An Approach to the Synthesis of Thioesters and Selenoesters Promoted by Rongalite®

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Rongalite® promotes cleavage of diaryldisulfides generating the corresponding chalcogenolate anions that then undergo facile reaction with N-acylbenzotriazoles in the presence of K₂CO₃ to afford thioesters in good to excellent yields. The important features of this methodology are no requirement of metal catalysts, without any expensive reagent and high yields. It is noteworthy that the reactions of diphenyl diselenide with N-acylbenzotriazoles are also conducted to afford selenoesters in good yields under the standard conditions.

Keywords: Rongalite®, thioesters, selenoesters, N-acylbenzotriazoles, diaryl disulfide, diphenyldiselenide

Introduction

Thioesters have become increasingly important in the past few years because they have proven to be extremely useful intermediates for the preparation of heterocycles¹ and diverse ketones,² acyl radicals,³ and biologically active compounds.⁴ The typical procedure for the synthesis of thioesters involves the reaction of acylhalides with thiols,⁵ thiol sodium salts⁶ or disulfides.⁷ In addition, carboxylic acids are also transformed into thioesters by treatment with arylthiocyanates and tributyl phosphine in dichloromethane⁸ or with thiols by activated using tetramethyl fluoroformamidinium hexafluorophosphate,⁹ diphosgene¹⁰ and polyphosphate ester.¹¹ Recently, Katritzky and co-workers¹² introduced a new procedure for preparation of thioesters utilizing N-acylbenzotriazoles. Some other methods include palladium-catalyzed thiocarbonylation of iodoarenes with thiols in ionic liquid,¹³ rhodium-catalyzed alkylthio exchange reaction of thioester and disulfide,¹⁴ KF/Al₂O₃-catalyzed reaction of N-acylphthalimides with thiols¹⁵ and copper-catalyzed coupling of aryl iodides and thiobenzoic acid.¹⁶ However, these methods usually suffer from one or more limitations such as the use of unpleasant odor substrates thiols and expensive, toxic or metallic catalysts, long reaction times, unsatisfactory yields, as well as elevated temperature. Therefore, developing versatile approaches to synthesize thioesters still remains a highly desired goal in organic synthesis.

In continuation of our researches in developing novel synthetic routes for the formations of carbon-sulfur bonds¹⁷ and Rongalite®-promoted organic reactions,¹⁸ we here demonstrate further extension of this work together with application of Rongalite® (sodium formaldehyde sulfoxylate, HOCH₂SO₃Na) as an inexpensive reagent for the cleavage of diaryl disulfides or diphenyldiselenide and subsequent reaction with N-acylbenzotriazoles (Bt=1H-benzo[d][1,2,3]triazol-1-yl) to provide thioesters and selenoesters (Scheme 1).
Results and Discussion

At the onset of this work, we have investigated a variety of conditions with the model reaction of (1H-benzo[d] [1,2,3]triazol-1-yl)(phenyl)methanone (1a) and diphenyl disulfide (2a) using Rongalite® as promoter (Table 1).

First, we examined different solvents such as toluene, CH₂Cl₂, CH₃CN, H₂O, CH₃CH₂OH and DMF. Among the solvents screened, it was found that DMF is a much better solvent than all others tested (Table 1, entries 1-6).

Next, we evaluated the loading amount of Rongalite®. No reaction was observed in the absence of Rongalite® and both starting materials were recovered in quantitative yields (Table 1, entry 7). In order to confirm, the amount of Rongalite® required for the above transformation, different experiments were carried out by varying the amount of Rongalite® (Table 1, entries 8-12). These results clearly indicate that, the use of 3 equiv. of Rongalite® is sufficient to promote the reaction in excellent yield.

On the other hand, among the bases such as KF, Et₃N, K₃PO₄, K₂CO₃ and Cs₂CO₃ tested, K₂CO₃ was found to be the best (Table 1, entries 6 and 13-16). We also checked the effect of the amount of K₂CO₃, the desired product 3a was afforded in 49% without K₂CO₃, increasing the amount of K₂CO₃ to 2 equiv., it was found that 1.5 equiv. resulted in excellent yield (Table 1, entries 17-20).

