Supporting Information

Mild and Selective Organocatalytic Iodination of Activated Aromatic Compounds

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Table of contents

General remarks ......................................................................................................................... 2
Synthesis of (thio)urea catalysts ................................................................................................. 2
  N-methyl-3,5-bis(trifluoromethyl)aniline .............................................................................. 2
  N,N’-dimethyl-N,N’-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T4) ........................................ 3
  N-methyl-N,N’-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T5) ............................................... 3
General procedure for the iodination of aromatic compounds ................................................... 4
  1-iodo-3,4-dimethoxybenzene (1a) ........................................................................................ 4
  1-iodo-3,4-dimethylbenzene (2a) .......................................................................................... 5
  2-chloro-1-iodo-4-methoxybenzene (3a) .............................................................................. 5
  2-iodo-5-methoxybenzaldehyde (4a) ................................................................................... 5
  4-idoacetoisole (5a) ..................................................................................................... 6
  1-iodo-4-methoxynaphthalene (6a) ..................................................................................... 6
  1-iodo-2-methoxynaphthalene (7a) ..................................................................................... 6
  1-iodo-2,4,6-trimethylbenzene (8a) .................................................................................... 7
  1-iodo-2,4,6-trimethoxybenzene (9a) .................................................................................. 7
  4-iodoacetanalide (10a) .................................................................................................... 7
Kinetic investigations ............................................................................................................... 8
Sulfur-iodine complex formation .......................................................................................... 10
References ................................................................................................................................. 13
Appendix .................................................................................................................................. 13
General remarks

Melting points were recorded on a Krüss KSP1N melting-point meter and are uncorrected. IR spectra were obtained using a Brucker Alpha FT-IR spectrometer. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV400, or a Bruker AV600 spectrometer, using TMS as the internal standard with chemical shifts given in ppm relative to TMS, or the respective solvent residual peaks. HRMS spectra were recorded on a Thermo Finnigan MAT 95 mass spectrometer or on an AP MALDI Q Exactive Mass Spectrometer (Thermo Fisher Scientific). C-H-N analyses were performed on a Thermo Flash EA 1112 device. Column chromatography was conducted using Merck silica gel 60 (0.040–0.063 mm). Starting materials, solvents, and reagents were purchased from commercial sources, unless otherwise noted and were used without purification. Argon was passed through concentrated sulfuric acid, CaCl$_2$ and P$_2$O$_5$ columns to remove residual water.

Synthesis of (thio)urea catalysts

The (thio)urea derivatives were synthesized according to literature procedures$^1$ unless otherwise noted.

$N$-methyl-3,5-bis(trifluoromethyl)aniline$^2$

[CAS Reg. No. 42450-72-6] A dry 25 mL two necked flask was equipped with argon inlet and septum. The system was purged with argon and was charged with 3,5-bis(trifluoromethyl)aniline (1.47 g, 1.0 mL, 6.4 mmol) and dry DCM (14 mL). The mixture was cooled to 0°C with an ice bath and (2.7 mL, 19 mmol) trifluoroacetic anhydride was added with a syringe through the septum. Then the solution was allowed to warm to room temperature and was stirred for 20 min. The volatiles were evaporated in vacuo and the residue was redissolved in acetone (15 mL). Anhydrous K$_2$CO$_3$ (1.77 g, 12.8 mmol) was added followed by methyl iodide (1.2 mL, 19 mmol). This mixture was refluxed for 2 h then the precipitate was filtered off and the filtrate was concentrated in vacuo. Water (5 mL), methanol (25 mL), and K$_2$CO$_3$ (0.88 g, 6.3 mmol) were added; the mixture was stirred for 1 h at room temperature. The bulk of the methanol was distilled off and the crude product was extracted with DCM (30 mL), which was subsequently washed with water (2×10 mL) and brine (10 mL). The organic phase was dried over Na$_2$SO$_4$ and concentrated to yield the 1.36 g (87%) $N$-methyl-3,5-bis(trifluoromethyl)aniline as a yellow oil. The product was used
without further purification. $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.16$ (s, 1H, para-H), 6.94 (s, 2H, ortho-H), 4.41 (br s, 1H, NH), 2.91 (s, 3H, CH$_3$); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.5, 132.4 (q, $J = 32$ Hz), 123.5 (q, $J = 275$ Hz), 111.6, 110.2, 30.4.

