Scalable Synthesis of 1,3,4,5-Tetraaryl Imidazolium Salts as Precursors of Sterically Demanding *N*-Heterocyclic Carbenes

Cengiz Azap^{a,1}Anna Christoffers^{a,2}Renat Kadyrov^{a,b} ^a EVONIK Resource Efficiency GmbH, Rodenbacher Chaussee 4, 63457 Hanau, Germany^b Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 25068 Řež, Czech Republic
kadyrov@iic.cas.cz

Received: 05.11.2019

Accepted after revision: 15.11.2019

Published online: 23.01.2020

DOI: 10.1055/s-0039-1690338; Art ID: so-2019-d0032-ppsp

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Abstract A convenient, large-scale, and cost-efficient synthesis of 4,5-diarylsubstituted *N,N*-diarylthioureas is described. A variety of 1,3,4,5-tetraaryl imidazolium salts with increasing electron donation and steric bulk of the *N*-aryl groups was synthesized in good yields. In the key step, readily available *N,N'*-diarylthioureas and benzoin/anisoin are coupled to give imidazole-2-thiones, followed by imidazolium salt formation by oxidative desulfurization. In this way, *N,N*-diarylthioureas with 2-methoxy, 2-methyl, and 2-isopropyl substituents could be obtained; the synthesis of their 2-*tert*-butyl, 2,6-dimethyl, and 2,6-diisopropyl analogues failed.

Key words carbene ligands, heterocycles, imidazolium salts, imidazolinthiones, thioureas

N-Heterocyclic carbenes (NHCs) have attracted considerable attention as alternatives for widely used phosphine complexes in homogeneous catalysis.³ Among them, sterically demanding and electron-rich carbenes have been successfully utilized in most catalytic transformations. Particu-

larly, QSAR analysis shows that imidazolylidene ligands with the backbone carbon atoms substituted by phenyl groups most efficiently promote catalytic activity of second-generation Ru catalysts in olefin metathesis.⁴ As a part of our efforts to provide access to effective metathesis catalysts, we were interested in a cost-effective and easily scalable synthesis of 1,3,4,5-tetraaryl imidazolium salts.⁵ Especially, we are seeking methods and procedures that are applicable industrially, avoiding chromatographic separation.

Over the past decades, many synthetic methods for the preparation of imidazolium salts have been reported.^{6,7} Although, the first synthesis of a tetraarylthiourea salt was established almost 50 years ago, examples of 4,5-diaryl-substituted imidazolium salts are rare.⁸ Recently, one highly sterically demanding example (*Ar* = Mes) was reported (Scheme 1, A).^{8d} Most recently, an aldimine coupling followed by cyclization with formaldehyde was used for the preparation of a wide variety of 4,5-diaryl-substituted NHCs with *para*-substituted *N*-phenyl groups (Scheme 1, B).^{8e,f} An interesting method for formation of 1,3,4,5-tetraarylthioureas is reaction of benzyl dianil with sodium in diethyl ether followed by addition of carbon disulfide (Scheme 1, C).^{8g}

Unfortunately, protocols A and C are not really scalable and protocol B is restricted to the preparation of imidazolium salts with *para*-substituents on the *N*-aryl groups. The

Scheme 1 Routes to 1,3,4,5-tetraarylthioureas

Scheme 2 Synthesis of 1,3,4,5-tetraarylimidazolium salts used in this work (route D)

strategy outlined in Scheme 2 appears to be the most convenient synthetic route for the large-scale and cost-efficient preparation of 4,5-diaryl-substituted imidazolium salts with sterically demanding *N*-aryl groups.

A number of synthetic protocols to access 1,3-disubstituted thioureas **1** have been reported.⁹ Past approaches include reaction of thiophosgene,¹⁰ isothiocyanates,¹¹ and 1,1'-thiocarbonyldiimidazole¹² with amines. Recently, the direct conversion of aniline and CS₂ into thiourea **1** has been developed.^{9b,13} After initial experiments, applying different published approaches, we found that *N,N*-diarylthioureas **1c-i** and **1m** could be generated in good yields by the reaction of the amine with the CS₂ in water; whereas heating under reflux for 6 h in diglyme was required for the formation of thioureas **1j** and **1k** bearing isopropyl- and *tert*-butyl groups at the *ortho*-positions, respectively. Furthermore, thioureas **1a**, **1b**, and **1n** were obtained in better yields by using the latter method. The substitution patterns of the *N*-aryl groups were selected on the basis of availability of the corresponding anilines on large scale, including electron-rich (**c**, **d**, **e**) and with increased steric demand (**g-k**, **m**, **n**) substrates.

It should be noted at this point that only benzoin and anisoin are commercially available; therefore, no more benzoin derivatives were used in this survey. To introduce other substitution patterns into the aryl-groups at positions 4 and 5 requires significant synthetic effort.¹⁴

Imidazolin-2-thiones were obtained in good to excellent yields by condensation of the *N,N*-diaryllureas with benzoin or anisoin in acetic acid,¹⁵ although the imidazolin-2-thione **2j**, bearing an isopropyl-group at the *ortho*-position, was isolated in reduced yield. Imidazolin-2-thiones with *ortho*-substituents were obtained as a pair of diastereoisomers but because the products of the subsequent oxidation, imidazolium salts **3g-4i**, do not exhibit atropoisomerism we did not separate the diastereoisomers. When the condensation was attempted with thioureas **1k**, **1m**, and **1n**, no imid-

azolin-2-thiones were produced. Instead 2-[(2-*tert*-butylphenyl)amino]-1,2-diphenylethanone (**5**) was isolated (see Table 1 below). Attempts to achieve the cyclization in boiling hexanol in the presence of catalytic amounts of hydrochloric acid¹⁶ were unsuccessful. It should be noted that attempts to form *N,N*-bis(2-*tert*-butylphenyl)-4,5-dimethylimidazolin-2-thione failed, as reported by Bach et al.¹⁷ Interestingly, reaction of *N,N*-bis(3-pyridinyl)thiourea **1l** with benzoin under similar conditions in acetic acid gave 2-[(3-pyridyl)amino]-1,2-diphenylethanone (**6**) in excellent yield.

Oxidative desulfurization was performed using H₂O₂ in acetic acid. The initial products of oxidative desulfurization – the hydrogen sulfates^{8b,c} were obtained as viscous syrups after careful removal of acetic acid. Ion exchange with NaClO₄ gave perchlorates **3a-j** effectively as analytically pure compounds. A mixture of two diastereoisomers was formed in the case of *ortho*-isopropyl-substituted imidazolium salt **3j**, as in the case of the 4,5-dimethyl analogue.¹⁷ We expect that the carbene generated from **3j** will not exhibit atropoisomerism because rotation around the *N*-Ar bond in the carbenes is not restricted.¹⁷ Therefore, no further attempts to separate the diastereoisomers were undertaken. Ion exchange with BaCl₂ furnished imidazolium chlorides **4a-i**. Unfortunately, desulfurization of **2j** and ion exchange with BaCl₂ did not give a crystalline product; therefore, no further attempts to purify this chloride salt were undertaken.

In conclusion, we have reported a convenient, large-scale and cost-efficient synthesis of 4,5-diarylsubstituted imidazolium salts with electron-rich, and sterically demanding *N*-aryl groups (Table 1). In this way, *N,N*-diarylimidazolium salts with *ortho*-methoxy, *ortho*-methyl, and *ortho*-isopropyl substituents can be obtained; whereas the synthesis of their 2-*tert*-butyl, 2,6-dimethyl, and 2,6-di-isopropyl analogues failed.

Table 1 Yields of the Prepared Compounds

Thiourea 1	Yield (%)	Imidazolin-2-thione 2	Yield (%)	Imidazolium perchlorate 3	Yield (%)	Imidazolium chloride 4	Yield (%)
47		76		88		68
85		86		90		73
78		88		74		89
72		61		31		45
68		87		64		54
56		91		89		81
56		61		54		58
98		63		51		69
62		76		70		70
56		31		81	–	–

Table 1 (continued)

Thiourea 1	Yield (%)	Imidazolin-2-thione 2	Yield (%)	Imidazolium perchlorate 3	Yield (%)	Imidazolium chloride 4	Yield (%)
38		51	–	–	–	–
1k		5
35		95	–	–	–	–
1l		6					

All starting materials and solvents were obtained from commercial suppliers and were used without further purification. 2-Methyl-5-*tert*-butylaniline was prepared according to the reported procedure.¹⁸ Melting points of all synthesized compounds were determined in open capillaries and are uncorrected. NMR spectra were recorded with a Bruker Avance 400 (¹H: 400 MHz, ¹³C: 101 MHz), Bruker Avance 600 (¹H: 601 MHz, ¹³C: 151 MHz), or Jeol ECZ-600 R (¹H: 600 MHz, ¹³C: 151 MHz) spectrometer; chemical shifts are given in δ ppm. IR spectra were recorded with a Bruker Tensor 27 spectrophotometer equipped with a 'GoldenGate' diamond ATR unit.

General Procedures for the Synthesis of Thioureas **1**

General Procedure A: A stirred mixture of aniline (1 mol), sulfur (2 g), and potassium carbonate (2 g) in water (700 mL) was heated to 80 °C, carbon disulfide (0.6–1.0 mol) was added dropwise over 60 min and the mixture was then heated to reflux for 6 h. After cooling to ambient temperature, the precipitated product was filtered off, washed with 1 M hydrochloric acid, then with water, sucked as dry as possible and the crude product was recrystallized from boiling ethanol.

