JOC The Journal of Organic Chemistry

NOTE

pubs.acs.org/joc

Carbene-Mediated Transformations of 1-(Benzylideneamino)benzimidazoles

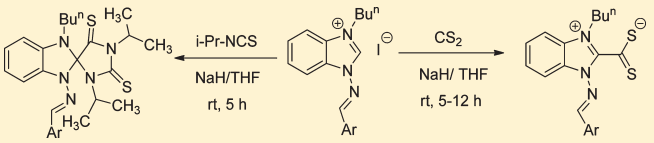
Alan R. Katritzky,*[,‡] Davit Jishkariani,[‡] Rajeev Sakhuja,[‡] C. Dennis Hall,[‡] and Peter J. Steel[§]

[‡]Center for Heterocyclic Compounds, Department of Chemistry, University of Florida, Gainesville, Florida 32611-7200, United States

[§]Chemistry Department, University of Canterbury, Christchurch, New Zealand *E-mail: katritzky@chem.ufl.edu.

Supporting Information

ABSTRACT: Carbene-mediated transformations of *N*-(3-butylbenzimidazol-3-ium-1-yl)-1-arylmethanimine *iodides* with carbon disulfide and benzoyl isothiocyanate gave the corresponding NHC·CS_2 betaines in 68−85% and benzoyl-[1-butyl-3-[(*E*)-(aryl)-methyleneamino]benzimidazol-1-ium-2-carbothioyl]azanides, respectively, in 74−85% yields. However, reaction with excess isopropyl isothiocyanate in NaH/THF at room temperature yielded the 1-butyl-1′,3′-diisopropyl-3-[(*E*)-(aryl)methyleneamino]spiro[benzimidazole-2,5′-imidazolidine]-2′,4′-dithiones (74−77%).



Carbenes derived from nitrogen heterocycles (NHC) are well-known organocataysts for benzoin condensations,[1,2] Stetter[3,4] and Staudinger reactions,[5] oxidative amidation,[6] annulation of enals,[7] ring-opening polymerizations,[8,9] transesterifications,[10,11] and other transformations;[12] they are also versatile ligands for transition metals.[13−15] The σ-donating ability and strong nucleophilic character of NHC offers opportunities for the construction of substituted heterocycles[16−21] and novel molecular frameworks.[22,23]

An important property of NHCs is the ability to react with CO_2,[24−26] CS_2,[27−29] and isothiocyanates[27,29] to form imidazol-2-ylidene, 1,3-thiazol-2-ylidene,[17,30] 1,2,4-triazol-3-ylidene,[17,31,32] and isothiazol-3-ylidene adducts.

A wide range of stable benzimidazolium or imidazol(in)ium−CS_2 adducts have been studied as novel ionic liquids,[25,27,33] as catalysts in the cyanosilylation of aldehydes,[34] as intermediates for sulfur heterocycles,[35] ligands for gold complexes, surface units for gold nanoparticles,[36] and promising antifungal and antibacterial agents.[29,37]

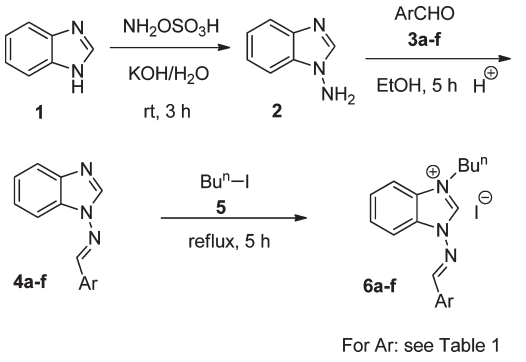
NHC zwitterionic betaine adducts with isothiocyanates (NHC·RNCS) are powerful intermediates for the synthesis of a variety of heterocycles.[38,39] Thus, Cheng and co-workers utilized 2-thiocarbamoyl benzimidazolium, imidazolium, and triazolium zwitterionic inner salts in [3 + 2] cycloaddition reactions, resulting in spiro-heterocycles.[38,39]

Most literature NHC examples are based on imidazole and benzimidazole nuclei bearing various alkyl or aryl groups on nitrogen. An early report by Balch described a template synthesis of an N-amino-substituted N-heterocyclic carbene.[40] Lassaletta described the synthesis and application of a class of N-heterocyclic carbenes based on bis(*N*,*N*-dialkylamino)imidazolin-2-ylidines.[41,42]

However, we found no literature reports of NHC·CS_2 or NHC·RNCS betaines or spirocyclic derivatives of *N*-(arylmethyleneimino)benzimidazoles. Herein, we describe our results from the carbene-mediated transformations of 1-(benzylideneamino)-benzimidazoles.

1-Aminobenzimidazole (**2**) was synthesized from benzimidazole (**1**) and hydroxylamine-*O*-sulfonic acid in 75% yield following a literature procedure.[43] *N*-(Arylmethyleneimino)benzimidazoles **4a**−**f** were synthesized in 69−94% yield by the reaction of 1-aminobenzimidazole **2** with aldehydes **3a**−**f**, in ethanol in the presence of a catalytic quantity of sulfuric acid[44] (Scheme 1, Table 1). Quaternization of *N*-(arylmethyleneimino)benzimidazoles **4a**−**f** with butyl iodide **5** gave the corresponding 3-butyl-*N*-(arylmethyleneimino)-benzimidazolium iodides **6a**−**f** in quantitative yields (Scheme 1, Table 1).

Scheme 1



For Ar: see Table 1

1,3-Dimethylbenzimidazolium iodide (**7**) was synthesized from benzimidazole following a literature procedure.[48] The singlet carbene generated in situ at the C-2 position of 1,3-dimethylbenzimidazolium iodide **7** by treatment with sodium hydride, on reaction with carbon disulfide **8**, gave 1,3-dimethylbenzimidazol-3-ium-2-carbodithioate (**10**) in 85% yield (Scheme 2). Deprotonation of

Received: January 21, 2011
Published: April 11, 2011

Table 1. Synthesis of *N*-(Arylmethyleneimino)benzimidazoles and Their Quaternized Salts

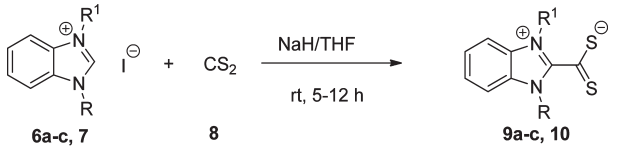
		products **4a**–**f**		products **6a**–**f**	
entry	Ar	yield (%)	mp (°C)	yield (%)	mp (°C)
a	4-CH_3O–C_6H_4	92	93–95	100	154–155
b	C_6H_5	94	125[a]	100	171–172
c	4-Br-2-thiophenyl	69	174–175	100	175–176
d	4-CH_3–C_6H_4	82	74–75	100	167–169
e	4-NO_2–C_6H_4	79	225–226[b]	100	217–219
f	4-Et_2N–C_6H_4	91	118[c]	100	151–152

[a] Literature[45] mp 125–126 °C. [b] Literature[46] mp 223 °C. [c] Literature[47] mp not available.

