Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Informations

The thiocarbonyl 'S' is softer than thiolate 'S': A catalyst-free one-pot synthesis of isothiocyanates in water

Latonglila Jamir, Abdur Rezzak Ali, Harisadhan Ghosh, Francis A. S. Chipem and Bhisma K. Patel*

Department of Chemistry, Indian Institute of Technology Guwahati

Email: *patel@iitg.ernet.in*

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General information:

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulphate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60-120 mesh size) was used for the column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25mm). NMR spectra were recorded in $CDCl_3$ with tetramethylsilane as the internal standard for ^{1}H NMR (400 MHz) $CDCl_3$ solvent as the internal standard for ^{13}C NMR (100 MHz).

Method 1: General Procedure for the Reaction of the in situ Generated Dithiocarbamate Salt with Methyl Acrylate in an Aqueous Buffer of Different pH.

To an ice cooled aqueous buffer (5 mL) (1M, K_2HPO_4 +KH_2PO_4) was added aniline (1 mmol) followed by CS_2 (2.5 mmol) and the reaction mixture was stirred for 0.5 hrs. Methyl acrylate (1.5 mmol) was added to the above reaction mixture and stirring was continued. The pH of the reaction as well as the progress of the reaction was monitored at different time intervals. After stirring for 0.5 hrs, the reaction mixture was extracted with ethyl acetate (2 x10 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4. The crude reaction mixture so obtained was purified over a column of silica gel.

Method 2: General Procedure for the Reaction of the Preformed Dithiocarbamate Triethylammonium Salt with Methyl Acrylate in an Aqueous Buffer of Different pH.

To an ice cooled aqueous buffer (5 mL) (1M, K_2HPO_4 +KH_2PO_4) was added dithiocarbamate triethylammonium salt (1 mmol) followed by methyl acrylate (1.5 mmol) and the reaction mixture was vigorously stirred. The pH of the reaction as well as the progress of the reaction was monitored at intervals. After stirring for 0.5 hrs, the reaction mixture was extracted with ethyl acetate (2 x10 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4. The crude reaction mixture so obtained was purified over a column of silica gel

Method 3: General Procedure for the Reaction of the in situ Generated Dithiocarbamate Triethylammonium Salt with Methyl Acrylate in an Aqueous Buffer of Different pH.

To an ice cooled aqueous buffer (5 mL) (1M, K_2HPO_4 +KH_2PO_4) was added aniline (1 mmol), CS_2 (2.5 mmol), Et_3N (3 mmol) and stirred for 0.5 hrs followed by addition of methyl acrylate (1.5 mmol) and the reaction mixture was vigorously stirred.

The pH of the reaction as well as progress of the reaction was monitored at intervals. After stirring for an additional 0.5 hrs, the reaction mixture was extracted with ethyl acetate (2 x10 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4. The crude reaction mixture so obtained was purified over a column of silica gel

Method 4: General Procedure for the Reaction of the insitu Generated Dithiocarbamate Triethylammonium Salt with Methyl Acrylate in Water.

Aniline (1 mmol) was taken in water (5 mL) to which was added triethylamine (3 mmol) followed by addition of CS_2 (2.5 mmol) in ice cold condition and the reaction mixture was stirred for 0.5 hrs. Methyl acrylate (1.5 mmol) was added and the reaction mixture was vigorously stirred. The pH of the reaction as well as progress of the reaction was monitored at intervals. After stirring for an additional 0.5 hrs, the pH of the reaction was found to be 10.5. The reaction mixture was extracted with ethyl acetate (2 x10 mL). The ethyl acetate layer was dried over anhydrous Na_2SO_4. The crude reaction mixture so obtained was purified over a column of silica gel

Method 5: General Procedure for the Reaction of the insitu Generated Dithiocarbamate Pyridinium Salt with Methyl Acrylate in Water.

Same as method 4, except that pyridine was taken instead of triethylamine and the pH of the reaction mixture was found to be 9.2 at the end of the reaction.

Method 6: General Procedure for the Reaction of the insitu Generated Dithiocarbamate $DBUH^+$ Salt with Methyl Acrylate in Water.

Same as method 4, except that DBU was taken instead of triethylamine and the pH of the reaction mixture was found to be 8.4 at the end of the reaction.

General Procedure for the Preparation of Aliphatic Isothiocyanate from its Dithiocarbamate Triethylammonium Salt.

To a solution/suspension of cyclohexyl dithiocarbamate triethylammonium salt **15** (5 mmol) in dioxane (10 mL) was added methyl acrylate (8 mmol). The reaction mixture was stirred at room temperature for 1.5 h during which formation of *thia*-Michael adduct was observed. To this reaction mixture, NaOH (15 mmol) was added and stirred for 3 h. The resultant isothiocyanate (**15a**) was extracted with hexane (2 x 10 mL) and the hexane layer was dried over anhydrous Na_2SO_4. The crude isothiocyanate so obtained was purified over a short column of silica gel using 100% hexane as the eluent to give product **15a** in 71% isolated yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28-1.96 (m, 10H), 3.67 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 23.0, 24.9, 33.0, 55.2, 129.6 ppm. IR (KBr) 2937, 2858, 2175, 2102, 2060, 1450, 1361, 1320, 986, 891, 720, 702 cm^{-1}. Anal. Calcd for $C_7H_{11}NS$ (141.23): C 59.53, H 7.85, N 9.92, S 22.70; Found C 59.50, H 7.81, N 9.88, S 22.74.

Computational Details:

The computations were performed with the development version of Gaussian 03W[23]. The molecular geometries were optimized employing Berny optimization algorithm contained within the program by density functional calculation in spin restricted shell wave function manner. The minimum energy nature of the optimized geometries was verified from vibrational frequency analysis.

The functional used in the calculation was B3LYP where the gradient corrected exchange functional of Becke (B)[24] and the correlation functional of Lee, Yang and Paar (LYP)[25] were employed. The standard 6-31G(d) was used as the basis set which includes polarization functions (d orbitals) for C, N, O and S atoms in the molecules studied.

References:

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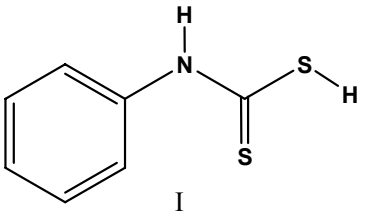
C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople; *Gaussian 03*, Revision E.01, Gaussian, Inc., Wallingford CT, **2004**.

24. Becke A.D.; *J. Chem. Phys.*, **1993**, *98*, 5648.
25. Lee, C.; Yang, W.; Parr, R.G. *Phys. Rev. B*, **1988**, *37*, 785.



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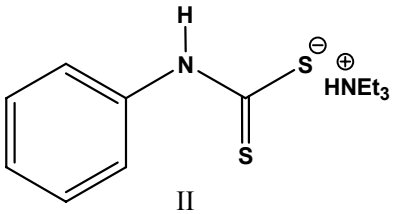

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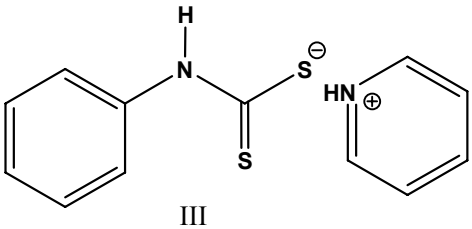

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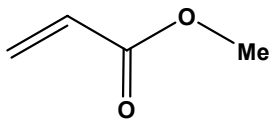

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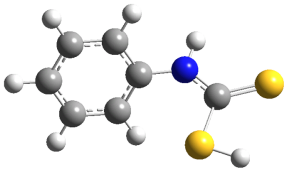

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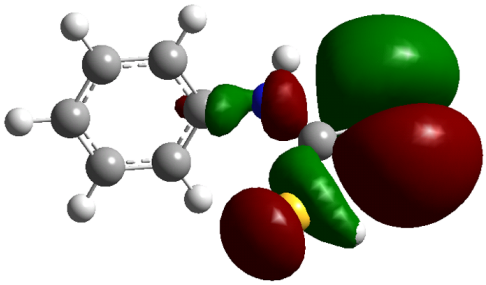

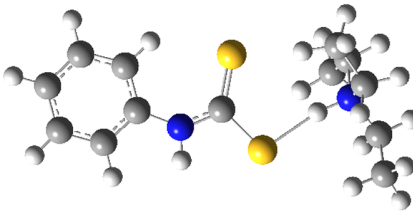

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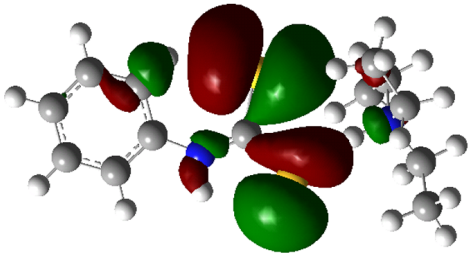


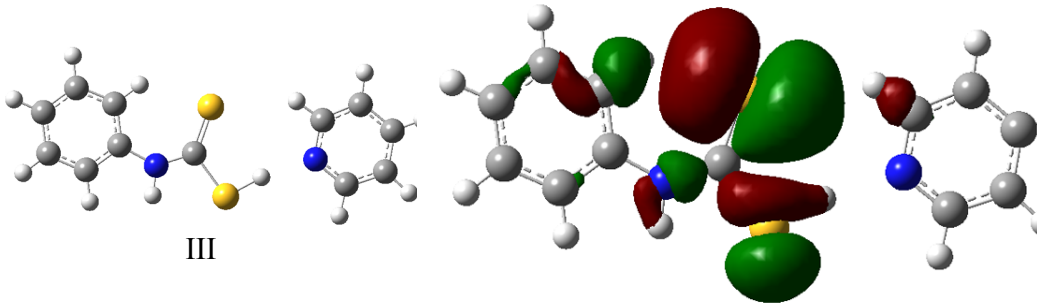


Figure 1. The highest occupied molecular orbital (HOMO) structures of the optimized compounds I, II and III.

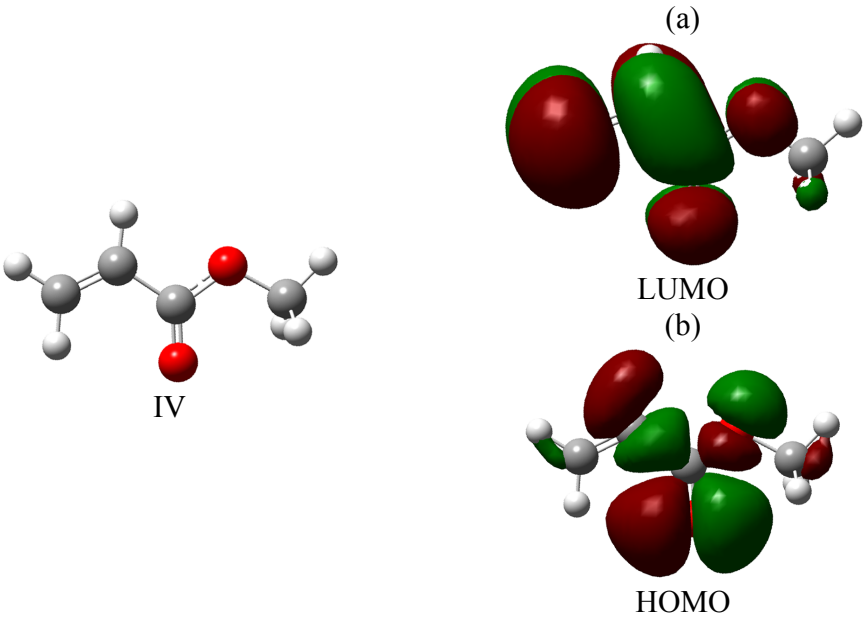
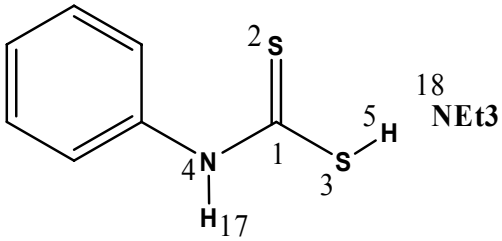


Figure 2. The LUMO (a) and HOMO (b) of methyl acrylate.

Table 1: Orbital coefficients of selected atoms of different ion-pairs. The values within the parentheses are the charges on the atoms



Atom Numbering

Atoms	Compound I	Compound II	Compound III
C1	-0.0696 (0.002)	0.0588 (0.036)	0.0959 (0.027)
S2	0.5663 (-0.238)	0.5647 (-0.357)	0.6210 (-0.232)
S3	0.1637 (0.017)	-0.3512 (-0.398)	0.2419 (-0.071)
N4	0.2412 (-0.608)	0.0659 (-0.644)	-0.1658 (-0.652)

H5	-0.0380 (0.134)	0.0564 (0.354)	0.0341 (0.160)
N18	-	-0.0752 (-0.489)	-0.0201 (-0.449)

The optimized structures in Cartesian coordinates obtained from B3LYP/6-31G(d) calculations are given below:

Compound I

C	-1.68784481	-0.13026309	0.03984897
S	-3.20528045	-0.77425931	0.27552529
S	-1.40280992	1.50413211	-0.63977183
N	-0.55986183	-0.82821487	0.32779867
H	-2.71686213	1.73466770	-0.81760764
C	0.81048532	-0.45082147	0.19590584
C	1.66734342	-1.28270975	-0.53509505
C	3.02071314	-0.96654974	-0.63817821
C	3.52223902	0.18401687	-0.02542129
C	2.66632343	1.00893506	0.70583527
C	1.31434347	0.68921840	0.83312427
H	1.26645858	-2.16509546	-1.02628374
H	3.68099373	-1.61500482	-1.20701546
H	4.57593365	0.43270760	-0.11297121
H	3.05248035	1.89718762	1.19761613
H	0.65619488	1.30841701	1.43312304
H	-0.74833836	-1.78429805	0.61037381

Compound II

C	0.62962019	0.29233088	0.00581211
S	0.35432611	-1.38352065	0.02682387
S	-0.63751579	1.50400666	0.00363041
N	1.87555232	0.86242334	-0.00845443
H	-2.29118527	0.31805736	-0.01328679
C	3.20160029	0.38362596	-0.01074835
C	3.58855818	-0.96580020	0.00416971
C	4.94536353	-1.29303236	-0.00027267
C	5.93359491	-0.30943699	-0.01910491
C	5.54908466	1.03338496	-0.03378170
C	4.20198953	1.37591119	-0.02966920
H	2.83248501	-1.73741634	0.01886855
H	5.22677602	-2.34317990	0.01146956
H	6.98532855	-0.58182137	-0.02224788
H	6.29906107	1.82000794	-0.04848561
H	3.91259150	2.42530475	-0.04122855
H	1.82224457	1.87539439	-0.01996648
N	-3.28067473	-0.13646767	0.00056889
C	-4.18229241	0.88673399	0.64261859
H	-3.72664583	1.11893278	1.60565902
H	-5.14631537	0.39781791	0.82511413
C	-3.66349566	-0.40339652	-1.43313216
H	-4.73074396	-0.65575347	-1.43914052
H	-3.53341932	0.54671919	-1.95309538
C	-3.19379654	-1.40027792	0.82150398
H	-2.43567229	-2.01207454	0.33462732

H	-4.17060962	-1.89463439	0.75337667
C	-4.35516412	2.17636805	-0.15629134
H	-4.94810613	2.03800351	-1.06448217
H	-4.88456951	2.89785204	0.47462575
H	-3.38862583	2.61258472	-0.42454739
C	-2.82643844	-1.47591189	-2.12254602
H	-3.06770424	-2.48462344	-1.77603661
H	-3.03939403	-1.43486255	-3.19595296
H	-1.75642932	-1.30382406	-1.97090656
C	-2.76937671	-1.16765857	2.26746687
H	-3.53365375	-0.66666441	2.86891963
H	-2.57769726	-2.14436843	2.72296317
H	-1.83630788	-0.59796116	2.30553393

Compound III

C	0.65016364	-0.37554767	-0.00015076
S	0.17168014	1.21911994	-0.00016116
S	-0.49552110	-1.75839280	-0.00009352
N	1.92380466	-0.85786359	-0.00017929
H	-1.67174968	-1.03966951	-0.00009313
C	3.20331937	-0.25325429	-0.00002117
C	4.29106288	-1.14573479	-0.00002499
C	5.59782522	-0.67215698	0.00009731
C	5.84649122	0.70227511	0.00022768
C	4.76834471	1.58601149	0.00022471
C	3.45002196	1.12698707	0.00009919
H	4.10705402	-2.21872610	-0.00012208
H	6.42176515	-1.38039118	0.00009345
H	6.86622948	1.07620653	0.00032511
H	4.94552183	2.65817970	0.00031949
H	2.62390368	1.82258547	0.00008810
H	1.98538005	-1.87059254	-0.00033722
N	-3.47806742	-0.33042249	-0.00009211
C	-3.64850489	0.99901388	-0.00025259
C	-4.90772509	1.59998329	-0.00011653
C	-6.03861897	0.78447246	0.00018426
C	-5.86740700	-0.59998184	0.00035637
C	-4.56889443	-1.10750293	0.00022134
H	-2.73437061	1.58728272	-0.00040866
H	-4.99326055	2.68232754	-0.00022010
H	-7.03494304	1.21837480	0.00030552
H	-6.71793126	-1.27488108	0.00060026
H	-4.39277599	-2.18171688	0.00035519

Compound IV

C	0.04366976	0.11747061	-0.00069730
C	1.31732520	-0.64647378	-0.00011502
C	2.49187183	-0.01298190	0.00032487
O	-0.06045630	1.32760624	-0.00004356
O	-1.01712643	-0.72537796	-0.00012884
H	1.23952089	-1.72968739	-0.00009983
H	3.43323913	-0.55394036	0.00069013
H	2.52950572	1.07272277	0.00029640

C	-2.30332717	-0.08833113	0.00034033
H	-3.03295660	-0.89876613	0.00076621
H	-2.42256423	0.53699433	0.88941906
H	-2.42332076	0.53674769	-0.88881006

Spectral Data

1-Isothiocyanato-benzene (1a): Oily; ^{1}H NMR (400 MHz, $CDCl_3$)**:** δ 7.21-7.37 (m, 5H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.8, 127.4, 129.6, 131.3, 135.3 ppm. IR (KBr): 3064, 2164, 2063, 1591, 1489, 1474, 1451, 1070, 927, 905, 749, 684 cm^{-1}. Anal. Calcd for C_7H_5NS (135.19): C 62.19, H 3.73, N 10.36, S 23.72; Found C 62.22, H 3.71, N 10.35, S 23.73.

