Supporting Information for:

Siloxy-Ether Functionalized Resins for Chemoselective Enrichment of Carboxylic Acids

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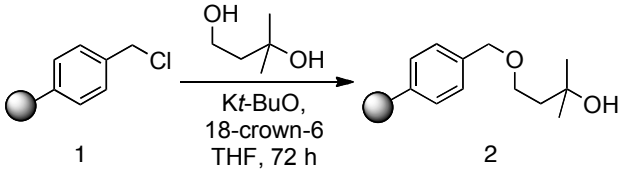
Supporting Information Contents

Methods:

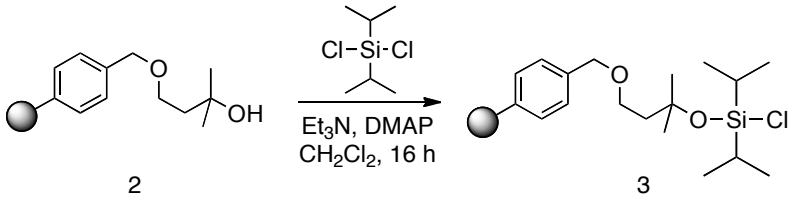
Appendix B. FT-IR (KBr pellet) of resins shown in **Supporting Information Table S2.**

Methods

Resin Synthesis



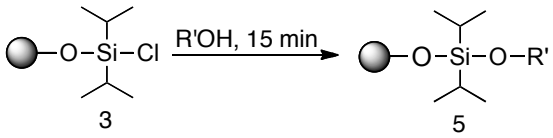
To a 50 mL oven-dried round bottom flask was added 25 mL of anhydrous THF and 2.0 g (2.1 mL, 19 mmol, 3.0 eq) of 3-methyl-1,3-butanediol. This solution was placed under Ar and cooled to 0°C in an ice bath. Next, a 1 M solution of potassium *t*-butoxide (2.2 g, 19 mmol, 3.0 eq) in THF (20 mL) was added followed by 5.2 g (19 mmol, 3.0 eq) of 18-crown-6. This mixture was stirred for 1 h at 0°C and then 3 h at room temperature. During the warm-up to room temperature, the solution turned from clear to light yellow. This yellow solution was then transferred via syringe to a 250 mL amber bottle with a rubber septum where 5.0 g of Merrifield resin (1.3 mmol/g) and 20 mL of THF had been placed and allowed to swell under Ar for 2 h. This resin suspension was capped and allowed to shake for 72 h at room temperature. The golden resin was then transferred to a peptide synthesis vessel with THF. The resin was subjected to the following wash protocol: THF (2 x 20 mL), DMF (3 x 10 mL), 1:1 DMF:H_2O (3 x 100 mL), DMF (3 x 100 mL), THF (3 x 100 mL), and CH_2Cl_2 (3 X 100 mL). The vessel was placed in a desiccator under vacuum for 12 h to dry the resin. It was assumed that the initial Merrifield resin was completely transformed into **2**, and the original loading capacity of 1.3 mmol/g was assumed for the next reaction.



2 3

A 20 mL scintillation vial was charged with 200 mg (0.26 mmol) of **2** (loading capacity 1.3 mmol/g) and equipped with a rubber septum. After flushing the resin with Ar for 10 minutes, the vial was charged with 3 mL of anhydrous CH_2Cl_2 and the resin was allowed to swell for 5 min. To the swollen resin was added 263 µL (1.8 mmol, 7.0 eq) of freshly distilled Et_3N, 160 µL (1.3 mmol, 5.0 eq) of dichlorodiisopropyl silane and 318 mg (2.9 mmol, 10.0 eq) of DMAP. The vial was then capped and the reaction was agitated for 16 h at room temperature. The resin was filtered over a 10 mL fritted polypropylene column and washed with 2 x 4 mL anhydrous CH_2Cl_2 and used immediately to avoid undesired hydrolysis.

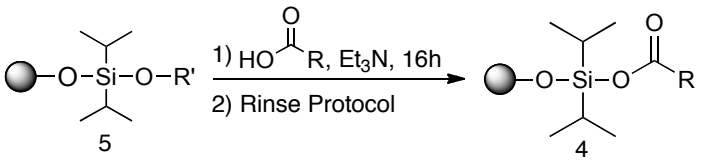
Alcoholysis Procedure



3 5

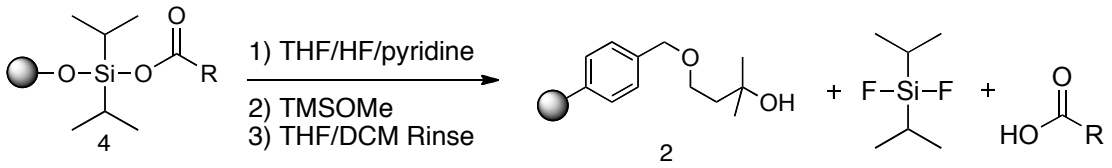
Before rinsing **3** with anhydrous CH_2Cl_2 to remove excess Et_3N and DMAP, 500 µL or 500 mg of an alcohol was added and the vial re-capped. This promoted the hydrolysis of the Si-Cl bond to the corresponding siloxyl ether. After agitation for 15 min at room temperature, the resin was rinsed with 2 x 5 mL anhydrous CH_2Cl_2. The resin was then re-swollen in 2.5 mL of CH_2Cl_2 and aliquoted into 5 different vials (4 reaction and 1 discard vial).

Coupling Procedure



To **5** (40 mg 0.015 mmol) was added 50 µL of freshly distilled Et_3N (0.35 mmol, 20 eq) followed by 100 µL of a mixture of model carboxylic acids in a DMSO/THF solution. The solution contained four carboxylic acids, 0.1 equivalent of each, and 400 µL of anhydrous THF and 100 µL of DMSO. The coupling reactions were gently agitated at room temperature overnight. The resin was transferred to a 2 mL fritted polypropylene column and subjected to the standard wash protocol.

Cleavage of Model Carboxylic Acids from Resin



Coupled resin was transferred to polypropylene vials (2 mL). To the resin was added 100 µL of a freshly prepared solution of 500/50/50 µL (v/v) of THF/HF•pyridine(70/30 wt%)/pyridine (2 mmol of HF, 45 eq) and the reaction was gently agitated at room temperature for 3 h. To this was added 500 µL of TMSOMe (3.6 mmol, 82 eq) to quench excess HF and the resin was agitated for an additional 30 minutes at room temperature. The resin was washed with THF and CH_2Cl_2 and filtered over a 1 mL fritted polypropylene column into a 5 mL vial. This solution was then concentrated and the sample was analyzed by dissolving the sample in 2 mL of 2:1:1 H_2O/THF/MeOH and injecting 1 µL onto a LC-MS-TOF and comparing peak area to the corresponding standard curve data.

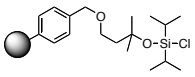
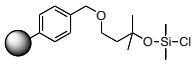
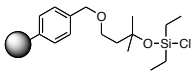
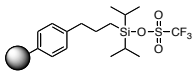
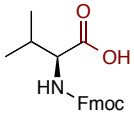
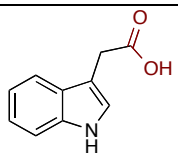
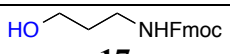
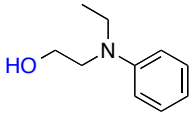
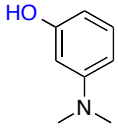
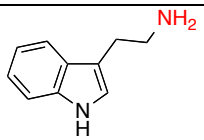
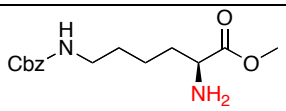
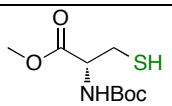
Standard Resin Wash Protocol.

Coupled resin (40 mg) is transferred to a fritted vessel and rinsed as follows: CH_2Cl_2 (suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), THF (suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), DMSO/ CH_2Cl_2 (1:1, suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), THF (suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), DMSO/ CH_2Cl_2 (1:1, suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), CH_2Cl_2 (suspend resin in 2 mL for 10 min, rinse 2 x 2 mL), toluene (3 x 2 mL), DMF (3 x 2 mL), CH_2Cl_2 (3 x 2 mL), hexanes (3 x 2 mL), CH_2Cl_2/MeOH (3 x 2 mL), CH_2Cl_2 (3 x 2 mL). The resin is then allowed to dry in a vacuum desiccator for at least 1 h before HF cleavage.

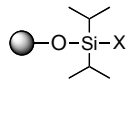
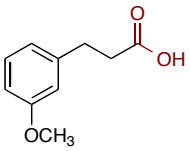
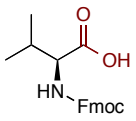
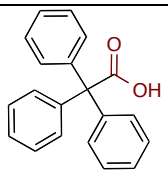
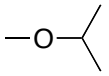
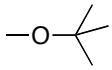
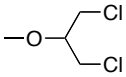
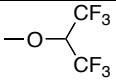
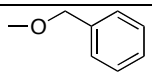
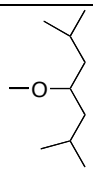
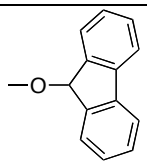
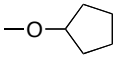
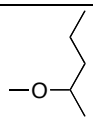
Determination of resin loading capacity.

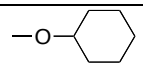
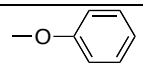
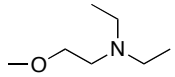
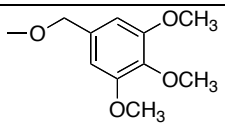
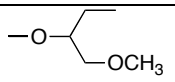
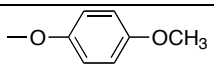
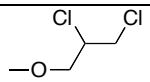
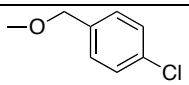
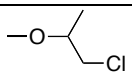
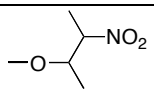
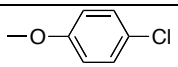
For each of the resins, 200 mg (1.3 mmol/g, 0.26 mmol) of **3** was placed in a dry 20 mL scintillation vial. The resin was swollen with 3 mL of anhydrous CH_2Cl_2 under Ar. Next, 300 µL (8.0 equiv, 2.1 mmol) of freshly distilled Et_3N was added, followed by 250 µL (6.0 equiv, 1.7 mmol) of dichlorodiisopropyl silane. 318 mg of DMAP (10.0 equiv, 2.6 mmol) was added and the vial was capped and allowed to agitate at room temperature for 16 h. For resins **6-10** and **S9-S26**, after overnight reaction with the silane, 500 mg or 500 µL of the corresponding alcohol was added, the vial was re-capped, and allowed to agitate for 15 additional min at room temperature. The resin was transferred to a 10 mL biospin vial and rinsed under Ar with anhydrous CH_2Cl_2 (2 x 2 mL). Next, 2.5 mL of anhydrous CH_2Cl_2 was added to the resin and allowed to swell for 1 min. The resin was aliquoted into five 2 mL vials (40 mg of resin into each). Four aliquots acted as replicate reactions and the fifth was discarded. A control resin was synthesized utilizing chlorodiispropylsilane (**S27**) (same equiv as previously mentioned), which had no appropriate

leaving group. To each of the vials was added 50 μL (0.7 mmol) of freshly distilled Et_3N and 3.0 equiv (as compared to the assumed loading capacity of the resin; 0.16 mmol for each resin aliquot) of a model acid dissolved in 500 μL of anhydrous THF. The reactions were agitated overnight at room temperature. Resin was transferred to a 2 mL biospin vessel and subjected to the standard wash protocol. The resins were dried for 1 h at room temperature in a vacuum desiccator at 30 mmHg. Coupled resin was then transferred to polypropylene vials (2 mL). To the resin was added 500/50/50 μL (v/v) of a freshly prepared solution of THF/HF•pyridine(70/30 wt%)/pyridine (1.6 mmol of HF) and the reaction was gently agitated at room temperature for 3 h. To this was added 500 μL of TMSOMe (3.6 mmol) to quench excess HF and the resin was agitated for an additional 30 min at room temperature. The resin was washed with THF (3 x 1 mL) followed by CH_2Cl_2 (3 x 1 mL) and filtered over a 1 mL fritted polypropylene column into a 5 mL vial. The rinse was concentrated under reduced pressure with no additional heating and the sample was redissolved in 5 mL of 2:1:1 H_2O/THF/MeOH. Analysis was performed by injection of 1 μL of this solution onto a LC-MS-TOF and comparing the observed peak area to that of standard curve data. The average of the four replicates was used as the loading capacity for all subsequent coupling experiments. The loading capacity for all 25 synthesized resins is shown in **Supporting Table S2**.

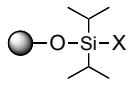
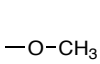
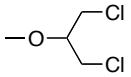
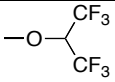
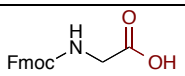
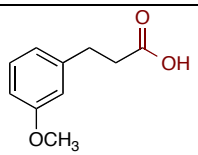
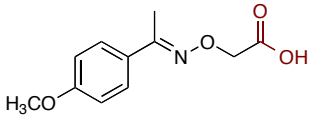
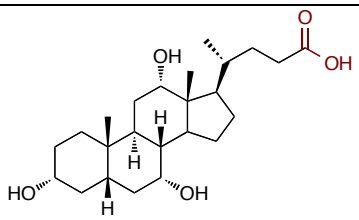
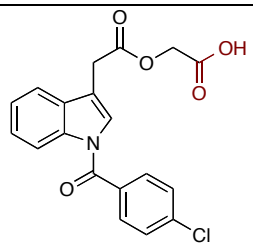
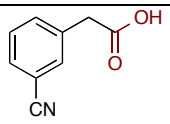
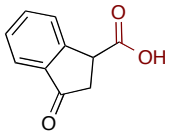
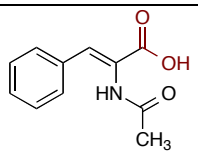
	 **3**	 **S1**	 **S2**	 **S3**
 **S4**	85%	10%	31%	38%
 **S5**	98%	22%	25%	96%
 **17**	18%	52%	58%	63%
 **S6**	6%	90%	74%	70%
 **18**	10%	52%	41%	53%
 **S7**	0%	2%	4%	3%
 **19**	0%	0%	0%	45%
 **20**	3%	11%	0%	46%

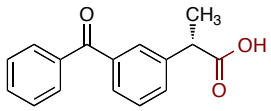
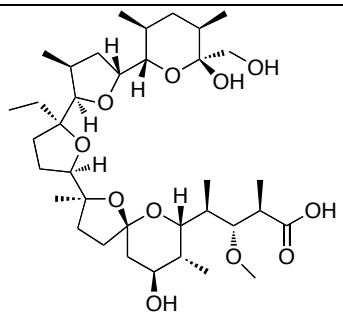
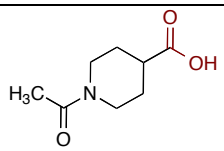
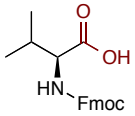
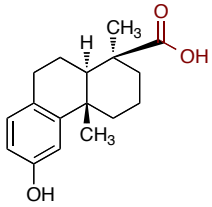
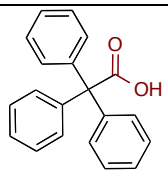
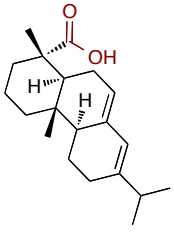
Supporting Information Table S1. Comparison of the capture abilities of several dialkyl siloxyl chloride resins and a diisopropylsilyl triflate resin. Each value is an average of four replicates.

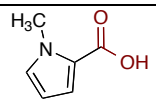
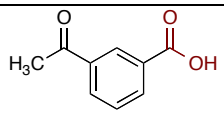
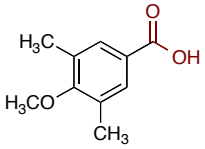
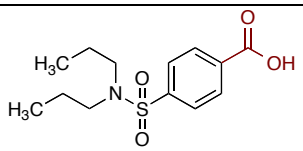
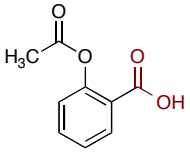
 X =	 11	 S4	 S8	Average
 **3**	0.72	0.40	0.22	0.45
 **6**	0.10	0.12	0.04	0.09
 **7**	0.31	0.16	0.04	0.17
 **8**	0.43	0.38	0.18	0.33
 **9**	0.55	0.32	0.28	0.38
 **10**	0.45	0.28	0.12	0.28
 **S9**	0.10	0.11	0.12	0.11
 **S10**	0.01	0.01	0.01	0.01
 **S11**	0.70	0.38	0.08	0.39
 **S12**	0.35	0.20	0.14	0.23
 **S13**	0.30	0.15	0.12	0.19
 **S14**	0.50	0.28	0.1	0.29

 **S15**	0.22	0.10	0.10	0.11
 **S16**	0.30	0.14	0.11	0.18
 **S17**	0.011	0.020	0.013	0.015
 **S18**	0.16	0.010	0.10	0.10
 **S19**	0.55	0.32	0.1	0.32
 **S20**	0.31	0.21	0.10	0.20
 **S21**	0.19	0.22	0.10	0.16
 **S22**	0.030	0.030	0.030	0.030
 **S23**	0.31	0.25	0.26	0.27
 **S24**	0.42	0.30	0.21	0.31
 **S25**	0.13	0.10	0.11	0.11
 **S26**	0	0	0	0
 **S27**	0	0	0	0

Supporting Information Table S2. Synthesized diisopropyl disiloxyl resins and their corresponding loading capacities. Loading capacities of synthesized resins in mmol/g. Each value is an average of four replicates.

			X =		
	 **6**	 **7**	 **8**	 **9**	 **10**
 **S28**	5%	66%	50%	52%	72%
 **11**	25%	95%	75%	95%	95%
 **S29**	87%	99%	70%	99%	99%
 **12**	73%	94%	53%	81%	47%
 **S30**	0%	3%	2%	15%	5%
 **S31**	82%	91%	71%	88%	2%
 **S32**	44%	63%	55%	89%	71%
 **S33**	71%	92%	62%	99%	99%

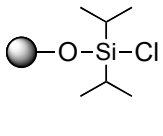
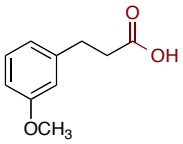
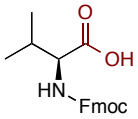
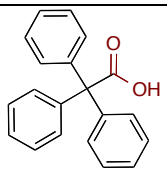
 **S34**	65%	82%	64%	86%	84%
 **13**	43%	13%	82%	72%	80%
 **14**	52%	75%	67%	95%	90%
 **S4**	13%	74%	58%	69%	81%
 **S35**	22%	22%	7%	30%	8%
 **S8**	69%	99%	21%	99%	93%
 **15**	35%	42%	22%	84%	63%

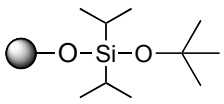
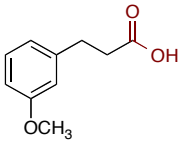
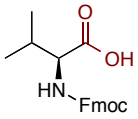
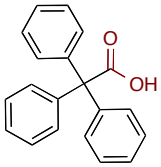
 **S36**	2%	76%	70%	87%	84%
 **S37**	5%	89%	75%	87%	95%
 **S38**	34%	92%	75%	99%	82%
 **16**	55%	50%	49%	85%	69%
 **S39**	1%	6%	5%	8%	4%

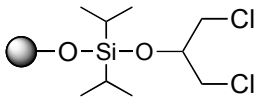
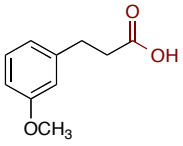
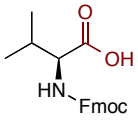
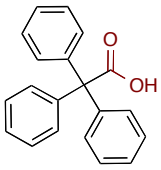
Supporting Information Table S3. Enrichment yields for resins **6**, **7**, **8**, **9**, and **10** with a model set of carboxylic acids.

Demonstration of resin regeneration.

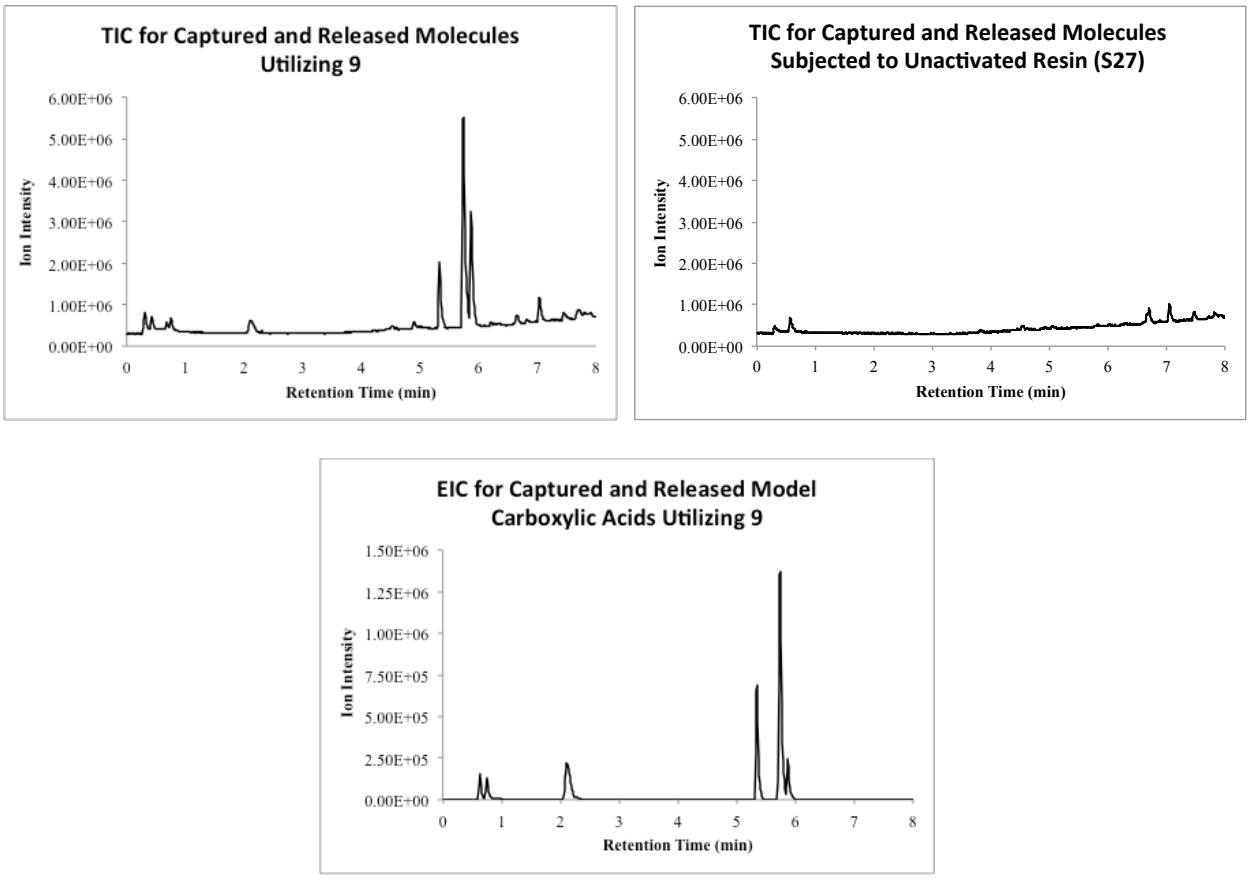
Each resin was coupled as in the *Loading Capacity Experiment section*, with the exception that the resins had previously been coupled to acids and subjected to cleavage conditions resulting in regeneration of **2**. Averaging of four replicates gave the loading capacities as shown below.

 **3**	 **11**	 **S4**	 **S8**	Average
Initial	0.72	0.40	0.22	0.45
Recycled	0.70	0.38	0.24	0.44

 **8**	 **11**	 **S4**	 **S8**	Average
Initial	0.43	0.38	0.18	0.33
Recycled	0.46	0.31	0.22	0.33

 **9**	 **11**	 **S4**	 **S8**	Average
Initial	0.55	0.32	0.28	0.38
Recycled	0.49	0.27	0.27	0.34

Supporting Information Table S4. Demonstration of the regenerative properties of the developed capture resins. This resin can be re-used for multiple cycles without a substantial decrease in loading capacity.



Supporting Information Figure S1. Representative TIC and EIC traces of enriched carboxylic acids utilizing resin **9**. Six carboxylic acids [3-acetylbenzoic acid (**S39**), 3-cyanophenylacetic acid (**S31**), 3-(3-methoxyphenyl)propionic acid (**11**), Fmoc-Gly-OH (**S28**), Fmoc-Val-OH (**S4**), and Acemtacin (**S30**) in the order that they appear on the chromatogram] were subjected to enrichment. **Top Left**. TIC of captured and released molecules. **Top Right**. TIC of unactivated resin (**S27**) that was subjected to coupling conditions and the mixture of the six carboxylic acids. This shows that capture and release of carboxylic acid-containing molecules is dependent upon the disiloxane moiety present on resin **9**. **Bottom.** The EIC for the captured and released molecules that were subjected to chemoselective coupling with **9**.

	Peak Area Prior to Capture	Peak Area After Capture
3-oxo-1-indancarboxylic acid (**S32**)	546446	478384
Probenecid (**16**)	3663340	2799309
3,5-dimethyl-4-methoxybenzoic acid (**S38**)	1518457	1308679
Abietic Acid (**15**)	2414543	1565820
Fmoc-Amino-Propanol (**17**)	4455509	4559
3-(dimethylamino)phenol (**18**)	4043524	21738
Trypatamine (**S7**)	203403	611
H-Lyz(Z)-OMe (**19**)	36329688	453279
Boc-Cys-OMe (**20**)	100590	2378

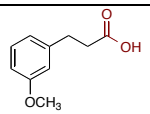
Compounds	Peak Ratio Before Capture	Normalization Factor	Peak Ratio After Capture	Normalized Ratio After Capture
S32:17	0.12	8.15	104.93	855.57
S32:18	0.14	7.40	22.01	162.84
S32:S7	2.69	0.37	782.95	291.44
S32:19	0.02	66.48	1.06	70.17
S32:20	0.55	1.83	201.17	368.36
S38:17	0.34	2.93	287.05	842.28
S38:18	0.38	2.66	60.20	160.31
S38:S7	7.47	0.13	2141.86	286.91
S38:19	0.04	23.93	2.89	69.08
S38:20	1.52	0.66	550.33	362.64
16:17	0.82	1.22	614.02	746.79
16:18	0.91	1.10	128.77	142.14
16:S7	18.01	0.06	4581.52	254.38
16:19	0.10	9.92	6.18	61.24
16:20	3.66	0.27	1177.17	321.53
15:17	0.54	1.85	343.46	633.77
15:18	0.60	1.67	72.03	120.63
15:S7	11.87	0.08	2562.72	215.89
15:19	0.07	15.05	3.45	51.98
15:20	2.41	0.41	658.46	272.87

Compounds	Average of Enrichment Ratio
Carboxylic Acid to Primary Alcohol	770
Carboxylic Acid to Phenol	147
Carboxylic Acid to Primary Amine	262
Carboxylic Acid to Secondary Amine	63
Carboxylic Acid to Thiol	331

Supporting Information Table S5. Ratios of enrichment of carboxylic acids compared to those molecules with no carboxylic acid moiety. To illustrate that the carboxylic acid-containing compounds are being dramatically enriched in comparison to the molecules containing other functional groups, we calculated the ratio of enrichment. The ratio of each carboxylic acid to the chemoselective set of compounds was calculated and normalized. Normalization is required given that although an equivalent number of moles of each compound were used, the ionization efficiency of each compound is unique, making the observed peak areas dramatically different. Accordingly, the initial ratios were normalized to a 1:1 ratio and this factor was applied to the post-capture data. In all cases, following the capture and release protocol at least a 63-fold enrichment of the carboxylic acids was seen in comparison to the non-carboxylic acid compounds. These data were obtained from the *Streptomyces cinnamonensis* extract enrichment experiment.

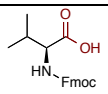
Model Carboxylic Acid	Peak Area Following Exposure to Activated Resin (9)	Peak Area Following Exposure to Unactivated Resin (S27)	Ratio of Enrichment (Activated/Unactivated resin)
3-oxo-1-indancarboxylic acid (**S32**)	478384	1213	394
Probenecid (**16**)	2799309	5463	512
3,5-dimethyl-4-methoxybenzoic acid (**S38**)	1308679	3152	415
Abietic Acid (**15**)	1565820	2244	698

Supporting Information Table S6. Ratios of enrichment of carboxylic acids subjected to activated resin versus unactivated resin. The *Streptomyces cinnamonensis* extract (containing the full chemoselective set and four additional acids) was subjected separately to activated resin (**9**) and an unactivated control (**S27**). The peak areas obtained following performance of the release protocol from both resin samples are shown above. These data clearly illustrate that the observed enrichment of the acids is only a result of specific capture by the activated disiloxane moiety and not due to non-specific binding to the resin.



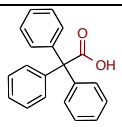
11

mmol of natural product background	mmol of model acid added	Ratio of natural product background to model carboxylic acid (mmol)	Percent Recovery of model carboxylic acid
0.012	0.0076	2:1	96%
0.012	0.00152	8:1	94%
0.012	0.00076	16:1	94%
0.012	0.000152	80:1	91%
0.012	0.000076	160:1	95%
0.012	0.0000152	800:1	92%



S4

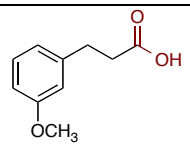
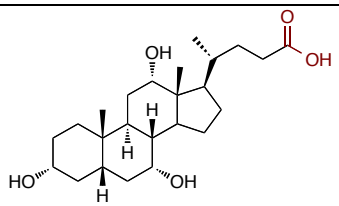
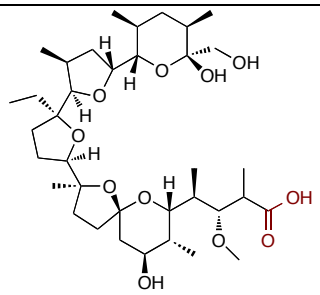
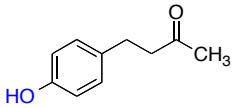
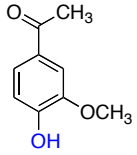
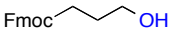
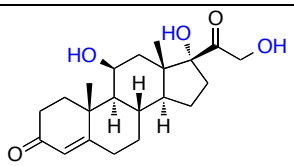
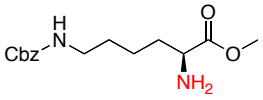
mmol of natural product background	mmol of model acid added	Ratio of natural product background to model carboxylic acid (mmol)	Percent Recovery of model carboxylic acid
0.012	0.0076	2:1	85%
0.012	0.00152	8:1	95%
0.012	0.00076	16:1	85%
0.012	0.000152	80:1	75%
0.012	0.000076	160:1	78%
0.012	0.0000152	800:1	57%

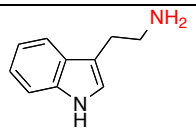
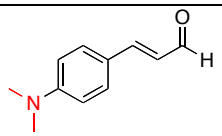


S8

mmol of natural product background	mmol of model acid added	Ratio of natural product background to model carboxylic acid (mmol)	Percent Recovery of model carboxylic acid
0.012	0.0076	2:1	84%
0.012	0.00152	8:1	91%
0.012	0.00076	16:1	83%
0.012	0.000152	80:1	87%
0.012	0.000076	160:1	83%
0.012	0.0000152	800:1	92%

Supporting Information Table S7. Dynamic range of the capture efficiency of resin **9** in a background of a crude natural product mixture. The average molecular weight of the extract material was assumed to be 350 g/mol for the purpose of calculation of "mmol of natural product background."

