SUPPORTING INFORMATION

IODIDE-CATALYZED SYNTHESIS OF SECONDARY THIOCARBAMATES FROM ISOCYANIDES AND THIOSULFONATES.

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2 General information

Unless stated otherwise, all solvents and commercially available reagents were used as received. Heptane, which was used for flash chromatography, was distilled prior to use. Non-commercial starting materials were prepared as described below or according to literature procedures. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Advance 400 at ambient temperature using the deuterated solvent as internal standard (^{1}H: δ 2.50 ppm and ^{13}C[^{1}H]: δ 39.52 ppm for DMSO-d_6, ^{1}H: δ 7.26 ppm and ^{13}C[^{1}H]: δ 77.16 ppm for $CDCl_3$, ^{1}H: δ 5.98 ppm and ^{13}C[^{1}H]: δ 73.80 ppm for $C_2D_2Cl_4$). Chemical shifts (δ) are given in ppm and coupling constants (J) are quoted in hertz (Hz). Multiplicities are described as s (singlet), d (doublet), t (triplet), q (quartet), hp (heptuplet), m (multiplet), br (broad) or combinations thereof. ^{13}C-NMR spectra were recorded with complete proton decoupling. For high resolution mass-spectrometric analysis, samples were dissolved in MeOH or CH_3CN and diluted to a concentration of approximately 10^{-5} mol/L. 2 µL was injected using a CapLC system and electrosprayed through the nanoelectrospray source. The nanoelectrospray source was operated in positive ion mode at an electrospray potential of 1.7 kV. The eluent used was 30 % A (H_2O 0.1% formic acid) and 70 % B (CH_3CN/H_2O 95/5 0.1 % formic acid) at a flow rate of 6 µL/min. Samples were injected with an interval of 3 minutes. Before analysis and after each seventh sample a 2 µL volume of a 0.025 % H_3PO_4 solution (50/50 MeOH/H_2O) was injected and used as lock mass. The MS was calibrated prior to use with a 0.015 % H_3PO_4 solution. The spectra were lock mass corrected using the known mass of the nearest H_3PO_4 cluster. The X-band continuous wave electron paramagnetic resonance (CW EPR) experiments were performed on a Bruker E580 Elexsys spectrometer with a mw frequency of 9.6609 GHz. The EPR spectra were recorded with a modulation amplitude of 0.1 mT, a microwave power of 1.5 mW and a modulation frequency of 100 kHz. The solutions were inserted in a glass capillary to avoid spectrometer tuning problems at room temperature. Flash chromatography was performed either manual on SiO_2 (particle size 40-63 µm, pore diameter 60 Å) using the indicated eluent and visualized by UV detection (254 nm) or on an automated chromatography system (Biotage® / Combiflash®Rf) with on-line UV detection using Silica Flash Cartridges (40g, Grace®).

3 Reaction Optimization

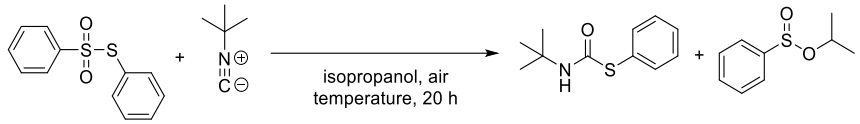
3.1 General procedure

A 10 mL round-bottom flask was charged with *S*-phenyl benzenethiosulfonate (**1a**, 125 mg, 0.5 mmol), *tert*-butylisocyanide (**2a**), isopropanol (0.5 mL) and additive. The flask was equipped with a reflux condenser and the reaction mixture was stirred for the indicated time and temperature under air atmosphere. The mixture was concentrated and dried under vacuum. 1,3,5-Trimethoxybenzene was added, as internal standard, and everything was dissolved in $CDCl_3$. Subsequently, a ^{1}H-NMR was recorded and signals were integrated versus the internal standard.

3.2 A new route towards thiocarbamates

The synthesis of *S*-phenyl *tert*-butylthiocarbamate (**3a**) from *S*-phenyl benzenethiosulfonate (**1a**) and *tert*-butyl isocyanide (**2a**) was chosen as test system for the optimization and the general procedure was applied. After some initial screening, we were pleased to observe a high yield of **3a** when isopropanol was used as solvent (Table S1, entry 1). Besides **3a**, isopropyl benzenesulfinate (**4a**) was also formed, indicating that the solvent is also acting as a reagent. Subsequently, the ratio between reagents **1a** and **2a** was altered (entries 1-4). Entry 4 indicates that the yield reduces when 1.2 equivalents of *tert*-butyl isocyanide (**2a**) was used at 75°C. Pleasingly, with this **2a** loading the temperature could be reduced to 30 °C (entries 4, 8 and 9). Unexpectedly, a yield reduction of around 31% arose when two different batches (A and B) of **1a** were used at 30°C and 1.5 equivalents of **2a** (entries 5-6). A similar trend was also observed with 1.2 equivalents of **2a** (entries 7-8).

Table S1: Effect of 1a/2a ratio, temperature and method used to prepare 1a.[a]



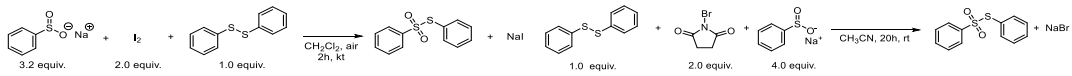
1a **2a** **3a** **4a**

entry	ELN code	batch **1a**	**2a** (equiv.)	temperature (°C)	yield **3a** (%)[b]	yield **4a** (%)[b]
1	PMSA624	A	2.5	75	84	96
2	PMSA630	A	2.0	75	86	96
3	PMSA626	A	1.5	75	89	93
4	PMSA629	A	1.2	75	71	78
5	PMSA637	A	1.5	30	78	84
6	PMSA895	B	1.5	30	47	45
7	PMSA939	B	1.2	30	48	51
8	PMSA944	A	1.2	30	66	66
9	PMSA942	A[c]	1.2	30	47	51
10	PMSA940	B[d]	1.2	30	94	93

[a] *Reaction conditions*: *S*-phenyl benzenethiosulfonate (**1a,** 125 mg, 0.5 mmol, 1.0 equiv), *tert*-butyl isocyanide (**2a,** y equiv), isopropanol (0.5 mL, 13 equiv), temperature (x °C), 20 h, air. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] Batch A was purified by flash chromatography prior to use. [d] 10 mol % of NaI was added.

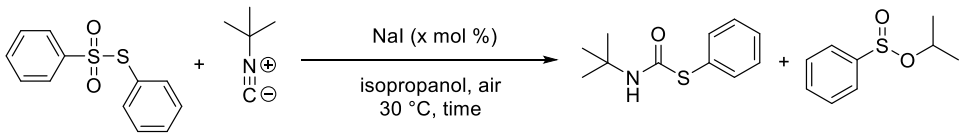
We subsequently had a closer look into the preparation of these batches (Table S2). Batch A was made by the I_2 method (Fujiki method)[1] and batch B by the NBS-mediated transformation (Wu method) (Table S2).[2] We reasoned that during the workup of batch A the washing with water might not have been sufficient to remove all the NaI present, which is formed by the reduction of I_2 with $Na_2S_2O_3$. As no column chromatography was required for purification of **1a** via the iodine method, NaI presumably remained in this batch. When **1a** was prepared via the NBS-method, NaBr is formed. As with the Wu method flash chromatography is used for the purification of **1a** no inorganic salt remains in batch B. The difference in yield might therefore be due to the difference in the concentration of NaI acting as a catalyst (Table S1, entries 5, 6 and 7, 8). If this hypothesis is true, then adding NaI should promote the coupling between **1a** and **2a**. When **1a** prepared by the NBS-method (batch B) (salt free) was used and a reaction with and without addition of 10 mol % NaI were compared at 30°C, the yield doubled, 48% to 94% (Table S1, entries 7 and 10). Performing the experiment with a batch of **1a**, prepared by the Fujiki method but additionally purified by column chromatography, also gave 47% **3a** (Table S1, entry 9). These experiments prove that NaI acts as a catalyst in the coupling of **1a** and **2a**. Further optimization was therefore performed in the presence of this additive.

Table S2: Methods used to prepare *S*-phenyl benzenethiosulfonate (1a)

method	Fujiki method[1]	Wu method[2]
Batch thiosulfonate	A	B
Reaction scheme		
Work-up	1) Reduction iodine to iodide with $Na_2S_2O_3$ 2) Washing with water 3) Extraction water layer with EtOAc (3x) 4) Drying organic layer with MgSO4	1) Removal of CH_3CN 2) Redissolve in EtOAc, washing with water 3) Extraction water layer with EtOAc (3x) 4) Drying organic layer with MgSO4 5) Column chromatography

Because of the importance of NaI in the reaction, thiosulfonate **1a** prepared by the Wu method (Table S2) was used in further experiments.[2] The catalyst loading could be lowered to 5 mol % without loss in yield with 1.5 equivalents **2a** (Table S3, entries 1 and 3). With this NaI loading the reaction time could be reduced to 4 hours and the isocyanide excess to 1.2 equivalents (entries 4-7). Further lowering of the catalyst loading diminished the yield so the optimal amount of NaI is 5 mol % (entries 5, 8-9). A blanc reaction omitting the catalyst under the reaction conditions of entry 5 revealed that *S*-phenyl *tert*-butylthiocarbamate (**3a**) and isopropyl benzenesulfinate (**4a**) could only be formed in respectively 19% and 20% yield (entry 10). Addition of 5 mol % of NaI as catalyst therefore increases the yield of **3a** and **4a** with 74% and 73%, respectively (entries 5 and 10).

Table S3: Effect of NaI loading, time, 1a/2a ratio at 30 °C.[a]



1a **2a** **3a** **4a**

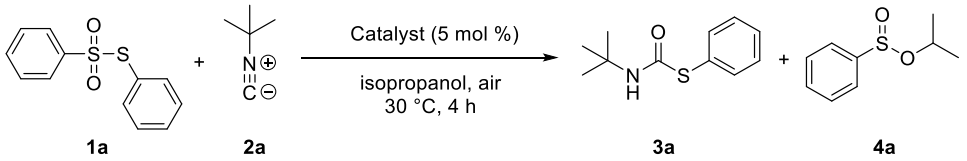
entry	ELN code	**2a** (equiv.)	NaI (mol %)	time (h)	yield **3a** (%)[b]	yield **4a** (%)[b]
1	PMSA668	1.5	10	20	94	96
2	PMSA940	1.2	10	20	94	93
3	PMSA680	1.5	5	20	95	94
4	PMSA695	1.5	5	4	96	93
5	PMSA894/702	1.2	5	4	93 (95)[c]	93 (90)[c]
6	PMSA887	1.0	5	4	76	78
7	PMSA891	1.2	5	2	79	81
8	PMSA892	1.2	2.5	4	69	68
9	PMSA893	1.2	1	4	51	51
10	PMSA887	1.2	0	4	19	20

[a] *Reaction conditions*: *S*-phenyl benzenethiosulfonate (**1a,** 125 mg, 0.5 mmol, 1.0 equiv), *tert*-butyl isocyanide (**2a**, y equiv), NaI (x mol %), isopropanol (0.5 mL, 13.0 equiv), 30 °C, time, air. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield.

We wondered whether other iodide salts could also promote the coupling of *S*-phenyl benzenethiosulfonate (**1a**) and *tert*-butyl isocyanide (**2a**). We first evaluated six different cations under the optimal reaction conditions (Table S4, entries 2, 5-9). Sodium was found to be the best cation for iodide. When different sodium (entries 2-4) and tetrabutylammonium (entries 9-11) halides were compared, only the iodide salts performed significantly better than the blanc reaction (entry 1). I_2 also had an effect on the reaction but significantly less than NaI (entry 12). The optimal reactions conditions are **1a** (1.0 mmol), **2a** (1.2 mmol), NaI (5 mol %), isopropanol (0.5 mL), 30 °C, 4 h, air (entry 2).

In Table S5 different solvents were evaluated for the desired reaction under otherwise optimal reaction conditions. The solvent turned out to have a huge effect on the efficiency of the transformation. Alcohols are optimal and these also act as a reagent, resulting in the formation of the corresponding alkyl benzenesulfinates (entries 1-4). Thiocarbamate **3a** was also formed in other solvents, although only in a very low amount (entries 5-9). Isopropanol was selected as reaction partner based on the published green solvents guides.[3]

Table S4: Effect of the catalyst.[a]

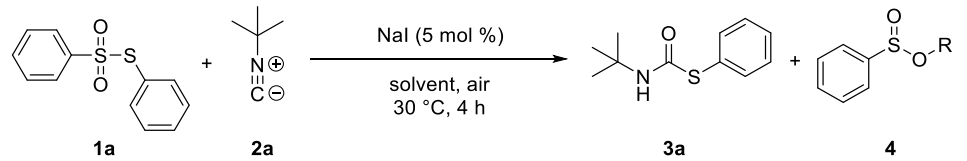


1a 2a 3a 4a

entry	ELN code	catalyst	yield **3a** (%)[b]	yield **4a** (%)[b]
1	PMSA887	/	19	20
2	PMSA894/702	NaI	93 (95)[c]	93 (90)[c]
3	PMSA936	NaBr	34	33
4	PMSA937	NaCl	25	27
5	PMSA921	KI	42	42
6	PMSA922	LiI	81	81
7	PMSA923	CsI	34	30
8	PMSA888	CuI	43	45
9	PMSA884	NBu_4I	44	48
10	PMSA886	NBu_4Br	27	30
11	PMSA885	NBu_4Cl	23	26
12[d]	PMSA890	I_2	46	48

[a] *Reaction conditions: S*-phenyl benzenethiosulfonate (**1a**, 125 mg, 0.5 mmol, 1.0 equiv), *tert*-butyl isocyanide (**2a**, 68 µL, 0.6 mmol, 1.2 equiv), catalyst (5 mol %), isopropanol (0.5 mL, 13.0 equiv), 30 °C, 4 h, air. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield. [d] I_2 (3.2 mg, 2.5 mol %) was added to the reaction.

Table S5: Effect of the solvent.[a]



1a 2a 3a 4

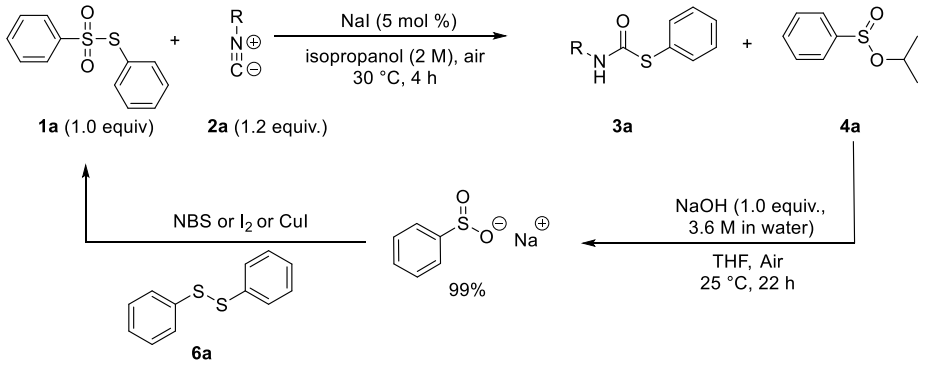
entry	ELN code	solvent	R	yield **3a** (%)[b]	yield **4** (%)[b]
1	PMSA929	*n*-BuOH	Butyl	81	84
2	PMSA894/702	Isopropanol	Isopropyl	93 (95)[c]	93 (90)[c]
3	PMSA928	EtOH	Ethyl	89	90
4	PMSA933	MeOH	Methyl	95	78
5	PMSA931	n-BuOAc	/	5	/
6	PMSA930	2-MeTHF	/	12	/
7	PMSA932	Toluene	/	0	/
8	PMSA934	1,4-dioxane	/	18	/
9	PMSA935	CH_3CN	/	12	/

[a] *Reaction conditions: S*-phenyl benzenethiosulfonate (**1a**, 125 mg, 0.5 mmol, 1.0 equiv), *tert*-butyl isocyanide (**2a**, 68 µL, 0.6 mmol, 1.2 equiv), NaI (5 mol %), solvent (13.0 equiv), 30 °C, 4 h, air. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield.

4 Transformation of isopropyl benzenesulfinate into *S*-phenyl benzenethiosulfonate.

Our new method towards thiocarbamates generates isopropyl benzenesulfinate (**4a**) as a side compound (Scheme S1). We wondered whether we would be able to transform this waste compound into sodium benzenesulfinate. After all, this sodium salt is used both in the method of Wu[2] and *Fujiki*[1] for the preparation of the *S*-phenyl benzenesulfinate reagent (**1a**) via reaction with **6a** (Scheme S1). Alternatively, Cu-catalyzed coupling in air also delivers **1a**.[4] In In this way the generated waste can be reused. Based on a hydrolysis method reported by Braverman,[5] sodium benzenesulfinate could be obtained quantitatively illustrating the potential recycling of this compound (Scheme S1). A similar strategy can be used for the other alkyl and aryl benzenesulfinate reagents used in this work.

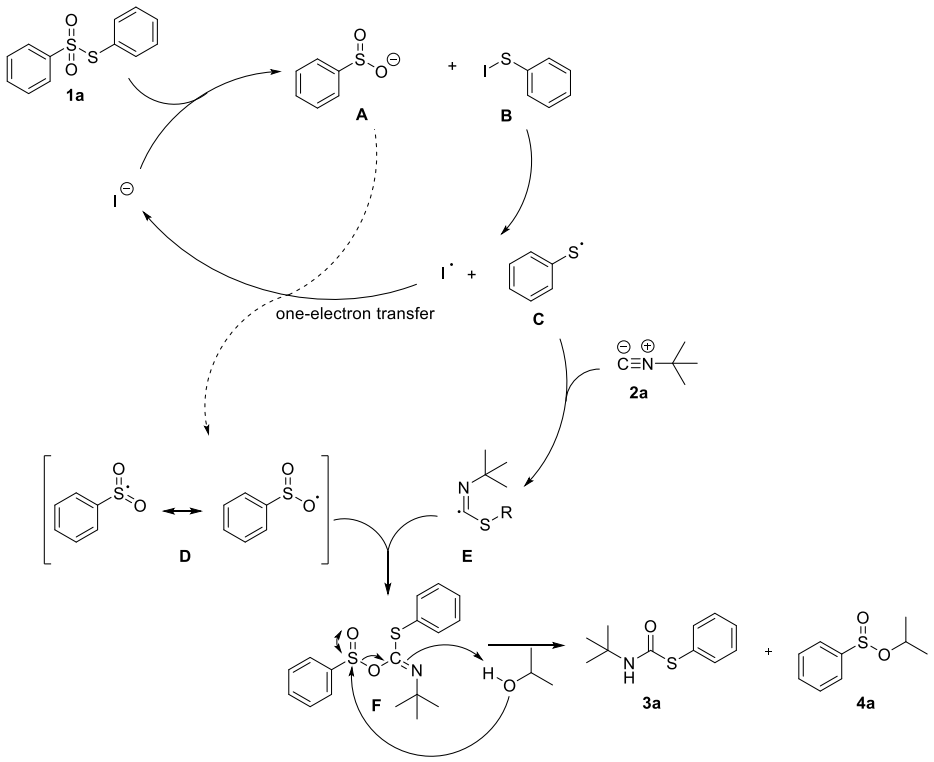
Scheme S1: Reuse of isopropyl benzenesulfinate (4a) for the synthesis of 1a by hydrolysis of 4a with NaOH.



5 Mechanism

Based on the results of different control reactions, which will be discussed in this section, a radical reaction mechanism is proposed as outlined in Scheme S2. First, **1a** reacts with sodium iodide yielding benzenesulfinate (**A**) and PhSI (**B**).[6] Then **B** undergoes homolytic cleavage to yield the thiophenol radical **C**.[7] Subsequently, **C** adds to isocyanide **2a** furnishing radical **E**. Reaction of **E** with benzenesulfinate radical **D** forms intermediate **F**. Finally, alcoholysis of intermediate **F** with isopropanol generates **3a** and **4a**. Intermediate **D** is formed via electron transfer from benzene sulfinate **A** to the iodine radical, which is plausible based on its low oxidation potential.[8] Regeneration of iodide justifies its role as a catalyst.

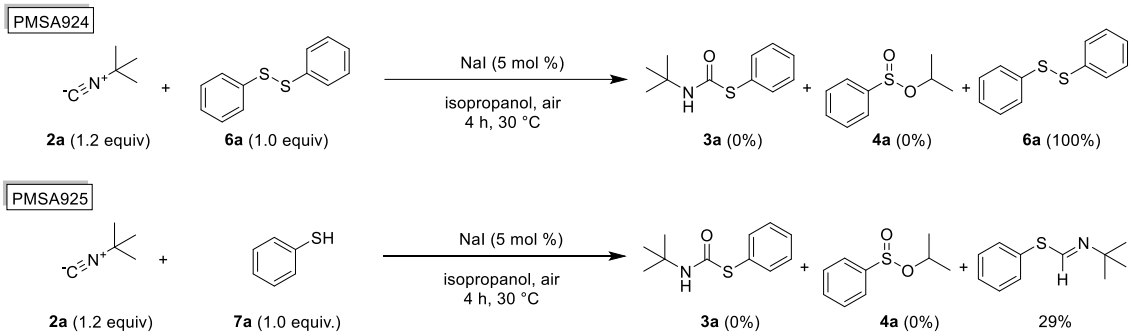
Scheme S2: Proposed mechanism for the iodide-catalyzed reaction of 1a with 2a.



5.1 Sulfenylating agent

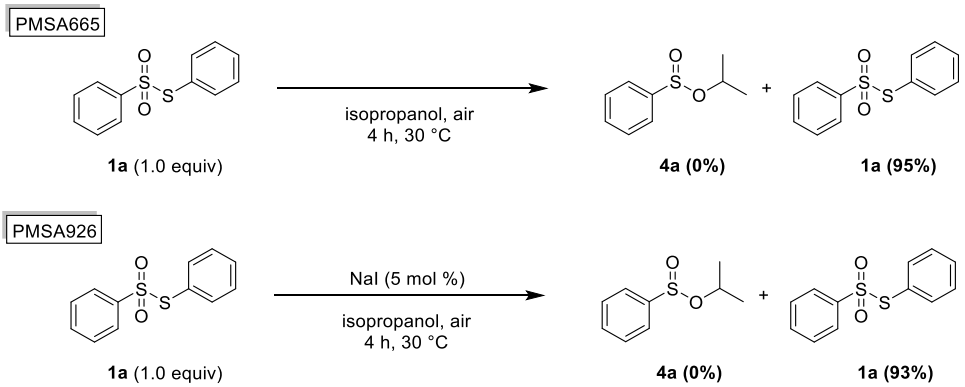
Scheme S3 shows that the choice of the appropriate sulfenylating agent is essential for the desired coupling as diphenyl disulfide (**6a**) or thiophenol (**7a**) did not lead to the formation of *S*-phenyl *tert*-butylthiocarbamate (**3a**) and isopropyl benzenesulfinate (**4a**). In the reaction of *tert*-butyl isocyanide (**2a**) with benzenethiol, a low amount of *S*-phenyl *N*-*tert*-butylthioformimidate was formed in accordance with previous observations of Seagusa.[9] These experiments prove that the reaction of **3a** and **4a** is specific to the thiosulfonate class as sulfenylating agents.

Scheme S3: Attempts to use diphenyl disulfide (6a) and thiophenol (7a) as sulfenylating agent.



Subsequently, it was evaluated whether **4a** can be formed in the absence of **2a**. Scheme S4 reveals that in the absence of **2a** no reaction occurs and *S*-phenyl benzenethiosulfonate (**2a**) is fully recovered, both in the presence and absence of NaI (Scheme 4). **4a** is therefore a side compound formed in the reaction delivering thiocarbamate **3a**.

Scheme S4: Involvement of isocyanide 2a in the formation of isopropyl benzenesulfinate (4a).



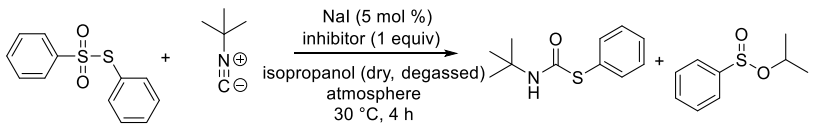
5.2 Oxygen atom source for thiocarbamate

There are four species which could deliver the oxygen in the thiocarbamate reaction product **4a**:

- Water
- Isopropanol
- Oxygen
- Thiosulfonate

When the reaction was performed under dry conditions (argon, dry oxygen and dry, degassed isopropanol), no difference in yield was observed for *S*-phenyl *tert*-butylthiocarbamate (**3a**) and isopropyl benzenesulfinate (**4a**) (Table S6, entries 2 and 3). These results exclude that oxygen or water are the oxygen source for the thiocarbamate. In addition, we earlier found that in other solvents (2-MeTHF, 1,4-dioxane and acetonitrile) also reaction product was formed, albeit in a low yield (Table S5, entries 6, 8-9), meaning that **3a** can also be formed without isopropanol. The only remaining oxygen source for the thiocarbamate formation is therefore *S*-phenyl benzenethiosulfonate (**1a**).

Table S6: Control reactions to support the mechanism[a]



1a (1.0 equiv) **2a** (1.2 equiv) **3a** **4a**

entry	ELN code	atmosphere	inhibitor	yield **3a** (%)[b]	yield **4a** (%)[b]
1	PMSA894	Air	/	93	93
2	PMSA909	Oxygen (dry)	/	88	87
3	PMSA908	Argon	/	91	90
4	PMSA911	Argon	TEMPO	56[c]	36[c]
5	PMSA906	Argon	Galvinoxyl	34[c]	32[c]
6	PMSA907	Argon	1,1-diphenylethylene	86	84
7	PMSA912	Argon	BHT	56[c]	37[c]

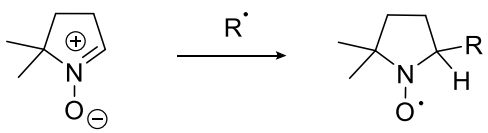
[a] *Reaction conditions: S*-phenyl benzenethiosulfonate (**1a**, 125 mg, 0.5 mmol, 1.0 equiv), *tert*-butyl isocyanide (**2a**, 68 µL, 0.6 mmol, 1.2 equiv), sodium iodide (3.8 mg, 0.025 mmol, 5 mol %), isopropanol (0.5 mL, 13 equiv), 30 °C, 4 h, atmosphere. [b] ^{1}H-NMR yield using 1,3,5-trimethoxybenzene as internal standard. [c] Isolated yield.

5.3 Radical or ionic reaction

To examine if a radical is involved in the mechanism, different radical inhibitors were added to the reaction (Table S6, entries 4-7). Three of the four tested radical inhibitors show a clear decrease in yield of *S*-phenyl *tert*-butylthiocarbamate (**3a**) and isopropyl benzenesulfinate (**4a**). This points towards a radical reaction. EPR experiments with DMPO trapping of the reaction mixture were performed to confirm this. Trapped radicals with structures in accordance to D and E were observed. Interestingly, even when NaI was omitted from the reaction mixture, D was still detected meaning that the background reaction (Table S4, entry 1) is also radical in nature and does not involve a direct insertion reaction of the isocyanide. Control experiments on isopropanol, **1a** in isopropanol and **2a** in isopropanol with added DMPO did not reveal the presence of a trapped radical.

DMPO (5,5-dimethyl-1-pyrroline *N*-oxide) acts as an efficient trap for short lived radicals via the reaction given in Scheme S5. The resulting DMPO adduct is in general a radical with a long enough life time to allow detection by EPR spectroscopy. The EPR spectra are characterized by the hyperfine couplings of the nitroxide nitrogen (a_N), the β-protons ($a_{H\beta}$) and in some cases the γ-protons ($a_{H\gamma}$). This set of parameters is dependent on the trapped radical. Here, DMPO was added to the reaction mixture and aliquots were taken at different stages of the reaction for EPR analysis. Several control experiments were also performed as indicated below.

Scheme S5: Spin-trapping mechanism with DMPO.



From Figure S1 it becomes clear that DMPO does not trap any radical as long as **1a** and **2a** are not both in the reaction mixture (Figure S1 a-c). In a mixture of **1a** and **2a** with DMPO in isopropanol without the catalyst (NaI), DMPO traps already organic radicals (Figure S1 d). The EPR intensity increases considerably after addition of NaI to the mixture (Figure S1 e). Heating of the sample to 30°C initially increases the EPR intensity further (Figure S1 f), which then decays in the next 10 min (Figure S1 g, h) to a signal that remains more or less

identical in the continuation of the reaction (Figure S1 i, j). The latter decrease in intensity may be related to the limited life-time of the trapped radicals.

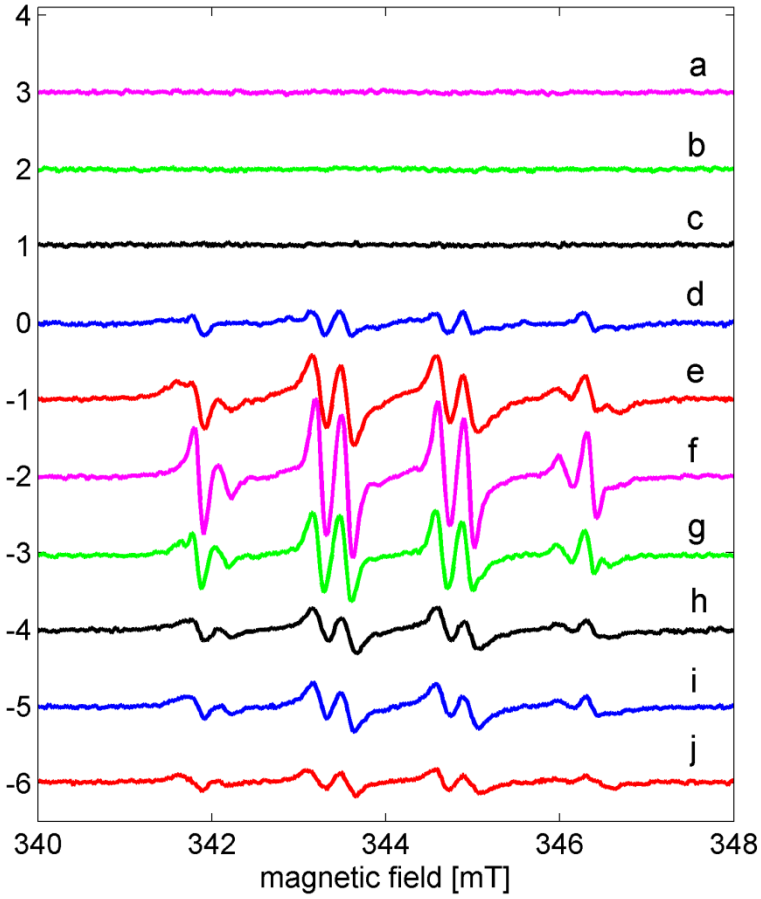


Figure S1: Room-temperature X-band EPR spectra of (a) DMPO in isopropanol, (b) DMPO + **1a** in isopropanol, (c) DMPO + **2a** in isopropanol, (d) DMPO + **1a** + **2a** in isopropanol, (e) DMPO + **1a** + **2a** + NaI in isopropanol, and (f-j) Reaction mixture of DMPO + **1a** + **2a** + NaI in isopropanol at 30oC. Aliquots taken after (f) 5 min, (g) 10 min, (h) 15 min, (i) 20 min, (j) 90 min. The spectra are shown such as to represent their true relative intensity. [Aliquots were taken every 5 min in the reaction but no relevant changes were observed after 15 min. of reaction].

Figure S2 shows the spectrum of the mixture of DMPO + **1a** + **2a** in isopropanol. The spectrum consists of six-line spectrum overlaid on a noisy background. The corresponding EPR simulation parameters are given in

Table S7 (DMPO adduct of R1), together with the known coupling parameters for DMPO adducts of a number of relevant radicals. Trapping of carbon radicals leads to $a_{H\beta}$ -values ≥ 2.0 mT, which rules out that R1 is a carbon radical. The observed parameters of R1 are closest (but not fully identical) to the ones observed for trapping of $NaSO_3^{\bullet}$ [10] or $C_6H_5SO_2^{\bullet}$,[11] which suggests that R1 is radical D in the reaction Scheme S2 of the main text. The deviations in the observed EPR parameters may result from the difference in solvent. The intensity of DMPO-R1 increases when NaI is added (Figure S1 e) and further upon heating to 30°C (Figure S1f). It remains present during the whole reaction time (Figure S1 g-i).

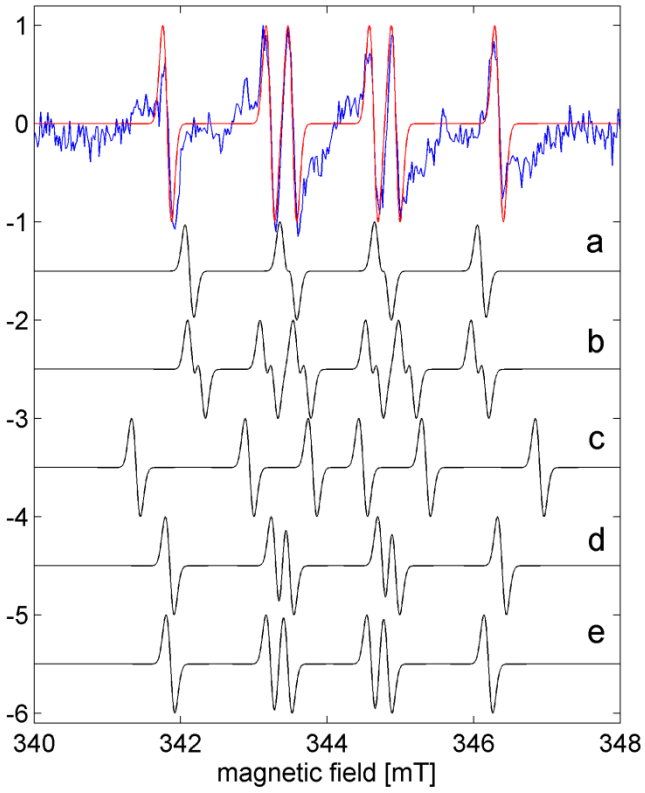


Figure S2: (blue) Experimental room-temperature X-band EPR spectra of DMPO + 1a + 2a in isopropanol. (red) simulation using parameters of R1 (Table S7). (black) Simulations using reported EPR parameters for the DMPO adducts of (a) $PhS^{\bullet}$ in toluene,[12] (b) $iPrO^{\bullet}$ in various solvents,[13] (c) $^{\bullet}C(CH_3)_2OH$ in various solvents,[13] (d) $NaSO_3^{\bullet}$ in water[10] and e) $C_6H_5SO_2^{\bullet}$ in water[11].

Table S7: EPR simulation parameters of the DMPO adducts observed in this work in comparison to reported parameters.

DMPO adducts of	G	a_N /mT	$a_{H\beta}$ /mT	$a_{H\gamma}$ /mT	Reference
R1	2.0062 ± 0.0001	1.41 ± 0.02	1.71 ± 0.02	-	This work
R2	2.0060 ± 0.0001	1.47 ± 0.03	1.47 ± 0.03	0.37	This work
R3	2.0060 ± 0.0001	1.27 ± 0.02	1.40 ± 0.02	-	This work
$PhS^{\bullet}$	2.006	1.29	1.41	-	[12]
$iPrO^{\bullet}$	2.0058	1.44	0.99	0.13	[13]
$^{\bullet}C(CH_3)_2OH$	2.0058	1.55	2.41	-	[13]
$NaSO_3^{\bullet}$	n.r.	1.45	1.625	-	[10]

Figure S3 shows the normalized EPR spectra after addition of NaI and heating and during the reaction. Besides the components of DMPO-R1, additional lines are observed that are best recognized in the high and low-field areas (dashed and green dashed-dotted lines). Inspection of the spectra shows that the relative intensities of the peaks indicated with dashed and dotted lines are not constant, indicating that at least two additional DMPO adducts are present. However, the exact parameters of the contributions are hard to determine and especially the results for DMPO-R2 should be considered with caution, since no perfect fit could be obtained. The parameters DMPO-R3 match those of the DMPO adduct of $PhS^{\bullet}$,[12] where the small difference may arise from the fact that toluene was used as a solvent in the cited work. The

EPR parameters of DMPO-R2 are very unusual. DMPO adducts of hydroxyl radicals lead to spectra with similar couplings to the nitrogen and β-protons, but do not show such a high coupling to the γ protons. However, as said before, the EPR parameters of this contribution should be treated with caution, since only the outer peaks can be observed well.

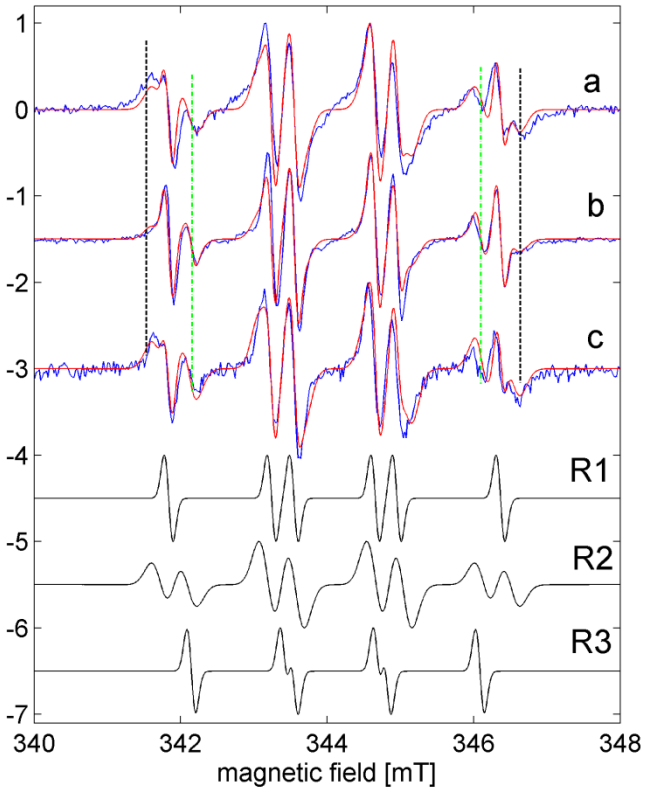
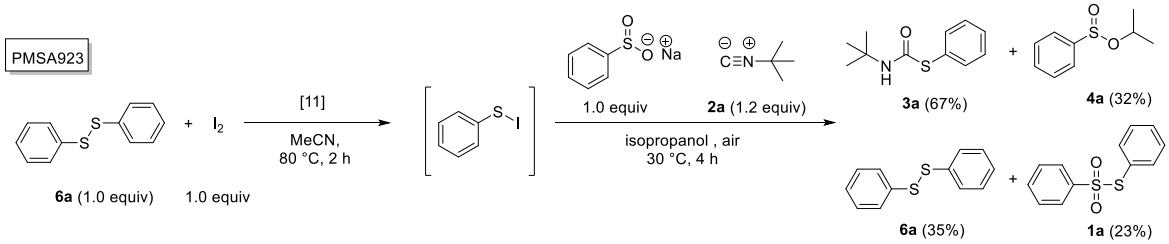


Figure S3: (blue) Experimental X-band EPR spectra of (a) DMPO + **1a** + **2a** + NaI in isopropanol (directly after mixing at room temperature), and after 5 minutes (b) and 50 minutes (c) at 30 °C. The spectra are shown normalized. (red) Corresponding simulations taking into account different relative amounts of the DMPO-adducts of R1, R2 and R3. (black) Individual EPR spectra of the three DMPO-adducts used in the simulation.

5.4 Involvement of PhSI

In literature, PhSI is described as an unstable compound which disproportionates into diphenyl disulfide (**6a**).[14] PhSI can also be generated *in situ* from diphenyl disulfide and iodine.[6] We therefore carried out a control experiment with PhSI, generated *in situ* following the reported procedure, and that mixture was subsequently added to a solution of sodium benzenesulfinate, *tert*-butyl isocyanide (**2a**) and isopropanol (Scheme S6) without intermediate workup. *S*-phenyl *tert*-butylthiocarbamate (**3a**) and isopropyl benzenesulfinate (**4a**) were both obtained, which suggest that PhSI is indeed involved as an intermediate in our transformation. The formation of thiosulfonate **1a** is in accordance with the thiosulfonate synthesis reported by Fujiki involving **6a**, sodium benzene sulfinate and I_2.[1]

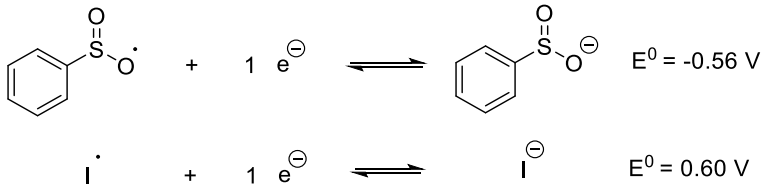
Scheme S6: *In situ* generation of PhSI and its reaction with sodium benzenesulfinate and isocyanide 2a.



5.5 Standard potential of sodium benzenesulfinate and iodide

The standard potential of sodium benzenesulfinate in a 0.1 M R_4NBF_4 acetonitrile solution vs. ferrocene redox couple (Fc^+/Fc) is -0.56 V.[8] The standard potential of I^- in a 0.1 M R_4NBF_4 acetonitrile solution vs. Fc^+/Fc is 0.60 V.[15] Sodium benzenesulfinate is therefore easily oxidized and able to donate an electron to iodine radical.

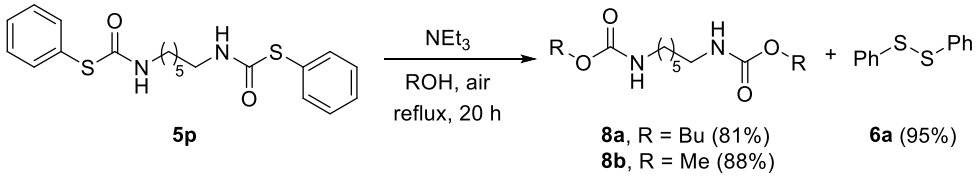
Scheme S7: Standard potential of sodium benzenesulfinate and iodide.



6 Synthesis of biscarbamates

To illustrate the synthetic potential of our newly developed transformation, *S,S'*-diphenyl hexane-1,6-diylbisthiocarbamate (**5p**) was transformed in high yield into dialkyl hexane-1,6-diylbiscarbamates (**8a-b**) by reaction with an alcohol using NEt_3 as a base (Scheme S8).[16] No waste resulting from the thiophenol leaving group is generated as it can easily be recovered as diphenyldisulfide (**6a**), which can be transformed into **1a** by selective oxidation.[1-2, 4, 17] **8a-b** can be used for polyurethane synthesis by polycondensation with a diol. Dicarbamates are considered as one of the most promising alternative reagents towards polyurethanes.[18] In order to achieve a more sustainable polyurethane production isocyanate and phosgene-free methods are required for the synthesis of the polymer precursors. 1,6-Diisocyanohexane (**2p**) was synthesized from hexamethylenediamine via the Hofmann synthesis or dehydration of the corresponding diformamide.

Scheme S8: Synthesis of bicarbamates 8.

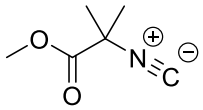


7 Experimental

7.1 Synthesis of isocyanides

Methyl 2-isocyano-2-methylpropanoate (2b) [PMS-TIO022]

The isocyanide was prepared according to a slightly adapted literature procedure.[19]

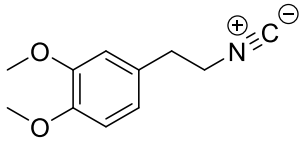


2-Methylalanine (5.16 g, 50.0 mmol, 1.0 equiv.) is dissolved in MeOH (15.0 mL) and thionyl chloride (4.4 mL, 60 mmol, 1.2 equiv.) is added at 0 °C. The reaction is stirred at room temperature overnight. The volatiles were removed *in vacuo* to give a white solid, which is used in the next step without further purification. The crude was dissolved in formic acid (18.0 mL) to which a solution of sodium formate (3.40 g, 50.0 mmol, 1.0 equiv.) in formic acid (6.0 mL) was added. The resulting suspension was heated at 40 °C for 2 hours. NaCl was filtered off over a Celite pad and the mixture was concentrated. A fresh solution of acetic formic anhydride was prepared, by stirring acetic anhydride (14.1 mL, 150.0 mmol, 3.0 equiv.) and formic acid (1.9 mL, 50.0 mmol, 1.0 equiv.) at 80 °C for 2 hours, and added. The reaction mixture is heated overnight at 80 °C. A Na_2CO_3 solution (30 mL, 1 M) was added and the organic layer is extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with a Na_2CO_3 solution (2 x 30 mL, 1 M), and dried over $MgSO_4$. The volatiles were removed *in vacuo* to give the formamide as yellow oil, which was used in the next step without further purification. The formamide was dissolved in CH_2Cl_2 (50.0 mL) and triethylamine (27.8 mL, 200.0 mmol, 4.0 equiv.) was added. Subsequently, a solution of phosphoryl chloride (5.6 mL, 60.0 mmol, 1.2 equiv.) in CH_2Cl_2 (15.0 mL) was added dropwise at -20 °C (Ice/NaCl). Saturated $NaHCO_3$ solution (20 mL) was added and the organic layer was washed with $NaHCO_3$ (30 mL), brine (2 x 30 mL) and dried over $MgSO_4$. The product was purified by manual flash chromatography using Heptane / EtOAc (9:1) as eluent. Methyl 2-isocyano-2-methylpropanoate was obtained in 25% (1.56 g) yield. The spectral data are in accordance with the literature.[19]

Yellow oil, R_f = 0.57 in Heptane / EtOAc (4:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H), 1.67 (s, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.2 (C), 158.2 (C), 59.6 (C), 53.7 (CH_3), 27.7 (CH_3) ppm. HRMS (ESI) for $C_6H_{10}NO_2$ $[M+H]^+$ calcd. 128.0706, found 128.0709.

4-(2-Isocyanoethyl)-1,2-dimethoxybenzene (2k) [PMSA817]

This compound was prepared according to a literature procedure.[20]

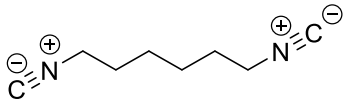


3,4-Dimethoxyphenethylamine (1.67 mL, 10.0 mmol, 1.0 equiv.) was dissolved in ethyl formate (15.0 mL, 186.0 mmol, 18.6 equiv.) and heated at 80 °C for 4 hours. The reaction mixture was concentrated *in vacuo* to afford the desired formamide product, which was used in the next step without purification. The crude formamide was dissolved in dry 2-MeTHF (15.0 mL), the solution flushed with argon and cooled to 0 °C. Triethylamine (7.0 mL, 50.3 mmol, 5.0 equiv.) was added, followed by phosphorus oxychloride (1.1 mL, 12.0 mmol, 1.2 equiv.) dropwise over 10 minutes. The reaction mixture was stirred at 0 °C for 1 hour. Ice water (50.0 mL) was added and the reaction was stirred for 10 minutes. The mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine (15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The oily residue was purified via an automated flash chromatography system applying a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). 4-(2-Isocyanoethyl)-1,2-dimethoxybenzene was obtained in 75% (1.428 g) yield. The spectral data are in accordance with the literature.[20]

Off-white solid, m.p.: 51-52 °C (lit.: 52-53 °C),[21] R_f = 0.39 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 6.83 (d, *J* = 8.0 Hz, 1H), 6.77 (dd, *J* = 10.5, 2.2 Hz, 2H), 3.88 (d, *J* = 6.8 Hz, 6H 6H), 3.58 (t, *J* = 7.0 Hz, 2H), 2.93 (t, *J* = 6.9 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 156.8 (t, *J* = 5.4 Hz, C)*, 149.3 (C), 148.5 (C), 129.4 (C), 120.9 (CH), 112.1 (CH), 111.7 (CH), 56.1 (CH_3), 56.1 (CH_3), 43.4 (t, *J* = 6.6 Hz, CH_2)*, 35.5 (CH_2) ppm. HRMS (ESI) for $C_{11}H_{14}NO_2$ $[M+H]^+$ calcd. 192.1019, found 192.1023.

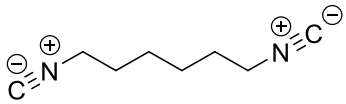
1,6-Diisocyanohexane (2p) [PMSA841b]

This compound was prepared according to a literature procedure.[22]



Hexamethylenediamine (581 mg, 5.0 mmol, 1.0 equiv.) was dissolved in ethyl formate (7.5 mL, 93 mmol, 18.6 equiv.) and heated at 80 °C overnight. The reaction mixture was concentrated *in vacuo* to afford the desired formamide product, which was used in the next step without purification. The crude formamide was dissolved in CH_2Cl_2 (15.0 mL) and cooled to 0 °C. Triethylamine (7.0 mL, 50.3 mmol, 10 equiv.) was added, followed by phosphorus oxychloride (1.1 mL, 12.0 mmol, 2.4 equiv.) dropwise over 10 minutes. The reaction mixture was stirred at room temperature for 2 hours. Ice water (20.0 mL) containing K_2CO_3 (4.0 g) was added and the reaction was stirred for 10 minutes. The mixture was extracted with EtOAc (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The oily residue was purified via flash chromatography using Heptane / EtOAc (4:1→2:1) as eluent. 1,6-Diisocyanohexane was obtained in 52% (355 mg) yield. The spectral data are in accordance with the literature.[22]

Alternatively, 1,6-diisocyanohexane could be directly prepared from hexamethylenediamine without first preparing the diformamide by using the Hofmann carbylamine approach.[23]



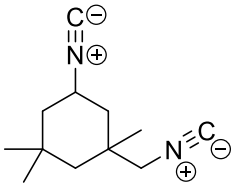
A 100 mL three-necked round-bottom flask was equipped with a stirring bar, reflux-condensor and a dropping funnel. The flask was charged with water (10 mL) and stirring was begun while NaOH (10.0 g, 250 mmol, 50.0 equiv.) was added in portions in order to maintain efficient stirring. A mixture of $CHCl_3$ (870 µL, 11.0 mmol, 2.2 equiv.), hexamethylenediamine (581 mg, 5.0 mmol, 1.0 equiv.) and benzyltriethylammonium chloride (228 mg, 1.0 mmol, 0.2 equiv.) in CH_2Cl_2 (10 mL) was added dropwise over 15 minutes. The reaction mixture was stirred for 24

* The ^{13}C-NMR spectra of certain aliphatic isonitriles exhibit a three-line multiplet which can be assigned to the isonitrile carbon resonance. In theory a 1:1:1 multiplet would be expected for the ^{13}C-^{14}N coupling between the nitrogen atom and the adjacent carbon atom. For further explanation see: (a) Morishima, I.; Mizuno, A.; Yonezawa, T.; Goto, K. *J. Chem. Soc. D: Chem. Comm.* **1970**, 1321. (b) Stephany, R. W.; de Bie, M. J. A.; Drenth, W. *Org. Magn. Res.* **1974**, *6*, 45. (c) Brady, S. F.; Clardy, J. *Angew. Chem. Int. Ed.* **2005**, *44*, 7063. (d) Cronin, D. L.; Wilkinson, J. R.; Todd, L. J. *J. Magn. Res.***1975**, *17*, 353.

hours. The reaction mixture is diluted with ice water (15 mL) and the organic layer is separated. The water layer is extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with water (50 mL) and brine (15 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The oily residue was purified via flash chromatography using Heptane / EtOAc (4:1→2:1) as eluent. 1,6-Diisocyanohexane was obtained in 31% (209 mg) yield. The spectral data are in accordance with the literature.[22]

Yellow oil, R_f = 0.32 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.43-3.41 (m, 4H), 1.71 (br s, 4H), 1.52-1.49 (m, 4H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 156.4 (t, *J* = 5.7 Hz, C)*, 41.5 (t, *J* = 6.5 Hz, CH_2)*, 29.0 (CH_2), 25.7 (CH_2) ppm. HRMS (ESI) for $C_8H_{13}N_2$ $[M+H]^+$ calcd. 137.1073, found 137.1082.

5-Isocyano-1-(isocyanomethyl)-1,3,3-trimethylcyclohexane (2q) [PMSA842]

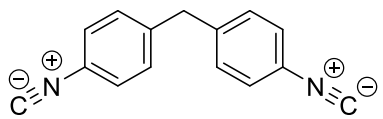


Isophoronediamine (3:1 mixture of cis and trans, 1.703 g, 10.0 mmol, 1.0 equiv.) was dissolved in triethylamine (1.4 mL, 10.0 mmol, 1.0 equiv.) and ethylformate (15.0 mL, 186 mmol, 18.6 equiv.) and heated at 80°C overnight. The reaction mixture was concentrated *in vacuo* to afford the desired formamide product, which was used in the next step without purification. The crude formamide was dissolved in CH_2Cl_2 (15.0 mL) and cooled to 0 °C. Triethylamine (13.9 mL, 100.0 mmol, 10.0 equiv.) was added, followed by phosphorusoxychloride (2.2 mL, 24.0 mmol, 2.4 equiv.) dropwise over 10 minutes. The reaction mixture was stirred at 0 °C for 30 minutes and subsequently for 2 hours at room temperature. Ice water (50.0 mL) containing K_2CO_3 (10.0 g) was added and the reaction was stirred for 10 minutes. The mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$, filtered and concentrated. The oily residue was purified via flash chromatography using Heptane / EtOAc (4:1→2:1) as eluent. 5-Isocyano-1-(isocyanomethyl)-1,3,3-trimethylcyclohexane was obtained in 69% (1.321 mg, 1:3 mixture of cis and trans determined via the ^{1}H-NMR signals at 3.74 ppm and 3.58 ppm) yield. No spectroscopic data are available in literature.

Orange oil, R_f = 0.61 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 3.77-3.56 (m, 2H), 3.32 (q, *J* = 15.0 Hz, 1H), 3.11 (s, 3H), 2.06-1.90 (m, 4H), 1.58-1.28 (m, 6H), 1.18-1.09 (m, 8H), 1.02-0.97 (m, 12H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.2 (t, *J* = 5.3 Hz, minor, C)*, 158.1 (t, *J* = 5.3 Hz, major, C)*, 155.5 (t, *J* = 5.0 Hz, minor, C)*, 155.3 (t, *J* = 5.0 Hz, major, C)*, 55.5 (t, *J* = 6.4 Hz, major, CH_2)*, 49.8 (t, *J* = 6.4 Hz, minor, CH_2)*, 47.1 (t, *J* = 6.5 Hz, major, CH)*, 46.9 (t, *J* = 6.5 Hz, minor, CH)*, 46.8 (major, CH_2), 46.8 (minor, CH_2), 45.6 (minor, CH_2), 45.6 (major, CH_2), 35.2 (t, *J* = 1.3 Hz, major, C)*, 35.0 (t, *J* = 1.3 Hz, minor, C)*, 34.3 (major, CH_3), 34.1 (minor, CH_3), 31.4 (t, *J* = 1.4 Hz, major, C)*, 31.2 (t, *J* = 1.4 Hz, minor, C)*, 29.4 (minor CH_3), 27.3 (major, CH_3), 26.7 (minor, CH_3), 23.1 (major, CH_3) ppm. HRMS (ESI) for $C_{12}H_{19}N_2$ $[M+H]^+$ calcd. 191.1543, found 191.1550.
The compound was visualized on TLC by staining with $KMnO_4$.

1,1'-Methylenebis(4-isocyanobenzene) (2r) [PMSA769 and 774]

This compound was prepared according to a literature procedure.[24]



4,4'-Diaminodiphenylmethane (793 mg, 4.0 mmol, 1.0 equiv.) was dissolved in toluene (20.0 mL), and formic acid (600 µL, 20.0 mmol, 4.0 equiv.) and the mixture was refluxed for 8 hours. The reaction mixture was concentrated *in vacuo* to afford the desired formamide product, which was used in the next step without purification. The crude formamide was dissolved in CH_2Cl_2 (20.0 mL) and cooled to 0 °C. Triethylamine (4.0 mL, 28.8 mmol, 7.2 equiv.) was added, followed by phosphorus oxychloride (895 µL, 9.60 mmol, 2.4 equiv.) dropwise over 10 minutes. The reaction mixture was stirred at room temperature for 2 hours. Ice water (20.0 mL) containing Na_2CO_3 (25 g in 100 mL) was added and the reaction was stirred for 10 minutes. The mixture was extracted with CH_2Cl_2 (3 x 15 mL). The combined organic layers were washed with brine (4 x 25 mL), dried over anhydrous $MgSO_4$, filtered and concentrated. The oily residue was purified via an automated flash chromatography system applying a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). 1,1'-Methylenebis(4-isocyanobenzene) was obtained in 52% (355 mg) yield. The spectral data are in accordance with the literature.[24]

White solid, m.p.: 137-138 °C (lit.: 131-132 °C),[25] R_f = 0.18 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31 (d, *J* = 8.3 Hz, 4H), 7.17 (d, *J* = 8.3 Hz, 4H), 4.01 (s, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.4 (C), 141.6 (C), 130.0 (CH), 126.8 (CH), 125.3 (C), 41.3 (CH_2) ppm. HRMS (ESI) for $C_{15}H_{11}N_2$ $[M+H]^+$ calcd. 219.0917, found 219.0921.

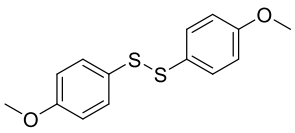
7.2 Synthesis of disulfides

General procedure A

This general procedure was adapted from a literature procedure.[26]

To a stirred solution of thiol (1.0 equiv.) in EtOAc (15 mL) at 0 °C was added sodium iodide (0.1 equiv.) and hydrogen peroxide (1.0 equiv.). The mixture was stirred at room temperature for 30 minutes. Saturated aqueous $Na_2S_2O_3$ (15 mL) was added, and the resulting mixture was extracted with EtOAc (3 x 15 mL). The combined organic phases were washed with brine (15 mL) and dried ($MgSO_4$). After the evaporation of the solvent the disulfide was obtained.

1,1'-Disulfanediylbis(4-methoxybenzene) (6f) [PMSA566a]

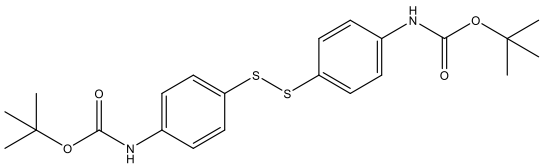


The general procedure A was applied using 4-methoxybenzenethiol (1.23 mL, 10.0 mmol, 1.0 equiv.), NaI (150 mg, 1.0 mmol, 0.1 equiv.) and H_2O_2 (568 µL, 10.0 mmol, 1.0 equiv.). After work-up, 1,1'-Disulfanediylbis(4-methoxybenzene) was obtained in quantitative yield. The spectroscopic data are in accordance with literature.[27]

Red oil, R_f = 0.50 in Heptane / CH_2Cl_2 (1:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42-7.38 (m, 4H)†, 6.85-6.62 (m, 4H)†, 3.80 (s, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 160.0 (C), 132.8 (CH), 128.6 (C), 114.8 (CH), 55.5 (CH_3) ppm. HRMS (ESI) for $C_{14}H_{15}O_2S_2$ $[M+H]^+$ calcd. 279.0508, found 279.0525.

Di-*tert*-butyl [disulfanediyldi(4,1-phenylene)]biscarbamate (6h) [PMSA785/795/803]

This product was prepared according to a slightly adapted literature procedure.[28]

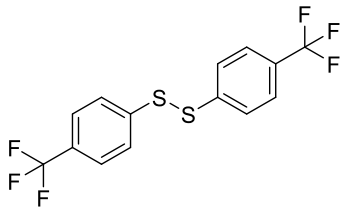


Di-*tert*-butyldicarbonate (2.62 g, 12.0 mmol, 4.0 equiv.) was added dropwise to a solution of 4-aminophenyldisulfide (745 mg, 3.0 mmol, 1.0 equiv.) and triethylamine (1.7 mL, 12.0 mmol, 4.0 equiv.) in DMF (2 mL). The reaction mixture was stirred in a preheated oil bath at 30 °C for 18 hours. Subsequently the solvent was evaporated and the product was purified by an automated flash chromatography system applying a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). Di-*tert*-butyl [disulfanediyldi(4,1-phenylene)]biscarbamate was obtained in 42% (567 mg) yield. No spectroscopic data are available in literature.

White solid, m.p.: 189-190 °C, R_f = 0.46 in heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.41-7.38 (m, 4H)†, 7.31-7.28 (m, 4H)†, 6.46 (br s, 2H), 1.51 (s, 18H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 152.6 (C), 138.6 (C), 131.2 (CH), 131.0 (C), 119.1(CH), 81.0 (C), 28.5 (CH_3) ppm. HRMS (ESI) for $C_{22}H_{29}N_2O_4S_2$ $[M+H]^+$ calcd. 449.1563, found 449.1565.

† The splitting of the signals can be explained by spin-coupling of chemical equivalent nuclei. For further explanation see: R. M. Silverstein, F. X. Webster, D. J. Kiemle, *Spectrometic identification of organic compounds*, (Ed: D. Brennan), *Wiley*, **2005**, 7th edition, 162-164.

1,1'-Disulfanediylbis[(4-(trifluoromethyl)benzene] (6j) [PMSA801]

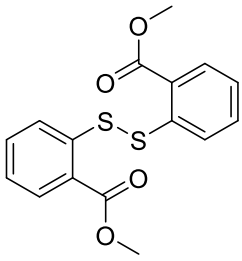


The general procedure A was applied using 4-(trifluoromethyl)thiophenol (548 µL, 4.0 mmol, 1.0 equiv.), NaI (60 mg, 0.4 mmol, 0.1 equiv.) and H_2O_2 (227 µL, 30%, 4.0 mmol, 1.0 equiv.). 1,1'-disulfanediylbis[(4-(trifluoromethyl)benzene] was obtained in quantitative yield. No spectroscopic data in $CDCl_3$ have been reported in literature.

Yellow solid, m.p.: 56-57 °C, R_f = 0.79 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.56 (m, 8H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 141.0 (C), 129.6 (q, J_{C-F} = 32.8 Hz, C), 126.8 (CH), 126.3 (q, J_{C-F} = 3.8 Hz, CH), 124.0 (q, J_{C-F} = 272.0 Hz, C) ppm. HRMS (ESI) for $C_{14}H_9F_6S_2$ $[M+H]^+$ calcd. 355.0044, found 355.0046.

Dimethyl 2,2'-disulfanediyldibenzoate (6l) [PMSA754]

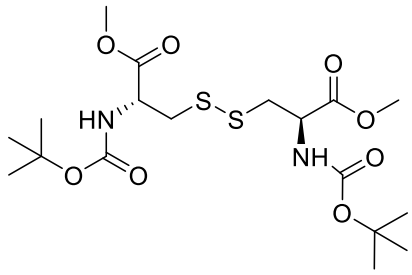
This compound was prepared according to an adapted literature procedure.[29]



2,2'-Dithiosalicylic acid (3.06 g, 10.0 mmol, 1.0 equiv.) was dissolved in thionyl chloride (15.2 mL, 210.0 mmol, 21.0 equiv.) and refluxed for 2 hours. The excess thionyl chloride was evaporated to give a brown solid. To this solid was slowly added triethylamine (15.3 mL, 110 mmol, 11.0 equiv.) and methanol (30.4 mL, 750 mmol, 75.0 equiv.). The mixture was stirred and refluxed for 2 hours. The reaction mixture was evaporated under reduced pressure to give a brown solid, which was dissolved in $CHCl_3$ (50 mL). This solution was washed with H_2O (3 x 50 mL), dried over anhydrous $MgSO_4$ and concentrated. Dimethyl 2,2'-disulfanediyldibenzoate was obtained in 92% (3.08 g) yield. The spectral data are in accordance with the literature.[30]

Brown solid, m.p.: 124-125°C (literature: 124-125°C)[31], R_f = 0.58 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.06 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.76 (d, *J* = 8.2 Hz, 2H), 7.43-7.38 (m, 2H), 7.25-7.20 (m, 2H), 3.98 (s, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.0 (C), 140.5 (C), 133.2 (CH), 131.6 (CH), 127.5(C), 126.0 (CH), 125.6 (CH), 52.5 (CH_3) ppm. HRMS (ESI) for $C_{16}H_{15}O_4S_2$ $[M+H]^+$ calcd. 335.0406, found 335.0419.

Dimethyl *N,N'*-bis(*tert*-butoxycarbonyl)-*L*-cystinate (6r) [PMSA567a]



The general procedure A was applied using *N*-(*tert*-butoxycarbonyl)-*L*-cysteine methyl ester (1.03 mL, 5.0 mmol, 1.0 equiv.), NaI (7.49 mg, 0.05 mmol, 0.01 equiv.) and 30% H_2O_2 (551 µL, 5.0 mmol, 1.0 equiv.) Dimethyl *N,N'*-bis(*tert*-butoxycarbonyl)-*L*-cystinate was obtained quantitatively (2.377 g). This spectral data are in accordance with literature.[32]

White solid, m.p: 99-100 °C, R_f = 0.30 in Heptane / EtOAc (4:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.36 (br s, 2H), 4.59 (br s, 2H), 3.76 (s, 6H), 3.15 (d, *J* = 4.7 Hz, 4H), 1.45 (s, 18H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 171.3 (C), 155.2 (C), 80.4 (C), 52.9 (CH), 52.8 (CH_3), 41.4 (CH_2), 28.4 (CH_3) ppm. HRMS (ESI) for $C_{18}H_{33}O_8N_2S_2$ $[M+H]^+$ calcd. 469.1673, found 469.1682.

7.3 Synthesis of thiosulfonates

General procedure B:

This general procedure was adapted from a literature procedure.[2]

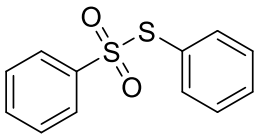
A mixture of sodium sulfinate (4.0 equiv.), disulfide (1.0 equiv.) and *N*-bromosuccinimide (2.0 equiv.) in acetonitrile (15.0 mL) was stirred at room temperature for the indicated time. Subsequently, the solvent was evaporated, the residue was redisolved in EtOAc, washed with water (15 mL) and extracted with EtOAc (3 x 15 mL). The combined organic phases were dried over $MgSO_4$. After filtration and concentration, the residue was purified by flash chromatography.

General procedure C:

This general procedure was adapted from a literature procedure.[1]

To a mixture of sodium sulfinate (3.2 equiv.) and disulfide (1.0 equiv.) in CH_2Cl_2 (20.0 mL) was added I_2 (2.0 equiv.) while mixing. The mixture was stirred until the disulfide was consumed, then CH_2Cl_2 (50 mL) was added followed by aqueous $Na_2S_2O_3$ (1 M, 10 mL). The organic layer was washed with H_2O (3 x 50 mL) and dried over $MgSO_4$. The organic layer was concentrated under reduced pressure. If necessary the product was purified by flash chromatography.

***S*-phenyl benzenethiosulfonate (1a) [PMSA-JVW08]**



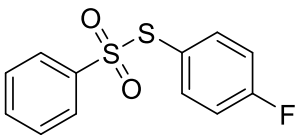
The general procedure B was applied using sodium benzenesulfinate (1.643 g, 10.0 mmol, 4.0 equiv.), diphenyldisulfide (547 mg, 2.5 mmol, 1.0 equiv.) and *N*-bromosuccinimide (893 mg, 5.0 mmol, 2.0 equiv.) for 24 hours. The compound was purified by flash chromatography with Heptane / Acetone (9:1) as eluent. *S*-phenyl benzenethiosulfonate was obtained in 70% (880 mg) yield.

OR

The general procedure C was applied using sodium benzenesulfinate (1.051 g, 6.4 mmol, 3.2 equiv.), diphenyl disulfide (437 mg, 2.0 mmol, 1.0 equiv.) and I_2 (1.015 g, 4.0 mmol, 2.0 equiv.). The mixture was stirred for 2 hours. *S*-phenyl benzenethiosulfonate was obtained in 96% (966 mg) yield. The spectral data are in accordance with literature.[1]

White solid, m.p.: 45-47 °C (literature. 41-42 °C)[33], R_f = 0.58 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 3H), 7.49-7.40 (m, 3H), 7.37-7.31 (m, 4H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.2 (C), 136.8 (CH), 133.8 (C), 131.5 (C), 129.6 (CH), 128.9 (CH), 128.1 (C), 127.7 (CH) ppm. HRMS (ESI) for $C_{12}H_{11}O_2S_2$ $[M+H]^+$ calcd. 251.0200, found 251.0210.

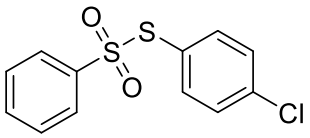
***S*-(4-fluorophenyl) benzenethiosulfonate (1b) [PMSA-JVW15]**



The general procedure C was applied using sodium benzenesulfinate (1.325 g, 8.1 mmol, 3.2 equiv.), bis-(4-fluorophenyl) disulfide (0.637 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.266 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 1.5 hours. *S*-(4-fluorophenyl) benzenethiosulfonate was obtained in 88% (1.184 g) yield. The spectral data are in accordance with literature.[1]

Orange solid, m.p.: 51-52 °C (literature 52-53 °C)[1], R_f = 0.43 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 3H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 2H), 7.02 (t, J = 8.6 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.0 (d, $J_{C\text{-}F}$ = 254.0 Hz, C), 143.0 (CH), 139.0 (d, $J_{C\text{-}F}$ = 9.1 Hz, CH), 134.0 (C), 129.1 (CH), 127.8 (CH), 123.6 (d, $J_{C\text{-}F}$ = 3.4 Hz, C), 117.0 (d, $J_{C\text{-}F}$ = 22.3 Hz, CH) ppm. HRMS (ESI) for $C_{12}H_{10}FO_2S_2$ $[M+H]^+$ calcd. 269.0101, found 269.0109.

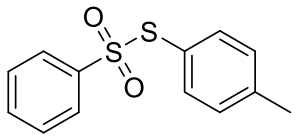
***S*-(4-chlorophenyl) benzenethiosulfonate (1c) [PMSA-JVW10]**



The general procedure C was applied using sodium benzenesulfinate (1.318 g, 8.0 mmol, 3.2 equiv.), bis-(4-chlorophenyl) disulfide (0.719 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.266 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 3 hours. The product was purified by an automated flash chromatography system using a Heptane / Acetone gradient (from 100% Heptane to 50% Acetone, 25 mL/min). *S*-(4-chlorophenyl) benzenethiosulfonate was obtained in 68% (0.975 g) yield. No spectral data are reported in literature.

Yellow crystals, m.p.: 68-69 °C, Rf = 0.46 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61-7.58 (m, 3H), 7.47-7.43 (m, 2H), 7.33-7.27 (m, 4H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.1(C), 138.5 (C), 137.9 (CH), 134.0 (CH), 129.9 (CH), 129.1 (CH), 127.7 (CH), 126.5 (C) ppm. HRMS (ESI) for $C_{12}H_9ClO_2S_2Na$ $[M+Na]^+$ calcd. 306.9630, found 306.9632.

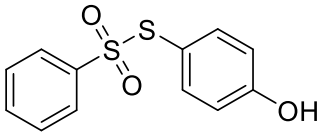
***S*-(4-methylphenyl) benzenethiosulfonate (1d) [PMSA-JVW26]**



The general procedure B was applied using sodium benzenesulfinate (1.645 g, 10.0 mmol, 4.0 equiv.), bis(*p*-tolyl)disulfide (620 mg, 2.5 mmol, 1.0 equiv.) and *N*-bromosuccinimide (893 mg, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 23 hours. The compound was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 10% EtOAc, 25 mL/min). *S*-(4-methylphenyl) benzenethiosulfonate was obtained in 69% (915 mg) yield. The spectral data are in accordance with literature.[4]

White solid, m.p.: 51-52 °C (literature 52-53°C)[1], Rf = 0.62 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.56 (m, 3H), 7.45-7.41 (m, 2H), 7.24-7.21 (m, 2H), 7.15-7.13 (m, 2H), 2.38 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 143.2 (C), 142.3 (C), 136.6 (CH), 133.7 (CH), 130.4(CH), 128.9 (CH), 127.7 (CH), 124.5 (C), 21.6 (CH_3) ppm. HRMS (ESI) for $C_{13}H_{13}O_2S_2$ $[M+H]^+$ calcd. 265.0351, found 265.0354.

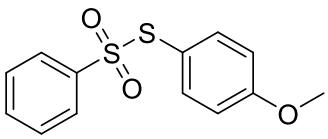
***S*-(4-hydroxyphenyl) benzenethiosulfonate (1e) [PMSA751]**



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), 4,4'-dithiodiphenol (626 mg, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 5.5 hours. The product was purified by an automated flash chromatography system using a Heptane / Acetone gradient (from 100% Heptane to 50% Acetone, 25 mL/min). *S*-(4-hydroxyphenyl) benzenethiosulfonate was obtained in 29% (381 mg) yield. No spectroscopic data are available in literature.