1-Isothiocyanato-4-methyl-benzene (2a): Oily; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.33 (s, 3H), 7.06-7.13 (m, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.2, 125.4, 128.2, 130.1, 134.4, 137.4 ppm. IR (KBr): 2920, 2094, 1503, 929, 812, 790, 497 cm^{-1}. Anal. Calcd for C_8H_7NS (149.15): C 64.36, H 4.73, N 9.39, S 21.51; Found C 64.32, H 4.75, N 9.41, S 21.56.

1-Isothiocyanato-4-methoxy-benzene (3a): Oily; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.80 (s, 3H), 6.85 (d, 2H, *J* = 8.8 Hz), 7.16 (d, 2H, *J* = 8.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 114.6, 123.2, 126.8, 133.7, 158.4 ppm. IR (KBr): 3000, 2956, 2835, 2170, 2098, 1580, 1599, 1503, 1459, 1440, 1292, 1251, 1179, 1166, 1028, 927, 824, 614, 513 cm^{-1}. Anal. Calcd for C_8H_7NOS (165.22): C 58.16, H 4.27, N 8.48, S 19.40; Found C 58.08, H 4.23, N 8.34, S 19.34.

1-Bromo-4-isothiocyanato-benzene (4a): White solid, M.p. 58 ^{o}C (Lit[1a] 58^{o}C), ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, 2H, *J* = 8.8 Hz), 7.47 (d, 2H, *J* = 8.8 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.8, 127.2, 130.5, 132.8, 136.9 ppm. IR (KBr): 3074, 2925, 2171, 2071, 1578, 1478, 1474, 1399, 1067, 1011, 923, 818, 490, 438 cm^{-1}. Anal. Calcd

for C_7H_4BrNS (214.03): C 39.24, H 1.88, N 6.54, S 14.99; Found C 39.21, H 1.93, N 6.50, S 15.04.

4-Isothiocyanato-benzonitrile (5a): White solid; mp 119-120 ^oC (Lit[21]121 ^oC; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 110.6, 117.9, 126.5, 133.6, 135.9, 139.4 ppm; IR (KBr) 3435, 2197, 2124, 2104, 1591, 1492, 1277, 933, 836, 544 cm^{-1}. Anal. Calcd for $C_8H_4N_2S$ (166.13): C 59.95, H 2.51, N 17.49, S 20.03; Found C 59.98, H 2.49, N 17.45, S 19.98.

(Lit 21. Hunig, S, Lehmann, H.; Grimmer, G.;. *Liebigs Ann. Chem.* **1953**, *579*, 77)..

1-Isothiocyanato-4-trifluoromethyl-benzene (6a): White solid; mp 43 ^oC (Lit[22] bp 205-207 ^oC); ^1H NMR ($CDCl_3$, 400 MHz) δ 7.32 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 122.4, 125.1, 126.1, 126.9, 127.0, 129.0, 129.4, 135.15, 138.4 ppm; IR (KBr) 3427, 2081, 1613, 1413, 1325, 1137, 1106, 1066, 839, 590 cm^{-1}. Anal. Calcd for $C_8H_4F_3NS$ (203.12): C 47.26, H 1.98, N 6.89, S 15.79; Found C 47.22, H 1.96, N 6.91, S 15.75.

(**Lit 22.** Kurzer, F.; Candle, J. *Tetrahedron,* **1963**, *19*, 1603.

1-Isothiocyanato-3-nitro-benzene (7a): Oily; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 2H), 8.06 (s, 1H), 8.11-8.14 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$) δ 120.7, 121.9, 130.6, 131.6, 133.3, 139.6, 148.8 ppm. IR (KBr): 3091, 3074, 2227, 2161, 2106, 1526, 1470, 1348, 1302, 892, 809, 736, 665 cm^{-1}. Anal. Calcd for $C_7H_4N_2O_2S$ (180.13): C 46.63, H 2.23, N 15.55, S 17.81; Found C 46.65, H 2.26, N 15.51, S 17.78.

1-Isothiocyanato-2,4-dimethyl-benzene (8a): Oily; ^1H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 2.33 (s, 3H), 6.96 (d, 1H, J = 9.2 Hz), 7.01 (s, 1H), 7.07 (d, 1H, J = 8.0 Hz) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 18.2, 21.1, 125.6, 127.4, 131.2, 134.6, 137.4 ppm. IR (KBr): 2920, 2131, 2085, 1490, 1455, 1379, 1229, 1036, 947, 901, 875, 812 cm^{-1}. Anal.

Calcd for C_9H_9NS (163.17): calcd. C 66.19, H 5.55, N 8.58, S 19.66; Found C 66.15, H 5.52, N 8.63, S 19.64.

4-Isothiocyanato-1,2-dimethyl-benzene (9a): Oily; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.22 (s, 3H), 2.23 (s, 3H), 6.94 (d, 1H, J = 8.0 Hz), 6.98 (s, 1H), 7.07 (d, 1H, J = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.6, 19.7, 123.0, 126.7, 128.5, 130.6, 134.2, 136.4, 138.2 ppm; IR (KBr) 3027, 2973, 2943, 2921, 2109, 2060, 1610, 1574, 1494, 1448, 1384, 1020, 971, 871, 831, 812 cm^{-1}. Anal. Calcd for C_9H_9NS (163.17): C 66.19, H 5.55, N 8.58, S 19.66; Found C 66.19, H 5.55, N 8.58, S 19.66.

2-Bromo-1-isothiocyanato-4-methoxy-benzene (10a): White solid; mp. 77 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (s, 3H), 6.82 (m, 1H), 7.11 (m, 1H), 7.18 (d, 1H, J = 8.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 56.0, 114.4, 118.5, 121.6, 124.1, 127.7, 136.7, 158.8 ppm; IR (KBr) 2972, 2125, 1594, 1560, 1483, 1296, 1263, 1220, 1039, 807, 617 cm^{-1}. Anal. Calcd for C_8H_6BrNOS (244.05): C 39.33, H 2.47, N 5.73, S 3.14; Found C 39.29, H 2.52, N 5.70, S 3.11.

2-(3-Bromo-4-isothiocyanato-phenyl)-2-methyl-[1,3]dithiolane (11a): White solid; mp. 79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.10 (s, 3H), 3.34 (m, 2H), 3.65 (m, 2H), 7.17 (d, 1H, J = 8.4 Hz), 7.66 (dd, 1H, J_1 = 8.4 Hz, J_2= 2.4 Hz), 7.99 (d, 1H, J = 2.0 Hz) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 33.3, 40.7, 67.5, 120.4, 126.4, 127.2, 130.1, 131.9, 137.9, 147.3 ppm; IR (KBr) 2920, 2853, 2057, 1446, 1378, 1153, 1022, 865, 844, 663, 545 cm^{-1}. Anal. Calcd for $C_{11}H_{10}BrNS_3$: C, 39.75; H, 3.03; N, 4.22; S, 28.95. Found C, 39.79; H, 3.01; N, 4.20; S, 28.91. MS (AP$^+$) Calcd for $C_{11}H_{10}BrNS_3$, 330.91; Found, (M^+) 330.95; $[M+2]^+$ 332.95.

1-Iodo-2-isothiocyanato-4,5-dimethyl-benzene (12a): White solid; mp. 54 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.22 (s, 3H), 6.99 (s, 1H), 7.30 (s, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.4, 19.5, 117.2, 124.1, 127.8, 129.3, 133.8, 137.4, 137.9 ppm; IR (KBr) 2922, 2853, 2192, 2118, 1472, 1372, 1273, 1076, 1048, 933, 882, 824, 708 cm^{-1}.

Anal. Calcd for C_9H_8INS: C, 37.39; H, 2.79; N, 4.84; S, 11.09. Found C, 37.42; H, 2.81; N, 4.81; S, 11.06. MS (AP^+) Calcd for C_9H_8INS, 288.94; Found, (M^+) 288.97.

1-(1-Isothiocyanato-ethyl)-naphthalene (13a): Oily; [α] = +48°; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (d, 3H, *J* = 6.8 Hz), 6.08 (m, 1H), 8.00 (d, 1H, *J* = 6.8 Hz), 8.21 (d, 1H, *J* = 8.4 Hz), 8.29 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.0, 54.1, 122.3, 123.1, 125.5, 126.0, 126.8, 129.0, 129.3, 129.5, 132.5, 133.9, 135.5 ppm; IR (KBr) 3051, 2985, 2094, 1599, 1511, 1360, 1324, 1171, 1001, 799, 775, 606 cm^{-1}. Anal. Calcd for $C_{13}H_{11}NS$ (213.19): C 73.13, H 5.20, N 6.57, S 15.04; Found C 73.11, H 5.23, N 6.53, S 15.10.

5-(Isothiocyanatomethyl)benzo[d][1,3]dioxole (14a): White solid; M.p. 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (s, 2H), 5.98 (s, 2H), 6.74-6.80 (m, 3H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 48.7, 101.5, 107.7, 108.6, 120.7, 128.0, 132.1, 147.8, 148.2 ppm. IR (KBr): 2895, 2087, 1503, 1445, 1369, 1322, 1251, 1101, 1028, 924 cm^{-1}. Anal. Calcd for $C_9H_7NO_2S$ (193.23): C 55.95, H 3.65, N 7.25, S 16.56; Found C 56.12, H 3.71, N 7.13, S 16.45. MS (ESI): 195 (M+2).

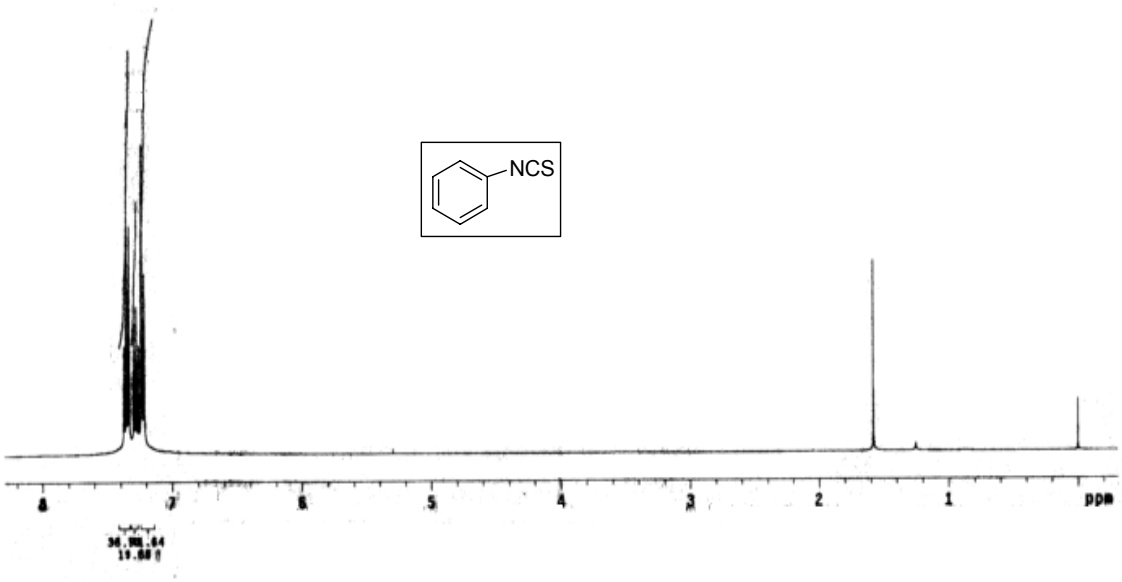
Isothiocyanato-cyclohexane (15a): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.28-1.96 (m, 10H), 3.67 (m, 1H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 23.0, 24.9, 33.0, 55.2, 129.6 ppm. IR (KBr): 2937, 2858, 2175, 2102, 2060, 1450, 1361, 1320, 986, 891, 720, 702 cm^{-1}. Anal. Calcd for $C_7H_{11}NS$ (141.23): C 59.53, H 7.85, N 9.92, S 22.70; Found C 59.50, H 7.81, N 9.88, S 22.74.

1-Isothiocyanato-octadecane (16a): Gummy, ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.879 (t, *J* = 6.8 Hz, 3H), 1.25 (m, 28H), 1.71-1.72 (m, 4H), 3.50 (t, *J* = 6.4 Hz, 2H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 14.3, 22.8, 26.7, 29.0, 29.5, 29.7, 29.8, 30.1, 32.1, 45.2 ppm; IR (KBr) 2923, 2853, 2185, 2096, 1463, 1455, 1346, 721 $cm^{-1.}$ Anal. Calcd for $C_{19}H_{37}NS$: C, 73.24; H, 11.97; N, 4.50; S, 10.29. Found C, 73.27; H, 12.01; N, 4.48; S, 10.25. MS (ES^-) Calcd for $C_{19}H_{37}NS$, 311.26; Found, (M^+) 311.19.

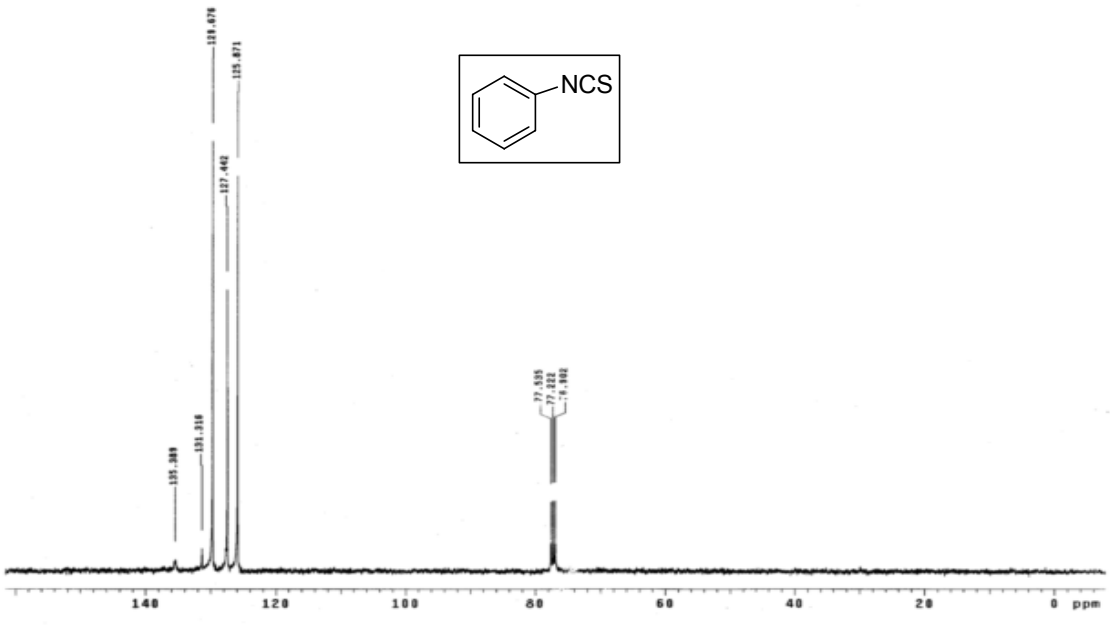
3-(2-Methoxycarbonyl-ethyldisulfanyl)-propionic acid methyl ester: Oily liquid ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.62 (t, J = 7.2 Hz, 2 x 2H), 2.80 (t, J = 7.2 Hz, 2 x 2H), 3.70 (s, 2 x 3H) ppm; ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.8, 34.4, 51.7, 172.1 ppm; IR (KBr) 2953, 2847, 1738, 1732, 1436, 1359, 1248, 1173, 980, 828, 697 cm^{-1}.