N-(3-butylbenzimidazol-3-ium-1-yl)-1-(aryl)methanimine iodides **6a**–**c** using sodium hydride, followed by reaction with carbon disulfide **8** at room temperature, formed the corresponding NHC·CS_2 betaines (**9a**–**c**) (68–76%) (Scheme 2, Table 2). Isolation of the NHC·CS_2 betaine adducts was achieved by crystallization techniques in all cases. The structure of one representative example, **9a**, was confirmed by single-crystal X-ray diffraction (Figure 1).

More interesting results were obtained when the reaction of benzimidazolium salts with isopropyl isothiocyanate was carried out under similar experimental conditions. 1,3-Dimethylbenzimidazolium iodide (**7**) on reaction with excess of isopropyl isothiocyanate (**11**) in the presence of sodium hydride/THF at room temperature gave (1,3-dimethylbenzimidazol-3-ium-2-carbothioyl)-isopropylazanide (**12**) in 86% yield (Scheme 3).

Scheme 2



For R and R^1: see Table 2

Table 2. Synthesis of NHC·CS_2 Betaine Adducts

reactant	product	R	R^1	yield (%)	mp (°C)
6a	**9a**	–N=CH-(4-CH_3O–C_6H_4)	Bu^n	70	160–161
6b	**9b**	–N=CH–C_6H_5	Bu^n	76	171–172
6c	**9c**	–N=CH-(4-Br-2-thiophenyl)	Bu^n	68	170–173
7	**10**	CH_3	CH_3	85	235–236[a]

[a] Literature[37] mp 237–238 °C.

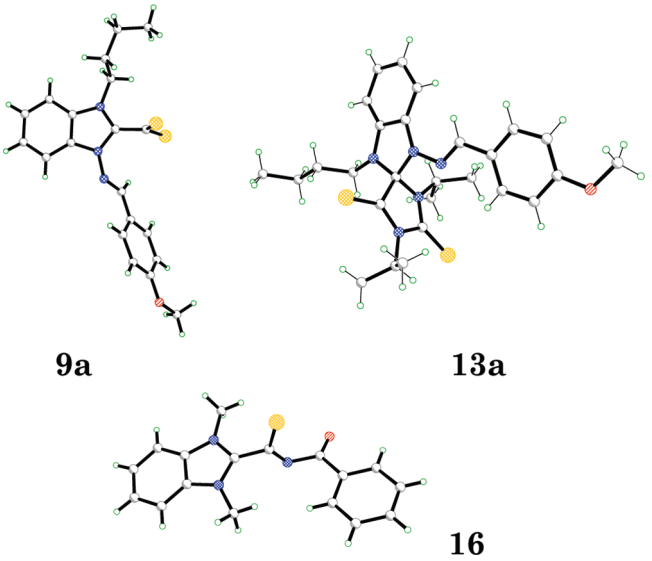
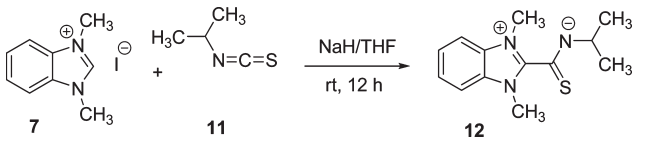


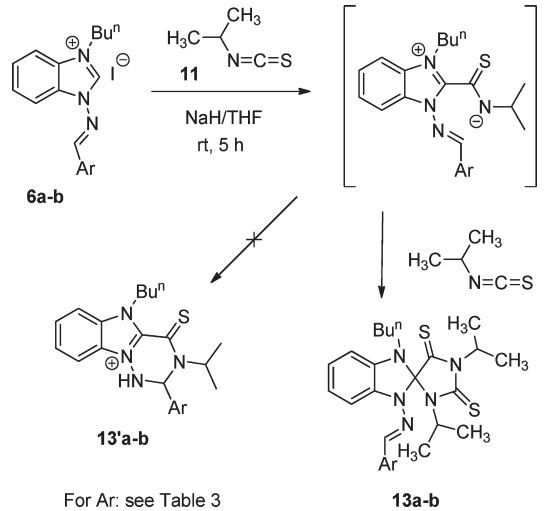
Figure 1. X-ray structures of **9a**, **13a**, and **16**.

Scheme 3



However, the reaction of *N*-(3-butylbenzimidazol-3-ium-1-yl)-1-(aryl)methanimine iodides (**6a**,**b**) with excess of isopropyl isothiocyanate **11** in the presence of NaH/THF at room temperature led to the formation of red crystalline compounds (**13a**,**b**) in 74–77% yield (Scheme 4, Table 3). The ^1H and ^{13}C NMR spectra were complex and did not correspond to the formation of a betaine intermediate (Scheme 4). In fact, the spectroscopic data revealed two isopropyl groups, and the structure of representative example **13a** was confirmed by single-crystal X-ray diffraction studies (Figure 1). The X-ray crystallographic data proved the formation of 1-butyl-1′,3′-diisopropyl-3-[(*E*)-(aryl)methyleneamino]spiro[benzimidazole-2,5′-imidazolidine]-2′,4′-dithiones (**13a**,**b**), resulting from the addition of a second molecule of isopropyl isothiocyanate to the NHC·RNCS betaine adduct. In fact, with an imine function in the side chain, we were unable to isolate NHC·RNCS betaine adducts because the corresponding adducts reacted further with heteroallene even when the reagents were present in stoichiometric (1:1) or substoichiometric quantities. This result indicates that the intermolecular formation of **13a**,**b** is preferred over the intramolecular cyclization to **13′a**,**b** (Scheme 4). However, in the case of 1,3-dimethylbenzimidazolium iodide **7**, the reaction stopped at the NHC·RNCS betaine step and no spirocyclic product was observed even in presence of excess isopropyl isothiocyanate or at elevated temperatures.

