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SUPPORTING INFORMATION

Title: Reaction of Thiolesters with Nitrogen Ylides
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Melting points were determined on a Kofler block and are not corrected. NMR spectra (δ, ppm; *J*, Hz) were measured on a Varian Unity 500 and/or Bruker Avance-400 instruments in hexadeuterated dimethyl sulfoxide or $CDCl_3$ and referenced to the solvent signal. Mass spectra were measured on a ZAB-EQ (VG Analytical) spectrometer using the FAB ionization. UPLC-MS was performed on Acquity UPLC Instrument (Waters Corporation).

1. *Deuterium exchange in butyl quaternary salts* **1a–1e**

Preparation of 1-butylpyridinium bromide (**1a**), 3-aminocarbonyl-1-butylpyridinium bromide (**1b**), 4-aminocarbonyl-1-butylpyridinium bromide (**1c**), butyltriethylammonium bromide (**1d**), and butyltriphenylphosphonium bromide (**1e**)

The title quaternary bromides were prepared by a 8-h refluxing of acetonitrile solutions of the corresponding base and equimolar amount of 1-bromobutane. After cooling, the salts **1** were filtered and characterized.

1-Butylpyridinium bromide (**1a**): Yield 85%, M.p. 95-97 ºC, ref.[1a] 97-98 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): 0.89 (t, 3H, J_{vic} = 7.3, CH_3); 1.27 (m, 2H, CH_2-3); 1.89 (m, 2H, CH_2-2); 4.66 (t, 2H, J_{vic} = 7.3 CH_2-1); 8.18 (m, 2H, H-3,5-Py); 8.62 (m, 1H, H-4-Py); 9.20 (m, 2H, H-2,6-Py).

3-Aminocarbonyl-1-butylpyridinium bromide (**1b**): Yield 78%, M.p. 166-168 ºC, ref.[1b] 169 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): 0.91 (t, 3H, J_{vic} = 7.3, CH_3); 1.32 (m, 2H, CH_2-3); 1.93 (m, 2H, CH_2-2); 4.68 (t, 2H, J_{vic} = 7.3 CH_2-1); 8.18 (bs, 1H, NH_aH_b); 8.28 (m, 1H, H-5-Py); 8.61 (bs, 1H, NH_aH_b); 8.96 (m, 1H, H-4-Py); 9.27 (m, 1H, H-6-Py); 9.57 (m, 1H, H-2-Py).

4-Aminocarbonyl-1-butylpyridinium bromide (**1c**): Yield 82%, M.p. 147-149 ºC, ref.[1c] 154-156 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): 0.90 (t, 3H, J_{vic} = 7.3, CH_3); 1.30 (m, 2H, CH_2-3); 1.91 (m, 2H, CH_2-2); 4.67 (t, 2H, J_{vic} = 7.3 CH_2-1); 8.29 (bs, 1H, NH_aH_b); 8.48 (m, 2H, H-3,5-Py); 8.73 (bs, 1H, NH_aH_b); 9.34 (m, 2H, H-2,6-Py).

Butyltriethylammonium bromide (**1d**): Yield 51%, M.p. 215-217 ºC, ref.[1d] 212-215 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): 0.93 (t, 3H, J_{vic} = 7.3, CH_3-4); 1.32 (m, 2H, CH_2-3); 1.16 (m, 9H, CH_3-amine); 1.56 (m, 2H, CH_2-2); 3.12 (t, 2H, J_{vic} = 7.3 CH_2-1); 3.22 (m, 6H, CH_2-amine).

Butyltriphenylphosphonium bromide (**1e**):): Yield 72%, M.p. 241-241.5 ºC, ref.[1e] 239-241 ºC. ^{1}H NMR (400 MHz, DMSO-d_6): 0.88 (t, 3H, J_{vic} = 7.3, CH_3); 1.49 (m, 4H, CH_2-2,3); 3.62 (t, 2H, J_{vic} = 7.3 CH_2-1); 7.74-7.93 (m, 15H, 3xPh).

Deuterium exchange:

To the $(CD_3)_2SO$ solution of bromide **1a–1e** (approx. 15 mg bromide in 0.5 mL of the solvent) was added one drop D_2O. Deuterium exchange was observed by NMR spectroscopy.

a) *After 10 min at RT*: only the exchange of ortho protons of the pyridinium ring was observed (in compound **1a** 65% of H exchanged, **1b** 80%, **1c** 45%). No changes took place in the molecule **1d** and complete exchange of CH_2-1 in **1e** was observed.

b) *After heating to 90 ºC for 60 min*: complete exchange of CH_2-1 in **1a** as well as 55% exchange of CH_2-1 in **1c** were observed. In the NMR spectrum of nicotinamide derivative **1b** appeared signals of one or more degradation products. Spectra of compounds **1d** and **1e** remained as in the case a).

2. *4-(4-Aminocarbonylpyridinio)butan-1-yl-isothiuronium dibromide* (**5a**) *and 4-pyridiniobutan-1-yl-isothiuronium dibromide* (**5b**)

4-Aminocarbonyl-1-(4-bromobutan-1-yl)pyridinium bromide[2a] (**4a**) and 1-(4-bromobutan-1-yl)pyridinium bromide[2b] (**4b**) were prepared by a 7-h (2-h, resp.) refluxing of acetone solutions of the corresponding base and with 50% excess of 1,4-dibromobutane and one drop of DMF in the yield of 78% and 43%, resp. The obtained quaternary salt was dissolved in ethanol, equimolar amount of thiourea added and reaction mixture refluxed for 5 h. Analytically pure title dibromides **5a** and **5b** were obtained in 89%, resp. 65% yield by fitration of the cooled reaction mixture.

5a: M.p.: 203–206 ºC. Elemental analysis: For $C_{11}H_{18}Br_2N_4OS$ (414.160) calculated (%): C, 31.90; H, 4.38; Br, 38.59; N, 13.53; S, 7.74, found (%): C, 31.66; H, 4.25; Br, 38.39; N, 12.95; S, 7.90.

^{1}H NMR (400 MHz, DMSO-d_6): 1.62 (m, 2H, CH_2CH_2S); 2.04 (m, 2H, CH_2CH_2N); 3.21 (t, 2H, J_{vic} = 7.4, CH_2S); 4.71 (t, 2H, J_{vic} = 7.2 CH_2N); 8.29 (bs, 1H, NH_aH_b); 8.47 (m, 2H, H-3,5-Py); 8.70 (bs, 1H, NH_aH_b); 9.02 (bs, 4H, $C(NH_2)_2$); 9.30 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.02 (CH_2CH_2S); 29.31 (CH_2S), 29.31 (CH_2CH_2N); 59.86 (CH_2N); 125.84 (CH-3,5-Py); 145.64 (CH-2,6-Py); 148.04 (C-4-Py); 163.19 (CON); 169.58 ($SC(NH_2)_2$).

m/z 254 ($C_{11}H_{18}N_4OS^{2+}$)

5b: M.p.: 102–104 ºC. Elemental analysis: For $C_{10}H_{17}Br_2N_3S{\cdot}H_2O$ (389.150) calculated (%): C, 30.86; H, 4.92; N, 10.80, found (%): C, 30.83; H, 4.92; N, 10.47.

^{1}H NMR (400 MHz, DMSO-d_6): 1.61 (m, 2H, CH_2CH_2S); 2.03 (m, 2H, CH_2CH_2N); 3.22 (t, 2H, J_{vic} = 7.3, CH_2S); 4.68 (t, 2H, J_{vic} = 7.3 CH_2N); 8.19 (m, 2H, H-3,5-Py); 8.63 (m, 1H, H-4-Py); 8.98 (bs, 2H, $C(NH_2)_2$); 9.10 (bs, 2H, $C(NH_2)_2$); 9.16 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.06 (CH_2CH_2S); 29.32 (CH_2S), 29.38 (CH_2CH_2N); 59.69 (CH_2N); 128.06 (CH-3,5-Py); 144.69 (C-4-Py); 145.53 (CH-2,6-Py); 169.61 ($SC(NH_2)_2$).

m/z 211 ($C_{10}H_{17}N_3S^{2+}$)

3. *Alkaline hydrolysis of isothiouronium salt* **5** *followed by reaction with acyl chlorides and anhydrides – preparation of thiolesters* (**2a-2k**)

4-(4-Aminocarbonylpyridinio)butan-1-yl-isothiuronium dibromide (**5a**) or 4-pyridiniobutan-1-yl-isothiuronium dibromide (**5b**) (3 mmol) was dissolved in water, heated to ca. 80 ºC (5 mL) and the solution of NaOH (0.2 g, 5 mmol) in water (5 mL) was added. After 15 min stirring under Ar the corresponding anhydride (**2a**) or acyl chloride (**2b–2k**) (4 mmol) was added (liquid chlorides and anhydrides dropped as neat, solid ones dissolved in 3 ml THF) and the reaction mixture stirred at laboratory temperature for 10 min. The reaction mixture was washed with ether, the water layer acidified to pH 6 with 5% HCl and after removing of dissolved ether (evacuation for 3 min) mixed with the water solution of ammonium hexafluorophosphate. The precipitated thiolester **2a–2k** was filtered off and characterized (Table 1, yields are not optimized).

Table 1. Thiolesters **2a–2k**

No	R	Y	Yield [%]	M.p. ºC	Calculated/Found		
					%C	%H	%N
2a[a]	CH_3	$CONH_2$	65	97–106	34.62/34.45	4.60/4.08	6.73/6.77
2b[b]	$C_{11}H_{23}$	$CONH_2$	36	118–120	51.86/52.46	8.11/8.14	5.50/5.42
2c[a]	4-methylphenyl	$CONH_2$	90	87–105	43.90/43.85	4.71/4.78	5.69/5.74
2d[c]	4-chlorophenyl	$CONH_2$	40	129–135	-	-	-
2e[d]	3-pyridyl	$CONH_2$	57	115–120	-	-	-
2f[a]	2-thienyl	$CONH_2$	79	130–155	37.19/36.99	3.95/3.41	5.78/6.24
2g	2-furyl	$CONH_2$	64	163–165	40.01/39.49	3.80/3.74	6.22/6.26
2h	phenyl	H	62	125–126	46.05/46.10	4.35/4.35	3.36/3.24
2i[e]	$C_{11}H_{23}$	H	40	169–176	-	-	-
2j[f]	2-thienyl	H	65	91–100	-	-	-
2k[g]	2-furyl	H	60	89–92	-	-	-

[a] Monohydrate, [b] Bromide dihydrate, [c] HRMS: calculated 316.112885, found 316.111974, [d] HRMS: for protonated form calculated 350.086346, found 350.085578, [e] Bromide, HRMS: calculated 350.251762, found 350.252849, [f] HRMS: calculated 278.067333, found 278.068080, [g] HRMS: calculated 262.090176, found 262.089987.

4. *Cyclizations*

In the 10mL screw-cap sealed ampoule with magnetic stirrer, starting salt **2a-2k** (0.5 mmol) and Cs_2CO_3 (0.326 g, 1 mmol) were suspended in dry DMA (2 mL). The reaction mixture was stirred at 70–100 ºC (bath temperature) for 4–6 h under Ar atmosphere and then slowly cooled to laboratory temperature. According to the UPLC-MS control, the conversion of starting quaternary salts **2** was higher than 90%. The dark suspension was diluted with water (5 mL), acidified to pH 3–4 by 5% hydrochloric acid and extracted with ether containing few drops of hexane. After drying of ethereal portion with $MgSO_4$ and evaporation, the residue was purified by filtration through a layer of silica gel and washed with hexane containing 0–0.5% ether. After solvent evaporation pure tetrahydrothiophene derivative **3a–3h** was obtained (Table 2).

Table 2. Tetrahydrothiophenes **3a–3h**

No	R	Yield [%]	Calculated/Found		
			%C	%H	%S
3a[a]	CH_3	53(90[b])	-	-	-
3b	$C_{11}H_{23}$	42,48[c]	71.05/71.23	11.18/11.50	11.86/11.62
3c	4-methylphenyl	85	69.86/69.16	6.84/6.93	15.54/15.70
3d[d]	4-chlorophenyl	76	-	-	-
3e[e]	3-pyridyl	52	-	-	-
3f	2-thienyl	87,78[c]	54.51/54.40	5.08/5.14	32.34/32.05
3g	2-furyl	80,69[c]	59.32/59.06	5.53/5.45	17.59/17.70
3h[f]	phenyl	88[c]	-	-	-

[a] Ref.[3], [b] UPLC-MS, [c] Starting from the corresponding pyridinium quaternary salt, [d] Ref[4], [e] HRMS: for protonated form calculated 194.063961, found: 194.063507, [f] Ref[5].

NMR spectra of starting thiolesters **2a–2k** and tetrahydrothiophenes **3a–3h**

1-(4-Acetylthiobutyl)-4-aminocarbonylpyridinium hexafluorophosphate (**2a**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.55 (m, 2H, CH_2CH_2S); 1.98 (m, 2H, CH_2CH_2N); 2.31 (CH_3); 2.87 (t, 2H, J_{vic} = 7.3, CH_2S); 4.65 (t, 2H, J_{vic} = 7.3, CH_2N); 8.26 (bs, 1H, NH_aH_b); 8.43 (m, 2H, H-3,5-Py); 8.68 (bs, 1H, NH_aH_b); 9.22 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.64 (CH_2CH_2S); 27.52 (CH_2S); 29.60 (CH_2CH_2N); 30.46 (CH_3); 60.20 (CH_2N); 125.82 (CH-3,5-Py); 145.63 (CH-2,6-Py); 148.17 (C-4-Py); 163.27 (CON); 195.24 (COS).

4-Aminocarbonyl-1-(4-dodecanoylthiobutyl)pyridinium hexafluorophosphate (**2b**)

^{1}H NMR (400 MHz, DMSO-d_6): 0.85 (t, 3H, CH_3), 1.18-1.35 (m, 18H, CH_2-3 to CH_2-11 lauroyl), 1.58 (m, 2H, CH_2CH_2S); 1.89 (m, 2H, CH_2-2 lauroyl), 2.01 (m, 2H, CH_2CH_2N); 2.88 (t, 2H, J_{vic} = 7.3, CH_2S); 4.69 (t, 2H, J_{vic} = 7.3, CH_2N); 8.26 (bs, 1H, NH_aH_b); 8.46 (m, 2H, H-3,5-Py); 8.76 (bs, 1H, NH_aH_b); 9.26 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 13.82 (CH_3), 21.98-28.86 (9xC, CH_2-3 to CH_2-11 lauroyl), 25.70 (CH_2CH_2S); 28.93 (CH_2S); 29.68 (CH_2CH_2N); 43.29 (CH_2-2 lauroyl), 60.13 (CH_2N); 125.82 (CH-3,5-Py); 145.66 (CH-2,6-Py); 148.15 (C-4-Py); 163.22 (CON); 198.60 (COS).

4-Aminocarbonyl-1-[4-(4-methylbenzoylthio)butyl]pyridinium hexafluorophosphate (**2c**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.65 (m, 2H, CH_2CH_2S); 2.05 (m, 2H, CH_2CH_2N); 2.40 (s, 3H, CH_3); 3.09 (t, 2H, J_{vic} = 7.3, CH_2S); 4.68 (t, 2H, J_{vic} = 7.3, CH_2N); 7.38 (m, 2H, H-*m*-Ph); 7.80 (m, 2H, H-*o*-Ph); 8.28 (bs, 1H, NH_aH_b); 8.42 (m, 2H, H-3,5-Py); 8.66 (bs, 1H, NH_aH_b); 9.24 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 21.06 (CH_3); 25.69 (CH_2CH_2S); 27.39 (CH_2S); 29.79 (CH_2CH_2N); 60.13 (CH_2N); 126.75 (CH-3,5-Py); 127.01 (CH-*o*-Ph); 129.49 (CH-*m*-Ph); 133.72 (C-*i*-Ph); 144.40 (C-*p*-Ph); 145.59 (CH-2,6-Py); 148.38 (C-4-Py); 163.51 (CON); 190.43 (COS).

4-Aminocarbonyl-1-[4-(4-chlorobenzoylthio)butyl]pyridinium hexafluorophosphate (**2d**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.64 (m, 2H, CH_2CH_2S); 2.04 (m, 2H, CH_2CH_2N); 3.11 (t, 2H, J_{vic} = 7.3, CH_2S); 4.68 (t, 2H, J_{vic} = 7.3, CH_2N); 7.64 (m, 2H, H-*o*-Ph); 7.91 (m, 2H, H-*m*-Ph); 8.28 (bs, 1H, NH_aH_b); 8.43 (m, 2H, H-3,5-Py); 8.66 (bs, 1H, NH_aH_b); 9.24 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.54 (CH_2CH_2S); 27.68 (CH_2S); 29.76 (CH_2CH_2N); 60.12 (CH_2N); 125.82 (CH-3,5-Py); 128.52 (CH-*m*-Ph); 129.18 (CH-*o*-Ph); 134.87 (C-*i*-Ph); 138.71 (C-*p*-Ph); 145.59 (CH-2,6-Py); 148.17 (C-4-Py); 163.47 (CON); 189.99 (COS).