Spectra

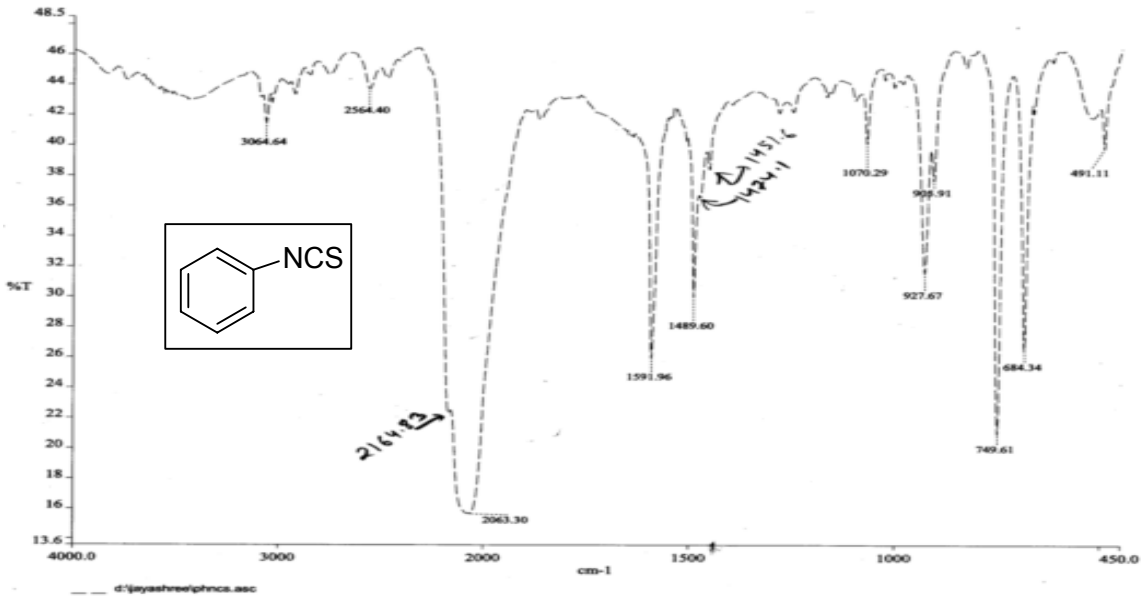
1-Isothiocyanato-benzene (1a): ^{1}H NMR ($CDCl_3$, 400 MHz):



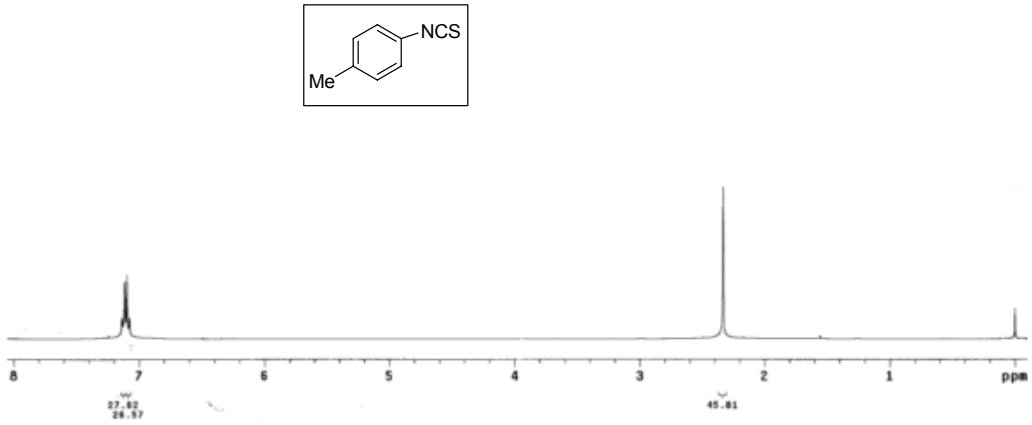
1-Isothiocyanato-benzene (1a): ^{13}C NMR (100 MHz, $CDCl_3$):



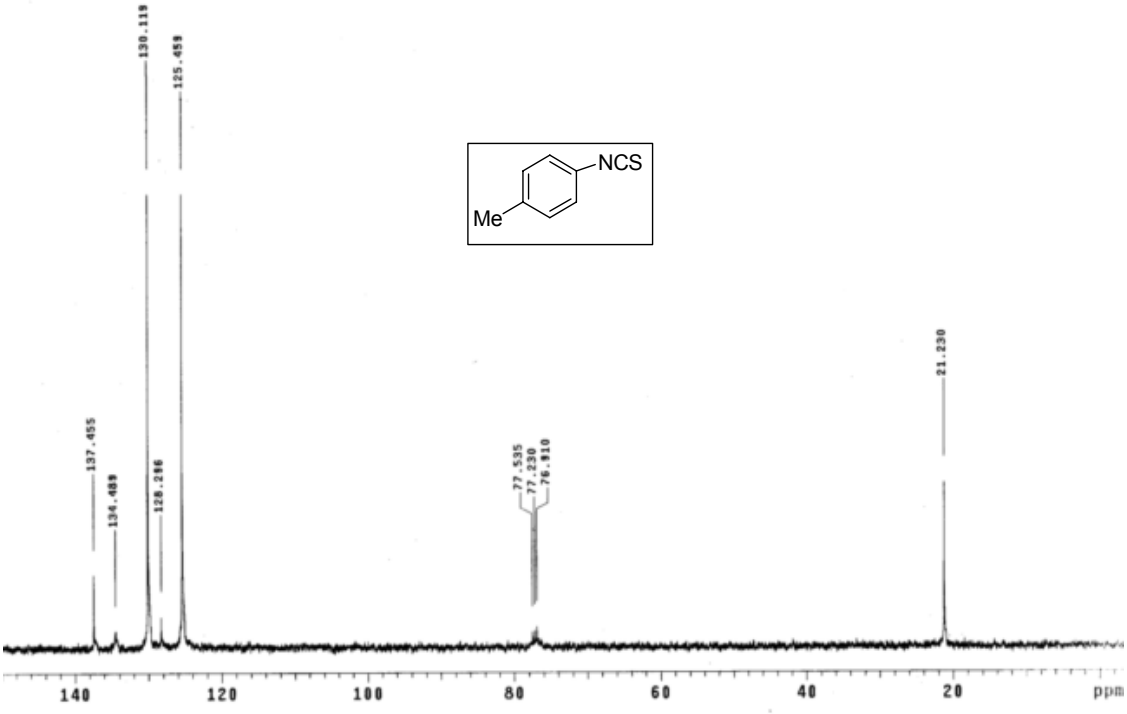
1-Isothiocyanato-benzene (1a): IR (KBr):



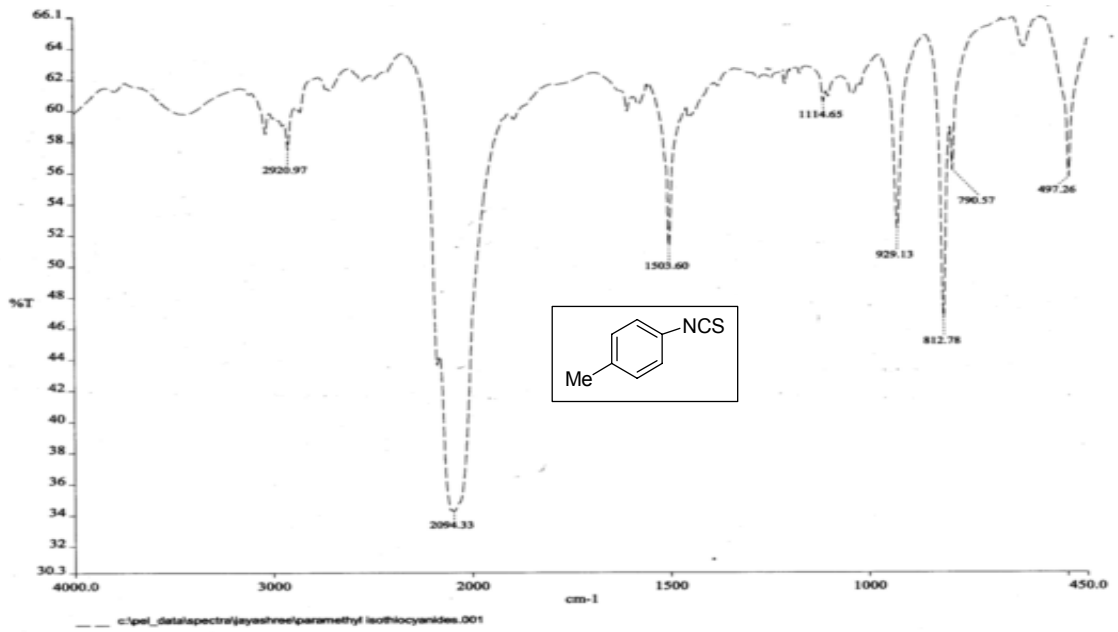
1-Isothiocyanato-4-methyl-benzene (2a): ^{1}H NMR (400 MHz, $CDCl_3$):



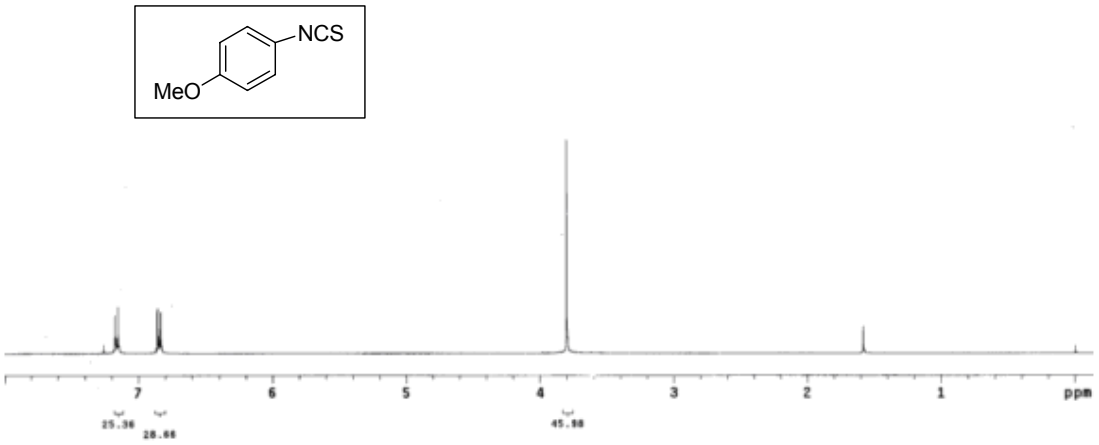
1-Isothiocyanato-4-methyl-benzene (2a): ^{13}C NMR (100 MHz, $CDCl_3$):



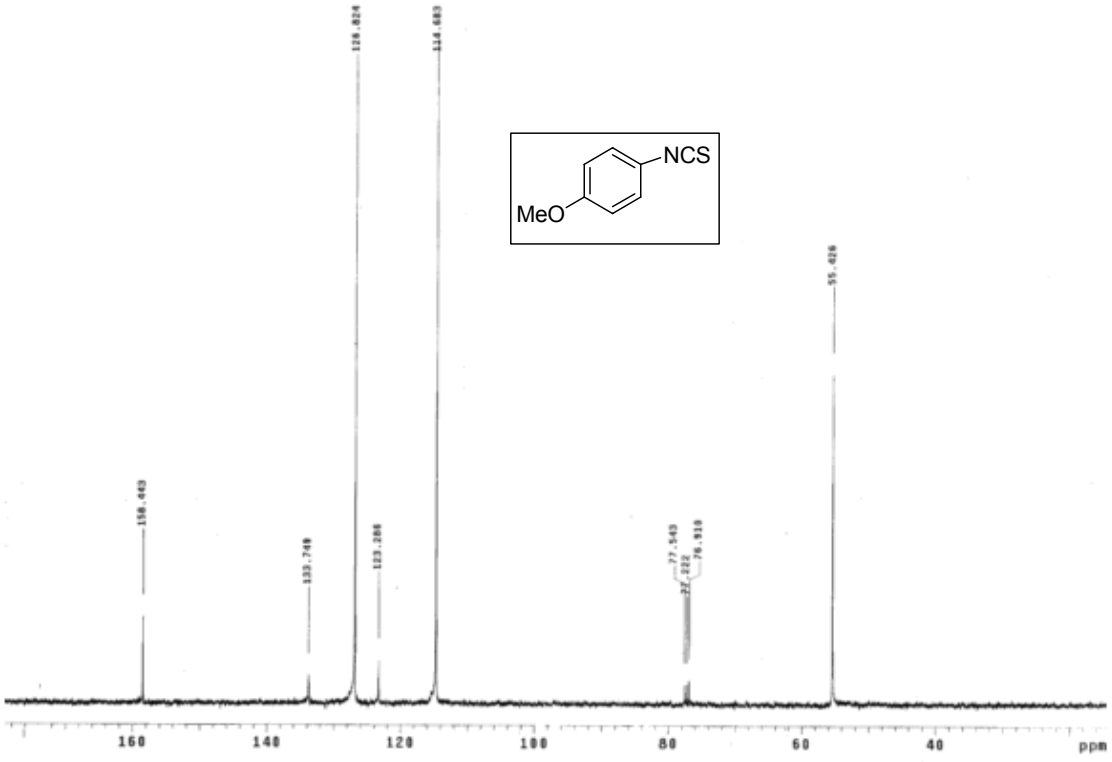
1-Isothiocyanato-4-methyl-benzene (2a): IR (KBr):



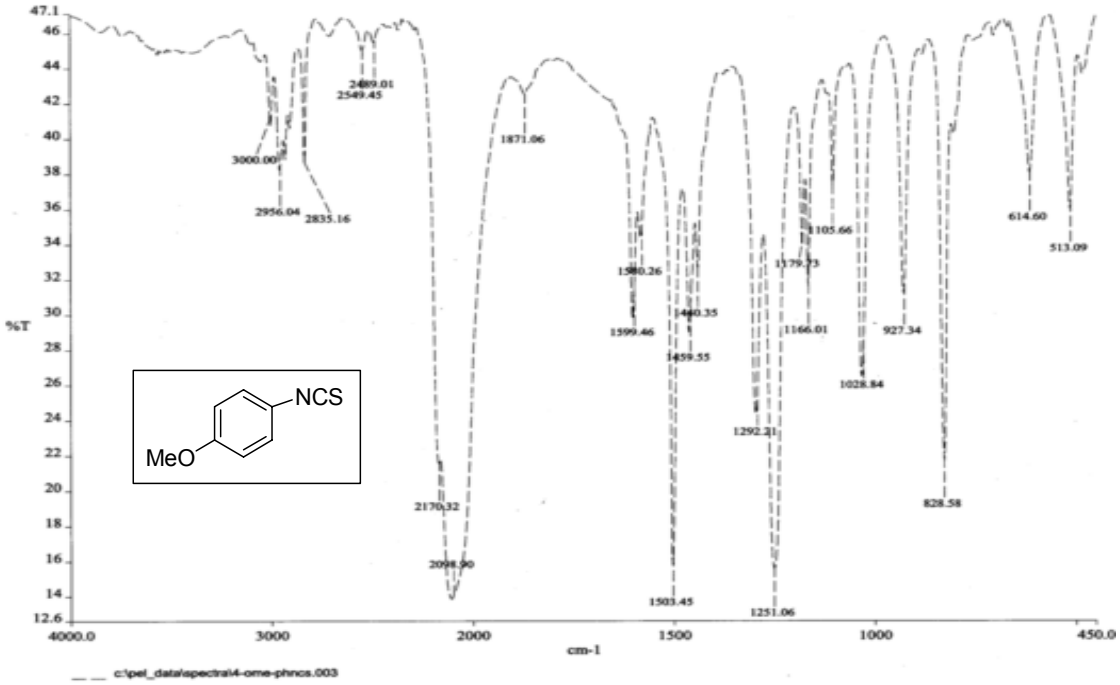
1-Isothiocyanato-4-methoxy-benzene (3a): ^{1}H NMR (400 MHz, $CDCl_3$):