Scheme 4



For Ar: see Table 3

Zwitterionic NHC·RNCS betaine intermediates were only isolated when a strongly deactivated isothiocyanate (benzoyl isothiocyanate) was used. Thus the reaction of benzimidazolium salts (**6a**–**c**, **7**) with equivalent amounts of benzoyl

dx.doi.org/10.1021/jo200088s |*J. Org. Chem.* 2011, 76, 4082–4087

Table 3. Synthesis of Spiro[imidazolidine-4,2′-indoline]-2,5-dithiones

reactant	product	Ar	yield (%)	mp (°C)
6a	**13a**	4-CH_3O−C_6H_4	77	141−142
6b	**13b**	C_6H_5	74	116−119

isothiocyanate (**14**) in the presence of NaH/THF led to benzoyl benzimidazolium-2-carbonothioyl)amides (**15a**−**c**, **16**) in 74−85% yield (Scheme 5, Table 4). The structure of representative example **16** was confirmed by single-crystal X-ray diffraction studies (Figure 1).

Scheme 5

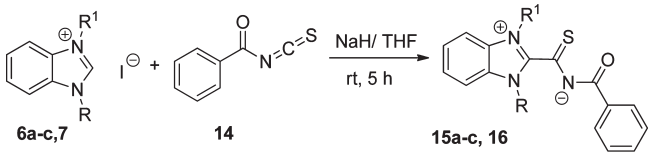


Table 4. Synthesis of NHC·RNCS Betaine Adducts

reactant	product	R	R^1	yield (%)	mp (°C)
6a	**15a**	−N=CH-(4-CH_3O−C_6H_4)	Bu^n	83	126−128
6b	**15b**	−N=CH−C_6H_5	Bu^n	77	125−127
6c	**15c**	−N=CH-(4-Br-2-thiophenyl)	Bu^n	74	151−154
7	**16**	CH_3	CH_3	85	207−210

In an extension of this work, we studied the influence of functional groups on *N*-1 nitrogen, on the amination of 1-aminobenzimidazole and its derivatives. Compounds **2** and **4a**−**f** were reacted with 2,4-dinitrophenyl hydroxylamine (**17**) to form **18** and **19a**−**f** in 0−80% yield.[49] We found that imines with electron-donating substituents in the side chain gave higher yields compared to those with electron-withdrawing groups, and aminated products of some derivatives were not detected at all (Scheme 6, Table 5).

Scheme 6

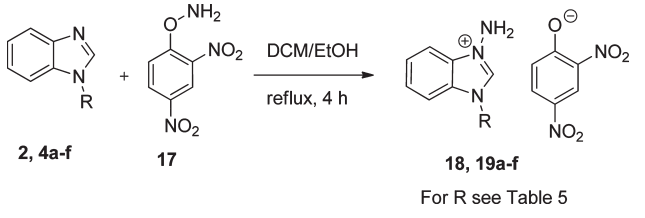


Table 5. Amination of 1-Aminobenzimidazole and Its Imine Derivatives

reactant	product	R	yield (%)	mp (°C)
2	**18**	−NH_2	80	166−168
4a	**19a**	−N=CH-(4-CH_3O−C_6H_4)	42	146−148
4b	**19b**	−N=CH−C_6H_5	0	
4c	**19c**	−N=CH-(4-Br-2-thiophenyl)	0	
4d	**19d**	−N=CH-(4-CH_3−C_6H_4)	40	132−134
4e	**19e**	−N=CH-(4-NO_2−C_6H_4)	0	
4f	**19f**	−N=CH-(4-Et_3N−C_6H_4)	60	180

EXPERIMENTAL SECTION

Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with TMS for ^1H (300 MHz) and ^{13}C (75 MHz) as an internal reference. Aminating agent **17** was prepared via a two-step literature procedure.[50] Elemental analysis was performed on a Carlo Erba-1106 instrument.

General Method for the Preparation of Imines 4a−f: 1-Aminobenzimidazole and corresponding aldehyde (1.05 equiv) were dissolved in absolute ethanol and stirred in the presence of a catalytic amount of sulfuric acid. After 5 h, the solvent was removed under reduced pressure and the imines were obtained by recrystallization from EtOAc/hexanes.

***N*-(Benzimidazol-1-yl)-1-(4-methoxyphenyl)methanimine (4a):** White microcrystals (92%), mp 93−95.0 °C; ^1H NMR ($CDCl_3$) δ 8.69 (s, 1H), 8.32 (s, 1H), 7.85−7.78 (m, 3H), 7.75−7.70 (m, 1H), 7.39−7.28 (m, 2H), 7.02−6.97 (m, 2H), 3.87 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 162.5, 152.2, 142.5, 136.5, 131.9, 129.9, 125.6, 123.9, 123.0, 120.7, 114.5, 110.8, 55.5. Anal. Calcd for $C_{15}H_{13}N_3O$: C, 71.70; H, 5.21; N, 16.72. Found: C, 71.87; H, 5.28; N, 16.78.

***N*-(Benzimidazol-1-yl)-1-phenyl-methanimine (4b):** White microcrystals (94%), mp 125.0 °C (lit.[45] mp 125−126 °C); ^1H NMR ($CDCl_3$) δ 8.76 (d, J = 2.7 Hz, 1H), 8.37 (s, 1H), 7.91−7.86 (m, 2H), 7.84−7.80 (m, 1H), 7.78−7.73 (m, 1H), 7.52−7.47 (m, 3H), 7.41−7.29 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 151.7, 142.5, 136.6, 132.9, 131.8, 131.6, 129.0, 128.1, 124.1, 123.1, 120.7, 110.8. Anal. Calcd for $C_{14}H_{11}N_3$: C, 76.00; H, 5.01; N, 18.99. Found: C, 75.82; H, 4.99; N, 19.07.

***N*-(Benzimidazol-1-yl)-1-(4-bromo-2-thienyl)methanimine (4c):** Colorless crystals (79%), mp 174.0−175.0 °C; ^1H NMR (DMSO-d_6) δ 9.36 (s, 1H), 8.90 (s, 1H), 7.99 (s, 1H), 7.78 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.69 (s, 1H), 7.39 (t, J = 7.5 Hz, 1H), 7.32 (t, J = 7.5 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 146.4, 141.6, 138.9, 137.4, 134.4, 131.4, 128.1, 123.8, 122.8, 119.9, 110.6, 109.6. Anal. Calcd for $C_{12}H_8BrN_3S$: C, 47.07; H, 2.63; N, 13.72. Found: C, 47.12; H, 2.59; N, 13.60.

***N*-(Benzimidazol-1-yl)-1-(*p*-tolyl)methanimine (4d):** White microcrystals (82%), mp 74−75.0 °C; ^1H NMR ($CDCl_3$) δ 8.71 (s, 1H), 8.38 (s, 1H), 7.83−7.72 (m, 4H), 7.39−7.25 (m, 4H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 152.4, 142.4, 142.3, 136.6, 131.9, 130.3, 129.8, 128.2, 124.1, 123.2, 120.7, 110.9, 21.7. Anal. Calcd for $C_{15}H_{13}N_3$: C, 76.57; H, 5.57; N, 17.86. Found: C, 76.67; H, 5.61; N, 17.99.