4-Aminocarbonyl-1-(4-nicotinoylthiobutyl)pyridinium hexafluorophosphate (**2e**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.68 (m, 2H, CH_2CH_2S); 2.06 (m, 2H, CH_2CH_2N); 3.15 (t, 2H, J_{vic} = 7.3, CH_2S); 4.69 (t, 2H, J_{vic} = 7.3, CH_2N); 7.61 (m, 1H, H-5-Nic); 8.25 (m, 1H, H-4-Nic); 8.27 (bs, 1H, NH_aH_b); 8.47 (m, 2H, H-3,5-Py); 8.74 (bs, 1H, NH_aH_b); 8.84 (m, 1H, H-6-Nic); 9.04 (m, 1H, H-2-Nic); 9.28 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.49 (CH_2CH_2S); 28.87 (CH_2S); 29.51 (CH_2CH_2N); 59.26 (CH_2N); 122.65 (CH-5-Nic); 126.47 (CH-3,5-Py); 134.02 (C-3-Nic); 136.22 (CH-4-Nic); 144.60 (CH-2,6-Py); 148.28 (C-4-Py);149.75 (CH-2-Nic); 150.47 (CH-6-Nic); 163.84 (CON); 193.89 (COS).

4-Aminocarbonyl-1-[4-(2-thienoyl)thiobutyl]pyridinium hexafluorophosphate (**2f**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.64 (m, 2H, CH_2CH_2S); 2.04 (m, 2H, CH_2CH_2N); 3.09 (t, 2H, J_{vic} = 7.3, CH_2S); 4.67 (t, 2H, J_{vic} = 7.3, CH_2N); 7.25 (m, 1H, H-4-thiophene); 7.88 (m, 1H, H-3-thiophene); 8.06 (m, 1H, H-5-thiophene); 8.27 (bs, 1H, NH_aH_b); 8.42 (m, 2H, H-3,5-Py); 8.65 (bs, 1H, NH_aH_b); 9.24 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.76 (CH_2CH_2S); 27.67 (CH_2S); 29.63 (CH_2CH_2N); 60.21 (CH_2N); 125.82 (CH-3,5-Py); 128.69 (CH-4-thiophene); 131.77 (CH-3-thiophene); 134.48 (CH-5-thiophene); 140.86 (C-2-thiophene);145.66 (CH-2,6-Py); 148.15 (C-4-Py); 163.27 (CON); 183.02 (COS).

4-Aminocarbonyl-1-[4-(2-furoyl)thiobutyl]pyridinium hexafluorophosphate (**2g**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.62 (m, 2H, CH_2CH_2S); 2.03 (m, 2H, CH_2CH_2N); 3.06 (t, 2H, J_{vic} = 7.3, CH_2S); 4.66 (t, 2H, J_{vic} = 7.3, CH_2N); 6.75 (m, 1H, H-4-furane); 7.37 (m, 1H, H-3-furane); 8.03 (m, 1H, H-5-furane); 8.27 (bs, 1H, NH_aH_b); 8.43 (m, 2H, H-3,5-Py); 8.64 (bs, 1H, NH_aH_b); 9.24 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.81 (CH_2CH_2S); 26.68 (CH_2S); 29.70 (CH_2CH_2N); 60.35 (CH_2N); 112.87 (CH-4-furane); 116.48 (CH-3-furane); 125.92 (CH-3,5-Py); 145.60 (CH-2,6-Py); 147.90 (CH-5-furane); 148.23 (C-4-Py); 149.87 (C-2-furane); 163.39 (CON); 179.42 (COS).

1-(4-Benzoylthiobutyl)pyridinium hexafluorophosphate (**2h**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.63 (m, 2H, CH_2CH_2S); 2.04 (m, 2H, CH_2CH_2N); 3.10 (t, 2H, J_{vic} = 7.3, CH_2S); 4.65 (t, 2H, J_{vic} = 7.3 CH_2N); 7.55 (m, 2H, H-*m*-Ph); 7.70 (m, 1H, H-*p*-Ph); 7.90 (m, 2H, H-*o*-Ph); 8.16 (m, 2H, H-3,5-Py); 8.60 (m, 1H, H-4-Py); 9.09 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.70 (CH_2CH_2S); 27.54 (CH_2S); 29.78 (CH_2CH_2N); 60.15 (CH_2N); 126.71 (CH-*o*-Ph); 128.08 (CH-3,5-Py); 129.07 (CH-*m*-Ph); 133.94 (CH-*p*-Ph); 136.25 (C-*i*-Ph); 144.72 (CH-4-Py); 145.47 (CH-2,6-Py); 191.04 (COS).

1-(4-Dodecanoylthiobutyl)pyridinium hexafluorophosphate (**2i**)

^{1}H NMR (400 MHz, DMSO-d_6): 0.86 (t, 3H, CH_3), 1.18-1.38 (m, 18H, CH_2-3 to CH_2-11 lauroyl), 1.58 (m, 2H, CH_2CH_2S); 1.89 (m, 2H, CH_2-2 lauroyl), 2.00 (m, 2H, CH_2CH_2N); 2.75 (t, 2H, J_{vic} = 7.3, CH_2S); 4.68 (t, 2H, J_{vic} = 7.3 CH_2N); 8.20 (m, 2H, H-3,5-Py); 8.63 (m, 1H, H-4-Py); 9.16 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 13.88 (CH_3), 22.03-28.94 (9xC, CH_2-3 to CH_2-11 lauroyl), 26.06 (CH_2CH_2S); 28.64 (CH_2S); 28.95 (CH_2CH_2N); 45.29 (CH_2-2 lauroyl), 60.03 (CH_2N); 128.08 (CH-3,5-Py); 144.75 (CH-4-Py); 145.50 (CH-2,6-Py); 198.02 (COS).

1-[4-(2-Thienoyl)thiobutyl]pyridinium hexafluorophosphate (**2j**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.62 (m, 2H, CH_2CH_2S); 2.03 (m, 2H, CH_2CH_2N); 3.09 (t, 2H, J_{vic} = 7.3, CH_2S); 4.63 (t, 2H, J_{vic} = 7.3, CH_2N); 7.26 (m, 1H, H-4-thiophene); 7.89 (m, 1H, H-3-thiophene); 8.06 (m, 1H, H-5-thiophene); 8.16 (m, 2H, H-3,5-Py); 8.60 (m, 1H, H-4-Py); 9.09 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.81 (CH_2CH_2S); 27.69 (CH_2S); 29.72 (CH_2CH_2N); 60.10 (CH_2N); 128.08 (CH-3,5-Py); 128.71 (CH-4-thiophene); 131.83 (CH-3-thiophene); 134.49 (CH-5-thiophene); 140.89 (C-2-thiophene);144.73 (CH-4-Py); 145.47 (CH-2,6-Py); 183.06 (COS).

1-[4-(2-Furoyl)thiobutyl]pyridinium hexafluorophosphate (**2k**)

^{1}H NMR (400 MHz, DMSO-d_6): 1.61 (m, 2H, CH_2CH_2S); 2.02 (m, 2H, CH_2CH_2N); 3.06 (t, 2H, J_{vic} = 7.3, CH_2S); 4.63 (t, 2H, J_{vic} = 7.3 CH_2N); 6.76 (m, 1H, H-4-furane); 7.38 (m, 1H, H-3-furane); 8.03 (m, 1H, H-5-furane); 8.16 (m, 2H, H-3,5-Py); 8.61 (m, 1H, H-4-Py); 9.10 (m, 2H, H-2,6-Py).

^{13}C NMR (100 MHz, DMSO-d_6): 25.85 (CH_2CH_2S); 26.70 (CH_2S); 29.77 (CH_2CH_2N); 60.01 (CH_2N); 112.93 (CH-4-furane); 116.54 (CH-3-furane); 128.19 (CH-3,5-Py); 144.74 (CH-4-Py); 145.66 (CH-2,6-Py); 147.94 (CH-5-furane); 149.90 (C-2-furane); 179.49 (COS).

Methyl 2-tetrahydrothienyl ketone (**3a**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.87 (m, 1H, H-3b); 2.03 (m, 1H, H-4b); 2.23 (s, 3H, CH_3); 2.31 (m, 1H, H-4^a); 2.67 (m, 1H, H-3^a); 2.88 (m, 2H, H-5); 3.93 (dd, 1H, $J_{2,3}$ = 7.0, 4.4, H-2).

^{13}C NMR (100 MHz, $CDCl_3$): 27.73 (CH_3); 30.69 (CH_2-4); 31.36 (CH_2-3); 33.83 (CH_2-5); 49.43 (CH-2); 205.64 (CO).

Undecanyl 2-tetrahydrothienyl ketone (**3b**)

^{1}H NMR (400 MHz, $CDCl_3$): 0.88 (t, 3H, CH_3-11‘); 1.30, 1.60 and 2.35 (3 x m, 20H, CH_2-1‘-CH_2-10‘); 1.86 (m, 1H, H-3b); 2.01-2.11 (m, 2H, H-4); 2.60 (m, 1H, H-3^a); 2.89 (m, 2H, H-5); 3.95 (dd, 1H, $J_{2,3}$ = 7.1, 4.1, H-2).

^{13}C NMR (100 MHz, $CDCl_3$): 14.05 (CH_3-11‘); 22.62-30.82 (9 x CH_2); 29.20 (CH_2-4); 31.36 (CH_2-3); 33.13 (CH_2-5); 40.69 (CH_2-1‘); 54.36 (CH-2); 207.89 (CO).

4-Methylphenyl 2-tetrahydrothienyl ketone (**3c**)

^{1}H NMR (600 MHz, $CDCl_3$): 1.98 (dddd, 1H, J_{gem} = 12.7, $J_{3b,4}$ = 8.5, 5.9, $J_{3b,2}$ = 7.1, H-3b); 2.15 (m, 1H, J_{gem} = 12.6, $J_{4b,5}$ = 6.3, 6.1, $J_{4b,3}$ = 5.9, H-4b); 2.23 (m, 1H, J_{gem} = 12.6, $J_{4a,3}$ = 8.5, 5.9, $J_{4a,5}$ = 7.4, 6.1, H-4^a); 2.41 (s, 3H, CH_3); 2.60 (dtd, 1H, J_{gem} = 12.7, $J_{3a,4}$ = 5.9, $J_{3a,2}$ = 4.4, H-3^a); 2.91 (ddd, 1H, J_{gem} = 10.2, $J_{5b,4}$ = 7.4, 6.3, H-5b); 2.95 (dt, 1H, J_{gem} = 10.2, $J_{5a,4}$ = 6.1, H-5^a); 4.72 (dd, 1H, $J_{2,3}$ = 7.1, 4.4, H-2); 7.26 (m, 2H, H-*m*-Tol); 7.85 (m, 2H, H-*o*-Tol).

^{13}C NMR (151 MHz, $CDCl_3$): 21.65 (CH_3); 31.17 (CH_2-4); 31.31 (CH_2-3); 33.94 (CH_2-5); 49.26 (CH-2); 128.69 (CH-*m*-Tol); 129.29 (CH-*o*-Tol); 133.35 (C-*i*-Tol); 143.97 (C-*p*-Tol); 202.24 (CO).

4-Chlorophenyl 2-tetrahydrothienyl ketone (**3d**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.99 (m, 1H, H-3b); 2.17 (m, H-4b); 2.58 (m, 1H, H-4^a); 2.75 (m, 1H, H-3^a); 2.95 (m, 2H, H-5); 4.67 (dd, 1H, $J_{2,3}$ = 7.1, 4.4, H-2); 7.43 (m, 2H, H-*m*-Ph); 7.87 (m, 2H, H-*o*-Ph).

^{13}C NMR (100 MHz, $CDCl_3$): 29.65 (CH_2-4); 31.10 (CH_2-3); 31.01 (CH_2-5); 49.33 (CH-2); 129.96 (CH-*m*-Ph); 131.49 (CH-*o*-Ph); 135.77 (C-*i*-Ph); 138.74 (C-*p*-Ph); 196.75 (CO).

3-Pyridyl 2-tetrahydrothienyl ketone (**3e**)

^{1}H NMR (500 MHz, $CDCl_3$): 2.02 (dddd, 1H, J_{gem} = 12.6, $J_{3b,4}$ = 8.9, 6.3, $J_{3b,2}$ = 7.0, H-3b-THT); 2.20 (m, 1H, H-4b-THT); 2.59-2.73 (m, 2H, H-3a,4a-THT); 2.95 (ddd, 1H, J_{gem} = 10.3, $J_{5b,4}$ = 7.2, 6.3, H-5b-THT); 2.97 (ddd, 1H, J_{gem} = 10.3, $J_{5a,4}$ = 6.7, 6.0, H-5a-THT); 4.69 0(dd, 1H, $J_{2,3}$ = 7.0, 3.9, H-2-THT); 7.53 (bdd, 1H, $J_{5,4}$ = 8.0, $J_{5,6}$ = 5.0, H-5-py); 8.33 (dt, 1H, $J_{4,5}$ = 8.0, $J_{4,6}$ = $J_{4,2}$ = 1.8, H-4-py); 8.81 (bd, 1H, $J_{6,5}$ = 5.0, H-6-py); 9.17 (bs, 1H, H-2-py).

^{13}C NMR (125.7 MHz, $CDCl_3$): 30.96 (CH_2-4-THT); 30.99 (CH_2-3-THT); 34.07 (CH_2-5-THT); 49.64 (CH-2-THT); 124.09 (CH-5-py); 131.76 (C-3-py); 137.25 (CH-4-py); 148.65 (CH-2-py); 151.86 (CH-6-py); 194.30 (CO).

2-Tetrahydrothienyl 2-thienyl ketone (**3f**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.99 (m, 1H, H-3b); 2.16 (m, 1H, H-4b); 2.23 (m, 1H, H-4^a); 2.56 (m, 1H, H-3^a); 2.93 (m, 1H, H-5b); 2.98 (m, 1H, H-5^a); 4.62 (dd, 1H, $J_{2,3}$ = 7.2, 4.3, H-2); 7.13 (dd, 1H, H-4-thiophene); 7.64 (d, 1H, H-3-thiophene); 7.69 (d, 1H, H-5-thiophene).

^{13}C NMR (100 MHz, $CDCl_3$): 31.10 (CH_2-4); 31.60 (CH_2-3); 33.97 (CH_2-5); 50.41 (CH-2); 128.04 (CH-4-thiophene); 132.10 (CH-3-thiophene); 133.76 (CH-5-thiophene); 143.21 (C-2-thiophene); 190.18 (CO).

2-Furyl 2-tetrahydrothienyl ketone (**3g**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.96 (m, 1H, H-3b); 2.14 (m, 1H, H-4b); 2.22 (m, 1H, H-4^a); 2.53 (m, 1H, H-3^a); 2.93 (m, 2H, H-5); 4.59 (dd, 1H, $J_{2,3}$ = 7.2, 4.3, H-2); 6.54 (dd, 1H, H-4-furane); 7.20 (d, 1H, H-3-furane); 7.60 (d, 1H, H-5-furane).

^{13}C NMR (100 MHz, $CDCl_3$): 30.96 (CH_2-4); 31.10 (CH_2-3); 33.58 (CH_2-5); 49.42 (CH-2); 112.20 (CH-4-furane); 117.63 (CH-3-furane); 146.48 (CH-5-furane); 151.80 (C-2-furane); 186.18 (CO).

Phenyl 2-tetrahydrothienyl ketone (**3h**)

^{1}H NMR (400 MHz, $CDCl_3$): 1.99 (m, 1H, H-3b); 2.16 (m, 1H, H-4b); 2.21 (m, 1H, H-4^a); 2.59 (m, 1H, H-3^a); 2.93 (m, 2H, H-5); 4.73 (dd, 1H, $J_{2,3}$ = 7.1, 4.4, H-2); 7.45 (m, 2H, H-*m*-Ph); 7.55 (m, 1H, H-*p*-Ph); 7.93 (m, 2H, H-*o*-Ph).

^{13}C NMR (100 MHz, $CDCl_3$): 31.17 (CH_2-4); 31.32 (CH_2-3); 33.95 (CH_2-5); 49.28 (CH-2); 128.69 (CH-*m*-Ph); 129.29 (CH-*o*-Ph); 133.35 (CH-*p*-Ph); 136.19 (C-*i*-Ph); 196.80 (CO).

