Syntheses and NMR-Spectra of NKR Substrates 2a-h and Product 3a

2-Nitrophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2a

Procedure:[1] 2-Nitrophenol (10.4 g, 75.0 mmol, 1 eq) and DABCO (10.5 g, 93.8 mmol, 1.25 eq) were dissolved in NMP (52 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (9.73 g, 78.8 mmol, 1.05 eq) in NMP (12 mL) was added dropwise within 7 min. The color of the reaction mixture changed from dark yellow to dark orange. The reaction was monitored by TLC (cyclohexane/EtOAc, 4:1, $R_f = 0.2$) and completed after 3.8 h at 50 °C. During the addition of water (120 mL) over a period of 20 min a yellow precipitate was formed. The reaction mixture was smoothly cooled down to rt. The precipitate was filtrated, washed with water (3 × 20 mL), and dried in high vacuum.

Yield: 15.6 g (69.0 mmol, 92%; Lit.:[1] 92%). Off-white solid.

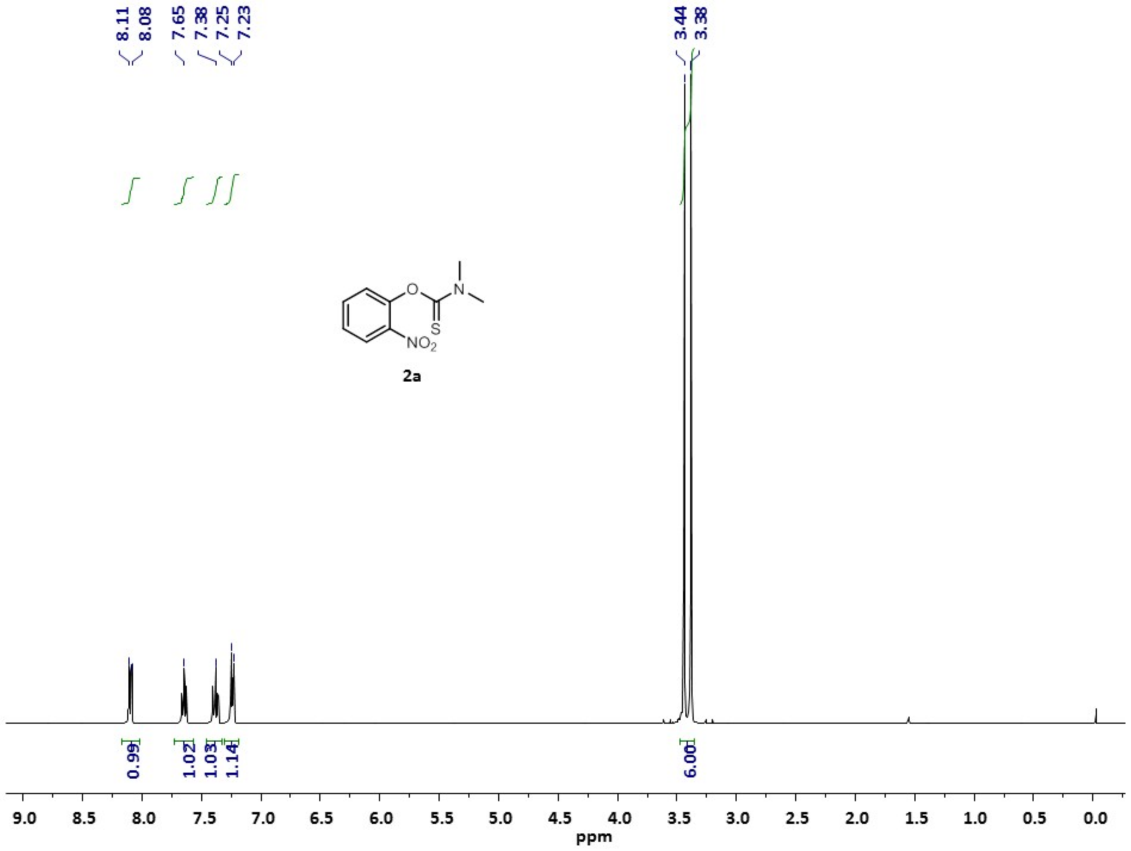
Mp: 125 °C. Lit.:[1] 120-121 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1603 (w, aryl, $\nu_{C=C}$), 1589 (w, aryl, $\nu_{C=C}$), 1547 (w, thiocarbamate, $\nu_{C=S}$), 1518 (m, aryl, $\nu_{C=C}$), 1475 (m, aryl, $\nu_{C=C}$), 1342 (m, NO_2, $\nu_{N=O}$), 1209 (m, ArC-O, ν_{C-O}), 1144 (m, C=S, $\nu_{C=S}$), 1111 (s, C=S, $\nu_{C=S}$), 1050 (m, C=S, $\nu_{C=S}$), 751 (s, aryl, ν_{C-H}); further absorption bands: 1391 (w), 1283 (m), 959 (w), 862 (w), 824 (w), 783 (s), 697 (s), 676 (m), 469 (w), 452 (w).

^1H-NMR (400.13 MHz, $CDCl_3$, 298 K):[1] δ_H (ppm) = 3.38 (3 H, s, NC*H*$_3$), 3.44 (3 H, s, NC*H*$_3$), 7.24 (1 H, dd, *J* = 8.1, 3.1 Hz, Ar*H*), 7.38 (1 H, td, *J* = 8.0, 1.3 Hz, Ar*H*), 7.65 (1 H, td, *J* = 7.8, 1.7 Hz, Ar*H*), 8.10 (1 H, dd, *J* = 8.2, 1.6 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, $CDCl_3$, 298 K):[1] δ_C (ppm) = 39.30 (1 C, N*C*H$_3$), 43.71 (1 C, N*C*H$_3$), 125.89 (1 C, Ar*C*), 126.71 (1 C, Ar*C*), 126.76 (1 C, Ar*C*), 134.64 (1 C, Ar*C*), 142.19 (1 C, Ar*C*), 147.40 (1 C, Ar*C*), 186.09 (1 C, *C*S).

MS (EI): calc. for $C_9H_{10}N_2O_3S$: 226.04, found: m/z = 72 [$O=C=NMe_2^+$], 88 [$S=C=NMe_2^+$], 181 [$PhO(CS)NMe_2^{\cdot} + H^+$], 227 [$M + H^+$].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7.65
7.38
7.25
7.23
3.44
3.38
0.99
1.02
1.03
1.14
6.00
2a
NO2
O
N
S
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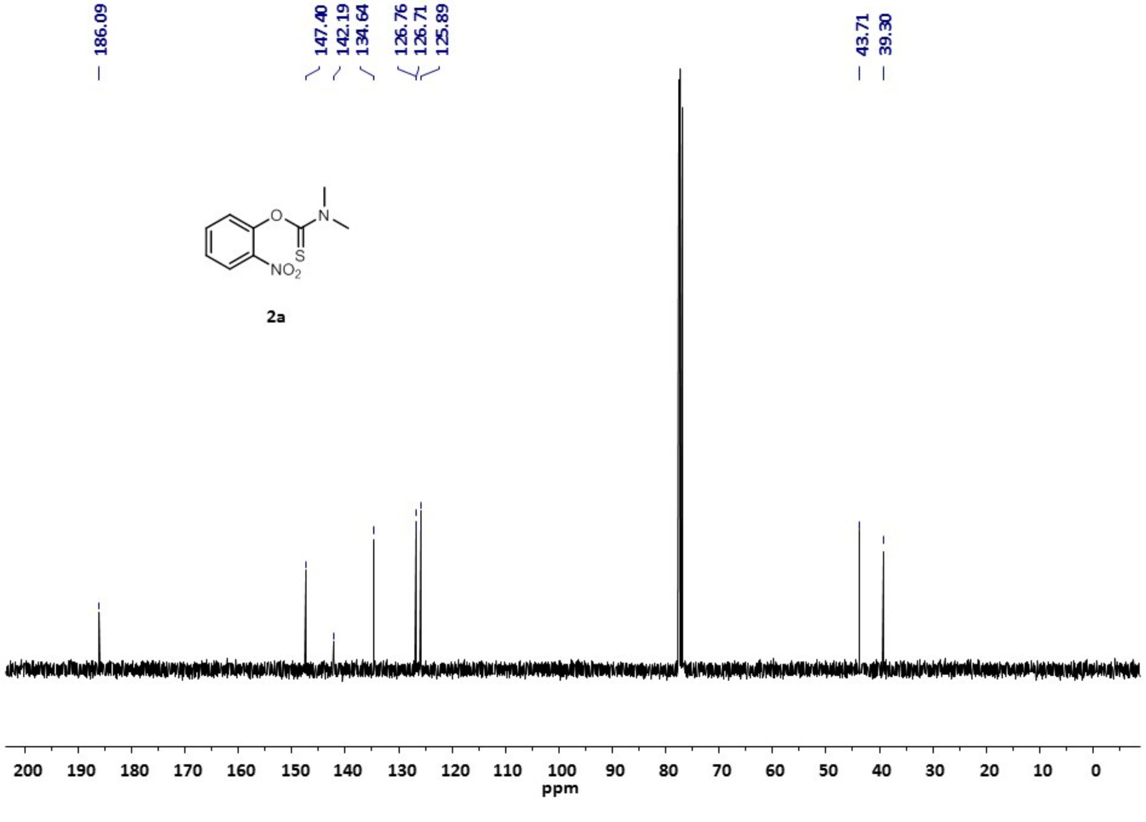
ppm


186.09
147.40
142.19
134.64
126.76
126.71
125.89
43.71
39.30
2a
NO2
O
N
S
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

4-Nitrophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2b

Procedure:[1] 4-Nitrophenol (5.00 g, 35.9 mmol, 1 eq) and DABCO (5.04 g, 44.9 mmol, 1.25 eq) were dissolved in NMP (26 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (4.66 g, 37.7 mmol, 1.05 eq) in NMP (7 mL) was added dropwise within 12 min. The color of the reaction mixture changed from pale to turbid yellow. The reaction was monitored by TLC (cyclohexane/EtOAc, 4:1) and completed after 2.5 h at 50 °C. During the addition of water (60 mL) over a period of 20 min a bright yellow precipitate was formed. The reaction mixture was smoothly cooled down to rt. The precipitate was filtrated, washed with water (3 × 20 mL), and dried in high vacuum at 50 °C.