***N*-(Benzimidazol-1-yl)-1-(4-nitrophenyl)methanimine (4e):** Yellow microcrystals (79%), mp 225−226 °C (lit.[46] mp 223 °C); ^1H NMR (DMSO-d_6) δ 9.36 (s, 1H), 9.03 (s, 1H), 8.40 (d, J = 7.8 Hz, 2H), 8.20 (d, J = 7.7 Hz, 2H), 7.90 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 7.8 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.34 (t, J = 7.5 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 150.1, 148.5, 141.7, 139.2, 137.1, 131.8, 128.8, 124.1, 123.0, 120.0, 110.8. Anal. Calcd for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.03; H, 3.70; N, 20.79.

4-[(*E*)-Benzimidazol-1-yliminomethyl]-*N*,*N*-diethylaniline (4f): Green crystals (91%), mp 118.0 °C (lit.[47] mp not available); ^1H NMR (DMSO-d_6) δ 8.96 (s, 1H), 8.89 (s, 1H), 7.77−7.70 (m 4H), 7.35 (t, J = 7.4 Hz, 1H), 7.27 (t, J = 7.6 Hz 1H), 6.78 (d, J = 9.0 Hz, 2H), 3.42 (q, J = 7.0 Hz, 4H), 1.13 (t, J = 6.9 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 154.6, 149.9, 141.5, 136.5, 132.0, 130.0, 123.2, 122.1, 119.7, 119.1, 111.0, 110.5, 43.7, 12.3. Anal. Calcd for $C_{18}H_{20}N_4$: C, 73.94; H, 6.89; N, 19.16. Found: C, 73.56; H, 7.00; N, 18.99.

General Method for the Preparation of *N*-(3-Butylbenzimidazol-3-ium-1-yl)-1-arylmethanimine iodides (6a−f): 1-Iodobutane (3 equiv) and the corresponding imines **4a**−**f** were heated with stirring at 100 °C in a round-bottom flask for 5 h without solvent. Excess 1-iodobutane was removed under reduced pressure at 50 °C to give the corresponding 3-butyl-*N*-(arylmethyleneimino)benzimidazolium iodides **6a**−**f** in quantitative yields.

***N*-(3-Butylbenzimidazol-3-ium-1-yl)-1-(4-methoxyphenyl)-methanimine iodide (6a):** White crystals (100%), mp 154.0−155.0 °C;

dx.doi.org/10.1021/jo200088s |*J. Org. Chem.* 2011, 76, 4082–4087

^{1}H NMR (DMSO-d_6) δ 10.57 (s, 1H), 9.38 (s, 1H), 8.23−8.20 (m, 1H), 8.13−8.09 (m, 1H), 8.02 (d, J = 8.8 Hz, 2H), 7.80−7.74 (m, 2H), 7.20 (d, J = 8.8 Hz, 2H), 4.59 (t, J = 7.3 Hz, 2H), 3.90 (s, 3H), 2.03 (quintet, J = 7.4 Hz, 2H), 1.45 (sextet, J = 7.3 Hz, 2H), 0.98 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 163.3, 162.1, 135.7, 131.3, 130.0, 129.4, 127.2, 126.9, 123.6, 114.9, 113.8, 113.1, 55.7, 47.1, 30.4, 19.1, 13.4. Anal. Calcd for $C_{19}H_{22}IN_3O$: C, 52.42; H, 5.09; N, 9.65. Found: C, 52.33; H, 5.15; N, 9.51.

***N*-(3-Butylbenzimidazol-3-ium-1-yl)-1-phenylmethanimine iodide (6b):** White crystals (100%), mp 171.0−172.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.58 (s, 1H), 9.44 (s, 1H), 8.25−8.15 (m, 2H), 8.08 (d, J = 6.9 Hz, 2H), 7.82−7.76 (m, 2H), 7.74−7.64 (m, 3H), 4.59 (t, J = 7.2 Hz, 2H), 2.02 (quintet, J = 7.5 Hz, 2H), 1.45 (sextet, J = 7.5 Hz, 2H), 0.98 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 162.6, 136.0, 133.3, 131.2, 130.0, 129.4, 129.3, 129.1, 127.3, 127.0, 113.9, 113.1, 47.1, 30.4, 19.1, 13.4. Anal. Calcd for $C_{18}H_{20}IN_3$: C, 53.35; H, 4.97; N, 10.37. Found: C, 53.06; H, 4.95; N, 10.18.

1-(4-Bromo-2-thienyl)-*N*-(3-butylbenzimidazol-3-ium-1-yl)-methanimine iodide (6c): Brown crystals (100%), mp 175.0−176.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.54 (s, 1H), 9.59 (s, 1H), 8.25−8.21 (m, 2H), 8.11−8.07 (m, 1H), 7.98 (s, 1H), 7.80−7.75 (m, 2H), 4.59 (t, J = 7.2 Hz, 2H), 2.01 (quintet, J = 7.2 Hz, 2H), 1.44 (sextet, J = 7.5 Hz, 2H), 0.97 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 155.5, 137.7, 136.5, 136.4, 131.4, 130.0, 129.0, 127.4, 127.0, 113.9, 113.0, 110.4, 47.1, 30.3, 19.0, 13.4. Anal. Calcd for $C_{16}H_{17}IBrN_3S$: C, 39.20; H, 3.50; N, 8.57. Found: C, 39.08; H, 3.60; N, 8.17.

***N*-(3-Butylbenzimidazol-3-ium-1-yl)-1-(*p*-tolyl)methanimine iodide (6d):** White crystals (100%), mp 167.0−169.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.55 (s, 1H), 9.38 (s, 1H), 8.23−8.19 (m, 1H), 8.17−8.12 (m, 1H), 7.97 (t, J = 8.1 Hz, 2H), 7.79−7.74 (m, 2H), 7.47 (d, J = 7.8 Hz, 2H), 4.59 (t, J = 7.2 Hz, 2H), 2.45 (s, 3H), 2.08−1.98 (m, 2H), 1.50−1.40 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 162.5, 143.9, 135.9, 130.0, 129.4, 129.2, 128.5, 127.3, 127.0, 113.9, 113.1, 47.1, 30.4, 21.4, 19.1, 13.4. Anal. Calcd for $C_{19}H_{22}IN_3$: C, 54.42; H, 5.29; N, 10.02. Found: C, 54.43; H, 5.31; N, 9.90.