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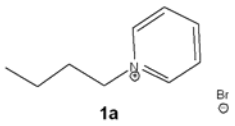

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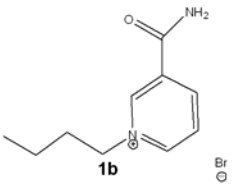

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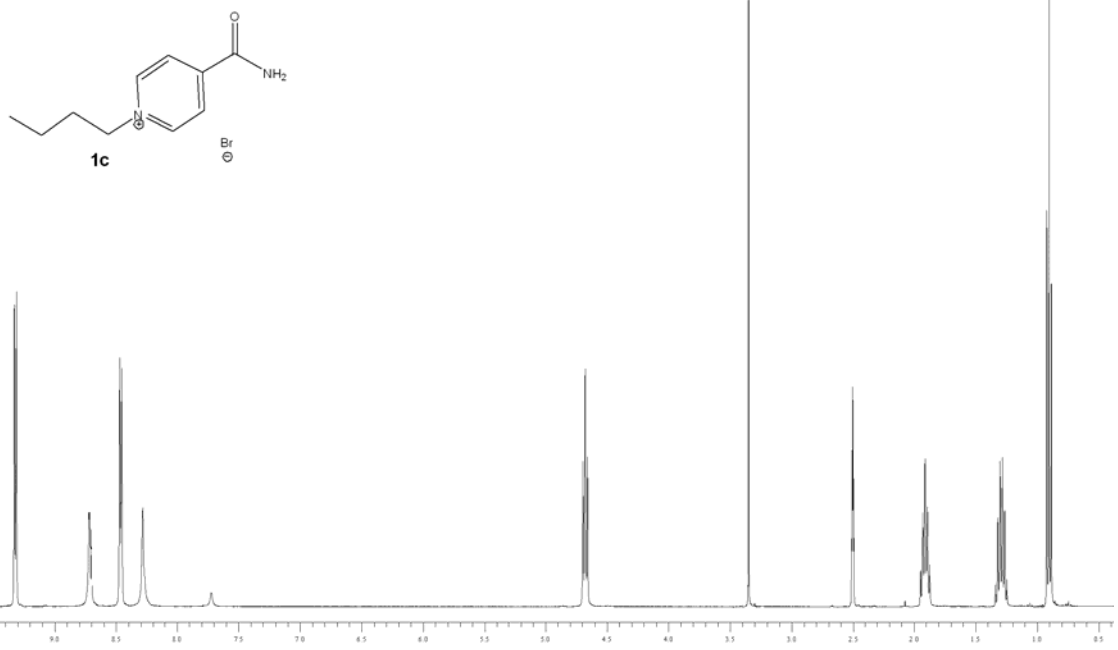

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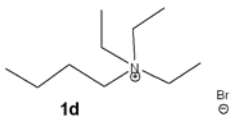

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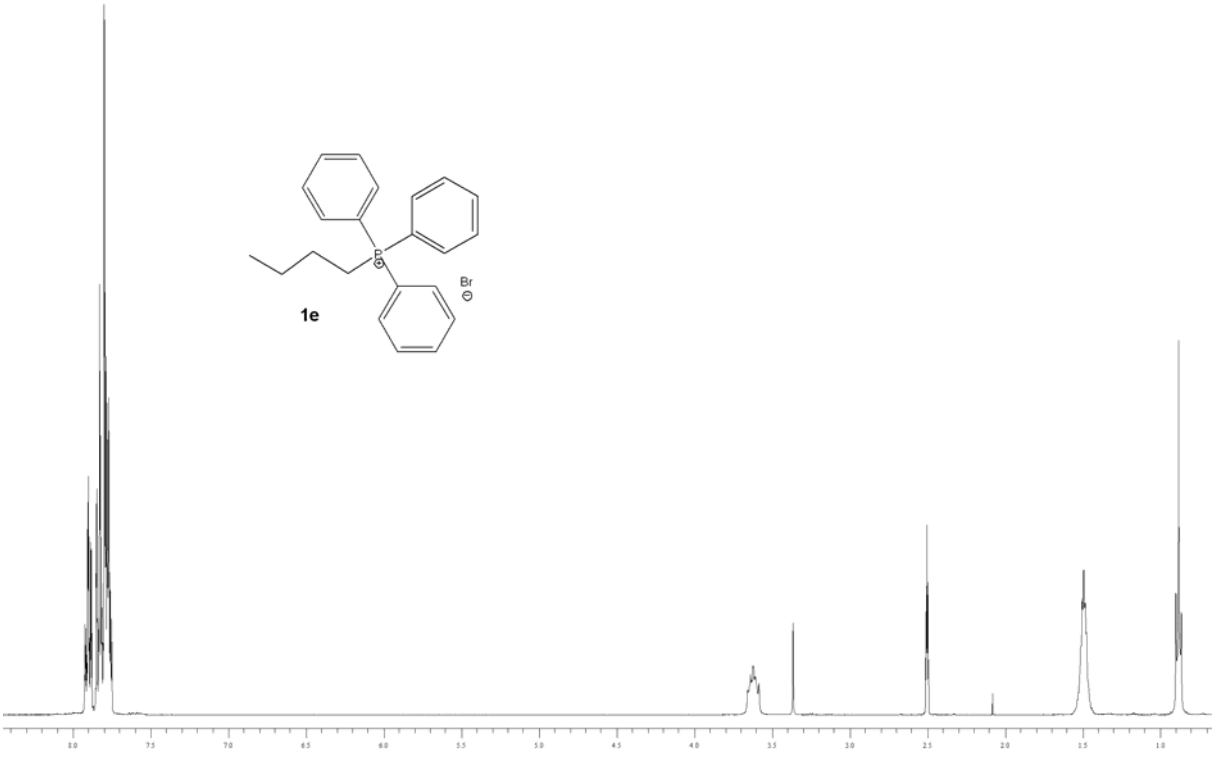
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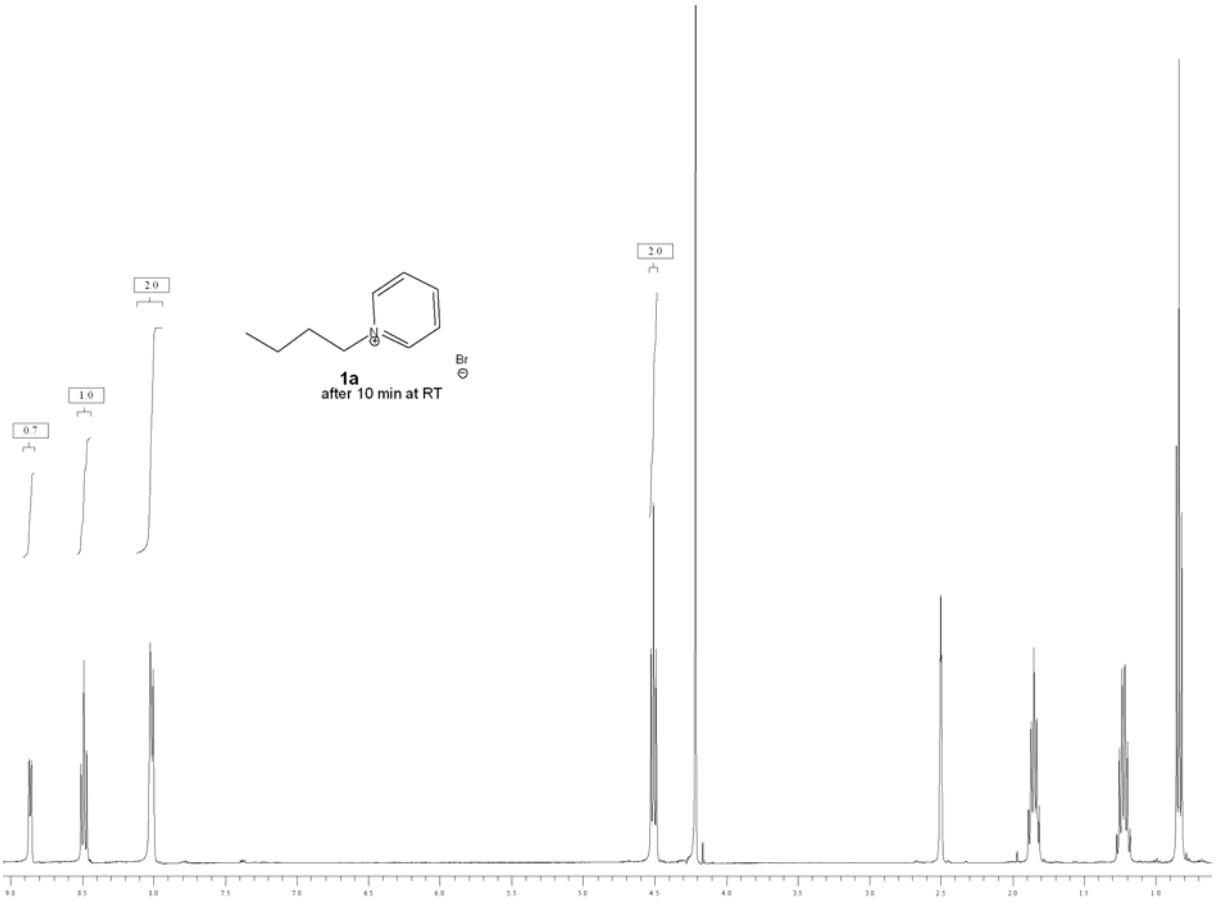
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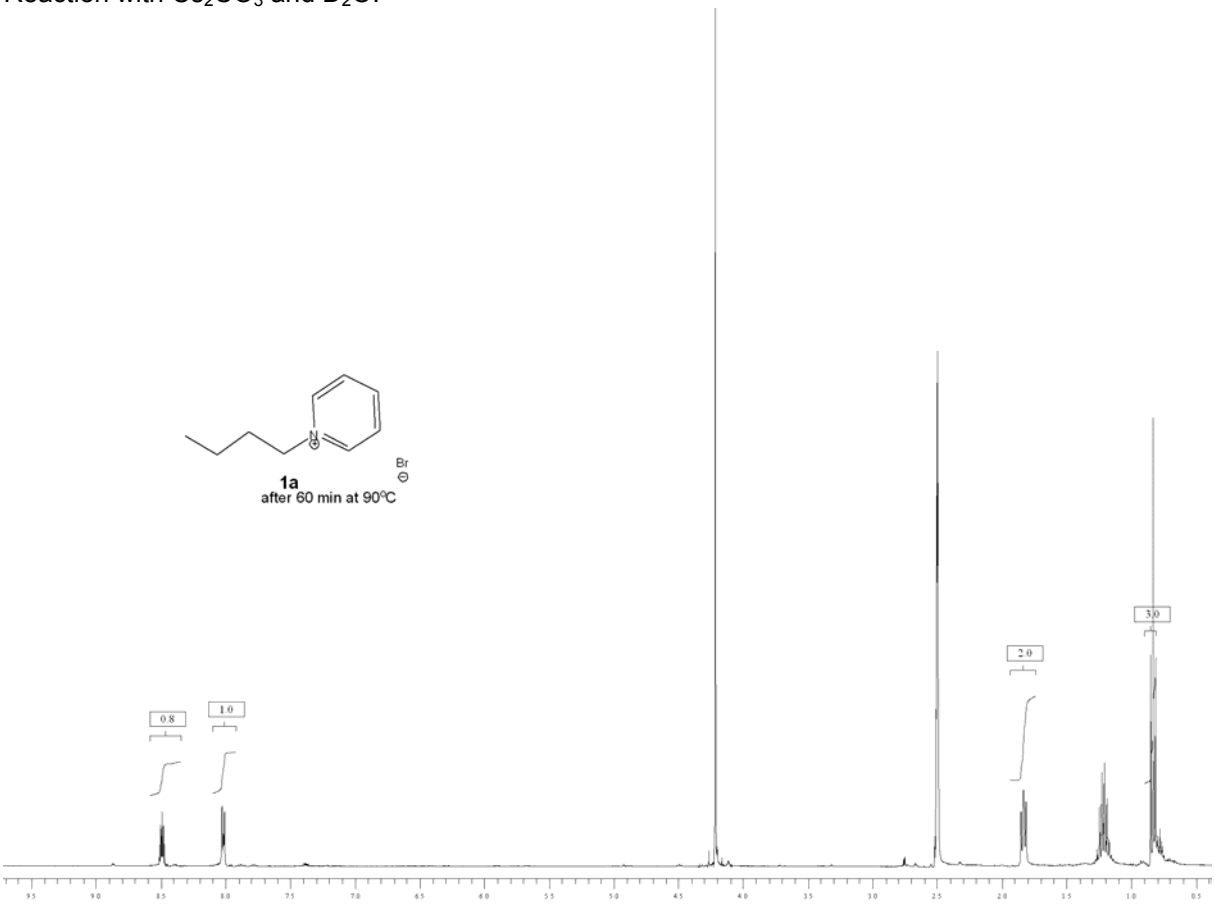

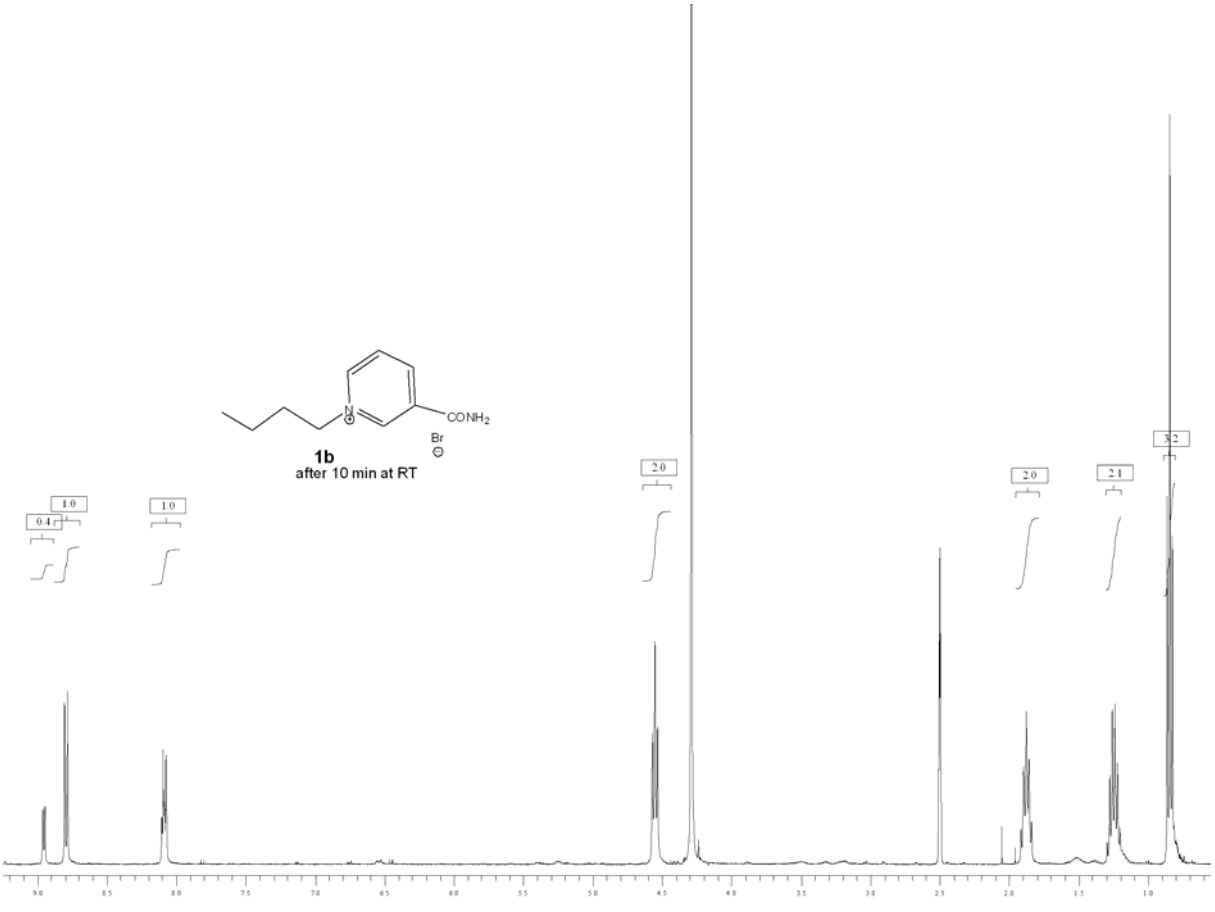

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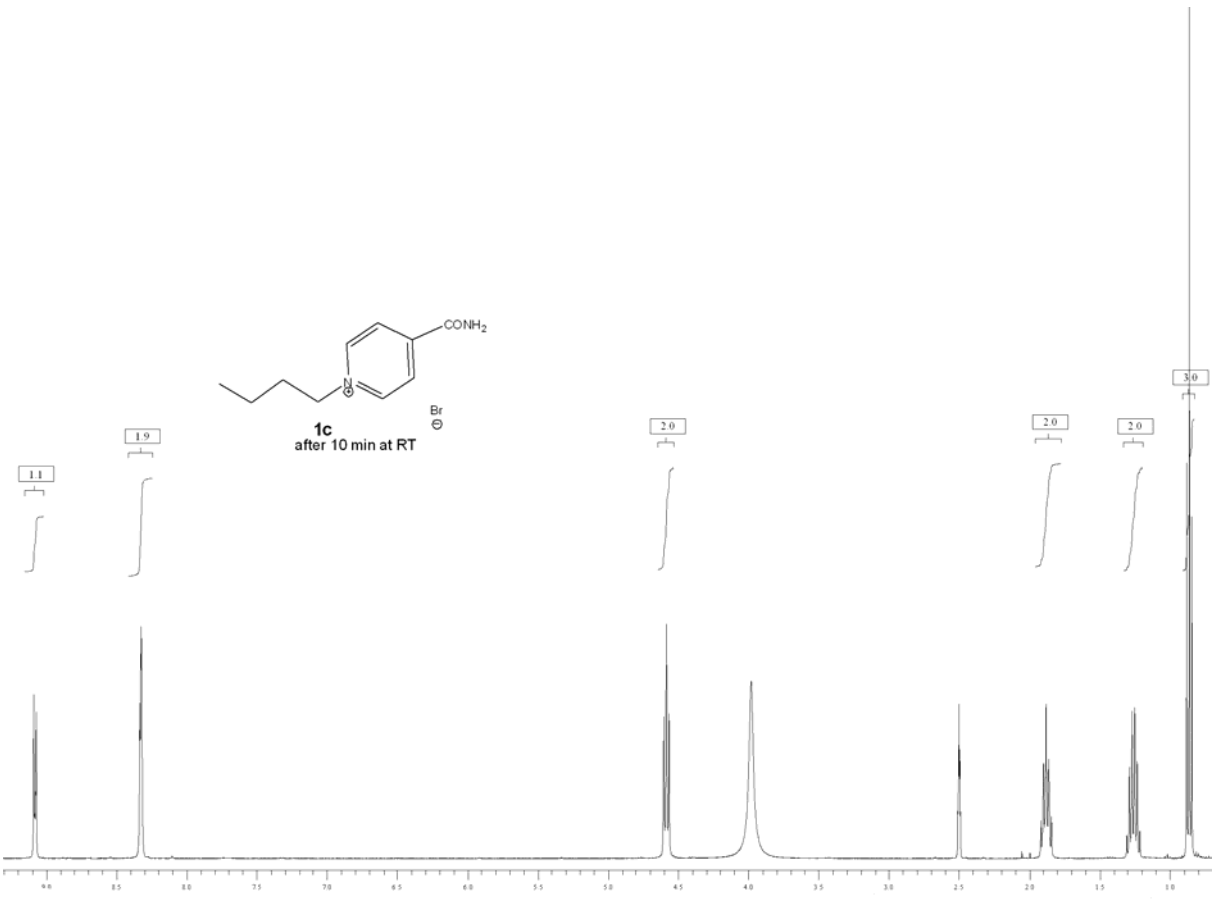

