Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Stereoselective Synthesis of 4-aminobenzothiazine using S-methyl-S-phenylsulfoximne

General information:

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware. THF was distilled over sodium-benzophenone before use. Dried 1,4-Dioxane was purchased from Leonid Chemicals pvt Ltd., India. Chromatographic separations were carried out by flash chromatography systems using Hi-Purit Flash Column Silica(NP) columns. Analytical thin layer chromatography was performed on EM Reagent 0.25 nm silica gel 60-F254 Aluminium sheets.

Optical rotations were measured on a Rudolph AUTOPOL IV automatic polarimeter. ^{1}H NMR were recorded on a Varian (400 MHz) spectrometer and is reported in ppm (δ) from tetramethylsilane (TMS: δ 0.0 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet), coupling constants (Hz), and integration. ^{13}C NMR spectra were recorded on a Varian (100 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with solvent resonance as the internal standard ($CDCl_3$: δ 77.0, DMSO: 40.0 and MeOH: 53.0 ppm).

2-bromobenzaldehyde(6630-33-7), 2-Methyl-2-propanesulfinamide(146374-27-8), (*S*)-(−)-2-Methyl-2-propanesulfinamide(343338-28-3), 2-Bromo-5-fluorobenzaldehyde (94569-84-3), 2-Bromo-5-(trifluoromethyl)benzaldehyde (102684-91-3), 6-Bromo-1,3-benzodioxole-5-carboxaldehyde (15930-53-7), 3,5-Dibromo-4-pyridinecarboxaldehyde (70201-42-2), 2-Chloro-3-quinolinecarboxaldehyde (73568-25-9), 3-Bromothiophene-2-carboxaldehyde (930-96-1) and 3-bromofuran-2-carbaldehyde (14757-78-9) were purchased from Sigma-Aldrich. 4-Bromo-1-methyl-1H-pyrazole-5-carboxaldehyde (473528-88-0) was purchased from Alfa-Aesar.
2-Bomo-5-Nitrobenzaldehyde (84459-32-5)[1], 5-Bromo-2-methoxy-4-pyridinecarboxaldehyde (936011-17-5)[2], S-Methyl-S-phenyl-N-(tert-butyldimethylsilyl)-sulfoximine (108947-72-4)[3]

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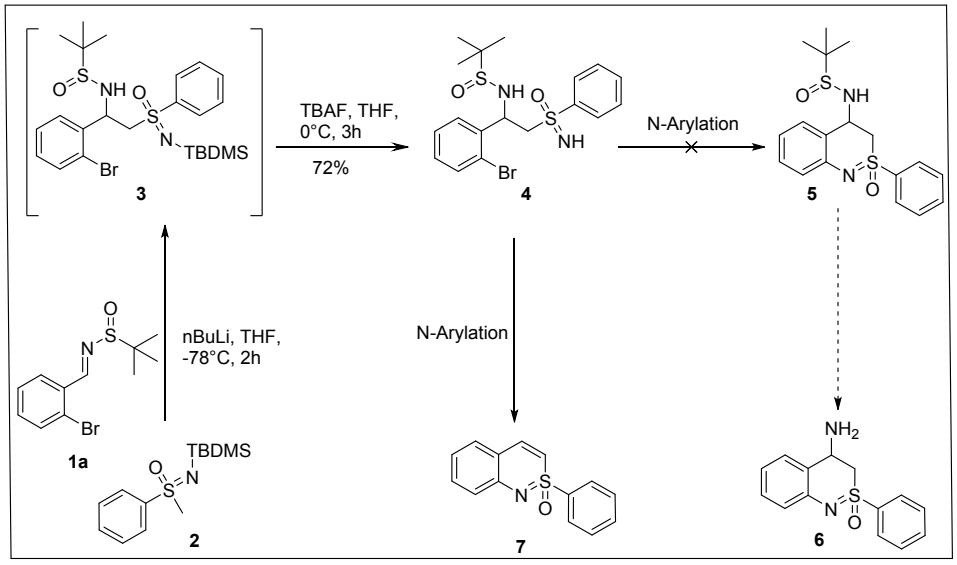
[1] Charles, A. B.; Oalmann, C.; Szczepankiewicz, B. G.; Caldwell, R.D.; Casaubon, R.; White, B. H.; Perni, R. B.; Karsten, K.; Disch, J. S.; Yee Ng, P.; Michael Fox, R.; WO2014186313, **2014**.

[2] Juteau, H.; Gallant, M.; Dube, D.; Roy, P.; Aspiotis, R.; Fortin, R.; Lacombe, P.; Mckay, D.; Yao-Hsiang Wu, T.; WO2009023964, **2009**.

[3] Pearson, A. J.; Blystone, S. L.; Nar, H.; Alan Pinkerton, A.; Roden, B. A; Yoon, J. *J. Am. Chem. Soc.*, **1989**, *111* (1), 134–144

were synthesized according to the literature report.

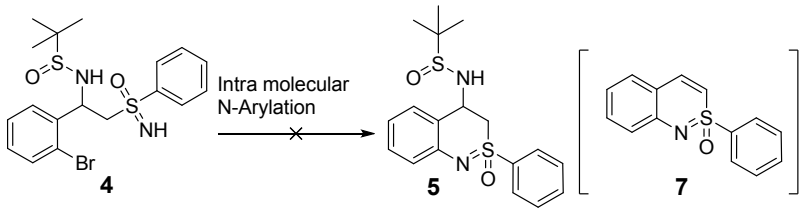
Scheme 1. Proposed Method for synthesis of 4-aminobenzothiazine



Synthesis of N-(1-(2-bromophenyl)-2-(phenylsulfonimidoyl)ethyl)-2-methylpropane-2-sulfinamide (4): To a stirred solution of S-Methyl-S-phenyl-N-(tert-butyldimethylsilyl)-sulfoximine **(2)** (0.3 g, 1.15 mmol) in THF (10 mL) was added nBuLi (1.6 M in THF) (0.86 mL, 1.33 mmol) at -78 °C and stirred for 30 min at that temperature, then added a solution of (RS, E) N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide **(1a)** (0.38 g, 1.33 mmol) in THF (5 mL) at -78 °C and stirred for another 1 h. After completion of starting material, reaction mixture was quenched with saturated NH_4Cl solution and extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated to get crude product. The crude product was dissolved in THF (15 mL), then added TBAF (1M in THF) (1.34 mL, 1.33 mmol) at 0 °C and stirred for another 3 h. After completion of starting material, reaction mixture was quenched with saturated NH_4Cl solution and extracted with DCM (3 x 50 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated to get crude product. Crude product was purified by flash chromatography (2% MeOH/DCM) to afford desired product. Off-white solid, Yield (0.35 g, 71.4%); ^{1}H NMR (400M Hz, DMSO) δ 7.80 (d, J = 6.8 Hz, 2H), 7.59 (t, J = 7.2 Hz, 1H), 7.52-7.46 (m, 4H), 7.24 (t, J = 7.2 Hz, 1H), 7.11 (t, J = 7.6 Hz, 1H), 6.13 (d, J = 6.8 Hz, 1H), 5.12 – 5.07 (m, 1H), 4.44 (s, 1H), 3.82-3.76 (m, 1H), 3.47 (dd, J = 14.4, 4.4 Hz, 1H), 1.08 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 142.4, 137.3, 133.3, 133.2, 129.99, 129.92, 129.27, 128.0, 127.9,

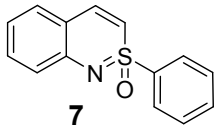
123.3, 61.3, 56.7, 54.5, 22.5. HRMS (ESI) m/z calcd for $C_{18}H_{23}BrN_2O_2S_2$ $[M + H]^+$ 443.0463 and 445.0442, found 443.0457 and 445.0439.

Table 1. Optimization conditions for intra-molecular N-arylation



Entry	Conditions	6(%)[a]	7(%)[a]
1	$Pd_2(dba)_3$ (5 mol%), Xantphos (7 mol%) $CsCO_3$, Dioxane, 90°C, 3h	0%	65%
2	$Pd_2(dba)_3$ (5 mol%), Ru-phos (7 mol%) K_2CO_3, Dioxane, 90°C, 3h	0%	43%
3	$Pd(OAc)_2$ (5 mol%), (+) BINAP (5 mol%) $CsCO_3$, Dioxane, 90°C, 3h	0%	58%
4	CuI, $CsCO_3$, Dioxane, 90°C, 8h	0%	0%
5	CuI, trans-1,2-Cyclohexanediamine, K_3PO_4, Dioxane, 90°C, 6h	0%	0%
6	CuI, DMEDA, K_3PO_4, Dioxane, 90°C, 6h	0%	0%

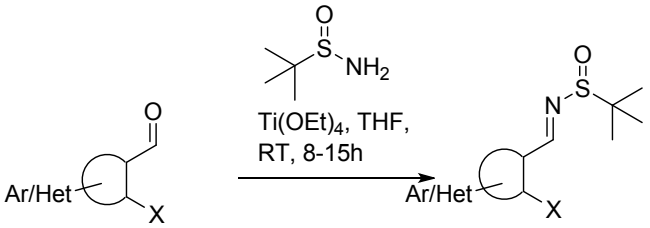
[a] Isolated yields



2-phenylbenzo[c][1,2]thiazine 2-oxide (7): ^{1}H NMR (400M Hz, $CDCl_3$) δ 7.90 (d, J = 7.2 Hz, 2H), 7.66 (d, J = 9.6 Hz, 1H), 7.61 (d, J = 6.8 Hz, 1H), 7.56 (t, J = 7.2 Hz, 2H), 7.44 (t, J = 7.2 Hz, 1H), 7.38-7.24 (m, 2H), 7.03 (t, J = 7.6 Hz, 1H), 6.38 (d, J = 10.0 Hz, 1H). Spectroscopic data is identical to those previously reported.[4]

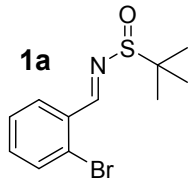
General procedure for synthesizing *tert*-butanesulfinyl aldimines from corresponding aldehydes and tert-butanesulfinamide:

[4] (a) Harmata, M.; Pavri, N. *Angew. Chem., Int. Ed*. **1999**, *38*, 2419-21. (b) Bolm, C.; Hildebrand, J. P. *Tetrahedron Lett*. **1998**, *37*, 5731.



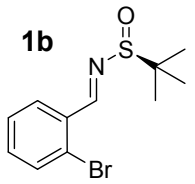
Where as X = Br or Cl

A flame-dried flask was cooled under a stream of N_2 and charged with the appropriate aldehyde (1.0 - 1.2 equiv) and sufficient THF to provide a 0.4 M solution. Neat $Ti(OEt)_4$ (2.0 equiv) was added, the reaction mixture was stirred at room temperature for 5 min, then tert-butanesulfinamide (1 equiv) was added. The resulting mixture was stirred at room temperature until the tert-butanesulfinamide had been completely consumed as judged by TLC analysis. The reaction mixture was poured into an equal volume of brine and stirred for 10 min before the resulting suspension was transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated under vacuum. The crude product was then purified by flash chromatography on silica gel.



(RS, E) N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide (1a).

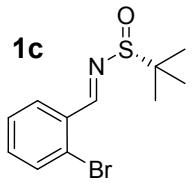
General Procedure: Clear viscous oil, Yield (94%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.98 (s, 1H), 8.03 (dd, J = 7.6, 1.6 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.40-7.32 (m, 2H), 1.27 (s, 9H). Spectroscopic data is identical to those previously reported[5].



(S, E) N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide (1b).

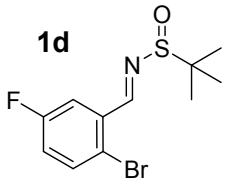
[5] Fan, R.; Pu, D.; Wen, F.; Yang, Y.; Wang, X. *J. Org. Chem*., **2008**, *73 (9),* 3623.

General Procedure: Clear viscous oil, Yield (94%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.97 (s, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.40-7.32 (m, 2H), 1.27 (s, 9H). Spectroscopic data is identical to those previously reported[6].



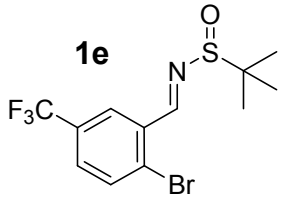
(R, E) N-(2-bromobenzylidene)-2-methylpropane-2-sulfinamide (1c).

General Procedure: Clear viscous oil, Yield (92%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.98 (s, 1H), 8.03 (d, J = 6.4 Hz, 1H), 7.64 (d, J = 7.2 Hz, 1H), 7.40-7.32 (m, 2H), 1.27 (s, 9H). Spectroscopic data is identical to those previously reported[7].



(RS, E) N-(2-bromo-5-fluorobenzylidene)-2-methylpropane-2-sulfinamide (1d).

General Procedure: Off white solid, Yield (95%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.91 (d, J = 1.6 Hz, 1H), 7.74 (dd, J = 9.2, 3.2 Hz, 1H), 7.61 (dd, J = 8.8, 5.2 Hz, 1 H), 7.11-7.06 (m, 1H), 1.27 (s, 9H). Spectroscopic data is identical to those previously reported[8].



(RS, E) N-(2-bromo-5-(trifluoromethyl)benzylidene)-2-methylpropane-2-sulfinamide (1e).

General Procedure: Off white solid, Yield (92%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.98 (s, 1H), 8.26 (s, 1H), 7.79 (d, J = 8.4 Hz, 1H), 7.58 (d, J = 7.6 Hz, 1H), 1.29 (s, 9H). Spectroscopic data is identical to those previously reported[9].

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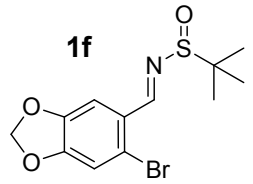
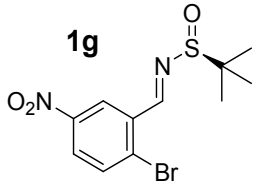
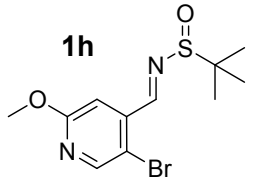
[6] Cheng, L.; Liu, L.; Sui, Y.; Wang, D.; Chen, Y.-J. *Tetrahedron: Asymmetry* **2007**, *18*, 1833.
[7] Cheng, L.; Liu, L.; Sui, Y.; Wang, D.; Chen, Y.-J. *Tetrahedron: Asymmetry* **2007**, *18*, 1833.
[8] Sirvent, J. A.; Foubelo, F.; Yus, M. *Eur. J. Org. Chem.* **2013**, (12), 2461-2471
[9] Patrick Shao, P.; Ye, F.; Vachal, P.; Sha, D.; Revathi Reddy, K.; Liu, J.; Sun, W.; WO 2013063217, **2013.**



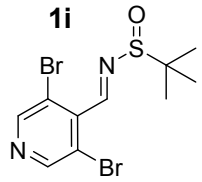
(RS, E) N-((6-bromobenzo[d][1,3]dioxol-5-yl)methylene)-2-methylpropane-2-sulfinamide (1f). General Procedure: Off white solid, Yield (90%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.86 (s, 1H), 7.50 (s, 1H), 7.06 (s, 1H), 6.05 (d, J = 1.2 Hz, 2H), 1.25 (s, 9H). Spectroscopic data is identical to those previously reported[10].



(S, E)-N-(2-bromo-5-nitrobenzylidene)-2-methylpropane-2-sulfinamide (1g). General Procedure: Off white solid, Yield (86%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.99 (s, 1H), 8.83 (d, J = 2.8 Hz, 1H), 8.17 (dd, J = 8.4, 2.4 Hz, 1H), 7.86 (d, J = 8.8 Hz, 1H), 1.31 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.3, 147.4, 134.8, 134.0, 132.4, 126.8, 124.2, 58.5, 22.7.

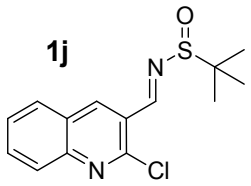


(RS, E) N-((5-bromo-2-methoxypyridin-4-yl)methylene)-2-methylpropane-2-sulfinamide (1h). General Procedure: Off white solid, Yield (89%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.83 (s, 1H), 8.37 (s, 1H), 7.28 (s, 1H), 3.95 (s, 3H), 1.27 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 163.8, 160.6, 150.0, 141.2, 113.0, 110.3, 58.5, 54.0, 22.6.



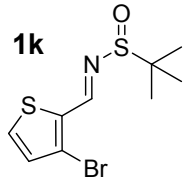
(RS, E) N-((3,5-dibromopyridin-4-yl)methylene)-2-methylpropane-2-sulfinamide (1i). General Procedure: Viscous oil, Yield (82%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.75 (s, 2H), 8.72 (s, 1H), 1.33 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.6, 151.6, 140.0, 120.9, 54.4, 22.68.

[10] Schultz, D. M.; Wolfe, J. P. *Org. Lett*, **2011,** *13(11),* 2962-2965;



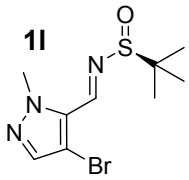
(RS, E) N-((2-chloroquinolin-3-yl)methylene)-2-methylpropane-2-sulfinamide (1j)[11].

General Procedure: Clear viscous oil, Yield (86%); ^{1}H NMR (400MHz, DMSO): δ 9.09 (s, 1H), 8.89 (s, 1H), 8.25 (d, J = 8.0Hz, 1H), 8.01(d, J = 8.4 Hz, 1H), 7.93 (t, J = 7.2 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 1.23 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 159.2, 150.0, 148.8, 138.7, 132.5, 128.8, 128.5, 127.8, 126.7, 125.7, 58.4, 22.7.

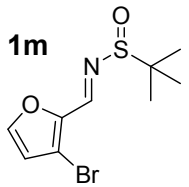


(RS, E) N-((3-bromothiophen-2-yl)methylene)-2-methylpropane-2-sulfinamide (1k).

General Procedure: Viscous oil, Yield (92%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.73 (s, 1H), 7.53 (d, J = 5.6 Hz, 1H), 7.09 (d, J = 5.6 Hz, 1H), 1.25 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 154.6, 134.8, 132.0, 131.6, 117.9, 58.1, 22.6.



(S, E) N-((4-bromo-1-methyl-1H-pyrazol-5-yl)methylene)-2-methylpropane-2-sulfinamide (1h) . General Procedure: Off white solid, Yield (91%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.59 (s, 1H), 7.5 (s, 1H), 4.17 (s, 3H), 1.27 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 149.7, 139.32, 133.7, 101.2, 57.7, 40.7, 22.4.



(RS, E) N-((3-bromofuran-2-yl)methylene)-2-methylpropane-2-sulfinamide (1m).

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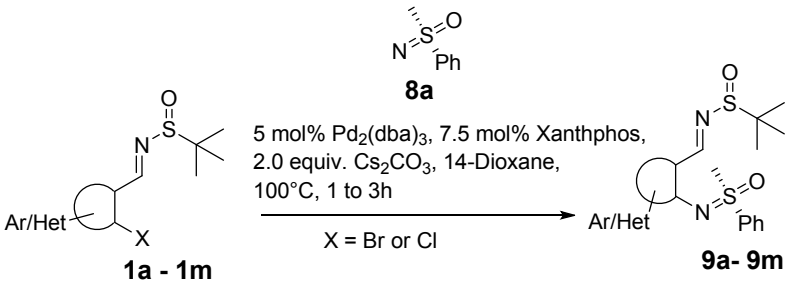
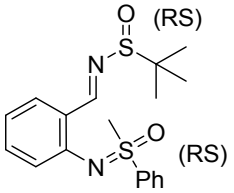
[11] Lemonnier, G.; Hijfte, N. V.; Poisson, T.; Couve-Bonnaire, S.; Pannecoucke, X. *J. Org. Chem.*, **2014**, 79 *(7),* 2916.

General Procedure: Viscous oil, Yield (90%); ^{1}H NMR (400M Hz, DMSO) δ 8.26 (s, 1H), 8.10 (d, J = 1.2 Hz, 1H), 7.0 (d, J = 1.2 Hz, 1H), 1.14 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 147.7, 147.1, 146.6, 116.3, 109.2, 57.8, 22.4.

General procedure for Buchwal-Harwing cross coupling reaction:



A sealed tube was charged with *tert*-butanesulfinyl aldimines (**1a – 1m**) (1.0 equiv), Sulfoximine (**8 or 8a**) (1.0 equiv) and Cs_2CO_3 and purged with Argon gas for 15min. Then added $Pd_2(dba)_3$ (0.05 equiv) and Xanthphos (0.075 equiv) and continued the Argon gas purging for further 10 min. After that reaction mixture was heated to 100°C for 1 to 3h and further reaction was monitored by TLC analysis. After completion of starting material, reaction mixture was cooled to room temperature, filtered through celite and filtrate was concentrated to get the crude product. The crude product was then purified by flash chromatography on silica gel.



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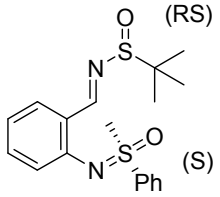
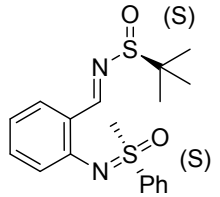
(9) (RS, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (96%); ^{1}H NMR (400M Hz, DMSO) δ 9.18 (s, 2H), 7.92-7.89 (m, 4H), 7.81 (d, J = 7.6 Hz, 2H), 7.67 (t, J = 7.6 Hz, 2H), 7.62-7.58 (m, 4H), 7.23-7.16 (m, 2H), 6.97 (d, J = 8.0 Hz, 1H), 6.92-6.87 (m, 3H), 3.47 (s, 6H), 1.17 (s, 9H), 1.16 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 161.1, 161.0, 146.86, 146.83, 139.0, 138.9, 133.4, 133.3, 132.9, 129.6, 129.5, 128.1, 127.9, 127.2, 122.6, 122.4, 121.6, 121.5, 57.4, 57.3, 46.1, 46.0, 22.57, 22.54. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1191.



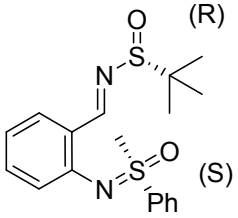
9a

(9a) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (94%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.368 (s, 1H), 9.361 (s, 1H), 7.96-7.92 (m, 6H), 7.61-7.57 (m, 2H), 7.55-7.50 (m, 4H), 7.19-7.13 (m, 2H), 7.09 (d, J = 8.0 Hz, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.92-6.89 (m, 2H), 3.29 (s, 6H), 1.289 (s, 9H), 1.282 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 161.1, 161.0, 146.82, 146.80, 139.1, 139.0, 133.44, 133.40, 132.9, 129.64, 129.62, 128.24, 128.22, 127.9, 127.38, 127.36, 122.6, 122.5, 121.6, 121.5, 57.5, 57.3, 46.2, 46.1, 22.6, 22.59. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1191.



9b

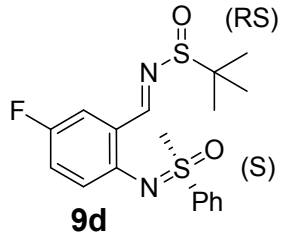
(9b) (S, S, E): General Procedure: Viscous oil, Yield (94%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.37 (s, 1H), 7.94 (t, J = 8.0 Hz, 3H), 7.59 (t, J = 7.2 Hz, 1H), 7.52 (t, J = 7.6 Hz, 2H), 7.17 (t, J = 7.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.2 Hz, 1H), 3.29 (s, 3H), 1.29 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 161.0, 146.8, 138.9, 133.3, 132.9, 129.5, 128.0, 127.8, 127.2, 122.6, 121.5, 57.3, 45.9, 22.4. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1191.



9c

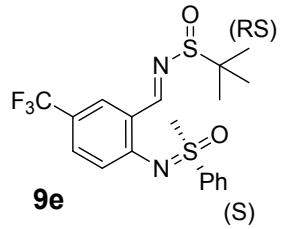
(9c) (S, R, E): General Procedure: Viscous oil, Yield (95%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.35 (s, 1H), 7.94-7.92 (m, 3H), 7.59 (t, J = 7.2 Hz, 1H), 7.53 (t, J = 8.0 Hz, 2H), 7.17-7.13 (m, 1H), 7.03 (d, J = 8.0 Hz, 1H), 6.90 (t, J = 7.6 Hz, 1H), 3.30 (s, 3H), 1.28 (s, 9H). ^{13}CNMR

(100MHz, $CDCl_3$): 161.1, 146.8, 139.0, 133.4, 133.0, 129.6, 128.2, 127.9, 127.3, 122.5, 121.5, 57.5, 46.2, 22.6. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1191.



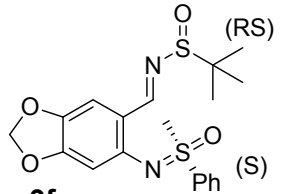
9d

(9d) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (94%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.30 - 9.28 (m, 2H), 7.92 (t, J = 7.2 Hz, 4H), 7.61 - 7.58 (m, 4H), 7.56 - 7.50 (m, 4H), 7.09 - 7.06 (m, 1H), 7.03 - 7.00 (m, 1H), 6.92 - 6.85 (m, 2H), 3.29 (s, 6H), 1.29 (s, 9H), 1.28 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.4, 160.3, 157.9 (d, J = 240.2 Hz, C), 157.8 (d, J = 240.2 Hz, C), 142.9, 138.9, 138.8, 133.55, 133.50, 129.7, 129.6, 128.4 (d, J = 7.0 Hz, C), 128.3 (J = 7.8 Hz, C), 124.1 (d, J = 7.0 Hz, C), 124.0 (d, J = 7.8 Hz, C), 120.1, 119.9, 113.6, 113.4, 57.7, 57.6, 46.2, 46.1, 22.67, 22.62. HRMS (ESI) m/z calcd for $C_{18}H_{21}FN_2O_2S_2$ $[M + H]^+$ 381.1107, found 381.1087.



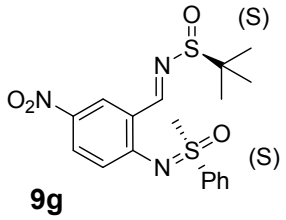
9e

(9e) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (96%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.349 (s, 1H), 9.340 (s, 1H), 8.17 (s, 1H), 8.16 (s, 1H), 7.94)m, 4H), 7.66 – 7.61 (m, 2H), 7.58-7.53 (m, 4H), 7.37-7.32 (m, 2H), 7.07 (d, J = 8.4 Hz, 1H), 6.97 (d, J = 12.4 Hz, 1H), 3.34 (s, 6H), 1.308 (s, 9H), 1.301 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.1, 160.0, 149.7, 138.5, 138.3, 133.8, 133.7, 129.86, 129.81, 129.16 (q, J = 3.1 Hz, C), 129.13 (q, J = 3.1 Hz, C), 128.1, 128.09, 127.06, 127.01, 125.1 (q, J = 3.1 Hz, C), 124.09 (q, J = 269Hz, C), 124.08 (q, J = 269Hz, C), 123.37 (q, J = 33.0Hz, C), 123.27 (q, J = 33.0Hz, C), 122.3, 122.1, 57.7, 57.6, 46.2, 46.4, 22.6, 22.5. HRMS (ESI) m/z calcd for $C_{19}H_{21}F_3N_2O_2S_2$ $[M + H]^+$ 431.1075, found 431.1061.



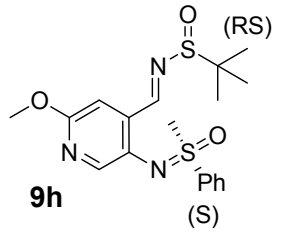
9f

(9f) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (92%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.049 (s, 1H), 9.040 (s, 1H), 7.89 (t, J = 7.2 Hz, 4H), 7.70 - 7.67 (m, 2H), 7.64 - 7.58 (m, 4H), 7.23 (s, 2H), 6.54 (s, 1H), 6.46 (s, 1H), 5.98-5.93 (m, 4H), 3.46 (s, 6H), 1.15 (s, 9H), 1.14 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.2, 160.0, 151.76, 151.74, 143.5, 143.4, 143.29, 143.22, 139.08, 139.01, 133.49, 133.43, 129.69, 129.64, 128.3, 128.2, 121.3, 121.2, 105.9, 103.6, 103.5, 101.4, 57.4, 57.2, 46.1, 46.0, 22.6, 22.5. HRMS (ESI) m/z calcd for $C_{19}H_{22}N_2O_4S_2$ $[M + H]^+$ 407.1099, found 407.1086.



9g

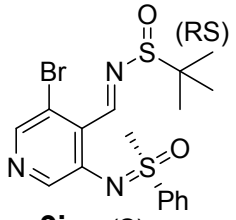
(9g) (S, S, E): General Procedure: Yellow oil, Yield (81%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.16 (s, 1H), 8.55 (d, J = 2.8 Hz, 1H), 8.06 (dd, J = 9.2, 2.8 Hz, 1H), 7.96 (d, J = 7.6 Hz, 2H), 7.74 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.2 Hz, 2H), 7.10 (d, J = 9.2 Hz, 1H), 3.64 (s, 3H), 1.20(s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 159.6, 152.8, 141.5, 138.0, 134.1, 129.9, 127.9, 127.3, 126.9, 123.9, 121.7,57.8, 46.6, 22.6. HRMS (ESI) m/z calcd for $C_{18}H_{21}N_3O_4S_2$ $[M + H]^+$ 408.1052, found 408.1055.



9h

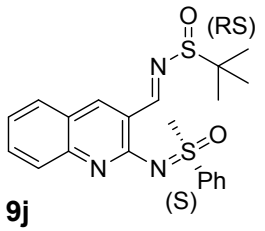
(9h) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (83%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.01 (s, 2H), 7.91 (t, J = 6.4 Hz, 4H), 7.86 (s, 1H), 7.79 (s, 1H), 7.68 (t, J = 7.6 Hz, 2H), 7.63 – 7.58 (m, 4H), 7.04 (s, 2H), 3.72 (s, 3H), 3.71 (s, 3H), 3.50 (s, 6H), 1.18 (s, 18H). ^{13}CNMR (100MHz, $CDCl_3$): 160.0, 159.9, 159.4, 159.3, 141.1, 141.0, 138.8, 138.7, 136.6,

135.6, 135.58, 133.54, 133.4, 129.7, 129.6, 128.2, 107.0, 58.1, 57.9, 53.5, 46.0, 45.9, 22.69, 22.65. HRMS (ESI) m/z calcd for $C_{18}H_{23}N_3O_3S_2$ $[M + H]^+$ 394.1259, found 394.1249.



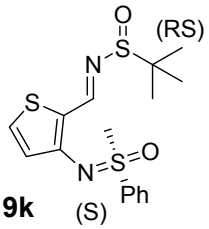
9i (S)

(9i) (S, RS, E): (Mixture of Isomers) General Procedure: Yellow solid, Yield (69%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.10 (s, 1H), 9.09 (s, 1H), 8.32 - 8.29 (m, 3H), 7.97 - 7.92 (m, 4H), 7.65 - 7.52 (m, 7H), 3.30 (s, 6H), 1.35 (s, 18H). ^{13}CNMR (100MHz, $CDCl_3$): 160.4, 145.46, 145.42, 142.98, 142.96, 142.39, 142.2, 138.2, 138.1, 133.9, 132.7,132.5, 129.9, 128.18, 128.15, 119.1, 118.8, 57.8, 57.7, 46.4, 46.2, 22.5. HRMS (ESI) m/z calcd for C18H16BrClN2O2 $[M + H]^+$ 407.0162 and 409.0141, found 407.0153 and 409.0131.



9j

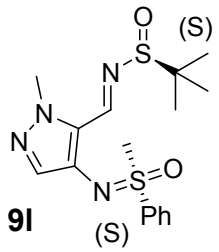
(9j) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (93%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.33 (s, 2H), 8.62 (d, J = 7.2 Hz, 2H), 8.09 (t, J = 9.6 Hz, 4H), 7.70 (t, J = 6.8 Hz, 2H), 7.62 - 7.48 (m, 10H), 7.30 - 7.28 (m, 2H), 3.54 (s, 3H), 3.49 (s, 3H), 1.32 (s, 9H), 1.31 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 160.9, 157.2, 157.1, 148.9, 148.8, 140.2, 140.1, 136.8, 133.0, 132.9, 130.9, 130.8, 129.4, 129.3, 128.65, 128.62, 127.7, 127.57, 127.54, 127.50, 127.3, 124.26, 124.24, 124.18, 124.14, 122.08, 122.03, 57.9, 57.8, 45.3, 45.1, 22.7. HRMS (ESI) m/z calcd for $C_{21}H_{23}N_3O_2S_2$ $[M + H]^+$ 414.1310, found 414.1305.



9k (S)

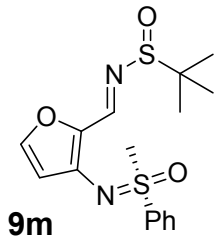
(9k) (S, RS, E): (Mixture of Isomers) General Procedure: Viscous oil, Yield (91%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 9.0 (s, 2H), 7.93 (t, J = 7.6 Hz, 4H), 7.62 (t, J = 8.0 Hz, 2H), 7.57 - 7.52

(m, 4H), 7.27 - 7.23 (m, 2H), 6.76 (d, *J* = 5.6 Hz, 1H), 6.71 (d, *J* = 5.2 Hz, 1H), 3.288 (s, 3H), 3.283 (s, 3H), 1.24 (s, 18H). ^{13}CNMR (100MHz, $CDCl_3$): 149.6, 149.5, 144.3, 144.2, 134.35, 134.34, 128.93, 128.90, 126.8, 124.98, 124.93, 123.38, 123.34, 120.0, 119.8, 119.0, 118.7, 52.7, 52.6, 41.2,41.1, 17.8, 17.5. HRMS (ESI) m/z calcd for $C_{16}H_{20}N_2O_2S_3$ $[M + H]^+$ 369.0765, found 369.0751.



9l

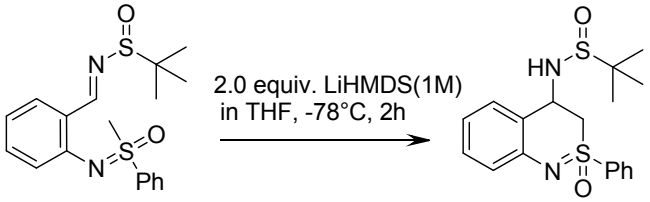
(9l) (S, S, E): General Procedure: Off-white solid Yield (85%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.50 (s, 1H), 7.90 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.2 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 3.93 (s, 3H), 3.47 (s, 3H), 1.15 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 149.7, 138.8, 133.4, 131.1, 129.6, 129.0, 128.4, 57.1, 45.2, 40.3, 22.4. HRMS (ESI) m/z calcd for $C_{16}H_{22}N_4O_2S_2$ $[M + H]^+$ 367.1262, found 367.1260.



9m

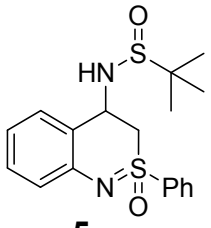
(9m) (S, RS, E): (Mixture of Isomers) General Procedure: Colorless oil, Yield (90%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.35 (s, 2H), 7.93 (d, *J* = 7.6 Hz, 4H), 7.71 (t, *J* = 7.6 Hz, 2H), 7.65 – 7.61 (m, 6H), 6.12 – 6.09 (m, 2H), 3.54 (s, 6H), 1.10 (s, 18H). ^{13}CNMR (100MHz, $CDCl_3$): 146.7, 146.5, 141.3, 140.3, 138.9, 133.7, 129.79, 129.74, 128.29, 128.23, 108.9, 108.7, 57.4, 57.3, 46.0, 45.8, 22.4. HRMS (ESI) m/z calcd for $C_{16}H_{20}N_2O_3S_2$ $[M + H]^+$ 353.0994, found 353.1011.

General procedure for intramolecular cyclization reaction:



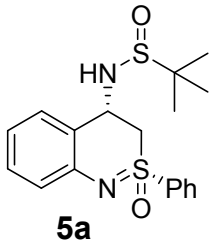
9 **5**

To a stirred solution of **(RS, RS, E) - (9)** (1.5 g. 4.14 mmol) in THF (25 mL) was added LiHMDS (1M in THF) (8.3 mL, 8.28 mmol) at -78°C and stirred for 2 h at the same temperature. After completion of starting material, reaction mixture was quenched with saturated NH_4Cl solution and the aqueous layer was extracted with EtOAc (3 x 50 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated to get crude product. Crude product was purified by flash chromatography (70% EtOAc/Hexane) to afford desired product. Off-white solid, Yield (1.43 g, 95%);



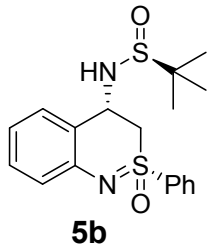
5

(5) 2-methyl-N-(2-oxido-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazin-4-yl)propane-2-sulfinamide: (Mixture of Diastereomers) Off-white solid: ^{1}H NMR (400M Hz, DMSO) δ 8.03-8.00 (m, 3.2H), 7.79 (t, J = 7.2 Hz, 1.74H), 7.71-7.66 (m, 4.1H), 7.48 (d, J = 7.6 Hz, 1.1H), 7.2 (t, J = 7.6 Hz, 1.7H), 6.91 (t, J = 8.0 Hz, 3.32H), 5.98 (d, J = 8.8 Hz, 0.63H), 5.80 (d, J = 9.2 Hz, 1H), 4.85-4.78 (m, 1.65H), 3.86-3.81 (m, 1.67H), 3.44 (t, J = 12.4 Hz, 1.1H), 3.23 (t, J = 12.8 Hz, 1.4H), 1.17 (s, 9H), 1.12 (s, 5.98H). ^{13}CNMR (100MHz, $CDCl_3$): 144.7, 144.5, 138.6, 137.5, 134.2, 134.0, 130.0, 129.8, 129.4, 129.0, 128.9, 127.5, 125.5, 124.3, 123.0, 122.9, 121.4, 120.8, 57.0, 56.2, 53.8, 53.7, 52.3, 51.9, 22.6, 22.4. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1198.



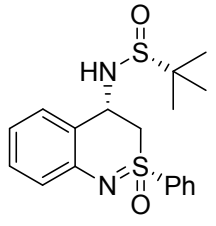
5a

(5a) 2-methyl-N-((2S,4S)-2-oxido-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazin-4-yl)propane-2-sulfinamide: (Mixture of Diastereomers) Off-white solid: ^{1}H NMR (400M Hz, DMSO) δ 8.03-8.02 (m, 3H), 7.79 (t, J = 7.2 Hz, 1.6H), 7.71-7.66 (m, 4.3H), 7.48 (d, J = 7.6 Hz, 0.68H), 7.2 (t, J = 7.6 Hz, 1.65H), 6.91 (t, J = 8.0 Hz, 3.17H), 5.98 (d, J = 8.8 Hz, 1H), 5.80 (d, J = 10.0 Hz, 0.55H), 4.88-4.82 (m, 1.6H), 3.87-3.82 (m, 1.53H), 3.44 (t, J = 12.0 Hz, 1.1H), 3.23 (t, J = 12.4 Hz, 1.1H), 1.17 (s, 5H), 1.12 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 143.7, 143.5, 137.6, 136.6, 133.2, 133.0, 129.0, 128.8, 128.5, 128.0, 127.9, 126.5, 124.5, 123.36, 123.32, 122.1, 122.0, 120.4, 119.8, 56.0, 55.3, 52.8, 52.7, 51.3, 50.9, 21.7, 21.4. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1198.



5b

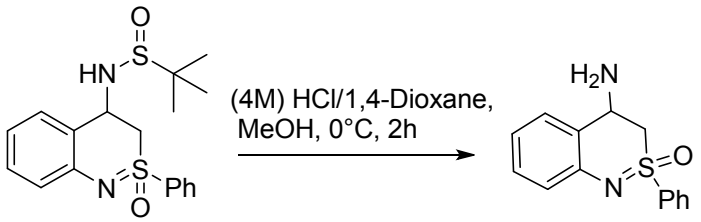
(5b) (S)-2-methyl-N-((2S,4S)-2-oxido-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazin-4-yl) propane-2-sulfinamide: Off-white solid: ^{1}H NMR (400M Hz, DMSO) δ 8.02 (d, J = 7.6 Hz, 2H), 7.79 (t, J = 7.2 Hz, 1H), 7.70 (t, J = 8.0 Hz, 2H), 7.48 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 7.6 Hz, 1H), 6.94-6.90 (m, 2H), 5.81 (d, J = 9.6 Hz, 1H), 4.84-4.80 (m, 1H), 3.83 (dd, J = 12.4, 4.8 Hz, 1H), 3.44 (t, J = 12.4Hz, 1H), 1.18 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 144.5 137.5, 134.2, 129.8, 129.5, 129.0, 125.5, 124.3, 123.0, 120.8, 57.0, 53.8, 52.3, 22.6. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ $[M + H]^+$ 363.1201, found 363.1198. $[\alpha]^{25}_D$ = -3.90 (c 1.02, $CHCl_3$).



5c

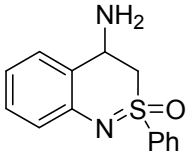
(5c) (R)-2-methyl-N-((2S,4S)-2-oxido-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazin-4-yl) propane-2-sulfinamide: Off-white solid: ^{1}H NMR (400M Hz, DMSO) δ 8.02 (d, J = 7.6 Hz, 2H), 7.80 (t, J = 7.2 Hz, 1H), 7.71-7.66 (m, 3H), 7.19 (t, J = 7.6 Hz, 1H), 6.91 (t, J = 8.4 Hz, 2H), 5.98 (d, J = 9.2 Hz, 1H), 4.88-4.81 (m, 1H), 3.84 (dd, J = 12.0, 4.8 Hz, 1H), 3.22 (t, J = 12.0Hz, 1H), 1.12 (s, 9H). ^{13}CNMR (100MHz, $CDCl_3$): 144.7, 138.6, 134.0, 130.0, 129.4, 128.9, 127.5, 124.3, 122.9, 121.4, 56.3, 53.7, 51.8, 22.4. HRMS (ESI) m/z calcd for $C_{18}H_{22}N_2O_2S_2$ [M + H]$^+$ 363.1201, found 363.1198. $[\alpha]^{25}_D$ = 27.77 (*c* 1.00, $CHCl_3$).

General procedure for deprotection of *tert*-butanesulfinyl group:



5 **6**

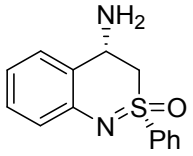
To a stirred solution of 2-methyl-N-(2-oxido-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazin-4-yl)propane-2-sulfinamide **(5)** (0.8 g, 2.20 mmol) in MeOH (15 mL) was added (4M) HCl in 1,4-Dioxane (3 mL) at 0°C and stirred for 2 h at that temperature. After completion of starting material, reaction mixture was concentrated under reduced pressure, basified the crude product with saturated $NaHCO_3$ solution and compound was extracted with DCM (3 x 20 mL). The combined organic extracts were washed with water, brine, dried over Na_2SO_4, filtered and concentrated to get crude product. Crude product was purified by flash chromatography (2% MeOH/DCM) to afford desired product.



6

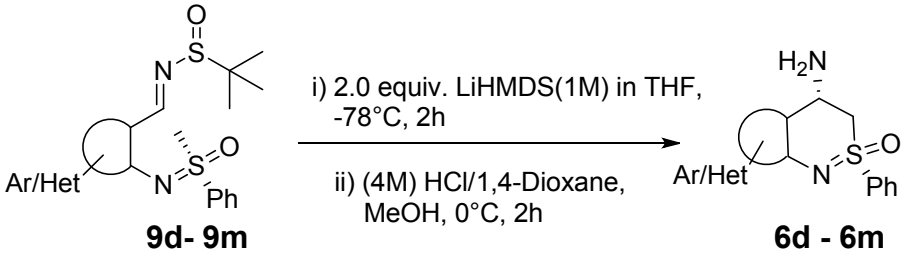
(6) 4-amino-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazine 2-oxide: Off-white solid, Yield (0.55g, 98%); ^{1}H NMR (400M Hz, DMSO) δ 7.98 (d, J = 7.2 Hz, 2H), 7.75 (t, J = 7.2 Hz, 1H), 7.68-7.61 (m, 3H), 7.12 (t, J = 7.2 Hz, 1H), 6.87 (d, J = 6.0 Hz, 2H), 4.27 (d, J = 9.6 Hz, 1H), 3.70-6.68 (m, 1H), 3.12 (t, J = 11.6 Hz, 1H), 2.21 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$+MeOD):

147.8, 142.0, 138.1, 133.4, 132.9, 132.6, 130.7, 128.6, 127.0, 125.1, 58.6, 49.7. HRMS (ESI) m/z calcd for $C_{14}H_{14}N_2OS$ $[M + H]^+$ 259.0905, found 259.0887.

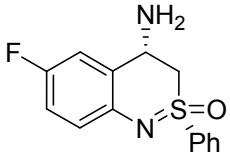


6a

(6a) (2S,4S)-4-amino-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazine 2-oxide: Off-white solid, ^{1}H NMR (400M Hz, DMSO) δ 7.98 (d, J = 7.6 Hz, 2H), 7.75 (t, J = 7.2 Hz, 1H), 7.68-7.62 (m, 3H), 7.12 (t, J = 7.2 Hz, 1H), 6.86 (t, J = 6.4 Hz, 2H), 4.27 (d, J = 9.2 Hz, 1H), 3.71-6.67 (m, 1H), 3.12 (t, J = 12.4 Hz, 1H), 2.15(bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 144.4, 138.6, 133.9, 129.4, 128.9, 128.8, 127.2, 124.9, 123.4, 120.8, 55.3, 46.3. HRMS (ESI) m/z calcd for $C_{14}H_{14}N_2OS$ $[M + H]^+$ 259.0905, found 259.0887. $[\alpha]^{25}_D$ = 7.35 (c 0.245, $CHCl_3$).

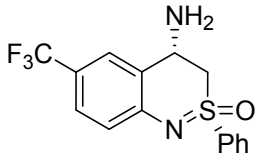


9d- 9m **6d - 6m**



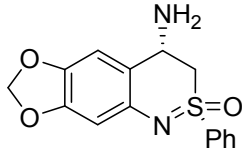
6d

(6d) (2S,4S)-4-amino-6-fluoro-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazine 2-oxide: Off-white solid, Yield (92%); ^{1}H NMR (400M Hz, DMSO) δ 7.98 (d, J = 7.2 Hz, 2H), 7.77 (t, J = 7.2 Hz, 1H), 7.67 (t, J = 8.0 Hz, 2H), 7.45 (dd, J = 10.0, 2.0 Hz, 1H), 6.99 - 6.94 (m, 1H), 6.88 - 6.85 (m, 1H), 4.27 - 4.24 (m, 1H), 3.71 (dd, J = 12.0, 4.4 Hz, 1H), 3.09 (t, J = 12.4, 1H), 2.27 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 157.7 (d, J = 237.9 Hz, C), 140.4, 138.3, 134.0, 129.4, 128.9, 128.5 (d, J = 6.2 Hz, C), 124.3 (d, J = 7.0 Hz, C), 115.4 (d, J = 22.4 Hz, C), 111.7 (d, J = 24.0 Hz, C), 55.0, 46.2. HRMS (ESI) m/z calcd for $C_{14}H_{13}FN_2OS$ $[M + H]^+$ 277.0811, found 277.0812. $[\alpha]^{25}_D$ = 2.5 (c 2.30, $CHCl_3$).



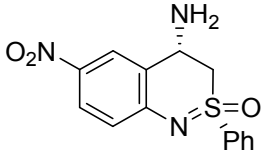
6e

(6e) (2S,4S)-4-amino-2-phenyl-6-(trifluoromethyl)-3,4-dihydrobenzo[c][1,2]thiazine 2-oxide: Off-white solid, Yield (91%); ^{1}H NMR (400M Hz, DMSO) δ 7.99 (d, J = 6.8 Hz, 3H), 7.79 (t, J = 7.6 Hz, 1H), 7.69 (t, J = 8.0 Hz,2H), 7.46 (d, J = 8.4 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 4.32 (d, J = 8.8 Hz, 1H), 3.81 (dd, J = 12.0, 4.4 Hz, 1H), 3.21 (t, J = 12.8 Hz, 1H), 2.33 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 148.0, 137.7, 134.2, 129.5, 128.8, 127.3, 125.9 (q, J = 3.9 Hz, C), 124.7 (q, J = 269C), 123.3, 122.49 (q, J = 3.9 Hz, C), 122.44 (q, J = 3.9 Hz, C), 54.9, 45.9. HRMS (ESI) m/z calcd for $C_{15}H_{13}F_3N_2OS$ $[M + H]^+$ 327.0779, found 327.0775.
$[\alpha]^{25}_D$ = -5.39 (*c* 2.00, $CHCl_3$).



6f

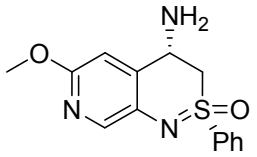
(6f) (2S,4S)-4-amino-2-phenyl-3,4-dihydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-c][1,2]thiazine 2-oxide: Off-white solid, Yield (86%); ^{1}H NMR (400M Hz, DMSO) δ 7.96 (d, J = 8.0 Hz, 2H), 7.74 (t, J = 7.6 Hz, 1H), 7.66 (t, J = 7.6 Hz, 2H), 7.19 (s, 1H), 6.47 (s, 1H), 5.88 (s, 2H), 4.16 (d, J = 9.2 Hz, 1H), 3.65 (dd, J = 12.0, 4.0 Hz, 1H), 3.03 (t, J = 12.4, 1H), 2.13 (bs, 2H). ^{13}CNMR (100MHz, DMSO): 147.2, 141.4, 139.5, 139.1, 134.3, 129.9, 128.7, 121.0, 106.0, 103.9, 100.8, 54.0, 46.0. HRMS (ESI) m/z calcd for $C_{15}H_{14}N_2O_3S$ $[M + Na]^+$ 325.0623, found 325.0621.
$[\alpha]^{25}_D$ = 25.7 (*c* 0.245, $CHCl_3$).



6g

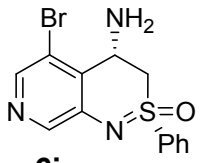
(6g) (2S,4S)-4-amino-6-nitro-2-phenyl-3,4-dihydrobenzo[c][1,2]thiazine 2-oxide: Yellow solid, Yield (78%); ^{1}H NMR (400M Hz, DMSO) δ 8.59 (d, J = 2.0 Hz, 2H), 8.04 (dd, J = 8.8, 3.2Hz, 1H), 8.00 (d, J = 7.2 Hz, 2H), 7.80 (t, J = 7.2 Hz, 1H), 7.70 (t, J = 8.0 Hz, 2H),7.01 (d, J = 8.8 Hz, 1H), 4.33 - 4.31 (m, 1H), 3.91(dd, J = 12.4, 4.4 Hz, 1H), 3.26 (t, J = 14.8, 1H), 2.39

(bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 151.9, 140.9, 136.9, 134.6, 129.6, 128.8, 127.4, 124.8, 123.2, 121.5, 54.3, 45.6. HRMS (ESI) m/z calcd for $C_{14}H_{13}N_3O_3S$ $[M + H]^+$ 304.0756, found 304.0768. $[\alpha]^{25}_D$ = -46.53 (*c* 0.26, $CHCl_3$).



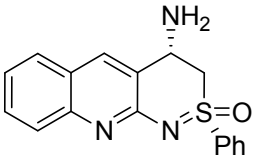
6h

(6h) (2S,4S)-4-amino-6-methoxy-2-phenyl-3,4-dihydropyrido[3,4-c][1,2]thiazine 2-oxide: Off-white solid, Yield (75%); ^{1}H NMR (400M Hz, DMSO) δ 7.98 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 6.8 Hz, 1H), 7.71 – 7.65 (m, 3H), 7.06 (s, 1H), 4.27 (dd, J = 12.8, 4.4 Hz, 1H), 3.77 (s, 3H), 3.73 (dd, J = 12.4, 4.8 Hz, 1H), 2.36 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 159.3, 140.0, 139.2, 138.0, 135.3, 134.1, 129.5, 129.0, 105.6, 54.7, 53.4, 45.8. HRMS (ESI) m/z calcd for $C_{14}H_{15}N_3O_2S$ $[M + H]^+$ 290.0963, found 290.0984. $[\alpha]^{25}_D$ = 35.83 (*c* 0.24, $CHCl_3$).



