Facile and mild displacement of nitrite ion in electron-deficient nitroarens by alkyl or aryl thiols in the presence of magnesium methoxide as solid base catalyst

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Experimental section:

General. All reactions were conducted in glassware with magnetic stirring. All the materials were of commercial reagent grade. IR spectra were recorded as KBr pellets on a Perkin-Elmer 781 spectrophotometer and an Impact 400 Nicolet FTIR spectrophotometer. \(^1\)H and \(^13\)C-NMR spectra were recorded in CDCl\(_3\) on a Bruker DRX-400 spectrometer with tetramethylsilane as internal reference. Mass spectra were recorded on a Finnigan MAT 44S instrument by Electron Impact (EI) Ionization mode with an ionization voltage of 70eV. Melting points were determined with a Thermo Scientific 9300 micro melting point apparatus and are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates Merck.

Catalyst preparation

Magnesium methoxide: A 1-l. round-bottomed flask fitted with an efficient mechanical stirrer, a reflux condenser and set up in a good hood in order to heating on an oil bath. In the flask is placed 0.2 mol 4.86 gr. metallic magnesium powder and 150 ml of absolute methanol.
However, initially the set up must stirred at room temperature about 2 hours (the reaction is very vigorous). The oil bath is turn on and heating is started until 60 degree of centigrade, this requires about four hours. After this time the reaction is complete, the mixture (white solid that suspension in alcohol) is cooled in a cold-water bath with vigorous stirring, filtered with suction through a sintered-glass funnel. The cake of the magnesium methoxide is well compressed and dried under vacuum and keeps in dry places without any moisture.

**Representative Procedure for the synthesis of thio compounds on the basis of \( S_{N}Ar \) reaction:**

2-(phenylthio)benzaldehyde (Table 2, Entry 1):

![Chemical Reaction]

The reaction of thiophenol with 2-nitrobenzaldehyde is representative. Magnesium methoxide that freshly prepared according to the above procedure (0.18 g, 2 mmol) was placed in a 20-mL reaction flask. \( N,N \)-Dimethylformamide (8 ml), 2-nitrobenzaldehyde (0.30 g, 2 mmol), and thiophenol (0.22 g, 2 mmol) were added and stirred at 80 °C for 4 hours. The progress of the reaction was monitored by TLC, after completion of the reaction, water (50 ml) was added, and the aqua’s solution was extracted twice by ethyl acetate (2 × 10 ml). The combined organic layer was dried over magnesium sulfate to adsorb the residual H₂O. Solvent were evaporated in a vacuum evaporator to give 3a as a yellow oil, followed by purification on silica gel afforded 2-phenylthiobenzaldehyde in excellent yield (0.37 gr. 87% yield). Yellow oil; IR (thin film): 3060
(H-Ar), 2846, 2738 (HCO), 1686 (C=O), 1584, 1445 (C=C, Ar), 1392, 1299, 1195, 751, 694. $^1$H-NMR (CDCl$_3$): 10.38 (s, 1 H, HC=O), 7.88 (s, 1 H, Ar), 7.26-7.43 (m, 7 H, Ar), 7.10 (s, 1 H, Ar). $^{13}$C-NMR (CDCl$_3$): 126.3, 128.4, 129.7, 130.3, 131.9, 133.1, 133.2, 133.7, 134.1, 141.5, 191.4. MS: 215 ([M+1]$^+$, 1.5), 215 (M$^+$, 12), 185 (45), 109 (74), 105 (23), 76 (100). Anal. calc. for C$_{13}$H$_{10}$OS (214.28): C 72.87, H 4.70; found: C 72.07, H 4.58.

4-(Phenylthio)benzaldehyde (Table 2, Entry 2):

![Chemical Structure](image)

