Supporting Information

Trifluoroacetic Anhydride–Catalyzed Oxidation of Isonitriles by DMSO: A Rapid, Convenient Synthesis of Isocyanates

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General Procedures:

^{1}H NMR spectra were taken on a Varian Inova-400 spectrometer using $CDCl_3$ with 0.05% v/v TMS or DMSO-d6 as solvents, recorded in δ (ppm), and referenced to TMS (0.00 ppm) or DMSO-d_6 (2.50 ppm). ^{13}C NMR spectra were taken on a Varian Inova-400 spectrometer using $CDCl_3$ with 0.05% v/v TMS as solvent, recorded in δ (ppm), and referenced to $CDCl_3$ (77.16 ppm for ^{13}C NMR). IR spectra were obtained using a Thermo Nicolet Avatar 370DTGS FT-IR spectrometer and recorded in wavenumbers (cm^{-1}). Melting points were measured using a Thomas Hoover Uni-melt Capillary Melting Point Apparatus. Mass spectra were measured at the Life Sciences Core Laboratories Center using ABI/MDS Sciex 4000 Q Trap. Chemicals were obtained from Aldrich, Acros, Aensar, or Fluka and used as received unless specified.

Reduction of Dibenzyl Sulfoxide to Dibenzylsulfide *[538-74-9]*

Dibenzyl sulfoxide (115 mg, 0.5 mmol, recrystallized from ethanol) was dissolved in dry CH_2Cl_2 (0.5 mL) and *t*-butyl isonitrile (74 μL, 0.65 mmol) under N_2 in a 25 mL RBF. After cooling the solution to 0 ^{o}C, TFAA (91μL, 0.65 mmol) was added dropwise. The resulting solution was stirred vigorously at 0 ^{o}C for 5 min, then warmed to rt and stirred for 5 min. The solution was then concentrated *in vacuo* to afford a white paste, which was purified by flash column chromatography (1:15 ethyl acetate:hexane, R_f=0.35) to afford the desired sulfide (94 mg, 88%) as a white solid.

Representative Procedure for the Catalytic Oxidation of Isonitriles to Isocyanates: Oxidation

of t-Butyl Isonitrile and Trapping with t-Butylamine.

A solution of *t*-butyl isonitrile (113 μL, 1 mmol) in dry CH_2Cl_2 (1 mL) and dry DMSO (78 μL, 1.1 mmol) under N_2 in a 25 mL RBF was cooled to -60 ^oC, then TFAA (7 μL, 0.05 mmol) was added. The resulting solution was stirred vigorously at -60 ^oC for 5 min, then warmed to rt and stirred for 5 min. After recooling the solution to -60 ^oC, *t*-butylamine (315 μL, 3 mmol) was added dropwise. The resulting solution was stirred at rt for 2 h, then concentrated *in vacuo* to afford a white solid. Water (3 mL) was added and the aqueous phase was extracted with ethyl acetate (4 x 5 mL). The combined organic extracts were washed with brine (2 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo* to afford di-*t*-butylurea (165 mg, 96%) as a white solid, m.p. 252 – 254 ^oC (sealed capillary tube) (lit.[1] 240 ^oC).

N-n-butyl-N'-tert-butylurea *[25347-96-0]*

Yield: 95%, m.p. 73–76 ^oC (lit.[2] 71–72 ^oC).

N-tert-butyl-N'-4-methoxyphenylurea

Yield: 61%, m.p. = 129 – 130. 5 ^oC (lit.[3] 128 – 130 ^oC).

N-tert-butyl-N'-2-morpholinoethylurea

Yield: 67%. IR (neat) 3350(s), 2961(s), 2926(m), 2856(m), 2811(m), 1638(s), 1558(s). ESI-MS (CH_3OH) 230 (M+H).

Representative Procedure for the Catalytic Oxidation of Isonitriles with Direct Isolation of the Isocyanate: Ethyl Isocyanatoacetate *[2949-22-6]*

A solution of ethyl isocyanoacetate (115 μL, 1 mmol) in dry CH_2Cl_2 (1 mL) and dry DMSO (78 μL, 1.1 mmol) under N_2 in a 25 mL RBF was cooled to -60 ^oC, then TFAA (7 μL, 0.05 mmol) was added. The resulting solution was stirred vigorously at -60 ^oC for 5 min, then warmed to rt and stirred for 5 min. Solvent was removed using a rotary evaporator and the residue concentrated *in vacuo* (0.2 Torr, 1-2 min) to afford ethyl isocyanatoacetate (122 mg,

95%) as a brown oil whose IR and ^{1}H NMR matched those in the Aldrich Spectral Library. IR (neat) 3349(m), 2986(m), 2254(s), 1747(s).