Yield: 7.38 g (32.6 mmol, 91%; Lit.:[1] 79%). Pale yellow solid.

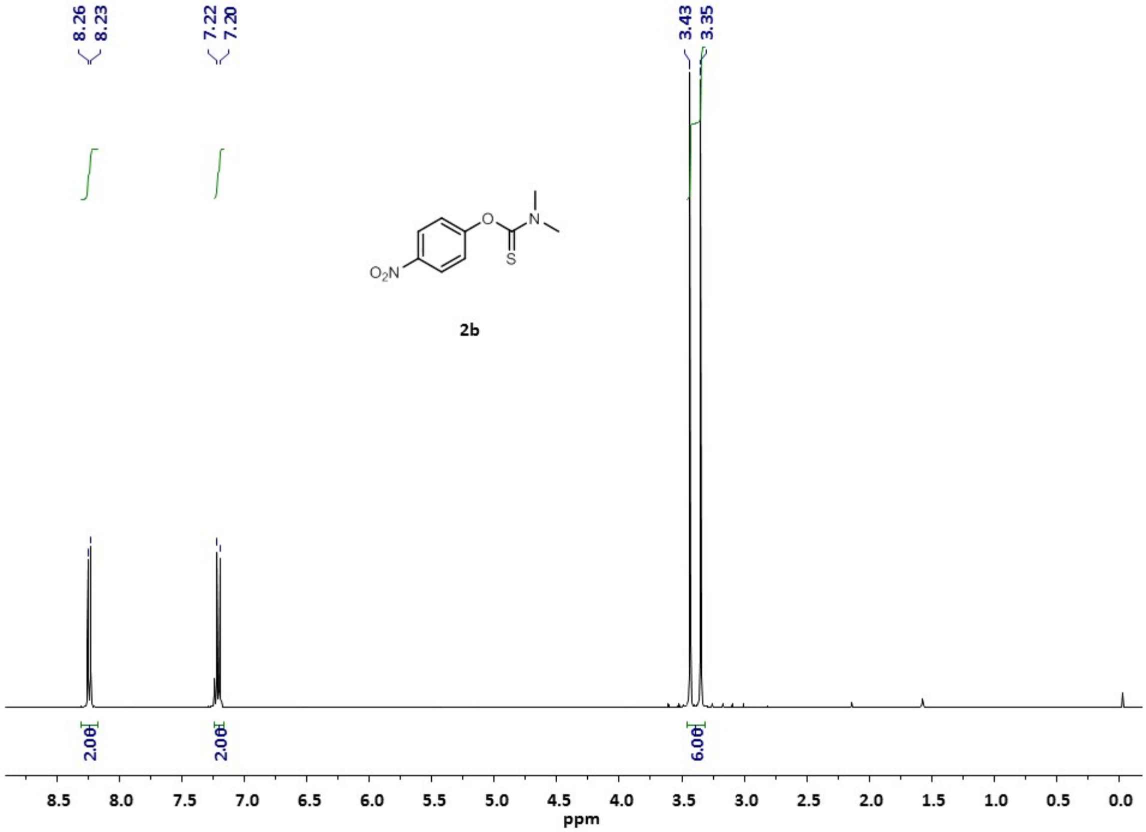
Mp: 148 °C. Lit.:[2] 150-153 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1612 (w, aryl, $\nu_{C=C}$), 1585 (w, aryl, $\nu_{C=C}$), 1539 (m, C=S, $\nu_{C=S}$), 1513 (s, aryl, $\nu_{C=C}$), 1478 (w, aryl, $\nu_{C=C}$), 1338 (s, NO_2, $\nu_{N=O}$), 1211 (s, ArC-O, ν_{C-O}), 1153 (m, C=S, $\nu_{C=S}$), 1125 (s, C=S, $\nu_{C=S}$), 1092 (s, C=S, $\nu_{C=S}$), 1058 (w, C=S, $\nu_{C=S}$), 894 (m, aryl, ν_{C-H}), 819 (m, aryl, ν_{C-H}); further absorption bands: 1413 (w), 1391 (m), 1284 (m), 1002 (m), 957 (w), 854 (s), 754 (m), 688 (s), 621 (w), 524 (w), 473 (m), 421 (w).

^{1}H-NMR (400.13 MHz, $CDCl_3$, 298 K):[1] δ_H (ppm) = 3.35 (3 H, s, NC*H*$_3$), 3.43 (3 H, s, NC*H*$_3$), 7.21 (2 H, d, *J* = 9.1 Hz, Ar*H*), 8.25 (2 H, d, *J* = 9.1 Hz, Ar*H*).

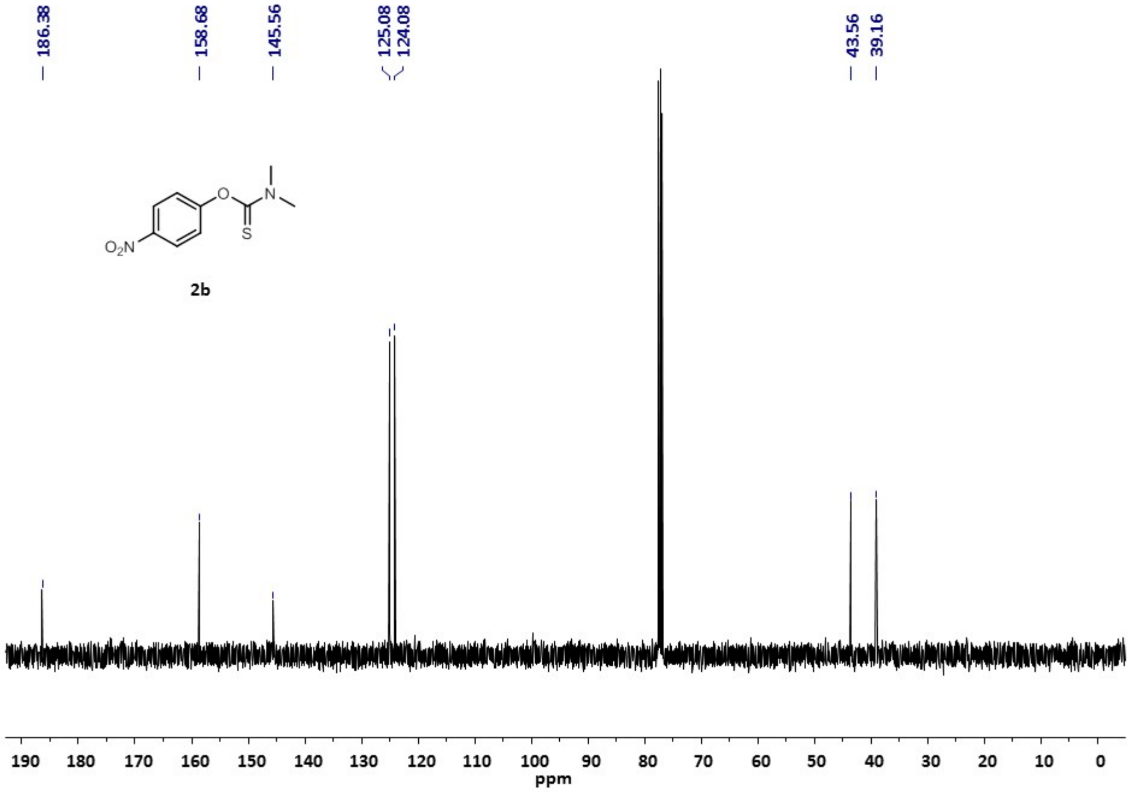
^{13}C-NMR (100.62 MHz, $CDCl_3$, 298 K):[1] δ_C (ppm) = 39.16 (1 C, N*C*H$_3$), 43.56 (1 C, N*C*H$_3$), 124.08 (2 C, Ar*C*), 125.08 (2 C, Ar*C*), 145.56 (1 C, Ar*C*), 158.68 (1 C, Ar*C*), 186.38 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_9H_{10}N_2O_3S$: 226.04, found: m/z = 72 [O=C=NMe$_2^+$], 88 [S=C=NMe$_2^+$], 227 [M + H$^+$].



2b

8.26
8.23
7.22
7.20
3.43
3.35
2.00
2.00
6.00
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
ppm
O
N
S
O2N



2b

186.38
158.68
145.56
125.08
124.08
43.56
39.16
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm
O
N
S
O2N

3-Nitrophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2c

Procedure:[1] 3-Nitrophenol (5.00 g, 35.9 mmol, 1 eq) and DABCO (5.04 g, 44.9 mmol, 1.25 eq) were dissolved in NMP (25 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (4.75 g, 38.4 mmol, 1.07 eq) in NMP (8 mL) was added dropwise within 5 min. The color of the reaction mixture changed from dark red to dark orange. The reaction was monitored by TLC (cyclohexane/EtOAc, 4:1) and completed after 5.8 h at 50 °C. During the addition of water (60 mL) over a period of 9 min a beige precipitate was formed. The reaction mixture was smoothly cooled down to rt. The precipitate was filtrated, washed with water (3 × 20 mL), and dried in high vacuum at 50 °C.

Yield: 7.55 g (33.4 mmol, 93%; Lit.:[1] 93%). Beige crystalline solid.