4-nitrobenzaldehyde: (0.30 g, 2 mmol); thiophenol: (0.22 g, 2 mmol); magnesium methoxide: (0.18 g, 2 mmol); solvent: DMF (8 ml); reaction time: 4 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H$_2$O. The solution was evaporated in vacuum evaporator to give 3b as a yellow oil, followed by purification on silica gel afforded 4-(phenylthio)benzaldehyde (0.38 gr. 88% yield). Yellow oil; IR (thin film): 3048, 2851, 2740 (HCO), 1692 (C=O), 1578, 1441 (C=C, Ar), 1380, 1303, 1205, 760, 681. $^1$H-NMR (CDCl$_3$): 9.90 (s, 1 H, HC=O), 7.70 (d, 2 H, Ar), 7.52 (s, 2 H, Ar), 7.42 (s, 3 H, Ar), 7.22 (d, 2 H, Ar). $^{13}$C-NMR (CDCl$_3$): 125.2, 127.7, 128.7, 131.1, 132.2, 134.1, 134.5, 142.0, 190.6. MS: 215 ([M+1]$^+$, 2.7), 215 (M$^+$, 25), 185 (32), 109 (38), 105 (10), 76 (100). Anal. calc. for C$_{13}$H$_{10}$OS (214.28): C 72.87, H 4.70; found: C 72.79, H 4.63.
4-(Phenylthio)acetophenone (Table 2, Entry 3):

![Chemical Structure]

4-nitroacetophenone: (0.33 g, 2 mmol); thiophenol: (0.22 g, 2 mmol); magnesium methoxide: (0.18 g, 2 mmol); solvent: DMF (8 ml); reaction time: 5 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H₂O. The solution was evaporated in vacuum evaporator to give 3c as a pale yellow oil, followed by purification on silica gel afforded 4-(phenylthio) acetophenone in excellent yield (0.383 gr. 84% yield). Yellow solid; M.p. 81-83 ºC; IR (KBr): 3051 (Ar-H), 2945 (CH₃), 1713 (C=O), 1592, 1432 (C=C, Ar), 1281, 1110, 753, 687. ¹H-NMR (CDCl₃): 8.12 (d, 2 H, Ar), 8.01 (d, 2 H, Ar), 7.26-7.31 (m, 7 H, Ar), 2.61 (s, 3 H, CH₃). ¹³C-NMR (CDCl₃): 26.7, 126.1, 129.0, 130.0, 130.9, 135.5, 139.1, 189.7. MS: 229 ([M+1]+, 3.8), 228 (M⁺, 39), 185 (65), 151 (41), 109 (31), 77 (100).

Anal. calc. for C₁₄H₁₂OS (214.28): C 73.65, H 5.30; found: C 73.02, H 5.14.

Methyl-4-(Phenylthio)benzoate (Table 2, Entry 4):

![Chemical Structure]

Methyl-4-nitrobenzoate: (0.36 g, 2 mmol); thiophenol: (0.22 g, 2 mmol); magnesium methoxide: (0.18 g, 2 mmol); solvent: DMF (8 ml); reaction time: 6 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H₂O. The solution was evaporated in vacuum evaporator to give 3d as a pale yellow oil, followed by
purification on silica gel afforded Methyl-4-(Phenylthio)benzoate in excellent yield (0.414 gr.
85% yield). IR (thin film): 3003 (ArH), 2954 (OCH₃), 1715 (C=O), 1591, 1438 (C=C, Ar), 1399,
1277, 1182, 1111, 847, 757, 693. ¹H-NMR (CDCl₃): 7.89 (d, 2 H, Ar), 7.50 (m, 2 H, Ar), 7.39-
7.42 (m, 3 H, Ar), 7.21 (d, 2 H, Ar), 3.90 (s, 3 H, OCH₃). ¹³C-NMR (CDCl₃): 52.1, 127.4, 127.5,
128.6, 129.6, 130.1, 132.3, 133.7, 144.4, 166.7. MS: 245 ([M+1]⁺, 2.2), 244 (M⁺, 13), 185 (34),
167 (21), 135 (63), 76 (100). Anal. calc. for C₁₄H₁₂O₂S: C 68.83, H 4.95; found: C 68.71, H 4.97.

4-(Phenylthio)benzonitrile (Table 2, Entry 5):

![Chemical structure](image)

4-nitrobenzonitrile: (0.3 g, 2 mmol); thiophenol: (0.22 g, 2 mmol); magnesium methoxide: (0.18
g, 2 mmol); solvent: DMF (8 ml); reaction time: 6 h; reaction temperature: 80 °C. The combined
organic layer was dried over magnesium sulfate to adsorb the residual H₂O. The solution was
evaporated in vacuum evaporator to give 3e as a pale yellow oil, followed by purification on
silica gel afforded 4-(Phenylthio)benzonitrile in excellent yield (0.328 gr. 78% yield). Yellow
oil; IR (thin film): 3066 (ArH), 2230 (C=N), 1568, 1474 (C=C, Ar), 1448. ¹H-NMR (CDCl₃):
7.64 (m, 2H, ArH), 7.28-7.39 (m, 5H, ArH), 7.07 (m, 2H, ArH). ¹³C-NMR (CDCl₃): 113.26,
118.65, 126.91, 128.34, 129.10, 130.90, 133.91, 134.86, 139.42. MS: 212 ([M+1]⁺, 14.2), 211
(M⁺, 100), 185 (41), 134 (38), 102 (65), 76 (25). Anal. calc. for C₁₃H₉NS: C 73.90, H 4.29, N
6.63; found: C 74.05, H 4.23, N 6.54.
2-(Phenylthio)nitrobenzene (Table 2, Entry 6):