$N,N'$-dimethyl-$N,N'$-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T4)

[CAS Reg. No. 1356253-41-2] We were unable to reproduce the final step of the reported procedure$^3$ and therefore developed our own method.

A dry 100 mL two necked flask was equipped with argon inlet. Under protective atmosphere the flask was charged with $N$-methyl-3,5-bis(trifluoromethyl)aniline (0.600 g, 2.5 mmol) and dry THF (10 mL). The solution was cooled to $-78^\circ$C in a dry ice/acetone bath and $n$-BuLi (1.6 M in hexanes, 1.6 mL, 2.6 mmol) was added dropwise via syringe. The yellow reaction mixture was stirred for 15 min followed by the addition of thiophosgene (100 $\mu$L, 1.3 mmol). The solution was stirred at $-78^\circ$C for an hour, and then it was allowed to warm to room temperature and stirred overnight. Saturated NH$_4$Cl solution (6 mL) was added to quench the reaction; the crude product was extracted with EtOAc (2$\times$40 mL). The combined organic phase was washed with water (2$\times$20 mL), dried over Na$_2$SO$_4$ and concentrated. Purification by column chromatography (Hexanes/Ethyl acetate 20/1) on silica gel furnished 59 mg yellow oil. Methanol (1 mL) was added and the precipitating white solid was filtered off and dried in vacuo to yield pure $N,N'$-dimethyl-$N,N'$-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T4) (43 mg, 3.3%) as a white solid. Mp 173–174 $^\circ$C; IR (KBr): 3038, 2935, 1615, 1473, 1380, 1278, 1181, 1147, 1035, 892, 846, 702, 682 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.48$ (s, 2H, para-H), 7.06 (s, 4H, ortho-H), 3.62 (s, 6H, CH$_3$); $^{13}$C NMR (150 MHz, CDCl$_3$): $\delta = 189.9$, 148.0, 132.9 (q, $J = 34.2$ Hz), 125.2, 122.4 (q, $J = 276.4$ Hz), 119.3, 44.8; HRMS (AP MALDI) $m/z$ [M+H]$^+$ calcd for C$_{19}$H$_{13}$F$_{12}$N$_2$S: 529.05968, found: 529.07468.

$N$-methyl-$N,N'$-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T5)

A dry 10 mL two necked flask was equipped with argon inlet. The flask was charged with $N$-methyl-3,5-bis(trifluoromethyl)aniline (0.5 g, 2.1 mmol) and dry DCM (2 mL). Under argon atmosphere DIPEA (0.35 mL, 2.1 mmol) and 3,5-bis(trifluoromethyl)phenylisothiocyanate (0.613 g, 413 $\mu$L, 2.3 mmol) was added and the reaction mixture was stirred overnight at room temperature. The solution was diluted with DCM (30 mL), washed with aqueous HCl solution (2$\times$10 mL, 5 $\text{V/V}\%$) and water (10 mL). The organic layer was dried over Na$_2$SO$_4$
and concentrated to furnish a yellow oil. The crude product was purified by column chromatography (Hexanes/DCM 1/1) on silica gel to give \(N\)-methyl-\(N,N'\)-di[3,5-bis(trifluoromethyl)phenyl]thiourea (T5) (0.55 g, 52%) as an off white solid. Mp 105–106°C; IR (KBr): 3378, 3085, 2948, 1475, 1430, 1377, 1279, 1179, 1135, 884, 703, 683 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.91\) (s, 1H, \(\text{para}-\text{H}\)), 7.80 (s, 2H, \(\text{ortho}-\text{H}\)), 7.75 (s, 2H, \(\text{ortho}-\text{H}\)), 7.67 (s, 1H, \(\text{para}-\text{H}\)), 7.05 (br s, 1H, \(\text{NH}\)), 3.77 (s, 3H, NCH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 182.2, 144.9, 140.0, 134.3\) (q, \(J = 35.6\) Hz), 132.1 (q, \(J = 35.6\) Hz), 127.4, 125.4, 122.8 (q, \(J = 273.4\) Hz), 122.4 (q, \(J = 273.4\) Hz), 122.4, 119.7, 43.9; HRMS (AP MALDI) \(m/z\) [M+H]\(^+\) calcd for C\(_{18}\)H\(_{11}\)F\(_{12}\)N\(_2\)S: 515.04404, found: 515.04464; Anal. calcd for C\(_{18}\)H\(_{10}\)F\(_{12}\)N\(_2\)S: C, 42.03; H, 1.96; N, 5.45. Found: C, 41.75; H, 2.02; N, 5.16.