General Procedure B: A mixture of 2-isopropylaniline (135.0 g, 1 mol), sulfur (1 g), and potassium carbonate (2 g) in diglyme (1 L) was heated to 80 °C, then carbon disulfide (38 g, 0.5 mol) was added over 1 h. The mixture was then slowly heated to 180 °C (bath temperature) and stirred at this temperature for 6 h. The reaction mixture was then allowed to cool overnight to ambient temperature. The precipitate was filtered off with suction, washed with 1 M hydrochloric acid, then with water, sucked as dry as possible, washed with hexane and dried in vacuum.

General Procedure for the Synthesis of Imidazolin-2-thiones **2**

Benzoin/anisoin (0.1 mol) and *N,N'*-diarylthiourea (0.1 mol) were heated to reflux in glacial acetic acid (150 mL) for 6–16 h and the mixture was then allowed to cool to ambient temperature. EtOH (50 mL) was added and the suspension was stirred in an ice bath to complete the precipitation. The precipitated product was filtered off with suction, washed with ethanol, then diethyl ether, and dried in vacuum.

General Procedure for the Synthesis of Perchlorates **3**

CAUTION: PERCHLORATES ARE POTENTIALLY EXPLOSIVE AND SHOULD BE TREATED AS POTENTIALLY HAZARDOUS COMPOUNDS.

To a solution of imidazolin-2-thione **2** (0.1 mol) in glacial acetic acid (200 mL), 35% aqueous H₂O₂ (34 mL, 0.4 mol) was added dropwise, allowing the temperature to rise to 50 °C, leading to a slightly turbid

mixture that was subsequently stirred at ambient temperature for 4 h. All volatiles were removed by rotary evaporation (**CAUTION: Do not evaporate to dryness. When preparing larger volumes, it is critical to ensure that any excess of hydrogen peroxide is destroyed before workup; otherwise, explosive decomposition may occur.**) The residue was dissolved in MeOH (200 mL) and treated with a solution of NaClO₄ (28.1 g, 0.2 mol) in a 2:1 (v/v) mixture of methanol/water (200 mL). A white solid precipitated upon additional stirring in an ice bath. The precipitate was filtered off and washed with water, diethyl ether and dried at r.t. in vacuum.

General Procedure for the Synthesis of Chlorides **4**

Hydrogen peroxide (35%; 53 mL, 0.65 mol) was added dropwise to a stirred suspension of imidazolin-2-thione **2** (0.2 mol) in glacial acetic acid (200 mL). An exothermic reaction occurred with the reaction mixture reaching 60 °C at the end of the addition and the solution was stirred for a further 4 h. All volatiles were removed by rotary evaporation (**CAUTION: Do not evaporate to dryness. When preparing larger volumes, it is critical to ensure that any excess of hydrogen peroxide is destroyed before workup; otherwise, explosive decomposition may occur.**) and the residue was dissolved in MeOH (500 mL). A solution of BaCl₂ (97.7 g, 0.4 mol) in water (200 mL) was added, and the suspension was filtered with suction through a G4 glass sinter covered with Celite®. The filtrate was evaporated and the residue was extracted with dichloromethane (3 × 100 mL). The combined organic layers were dried over MgSO₄, filtered, and the filtrate evaporated. The residue was triturated with diethyl ether, the solid product was filtered with suction, washed with diethyl ether, and dried in vacuum.

N,N'-Bis(4-ethoxycarbonylphenyl)thiourea (**1a**)¹⁹

According to **GP B**, the reaction of ethyl 4-aminobenzoate (82.6 g, 0.5 mol) and carbon disulfide (45 mL, 0.75 mol) and recrystallization from boiling water afforded **1a**. An analytically pure sample was obtained by recrystallization from ethanol.

Yield: 47% (44.1 g); mp 164–165 °C (Lit¹⁹ 165 °C).

IR (ATR): 3284br, 1681s, 1591s, 1524s, 1507s, 1408s, 1328s, 1286s, 1229s, 1174s, 849s, 765s, 734s, 650s, 614s, 572s cm⁻¹.

¹H NMR (400 MHz, DMSO-*d*₆): δ = 10.33 (s, 1 H), 7.93 (d, *J* = 8.7 Hz, 2 H), 7.69 (d, *J* = 8.7 Hz, 2 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

¹³C NMR (101 MHz, DMSO-*d*₆): δ = 179.09, 165.23, 143.71, 129.66, 125.04, 122.01, 60.44, 14.10.

Anal. Calcd for C₁₉H₂₀N₂O₄S: C, 61.27; H, 5.41; N, 7.52; S, 8.61. Found: C, 60.93; H, 5.38; N, 7.41; S, 8.72.

1,3-Bis(4-ethoxycarbonylphenyl)-4,5-diphenylimidazolin-2-thione (2a)

Reaction of thiourea **1a** (44.0 g, 0.12 mol) and benzoin (25.1 g, 0.12 mol) in acetic acid (170 mL) for 6 h afforded **2a**. An analytically pure sample was obtained by recrystallization from $\text{CHCl}_3/\text{EtOH}$.

Yield: 76% (49.1 g); mp 305–307 °C (dec.).

IR (ATR): 1715s, 1606m, 1512m, 1336s, 1269s, 1172m, 1099s, 741s, 693s, 597s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 8.02–7.96 (m, 4 H), 7.42–7.35 (m, 4 H), 7.11 (t, J = 7.4 Hz, 2 H), 7.05 (t, J = 7.6 Hz, 4 H), 6.92–6.87 (m, 4 H), 4.29 (q, J = 7.1 Hz, 4 H), 1.30 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 165.78, 165.69, 140.60, 130.54, 130.33, 130.26, 129.06, 128.64, 128.51, 128.47, 127.50, 61.25, 14.30.

Anal. Calcd for $\text{C}_{33}\text{H}_{28}\text{N}_2\text{O}_4\text{S}$: C, 72.24; H, 5.14; N, 5.11; S, 5.84. Found: C, 71.86; H, 5.15; N, 5.02; S, 5.96.

1,3-Bis(4-ethoxycarbonylphenyl)-4,5-diphenylimidazolium Perchlorate (3a)

Reaction of imidazolinethione **2a** (13.72 g, 25 mmol) and H_2O_2 (8.8 mL, 35%) in acetic acid (90 mL) afforded **3a**. An analytically pure sample was obtained by recrystallization from $\text{CHCl}_3/\text{Et}_2\text{O}$.

Yield: 88% (13.6 g); mp 336–338 °C (dec.).

IR (ATR): 1715s, 1607w, 1542m, 1276s, 1086s, 1020m, 772s, 702s, 621s cm^{-1} .

^1H NMR (601 MHz, $\text{DMSO}-d_6$): δ = 10.31 (s, 1 H), 8.14 (d, J = 8.5 Hz, 4 H), 7.70 (d, J = 8.5 Hz, 4 H), 7.41 (t, J = 7.3 Hz, 2 H), 7.36 (t, J = 7.4 Hz, 4 H), 7.26 (d, J = 7.2 Hz, 4 H), 4.35 (q, J = 7.1 Hz, 4 H), 1.34 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 165.05, 138.22, 137.58, 132.10, 132.06, 131.33, 131.04, 130.68, 129.35, 127.44, 125.07, 61.87, 14.54.

Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_8$: C, 64.24; H, 4.74; N, 4.54. Found: C, 64.05; H, 4.67; N, 4.42.

1,3-Bis(4-ethoxycarbonylphenyl)-4,5-diphenylimidazolium Chloride (4a)

Reaction of imidazolinethione **2a** (13.72 g, 25 mmol) and H_2O_2 (18 mL, 35%) in acetic acid (90 mL) afforded **4a** after crystallization from $\text{CH}_2\text{Cl}_2/\text{EtOAc}$.

Yield: 68% (9.4 g); mp 277–278 °C.

IR (ATR): 1702s, 1608w, 1560m, 1260s, 1175w, 1095s, 1025m, 869s, 771s, 692s cm^{-1} .

^1H NMR (601 MHz, $\text{DMSO}-d_6$): δ = 10.39 (s, 1 H), 8.15–8.11 (m, 4 H), 7.73 (d, J = 8.6 Hz, 4 H), 7.42–7.39 (m, 2 H), 7.36 (t, J = 7.4 Hz, 4 H), 7.30–7.26 (m, 4 H), 4.35 (q, J = 7.1 Hz, 4 H), 1.34 (t, J = 7.1 Hz, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 165.07, 138.26, 137.62, 132.06, 132.05, 131.36, 130.99, 130.65, 129.32, 127.50, 125.12, 61.86, 14.55.

Anal. Calcd for $\text{C}_{33}\text{H}_{29}\text{ClN}_2\text{O}_4$: C, 71.67; H, 5.29; N, 5.07. Found: C, 71.28; H, 5.20; N, 4.86.

N,N'-Bis(4-bromophenyl)thiourea (1b)^{20,21}

According to **GP B**, reaction of 4-bromoaniline (86.0 g, 0.5 mol) and carbon disulfide (45 mL, 0.75 mol), afforded **1b**. An analytically pure sample was obtained by recrystallization from ethanol.

Yield: 85% (81.8 g); mp 188–189 °C (Lit.²⁰ 188 °C).

IR (ATR): 3206m, 3013m, 1588m, 1530s, 1482s, 1305s, 1068s, 1008s, 821s, 717s cm^{-1} .

^1H NMR (601 MHz, $\text{DMSO}-d_6$): δ = 9.94 (s, 2 H), 7.54–7.51 (m, 4 H), 7.49–7.45 (m, 4 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 180.09, 139.25, 131.74, 126.11, 117.04.

NMR spectroscopic data for **1b** match those previously described.²¹

1,3-Bis(4-bromophenyl)-4,5-diphenylimidazolin-2-thione (2b)

Reaction of thiourea **1b** (77.22 g, 0.2 mol) and benzoin (42.42 g, 0.2 mol) in acetic acid (200 mL) for 11 h afforded **2b**.

Yield: 86% (96.8 g); mp 319–320 °C.

