Supplementary Information

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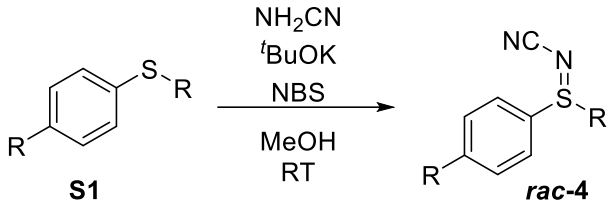
1. General Information

All reactions were performed in oven-dried glassware under a nitrogen atmosphere. Unless specified, all reagents and starting materials were purchased from commercial companies and used as received. Anhydrous solvents were freshly obtained from pure solvent system following standard procedures. Analytical thin layer chromatography (TLC) was performed using pre-coated silica gel plates. A Razel A 99 syringe pump was used for the slow addition of solutions. Visualisation was achieved by UV light (254 nm) or $KMnO_4$ and vanillin as stain. Flash chromatography was performed using silica gel and gradient solvent system (eluent: hexane: ethyl aetate/hexane: DCM). ^{1}H and ^{13}C NMR spectra were recorded on 400MHz Jeol ECS and Bruker AV and AM spectrometers. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), br s (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (double of triples), ddd (doublet of doublet of doublets), ddt (doublet of doublet of triplets), dtt (doublet of triplet of triplets), ddq (doublet of doublet of quintets), dddd (doublet of doublet of doublet of doublets), dtd (doublet of triplet of doublets), dt (doublet of triplets), dp (doublet of pentents), dq (doublet of quintets), td (triplet of doublets), tdd (triplet of doublet of doublets), tt (triplet of triplets), qd (quintet of doublets), qt (quintet of triplets) or m (multiplet). The number of protons (*n*) for a given resonance is indicated by *n*H and coupling constants are reported as a *J* value in Hz. Enantiomeric excess values were measured by an Agilent 1200 series HPLC. Unless stated otherwise, all chiral HPLC runs were carried out at 20 °C. High resolution mass spectra (HRMS) were obtained on a LC/HRMS TOF spectrometer using simultaneous electrospray (ESI).

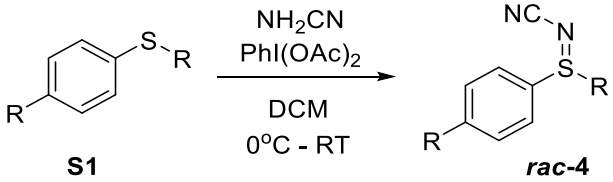
2. Experimental Procedures

General Procedure 2.1



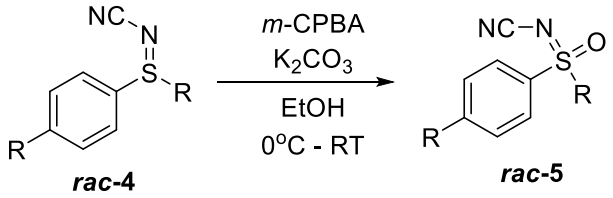
Adapted from Mancheno *et al*. [1] To a stirring solution of sulfide (4.08 mmol) in MeOH (10.0 mL) was added NH_2CN (2.00 eq.). Following this was added *t*BuOK (1.70 eq.) portion-wise followed by addition of NBS (1.30 eq.). The reaction was allowed to stir overnight. The solvent was removed *in vacuo* and the crude dissolved in saturated $Na_2S_2O_3$ (10 mL) which was extracted with EtOAc (3 x 30 mL), and the combined organic phase washed with saturated brine (30 mL), dried over $MgSO_4$, filtered, and the solvent removed *in vacuo* to afford the crude. Purification was *via* done flash column chromatography on silica gel.

General Procedure 2.2



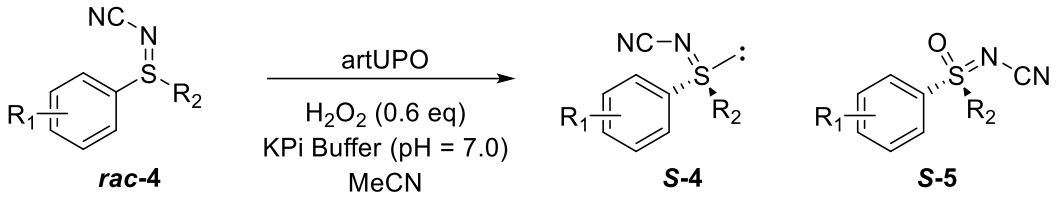
To a stirring solution of sulfide (4.08 mmol) and NH_2CN (2.00 eq.) in DCM (20.0 mL) at 0 °C were added $PhI(OAc)_2$ (1.10 eq.), after which the temperature was raised to RT. After stirring overnight, the solvent was removed *in vacuo* and the crude material dissolved in saturated $Na_2S_2O_3$ (10 mL). Following extraction with EtOAc (3 x 30 mL), the combined organic phase washed with saturated brine (30 mL), dried over $MgSO_4$, filtered, and the solvent removed *in vacuo*. Purification was done *via* flash column chromatography on silica gel.

2.3 Synthesis of Racemic Sulfoximine Standards



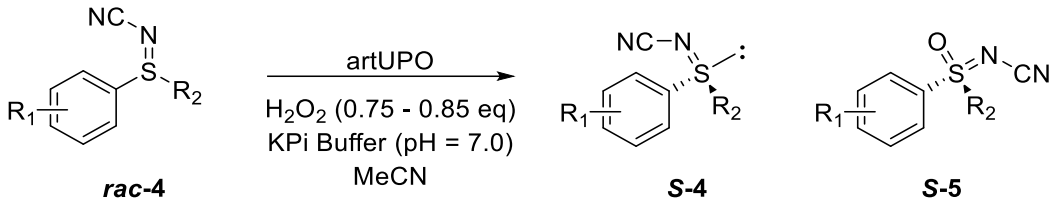
To a stirring solution of sulfilimine (0.600 mmol) in EtOH (5.00 mL) at 0 °C were added K_2CO_3 (3.00 eq.) followed by *m*-CPBA (2.00 eq.) before raising the reaction to RT. After overnight stirring, the solvent was removed *in vacuo* to afford a white solid, which was dissolved in saturated aq. $Na_2S_2O_3$ (10 mL) and extracted with EtOAc (3 x 30 mL). The combined organic phase was washed with saturated brine (50 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to afford crude material which was purified, where required, *via* flash column chromatography on silica gel.

2.4 General Procedure for 0.3 mmol artUPO Kinetic Resolution of Sulfilimines 4



Liquid artUPO secretate (1.00 mL, 0.8 U/mL) was added to KPi Buffer (24.0 mL, pH 7.00) at RT and stirred for five min, after which, a solution of sulfilimine (0.3 mmol) in MeCN (6.00 mL) was added. The reaction was initiated by the slow continuous addition of a H_2O_2 solution (0.180 mmol in 2 mL H_2O) over 4 h followed by stirring overnight. The reaction was extracted with Et_2O (3 x 30 mL), and the combined organic phase washed with saturated brine (40 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to afford the crude. For preparative reactions, the purified product were isolated following flash column chromatography on silica gel.

2.5 General Procedure for ≈1.0 mmol artUPO Kinetic Resolution of Sulfilimines 4



Liquid artUPO secretate (2.50 mL, 0.8 U/mL) was added to KPi Buffer (40.0 mL, pH 7.0) at RT and stirred for five min, after which, a solution of sulfilimine (1.00 mmol) in MeCN (10.0 mL) was added. The reaction was initiated by the slow continuous addition of a H_2O_2 solution (0.600–0.800 mmol in 2.00 mL H_2O, see below for specific amounts for individual substrates) over 4 h. After H_2O_2 addition was complete, a sample of the reaction mixture (1.00 mL) was subjected to standard aqueous work-up (extract with EtOAc, wash with brine) before analysis of the resulting sample using ^{1}H NMR to measure conversion. If 50% conversion was not observed, a further 0.05–0.15 equivalents of H_2O_2 was added over 1 h, before re-analysing as described above. When 50% conversion was reached, the reaction was extracted with Et_2O (3 x 30 mL), and the combined organic phase washed with saturated brine (40 mL), dried over $MgSO_4$, filtered and the solvent removed *in vacuo* to afford the crude. Purified products for preparative reactions were isolated following flash column chromatography on silica gel.

<u>H_2O_2 quantities used for scale ups</u>:

rac-4b: Initial H_2O_2 infusion of 0.60 equiv., followed by an additional 0.10 equiv. H_2O_2 infusion. 1.07 mmol scale.

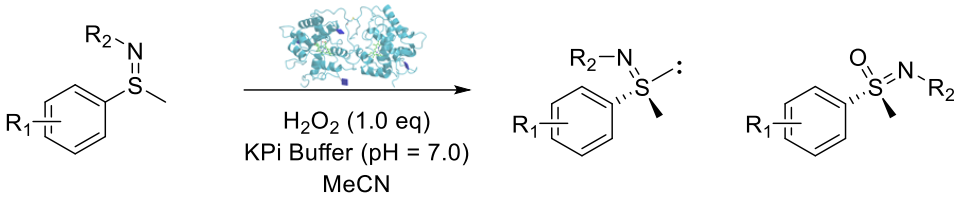
rac-4e: Initial H_2O_2 infusion of 0.65 equiv., followed by an additional 0.15 mmol H_2O_2 infusion. 1.20 mmol scale.

rac-4j: Initial H_2O_2 infusion of 0.70 equiv. No additional H_2O_2 infusion. 1.00 mmol scale.

rac-4t: Initial H_2O_2 infusion of 0.75 equiv., followed by an additional 0.05 equiv. H_2O_2 infusion. 1.07 mmol scale.

rac-4u: Initial H_2O_2 infusion of 0.80 equiv. No additional H_2O_2 infusion. 1.00 mmol scale.

2.6. Screening for UPOs



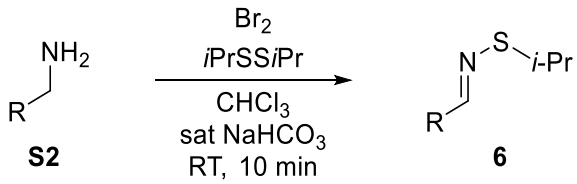
In order to investigate the feasibility of successfully sulifilimine oxidation by UPOs, we first synthesised three substrates to test for activity. Unless otherwise specified, the reactions were carried out following general procedure **2.4** with 0.2 mmol substrate. Unless otherwise specified, conversion was determined by comparing the intensity of the methyl peaks of the sulfilimine and sulfoximine in the ^{1}H NMR spectra of the crude material.

Entry	R_1	R_2	Conversion (%)	
			***r*AaeUPO-PaDa-I**	**art-UPO**
1	H	CN	11	39
2	H	$C(O)CF_3$	0	14
3	4-MeO	CN	11	65[a,b]

[a] Reaction carried out on a 60 mL scale with 0.6 mmol substrate

[b] Isolated yield following purification via flash chromatography on silica gel

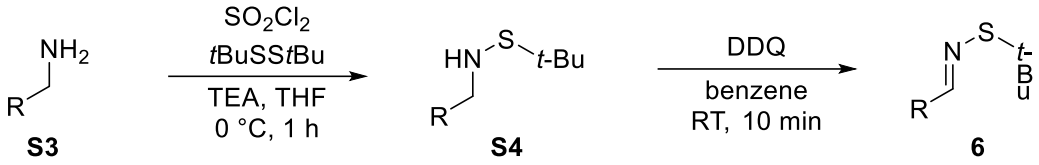
2.7 General procedure for the synthesis of *i*-Pr *N*-sulfenylimines (6) [2]



To a round bottom flask containing a magnetic stirring bar was added the appropriate amine **S1** (6 mmol, 3.0 equiv.) and diisopropyl disulfide (2 mmol, 0.34 mL, 1.0 equiv.) in $CHCl_3$ (24 mL) and sat. aq. $NaHCO_3$ (40 mL). The resulting reaction mixture was stirred vigorously by adding Br_2 (10 mmol, 0.52 mL, 5.0 equiv.) solution in DCM (4 mL) slowly. After the addition,

the reaction mixture was stirred at room temperature for a further 10 min, open to air. Upon completion (a colour change to light yellow was noted), the reaction mixture was quenched by the addition of saturated aq. $Na_2S_2O_3$ (30 mL). The reaction mixture was then extracted with DCM (3 × 20 mL). The combined organic phases were washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent specified later for each compound) to give the corresponding *N*-sulfenylimines (**1**).

2.8 General procedure for the synthesis of *t*-Bu *N*-sulfenylimines (6) [3]

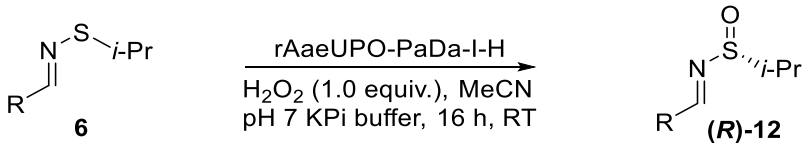


To a flame dried round bottom flask containing a magnetic stirring bar was added the di-*t*-butyl disulfide (5 mmol, 1.0 mL, 1.0 equiv.) anhydrous THF (40 mL) at 0 °C under an argon atmosphere. The sulfuryl dichloride (5.5 mmol, 0.45 mL, 1.1 equiv.) was added slowly and the resulting reaction mixture was stirred at the same temperature for 30 min. Upon completion, the solution was slowly transferred to another flame dried round bottom flask containing the appropriate amine **S2** (10 mmol, 2.0 equiv.) and TEA (15 mmol, 2.0 mL, 3.0 equiv.) in anhydrous THF (20 mL) at 0 °C. The resulting mixture was stirred at the same temperature for another 30 min. On completion, the reaction mixture was filtrated through a pad of Celite and rinsed with EtOAc (10 mL). The filtrate was concentrated under reduced pressure to give a residue that was purified by flash column chromatography on silica gel to give the corresponding compound **S3**.

To a flame dried round bottom flask containing a magnetic stirring bar was added **S3** (1.0 equiv.) in anhydrous benzene (10 mL) under an argon atmosphere. DDQ (1.1 equiv.) was added to the solution in one portion and the resulting mixture was stirred at room temperature for 10

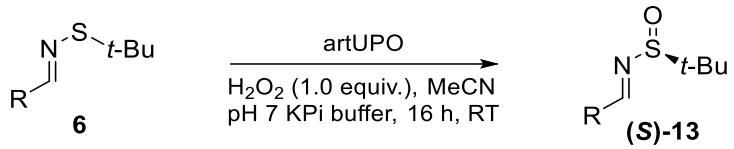
min. Upon completion, the reaction was quenched by the addition of saturated aq. $NaHCO_3$ (50 mL). The reaction mixture was then extracted with DCM (3 × 20 mL). The combined organic phases were washed with water (50 mL) and brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give a residue that was purified by flash column chromatography on silica gel (eluent specified later for each compound) to give the corresponding *N*-sulfenylimines (**6**).

2.9 General procedure for the *r*AaeUPO biotransformations with *i*-Pr *N*-sulfenylimines



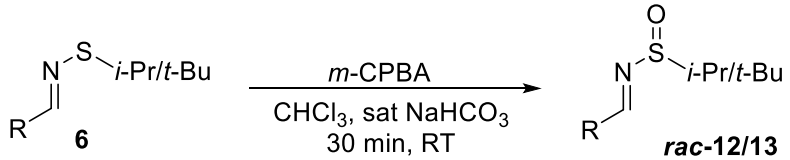
To a round bottom flask containing a magnetic stirring bar was added r*Aae*UPO-PaDa-I-H (1.3 mL, 57 U/mL) and KPi buffer (10 mL, 0.1 mmol/mL, pH = 7, 10 mL). The solution was diluted by the addition of deionised water (2.7 mL), followed by addition of the appropriate *i*-Pr *N*-sulfenylimines **6** (0.2 mmol, 1.0 equiv.,) in MeCN (4 mL). Next, H_2O_2 solution (2 mL, 0.1 mmol/ml, 1.0 equiv.) was added over a 10 h period, using a syringe pump. After the H_2O_2 addition was complete, the reaction was then stirred at room temperature for a further 6 h. The reaction mixture was then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were then washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: specified later for each compound) to provide the corresponding *N*-sulfinyl imine product **(*R*)-12**.

2.10 General procedure for the artUPO biotransformations with *t*-Bu *N*-sulfenylimines



To a round bottom flask containing a magnetic stirring bar was added liquid artUPO secretate (1.0 mL, 0.8 U/mL) and KPi buffer (100 mM, pH = 7, 10 mL). The solution was diluted by the addition of deionised water (3 mL), followed by addition of the appropriate *t*-Bu *N*-sulfenylimine **6** (0.2 mmol, 1.0 equiv., final concentration 10 mM) in MeCN (4 mL). Next, 2 mL of a 100 mM H_2O_2 solution (prepared from 22 µL 30% H_2O_2 in 2 mL deionised water) was added over a 10 h period, using a syringe pump. After the H_2O_2 addition was complete, the reaction was then stirred at room temperature for a further 6 h. The reaction mixture was then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were then washed with brine (20 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: specified later for each compound) to provide the corresponding *N*-sulfinyl imine product **(*S*)-13**.

2.11 Racemic *N*-sulfinyl imine synthesis [4]

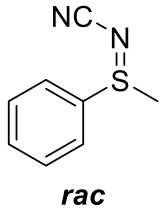


To a round bottom flask containing a magnetic stirring bar was added corresponding *N*-sulfenylimines (0.1 mmol, 1.0 equiv.) in $CHCl_3$ (3 mL), which was followed by the addition of sat $NaHCO_3$ (0.4 mL) and *m*-CPBA (25 mg, 0.11 mmol, 1.1 equiv.) in one portion and the resulting reaction mixture was stirred at room temperature for 30 min. Upon completion, the reaction mixture was quenched by adding excess neat KOH and dried over anhydrous $MgSO_4$ which was then filtered and concentrated *in vacuo* to give the crude product mixture. The

products afforded were of sufficient purity to be used as standards for HPLC analysis without additional purification.

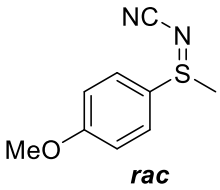
3. Compound data

N-(cyano) methyl phenyl sulfilimine (4a) [1]



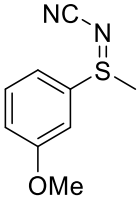
Synthesised from phenyl methyl sulfane using general procedure **2.1**. Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 2:3). Data for **4a:** as a yellow oil (0.560 g, 84% yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.82 – 7.78 (m, 2H), 7.66 – 7.58 (m, 3H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.3, 133.3, 130.5, 126.1, 120.4, 36.6.

N-(cyano) methyl 4-methoxyphenyl sulfilimine (4b) [1]



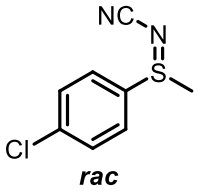
Synthesised from (4-methoxyphenyl)(methyl)sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: EtOAc: MeOH = 19:1). Data for **4b:** as a white solid (0.630 g, 80% yield); ^{1}H NMR (400 MHz, *chloroform-d)* δ 7.78 – 7.69 (m, 2H), 7.11 – 7.02 (m, 2H), 3.86 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 163.7, 128.5, 126.7, 120.6, 115.8, 55.9, 36.2; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaOS$ $(MNa)^+$ 217.0407, found 217.0412.

N-(cyano) methyl 3-methoxyphenyl sulfilimine (4c)



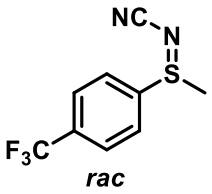
Synthesised from (3-methoxyphenyl) (methyl)sulfane using general procedure **2.1**. Purification via flash column chromatography on silica gel (eluent: hexane: EtOAc = 4:1); as a light yellow oil (0.500 g, 63 % Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.47 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.24 (m, 2H), 7.15 – 7.08 (m, 1H), 3.87 (s, 2H), 2.99 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 160.9, 137.4, 131.4, 120.5, 119.4, 117.9, 110.5, 55.9, 36.9; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaOS$ $(MNa)^+$ 217.0412, found 217.0399; IR film: vmax/cm^{-1} 3007, 2141 (C≡N stretch), 1593, 1481, 1241, 1148, 1029, 760, 680.

***N*-(cyano) methyl 4-chlorophenyl sulfilimine (4d) [5]**



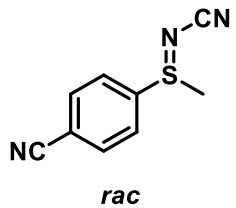
Synthesised from (4-chlorophenyl) (methyl) sulfane using general procedure **2.1.** Purification via flash column chromatography on silica gel (eluent: hexane: EtOAc = 3:7); as a white solid (0.320 g, 40% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.72 (m, 2H), 7.62 – 7.57 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 140.0, 134.8, 130.8, 127.5, 36.8; HRMS (ESI, m/z) m/z calculated for $C_8H_7{}^{35}ClN_2NaS$ $(MNa)^+$ 220.9916, found 220.9914.

***N*-(cyano) methyl 4-trifluorophenyl sulfilimine (4e) [6]**



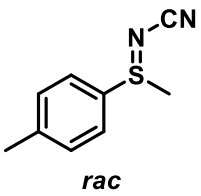
Synthesised from (4-(trifluoromethyl) phenyl (methyl) sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 2: 3); as a yellow oil (0.700 g, 74 % Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 3.07 (s, 3H); ^{13}C NMR (151 MHz, *Chloroform-d*) δ 140.5, 135.1 (q, *J* = 33.5 Hz), 127.4 (q, *J* = 3.8 Hz), 126.4, 123.0 (q, *J* = 273.4 Hz), 119.6, 36.8; ^{19}F NMR (376 MHz*, chloroform-d*) δ –63.09; HRMS (ESI, m/z) m/z calculated for $C_9H_7F_3N_2NaS$ $(MNa)^+$ 255.0180, found 255.0181.

***N*-(cyano) methyl 4-cyanophenyl sulfilimine (4f) [7]**



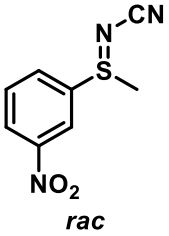
Synthesised from (4-cyanophenyl) (methyl) sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7); as a white solid (0.640 g, 83% yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.96 – 7.88 (m, 4H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ ^{13}C NMR (101 MHz, CHLOROFORM-*D*) δ 141.5, 134.0, 126.7, 119.6, 117.0, 117.0, 37.0.

***N*-(cyano) methyl 4-methylphenyl sulfilimine (4g)**



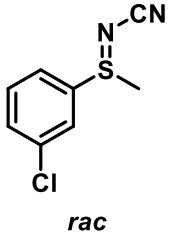
Synthesised from p-tolyl sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 7:11); as a white solid (0.580 g, 80% Yield); Mp = 86 – 89 °C; ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.71 – 7.64 (m, 2H), 7.43 – 7.35 (m, 2H), 3.00 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 144.4, 133.0, 131.1, 126.2, 120.6, 36.4, 21.7; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaS$ $(MNa)^+$ 201.0462, found 201.0455; IR film: νmax/cm^{-1} 2996, 2136, 1592, 1416,1147, 750, 559, 501.

***N*-(cyano) methyl 3-nitrophenyl sulfilimine (4h)**



Synthesised from (3-nitrophenyl) (methyl) sulfane using general procedure **2.2.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 1:4); as a red oil (0.290 g, 32% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.61 (t, *J* = 2.1 Hz, 1H), 8.50 (ddd, *J* = 8.2, 2.1, 1.0 Hz, 1H), 8.26 – 8.18 (m, 1H), 7.89 (t, *J* = 8.2 Hz, 1H), 3.12 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 149.0, 139.0, 132.0, 131.5, 127.7, 121.3, 119.5, 37.2; HRMS (ESI, m/z) m/z calculated for $C_8H_7N_3NaO_2S$ $(MNa)^+$ 232.0157, found 232.0157; IR film: νmax/cm^{-1} 3069, 2922, 2153, 1525, 1347, 1170, 734.

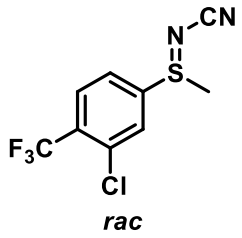
***N*-(cyano) methyl 3-chlorophenyl sulfilimine (4i)**



Synthesised from (3-chlorophenyl) (methyl) sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:1 to EtOAc); as a white solid (0.670 g, 84% Yield); M.p. = 79 – 81 °C; ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.76 (m, 1H), 7.70 – 7.66 (m, 1H), 7.61 – 7.53 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 138.2,

136.7, 133.4, 131.7, 125.9, 124.0, 37.1; HRMS (ESI, m/z) m/z calculated for $C_8H_7{}^{35}ClN_2NaS$ $(MNa)^+$ 220.9916, found 220.9911.

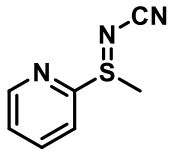
_N_-(cyano) methyl 3-chloro-4-(trifluoromethyl)phenyl sulfilimine (4j)



rac

Synthesised from (3-chlorophenyl)-(methyl) sulfane using general procedure **2.1.** Purififcation via flash chromatography on silica gel (eluent: EtOAc); as a yellow oil (0.540 g, 82% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.96 – 7.92 (m, 2H), 7.83 – 7.79 (m, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 141.8, 135.1, 132.6 (q, *J* = 32.4 Hz), 129.6 (q, *J* = 4.9 Hz) 128.5, 124.1, 122.0 (q, *J* = 273.8 Hz), 37.3; ^{19}F NMR (376 MHz, *chloroform-d*) δ -63.1; HRMS (ESI, m/z) m/z calculated for $C_9H_6{}^{35}ClF_3N_2NaS$ $(MNa)^+$ 288.9790, found 288.9792; IR film: vmax/cm^{-1} 3043, 2149, 1606, 1403, 1321, 1168, 1126, 840, 700, 595.

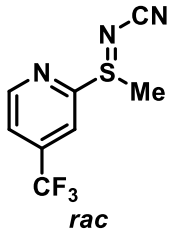
_N_-(cyano) methyl 2-pyridyl sulfilimine (4k) [1]



rac

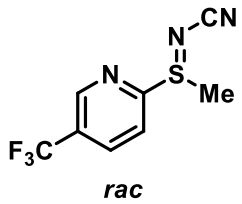
Synthesised from 2-pyridyl methyl sulfane using general procedure **2.1**. Purification via flash chromatography on silica gel (eluent: EtOAc); as a white solid (0.450 g, 66% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.67 – 8.64 (m, 1H), 8.07 (dt, *J* = 7.8, 1.1 Hz, 1H), 8.00 (td, *J* = 7.8, 1.1 Hz, 1H), 7.50 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 3.15 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 156.6, 150.6, 139.1, 126.2, 121.8, 120.1, 119.3, 33.9; HRMS (ESI, m/z) m/z calculated for $C_7H_7N_3NaS$ $(MNa)^+$ 188.0258, found 188.0251.

***N*-(cyano) methyl (4-trifluoromethyl-2-pyridyl) sulfilimine (4l)**



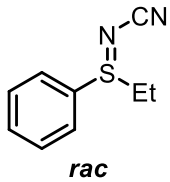
Synthesised from 2-(methylthio)-4-(trifluoromethyl) pyridine. Purification via flash chromatography (eluent: hexane: EtOAc = 2:3); as a yellow oil (0.650 g, 71% Yield); ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.89 (d, *J* = 5.1 Hz, 1H), 8.31 (s, 1H), 7.75 (d, *J* = 5.0 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.8, 151.8, 141.7 (q, *J* = 34.7 Hz), 122.1 (q, *J* = 3.4 Hz), 121.9 (q, *J* = 274 Hz), 119.6, 118.1 (q, *J* = 3.4 Hz), 34.5; HRMS (ESI, m/z) m/z calculated for $C_8H_6F_3N_3NaS$ $(MNa)^+$ 256.0132, found 256.0129; IR film: νmax/cm^{-1} 3075, 2150, 1322, 1172, 1129, 858, 660, 460.

***N*-(cyano) methyl (5-trifluoromethyl-2-pyridyl) sulfilimine (4m)**



Synthesised from 2-(methylthio)-5-(trifluoromethyl) pyridine. Purifciation via flash chromatography (eluent: hexane: EtOAc = 2:3); as a red oil (0.450 g, 49% Yield); ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.97 – 8.92 (s, 1H), 8.27 (d, *J* = 1.5 Hz, 2H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 160.7, 147.7 (q, *J* = 3.5 z), 136.5 (q, *J* = 3.5 Hz), 129.2 (q, *J* = 33.8 Hz), 122.6 (*J* = 273.2 Hz), 122.1, 119.5, 34.1; ^{19}F NMR (376 MHz, *chloroform-d*) δ -62.41; HRMS (ESI, m/z) m/z calculated for $C_8H_6F_3N_3NaS$ $(MNa)^+$ 256.0127, found 256.0129; IR film: νmax/cm^{-1} 3014, 2152, 1713, 1592, 1324, 1101, 1071, 773, 549.

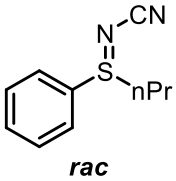
***N*-(cyano) ethyl phenyl sulfilimine (4n)**



Synthesised from ethyl phenyl sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:1 to EtOAc); as a colourless oil (1.26 g, 98% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.74 (m, 2H), 7.65 – 7.56 (m, 3H), 3.26 (dq, *J* = 13.1, 7.4 Hz, 1H), 3.13 (dq, *J* = 13.1, 7.4 Hz, 1H), 1.37 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ

134.6, 133.2, 130.3, 126.5, 121.3, 46.7, 8.1; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaS$ $(MNa)^+$ 201.0462, found 201.0463; IR film: νmax/cm^{-1} 3059, 2141, 1711, 1444, 1170, 686, 583.

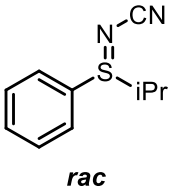
_N_-(cyano) propyl phenyl sulfilimine (4o)



rac

Synthesised from propyl phenyl sulfide using general procedure **2.1**. Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 2:8); as a colourless oil (0.590 g, 76% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.83 – 7.69 (m, 2H), 7.67 – 7.51 (m, 3H), 3.28 (ddd, *J* = 12.9, 7.9, 6.2 Hz, 1H), 2.99 (ddd, *J* = 12.9, 8.4, 7.3 Hz, 1H), 1.91 – 1.73 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.2, 133.2, 130.4, 126.4, 121.2, 54.4, 17.3, 13.0; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$ $(MNa)^+$ 217.0412, found 217.0407; IR film: νmax/cm^{-1} 2967, 2934, 2141, 1444, 1149, 747, 668, 486.

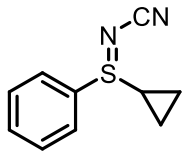
_N_-(cyano) iso-propyl phenyl sulfilimine (4p) [6]



rac

Synthesised from isopropyl phenyl sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 1:4 to EtOAc); as a colourless oil (0.630 g, 81% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.76 – 7.72 (m, 2H), 7.65 – 7.55 (m, 3H), 3.34 (hept, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 133.1, 132.9, 130.1, 127.2, 122.2, 54.3, 16.9, 15.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$ $(MNa)^+$ 215.0613, found 215.0613; IR film: νmax/cm^{-1} 3059, 2145, 1633, 1443, 1155, 1081, 747, 483.

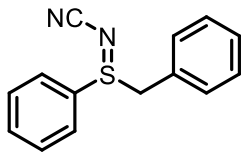
***N*-(cyano) cyclopropyl phenyl sulfilimine (4q)**



rac

Synthesised from cyclopropyl phenyl sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent hexane: EtOAc = 3:7); as a golden oil (0.750 g, 70% yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.83 – 7.73 (m, 1H), 7.66 – 7.54 (m, 2H), 2.76 – 2.64 (m, 1H), 1.49 – 1.34 (m, 1H), 1.31 – 1.14 (m, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.0, 132.9, 130.2, 128.6, 128.5, 127.3, 126.4, 121.3, 29.7, 28.5, 5.6, 4.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{10}N_2NaS$ $(MNa)^+$ 213.0462, found 213.0461; IR film: νmax/cm^{-1} 3025, 2143, 1703, 1444, 1156, 747, 685, 467.

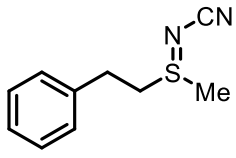
***N*-(cyano) benzyl phenyl sulfilimine (4r) [8]**



rac

Synthesised from benzyl phenyl sulfane using general procedure **2.2.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 1:4); as a white, gum-like solid (1.08 g, 90% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.67 – 7.56 (m, 3H), 7.56 – 7.47 (m, 2H), 7.41 – 7.21 (m, 3H), 7.18 – 7.11 (m, 2H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.27 (d, *J* = 12.6 Hz, 1H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 134.3, 133.3, 130.8, 130.1, 129.8, 129.3, 127.4, 126.9, 120.9, 58.8.

***N*-(cyano) phenethyl methyl sulfilimine (4s)**

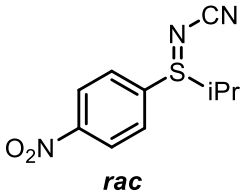


rac

Synthesised from phenethyl methyl sulfane using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7); as a brown solid (0.400 g, 51% Yield); M.p. (°C) 68 – 70; ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 3.49 – 3.41 (m, 1H), 3.22 – 3.06 (m, 3H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.9, 129.3, 128.7, 127.6, 119.9, 51.4, 32.8, 29.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$

(MNa)$^+$ 215.0619, found 215.0618; IR film: νmax/cm^{-1} 3028, 2130, 1602, 1454, 1154, 972, 770, 695, 556, 494

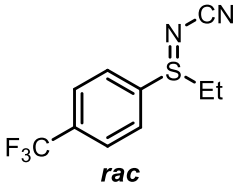
_N_-(cyano) methyl 4-nitrophenyl sulfilimine (4t)



rac

Synthesised from isopropyl 4-nitrophenyl sulfane following general procedure **2.2.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:4 to EtOAc); as a red oil (0.860 g, 86% yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.44 – 8.33 (m, 2H), 7.98 – 7.91 (m, 2H), 3.40 (hept, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H), 1.24 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 150.3, 139.6, 128.4, 128.1, 124.9, 121.5, 55.2, 16.9, 14.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_3NaO_2S$ (MNa)$^+$ 260.0470, found 260.0464; IR film: νmax/cm^{-1} 3027, 2152, 1525, 1345, 1157, 852, 742, 492.

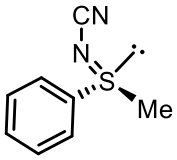
_N_-(cyano) methyl 4-trifluorophenyl sulfilimine (4u)



rac

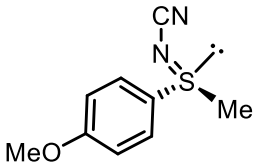
Synthesised from 4-trifluorophenyl methyl sulfane following general procedure **2.1.** Purification via flash chromatography on silica gel (eluent: EtOAc); as a yellow oil (0.660 g, 62% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 3.33 – 3.11 (m, 2H), 1.41 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 138.9, 135.02 (q, *J* = 32.7), 127.4 (q, *J* = 3.7 Hz), 126.9, 123.0 (q, *J* = 273 Hz) 120.7, 47.2, 7.9; ^{19}F NMR (376 MHz, *chloroform-d*) δ -63.06; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{10}F_3N_2NaS$ (MNa)$^+$ 269.0336, found 269.0328; IR film: νmax/cm^{-1} 3043, 2149, 1606, 1403, 1321, 1168, 1012, 840, 761, 595.

***(S)-N*-(cyano) methyl phenyl sulfilimine (*(S)*-4a) [1]**



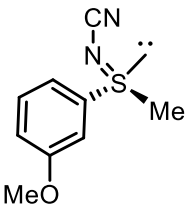
Synthesised from *N*-(cyano) methyl phenyl sulfilimine (49.0 mg, 0.300 mmol) using general procedure **2.4**. Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 2:3); as a colourless oil (20.0 mg, 35% yield); $[\alpha]_D^{20} = -1.59$, (c =1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.82 – 7.78 (m, 2H), 7.66 – 7.58 (m, 3H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.3, 133.3, 130.5, 126.1, 120.4, 36.6; HPLC Data: 32% *ee*, determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/isopropanol: 65:35): tr (minor) = 27.01, tr (major) = 25.0. See section 4.0 for images depicting the HPLC trace.

***(S)-N*-(cyano) methyl 4-methoxyphenyl sulfilimine (*(S)*-4b) [1]**



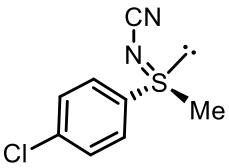
Synthesised from *N*-(cyano) methyl 4-methoxyphenyl sulfilimine (208 mg, 1.07 mmol) using general procedure **2.5.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:4 to EtOAc: MeOH = 19:1); as a white solid (53.0 mg, 26% Yield); $[\alpha]_D^{20} = -75.1$, (c =1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d)* δ 7.78 – 7.69 (m, 2H), 7.11 – 7.02 (m, 2H), 3.86 (s, 3H), 3.00 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 163.7, 128.5, 126.7, 120.6, 115.8, 55.9, 36.2; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaOS$ $(MNa)^+$ 217.0407, found 217.0412; HPLC Data: 73% *ee*, determined by HPLC (AD-H, flow rate: 0.8 mL/min, hexane/isopropanol: 80:20) tr (minor) = 19.47 min, tr (major) = 17.80 min. See section 4.0 for images depicting the HPLC trace.

***(S)-N*-(cyano) methyl 3-methoxyphenyl sulfilimine (*(S)*-4c)**



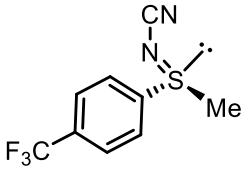
Synthesised from *N*-(cyano) methyl 3-methoxyphenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 1:1); as a yellow oil (21.0 mg, 36% Yield); $[\alpha]_D^{20}$ = –23.34, (c =1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.47 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.24 (m, 2H), 7.15 – 7.08 (m, 1H), 3.87 (s, 2H), 2.99 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 160.9, 137.4, 131.4, 120.5, 119.4, 117.9, 110.5, 55.9, 36.9; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaOS$ $(MNa)^+$ 217.0412, found 217.0399; IR film: νmax/cm^{-1} 3007, 2141 (C≡N stretch), 1593, 1481, 1241, 1148, 1029, 760, 680; ; HPLC Data: 38% *ee*, determined by HPLC (AD-H, flow rate: 1.0 mL/min, hexane/isopropanol: 85:15) tr (minor) = 18.80 min, tr (major) = 17.89 min. See section 4.0 for images depicting the HPLC trace.

***(S)-N*-(cyano) methyl 4-chlorophenyl sulfilimine (*(S)*-4d) [2]**



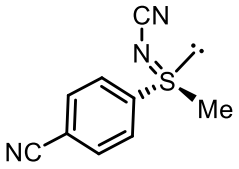
Synthesised from *N*-(cyano) methyl 4-chlorophenyl sulfilimine (99.0 mg, 0.500 mmol) using general procedure **2.4**. Purification via flash column chromatography (gradient eluent: hexane: EtOAc = 2: 3 to EtOAc); as a white solid (38.0 mg, 38% yield); $[\alpha]_D^{20}$ = –71.75 (c =1.5 in chloroform,); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.72 (m, 2H), 7.62 – 7.57 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 140.0, 134.8, 130.8, 127.5, 36.8; HRMS (ESI, m/z) m/z calculated for $C_8H_7ClN_2NaS$ $(MNa)^+$ 220.9916, found 220.9914; [Note: The CN peak is not present in the ^{13}C NMR spectra recorded. In the cited literature,[2] the CN is very weak and barely visible]; HPLC Data: 59% *ee* determined by HPLC (AD-H Chiralcel Column; flow rate: 1.0 mL/ min, hexane/isopropanol = 90:10, column temperature: 30 °C) tr (minor) = 29.96 min, tr (major) = 25.76 min. See section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 4-trifluorophenyl sulfilimine (*(S)*-4e) [6]



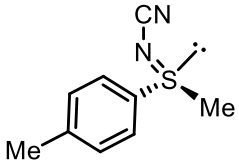
Synthesised from *N*-(cyano) methyl 4-trifluorophenyl sulfilimine (278 mg, 1.20 mmol) following general procedure **2.5.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 2:3); as a colourless oil (119 mg, 43% Yield); $[\alpha]_D^{20} = -120.24$, (c =1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.89 (d, *J* = 8.7 Hz, 2H), 3.07 (s, 3H); ^{13}C NMR (151 MHz, Chloroform-d) δ 140.5, 135.1 (q, *J* = 33.5 Hz), 127.4 (q, *J* = 3.8 Hz), 126.4, 123.0 (q, *J* = 273.4 Hz), 119.6, 36.8; ^{19}F NMR (376 MHz, *chloroform-d*) δ –63.09; HRMS (ESI, m/z) m/z calculated for $C_9H_7F_3N_2NaS$ $(MNa)^+$ 255.0180, found 255.0181; HPLC Data: > 99% *ee* determined by HPLC (AD-H; flow rate: 0.8 mL/ min, hexane/ isopropanol = 80:20) tr (minor) = 12.06, tr (major) = 11.34 min. See section 4.0 for images depicting the HPLC trace.

***(S)*-*N*-(cyano) methyl 4-nitrilephenyl sulfilimine (*(S)*-4f) [7]**



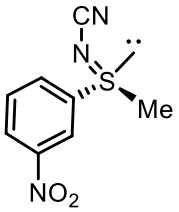
Synthesised from *N*-(cyano) methyl 4-nitrilephenyl sulfilimine (57.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7 to EtOAc: MeOH = 9:1); as a white solid (32.0 mg, 55% yield); $[\alpha]_D^{20} = -46.05$ (c =1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.96 – 7.88 (m, 4H), 3.06 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 141.5, 134.0, 126.7, 119.6, 117.0, 117.0, 37.0.; HPLC Data: 34% *ee* determined by HPLC (AS-H, flow rate: 1.0 mL/min, hexane/ isopropanol = 70:30, column temperature = 30 °C) tr (minor) = 51.28 min, tr (major) = 39.54 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 4-methylphenyl sulfilimine (*(S)*-4g)



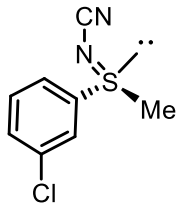
Synthesised from *N*-(cyano) methyl 4-methylphenyl sulfilimine (55.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 3:7 to EtOAc); as a white solid (30.0 mg, 54% Yield); M.p. = 86 – 89 °C; $[\alpha]_D^{20} = -42.94$ (c = 1.00 in chloroform); ^{1}H NMR (400 MHz*, chloroform-d*) δ 7.71 – 7.64 (m, 2H), 7.43 – 7.35 (m, 2H), 3.00 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 144.4, 133.0, 131.1, 126.2, 120.6, 36.4, 21.7; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaS$ $(MNa)^+$ 201.0462, found 201.0455 IR film: νmax/cm^{-1} 2996, 2136, 1592, 1416,1147, 750, 559, 501; HPLC Data: 46% *ee* determined by HPLC (AD-H, flow rate: 1.00 mL/ min, hexane/ isopropanol = 85:15) tr (minor) = 18.95 min, tr (major) = 16.02 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 3-nitrophenyl sulfilimine (*(S)*-4h)



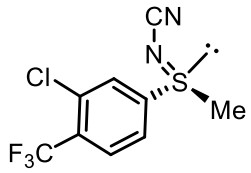
Synthesised from *N*-(cyano) methyl 3-nitrophenyl sulfilimine (63.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:1 to EtOAc); as a red oil (25.0 mg, 37% Yield); $[\alpha]_D^{20} = -45.24$ (c = 0.6 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.61 (t, *J* = 2.0 Hz, 1H), 8.50 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.26 – 8.18 (m, 1H), 7.89 (t, *J* = 8.2 Hz, 1H), 3.12 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 149.0, 139.0, 132.0, 131.5, 127.7, 121.3, 119.5, 37.2; HRMS (ESI, m/z) m/z calculated for $C_8H_7N_3NaO_2S$ $(MNa)^+$ 232.0157, found 232.0157; IR film: νmax/cm^{-1} 3069, 2922, 2153, 1525, 1347, 1170, 734; HPLC Data: 44% *ee* determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/ isopropanol: 60:40; column temperature: 30 °C) tr (minor) = 43.19 min, tr (major) = 47.35 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 3-chlorophenyl sulfilimine (*(S)*-4i)



Synthesised from *N*-(cyano) methyl 3-nitrophenyl sulfilimine (59.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 3:7 to EtOAc); as a white solid (26.0 mg, 44% Yield); $[\alpha]_D^{20}$ = –66.55 (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.76 (m, 1H), 7.70 – 7.66 (m, 1H), 7.61 – 7.53 (m, 2H), 3.02 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 138.2, 136.7, 133.4, 131.7, 125.9, 124.0, 37.1; HRMS (ESI, m/z) m/z calculated for $C_8H_7{}^{35}ClN_2NaS$ $(MNa)^+$ 220.9916, found 220.9911; HPLC Data: 44% *ee* as determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/ isopropanol: 65:35; column temperature: 30 °C) tr (minor) = 26.18 min, tr (major) = 24.02 min. See Section 4.0 for images depicting the HPLC trace.

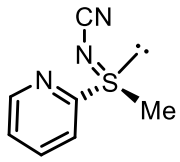
(*S*)-*N*-cyano methyl 3-chloro-4-(trifluoromethyl)phenyl sulfilimine (*(S)*-4j)



Synthesised from *N*-cyano methyl 3-chloro-4-(trifluoromethyl) phenyl sulfilimine (270 mg, 1.00 mmol) using general procedure **2.5.** Purififcation via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 1:4); as a colourless oil (122 mg, 45% Yield); $[\alpha]_D^{20}$ = – 122.51 (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.96 – 7.92 (m, 2H), 7.83 – 7.79 (m, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 141.8, 135.1, 132.6 (q, *J* = 32.4 Hz), 129.6 (q, *J* = 4.9 Hz) 128.5, 124.1, 122.0 (q, *J* = 273.8 Hz), 119.5, 37.3; ^{19}F NMR (376 MHz, *chloroform-d*) δ –63.1; HRMS (ESI, m/z) m/z calculated for $C_9H_6{}^{35}ClF_3N_2NaS$ $(MNa)^+$ 288.9790, found 288.9792; IR film: νmax/cm^{-1} IR film: νmax/cm^{-1} 3043, 2149, 1606, 1403, 1321, 1168, 1126, 840, 700, 595; HPLC Data: > 99% *ee* determined

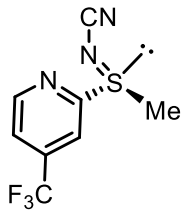
by HPLC (AS-H, flow rate: 0.80 mL/min, hexane/isopropanol: 70/30) tr (major) = 15.49. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 2-pridyl sulfilimine (*(S)*-4k) [1]



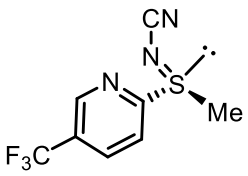
Synthesised from 2-pridyl methyl sulfane (49.5 mg, 0.300 mmol) using general procedure **2.4**. Purification via flash chromatography on silica gel (eluent: EtOAc); as a white solid (20.0 mg, 40% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.67 – 8.64 (m, 1H), 8.07 (dt, *J* = 8.0, 1.1 Hz, 1H), 8.00 (td, *J* = 7.5, 1.7 Hz, 1H), 7.50 (ddd, *J* = 7.5, 4.7, 1.1 Hz, 1H), 3.15 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 156.6, 150.6, 139.1, 126.2, 121.8, 120.1, 119.3, 33.9; HRMS (ESI, m/z) m/z calculated for $C_7H_7N_3NaS$ $(MNa)^+$ 188.0258, found 188.0251.

(*S*)-*N*-(cyano) methyl (4-trifluoromethyl-2-pyridyl) sulfilimine (*(S)*-4l)



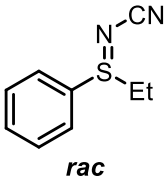
Synthesised from *N*-(cyano) methyl (4-trifluoromethyl-2-pyridyl) sulfilimine (71.0 mg, 0.300 mmol). Purification via flash chromatography (eluent: hexane: EtOAc = 2:3); as a yellow oil (35.0 mg, 50% Yield); $[\alpha]_D^{20} = -27.35$ (c = 1.0 in chloroform, measured indirectly after oxidation with *m*-CPBA via general procedure **2.3**), ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.89 (d, *J* = 5.1 Hz, 1H), 8.31 (s, 1H), 7.75 (d, *J* = 5.1 Hz, 1H), 3.22 (s, 3H); ^{13}C NMR (101 MHz, chloroform-*d*) δ 158.8, 151.8, 141.7 (q, *J* = 34.7 Hz), 122.1 (q, *J* = 3.4 Hz), 121.9 (q, *J* = 274 Hz), 119.6, 118.1 (q, *J* = 3.4 Hz), 34.5; HRMS (ESI, m/z) m/z calculated for $C_8H_6F_3N_3NaS$ $(MNa)^+$ 256.0132, found 256.0129; IR film: νmax/cm^{-1} 3075, 2150, 1322, 1172, 1129, 858, 660, 460; HPLC Data: 35% *ee* determined by HPLC (AD-H, flow rate: 1.00 mL/ min, hexane: isopropanol = 85:15) tr (minor) = 15.60 min, tr (major) = 14.08.

(*S*)-*N*-(cyano) (5-trifluoromethyl-2-pyridyl) sulfilimine (*(S)*-4m)



Synthesised *N*-(cyano) methyl (5-trifluoromethyl-2-pyridyl) sulfilimine (60.0 mg, 0.250 mmol) using general procedure **2.4.** Purifciation via flash chromatography (eluent: hexane: EtOAc = 2:3); as a red oil (30.0 mg, 53% Yield); $[\alpha]_D^{21.5} = -32.96$ (c = 0.50 in chloroform, measured indirectly after oxidation with *m*-CPBA via general procedure **2.3**); ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.97 – 8.92 (s, 1H), 8.27 (d, *J* = 1.5 Hz, 2H), 3.23 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 160.7, 147.7 (q, *J* = 3.5 Hz), 136.5 (q, *J* = 3.5 Hz), 129.2 (q, *J* = 33.8 Hz), 122.6 (*J* = 273.2 Hz), 122.1, 119.5, 34.1; ^{19}F NMR (376 MHz, *chloroform-d*) δ –62.41; HRMS (ESI, m/z) m/z calculated for $C_8H_6F_3N_3NaS$ $(MNa)^+$ 256.0127, found 256.0129; IR film: νmax/cm^{-1} 3014, 2152, 1713, 1592, 1324, 1101, 1071, 773, 549; HPLC Data: 40% *ee* determined by HPLC (AD-H, flowrate: 0.8 mL/ min, hexane: isopropanol = 85:15) tr (minor) = 20.17 min, tr (major) = 22.56 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-N-(cyano) ethyl phenyl sulfilimine (*(S)*-4n)



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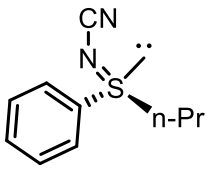
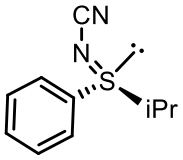
Synthesised from N-(cyano) ethyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a colourless oil (22.0 mg, 48% Yield); $[\alpha]_D^{21.5} = -51.45$ (c = 1.00 in chlorform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.78 – 7.74 (m, 2H), 7.65 – 7.56 (m, 3H), 3.26 (dq, *J* = 13.1, 7.4 Hz, 1H), 3.13 (dq, *J* = 13.1, 7.4 Hz, 1H), 1.37 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 134.6, 133.2, 130.3, 126.5, 121.3, 46.7, 8.1; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaS$ $(MNa)^+$ 201.0462, found 201.0463.; IR film: νmax/cm^{-1} 3059, 2141, 1711, 1444, 1170, 686, 583; HPLC Data: 28% *ee* determined by HPLC (AD-H, flow rate: 0.8 mL/ min, hexane: isopropanol = 80:20) tr (minor) = 14.90 min, tr (major) = 13.90 min. See Section 4.0 for images of the HPLC trace.

(*S*)-*N*-(cyano) propyl phenyl sulfilimine (*(S)*-4o)



Synthesised from *N*-(cyano) propyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.1**. Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:8 to EtOAc); as a golden oil (0.590 g, 59% Yield); $[\alpha]_D^{21.5}$ = – 33.38 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.83 – 7.69 (m, 2H), 7.67 – 7.51 (m, 3H), 3.28 (ddd, *J* = 12.9, 7.9, 6.2 Hz, 1H), 2.99 (ddd, *J* = 12.9, 8.4, 7.3 Hz, 1H), 1.91 – 1.73 (m, 2H), 1.09 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.2, 133.2, 130.4, 126.4, 121.2, 54.4, 17.3, 13.0; IR film: νmax/cm^{-1} 2967, 2934, 2141, 1444, 1149, 747, 668, 486; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$ $(MNa)^+$ 217.0412, found 217.0407; HPLC Data: 12% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/min, hexane/isopropanol = 95:5, column temperature: 30 °C) tr (minor) = 62.51 min, tr (major) = 59.80 min. See Section 4.0 for images depicting the HPLC trace.

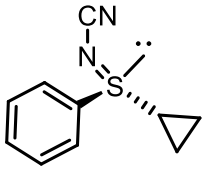
(*S*)-*N*-(cyano) iso-propyl phenyl sulfilimine (*(S)*-4p) [6]



Synthesised from *N*-(cyano) iso-propyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 1:1 to hexane: EtOAc = 1:4); as a colourless oil (37.0 mg, 63% Yield); $[\alpha]_D^{20}$ = – 56.93 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.76 – 7.72 (m, 2H), 7.65 – 7.55 (m, 3H), 3.34 (hept, *J* = 6.8 Hz, 1H), 1.35 (d, *J* = 6.8 Hz, 3H), 1.26 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 133.1, 132.9, 130.1, 127.2, 122.2, 54.3, 16.9, 15.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$ $(MNa)^+$ 215.0613, found 215.0613; IR film: νmax/cm^{-1} 3059, 2145, 1633, 1443, 1155, 1081, 747, 483; HPLC Data: 26% *ee* determined by HPLC (AS-H, flowrate: 1.00 mL/ min, hexane:

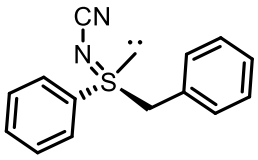
isopropanol = 70:30) tr (minor) = 39.49 min, tr (major) = 28.21 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) cyclopropyl phenyl sulfilimine (*(S)*-4q)



Synthesised from *N*-(cyano) cyclopropyl phenyl sulfilimine (57.0 mg, 0.300 mmol) using general procedure **2.1.** Purification via flash chromatography on silica gel (eluent hexane: EtOAc = 3:7); as a golden oil (26.0 mg, 46% yield); $[\alpha]_D^{20} = -30.82$ (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.83 – 7.73 (m, 1H), 7.66 – 7.54 (m, 2H), 2.76 – 2.64 (m, 1H), 1.49 – 1.34 (m, 1H), 1.31 – 1.14 (m, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.0, 132.9, 130.2, 128.6, 128.5, 127.3, 126.4, 121.3, 29.7, 28.5, 5.6, 4.6; IR film: νmax/cm^{-1} 3025, 2143, 1703, 1444, 1156, 747, 685, 467; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{10}N_2NaS$ $(MNa)^+$ 213.0462, found 213.0461**;** HPLC Data: 34% *ee*, determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 85:15, column temperature: 30 °C) tr (minor) = 17.71 min, tr (major) = 18.58 min. The *ee* was measured by first oxidising the recovered sulfilimine to the corresponding sulfoximine using general procedure **2.3**. See Section 4.0 for images depicting the HPLC trace.

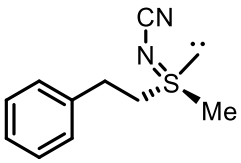
(*S*)-*N*-(cyano) benzyl phenyl sulfilimine (*(S)*-4r) [8]



Synthesised from *N*-(cyano) benzyl phenyl sulfilimine (73.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3: 7); as a white, gum-like solid (40.0 mg, 55% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.67 – 7.56 (m, 3H), 7.56 – 7.47 (m, 2H), 7.41 – 7.21 (m, 3H), 7.18 – 7.11 (m, 2H), 4.56 (d, *J* = 12.6 Hz, 1H), 4.27 (d, *J* = 12.6 Hz, 1H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 134.3, 133.3, 130.8, 130.1, 129.8, 129.3, 127.4, 126.9, 120.9, 58.8; HPLC Data: 16% *ee* determined by HPLC (AS-H,

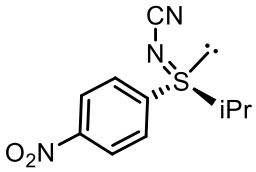
flowrate: 0.8 mL/ min, hexane: isopropanol = 65:35) tr (minor) = 34.12 min, tr (major) = 41.41 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) phenethyl methyl sulfilimine (*(S)*-4s)



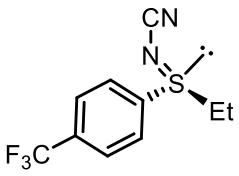
Synthesised from *N*-(cyano) phenethyl methyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7); as a golden oil (19.0 mg, 31% Yield); $[\alpha]_D^{20} = -29.16$ (c = 1.00 in chloroform); M.p. (°C) 68 – 70; ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 2H), 7.26 – 7.23 (m, 1H), 3.49 – 3.41 (m, 1H), 3.22 – 3.06 (m, 3H), 2.75 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.9, 129.3, 128.7, 127.6, 119.9, 51.4, 32.8, 29.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaS$ $(MNa)^+$ 215.0619, found 215.0618; IR film: νmax/cm^{-1} 3028, 2130, 1602, 1454, 1154, 972, 770, 695, 556, 494.

(*S*)-*N*-(cyano) isopropyl 4-nitrophenyl sulfilimine (*(S)*-4t)



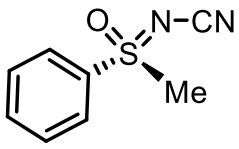
Synthesised from *N*-(cyano) isopropyl 4-nitrophenyl sulfilimine (238 mg, 1.00 mmol) following general procedure **2.5.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a red oil (111 mg, 47% yield); $[\alpha]_D^{20} = -186.09$ (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.44 – 8.33 (m, 2H), 7.98 – 7.91 (m, 2H), 3.40 (hept, *J* = 6.7 Hz, 1H), 1.35 (d, *J* = 6.7 Hz, 3H), 1.24 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 150.3, 139.6, 128.4, 128.1, 124.9, 121.5, 55.2, 16.9, 14.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_3NaO_2S$ $(MNa)^+$ 260.0470, found 260.0464; IR film: νmax/cm^{-1} 3027, 2152, 1525, 1345, 1157, 852, 742, 492; HPLC Data: 84% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 80:20) tr (minor) = 19.61 min, tr (major) = 17.97 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) ethyl 4-trifluorophenyl sulfilimine (*(S)*-4u)



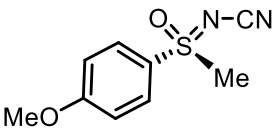
Synthesised from *N*-(cyano) ethyl 4-trifluorophenyl ethyl sulfilimine (246 mg, 1.00 mmol) using general procedure **2.5.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a colourless oil (109 mg, 47% Yield); $[\alpha]_D^{20} = -194.67$ (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 2H), 3.33 – 3.11 (m, 2H), 1.41 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 138.9, 135.02 (*J* = 32.7), 127.4 (q, *J* = 3.7 Hz), 126.9, 123.0 (q, *J* = 273 Hz) 120.7, 47.2, 7.9; ^{19}F NMR (376 MHz, *chloroform-d*) δ –63.06; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{10}F_3N_2NaS$ $(MNa)^+$ 269.0336, found 269.0328; IR film: νmax/cm^{-1} 3043, 2149, 1606, 1403, 1321, 1168, 1012, 840, 761, 595**;** HPLC Data: > 99% *ee* determined by HPLC (AS-H, flowrate: 0.80 mL/ min, hexane: isopropanol = 70:30) tr (major) = 14.70 min, tr (minor) = 17.29 min.

***(S)*-*N*-(cyano) methyl phenyl sulfoximine ((*S*)-5a) [1]**



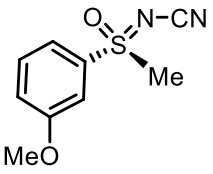
Synthesised from *N*-(cyano) methyl phenyl sulfilimine (49.0 mg, 0.300 mmol) using general procedure **2.4**. Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 2:3); as a colourless oil (16.0 mg, 22% yield); $[\alpha]_D^{20} = +46.54$ (c = 1.00 in chloroform), Lit $[\alpha]_D = +196$ (c = 0.41 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.98 – 7.94 (m, 2H), 7.76 (tt, *J* = 7.8, 1.3 Hz, 1H), 7.68 – 7.63 (dd, *J* = 8.5, 7.2 Hz, 2H), 3.32 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.9, 135.5, 130.3, 127.8, 127.5, 112.0, 44.7; HPLC Data: 74% *ee*, determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/isopropanol: 65:35): tr (minor) = 23.51 min, tr (major) = 26.63 min. See section 4.0 for images depicting the HPLC trace.

***(S)-N*-(cyano) methyl 4-methoxyphenyl sulfoximine ((*S*)-5b) [1]**



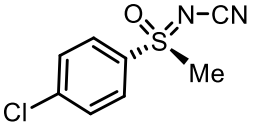
Synthesised from *N*-(cyano) methyl 4-methoxyphenyl sulfilimine (208 mg, 1.07 mmol) using general procedure **2.5.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:4 to EtOAc: MeOH = 19:1); as a white solid (93.0 mg, 41% Yield); $[\alpha]_D^{20}$ = +174.72 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.94 – 7.85 (m, 2H), 7.12 – 7.05 (m, 2H), 3.90 (s, 3H), 3.30 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 165.2, 130.4, 126.7, 115.6, 112.3, 56.1, 45.3; HPLC Data: 90% *ee* determined by HPLC (AD-H, flow rate: 0.80 mL/min, hexane/isopropanol: 80:20) tr (minor) = 21.95 min, tr (major) = 23.20 min. See section 4.0 for images depicting the HPLC trace.

***(S)-N*-(cyano) methyl 3-methoxyphenyl sulfilimine ((*S*)-5c) [9]**



Synthesised from *N*-(cyano) methyl 3-methoxyphenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 1:1); as a colourless oil (18.0 mg, 29% Yield); $[\alpha]_D^{20}$ = + 75.14 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.61 – 7.54 (m, 2H), 7.47 – 7.44 (m, 1H), 7.30 – 7.27 (m, 1H), 3.91 (s, 3H), 3.33 (s, 3H); ^{13}C NMR (101 MHz, chloroform-*d*) δ 160.8, 137.3, 131.5, 122.0, 120.0, 112.5, 111.9, 56.1, 44.9; HPLC Data: 90% *ee* determined by HPLC (AD-H, flow-rate: 0.8 mL/min, hexane/isopropanol: 80/20) tr (minor) = 17.20 min, tr (major) 19.24 min. See Section 4.0 for images depicting the HPLC trace.

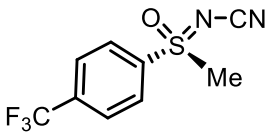
(*S*)-*N*-(cyano) methyl 4-chlorophenyl sulfoximine ((*S*)-5d) [9]



Synthesised from *N*-(cyano) methyl 4-chlorophenyl sulfilimine (99.0 mg, 0.500 mmol) using general procedure **2.4**. Purification via flash

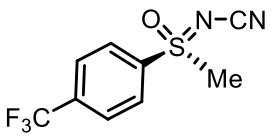
column chromatography (gradient eluent: hexane: EtOAc = 2: 3 to EtOAc); as a colourless oil (49.0 mg, 46% yield); $[\alpha]_D^{20}$ = +124.58 (c =1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.97 – 7.89 (m, 2H), 7.69 – 7.61 (m, 2H), 3.35 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 142.7, 134.5, 130.7, 129.5, 111.6, 44.9; HRMS (ESI, m/z) m/z calculated for $C_8H_7ClN_2NaOS$ $(MNa)^+$ 236.9865, found 236.9871; HPLC Data: 90% *ee* determined by HPLC (AD-H Chiralcel Column; flow rate: 1.0 mL/ min, hexane/isopropanol = 90:10, column temperature: 30 °C) tr (minor) = 32.58 min, tr (major) = 40.14 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 4-trifluorophenyl sulfoximine ((*S*)-5e) [9]



Synthesised from *N*-(cyano) methyl 4-trifluorophenyl sulfilimine (278 mg, 1.20 mmol) following general procedure **2.5**. Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 2:3); as a colourless oil (147 mg, 44 % yield); $[\alpha]_D^{20}$ = + 123.75, (c =1.00 in chloroform); ^{1}H NMR (400 MHz*, chloroform-d*) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.96 (d, *J* = 8.2 Hz, 2H), 3.39 (s, 3H; C***H*₃**); ^{13}C NMR (101 MHz, *chloroform-d)* δ 139.9, 137.2 (q, *J* = 37.2 Hz), 128.9, 127.59 (q, *J* = 3.6 Hz), 122.8 (q, *J* = 273 Hz) , 111.3, 44.7; ^{19}F NMR (376 MHz, *chloroform-d*) δ −63.30; HRMS (ESI, m/z) m/z calculated for $C_9H_7F_3N_2NaOS$ $(MNa)^+$ 271.0123, found 271.0123; IR film: vmax/cm^{-1} 2924 (C-H stretch), 2197, 1403, 1320, 824; HPLC Data: 94% *ee* as determined by HPLC (AD-H; flow rate: 0.8 mL/ min, hexane/ isopropanol = 80:20) tr (minor) = 11.40 min, tr (major) = 13.12 min. See Section 4.0 for images depicting the HPLC trace.

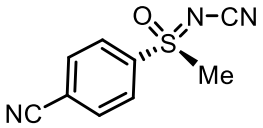
(*R*)-*N*-(cyano) methyl 4-trifluorophenyl sulfoximine ((*S*)-5e)



Synthesised from **4e** (119 mg, 0.513 mmol) following general procedure **2.3**. Purification via flash chromatography on silica gel

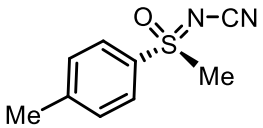
(gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 2:3); as a colourless oil (108 mg, 87 % Yield); $[\alpha]_D^{20} = -124.85$, (c =1.00 in chloroform); All other spectroscopic data were identical to those above.

***(S)*-*N*-(cyano) methyl 4-cyanophenyl sulfoximine ((*S*)-5f) [8]**



Synthesised from *N*-(cyano) methyl 4-cyanophenyl sulfilimine (57.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7 to EtOAc: MeOH = 9:1); as a colourless oil, (20.0 mg, 33% Yield); $[\alpha]_D^{20} = +119.1$, (c =1.36 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.19 – 8.10 (m, 2H), 8.05 – 7.96 (m, 2H), 3.40 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 140.5, 134.1, 128.9, 119.4, 116.6, 111.0, 44.6; HRMS (ESI, m/z) m/z calculated for $C_9H_7N_3NaOS$ $(MNa)^+$ 228.0208, found 228.0208; IR film: νmax/cm^{-1} 3093, 2923, 2197, 1399, 1251, 826; HPLC Data: 80% *ee* determined by HPLC (AS-H, flow rate: 1.0 mL/min, hexane/ isopropanol = 70:30, column temperature = 30 °C) tr (minor) = 70.64 min, tr (major) = 66.07 min. See Section 4.0 for pictures depicting the HPLC trace.

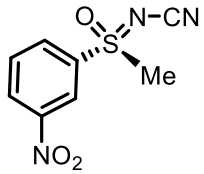
(*S*)-*N*-(cyano) methyl 4-methylphenyl sulfilimine ((*S*)-5g) [10]



Synthesised from *N*-(cyano) methyl 4-methylphenyl sulfilimine (55.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 3:7 to EtOAc); as a white solid (21.0 mg, 38% Yield); $[\alpha]_D^{20} = +115.79$ (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.90 – 7.83 (m, 2H), 7.51 – 7.43 (m, 2H), 3.31 (s, 3H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 147.1, 133.0, 1301.0, 128.1, 112.1, 45.1, 21.9; HPLC Data: 88% *ee* determined by HPLC (AD-H, flow rate: 1.00 mL/ min, hexane/ isopropanol = 85:15) tr

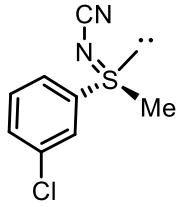
(minor) = 18.91 min, tr (major) = 22.71 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 3-nitrophenyl sulfoximine ((*S*)-5h) [11]



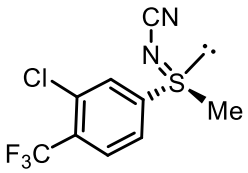
Synthesised from *N*-(cyano) methyl 3-nitrophenyl sulfilimine (63.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:1 to EtOAc); as a yellow oil (25.0 mg, 38% yield), $[\alpha]_D^{20}$ = +107.77 (c = 0.8 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.85 (t, *J* = 1.9 Hz, 1H), 8.65 (ddd, *J* = 8.2, 1.9, 1.0 Hz, 1H), 8.35 (ddd, *J* = 7.9, 1.9, 1.0 Hz, 1H), 7.96 (app. t, *J* = 8.1 Hz, 1H), 3.45 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 149.1, 138.6, 133.5, 132.0, 130.0, 123.7, 110.8, 44.7; HRMS (ESI, m/z) m/z calculated for $C_8H_7N_3NaO_3S$ $(MNa)^+$ 248.0106, found 248.0099; HPLC Data: 82% *ee* determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/ isopropanol: 60:40; column temperature: 30 °C) tr (minor) = 34.45 min, tr (major) = 41.58 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 3-chlorophenyl sulfoximine ((*S*)-5i) [12]



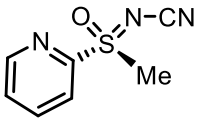
Synthesised from *N*-(cyano) methyl 3-chlorophenyl sulfilimine (59.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 1:1 to EtOAc); as a red solid (23.0 mg, 36% Yield), $[\alpha]_D^{20}$ = +103.25 (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.98 (t, *J* = 2.0 Hz, 1H), 7.91 – 7.88 (m, 1H), 7.78 – 7.74 (m, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 3.36 (s, 3H); ^{13}C NMR (101 MHz, chloroform-*d*) δ 138.0, 136.8, 135.8, 131.7, 128.1, 126.2, 111.4, 44.9; HPLC Data: 80% *ee* as determined by HPLC (AS-H, flow rate: 0.8 mL/min, hexane/ isopropanol: 60:40; column temperature: 30 °C) tr (minor) = 16.57 min, tr (major) = 22.03 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-cyano methyl 3-chloro-4-(trifluoromethyl)phenyl sulfoximine ((*S*)-5j)



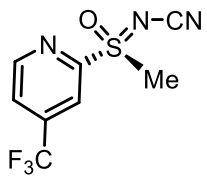
Synthesised from *N*-cyano methyl 3-chloro-4-(trifluoromethyl) phenyl sulfilimine (270 mg, 1.00 mmol) using general procedure **2.5.** Purififcation via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:3 to hexane: EtOAc = 1:4); as a white solid (132 mg, 47% Yield); Mp (°C) = 97 – 98; $[\alpha]_D^{20}$ = 106.16 (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, chloroform-*d*) δ 8.16 – 8.14 (m, 1H), 8.05 – 7.99 (m, 2H), 3.41 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 141.04, 135.2 (q, *J* =1.4 Hz), 135.0 (q, *J* =32.4 Hz), 131.0, 129.8 (q, *J* = 5.4 Hz), 126.4, 121.7 (q, *J* = 273.8 Hz), 110.8, 44.7; ^{19}F NMR (376 MHz, *chloroform-d*) δ –63.40; HRMS (ESI, m/z) m/z calculated for $C_9H_6ClF_3N_2NaSO$ $(MNa)^+$ 304.9739, found 304.9737; IR film: νmax/cm^{-1} 3035, 2189, 1588, 1391, 1310, 1249, 1105, 1027, 969, 827, 554, 454; HPLC Data: 98% *ee* determined by HPLC (AS-H, flow rate: 0.80 mL/min, hexane/isopropanol: 70/30) tr (minor) = 14.77 min, tr (major) = 16.49 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl 2-pyridyl sulfoximine ((*S*)-5k) [1]



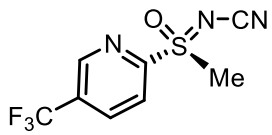
Synthesised from 2-pridyl methyl sulfane (49.5 mg, 0.300 mmol) using general procedure **2.4**. Purification *via* flash chromatography on silica gel (eluent: EtOAc); as a white solid (23.0 mg, 40% Yield); $[\alpha]_D^{20}$ = +17.87 (c = 1.0 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.79 (ddd, *J* = 4.7, 1.8, 1.0 Hz, 1H), 8.20 (dt, *J* = 7.8, 1.0 Hz, 1H), 8.09 (td, *J* = 7.8, 1.8 Hz, 1H), 7.69 (ddd, *J* = 7.8, 4.7, 1.0 Hz, 1H), 3.51 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 154.7, 150.9, 139.2, 128.9, 122.6, 111.6, 39.8; HRMS (ESI, m/z) m/z calculated for $C_7H_7N_3NaOS$ $(MNa)^+$ 204.0208, found 204.0203; HPLC Data: 64% *ee* determined by HPLC (AD-H, flow rate: 0.8 mL/ min, hexane: isopropanol = 80:20), tr (minor) = 23.24 min, tr (major) = 21.65 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl (4-trifluoromethyl-2-pyridyl) sulfoximine ((*S*)-5l)



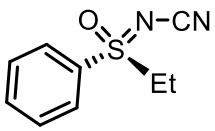
Synthesised from *N*-(cyano) (4-trifluoromethyl-2-pyridyl) sulfilimine (71.0 mg, 0.300 mmol). Purification *via* flash chromatography (eluent: hexane: EtOAc = 2:3); as a white crystaline solid (20 mg; 27% Yield); Mp (°C) = 106; $[\alpha]_D^{20}$ = +34.63 (c = 0.79 in chloroform); ^{1}H NMR (400 MHz, chloroform-*d*) δ 9.04 – 9.00 (m, 1H), 8.43 – 8.40 (m, 1H), 7.94 – 7.90 (m, 1H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, chloroform-*d*) δ 156.3, 152.2, 141.8 (q, *J* = 36.4 Hz), 124.8 (q, *J* = 3.4 Hz), 121.7 (q, *J* = 274 Hz) , 118.9 (q, *J* = 3.4 Hz), 110.9, 40.0; ^{19}F NMR (376 MHz, chloroform-*d*) δ –64.49; HRMS (ESI, m/z) m/z calculated for $C_8H_6F_3N_3NaOS$ $(MNa)^+$ 272.0081, found 272.0079: IR film: νmax/cm^{-1} 2924, 2201, 1326 (S=O), 1257, 1144, 989, 751, 662, 489; HPLC Data: 90% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane/ isopropanol: 85:15, column temperature: 30 °C) tr (minor) = 14.09 min, tr (major) = 15.67 min. See Section 4.0 depicting the HPLC trace.

(*S*)-*N*-(cyano) methyl (5-trifluoromethyl-2-pyridyl) sulfoximine ((*S*)-5m)



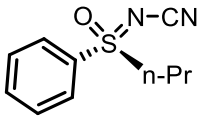
Synthesised *N*-(cyano) (5-trifluoromethyl-2-pyridyl) sulfilimine (60.0 mg, 0.250 mmol) using general procedure **2.4.** Purifciation via flash chromatography (eluent: hexane: EtOAc = 2:3); as a yellow oil (20.0 mg, 30% Yield); $[\alpha]_D^{20}$ = + 81.37, (c =1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 9.10 – 9.03 (m, 1H), 8.39 – 8.33 (m, 2H), 3.57 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 157.9, 148.0 (q, *J* = 4.0 Hz), 136.6 (q, *J* = 3.6 Hz), 131.5 (q, *J* = 34.5 Hz), 122.2, 122.2 (q, *J* = 273 Hz), 111.0, 39.6; HRMS (ESI, m/z) m/z calculated for $[C_8H_6F_3N_3NaOS]^+$ = 272.0081, found 272.0076; IR film: νmax/cm^{-1} 3015, 2923, 2199, 1594, 1327, 1140, 827; HPLC Data: 90% *ee* determined by HPLC (AD-H, flowrate: 0.8 mL/ min, hexane: isopropanol = 85:15) tr (minor) = 22.34 min, tr (major) = 19.94 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-N-(cyano) ethyl phenyl sulfoximine ((*S*)-5n) [12]



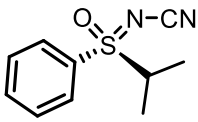
Synthesised from N-(cyano) ethyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification *via* flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a colourless oil (22.0 mg, 48% Yield); $[\alpha]_D^{21.5}$ = + 58.52 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.00 – 7.91 (m, 2H), 7.79 (tt, 1H), 7.74 – 7.64 (m, 2H), 3.45 (dq, *J* = 14.7, 7.4 Hz, 1H), 3.38 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.34 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.5, 134.1, 130.3, 128.8, 112.2, 51.6, 7.2; HRMS (ESI, m/z) m/z calculated for $C_9H_{10}N_2NaOS$ $(MNa)^+$ 217.0412, found 217.0407; HPLC Data: 50% *ee* determined by HPLC (AD-H, flow rate: 0.8 mL/ min, hexane: isopropanol = 80:20) tr (minor) = 17.28 min, tr (major) = 18.70 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-N-(cyano) n-propyl phenyl sulfoximine ((*S*)-5o) [12]



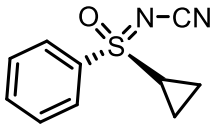
Synthesised from *N*-(cyano) propyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.1**. Purification *via* flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 7:8 to EtOAc); as a colourless oil (17.0 mg, 27% Yield); $[\alpha]_D^{21.5}$ = + 55.75 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.98 – 7.91 (m, 2H), 7.78 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.72 – 7.63 (m, 2H), 3.44 – 3.36 (m, 1H), 3.34 – 3.26 (m, 1H), 1.92 – 1.66 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.5, 134.8, 130.3, 128.6, 112.2, 58.4, 16.3, 12.6; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaOS$ $(MNa)^+$ 231.0568, found 231.0568; IR film: νmax/cm^{-1} 2971, 2191, 1447, 1240, 1183, 1091, 824, 750, 727, 541, 473; HPLC Data: 42% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 90:10) tr (minor) = 34.11 min, tr (major) = 35.85 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-N-(cyano) iso-propyl phenyl sulfoximine ((*S*)-5p)



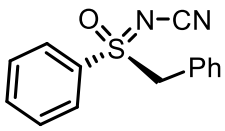
Synthesised from *N*-(cyano) iso-propyl phenyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4.** Purification *via* flash chromatography on silica gel (eluent: hexane: EtOAc = 1:1 to hexane: EtOAc = 1:4); as a golden oil (22 mg, 35% Yield); $[\alpha]_D^{20}$ = +71.05 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.94 – 7.87 (m, 2H), 7.82 – 7.74 (m, 1H), 7.71 – 7.63 (m, 2H), 3.51 (hept, *J* = 6.8 Hz, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.4, 132.7, 130.1, 129.6, 112.6, 57.8, 15.8, 15.3; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_2NaOS$ $(MNa)^+$ 231.0568, found, 231.0558; IR film: νmax/cm^{-1} 2985, 2191, 1448, 1446, 1234, 1189, 1087, 826, 721, 687, 554; HPLC Data: 76% *ee* (AS-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 70:30) tr (minor) = 19.65 min, tr (major) = 21.38 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) cyclopropyl phenyl sulfoximine ((*S*)-5q) [12]



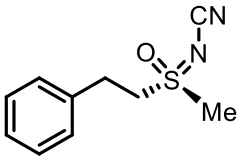
Synthesised from *N*-(cyano) cyclopropyl phenyl sulfilimine (57.0 mg, 0.300 mmol) using general procedure **2.1.** Purification *via* flash chromatography on silica gel (eluent hexane: EtOAc = 3:7); as a golden oil (13 mg, 21% Yield); $[\alpha]_D^{21.1}$ = +38.23 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.98 – 7.93 (m, 2H), 7.77 (tt, *J* = 7.8, 1.4 Hz, 1H), 7.69 – 7.63 (m, 2H), 2.73 – 2.65 (m, 1H), 1.74 – 1.67 (m, 1H), 1.43 – 1.28 (m, 3H), 1.16 – 1.08 (m, 1H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 136.5, 135.2, 130.2, 128.1, 112.2, 33.7, 7.2, 6.1; HPLC Data: 74% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 85:15, column temperature: 30 °C) tr (minor) = 17.3 min, tr (major) = 16.59 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) benzyl phenyl sulfoximine ((*S*)-5r) [8]



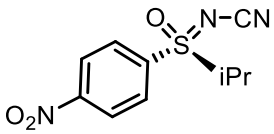
Synthesised from *N*-(cyano) benzyl phenyl sulfilimine (73.0 mg, 0.300 mmol) using general procedure **2.4.** Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3: 7); as a white solid (21 mg, 27% Yield); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.75 – 7.69 (m, 1H), 7.65 – 7.61 (m, 2H), 7.56 – 7.51 (m, 2H), 7.40 – 7.35 (m, 1H), 7.31 – 7.27 (m, 2H), 7.06 – 7.03 (m, 2H), 4.62 (s, 2H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.5, 133.2, 131.4, 130.1, 129.8, 129.3, 129.1, 125.6, 112.3, 63.5; HPLC Data: 56% *ee* determined by HPLC (AS-H, flowrate: 0.8 mL/ min, hexane: isopropanol = 65:35) tr (minor) = 29.58 min, tr (major) = 25.28 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) phenethyl methyl sulfoximine ((*S*)-5s)



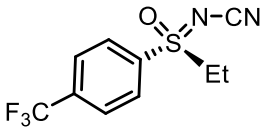
Synthesised from *N*-(cyano) phenethyl methyl sulfilimine (58.0 mg, 0.300 mmol) using general procedure **2.4**. Purification via flash chromatography on silica gel (eluent: hexane: EtOAc = 3:7); as a white solid (21 mg, 36% Yield); $[\alpha]_D^{20}$ = +9.70 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 7.39 – 7.34 (m, 2H), 7.33 – 7.26 (m, 2H), 7.26 – 7.24 (m, 1H), 3.76 – 3.67 (m, 1H), 3.65 – 3.56 (m, 1H), 3.28 – 3.22 (m, 2H), 3.04 (s, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 135.8, 129.4, 128.7, 127.9, 112.1, 56.5, 41.0, 28.8; $C_{10}H_{12}N_2NaOS$ $(MNa)^+$ 231.0568, found, 231.0564; IR film: ν_{max}/cm^{-1} 2923, 2192, 1455, 1245, 1131, 820, 701; HPLC Data: 60% *ee* determined by HPLC (AS-H, flowrate: 1.0 mL/min, hexane: isopropanol = 70:30) tr (minor) = 29.83 min, tr (major) = 25.02 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) isopropyl 4-nitropheneyl sulfoximine ((*S*)-5t)



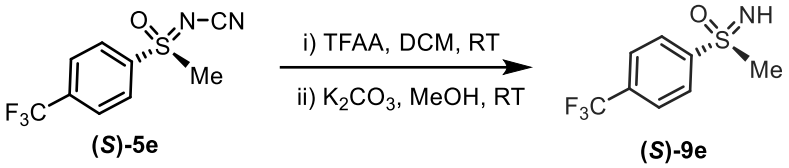
Synthesised from *N*-(cyano) isopropyl 4-nitropheneyl sulfilimine (238 mg, 1.00 mmol) following general procedure **2.5**. Purification via flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a white solid (111 mg, 44% yield); M.p. 111 – 112 °C; $[\alpha]_D^{20}$ = +178.19 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.54 – 8.50 (m, 2H), 8.17 – 8.13 (m, 2H), 3.59 (hept, *J* = 6.9 Hz, 1H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.38 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 163.1, 151.9, 139.0, 131.2, 125.2, 111.5, 58.1, 15.8, 15.2; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{12}N_3NaO_3S$ $(MNa)^+$ 276.0413, found 276.0419; IR film: νmax/cm^{-1} 3104, 2987, 2198, 1534, 1353, 1242, 827, 734, 493; HPLC Data: 90% *ee* determined by HPLC (AD-H, flowrate: 1.00 mL/ min, hexane: isopropanol = 80:20) tr (minor) = 24.12 min, tr (major) = 26.89 min. See Section 4.0 for images depicting the HPLC trace.

(*S*)-*N*-(cyano) ethyl 4-trifluorophenyl sulfoximine ((*S*)-5u)



Synthesised from *N*-(cyano) ethyl 4-trifluorophenyl sulfilimine (246 mg, 1.0 mmol) using general procedure **2.5.** Purification *via* flash chromatography on silica gel (gradient eluent: hexane: EtOAc = 2:3 to EtOAc); as a colourless oil (120 mg, 46% Yield); $[\alpha]_D^{20}$ = +122.51 (c = 1.00 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H), 3.58 – 3.36 (m, 2H), 1.39 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, *chloroform-d*) δ 138.0, 137.1 (q, *J* = 33.8), 129.6, 127.5 (q, *J* = 3.4 Hz), 122.8 (q, *J* = 273.1 Hz), 111.5, 51.6, 7.1; ^{19}F NMR (376 MHz, *chloroform-d*) δ –63.28; HRMS (ESI, m/z) m/z calculated for $C_{10}H_{10}F_3N_2NaSO$ $(MNa)^+$ 285.0285, found 285.0281; IR film: νmax/cm^{-1} 3051, 2196, 1404, 1321, 1174, 1091, 831, 719, 540**;** HPLC Data: 96% *ee* determined by HPLC (AS-H, flowrate: 0.80 mL/ min, hexane: isopropanol = 70:30) tr (minor) = 13.79 tr (major) = 15.69 min. See Section 4.0 for images depicting the HPLC trace

Synthesis of *S*-methyl-S-[4-(trifluoromethyl)phenyl]-sulfoximine ((*S*)-9e) [13]

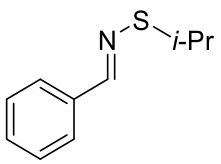


(*S*)-5e 95% *ee*

(*S*)-9e 95% *ee*

To a stirring solution of **(*S*)-5e** (144 mg, 0.580 mmol) in DCM (8.00 mL) was added TFAA (0.250 mL, 1.74 mmol) at 0 °C before the reaction temperature was raised to RT and stirred for 3 h. A further aliquot of TFAA (0.250 mL, 1.74 mmol) was added and the reaction stirred for 16 h. The solvent was removed *in vacuo* and the crude material dissolved in dry MeOH (10.0 mL) and stirred with solid K_2CO_3 (350 mg, 2.5 mmol) for 4 h, upon which, the solvent was removed *in vacuo* and the resultant crude dissolved in H_2O (10 mL). The reaction was extracted with EtOAc (3 x 30 mL), and the combined organic phase washed with saturated brine (40 mL), dried over $MgSO_4$, filtered, and the solvent removed *in vacuo* to afford a white solid. Purification via flash column chromatography on silica gel (eluent: hexane: EtOAc = 1:4) afforded (*S*)-**9e** as white crystals (100 mg, 83% Yield). $[\alpha]_D^{20.9}$ = +16.62 (c = 1.00 in chlorform), Lit $[\alpha]_D^{25}$ = +16.3 (c = 1.1 in chloroform); ^{1}H NMR (400 MHz, *chloroform-d*) δ 8.14 (d, *J* = 7.6 Hz, 2H), 7.81 (d, *J* = 7.6 Hz, 2H), 3.11 (d, *J* = 1.5 Hz, 3H), 2.71 (br s, 1H, N-***H***); ^{13}C NMR (101 MHz, *chloroform-d)* δ 147.3, 134.8 (q, *J* = 33.0 Hz), 128.5, 126.5 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 273 Hz), 46.1; ^{19}F NMR (376 MHz, *chloroform-d*) δ –62.99.

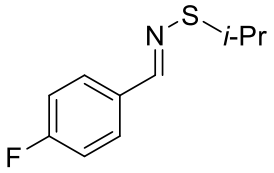
(*E*)-*N*-benzylidene-*S*-isopropylthiohydroxylamine (6a-*i*Pr)



Synthesised from benzylamine (0.660 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (270 mg, 24% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.47 (s, 1H), 7.68 – 7.57 (m, 2H), 7.42 – 7.32 (m, 3H), 3.56 (hept,

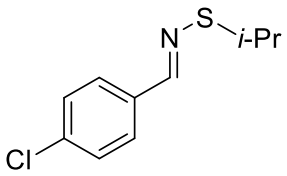
J = 6.8 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 156.1, 136.8, 129.8, 128.7, 127.0, 40.6, 21.7; HRMS (ESI) calcd. for $C_{10}H_{14}NS$ (MH^+): 180.0847, found 180.0841; IR (film): νmax/cm^{-1} 2960, 1447, 1239, 749, 689.

(*E*)-*N*-(4-fluorobenzylidene)-*S*-isopropylthiohydroxylamine (6b-*i*Pr)



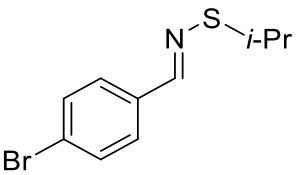
Synthesised from (4-fluorophenyl)methanamine (752 mg, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (70.0 mg, 7% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.42 (s, 1H), 7.69 – 7.54 (m, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 3.54 (pd, *J* = 6.8, 0.9 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 164.9, 154.5, 128.7 (d, *J* = 9.1 Hz), 115.6 (d, *J* = 22.2 Hz), 40.6, 21.6; HRMS (ESI) calcd. for $C_{10}H_{13}FNS$ (MH^+): 198.0753, found 198.0747; IR (film): νmax/cm^{-1} 2961, 1506, 1227, 830.

(*E*)-*N*-(4-chlorobenzylidene)-*S*-isopropylthiohydroxylamine (6c-*i*Pr)



Synthesised from (4-chlorophenyl)methanamine (0.730 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (150 mg, 15% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.41 (s, 1H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 3.54 (dt, *J* = 13.5, 6.9 Hz, 1H), 1.42 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, *Chloroform-d*) δ 154.4, 135.6, 135.2, 128.8, 128.0, 40.7, 21.5; HRMS (ESI) calcd. for $C_{10}H_{13}{}^{35}ClNS$ (MH^+): 214.0457, found 214.0452; IR (film): νmax/cm^{-1} 2961, 1488, 1086, 818.

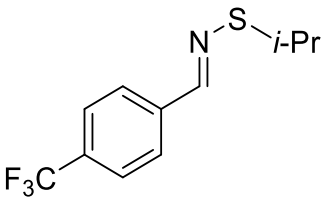
(*E*)-*N*-(4-bromobenzylidene)-*S*-isopropylthiohydroxylamine (6d-*i*Pr)



Synthesised from (4-bromophenyl)methanamine (1.10 g, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow

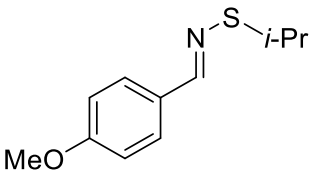
oil (73.0 mg, 6% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.39 (s, 1H), 7.58 – 7.39 (m, 4H), 3.54 (hept, *J* = 6.8 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 154.6, 135.7, 131.9, 128.3, 124.1, 40.8, 21.6; HRMS (ESI) calcd. for $C_{10}H_{13}{}^{79}BrNS$ (MH^+): 259.9926, found 259.9932; IR (film): νmax/cm^{-1} 2961, 1588, 1485, 1239, 1068, 1008, 816.

(*E*)-*S*-isopropyl-*N*-(4-(trifluoromethyl)benzylidene)thiohydroxylamine (6e-*i*Pr)



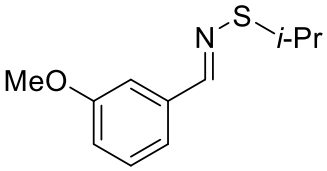
Synthesised from (4-(trifluoromethyl)phenyl)methanamine (0.860 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (150 mg, 12% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.47 (s, 1H), 7.79 – 7.54 (m, 4H), 3.61 – 3.47 (m, 1H), 1.42 (d, *J* = 7.0 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 154.1, 139.6, 131.2 (q, *J* = 40.4 Hz), 127.0, 125.6 (q, *J* = 3.8 Hz), 125.5 (q, *J* = 278.7Hz), 40.9, 21.6; HRMS (ESI) calcd. for $C_{11}H_{13}F_3NS$ (MH^+): 248.0721, found 248.0725; IR (film): νmax/cm^{-1} 2965, 1616, 1320, 1163, 1122, 1064, 832.

(*E*)-*S*-isopropyl-*N*-(4-methoxybenzylidene)thiohydroxylamine (6f-*i*Pr)



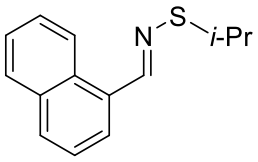
Synthesised from (4-methoxyphenyl)methanamine (0.860 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (120 mg, 14% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.40 (s, 1H), 7.56 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 3.54 (hept, *J* = 6.8 Hz, 1H), 1.41 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.0, 155.8, 130.1, 128.5, 114.1, 55.4, 40.5, 21.7. HRMS (ESI) calcd. for $C_{11}H_{16}ONS$ (MH^+): 210.0953, found 210.0950; IR (film): νmax/cm^{-1} 2960, 1606, 1509, 1246, 1165, 1031, 829.

(*E*)-S-isopropyl-*N*-(3-methoxybenzylidene)thiohydroxylamine (6g-*i*Pr)



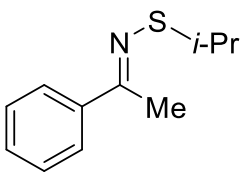
Synthesised from (3-methoxyphenyl)methanamine (0.860 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (163 mg, 15% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.43 (s, 1H), 7.29 (t, *J* = 7.9 Hz, 1H), 7.21 (dd, *J* = 2.7, 1.3 Hz, 1H), 7.15 (dt, *J* = 7.9, 1.3 Hz, 1H), 6.91 (ddd, *J* = 7.9, 2.7, 1.3 Hz, 1H), 3.84 (s, 3H), 3.56 (hept, *J* = 6.8 Hz, 1H), 1.42 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 159.8, 155.8, 138.1, 129.5, 120.0, 116.1, 110.9, 55.3, 40.5, 21.6; HRMS (ESI) calcd. for $C_{11}H_{16}ONS$ (MH^+): 210.0953, found 210.0937; IR (film): νmax/cm^{-1} 2960, 1598, 1463, 1262, 1151, 1044, 779, 686.

(*E*)-*S*-isopropyl-*N*-(naphthalen-1-ylmethylene)thiohydroxylamine (6h-*i*Pr)



Synthesised from naphthalen-1-ylmethanamine (943 mg, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (29.0 mg, 3% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 9.14 (s, 1H), 8.82 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 8.2, 4.3 Hz, 2H), 7.79 (d, *J* = 6.5 Hz, 1H), 7.59 – 7.46 (m, 3H), 3.65 (hept, *J* = 6.5 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 156.1, 134.0, 132.2, 130.6, 130.5, 128.7, 127.8, 127.2, 126.1, 125.4, 124.4, 40.8, 21.9; HRMS (ESI) calcd. for $C_{14}H_{16}NS$ (MH^+): 230.1003, found 230.1002; IR (film): νmax/cm^{-1} 2958, 1567, 1432, 1128, 854.

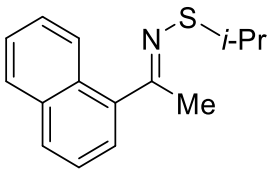
(*E*)-*S*-isopropyl-*N*-(1-phenylethylidene)thiohydroxylamine (6i-*i*Pr)



Synthesised from 1-phenylethan-1-amine (0.770 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (240 mg, 31% yield); ^{1}H

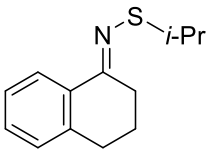
NMR (400 MHz, *Chloroform-d*) δ 7.76 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.45 – 7.32 (m, 3H), 3.54 (hept, *J* = 6.8 Hz, 1H), 2.37 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 6H).^{13}C NMR (101 MHz, *Chloroform-d*) δ 159.8, 139.8, 128.9, 128.3, 125.9, 41.0, 21.8, 19.5; HRMS (ESI) calcd. for $C_{11}H_{16}NS$ (MH^+): 194.1003, found 194.0998; IR (film): νmax/cm^{-1} 2960, 1444, 1363, 1238, 757, 689.

_S_-isopropyl-_N_-(1-(naphthalen-1-yl)ethylidene)thiohydroxylamine (6j-*i*Pr)



Synthesised from 1-(naphthalen-1-yl)ethan-1-amine (1.02 g, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (320 mg, 65% yield, *E/Z* 5:1); ^{1}H NMR (400 MHz, *Chloroform-d*) *E* isomer: δ 8.22 – 8.17 (m, 1H), 7.89 – 7.82 (m, 2H), 7.52 – 7.44 (m, 4H), 3.58 (heptd, *J* = 6.8, 0.9 Hz, 1H), 2.50 (d, *J* = 0.9 Hz, 3H), 1.46 (dd, *J* = 6.8, 0.9 Hz, 6H); *Z* isomer: δ 7.93 – 7.89 (m, 1H), 7.70 – 7.64 (m, 1H), 7.56 – 7.52 (m, 4H), 7.28 (dt, *J* = 6.8, 1.0 Hz, 1H), 3.43 (heptd, *J* = 6.8, 1.0 Hz, 1H), 2.48 (d, *J* = 0.8 Hz, 3H), 1.32 – 1.30 (m, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) *E* isomer: δ 163.3, 140.0, 134.1, 130.5, 128.9, 128.5, 126.4, 126.0, 125.9, 125.2, 125.2, 41.0, 31.7, 24.5, 22.0; *Z* isomer: δ 164.7, 139.1, 133.8, 130.5, 128.8, 128.7, 127.6, 126.7, 125.7, 124.9, 122.9, 40.6, 29.6, 22.8, 21.6; HRMS (ESI) calcd. for $C_{15}H_{18}NS$ (MH^+): 244.1154, found 244.1152; IR (film): νmax/cm^{-1} 2960, 1508, 1237, 794, 769.

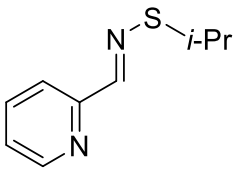
(*E*)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)-*S*-isopropylthiohydroxylamine (6k-*i*Pr)



Synthesised from 1,2,3,4,4a,8a-hexahydronaphthalen-1-amine (0.900 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); red oil (135 mg, 15% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.13 – 8.00 (m, 1H), 7.24 – 7.19 (m, 2H), 7.14 – 7.09 (m, 1H), 3.49 (heptd, *J* = 6.8, 1.8 Hz, 1H), 2.78 (t, *J* = 6.8 Hz, 2H), 2.59 (td, *J* =

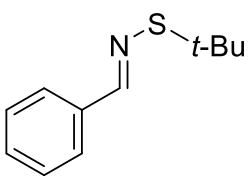
6.8, 1.8 Hz, 2H), 2.01 – 1.90 (m, 2H), 1.44 (dd, *J* = 6.8, 1.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 159.6, 138.7, 134.2, 128.8, 128.3, 126.3, 125.0, 40.8, 31.9, 29.7, 22.2, 21.7; HRMS (ESI) calcd. for $C_{13}H_{18}NS$ (MH^+): 220.1154, found 220.1152; IR (film): νmax/cm^{-1} 2928, 1451, 1237, 759.

(*E*)-*S*-isopropyl-*N*-(pyridin-2-ylmethylene)thiohydroxylamine (6l-*i*Pr)



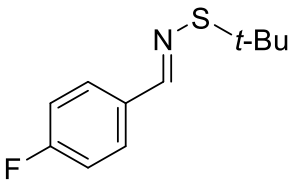
Synthesised from pyridin-2-ylmethanamine (0.620 mL, 6.00 mmol) using general procedure **2.1**. Purified by flash column chromatography on silica gel (eluent: DCM : MeOH = 50:1); brown oil (320 mg, 44% yield); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.59 – 8.58 (m, 1H), 8.54 (s, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 7.8, Hz, 1H), 7.26 – 7.21 (m, 1H), 3.59 (hept, *J* = 6.8 Hz, 1H), 1.43 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 156.3, 149.3, 136.3, 123.8, 120.2, 40.6, 21.4; HRMS (ESI) calcd. for $C_9H_{13}N_2S$ (MH^+): 181.0799, found 181.0792; IR (film): νmax/cm^{-1} 2961, 1464, 1432, 768.

(*E*)-*N*-benzylidene-*S*-(*tert*-butyl)thiohydroxylamine (6a-*t*Bu) [14]



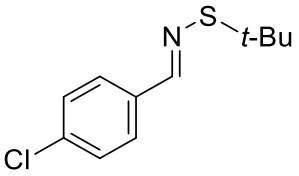
Synthesised from benzylamine (1.30 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (350 mg, 36% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.47 (s, 1H), 7.68 – 7.58 (m, 2H), 7.44 – 7.32 (m, 3H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 155.3, 137.0, 129.6, 128.5, 126.8, 47.0, 29.2.

(*E*)-*S*-(*tert*-butyl)-*N*-(4-fluorobenzylidene)thiohydroxylamine (6b-*t*Bu)



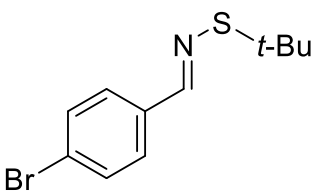
Synthesised from (4-fluorophenyl)methanamine (1.10 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: DCM : MeOH = 50:1); yellow oil (528 mg, 50% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.43 (s, 1H), 7.62 (dd, *J* = 8.7, 5.6 Hz, 2H), 7.06 (t, *J* = 8.7 Hz, 2H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 163.7 (d, *J* = 242.4 Hz), 154.0, 133.5 (d, *J* = 10.1 Hz), 128.7 (d, *J* = 10.1 Hz), 115.7 (d, *J* = 20.2 Hz), 47.1, 29.3; HRMS (ESI) calcd. for $C_{11}H_{15}FNS$ (MH^+): 212.0909, found 212.0904; IR (film): νmax/cm^{-1} 2961, 1599, 1507, 1228, 1151, 832.

(*E*)-*S*-(*tert*-butyl)-*N*-(4-chlorobenzylidene)thiohydroxylamine (6c-*t*Bu)



Synthesised from (4-chlorophenyl)methanamine (1.20 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: Hexane : DCM = 5:1); yellow oil (530 mg, 47% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.40 (s, 1H), 7.54 (d, *J* = 8.6 Hz, 2H), 7.32 (d, *J* = 8.6 Hz, 2H), 1.44 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 153.9, 135.5, 128.9, 128.0, 47.3, 29.3; HRMS (ESI) calcd. for $C_{11}H_{15}{}^{35}ClNS$ (MH^+): 228.0614, found 228.0608; IR (film): νmax/cm^{-1} 2960, 1488, 1360, 1165, 1086, 818.

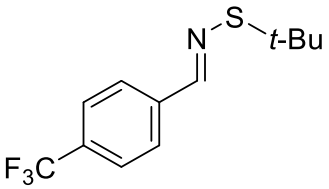
(*E*)-*N*-(4-bromobenzylidene)-*S*-(*tert*-butyl)thiohydroxylamine (6d-*t*Bu)



Synthesised from (4-bromophenyl)methanamine (1.80 g, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: Hexane : DCM = 5:1); yellow oil (408 mg, 30% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.40 (s, 1H), 7.52 – 7.47 (m, 4H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 153.9, 135.9, 131.8,

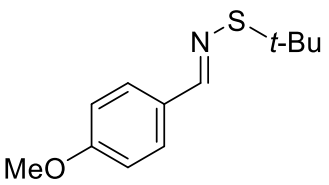
128.2, 123.9, 47.3, 29.3; HRMS (ESI) calcd. for $C_{11}H_{15}{}^{79}BrNS$ (MH^+): 272.0109 and 274.0088, found 272.0103 and 274.0082; IR (film): νmax/cm^{-1} 2959, 1485, 1360, 1165, 1069, 1008, 814.

(*E*)-*S*-(*tert*-butyl)-*N*-(4-(trifluoromethyl)benzylidene)thiohydroxylamine (6e-*t*Bu)



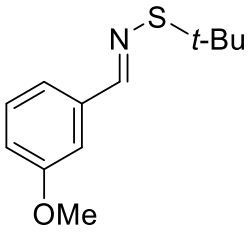
Synthesised from (4-(trifluoromethyl)phenyl)methanamine (1.40 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (385 mg, 30% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.49 (s, 1H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 8.1 Hz, 2H), 1.47 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 153.4, 139.8, 131.1 (q, *J* = 32.5 Hz), 126.9, 125.7 (q, *J* = 273.7 Hz), 125.62 (q, *J* = 3.8 Hz), 47.5, 29.3; HRMS (ESI) calcd. for $C_{12}H_{15}F_3NS$ (MH^+): 262.0877, found 262.0876; IR (film): νmax/cm^{-1} 2963, 1616, 1320, 1163, 1122, 1064, 831.

(*E*)-*S*-(*tert*-butyl)-*N*-(4-methoxybenzylidene)thiohydroxylamine (6f-*t*Bu)



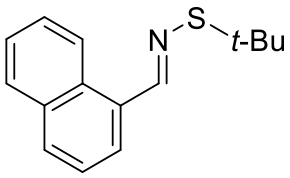
Synthesised from (4-methoxyphenyl)methanamine (1.30 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (220 mg, 20% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.41 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 160.9, 155.0, 130.3, 128.3, 113.9, 55.3, 46.8, 29.2; HRMS (ESI) calcd. for $C_{12}H_{18}NOS$ (MH^+): 224.1103, found 224.1104; IR (film): νmax/cm^{-1} 2959, 1606, 1509, 1246, 1163, 828.

(*E*)-*S*-(*tert*-butyl)-*N*-(3-methoxybenzylidene)thiohydroxylamine (6g-*t*Bu)



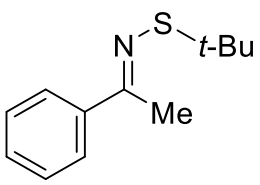
Synthesised from (3-methoxyphenyl)methanamine (1.30 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (669 mg, 60% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.42 (s, 1H), 7.32 – 7.12 (m, 3H), 6.95 – 6.84 (m, 1H), 3.82 (s, 3H), 1.45 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 159.9, 155.2, 138.4, 129.6, 120.0, 115.8, 111.2, 55.4, 47.1, 29.3; HRMS (ESI) calcd. for $C_{12}H_{18}NOS$ (MH^+): 224.1103, found 224.1096; IR (film): νmax/cm^{-1} 2959, 1601, 1457, 1262, 1043, 779, 686.

(*E*)-*S*-(*tert*-butyl)-*N*-(naphthalen-1-ylmethylene)thiohydroxylamine (6h-*t*Bu)



Synthesised from naphthalen-1-ylmethanamine (1.40 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (480 mg, 40% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 9.14 (s, 1H), 9.00 – 8.85 (m, 1H), 7.93 – 7.75 (m, 3H), 7.63 – 7.43 (m, 3H), 1.55 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 155.6, 134.0, 132.3, 130.6, 130.4, 128.7, 127.9, 127.2, 126.1, 125.4, 124.6, 47.3, 29.5; HRMS (ESI) calcd. for $C_{15}H_{18}NS$ (MH^+): 244.1154, found 244.1157; IR (film): νmax/cm^{-1} 2959, 1454, 1360, 1164, 769.

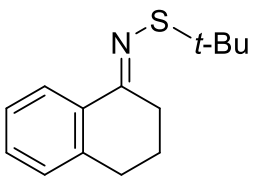
(*E*)-*S*-(*tert*-butyl)-*N*-(1-phenylethylidene)thiohydroxylamine (6i-*t*Bu)



Synthesised from 1-phenylethan-1-amine (1.30 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (1.00 g, 96% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.86 – 7.68 (m, 2H), 7.47 – 7.30 (m,

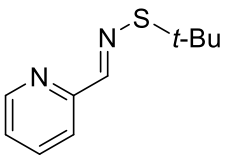
3H), 2.34 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 158.8, 139.9, 128.8, 128.3, 125.8, 46.8, 29.4, 19.5; HRMS (ESI) calcd. for $C_{12}H_{18}NS$ (MH^+): 208.1160, found 208.1157; IR (film): νmax/cm^{-1} 2959, 1337, 800, 774.

(*E*)-*S*-(*tert*-butyl)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)thiohydroxylamine (6k-*t*Bu)



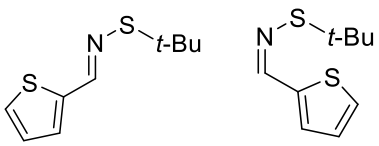
Synthesised from 1,2,3,4-tetrahydronaphthalen-1-amine (1.40 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (620 mg, 53% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.16 – 7.99 (m, 1H), 7.25 – 7.19 (m, 2H), 7.12 – 7.09 (m, 1H), 2.82 – 2.73 (m, 2H), 2.58 (t, *J* = 6.6 Hz, 2H), 2.00 – 1.88 (m, 2H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 158.8, 138.8, 134.5, 128.8, 128.4, 126.4, 125.1, 46.7, 32.1, 29.8, 29.4, 22.3, 14.2; HRMS (ESI) calcd. for $C_{14}H_{20}NS$ (MH^+): 234.1311, found 234.1316; IR (film): νmax/cm^{-1} 2957, 1453, 1359, 1163, 759, 730.

(*E*)-*S*-(*tert*-butyl)-*N*-(pyridin-2-ylmethylene)thiohydroxylamine (6l-*t*Bu)



Synthesised from pyridin-2-ylmethanamine (1.10 g, 10.0 mmol) using general procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: DCM : MeOH = 50:1); yellow oil (420 mg, 43% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.58 – 8.53 (m, 2H), 7.94 – 7.91 (m, 1H), 7.71 – 7.67 (m, 1H), 7.25 – 7.20 (m, 1H), 1.46 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 156.0, 154.8, 149.2, 136.3, 123.8, 120.0, 47.4, 29.2; HRMS (ESI) calcd. for $C_{10}H_{14}N_2NaS$ (MNa^+): 217.0770, found 217.0771; IR (film): νmax/cm^{-1} 2960, 1567, 1461, 1432, 1361, 1164, 767.

***S*-(*tert*-butyl)-*N*-(thiophen-2-ylmethylene)thiohydroxylamine (6m-*t*Bu)**

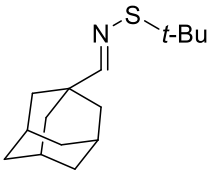


Synthesised from thiophen-2-ylmethanamine (1.00 mL, 10.0 mmol) using general procedure **2.2**. Purified by flash column

chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow oil (650 mg, 65% yield over two steps, *E/Z* 10:3); *E* isomer: ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.54 (s, 1H), 7.33 (dd, *J* = 5.0, 1.2 Hz, 1H), 7.12 (ddd, *J* = 3.6, 1.2, 0.6 Hz, 1H), 7.03 (ddd, *J* = 5.0, 3.6, 0.6 Hz, 1H), 1.44 (s, 9H); *Z* isomer: ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.49 (s, 1H), 7.62 (ddd, *J* = 5.0, 1.2, 0.5 Hz, 1H), 7.47 (ddd, *J* = 3.8, 1.2, 0.5 Hz, 1H), 7.16 (dd, *J* = 5.0, 3.8 Hz, 1H), 1.48 (s, 9H); *E* isomer: ^{13}C NMR (101 MHz, *Chloroform-d*) δ 149.3, 139.2, 128.1, 127.6, 127.3, 47.3, 29.2; *Z* isomer: ^{13}C NMR (101 MHz, *Chloroform-d*) δ 145.8, 143.9, 131.6, 130.6, 48.3, 29.0; HRMS (ESI) calcd. for $C_9H_{14}NS_2$ (MH^+): 200.0562, found 200.0570; IR (film): νmax/cm^{-1} 2959, 1360, 1163, 701.

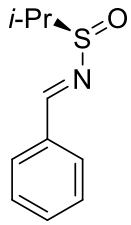
_N_-((_E_)-((3r,5r,7r)-adamantan-1-yl)methylene)-_S_-(_tert_-butyl)thiohydroxylamine (6n-_t_Bu)

Synthesised from ((3r,5r,7r)-adamantan-1-yl)methanamine (1.65 g, 10.0 mmol) using general



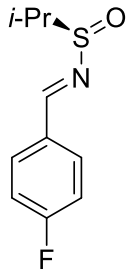
procedure **2.2**. Purified by flash column chromatography on silica gel (eluent: hexane : DCM = 5:1); yellow waxy solid (1.00 g, 81% yield over two steps); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.62 (s, 1H), 2.01 – 1.99 (m, 3H), 1.73 – 1.64 (m, 12H), 1.37 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 167.9, 46.3, 40.8, 39.5, 36.9, 31.7, 30.7, 29.1, 28.2; HRMS (ESI) calcd. for $C_{15}H_{26}NS$ (MH^+): 252.1780, found 252.1782; IR (film): ν_{max}/cm^{-1} 2902, 2848, 1452, 1360, 1165, 739.

(*R*,*E*)-*N*-benzylidenepropane-2-sulfinamide ((*R*)-12a) [15]



Synthesised from (*E*)-*N*-benzylidene-*S*-isopropylthiohydroxylamine (36.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (20.0 mg, 51% yield); $[\alpha]_D^{20} = -72.23$ (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20} = -112$ (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.59 (s, 1H), 7.88 – 7.82 (m, 2H), 7.56 – 7.44 (m, 3H), 2.98 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.5, 133.9, 132.5, 129.4, 128.9, 53.9, 14.7, 13.5; HRMS (ESI) calcd. for $C_{10}H_{14}NOS$ (MH^+): 196.0796, found 196.0791; IR (film): νmax/cm^{-1} 2933, 1581, 1185, 802; HPLC data: 98% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 9.01 min, tr(major) = 10.24 min. See Section 4 for images depicting the HPLC traces.

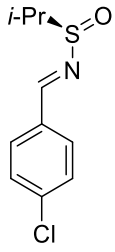
(*R*,*E*)-*N*-(4-fluorobenzylidene)propane-2-sulfinamide ((*R*)-12b)



Synthesised from (*E*)-*N*-(4-fluorobenzylidene)-*S*-isopropylthiohydroxylamine (40.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (30.0 mg, 70% yield); $[\alpha]_D^{20} = -29.92$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.54 (s, 1H), 7.96 – 7.79 (m, 2H), 7.25 – 7.09 (m, 2H), 2.96 (hept, *J* = 6.9 Hz, 1H), 1.25 (dd, *J* = 35.1, 6.9 Hz, 6H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 165.4 (d, *J* = 254.3 Hz), 161.2, 131.7 (d, *J* = 9.1 Hz), 130.5 (d, *J* = 3.1 Hz), 116.3 (d, *J* = 22.1 Hz), 54.0, 14.8, 13.6; ^{19}F NMR (376 MHz, *Chloroform-d*) δ −105.69; HRMS (ESI) calcd. for $C_{10}H_{12}FNONaS$ (MNa^+): 236.0521, found 236.0514; IR (film): νmax/cm^{-1} 2930, 1582, 1508, 1231, 1086; HPLC data: 99% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min,

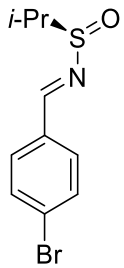
hexane/propanol: 95:5): tr(minor)= 7.50 min, tr(major)= 10.54 min. See Section 4 for images depicting the HPLC traces.