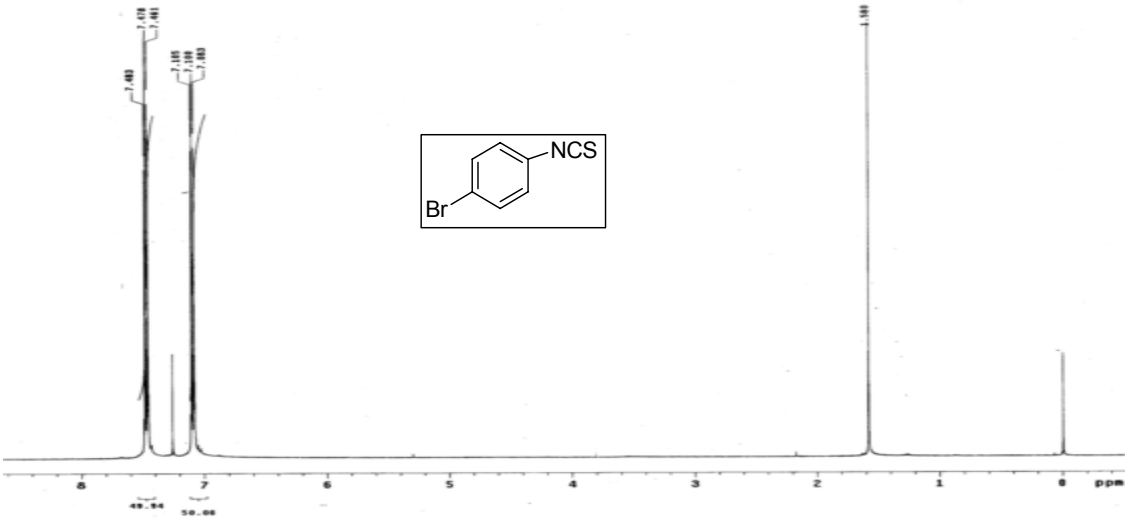
1-Isothiocyanato-4-methoxy-benzene (3a): ^{13}C NMR (100 MHz, $CDCl_3$):



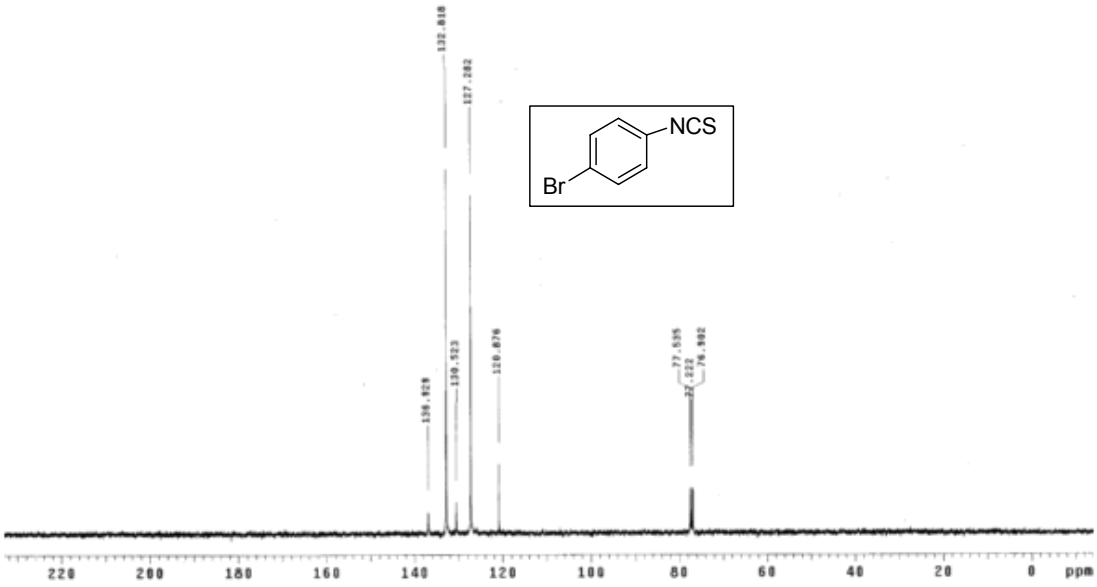
1-Isothiocyanato-4-methoxy-benzene (3a): IR (KBr):



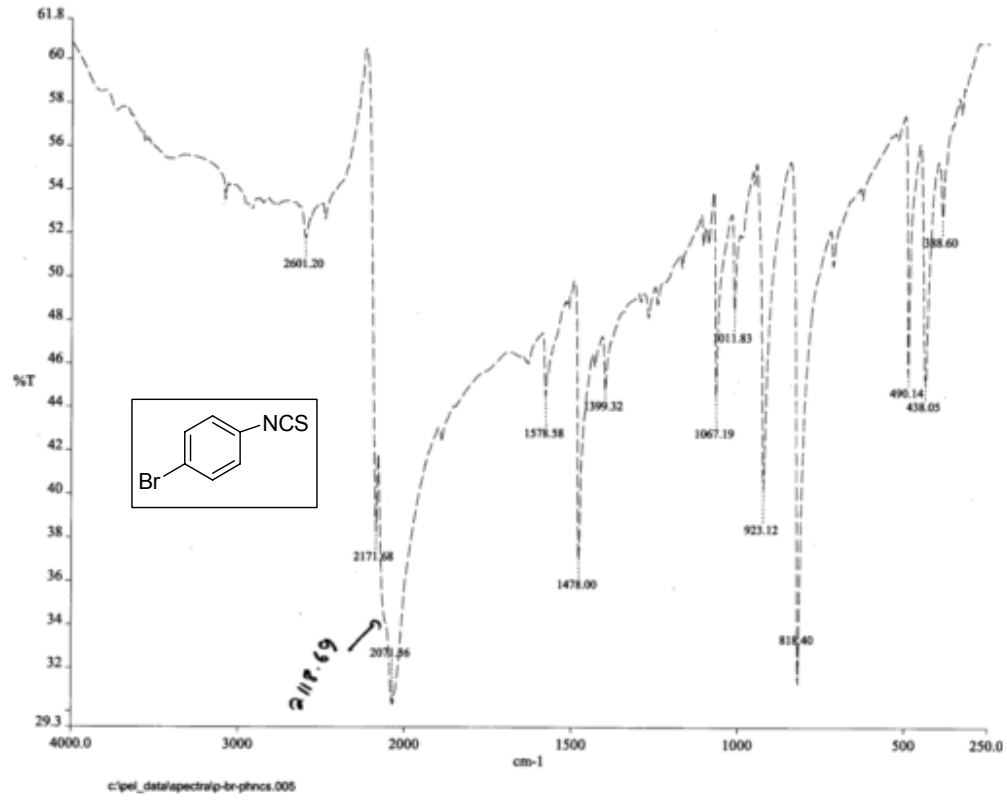
1-Bromo-4-isothiocyanato-benzene (4a): ^{1}H NMR (400 MHz, $CDCl_3$):



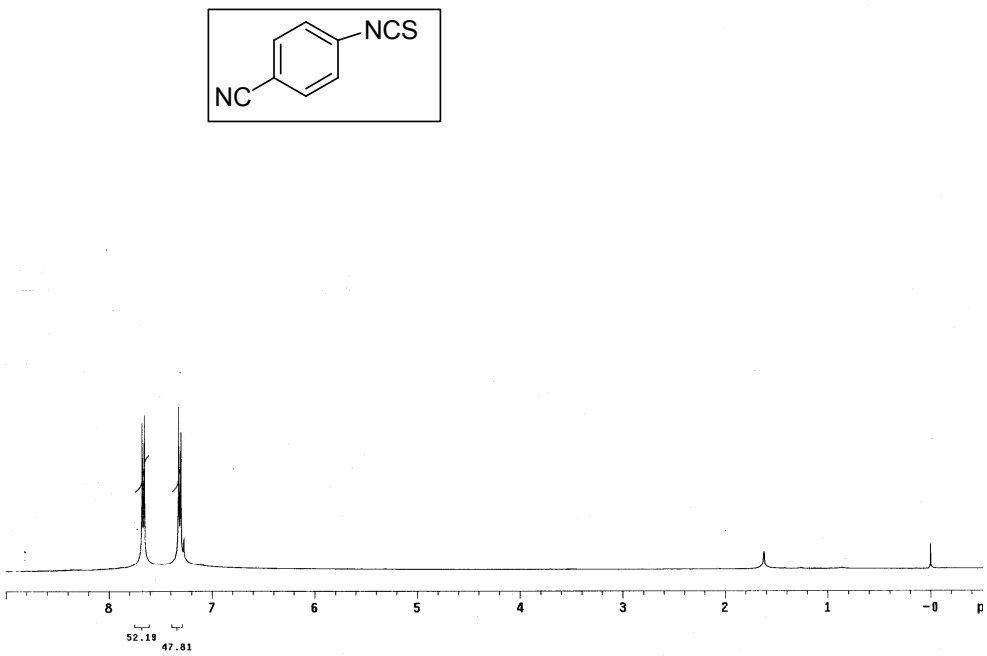
1-Bromo-4-isothiocyanato-benzene (4a): ^{13}C NMR (100 MHz, $CDCl_3$):



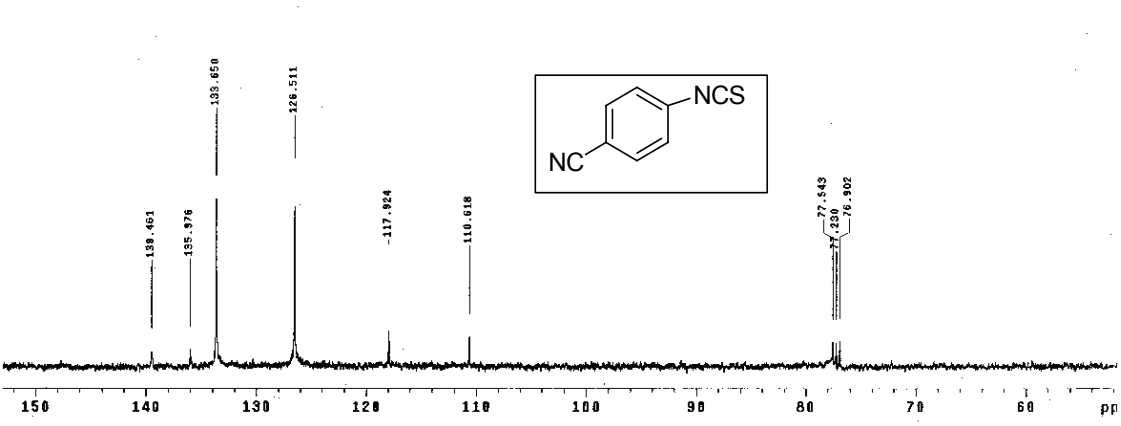
1-Bromo-4-isothiocyanato-benzene (4a): IR(KBr):



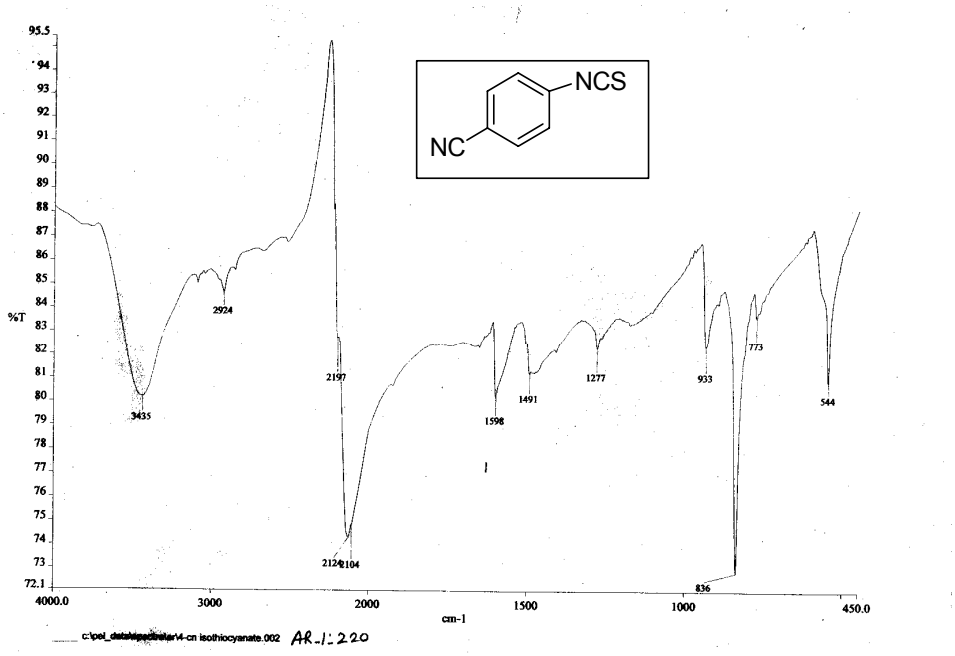
4-Isothiocyanato-benzonitrile (5a): ^{1}H NMR ($CDCl_3$, 400 MHz):



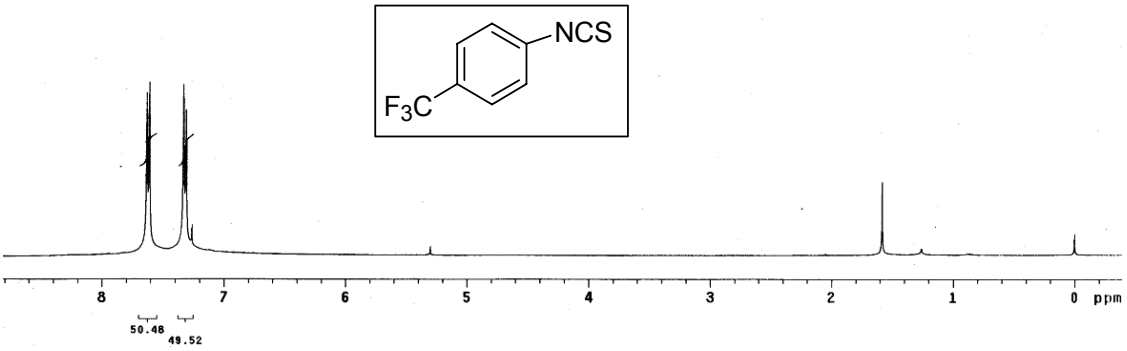
4-Isothiocyanato-benzonitrile (5a): ^{13}C NMR (100 MHz, $CDCl_3$):



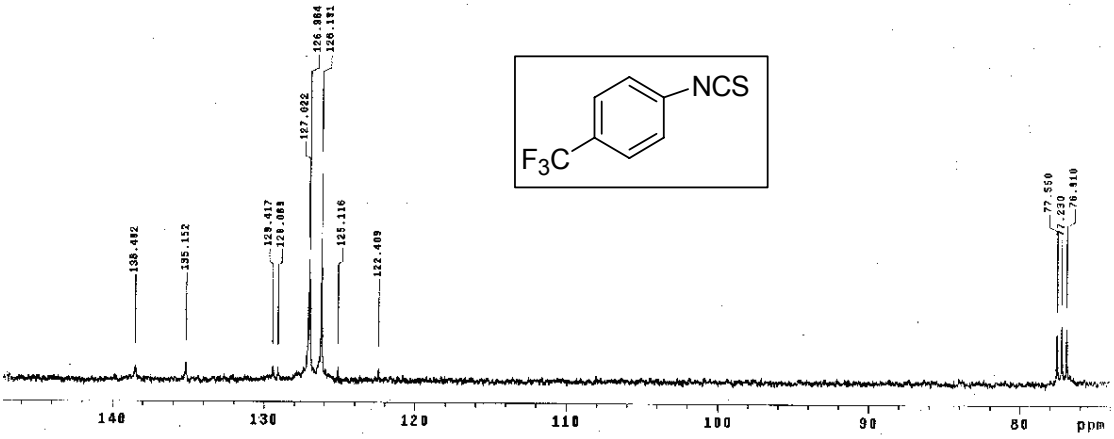
4-Isothiocyanato-benzonitrile (5a): IR(KBr):