Molecule	Recovery Yield from Extraction of Basic Fraction	Recovery Yield from Extraction of Acidic Fraction	Recovery Yield Utilizing Resin 9
 **11**	0%	40%	95%
 **12**	0%	83%	81%
 **13**	34%	0%	72%
Compounds Containing Functional Groups Not Enriched With Resin 9			
 **S42**	61%	0%	ND*
 **S43**	0%	64%	ND*
 **17**	49%	0%	0%
 **S44**	20%	0%	ND*
 **19**	69%	0%	0%

 **S7**	23%	0%	0%
 **S45**	20%	0%	ND*

*ND = these molecules do not contain a carboxylic acid moiety and would not be captured and released by **9**. Based upon previous results with our chemoselective set of molecules, we expect these yields would be zero.

Supporting Information Table S8. Comparison of the recovery yields obtained from performing a standard acid/base organic extraction to yields achieved utilizing resin **9**. Broth obtained from growth of *Streptomyces cinnamonensis* was spiked with model compounds. It was made basic (pH 10.5) and extracted and then acidified (pH 2.5) and extracted again. As expected, carboxylic acids **11** and **12** were found in the material extracted following acidification of the aqueous broth. Although monensin (**13**) contains a carboxylic acid, it was present in the organic layer obtained following extraction of the basified broth. This is likely due to its relatively hydrophobic character and highlights the utility of a strategy to enrich all compounds containing this functional group regardless of their solubility properties. Application of **9** to the isolation of carboxylic acid-containing compounds resulted in similar or better yields than those obtained by organic extraction (**11**-**13**). Compounds that would not be enriched with resin **9** were also examined. Amines (**19**, **S7**, **S45**) and alcohols (**17**, **S44**) were found in the extraction from the basic fraction as expected. Phenol-containing compounds (**S42**, **S43**) were present in the organic layer following extraction of both the basic and the subsequently acidified broth, suggesting that these compounds were parsed based upon both acidity and hydrophobicity.

Preparation of Streptomyces cinnamonensis extract.

Streptomyces cinnamonensis was purchased from ATCC as a freeze-dried pellet. Cell cultures were started utilizing 5 mL of ISP Medium 1. After 3 days of incubation at 28^{o}C at 175 rpm, these 5 mL cultures were transferred to 100 mL of ISP Medium 1 and again incubated for 3 days under the previous conditions. Finally, the 100 mL cultures were transferred to 4 L flasks that contained 1 L of ISP Medium 1. These cultures were incubated for 7 days. After this time, the culture was transferred to Nalgene centrifuge vessels and spun at 7000 rpm for 35 min. The broth was decanted from the cell pellet into a 2 L flask. To the broth was then added 10 g of XAD-16 resin. The flask was then shaken at 175 rpm overnight. The resin was transferred to a 500 mL peptide synthesis vessel and rinsed with 100 mL of H_2O X 2. The resin was then subjected to the following wash protocol to elute off all compounds from the resin: MeOH 100 mL, ACN 100 mL, EtOAc 100 mL, Acetone 100 mL, EtOAc 100 mL, ACN 100 mL, MeOH 100 mL. The washes were combined and concentrated to yield 297 mg of crude material. From the extract, it was determined via LC-MS-TOF analysis that the sample contained 46 nmol of Monensin per 1 mg of crude material.

*Enrichment of endogenously produced Monensin (**13**).*

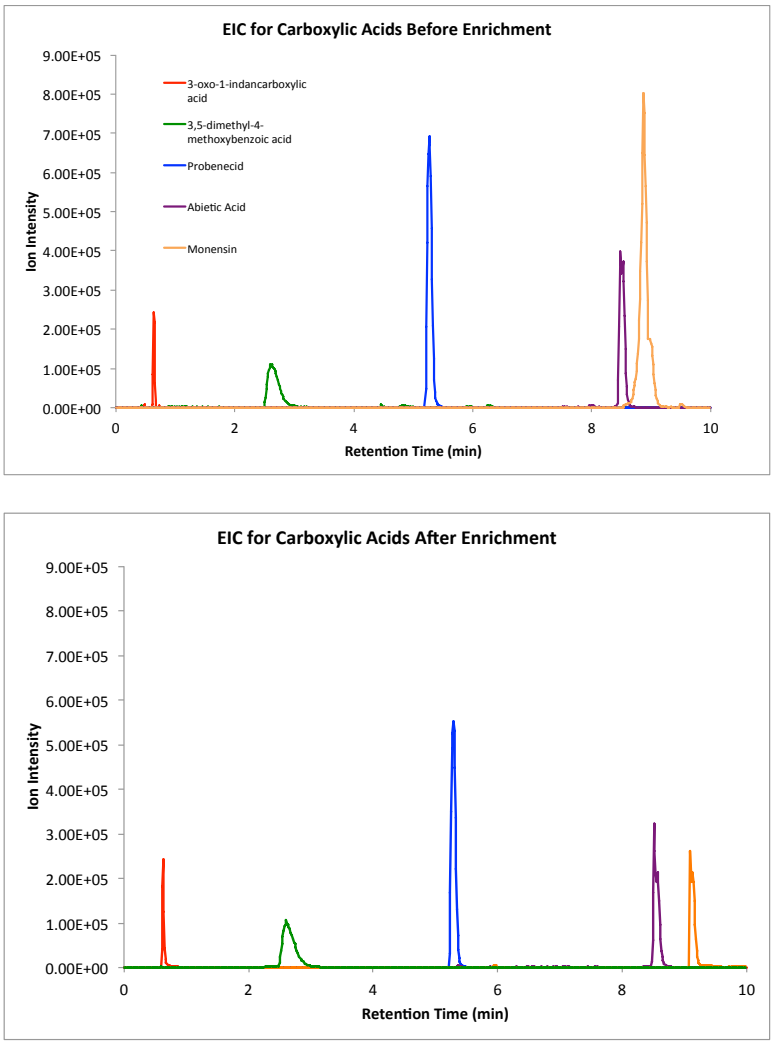
Bacterial extract material (12 mg) was dissolved in 600 μL of anhydrous THF and 500 μL of anhydrous DMSO. The chemoselective compound mixture (1.9 mL solution containing 46 nmol each of Boc-Cys-OMe, tryptamine, H-Lys(Z)-OMe, Fmoc-aminopropanol, 3-(dimethylamino)phenol, 3-oxo-1-indancarboxylic acid, Probenecid, 3,5-dimethyl-4-methoxybenzoic acid, and Abietic acid in 90% THF/10% DMSO) was added, which brought the total volume of the solution to 3 mL. Six 2 mL vials were charged with 40 mg (‘‘3 equivalents’’;

see below) of **9**, which was synthesized as previously described. The resin was then swollen in 500 µL of DCM and 300 µL of Et_3N was added, followed by 500 µL of the above extract/chemoselective solution. This amount of resin was chosen by estimation of the theoretical number of moles of material in the bacterial extract based on the assumption that the average compound molecular weight was 350 Da. The vials were capped and agitated overnight at room temperature. The resin was transferred to 2 mL biospin vessels and subjected to the wash protocol described previously. The resin vessels were dried for 1 h in a vacuum desiccator at 30 mmHg. The dried resin was transferred to 2 mL polypropylene vials and swollen with 500 µL of anhydrous THF. To each vial was added 100 µL of a 50/50 mixture (v/v) of HF/pyridine (70/30 wt%)/pyridine. The vials were capped and agitated for 3 h at room temperature. After this time, 500 µL of TMSOMe was added to quench excess HF and the resin was agitated for an additional 30 min at room temperature. The resin was washed with THF (3 X 2 mL), DCM (3 X 2 mL), and filtered over a 2 mL fritted polypropylene column into a 5 mL vial. This solution was then concentrated under reduced pressure with no heating and the sample was dissolved in 200 µL of 2:1:1 H_2O/THF/MeOH. Analysis was performed by injection of 5 µL of this solution onto a LC-MS-TOF and comparing the observed peak area to that of standard curve data.

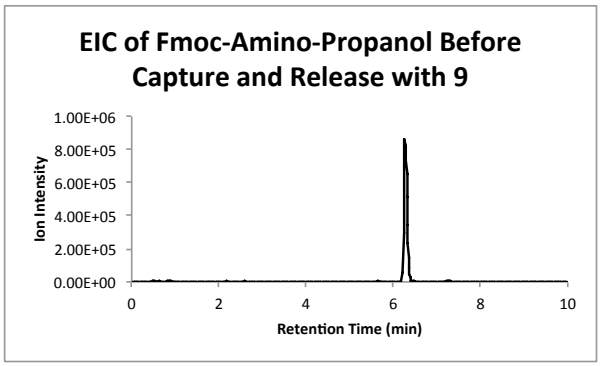
Organic extraction of model compounds from a crude broth background

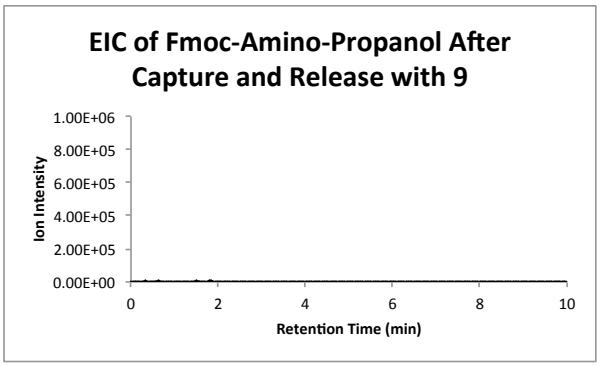
15 mg of a crude extract of the concentrated broth from *Streptomyces cinnamonensis* was dissolved in 50 mL of a 3% NH_4OH solution (pH = 10.5). To this was spiked in 0.5 mg of **11**, **12**, **13**, **S42**, **S43**, **17**, **S44**, **19**, **S7**, and **S45**. This basic aqueous layer was extracted three times with 50 mL of ethyl acetate. These organic layers were then combined and concentrated. The basic organic layer was then acidified using concentrated HCl (approximately 2 mL) to yield an

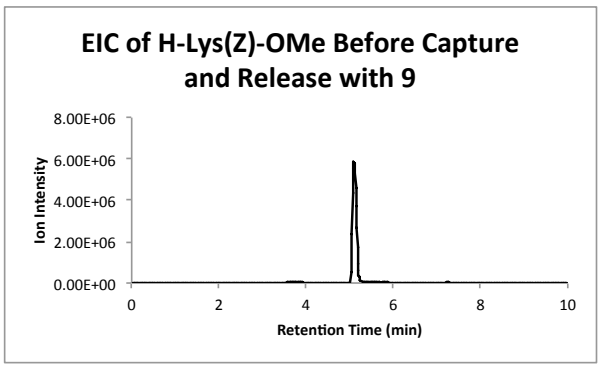
aqueous phase with a pH of 2.5. This acidic aqueous layer was extracted three times with 50 mL of ethyl acetate. The organic layers were combined and concentrated. Recovery yields were calculated for all model compounds after dissolving the resulting pools in 3 mL of 50/25/25 H_2O/THF/MeOH, injecting 1 μL of this solution onto an LC-MS-TOF, and comparing the corresponding ion peak areas to those obtained from a standard curve. These yields are shown in **Supporting Information Table S8**. Extraction protocol adapted from *Natural Products Isolation.* Ed. Sarker, S. D.; Latif, Z.; Gray, A. I. Humana Press Inc., Totowa, New Jersey, 2006.

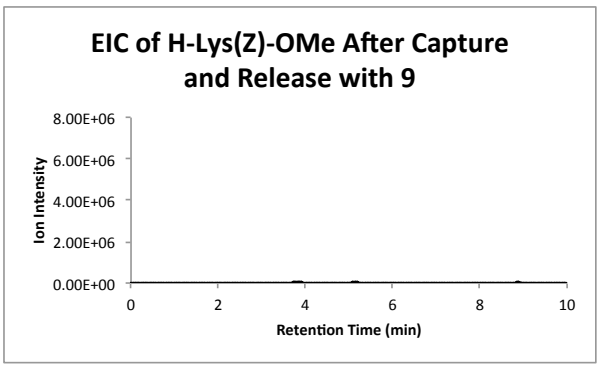


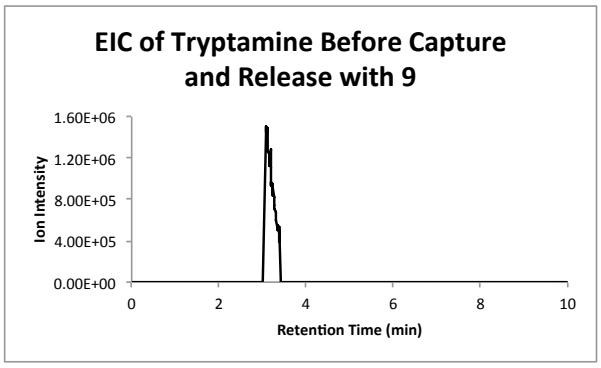
Supporting Information Figure S2. EIC traces for the carboxylic acids in the experiment from *Streptomyces cinnamonensis* extract both before and after enrichment with resin **9**. **Top**. Carboxylic acids prior to enrichment protocol. 46 nmol of each carboxylic acid standard was doped into 12 mg of the extract material. **Bottom**. Carboxylic acid EIC after enrichment.

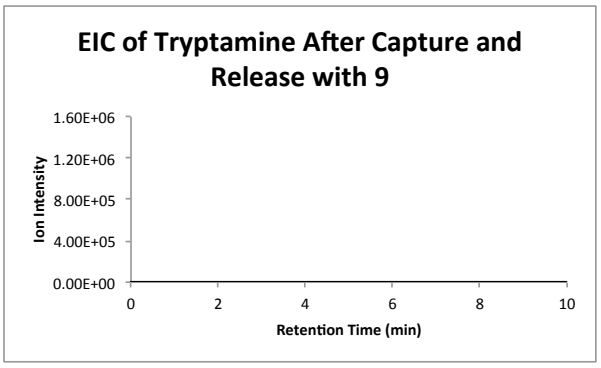

EIC of Fmoc-Amino-Propanol Before Capture and Release with 9
Ion Intensity
1.00E+06
8.00E+05
6.00E+05
4.00E+05
2.00E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)

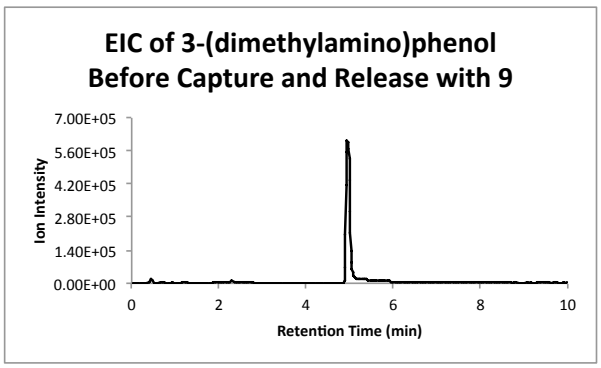

EIC of Fmoc-Amino-Propanol After Capture and Release with 9
Ion Intensity
1.00E+06
8.00E+05
6.00E+05
4.00E+05
2.00E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)

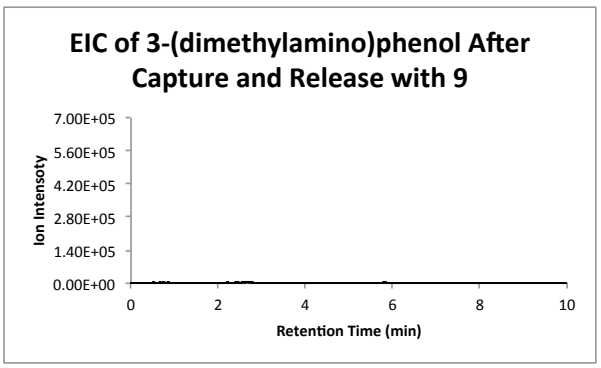

EIC of H-Lys(Z)-OMe Before Capture and Release with 9
Ion Intensity
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
0
2
4
6
8
10
Retention Time (min)

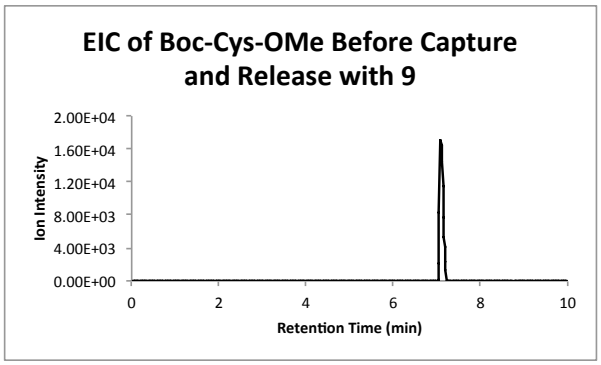

EIC of H-Lys(Z)-OMe After Capture and Release with 9
Ion Intensity
8.00E+06
6.00E+06
4.00E+06
2.00E+06
0.00E+00
0
2
4
6
8
10
Retention Time (min)

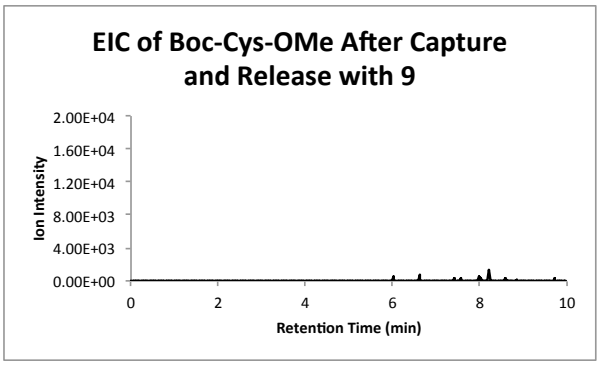

EIC of Tryptamine Before Capture and Release with 9
Ion Intensity
1.60E+06
1.20E+06
8.00E+05
4.00E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)


EIC of Tryptamine After Capture and Release with 9
Ion Intensity
1.60E+06
1.20E+06
8.00E+05
4.00E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)


EIC of 3-(dimethylamino)phenol Before Capture and Release with 9
Ion Intensity
7.00E+05
5.60E+05
4.20E+05
2.80E+05
1.40E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)


EIC of 3-(dimethylamino)phenol After Capture and Release with 9
Ion Intensoty
7.00E+05
5.60E+05
4.20E+05
2.80E+05
1.40E+05
0.00E+00
0
2
4
6
8
10
Retention Time (min)

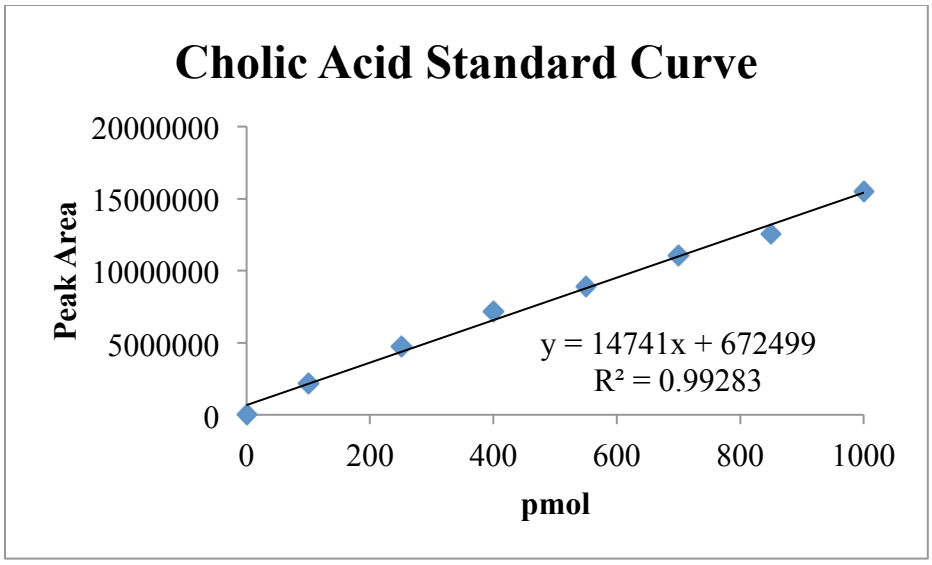




Supporting Information Figure S3. Demonstration of chemoselectivity during carboxylic acid enrichment experiment from *Streptomyces cinnamonensis* extract. The left column represents the amount of each compound that was spiked into the bacterial broth. As the right column shows, these molecules were not captured, demonstrating that in a biological setting **9** retains its chemoselectivity for carboxylic acids.

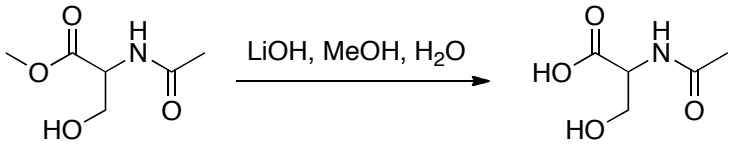
Protocol for acquisition, analysis, and calculation of enrichment yields using LC-MS-TOF spectral data.

For each model compound, a standard curve was generated from solutions with known concentrations. All compounds were dissolved in 2:1:1 H_2O:MeOH:THF to yield the concentrations required to provide 1000 pmol, 700 pmol, 560 pmol, 420 pmol, 280 pmol, 140 pmol, and 1 pmol in separate 1 μL injections into the LC-MS-TOF. For all compounds, the optimal fragmentation voltage for the desired ion was determined by assessment of the 700 pmol injection at 50V, 100V, 125V, 150V, 175V, 200V, 225V, and 250V. The fragmentation voltage yielding the highest ion intensity was selected. Following this analysis, all samples were run at each optimal voltage determined for each compound included in the sample. Standard curves were generated for all model compounds by running two independent sets of samples. A representative graph is shown for cholic acid (**12**) (**Supporting Information Figure S4**). Unknown samples were quantified by comparison to the generated standard curves. All reactions were run in quartet. The average number of pmoles obtained from the capture and release of each model compound was compared to the initial pmoles added to the reaction giving an enrichment yield as a percentage (i.e., moles obtained following capture and release divided by moles initially added to the experiment).

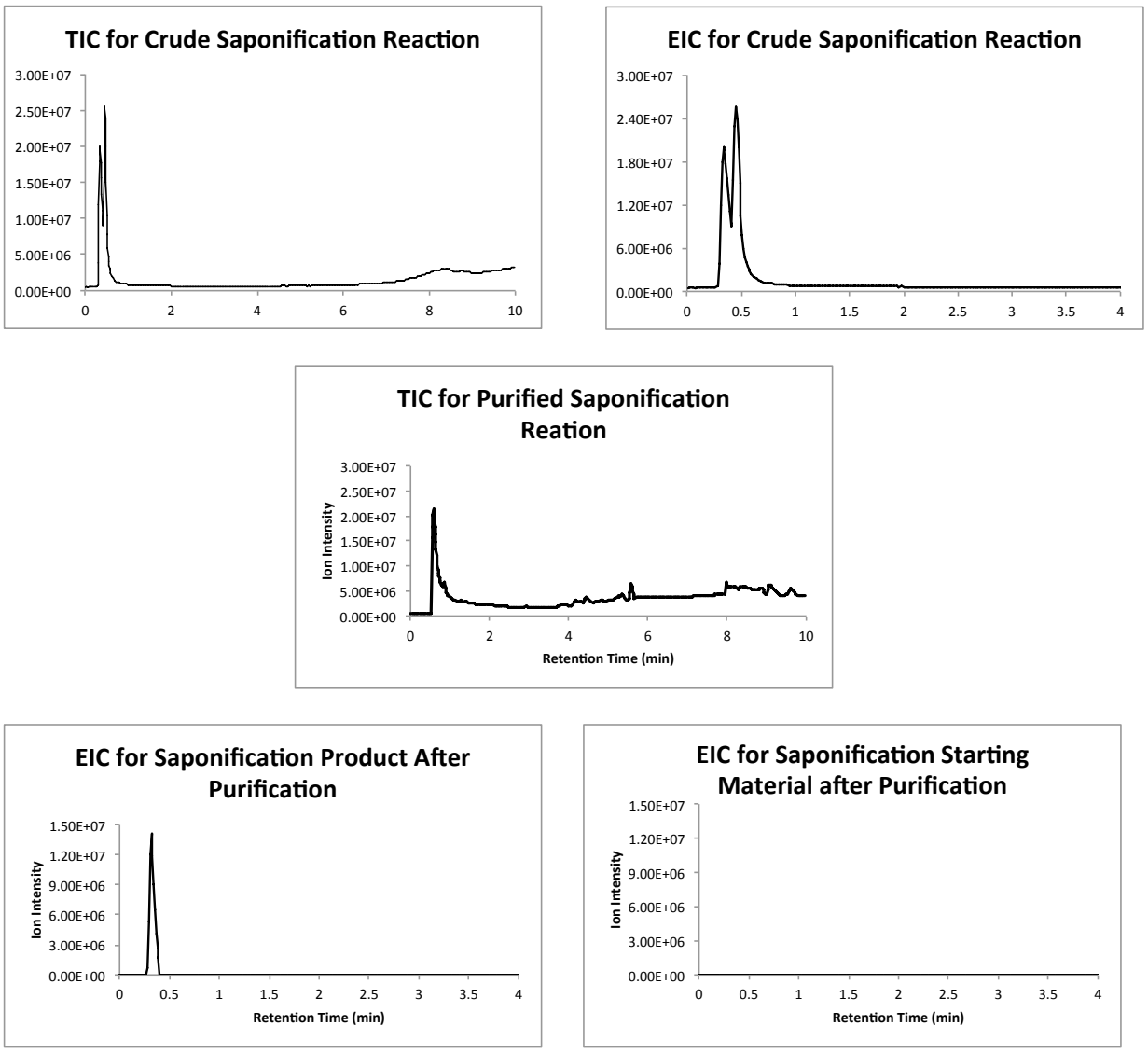


Supporting Information Figure S4. Representative standard curve for carboxylic acid capture quantification. Unknowns were quantified using the generated equation from each graph. This is an example standard curve for cholic acid (**12**).

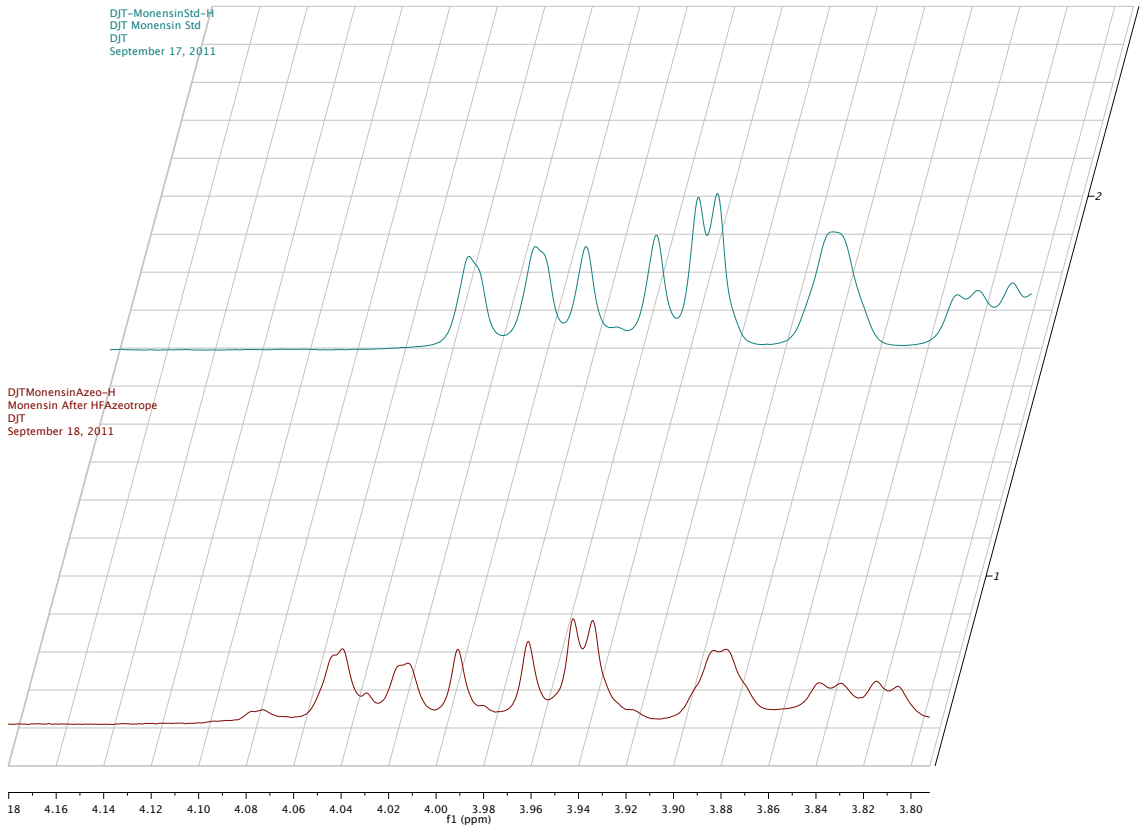
Saponification Reaction



To a 25 mL roundbottom flask was added 20 mg of Ac-Ser-OMe (1.0 equiv, 0.12 mmol) dissolved in 5 mL of MeOH and 1 mL of H_2O. Next, 30 mg of LiOH (0.24 mmol, 2.0 equiv) was added to the flask and stirred for 30 min. The crude reaction mixture was concentrated to yield a mixture of Ac-Ser-OMe (starting material), Ac-Ser-OH (product), excess LiOH, and other reaction by-products. This crude mixture was dissolved in 4 mL of THF and 1 mL of DMSO and subjected to coupling conditions with 500 mg of **9** as described. After agitating the resin overnight, it was subjected to the standard wash protocol, dried for 1 h in a vacuum dessicator at 30 mmHg, and subjected to the cleavege conditions using HF/pyridine/pyridine as described previously. After quneching the excess HF with TMSOMe, the resin was washed twice with 2 mL of THF and once with 2 mL of CH_2Cl_2. This solution was concentrated to yield only the corresponding product of this saponification reaction (15 mg, 83% purified yield) as determined by LC-MS-TOF analysis as shown in **Supporting Information Figure S5**.



Supporting Information Figure S5. Example of the utility of **9** as a purification scavenger to isolate the desired product from a crude saponification reaction containing remaining starting material, side products, lithium salt, and product. The chemoselectivity of our method enables ready separation of the carboxylic acid-containing product from the starting material, which only displays an alcohol. The high polarity of both species would make traditional separation methods difficult to implement for their separation. Product was obtained in a 83% yield and high purity. Thus, our resin can be used to isolate natural products that contain the carboxylic acid functional group, as well as a purify such compounds following solution phase synthesis. **Top Left**. TIC of the crude reaction showing that both starting material (t_R=0.35 min) and product (t_R=0.56 min) are present. **Top Right**. Extracted ion chromatograph of the starting material and product in the crude sample. **Middle**. TIC of the carboxylic acid-enriched sample showing only the presence of the product. **Bottom Left**. Extracted ion chromatograph of the product from the purified sample. **Bottom Right**. Extracted ion chromatograph of the starting material from the purified sample.