Table 1. Screening conditions for the synthesis of thioesters

<table>
<thead>
<tr>
<th>Entry</th>
<th>Rongalite® (equiv.)</th>
<th>Solvent</th>
<th>Base</th>
<th>Yield (%)³</th>
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<td>1</td>
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<td>toluene</td>
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<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>H₂O</td>
<td>K₂CO₃</td>
<td>NR</td>
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<tr>
<td>3</td>
<td>3</td>
<td>CH₂Cl₂</td>
<td>K₂CO₃</td>
<td>NR</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>CH₃CH₂OH</td>
<td>K₂CO₃</td>
<td>trace</td>
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<tr>
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<tr>
<td>6</td>
<td>3</td>
<td>DMF</td>
<td>K₂CO₃</td>
<td>92</td>
</tr>
<tr>
<td>7</td>
<td>-</td>
<td>DMF</td>
<td>K₂CO₃</td>
<td>-</td>
</tr>
<tr>
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<td>1</td>
<td>DMF</td>
<td>K₂CO₃</td>
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<td>10</td>
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<td>K₂CO₃</td>
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<td>KF·2H₂O</td>
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<td>DMF</td>
<td>Et₃N</td>
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<td>K₃PO₄</td>
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<td>Cs₂CO₃</td>
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<td>K₂CO₃</td>
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<td>20</td>
<td>3</td>
<td>DMF</td>
<td>K₂CO₃</td>
<td>86</td>
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</table>

aReaction conditions: 1H-1,2,3-benzotriazol-1-yl (phenyl) methanone 1a (0.4 mmol), 1,2-diphenyl disulfane 2a (0.2 mmol), HOC₃H₄SO₃Na, base, solvent, r.t., 5 min. bIsolated yields. cWithout K₂CO₃. d0.5 equiv. of K₂CO₃. e1 equiv. of K₂CO₃. f2 equiv. of K₂CO₃. NR = No Reaction.
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Table 2. Synthesis of diverse thiol esters from N-acylbenzotriazoles with disulfides

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹ (1)</th>
<th>R²</th>
<th>time / min</th>
<th>Product</th>
<th>Yield / (%)³</th>
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<tbody>
<tr>
<td>1</td>
<td>C₆H₅ (1a)</td>
<td>C₆H₅</td>
<td>5</td>
<td>3a</td>
<td>92</td>
</tr>
<tr>
<td>2</td>
<td>C₆H₅ (1a)</td>
<td>p-(Me)C₆H₄</td>
<td>5</td>
<td>3b</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>C₆H₅ (1a)</td>
<td>p-(Cl)C₆H₄</td>
<td>5</td>
<td>3c</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>p-(MeO)C₆H₅ (1b)</td>
<td>C₆H₅</td>
<td>5</td>
<td>3d</td>
<td>97</td>
</tr>
<tr>
<td>5</td>
<td>p-(MeO)C₆H₅ (1b)</td>
<td>p-(Me)C₆H₄</td>
<td>5</td>
<td>3e</td>
<td>93</td>
</tr>
<tr>
<td>6</td>
<td>p-(MeO)C₆H₅ (1b)</td>
<td>p-(Cl)C₆H₄</td>
<td>5</td>
<td>3f</td>
<td>98</td>
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<tr>
<td>7</td>
<td>o-(IC₆H₄ (1c)</td>
<td>C₆H₅</td>
<td>15</td>
<td>3g</td>
<td>92</td>
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<tr>
<td>8</td>
<td>o-(IC₆H₄ (1c)</td>
<td>p-(Me)C₆H₄</td>
<td>15</td>
<td>3h</td>
<td>93</td>
</tr>
<tr>
<td>9</td>
<td>o-(IC₆H₄ (1c)</td>
<td>p-(Cl)C₆H₄</td>
<td>15</td>
<td>3i</td>
<td>88</td>
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<td>Et (1d)</td>
<td>C₆H₅</td>
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<td>3j</td>
<td>82</td>
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<tr>
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<td>Et (1d)</td>
<td>p-(Me)C₆H₄</td>
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<td>3k</td>
<td>83</td>
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<tr>
<td>12</td>
<td>Et (1d)</td>
<td>p-(Cl)C₆H₄</td>
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<td>80</td>
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<td>C₆H₅</td>
<td>20</td>
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<tr>
<td>14</td>
<td>2-furyl (1e)</td>
<td>p-(Me)C₆H₄</td>
<td>20</td>
<td>3n</td>
<td>67</td>
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</tbody>
</table>

³Reaction conditions: N-acylbenzotriazoles 1 (0.4 mmol), disulfides 2 (0.2 mmol), HOCH₂SO₂Na (0.6 mmol), K₂CO₃ (0.3 mmol), DMF (3 mL), r.t., 5-30 min. Isolated yield.