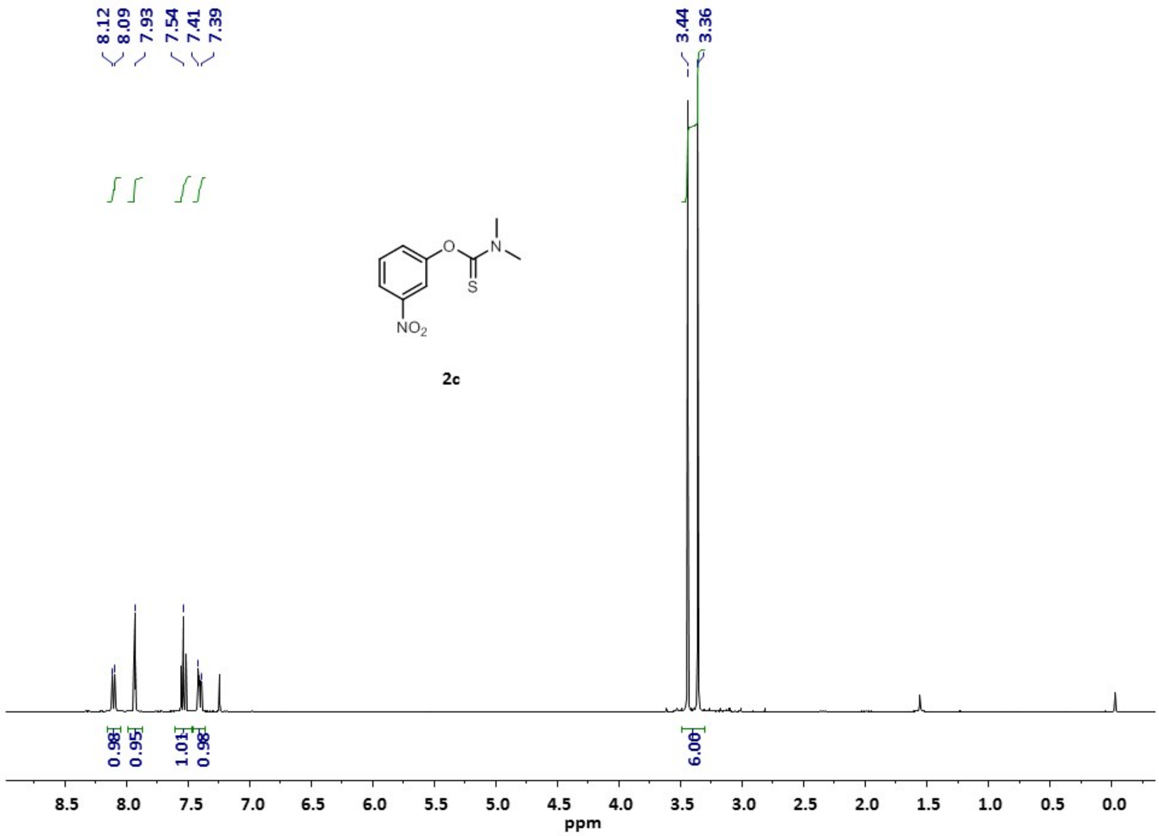
Mp: 149 °C. Lit.:[2] 153-155 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1550 (w, thiocarbamate, $\nu_{C=S}$), 1519 (s, aryl, $\nu_{C=C}$), 1470 (w, aryl, $\nu_{C=C}$), 1343 (s, NO_2, $\nu_{N=O}$), 1211 (s, ArC-O, ν_{C-O}), 1162 (w, C=S, $\nu_{C=S}$), 1121 (s, C=S, $\nu_{C=S}$), 1076 (m, C=S, $\nu_{C=S}$), 894 (m, aryl, ν_{C-H}), 807 (m, aryl, ν_{C-H}); further absorption bands: 1412 (w), 1391 (w), 1284 (m), 999 (w), 904 (w), 742 (m), 702 (m), 679 (m), 525 (w), 481 (w), 448 (w), 413 (w).

^{1}H-NMR (400.13 MHz, $CDCl_3$, 298 K):[1] δ_H (ppm) = 3.36 (3 H, s, NC*H*$_3$), 3.44 (3 H, s, NC*H*$_3$), 7.40 (1 H, d, *J* = 8.1 Hz, Ar*H*), 7.54 (1 H, t, *J* = 8.2 Hz, Ar*H*), 7.93 (1 H, t, *J* = 2.3 Hz, Ar*H*), 8.10 (1 H, d, *J* = 8.2 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, $CDCl_3$, 298 K):[1] δ_C (ppm) = 39.11 (1 C, N*C*H$_3$), 43.65 (1 C, N*C*H$_3$), 118.87 (1 C, Ar*C*), 121.05 (1 C, Ar*C*), 129.76 (2 C, Ar*C*), 148.78 (1 C, Ar*C*), 154.32 (1 C, Ar*C*), 186.88 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_9H_{10}N_2O_3S$: 226.04, found: m/z = 72 [$O=C=NMe_2^+$], 88 [$S=C=NMe_2^+$], 227 [$M + H^+$].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7.54
7.41
7.39
3.44
3.36
0.98
0.95
1.01
0.98
6.00
O
N
S
NO2
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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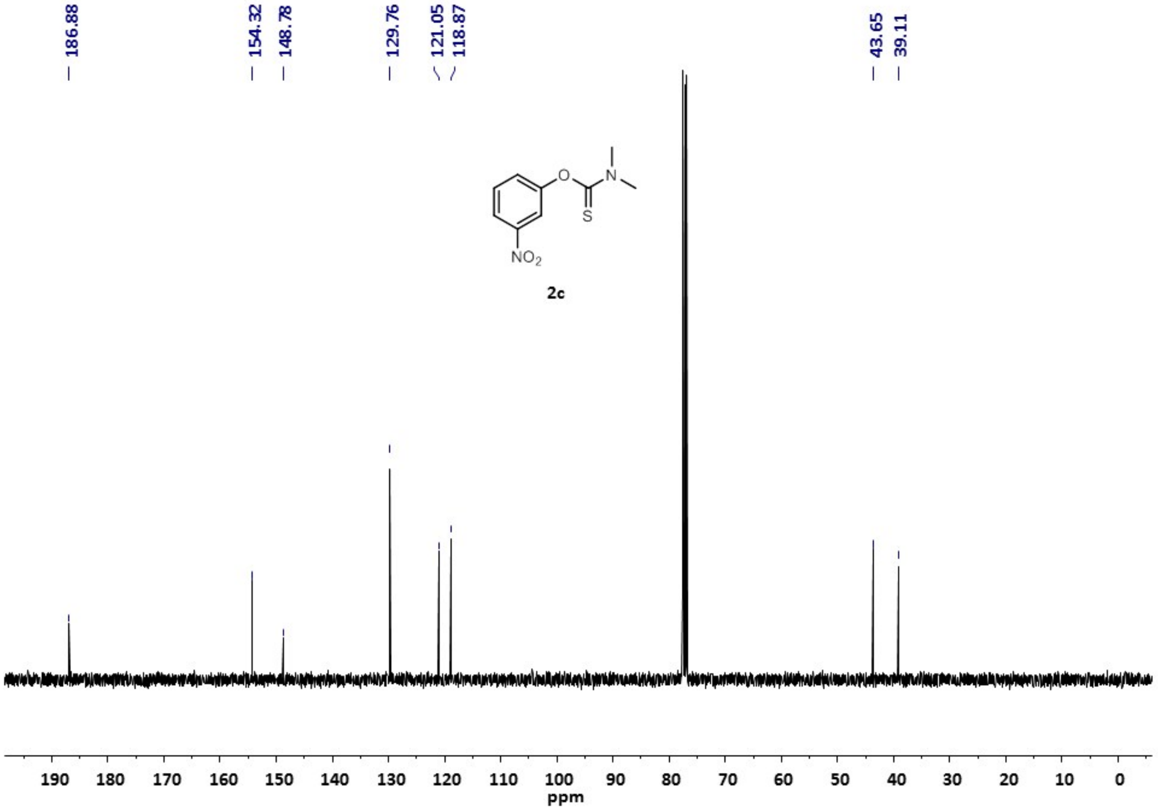
1.0
0.5
0.0
ppm

2c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148.78
129.76
121.05
118.87
43.65
39.11
O
N
S
NO2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

2c

4-Cyanophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2d

Procedure:[1] 4-Cyanophenol (5.00 g, 42.0 mmol, 1 eq) and DABCO (6.12 g, 54.6 mmol, 1.3 eq) were dissolved in NMP (25 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (5.71 g, 46.2 mmol, 1.1 eq) in NMP (8 mL) was added dropwise within 7 min. After stirring for 3 h at 50 °C, the reaction mixture was cooled down to rt and water (100 mL) was added over a period of 15 min. The original yellow solid dissolved and colorless as well as yellow impure product precipitated out of solution. Both precipitates were recrystallized with EtOH (50 mL), filtrated, washed with water (2 × 25 mL), and dried under high vacuum at 50 °C.

Yield: 7.62 g (37.0 mmol, 88%; Lit.:[1] 93%). Colorless solid.