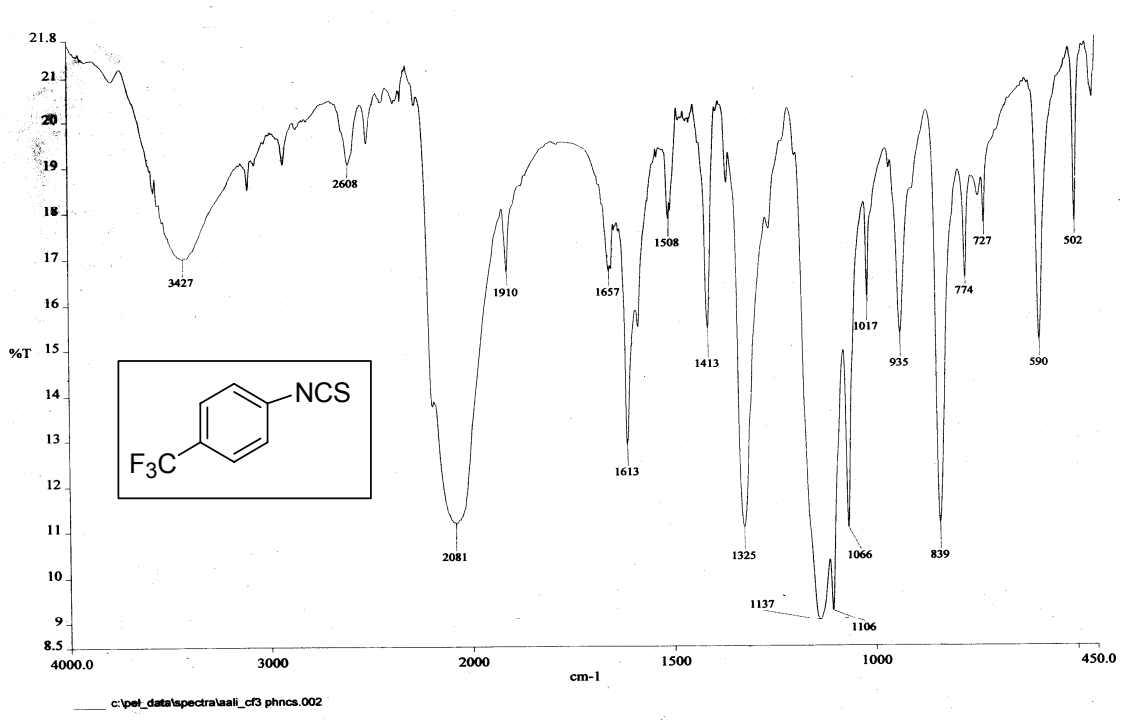
1-Isothiocyanato-4-trifluoromethyl-benzene (6a): ^{1}H NMR (400 MHz, $CDCl_3$):



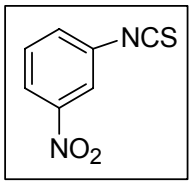
1-Isothiocyanato-4-trifluoromethyl-benzene (6a): ^{13}C NMR (100 MHz, $CDCl_3$):

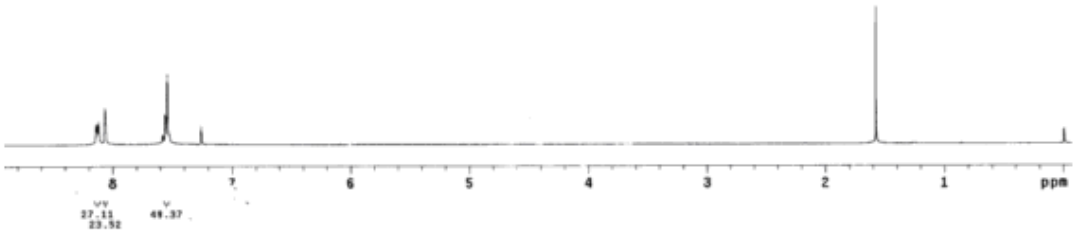


1-Isothiocyanato-4-trifluoromethyl-benzene (6a): IR (KBr):

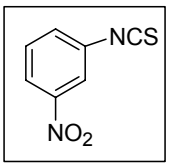


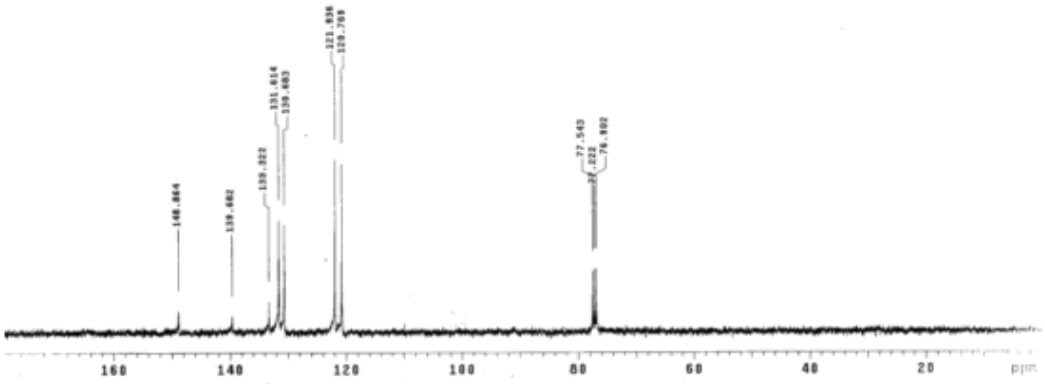
1-Isothiocyanato-3-nitro-benzene (7a): ^{1}H NMR (400 MHz, $CDCl_3$):



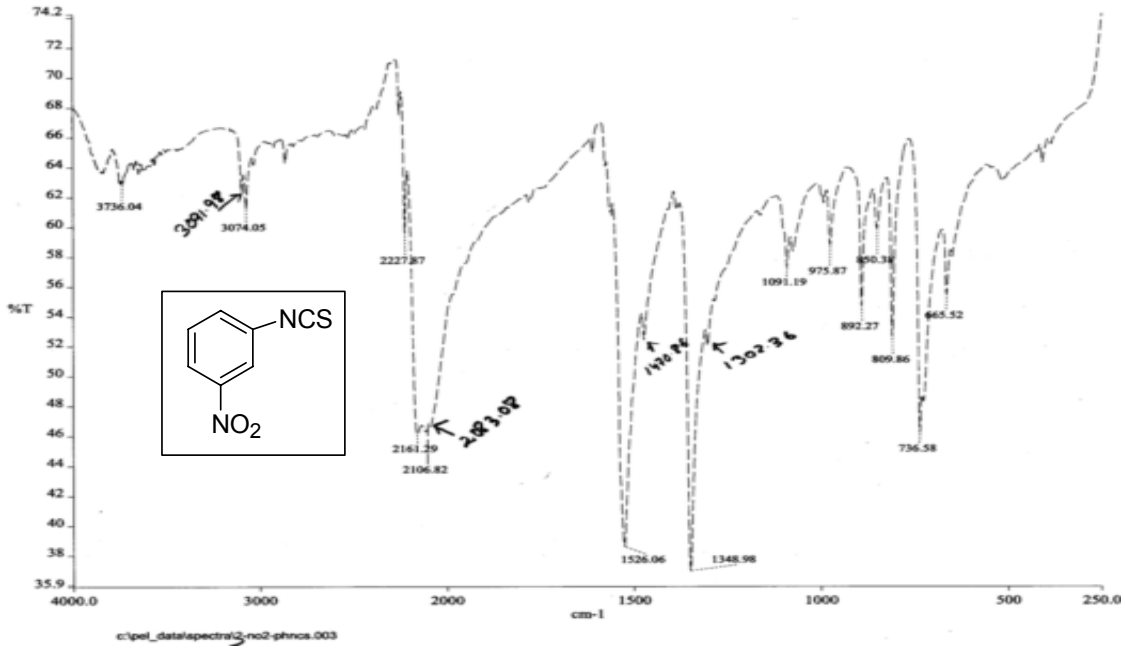


1-Isothiocyanato-3-nitro-benzene (7a): ^{13}C NMR (100 MHz, $CDCl_3$):

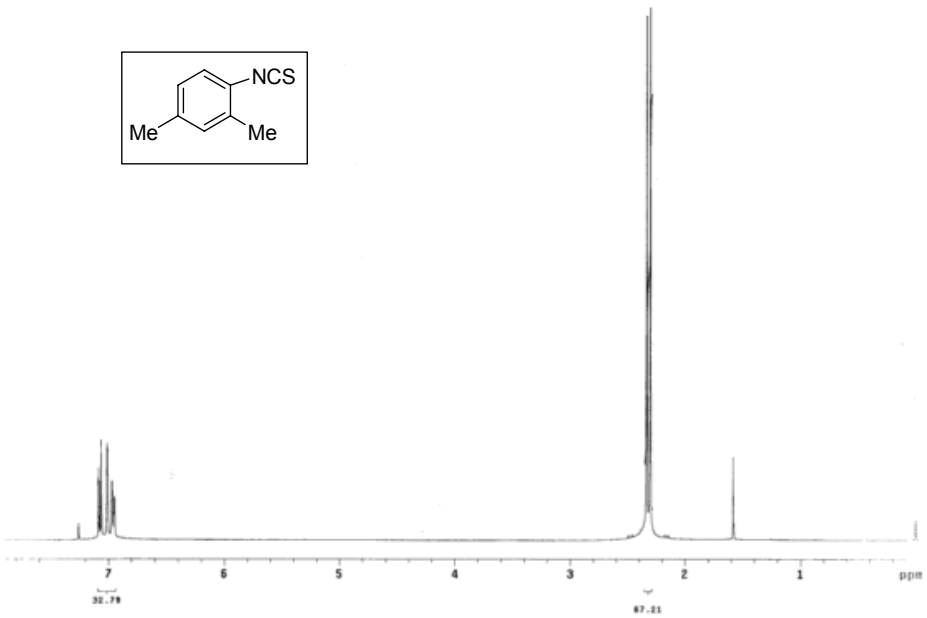




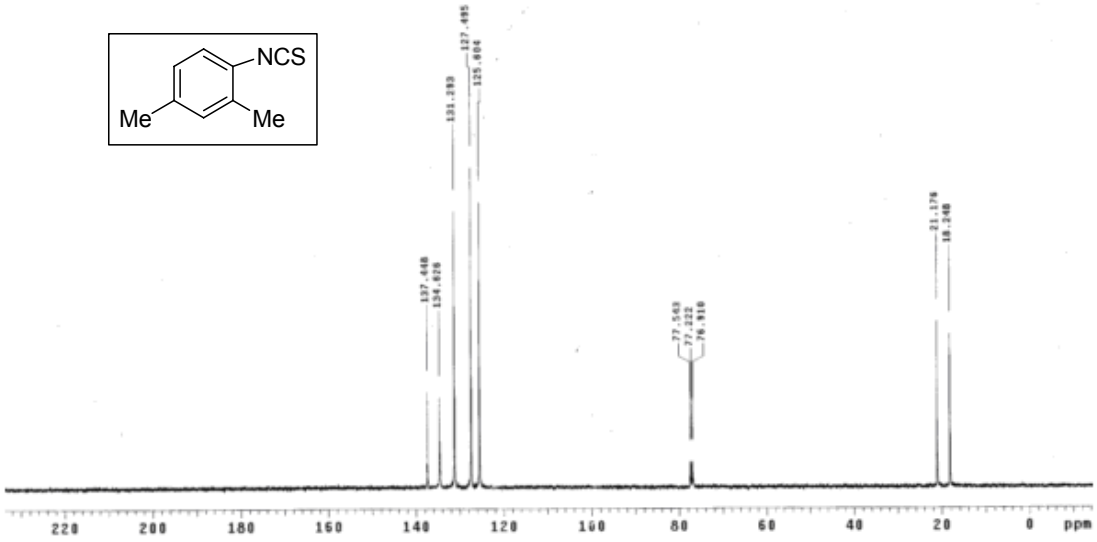
1-Isothiocyanato -3-nitro-benzene (7a): IR (KBr):



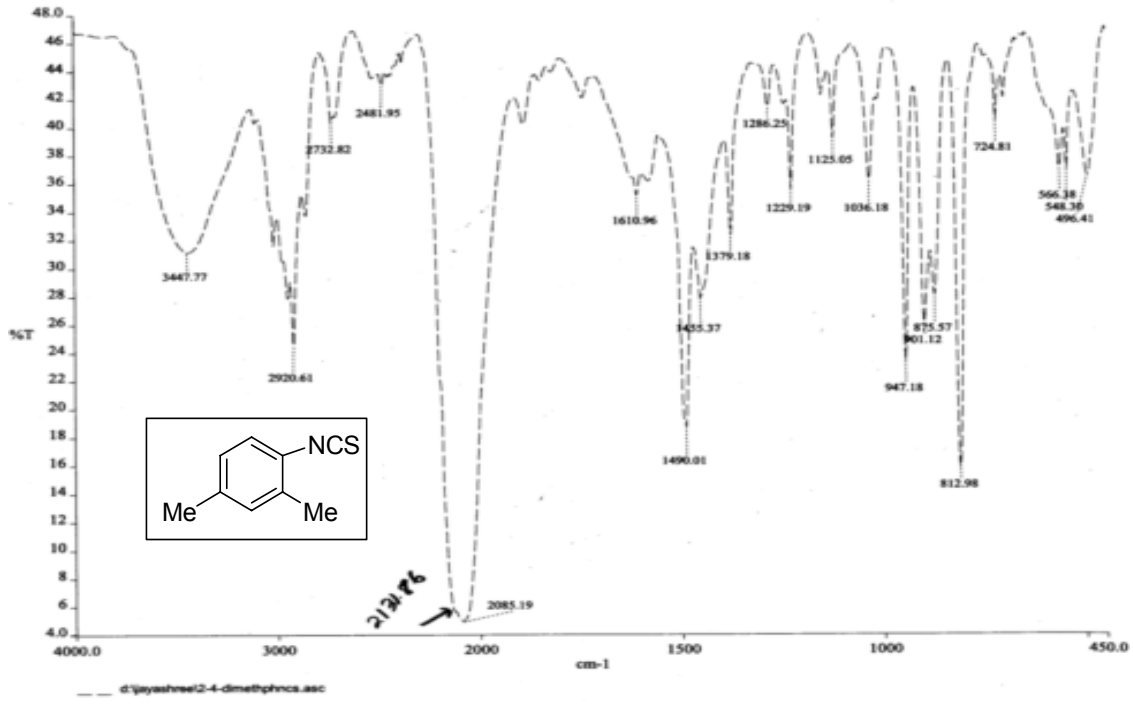
1-Isothiocyanato-2,4-dimethyl-benzene (8a): ^{1}H NMR (400 MHz, $CDCl_3$):



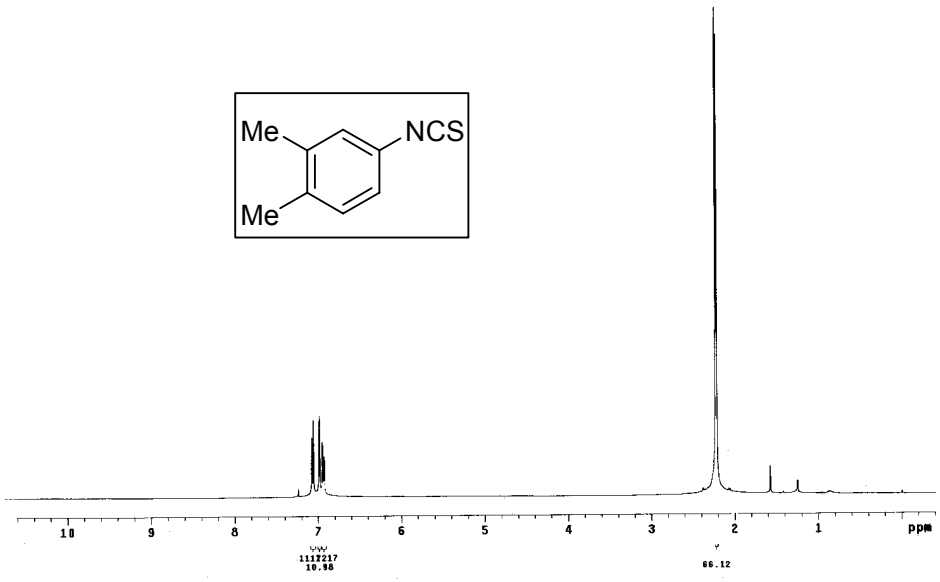
1-Isothiocyanato-2,4-dimethyl-benzene (8a): ^{13}C NMR (100 MHz, $CDCl_3$):



