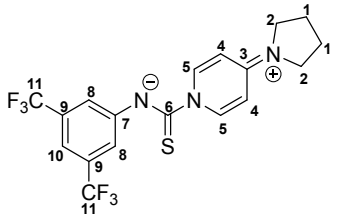
Supporting Information

Synthesis of catalyst 5[33]

4-pyrrolidinopyridine (0.74 g, 5.00 mmol) was added to a solution of 3,5-bis(trifluromethyl)phenyl isothiocyanate (0.92 mL, 5.00 mmol) in toluene (10 mL) in a 25 mL round-bottom flask. The mixture was then stirred at ambient temperature for 2 h. The precipitated solid was filtered and recrystallized from toluene. The product was filtrated and dried under vacuum to give a yellow solid (1.47 g, 0.35 mmol, yield: 70 %, mp. = 132 - 133 °C).



^{1}H-NMR (500 MHz, CD_3CN)

δ (ppm) = 2.00-2.14 (m, 4 H, $^{1}CH_2$), 3.13-3.69 (m, 4 H, $^{2}CH_2$), 6.45-6.72 (2H, ^{4}CH), 7.61-7.96 (m, 3 H, $^{8,10}CH$), 8,10-8.12 and 9.59-9.61 (m, 2 H, ^{5}CH).

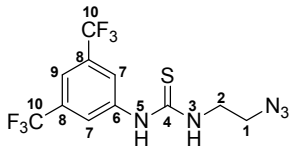
^{13}C-NMR (125 MHz, CD_3CN)

δ (ppm) = 24.77 and 24.94 (2 C, $^{1}CH_2$), 46.76 and 48.73 (2 C, $^{2}CH_2$), 105.91 and 106.91 (2 C, ^{4}CH), 120.85 (1 C, ^{10}CH), 123.31 (2 C, $^{11}CF_3$), 126.69 (2 C, ^{8}CH), 137.99 (2 C, $^{9}C_q$), 148.97 (2 C, ^{5}CH), 151.93 (1 C, $^{7}C_q$), 153.88 and 155.15 (1 C, $^{3}C_q$)

Synthesis of catalyst 6[32]

Step 1:

Sodium azide (0.96 g, 14.6 mmol) was added to a solution of bromoethylamine hydrobromide (1.00 g, 4.88 mmol) in bidistilled water (5 mL) at room temperature. The mixture was then stirred at 80 °C over night and a red solution was formed. After cooling to room temperature the mixture was neutralized with potassium hydroxide (1.60 g, 28.5 mmol) and extracted with diethyl ether (3x50 mL). The organic extracts were dried over anhydrous sodium sulfate. The diethyl ether was removed under a flow of nitrogen. Then anhydrous THF (25 mL) and 3,5-bis(trifluromethyl)phenyl isothiocyanate were added to the flask. The mixture was stirred under argon atmosphere at room temperature for 3 h. THF was removed *in vacuo* and a further purification followed by flash chromatography over silica gel using ethyl acetate/*n*-hexane (3:7, R_f = 0.40) to afford a colorless solid (1.00 g, 2.81 mmol, yield: 57 %).



^{1}H-NMR (500 MHz, $CDCl_3$)

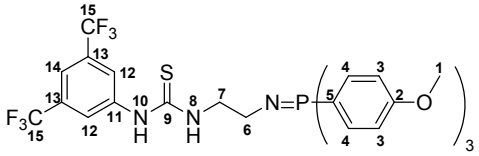
δ (ppm)= 3.67 (m, 2 H, $^{1}CH_2$), 3.83 (m, 2 H, $^{2}CH_2$), 6.44 (b, 1 H, ^{3}NH), 7.75 (s, 1 H, ^{9}CH), 7.80 (s, 2 H, ^{7}CH), 8.31 (b, 1 H, ^{5}NH)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 44.36 (1 C, $^{2}CH_2$), 50.28 (1 C, $^{1}CH_2$), 122.70 (q, 2 C, J_{CF} = 273 Hz, $^{10}CF_3$), 120.01 (1 C, ^{9}CH), 124.21 (2 C, ^{7}CH), 133.26 (t, 2 C, J_{CF} = 34 Hz, $^{8}C_q$), 138.43 (1 C, $^{6}C_q$), 181.14 (1 C, $^{4}C_q$)

Step 2:

The 1-(2-azidoethyl)-3-(3,5-bis(trifluoromethyl)phenyl)thiourea from step 1 (1.00 g, 2.81 mmol) and tris(4-methoxy)phenyl phosphine (0.99 g, 2.81 mmol) were dissolved in anhydrous diethyl ether (9 mL) in a round-bottom flask. The mixture was stirred at room temperature under argon atmosphere over night. The precipitated solid was filtrated, washed with *n*-pentane (30 mL) and dried under vacuum at room temperature to give a colorless solid (1.57 g, 2.30 mmol, yield: 82 %, mp. = 109 - 111°C).



^{1}H-NMR (500 MHz, $CDCl_3$)

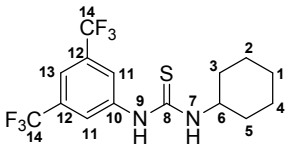
δ (ppm)= 3.08 (m, 2 H, $^{6}CH_2$), 3.63 (b, 2 H, $^{7}CH_2$), 3.83 (s, 9 H, $^{1}CH_3$), 6.96 (m, 6 H, ^{3}CH), 7.27 (s, 1 H, ^{14}CH), 7.46 (m, 6 H, ^{4}CH), 7.54 (s, 2 H, ^{12}CH)

^{13}C-NMR (125 MHz, $CDCl_3$)