With the optimal conditions in hand, the scope of both disulfides and N-acylbenzotriazoles were explored and the results are summarized in (Table 2). As expected, this reaction proceeded smoothly and the desired products were afforded in good to excellent yields. A series of N-acylbenzotriazoles with either electron-donating or electron-withdrawing groups attached to aromatic ring were investigated. The substitution groups on the aromatic ring had no obvious effect on the yield. We also examined reaction of aliphatic N-acylbenzotriazole such as 1-(1H-benzo[d][1,2,3]triazol-1-yl)propan-1-one (1d), the desired products of 3j-3l were afforded in good yields (Table 2, entries 10-12). Similarly, 3m and 3n were afforded from heterocyclic N-acylbenzotriazole such as (1H-benzo[d][1,2,3]triazol-1-yl)(furan-2-yl)methanone (1e) in moderate yields (Table 2, entries 13-14). Unfortunately, attempt to acylation of dibenzyl disulfide, an aliphatic disulfide, with (1H-benzo[d][1,2,3]triazol-1-yl)(phenyl)methanone (1a) failed to give the expected thioesters.

Interestingly, when cinnamic N-acylbenzotriazole (1f) was used, the corresponding multi-sulfur substitution compounds of 4a-4c were afforded in moderate yields (Scheme 2).

On the other hand, we extended this method to prepare selenoesters starting from N-acylbenzotriazoles. Selenoesters are important intermediates in several organic reactions.
transformations. Selenoesters have been used as precursors of acyl radicals\textsuperscript{19} and anions,\textsuperscript{20} mild acyl transfer reagents,\textsuperscript{21} intermediates in the synthesis of ketones,\textsuperscript{22} and for asymmetric aldol reactions.\textsuperscript{23} Under the same conditions, we used diphenyldiselenide as source of selenolate anion, the reaction with \(N\)-acylbenzotriazoles afforded the corresponding selenoesters \(5a-5d\) in the presence of Rongalite\textsuperscript{®} and \(K_2CO_3\) (Scheme 3). However, acylation of aliphatic diselenide, such as dibenzyl diselenide and dimethyl diselenide, was still unsuccessful under the standard conditions.

In summary, \(N\)-acylbenzotriazoles have been introduced as new efficient \(S\)-acylating reagents. The reactions have been demonstrated under mild conditions to give diverse thioesters and selenoesters with moderate to good yield. Rongalite\textsuperscript{®} as an inexpensive promoting reagent for these transformations can be substantiated by short reaction times, which is an additional advantage of this protocol. Efforts to explore the detailed mechanism and further applications of the present system in other transformations using disulfide and diselenide as a reaction partner are ongoing in our group.

**Experimental**

Chemicals and solvents were either purchased or synthesized by standard techniques. The reagents of \(N\)-acylbenzotriazoles were synthesized by reaction of the corresponding carboxylic acids with BtH and SOCl\textsubscript{2} following the reported one-step general procedure.\textsuperscript{24} Melting points were recorded on Digital Melting Point Apparatus WRS-1B and are uncorrected. \(^1\)H NMR and \(^{13}\)C NMR spectra were taken on a Bruker DPX300 spectrometer using CDCl\textsubscript{3} or DMSO-\(d_6\) as the solvent with tetramethylsilane (TMS) as an internal standard at room temperature. Chemical shifts were given in \(\delta\) relative to TMS, the coupling constants \(J\) are given in Hz. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GCMS-QP2010). Elemental analysis was determined on a Carlo-Erba 1108 instrument.

**General procedure for the preparation of thioesters 3, 4 and selenoesters 5**

A mixture of \(N\)-acylbenzotriazoles 1 (0.4 mmol), diaryl disulfides 2 or diphenyldiselenide (0.2 mmol), Rongalite\textsuperscript{®} (3 equiv.), and \(K_2CO_3\) (1.5 equiv.) in DMF (3 mL) was stirred for the corresponding time at room temperature under air. After the reaction was finished, the reaction mixture was washed with water, extracted with ethyl acetate (3 × 10 mL), the organic phase was separated and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under vacuum.