Supporting Information Figure S6. ^{1}H NMR comparison of monensin standard before and after treatment with HF/pyridine cleavage conditions (pH~3.5). The spiroketal portion of monensin has been reported to be acid sensitive resulting in epimerization. We confirmed that our conditions do not cause epimerization. The top spectrum in green illustrates the monensin spiroketal portion (*J. Org. Chem*. **2009**, *74*, 7774–7780). The bottom spectrum in red confirms that the spiroketal portion of monensin is not epimerized after exposure to the pyridine buffered HF/pyridine cocktail used for cleavage of carboxylic acid-containing molecule from resin. Epimerization results in dramatic changes in both chemical shift values and coupling patterns of the observed protons in this region, which we do not observe.

Resin Characterization Data.

2: FT-IR (on-bead KBr pellet) ν_{max}: 3466, 3059, 2849, 1384, 1149, 1087 cm^{-1}; gel phase ^{13}C NMR (125MHz, $CDCl_3$) δ 73.1, 70.4, 67.4, 41.4, 40.3, 29.3

3: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2920, 1057, 883, 611 cm^{-1}; gel phase ^{13}C NMR (125MHz, $CDCl_3$) δ 76.4, 73.3, 67.5, 44.5, 41.0, 30.4, 17.6, 16.8

6: FT-IR (on-bead KBr pellet) ν_{max}: 3060, 2973, 2930, 1012, 882 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.6, 67.9, 51.3, 44.8, 41.0, 30.7, 18.2, 18.1, 13.8

7: FT-IR (on-bead KBr pellet) ν_{max}:3059, 2922, 1028, 880 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 73.5, 67.6, 65.3, 44.5, 41.0, 30.7, 30.4, 26.4, 18.3, 18.2 14.3

8: FT-IR (on-bead KBr pellet) ν_{max}: 3082, 2935, 1046, 906 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.3, 73.4, 67.6, 44.5, 41.0, 30.4, 17.6, 16.8

9: FT-IR (on-bead KBr pellet) ν_{max}: 3058, 2855, 1153, 882, 695 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.3, 73.8, 71.9, 67.6, 46.1, 44.5, 41.0, 30.9, 30.4, 18.0, 17.9, 17.6, 16.8, 14.3

10: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2926, 1264, 1223, 1068, 818 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 121.3, 76.4, 75.3, 73.8, 67.5, 44.5, 41.0, 30.9, 30.4, 18.0, 17.9, 17.7, 16.8, 14.3

S9: FT-IR (on-bead KBr pellet) ν_{max}: 3061, 2924, 1088, 885 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.6, 67.8, 58.9, 44.8, 41.0, 30.7, 19.0, 18.3, 18.2, 14.0

S10: FT-IR (on-bead KBr pellet) ν_{max}: 3026, 2925, 1025, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.0, 128.7, 127.4, 126.5, 73.8, 67.8, 65.1, 44.8, 41.0, 30.8, 18.3, 18.2, 14.0

S11: FT-IR (on-bead KBr pellet) ν_{max}: 3024, 2929, 1099, 884 ;gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 73.3, 67.4, 56.4, 44.5, 41.0, 30.4, 23.4, 17.6, 16.8

S12: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2926, 1748, 1061 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 140.5, 129.1, 128.0, 126.0, 120.3, 76.3, 75.9, 74.4, 67.6, 44.5, 41.0, 30.9, 18.4, 17.9, 17.6, 16.8, 14.9, 14.3

S13: FT-IR (on-bead KBr pellet) ν_{max}: 3059, 2965, 1601, 1053, 882 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.3, 74.7, 73.5, 67.6, 44.5, 41.0, 36.5, 30.7, 23.8, 18.2, 17.6, 16.8, 14.2

S14: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2870, 1492, 1450, 1045, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 73.5, 68.9, 44.8, 42.7, 41.0, 30.4, 23.8, 19.1, 18.3, 17.6, 16.8, 14.5

S15: FT-IR (on-bead KBr pellet) ν_{max}: 3081, 2942, 1720, 1045, 884 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 75.0, 72.9, 67.3, 44.4, 41.0, 36.6, 32.2, 31.9, 30.9, 30.4, 26.0, 25.4, 25.1, 17.9, 17.6, 16.8, 14.3

S16: FT-IR (on-bead KBr pellet) ν_{max}: 3023, 2922, 2362, 2335, 1029, 882 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 129.9, 121.7, 120.3, 74.7, 73.3, 67.7, 44.6, 41.1, 30.6, 18.1, 18.0, 17.6, 16.8, 14.5

S17: FT-IR (on-bead KBr pellet) ν_{max}: 3058, 3025, 2930, 1160, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.7, 67.9, 62.0, 46.4, 44.8, 41.0, 30.7, 18.2, 17.8, 13.9

S18: FT-IR (on-bead KBr pellet) ν_{max}: 3024, 2919, 1364, 1330, 1070, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 137.3, 103.2, 73.8, 67.8, 64.9, 60.9, 56.4, 44.8, 41.0, 30.8, 18.1, 14.0

S19: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2921, 1244, 1055, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.6, 76.4, 73.3, 67.4, 59.2, 44.5, 41.0, 30.4, 21.9, 18.2, 17.6, 16.8, 9.4

S20: FT-IR (on-bead KBr pellet) ν_{max}: 3059, 3025, 2930, 1058, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.6, 149.6, 120.7, 114.9, 76.4, 74.6, 67.5, 56.0, 44.5, 41.0, 30.4, 18.0, 17.6, 16.8, 14.5

S21: FT-IR (on-bead KBr pellet) ν_{max}: 3026, 2920, 2865, 1245, 1030, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 74.0, 67.8, 64.0, 60.9, 45.7, 44.8, 41.0, 30.7, 18.0, 14.3, 13.9

S22: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2926, 1082, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 132.8, 128.8, 127.9, 73.9, 67.6, 64.4, 44.8, 41.1, 30.8, 18.2, 18.1, 14.0

S23: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2920, 1057, 883, 753 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 73.9, 73.3, 68.8, 58.2, 44.4, 41.1, 30.7, 30.4, 21.9, 21.8, 18.1, 17.6, 18.8, 14.3, 13.9

S24: FT-IR (on-bead KBr pellet) ν_{max}: 3025, 2921, 1600, 1162, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.4, 73.3, 67.7, 44.5, 41.0, 30.9, 30.4, 17.9, 17.6, 16.8, 15.0, 14.3

S25: FT-IR (on-bead KBr pellet) ν_{max}: 3024, 2922, 1259, 1035, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 129.8, 126.4, 121.6, 74.9, 73.4, 67.7, 44.7, 41.1, 30.6, 18.0, 17.9, 17.6, 16.8, 14.5

S26: FT-IR (on-bead KBr pellet) ν_{max}: 3459, 3025, 2938, 1169, 1035, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.6, 67.5, 47.2, 43.3, 40.9, 40.4, 30.8, 17.9, 14.3, 8.9

S27: FT-IR (on-bead KBr pellet) ν_{max}: 3060, 2920, 2175, 1033, 884 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.6, 66.9, 43.8, 40.4, 29.6, 17.7, 17.5, 13.0

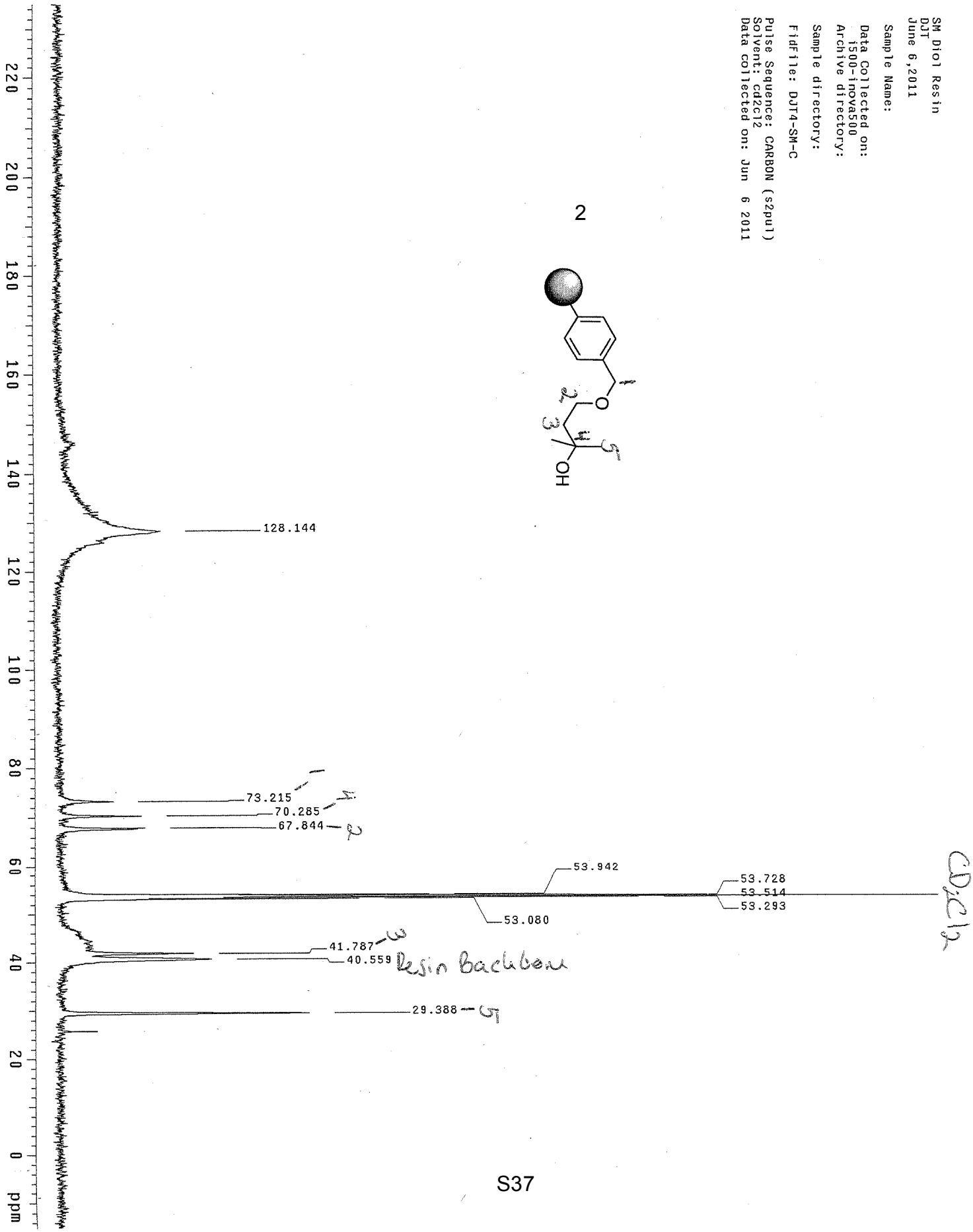
Dimethyl-Cl (S1) FT-IR (on-bead KBr pellet) ν_{max}: 3060, 2923, 1086, 698 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 76.1, 70.5, 66.7, 43.5, 40.3, 29.3, 4.7.

Diethyl-Cl (S2) FT-IR (on-bead KBr pellet) ν_{max}: 3060, 2911, 1042, 887, 591 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 75.9, 72.7, 66.8, 43.7, 40.5, 29.8, 10.3, 6.5.

Diethyl-OMe (S40) FT-IR (on-bead KBr pellet) ν_{max}: 3060, 2920, 2870, 1067, 883 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.5, 67.6, 50.3, 44.4, 40.8, 30.4, 7.0, 6.0.

Diisopropylsilyl-OCH(CH_2Cl)$_2$ (S41) FT-IR (on-bead KBr pellet) ν_{max}: 3082, 2916, 1025, 881, 820 cm^{-1}; gel phase ^{13}C NMR (125 MHz, $CDCl_3$) δ 72.5, 46.4, 41.1, 26.1, 18.0, 13.6, 13.4.

Appendix A. ^{13}C gel-phase NMR of resins shown in Supporting Information Table S2



DJT 4-175-22
DJT
June 21, 2011

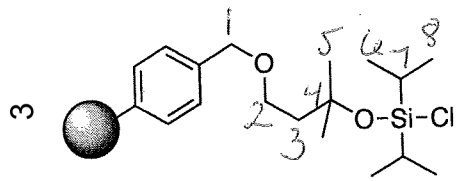
Sample Name:

Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011



DJT 4-171-B
DJT
June 5, 2011

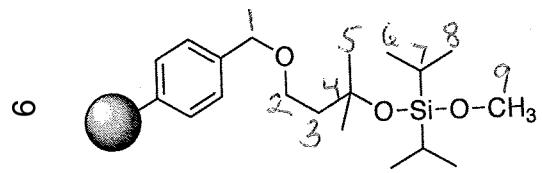
Sample Name:

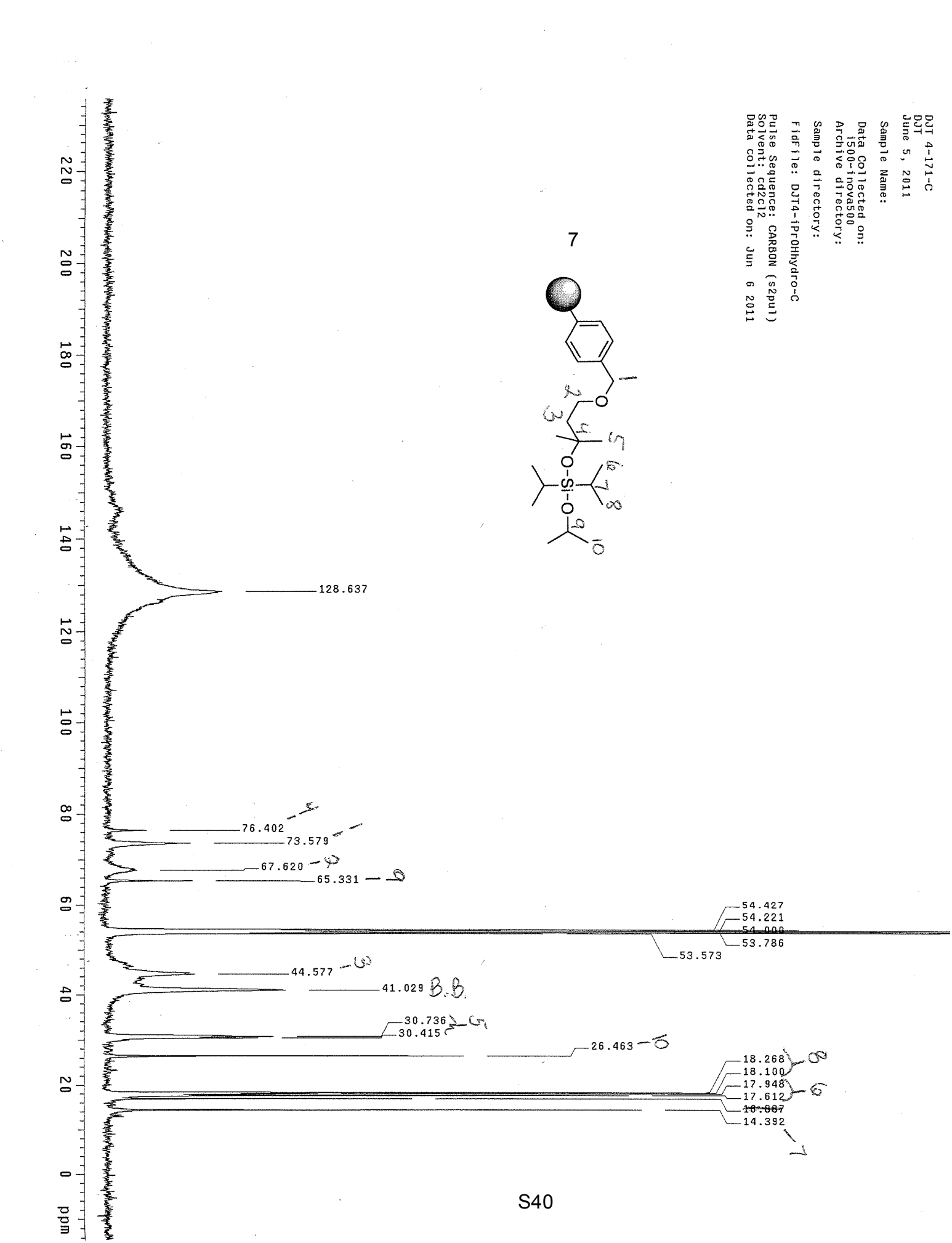
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: DJT4-MeOHhydro-C

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 6 2011




DJT 4-171-C
DJT
June 5, 2011
Sample Name:
Data Collected on:
I500-Inova500
Archive directory:
Sample directory:
FidFile: DJT4-iPrOHhydro-C
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 6 2011
7
O
O-Si-O
128.637
76.402
73.579
67.620
65.331
54.427
54.221
54.000
53.786
53.573
44.577
41.029
30.736
30.415
26.463
18.268
18.100
17.948
17.612
16.887
14.392
220
200
180
160
140
120
100
80
60
40
20
0
ppm

DJT 4-175-3
DJT
June 14, 2011

Sample Name:

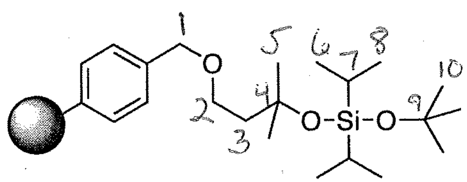
Data Collected on:
i500-inova500
Archive directory:

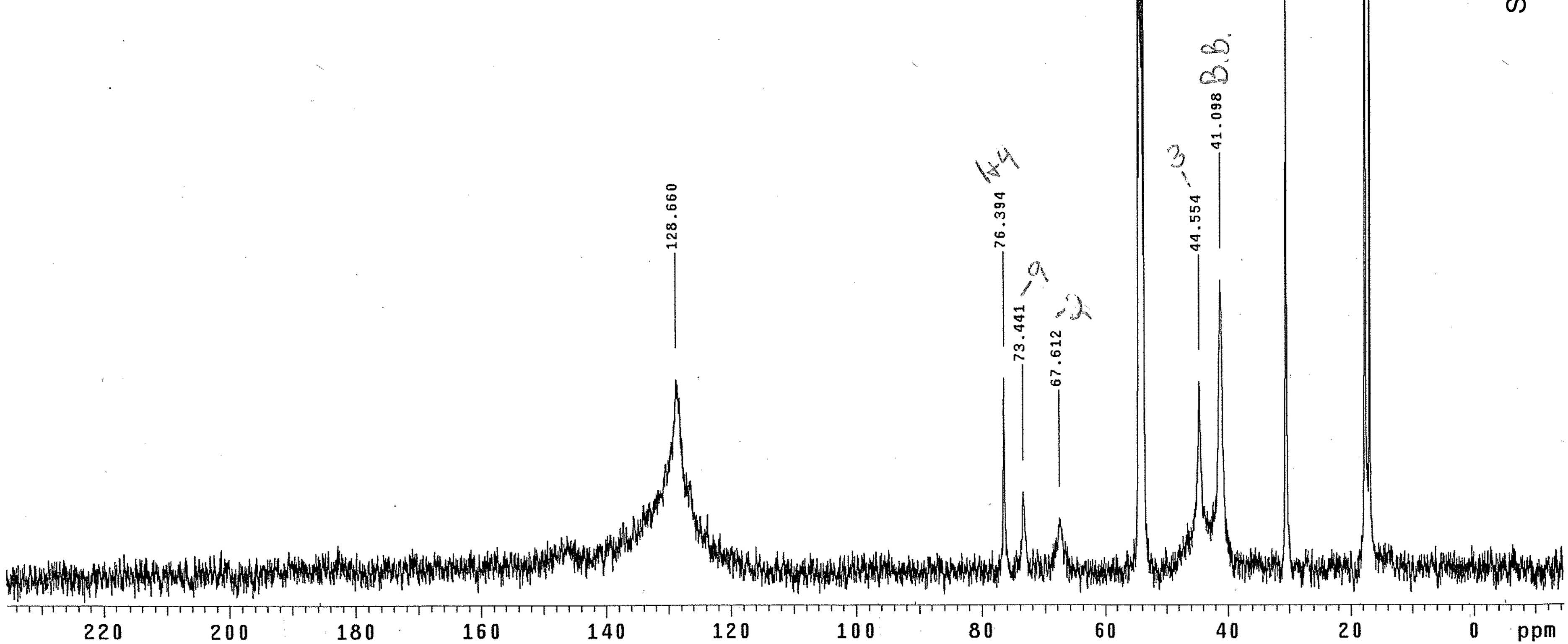
Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011

8





DJT 4-171-A
DJT
June 5, 2011

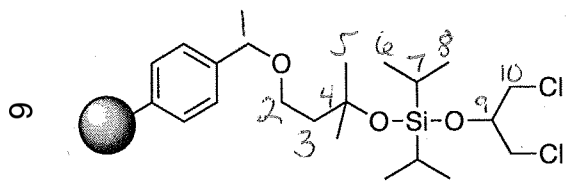
Sample Name:

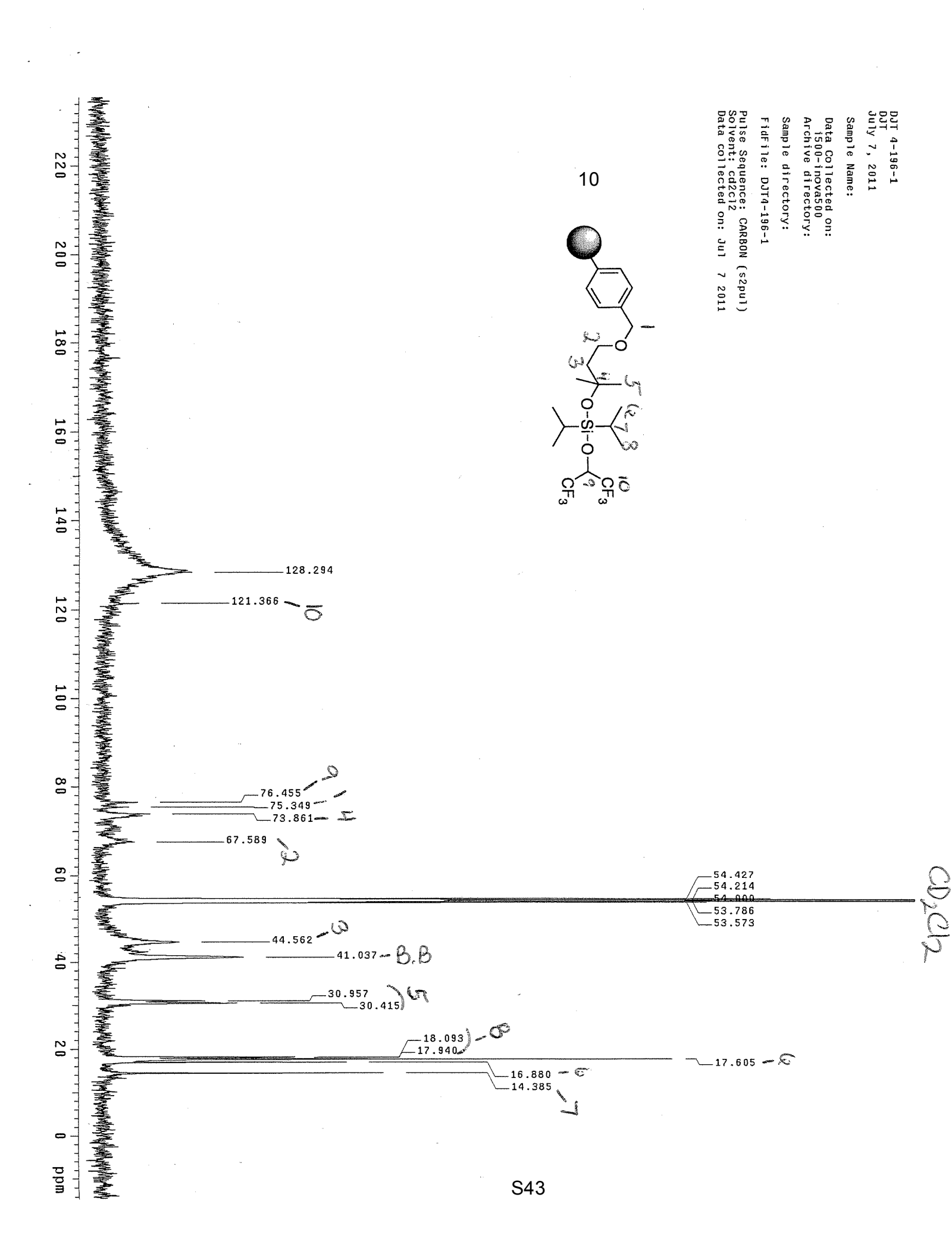
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: DJT4-dichlorhydro-C

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 6 2011




DJT 4-196-1
DJT
July 7, 2011
Sample Name:
Data Collected on:
i500-inova500
Archive directory:
Sample directory:
FidFile: DJT4-196-1
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jul 7 2011
10
128.294
121.366
76.455
75.349
73.861
67.589
54.427
54.214
54.000
53.786
53.573
44.562
41.037
30.957
30.415
18.093
17.940
17.605
16.880
14.385
CD2Cl2
ppm

DJT 3-123
DJT
July 10, 2010

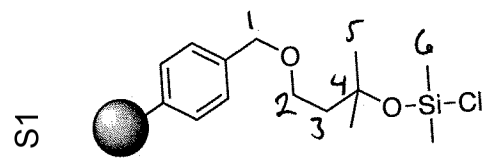
Sample Name:

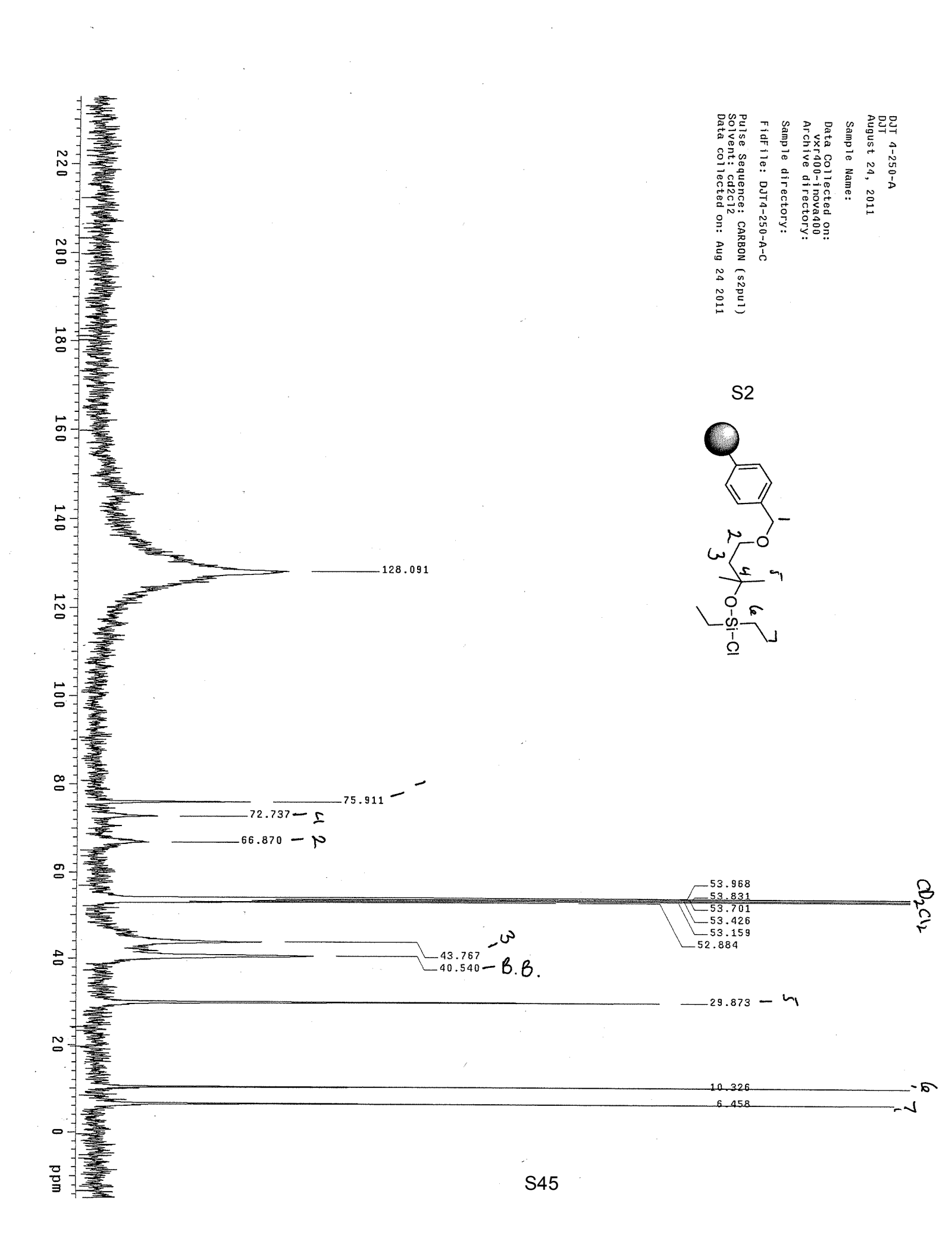
Data Collected on:
i500-inova500
Archive directory:

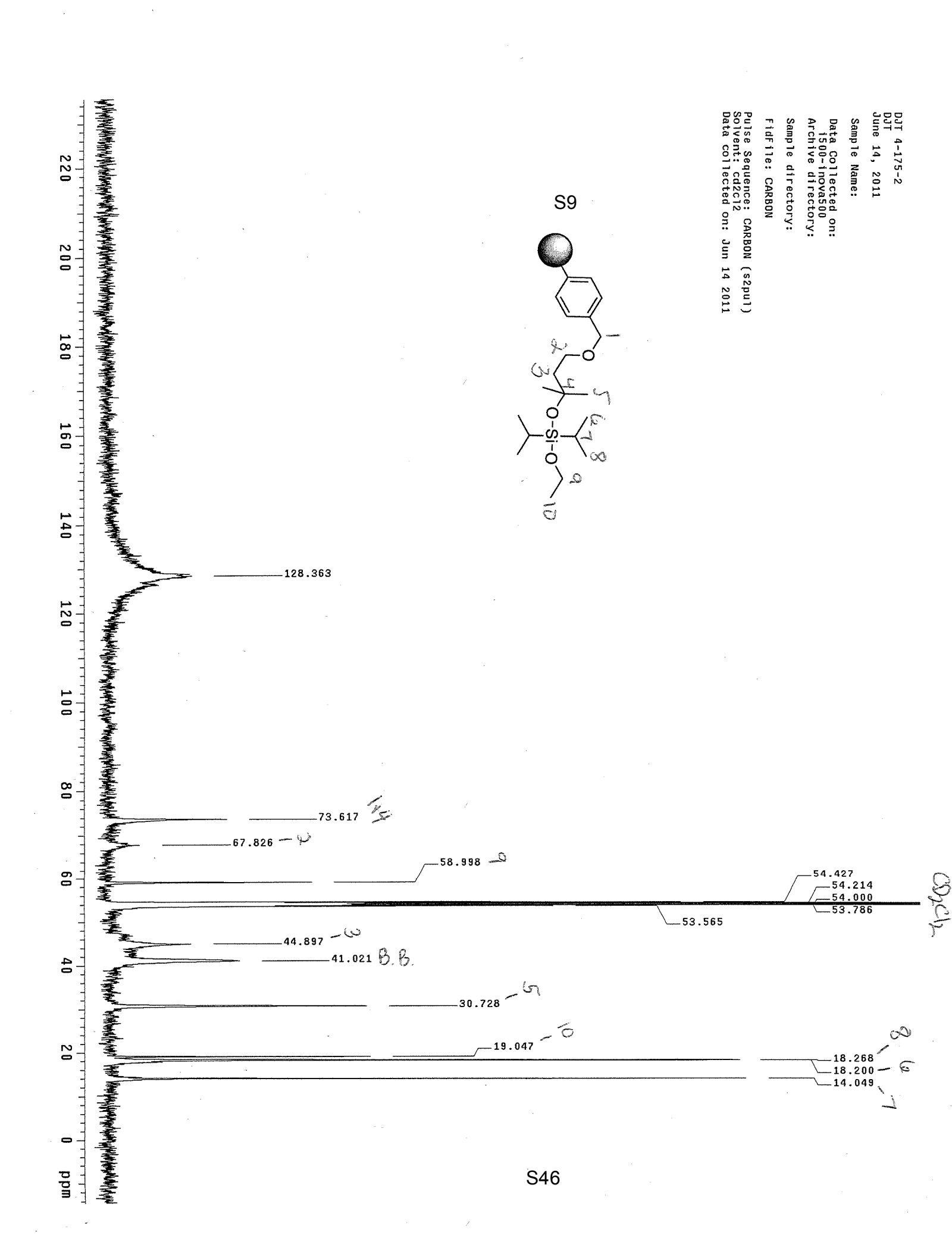
Sample directory:

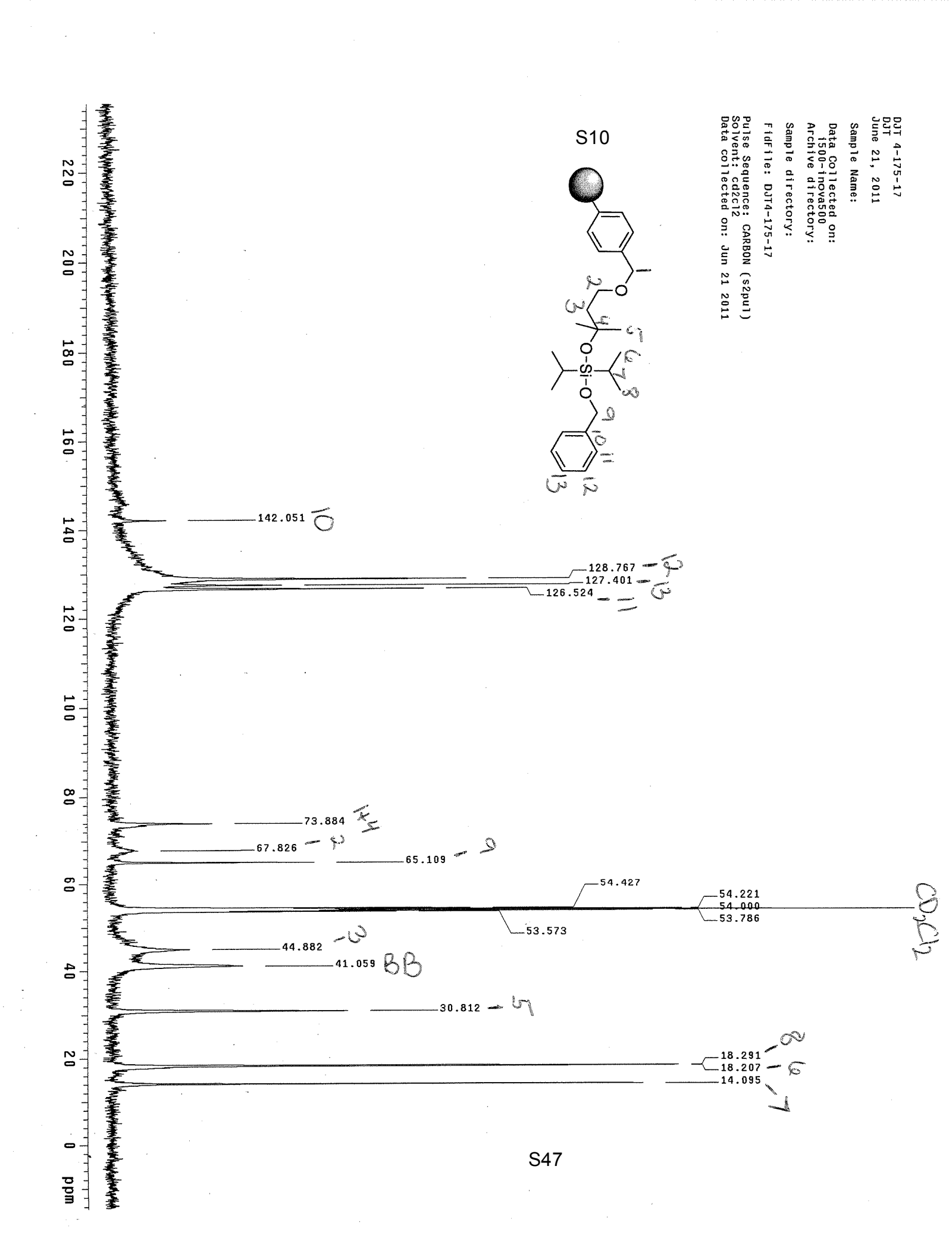
FidFile: DJT3-123-C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jul 10 2010




DJT 4-250-A
DJT
August 24, 2011
Sample Name:
Data Collected on:
vxr400-inova400
Archive directory:
Sample directory:
FidFile: DJT4-250-A-C
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Aug 24 2011
S2
128.091
75.911
72.737
66.870
53.968
53.831
53.701
53.426
53.159
52.884
43.767
40.540
29.873
10.326
6.458
CD2Cl2
B.B.
ppm


DJT 4-175-2
DJT
June 14, 2011
Sample Name:
Data Collected on:
1500-inova500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011
S9
128.363
73.617
67.826
58.998
54.427
54.214
54.000
53.786
53.565
44.897
41.021
30.728
19.047
18.268
18.200
14.049
CD2Cl2
B.B.
220
200
180
160
140
120
100
80
60
40
20
0
ppm


DJT 4-175-17
DJT
June 21, 2011
Sample Name:
Data Collected on:
i500-inova500
Archive directory:
Sample directory:
FidFile: DJT4-175-17
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011
S10
142.051
128.767
127.401
126.524
73.884
67.826
65.109
54.427
54.221
54.000
53.786
53.573
44.882
41.059
30.812
18.291
18.207
14.095
CD2Cl2
ppm

DJT 4-175-1
DJT
June 14, 2011

Sample Name:

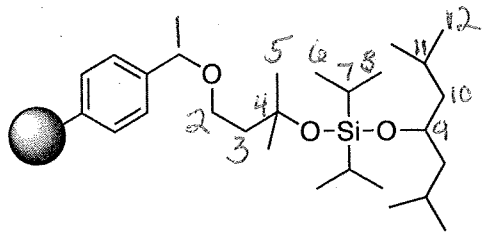
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

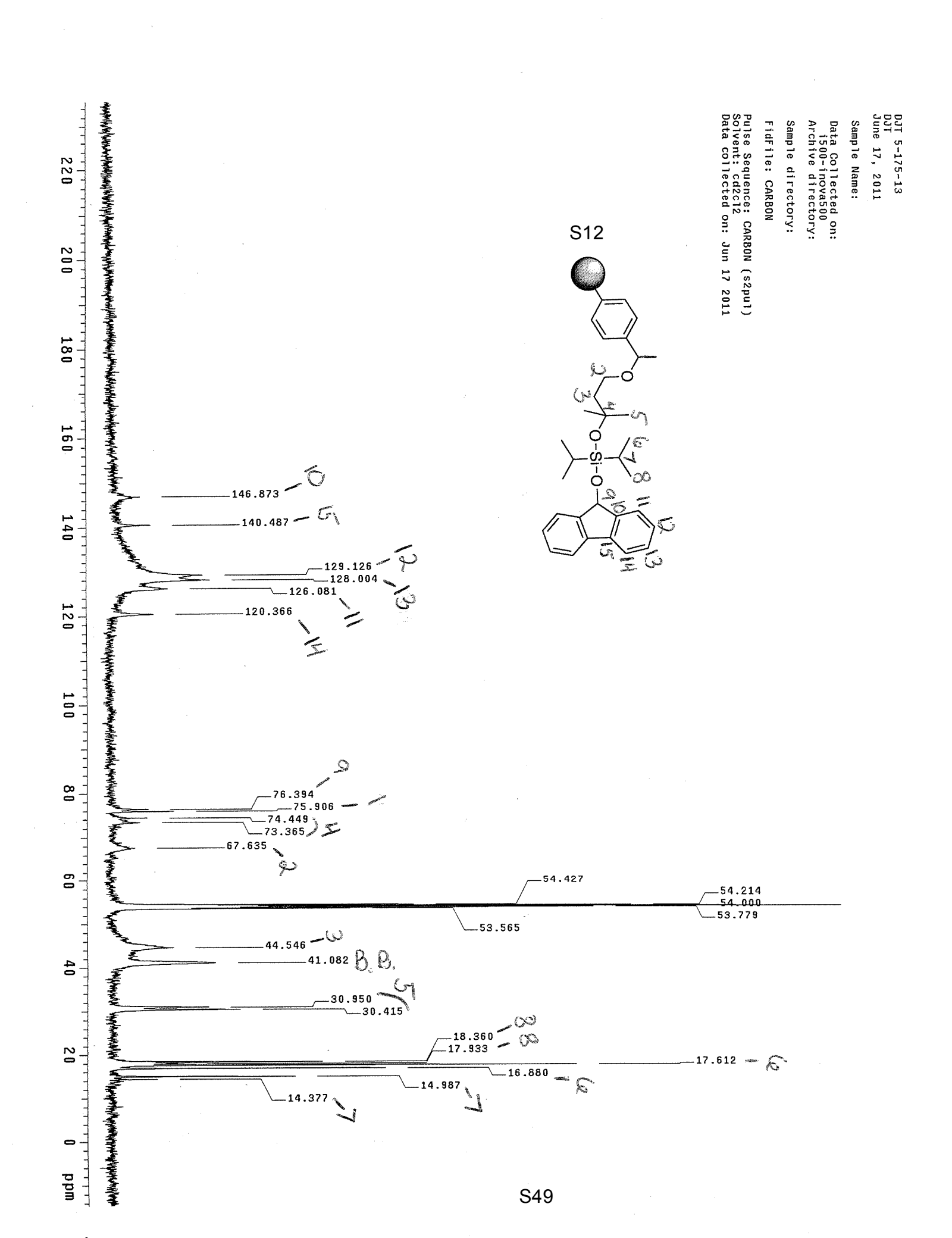
FidFile: CARBON

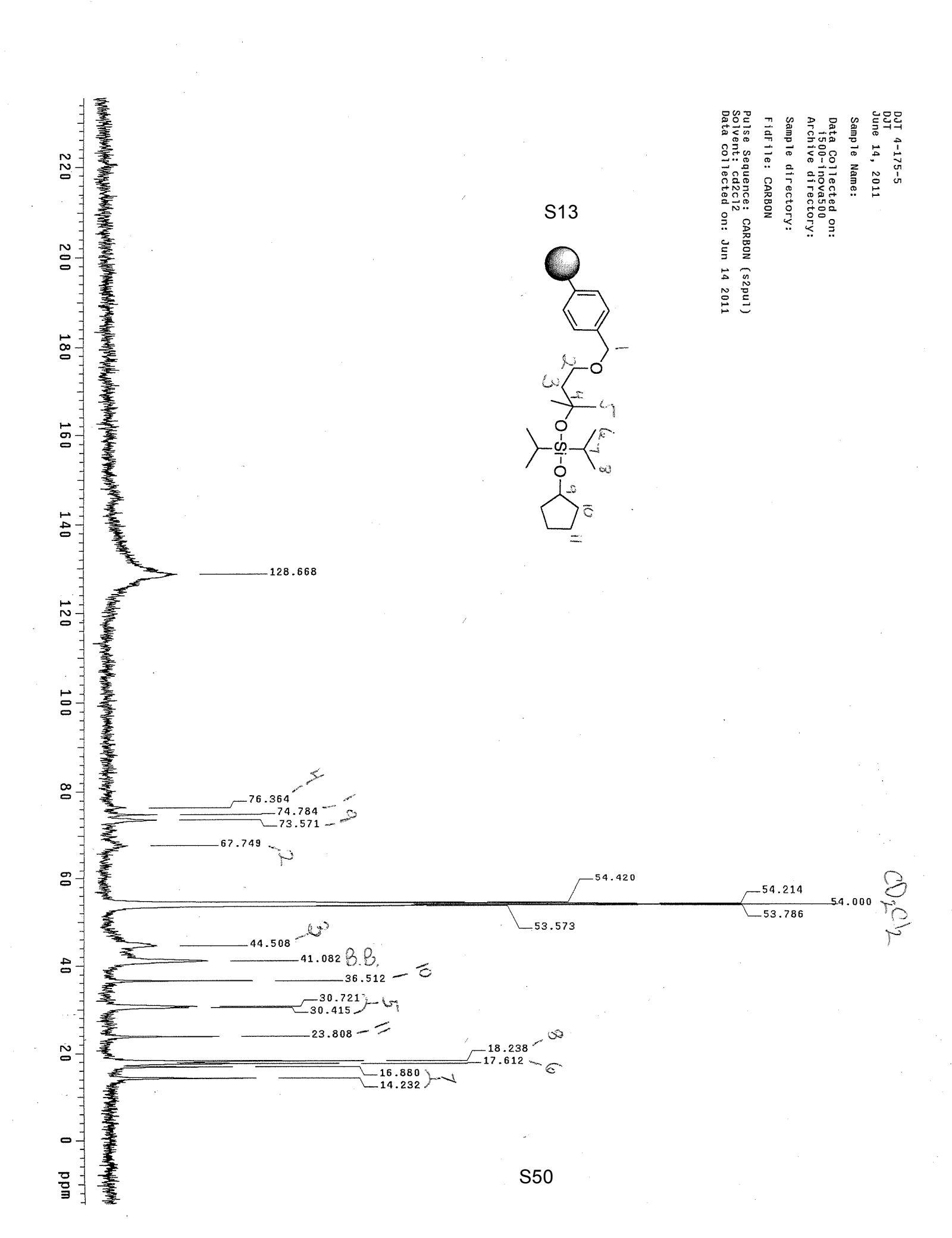
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011

S11



S48


DJT 5-175-13
DJT
June 17, 2011
Sample Name:
Data Collected on:
I500-inova500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 17 2011
S12
146.873
140.487
129.126
128.004
126.081
120.366
76.394
75.906
74.449
73.365
67.635
54.427
54.214
54.000
53.779
53.565
44.546
41.082
30.950
30.415
18.360
17.933
17.612
16.880
14.987
14.377
220
200
180
160
140
120
100
80
60
40
20
0
ppm


DJT 4-175-5
DJT
June 14, 2011
Sample Name:
Data Collected on:
1500-Inova500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011
S13
128.668
76.364
74.784
73.571
67.749
54.420
54.214
54.000
53.786
53.573
44.508
41.082
36.512
30.721
30.415
23.808
18.238
17.612
16.880
14.232
CD2Cl2
B.B.
220
200
180
160
140
120
100
80
60
40
20
0
ppm

DJT 4-175-6
DJT
June 14, 2011

Sample Name:

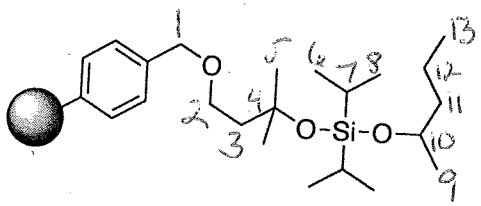
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011

S14



S51

DJT 4-175-4
DJT
June 14, 2011

Sample Name:

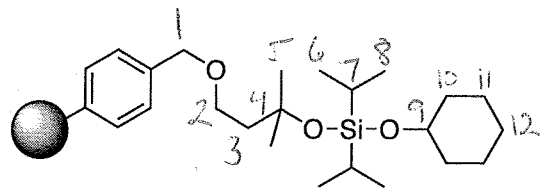
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011

S15



S52

DJT 4-175-7
DJT
June 14, 2011

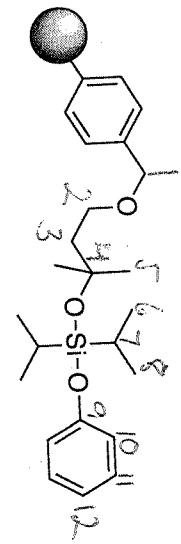
Sample Name:

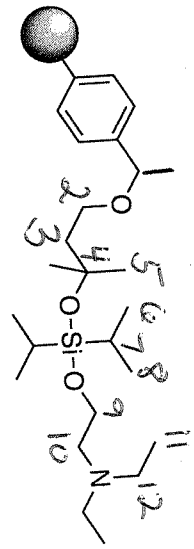
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: DJT4-175-7

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011





DJT 4-175-14
DJT
June 17, 2011

Sample Name:

Data Collected on:
i500-Inova500
Archive directory:

Sample directory:

FidFile: DJT4-175-14

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 17 2011

128.286
107.113
73.716
67.917
62.004
54.427
54.214
54.000
53.779
53.565
46.431
44.852
41.067
39.495
30.736
18.207
13.957

ppm

DJT 4-175-12
DJT
June 17, 2011

Sample Name:

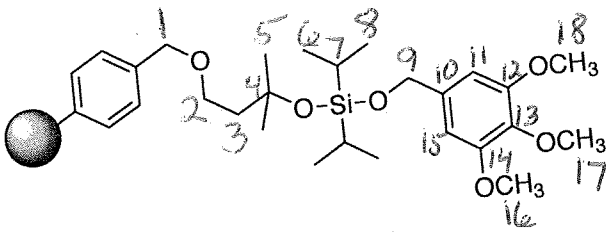
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 17 2011

S18



S55

DJT 4-175-10
DJT
June 17, 2011

Sample Name:

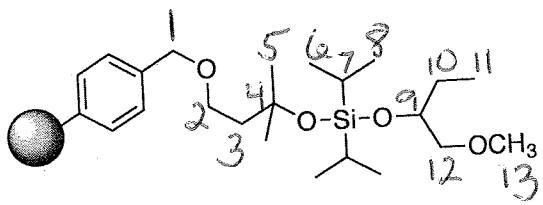
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

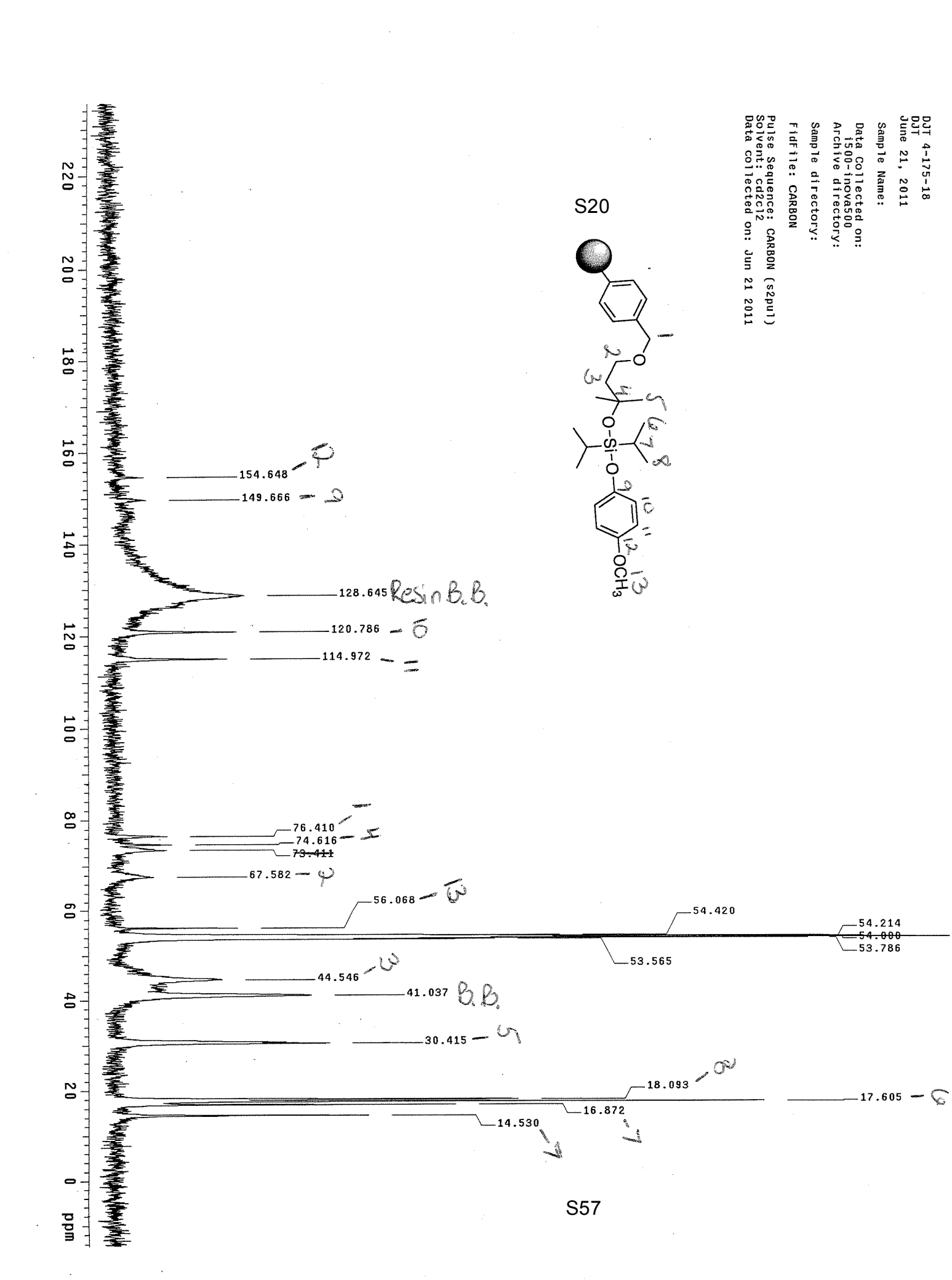
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 17 2011

S19



S56


DJT 4-175-18
DJT
June 21, 2011
Sample Name:
Data Collected on:
i500-inova500
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011
S20
154.648
149.666
128.645
Resin B.B.
120.786
114.972
76.410
74.616
73.411
67.582
56.068
54.420
54.214
54.000
53.786
53.565
44.546
41.037
B.B.
30.415
18.093
17.605
16.872
14.530
220
200
180
160
140
120
100
80
60
40
20
0
ppm

DJT 4-175-19
DJT
June 21, 2011

Sample Name:

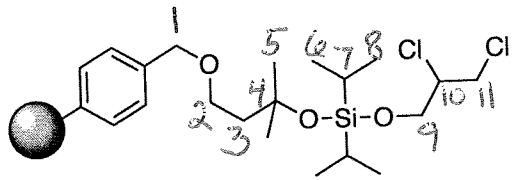
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011

S21



S58

DJT 4-175-11
DJT
June 17, 2011

Sample Name:

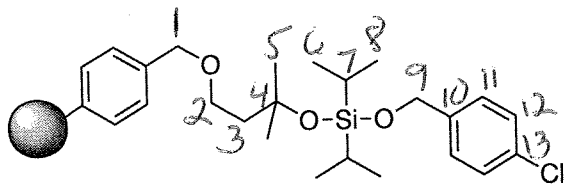
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 17 2011

S22



S59

DJT 4-175-21
DJT
June 21, 2011

Sample Name:

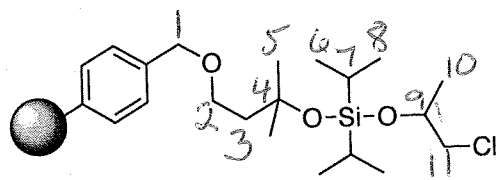
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

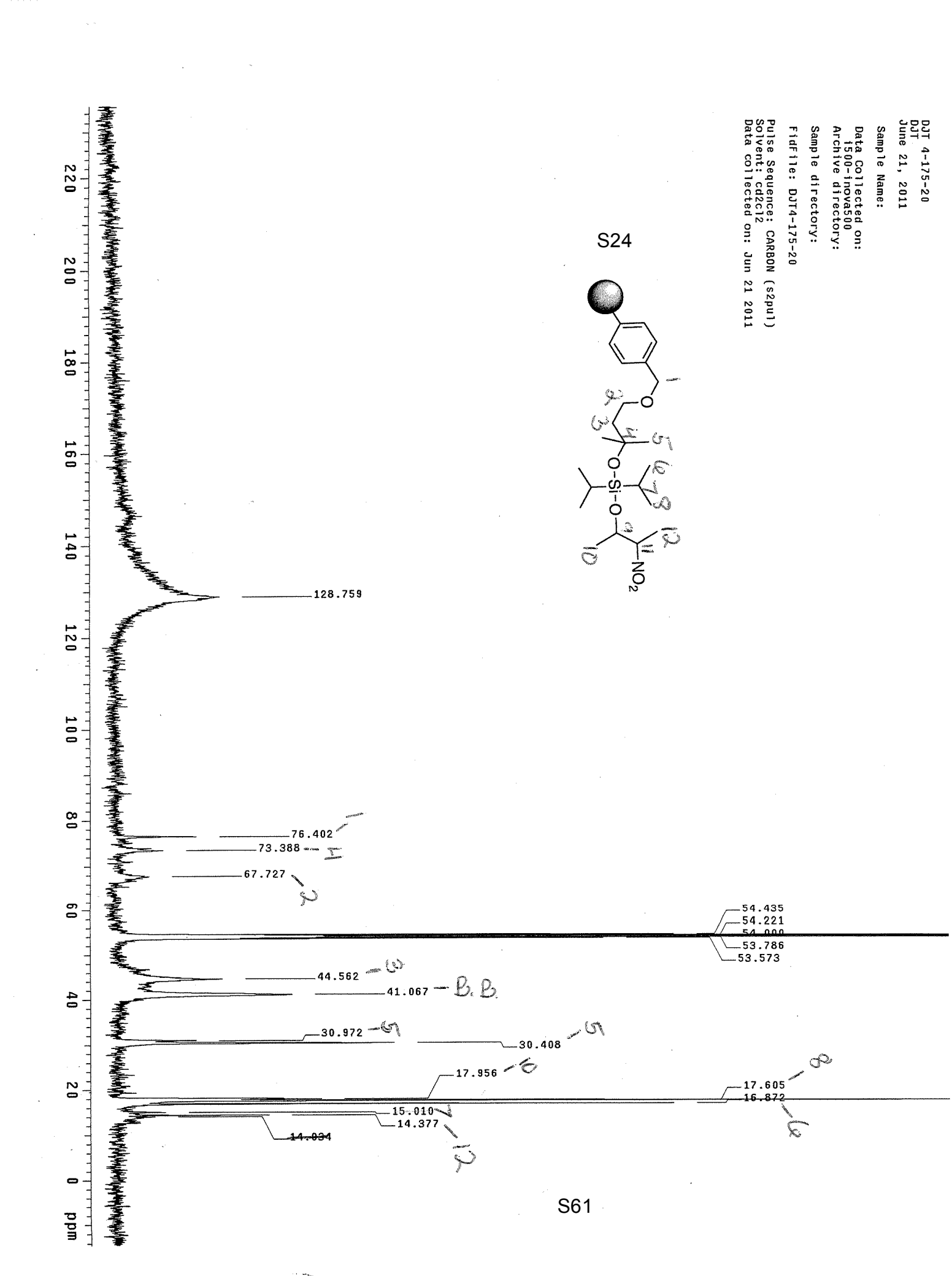
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011

S23



S60


DJT 4-175-20
DJT
June 21, 2011
Sample Name:
Data Collected on:
i500-inova500
Archive directory:
Sample directory:
FidFile: DJT4-175-20
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 21 2011
S24
128.759
76.402
73.388
67.727
54.435
54.221
53.786
53.573
44.562
41.067
30.972
30.408
17.956
17.605
16.872
15.010
14.377
14.034
220
200
180
160
140
120
100
80
60
40
20
0
ppm

DJT 4-175-8
DJT
June 14, 2011

Sample Name:

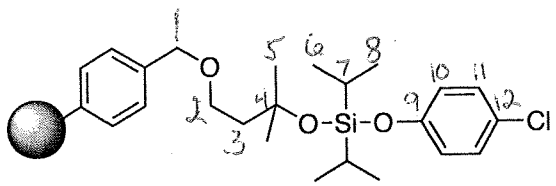
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

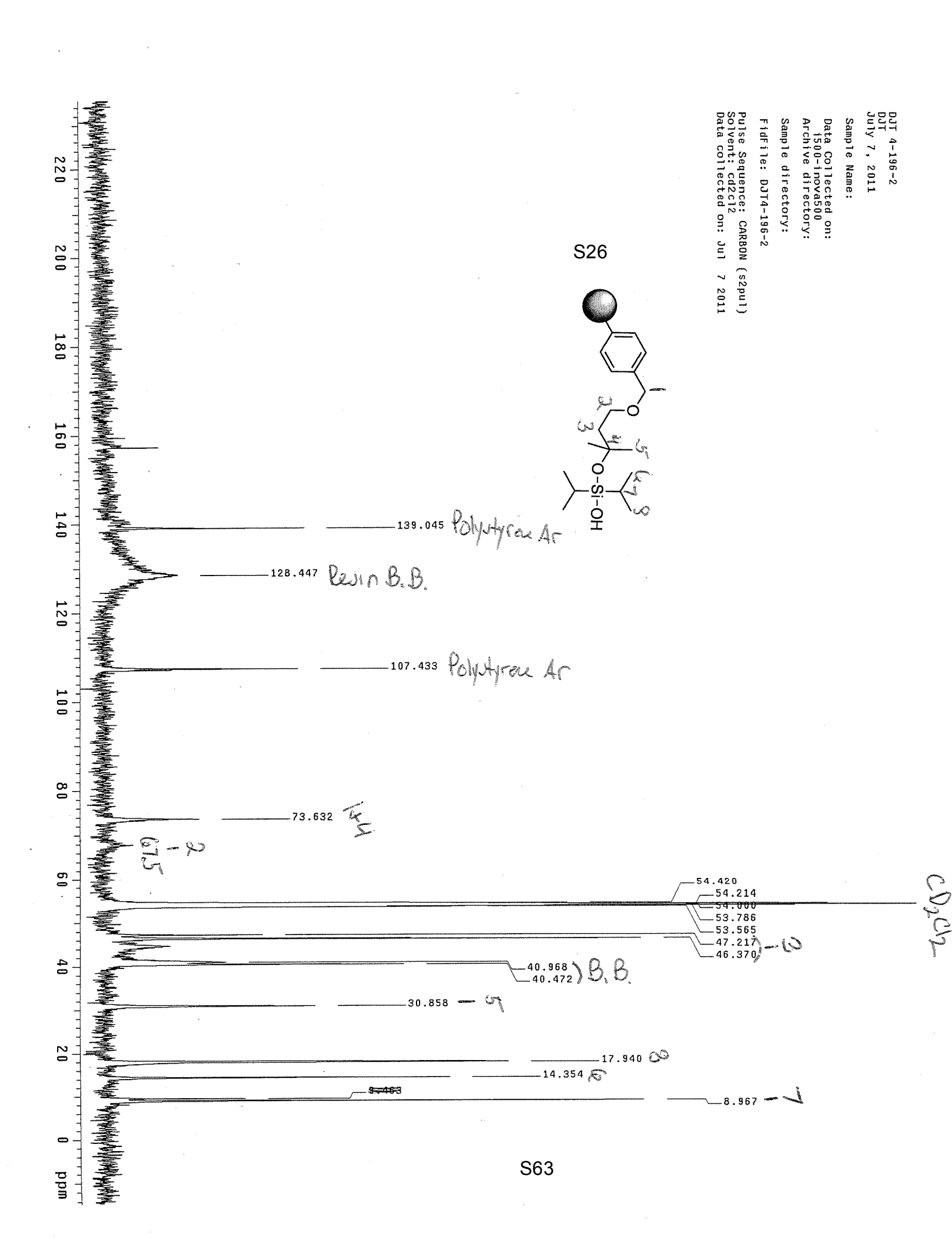
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jun 14 2011