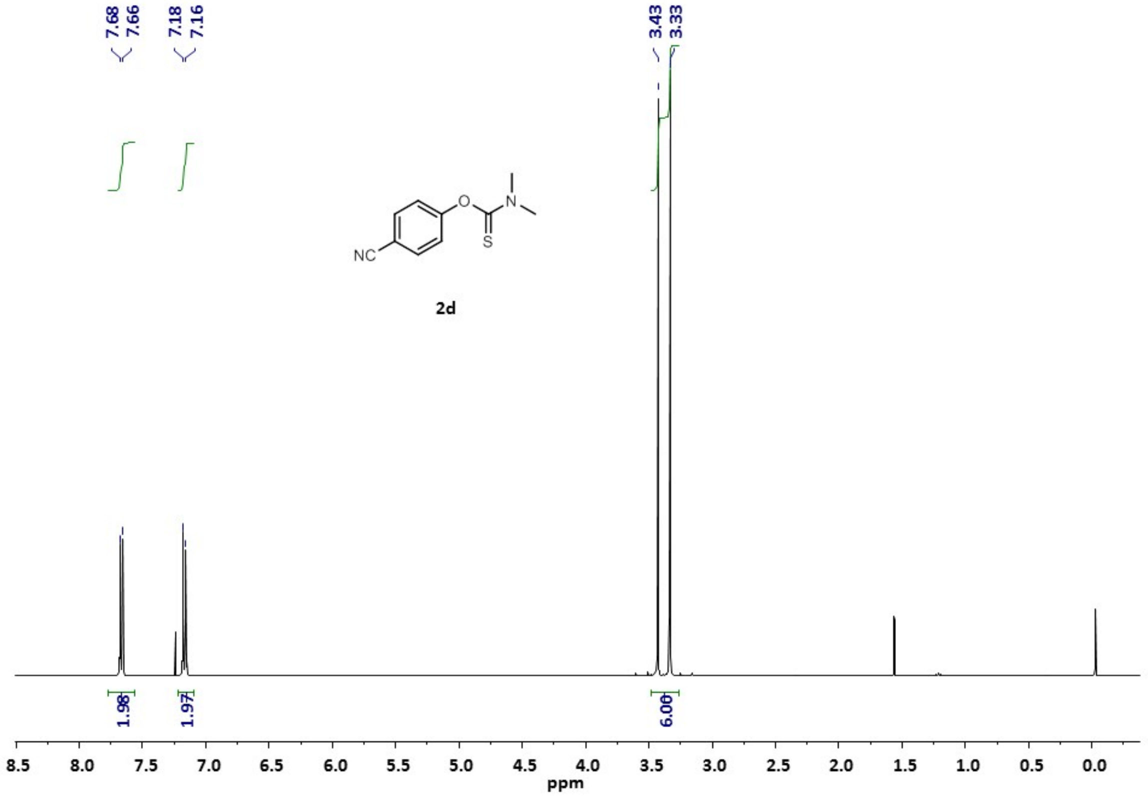
Mp: 114 °C. Lit.:[1] 111-112 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 2223 (m, C≡N, $\nu_{\mathrm{C\equiv N}}$), 1600 (m, aryl, $\nu_{\mathrm{s\ C=C}}$), 1499 (s, aryl, $\nu_{\mathrm{as\ C=C}}$, 1457 (w CH$_3$, $\delta_{\mathrm{C\text{-}H}}$), 1163 (s, C=S, $\nu_{\mathrm{C=S}}$), 1115 (s, C=S, $\nu_{\mathrm{C=S}}$), 1101 (s, C=S, $\nu_{\mathrm{C=S}}$), 1057 (w, C=S, $\nu_{\mathrm{C=S}}$), 834 (m, aryl, $\delta_{\mathrm{C\text{-}H}}$); further absorption bands: 1543 (m), 1398 (m), 1286 (m), 1208 (s), 1017 (m), 974 (w), 853 (s), 740 (w), 732 (m), 712 (w), 668 (w), 646 (w), 622 (w).

^{1}H-NMR (400.13 MHz, CDCl$_3$, 298 K):[1] δ_H (ppm) = 3.33 (3 H, s, NC*H*$_3$), 3.43 (3 H, s, NC*H*$_3$), 7.17 (2 H, d, *J* = 8.9 Hz, Ar*H*), 7.67 (2 H, d, *J* = 8.7 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, CDCl$_3$, 298 K):[1] δ_C (ppm) = 39.10 (1 C, N*C*H$_3$), 43.52 (1 C, N*C*H$_3$), 109.90 (1 C, Ar*C*), 118.50 (1 C, *C*N), 124.32 (2 C, Ar*C*), 133.52 (2 C, Ar*C*), 157.21, 186.54 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_{10}H_{10}N_2OS$: 206.26, found: m/z = 268 [M - CN + S=C=NMe$_2^+$], 279 [M - CH$_3$ + S=C=NMe$_2^+$], 449 [2(M - CN) + S=C=NMe$_2^+$].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3.33
NC
O
N
S
2d
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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
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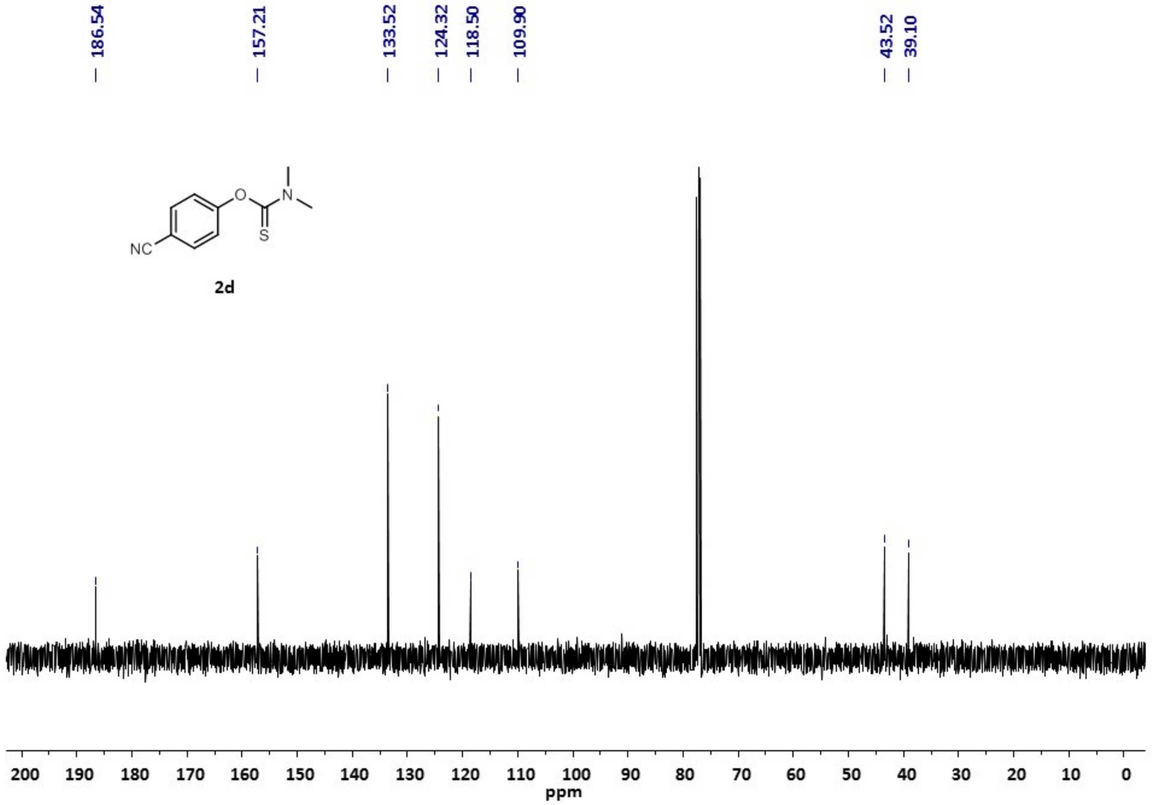
1.5
1.0
0.5
0.0
ppm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124.32
118.50
109.90
43.52
39.10
NC
O
N
S
2d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4-Acetylphenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2e

Procedure:[3] 4-Hydroxyacetophenone (6.81 g, 50.0 mmol, 1 eq) and DABCO (14.0 g, 125 mmol, 2.5 eq) were dissolved in DMF (60 mL) and stirred at 65 °C. Then dimethylthiocarbamoyl chloride (7.66 g, 62.0 mmol, 1.24 eq) was slowly added to the solution. After stirring for 1.5 h at 65 °C, the reaction mixture was poured onto crushed ice, which was priorly diluted with water (30 mL). The reaction mixture was acidified to pH 3 with 6N HCl while stirring vigorously. The colorless precipitate was filtrated, washed with water (2 × 25 mL), and dried under high vacuum at 50 °C.

Yield: 10.7 g (48.1 mmol, 96%; Lit.:[3] 91%). Colorless solid.

Mp: 100-103 °C. Lit.:[4] 102-103 °C.

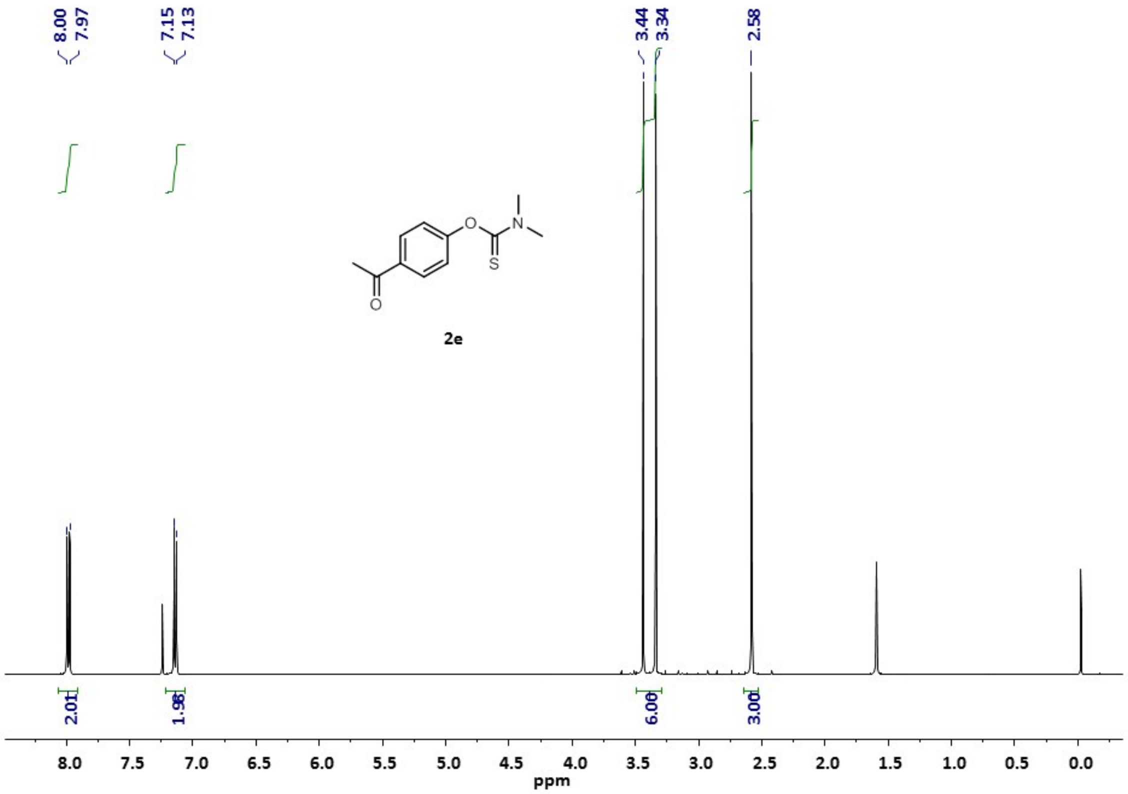
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1595 (w, aryl, $\nu_{s\ C=C}$), 1500 (m, aryl, $\nu_{as\ C=C}$), 1388 (w, CH$_3$, $\delta_{s\ C\text{-}H}$), 1204 (m, C=S, $\nu_{C=S}$), 1166 (m, C=S, $\nu_{C=S}$), 1128 (s, C=S, $\nu_{C=S}$), 1071 (w, C=S, $\nu_{C=S}$), 1058 (w, C=S, $\nu_{C=S}$), 840 (w, aryl, $\delta_{C\text{-}H}$), 826 (w, aryl, $\delta_{C\text{-}H}$); further absorption bands: 1678 (s), 1534 (m), 1403 (w), 1356 (m), 1286 (m), 1268 (m), 1235 (m), 1010 (m), 974 (w), 955 (w), 849 (m), 734 (w), 720 (w), 655 (w), 620 (w).