White solid, m.p.: 117-118 °C, R_f = 0.55 in Heptane / Acetone (1:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.62-7.55 (m, 3H), 7.47-7.41 (m, 2H), 7.24-7.19 (m, 2H)†, 6.81-6.71 (m, 2H)†, 5.41 (s, 1H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 158.9 (C), 143.1 (C), 138.8 (CH), 133.8 (CH), 129.0 (CH), 127.7 (CH), 118.8 (C), 116.8 (CH) ppm. HRMS (ESI) for $C_{12}H_{11}O_3S_2$ $[M+H]^+$ calcd. 267.0144, found 267.0151.

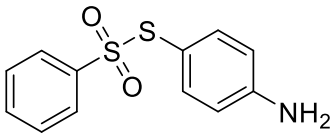
***S*-(4-methoxyphenyl) benzenethiosulfonate (1f) [PMSA-JVW07]**



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), 1,1'-disulfanediylbis(4-methoxybenzene) (**6f**, 0.697 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 3 hours. *S*-(4-methoxyphenyl) benzenethiosulfonate was obtained in 98% (1.373 g) yield. No spectroscopic data are available in literature.

Brown solid, m.p.: 57-58 °C, R_f = 0.34 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59-7.55 (m, 3H), 7.45-7.41 (m, 2H), 7.27-7.23 (m, 2H)†, 6.85-6.82 (m, 2H) †, 3.82 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 162.5 (C), 143.2 (C), 138.5 (CH), 133.6 (CH), 128.9 (CH), 127.7 (CH), 118.7 (C), 115.1 (CH), 55.6 (CH_3) ppm. HRMS (ESI) for $C_{13}H_{13}O_3S_2$ $[M+H]^+$ calcd. 281.0301, found 281.0316.

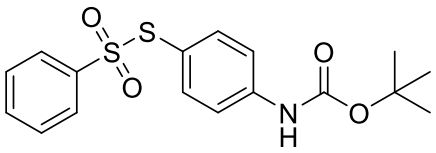
_S_-(4-aminophenyl) benzenethiosulfonate (1g) [PMSA747]



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), 4-aminophenyl disulfide (621 mg, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 6 hours. *S*-(4-aminophenyl) benzenethiosulfonate was obtained in 87% (1.156 g) yield. No spectroscopic data are available in literature.

Brown solid, m.p.: 128-129 °C, R_f = 0.48 in Heptane / EtOAc / NEt_3 (50:50:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64-7.52 (m, 3H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H)†, 6.56 (d, *J* = 8.6 Hz, 2H)†, 3.65 (br s, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 149.9 (C), 143.3 (C), 138.5 (CH), 133.5 (CH), 128.9 (CH), 127.8 (CH), 115.4 (CH), 114.9 (C) ppm. HRMS (ESI) for $C_{12}H_{12}NO_2S_2$ $[M+H]^+$ calcd. 266.0304, found 266.0297.

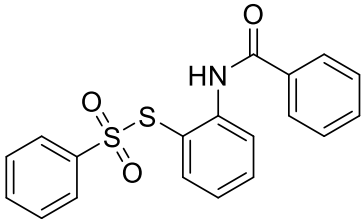
_S_-(4-(*tert*-butoxycarbonylamino)phenyl) benzenethiosulfonate (1h) [PMSA799/805]



The general procedure C was applied using sodium benzenesulfinate (657 mg, 4.0 mmol, 3.2 equiv.), Di-*tert*-butyl [disulfanediyldi(4,1-phenylene)]biscarbamate (**6h**, 561 mg, 1.25 mmol, 1.0 equiv.) and I_2 (635 mg, 2.5 mmol, 2.0 equiv.). The mixture was stirred for 15 hours. *S*-(4-(*tert*-butoxycarbonylamino)phenyl) benzenethiosulfonate was obtained in 64% (582 mg) yield. No spectroscopic data are available in literature.

Off-white solid, m.p.: 162-163 °C, R_f = 0.50 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.55 (m, 3H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.7 Hz, 2H), 7.25 (d, *J* = 8.7 Hz, 2H), 6.67 (br s, 1H), 1.52 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 152.3 (C), 143.3 (C), 141.9 (C), 137.8 (CH), 133.7 (C), 129.0 (CH), 127.7 (CH), 120.8 (CH), 118.7 (CH), 81.5 (C), 28.4 (CH_3) ppm. HRMS (ESI) for $C_{17}H_{20}NO_4S_2$ $[M+H]^+$ calcd. 366.0828, found 366.0827.

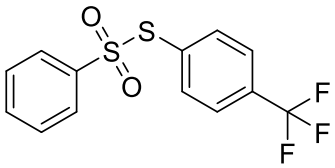
_S_-(2-benzamidophenyl) benzenethiosulfonate (1i) [PMSA748]



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), 2,2'-dibenzamidodiphenyl disulfide (1.141 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 4.5 hours. *S*-(2-benzamidophenyl) benzenethiosulfonate was obtained in 94% (1.744 g) yield. No spectroscopic data are available in literature.

Off-white solid, m.p.: 156-157 °C, R_f = 0.34 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.07 (s, 1H), 8.51 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.91-7.86 (m, 2H), 7.61-7.47 (m, 7H), 7.34 (m, 2H), 7.13 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.00 (td, *J* = 7.6, 1.3 Hz, 1H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.2 (C), 142.1(C), 141.4 (C), 138.4 (CH), 134.4 (CH), 134.3 (C), 133.8 (CH), 132.4 (CH), 129.2 (CH), 129.0 (CH), 127.7 (CH), 127.4 (CH), 124.8 (CH), 122.5 (CH), 116.9 (C) ppm. HRMS (ESI) for $C_{19}H_{16}NO_3S_2$ $[M+H]^+$ calcd. 370.0566, found 370.0580.

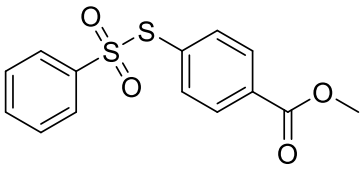
***S*-(4-(trifluoromethyl)phenyl) benzenethiosulfonate (1j) [PMSA804]**



The general procedure C was applied using sodium benzenesulfinate (788 mg, 4.80 mmol, 3.2 equiv.), 1,1'-disulfanediylbis[(4-(trifluoromethyl)benzene] (**6j**, 532 mg, 1.5 mmol, 1.0 equiv.) and I_2 (761 mg, 3.0 mmol, 2.0 equiv.). The mixture was stirred for 25 hours. *S*-(4-(trifluoromethyl)phenyl) benzenethiosulfonate was obtained in 58% (556 mg) yield. No spectroscopic data are available in literature.

Colorless oil, R_f = 0.31 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 5H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.45 (t, *J* = 7.8 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 148.1 (C), 136.7 (CH), 134.2 (CH), 133.4 (q, J_{C-F}= 33.1 Hz, C), 132.5 (C), 129.2 (CH), 127.7 (CH), 126.4 (q, J_{C-F}= 3.7 Hz, CH), 123.6 (q, J_{C-F}= 272.7 Hz, C) ppm. HRMS (ESI) for $C_{13}H_{10}F_3O_2S_2$ $[M+H]^+$ calcd. 319.0069, found 319.0077.

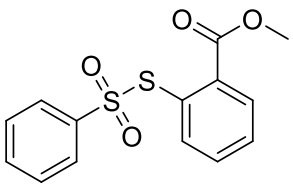
Methyl 4-[(benzenesulfonyl)sulfanyl]benzoate (1k) [PMSA813]



The general procedure C was applied using sodium benzenesulfinate (0.368 g, 2.24 mmol, 3.2 equiv.), dimethyl 4,4'-disulfanediyldibenzoate (0.234 g, 0.7 mmol, 1.0 equiv.) and I_2 (0.355 g, 1.4 mmol, 2.0 equiv.). The mixture was stirred for 25 hours. Methyl 4-[(benzenesulfonyl)sulfanyl]benzoate was obtained in 44% (190 mg) yield. No spectroscopic data are available in literature.

White solid, m.p.: 86-87 °C, R_f = 0.51 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.00-7.87 (m, 2H)†, 7.61-7.57 (m, 3H), 7.46-7.41 (m, 4H), 3.94 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.2 (C), 143.2 (C), 136.4 (CH), 134.1 (CH), 133.2 (C), 132.8 (C), 130.5 (CH), 129.1 (CH), 127.7 (CH), 52.7 (CH_3) ppm. HRMS (ESI) for $C_{14}H_{13}O_4S_2$ $[M+H]^+$ calcd. 309.0250, found 309.0247.

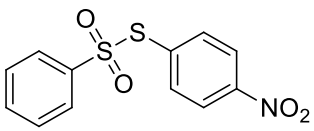
Methyl 2-[(benzenesulfonyl)sulfanyl]benzoate (1l) [PMSA757]



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), dimethyl 2,2'-disulfanediyldibenzoate (**6l**, 0.836 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 21 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 10% EtOAc, 25 mL/min). Methyl 2-[(benzenesulfonyl)sulfanyl]benzoate was obtained in 70% (1.084 g) yield. No spectroscopic data are available in literature.

Yellow oil, R_f = 0.11 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.76-7.66 (m, 2H), 7.58-7.47 (m, 5H), 7.43-7.34 (m, 2H), 3.70 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.3 (C), 143.5 (C), 138.6 (CH), 136.3 (C), 133.8 (CH), 132.2 (CH), 131.1 (CH), 130.9 (CH), 129.0 (CH_2), 127.8 (C), 127.5 (CH), 52.5 (CH_3) ppm. HRMS (ESI) for $C_{14}H_{12}O_4S_2Na$ $[M+Na]^+$ calcd. 331.0075, found 331.0081.

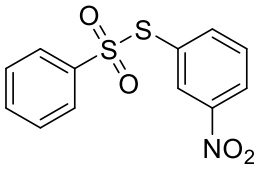
***S*-(4-nitrophenyl) benzenethiosulfonate (1m) (PMSA572)**



The general procedure C was applied using sodium benzenesulfinate (1.051 g, 6.4 mmol, 3.2 equiv.), di-(4-nitrophenyl)disulfide (0.617 g, 2.0 mmol, 1.0 equiv.) and I_2 (1.015 g, 4.0 mmol, 2.0 equiv.) The mixture was stirred for 6 hours. The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 60% CH_2Cl_2, 25 mL/min). *S*-(4-nitrophenyl) benzenethiosulfonate was obtained in 52% (612 mg) yield. No spectroscopic data are available in literature.

White solid, m.p.: 106-107 °C, R_f = 0.27 in Heptane / CH_2Cl_2 (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.33 (dd, *J* = 8.3, 1.1 Hz, 1H), 8.08 (t, *J* = 1.8 Hz, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.65-7.57 (m, 4H), 7.47 (t, *J* = 7.8 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.8 (C), 142.5 (C), 134.5 (CH), 131.0 (CH), 130.5 (C), 129.4 (CH), 127.7 (CH), 126.2 (CH) ppm. HRMS (ESI) for $C_{12}H_{10}NO_4S_2$ $[M+H]^+$ calcd. 296.0046, found 296.0064.

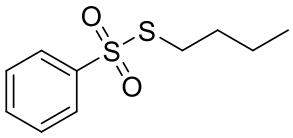
_S_-(3-nitrophenyl) benzenethiosulfonate (1n) [PMSA362, PMSA555]



The general procedure B was applied using sodium benzenesulfinate (3.940 g, 24.0 mmol, 4.0 equiv.), bis-(3-nitrophenyl)disulfide (1.850 g, 6.0 mmol, 1.0 equiv.) and *N*-bromosuccinimide (2.136 g, 12.0 mmol, 2.0 equiv.). The mixture was stirred for 22 hours. The product was purified by an automated flash chromatography system using a Heptane / Acetone gradient (from 100% Heptane to 10% Acetone, 25 mL/min). *S*-(3-nitrophenyl) benzenethiosulfonate was obtained in 86% (3.06 g) yield. No spectroscopic data are available in literature.

Yellow solid, m.p: 99-100 °C, R_f = 0.25 in Heptane / Acetone (4:1), ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.42 (ddd, *J* = 8.0, 2.3, 1.2 Hz, 1H), 8.01 (t, *J* = 1.9 Hz, 1H), 7.83-7.73 (m, 3H), 7.60-7.56 (m, 4H) ppm. ^{13}C-NMR (101 MHz, DMSO-d_6): δ 147.8 (C), 142.4 (CH), 141.5 (C), 134.9 (CH), 131.3 (CH), 130.2 (CH), 129.7 (CH), 129.0 (C), 127.3 (CH), 126.5 (CH) ppm. HRMS (ESI) for $C_{12}H_{10}NO_4S_2$ $[M+H]^+$ calcd. 296.0046, found 296.0049.

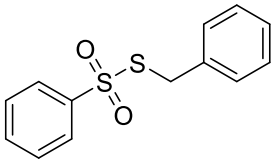
_S_-butyl benzenethiosulfonate (1p) [PMSA-JVW16]



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), dibutyldisulfide (446 mg, 2.5 mmol, 1.0 equiv.) and I_2 (1.272 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 3 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-butyl benzenethiosulfonate was obtained in 81% (938 mg) yield. No spectroscopic data are available in literature.

Colorless oil, R_f = 0.48 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95-7.93 (m, 2H), 7.65-7.61 (m, 1H), 7.57-7.54 (m, 2H), 3.01 (t, *J* = 7.0 Hz, 2H), 1.60-1.54 (m, 2H), 1.36-1.29 (m, 2H), 0.85 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 145.2 (C), 133.7 (CH), 129.4 (CH), 127.1 (CH), 35.9 (CH_2), 30.8 (CH_2), 21.8 (CH_2), 13.5 (CH_3) ppm. HRMS (ESI) for $C_{10}H_{15}O_2S_2$ $[M+H]^+$ calcd. 231.0508, found 231.0515.

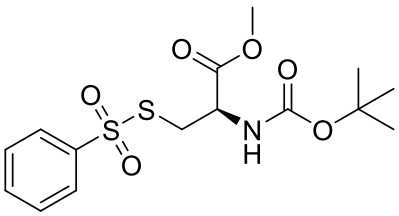
_S_-benzyl benzenethiosulfonate (1q) [PMSA-JVW31]



The general procedure B was applied using sodium benzenesulfinate (1.667 g, 10.0 mmol, 4.0 equiv.), dibenzyldisulfide (0.622 g, 2.5 mmol, 1.0 equiv.) and *N*-bromosuccinimide (0.890 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 17 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 5% EtOAc, 25 mL/min). *S*-benzyl benzenethiosulfonate was obtained in 77% (1.024 g) yield. Spectroscopic data are in accordance with literature.[34]

White solid, m.p.: 41-42 °C (literature 39-41 °C)[34], R_f = 0.45 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85-7.82 (m, 2H), 7.59 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.50-7.46 (m, 2H), 7.24-7.16 (m, 5H), 4.27 (s, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 145.0 (C), 133.7 (C), 133.7 (CH), 129.3 (CH), 129.2 (CH), 128.9 (CH), 128.2 (CH), 127.0 (CH), 40.5 (CH_2) ppm. HRMS (ESI) for $C_{13}H_{12}O_2S_2Na$ $[M+H]^+$ calcd. 287.0176, found 287.0187.

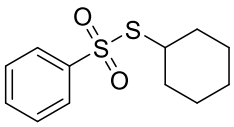
(*2R*)-*S*-2-(*tert*-butoxycarbonyl)amino-2-methoxycarbonylethyl benzenethiosulfonate (1r) [PMSA741]



The general procedure C was applied using sodium benzenesulfinate (1.051 g, 6.4 mmol, 3.2 equiv.), dimethyl *N,N'*-bis(*tert*-butoxycarbonyl)-*L*-cystinate (**6r**, 0.937 g, 2.0 mmol, 1.0 equiv.) and I_2 (1.015 g, 4.0 mmol, 2.0 equiv.). The mixture was stirred for 18 hours. (*2R*)-*S*-2-(*tert*-butoxycarbonyl)amino-2-methoxycarbonylethyl benzenethiosulfonate was obtained in 92% (1.384 g) yield. The spectroscopic data are in accordance with literature.[35]

Yellow solid, m.p.: 71-72 °C, R_f = 0.49 in Heptane / EtOAc (1:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95-7.92 (m, 2H), 7.68-7.62 (m, 1H), 7.60-7.55 (m, 2H), 5.29 (s, 1H), 4.56 (br s, 1H), 3.74 (s, 3H), 3.54 (dd, *J* = 13.8, 5.0 Hz, 1H), 3.42 (dd, *J* = 13.8, 5.3 Hz, 1H), 1.44 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.3 (C), 155.1 (C), 144.7 (C), 134.1 (CH), 129.6 (CH), 127.3 (CH), 80.8 (C), 53.1(CH_3), 53.0(CH), 38.0 (CH_2), 28.4 (CH_3) ppm. HRMS (ESI) for $C_{15}H_{22}NO_6S_2$ $[M+H]^+$ calcd. 376.0883, found 376.0902.

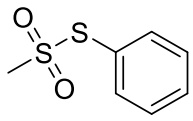
***S*-cylohexyl benzenethiosulfonate (1s) [PMSA944]**



The general procedure C was applied using sodium benzenesulfinate (1.313 g, 8.0 mmol, 3.2 equiv.), dicylcohexyldisulfide (551 µL, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 22 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 10% EtOAc, 25 mL/min). *S*-cyclohexyl benzenethiosulfonate was obtained in 90% (1.152 g) yield. Spectroscopic data are in accordance with literature.[1]

Colorless oil, R_f = 0.29 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 7.3 Hz, 2H), 7.62 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 1.93-1.90 (m, 2H), 1.67-1.63 (m, 2H), 1.50-1.23 (m, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 146.0 (C), 133.6 (CH), 129.4 (CH), 127.0 (CH), 50.6 (CH_2), 33.6 (CH_2), 25.8 (CH), 25.3 (CH_2) ppm. HRMS (ESI) for $C_{12}H_{17}O_2S_2$ $[M+H]^+$ calcd. 257.0664, found 257.0674.

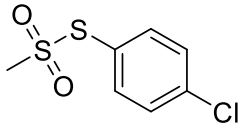
***S*-phenyl methanethiosulfonate (1t) [JVW04b]**



The general procedure C was applied using sodium methanesulfinate (0.817 g, 8.0 mmol, 3.2 equiv.), diphenyldisulfide (0.549 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 44 hours. The product was purified by an automated flash chromatography system using a Heptane / Acetone gradient (from 100% Heptane to 20% Acetone, 25 mL/min). *S*-phenyl methanethiosulfonate was obtained in 29% (0.272 g) yield. No spectroscopic data are available in literature.

Yellow solid, m.p.: 82-83 °C, R_f = 0.36 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73-7.71 (m, 2H), 7.57-7.53 (m, 1H), 7.51-7.47 (m, 2H), 3.18 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 136.4 (CH), 131.8 (CH), 130.1 (CH), 128.2 (C), 47.6 (CH_3) ppm. HRMS (ESI) for $C_7H_9O_2S_2$ $[M+H]^+$ calcd. 189.0038, found 189.0051.

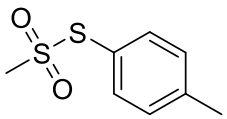
***S*-(4-chlorophenyl) methanethiosulfonate (1u) (TIO-001)**



The general procedure B was applied using sodium methanesulfinate (817 mg, 8.0 mmol, 4.0 equiv.), bis-(*p*-chlorophenyl)disulfide (574 mg, 1.0 mmol, 1.0 equiv.) and *N*-bromosuccinimide (712 mg, 2.0 mmol, 2.0 equiv.) for 24 hours. The compound was purified by flash column chromatography with Heptane / Acetone (9:1) as eluent. A second purification was done with Heptane / CH_2Cl_2 (7:3). *S*-(4-chlorophenyl) methanethiosulfonate was obtained in 30% (265 mg) yield. The spectroscopic data are in accordance with literature.[32]

White solid, m.p.: 100-102 °C (lit. 100-102°C)[32], R_f = 0.18 in Heptane / Acetone (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.66-7.63 (m, 2H)†, 7.48-7.44 (m, 2H)†, 3.19 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 138.7 (C), 137.5 (CH), 130.4 (CH), 126.5(C), 47.8 (CH_3) ppm. HRMS (ESI) for $C_7H_7ClO_2S_2Na$ $[M+Na]^+$ calcd. 244.9474, found 244.9462.

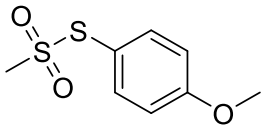
_S_-(4-methylphenyl) methanethiosulfonate (1v) [PMSA-JVW18]



The general procedure C was applied using sodium methanesulfinate (0.817 g, 8.0 mmol, 3.2 equiv.), bis(4-methylphenyl)disulfide (0.549 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 44 hours. The product was purified by an automated flash chromatography system using a Heptane / Acetone gradient (from 100% Heptane to 20% Acetone, 25 mL/min). *S*-(4-methylphenyl) methanethiosulfonate was obtained in 29% (0.272 g) yield. The spectroscopic data are in accordance with literature.[4]

Yellow solid, m.p.: 46-47 °C, R_f = 0.36 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 3.16 (s, 3H), 2.41 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 142.6 (C), 136.3 (CH), 130.8 (CH), 124.7 (C), 47.3 (CH_3), 21.6 (CH_3) ppm. HRMS (ESI) for $C_8H_{10}O_2S_2Na$ $[M+Na]^+$ calcd. 225.0020, found 225.0029.

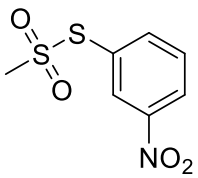
_S_-(4-methoxyphenyl) methanethiosulfonate (1w) [PMSA566b]



The general procedure C was applied using sodium methanesulfinate (0.817 g, 8.0 mmol, 3.2 equiv.), bis(4-methoxyphenyl)disulfide (12i, 0.696 g, 2.5 mmol, 1.0 equiv.) and I_2 (1.269 g, 5.0 mmol, 2.0 equiv.). The mixture was stirred for 20 hours. *S*-(4-methoxyphenyl) methanethiosulfonate was obtained in 54% (0.590 g) yield. The spectroscopic data are in accordance with literature.[1]

Red oil, R_f = 0.27 in Heptane / CH_2Cl_2 (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.64-7.60 (m, 2H)†, 7.00-6.96 (m, 2H)†, 3.86 (s, 3H), 3.15 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 162.7 (C), 138.2 (CH), 118.8 (C), 115.6 (CH), 55.7 (CH_3), 47.1 (CH_3) ppm. HRMS (ESI) for $C_8H_{11}O_3S_2$ $[M+H]^+$ calcd. 219.0144, found 219.0156.

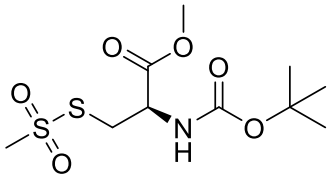
_S_-(3-nitrophenyl) methanethiosulfonate (1x) [PMSA571]



The general procedure B was applied using sodium methanesulfinate (817 mg, 8 mmol, 4 equiv.), bis-(3-nitrophenyl)disulfide (617 mg, 2.0 mmol, 1.0 equiv.) and *N*-bromosuccinimide (712 mg, 4.0 mmol, 2.0 equiv.). The mixture was stirred for 22 hours. The product was purified by an automated flash chromatography applying a Heptane / Acetone gradient (from 100% Heptane to 10% Acetone, 25 mL/min). *S*-(3-nitrophenyl) methanethiosulfonate was obtained in 59% (547 mg) yield. No spectroscopic data are reported in literature.

Yellow oil, R_f = 0.33 in Heptane / Acetone (2:1), ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.50 (t, *J* = 2.0 Hz, 1H), 8.48-8.44 (m, 1H), 8.18-8.16 (m, 1H), 7.85 (t, *J* = 8.0 Hz, 1H), 3.50 (s, 3H) ppm. ^{13}C-NMR (101 MHz, DMSO-d_6): δ 148.2 (C), 142.3 (CH), 131.3 (CH), 130.3 (CH), 129.4 (C), 126.2 (CH), 48.5 (CH_3) ppm. HRMS (ESI) for $C_7H_8NO_4S_2$ $[M+H]^+$ calcd. 233.9889, found 233.9901.

(*2R*)-*S*-2-(*tert*-butoxycarbonyl)amino-2-methoxycarbonylethyl methanethiosulfonate (1y) [PMSA740]



The general procedure C was applied using sodium methanesulfinate (0.853 g, 6.4 mmol, 3.2 equiv.), dimethyl *N,N'*-bis(tert-butoxycarbonyl)-*L*-cystinate (**6r**, 0.937 g, 2.0 mmol, 1.0 equiv.) and I_2 (1.015 g, 4.0 mmol, 2.0 equiv.). The mixture was stirred for 18 hours. (*2R*)-*S*-2-(*tert*-butoxycarbonyl)amino-2-methoxycarbonylethyl methanethiosulfonate was obtained in 82% (1.024 g) yield. No spectroscopic data are reported in literature.

Yellow solid, m.p.: 71-72 °C, R_f = 0.49 in Heptane / EtOAc (1:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.38 (br s, 1H), 4.62 (br s, 1H), 3.79 (s, 3H), 3.76-3.70 (m, 1H), 3.53 (dd, *J* = 14.4, 6.0 Hz, 1H), 3.37 (s, 3H), 1.45 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 170.4 (C), 155.1 (C), 80.9 (C), 53.4 (CH), 53.1 (CH_3), 51.0 (CH_3), 38.7 (CH_2), 28.4 (CH_3) ppm. HRMS (ESI) for $C_{10}H_{20}NO_6S_2$ $[M+H]^+$ calcd. 314.0727, found 314.0745.

7.4 Synthesis of thiocarbamates

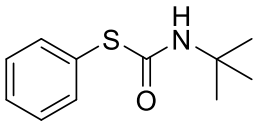
General procedure D:

A 10 mL round-bottom flask was charged with sodium iodide (7.5 mg, 0.05 mmol, 5 mol %), *S*-aryl/alkyl benzenethiosulfonate (1.0 mmol, 1.0 equiv.), isocyanide (1.2 mmol, 1.2 equiv.) and isopropanol (0.5 mL, 6.5 mmol, 6.5 equiv.). The reaction mixture was stirred under air in a preheated oil bath at 30 °C for 4 hours. Subsequently, the solvent was removed under reduced pressure and the product was purified by an automated flash chromatography system using silica cartridges and the eluent indicated below.

General procedure E:

A 10 mL round-bottom flask was charged with sodium iodide (7.5 mg, 0.05 mmol, 5 mol %), *S*-aryl/alkyl methanethiosulfonate (1.0 mmol, 1.0 equiv.), isocyanide (1.2 mmol, 1.2 equiv.), and isopropanol (0.5 mL, 6.5 mmol, 6.5 equiv.). The reaction mixture was stirred under air in a preheated oil bath at 40 °C for 6 hours. Subsequently, the solvent was removed under reduced pressure and the product was filtered through a plug of silica using EtOAc (50mL) as eluent. The solvent was removed solvent was removed under reduced pressure to obtain the desired thiocarbamate.

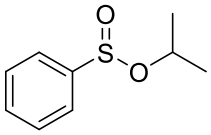
***S*-phenyl *tert*-butylthiocarbamate (3a) [PMSA702]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 20% CH_2Cl_2, 25 mL/min). *S*-phenyl *tert*-butylthiocarbamate was obtained in 97% (204 mg) yield. If general procedure E was applied with **1t** as thiosulfonate, **3a** was obtained in 98% (170 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 114-115 °C (lit. 115 °C)[36], R_f = 0.49 in Heptane / CH_2Cl_2 (1:2), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55-7.52 (m, 2H), 7.40-7.39 (m, 3H), 5.18 (br s, 1H), 1.32 (s, 9H). ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.1 (C), 135.5 (CH), 129.4 (CH), 129.4 (CH), 129.3 (C), 53.6 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{16}NOS$ $[M+H]^+$ calcd. 210.0947, found 210.0956.

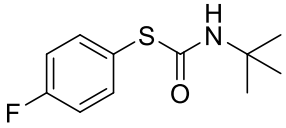
Isopropyl benzenesulfinate (4a) [PMSA724]



This compound was isolated together with compound **3a** in 92% (170 mg) yield. No spectral data are reported in literature.

Yellow oil, R_f = 0.31 in Heptane / CH_2Cl_2 (1:2), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.73–7.71 (m, 2H), 7.54-7.51 (m, 3H), 4.62 (hp, *J* = 6.2 Hz, 1H), 1.39 (d, *J* = 6.2 Hz, 3H), 1.25 (d, *J* = 6.2 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 145.9 (C), 132.0 (CH), 129.1 (CH), 125.2 (CH), 73.1 (C), 24.1 (CH_3), 23.9 (CH_3) ppm. HRMS (ESI) for $C_9H_{13}O_2S$ $[M+H]^+$ calcd. 185.0631, found 185.0637.

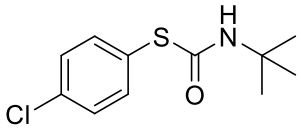
***S*-(4-fluorophenyl) *tert*-butylthiocarbamate (3b) [PMSA721]**



The general procedure D was applied using *S*-(4-fluorophenyl) benzenethiosulfonate (**1b**, 268 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 20% CH_2Cl_2, 25 mL/min). *S*-(4-fluorophenyl) *tert*-butylthiocarbamate was obtained in 95% (216 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 98-99 °C, R_f = 0.23 in Heptane / CH_2Cl_2 (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.0, 5.6 Hz, 2H), 7.08 (t, *J* = 8.5 Hz, 2H), 5.17 (br s, 1H), 1.34 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.8 (d, J_{C-F} = 1.3 Hz, C), 163.6 (d, J_{C-F} = 250.0 Hz, C), 137.6 (d, J_{C-F} = 8.6 Hz, CH), 124.5 (d, J_{C-F} = 3.5 Hz, C), 116.5 (d, J_{C-F} = 22.1 Hz, CH), 53.8 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{15}NOSF$ $[M+H]^+$ calcd. 228.0853, found 228.0855.

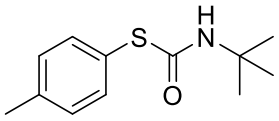
_S_-(4-chlorophenyl) _tert_-butylthiocarbamate (3c) [PMSA707]



The general procedure D was applied using *S*-(4-chlorophenyl) benzenethiosulfonate (**1c**, 285 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 20% CH_2Cl_2, 25 mL/min). *S*-(4-chlorophenyl) *tert*-butylthiocarbamate was obtained in 98% (239 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 66% (121 mg) yield. If general procedure E was applied with **1u** as thiosulfonate, **3c** was obtained in 99% (241 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 145-146 °C, R_f = 0.64 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.7 Hz, 2H)†, 7.36 (d, *J* = 8.7 Hz, 2H)†, 5.19 (br s, 1H), 1.35 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.3 (C), 136.7 (CH_3), 135.8 (C), 129.5 (CH_3), 127.7 (C), 53.9 (C), 29.1 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{15}NOSCl$ $[M+H]^+$ calcd. 244.0557, found 244.0563.

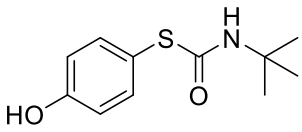
_S_-(4-methylphenyl) _tert_-butylthiocarbamate (3d) [PMSA708/739]



The general procedure D was applied using *S*-(4-methylphenyl) benzenethiosulfonate (**1d**, 264 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 30% CH_2Cl_2, 25 mL/min). *S*-(4-methylphenyl) *tert*-butylthiocarbamate was obtained in 91% (204 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 65% (120 mg) yield. If general procedure E was applied with **1v** as thiosulfonate, **3d** was obtained in 81% (180 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 116-117 °C (lit. 118 °C)[37], R_f = 0.28 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.1 Hz, 2H)†, 7.20 (d, *J* = 7.9 Hz, 2H)†, 5.16 (br s, 1H), 2.37 (s, 3H), 1.32 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.6 (C), 139.8 (C), 135.6 (CH), 130.2 (CH), 125.8 (C), 53.5 (C), 29.0 (CH_3), 21.5 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{18}NOS$ $[M+H]^+$ calcd. 224.1104, found 224.1117.

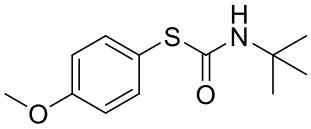
_S_-(4-hydroxyphenyl) _tert_-butylthiocarbamate (3e) [PMSA758]



The general procedure D was applied using *S*-(4-hydroxyphenyl) benzenethiosulfonate (**1e**, 266 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). *S*-(4-hydroxyphenyl) *tert*-butylthiocarbamate was obtained in 87% (195 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 84% (102 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 142-143 °C, R_f = 0.26 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31-7.27 (m, 2H), 6.95 (br s, 1H), 6.69-6.65 (m, 2H), 5.34 (br s, 1H), 1.35 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.1 (C), 158.1 (C), 137.5 (CH), 118.1 (CH), 117.0 (C), 53.8 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{16}NO_2S$ $[M+H]^+$ calcd. 226.0896, found 226.0909.

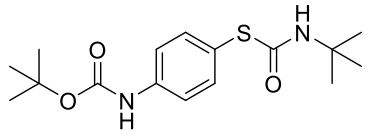
***S*-(4-methoxyphenyl) *tert*-butylthiocarbamate (3f) [PMSA706/711]**



The general procedure D was applied using *S*-(4-methoxyphenyl) benzenethiosulfonate (**1f**, 280 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-(4-methoxyphenyl) *tert*-butylthiocarbamate was obtained in 99% (237 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 87% (160 mg) yield. If general procedure E was applied with **1w** as thiosulfonate, **3f** was obtained in 99% (237 mg) yield. No spectroscopic data are reported in literature.

Off-white solid, m.p.: 83-84 °C, R_f = 0.17 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.8 Hz, 2H)†, 6.93 (d, *J* = 8.8 Hz, 2H)†, 5.15 (br s, 1H), 3.82 (s, 3H), 1.31 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.1 (C), 160.9 (C), 137.4 (CH), 120.1 (C), 115.1 (CH), 55.6 (CH_3), 53.5 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{18}NO_2S$ $[M+H]^+$ calcd. 240.1053, found 240.1056.

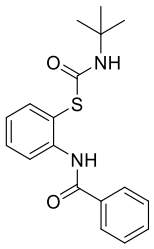
***Tert*-butyl (4-((*tert*-butylcarbamoyl)sulfanyl)phenyl)carbamate (3h) [PMSA800/819]**



The general procedure D was applied using *S*-(4-(*tert*-butoxycarbonyl)aminophenyl) benzenethiosulfonate (**1h**, 365 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 0.57 mmol, 1.2 equiv.). The reaction was stirred for 15 hours at 50 °C. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *Tert*-butyl [4-((*tert*-butylcarbamoyl)sulfanyl)phenyl]carbamate was obtained in 91% (304 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 81% (149 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 72-73 °C, R_f = 0.38 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.45-7.39 (m, 4H), 6.61 (br s, 1H), 5.15 (br s, 1H), 1.52 (s, 9H), 1.31 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.8 (C), 152.5 (C), 140.0 (C), 136.6 (CH), 122.5 (C), 119.0 (CH), 81.1 (C), 53.5 (C), 29.0 (CH_3), 28.5 (CH_3) ppm. HRMS (ESI) for $C_{16}H_{25}N_2O_3S$ $[M+H]^+$ calcd. 325.1580, found 325.1580.

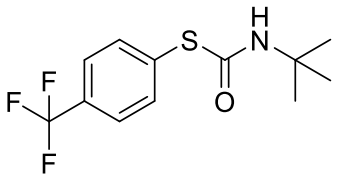
***S*-(2-benzamidophenyl)-*tert*-butylthiocarbamate (3i) [PMSA759]**



The general procedure D was applied using *S*-(2-benzamidophenyl) benzenethiosulfonate (**1i**, 369 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). The compound was repurified using the same eluent system. *S*-(2-benzamidophenyl) *tert*-butylthiocarbamate was obtained in 69% (226 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 75% (138 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 115-116 °C, R_f = 0.43 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.25 (s, 1H), 8.46 (d, *J* = 8.2 Hz, 1H), 7.95-7.93 (m, 2H), 7.57-7.46 (m, 5H), 7.16 (td, *J* = 7.6, 1.2 Hz, 1H), 5.39 (s, 1H), 1.30 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.4 (C), 163.2 (C), 140.6 (C), 136.6 (CH), 134.8 (C), 132.1 (CH), 131.8 (CH), 128.9 (CH), 127.4 (CH), 125.0 (CH), 122.9 (CH), 119.1 (C), 54.1 (C), 28.8 (CH_3) ppm. HRMS (ESI) for $C_{18}H_{21}N_2O_2S$ $[M+H]^+$ calcd. 329.1318, found 329.1314.

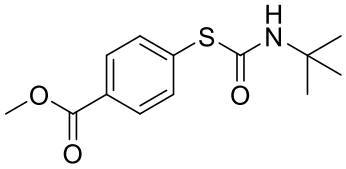
_S_-(4-(trifluoromethyl)phenyl) _tert_-butylthiocarbamate (3j) [PMSA808]



The general procedure D was applied using _S_-(4-trifluoromethylphenyl) benzenethiosulfonate (**1j**, 318 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 40% CH_2Cl_2, 25 mL/min). _S_-(4-(trifluoromethyl)phenyl) _tert_-butylthiocarbamate was obtained in 79% (219 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 114-115 °C, R_f = 0.21 in Heptane / CH_2Cl_2 (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.63 (m, 4H), 5.23 (br s, 1H), 1.37 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 162.4 (C), 135.2 (CH), 133.9 (C), 131.1 (q, J_{C-F} = 32.8 Hz, C), 125.9 (q, J_{C-F} = 3.7 Hz, CH), 124.0 (q, J_{C-F} = 272.3 Hz, C), 54.1 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{15}F_3NOS$ $[M+H]^+$ calcd. 278.0821, found 278.0818.

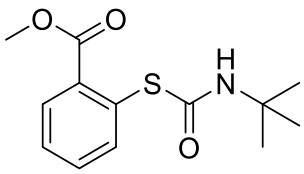
Methyl 4-((_tert_-butylcarbamoyl)sulfanyl)benzoate (3k) [PMSA815]



The general procedure D was applied using methyl 4-[(benzenesulfonyl)sulfanyl]benzoate (**1k**, 147 mg, 0.48 mmol, 1.0 equiv.), _tert_-butyl isocyanide (65 µL, 0.57 mmol, 1.2 equiv.) and sodium iodide (3.6 mg, 0.024 mmol, 5 mol %). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). Methyl 4-((_tert_-butylcarbamoyl)sulfanyl)benzoate was obtained in 82% (105 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 72% (133 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 101-102 °C, R_f = 0.12 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.03 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 5.23 (br s, 1H), 3.92 (s, 3H), 1.36 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.6 (C), 162.5 (C), 135.1 (C), 134.6 (CH), 130.6 (C), 130.2 (CH), 54.0 (C), 52.4 (CH_3), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{13}H_{18}NO_3S$ $[M+H]^+$ calcd. 268.1002, found 268.0995.

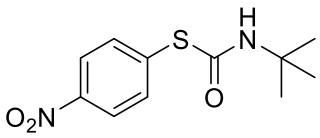
Methyl 2-(_tert_-butylcarbamoyl)sulfanyl)benzoate (3l) [PMSA760]



The general procedure D was applied using methyl 2-[(benzenesulfonyl)sulfanyl]benzoate (**1l**, 308 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). Methyl 2-(_tert_-butylcarbamoyl)thio)benzoate was obtained in 86% (231 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 91% (167 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 97-98 °C, R_f = 0.26 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (dd, J = 7.7, 1.5 Hz, 1H), 7.67 (dd, J = 7.8, 1.0 Hz, 1H), 7.48 (td, J = 7.6, 1.6 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 5.35 (br s, 1H), 3.89 (s, 3H), 1.34 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 167.3 (C), 163.2 (C), 136.6 (CH), 134.4 (C), 131.8 (CH), 130.7 (CH), 130.2 (C), 128.7 (CH), 53.8 (C), 52.4 (CH_3), 28.9 (CH_3) ppm. HRMS (ESI) for $C_{13}H_{18}NO_3S$ $[M+H]^+$ calcd. 268.1002, found 268.0995.

_S_-(4-nitrophenyl) _tert_-butylthiocarbamate (3m) [PMSA782]

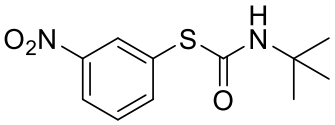


The general procedure D was applied using _S_-(4-nitrophenyl) benzenethiosulfonate (**1m**, 295 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). The product was repurified by automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 50% CH_2Cl_2, 25 mL/min). _S_-(4-nitrophenyl) _tert_-butylthiocarbamate was ob-

tained in 48% (122 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 69% (127 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 129-130 °C, R_f = 0.48 in Heptane / CH_2Cl_2 (1:2), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.22-8.19 (m, 2H), 7.70-7.66 (m, 2H), 5.29 (br s, 1H), 1.38 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 161.2 (C), 147.9 (C), 138.1 (C), 134.9 (CH), 123.9 (CH), 54.3 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{15}N_2O_3S$ $[M+H]^+$ calcd. 255.0798, found 255.0806.

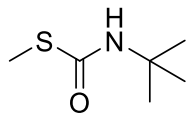
***S*-(3-nitrophenyl) *tert*-butylthiocarbamate (3n) [PMSA722/735]**



The general procedure D was applied using *S*-(3-nitrophenyl) benzenethiosulfonate (**1n**, 295 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). The product was repurified by automated flash chromatography system using a Heptane / CH_2Cl_2 gradient (from 100% Heptane to 50% CH_2Cl_2, 25 mL/min). *S*-(3-nitrophenyl) *tert*-butylthiocarbamate was obtained in 41% (105 mg) yield. If general procedure E was applied with **1x** as thiosulfonate, **3n** was obtained in 69% (175 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 40% (74 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 107-108 °C, R_f = 0.06 in Heptane / CH_2Cl_2 (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.37 (t, *J* = 1.9 Hz, 1H), 8.23 (ddd, *J* = 8.3, 2.2, 1.0 Hz, 1H), 7.85-7.83 (m, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 5.26 (br s, 1H), 1.38 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 161.8 (C), 148.5 (C), 141.1 (CH), 131.6 (C), 129.8 (CH), 129.7 (CH), 123.9 (CH), 54.3 (C), 29.0 (CH_3) ppm. HRMS (ESI) for $C_{11}H_{15}N_2O_3S$ $[M+H]^+$ calcd. 255.0798, found 255.0791.

***S*-methyl tert-butylthiocarbamate (3o) [PMSA737/862a]**

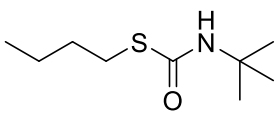


The general procedure E was applied using *S*-methyl methanethiosulfonate (94 µL, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The reaction mixture was stirred at 50 °C for 15 hours. *S*-methyl *tert*-butylthiocarbamate was obtained in 92% (136 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 85-86 °C (lit. 88 °C)[37], R_f = 0.36 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.17 (br s, 1H), 2.30 (s, 3H), 1.35 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.0 (C), 53.3 (C), 29.1 (CH_3), 12.5 (CH_3) ppm. HRMS (ESI) for $C_6H_{14}NOS$ $[M+H]^+$ calcd. 148.0791, found 148.0792.

Remark: The product was visualized on TLC via staining with $KMnO_4$.

***S*-butyl *tert*-butylthiocarbamate (3p) [PMSA715]**

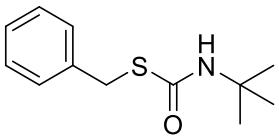


The general procedure D was applied using *S*-butyl benzenethiosulfonate (**1p**, 230 mg, 1.0 mmol, 1.0 equiv.) and *tert*-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-butyl *tert*-butylthiocarbamate was obtained in 81% (154 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 89% (174 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 42-43 °C, R_f = 0.50 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.12 (br s, 1H), 2.85 (t, *J* = 7.3 Hz, 2H), 1.60-1.55 (m, 2H), 1.44-1.36 (m, 2H), 1.35 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.7 (C), 53.3 (C), 32.8 (CH_2), 29.9 (CH_2), 29.2 (CH_3), 22.1 (CH_2), 13.8 (CH_3) ppm. HRMS (ESI) for $C_9H_{20}NOS$ $[M+H]^+$ calcd. 190.1260, found 190.1261.

Remark: The product was visualized on TLC via staining with $KMnO_4$.

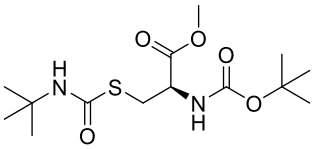
_S_-benzyl _tert_-butylthiocarbamate (3q) [PMSA720]



The general procedure D was applied using _S_-benzyl benzenethiosulfonate (**1q**, 264 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). _S_-benzyl _tert_-butylthiocarbamate was obtained in 88% (197 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 82% (157 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 74-75 °C, R_f = 0.38 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.31- 7.21 (m, 5H), 5.12 (br s, 1H), 4.11 (s, 2H), 1.36 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.9 (C), 138.7 (C), 129.0 (CH), 128.7 (CH), 127.2 (CH), 53.5 (C), 34.4 (CH_2), 29.1 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{18}NOS$ $[M+H]^+$ calcd. 224.1104, found 224.1110.
Remark: The product was visualized on TLC via staining with $KMnO_4$.

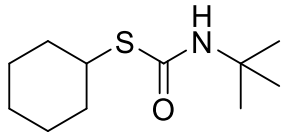
Methyl _N_-(_tert_-butoxycarbonyl)-_S_-(_tert_-butylcarbamoyl)-_L_-cysteinate (3r) [PMSA749]



The general procedure D was applied using methyl 2-((_tert_-butoxycarbonyl)amino)-3-((phenylsulfonyl)thio)propanoate (**1r**, 375 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). Methyl _N_-(_tert_-butoxycarbonyl)-_S_-(_tert_-butylcarbamoyl)-_L_-cysteinate was obtained in 79% (263 mg) yield. If general procedure E was applied with **1y** as thiosulfonate, **3r** was obtained in 97% (129 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 132-133 °C, R_f = 0.38 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.44 (d, _J_ = 7.2 Hz, 1H), 5.18 (br s, 1H), 4.49 (d, _J_ = 6.4 Hz, 1H), 3.74 (s, 3H), 3.31 (d, _J_ = 5.4 Hz, 2H), 1.44 (s, 9H), 1.35 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 171.4 (C), 164.1 (C), 155.4 (C), 80.0 (C), 54.1 (C), 53.7 (CH), 52.6 (CH_3), 32.2 (CH_2), 29.0 (CH_3), 28.4 (CH_3) ppm. HRMS (ESI) for $C_{14}H_{27}N_2O_5S$ $[M+H]^+$ calcd. 335.1635, found 335.1646.
Remark: The product was visualized on TLC via staining with $KMnO_4$.

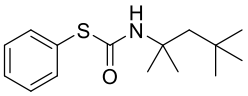
_S_-cyclohexyl _tert_-butylthiocarbamate (3s) [PMSA947]



The general procedure D was applied using _S_-cylohexyl benzenethiosulfonate (**1t**, 256 mg, 1.0 mmol, 1.0 equiv.) and _tert_-butyl isocyanide (136 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). _S_-cyclohexyl _tert_-butylthiocarbamate was obtained in 81% (175 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 80% (147 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 104-105 °C, R_f = 0.44 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 5.09 (br s, 1H), 3.40-3.35 (m, 1H), 2.00-1.95 (m, 2H), 1.70-1.67 (m, 1H), 1.59-1.37 (m, 5H), 1.34 (s, 9H), 1.27-1.21 (m, 1H). ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.6 (C), 53.2 (C), 43.8 (CH), 34.1 (CH_2), 29.1 (CH_3), 26.3 (CH_2), 25.7 (CH_2) ppm. HRMS (ESI) for $C_{11}H_{22}NOS$ $[M+H]^+$ calcd. 216.1417, found 216.1423.
Remark: The product was visualized on TLC via staining with $KMnO_4$.

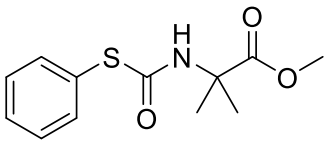
_S_-phenyl (2,4,4-trimethyl-2-pentanyl)thiocarbamate (5a) [PMSA772]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 1,1,3,3-tetramethylbutyl isocyanide (210 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl (2,4,4-trimethyl-2-pentanyl)thiocarbamate was obtained in 90% (240 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 91% (167 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 85-86 °C, R_f = 0.38 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.55-7.53 (m, 2H), 7.41-7.39 (m, 3H), 5.14 (br s, 1H), 1.66 (s, 2H), 1.37 (s, 6H), 0.96 (s, 9H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.9 (C), 135.7 (CH), 129.6 (CH), 129.5 (CH), 129.4 (C), 57.4 (C), 52.1 (CH_2), 31.7 (C), 31.5 (CH_3), 29.4 (CH_3) ppm. HRMS (ESI) for $C_{15}H_{24}NOS$ $[M+H]^+$ calcd. 266.1573, found 266.1584.

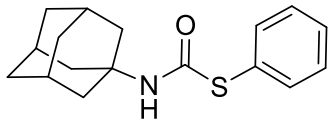
Methyl 2-methyl-*N*-[(phenylsulfanyl)carbonyl]alaninate (5b) [PMSA766/794]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and methyl 2-isocyano-2-methylpropanoate (**2b**, 153 mg, 1.2 mmol, 1.2 equiv.). The reaction was stirred for 15 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). Methyl 2-methyl-*N*-[(phenylsulfanyl)carbonyl]alaninate was obtained in 84% (213 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 69% (127 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 100-101 °C, R_f = 0.38 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57-7.54 (m, 2H), 7.43-7.40 (m, 3H), 6.11 (br s, 1H), 3.74 (s, 3H), 1.57 (s, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 174.8 (C), 165.1 (C), 135.6 (CH), 129.7 (CH), 129.5 (CH), 128.7 (C), 58.6 (C), 53.0 (CH_3), 24.8 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{16}NO_3S$ $[M+H]^+$ calcd. 254.0845, found 254.0845.

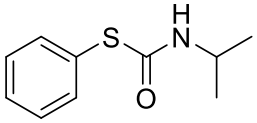
_S_-phenyl (1-adamantyl)thiocarbamate (5c) [PMSA726]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 1-adamantyl isocyanide (193 mg, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl (1-adamantyl)thiocarbamate was obtained in 90% (258 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 88% (162 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 137-138 °C, R_f = 0.67 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.54-7.50 (m, 2H), 7.40-7.38 (m, 3H), 5.05 (br s, 1H), 2.06 (s, 3H), 1.95 (d, *J* = 3.0 Hz, 6H), 1.65 (br s, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 163.7 (C), 135.5 (CH), 129.5 (C), 129.4 (CH), 129.4 (CH), 54.4 (C), 41.9 (CH_2), 36.4 (CH_2), 29.7 (CH) ppm. HRMS (ESI) for $C_{17}H_{22}NOS$ $[M+H]^+$ calcd. 288.1417, found 288.1419.

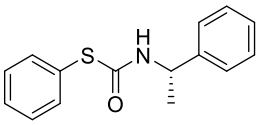
_S_-phenyl isopropylthiocarbamate (5d) [PMSA709]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and isopropyl isocyanide (113 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). *S*-phenyl isopropylthiocarbamate was obtained in 99% (195 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 90% (166 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 98-99 °C, R_f = 0.15 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.41-7.40 (m, 3H), 5.12 (br s, 1H), 4.03 (hp, *J* = 6.7 Hz, 1H), 1.14 (d, *J* = 6.5 Hz, 6 H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.0 (C), 135.5 (CH), 129.6 (CH), 129.5 (CH), 129.0 (C), 44.1 (CH), 22.8 (CH_3) ppm. HRMS (ESI) for $C_{10}H_{14}NOS$ $[M+H]^+$ calcd. 196.0791, found 196.0790.

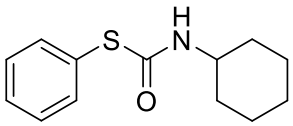
(*S*)-*S*-phenyl (1-phenylethyl)thiocarbamate (5e) [PMSA767]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and (*S*)-(-)-*α*-methylbenzyl isocyanide (162 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). (*S*)-*S*-phenyl (1-phenylethyl)thiocarbamate was obtained in 92% (237 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 75% (138 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 86-87 °C, R_f = 0.62 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): 7.54 (dd, *J* = 6.5, 2.9 Hz, 2H), 7.41-7.37 (m, 3H), 7.34-7.31 (m, 2H), 7.27-7.23 (m, 3H), 5.55 (br s, 1H), 5.06 (p, *J* = 6.8 Hz, 1H), 1.47 (d, *J* = 6.9 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.3 (C), 142.7 (C), 135.6 (CH), 129.7 (CH), 129.5 (CH), 128.9 (CH), 128.7 (C), 127.7 (CH), 126.2 (CH), 51.3 (CH), 22.0 (CH_3) ppm. HRMS (ESI) for $C_{15}H_{16}NOS$ $[M+H]^+$ calcd. 258.0947, found 258.0951.

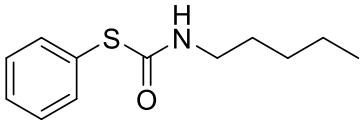
***S*-phenyl cyclohexylthiocarbamate (5f) [PMSA725]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and cyclohexyl isocyanide (149 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl cyclohexylthiocarbamate was obtained in 89% (210 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 72% (132 mg) yield. The spectroscopic data are slightly different than those reported in literature.[38]

White solid, m.p.: 112-113 °C (lit.: 114 °C)[37], R_f = 0.50 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57-7.53 (m, 2H), 7.44-7.38 (m, 3H), 5.18 (br s, 1H), 3.72 (br s, 1H), 1.90 (d, *J* = 9.3 Hz, 2H), 1.69-1.55 (m, 3H), 1.40-1.25 (m, 2H), 1.16-1.10 (m, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 165.0 (C), 135.5 (CH), 129.6 (CH), 129.5 (CH), 129.1 (C), 50.7 (CH), 33.0 (CH_2), 25.5 (CH_2), 24.7 (CH_2) ppm. HRMS (ESI) for $C_{13}H_{18}NOS$ $[M+H]^+$ calcd. 236.1104, found 236.1107.

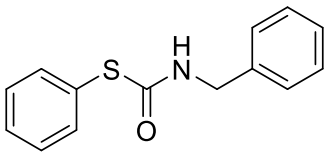
***S*-phenyl pentylthiocarbamate (5g) [PMSA718]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and *n*-pentyl isocyanide (161 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl pentylthiocarbamate was obtained in 89% (199 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 86% (158 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 36-37 °C, R_f = 0.11 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 2H), 7.42-7.40 (m, 3H), 5.28 (br s, 1H), 3.25 (dd, *J* = 13.3, 6.7 Hz, 2H), 1.49-1.43 (m, 2H), 1.32-1.23 (m, 4H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.1 (C), 135.6 (CH), 129.8 (CH), 129.6 (CH), 129.0 (C), 41.7 (CH_2), 29.4 (CH_2), 29.0 (CH_2), 22.4 (CH_2), 14.1 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{18}NOS$ $[M+H]^+$ calcd. 224.1104, found 224.1105.

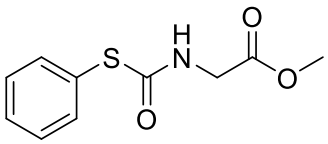
_S_-phenyl benzylthiocarbamate (5h) [PMSA729]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and benzyl isocyanide (146 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl benzylthiocarbamate was obtained in 77% (188 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 66% (121 mg) yield. The spectroscopic data are in accordance with literature.[39]

White solid, m.p.: 88-89 °C (lit.: 90-91 °C)[39], R_f = 0.12 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.57 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.44-7.37 (m, 3H), 7.35-7.20 (m, 5H), 5.62 (br s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.4 (C), 137.7 (C), 135.6 (CH), 129.8 (CH), 129.6 (CH), 128.9 (CH), 128.6 (C), 127.9 (CH), 127.8 (CH), 45.5 (CH_2) ppm. HRMS (ESI) for $C_{14}H_{14}NOS$ $[M+H]^+$ calcd. 244.0791, found 244.0802.

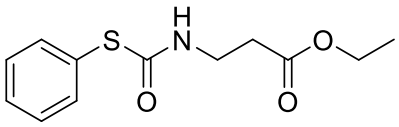
Methyl _N_-[(phenylsulfanyl)carbonyl]glycinate (5i) [PMSA724/778]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and methyl isocyanoacetate (109 µL, 1.2 mmol, 1.2 equiv.). The reaction mixture was stirred for 15 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). Methyl *N*-[(phenylsulfanyl)carbonyl]glycinate was obtained in 85% (191 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 55% (102 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.: 117-118 °C (literature: 117-118 °C)[40], R_f = 0.20 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.58 (m, 2H), 7.45-7.40 (m, 3H), 5.86 (br s, 1H), 4.05 (d, *J* = 5.1 Hz, 2H), 3.75 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 169.9 (C), 167.0 (C), 135.7 (CH), 130.1 (CH), 129.8 (CH), 128.2 (CH_3), 52.6 (CH_3), 42.7 (CH_2) ppm. HRMS (ESI) for $C_{10}H_{12}NO_3S$ $[M+H]^+$ calcd. 226.0532, found 226.0544.

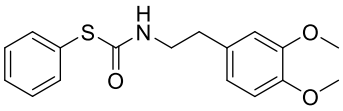
Ethyl _N_-[(phenylsulfanyl)carbonyl]-ß-alaninate (5j) [PMSA723]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and ethyl isocyanopropionate (153 µL, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). Ethyl *N*-[(phenylsulfanyl)carbonyl]-ß-alaninate was obtained in 91% (230 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 77% (142 mg) yield. No spectroscopic data are reported in literature.

Yellow oil, R_f = 0.08 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56-7.54 (m, 2H), 7.42-7.41 (m, 3H), 5.94 (br s, 1 H), 4.12 (q, *J* = 7.1 Hz, 2H), 3.52 (q, *J* = 5.9 Hz, 2H), 2.52 (t, *J* = 5.8 Hz, 2H), 1.25 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 172.3 (C), 166.5 (C), 135.6 (CH), 129.9 (CH), 129.6 (CH), 128.6 (C), 61.0 (CH_2), 36.9 (CH_2), 34.2 (CH_2), 14.3 (CH_3) ppm. HRMS (ESI) for $C_{12}H_{16}NO_3S$ $[M+H]^+$ calcd. 254.0845, found 254.0853.

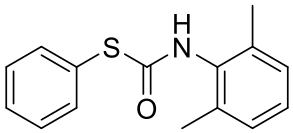
***S*-phenyl [2-(3,4-dimethoxyphenyl)ethyl]thiocarbamate (5k) [PMSA773/822]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 4-(2-isocyanoethyl)-1,2-dimethoxybenzene (**2k**, 229 mg, 1.2 mmol, 1.2 equiv.). The reaction mixture was stirred for 15 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl [2-(3,4-dimethoxyphenyl)ethyl]thiocarbamate was obtained in 89% (284 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 82% (151 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p: 68-69 °C, R_f = 0.05 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): 7.48 (dd, *J* = 7.8, 1.5 Hz, 2H), 7.41-7.33 (m, 3H), 6.77 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 6.62 (d, *J* = 9.3 Hz, 1H), 5.33 (br s, 1H), 3.87 (s, 3H), 3.86 (s, 3H), 3.49 (q, *J* = 6.7 Hz, 2H), 2.73 (t, *J* = 6.8 Hz, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.3 (C), 149.3 (C), 147.9 (C), 135.6 (CH), 130.9 (C), 129.8 (CH), 129.6 (CH), 128.6 (C), 120.7 (CH), 112.0 (CH), 111.6 (CH), 56.1 (CH_2), 56.0 (CH_2), 42.7 (CH_3), 35.1 (CH_3) ppm. HRMS (ESI) for $C_{17}H_{20}NO_3S$ $[M+H]^+$ calcd. 318.1158, found 318.1178.

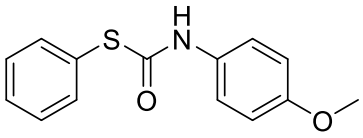
***S*-phenyl (2,6-dimethylphenyl)thiocarbamate (5m) [PMSA710/781]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 2,6-dimethylphenyl isocyanide (157 mg, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl (2,6-dimethylphenyl)thiocarbamate was obtained in 92% (238 mg) yield. No spectroscopic data are reported in literature. Due to the existence of rotamers, the spectra were recorded at 100°C in $C_2D_2Cl_4$.

White solid, m.p.: 156-157°C, R_f = 0.13 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $C_2D_2Cl_4$): δ 7.68-7.74 (m, 2H), 7.46-7.45 (m, 3H), 7.20-7.11 (m, 3H), 6.58 (br s, 1H), 2.32 (s, 6H) ppm. ^{13}C-NMR (101 MHz, $C_2D_2Cl_4$): δ 165.4 (C), 136.2 (C), 135.1 (CH), 133.5 (C), 129.4 (CH), 129.2 (CH), 128.9 (C), 128.2 (CH), 127.9 (CH), 18.0 (CH_3) ppm. HRMS (ESI) for $C_{15}H_{16}NOS$ $[M+H]^+$ calcd. 258.0947, found 258.0946.

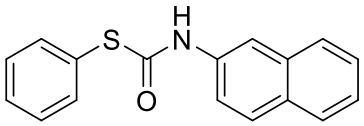
***S*-phenyl (4-methoxyphenyl)thiocarbamate (5n) [PMSA717]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 4-methoxyphenyl isocyanide (160 mg, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). *S*-phenyl (4-methoxyphenyl)thiocarbamate was obtained in 89% (230 mg) yield. No spectroscopic data are reported in literature.

Yellow solid, m.p.: 92-93 °C, R_f = 0.22 in Heptane / EtOAc (9:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.61-7.59 (m, 2H), 7.45-7.43 (m, 3H), 7.29-7.25 (m, 2H), 6.95 (br s, 1H), 6.83 (d, *J* = 9.0 Hz, 2H)†, 3.77 (s, 3H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.0 (C), 135.7 (CH), 130.7 (C), 129.9 (CH), 129.6 (CH), 128.4 (CH), 127.7 (C), 121.5 (br, C), 114.4 (CH), 55.6 (CH_3) ppm. HRMS (ESI) for $C_{14}H_{14}NO_2S$ $[M+H]^+$ calcd. 260.0740, found 260.0754.

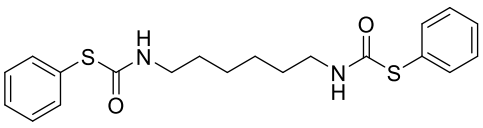
***S*-phenyl naphthalen-2-ylthiocarbamate (5o) [PMSA768]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 1.0 equiv.) and 2-naphthylisocyanide (184 mg, 1.2 mmol, 1.2 equiv.). The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 20% EtOAc, 25 mL/min). The product was subsequently recrystallized from heptane. *S*-phenyl naphthalen-2-ylthiocarbamate was obtained in 66% (186 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 43% (79 mg) yield. No spectroscopic data are reported in literature.

Orange crystals, m.p.: 114-115 °C, R_f = 0.19 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.04 (d, *J* = 1.8 Hz, 1H), 7.74 (t, *J* = 9.2 Hz, 3H), 7.65-7.63 (m, 2H), 7.49-7.36 (m, 5H), 7.31 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.25 (br s, 1H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.6 (C), 135.8 (CH), 135.1 (C), 133.9 (C), 130.9 (C), 130.2 (CH), 129.7 (CH), 129.1 (CH), 128.2 (C), 127.8 (CH), 127.7 (CH), 126.8 (CH), 125.4 (CH), 119.5 (CH), 116.6 (CH) ppm. HRMS (ESI) for $C_{17}H_{14}NOS$ $[M+H]^+$ calcd. 280.0791, found 280.0796.

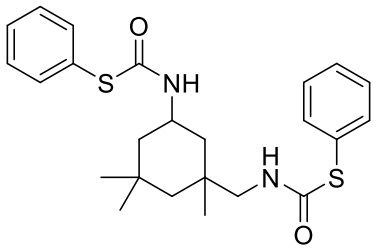
***S,S'*-diphenyl hexane-1,6-diylbisthiocarbamate (5p) [PMSA843/844]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 2.0 equiv.) and 1,6-diisocyanohexane (**2p**, 68 mg, 0.5 mmol, 1.0 equiv.) and sodium iodide (7.5 mg, 0.05 mmol, 0.1 equiv.). The reaction mixture stirred for 15 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 50% EtOAc, 25 mL/min). *S,S'*-diphenyl hexane-1,6-diylbisthiocarbamate was obtained in 88% (171 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 88% (162 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.:127-128 °C, R_f = 0.30 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.56 (m, 4H), 7.42-7.41 (m, 6H), 5.37 (br s, 2H), 3.24 (dd, *J* = 13.1, 6.6 Hz, 4H), 1.46 (br s, 4H), 1.26 (br s, 4H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 166.2 (C), 135.6 (CH), 129.8 (CH), 129.6 (CH), 128.9 (C), 41.3 (CH_2), 29.6 (CH_2), 26.1 (CH_2) ppm. HRMS (ESI) for $C_{20}H_{25}N_2O_2S_2$ $[M+H]^+$ calcd. 389.1352, found 389.1367.

***S*-phenyl [(1,3,3-trimethyl-5-[((phenylsulfanyl)carbonyl)amino]cyclohexyl)methyl] thiocarbamate (5q) [PMSA845, 876]**



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 250 mg, 1.0 mmol, 2.0 equiv.) and 5-isocyano-1-(isocyanomethyl)-1,3,3-trimethylcyclohexane (**2q**, 95 mg, 0.5 mmol, 1.0 equiv.) and sodium iodide (7.5 mg, 0.05 mmol, 0.1 equiv.). The reaction mixture was stirred for 15 hours. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 50% EtOAc, 25 mL/min). *S*-phenyl [(1,3,3-trimethyl-5-[((phenylsulfanyl)carbonyl)amino]cyclohexyl)methyl] thiocarbamate was obtained in 76% (168 mg, mixture of two diastereoisomers, ratio 1:3) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 42% (77 mg) yield. No spectroscopic data are reported in literature.

Diastereoisomer 1 (Minor)

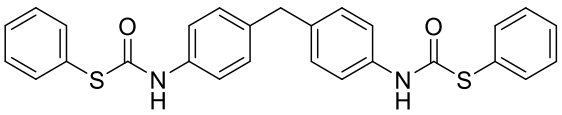
White solid, m.p.: 168-169 °C, R_f = 0.52 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.49 (m, 4H), 7.42-7.39 (m, 6H), 5.29 (br s, 1H), 5.13 (d, *J* = 6.5 Hz, 1H), 3.98 (br s, 1H), 3.35 (dd, J = 13.4, 6.4 Hz, 1H), 3.20 (dd, *J* = 15.9, 14.0 Hz, 1H), 1.75 (d, *J* = 12.3 Hz, 1H), 1.70-1.66 (m, 1H), 1.17-1.13 (m, 1H), 1.01-0.74 (m, 12H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.4 (C), 165.3 (C), 135.8 (CH), 135.6 (CH), 130.0 (CH), 129.8 (CH), 129.7 (CH), 129.5 (CH), 129.0 (C), 128.7 (C), 47.6 (CH_2), 47.2 (CH_2), 45.7 (CH), 45.4 (C),

42.2 (C), 36.6 (CH_2), 34.9 (CH_3), 31.9 (CH_2), 29.9 (CH_3), 27.3 (CH_3) ppm. HRMS (ESI) for $C_{24}H_{30}NaN_2O_2S_2$ $[M+H]^+$ calcd. 465.1641, found 465.1648.

Diastereoisomer 2 (Major)

White solid, m.p.: 169-170 °C, R_f = 0.45 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60-7.53 (m, 4H), 7.43-7.39 (m, 6H), 5.36 (br s, 1H), 5.17 (d, *J* = 7.4 Hz, 1H), 4.04 (br s, 1H), 2.97 (d, *J* = 6.4 Hz, 2H), 1.71 (d, *J* = 11.9 Hz, 1H), 1.63 (d, *J* = 11.9 Hz, 1H), 1.11-0.79 (m, 13H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.6 (C), 165.3 (C), 135.7 (CH), 135.6 (CH), 130.0 (CH), 129.7 (CH), 129.7 (CH), 129.5 (CH), 128.9 (C), 128.7 (C), 54.8 (CH_2), 47.1 (CH_2), 45.9 (CH), 45.6 (C), 41.4 (C), 36.8 (CH_2), 35.1 (CH_3), 32.0 (CH_2), 27.7 (CH_3), 23.3 (CH_3) ppm. HRMS (ESI) for $C_{24}H_{30}NaN_2O_2S_2$ $[M+H]^+$ calcd. 465.1641, found 465.1648.

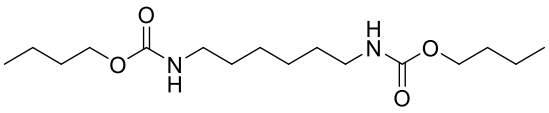
_S,S'_-diphenyl [methylenedi(4,1-phenylene)]bisthiocarbamate (5r) [PMSA776/824]



The general procedure D was applied using *S*-phenyl benzenethiosulfonate (**1a**, 313 mg, 1.0 mmol, 2.0 equiv.) and 1,1'-methylenebis(4-isocyanobenzene) (**2r**, 109 mg, 0.5 mmol, 1.0 equiv.) and sodium iodide (7.5 mg, 0.05 mmol, 0.1 equiv.). The reaction mixture was stirred for 15 hours at 50 °C. The product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 50% EtOAc, 25 mL/min). *S,S'*-diphenyl [methylenedi(4,1-phenylene)]bisthiocarbamate was obtained in 49% (114 mg) yield. Isopropyl benzenesulfinate (**4a**) was isolated in 43% (79 mg) yield. No spectroscopic data are reported in literature.

White solid, m.p.:162-163 °C, R_f = 0.42 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.60 (dd, *J* = 6.4, 3.0 Hz, 4H), 7.45 (m, 6H), 7.27 (d, *J* = 8.4 Hz, 4H), 7.07 (d, *J* = 8.4 Hz, 4H), 6.99 (br s, 2H), 3.87 (s, 2H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 164.5 (C), 137.5 (C), 135.8 (CH), 135.7 (CH), 130.0 (CH), 129.7 (CH), 129.6 (CH), 128.2 (C), 120.0 (C), 40.8 (CH_2) ppm. HRMS (ESI) for $C_{27}H_{23}N_2O_2S_2$ $[M+H]^+$ calcd. 471.1195, found 471.1204.

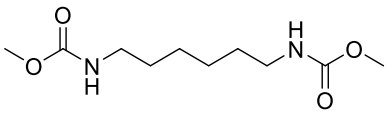
Dibutyl hexane-1,6-diylbiscarbamate (8a) [PMSA883]



S,S'-diphenyl hexane-1,6-diyldithiocarbamate (**5p**, 76 mg, 0.2 mmol, 1.0 equiv.) was dissolved in *n*-butanol (1.0 mL). To this mixture was added triethylamine (120 µL, 0.9 mmol, 4.4 equiv.). The reaction mixture was refluxed for 16 hours. The reaction mixture was concentrated *in vacuo* and the product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 30% EtOAc, 25 mL/min). The product was repurified by flash chromatography using Heptane/EtOAc (2:1) as eluent. Dibutyl hexane-1,6-diylbiscarbamate was obtained in 91% (56 mg) yield. Phenyl disulfide was isolated as side compound in 95% (41 mg) yield. Spectroscopic data are in accordance with literature.[41]

White solid, m.p.: 91-92 °C (lit.: 91 °C)[42], R_f = 0.47 in Heptane / EtOAc (2:1), ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.63 (br s, 2H), 4.05 (t, *J* = 6.4 Hz, 4H), 3.16 (d, *J* = 6.3 Hz, 4H), 1.64-1.57 (m, 4H), 1.52-1.48 (m, 4H), 1.36 (m, 8H), 0.93 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.0 (C), 64.8 (CH_2), 40.9 (CH_2), 31.3 (CH_2), 30.1 (CH_2), 26.4 (CH_2), 19.3 (CH_2), 13.9 (CH_3) ppm. HRMS (ESI) for $C_{16}H_{33}N_2O_4$ $[M+H]^+$ calcd. 317.2435, found 317.2433.