6i

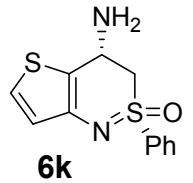
(6i) (2S,4S)-4-amino-5-bromo-2-phenyl-3,4-dihydropyrido[3,4-c][1,2]thiazine 2-oxide: Off-white solid, Yield (72%); ^{1}H NMR (400M Hz, $CDCl_3$) δ 8.37 (s, 1H), 8.29 (s, 1H), 8.10 (d, J = 8.0 Hz, 2H), 7.69 (t, J = 7.2 Hz, 1H), 7.61 (t, J = 8.0 Hz, 2H), 4.65 (d, J = 3.2 Hz, 1H), 4.04 (d, J = 15.2 Hz, 1H), 3.49 (dd, J = 14.8, 5.2 Hz, 1H), 1.45 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 145.1, 143.7, 142.2, 139.9, 134.1, 131.4, 129.6, 128.4, 121.1, 55.0, 48.5. HRMS (ESI) m/z calcd for $C_{13}H_{12}BrN_3OS$ $[M + H]^+$ 337.9963 and 339.9942, found 337.9958 and 339.9937.
$[\alpha]^{25}_D$ = -66.10 (*c* 1.00, $CHCl_3$).



6j

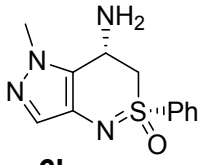
(6j) (2S,4S)-4-amino-2-phenyl-3,4-dihydro-[1,2]thiazino[3,4-b]quinoline 2-oxide: Off-white solid, Yield (88%); ^{1}H NMR (400M Hz, DMSO) δ 8.46 (s, 1H), 8.05 (d, J = 8.0 Hz, 2H), 7.83-7.78 (m, 2H), 7.71 (t, J = 8.0 Hz, 3H), 7.58 (t, J = 7.2 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 4.48 (d, J = 9.2 Hz, 1H), 3.91 (dd, J = 12.4,4.0 Hz, 1H), 3.35 (t, J = 12.4 Hz, 1H), 2.39 (bs, 2H). ^{13}CNMR

(100MHz, $CDCl_3$): 155.0, 147.6, 137.5, 134.2, 133.45, 134.42, 129.5, 129.4, 128.8, 127.36, 127.32, 124.9, 124.3, 124.0, 55.3, 46.0. HRMS (ESI) m/z calcd for $C_{17}H_{15}N_3OS$ $[M + H]^+$ 310.1014, found 310.1007. $[\alpha]^{25}_D = 149.63$ (*c* 2.00, $CHCl_3$).



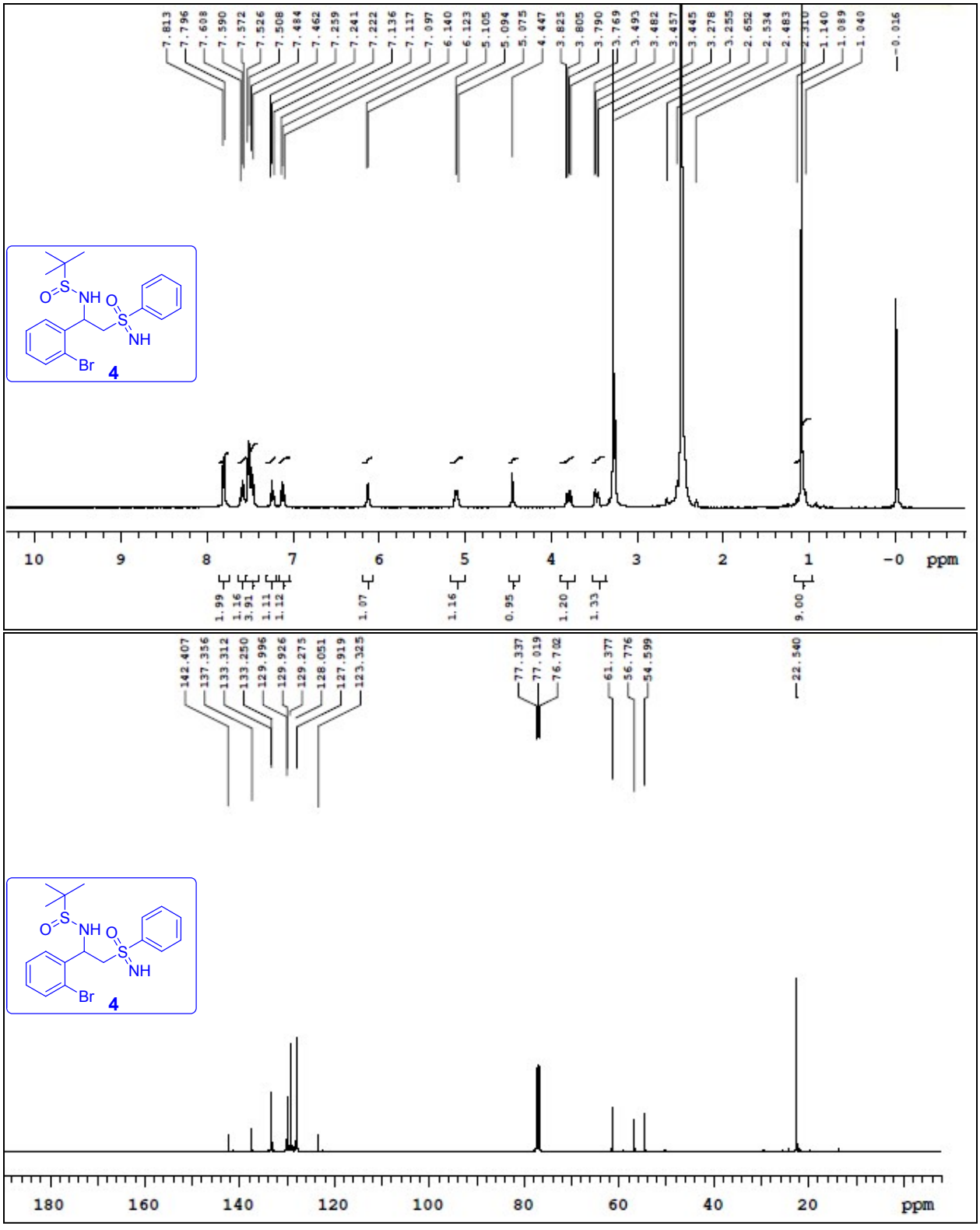
6k

(6k) (2S,4R)-4-amino-2-phenyl-3,4-dihydrothieno[3,2-c][1,2]thiazine 2-oxide: Off-white solid, Yield (90%); ^{1}H NMR (400M Hz, DMSO) δ 8.02 (d, J = 6.8 Hz, 2H), 7.79 (t, J = 7.2 Hz, 1H), 7.69 (t, J = 8.0 Hz, 2H), 7.28 (d, J = 5.2 Hz, 1H), 6.70 (d, J = 6.0 Hz, 1H), 4.30 (dd, J = 12.4, 5.2 Hz, 1H), 3.69 (dd, J = 11.6, 5.6 Hz, 1H), 2.97 (t, J = 12.0 Hz, 1H), 2.33 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 142.8, 136.6, 134.3, 129.5, 129.1, 125.2, 122.7, 117.9, 55.2, 45.4. HRMS (ESI) m/z calcd for $C_{12}H_{12}N_2OS_2$ $[M + Na]^+$ 287.0289, found 287.0285.
$[\alpha]^{25}_D = 29.17$ (*c* 2.20, $CHCl_3$).



6l

(6l) (5S,7S)-7-amino-1-methyl-5-phenyl-6,7-dihydro-1H-pyrazolo[4,3-c][1,2]thiazine 5-oxide: Off-white solid, Yield (89%); ^{1}H NMR (400M Hz, DMSO) δ 7.99 (d, J = 8.0 Hz, 2H), 7.77 (t, J = 7.6 Hz, 1H), 7.67 (t, J = 8.0 Hz, 2H), 7.01 (s, 1H), 4.51 (bs, 1H), 3.90 (s, 3H), 3.61 (dd, J = 12.0, 6.0 Hz, 1H), 3.24 (t, J = 12.0 Hz, 1H), 2.07 (bs, 2H). ^{13}CNMR (100MHz, $CDCl_3$): 137.0, 134.2, 130.9, 129.5, 128.8, 128.6, 124.3, 56.6, 44.3, 39.1. HRMS (ESI) m/z calcd for $C_{12}H_{14}N_4OS$ $[M + H]^+$ 263.0967, found 263.0950. $[\alpha]^{25}_D = -9.39$ (*c* 0.245, $CHCl_3$).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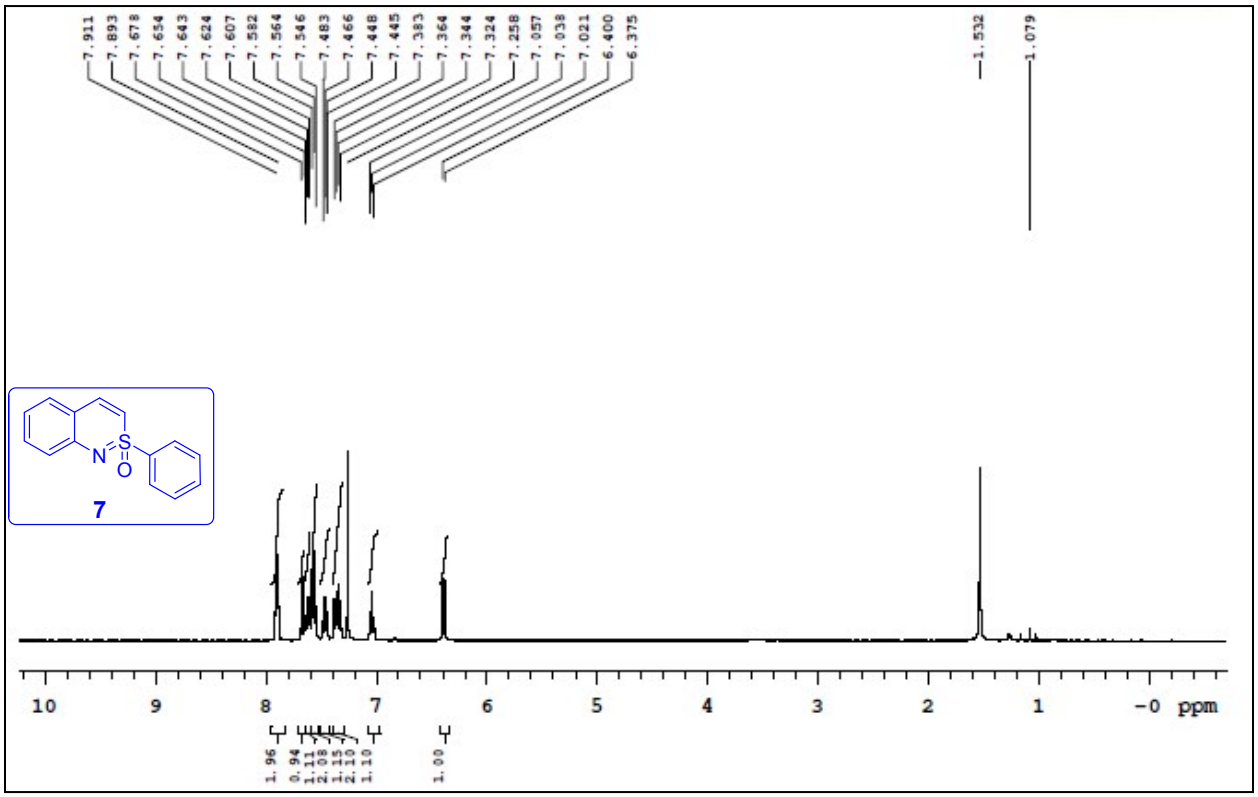
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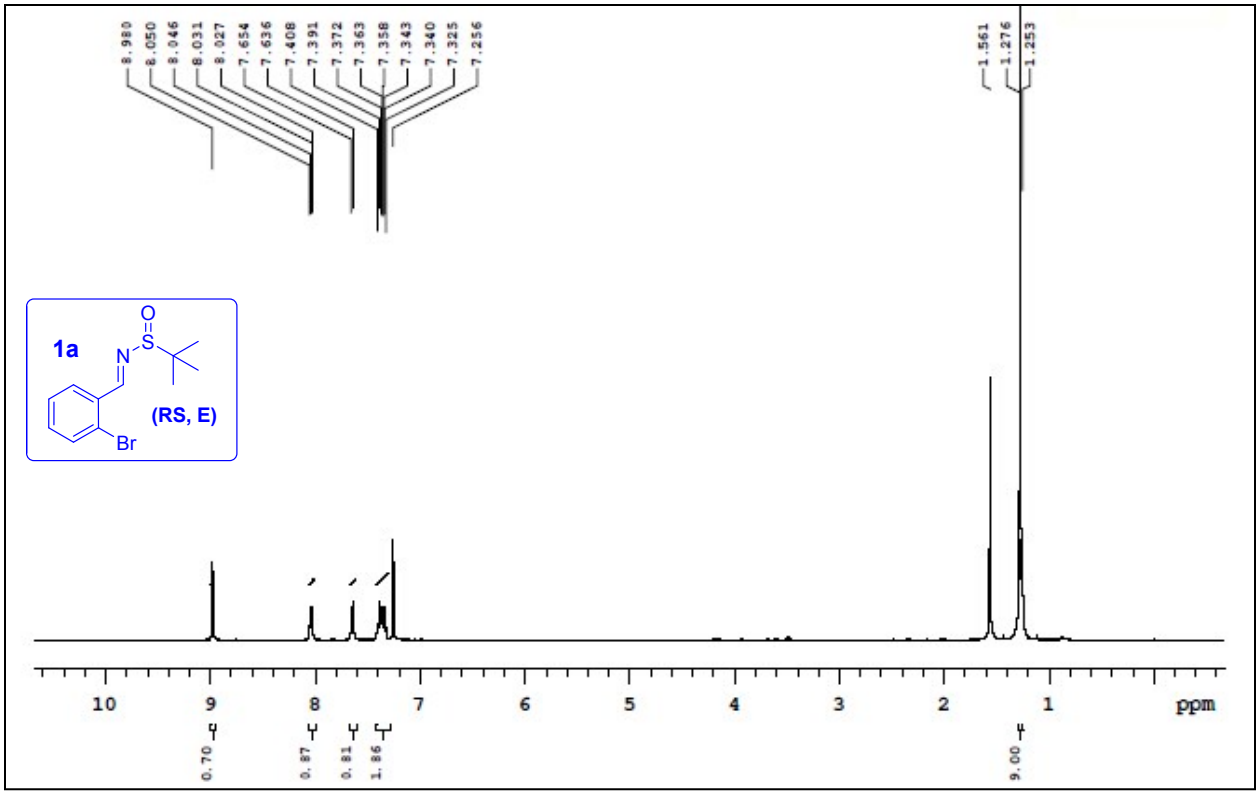
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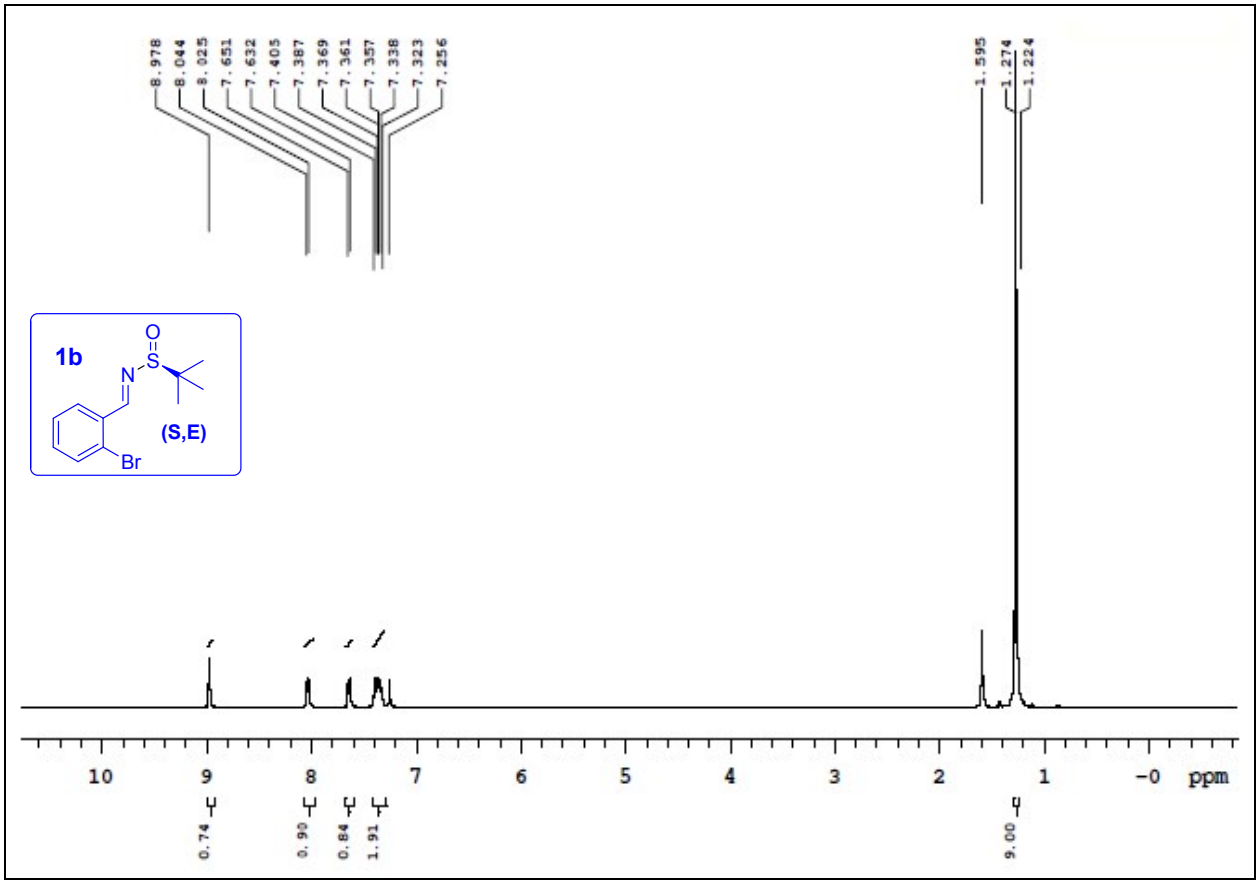
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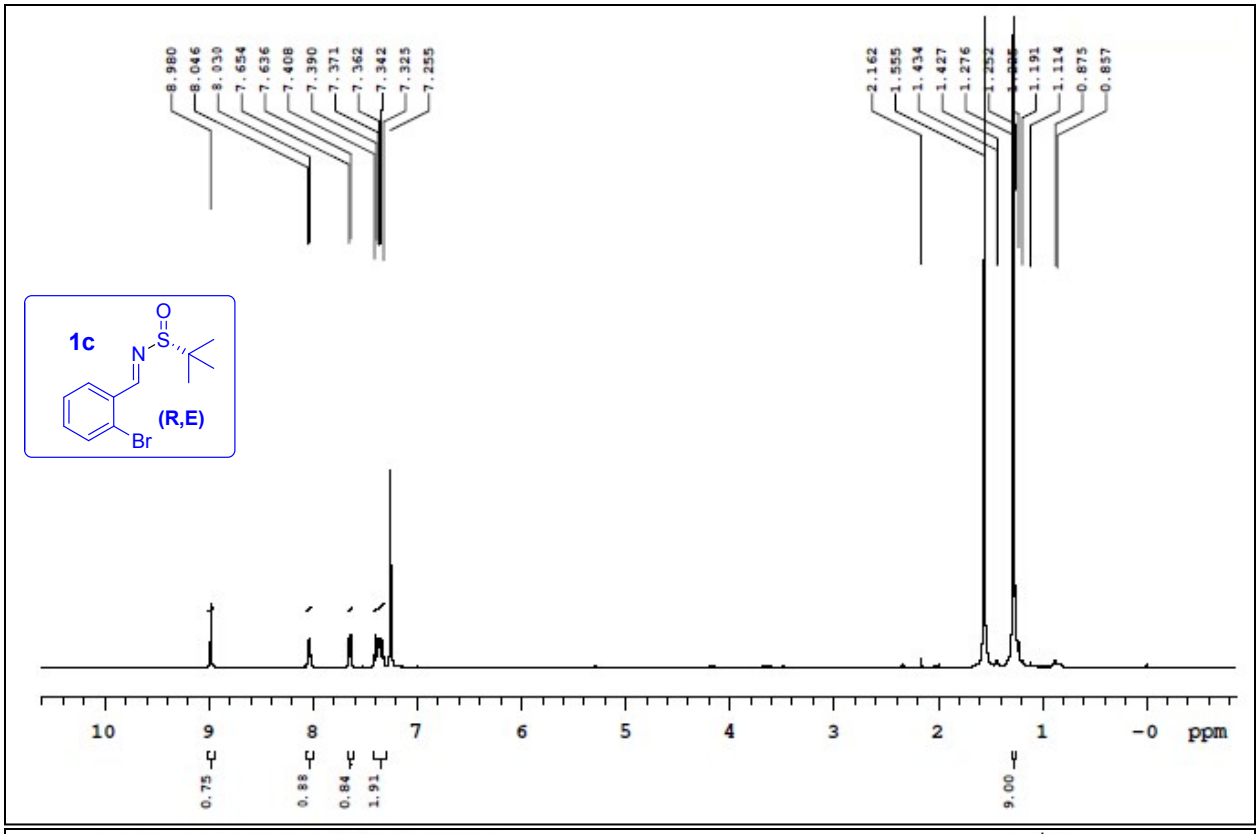
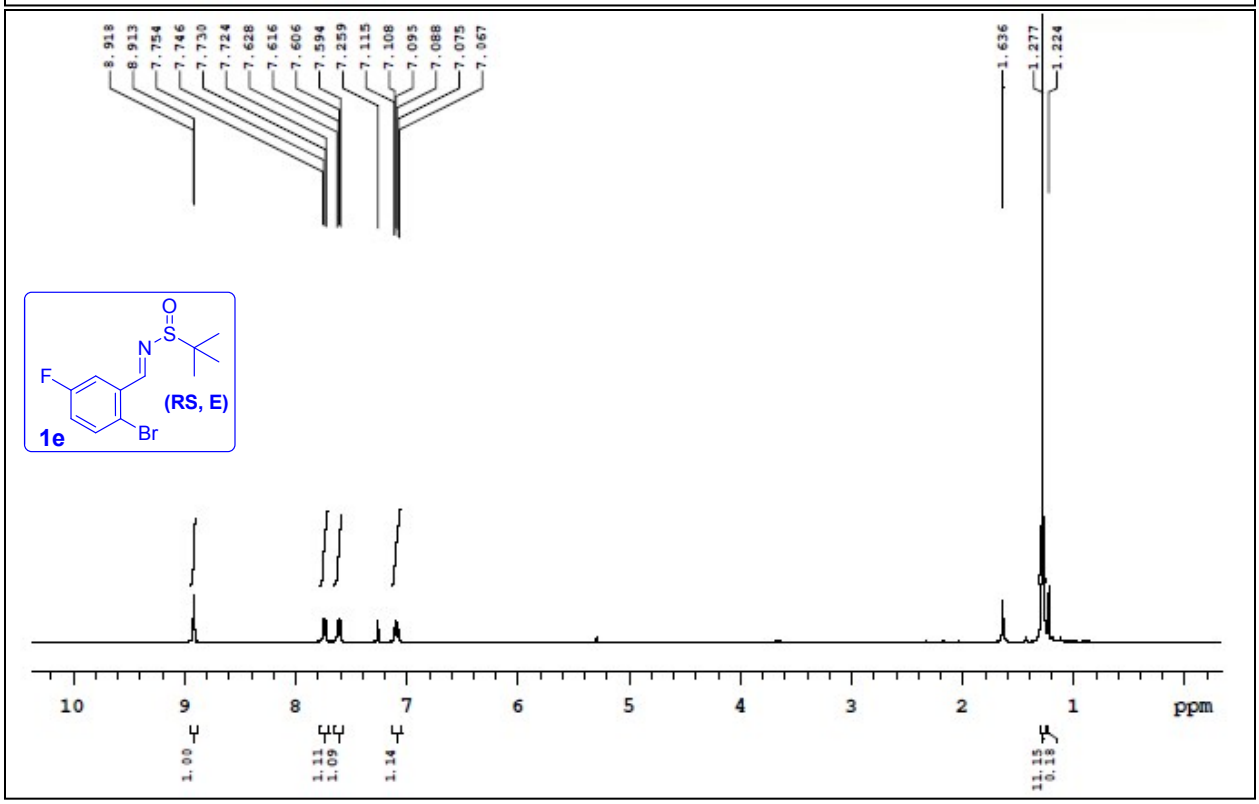
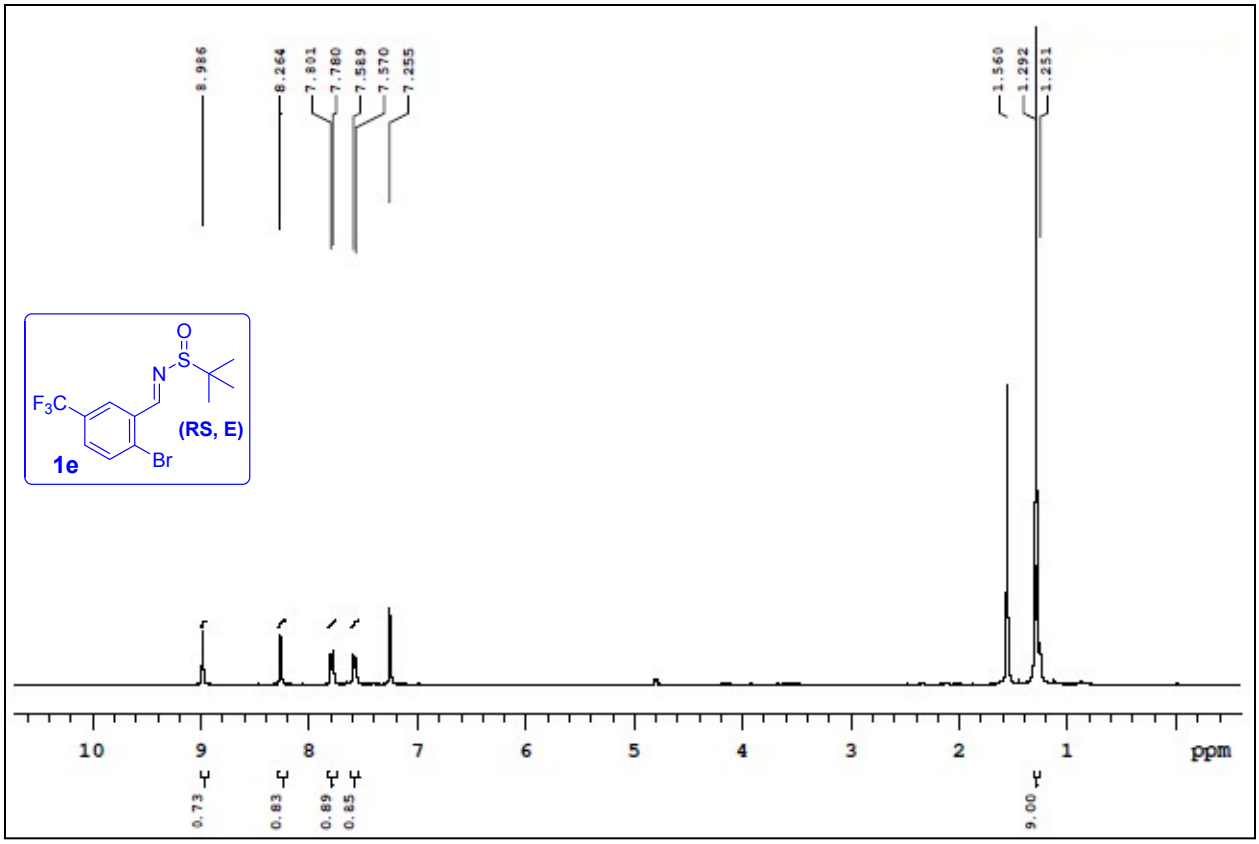
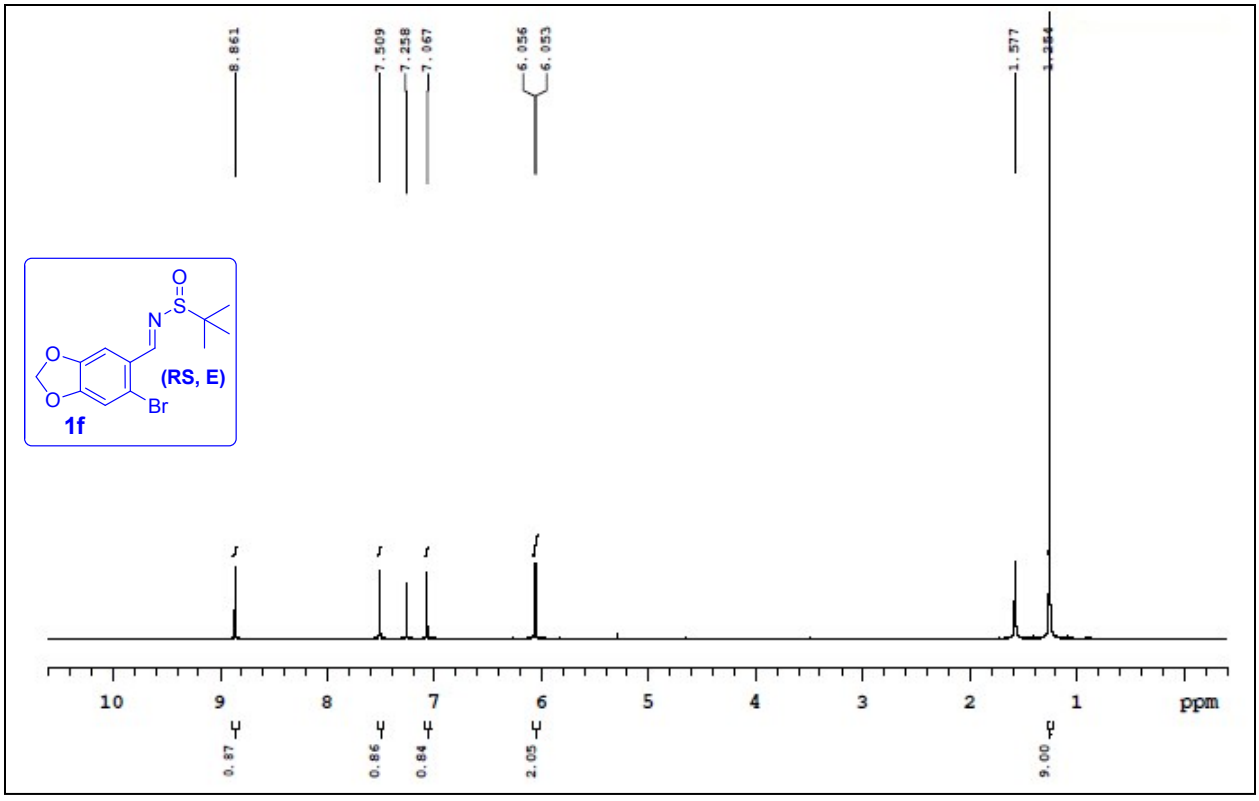
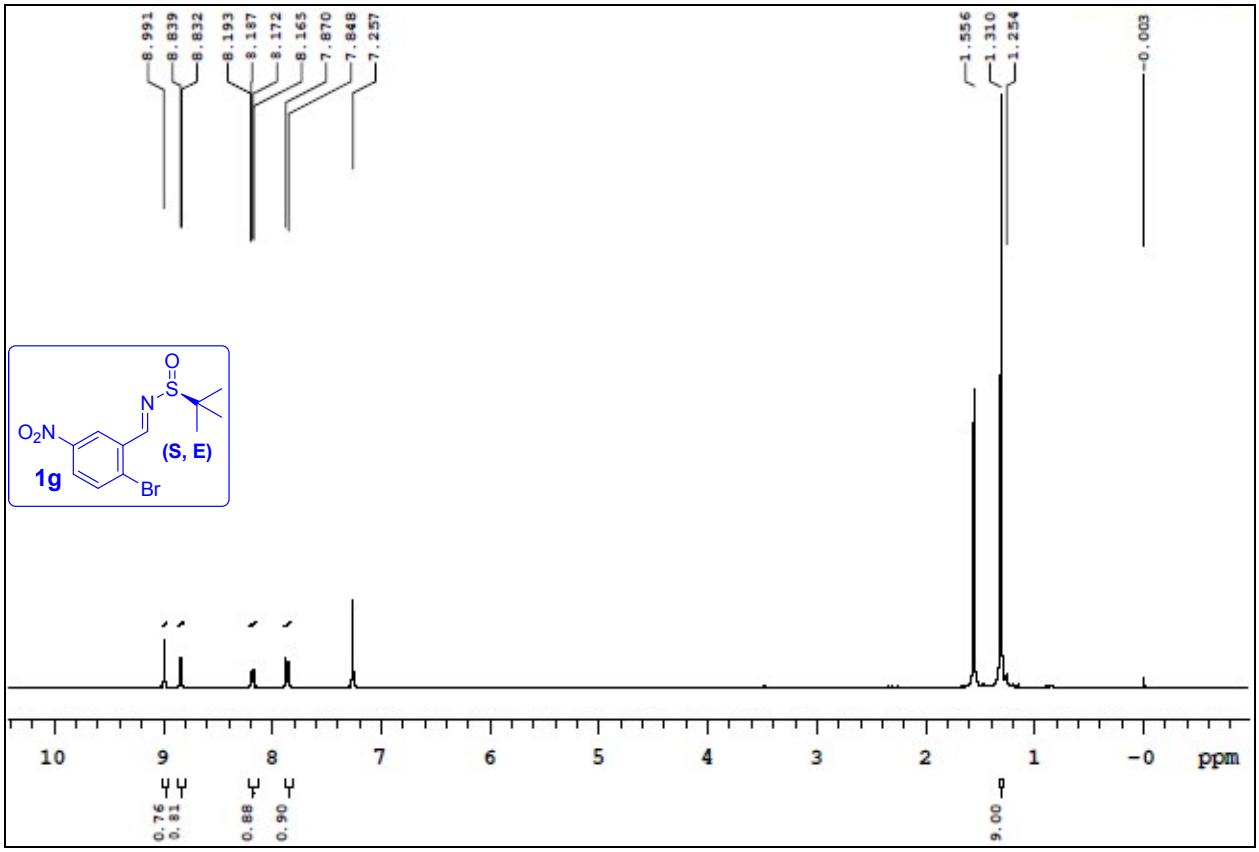
1b
(S,E)
Br
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.74
0.90
0.84
1.91
9.00

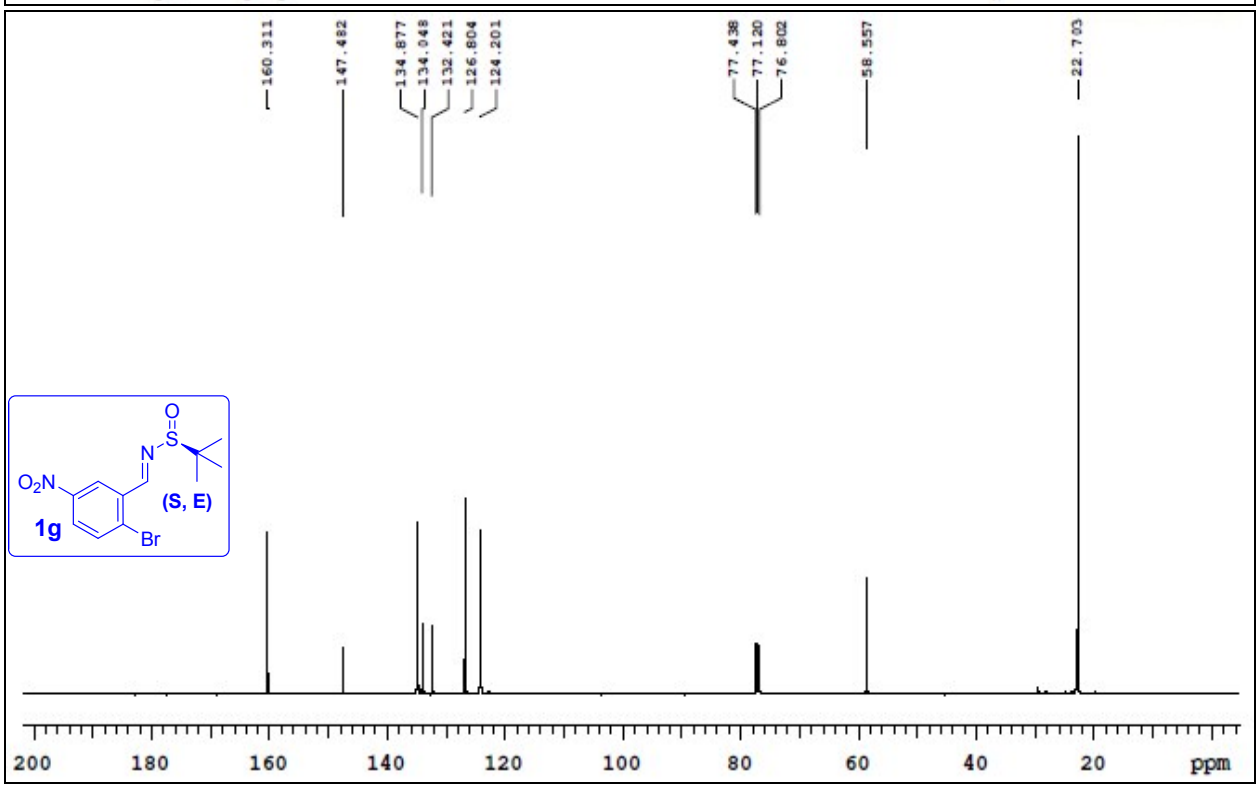

8.980
8.046
8.030
7.654
7.636
7.408
7.390
7.371
7.362
7.342
7.325
7.255
2.162
1.555
1.434
1.427
1.276
1.252
1.191
1.114
0.875
0.857
1c
(R,E)
Br
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.75
0.88
0.84
1.91
9.00

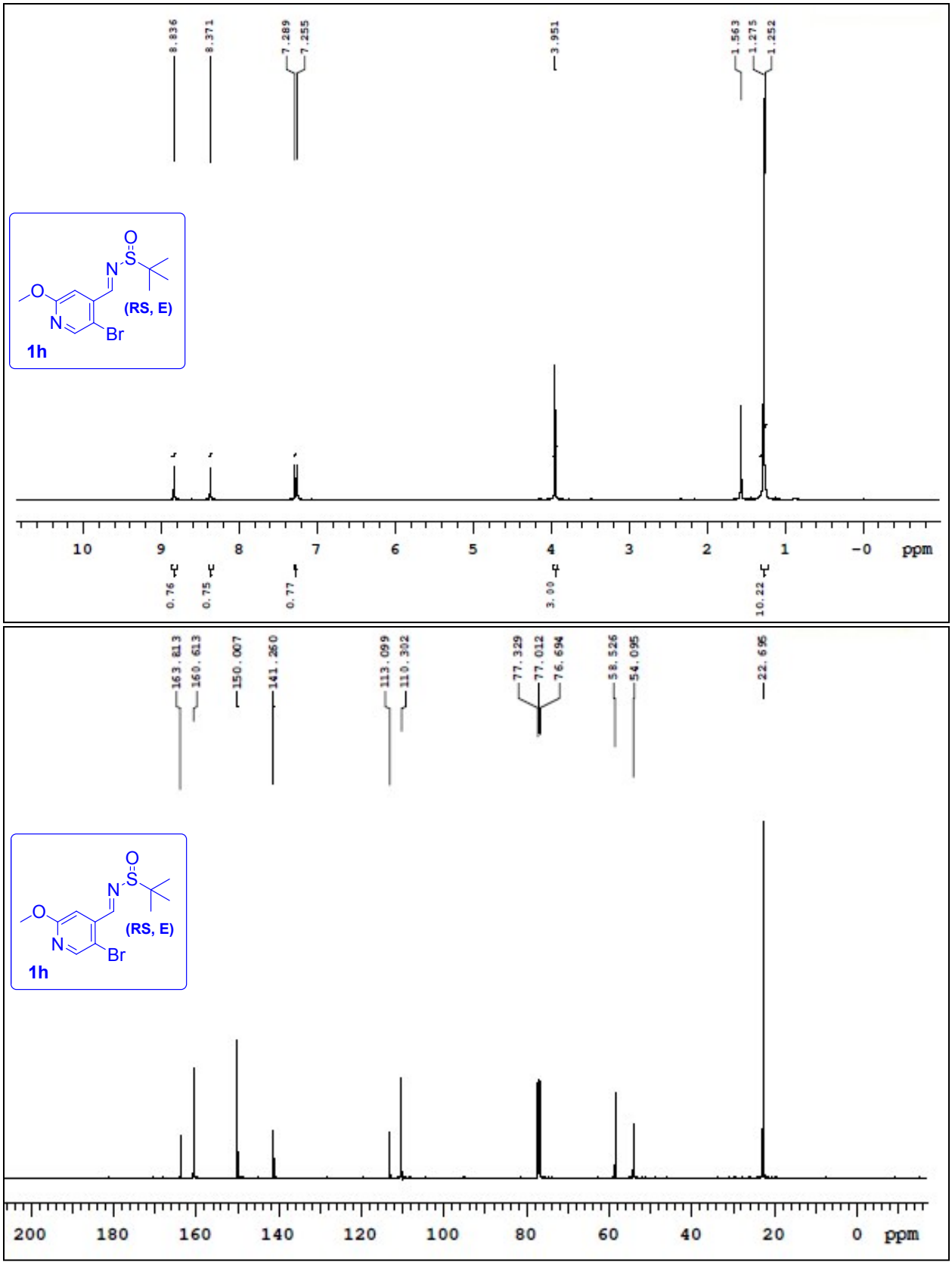

8.918
8.913
7.754
7.746
7.730
7.724
7.628
7.616
7.606
7.594
7.259
7.115
7.108
7.095
7.088
7.075
7.067
1.636
1.277
1.224
(RS, E)
1e
F
Br
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.11
1.09
1.14
11.15
0.18

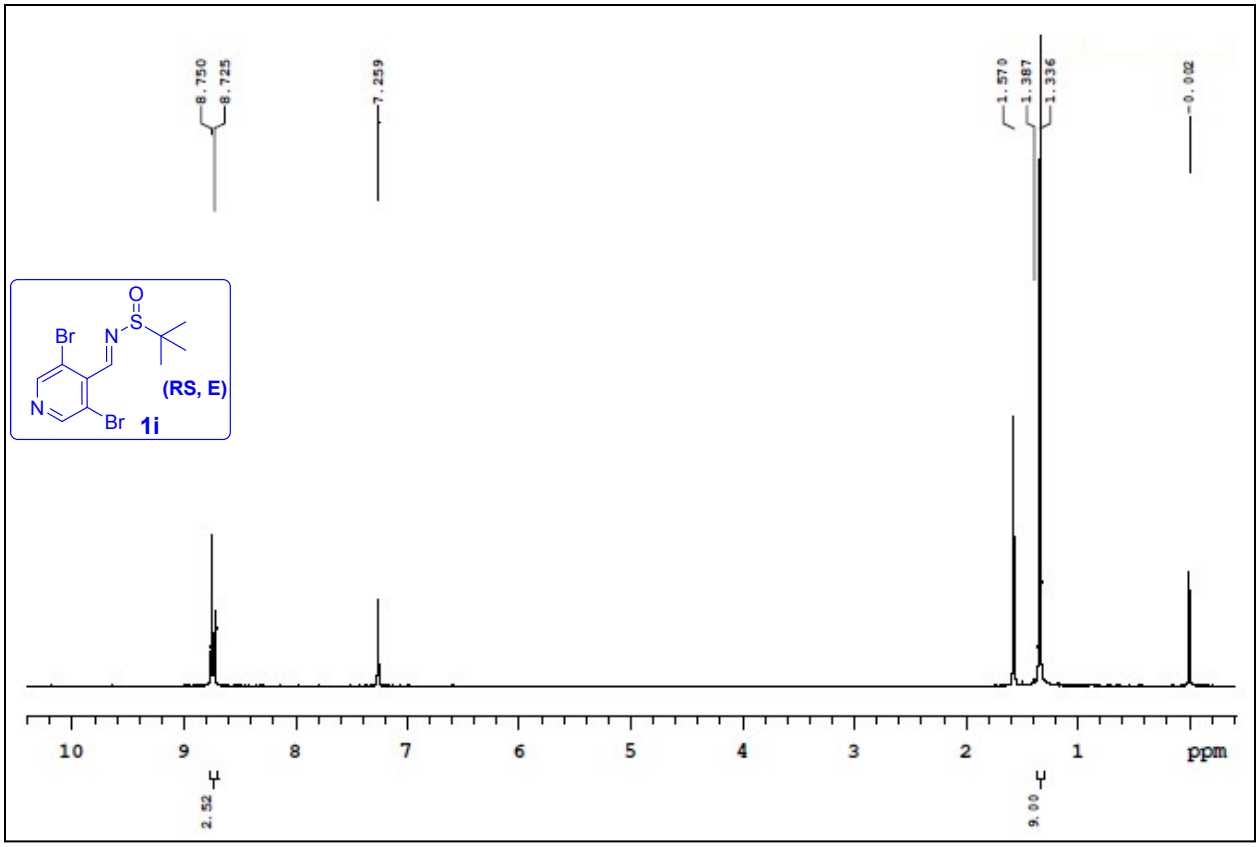

8.986
8.264
7.801
7.780
7.589
7.570
7.255
1.560
1.292
1.251
O
S
N
F3C
Br
(RS, E)
1e
10
9
8
7
6
5
4
3
2
1
ppm
0.73
0.83
0.89
0.85
9.00

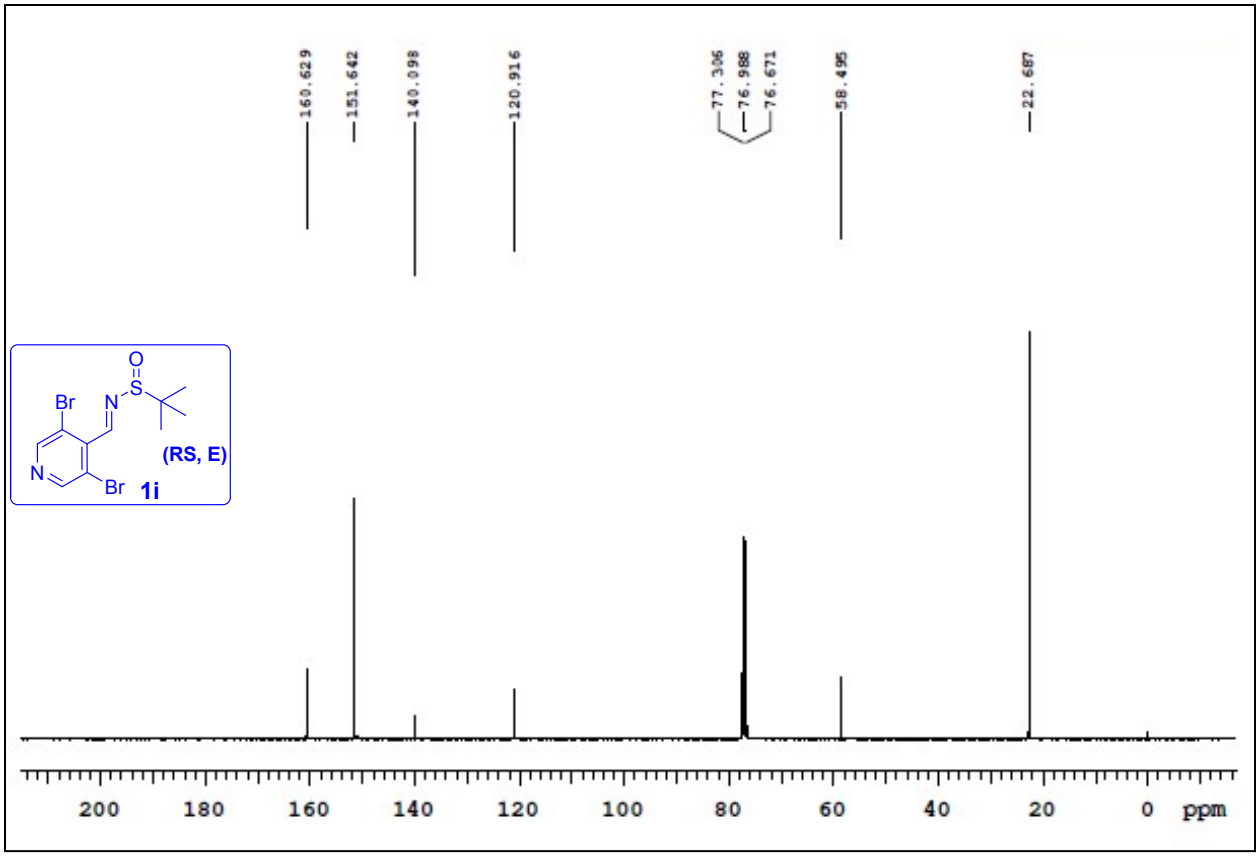

8.861
7.509
7.258
7.067
6.056
6.053
1.577
1.284
O
S
N
O
O
Br
(RS, E)
1f
10
9
8
7
6
5
4
3
2
1
ppm
0.87
0.86
0.84
2.05
9.00

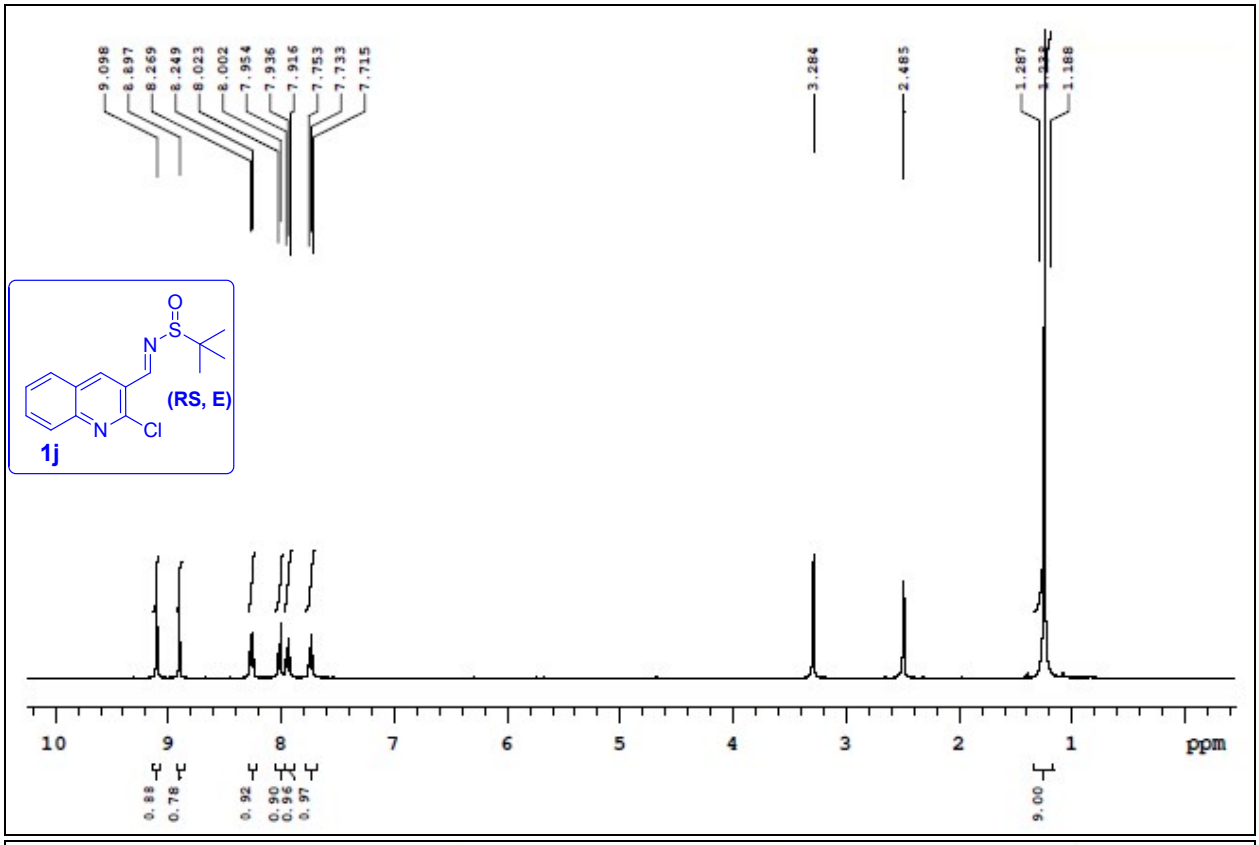

8.991
8.839
8.832
8.193
8.187
8.172
8.165
7.870
7.848
7.257
1.556
1.310
1.254
0.003
O
S
N
O2N
(S, E)
1g
Br
10
9
8
7
6
5
4
3
2
1
0
ppm
0.76
0.81
0.88
0.90
9.00