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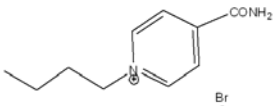

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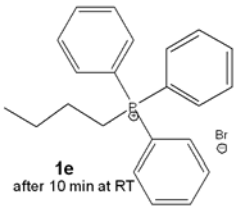

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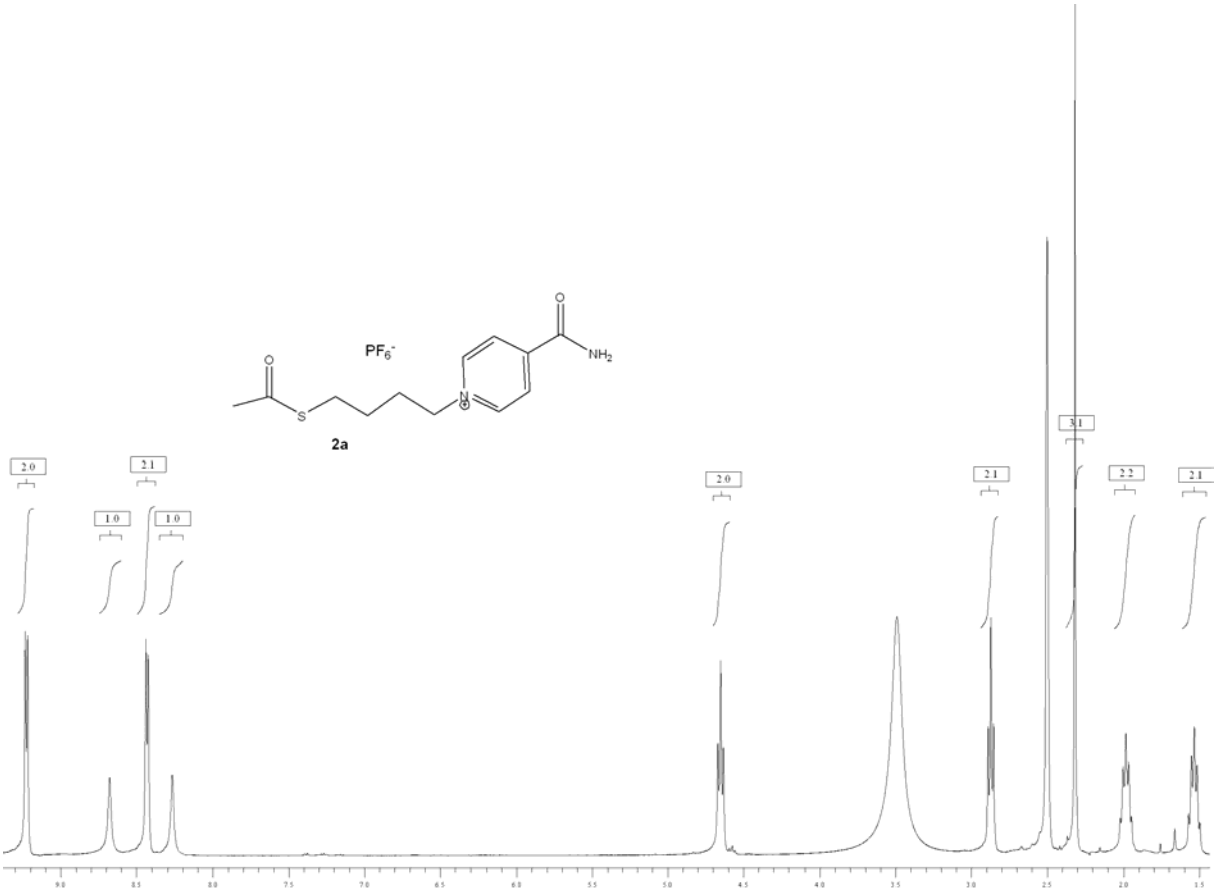
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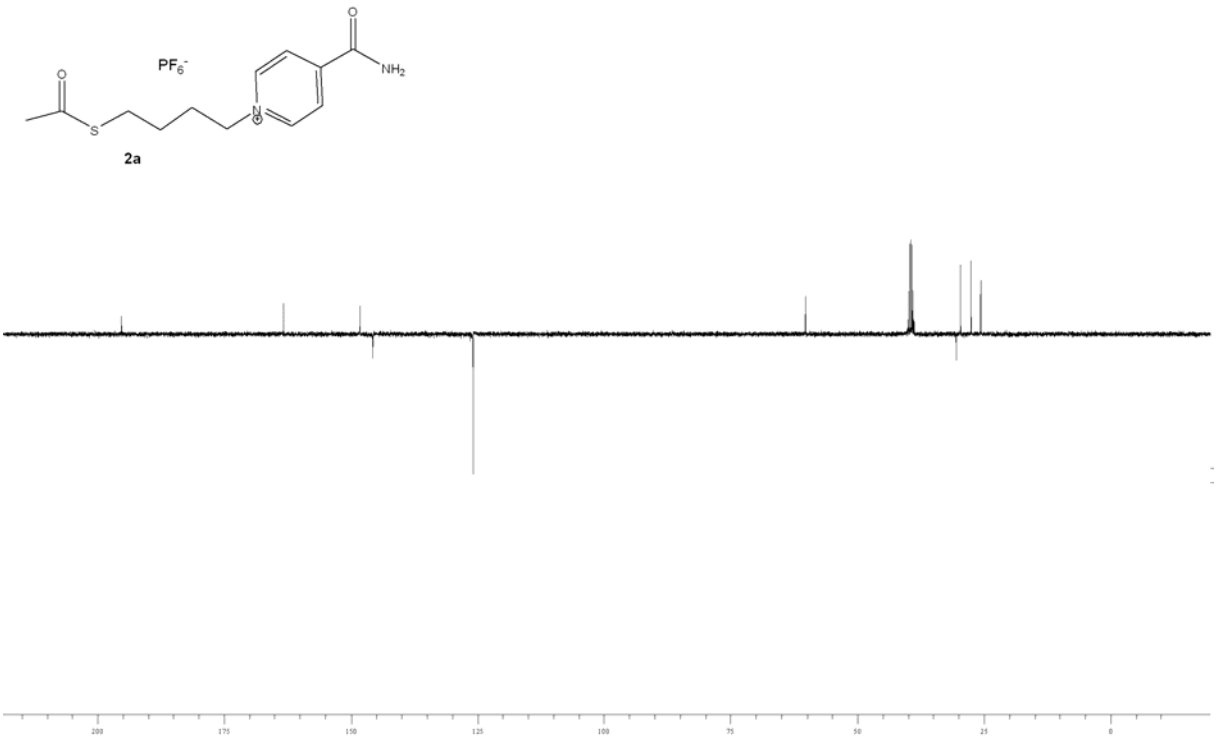
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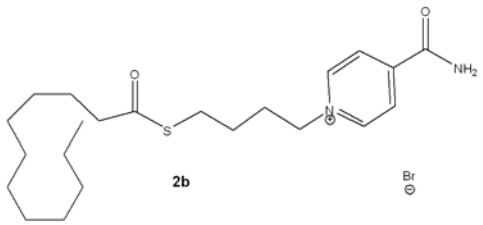
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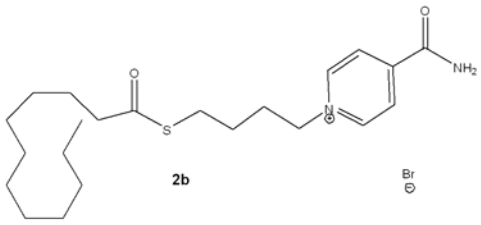
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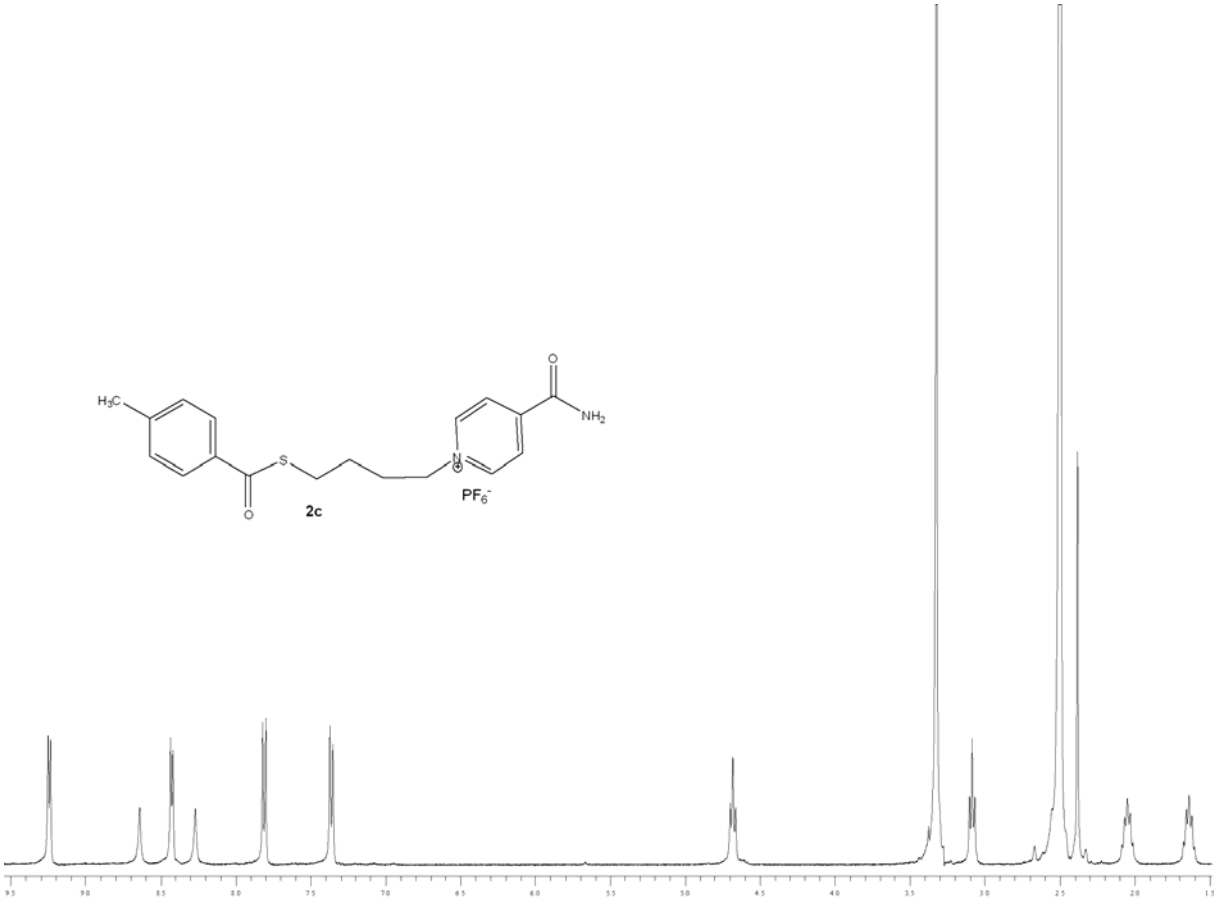

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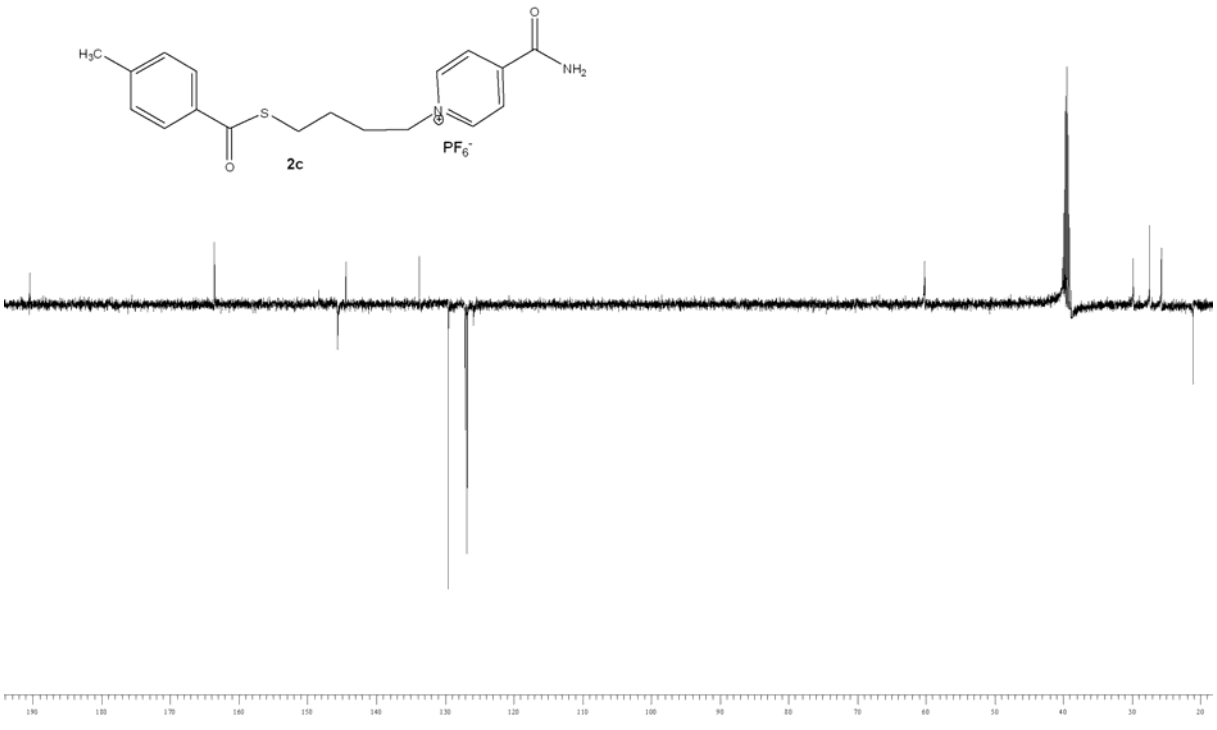