The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product thioesters 3 or selenoesters 5. If cinnamic \(N\)-acylbenzotriazole 1f was used the reaction substrate, the amount of diaryl disulfides 2 is 0.4 mmol.

**Supplementary Information**

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

**Acknowledgments**

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**References**

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Description of the Products

Compounds 3a-3h, 3j-3m, 3o-3p, 4a-4d are known, compounds 3i, 3n and 3q are new and described below.

S-Phenyl thiobenzoate (3a)
White solid; mp 51-52 °C (Lit.1 mp 54-58 °C); 1H NMR (300 MHz, CDCl3): δ 7.45-7.62 (m, 8H), 8.02-8.05 (m, 2H); 13C NMR (125 MHz, CDCl3): δ 127.49, 127.54, 128.81, 129.30, 129.55, 133.70, 135.14, 136.75, 190.08.

S-4-Tolyl thiobenzoate (3b)
White solid; mp 70-71 °C (Lit.2 mp 65-66 °C); 1H NMR (300 MHz, CDCl3): δ 2.41 (s, 3H), 7.29-7.61 (m, 7H), 8.01-8.05 (m, 2H); 13C NMR (125 MHz, CDCl3): δ 21.29, 123.71, 127.38, 128.63, 130.02, 133.48, 134.94, 136.64, 139.71, 190.44.

S-4-Chlorophenyl thiobenzoate (3c)
White solid; mp 71-72 °C (Lit.3 mp 73-74°C); 1H NMR (300 MHz, CDCl3): δ 7.44-7.63 (m, 7H), 8.00-8.03 (m, 2H); 13C NMR (125 MHz, CDCl3): δ 125.81, 127.47, 128.78, 129.46, 133.82, 135.94, 136.27, 136.32, 189.55.

S-Phenyl, 4-methoxythiobenzoate (3d)
White solid; mp 93-94 °C (Lit.4 mp 98-101 °C); 1H NMR (300 MHz, CDCl3): δ 3.80 (s, 3H), 6.88 (d, J 9 Hz, 2H), 7.35-7.44 (m, 5H), 7.93 (d, J 9Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 55.55, 113.94, 127.71, 129.17, 129.36, 129.47, 135.19, 164.03, 188.57.

S-4-Tolyl 4-methoxythiobenzoate (3e)
White solid; mp 59-62 °C; 1H NMR (300 MHz, CDCl3): δ 2.41 (s, 3H), 3.89 (s, 3H), 6.96 (d, J 9 Hz, 2H), 7.25-7.28 (m, 2H), 7.40 (d, J 8Hz, 2H), 8.01 (d, J 9Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 20.31, 54.50, 112.87, 123.10, 128.65, 128.99, 134.08, 138.57, 162.93, 187.94.

S-4-Chlorophenyl 4-methoxythiobenzoate (3f)
White solid; mp 93-94 °C (Lit.5 mp 98-101 °C); 1H NMR (300 MHz, CDCl3): δ 3.81 (s, 3H), 6.88-6.91 (m, 2H), 7.35 (m, 4H), 7.92 (d, J 6.9 Hz, 2H); 13C NMR (125 MHz, CDCl3): δ 55.57, 114.01, 126.22, 129.16, 129.41, 129.77, 135.81, 136.39, 164.18, 188.00.

S-Phenyl 2-iodothiobenzoate (3g)
White solid; mp 93-94 °C (Lit.6 mp 98-101 °C); 1H NMR (300 MHz, CDCl3): δ 7.19 (t, 1H), 7.45-7.60 (m, 6H), 8.01-8.03 (m, 2H); 13C NMR (125 MHz, CDCl3): δ 127.49, 127.54, 128.81, 129.46, 133.82, 135.94, 136.27, 136.32, 189.55.

S-4-Tolyl 2-iodothiobenzoate (3h)
White solid; mp 94-95 °C; 1H NMR (300 MHz, CDCl3): δ 2.41 (s, 3H), 7.18 (t, 1H), 7.27-7.47 (m, 5H), 7.71 (d, J 8 Hz, 1H), 7.96 (d, J 8 Hz, 1H); 13C NMR (125 MHz, CDCl3): δ 21.54, 123.99, 128.00, 128.57, 129.98, 130.23, 132.36, 134.55, 140.08, 140.82, 142.58, 192.80.