IR (ATR): 2948w, 1487s, 1356s, 1069m, 1012m, 749s, 696s, 661m cm^{-1} .

^1H NMR (601 MHz, $\text{DMSO}-d_6$): δ = 7.63–7.59 (m, 2 H), 7.37–7.33 (m, 2 H), 7.25–7.19 (m, 3 H), 7.16 (dt, J = 3.9, 2.3 Hz, 2 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 165.29, 136.55, 132.24, 131.75, 131.10, 129.10, 128.72, 128.51, 128.07, 122.03.

Anal. Calcd for $\text{C}_{27}\text{H}_{18}\text{Br}_2\text{N}_2\text{S}$: C, 57.67; H, 3.23; N, 4.98; S, 5.70. Found: C, 57.38; H, 3.30; N, 4.79; S, 5.92.

1,3-Bis(4-bromophenyl)-4,5-diphenylimidazolium Perchlorate (3b)

Reaction of imidazolinethione **2b** (22.49 g, 40 mmol) and H_2O_2 (13.7 mL, 35%) in acetic acid (90 mL) afforded product **3b**.

Yield: 90% (22.6 g); mp 319–320 °C (dec.).

IR (ATR): 1545m, 1485s, 1079s, 1012s, 1013s, 831m, 751s, 696s cm^{-1} .

^1H NMR (601 MHz, $\text{DMSO}-d_6$): δ = 10.18 (s, 1 H), 7.84–7.80 (m, 4 H), 7.52–7.48 (m, 4 H), 7.43–7.39 (m, 2 H), 7.39–7.34 (m, 4 H), 7.28–7.25 (m, 4 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 138.03, 133.30, 133.27, 132.00, 131.36, 130.64, 129.32, 128.99, 125.12, 124.33.

Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{Br}_2\text{ClN}_2\text{O}_4$: C, 51.42; H, 3.04; N, 4.44. Found: C, 51.19; H, 3.09; N, 4.35.

1,3-Bis(4-bromophenyl)-4,5-diphenylimidazolium Chloride (4b)

Reaction of imidazolinethione **2b** (22.49 g, 40 mmol) and H_2O_2 (12 mL, 35%) in acetic acid (100 mL) afforded product **4b** after crystallization from $\text{CH}_2\text{Cl}_2/\text{EtOAc}$.

Yield: 73% (16.5 g); mp 292–293 °C (dec.).

IR (ATR): 2970br, 1547s, 1483s, 1249m, 1017s, 830s, 750s, 695s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 10.56 (s, 1 H), 7.58 (d, J = 8.7 Hz, 4 H), 7.49 (d, J = 8.7 Hz, 4 H), 7.29 (t, J = 7.5 Hz, 2 H), 7.21 (t, J = 7.9 Hz, 4 H), 7.11 (dd, J = 8.2, 1.0 Hz, 4 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 137.41, 133.11, 132.32, 132.26, 130.91, 130.40, 129.04, 128.08, 124.99, 124.36.

Anal. Calcd for $\text{C}_{27}\text{H}_{19}\text{Br}_2\text{ClN}_2$: C, 57.22; H, 3.38; N, 4.94. Found: C, 56.84; H, 3.42; N, 4.85.

N,N'-Bis(4-methoxyphenyl)thiourea (1c)^{22–24}

According to **GP A**, reaction of *p*-anisidine (123.2 g, 1 mol) and carbon disulfide (33 mL, 0.55 mol), afforded **1c** after recrystallization from EtOH.

Yield: 78% (224.9 g); mp 194–195 °C (dec.) (Lit. 188–189 °C,²² 198 °C²³).

IR (ATR): 3222br, 1612m, 1537s, 1507s, 1337s, 1284s, 1235s, 1032s, 837s, 725s, 671s, 581s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.37 (s, 2 H), 7.29 (d, J = 8.9 Hz, 4 H), 6.86 (d, J = 8.9 Hz, 4 H), 3.71 (s, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 180.80, 157.07, 132.81, 126.61, 114.19, 55.78.

NMR spectroscopic data of **1c** match those previously described.²⁴

1,3-Bis(4-methoxyphenyl)-4,5-diphenylimidazolin-2-thione (**2c**)

Reaction of thiourea **1c** (34.41 g, 0.12 mol) and benzoin (25.2 g, 0.12 mol) in acetic acid (100 mL) for 11 h and crystallization of the resultant product from EtOH afforded **2c**.

Yield: 88% (48.87 g); mp 271–272 °C.

IR (ATR): 1597m, 1511s, 1441s, 1340s, 1298s, 1241s, 1165s, 1028s, 836s, 784s, 696s, 576s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 7.23 (d, J = 8.6 Hz, 4 H), 7.13 (dt, J = 8.2, 4.1 Hz, 6 H), 7.09 (d, J = 6.6 Hz, 4 H), 6.88 (d, J = 8.6 Hz, 4 H), 3.71 (s, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 165.95, 159.23, 131.14, 130.76, 130.18, 128.81, 128.69, 128.61, 114.36, 55.82.

Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$: C, 74.97; H, 5.21; N, 6.03; S, 6.90. Found: C, 74.69; H, 5.20; N, 5.95; S, 6.92.

1,3-Bis(4-methoxyphenyl)-4,5-diphenylimidazolium Perchlorate (**3c**)

Reaction of imidazolinethione **2c** (10.0 g, 22 mmol) and H_2O_2 (7.8 mL, 35%) in acetic acid (100 mL) afforded **3c** after recrystallization from MeOH (1 L).

Yield: 74% (8.45 g); mp 289–291 °C.

IR (ATR): 1546m, 1508s, 1447m, 1253s, 1177m, 1088s, 833s, 697s, 621s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.97 (s, 1 H), 7.48–7.40 (m, 4 H), 7.32 (dd, J = 11.1, 3.9 Hz, 2 H), 7.28 (t, J = 7.5 Hz, 4 H), 7.25–7.20 (m, 4 H), 7.04 (dd, J = 14.0, 5.5 Hz, 4 H), 3.75 (s, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 160.88, 137.83, 132.27, 131.46, 130.37, 129.13, 128.44, 126.82, 125.76, 115.28, 56.18.

Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{ClN}_2\text{O}_6$: C, 65.35; H, 4.73; N, 5.26. Found: C, 64.64; H, 4.52; N, 4.95.

1,3-Bis(4-methoxyphenyl)-4,5-diphenylimidazolium Chloride (**4c**)^{8c}

Reaction of imidazolinethione **2c** (23.2 g, 50 mmol) and H_2O_2 (18 mL, 35%) in acetic acid (150 mL) afforded **4c**. An analytical pure sample was obtained by recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$. Yield: 89% (20.83 g); mp 143–144 °C.

IR (ATR): 3231w, 1550s, 1507s, 1449m, 1236s, 1177s, 1019s, 834s, 785s, 699s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 10.37 (s, 1 H), 7.63 (d, J = 8.9 Hz, 4 H), 7.32 (t, J = 7.5 Hz, 2 H), 7.25 (t, J = 7.7 Hz, 4 H), 7.17 (d, J = 7.4 Hz, 4 H), 6.90 (d, J = 8.9 Hz, 4 H), 3.79 (s, 6 H).

^1H NMR data were in accordance with reported data.^{8c}

^{13}C NMR (151 MHz, CDCl_3): δ = 160.72, 137.32, 132.10, 130.95, 129.96, 128.80, 127.81, 126.11, 125.03, 114.89, 55.58.

Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{ClN}_2\text{O}_2$: C, 74.27; H, 5.37; N, 5.97. Found: C, 73.59; H, 5.40; N, 5.57.

N,N'-Bis(4-dimethylaminophenyl)thiourea (**1d**)²²

According to **GP A**, reaction of *N,N*-dimethyl-*p*-phenylenediamine (50.0 g, 0.37 mol) and carbon disulfide (12 mL, 0.2 mol), followed by recrystallization from EtOH afforded **1d**.

Yield: 72% (41.9 g); mp 189–190 °C (dec.) (Lit.²² 185–186 °C).

IR (ATR): 3300–3100br, 2884m, 1611s, 1519s, 1367s, 1231s, 1174s, 945s, 818s, 721s, 673s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.08 (s, 2 H), 7.16 (d, J = 8.9 Hz, 4 H), 6.65 (d, J = 9.0 Hz, 4 H), 2.84 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 180.51, 148.67, 129.09, 126.39, 112.81, 40.93.

Anal. Calcd for $\text{C}_{17}\text{H}_{22}\text{N}_4\text{S}$: C, 64.93; H, 7.05; N, 17.82; S, 10.20. Found: C, 64.70; H, 7.02; N, 17.71; S, 10.31.

1,3-Bis(4-dimethylaminophenyl)-4,5-di(4-methoxyphenyl)imidazolin-2-thione (**2d**)

Reaction of thiourea **1d** (31.45 g, 0.1 mol) and anisoin (27.2 g, 0.1 mol) in acetic acid (100 mL) for 7 h afforded **2d** after recrystallization from EtOH. An analytically pure sample was obtained by recrystallization from $\text{CHCl}_3/\text{EtOH}$.

Yield: 61% (33.6 g); mp 250–251 °C (dec.).

IR (ATR): 1610s, 1516s, 1342s, 1247s, 1172s, 1026s, 803s, 757s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 7.17 (d, J = 8.2 Hz, 4 H), 6.91 (d, J = 8.4 Hz, 4 H), 6.66 (d, J = 8.4 Hz, 4 H), 6.64 (d, J = 8.4 Hz, 4 H), 3.71 (s, 6 H), 2.95 (s, 12 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 165.44, 158.95, 149.83, 131.77, 129.45, 128.03, 126.22, 121.11, 113.57, 112.16, 55.06, 40.48.