(*R*,*E*)-*N*-(4-chlorobenzylidene)propane-2-sulfinamide ((*R*)-12c)



Synthesised from (*E*)-*S*-isopropyl-*N*-(4-chlorobenzylidene)thiohydroxylamine (43.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (37.0 mg, 80% yield); $[\alpha]_D^{20} = -56.37$ (c = 1.5, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.54 (s, 1H), 7.79 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 2.97 (hept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.4, 138.8, 132.5, 130.6, 129.4, 54.0, 14.9, 13.7; HRMS (ESI) calcd. for $C_{10}H_{13}{}^{35}ClNOS$ (MH^+): 230.0406, found 230.0401; IR (film): νmax/cm^{-1} 2924, 1591, 1085, 825; HPLC data: 98% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 7.81 min, tr(major) = 11.51 min. See Section 4 for images depicting the HPLC traces.

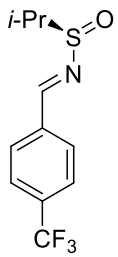
(*R*,*E*)-*N*-(4-bromobenzylidene)propane-2-sulfinamide ((*R*)-12d)



Synthesised from (*E*)-*N*-(4-bromobenzylidene)-*S*-isopropylthiohydroxylamine (26.0 mg, 0.100 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (17.0 mg, 62% yield); $[\alpha]_D^{20} = -13.57$ (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.53 (s, 1H), 7.72 (d, *J* = 8.6 Hz, 2H), 7.62 (d, *J* = 8.6 Hz, 2H), 2.98 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.5, 132.9, 132.4, 130.8, 127.4, 54.0, 14.9, 13.7; HRMS (ESI) calcd. for $C_{10}H_{12}{}^{79}BrNONaS$ (MNa^+): 297.9700 and 295.9721, found 297.9694 and 295.9718; IR (film): νmax/cm^{-1} 2924, 1608, 1088, 821; HPLC data: 99% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0

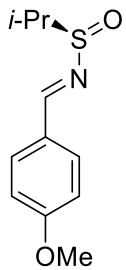
mL/min, hexane/propanol: 95:5): tr(minor)= 8.44 min, tr(major)= 12.79 min. See Section 4 for images depicting the HPLC traces.

(*R*,*E*)-*N*-(4-(trifluoromethyl)benzylidene)propane-2-sulfinamide ((*R*)-12e)



Synthesised from (*E*)-*S*-isopropyl-*N*-(4-trifluoromethylbenzylidene)thiohydroxylamine (50.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (31 mg, 60% yield); $[\alpha]_D^{20}$ = −100.14 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.63 (s, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 3.01 (hept, *J* = 6.9 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 1.23 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.4, 136.8, 133.8 (q, *J* = 32.6 Hz), 129.6, 126.1 (q, *J* = 3.8 Hz), 123.2 (q, *J* = 274.2 Hz), 54.1, 14.9, 13.7; ^{19}F NMR (376 MHz, *Chloroform-d*) δ –62.94; HRMS (ESI) calcd. for $C_{11}H_{12}F_3NONaS$ (MNa^+): 286.0489, found 286.0486; IR (film): νmax/cm^{-1} 2933, 1322, 1121, 1065; HPLC data: 98% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 7.42 min, tr(major) = 15.36 min. See Section 4 for images depicting the HPLC traces.

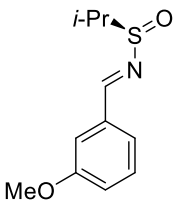
(*R*,*E*)-*N*-(4-methoxybenzylidene)propane-2-sulfinamide ((*R*)-12f) [15]



Synthesised from (*E*)-*S*-isopropyl-*N*-(4-methoxybenzylidene)thiohydroxylamine (23.0 mg, 0.100 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (18.0 mg, 74% yield); $[\alpha]_D^{20}$ = −34.84 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 71 for the opposite *S* isomer (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.51 (s, 1H), 7.80 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H), 2.94 (hept, *J* = 6.9 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 163.1, 161.6, 131.3, 127.2, 114.4, 55.5, 53.9, 14.8, 13.5; HRMS (ESI) calcd. for $C_{11}H_{16}NO_2S$ (MH^+): 226.0902, found

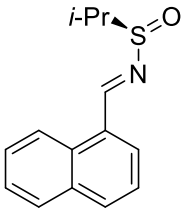
226.0897; IR (film): νmax/cm^{-1} 2965, 1594, 1568, 1511, 1253, 1028; HPLC data: 98% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor)= 10.05 min, tr(major) = 12.57 min. See Section 4 for images depicting the HPLC traces.

(*R*,*E*)-*N*-(3-methoxybenzylidene)propane-2-sulfinamide ((*R*)-12g)[16]



Synthesised from (*E*)-*S*-isopropyl-*N*-(3-methoxybenzylidene)thiohydroxylamine (42.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (25.0 mg, 56% yield); $[\alpha]_D^{20}$ = −47.78 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = −74.8 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.55 (s, 1H), 7.42 – 7.34 (m, 3H), 7.07 (dt, *J* = 6.9, 2.7 Hz, 1H), 3.86 (s, 3H), 2.98 (hept, *J* = 6.9 Hz, 1H), 1.31 (d, *J* = 6.9 Hz, 3H), 1.22 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.4, 160.0, 135.2, 130.0, 122.6, 119.0, 112.9, 55.4, 53.8, 14.8, 13.5; HRMS (ESI) calcd. for $C_{11}H_{15}NO_2NaS$ (MNa^+): 248.0721, found 248.0717; IR (film): νmax/cm^{-1} 2965, 1607, 1577, 1266, 1085; HPLC data: 94% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 9.14 min, tr(major) = 11.22 min. See Section 4 for images depicting the HPLC traces.

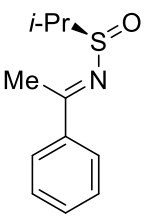
(*R*,*E*)-*N*-(naphthalen-1-ylmethylene)propane-2-sulfinamide ((*R*)-12h)



Synthesised from (*E*)-*S*-isopropyl-*N*-(naphthalen-1-ylmethylene)thiohydroxylamine (23.0 mg, 0.100 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (11.0 mg, 45% yield); $[\alpha]_D^{20}$ = −2.08 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 9.17 (s, 1H), 9.02 (dd, *J* = 8.5, 1.1 Hz, 1H),

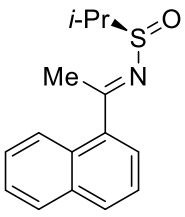
8.13 – 7.99 (m, 2H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.71 – 7.56 (m, 3H), 3.06 (hept, *J* = 6.9 Hz, 1H), 1.37 (d, *J* = 6.9 Hz, 3H), 1.29 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.4, 134.0, 133.4, 132.0, 131.3, 129.4, 128.9, 128.1, 126.6, 125.3, 124.5, 54.1, 14.9, 13.8; HRMS (ESI) calcd. for $C_{14}H_{15}NONaS$ (MNa^+): 268.0772, found 268.0768; IR (film): νmax/cm^{-1} 2927, 1582, 1087, 774; HPLC data: 93% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 24.51 min, tr(major)= 22.23 min. See Section 4 for images depicting the HPLC traces.

(*R*,*E*)-*N*-(1-phenylethylidene)propane-2-sulfinamide ((*R*)-12i)



Synthesised from (*E*)-*S*-isopropyl-*N*-(1-phenylethylidene)thiohydroxylamine (40.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (31.0 mg, 74% yield); $[\alpha]_D^{20}$ = −6.4 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.52 – 7.39 (m, 3H), 3.01 (hept, *J* = 6.9 Hz, 1H), 2.76 (s, 3H), 1.35 (d, *J* = 4.1 Hz, 1H), 1.34 (d, *J* = 4.1 Hz, 1H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 176.2, 138.6, 131.7, 128.5, 127.2, 54.7, 19.8, 14.7, 14.4; HRMS (ESI) calcd. for $C_{11}H_{15}NNaOS$ (MNa^+): 232.0772, found 232.0767; IR (film): νmax/cm^{-1} 2985, 1565, 1460, 1224, 785; HPLC data: 97% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 12.07 min, tr(major) = 10.51 min. See Section 4 for images depicting the HPLC traces.

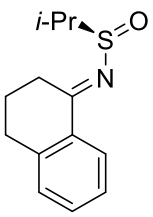
(*R*)-*N*-(1-(naphthalen-1-yl)ethylidene)propane-2-sulfinamide ((*R*)-12j)



Synthesised from *S*-isopropyl-*N*-(1-(naphthalen-1-yl)ethylidene)thiohydroxylamine (122 mg, 0.500 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (45.0 mg, 35% yield, *E/Z* 2:1); $[\alpha]_D^{20}$ = −40.3 (c = 1.0,

$CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.23 – 8.15 (m, 1H, *Z* isomer), 7.91– 7.89 (m, 3H, *E*+*Z* isomer), 7.60 – 7.42 (m, 6H, *E*+*Z* isomer), 3.06 (hept, *J* = 6.9 Hz, 1H, *E* isomer), 2.87 (s, 3H, *E* isomer), 2.79 (p, *J* = 7.4 Hz, 3H, *Z* isomer), 2.64 (s, 3H, *Z* isomer), 1.36 (d, *J* = 1.9 Hz, 3H, *E* isomer), 1.34 (d, *J* = 1.9 Hz, 3H, *E* isomer), 1.23 (d, *J* = 7.0 Hz, 3H, *Z* isomer), 1.16 (d, *J* = 7.0 Hz, 3H, *Z* isomer); ^{13}C NMR (101 MHz, *Chloroform-d*) *E* isomer: δ 181.1, 139.0, 133.8, 130.2, 128.6, 126.9, 126.2, 125.1, 125.0, 124.9, 54.4, 24.9, 14.9, 14.1; *Z* isomer: δ 133.2, 129.4, 129.3, 129.0, 126.4, 123.9, 123.6, 122.4, 53.6, 30.7, 13.9 (two peaks missing from this isomer); HRMS (ESI) calcd. for $C_{15}H_{17}NONaS$ (MNa^+): 282.0929, found 282.0926; IR (film): νmax/cm^{-1} 2926, 1738, 1237, 1045, 730; HPLC data: 99% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 15.86 min, tr(major) = 14.54 min. See Section 4 for images depicting the HPLC traces.

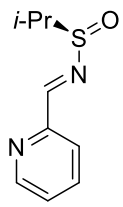
(*R*,*E*)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)propane-2-sulfinamide ((*R*)-12k)



Synthesised from (*E*)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)-*S*-isopropylthiohydroxylamine (22.0 mg, 0.100 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (21.0 mg, 89% yield); $[\alpha]_D^{20}$ = 1.94 (c = 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.18 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.39 (td, *J* = 7.8, 1.4 Hz, 1H), 7.28 – 7.23 (m, 2H), 7.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 3.28 (ddd, *J* = 17.4, 9.0, 4.9 Hz, 1H), 3.07 – 2.96 (m, 2H), 2.90 – 2.85 (m, 2H), 2.09 – 1.92 (m, 2H), 1.36 (d, *J* = 4.8 Hz, 3H), 1.34 (d, *J* = 4.8 Hz, 3H)); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 176.8, 142.3, 132.9, 132.1, 129.0, 127.2, 126.6, 54.7, 32.4, 29.6, 22.7, 14.7, 14.6; HRMS (ESI) calcd. for $C_{13}H_{17}NONaS$ (MNa^+): 258.0929, found 258.0926; IR (film): νmax/cm^{-1} 2927, 1583, 1509, 1231, 1087; HPLC data: 93% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5):

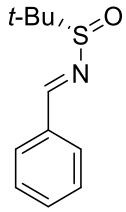
tr(minor)= 14.70 min, tr(major)= 10.75 min. See Section 4 for images depicting the HPLC traces.

(*R*,*E*)-*N*-(pyridin-2-ylmethylene)propane-2-sulfinamide ((*R*)-12l)



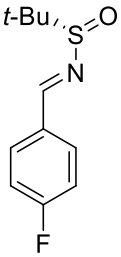
Synthesised from (*E*)-*S*-isopropyl-*N*-(pyridin-2-ylmethylene)thiohydroxylamine (36.0 mg, 0.200 mmol) using general procedure **2.3**. Purified by flash column chromatography on silica gel (eluent: DCM : MeOH = 25:1); brown oil (28.0 mg, 71% yield); $[\alpha]_D^{20}$ = −67.66 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.75 (ddd, *J* = 4.8, 1.2, 0.9 Hz, 1H), 8.69 (s, 1H), 7.98 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.87 – 7.77 (m, 1H), 7.40 (ddd, *J* = 7.7, 4.8, 1.2 Hz, 1H), 3.05 (hept, *J* = 6.9 Hz, 1H), 1.33 (d, *J* = 6.9 Hz, 3H), 1.21 (d, *J* = 6.9 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 163.4, 152.3, 150.4, 136.9, 126.1, 123.7, 53.8, 15.2, 13.4; HRMS (ESI) calcd. for $C_9H_{13}N_2OS$ (MH^+): 197.0749, found 197.0743; IR (film): νmax/cm^{-1} 2988, 1587, 1464, 1124, 785; HPLC data: 90% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 15.75 min, tr(major) = 18.34 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-*N*-benzylidene-2-methylpropane-2-sulfinamide ((*S*)-13a) [17]



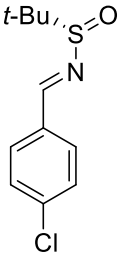
Synthesised from (*E*)-*N*-benzylidene-*S*-(*tert*-butyl)thiohydroxylamine (40.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (37.0 mg, 88% yield); $[\alpha]_D^{20}$ = 75.62 (c = 1, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 122.38 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.59 (s, 1H), 7.85 (dt, *J* = 6.7, 1.6 Hz, 2H), 7.57 – 7.43 (m, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.8, 134.2, 132.5, 129.5, 129.0, 57.9, 22.7; HPLC data: 99% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 14.45 min, tr(major) = 13.60 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-*N*-(4-fluorobenzylidene)-2-methylpropane-2-sulfinamide ((*S*)-13b) [18]



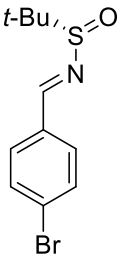
Synthesised from (*E*)-*S*-(*tert*-butyl)-N-(4-fluorobenzylidene)thiohydroxylamine (43.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (32.0 mg, 70% yield); $[\alpha]_D^{20}$ = 117.66 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.54 (s, 1H), 7.86 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.15 (t, *J* = 8.7 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 165.3 (d, *J* = 254.0 Hz), 161.4, 131.6 (d, *J* = 9.1 Hz), 130.6 (d, *J* = 2.9 Hz), 116.3 (d, *J* = 22.2 Hz), 57.9, 22.7; ^{19}F NMR (376 MHz, Chloroform-d) δ –105.8; HPLC data: 94% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 14.49 min, tr(major) = 13.39 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-*N*-(4-chlorobenzylidene)-2-methylpropane-2-sulfinamide ((*S*)-13c) [17]



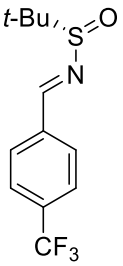
Synthesised from (*E*)-*S*-(*tert*-butyl)-N-(4-chlorobenzylidene)thiohydroxylamine (45.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (39.0 mg, 80% yield); $[\alpha]_D^{20}$ = 67.17 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 77.1 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.54 (s, 1H), 7.78 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 1.25 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.4, 138.6, 132.5, 130.5, 129.3, 129.3, 57.9, 22.6; HPLC data: 98% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 15.02 min, tr(major) = 13.78 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-*N*-(4-bromobenzylidene)-2-methylpropane-2-sulfinamide ((*S*)-13d) [19]



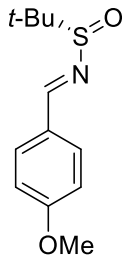
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(4-bromobenzylidene)thiohydroxylamine (55.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (38.0 mg, 66% yield); $[\alpha]_D^{20}$ = 74.58 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.53 (s, 1H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.7, 133.0, 132.4, 130.8, 127.3, 58.0, 22.7; HPLC data: 99% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor)= 13.46 min, tr(major)= 14.60 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-2-methyl-*N*-(4-(trifluoromethyl)benzylidene)propane-2-sulfinamide ((*S*)-13e) [20]



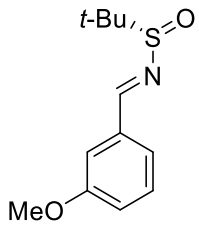
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(4-trifluoromethylbenzylidene)thiohydroxylamine (53.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (30.0 mg, 54% yield); $[\alpha]_D^{20}$ = 77.42 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 74.9 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.63 (s, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.74 (d, *J* = 8.0 Hz, 2H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 161.6, 136.9, 133.7 (q, *J* = 32.8 Hz), 129.6, 126.0 (q, *J* = 3.8 Hz), 125.8 (q, *J* = 273.7 Hz), 58.3, 22.7; ^{19}F NMR (376 MHz, Chloroform-d) δ −62.9; HPLC data: 98% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 11.01 min, tr(major) = 9.44 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-*N*-(4-methoxybenzylidene)-2-methylpropane-2-sulfinamide ((*S*)-13f) [21]



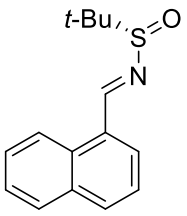
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(4-methoxybenzylidene)thiohydroxylamine (45.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (40.0 mg, 83% yield); $[\alpha]_D^{20}$ = 92.11 (c = 1, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 45.4 (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.50 (s, 1H), 7.80 (d, *J* = 9.0 Hz, 2H), 6.96 (d, *J* = 9.0 Hz, 2H), 3.86 (s, 3H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 163.0, 161.7, 131.2, 127.3, 114.3, 57.5, 55.5, 22.5; HPLC data: 96% *ee*, determined by HPLC (AD-H column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 14.92 min, tr(major) = 15.61 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-*N*-(3-methoxybenzylidene)-2-methylpropane-2-sulfinamide ((*S*)-13g) [17]



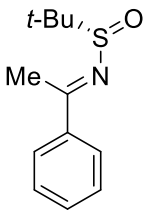
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(3-methoxybenzylidene)thiohydroxylamine (45.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); yellow oil (35.0 mg, 72% yield); $[\alpha]_D^{20}$ = 86.70 (c = 1, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 76.7 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.55 (s, 1H), 7.43 – 7.35 (m, 3H), 7.12 – 7.03 (m, 1H), 3.86 (s, 3H), 1.26 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.6, 160.0, 135.4, 130.0, 122.5, 118.8, 113.1, 57.8, 55.4, 22.6; HPLC data: 96% *ee*, determined by HPLC (AD-H column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 10.40 min, tr(major) = 9.59 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-2-methyl-*N*-(naphthalen-1-ylmethylene)propane-2-sulfinamide ((*S*)-13h) [22]



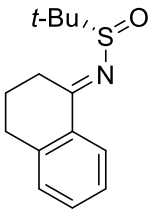
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(naphthalen-1-ylmethylene)thiohydroxylamine (50.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (28.0 mg, 55% yield); $[\alpha]_D^{20}$ = 6.02 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 1.45 (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 9.16 (s, 1H), 9.04 (d, *J* = 8.5 Hz, 1H), 8.05 (d, *J* = 7.4 Hz, 1H), 8.02 (d, *J* = 8.5 Hz, 1H); 7.93 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.62 (m, 1H), 7.61 – 7.56 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 162.6, 134.0, 133.4, 132.1, 131.3, 129.5, 128.9, 128.1, 126.6, 125.3, 124.5, 57.8, 22.7; HPLC data: 95% *ee*, determined by HPLC (IBN5 column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 9.74 min, tr(major) = 7.79 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-2-methyl-*N*-(1-phenylethylidene)propane-2-sulfinamide ((*S*)-13i) [23]



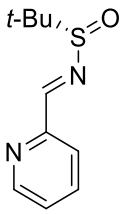
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(1-phenylethylidene)thiohydroxylamine (42.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (27.0 mg, 61% yield); $[\alpha]_D^{20}$ = 5.19 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 13 (c = 1.03, CH_2Cl_2); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.89 (d, *J* = 7.3 Hz, 2H), 7.54 – 7.39 (m, 3H), 2.77 (s, 3H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 176.5, 138.9, 131.8, 128.6, 127.3, 57.5, 22.6, 19.9; HPLC data: 98% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor)= 34.77 min, tr(major)= 41.62 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-*N*-(3,4-dihydronaphthalen-1(2H)-ylidene)-2-methylpropane-2-sulfinamide ((*S*)-13k)[23]



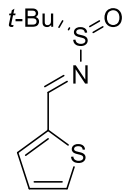
Synthesised from (*E*)-*S*-(*tert*-butyl)-N-(3,4-dihydronaphthalen-1(2H)-ylidene)thiohydroxylamine (47.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); colourless oil (21.0 mg, 42% yield); $[\alpha]_D^{20}$ = 20.08 (c = 1.00, $CHCl_3$), Lit. $[\alpha]^{20}_D$ = 27 (c = 0.84, CH_2Cl_2); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.17 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.38 (td, *J* = 7.9, 1.4 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.21 – 7.13 (m, 1H), 3.32 – 3.22 (m, 1H), 3.09 – 3.02 (m, 1H), 2.89 – 2.86 (m, 2H), 2.07 – 1.91 (m, 2H), 1.32 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 177.1, 142.3, 133.2, 132.1, 129.0, 127.1, 126.6, 57.3, 32.5, 29.6, 22.8, 22.6; HPLC data: 97% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 35.41 min, tr(major) = 38.59 min. See Section 4 for images depicting the HPLC traces.

(*S,E*)-2-methyl-*N*-(pyridin-2-ylmethylene)propane-2-sulfinamide ((*S*)-13l) [24]



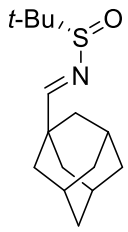
Synthesised from (*E*)-*S*-(*tert*-butyl)-*N*-(pyridin-2-ylmethylene)thiohydroxylamine (39.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: DCM : MeOH = 50:1); black oil (34.0 mg, 81% yield); $[\alpha]_D^{20}$ = 142.59 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.74 (ddd, *J* = 4.8, 1.5, 0.8 Hz, 1H), 8.69 (s, 1H), 8.01 (dt, *J* = 7.9, 1.5 Hz, 1H), 7.81 (tdd, *J* = 7.9, 1.5, 0.8 Hz, 1H), 7.40 (ddd, *J* = 7.9, 4.8, 1.5 Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 163.8, 152.5, 150.3, 136.9, 126.0, 123.2, 58.2, 22.8; HPLC data: 92% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 14.93 min, tr(major) = 11.54 min. See Section 4 for images depicting the HPLC traces.

(*S*,*E*)-2-methyl-*N*-(thiophen-2-ylmethylene)propane-2-sulfinamide (*S*)-13m [24]



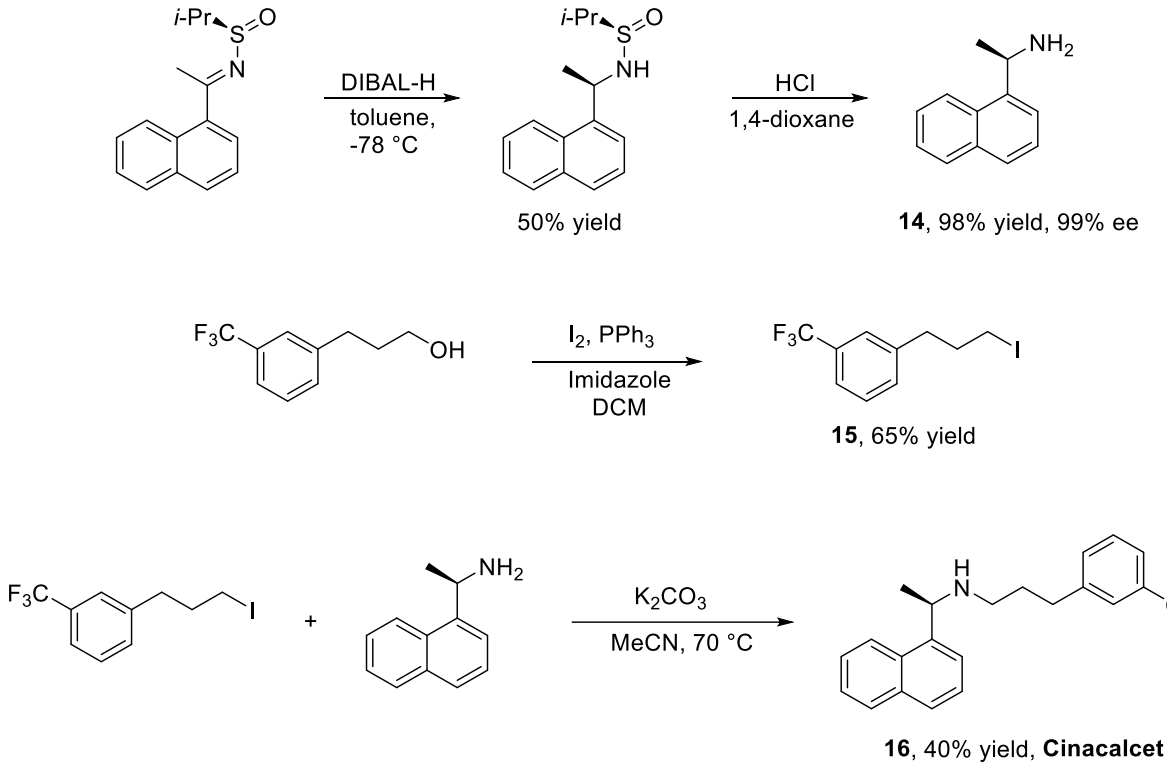
Synthesised from *S*-(*tert*-butyl)-*N*-(thiophen-2-ylmethylene)thiohydroxylamine (40.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); black solid (26.0 mg, 60% yield); $[\alpha]_D^{20}$ = 5.06 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 8.67 (d, *J* = 1.1 Hz, 1H), 7.58 (dt, *J* = 5.0, 1.1 Hz, 1H), 7.53 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.14 (dd, *J* = 5.0, 3.7 Hz, 1H), 1.24 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 155.5, 140.6, 133.9, 132.4, 128.2, 58.0, 22.6; HPLC data: 90% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 17.83 min, tr(major) = 16.53 min. See Section 4 for images depicting the HPLC traces.

(*S*)-*N*-((*E*)-((1s,3R)-adamantan-1-yl)methylene)-2-methylpropane-2-sulfinamide ((*S*)-13n) [25]



Synthesised from *N*-((*E*)-((3r,5r,7r)-adamantan-1-yl)methylene)-*S*-(*tert*-butyl)thiohydroxylamine (50.0 mg, 0.200 mmol) using general procedure **2.4**. Purified by flash column chromatography on silica gel (eluent: hexane : EtOAc = 10:1); white solid (5.00 mg, 10% yield); $[\alpha]_D^{20}$ =112.74 (c = 0.25 $CHCl_3$), Lit. $[\alpha]^{20}_D$ = −163.2 (c = 0.5, $CHCl_3$) for *R* isomer; ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.78 (s, 1H), 2.06 (s, 3H), 1.79 – 1.68 (m, 12H), 1.18 (s, 9H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 175.2, 56.5, 40.2, 39.2, 36.7, 27.9, 22.4; HPLC data: 80% *ee*, determined by HPLC (IC column, flow rate: 1.0 mL/min, hexane/propanol: 95:5): tr(minor) = 11.22 min, tr(major) = 10.53 min. See Section 4 for images depicting the HPLC traces.

Cinacalcet synthesis [26 – 29]



To a flame dried round bottom flask containing a magnetic stirring bar was added ((*R,E*)-*N*-(1-(naphthalen-1-yl)ethylidene)propane-2-sulfinamide (25.0 mg, 0.100 mmol, 1.0 equiv.) in dry toluene (1 mL). The solution was then cool down to –78 °C, which was followed by the addition of 1.0 M DIBAL-H in toluene (0.200 mL, 0.200 mmol, 2.0 equiv.) dropwise and the remaining mixture was stirred at the same temperature for 1 h. Upon completion, the reaction mixture was quenched by adding sat. aq. NH_4Cl (5 mL) and then extracted with ethyl acetate (3 × 5 mL). The combined organic phases were then washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: hexane : EtOAc 10:4) to provide the (*R*)-*N*-((*R*)-1-(naphthalen-1-yl)ethyl)propane-2-sulfinamide (13.0 mg, 50% yield).

To a flame dried round bottom flask containing a magnetic stirring bar was added (*R*)-*N*-((*R*)-1-(naphthalen-1-yl)ethyl)propane-2-sulfinamide (13.0 mg, 0.050 mmol, 1.0 equiv.) in MeOH (50.0 μL). which was followed by the addition of 4.0 M HCl in 1,4-dioxane (25.0 μL, 0.100

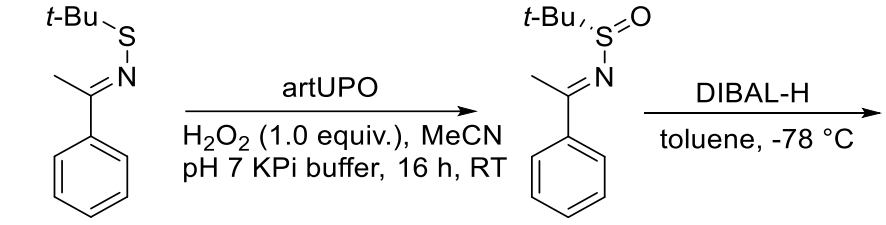
mmol, 2.0 equiv.) dropwise and the remain mixture was stirred at the room temperature for 30 min. Upon completion, the reaction was concentrated in *vacuo* and the remain residue was dissolved in water (10 mL) and the solution was washed with Et_2O (10 mL). The aqueous phase was then adjusted to pH 11 by using sat aq. NaOH solution which was then extracted with ethyl acetate (3 × 5 mL) The combined organic phases were then washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the (*R*)-1-(naphthalen-1-yl)ethan-1-amine **14** (8.4 mg, 98% yield) which was pure enough for next step.

To a flame dried round bottom flask containing a magnetic stirring bar was added 3-(3-(trifluoromethyl)phenyl)propan-1-ol (204 mg, 1.00 mmol, 1.0 equiv.) in DCM (5.00 mL), which was followed by the addition of imidazole (8.20 mg, 0.100 mmol, 0.1 equiv.) and triphenylphosphine (289 mg, 1.10 mmol, 1.1 equiv.). at room temperature. The I_2 (254 mg, 1.00 mmol, 1.0 equiv.) was added portionwise and the mixture was then stirred at room temperature for 1 h. Upon finished, the reaction was quenched by sat $Na_2S_2O_3$ (10 mL) and extracted with DCM (3 × 10 mL). The combined organic phases were then washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: hexane : EtOAc 20: 1) to provide 1-(3-iodopropyl)-3-(trifluoromethyl)benzene **15** (204 mg, 65% yield).

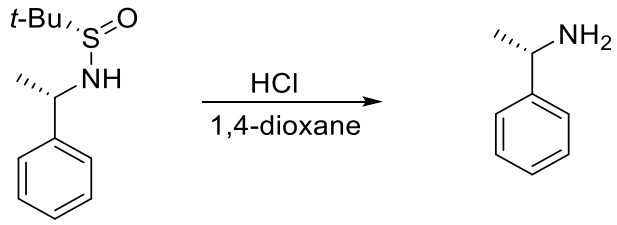
To a small vial containing a magnetic stirring bar was added (*R*)-1-(naphthalen-1-yl)ethan-1-amine (8.40 mg, 0.050 mmol, 1.0 equiv.), K_2CO_3 (8.30 mg, 0.060 mmol, 1.2 equiv.) and 1-(3-iodopropyl)-3-(trifluoromethyl)benzene (20.0 mg, 0.060, 1.2 equiv.) in MeCN (2 mL). The vial was then sealed and the mixture was stirred at 70 °C overnight. Upon completion, the reaction was cool down to room temperature and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: hexane : EtOAc 1:1) to provide Cinacalcet **16** as white solid (7.00 mg, 40% yield, 20% yield over three steps); $[\alpha]_D^{20}$ = 13.85 (c = 0.7, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = 20 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz,

Chloroform-d) δ 8.23 – 8.11 (m, 1H), 7.88 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.76 (dt, *J* = 8.0, 1.6 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 1H), 7.55 – 7.29 (m, 7H), 4.64 (q, *J* = 6.6 Hz, 1H), 2.77 – 2.54 (m, 4H), 1.85 (p, *J* = 7.4 Hz, 2H), 1.51 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 143.1, 134.1, 131.8, 131.4, 130.5, 129.1, 128.7, 127.3, 125.9, 125.8, 125.4, 125.1, 125.1, 123.0, 122.8, 122.7, 53.8, 47.3, 33.5, 31.9, 23.7 some peaks missing like CF_3; the NMR spectra is matched with literature; ^{19}F NMR (376 MHz, Chloroform-d) δ –62.4.

Large scale synthesis and further transformation [26,27, 30]



6j-*t*Bu, 3 mmol, 622 mg **(*S*)-13i**, 60% yield, 98% ee



17, 99% yield, dr > 20:1 **18**, 99% yield, precursor for **Mavacamten**

To a round bottom flask containing a magnetic stirring bar was added artUPO 15 mL (final concentration 0.25 g/mL) and KPi buffer (100 mM, pH = 7, 180 mL). The solution was diluted by the addition of deionised water (57 mL), followed by addition of the (*E*)-*S*-(*tert*-butyl)-*N*-(1-phenylethylidene)thiohydroxylamine (622 mg, 3.0 mmol, 1.0 equiv., final concentration 10 mM) in MeCN (72 mL). Next, 36 mL of an 83 mM H_2O_2 solution (prepared from 400 μL 30% H_2O_2 in 36 mL deionised water) was added over a 10 h period, using a syringe pump. After the H_2O_2 addition was complete, the reaction was then stirred at room temperature for a further 6 h. The reaction mixture was then extracted with ethyl acetate (3 × 50 mL). The combined organic phases were then washed with brine (50 mL), dried over anhydrous $MgSO_4$ and

concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: hexane : EtOAc 10:1) to provide the (*S,E*)-2-methyl-*N*-(1-phenylethylidene)propane-2-sulfinamide **(*S*)-13j** (400 mg, 60% yield).

To a flame dried round bottom flask containing a magnetic stirring bar was added (*S,E*)-2-methyl-*N*-(1-phenylethylidene)propane-2-sulfinamide (270 mg, 1 mmol, 1.0 equiv.) in dry toluene (10 mL). The solution was then cool down to −78 °C, which was followed by the addition of 1.0 M DIBAL-H in toluene (2 mL, 2 mmol, 2.0 equiv.) dropwise and the remain mixture was stirred at the same temperature for 1 h. Upon completion, the reaction mixture was quenched by adding sat NH_4Cl (20 mL) and then extracted with ethyl acetate (3 × 20 mL). The combined organic phases were then washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give the crude product mixture, which was purified by flash column chromatography on silica gel (eluent: hexane : EtOAc 10: 4) to provide the (*S*)-2-methyl-*N*-((*S*)-1-phenylethyl)propane-2-sulfinamide **17** (225 mg, 99% yield).

To a flame dried round bottom flask containing a magnetic stirring bar was added (*S*)-2-methyl-*N*-((*S*)-1-phenylethyl)propane-2-sulfinamide (225 mg, 1.0 mmol, 1.0 equiv.) in MeOH (10 mL). which was followed by the addition of 4.0 M HCl in 1,4-dioxane (0.5 mL, 2 mmol, 2.0 equiv.) dropwise and the remain mixture was stirred at the room temperature for 30 min. Upon completion, the reaction was concentrated in *vacuo* and the remain residue was dissolved in water (20 mL) and the solution was washed with EtO_2 (20 mL). The aqueous phase was then adjusted to pH 11 by using sat aq. NaOH solution which was then extracted with ethyl acetate (3 × 20 mL) The combined organic phases were then washed with brine (10 mL), dried over anhydrous $MgSO_4$ and concentrated *in vacuo* to give (*S*)-1-phenylethan-1-amine **18** (107 mg, 99% yield) without any purification as light yellow oil (107 mg, 59% yield over three steps); $[\alpha]_D^{20}$ = −26.53 (c = 1.0, $CHCl_3$), Lit. $[\alpha]_D^{20}$ = −30.6 (c = 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, *Chloroform-d*) δ 7.35 – 7.28 (m, 4H), 7.25 – 7.19 (m, 1H), 4.09 (q, *J* = 7.0 Hz, 1H), 1.48 (s,

2H), 1.37 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (101 MHz, *Chloroform-d*) δ 147.9, 128.6, 126.9, 125.8, 51.4, 25.8.

HPLC Data: >99 % *ee* determined by HPLC (IBN5, flow rate: 1.0 mL/ min, hexane/ isopropanol = 95:5) tr (minor) = 12.51 min, tr (major) = 10.99 min. See Section 4.0 for images depicting the HPLC trace.

4) Enzyme production

Production of rAaeUPO-PaDa-I-H and artUPO used in this manuscript: The cloning and expression of rAaeUPO-PaDa-I-H and artUPO and their preparation from fermentations of Pichia pastoris was done described previously.[31,32]

5) HPLC Data

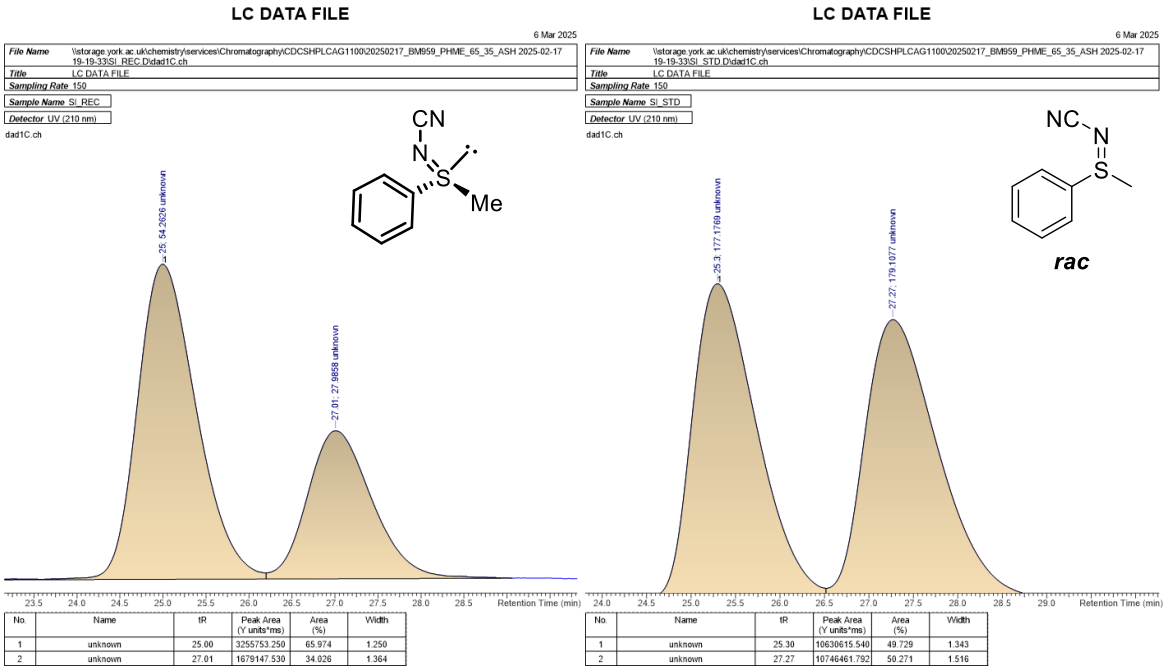


Figure S1. HPLC trace for **(*S*)-4a**

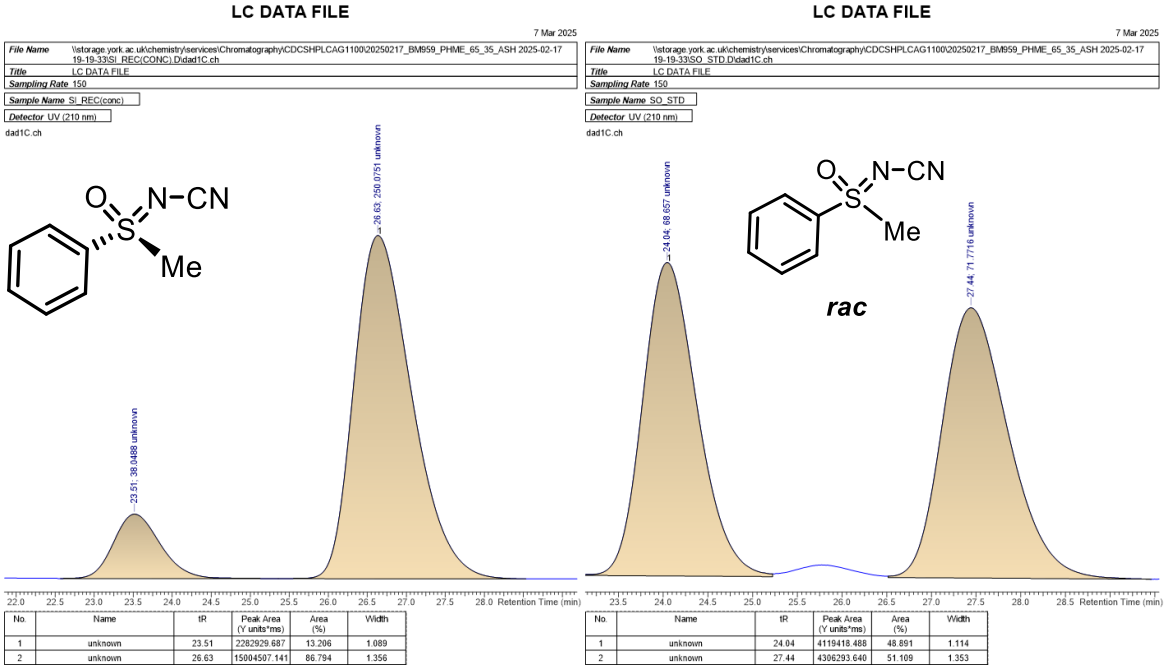


Figure S2. HPLC trace for **(*S*)-5a**

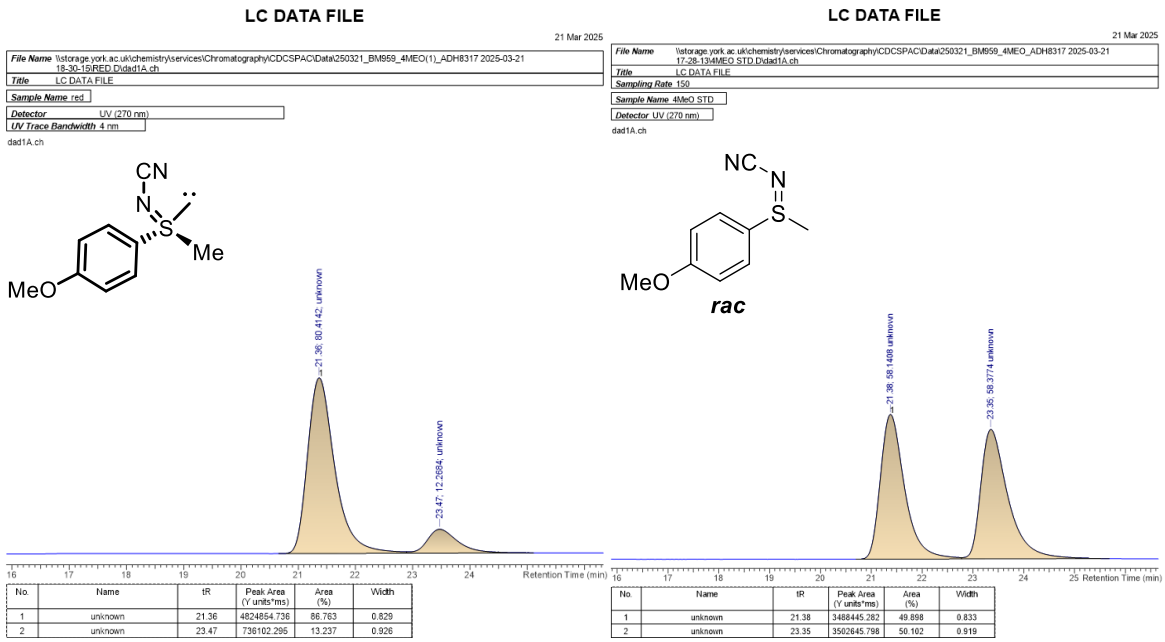


Figure S3. HPLC Data for **(*S*)-4b**

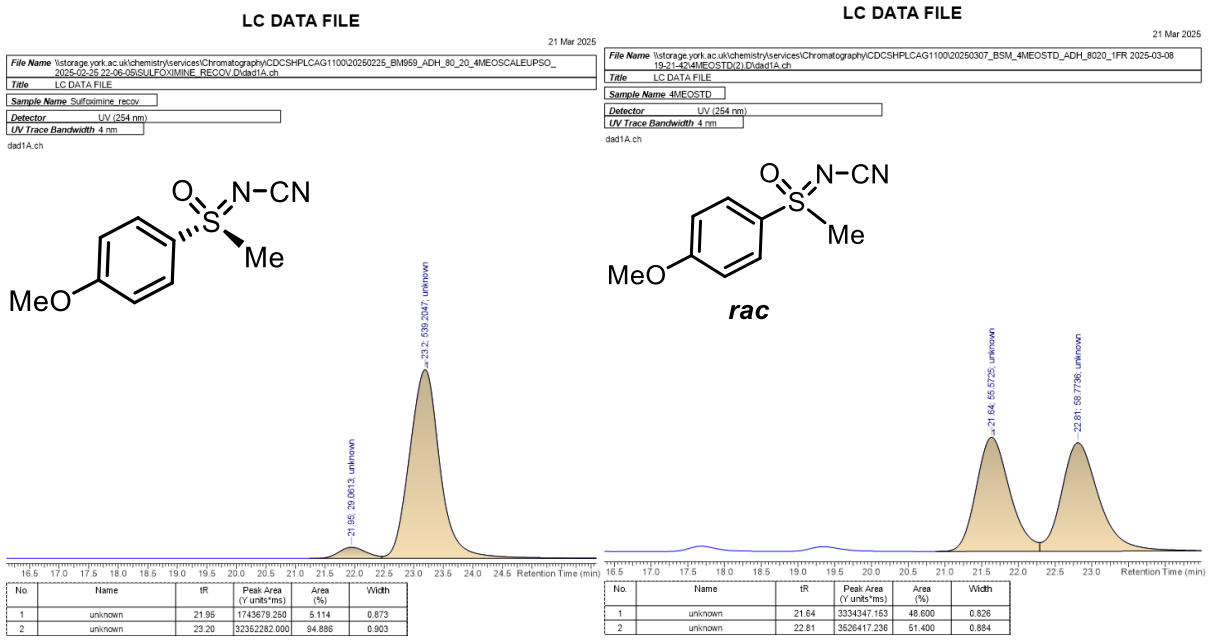


Figure S4. HPLC Data for **(*S*)-5b**

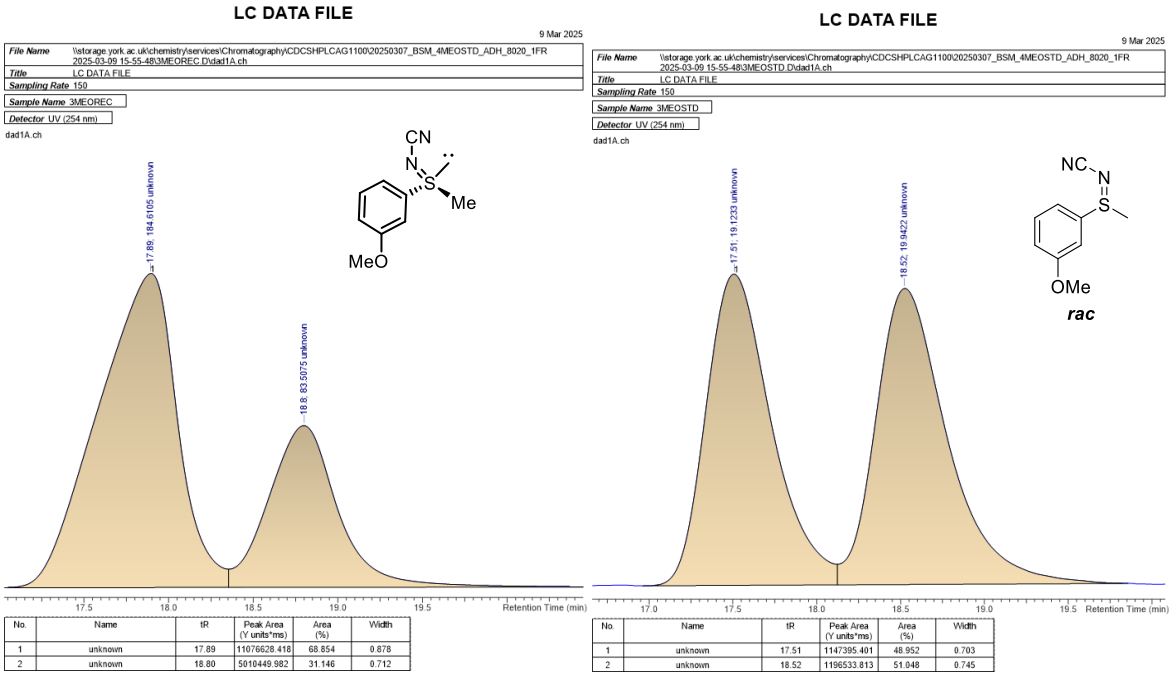


Figure S5. HPLC Data for **(*S*)-4c**

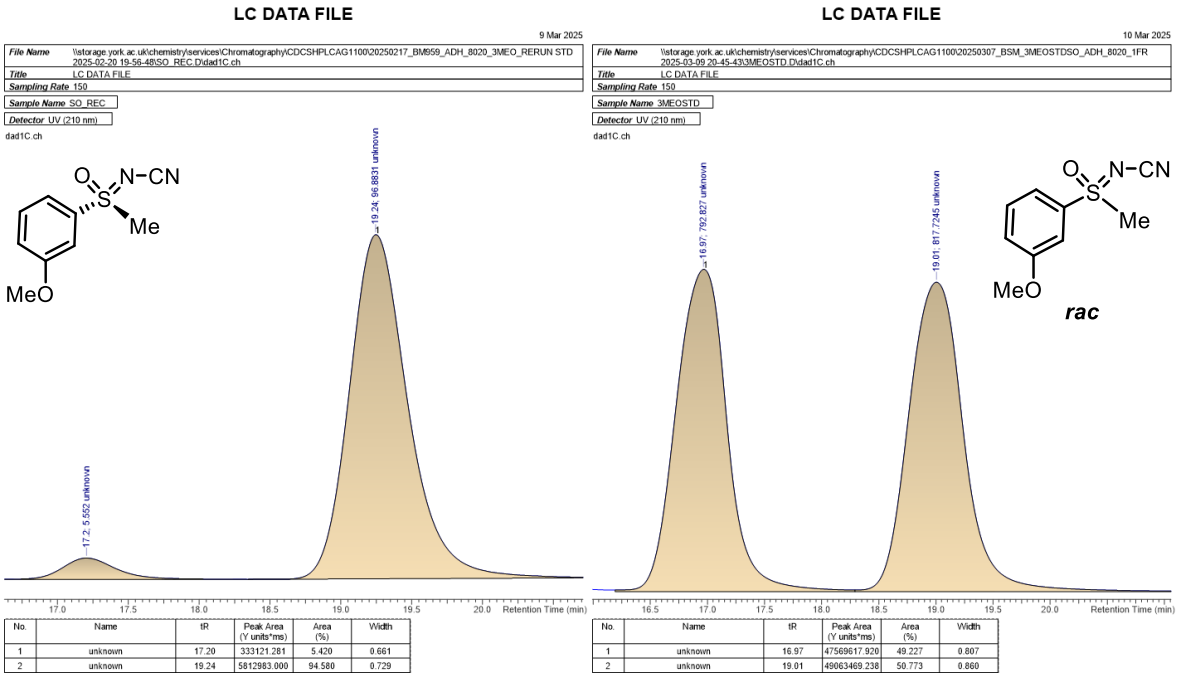


Figure S6. HPLC Data for **(*S*)-5c**

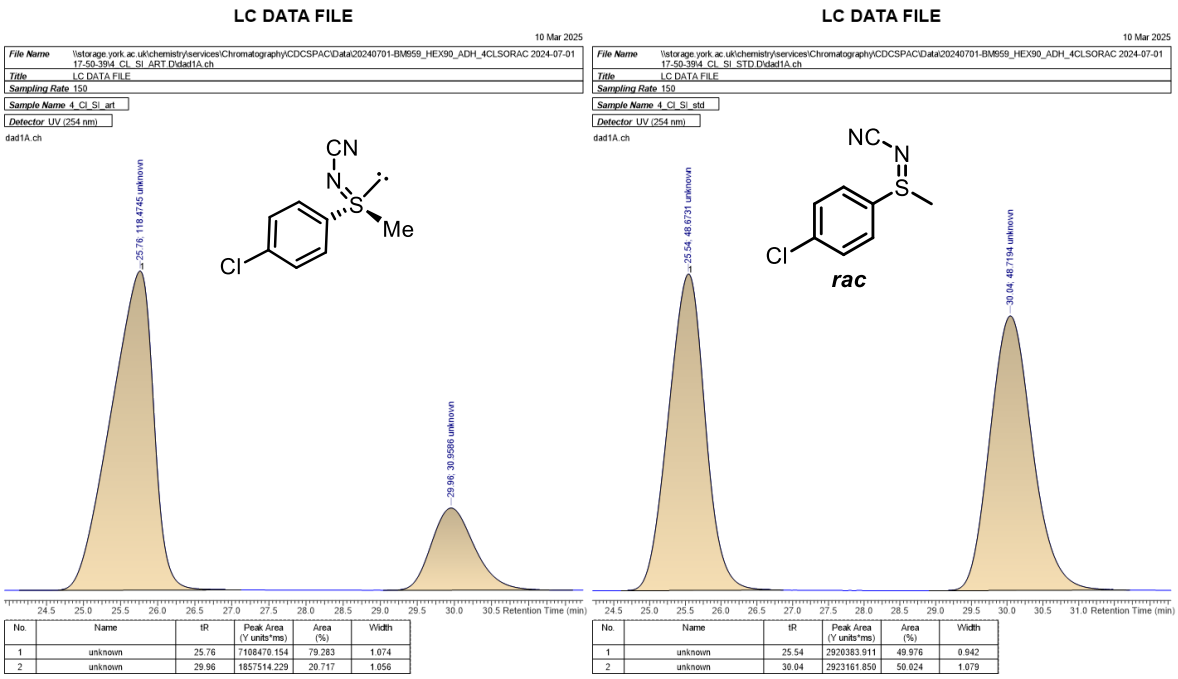


Figure S7. HPLC Data for **(*S*)-4d**

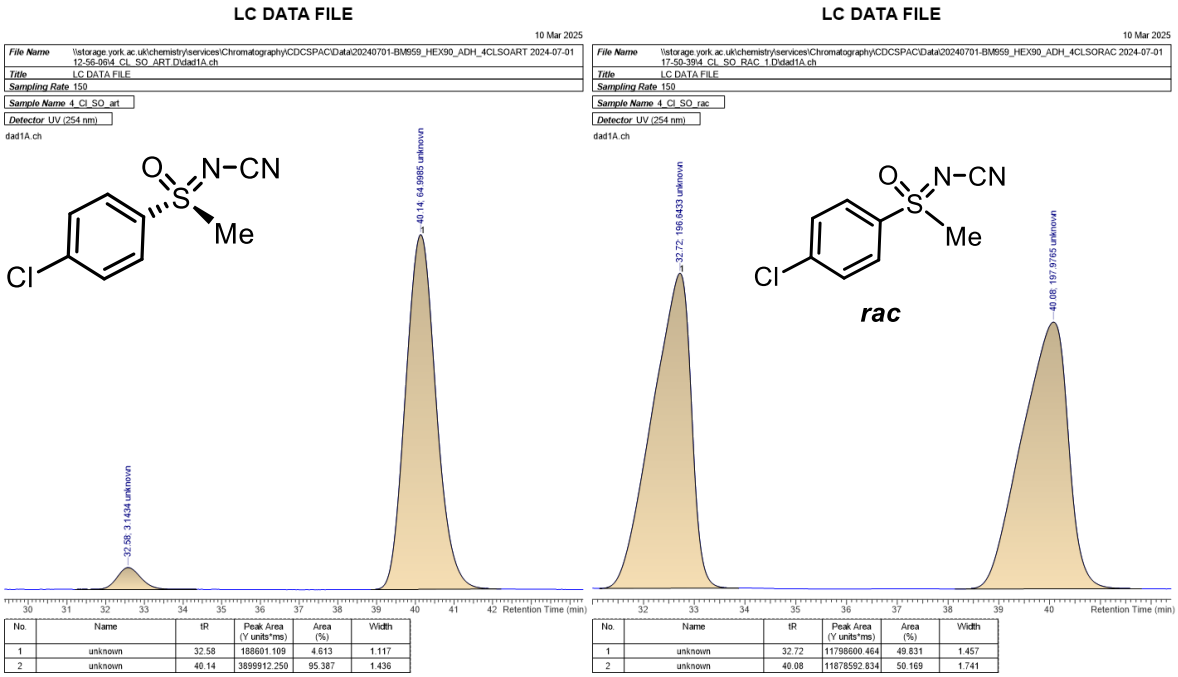


Figure S8. HPLC Data for **(*S*)-5d**

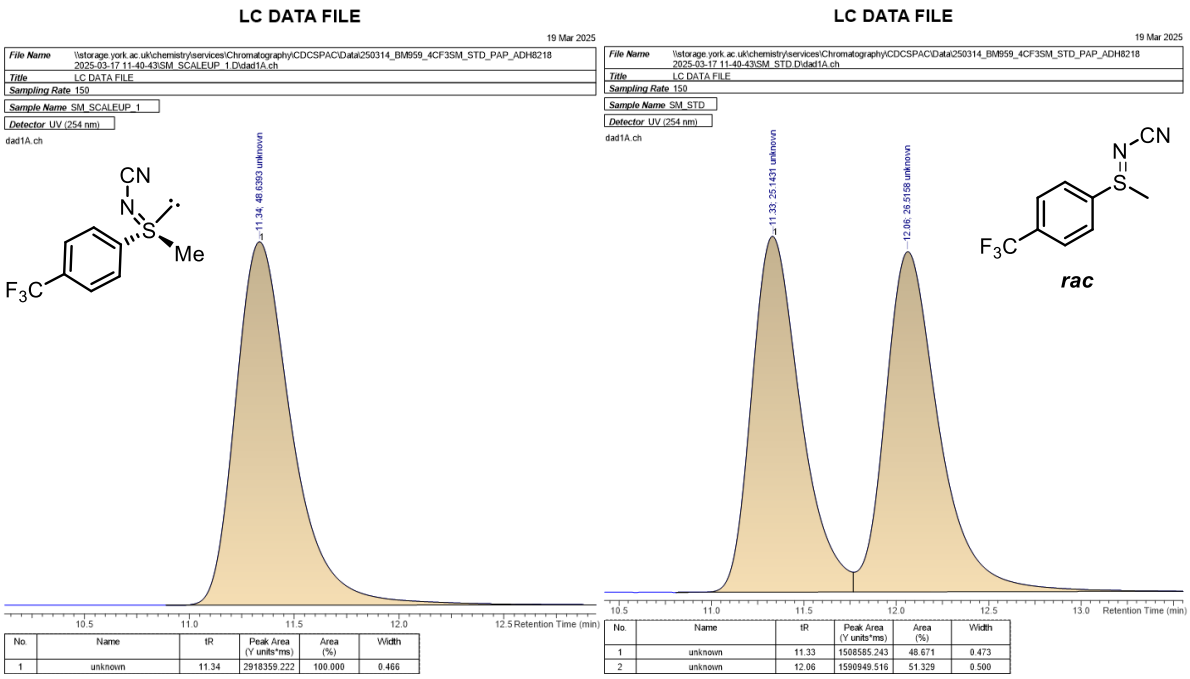


Figure S9. HPLC Data for **(*S*)-4e**

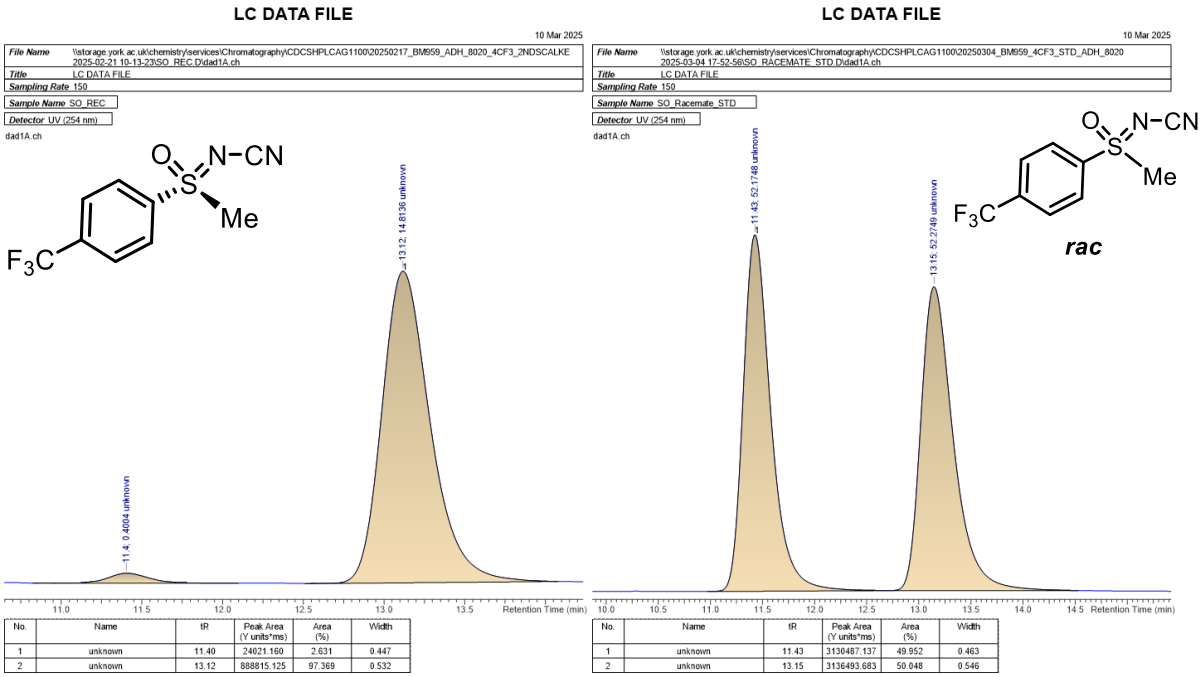


Figure S10. HPLC Data for **(*S*)-5e**

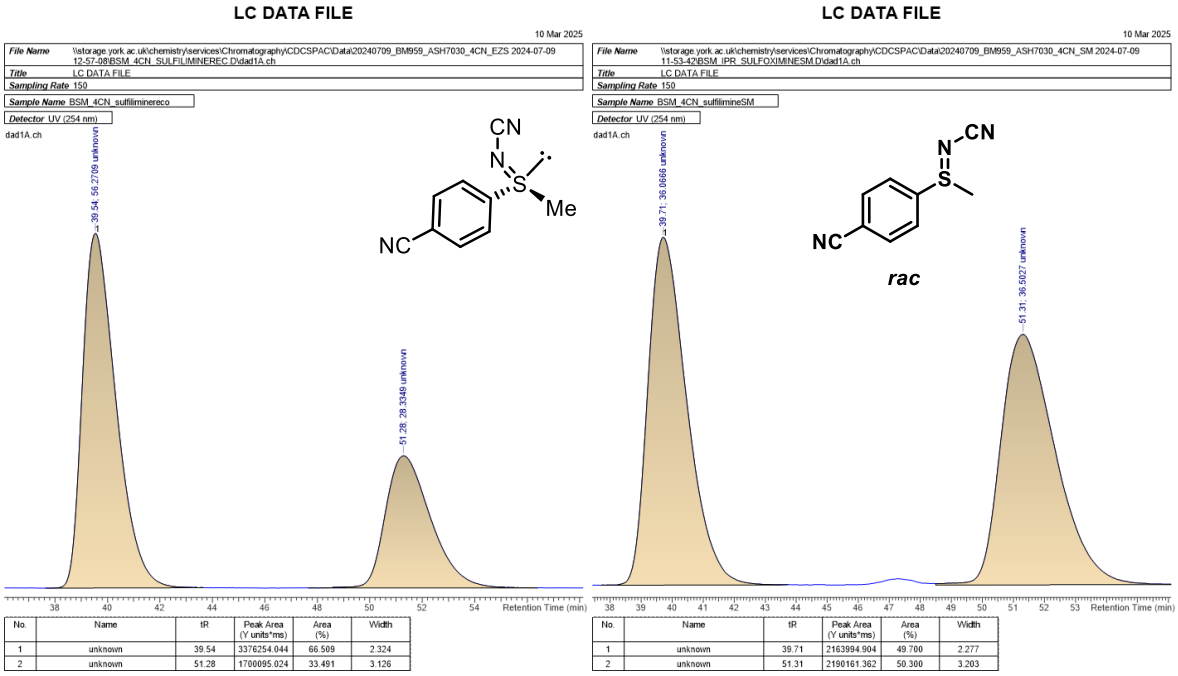


Figure 12. HPLC Data for **(*S*)-4f**

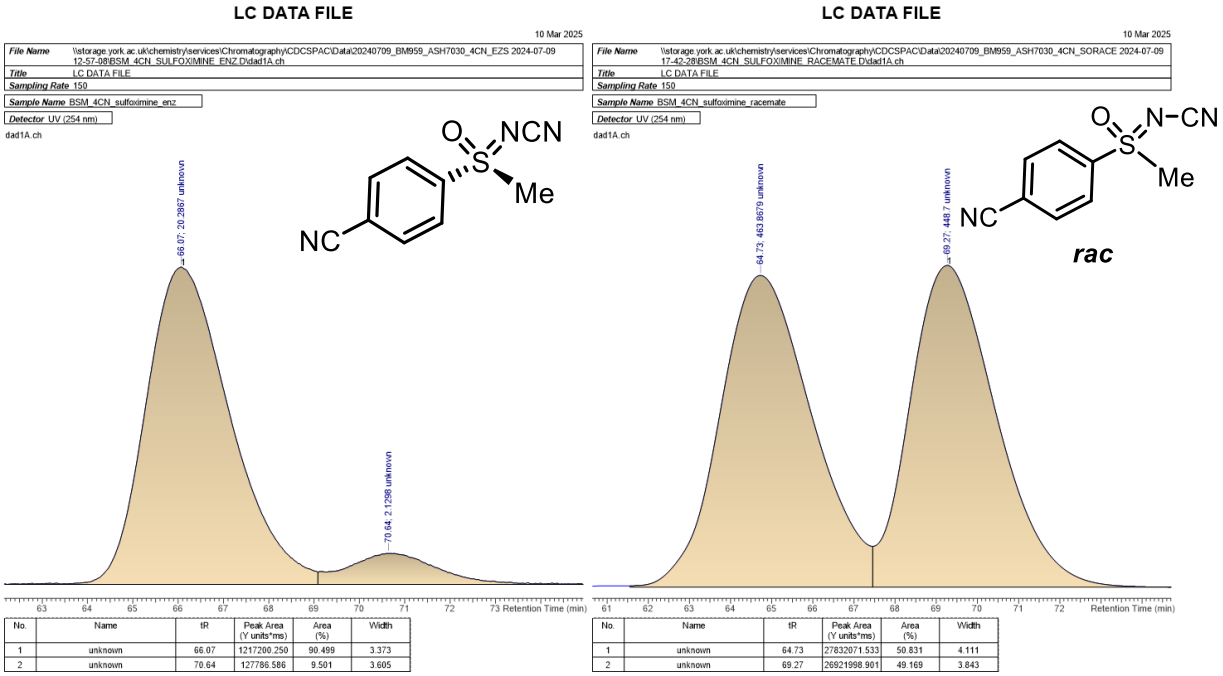


Figure S13. HPLC Data for **(*S*)-5f**

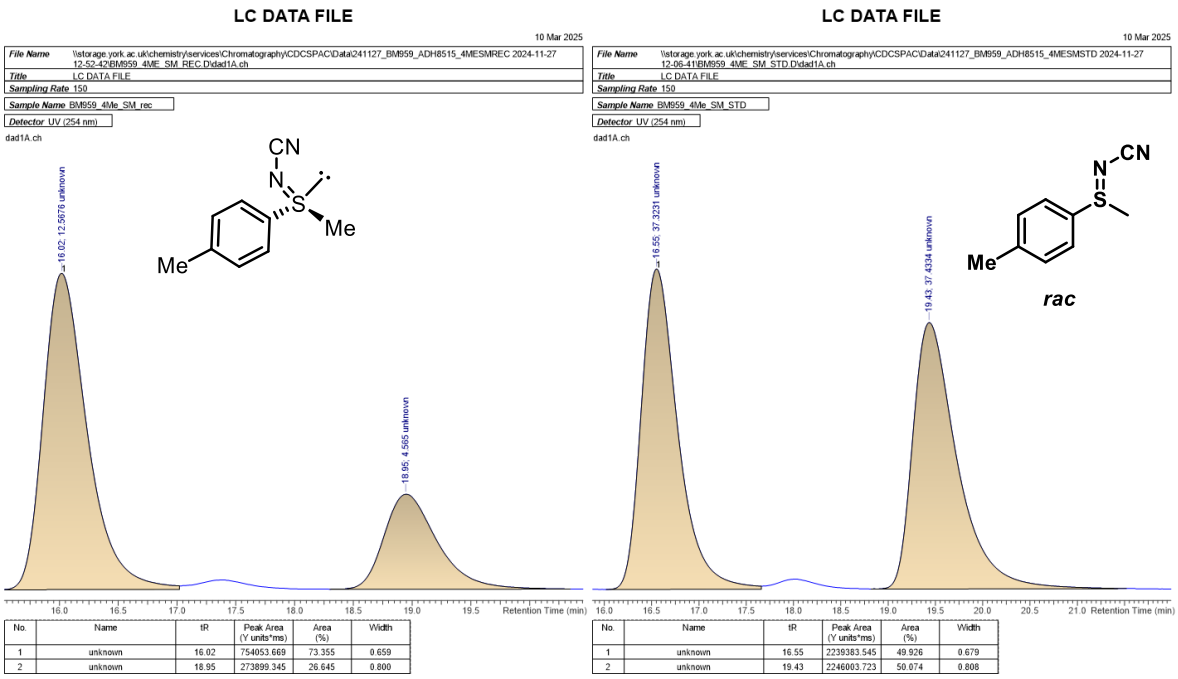


Figure S14. HPLC Data for **(*S*)-4g**

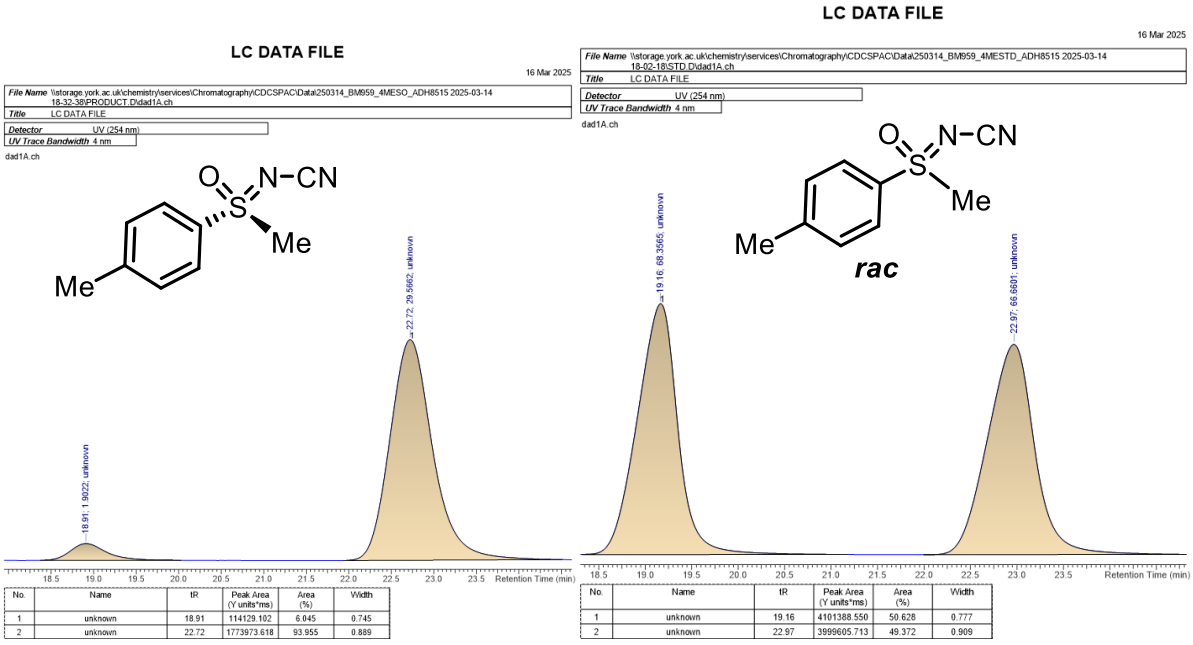


Figure S15. HPLC Data for **(*S*)-5g**

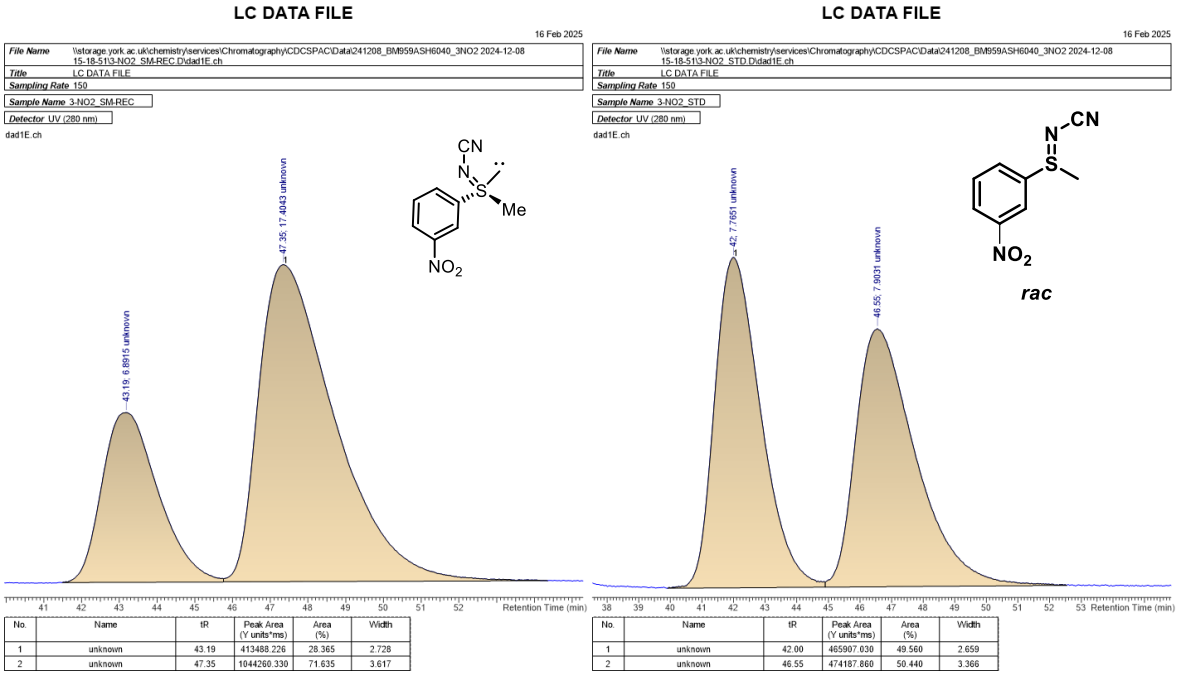


Figure S16. HPLC Data for **(*S*)-4h**

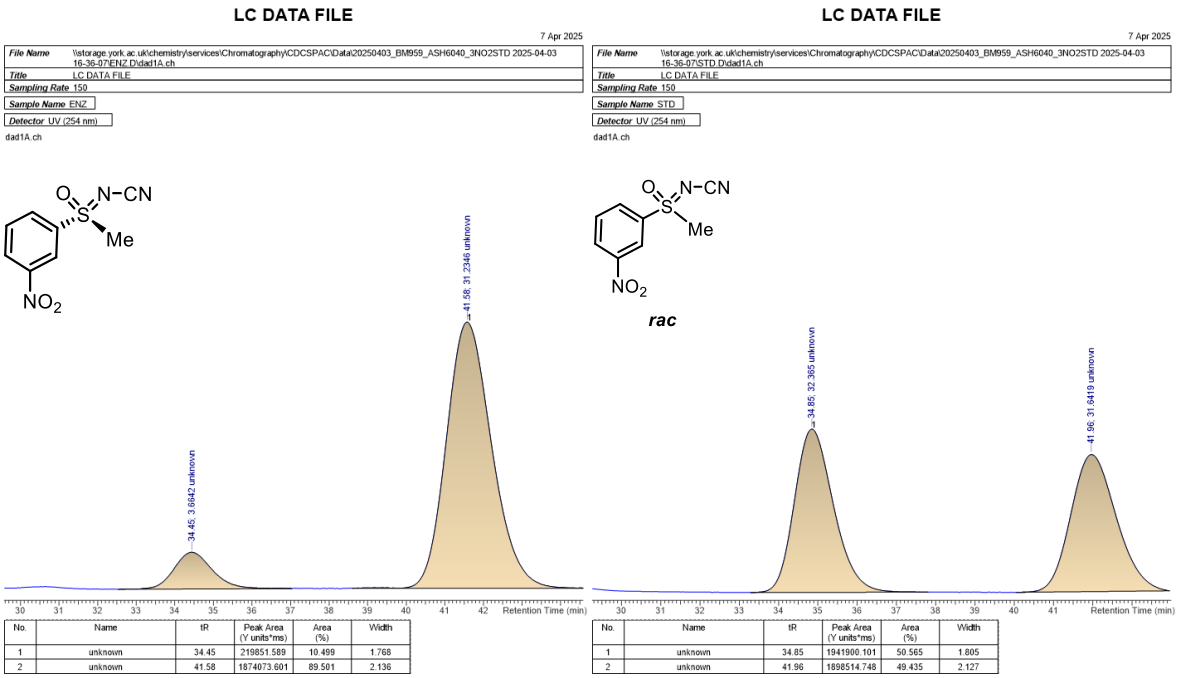


Figure S17. HPLC Data for **(*S*)-5h**

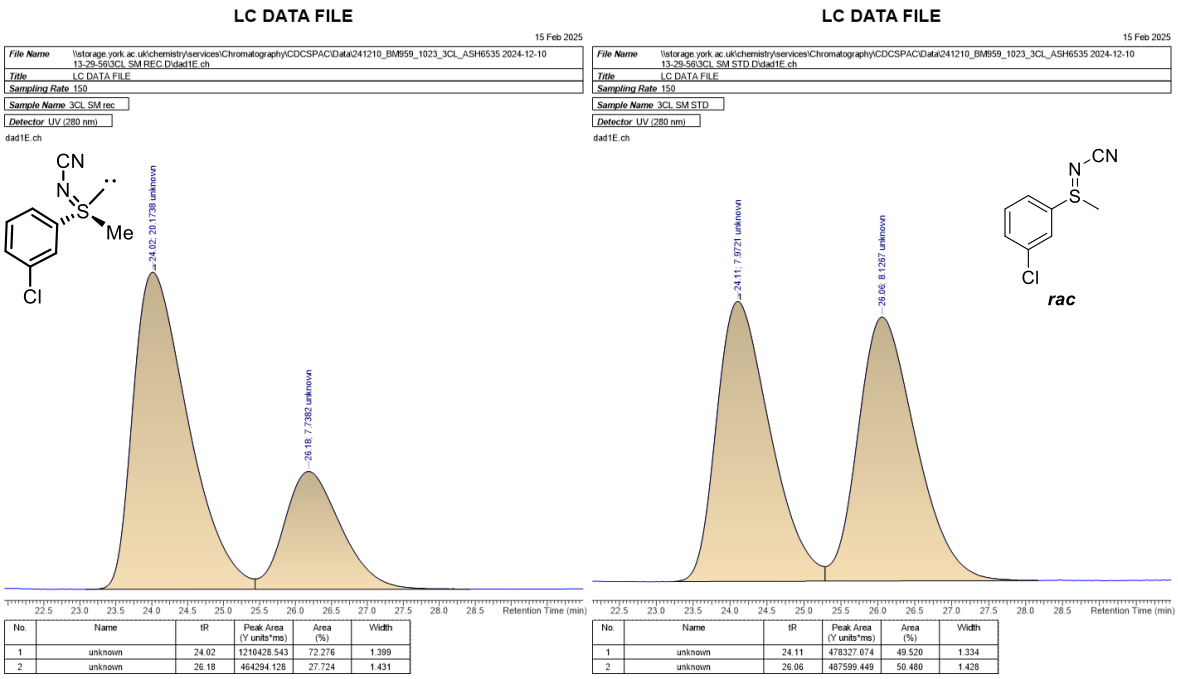


Figure S18. HPLC Data for **(*S*)-4i**

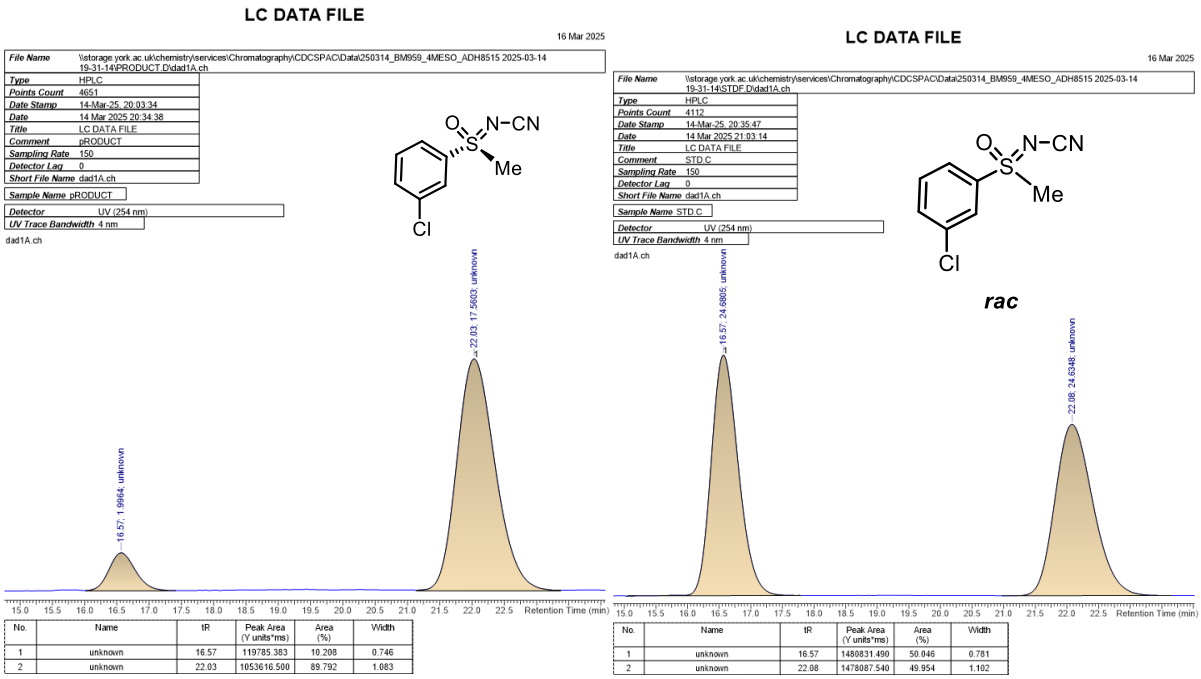


Figure S19. Data for **(*S*)-5i**

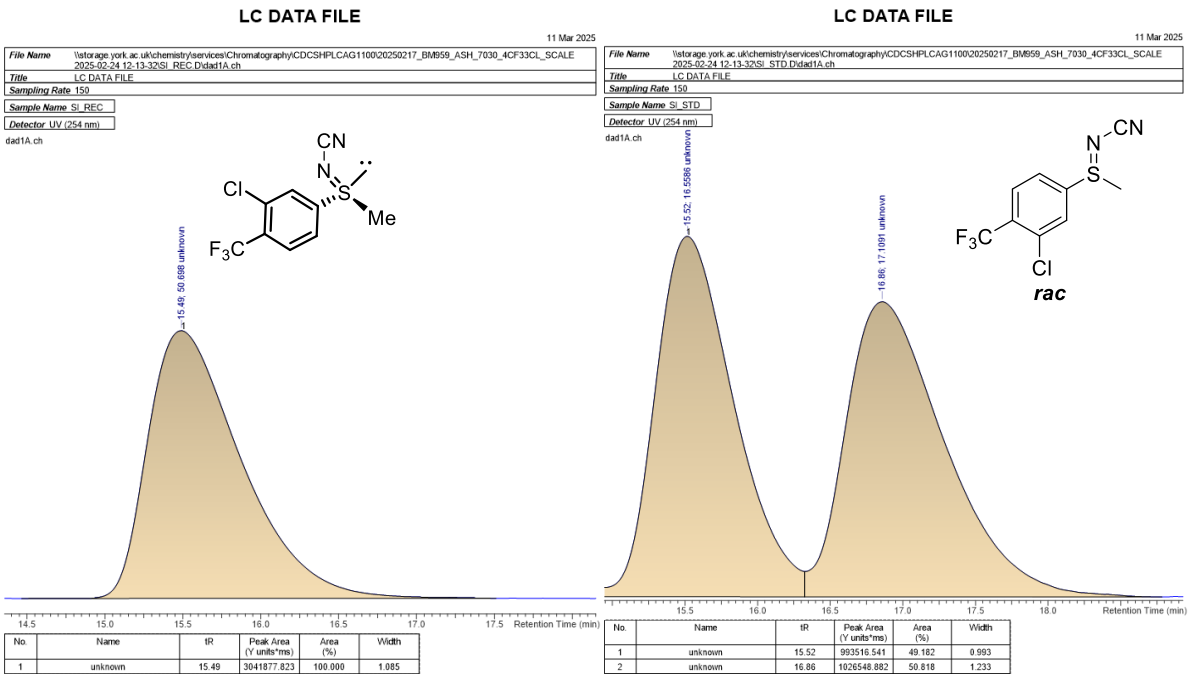


Figure S20. HPLC Data for **(*S*)-4j**

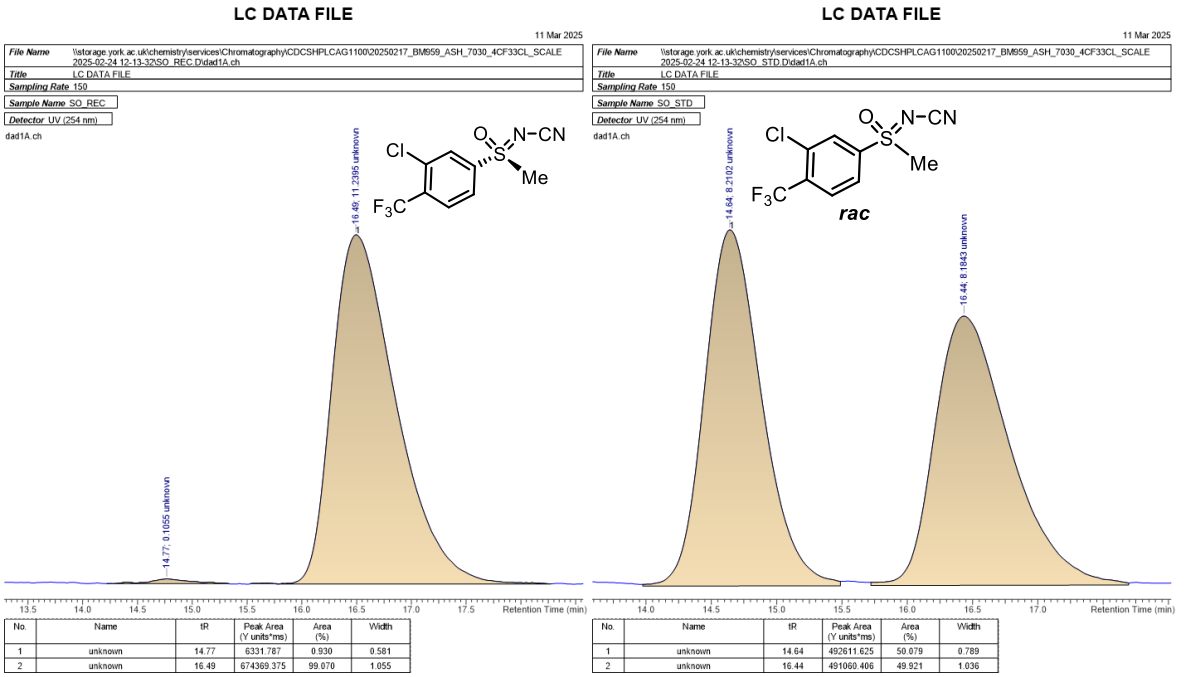


Figure S21. HPLC Data for **(*S*)-5j**

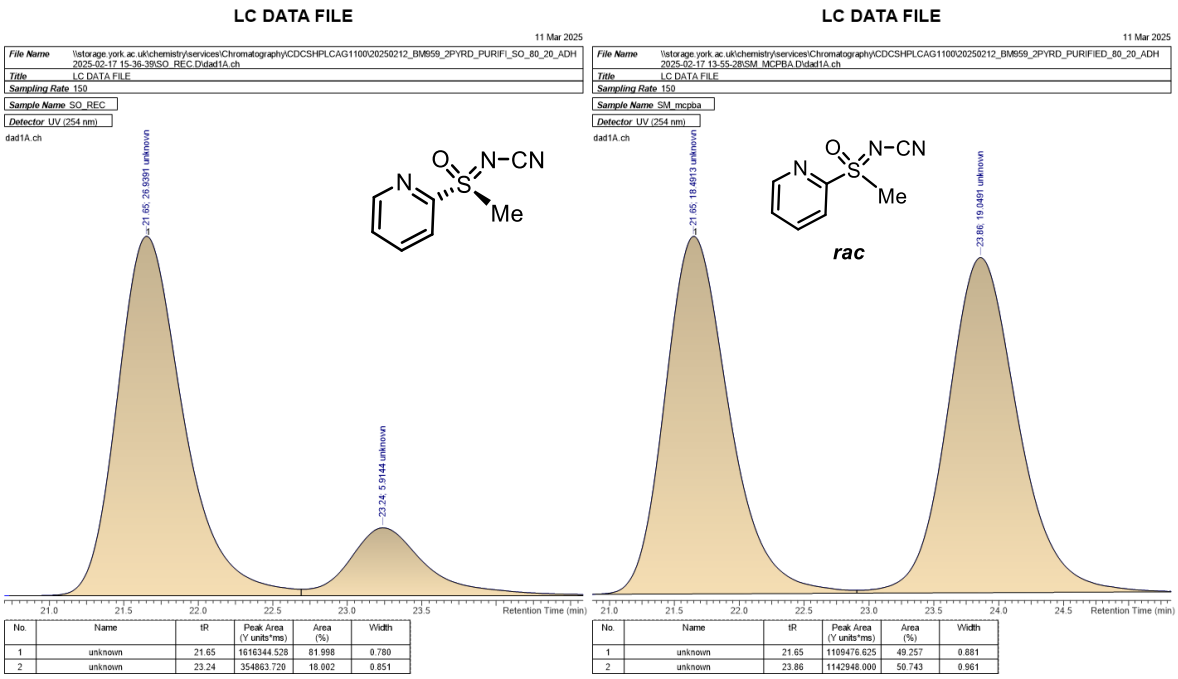
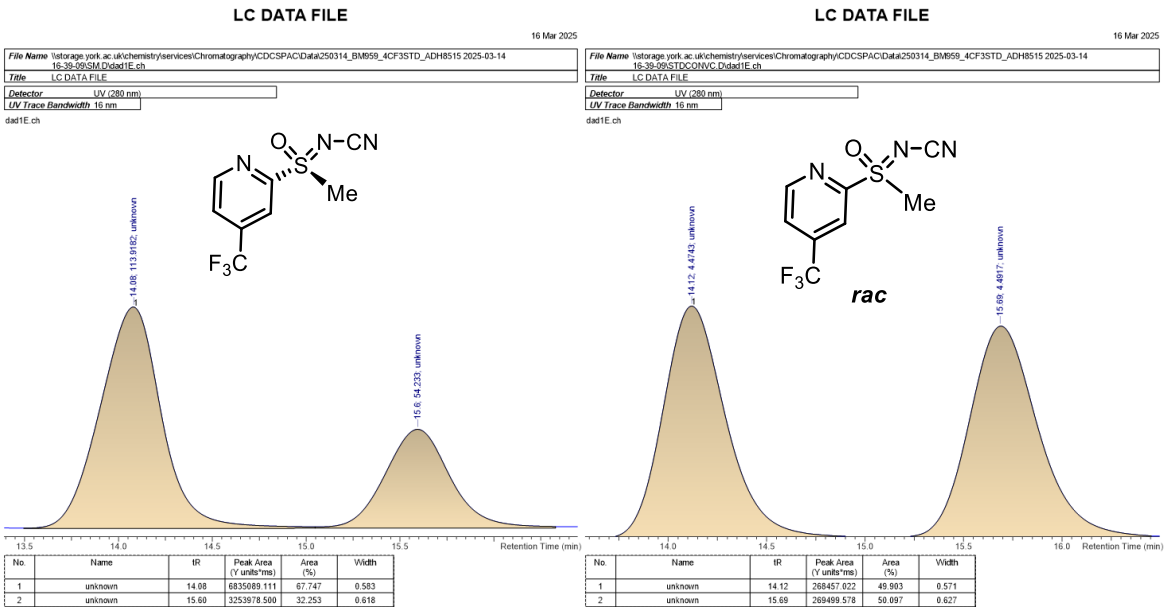


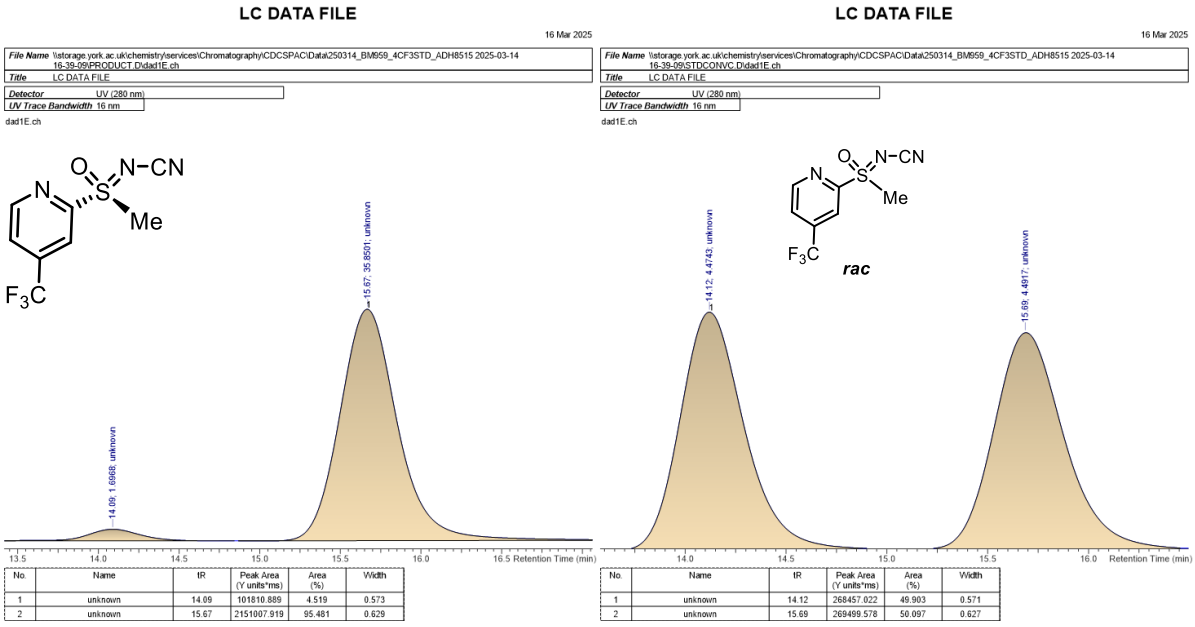
Figure S22. HPLC Data for **(*S*)-5k**



No.	Name	tR	Peak Area (Y units*ms)	Area (%)	Width
1	unknovn	14.08	6835089.111	67.747	0.583
2	unknovn	15.60	3253978.500	32.253	0.618

No.	Name	tR	Peak Area (Y units*ms)	Area (%)	Width
1	unknown	14.12	268457.022	49.903	0.571
2	unknown	15.69	269499.578	50.097	0.627

Figure S23. HPLC Data for **(*S*)-4l**



No.	Name	tR	Peak Area (Y units*ms)	Area (%)	Width
1	unknovn	14.09	101810.889	4.519	0.573
2	unknovn	15.67	2151007.919	95.481	0.629

No.	Name	tR	Peak Area (Y units*ms)	Area (%)	Width
1	unknown	14.12	268457.022	49.903	0.571
2	unknown	15.69	269499.578	50.097	0.627