\[
\begin{align*}
\text{SH} & \quad + \quad \text{NO}_2\text{NO}_2 \\
& \quad \rightarrow \quad \text{NO}_2\text{NO}_2 \quad \text{S}
\end{align*}
\]

1,2-dinitrobenzene: (0.335 g, 2 mmol); thiophenol: (0.22 g, 2 mmol); magnesium methoxide: (0.18 g, 2 mmol); solvent: DMF (7 ml); reaction time: 5 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H2O. The solution was evaporated in vacuum evaporator to give 3f as a orange yellowish oil, followed by purification on silica gel afforded 4-(phenylthio)benzaldehyde in excellent yield (0.374 gr. 81% yield). Orange oil; IR (thin film): 3064 (ArH), 1588, 1512, 1445, 1336, 790, 733, 693. \(^1\)H-NMR (CDCl\textsubscript{3}): 8.22 (d, 2 H, Ar), 7.59 (d, 2 H, Ar), 7.49 (s, 3 H, Ar), 7.20-7.36 (m, 3 H, Ar), 6.86 (d, 1 H, Ar). \(^{13}\)C-NMR (CDCl\textsubscript{3}): 125.0, 125.5, 128.3, 130.0, 130.1, 130.9, 131.6, 133.5, 135.9, 139.4, 144.9. MS: 232 ([M+1]$^+$, 13), 231 ($M^+$, 100), 185 (74), 154 (60), 122 (23), 76 (11). Anal. calc. for C\textsubscript{12}H\textsubscript{9}NO\textsubscript{2}S (214.28): C 62.32, H 3.92, N 6.06; found: C 62.25, H 3.90, N 5.94.

1,3-Di(2-formylphenylthio)propane (Table 3, Entry 1):

\[
\begin{align*}
\text{NO}_2\text{O} & \quad + \quad \text{HS} - \text{SH} \\
& \quad \rightarrow \quad \text{S} - \text{O} - \text{S} - \text{S} - \text{O} - \text{S}
\end{align*}
\]

2-nitrobenzaldehyde: (0.60 g, 4 mmol); propane-1,3-dithiol: (0.22 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 7 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H\textsubscript{2}O. The solution was evaporated in vacuum evaporator to give 3g as a pale yellow solid, followed by purification on silica gel afforded 1,3-di(2-formylphenylthio)propane in excellent yield (0.512
1,3-Di(4-formylphenylthio)propane (Table 3, Entry 2):

\[
\begin{align*}
\text{4-nitrobenzaldehyde: (0.60 g, 4 mmol); propane-1,3-dithiol: (0.22 g, 2 mmol); magnesium} \\
\text{methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 7 h; reaction temperature:} \\
\text{80 °C. The combined organic layer was dried over magnesium sulfate to adsorb the residual H}_2\text{O.}
\end{align*}
\]

The solution was evaporated in vacuum evaporator to give 3h as a pale yellow solid, followed by purification on silica gel afforded 1,3-Di(2-formylphenylthio)propane in excellent yield (0.537 gr. 85% yield). IR (KBr): 3054 (ArH), 2940 (RH), 2817, 2727 (CHO), 1693 (C=O), 1588, 1487 (C=C, Ar), 1087, 836, 808. ¹H-NMR (CDCl₃): 10.14 (s, 2 H, HC=O), 7.84 (d, 4 H, Ar), 7.10 (d, 4 H, Ar), 3.18 (s, 4 H, RH), 2.15 (s, 2 H, RH). ¹³C-NMR (CDCl₃): 27.81, 38.18, 129.69, 128.84, 134.10, 143.83, 197.08. MS: 317 ([(M+1]⁺, 7.5), 316 (M⁺, 38), 258 (34), 105 (17), 76 (100). Anal. calc. for C₁₇H₁₆O₂S₂: C 64.53, H 5.10; found: C 64.48, H 4.94.
1,3-Di(4-acetylpenthenylthio)propane (Table 3, Entry 3):