Anal. Calcd for $\text{C}_{33}\text{H}_{34}\text{N}_4\text{O}_2\text{S}$: C, 71.97; H, 6.22; N, 10.17; S, 5.82. Found: C, 71.64; H, 6.11; N, 10.02; S, 5.39.

1,3-Bis(4-dimethylaminophenyl)-4,5-di(4-methoxyphenyl)imidazolium Perchlorate (**3d**)

Reaction of imidazolinethione **2d** (10.4 g, 20 mmol) and H_2O_2 (6 mL, 35%) in acetic acid (90 mL) afforded, after crystallization from methanol, product **3d**. An analytically pure sample was obtained by recrystallization from $\text{CHCl}_3/\text{MeOH}$.

Yield: 31% (3.4 g); mp 174–175 °C.

IR (ATR): 1612m, 1518s, 1244s, 1180m, 1089s, 818s, 620s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.73 (s, 1 H), 7.24 (d, J = 8.6 Hz, 4 H), 7.13 (d, J = 8.4 Hz, 4 H), 6.84 (d, J = 8.5 Hz, 4 H), 6.71 (d, J = 8.8 Hz, 4 H), 3.67 (s, 6 H), 2.90 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 160.43, 151.36, 136.90, 132.88, 131.92, 127.53, 122.40, 118.13, 114.59, 112.27, 55.67, 40.34.

Anal. Calcd for $\text{C}_{33}\text{H}_{35}\text{ClN}_4\text{O}_6$: C, 64.02; H, 5.70; N, 9.05. Found: C, 63.62; H, 5.32; N, 8.91.

1,3-Bis(4-dimethylaminophenyl)-4,5-di(4-methoxyphenyl)imidazolium Chloride (**4d**)

Reaction of imidazolinethione **2d** (12.21 g, 22 mmol) and H_2O_2 (8 mL, 35%) in acetic acid (80 mL) afforded **4d**.

Yield: 45% (5.53 g); mp 110–112 °C.

IR (ATR): 1715m, 1518s, 1445m, 1228s, 1178s, 1025m, 821s, 605s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 8.52 (s, 1 H), 7.32 (d, J = 9.0 Hz, 1 H), 7.12 (d, J = 8.8 Hz, 1 H), 6.69 (d, J = 8.8 Hz, 1 H), 6.59 (d, J = 9.0 Hz, 1 H), 3.70 (s, 6 H), 2.93 (s, 12 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 160.26, 150.99, 134.22, 132.55, 132.41, 127.19, 122.05, 117.56, 114.05, 112.10, 55.17, 40.24.

Anal. Calcd for $\text{C}_{33}\text{H}_{35}\text{ClN}_4\text{O}_2$: C, 71.40; H, 6.36; N, 10.09. Found: C, 71.01; H, 6.34; N, 9.87.

***N,N'*-Bis(3,5-dimethylphenyl)thiourea (1e)²⁵**

According to **GP A**, reaction of 3,5-dimethylaniline (121.2 g, 1 mol) and carbon disulfide (42 g, 0.55 mol), after recrystallization from EtOH (800 mL) afforded **1e**.

Yield: 68% (96.1 g); mp 150–151 °C.

IR (ATR): 3347s, 3200–2900br, 1607s, 1536s, 1508s, 1303s, 1272s, 1228s, 854s, 700s, 652s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.49 (s, 2 H), 7.02 (s, 4 H), 6.73 (s, 2 H), 2.21 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 179.98, 139.74, 137.96, 126.58, 122.07, 21.48.

NMR data were in accordance with those described.²⁵

1,3-Bis(3,5-dimethylphenyl)-4,5-diphenylimidazolin-2-thione (2e)

Reaction of thiourea **1e** (67.5 g, 0.25 mol) and benzoin (53.0 g, 0.25 mol) in acetic acid (100 mL) for 10 h afforded **2e**.

Yield: 87% (100.2 g); mp 239–240 °C.

IR (ATR): 1594m, 1328s, 1258w, 723s, 689s, 610s, 581s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 7.24–7.01 (m, 10 H), 6.92 (s, 6 H), 2.17 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 165.50, 138.29, 137.31, 131.08, 130.24, 128.81, 128.64, 128.58, 128.53, 127.20, 21.18.

Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{S}$: C, 80.83; H, 6.13; N, 6.08; S, 6.96. Found: C, 79.95; H, 6.11; N, 5.95; S, 7.32.

1,3-Bis(3,5-dimethylphenyl)-4,5-diphenylimidazolium Perchlorate (3e)

Reaction of imidazolinethione **2e** (37.1 g, 80 mmol) and H_2O_2 (28 mL, 35%) in acetic acid (150 mL) afforded **3e**. An analytically pure sample was obtained by recrystallization from $\text{CHCl}_3/\text{Et}_2\text{O}$.

Yield: 64% (27.1 g); mp 276–277 °C.

IR (ATR): 1542m, 1083s, 864m, 772m, 697s, 621s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 10.00 (s, 1 H), 7.36–7.32 (m, 2 H), 7.30 (t, J = 7.4 Hz, 4 H), 7.22 (d, J = 7.3 Hz, 4 H), 7.16 (s, 2 H), 7.12 (s, 4 H), 2.23 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 139.68, 137.65, 133.99, 132.19, 132.04, 131.42, 130.49, 129.18, 125.61, 124.42, 21.18.

Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{ClN}_2\text{O}_4$: C, 70.38; H, 5.53; N, 5.30. Found: C, 69.91; H, 5.51; N, 5.01.

1,3-Bis(3,5-dimethylphenyl)-4,5-diphenylimidazolium Chloride (4e)

Reaction of imidazolinethione **2e** (6.9 g, 15 mmol) and H_2O_2 (5.3 mL, 35%) in acetic acid (50 mL) afforded **4e**.

Yield: 54% (3.77 g); mp 222–224 °C (dec.).

IR (ATR): 1719m, 1540m, 1256m, 1022m, 859m, 690s cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 10.35 (s, 1 H), 7.35–7.30 (m, 2 H), 7.27 (d, J = 2.5 Hz, 2 H), 7.25–7.22 (m, 6 H), 7.19–7.14 (m, 4 H), 7.04 (s, 2 H), 2.28 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 139.80, 137.06, 133.20, 132.00, 131.93, 130.90, 129.90, 128.70, 125.12, 123.93, 21.14.

Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{ClN}_2$: C, 80.07; H, 6.29; N, 6.02. Found: C, 79.52; H, 6.22; N, 5.85.

1,3-Bis(3,5-dimethylphenyl)-4,5-di(4-methoxyphenyl)imidazolin-2-thione (2f)

Reaction of thiourea **1e** (96.0 g, 0.34 mol) and anisoin (91.0 g, 0.34 mol) in acetic acid (400 mL) for 12 h, after recrystallization from EtOH (1 L) afforded **2f**.

Yield: 91% (161.2 g); mp 267–268 °C (dec.).

IR (ATR): 1605m, 1505s, 1364s, 1327s, 1293s, 1246s, 1174s, 827s, 755s cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 6.97–6.93 (m, 6 H), 6.92–6.87 (m, 4 H), 6.65–6.60 (m, 4 H), 3.69 (s, 6 H), 2.27 (s, 12 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 164.71, 159.14, 138.47, 137.00, 131.72, 130.37, 128.04, 126.74, 120.70, 113.57, 55.08, 21.23.

Anal. Calcd for $\text{C}_{33}\text{H}_{32}\text{N}_2\text{O}_2\text{S}$: C, 76.12; H, 6.19; N, 5.38; S, 6.16. Found: C, 75.89; H, 6.20; N, 5.19; S, 6.49.

1,3-Bis(3,5-dimethylphenyl)-4,5-di(4-methoxyphenyl)imidazolium Perchlorate (3f)

Reaction of imidazolinethione **2f** (52.0 g, 0.1 mol) and H_2O_2 (34 mL, 35%) in acetic acid (150 mL) afforded **3f**.

Yield: 89% (52.3 g); mp 274–275 °C (dec.).

IR (ATR): 1614m, 1506m, 1473m, 1255s, 1082s, 841s, 620s cm^{-1} .

^1H NMR (400 MHz, CDCl_3): δ = 9.70 (s, 1 H), 7.22 (s, 4 H), 7.09 (t, J = 8.4 Hz, 4 H), 7.02 (s, 2 H), 6.72 (d, J = 8.4 Hz, 4 H), 3.72 (s, 6 H), 2.27 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 160.63, 139.62, 137.09, 134.17, 132.89, 132.12, 131.84, 124.52, 117.63, 114.63, 55.71, 21.20.

Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{ClN}_2\text{O}_6$: C, 67.28; H, 5.65; N, 4.76. Found: C, 66.57; H, 5.61; N, 4.65.

1,3-Bis(3,5-dimethylphenyl)-4,5-di(4-methoxyphenyl)imidazolium Chloride (4f)

Reaction of imidazolinethione **2f** (104.0 g, 0.2 mol) and H_2O_2 (53 mL, 35%) in acetic acid (200 mL) afforded **4f**.

Yield: 81% (84.5 g); mp 216–217 °C (dec.).

IR (ATR): 1543m, 1249s, 1176s, 1023s, 833s, 695s, 584s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.94 (s, 1 H), 7.18–7.13 (m, 10 H), 6.84 (d, J = 7.9 Hz, 4 H), 3.66 (d, J = 0.7 Hz, 6 H), 2.23 (s, 12 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 160.65, 139.57, 137.14, 134.19, 132.93, 132.08, 131.85, 124.55, 117.68, 114.62, 55.74, 21.18.

Anal. Calcd for $\text{C}_{33}\text{H}_{33}\text{ClN}_2\text{O}_2$: C, 75.48; H, 6.33; Cl, N, 5.34. Found: C, 74.65; H, 6.24; N, 5.06.