Figure S24. HPLC Data for **(*S*)-5l**

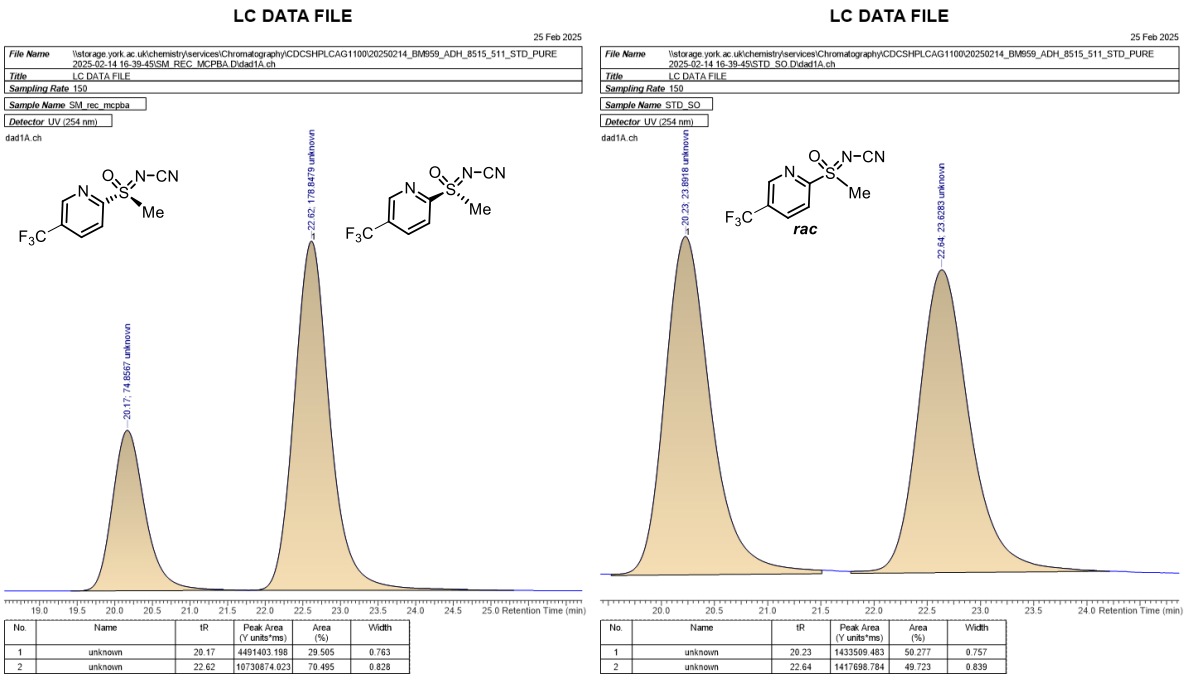


Figure S25. HPLC Data for **(*S*)-4m** following m-CPBA Oxidation

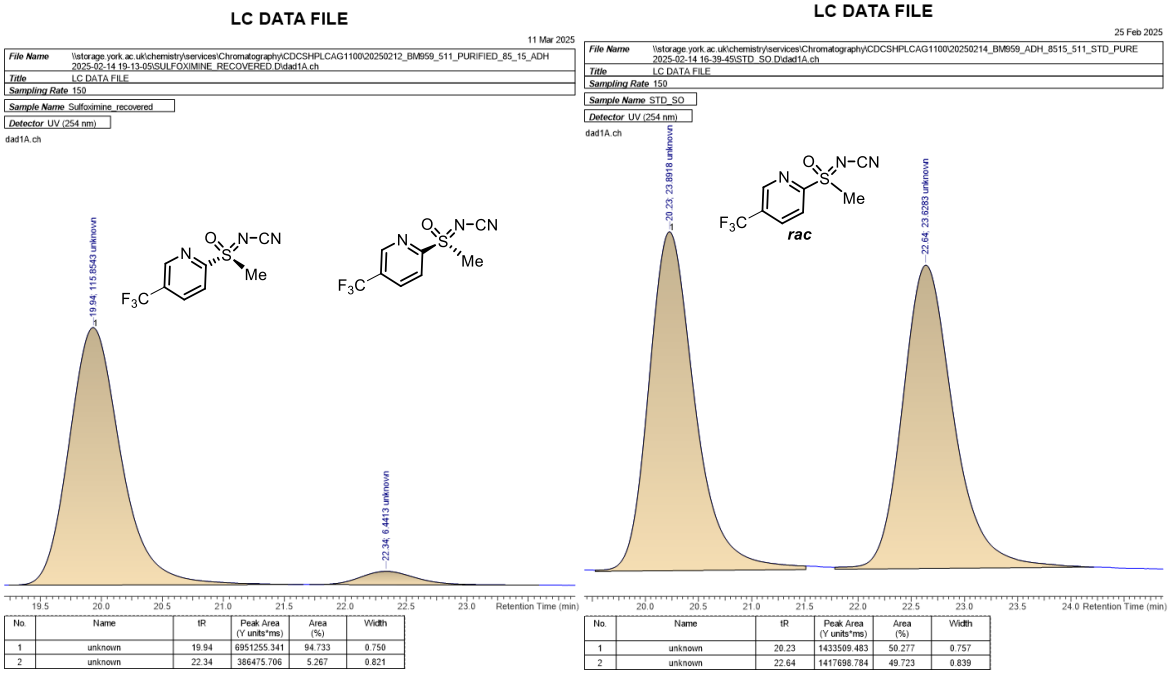


Figure S26. HPLC Data for **(*S*)-5m**

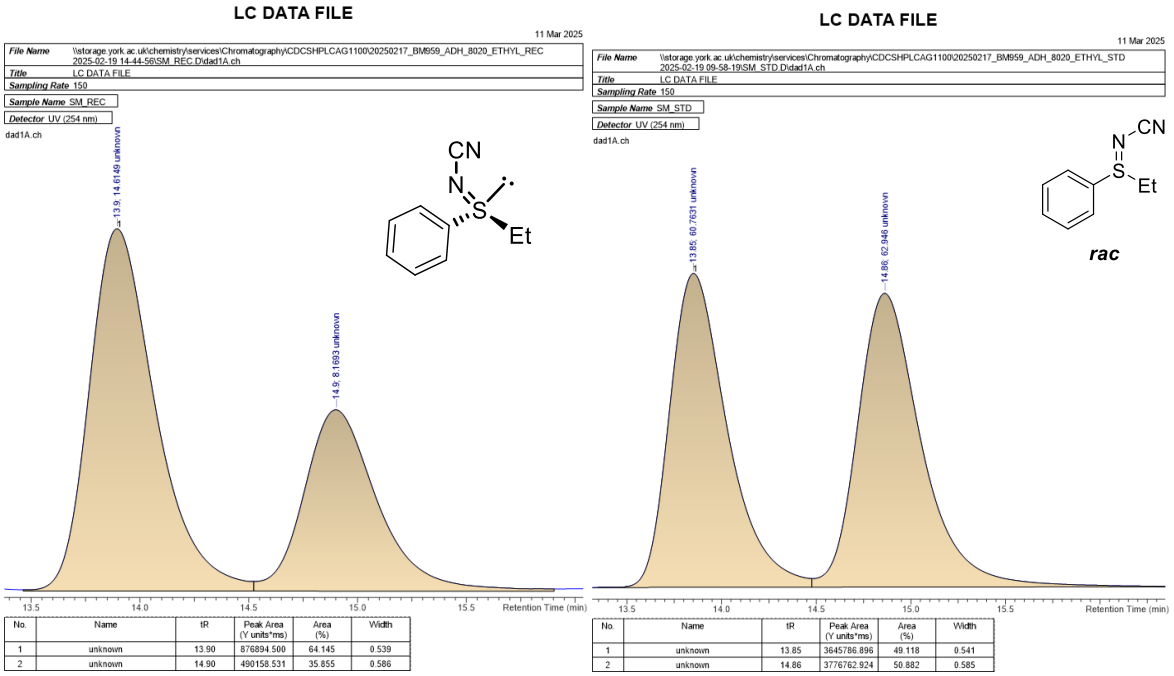


Figure S27. HPLC Data for **(*S*)-4n**

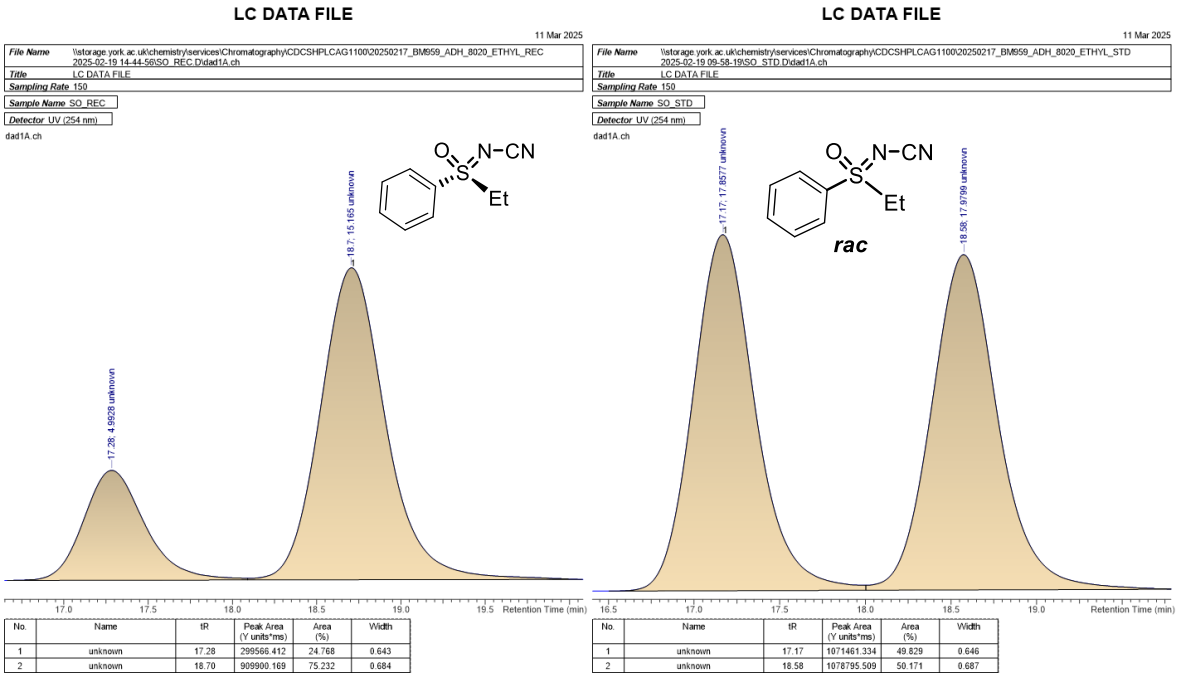


Figure S28. HPLC Data for **(*S*)-5n**

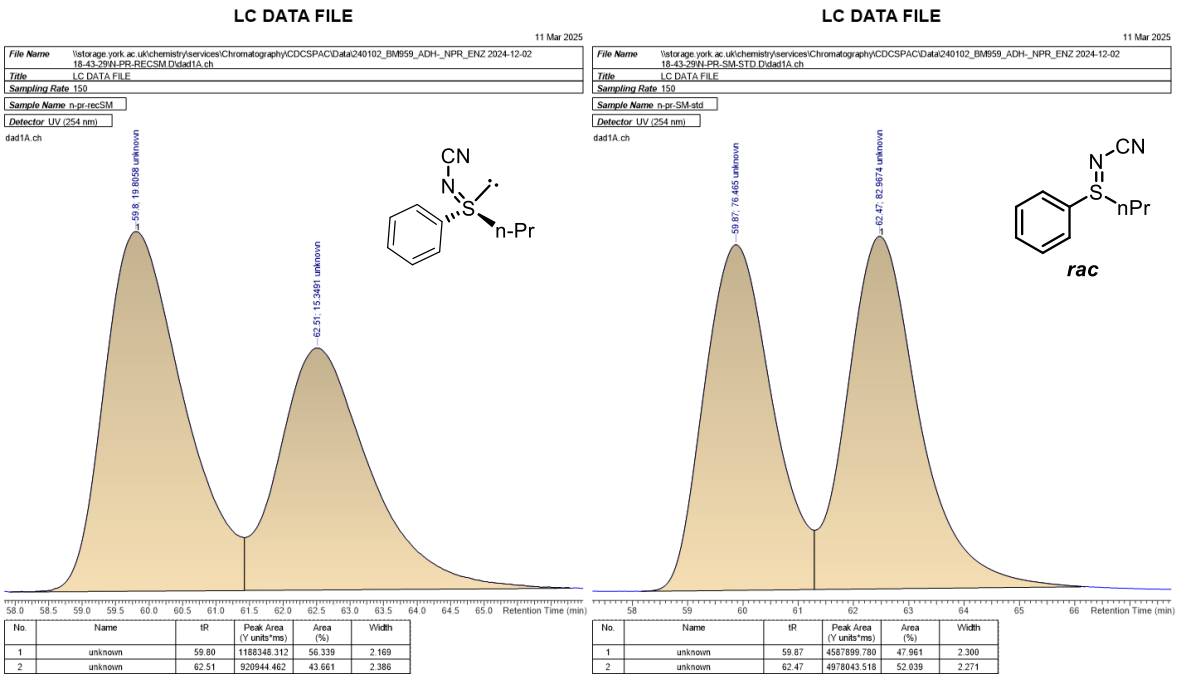


Figure S29. HPLC Data for **(*S*)-4o**

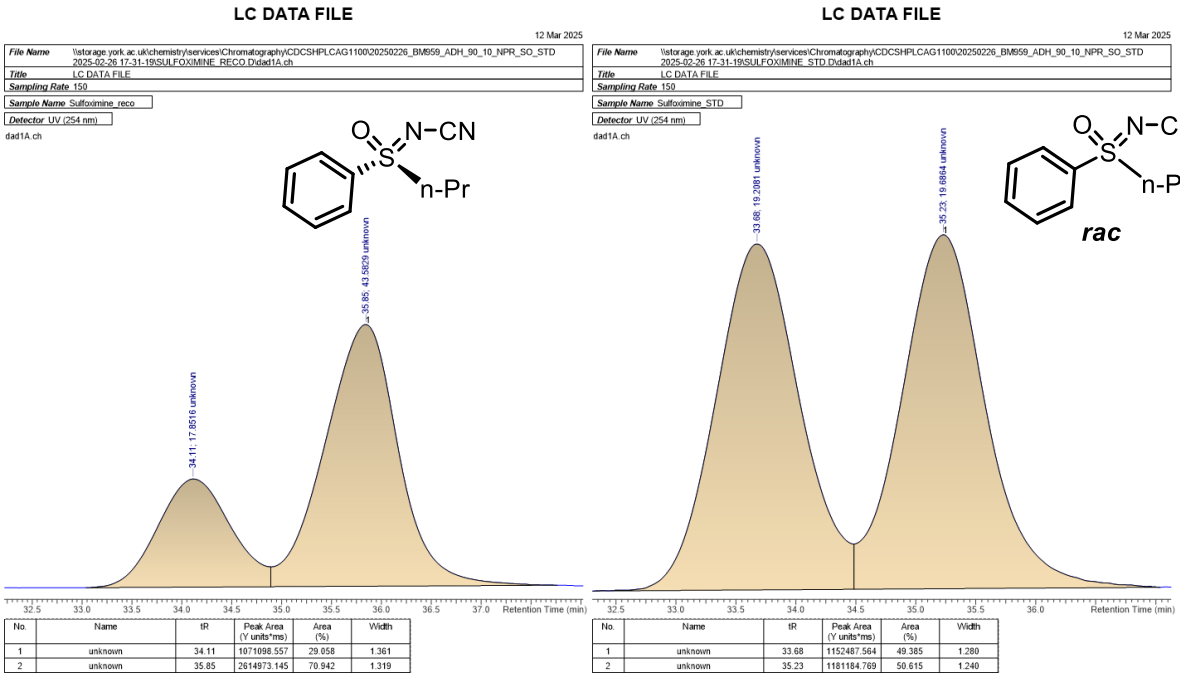


Figure S30. HPLC Data for **(*S*)-5o**

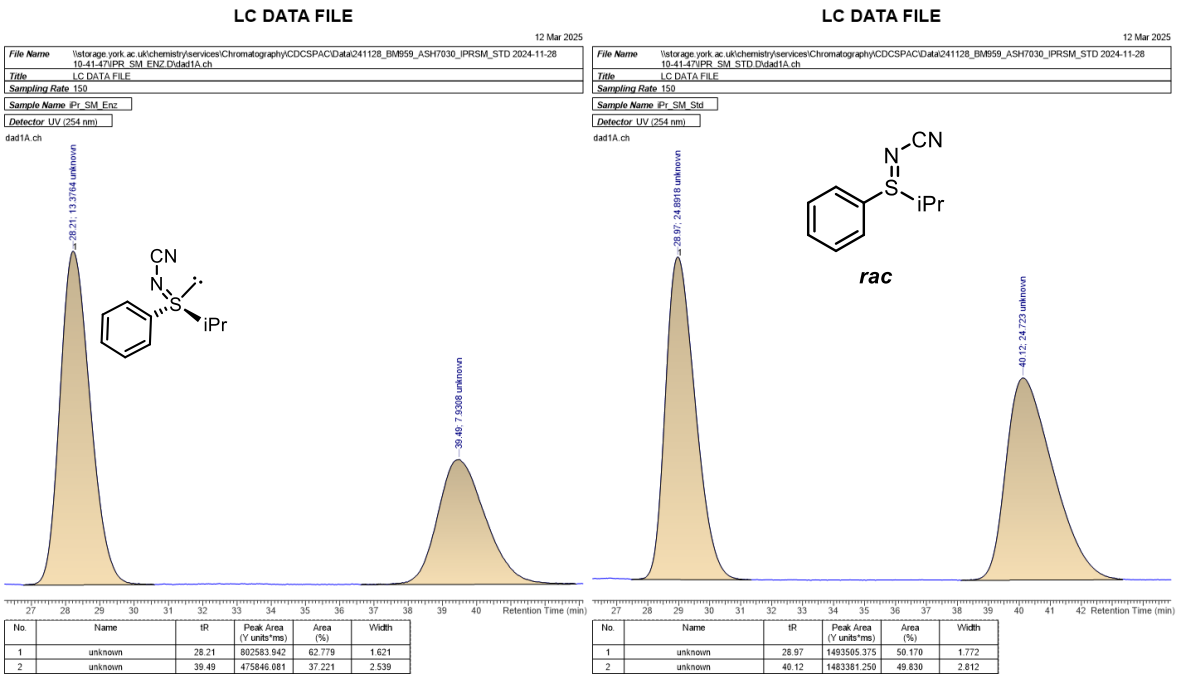


Figure S31. HPLC Data for **(*S*)-4p**

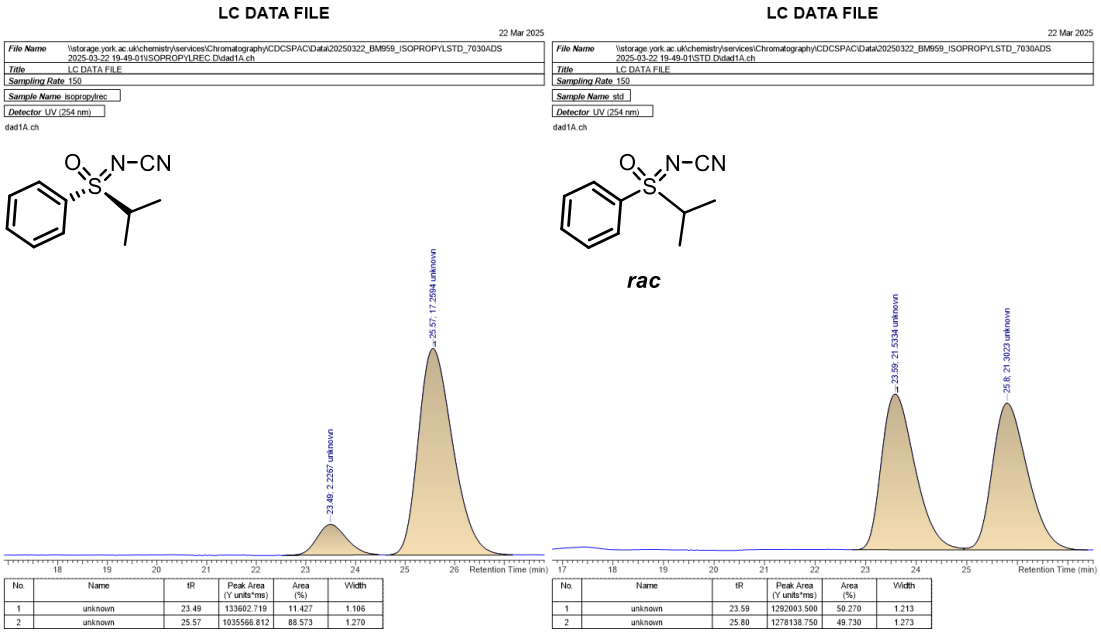


Figure S32. HPLC Data for **(*S*)-5p**

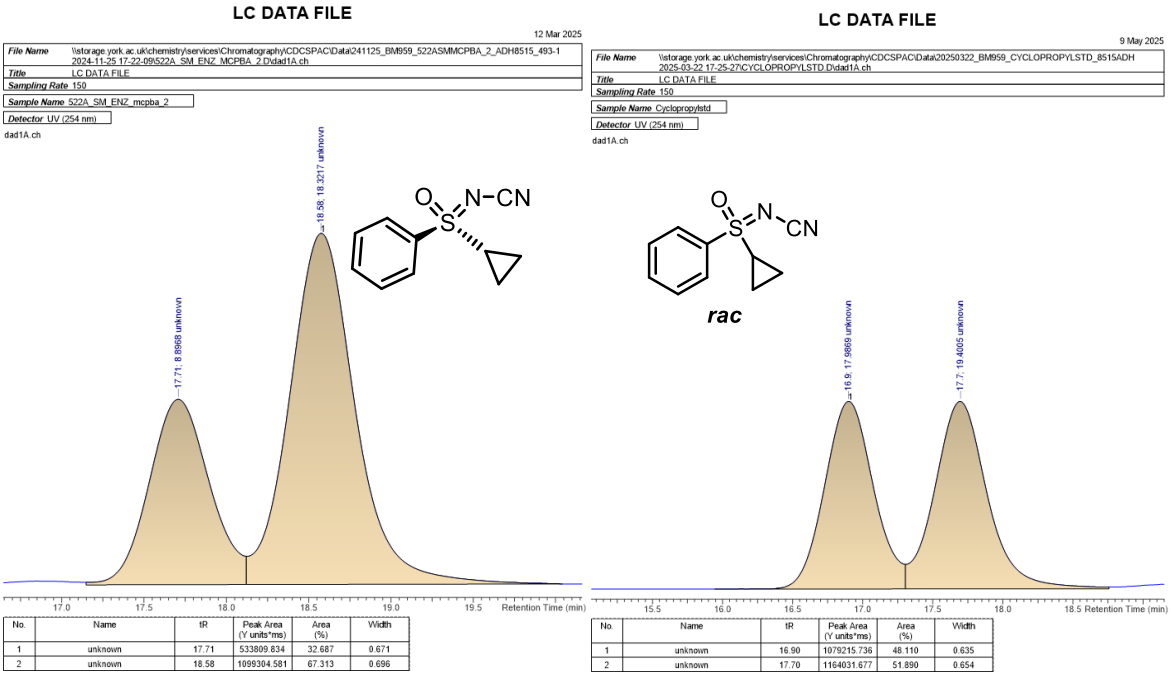


Figure S33. HPLC Data for **(*S*)-4q**

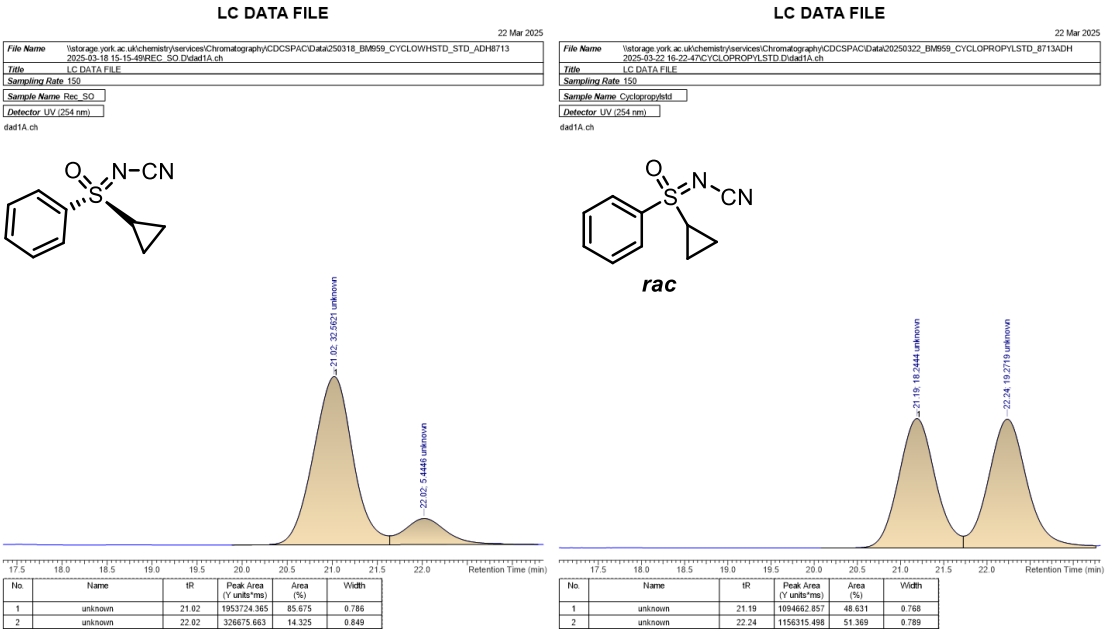


Figure S34. HPLC Data for **(*S*)-5q**

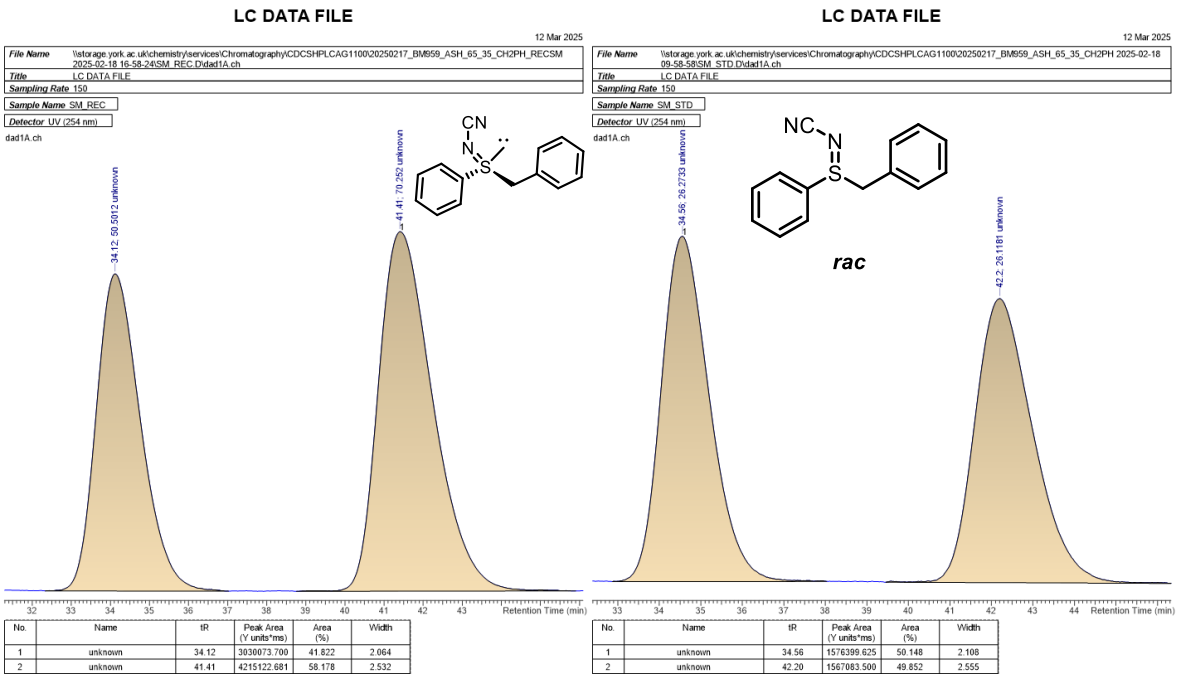


Figure S35. HPLC Data for **(*S*)-4r**

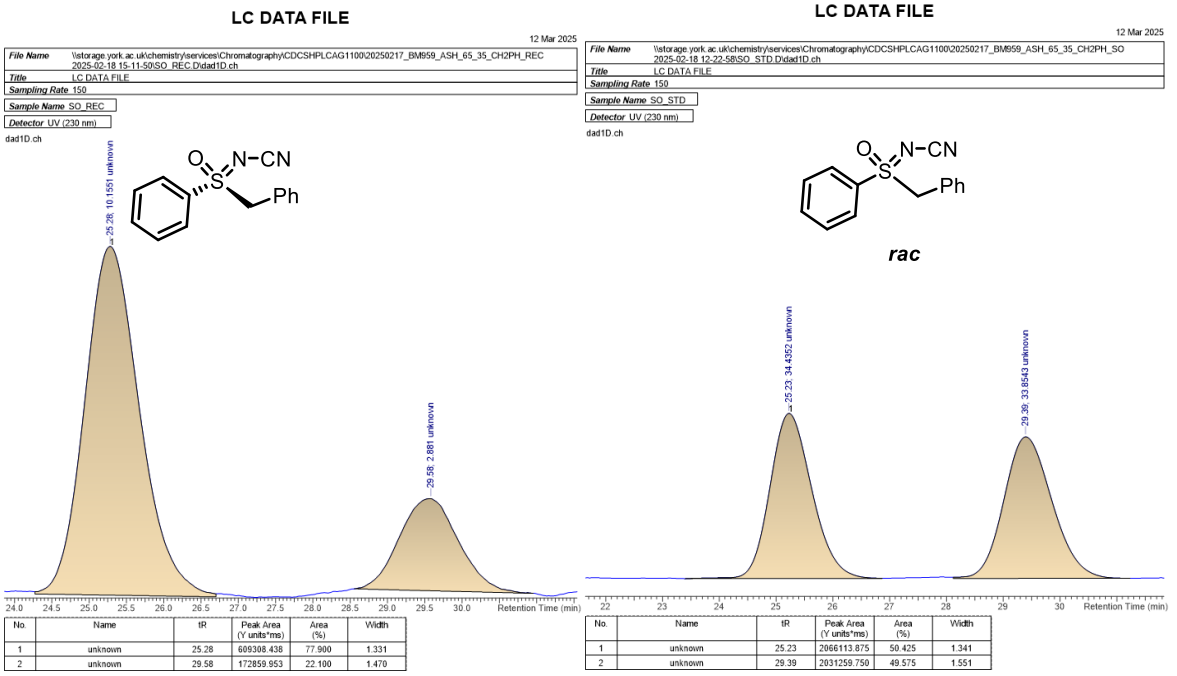


Figure S36. HPLC Data for **(*S*)-5r**

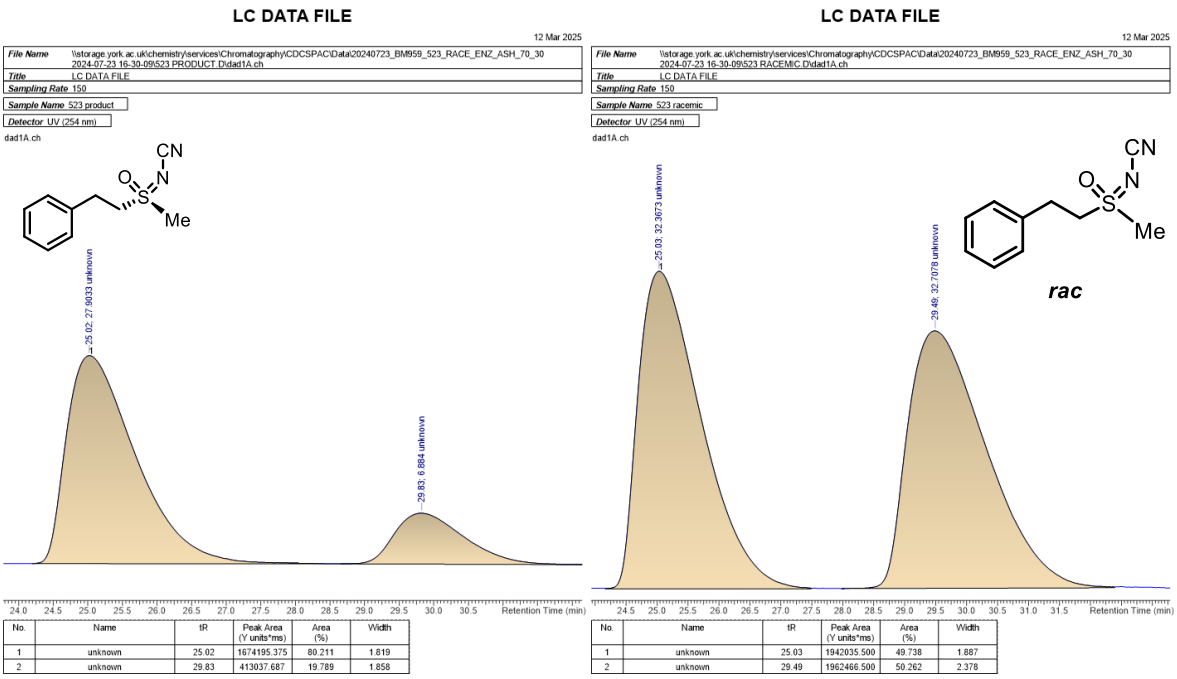


Figure S37. HPLC Data for **(*S*)-5s**

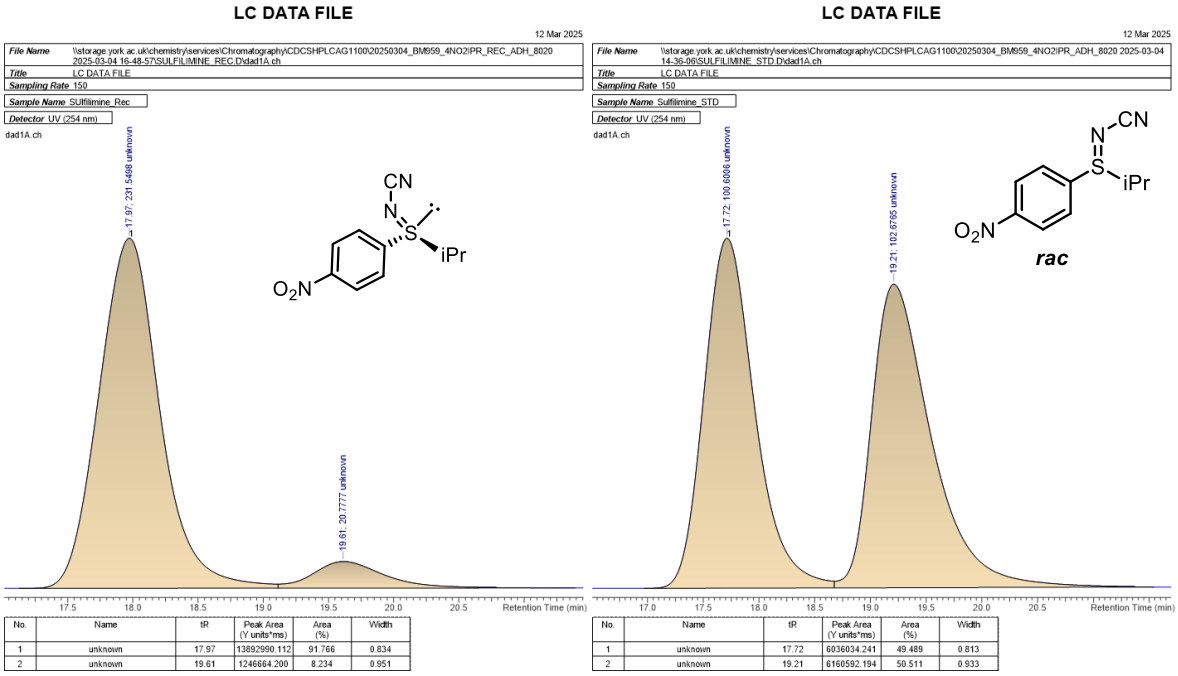


Figure S38. HPLC trace for **(*S*)-4t**

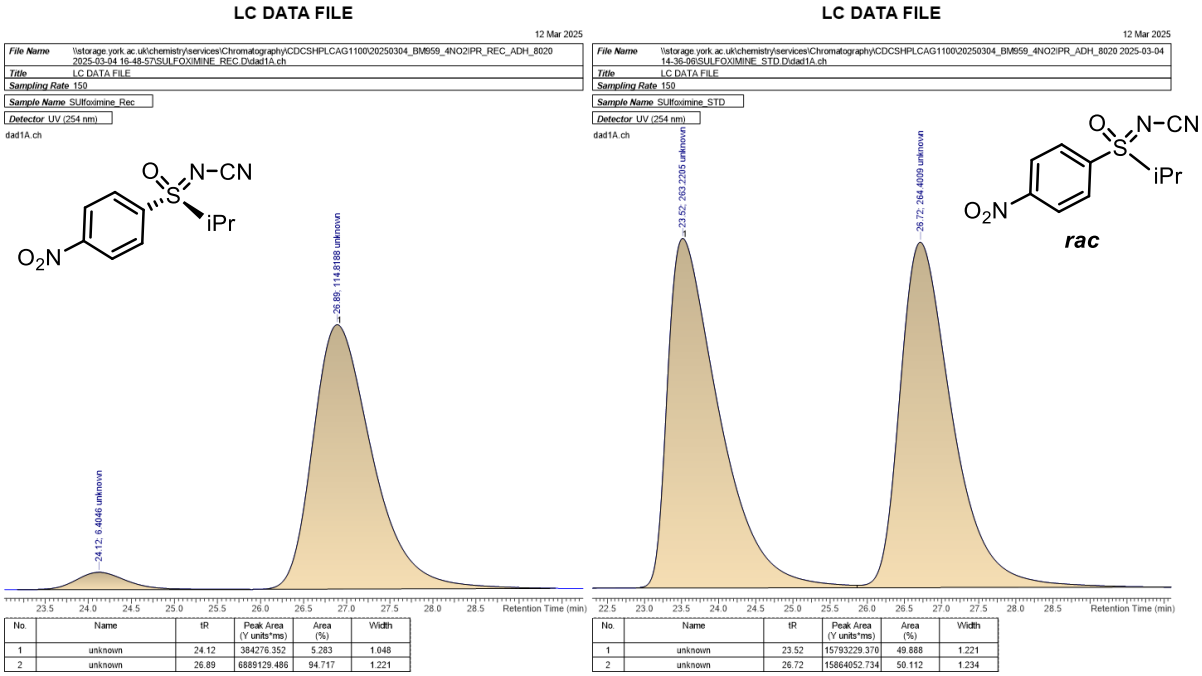


Figure S39. HPLC trace for **(*S*)-5t**

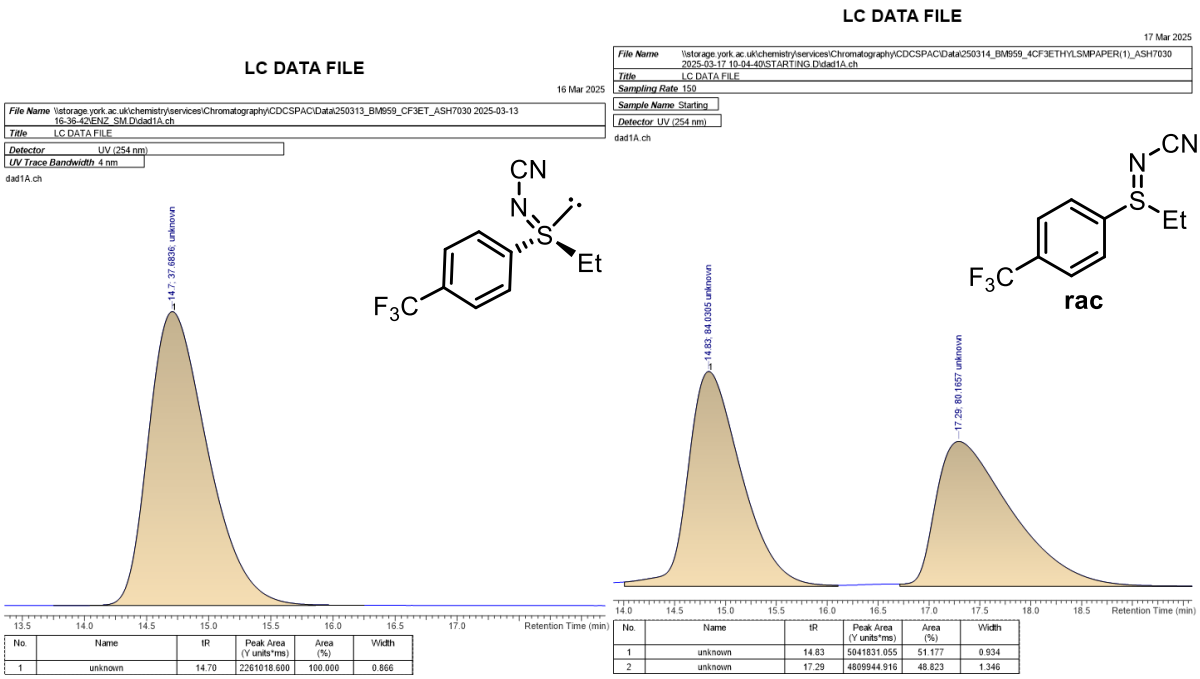


Figure S40. HPLC Data for **(*S*)-4u**

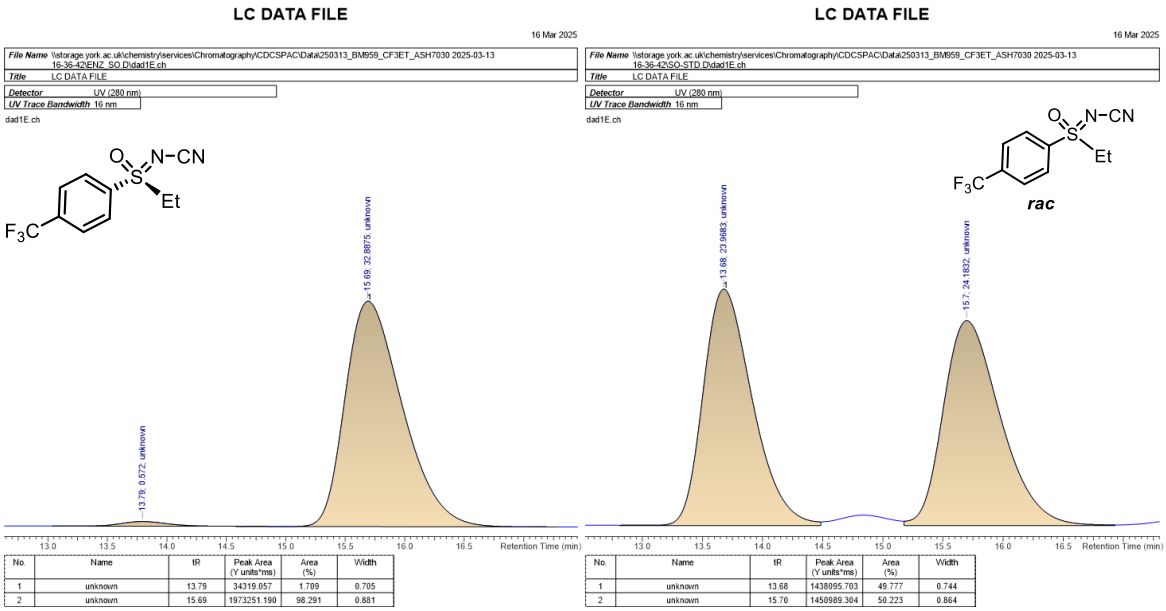


Figure S41. HPLC Data for **(*S*)-5u**

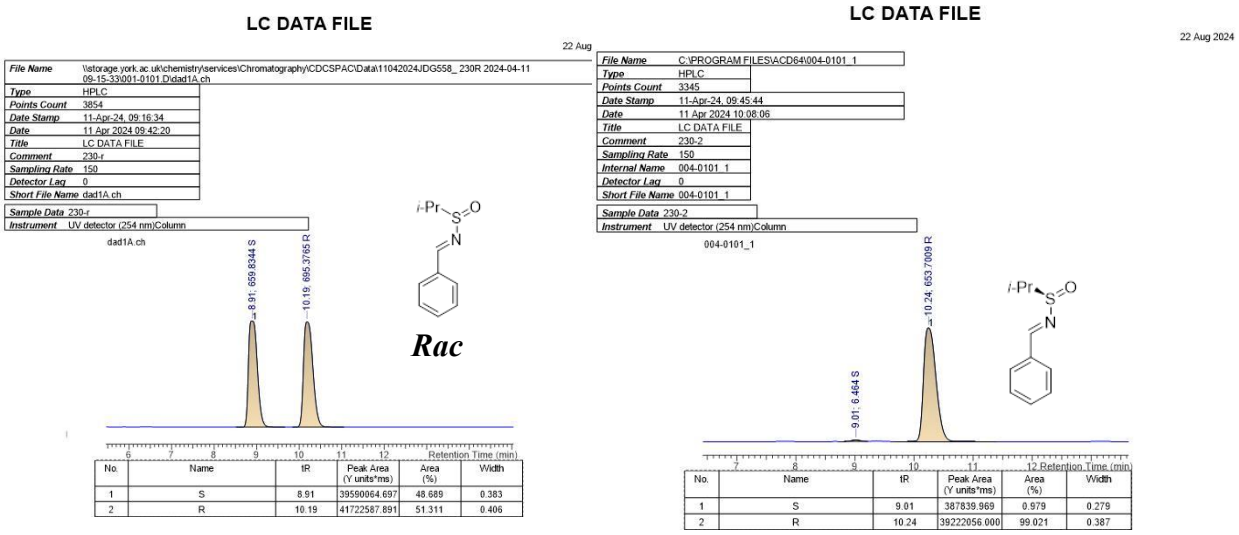


Figure S42. HPLC Data for **(*R*)-12a**

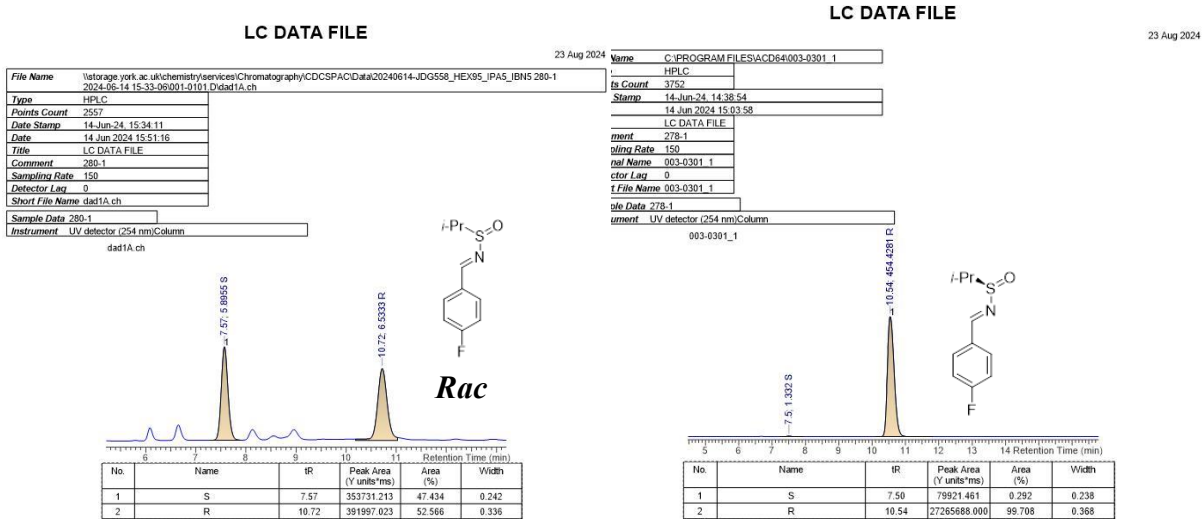
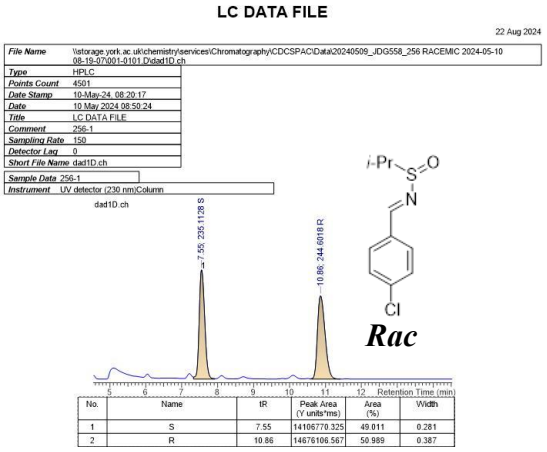


Figure S43. HPLC Data for **(*R*)-12b**



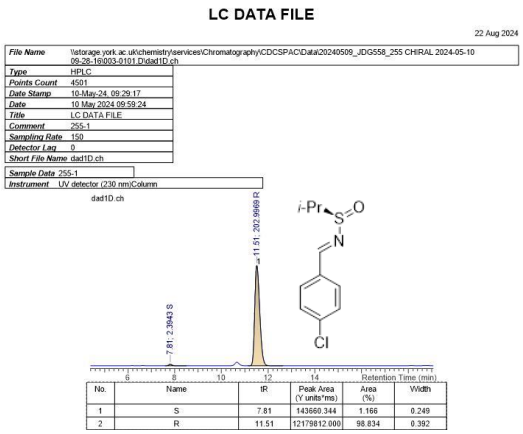
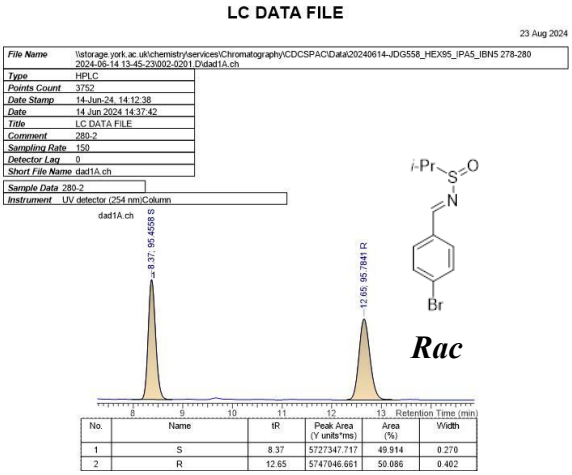


Figure S44. HPLC Data for **(*R*)-12c**



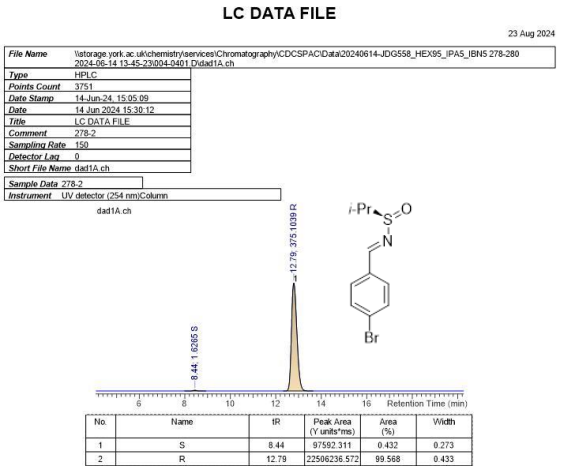
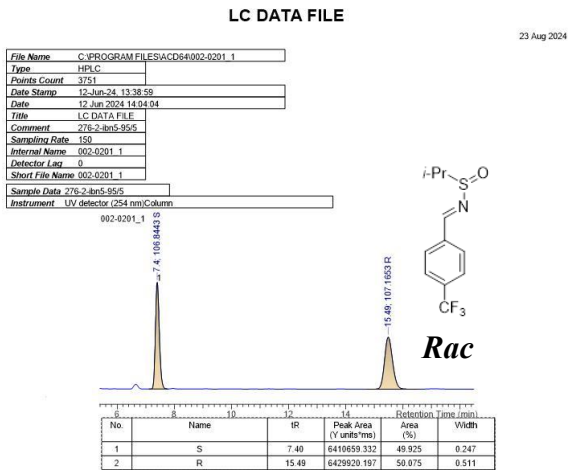


Figure S45. HPLC Data for **(*R*)-12d**



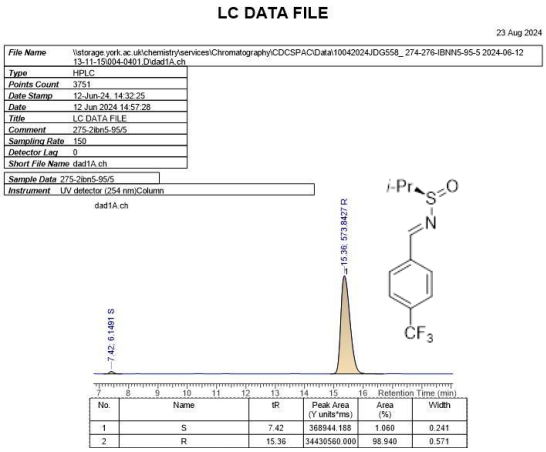
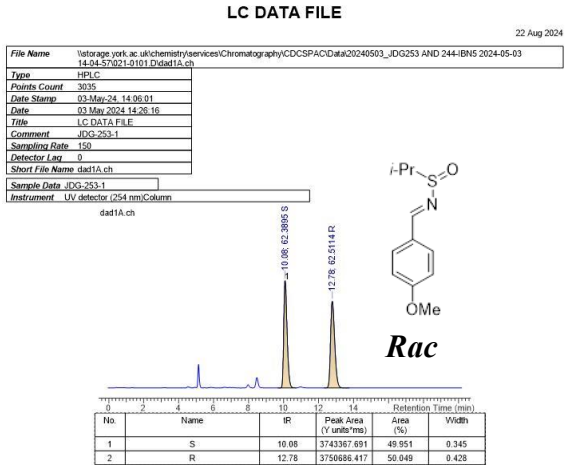


Figure S46. HPLC Data for **(*R*)-12e**



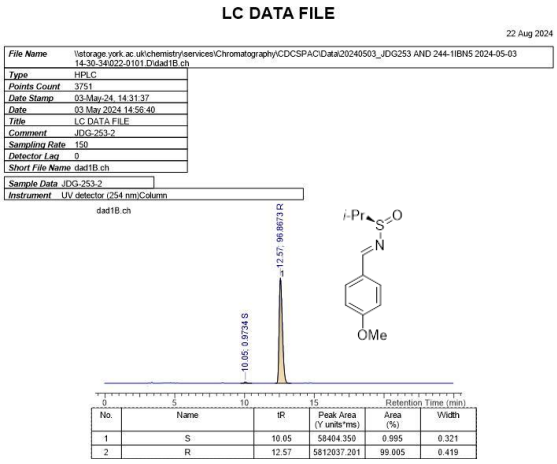
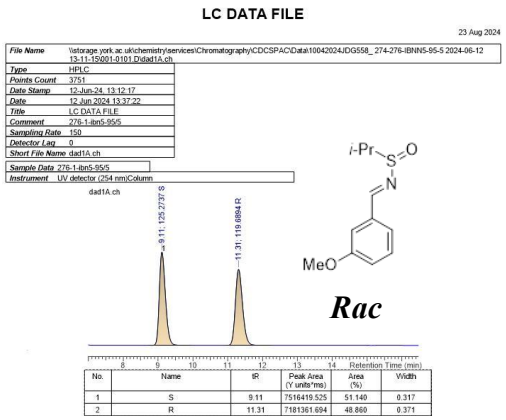


Figure S47. HPLC Data for **(*R*)-12f**



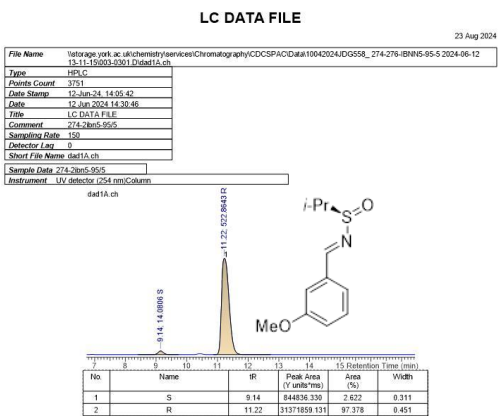


Figure S48. HPLC Data for **(*R*)-12g**

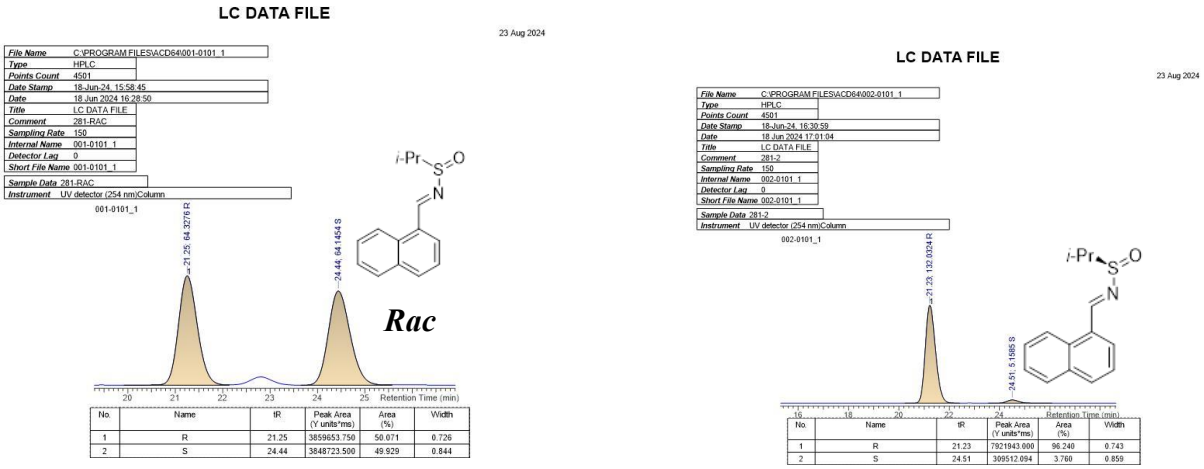


Figure S49. HPLC Data for **(*R*)-12h**

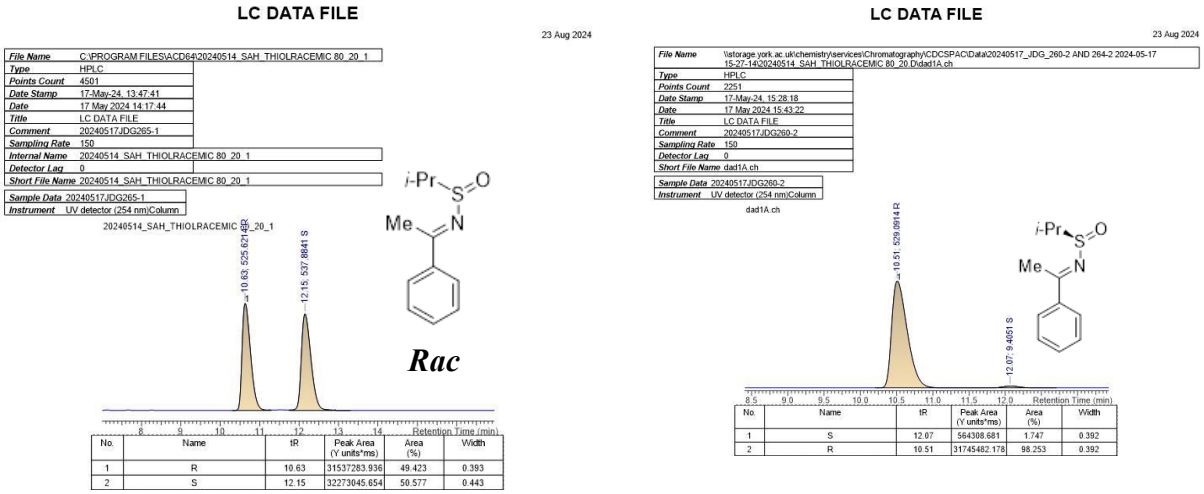
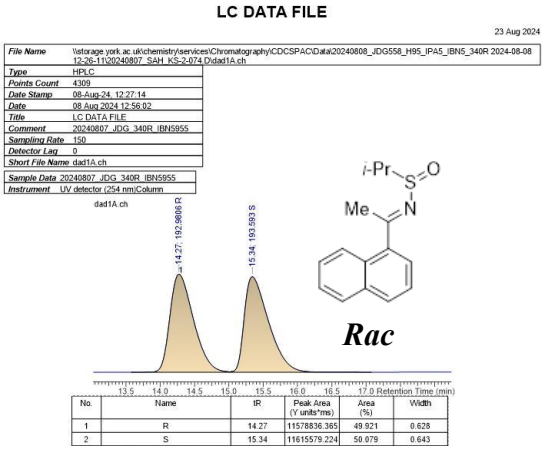


Figure S50. HPLC Data for **(*R*)-12i**



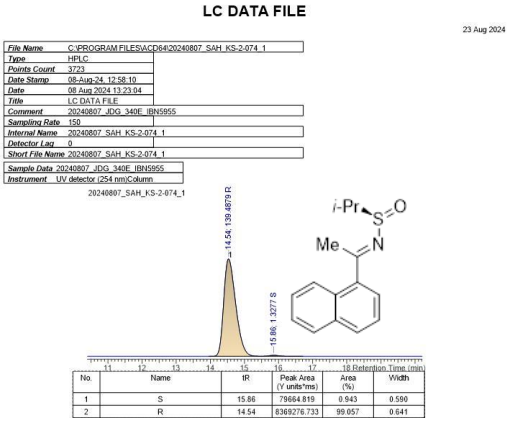
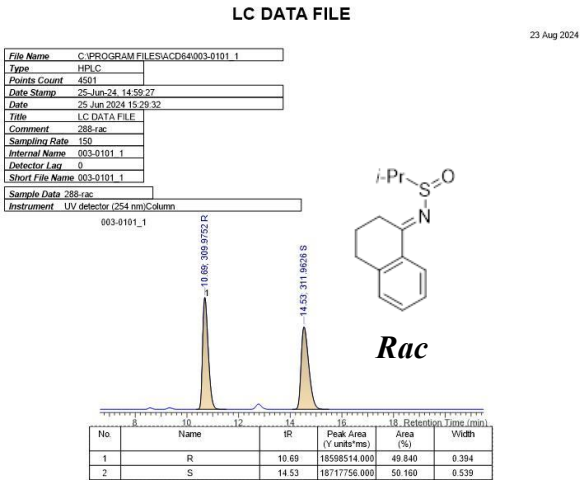


Figure S51. HPLC Data for **(*R*)-12j**



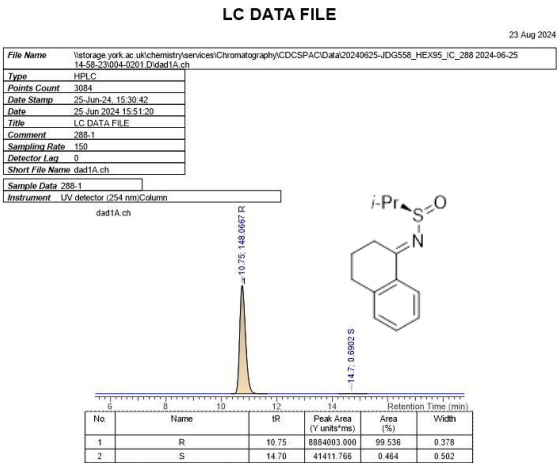
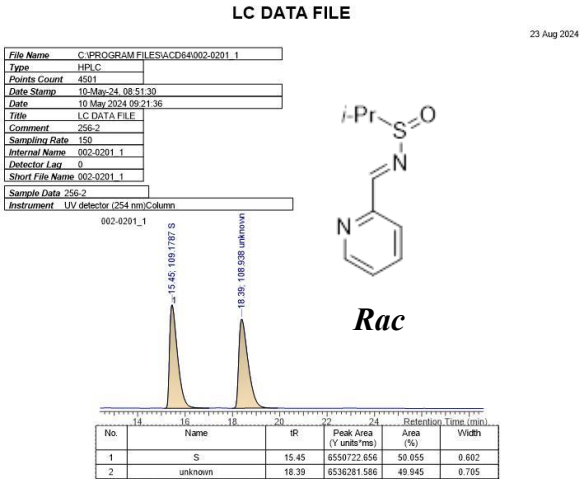


Figure S52. HPLC Data for **(*R*)-12k**



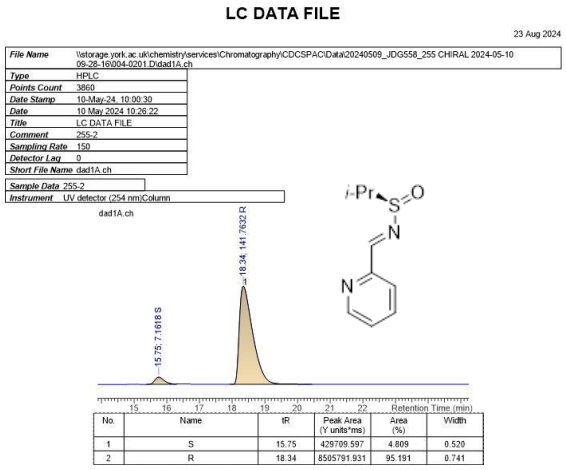
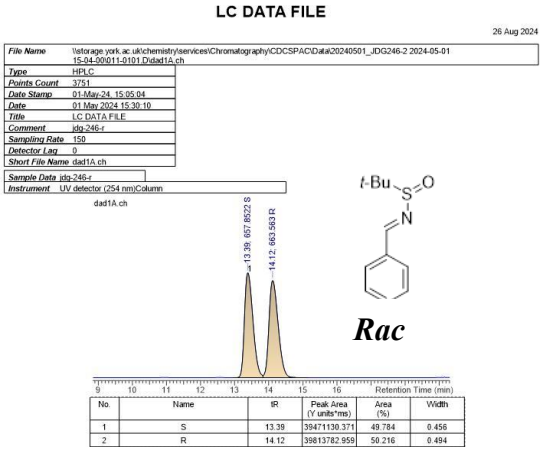


Figure S53. HPLC Data for **(*R*)-12l**



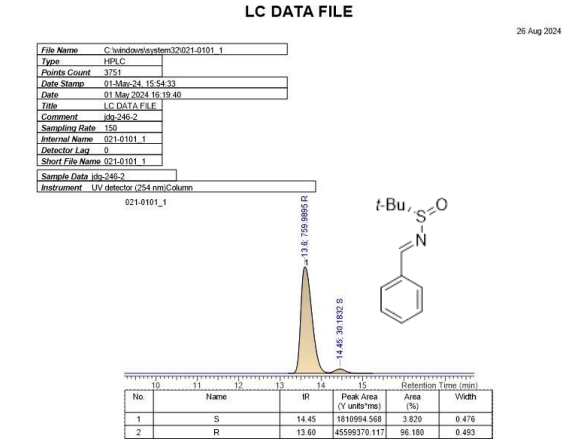
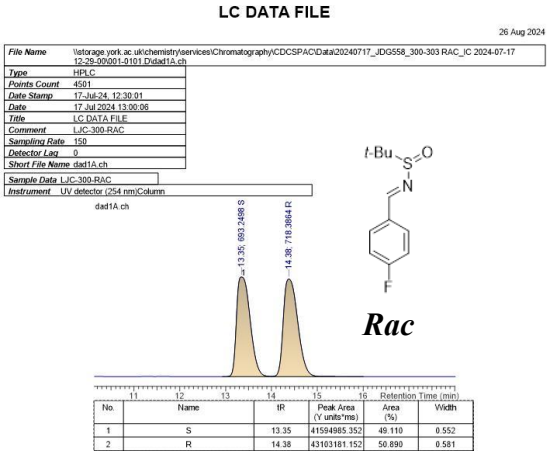


Figure S54. HPLC Data for **(*S*)-13a**



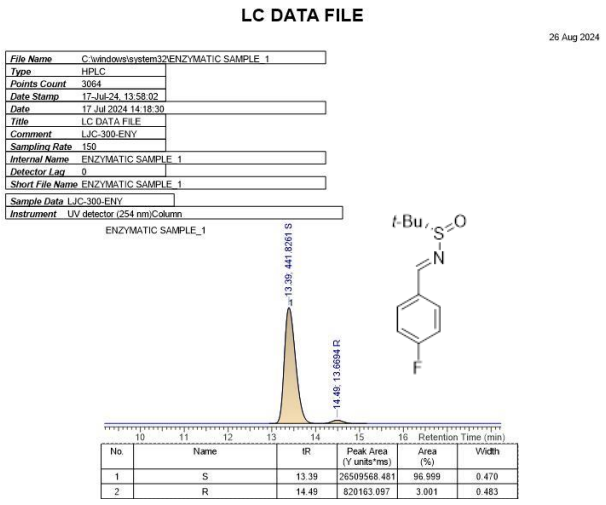
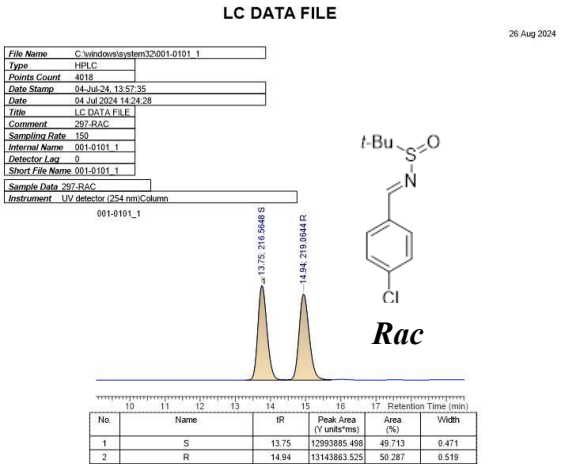


Figure S55. HPLC Data for **(*S*)-13b**



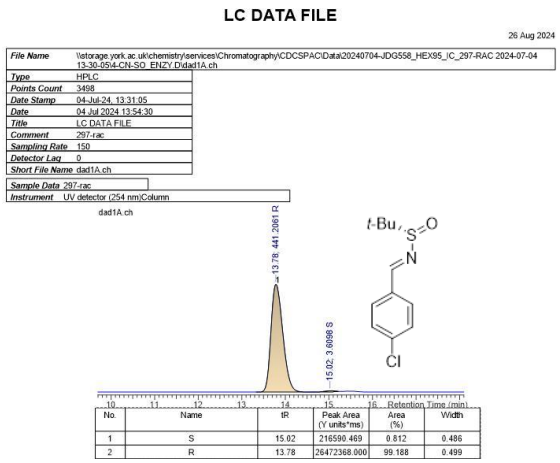
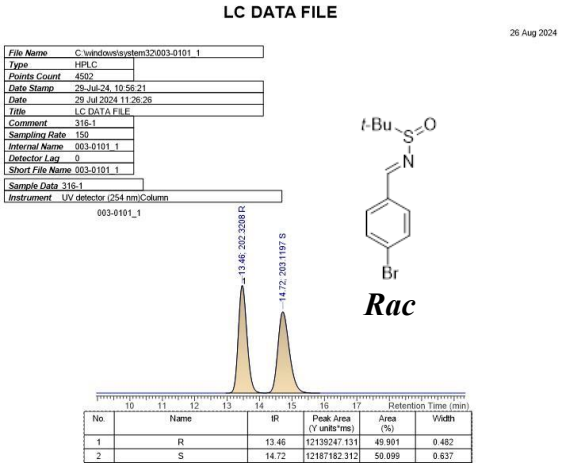


Figure S56. HPLC Data for **(*S*)-13c**



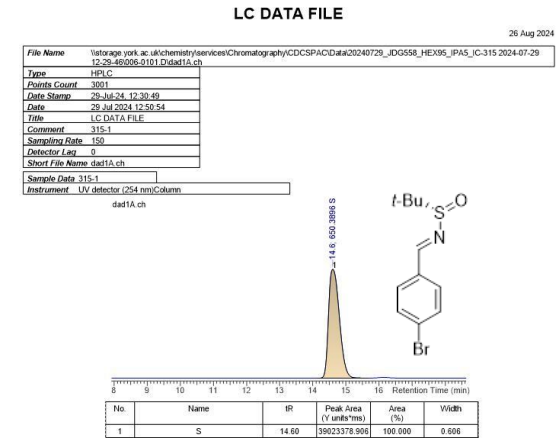
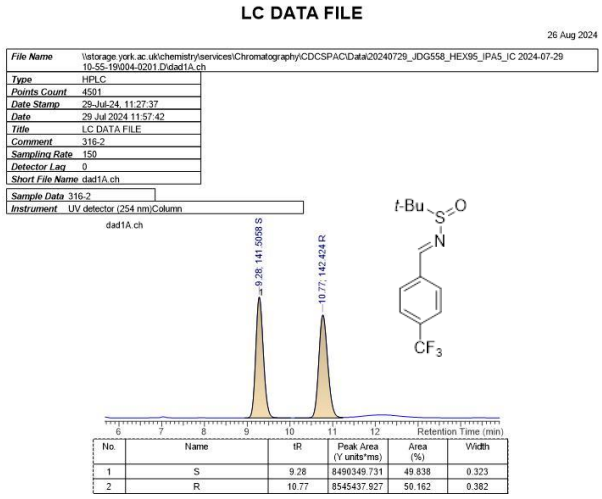


Figure S57. HPLC Data for **(*S*)-13d**



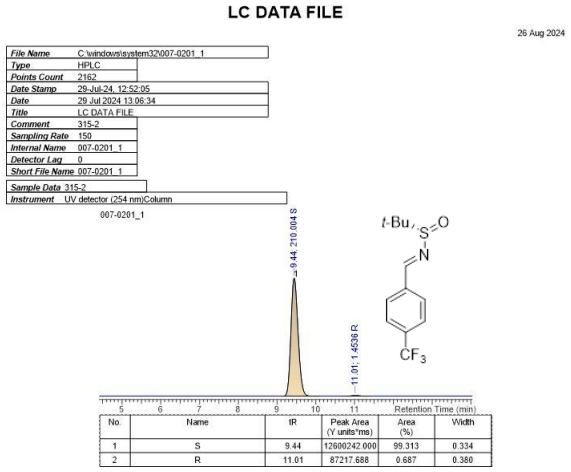
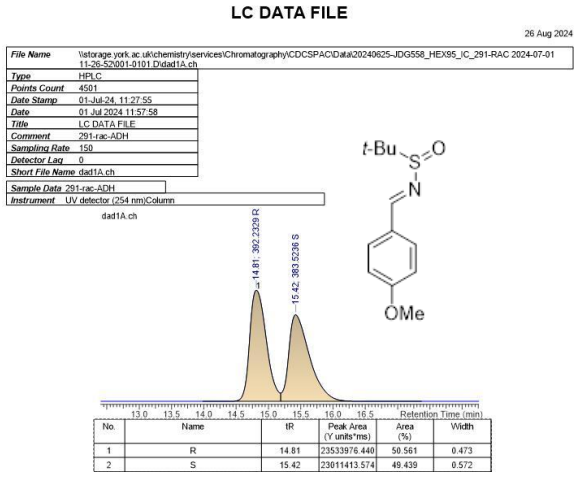


Figure S58. HPLC Data for **(*S*)-13e**



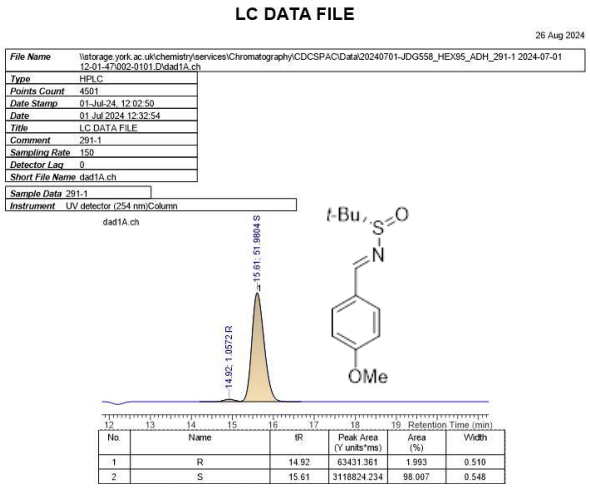
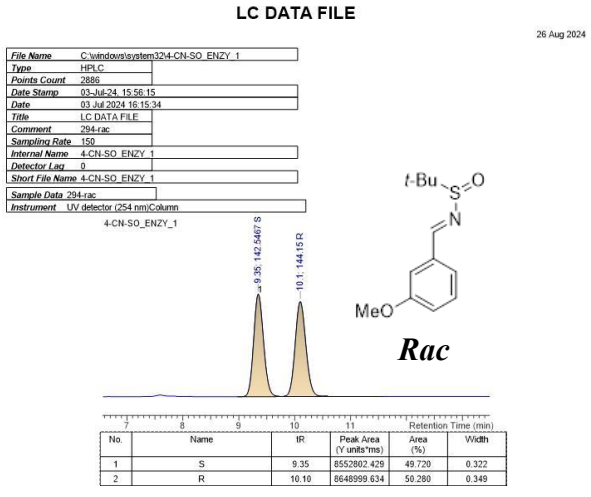


Figure S59. HPLC Data for **(*S*)-13f**



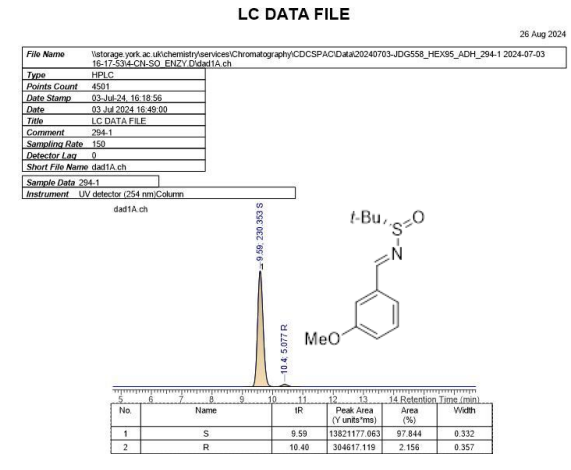
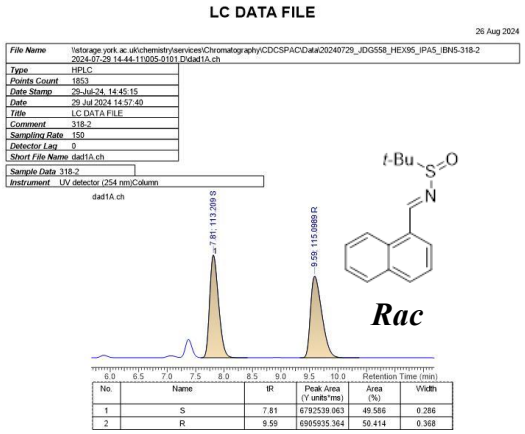


Figure S60. HPLC Data for**(*S*)-13g**



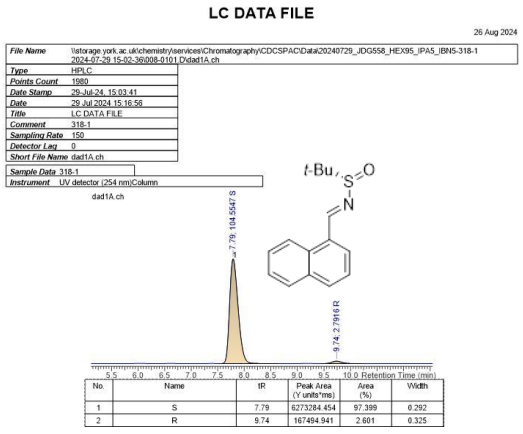
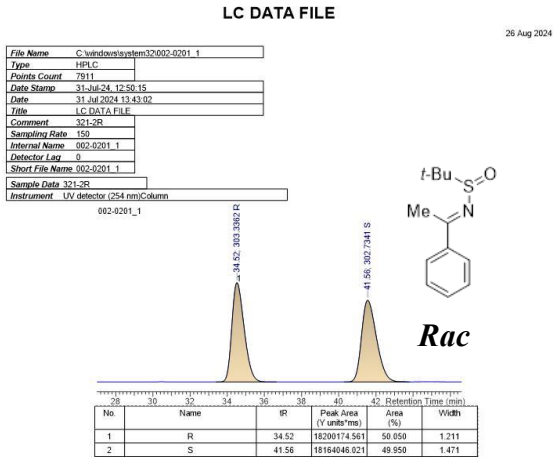


Figure S61. HPLC Data for **(*S*)-13h**



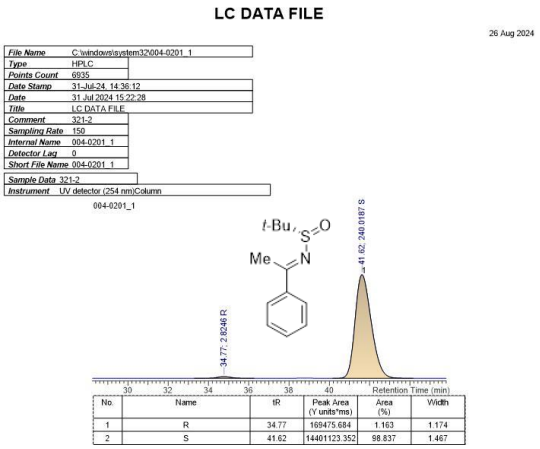
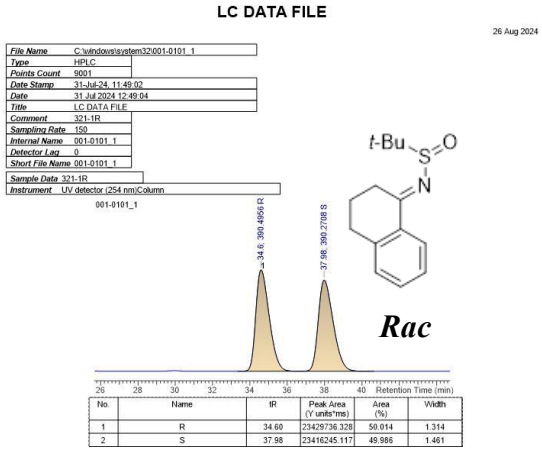


Figure S62. HPLC Data for **(*S*)-13i**



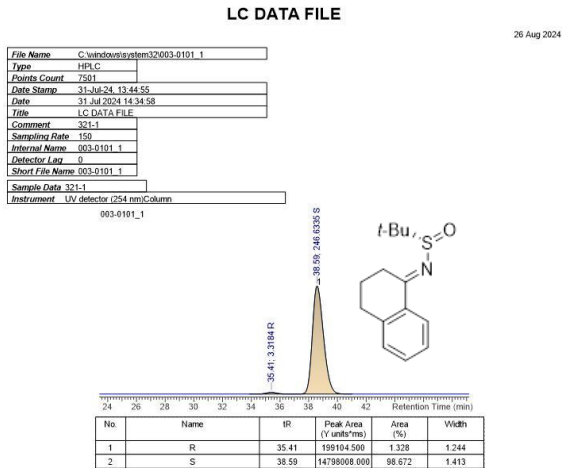
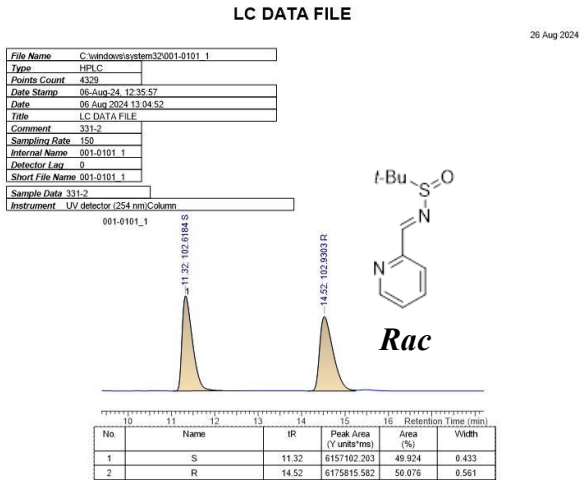


Figure S63. HPLC Data for **(*S*)-13k**



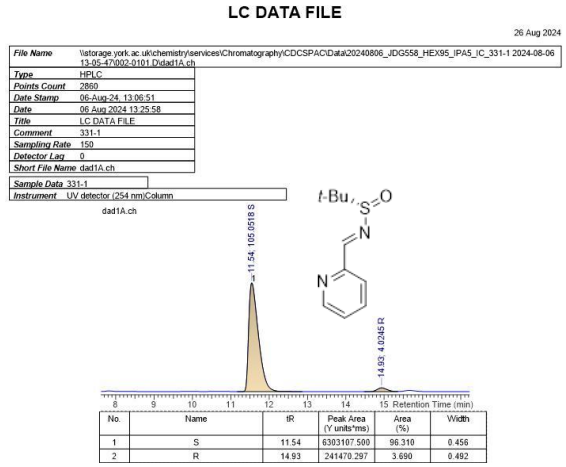
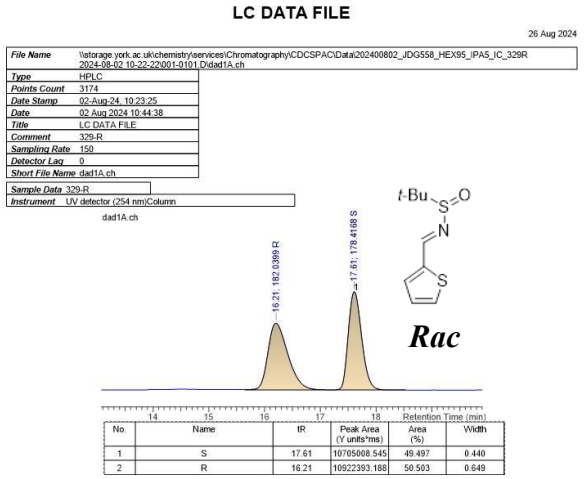


Figure S64. HPLC Data for **(*S*)-13l**



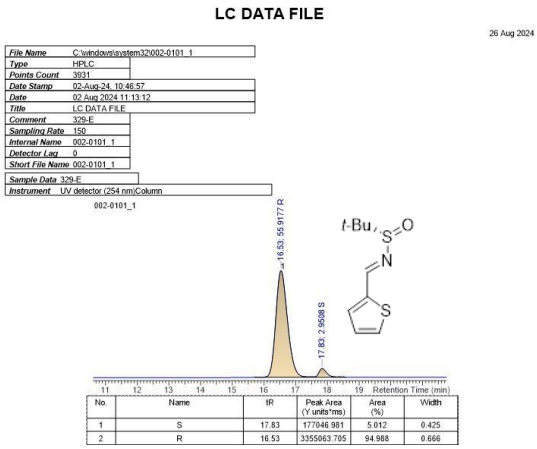
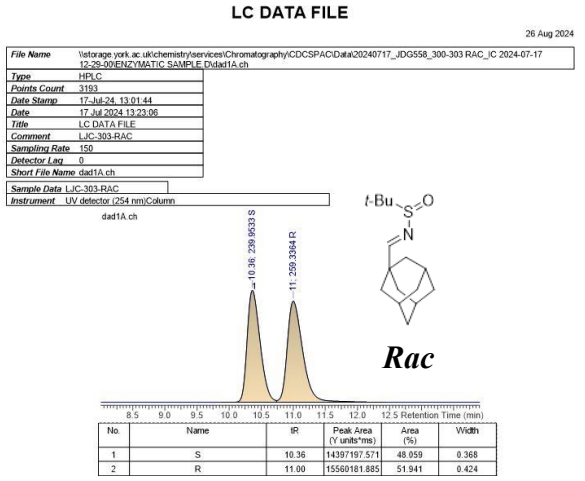


Figure S65. HPLC Data for **(*S*)-13m**



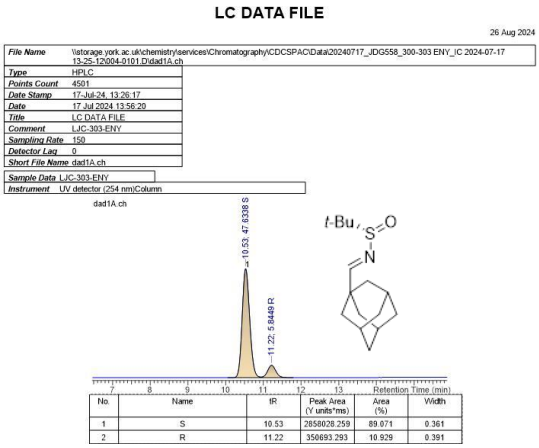
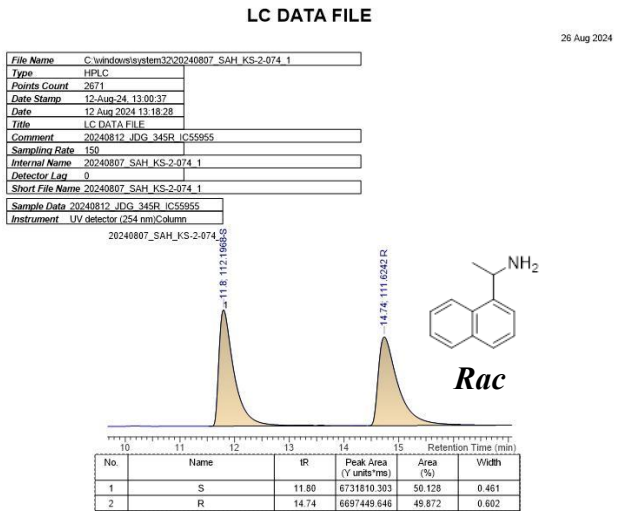


Figure S66. HPLC Data for **(*S*)-13n**



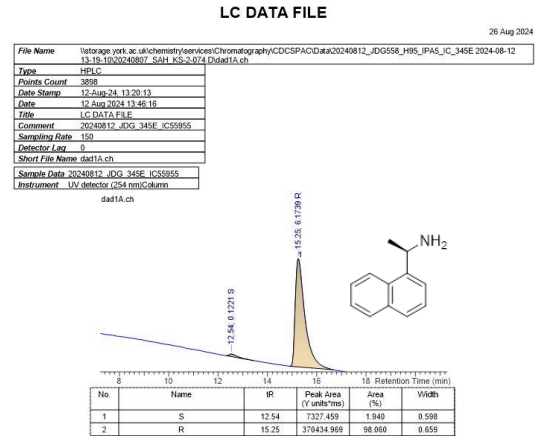
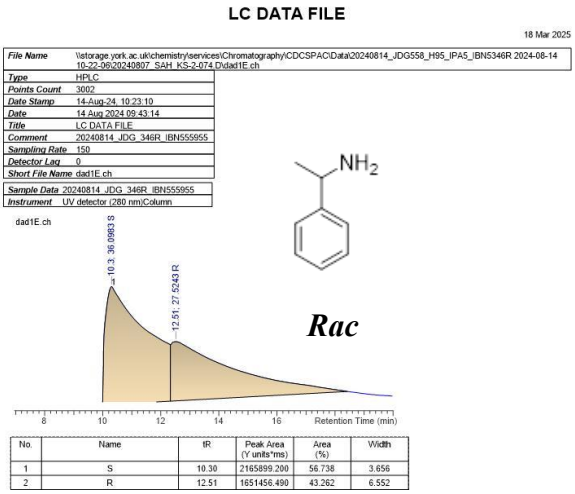


Figure S67. HPLC Data for **14**



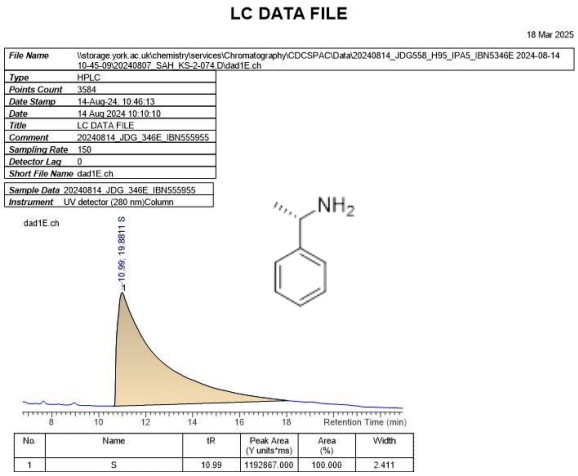


Figure S68. HPLC Data for **18**

6) Molecular Docking

Automated docking was performed using AUTODOCK VINA 1.1.2.[33] Coordinates for the ligands (*R*)-**4e** and **6** were prepared using ELBOW[34] in PHENIX.[35] The appropriate pdbqt files for the models of artUPO and r*Aae*UPO-Pada-I-H and the ligands were prepared in AUTODOCK Tools from structures with PDB codes 7ZNM[32] and 6EL0[36] respectively and into each of which had been modelled heme with Compound I from P450 structure 1DZ9.[37] The active site of artUPO was contained in a grid size of 34 Å × 34 Å × 34 Å (corresponding to x, y, z) with 1 Å spacing, centred around the catalytic centre at positions -2.55 Å × 5.28 Å × -27.21 Å (corresponding to x, y, z). The active site of r*Aae*UPO-PaDa-I was contained in grid sizes of 34 Å × 34 Å × 34 Å (corresponding to x, y, z) with 1 Å spacing, centred around the catalytic centre at positions -2.26 Å × 4.29 Å × -25.20 Å (corresponding to x, y, z). These values were generated using AutoGrid in the AUTODOCK Tools interface. The dockings were performed by VINA, therefore the posed dockings were below 2 Å r.m.s.d. The results generated by VINA were visualised in AUTODOCK Tools 1.5.6 where the ligand conformations were assessed based upon lowest VINA energy. Figure SXA shows the active site of artUPO with substrate (*R*)-**4e**; Figure SXB shows a superimposition of the active sites of artUPO and r*Aae*UPO-PaDa-I-H with substrate **6**.

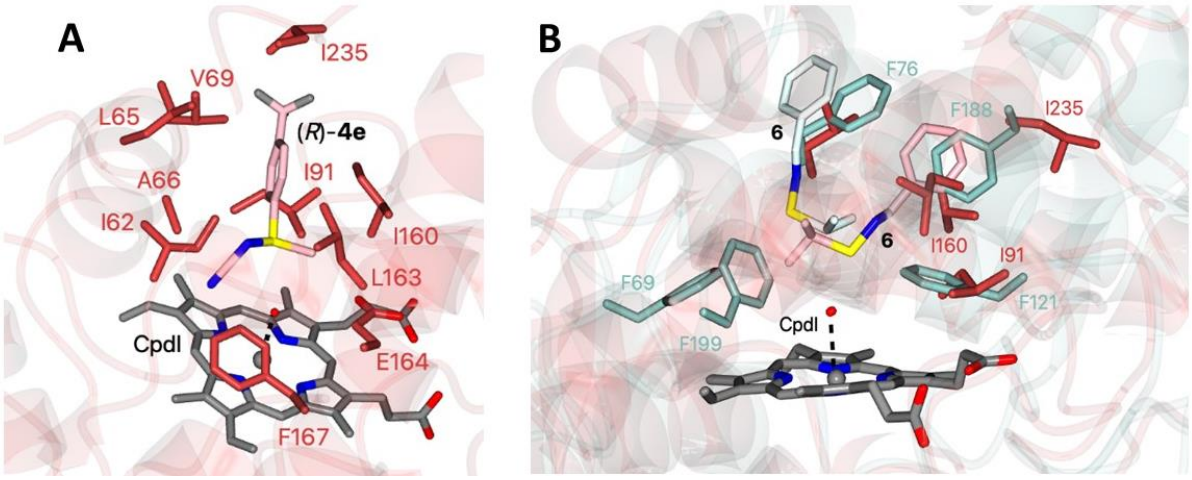
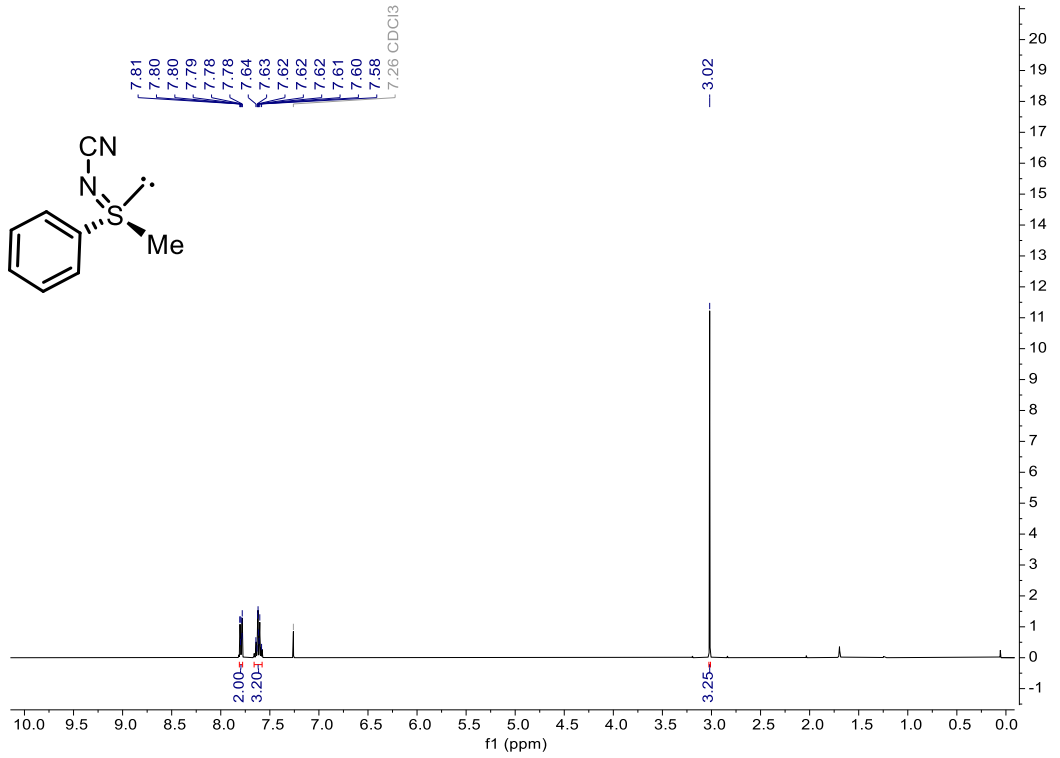
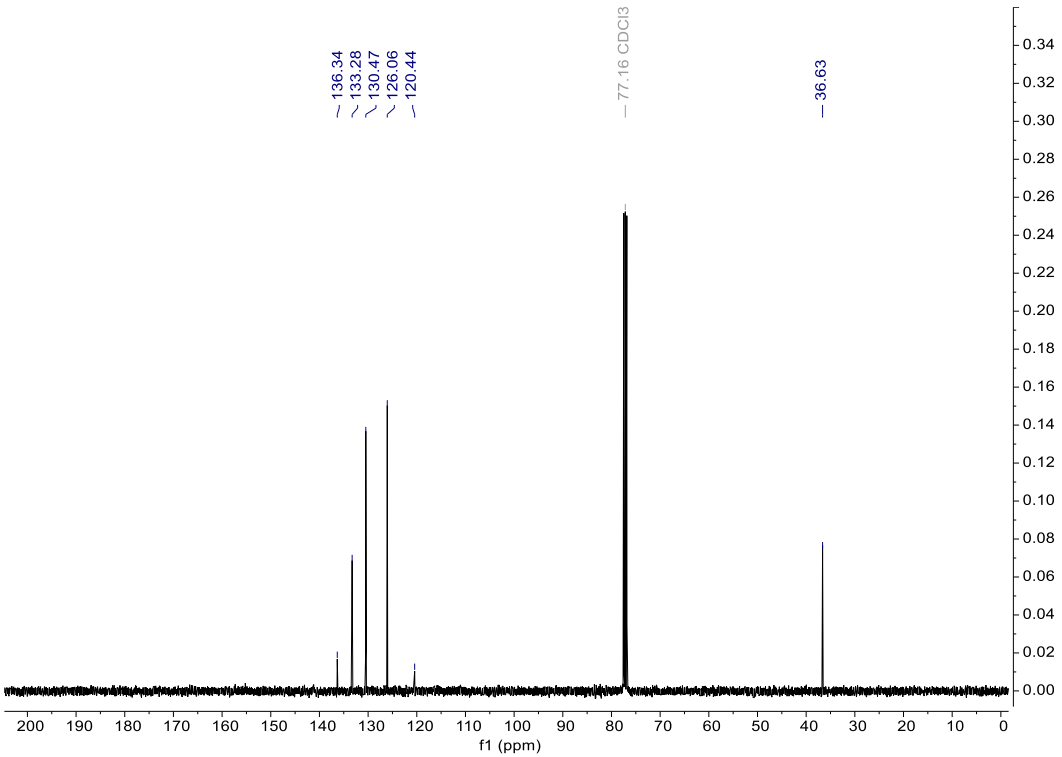


Figure S69. A. Active site of artUPO (from 7ZNM; carbon atoms in red) with (*R*)-**4e** modelled using Autodock VINA.[33] **B**. Superimposition of active sites of artUPO (from 7ZNM; carbon atoms in red) and *Aae*UPO-PaDa-I (from 6EL0; blue) with **6** (pink for artUPO and light blue for *Aae*UPO-PaDa-I) modelled using Autodock VINA.[33]

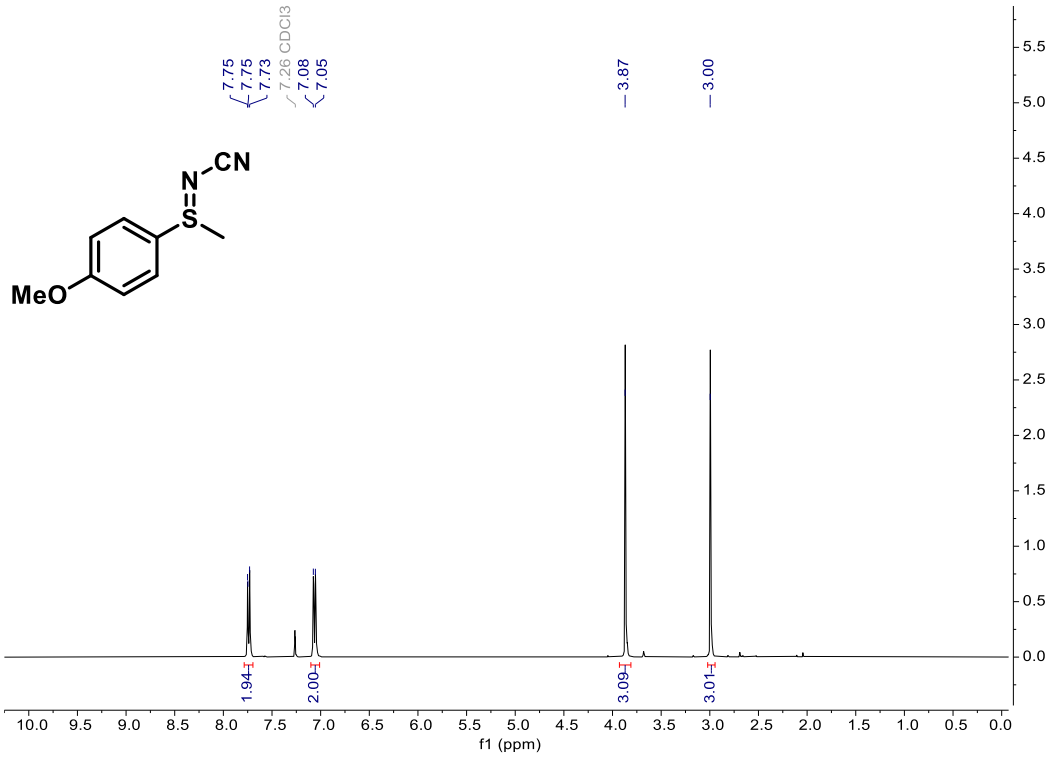
7) ^{1}H, ^{13}C and ^{19}F NMR spectra

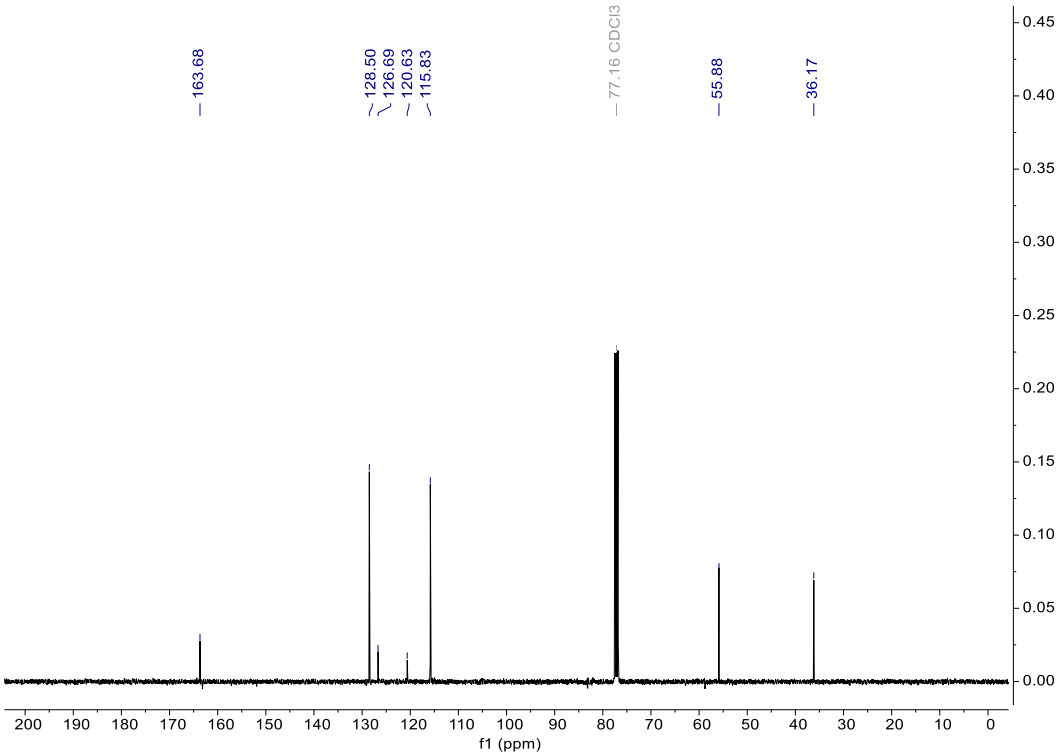
Data for **4a**



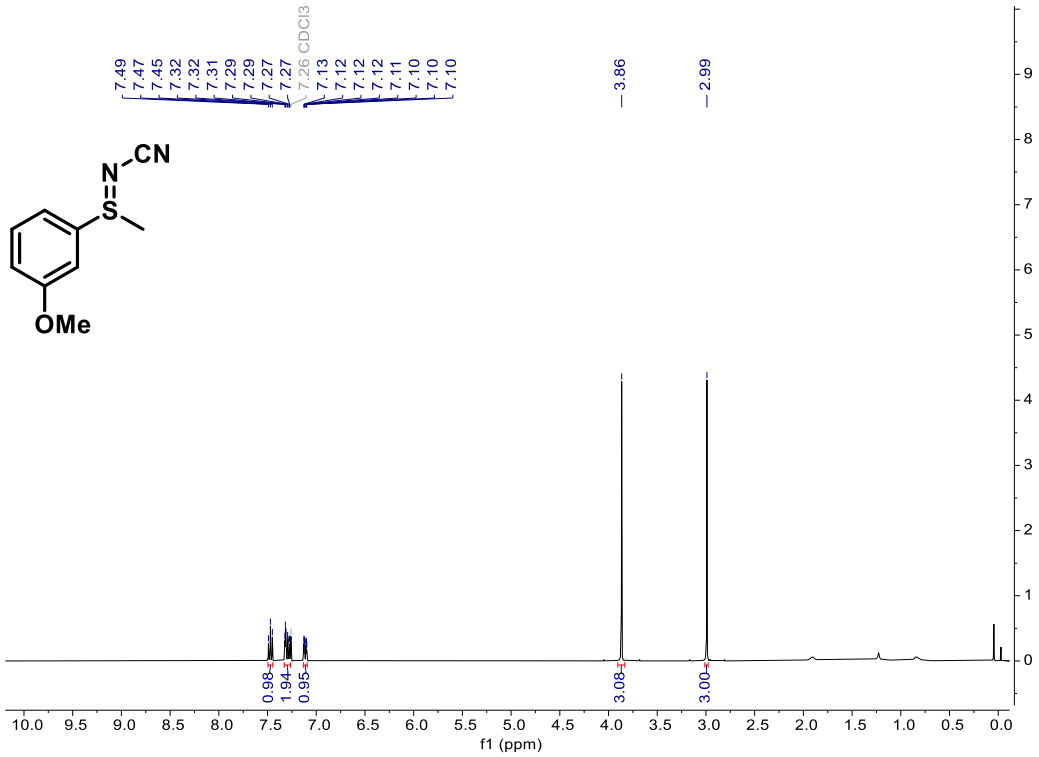


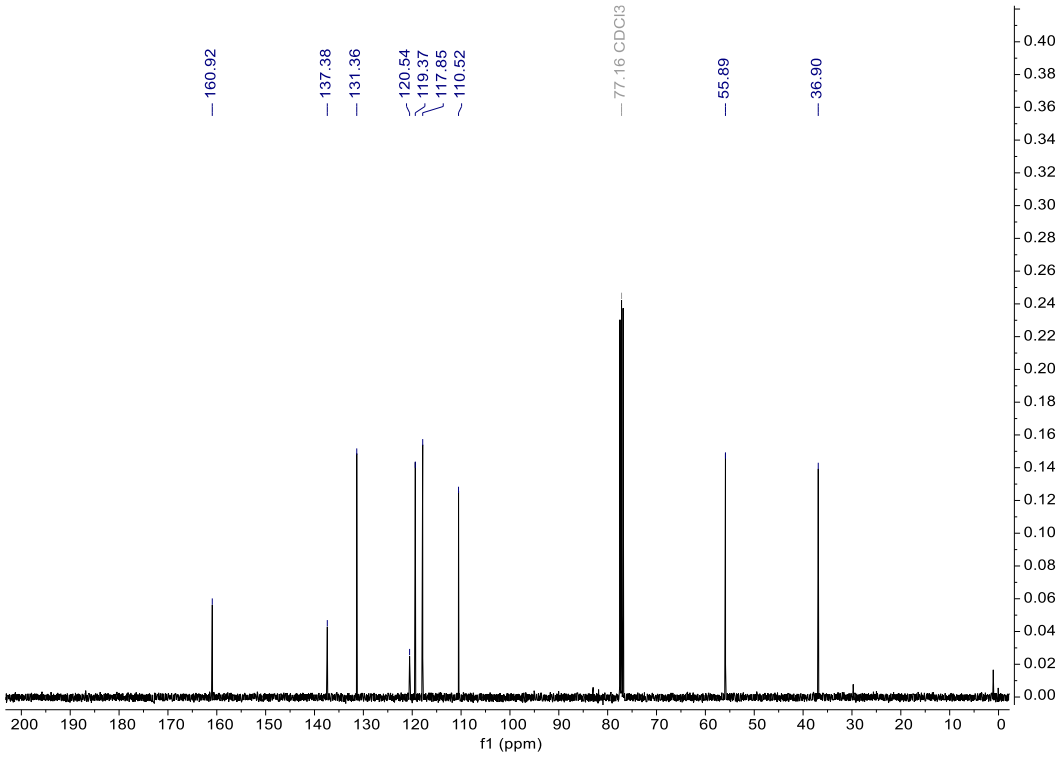
Data for **4b**


7.75
7.75
7.73
7.26 CDCl3
7.08
7.05
3.87
3.00
N
CN
S
MeO
1.94
2.00
3.09
3.01
f1 (ppm)

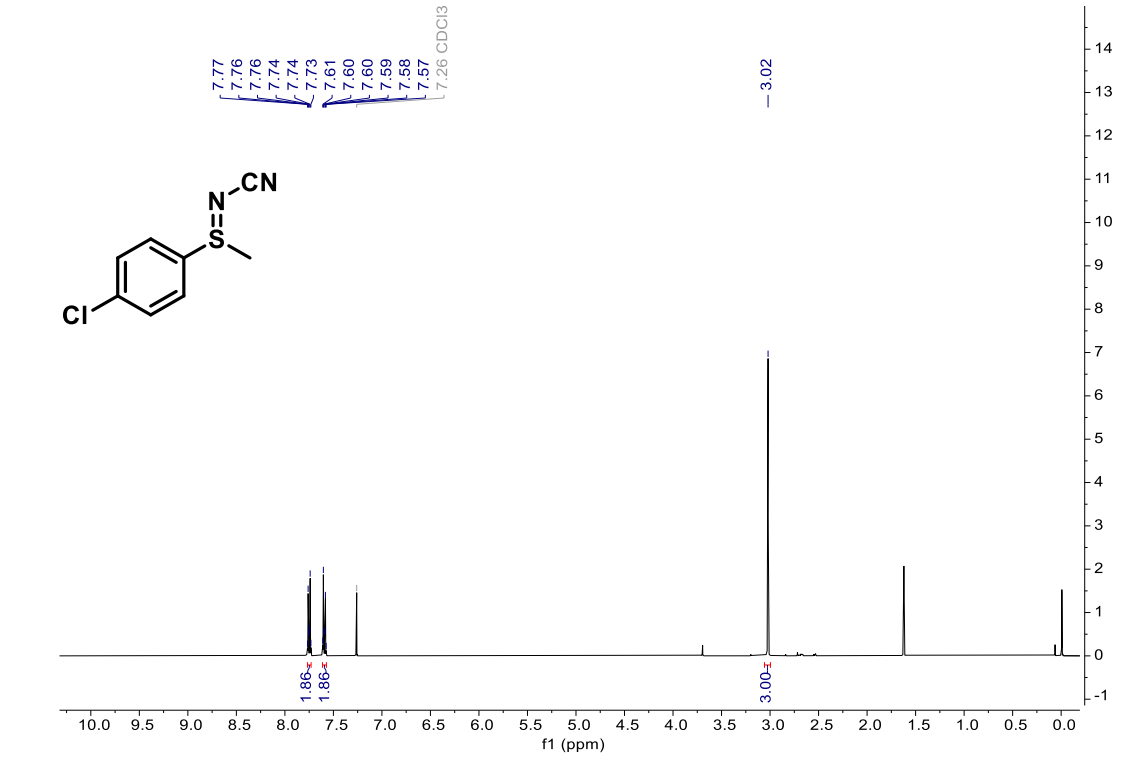

163.68
128.50
126.69
120.63
115.83
77.16 CDCl3
55.88
36.17
f1 (ppm)

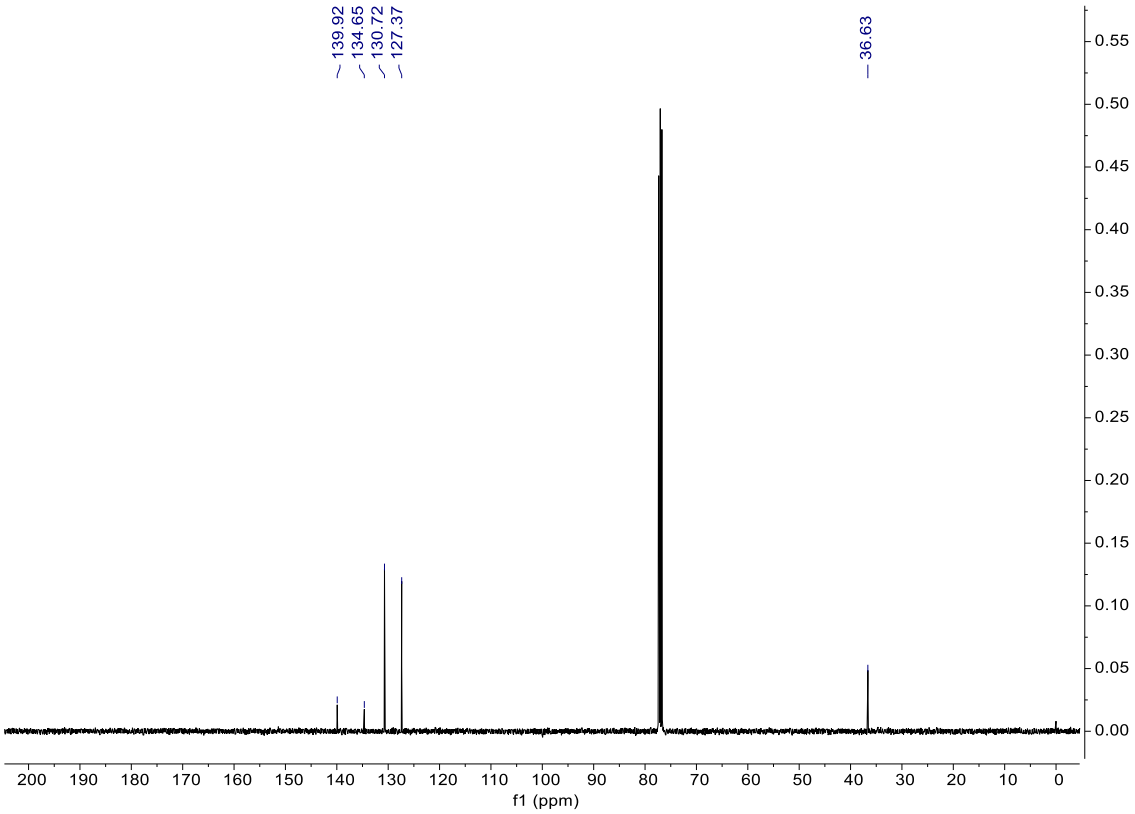
Data for **4c**:


7.49
7.47
7.45
7.32
7.32
7.31
7.29
7.29
7.27
7.27
7.26 CDCl3
7.13
7.12
7.12
7.12
7.11
7.10
7.10
7.10
3.86
2.99
CN
N
S
OMe
0.98
1.94
0.95
3.08
3.00
f1 (ppm)

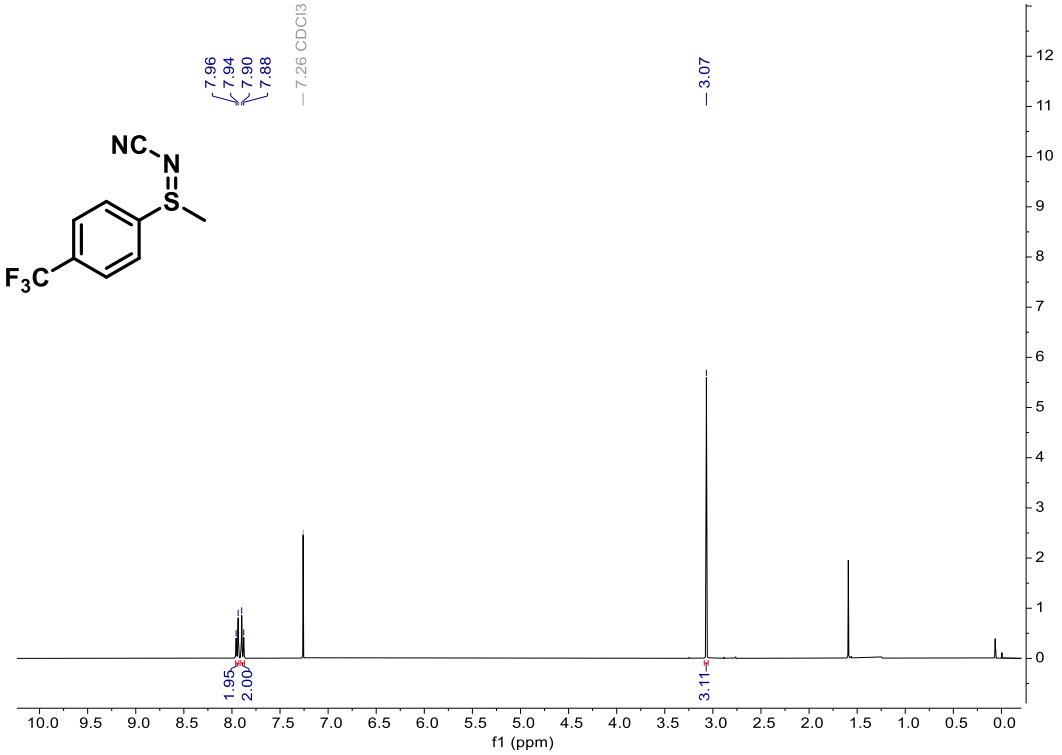

160.92
137.38
131.36
120.54
119.37
117.85
110.52
77.16 CDCl3
55.89
36.90
f1 (ppm)

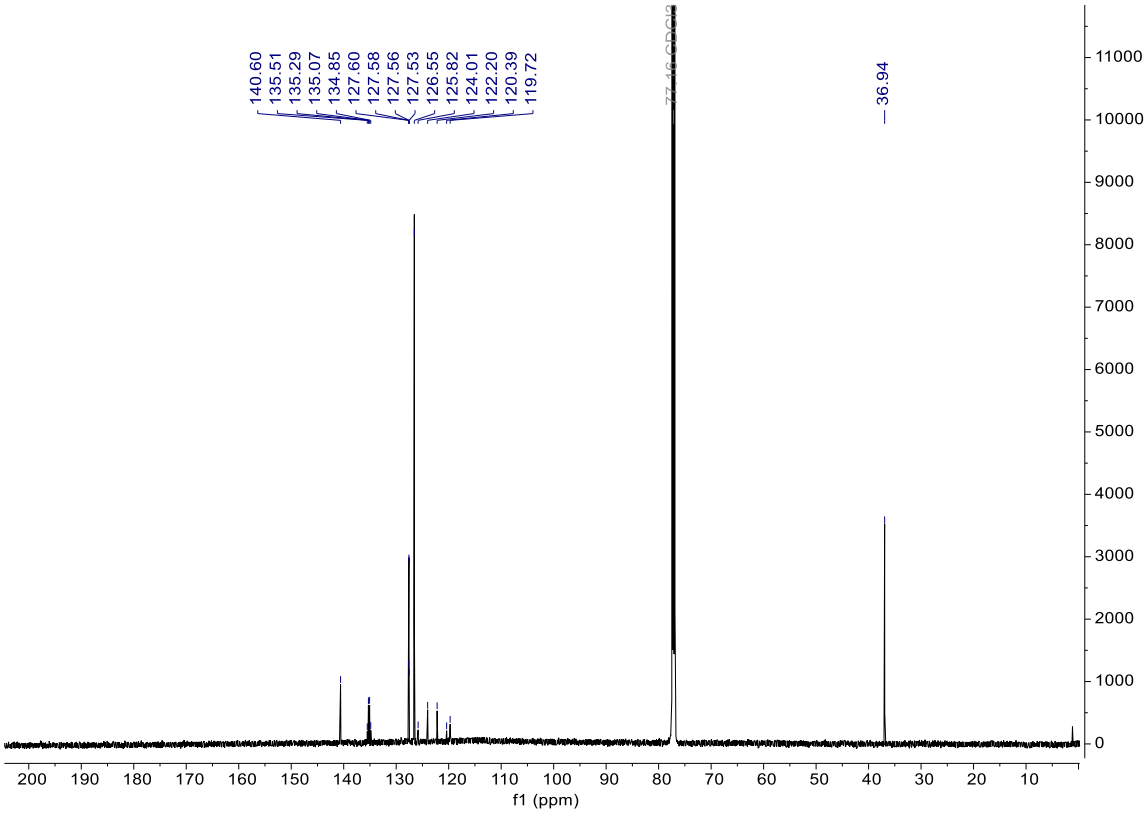
Data for **4d:**


7.77
7.76
7.76
7.74
7.74
7.73
7.61
7.60
7.60
7.59
7.58
7.57
7.26 CDCl3
3.02
CN
N
S
Cl
1.86
1.86
3.00
f1 (ppm)

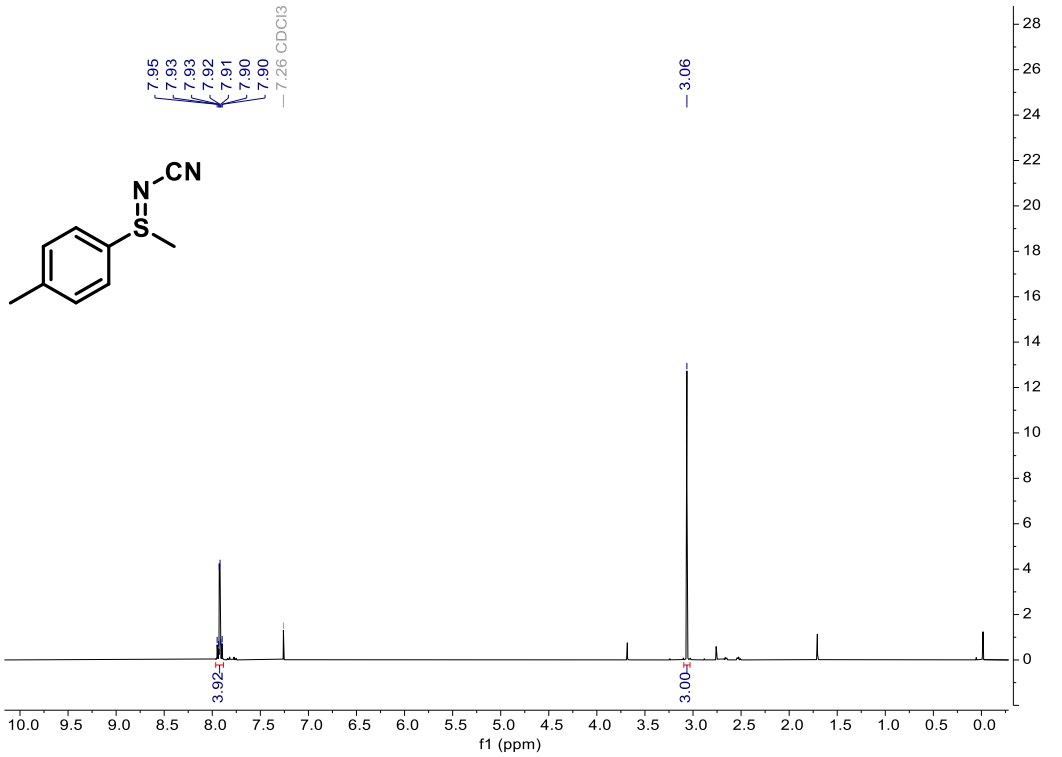

139.92
134.65
130.72
127.37
36.63
f1 (ppm)

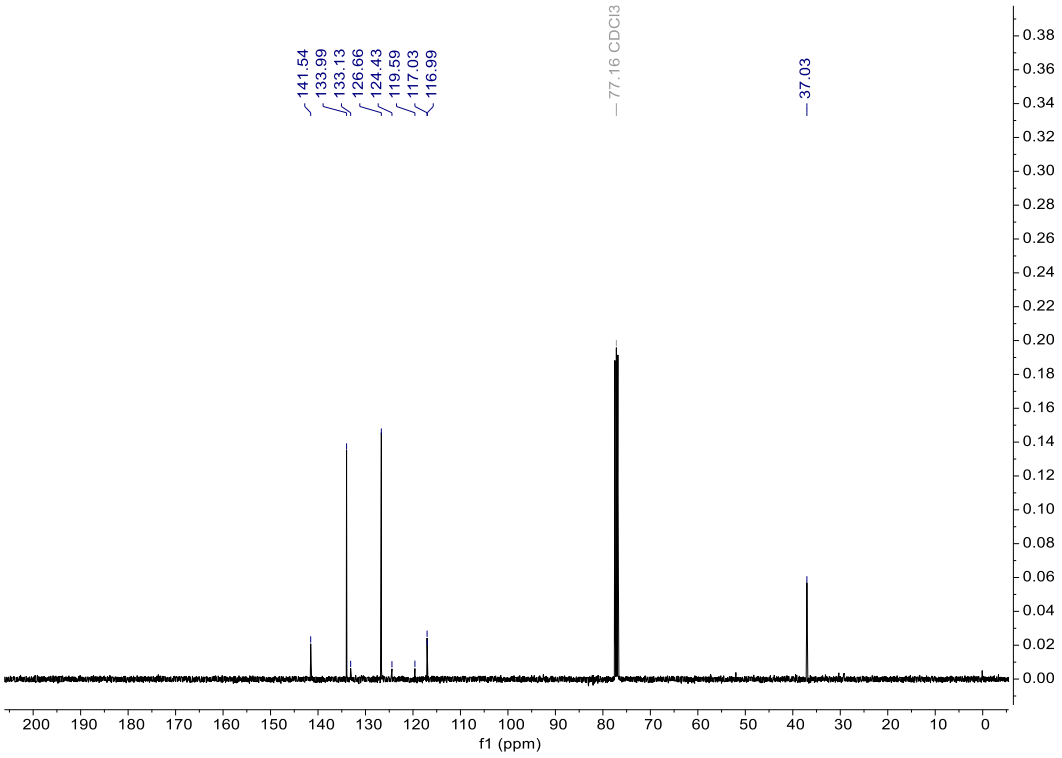
Data for **4e**


7.96
7.94
7.90
7.88
7.26 CDCl3
3.07
NC
N
S
F3C
1.95
2.00
3.11
f1 (ppm)

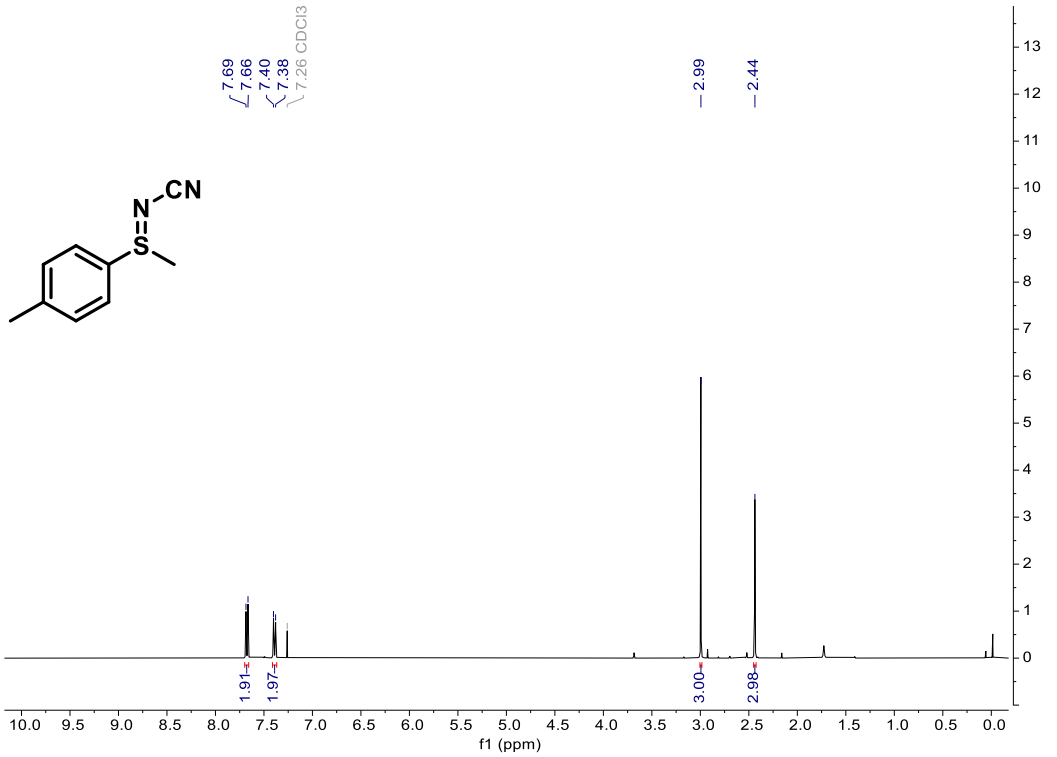

140.60
135.51
135.29
135.07
134.85
127.60
127.58
127.56
127.53
126.55
125.82
124.01
122.20
120.39
119.72
77.16 CDCl3
36.94
f1 (ppm)