^{1}H-NMR (400.13 MHz, CDCl$_3$, 298 K):[3] δ_H (ppm) = 2.58 (3 H, s, COC*H*$_3$), 3.34 (3 H, s, NC*H*$_3$), 3.44 (3 H, s, NC*H*$_3$), 7.14 (2 H, d, *J* = 8.7 Hz, Ar*H*), 7.99 (2 H, d, *J* = 8.5 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, CDCl$_3$, 298 K): δ_C (ppm) = 26.81 (1 C, CO*C*H$_3$)), 39.07 (1 C, N*C*H$_3$), 43.50 (1 C, N*C*H$_3$), 123.31 (2 C, Ar*C*), 129.90 (2 C, Ar*C*), 147.86 (1 C, Ar*C*), 157.49 (1 C, Ar*C*), 187.11 (1 C, *C*S), 197.08 (1 C, *C*O).

MS (MALDI-ToF, om): calc. for $C_{11}H_{13}NO_2S$: 223.29, found: m/z = 224 [M + H$^+$], 268 [M - COMe + S=C=NMe$_2^+$].

MS (MALDI-ToF, dhb): calc. for $C_{11}H_{13}NO_2S$: 223.29, found: m/z = 224 [M + H$^+$].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7.15
7.13
3.44
3.34
2.58
2e
2.01
1.98
6.00
3.00
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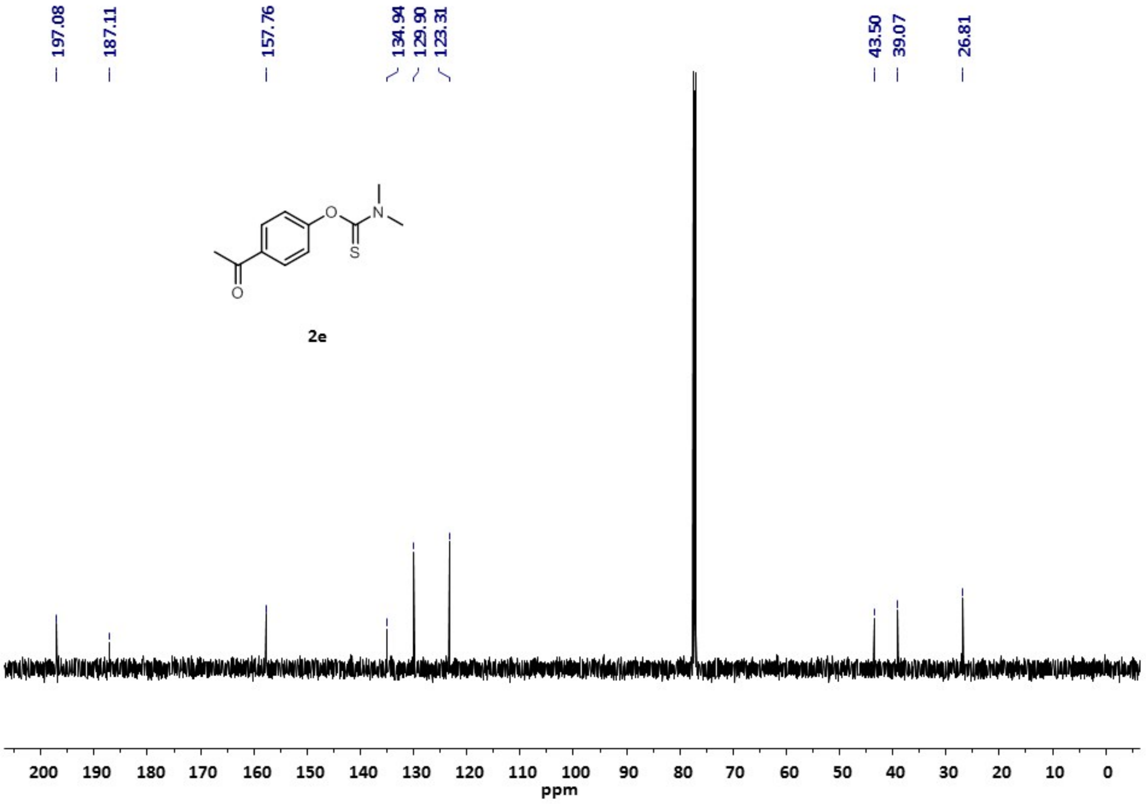
ppm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187.11
157.76
134.94
129.90
123.31
43.50
39.07
26.81
2e
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

4-Bromophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2f

Procedure:[1] 4-Bromophenol (5.00 g, 28.9 mmol, 1 eq) and DABCO (4.21 g, 37.6 mmol, 1.3 eq) were dissolved in NMP (25 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (3.93 g, 31.8 mmol, 1.1 eq) in NMP (8 mL) was added dropwise within 15 min. After stirring for 2.5 h at 50 °C, the reaction mixture was cooled down to rt and water (60 mL) was added over a period of 15 min. The original pale yellow solid dissolved and the colorless product precipitated out of solution. The product was filtrated, washed with water (2 × 25 mL), and dried in high vacuum at 50 °C.

Yield: 6.29 g (24.2 mmol, 84%; Lit.:[1] 84%). Colorless solid.

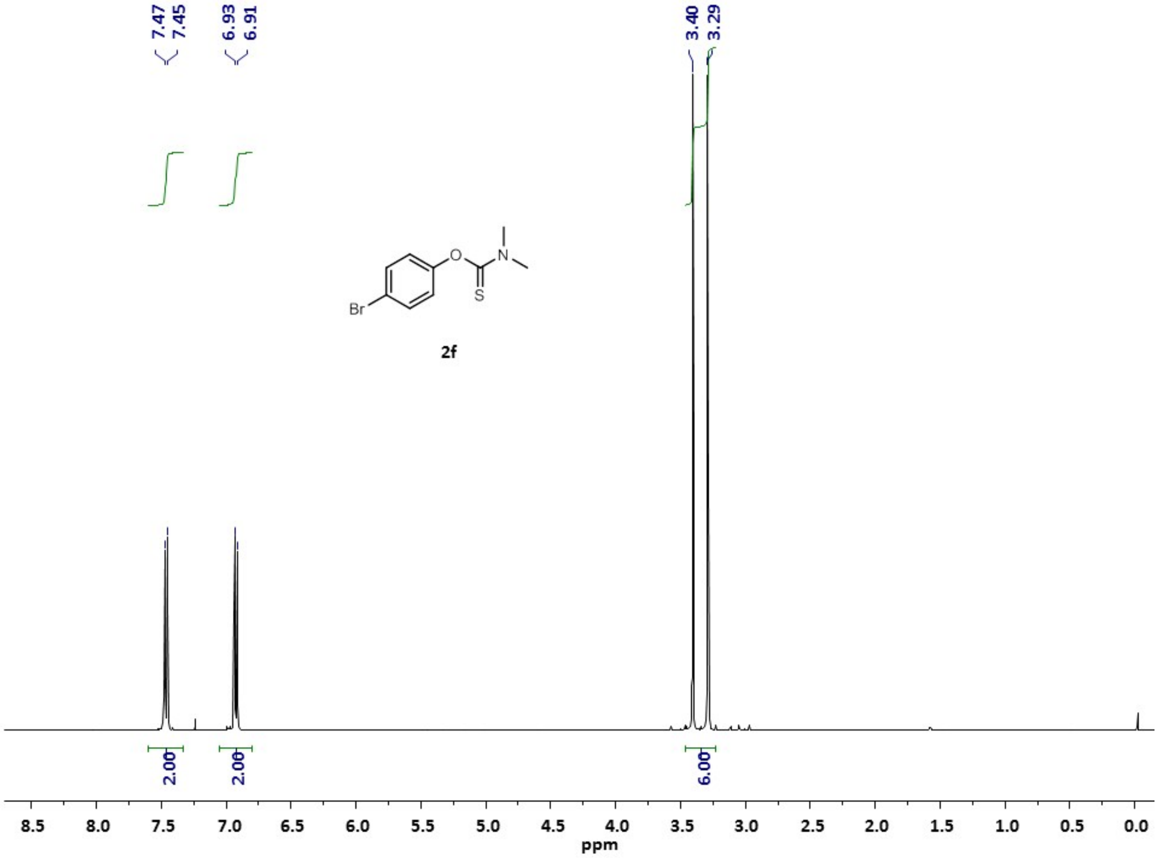
Mp: 68 °C. Lit.:[1] 84-85 °C.

IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1583 (w, aryl, $\nu_{s\ C=C}$), 1415 (w, aryl, $\nu_{as\ C=C}$), 1177 (w, C=S, $\nu_{C=S}$), 1158 (m, C=S, $\nu_{C=S}$), 1123 (s, C=S, $\nu_{C=S}$), 1089 (m, C=S, $\nu_{C=S}$), 1062 (s, ArC-Br, ν_{C-Br}), 830 (m, aryl, δ_{C-H}), 818 (w, aryl, δ_{C-H}), 643 (w, ArC-Br, ν_{C-Br}), 629 (w, ArC-Br, ν_{C-Br}); further absorption bands: 1540 (w), 1477 (m), 1395 (m), 1284 (m), 1206 (s), 1008 (s), 935 (w), 711 (w), 685 (m).

^{1}H-NMR (400.13 MHz, CDCl$_3$, 298 K):[1] δ_H (ppm) = 3.29 (3 H, s, NC*H*$_3$), 3.40 (3 H, s, NC*H*$_3$), 6.92 (2 H, d, *J* = 9.0 Hz, Ar*H*), 7.46 (2 H, d, *J* = 8.8 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, CDCl$_3$, 298 K):[1] δ_C (ppm) = 38.93 (1 C, N*C*H$_3$), 43.48 (1 C, N*C*H$_3$), 119.25 (1 C, Ar*C*), 124.80 (2 C, Ar*C*), 132.36 (2 C, Ar*C*), 153.16 (1 C, Ar*C*), 187.46 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_9H_{10}BrNOS$: 260.15, found: m/z = 243 [M$^+$ - CH$_4$], 268 [M - Br + S=C=NMe$_2^+$], 449 [2(M - Br) + S=C=NMe$_2^+$].



7.47
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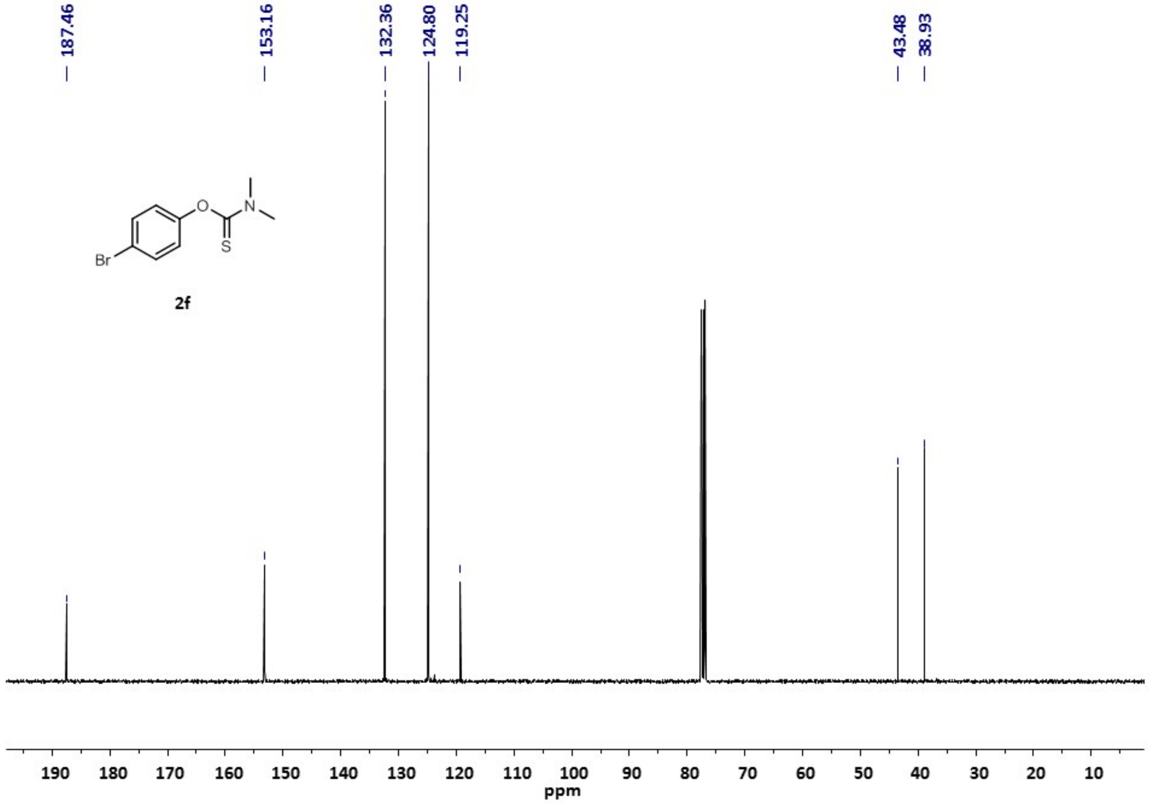
6.93
6.91
3.40
3.29
Br
O
N
S
2f
2.00
2.00
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm



187.46
153.16
132.36
124.80
119.25
43.48
38.93
Br
O
N
S
2f
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
ppm

4-Fluorophenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2g

Procedure:[1] 4-Fluorophenol (8.97 g, 80.0 mmol, 1 eq) and DABCO (11.2 g, 100 mmol, 1.25 eq) were dissolved in NMP (45 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (10.6 g, 85.6 mmol, 1.07 eq) in NMP (10 mL) was added dropwise within 7 min. After stirring for 5 h at 50 °C, the temperature was hold at 50 °C and water (130 mL) was added over a period of 15 min dissolving the priorly formed yellow solid. The reaction mixture was smoothly cooled down to 0 °C and stirred at this temperature for 30 min. The formed precipitate was recrystallized with EtOH (25 mL), filtrated and washed with water (2 × 25 mL). These steps were repeated for the impure product precipitated from the filtrate solution. The collected solids were dried under high vacuum at 50 °C.

Yield: 13.3 g (66.6 mmol, 83%; Lit.:[1] 80%). Colorless solid.

Mp: 75-77 °C. Lit.:[1] 75-77 °C.

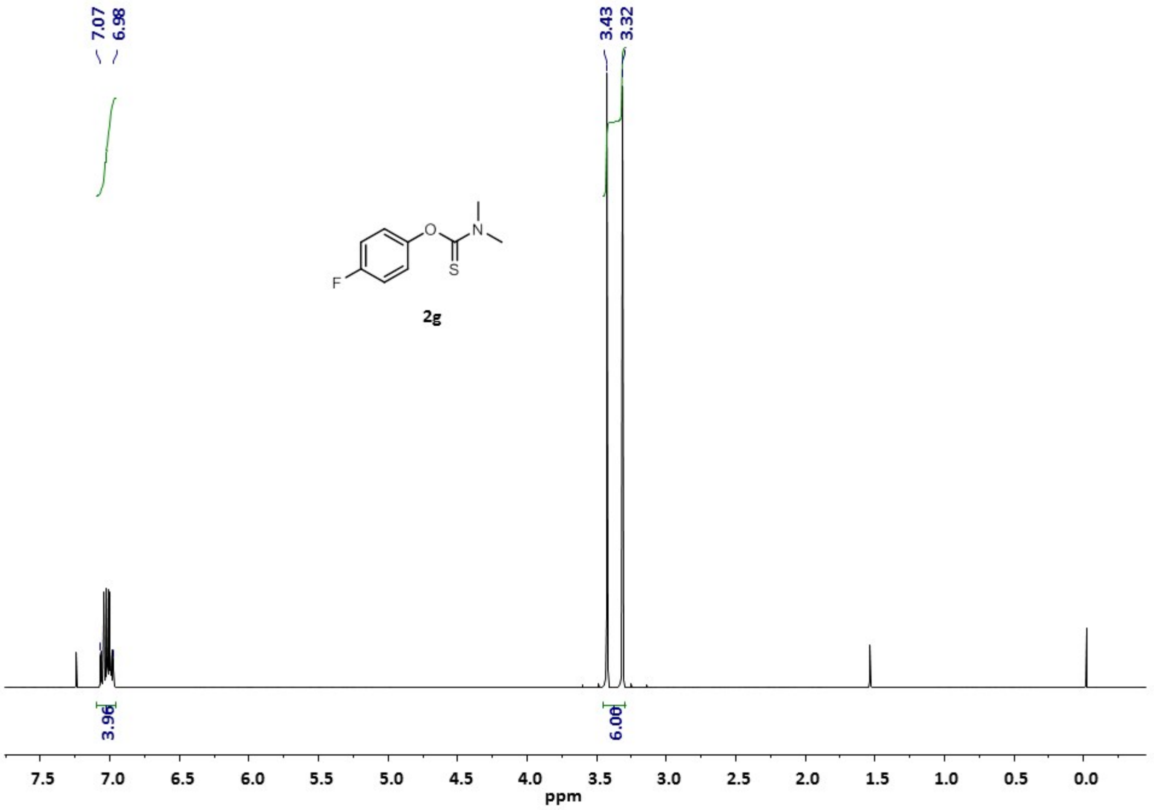
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1494 (s, aryl, $\nu_{as\ C=C}$), 1388 (m, CH_3, $\delta_{s\ C\text{-}H}$), 1284 (m, ArC-F, $\nu_{C\text{-}F}$), 1229 (w, ArC-F, $\nu_{C\text{-}F}$), 1186 (s, C=S, $\nu_{C=S}$), 1130 (s, C=S, $\nu_{C=S}$), 1085 (m, C=S, $\nu_{C=S}$), 836 (s, aryl, $\delta_{C\text{-}H}$); further absorption bands: 1534 (w), 1409 (w), 1014 (w), 1005 (m), 949 (w), 933 (w), 777 (s), 716 (m), 657 (w), 641 (w), 627 (w).

^{1}H-NMR (400.13 MHz, $CDCl_3$, 298 K):[1] δ_H (ppm) = 3.32 (3 H, s, NC*H*$_3$), 3.43 (3 H, s, NC*H*$_3$), 6.97-7.08 (4 H, m, Ar*H*).