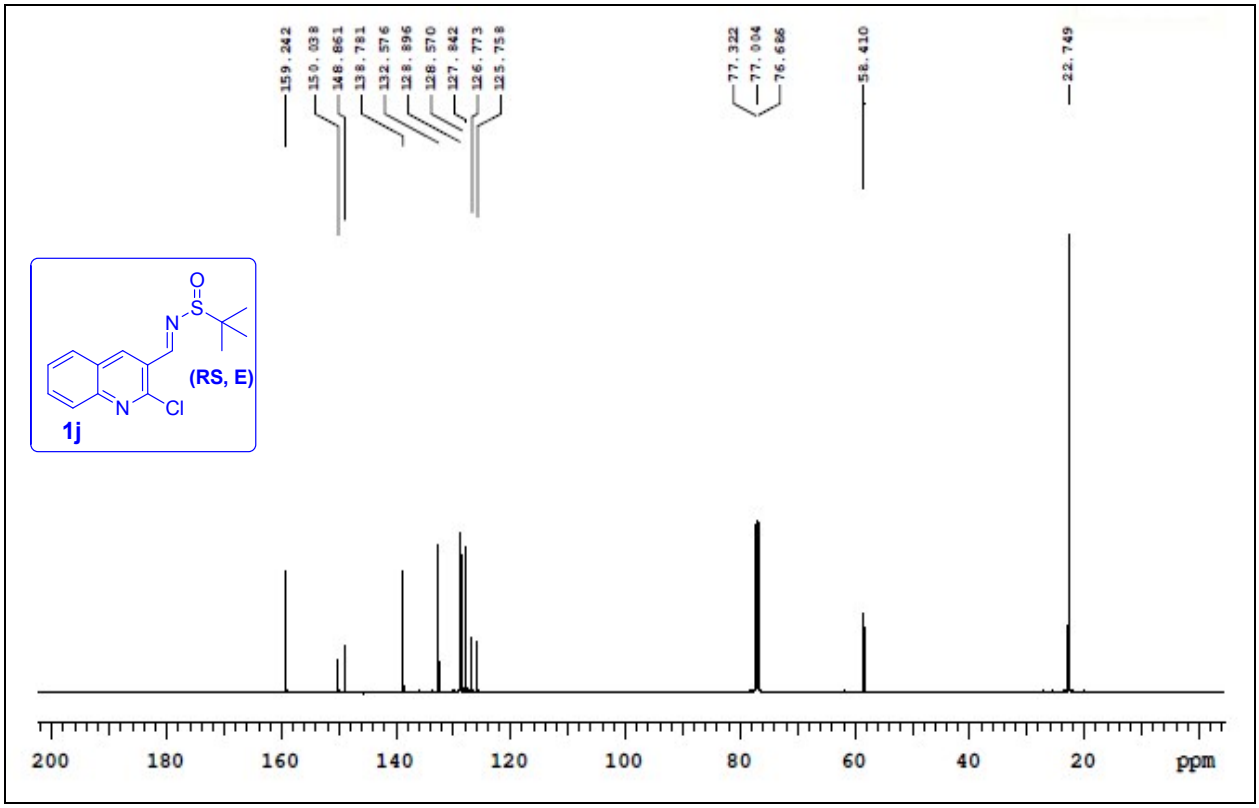

160.311
147.482
134.877
134.048
132.421
126.804
124.201
77.438
77.120
76.802
58.557
22.703
O
S
N
O2N
(S, E)
1g
Br
200
180
160
140
120
100
80
60
40
20
ppm

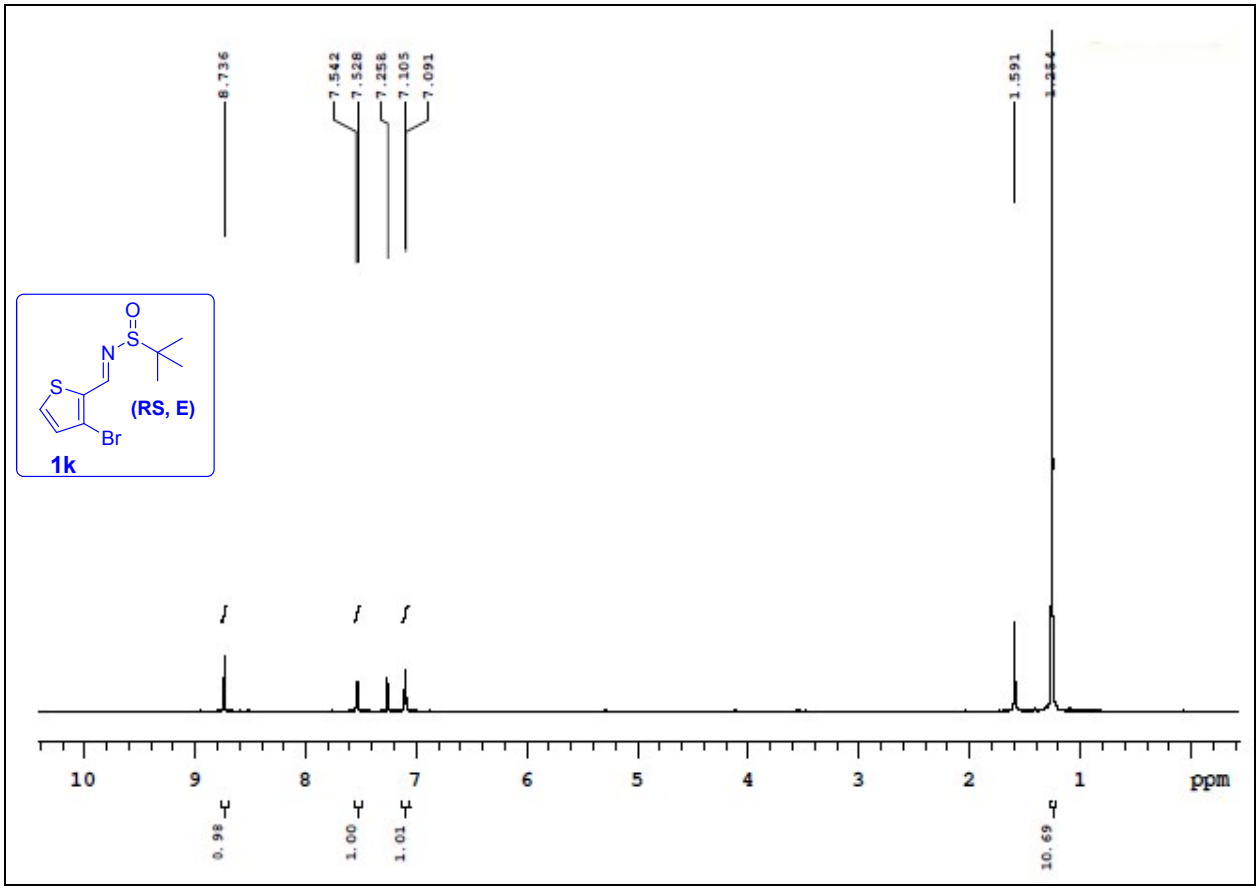

8.836
8.371
7.289
7.255
3.951
1.563
1.275
1.252
(RS, E)
1h
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.76
0.75
0.77
3.00
10.22
163.813
160.613
150.007
141.260
113.099
110.302
77.329
77.012
76.694
58.526
54.095
22.695
(RS, E)
1h
200
180
160
140
120
100
80
60
40
20
0
ppm

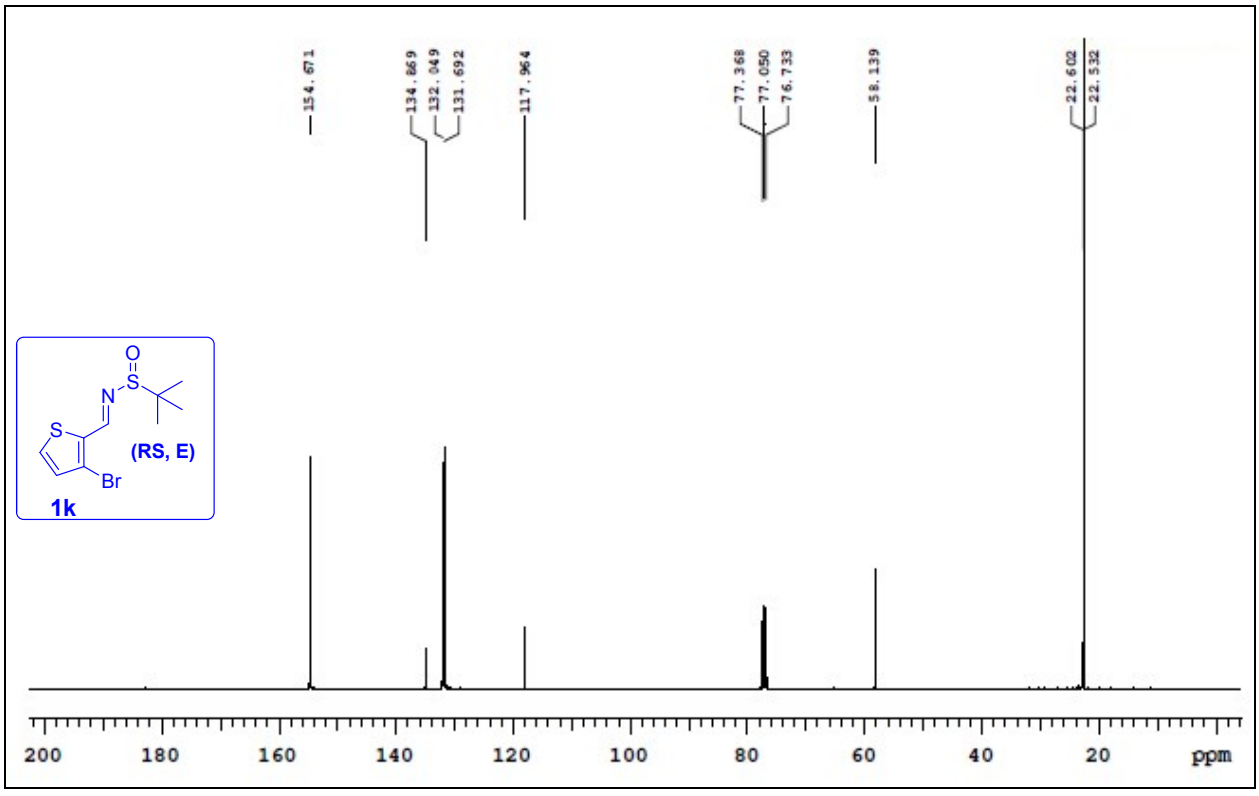

8.750
8.725
7.259
1.570
1.387
1.336
0.002
Br
N
O
S
Br
(RS, E)
1i
10
9
8
7
6
5
4
3
2
1
ppm
2.52
9.00

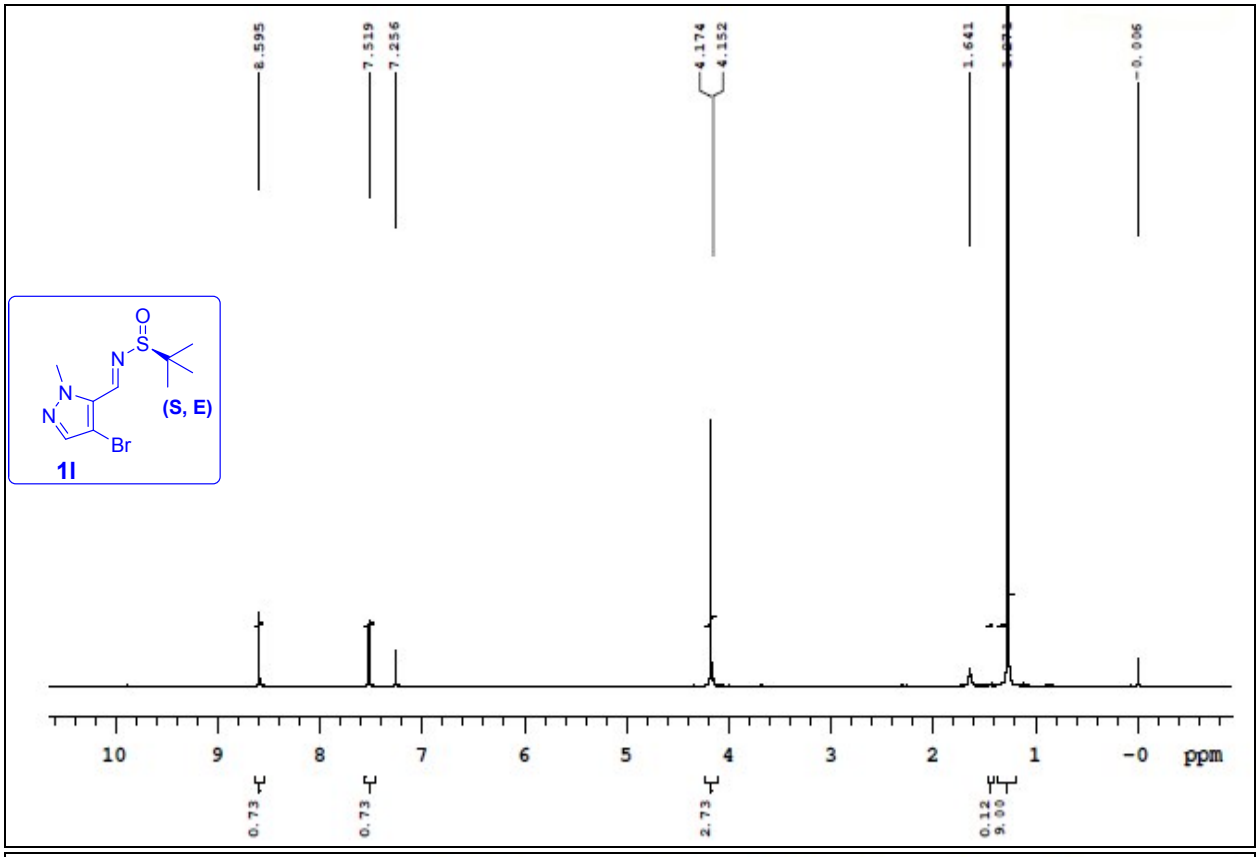

160.629
151.642
140.098
120.916
77.306
76.988
76.671
58.495
22.687
Br
N
O
S
Br
(RS, E)
1i
200
180
160
140
120
100
80
60
40
20
0
ppm

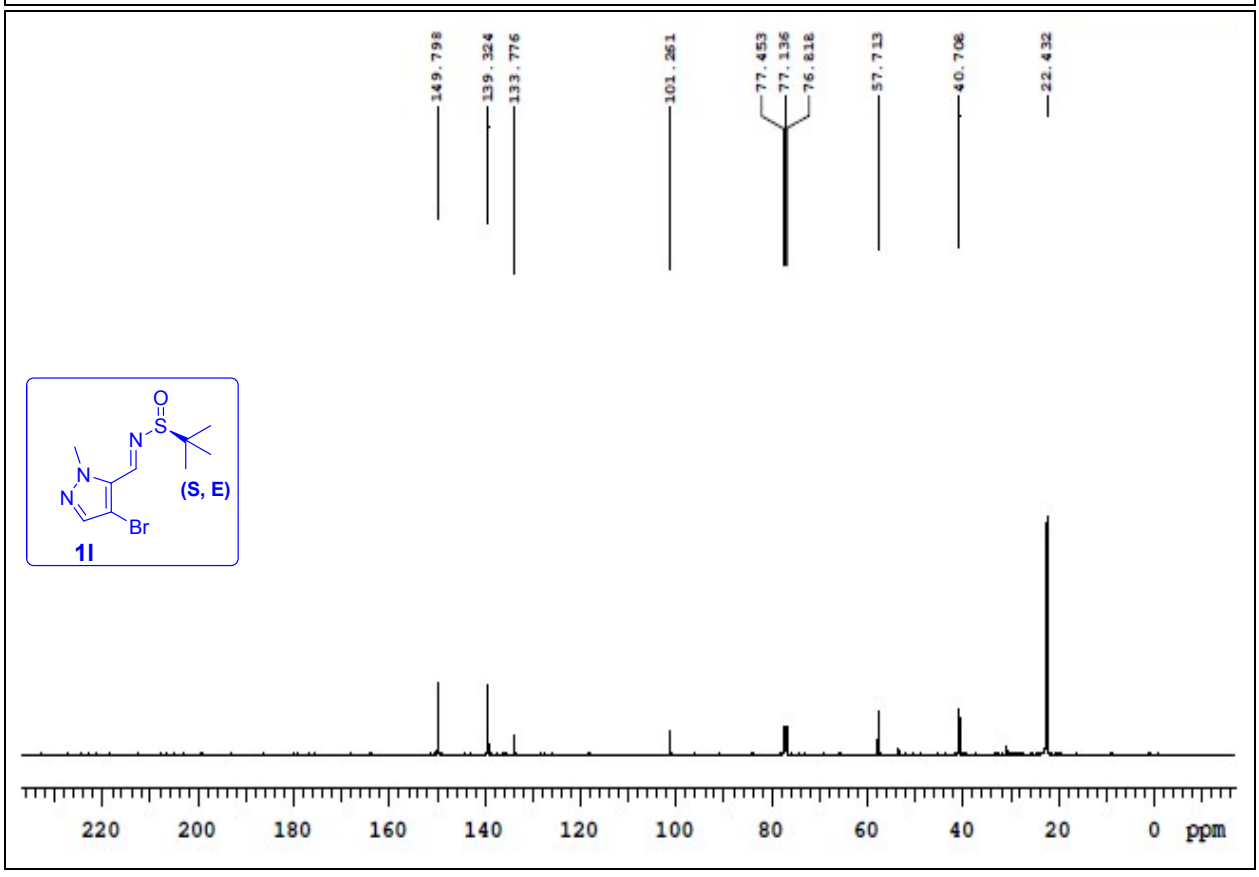

9.098
8.897
8.269
8.249
8.023
8.002
7.954
7.936
7.916
7.753
7.733
7.715
3.284
2.485
1.287
1.188
(RS, E)
1j
10
9
8
7
6
5
4
3
2
1
ppm
0.88
0.78
0.92
0.90
0.96
0.97
9.00

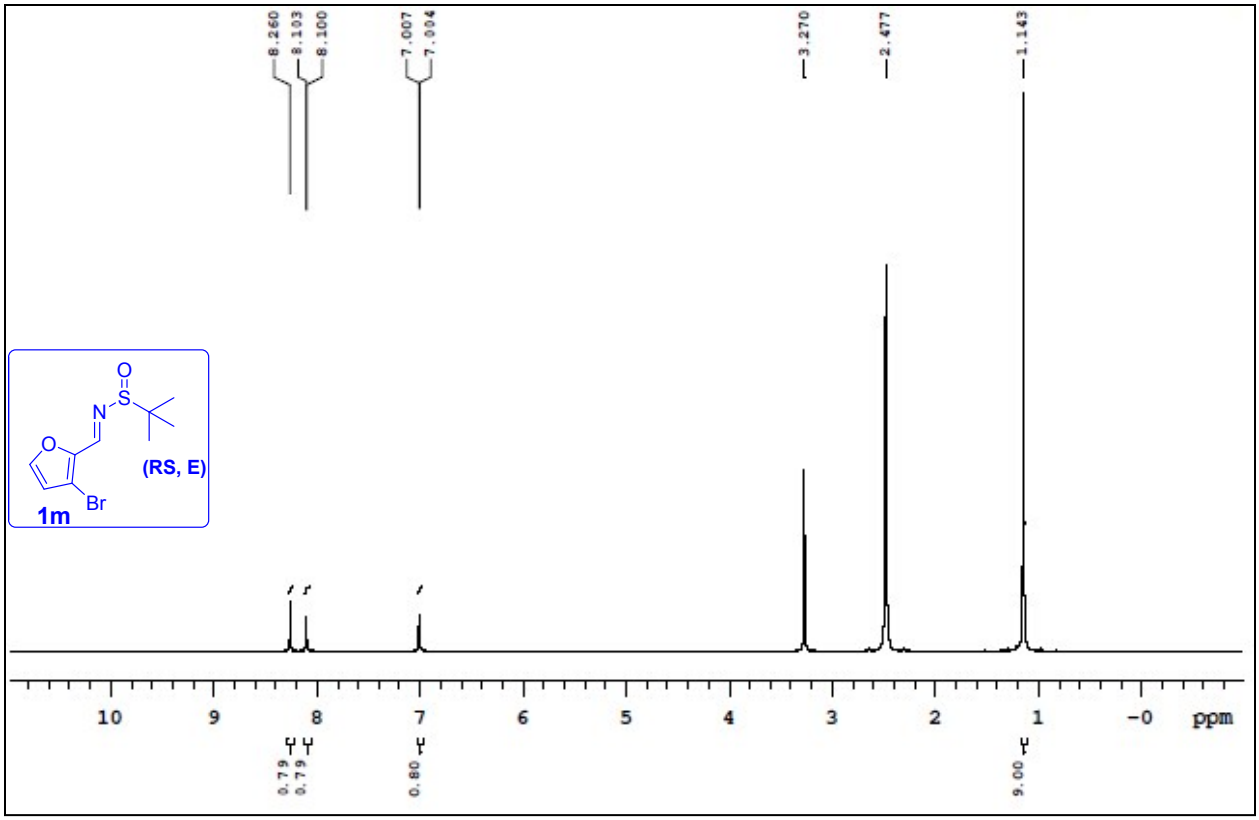

159.242
150.038
148.861
138.781
132.576
128.896
128.570
127.842
126.773
125.758
77.322
77.004
76.686
58.410
22.749
(RS, E)
1j
200
180
160
140
120
100
80
60
40
20
ppm

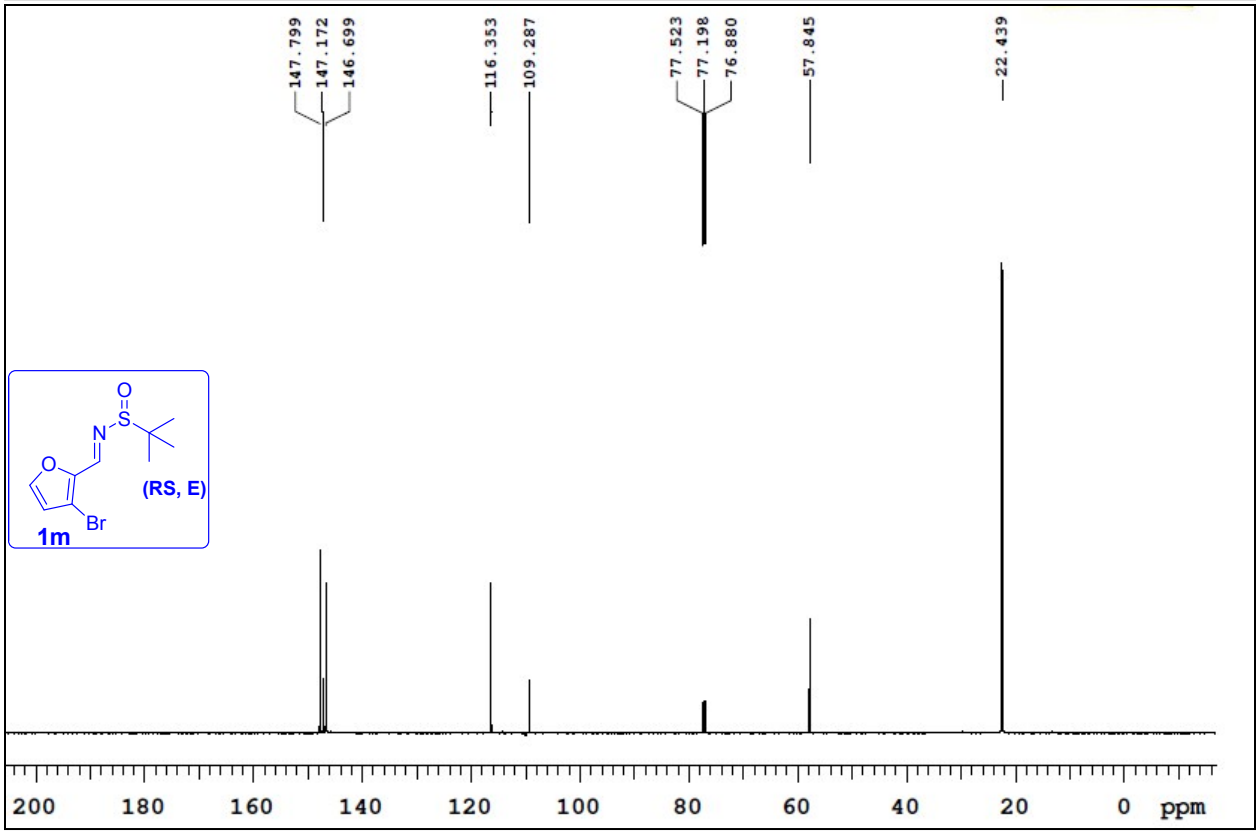

8.736
7.542
7.528
7.258
7.105
7.091
1.591
1.284
(RS, E)
1k
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.01
10.69

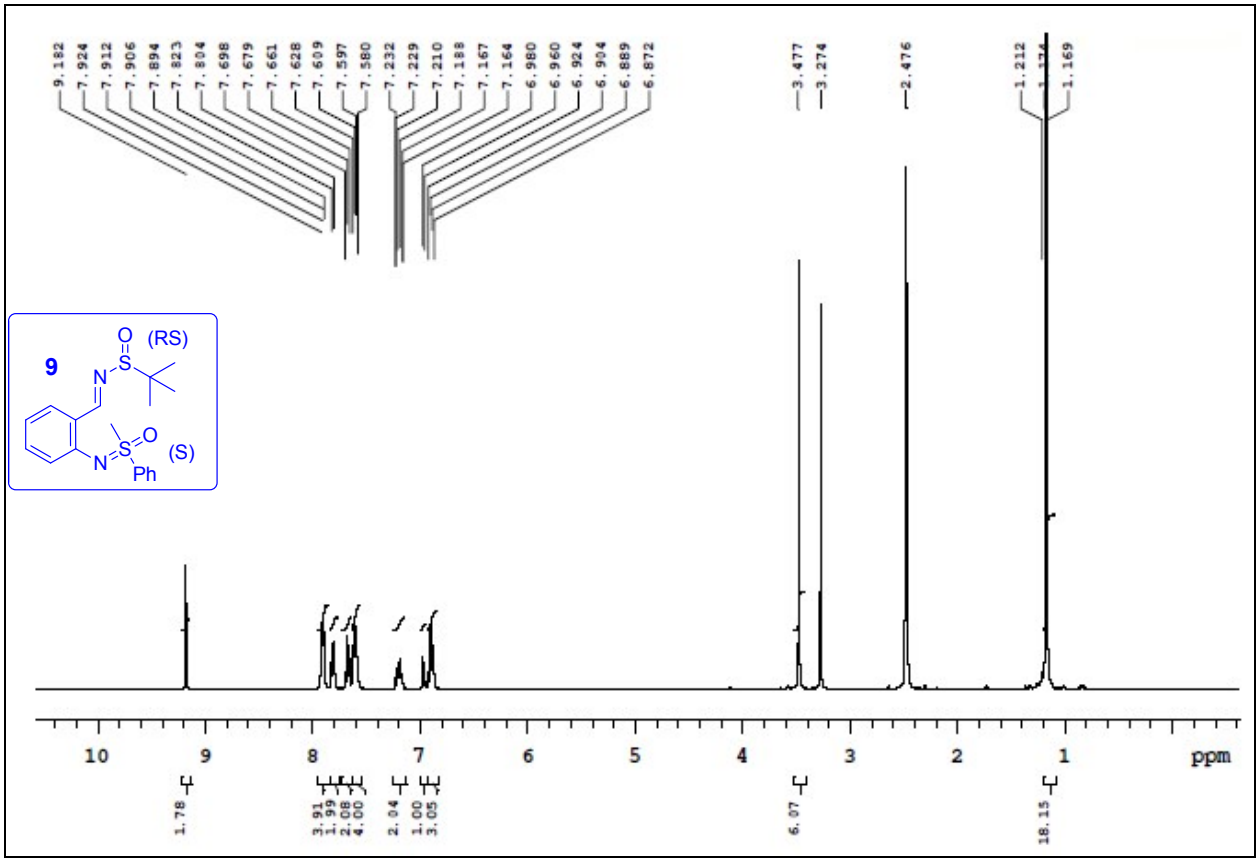

154.671
134.869
132.049
131.692
117.964
77.368
77.050
76.733
58.139
22.602
22.532
(RS, E)
1k
200
180
160
140
120
100
80
60
40
20
ppm

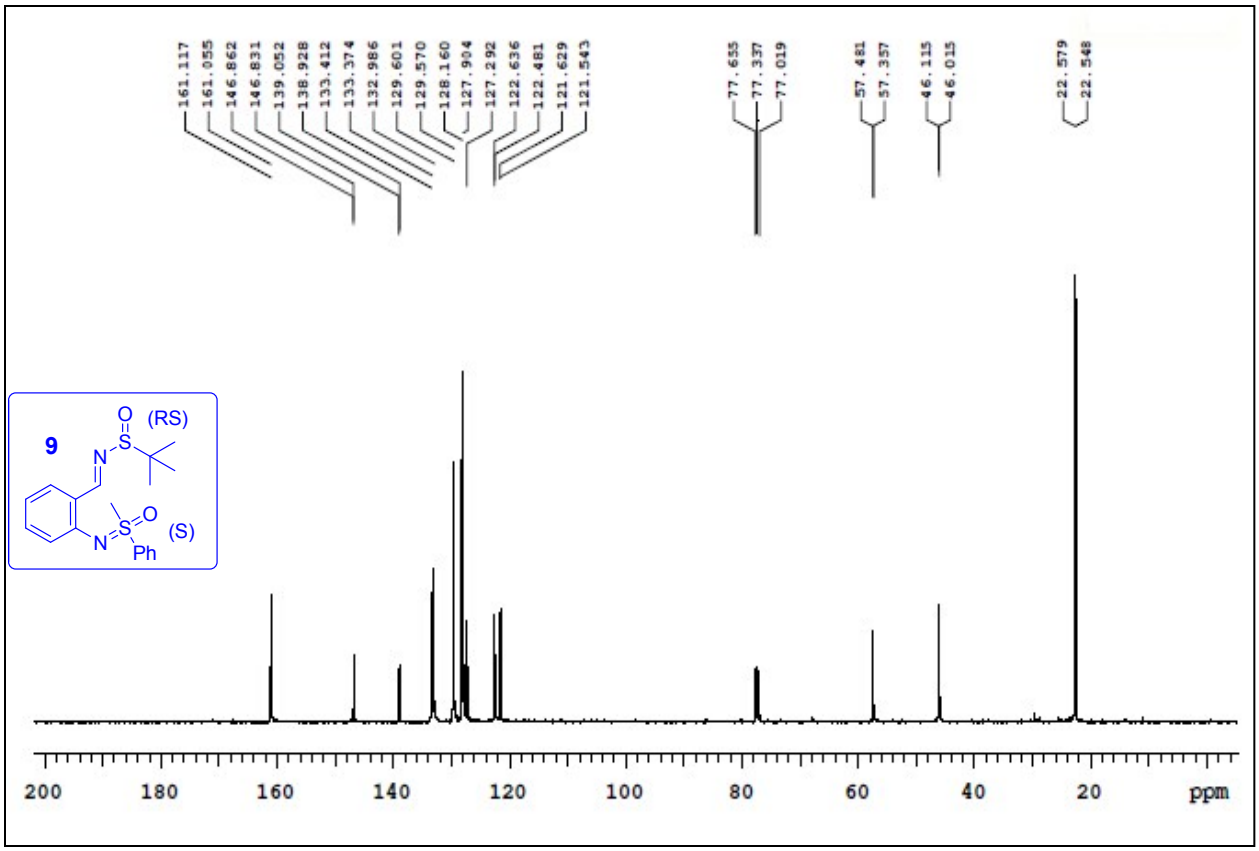

8.595
7.519
7.256
4.174
4.152
1.641
0.006
(S, E)
Br
1l
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.73
0.73
2.73
0.12
9.00


149.798
139.324
133.776
101.261
77.453
77.136
76.818
57.713
40.708
22.432
(S, E)
Br
1l
220
200
180
160
140
120
100
80
60
40
20
0
ppm


8.260
8.103
8.100
7.007
7.004
3.270
2.477
1.143
(RS, E)
1m
Br
10
9
8
7
6
5
4
3
2
1
−0
ppm
0.79
0.79
0.80
9.00


147.799
147.172
146.699
116.353
109.287
77.523
77.198
76.880
57.845
22.439
(RS, E)
1m
Br
200
180
160
140
120
100
80
60
40
20
0
ppm