***N*-(3-Butylbenzimidazol-3-ium-1-yl)-1-(4-nitrophenyl)methanimine iodide (6e):** Brown crystals (100%), mp 217.0−219.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.57 (s, 1H), 9.55 (s, 1H), 8.47 (d, J = 8.4 Hz, 2H), 8.32 (d, J = 8.7 Hz, 2H), 8.28−8.20 (m, 2H), 7.83−7.77 (m, 2H), 4.60 (t, J = 7.2 Hz, 2H), 2.01 (quintet, J = 7.4 Hz, 2H), 1.44 (sextet, J = 7.8 Hz, 2H), 0.97 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 160.0, 149.8, 137.0, 136.5, 130.3, 130.1, 129.4, 127.6, 127.3, 124.4, 114.0, 113.3, 47.2, 30.4, 19.1, 13.4. Anal. Calcd for $C_{18}H_{19}IN_4O_2$: C, 48.01; H, 4.25; N, 12.44. Found: C, 47.73; H, 4.14; N, 12.18.

4-[(*E*)-(3-Butylbenzimidazol-3-ium-1-yl)iminomethyl]-*N*,*N*-diethylaniline iodide (6f): Yellow microcrystals (100%), mp 151.0−152.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.35 (s, 1H), 9.03 (s, 1H), 8.18−8.14 (m, 1H), 8.07−8.03 (m, 1H), 7.80 (d, J = 9.0 Hz, 2H), 7.74−7.71 (m, 2H), 6.85 (d, J = 9.0 Hz, 2H), 4.53 (t, J = 7.2 Hz, 2H), 3.47 (q, J = 6.8 Hz, 4H), 1.97 (quintet J = 7.5 Hz, 2H), 1.41 (sextet, J = 7.5 Hz, 2H), 1.15 (t, J = 7.0 Hz, 6H), 0.95 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 163.0, 151.3, 135.5, 131.6, 130.1, 129.5, 126.9, 126.9, 116.9, 113.7, 113.1, 111.3, 46.8, 44.0, 30.6, 19.1, 13.4, 12.4. Anal. Calcd for $C_{22}H_{29}IN_4$: C, 55.47; H, 6.14; N, 11.76. Found: C, 55.11; H, 6.13; N, 11.57.

1,3-Dimethylbenzimidazol-3-ium iodide (7): White needles (94%), mp 193.0 °C (lit.[48] mp 190−191 °C); ^{1}H NMR (DMSO-d_6) δ 9.76 (s, 1H), 8.12−7.98 (m, 2H), 7.76−7.65 (m, 2H), 4.12 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 142.8, 131.4, 126.2, 113.2, 33.5.

General Method for the Preparation of NHC·CS_2 Betaines 9a−c, 10: Sodium hydride (1.2 equiv) was added to a mixture of carbon disulfide (2 equiv) and 1,3-dimethylbenzimidazolium iodide **7** or *N*-(3-butylbenzimidazol-3-ium-1-yl)-1-(aryl)methanimine iodides **6a−c** in dry THF and stirred for 5 h (12 h in the case of **7**) at room temperature under argon. The solution was filtered, the filtrate concentrated under reduced pressure, and the residue was recrystallized from EtOH to obtain the corresponding NHC·CS_2 betaines **9a−c**, **10**.

1-Butyl-3-[(*E*)-(4-methoxyphenyl)methyleneamino]benzimidazol-1-ium-2-carbodithioate (9a): Red crystals (70%), mp 160.0−161.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.25 (s, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.93−7.87 (m, 3H), 7.73−7.61 (m, 2H), 7.14 (d, J = 8.7 Hz, 2H), 4.44 (t, J = 7.7 Hz, 2H), 3.87 (s, 3H), 1.91 (quintet, J = 7.5 Hz, 2H), 1.38 (sextet, J = 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 222.6, 168.2, 163.5, 146.6, 131.4, 128.1, 127.3, 126.6, 123.6, 114.7, 113.5, 112.8, 55.7, 44.7, 30.4, 19.3, 13.4.

1-[(*E*)-Benzylideneamino]-3-butylbenzimidazol-3-ium-2-carbodithioate (9b): Red crystals (76%), mp 171.0−172.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.38 (s, 1H), 8.09−8.05 (m, 1H), 8.00−7.92 (m, 3H), 7.74−7.65 (m, 3H), 7.64−7.56 (m, 2H), 4.45 (t, J = 7.7 Hz, 2H), 1.92 (quintet, J = 7.2 Hz, 2H), 1.39 (sextet, J = 7.4 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 222.5, 168.2, 146.6, 133.5, 131.3, 129.2, 129.1, 128.2, 127.2, 126.7, 113.5, 113.0, 44.7, 40.3, 30.4, 19.3, 13.4. Anal. Calcd for $C_{19}H_{19}N_3S_2$: C, 64.56; H, 5.42; N, 11.89. Found: C, 64.34; H, 5.47; N, 11.85.

1-[(*E*)-(4-Bromo-2-thienyl)methyleneamino]-3-butylbenzimidazol-3-ium-2-carbodithioate (9c): Red crystals (68%), mp 170.0−173.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.47 (s, 1H), 8.16 (s, 1H), 8.10−8.03 (m, 1H), 7.98−7.93 (m, 1H), 7.90 (s, 1H), 7.75−7.65 (m, 2H), 4.46−4.38 (m, 2H), 1.95−1.85 (m 2H), 1.45−1.32 (m, 2H), 0.89 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 221.9, 160.7, 146.6, 138.4, 136.3, 131.4, 128.2, 127.0, 126.8, 113.6, 112.9, 110.2, 44.8, 30.3, 19.3, 13.4. Anal. Calcd for $C_{17}H_{16}BrN_3S_3$: C, 46.57; H, 3.68; N, 9.58. Found: C, 46.26; H, 3.53; N, 9.30.

1,3-Dimethylbenzimidazol-3-ium-2-carbodithioate (10): Red crystals (85%), mp 235.0−236.0 °C (lit.[37] mp 237−238 °C); ^{1}H NMR (DMSO-d_6) δ 7.92 (dd, J = 6.0, 3.0 Hz, 2H), 7.64 (dd, J = 6.0, 3.0 Hz, 2H), 3.88 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 223.8, 151.5, 129.9, 126.0, 112.9, 31.0. Anal. Calcd for $C_{10}H_{10}N_2S_2$: C, 54.02; H, 4.53; N, 12.60. Found: C, 53.87; H, 4.44; N, 12.39.

(1,3-Dimethylbenzimidazol-3-ium-2-carbothioyl)isopropylazanide (12): Colorless crystals (86%), mp 140.0−141.0 °C; ^{1}H NMR (DMSO-d_6) δ 8.14 (dd, J = 6.3, 3.0 Hz, 2H), 7.74 (dd, J = 6.3, 3.0 Hz, 2H), 3.99 (s, 6H), 1.37 (d, J = 6.6 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 173.9, 145.1, 130.5, 127.3, 113.7, 47.8, 32.2, 20.2. Anal. Calcd for $C_{13}H_{17}N_3S\cdot H_2O$: C, 58.84; H, 7.22; N, 15.83. Found: C, 58.97; H, 7.40; N, 15.86.