4-nitroacetophenone: (0.66 g, 4 mmol); propane-1,3-dithiol: (0.22 g, 2.0 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 8 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H2O. The solution was evaporated in vacuum evaporator to give 3i as a pale yellow solid, followed by purification on silica gel afforded 4-(phenylthio)benzaldehyde in excellent yield (0.520 gr. 77% yield). Pale yellow solid: M.p. 94-96 ºC. IR (KBr): 3065, 3003 (ArH), 2929 (RH), 1674 (C=O), 1586, 1488 (C=C, Ar), 1264, 835, 755, 588. \(^1\)H-NMR (CDCl₃): 7.85 (d, 4 H, Ar), 7.29 (d, 4 H, Ar), 3.15 (t, 4 H, RH), 2.57 (s, 3 H, CH₃), 2.07 (t, 2 H, RH). \(^13\)C-NMR (CDCl₃): 25.11, 30.41, 34.17, 129.74, 133.02, 134.83, 145.15, 195.03. MS: 345 ([M+1]^+, 22), 344 (M^+, 100), 301 (55), 258 (40), 225 (36). Anal. calc. for C₁₉H₂₀O₂S₂ (214.28): C 66.24, H 5.85; found: C 66.11, H 5.78.

1,3-Di(4-methoxycarbonylphenylthio)propane (Table 3, Entry 4):

Methyl 4-nitrobenzoate: (0.72 g, 4 mmol); propane-1,3-dithiol: (0.22 g, 2.0 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 8 h; reaction temperature: 80 ºC. The combined organic layer was dried over magnesium sulfate to adsorb the residual H₂O. The solution was evaporated in vacuum evaporator to give 3j as a white solid, followed by purification on silica gel afforded 1,3-Di(4-methoxycarbonylphenylthio)propane in excellent yield (0.536 gr. 78% yield). White solid: M.p. 71-73 ºC. IR (KBr): 3060, 2846, 2738 (HCO),
1686 (C=O), 1584, 1445 (C=C, Ar), 1392, 1299, 1195, 751, 694. $^1$H-NMR (CDCl$_3$): 7.92 ($d$, 4 H, Ar), 7.28 ($d$, 4 H, Ar), 3.91 ($s$, 3 H, OCH$_3$), 3.14 ($t$, 4 H, RH), 2.06 ($t$, 2 H, RH). $^{13}$C-NMR (CDCl$_3$): 30.02, 35.48, 52.81, 128.14, 130.47, 133.54, 144.60, 166.17. MS: 377 ([M+1]$^+$, 22), 376 ($M^+$, 100), 317 (47), 258 (61), 241 (14), 135 (7), 76 (24). Anal. calc. for C$_{19}$H$_{20}$O$_4$S$_2$: C 60.6, H 5.3; found: C 60.6, H 5.1.

1,3-Di(4-benzonitrilthio)propane (Table 3, Entry 5):

\[
\text{NO}_2 \text{NC} \xrightarrow{\text{SH} \text{SH}} \text{NC} \text{CN}
\]

4-nitrobenzonitrile: (0.60 g, 4.0 mmol); propane-1,3-dithiol: (0.22 g, 2.0 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 9 h; reaction temperature: 80 °C. The combined organic layer was dried over magnesium sulfate to adsorb the residual H$_2$O. The solution was evaporated in vacuum evaporator to give 3k as a dark yellow solid, followed by purification on silica gel afforded 1,3-Di(4-benzonitrilthio)propane in excellent yield (0.385 gr, 71% yield). Yellow solid: M.p. 102-104 °C. IR (KBr): 3060 (ArH), 2967 (RH), 2216 (C≡N), 1551, 1470 (C=C, Ar), 1351, 1214, 897. $^1$H-NMR (CDCl$_3$): 7.46-7.58 ($m$, 8H, ArH), 2.74 ($t$, 4H, RH), 2.08 ($m$, 2H, RH). $^{13}$C-NMR (CDCl$_3$): 30.54, 34.09, 116.41, 119.04, 132.01, 135.48, 141.46. MS: 311 ([M+1]$^+$, 20), 310 ($M^+$, 100), 258 (36), 208 (15), 102 (9), 76 (20). Anal. calc. for C$_{17}$H$_{14}$N$_2$S$_2$: C 65.77, H 4.55, N 9.02; found: C 65.68, H 4.60, N 9.07.
1,3-Di(2-nitrophenylthio)propane (Table 3, Entry 6):

\[
\begin{align*}
\text{NO}_2 & + \text{HS-SH} \rightarrow \text{NO}_2 \text{O}_2\text{N-S-S-}
\end{align*}
\]