9.182
7.924
7.912
7.906
7.894
7.823
7.804
7.698
7.679
7.661
7.628
7.609
7.597
7.580
7.232
7.229
7.210
7.188
7.167
7.164
6.980
6.960
6.924
6.904
6.889
6.872
3.477
3.274
2.476
1.212
1.174
1.169
9
(RS)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
ppm
1.78
3.91
1.99
2.08
4.00
2.04
1.00
3.05
6.07
18.15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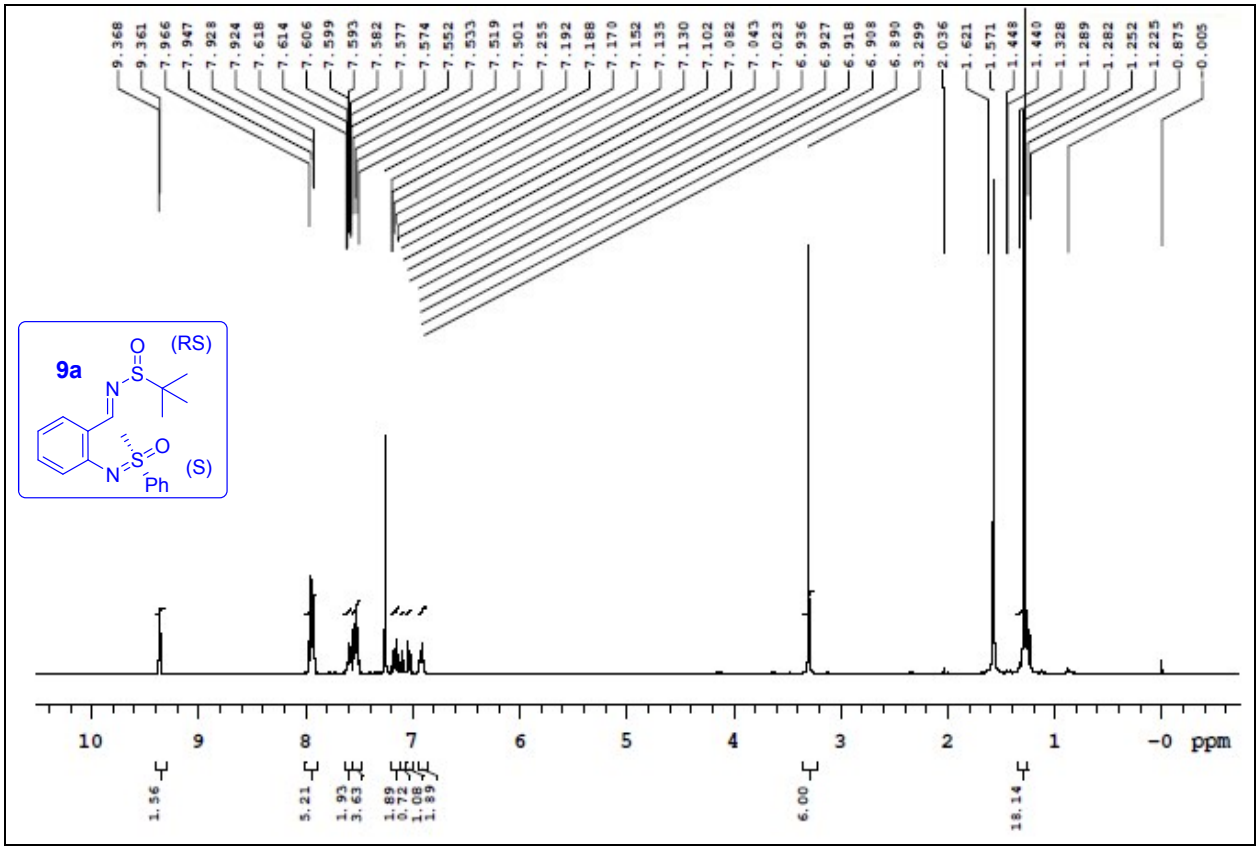
146.862
146.831
139.052
138.928
133.412
133.374
132.986
129.601
129.570
128.160
127.904
127.292
122.636
122.481
121.629
121.543
77.655
77.337
77.019
57.481
57.357
46.115
46.015
22.579
22.548
9
(RS)
(S)
Ph
200
180
160
140
120
100
80
60
40
20
ppm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9.361
7.966
7.947
7.928
7.924
7.618
7.614
7.606
7.599
7.593
7.582
7.577
7.574
7.552
7.533
7.519
7.301
7.255
7.192
7.188
7.170
7.152
7.135
7.130
7.102
7.082
7.043
7.023
6.936
6.927
6.918
6.938
6.890
3.299
2.036
1.621
1.571
1.448
1.440
1.328
1.289
1.282
1.252
1.225
0.875
0.005
9a
(RS)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
-0
ppm
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5.21
1.93
3.63
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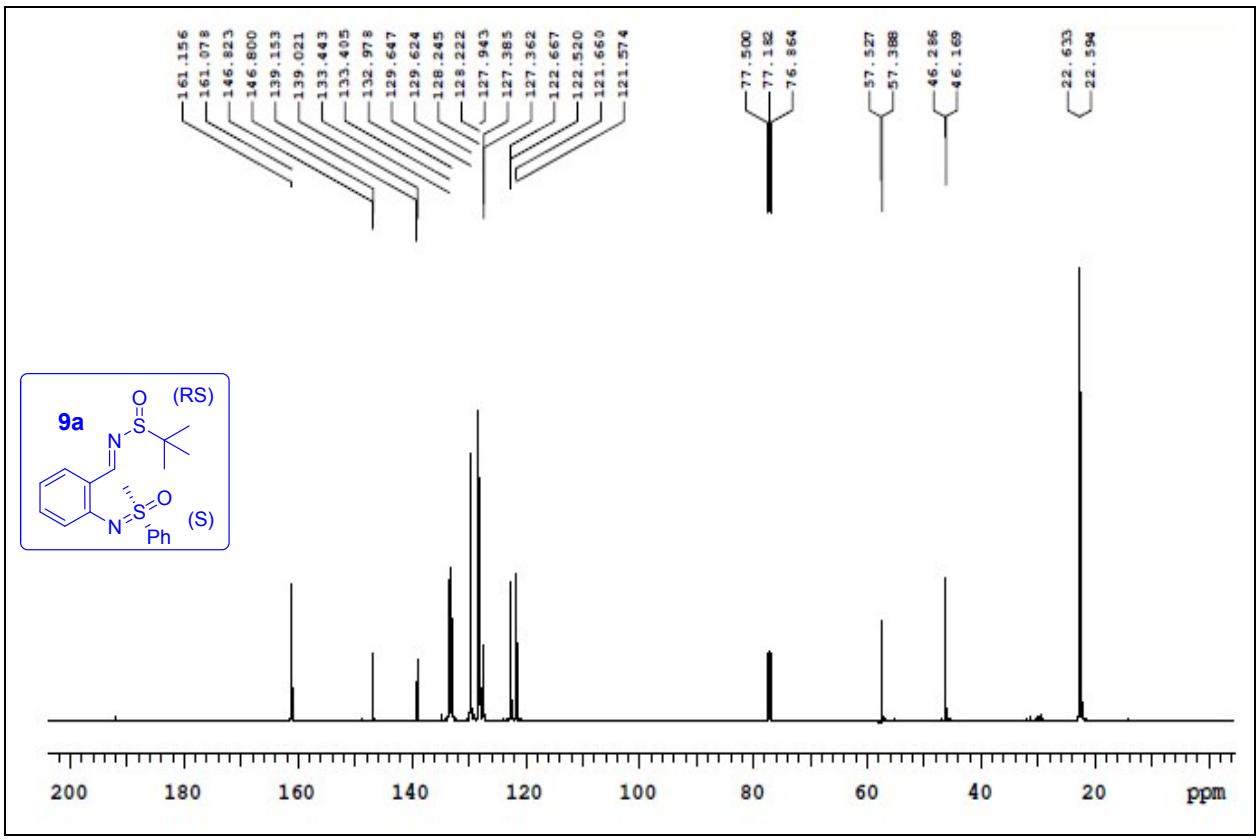
0.72
1.08
1.89
6.00
18.14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161.078
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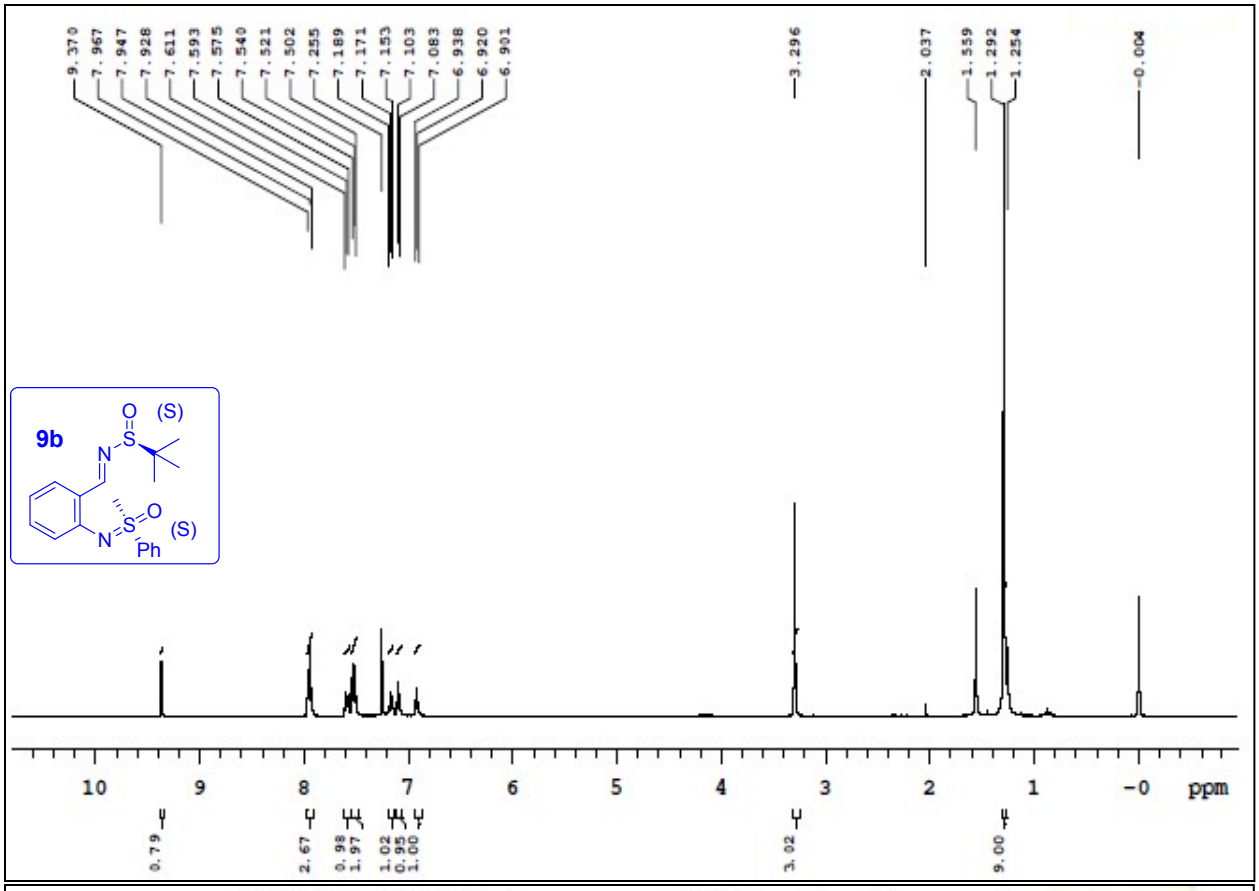
146.800
139.153
139.021
133.443
133.405
132.978
129.647
129.624
128.245
128.222
127.943
127.385
127.362
122.667
122.520
121.660
121.574
77.500
77.182
76.864
57.527
57.388
46.286
46.169
22.633
22.594
9a
(RS)
(S)
Ph
200
180
160
140
120
100
80
60
40
20
ppm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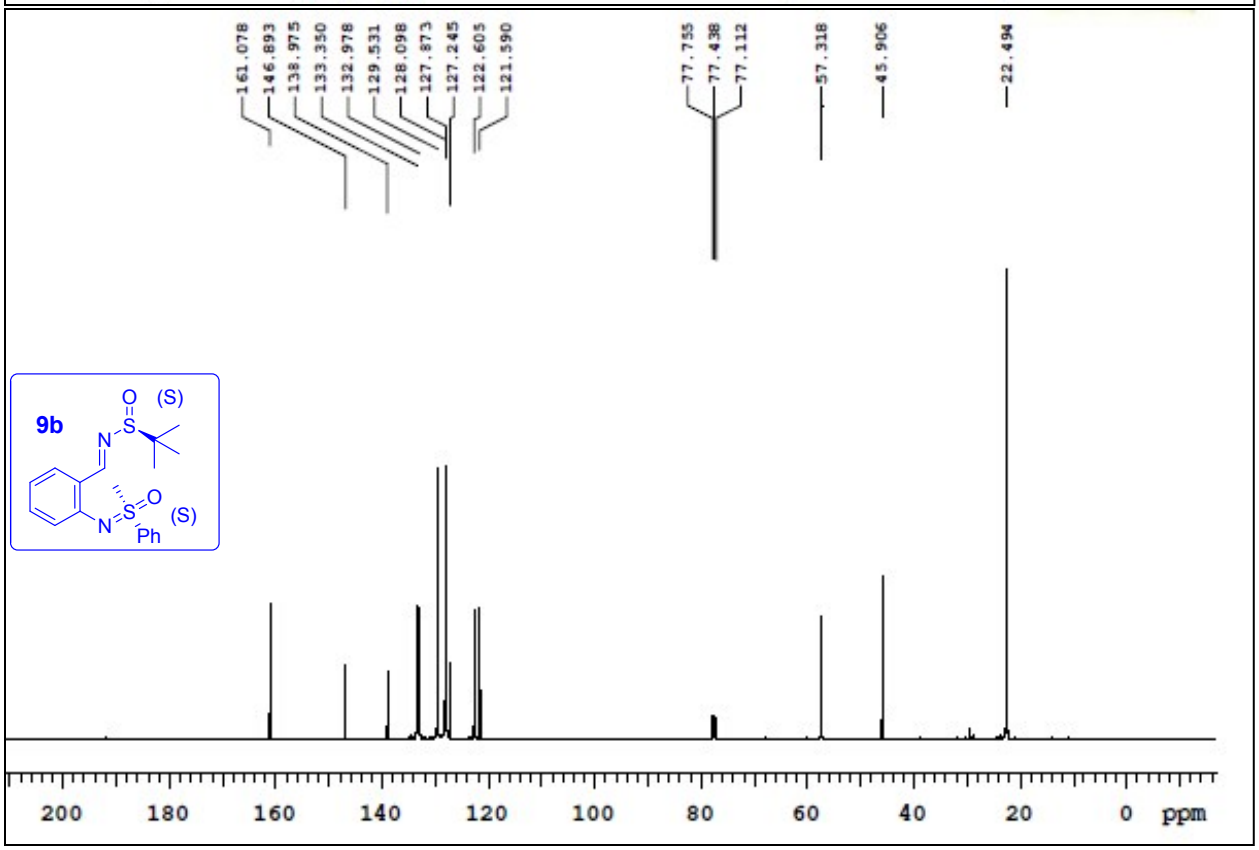
7.967
7.947
7.928
7.611
7.593
7.575
7.540
7.521
7.502
7.255
7.189
7.171
7.153
7.103
7.083
6.938
6.920
6.901
3.296
2.037
1.559
1.292
1.254
-0.004
9b
(S)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.79
2.67
0.98
1.97
1.02
0.95
1.00
3.02
9.00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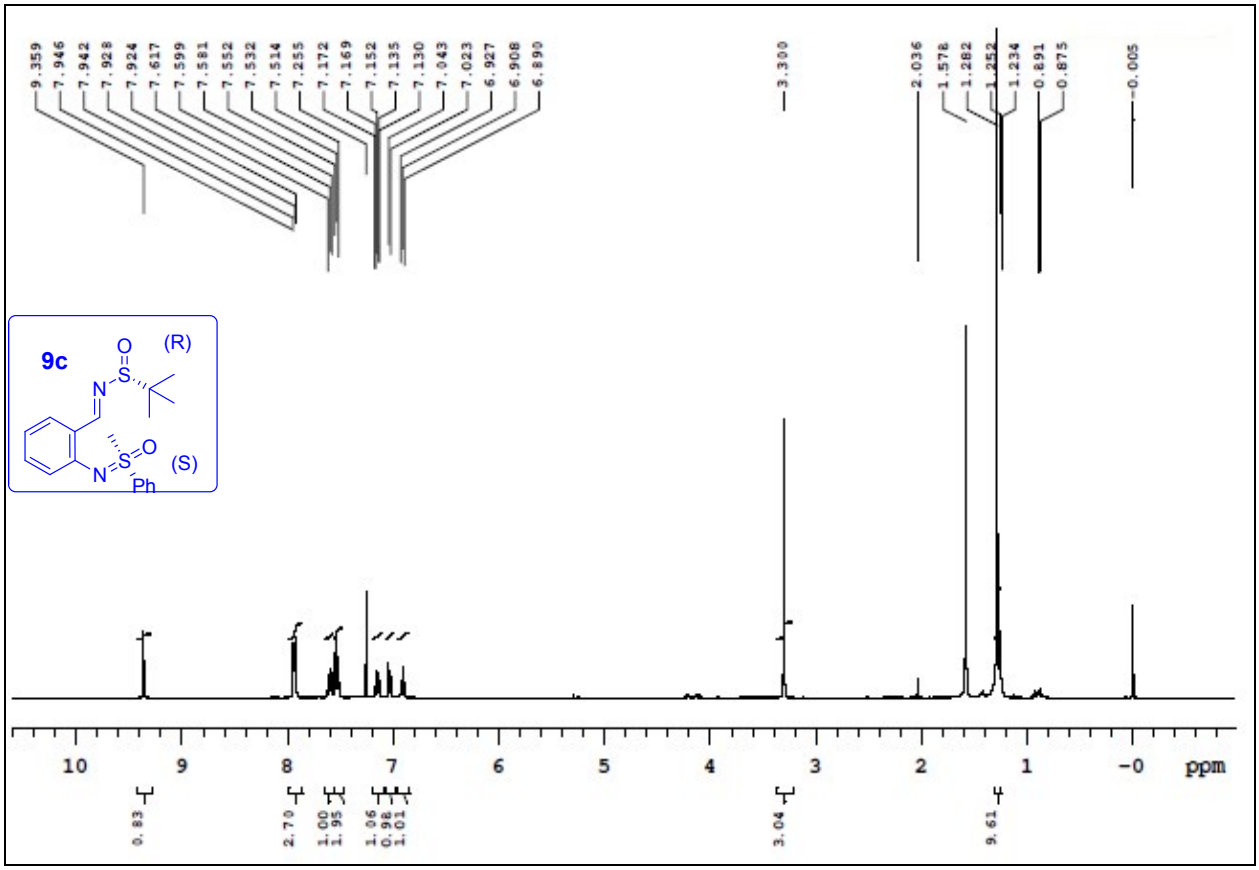
146.893
138.975
133.350
132.978
129.531
128.098
127.873
127.245
122.605
121.590
77.755
77.438
77.112
57.318
45.906
22.494
9b
(S)
(S)
Ph
200
180
160
140
120
100
80
60
40
20
0
ppm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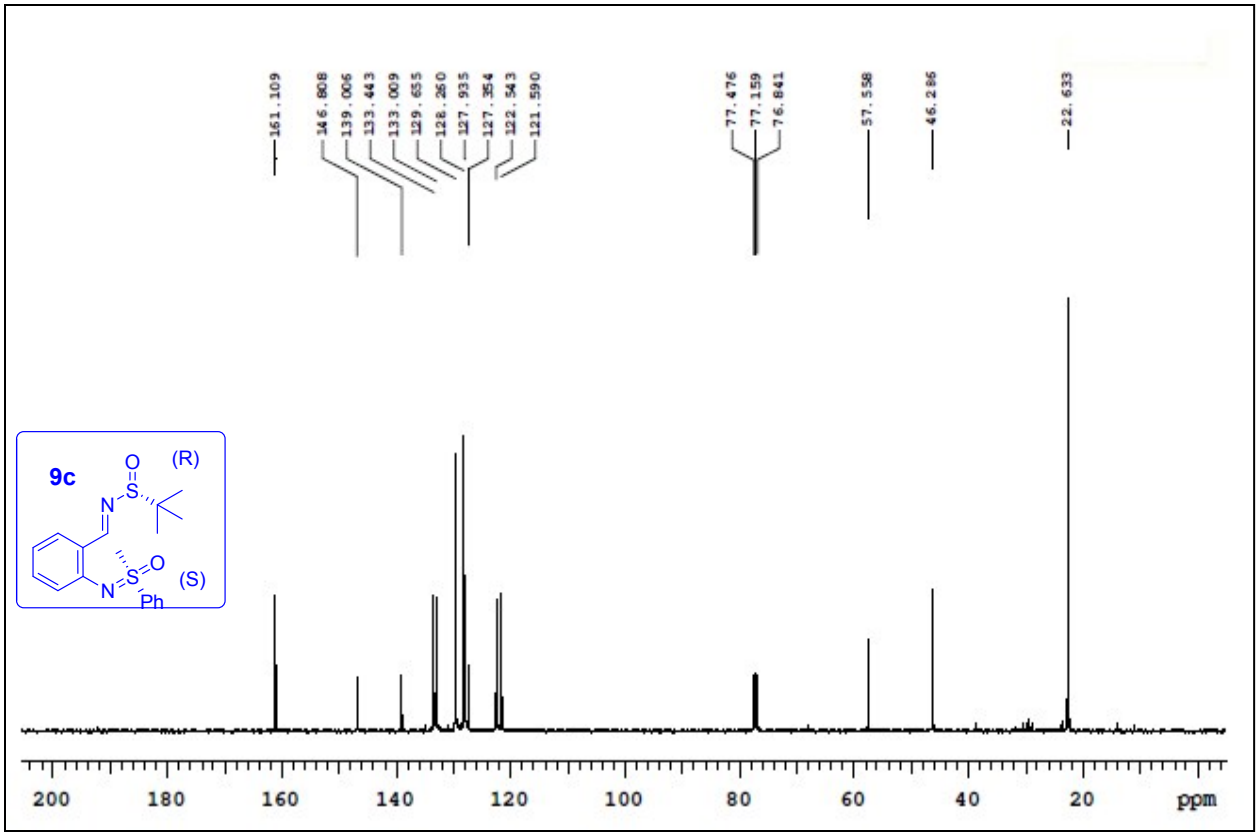
7.946
7.942
7.928
7.924
7.617
7.599
7.581
7.552
7.532
7.514
7.255
7.172
7.169
7.152
7.135
7.130
7.043
7.023
6.927
6.908
6.890
3.300
2.036
1.578
1.282
1.252
1.234
0.891
0.875
0.005
9c
(R)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
-0
ppm
0.83
2.70
1.00
1.95
1.06
0.98
1.01
3.04
9.61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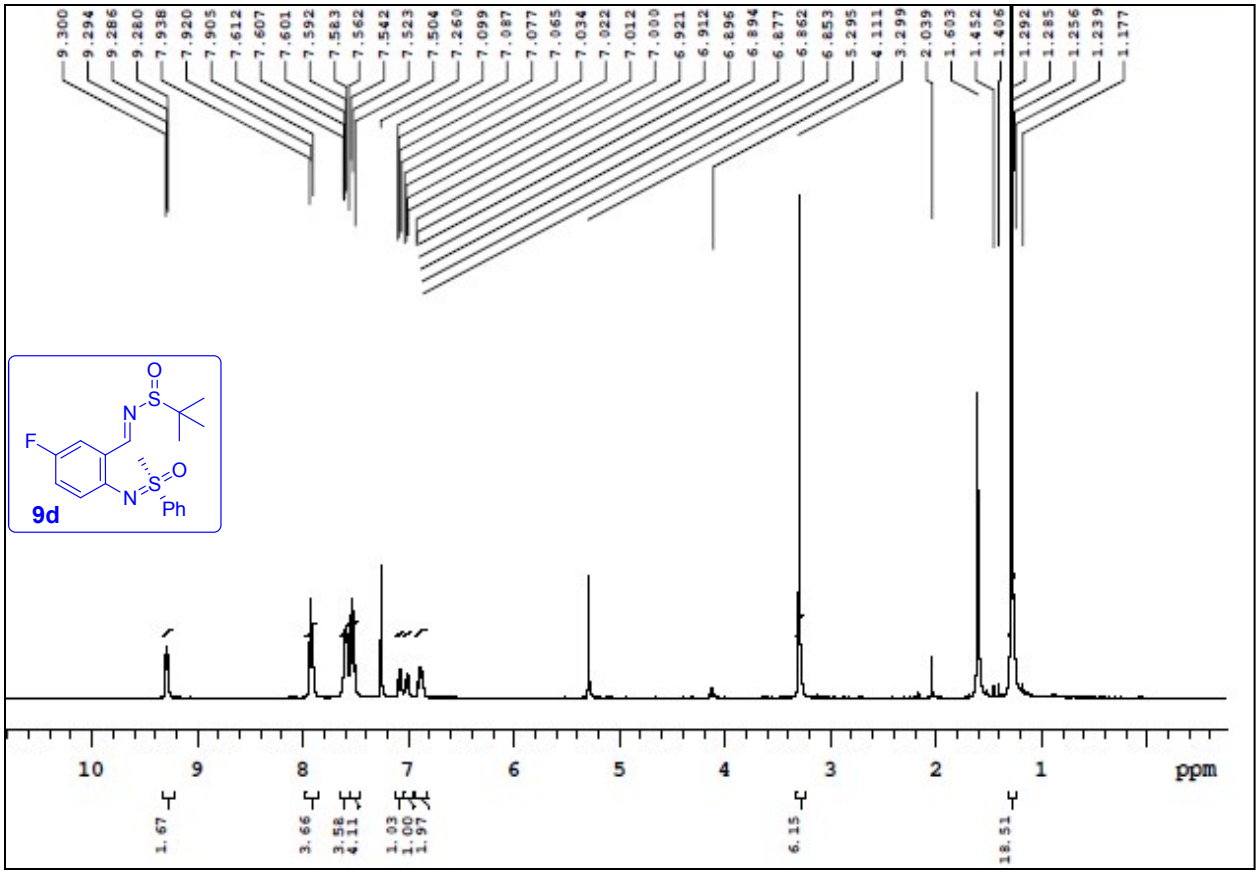
139.006
133.443
133.009
129.655
128.260
127.935
127.354
122.543
121.590
77.476
77.159
76.841
57.558
46.286
22.633
9c
(R)
(S)
Ph
200
180
160
140
120
100
80
60
40
20
ppm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9.280
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7.905
7.612
7.607
7.601
7.592
7.583
7.562
7.542
7.523
7.504
7.260
7.099
7.087
7.077
7.065
7.034
7.022
7.012
7.000
6.921
6.912
6.896
6.894
6.877
6.862
6.853
5.295
4.111
3.299
2.039
1.603
1.452
1.406
1.292
1.285
1.256
1.239
1.177
9d
10
9
8
7
6
5
4
3
2
1
ppm
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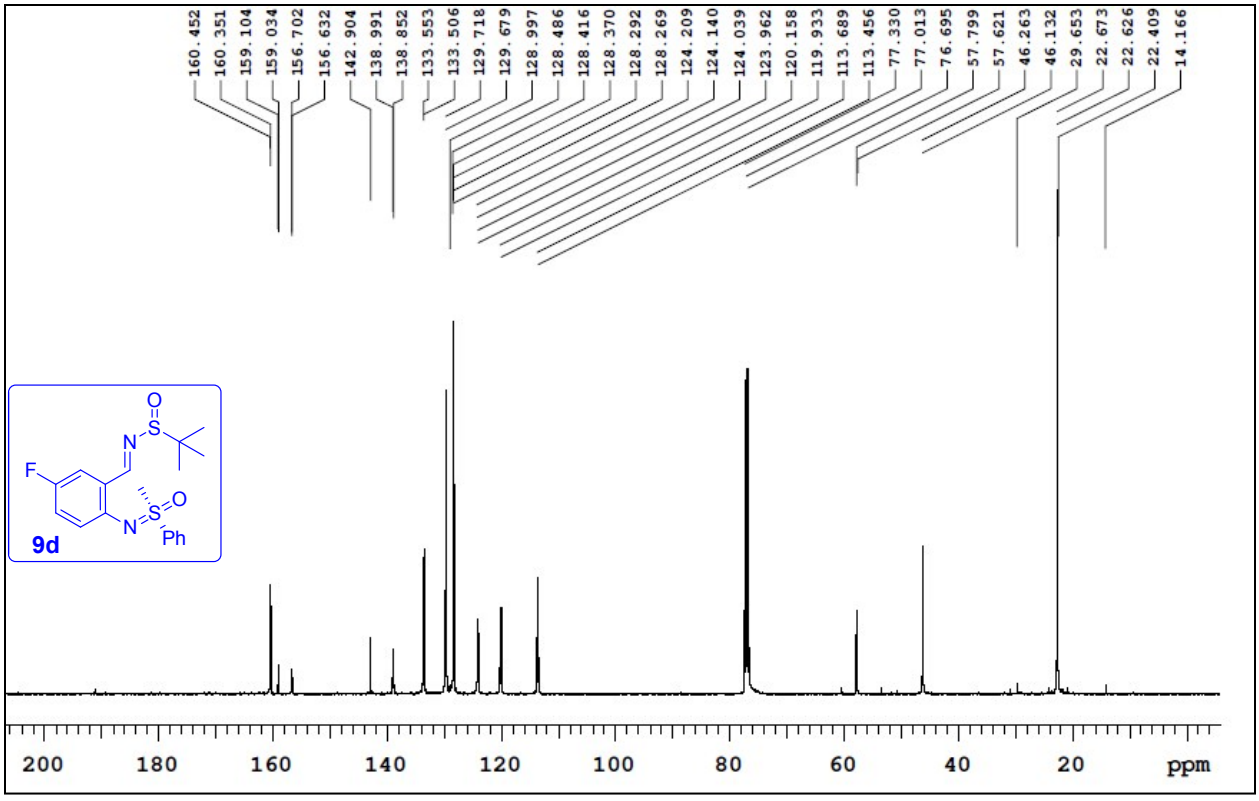
18.51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160.351
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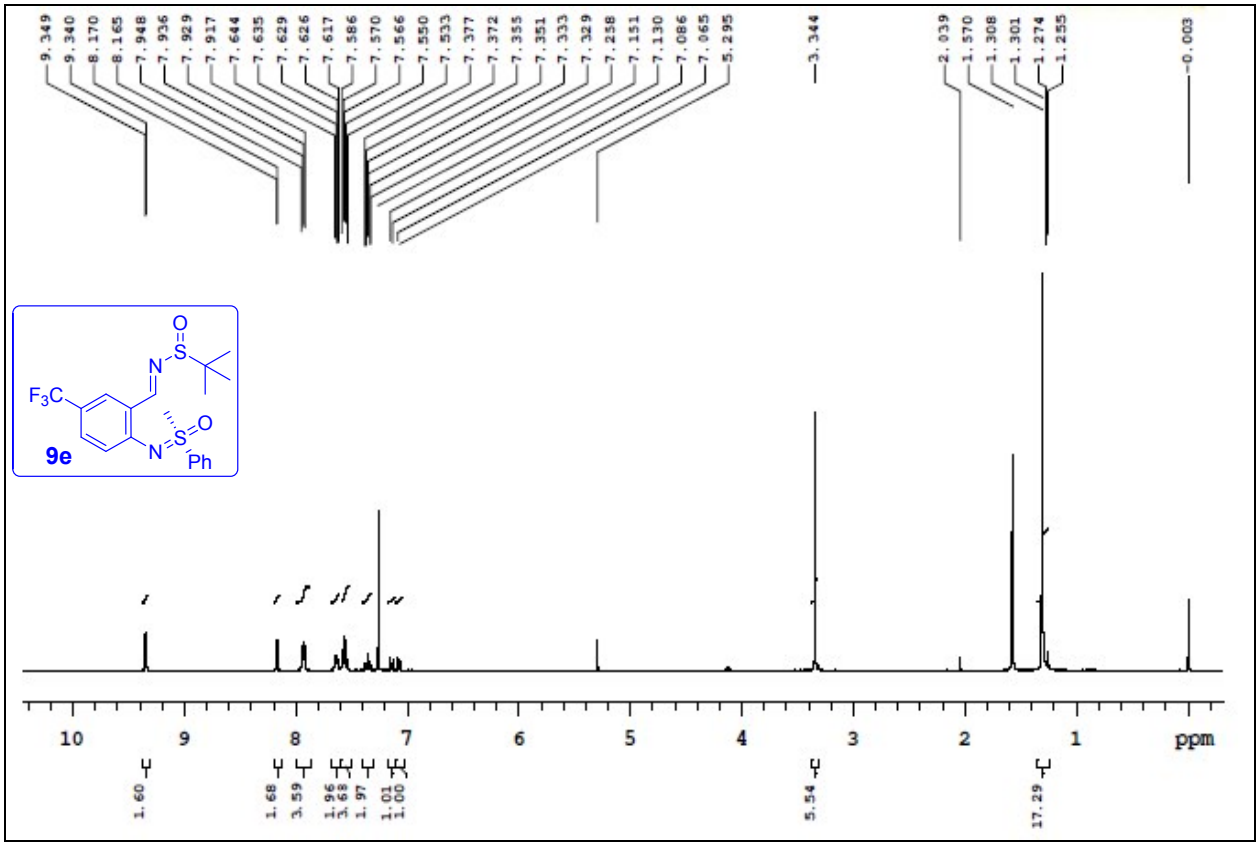
159.034
156.702
156.632
142.904
138.991
138.852
133.553
133.506
129.718
129.679
128.997
128.486
128.416
128.370
128.292
128.269
124.209
124.140
124.039
123.962
120.158
119.933
113.689
113.456
77.330
77.013
76.695
57.799
57.621
46.263
46.132
29.653
22.673
22.626
22.409
14.166
9d
200
180
160
140
120
100
80
60
40
20
ppm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8.170
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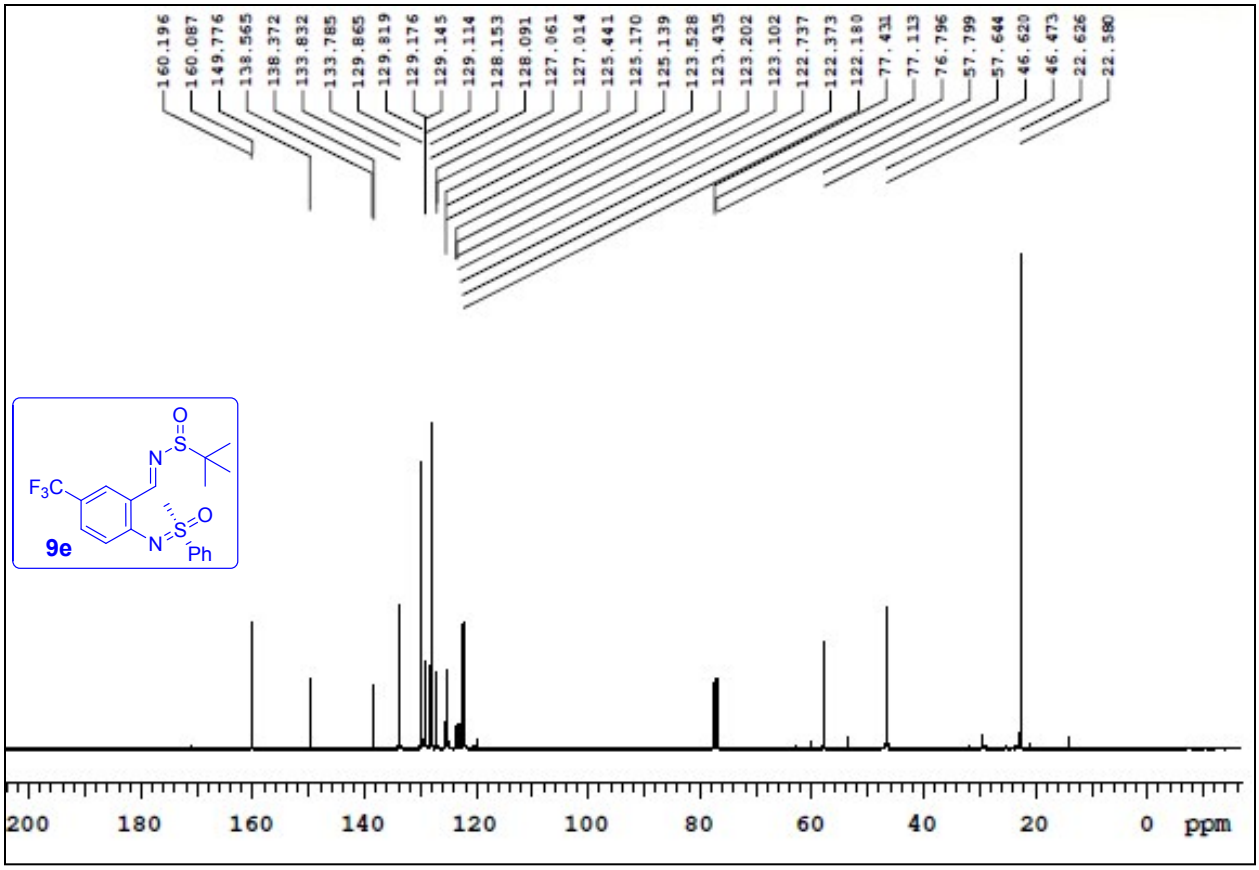
7.917
7.644
7.635
7.629
7.626
7.617
7.586
7.570
7.566
7.550
7.533
7.377
7.372
7.355
7.351
7.333
7.329
7.258
7.151
7.130
7.086
7.065
5.295
3.344
2.039
1.570
1.308
1.301
1.274
1.255
0.003
9e
10
9
8
7
6
5
4
3
2
1
ppm
1.60
1.68
3.59
1.96
3.68
1.97
1.01
1.00
5.54
17.29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149.776
138.565
138.372
133.832
133.785
129.865
129.819
129.176
129.145
129.114
128.153
128.091
127.061
127.014
125.441
125.170
125.139
123.528
123.435
123.202
123.102
122.737
122.373
122.180
77.431
77.113
76.796
57.799
57.644
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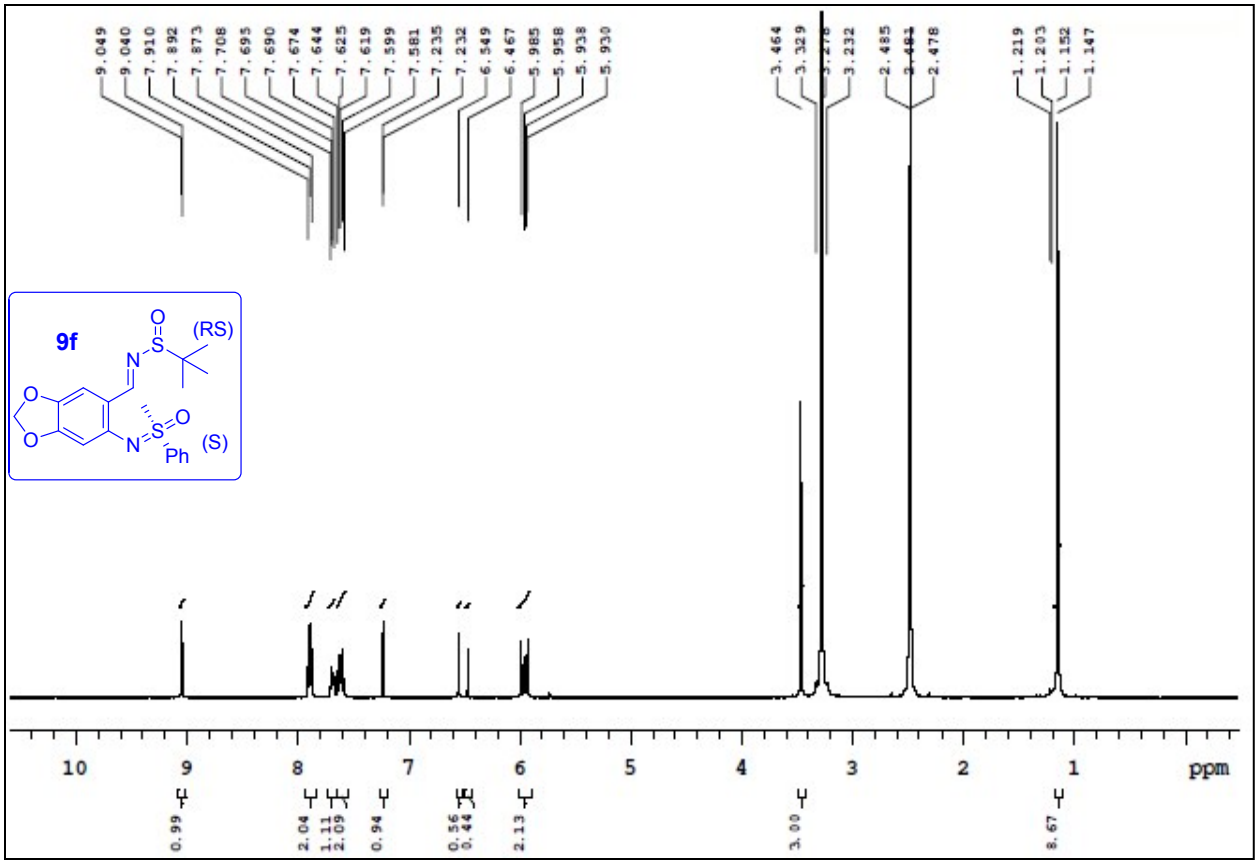
46.473
22.626
22.580
9e
200
180
160
140
120
100
80
60
40
20
0
ppm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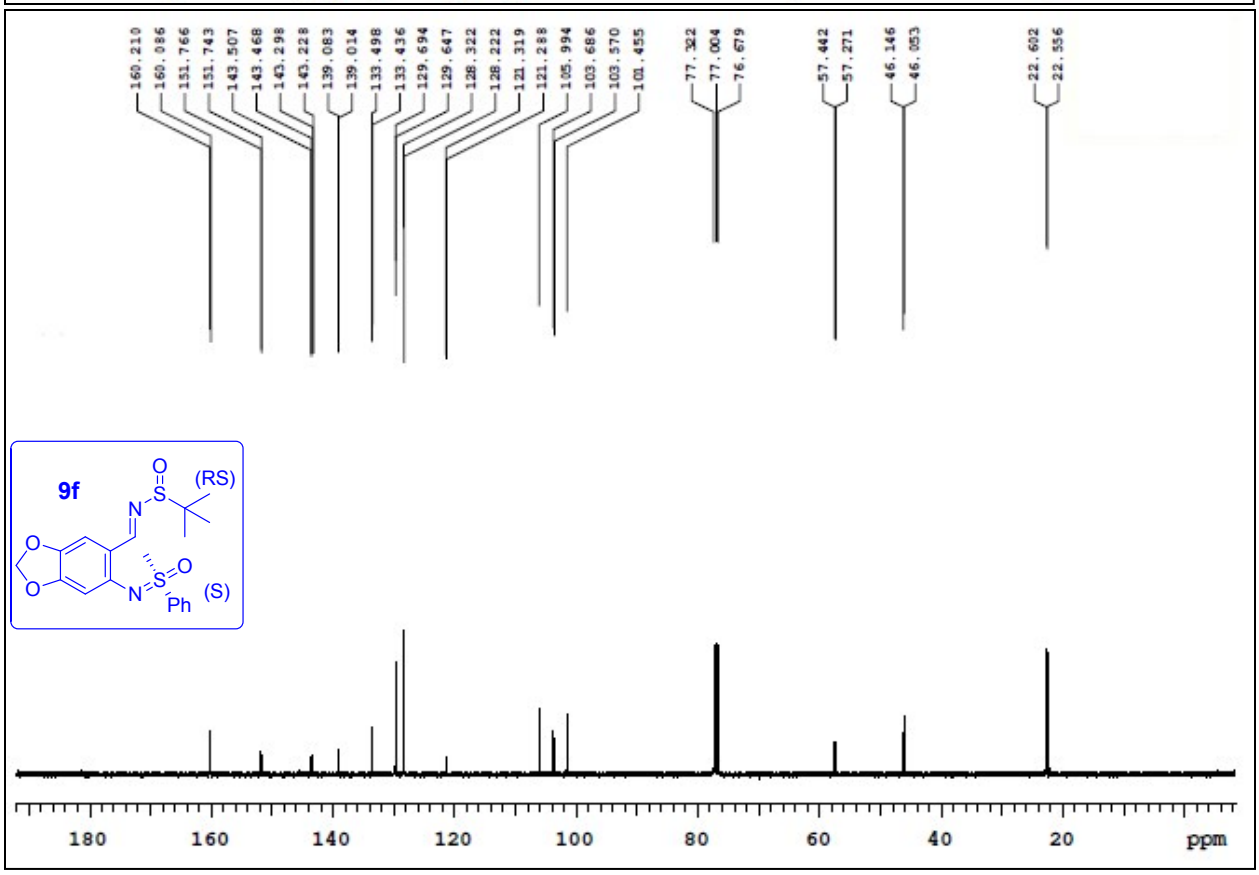
7.873
7.708
7.695
7.690
7.674
7.644
7.625
7.619
7.599
7.581
7.235
7.232
6.549
6.467
5.985
5.958
5.938
5.930
3.464
3.329
3.278
3.232
2.485
2.481
2.478
1.219
1.203
1.152
1.147
9f
(RS)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
ppm
0.99
2.04
1.11
2.09
0.94
0.56
0.44
2.13
3.00
8.67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151.766
151.743
143.507
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143.228
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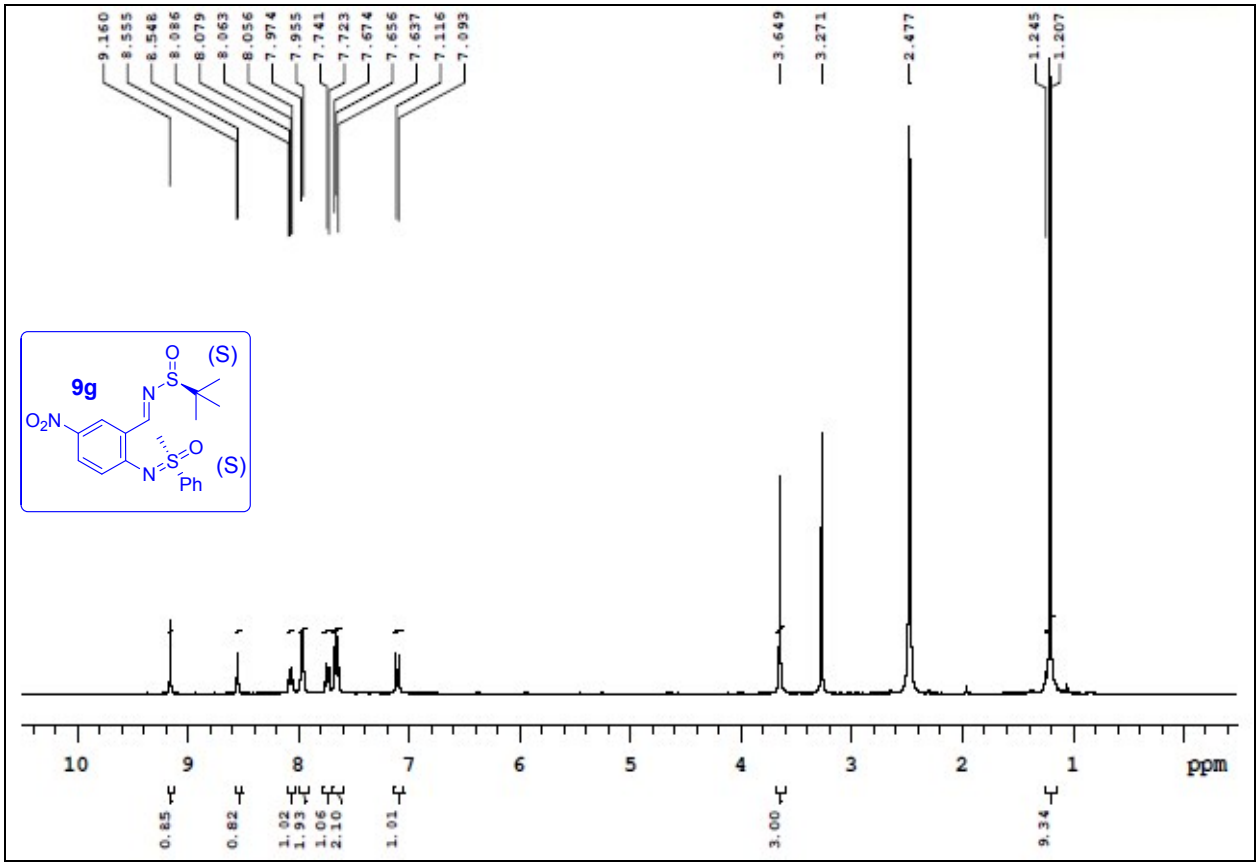
133.498
133.436
129.694
129.647
128.322
128.222
121.319
121.288
105.994
103.686
103.570
101.455
77.322
77.004
76.679
57.442
57.271
46.146
46.053
22.602
22.556
9f
(RS)
(S)
Ph
180
160
140
120
100
80
60
40
20
ppm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8.555
8.548
8.086
8.079
8.063
8.056
7.974
7.955
7.741
7.723
7.674
7.656
7.637
7.116
7.093
3.649
3.271
2.477
1.245
1.207
9g
(S)
(S)
Ph
10
9
8
7
6
5
4
3
2
1
ppm
0.85
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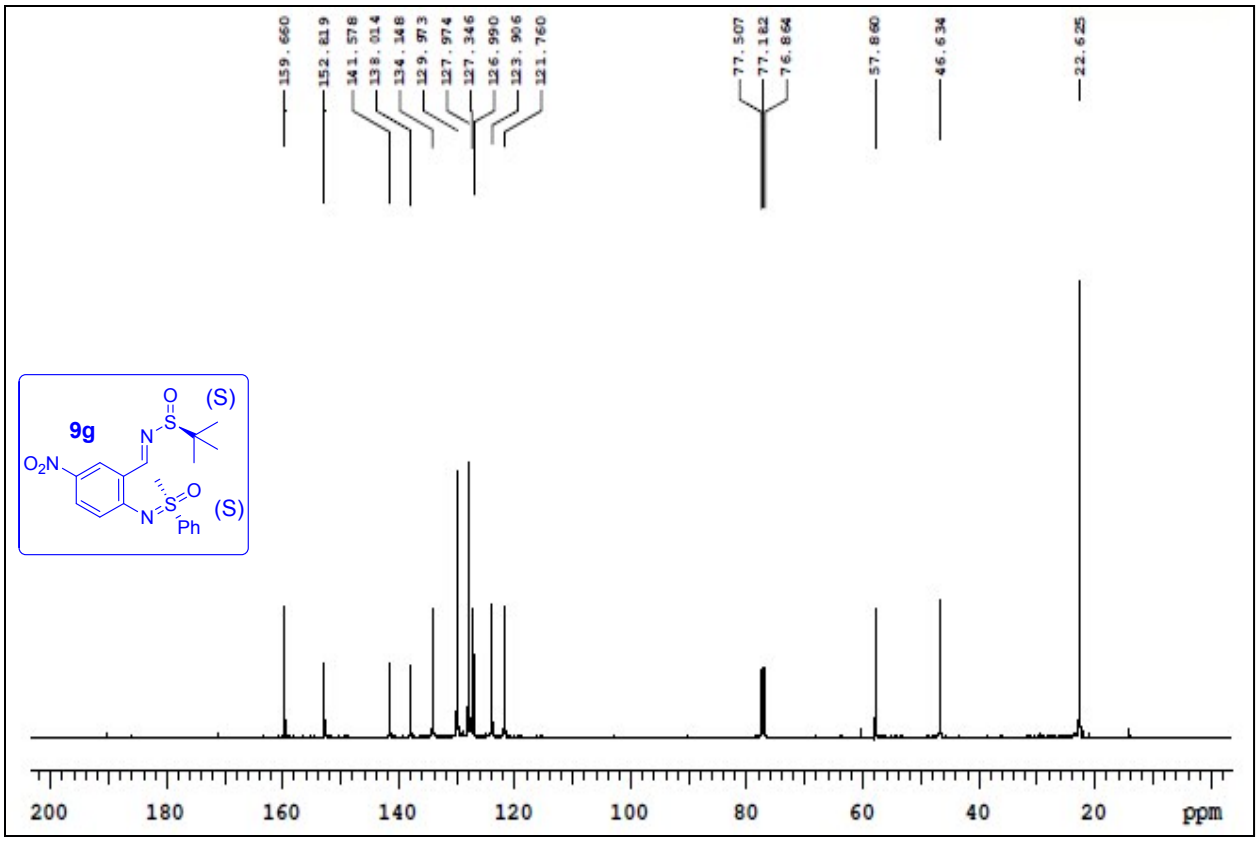
1.93
1.06
2.10
1.01
3.00
9.34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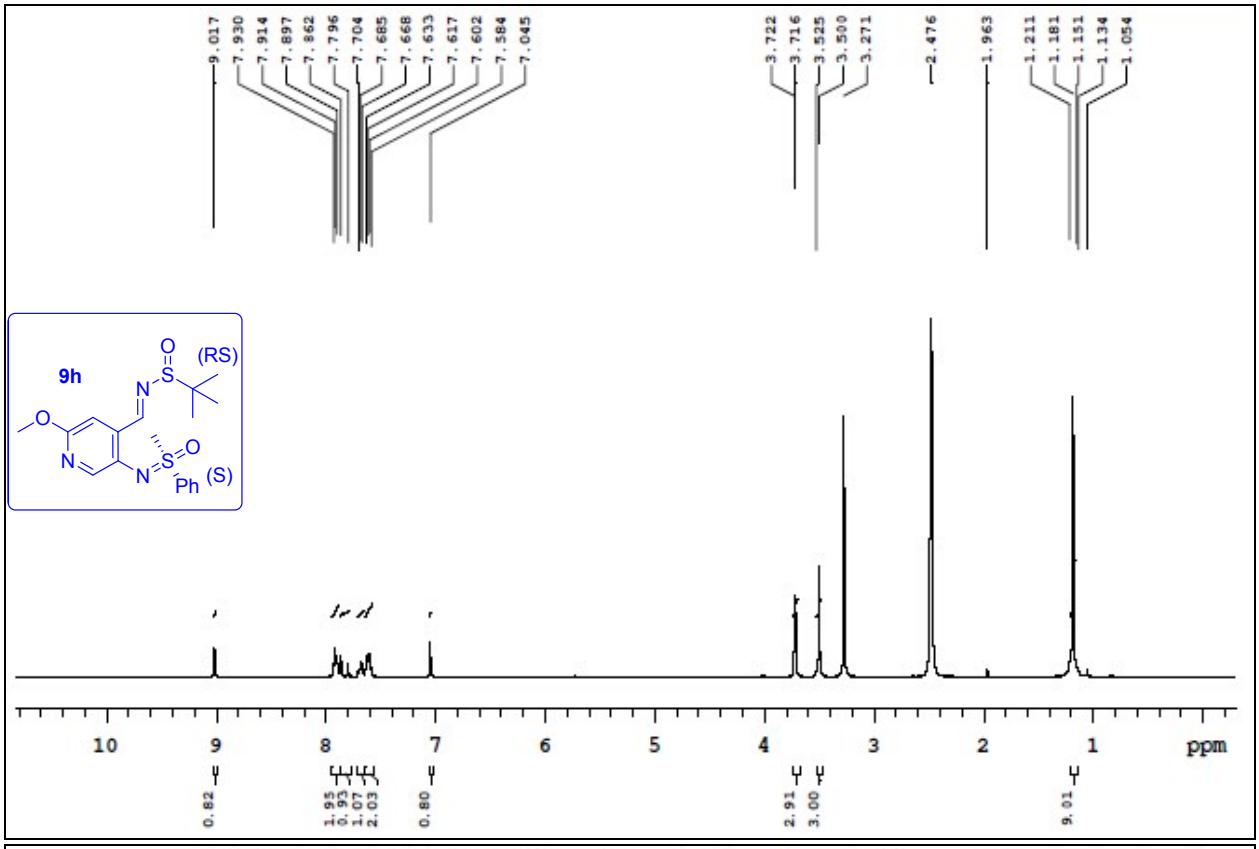
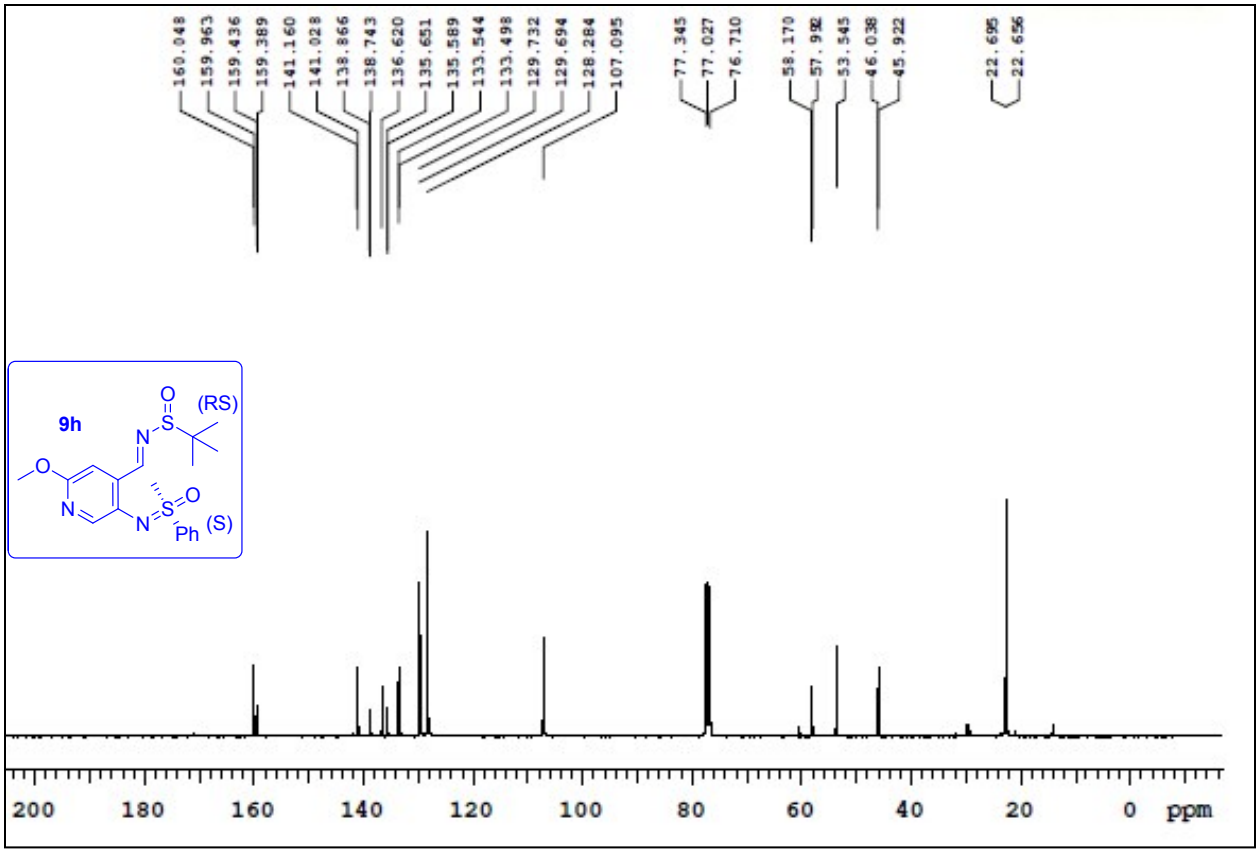
141.578
138.014
134.148
129.973
127.974
127.346
126.990
123.906
121.760
77.507
77.182
76.864
57.860
46.634
22.625
9g
(S)
(S)
Ph
200
180
160
140
120
100
80
60
40
20
ppm


9h
(RS)
(S)
Ph
9.017
7.930
7.914
7.897
7.862
7.796
7.704
7.685
7.668
7.633
7.617
7.602
7.584
7.045
3.722
3.716
3.525
3.500
3.271
2.476
1.963
1.211
1.181
1.151
1.134
1.054
0.82
1.95
0.93
1.07
2.03
0.80
2.91
3.00
9.01
ppm