***N,N'*-Bis(2-methoxyphenyl)thiourea (1g)²⁶**

According to **GP A**, reaction of *o*-anisidine (61.53 g, 0.5 mol) and carbon disulfide (22.8 g, 0.3 mol), after recrystallization from EtOH (200 mL) afforded **1g**.

Yield: 56% (39.4 g); mp 136–137 °C (Lit.²⁶ 132–134 °C).

IR (ATR): 3200–3100 br, 2958 br, 1509s, 1490s, 1455s, 1313s, 1258s, 1231s, 1163s, 1112s, 1024s, 778s, 754s, 645s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.33 (s, 1 H), 7.93 (dd, J = 7.9, 1.0 Hz, 1 H), 7.14–7.09 (m, 1 H), 7.03 (dd, J = 8.2, 1.1 Hz, 1 H), 6.92–6.87 (m, 1 H), 3.79 (s, 3 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 180.00, 152.26, 128.15, 126.31, 120.34, 111.96, 56.23.

Anal. Calcd for $\text{C}_{15}\text{H}_{16}\text{N}_2\text{O}_2\text{S}$: C, 62.48; H, 5.59; N, 9.71; S, 11.12. Found: C, 62.41; H, 5.60; N, 9.65; S, 11.10.

1,3-Bis(2-methoxyphenyl)-4,5-diphenylimidazolin-2-thione (2g)

Reaction of thiourea **1g** (39.4 g, 0.14 mol) and benzoin (28.8 g, 0.14 mol) in acetic acid (70 mL) for 6 h afforded **2g**. An analytically pure sample was obtained by recrystallization from CHCl_3 .

Yield: 61% (38.5 g); mp 242–243 °C.

IR (ATR): 1502m, 1377m, 1346s, 1253m, 1019m, 750s, 700s, 570s cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 7.59 (d, J = 7.6 Hz, 2 H), 7.32 (t, J = 7.7 Hz, 2 H), 7.14–7.10 (m, 2 H), 7.06 (dd, J = 15.0, 7.6 Hz, 6 H), 7.02 (d, J = 7.4 Hz, 4 H), 6.83 (d, J = 8.3 Hz, 2 H), 3.53 (s, 6 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 154.73, 131.27, 130.44, 129.91, 128.77, 128.71, 127.89, 127.74, 125.95, 120.66, 112.35, 55.54.

Anal. Calcd for $\text{C}_{29}\text{H}_{24}\text{N}_2\text{O}_2\text{S}$: C, 74.97; H, 5.21; N, 6.03; S, 6.90. Found: C, 74.37; H, 5.20; N, 5.89; S, 6.91.

1,3-Bi-(2-methoxyphenyl)-4,5-diphenylimidazolium Perchlorate (3g)

Reaction of imidazolinethione **2g** (23.1 g, 50 mmol) and H_2O_2 (18 mL, 35%) in acetic acid (50 mL) afforded **3g**.

Yield: 54% (14.4 g); mp 197–200 °C.

IR (ATR): 1548m, 1442m, 1259m, 1083s, 761s, 695s, 623s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 9.95 (s, 1 H), 7.56 (dd, J = 7.8, 1.4 Hz, 2 H), 7.50–7.43 (m, 2 H), 7.29–7.23 (m, 2 H), 7.20 (t, J = 7.6 Hz, 4 H), 7.12 (dd, J = 12.1, 4.6 Hz, 2 H), 7.11–7.07 (m, 4 H), 7.04 (dd, J = 11.3, 4.0 Hz, 2 H), 3.56 (s, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 153.89, 139.22, 133.12, 132.37, 130.56, 130.36, 129.08, 128.98, 125.65, 122.30, 121.50, 113.64, 56.58.

Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{ClN}_2\text{O}_6$: C, 65.35; H, 4.73; N, 5.26. Found: C, 64.84; H, 4.71; N, 5.23.

1,3-Bis(2-methoxyphenyl)-4,5-diphenylimidazolium Chloride (4g)

Reaction of imidazolinethione **2g** (18.57 g, 40 mmol) and H_2O_2 (14 mL, 35%) in acetic acid (100 mL) afforded **4g**.

Yield: 58% (10.9 g); mp 181–183 °C.

IR (ATR): 1547m, 1286s, 1256s, 1127w, 1018s, 752s, 701s, 666m cm^{-1} .

^1H NMR (601 MHz, CDCl_3): δ = 8.76 (s, 1 H), 7.72 (dd, J = 7.9, 1.4 Hz, 2 H), 7.43 (td, J = 8.4, 1.5 Hz, 2 H), 7.26 (dq, J = 3.4, 1.6 Hz, 2 H), 7.21–7.15 (m, 8 H), 7.01 (td, J = 7.8, 0.8 Hz, 2 H), 6.96 (d, J = 8.4 Hz, 2 H), 3.70 (s, 6 H).

^{13}C NMR (151 MHz, CDCl_3): δ = 153.46, 137.02, 132.68, 132.40, 130.42, 129.71, 129.27, 128.43, 125.34, 122.00, 121.51, 112.07, 55.90.

Anal. Calcd for $\text{C}_{29}\text{H}_{25}\text{ClN}_2\text{O}_2$: C, 74.27; H, 5.37; N, 5.97. Found: C, 73.71; H, 5.25; N, 5.78.

N,N'-Bis(2,4-dimethylphenyl)thiourea (1h)^{9b}

According to **GP A**, reaction of 2,4-dimethylaniline (65.0 g, 0.5 mol) and carbon disulfide (30 mL, 0.5 mol), after recrystallization from EtOH (300 mL) afforded **1h**.

Yield: 98% (70.1 g); mp 155–156 °C (Lit.^{9b} 214 °C).

IR (ATR): 3196br, 1550s, 1462s, 1263s, 1144s, 696s cm^{-1} .

^1H NMR (600 MHz, $\text{DMSO}-d_6$): δ = 8.91 (s, 2 H), 7.07 (d, J = 7.9 Hz, 2 H), 7.01 (s, 2 H), 6.95 (d, J = 7.8 Hz, 2 H), 2.23 (s, 6 H), 2.16 (s, 6 H).

^{13}C NMR (151 MHz, $\text{DMSO}-d_6$): δ = 181.91, 136.21, 135.77, 135.39, 131.40, 128.66, 127.22, 21.11, 18.24.

Anal. Calcd for $\text{C}_{17}\text{H}_{20}\text{N}_2\text{S}$: C, 71.79; H, 7.09; N, 9.85; S, 11.27. Found: C, 71.15; H, 7.05; N, 9.65; S, 11.92.

1,3-Bis(2,4-dimethylphenyl)-4,5-diphenylimidazolin-2-thione (2h)

Reaction of thiourea **1h** (20.2 g, 70 mmol) and benzoin (14.85 g, 70 mmol) in acetic acid (100 mL) for 7 h afforded **2h**, as a mixture of two isomers (4:3) after recrystallization from $\text{CHCl}_3/\text{EtOH}$ in isomer ratio 7:2.

Yield: 63% (20.3 g); mp 235–237 °C.

IR (ATR): 1502m, 1339s, 757m, 694s, 576s cm^{-1} .

^1H (601 MHz, CDCl_3): δ (major isomer) = 7.14 (d, J = 7.9 Hz, 2 H), 7.10–7.05 (m, 2 H), 7.01 (dd, J = 10.3, 4.7 Hz, 4 H), 6.98 (d, J = 7.8 Hz, 2 H), 6.96–6.91 (m, 6 H), 2.23 (s, 6 H), 2.07 (s, 6 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 165.17, 139.17, 135.96, 133.53, 131.88, 130.17, 129.41, 129.04, 128.18, 128.16, 127.56, 21.28, 18.16.

Anal. Calcd for $\text{C}_{31}\text{H}_{28}\text{N}_2\text{S}$: C, 80.83; H, 6.13; N, 6.08; S, 6.96. Found: C, 80.54; H, 6.15; N, 5.96; S, 6.95.

1,3-Bis(2,4-dimethylphenyl)-4,5-diphenylimidazolium Perchlorate (3h)

Reaction of imidazolinethione **2h** (9.12 g, 20 mmol) and H_2O_2 (7 mL, 35%) in acetic acid (50 mL) afforded **3h**.

Yield: 51% (5.4 g); mp 262–264 °C.

IR (ATR): 1537m, 1079s, 822m, 784m, 622m cm^{-1} .

^1H NMR (600 MHz, 80 °C, $\text{DMSO}-d_6$): δ = 9.84 (s, 1 H), 7.50 (d, J = 7.6 Hz, 2 H), 7.31 (ddd, J = 6.2, 3.2, 1.5 Hz, 2 H), 7.28–7.22 (m, 8 H), 7.21–7.15 (m, 4 H), 2.30 (s, 6 H), 2.13 (s, 6 H).

^{13}C NMR (151 MHz, 80 °C, $\text{DMSO}-d_6$): δ = 141.49, 138.43, 134.85, 132.95, 132.30, 131.11, 130.67, 130.52, 129.06, 128.59, 128.16, 125.54, 21.10, 17.42.

Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{ClN}_2\text{O}_4$: C, 70.38; H, 5.53; N, 5.30. Found: C, 70.32; H, 5.51; N, 5.25.

1,3-Bis(2,4-dimethylphenyl)-4,5-diphenylimidazolium Chloride (4h)

Reaction of imidazolinethione **2h** (4.61 g, 10 mmol) and H_2O_2 (3.5 mL, 35%) in acetic acid (25 mL) afforded **4h**.

Yield: 69% (3.2 g); mp 248–249 °C (dec.).

IR (ATR): 2892m, 1531s, 1443m, 1228s, 825m, 785s, 696s, 565m cm^{-1} .