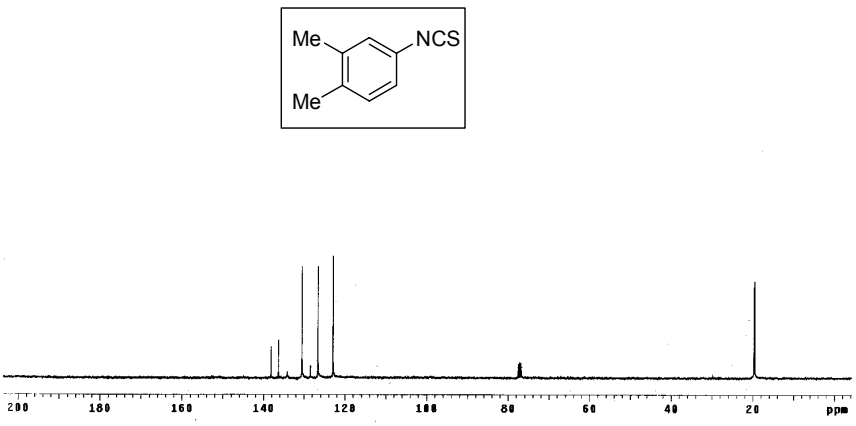
1-Isothiocyanato-2, 4-dimethyl-benzene (8a): IR (KBr):



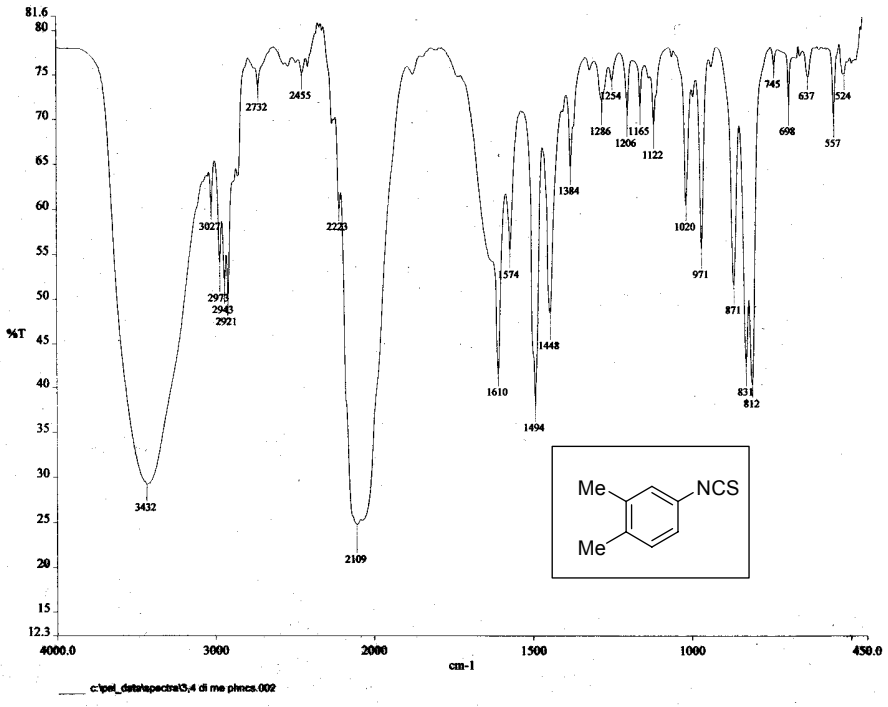
4-Isothiocyanato-1,2-dimethyl-benzene (9a): ^{1}H NMR (400 MHz, $CDCl_3$):



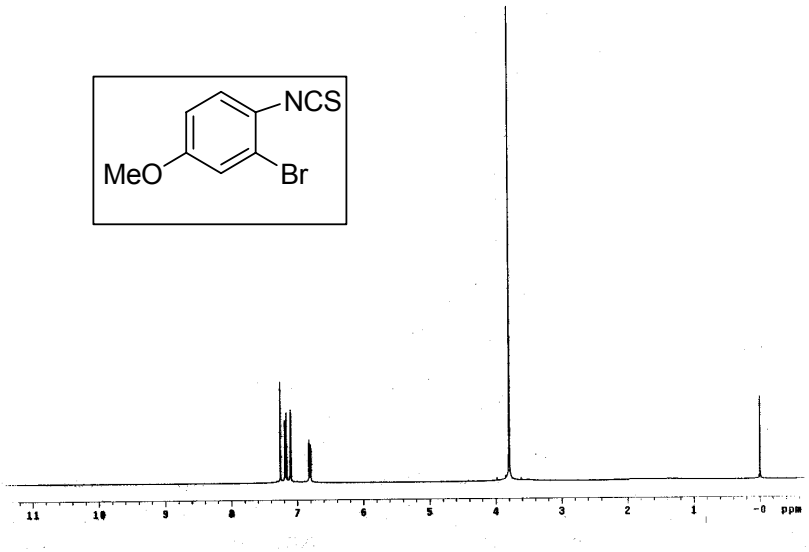
4-Isothiocyanato-1,2-dimethyl-benzene (9a): ^{13}C NMR (100 MHz, $CDCl_3$):



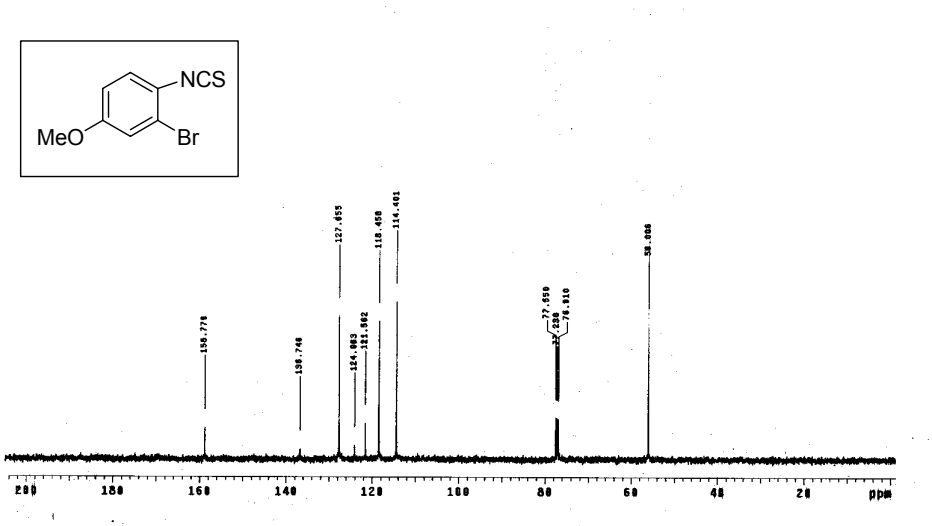
4-Isothiocyanato-1,2-dimethyl-benzene (9a): IR(KBr):



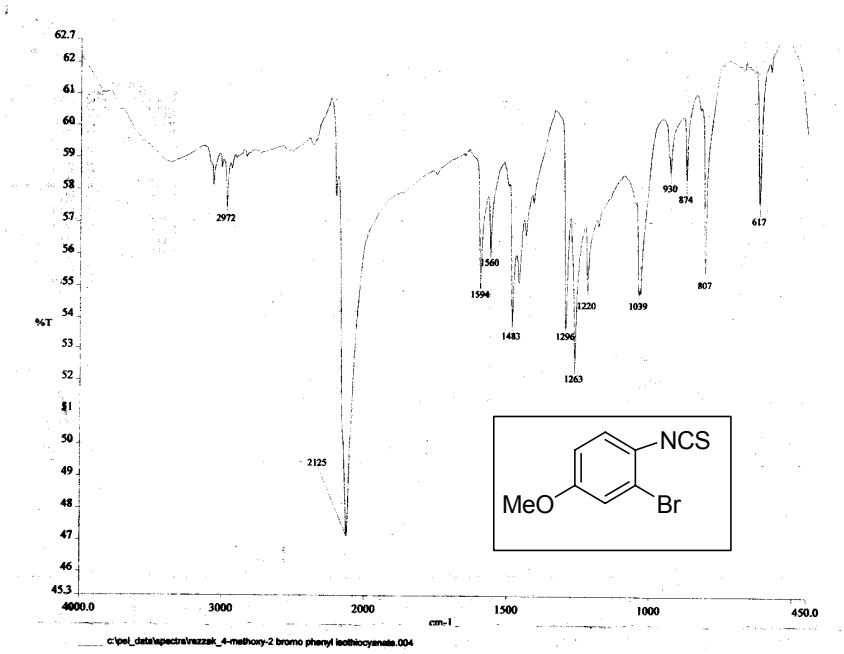
2-Bromo-1-isothiocyanato-4-methoxy-benzene (10a): ^{1}H NMR (400 MHz, $CDCl_3$):



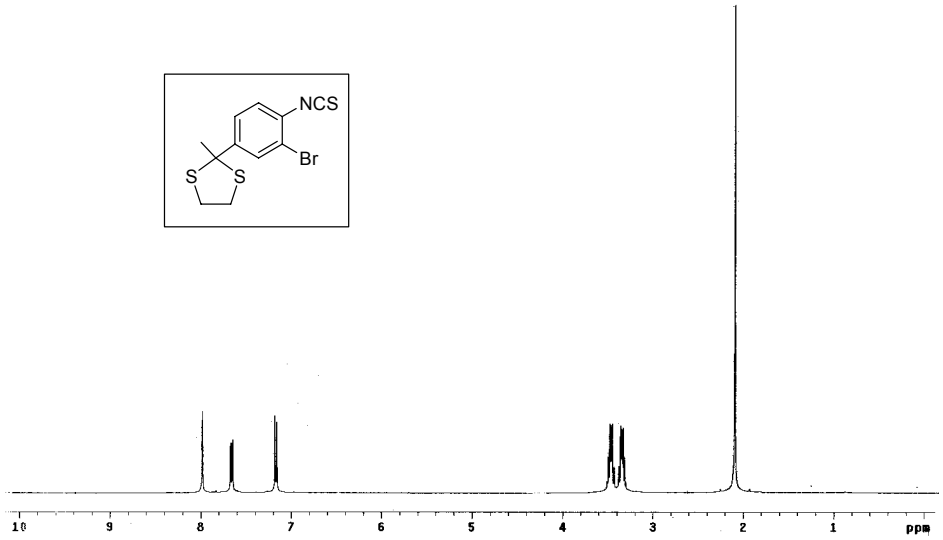
2-Bromo-1-isothiocyanato-4-methoxy-benzene (10a): ^{13}C NMR (100 MHz, $CDCl_3$):



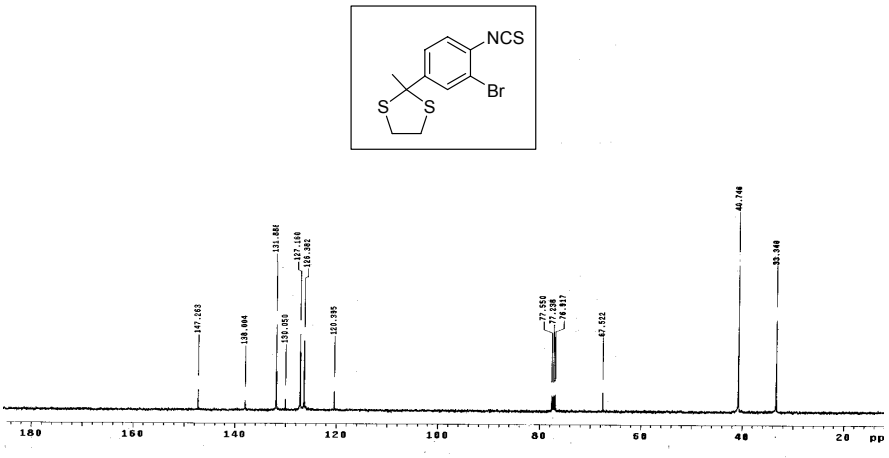
2-Bromo-1-isothiocyanato-4-methoxy-benzene (10a): IR(KBr):



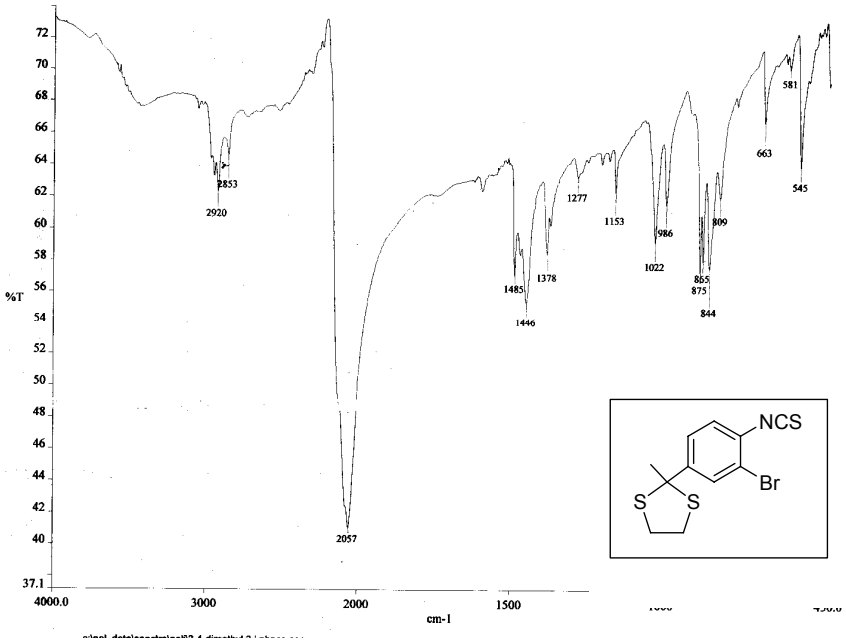
2-(3-Bromo-4-isothiocyanato-phenyl)-2-methyl-[1,3]dithiolane (11a): ^{1}H NMR (400 MHz, $CDCl_3$):



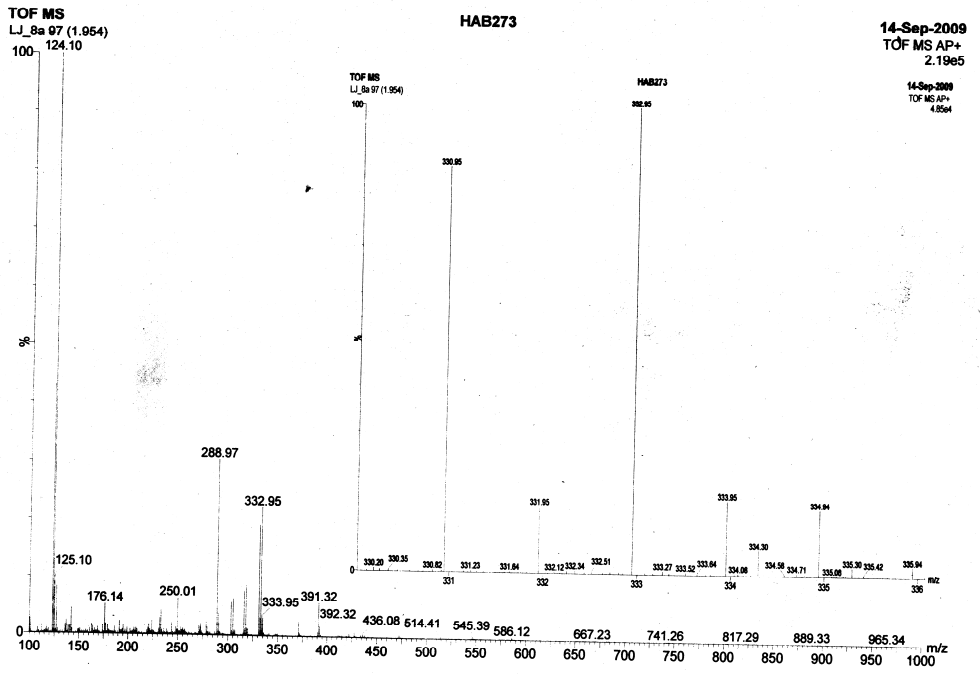
2-(3-Bromo-4-isothiocyanato-phenyl)-2-methyl-[1,3]dithiolane (11a): ^{13}C NMR (100 MHz, $CDCl_3$):



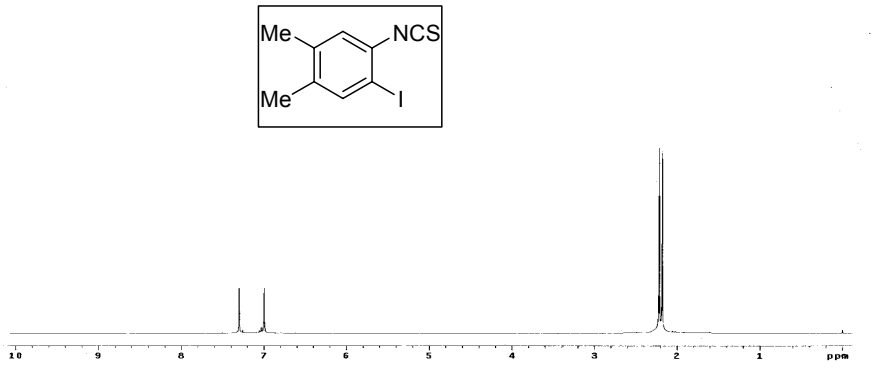
2-(3-Bromo-4-isothiocyanato-phenyl)-2-methyl-[1,3]dithiolane (11a): IR(KBr):