S-4-Chlorophenyl 2-iodothiobenzoate (3i)
White solid; mp 90-92 °C; 1H NMR (300 MHz, CDCl3): δ 7.20-7.21 (m, 1H), 7.43-7.51 (m, 5H), 7.69-7.72 (m, 1H), 7.96-7.99 (m, 1H); 13C NMR (125 MHz, CDCl3): δ 21.54, 123.99, 128.00, 128.57, 129.98, 130.23, 132.36, 134.55, 140.08, 140.82, 142.58, 192.80.

ESI-MS: m/z (%): 376 ([M+2]+, 32), 374 (M+, 100). Anal. calc. for C13H8Cl3OS: C, 41.68; H, 2.15; Found: C, 41.72; H, 2.21.
S-Phenyl thiopropionate (3j)

Oil; 'H NMR (300 MHz, CDCl₃): δ 1.24 (t, J 7.5 Hz, 3H), 2.70 (q, J 7.49 Hz, 2H), 7.42-7.43 (m, 5H); ¹³C NMR (125 MHz, CDCl₃): δ 8.75, 36.09, 126.91, 128.12, 128.26, 133.50, 197.13.

S-4-Tolyl thiopropionate (3k)

Oil; 'H NMR (300 MHz, CDCl₃): δ 1.21 (t, J 7.47 Hz, 3H), 2.36 (s, 3H), 2.67 (q, J 7.50 Hz, 2H), 7.19-7.30 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 9.53, 21.20, 36.90, 124.30, 129.89, 134.39, 139.43, 198.57.

S-Phenyl 2-Furancarbothioate (3m)

White solid; mp 51-52 °C (Lit.¹⁵ mp 51-52 °C); 'H NMR (300 MHz, CDCl₃): δ 6.65-6.60 (m, 1H), 7.27 (d, J 3.6 Hz, 1H), 7.46-7.63 (m, 5H), 7.64 (s, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 111.39, 115.21, 125.23, 128.23, 128.55, 134.12, 145.45, 149.39, 177.59.

S-4-Chlorophenyl thiopropionate (3l)

Oil; 'H NMR (300 MHz, CDCl₃): δ 1.23 (t, J 7.48 Hz, 3H), 2.69 (q, J 7.48 Hz, 2H), 7.32-7.41 (m, 4H); ¹³C NMR (125 MHz, CDCl₃): δ 8.43, 36.09, 126.87, 128.12, 128.26, 133.50, 197.16.

S-Phenyl 3-phenyl-3-(phenylthio)propanethioate (4a)¹²

White solid; mp 74-76 °C; 'H NMR (300 MHz, CDCl₃): δ 3.27 (d, J 6 Hz, 2H), 4.75 (t, J 6 Hz, 1H), 7.23-7.43 (m, 15H); ¹³C NMR (125 MHz, CDCl₃): δ 49.28, 49.42, 127.37, 127.70, 128.82, 128.54, 128.94, 129.18, 129.48, 133.67, 134.39, 139.97, 194.59.

S-4-Chlorophenyl 3-(4-chlorophenylthio)-3-phenylpropanethioate (4c)

White solid; mp 63-65 °C; 'H NMR (300 MHz, CDCl₃): δ 3.24 (d, J 7.5 Hz, 2H), 4.69 (t, J 7.6 Hz, 1H), 7.19-7.43 (m, 13H); ¹³C NMR (125 MHz, CDCl₃): δ 49.22, 49.43, 123.9, 125.6, 1207.7, 128.6, 129.4, 130.9, 131.8, 134.2, 135.5, 135.8, 139.5, 141.9, 193.9. ESI-MS: m/z (%): 422 ([M+4]¹⁰, 10), 420 ([M+2]¹⁰, 36), 418 (M⁺, 100). Anal. calc. for C₁₉H₂₃Cl₂O₂S: C, 60.14; H, 3.85; Found: C, 60.08; H, 3.94.

Se-Phenyl selenobenzoate (5a)

Yellow solid; mp 40-41 °C (Lit.¹³ mp 37-38 °C); 'H NMR (300 MHz, CDCl₃): δ 7.43-7.52 (m, 5H), 7.60-7.63 (m, 3H), 7.93-7.96 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 125.78, 127.30, 128.91, 129.02, 129.33, 133.84, 136.29, 138.52, 192.30.