δ (ppm) = 46.70 (d, 1 C, J_{CP}=14.6 Hz, $^{6}CH_2$), 47.00 (1 C, $^{7}CH_2$), 55.48(1 C, $^{1}CH_3$), 115.13 (d, 1 C, J_{cp}=85.9 Hz, ^{5}CH), 115.00 (d, 2 C, J_{CP}=13.6 Hz, ^{4}CH), 116.33, (1 C, ^{14}CH), 123.64 (q, 2 C, J_{CF}=272.7 Hz, $^{15}CF_3$), 124.20 (2 C, ^{12}CH), 130.54 (q, 2 C, J_{CF}=32.7 Hz, $^{13}C_q$), 134.69 (d, 2 C, J_{CP}=11.5 Hz, ^{3}CH), 149.09 (1 C, $^{11}C_q$), 163.65 (d, 1 C, J_{cp}=2.8 Hz, $^{2}C_q$)

Synthesis of catalyst 7[34]

Cyclohexaneamine (0.42 mL, 3.70 mmol) was added to a solution of 3,5-bis(trifluromethyl)phenyl isothiocyanate (0.68 mL, 3.70 mmol) in THF (4 mL). The mixture was then stirred at 30 °C for 2 h. THF was removed *in vacuo* and an off-white solid was obtained. The solid was washed with *n*-pentane (4x10 mL) to obtain a white solid (1.34 g, 3.62 mmol, yield: 98%, mp. = 167 - 168 °C).



^{1}H-NMR (500 MHz, DMSO-d6)

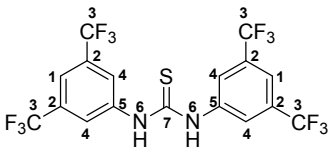
δ (ppm)= 1.20-1.94 (m, 10 H, $^{1\text{-}5}CH_2$), 4.12 (b, 1 H, ^{6}CH), 7.70 (s, 1 H, ^{13}CH), 8.13 (b, 1 H, ^{7}NH), 8.25 (b, 2 H, ^{11}CH), 9.84 (b, 1 H, ^{9}NH)

^{13}C-NMR (125 MHz, DMSO-d6)

δ (ppm) = 24.88 (2 C, $^{2,4}CH_2$), 25.55 (1 C, $^{1}CH_2$), 32.06 (2 C, $^{3,5}CH_2$), 52.75 (1 C, ^{6}CH), 116.30 (1 C, ^{13}CH), 122.21 (2 C, ^{11}CH), 123.73 (q, 2 C, J_{CF}=272.8 Hz, $^{14}CF_3$), 130.56 (q, 2 C, J_{CF}=32.4 Hz, $^{12}C_q$), 142.51 (1 C, $^{10}C_q$), 179.68 (1 C, $^{8}C_q$)

Synthesis of catalyst 8[34]

3,5-Bis(trifluromethyl)phenyl isothiocyanate (0.5 mL, 2.70 mmol) was added to a solution of 3,5-bis(trifluromethyl)aniline (0.4 mL, 2.67 mmol) in THF (5 mL) in a 25 mL round-bottom flask. The mixture was then stirred at 50 °C for 4 d. THF was removed *in vacuo* and yellow oil was obtained. After the purification by flash chromatography over silica gel using ethyl acetate/*n*-hexane (2 : 8, R_f = 0.41) a white solid was obtained (0.92 g, 1.81 mmol, yield: 70 %, mp. = 162 - 163 °C).

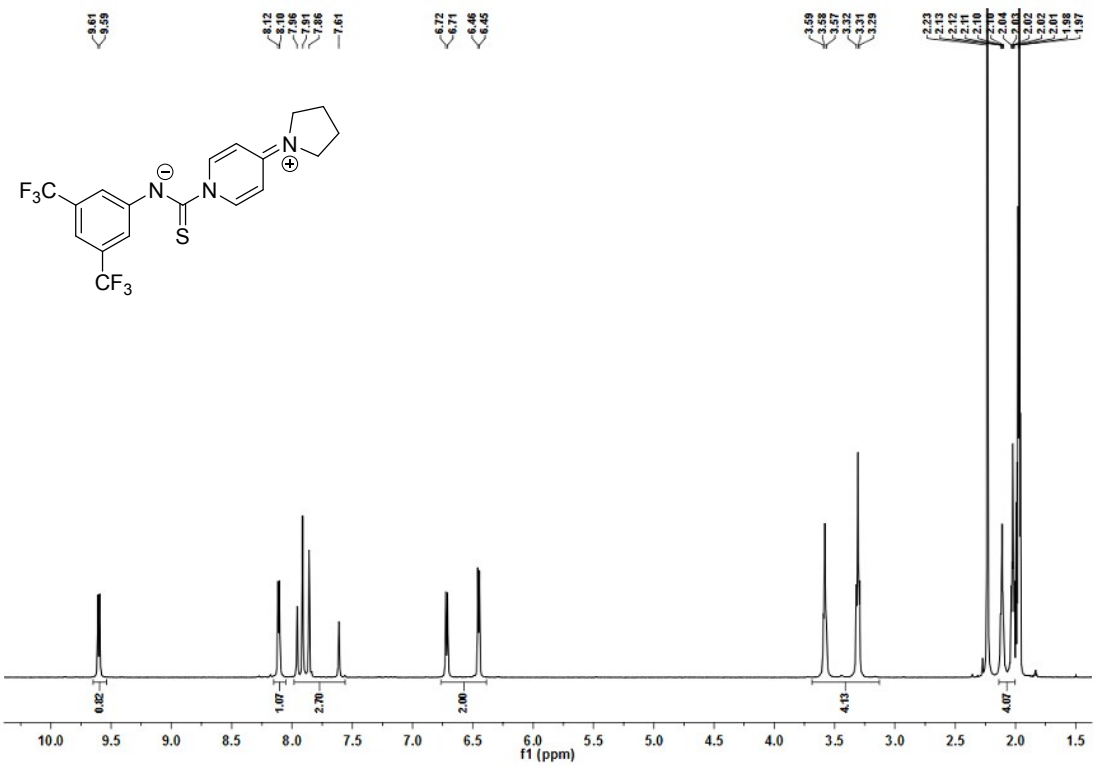


^{1}H-NMR (500 MHz, DMSO-d6)