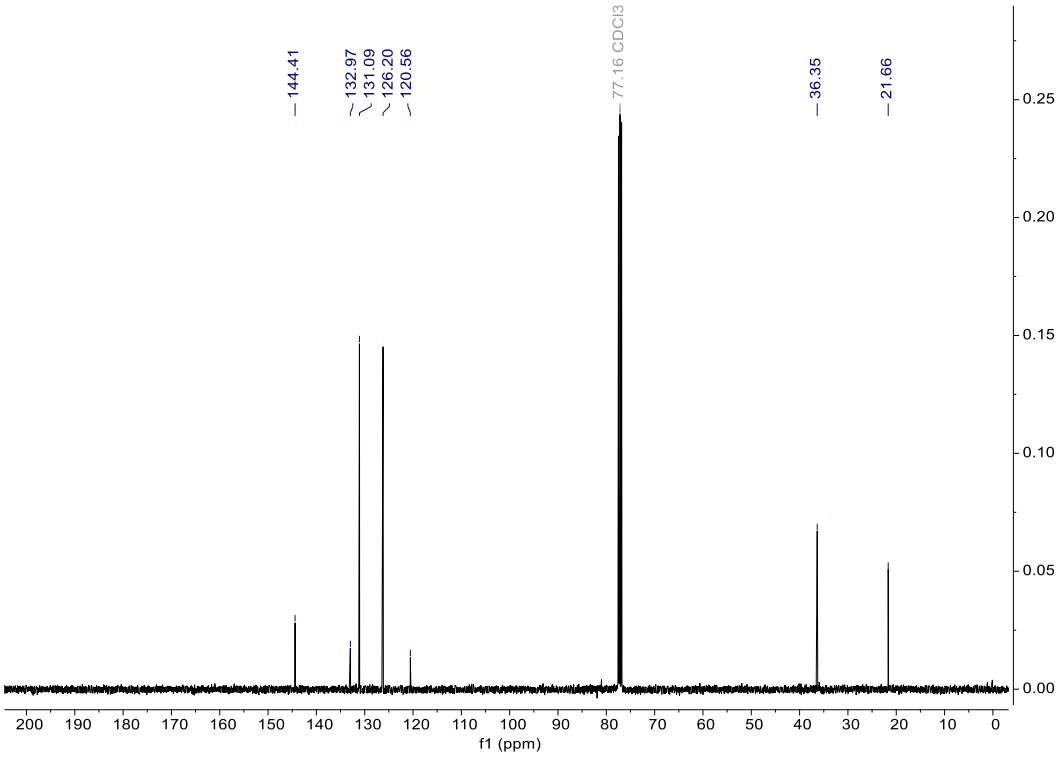
Data for **4f:**


7.95
7.93
7.93
7.92
7.91
7.90
7.90
7.26 CDCl3
3.06
CN
N
S
3.92
3.00
f1 (ppm)

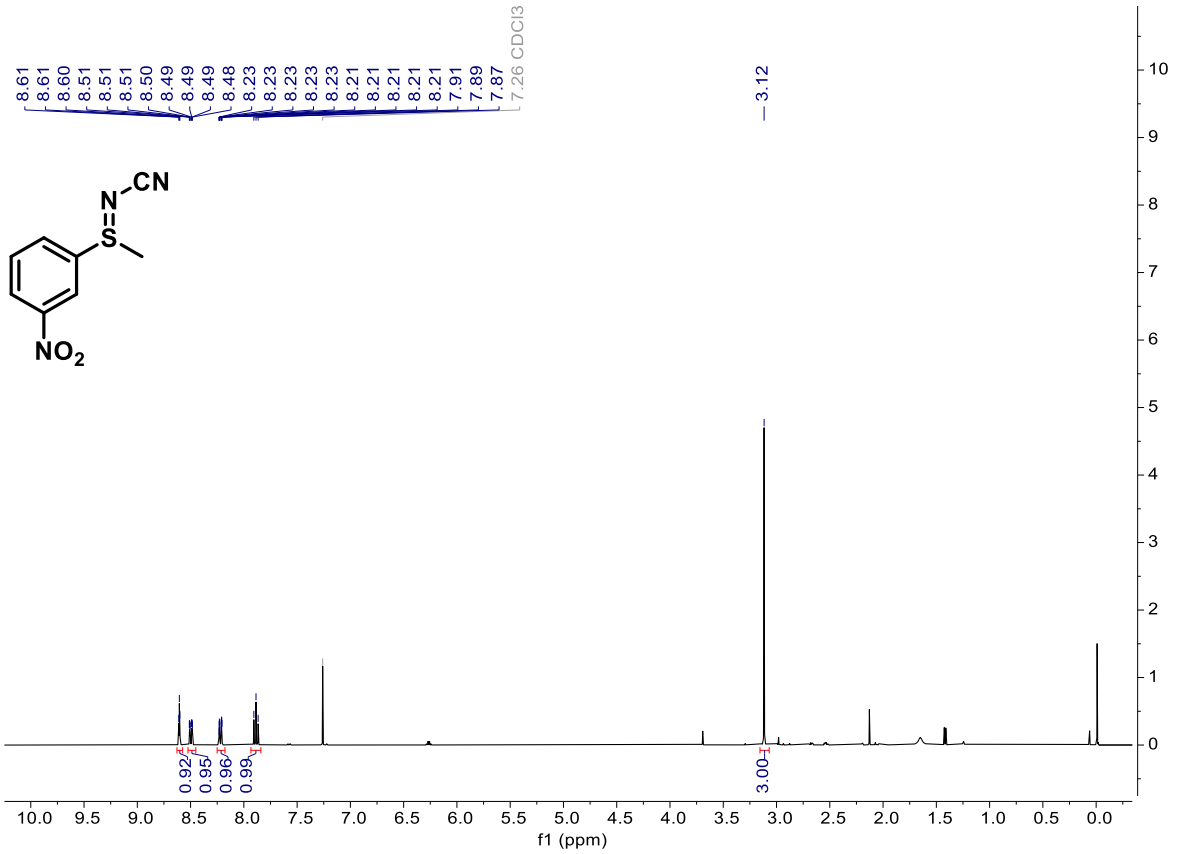

141.54
133.99
133.13
126.66
124.43
119.59
117.03
116.99
77.16 CDCl3
37.03
f1 (ppm)

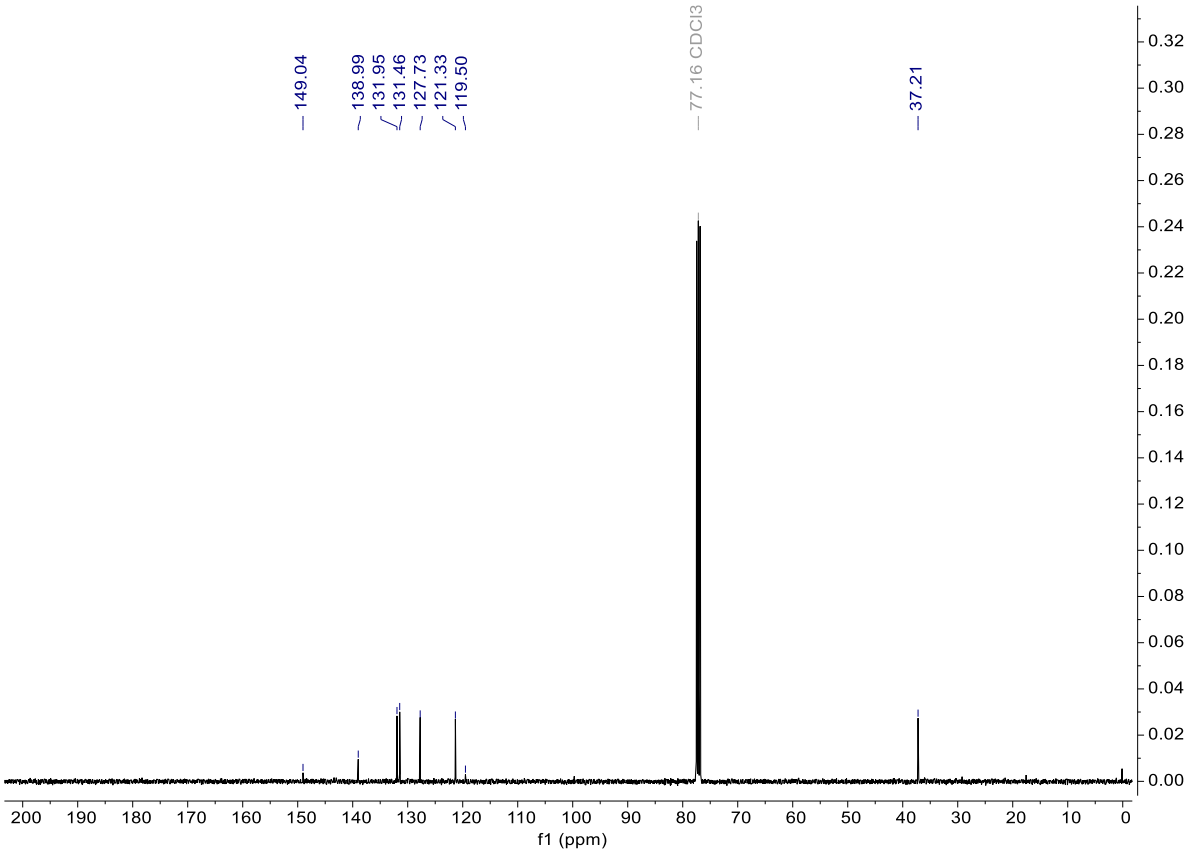
Data for **4g**


7.69
7.66
7.40
7.38
7.26 CDCl3
2.99
2.44
1.91
1.97
3.00
2.98
f1 (ppm)

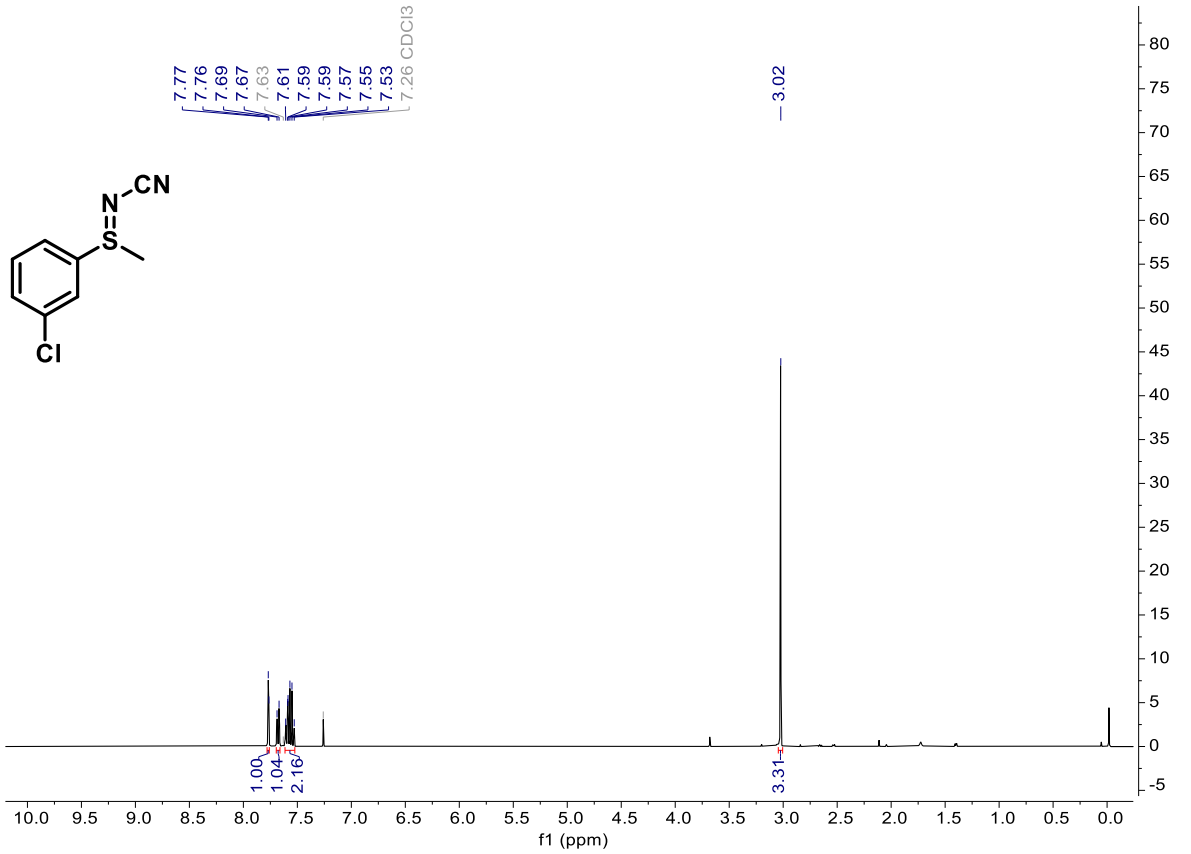

144.41
132.97
131.09
126.20
120.56
77.16 CDCl3
36.35
21.66
f1 (ppm)

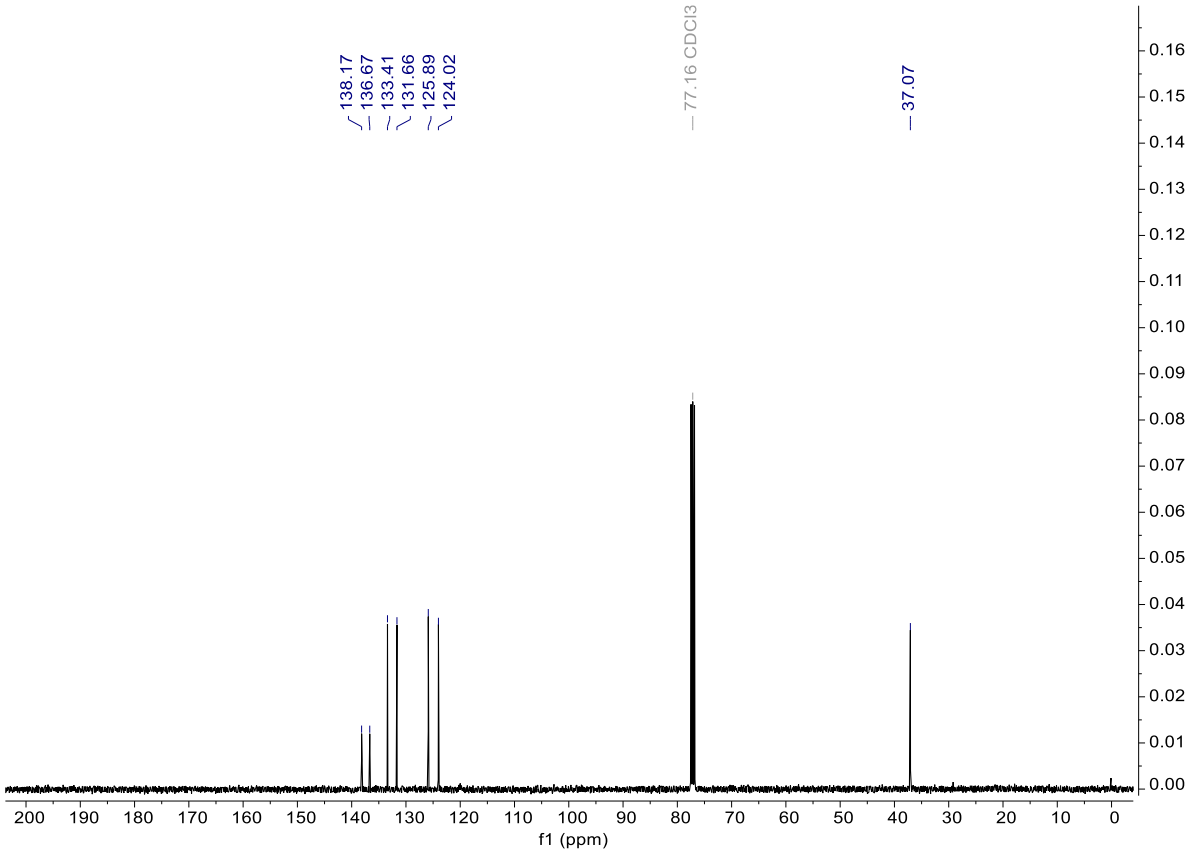
Data for **4h**


8.61
8.61
8.60
8.51
8.51
8.51
8.50
8.49
8.49
8.49
8.48
8.23
8.23
8.23
8.23
8.21
8.21
8.21
8.21
7.91
7.89
7.87
7.26 CDCl3
3.12
CN
N
S
NO2
0.92
0.95
0.96
0.99
3.00
f1 (ppm)

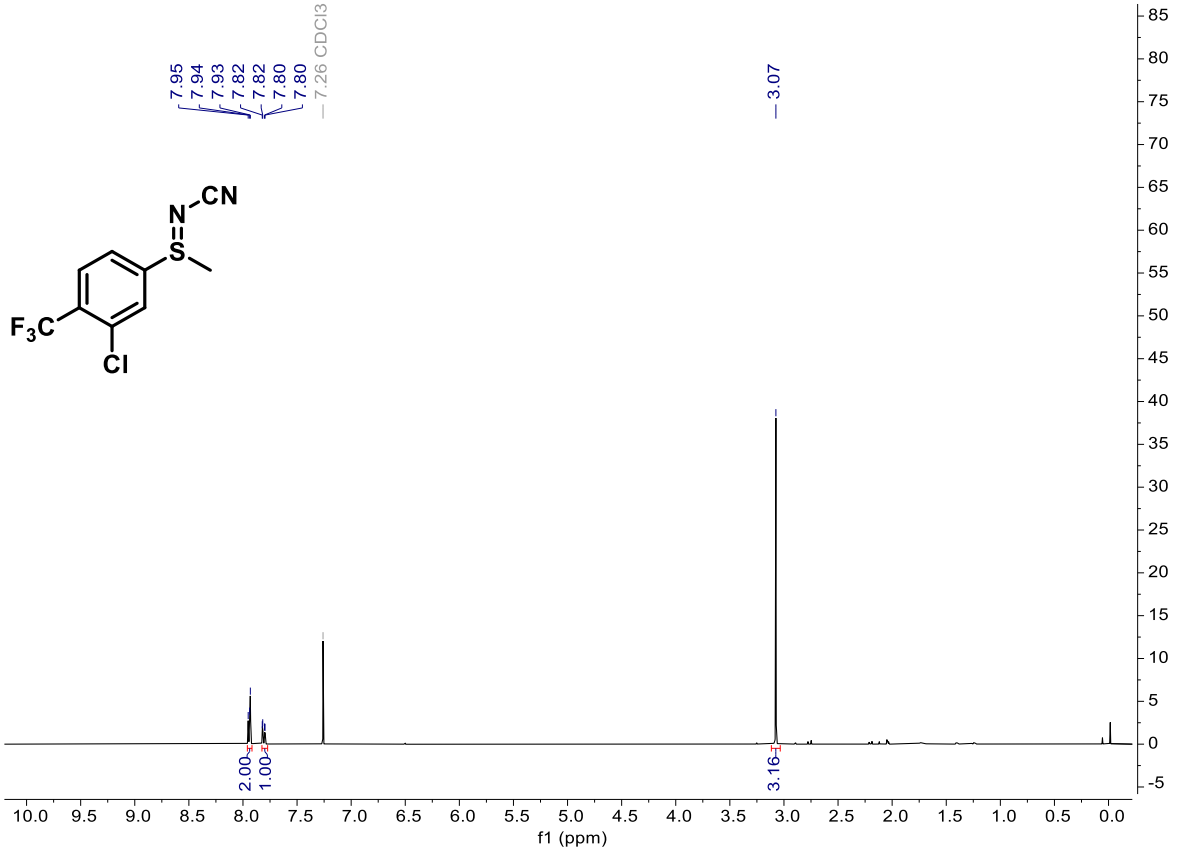

149.04
138.99
131.95
131.46
127.73
121.33
119.50
77.16 CDCl3
37.21
f1 (ppm)

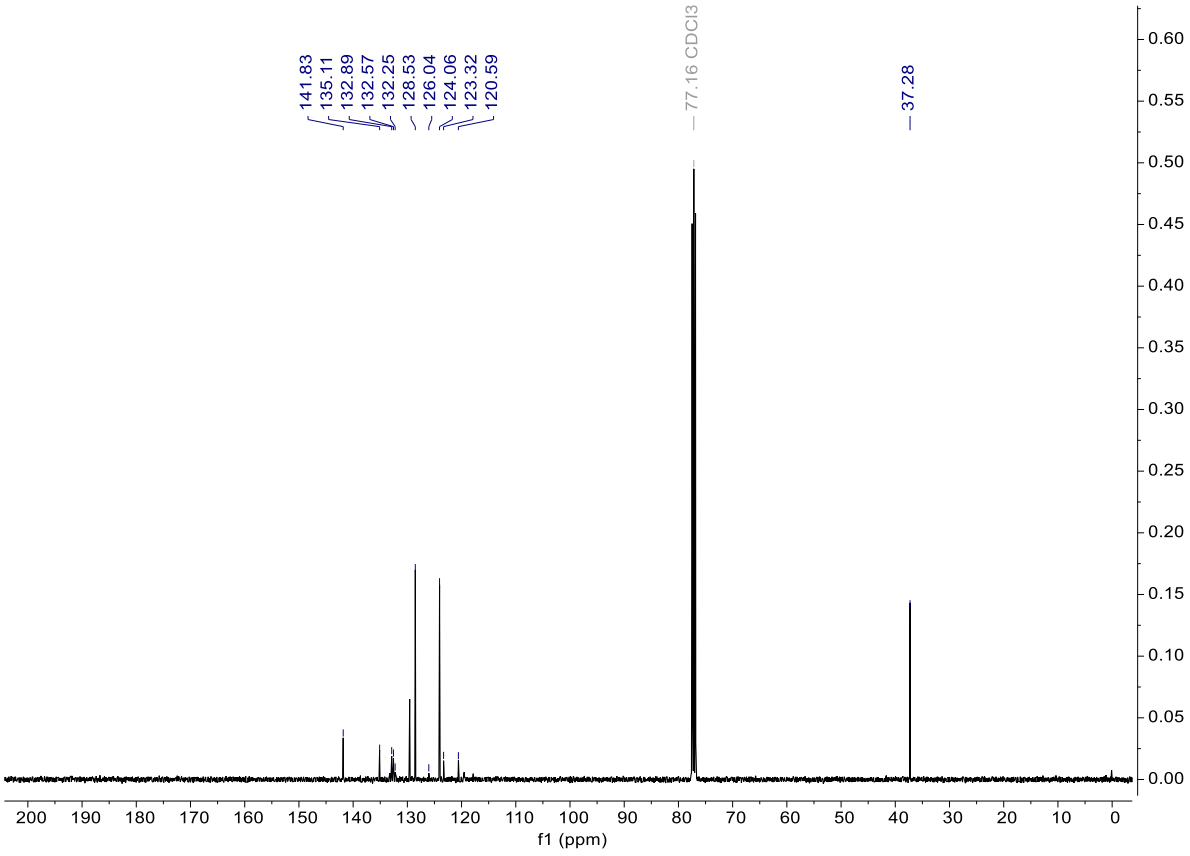
Data for **4i**


7.77
7.76
7.69
7.67
7.63
7.61
7.59
7.59
7.57
7.55
7.53
7.26 CDCl3
3.02
CN
N
S
Cl
1.00
1.04
2.16
3.31
f1 (ppm)

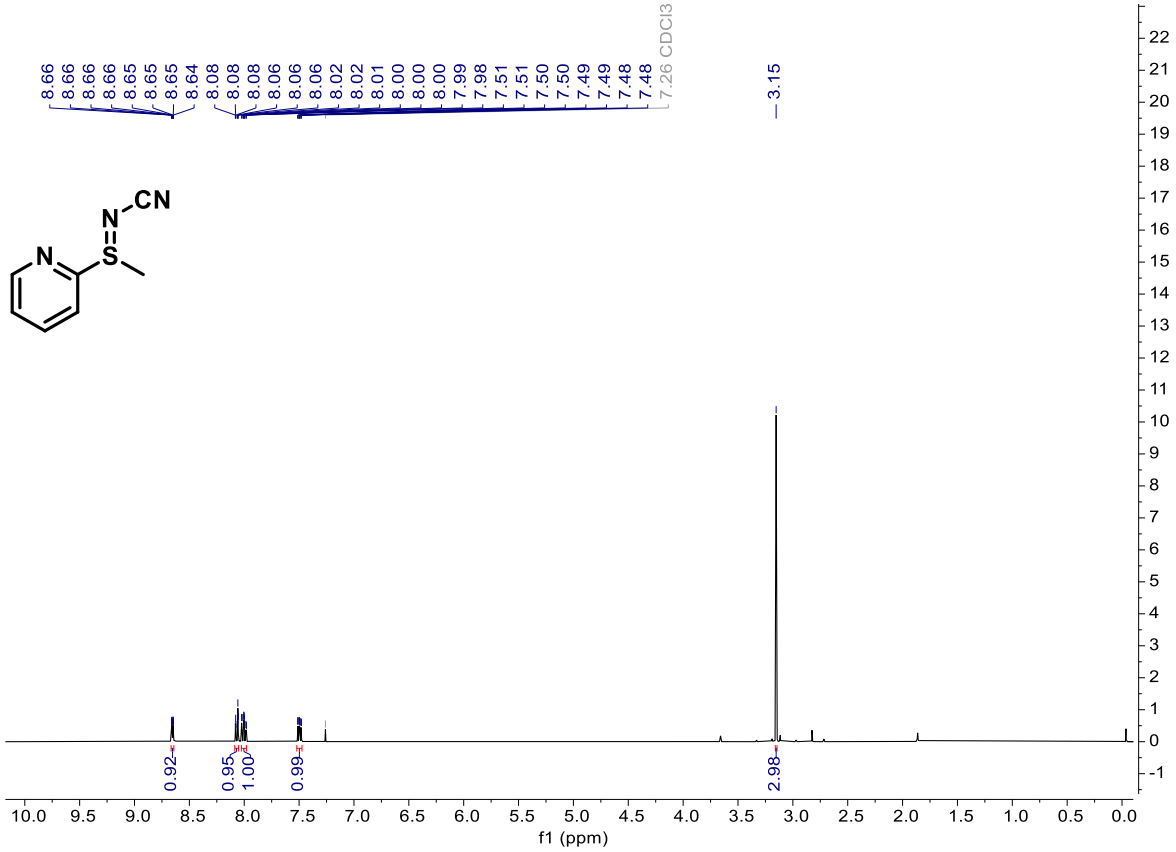

138.17
136.67
133.41
131.66
125.89
124.02
77.16 CDCl3
37.07
f1 (ppm)

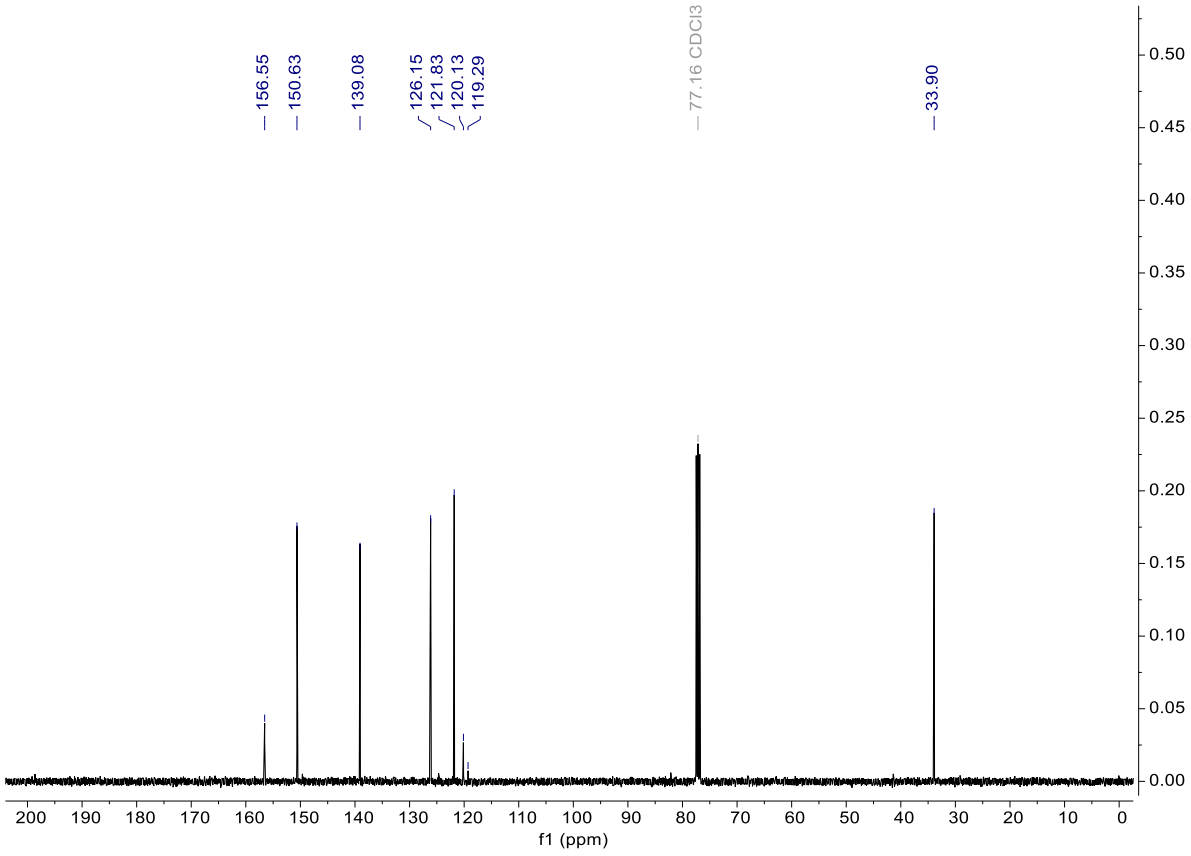
Data for **4j:**


7.95
7.94
7.93
7.82
7.82
7.80
7.80
7.26 CDCl3
3.07
N
CN
S
F3C
Cl
2.00
1.00
3.16
f1 (ppm)

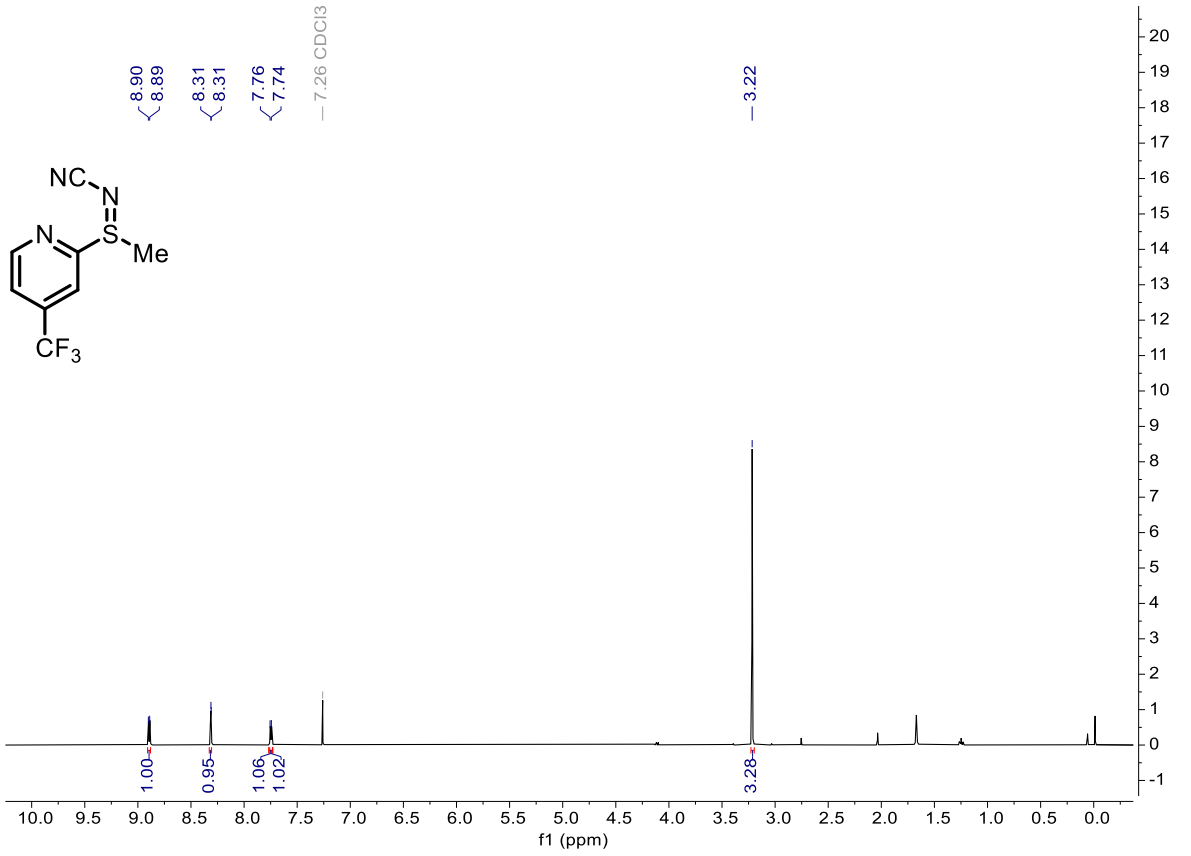

141.83
135.11
132.89
132.57
132.25
128.53
126.04
124.06
123.32
120.59
77.16 CDCl3
37.28
f1 (ppm)

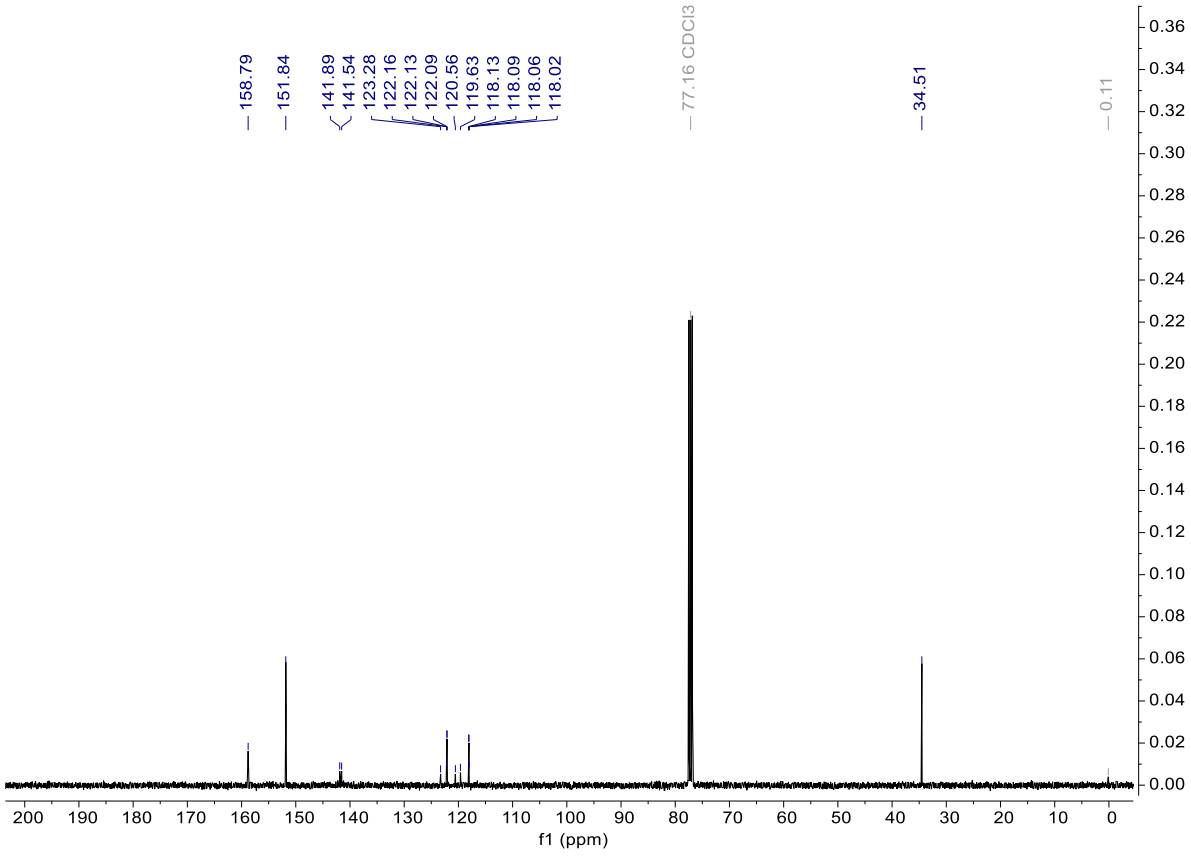
Data for **4k**


8.66
8.66
8.66
8.66
8.65
8.65
8.65
8.64
8.08
8.08
8.08
8.06
8.06
8.06
8.02
8.02
8.01
8.00
8.00
8.00
8.00
7.99
7.98
7.51
7.51
7.50
7.50
7.49
7.49
7.48
7.48
7.26 CDCl3
3.15
CN
N
S
N
0.92
0.95
1.00
0.99
2.98
f1 (ppm)

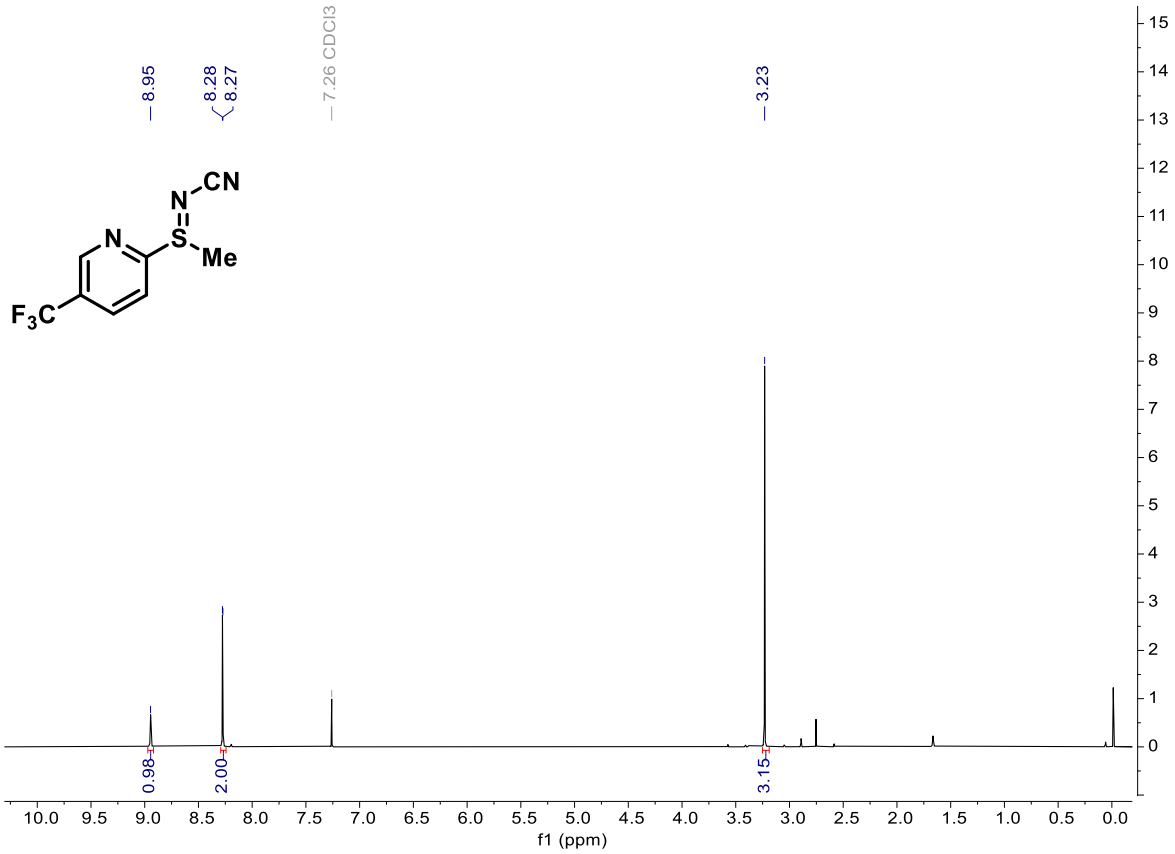

156.55
150.63
139.08
126.15
121.83
120.13
119.29
77.16 CDCl3
33.90
f1 (ppm)

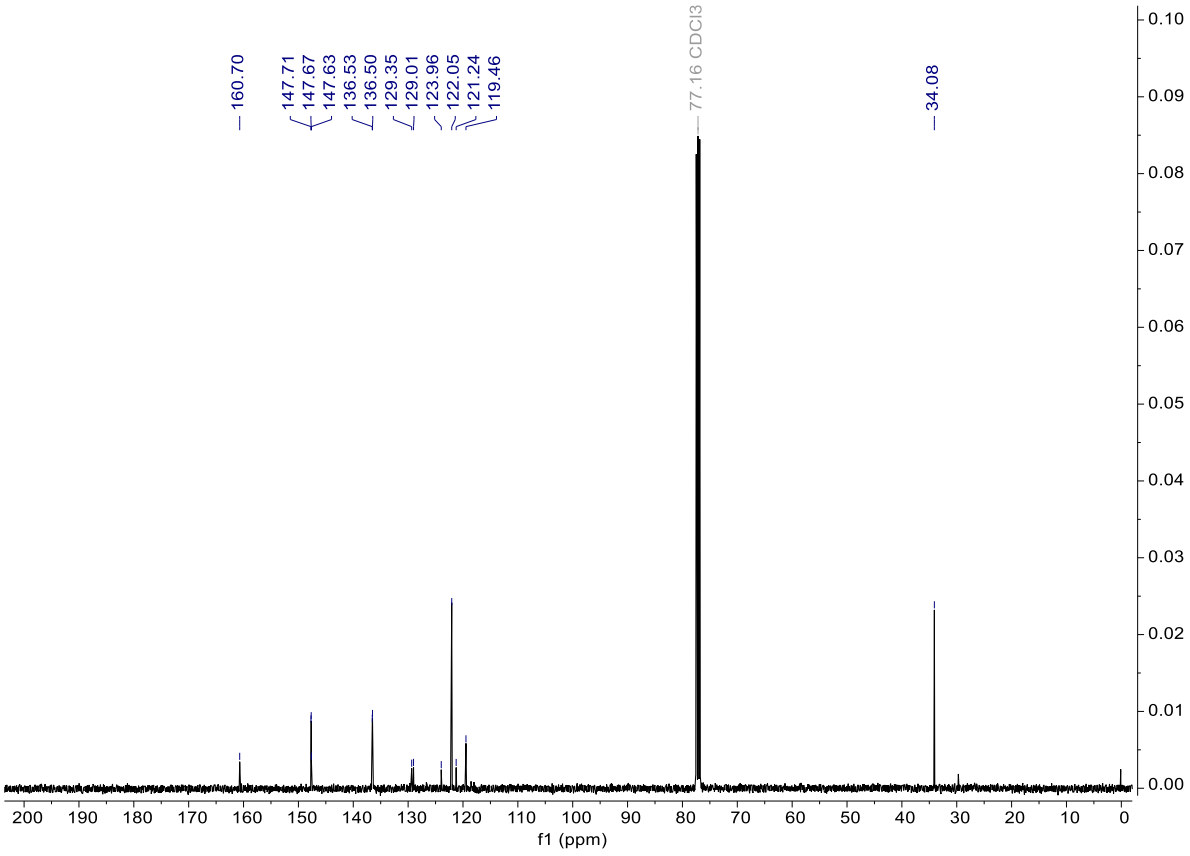
Data for **4l**


8.90
8.89
8.31
8.31
7.76
7.74
7.26 CDCl3
3.22
NC
N
S
Me
N
CF3
1.00
0.95
1.06
1.02
3.28
f1 (ppm)

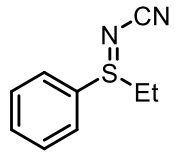

158.79
151.84
141.89
141.54
123.28
122.16
122.13
122.09
120.56
119.63
118.13
118.09
118.06
118.02
77.16 CDCl3
34.51
0.11
f1 (ppm)

Data for **4m**

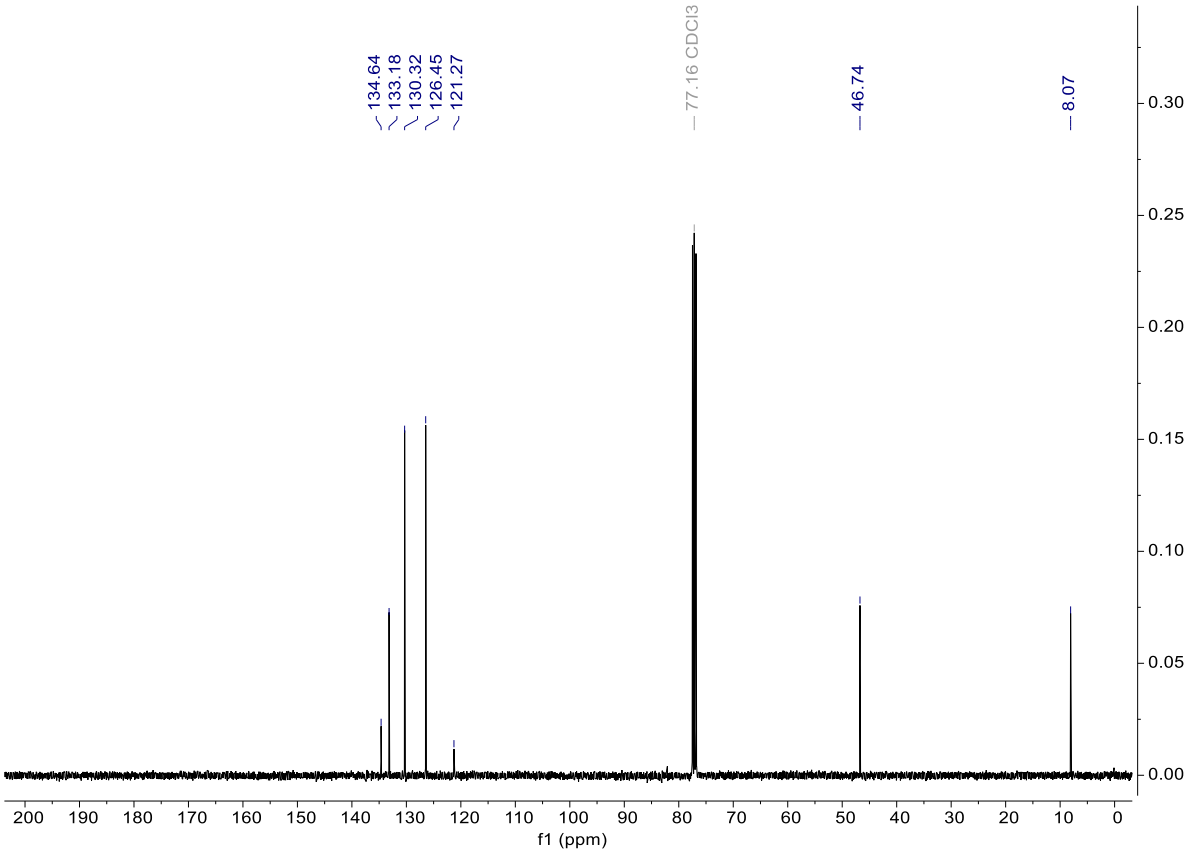

8.95
8.28
8.27
7.26 CDCl3
3.23
N
CN
S
Me
N
F3C
0.98
2.00
3.15
f1 (ppm)


160.70
147.71
147.67
147.63
136.53
136.50
129.35
129.01
123.96
122.05
121.24
119.46
77.16 CDCl3
34.08
f1 (ppm)

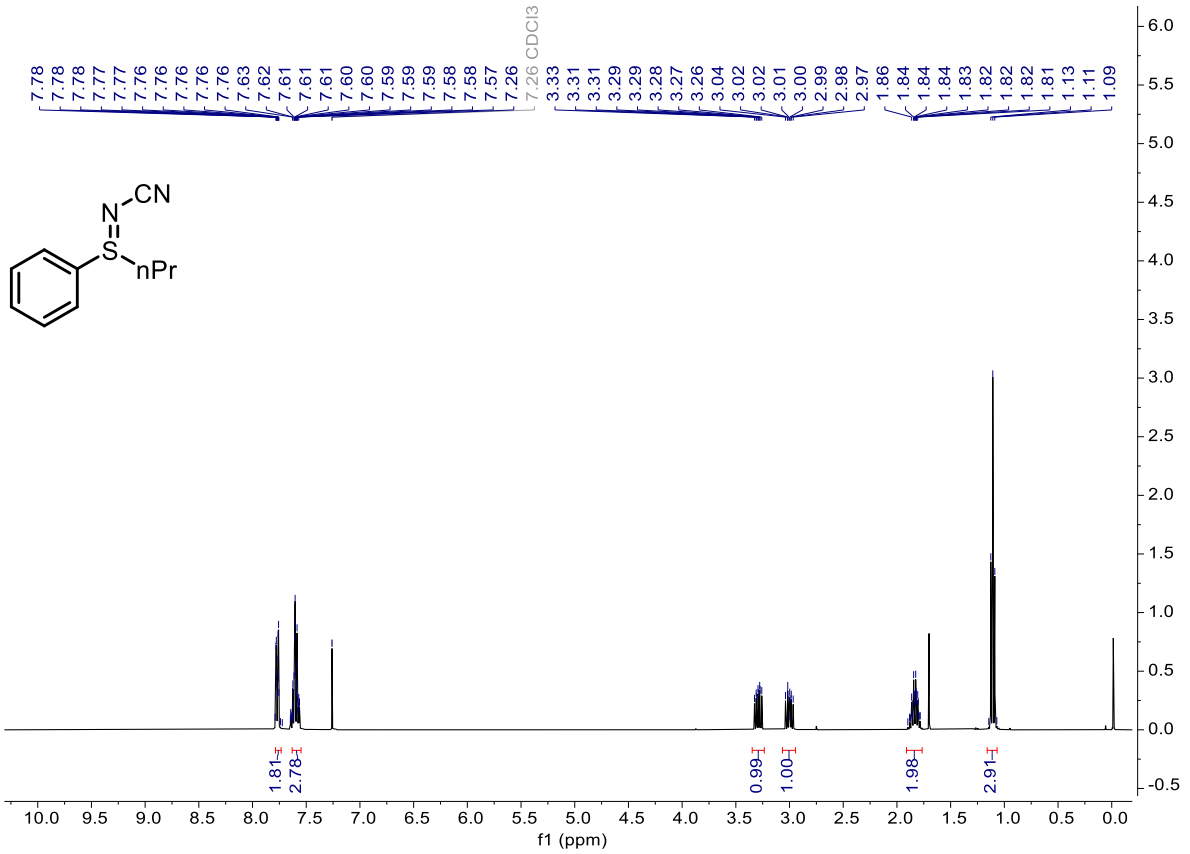
Data for **4n**

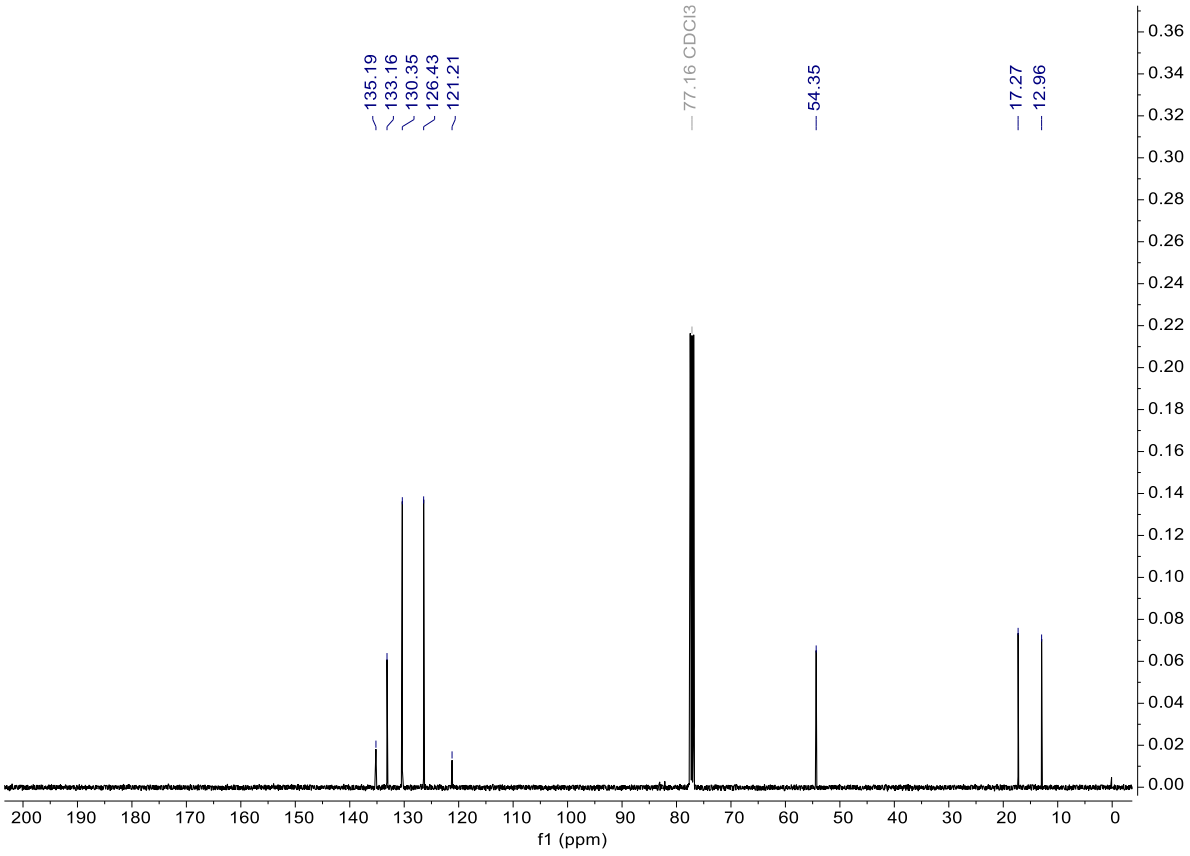

CN
N
S
Et

7.26 CDCl3
1.88
3.01
1.04
1.04
3.00
f1 (ppm)

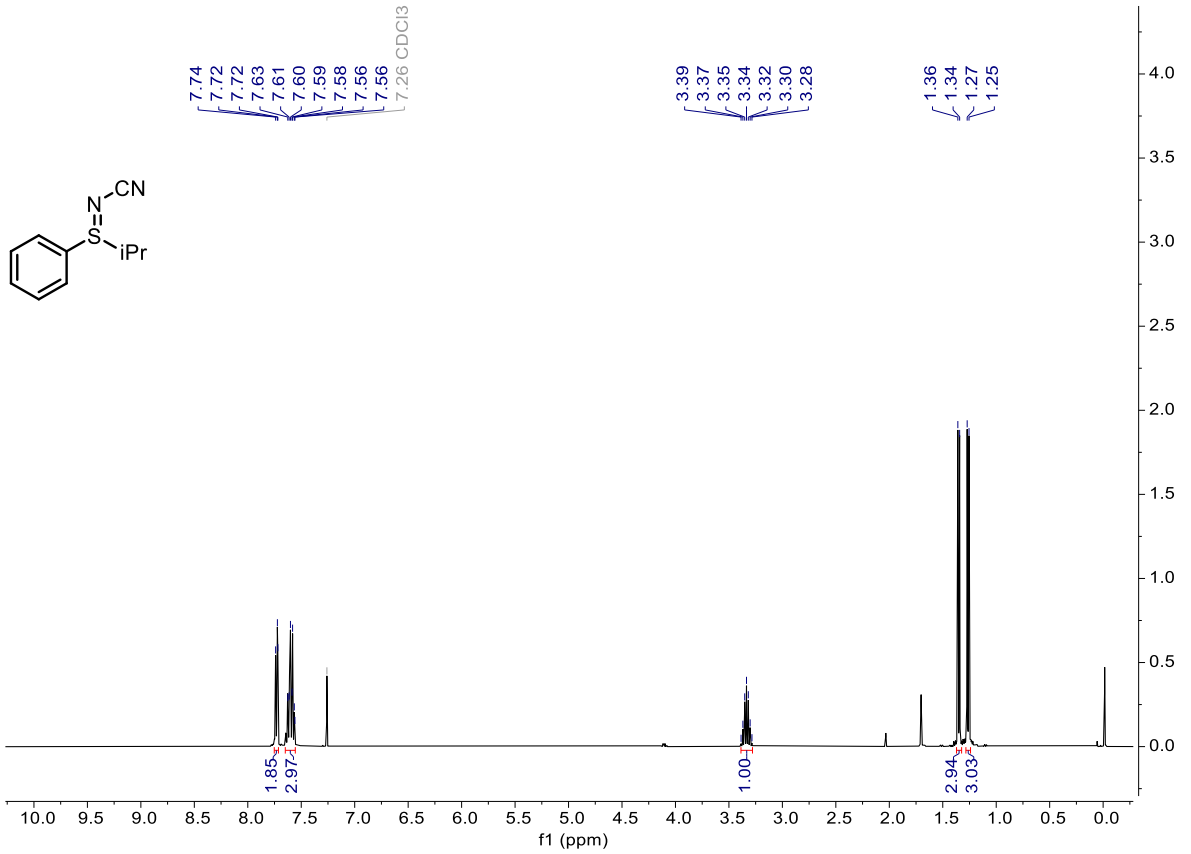

134.64
133.18
130.32
126.45
121.27
77.16 CDCl3
46.74
8.07
f1 (ppm)

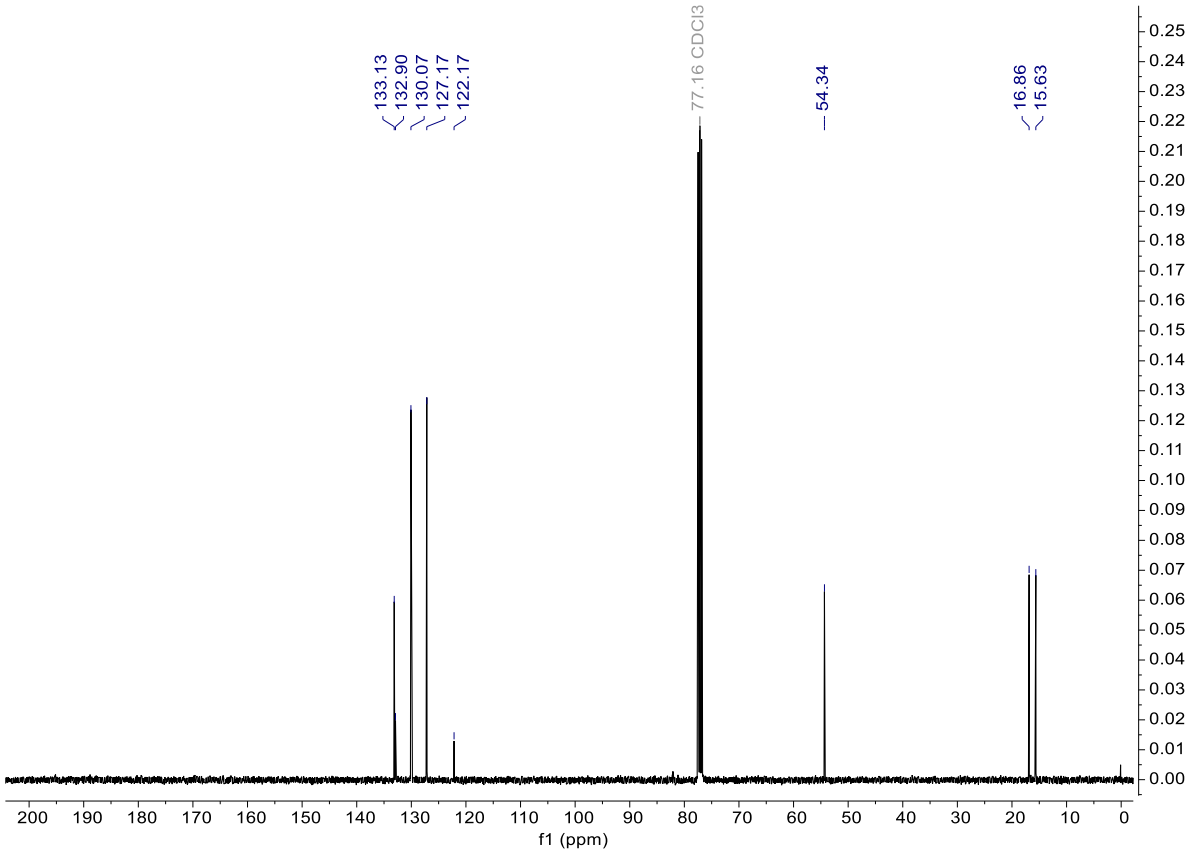
Data for **4o**


7.78 7.78 7.78 7.77 7.77 7.76 7.76 7.76 7.76 7.76 7.63 7.62 7.61 7.61 7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.26 CDCl3
3.33 3.31 3.31 3.29 3.29 3.28 3.27 3.26 3.04 3.02 3.02 3.01 3.00 2.99 2.98 2.97
1.86 1.84 1.84 1.84 1.83 1.82 1.82 1.82 1.81 1.13 1.11 1.09
CN
N
S
nPr
1.81 2.78 0.99 1.00 1.98 2.91
f1 (ppm)

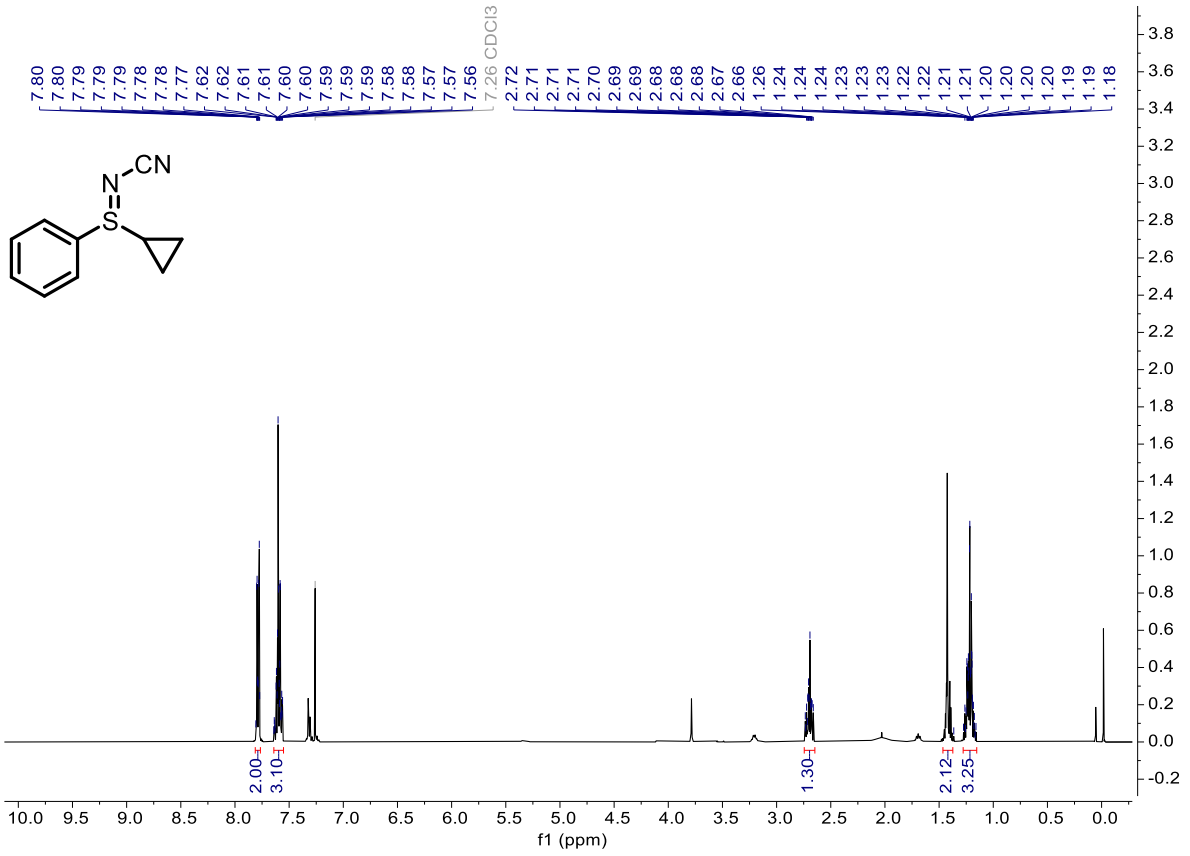

135.19 133.16 130.35 126.43 121.21
77.16 CDCl3
54.35
17.27 12.96
f1 (ppm)

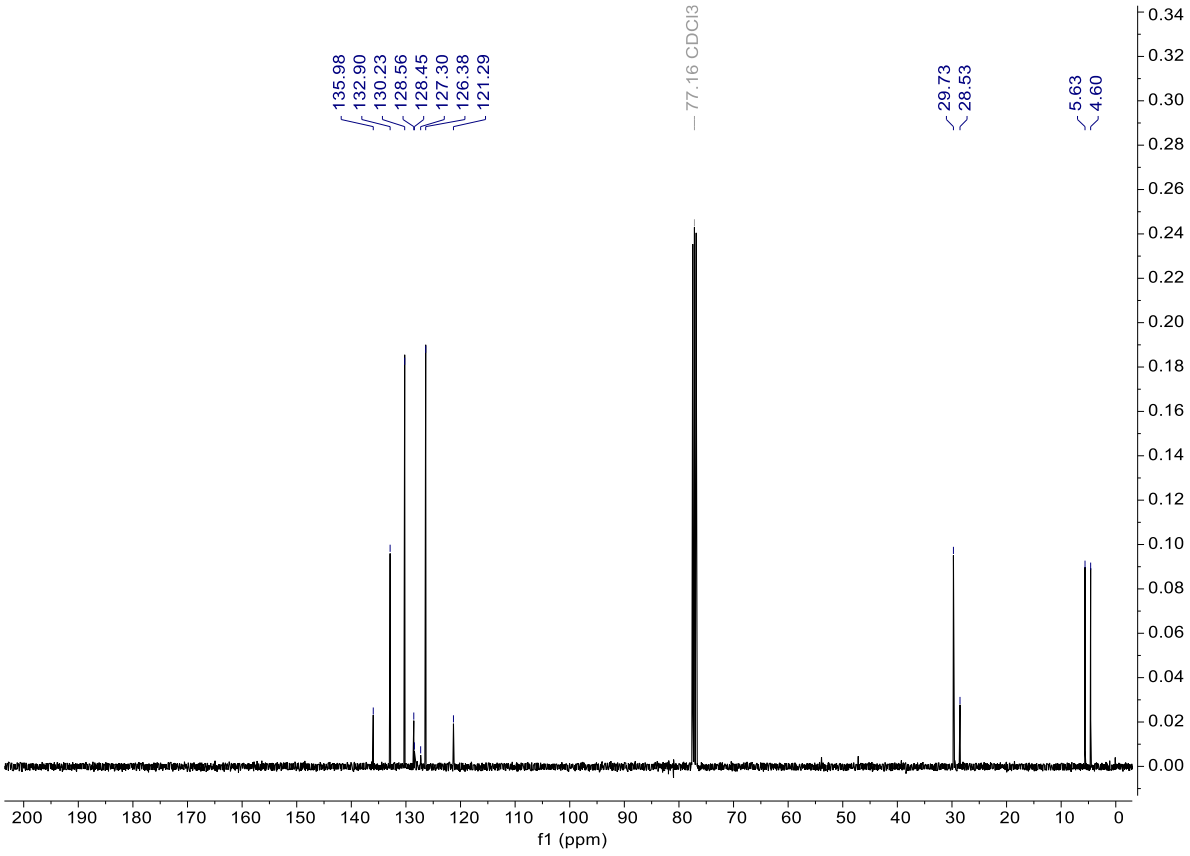
Data for **4p**


7.74
7.72
7.72
7.63
7.61
7.60
7.59
7.58
7.56
7.56
7.26 CDCl3
3.39
3.37
3.35
3.34
3.32
3.30
3.28
1.36
1.34
1.27
1.25
CN
N
S
iPr
1.85
2.97
1.00
2.94
3.03
f1 (ppm)

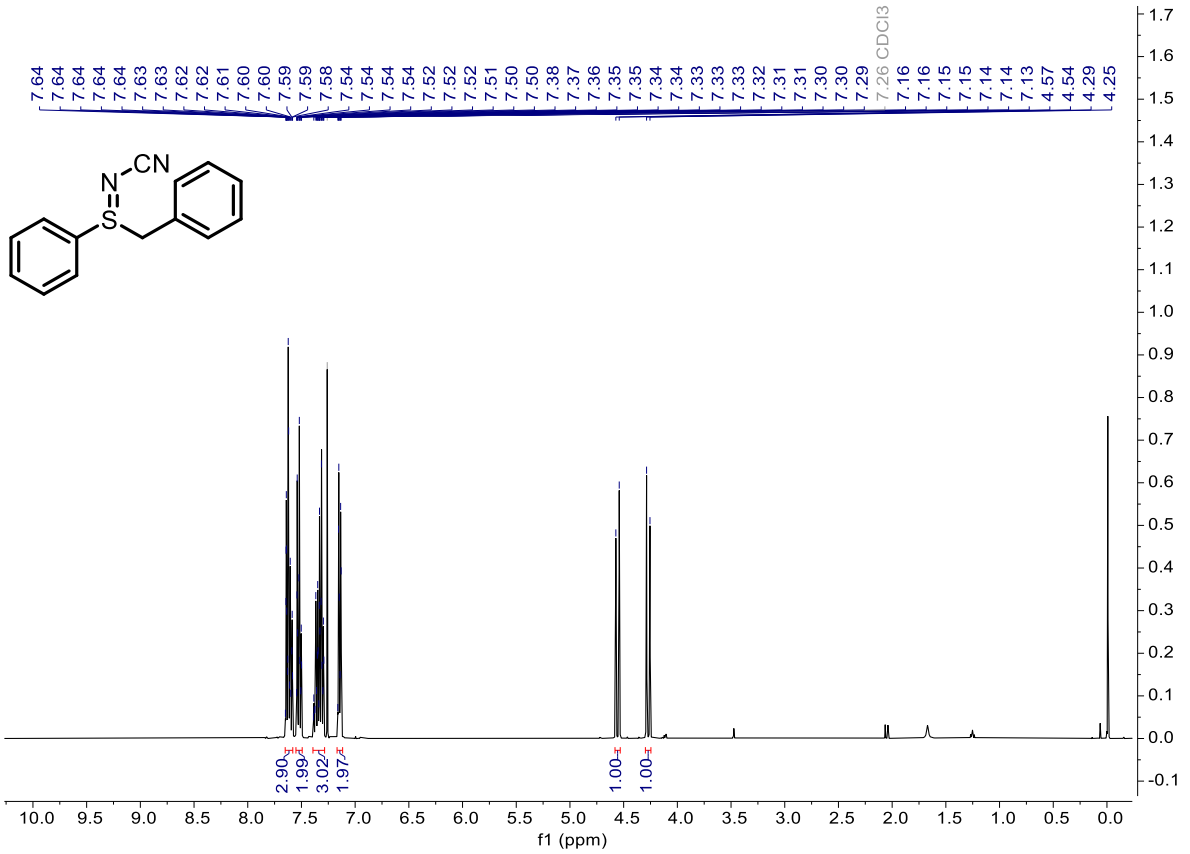

133.13
132.90
130.07
127.17
122.17
77.16 CDCl3
54.34
16.86
15.63
f1 (ppm)

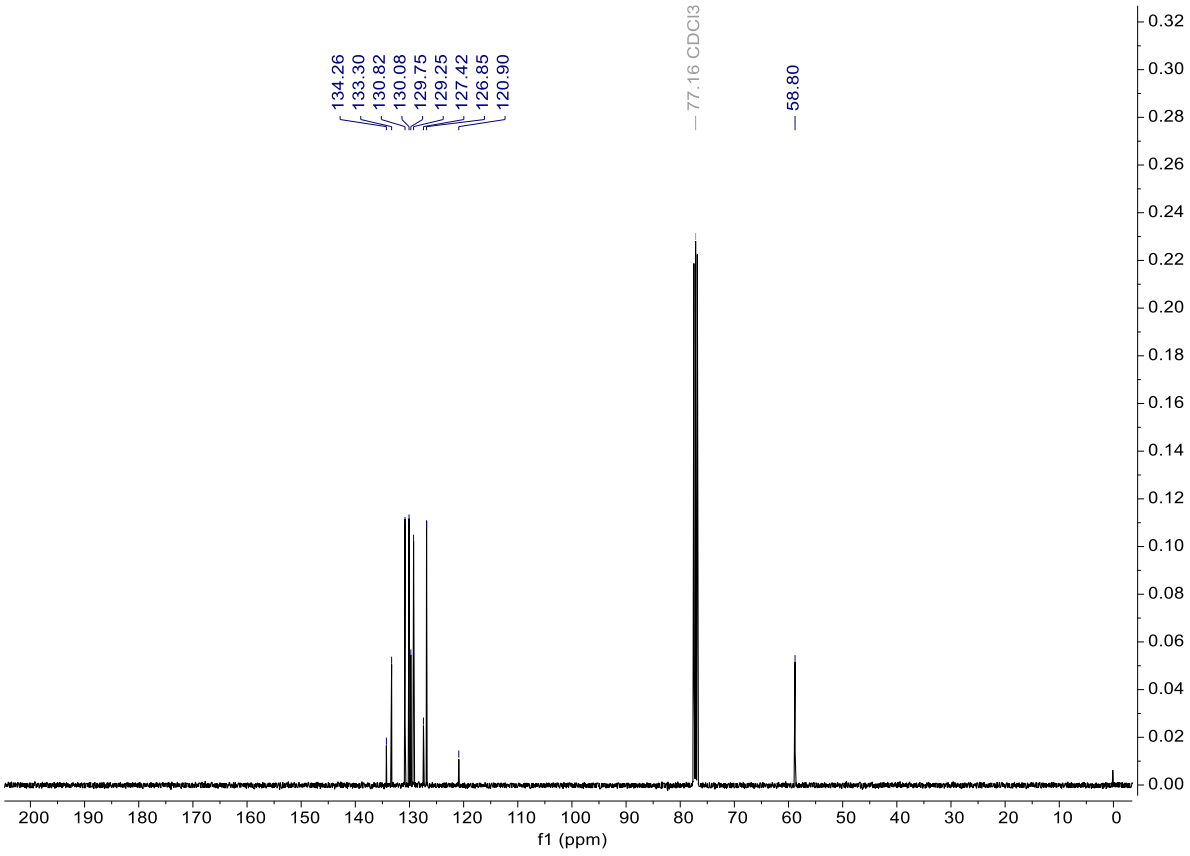
Data for **4q**


7.80 7.80 7.79 7.79 7.79 7.78 7.78 7.77 7.62 7.62 7.61 7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.57 7.56
7.26 CDCl3
2.72 2.71 2.71 2.71 2.70 2.69 2.69 2.68 2.68 2.68 2.67 2.66 1.26 1.24 1.24 1.24 1.23 1.23 1.23 1.22 1.22 1.21 1.21 1.20 1.20 1.20 1.20 1.19 1.19 1.18
CN
N
S
2.00
3.10
1.30
2.12
3.25
f1 (ppm)

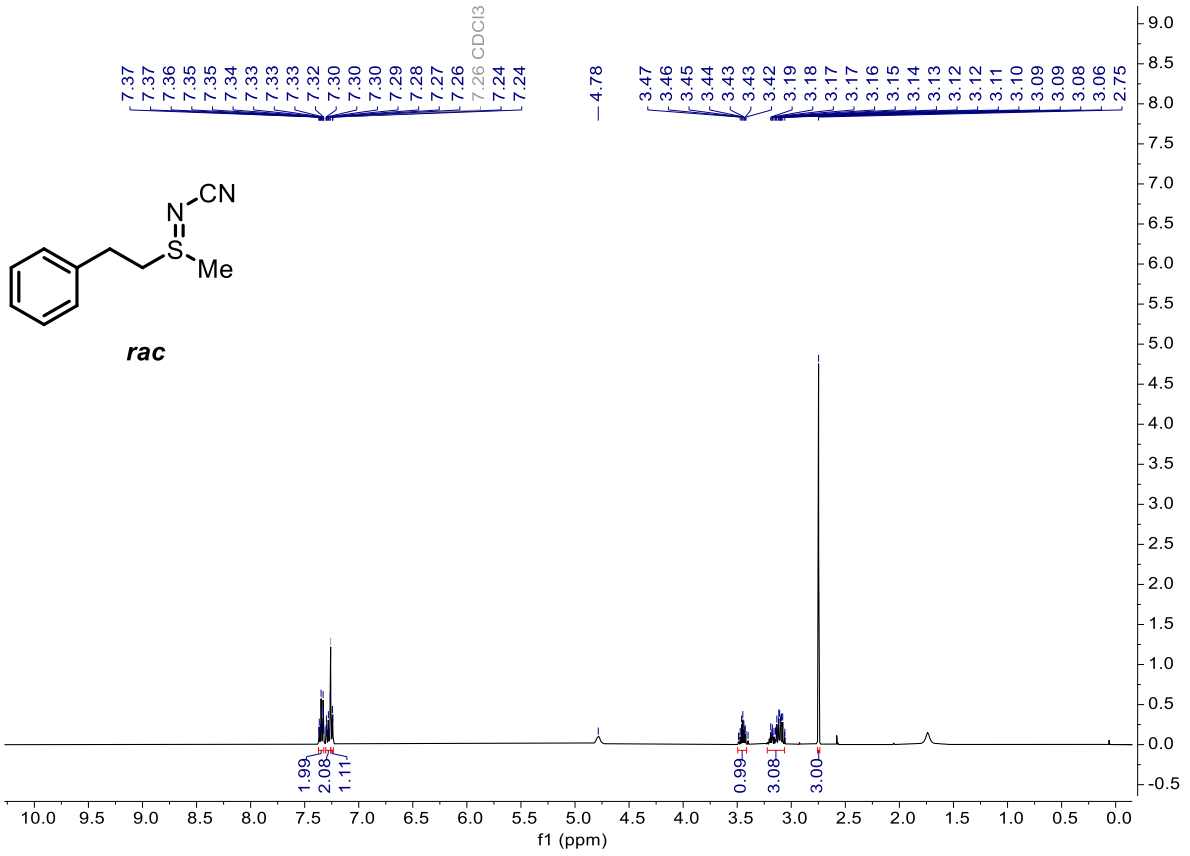

135.98
132.90
130.23
128.56
128.45
127.30
126.38
121.29
77.16 CDCl3
29.73
28.53
5.63
4.60
f1 (ppm)

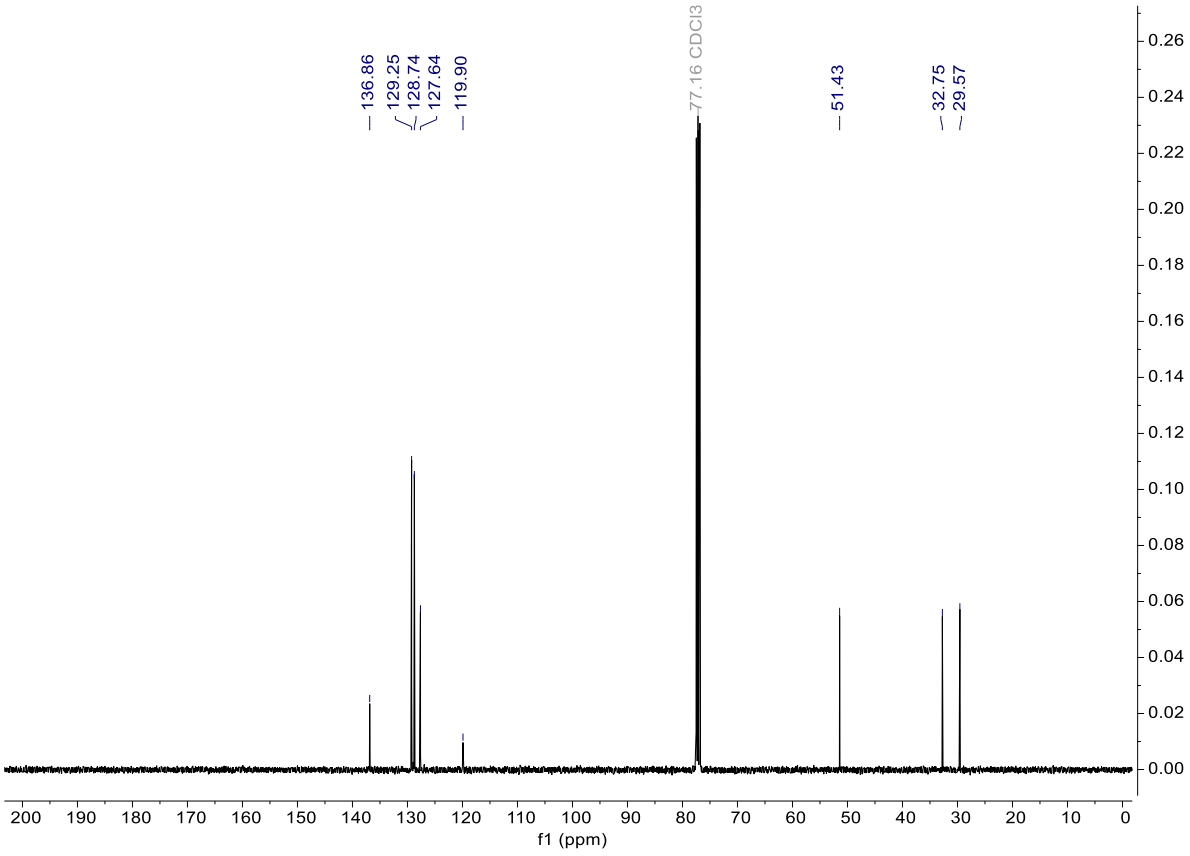
Data for **4r**


7.64 7.64 7.64 7.64 7.64 7.63 7.63 7.62 7.62 7.61 7.60 7.60 7.59 7.59 7.58 7.54 7.54 7.54 7.54 7.52 7.52 7.52 7.51 7.50 7.50 7.38 7.37 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.33 7.32 7.31 7.31 7.30 7.30 7.29 7.26 CDCl3 7.16 7.16 7.15 7.15 7.14 7.14 7.13 4.57 4.54 4.29 4.25
N
CN
S
2.90
1.99
3.02
1.97
1.00
1.00
f1 (ppm)

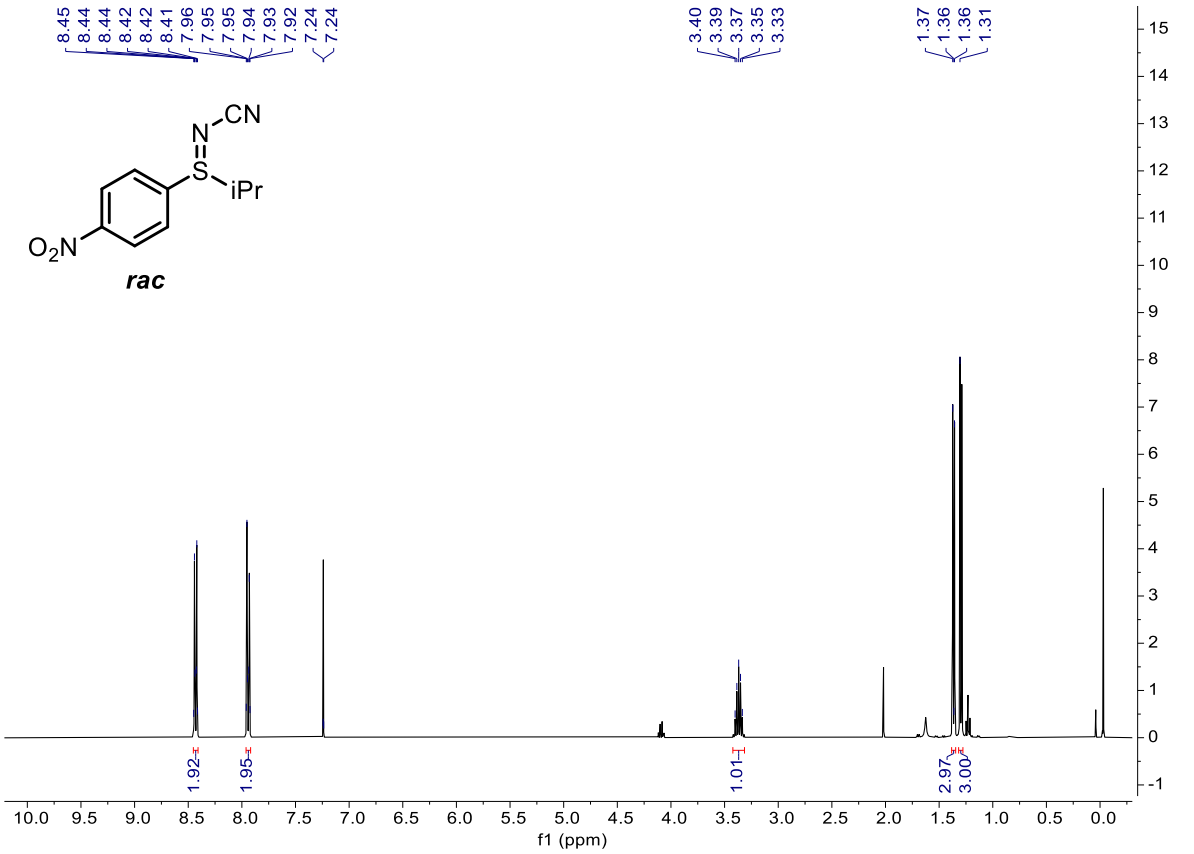

134.26 133.30 130.82 130.08 129.75 129.25 127.42 126.85 120.90
77.16 CDCl3
58.80
f1 (ppm)

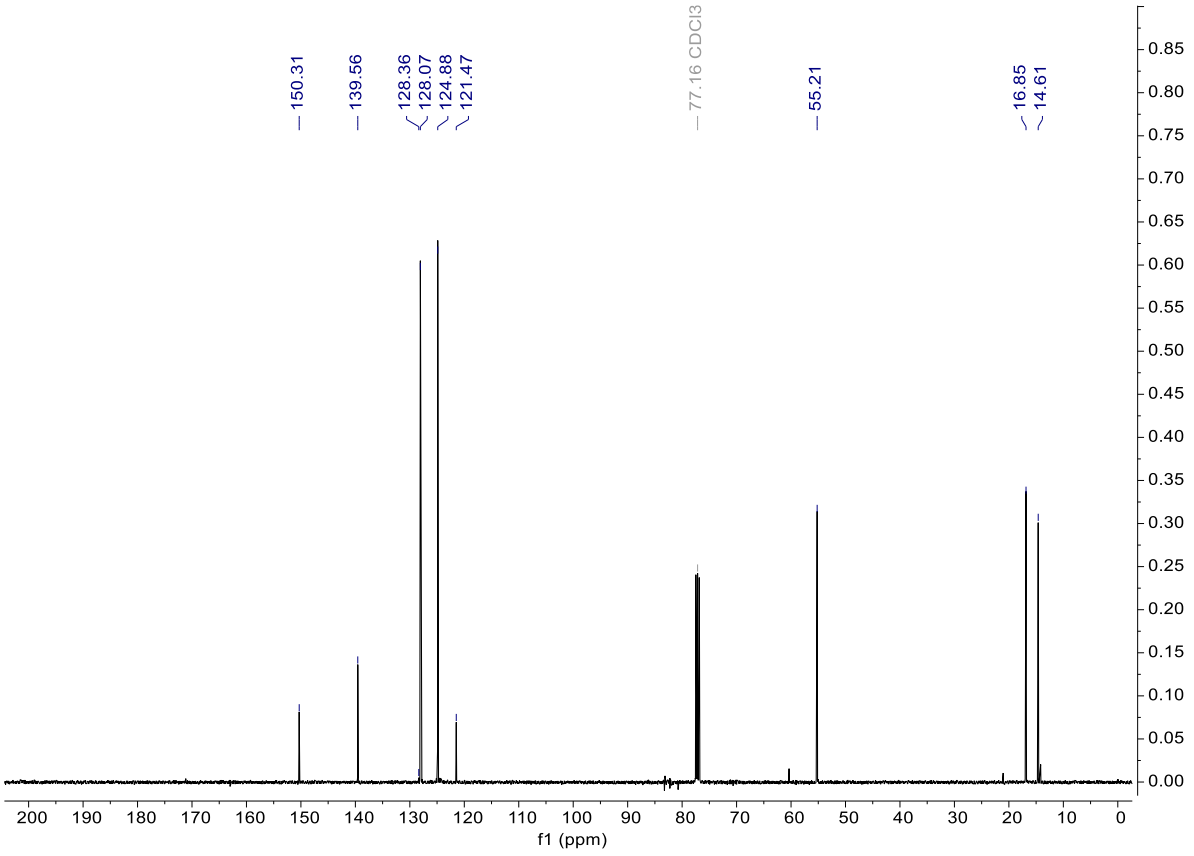
Data for **4s**


7.37
7.37
7.36
7.35
7.35
7.34
7.33
7.33
7.33
7.32
7.30
7.30
7.30
7.29
7.28
7.27
7.26
7.26 CDCl3
7.24
7.24
4.78
3.47
3.46
3.45
3.44
3.43
3.43
3.42
3.19
3.18
3.17
3.17
3.16
3.15
3.14
3.13
3.12
3.12
3.11
3.10
3.09
3.09
3.08
3.06
2.75
CN
N
S
Me
rac
1.99
2.08
1.11
0.99
3.08
3.00
f1 (ppm)

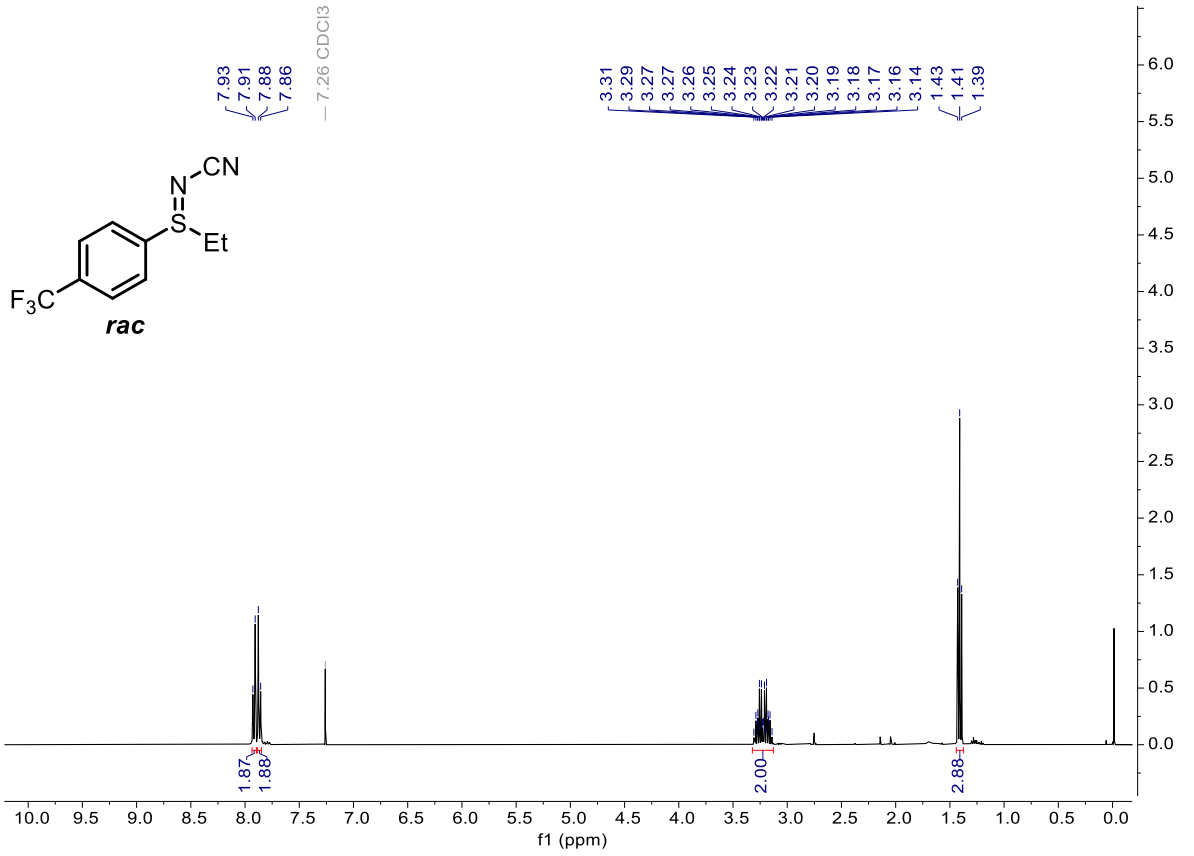

136.86
129.25
128.74
127.64
119.90
77.16 CDCl3
51.43
32.75
29.57
f1 (ppm)

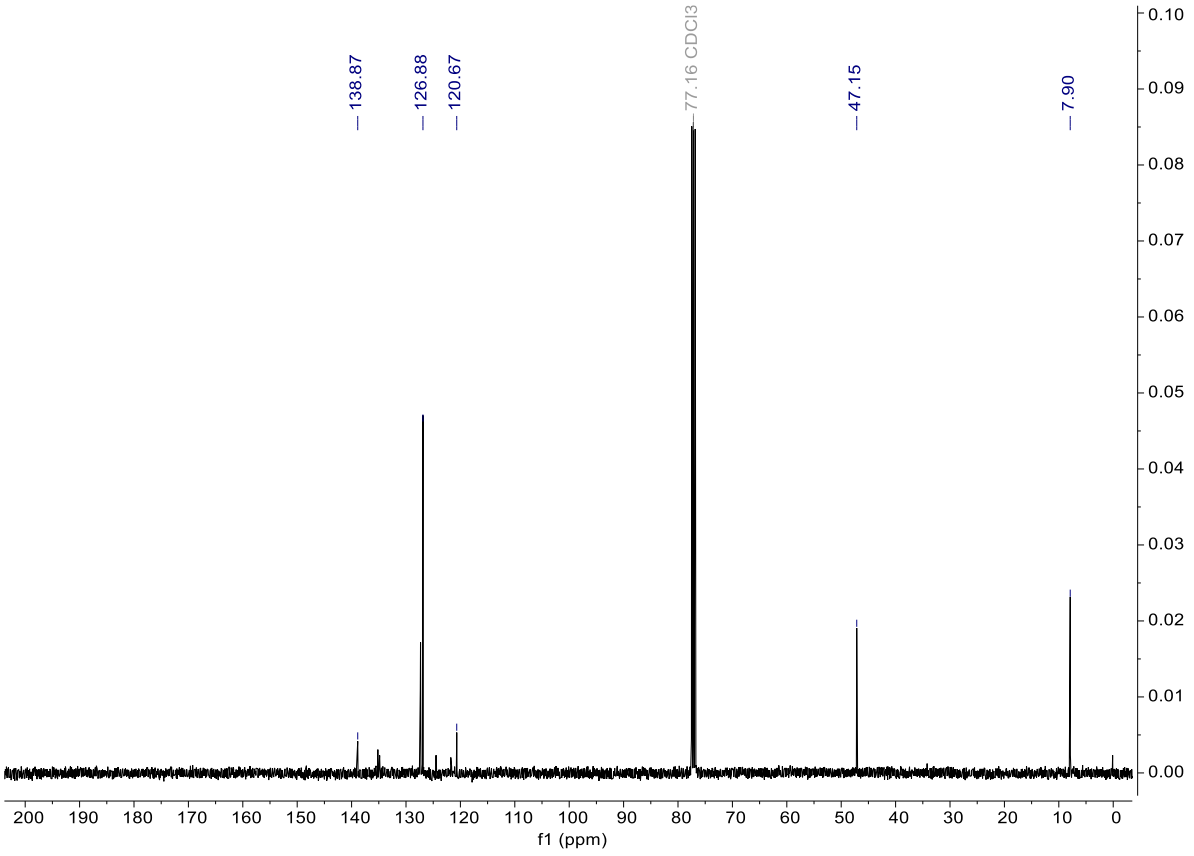
Data for **4t**


8.45
8.44
8.44
8.42
8.42
8.41
7.96
7.95
7.95
7.94
7.93
7.92
7.24
7.24
3.40
3.39
3.37
3.35
3.33
1.37
1.36
1.36
1.31
N
CN
S
iPr
O2N
rac
1.92
1.95
1.01
2.97
3.00
f1 (ppm)

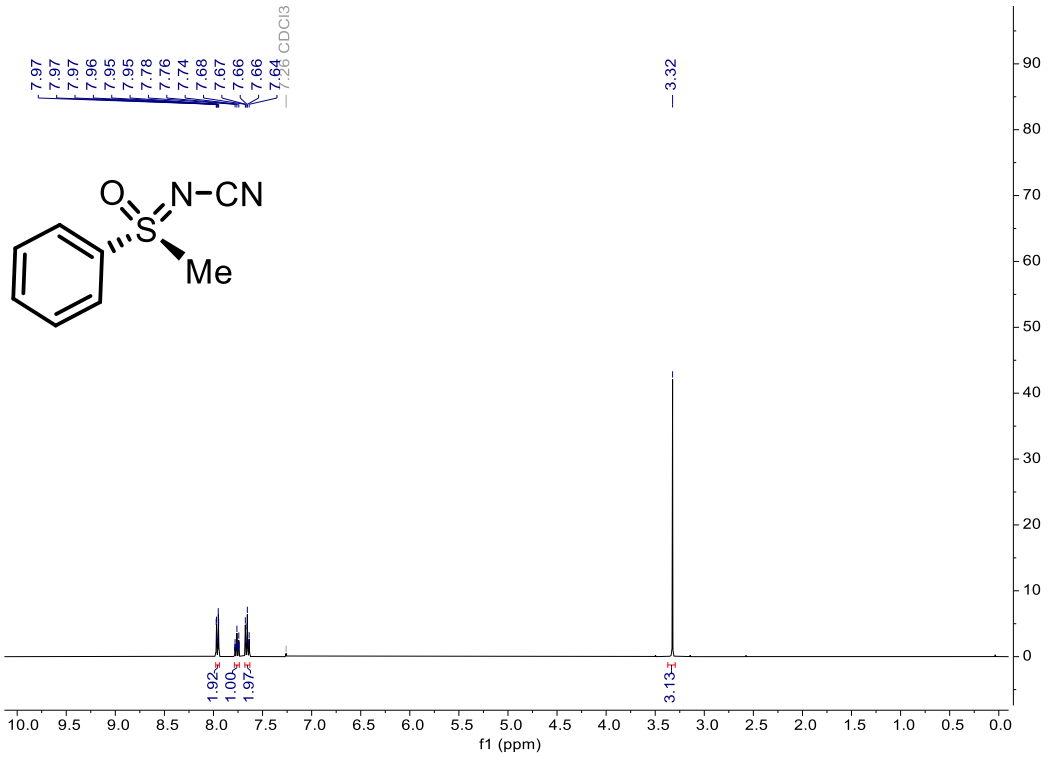

150.31
139.56
128.36
128.07
124.88
121.47
77.16 CDCl3
55.21
16.85
14.61
f1 (ppm)

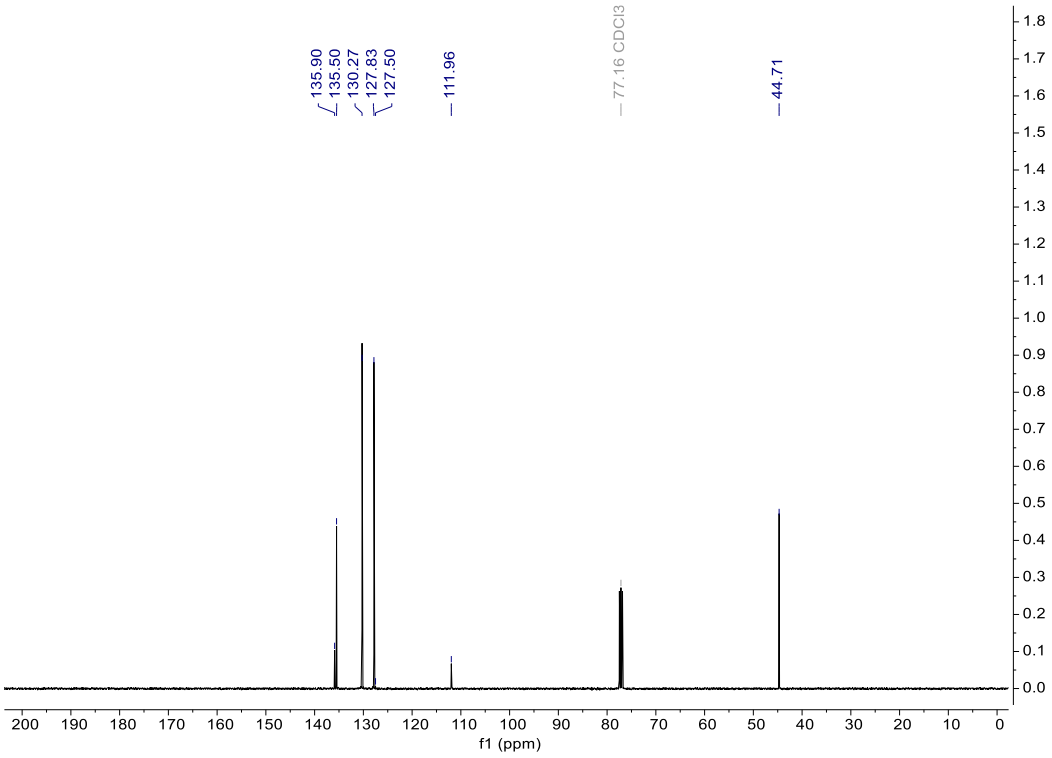
Data for **4u**


7.93
7.91
7.88
7.86
7.26 CDCl3
3.31
3.29
3.27
3.27
3.26
3.25
3.24
3.23
3.22
3.21
3.20
3.19
3.18
3.17
3.16
3.14
1.43
1.41
1.39
N
CN
S
Et
F3C
rac
1.87
1.88
2.00
2.88
f1 (ppm)

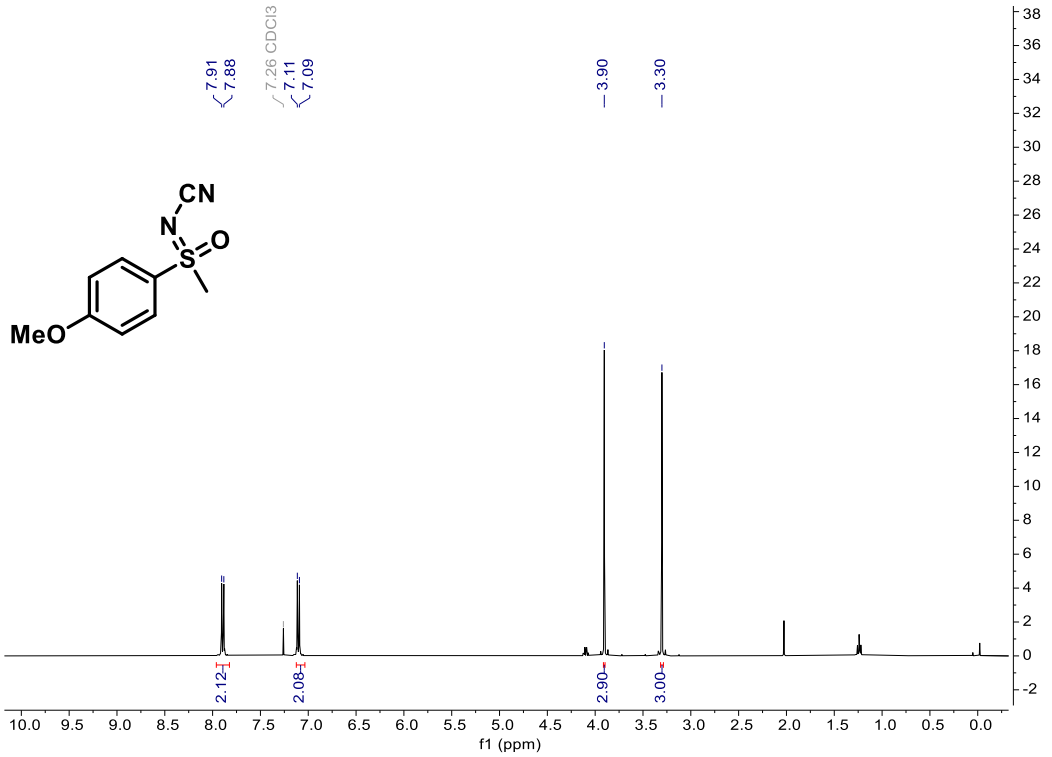

138.87
126.88
120.67
77.16 CDCl3
47.15
7.90
f1 (ppm)

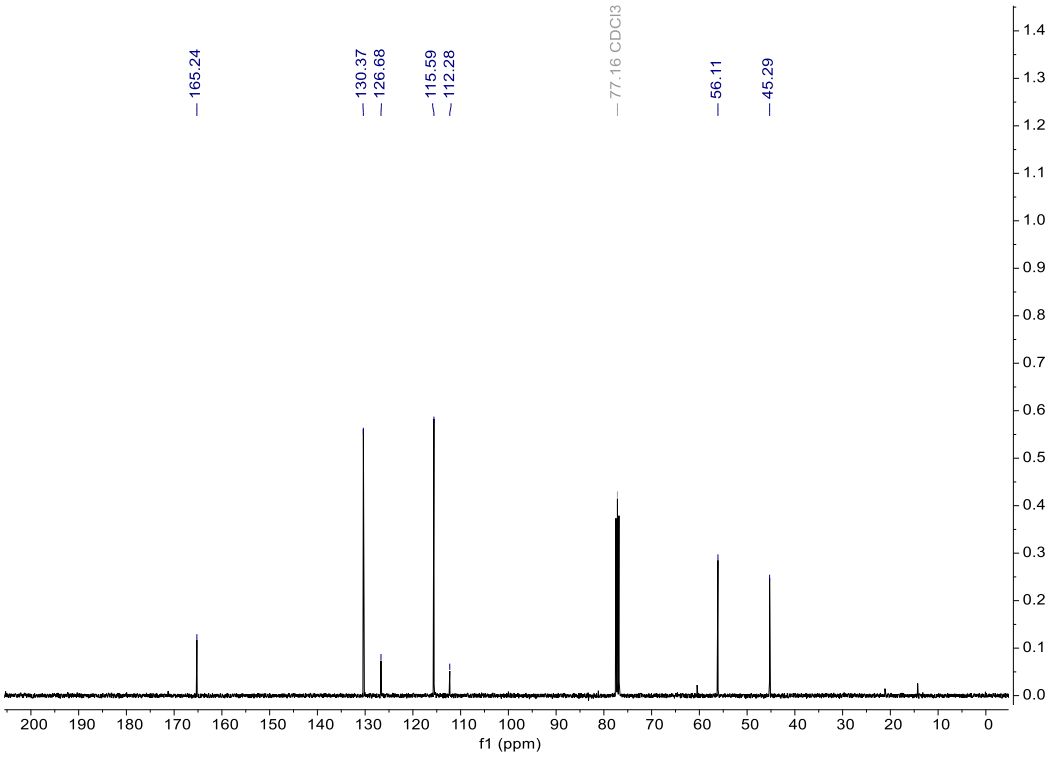
Data for **5a**


7.97
7.97
7.97
7.96
7.95
7.95
7.78
7.76
7.74
7.68
7.67
7.66
7.66
7.64
7.26 CDCl3
3.32
O
N−CN
S
Me
1.92
1.00
1.97
3.13
f1 (ppm)

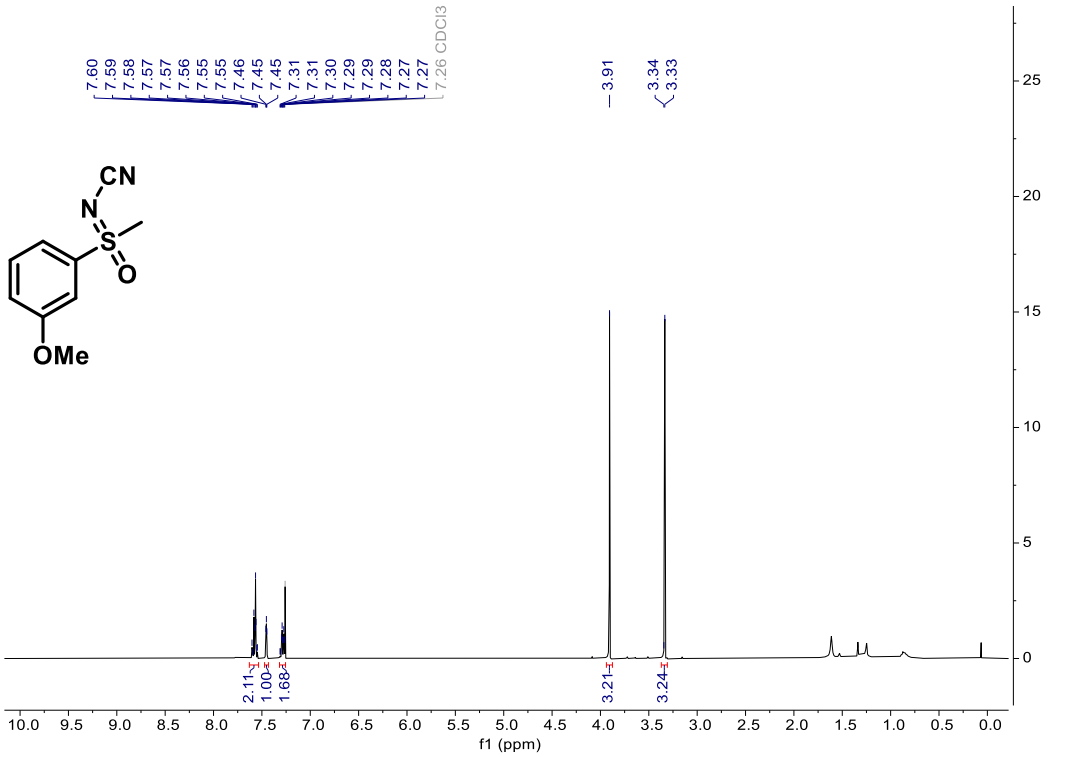

135.90
135.50
130.27
127.83
127.50
111.96
77.16 CDCl3
44.71
f1 (ppm)

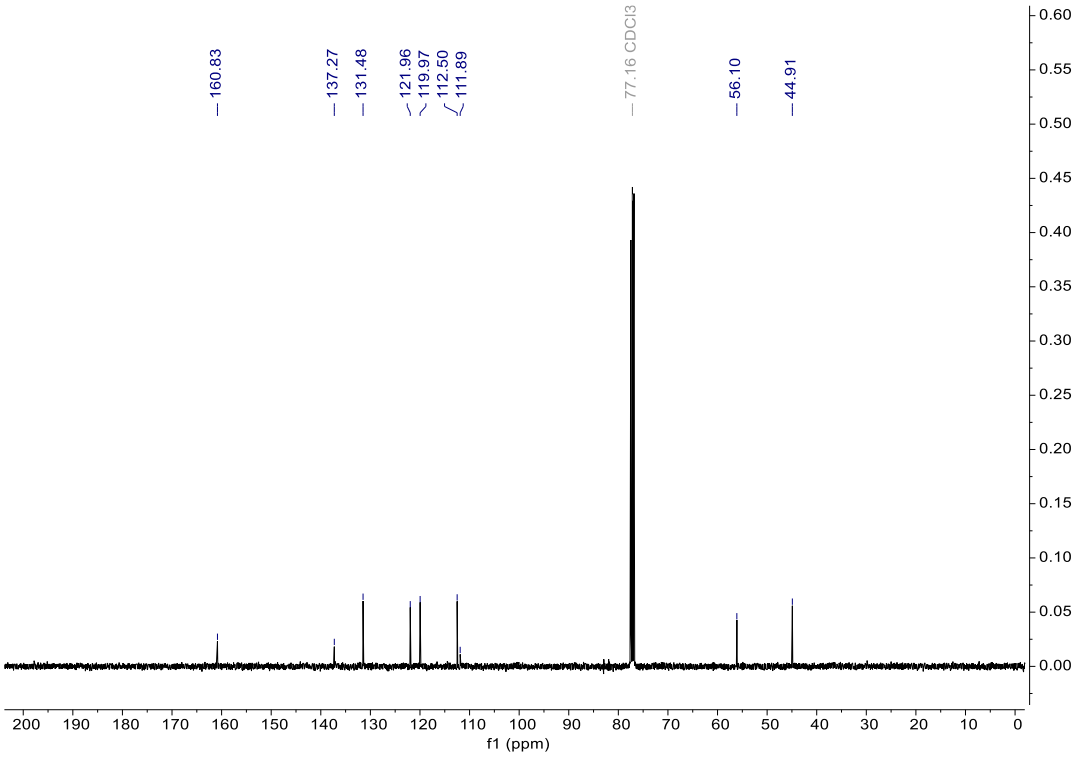
Data for **5b**


7.91
7.88
7.26 CDCl3
7.11
7.09
3.90
3.30
CN
N
S
O
MeO
2.12
2.08
2.90
3.00
f1 (ppm)