Dimethyl hexane-1,6-diylbiscarbamate (8b) [PMSA916]



S,S'-diphenyl hexane-1,6-diyldithiocarbamate (**5p**, 76 mg, 0.2 mmol, 1.0 equiv.) was dissolved in methanol (1.0 mL). To this mixture was added triethylamine (120 µL, 0.9 mmol, 4.4 equiv.). The reaction mixture was refluxed for 20 hours. The reaction mixture was concentrated *in vacuo* and the product was purified by an automated flash chromatography system using a Heptane / EtOAc gradient (from 100% Heptane to 100% EtOAc, 25 mL/min). Dimethyl hexane-1,6-diylbiscarbamate was obtained in 88% (41 mg) yield. Phenyl disulfide was isolated as side compound in 92% (41 mg) yield. Spectroscopic data are in accordance with literature.[43]

White solid, m.p.: 113-114°C (lit.: 113 °C)[44], ^{1}H-NMR (400 MHz, $CDCl_3$): δ 4.69 (br s, 2H), 4.69 (s, 6H), 3.16 (d, J = 6.3 Hz, 4H), 1.64-1.47 (m, 4H), 1.35-1.31 (m, 4H) ppm. ^{13}C-NMR (101 MHz, $CDCl_3$): δ 157.3 (C), 52.1 (CH_2), 41.0 (CH_2), 30.1 (CH_2), 26.4 (CH_3) ppm. HRMS (ESI) for $C_{10}H_{21}N_2O_4Na$ $[M+Na]^+$ calcd. 255.1321, found 255.1325.

8 References

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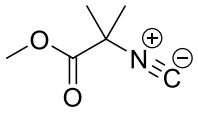
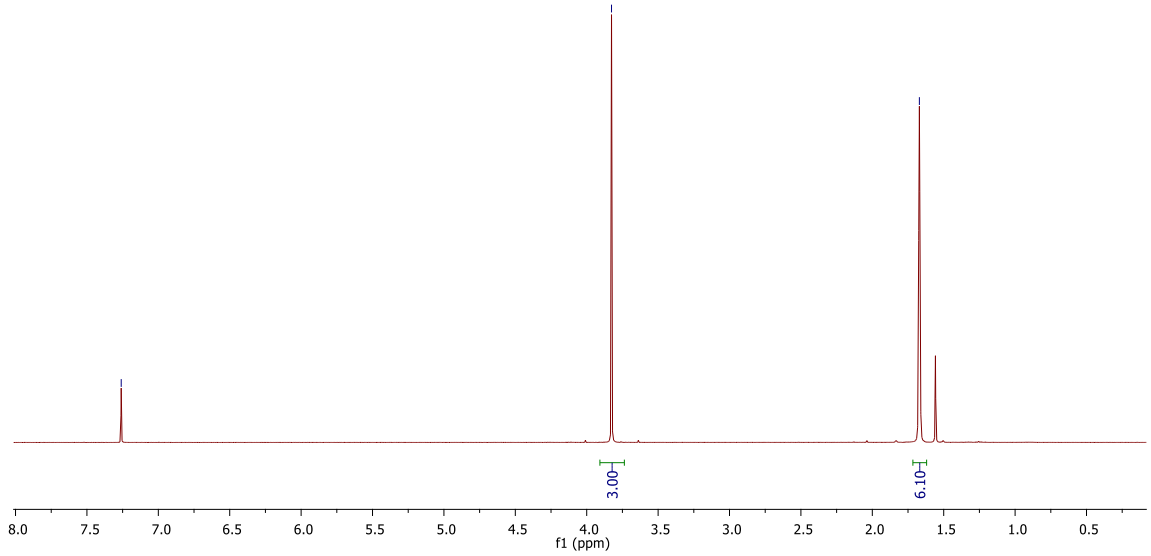
9 Annex: Copies of the ^{1}H and ^{13}C spectra

9.1 Synthesis of isocyanides

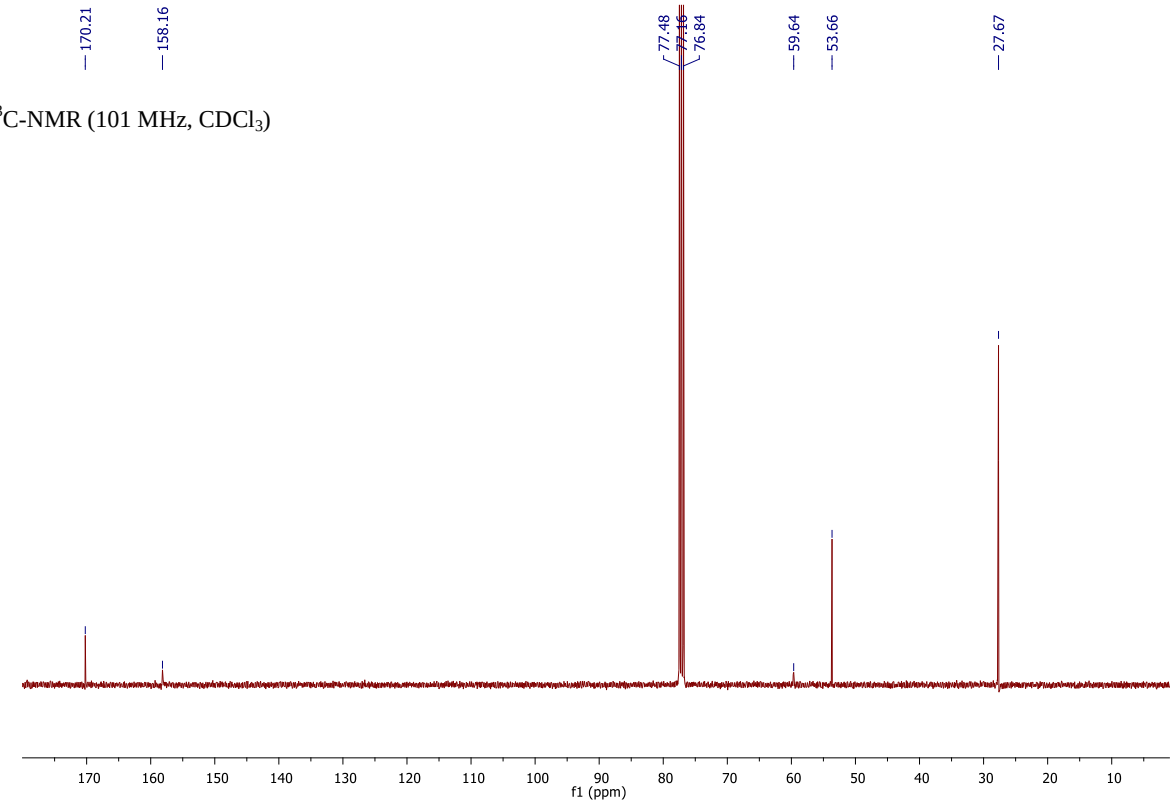
^{1}H-NMR (400 MHz, $CDCl_3$)

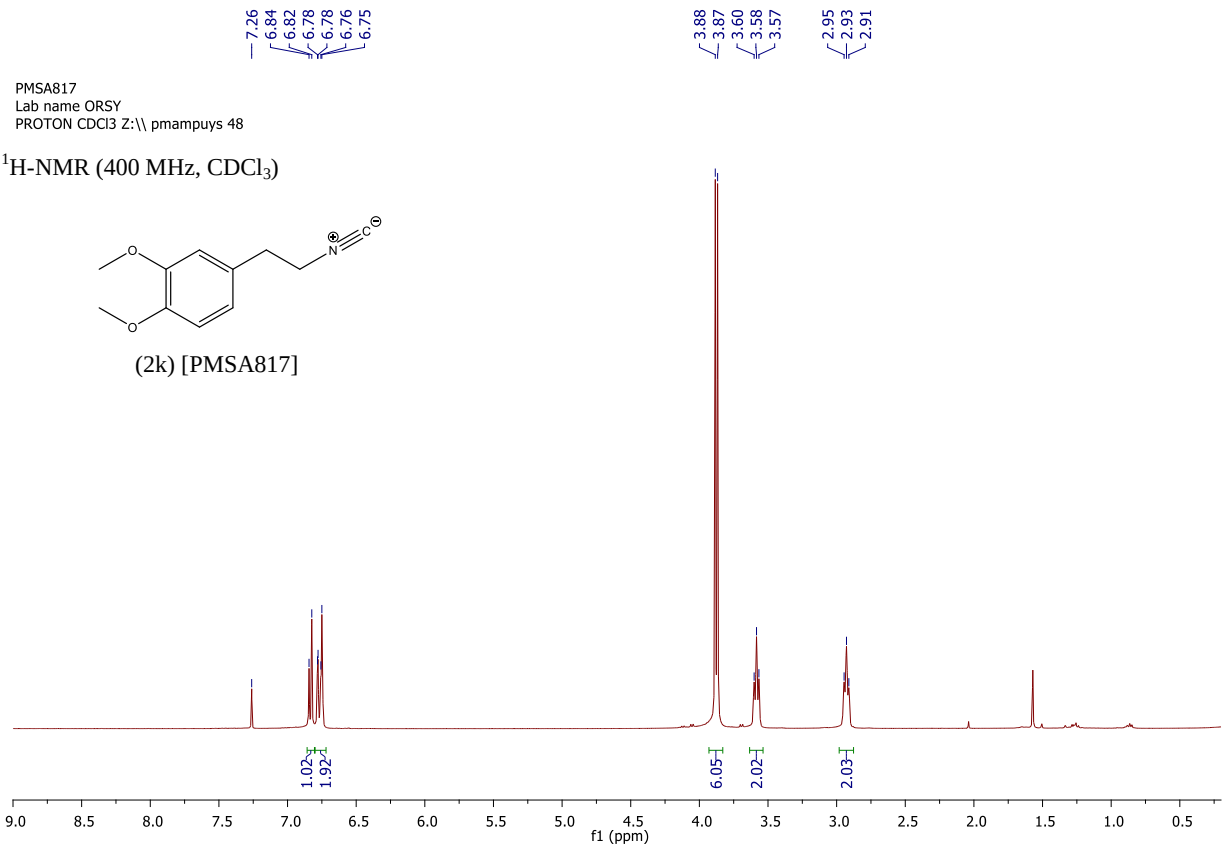


(2b) [PMSA-TIO022]



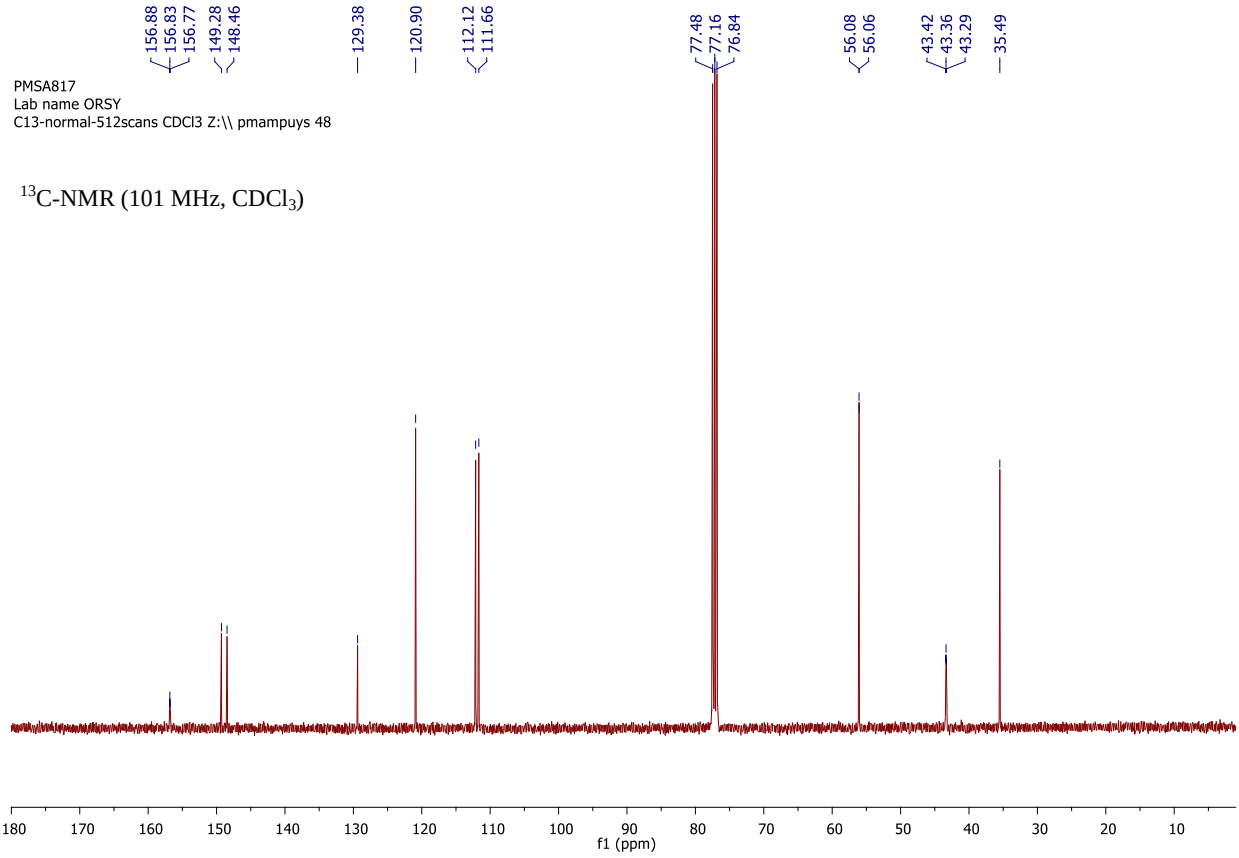
^{13}C-NMR (101 MHz, $CDCl_3$)



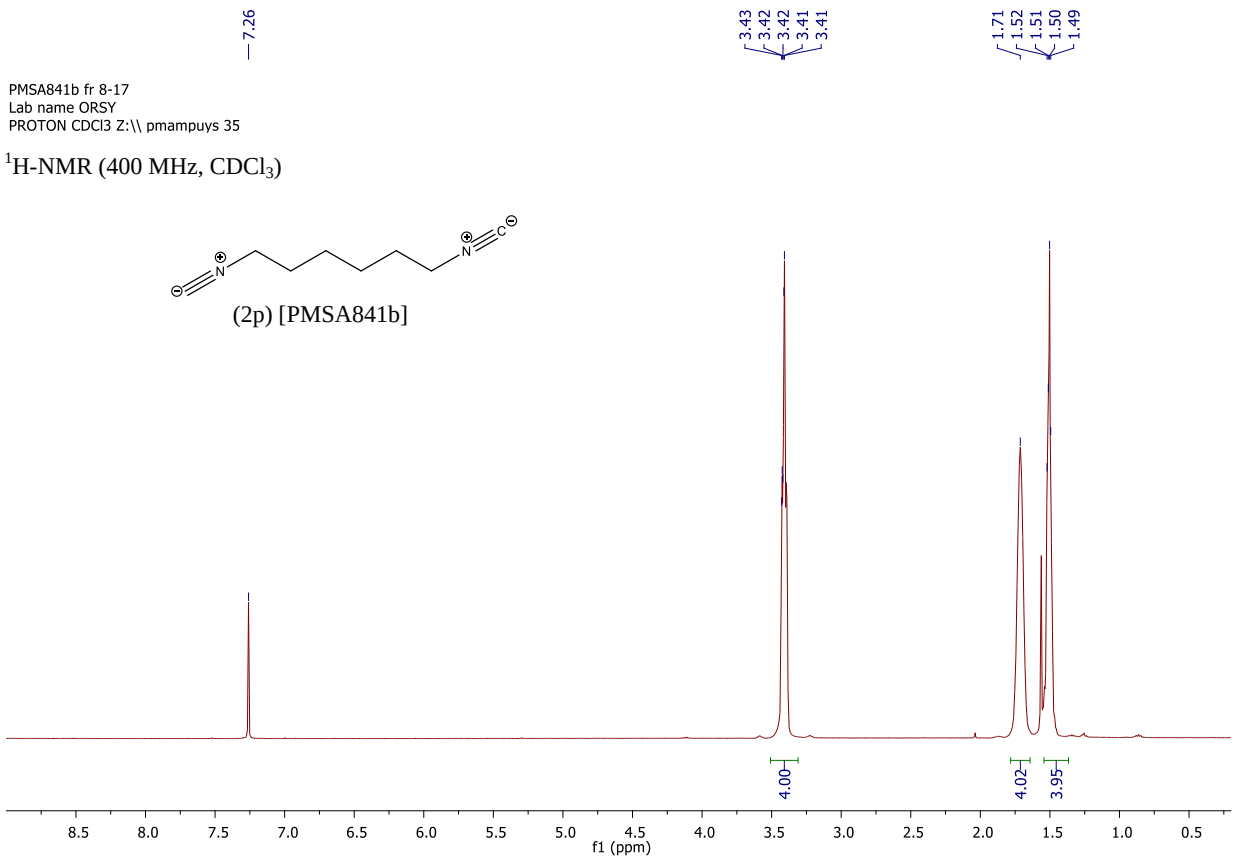


^{1}H-NMR (400 MHz, $CDCl_3$)

(2k) [PMSA817]

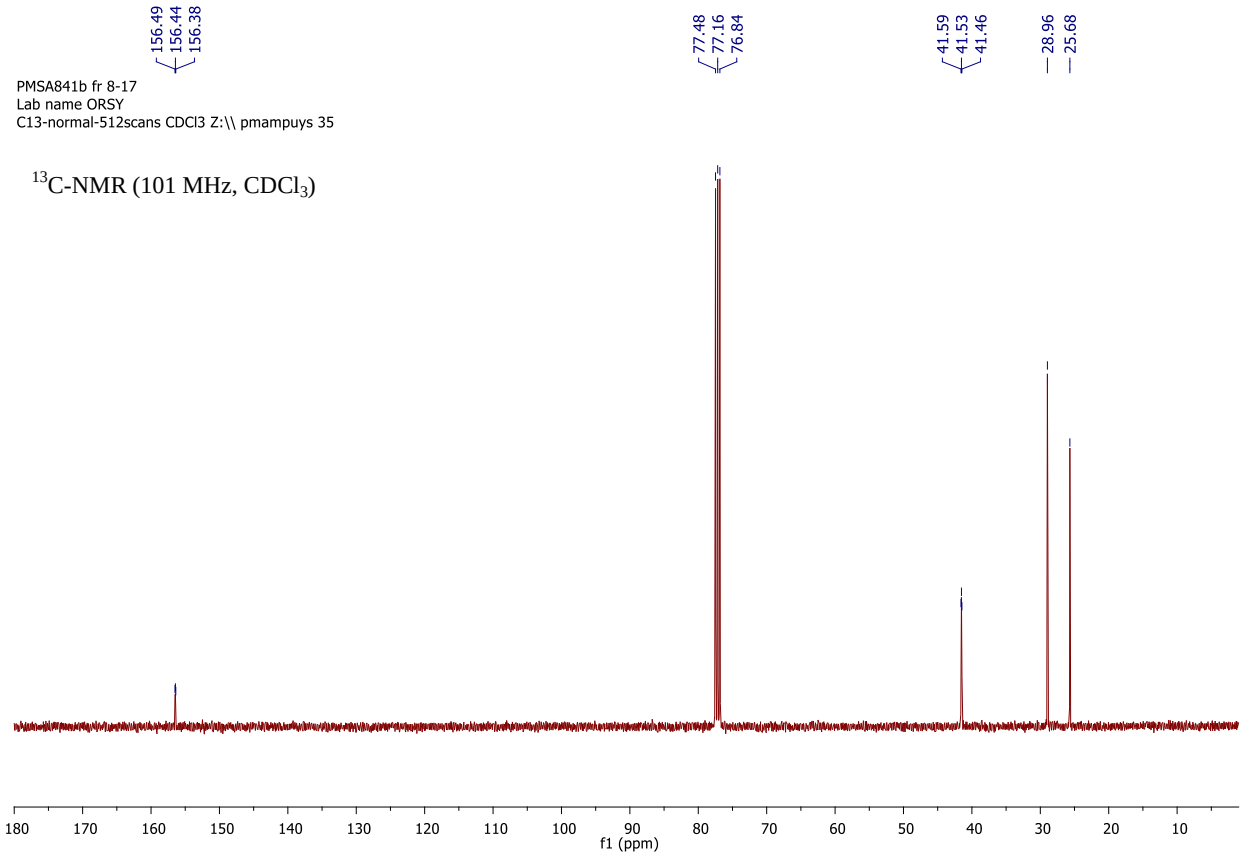


^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

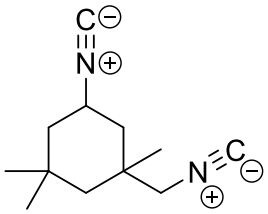
(2p) [PMSA841b]



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

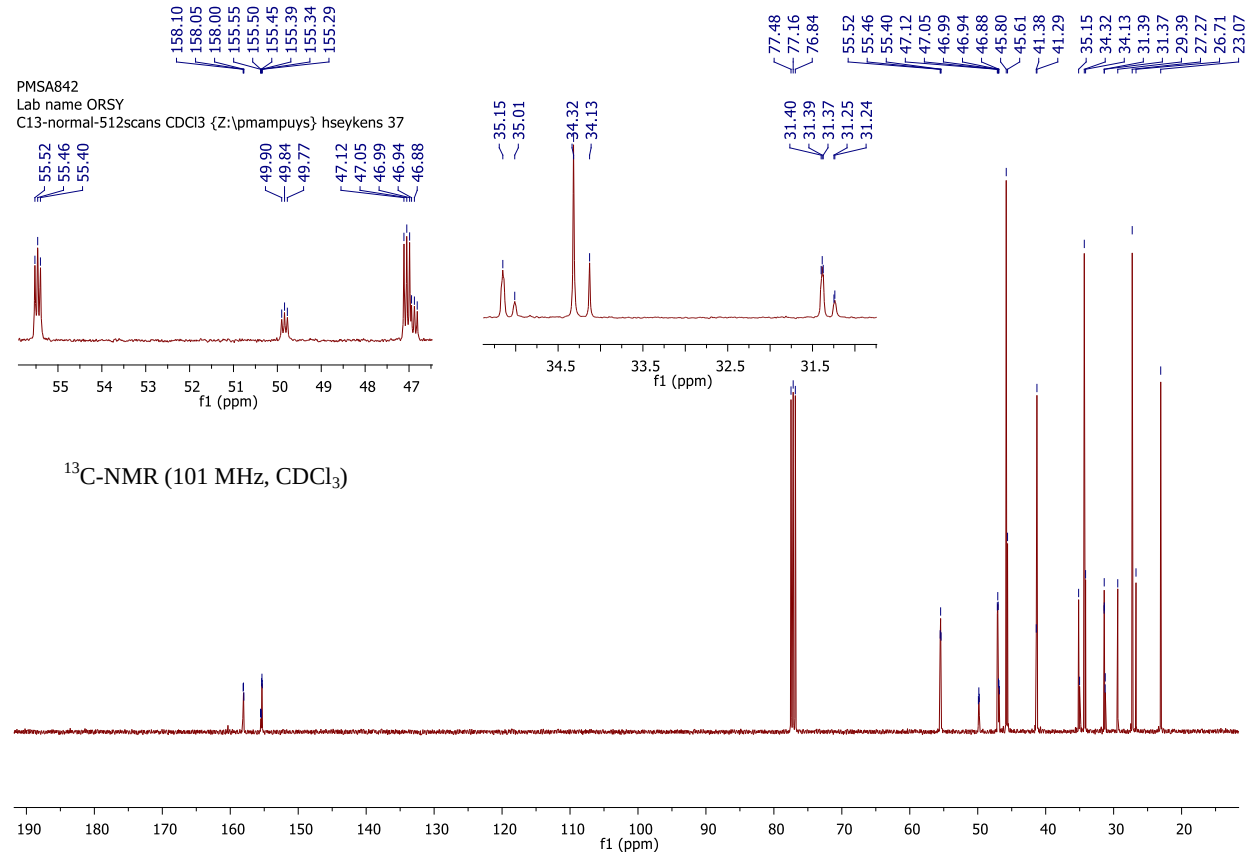
PMSA842
Lab name ORSY
PROTON CDCl3 {Z:\pmampuys} hseykens 37

^{1}H-NMR (400 MHz, $CDCl_3$)

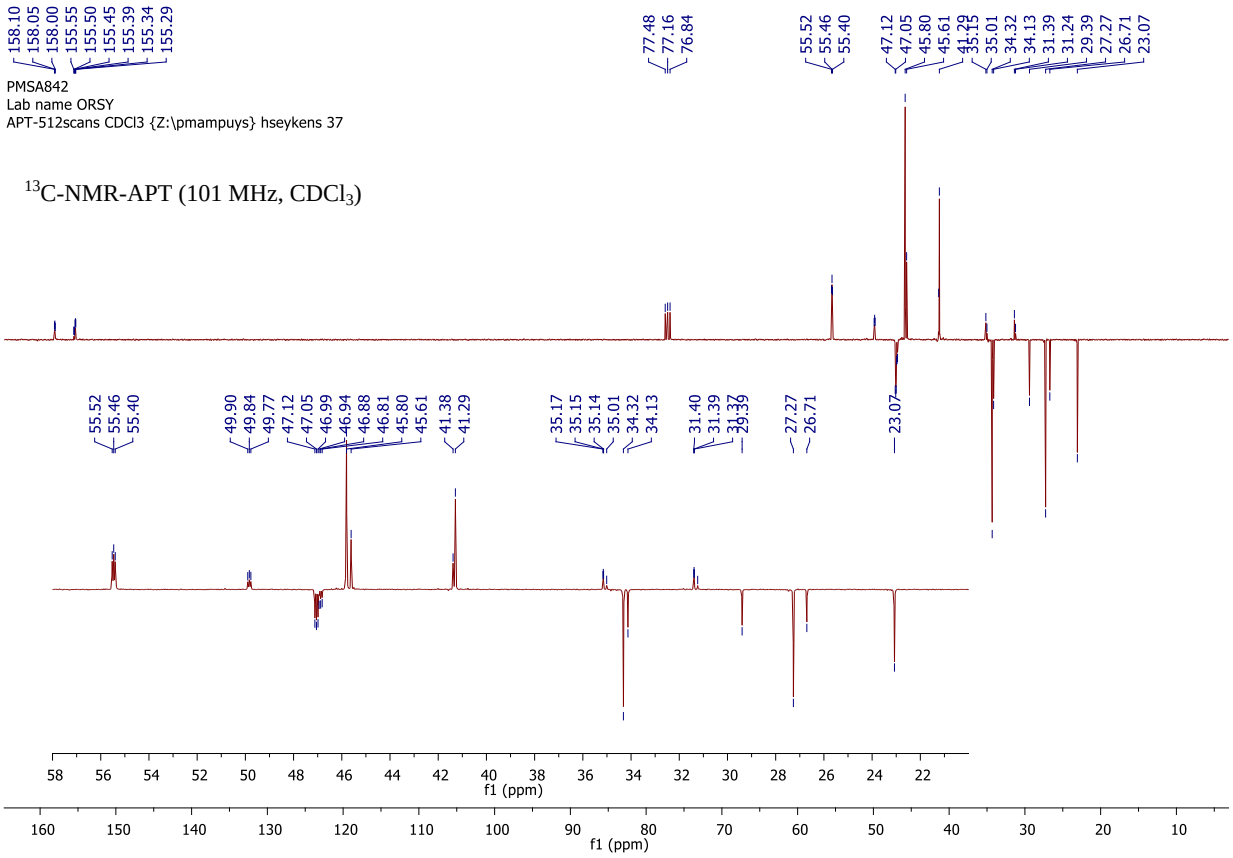


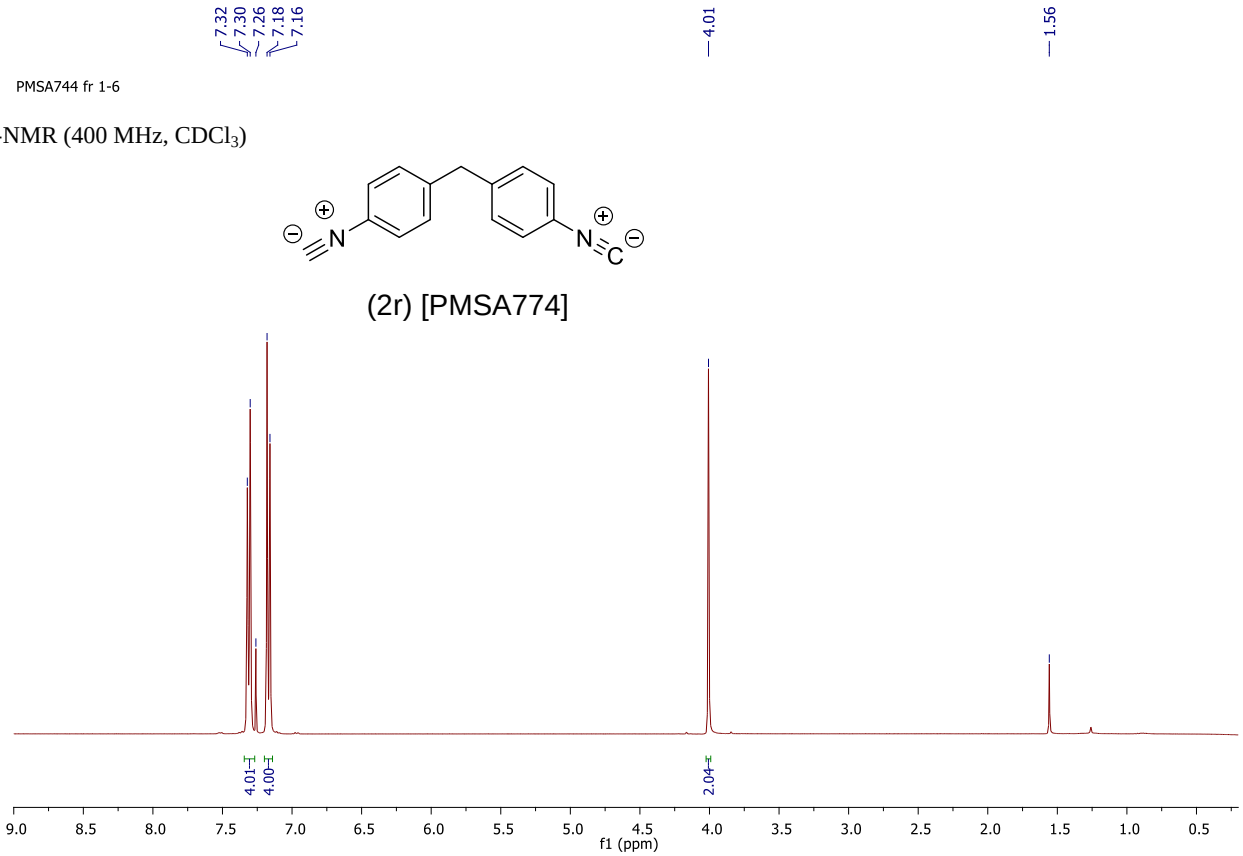
(2q) [PMSA842]

PMSA842
Lab name ORSY
C13-normal-512scans CDCl3 {Z:\pmampuys} hseykens 37



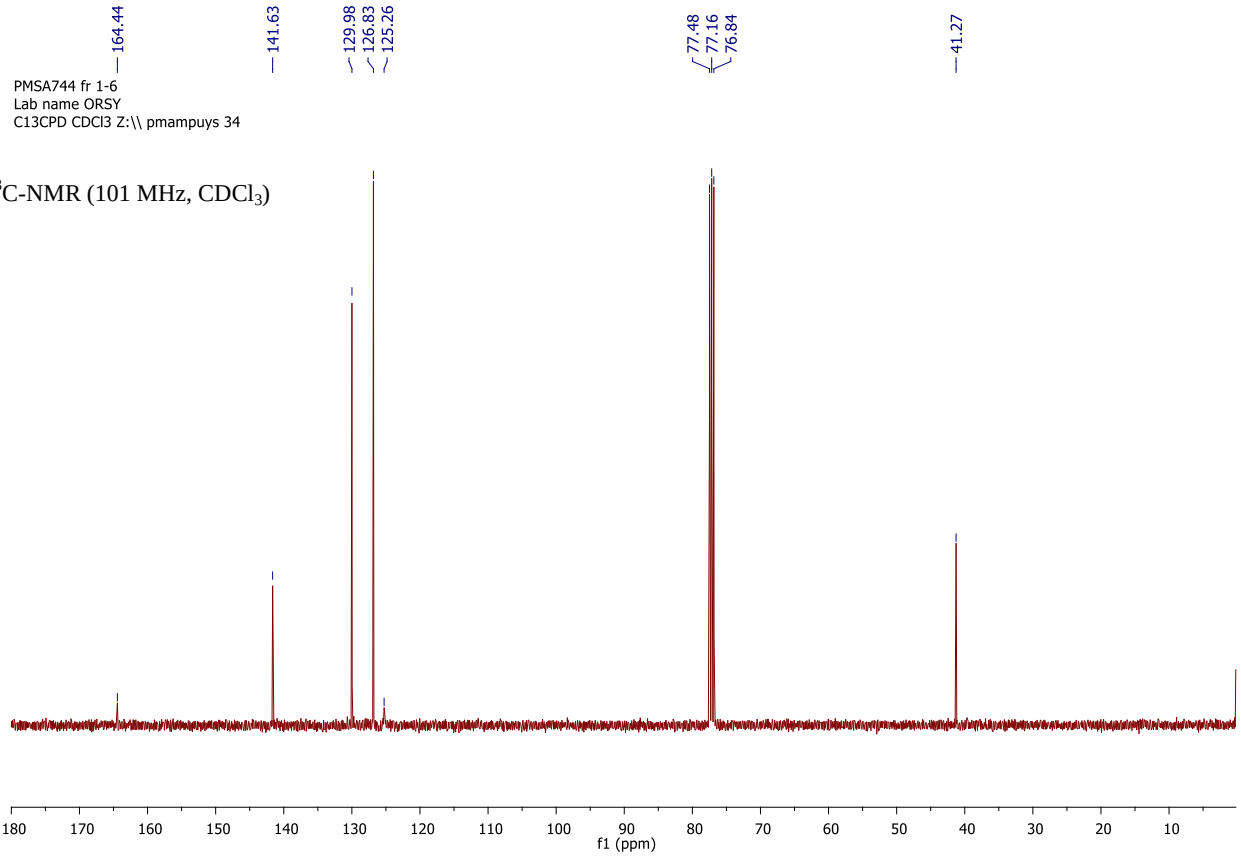
^{13}C-NMR (101 MHz, $CDCl_3$)


158.10
158.05
158.00
155.55
155.50
155.45
155.39
155.34
155.29
77.48
77.16
76.84
55.52
55.46
55.40
47.12
47.05
45.80
45.61
41.29
35.15
35.01
34.32
34.13
31.39
31.24
29.39
27.27
26.71
23.07
PMSA842
Lab name ORSY
APT-512scans CDCl3 {Z:\pmampuys} hseykens 37
13C-NMR-APT (101 MHz, CDCl3)
f1 (ppm)
f1 (ppm)



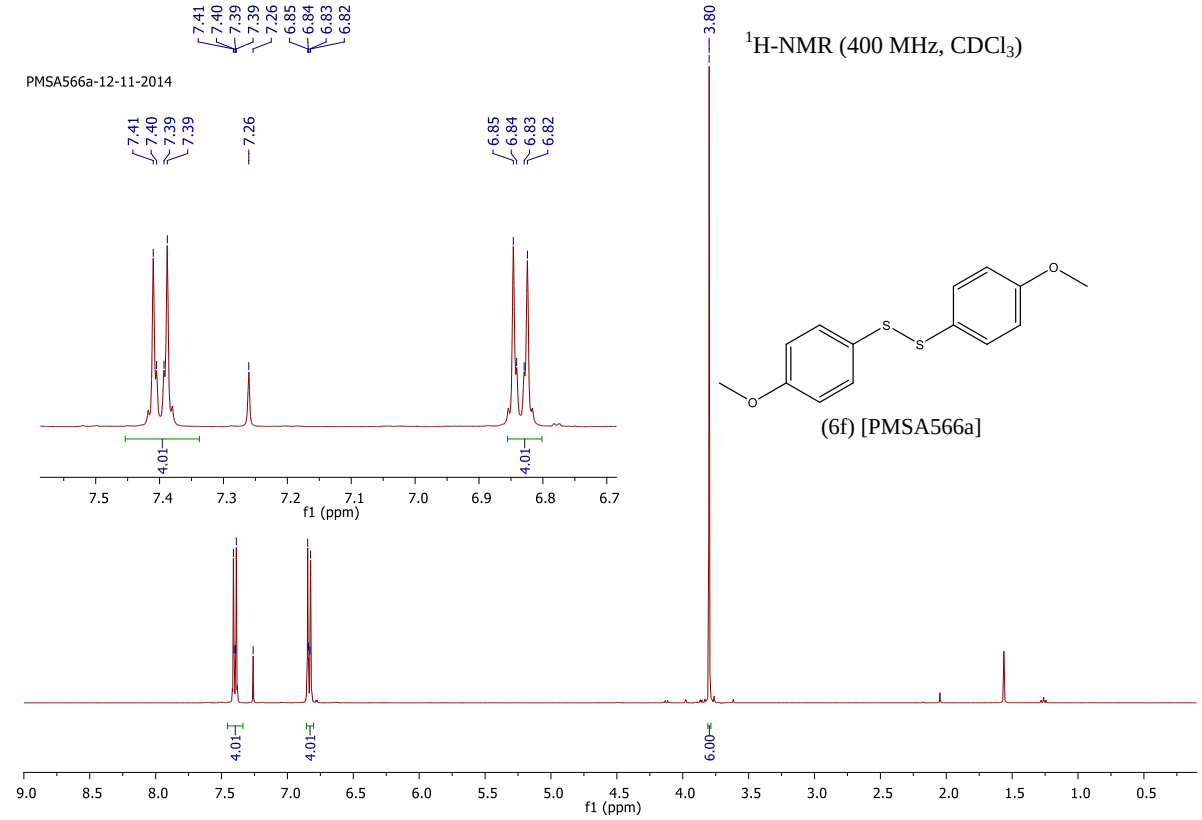
^{1}H-NMR (400 MHz, $CDCl_3$)

(2r) [PMSA774]



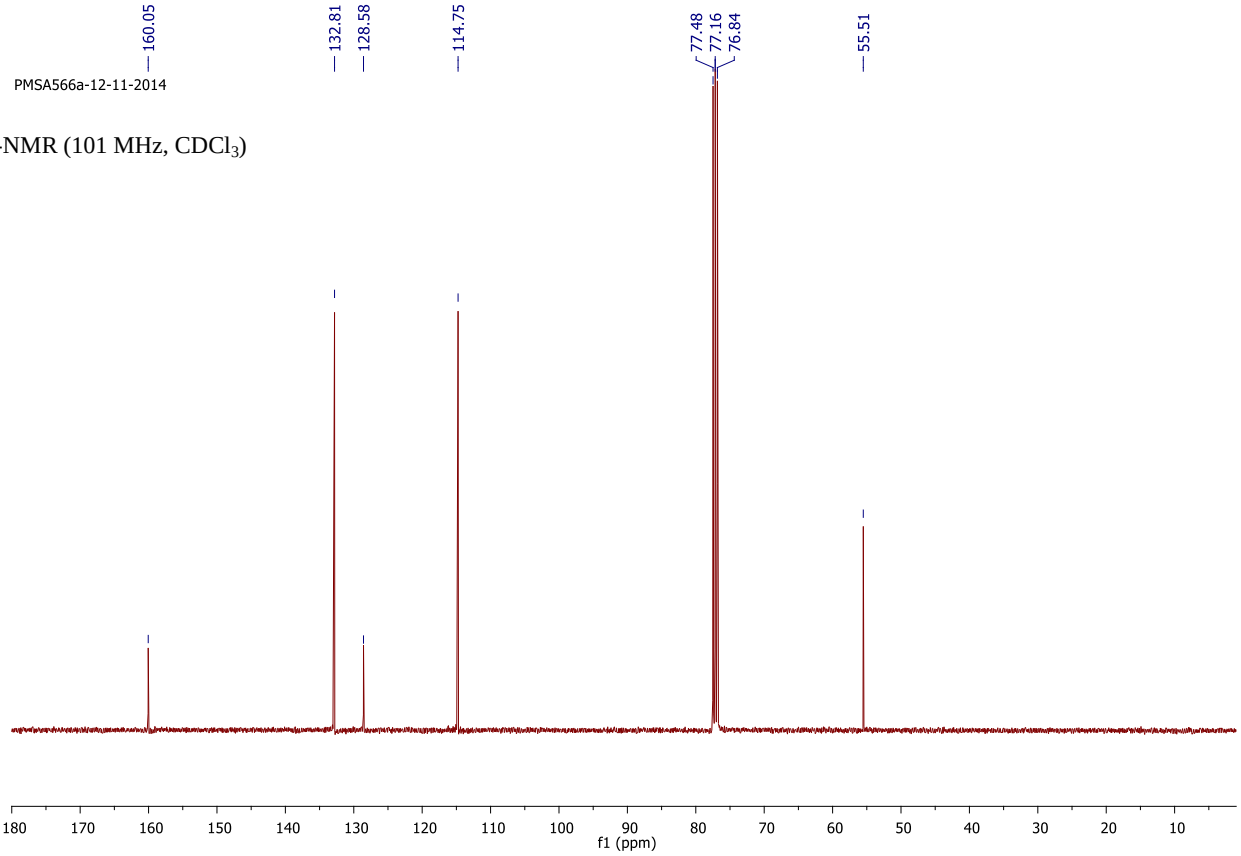
^{13}C-NMR (101 MHz, $CDCl_3$)

9.2 Synthesis of disulfides

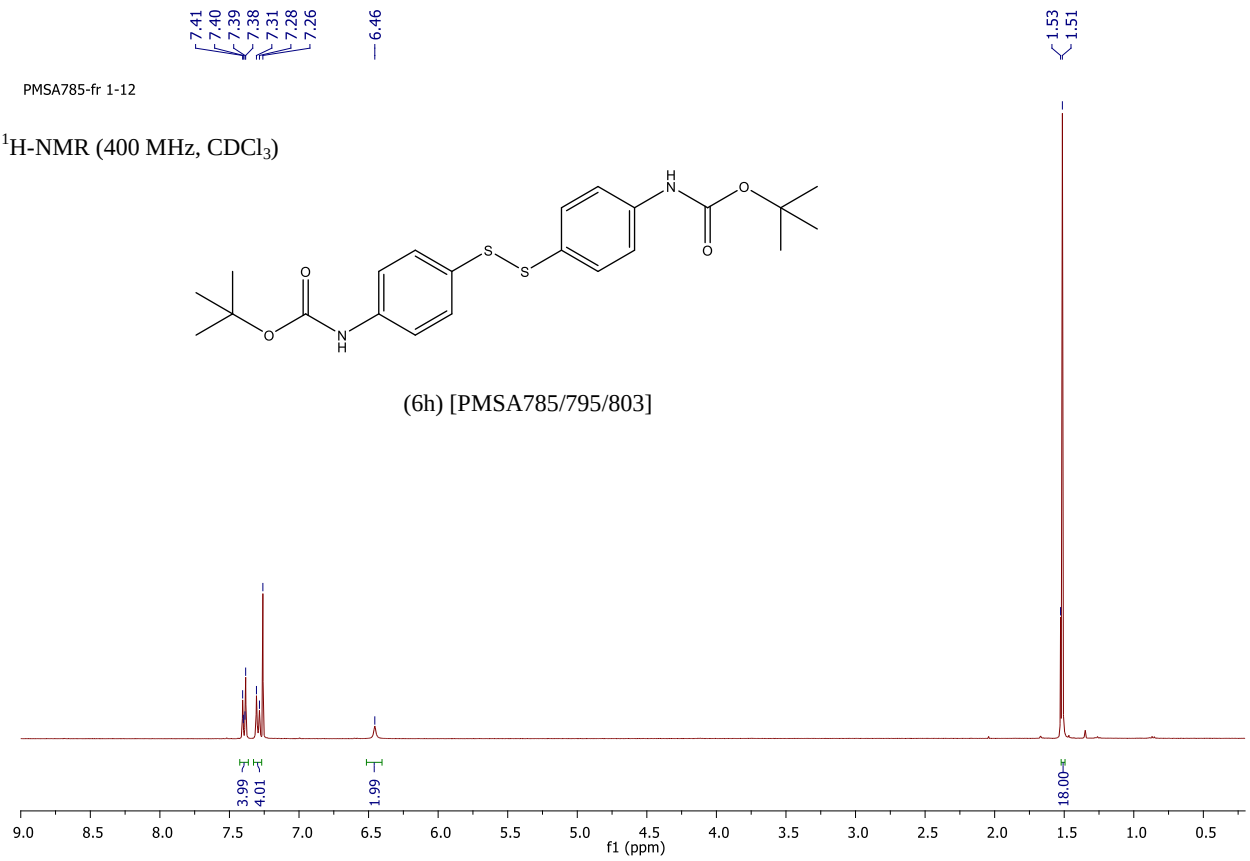


^{1}H-NMR (400 MHz, $CDCl_3$)

(6f) [PMSA566a]

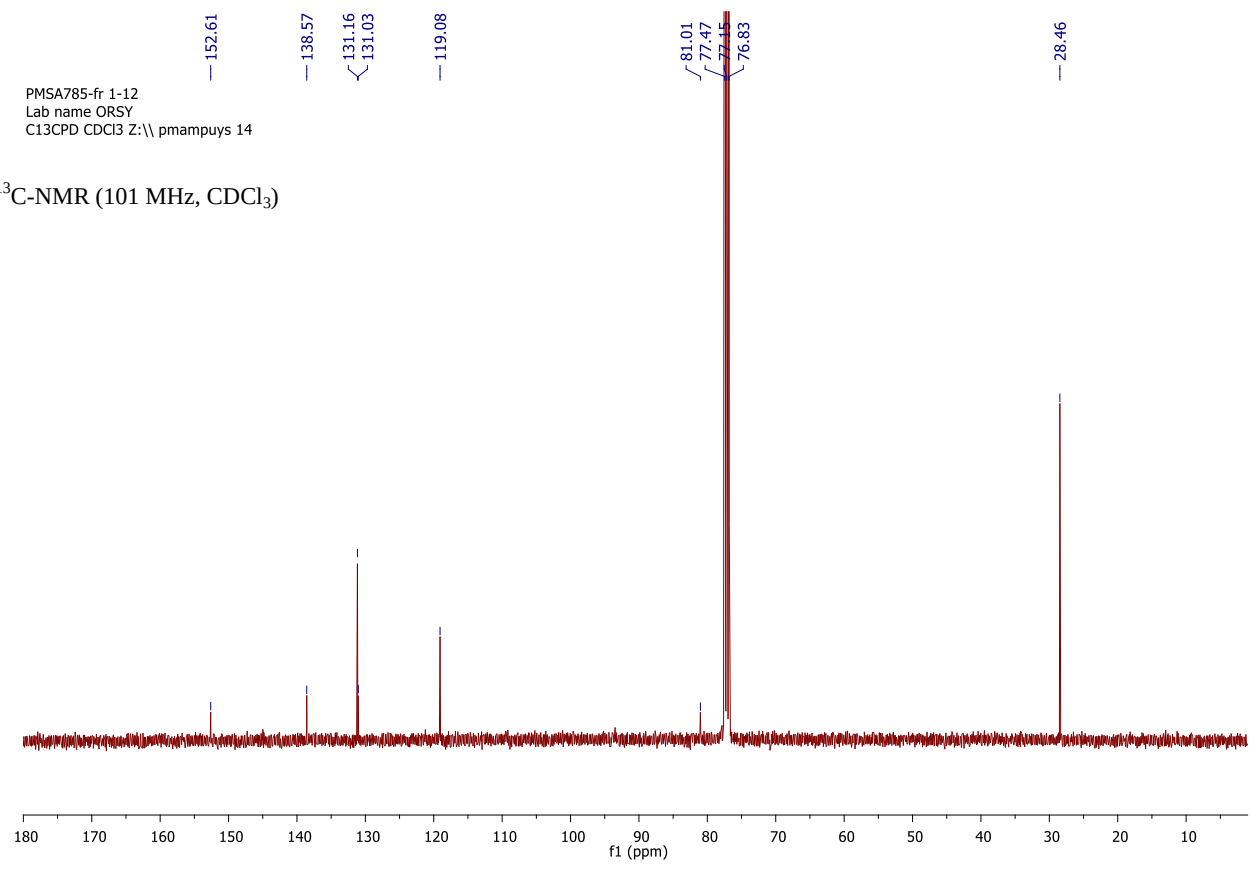


^{13}C-NMR (101 MHz, $CDCl_3$)

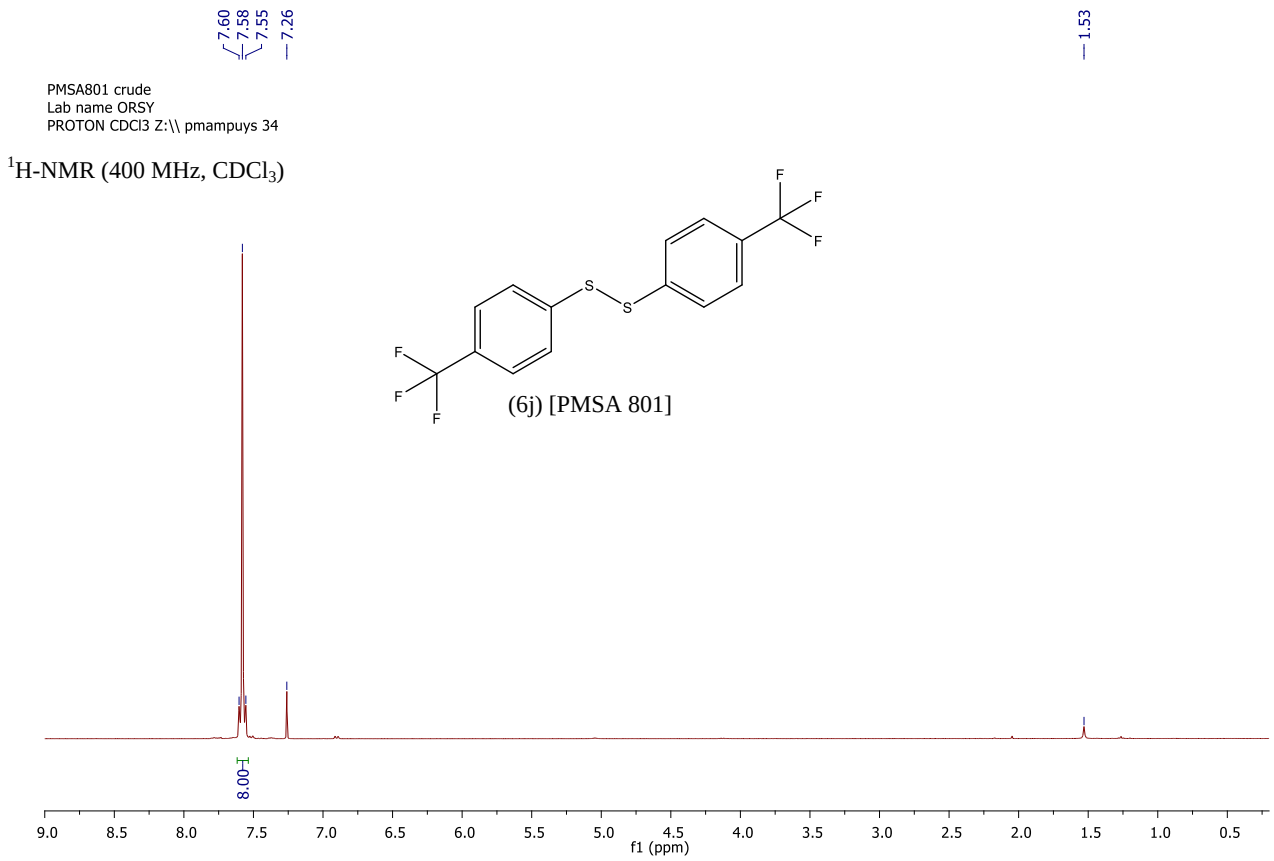


^{1}H-NMR (400 MHz, $CDCl_3$)

(6h) [PMSA785/795/803]



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



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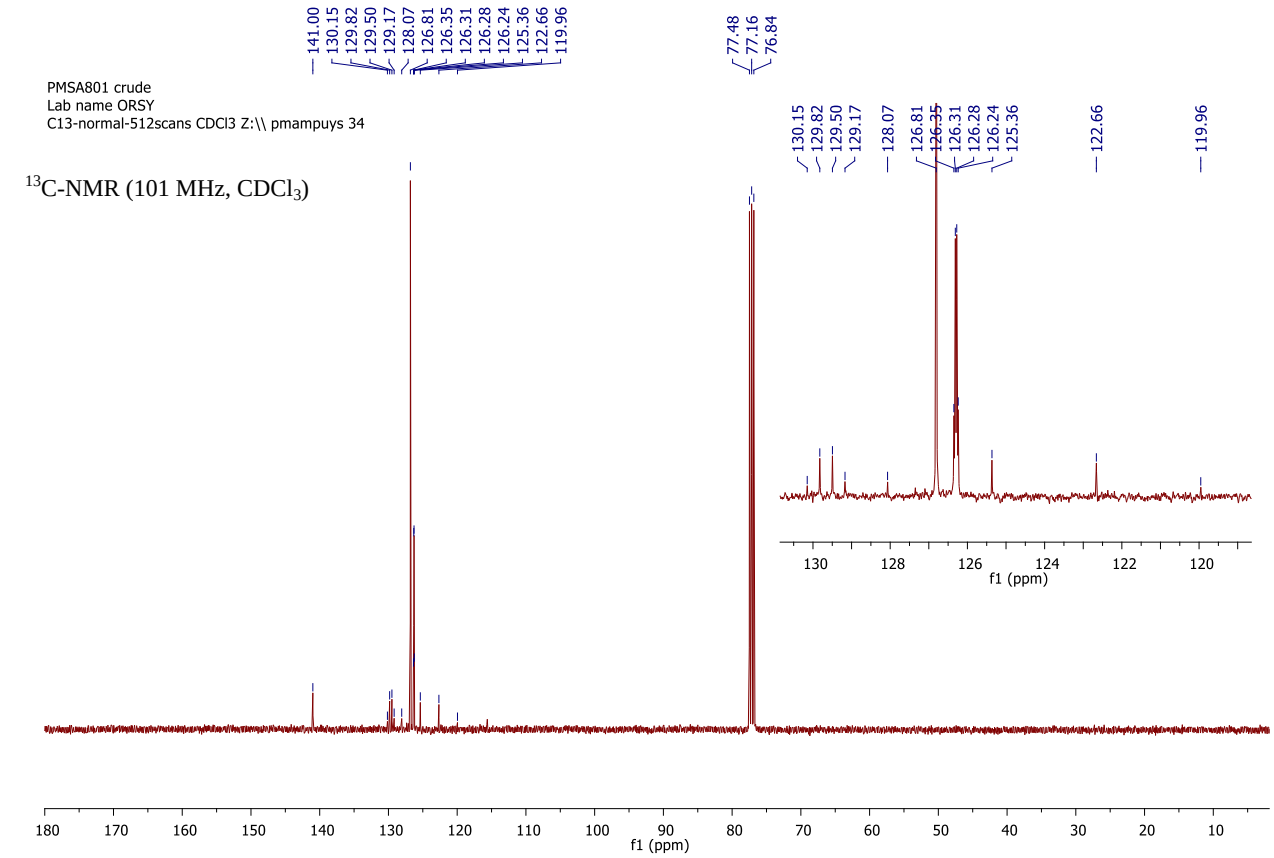
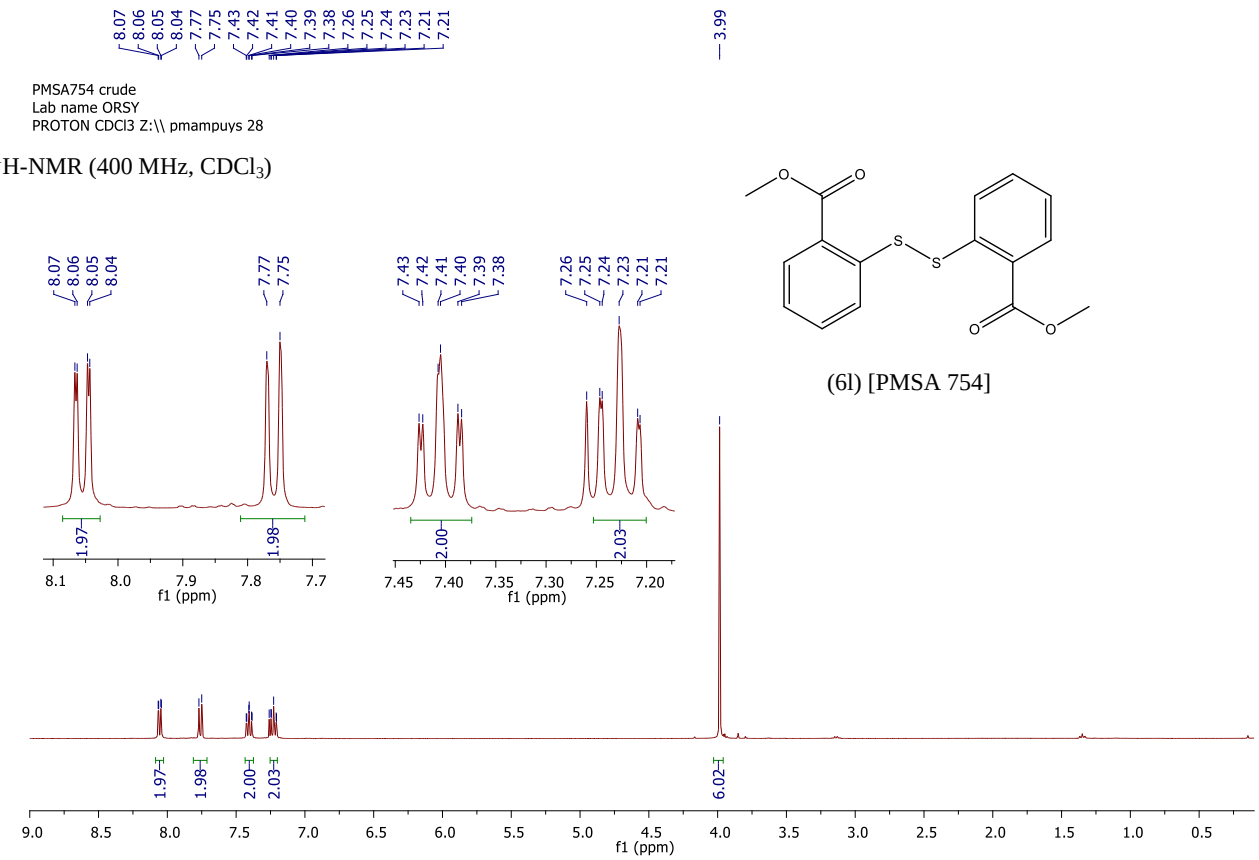
(6j) [PMSA 801]

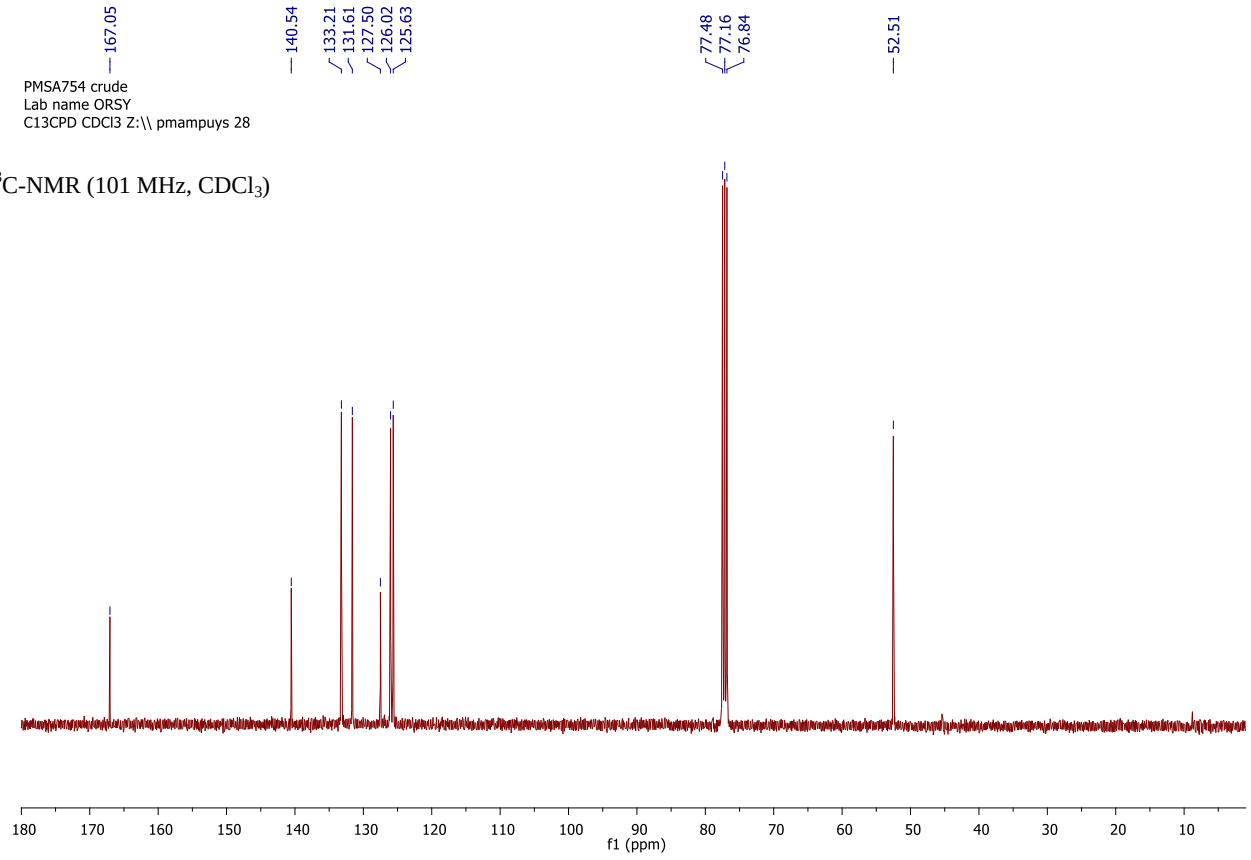


^{13}C-NMR (101 MHz, $CDCl_3$)



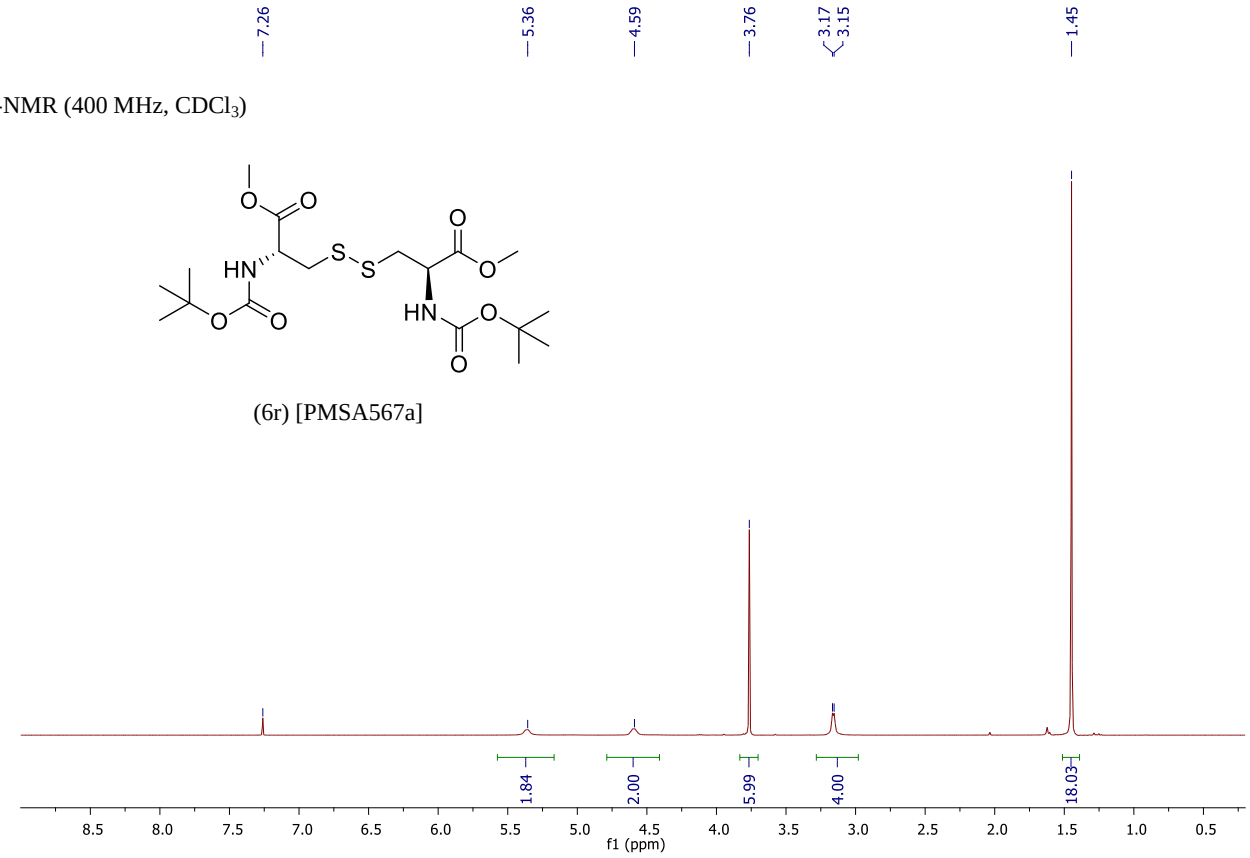
^{1}H-NMR (400 MHz, $CDCl_3$)

(6l) [PMSA 754]



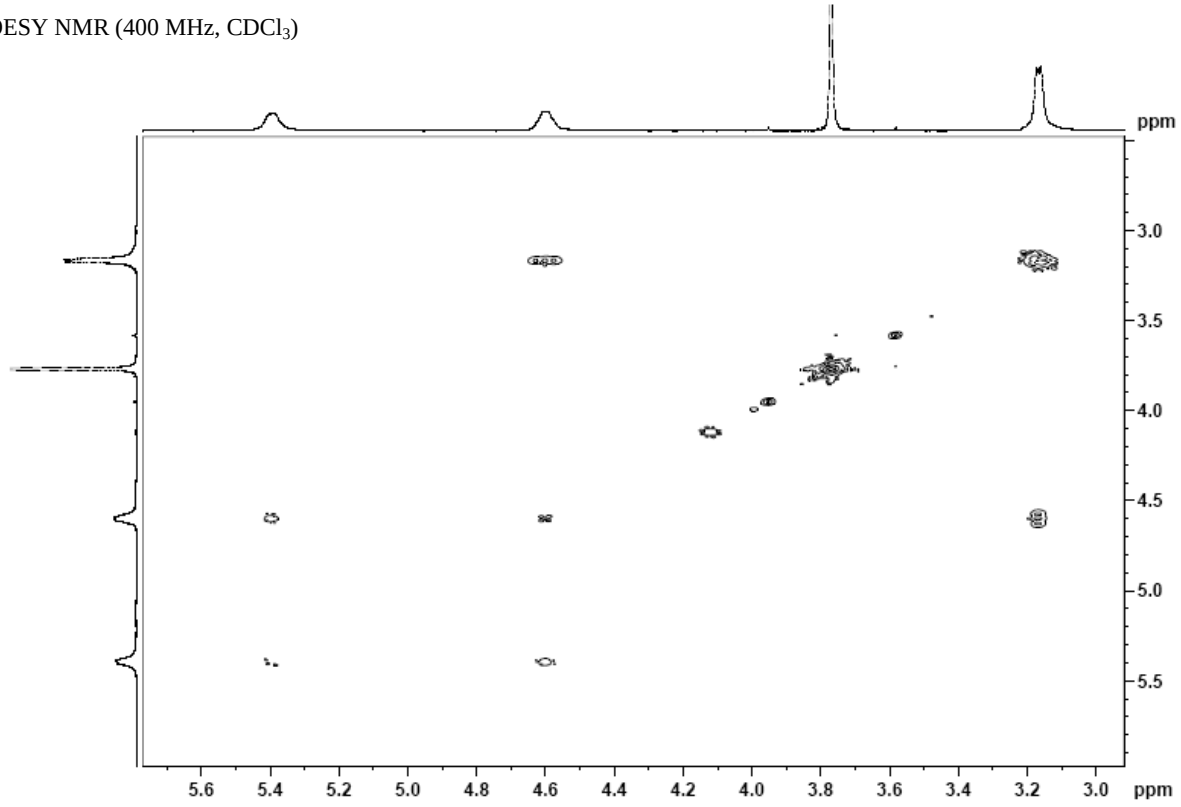
^{13}C-NMR (101 MHz, $CDCl_3$)

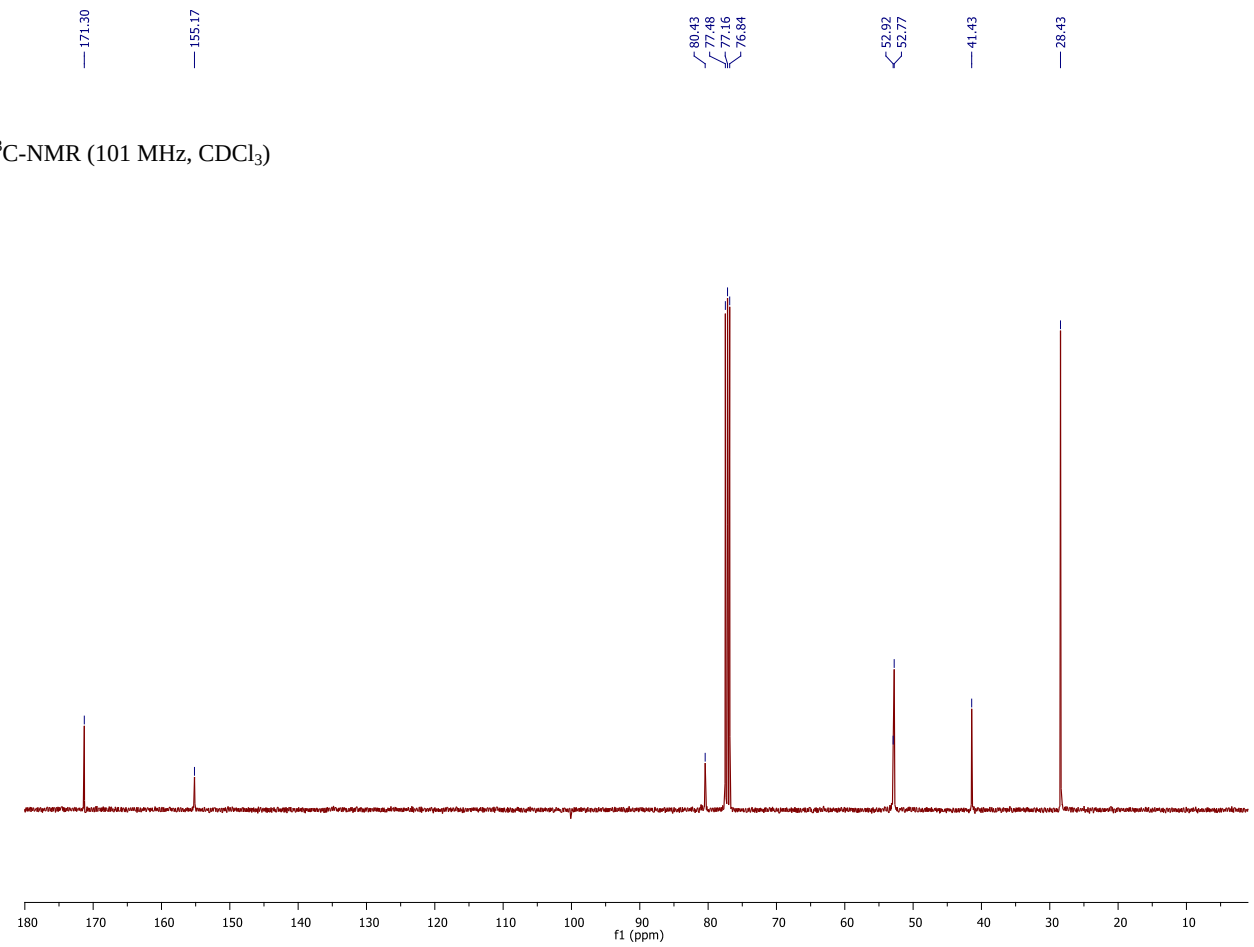
^{1}H-NMR (400 MHz, $CDCl_3$)



(6r) [PMSA567a]

COESY NMR (400 MHz, $CDCl_3$)