9h
(RS)
(S)
Ph
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159.963
159.436
159.389
141.160
141.028
138.866
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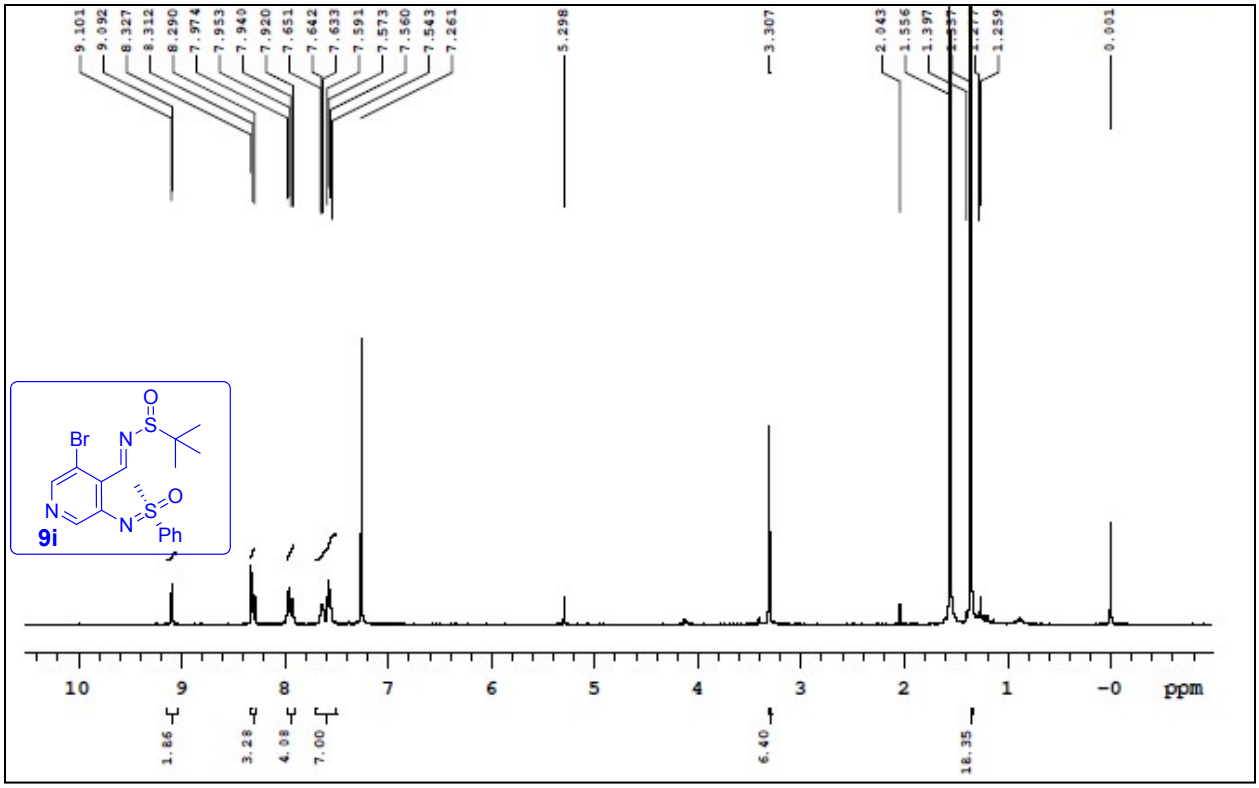
136.620
135.651
135.589
133.544
133.498
129.732
129.694
128.284
107.095
77.345
77.027
76.710
58.170
57.982
53.545
46.038
45.922
22.695
22.656
ppm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9.092
8.327
8.312
8.290
7.974
7.953
7.940
7.920
7.651
7.642
7.633
7.591
7.573
7.560
7.543
7.261
5.298
3.307
2.043
1.556
1.397
1.259
0.001
Br
N
S
O
Ph
9i
10
9
8
7
6
5
4
3
2
1
−0
ppm
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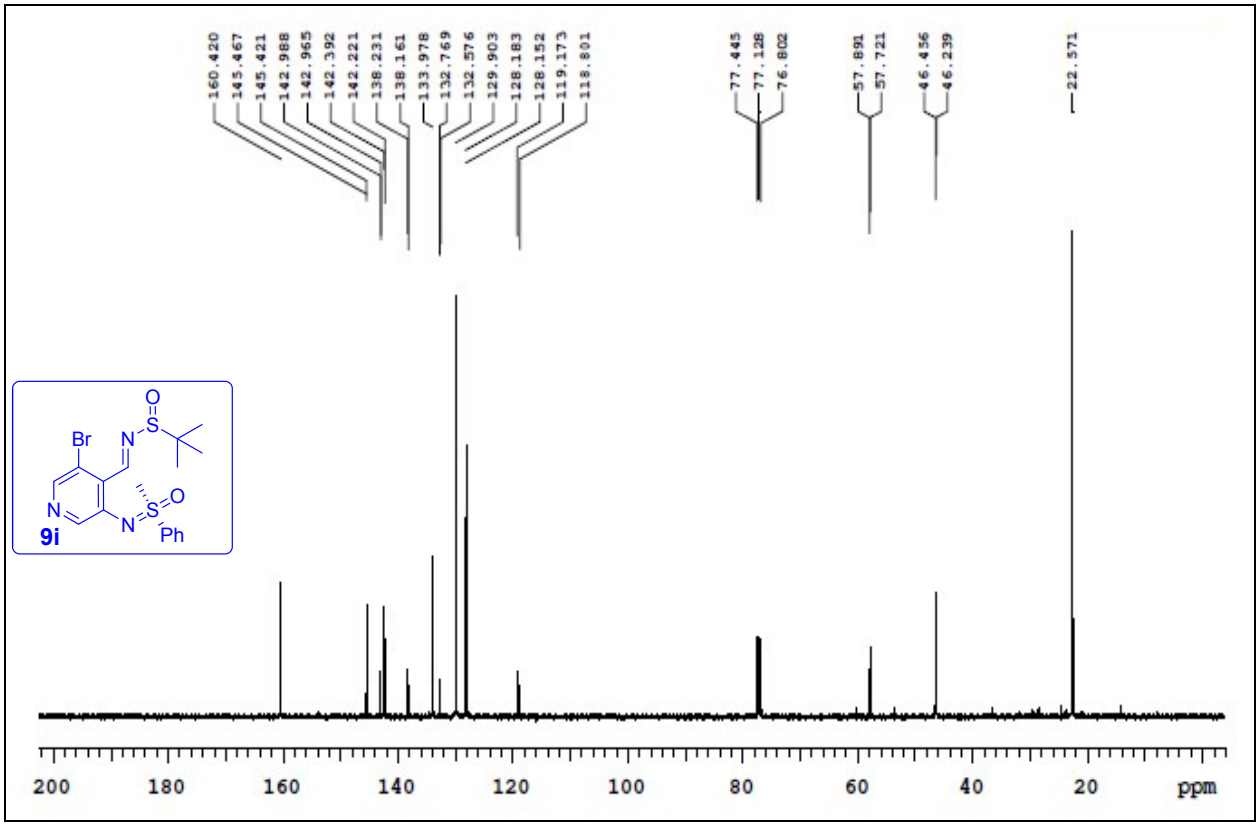
3.28
4.08
7.00
6.40
18.35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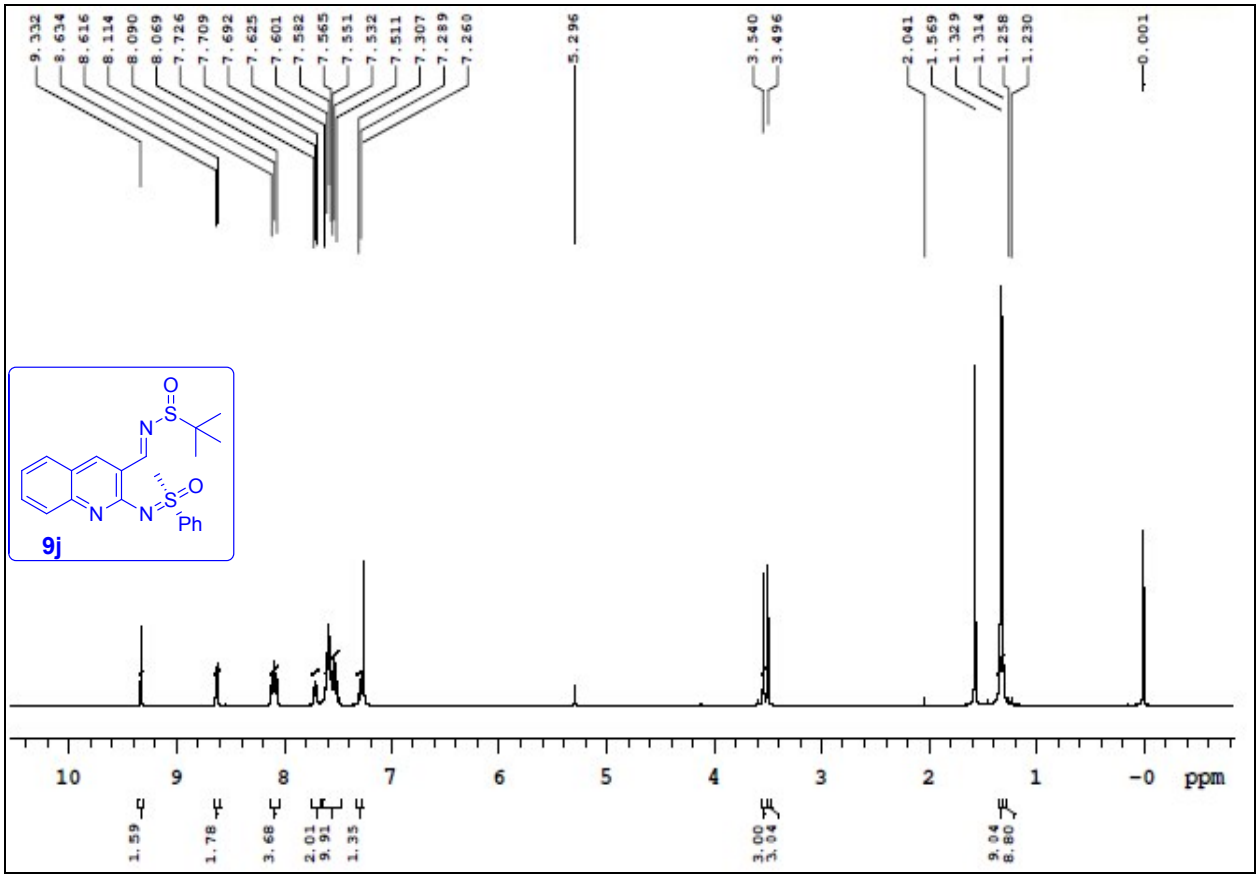
142.392
142.221
138.231
138.161
133.978
132.769
132.576
129.903
128.183
128.152
119.173
118.801
77.445
77.128
76.802
57.891
57.721
46.456
46.239
22.571
Br
N
S
O
Ph
9i
200
180
160
140
120
100
80
60
40
20
ppm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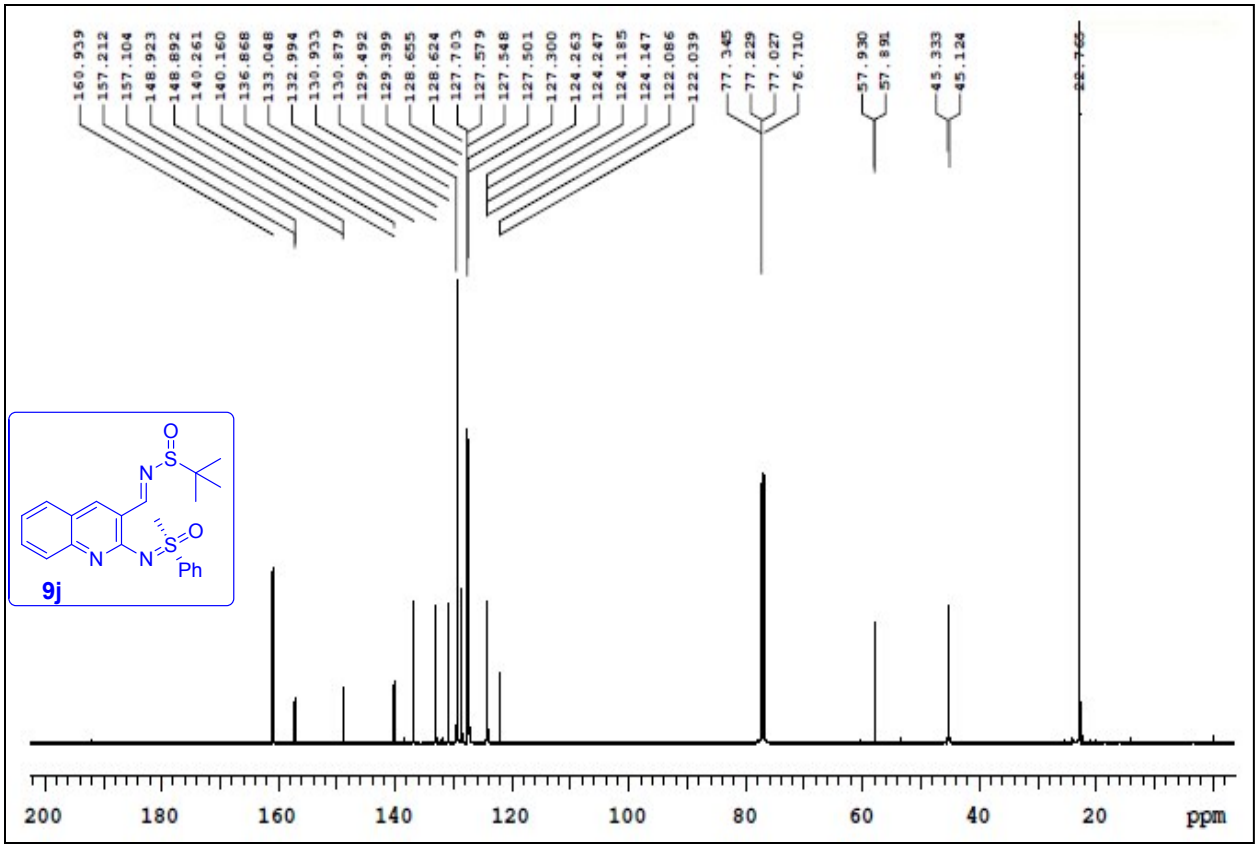
8.616
8.114
8.090
8.069
7.726
7.709
7.692
7.625
7.601
7.582
7.565
7.551
7.532
7.511
7.307
7.289
7.260
5.296
3.540
3.496
2.041
1.569
1.329
1.314
1.258
1.230
0.001
9j
10
9
8
7
6
5
4
3
2
1
-0
ppm
1.59
1.78
3.68
2.01
9.91
1.35
3.00
3.04
9.04
8.80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148.923
148.892
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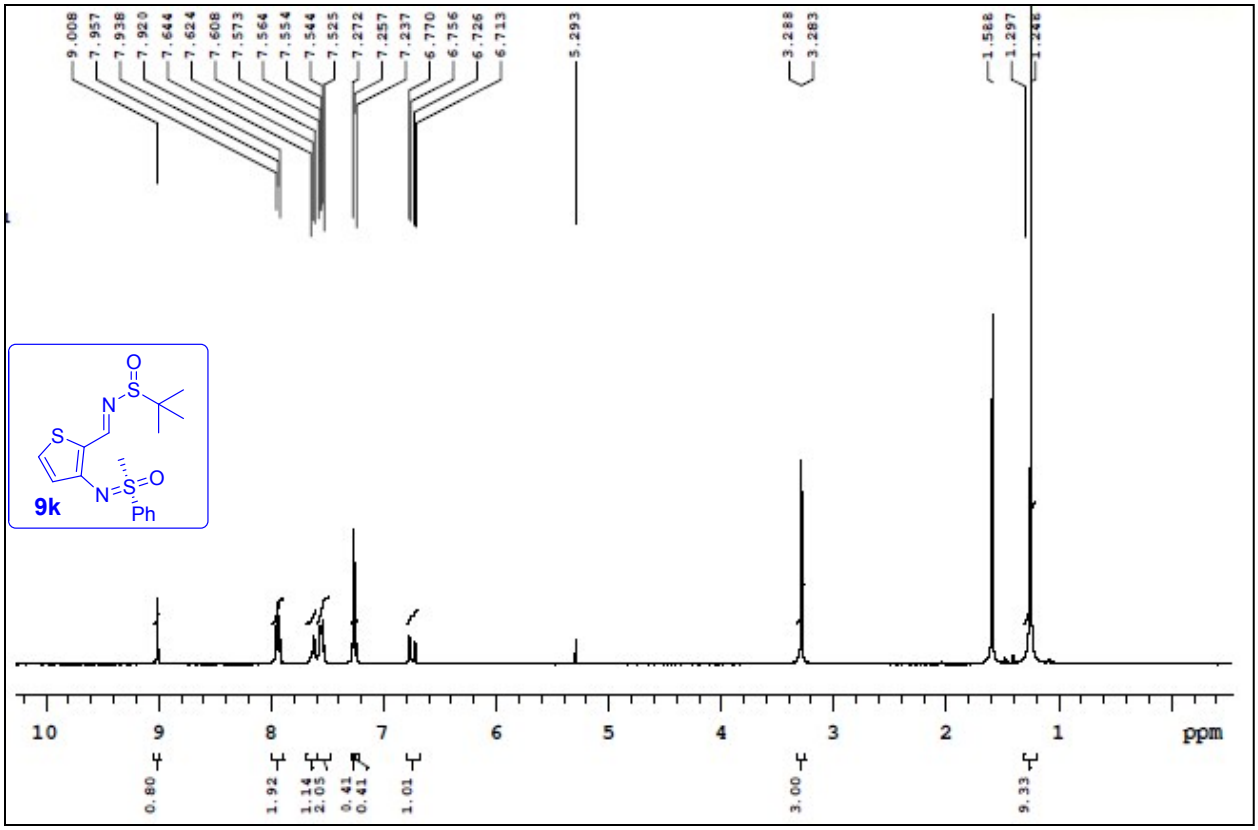
136.868
133.048
132.994
130.933
130.879
129.492
129.399
128.655
128.624
127.703
127.579
127.548
127.501
127.300
124.263
124.247
124.185
124.147
122.086
122.039
77.345
77.229
77.027
76.710
57.930
57.891
45.333
45.124
28.765
9j
200
180
160
140
120
100
80
60
40
20
ppm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7.644
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7.608
7.573
7.564
7.554
7.544
7.525
7.272
7.257
7.237
6.770
6.756
6.726
6.713
5.293
3.288
3.283
1.588
1.297
1.248
9k
10
9
8
7
6
5
4
3
2
1
ppm
0.80
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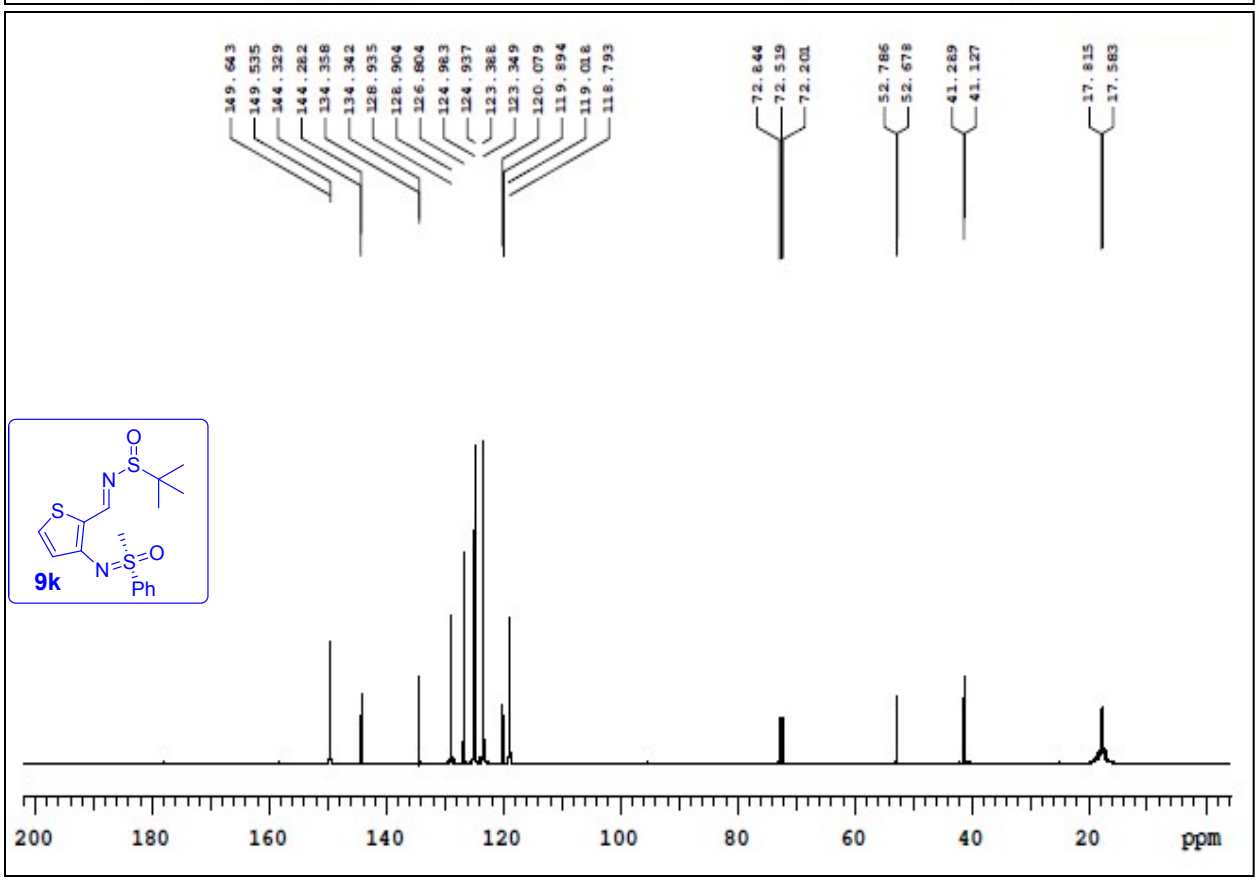
1.14
2.05
0.41
0.41
1.01
3.00
9.33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144.282
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134.342
128.935
128.904
126.804
124.983
124.937
123.388
123.349
120.079
119.894
119.018
118.793
72.644
72.519
72.201
52.786
52.678
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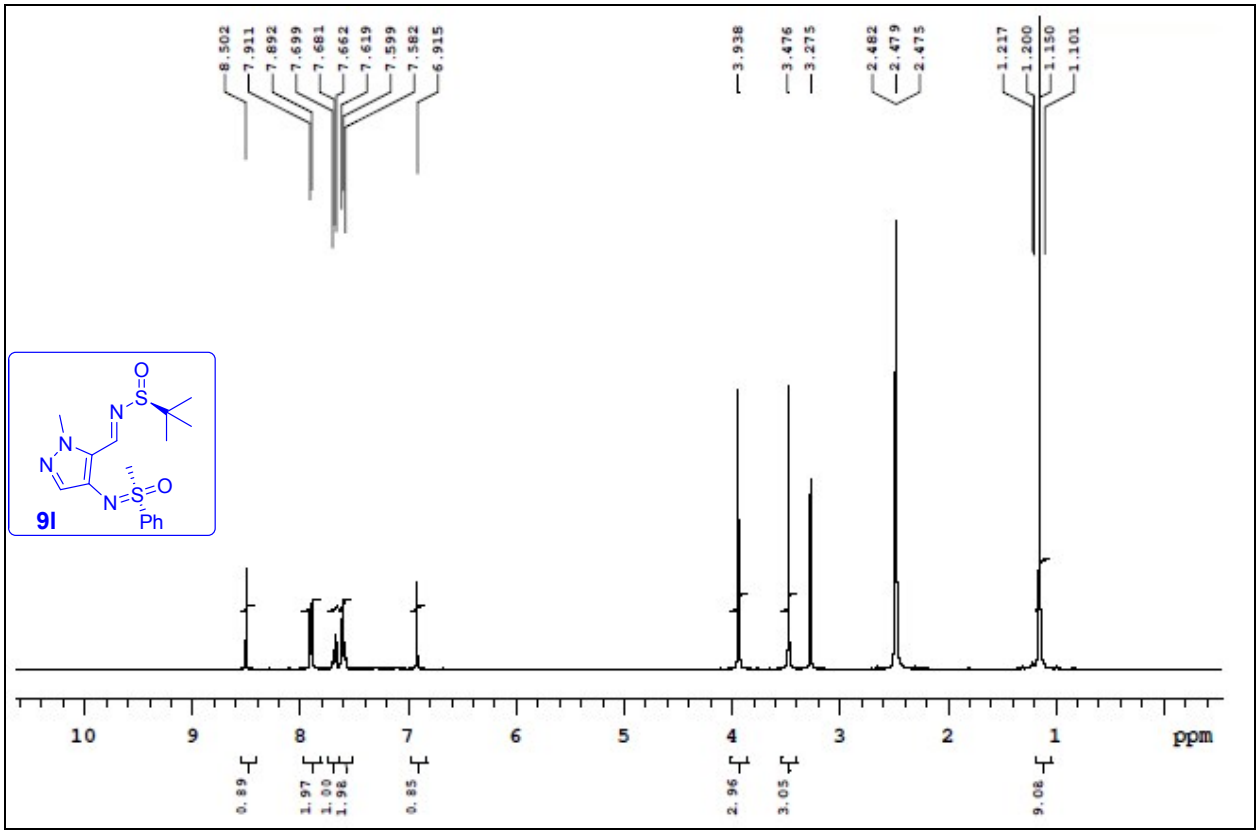
17.815
17.583
9k
200
180
160
140
120
100
80
60
40
20
ppm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7.619
7.599
7.582
6.915
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3.476
3.275
2.482
2.479
2.475
1.217
1.200
1.150
1.101
9l
Ph
10
9
8
7
6
5
4
3
2
1
ppm
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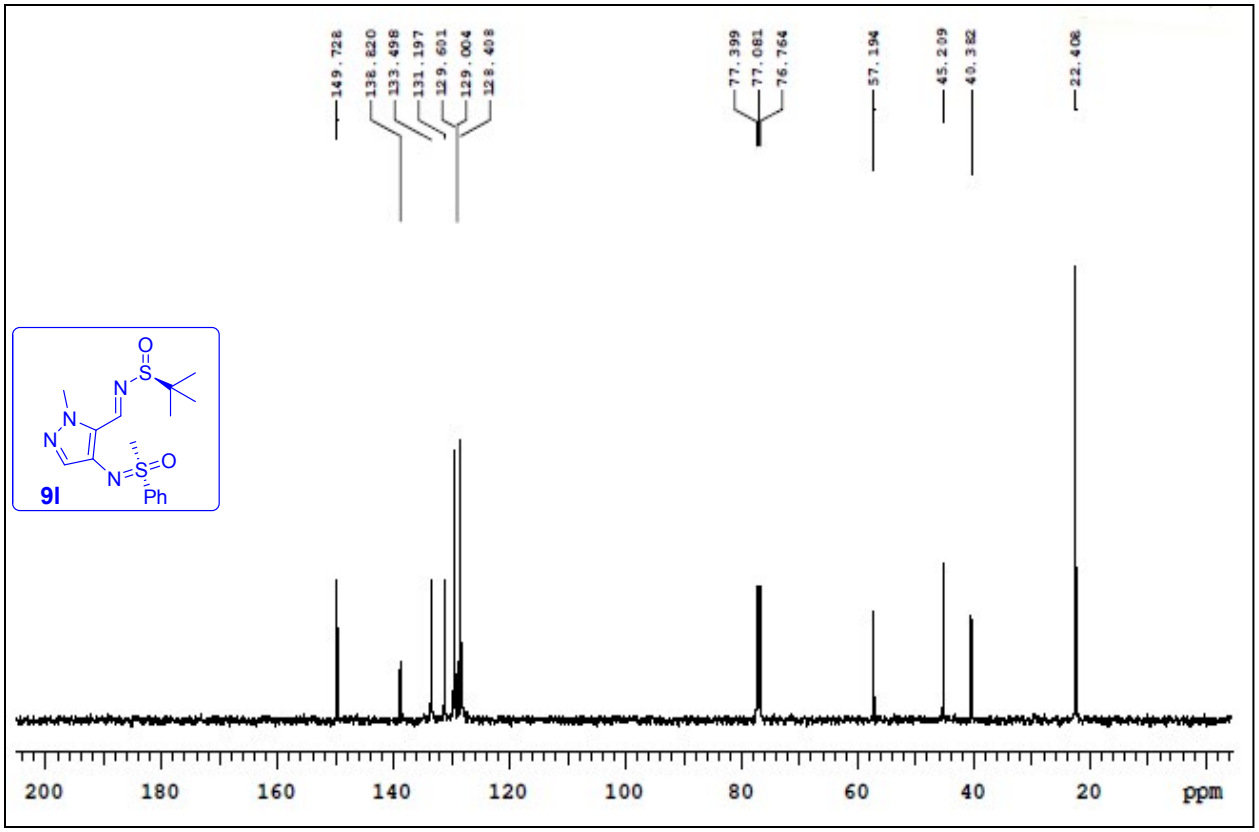
1.00
1.98
0.85
2.96
3.05
9.08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22.408
9l
Ph
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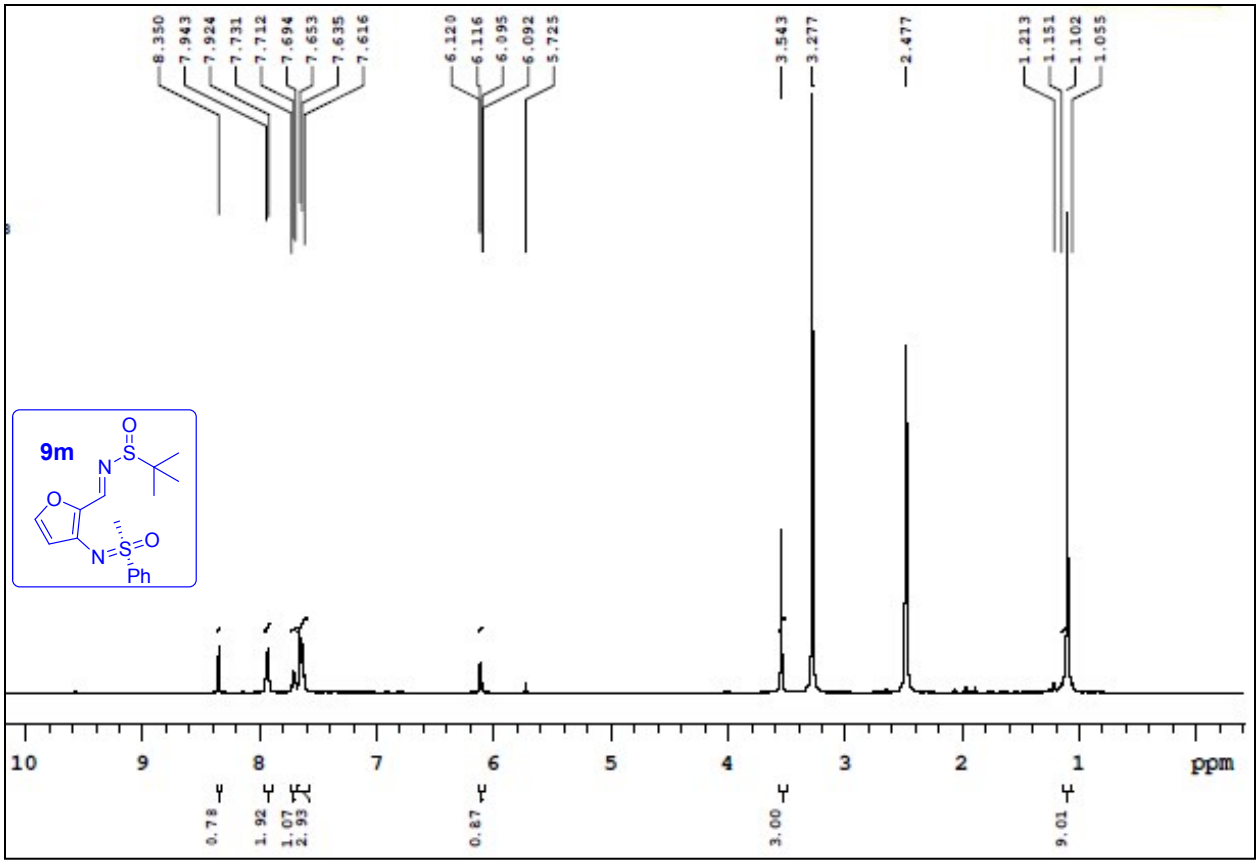
140
120
100
80
60
40
20
ppm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7.635
7.616
6.120
6.116
6.095
6.092
5.725
3.543
3.277
2.477
1.213
1.151
1.102
1.055
9m
Ph
10
9
8
7
6
5
4
3
2
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1.07
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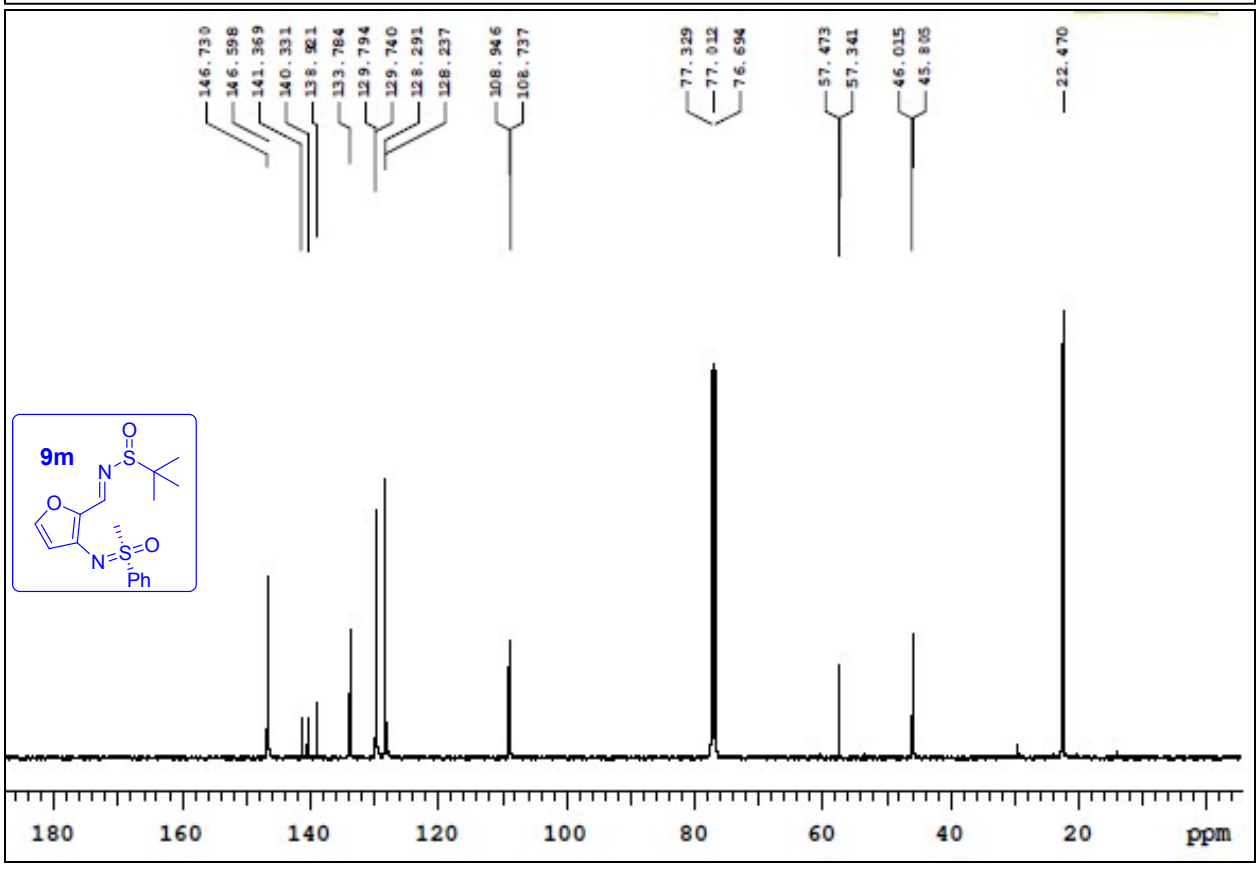
3.00
9.01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141.369
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129.740
128.291
128.237
108.946
108.737
77.329
77.012
76.694
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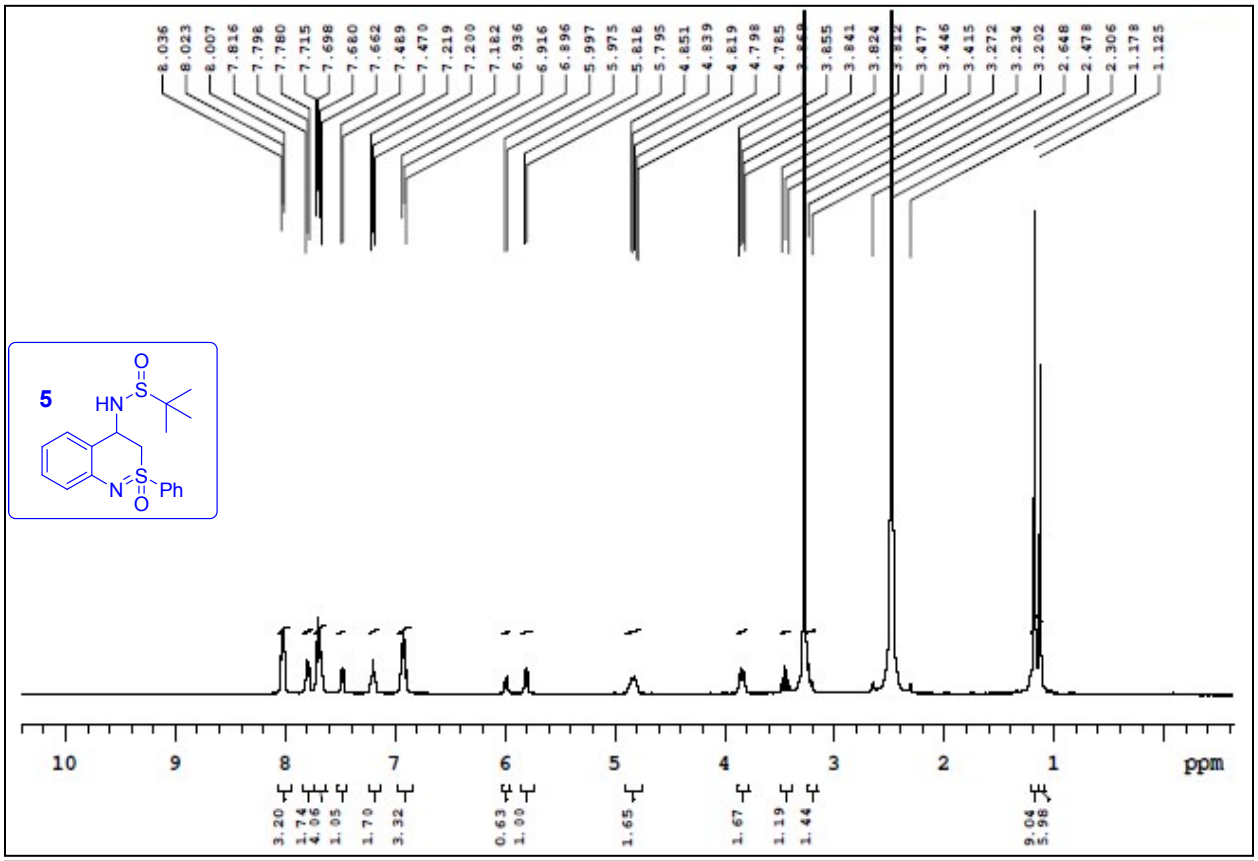
46.015
45.805
22.470
9m
Ph
180
160
140
120
100
80
60
40
20
ppm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8.007
7.816
7.798
7.780
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7.698
7.680
7.662
7.489
7.470
7.219
7.200
7.182
6.936
6.916
6.896
5.997
5.975
5.818
5.795
4.851
4.839
4.819
4.798
4.785
3.855
3.841
3.824
3.812
3.477
3.446
3.415
3.272
3.234
3.202
2.648
2.478
2.306
1.178
1.125
5
HN
O
S
N
S
Ph
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9
8
7
6
5
4
3
2
1
ppm
3.20
1.74
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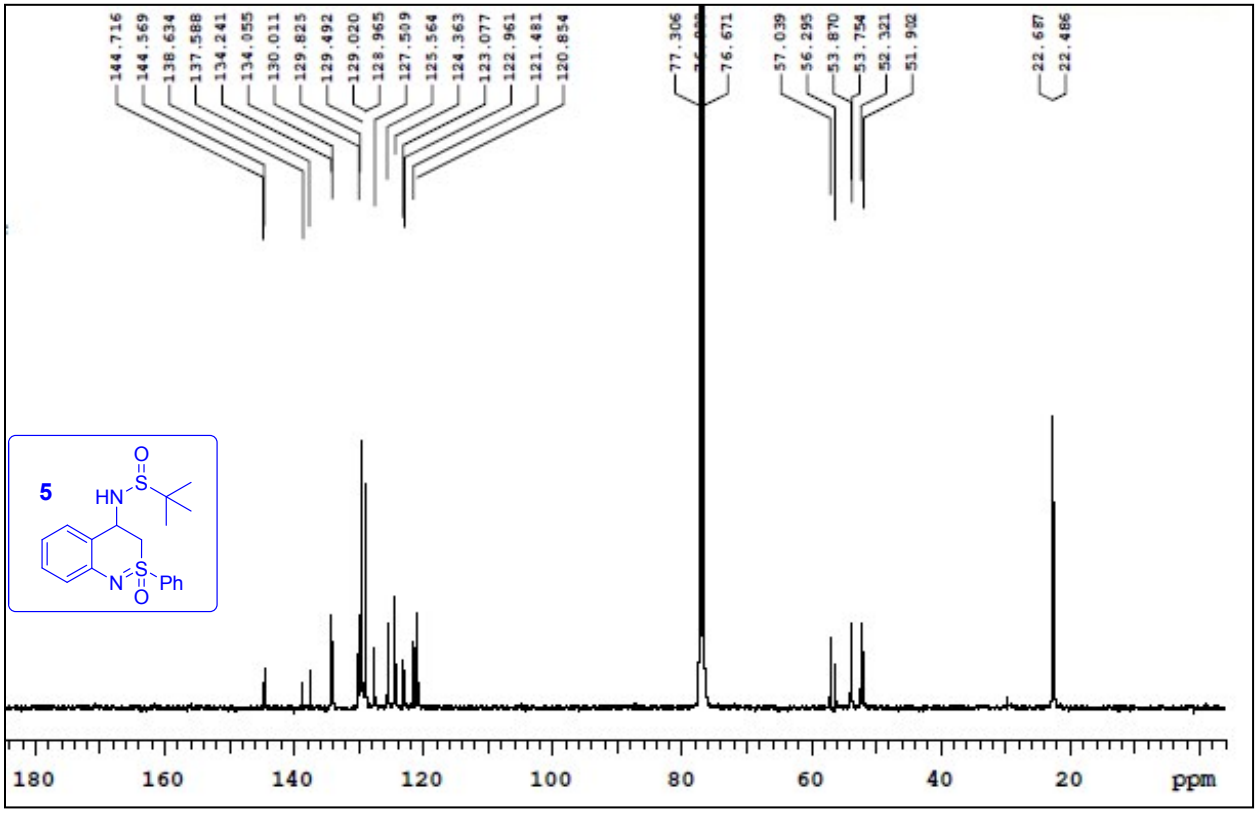
9.04
5.98


144.716
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130.011
129.825
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129.020
128.965
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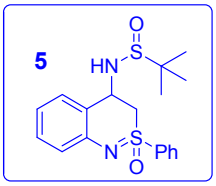
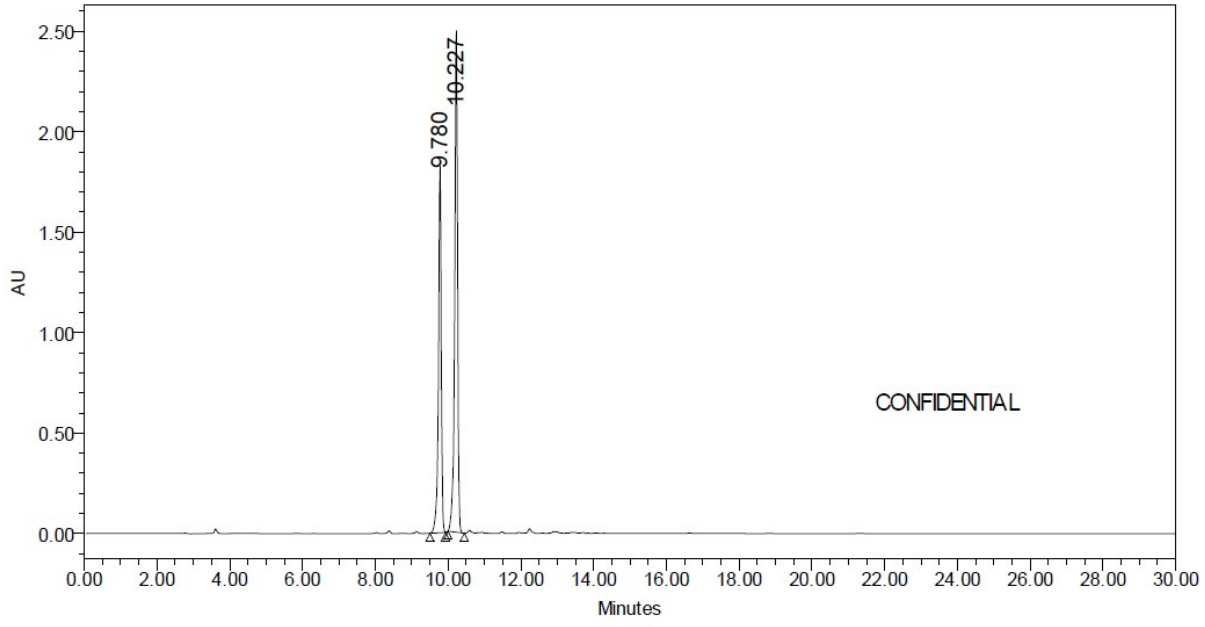
125.564
124.363
123.077
122.961
121.481
120.854
77.306
76.671
57.039
56.295
53.870
53.754
52.321
51.902
22.687
22.486
5
HN
O
S
N
S
Ph
O
180
160
140
120
100
80
60
40
20
ppm

JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-009-RS	Acquired By:	anachem
Test Type:	HPLC / UV	Sample Set Name:	CHEMSIL_TFA_GRA
Acq. Method Set:	CHEMSIL_TFA_GRA_HPLC2	Vial:	105
Injection Volume:	20.00 ul	Proc. Chnl. Descr.:	254
Date Acquired:	10/20/2015 1:24:18 AM IST	Date Processed:	10/20/2015 8:47:29 AM IST

Analytical Conditions:
Column :Column :Chemsil C18(250mm X 4.6mm X 5mic)
Mobile phase(A) : 0.01% TFA in water
Mobile phase(B) : ACN
Flow rate : 1.0 mL/min
T/%B: 0/20,10/80, 25/80,27/20,30/20



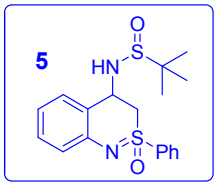


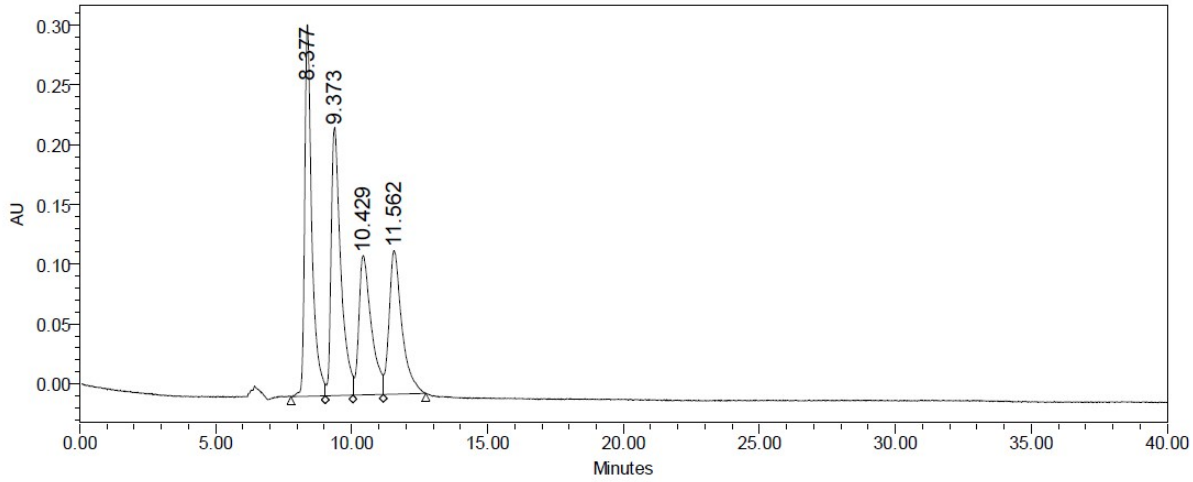
	RT	Area	% Area
1	9.780	9715848	41.59
2	10.227	13647604	58.41

JUBILANT BIOSYS, BANGALORE

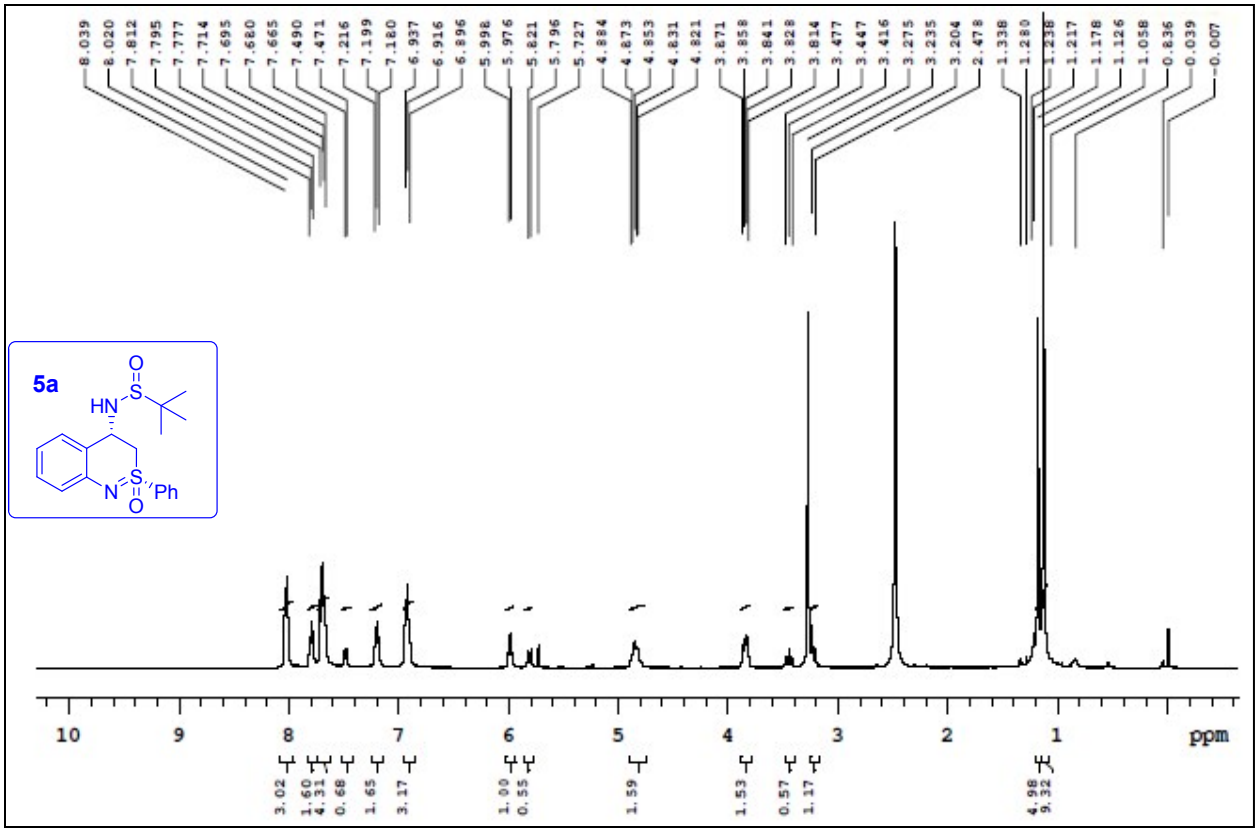
Sample Name:	JBPHD1-JBL-C-1529-009-RS	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	254.0nm
Sample Set Name:	IA_CHIRAL_HPLC1	Vial:	48
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	10/13/2015 4:08:37 PM IST	Date Processed:	10/14/2015 11:22:06 AM IST

Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase : IPA(100%)
Flow rate : 0.5 mL/min





	RT	Area	% Area
1	8.377	5672295	30.07
2	9.373	5511007	29.22
3	10.429	3734211	19.80
4	11.562	3946098	20.92


8.039
8.020
7.812
7.795
7.777
7.714
7.695
7.680
7.665
7.490
7.471
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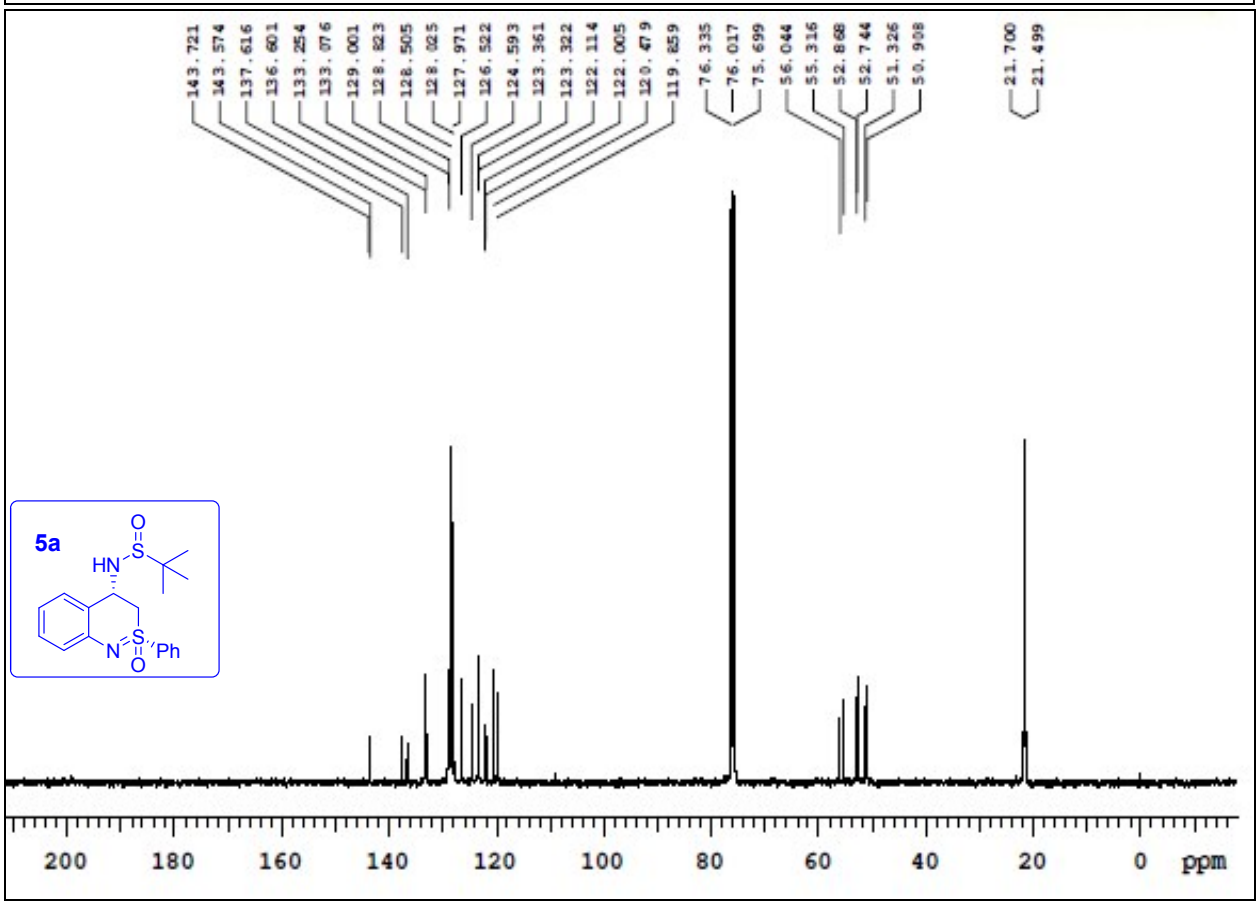
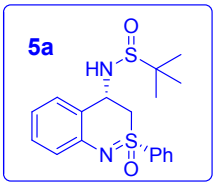
7.199
7.180
6.937
6.916
6.896
5.998
5.976
5.821
5.796
5.727
4.884
4.873
4.853
4.831
4.821
3.871
3.858
3.841
3.828
3.814
3.477
3.447
3.416
3.275
3.235
3.204
2.478
1.338
1.280
1.238
1.217
1.178
1.126
1.058
0.836
0.039
0.007
5a
HN
S
O
N
S
Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
3.02
1.60
4.31
0.68
1.65
3.17
1.00
0.55
1.59
1.53
0.57
1.17
4.98
9.32

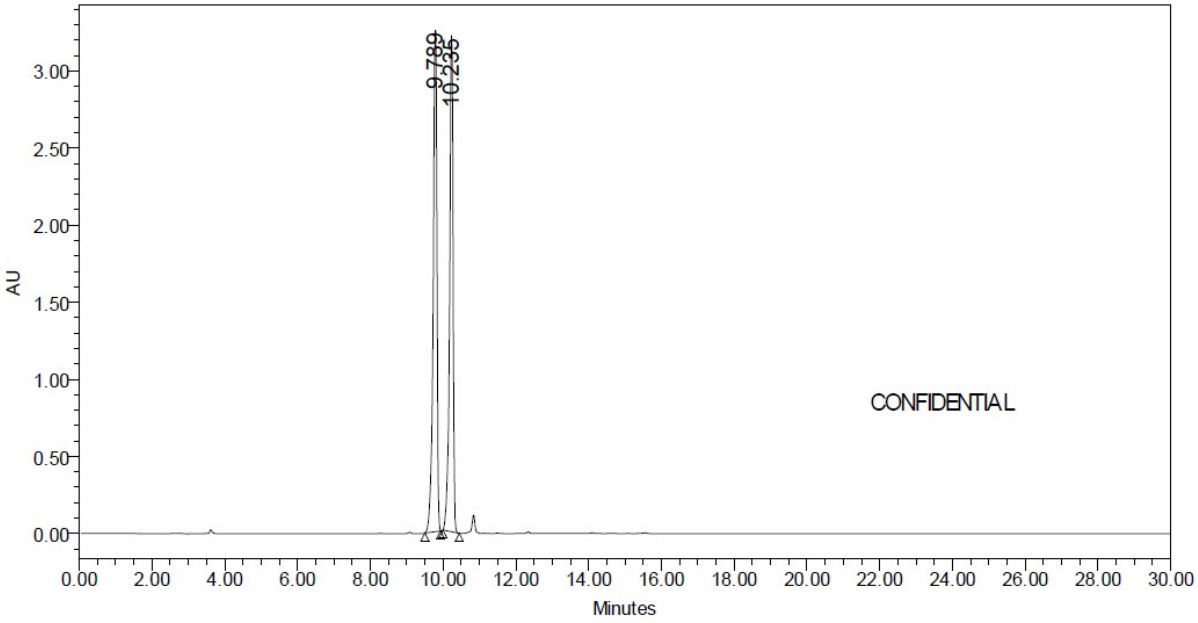

143.721
143.574
137.616
136.601
133.254
133.076
129.001
128.823
128.505
128.025
127.971
126.522
124.593
123.361
123.322
122.114
122.005
120.479
119.859
76.335
76.017
75.699
56.044
55.316
52.868
52.744
51.326
50.908
21.700
21.499
5a
HN
S
O
N
S
Ph
O
200
180
160
140
120
100
80
60
40
20
0
ppm

JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-009-S0	Acquired By:	anachem
Test Type:	HPLC / UV	Sample Set Name:	CHEMSIL_TFA_GRA
Acq. Method Set:	CHEMSIL_TFA_GRA_HPLC2	Vial:	104
Injection Volume:	20.00 ul	Proc. Chnl. Descr.:	254
Date Acquired:	10/20/2015 12:53:19 AM IST	Date Processed:	10/20/2015 8:47:07 AM IST

Analytical Conditions:
Column :Column :Chemsil C18(250mm X 4.6mm X 5mic)
Mobile phase(A) : 0.01% TFA in water
Mobile phase(B) : ACN
Flow rate : 1.0 mL/min
T/%B: 0/20,10/80, 25/80,27/20,30/20



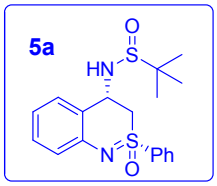


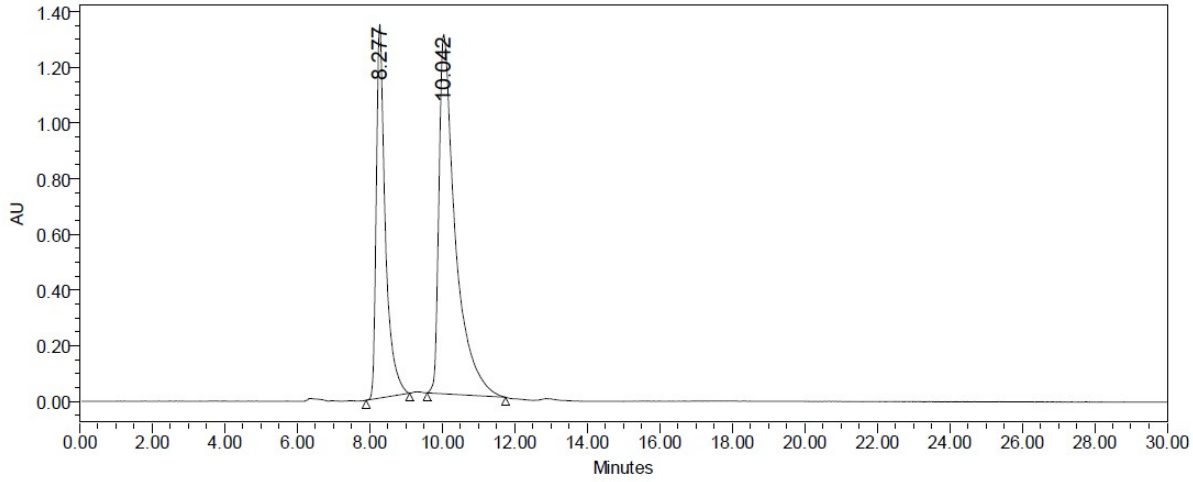
	RT	Area	% Area
1	9.789	23477787	52.57
2	10.235	21181739	47.43