General Method for the Preparation of Spirocyclic Derivatives (13a,b): Sodium hydride (1.2 equiv) was added to a mixture of isopropyl isothiocyanate (2.2 equiv) and the corresponding *N*-(3-butylbenzimidazol-3-ium-1-yl)-1-(aryl)methanimine iodides **6a**, in dry THF and stirred for 5 h at room temperature under argon. The solution was filtered, the filtrate concentrated under reduced pressure, and the residue was recrystallized from EtOAc to obtain pure spirocyclic derivatives **13a,b** as red crystals.

1-Butyl-1′,3′-diisopropyl-3-[(*E*)-(4-methoxyphenyl)methyleneamino]spiro[benzimidazole-2,5′-imidazolidine]-2′,4′-dithione (13a): Red crystals (77%), mp 141.0−142.0 °C; ^{1}H NMR (DMSO-d_6) δ 7.84 (s, 1H), 7.51 (d, J = 8.7 Hz, 2H), 7.26 (d, J = 7.2 Hz, 1H), 6.97 (d, J = 8.7 Hz, 2H), 6.83 (t, J = 7.5 Hz, 1H), 6.72 (t, J = 7.3 Hz, 1H), 6.65 (d, J = 7.5 Hz, 1H), 5.68 (br s, 1H), 4.13−4.03 (m, 1H), 3.77 (s, 3H), 3.19−2.96 (m, 2H), 1.65−1.52 (m, 8H), 1.38−1.29 (m, 5H), 1.23 (d, J = 6.9 Hz, 3H), 0.86 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 160.3, 139.6, 136.6, 132.2, 127.4, 121.4, 118.2, 114.3, 107.8, 104.8, 103.9, 99.4, 55.2, 42.8, 29.6, 19.8, 19.0, 17.9, 13.5. Anal. Calcd for $C_{27}H_{35}N_5OS_2$: C, 63.62; H, 6.92; N, 13.74. Found: C, 63.80; H, 7.21; N, 13.76.

1-[(*E*)-Benzylideneamino]-3-butyl-1′,3′-diisopropylspiro-[benzimidazole-2,5′-imidazolidine]-2′,4′-dithione (13b): Red crystals (74%), mp 116.0−119.0 °C; ^{1}H NMR (DMSO-d_6) δ 7.85 (s, 1H), 7.61−7.55 (m, 2H), 7.42−7.30 (m, 4H), 6.86 (t, J = 7.7 Hz, 1H), 6.74 (t, J = 7.7 Hz, 1H), 6.67 (d, J = 7.6 Hz, 1H), 5.68 (br s, 1H), 4.16−4.05 (m, 1H), 3.20−2.97 (m, 2H), 1.64−1.48 (m, 8H), 1.38−1.29 (m, 5H), 1.23

(d, J = 7.0 Hz, 3H), 0.86 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 139.0, 136.6, 134.8, 131.9, 129.2, 128.7, 125.8, 121.8, 118.2, 108.3, 105.0, 103.6, 42.8, 29.5, 19.8, 19.0, 17.9, 13.6. Anal. Calcd for $C_{26}H_{33}N_5S_2$: C, 65.10; H, 6.93; N, 14.60. Found: C, 65.10; H, 7.06; N, 14.58.

General Method for the Preparation of NHC·RC(O)NCS Betaines 15a−c, 16. Sodium hydride (1.2 equiv) was added to a mixture of benzoylisothiocyanate and the corresponding *N*-(3-butylbenzimidazol-3-ium-1-yl)-1-(aryl)methanimine iodides **6a−c** in 1/1 molar ratio in dry THF and stirred for 5 h (12 h in the case of **7**) at room temperature under argon. The solution was filtered, the filtrate concentrated under reduced pressure, and the residue was purified by flash chromatography using EtOAc/hexanes to obtain betaine adducts **15a−c**, **16**.

Benzoyl-[1-butyl-3-[(*E*)-(4-methoxyphenyl)methyleneamino]benzimidazol-1-ium-2-carbothioyl]azanide (15a): Yellow microcrystals (83%), mp 126.0−128.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.35 (s, 1H), 8.13 (d, J = 8.1 Hz, 1H), 8.03−7.94 (m, 5H), 7.75−7.65 (m, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.7 Hz, 2H), 7.18 (d, J = 8.7 Hz, 2H), 4.63 (t, J = 7.2 Hz, 2H), 3.89 (s, 3H), 2.02−1.92 (m, 2H), 1.47−1.36 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 179.1, 169.8, 168.2, 163.6, 145.1, 133.7, 132.3, 131.6, 129.2, 128.9, 128.3, 127.5, 126.8, 123.8, 114.8, 113.6, 113.2, 55.7, 45.2, 30.6, 19.4, 13.5. Anal. Calcd for $C_{27}H_{26}N_4O_2S$: C, 68.91; H, 5.57; N, 11.91. Found: C, 68.63; H, 5.63; N, 11.73.

Benzoyl-[1-[(*E*)-benzylideneamino]-3-butylbenzimidazol-3-ium-2-carbothioyl]azanide (15b): Yellow crystals (77%), mp 125.0−127.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.48 (s, 1H), 8.18−8.08 (m, 2H), 8.04−7.94 (m, 4H), 7.78−7.69 (m, 3H), 7.63 (t, J = 7.4 Hz, 2H), 7.53 (t, J = 7.4 Hz, 1H), 7.34 (t, J = 7.5 Hz, 2H), 4.64 (t, J = 7.3 Hz, 2H), 2.05−1.93 (m, 2H), 1.43 (sextet, J = 7.4 Hz, 2H), 0.92 (t, J = 7.3 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 179.0, 169.8, 168.1, 145.3, 133.7, 133.5, 132.3, 131.3, 129.3, 129.1, 128.9, 128.2, 127.2, 126.9, 126.9, 113.6, 113.2, 45.2, 30.5, 19.3, 13.4. Anal. Calcd for $C_{26}H_{24}N_4OS$: C, 70.88; H, 5.49; N, 12.72. Found: C, 70.57; H, 5.60; N, 12.51.