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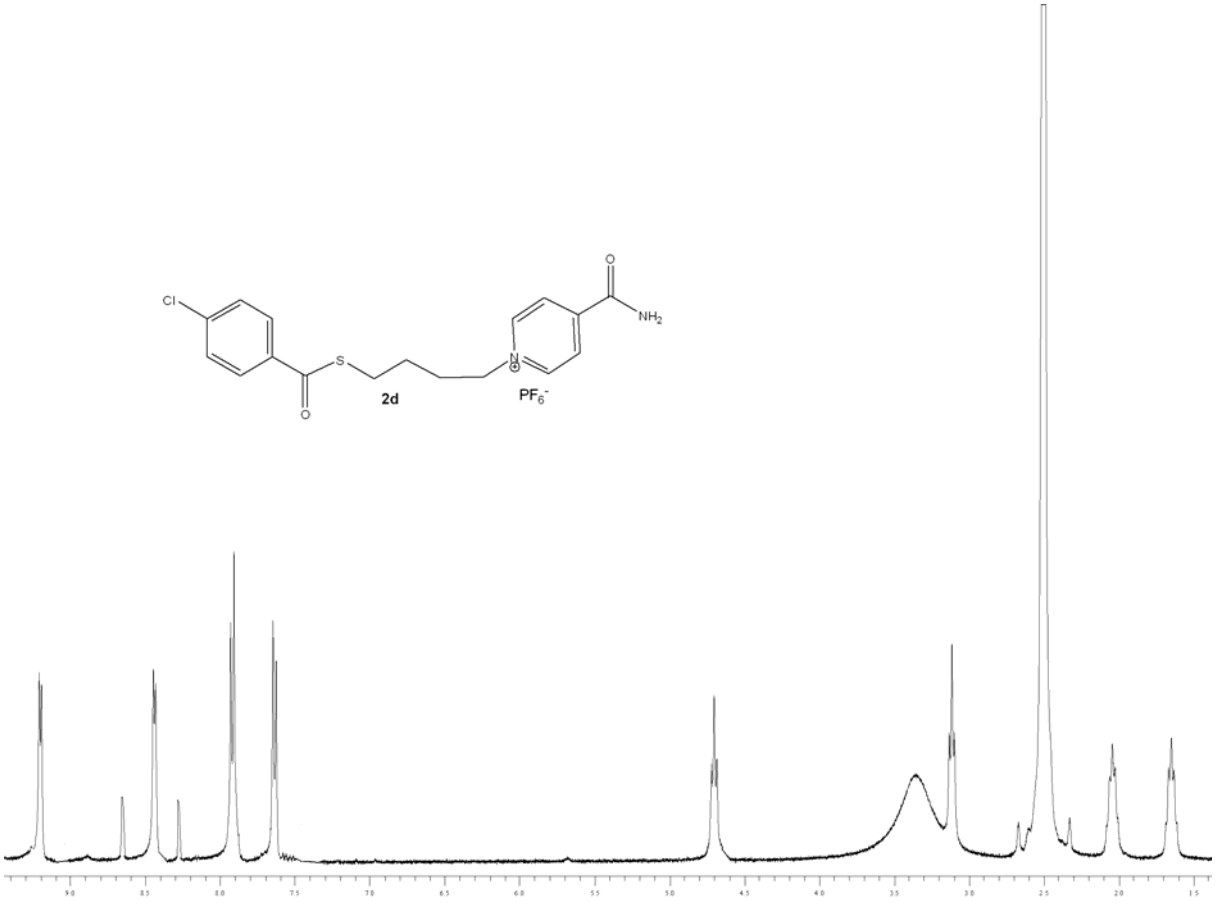
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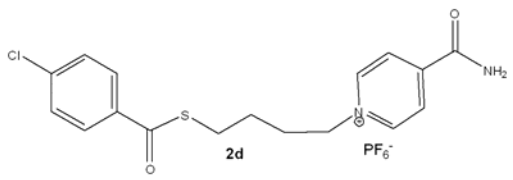
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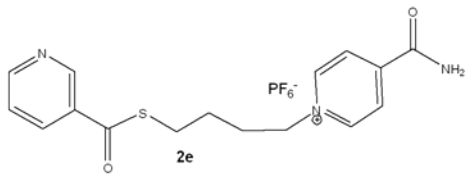
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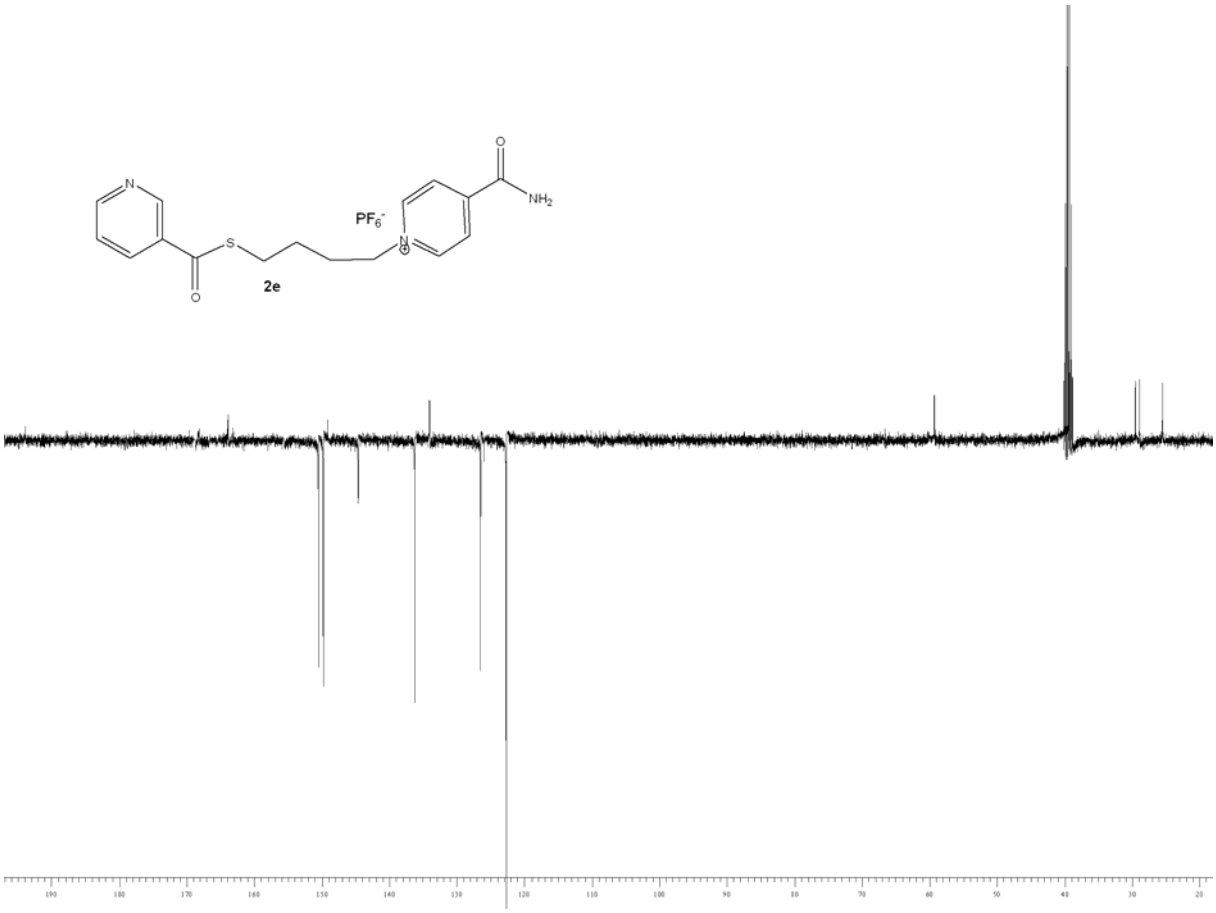
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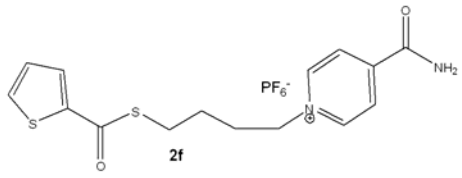
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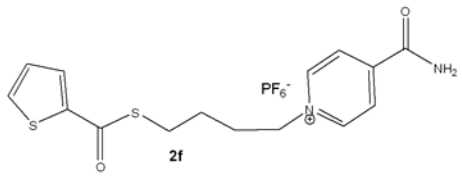
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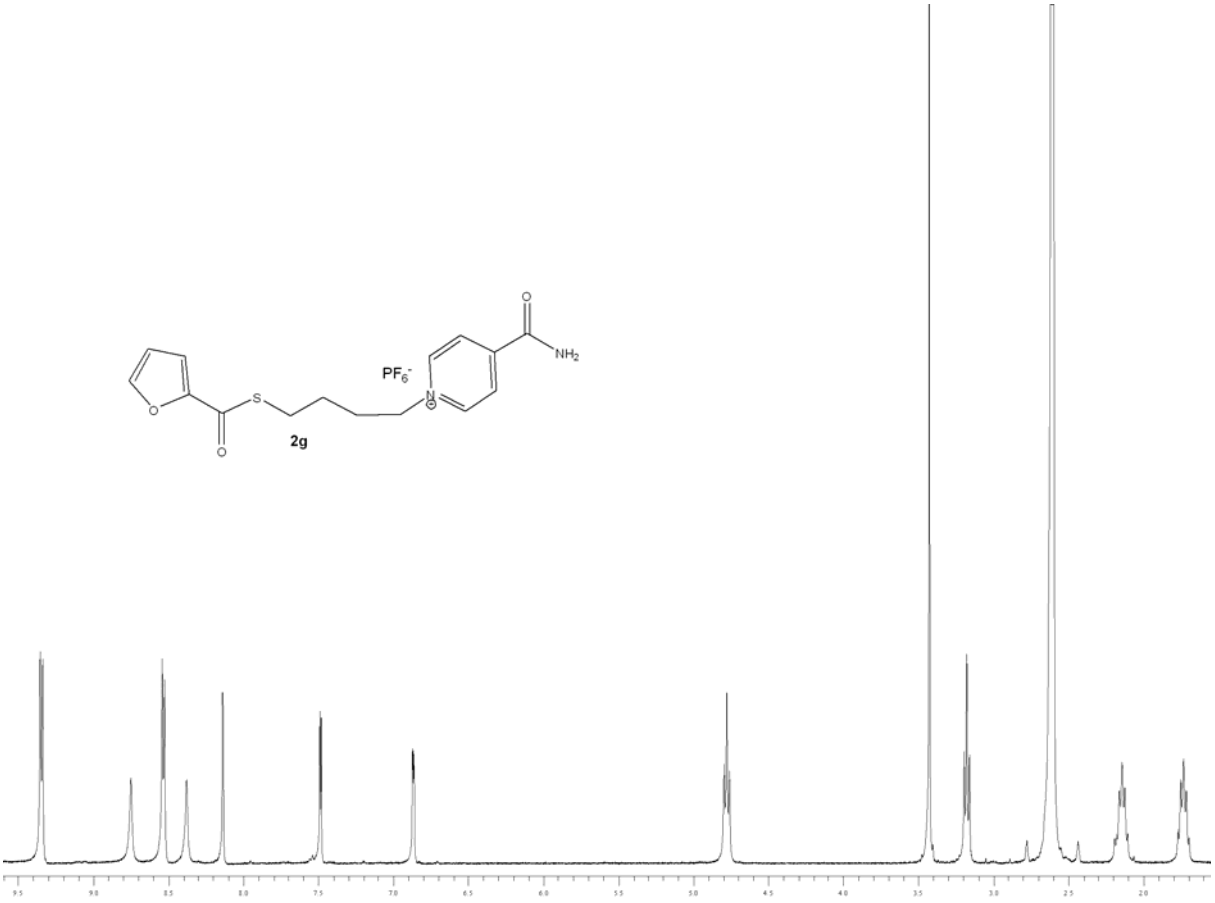
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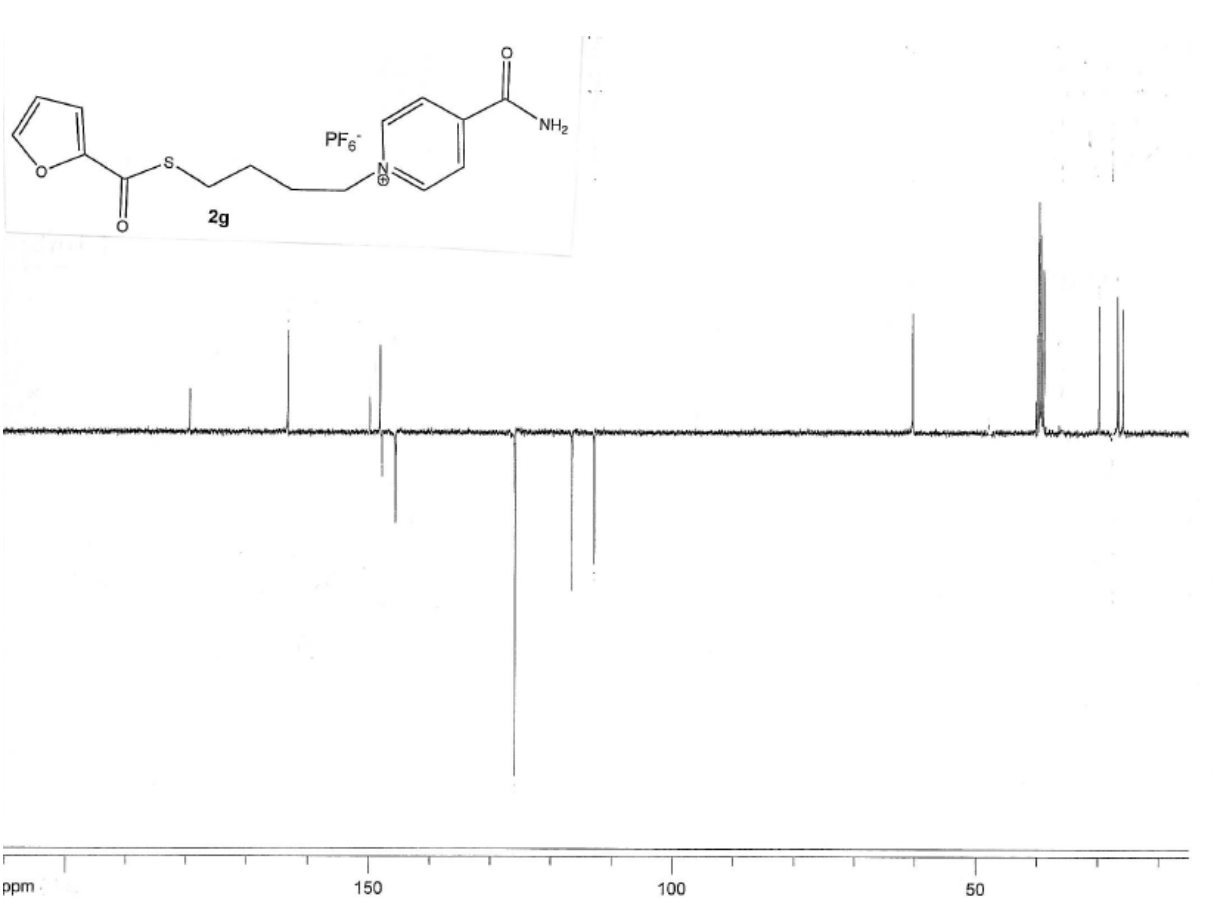
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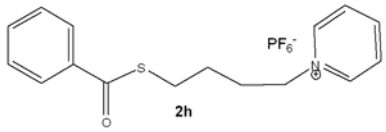

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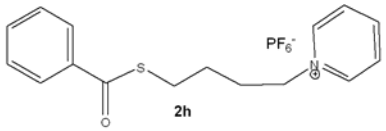

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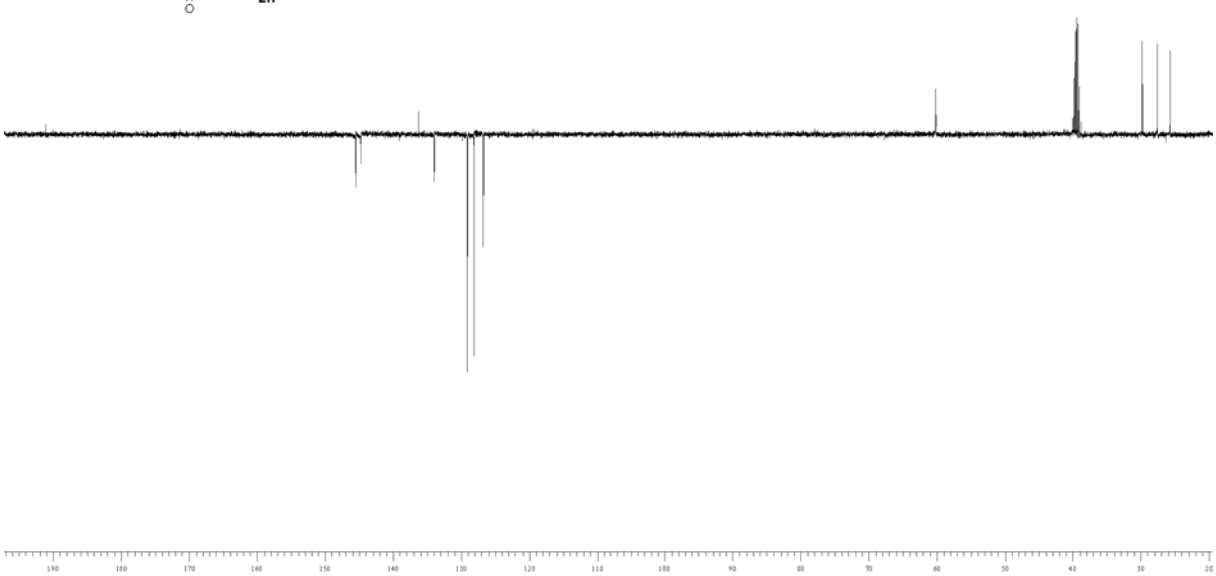