δ (ppm) = 7.84 (s, 2 H, ^{6}NH), 8.23 (s, 4 H, ^{2}CH), 10.63 (s, 2 H, ^{1}CH)

^{13}C-NMR (125 MHz, DMSO-d6)

δ (ppm) = 122.93 (4 C, ^{1}CH), 128.38 (q, 4 C, J_{CF}=272.7 Hz, $^{3}CF_3$), 129.30 (4 C, ^{4}CH),135.58 (q, 4 C, J_{CF}=33.0 Hz, $^{2}C_q$), 146.40 (2 C, $^{5}C_q$), 185.84 (1 C, $^{7}C_q$)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3.58
3.57
3.32
3.31
3.29
2.23
2.13
2.12
2.11
2.10
2.04
2.02
2.02
2.01
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1.97
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CF3
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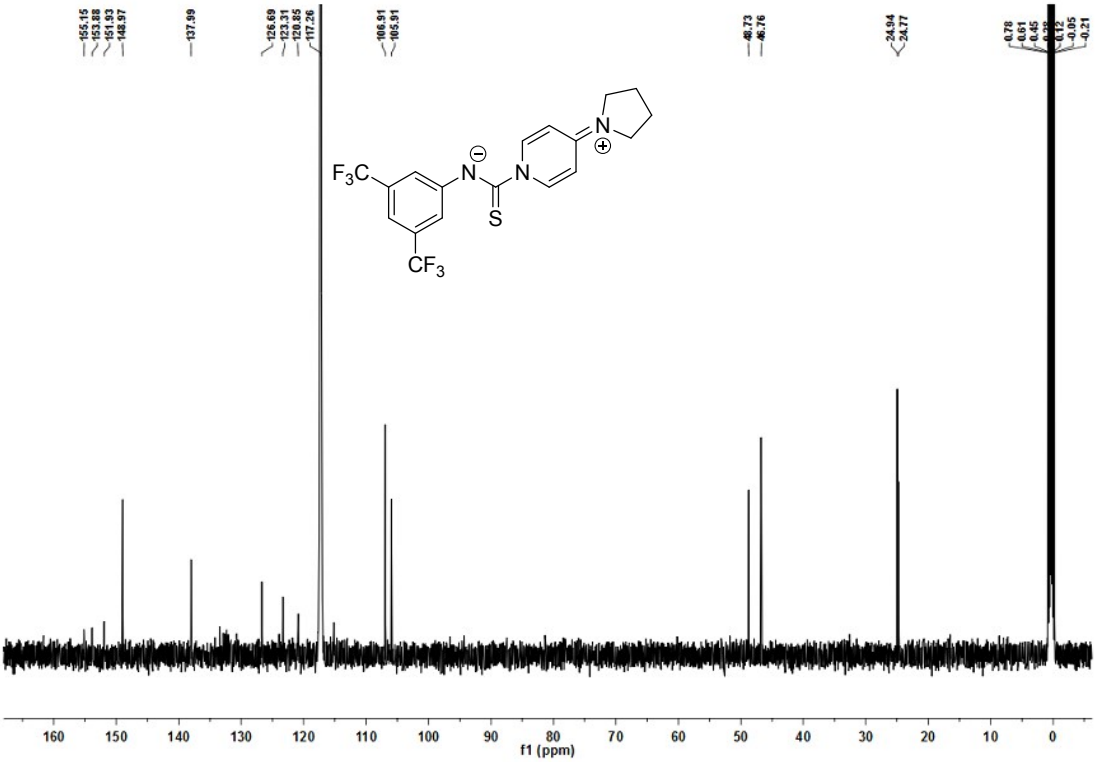
f1 (ppm)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46.76
24.94
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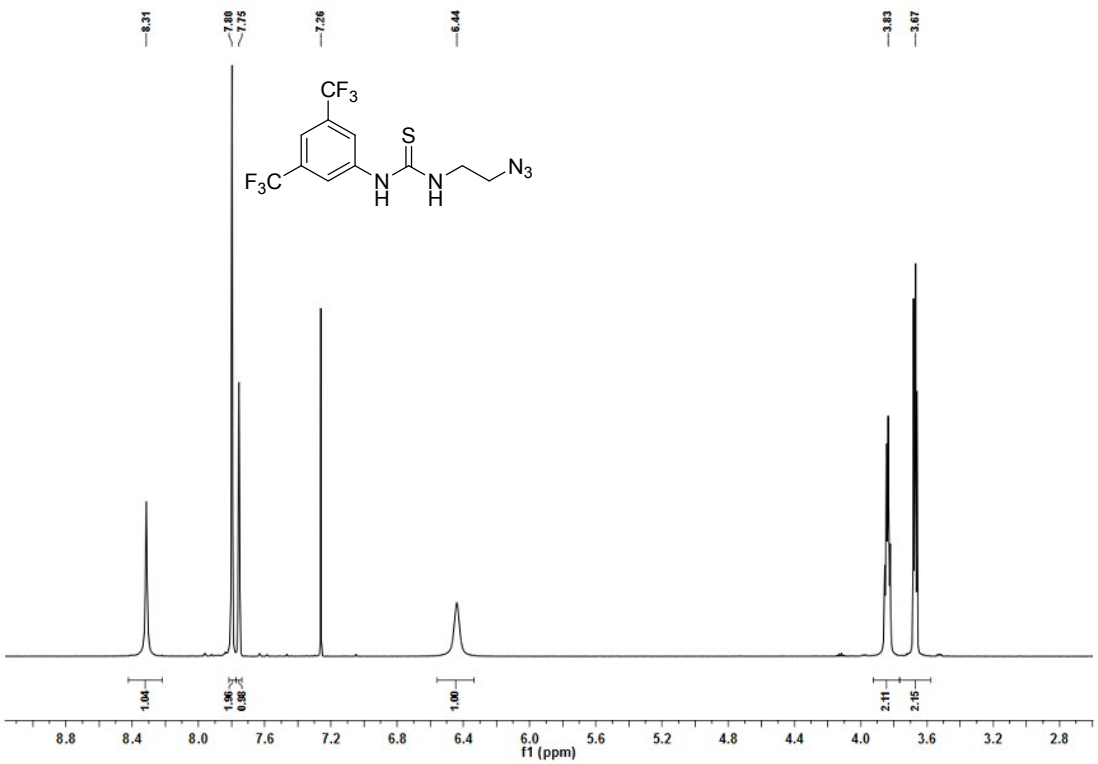
F3C
CF3
N
S
f1 (ppm)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1.00
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2.15
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8.0
7.6
7.2