**General procedure for the iodination of aromatic compounds**

A dry Schlenk tube was equipped with stirring bar and was purged with argon. T1 (30 mg, 0.06 mmol, 10%) was placed in the reaction vessel followed by dry acetonitrile (2 mL) and the respective aromatic compound (0.60 mmol). DIH (171 mg, 0.45 mmol, 0.75 eq) was added in one portion, and the mixture was stirred at room temperature. The progression of the reaction was followed by GCMS or TLC. After no further conversion was observed aqueous Na\(_2\)S\(_2\)O\(_3\) solution (20 mL, 10m/m\%) was added. The resulting mixture was extracted with DCM (3×20 mL), the combined organic phase was dried over Na\(_2\)SO\(_4\) and concentrated. The crude product was purified by column chromatography. Impurity profile was determined prior to chromatography using \(^1\)H NMR spectroscopy.

**1-iodo-3,4-dimethoxybenzene (1a)**

[CAS Reg. No. 5460-32-2] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 10/1) to furnish 137 mg (86%) 1-iodo-3,4-dimethoxybenzene as a white solid. Mp 31–32°C; IR (KBr): 2955, 2927, 2835, 1580, 1501, 1250, 1176, 1135, 1020, 836, 797 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.23\) (dd, \(J_1 = 8.6\) Hz, \(J_2 = 2.1\) Hz, 1H, H-6), 7.12 (d, \(J = 2.1\) Hz, 1H, H-2), 6.62 (d, \(J = 8.6\) Hz, 1H, H-5), 3.86 (s, 3H, CH\(_3\)), 3.85 (s, 3H, CH\(_3\)); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 149.8, 149.1, 129.8, 120.3, 113.1, 82.4, 56.1, 55.9\); HRMS (EI) \(m/z\) calcd for C\(_8\)H\(_9\)IO\(_2\): 263.965, found: 263.968. Byproduct: 1-iodo-2,3-dimethoxybenzene (2%).

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S4
1-iodo-3,4-dimethylbenzene (2a)
[CAS Reg. No. 31599-61-8] The crude product was subjected to column chromatography on silica gel (Hexanes/Ethyl acetate 20/1) to furnish 91 mg colorless oil. NMR spectroscopy confirmed the structure of the desired product and revealed that the sample contained 1-iodo-2,3-dimethylbenzene (16%), which we were unable to separate in any of the further attempts. Thus the product reported here is a mixture of 1-iodo-3,4-dimethylbenzene and 1-iodo-2,3-dimethylbenzene. Yield: 65% for 2a+2a′. 1H NMR (400 MHz, CDCl3): δ = 7.49 (br s, 1H), 7.42 (d, J = 7.7 Hz, 1H), 6.87 (d, J = 7.7 Hz, 1H), 2.22 (s, 6H); 13C NMR (100 MHz, CDCl3): δ = 139.2, 138.2, 136.2, 134.8, 131.5, 90.7, 19.5, 19.4; HRMS (EI) m/z calcd for C8H9I: 231.975, found: 231.975.