^{13}C-NMR (100.62 MHz, $CDCl_3$, 298 K):[1] δ_C (ppm) = 38.89 (1 C, N*C*H$_3$), 43.53 (1 C, N*C*H$_3$), 116.01 (2 C, d, *J* = 23.9 Hz, Ar*C*), 124.37 (2 C, d, *J* = 8.8 Hz, Ar*C*), 150.06 (1 C, d, *J* = 2.9 Hz, Ar*C*), 159.29 and 161.72 (1 C, d, *J* = 244.5 Hz, Ar*C*), 188.02 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_9H_{10}FNOS$: 199.24, found: m/z = 268 [M - F + S=C=NMe$_2^+$].

MS (MALDI-ToF, dhb): calc. for $C_9H_{10}FNOS$: 199.24, found: m/z = 200 [M + H$^+$].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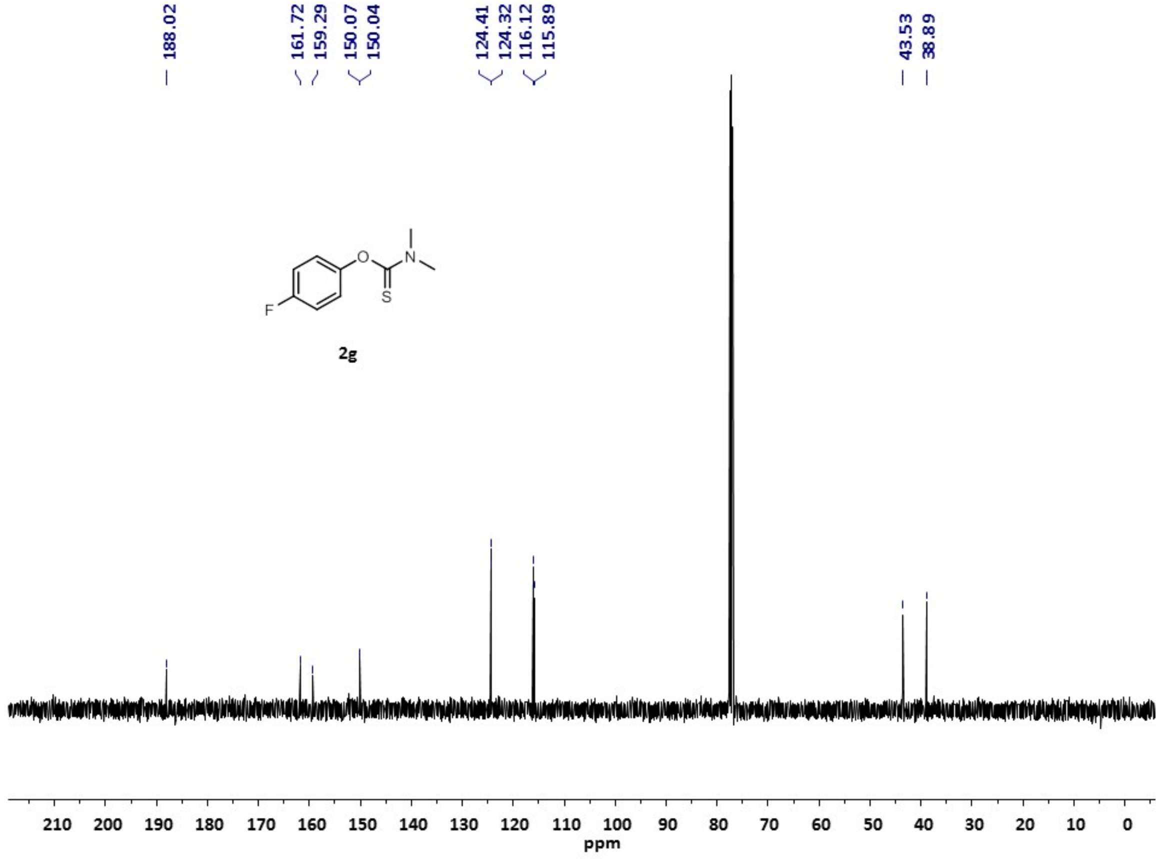
6.98
3.43
3.32
F
O
N
S
2g
3.96
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm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161.72
159.29
150.07
150.04
124.41
124.32
116.12
115.89
43.53
38.89
F
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S
2g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

4-Methoxyphenyl-*N*,*N*-dimethyl-*O*-thiocarbamate 2h

Procedure:[1] 4-Methoxyphenol (8.69 g, 70.0 mmol, 1 eq) and DABCO (9.81 g, 87.5 mmol, 1.25 eq) were dissolved in NMP (43 mL) and stirred at 50 °C. A solution of dimethylthiocarbamoyl chloride (9.26 g, 74.9 mmol, 1.07 eq) in NMP (9 mL) was added dropwise within 6 min. After stirring for 3.7 h at 50 °C, the temperature was hold at 50 °C and water (115 mL) was added over a period of 20 min dissolving the priorly formed solid. The reaction mixture was smoothly cooled down to 0 °C and stirred at this temperature for 45 min. The formed precipitate was washed with water (2 × 25 mL). The filtrate was extracted with MTBE (3 × 50 mL) and the solvent was distilled. The raw products were each recrystallized in EtOH (20 mL), filtrated, and washed with water (2 × 25 mL). The collected product was dried under high vacuum at 50 °C.

Yield: 8.70 g (41.2 mmol, 59%; Lit.:[1] 49%). Colorless solid.

Mp: 80-82 °C. Lit.:[1] 82-83 °C.

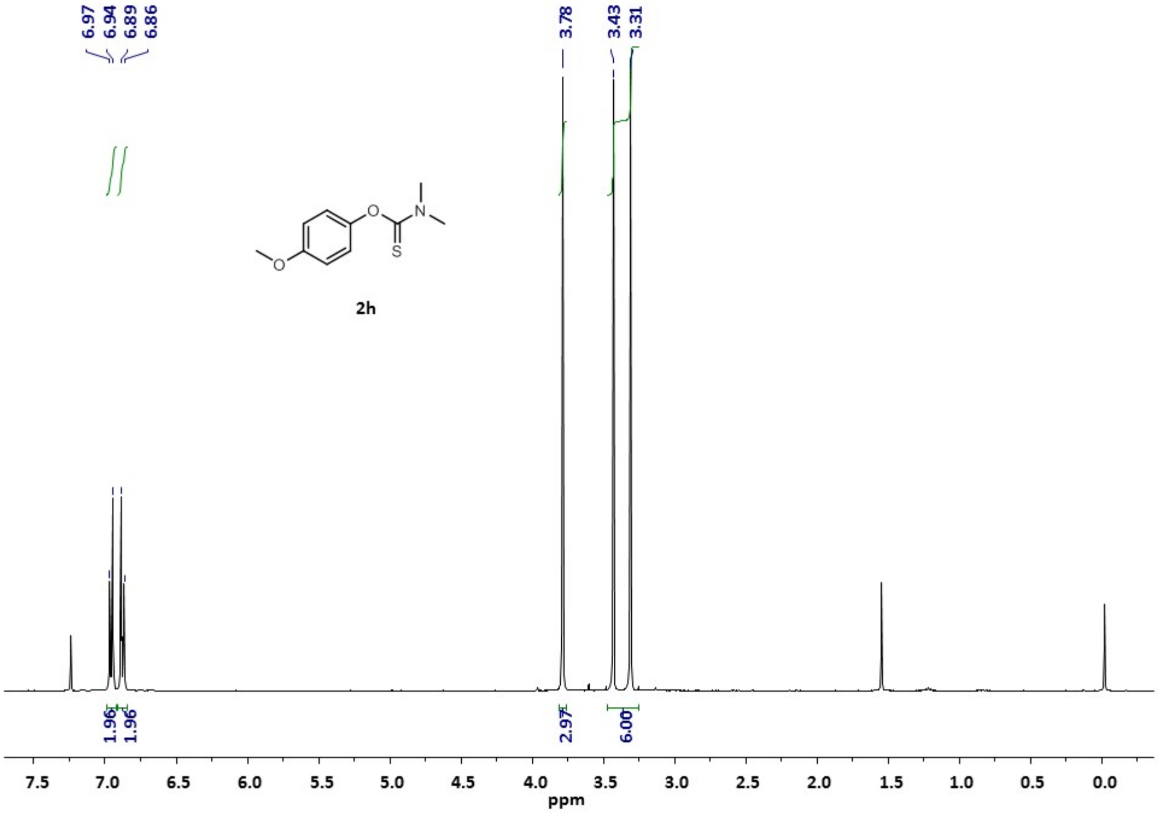
IR (ATR): $\tilde{\nu}$ (cm^{-1}) = 1598 (w, aryl, $\nu_{s\ C=C}$), 1499 (m, aryl, $\nu_{as\ C=C}$), 1465 (w, CH_3, $\delta_{C\text{-}H}$), 1456 (w, CH_3, $\delta_{C\text{-}H}$), 1445 (w, CH3, $\delta_{C\text{-}H}$), 1200 (m, C=S, $\nu_{C=S}$), 1157 (w, C=S, $\nu_{C=S}$), 1128 (s, C=S, $\nu_{C=S}$), 1097 (m, C=S, $\nu_{C=S}$), 1061 (w, C=S, $\nu_{C=S}$), 832 (s, aryl, $\delta_{C\text{-}H}$), 799 (w, aryl, $\delta_{C\text{-}H}$); further absorption bands: 1540 (w), 1413 (w), 1396 (w), 1295 (w), 1284 (m), 1250 (w), 1030 (m), 1005 (w), 949 (w), 922 (w), 765 (m), 721 (w), 658 (w), 641 (w).

^1H-NMR (400.13 MHz, $CDCl_3$, 298 K):[1] δ_H (ppm) = 3.31 (3 H, s, NCH_3), 3.43 (3 H, s, NCH_3), 3.78 (3 H, s, OCH_3), 6.88 (2 H, d, *J* = 9.1 Hz, Ar*H*), 6.96 (2 H, d, *J* = 9.1 Hz, Ar*H*).