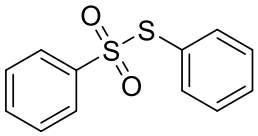




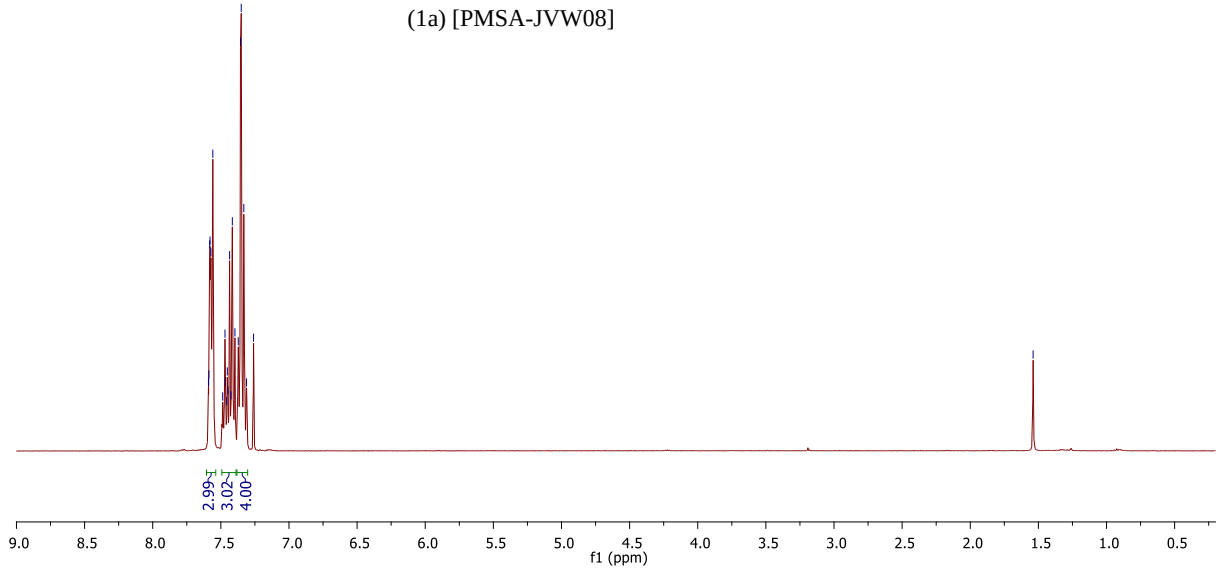
^{13}C-NMR (101 MHz, $CDCl_3$)

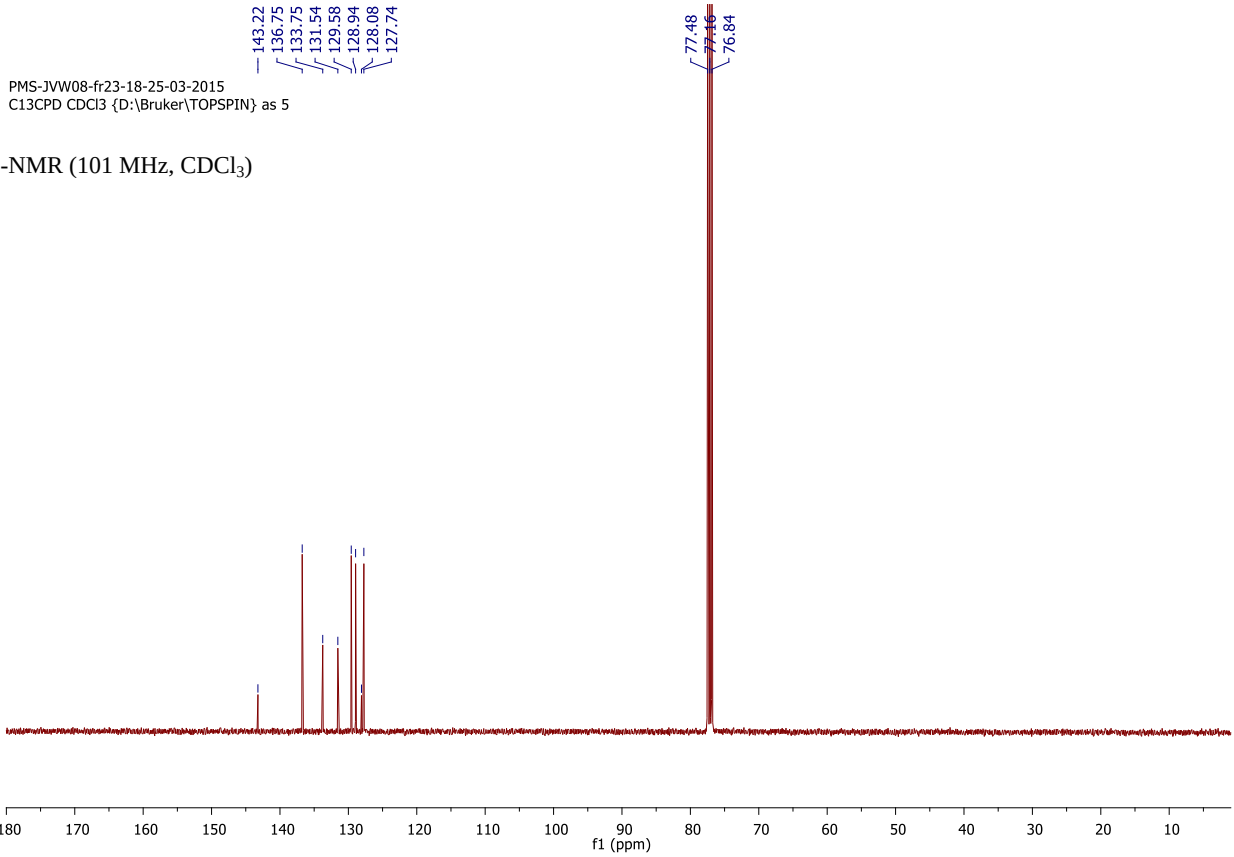
9.3 Synthesis of thiosulfonates

^{1}H-NMR (400 MHz, $CDCl_3$)



(1a) [PMSA-JVW08]

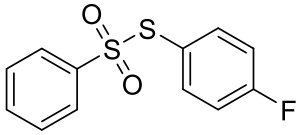




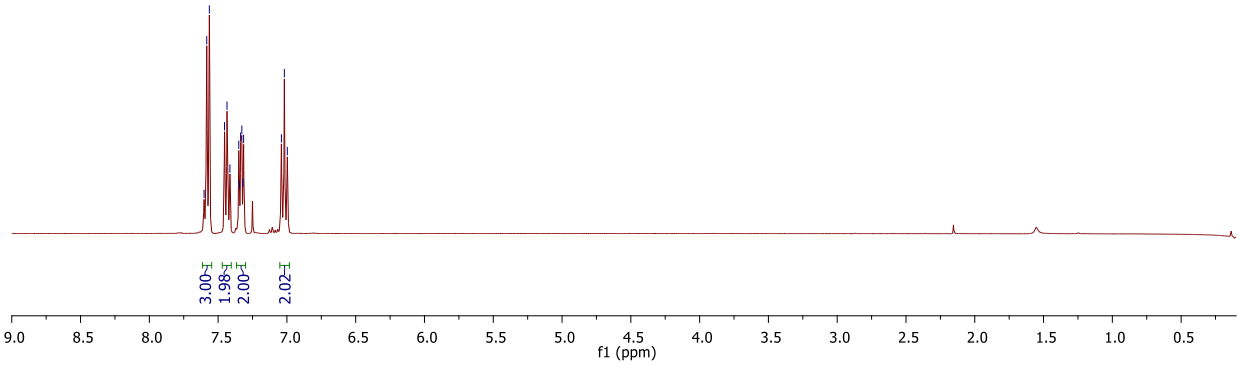
^{13}C-NMR (101 MHz, $CDCl_3$)

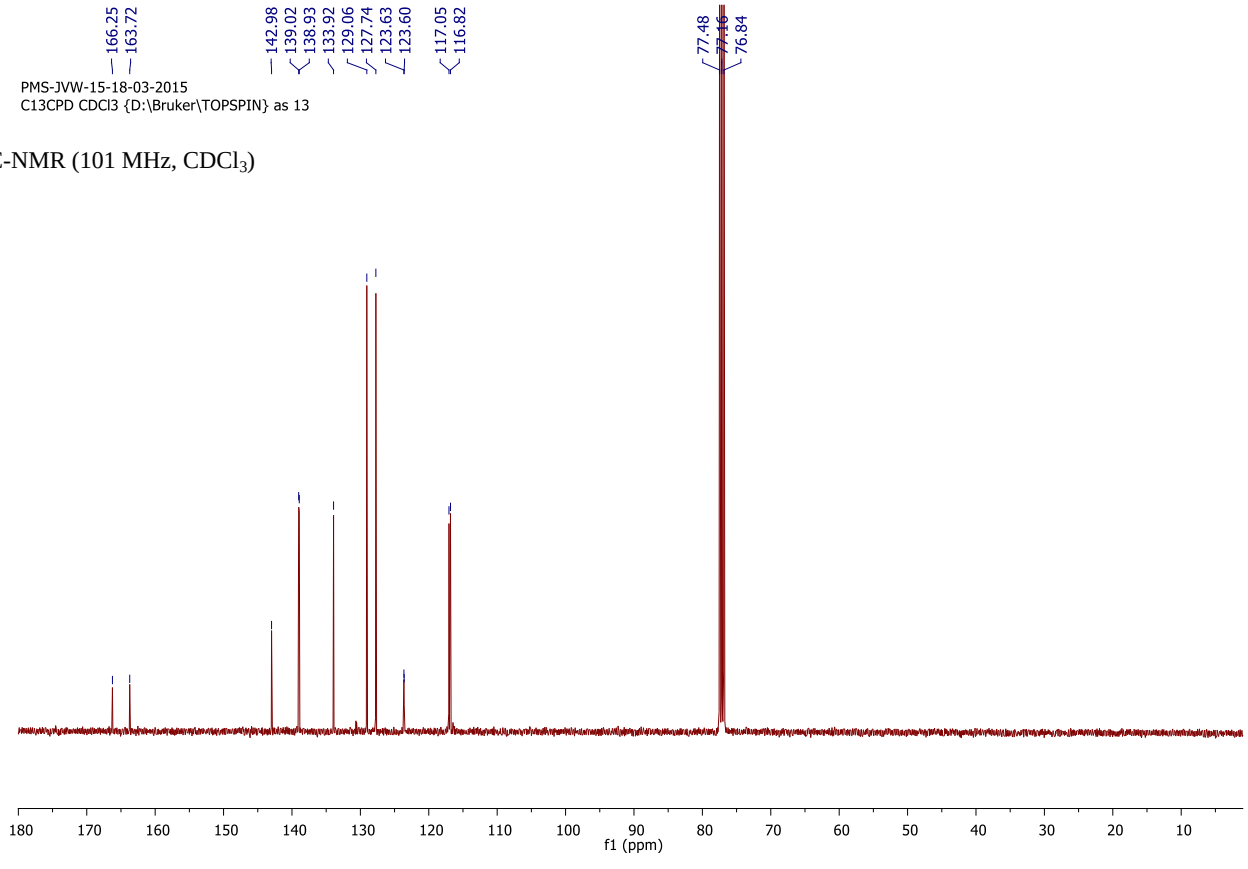
PMS-JVW15-Pieter-17-03-15
PROTON CDCl3 {D:\Bruker\TOPSPIN} hseykens 17

^{1}H-NMR (400 MHz, $CDCl_3$)



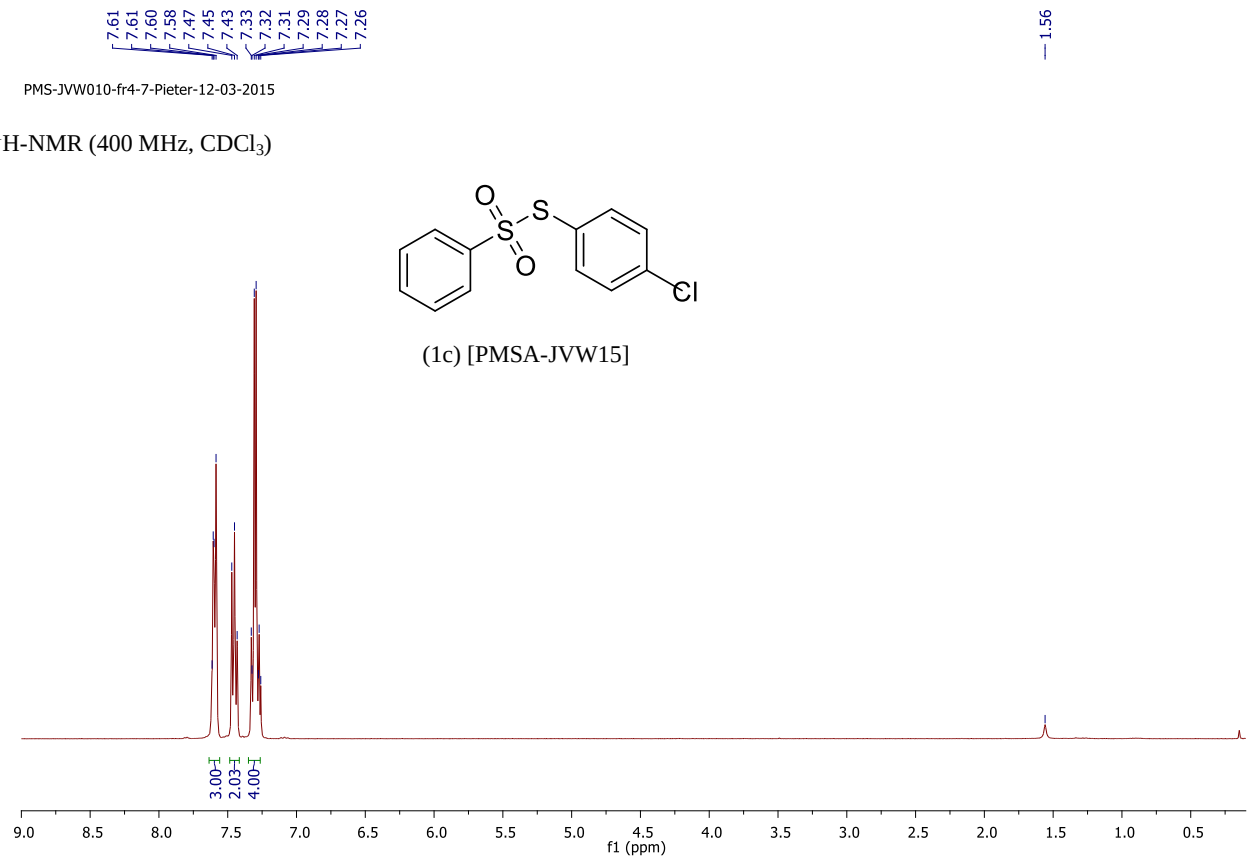
(1b) [PMSA-JVW15]





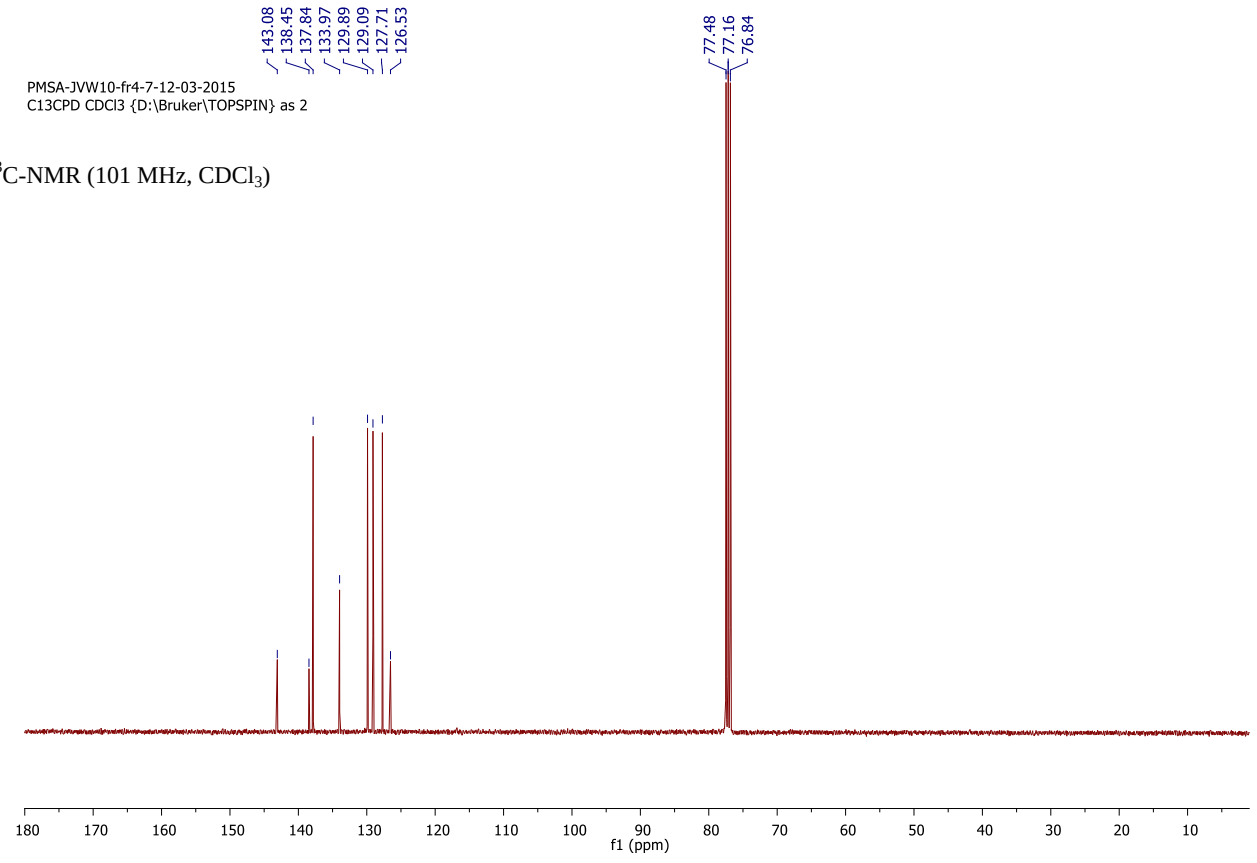
PMS-JVW-15-18-03-2015
C13CPD CDCl3 {D:\Bruker\TOPSPIN} as 13

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

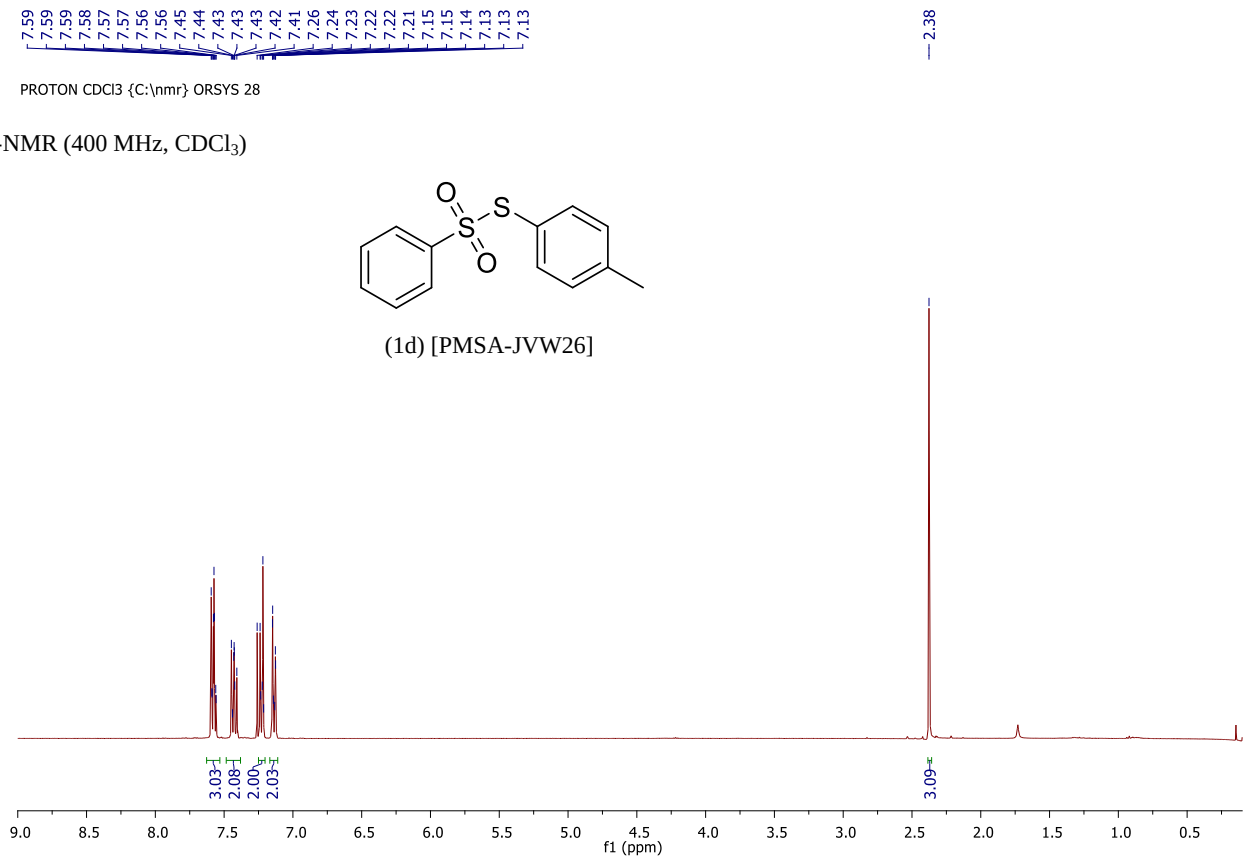


^{1}H-NMR (400 MHz, $CDCl_3$)

(1c) [PMSA-JVW15]

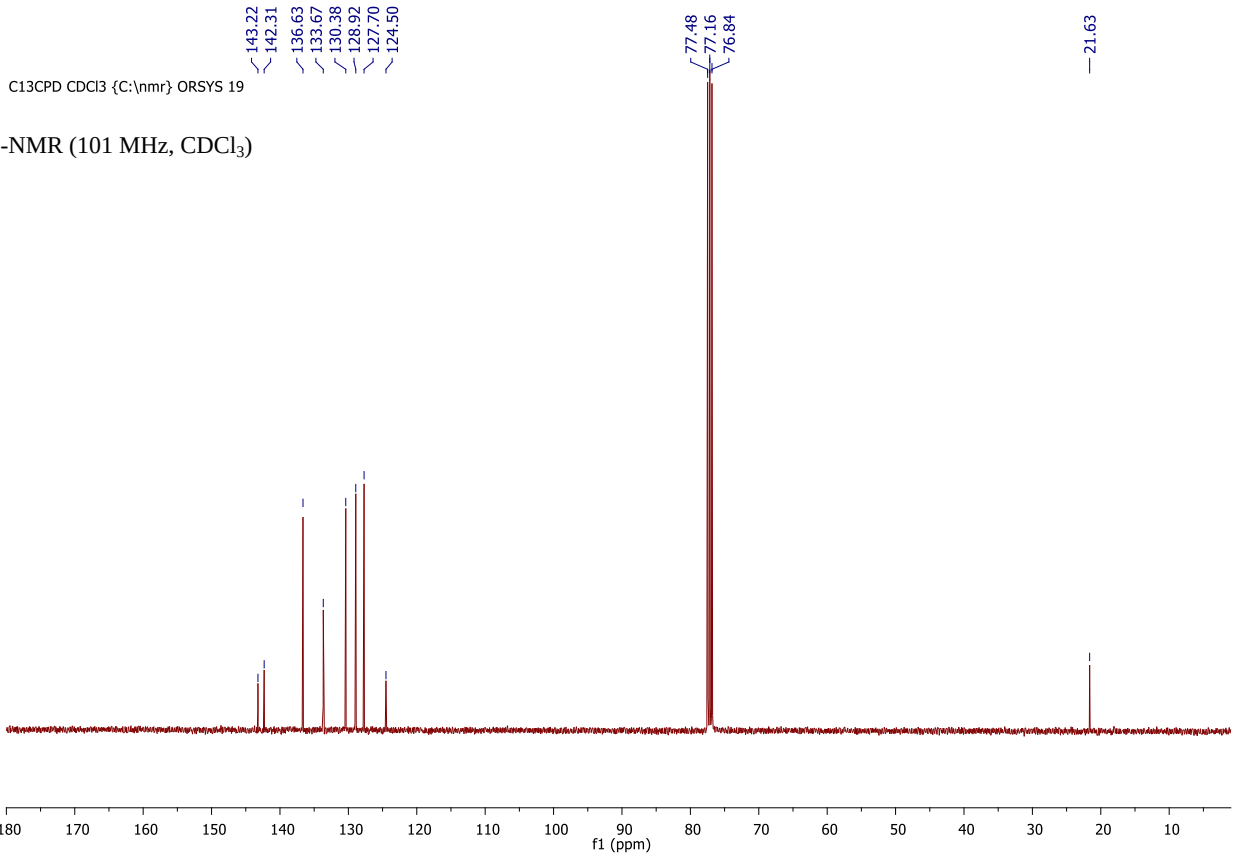


^{13}C-NMR (101 MHz, $CDCl_3$)



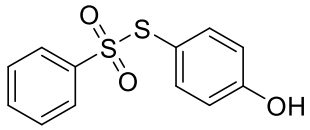
^{1}H-NMR (400 MHz, $CDCl_3$)

(1d) [PMSA-JVW26]

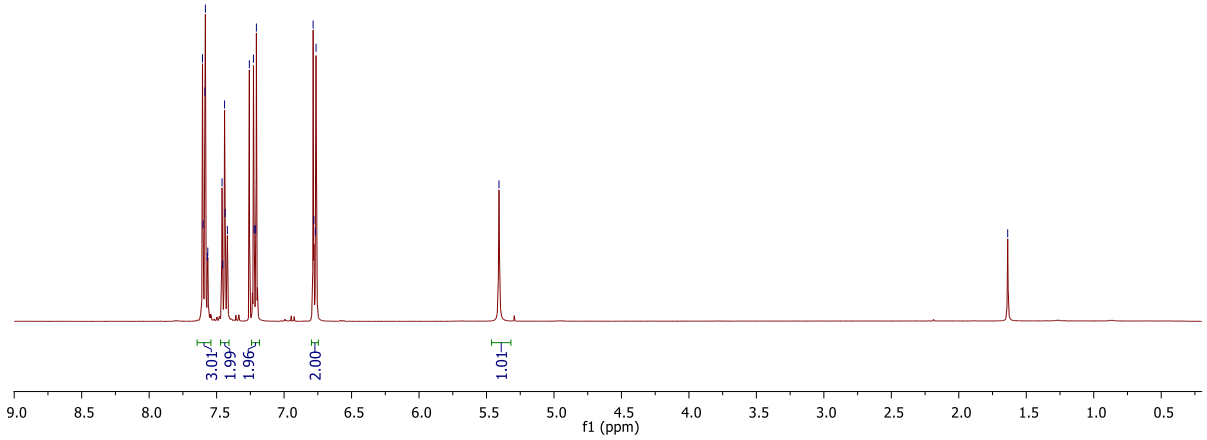


^{13}C-NMR (101 MHz, $CDCl_3$)

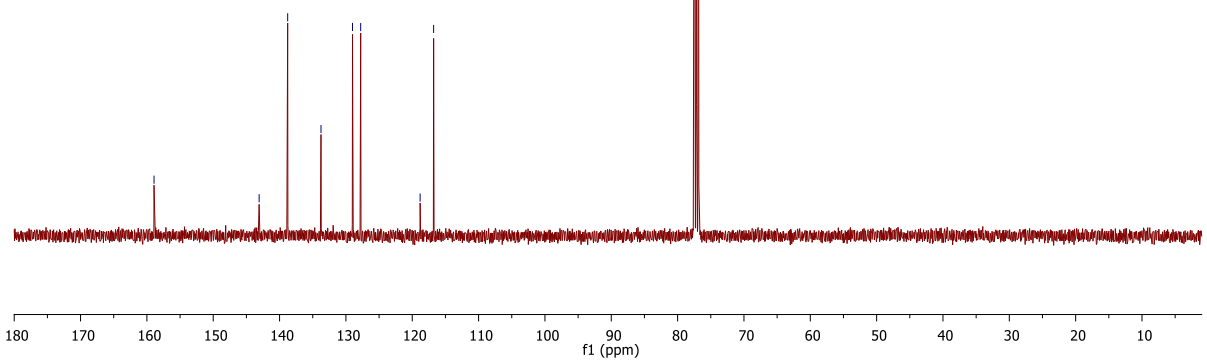
^{1}H-NMR (400 MHz, $CDCl_3$)

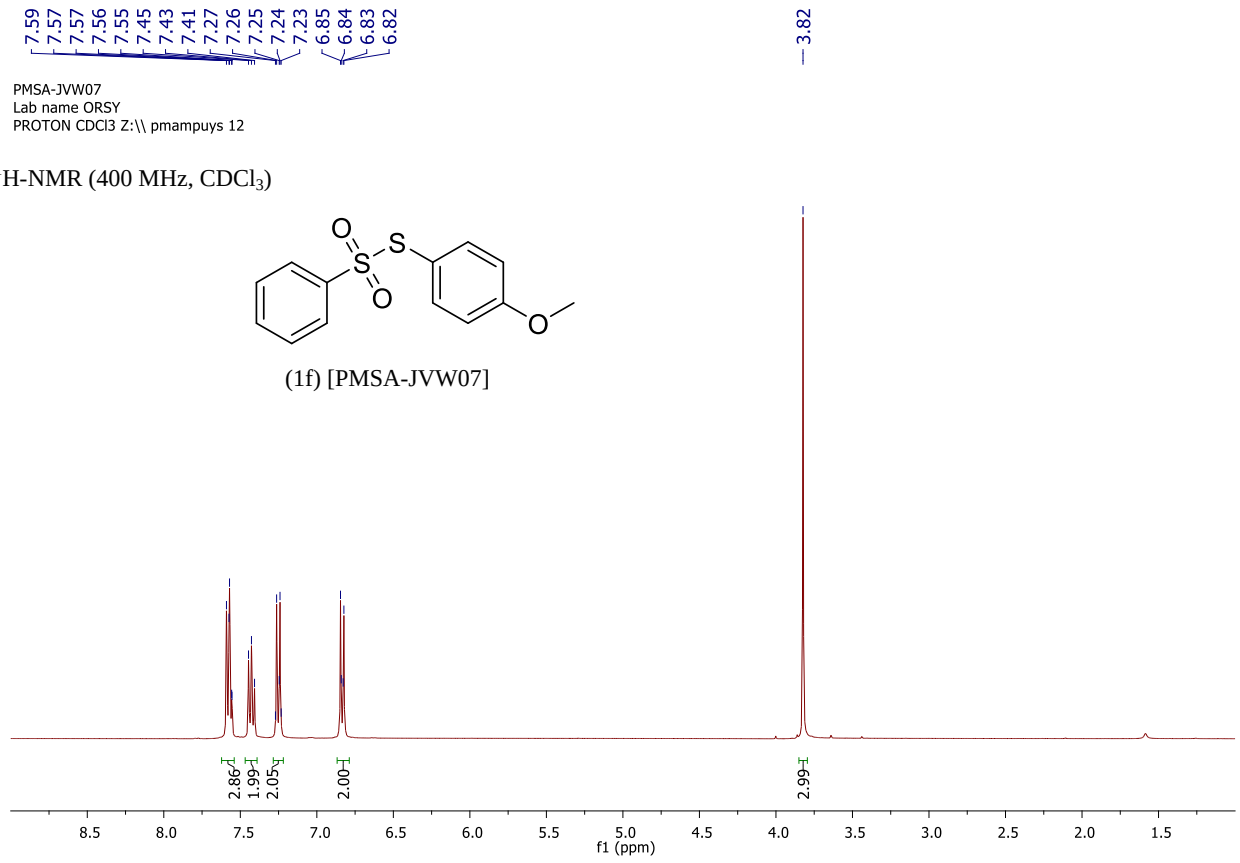


(1e) [PMSA 751]



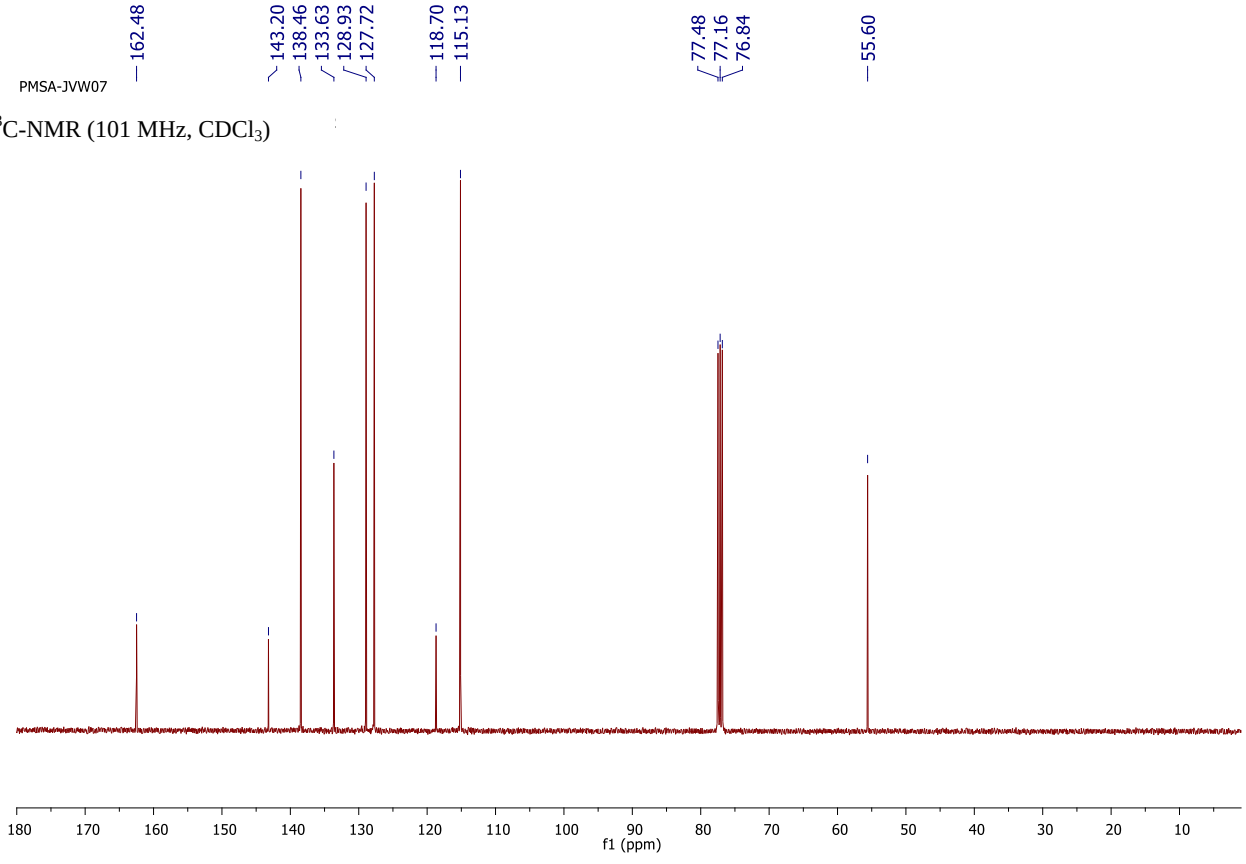
^{13}C-NMR (101 MHz, $CDCl_3$)





^{1}H-NMR (400 MHz, $CDCl_3$)

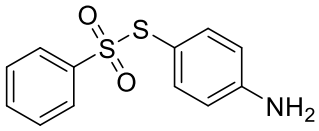
(1f) [PMSA-JVW07]



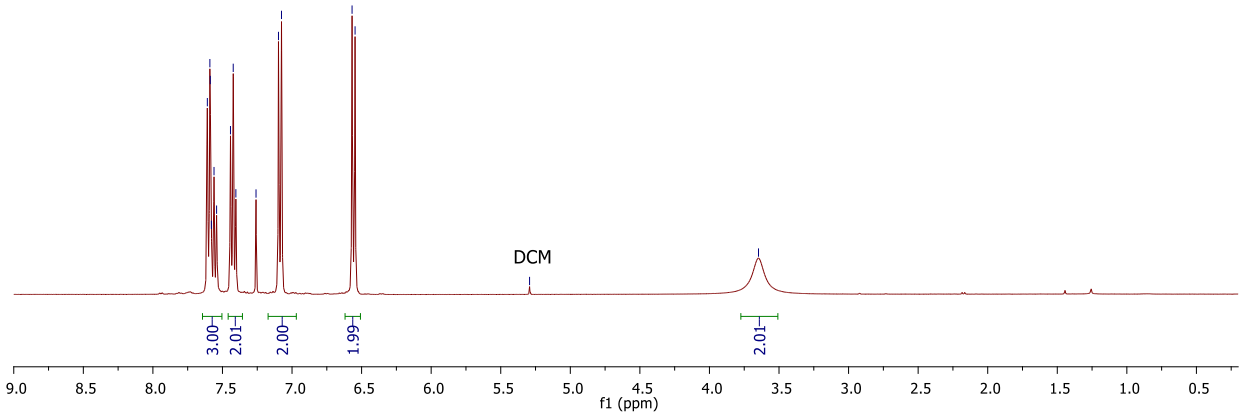
^{13}C-NMR (101 MHz, $CDCl_3$)

Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 11

^{1}H-NMR (400 MHz, $CDCl_3$)

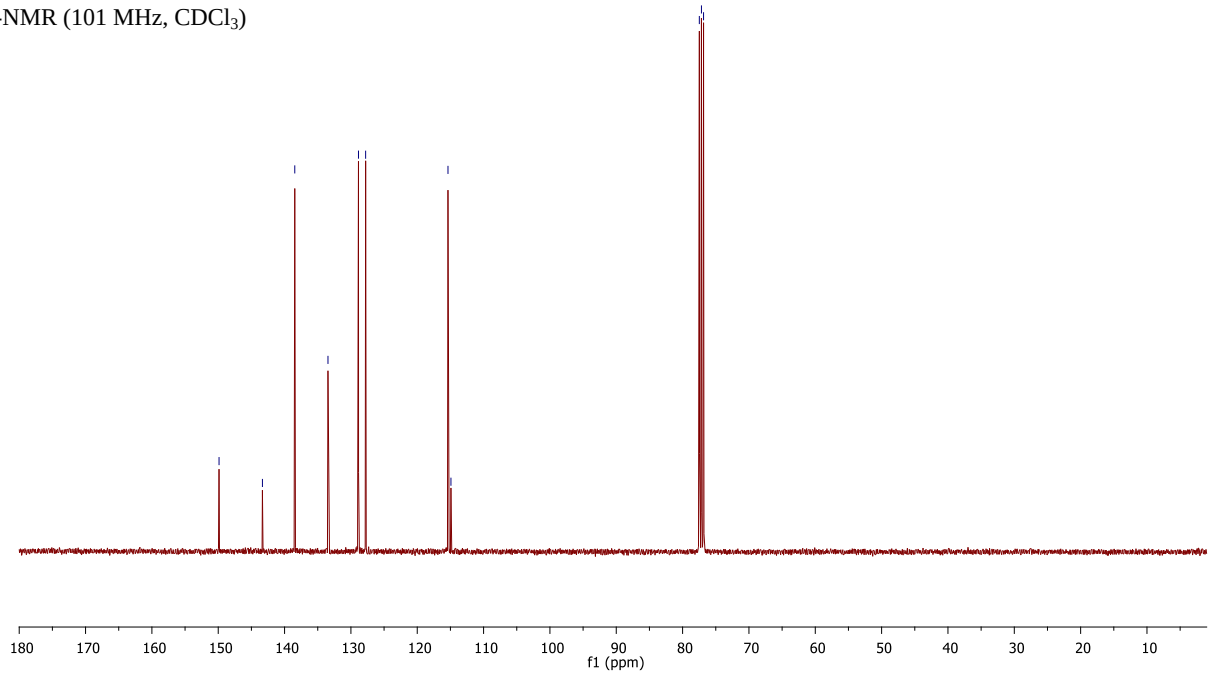


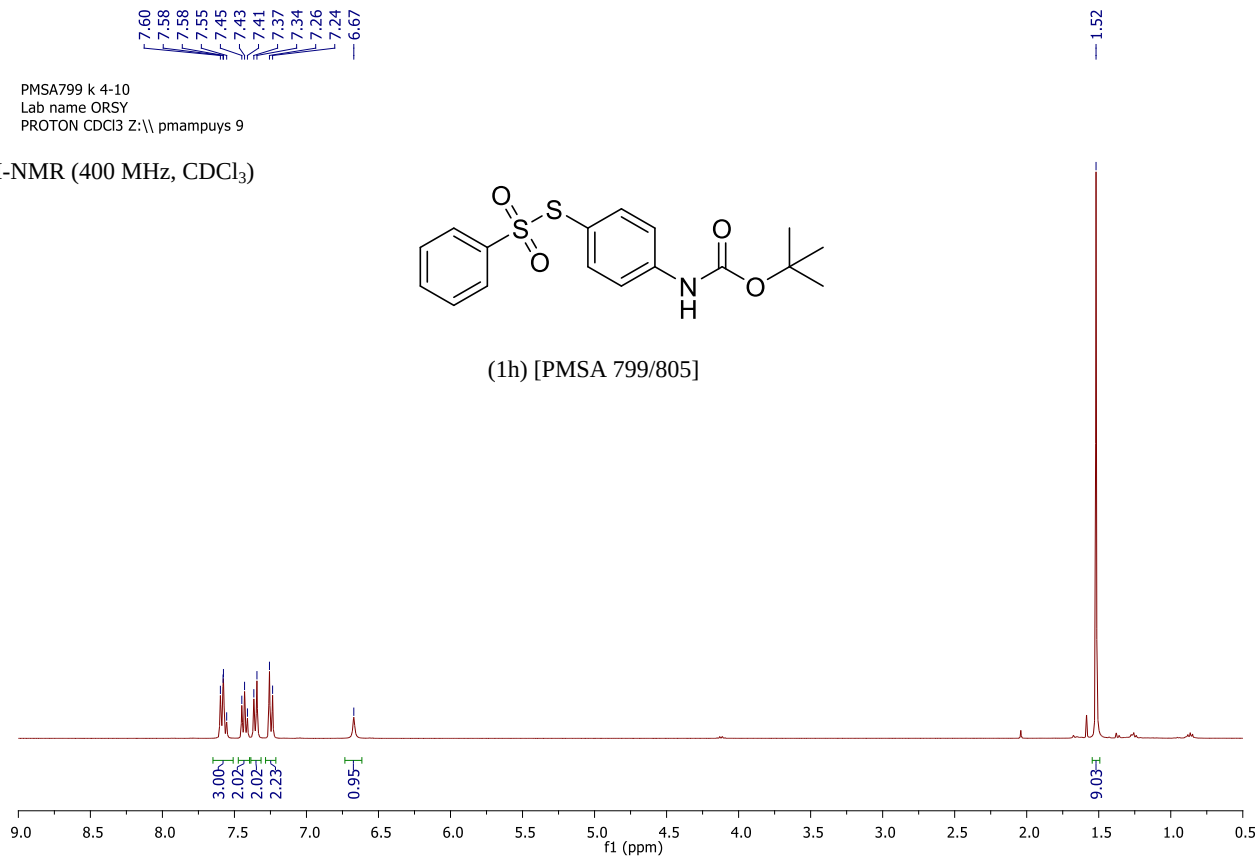
(1g) [PMSA 747]



PMSA747
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 2

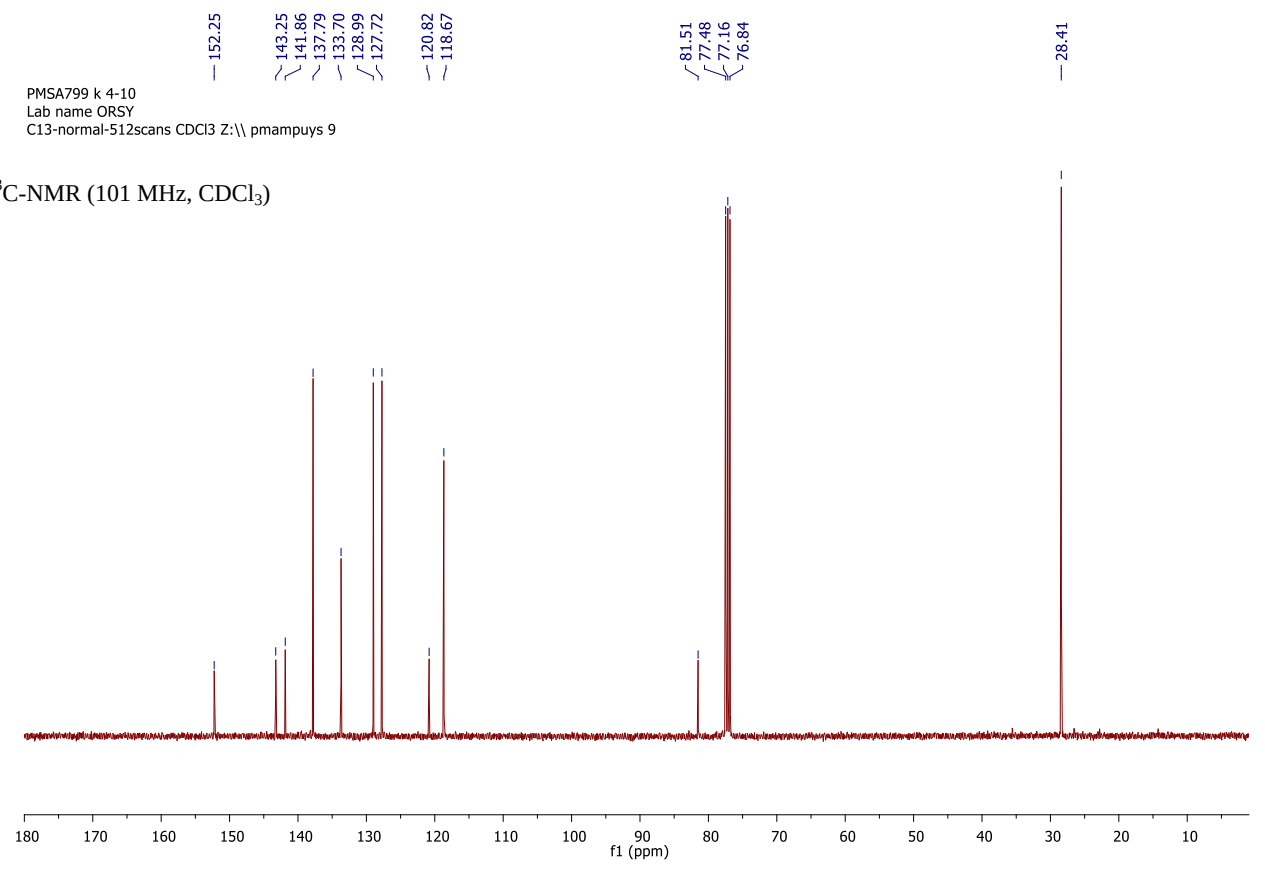
^{13}C-NMR (101 MHz, $CDCl_3$)



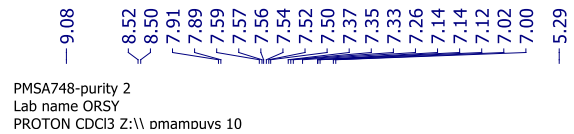


^{1}H-NMR (400 MHz, $CDCl_3$)

(1h) [PMSA 799/805]

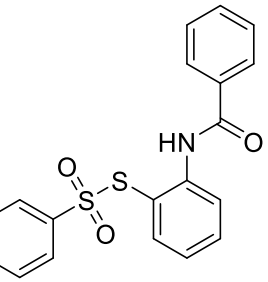


^{13}C-NMR (101 MHz, $CDCl_3$)

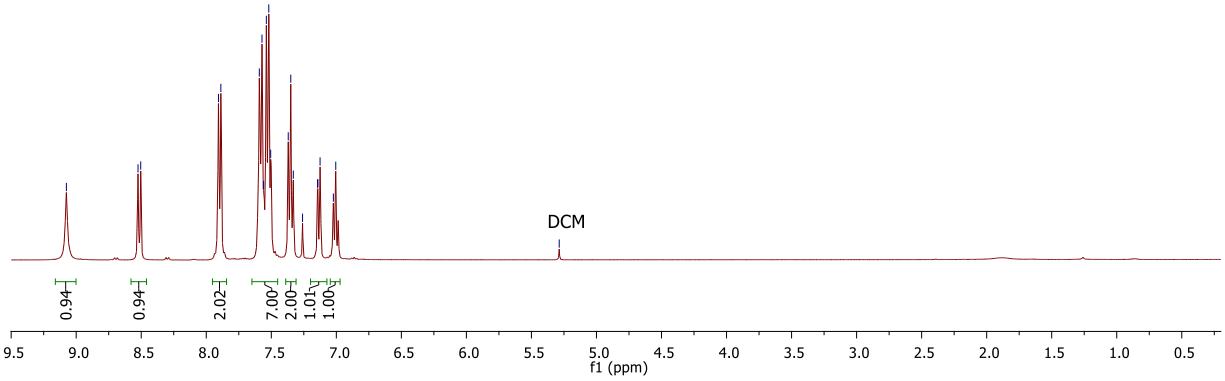


PMSA748-purity 2
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 10

^{1}H-NMR (400 MHz, $CDCl_3$)

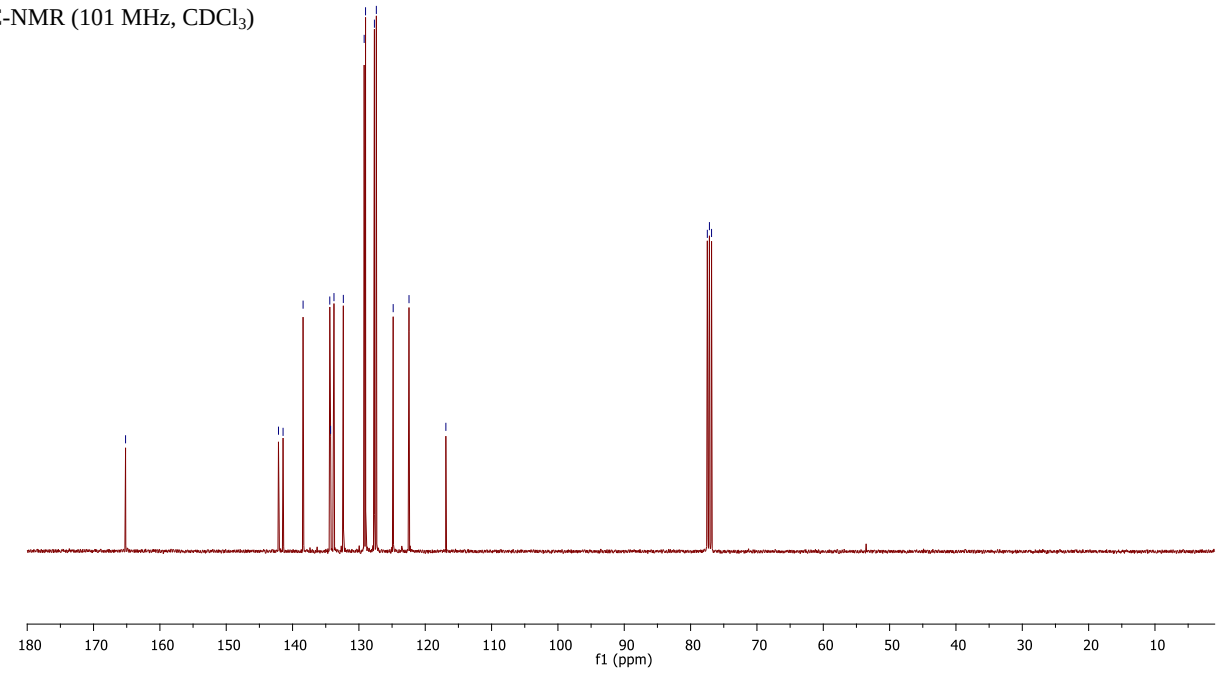


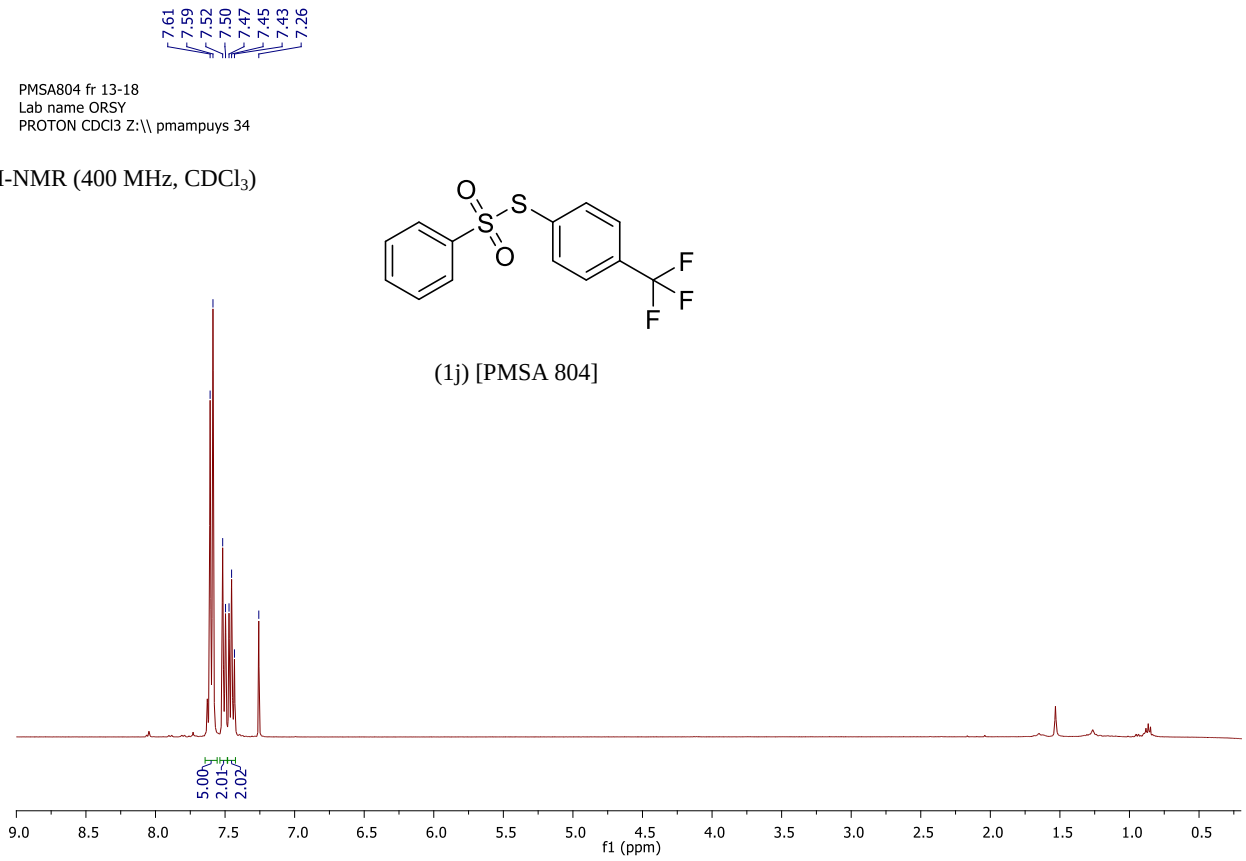
(1i) [PMSA 748]



PMSA748
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 18

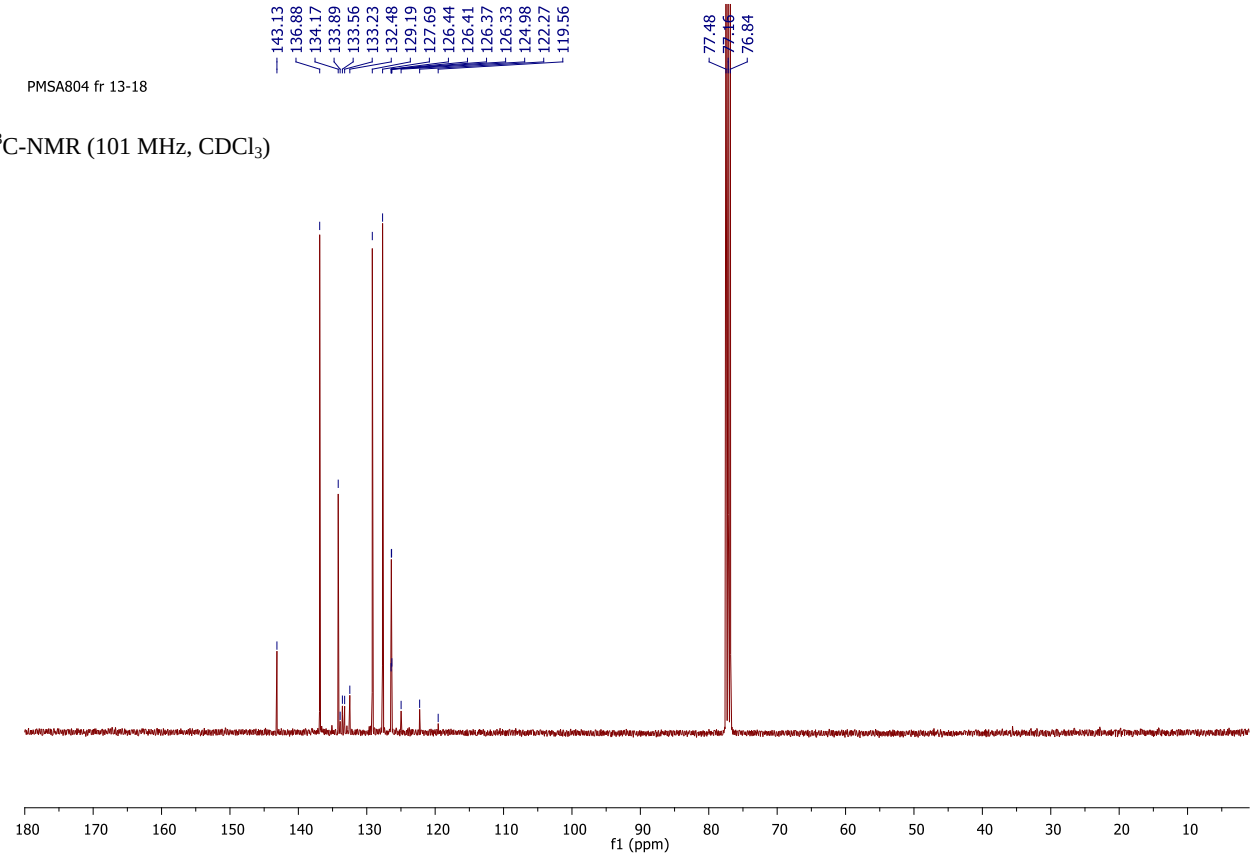
^{13}C-NMR (101 MHz, $CDCl_3$)





^{1}H-NMR (400 MHz, $CDCl_3$)

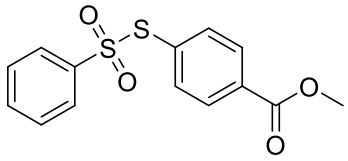
(1j) [PMSA 804]



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

PMSA813 fr4-8

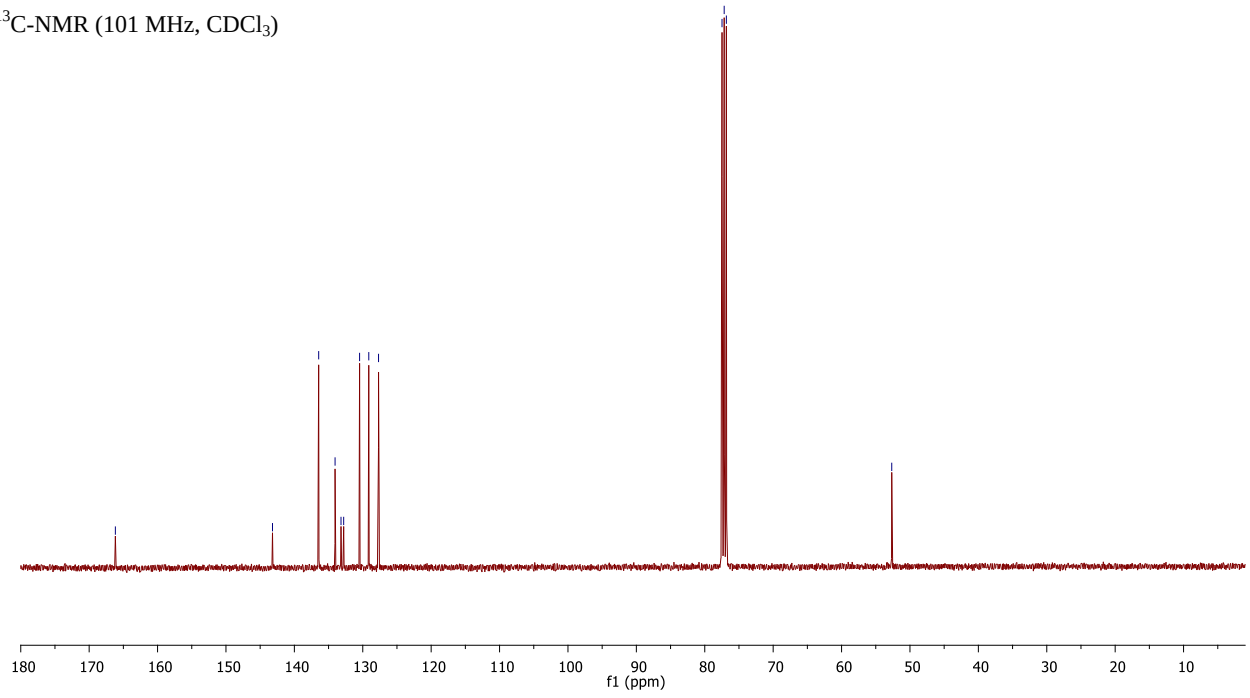
^{1}H-NMR (400 MHz, $CDCl_3$)

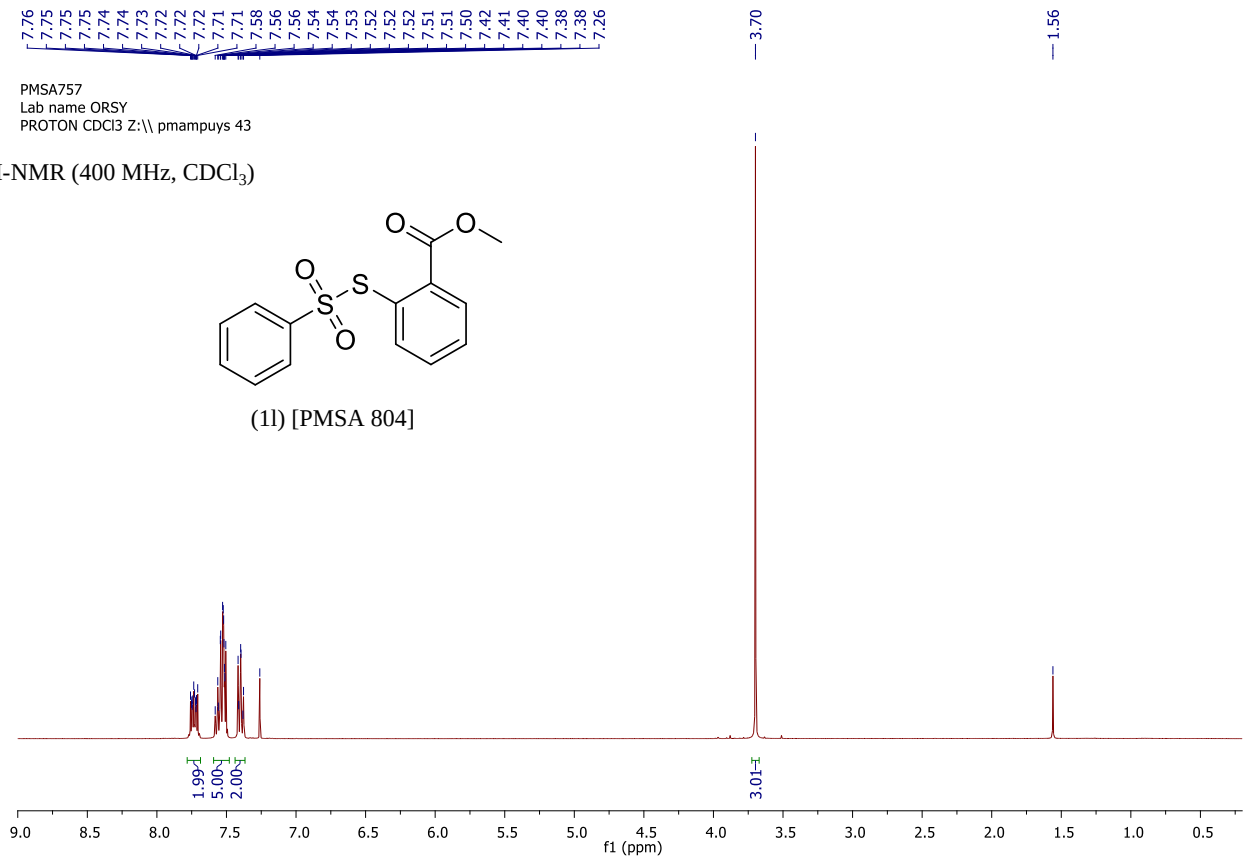


(1k) [PMSA 813]

PMSA813 fr4-8
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 30

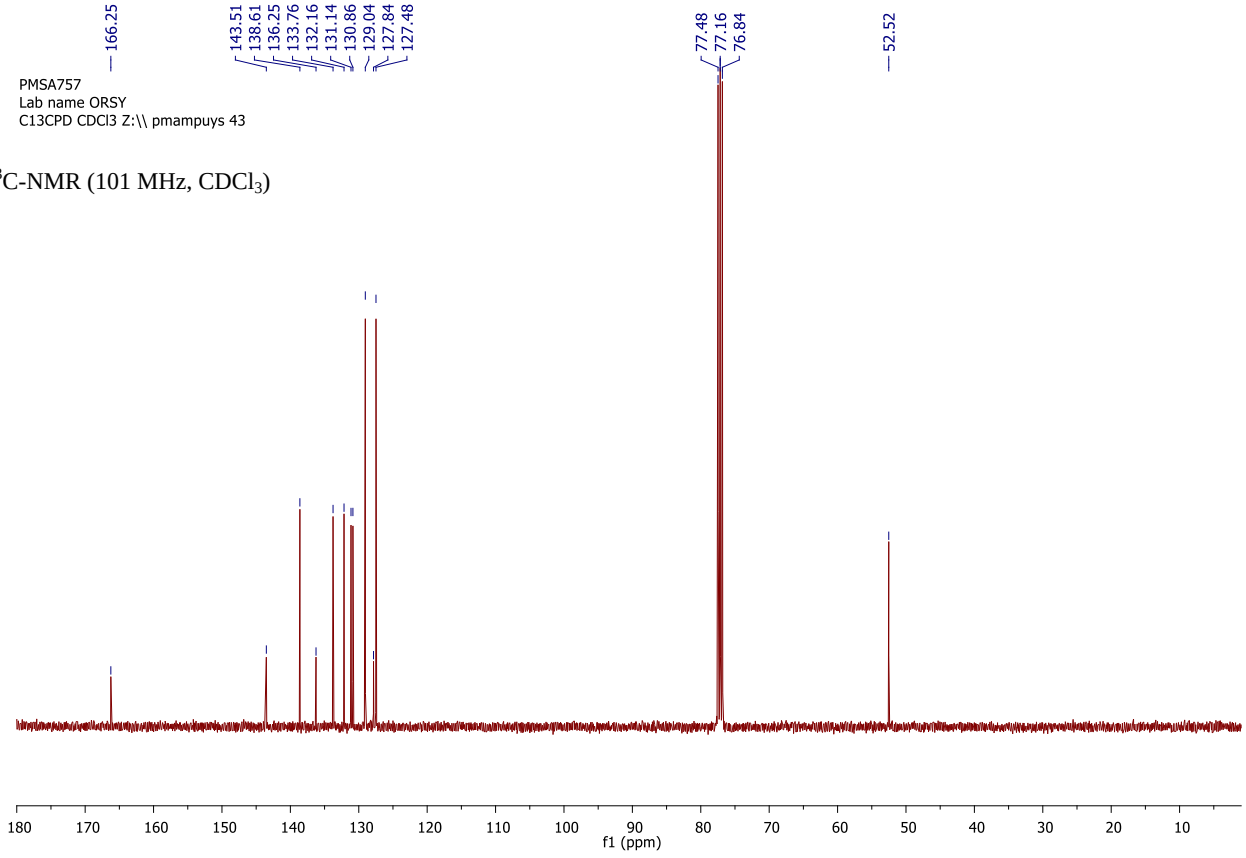
^{13}C-NMR (101 MHz, $CDCl_3$)



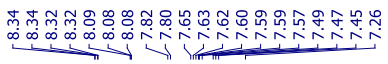


^{1}H-NMR (400 MHz, $CDCl_3$)

(1l) [PMSA 804]

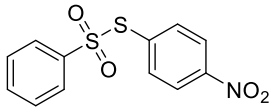


^{13}C-NMR (101 MHz, $CDCl_3$)

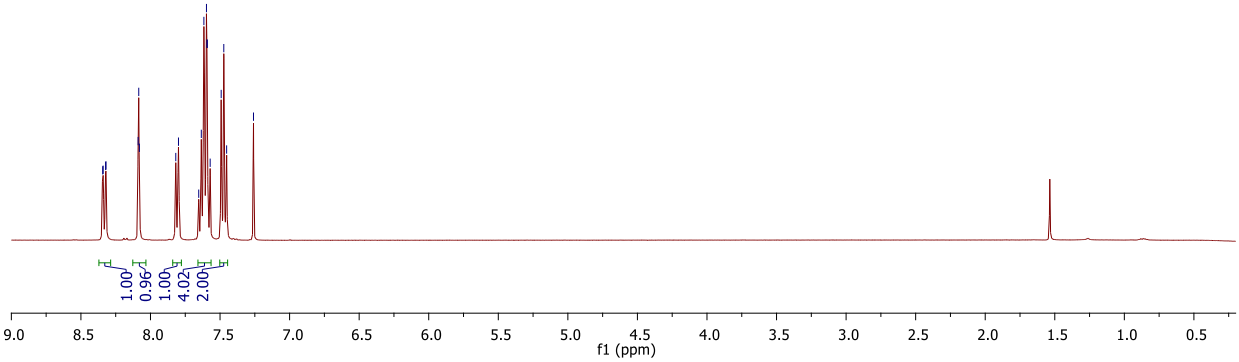


PMSA572
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 6

^{1}H-NMR (400 MHz, $CDCl_3$)

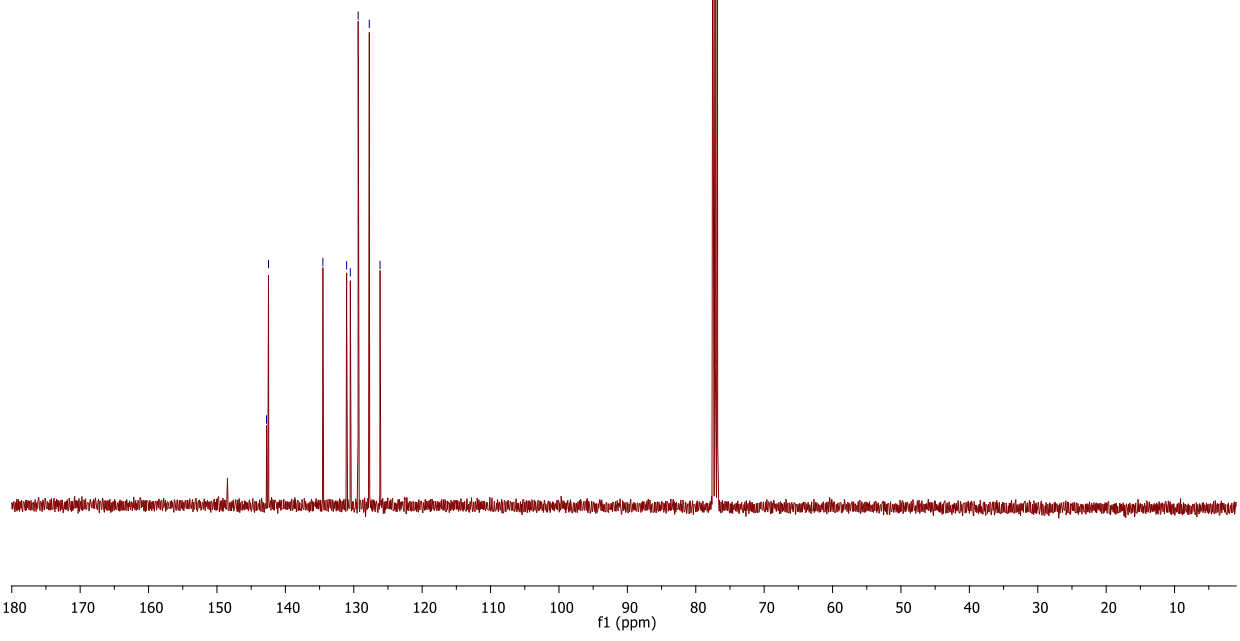


(1m) [PMSA572]