Byproduct: 1-iodo-2,3-dimethylbenzene (16%).

2-chloro-1-iodo-4-methoxybenzene (3a)
[CAS Reg. No. 219735-98-5] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 20/1) to furnish 123 mg (76%) 2-chloro-1-iodo-4-methoxybenzene as a colorless oil. IR (film): 3006, 2962, 2936, 2835, 1583, 1563, 1468, 1436, 1294, 1263, 1227, 1099, 1040, 871, 859, 801, 593 cm⁻¹; 1H NMR (400 MHz, CDCl3): δ = 7.68 (d, J = 8.8 Hz, 1H, H-6), 7.02 (d, J = 2.9 Hz, 1H, H-3), 6.57 (dd, J1 = 8.8 Hz, J2 = 2.9 Hz, 1H, H-5), 3.78 (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ = 160.5, 140.3, 139.0, 115.3, 114.9, 86.6, 55.7; HRMS (EI) m/z calcd for C7H6ClO: 267.915, found: 267.915.

Byproduct: 1-iodo-2-methoxy-4-chlorobenzene (10%).

2-iodo-5-methoxybenzaldehyde (4a)
[CAS Reg. No. 77287-58-2] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 15/1) to furnish 103 mg (66%) 2-iodo-5-methoxybenzaldehyde as a white solid. Mp 112–113°C; IR (KBr): 3004, 2976, 2937, 2860, 2839, 1668, 1593, 1563, 1469, 1301, 1280, 1245, 1199, 934, 820, 647 cm⁻¹; 1H NMR (400 MHz, CDCl3): δ = 10.02 (s, 1H, CHO), 7.80 (d, J = 8.7 Hz, 1H, H-3), 7.42 (d, J = 3.1 Hz, 1H, H-6), 6.92 (dd, J1 = 8.7 Hz, J2 = 3.1 Hz, 1H, H-4), 3.84 (s, 3H, CH3); 13C NMR (100 MHz, CDCl3): δ = 195.7, 160.3, 141.0, 135.7, 123.5, 113.5, 89.9, 55.7; HRMS (EI) m/z calcd for C8H7IO2: 261.949, found: 261.950.

Byproduct: 4-iodo-3-methoxybenzaldehyde (15%).

S5
4-idoanisole (5a)
[CAS Reg. No. 696-62-8] The crude product was purified by column chromatography on silica gel (Pentanes/DCM 3/1) to furnish 120 mg (85%) 4-idoanisole as a white solid. Mp 49–50°C; IR (KBr): 3006, 2966, 2937, 2838, 1586, 1485, 1455, 1286, 1242, 1176, 1028, 833, 813, 586, 510 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 7.58–7.53 (m, 2H, ortho-H), 6.71–6.65 (m, 2H, meta-H), 3.78 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 159.5, 138.2, 116.4, 82.7, 55.3; HRMS (EI) m/z calcd for C₇H₇IO: 233.954, found: 233.955.
Byproduct: 2-iodoanisole (3%).

1-ido-4-methoxynaphthalene (6a)
[CAS Reg. No. 2607-25-2] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 10/1) to furnish 151 mg (89%) 1-ido-4-methoxynaphthalene as a yellowish solid. Mp 54–55°C; IR (KBr): 2964, 2932, 2838, 1586, 1454, 1416, 1366, 1316, 1261, 1242, 1085, 816, 808, 774, 759 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.24 (d, J = 8.3 Hz, 1H, H-2), 8.03 (d, J = 8.3 Hz, 1H, H-8), 7.95 (d, J = 8.2 Hz, 1H, H-5), 7.63–7.48 (m, 2H, H-6,7), 6.59 (d, J = 8.2 Hz, 1H, H-3), 3.99 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 156.3, 136.9, 134.7, 131.8, 128.2, 126.6, 126.0, 122.5, 105.6, 88.2, 55.7; HRMS (EI) m/z calcd for C₁₁H₉IO: 283.970, found: 283.970.
Byproduct: No byproduct was detected.