^1H NMR (600 MHz, 80 °C, $\text{DMSO}-d_6$): δ = 9.96 (s, 1 H), 7.54 (d, J = 7.8 Hz, 2 H), 7.33–7.28 (m, 2 H), 7.27–7.21 (m, 8 H), 7.18 (s, 2 H), 7.16 (d, J = 8.0 Hz, 2 H), 2.29 (s, 6 H), 2.14 (s, 6 H).

^{13}C NMR (151 MHz, 80 °C, $\text{DMSO}-d_6$): δ = 141.40, 138.52, 134.84, 132.89, 132.24, 131.13, 130.71, 130.47, 129.02, 128.67, 128.10, 125.60, 21.10, 17.46.

Anal. Calcd for $\text{C}_{31}\text{H}_{29}\text{ClN}_2$: C, 80.07; H, 6.29; N, 6.02. Found: C, 79.66; H, 6.22; N, 5.95.

***N,N'*-Bis(2-methyl-5-*tert*-butylphenyl)thiourea (1i)**

According to **GP A**, reaction of 2-methyl-5-*tert*-butylaniline (194.0 g, 92%, 1.1 mol) and carbon disulfide (79 g, 1 mol), after recrystallization from 90% EtOH (600 mL) afforded **1i**.

Yield: 62% (125.1 g); mp 152–153 °C.

IR (ATR): 3187br, 2962s, 1535s, 1410s, 1293s, 1258s, 1222s, 808s, 733s, 600s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.02 (s, 2 H), 7.26 (s, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 2.19 (s, 6 H), 1.23 (s, 18 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 181.43, 149.10, 137.84, 132.14, 130.49, 125.20, 123.84, 34.59, 31.66, 17.88.

Anal. Calcd for C₂₃H₃₂N₂S: C, 74.95; H, 8.75; N, 7.60; S, 8.70. Found: C, 74.25; H, 8.65; N, 7.41; S, 9.25.

1,3-Bis(2-methyl-5-*tert*-butylphenyl)-4,5-di(4-methoxyphenyl)-imidazolin-2-thione (2i)

Reaction of thiourea **1i** (29.5 g, 80 mmol) and anisoin (21.8 g, 80 mmol) in acetic acid (400 mL) for 22 h, followed by purification by column chromatography using hexane–EtOAc (5:1) afforded **2i** as a mixture of two isomers (1:1). Recrystallization from diethyl ether/hexane gave the pure isomer.

Yield: 76% (36.8 g); mp 207–208 °C.

IR (ATR): 3000–2900br, 1505s, 1346s, 1252s, 1022m, 830s, 626m, 562s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 7.22 (dd, *J* = 8.0, 1.6 Hz, 2 H), 7.18 (s, 2 H), 7.12 (d, *J* = 8.0 Hz, 2 H), 7.00 (d, *J* = 8.7 Hz, 4 H), 6.63 (d, *J* = 8.7 Hz, 4 H), 3.58 (s, 6 H), 2.10 (s, 6 H), 1.18 (s, 18 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 163.58, 159.52, 149.46, 136.29, 133.66, 132.31, 130.66, 128.25, 127.28, 125.87, 120.91, 113.92, 55.54, 34.59, 31.50, 17.99.

Anal. Calcd for C₃₉H₄₄N₂O₂S: C, 77.45; H, 7.33; N, 4.63; S, 5.30. Found: C, 77.05; H, 7.35; N, 4.45; S, 5.30.

1,3-Bis(2-methyl-5-*tert*-butylphenyl)-4,5-di(4-methoxyphenyl)imidazolium perchlorate (3i)

H₂O₂ (52 mL, 35%) was carefully added to the reaction solution of imidazolinethione **2i** (150 mmol) in acetic acid (250 mL) from the previous step. The temperature was allowed to rise to 60 °C and the mixture was stirred at ambient temperature for 4 h. All volatiles were removed by rotary evaporation and the residue was dissolved in MeOH (200 mL) and treated with a solution of NaClO₄ (28.1 g, 0.2 mol) dissolved in a 2:1 (v/v) mixture of methanol/water (200 mL). A white solid precipitated. The suspension was further stirred in an ice bath and the precipitate was then filtered off and washed with water, diethyl ether and dried in vacuo to obtain product **3i**.

Yield: 70% (71.1 g); mp 264–265 °C.

IR (ATR): 1521w, 1253m, 1089s, 1027m, 837m, 621m cm⁻¹.

¹H NMR (601 MHz, CDCl₃): δ = 8.60 (s, 1 H), 7.87 (s, 2 H), 7.39 (dd, *J* = 8.0, 1.5 Hz, 2 H), 7.17 (d, *J* = 8.1 Hz, 2 H), 7.09 (d, *J* = 8.1 Hz, 4 H), 6.72–6.67 (m, 4 H), 3.71 (s, 6 H), 2.11 (s, 6 H), 1.28 (s, 18 H).

¹³C NMR (151 MHz, CDCl₃): δ = 160.51, 151.77, 134.76, 132.76, 132.32, 132.08, 130.61, 127.77, 126.65, 117.11, 114.13, 55.23, 34.77, 31.06, 17.02.

Anal. Calcd for C₃₉H₄₅ClN₂O₆: C, 69.58; H, 6.74; N, 4.16. Found: C, 69.23; H, 6.56; N, 4.05.

1,3-Bis(2-methyl-5-*tert*-butylphenyl)-4,5-di(4-methoxyphenyl)-imidazolium Chloride Methanol (4i)

Reaction of imidazolinethione **2i** (36.29 g, 60 mmol) and H₂O₂ (18 mL, 35%) in acetic acid (150 mL) afforded **4i**. An analytically pure sample was obtained by recrystallization from MeOH/Et₂O at –18 °C.

Yield: 70% (26.6 g); mp 128–130 °C.

IR (ATR): 2963br, 1505s, 1444m, 1247s, 1182s, 1033s, 832s, 655m cm⁻¹.

¹H NMR (601 MHz, CDCl₃): δ = 10.69 (s, 1 H), 7.51 (br. s., 2 H), 7.37 (dd, *J* = 8.1, 1.9 Hz, 2 H), 7.21 (d, *J* = 8.1 Hz, 2 H), 6.96 (d, *J* = 8.1 Hz, 4 H), 6.74–6.67 (m, 4 H), 3.73 (s, 6 H), 3.41 (s, 3 H), 2.23 (s, 6 H), 1.25 (s, 18 H).

¹³C NMR (101 MHz, CDCl₃): δ = 160.51, 150.86, 138.17, 132.22, 131.74, 131.66, 131.20, 127.73, 125.65, 117.26, 114.26, 55.29, 50.54 (MeOH), 34.59, 31.11, 17.50.

Anal. Calcd for C₄₁H₄₈ClN₂O₄: C, 74.92; H, 7.70; N, 4.37. Found: C, 74.56; H, 7.71; N, 4.35.

***N,N'*-Bis(2-isopropylphenyl)thiourea (1j)**

According to **GP B**, reaction of 2-isopropylaniline (135.0 g, 1.0 mol) and carbon disulfide (42 g, 0.55 mol) in diglyme (200 mL), after recrystallization from MeOH (800 mL) afforded **1j**.

Yield: 56% (100.3 g); mp 157–158 °C.

IR (ATR): 3250–3050br, 1531s, 1498s, 1258s, 767m, 573s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 9.02 (s, 2 H), 7.29 (d, *J* = 7.7 Hz, 2 H), 7.24–7.20 (m, 2 H), 7.18–7.13 (m, 4 H), 3.14 (hept, *J* = 6.9 Hz, 2 H), 1.15 (d, *J* = 6.9 Hz, 12 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 182.89, 146.08, 137.02, 129.77, 127.79, 126.40, 126.22, 28.15, 23.70.

Anal. Calcd for C₁₉H₂₄N₂S: C, 73.03; H, 7.74; N, 8.97; S, 10.26. Found: C, 72.54; H, 7.61; N, 8.65; S, 10.65.

1,3-Bis(2-isopropylphenyl)-4,5-diphenylimidazolin-2-thione (2j)

Reaction of thiourea **1j** (9.77 g, 20 mmol) and benzoin (16.97 g, 80 mmol) in acetic acid (50 mL) for 17 h afforded **2j** as a mixture of two isomers (2:1).

Yield: 31% (12.1 g).

¹H NMR (600 MHz, DMSO-*d*₆): δ (major isomer) = 7.37–7.30 (m, 6 H), 7.23–7.18 (m, 2 H), 7.16–7.07 (m, 10 H), 2.79 (hept, *J* = 6.8 Hz, 2 H), 1.19 (d, *J* = 6.8 Hz, 6 H), 0.98 (d, *J* = 6.9 Hz, 6 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (major isomer) = 166.16, 146.73, 134.97, 131.21, 130.65, 130.08, 129.05, 128.94, 128.51, 128.25, 127.14, 126.67, 28.56, 24.37, 23.20.

Filtration of the component that was insoluble in hot EtOH gave the pure minor isomer. Mp 250–251 °C.

IR (ATR): 2962w, 1490m, 1340s, 751s, 695s, 598s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ (minor isomer) = 7.50–7.47 (m, 1 H), 7.26 (dd, *J* = 7.3, 1.4 Hz, 1 H), 7.23–7.18 (m, 4 H), 7.01 (dd, *J* = 4.8, 4.3 Hz, 2 H), 2.62–2.54 (m, 1 H), 1.11 (d, *J* = 6.8 Hz, 3 H), 0.61 (d, *J* = 6.8 Hz, 3 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (minor isomer) = 166.65, 146.52, 134.95, 131.40, 130.98, 130.13, 128.90, 128.61, 128.58, 128.35, 127.09, 126.71, 28.35, 24.75, 22.55.