^{13}C-NMR (100.62 MHz, $CDCl_3$, 298 K):[1] δ_C (ppm) = 38.83 (1 C, NCH_3), 43.49 (1 C, NCH_3), 55.71 (1 C, OCH_3), 114.35 (2 C, Ar*C*), 123.65 (2 C, Ar*C*), 147.86 (1 C, Ar*C*), 157.49 (1 C, Ar*C*), 188.59 (1 C, *C*S).

MS (MALDI-ToF, om): calc. for $C_{10}H_{13}NO_2S$: 211.28, found: m/z = 268 [M - OMe + $S=C=NMe_2^+$].

MS (MALDI-ToF, dhb): calc. for $C_{10}H_{13}NO_2S$: 211.28, found: m/z = 212 [M + H^+].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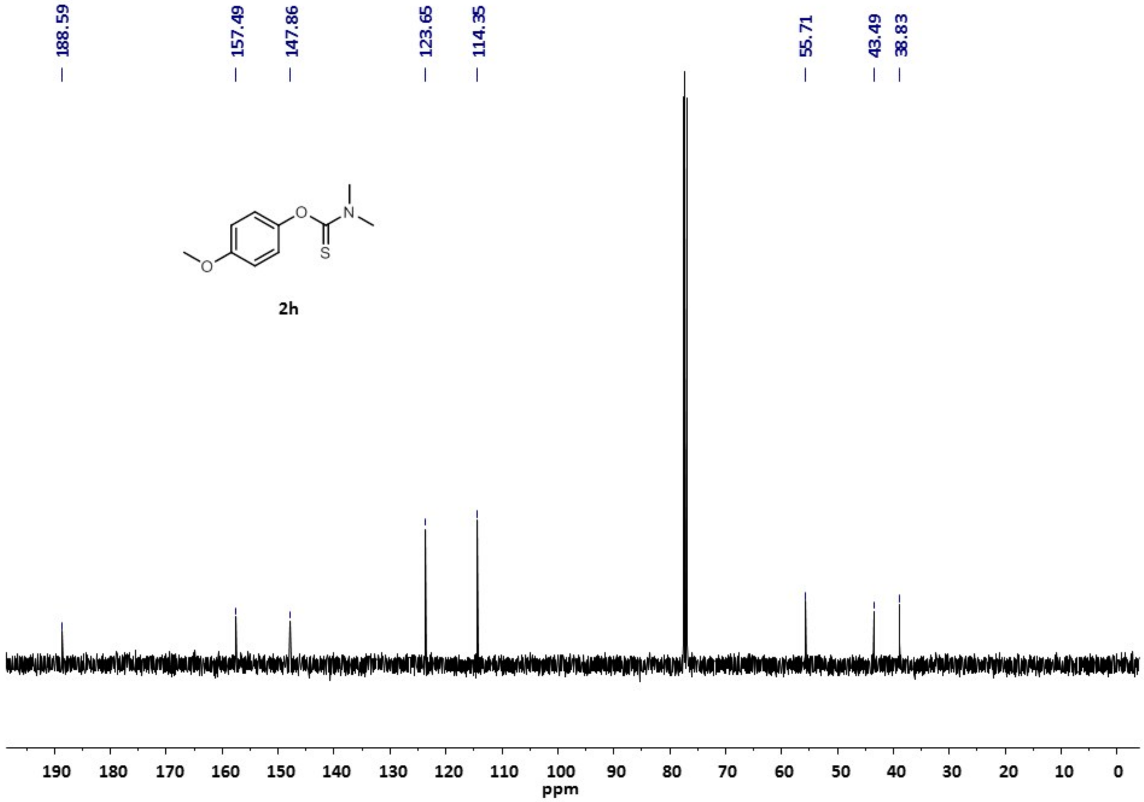
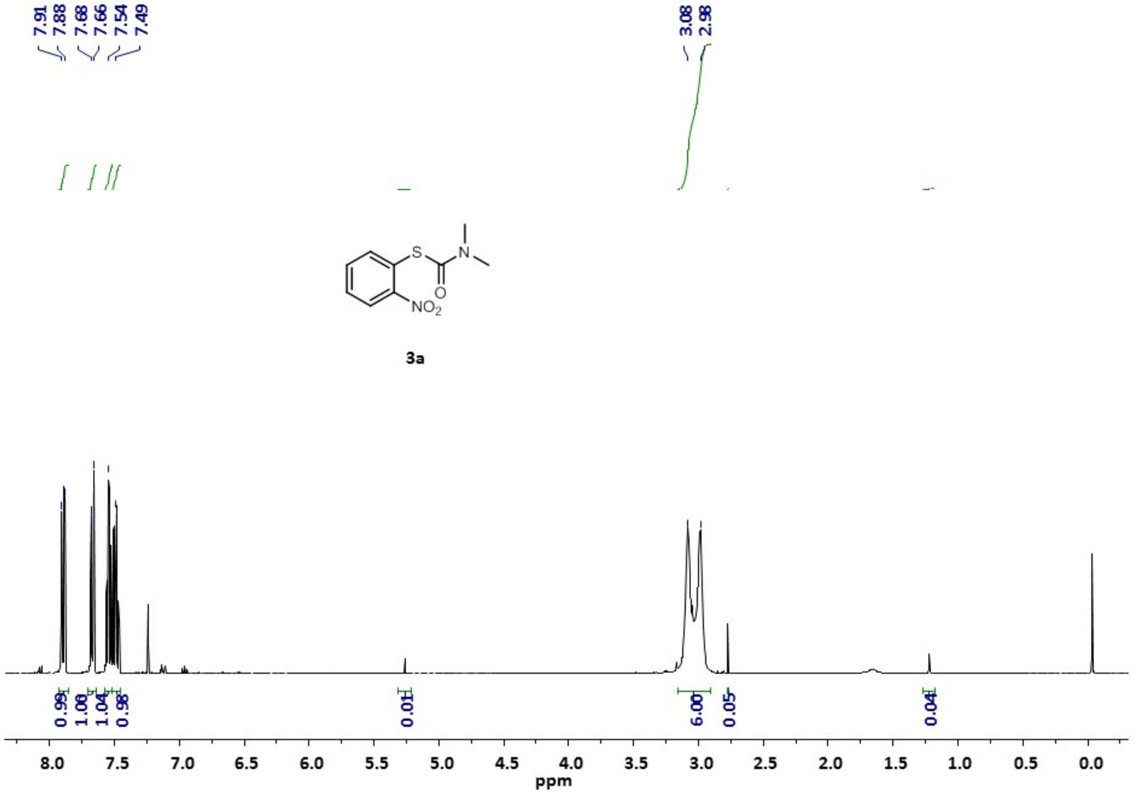
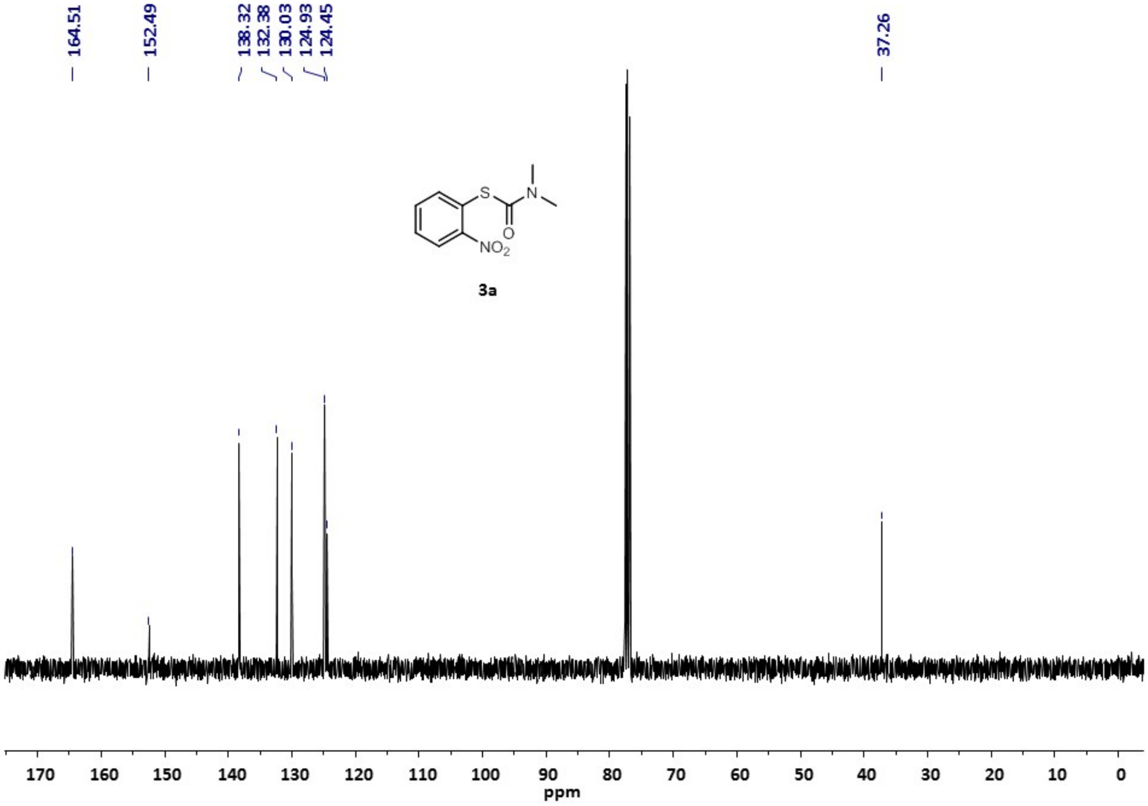
6.86
3.78
3.43
3.31
2h
1.96
1.96
2.97
6.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm


188.59
157.49
147.86
123.65
114.35
55.71
43.49
38.83
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


7.91
7.88
7.68
7.66
7.54
7.49
3.08
2.98
S
N
O
NO2
3a
0.99
1.00
1.04
0.98
0.01
6.00
0.05
0.04
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
ppm


164.51
152.49
138.32
132.38
130.03
124.93
124.45
37.26
S
N
O
NO2
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

Literature

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