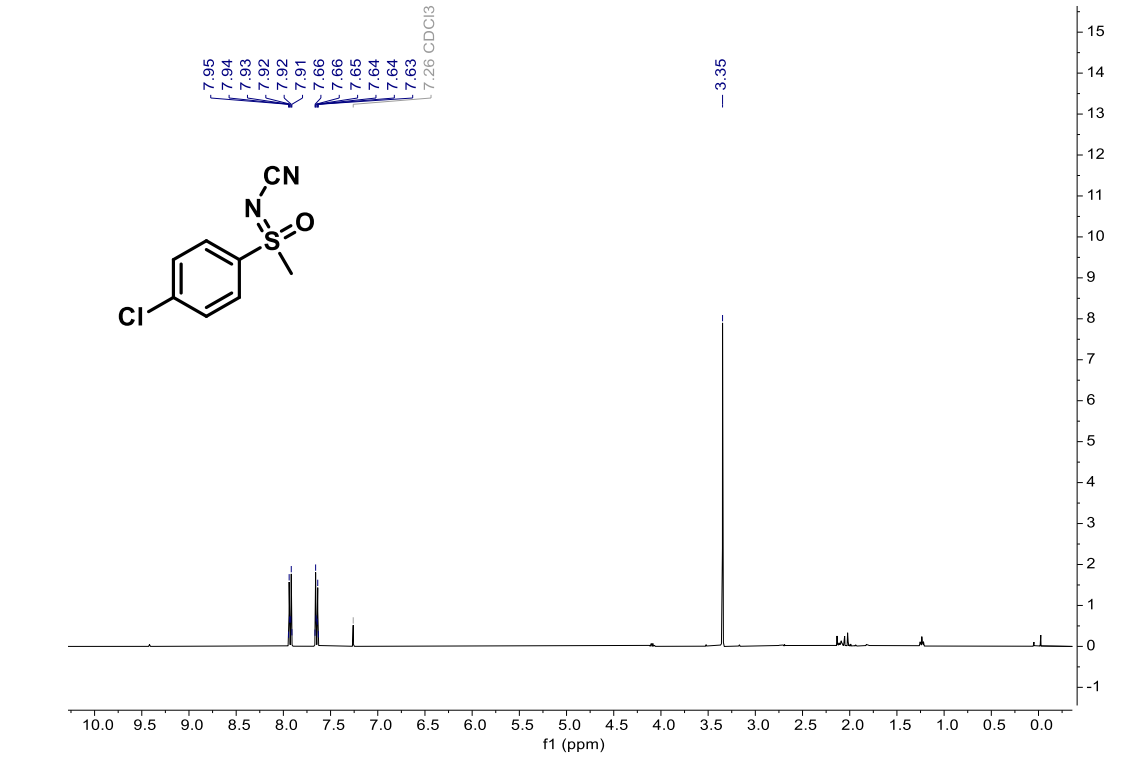

165.24
130.37
126.68
115.59
112.28
77.16 CDCl3
56.11
45.29
f1 (ppm)

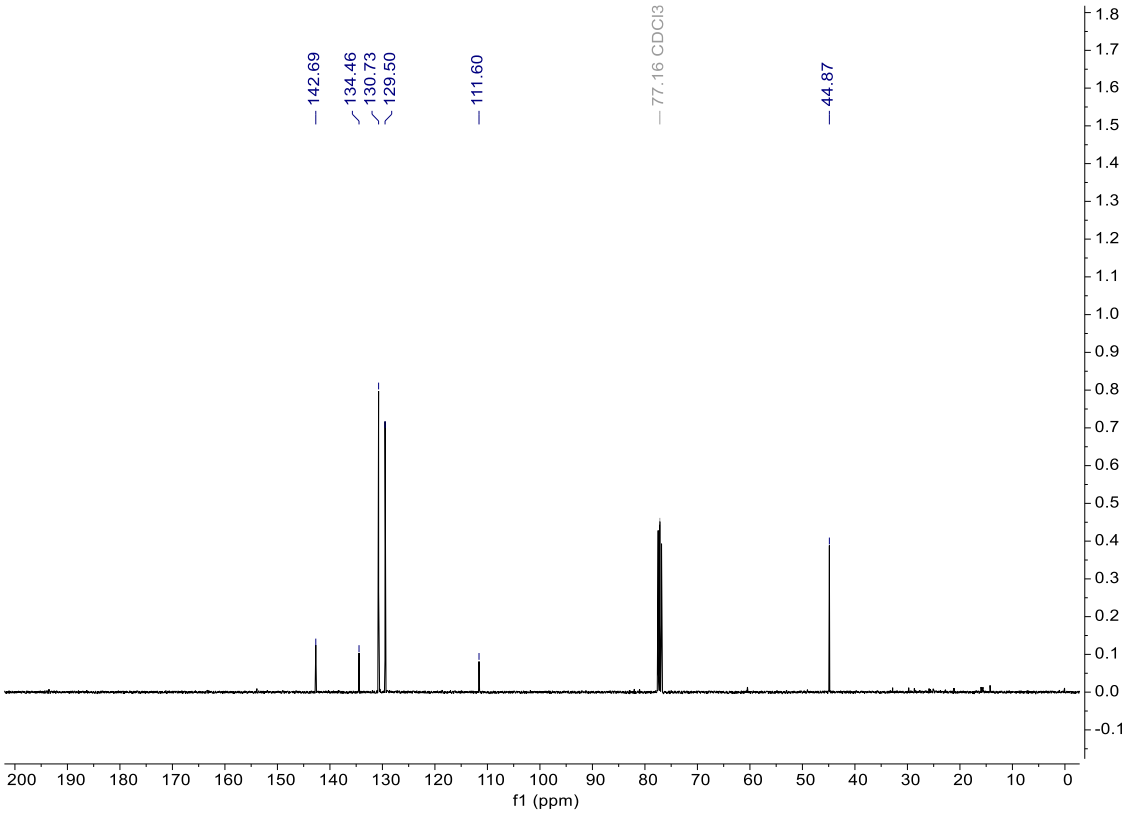
Data for **5c**


7.60
7.59
7.58
7.57
7.57
7.56
7.55
7.55
7.46
7.45
7.45
7.31
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26 CDCl3
3.91
3.34
3.33
CN
N
S
O
OMe
2.11
1.00
1.68
3.21
3.24
f1 (ppm)

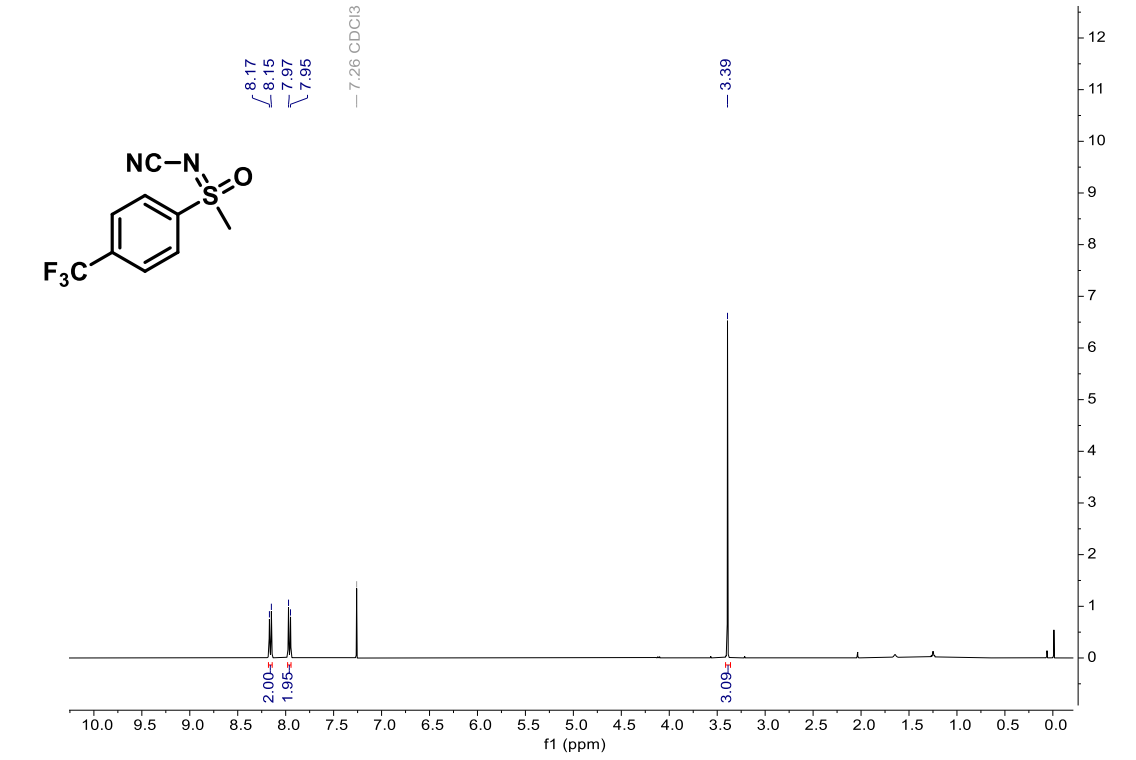

160.83
137.27
131.48
121.96
119.97
112.50
111.89
77.16 CDCl3
56.10
44.91
f1 (ppm)

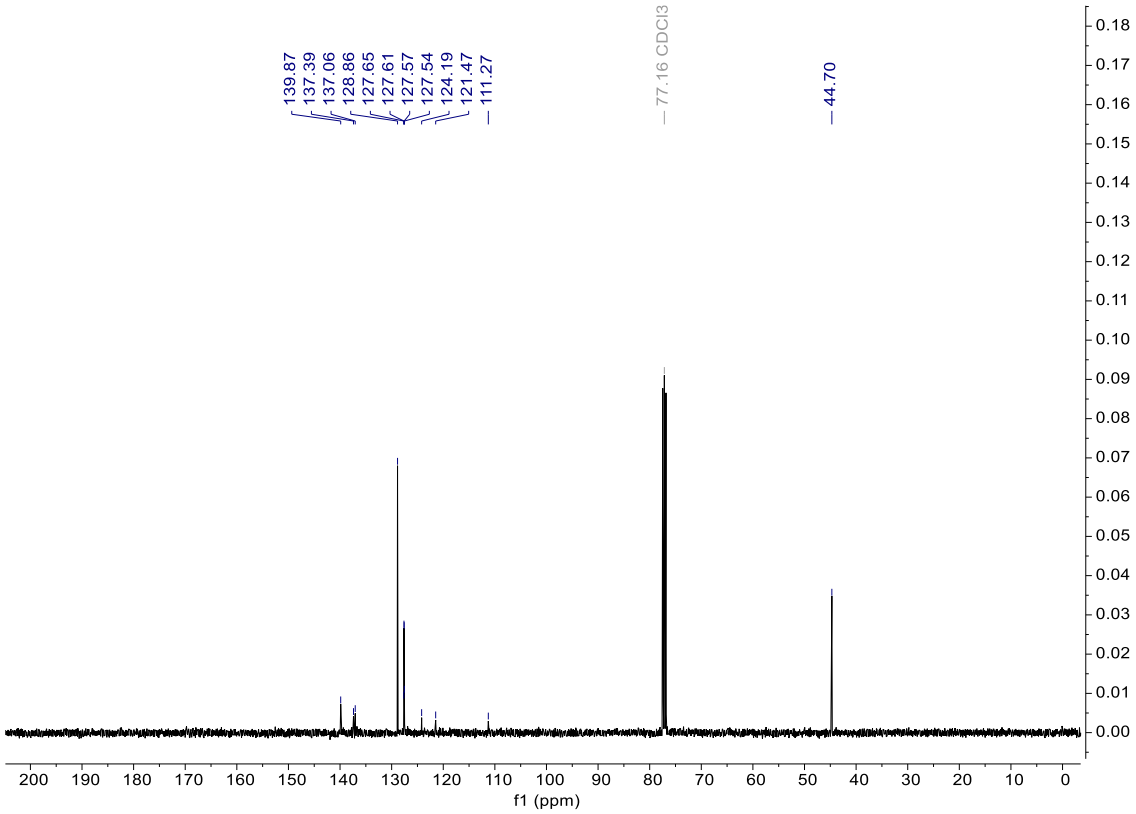
Data for **5d**


7.95
7.94
7.93
7.92
7.92
7.91
7.66
7.66
7.65
7.64
7.64
7.63
7.26 CDCl3
3.35
CN
N
S
O
Cl
f1 (ppm)

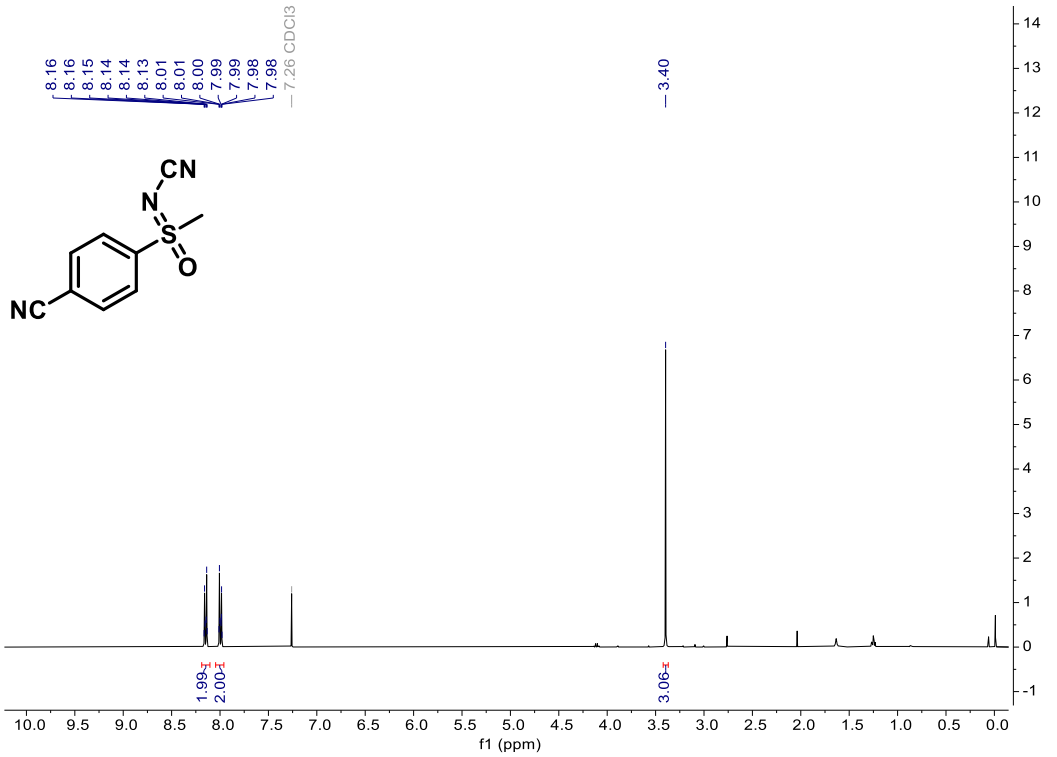

142.69
134.46
130.73
129.50
111.60
77.16 CDCl3
44.87
f1 (ppm)

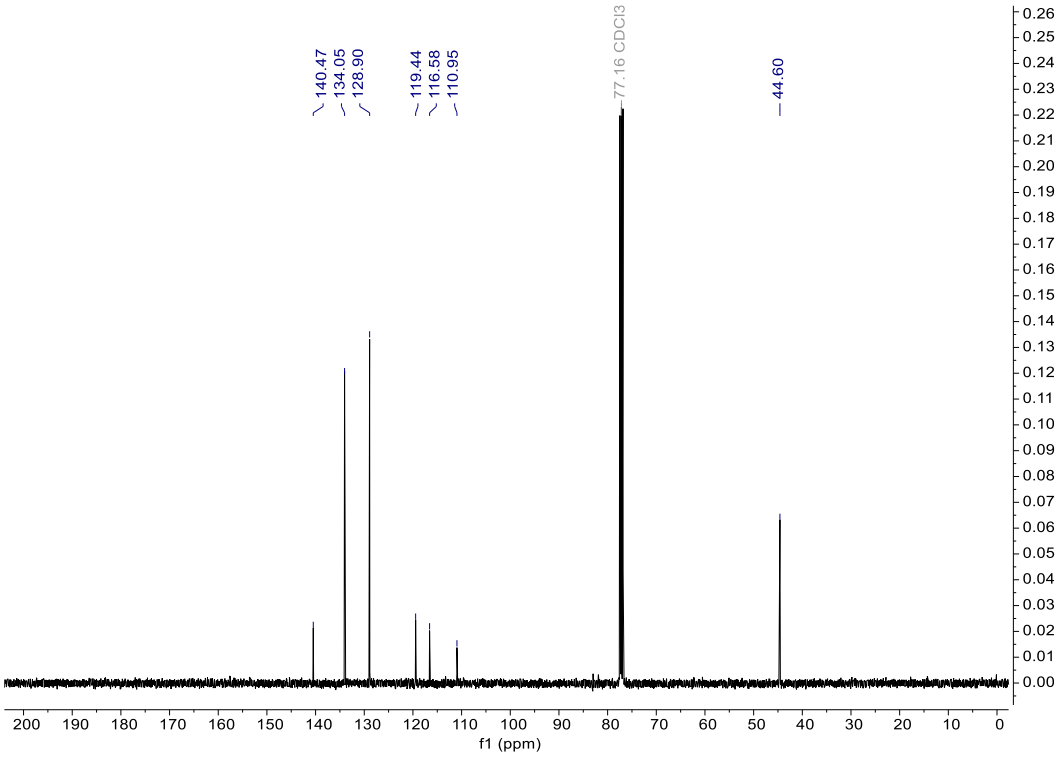
Data for **5e**


8.17
8.15
7.97
7.95
7.26 CDCl3
3.39
NC–N
S
O
F3C
2.00
1.95
3.09
f1 (ppm)

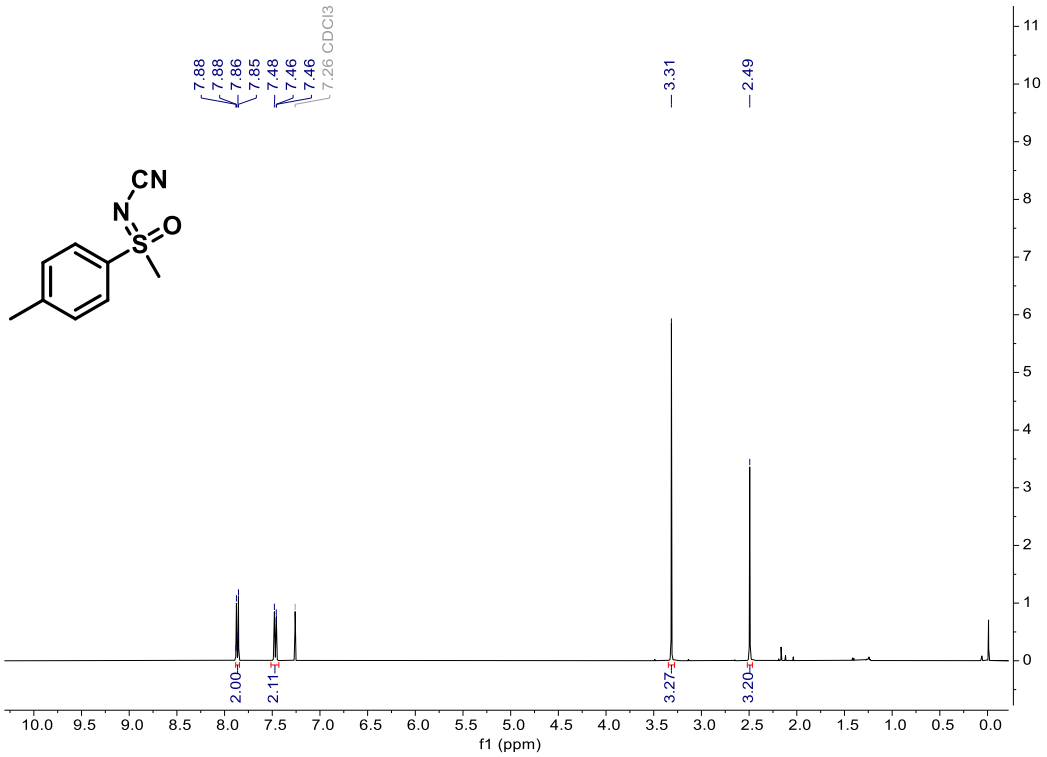

139.87
137.39
137.06
128.86
127.65
127.61
127.57
127.54
124.19
121.47
111.27
77.16 CDCl3
44.70
f1 (ppm)

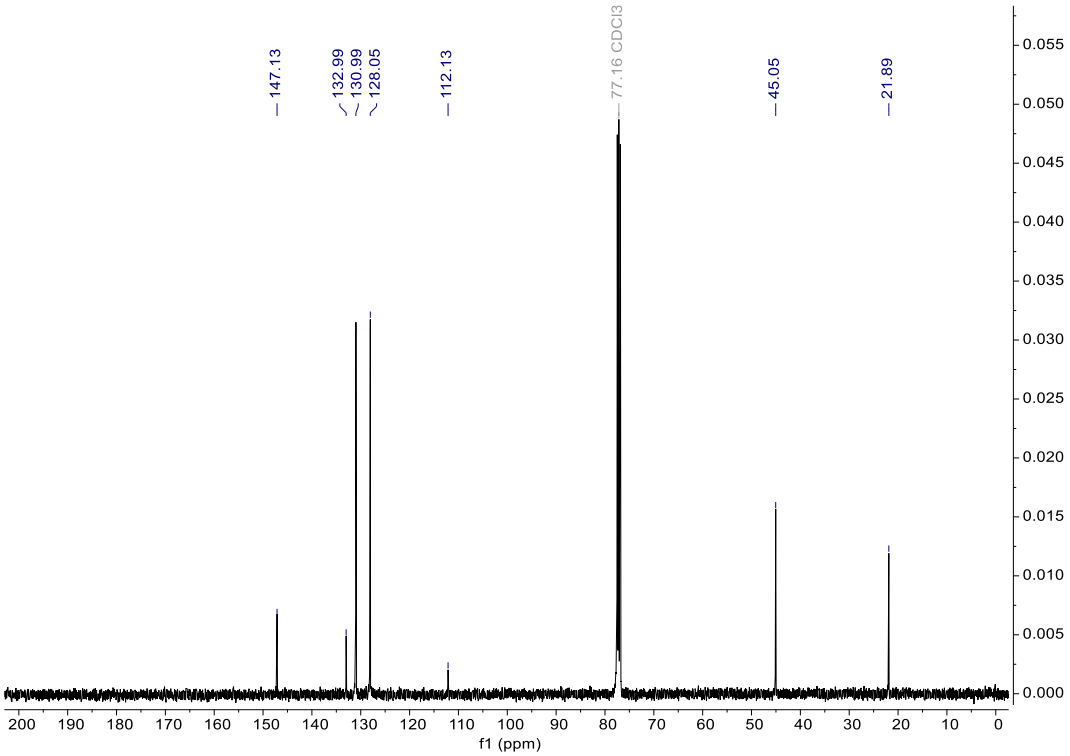
Data for **5f**


8.16
8.16
8.15
8.14
8.14
8.13
8.01
8.01
8.00
7.99
7.99
7.98
7.98
7.26 CDCl3
3.40
CN
N
S
O
NC
1.99
2.00
3.06
f1 (ppm)

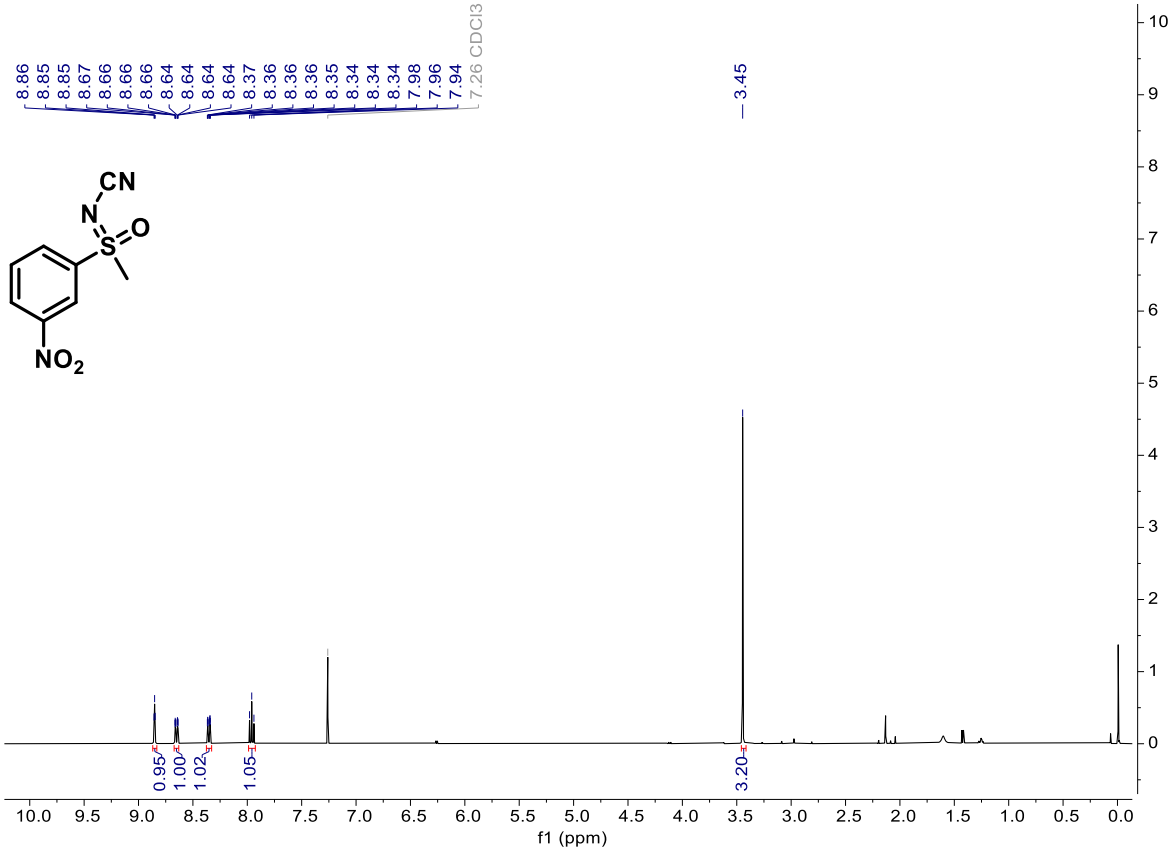

140.47
134.05
128.90
119.44
116.58
110.95
77.16 CDCl3
44.60
f1 (ppm)

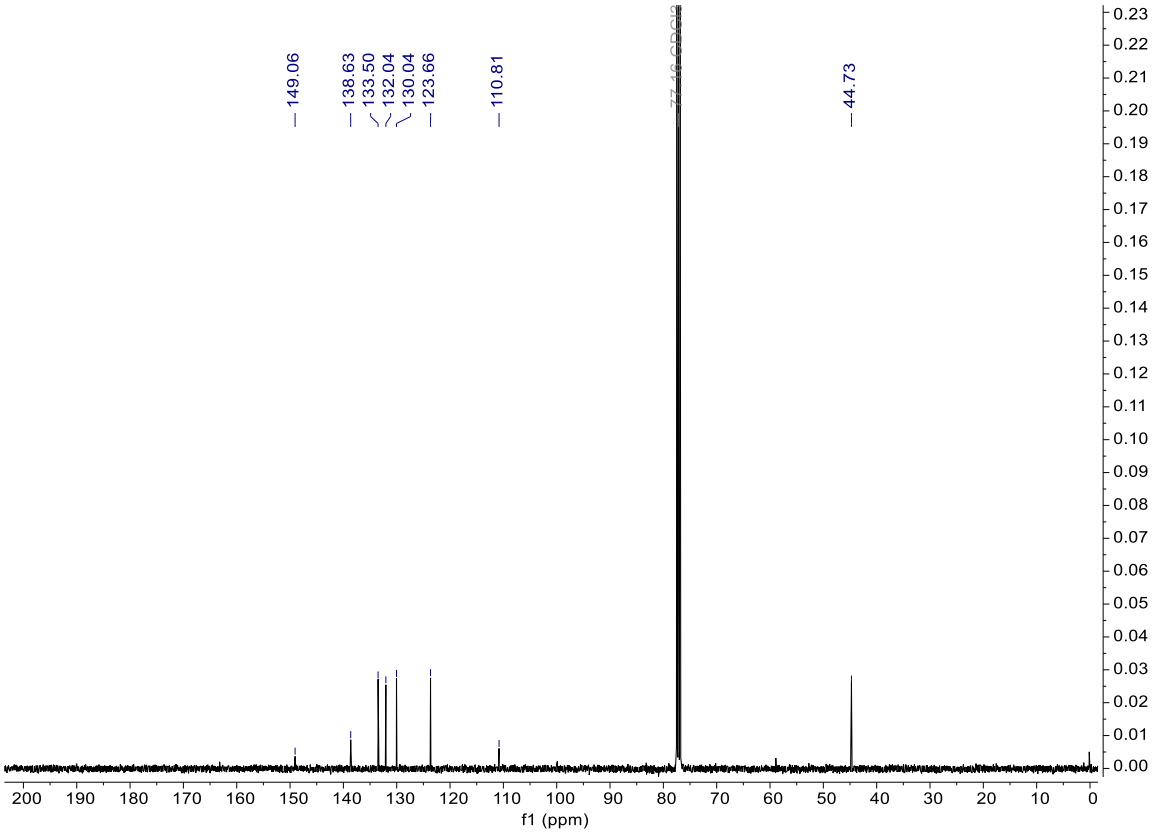
Data for **5g**


7.88
7.88
7.86
7.85
7.48
7.46
7.46
7.26 CDCl3
3.31
2.49
CN
N
S
O
2.00
2.11
3.27
3.20
f1 (ppm)

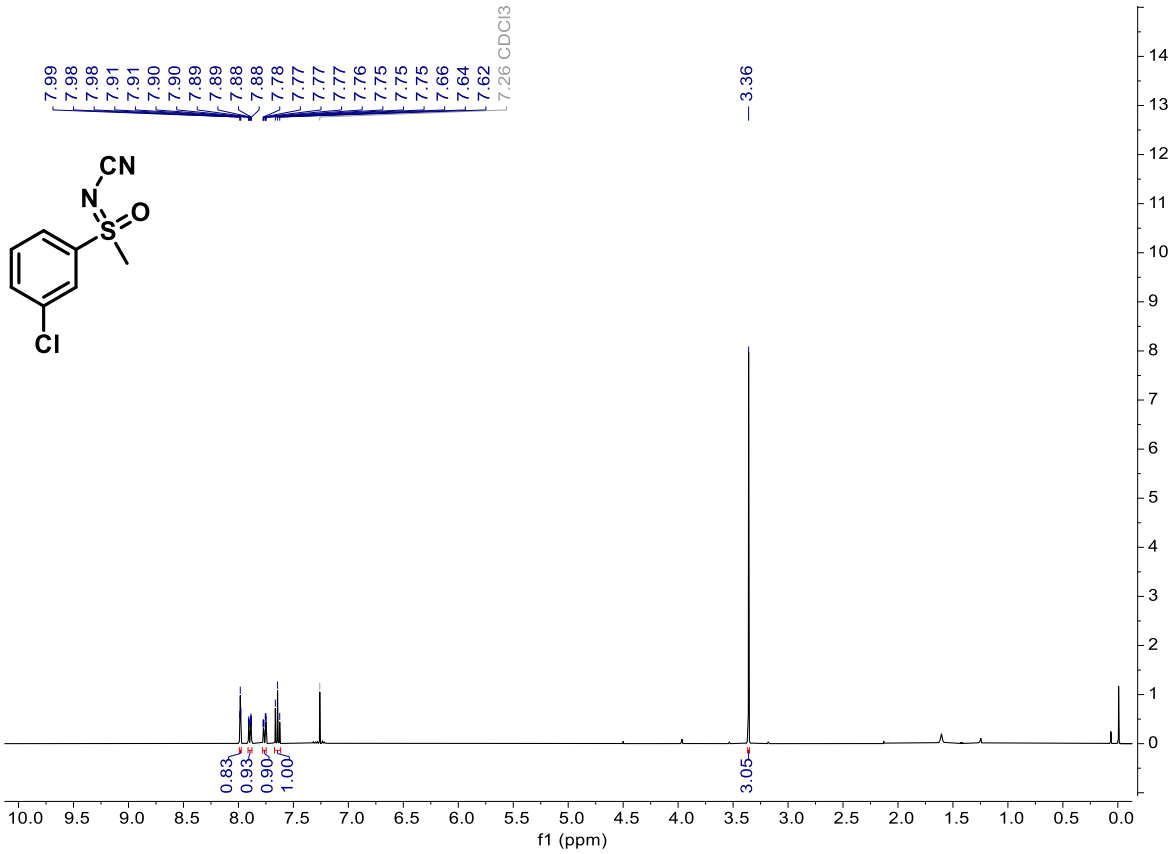

147.13
132.99
130.99
128.05
112.13
77.16 CDCl3
45.05
21.89
f1 (ppm)

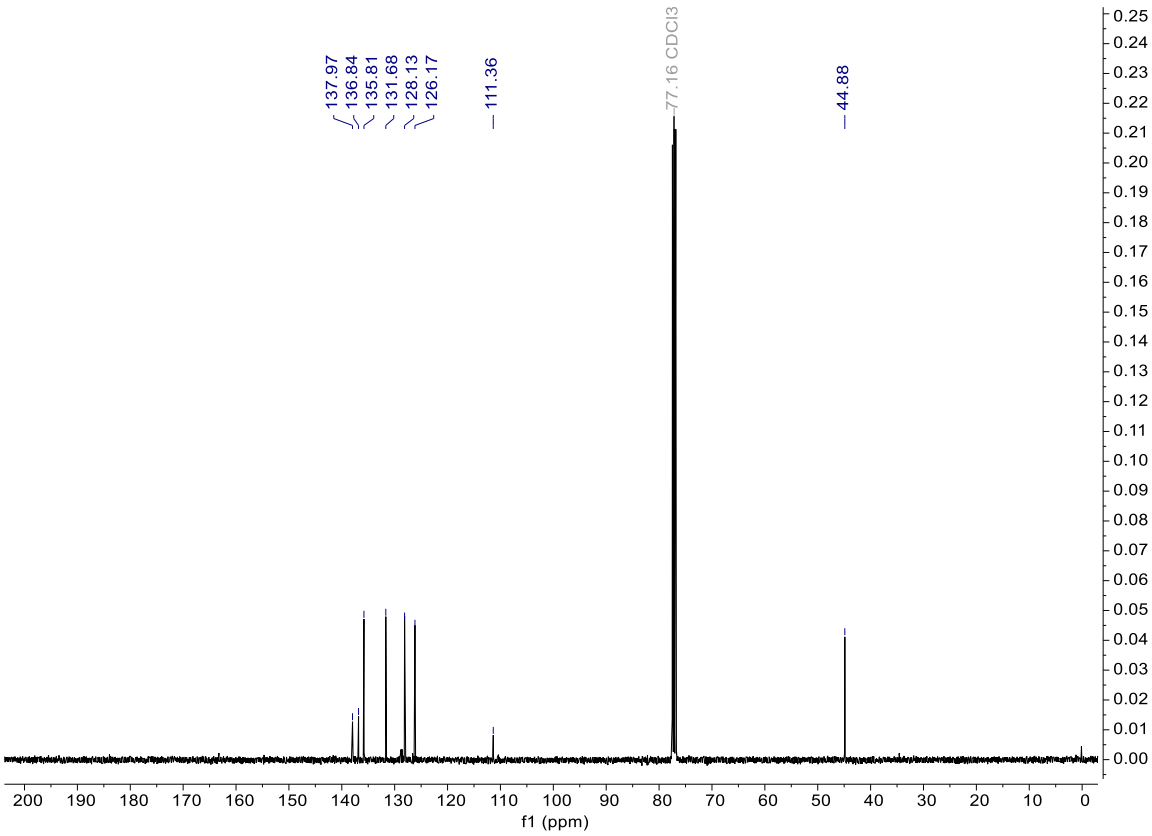
Data for **5h**:


8.86
8.85
8.85
8.67
8.66
8.66
8.66
8.64
8.64
8.64
8.64
8.37
8.36
8.36
8.36
8.35
8.34
8.34
8.34
7.98
7.96
7.94
7.26 CDCl3
3.45
CN
N
S
O
NO2
0.95
1.00
1.02
1.05
3.20
f1 (ppm)

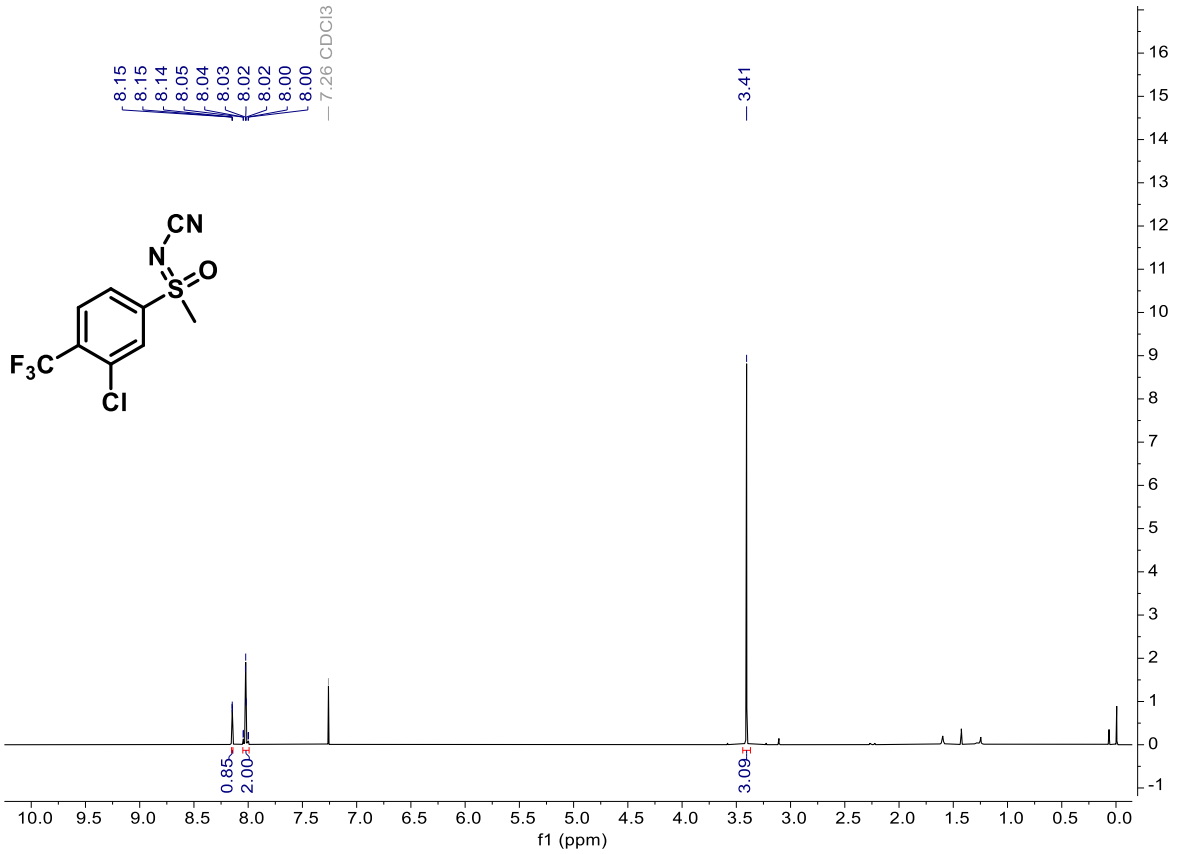

149.06
138.63
133.50
132.04
130.04
123.66
110.81
77.16 CDCl3
44.73
f1 (ppm)

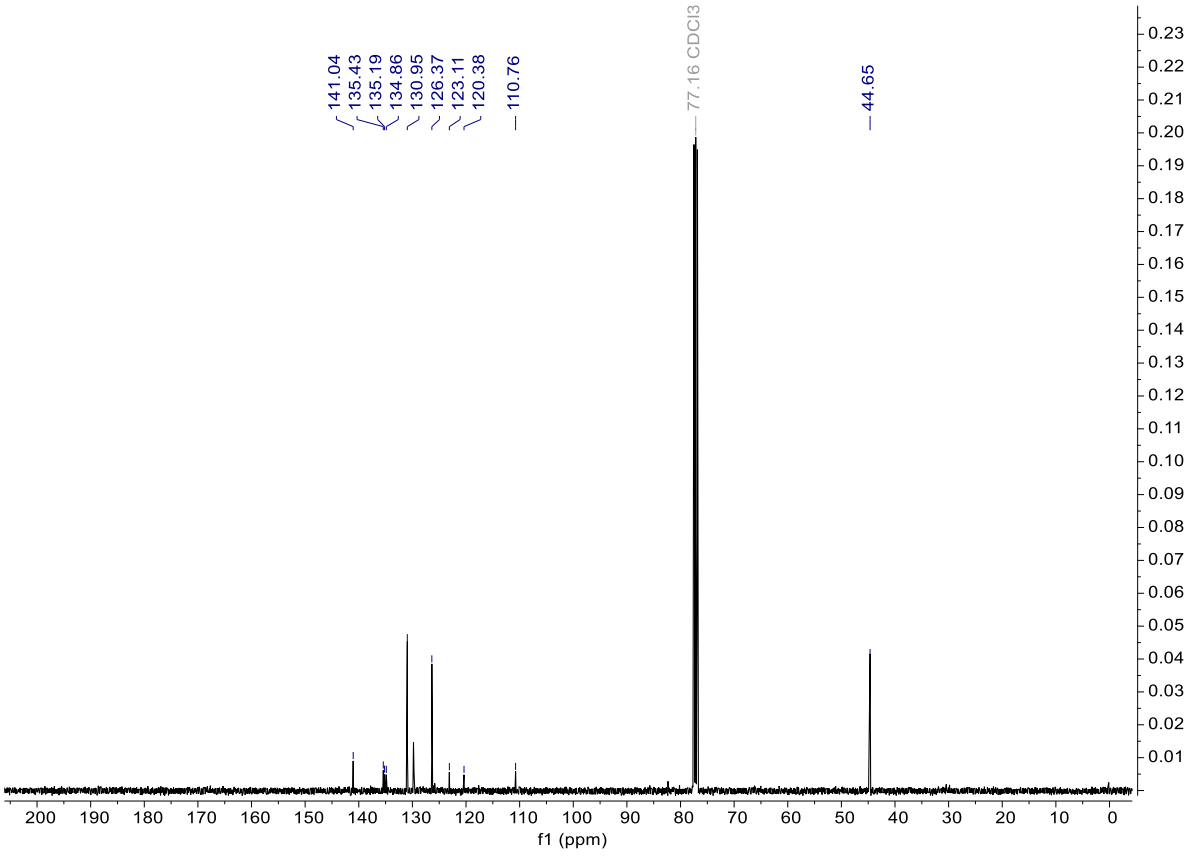
Data for **5i**


7.99
7.98
7.98
7.91
7.91
7.90
7.90
7.89
7.89
7.88
7.88
7.78
7.77
7.77
7.77
7.76
7.75
7.75
7.75
7.66
7.64
7.62
7.26 CDCl3
3.36
CN
N
S
O
Cl
0.83
0.93
0.90
1.00
3.05
f1 (ppm)

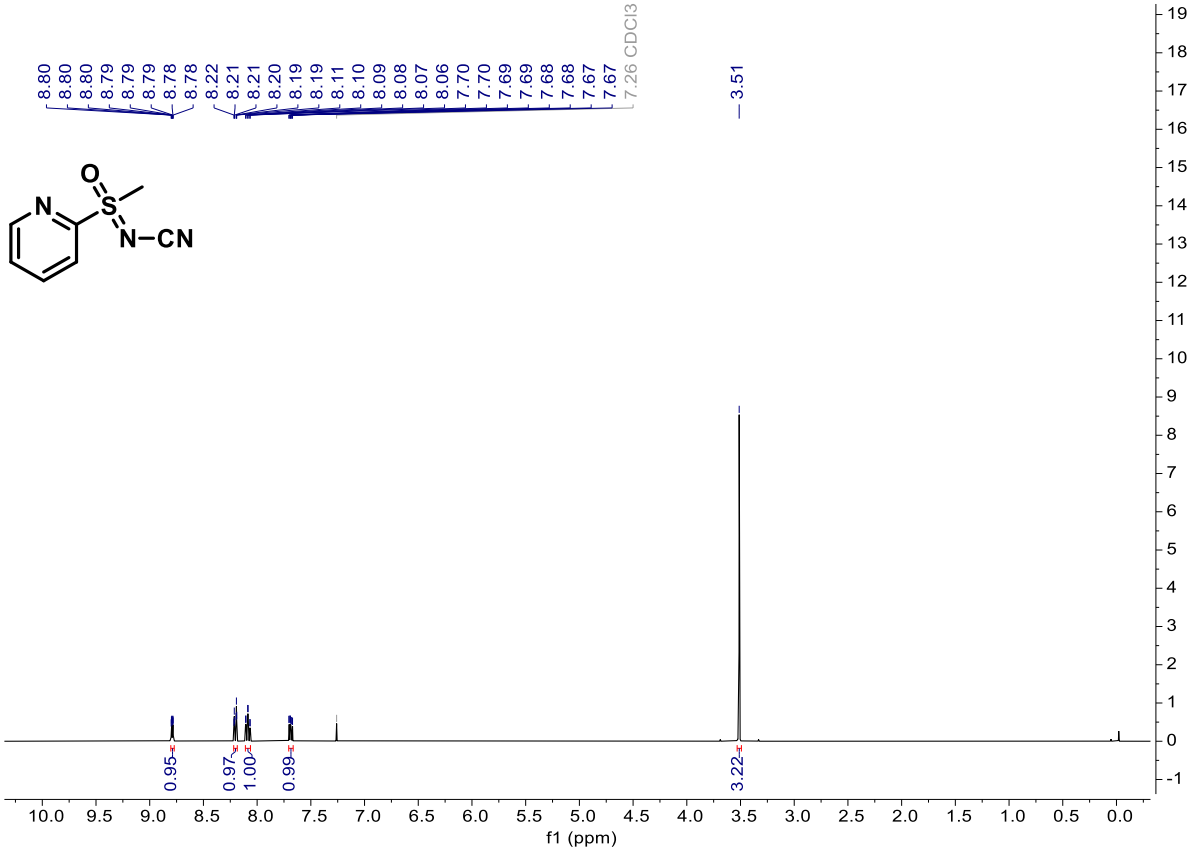

137.97
136.84
135.81
131.68
128.13
126.17
111.36
77.16 CDCl3
44.88
f1 (ppm)

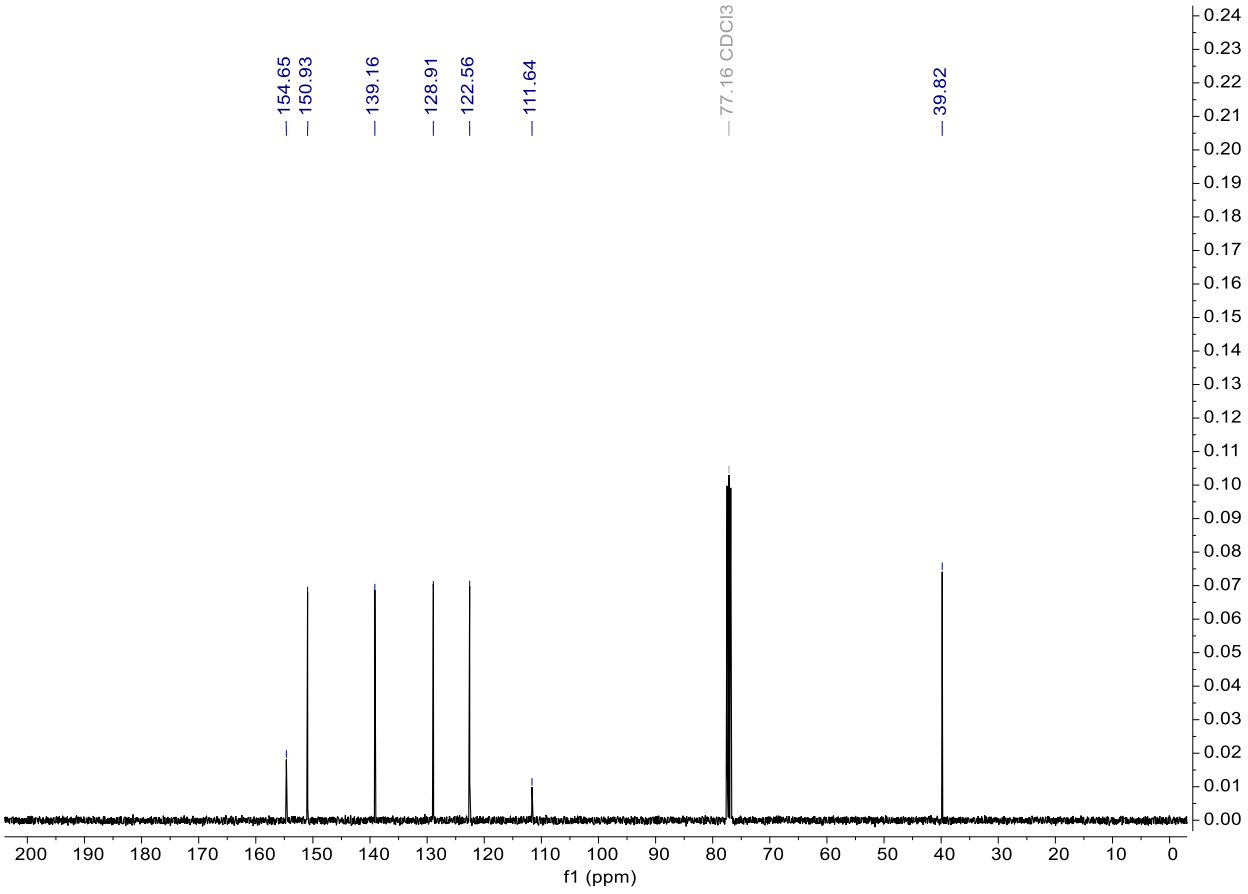
Data for **5j**


8.15
8.15
8.14
8.05
8.04
8.03
8.02
8.02
8.00
8.00
7.26 CDCl3
3.41
CN
N
S
O
F3C
Cl
0.85
2.00
3.09
f1 (ppm)

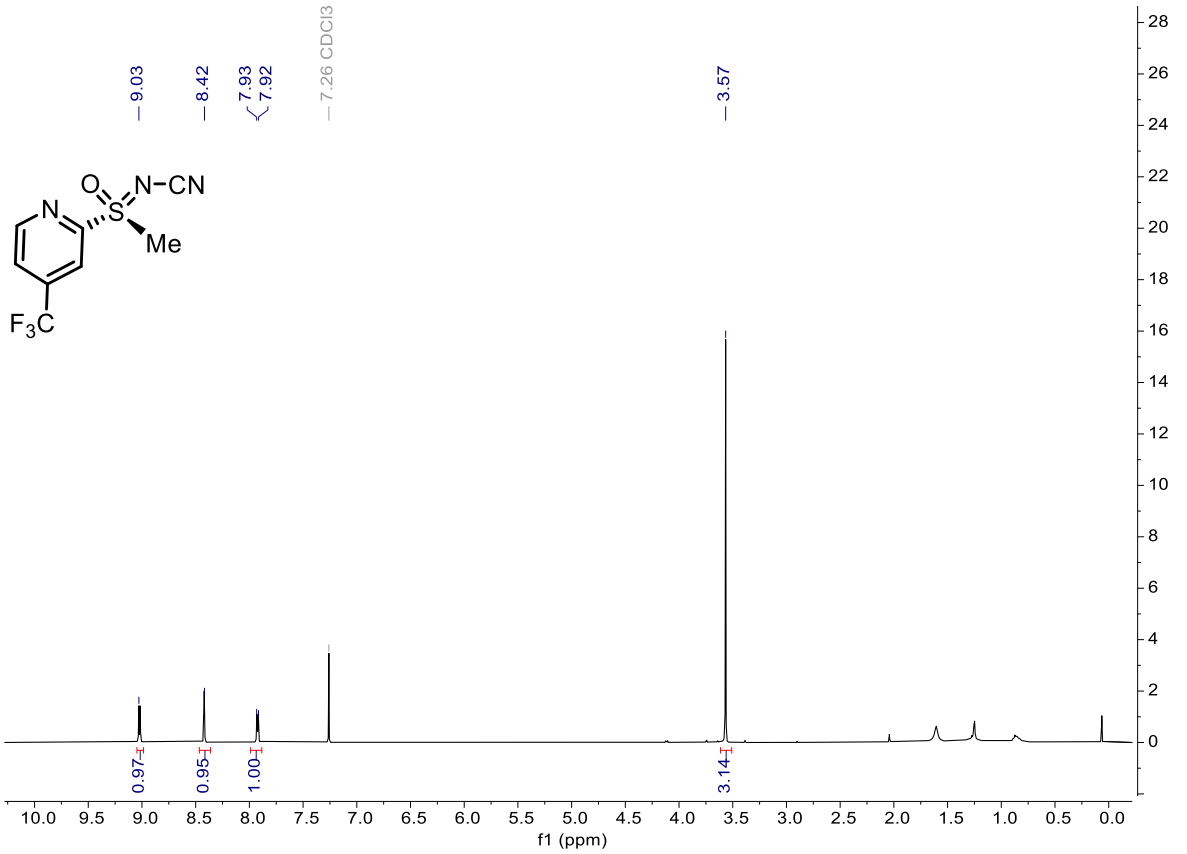

141.04
135.43
135.19
134.86
130.95
126.37
123.11
120.38
110.76
77.16 CDCl3
44.65
f1 (ppm)

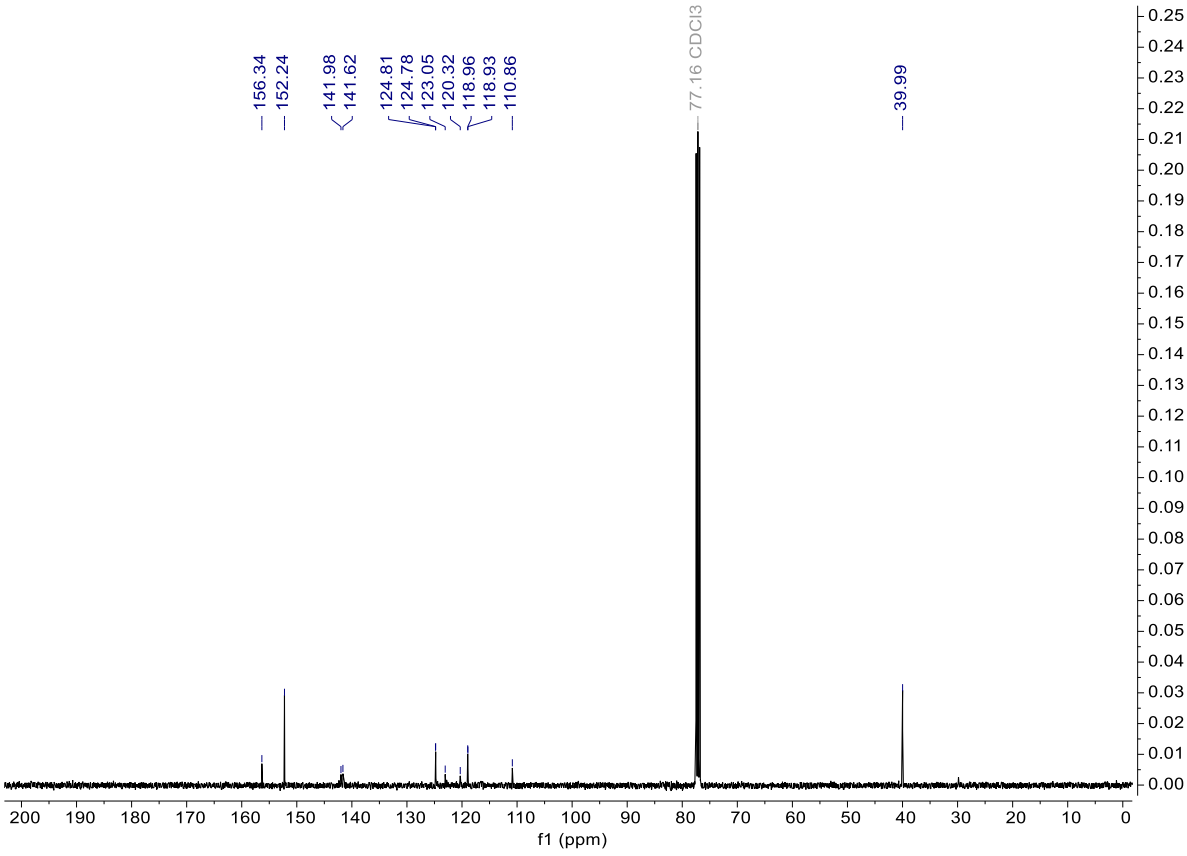
Data for **5k**


8.80
8.80
8.80
8.79
8.79
8.79
8.78
8.78
8.22
8.21
8.21
8.20
8.19
8.19
8.11
8.10
8.09
8.08
8.07
8.06
7.70
7.70
7.69
7.69
7.68
7.68
7.67
7.67
7.26 CDCl3
3.51
O
S
N
N–CN
0.95
0.97
1.00
0.99
3.22
f1 (ppm)

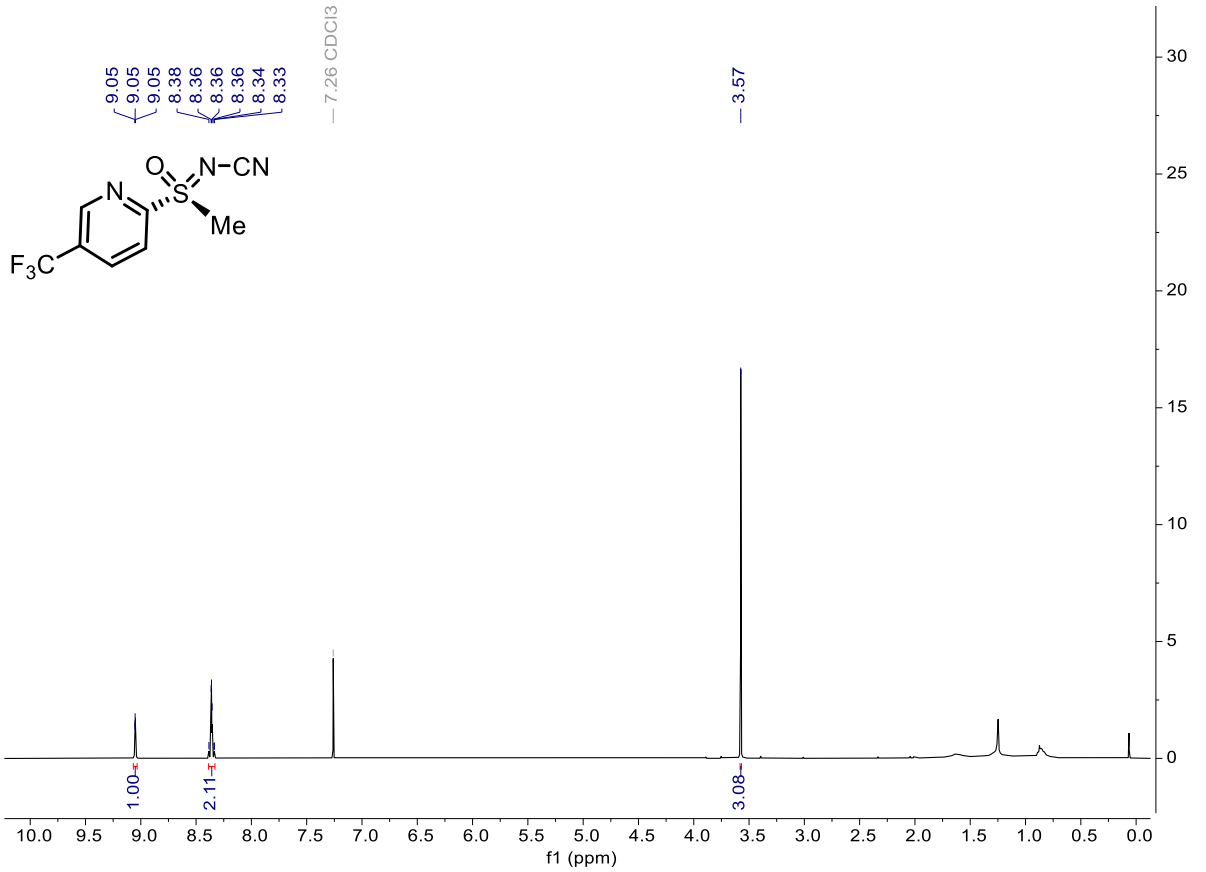

154.65
150.93
139.16
128.91
122.56
111.64
77.16 CDCl3
39.82
f1 (ppm)

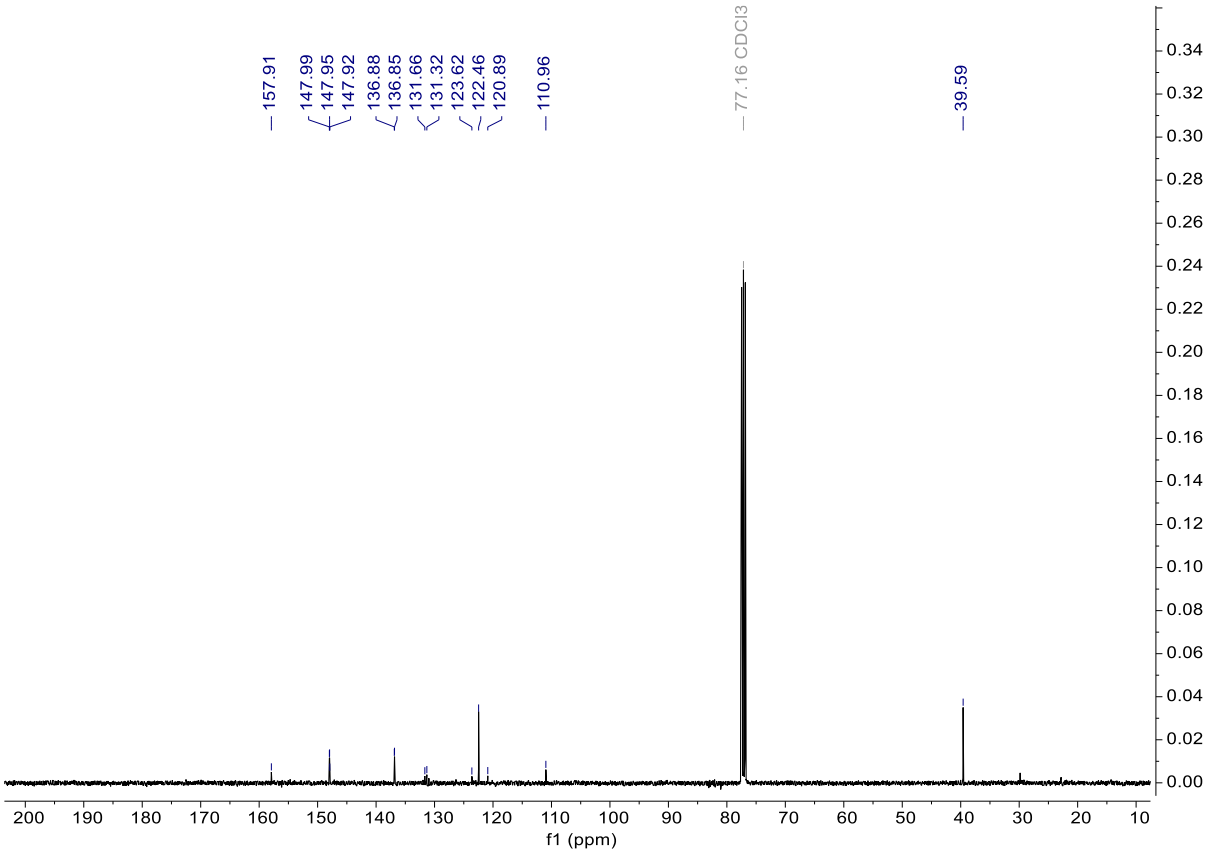
Data for **5l**


9.03
8.42
7.93
7.92
7.26 CDCl3
3.57
O
N–CN
S
N
Me
F3C
0.97
0.95
1.00
3.14
f1 (ppm)

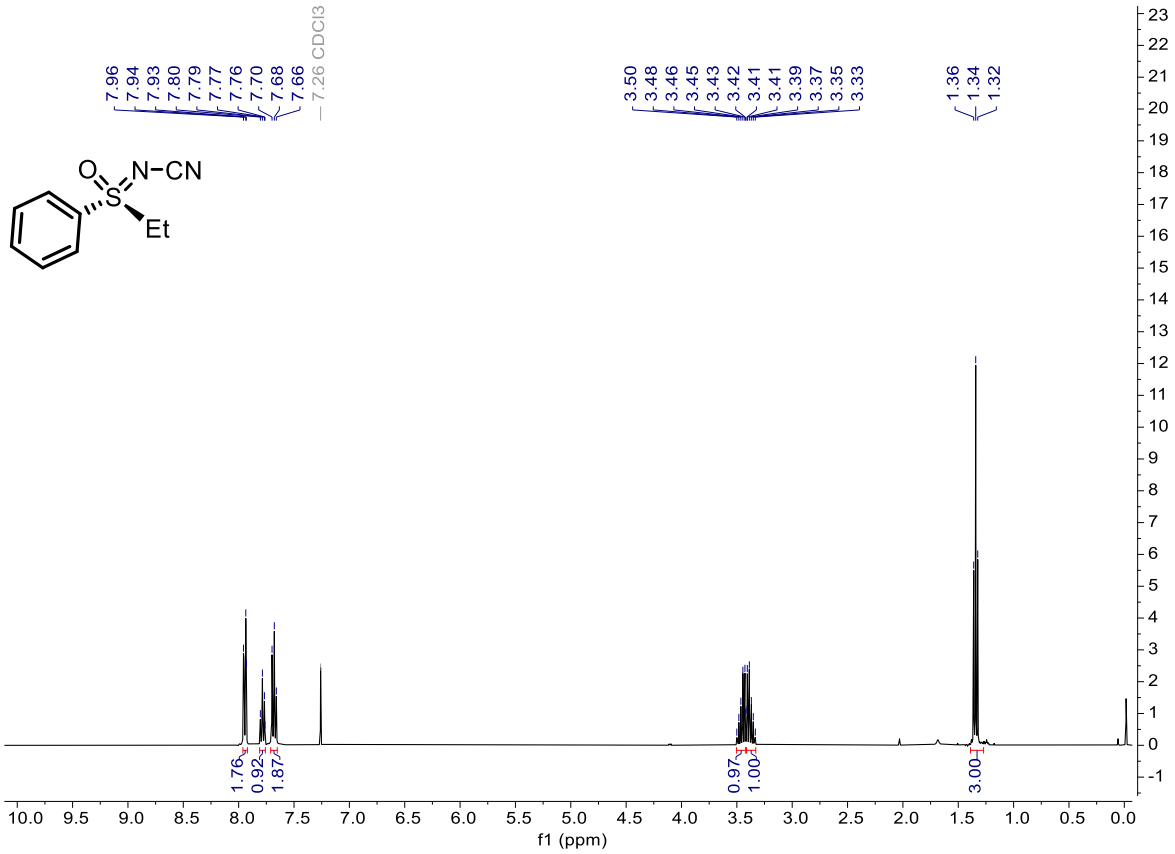

156.34
152.24
141.98
141.62
124.81
124.78
123.05
120.32
118.96
118.93
110.86
77.16 CDCl3
39.99
f1 (ppm)

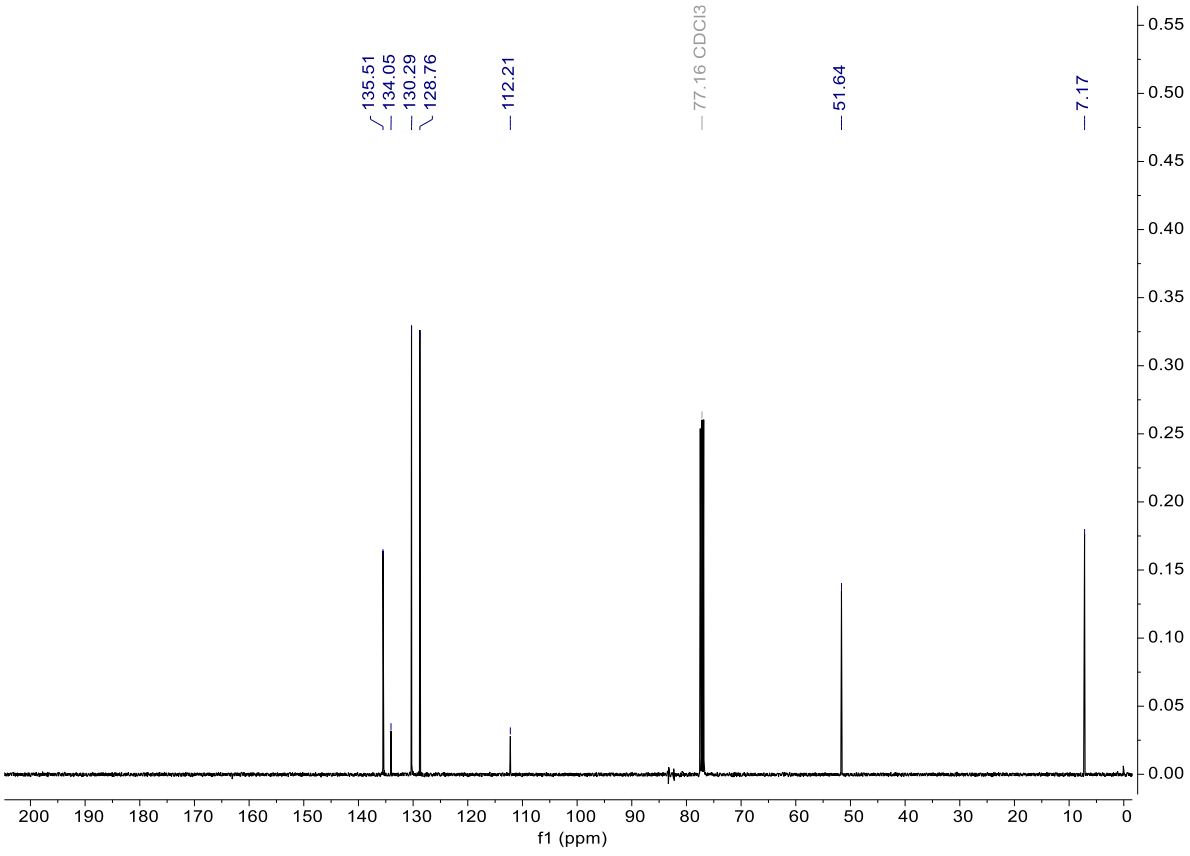
Data for **5m**:


9.05
9.05
9.05
8.38
8.36
8.36
8.36
8.34
8.33
7.26 CDCl3
3.57
O
N−CN
S
N
Me
F3C
1.00
2.11
3.08
f1 (ppm)

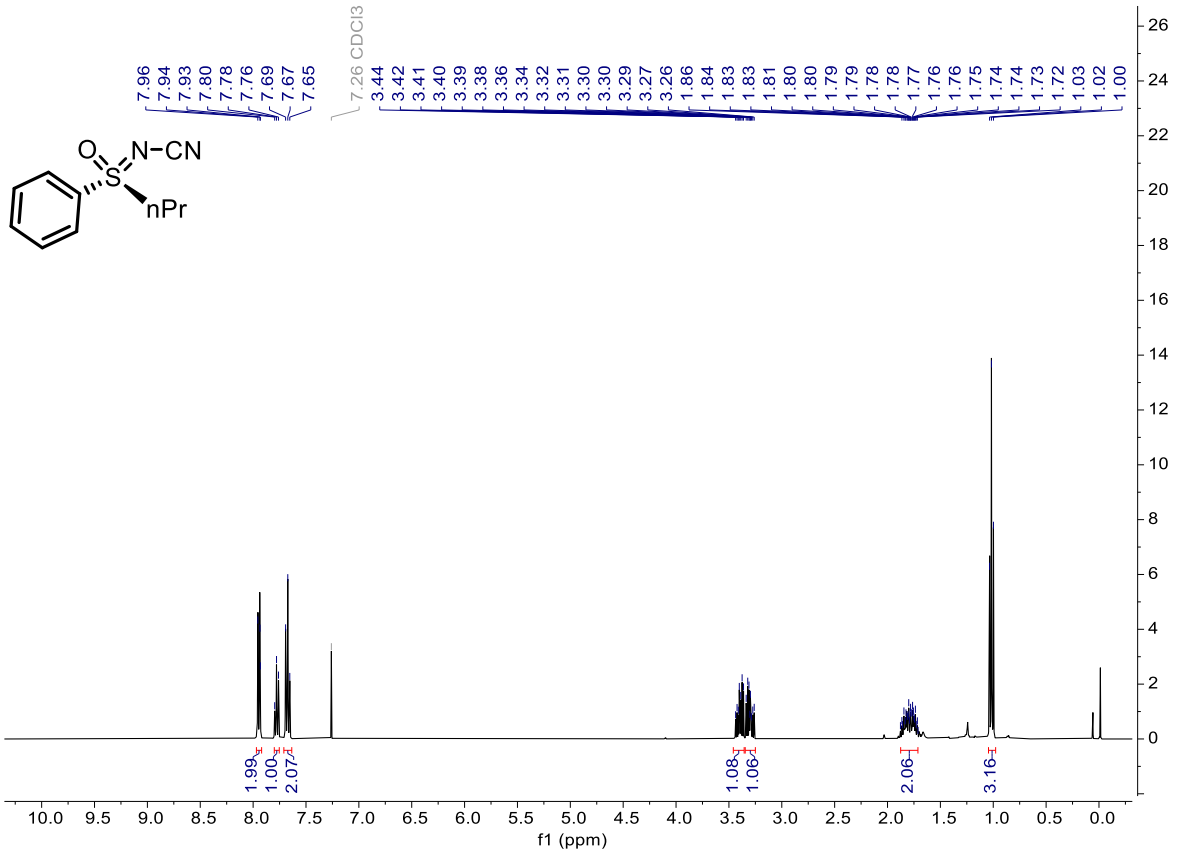

157.91
147.99
147.95
147.92
136.88
136.85
131.66
131.32
123.62
122.46
120.89
110.96
77.16 CDCl3
39.59
f1 (ppm)

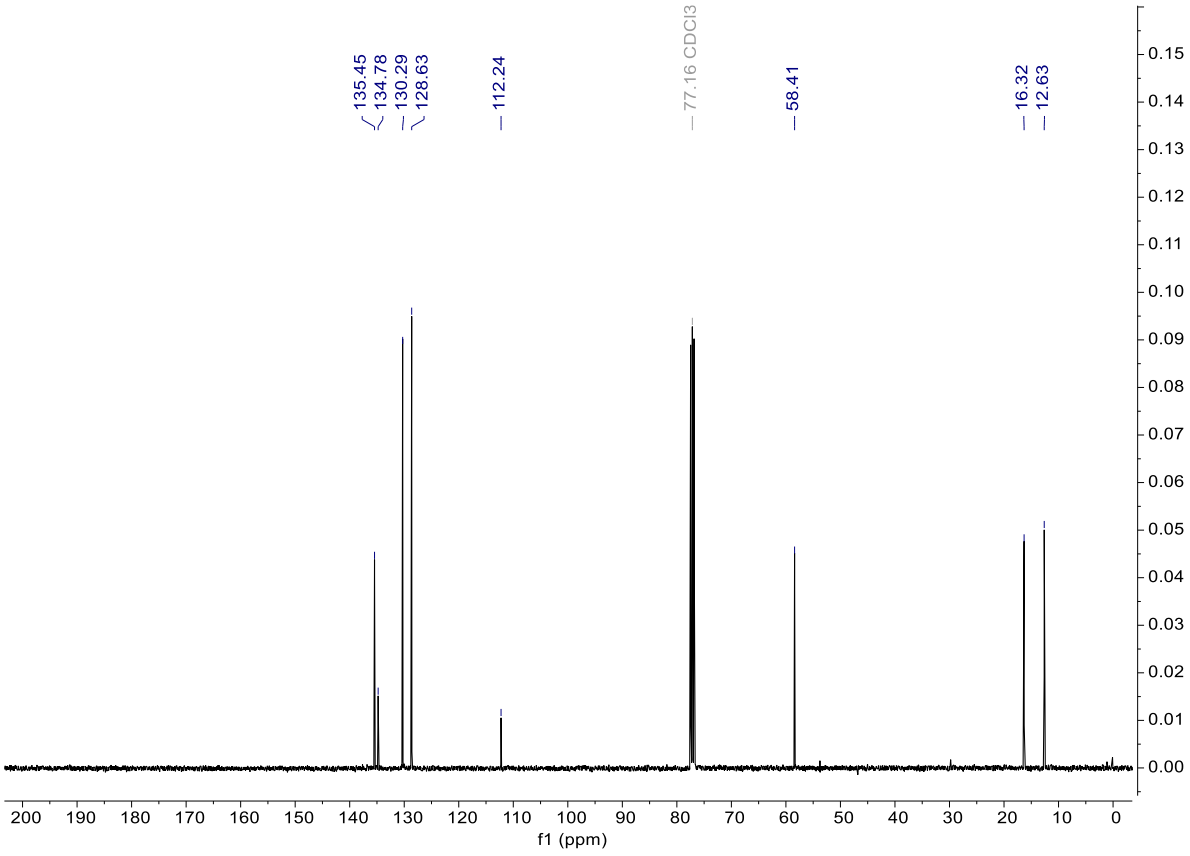
Data for **5n**


7.96
7.94
7.93
7.80
7.79
7.77
7.76
7.70
7.68
7.66
7.26 CDCl3
3.50
3.48
3.46
3.45
3.43
3.42
3.41
3.41
3.39
3.37
3.35
3.33
1.36
1.34
1.32
O
N−CN
S
Et
1.76
0.92
1.87
0.97
1.00
3.00
f1 (ppm)

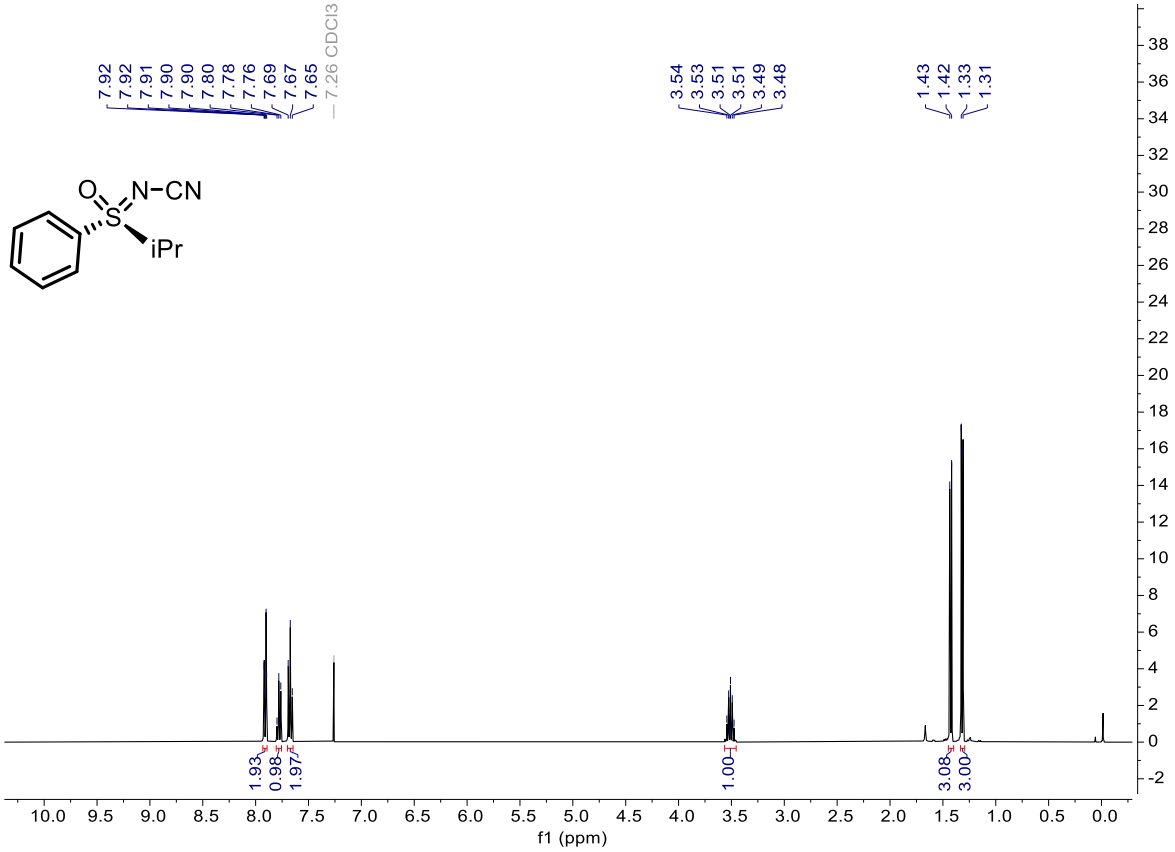

135.51
134.05
130.29
128.76
112.21
77.16 CDCl3
51.64
7.17
f1 (ppm)

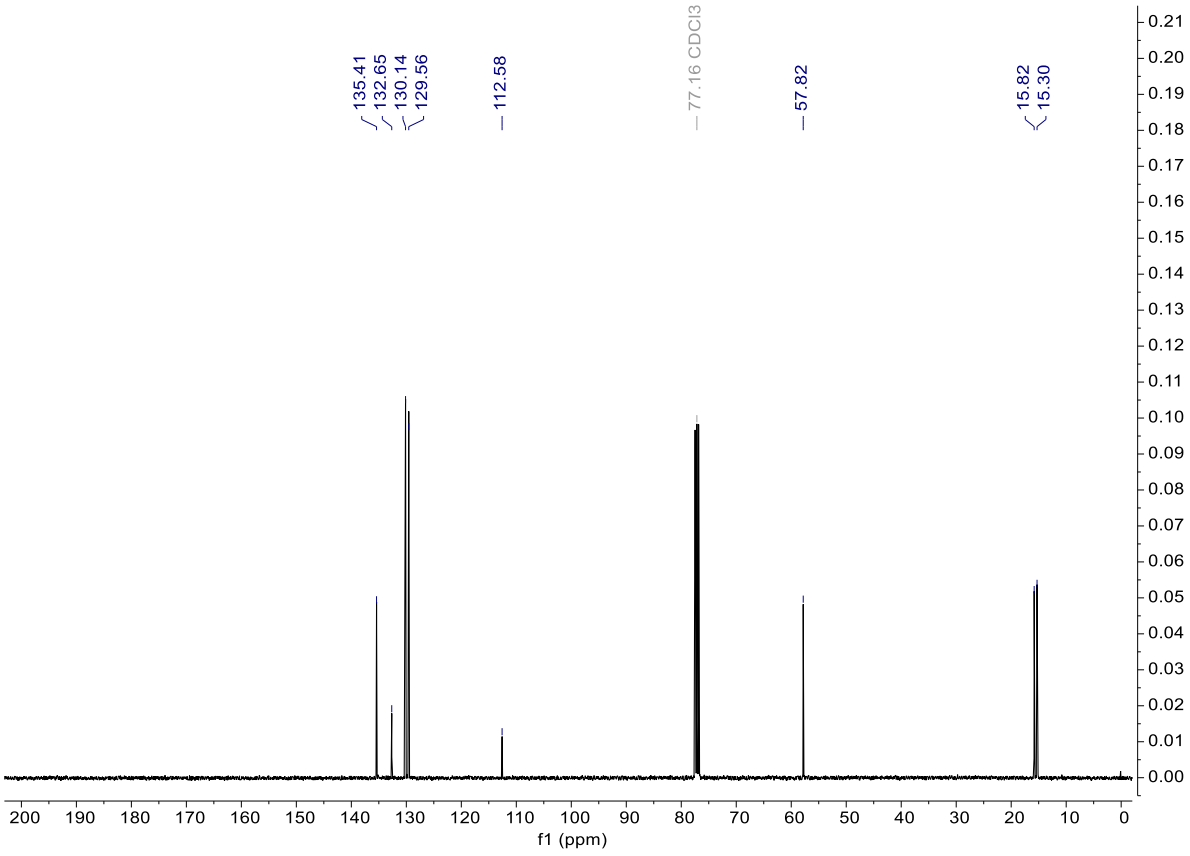
Data for **5o**


7.96
7.94
7.93
7.80
7.78
7.76
7.69
7.67
7.65
7.26 CDCl3
3.44
3.42
3.41
3.40
3.39
3.38
3.36
3.34
3.32
3.31
3.30
3.30
3.29
3.27
3.26
1.86
1.84
1.83
1.83
1.81
1.80
1.80
1.79
1.79
1.78
1.78
1.77
1.76
1.76
1.75
1.74
1.74
1.73
1.72
1.03
1.02
1.00
O
N−CN
S
nPr
1.99
1.00
2.07
1.08
1.06
2.06
3.16
f1 (ppm)

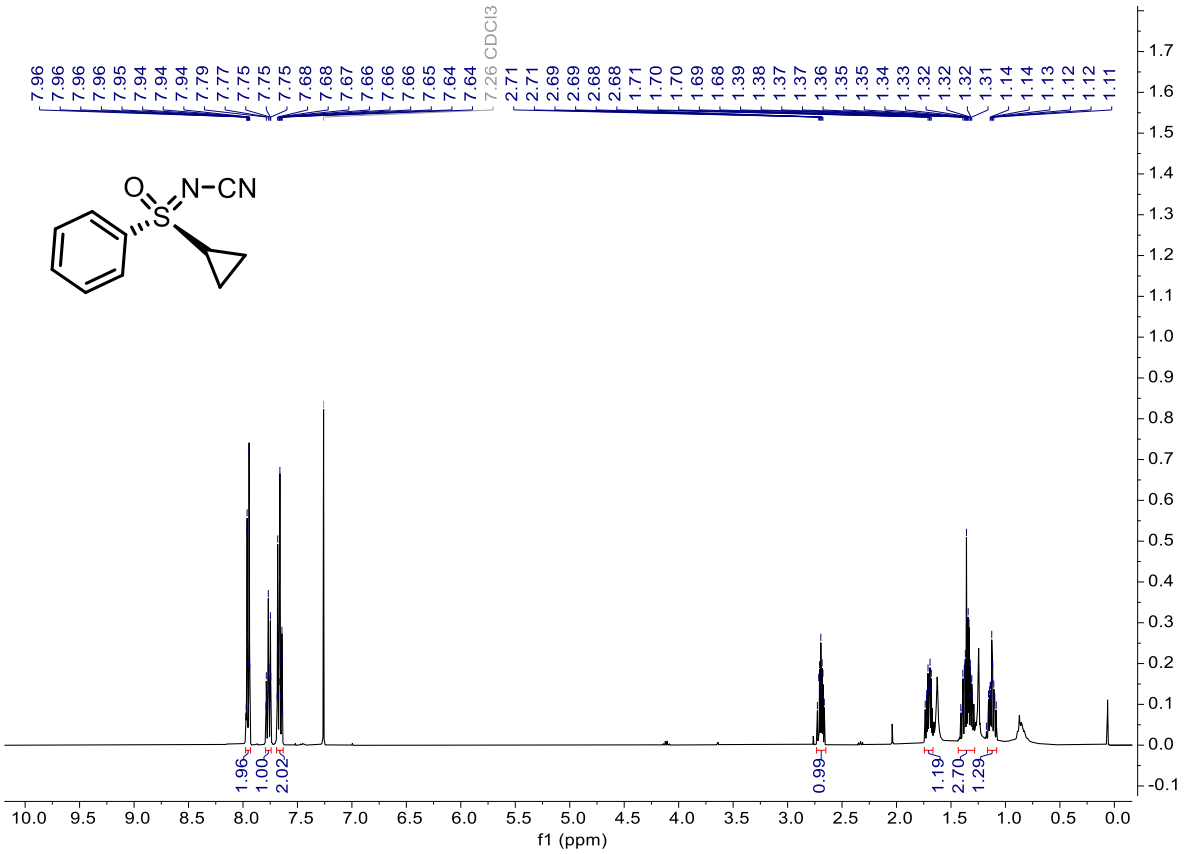

135.45
134.78
130.29
128.63
112.24
77.16 CDCl3
58.41
16.32
12.63
f1 (ppm)

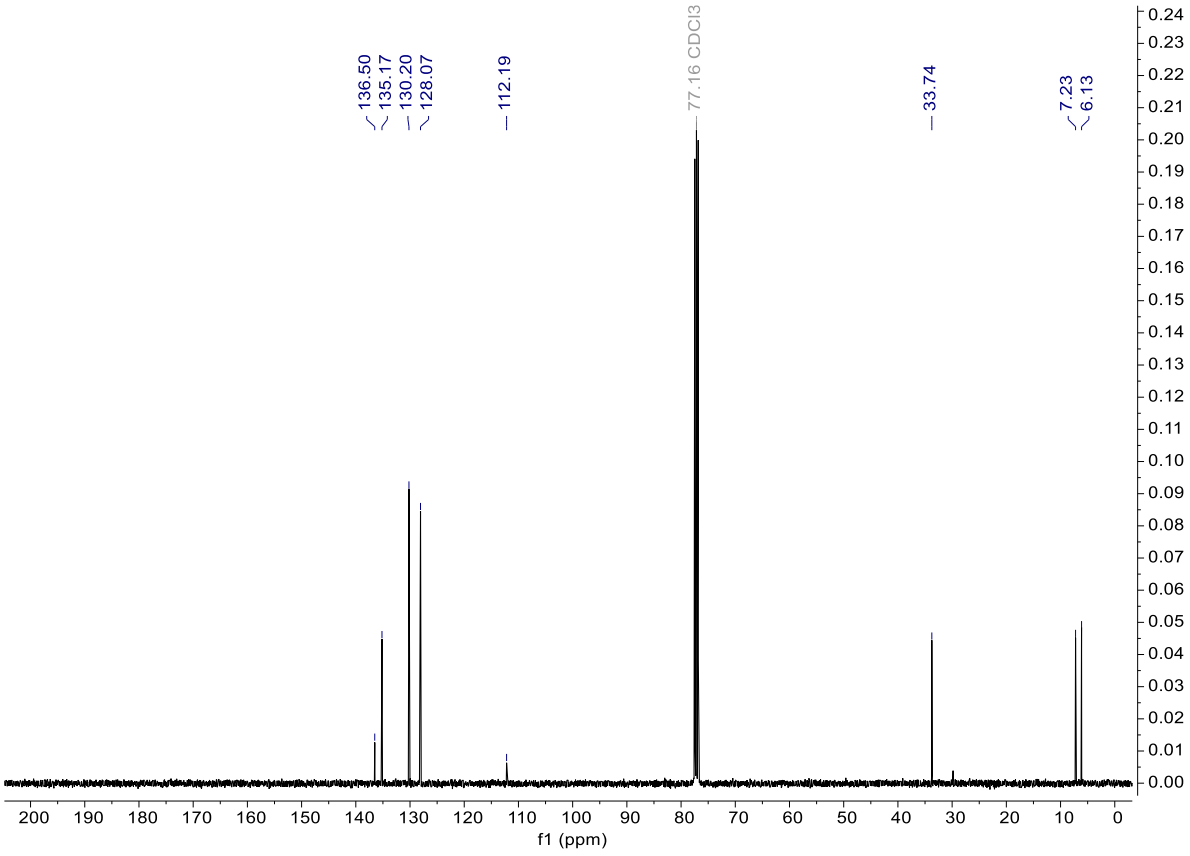
Data for **5p**


7.92
7.92
7.91
7.90
7.90
7.80
7.78
7.76
7.69
7.67
7.65
7.26 CDCl3
3.54
3.53
3.51
3.51
3.49
3.48
1.43
1.42
1.33
1.31
O
N−CN
S
iPr
1.93
0.98
1.97
1.00
3.08
3.00
f1 (ppm)

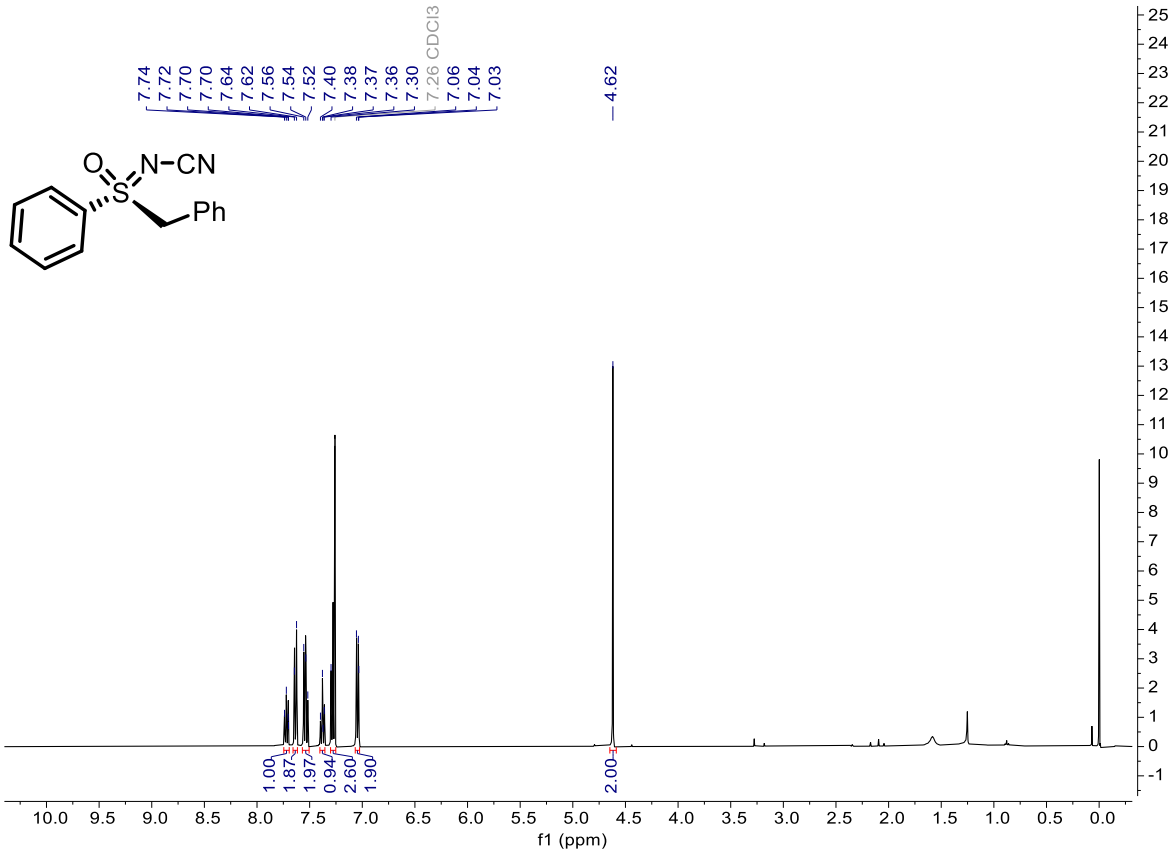

135.41
132.65
130.14
129.56
112.58
77.16 CDCl3
57.82
15.82
15.30
f1 (ppm)

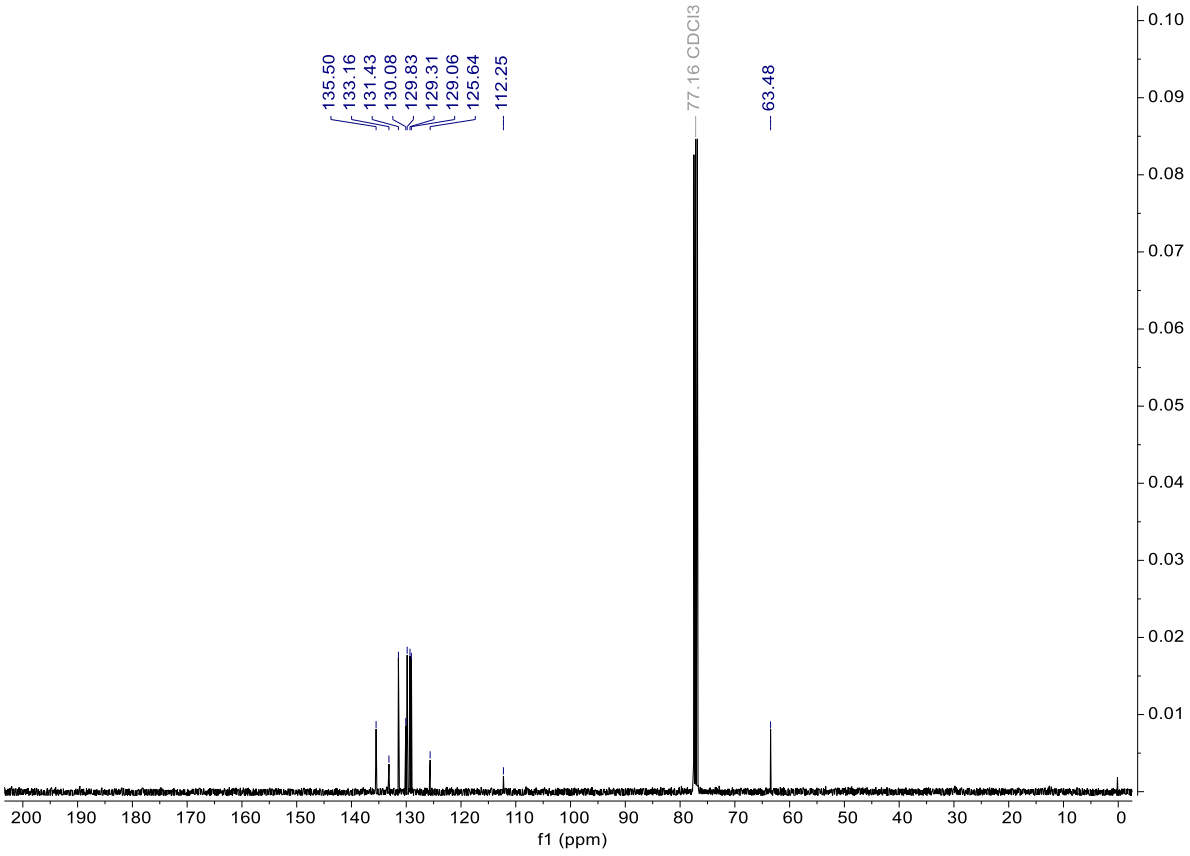
Data for **5q**


7.96 7.96 7.96 7.96 7.95 7.94 7.94 7.94 7.79 7.77 7.75 7.75 7.75 7.68 7.68 7.67 7.66 7.66 7.66 7.65 7.64 7.64
7.26 CDCl3
2.71 2.71 2.69 2.69 2.68 2.68 2.68 1.71 1.70 1.70 1.69 1.68 1.39 1.38 1.37 1.37 1.36 1.35 1.35 1.34 1.33 1.32 1.32 1.32 1.31 1.14 1.14 1.13 1.12 1.12 1.11
O
N−CN
S
1.96
1.00
2.02
0.99
1.19
2.70
1.29
f1 (ppm)

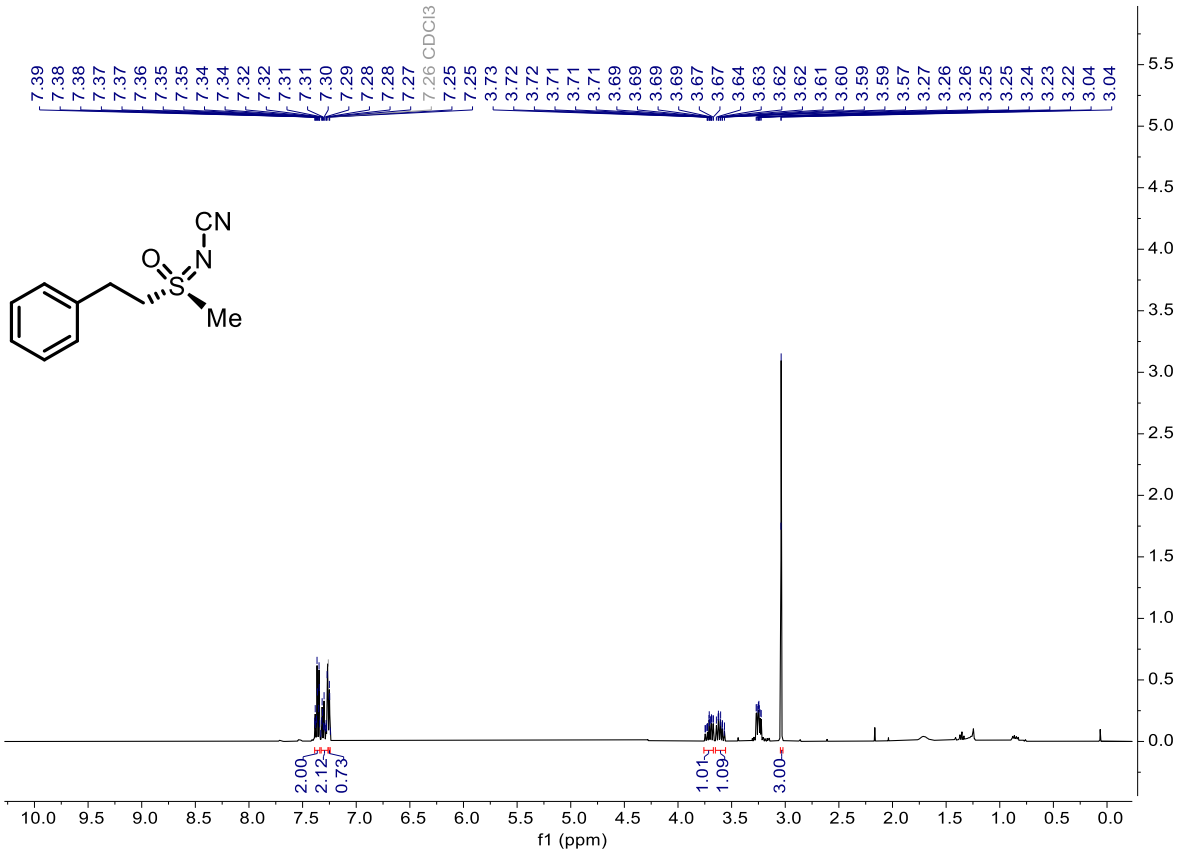

136.50
135.17
130.20
128.07
112.19
77.16 CDCl3
33.74
7.23
6.13
f1 (ppm)

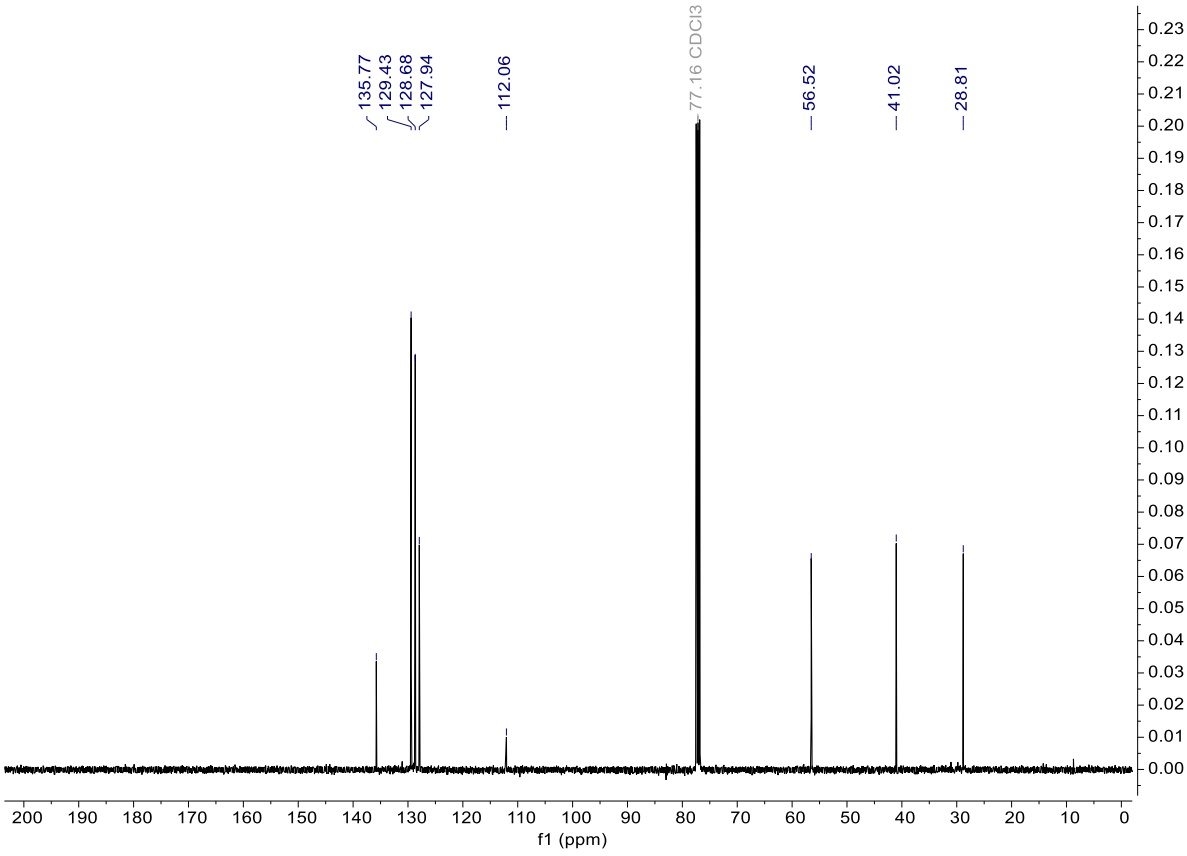
Data for **5r**


7.74
7.72
7.70
7.70
7.64
7.62
7.56
7.54
7.52
7.40
7.38
7.37
7.36
7.30
7.26 CDCl3
7.06
7.04
7.03
4.62
O
N−CN
S
Ph
1.00
1.87
1.97
0.94
2.60
1.90
2.00
f1 (ppm)

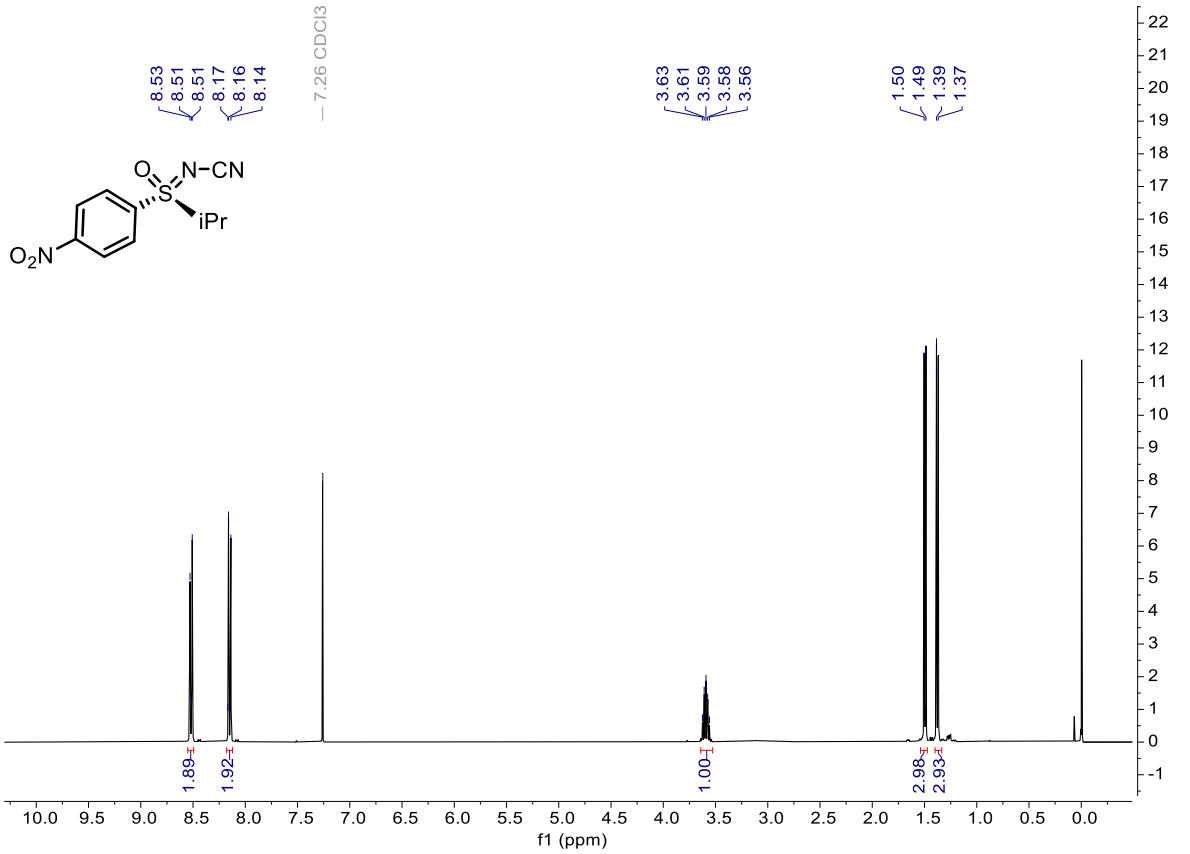

135.50
133.16
131.43
130.08
129.83
129.31
129.06
125.64
112.25
77.16 CDCl3
63.48
f1 (ppm)

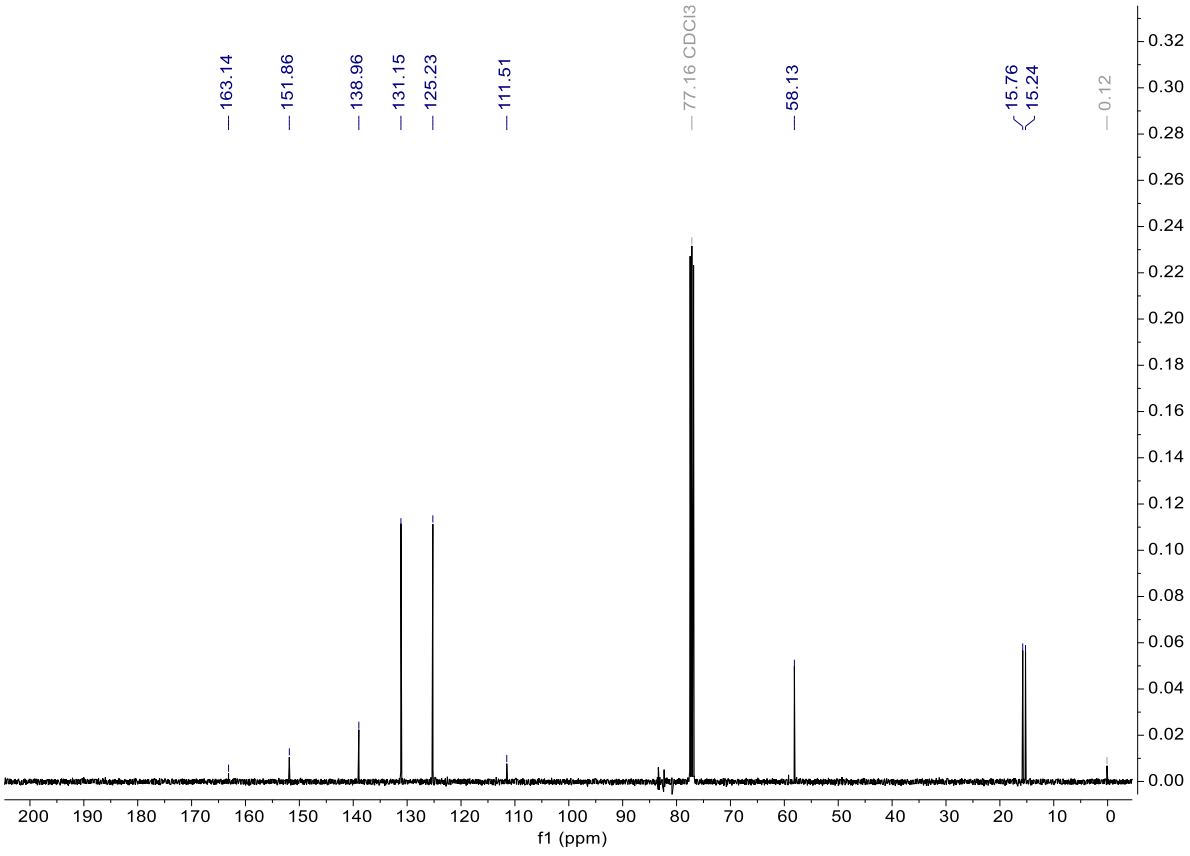
Data for **5s**


7.39 7.38 7.38 7.37 7.37 7.36 7.35 7.35 7.34 7.34 7.32 7.32 7.31 7.31 7.30 7.29 7.28 7.28 7.27 7.26 CDCl3 7.25 7.25
3.73 3.72 3.72 3.71 3.71 3.71 3.69 3.69 3.69 3.69 3.67 3.67 3.64 3.63 3.62 3.62 3.61 3.60 3.59 3.59 3.57 3.27 3.26 3.25 3.25 3.24 3.23 3.22 3.04 3.04
CN
O
N
S
Me
2.00 2.12 0.73 1.01 1.09 3.00
f1 (ppm)

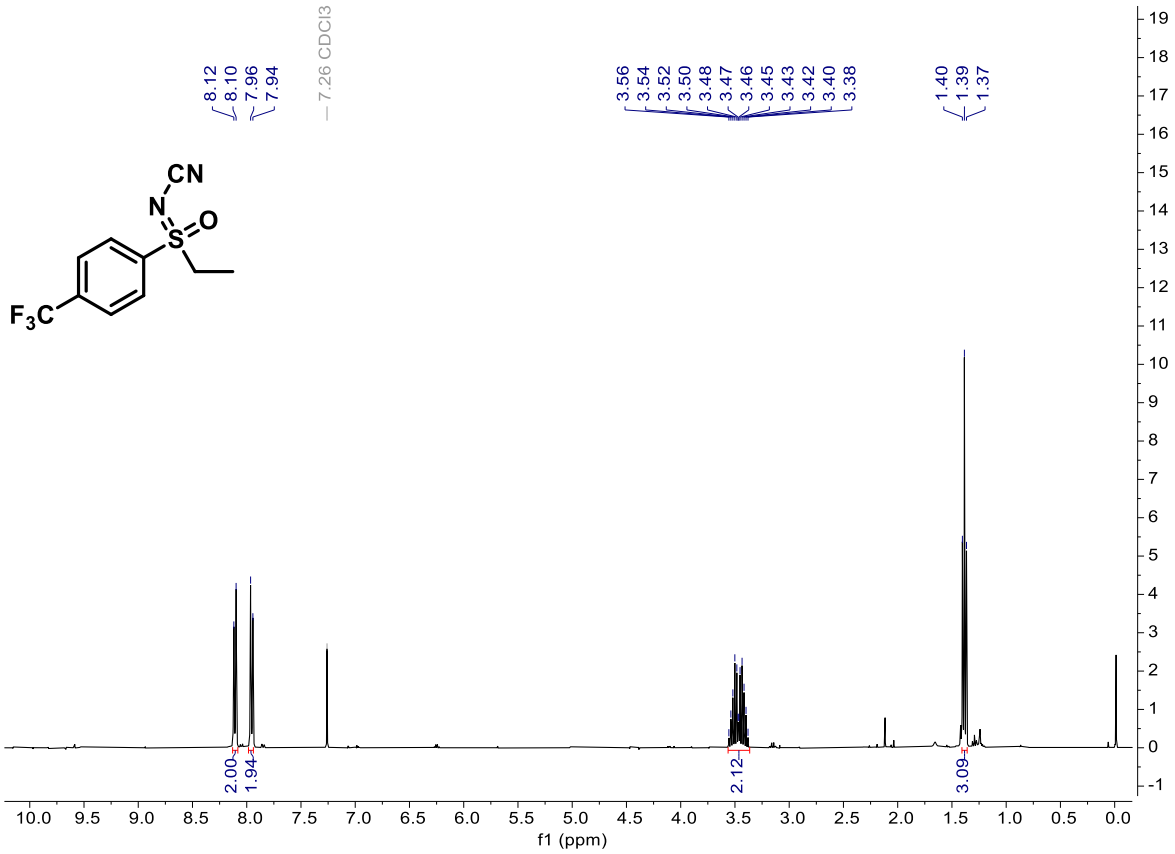

135.77 129.43 128.68 127.94 112.06 77.16 CDCl3 56.52 41.02 28.81
f1 (ppm)