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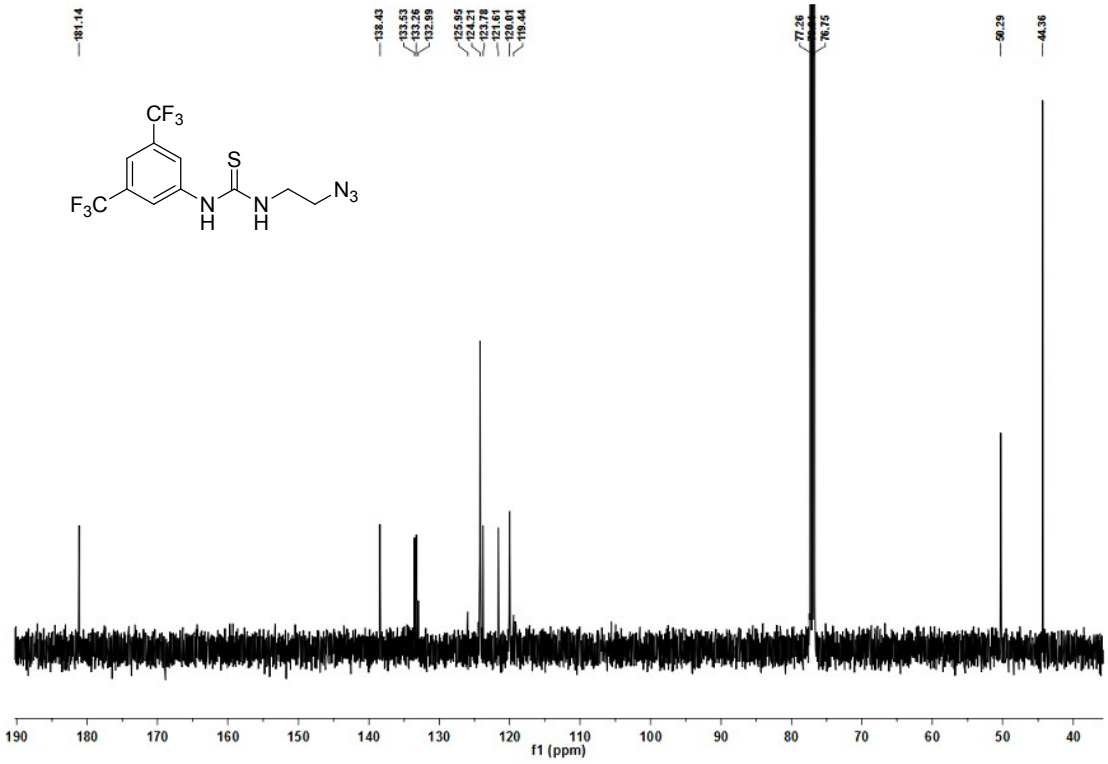
f1 (ppm)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80
70
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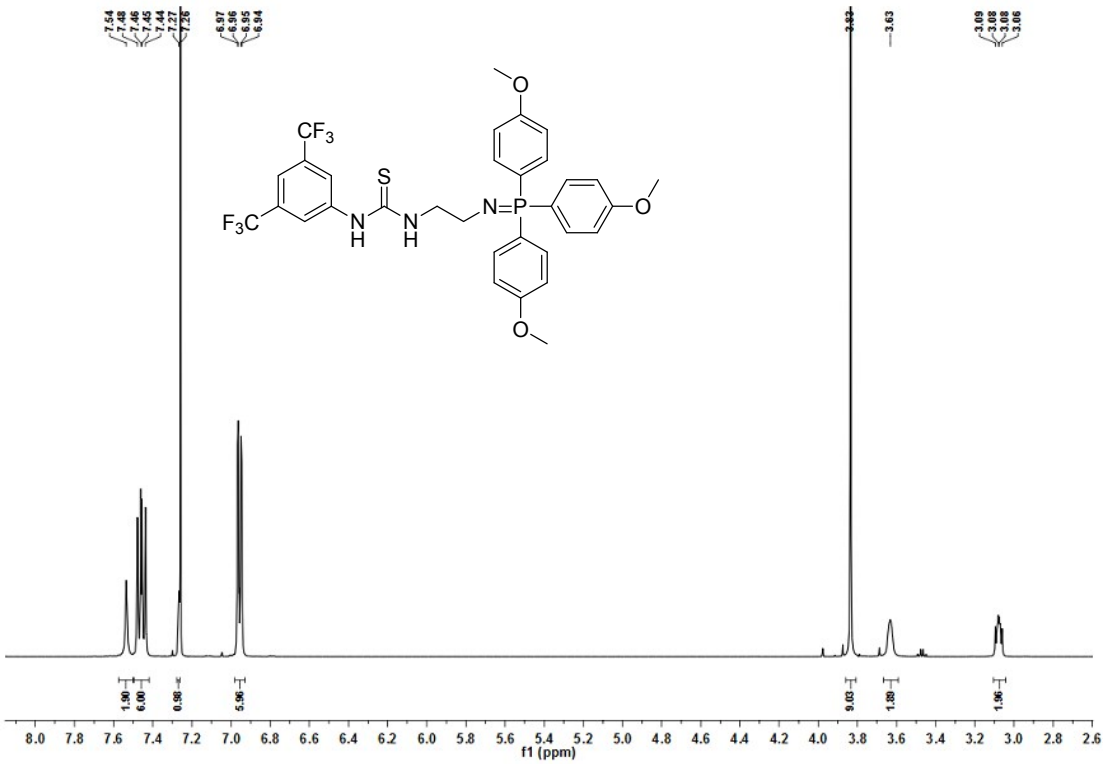
50
40
f1 (ppm)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3.08
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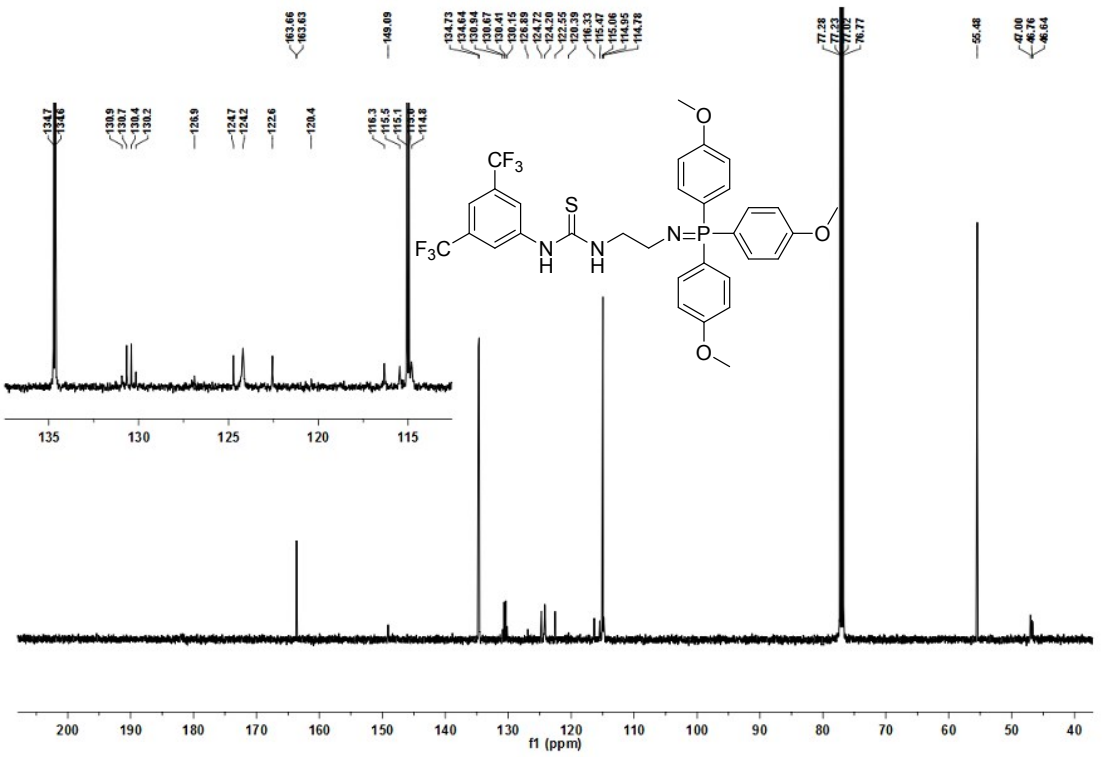
f1 (ppm)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114.95
114.78
77.28