JUBILANT BIOSYS, BANGALORE

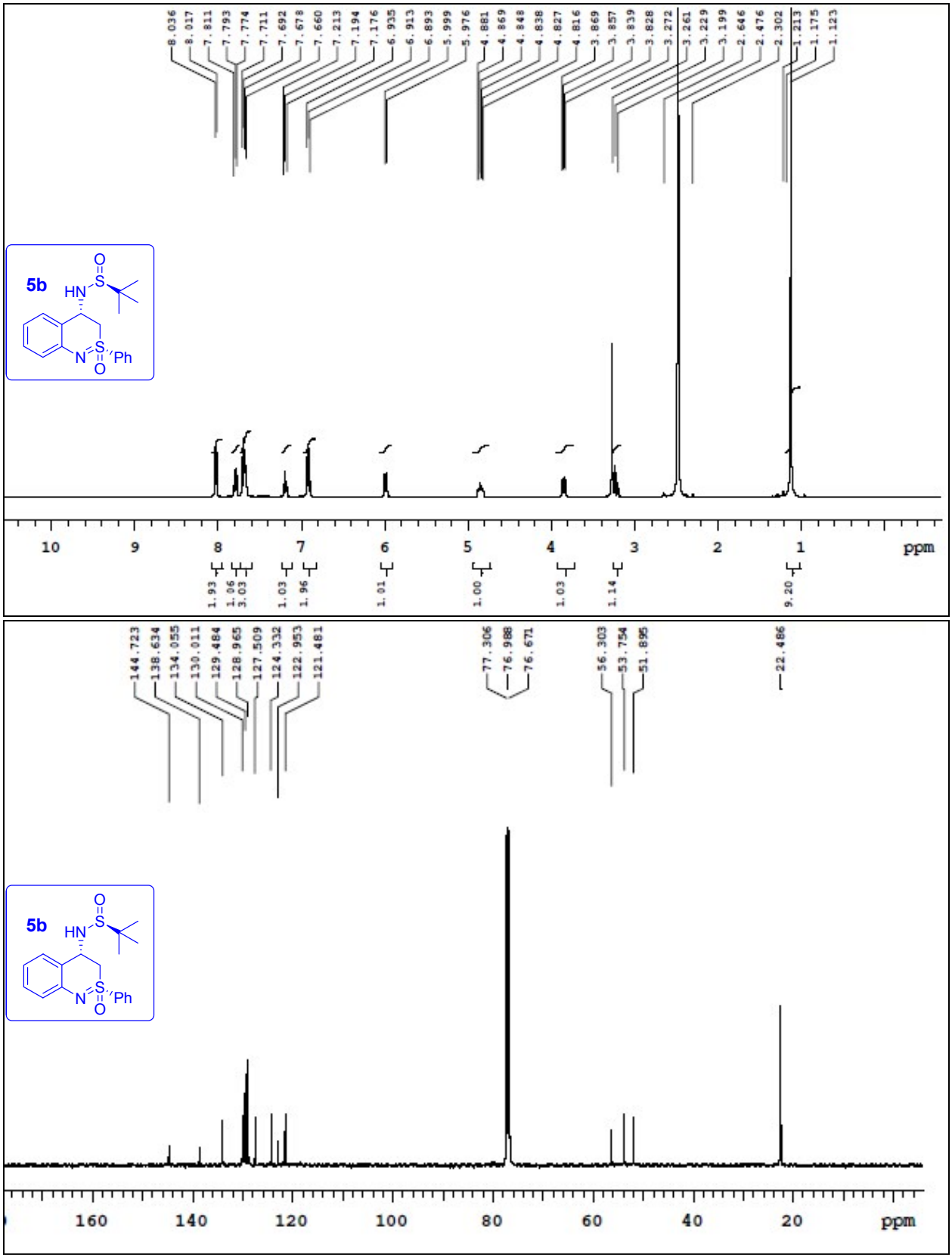
Sample Name:	JBPHD1-JBL-C-1529-009-S0	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	254.0nm
Sample Set Name:	IA_CHIRAL_HPLC1	Vial:	6
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	10/13/2015 5:51:33 PM IST	Date Processed:	10/14/2015 11:13:47 AM IST

Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase : IPA(100%)
Flow rate : 0.5 mL/min

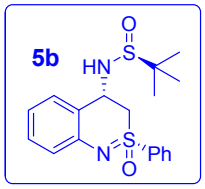




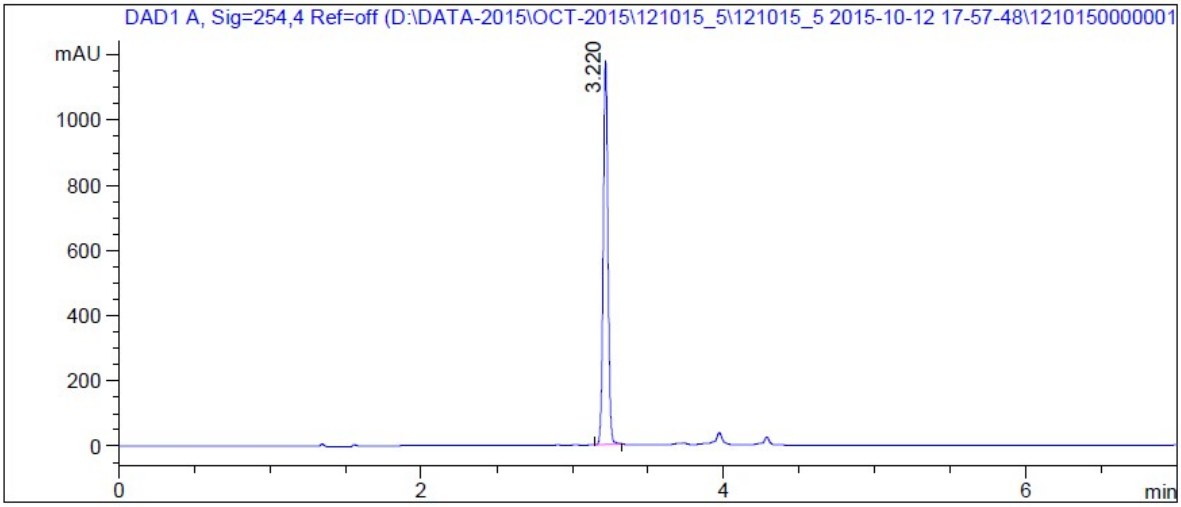
	RT	Area	% Area
1	8.277	23289466	36.62
2	10.042	40303360	63.38


8.036
8.017
7.811
7.793
7.774
7.711
7.692
7.678
7.660
7.213
7.194
7.176
6.935
6.913
6.893
5.999
5.976
4.881
4.869
4.848
4.838
4.827
4.816
3.869
3.857
3.839
3.828
3.272
3.261
3.229
3.199
2.646
2.476
2.302
1.213
1.175
1.123
5b
HN
O
S
N
S
Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
1.93
1.06
3.03
1.03
1.96
1.01
1.00
1.03
1.14
9.20
144.723
138.634
134.055
130.011
129.484
128.965
127.509
124.332
122.953
121.481
77.306
76.988
76.671
56.303
53.754
51.896
22.486
160
140
120
100
80
60
40
20
ppm

```
Injection Date  : Mon, 12. Oct. 2015            Seq Line   :          1
Sample Name     : JBPHD1-JBL-C-1529-009-0S                          P1-E-06
Acq Operator    : RAJESH                       Inj. No.   :          1
Data file:        D:\DATA-2015\OCT-2015\    ->  Inj. Vol.  :       2 µl
Injection Time    5:58:30 PM
Acq. Method     : D:\DATA-2015\OCT-2015\121015_5\121015_5 2015-10-12 1->
Analysis Method : C:\CHEM32\1\METHODS\KINETEX_1100MIN_A2B2_MET.M
Kinetex C18  (100mm X 4.6 mm X 2.6µm)
Mobile phase (A) : 0.1% TFA in  Water
Mobile phase (B) : ACN
Flow rate        :0.75ml/min
```



->

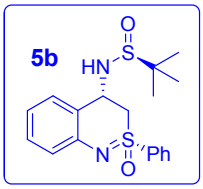


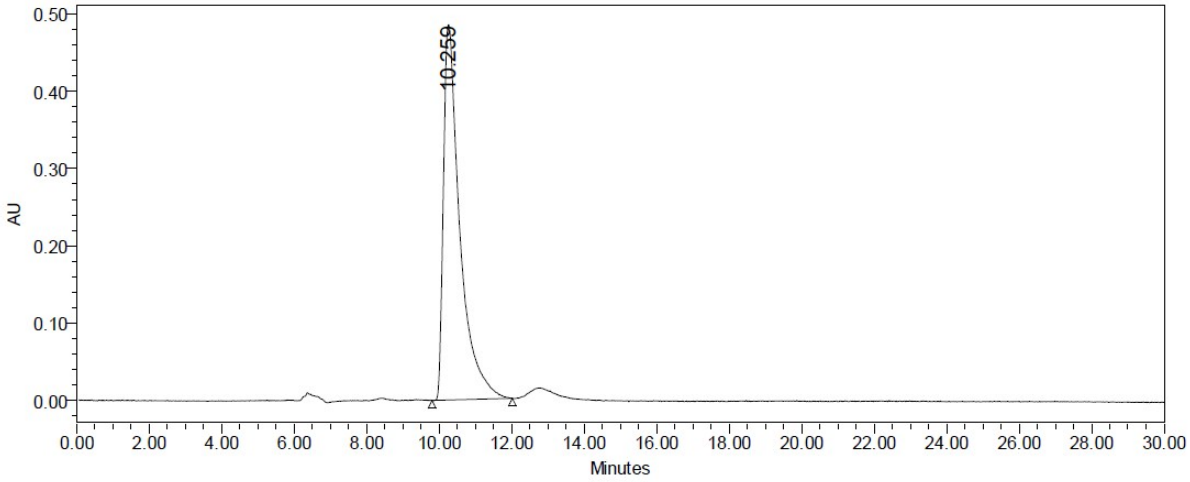

```
Signal  1:DAD1 A, Sig=254,4 Ref=off
|Peak|   RT    | Type  | Width |   Area    | Area % |
| #  |  [min]  |       | [min] |           |        |
|----|---------|-------|-------|-----------|--------|
|   1|    3.220|MM     |  0.036|  2518.973| 100.000|
-------------------------------------------------------
```

JUBILANT BIOSYS, BANGALORE

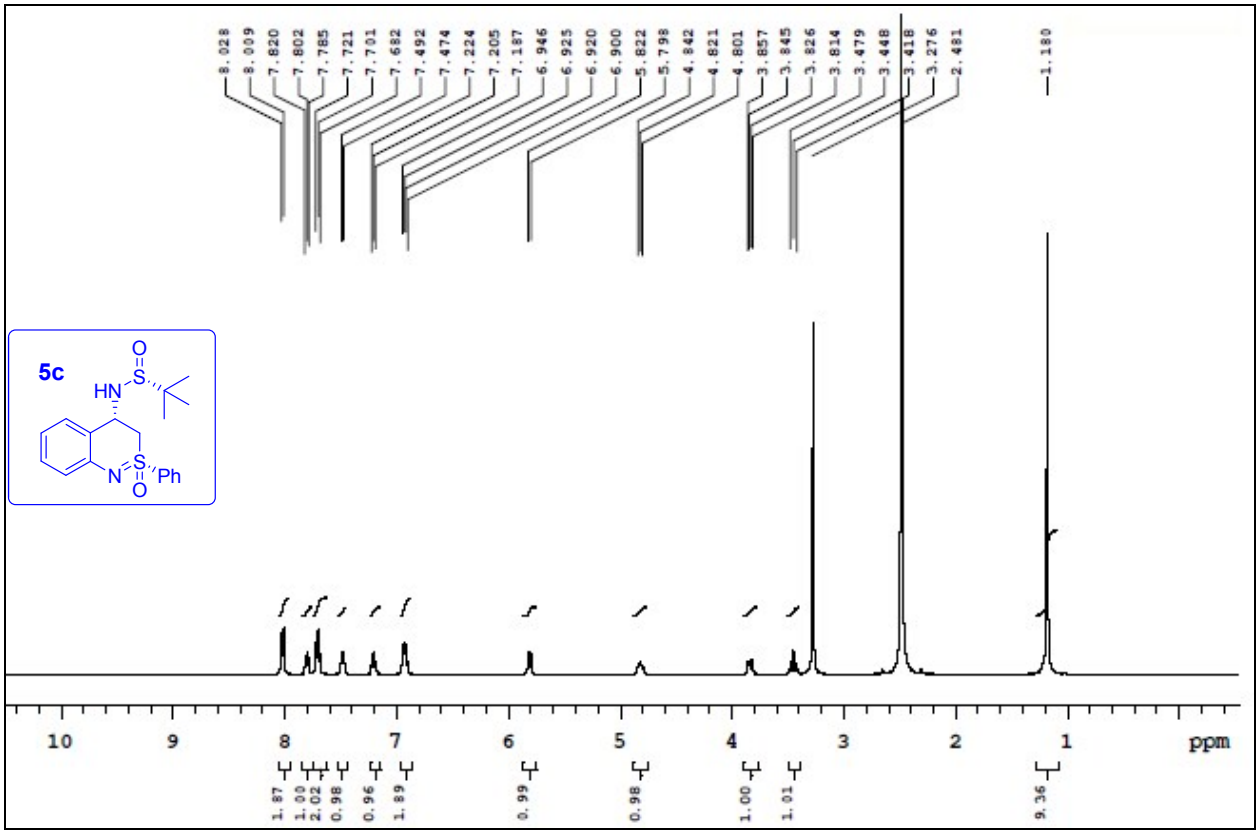
Sample Name:	JBPHD1-JBL-C-1529-009-0S	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	254.0nm@1
Sample Set Name:	IA_CHIRAL_HPLC1	Vial:	4
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	10/13/2015 4:49:40 PM IST	Date Processed:	10/14/2015 11:49:21 AM IST

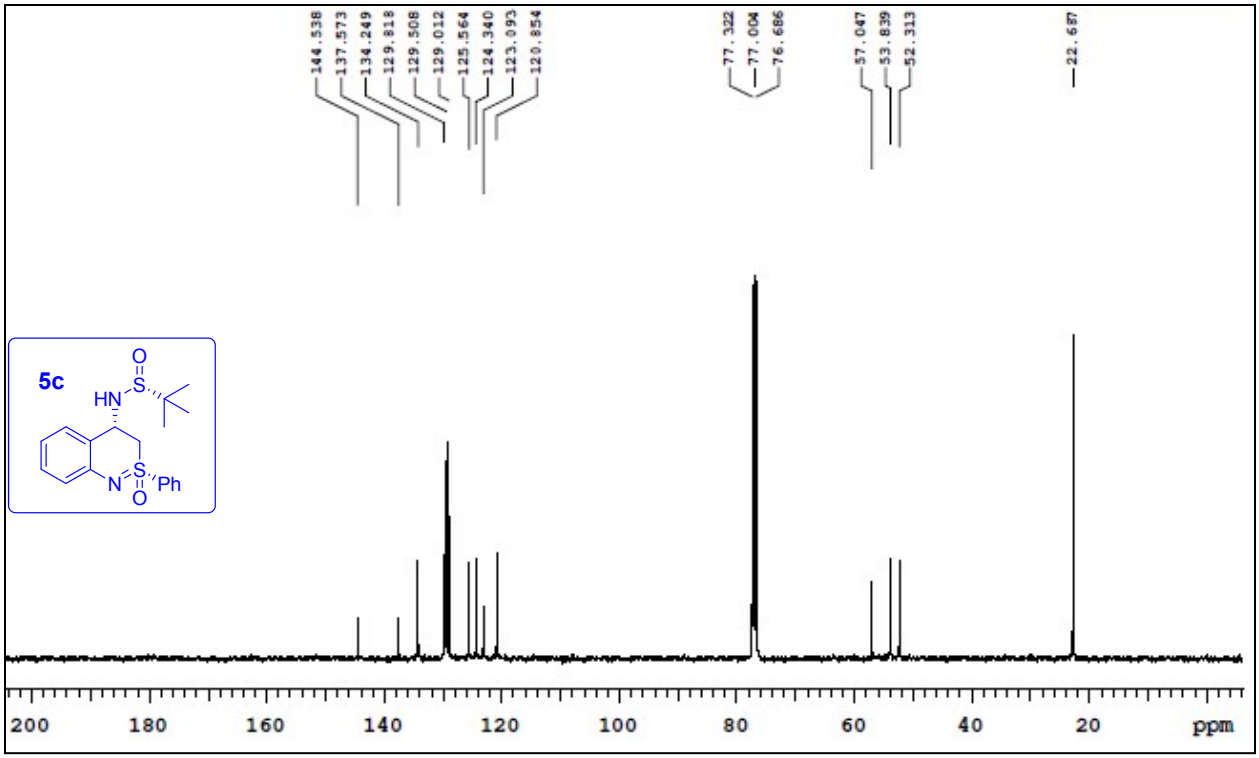
Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase : IPA(100%)
Flow rate : 0.5 mL/min



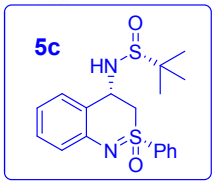


	RT	Area	% Area
1	10.259	15237206	100.00

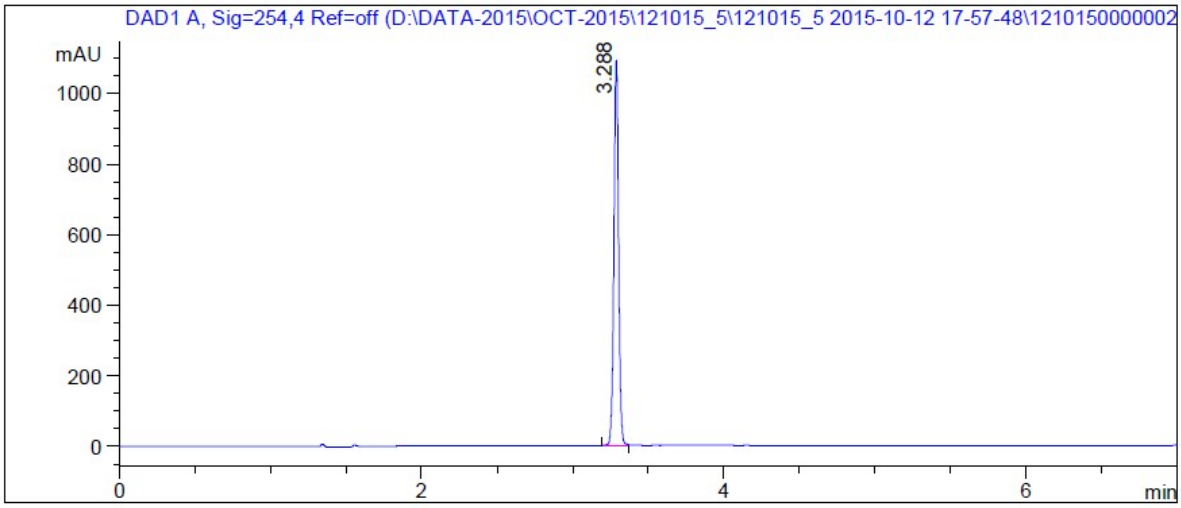

8.028
8.009
7.820
7.802
7.785
7.721
7.701
7.682
7.492
7.474
7.224
7.205
7.187
6.946
6.925
6.920
6.900
5.822
5.798
4.842
4.821
4.801
3.857
3.845
3.826
3.814
3.479
3.448
3.418
3.276
2.481
1.180
5c
HN
O
S
N
S
Ph
O
10
9
8
7
6
5
4
3
2
1
ppm
1.87
1.00
2.02
0.98
0.96
1.89
0.99
0.98
1.00
1.01
9.36


144.538
137.573
134.249
129.818
129.508
129.012
125.564
124.340
123.093
120.854
77.322
77.004
76.686
57.047
53.839
52.313
22.687
5c
HN
O
S
N
S
Ph
O
200
180
160
140
120
100
80
60
40
20
ppm

```
Injection Date  : Mon, 12. Oct. 2015            Seq Line   :          2
Sample Name     : JBPHD1-JBL-C-1529-009-0R                          P1-E-07
Acq Operator    : RAJESH                       Inj. No.   :          1
Data file:        D:\DATA-2015\OCT-2015\    ->  Inj. Vol.  :       2 µl
Injection Time    6:06:22 PM
Acq. Method     : D:\DATA-2015\OCT-2015\121015_5\121015_5 2015-10-12 1->
Analysis Method : C:\CHEM32\1\METHODS\KINETEX_1100MIN_A2B2_MET.M
Kinetex C18  (100mm X 4.6 mm X 2.6µm)
Mobile phase (A) : 0.1% TFA in  Water
Mobile phase (B) : ACN
Flow rate        :0.75ml/min
```



->

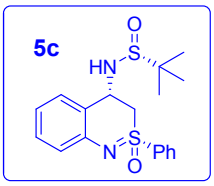


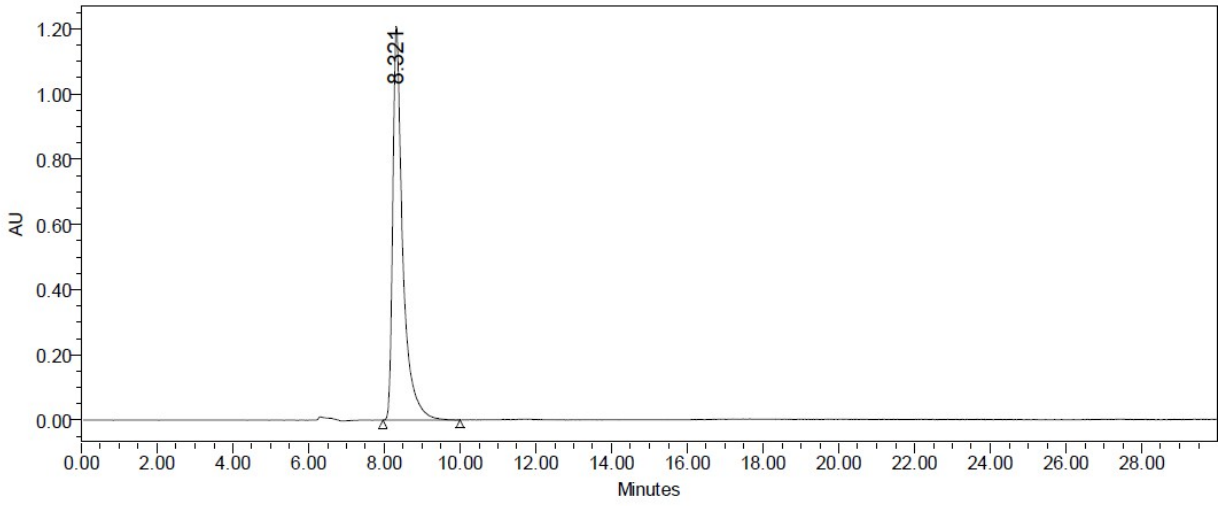

```
Signal  1:DAD1 A, Sig=254,4 Ref=off
|Peak|   RT    | Type  | Width |   Area    | Area % |
| #  |  [min]  |       | [min] |           |        |
|----|---------|-------|-------|-----------|--------|
|   1|    3.288|MM     |  0.036|  2345.900| 100.000|
-------------------------------------------------------
```

JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-009-0R	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	254.0nm@1
Sample Set Name:	IA_CHIRAL_HPLC1	Vial:	5
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 254.0 nm
Date Acquired:	10/13/2015 5:20:29 PM IST	Date Processed:	10/14/2015 11:49:31 AM IST

Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase : IPA(100%)
Flow rate : 0.5 mL/min

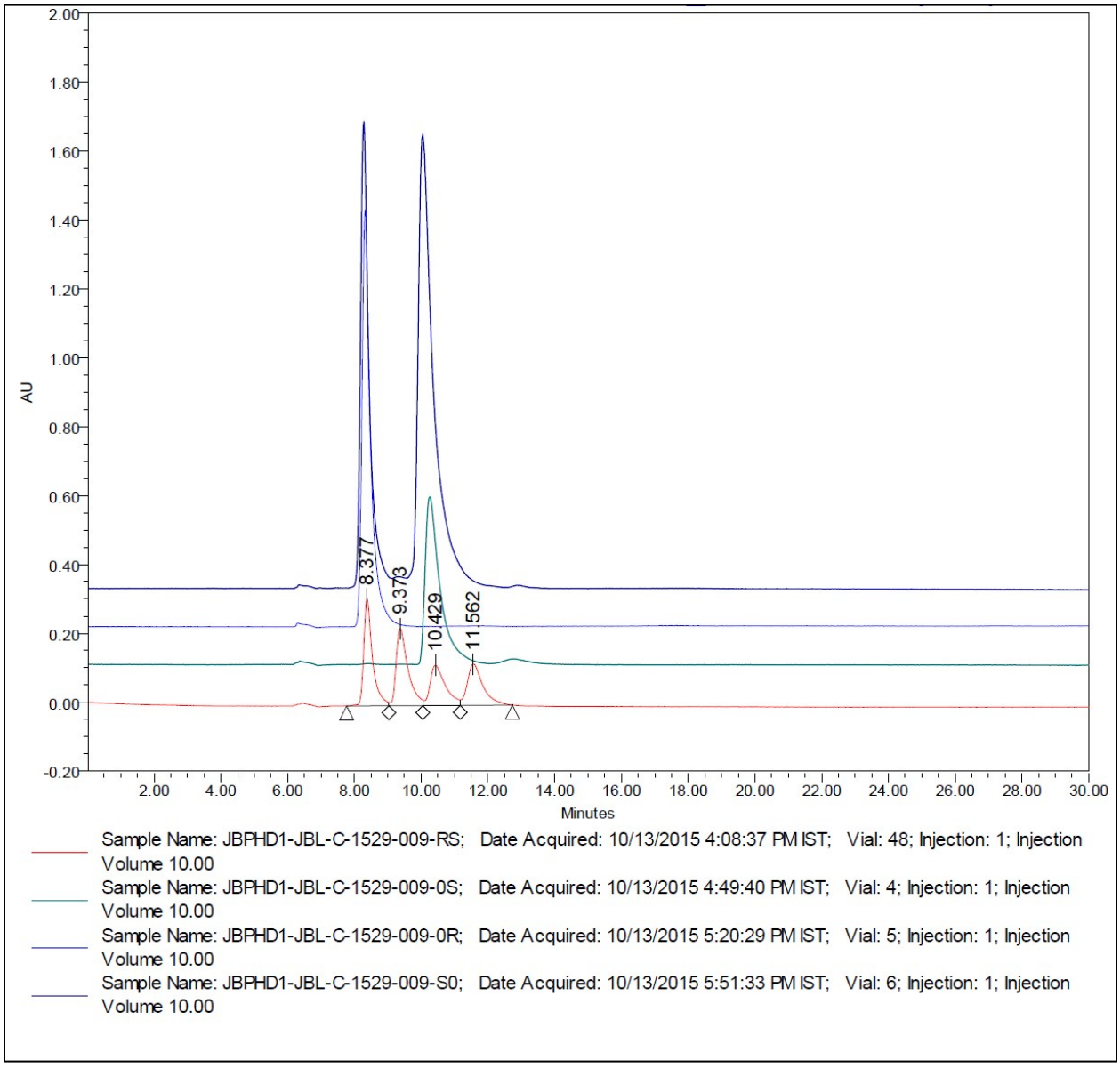


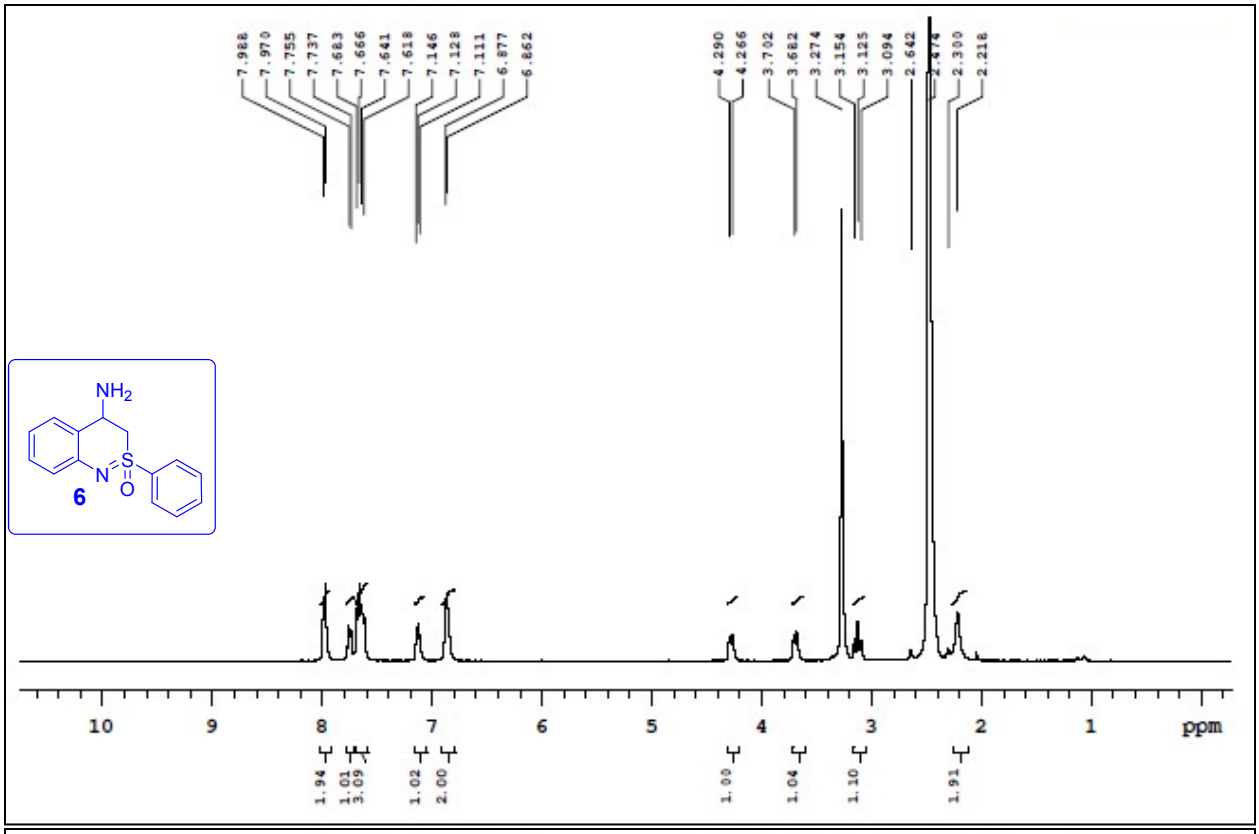


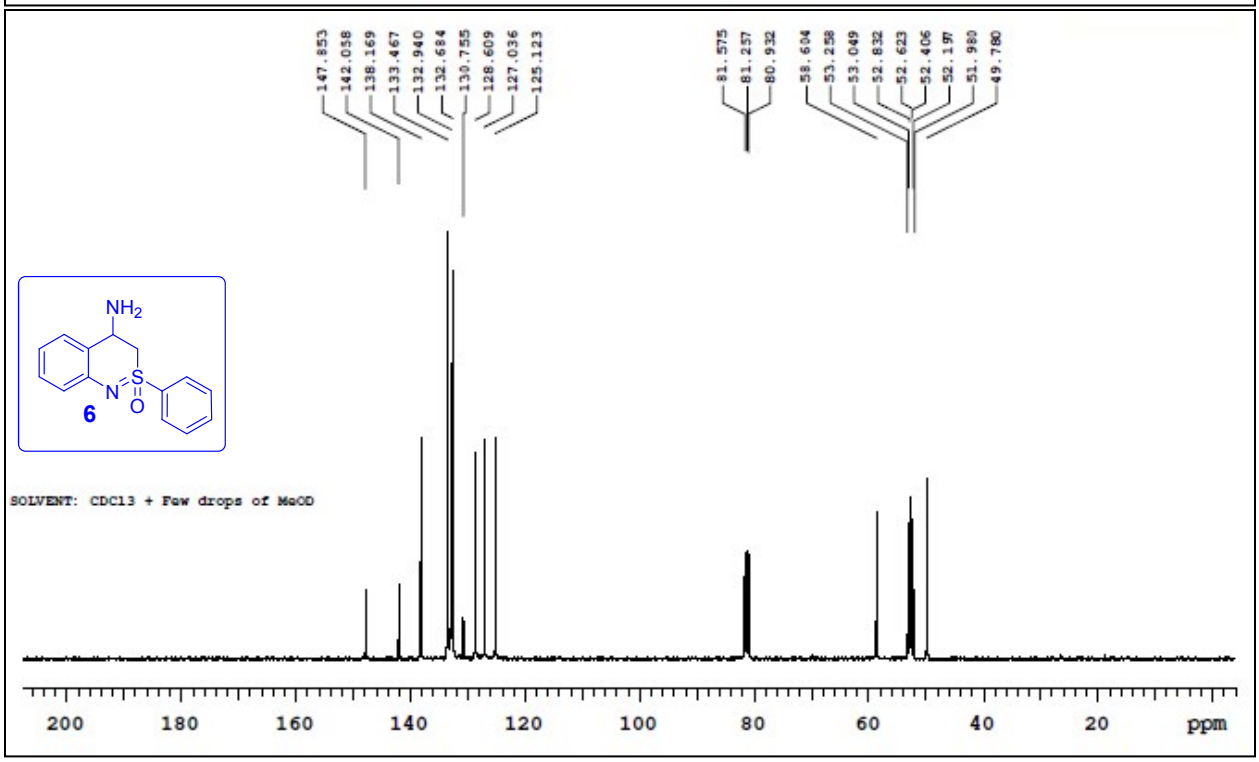
	RT	Area	% Area
1	8.321	22093652	100.00

Overplay report

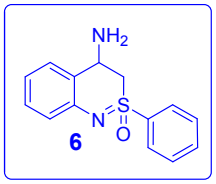
Sample Name	Compound No
JBPHD1-JBL-C-1529-009-RS	**5**
JBPHD1-JBL-C-1529-009-S0	**5a**
JBPHD1-JBL-C-1529-009-0S	**5b**
JBPHD1-JBL-C-1529-009-0R	**5c**

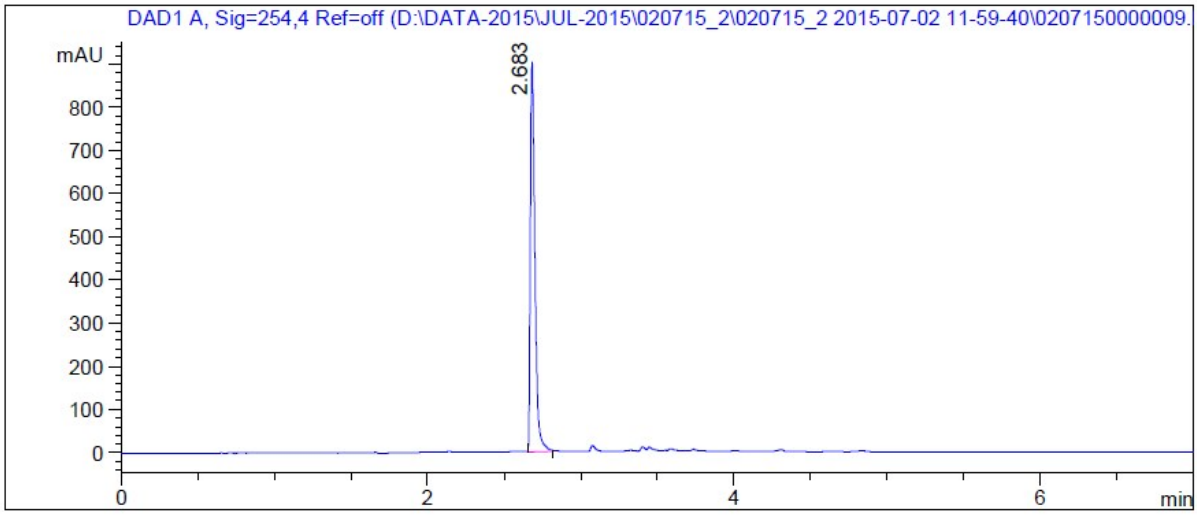



7.988
7.970
7.755
7.737
7.683
7.666
7.641
7.618
7.146
7.128
7.111
6.877
6.862
4.290
4.266
3.702
3.682
3.274
3.154
3.125
3.094
2.642
2.474
2.300
2.218
NH2
N
S
O
6
10
9
8
7
6
5
4
3
2
1
ppm
1.94
1.01
3.09
1.02
2.00
1.00
1.04
1.10
1.91


147.853
142.058
138.169
133.467
132.940
132.684
130.755
128.609
127.036
125.123
81.575
81.257
80.932
58.604
53.258
53.049
52.832
52.623
52.406
52.197
51.980
49.780
NH2
N
S
O
6
SOLVENT: CDCl3 + Few drops of MeOD
200
180
160
140
120
100
80
60
40
20
ppm

```
Data file:          D:\DATA-2015\JUL-2015\    ->  Inj. Vol.  :        2 µl
Injection Time      1:19:30 PM
Acq. Method       : D:\DATA-2015\JUL-2015\020715_2\020715_2 2015-07-02 1->
Analysis Method   : C:\CHEM32\1\METHODS\KINETEX_777MIN_A2B2_MET.M
Kinetex C18  (100mm X 4.6 mm X 2.6µm)
Mobile phase (A) :  0.1%TFA  in water
Mobile phase (B) : ACN
Flow rate         :0.75ml/min
```





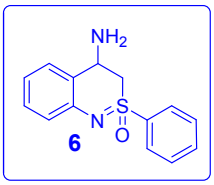
Signal 1:DAD1 A, Sig=254,4 Ref=off

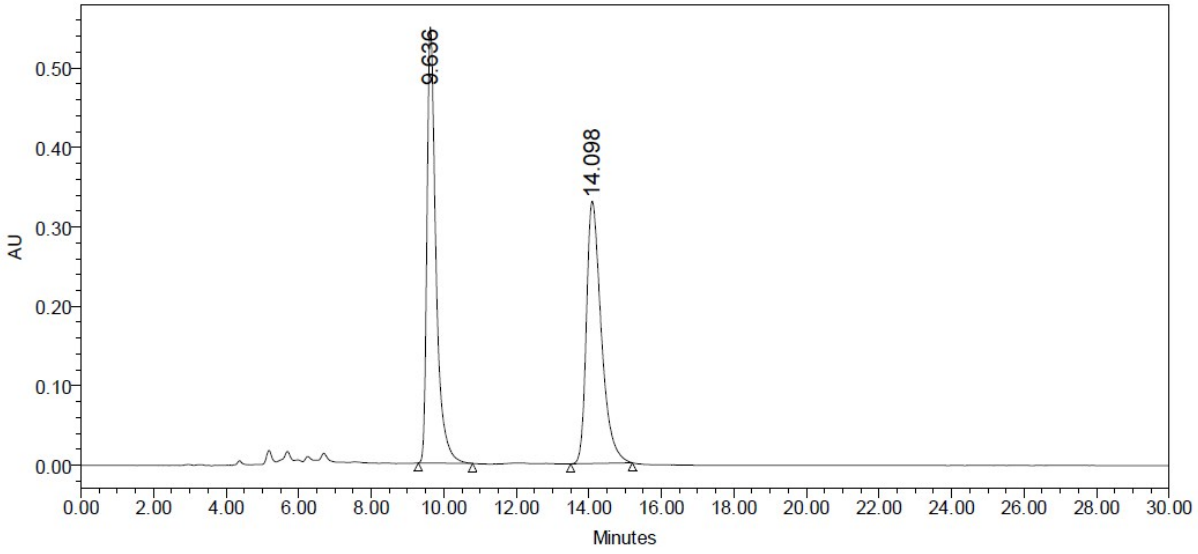
Peak #	RT [min]	Type	Width [min]	Area	Area %
1	2.683	MM	0.036	1931.627	100.000

JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-020-RS	Acquired By:	anachem
Test Type:	HPLC / UV	Sample Set Name:	IA_HEP_ETH_HPLC2
Acq. Method Set:	IA_HEP_ETH_HPLC2	Vial:	40
Injection Volume:	20.00 ul	Proc. Chnl. Descr.:	254nm
Date Acquired:	7/2/2015 8:51:06 PM IST	Date Processed:	7/3/2015 8:55:00 AM IST

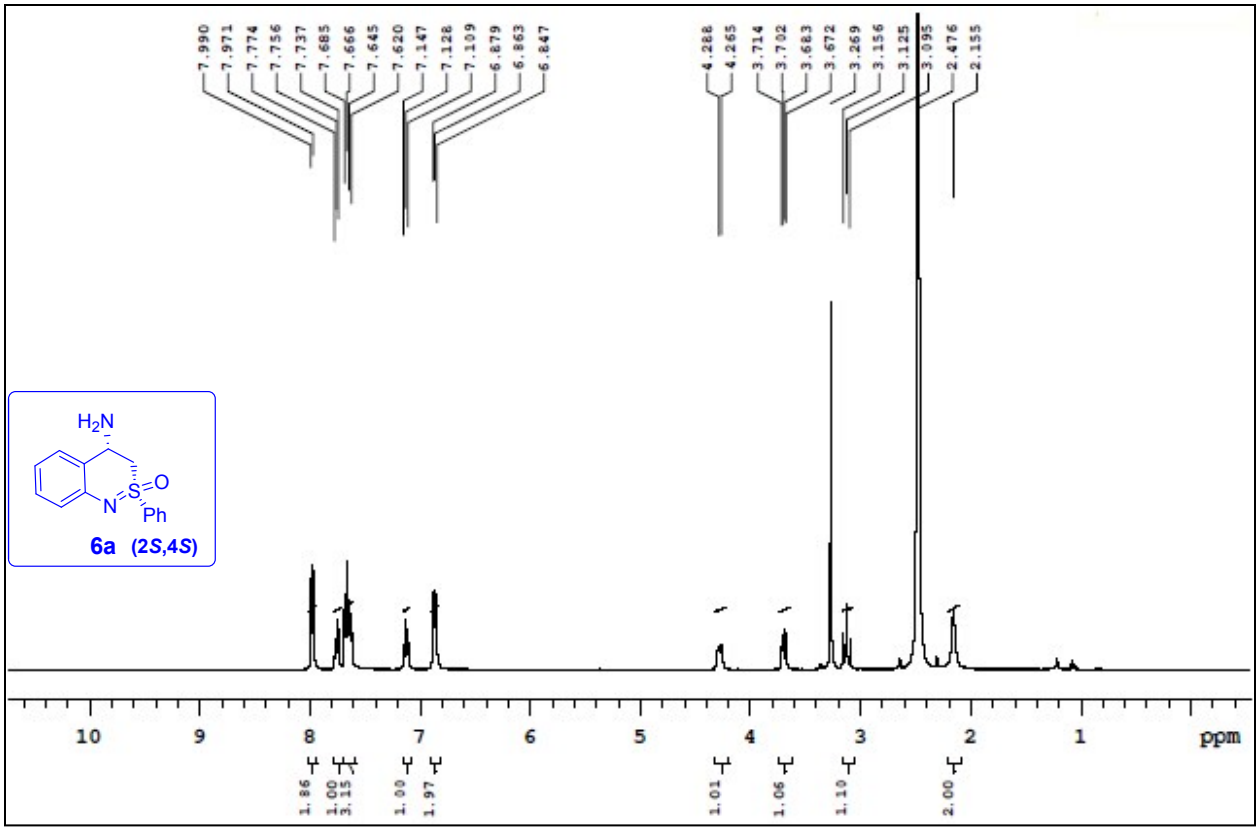
Analytical Conditions:
Column : CHIRALPAK IA (250mm X 4.6mmX 5mic)
Mobile phase(A) : HEPTANE:EtOHw ith 0.01% DEA (60:40)
Flow : 1ml/min

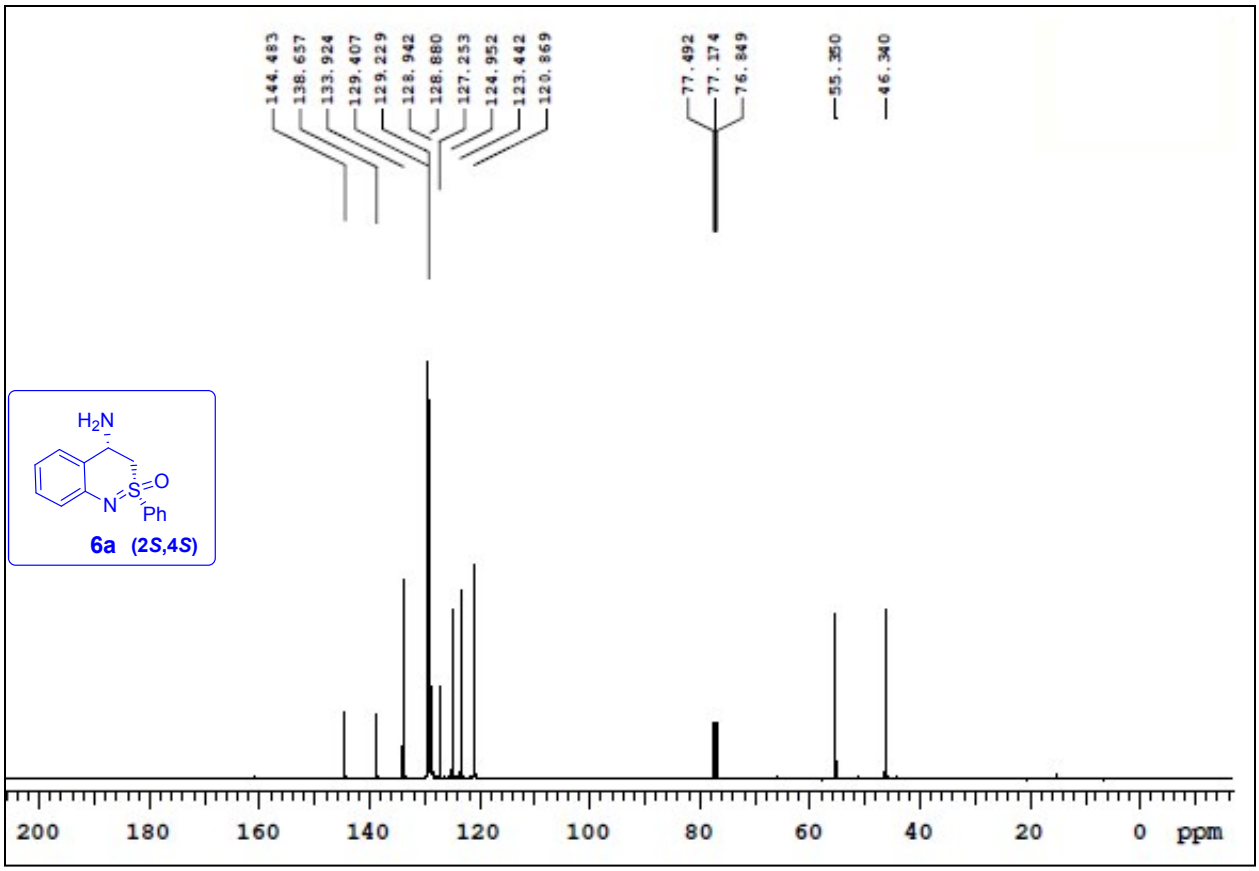




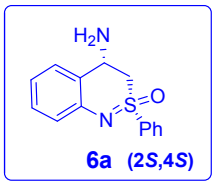
	RT	Area	% Area
1	9.636	9479070	50.26
2	14.098	9381795	49.74

CONFIDENTIAL

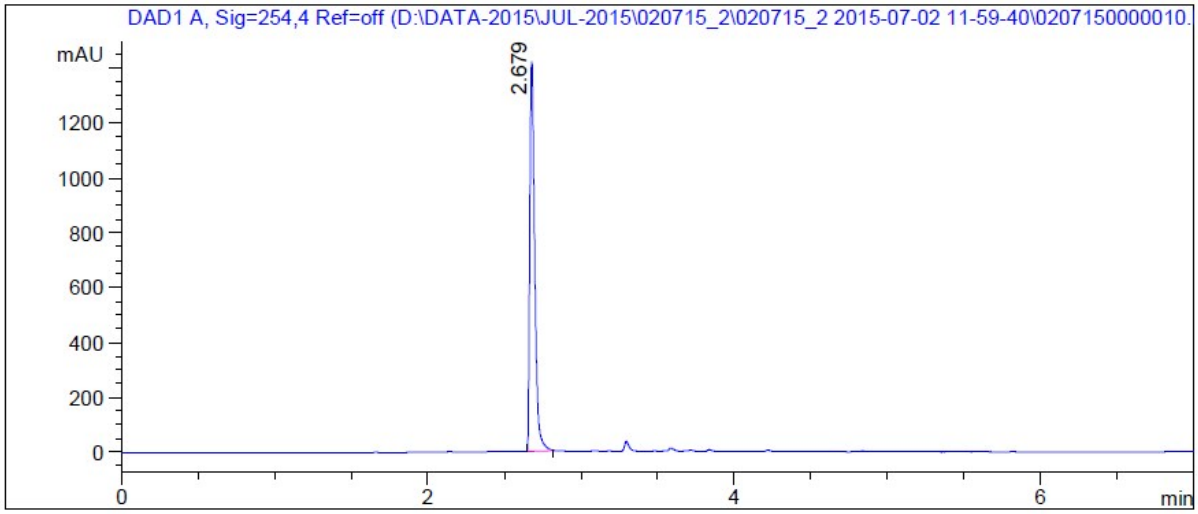

7.990
7.971
7.774
7.756
7.737
7.685
7.666
7.645
7.620
7.147
7.128
7.109
6.879
6.863
6.847
4.288
4.265
3.714
3.702
3.683
3.672
3.269
3.156
3.125
3.095
2.476
2.155
H_2N
O
S
N
Ph
6a (2S,4S)
10
9
8
7
6
5
4
3
2
1
ppm
1.86
1.00
3.15
1.00
1.97
1.01
1.06
1.10
2.00


144.483
138.657
133.924
129.407
129.229
128.942
128.880
127.253
124.952
123.442
120.869
77.492
77.174
76.849
55.350
46.340
H_2N
O
S
N
Ph
6a (2S,4S)
200
180
160
140
120
100
80
60
40
20
0
ppm

```
Data file:        D:\DATA-2015\JUL-2015\    ->  Inj. Vol.  :        2 µl
Injection Time    1:27:20 PM
Acq. Method     : D:\DATA-2015\JUL-2015\020715_2\020715_2 2015-07-02 1->
Analysis Method : C:\CHEM32\1\METHODS\KINETEX_777MIN_A2B2_MET.M
Kinetex C18  (100mm X 4.6 mm X 2.6µm)
Mobile phase (A) :  0.1%TFA  in water
Mobile phase (B) : ACN
Flow rate        :0.75ml/min
```



6a (2*S*,4*S*)