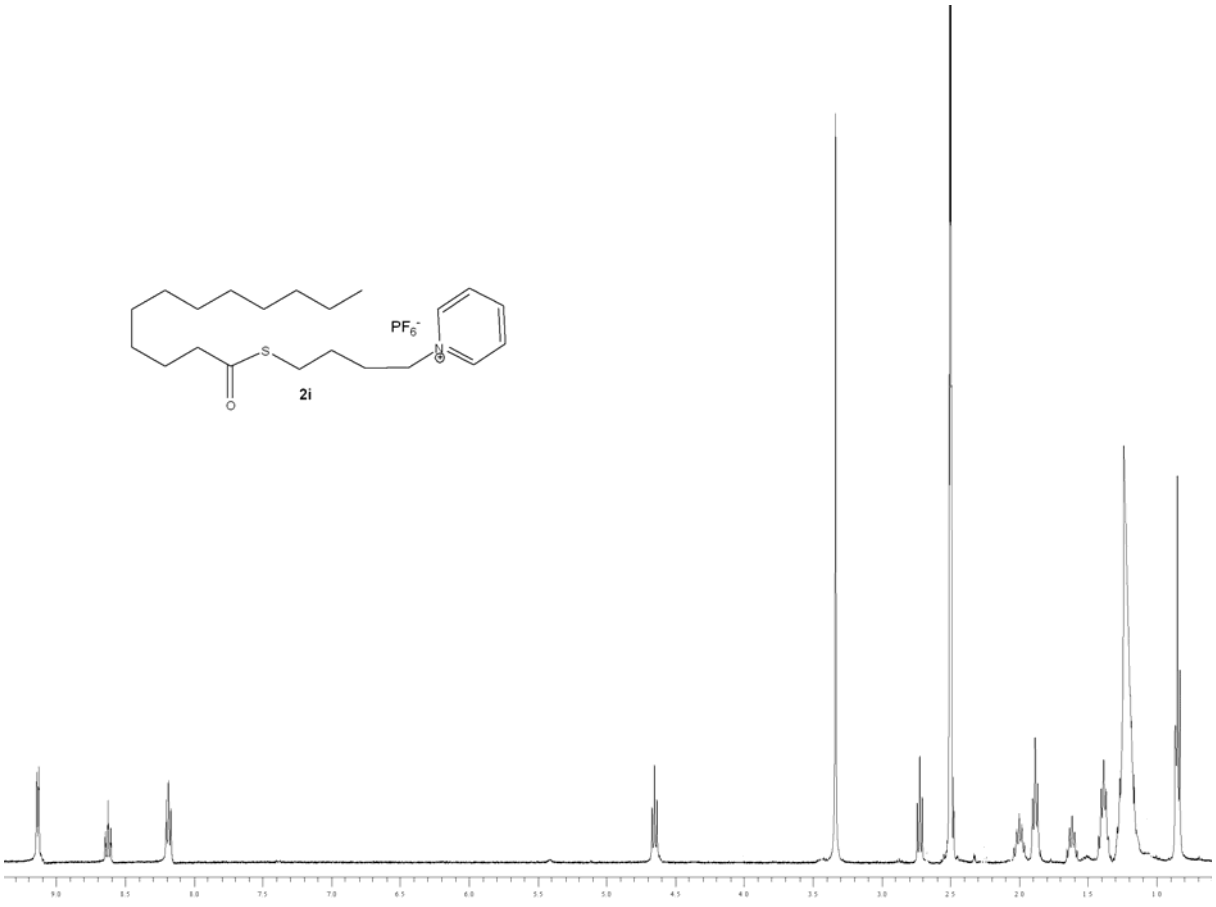
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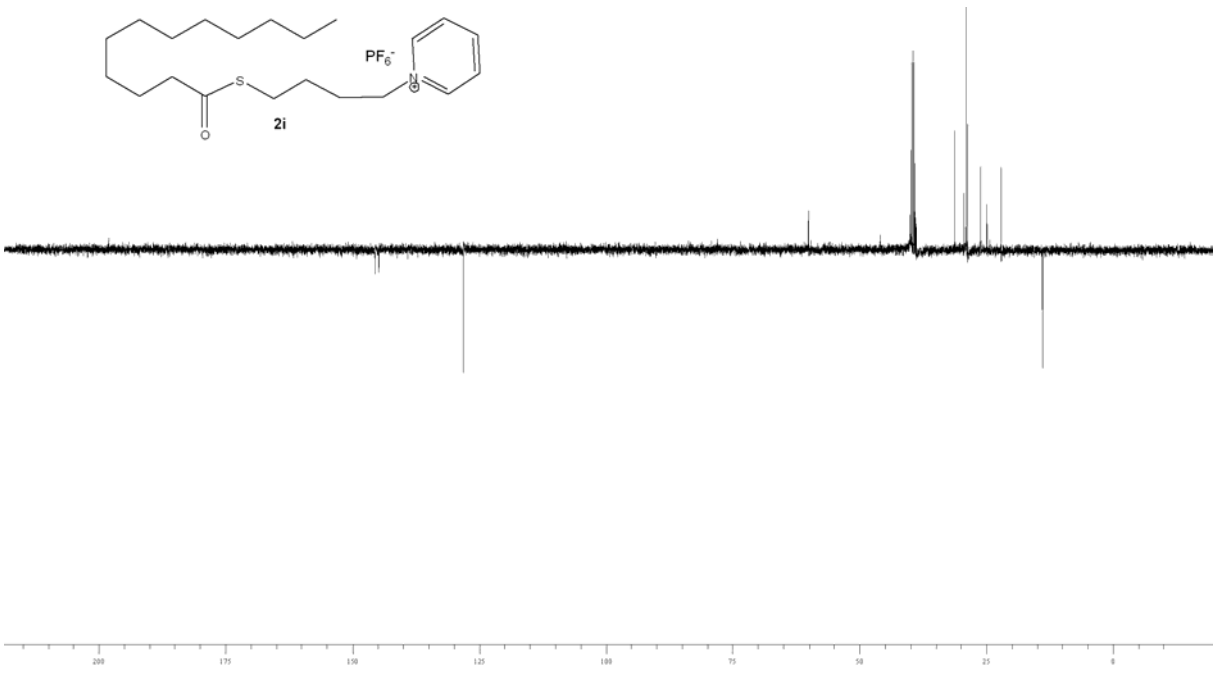
PF6-
S
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O
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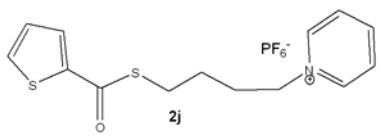

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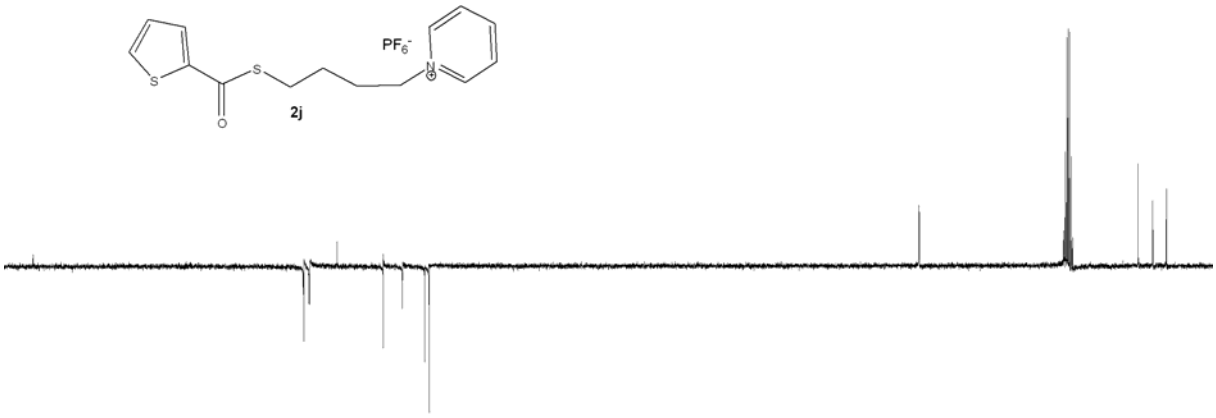

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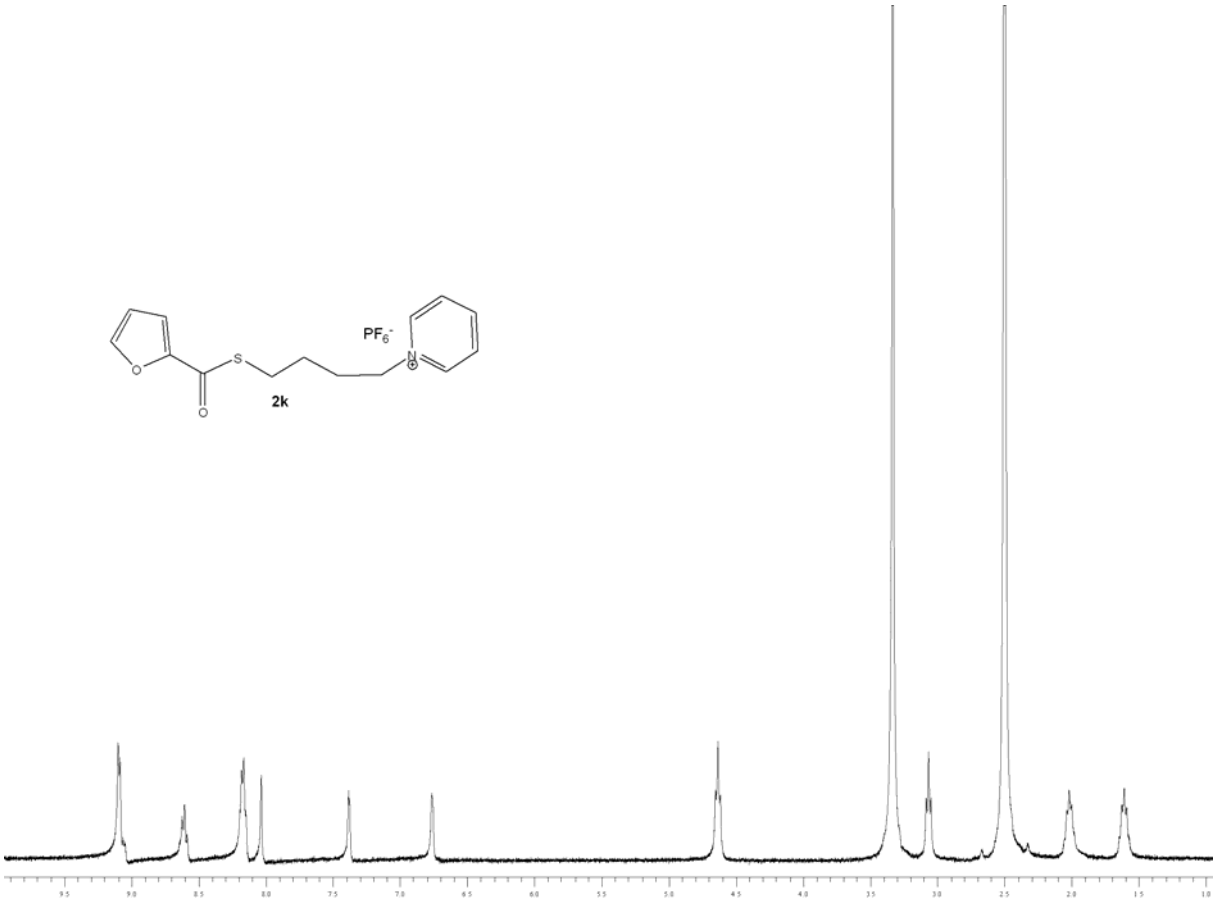

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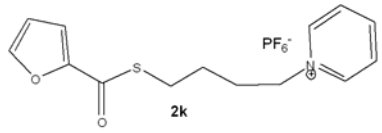

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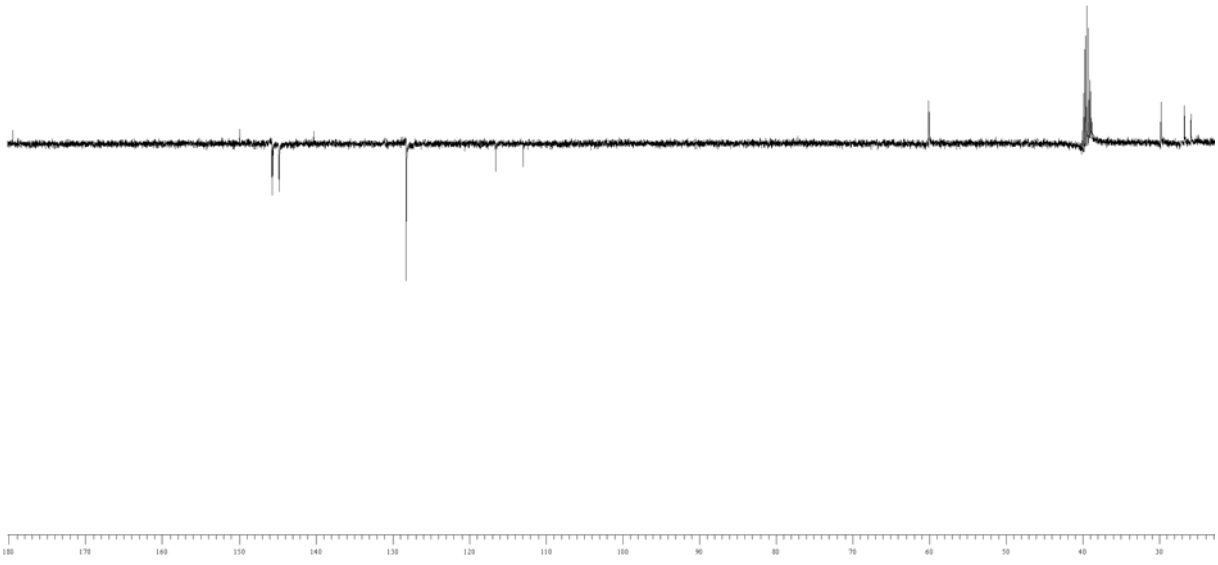

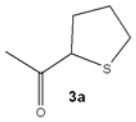

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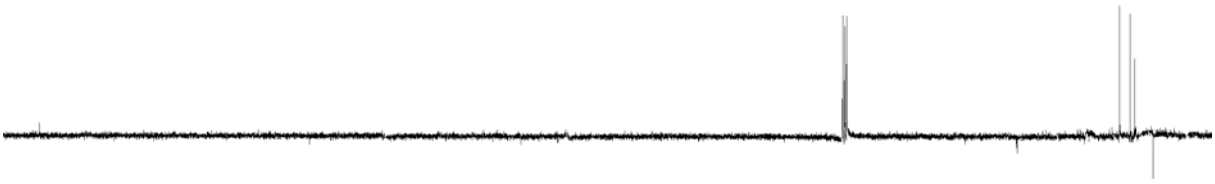

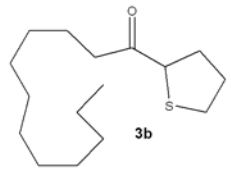

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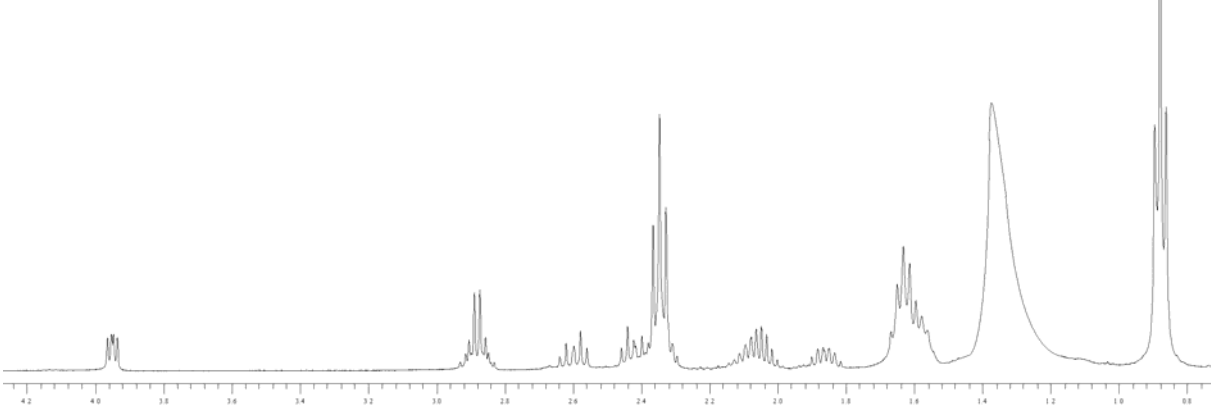