Se-phenyl 4-methoxyselenobenzoate (5b)

White solid; mp 56-58 °C (Lit.¹⁵ mp 61-62 °C); 'H NMR (300 MHz, CDCl₃): δ 6.96 (d, J 6.9Hz, 2H), 7.42-7.44 (m, 3H), 7.59-7.63 (m, 2H), 7.92 (d, J 6.9Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 55.52, 114.05, 125.97, 128.84, 129.22, 129.61, 131.25, 136.35, 164.14, 191.20.

Se-Phenyl 2-iodo seleno benzoate (5c)

Yellow solid; mp 59-60 °C (Lit.¹⁴ mp 76 °C); 'H NMR (300 MHz, CDCl₃): δ 7.18-7.18 (m, 1H), 7.43-7.45 (m, 4H), 7.63-7.69 (m, 3H), 7.96 (d, J 7.9Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ 90.20, 126.65, 128.01, 128.39, 129.17, 129.45, 132.53, 135.75, 140.97, 143.76, 195.61.

Se-Phenyl 2-Furancar box sul emo nate (5d)¹⁴

Oil; 'H NMR (300 MHz, CDCl₃): δ 6.59-6.60 (m, 1H), 7.21-7.23 (m, 1H), 7.41-7.44 (m, 3H), 7.58-7.63 (m, 3H); ¹³C NMR (125 MHz, CDCl₃): δ 112.77, 115.18, 124.74, 129.10, 129.32, 136.30, 146.57, 151.74, 180.72.

References


**Figure S1.** $^1$H NMR of 3a (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3a (125 MHz, CDCl$_3$).
Figure S2. $^1$H NMR of 3b (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3b (125 MHz, CDCl$_3$).
Figure S3. $^1$H NMR of 3c (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3c (125 MHz, CDCl$_3$).
Figure S4. $^1$H NMR of 3d (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3d (125 MHz, CDCl$_3$).
Figure S5. $^1$H NMR of 3e (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3e (125 MHz, CDCl$_3$).
Figure S6. $^1$H NMR of 3f (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3f (125 MHz, CDCl$_3$).
Figure S7. $^1$H NMR of 3g (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3g (125 MHz, CDCl$_3$).
Figure S8. $^1$H NMR of 3h (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3h (125 MHz, CDCl$_3$).
Figure S9. $^1$H NMR of 3i (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3i (125 MHz, CDCl$_3$).
Figure S10. $^1$H NMR of 3j (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3j (125 MHz, CDCl$_3$).
Figure S11. $^1$H NMR of 3k (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3k (125 MHz, CDCl$_3$).
Figure S12. $^1$H NMR of 3I (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3I (125 MHz, CDCl$_3$).
Figure S13. $^1$H NMR of 3m (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3m (125 MHz, CDCl$_3$).
Figure S14. $^1$H NMR of 3n (300 MHz, CDCl$_3$) and $^{13}$C NMR of 3n (125 MHz, CDCl$_3$).
Figure S15. $^1$H NMR of 4a (300 MHz, CDCl₃) and $^{13}$C NMR of 4a (125 MHz, CDCl₃).
Figure S16. $^1$H NMR of 4b (300 MHz, CDCl$_3$) and $^{13}$C NMR of 4b (125 MHz, CDCl$_3$).
Figure S17. $^1$H NMR of 4c (300 MHz, CDCl$_3$) and $^{13}$C NMR of 4c (125 MHz, CDCl$_3$).
Figure S18. $^1$H NMR of 5a (300 MHz, CDCl$_3$) and $^{13}$C NMR of 5a (125 MHz, CDCl$_3$).
Figure S19. $^1$H NMR of 5b (300 MHz, CDCl$_3$) and $^{13}$C NMR of 5b (125 MHz, CDCl$_3$).
Figure S20. $^1$H NMR of 5c (300 MHz, CDCl$_3$) and $^{13}$C NMR of 5c (125 MHz, CDCl$_3$).
Figure S21. $^1$H NMR of 5d (300 MHz, CDCl$_3$) and $^{13}$C NMR of 5d (125 MHz, CDCl$_3$).