S25



S62


DJT 4-196-2
DJT
July 7, 2011
Sample Name:
Data Collected on:
1500-inova500
Archive directory:
Sample directory:
FidFile: DJT4-196-2
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Jul 7 2011
S26
139.045 Polystyrene Ar
128.447 Resin B.B.
107.433 Polystyrene Ar
73.632
54.420
54.214
54.000
53.786
53.565
47.217
46.370
40.968
40.472
30.858
17.940
14.354
8.967
CD2Cl2
B.B.
ppm

DJT 2-24
DJT
August 27, 2009

Sample Name:

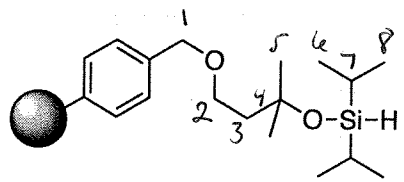
Data Collected on:
vxr400.chem.indiana.edu-inova400
Archive directory:

Sample directory:

Fidfile: DJT2-24-C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 27 2009

S27



S64

DJT 4-250-B
DJT
August 24, 2011

Sample Name:

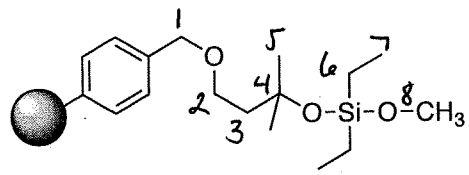
Data Collected on:
i500-inova500
Archive directory:

Sample directory:

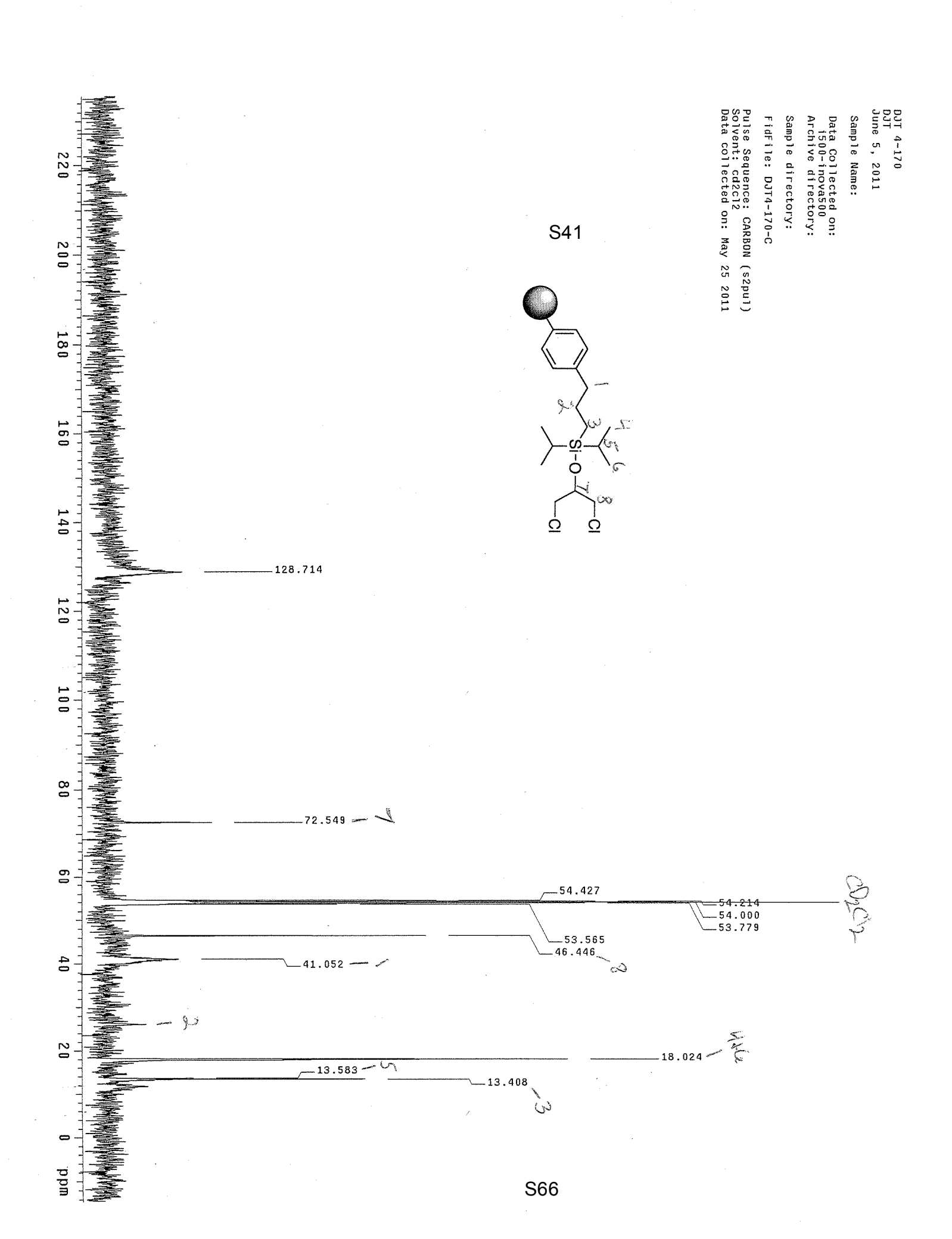
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: Aug 24 2011

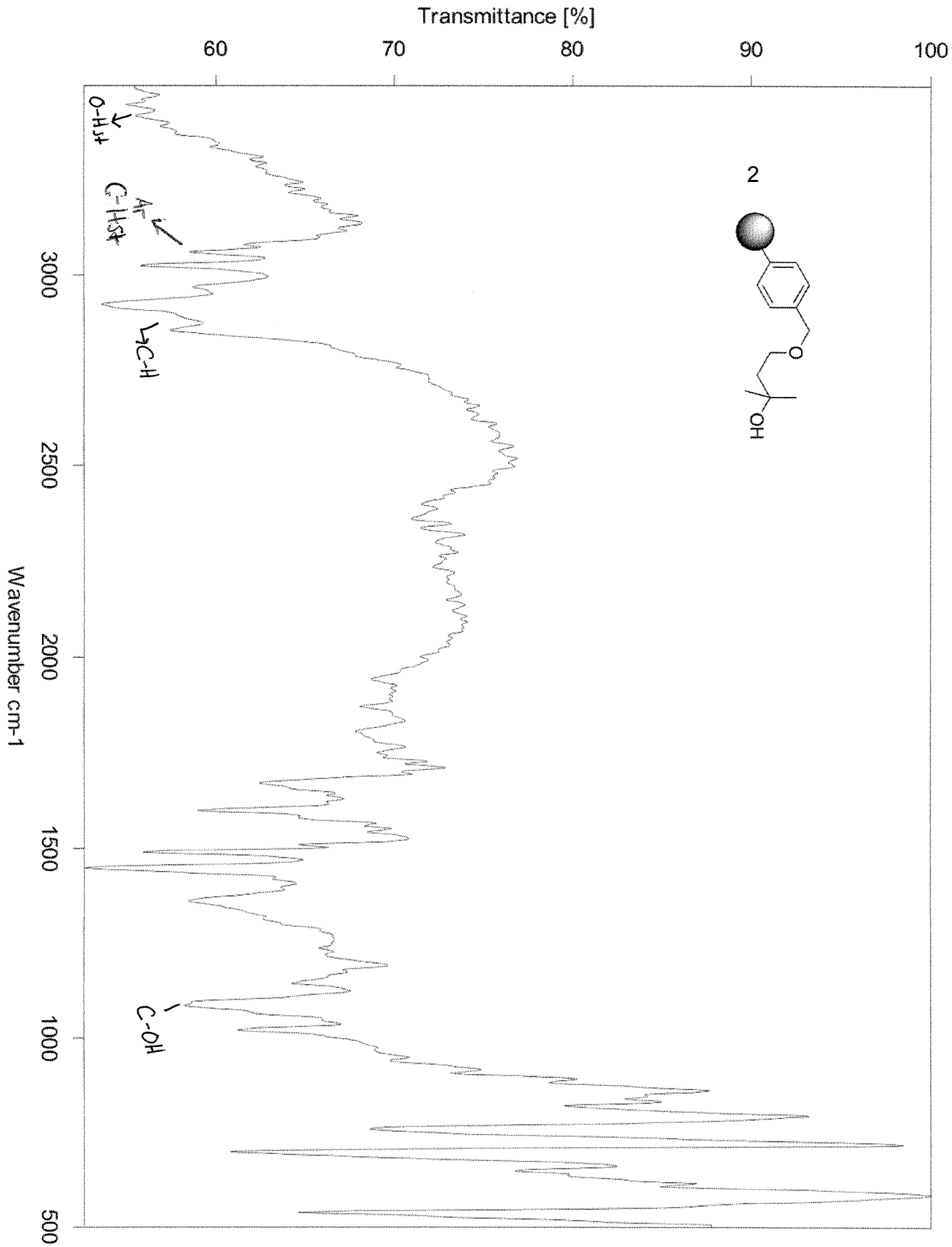
S40

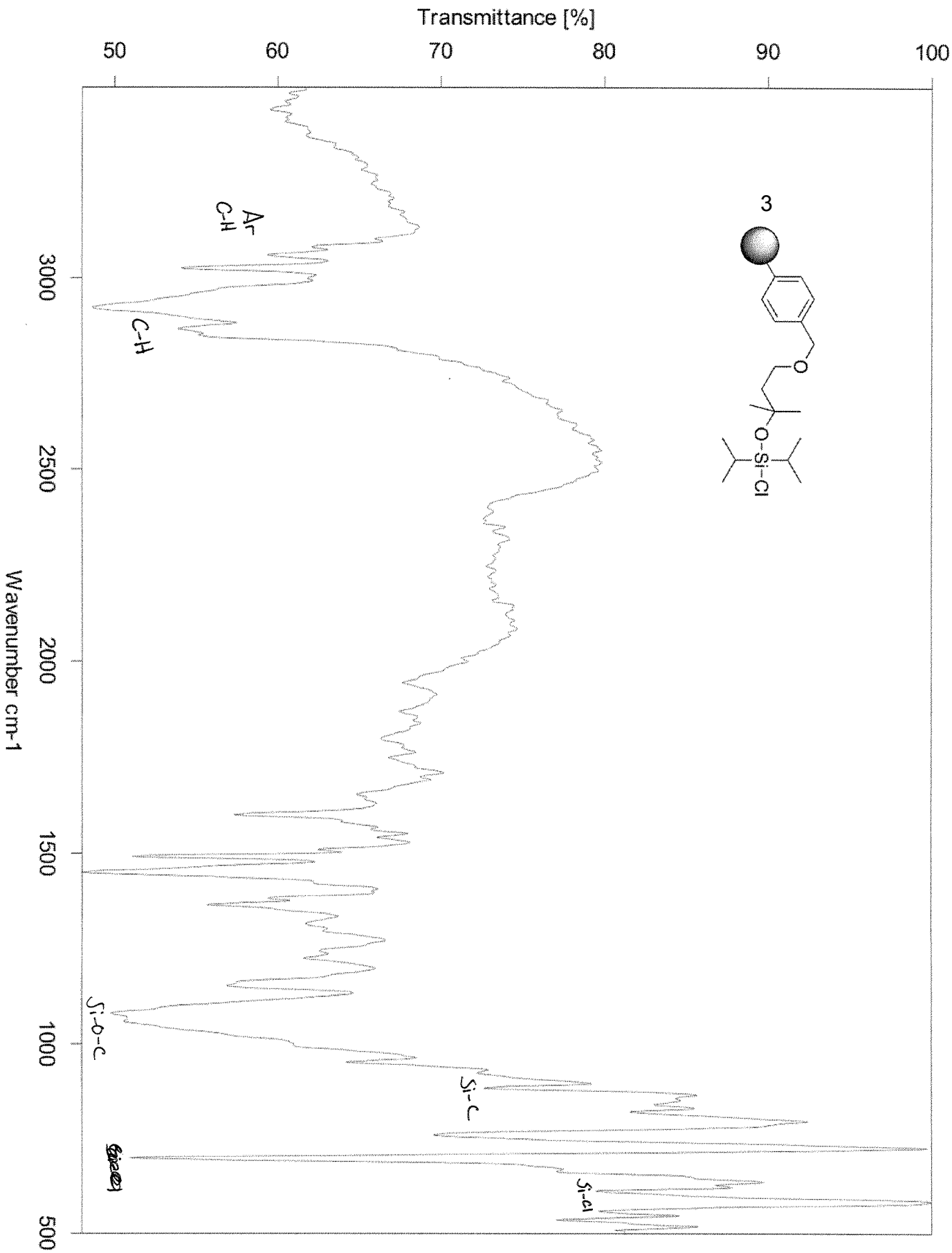


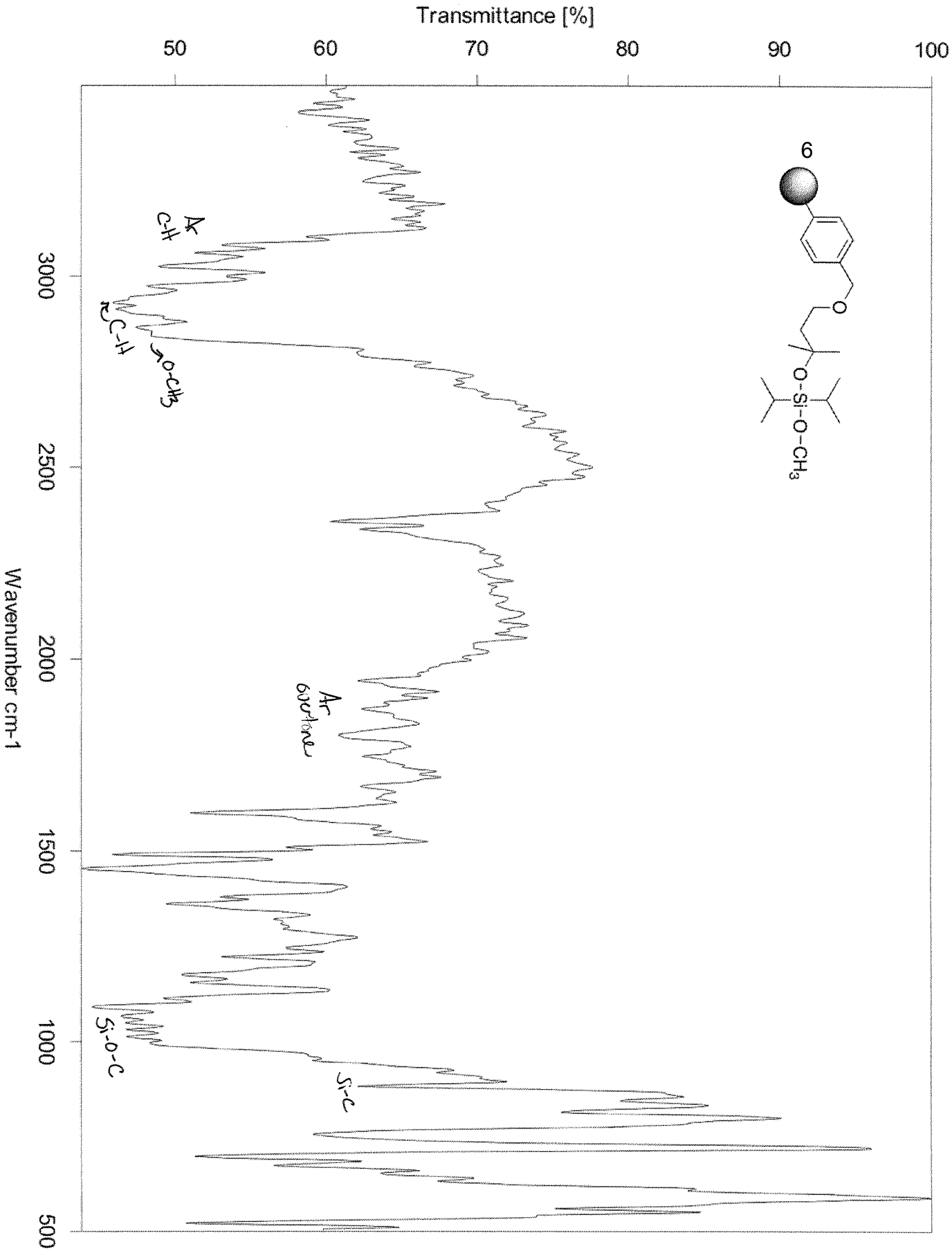
S65

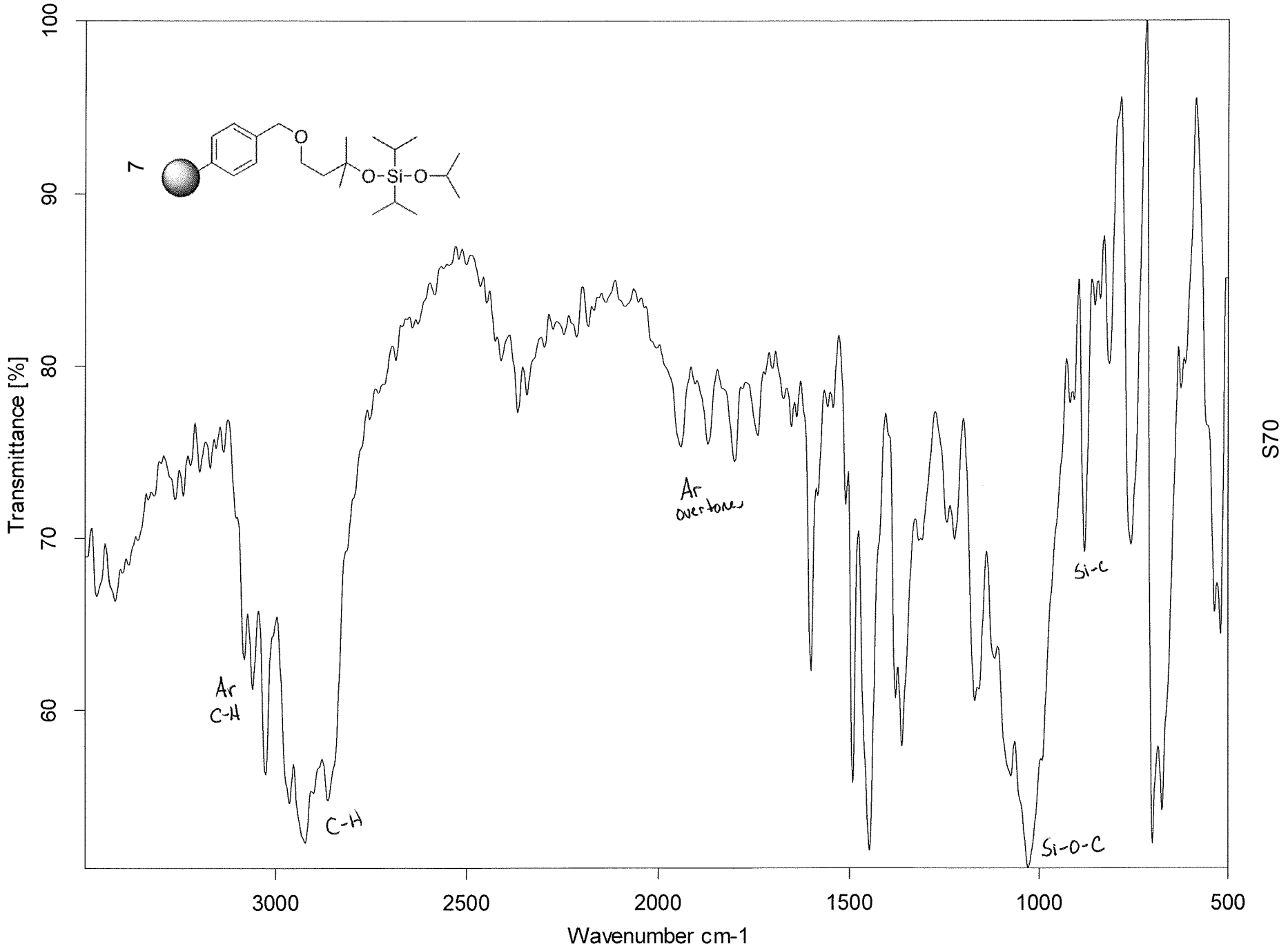

DJT 4-170
DJT
June 5, 2011
Sample Name:
Data Collected on:
i500-inova500
Archive directory:
Sample directory:
FidFile: DJT4-170-C
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: May 25 2011
Si
O
Cl
Cl
220
200
180
160
140
120
100
80
60
40
20
0
ppm
128.714
72.549
54.427
54.214
54.000
53.779
53.565
46.446
41.052
18.024
13.583
13.408

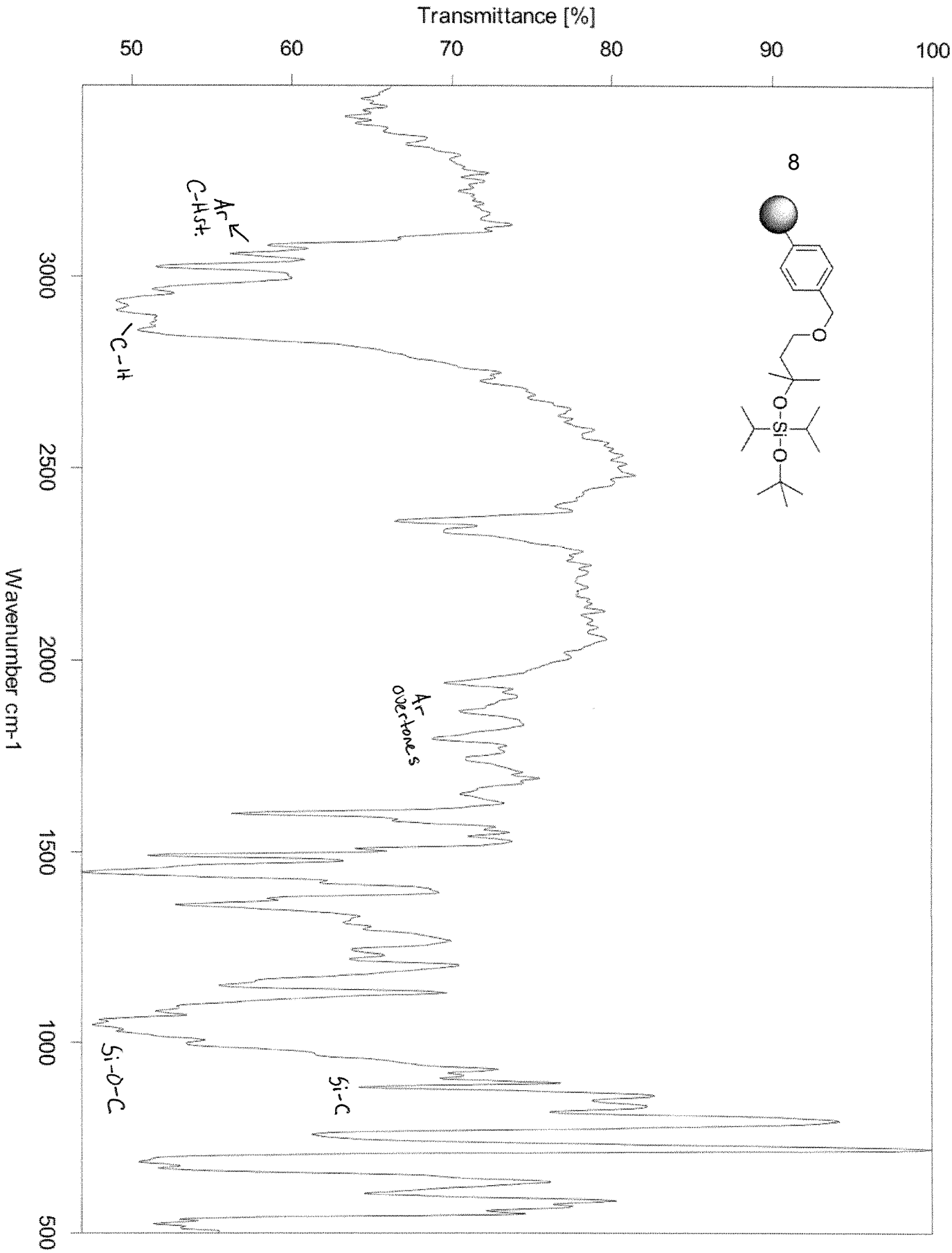
Appendix B. FT-IR (KBr pellet) of resins shown in Supporting Information Table S2.

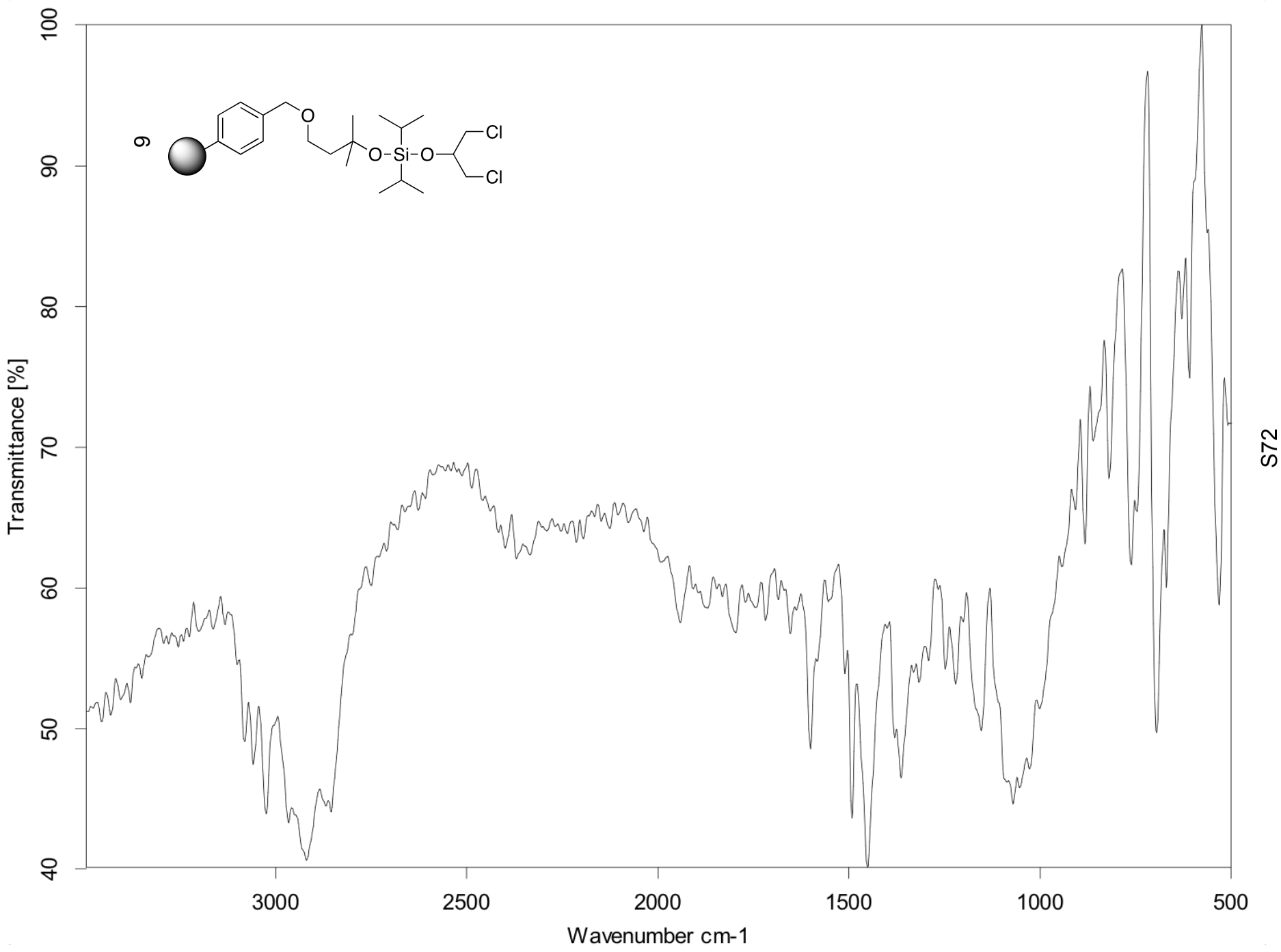


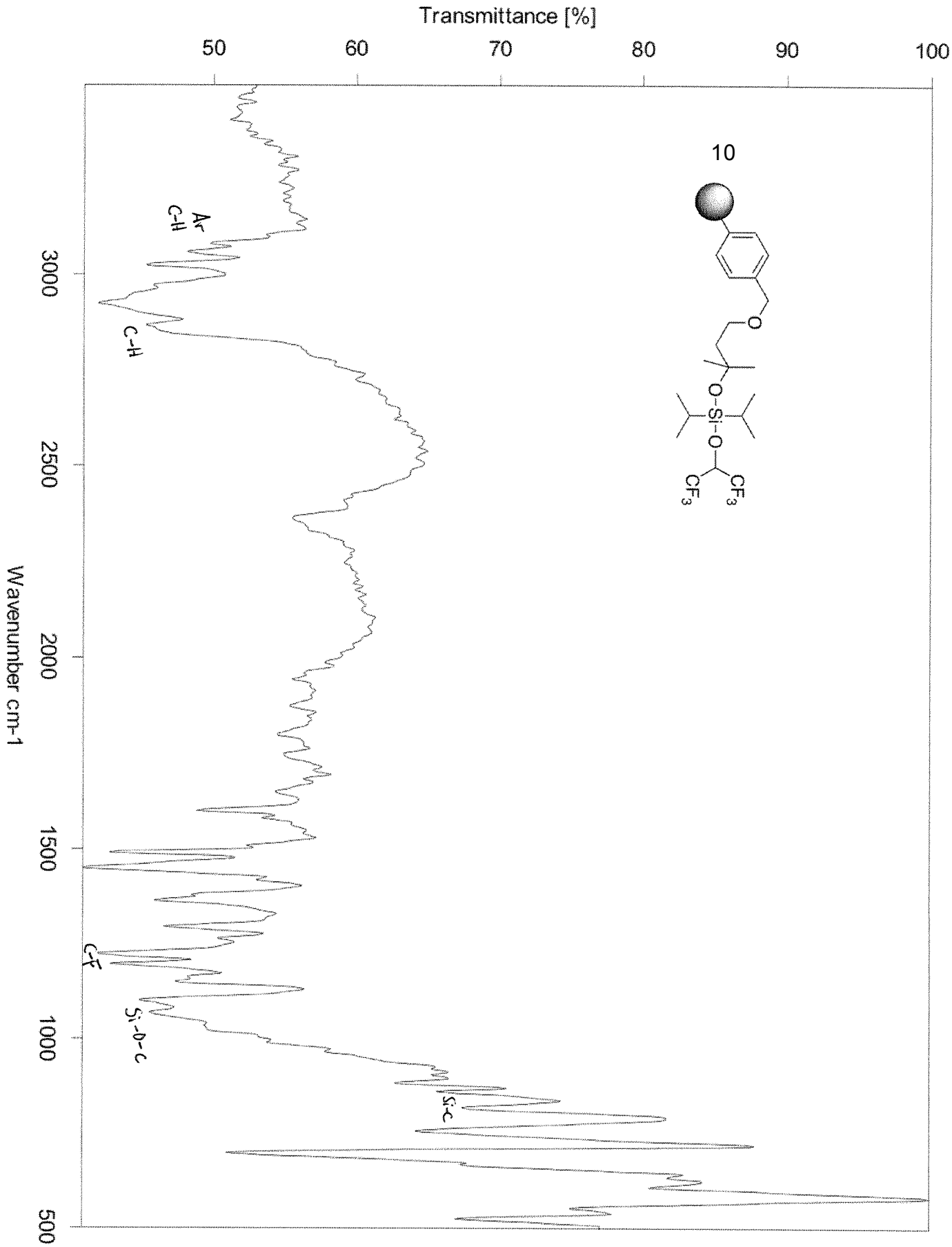

Transmittance [%]
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
Si-O-C
Si-C
Si-Cl
3
O
O-Si-Cl