Cyclohexyl isocyanate *[3173-53-3]*

Yield: 94%. IR and ^{1}H-NMR matched those in the Aldrich Spectral Library. IR (neat) 2937(s), 2858(m), 2263(s).

1. Baumgarter, H. E., Smith, H. L., and Staklis, A. *J. Org. Chem.* **1975**, *40*, 3554.
2. Linke, S., Tisue, G. T., and Lwowski, W. *J. Am. Chem. Soc.*, **1967**, *89*, 6308.
3. Groszek, G. *Org. Proc. Res. Dev.*, **2002**, *6*, 759.

S4

Parameter	Value
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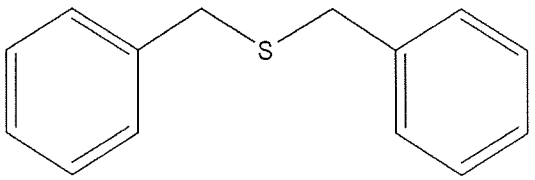
3 Acquisition Date	2011-01-24T14:21:33
4 Temperature	25.0
5 Nucleus	1H



S5

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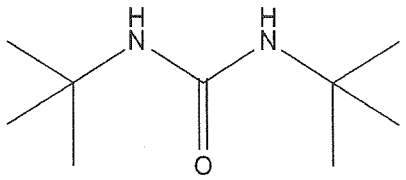
5 Nucleus	1H



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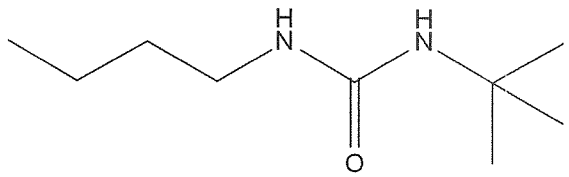
5 Nucleus	1H



S7

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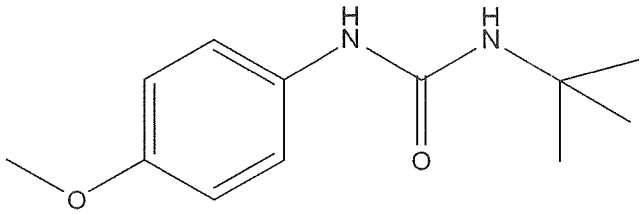
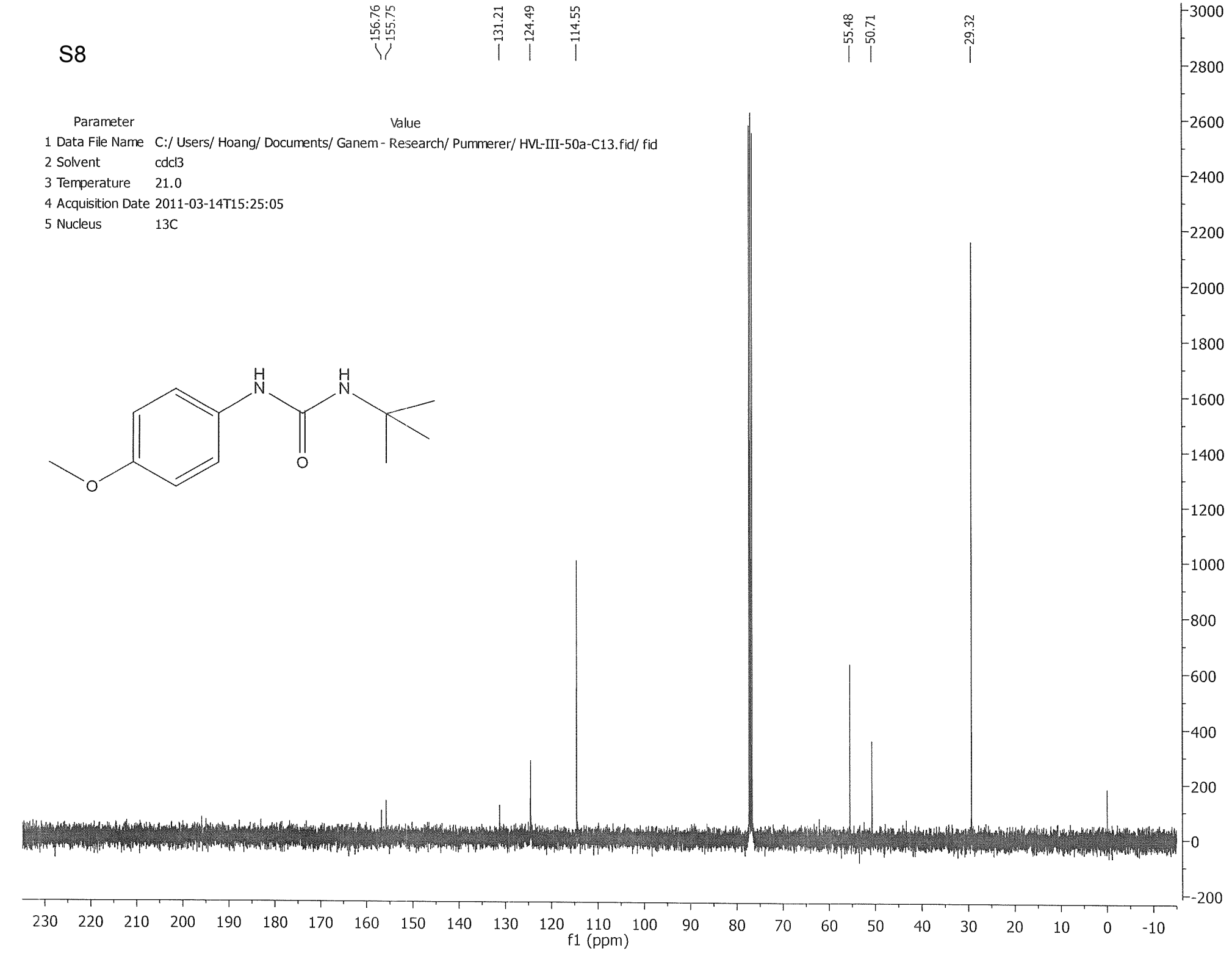
5 Nucleus	1H