Anal. Calcd for C₃₃H₃₂N₂S: C, 81.11; H, 6.60; N, 5.73; S, 6.56. Found: C, 79.88; H, 6.65; N, 5.54; S, 7.01.

1,3-Bis(2-isopropylphenyl)-4,5-diphenylimidazolium Perchlorate (3j)

Reaction of imidazolinethione **2j** (12.2 g, 25 mmol) and H₂O₂ (9 mL, 35%) in acetic acid (100 mL) afforded **3j** as a mixture of two isomers (2:1).

Yield: 81% (11.26 g); mp 238–241 °C.

IR (ATR): 1547m, 1445m, 1090s, 763s, 703s, 622s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ (major isomer) = 10.16 (s, 1 H), 7.69–7.67 (m, 2 H), 7.58–7.50 (m, 2 H), 7.33–7.20 (m, 14 H), 2.77 (sept, *J* = 6.8 Hz, 2 H), 1.13 (d, *J* = 6.8 Hz, 6 H), 1.00 (d, *J* = 6.8 Hz, 6 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (major isomer) = 145.59, 138.57, 133.07, 132.21, 131.41, 131.34, 130.59, 129.00, 128.86, 127.69, 127.57, 125.22, 28.35, 25.17, 22.62.

¹H NMR (600 MHz, DMSO-*d*₆): δ (minor isomer) = 10.09 (s, 1 H), 7.88–7.85 (m, 2 H), 7.58–7.49 (m, 4 H), 7.49–7.44 (m, 4 H), 7.41–7.37 (m, 4 H), 7.33–7.20 (m, 4 H), 2.74 (sept, *J* = 6.8 Hz, 2 H), 1.12 (d, *J* = 6.8 Hz, 6 H), 0.66 (d, *J* = 6.8 Hz, 6 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ (minor isomer) = 145.83, 138.18, 132.97, 132.27, 131.45, 131.32, 130.50, 129.43, 129.01, 127.80, 127.50, 125.50, 27.92, 25.39, 22.42.

Anal. Calcd for C₃₃H₃₃ClN₂O₄: C, 70.38; H, 5.53; N, 5.30. Found: C, 70.35; H, 5.69; N, 5.12.

***N,N'*-Bis(2-*tert*-butylphenyl)thiourea (1k)**

According to **GP B**, reaction of 2-*tert*-butylaniline (25.0 g, 0.168 mol) and carbon disulfide (7 g, 90 mmol) in diglyme (100 mL), after recrystallization from EtOH (80 mL) afforded **1k**.

Yield: 38% (10.9 g); mp 165–166 °C.

IR (ATR): 3374m, 3218br, 2961br, 1526s, 1479s, 1256s, 753s, 632s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.91 (s, 2 H), 7.40–7.35 (m, 2 H), 7.19–7.15 (m, 6 H), 1.36 (s, 18 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 183.20, 146.97, 138.03, 133.20, 127.60, 127.23, 126.70, 35.33, 31.38.

Anal. Calcd for C₂₁H₂₈N₂S: C, 74.07; H, 8.29; N, 8.23; S, 9.41. Found: C, 73.85; H, 8.26; N, 8.20; S, 9.48.

2-[(2-*tert*-Butylphenyl)amino]-1,2-diphenylethanone (5)

Reaction of thiourea **1k** (11.9 g, 35 mmol) and benzoin (7.41 g, 35 mmol) in acetic acid (50 mL) for 17 h, after recrystallization from diethyl ether/hexane afforded **5**.

Yield: 51% (6.1 g); mp 154–155 °C.

IR (ATR): 3461m, 2956br, 1683s, 1506s, 1448s, 1250s, 744s, 693s, 635s, 595s cm⁻¹.

¹H NMR (600 MHz, DMSO-*d*₆): δ = 8.14 (d, *J* = 8.0 Hz, 2 H), 7.61–7.54 (m, 1 H), 7.50 (d, *J* = 8.0 Hz, 2 H), 7.47 (t, *J* = 7.6 Hz, 2 H), 7.23 (t, *J* = 7.6 Hz, 2 H), 7.15–7.07 (m, 2 H), 6.89 (t, *J* = 7.6 Hz, 1 H), 6.72 (d, *J* = 8.1 Hz, 1 H), 6.53–6.47 (m, 2 H), 5.87 (d, *J* = 5.2 Hz, 1 H), 1.45 (s, 9 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 198.00, 155.50, 148.73, 143.79, 138.82, 134.86, 134.35, 133.25, 129.59, 129.30, 129.29, 128.69, 128.24, 127.15, 126.41, 117.17, 113.05, 61.88, 34.32, 30.17.

Anal. Calcd for C₂₄H₂₅NO: C, 83.93; H, 7.34; N, 4.08. Found: C, 83.65; H, 7.29; N, 4.01.

***N,N'*-Bis(3-pyridinyl)thiourea (1l)^{27,28}**

According to **GP B**, reaction of 3-aminopyridine (94.1 g, 1 mol) and carbon disulfide (38 mL, 0.63 mol) in diglyme (250 mL), after recrystallization from EtOH/H₂O (200/50 mL) afforded **1l**. An analytically pure sample was obtained by recrystallization from ethanol.

Yield: 35% (40.6 g); mp 178–179 °C (Lit.²⁷ 178–180 °C).

IR (ATR): 2971m, 2902m, 1580s, 1536s, 1414s, 1268s, 1252s, 1047s, 1024s, 1016s, 753s, 717s, 701s cm⁻¹.

¹H NMR (601 MHz, DMSO-*d*₆): δ = 10.08 (s, 2 H), 8.63 (dd, *J* = 2.6, 0.6 Hz, 2 H), 8.37 (dd, *J* = 4.7, 1.5 Hz, 2 H), 7.97 (ddd, *J* = 8.2, 2.6, 1.5 Hz, 2 H), 7.40 (ddd, *J* = 8.2, 4.7, 0.6 Hz, 2 H).

¹³C NMR (151 MHz, DMSO-*d*₆): δ = 181.47, 146.04, 145.99, 136.56, 132.04, 123.73.

NMR spectroscopic data of **1l** matched those previously described.²⁸

2-[(3-Pyridyl)amino]-1,2-diphenylethanone (6)

Reaction of thiourea **1l** (34.66 g, 0.15 mol) and benzoin (31.81 g, 0.15 mol) in acetic acid (150 mL) for 10 h afforded **6**. An analytically pure sample was obtained by recrystallization from EtOH/H₂O (1:1).

Yield: 95% (40.9 g); mp 141–142 °C.

IR (ATR): 3326w, 2336w, 1678s, 1589s, 1578s, 1342s, 795s, 755s, 711s, 700s, 691s, 681s, 668s, 618s cm⁻¹.

¹H NMR (601 MHz, CDCl₃): δ = 8.05 (d, *J* = 2.8 Hz, 1 H), 7.94–7.91 (m, 2 H), 7.86 (dd, *J* = 4.6, 1.3 Hz, 1 H), 7.49–7.45 (m, 1 H), 7.39–7.34 (m, 4 H), 7.22 (dd, *J* = 10.5, 4.8 Hz, 2 H), 7.16–7.12 (m, 1 H), 6.94 (dd, *J* = 8.3, 4.6 Hz, 1 H), 6.84 (ddd, *J* = 8.3, 2.9, 1.3 Hz, 1 H), 5.94 (d, *J* = 6.6 Hz, 1 H), 5.46 (d, *J* = 6.4 Hz, 1 H).

¹³C NMR (151 MHz, CDCl₃): δ = 196.28, 142.02, 139.30, 136.92, 136.44, 134.71, 133.76, 129.25, 128.91, 128.77, 128.43, 128.15, 123.64, 119.65, 62.25.

Anal. Calcd for C₁₉H₁₆N₂O: C, 79.14; H, 5.59; N, 9.72. Found: C, 79.51; H, 5.62; N, 9.81.

***N,N'*-Bis(2,4,6-trimethylphenyl)thiourea (1m)^{29,30}**

According to **GP A**, reaction of 2,4,6-trimethylaniline (65.0 g, 0.5 mol) and carbon disulfide (30 mL, 0.5 mol), after recrystallization from EtOH (300 mL) afforded **1m**.

Yield: 91% (70.9 g); mp 187–189 °C (Lit. 175 °C,^{9b} 202–203 °C²⁹).

IR (ATR): 3321m, 3250–3150br, 3100–2900br, 1519s, 1475s, 1246s, 1220s, 854m, 654m cm⁻¹.

¹H NMR (400 MHz, CDCl₃): δ = 7.94 (s, 1 H), 6.99 (s, 2 H), 6.84 (s, 2 H), 6.47 (s, 1 H), 2.38 (s, 6 H), 2.30 (s, 3 H), 2.22 (s, 3 H), 2.18 (s, 6 H).

¹³C NMR (101 MHz, CDCl₃): δ = 181.37, 139.17, 137.69, 137.29, 136.11, 133.16, 130.65, 129.79, 129.05, 21.01, 18.52, 18.10.

NMR spectroscopic data of **1m** matched those previously described.^{29,30}

***N,N'*-Bis(2,6-diisopropylphenyl)thiourea (1n)^{30,31}**

According to **GP B**, reaction of 2,6-diisopropylaniline (90%, 394 g, 2 mol) and carbon disulfide (91.4 g, 1.2 mol) in diglyme (1 L), afforded **1n**.

Yield: 39% (153.8 g); mp 223–224 °C (Lit.³¹ 242 °C).

IR (ATR): 3135m, 2959s, 1523s, 1463m, 1261s, 1234s, 800s, 481m cm⁻¹.