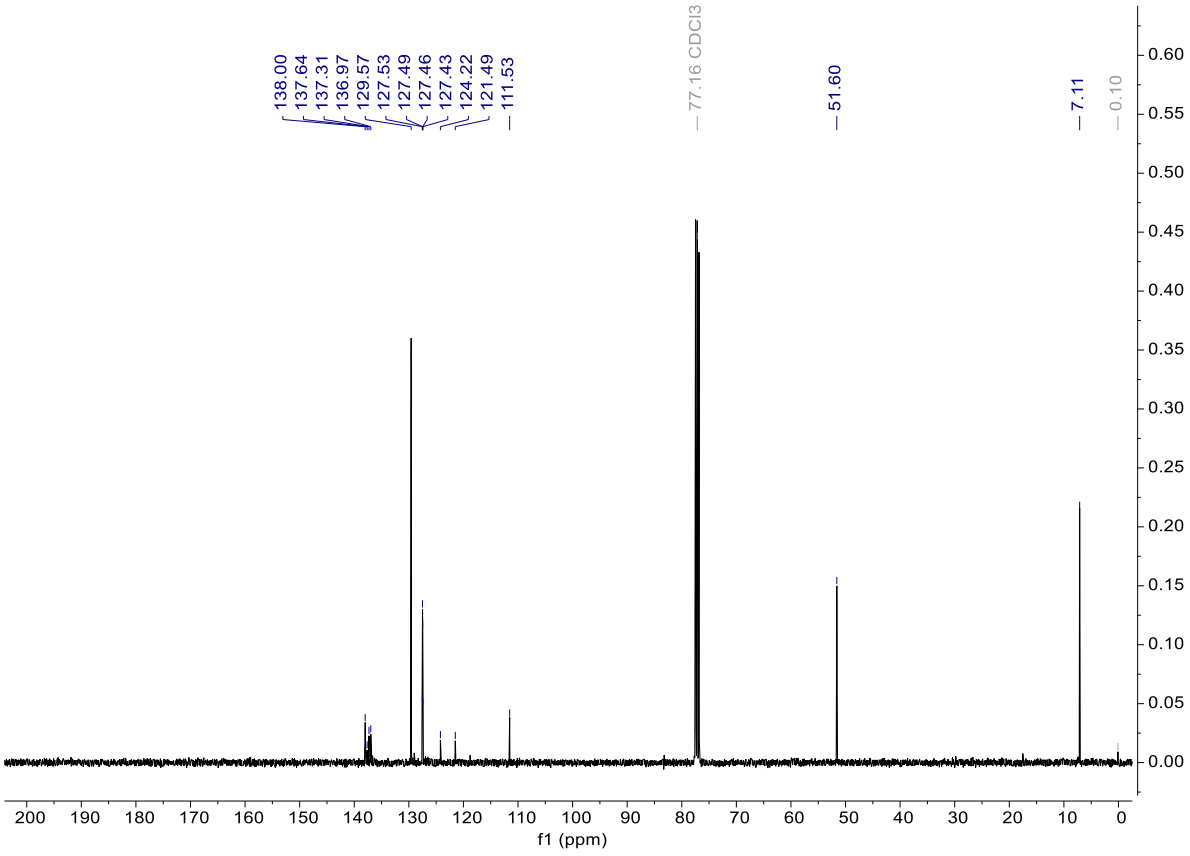
Data for **5t**:


8.53
8.51
8.51
8.17
8.16
8.14
7.26 CDCl3
3.63
3.61
3.59
3.58
3.56
1.50
1.49
1.39
1.37
O
N–CN
S
iPr
O2N
1.89
1.92
1.00
2.98
2.93
f1 (ppm)

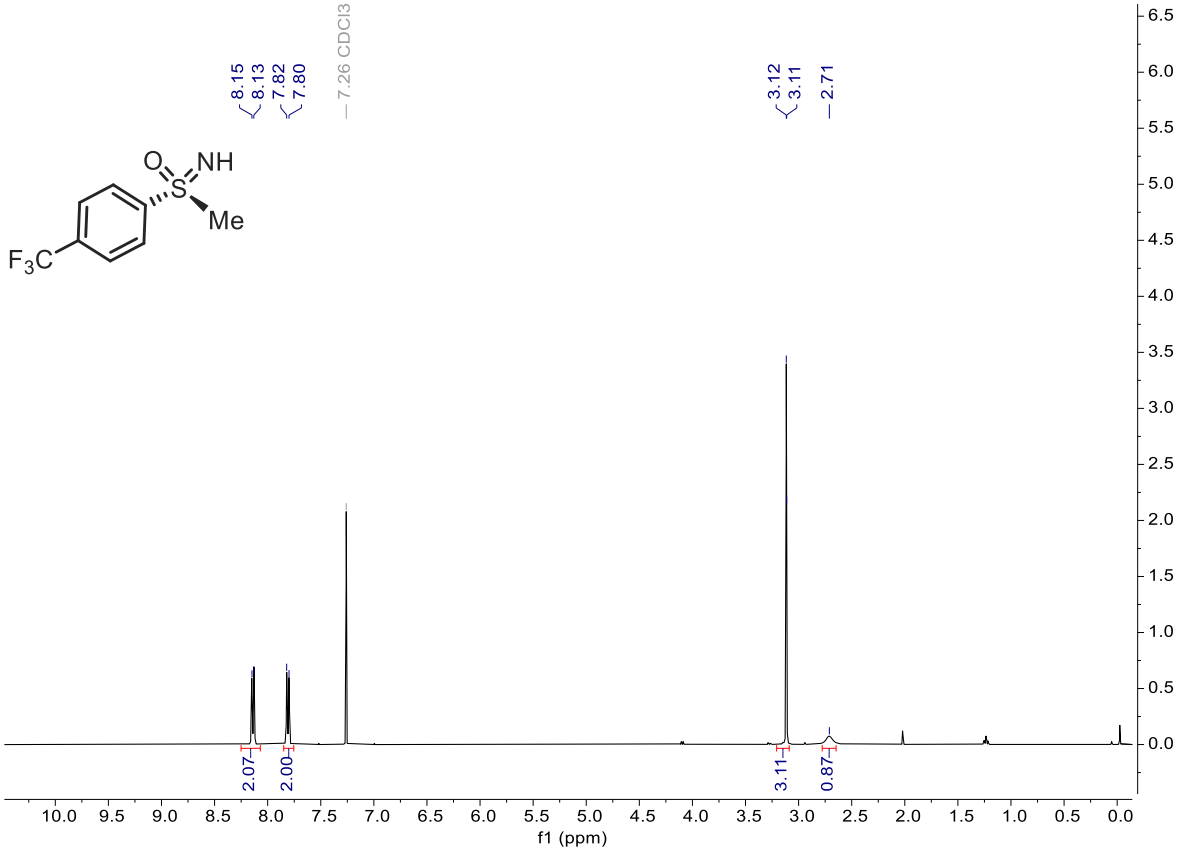

163.14
151.86
138.96
131.15
125.23
111.51
77.16 CDCl3
58.13
15.76
15.24
0.12
f1 (ppm)

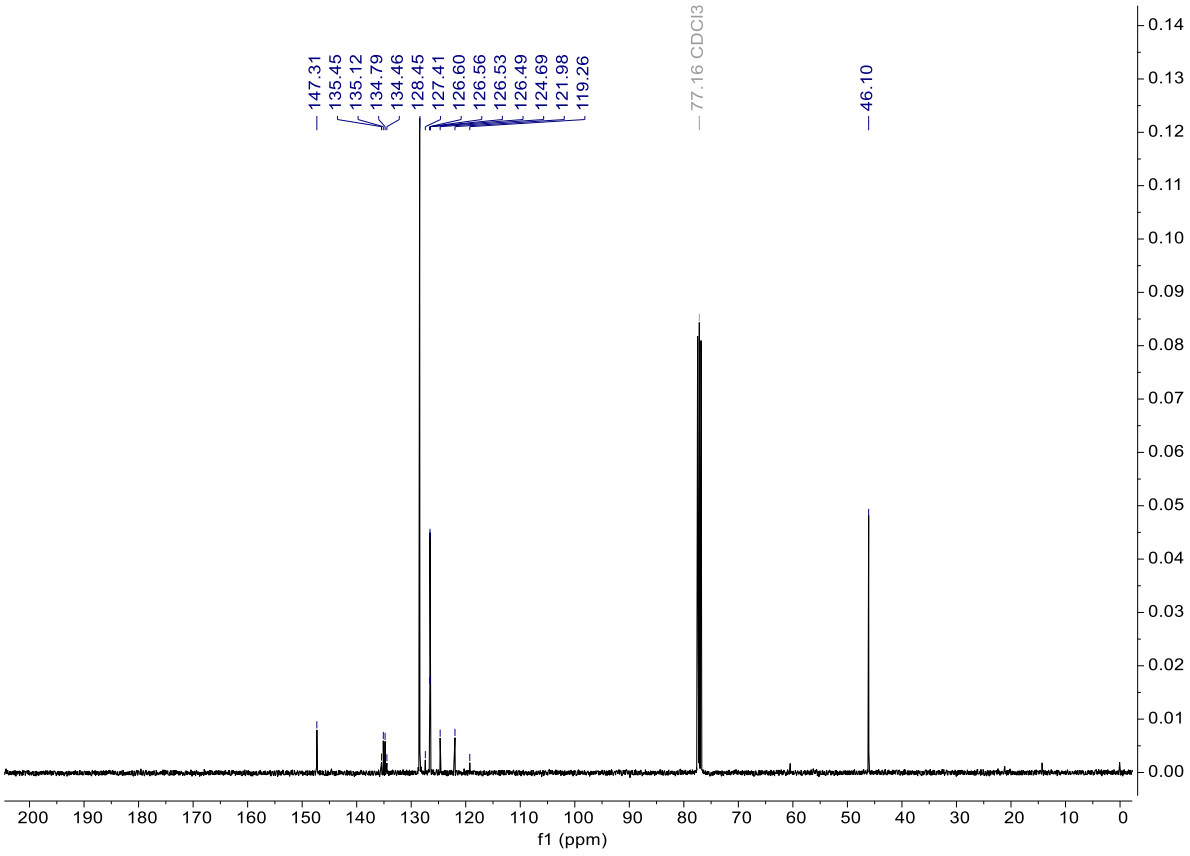
Data for **5u**:


8.12
8.10
7.96
7.94
7.26 CDCl3
3.56
3.54
3.52
3.50
3.48
3.47
3.46
3.45
3.43
3.42
3.40
3.38
1.40
1.39
1.37
CN
N
S
O
F3C
2.00
1.94
2.12
3.09
f1 (ppm)

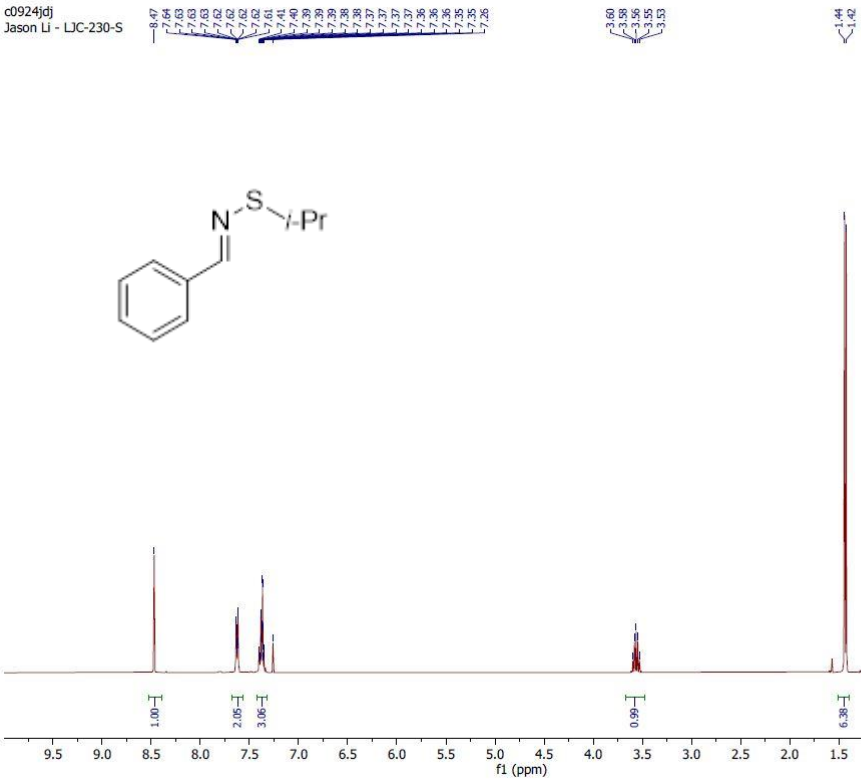

138.00
137.64
137.31
136.97
129.57
127.53
127.49
127.46
127.43
124.22
121.49
111.53
77.16 CDCl3
51.60
7.11
0.10
f1 (ppm)

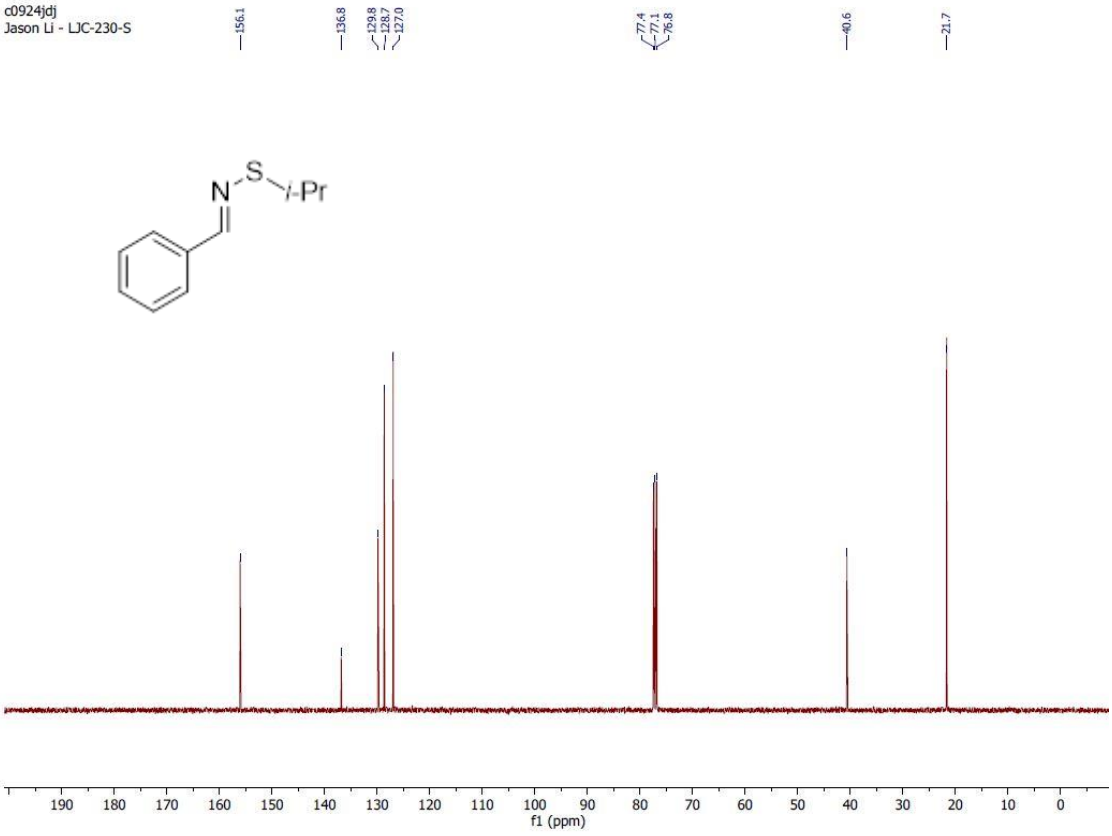
Data for **9e**


8.15
8.13
7.82
7.80
7.26 CDCl3
3.12
3.11
2.71
O
NH
S
Me
F3C
2.07
2.00
3.11
0.87
f1 (ppm)

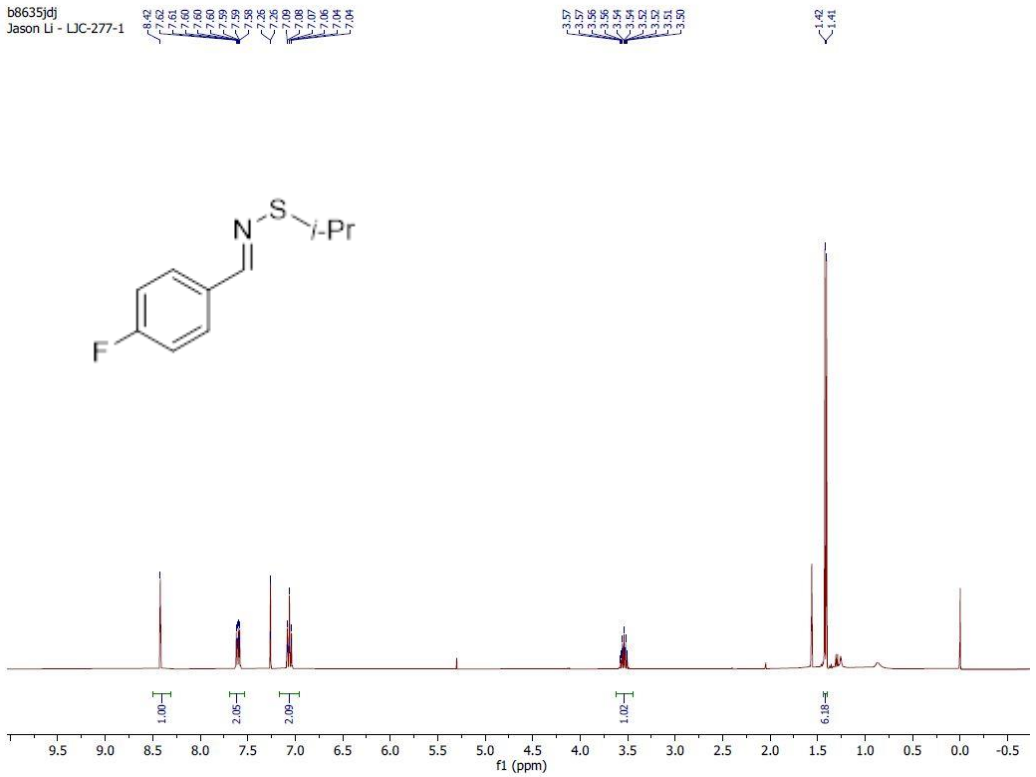

147.31
135.45
135.12
134.79
134.46
128.45
127.41
126.60
126.56
126.53
126.49
124.69
121.98
119.26
77.16 CDCl3
46.10
f1 (ppm)