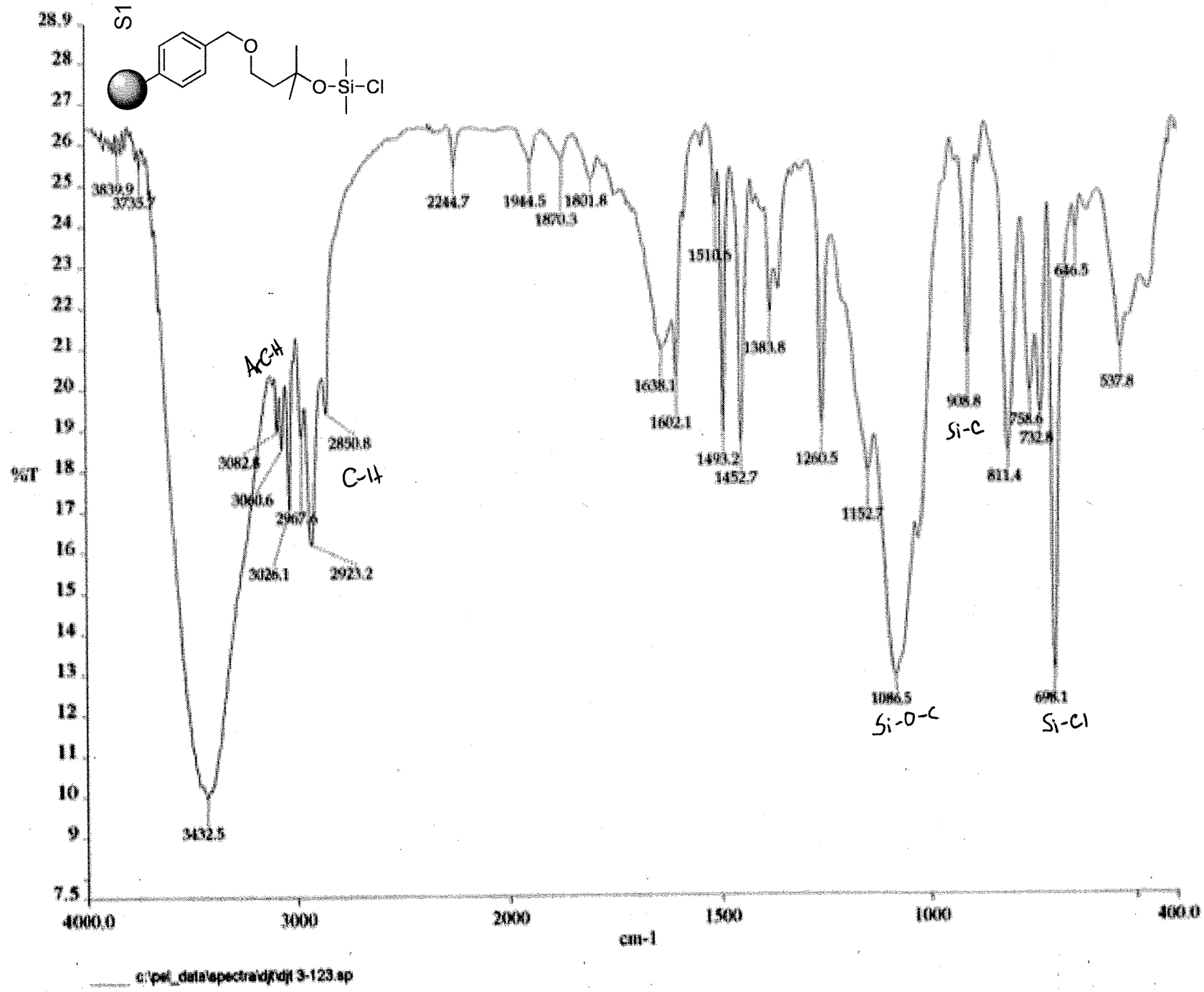

Transmittance [%]
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
O-CH3
Ar bonds
Si-O-C
Si-C
6
O
O-Si-O-CH3

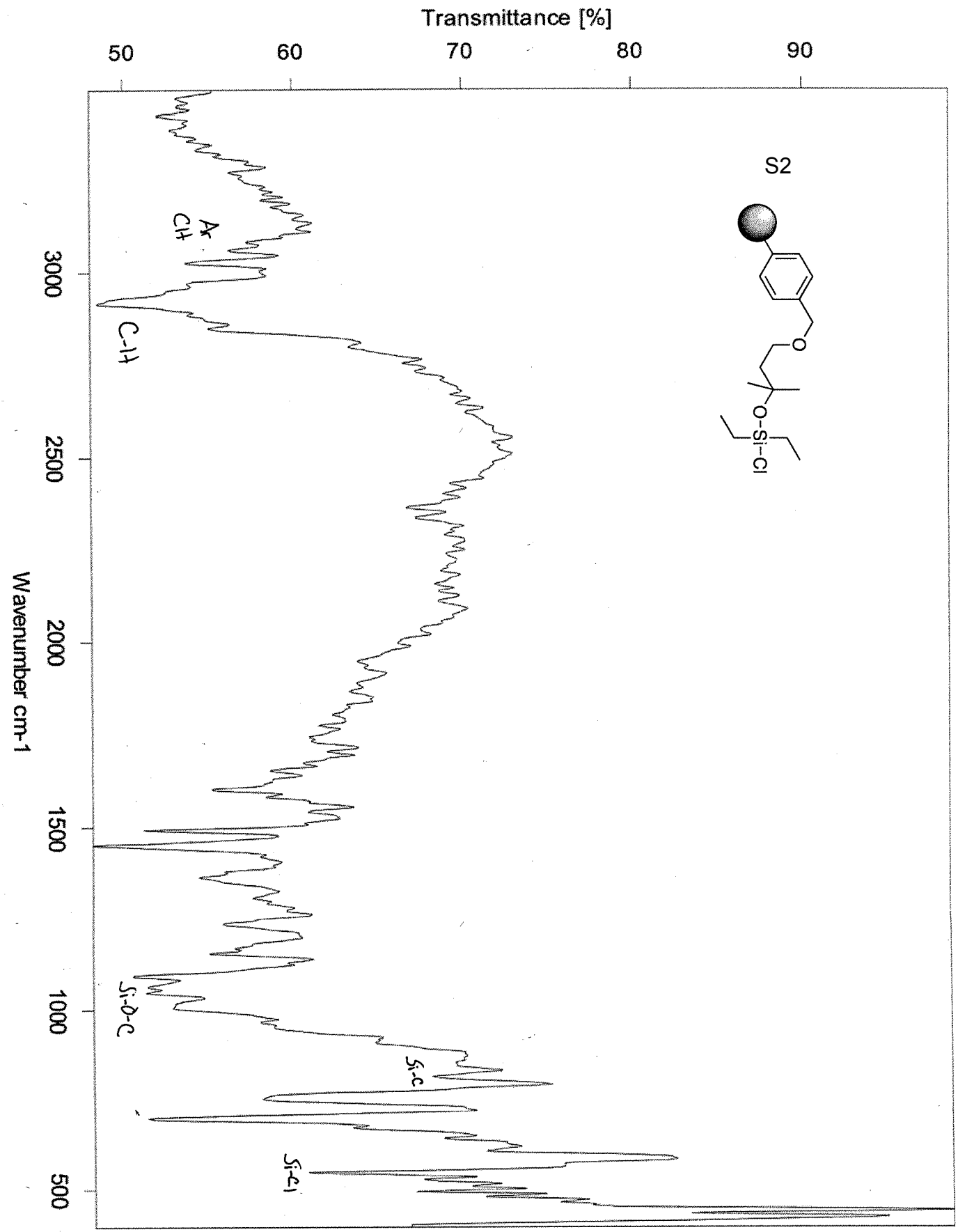

7
O
O-Si-O
Transmittance [%]
100
90
80
70
60
Ar
C-H
C-H
Ar
overtone
Si-C
Si-O-C
3000
2500
2000
1500
1000
500
Wavenumber cm-1
S70

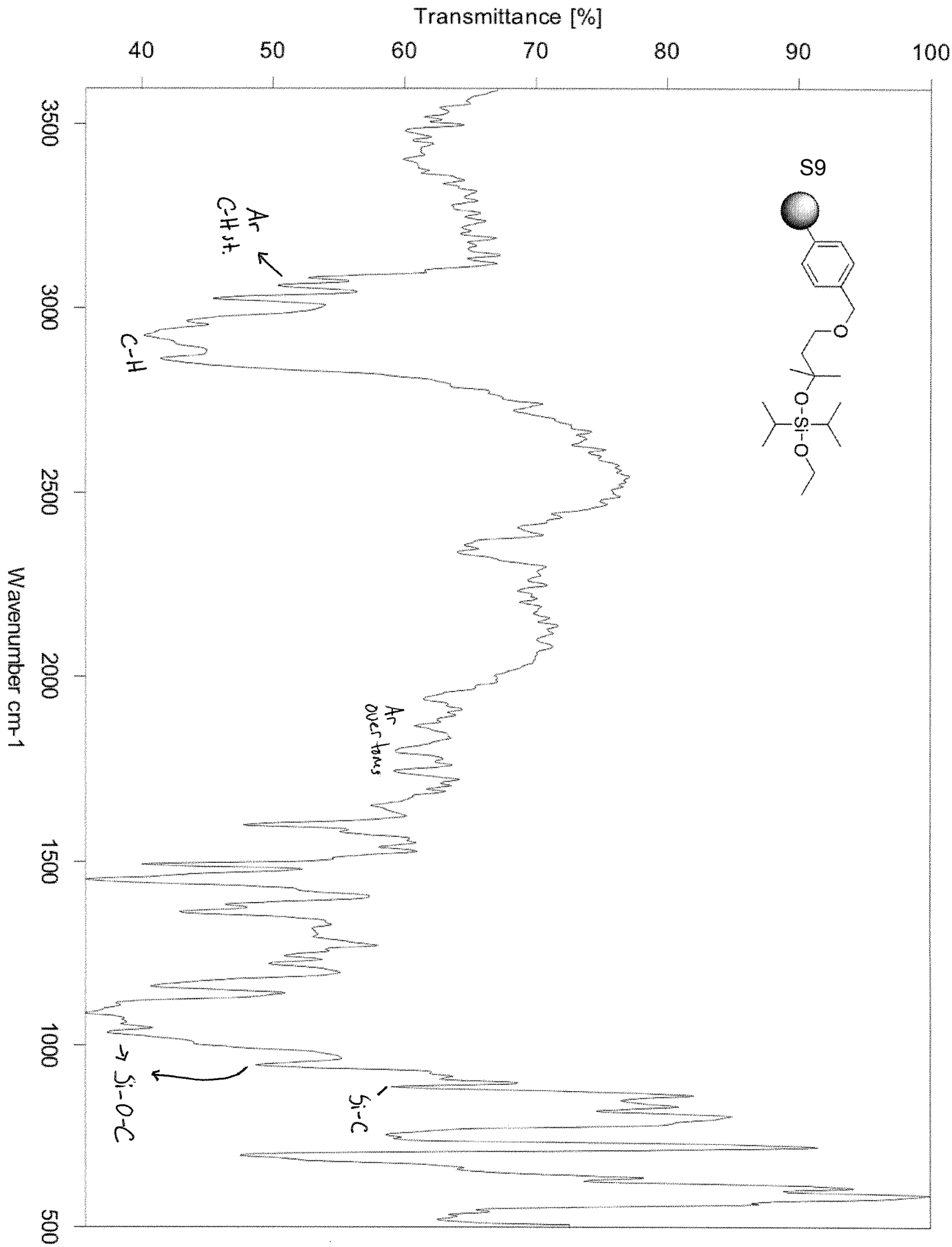

Transmittance [%]
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H st.
C-H
Ar overtones
Si-O-C
Si-C
8
O
O-Si-O

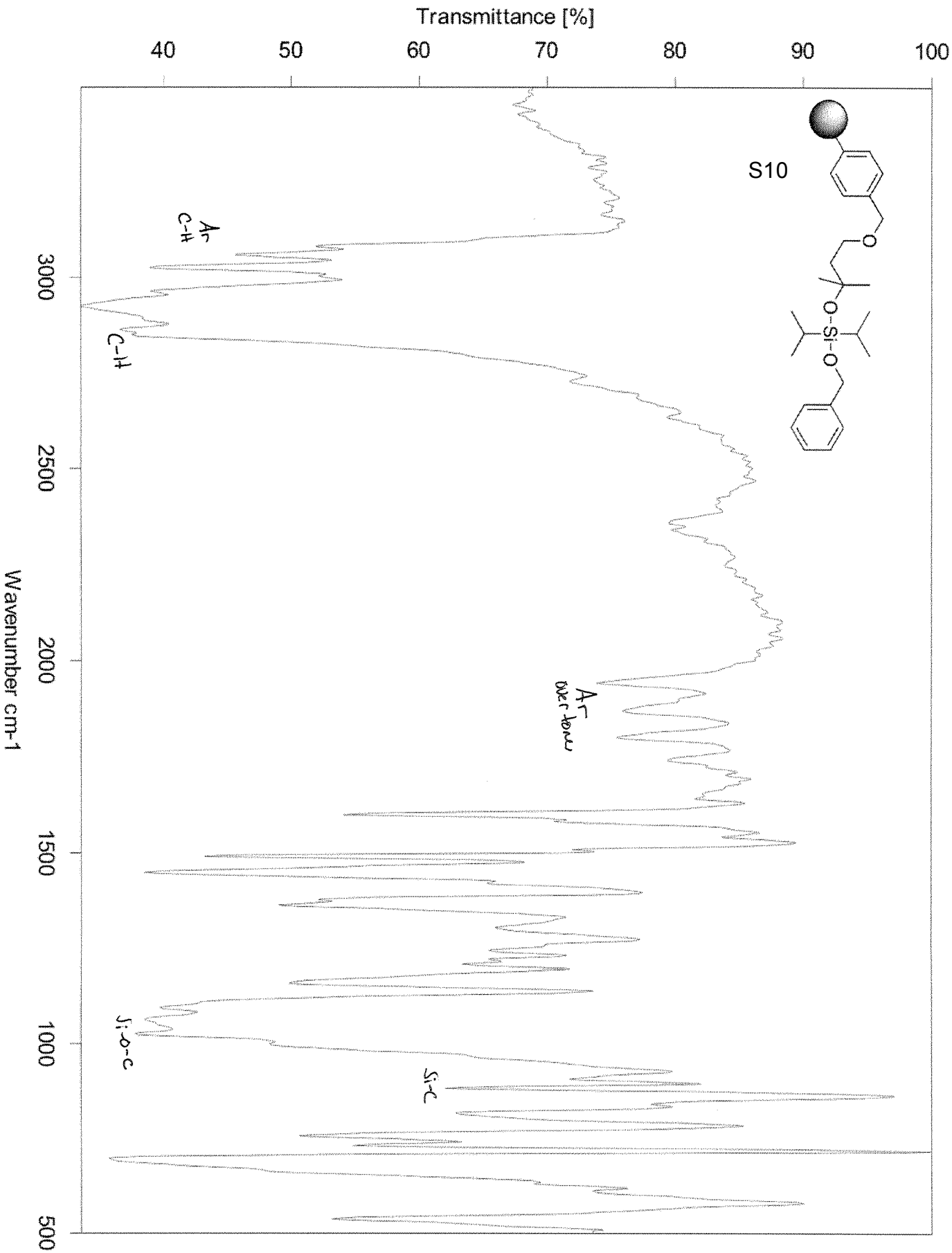

9
O
O-Si-O
Cl
Cl
Transmittance [%]
100
90
80
70
60
50
40
3000
2500
2000
1500
1000
500
Wavenumber cm-1
S72

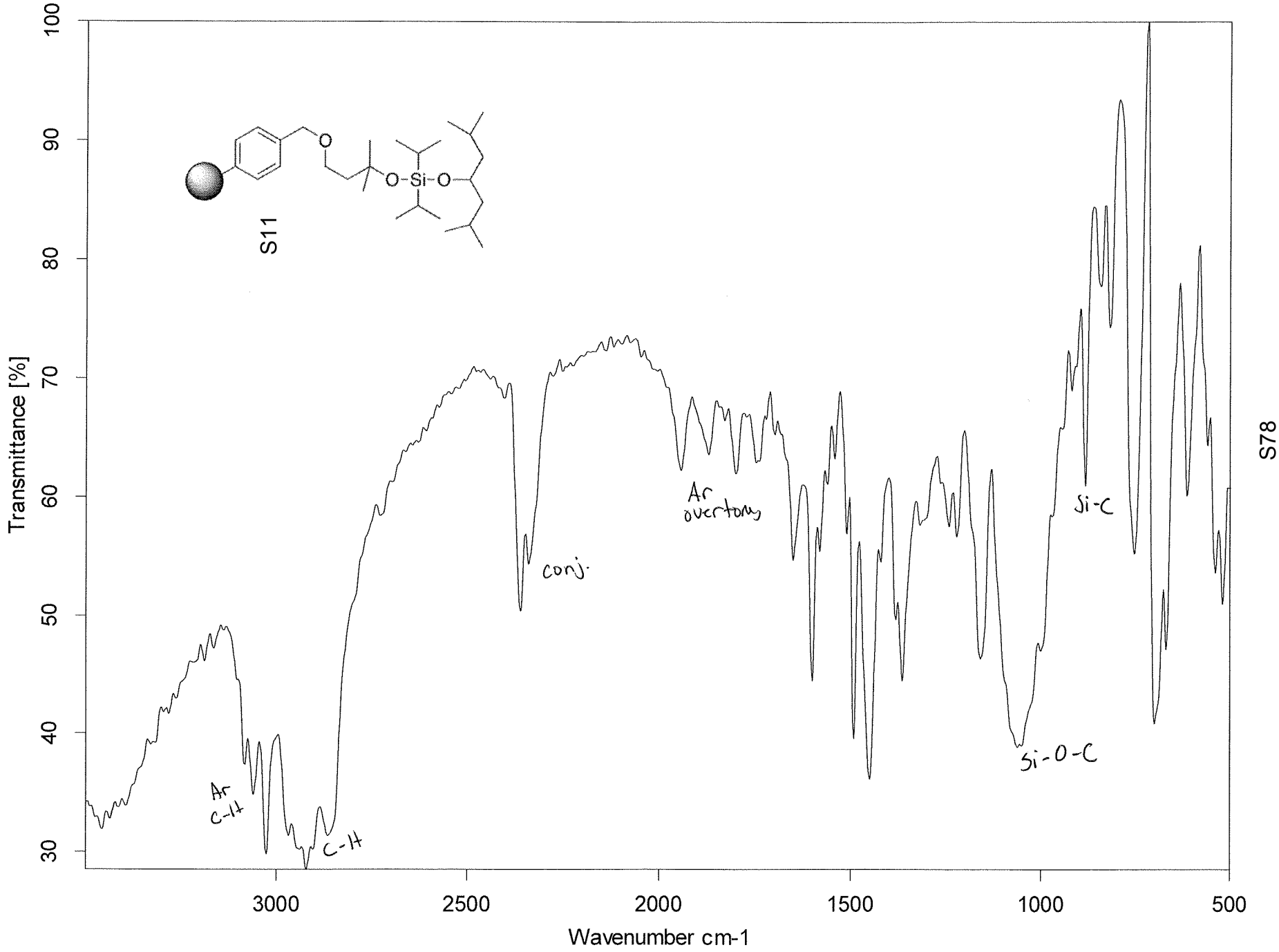

Transmittance [%]
50
60
70
80
90
100
10
Ar C-H
C-H
C-F
Si-O-C
Si-C
O
O-Si-O
CF3
CF3
Wavenumber cm-1
3000
2500
2000
1500
1000
500

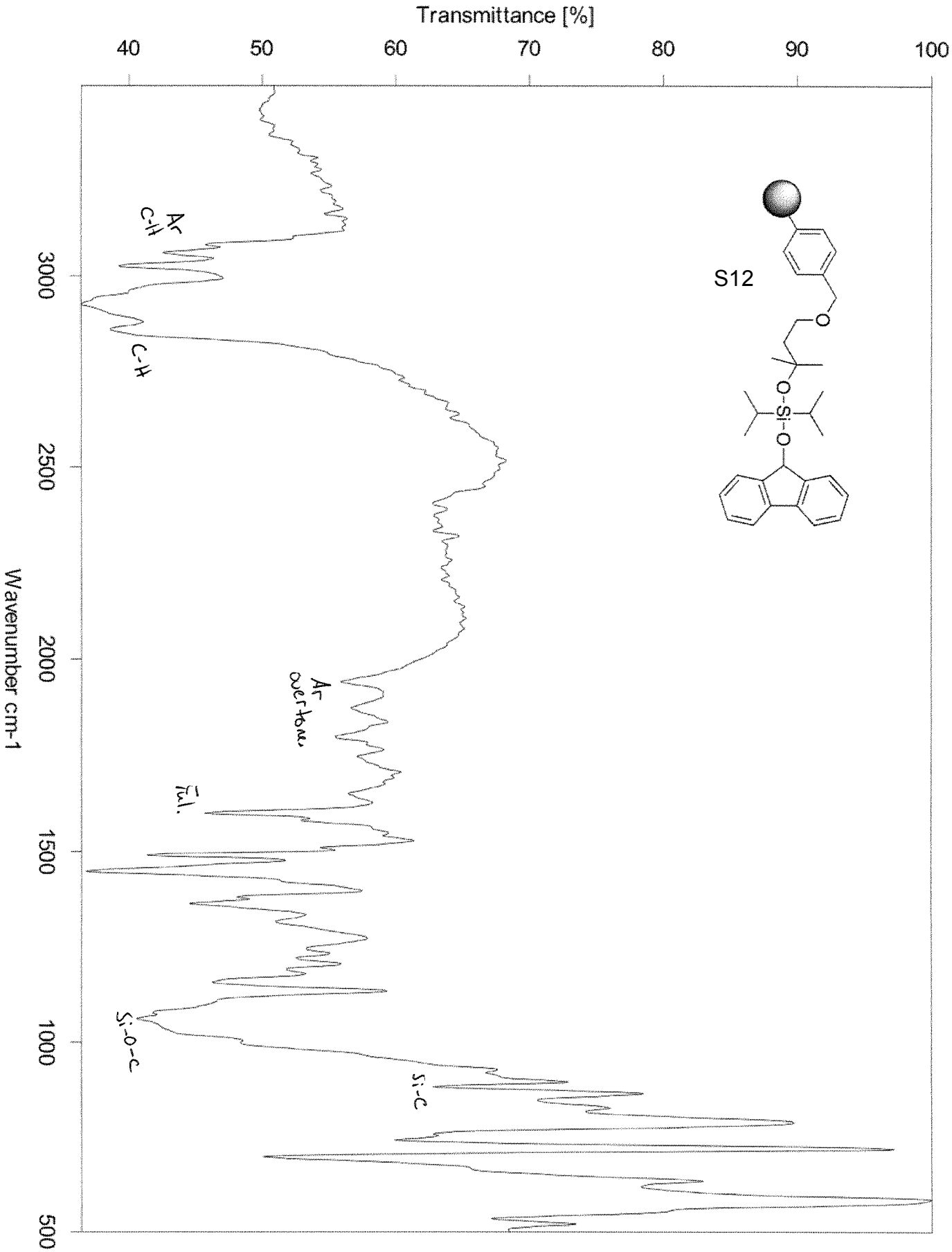

S1
O
O-Si-Cl
%T
cm-1
4000.0
3000
2000
1500
1000
400.0
3839.9
3735.7
3432.5
3082.8
3060.6
3026.1
2967.6
2923.2
2850.8
2244.7
1944.5
1870.3
1801.8
1638.1
1602.1
1510.6
1493.2
1452.7
1383.8
1260.5
1152.7
1086.5
908.8
811.4
758.6
732.8
698.1
646.5
537.8
Ac-H
C-H
Si-O-C
Si-C
Si-Cl
c:\pe_data\spectra\dj\ndj 3-123.sp

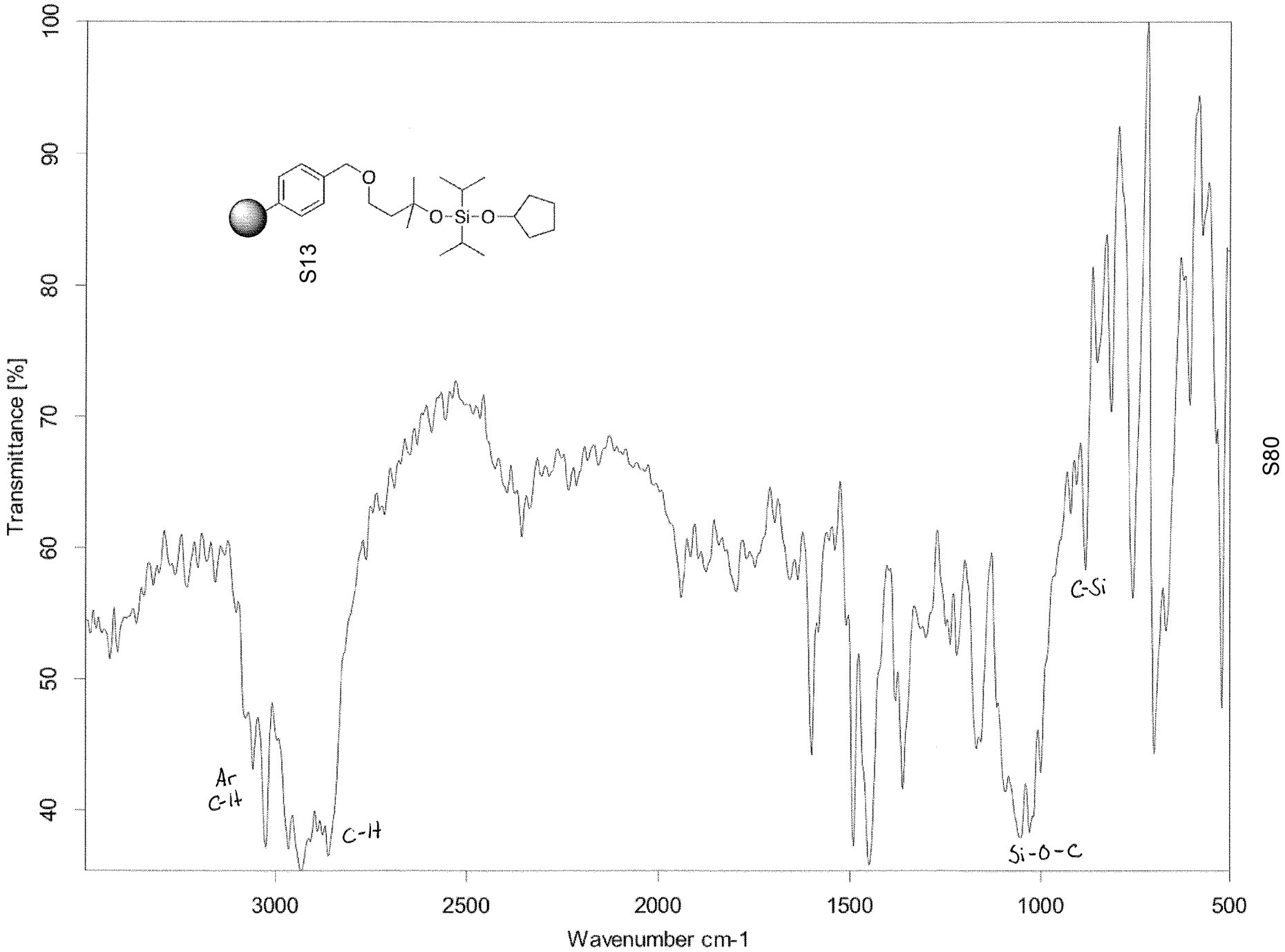

Transmittance [%]
50
60
70
80
90
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar CH
C-H
Si-O-C
Si-C
Si-Cl
S2
O
O-Si-Cl