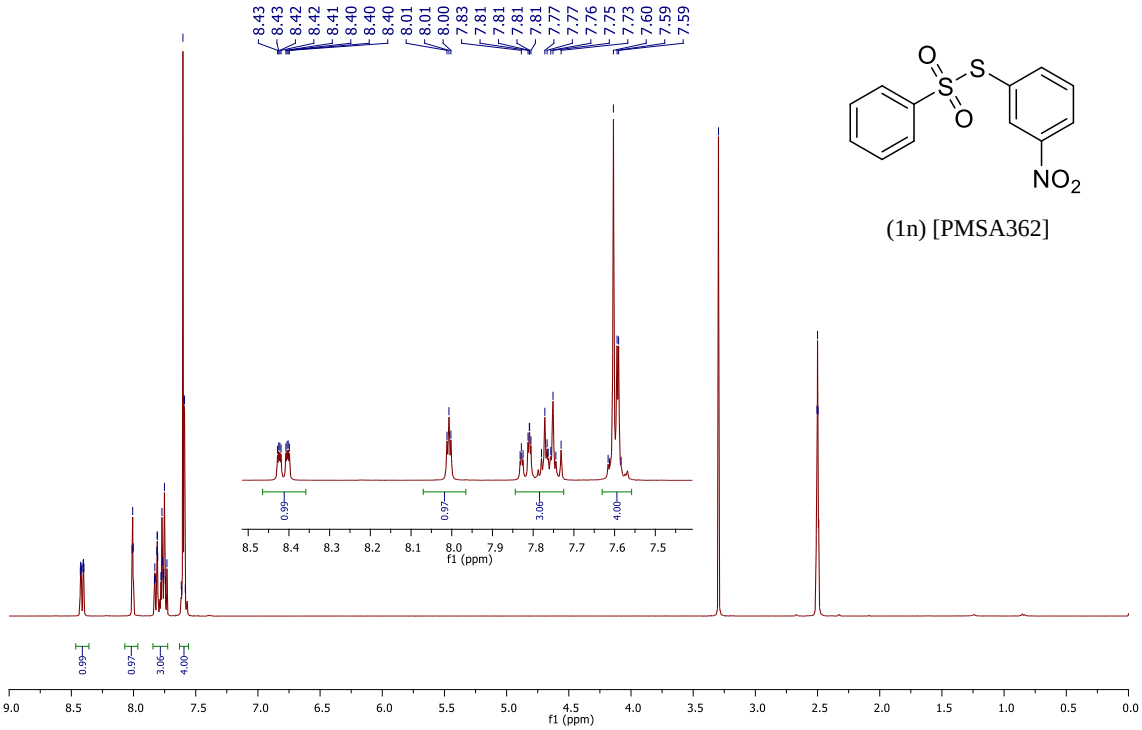


PMSA572
Lab name ORSY
C13-normal-512scans CDCl3 Z:\\ pmampuys 6

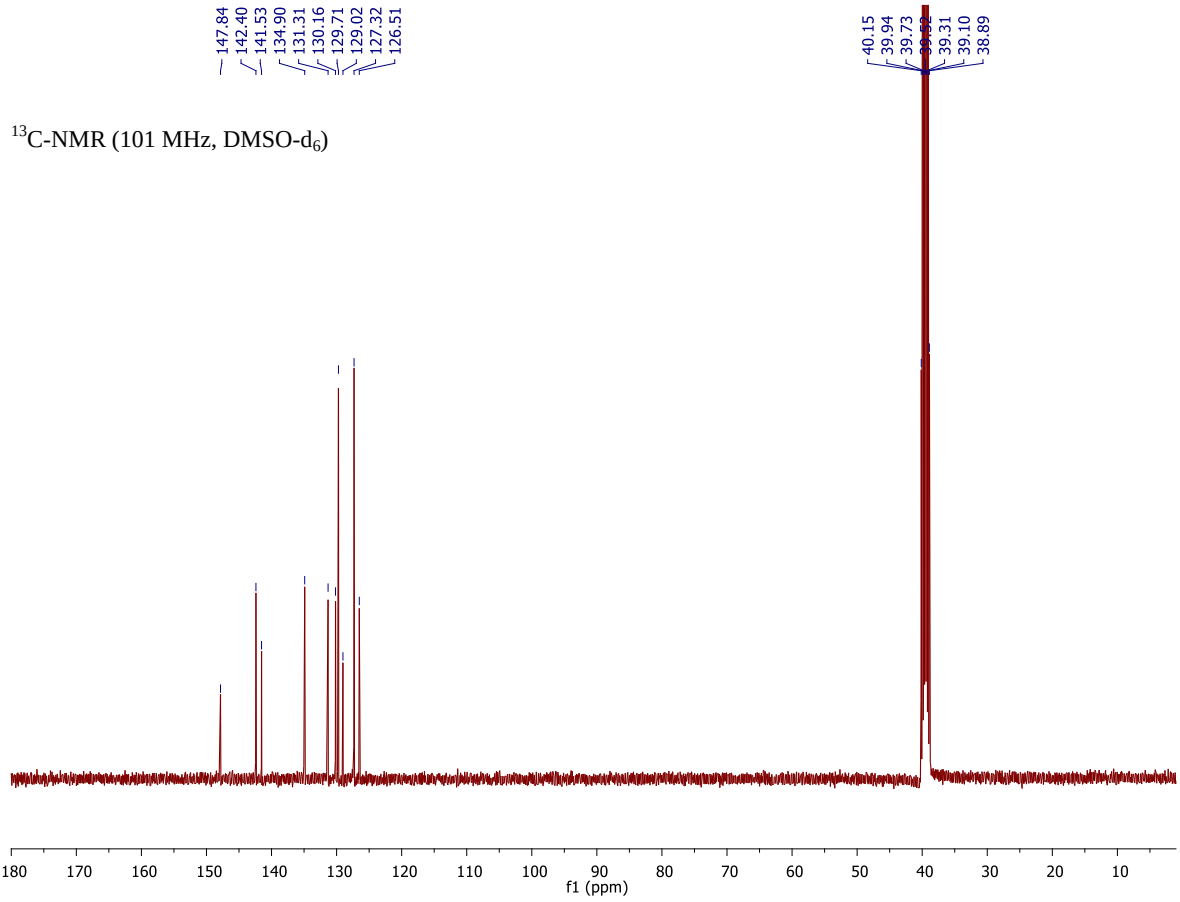
^{13}C-NMR (101 MHz, $CDCl_3$)



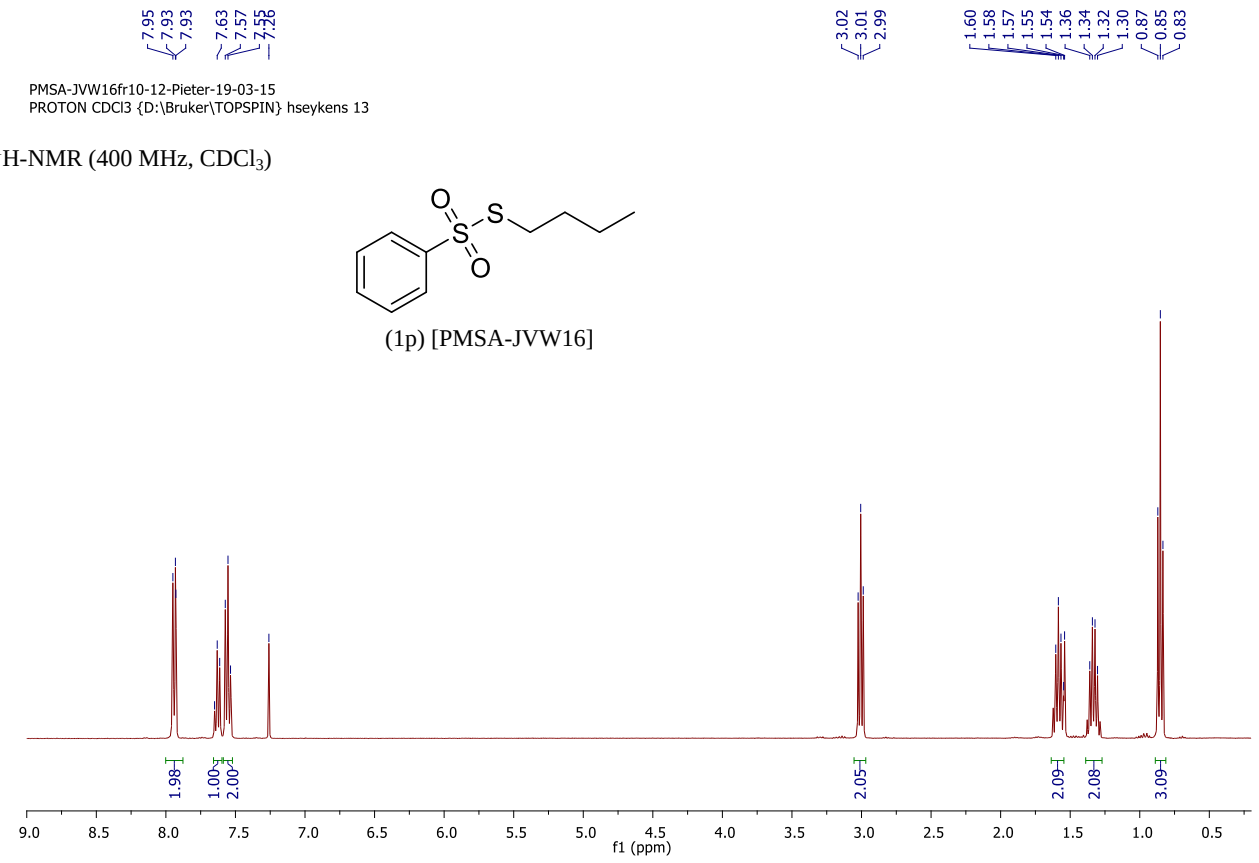
^{1}H-NMR (400 MHz, DMSO-d_6)



(1n) [PMSA362]

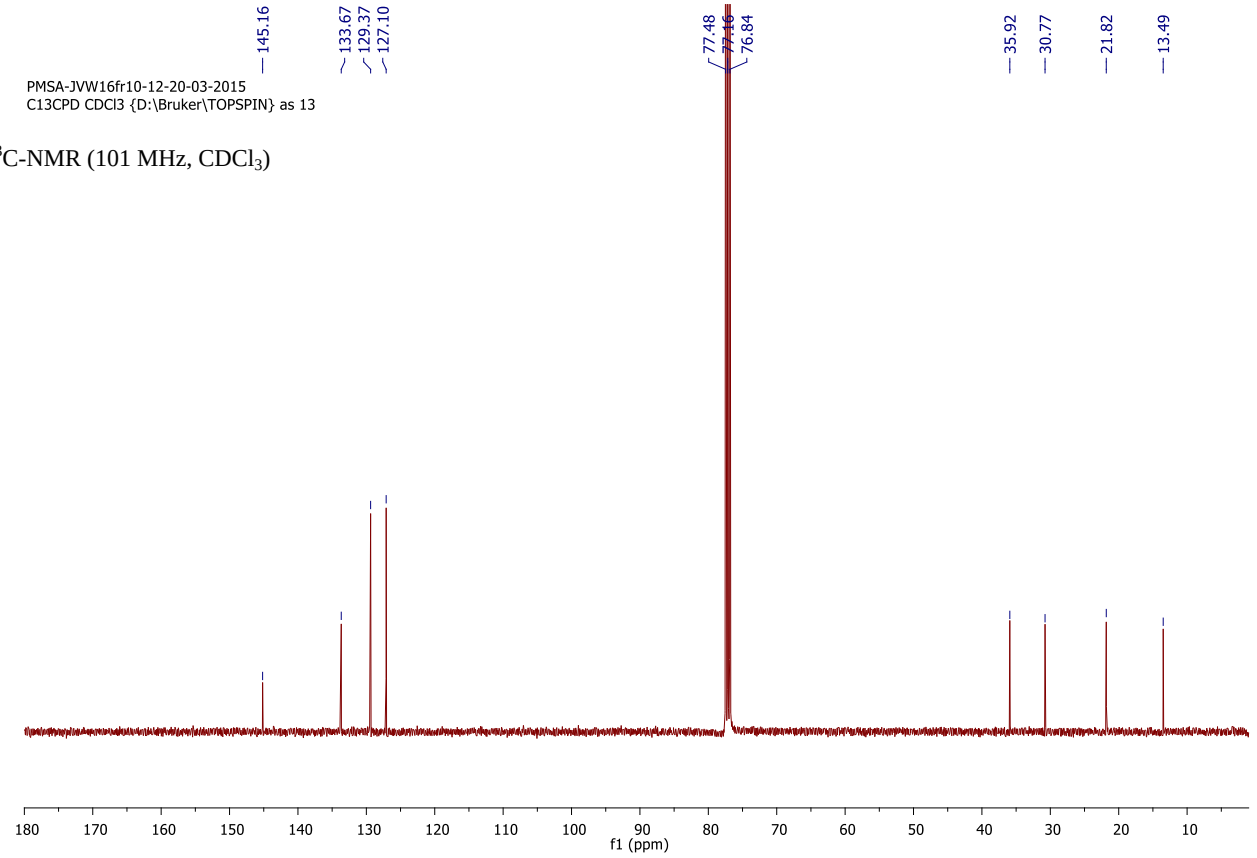


^{13}C-NMR (101 MHz, DMSO-d_6)

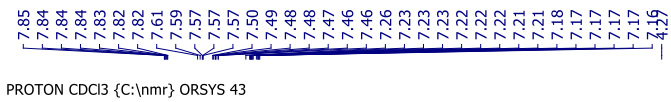


^{1}H-NMR (400 MHz, $CDCl_3$)

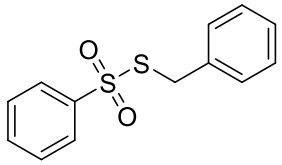
(1p) [PMSA-JVW16]



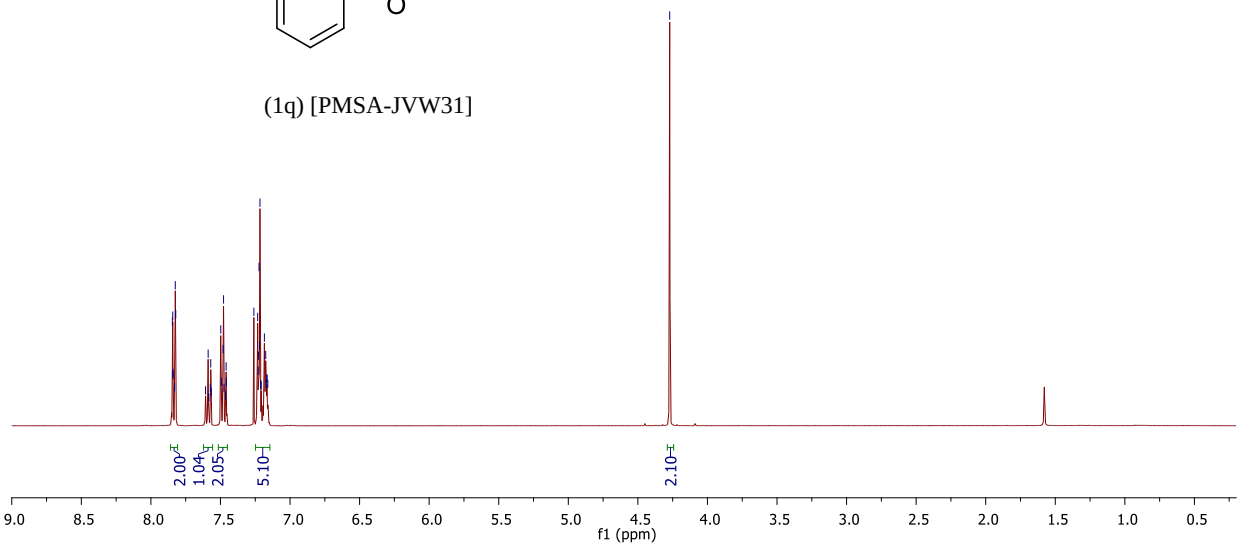
^{13}C-NMR (101 MHz, $CDCl_3$)

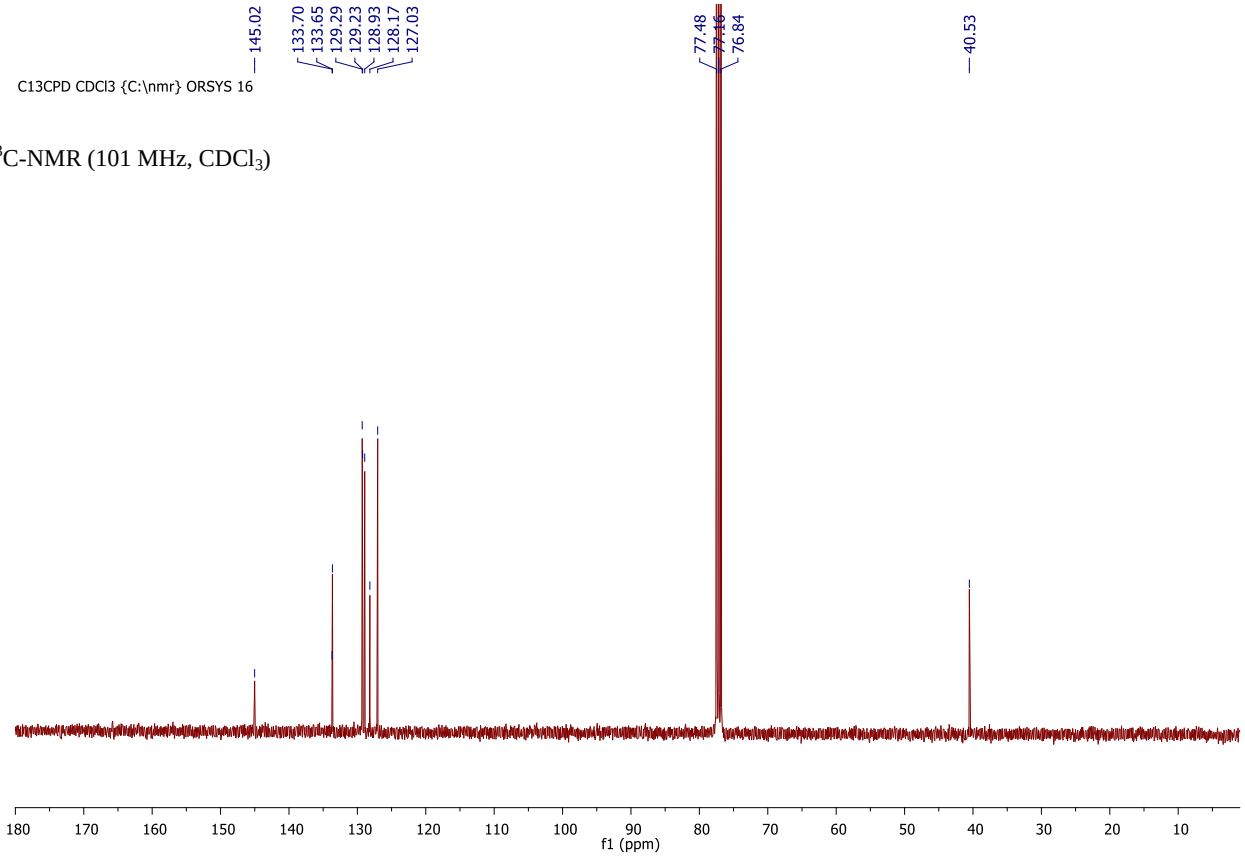


^{1}H-NMR (400 MHz, $CDCl_3$)

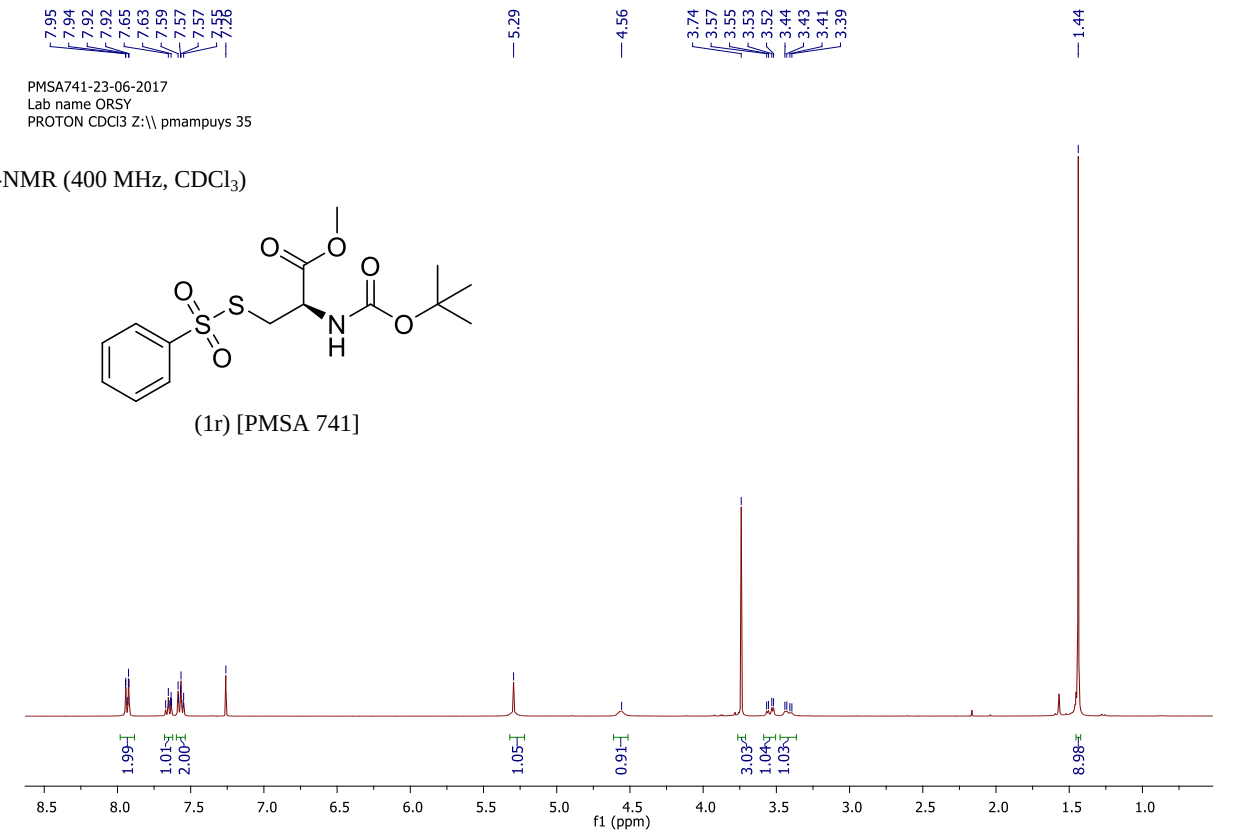


(1q) [PMSA-JVW31]



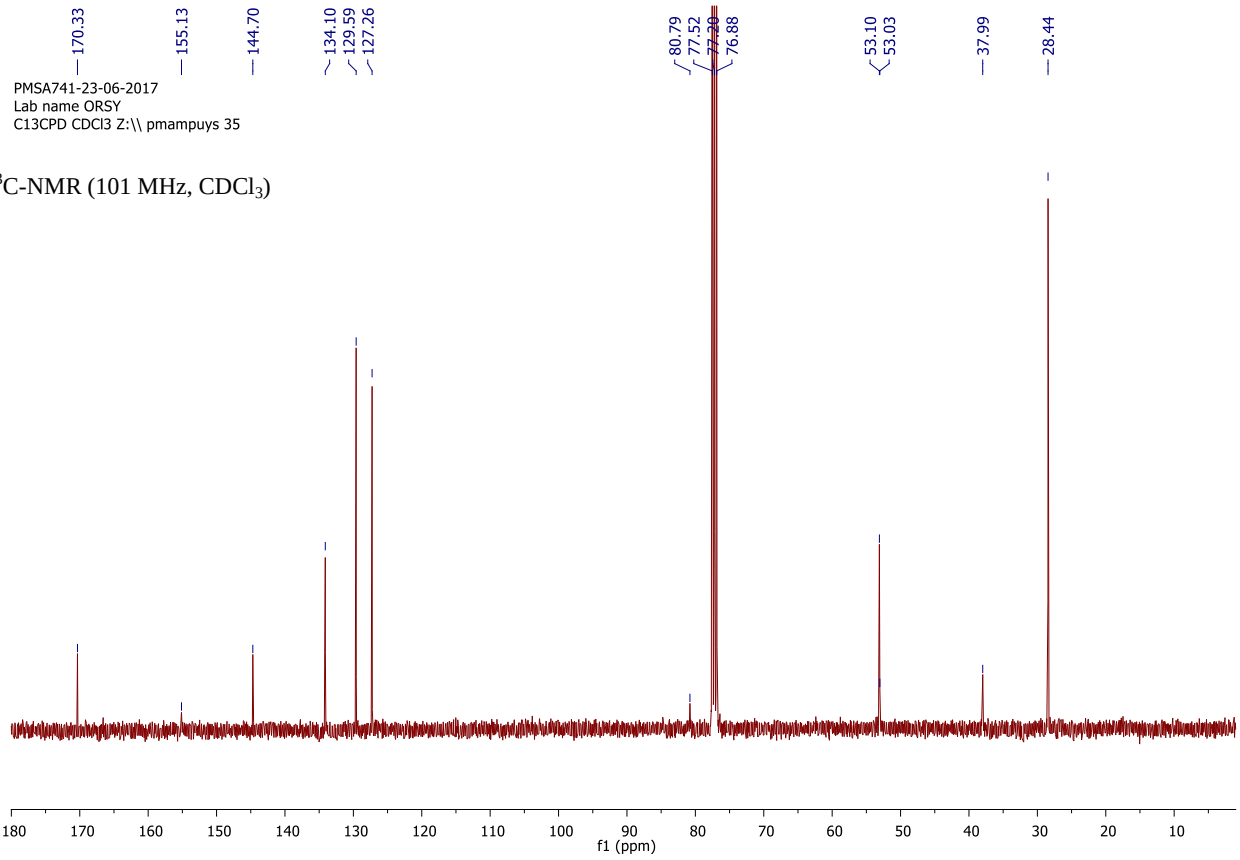


^{13}C-NMR (101 MHz, $CDCl_3$)

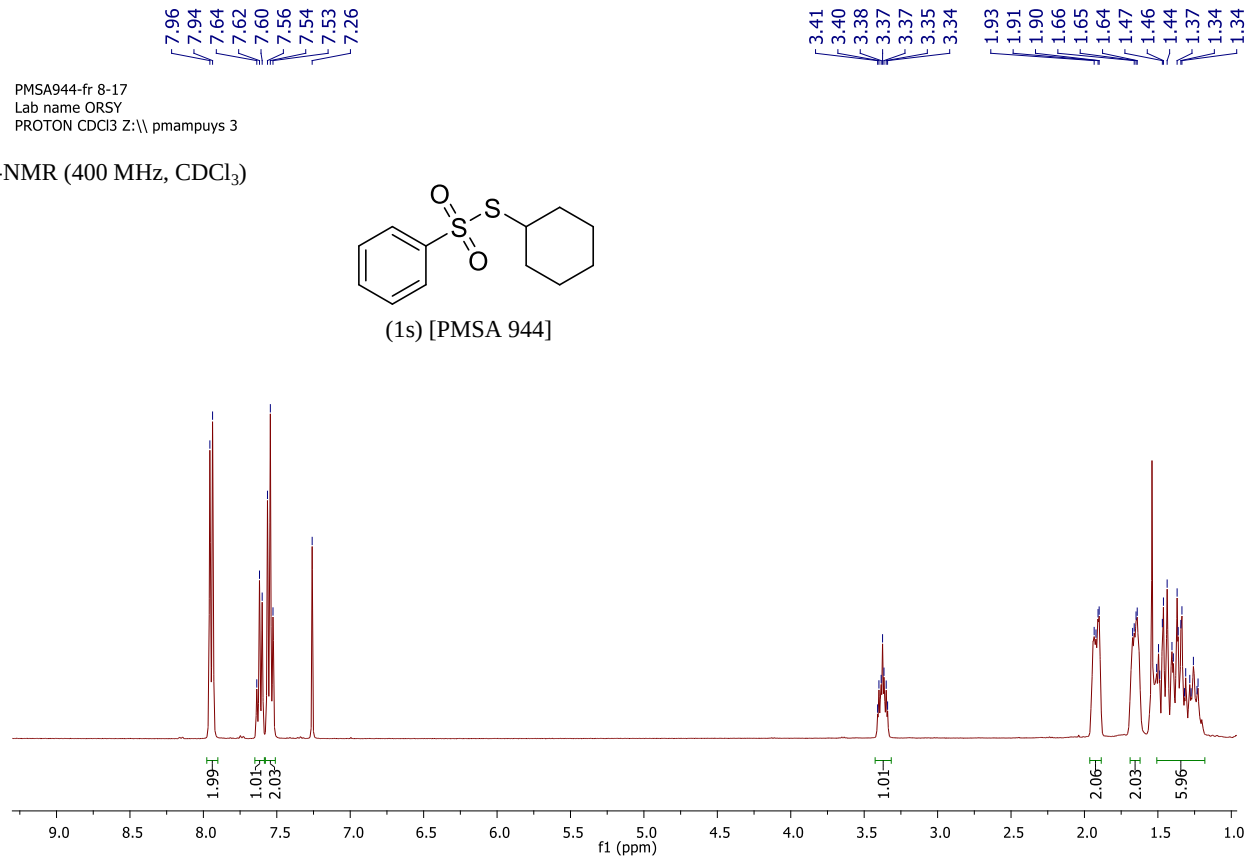


^{1}H-NMR (400 MHz, $CDCl_3$)

(1r) [PMSA 741]

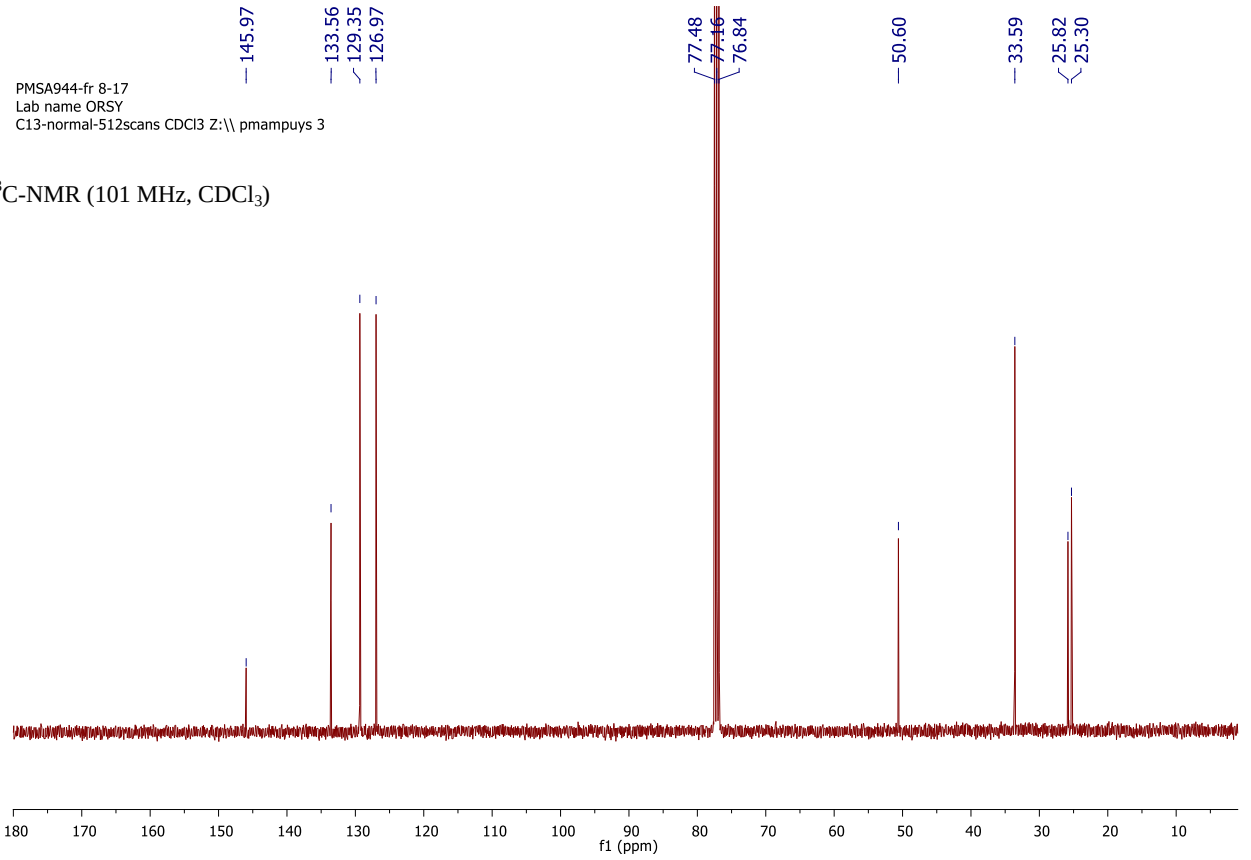


^{13}C-NMR (101 MHz, $CDCl_3$)

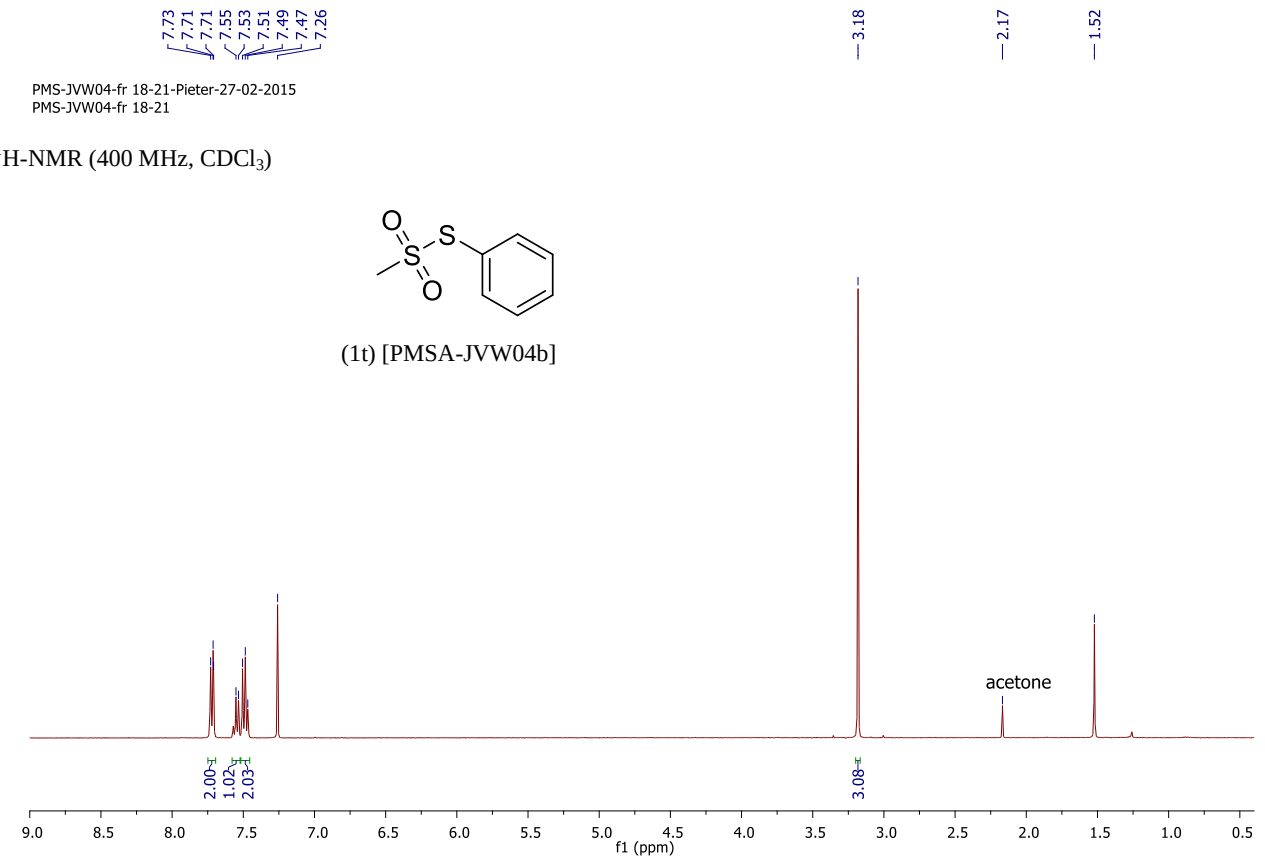


^{1}H-NMR (400 MHz, $CDCl_3$)

(1s) [PMSA 944]

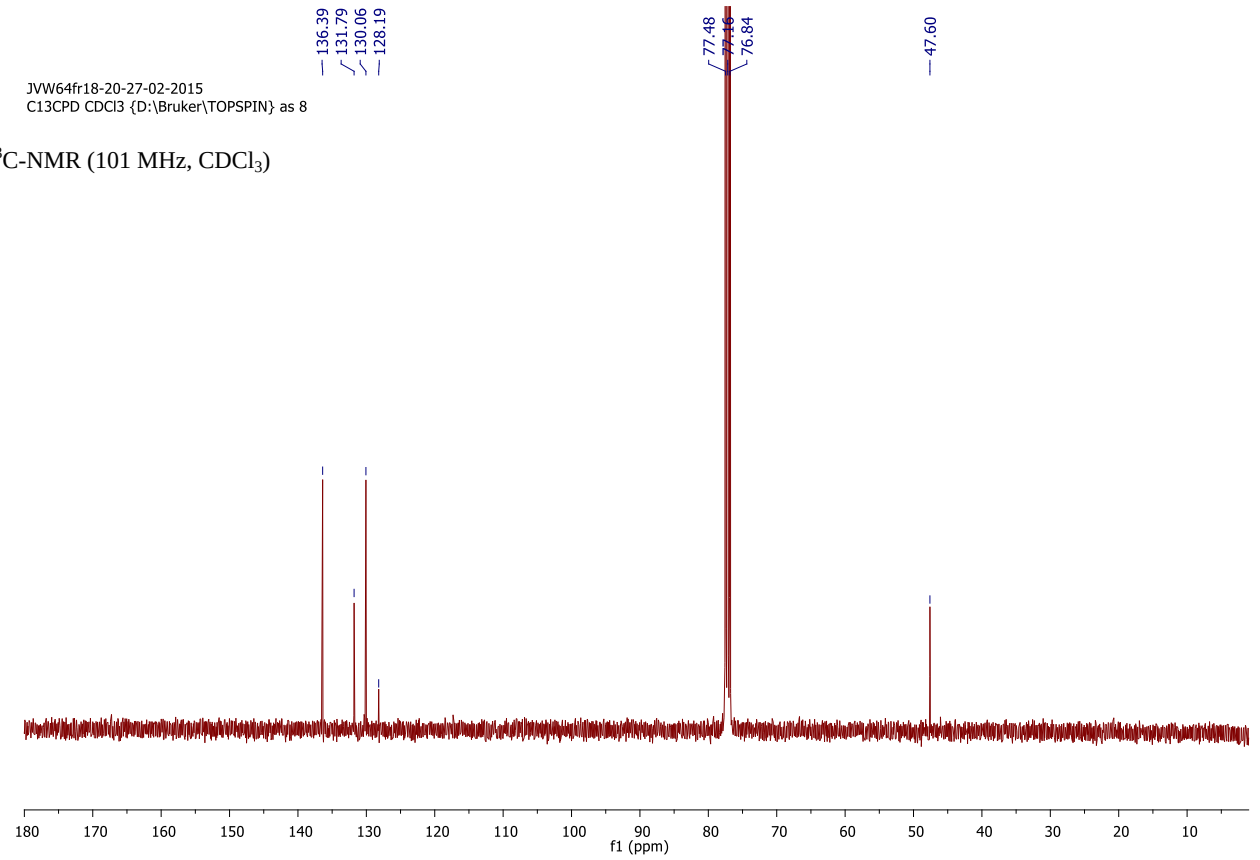


^{13}C-NMR (101 MHz, $CDCl_3$)



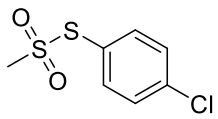
^{1}H-NMR (400 MHz, $CDCl_3$)

(1t) [PMSA-JVW04b]



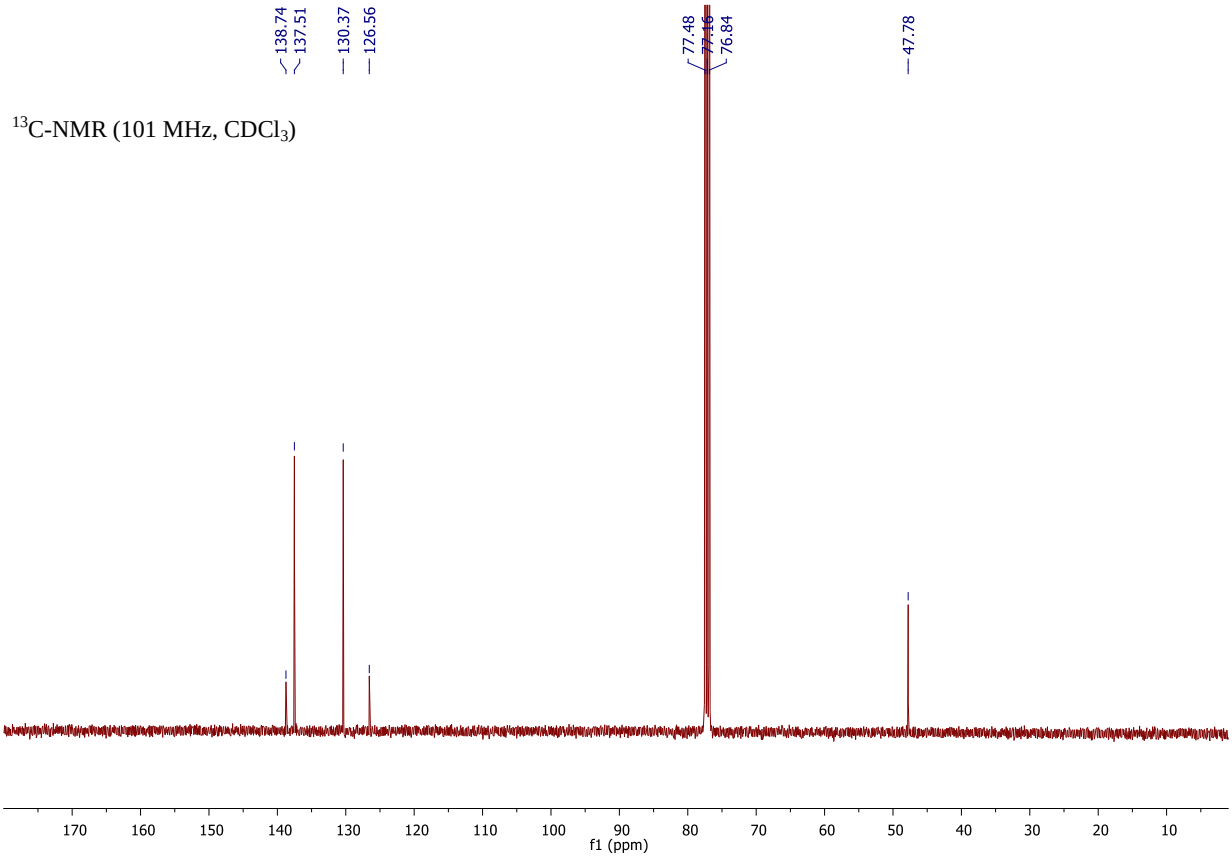
^{13}C-NMR (101 MHz, $CDCl_3$)

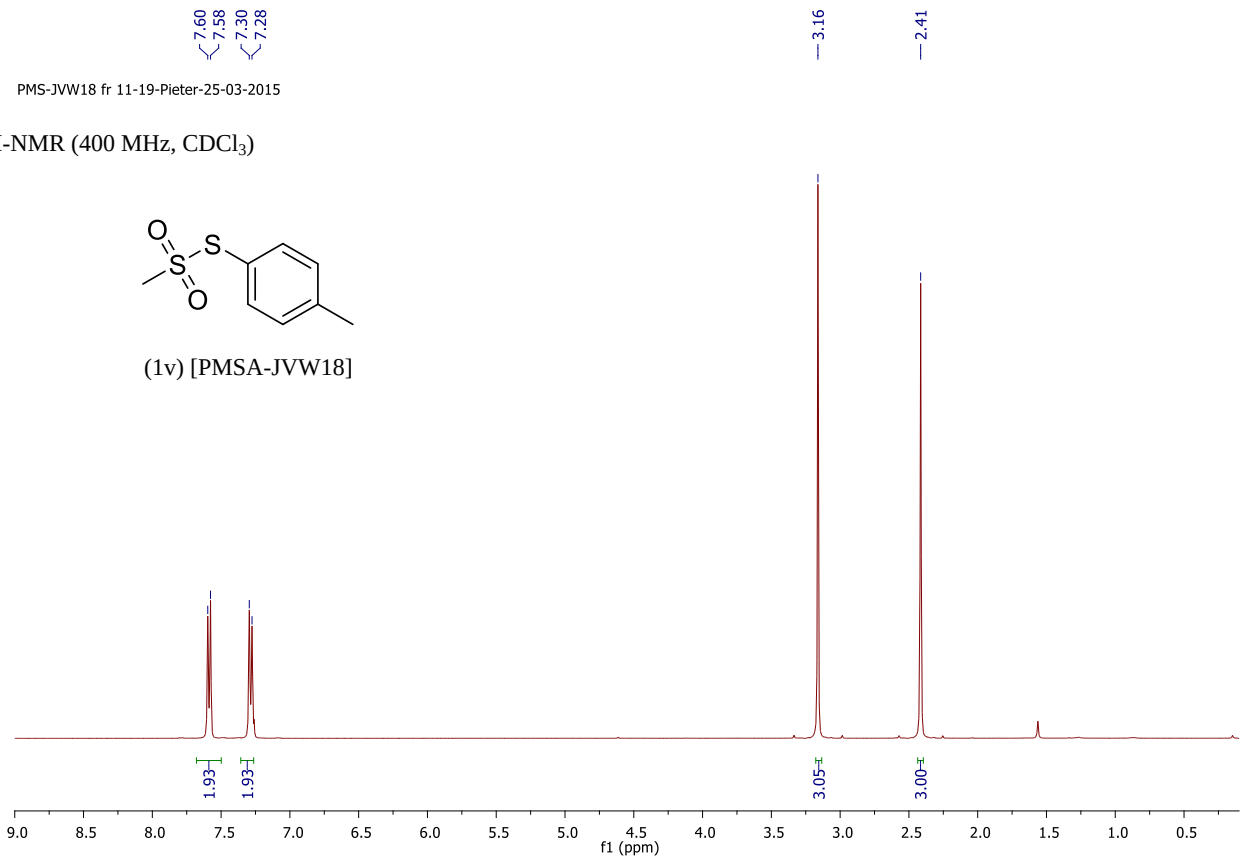
^{1}H-NMR (400 MHz, $CDCl_3$)



(1u) [PMS TIO-001]

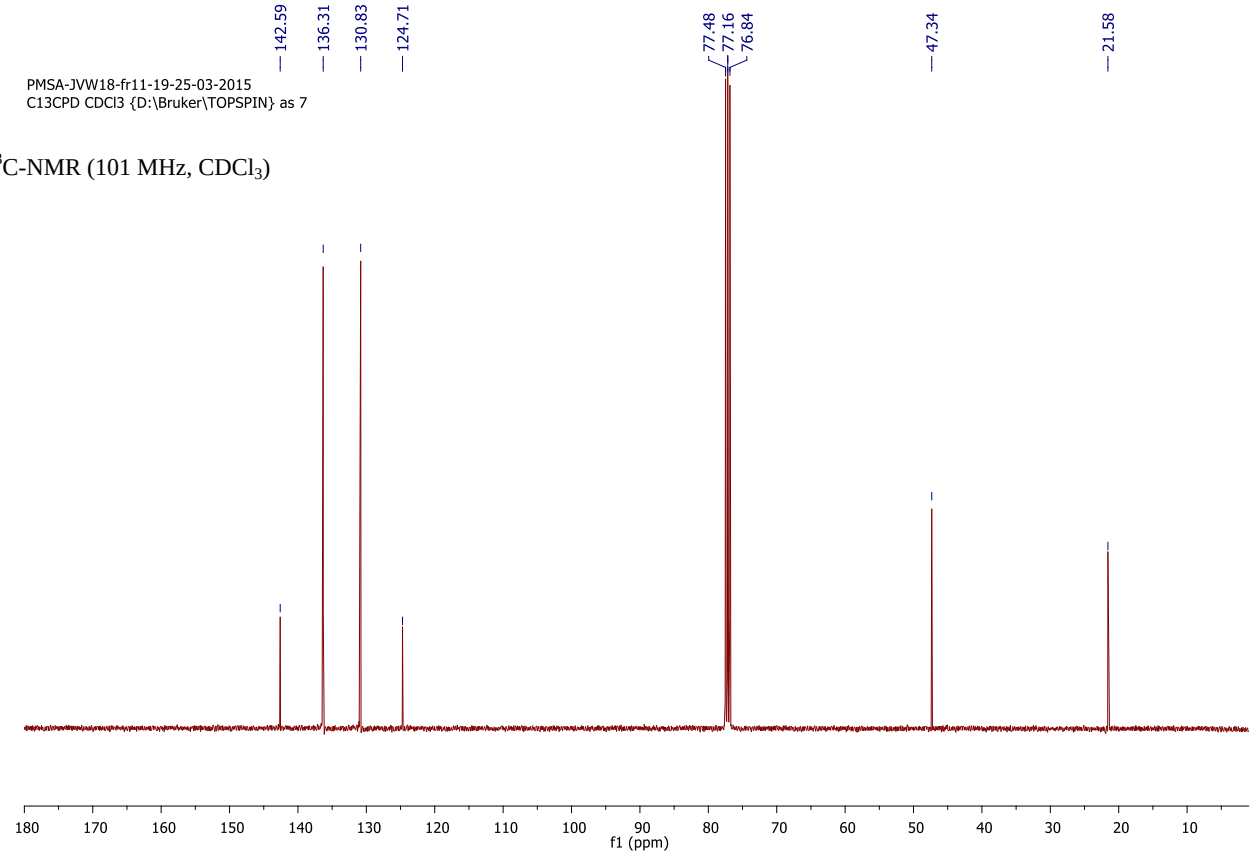
^{13}C-NMR (101 MHz, $CDCl_3$)





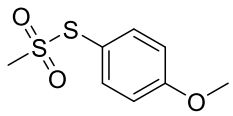
^{1}H-NMR (400 MHz, $CDCl_3$)

(1v) [PMSA-JVW18]

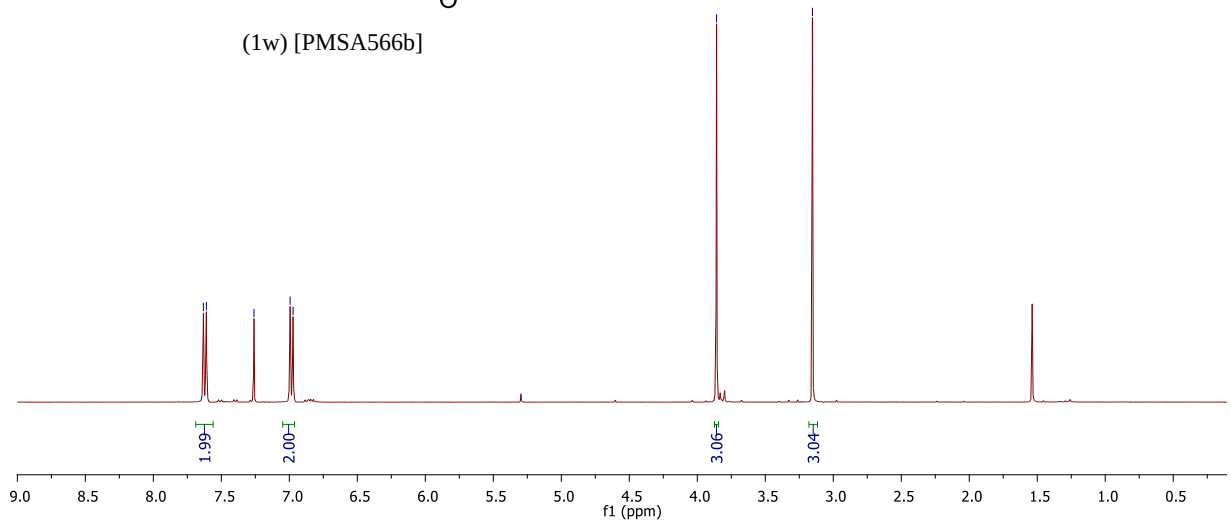


^{13}C-NMR (101 MHz, $CDCl_3$)

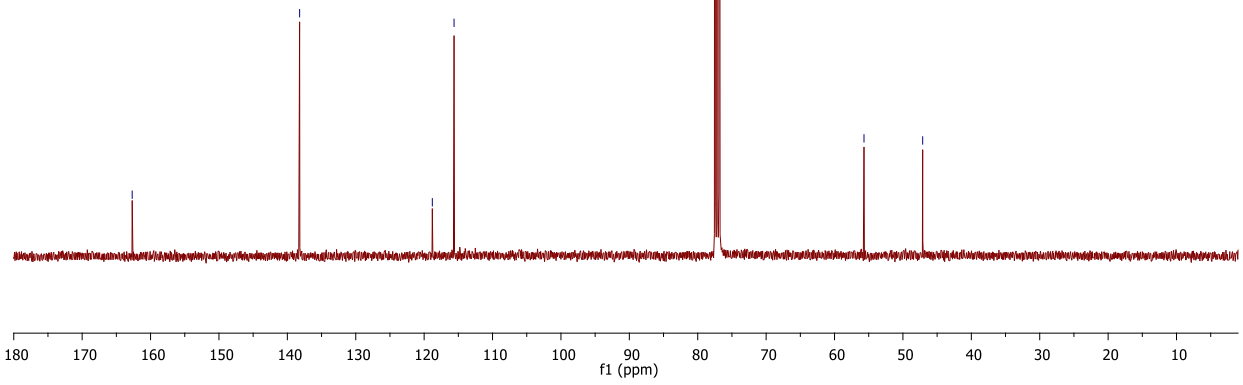
^{1}H-NMR (400 MHz, $CDCl_3$)

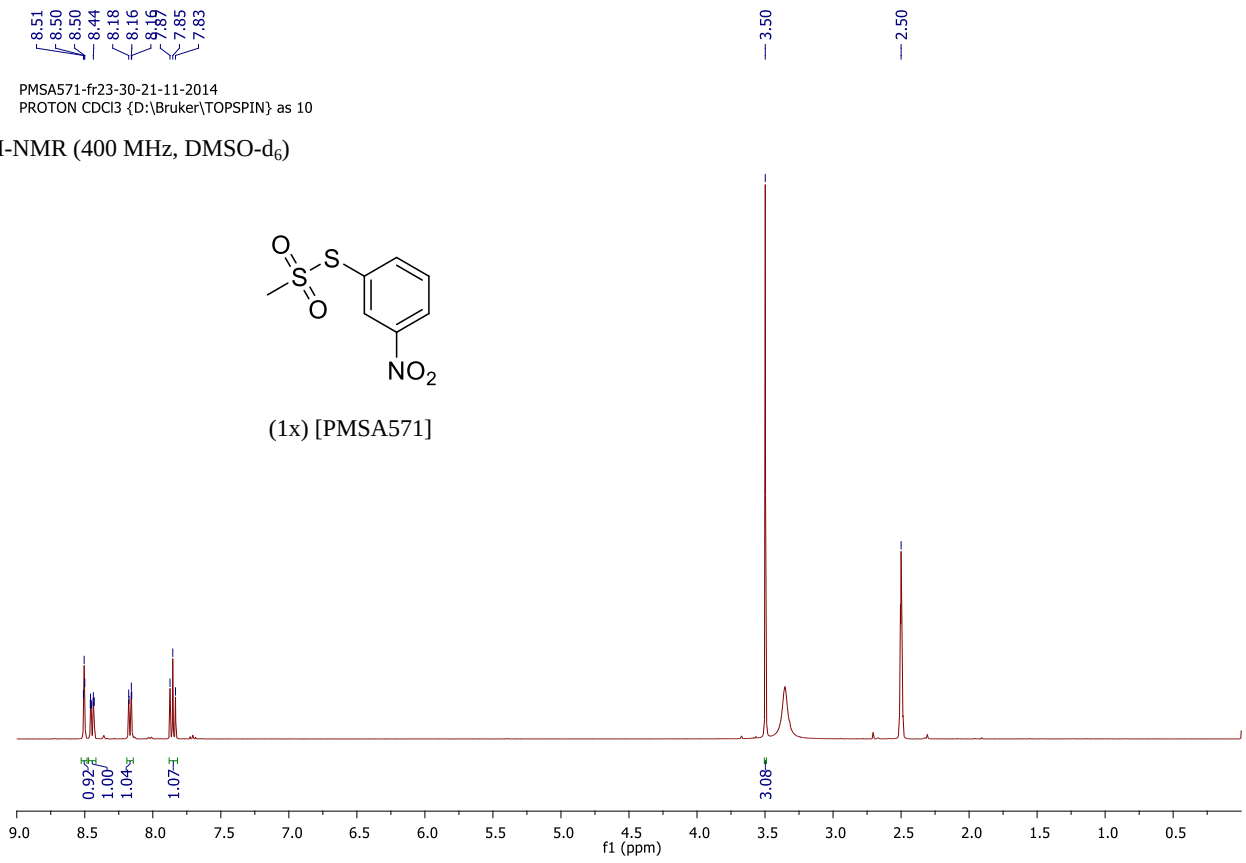


(1w) [PMSA566b]



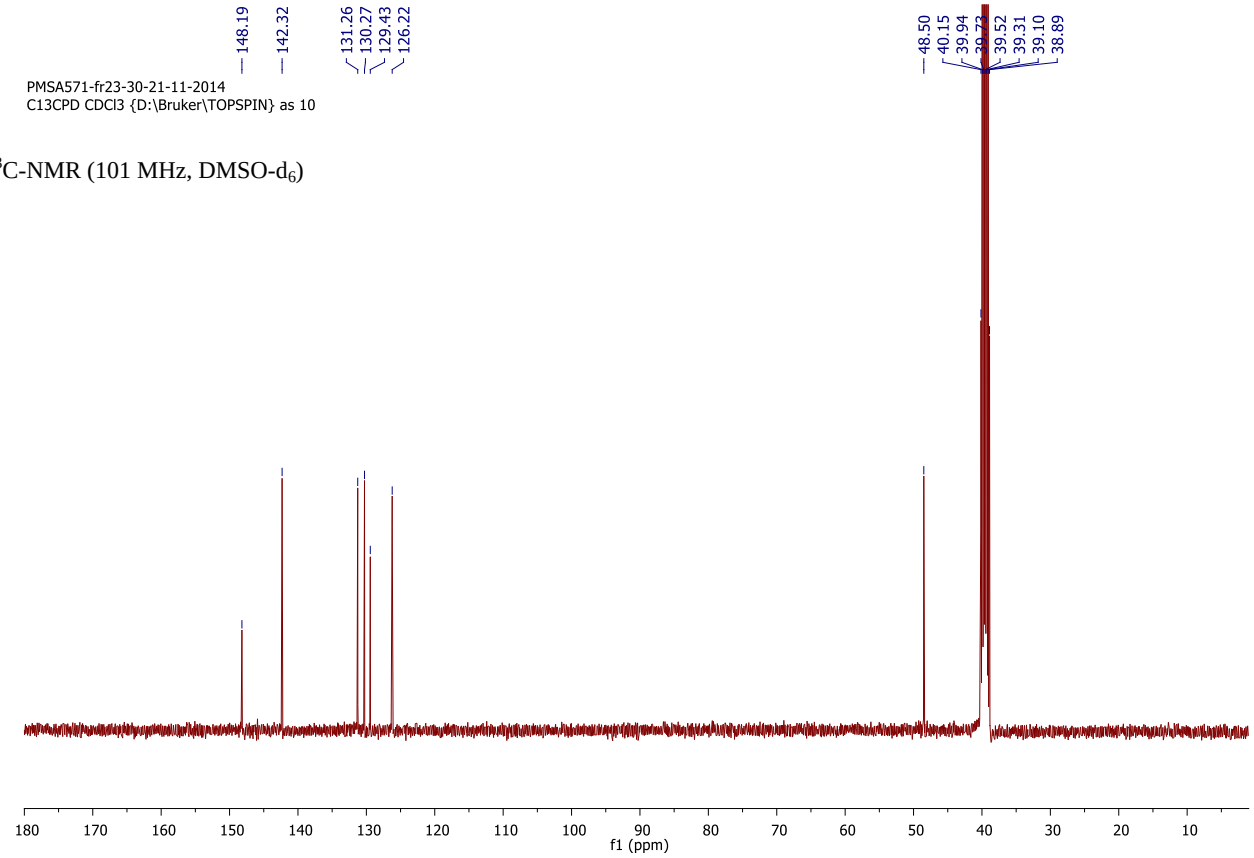
^{13}C-NMR (101 MHz, $CDCl_3$)





^{1}H-NMR (400 MHz, DMSO-d_6)

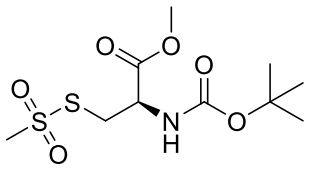
(1x) [PMSA571]



^{13}C-NMR (101 MHz, DMSO-d_6)

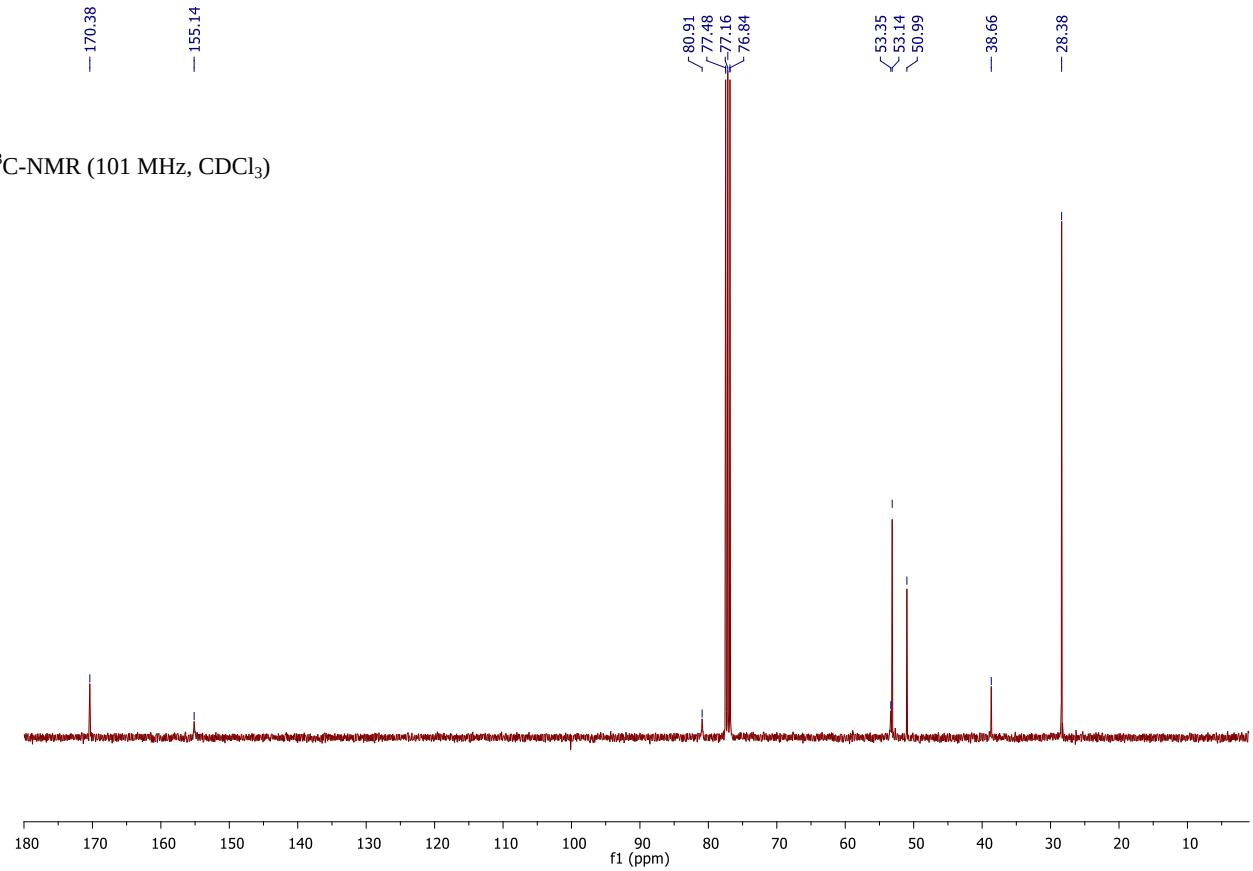
PMSA740-23-06-2015
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 8

^{1}H-NMR (400 MHz, $CDCl_3$)

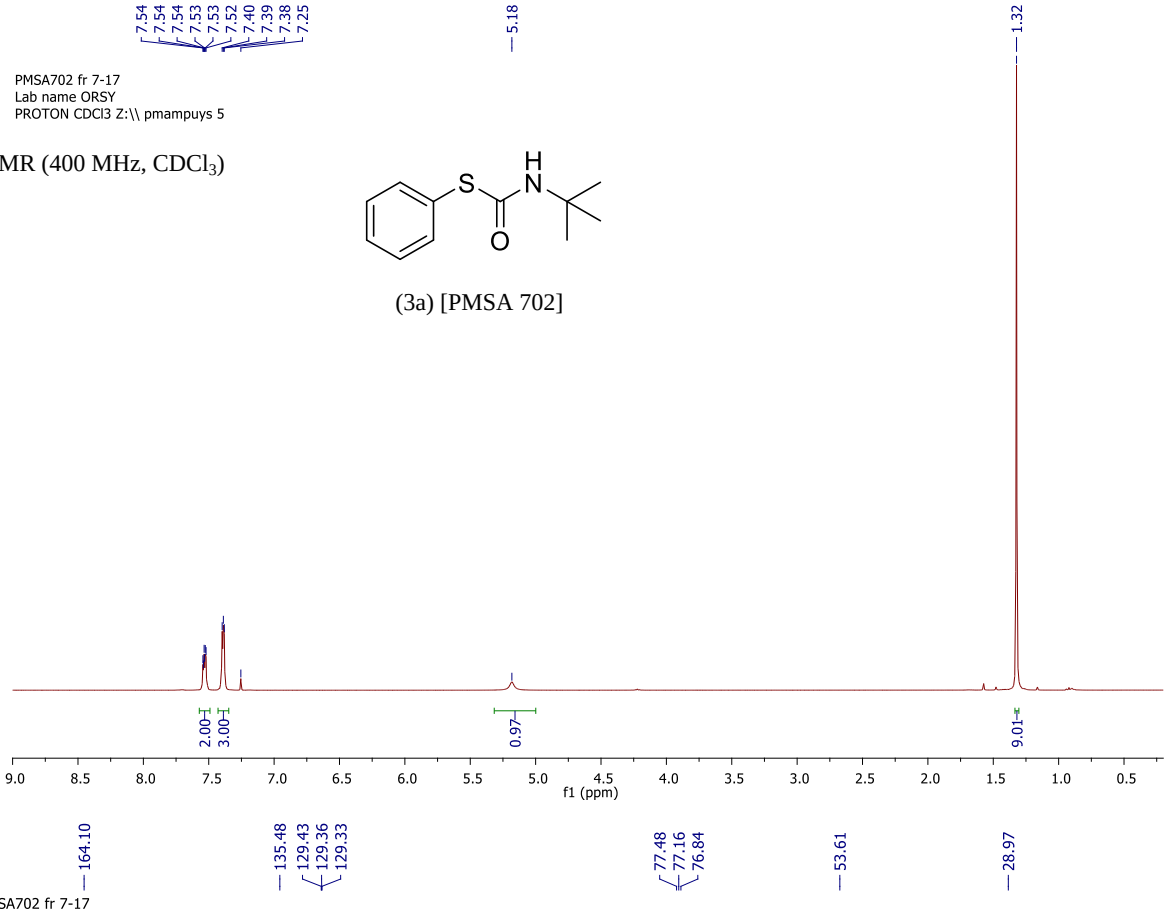


(1y) [PMSA 740]

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

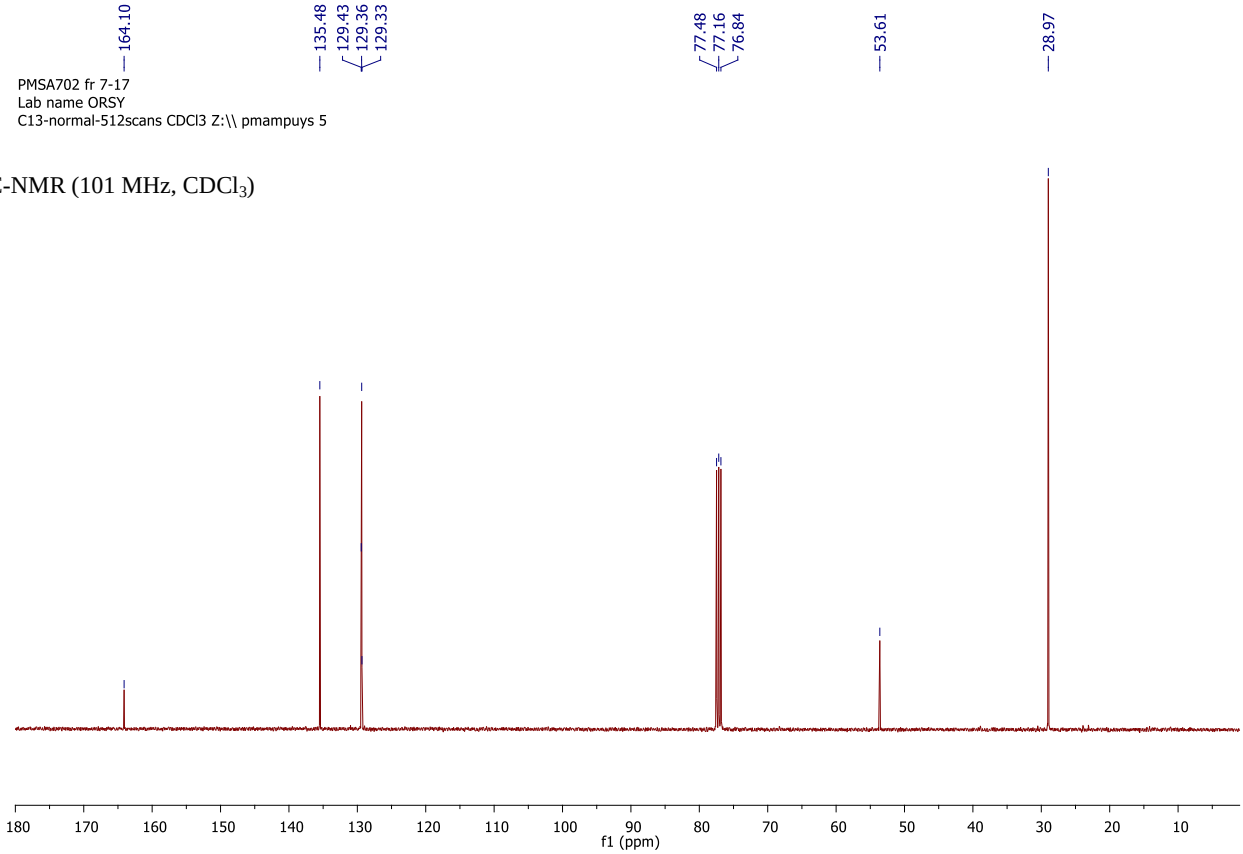


9.4 Synthesis of thiocarbamates



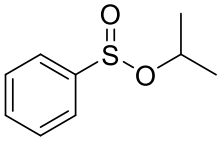
^{1}H-NMR (400 MHz, $CDCl_3$)

(3a) [PMSA 702]