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77.02
76.77
55.48
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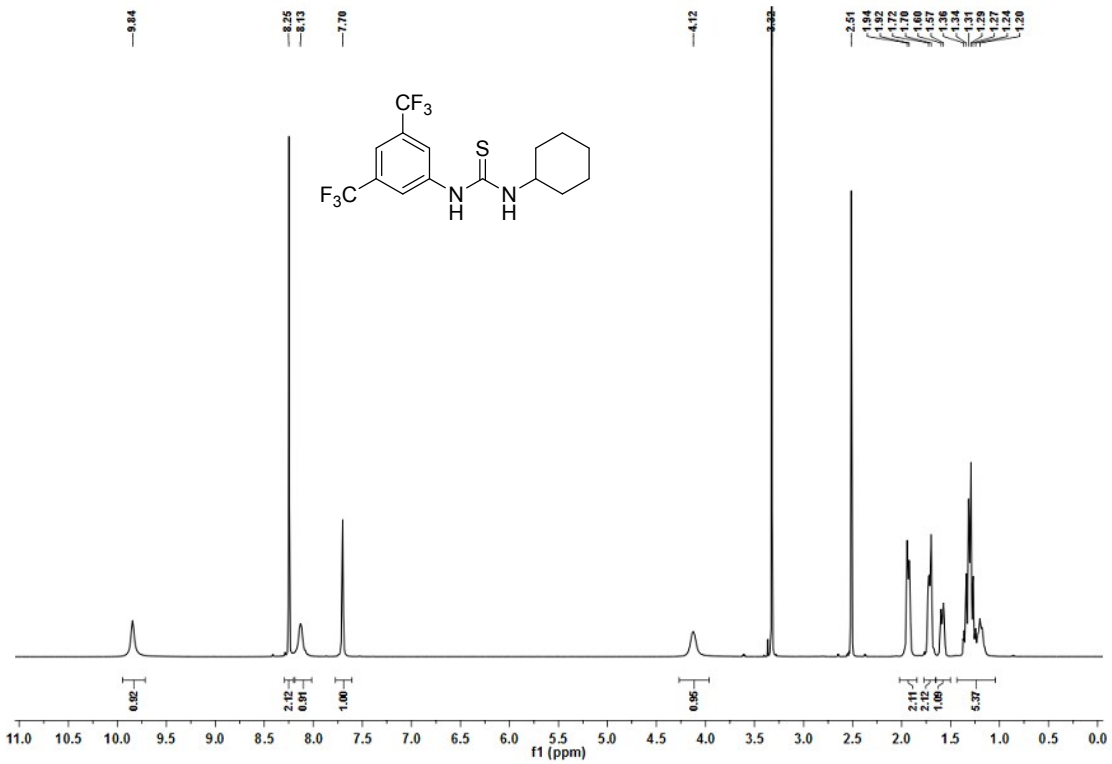
O
f1 (ppm)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1.31
1.29
1.27
1.24
1.20
CF3
F3C
S
N
H
N
H
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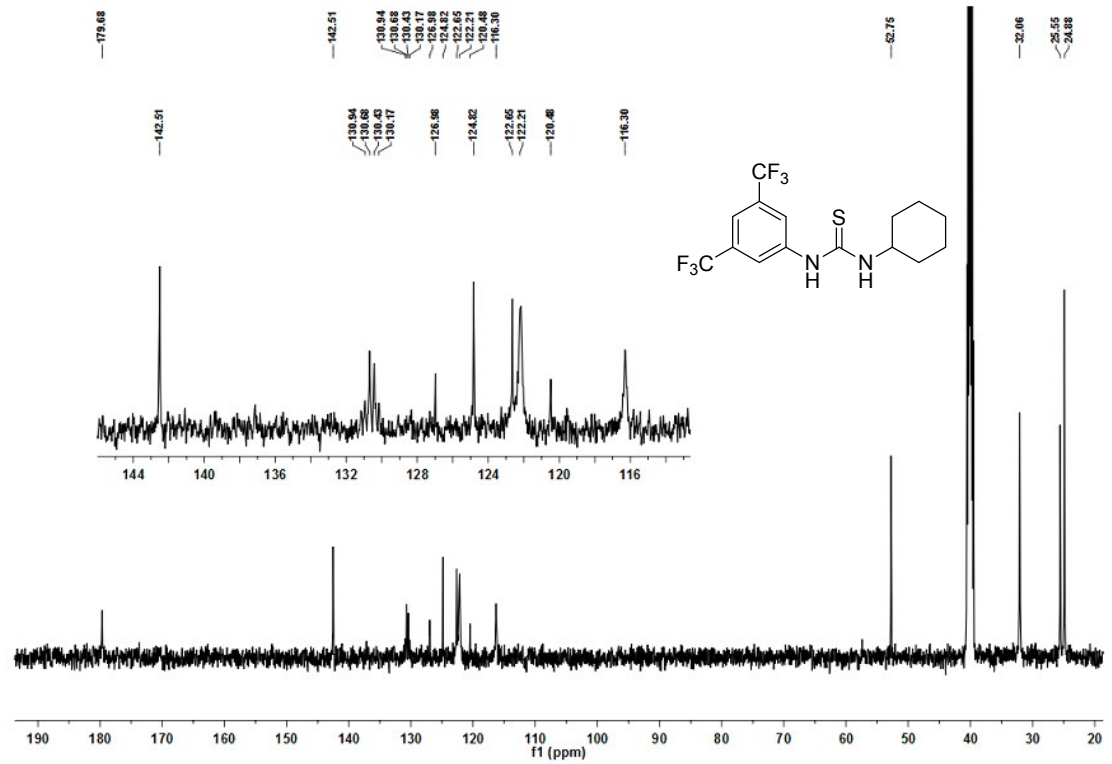
0.91
1.00
0.95
2.11
2.12
1.09
5.37
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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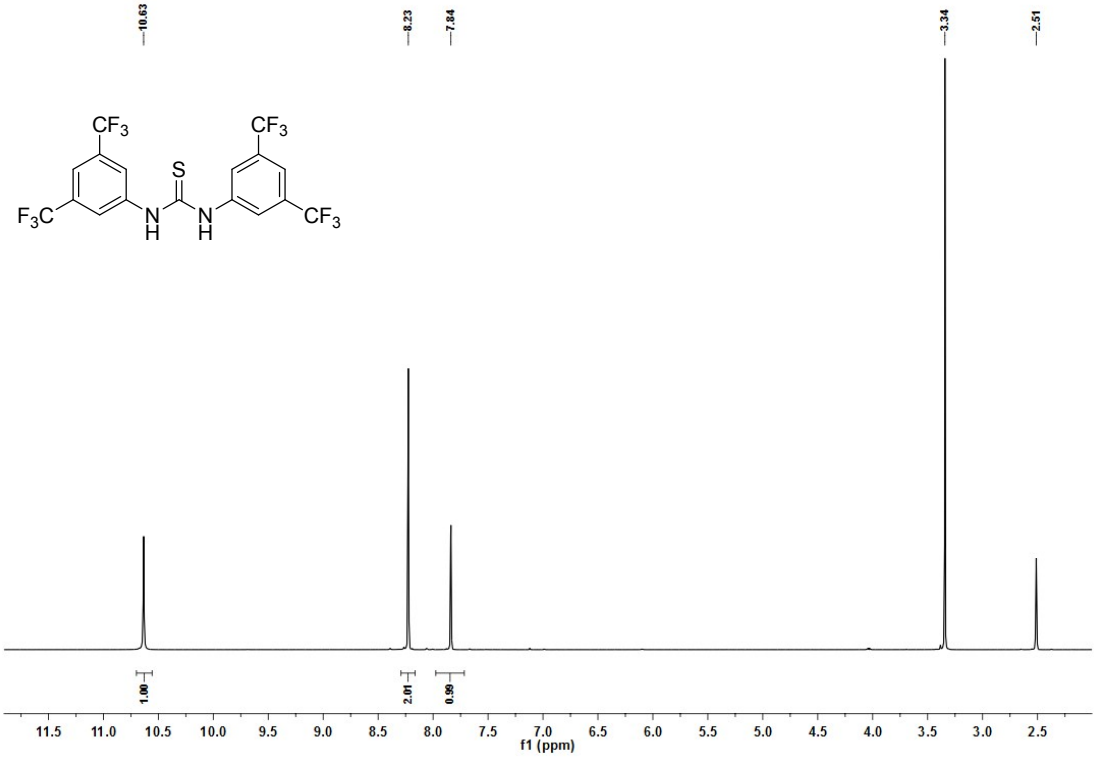