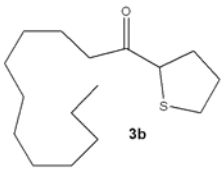

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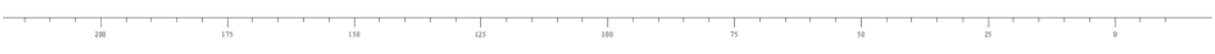
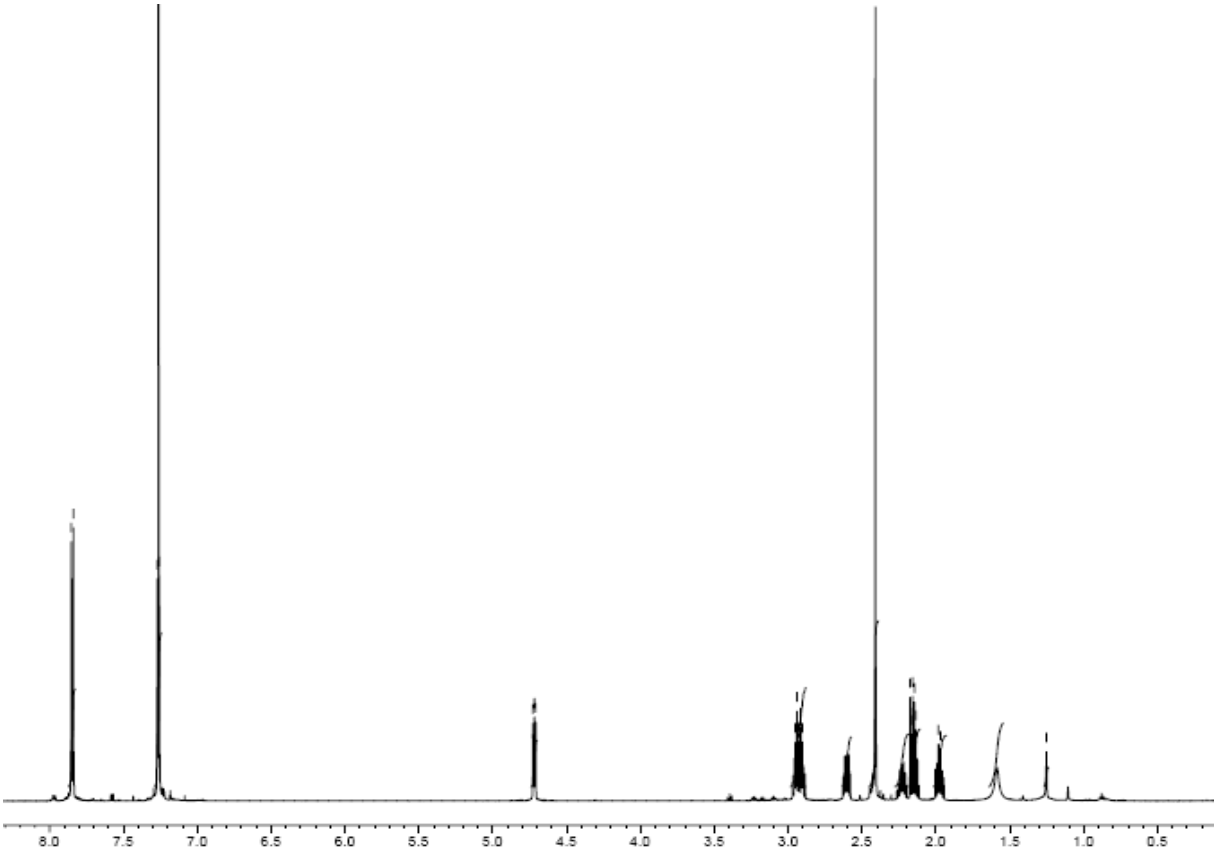
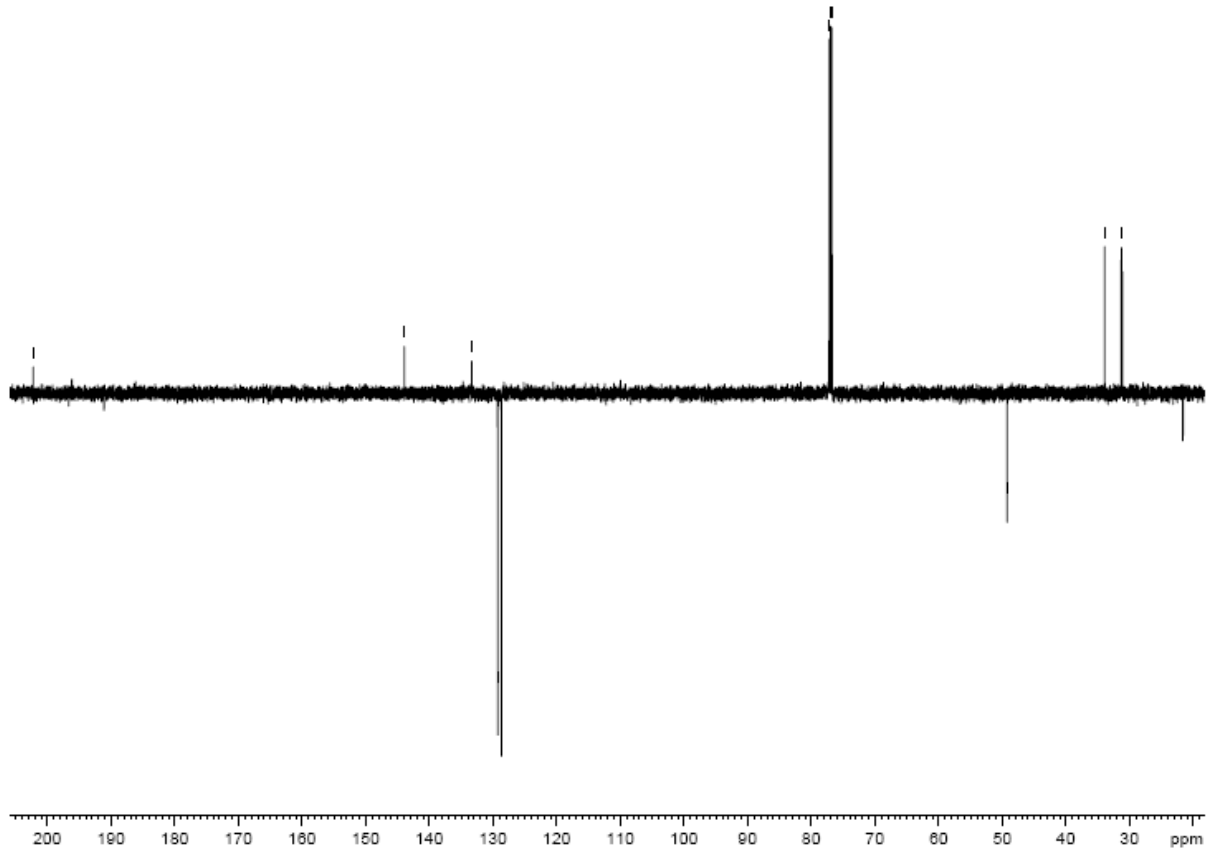
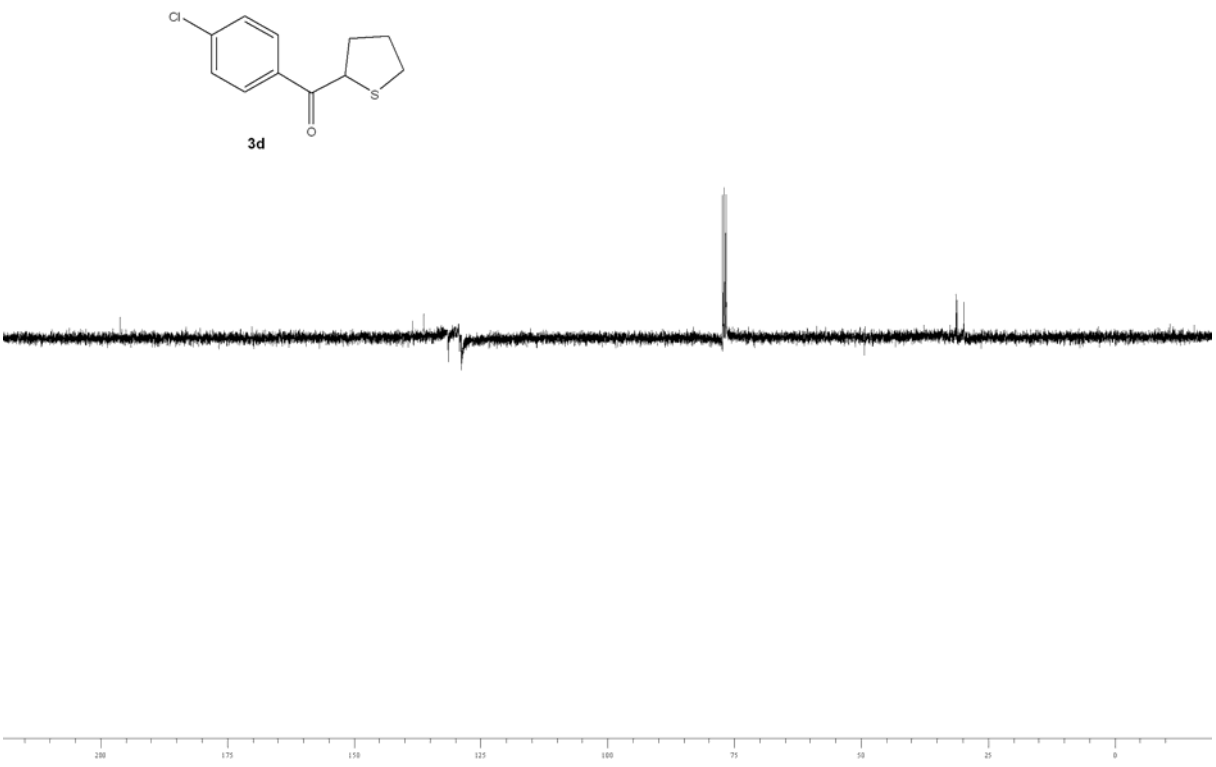


4-Methylphenyl 2-tetrahydrothienyl ketone (**3c**)

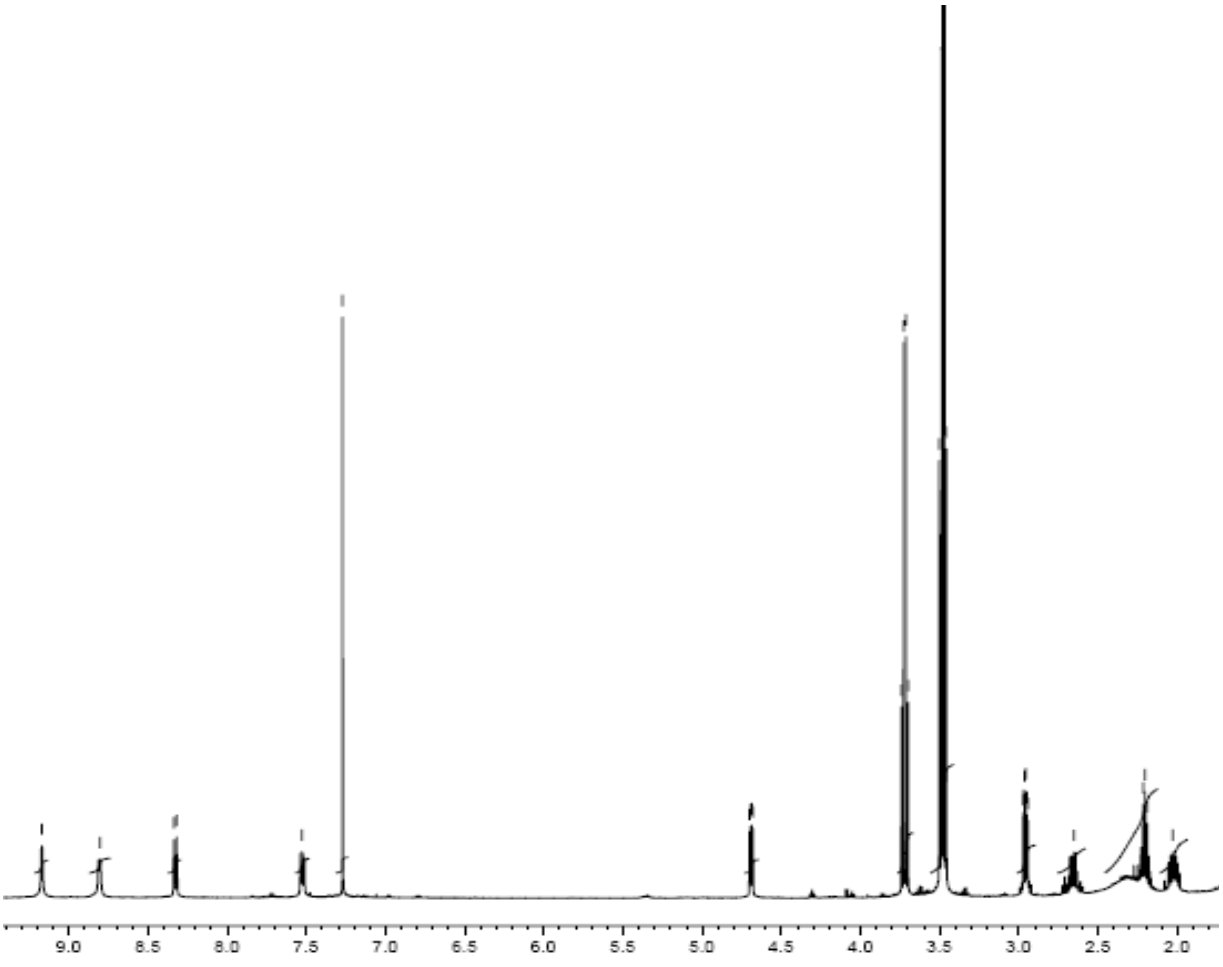


4-Methylphenyl 2-tetrahydrothienyl ketone (**3c**)

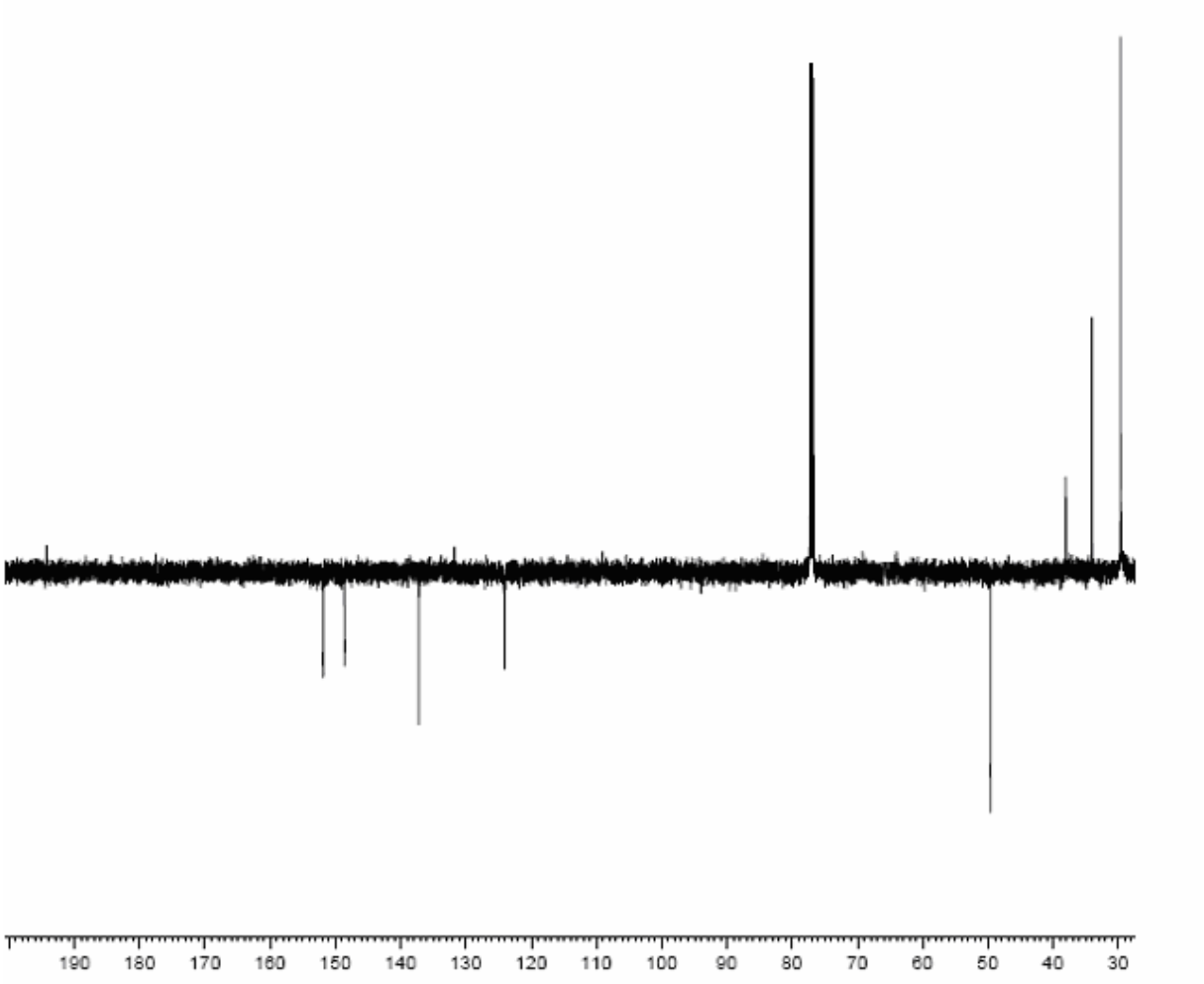


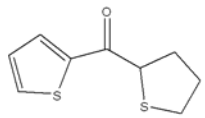


3-Pyridyl 2-tetrahydrothienyl ketone (**3e**)



3-Pyridyl 2-tetrahydrothienyl ketone (**3e**)





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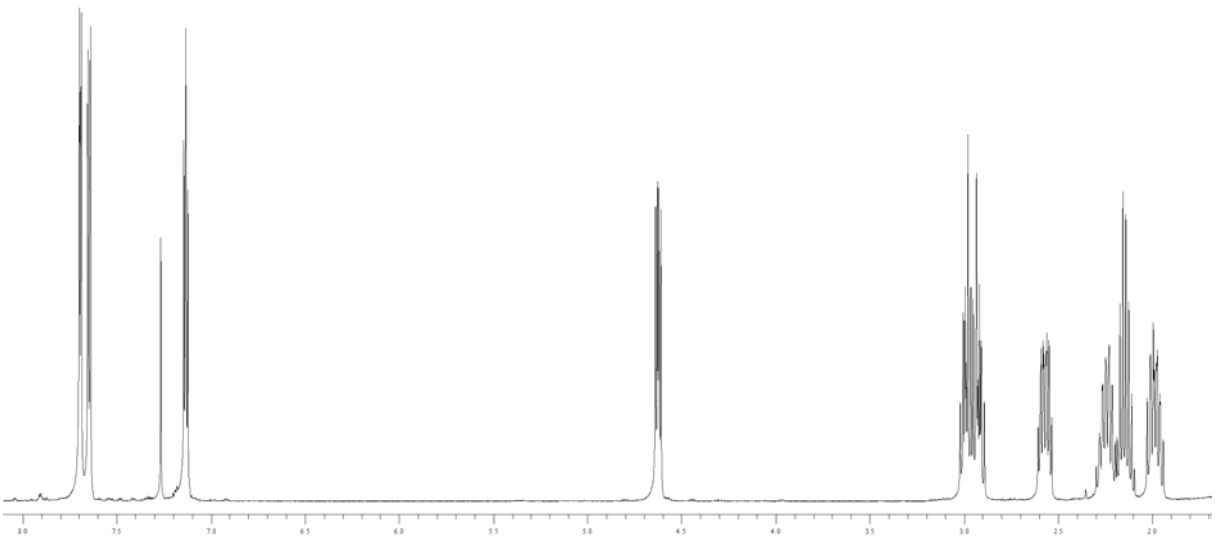