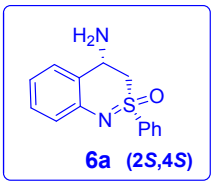
Signal 1:DAD1 A, Sig=254,4 Ref=off

Peak #	RT [min]	Type	Width [min]	Area	Area %
1	2.679	MM	0.038	3233.079	100.000

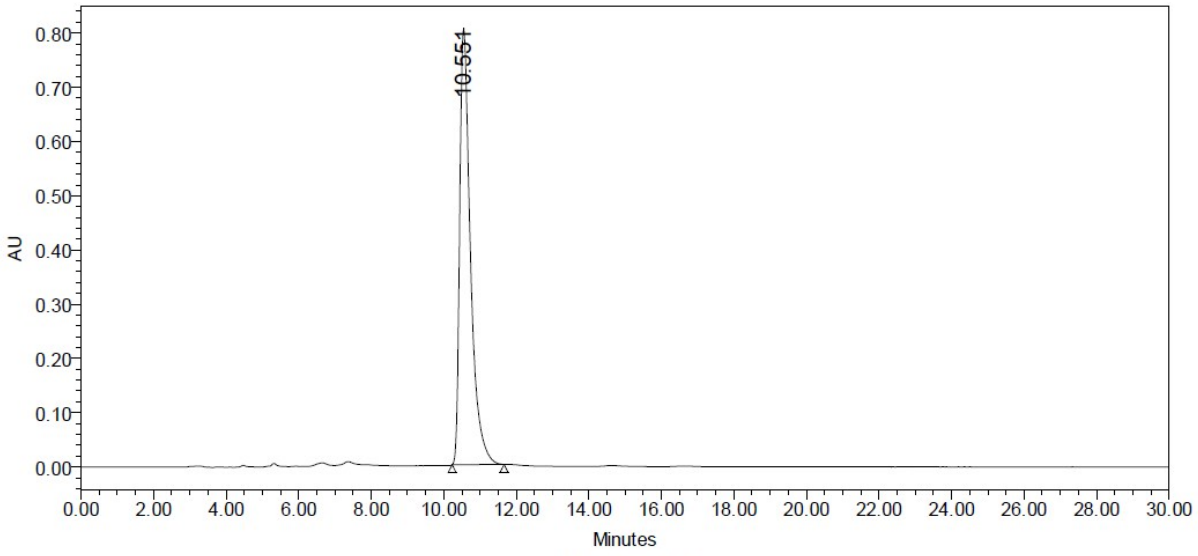
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-020-S0	Acquired By:	anachem
Test Type:	HPLC / UV	Sample Set Name:	IA_HEP_ETH_HPLC2
Acq. Method Set:	IA_HEP_ETH_HPLC2	Vial:	42
Injection Volume:	20.00 ul	Proc. Chnl. Descr.:	254nm
Date Acquired:	7/2/2015 7:18:18 PM IST	Date Processed:	7/3/2015 8:55:26 AM IST

Analytical Conditions:
Column : CHIRALPAK IA (250mm X 4.6mmX 5mic)
Mobile phase(A) : HEPTANE:EtOHw ith 0.01% DEA (60:40)
Flow : 1ml/min



6a (2S,4S)



	RT	Area	% Area
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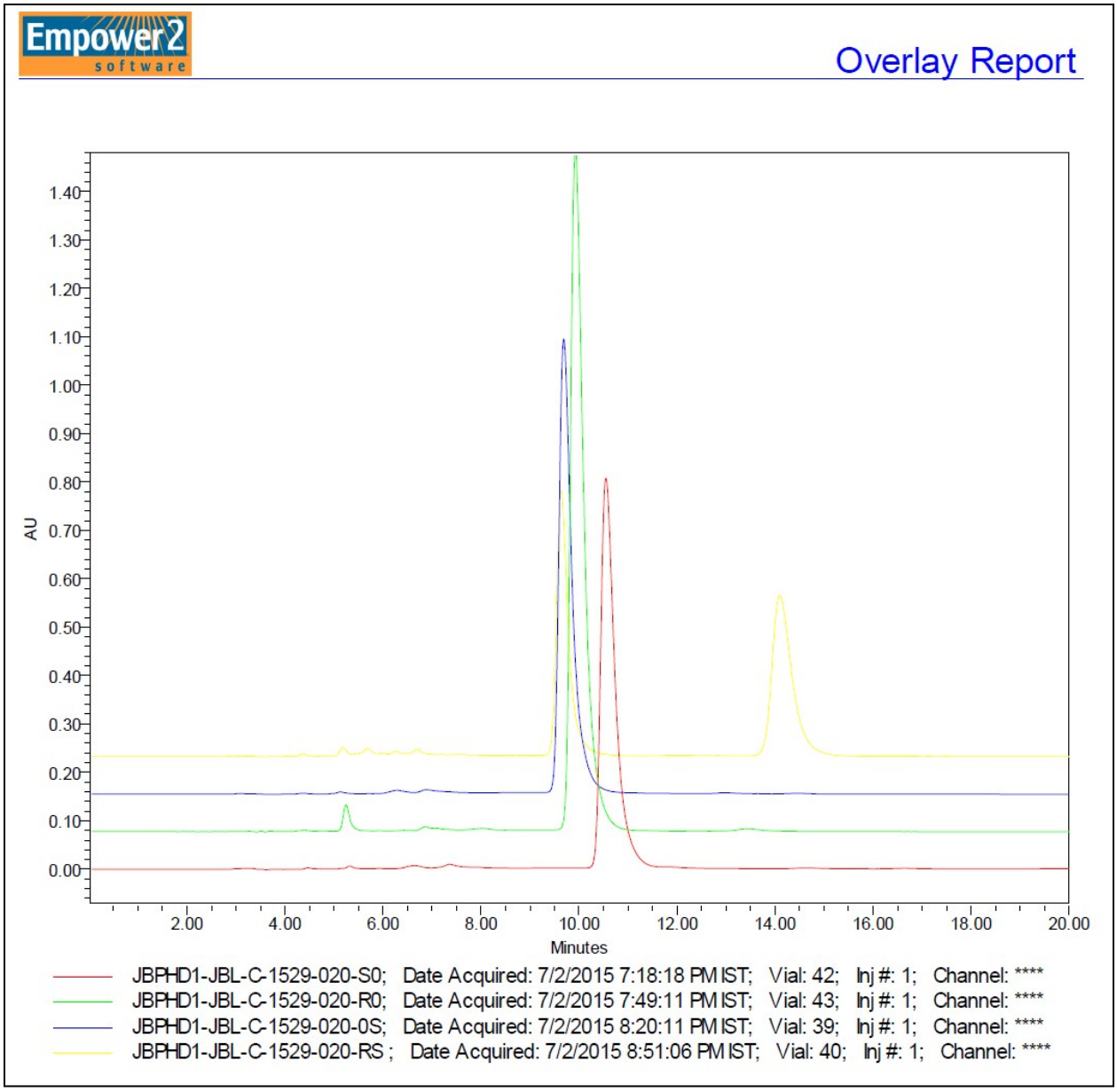
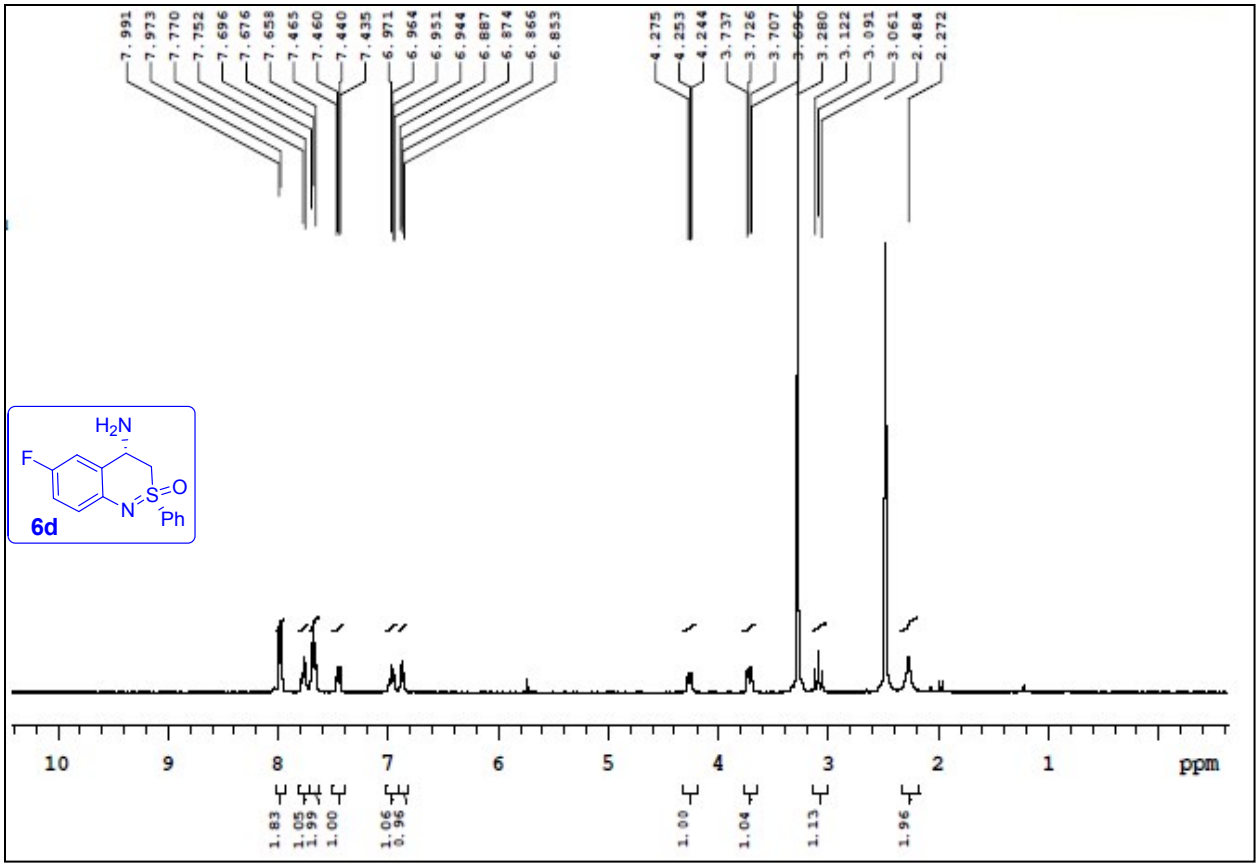
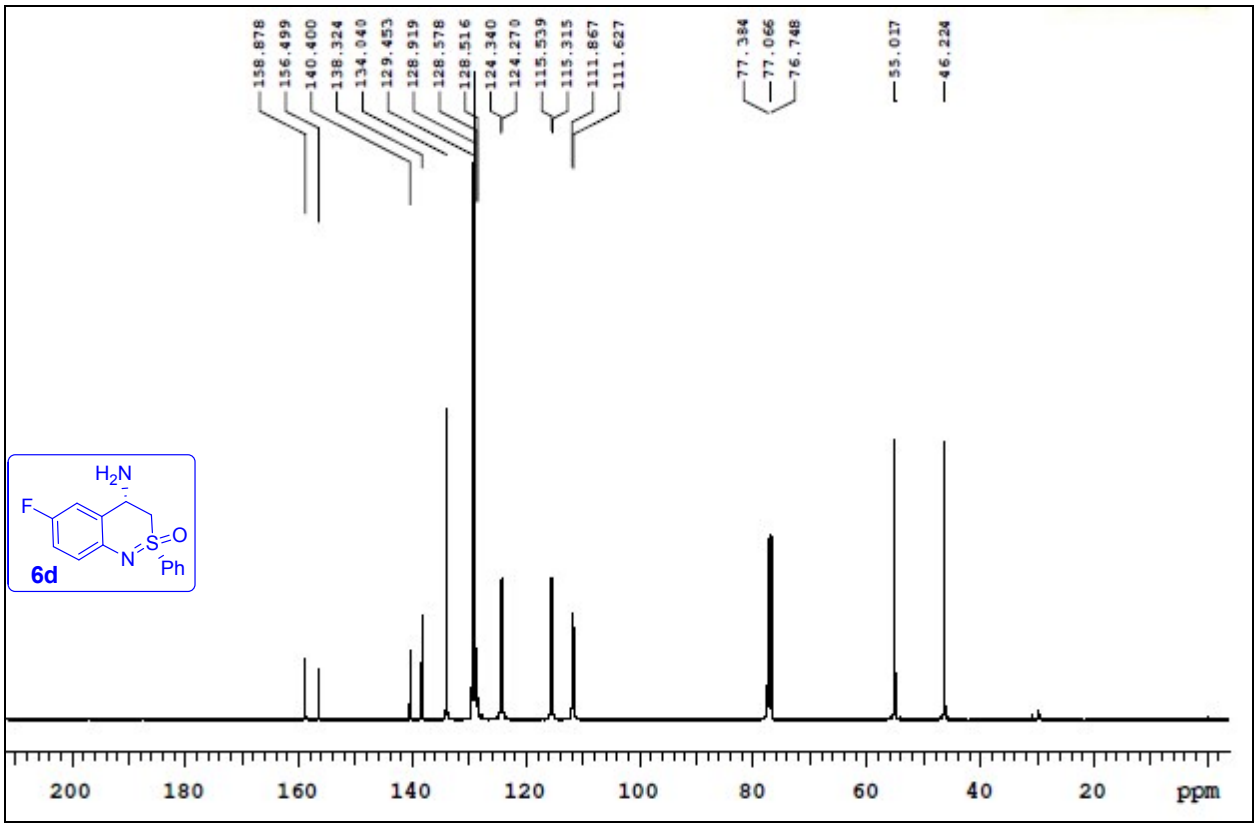
CONFIDENTIAL



Sample Name	Compound No
JBPHD1-JBL-C-1529-020-RS	**6**
JBPHD1-JBL-C-1529-020-S0	**6a**
JBPHD1-JBL-C-1529-020-0S	**6a**
JBPHD1-JBL-C-1529-020-0R	**6a**

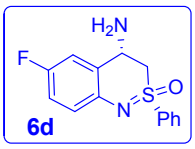

7.991
7.973
7.770
7.752
7.696
7.676
7.658
7.465
7.460
7.440
7.435
6.971
6.964
6.951
6.944
6.887
6.874
6.866
6.853
4.275
4.253
4.244
3.737
3.726
3.707
3.696
3.280
3.122
3.091
3.061
2.484
2.272
H2N
F
S
O
N
Ph
6d
10
9
8
7
6
5
4
3
2
1
ppm
1.83
1.05
1.99
1.00
1.06
0.96
1.00
1.04
1.13
1.96

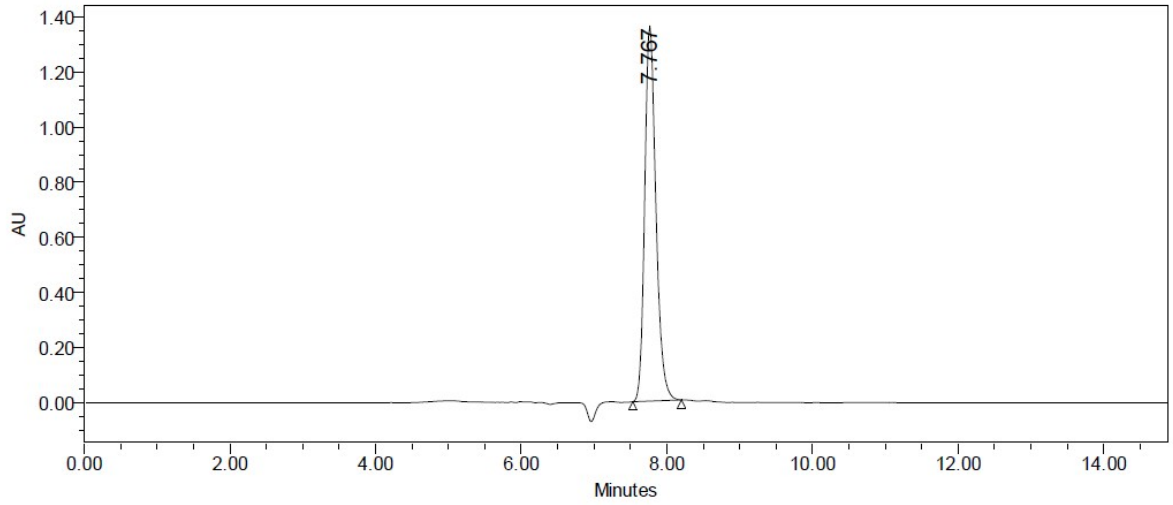

158.878
156.499
140.400
138.324
134.040
129.453
128.919
128.578
128.516
124.340
124.270
115.539
115.315
111.867
111.627
77.384
77.066
76.748
55.017
46.224
H2N
F
S
O
N
Ph
6d
200
180
160
140
120
100
80
60
40
20
ppm

JUBILANT BIOSYS, BANGALORE

Sample Name:	JBL-C-1033-171-02	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	230.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	104
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 230.0 nm
Date Acquired:	8/1/2011 1:40:41 PM IST	Date Processed:	8/1/2011 3:40:48 PM IST

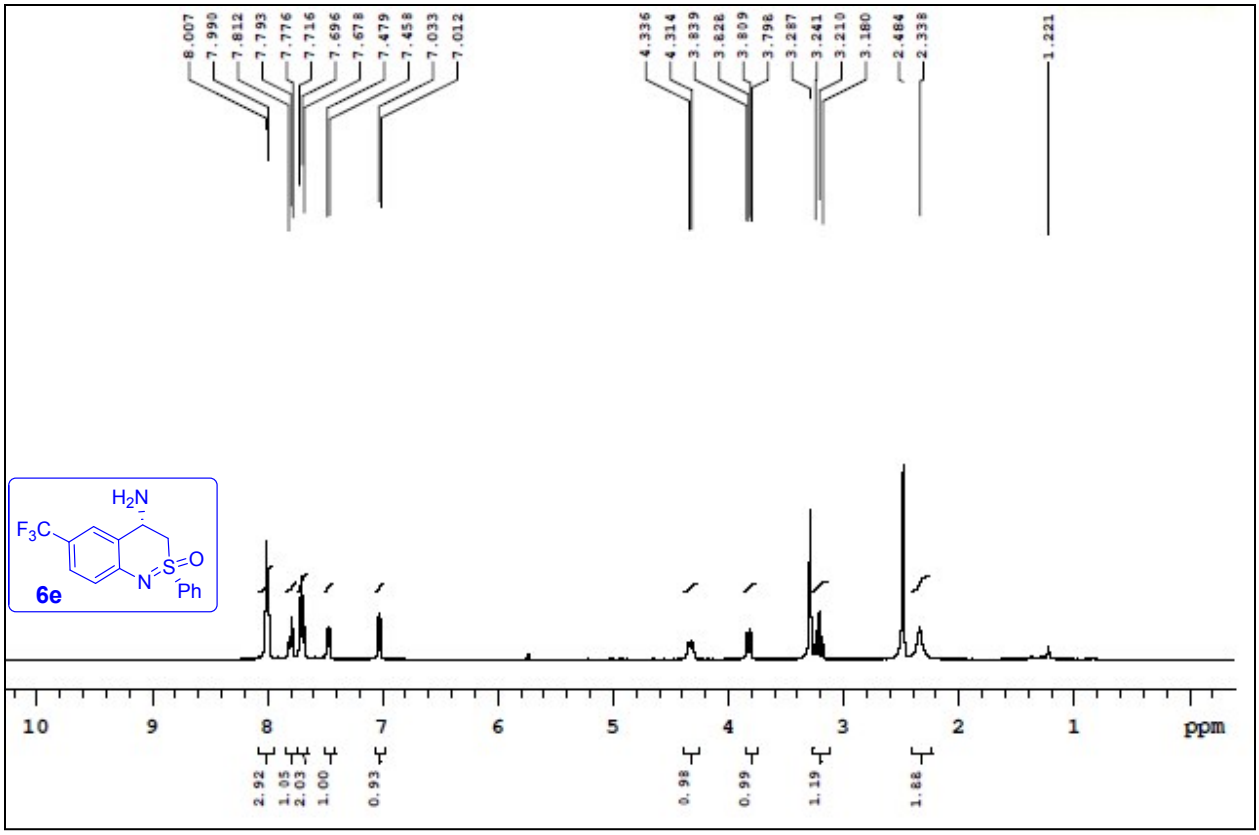
Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase :100% ETOH
Flow rate :0.5mL/min

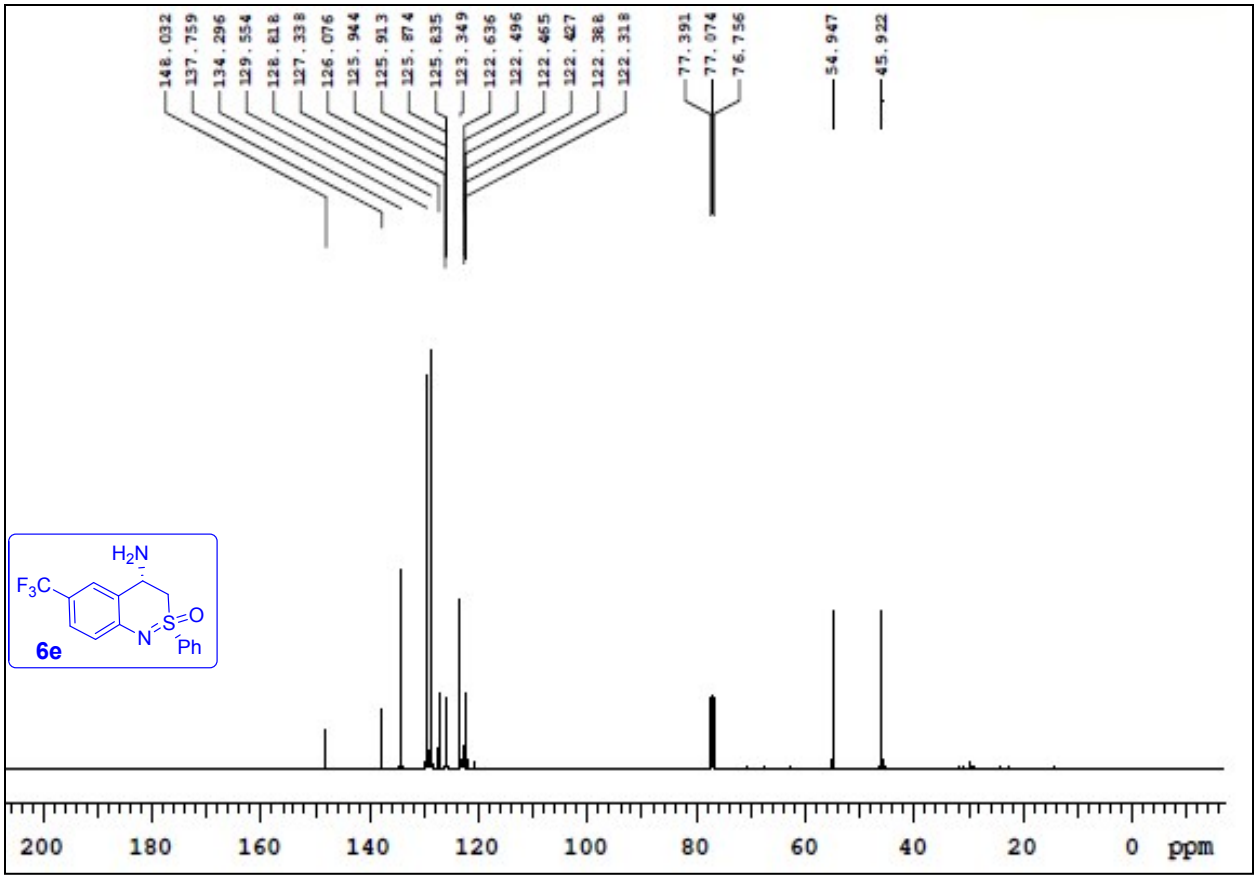




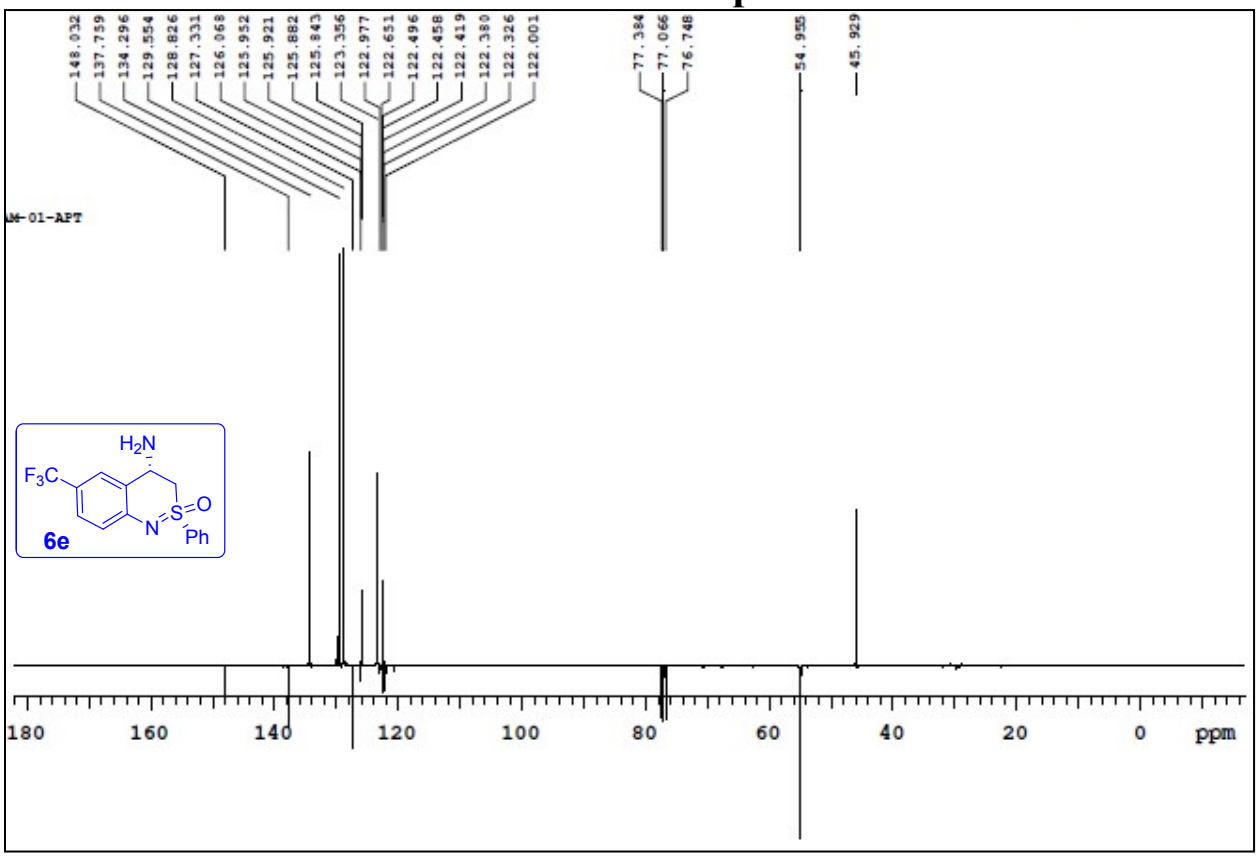
	RT	Area	% Area
1	7.767	14540240	100.00

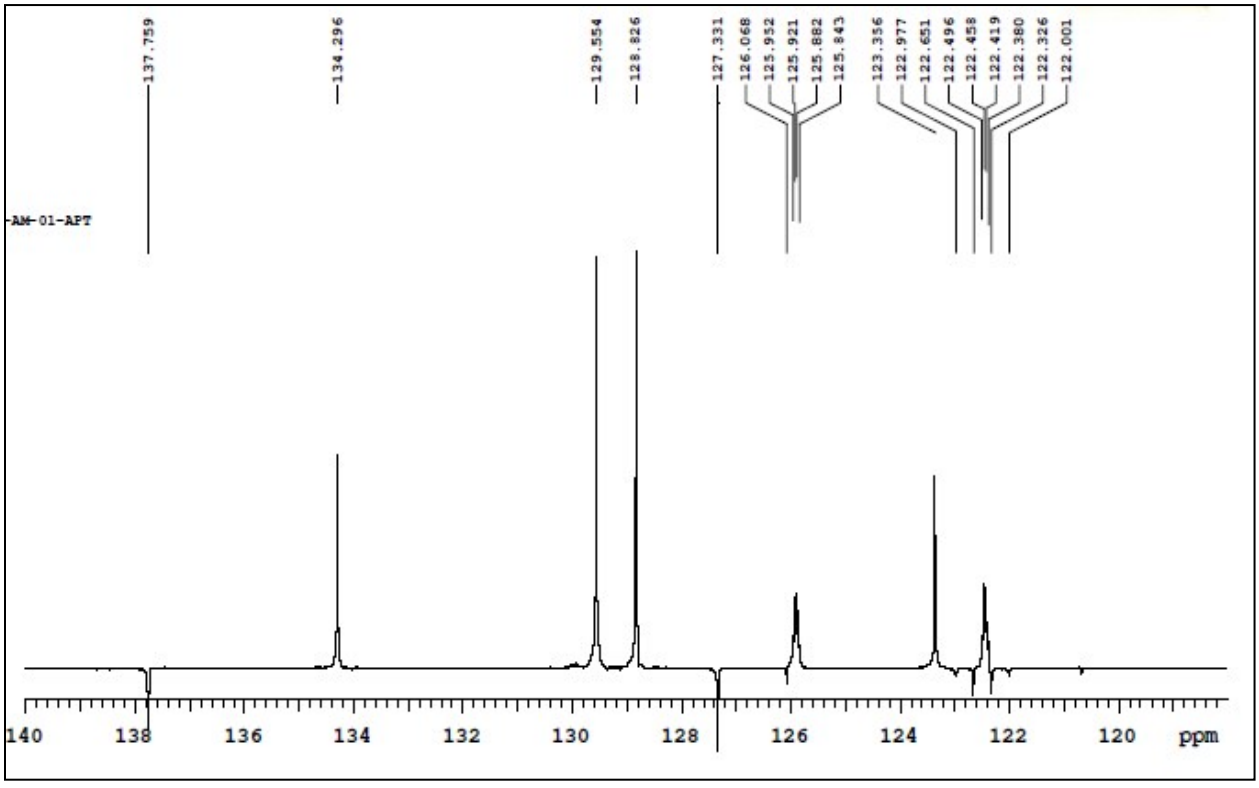
CONFIDENTIAL


8.007
7.990
7.812
7.793
7.776
7.716
7.696
7.678
7.479
7.458
7.033
7.012
4.336
4.314
3.839
3.828
3.809
3.798
3.287
3.241
3.210
3.180
2.484
2.338
1.221
H_2N
F_3C
N
S
O
Ph
6e
10
9
8
7
6
5
4
3
2
1
ppm
2.92
1.05
2.03
1.00
0.93
0.98
0.99
1.19
1.88


148.032
137.759
134.296
129.554
128.818
127.338
126.076
125.944
125.913
125.874
125.835
123.349
122.636
122.496
122.465
122.427
122.388
122.318
77.391
77.074
76.756
54.947
45.922
H_2N
F_3C
N
S
O
Ph
6e
200
180
160
140
120
100
80
60
40
20
0
ppm

6e APT NMR & Expansion

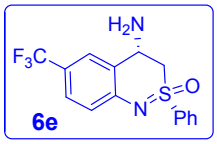




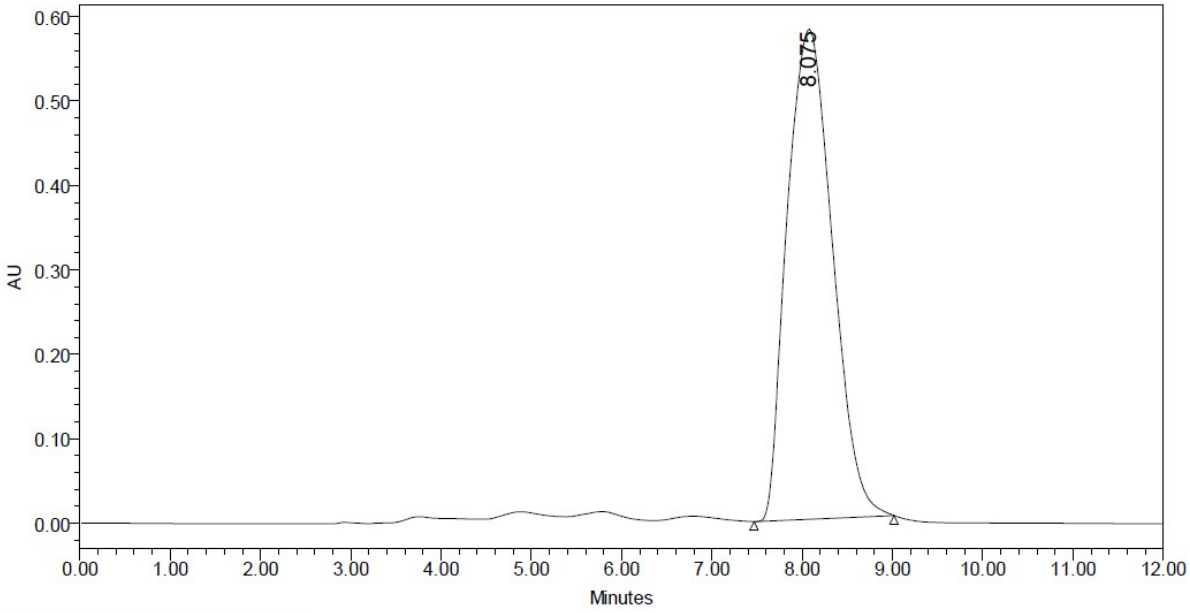
SAMPLE INFORMATION

Sample Name:	JBL-C-1033-181-AM-01	Acquired By:	anachem
Sample Type:	Unknown	Sample Set Name:	141111_1
Vial:	10	Acq. Method Set:	IA_8020_HPLC3_MET
Injection #:	1	Processing Method:	1
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	254nm
Date Acquired:	11/14/2011 12:26:33 PM IST		
Date Processed:	11/15/2011 10:30:50 AM IST		

Analytical Conditions:
Column :Chiralpak IA (250mm X 4.6mm)
Mobile phase A : Heptane
Mobile Phase B : EtOH with 0.1%DEA
Composition : 70:30
Flow rate : 1mL/min



6e



	RT	Area	% Area
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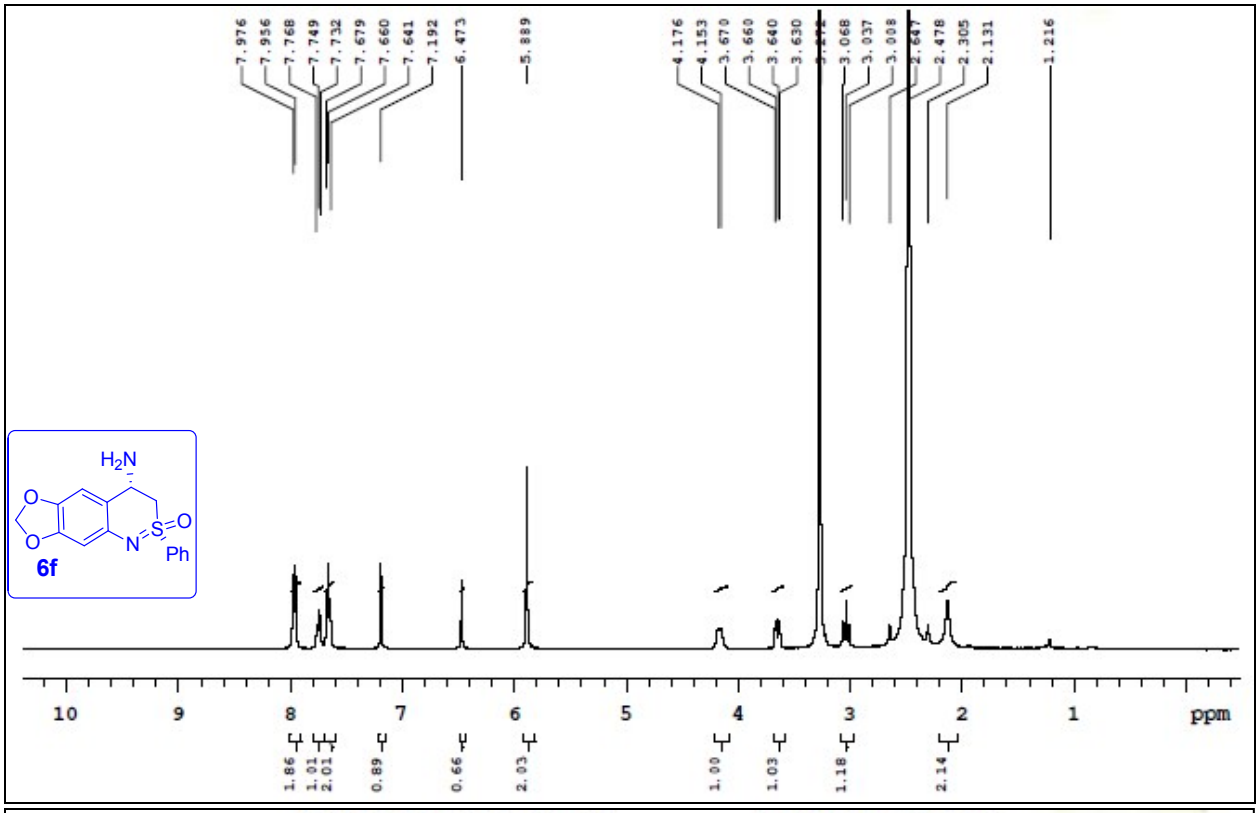
CONFIDENTIAL


7.976
7.956
7.768
7.749
7.732
7.679
7.660
7.641
7.192
6.473
5.889
4.176
4.153
3.670
3.660
3.640
3.630
3.068
3.037
3.008
2.647
2.478
2.305
2.131
1.216
H2N
O
O
N
S
O
Ph
6f
10
9
8
7
6
5
4
3
2
1
ppm
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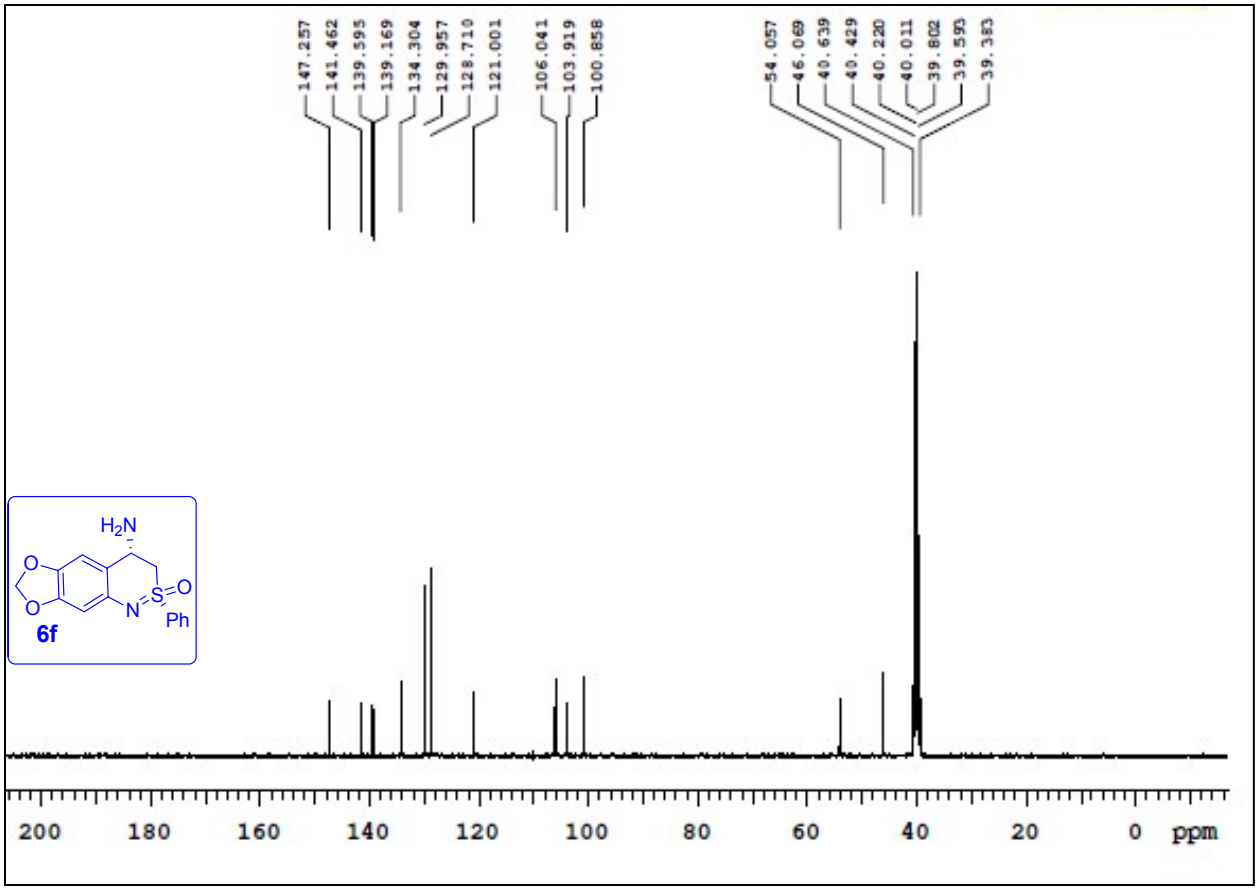
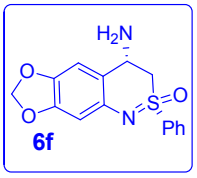
1.01
2.01
0.89
0.66
2.03
1.00
1.03
1.18
2.14


147.257
141.462
139.595
139.169
134.304
129.957
128.710
121.001
106.041
103.919
100.858
54.057
46.069
40.639
40.429
40.220
40.011
39.802
39.593
39.383
H2N
O
O
N
S
O
Ph
6f
200
180
160
140
120
100
80
60
40
20
0
ppm

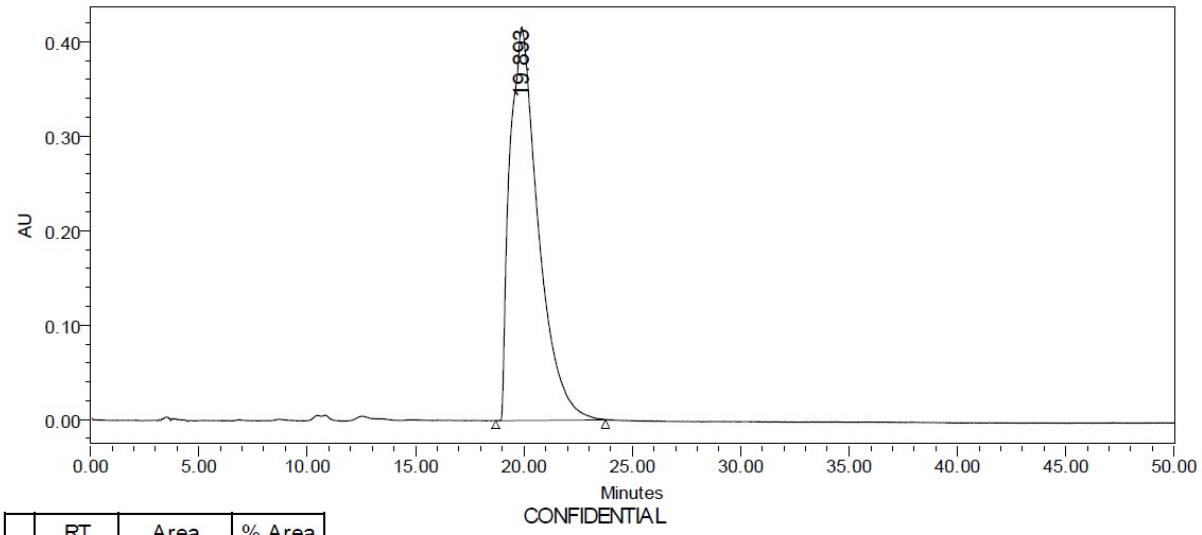
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-017-4A	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	249.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	16
Injection Volume:	25.00 ul	Proc. Chnl. Descr.:	PDA 249.0 nm
Date Acquired:	10/1/2015 3:00:19 PM IST	Date Processed:	10/1/2015 4:02:16 PM IST

Analytical conditions:
Column : chiralpak IA (250mm X 4.6mm X 5mic)
Mobile phase : nHexane: IPA w ith 0.1%DEA(60:40)
Flow rate :1.0mL/min

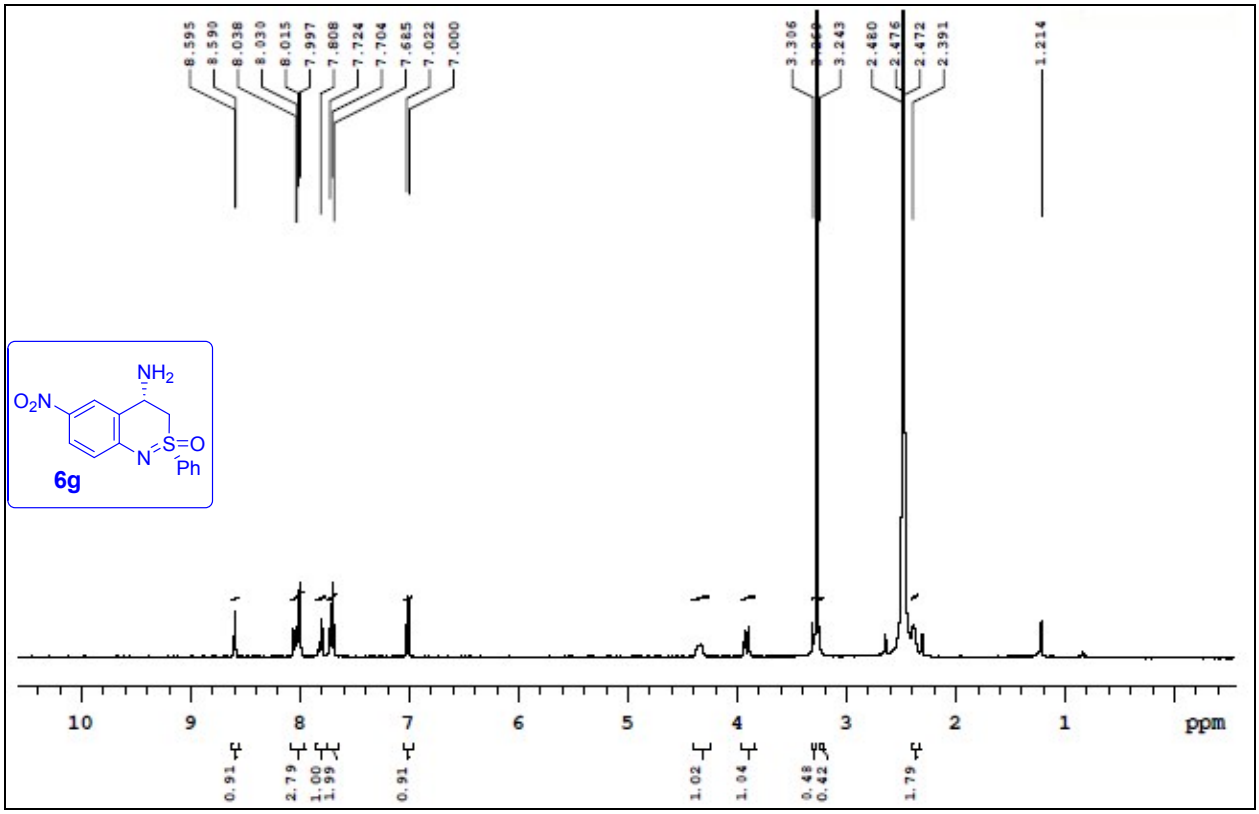


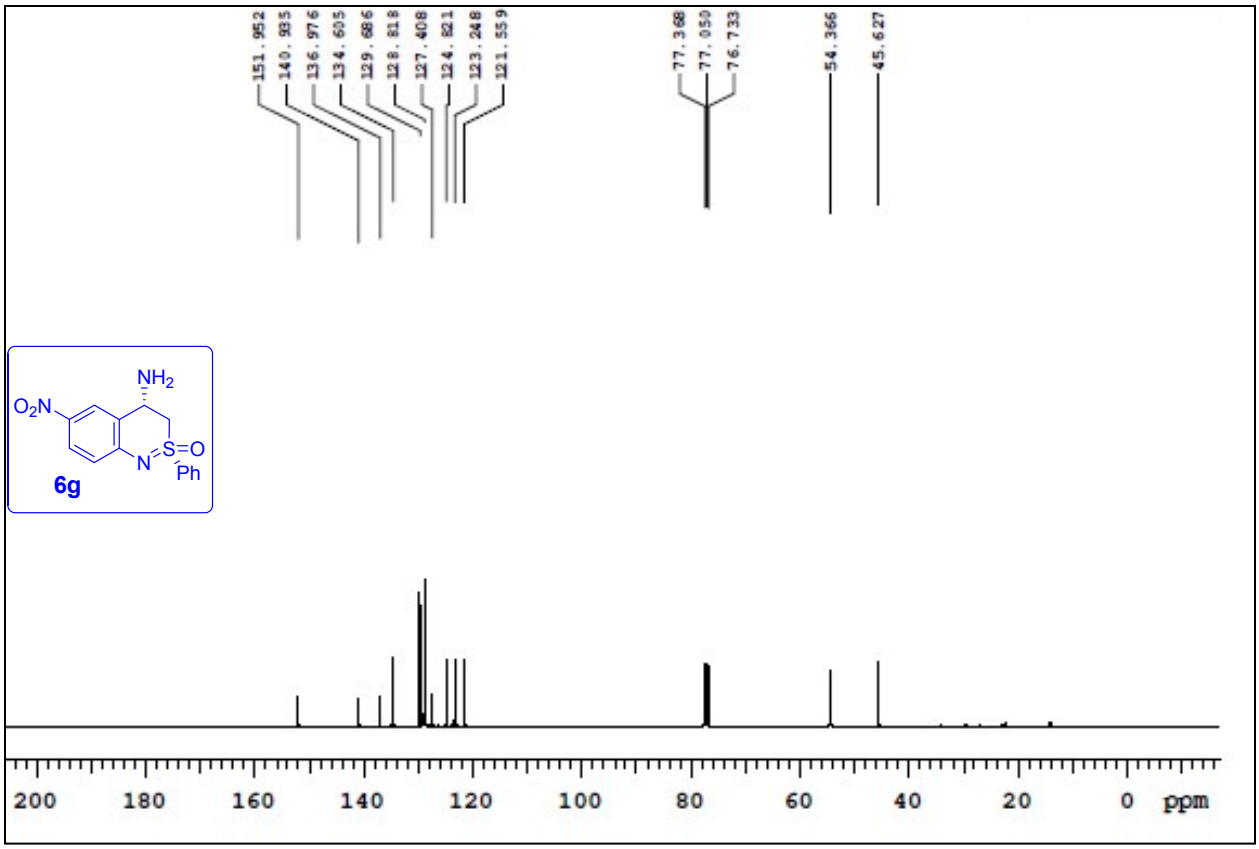
6f



CONFIDENTIAL

	RT	Area	% Area
1	19.893	37899916	100.00

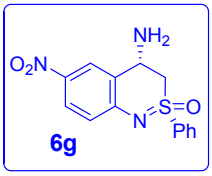

8.595
8.590
8.038
8.030
8.015
7.997
7.808
7.724
7.704
7.685
7.022
7.000
3.306
3.243
2.480
2.476
2.472
2.391
1.214
NH2
O2N
S=O
N
Ph
6g
10
9
8
7
6
5
4
3
2
1
ppm
0.91
2.79
1.00
1.99
0.91
1.02
1.04
0.48
0.42
1.79


151.952
140.935
136.976
134.605
129.686
128.818
127.408
124.821
123.248
121.559
77.368
77.050
76.733
54.366
45.627
NH2
O2N
S=O
N
Ph
6g
200
180
160
140
120
100
80
60
40
20
0
ppm

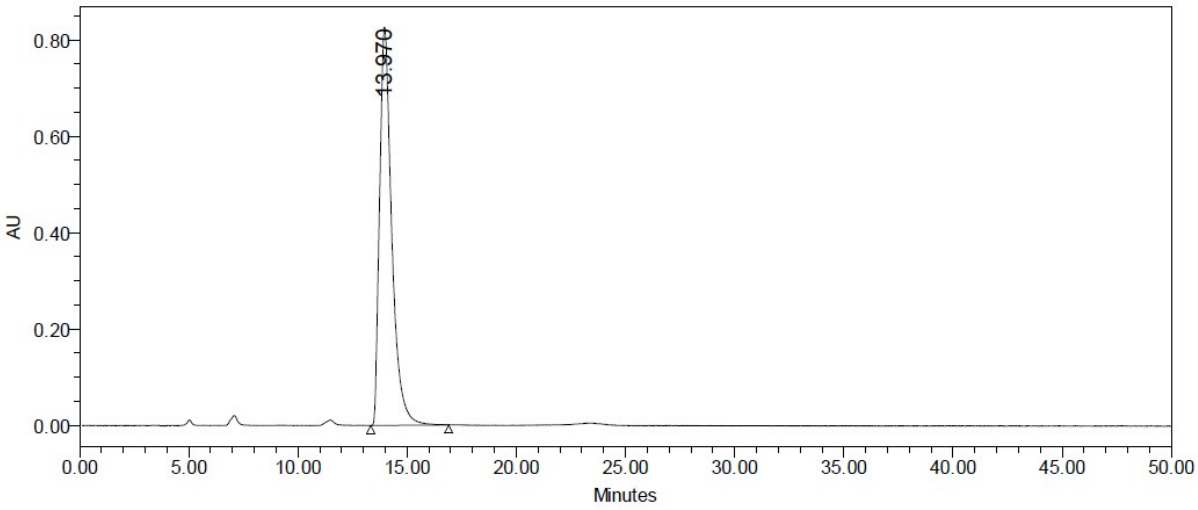
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-017-1B	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	340.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	7
Injection Volume:	25.00 ul	Proc. Chnl. Descr.:	PDA 340.0 nm
Date Acquired:	9/16/2015 2:26:09 AM IST	Date Processed:	9/16/2015 9:57:39 AM IST