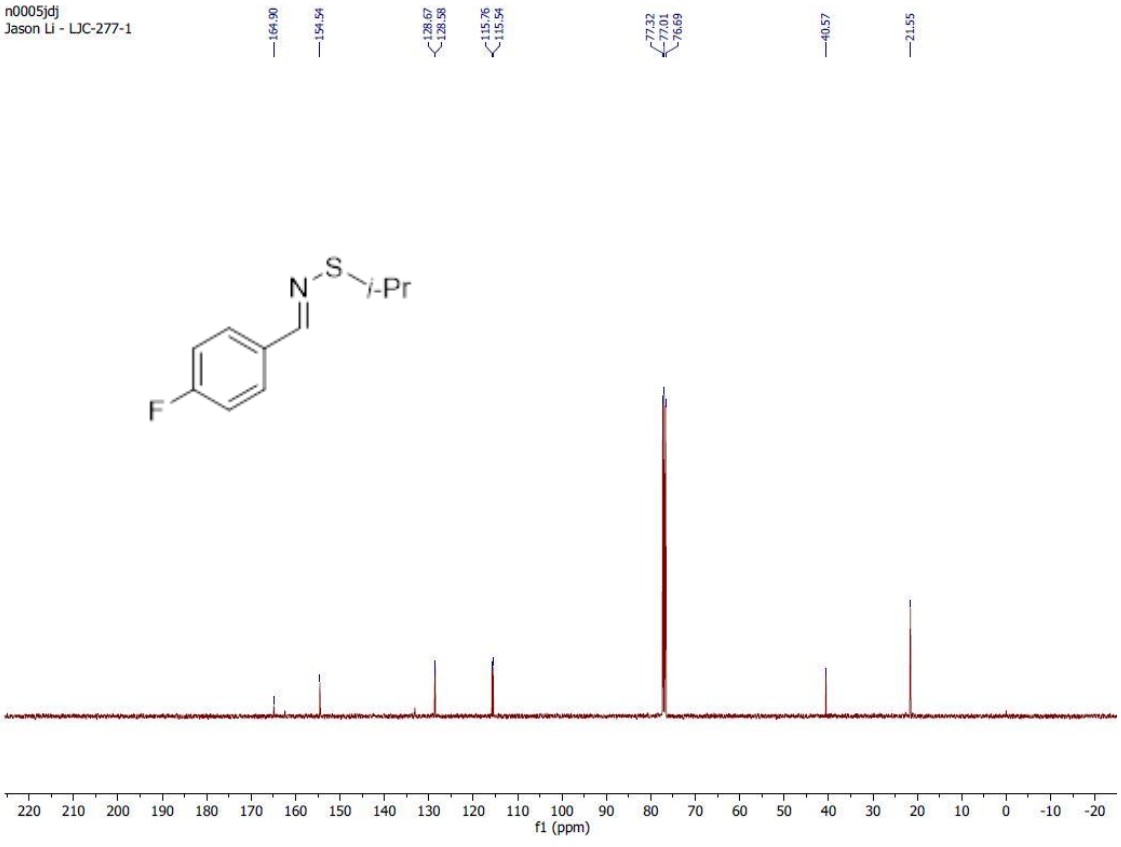
Data for **6a-*i*Pr**



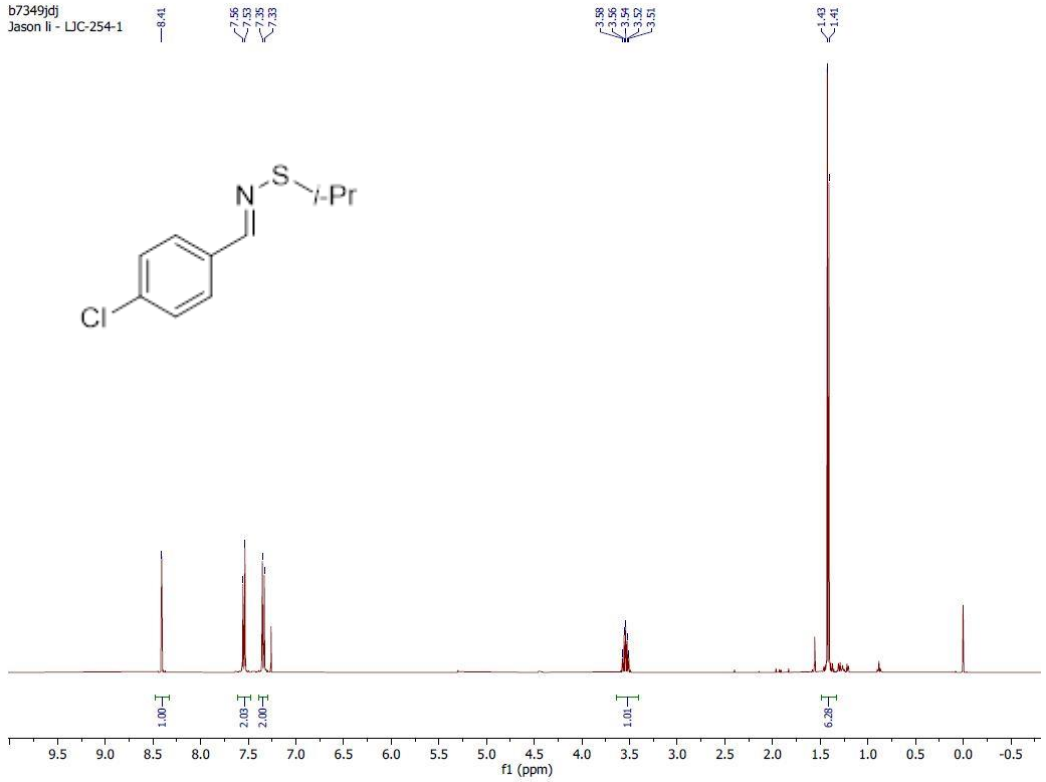


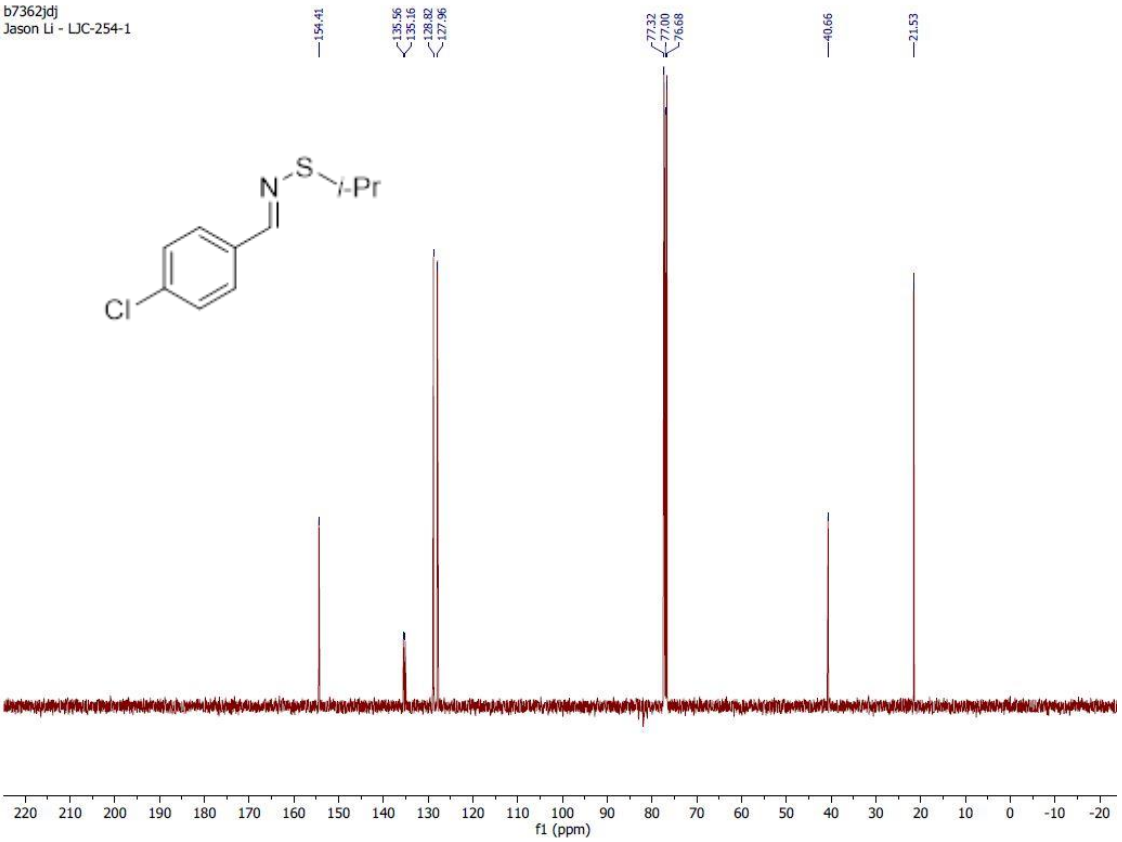
Data for **6b-*i*Pr**



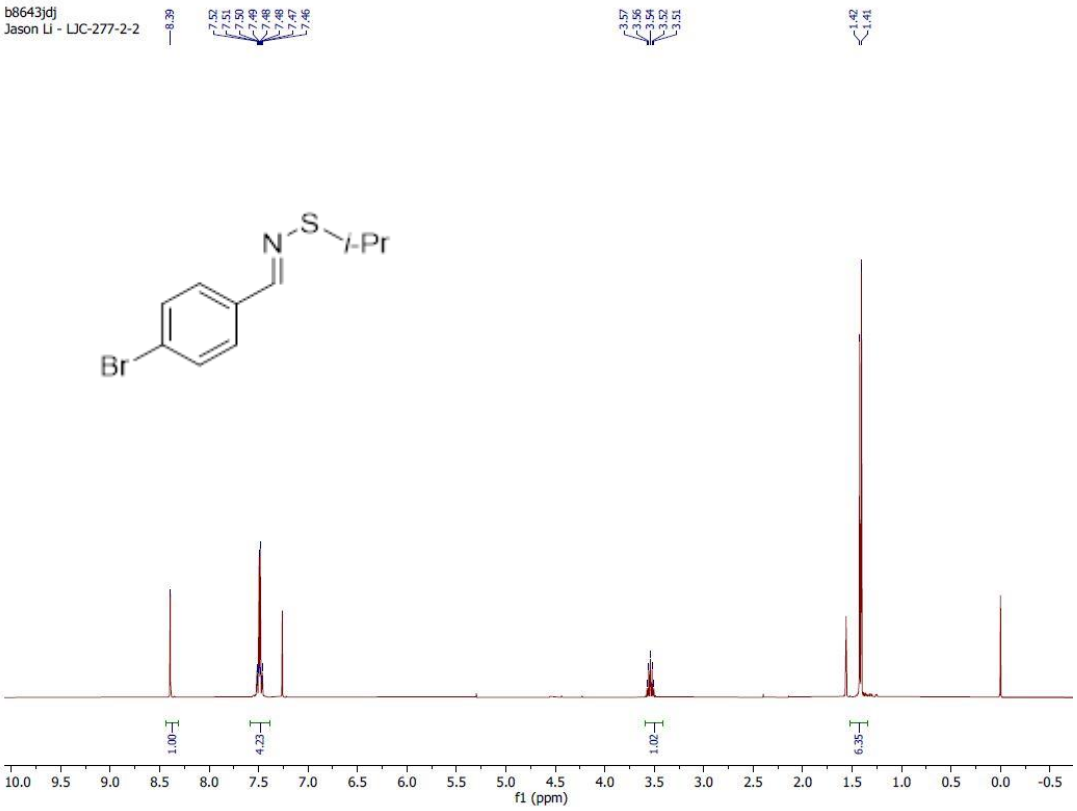


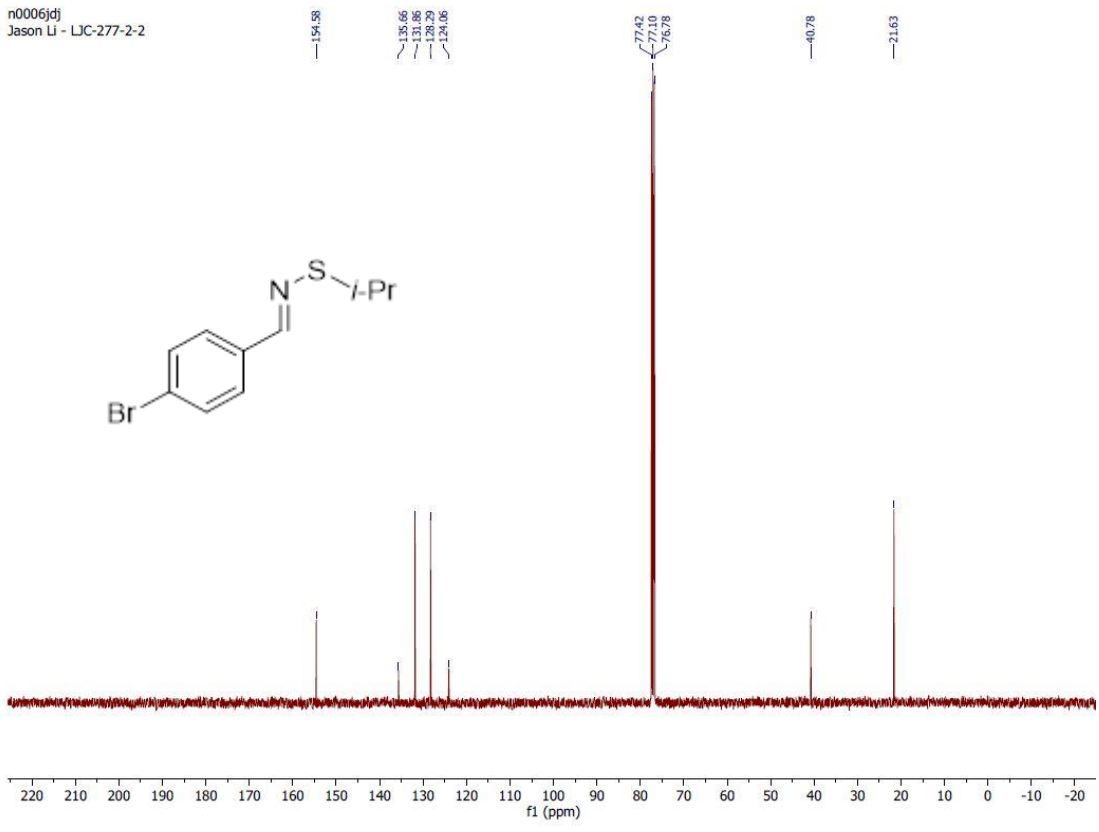
Data for **6c-*i*Pr**



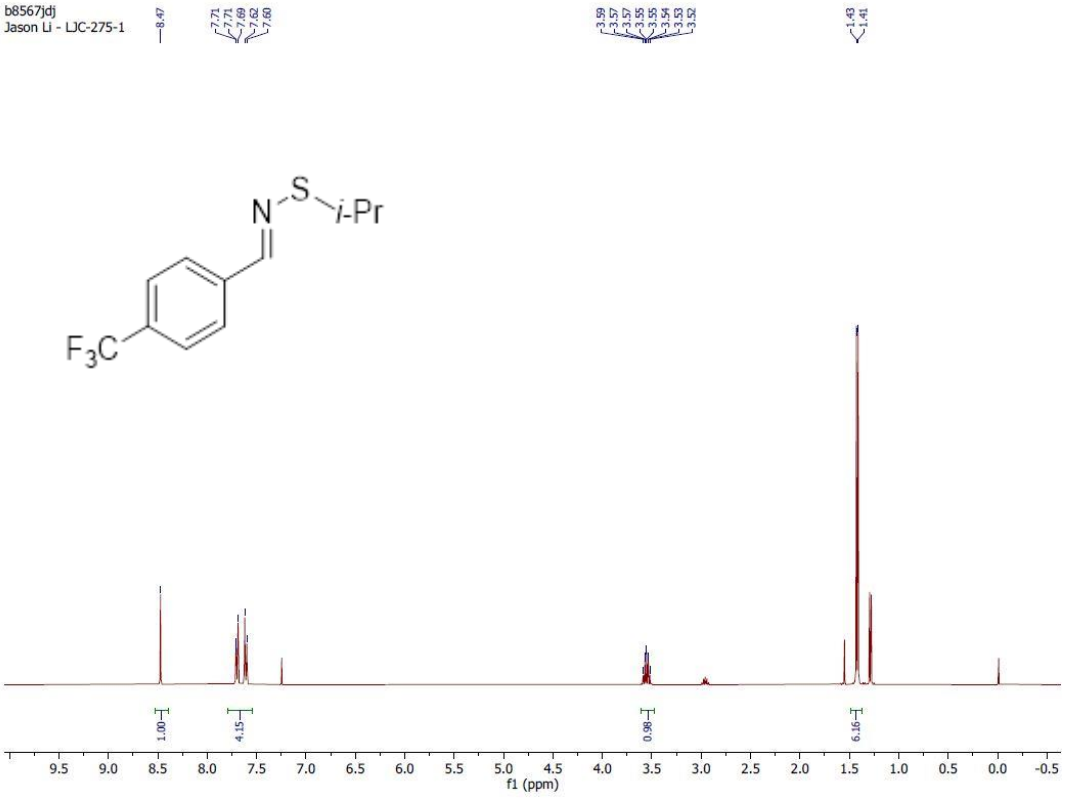


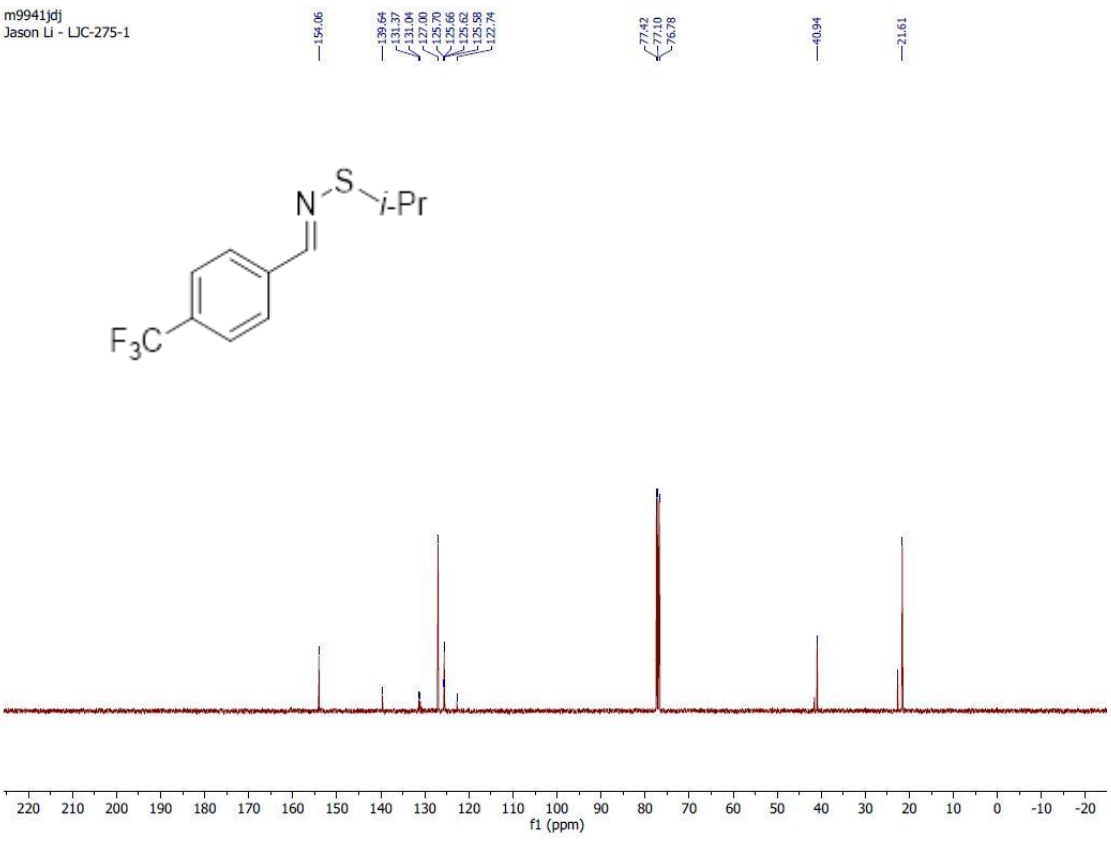
Data for **6d-*i*Pr**



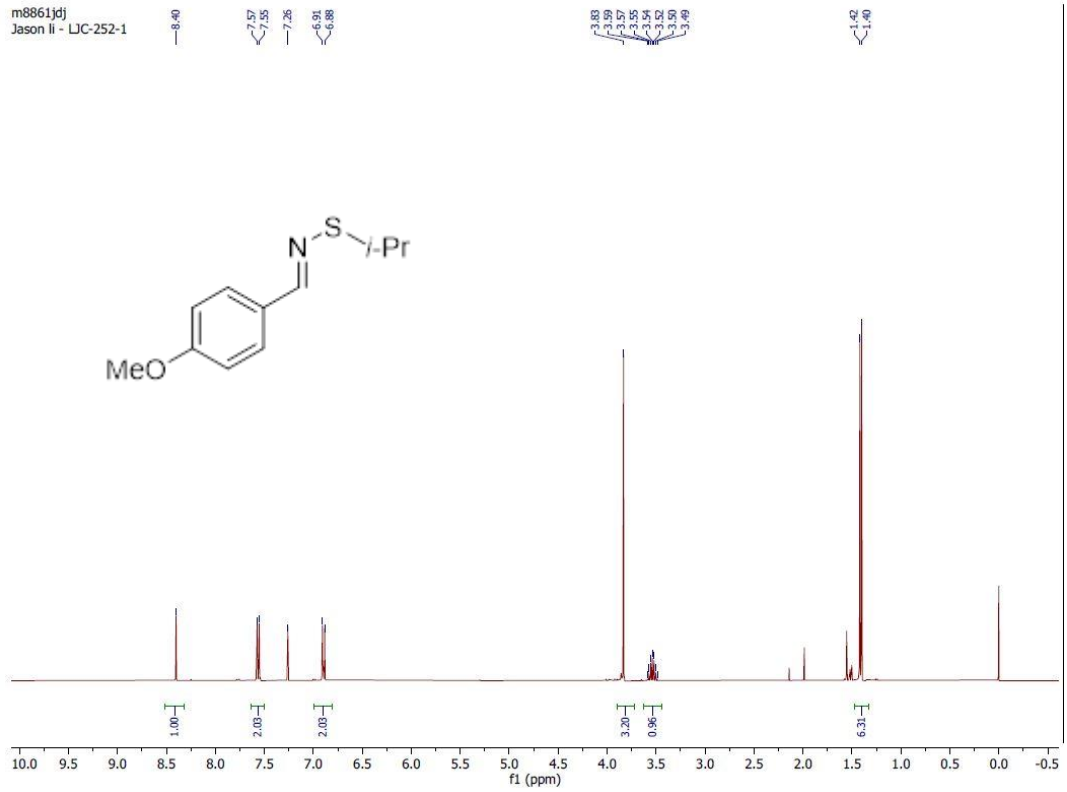


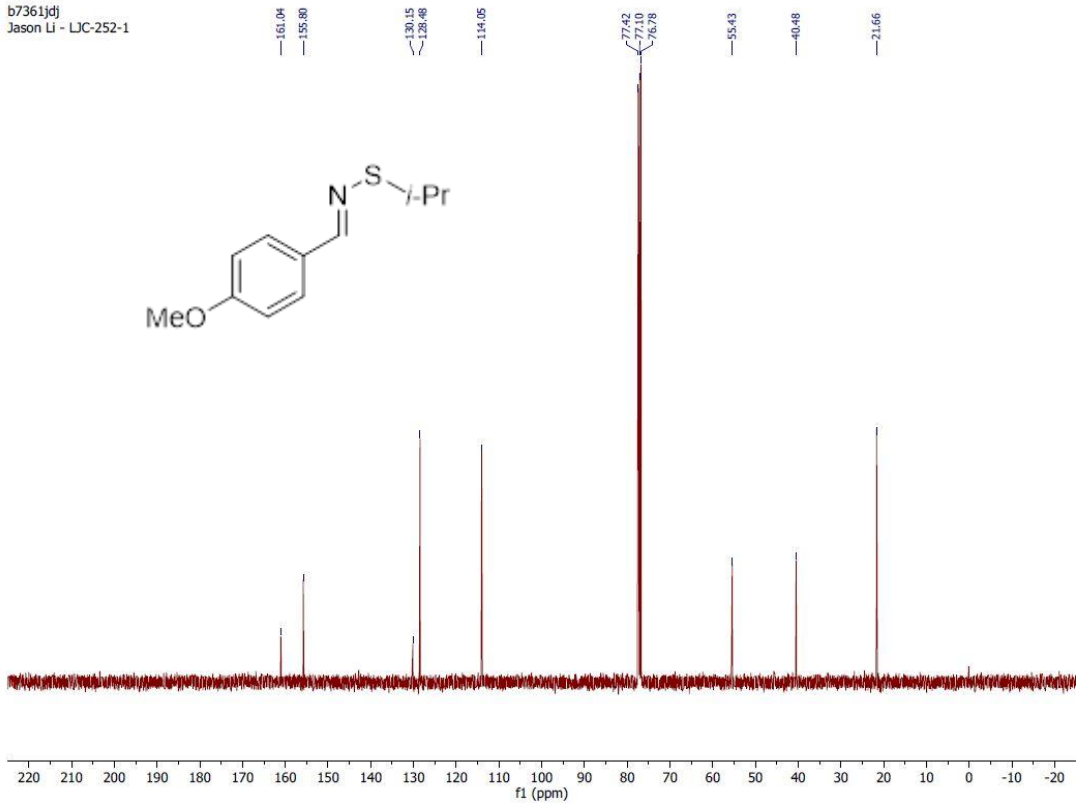
Data for **6e-*i*Pr**



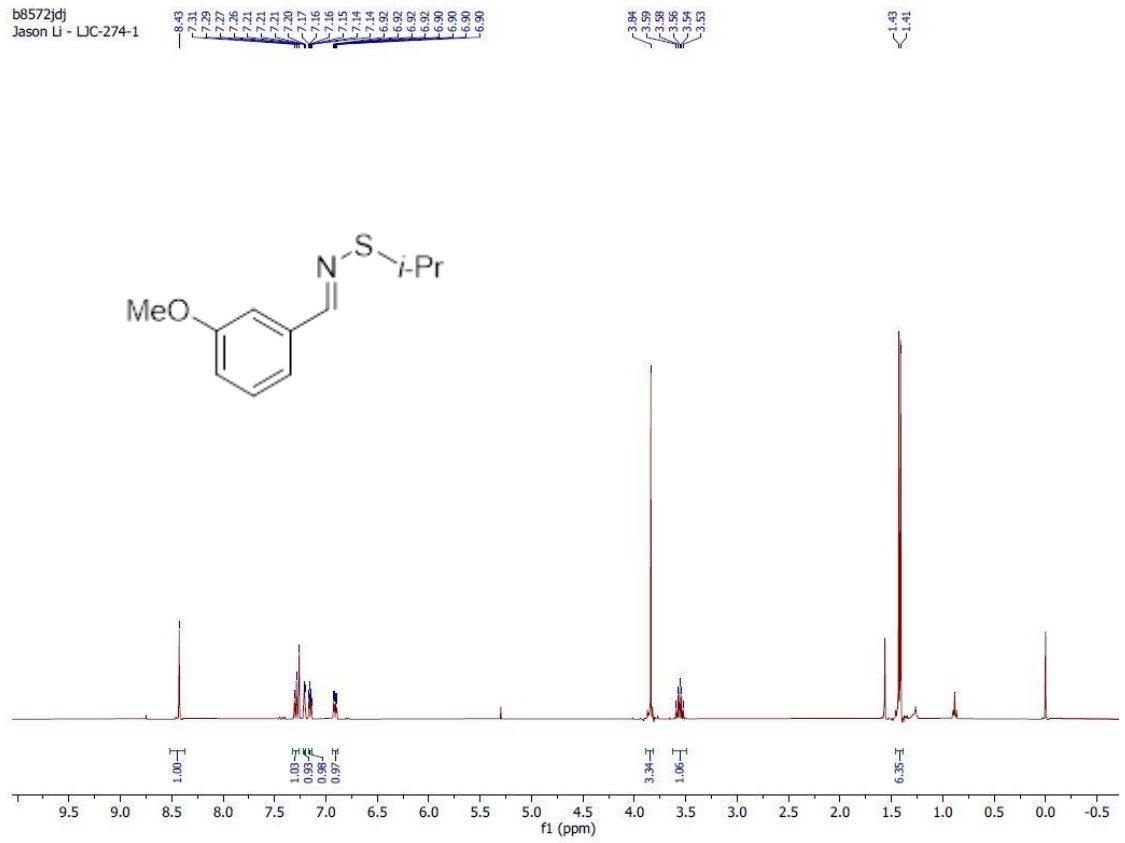


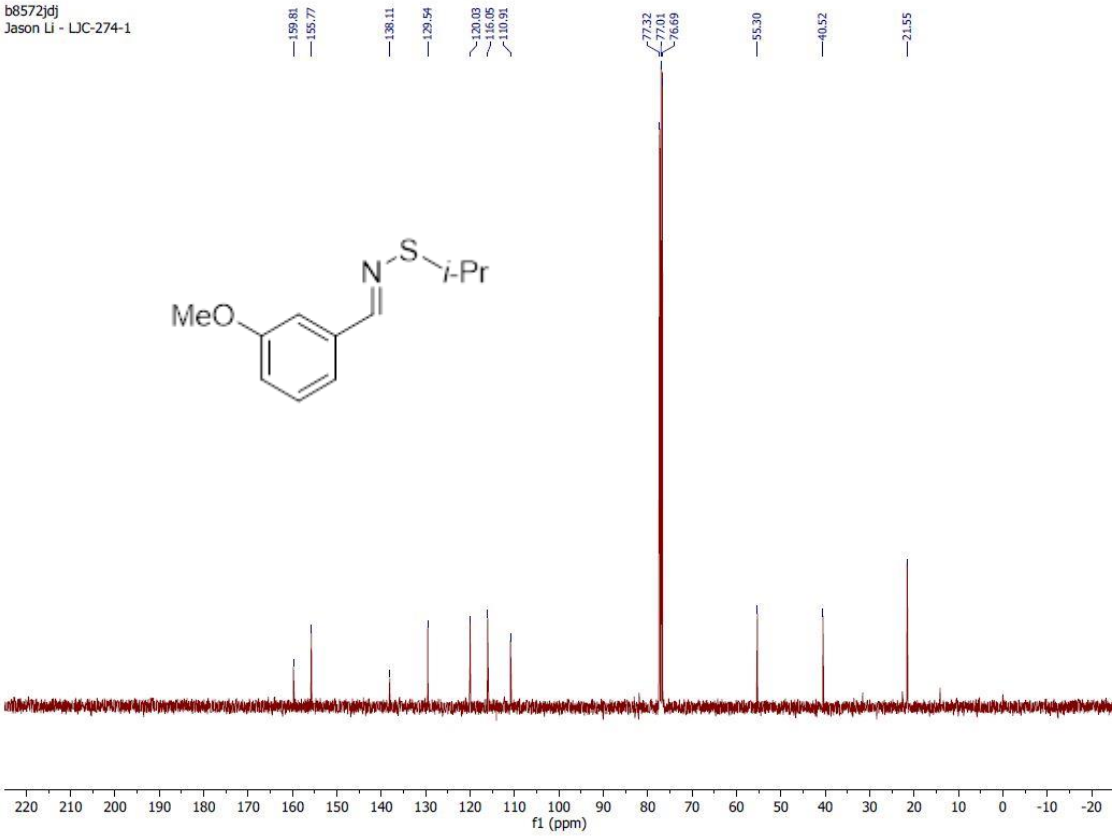
Data for **6f-*i*Pr**



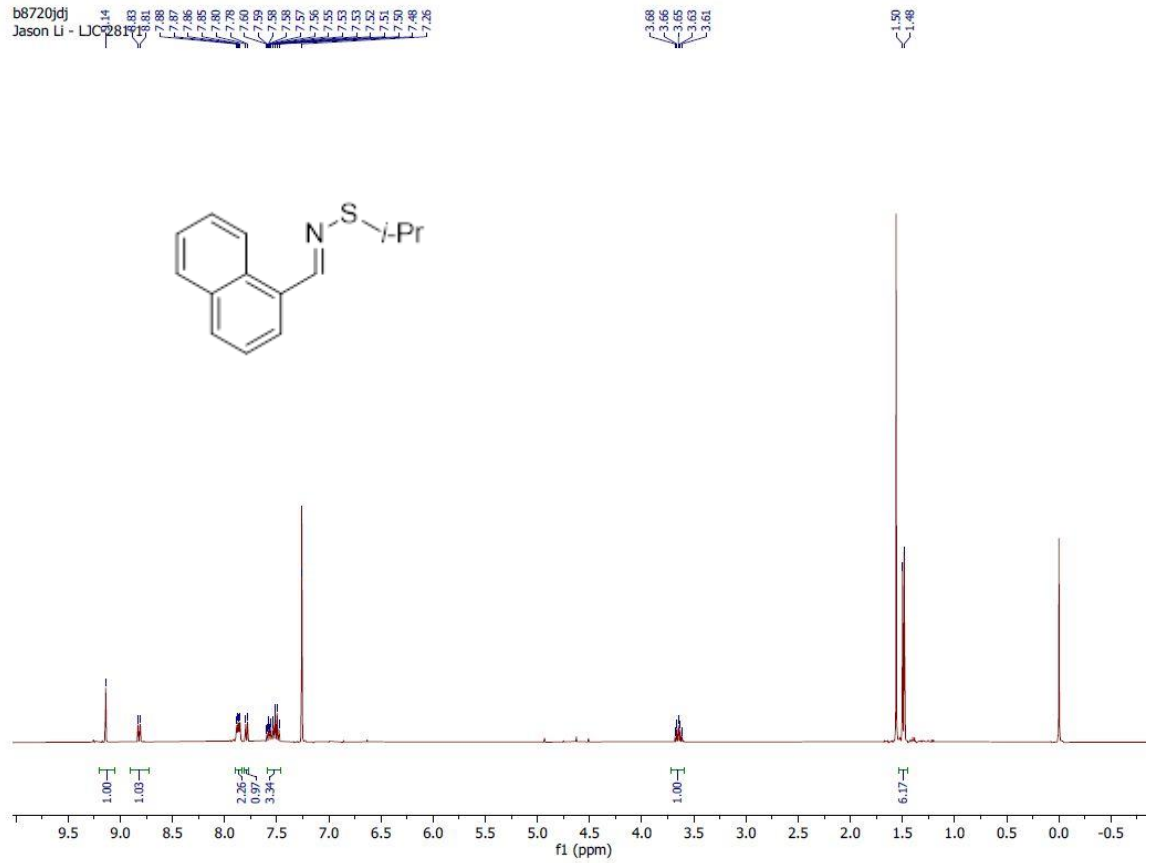


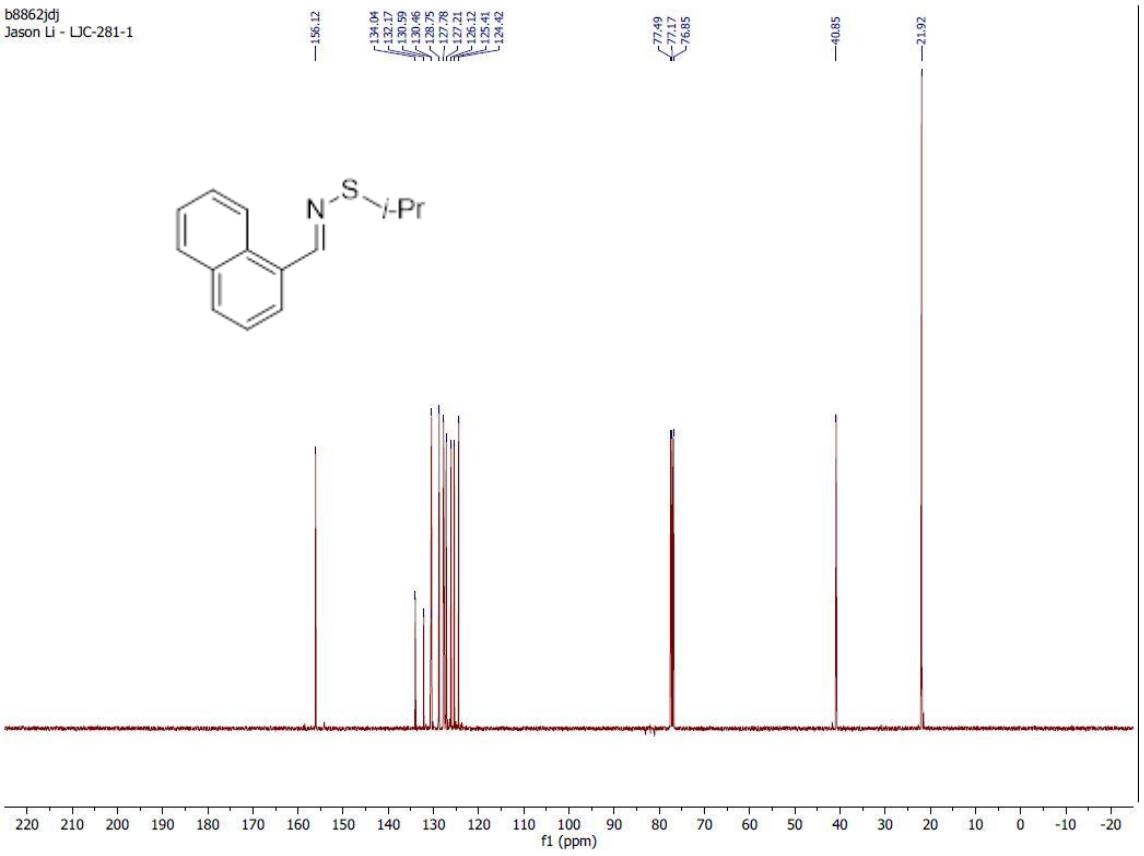
Data for **6g-*i*Pr**



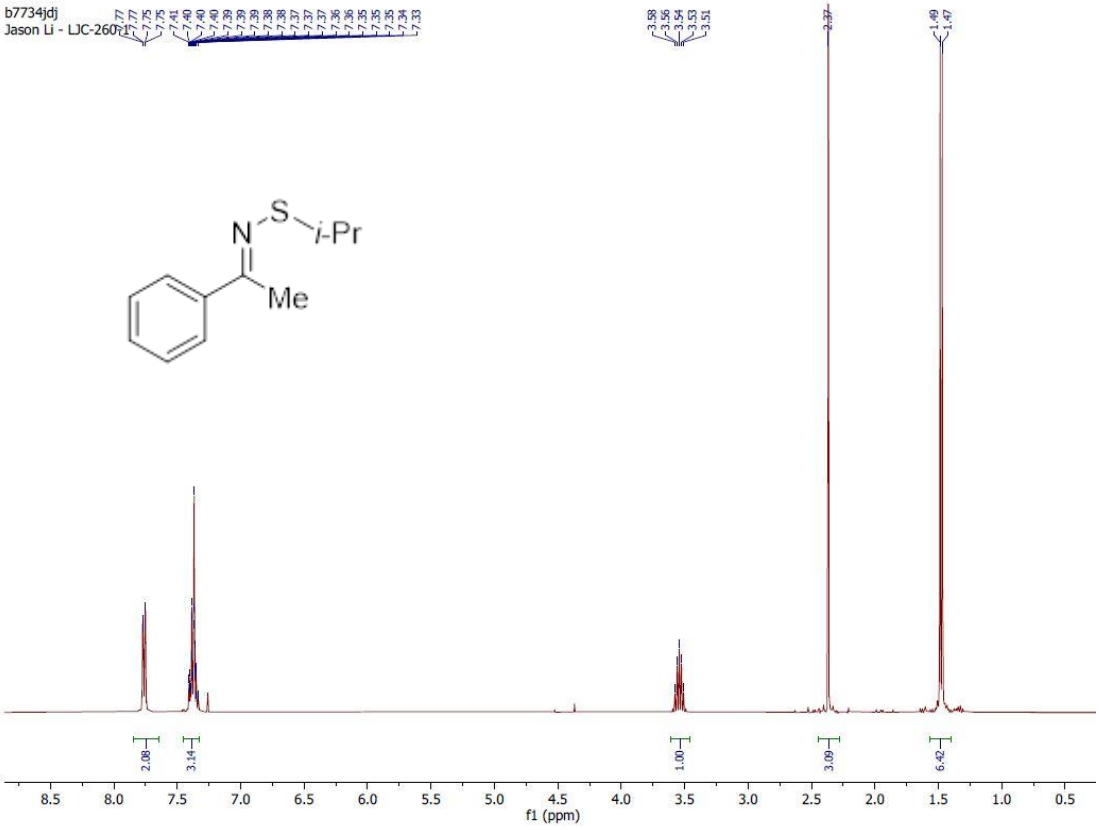


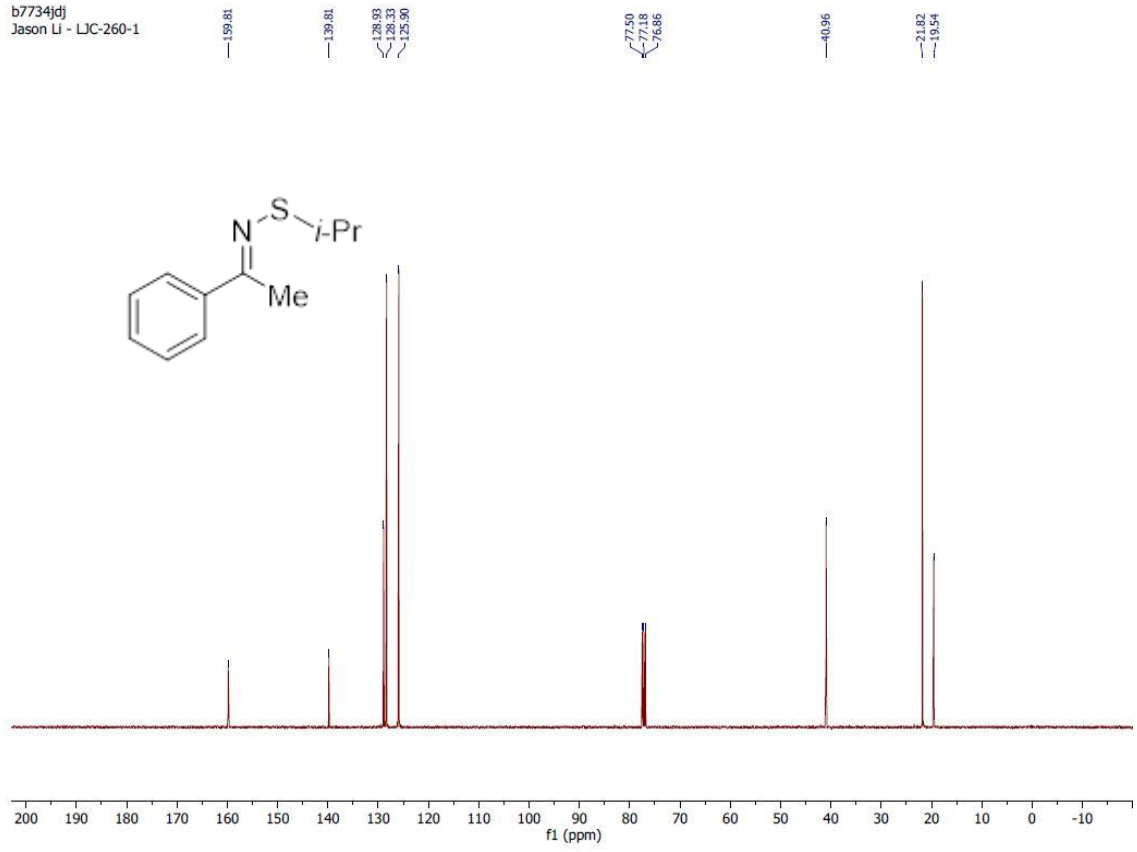
Data for **6h-*i*Pr**



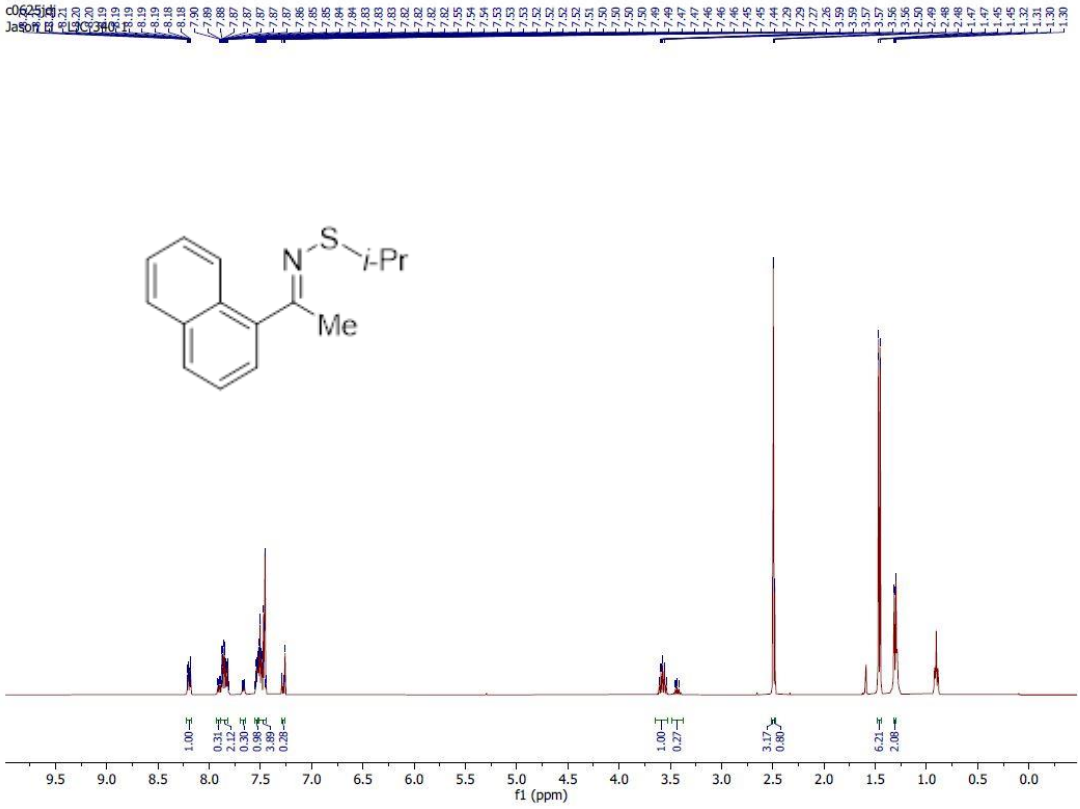


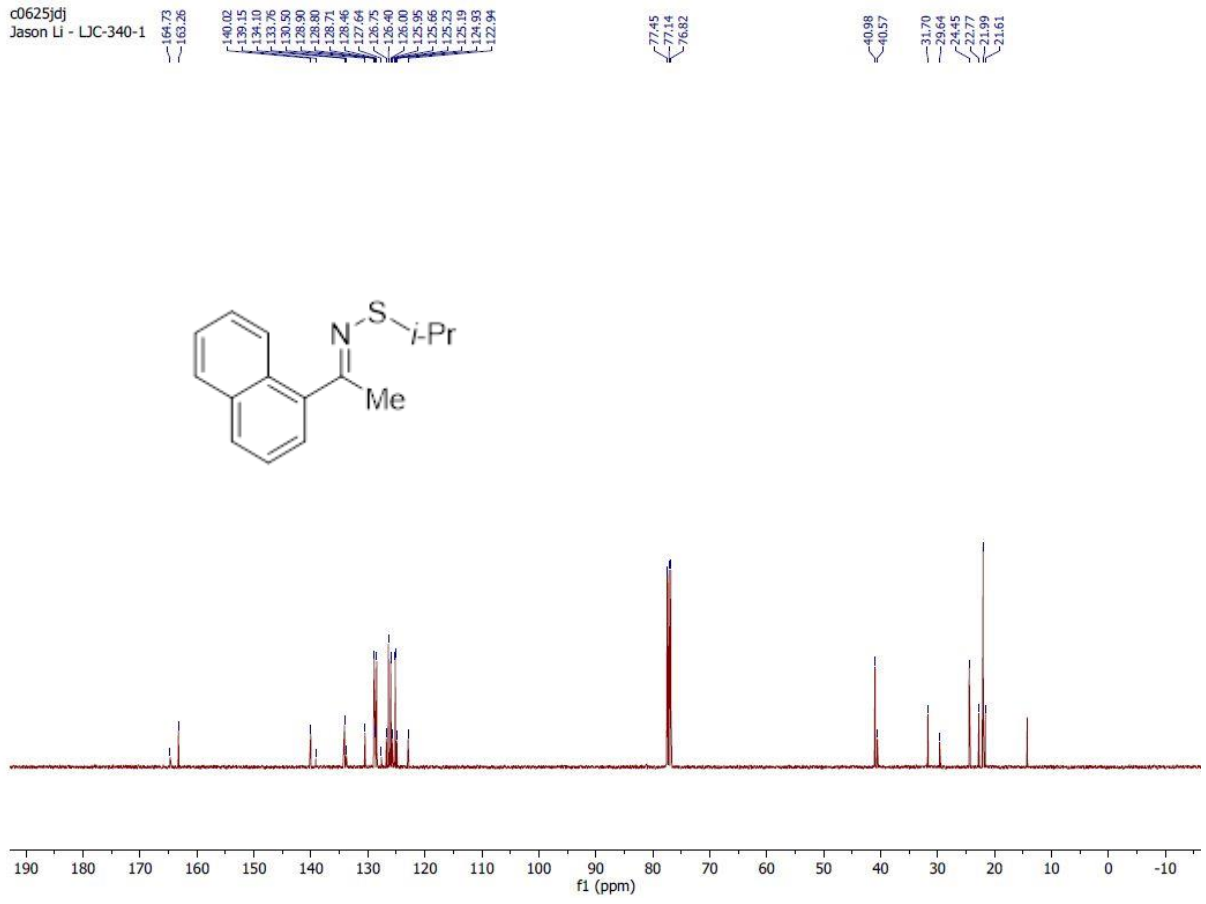
Data for **6i-*i*Pr**



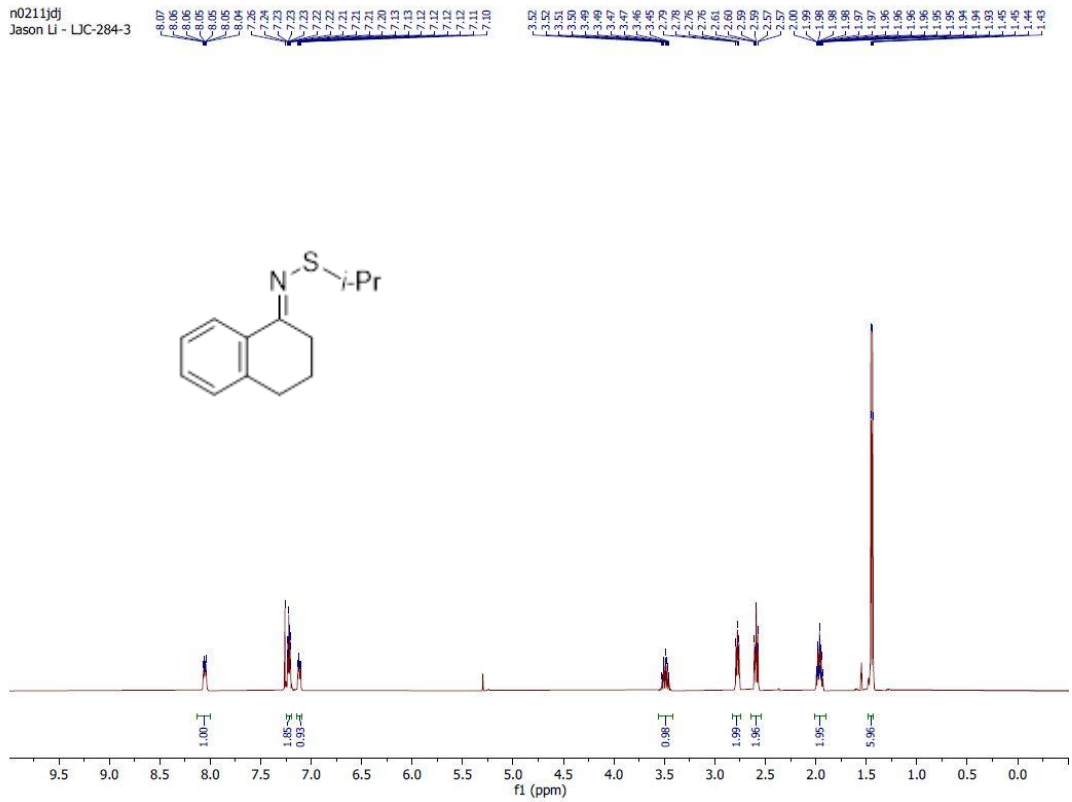


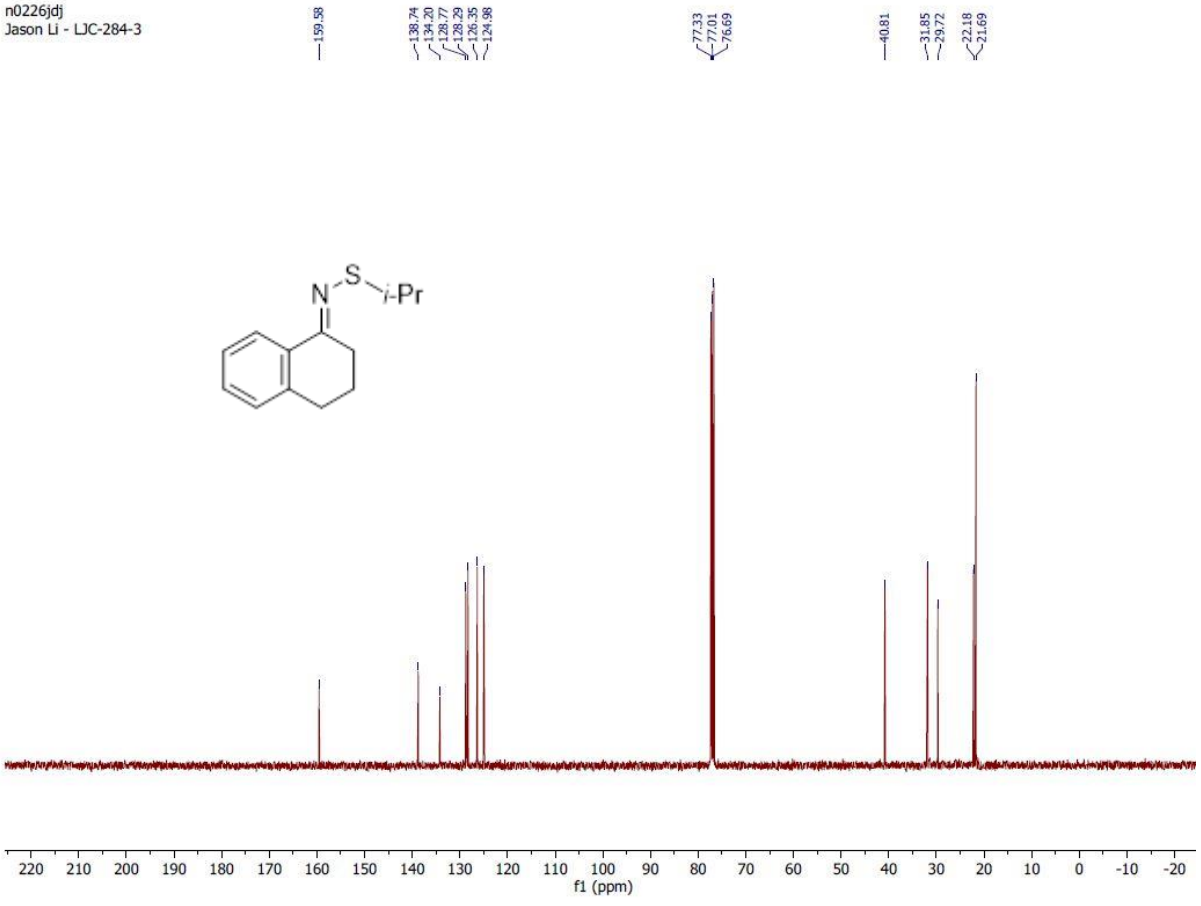
Data for **6j-*i*Pr**



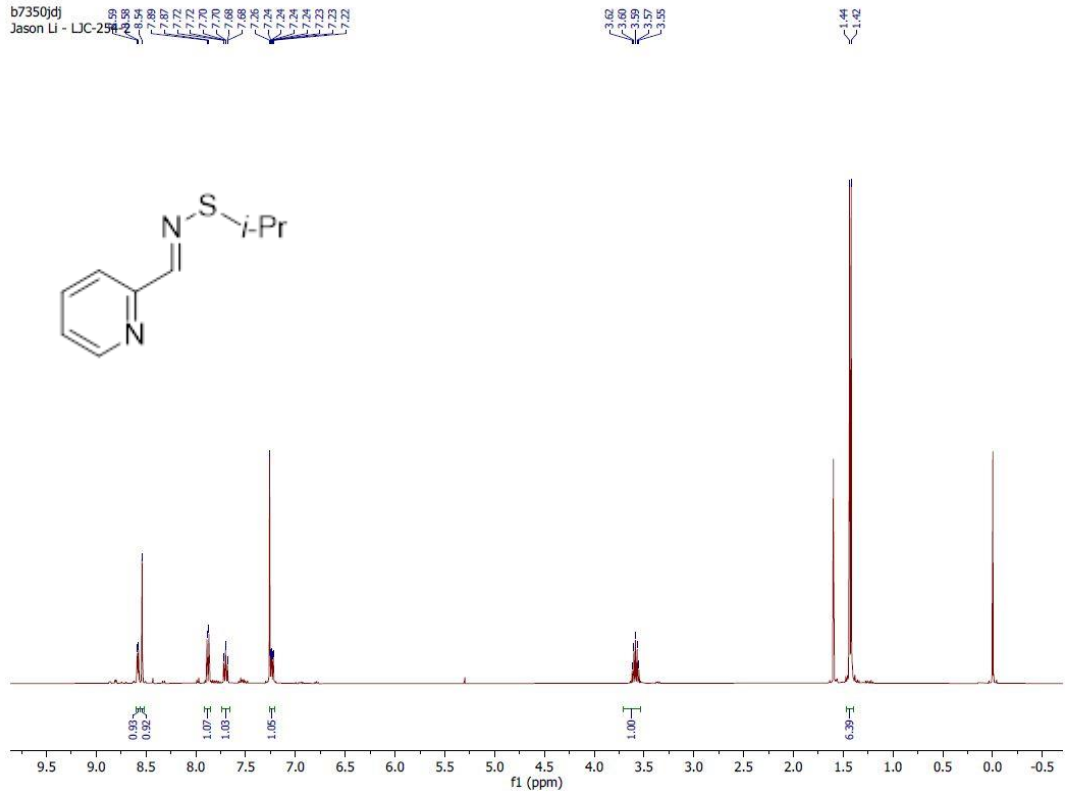


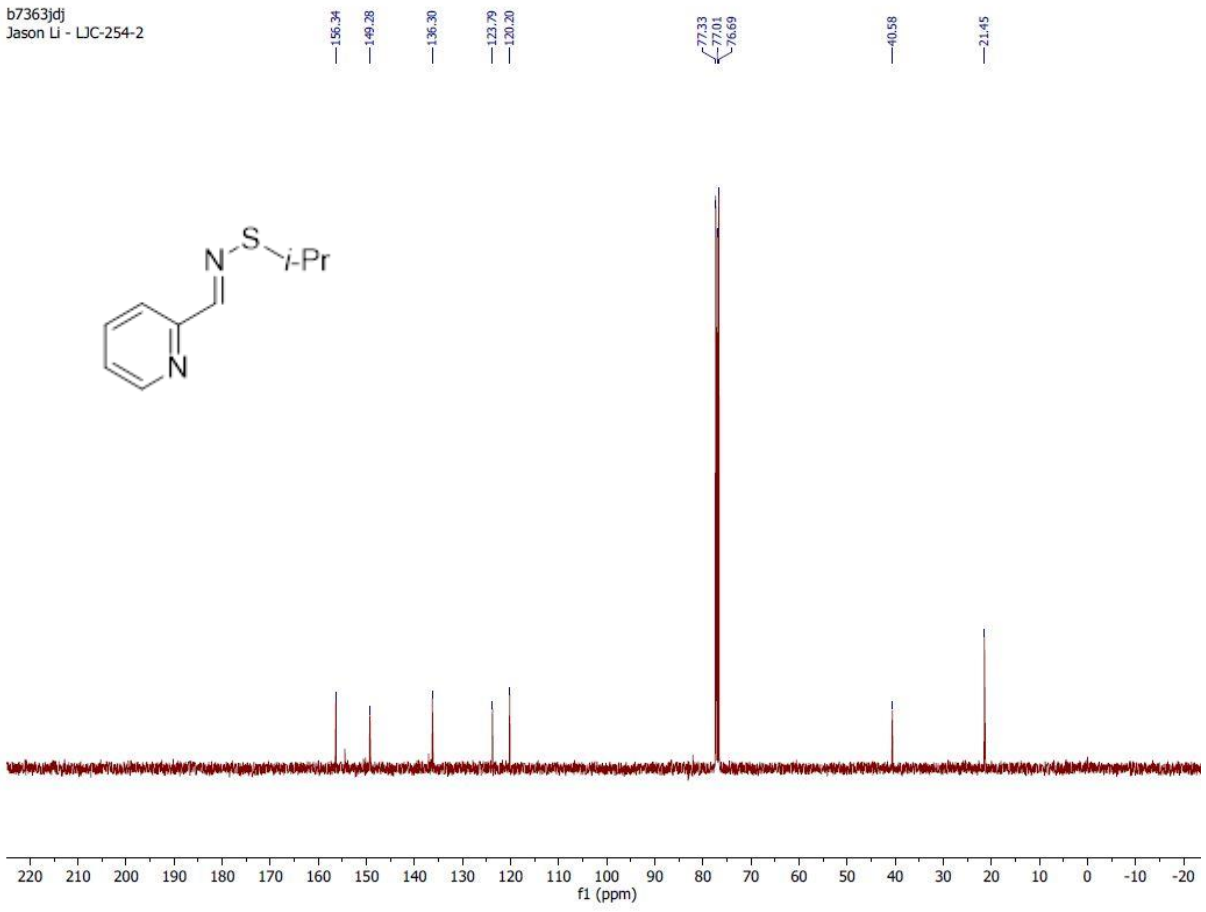
Data for **6k-*i*Pr**



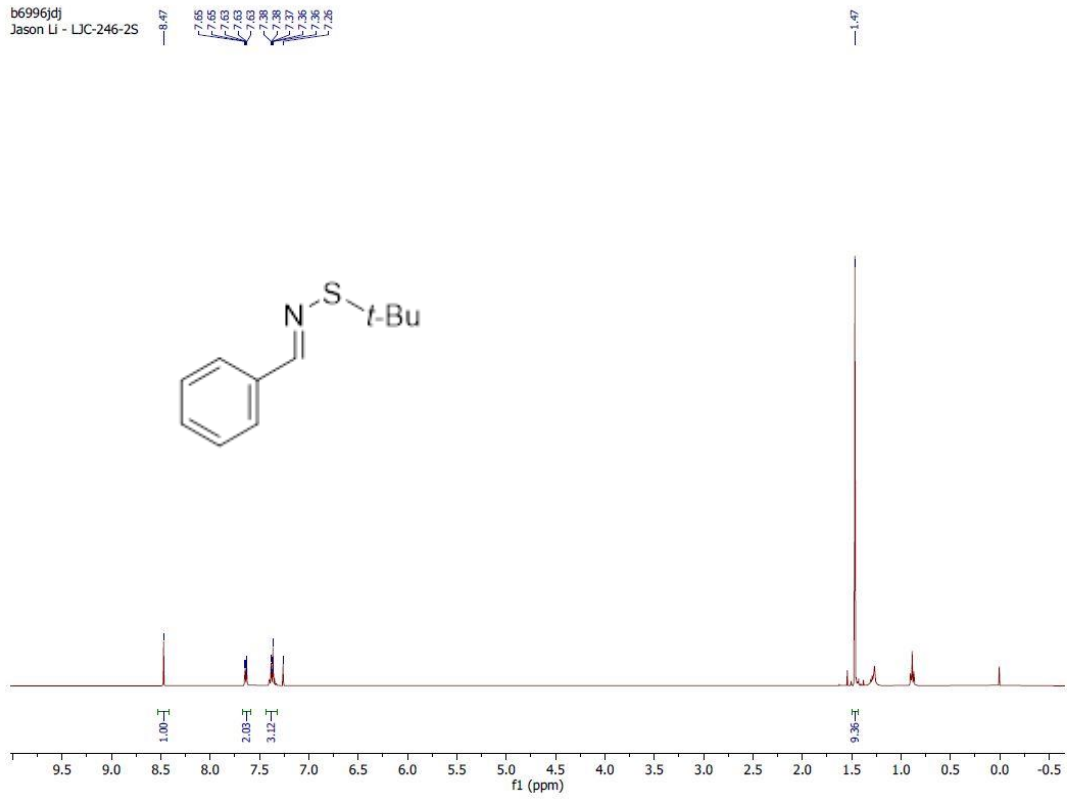


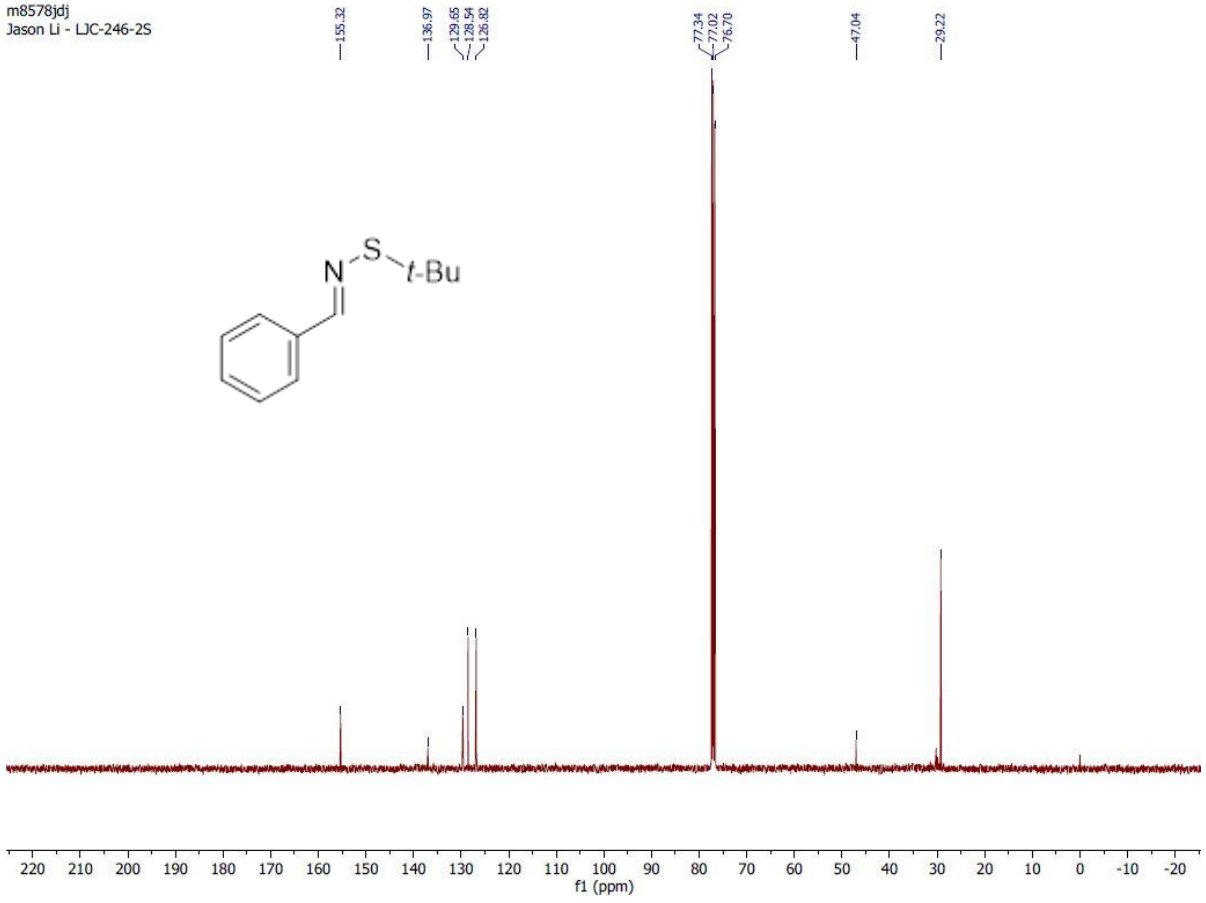
Data for **6l-*i*Pr**



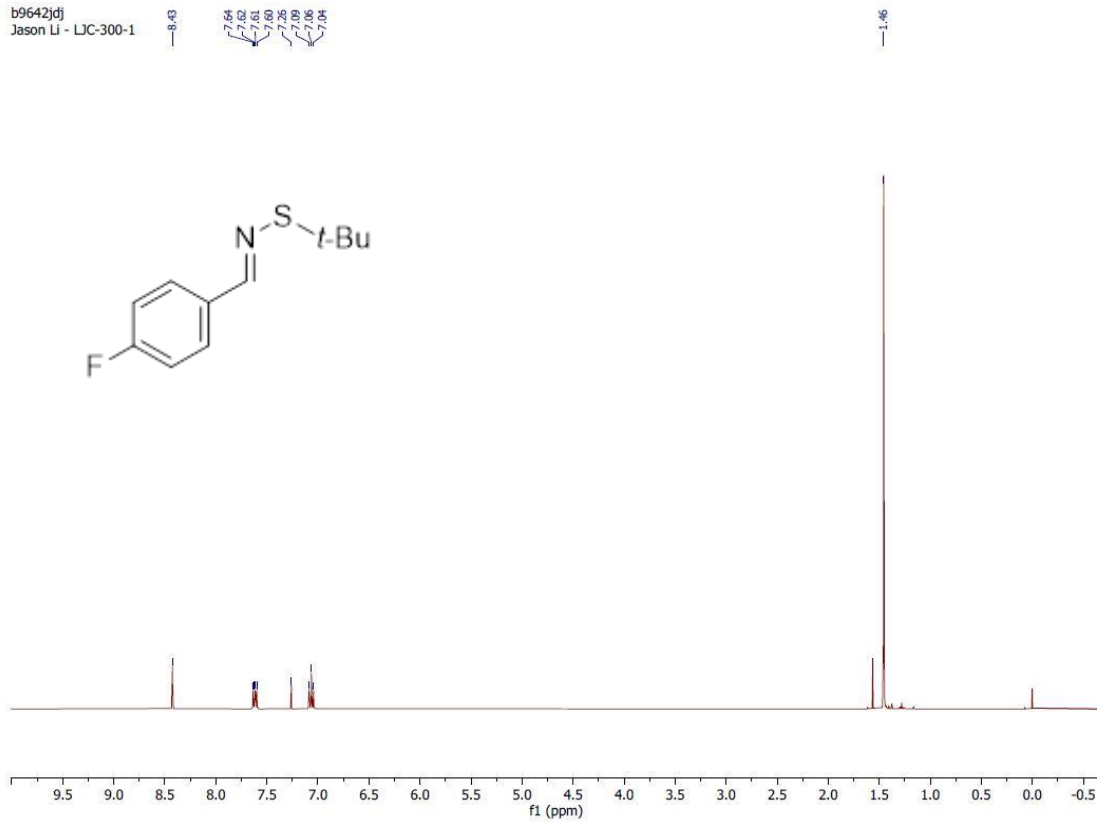


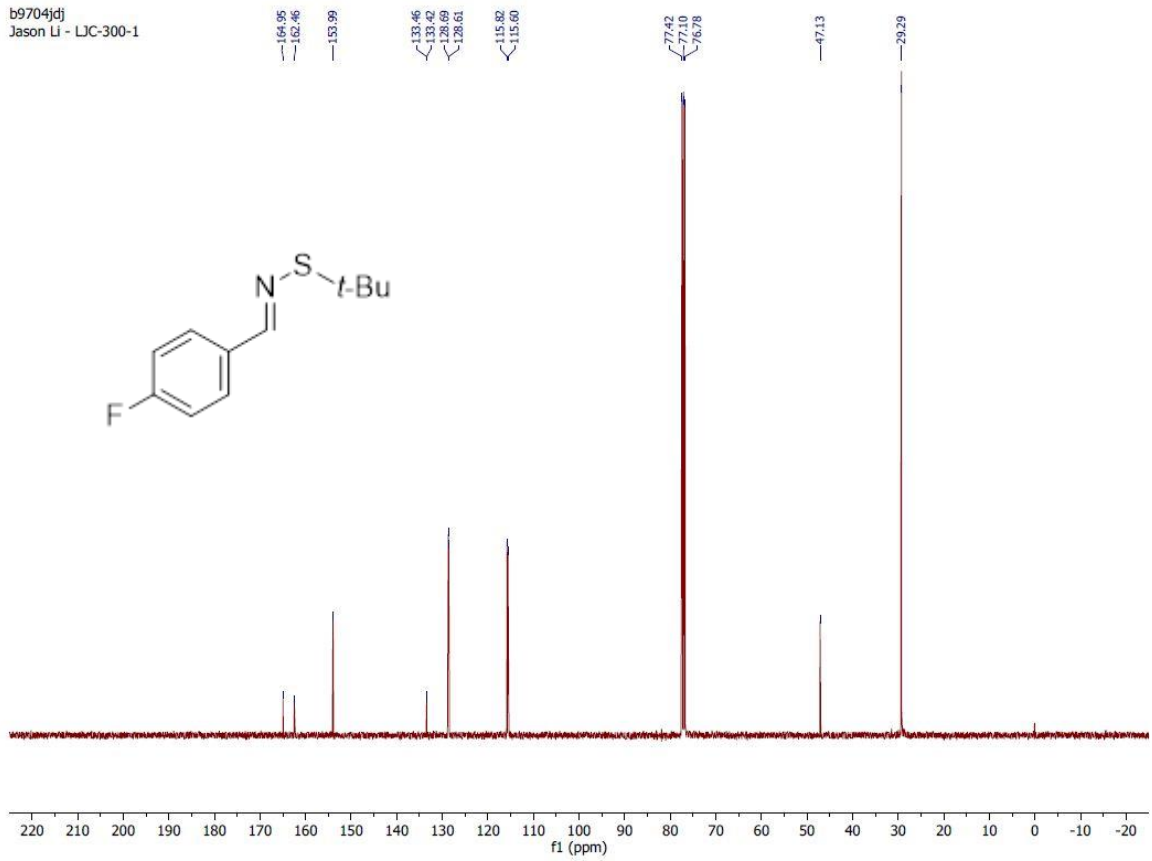
Data for **6a-*t*Bu**



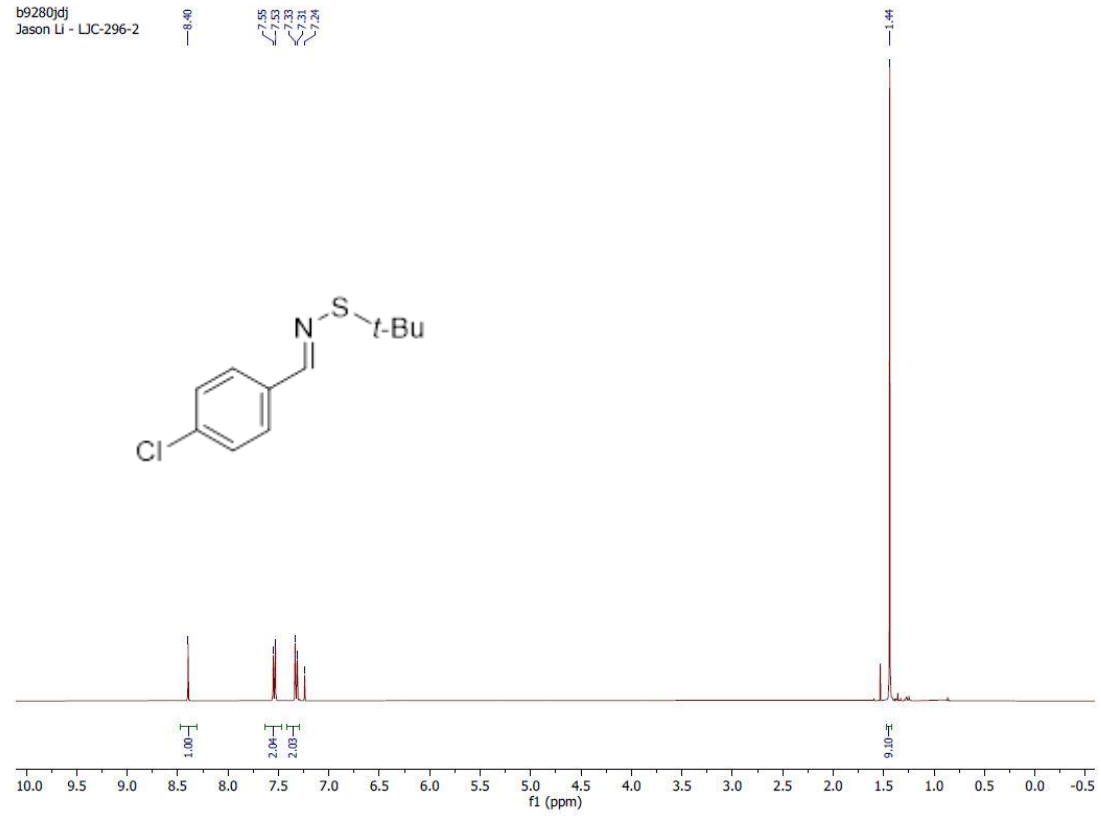


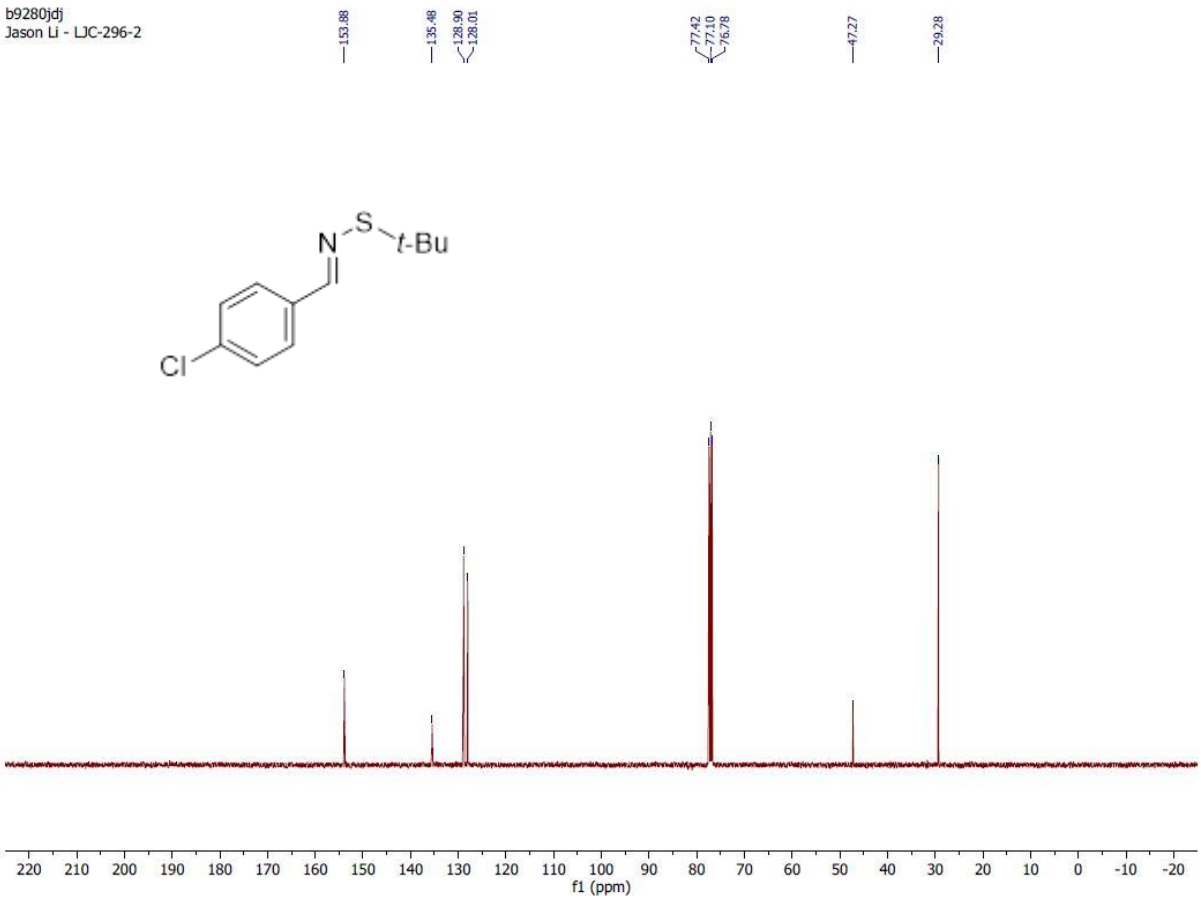
Data for **6b-*t*Bu**



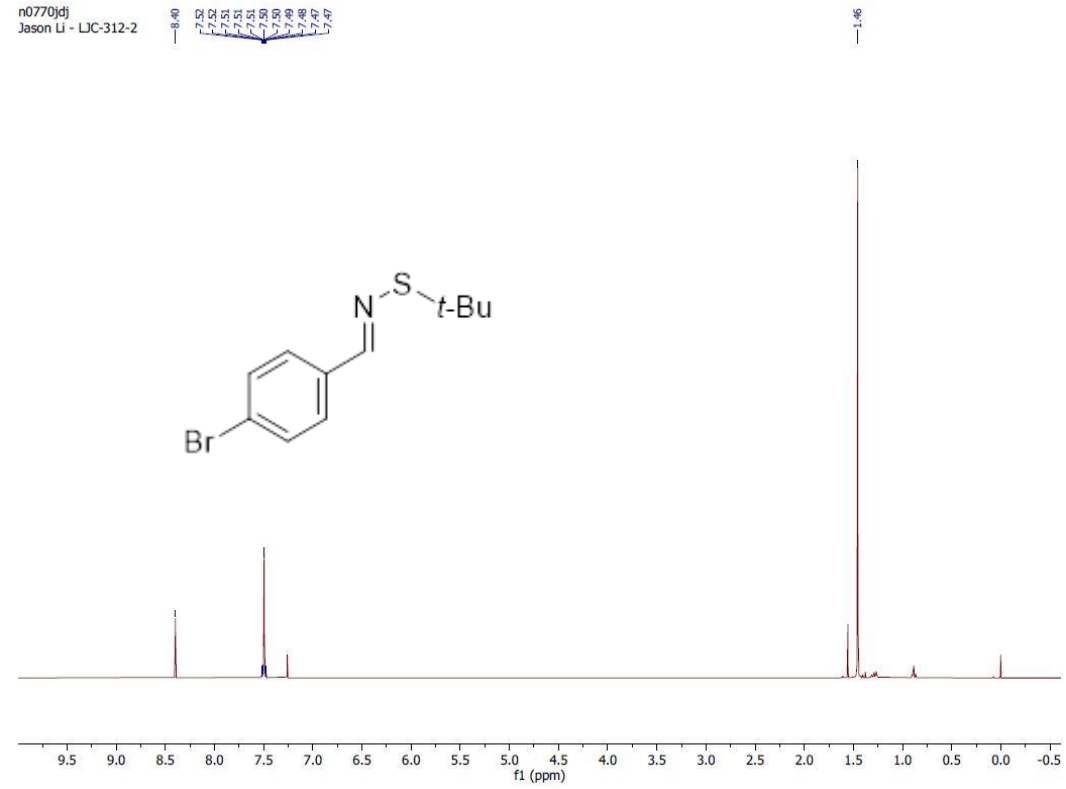


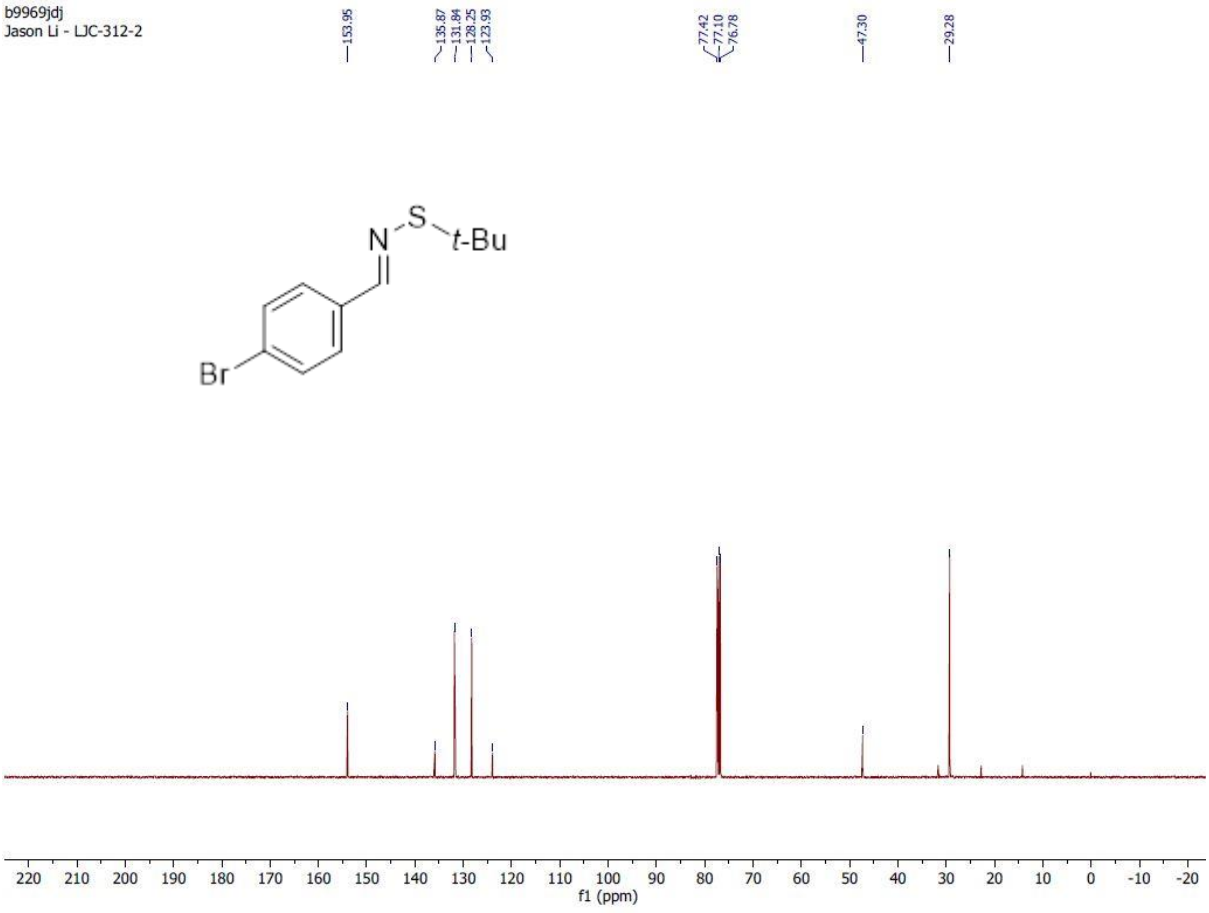
Data for **6c-*t*Bu**



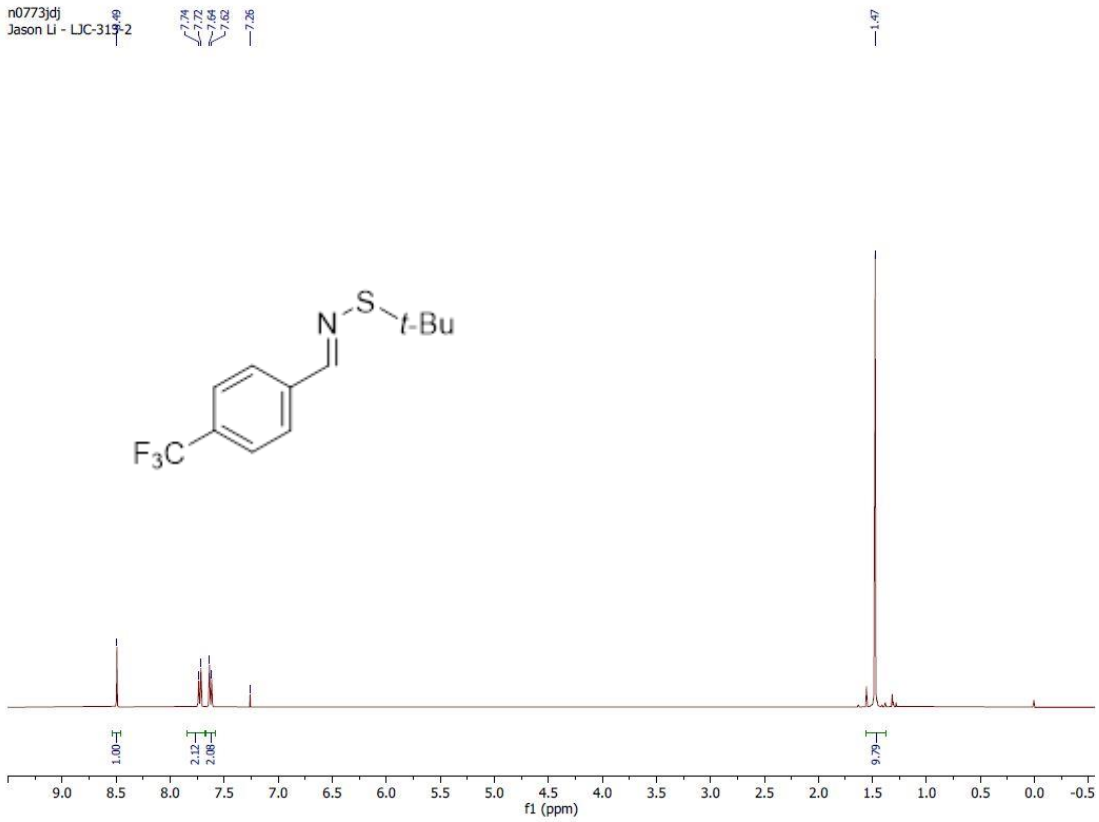


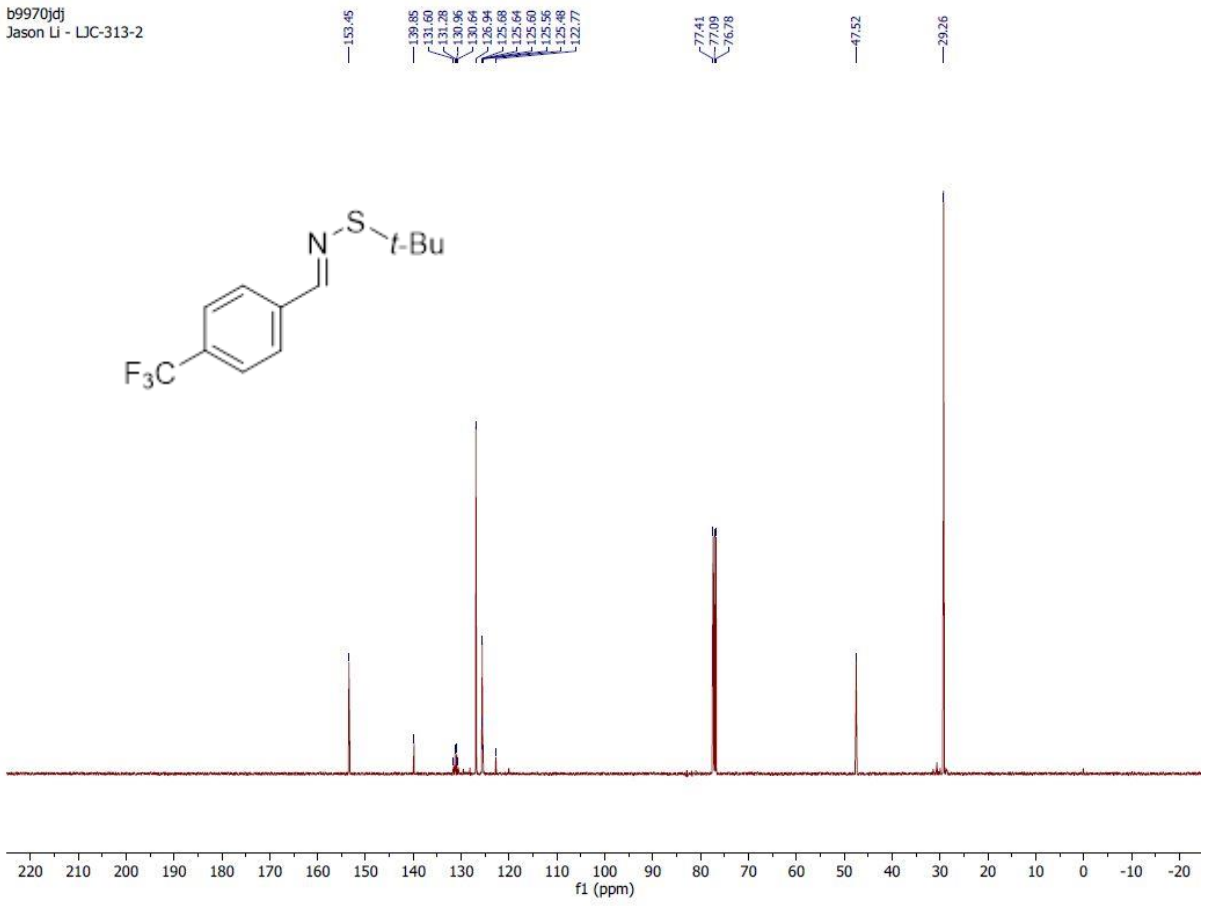
Data for **6d-*t*Bu**



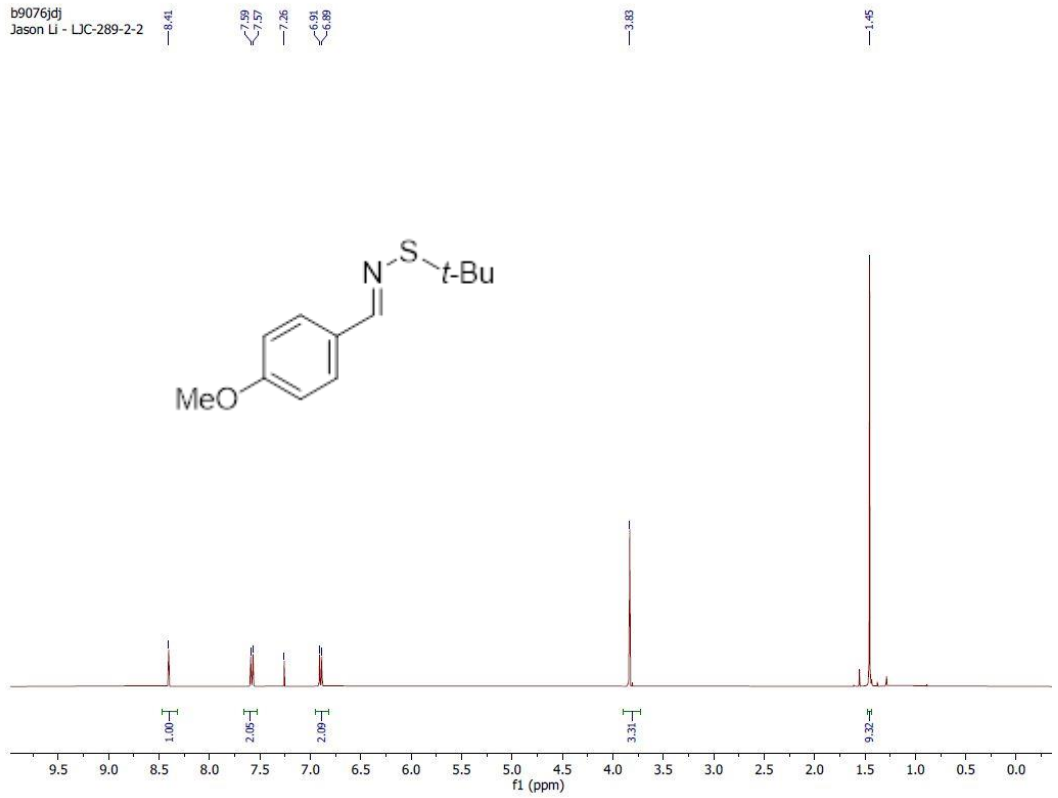


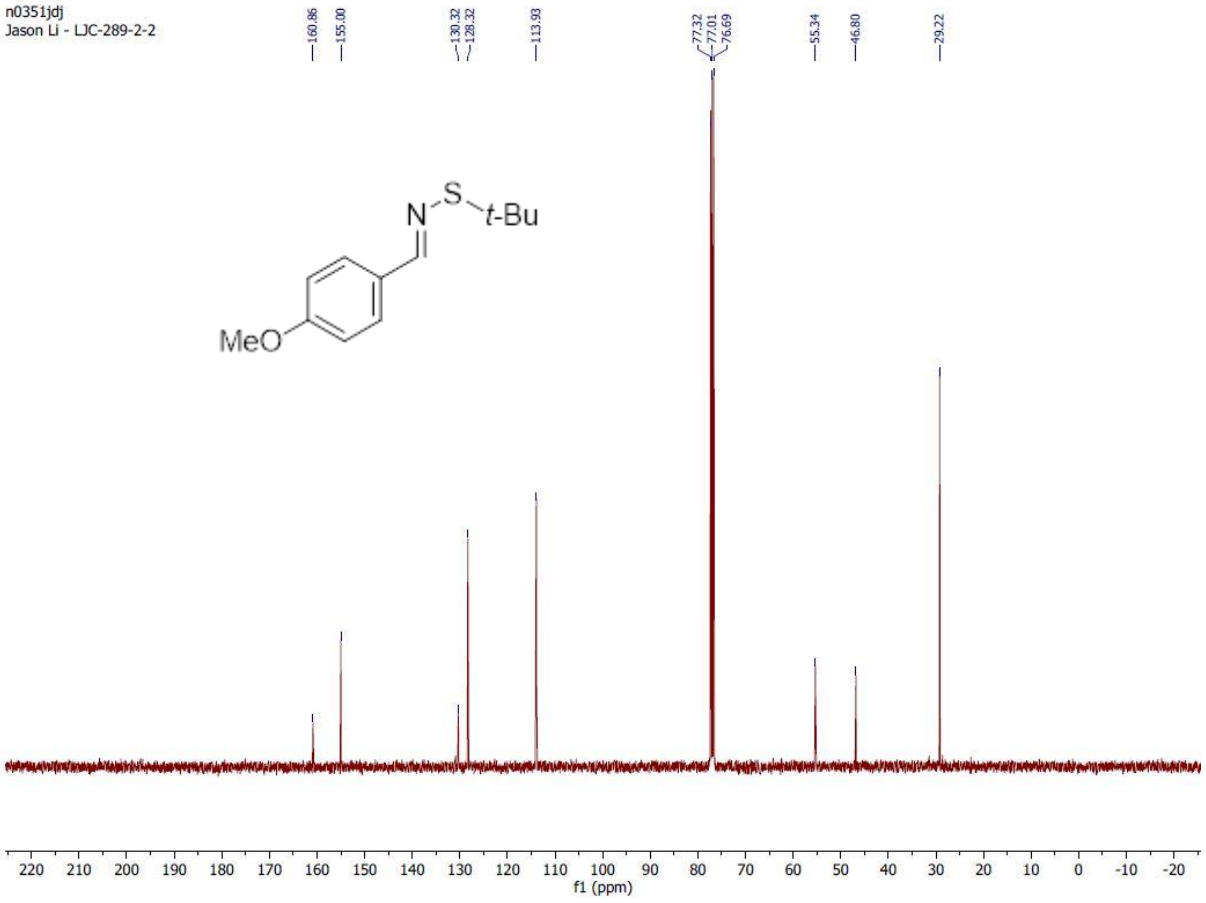
Data for **6e-*t*Bu**



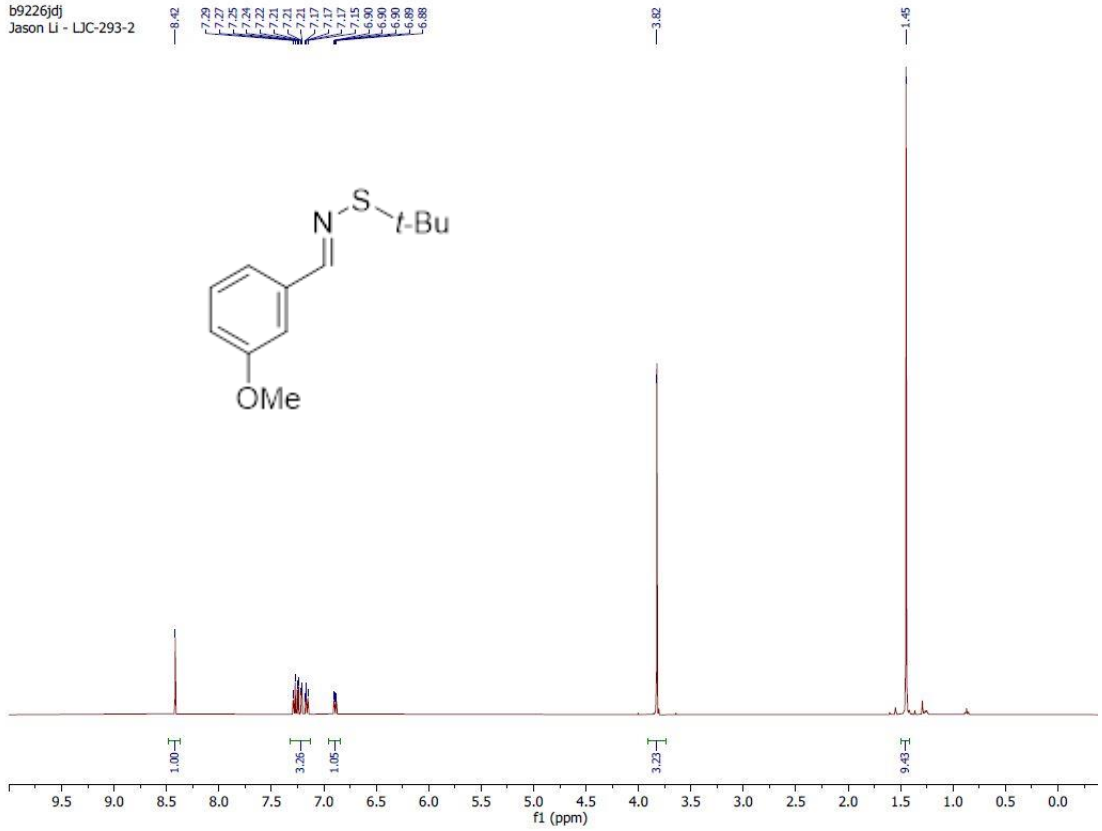


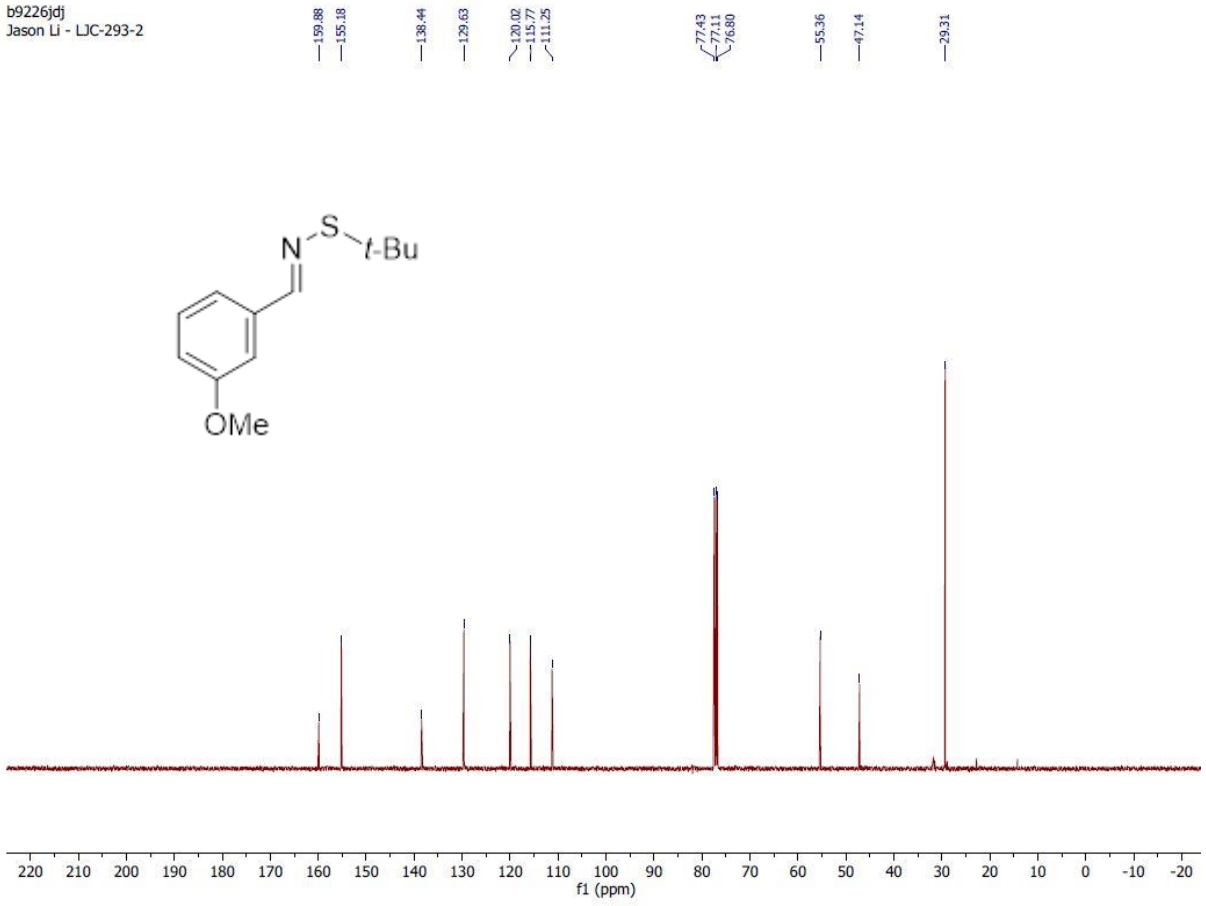
Data for **6f-*t*Bu**



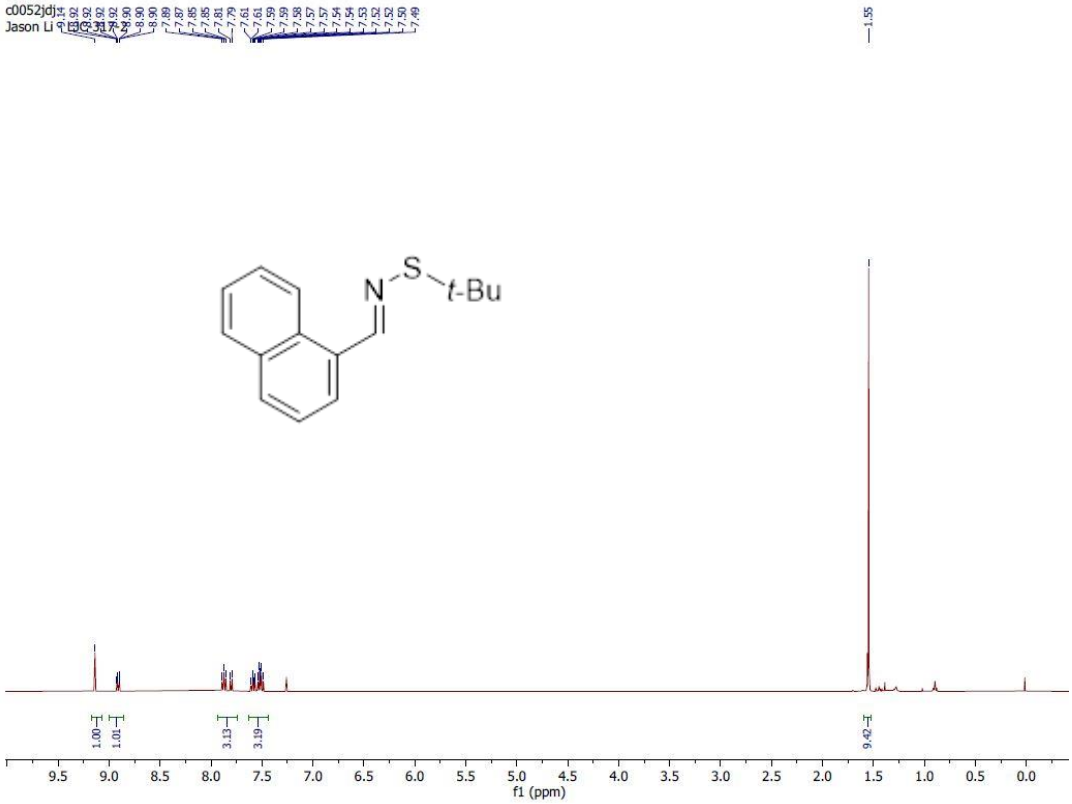


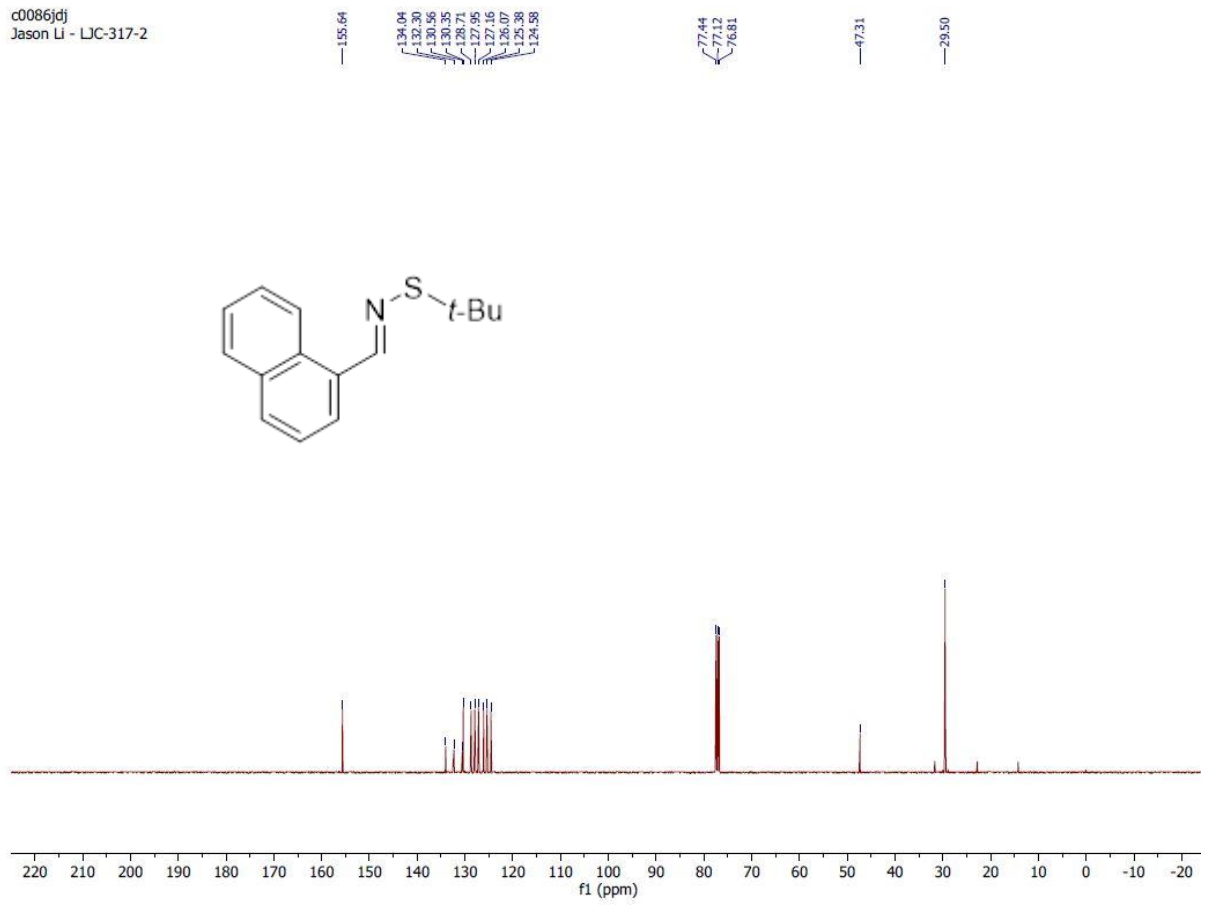
Data for **6g-*t*Bu**



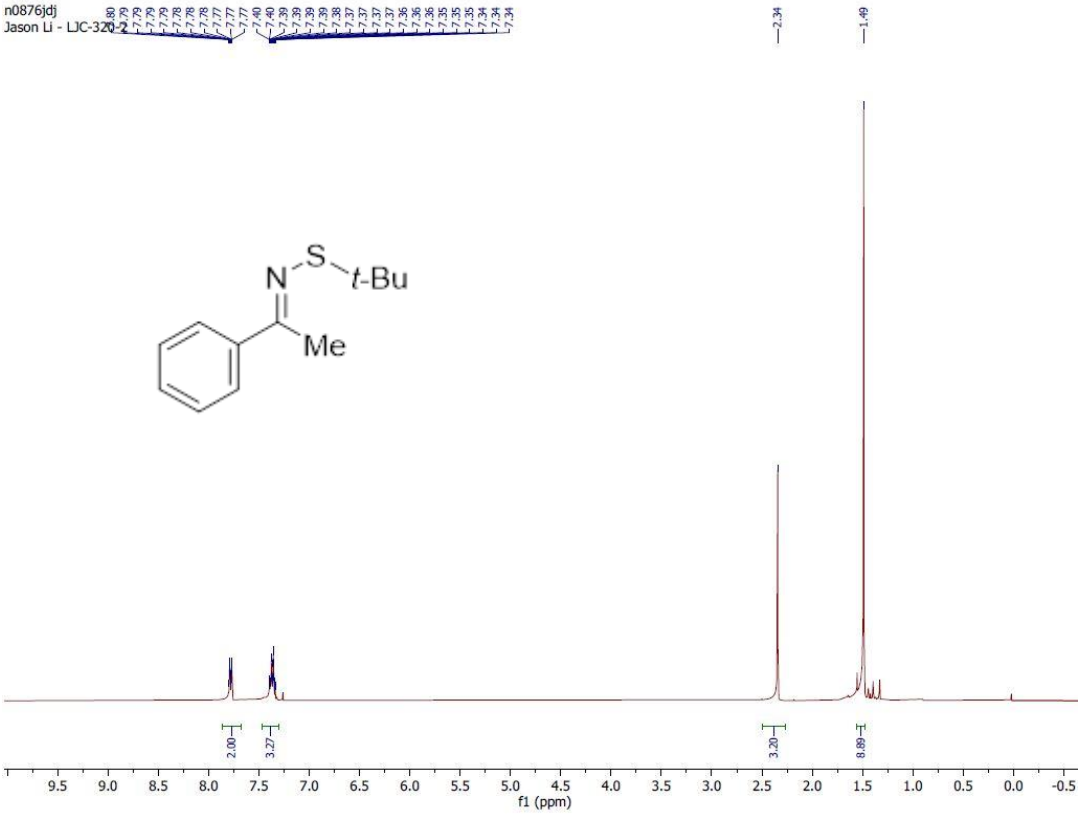


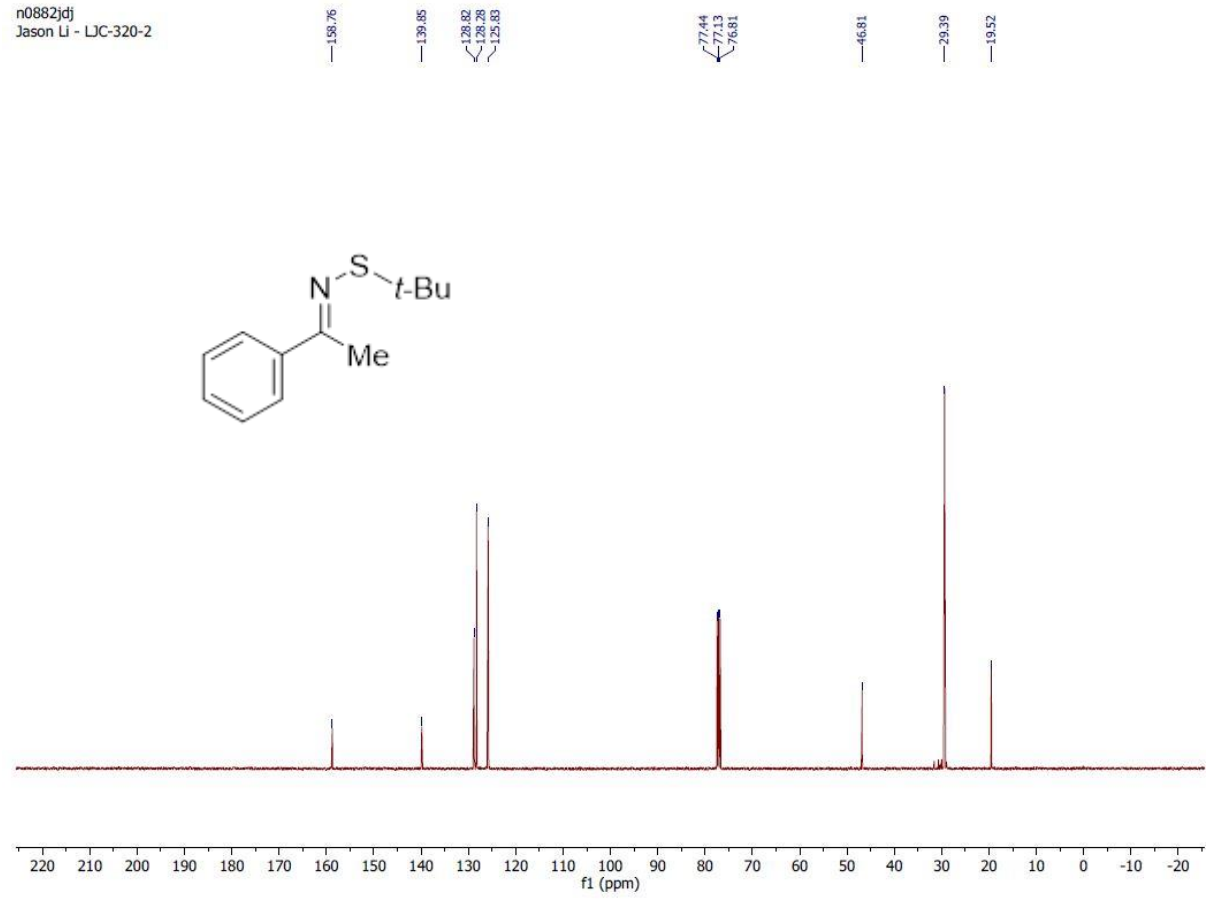
Data for **6h-*t*Bu**



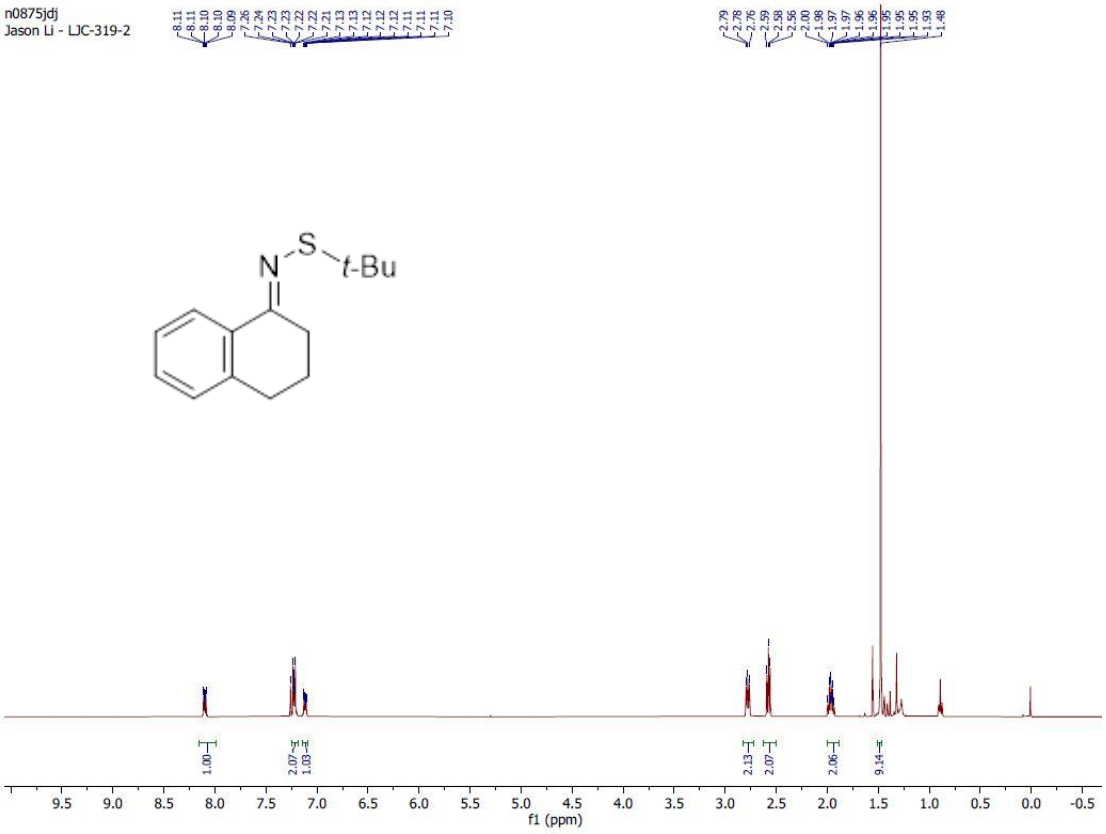


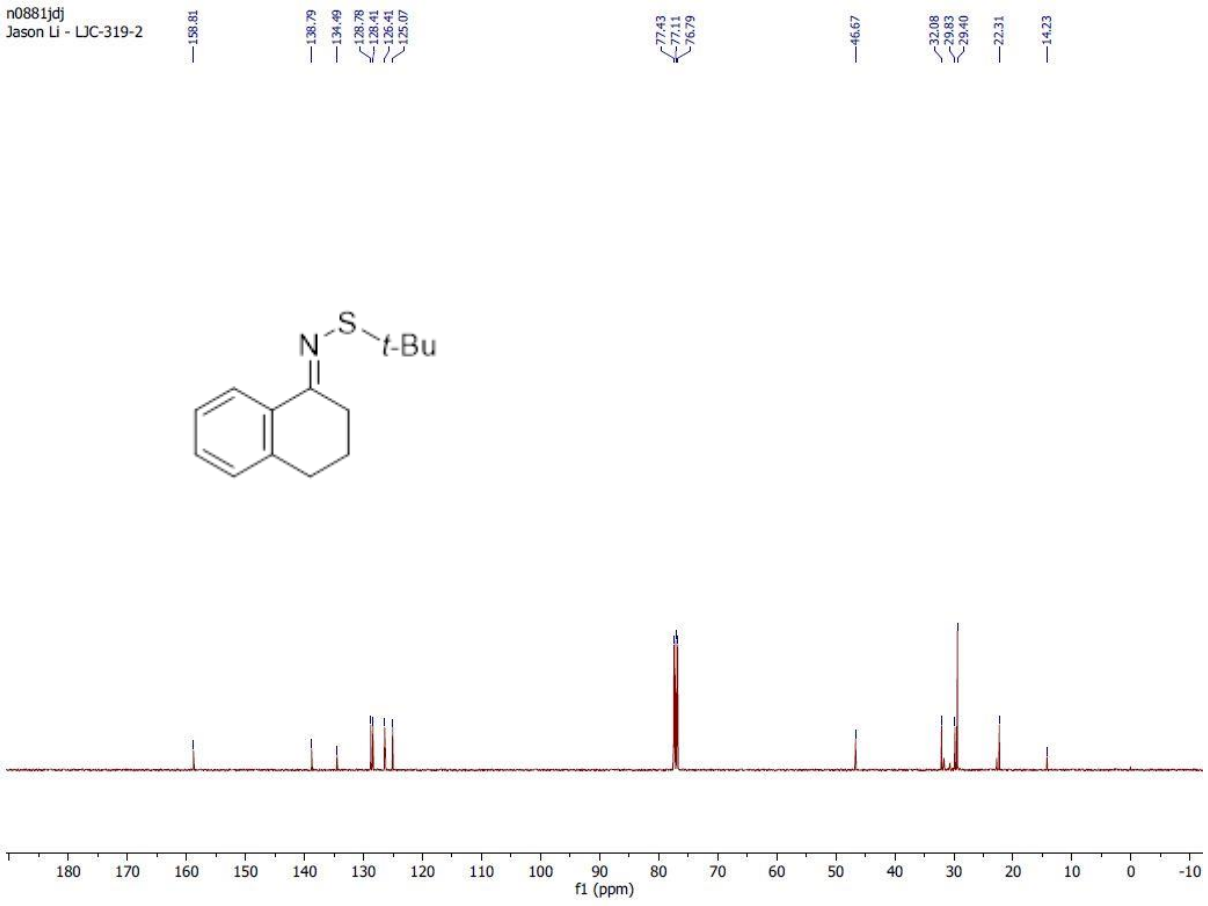
Data for **6i-*t*Bu**



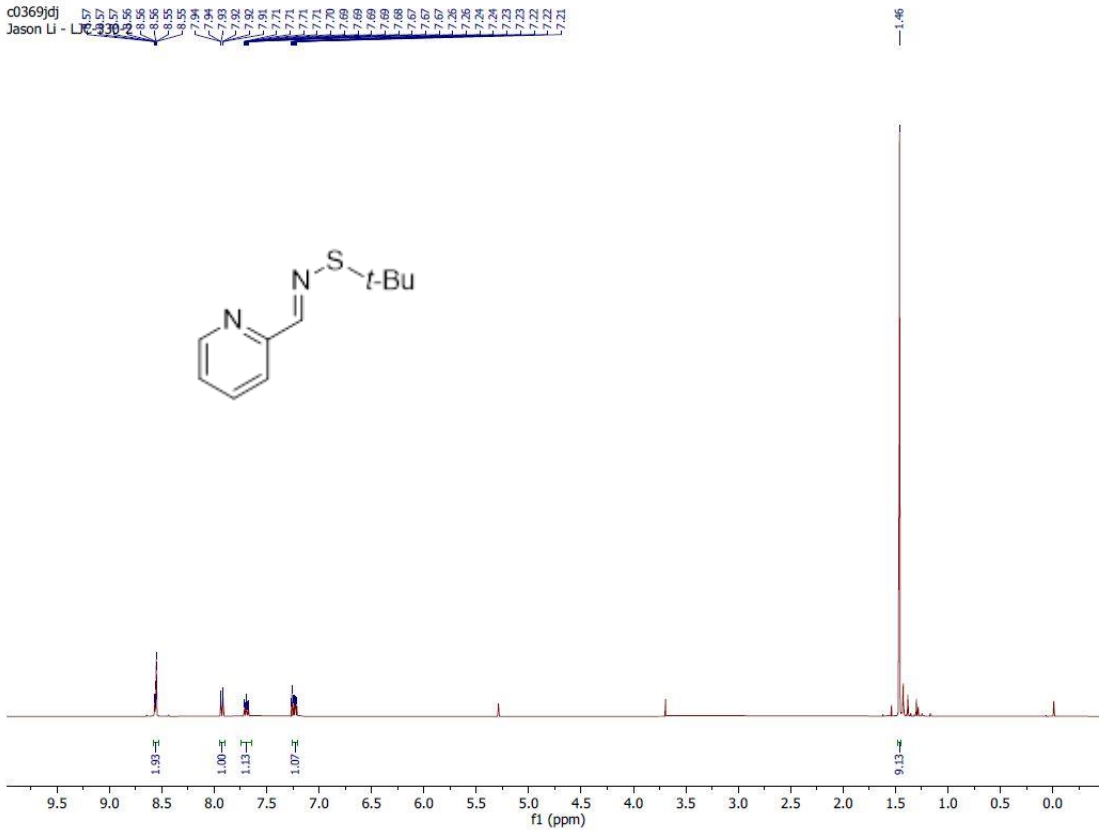


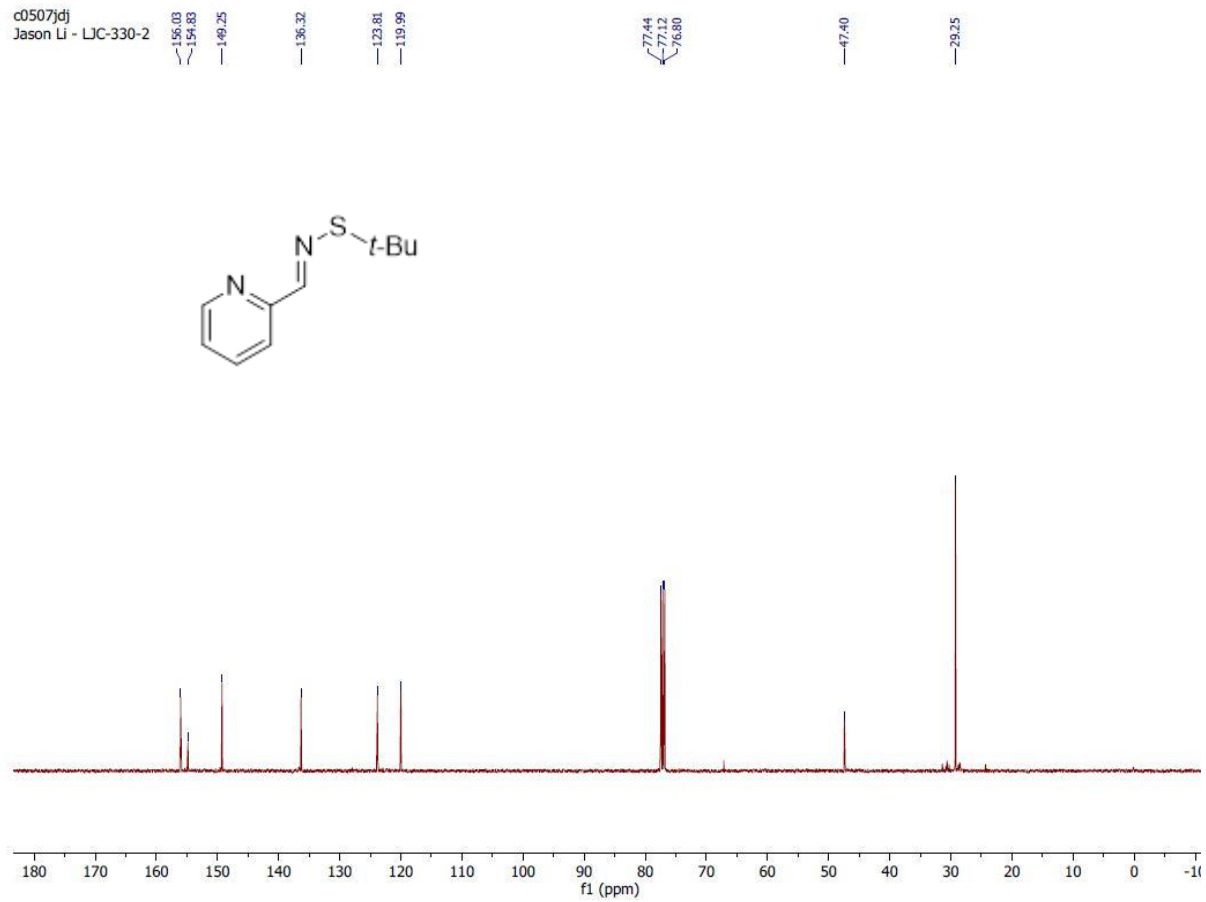
Data for **6k-*t*Bu**



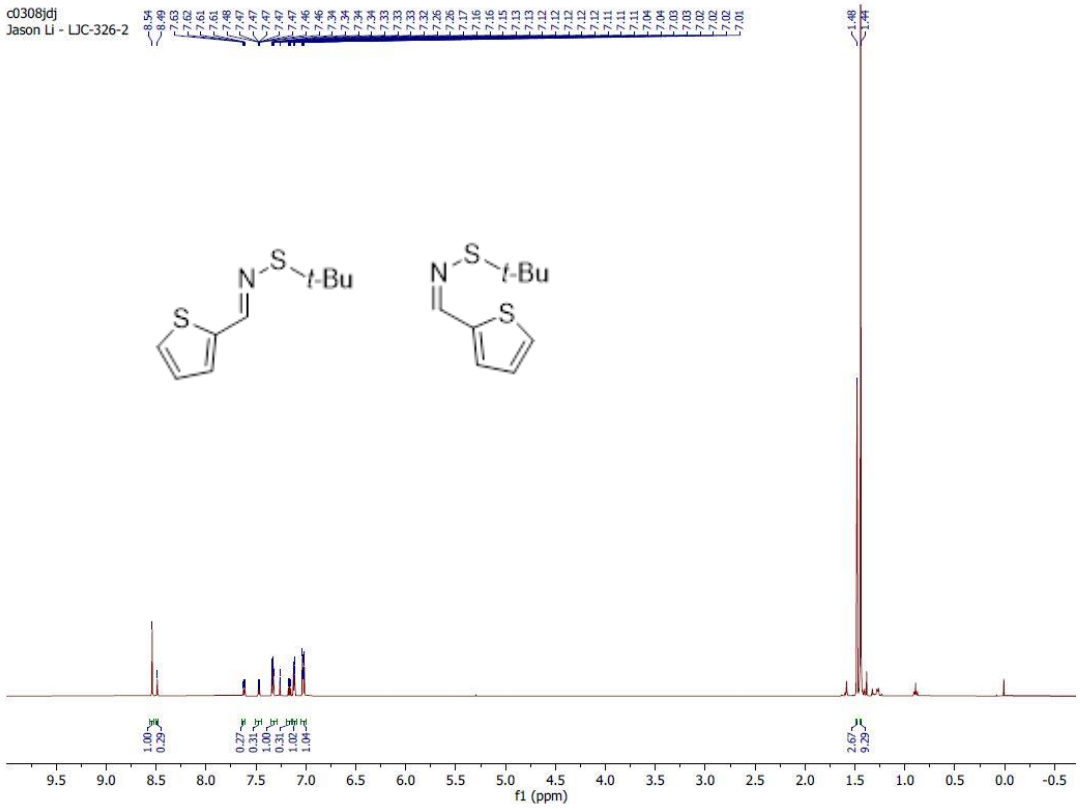


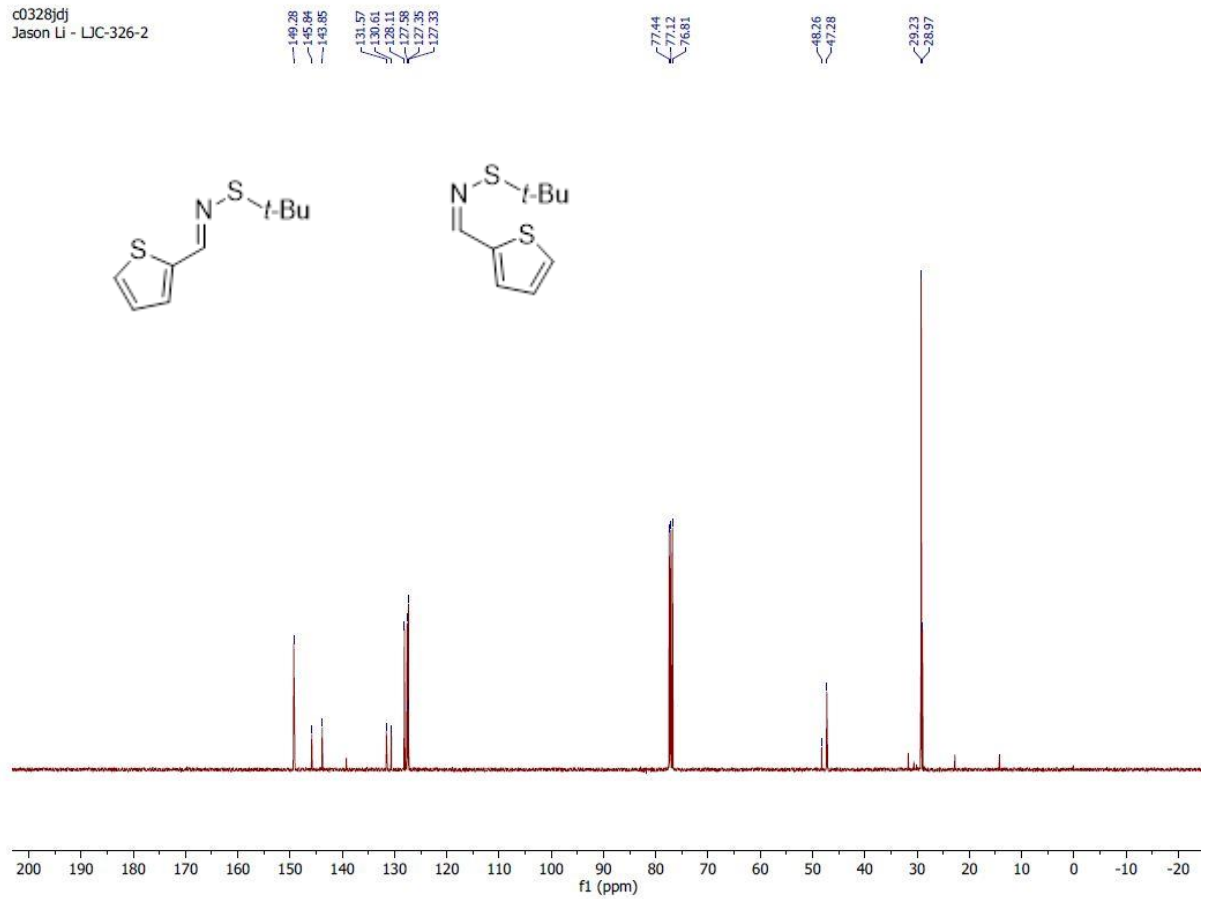
Data for **6l-*t*Bu**



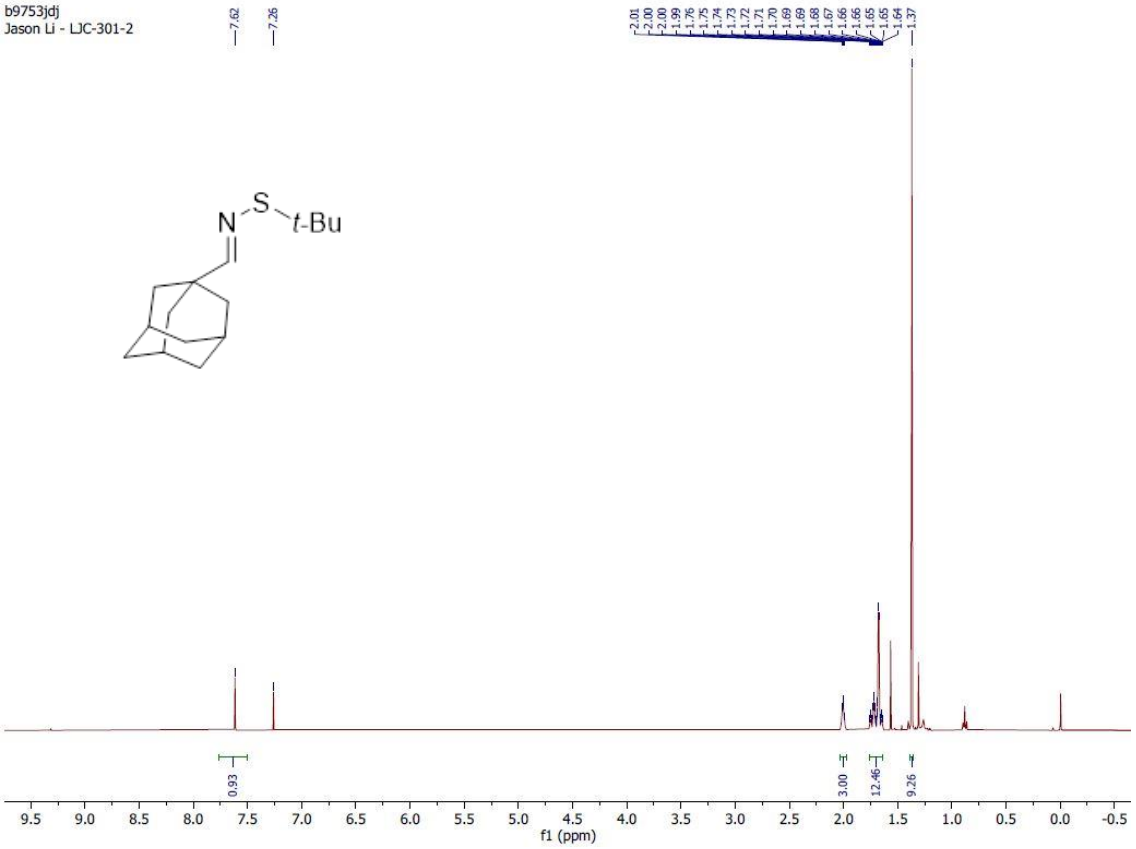


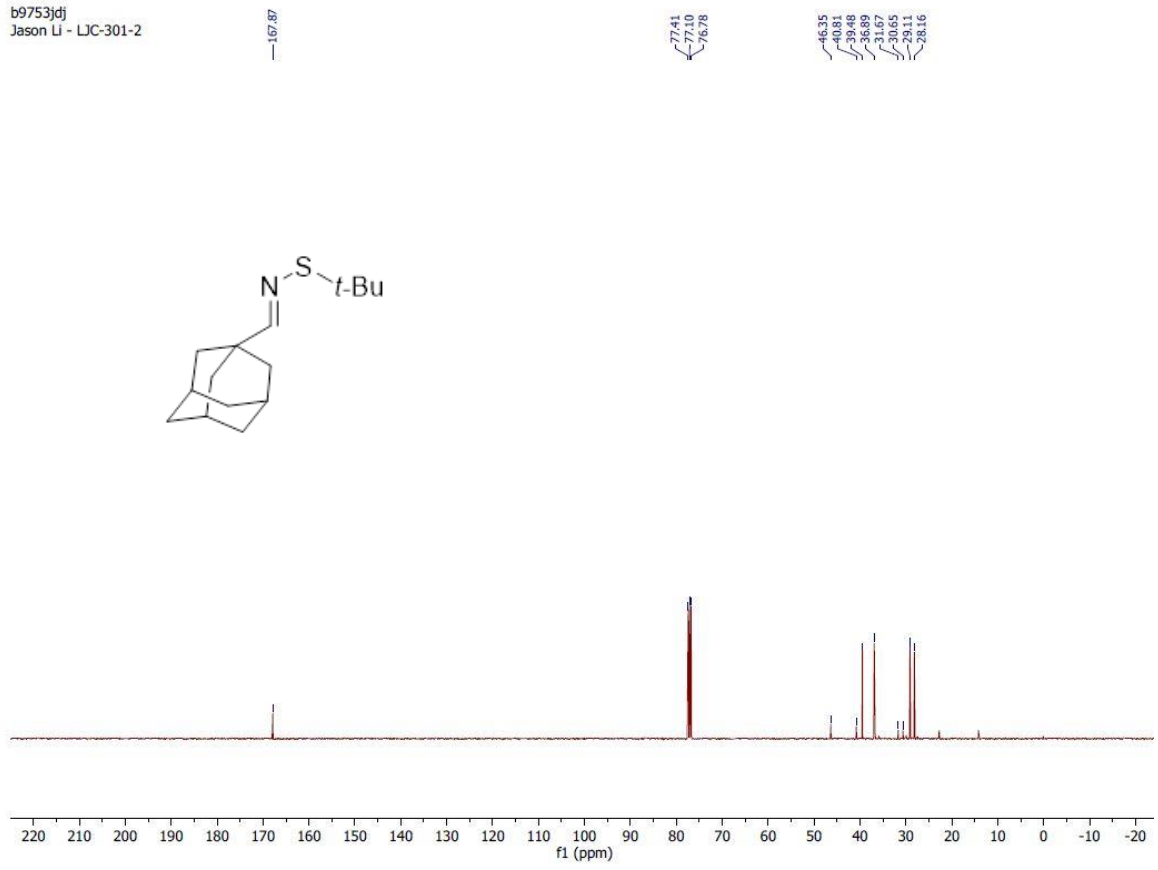
Data for **6m-*t*Bu**



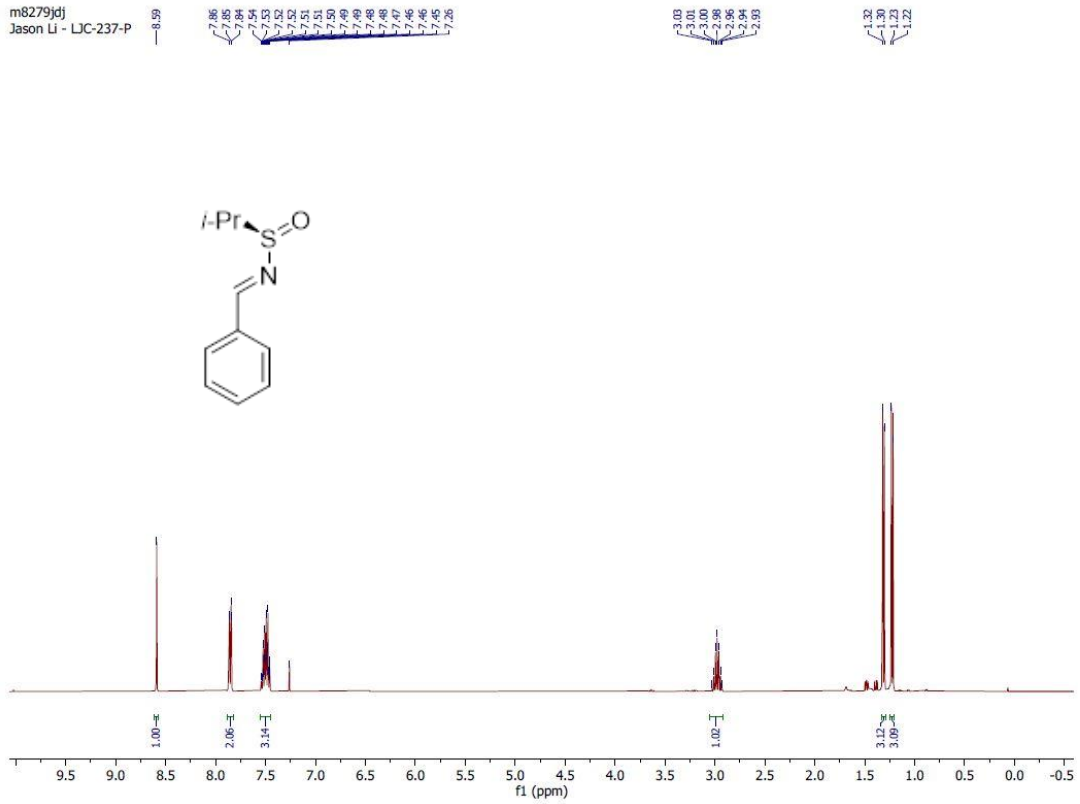


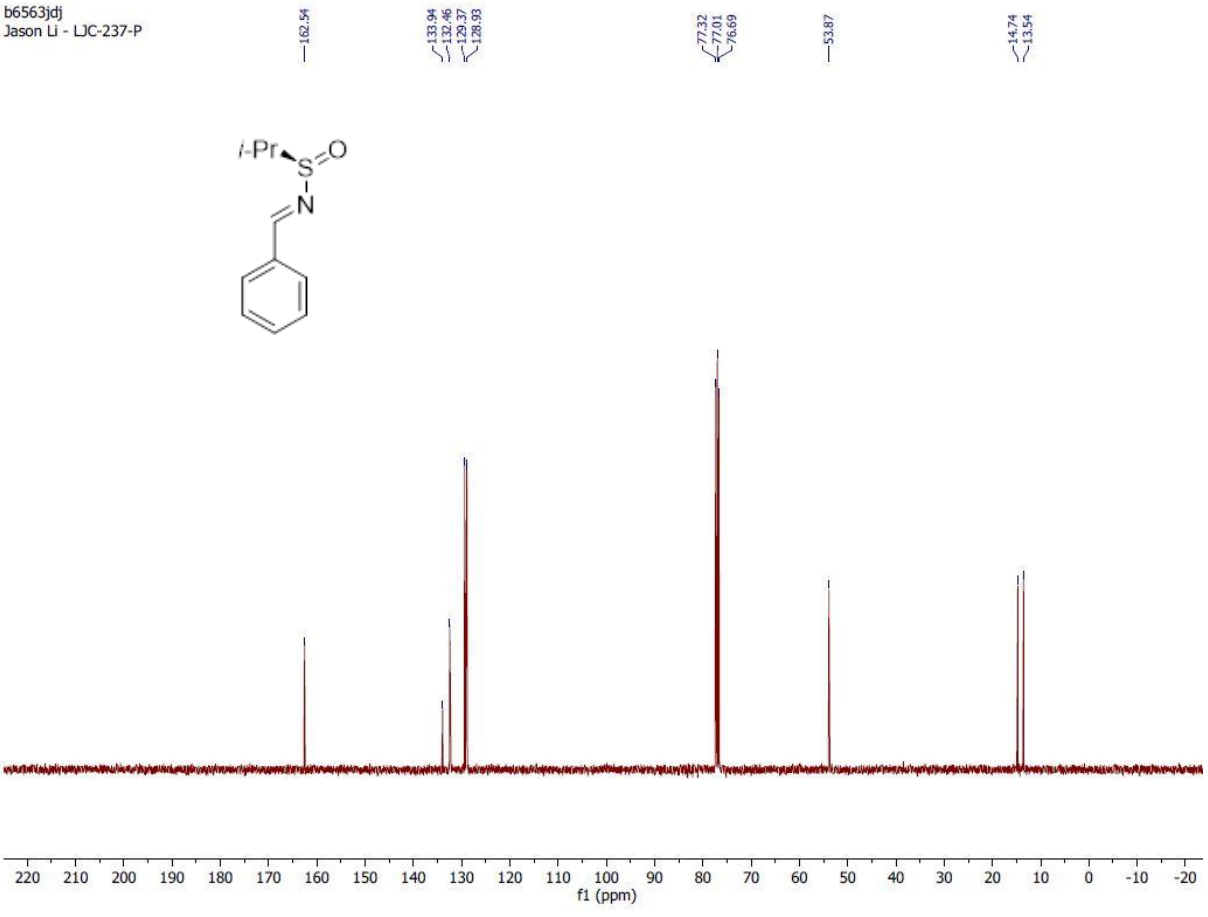
Data for **6n-*t*Bu**



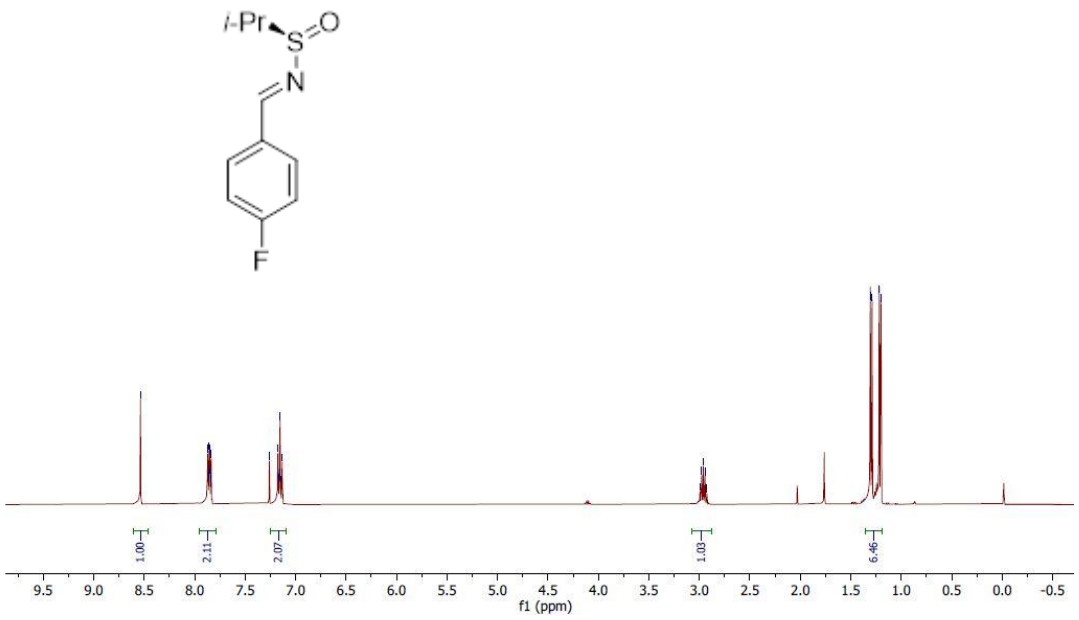


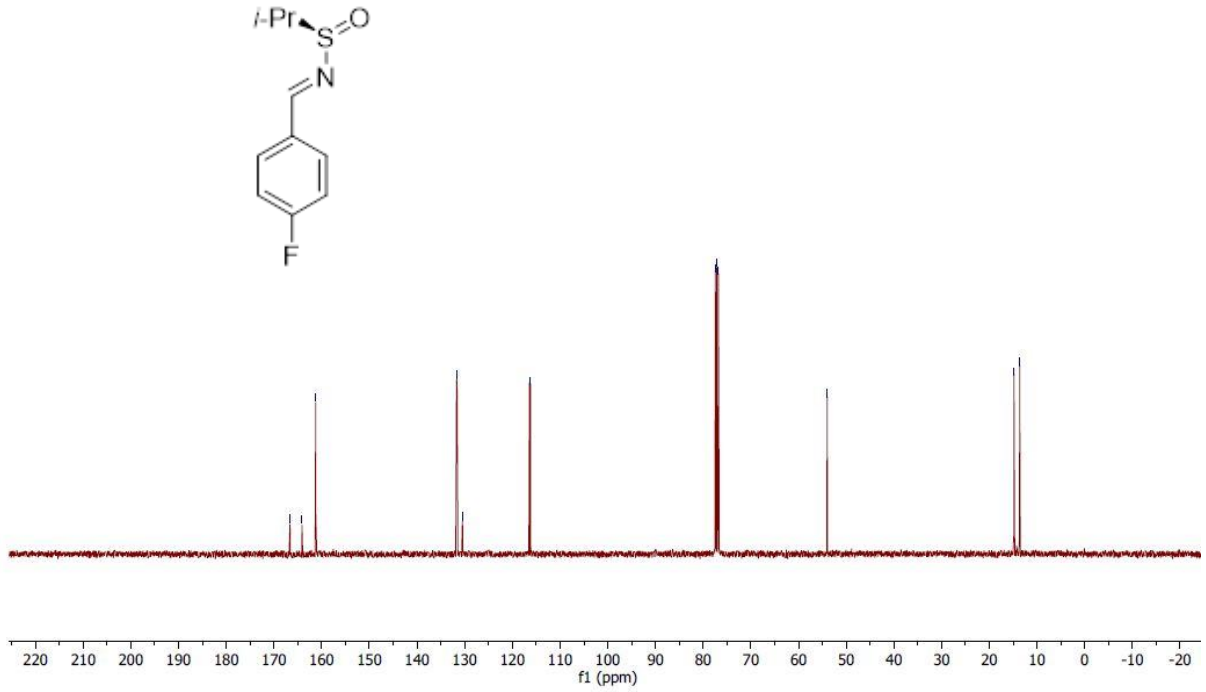
Data for **(*R*)-12a**

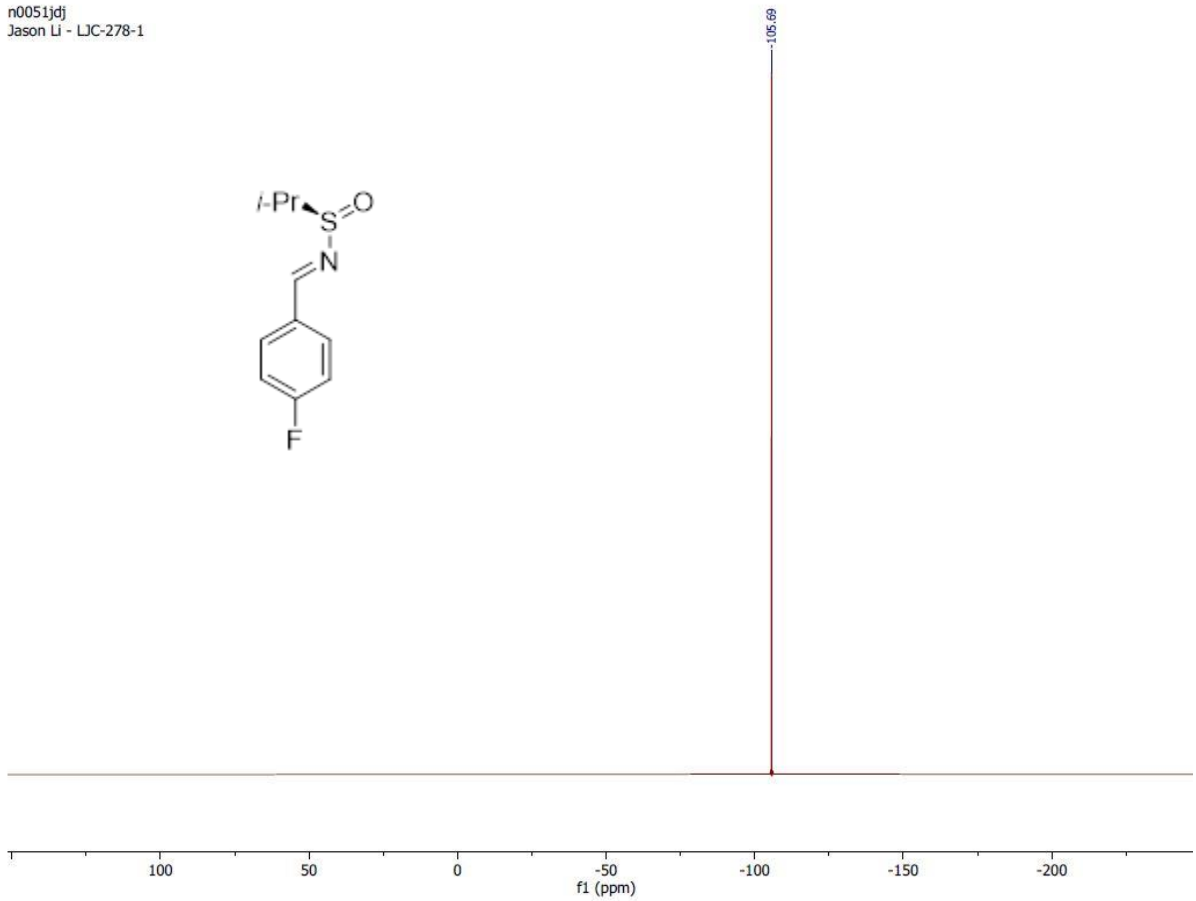




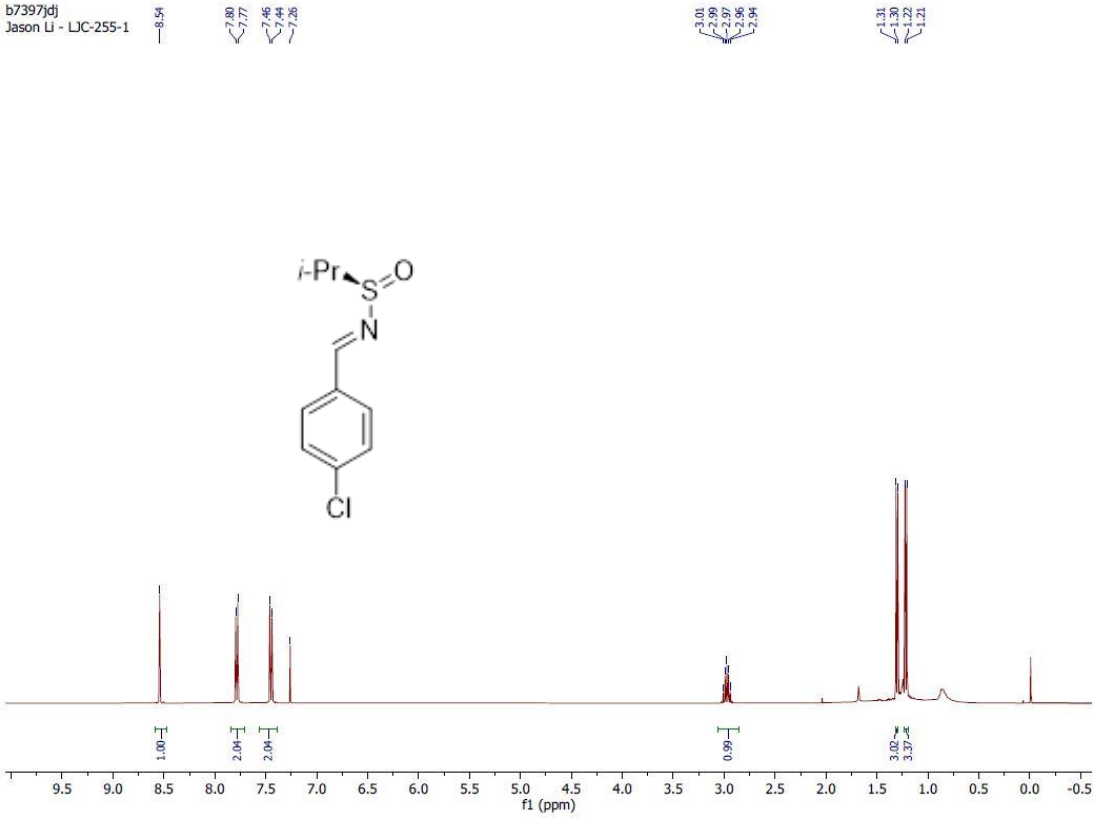
Data for **(*R*)-12b**

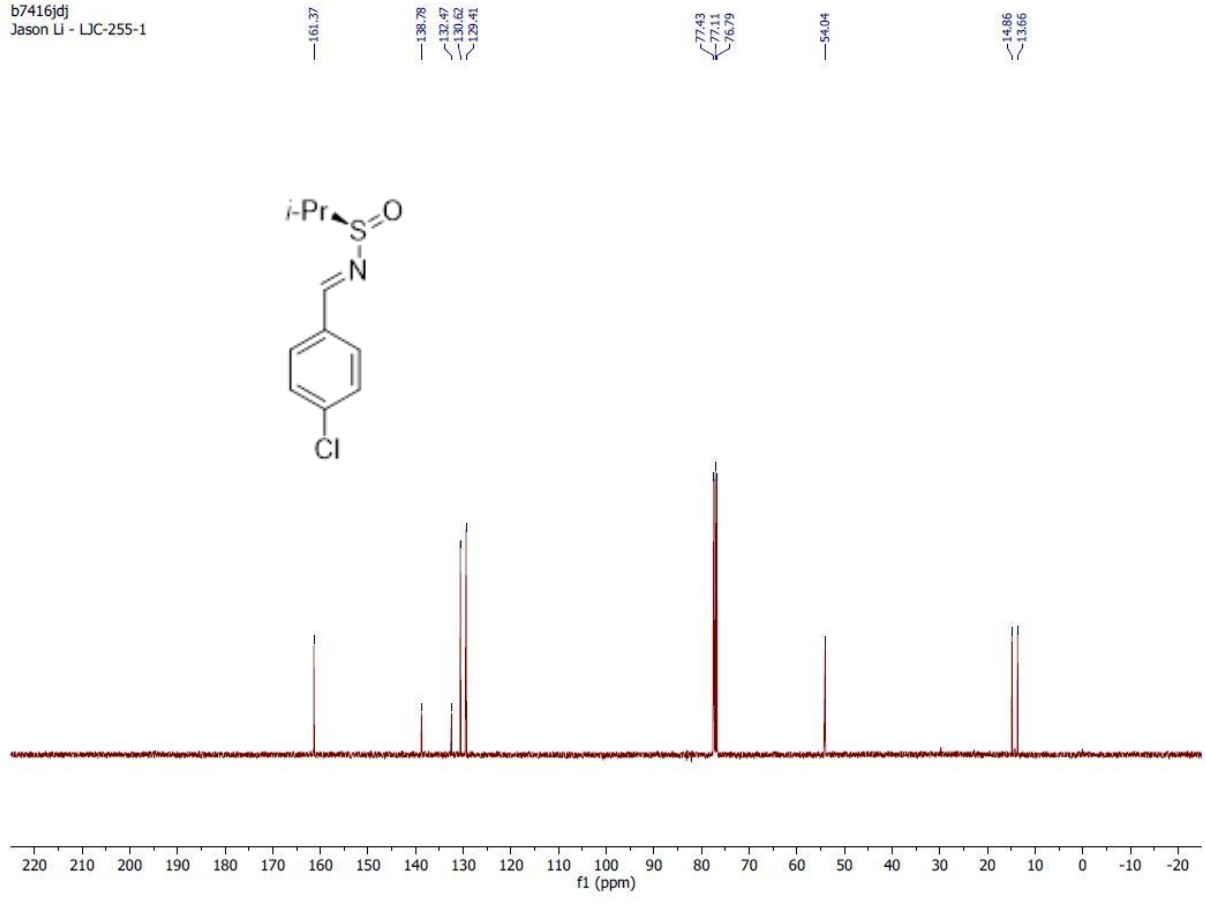




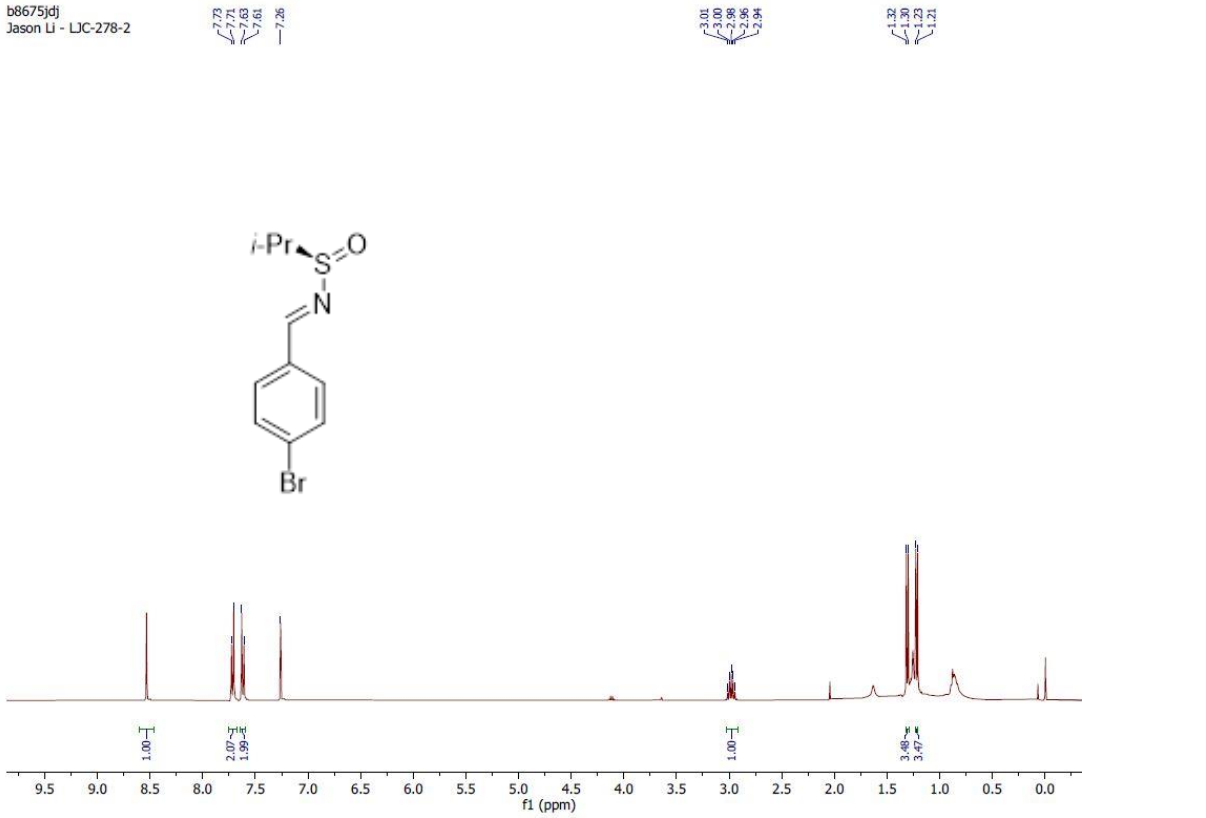

n0051jdj
Jason Li - LJC-278-1
-105.69
i-Pr
S
O
N
F
100
50
0
-50
-100
-150
-200
f1 (ppm)

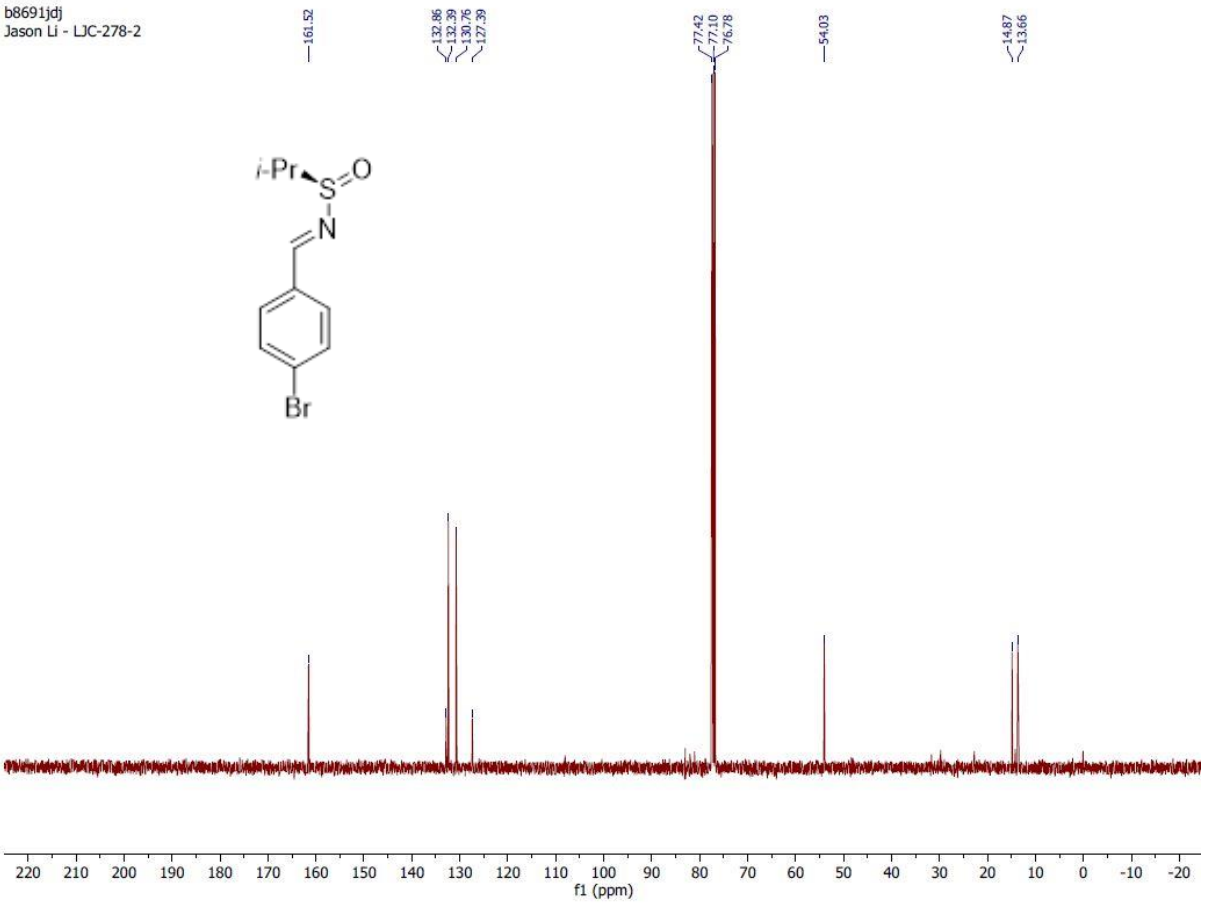
Data for **(*R*)-12c**



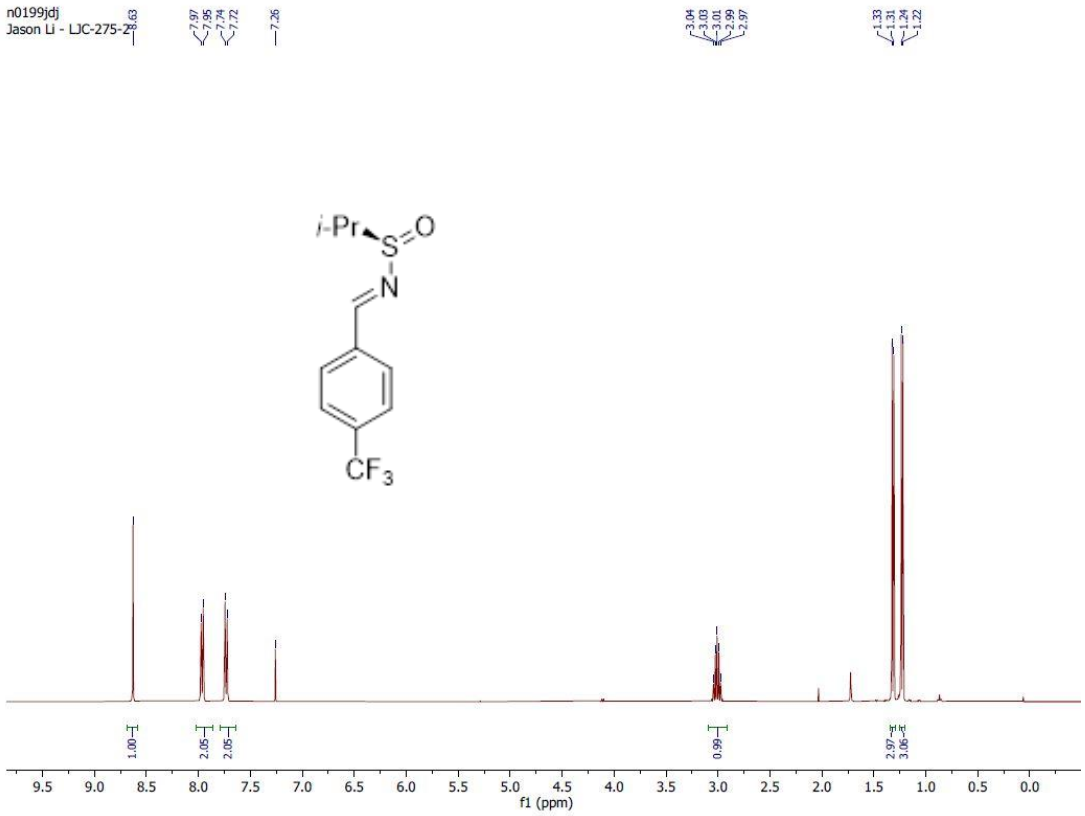


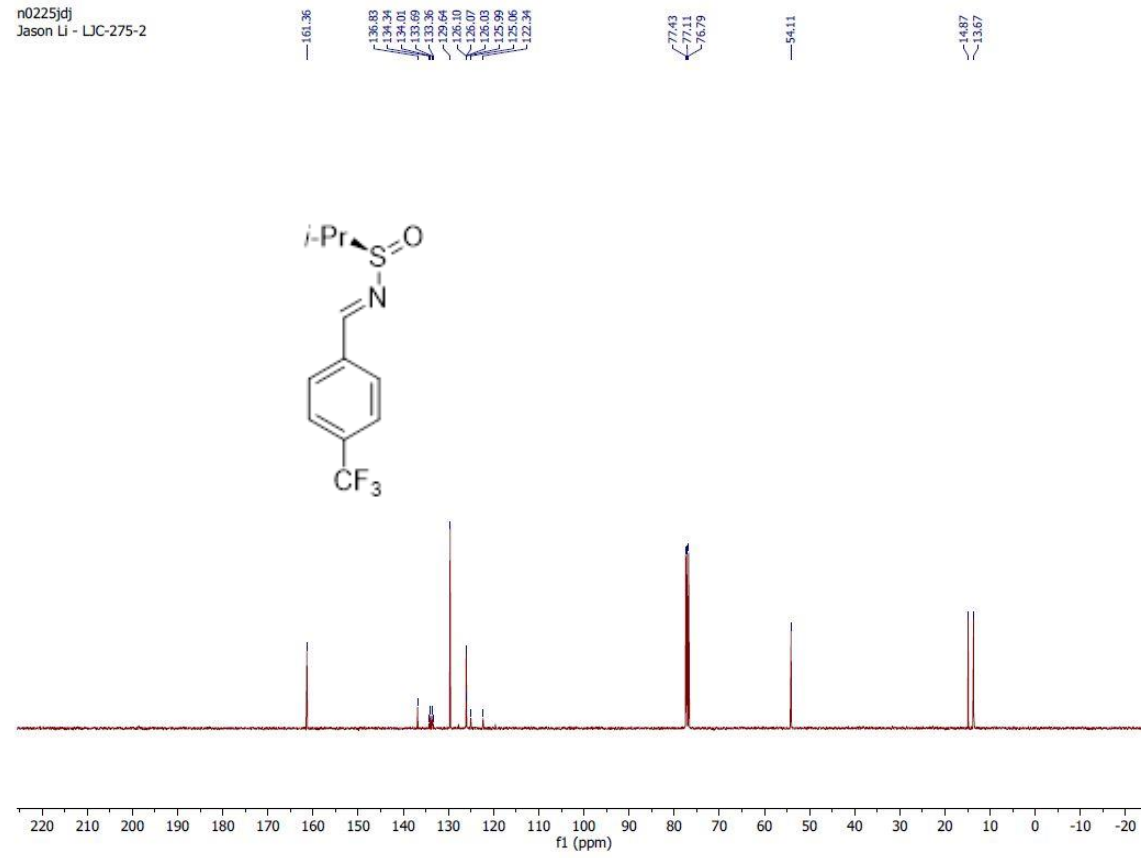
Data for **(*R*)-12d**

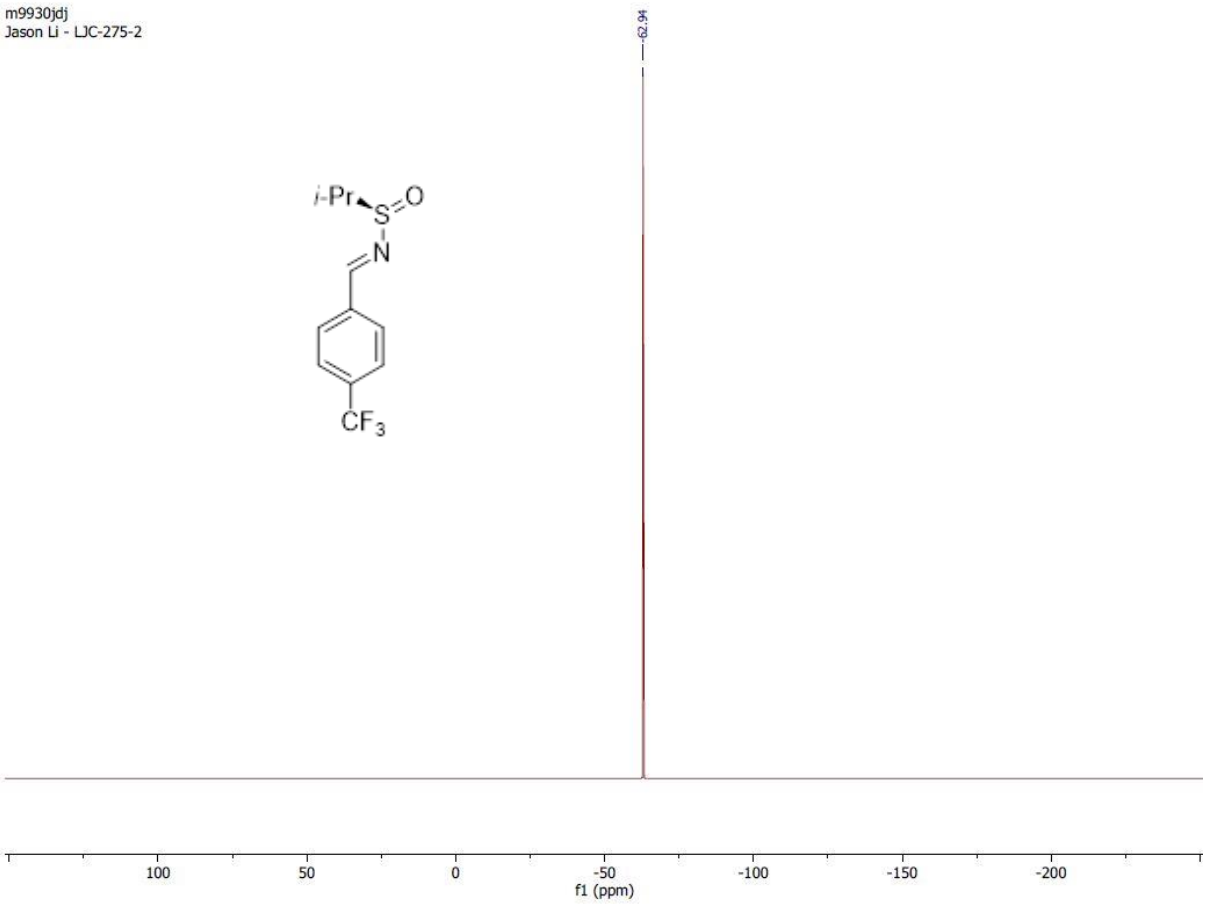




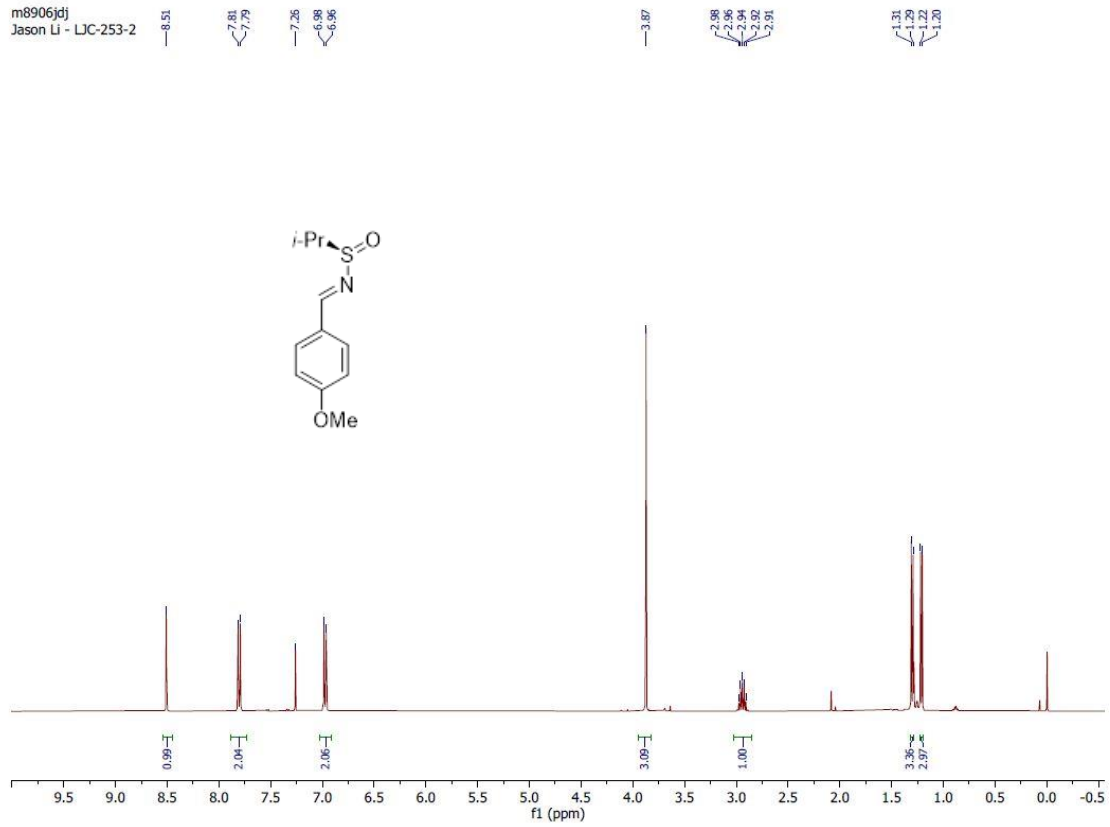
Data for **(*R*)-12e**

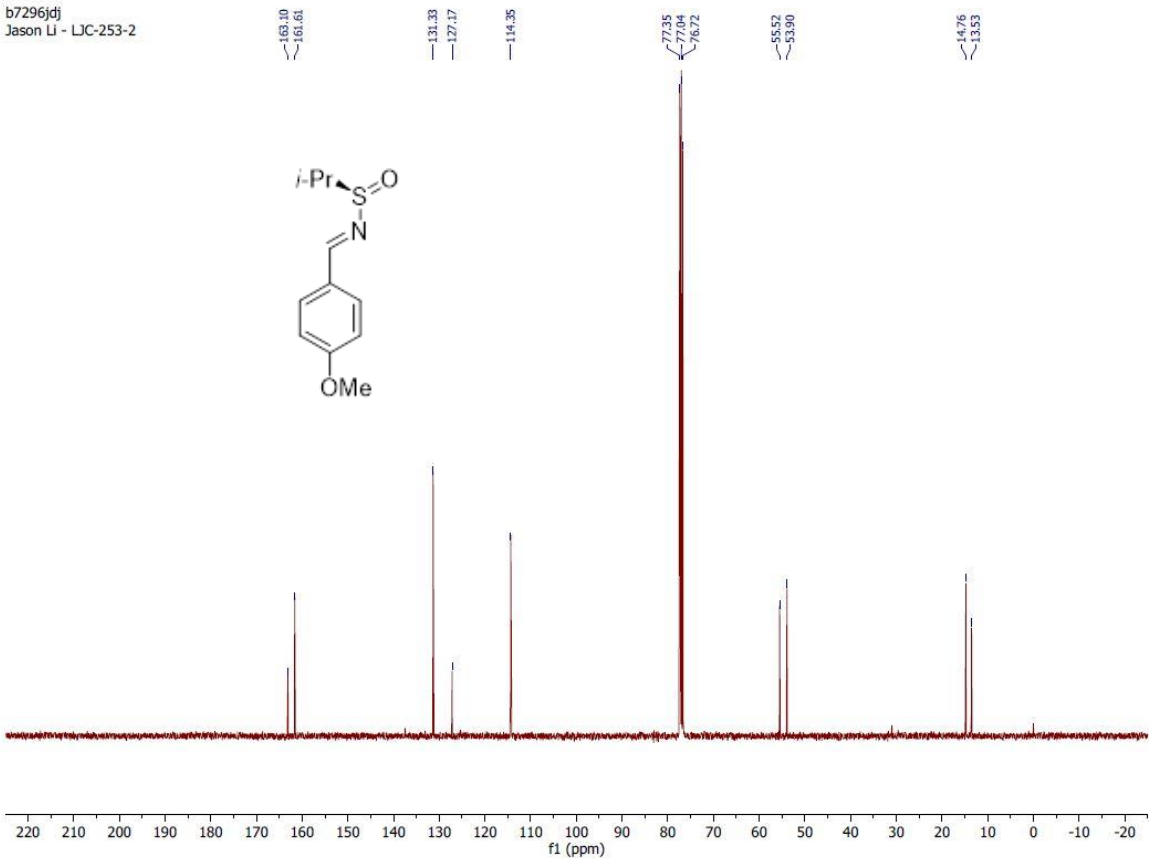




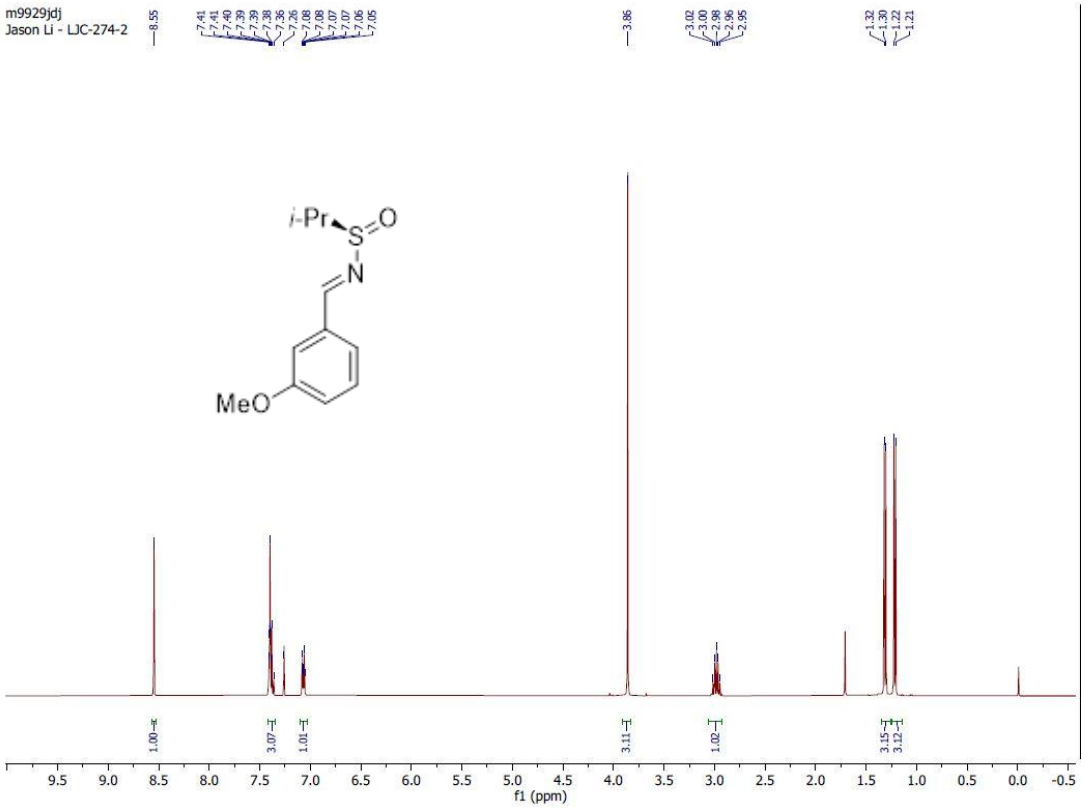

m9930jdj
Jason Li - LJC-275-2
-62.94
i-Pr
S
O
N
CF3
100
50
0
-50
-100
-150
-200
f1 (ppm)

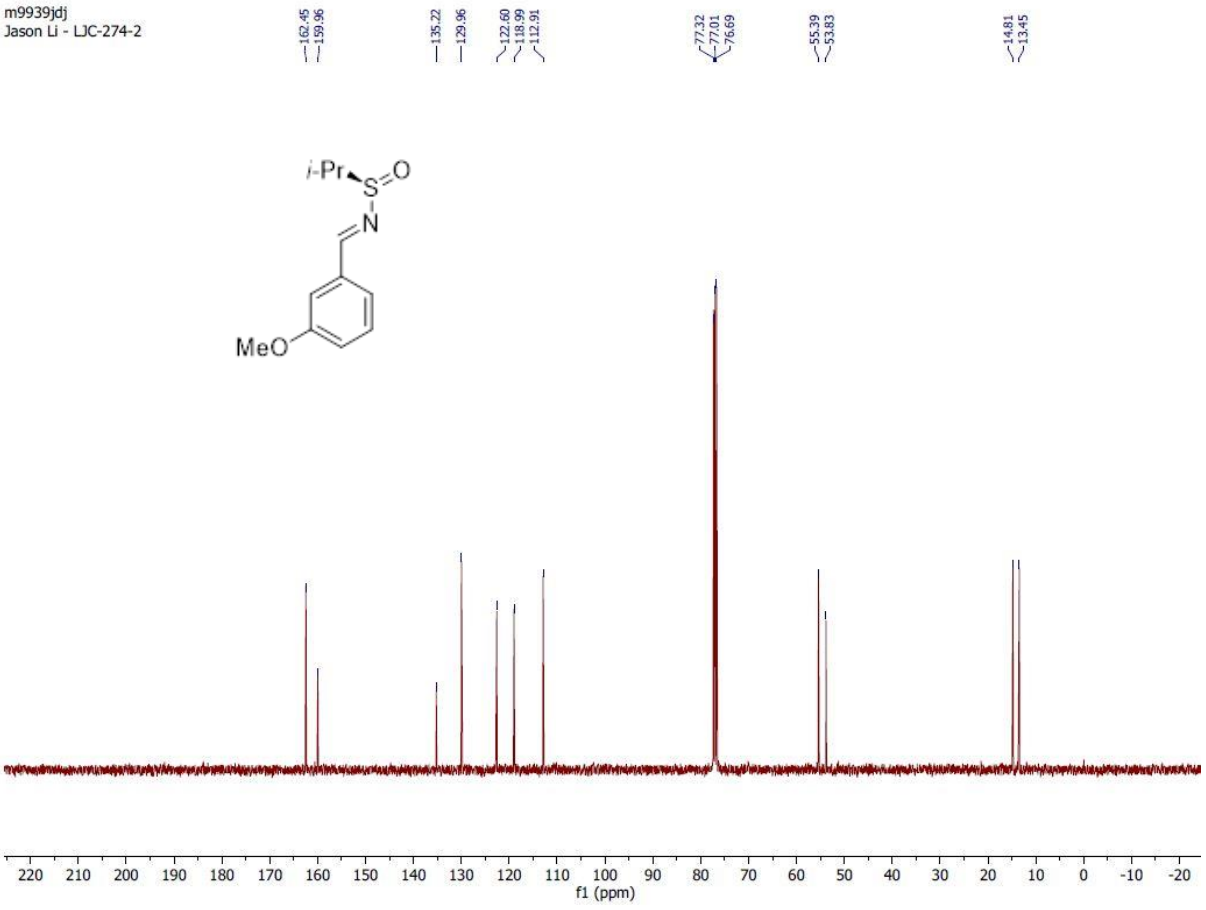
Data for **(*R*)-12f**



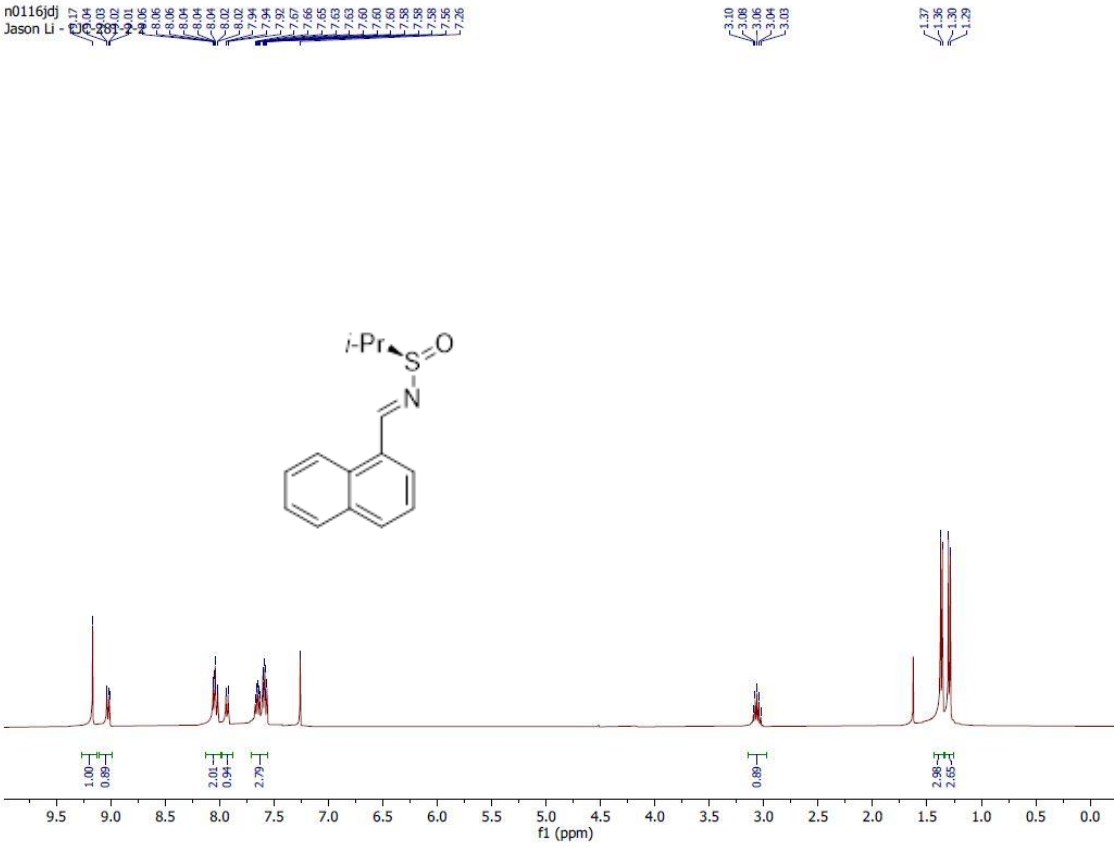


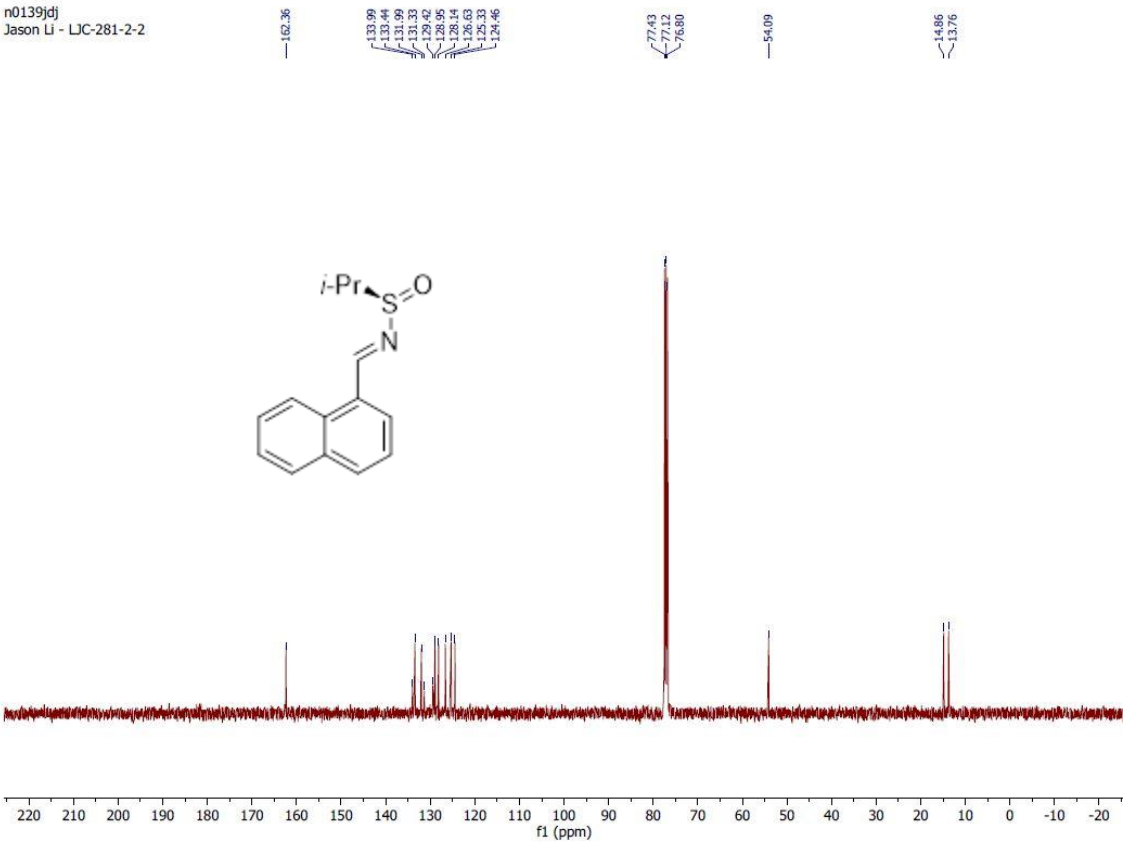
Data for **(*R*)-12g**



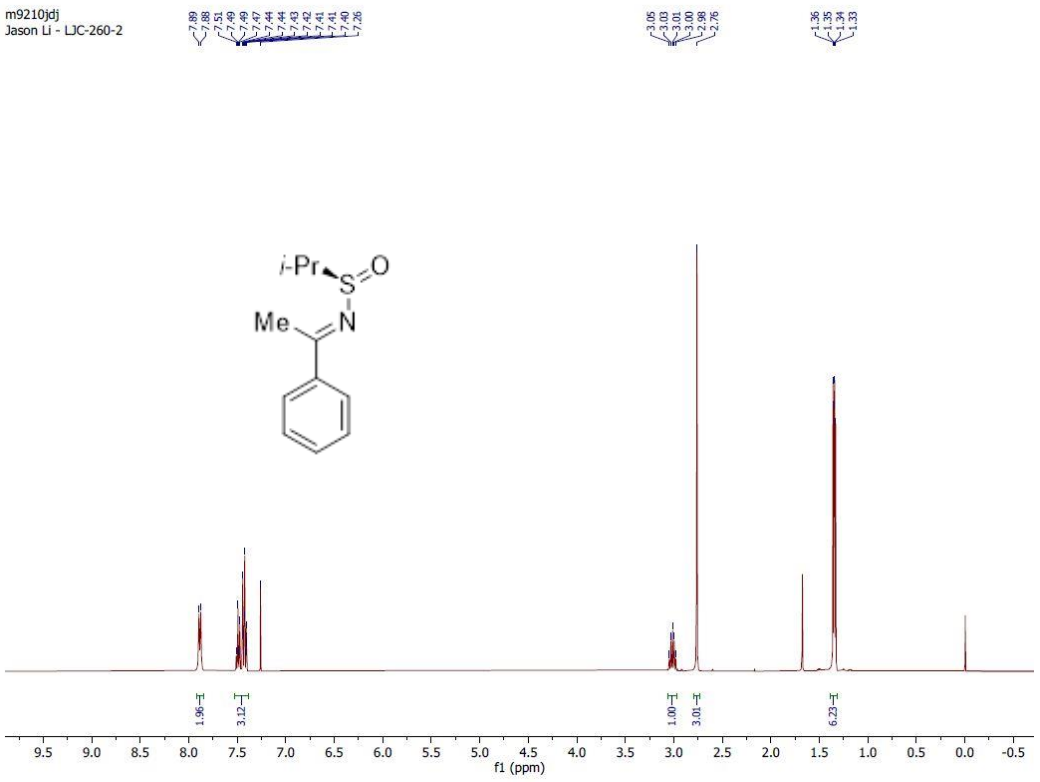


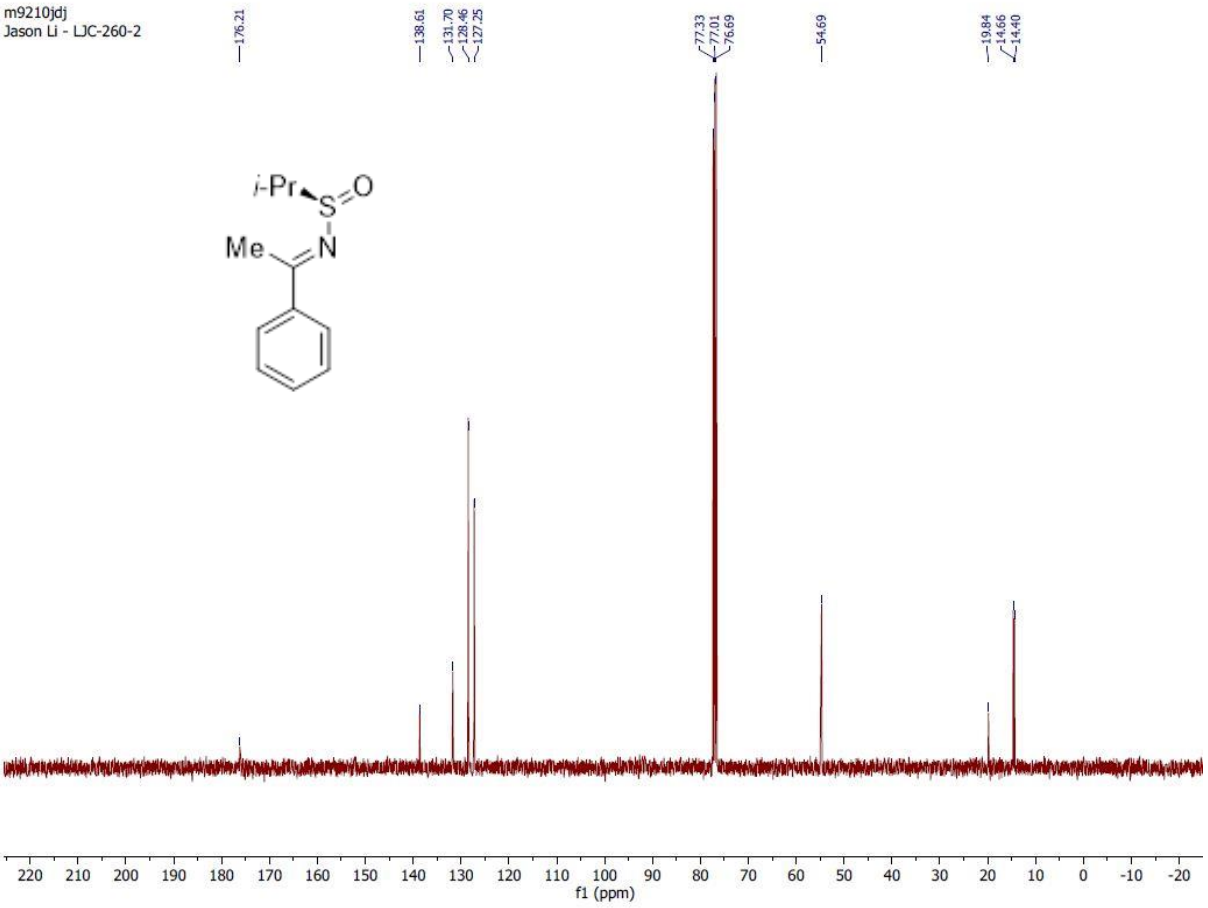
Data for **(*R*)-12h**



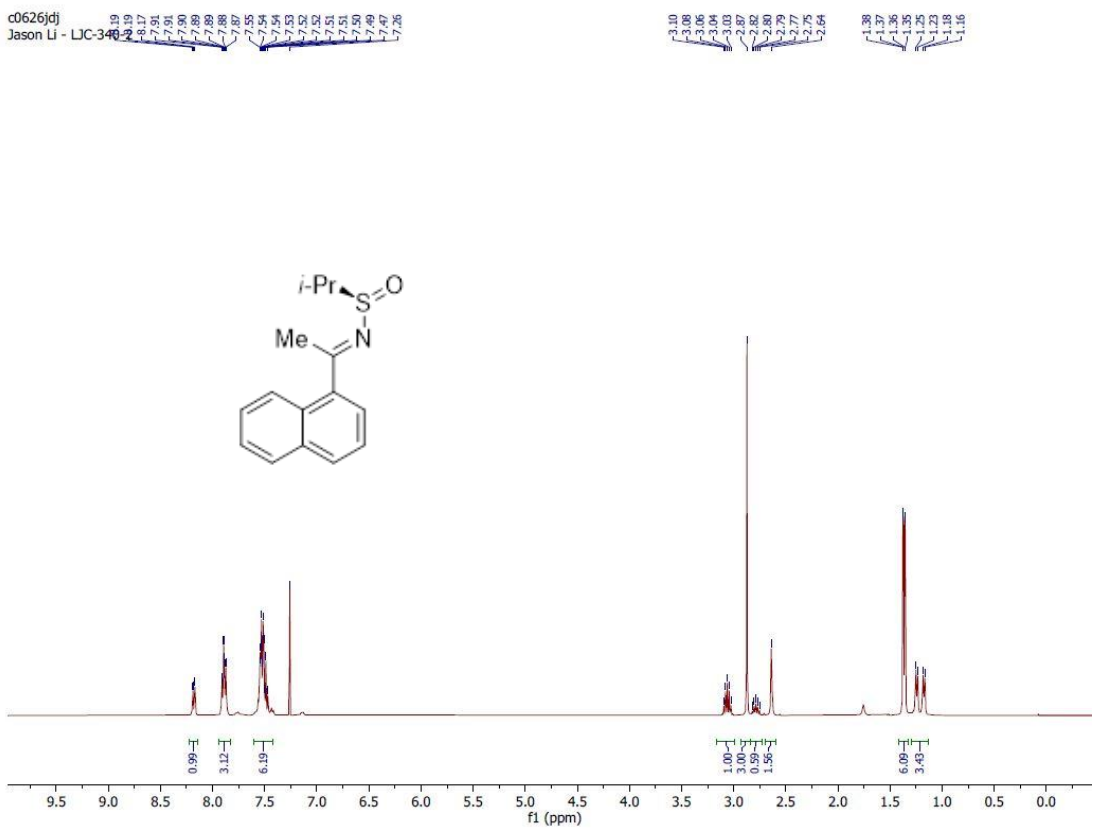


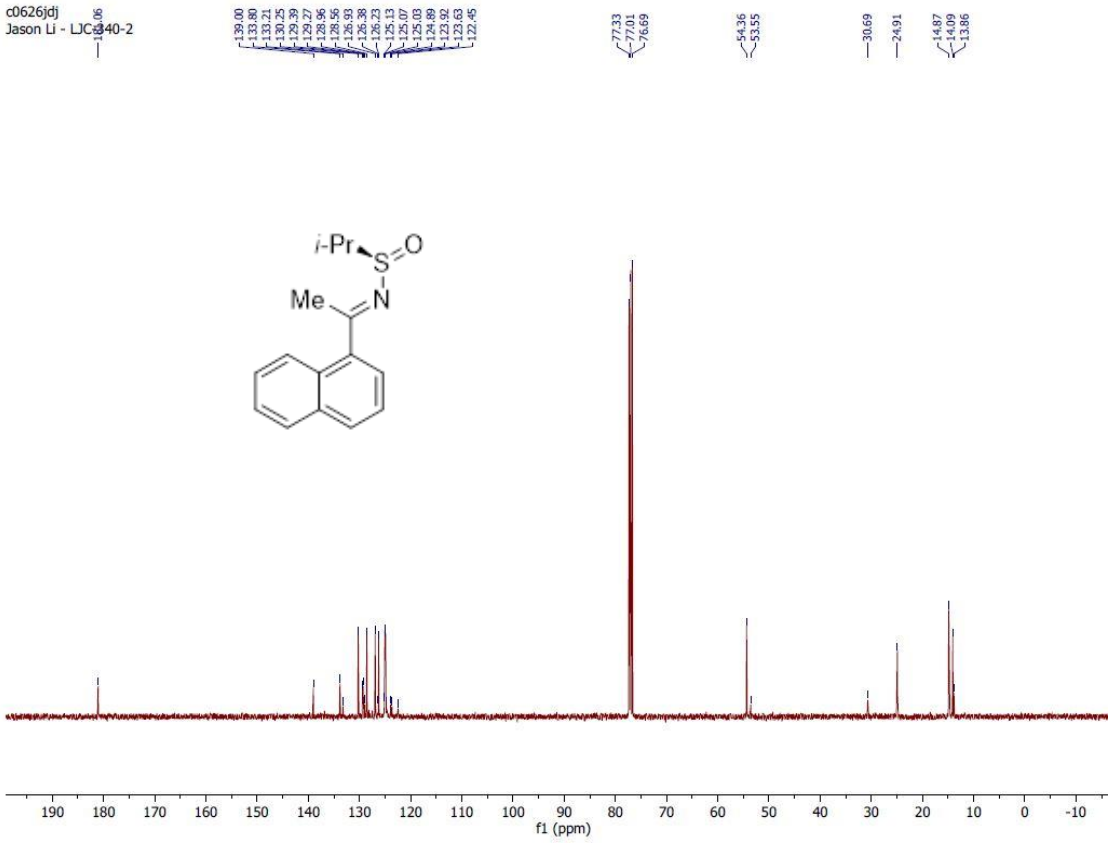
Data for **(*R*)-12i**



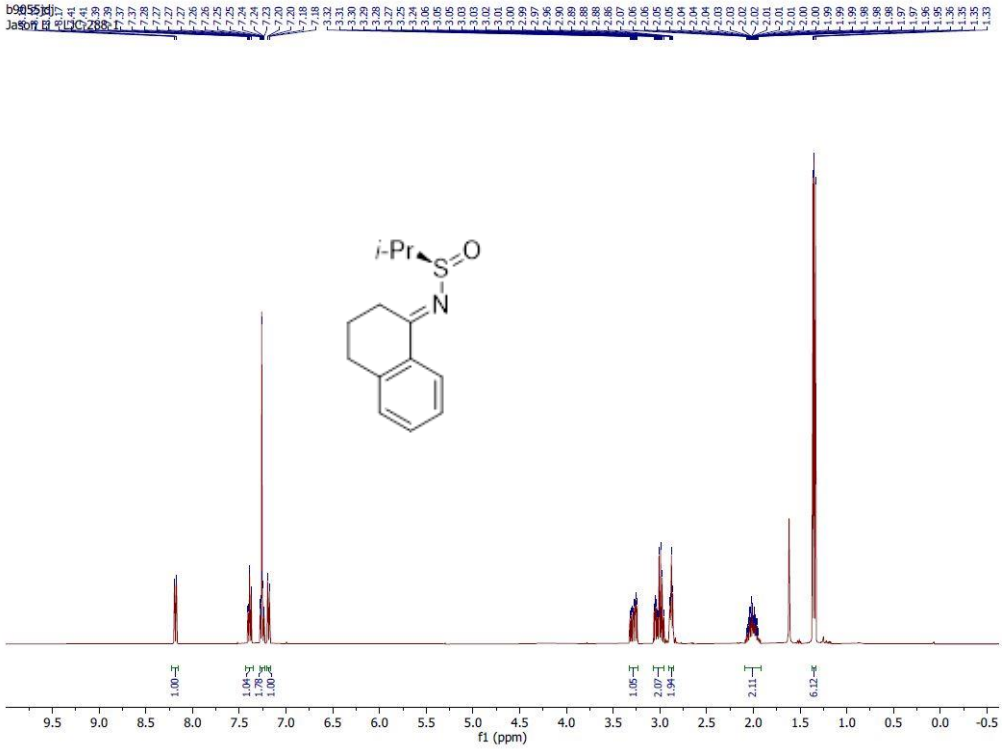


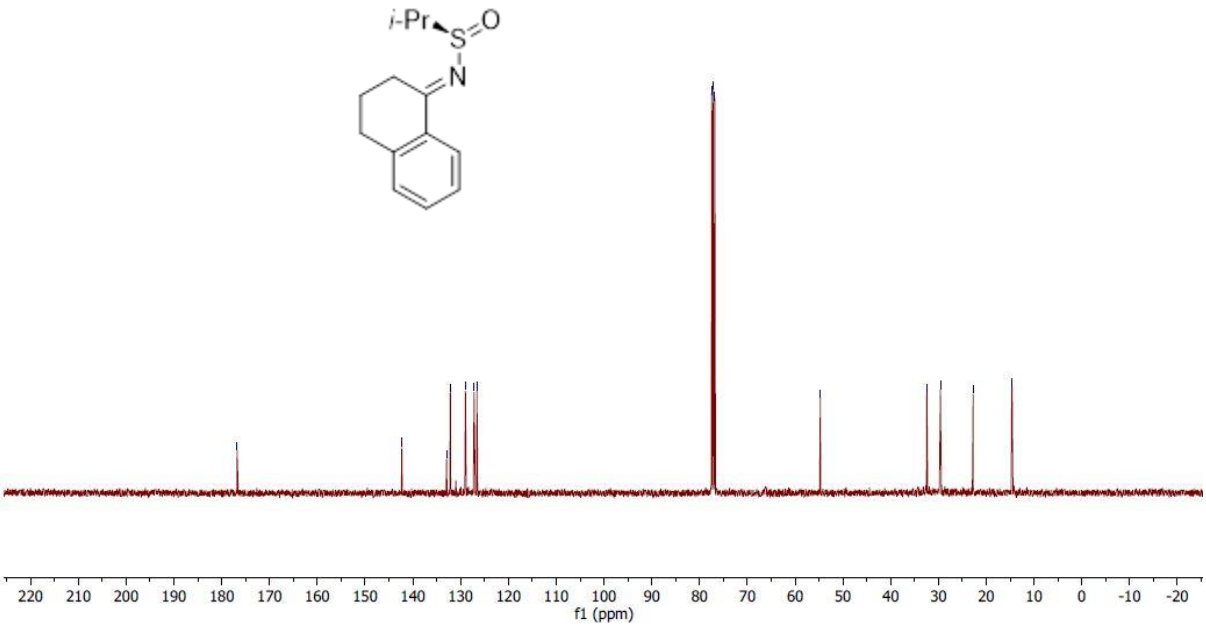
Data for **(*R*)-12j**





Data for **(*R*)-12k**





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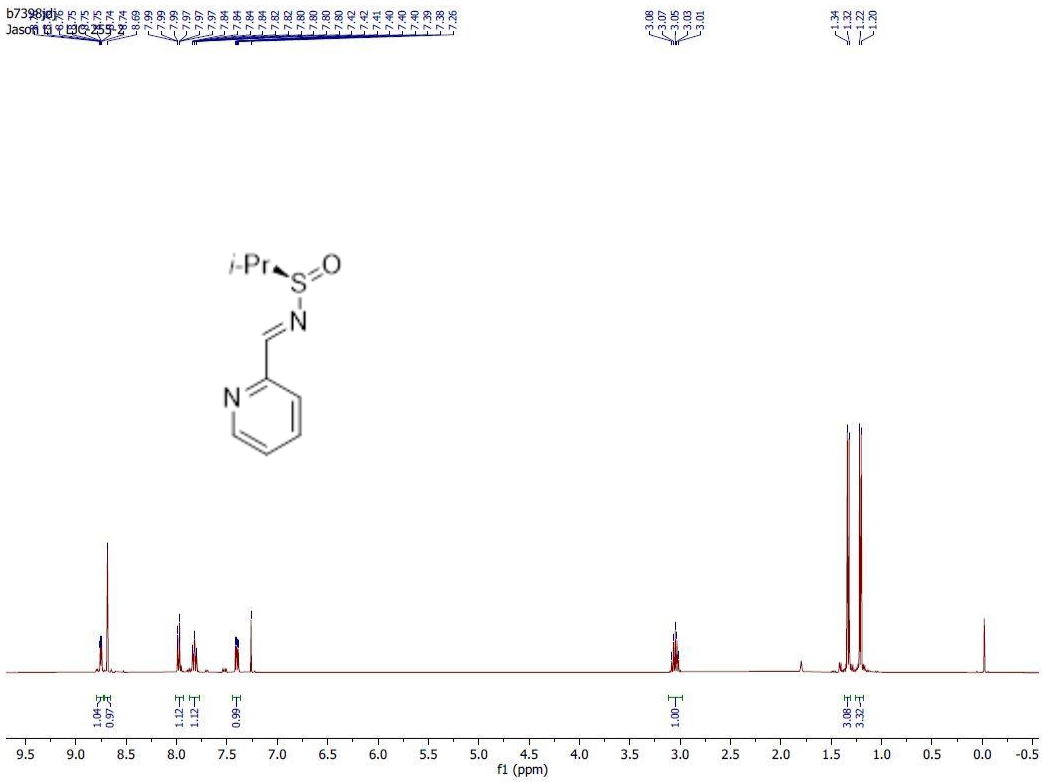