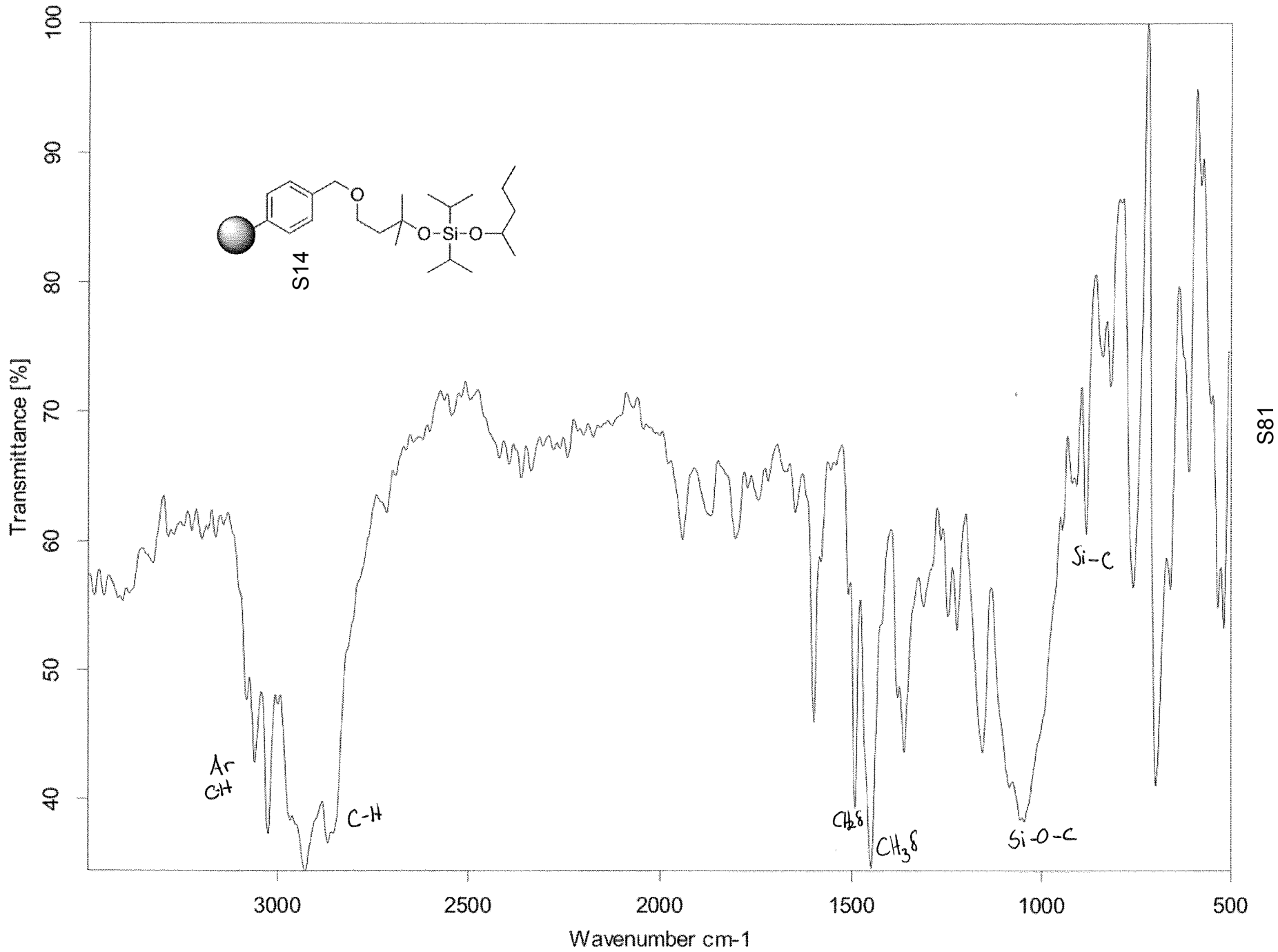

Transmittance [%]
40
50
60
70
80
90
100
Wavenumber cm-1
3500
3000
2500
2000
1500
1000
500
Ar C-H st.
C-H
Ar overtons
Si-O-C
Si-C
S9
O
O-Si-O

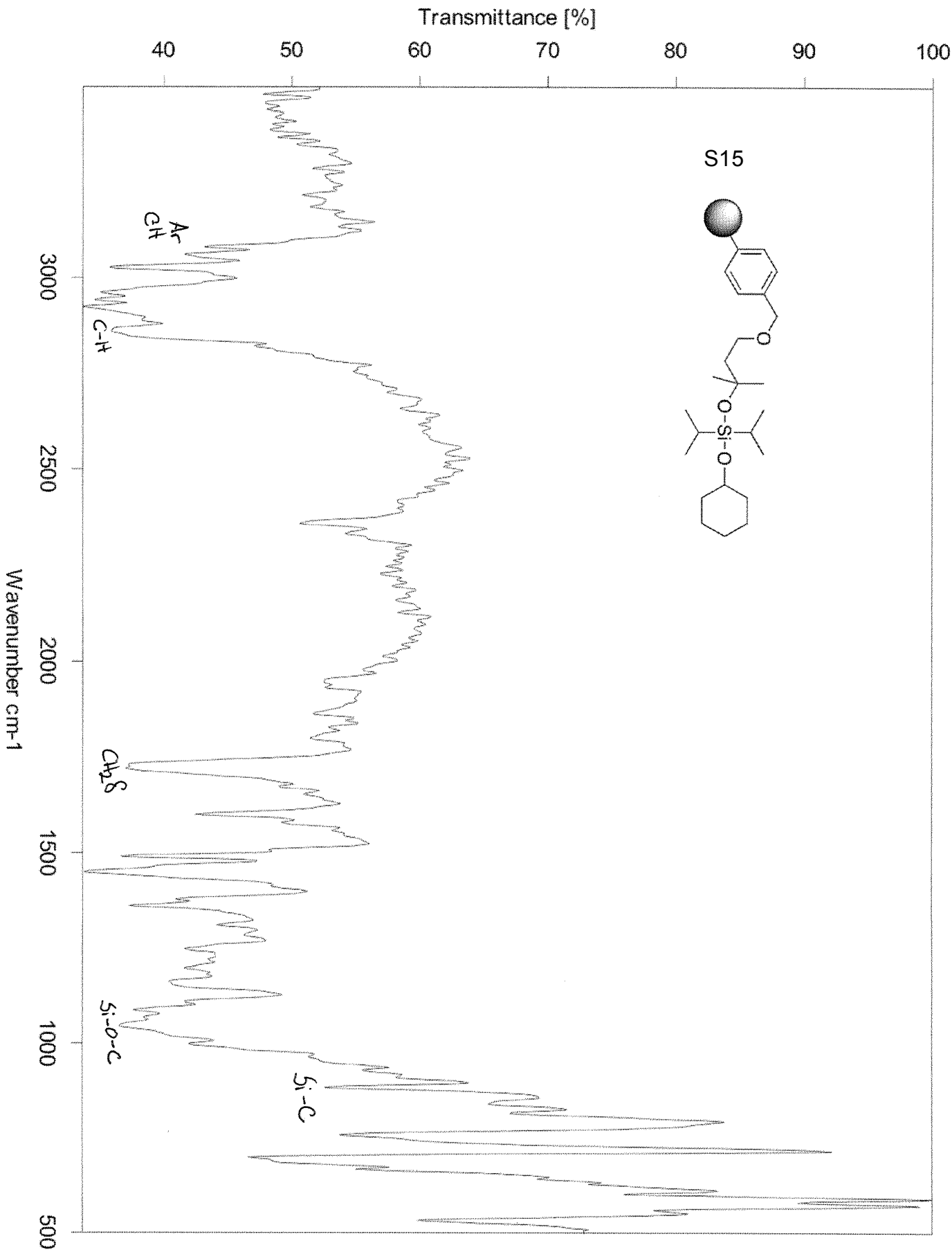

Transmittance [%]
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
S10
Ar C-H
C-H
Ar overtone
Si-O-C
Si-C

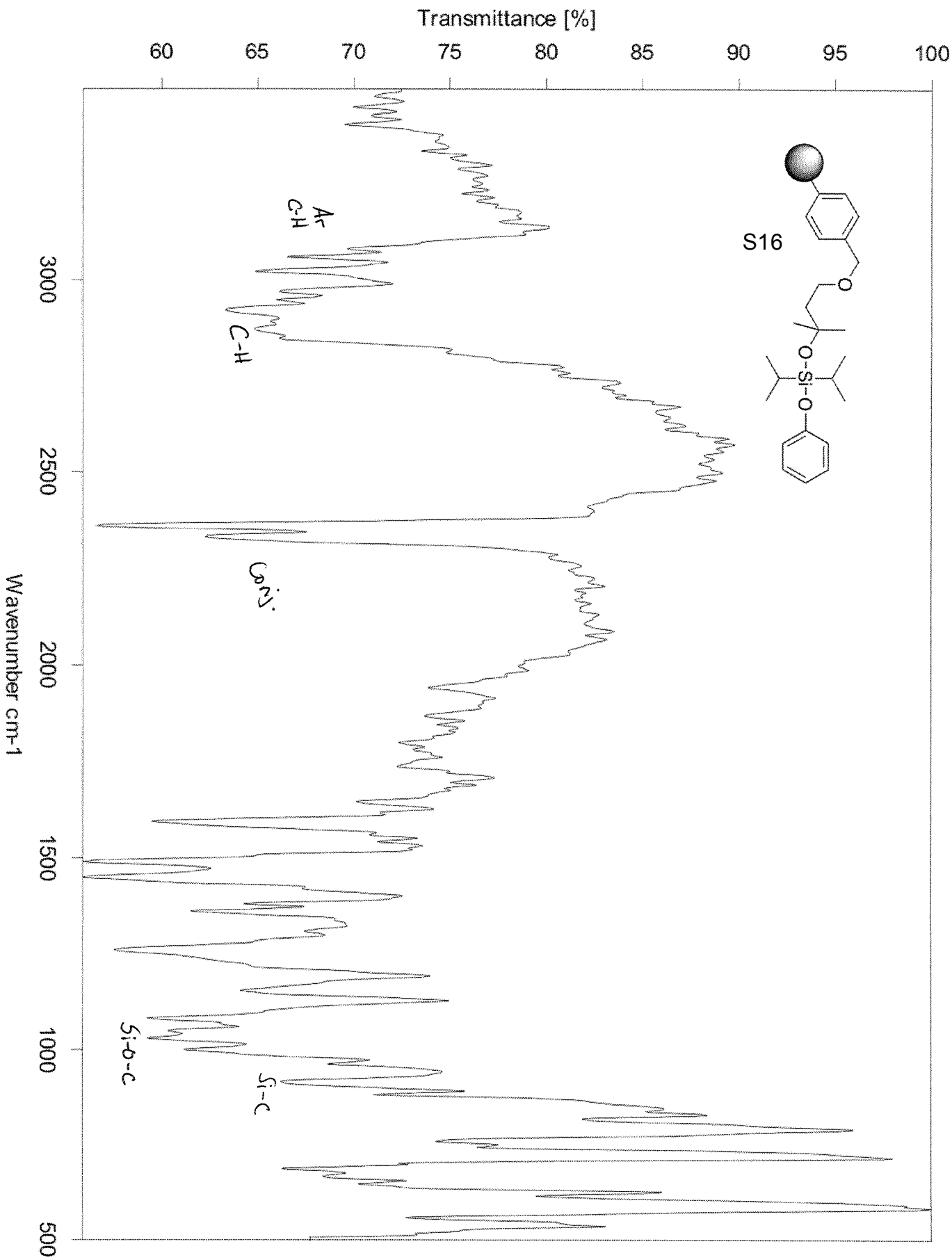

Transmittance [%]
100
90
80
70
60
50
40
30
3000
2500
2000
1500
1000
500
Wavenumber cm-1
S11
O
O-Si-O
Ar
C-H
C-H
conj.
Ar
overtone
Si-C
Si-O-C
S78

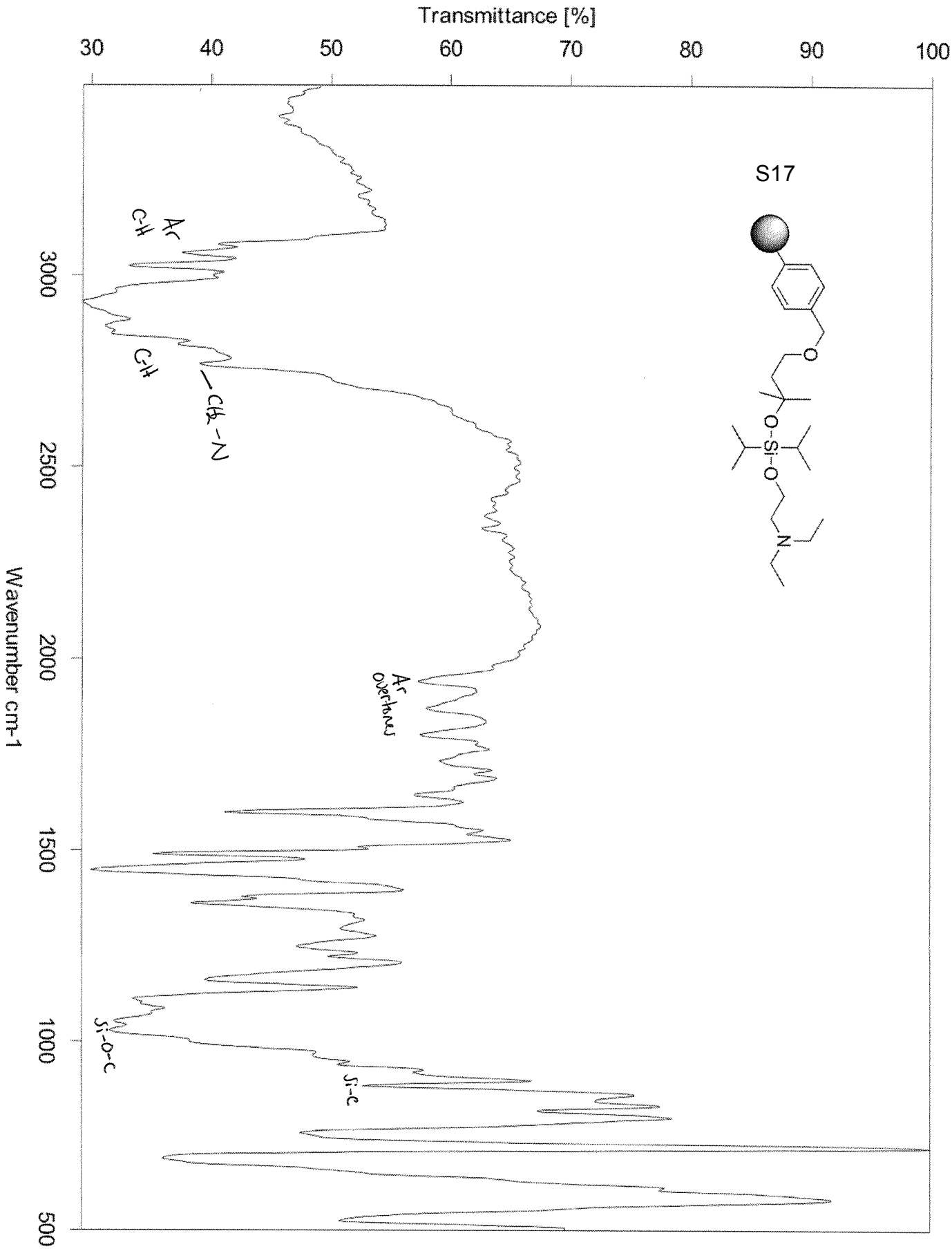

Transmittance [%]
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
Ar overtone
Si-O-C
Si-C
S12

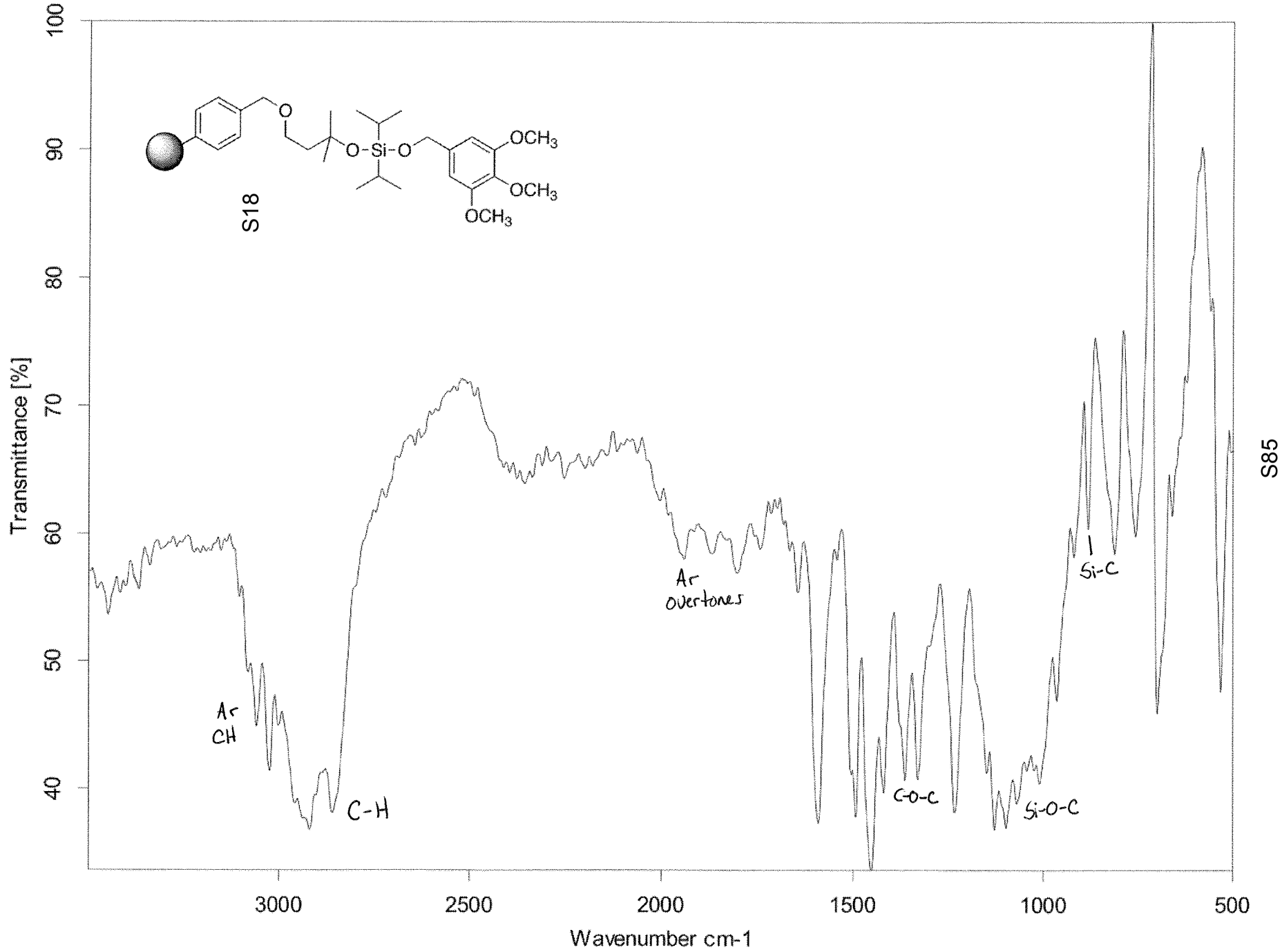

S13
O
O-Si-O
Transmittance [%]
100
90
80
70
60
50
40
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ar C-H
C-H
Si-O-C
C-Si
S80

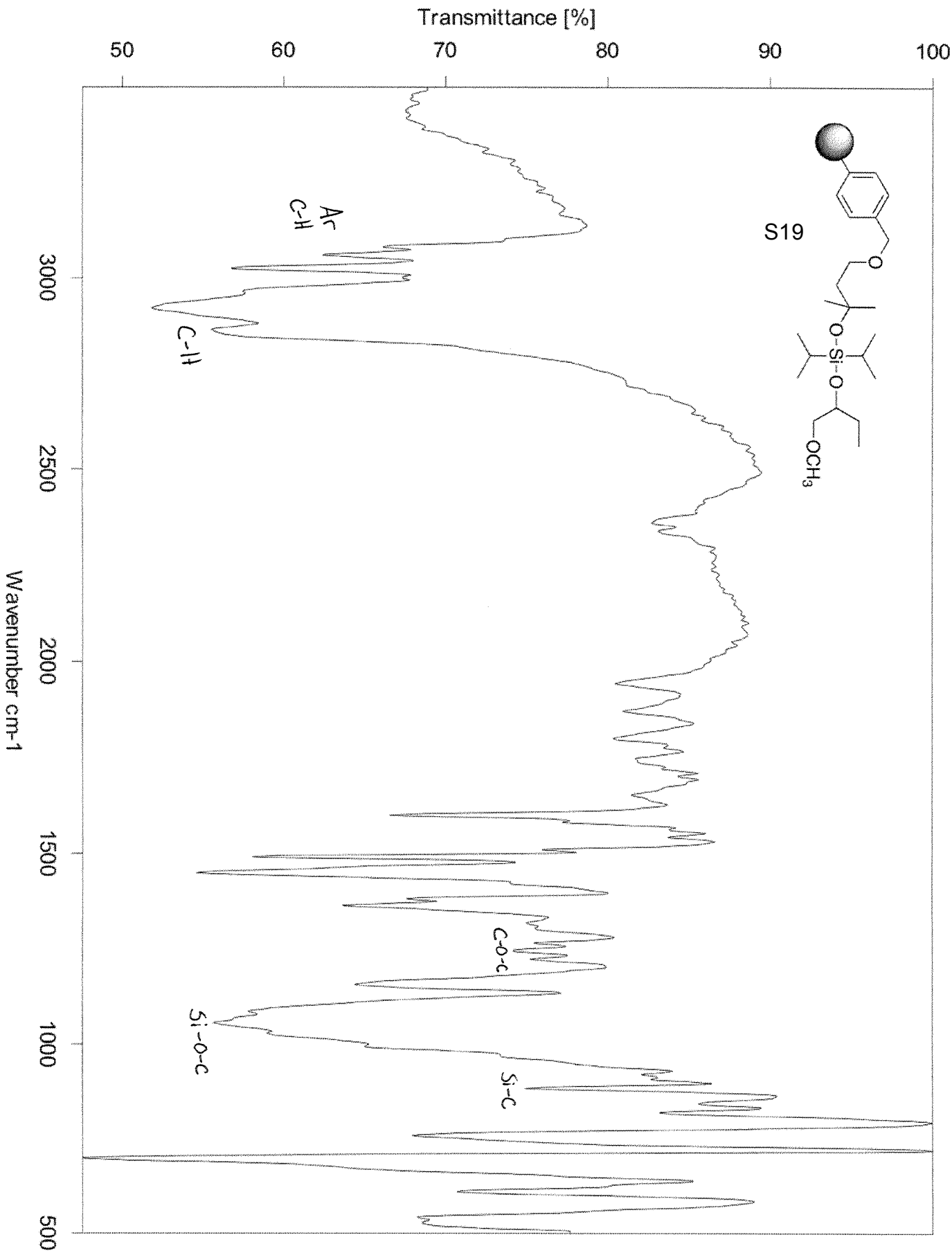

S14
O
O-Si-O
Transmittance [%]
100
90
80
70
60
50
40
Ar
C-H
C-H
CH2δ
CH3δ
Si-O-C
Si-C
3000
2500
2000
1500
1000
500
Wavenumber cm-1
S81

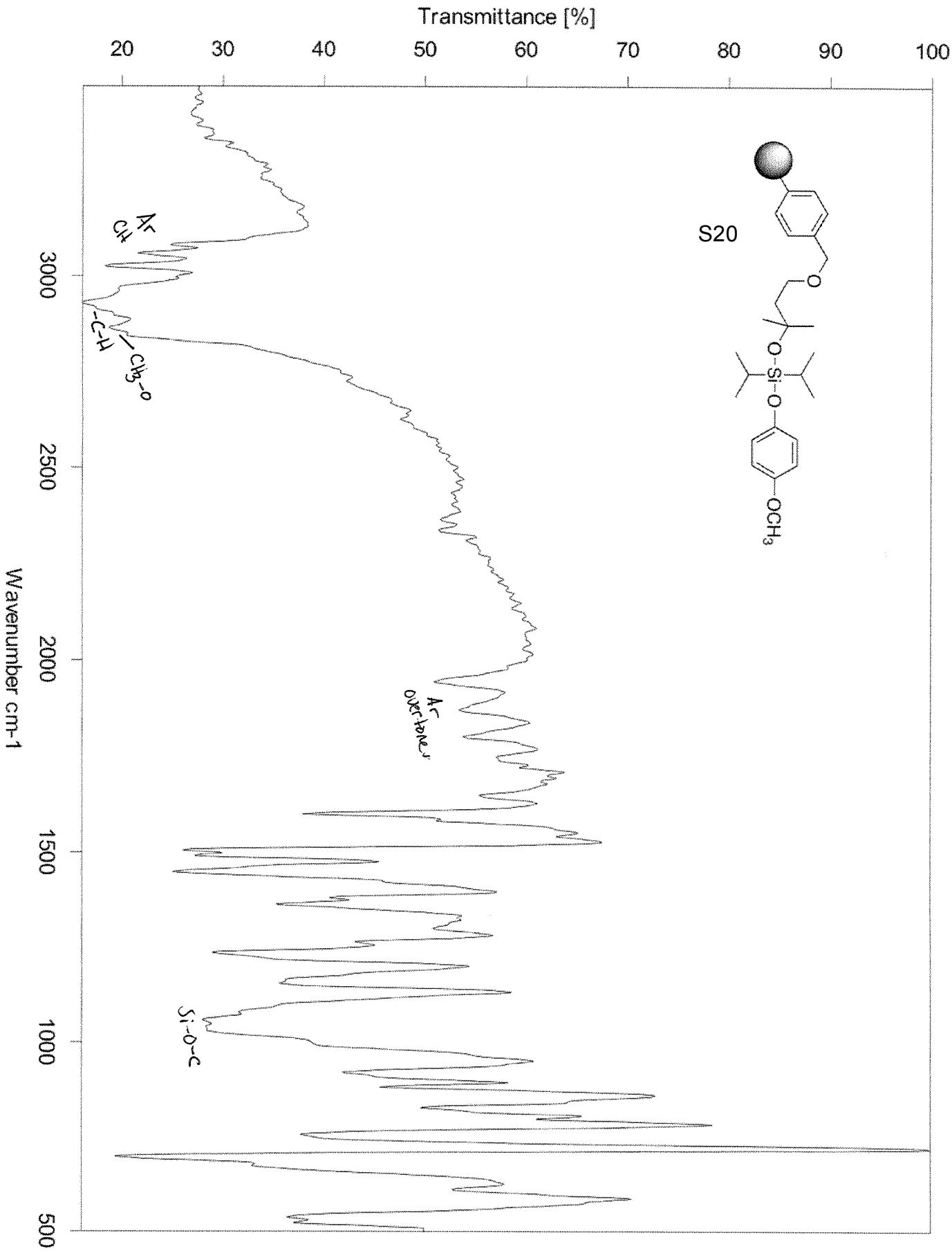

Transmittance [%]
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar CH
C-H
CH2 δ
Si-O-C
Si-C
S15

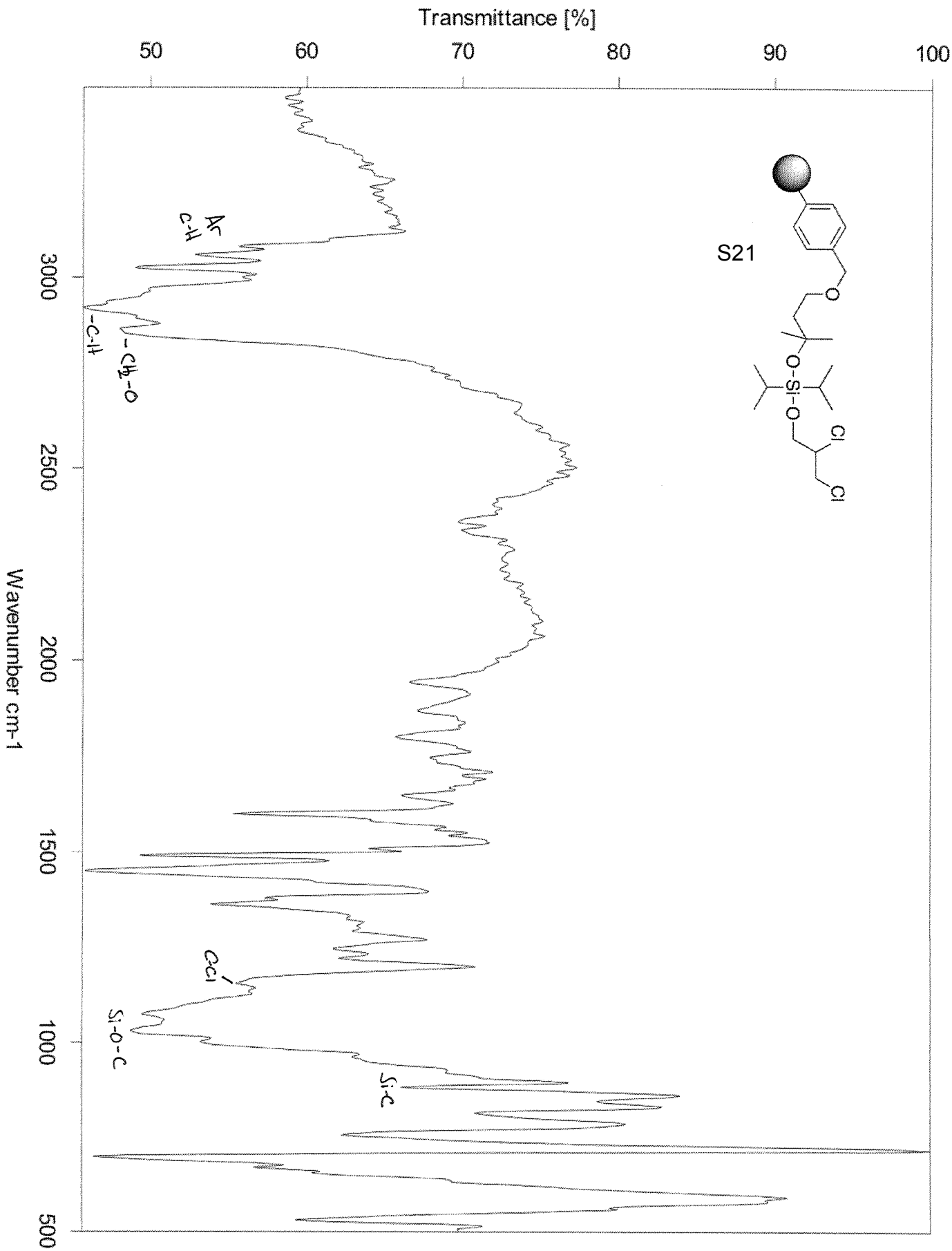

Transmittance [%]
60
65
70
75
80
85
90
95
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
Conj.
Si-O-C
Si-C
S16
O
O
Si
O