1-ido-2-methoxynaphthalene (7a)
[CAS Reg. No. 32721-21-4] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 10/1) to furnish 157 mg (92%) 1-ido-2-methoxynaphthalene as a white solid. Mp 85–86°C; IR (KBr): 3042, 2970, 2837, 1618, 1589, 1499, 1462, 1453, 1349, 1329, 1266, 1245, 1149, 1061, 1023, 804, 762, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ = 8.15 (d, J = 8.5 Hz, 1H, H-4), 7.82 (d, J = 8.9 Hz, 1H, H-5), 7.74 (d, J = 8.3 Hz, 1H, H-8), 7.58–7.52 (m, 1H, H-7), 7.42–7.36 (m, 1H, H-6), 7.20 (d, J = 8.9 Hz, 1H, H-3), 4.02 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃): δ = 156.7, 135.7, 131.2, 130.4, 129.9, 128.2, 128.1, 124.4, 112.9, 87.7, 57.2; HRMS (EI) m/z calcd for C₁₁H₉IO: 283.970, found: 283.970.
Byproduct: 1,6-diiodo-2-methoxynaphthalene (2%).
1-iodo-2,4,6-trimethylbenzene (8a)

[CAS Reg. No. 4028-63-1] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 50/1) to furnish 122 mg (83%) 1-iodo-2,4,6-trimethylbenzene as a white solid. Mp 29–30°C; IR (KBr): 3021, 2966, 2919, 2853, 1621, 1461, 1435, 1376, 1266, 1004, 949, 847 cm–1; 1H NMR (400 MHz, CDCl3): δ = 6.90 (s, 2H, Ar-H), 2.44 (s, 6H, otho-CH3), 2.25 (s, 3H, para-CH3); 13C NMR (100 MHz, CDCl3): δ = 141.8, 137.3, 128.0, 104.3, 29.5, 20.7; HRMS (EI) m/z calcd for C9H11I: 245.991, found: 245.992.

Byproduct: No byproduct was detected.

1-iodo-2,4,6-trimethoxybenzene (9a)

[CAS Reg. No. 2510-49-8] A dry Schlenk tube was equipped with stirring bar and was purged with argon. T1 (30 mg, 0.06 mmol, 10%) was placed in the reaction vessel followed by dry acetonitrile (2 mL) and 1,3,5-trimethoxybenzene (100.9 mg, 0.6 mmol). DIH (114 mg, 0.30 mmol, 0.5 eq) was added in one portion, and the mixture was stirred at room temperature. After 4 h aqueous Na2S2O3 solution (20 mL, 10m/m%) was added. The resulting mixture was extracted with DCM (3×20 mL), the combined organic phase was dried over Na2SO4 and concentrated. The crude product was purified by column chromatography on silica gel (Hexanes/Chloroform 1/1) to furnish 152 mg (86%) 1-iodo-2,4,6-trimethoxybenzene as a white solid. Mp 120–121°C; IR (KBr): 2964, 2931, 2835, 1583, 1467, 1403, 1343, 1226, 1208, 1160, 1125, 1070, 1016, 805 cm–1; 1H NMR (400 MHz, CDCl3): δ = 6.14 (s, 2H, Ar-H), 3.86 (s, 6H, otho-OCH3), 3.82 (s, 3H, para-OCH3); 13C NMR (100 MHz, CDCl3): δ = 162.2, 159.8, 91.2, 66.7, 56.5, 55.5; HRMS (EI) m/z calcd for C9H11IO3: 293.975, found: 293.975.

Byproduct: No byproduct was detected; the crude mixture contained starting material (13%).