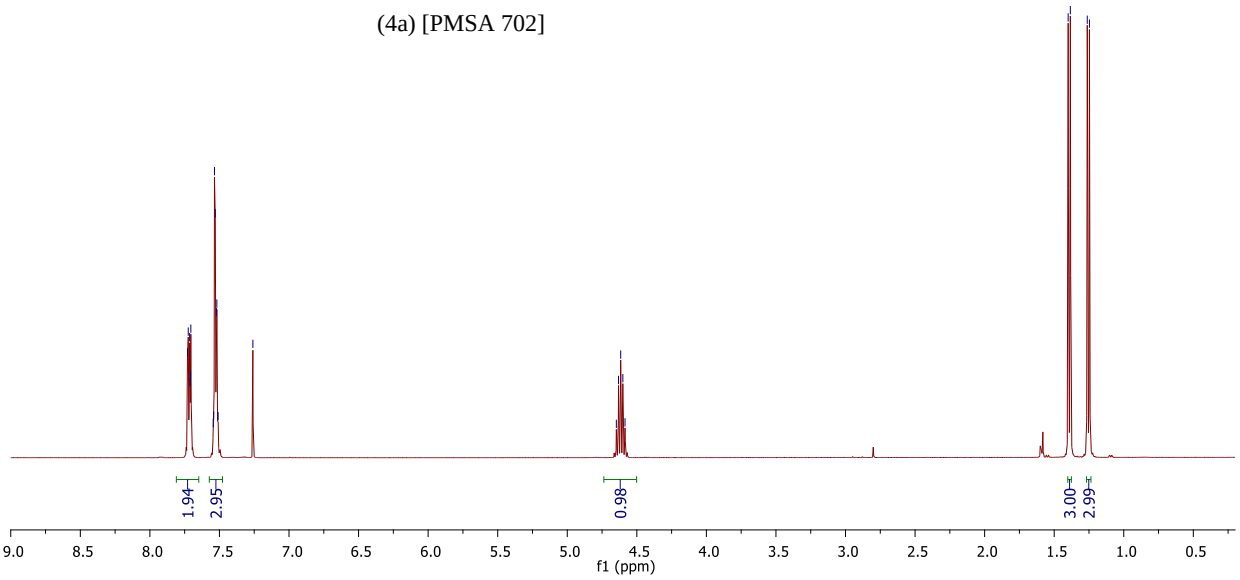


^{13}C-NMR (101 MHz, $CDCl_3$)

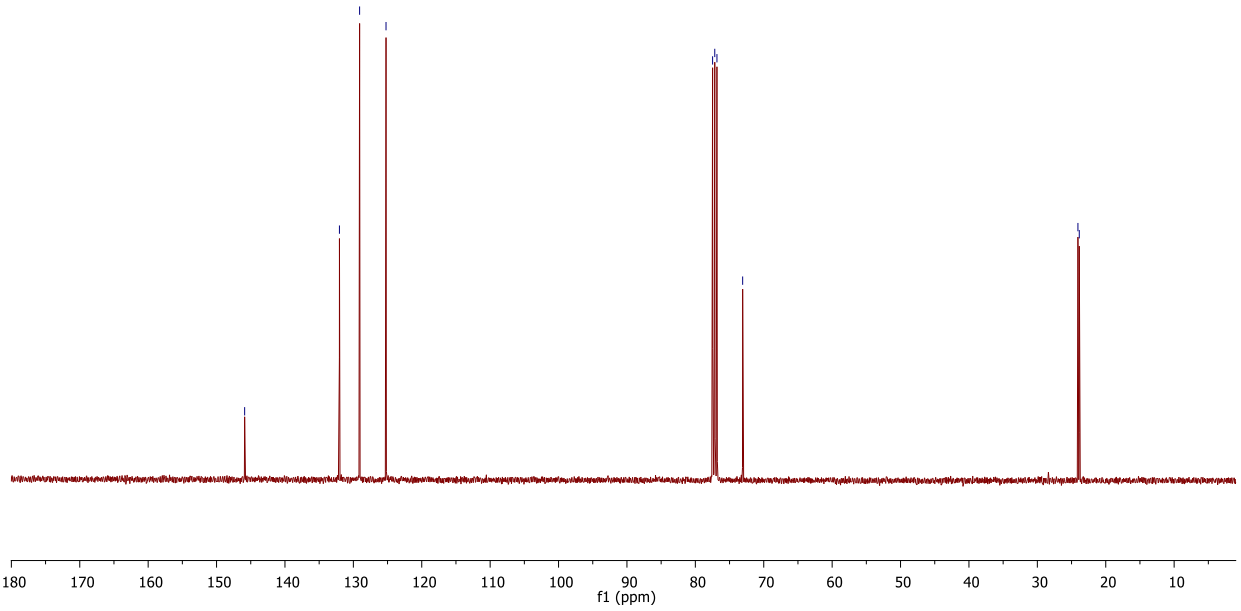
^{1}H-NMR (400 MHz, $CDCl_3$)

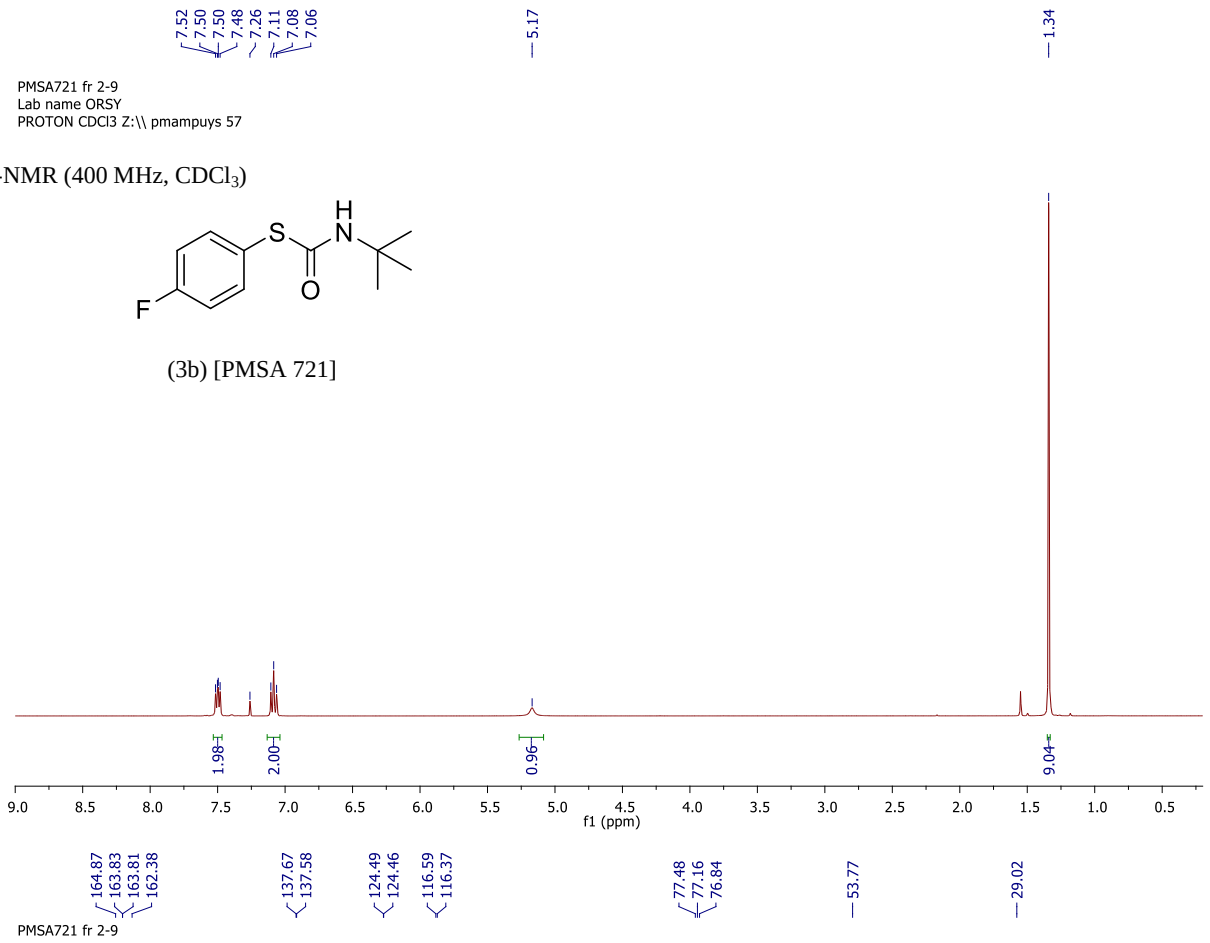


(4a) [PMSA 702]



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

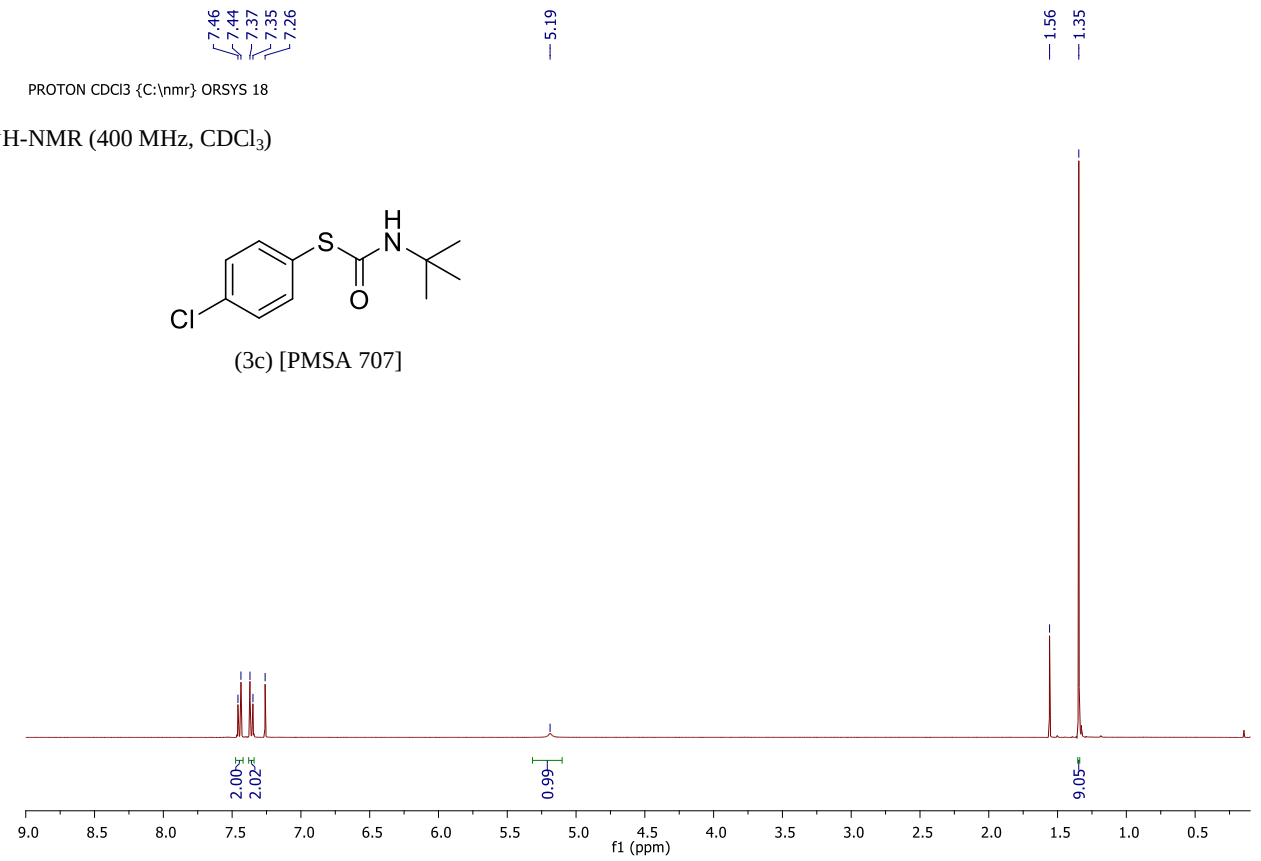




^{1}H-NMR (400 MHz, $CDCl_3$)

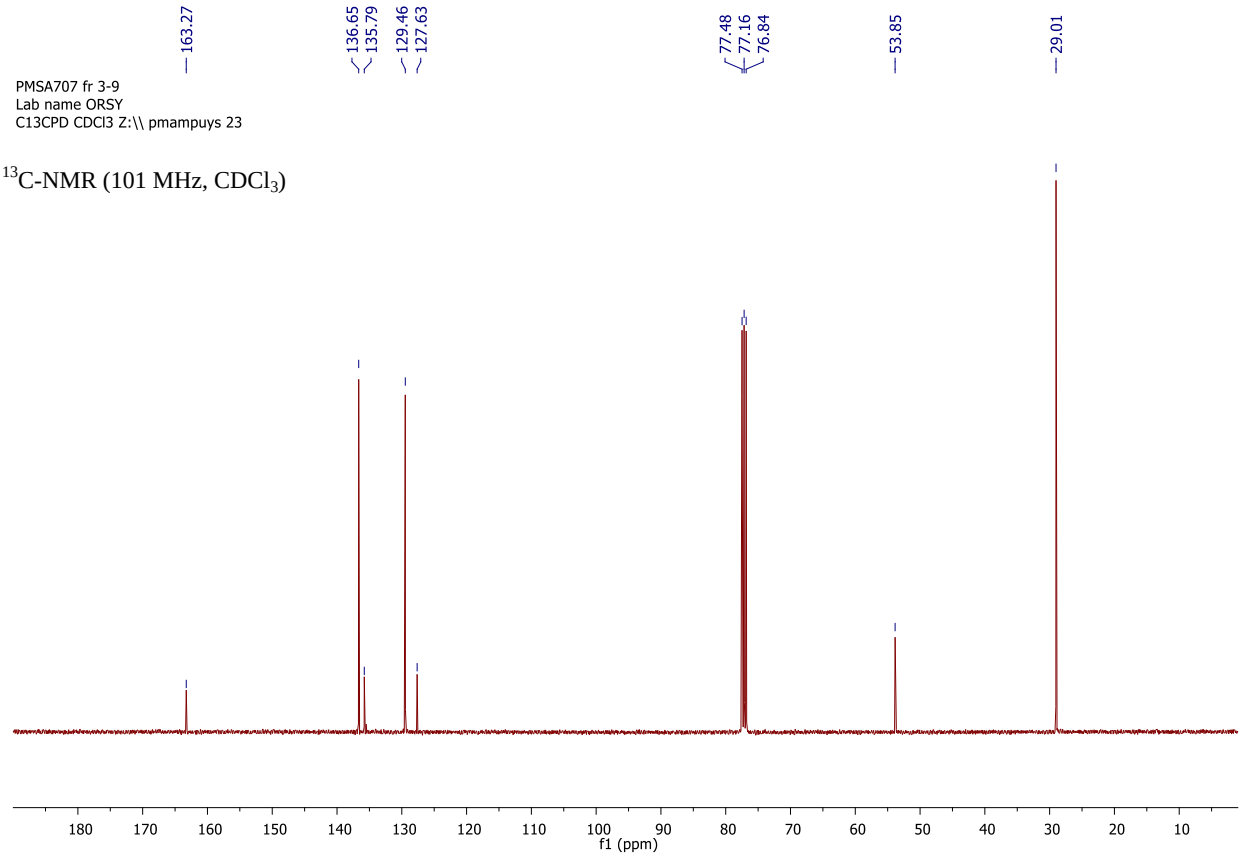
(3b) [PMSA 721]

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

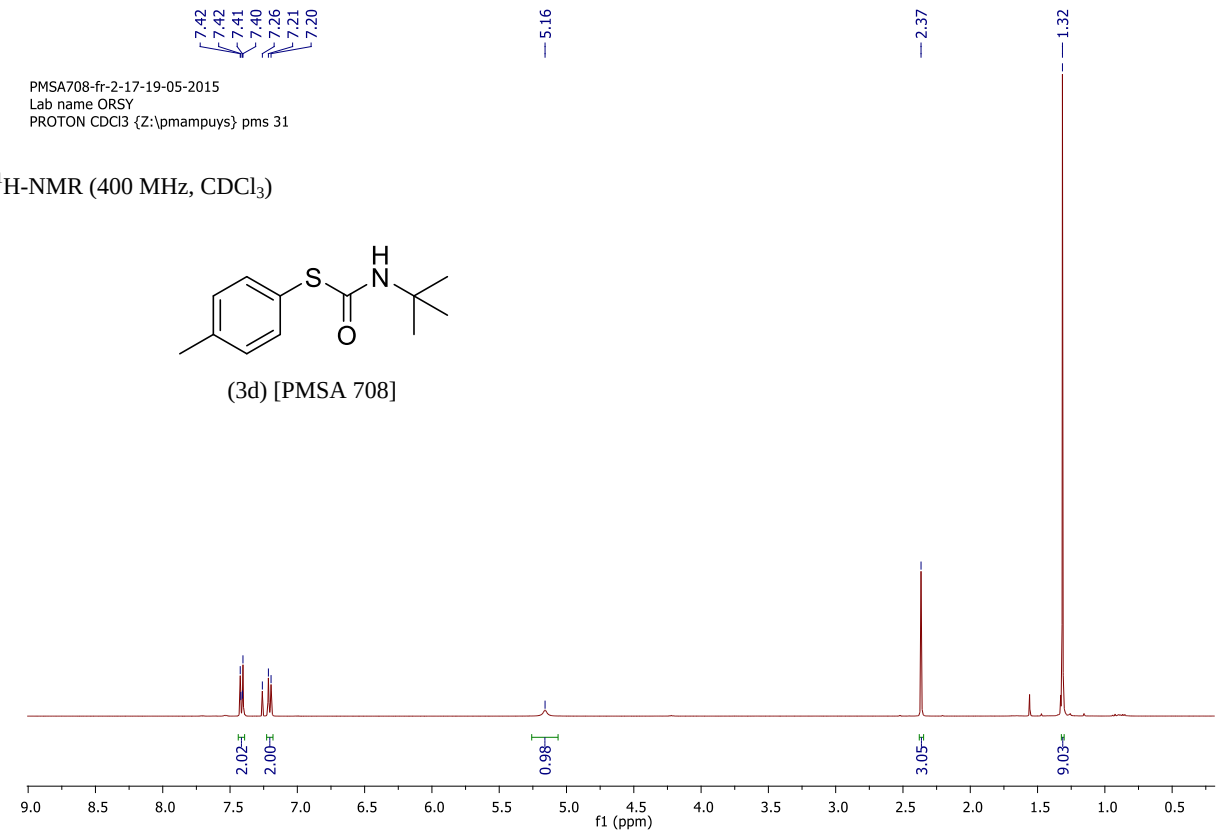


^{1}H-NMR (400 MHz, $CDCl_3$)

(3c) [PMSA 707]

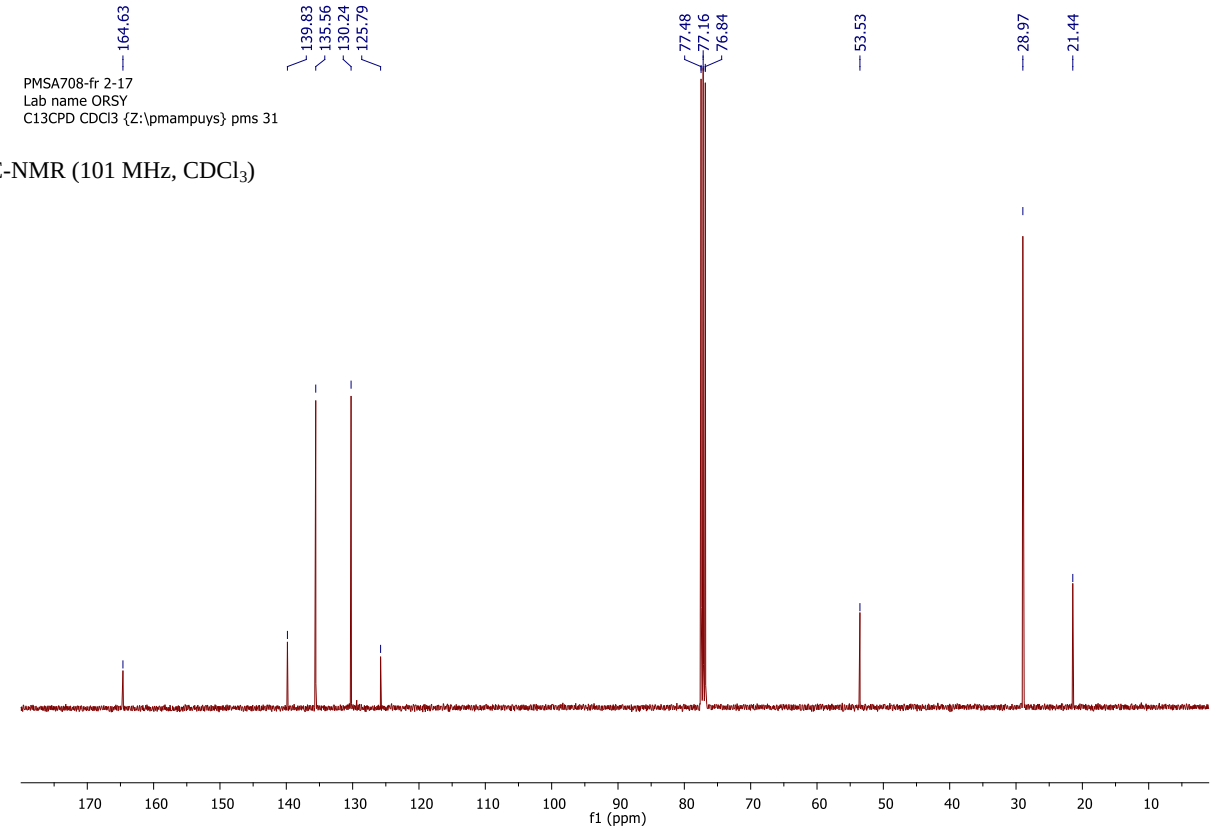


^{13}C-NMR (101 MHz, $CDCl_3$)

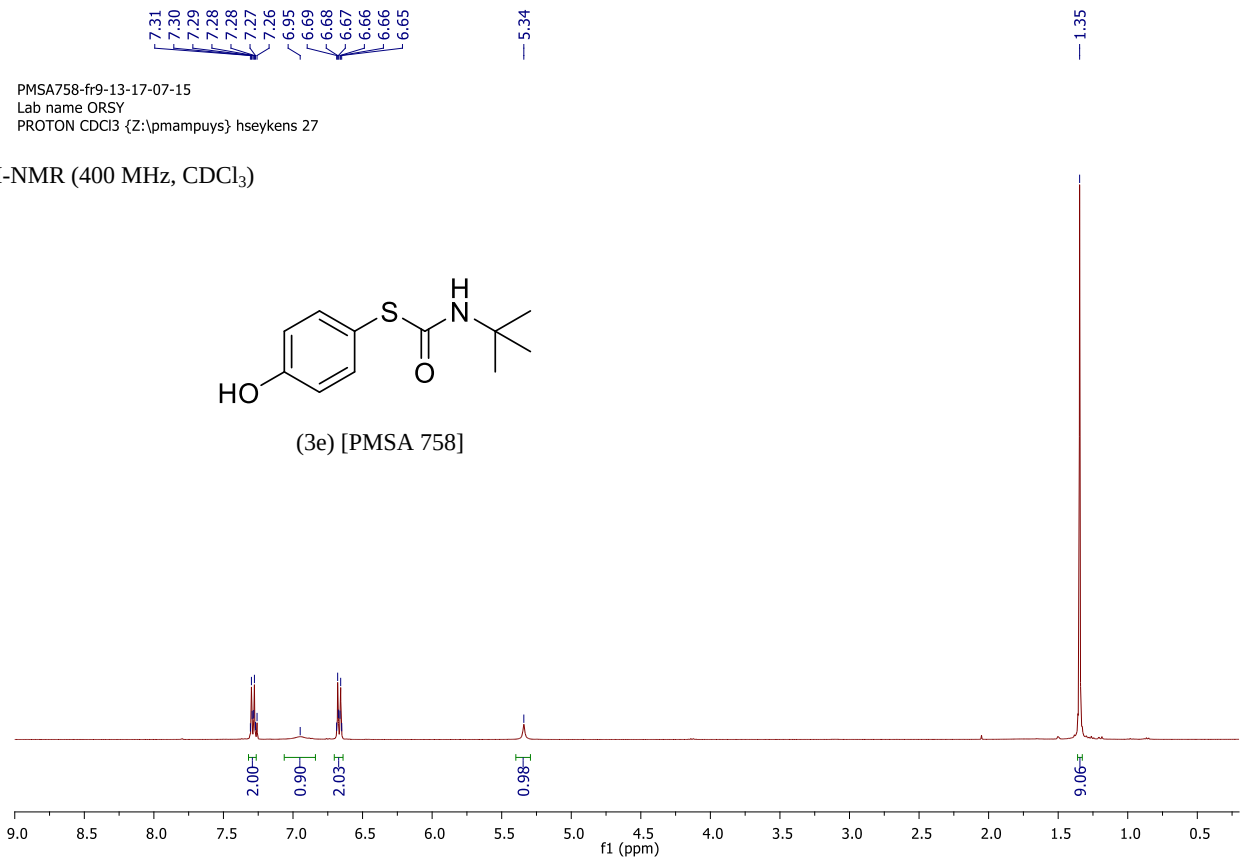


^{1}H-NMR (400 MHz, $CDCl_3$)

(3d) [PMSA 708]

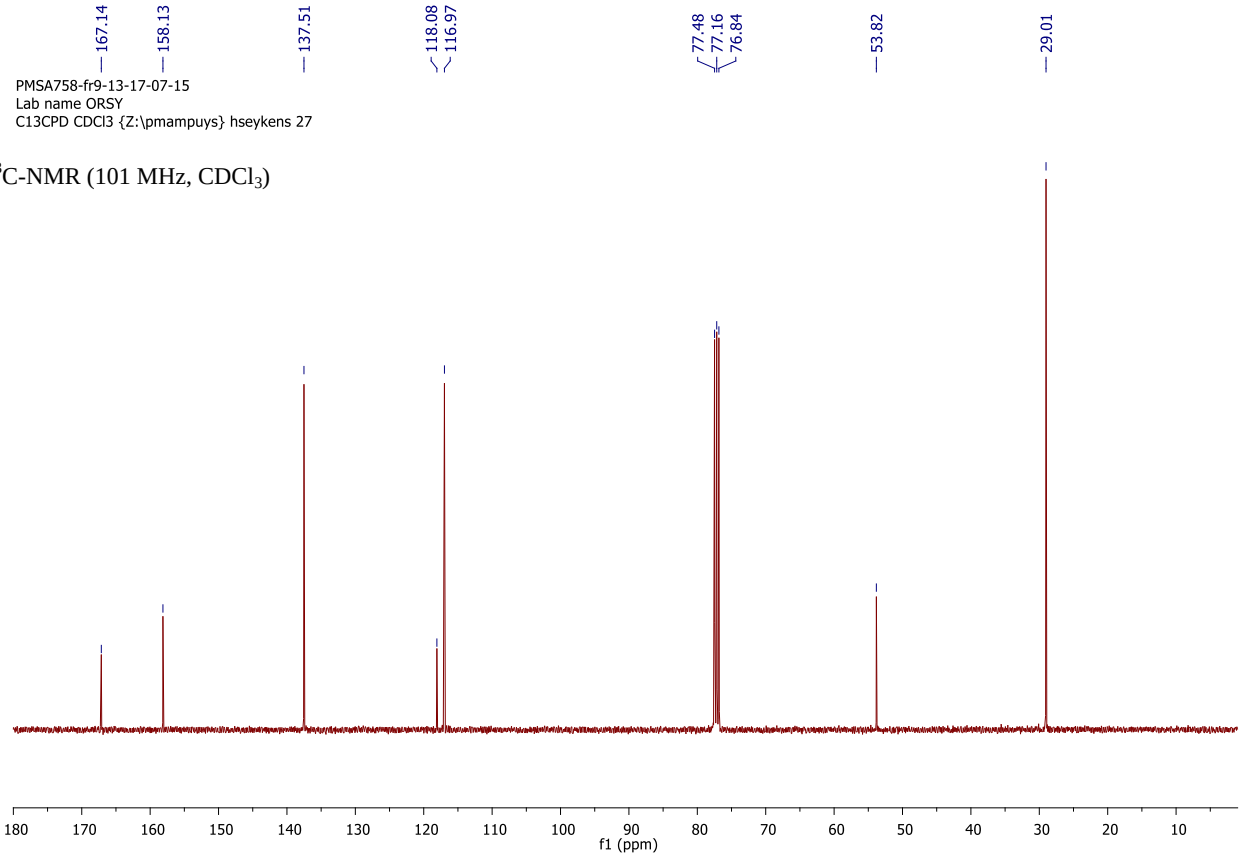


^{13}C-NMR (101 MHz, $CDCl_3$)

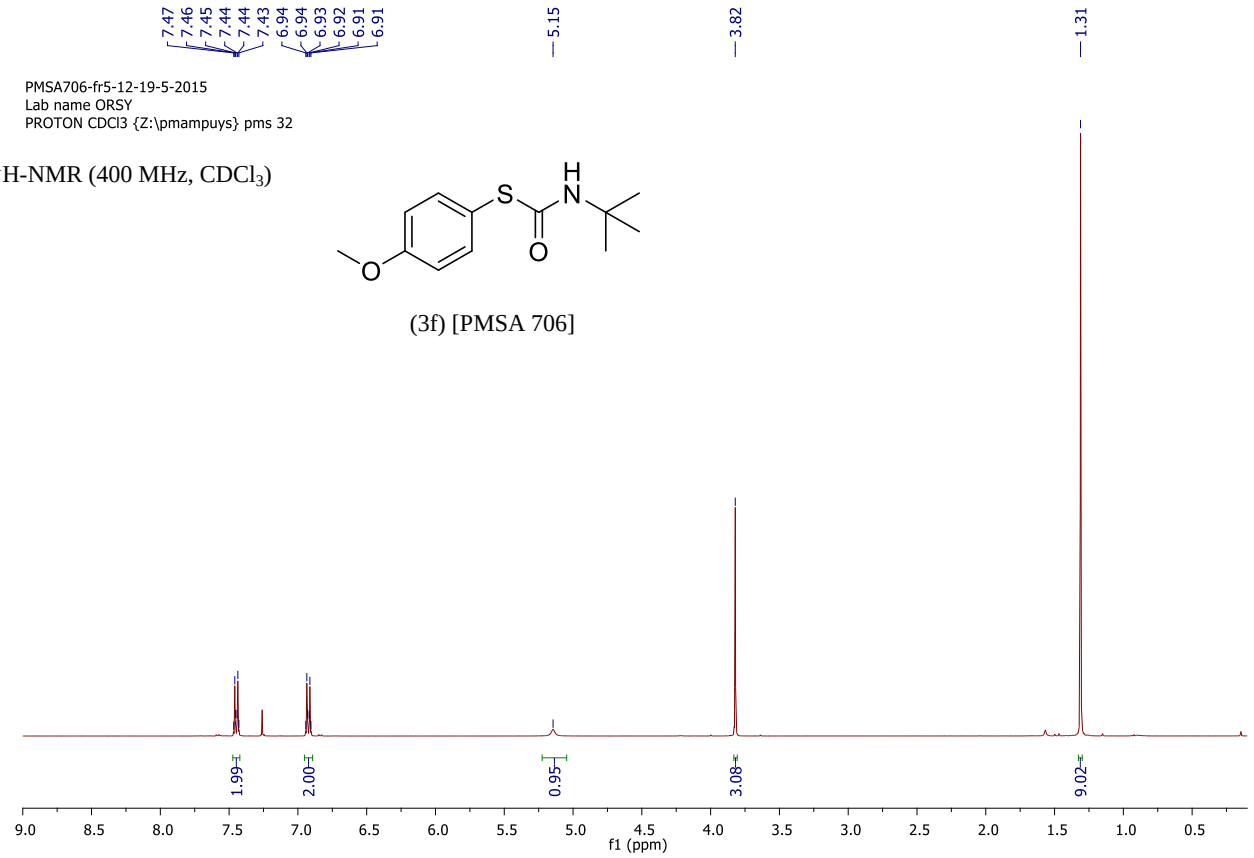


^{1}H-NMR (400 MHz, $CDCl_3$)

(3e) [PMSA 758]

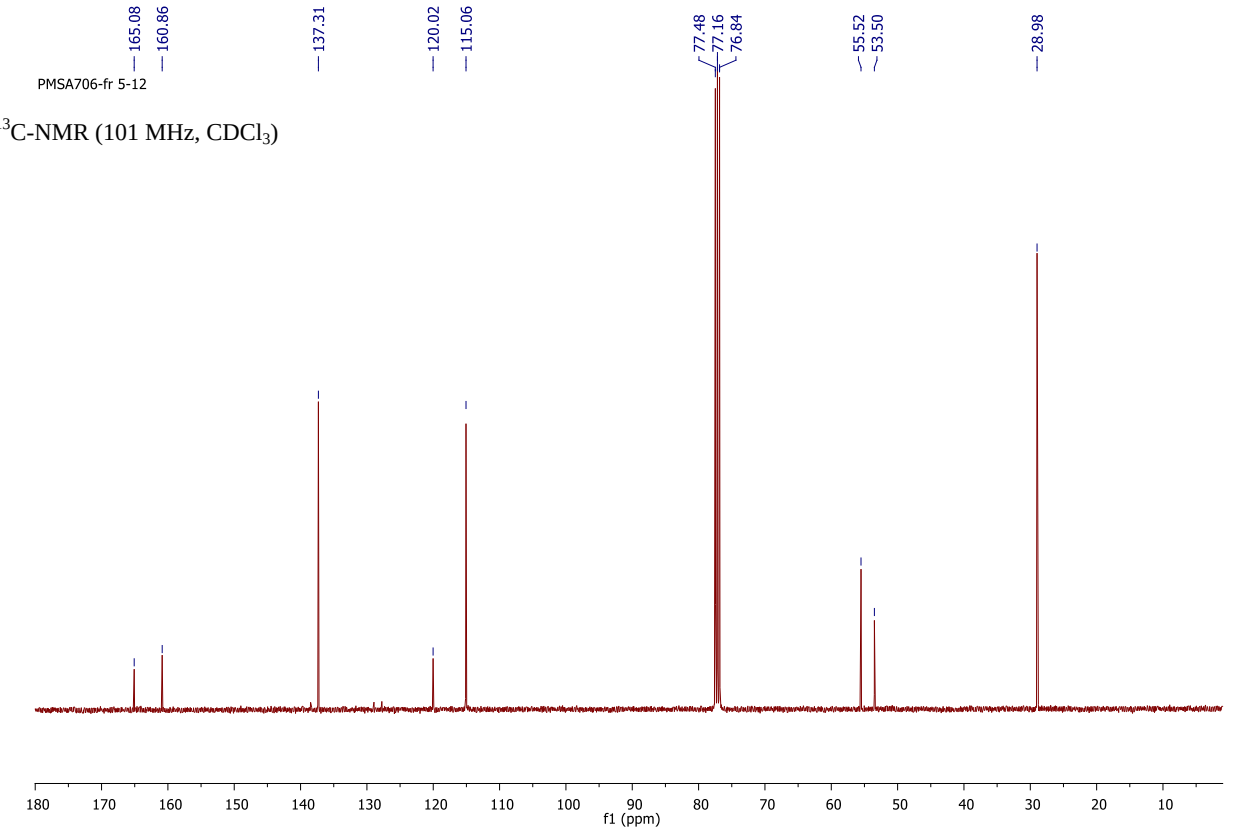


^{13}C-NMR (101 MHz, $CDCl_3$)

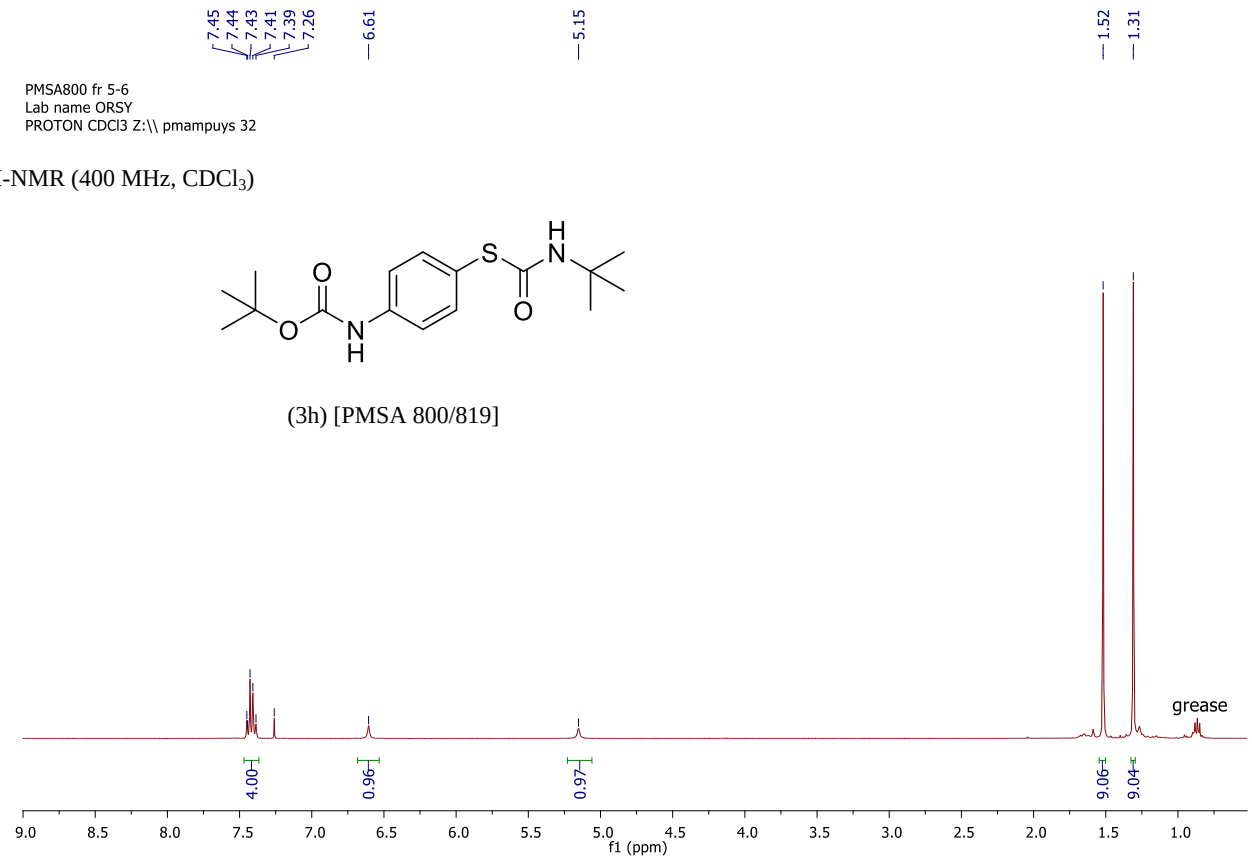


^{1}H-NMR (400 MHz, $CDCl_3$)

(3f) [PMSA 706]

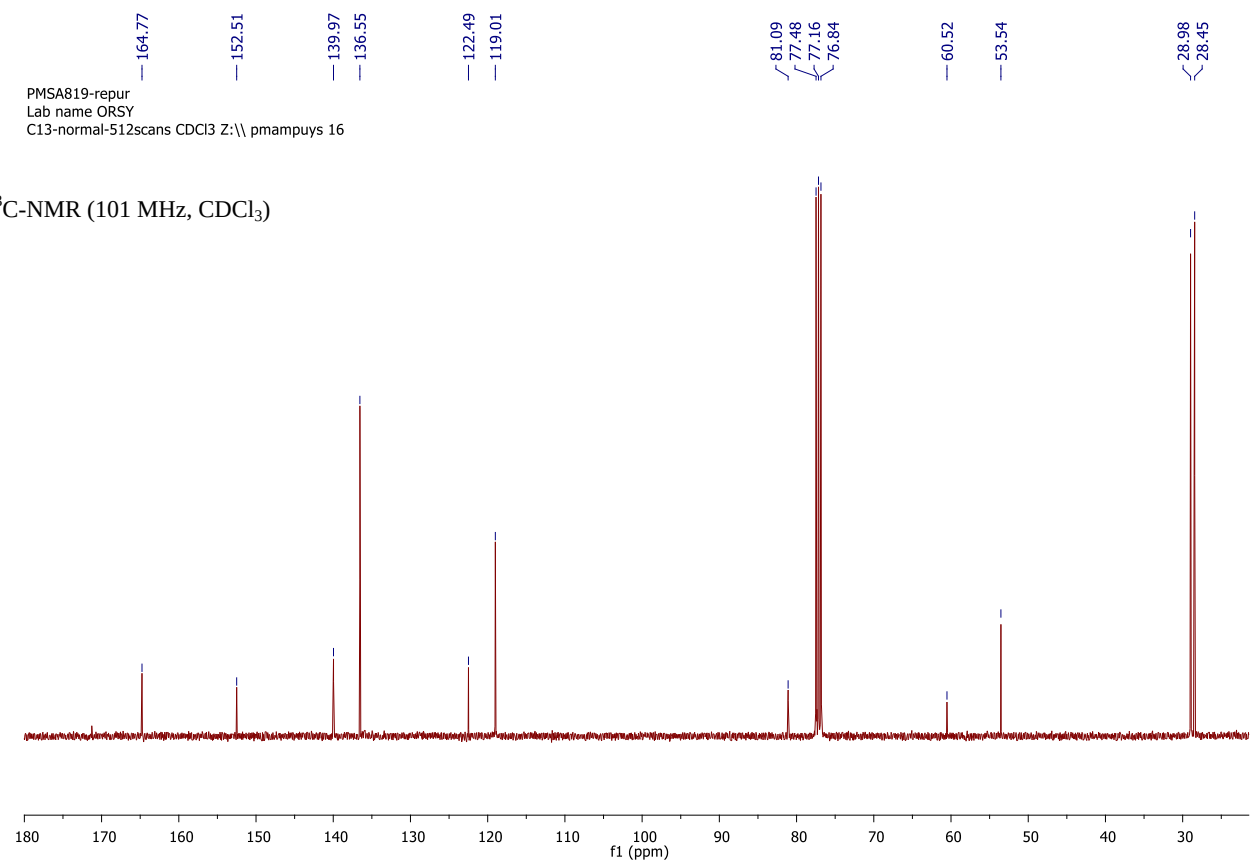


^{13}C-NMR (101 MHz, $CDCl_3$)

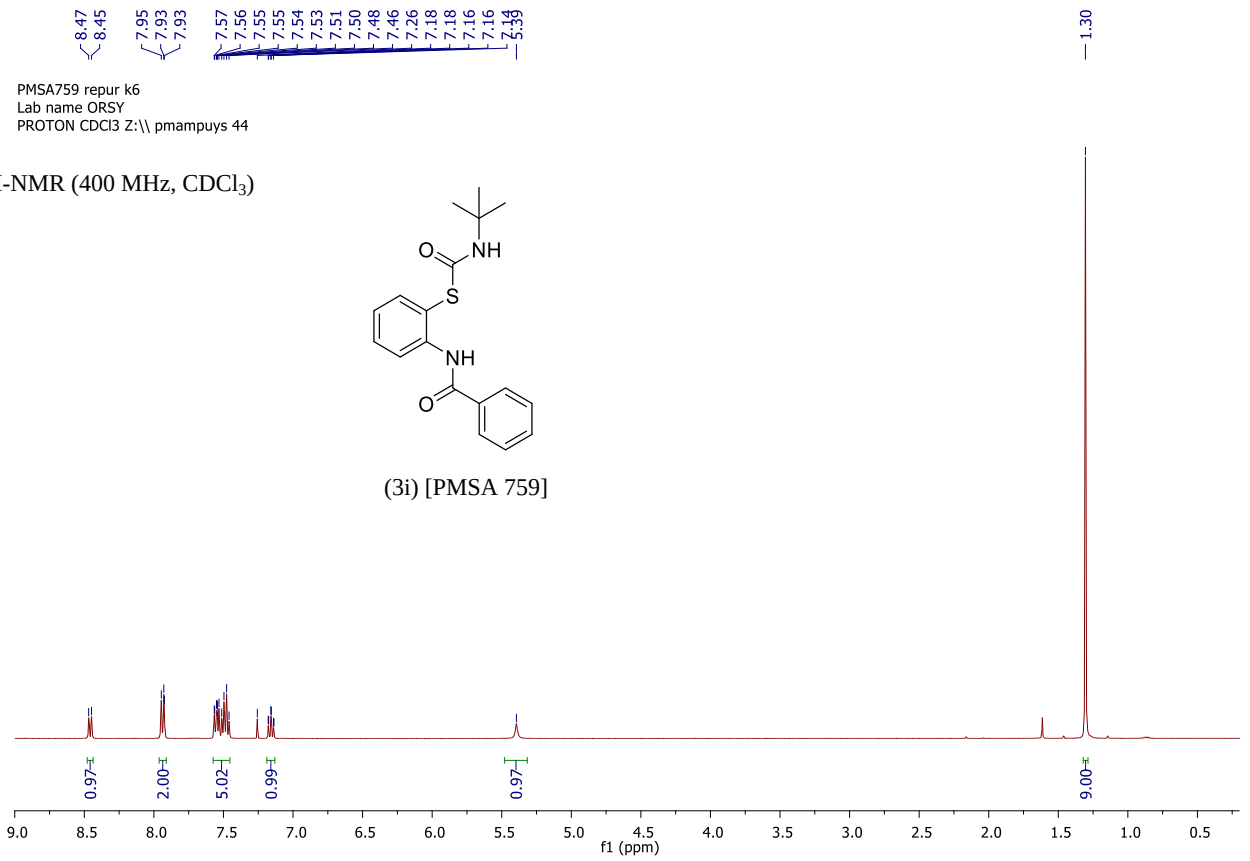


^{1}H-NMR (400 MHz, $CDCl_3$)

(3h) [PMSA 800/819]

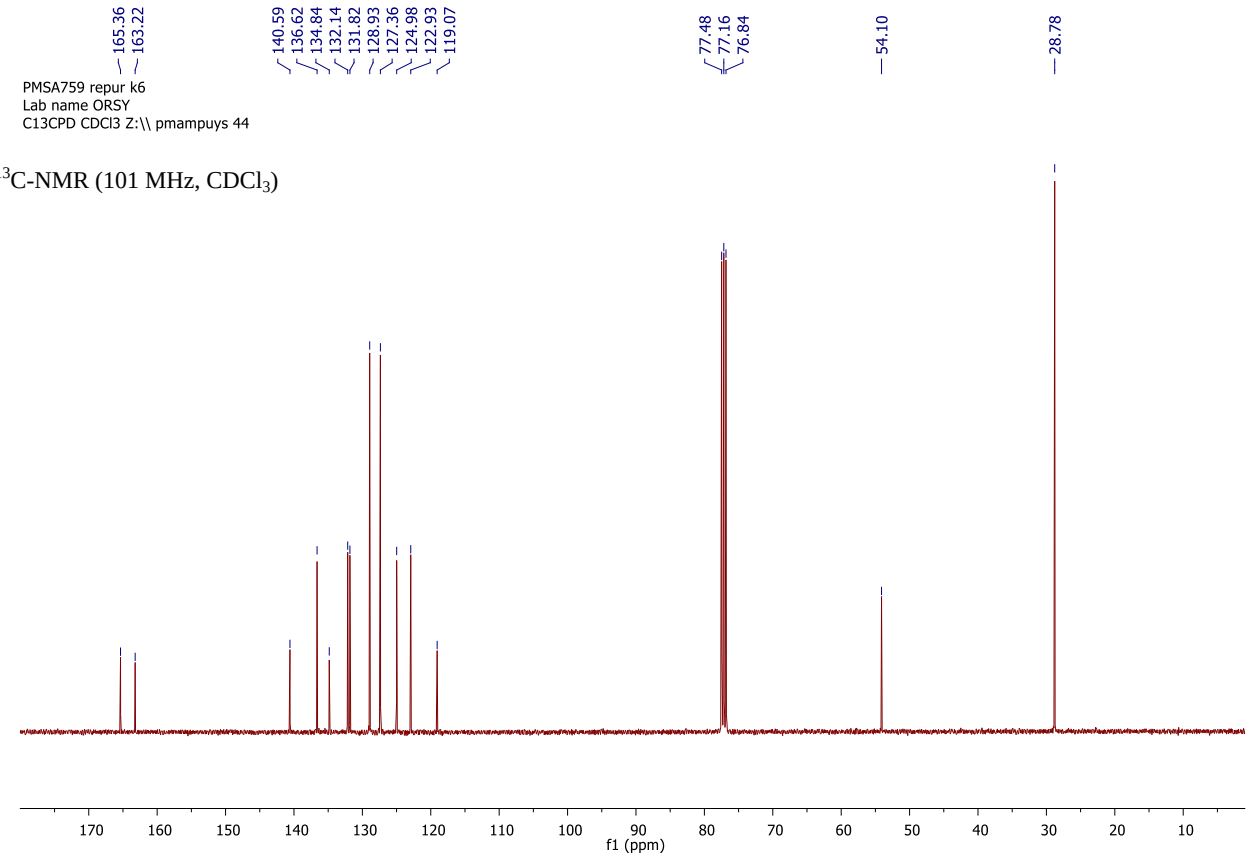


^{13}C-NMR (101 MHz, $CDCl_3$)

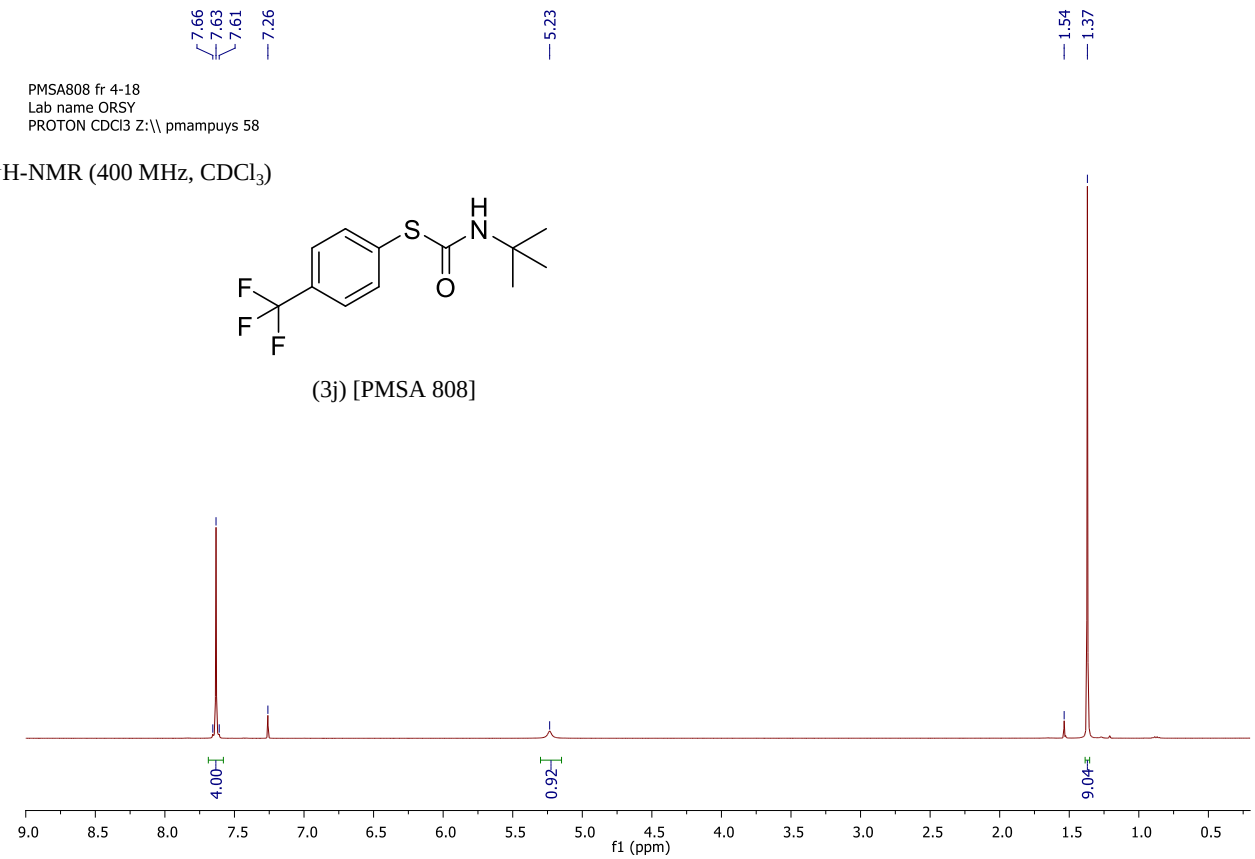


^{1}H-NMR (400 MHz, $CDCl_3$)

(3i) [PMSA 759]

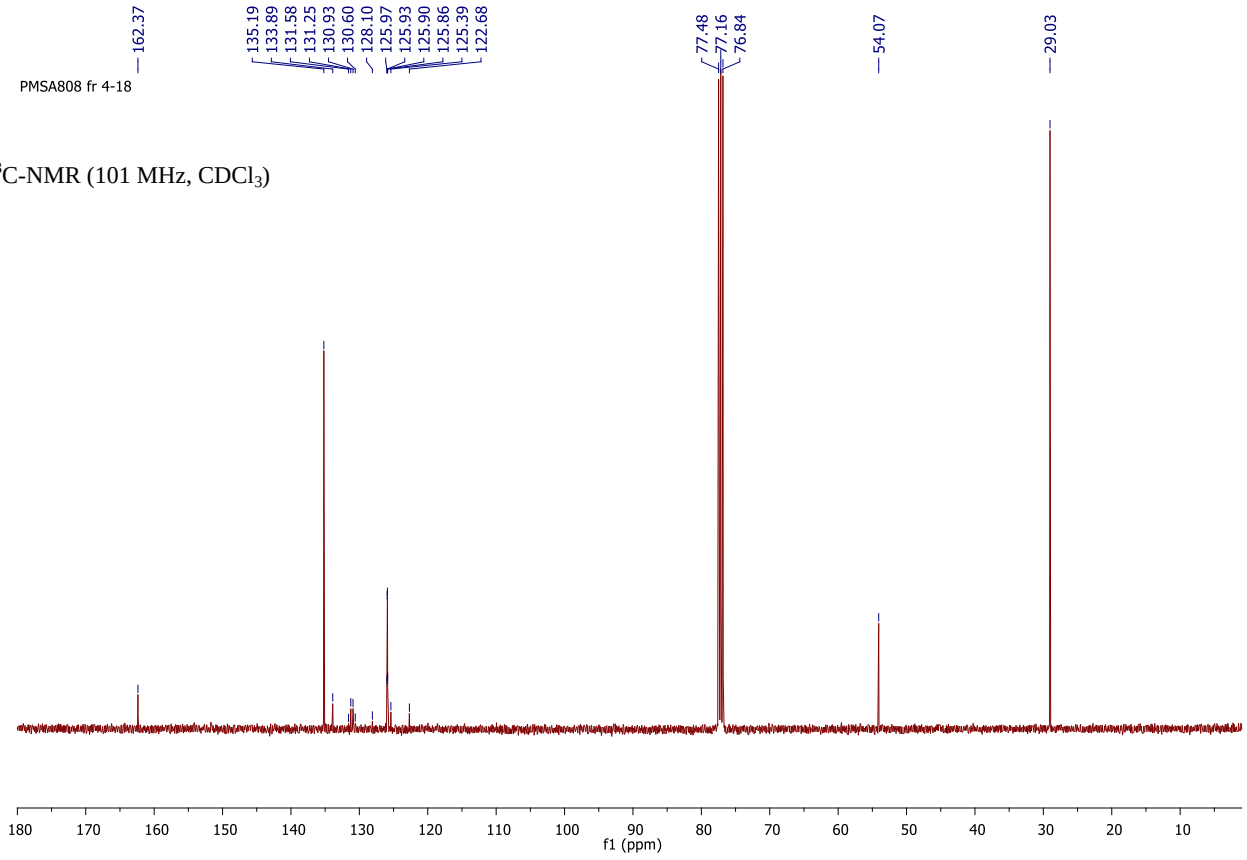


^{13}C-NMR (101 MHz, $CDCl_3$)

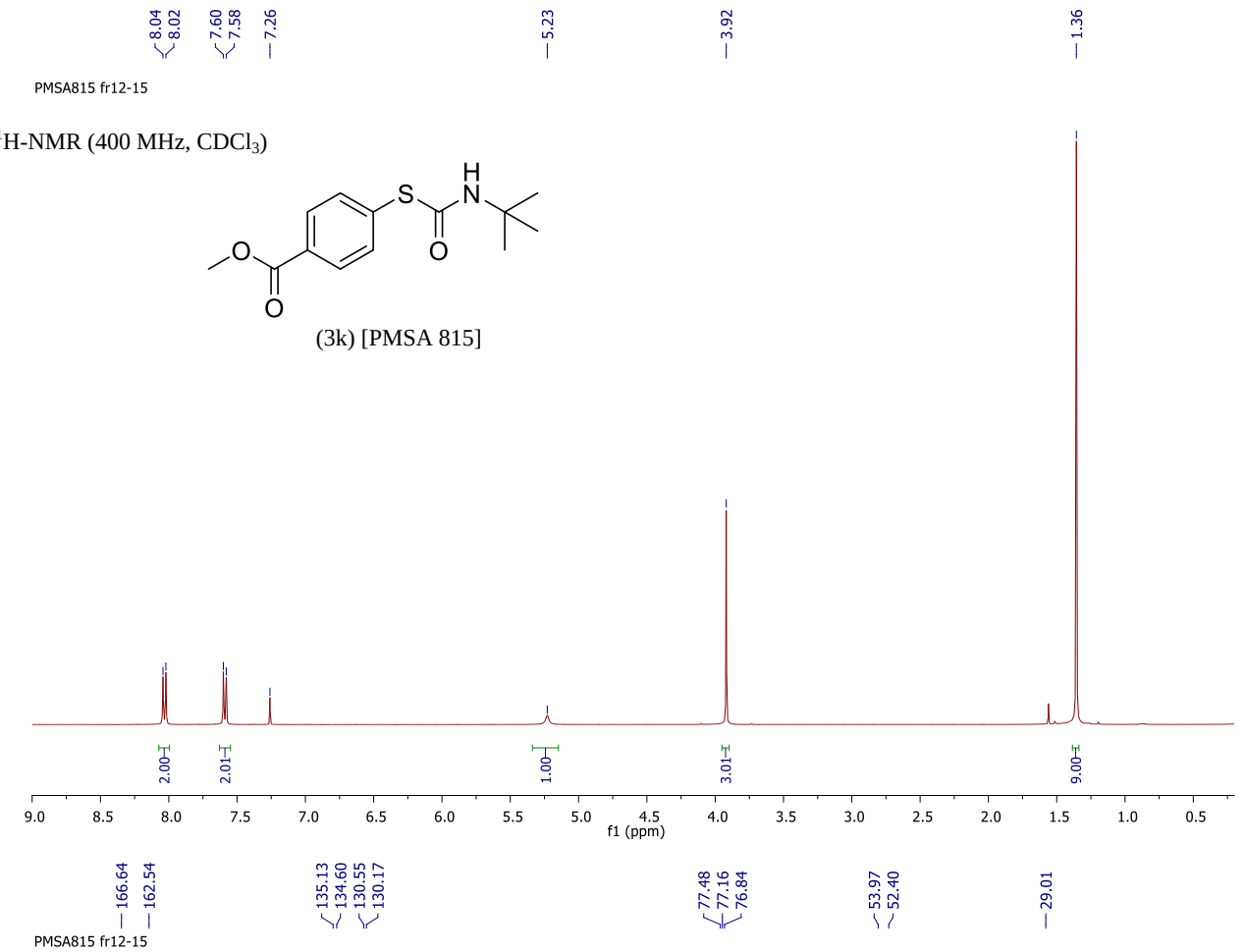


^{1}H-NMR (400 MHz, $CDCl_3$)

(3j) [PMSA 808]

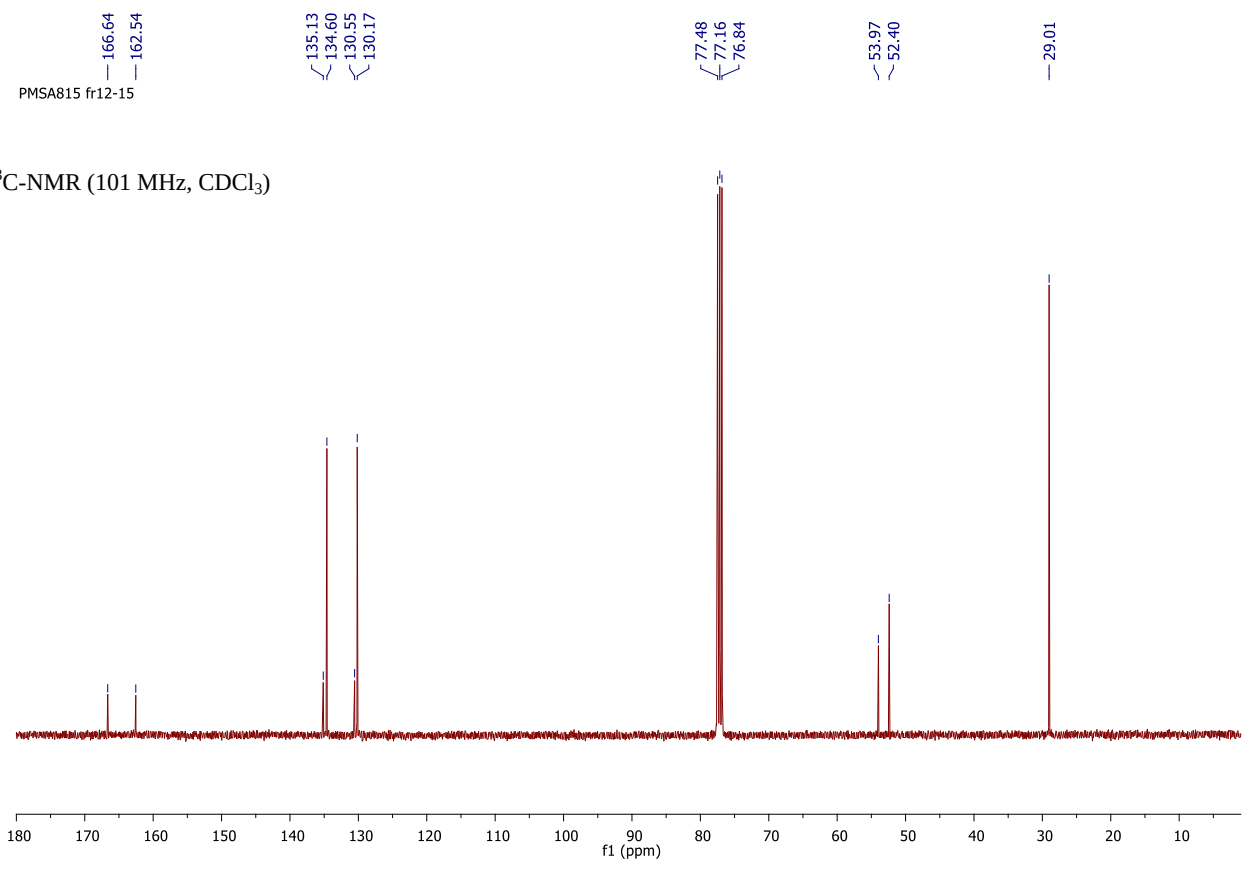


^{13}C-NMR (101 MHz, $CDCl_3$)

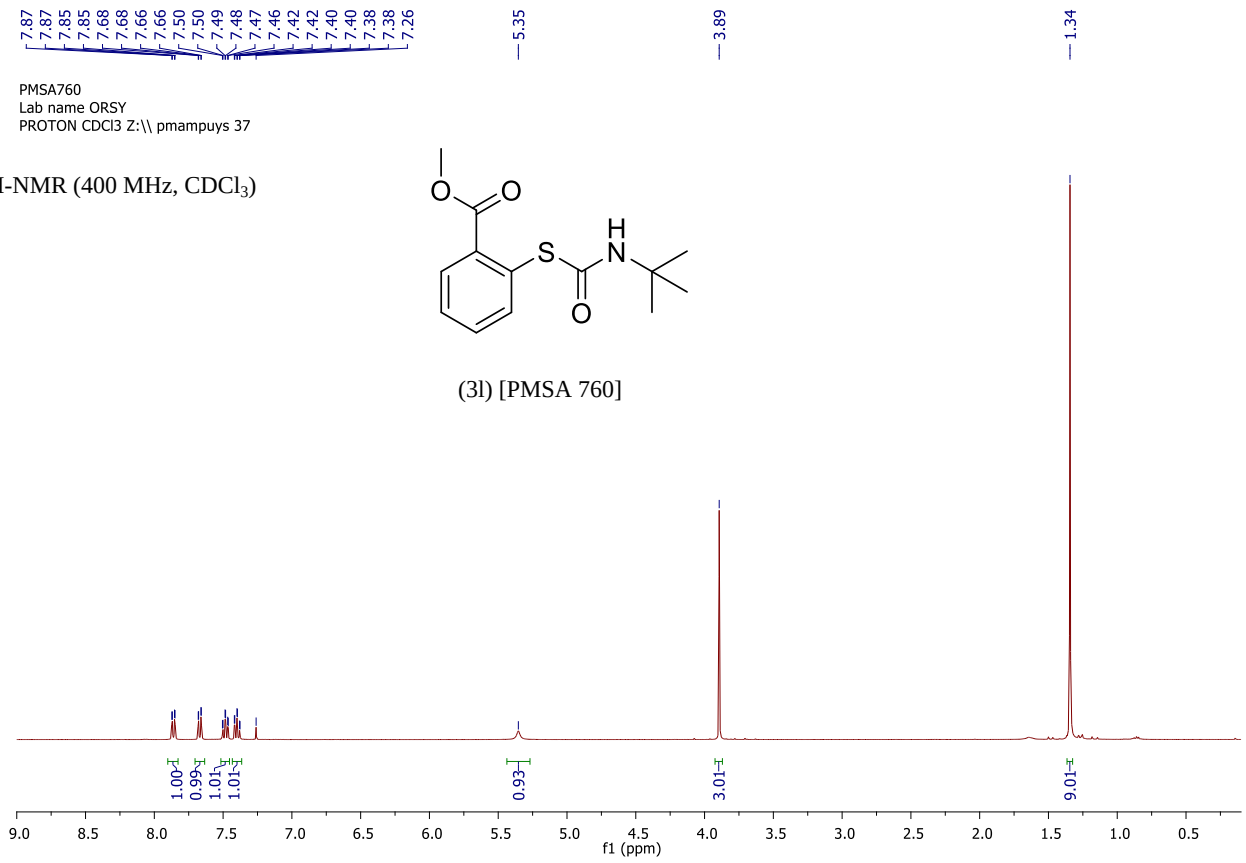


^{1}H-NMR (400 MHz, $CDCl_3$)

(3k) [PMSA 815]

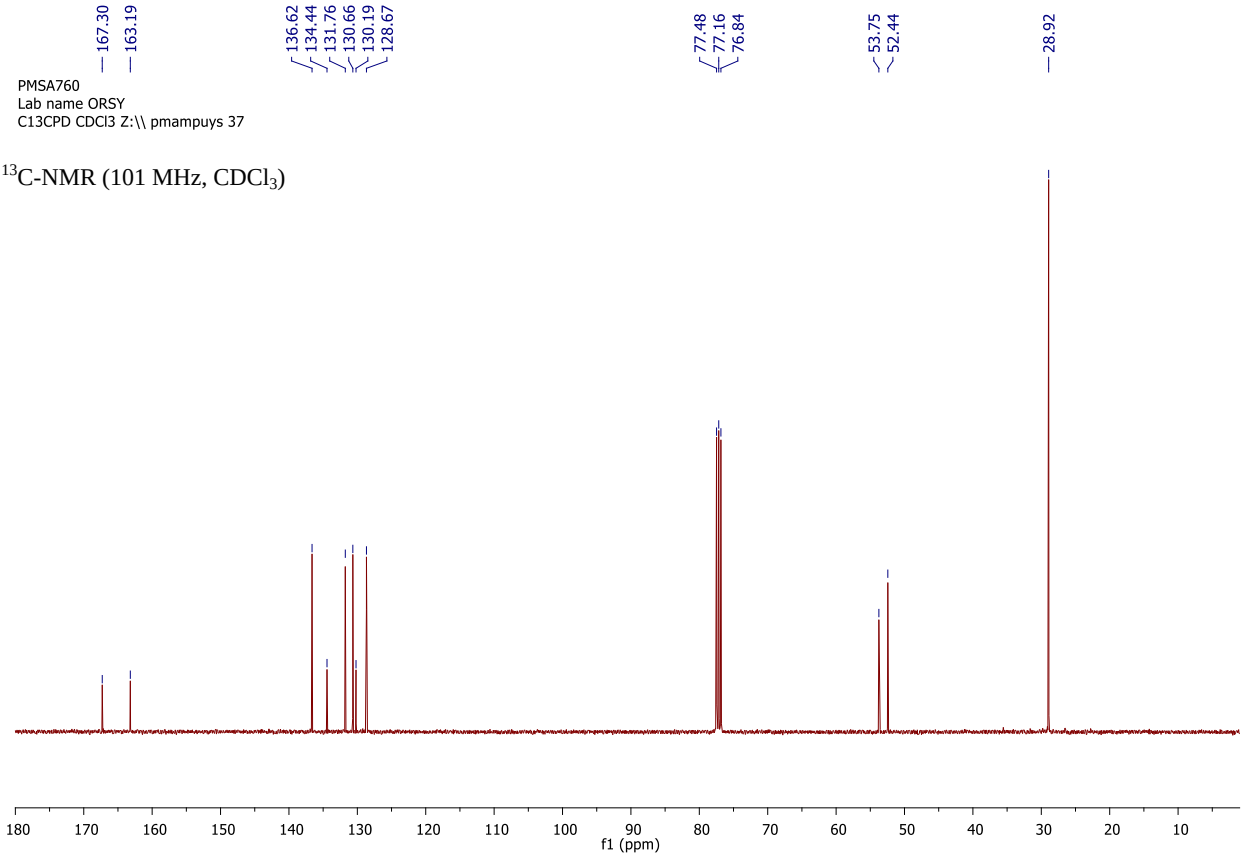


^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

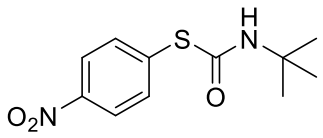
(3l) [PMSA 760]



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

PMSA782 fr 25-end
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 51

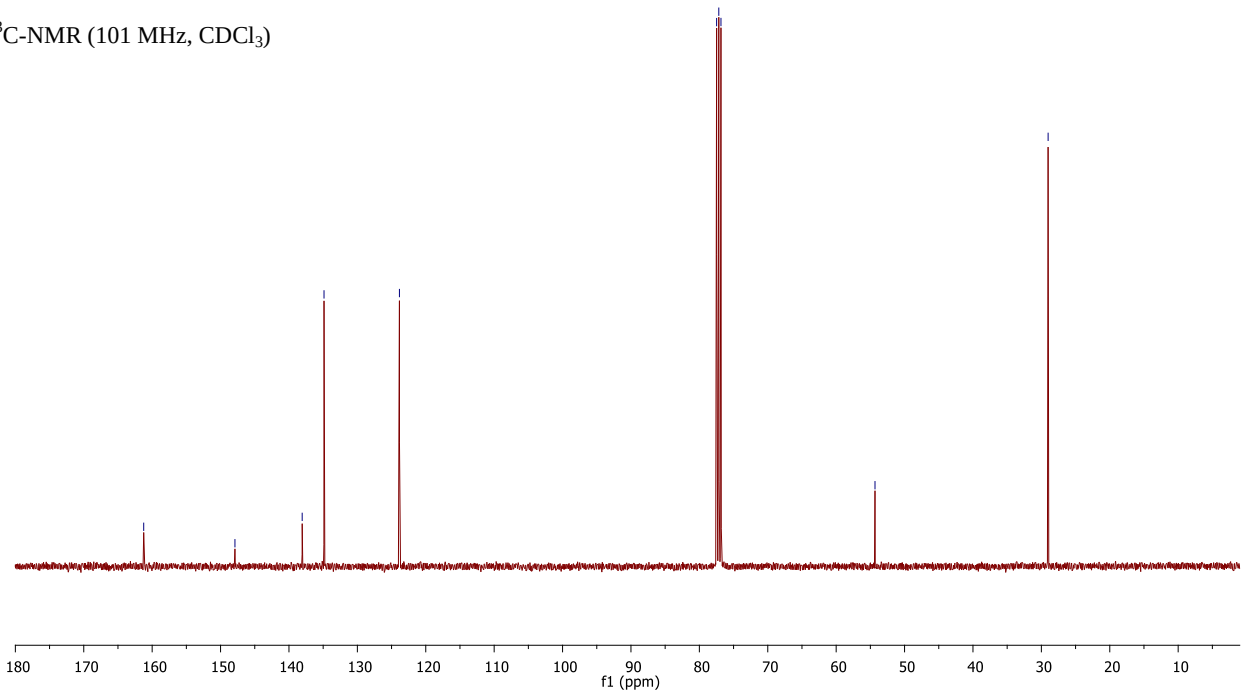
^{1}H-NMR (400 MHz, $CDCl_3$)