Benzoyl-[1-[(*E*)-(4-bromo-2-thienyl)methyleneamino]-3-butylbenzimidazol-3-ium-2-carbothioyl]azanide (15c): Yellow crystals (74%), mp 151.0−154.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.55 (s, 1H), 8.18 (s, 1H), 8.11 (d, J = 8.1 Hz, 1H), 8.05 (d, J = 7.3 Hz, 1H), 7.98 (d, J = 7.2 Hz, 2H), 7.87 (s, 1H), 7.75−7.66 (m, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.4 Hz, 2H), 4.61 (t, J = 7.2 Hz, 2H), 1.99−1.90 (m, 2H), 1.46−1.34 (m, 2H), 0.89 (t, J = 7.4 Hz, 3H); ^{13}C NMR (DMSO-d_6) δ 179.1, 170.1, 161.0, 145.6, 138.7, 136.5, 133.8, 132.5, 131.8, 129.4, 129.0, 128.6, 128.4, 127.1, 127.1, 113.8, 113.3, 110.4, 45.4, 30.5, 19.4, 13.5. Anal. Calcd for $C_{24}H_{21}BrN_4OS_2$: C, 54.86; H, 4.03; N, 10.66. Found: C, 55.19; H, 4.09; N, 10.42.

Benzoyl-(1,3-dimethylbenzimidazol-3-ium-2-carbothioyl)-azanide (16): Yellow crystals (85%), mp 207.0−210.0 °C; ^{1}H NMR (DMSO-d_6) δ 8.02−7.94 (m, 4H), 7.69−7.64 (m, 2H), 7.59 (d, J = 6.7 Hz, 1H), 7.55−7.48 (m, 2H), 4.02 (s, 6H); ^{13}C NMR (DMSO-d_6) δ 178.7, 172.0, 150.0, 134.2, 132.4, 130.4, 129.2, 128.5, 126.2, 113.1, 31.7.

General Method for Amination. To a solution of 1-aminobenzimidazole **2** or its imine derivatives **4a−f** in dichloromethane/ethanol (5:1) was added 1.2−1.5 equiv of *O*-(2,4-dinitrophenyl)hydroxylamine with stirring over a period of 2−3 min. The mixture was heated under reflux for 5−8 h. After cooling and standing for 30 min, the solid was filtered off, washed twice with ethyl acetate (20 mL), and dried under vacuum to obtain the corresponding 2,4-dinitrophenolate salts.

Benzimidazol-3-ium-1,3-diamine; 2,4-Dinitrophenolate (18): Brown microcrystals (80%), mp 166.0−168.0 °C; ^{1}H NMR (DMSO-d_6) δ 9.88 (s, 1H), 8.60 (d, J = 3.0 Hz, 1H), 7.93−7.87 (m, 2H), 7.80 (dd, J = 9.8, 3.2 Hz, 1H), 7.75−7.67 (m, 2H), 6.91 (s, 4H), 6.34 (d, J = 9.9 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 169.7, 142.4, 136.1, 131.0, 127.8, 127.5, 126.5, 126.1, 124.8, 112.9. Anal. Calcd for $C_{13}H_{12}N_6O_5$: C, 46.99; H, 3.64; N, 25.29. Found: C, 46.96; H, 3.49; N, 25.14.

3-[(*E*)-(4-Methoxyphenyl)methyleneamino]benzimidazol-1-ium-1-amine; 2,4-Dinitrophenolate (19a): Yellow microcrystals (42%), mp 146.0−148.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.40 (s, 1H), 9.23 (s, 1H), 8.58 (d, J = 3.9 Hz, 1H), 8.13−8.09 (m, 1H), 8.01−7.95 (m, 3H), 7.80−7.72 (m, 3H), 7.19 (d, J = 8.8 Hz, 2H), 7.13 (s, 2H), 6.30 (d, J = 9.8 Hz, 1H); ^{13}C NMR (DMSO-d_6) δ 170.3, 165.1, 163.4, 162.5, 136.0, 131.3, 131.1, 128.5, 127.4, 126.9, 126.5, 125.0, 123.7, 114.9, 113.3, 112.9, 109.2, 55.7. Anal. Calcd for $C_{21}H_{18}N_6O_6$: C, 56.00; H, 4.03; N, 18.66. Found: C, 55.86; H, 3.86; N, 18.58.

3-[(*E*)-*p*-Tolylmethyleneamino]benzimidazol-1-ium-1-amine; 2,4-Dinitrophenolate (19d): Brown microcrystals (40%), mp 132.0−134.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.45 (s, 1H), 9.28 (s, 1H), 8.58 (d, J = 3.3 Hz, 1H), 8.14−8.11 (m, 1H), 8.01−7.97 (m, 1H), 7.92 (d, J = 7.9 Hz, 2H), 7.80−7.72 (m, 3H), 7.45 (d, J = 7.9 Hz, 2H), 7.16 (s, 2H), 6.32 (d, J = 9.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (DMSO-d_6) δ 169.9, 162.5, 143.9, 136.0, 135.9, 131.0, 129.9, 129.1, 128.6, 128.5, 127.7, 127.5, 127.4, 126.9, 126.3, 124.8, 113.2, 112.9, 21.3. Anal. Calcd for $C_{21}H_{18}N_6O_5$: C, 58.06; H, 4.18; N, 19.35. Found: C, 57.64; H, 4.05; N, 19.38.

3-[(*E*)-[4-(Diethylamino)phenyl]methyleneamino]benzimidazol-1-ium-1-amine; 2,4-Dinitrophenolate (19f): Brown microcrystals (60%), mp 180.0 °C; ^{1}H NMR (DMSO-d_6) δ 10.38 (s, 1H), 9.01 (s, 1H), 8.63 (d, J = 2.7 Hz, 1H), 8.04 (d, J = 7.5 Hz, 1H), 7.98 (d, J = 7.8 Hz, 1H), 7.88 (dd, J = 9.6, 3.0 Hz, 1H), 7.80−7.68 (m, 4H), 7.09 (br s, 2H), 6.83 (d, J = 8.7 Hz, 2H), 6.50 (d, J = 9.6 Hz, 1H), 3.46 (q, J = 6.6 Hz, 4H), 1.16 (t, J = 6.8 Hz, 6H); ^{13}C NMR (DMSO-d_6) δ 168.6, 162.8, 151.2, 136.0, 135.7, 131.5, 131.1, 129.0, 128.5, 127.7, 127.0, 126.7, 125.5, 124.5, 117.0, 113.1, 112.8, 111.1, 43.9, 12.3. Anal. Calcd for $C_{24}H_{25}N_7O_5$: C, 58.65; H, 5.13; N, 19.95. Found: C, 58.32; H, 5.26; N, 19.88.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H and ^{13}C spectra for **4a−f**, **6a−f**, **7**, **9a−c**, **10**, **12**, **13a,b**, **15a−c**, **16**, **18**, **19a**, **19d**, and **19f** and the X-ray crystal structure and data of **9a**, **13a**, and **16** as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