Analytical Conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5im)
Mobile phase A : n-Hexane
Mobile phase B : 0.1% DEA Ethanol
Composition: 60:40
Flow rate : 1.0mL/min



6g



	RT	Area	% Area
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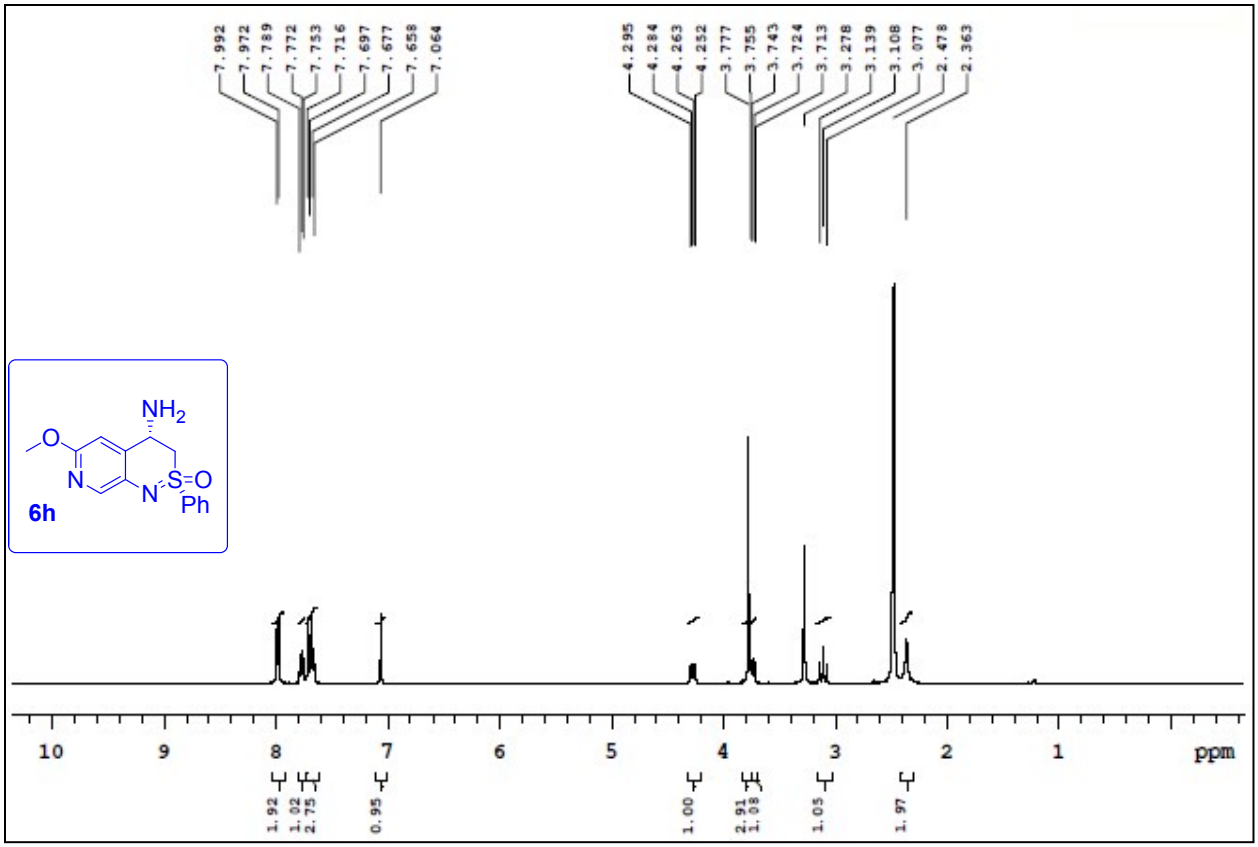
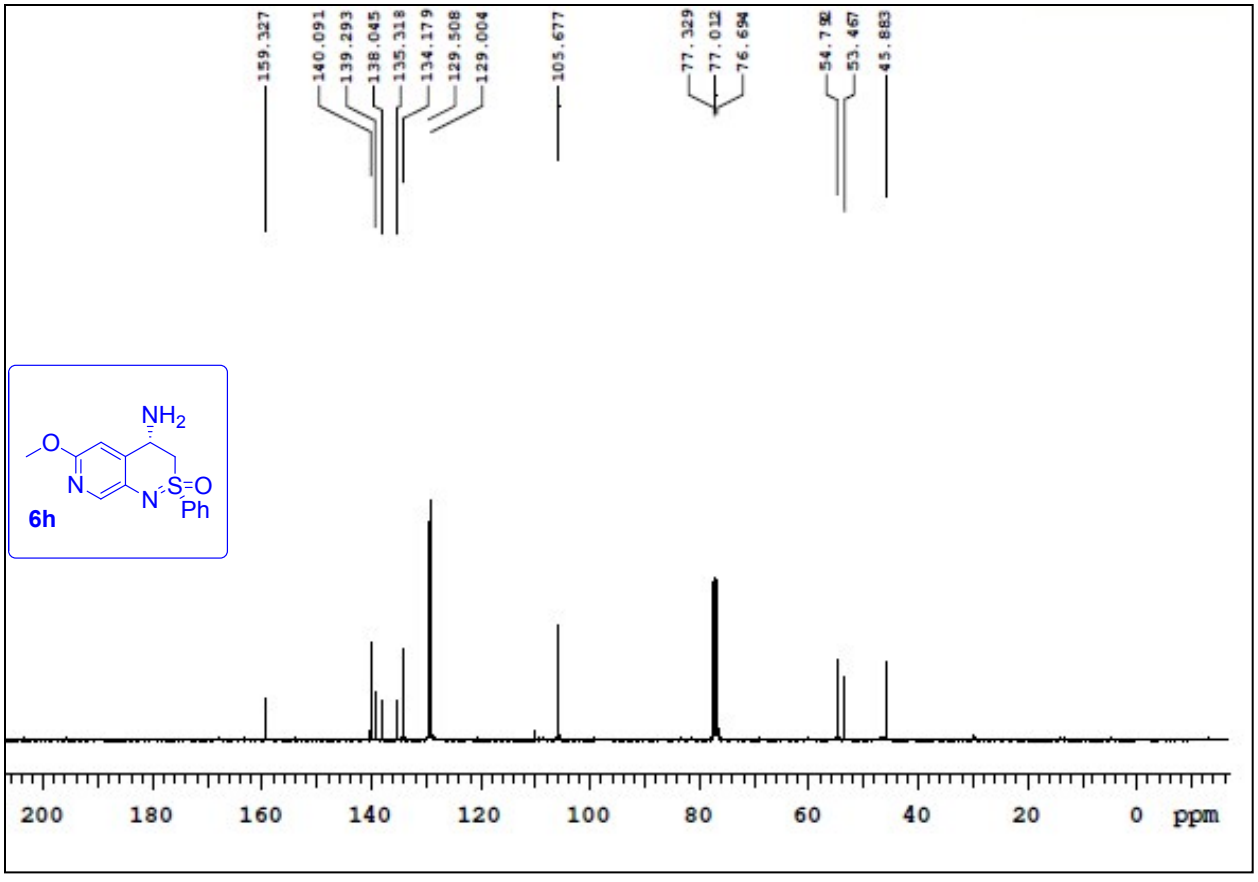
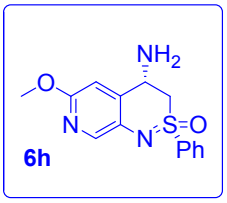

7.992
7.972
7.789
7.772
7.753
7.716
7.697
7.677
7.658
7.064
4.295
4.284
4.263
4.252
3.777
3.755
3.743
3.724
3.713
3.278
3.139
3.108
3.077
2.478
2.363
NH2
O
N
S=O
N
Ph
6h
10
9
8
7
6
5
4
3
2
1
ppm
1.92
1.02
2.75
0.95
1.00
2.91
1.08
1.05
1.97


159.327
140.091
139.293
138.045
135.318
134.179
129.508
129.004
105.677
77.329
77.012
76.694
54.792
53.467
45.883
NH2
O
N
S=O
N
Ph
6h
200
180
160
140
120
100
80
60
40
20
0
ppm

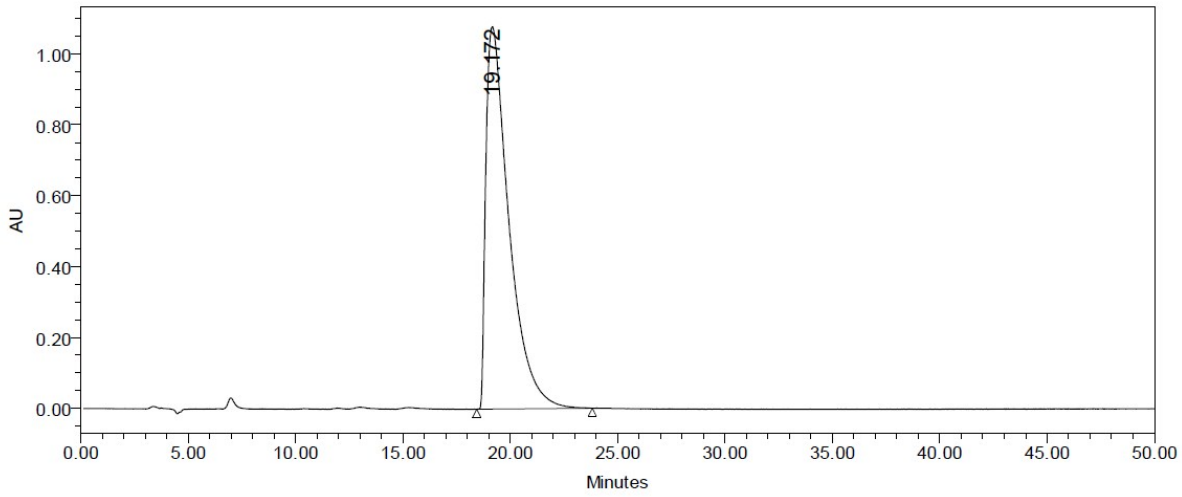
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-017-3C	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	238.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	19
Injection Volume:	25.00 ul	Proc. Chnl. Descr.:	PDA 238.0 nm
Date Acquired:	9/29/2015 1:26:26 PM IST	Date Processed:	9/29/2015 2:32:20 PM IST

Analytical Conditions:
Column :Chiralpak IA (250mm X 4.6mm)
Mobile phase A : n-Hexane B : IPA with 0.1%DEA
Composition: 60:40
Flow rate : 1.0mL/min
Single isomer



6h



	RT	Area	% Area
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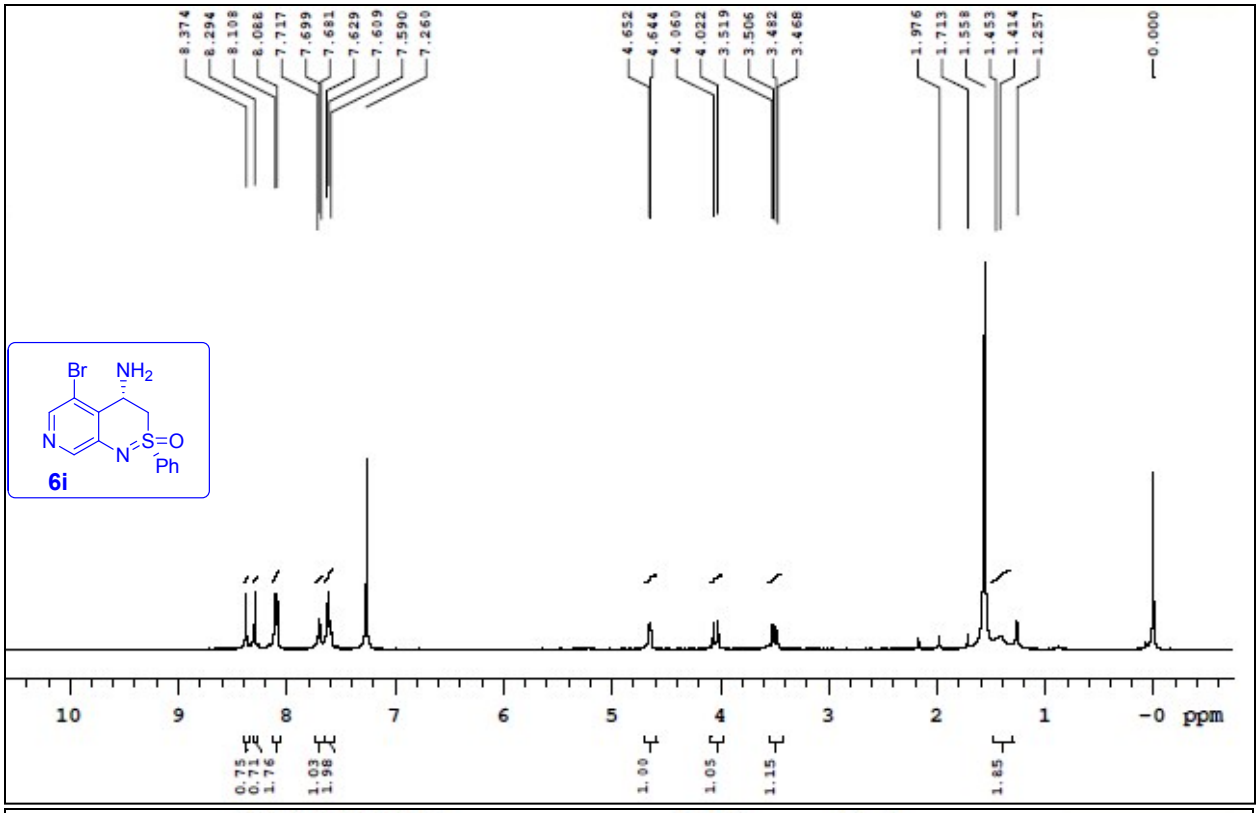
8.374
8.294
8.108
8.088
7.717
7.699
7.681
7.629
7.609
7.590
7.260
4.652
4.644
4.060
4.022
3.519
3.506
3.482
3.468
1.976
1.713
1.558
1.453
1.414
1.257
0.000
Br
NH2
N
S=O
N
Ph
6i
10
9
8
7
6
5
4
3
2
1
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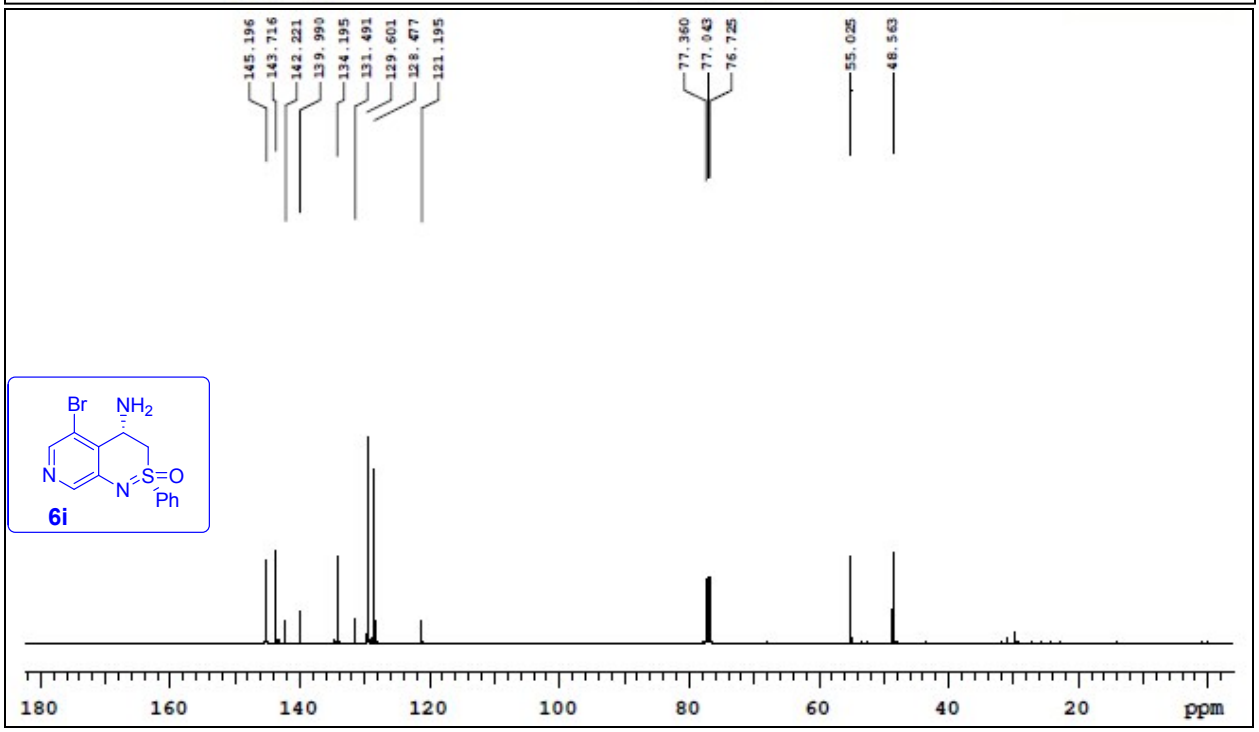
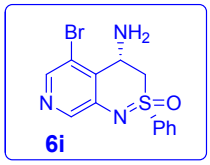
ppm
0.75
0.71
1.76
1.03
1.98
1.00
1.05
1.15
1.85


145.196
143.716
142.221
139.990
134.195
131.491
129.601
128.477
121.195
77.360
77.043
76.725
55.025
48.563
Br
NH2
N
S=O
N
Ph
6i
180
160
140
120
100
80
60
40
20
ppm

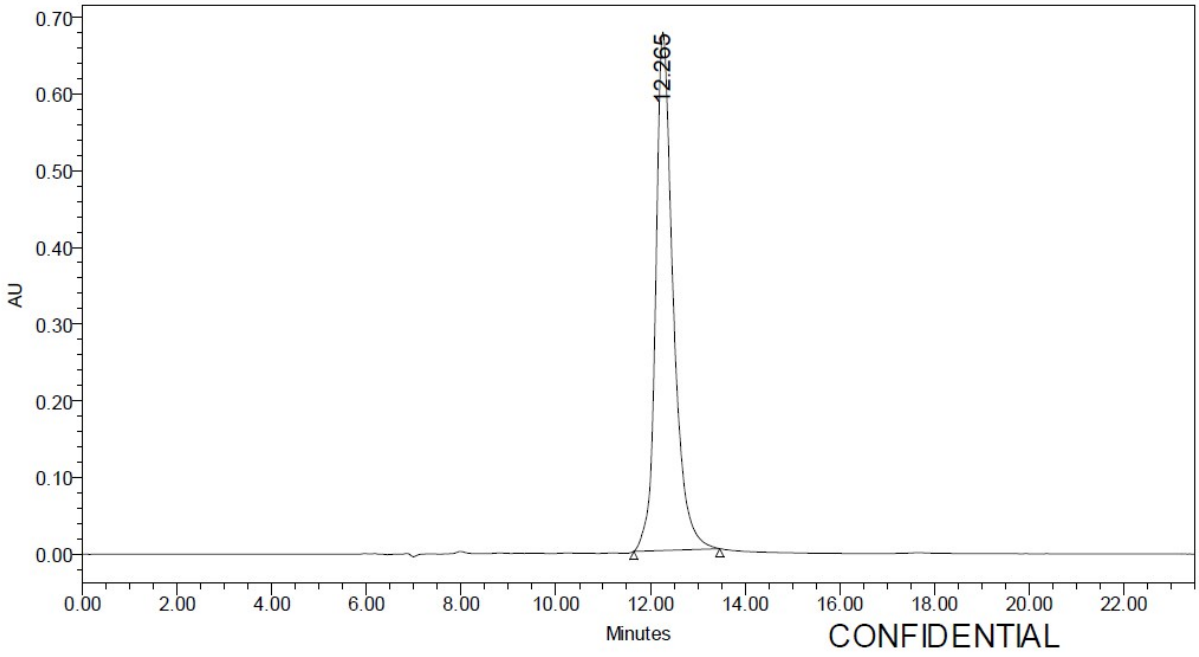
SAMPLE INFORMATION

Sample Name:	JBL-6801-061-AM	Acquired By:	anachem
Vial:	23	Sample Set Name:	211111_1
Injection #:	1	Acq. Method Set:	IA_100_ETH_HPLC3_MET
Injection Volume:	8.00 ul	Processing Method:	1
Run Time:	50.0 Minutes	Channel Name:	2487Channel 2
Date Acquired:	11/21/2011 1:22:05 PM IST	Proc. Chnl. Descr.:	254 nm
Date Processed:	11/21/2011 3:01:05 PM IST		

Analytical Conditions:
Column :Chiralpak IA (250mm X 4.6mm)
Mobile phase(B) : 100% EtOH
Flow rate : 0.5 mL/min



6i



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	RT	Area	% Area
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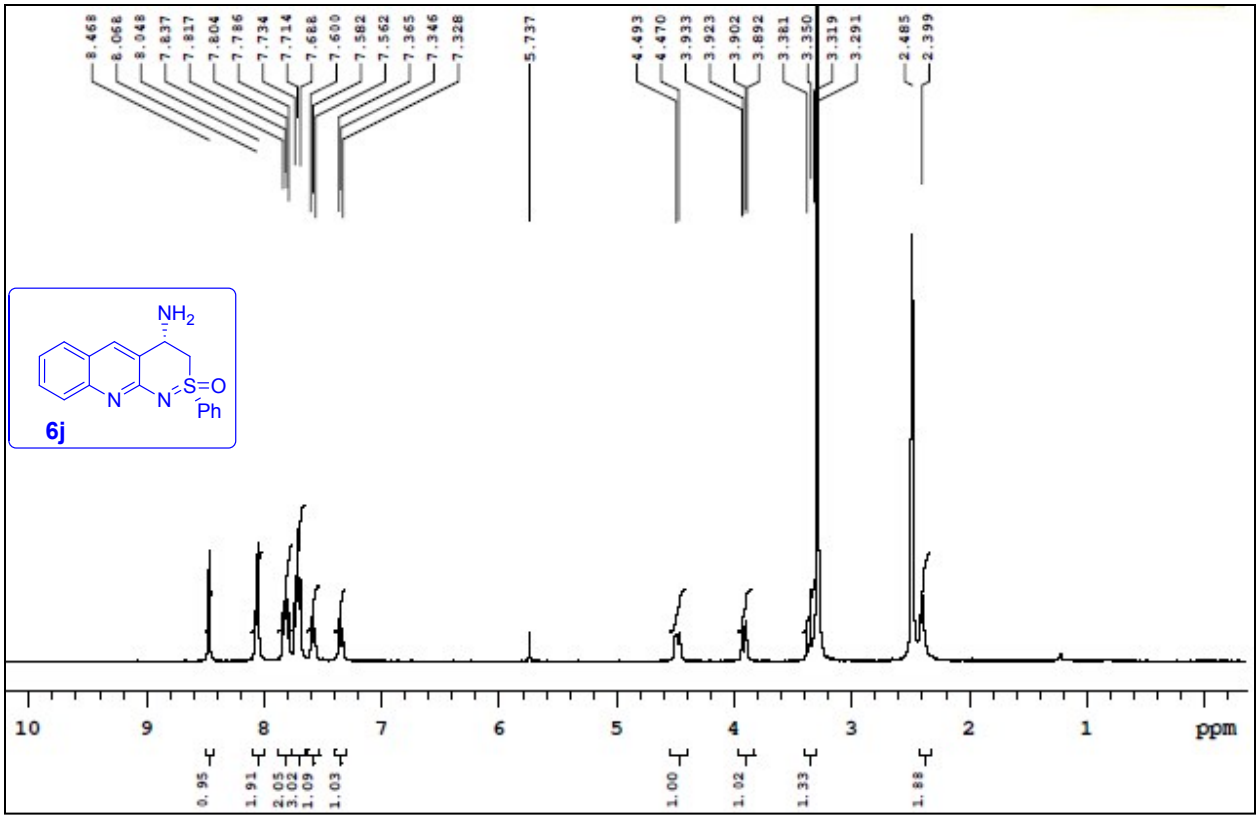
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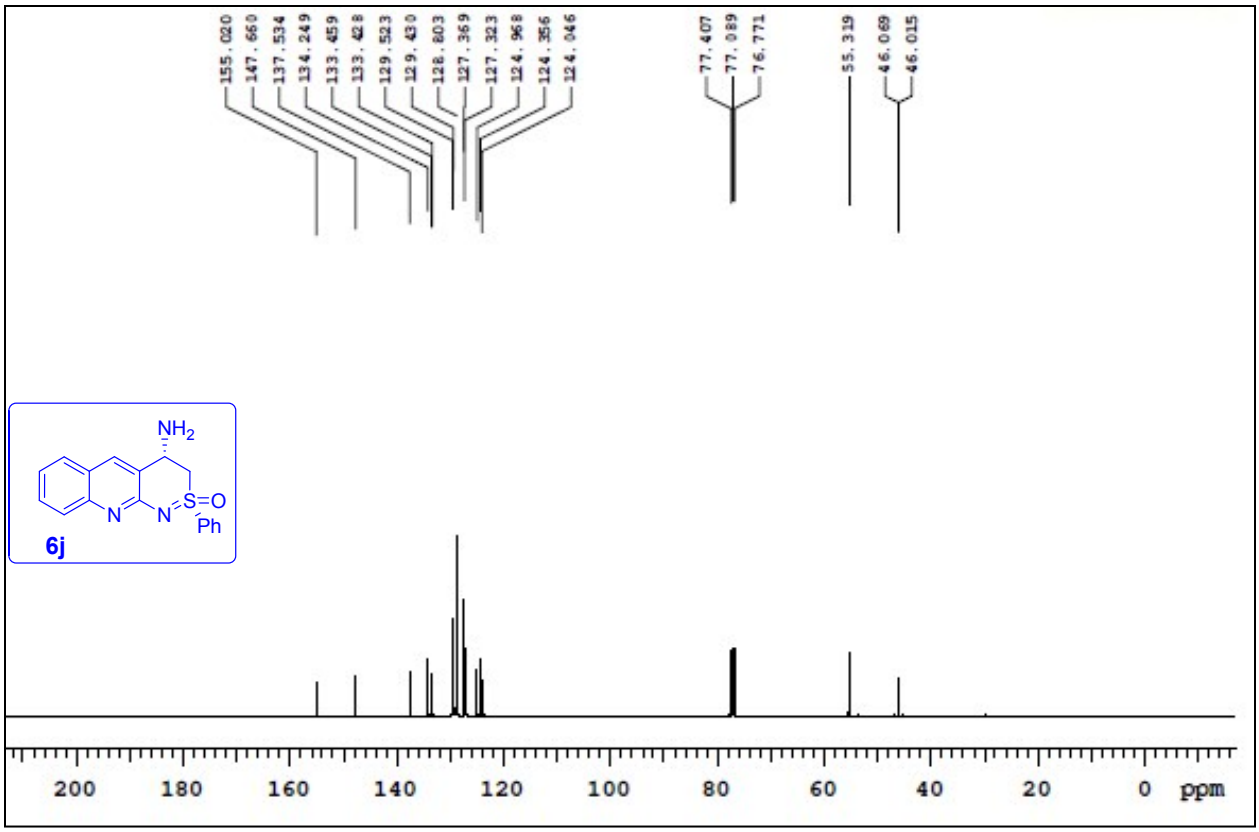
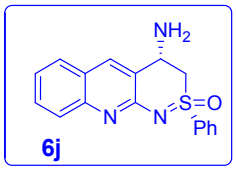
7.837
7.817
7.804
7.786
7.734
7.714
7.688
7.600
7.582
7.562
7.365
7.346
7.328
5.737
4.493
4.470
3.933
3.923
3.902
3.892
3.381
3.350
3.319
3.291
2.485
2.399
NH2
S=O
N
N
Ph
6j
10
9
8
7
6
5
4
3
2
1
ppm
0.95
1.91
2.05
3.02
1.09
1.03
1.00
1.02
1.33
1.88


155.020
147.660
137.534
134.249
133.459
133.428
129.523
129.430
128.803
127.369
127.323
124.968
124.356
124.046
77.407
77.089
76.771
55.319
46.069
46.015
NH2
S=O
N
N
Ph
6j
200
180
160
140
120
100
80
60
40
20
0
ppm

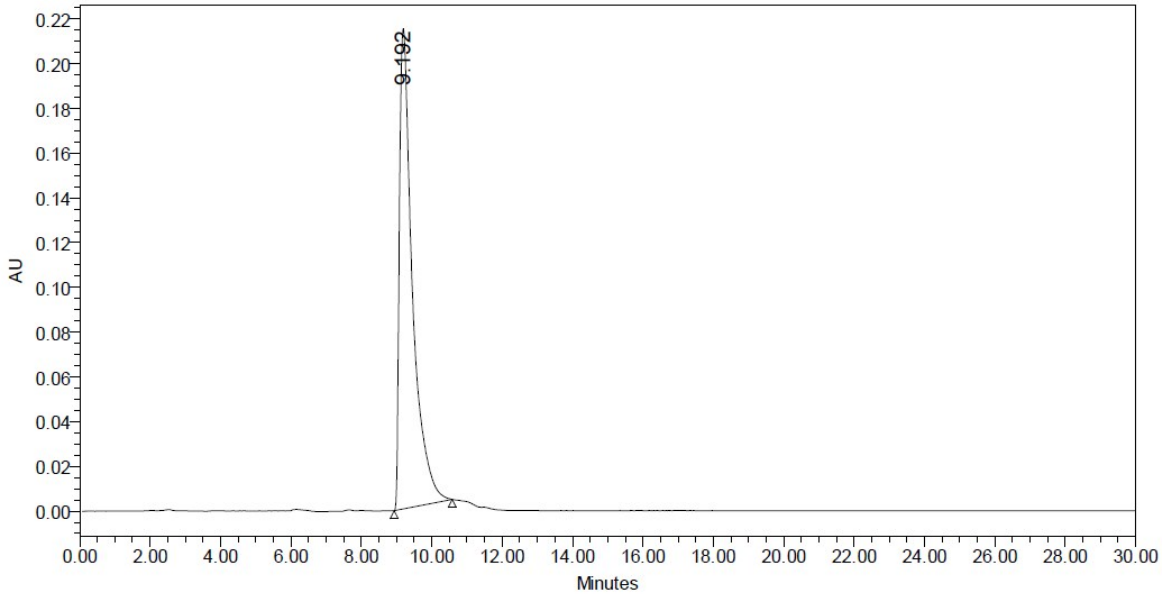
SAMPLE INFORMATION

Sample Name:	JBL-6801-062-AM-03	Acquired By:	anachem
		Sample Set Name:	281111_3
Vial:	8	Acq. Method Set:	IC_100_ETOH_HPLC3_MET
Injection #:	1	Processing Method:	Default
Injection Volume:	10.00 ul	Channel Name:	2487Channel 2
Run Time:	30.0 Minutes	Proc. Chnl. Descr.:	290nm
Date Acquired:	11/28/2011 7:32:53 PM IST		
Date Processed:	1/28/2016 3:31:37 PM IST		

Analytical Conditions:
Column :Chiralpak IC (250mm X 4.6mm)
Mobile phase(B) : Ethanol
Flow rate : 0.5 mL/min

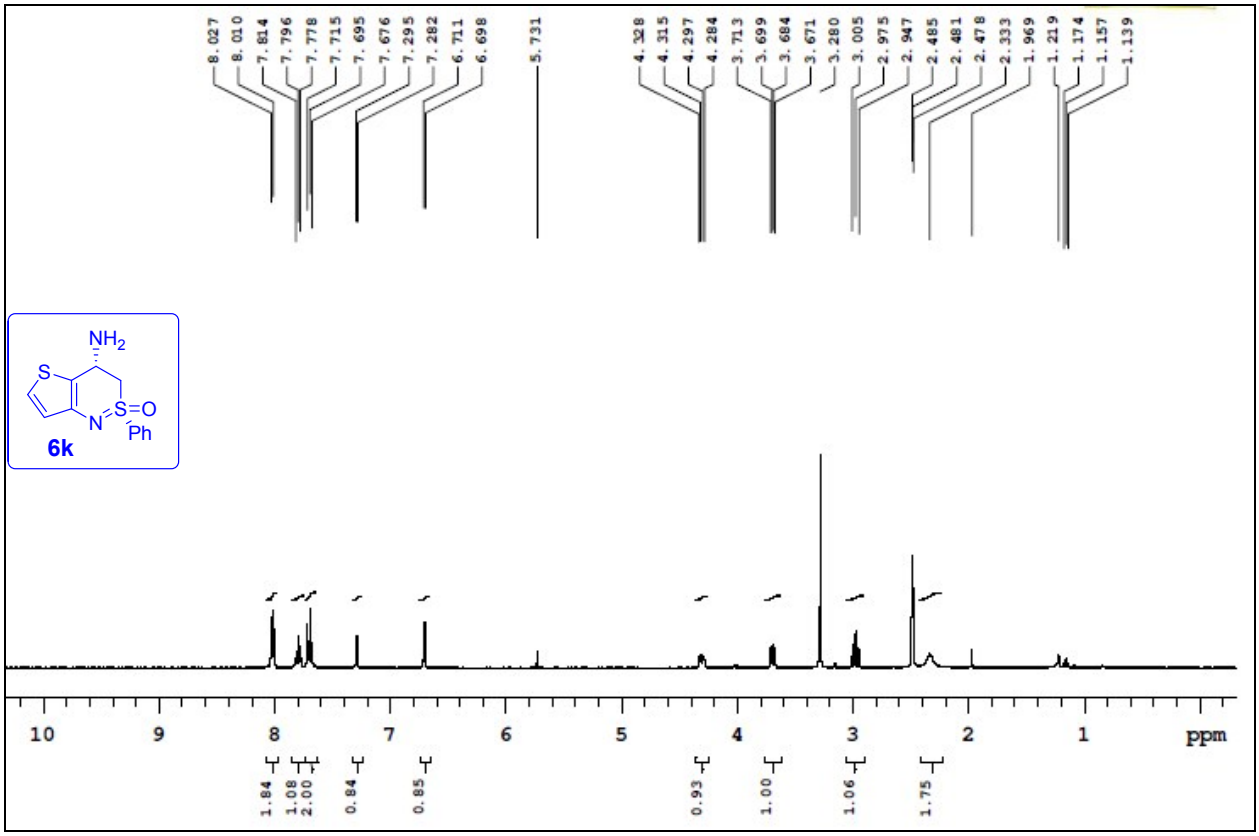


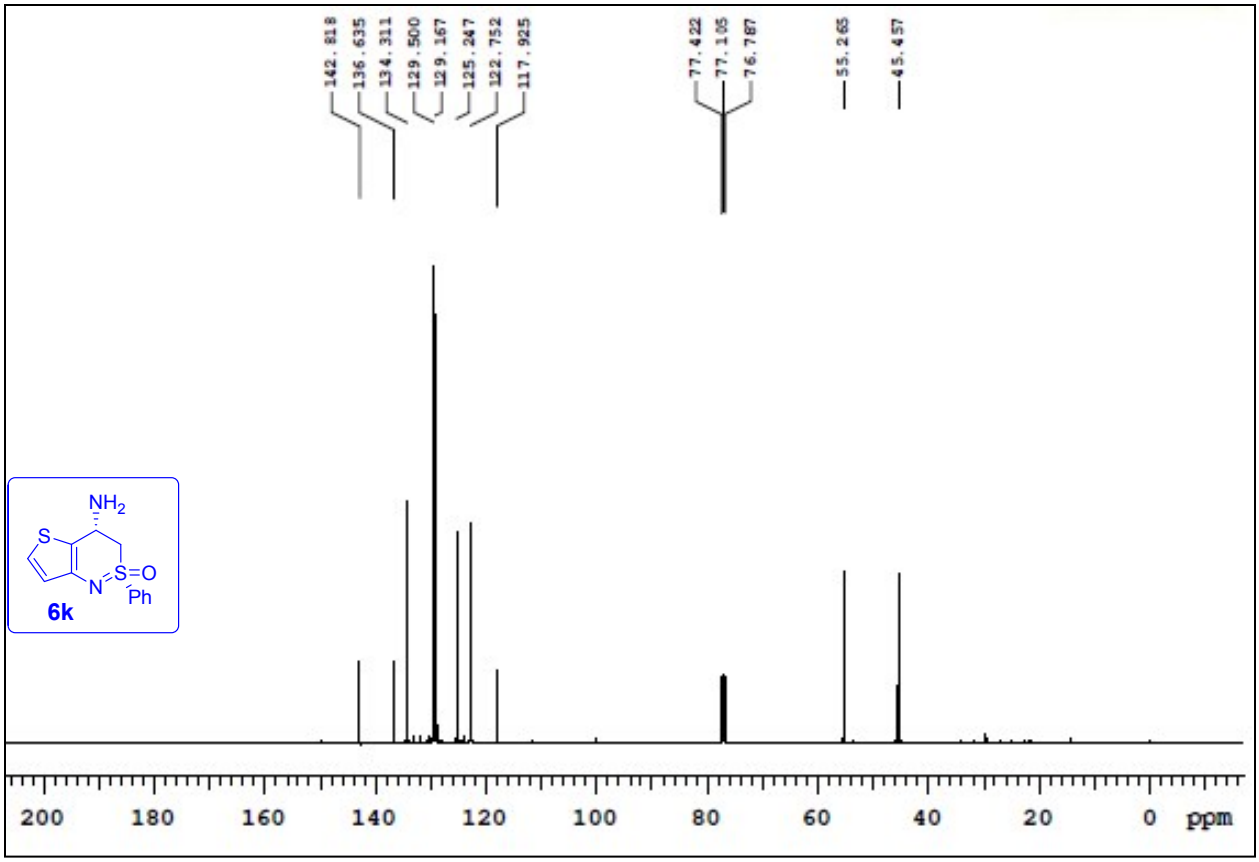
6j



	RT	Area	% Area
1	9.192	5532323	100.00

CONFIDENTIAL

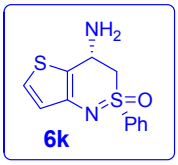

8.027
8.010
7.814
7.796
7.778
7.715
7.695
7.676
7.295
7.282
6.711
6.698
5.731
4.328
4.315
4.297
4.284
3.713
3.699
3.684
3.671
3.280
3.005
2.975
2.947
2.485
2.481
2.478
2.333
1.969
1.219
1.174
1.157
1.139
NH2
S
N
S=O
Ph
6k
10
9
8
7
6
5
4
3
2
1
ppm
1.84
1.08
2.00
0.84
0.85
0.93
1.00
1.06
1.75


142.818
136.635
134.311
129.500
129.167
125.247
122.752
117.925
77.422
77.105
76.787
55.265
45.457
NH2
S
N
S=O
Ph
6k
200
180
160
140
120
100
80
60
40
20
0
ppm

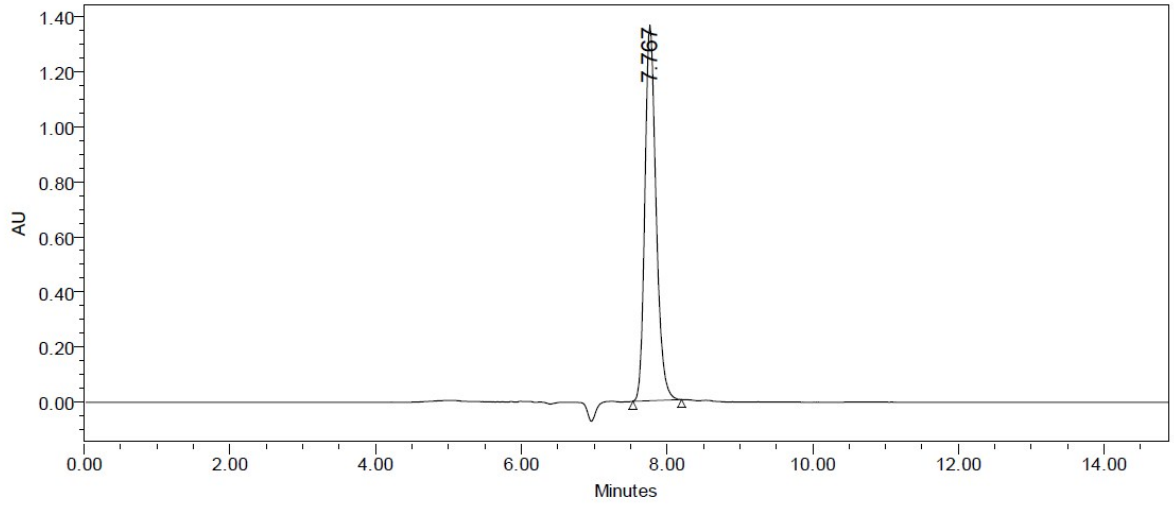
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBL-C-1033-171-02	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	230.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	104
Injection Volume:	10.00 ul	Proc. Chnl. Descr.:	PDA 230.0 nm
Date Acquired:	8/1/2011 1:40:41 PM IST	Date Processed:	8/1/2011 3:40:48 PM IST

Analytical conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5µm)
Mobile phase :100% ETOH
Flow rate :0.5mL/min

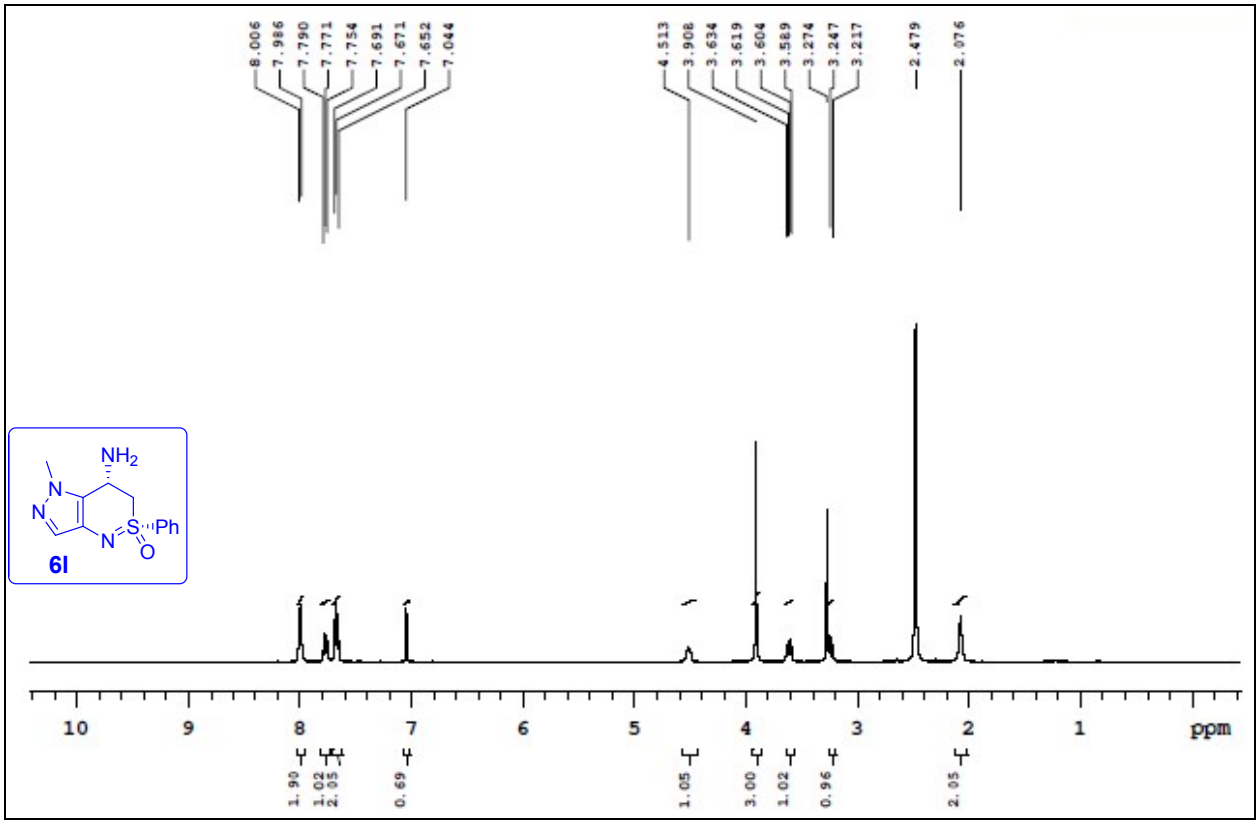


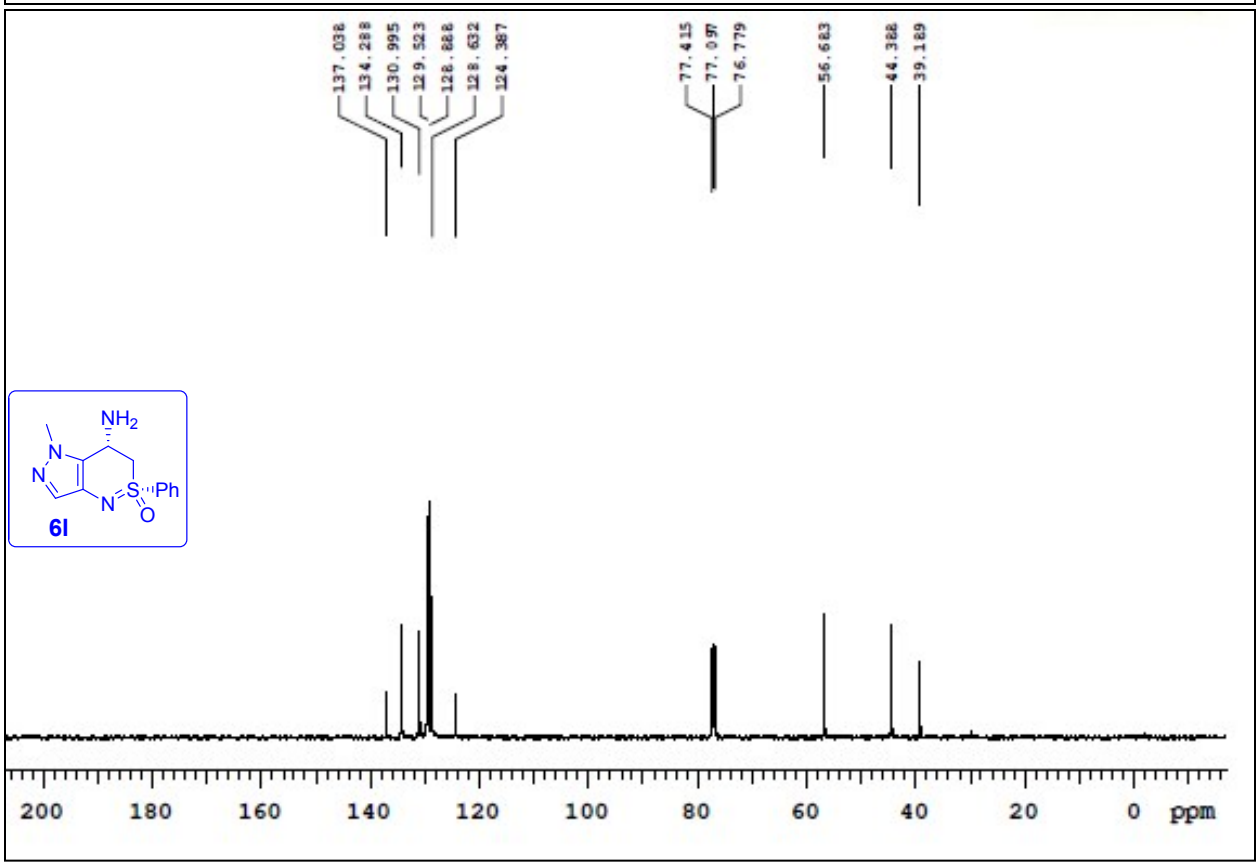
6k



	RT	Area	% Area
1	7.767	14540240	100.00

CONFIDENTIAL

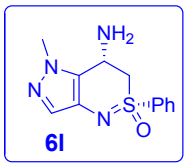

8.006
7.986
7.790
7.771
7.754
7.691
7.671
7.652
7.044
4.513
3.908
3.634
3.619
3.604
3.589
3.274
3.247
3.217
2.479
2.076
NH2
N
N
S
Ph
N
O
6l
10
9
8
7
6
5
4
3
2
1
ppm
1.90
1.02
2.05
0.69
1.05
3.00
1.02
0.96
2.05


137.038
134.288
130.995
129.523
128.888
128.632
124.387
77.415
77.097
76.779
56.683
44.388
39.189
NH2
N
N
S
Ph
N
O
6l
200
180
160
140
120
100
80
60
40
20
0
ppm

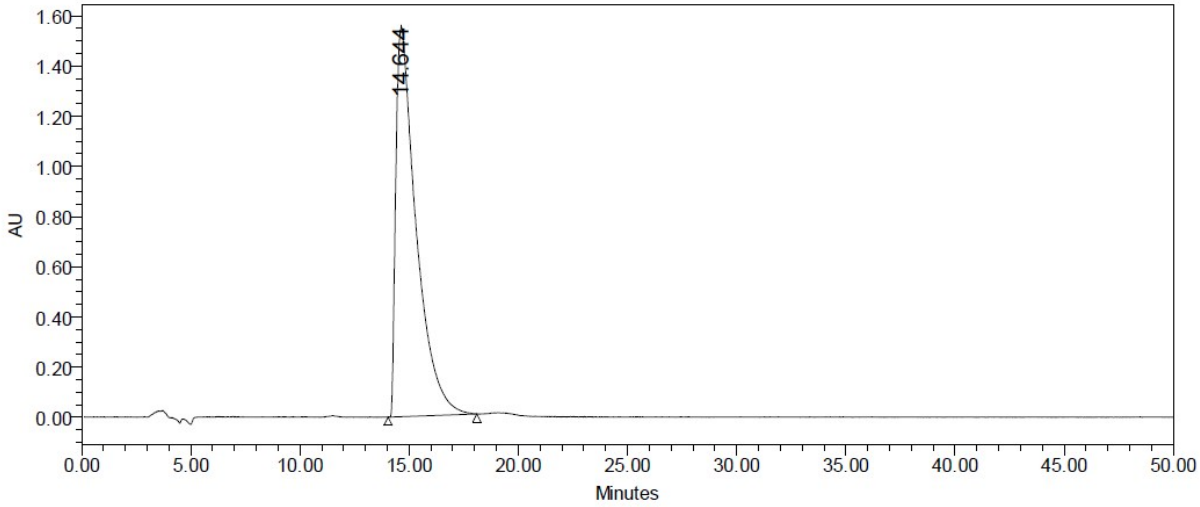
JUBILANT BIOSYS, BANGALORE

Sample Name:	JBPHD1-JBL-C-1529-017-2A	Processing Method:	IA_ACNDEA_GRA_INS
Test Type:	HPLC/PDA	Channel Name:	225.0nm
Sample Set Name:	IA_ACNDEA_HPLC1	Vial:	8
Injection Volume:	25.00 ul	Proc. Chnl. Descr.:	PDA 225.0 nm
Date Acquired:	9/16/2015 4:07:53 AM IST	Date Processed:	9/16/2015 9:59:32 AM IST

Analytical Conditions:
Column : CHIRALPAK IA (250 mm X 4.6mm X 5im)
Mobile phase A : n-Hexane
Mobile phase B : 0.1% DEA Ethanol
Composition: 60:40
Flow rate : 1.0mL/min



6l



	RT	Area	% Area
1	14.644	100373942	100.00