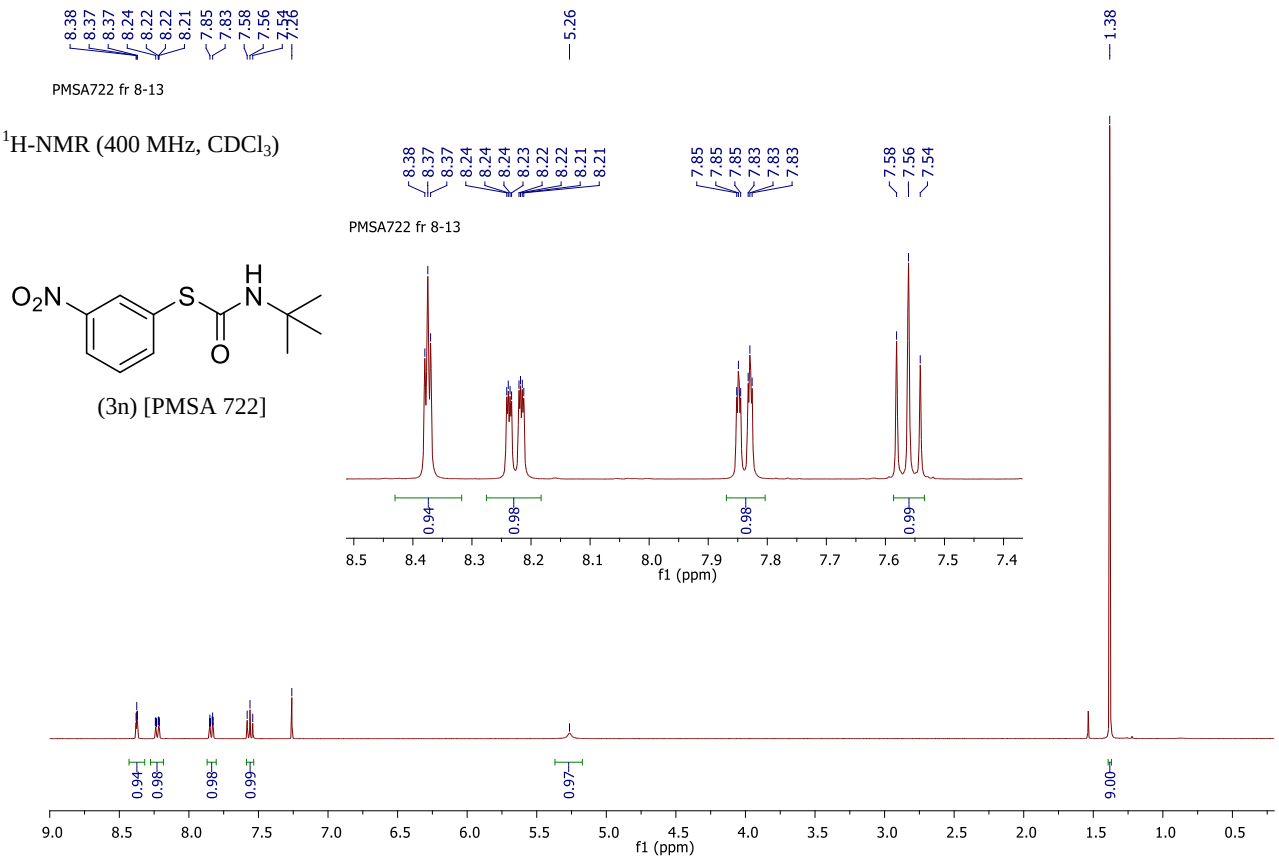


(3m) [PMSA 782]

PMSA782 fr 25-end
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 51

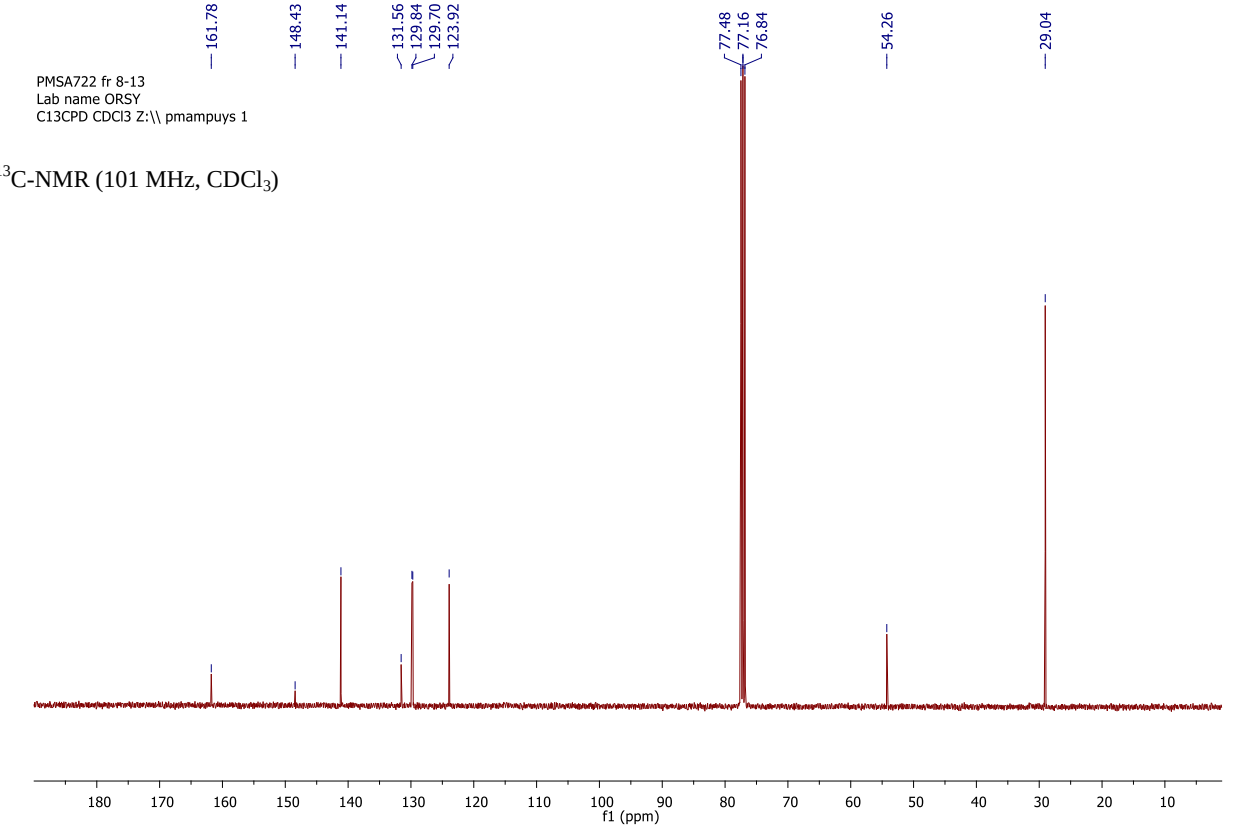
^{13}C-NMR (101 MHz, $CDCl_3$)



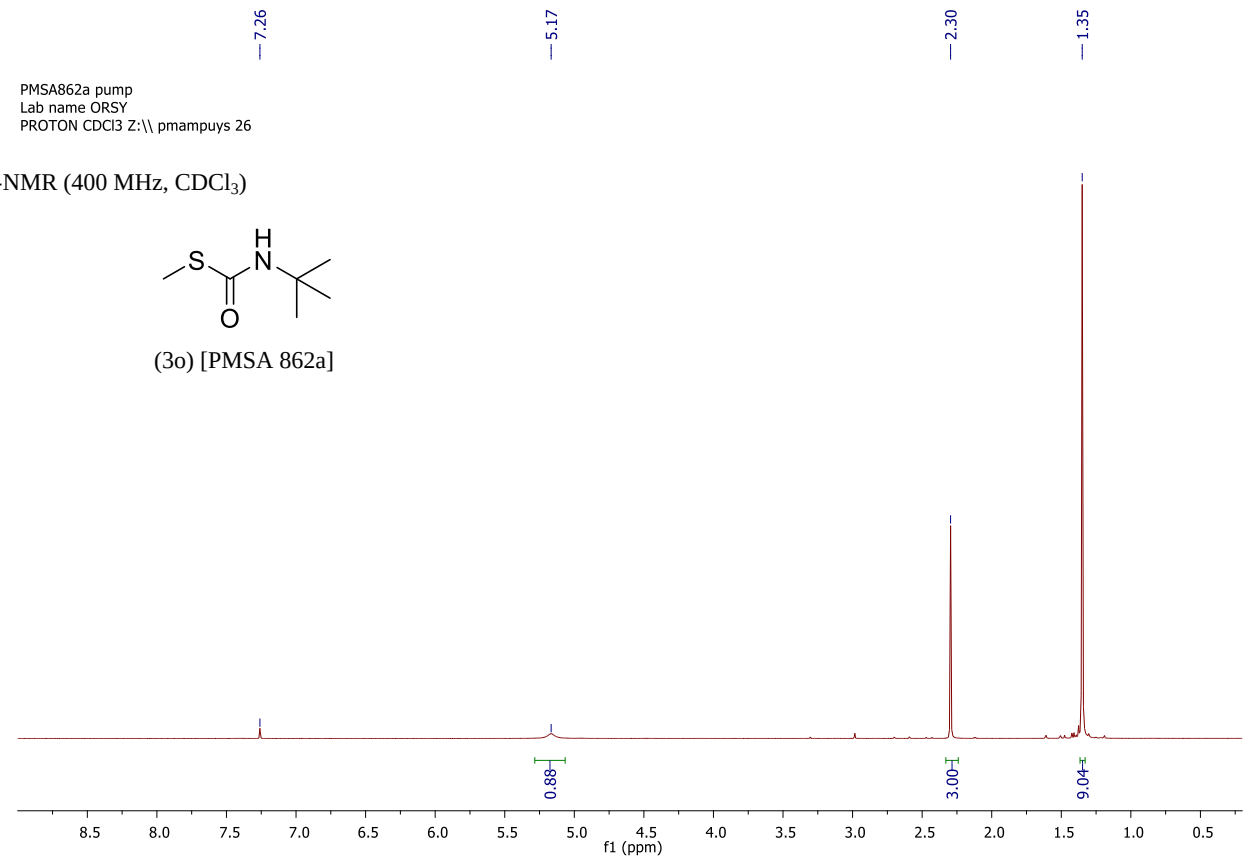


^{1}H-NMR (400 MHz, $CDCl_3$)

(3n) [PMSA 722]

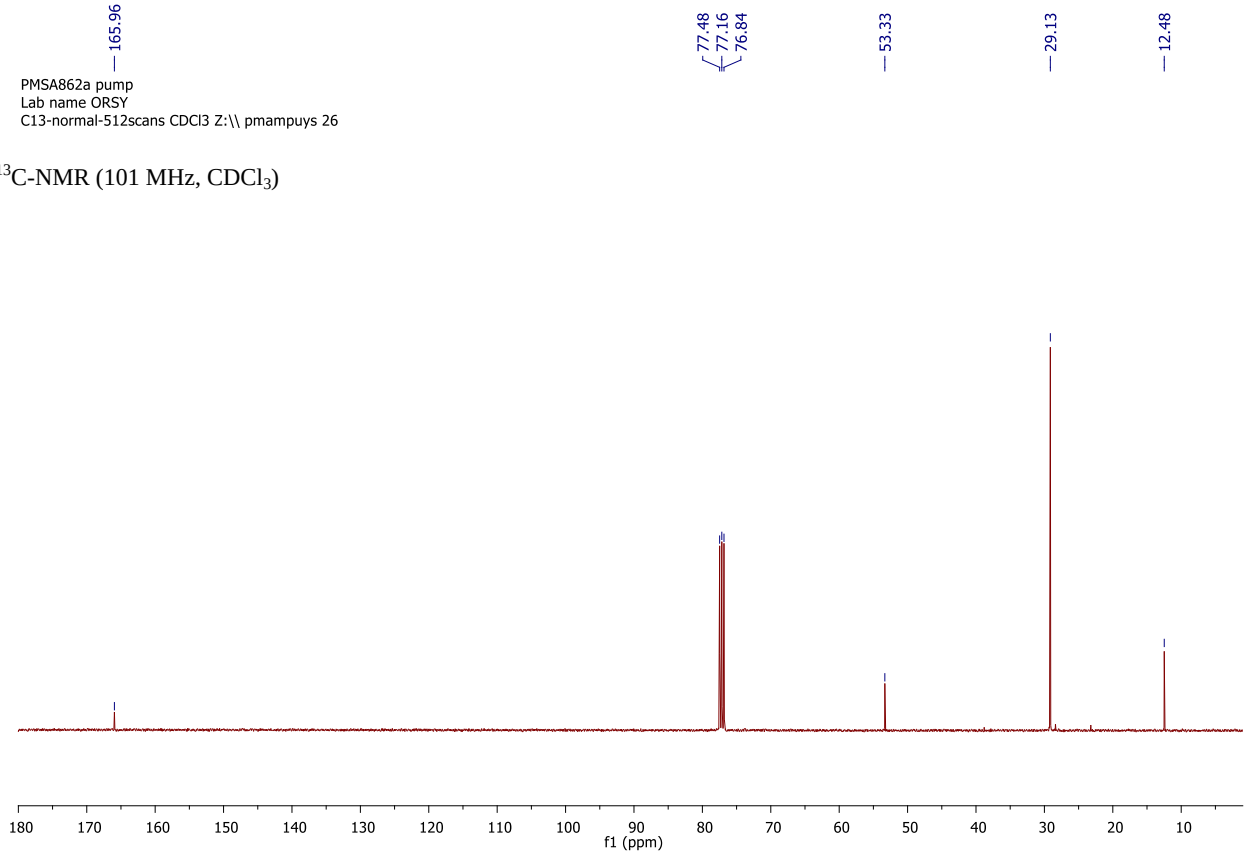


^{13}C-NMR (101 MHz, $CDCl_3$)

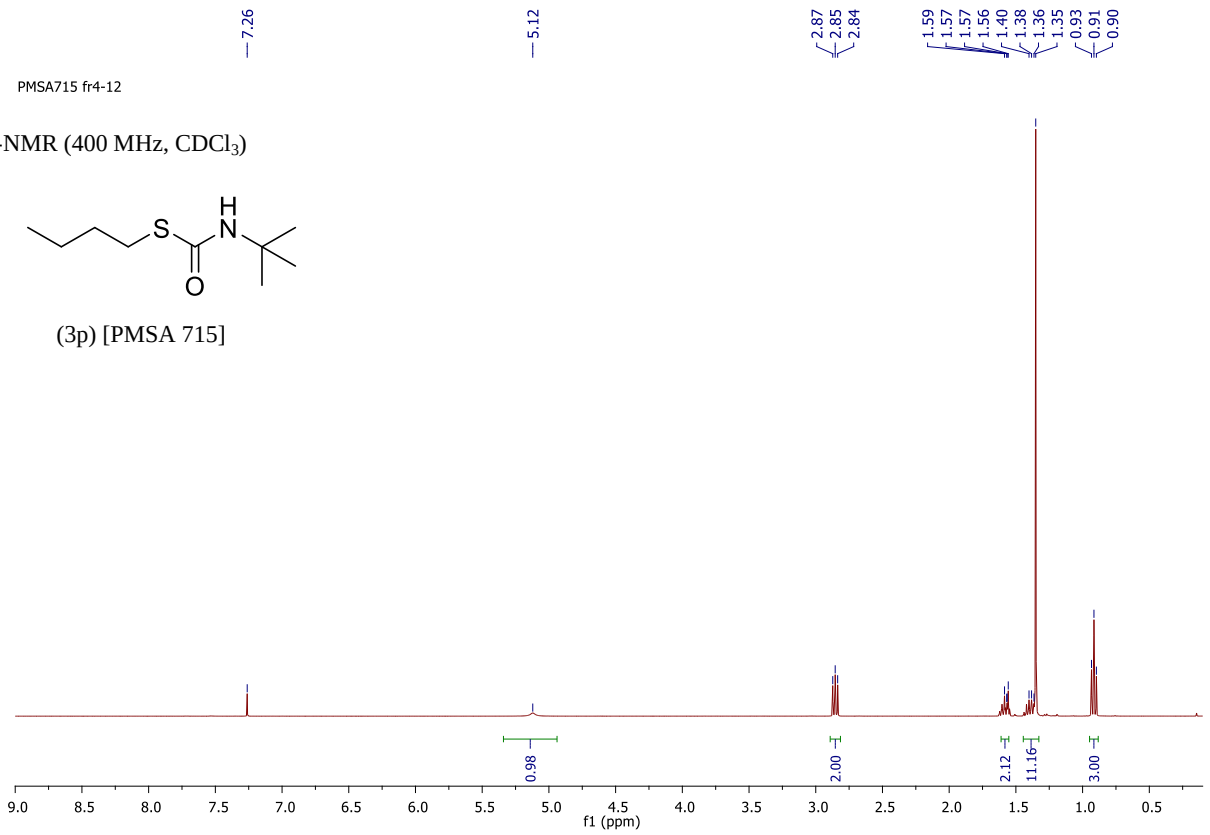


^{1}H-NMR (400 MHz, $CDCl_3$)

(3o) [PMSA 862a]

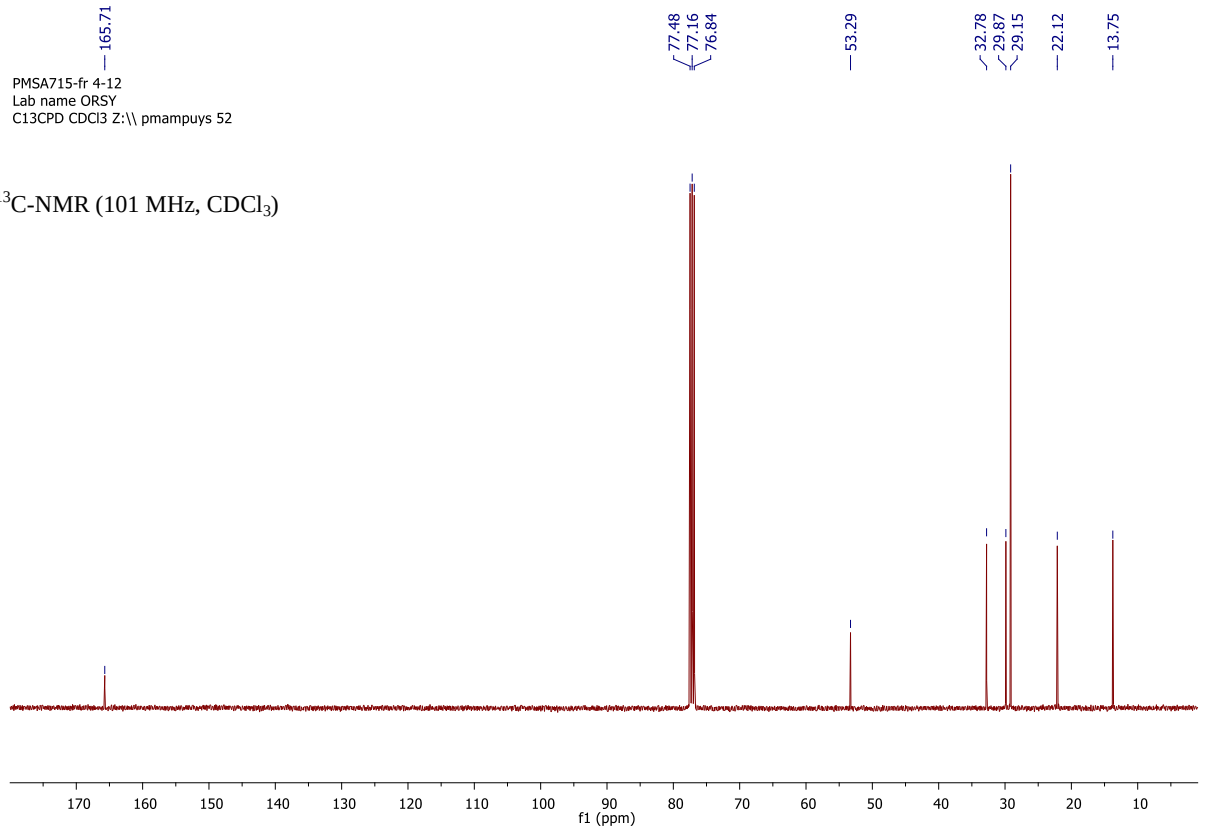


^{13}C-NMR (101 MHz, $CDCl_3$)

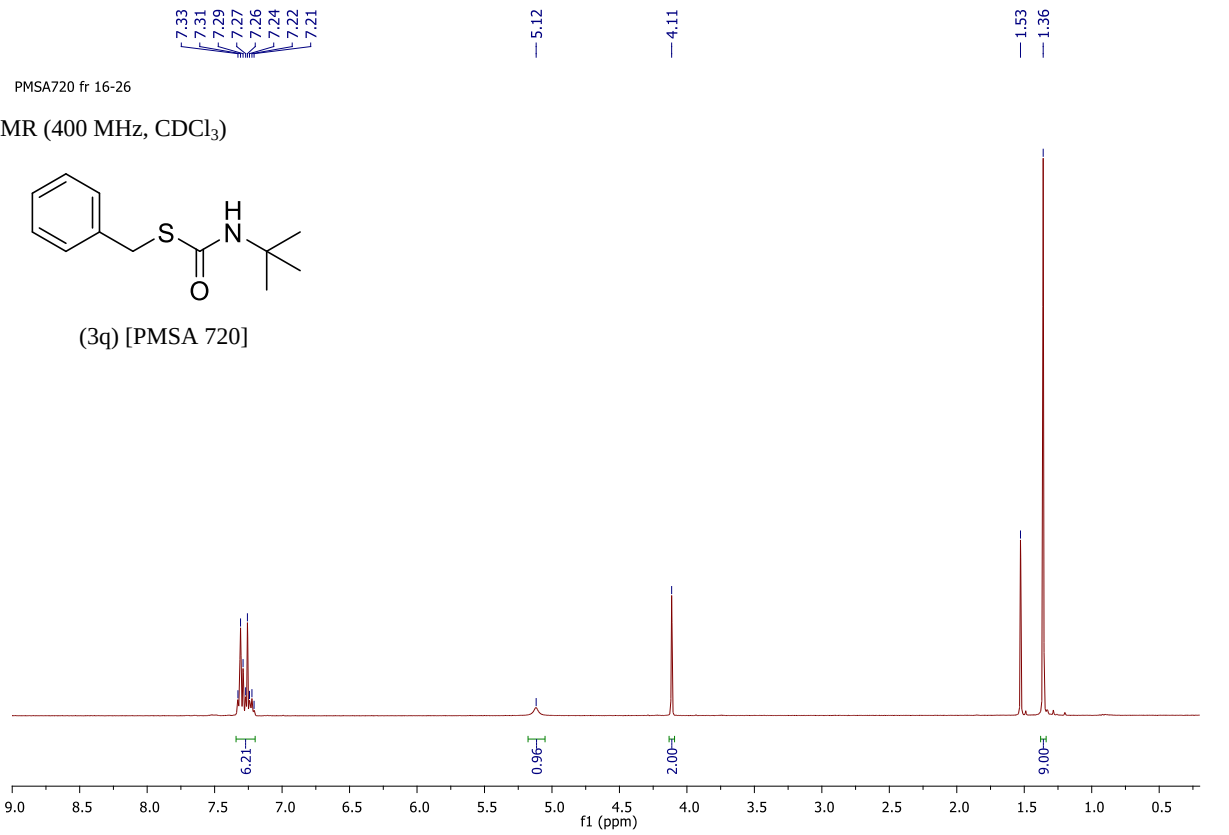


^{1}H-NMR (400 MHz, $CDCl_3$)

(3p) [PMSA 715]

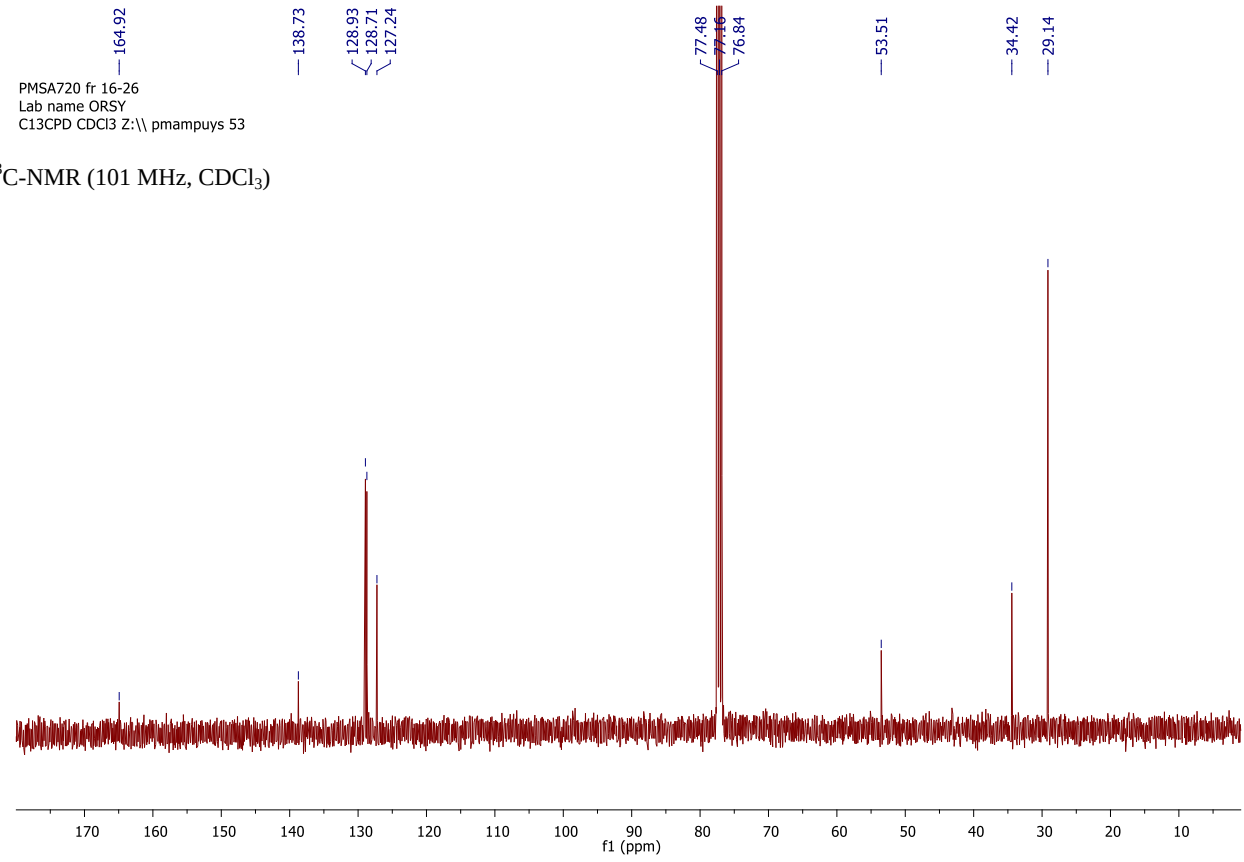


^{13}C-NMR (101 MHz, $CDCl_3$)

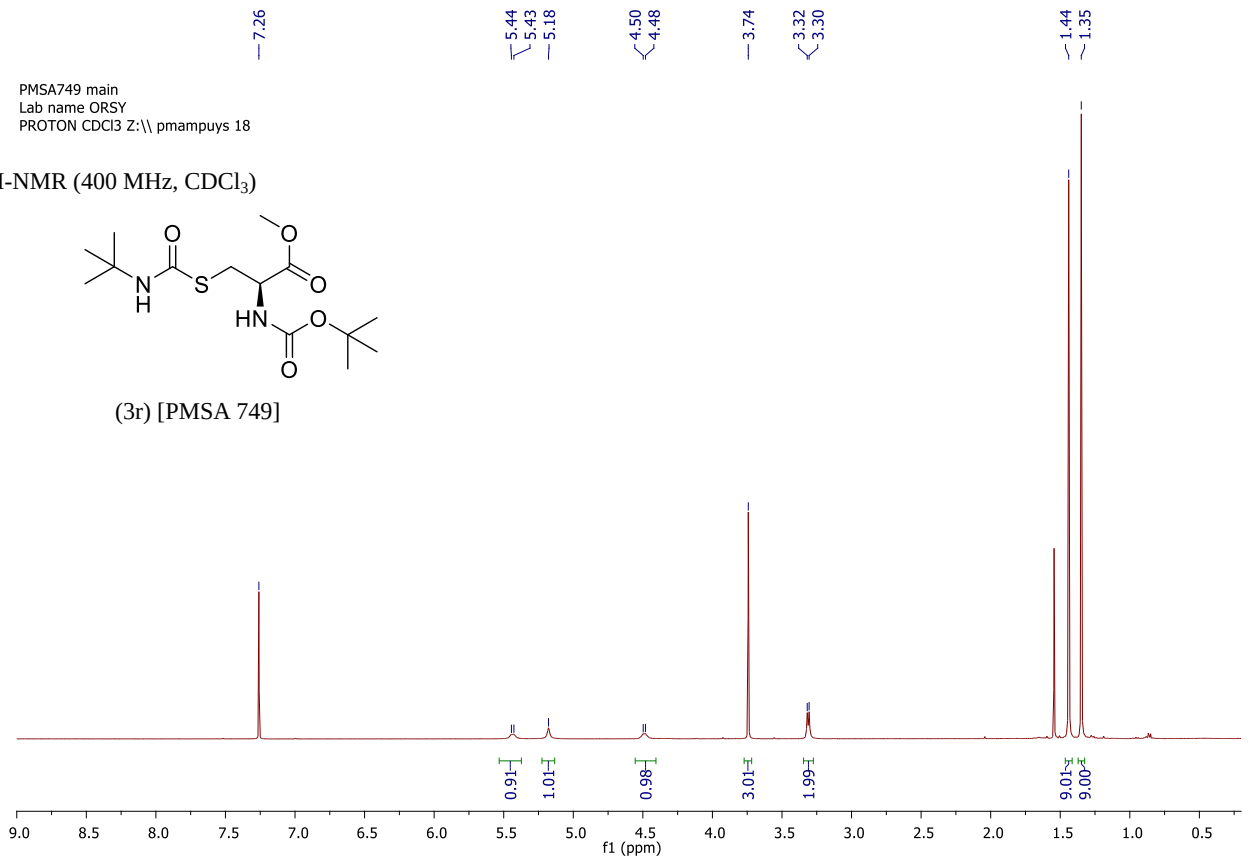


^{1}H-NMR (400 MHz, $CDCl_3$)

(3q) [PMSA 720]

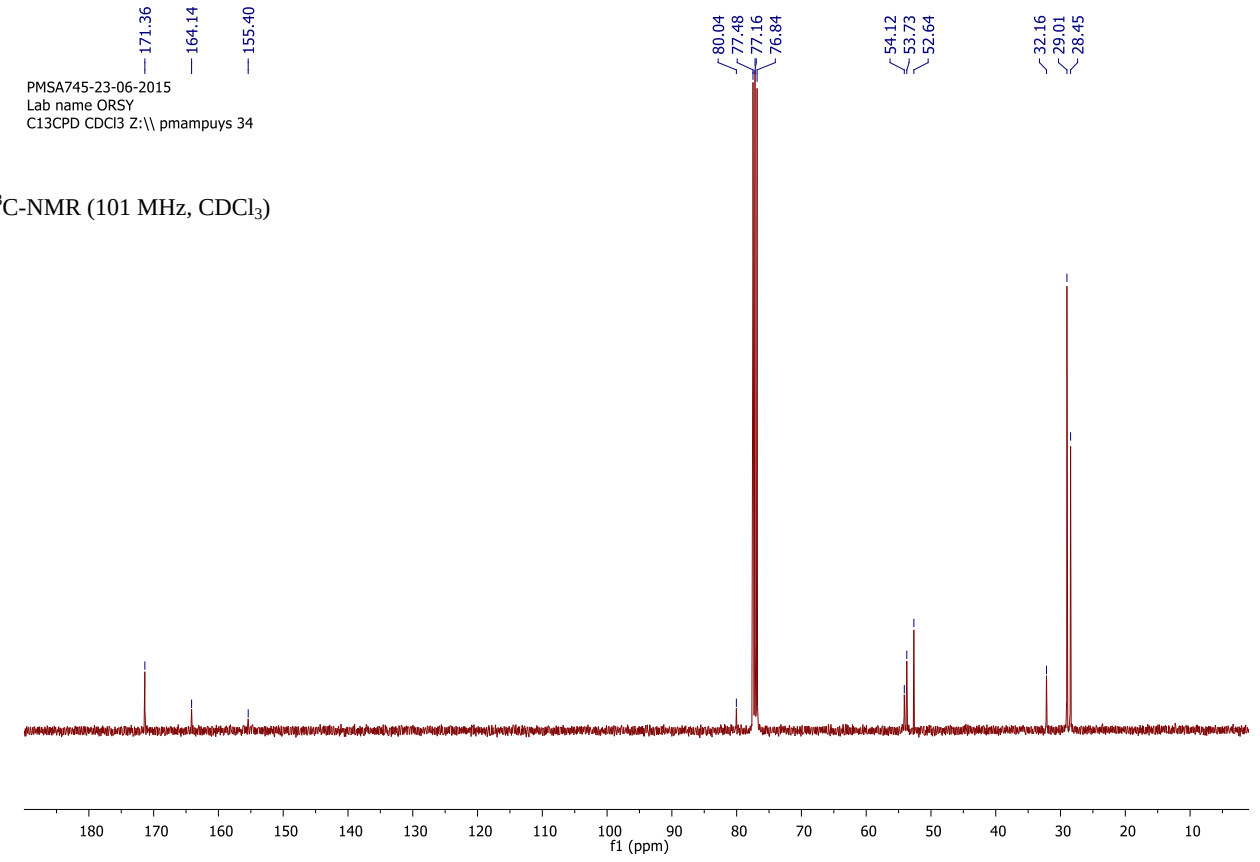


^{13}C-NMR (101 MHz, $CDCl_3$)

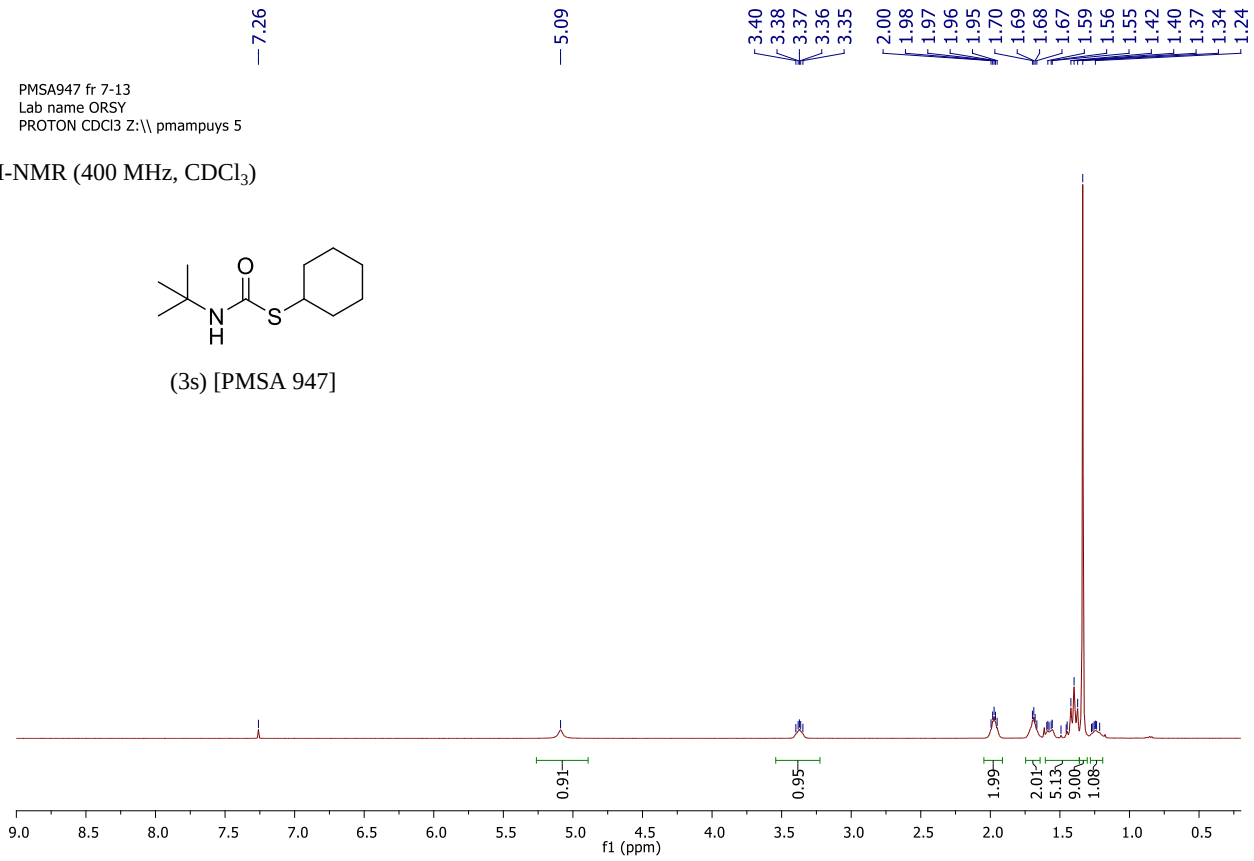


^{1}H-NMR (400 MHz, $CDCl_3$)

(3r) [PMSA 749]

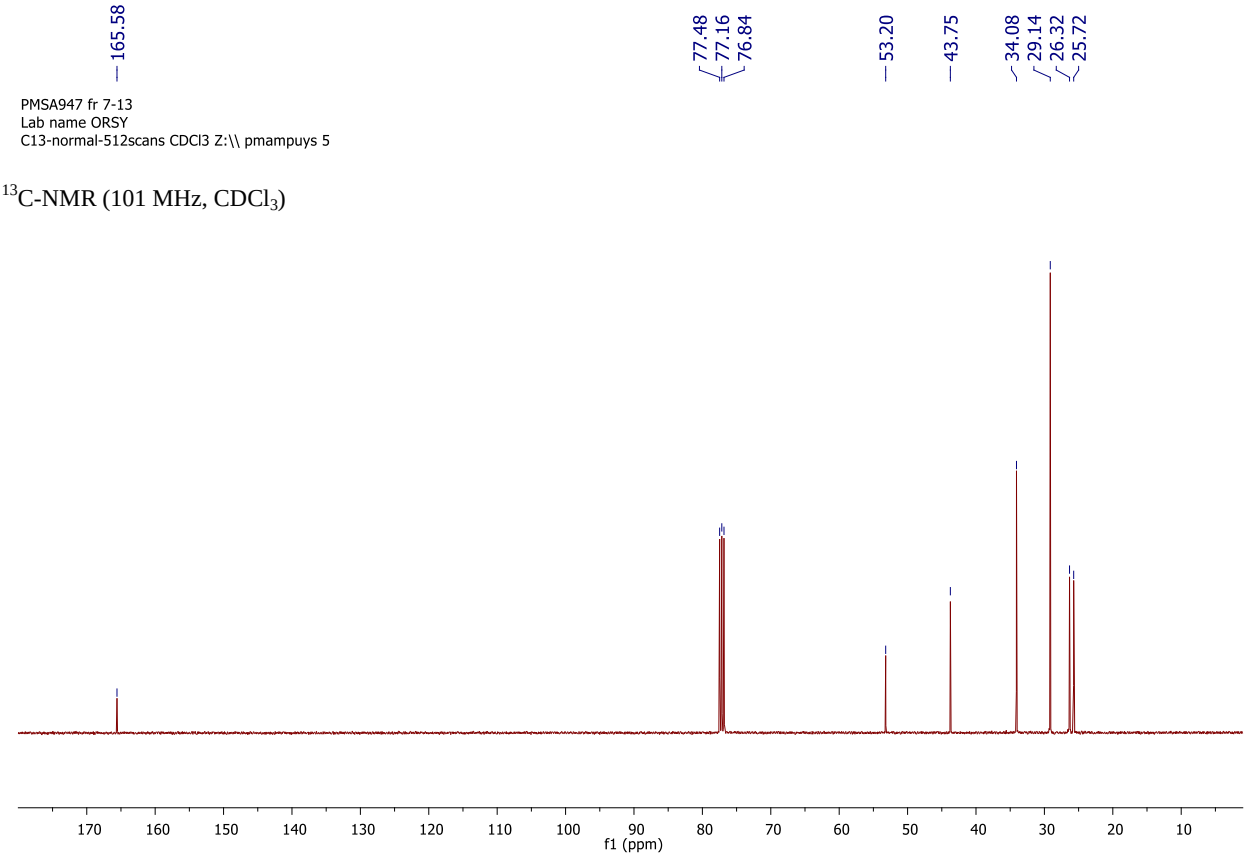


^{13}C-NMR (101 MHz, $CDCl_3$)

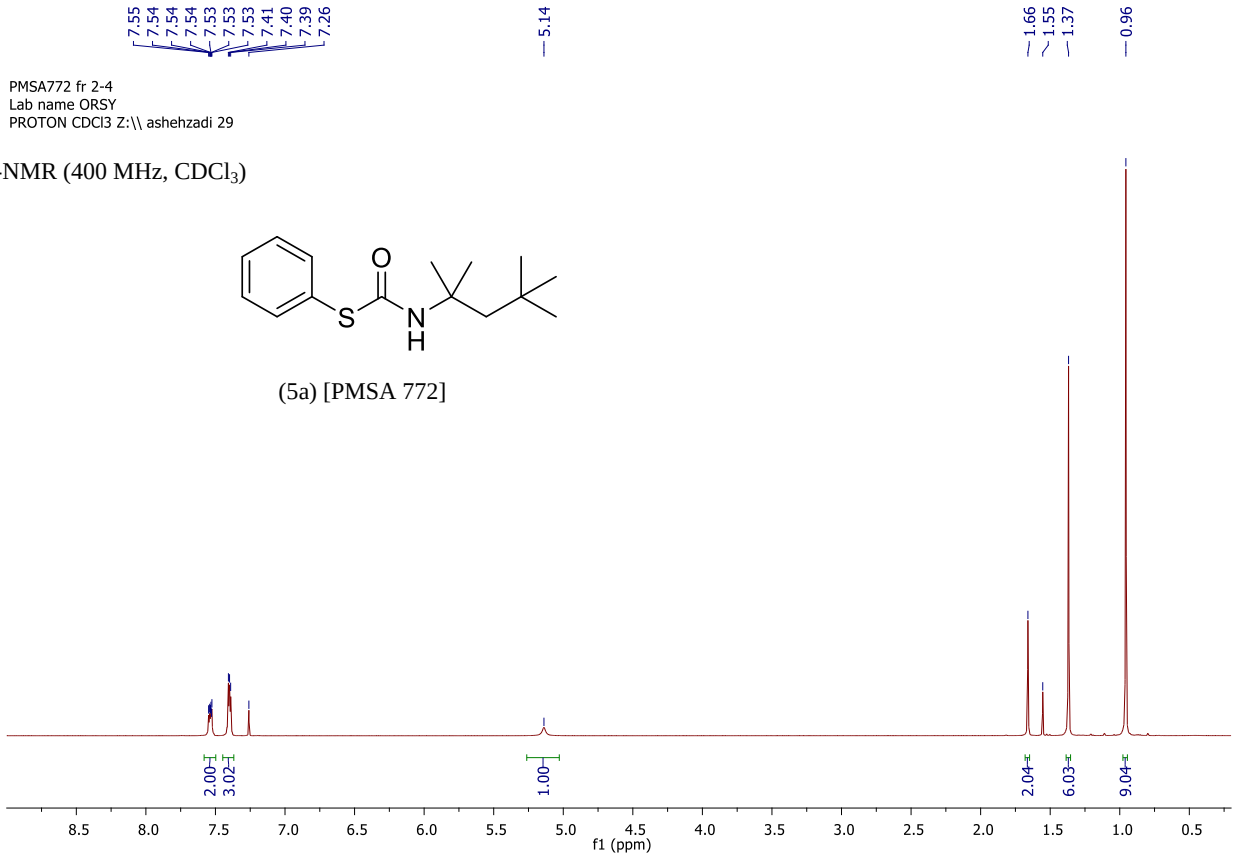


^{1}H-NMR (400 MHz, $CDCl_3$)

(3s) [PMSA 947]

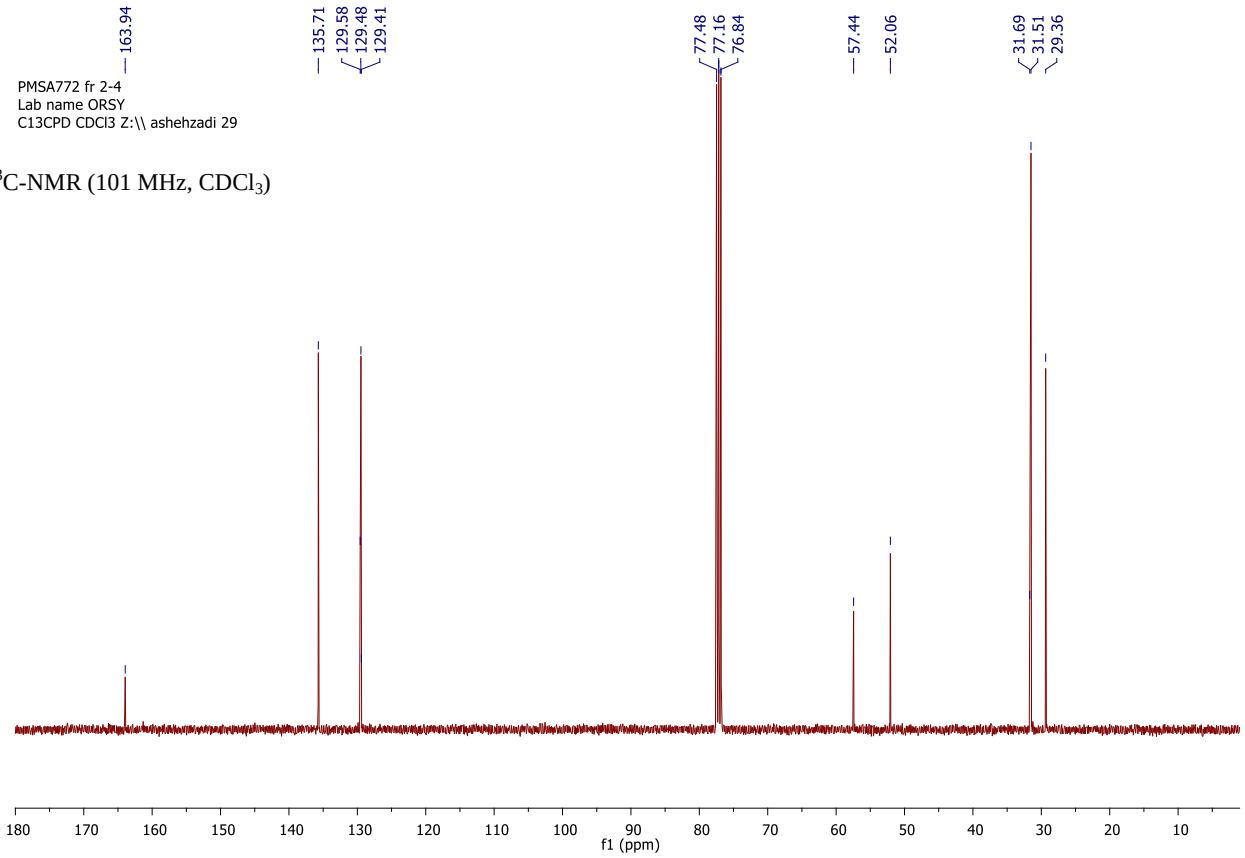


^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

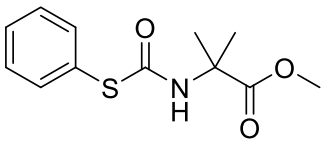
(5a) [PMSA 772]



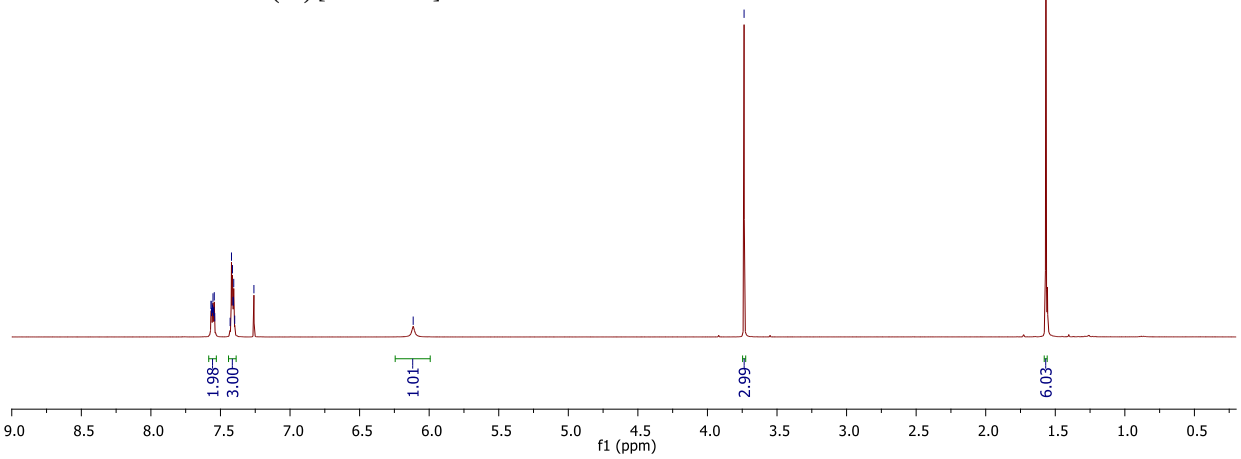
^{13}C-NMR (101 MHz, $CDCl_3$)

PMSA766 fr 8-14
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 10

^{1}H-NMR (400 MHz, $CDCl_3$)

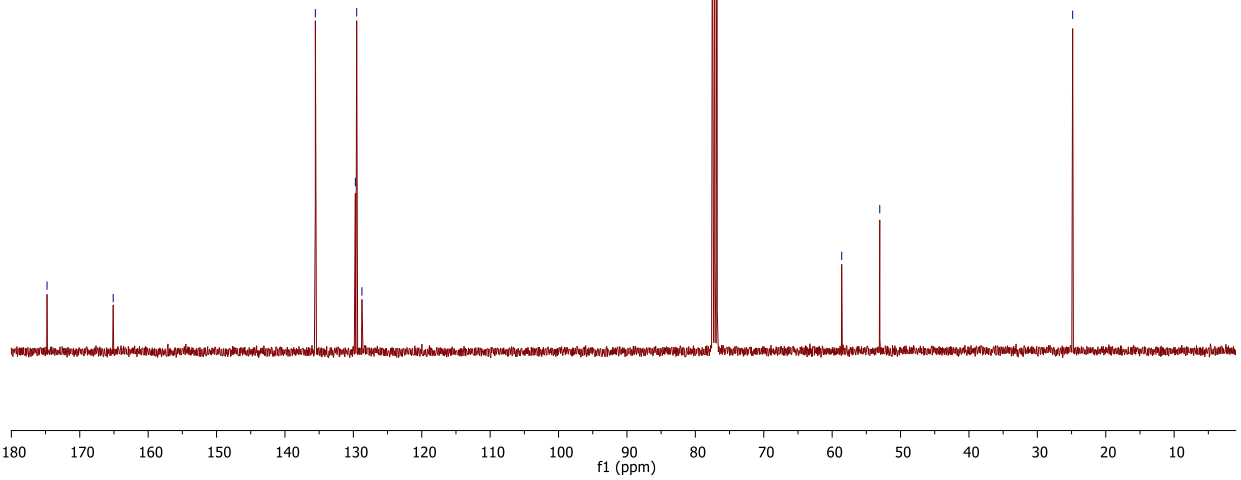


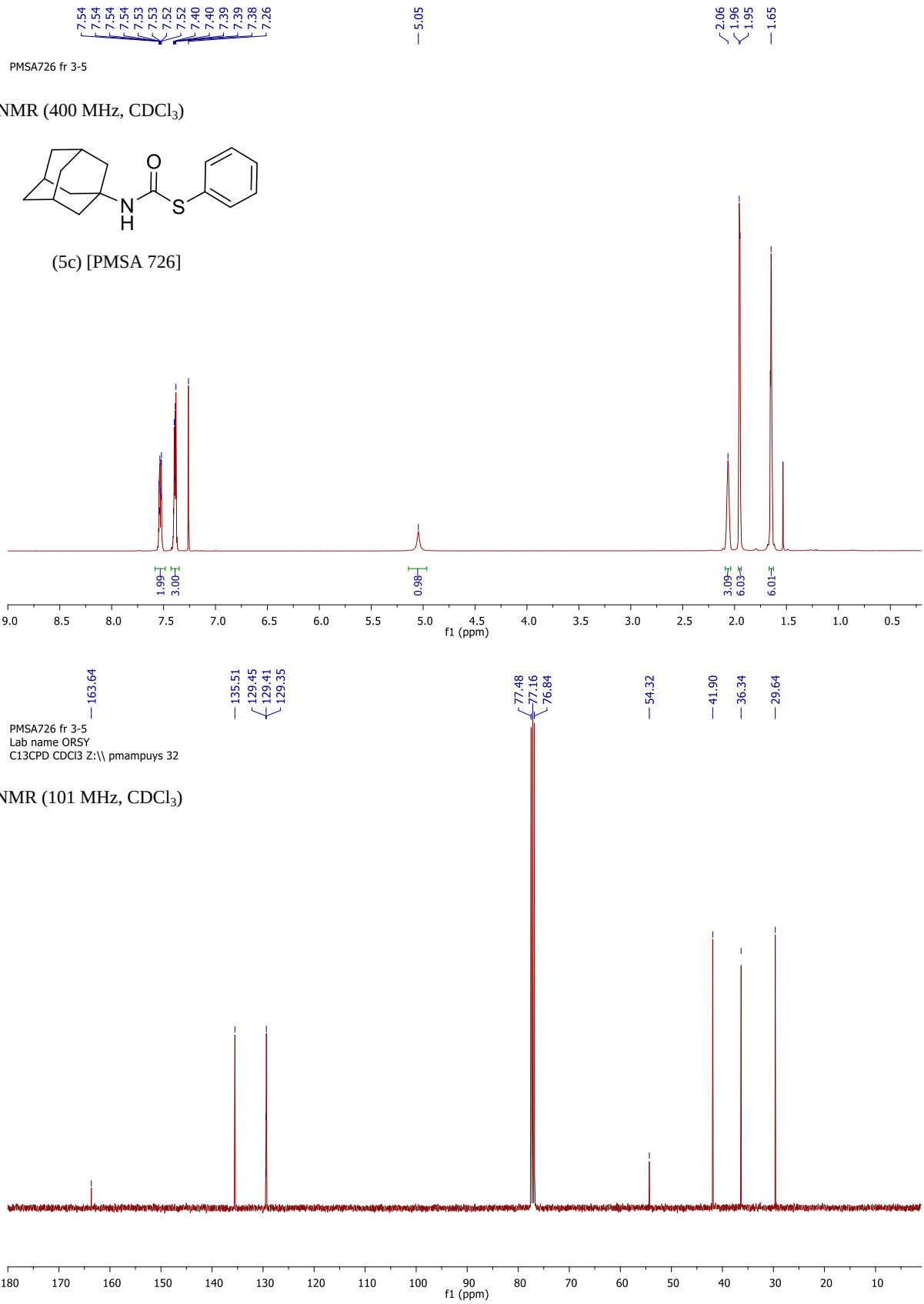
(5b) [PMSA 766]



PMSA766 fr 8-14
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 10

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

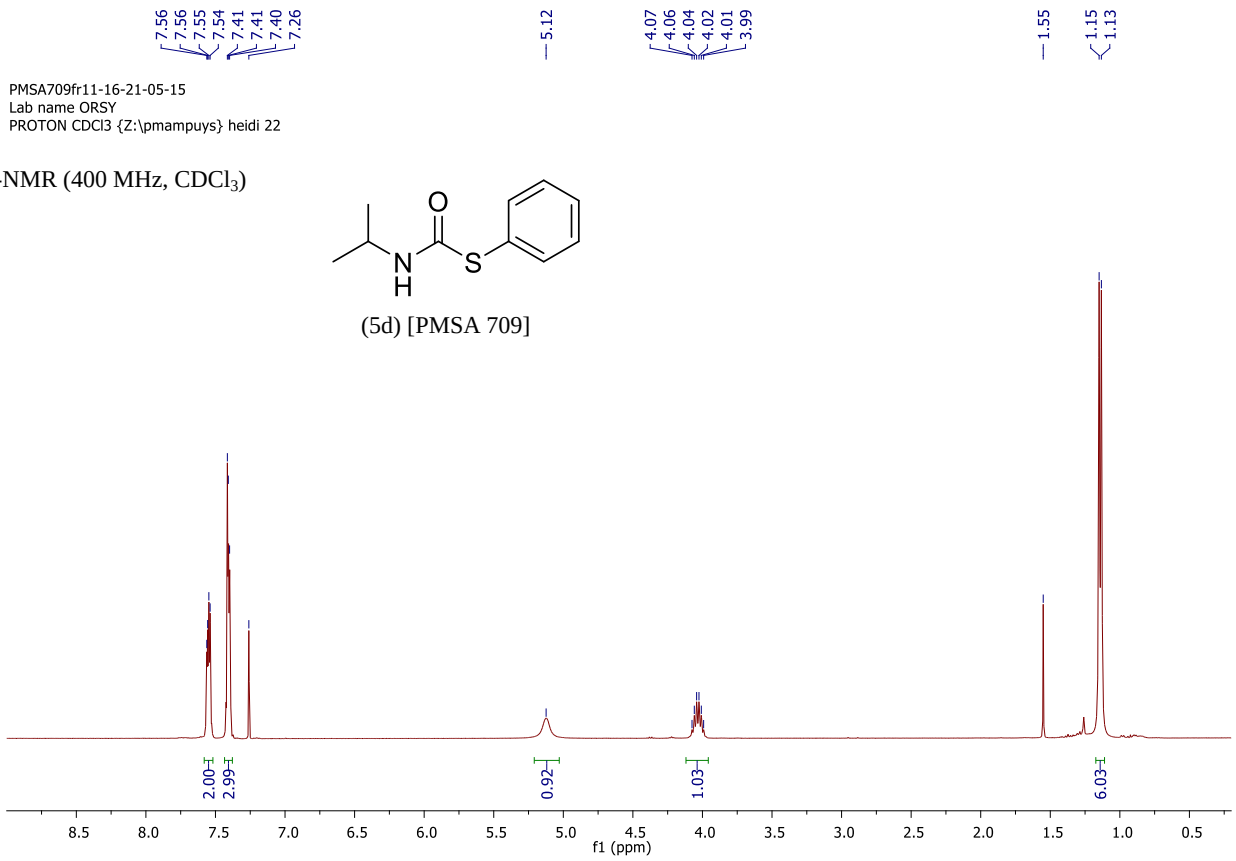




^{1}H-NMR (400 MHz, $CDCl_3$)

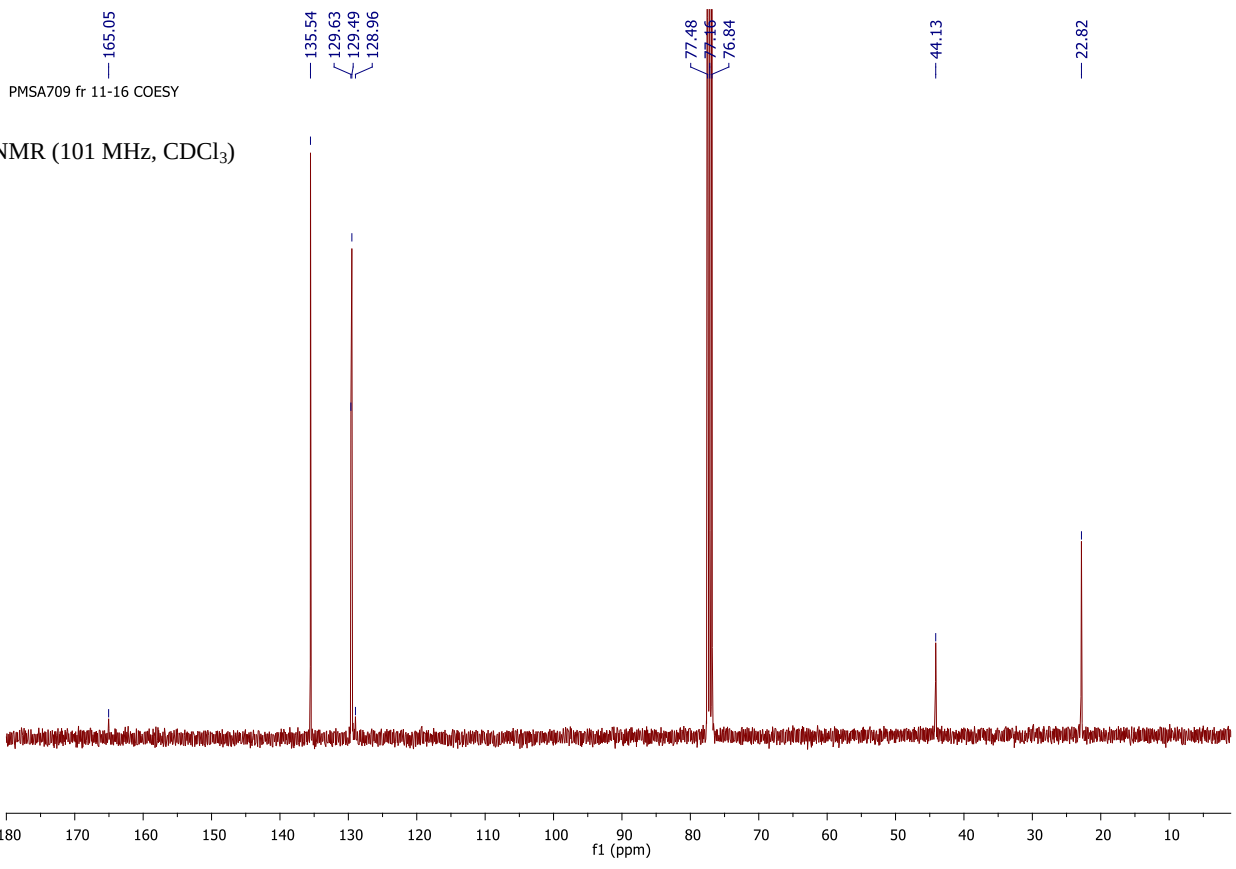
(5c) [PMSA 726]

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

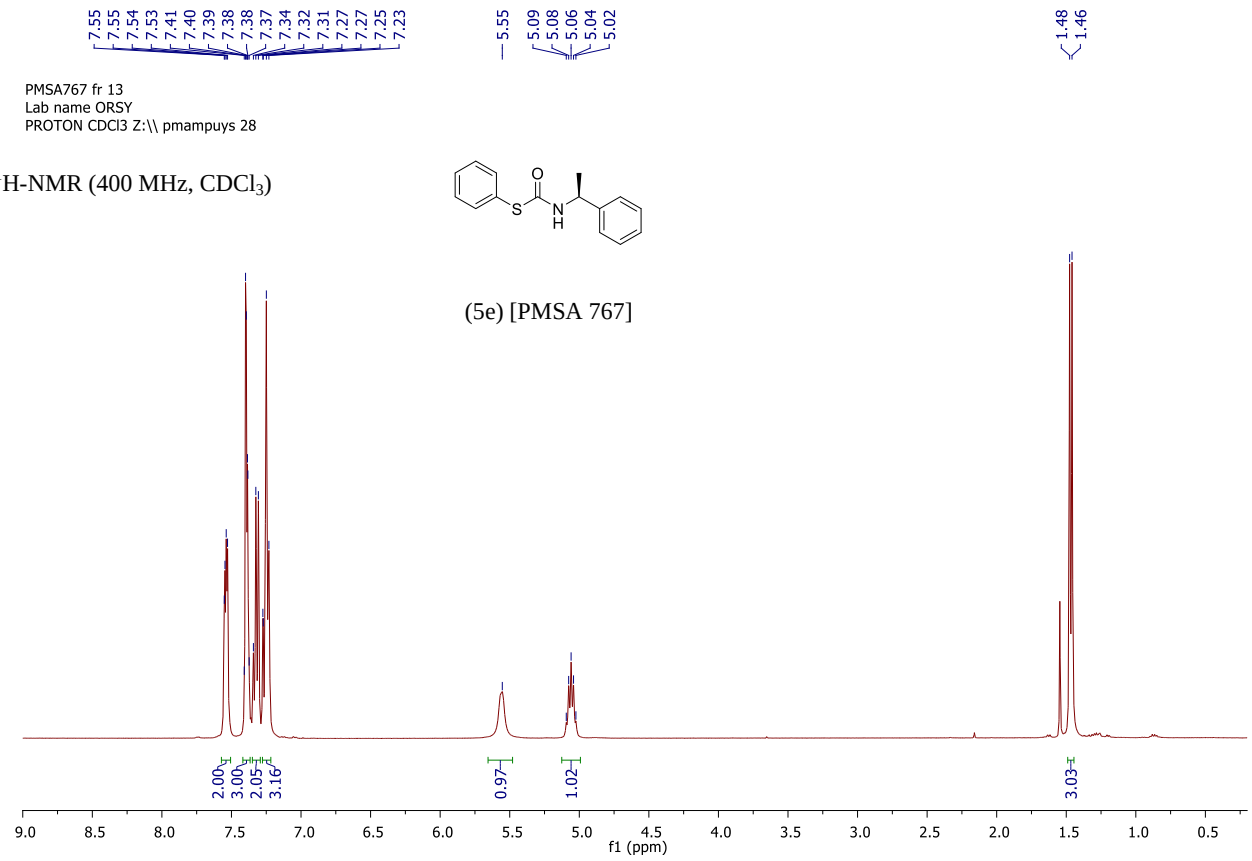


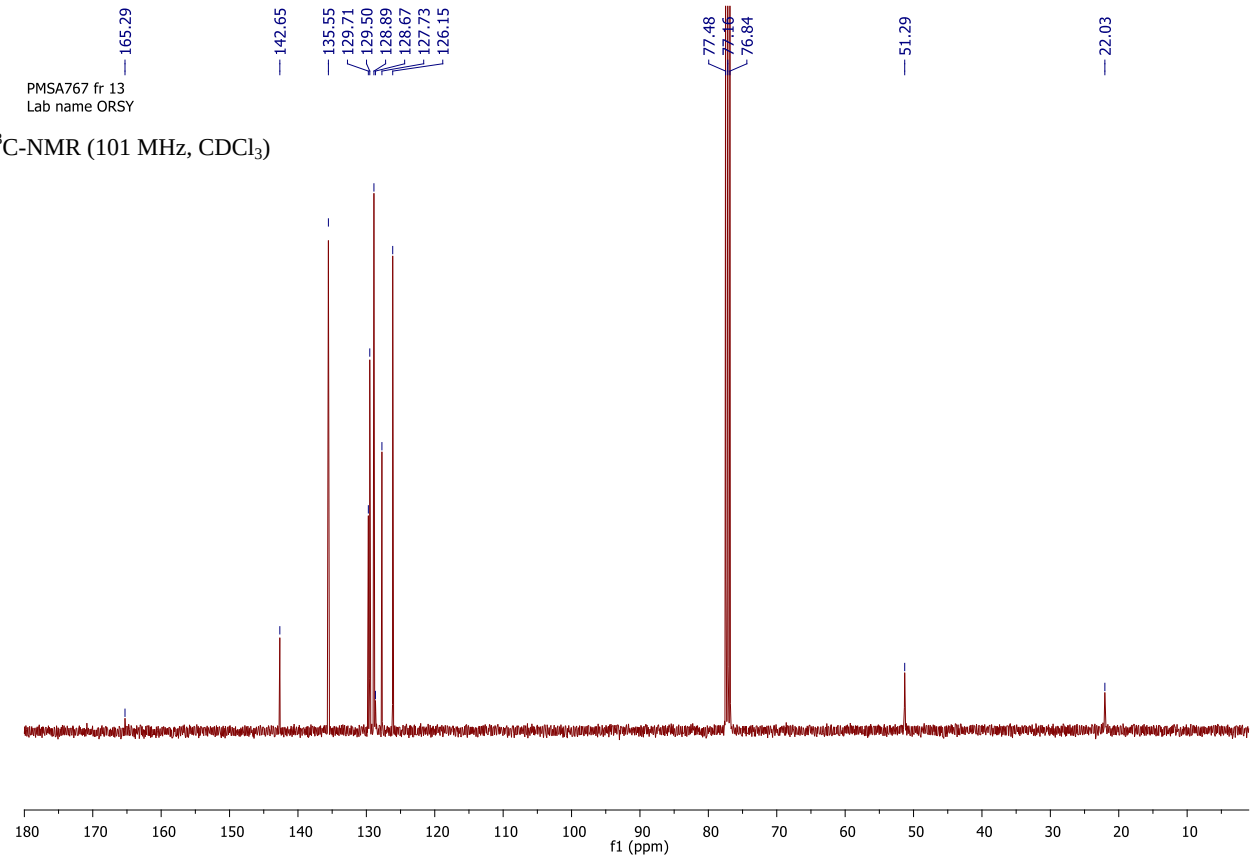
^{1}H-NMR (400 MHz, $CDCl_3$)

(5d) [PMSA 709]

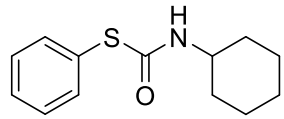


^{13}C-NMR (101 MHz, $CDCl_3$)

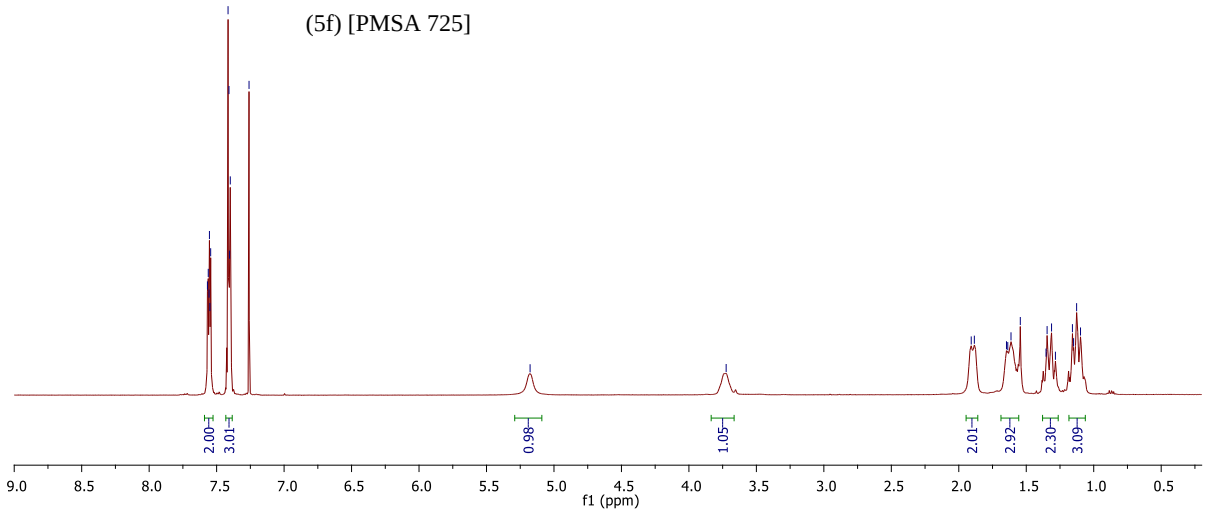

7.55
7.55
7.54
7.53
7.41
7.40
7.39
7.38
7.38
7.37
7.34
7.32
7.31
7.27
7.27
7.25
7.23
5.55
5.09
5.08
5.06
5.04
5.02
1.48
1.46
PMSA767 fr 13
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 28
1H-NMR (400 MHz, CDCl3)
O
S
N
H
(5e) [PMSA 767]
2.00
3.00
2.05
3.16
0.97
1.02
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