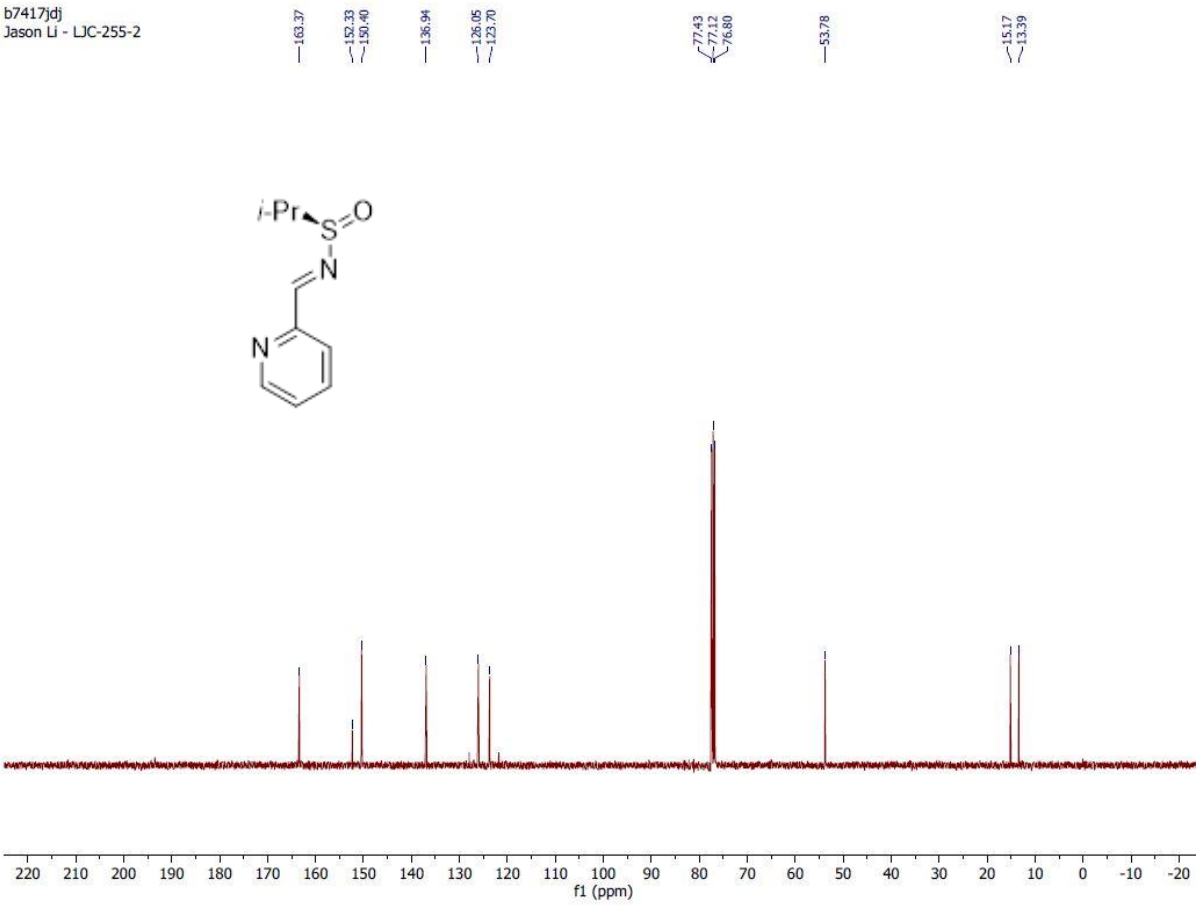

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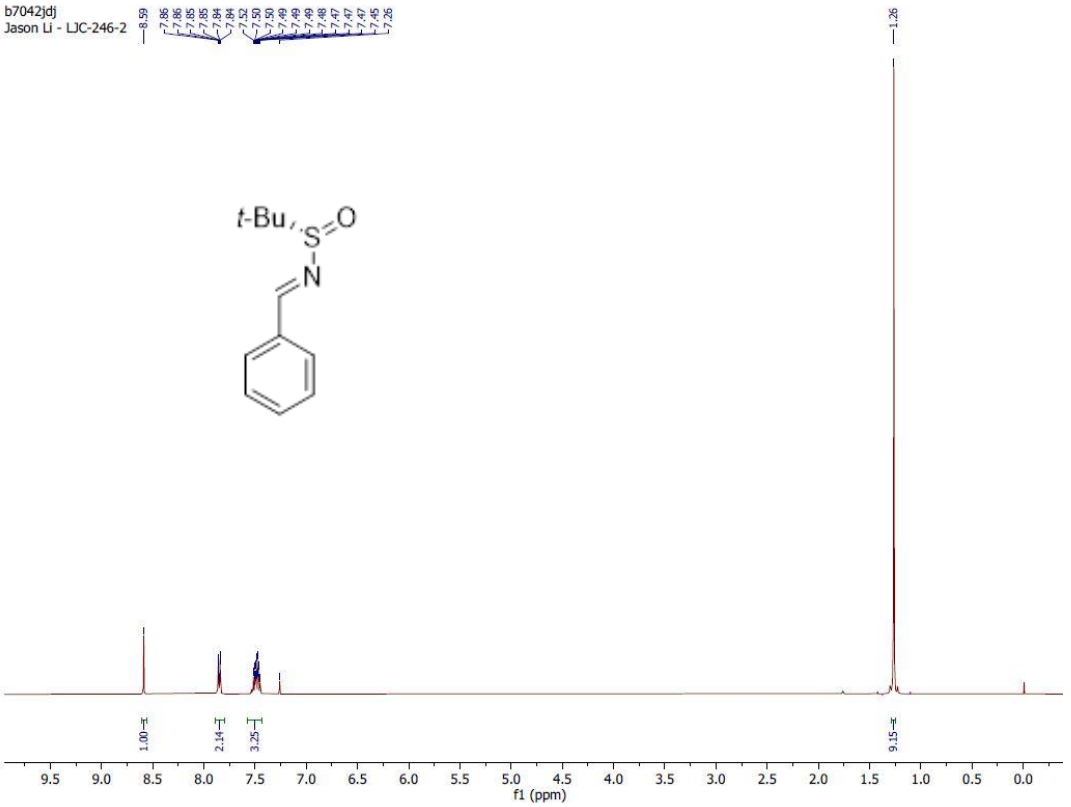

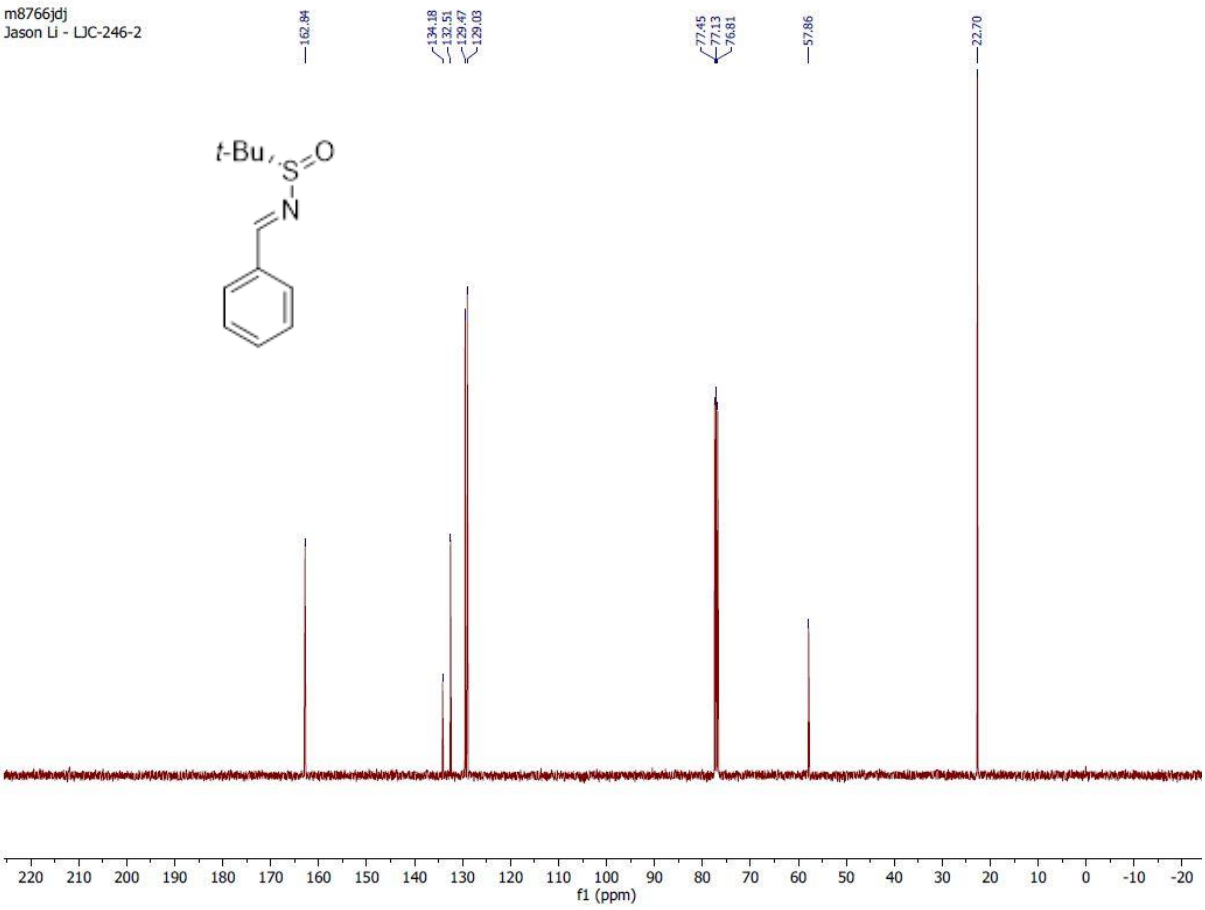

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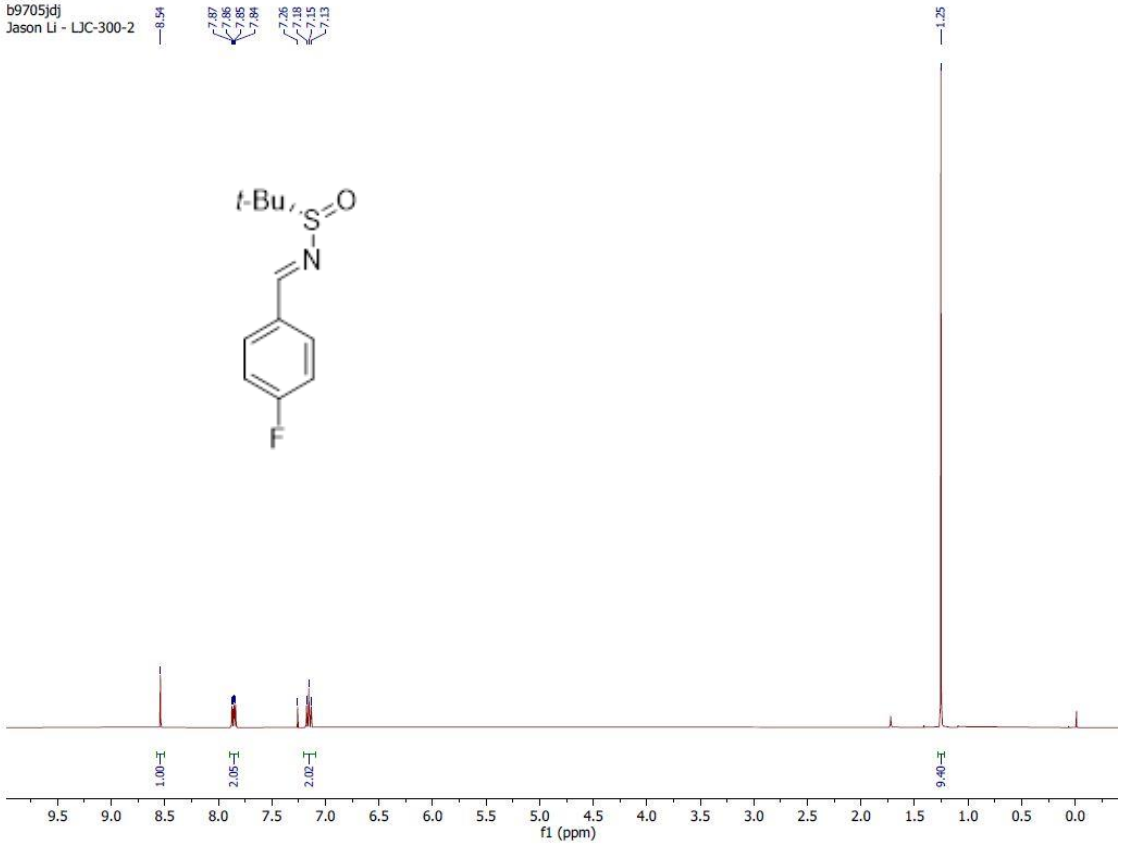
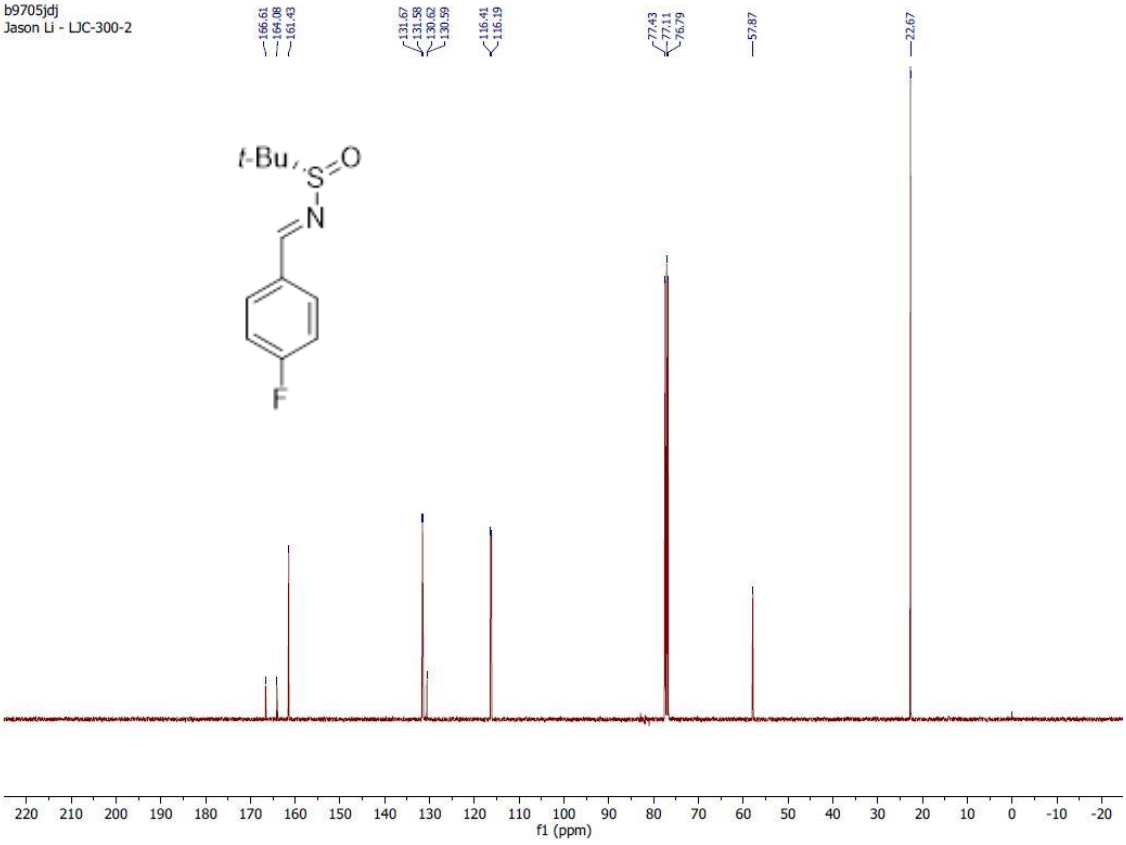
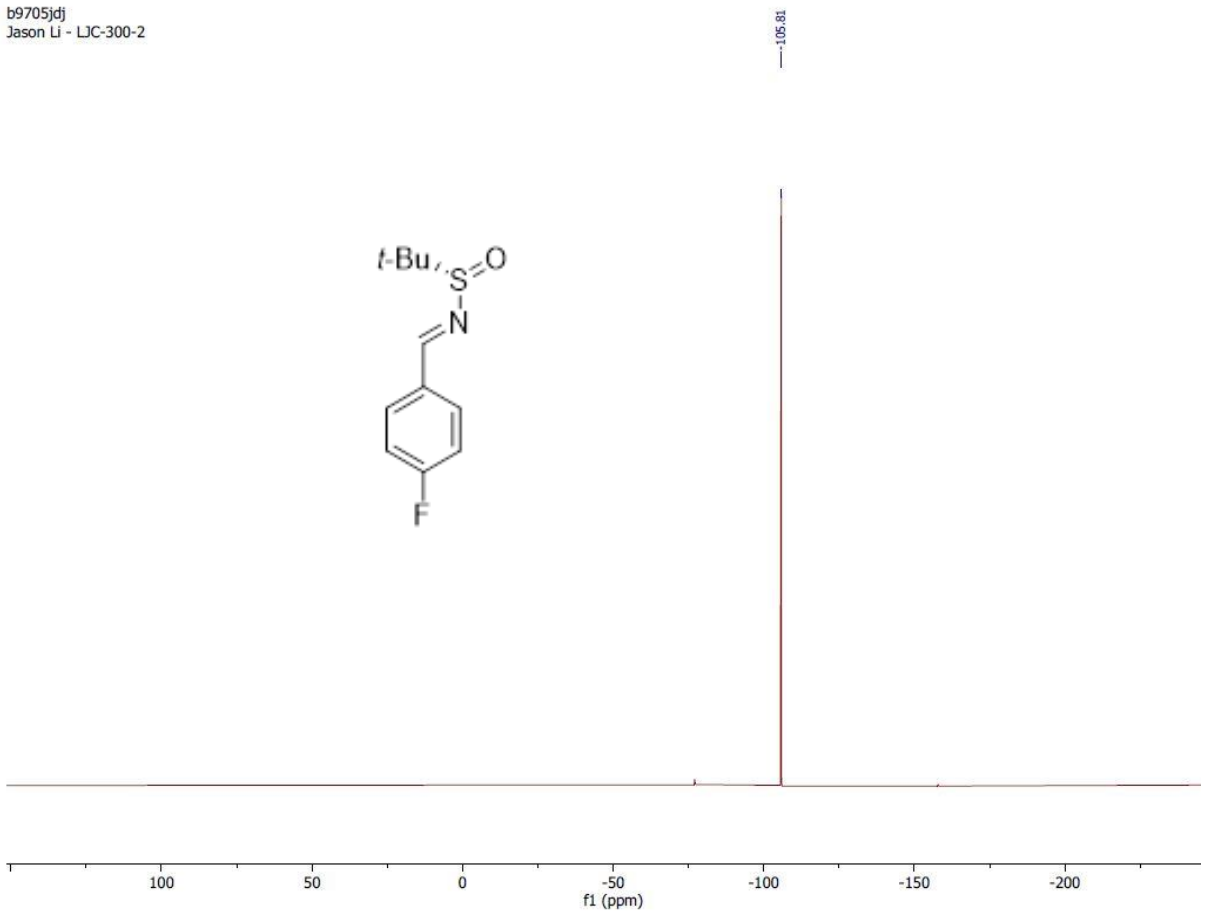
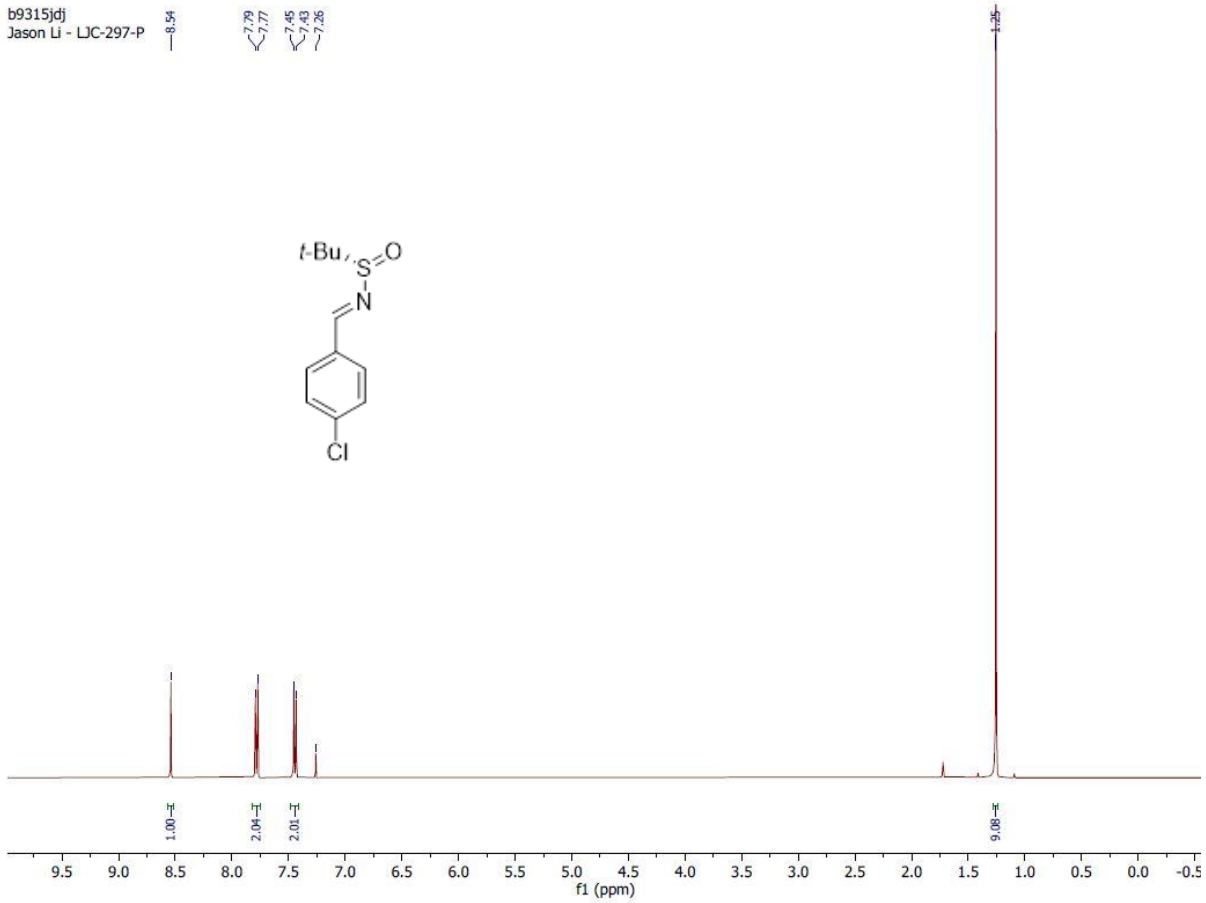
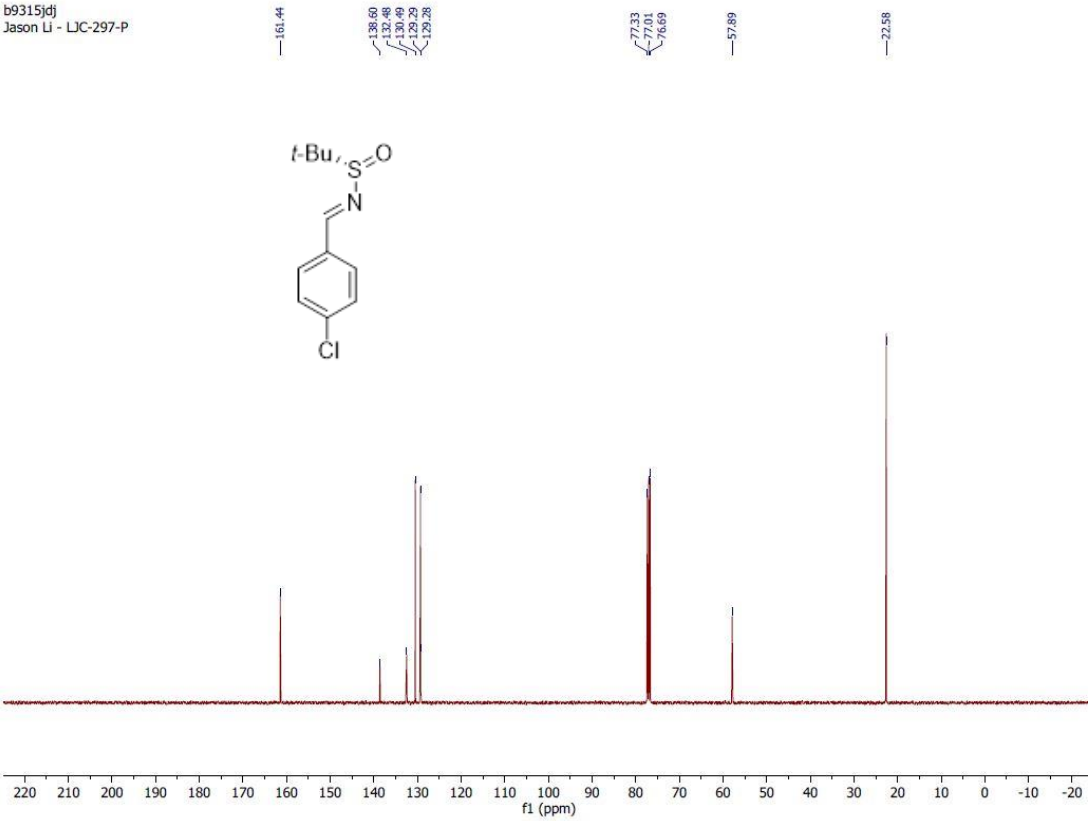





b9705jdj
Jason Li - LJC-300-2
-105.81
t-Bu
S
O
N
F
100
50
0
-50
-100
-150
-200
f1 (ppm)

Data for **(*S*)-13c**





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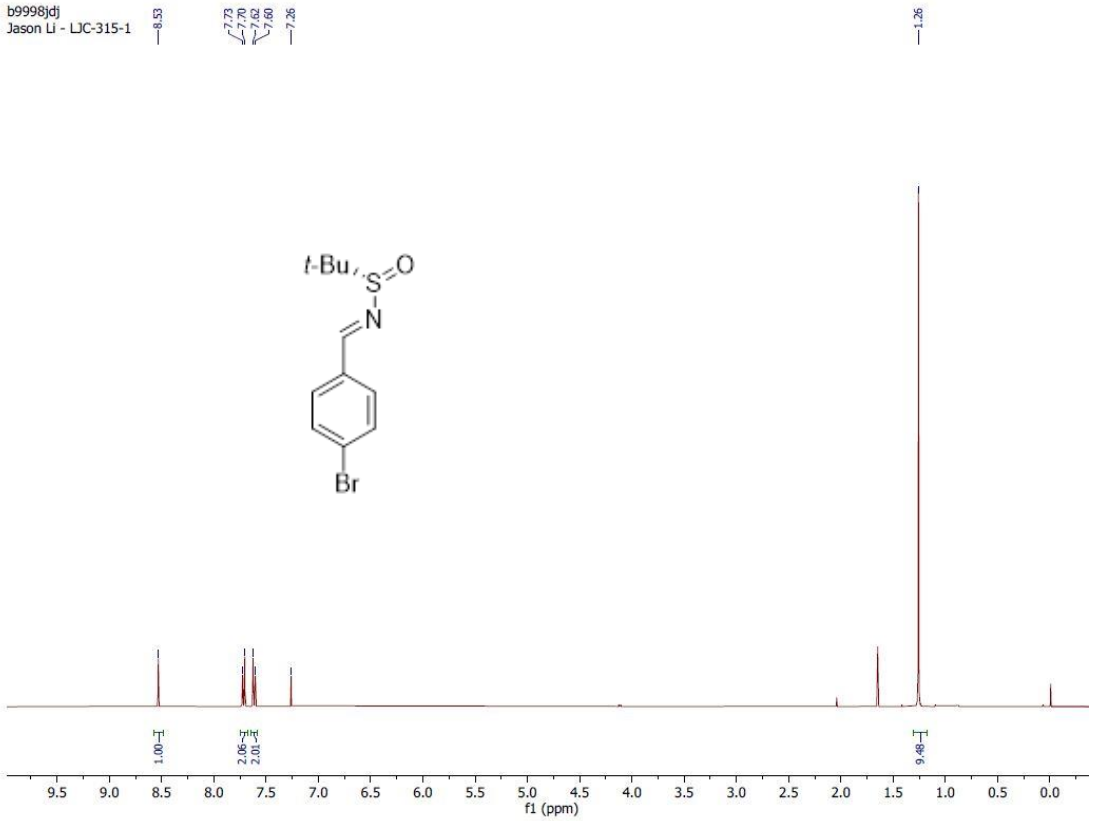

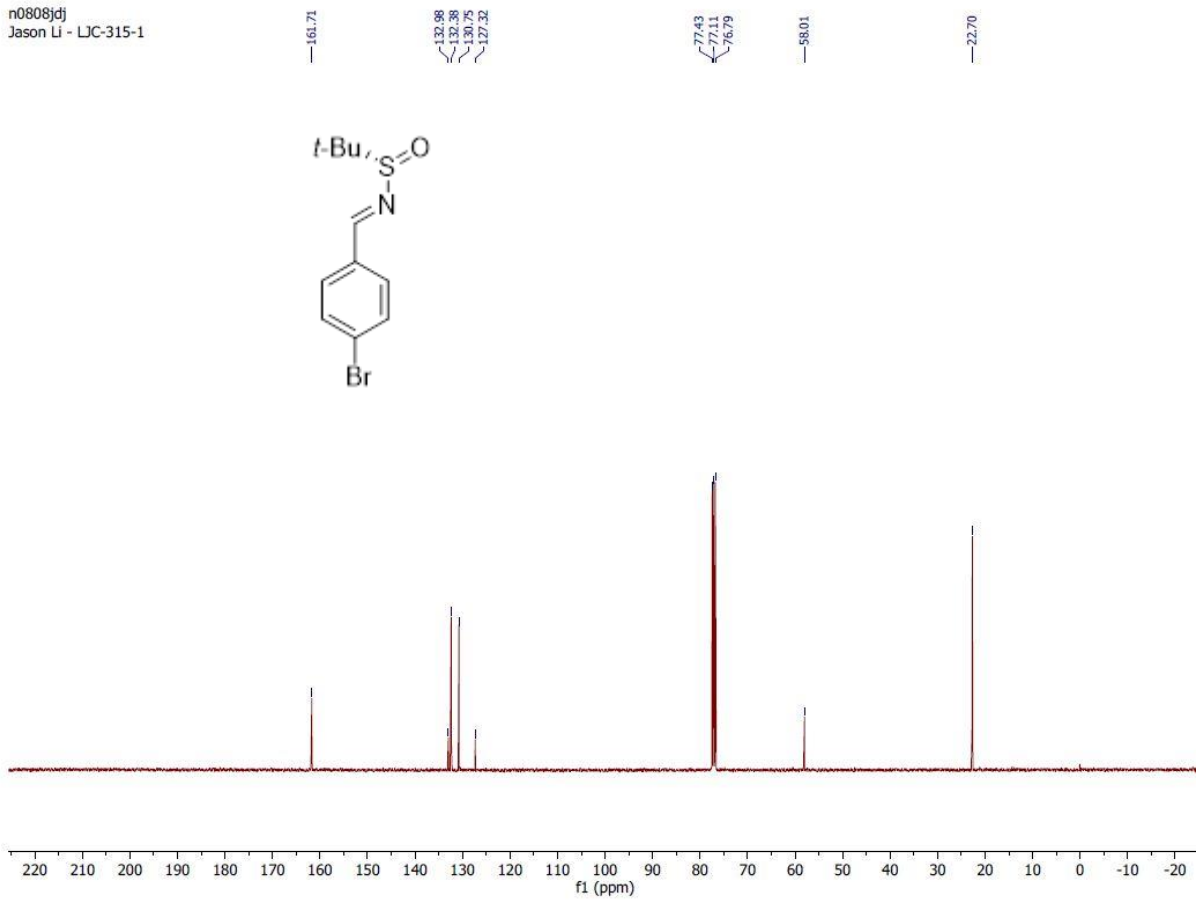

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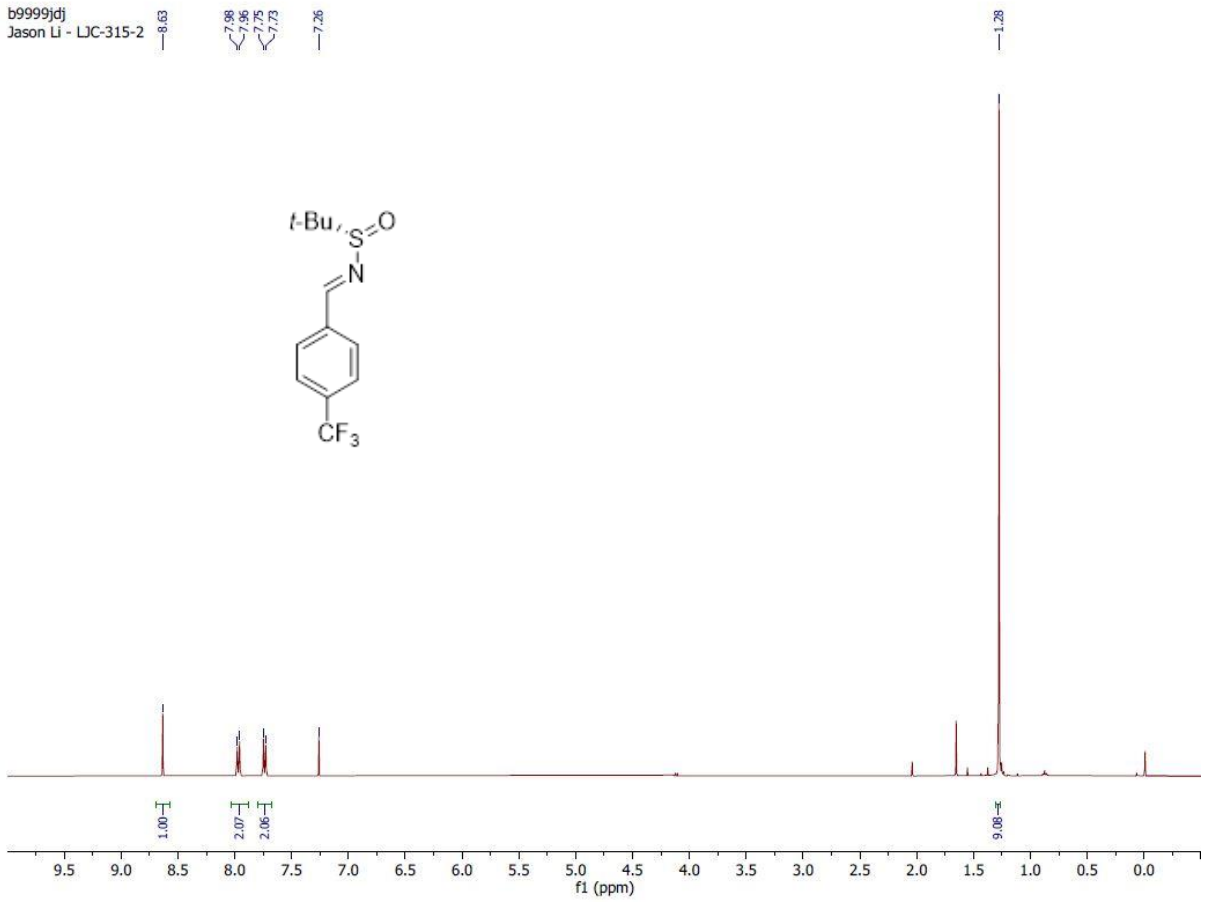
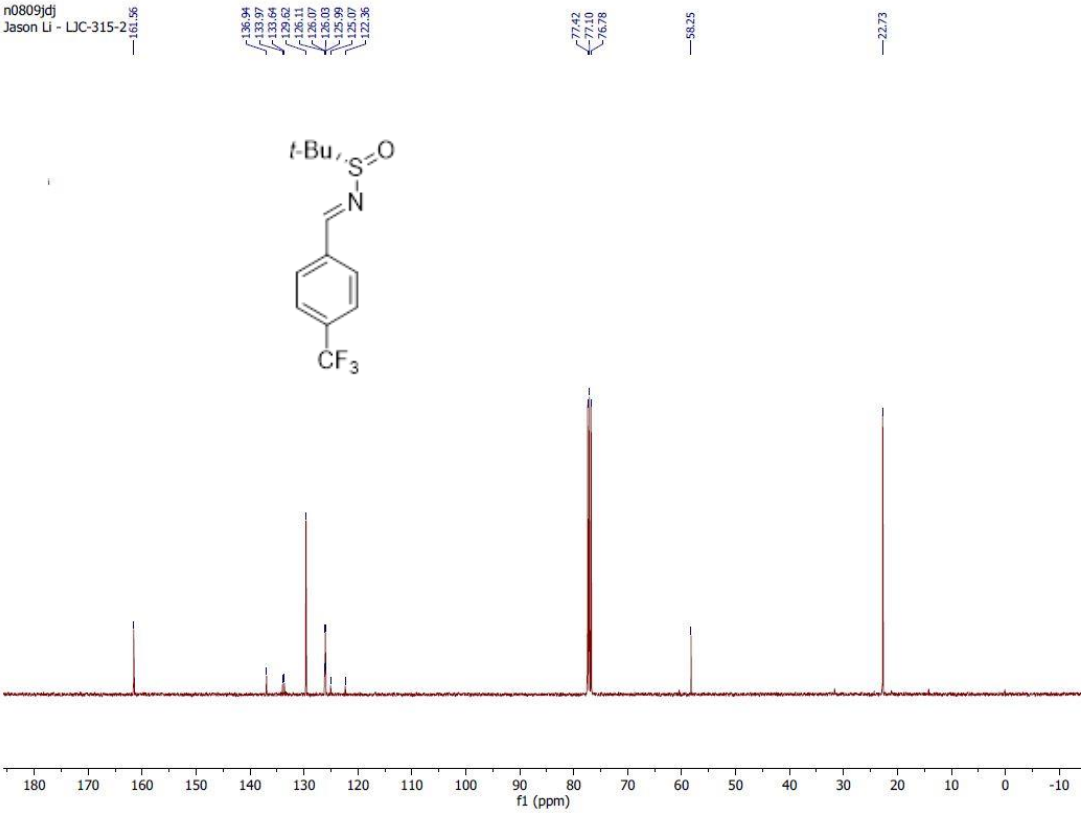
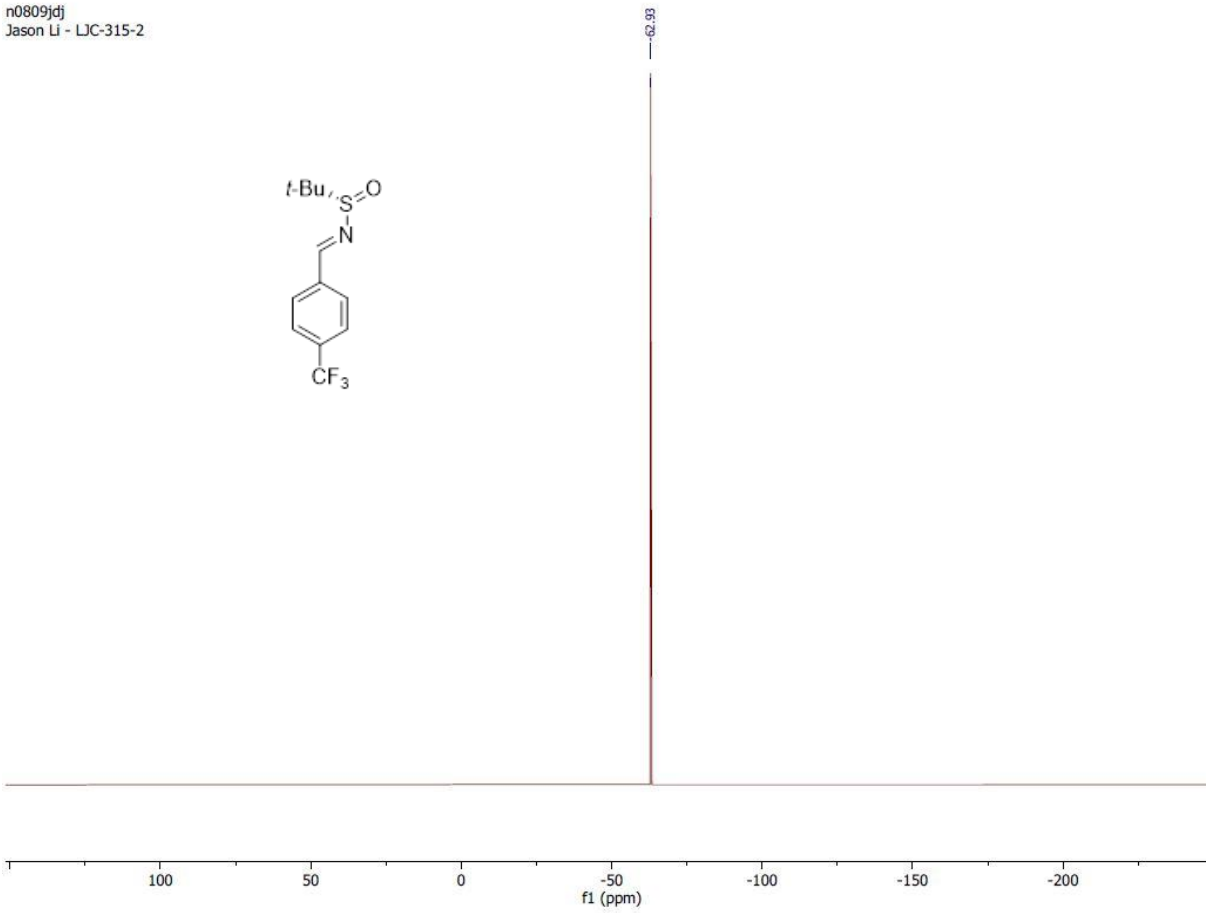
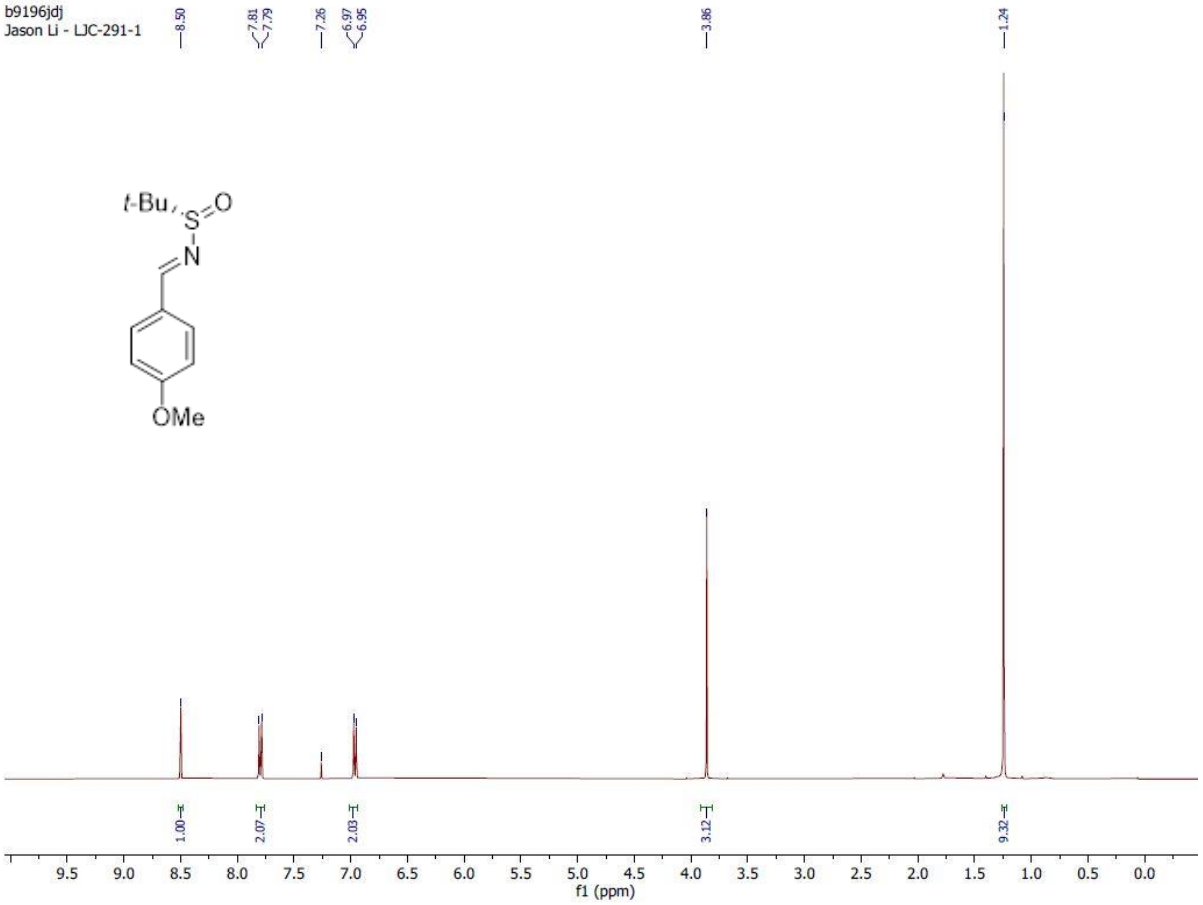
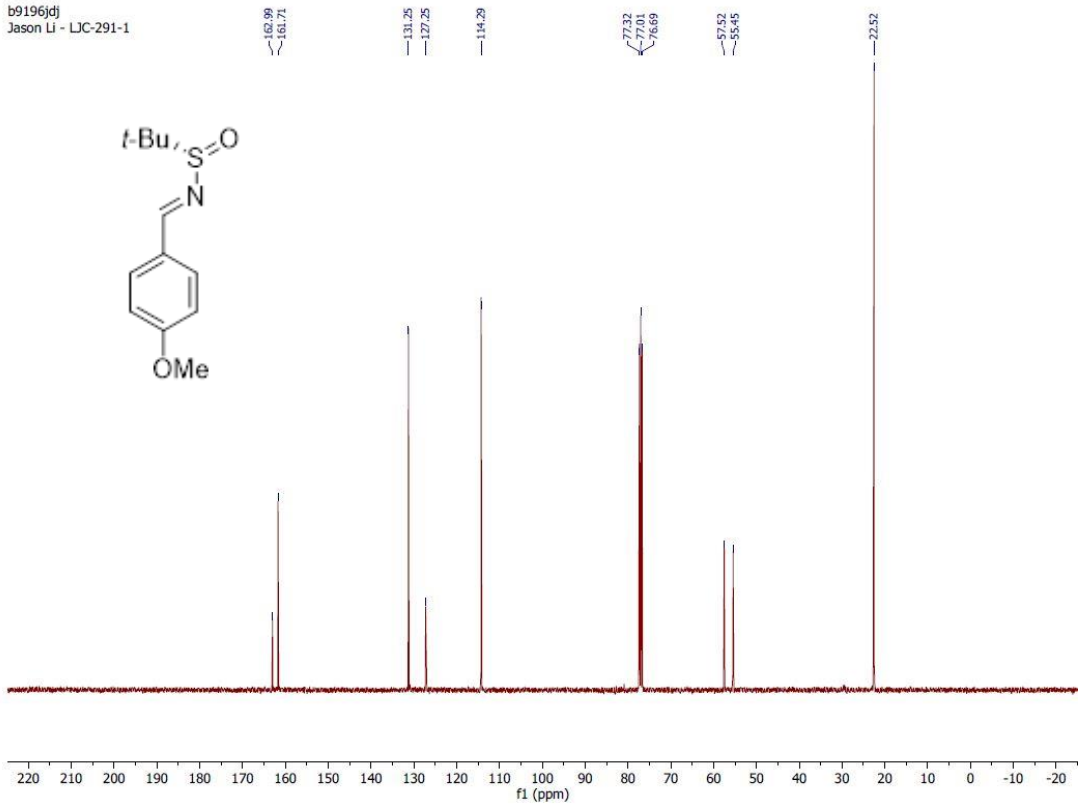





n0809jdj
Jason Li - LJC-315-2
-62.93
t-Bu
S
O
N
CF3
100
50
0
-50
-100
-150
-200
f1 (ppm)

Data for **(*S*)-13f**





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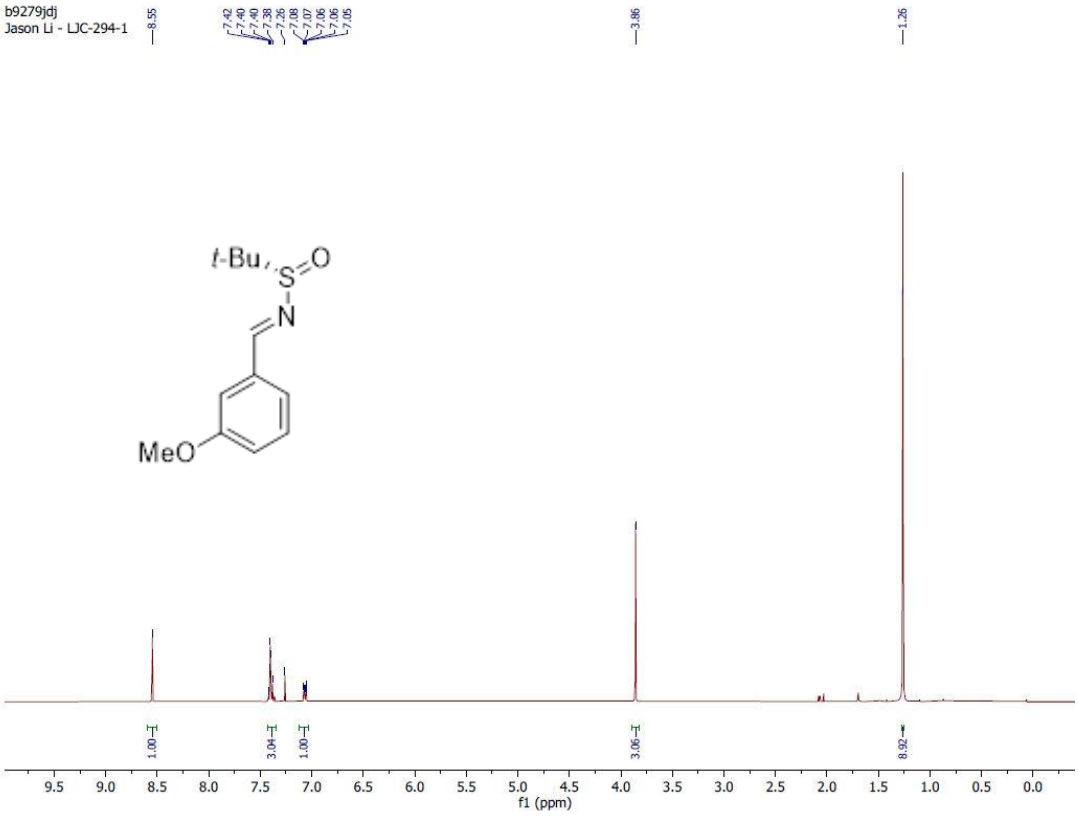

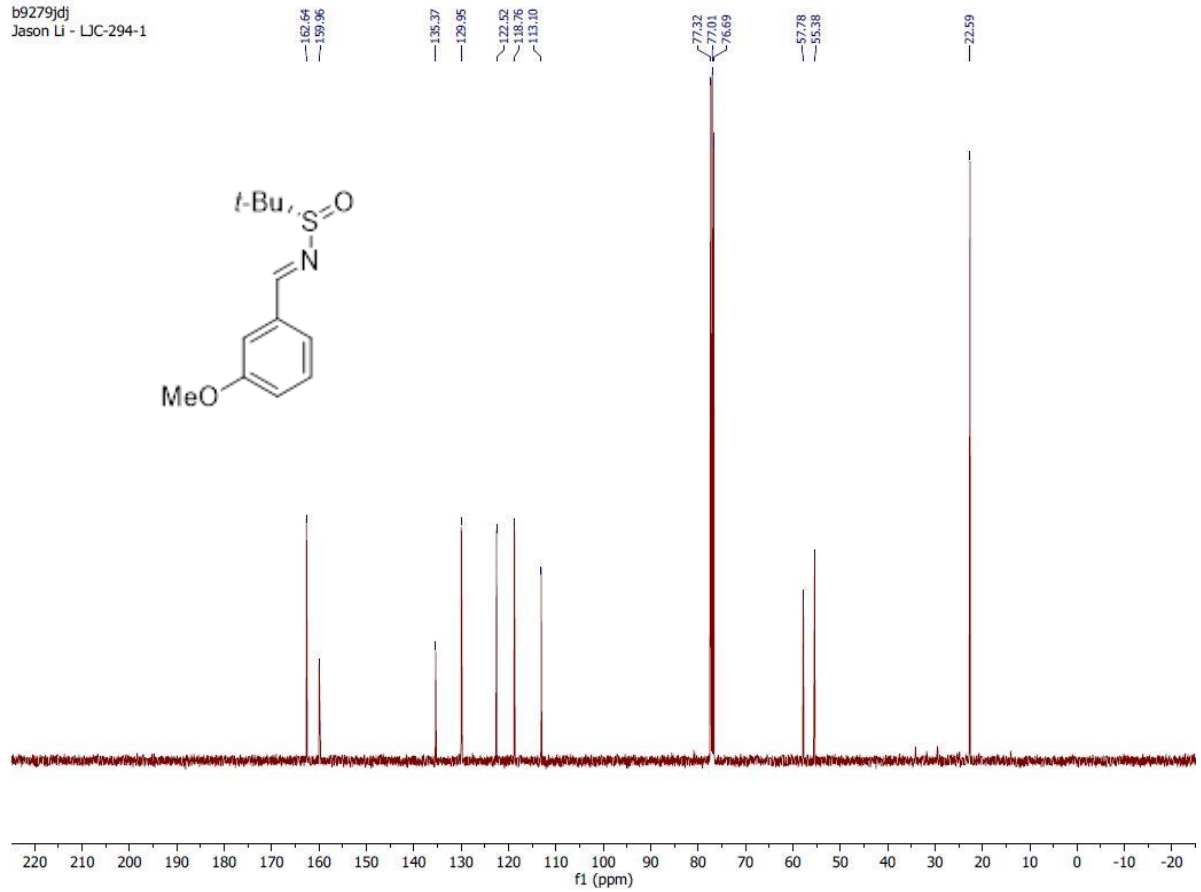

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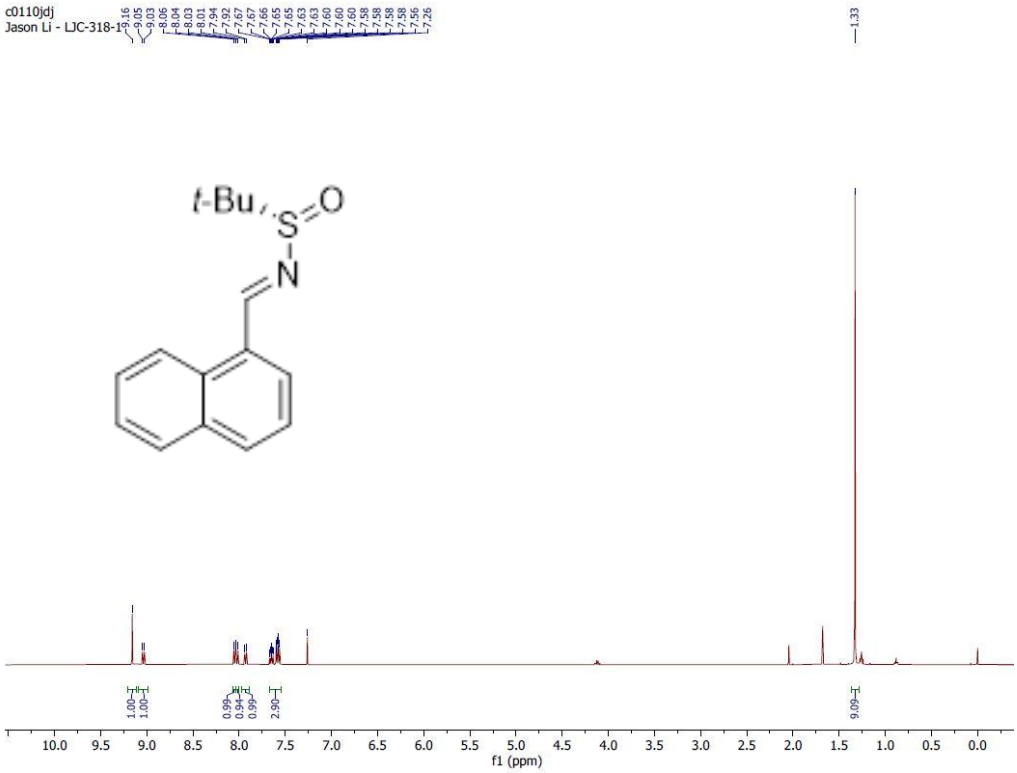

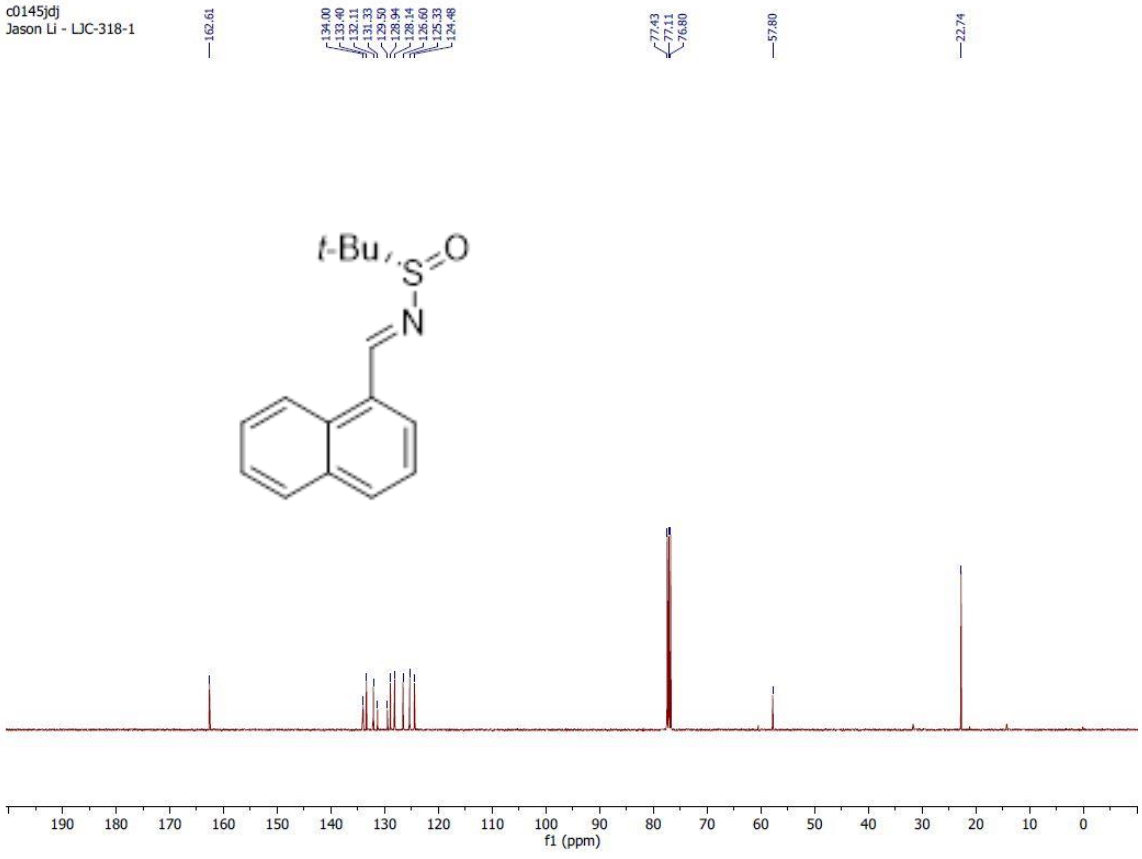

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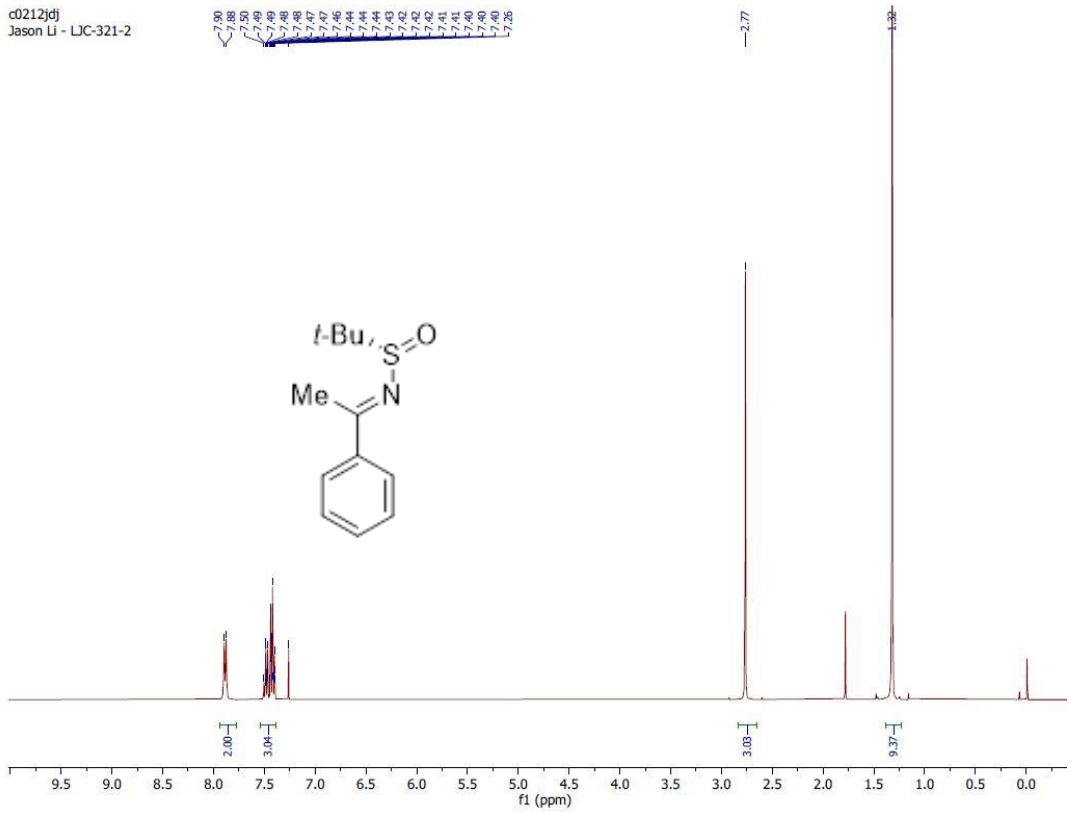

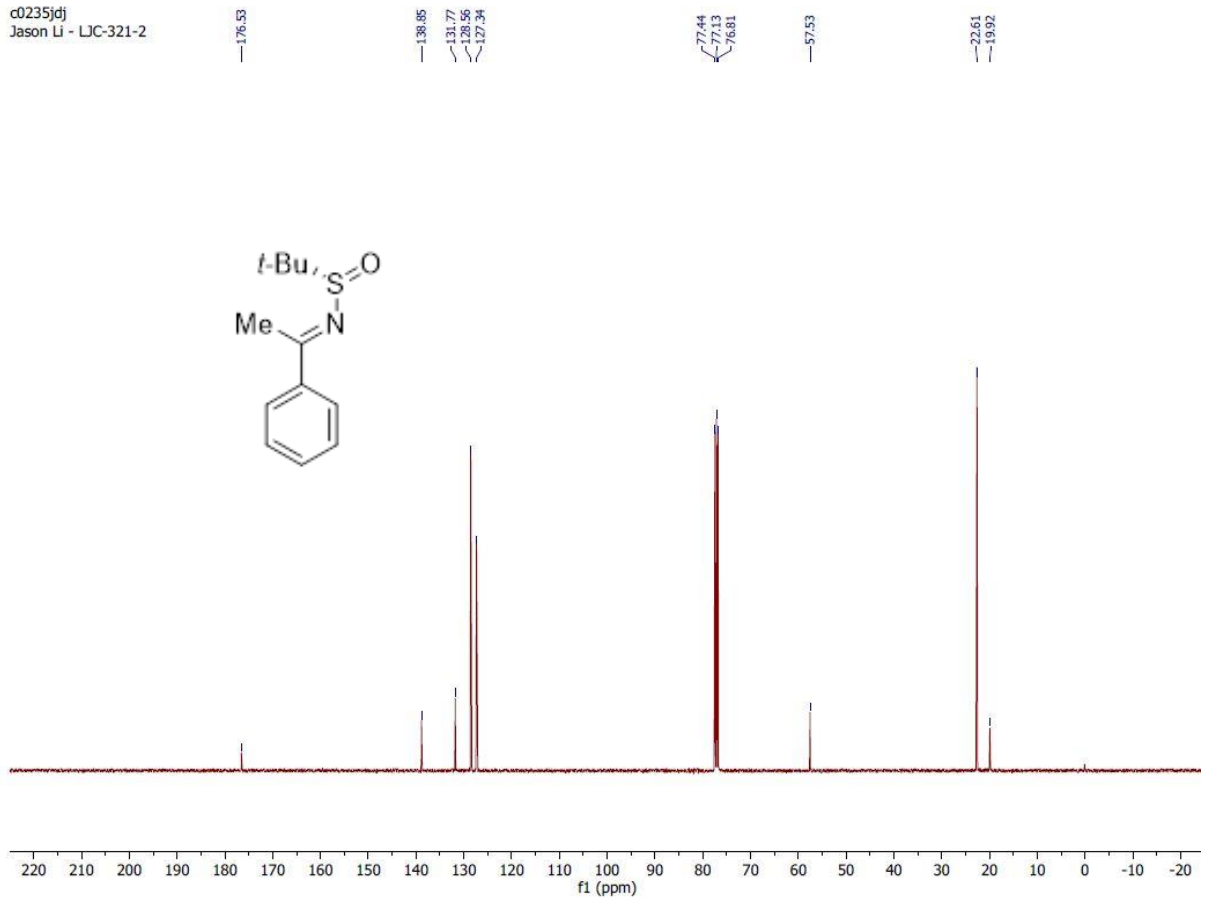

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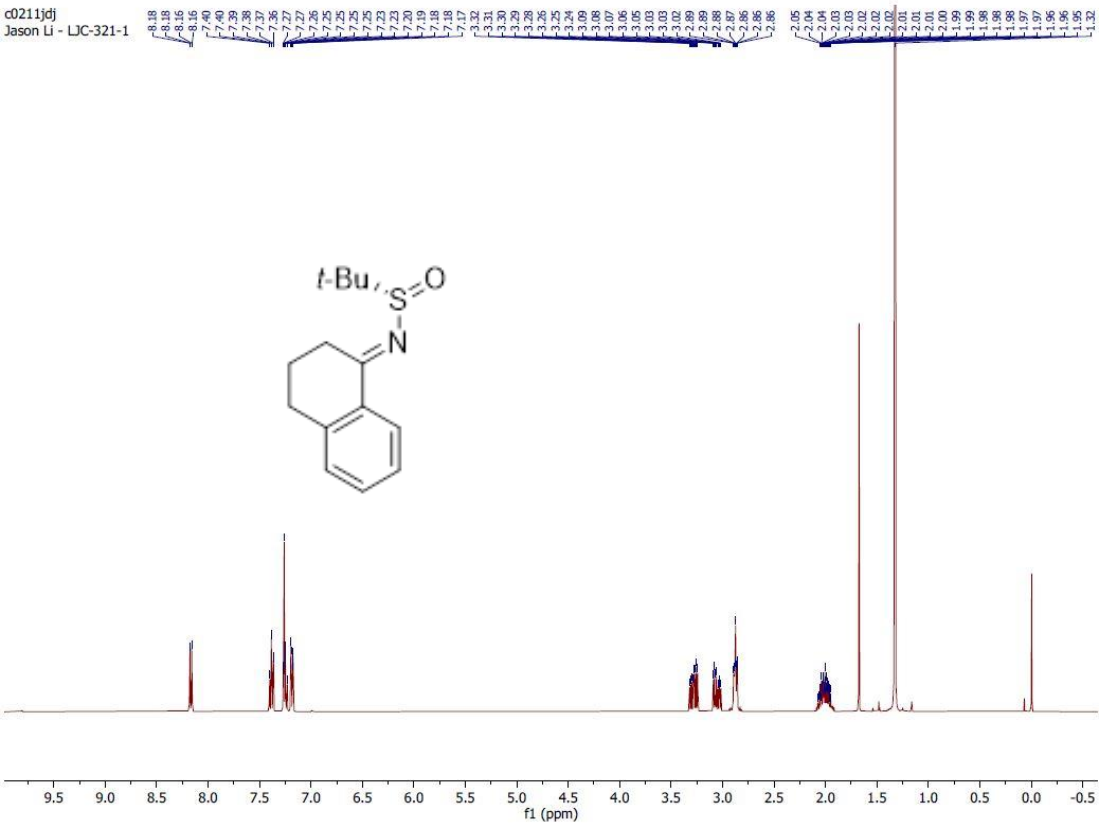

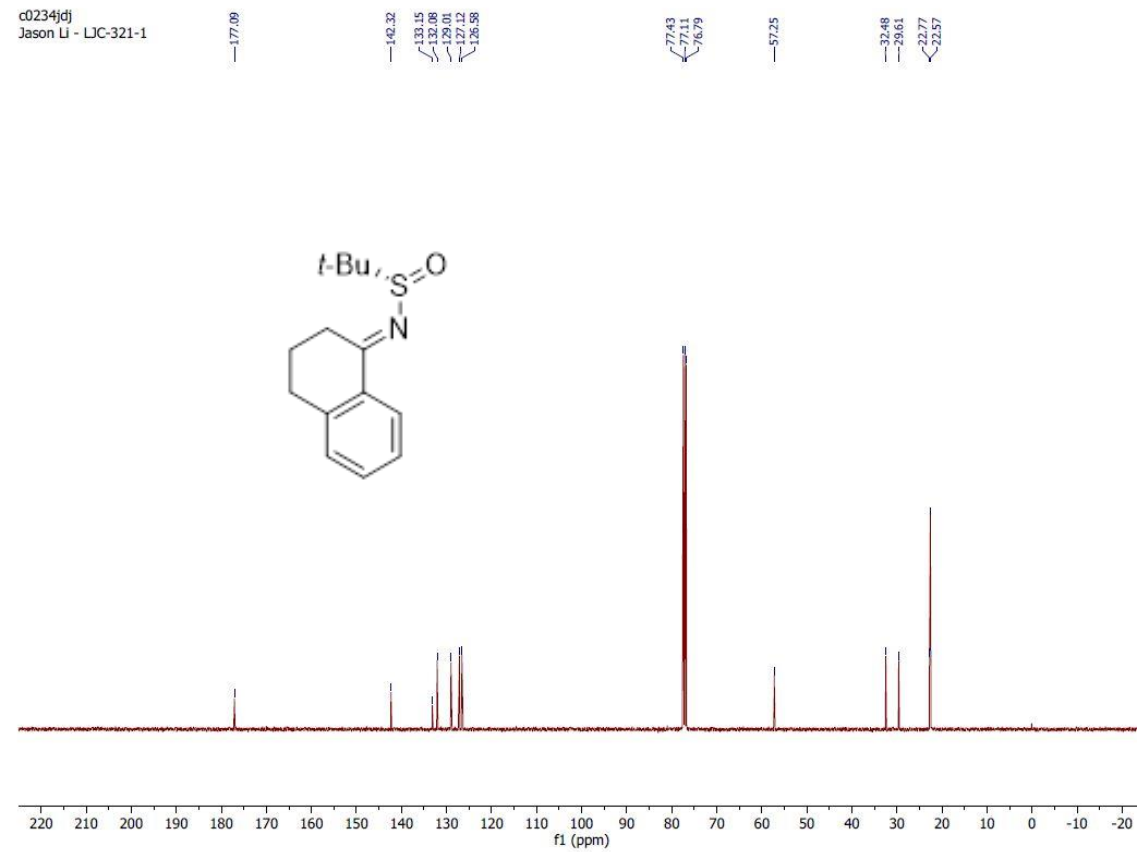

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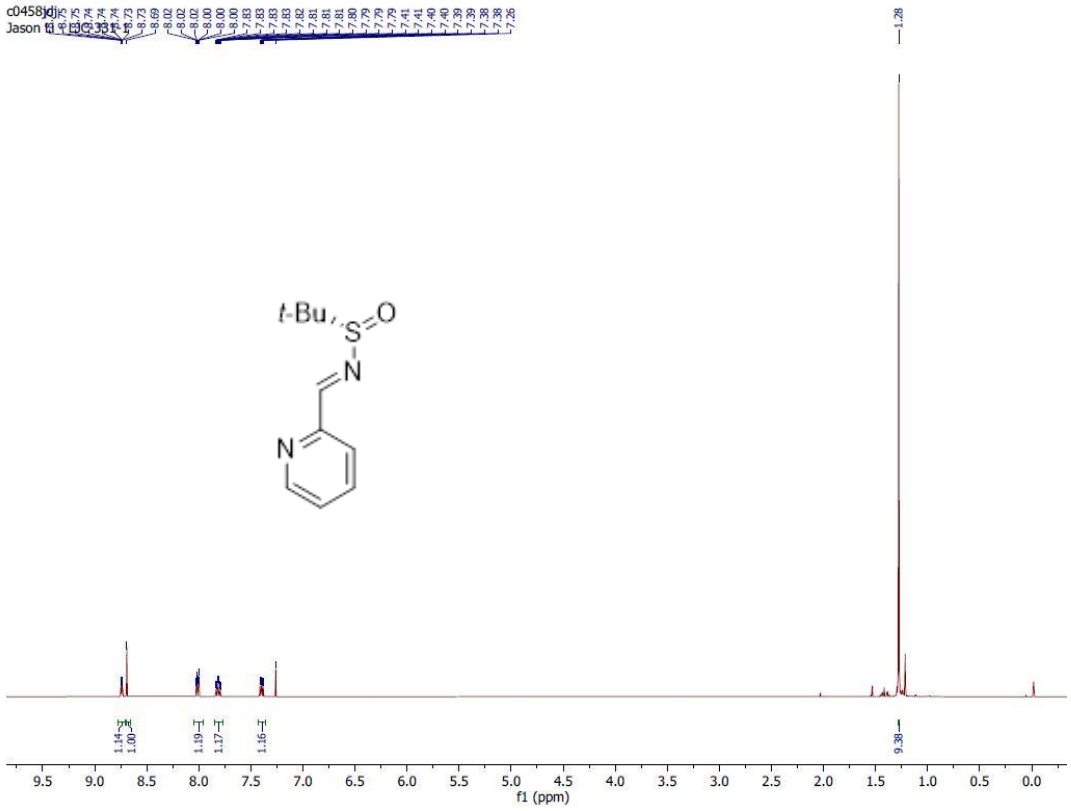

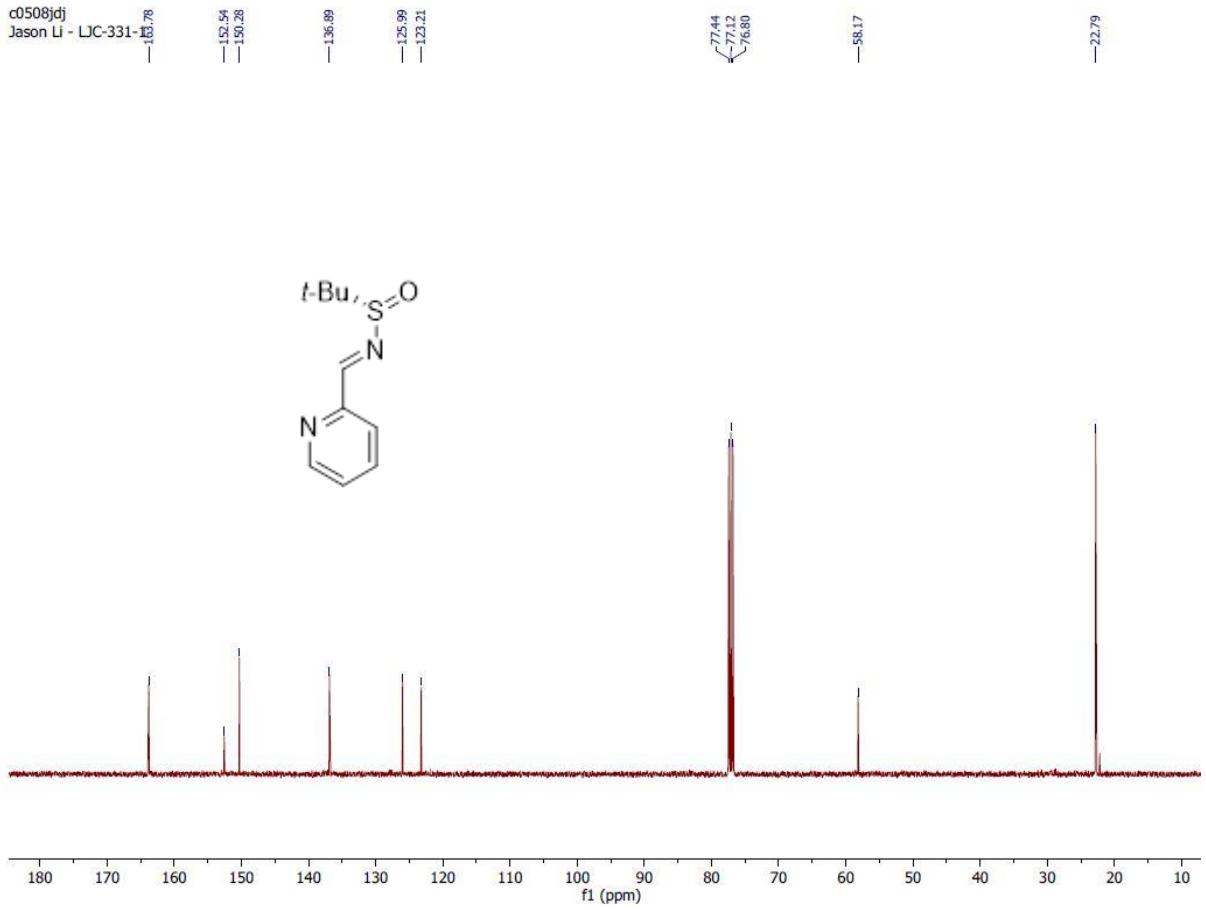

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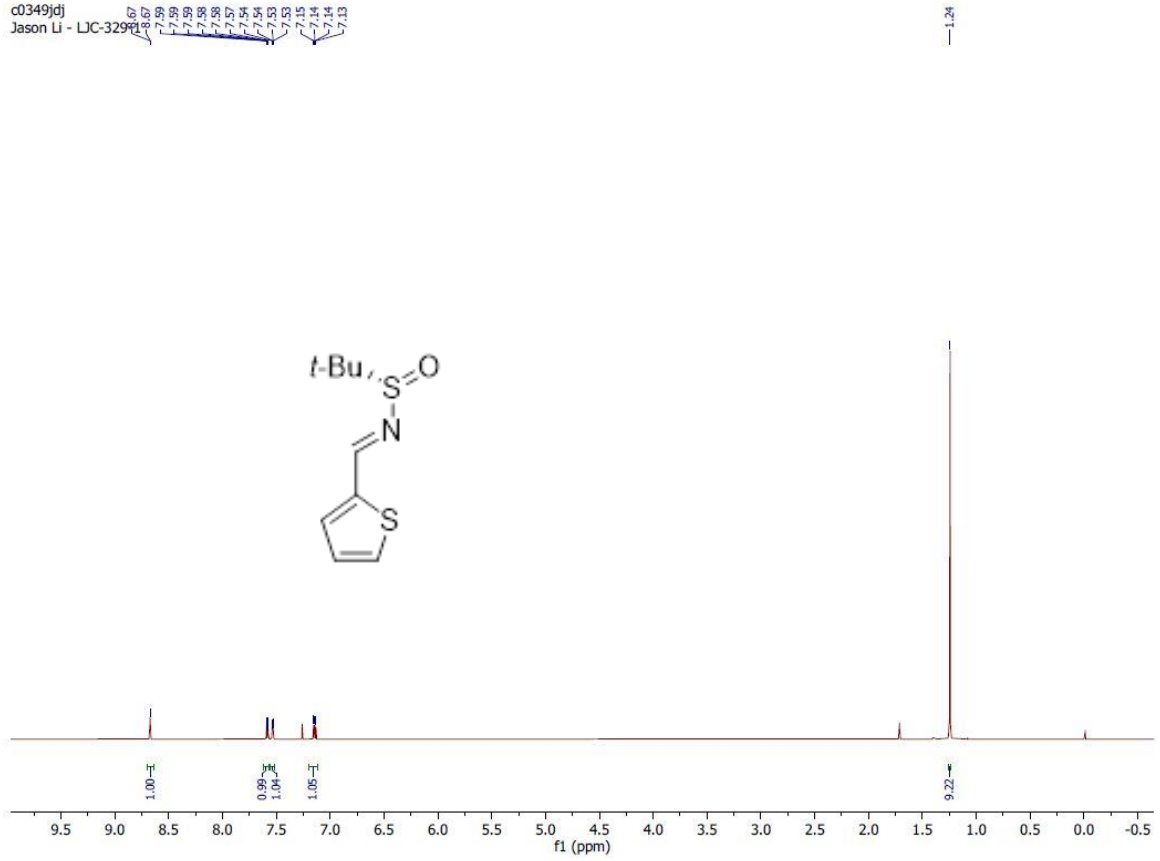

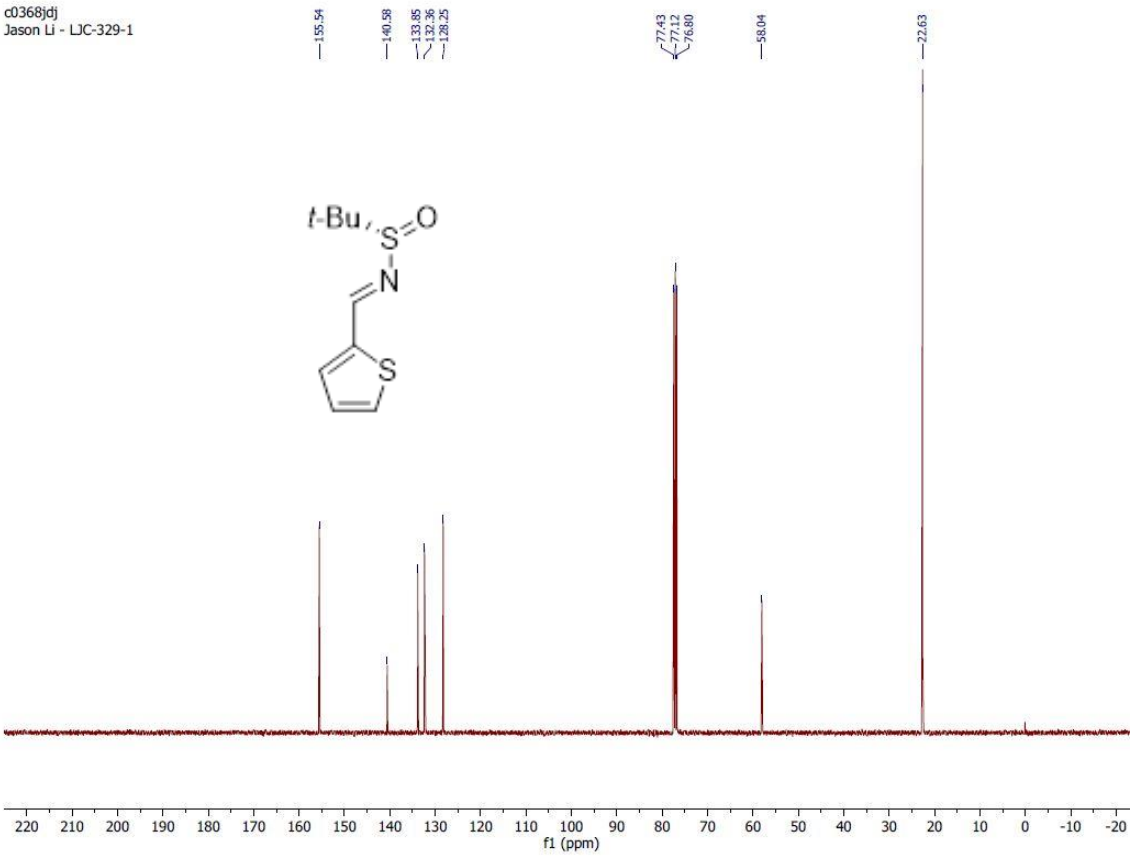

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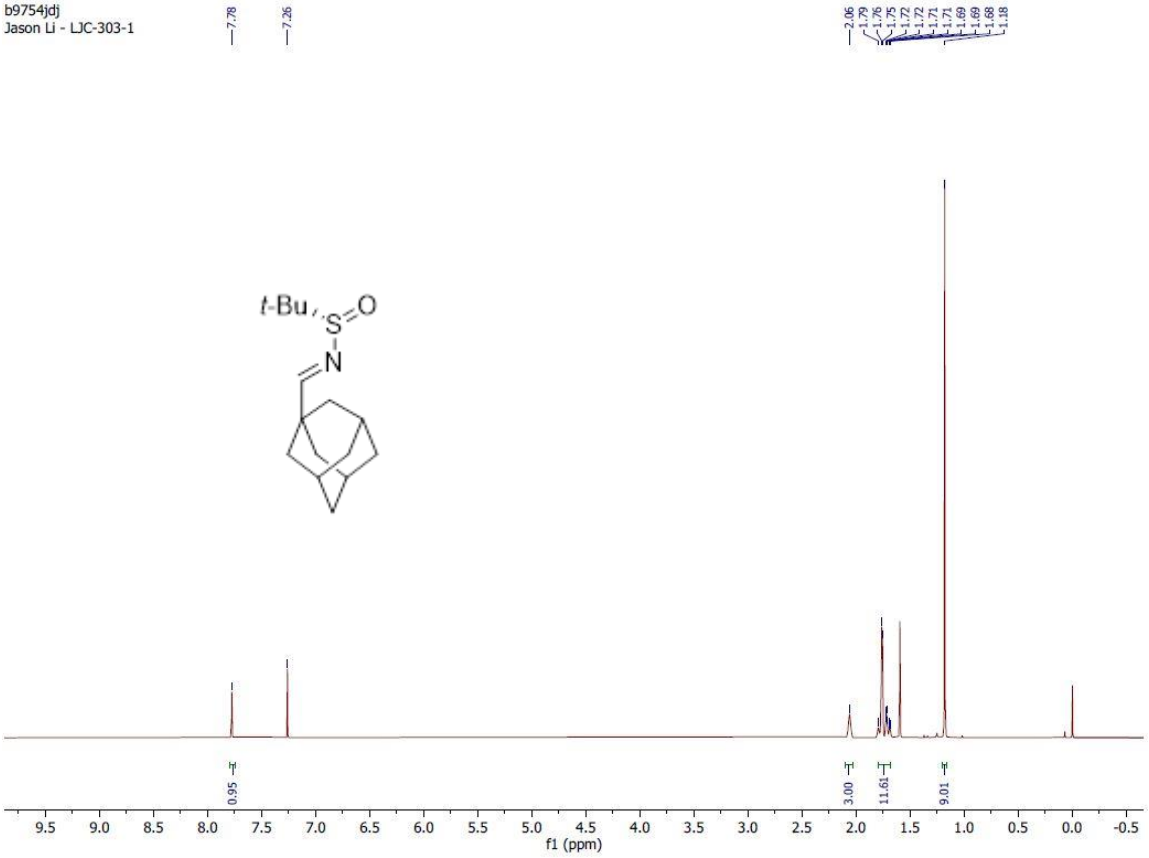
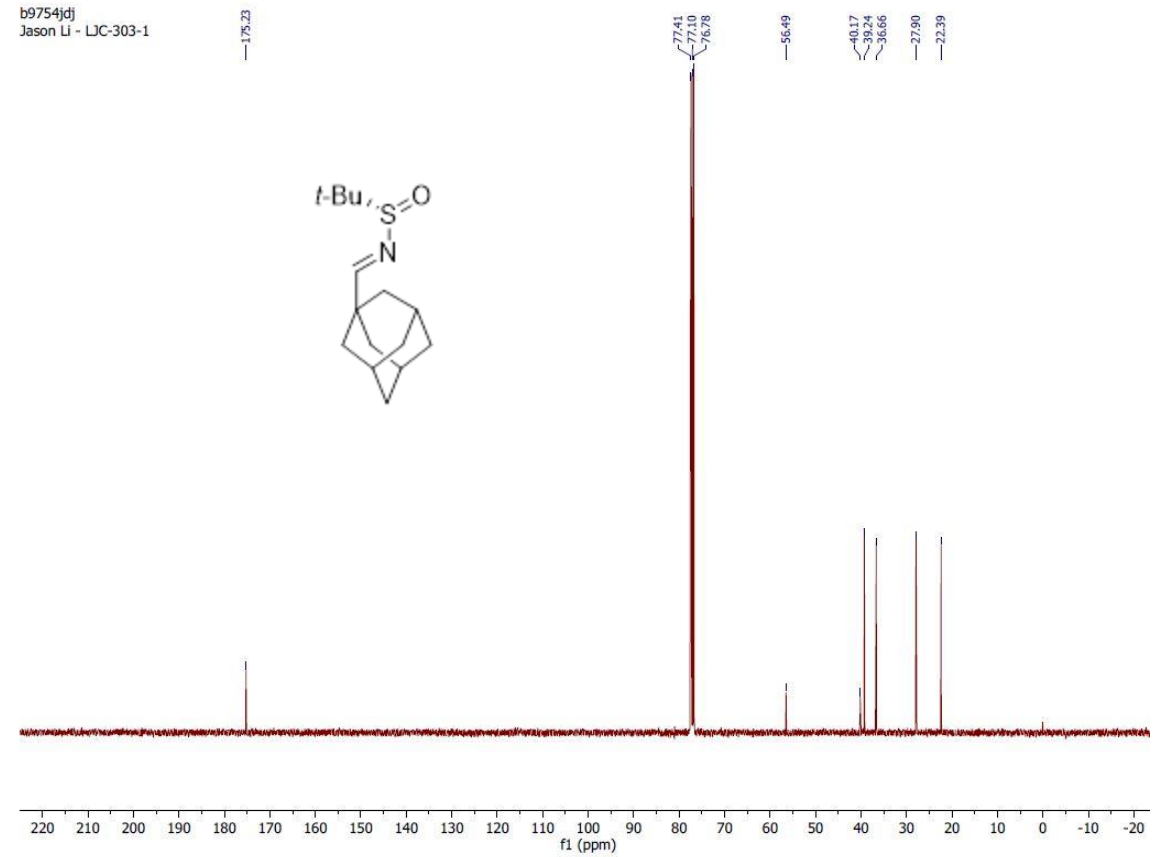
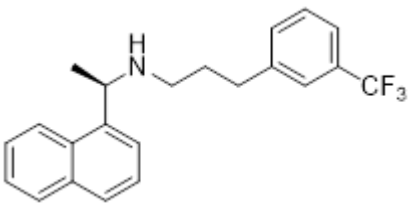
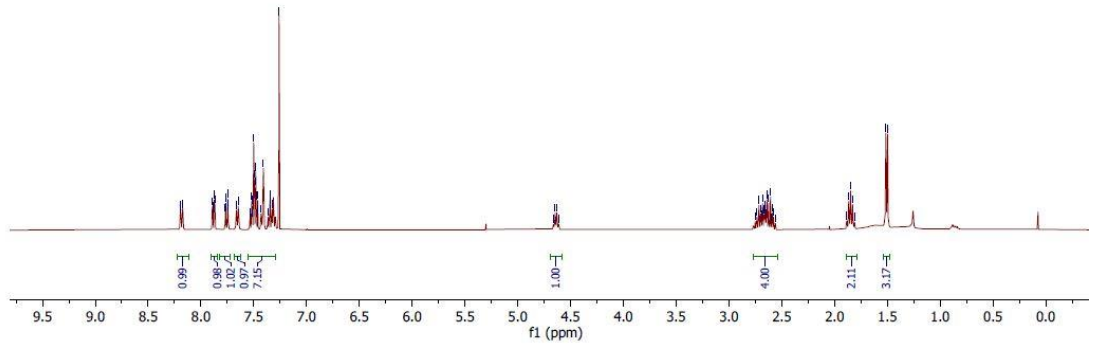


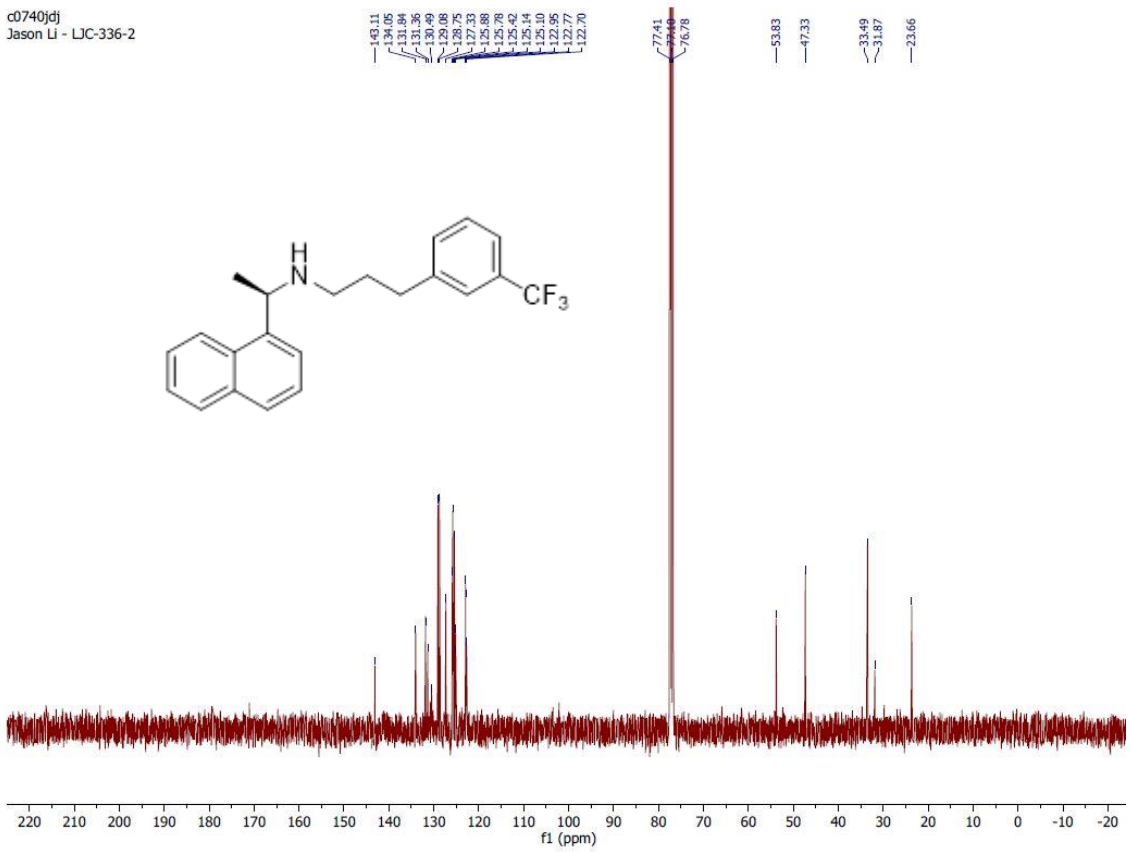


Data for **16**


c0715jdj
Jason Li - LJC-336-2

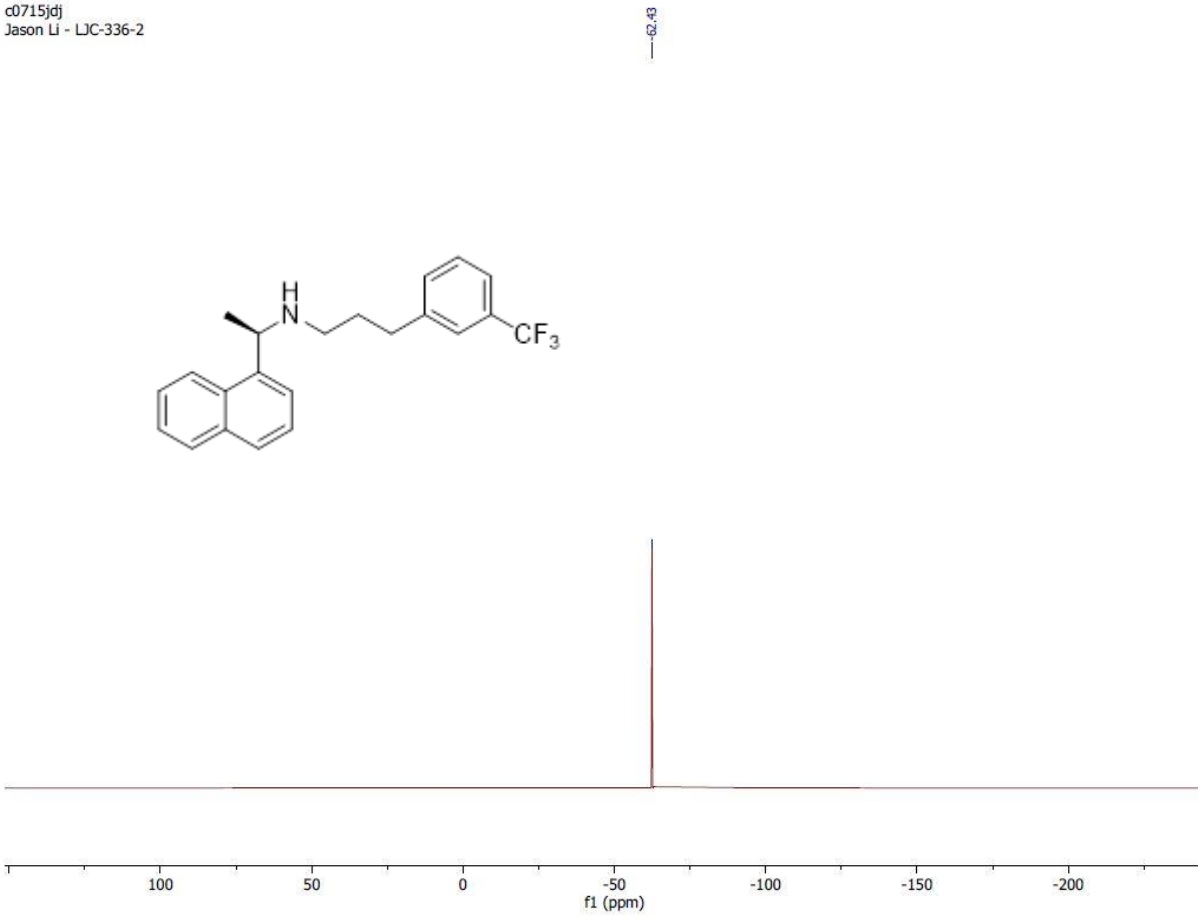

H
N
CF3


0.99
0.98
1.02
0.97
7.15
1.00
4.00
2.11
3.17
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


c0740jdj
Jason Li - LJC-336-2
143.11
134.05
131.84
131.36
130.49
129.08
128.75
127.33
125.88
125.78
125.42
125.14
125.10
122.95
122.77
122.70
77.41
77.16
76.78
53.83
47.33
33.49
31.87
23.66
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

H
N
CF3

c0715jdj
Jason Li - LJC-336-2



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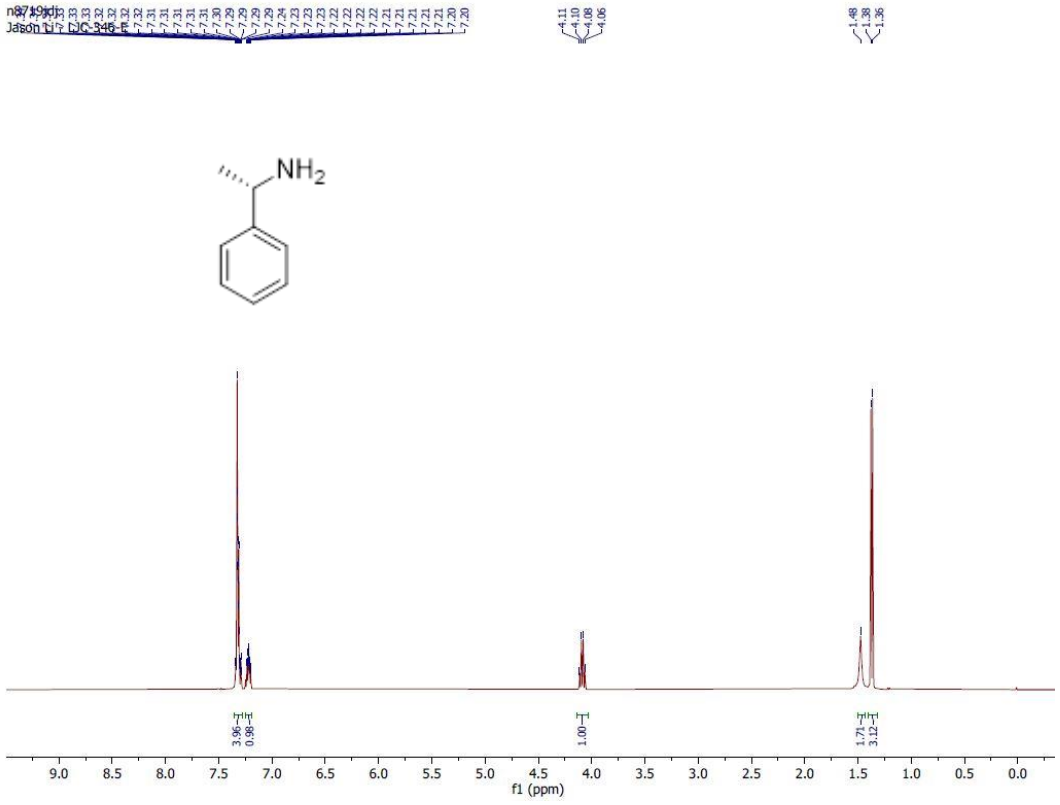
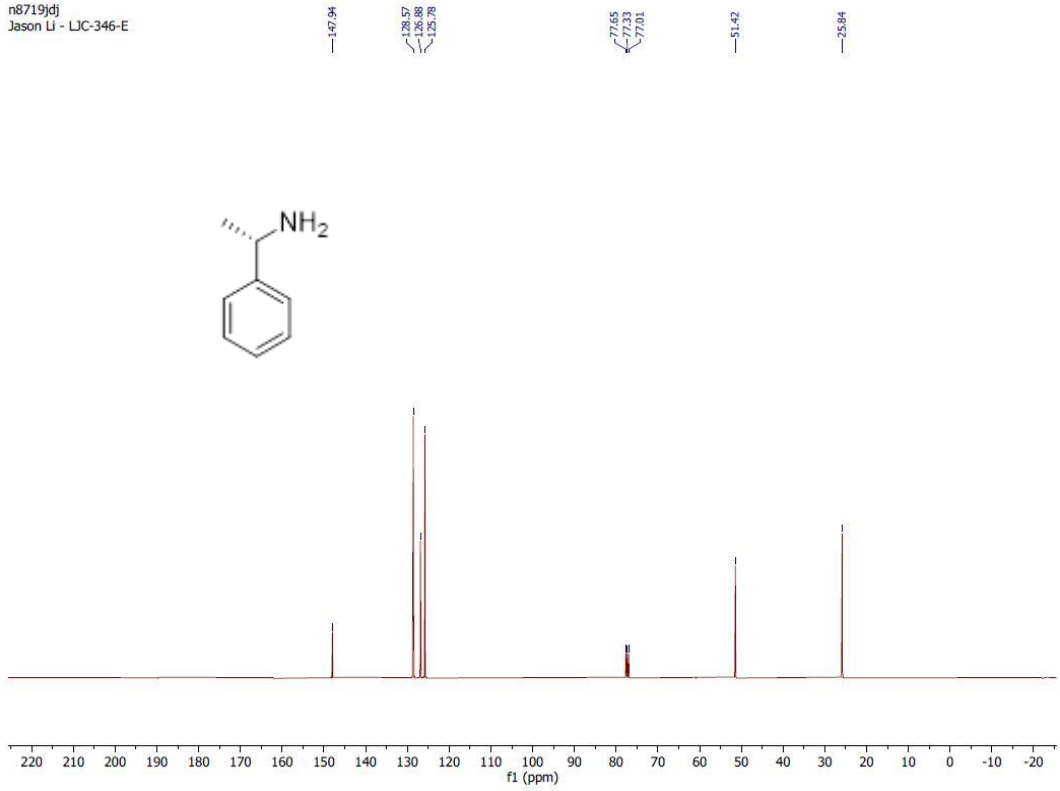

n8719jdj
Jason Li - LJC-346-E
NH2
3.96
0.98
1.00
1.71
3.12
f1 (ppm)


n8719jdj
Jason Li - LJC-346-E
147.94
128.57
126.88
125.78
77.65
77.33
77.01
51.42
25.84
NH2
f1 (ppm)

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