f1 (ppm)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CF3
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H
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0.99
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11.0
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10.0
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9.0
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8.0
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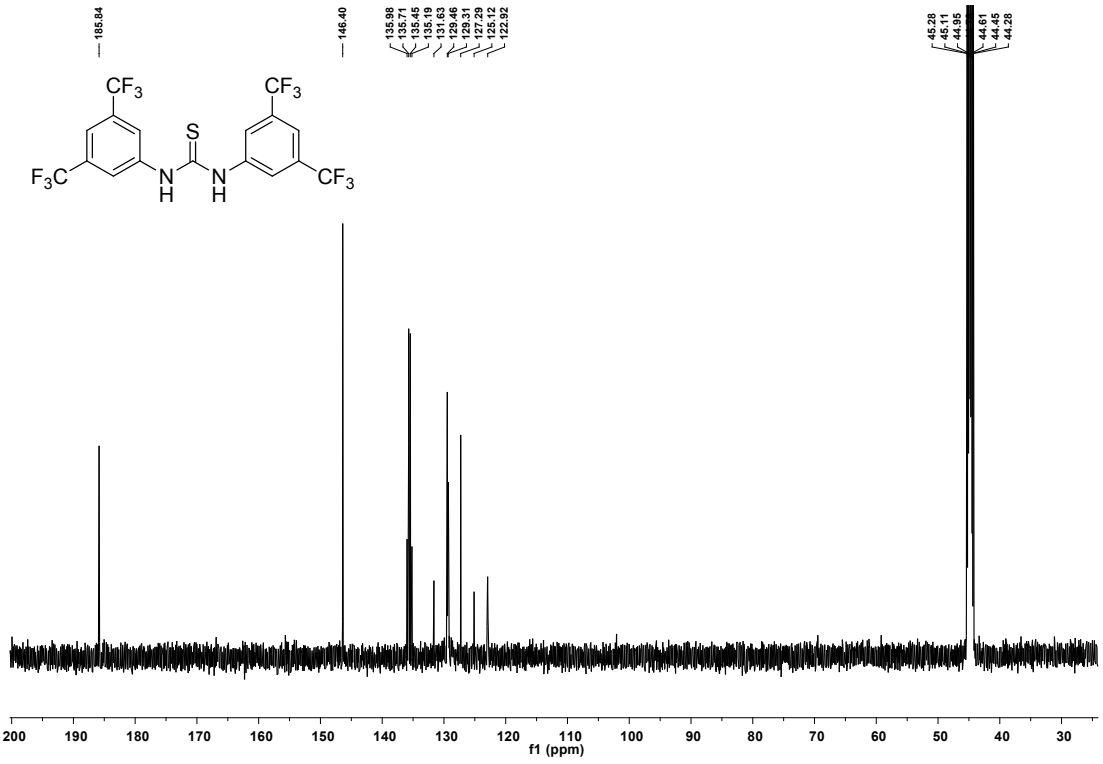