^1H NMR (601 MHz, CDCl_3): δ = 8.80 (s, 1 H), 7.31 (t, J = 7.7 Hz, 1 H), 7.22–7.17 (m, 3 H), 7.05 (t, J = 6.0 Hz, 2 H), 6.32 (s, 1 H), 3.34 (hept, J = 6.8 Hz, 2 H), 2.96 (hept, J = 6.8 Hz, 2 H), 1.29 (d, J = 6.9 Hz, 6 H), 1.23 (d, J = 6.8 Hz, 6 H), 1.18 (d, J = 6.8 Hz, 6 H), 0.96 (d, J = 6.9 Hz, 6 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 182.44, 148.14, 146.64, 132.74, 130.60, 130.11, 128.81, 124.23, 123.62, 28.89, 28.58, 26.01, 24.43, 23.84, 22.10.

NMR spectroscopic data for **1n** matched those previously described.³⁰

Acknowledgment

We are grateful to Prof. J. Christoffers from the Carl von Ossietzky University of Oldenburg for recording IR spectra and to Dr. O. Tok from the Institute of Inorganic Chemistry, Academy of Science of the Czech Republic for recording NMR spectra.

Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0039-1690338>.

References

- (1) Current address: C. Azap, Chemetall GmbH, Trakehner Str. 3, 60487 Frankfurt am Main, Germany.
- (2) Current address: A. Christoffers, Diapharm Analytics GmbH, Würzburger Str. 2, 26121 Oldenburg, Germany.
- (3) (a) Herrmann, W. A. *Kocher C Angew. Chem., Int. Ed. Engl.*; **1997**, *36*, 2163; *Angew. Chem.* **1997**, *109*, 2256. (b) Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39. (c) *N-Heterocyclic Carbenes in Transition Metal Catalysis*; Glorius, F., Ed.; Springer: Berlin, **2007**. (d) Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612. (e) Corberán, R.; Mas, E.; Peris-Marzá, E. *Eur. J. Inorg. Chem.* **2009**, 1700. (f) Hopkinson, M. N.; Richter, C.; Schedler, M.; Glorius, F. *Nature* **2014**, *510*, 485. (g) *N-Heterocyclic Carbenes: Effective Tools for Organometallic Synthesis*; Nolan, S. P., Ed.; Wiley-VCH: Weinheim, **2014**. (h) *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Diez-Gonzalez, S., Ed.; Royal Society of Chemistry: Cambridge, **2017**.
- (4) Occhipinti, G.; Bjørsvik, H.-R.; Jensen, V. R. *J. Am. Chem. Soc.* **2006**, *128*, 6952.
- (5) (a) Lübke, C.; Dumrath, A.; Neumann, H.; Beller, M.; Kadyrov, R. *ChemCatChem* **2014**, *6*, 105. (b) Kadyrov, R.; Azap, C.; Weidlich, S.; Wolf, D. *Top. Catal.* **2012**, *55*, 538. (c) Kadyrov, R.; Rosiak, A. *Chemistry Today* **2009**, *27*, 24.
- (6) For reviews, see: (a) Jahnke, M. C.; Hahn, F. E. In *N-Heterocyclic Carbenes: From Laboratory Curiosities to Efficient Synthetic Tools*; Diez-Gonzalez, S., Ed.; Royal Society of Chemistry: London, **2017**, 1–41. (b) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; Cesar, V. *Chem. Rev.* **2011**, *111*, 2705. (c) Zhong, R.; Lindhorst, A. C.; Groche, F. J.; Kühn, F. E. *Chem. Rev.* **2017**, *117*, 1970.
- (7) For selected references, see: (a) Herrmann, W. A.; Goossen, L. J.; Artus, G. R. J.; Köcher, C. *Organometallics* **1997**, *16*, 2472. (b) Arduengo, A. J. III.; Krafczyk, R.; Schmutzler, R. *Tetrahedron* **1999**, *55*, 14523. (c) Hirano, K.; Urban, S.; Wang, C.; Glorius, F. *Org. Lett.* **2009**, *11*, 1019; and references cited therein. (d) Lv, T.; Wang, Z.; You, J.; Lan, J.; Gao, G. *J. Org. Chem.* **2013**, *78*, 5723.
- (8) (a) Schönherr, H.-J.; Wanzlick, H.-W. *Justus Liebigs Ann. Chem.* **1970**, 731, 176. (b) Schönherr, H.-J.; Wanzlick, H.-W. *Chem. Ber.* **1970**, *103*, 1037. (c) Arduengo, A. J. III.; Goerlich, J. R.; Krafczyk, R.; Marshall, W. J. *Angew. Chem. Int. Ed.* **1998**, *37*, 1963; *Angew. Chem.* **1998**, *110*, 2062. (d) Dowe, A. P.; Li, H.; Pratt, R. C.; Lohmeijer, B. G. G.; Culkin, D. A.; Waymouth, R. M.; Hedrick, J. L. *Chem. Commun.* **2006**, 2881. (e) Ogle, J. W.; Zhang, J.; Reibenspies, J. H.; Abboud, K. A.; Miller, S. A. *Org. Lett.* **2008**, *10*, 3677. (f) Ogle, J. J. W.; Miller, S. A. *Chem. Commun.* **2009**, 5728. (g) Mehrotra, K. N.; Singh, G. *Synthesis* **1980**, 1001.
- (9) (a) Schroeder, D. C. *Chem. Rev.* **1955**, *55*, 181. (b) Azizi, N.; Khajeh-Amiri, A.; Ghafari, H.; Bolourtchian, M. *Mol. Diversity* **2011**, *15*, 157. (c) Li, Z.; Liu, D.; Chen, Y.; Yin, Y.; Wang, Z.; Sun, X. *J. Chem. Res.* **2016**, *40*, 515; and references cited therein.
- (10) Sharma, S. *Synthesis* **1978**, 803.
- (11) (a) Dyson, G.; George, H. J. *J. Chem. Soc.* **1924**, 1702. (b) Natarajan, A.; Guo, Y.; Arthanari, H.; Wagner, G.; Halperin, J. A.; Chorev, M. *J. Org. Chem.* **2005**, *70*, 6362. (c) Štrukil, V.; Igrec, M. D.; Fábán, L.; Eckert-Maksić, M.; Childs, S. L.; Reid, D. G.; Duer, M. J.; Halasz, I.; Mottilloe, C.; Friščić, T. *Green Chem.* **2012**, *14*, 2462.
- (12) Staab, H. A.; Walther, G. *Justus Liebigs Ann. Chem.* **1962**, 657, 98.
- (13) (a) Ballabeni, M.; Ballini, R.; Bigi, F.; Maggi, R.; Parrini, M.; Predieri, G.; Sartori, G. *J. Org. Chem.* **1999**, *64*, 1029. (b) Venkatesh, P.; Pandeya, S. N. *E-J. Chem.* **2009**, *6*, 495. (c) Maddani, M. R.; Prabhu, K. R. *J. Org. Chem.* **2010**, *75*, 2327.
- (14) Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, 5475.
- (15) (a) Biltz, H. *Ber. Dtsch. Chem. Ges.* **1907**, *40*, 4799. (b) Klüpfel, K. W.; Stumpf, H. R.; Behmenburg, H.; Neugebauer, W.; Süß, O.; Tomanek, M. German Patent Appl. DE 1060713, **1959**; *Chem. Abstr.* **1961**, *55*, 20735b.
- (16) Grimmett, M. R. In *Science of Synthesis*, Vol. 12; Neier, R., Ed.; Georg Thieme Verlag: Stuttgart, **2002**.
- (17) Pesch, J.; Harms, K.; Bach, T. *Eur. J. Org. Chem.* **2004**, 2025.
- (18) Carpenter, M. S.; Easter, W. M.; Wood, T. F. *J. Org. Chem.* **1951**, *16*, 586.
- (19) Dyson, G. M.; George, H. J.; Hunter, R. F. *J. Chem. Soc.* **1927**, 436.
- (20) Pohloudek-Fabini, R. *Arch. Pharm.* **1965**, *298*, 51.
- (21) Štrukil, V.; Gracin, D.; Magdysyuk, O. V.; Dinnebie, R. E.; Friscic, T. *Angew. Chem. Int. Ed.* **2015**, *54*, 8440.
- (22) Huebner, C. F.; Marsh, J. L.; Mizzoni, R. H.; Mull, R. P.; Schroeder, D. C.; Troxell, H. A.; Scholz, C. R. *J. Am. Chem. Soc.* **1953**, *75*, 2274.
- (23) Pasha, M. A.; Madhusudana Reddy, M. B. *Synth. Commun.* **2009**, *39*, 2928.
- (24) Natarajan, A.; Guo, Y.; Arthanari, H.; Wagner, G.; Halperin, J. A.; Chorev, M. *J. Org. Chem.* **2005**, *70*, 6362.
- (25) Lippert, K. M.; Hof, K.; Gerbig, D.; Ley, D.; Hausmann, H.; Guenther, S.; Schreiner, P. R. *Eur. J. Org. Chem.* **2012**, 5919.
- (26) Kokorev, G. I.; Yambushev, F. D. *Zh. Obshch. Khim.* **1987**, *57*, 1552.
- (27) Deady, L. W.; Ganame, D.; Hughes, A. B.; Quazi, N. H.; Zanatta, S. D. *Aust. J. Chem.* **2002**, *55*, 287.
- (28) Katritzky, A. R.; Witek, R. W.; Rodriguez-Garcia, V.; Mohapatra, P. P.; Rogers, J. W.; Cusido, J.; Abdel-Fattah, A. A. A.; Steel, P. J. *J. Org. Chem.* **2005**, *70*, 7866.
- (29) Yang, D.; Chen, Y.-C.; Zhu, N.-Y. *Org. Lett.* **2004**, *6*, 1577.
- (30) Findlater, M.; Hill, N. J.; Cowley, A. H. *Dalton Trans.* **2008**, 4419.
- (31) Walter, W.; Randau, G. *Justus Liebigs Ann. Chem.* **1969**, 722, 52.