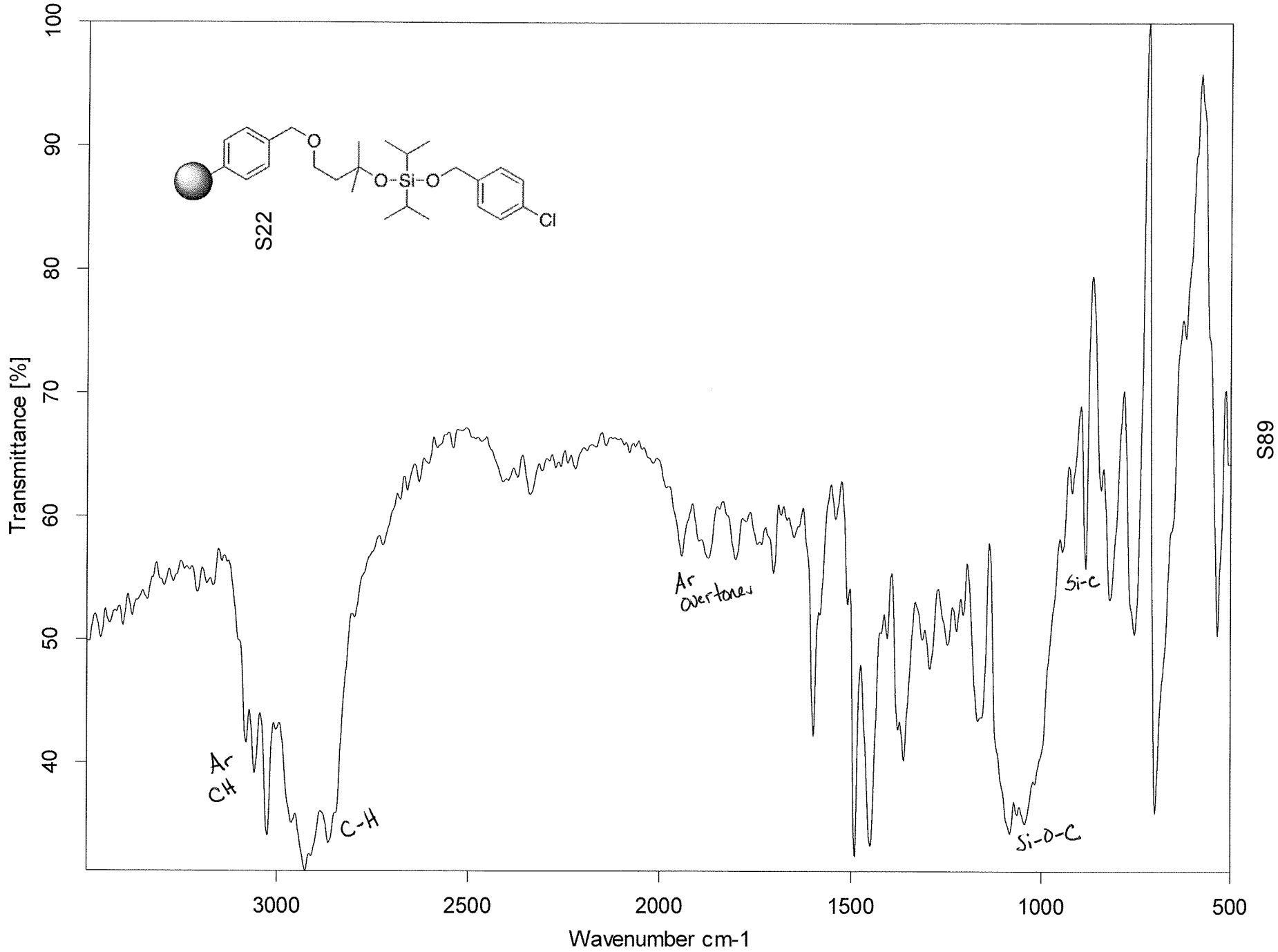

Transmittance [%]
30
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
—CH2-N
Ar overtones
Si-O-C
Si-C
S17
O
O-Si-O
N

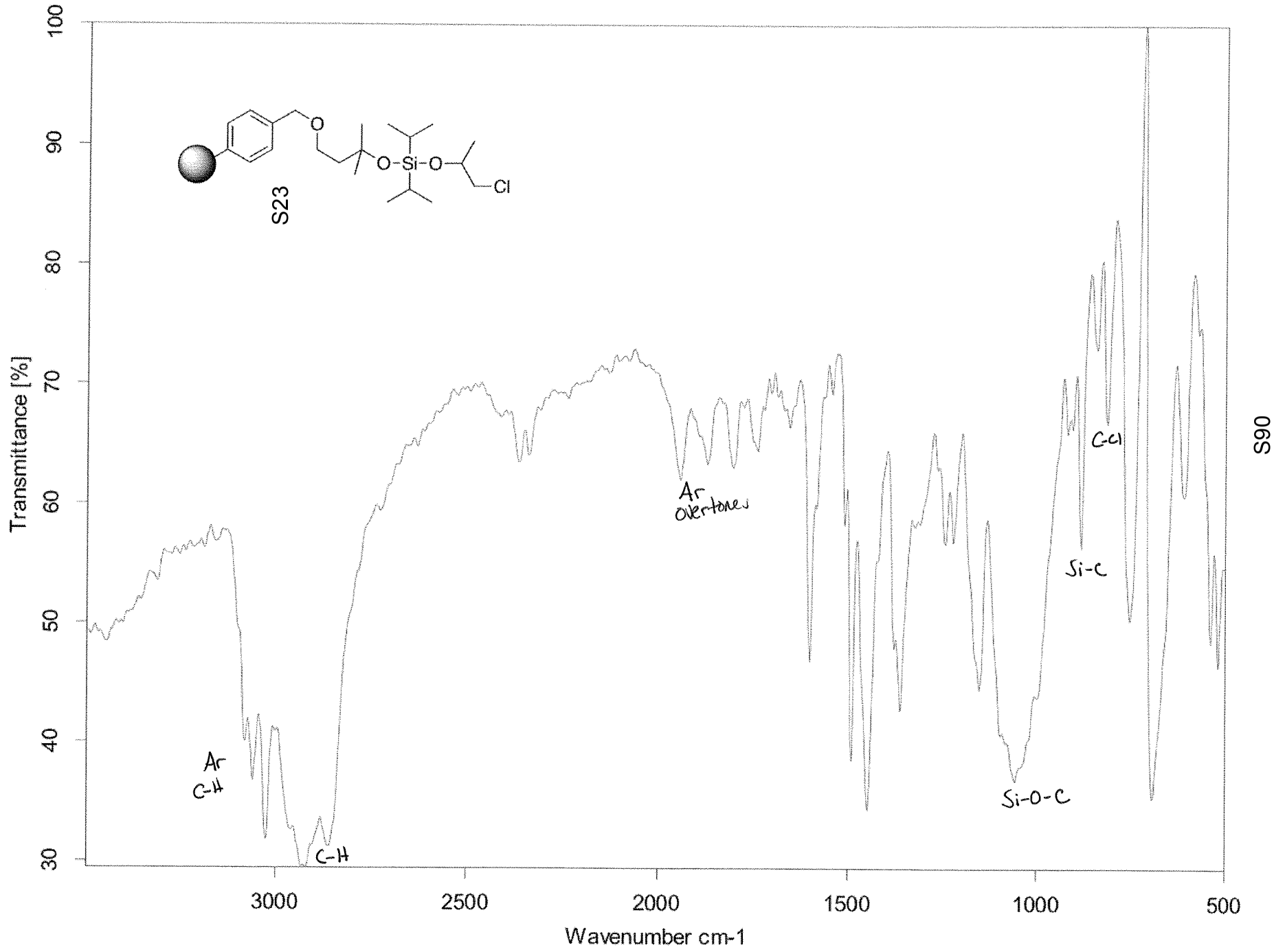

S18
OCH3
OCH3
OCH3
O
O-Si-O
Transmittance [%]
100
90
80
70
60
50
40
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ar
CH
C-H
Ar
overtones
C-O-C
Si-O-C
Si-C
S85

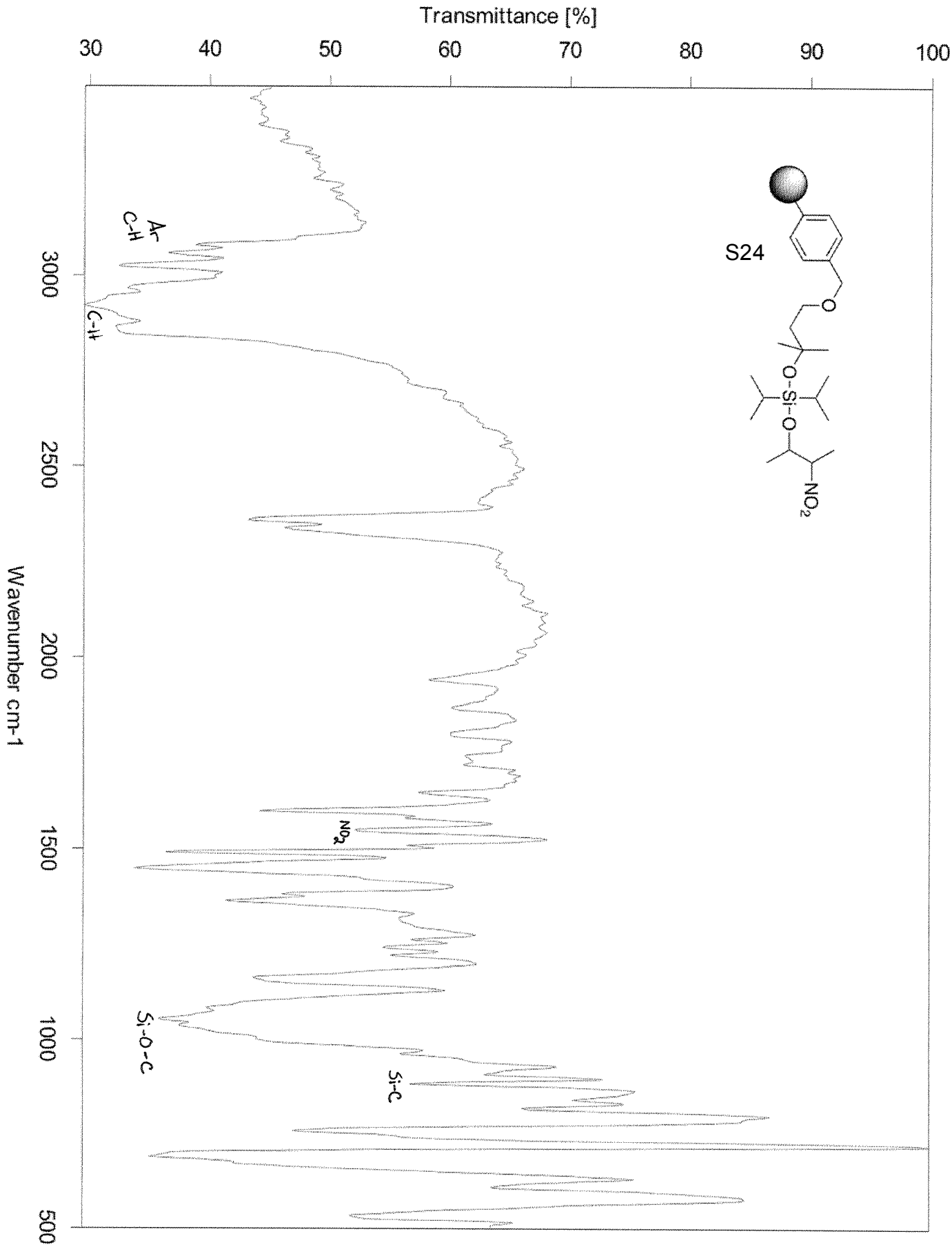

Transmittance [%]
50
60
70
80
90
100
Ar
C-H
C-H
C-O-C
Si-O-C
Si-C
S19
O
O
Si
O
OCH3
3000
2500
2000
1500
1000
500
Wavenumber cm-1

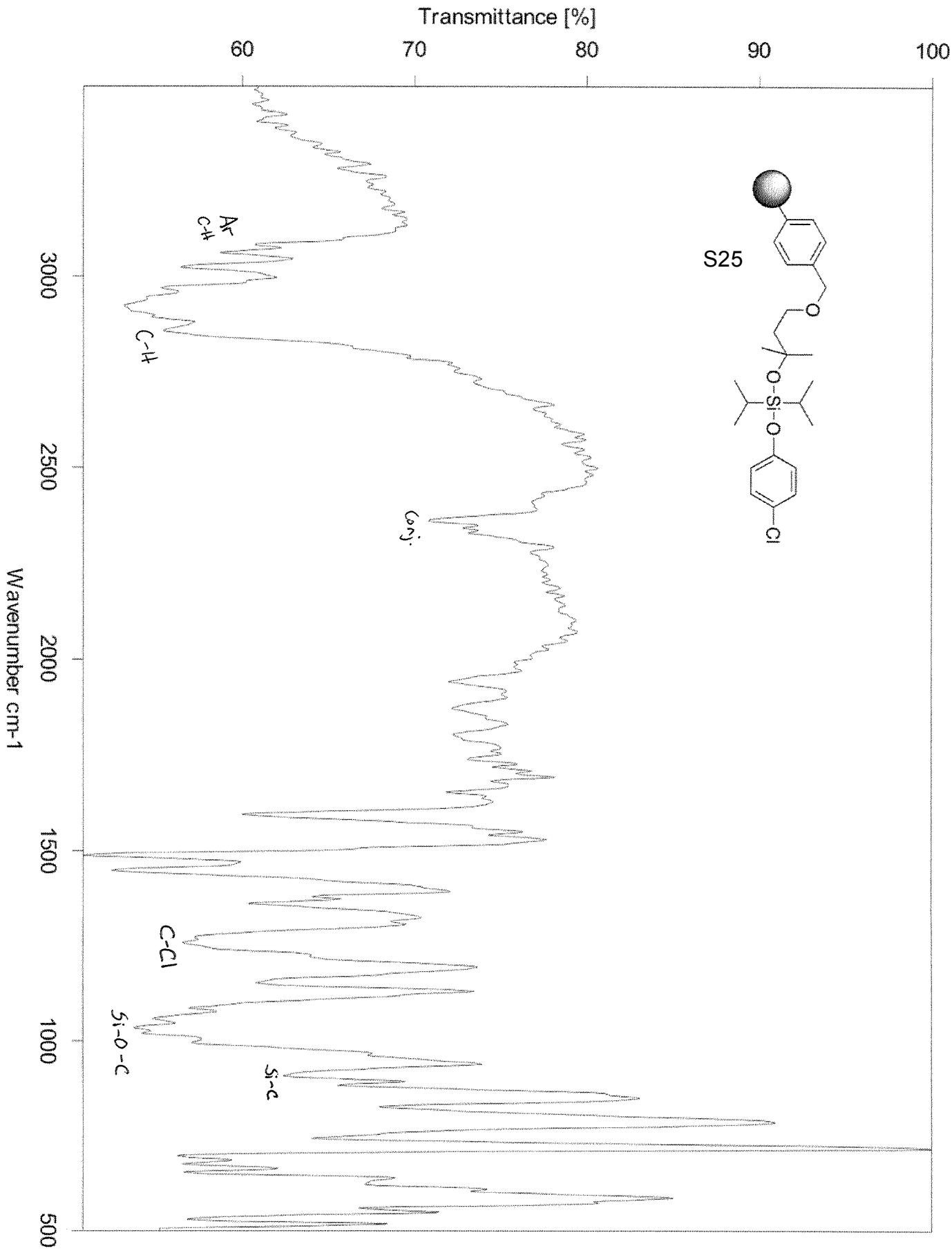

Transmittance [%]
20
30
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar CH
-C-H
CH3-O
Ar overtone
Si-O-C
S20
O
O
Si
O
OCH3

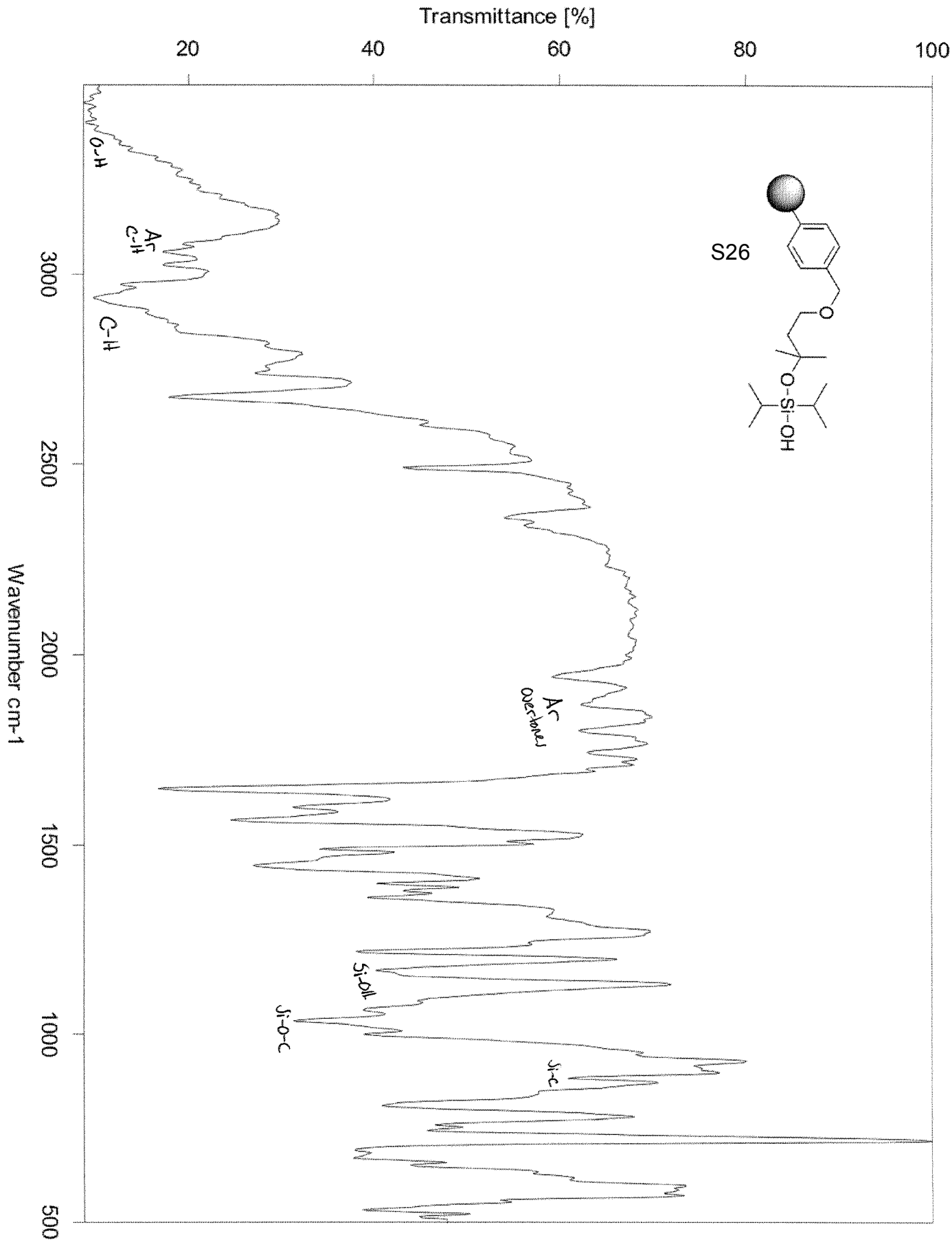

Transmittance [%]
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar c-H
-C-H
-CH2-O
C-Cl
Si-O-C
Si-C
S21
O
O-Si-O
Cl
Cl

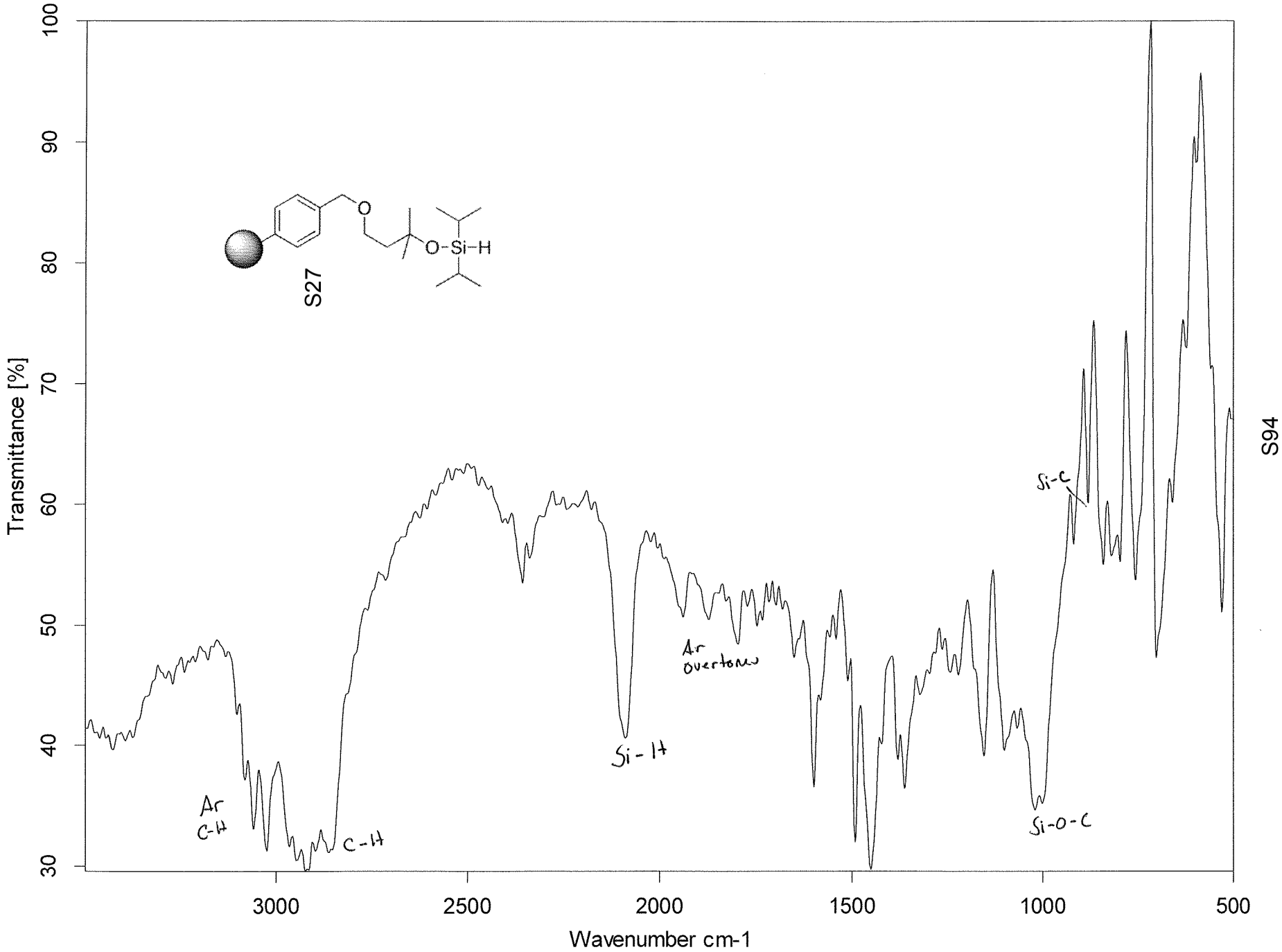

S22
Cl
Transmittance [%]
100
90
80
70
60
50
40
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ar CH
C-H
Ar overtones
Si-C
Si-O-C
S89

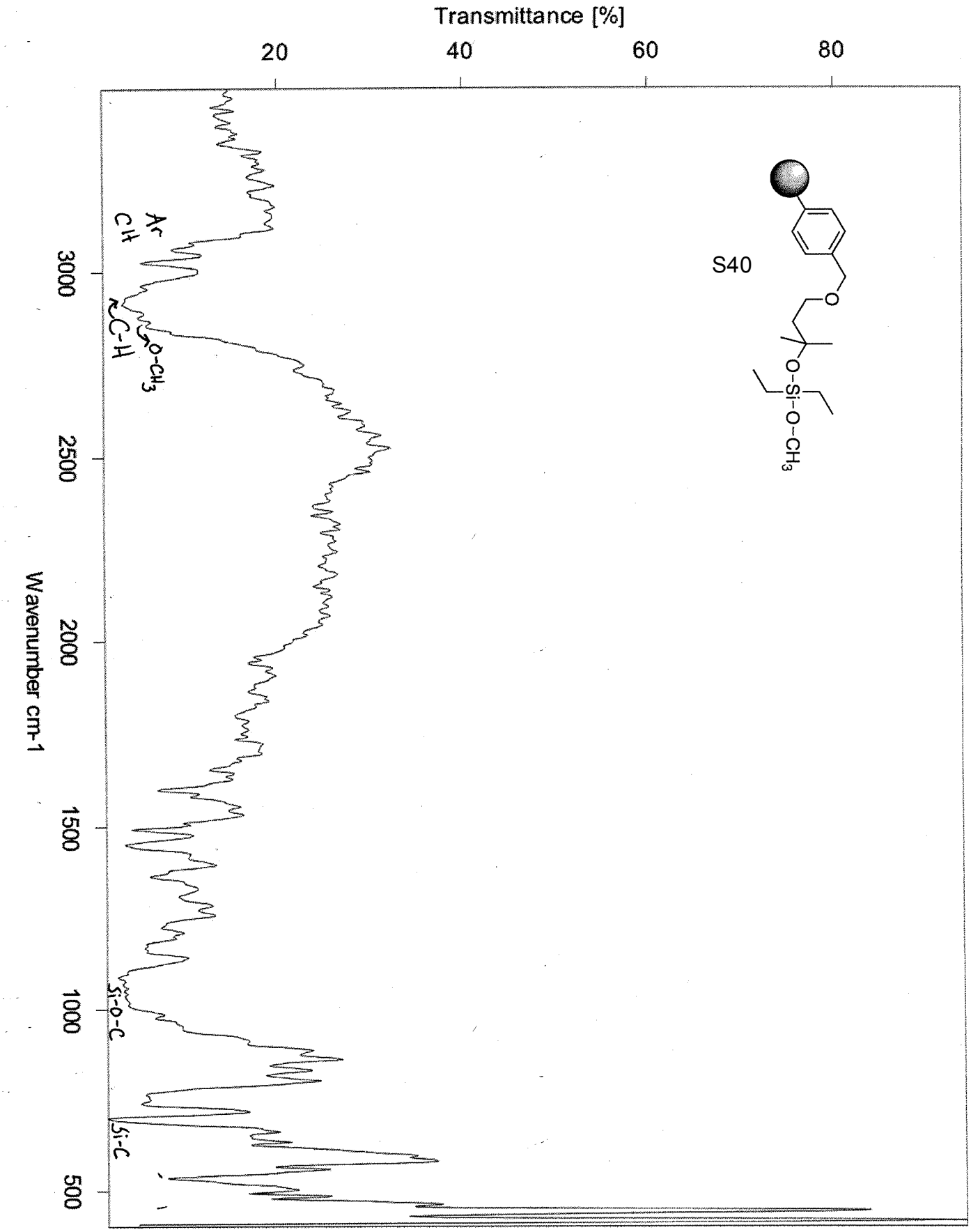

S23
O
O-Si-O
Cl
Transmittance [%]
100
90
80
70
60
50
40
30
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ar C-H
C-H
Ar overtones
Si-O-C
Si-C
C-Cl
S90

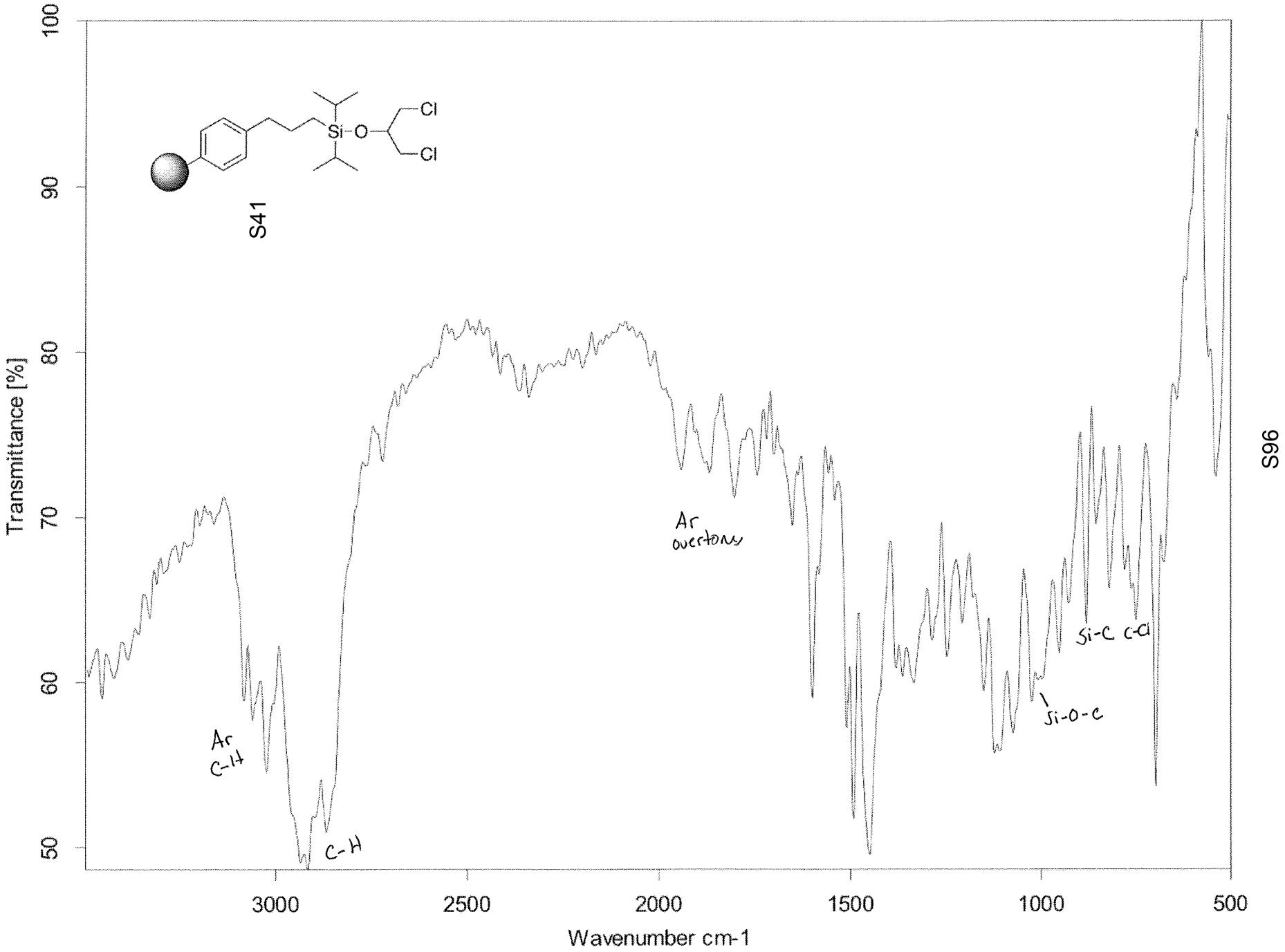

Transmittance [%]
30
40
50
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
NO2
Si-O-C
Si-C
S24
O
O-Si-O
NO2


Transmittance [%]
60
70
80
90
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
Ar C-H
C-H
Conj.
C-Cl
Si-O-C
Si-C
S25
O
O
Si
O
Cl


Transmittance [%]
20
40
60
80
100
Wavenumber cm-1
3000
2500
2000
1500
1000
500
O-H
Ar C-H
C-H
Ar overtones
Si-OH
Si-O-C
Si-C
S26
O
O-Si-OH


Transmittance [%]
100
90
80
70
60
50
40
30
3000
2500
2000
1500
1000
500
Wavenumber cm-1
O
O-Si-H
S27
Ar
C-H
C-H
Si-H
Ar
overtone
Si-C
Si-O-C
S94


Transmittance [%]
20
40
60
80
S40
O
O-Si-O-CH3
Ar C-H
O-CH3
C-H
Si-O-C
Si-C
Wavenumber cm-1
3000
2500
2000
1500
1000
500


S41
Cl
Cl
Si
O
Transmittance [%]
100
90
80
70
60
50
3000
2500
2000
1500
1000
500
Wavenumber cm-1
Ar
C-H
C-H
Ar
overtons
Si-O-C
Si-C
C-Cl
S96