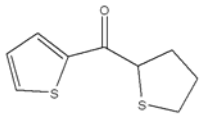

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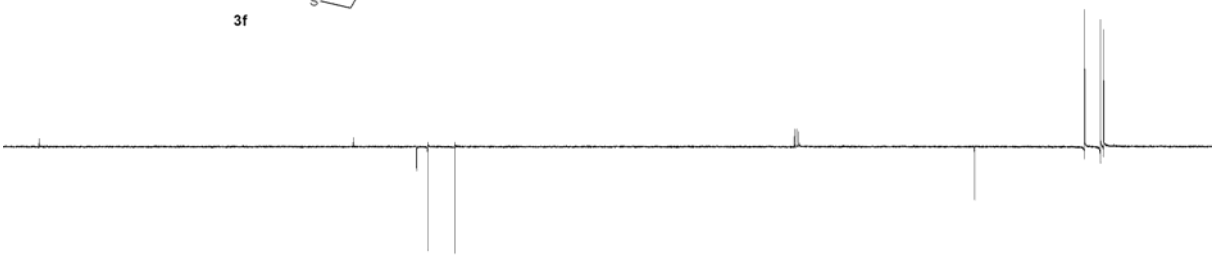

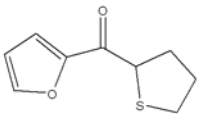

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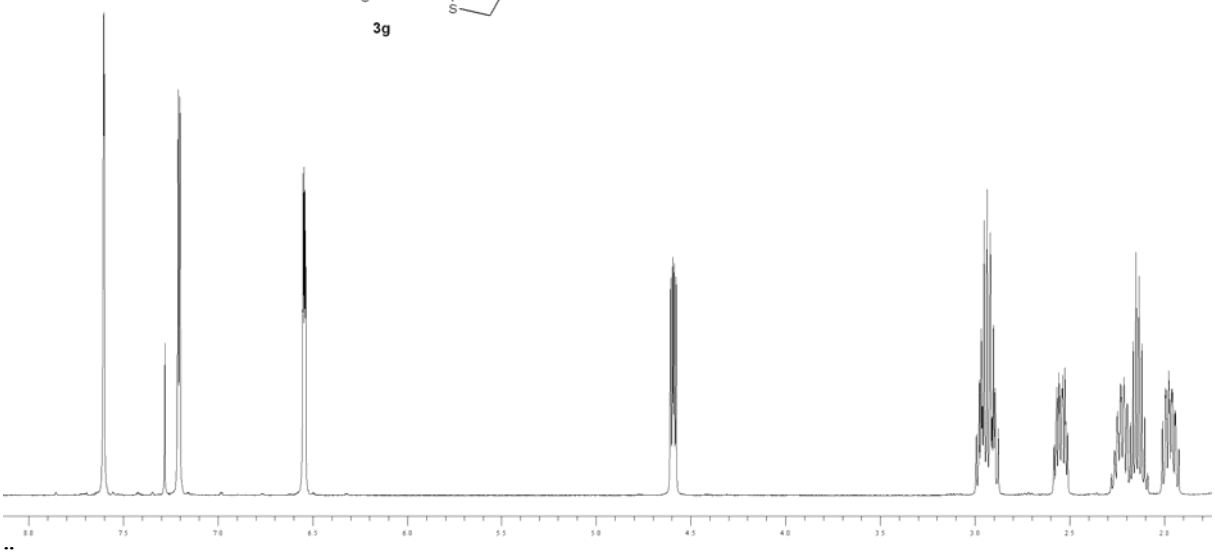

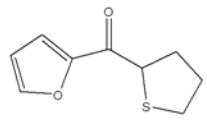

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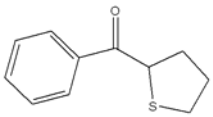

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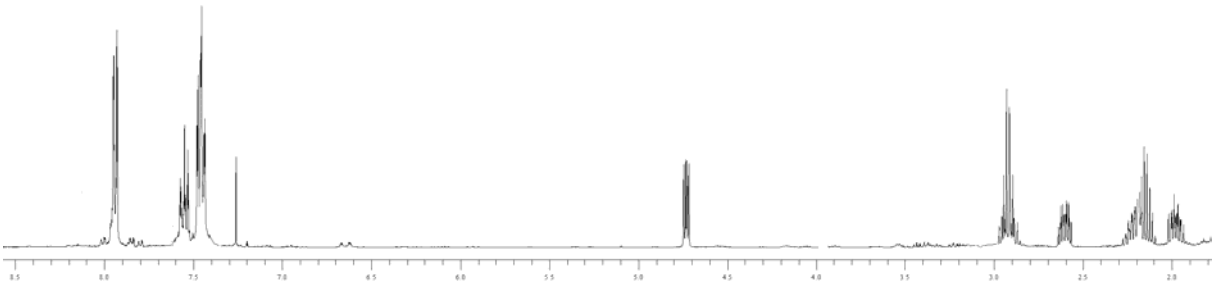

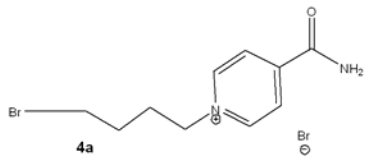

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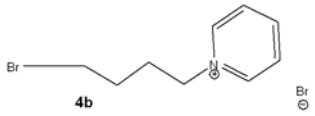

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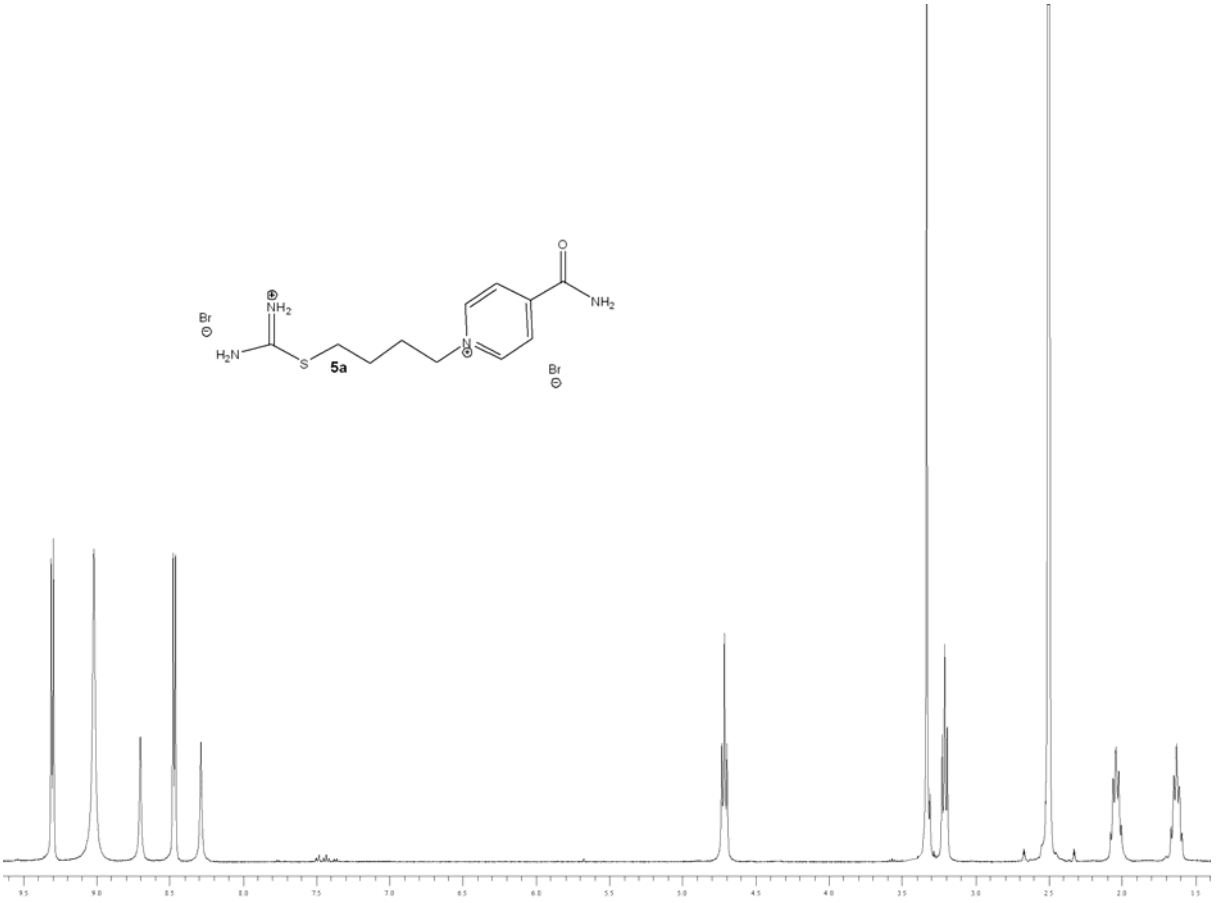
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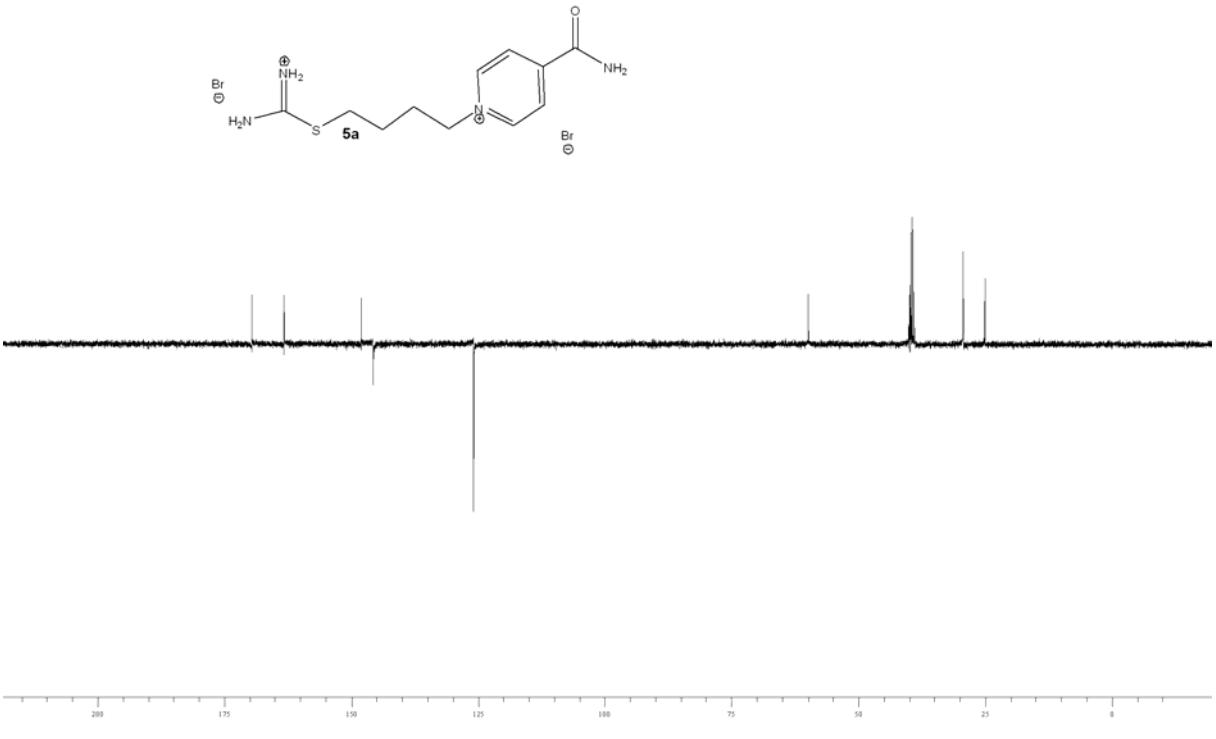
S
5a
N
O
NH2
Br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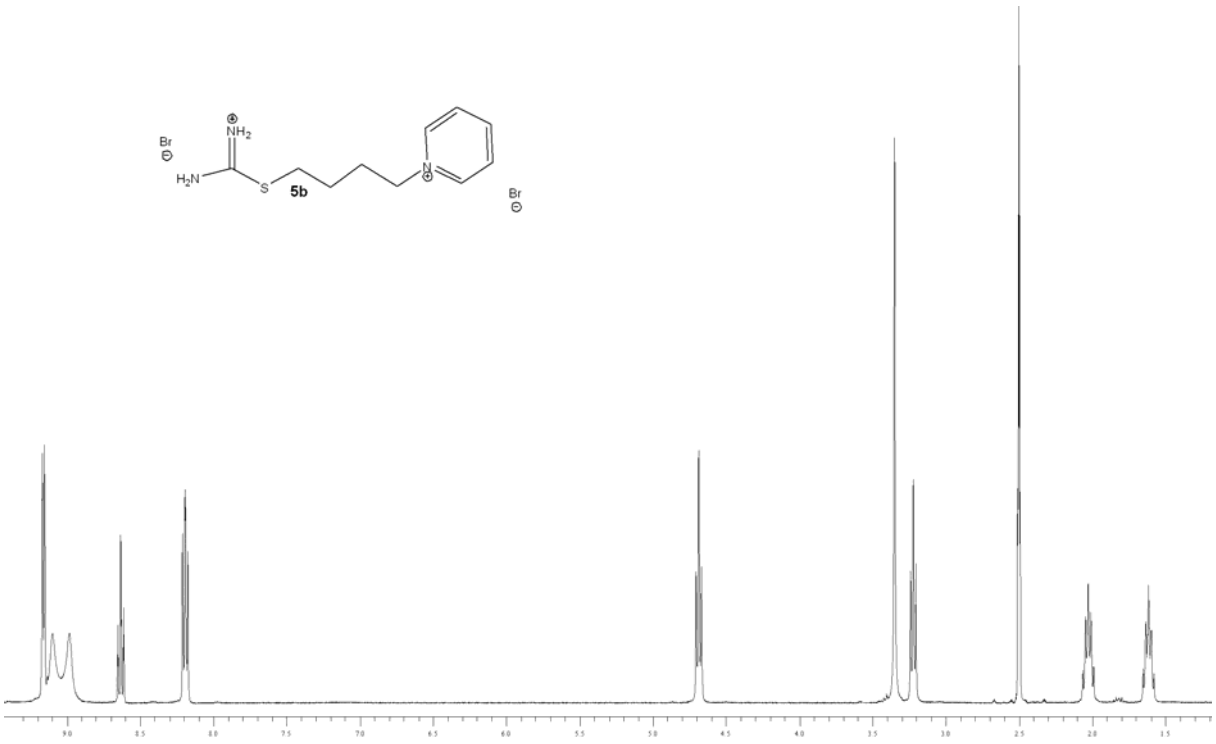
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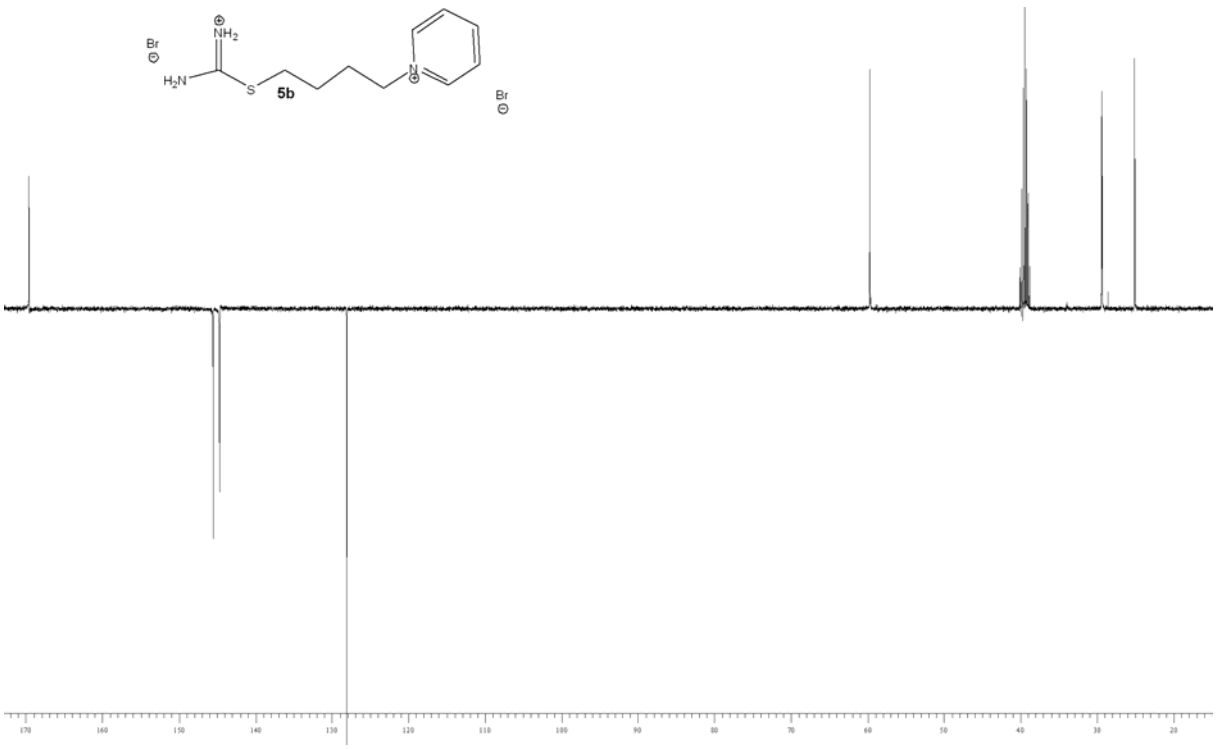
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