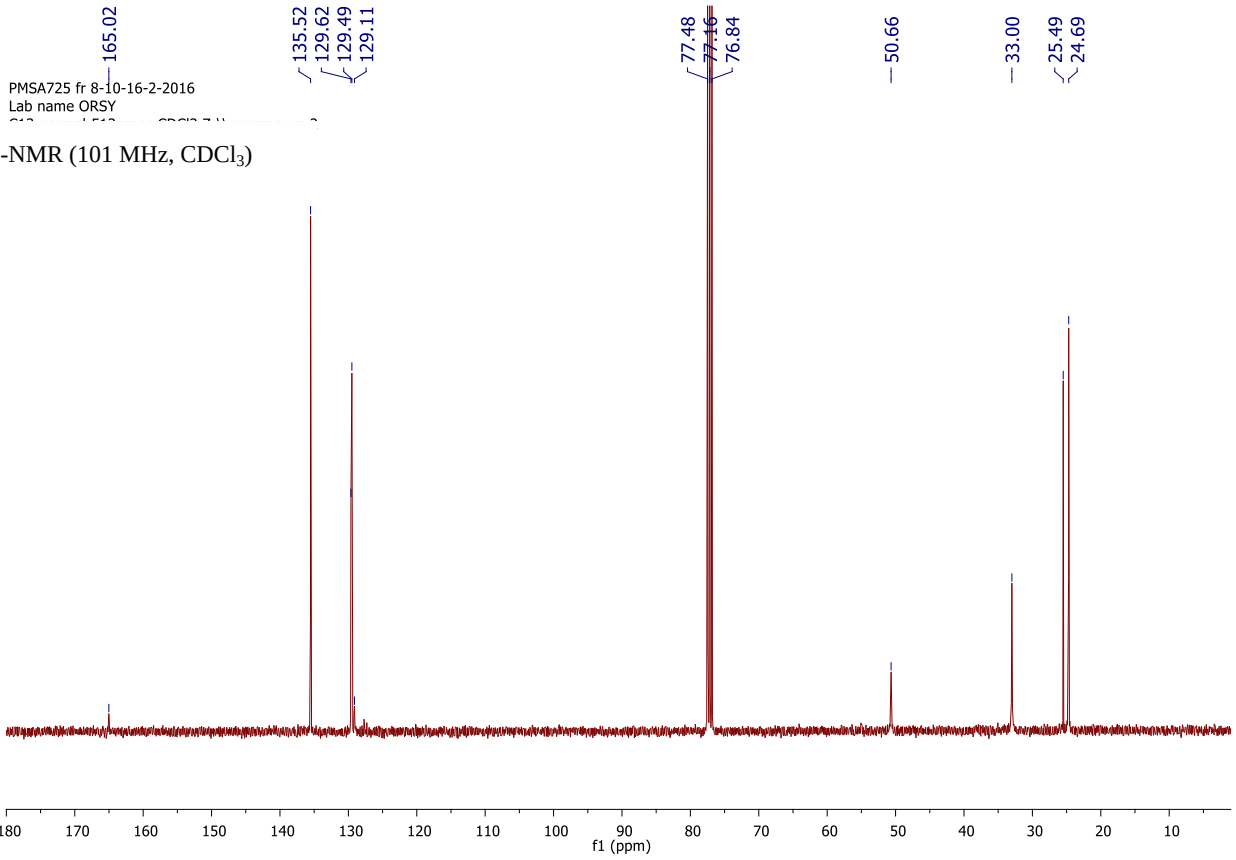

165.29
142.65
135.55
129.71
129.50
128.89
128.67
127.73
126.15
77.48
77.16
76.84
51.29
22.03
PMSA767 fr 13
Lab name ORSY
13C-NMR (101 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H-NMR (400 MHz, $CDCl_3$)



(5f) [PMSA 725]

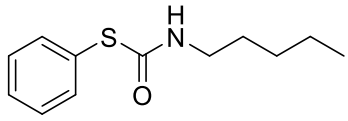




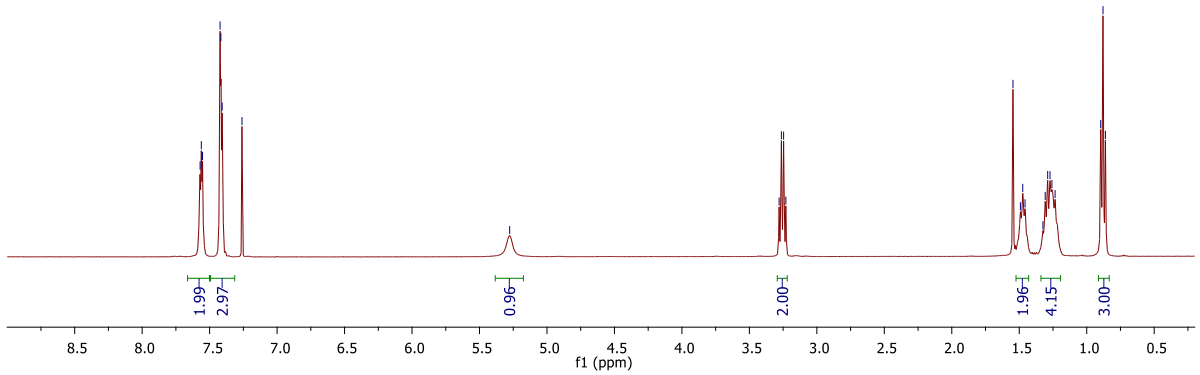
^{13}C-NMR (101 MHz, $CDCl_3$)

PMSA718 pur 2 fr 12-18
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 18

^{1}H-NMR (400 MHz, $CDCl_3$)

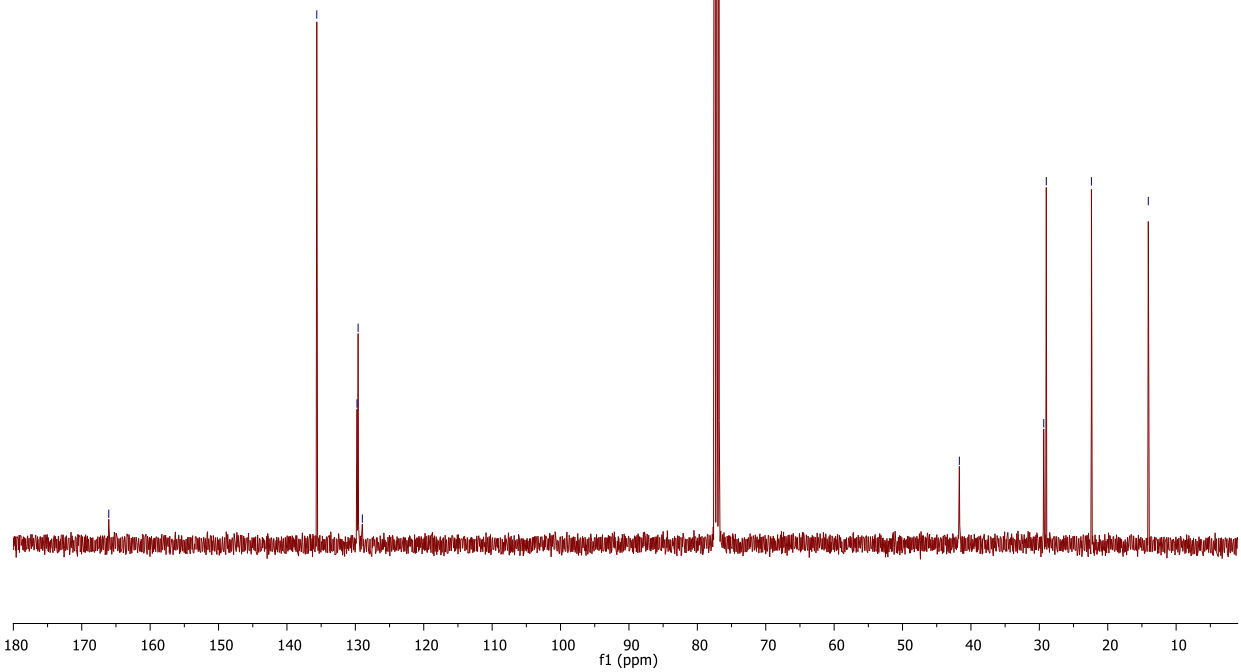


(5g) [PMSA 718]



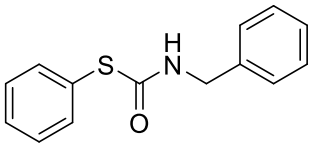
PMSA718 pur 2 fr 12-18

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

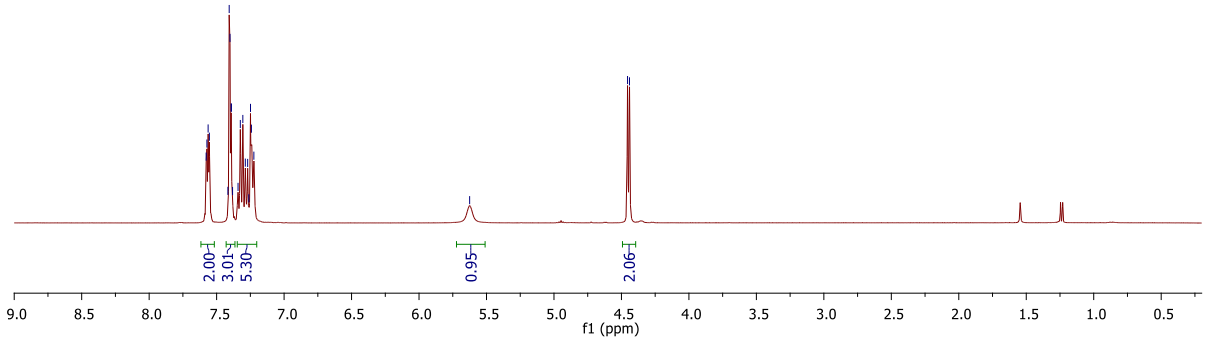


PMSA729fr12-16-06-15
Lab name ORSY
PROTON CDCl3 {Z:\pmampuys} hseykens 55

^{1}H-NMR (400 MHz, $CDCl_3$)

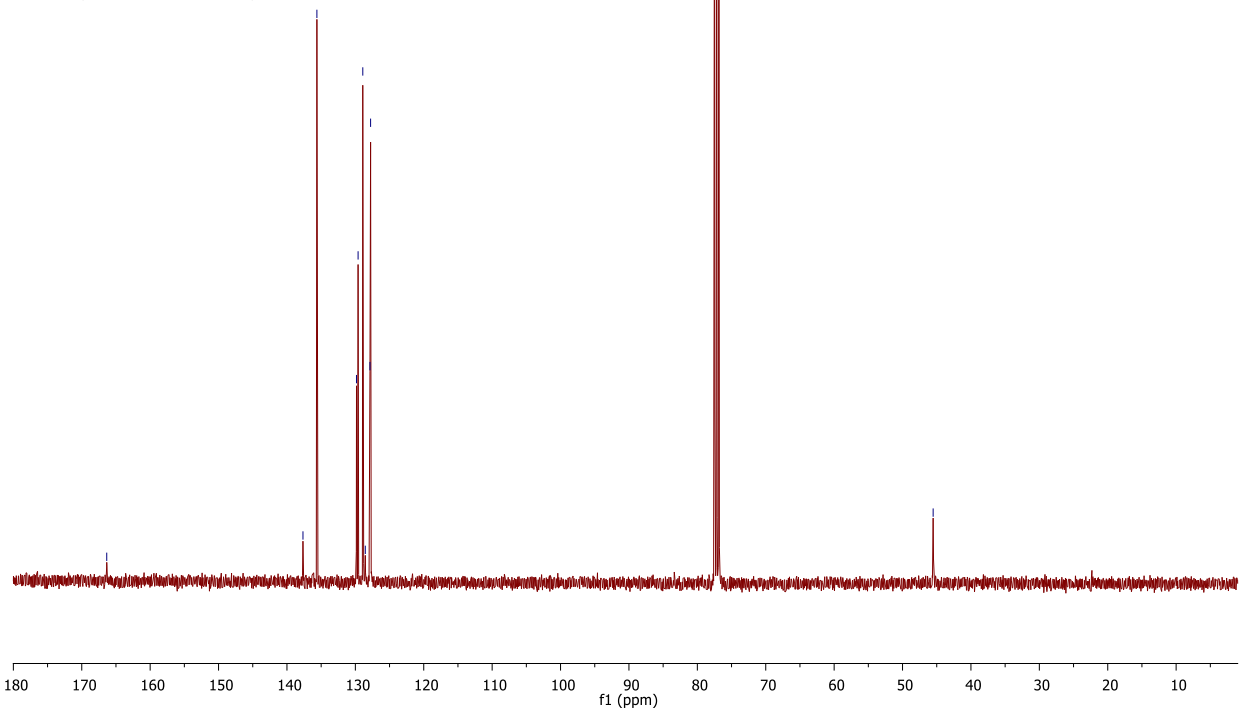


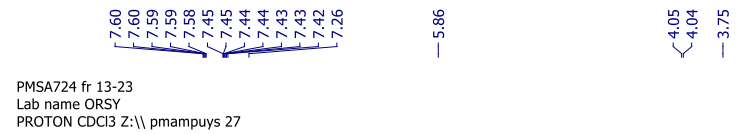
(5h) [PMSA 729]



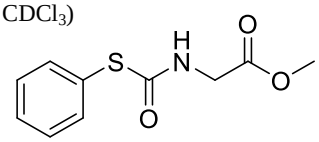
PMSA729 fr 12-16

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

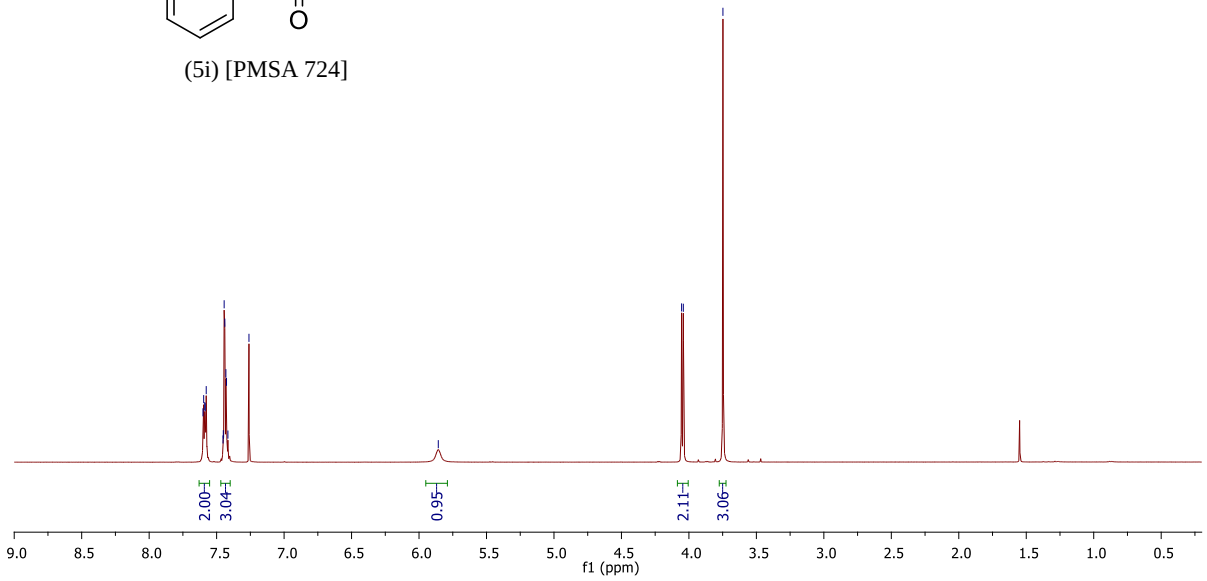


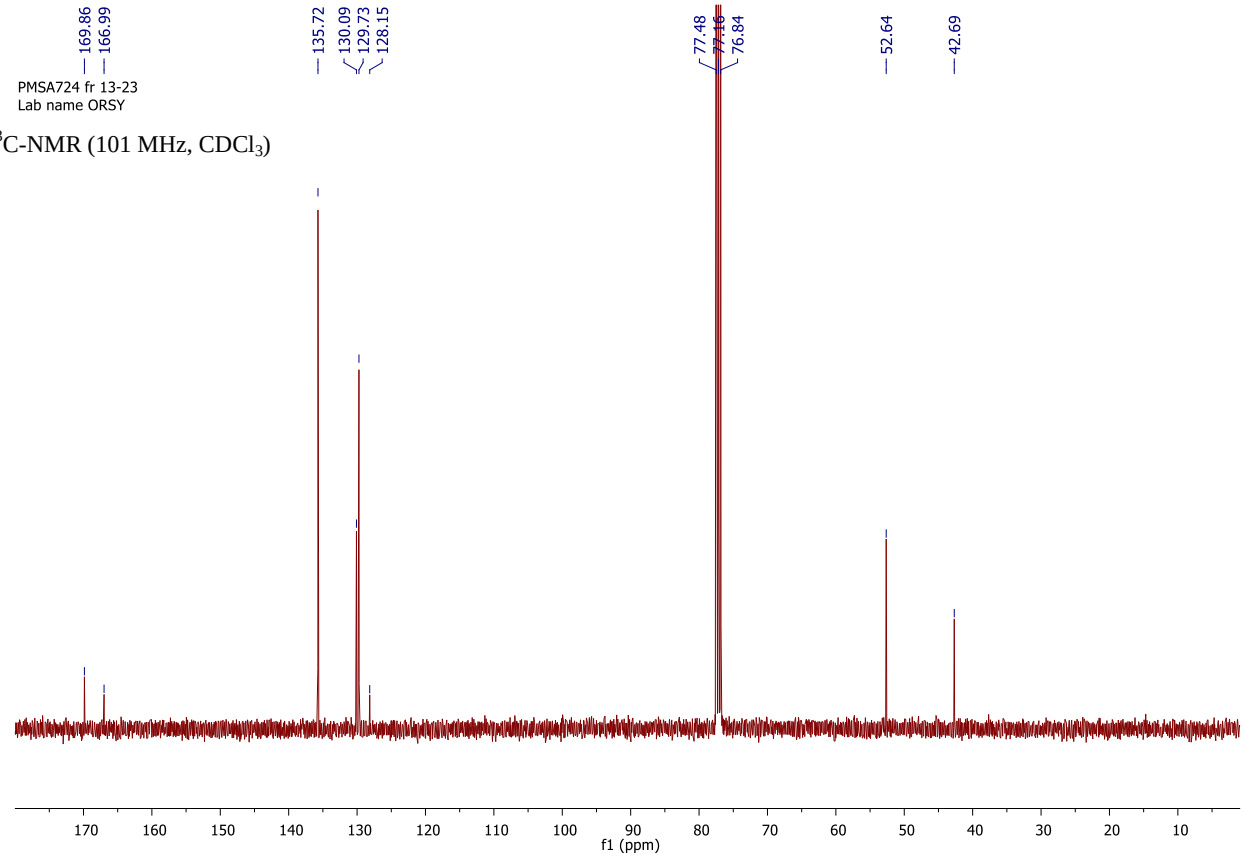


^{1}H-NMR (400 MHz, $CDCl_3$)



(5i) [PMSA 724]

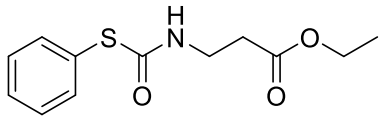




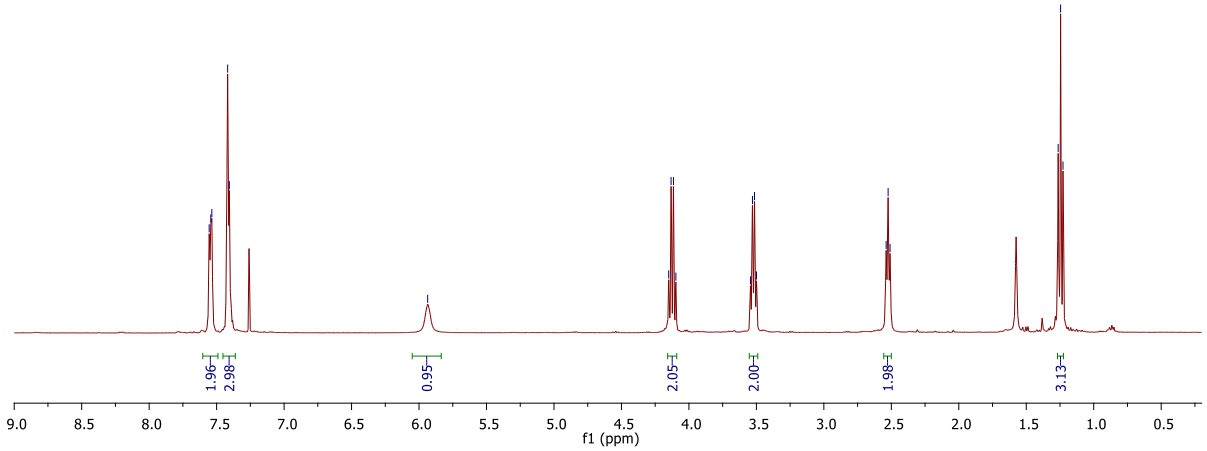
^{13}C-NMR (101 MHz, $CDCl_3$)

PMSA723 fr 10-15

^{1}H-NMR (400 MHz, $CDCl_3$)

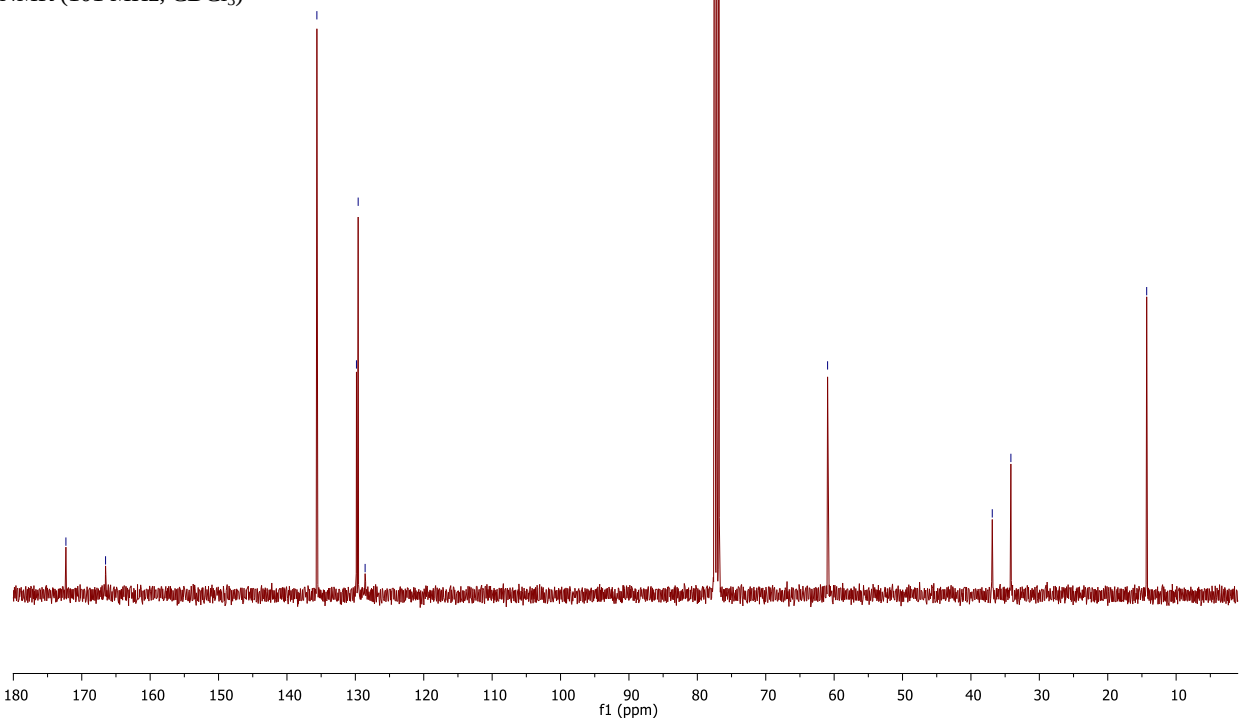


(5j) [PMSA 723]



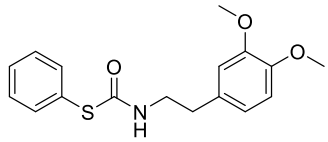
PMSA723-fr10-15

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

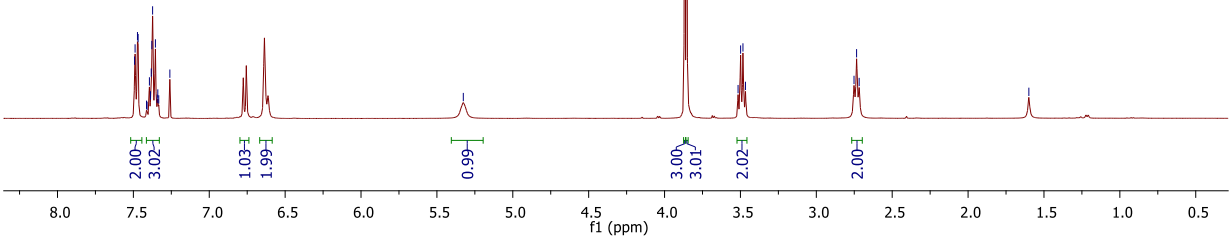


PMSA773 fr 32-36
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 43

^{1}H-NMR (400 MHz, $CDCl_3$)

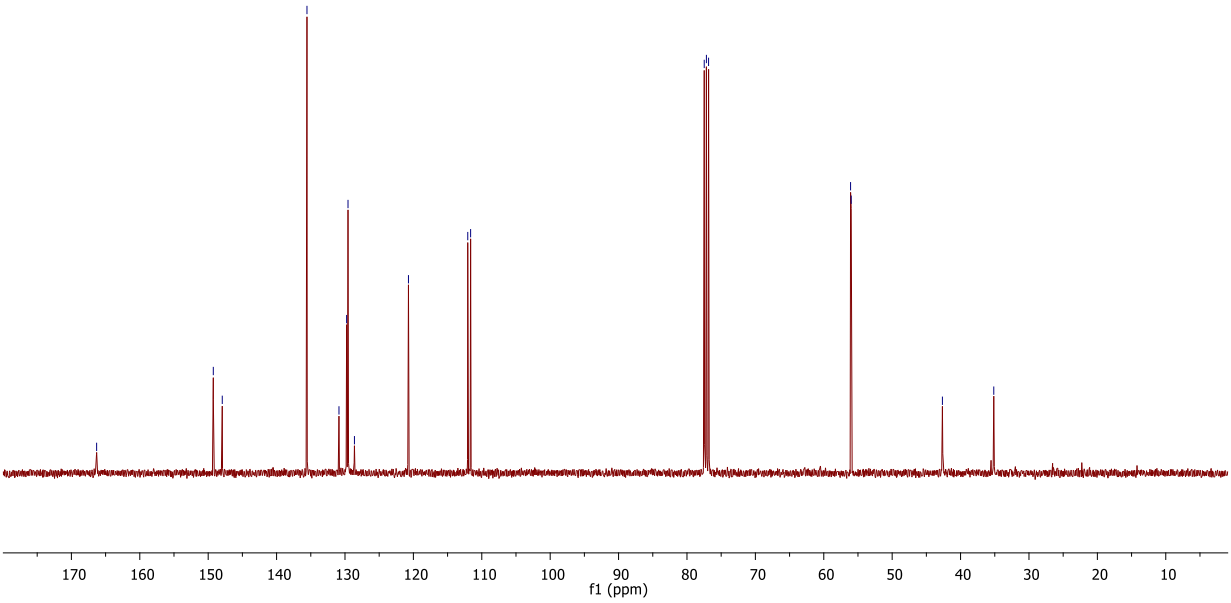


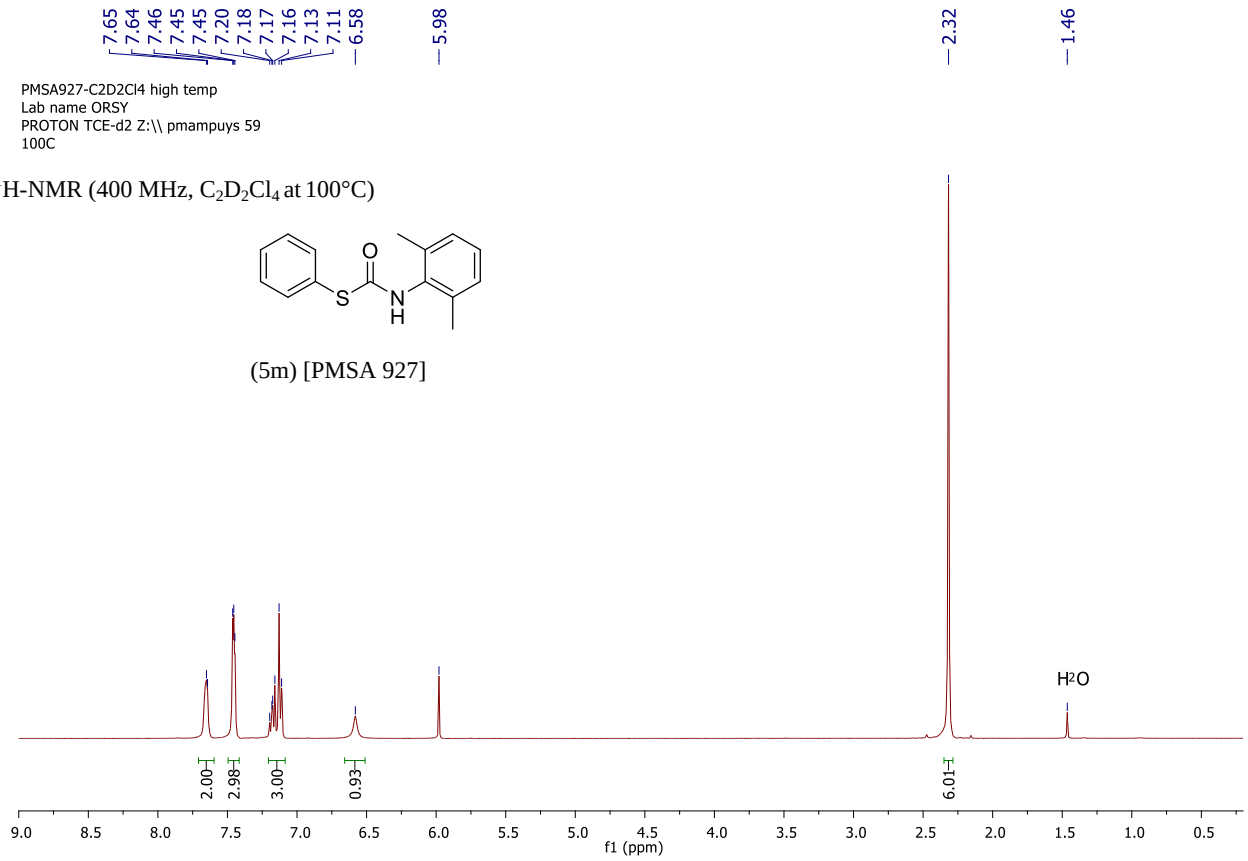
(5k) [PMSA 773]



PMSA773 fr 32-36

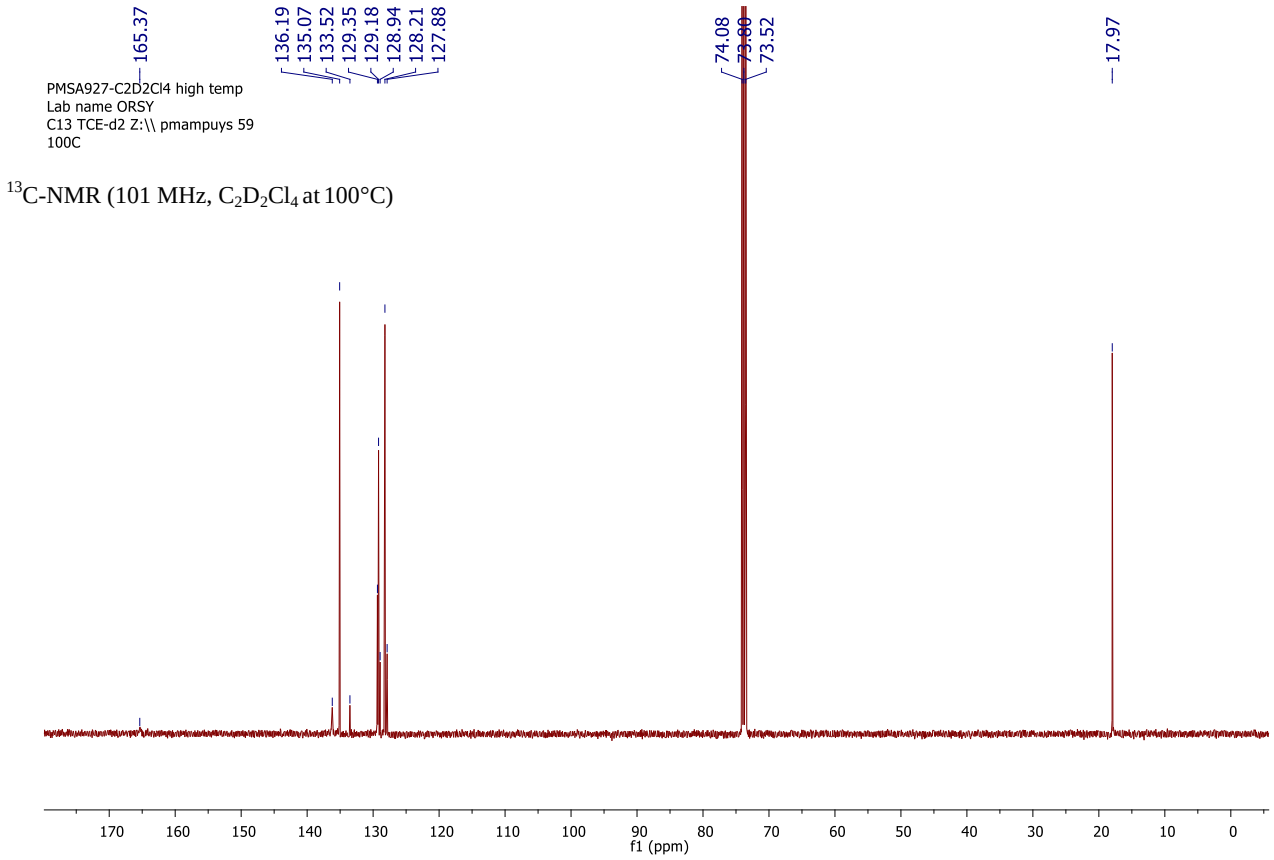
^{13}C-NMR (101 MHz, $CDCl_3$)





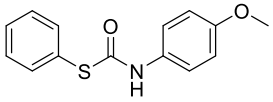
^{1}H-NMR (400 MHz, $C_2D_2Cl_4$ at 100°C)

(5m) [PMSA 927]

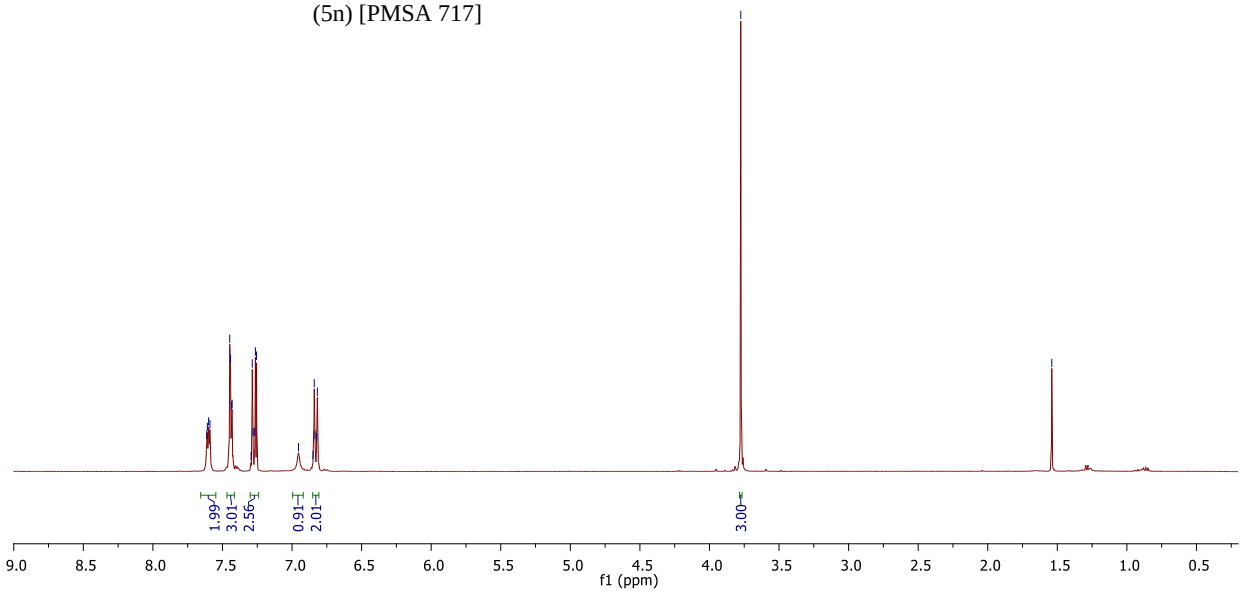


^{13}C-NMR (101 MHz, $C_2D_2Cl_4$ at 100°C)

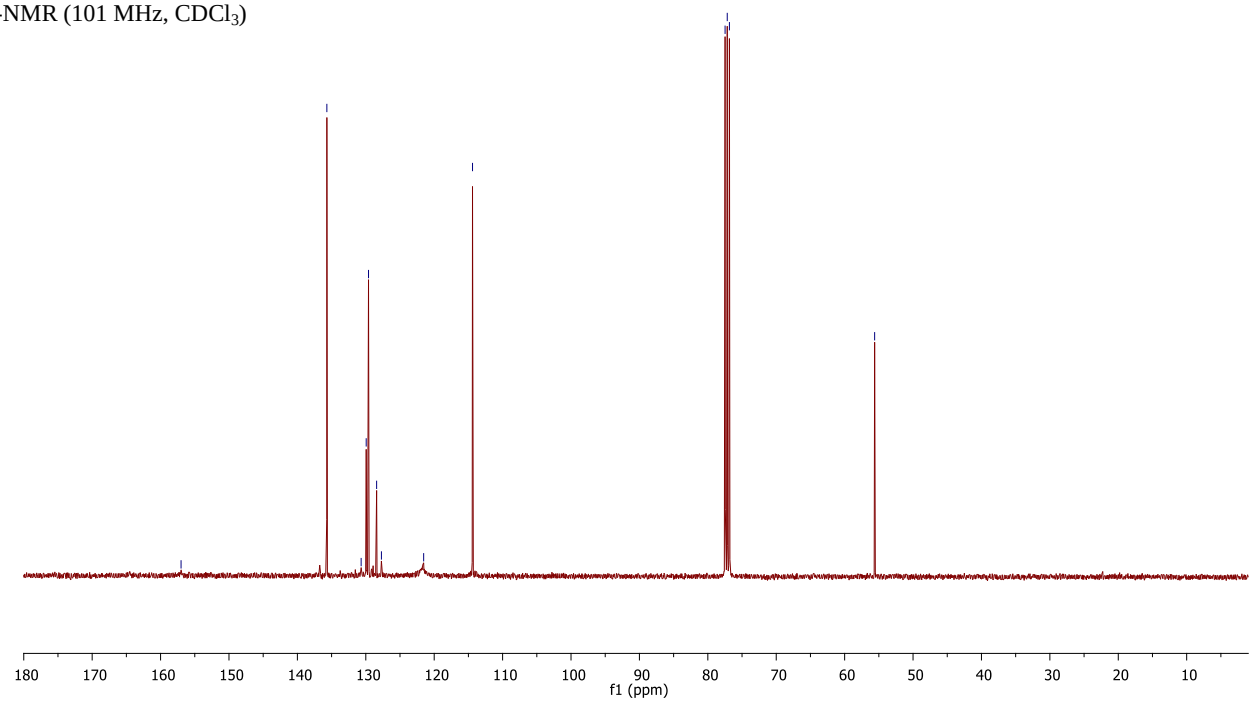
^{1}H-NMR (400 MHz, $CDCl_3$)

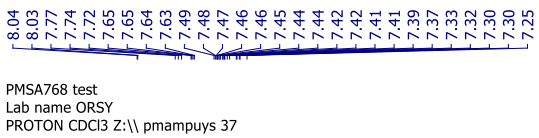


(5n) [PMSA 717]



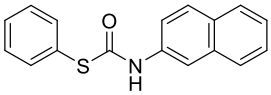
^{13}C-NMR (101 MHz, $CDCl_3$)



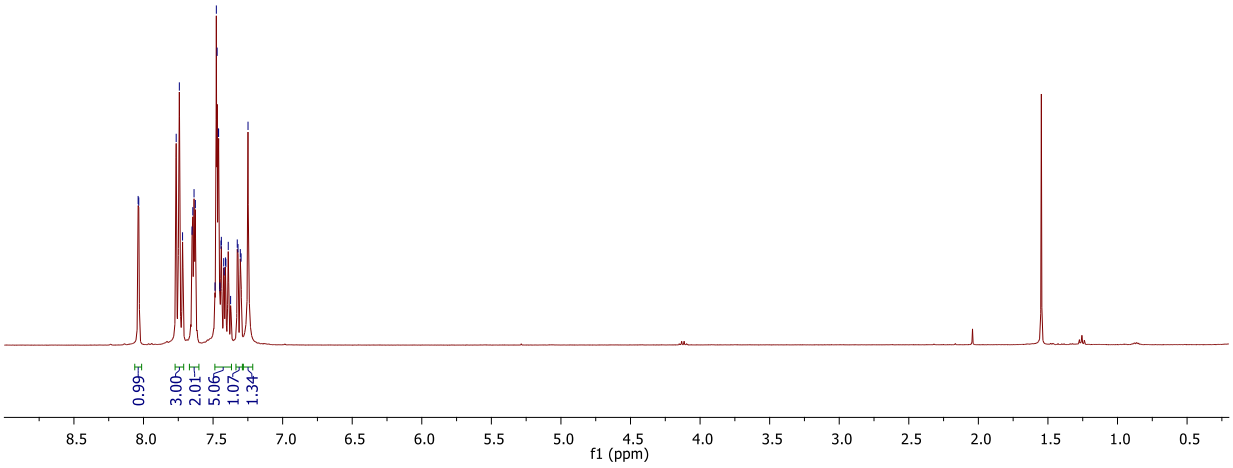


PMSA768 test
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 37

^{1}H-NMR (400 MHz, $CDCl_3$)

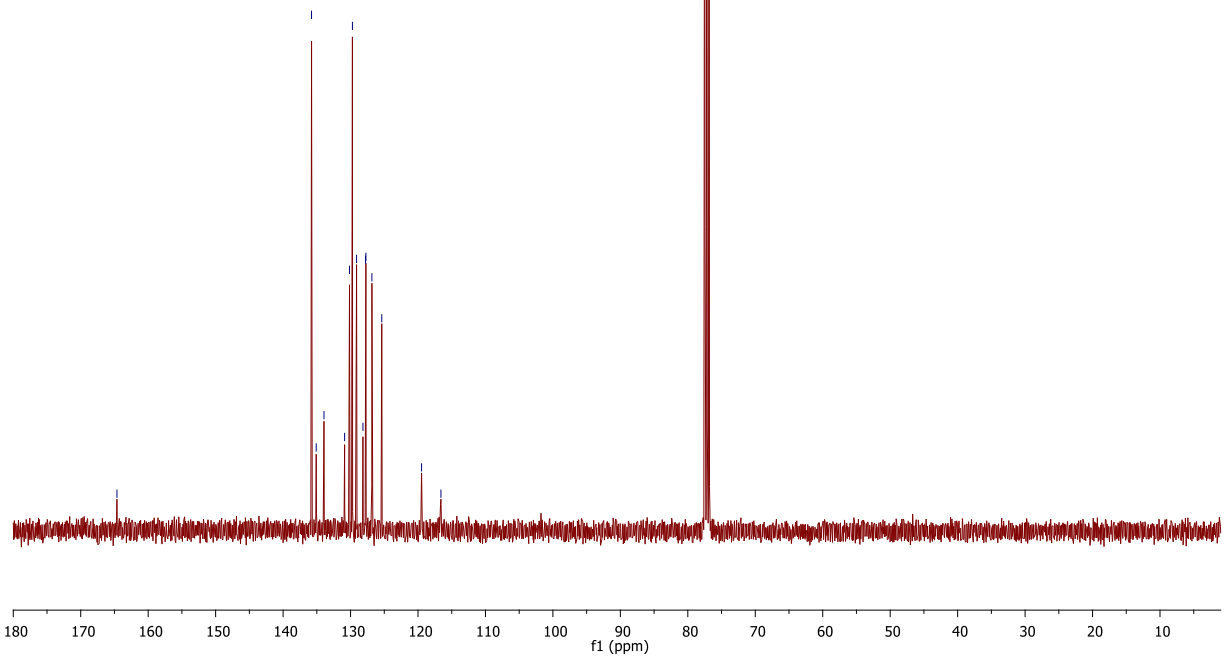


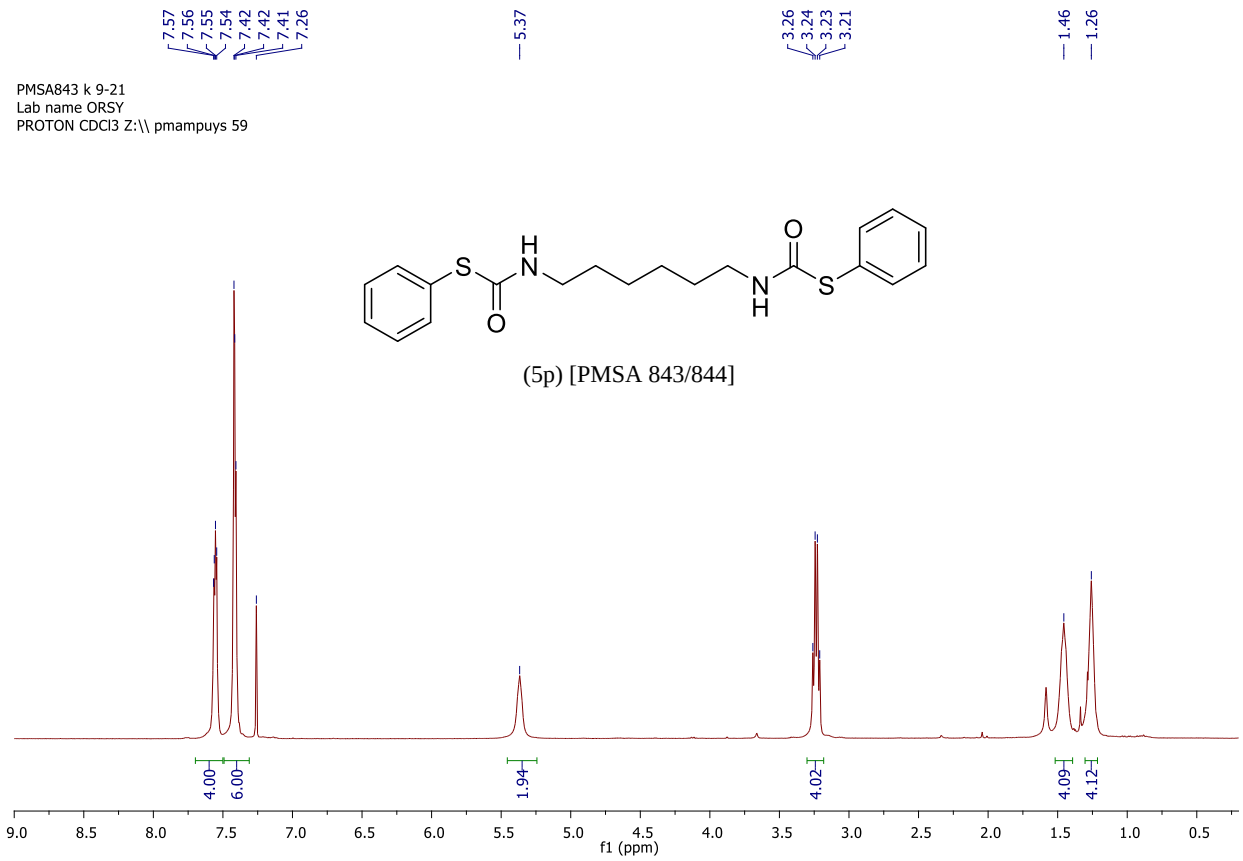
(5o) [PMSA 768]



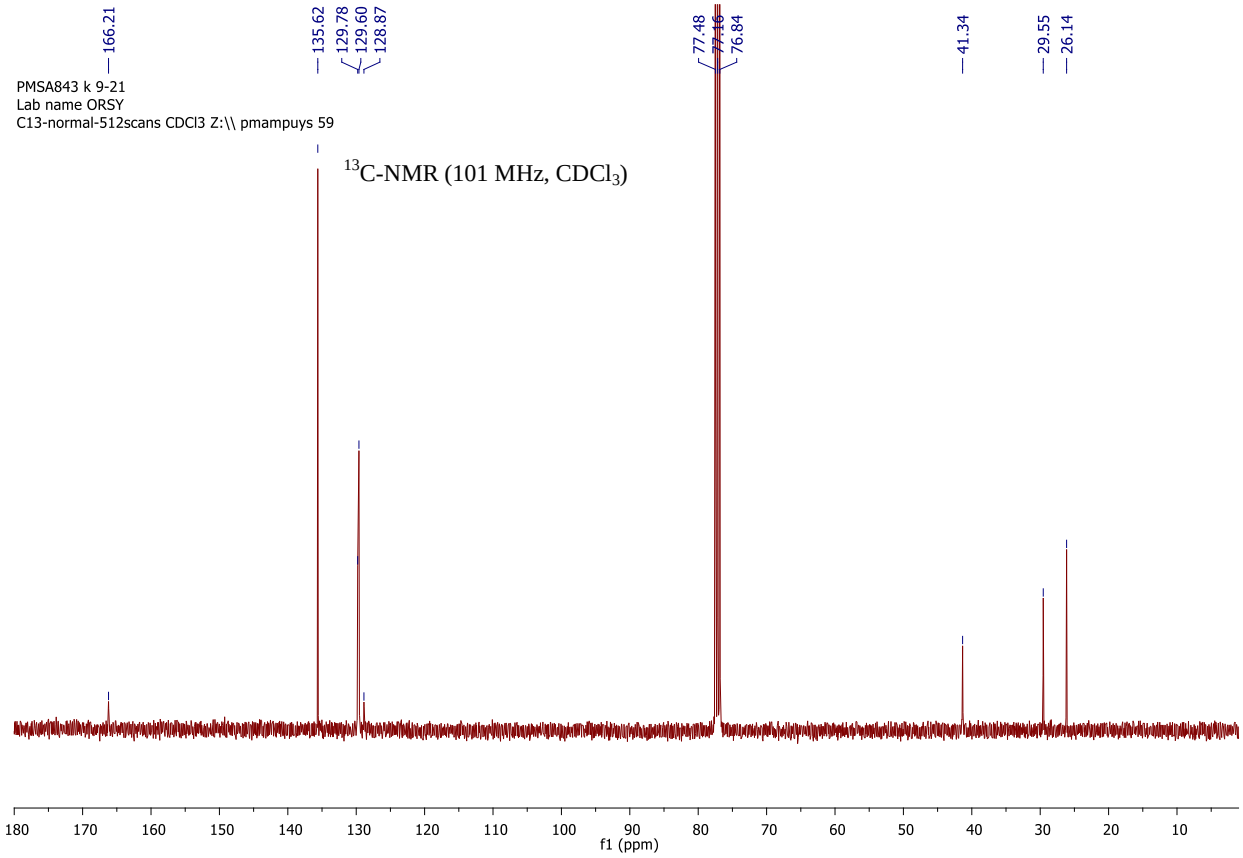
PMSA768 test
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 37

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



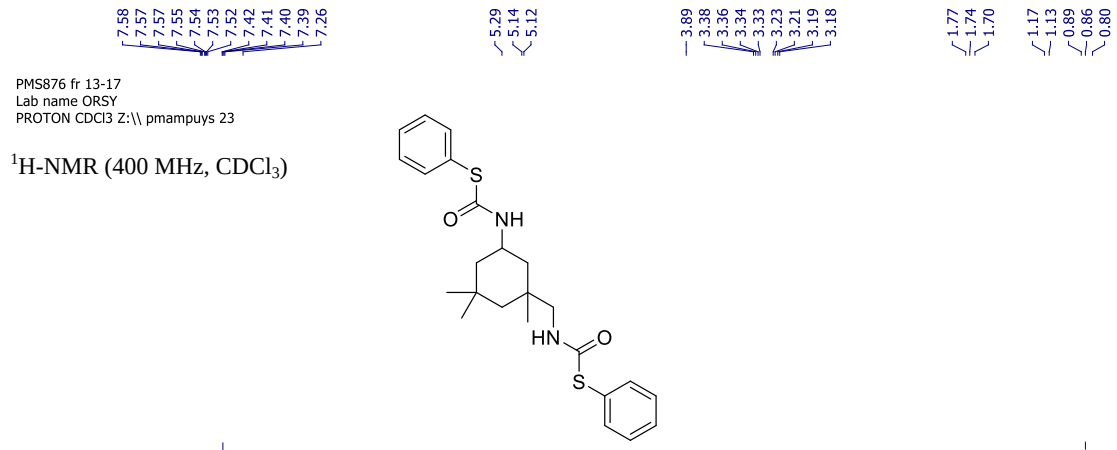


(5p) [PMSA 843/844]



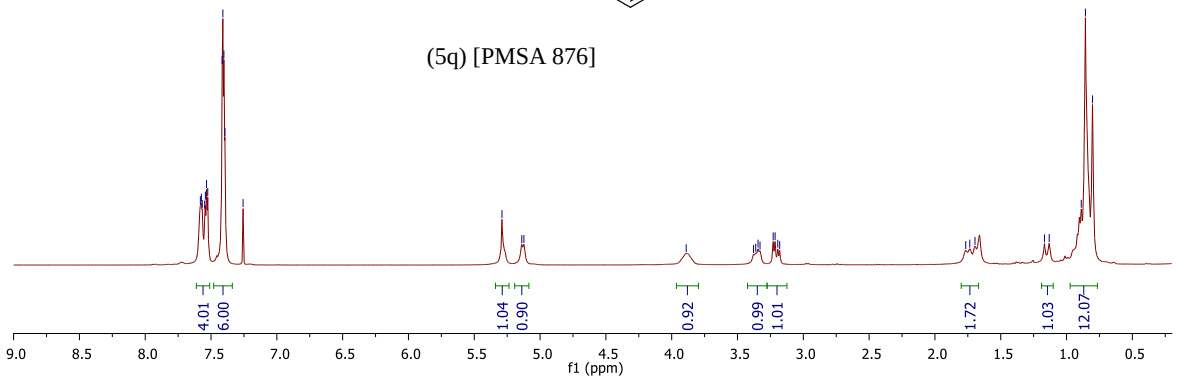
^{13}C-NMR (101 MHz, $CDCl_3$)

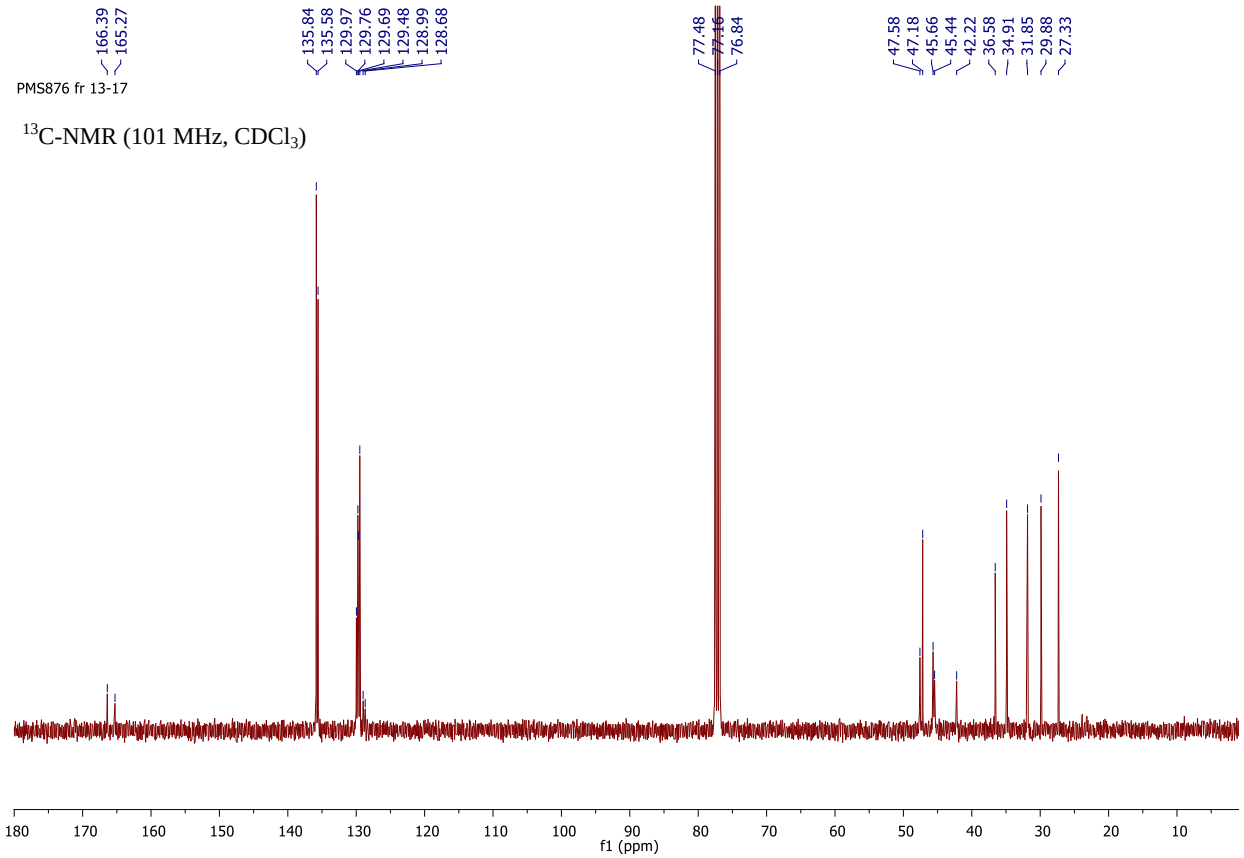
Diastereoisomer 1 (Minor)



^{1}H-NMR (400 MHz, $CDCl_3$)

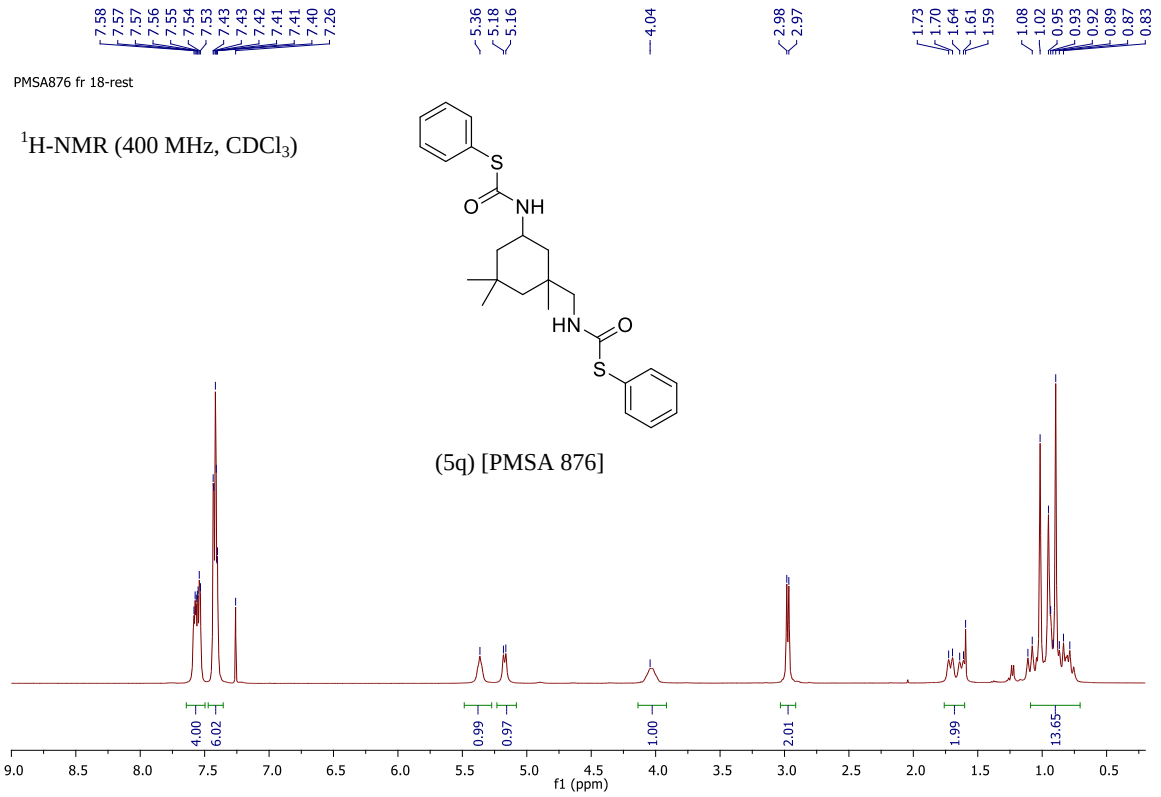
(5q) [PMSA 876]

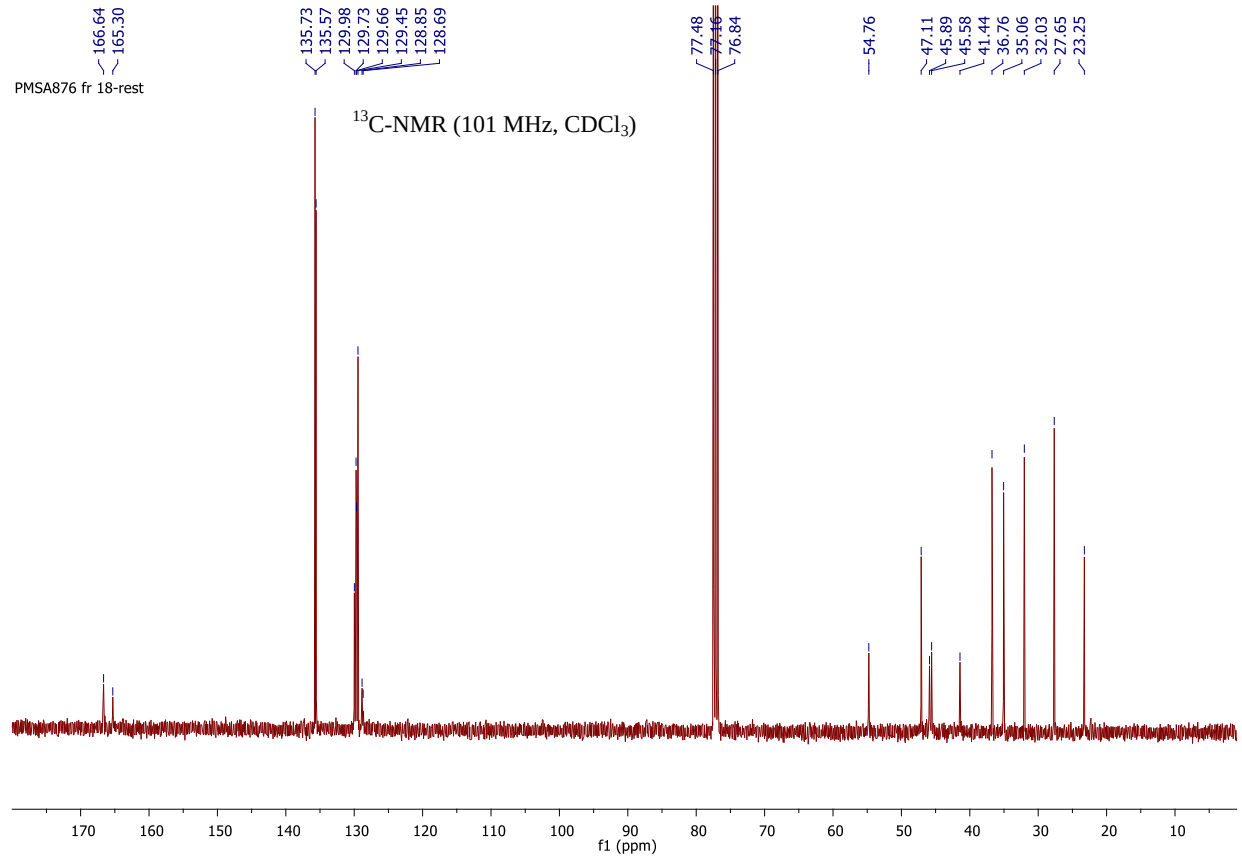


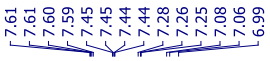


^{13}C-NMR (101 MHz, $CDCl_3$)

Diastereoisomer 2 (Major)

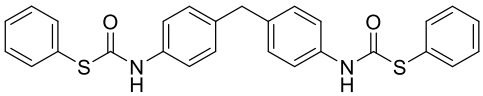




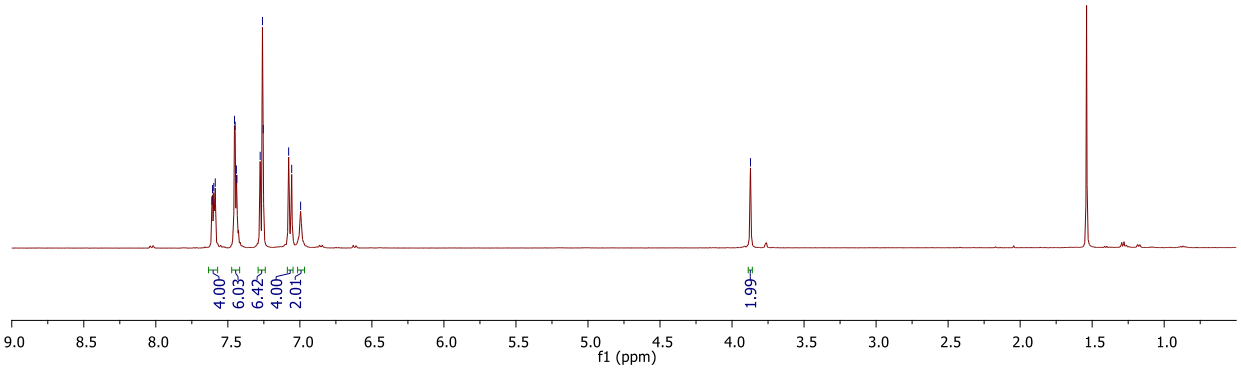


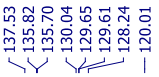
PMSA776 fr 20-23
Lab name ORSY
PROTON CDCl3 Z:\\ pmampuys 19

^{1}H-NMR (400 MHz, $CDCl_3$)



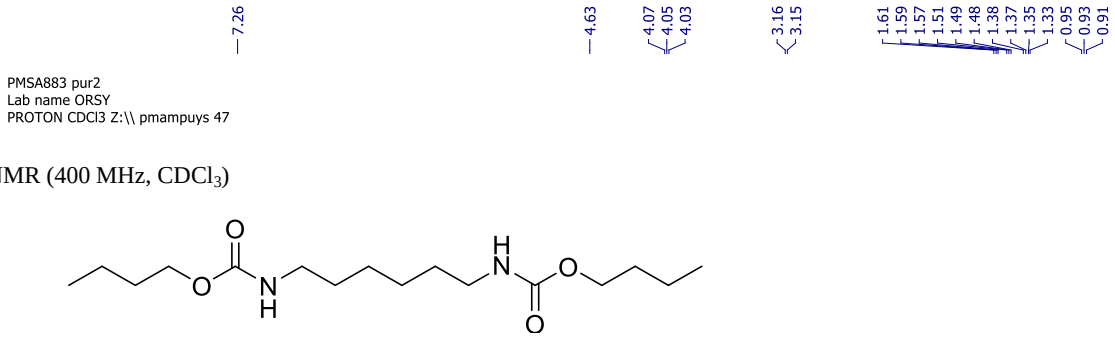
(5r) [PMSA 776/824]





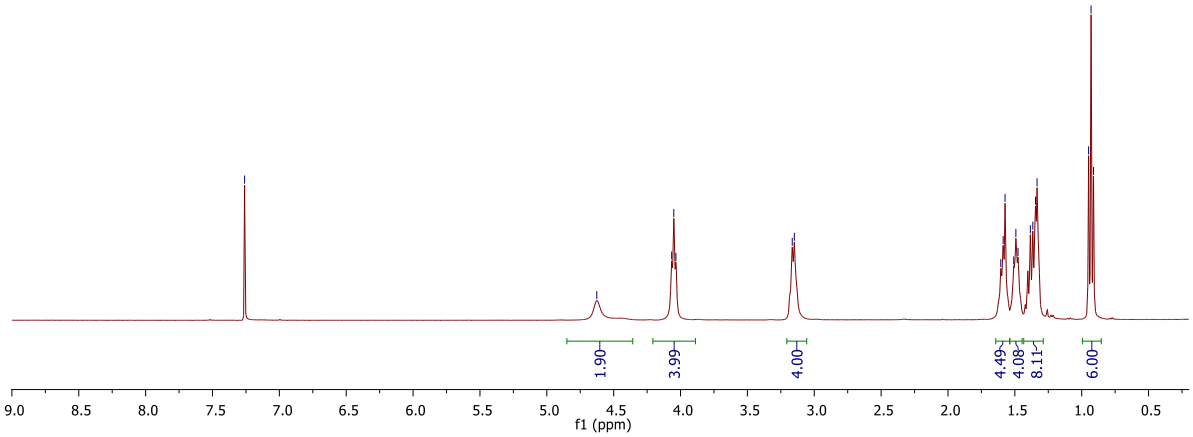
PMSA726 fr 20-23
Lab name ORSY
C13CPD CDCl3 Z:\\ pmampuys 40

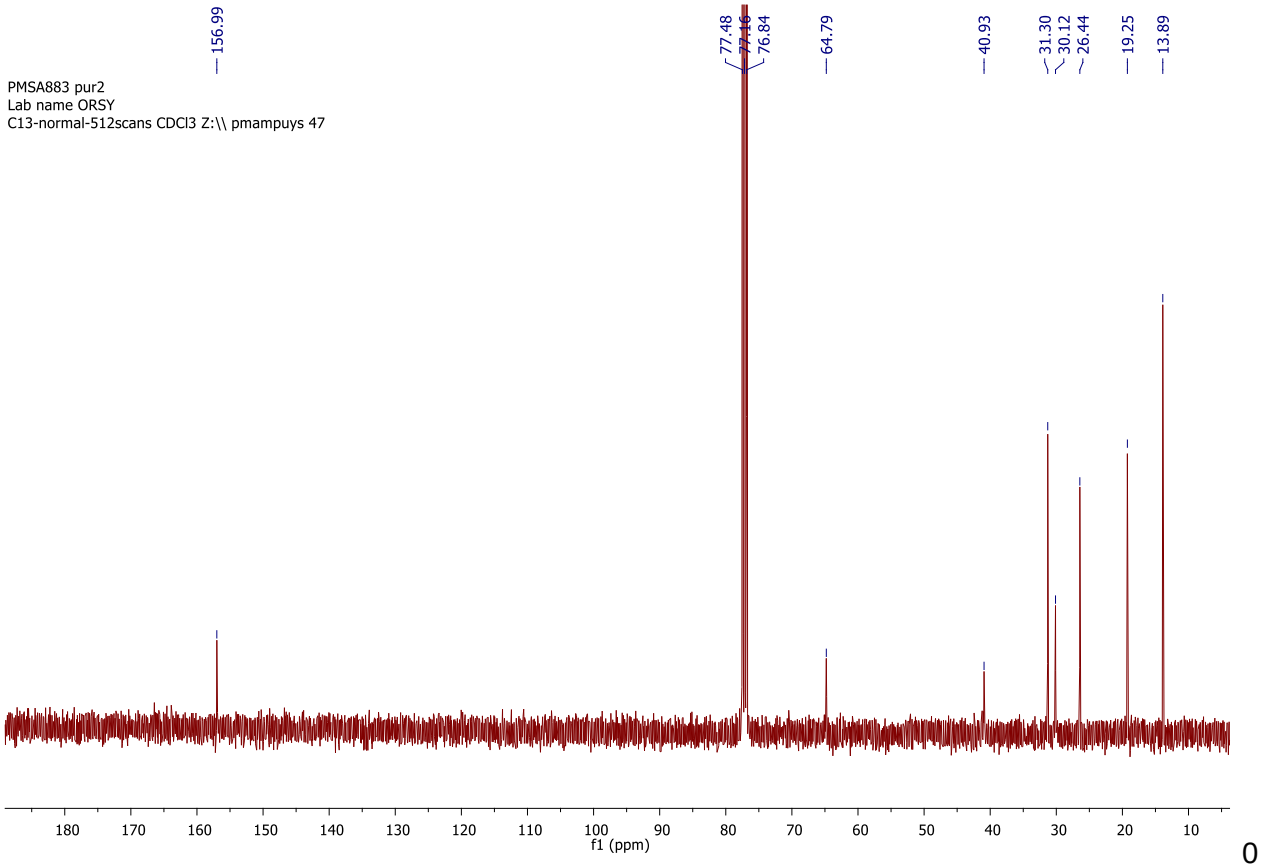
^{13}C-NMR (101 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)

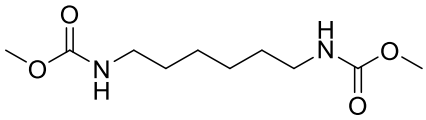
(8a) [PMSA 883]





0

^{1}H-NMR (400 MHz, $CDCl_3$)



(8b) [PMSA 916]