1,2-dinitrobenzene: (0.620 g, 4 mmol); propane-1,3-dithiol: (0.22 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 8 h; reaction temperature: 80 °C. The combined organic layer was dried over magnesium sulfate to adsorb the residual H₂O. The solution was evaporated in vacuum evaporator to give 31 as a dark orange oil, followed by purification on silica gel afforded 1,3-Di(2-nitrophenylthio)propane in excellent yield (0.532 gr. 76% yield). Yellow solid: M.p. 97-100 °C. IR (KBr): 3064 (ArH), 1579, 1517, 1450, 1339, 791, 727, 711. $^1$H-NMR (CDCl₃): 7.92 (d, 4 H, Ar), 7.28 (d, 4 H, Ar), 3.91 (s, 3 H, OCH₃), 3.14 (t, 4 H, RH), 2.06 (t, 2 H, RH). $^{13}$C-NMR (CDCl₃): 30.01, 33.48, 122.61, 128.07, 129.19, 130.11, 132.12, 140.80. MS: 351 ([M+1]$^+$, 19), 350 (M$^+$, 100), 304 (61), 258 (37), 228 (24), 122 (16), 76(30), 45(19). Anal. calc. for C₁₅H₁₄N₂O₄S₂: C 51.41, H 4.03, N 7.99; found: C 51.34, H 4.11, N 8.07.

3-(2-Formylphenylthio)propanoic acid (Table 3, Entry 7):

\[
\begin{align*}
\text{HS-COOH} & + \text{NO}_2 \rightarrow \text{S-COOH}
\end{align*}
\]

2-nitrobenzaldehyde: (0.30 g, 2 mmol); 3-mercaptopropanoic acid: (0.212 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (7 ml); reaction time: 10 h; reaction temperature: 80 °C. After the completion of the reaction, water (100 ml) was added to the
mixture and the solution has been acidic with hydrochloric acid and then added sodium hydrogen carbonate slowly to give 3m as a light yellow solid that precipitated near PH=8. The solid collected over filtrations, dissolving in ethanol and re-crystallized that afforded sodium 3-(2-Formylphenylthio)-propanoate in excellent yield (0.372 gr. 80% yield). Light yellow solid: M.p. 168-171. IR (KBr): 3431, 3028 (ArH), 2855, 2756 (HCO), 1705, 1680 (C=O), 1559, 1416 (C=C, Ar), 1271, 1200, 1195, 754. $^1$H-NMR (CDCl$_3$): 10.38 (s, 1 H, HC=O), 7.87 (d, 1 H, Ar), 7.56 (t, 1 H, Ar), 7.46 (d, 1 H, Ar), 7.36 (t, 1 H Ar), 3.23 (t, 2H, RH), 2.76 (t, 2H, RH). $^{13}$C-NMR (CDCl$_3$): 28.02, 33.42, 126.11, 128.75, 132.35, 134.20, 134.38, 140.26, 177.37, 191.67. MS: 233 ([M+1]$^+$, 7), 232 (M$,^+$, 65), 165 (100), 203 (45), 105 (15). Anal. calc. for C$_{10}$H$_9$NaO$_3$S: C 51.72, H 3.91; found: C 51.60, H 3.84.

3-(4-Acetylphenylthio)propanoic acid (Table 3, Entry 8):

4-nitroacetophenone: (0.33 g, 2 mmol); 3-mercaptopropanoic acid: (0.212 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 10 h; reaction temperature: 80 °C. After the completion of the reaction, water (100 ml) was added to the mixture and the solution has been acidic with hydrochloric acid and then added sodium hydrogen carbonate slowly to give 3n as a yellow solid that precipitated near PH=8. The solid collected over a filtered and dissolving in ethanol and re-crystallized that afforded sodium 3-(4-acetylphenylthio)propanoate in excellent yield (0.492 gr. 73% yield). Yellow solid: M.p. 141-143. IR (KBr): 3024 (ArH), 2962, (RH), 1704, 1681 (C=O), 1550, 1468 (C=C, Ar), 1274, 1201,
1H-NMR (CDCl3): 7.54 (d, 2 H, Ar), 7.36 (d, 2H, Ar), 3.31 (t, 2H, RH), 2.64 (t, 2H, RH), 2.27 (s, 3H, CH3). 13C-NMR (CDCl3): 25.85, 30.40, 36.18, 129.42, 133.71, 134.53, 145.24, 176.36, 197.54. MS: 247 ([M+1]+, 8), 246 (M+, 65), 203 (31), 179 (100), 119 (44), 76 (39). Anal. calc. for C11H11NaO3S (214.28): C 53.65, H 4.50; found: C 53.58, H 4.57.