2.5
f1 (ppm)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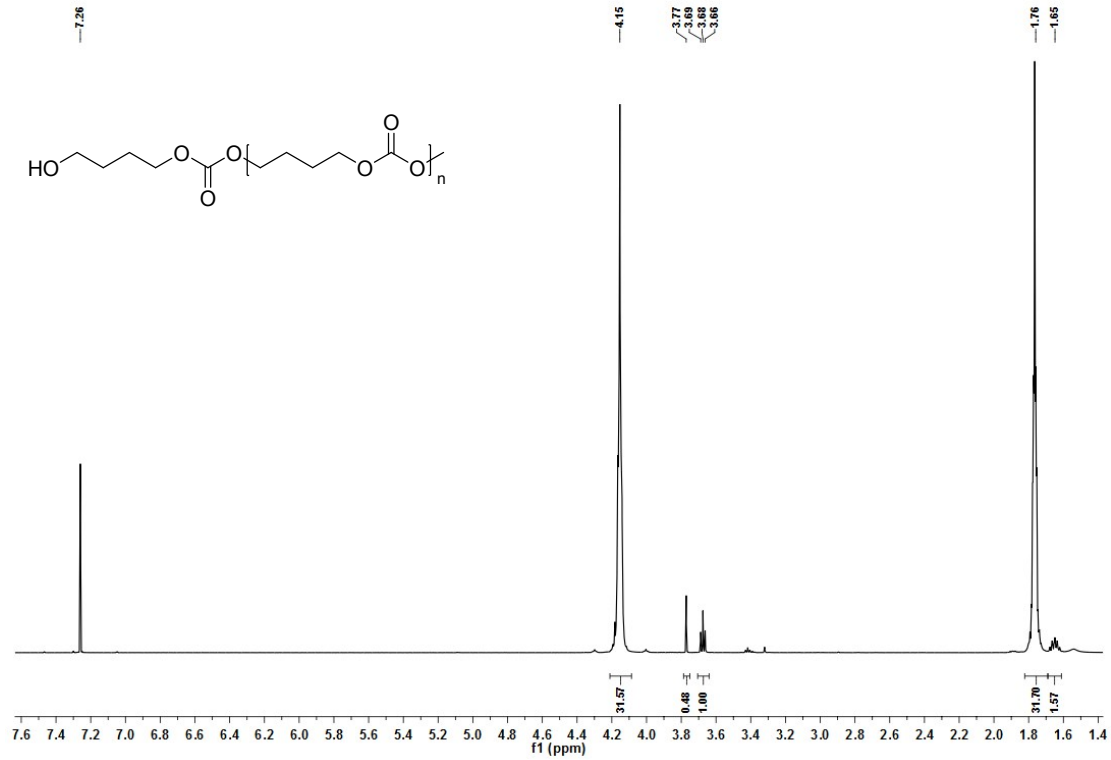
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1.57
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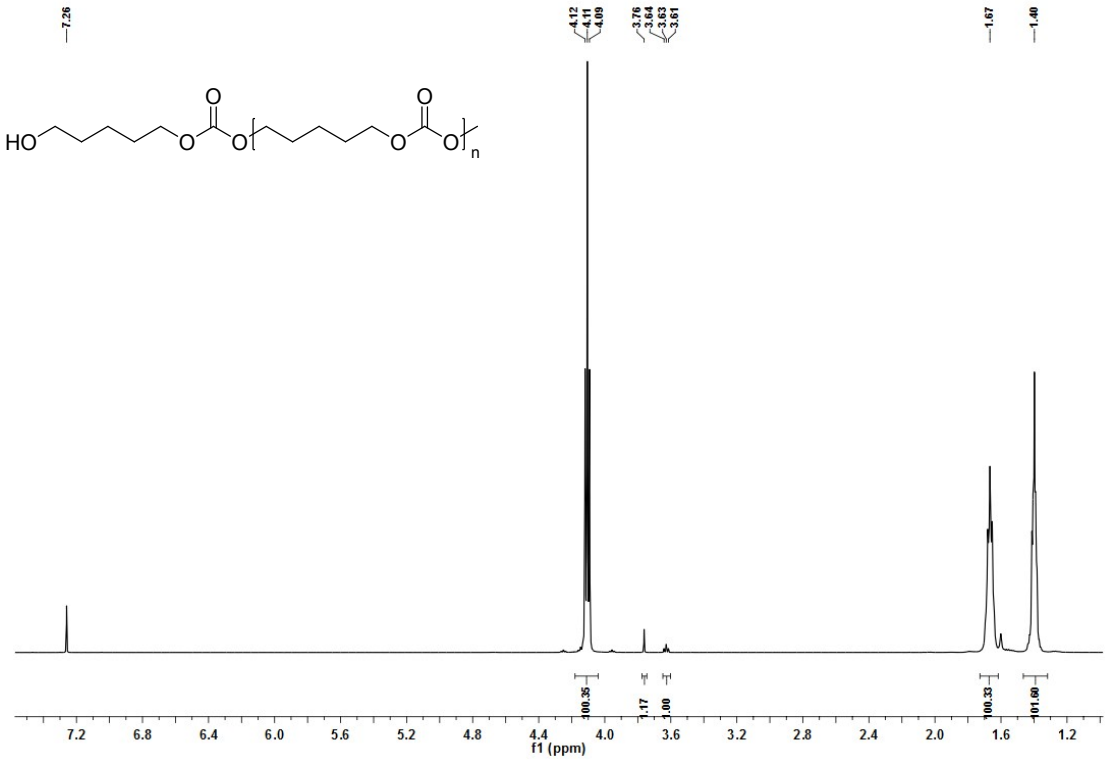
f1 (ppm)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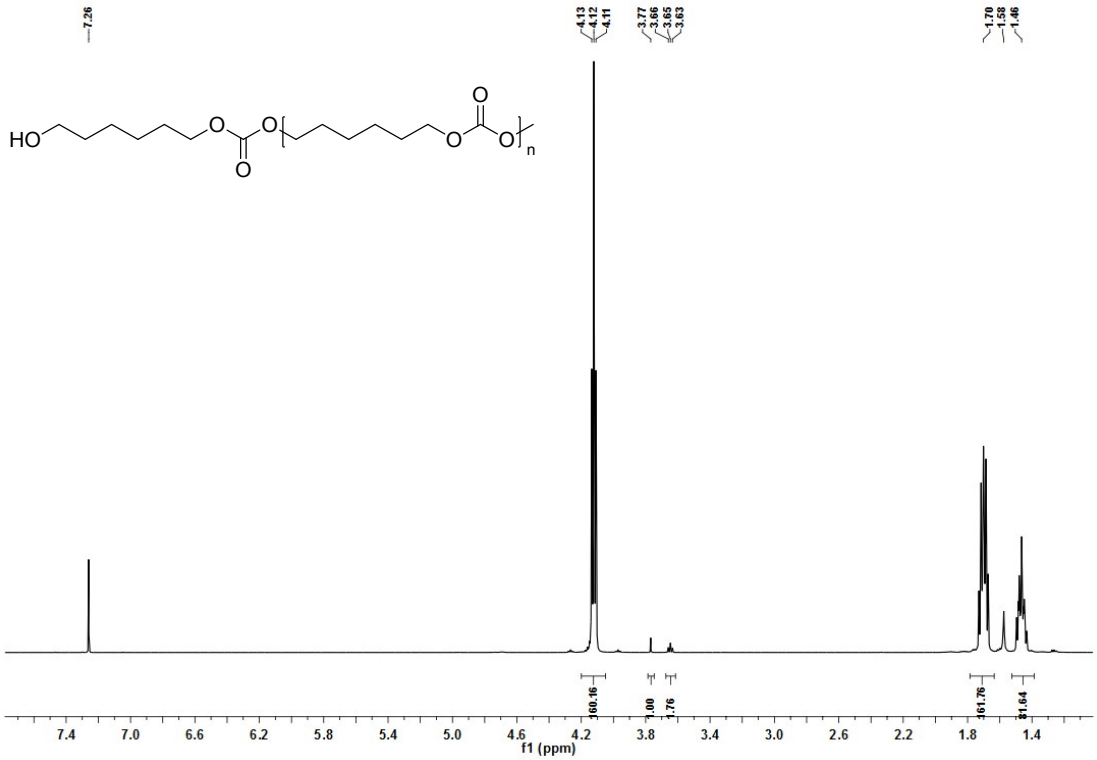
f1 (ppm)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3.8
3.4
3.0
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1.8
1.4
f1 (ppm)