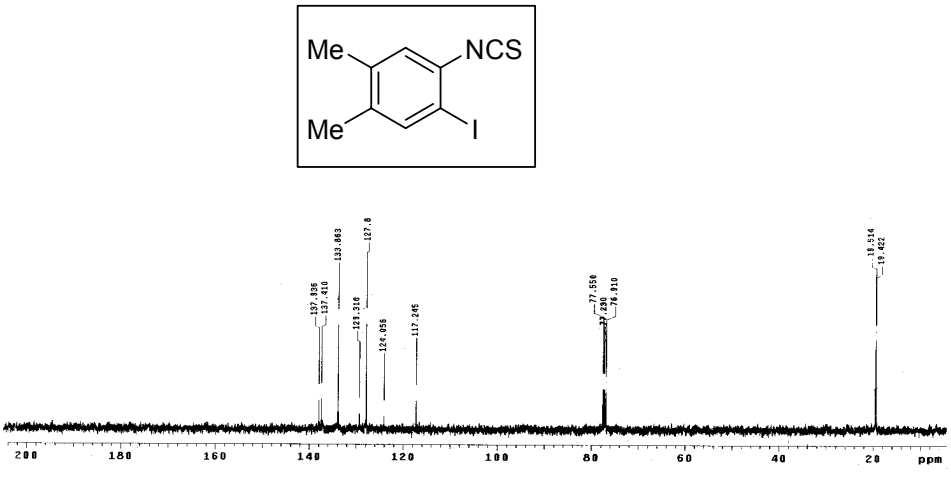
2-(3-Bromo-4-isothiocyanato-phenyl)-2-methyl-[1,3]dithiolane (11a): MS



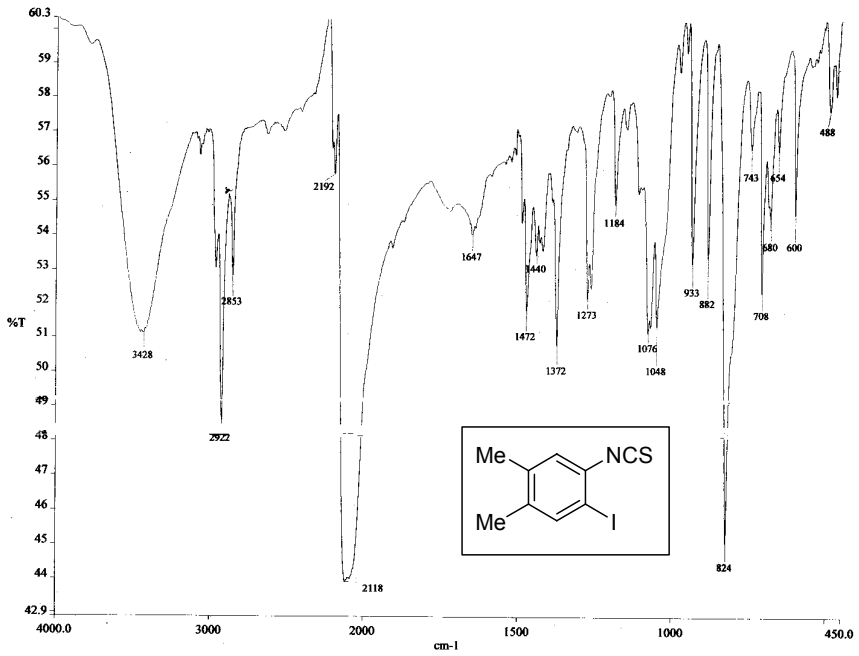
1-Iodo-2-isothiocyanato-4,5-dimethyl-benzene (12a): ^{1}H NMR (400 MHz, $CDCl_3$):



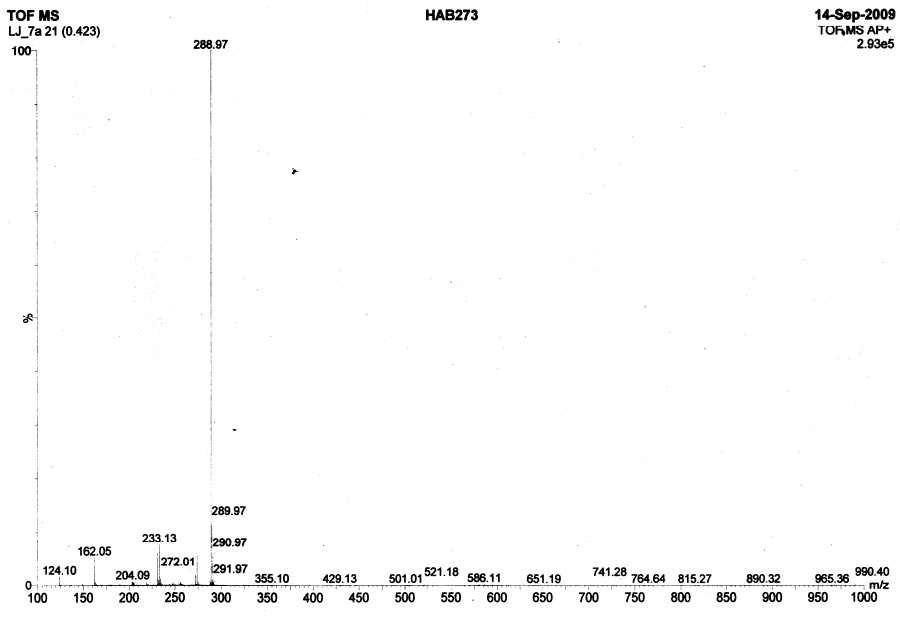
1-Iodo-2-isothiocyanato-4,5-dimethyl-benzene (12a): ^{13}C NMR (100 MHz, $CDCl_3$):



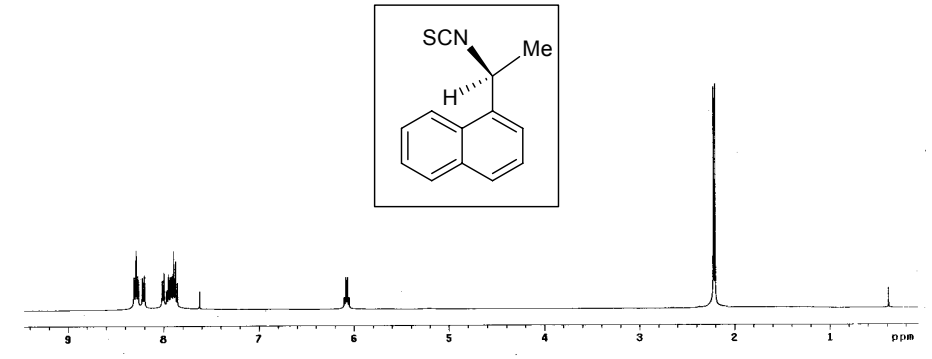
1-Iodo-2-isothiocyanato-4,5-dimethyl-benzene (12a): IR (KBr):



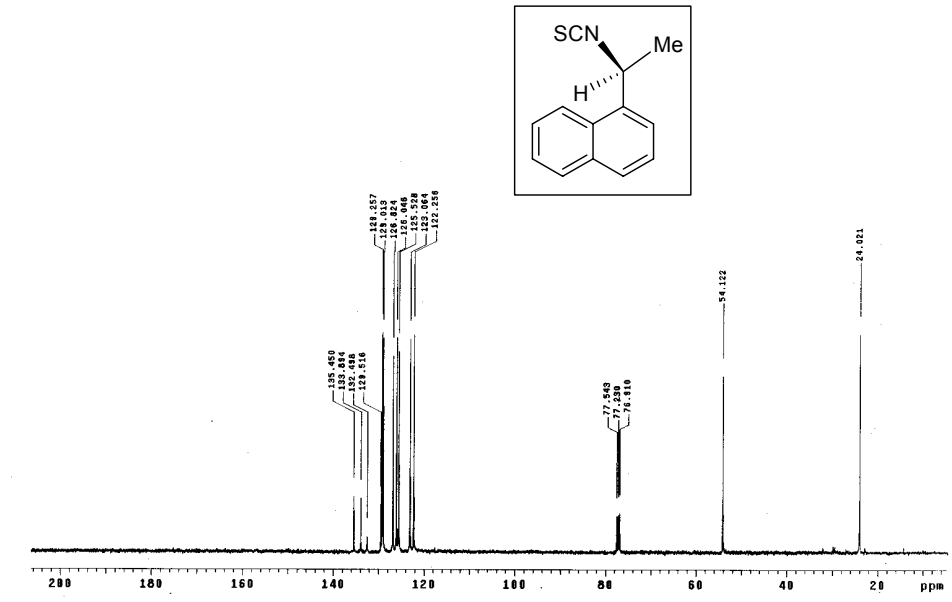
1-Iodo-2-isothiocyanato-4,5-dimethyl-benzene (12a): MS



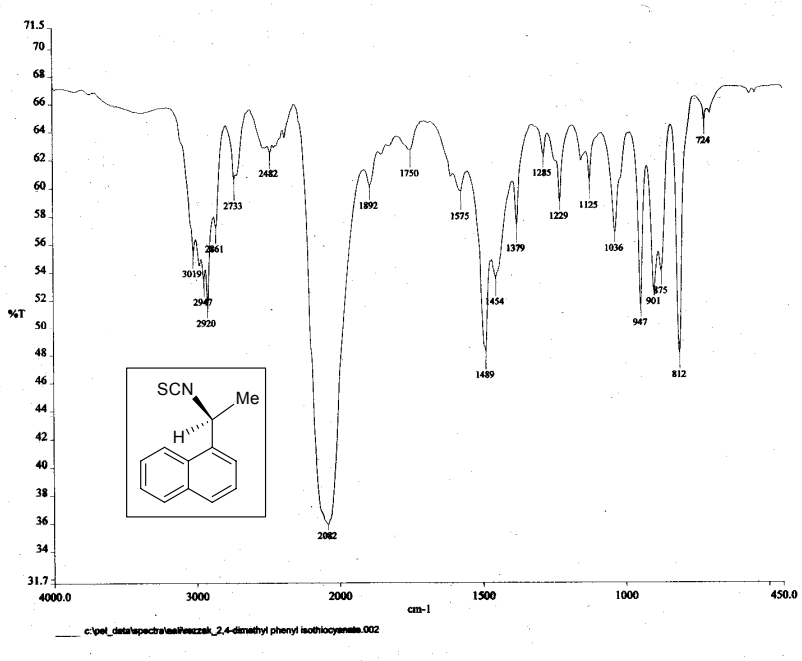
1-(1-Isothiocyanato-ethyl)-naphthalene (13a): ^{1}H NMR (400 MHz, $CDCl_3$):



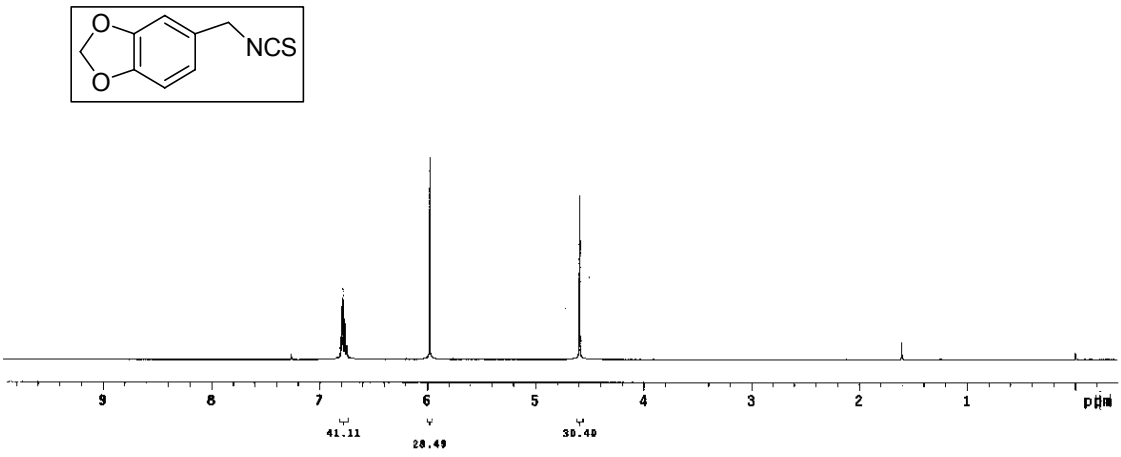
1-(1-Isothiocyanato-ethyl)-naphthalene (13a): ^{13}C NMR (100 MHz, $CDCl_3$):



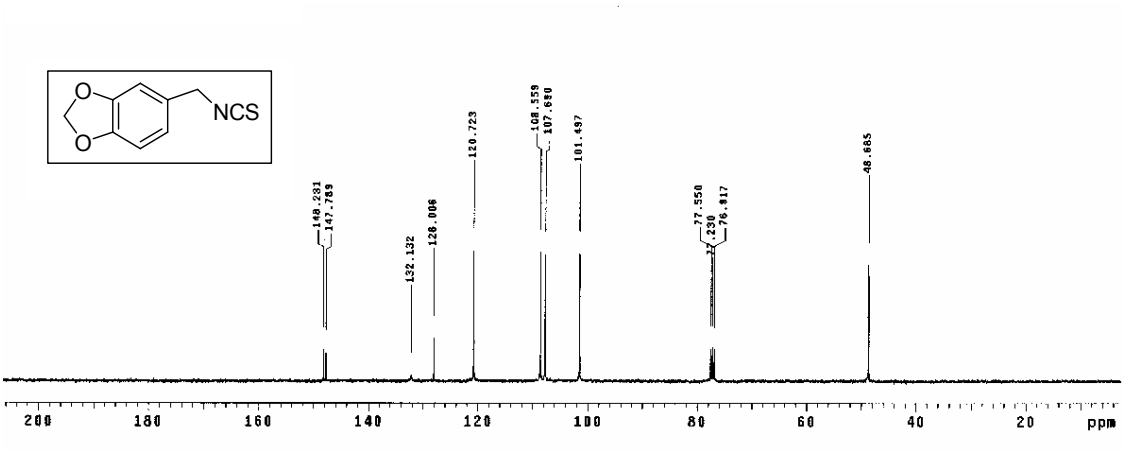
1-(1-isothiocyanato-ethyl)-naphthalene (13a): IR(KBr):



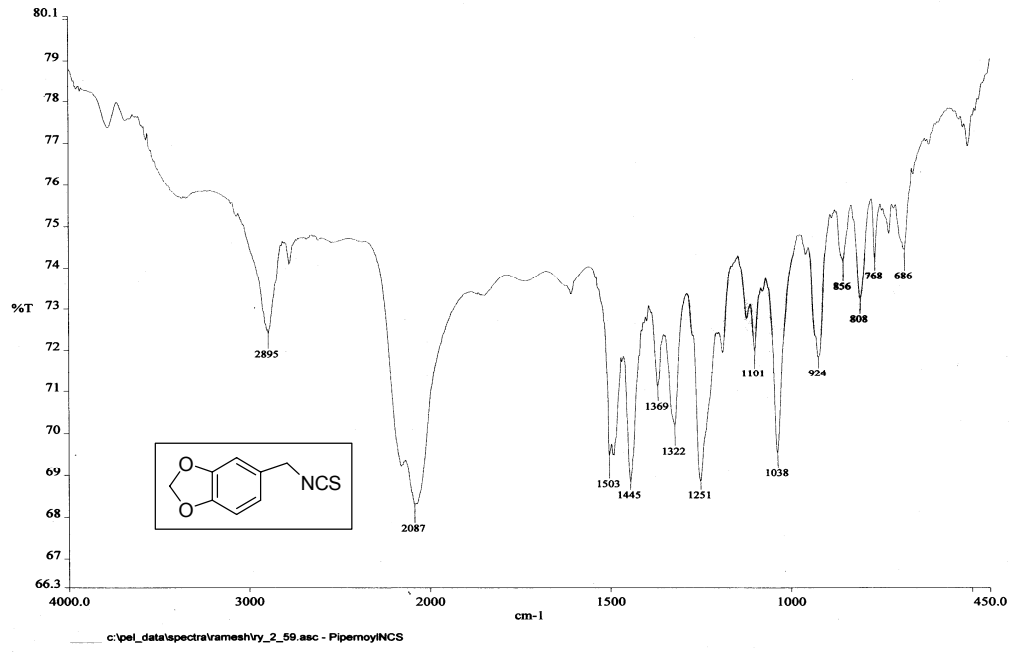
5-(Isothiocyanatomethyl)benzo[d][1,3]dioxole (14a): ^{1}HNMR. (400MHz, $CDCl_3$):