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155.75
131.21
124.49
114.55
55.48
50.71
29.32
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2 Solvent cdcl3
3 Temperature 21.0
4 Acquisition Date 2011-03-14T15:25:05
5 Nucleus 13C
H
N
H
N
O
O
f1 (ppm)

S9

Parameter	Value
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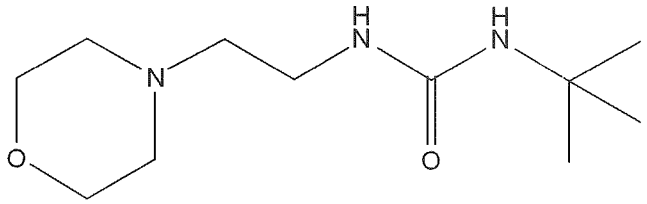
5 Nucleus	1H



S10

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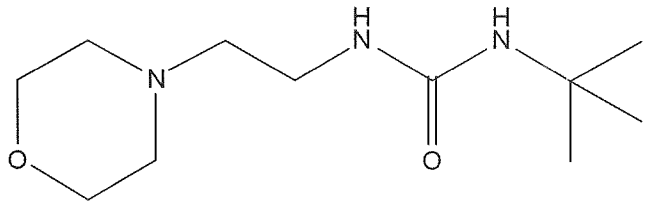
5 Nucleus	13C



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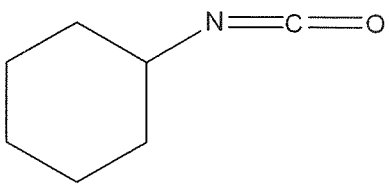
5 Nucleus	1H



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2 Solvent	cdcl3
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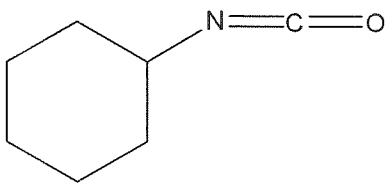
5 Nucleus	13C



S13

Parameter	Value
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3 Temperature	21.0
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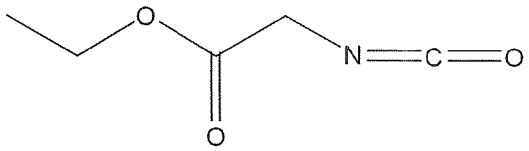
5 Nucleus	1H



S14

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5 Nucleus	13C