3-(2-Nitrophenylthio)propanoic acid (Table 3, Entry 9):

\[
\text{HS} \text{C} \text{O} + \begin{array}{c}
\text{NO}_2 \\
\text{NO}_2
\end{array}
\rightarrow \begin{array}{c}
\text{S} \\
\text{S}
\end{array}
\text{C} \text{O}
\]

1,2-dinitrobenzene: (0.336 g, 2 mmol); 3-mercaptopropanoic acid: (0.212 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 10 h; reaction temperature: 80 °C. After the completion of the reaction, water (100 ml) was added to the mixture and the solution has been acidic with hydrochloric acid and then added sodium hydrogen carbonate slowly to give 3o as a orange solid that precipitate near PH=8. The solid collected over a filtrations, dissolving in ethanol and re-crystallized that afforded sodium 3-(2-Nitrophenylthio)propanoate in excellent yield (0.350 gr. 71% yield). IR (KBr): 3035 (ArH), 1582, 1523, 1449, 1342, 794, 735, 702. 1H-NMR (CDCl3): 8.18 (d, 1 H, Ar), 8.08 (d, 1 H, Ar), 7.51 (t, 1 H, Ar), 7.28 (t, 1 H, Ar), 3.05 (t, 2H, RH), 2.87 (t, 2H, RH). 13C-NMR (CDCl3): 32.36, 37.68, 122.10, 128.74, 129.07, 130.94, 134.29, 141.17, 178.38. MS: 250 ([M+1]+, 4), 249 (M+, 37), 203 (100), 182 (20), 76 (34). Anal. calc. for C9H8NNaO4S: C 43.37, H 3.24, N 5.62; found: C 43.39, H 3.25, N 5.55.
3-(4-Formylphenylthio)propanoic acid (Table 3, Entry 10):

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\[
\begin{array}{c}
\text{HS} - \text{CH} - \text{CH} - \text{CH} - \text{COOH} + \text{NO}_2 \\
\text{O} \quad \text{S} \quad \text{O} \quad \text{O} \quad \text{H}
\end{array}
\]
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4-nitrobenzaldehyde: (0.30 g, 2 mmol); 3-mercaptopropanoic acid: (0.212 g, 2 mmol); magnesium methoxide: (0.43 g, 5.0 mmol); solvent: DMF (10 ml); reaction time: 10 h; reaction temperature: 80 °C. After the completion of the reaction, water (100 ml) was added to the mixture and the solution has been acidic with hydrochloric acid and then added sodium hydrogen carbonate slowly to give 3p as a pale yellow solid that precipitate near PH=8. The solid collected over a filtration, and dissolving in ethanol and re-crystallized that afforded sodium 3-(4-Formylphenylthio)propanoate in excellent yield (0.380 gr. 82% yield). Yellow solid: M.p. 132-133 °C. IR (KBr): 3008 (ArH), 2951, (RH), 2841, 2754 (HCO), 1701, 1684 (C=O), 1554, 1476 (C=C, Ar), 1279, 1211. \(^1\)H-NMR (CDCl\(_3\)): 10.32 (s, 1 H, HC=O), 7.47 (d, 2 H, Ar), 7.38 (d, 2H, Ar), 3.36 (t, 2H, RH), 2.75 (t, 2H, RH). \(^1\)C-NMR (CDCl\(_3\)): 32.86, 37.57, 130.52, 135.58, 136.18, 146.04, 177.62, 193.41. MS: 233 ([M+1]\(^+\), 2), 232 (M\(^+\), 17), 203 (44), 165 (100), 105 (28), 76 (18). Anal. calc. for C\(_{11}\)H\(_{11}\)NaO\(_3\)S: C 51.72, H 3.91; found: C 51.64, H 3.85.
6. Copy of $^1$H NMR and $^{13}$C NMR spectra for products