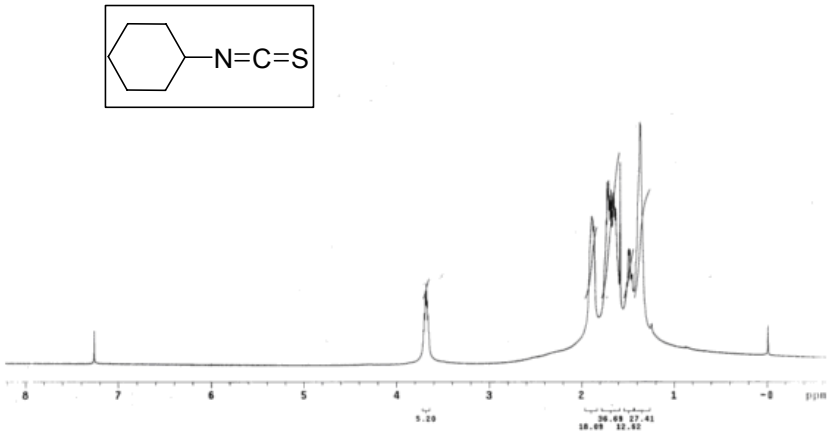
5-(Isothiocyanatomethyl)benzo[d][1,3]dioxole (14a): ^{13}C NMR (100 MHz, $CDCl_3$):



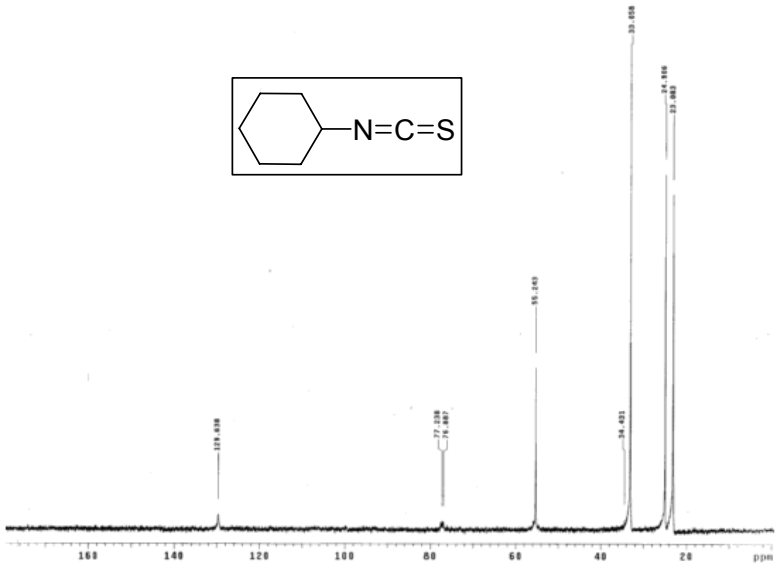
5-(Isothiocyanatomethyl)benzo[d][1,3]dioxole (14a): IR(KBr):



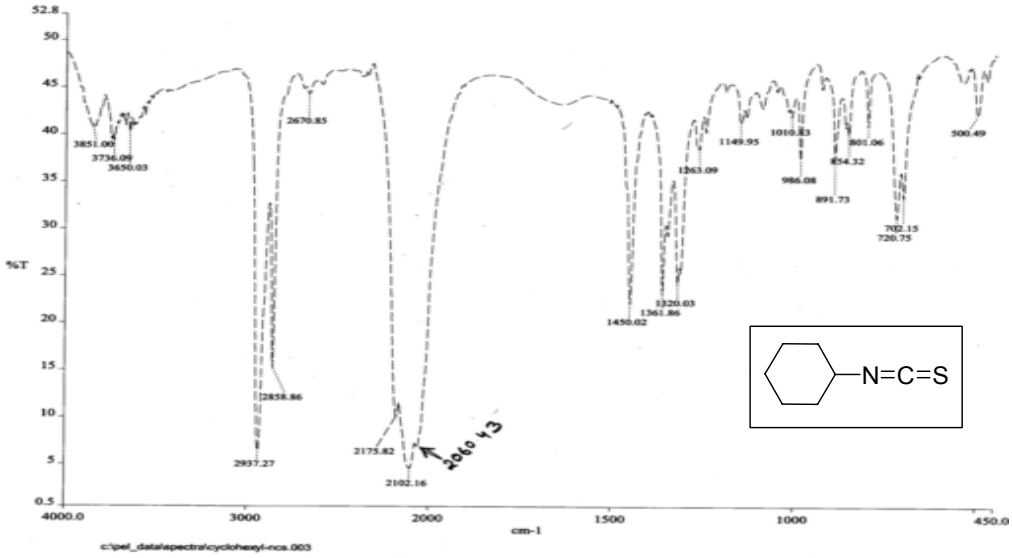
Isothiocyanato-cyclohexane (15a): ^{1}H NMR (400 MHz, $CDCl_3$):



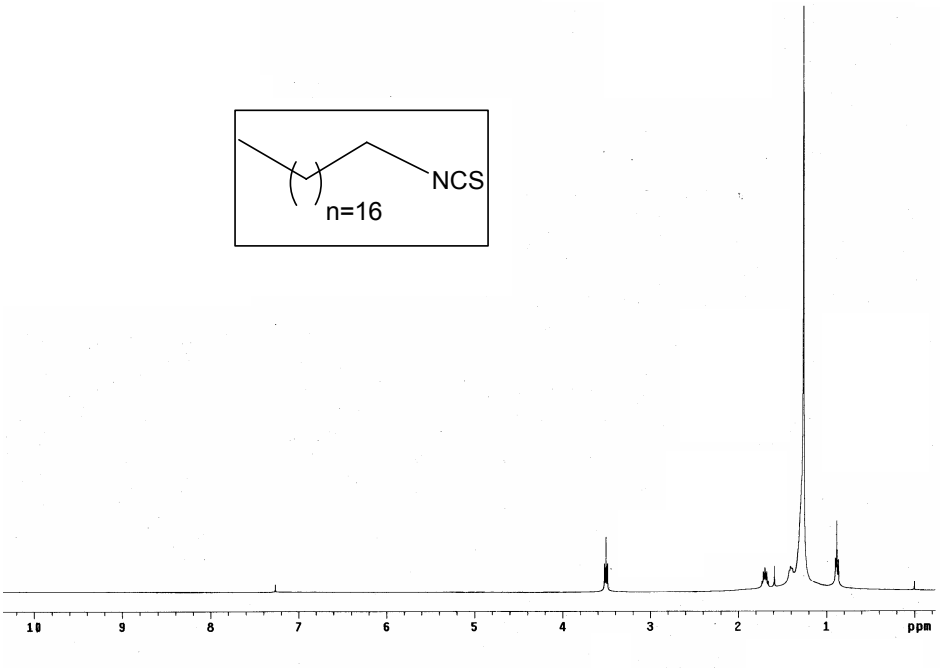
Isothiocyanato-cyclohexane (15a): ^{13}C NMR (100 MHz, $CDCl_3$):



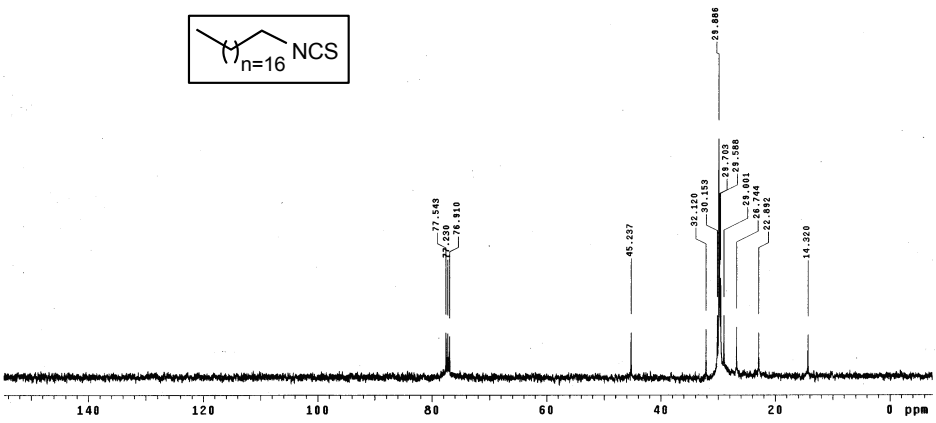
Isothiocyanato-cyclohexane (15a): IR (KBr):



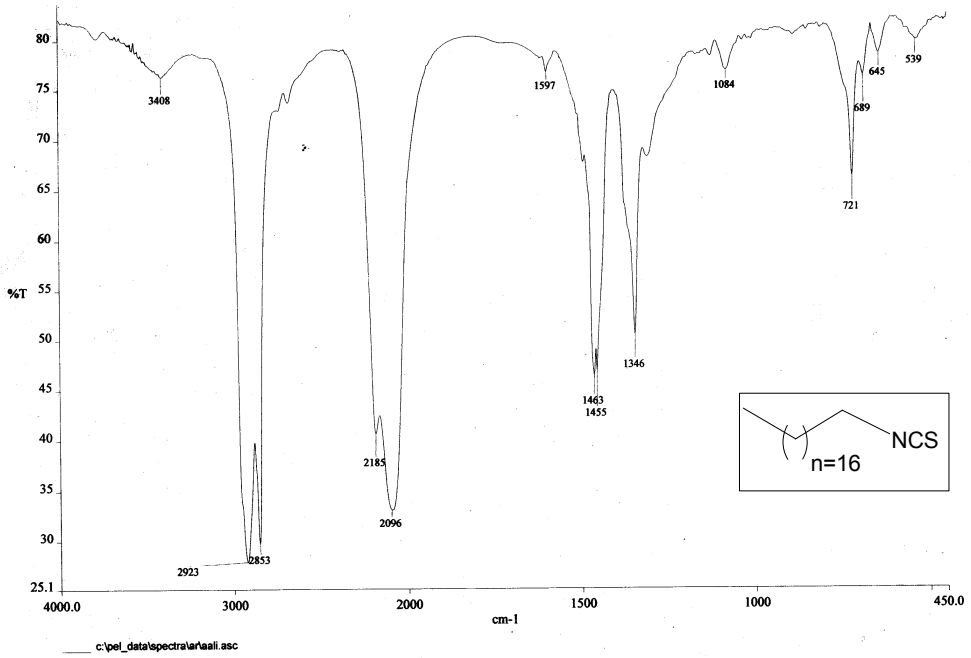
1-Isothiocyanato-octadecane (16a): ^{1}H NMR (400 MHz, $CDCl_3$):



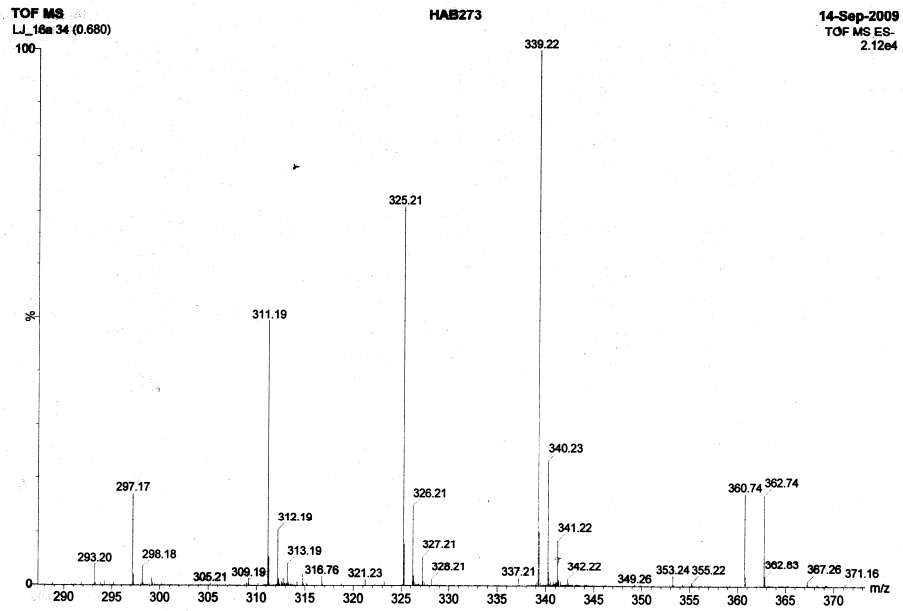
1-Isothiocyanato-octadecane (16a): ^{13}C NMR (100 MHz, $CDCl_3$):



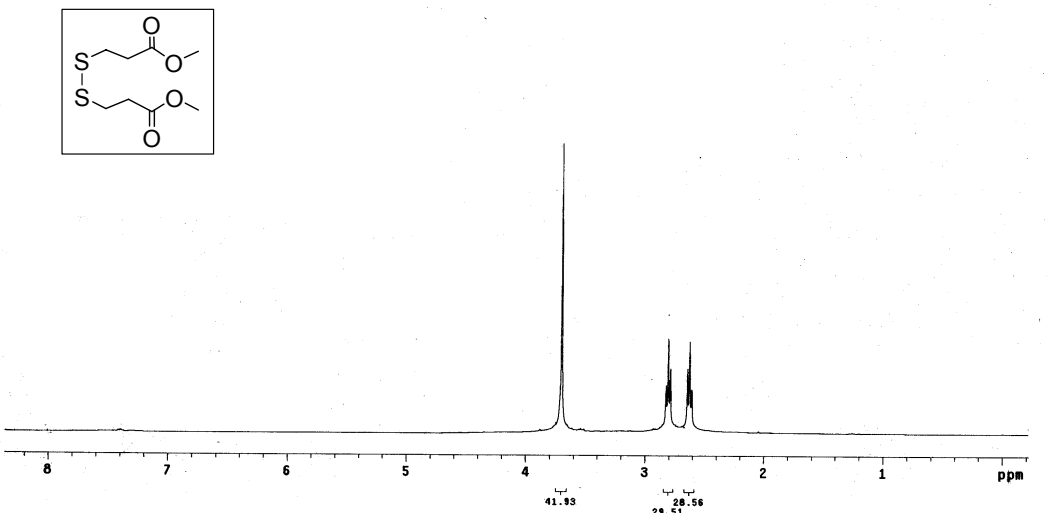
1-Isothiocyanato-octadecane (16a): IR (KBr):



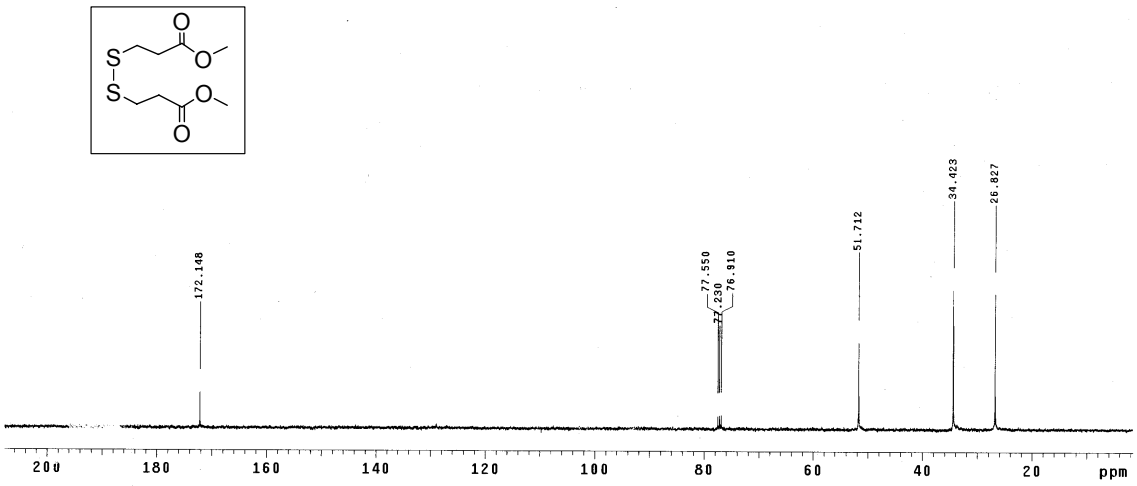
1-Isothiocyanato-octadecane (16a): MS



3-(2-Methoxycarbonyl-ethyldisulfanyl)-propionic acid methyl ester: ^{1}H NMR (400 MHz, $CDCl_3$):



3-(2-Methoxycarbonyl-ethyldisulfanyl)-propionic acid methyl ester: ^{13}C NMR (100 MHz, $CDCl_3$):



3-(2-Methoxycarbonyl-ethyldisulfanyl)-propionic acid methyl ester: IR (KBr):