4-iodoacetanilide (10a)

[CAS Reg. No. 622-50-4] The crude product was purified by column chromatography on silica gel (Hexanes/Ethyl acetate 1/1) to furnish 144 mg (92%) 4-iodoacetanilide as a white solid. Mp 184–185°C; IR (KBr): 3442, 3290, 3254, 3177, 3102, 1666, 1597, 1580, 1529, 1483, 1389, 1308, 1254, 1002, 817, 751 cm–1; 1H NMR (400 MHz, d6-DMSO): δ = 10.04 (s, 1H, NH), 7.62 (d, J = 8.5 Hz, 2H, meta-H), 7.42 (d, J = 8.5 Hz, 2H, ortho-H), 2.04 (s, 3H, COCH3); 13C NMR (100 MHz, d6-DMSO): δ = 168.4, 139.1, 137.3, 121.1, 86.3, 24.0; HRMS (EI) m/z calcd for C8H8INO: 260.965, found: 260.966.

Byproduct: No byproduct was detected.
Kinetic investigations

A dry Schlenk tube was equipped with stirring bar and was purged with argon. The corresponding catalyst was placed in the reaction vessel followed by dry $d_8$-THF (1 mL) and 1,2-dimethoxybenzene (41 mg, 38 μL, 0.3 mmol). DIH (85.5 mg, 0.23 mmol, 0.75 eq) was added in one portion, and 700 μL of the reaction mixture was transferred to an NMR tube; the sample was tempered to 25°C. The measurement was conducted on a Bruker AV600 spectrometer recording spectra every 10 minutes during the observed time period. Each $^1$H NMR spectrum was evaluated and the corresponding conversion value was calculated from the integral ratio of two specific peaks.

Starting material: $\delta$ 6.88–6.80 (m, 4H).

Product: $\delta$ 6.68 (d, $J = 8.6$ Hz, 1H).

Kinetic plots were generated by displaying these conversion data against the corresponding reaction times.

Figure 1 $^1$H NMR spectra of the reaction mixture in $d_8$-THF at different stages of the reaction.
**Figure 2** Additional amount of DIH was added to a T2 catalyzed iodination of 1,2-dimethoxybenzene in $d_8$-THF after the reaction came to a stop.

**Figure 3** Different catalyst loads of T1 in the iodination of 1,2-dimethoxybenzene in $d_8$-THF.
Sulfur-iodine complex formation

We decided to compare the $^{13}$C NMR spectra of some thiourea derivatives obtained in $d_8$-THF prior to and following the addition of an iodine source, in particularly the chemical shifts of the thiourea carbon atom. ICl was used instead of DIH to avoid peak interference from the latter. T1 showed high degree of decomposition under these conditions, which made unambiguous peak assignment difficult. T4 and cyclic thiourea derivative $N,N'$-dimethylimidazoline-2-thione on the other hand proved to be more robust donors. The observed thiourea carbon signals exhibited significant upfield shifts upon addition of ICl. This indicates a pronounced change in the electronic environment of the thiourea carbon atom, which is consistent with the formation of an [LS-I]$^+$ like species.

Representative procedure for these measurements as follows: a dry Schlenk tube was equipped with stirring bar and was purged with argon. T4 (30 mg, 0.57 mmol) was placed in the tube and was dissolved in dry $d_8$-THF (700 μL), which was freshly distilled from Na/benzophenone. The solution was transferred to an NMR tube and sealed. After a $^{13}$C NMR spectrum was obtained ICl (3.0 μL, 1 eq) was added and the spectral changes recorded.

Figure 4 $^{13}$C NMR spectra of T4 obtained in $d_8$-THF prior to the addition of ICl.
Figure 5 $^{13}$C NMR spectra of T4 obtained in $d_8$-THF following the addition of ICl.

Figure 6 $^{13}$C NMR spectra of $N,N'$-dimethylimidazole-2-thione obtained in $d_8$-THF prior to the addition of ICl.
**Figure 6** $^{13}$C NMR spectra of $N,N'$-dimethylimidazoline-2-thione obtained in $d_8$-THF following the addition of ICl.

**Figure 7** $^{13}$C NMR spectra of $N,N'$-dimethylimidazoline-2-thione obtained in $d_8$-THF prior to (red) and following (blue) the addition of ICl.
References


Appendix
5a

6a

Current Data Parameters

S18