■ REFERENCES

(1) Shimakawa, Y.; Morikawa, T.; Sakaguchi, S. *Tetrahedron Lett.* **2010**, *51*, 1786–1789.
(2) Enders, D.; Balensiefer, T. *Acc. Chem. Res.* **2004**, *37*, 534–541.
(3) Liu, Q.; Rovis, T. *J. Am. Chem. Soc.* **2006**, *128*, 2552–2553.
(4) DiRocco, D. A.; Oberg, K. M.; Dalton, D. M.; Rovis, T. *J. Am. Chem. Soc.* **2009**, *131*, 10872–10874.
(5) Zhang, Y.-R.; He, L.; Wu, X.; Shao, P.-L.; Ye, S. *Org. Lett.* **2008**, *10*, 277–280.
(6) De Sarkar, S.; Studer, A. *Org. Lett.* **2010**, *12*, 1992–1995.
(7) Yang, L.; Tan, B.; Wang, F.; Zhong, G. *J. Org. Chem.* **2009**, *74*, 1744–1746.
(8) Connor, E. F.; Nyce, G. W.; Myers, M.; Möck, A.; Hedrick, J. L. *J. Am. Chem. Soc.* **2002**, *124*, 914–915.
(9) Nyce, G. W.; Glauser, T.; Connor, E. F.; Möck, A.; Waymouth, R. M.; Hedrick, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 3046–3056.
(10) Csihony, S.; Nyce, G. W.; Sentman, A. C.; Waymouth, R. M.; Hedrick, J. L. *Polym. Prepr.* **2004**, *45*, 319–320.
(11) Grasa, G. A.; Kissling, R. M.; Nolan, S. P. *Org. Lett.* **2002**, *4*, 3583–3586.
(12) Marion, N.; Diez-González, S.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2007**, *46*, 2988–3000.
(13) Wanzlick, H. W. *Angew. Chem.* **1962**, *74*, 129–134.
(14) Choi, T.-L.; Grubbs, R. H. *Chem. Commun.* **2001**, 2648–2649.
(15) Uchida, T.; Katsuki, T. *Tetrahedron Lett.* **2009**, *50*, 4741–4743.
(16) Arduengo, A. J., III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361–363.

(17) Nair, V.; Bindu, S.; Sreekumar, V. *Angew. Chem., Int. Ed.* **2004**, *43*, 5130–5135.
(18) Wanzlick, H. W.; Schikora, E. *Angew. Chem.* **1960**, *72*, 494.
(19) Wanzlick, H. W.; Schoenherr, H. J. *Angew. Chem., Int. Ed. Engl.* **1968**, *7*, 141–142.
(20) Cheng, Y.; Meth-Cohn, O. *Chem. Rev.* **2004**, *104*, 2507–2530.
(21) Nair, V.; Rajesh, C.; Vinod, A. U.; Bindu, S.; Sreekanth, A. R.; Mathen, J. S.; Balagopal, L. *Acc. Chem. Res.* **2003**, *36*, 899–907.
(22) Ma, C.; Ding, H.; Zhang, Y.; Bian, M. *Angew. Chem., Int. Ed.* **2006**, *45*, 7793–7797.
(23) Nair, V.; Sreekumar, V.; Bindu, S.; Suresh, E. *Org. Lett.* **2005**, *7*, 2297–2300.
(24) Zhou, H.; Zhang, W.-Z.; Liu, C.-H.; Qu, J.-P.; Lu, X.-B. *J. Org. Chem.* **2008**, *73*, 8039–8044.
(25) Schoessler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931–1948.
(26) Duong, H. A.; Tekavec, T. N.; Arif, A. M.; Louie, J. *Chem. Commun.* **2004**, 112–113.
(27) Winberg, H. E.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2776–2777.
(28) Delaude, L.; Demonceau, A.; Wouters, J. *Eur. J. Inorg. Chem.* **2009**, 1882–1891.
(29) Küçükbay, H.; Durmaz, R.; Orhan, E.; Günal, S. *Farmaco* **2003**, *58*, 431–437.
(30) Pesch, J.; Harms, K.; Bach, T. *Eur. J. Org. Chem.* **2004**, 2025–2035.
(31) Coulembier, O.; Dove, A. P.; Pratt, R. C.; Sentman, A. C.; Culkin, D. A.; Mespouille, L.; Dubois, P.; Waymouth, R. M.; Hedrick, J. L. *Angew. Chem., Int. Ed.* **2005**, *44*, 4964–4968.
(32) Hardman, N. J.; Abrams, M. B.; Pribisko, M. A.; Gilbert, T. M.; Martin, R. L.; Kubas, G. J.; Baker, R. T. *Angew. Chem., Int. Ed.* **2004**, *43*, 1955–1958.
(33) Blanrue, A.; Wilhelm, R. *Synthesis* **2009**, 583–586.
(34) Blanrue, A.; Wilhelm, R. *Synlett* **2004**, 2621–2623.
(35) Krasuski, W.; Nikolaus, D.; Regitz, M. *Liebigs Ann. Chem.* **1982**, 1451–1465.
(36) Naeem, S.; Delaude, L.; White, A. J. P.; Wilton-Ely, J. D. E. T. *Inorg. Chem.* **2010**, *49*, 1784–1793.
(37) Kucukbay, H.; Cetinkaya, E.; Durmaz, R. *Arzneim. Forsch.* **1995**, *45*, 1331–1334.
(38) Li, J.-Q.; Liao, R.-Z.; Ding, W.-J.; Cheng, Y. *J. Org. Chem.* **2007**, *72*, 6266–6269.
(39) Cheng, Y.; Wang, B.; Wang, X.-R.; Zhang, J.-H.; Fang, D.-C. *J. Org. Chem.* **2009**, *74*, 2357–2367.
(40) Balch, A. L.; Parks, J. E. *J. Am. Chem. Soc.* **1974**, *96*, 4114–4121.
(41) Alcarazo, M. R.; Roseblade, S. J.; Alonso, E.; Fernández, R.; Alvarez, E.; Lahoz, F. J.; Lassaletta, J. M. *J. Am. Chem. Soc.* **2004**, *126*, 13242–13243.
(42) Ros, A.; Monge, D.; Alcarazo, M.; Álvarez, E.; Lassaletta, J. M.; Fernández, R. *Organometallics* **2006**, *25*, 6039–6046.
(43) Pozharskii, A. F.; Kuz′menko, V. V.; Bumber, A. A.; Petrov, E. S.; Terekhova, M. I.; Chikina, N. L.; Nanavyan, I. M. *Khim. Geterotsikl. Soedin.* **1989**, 221–227.
(44) Katritzky, A. R.; Laurenzo, K. S. *J. Org. Chem.* **1988**, *53*, 3978–3982.
(45) Sheng, M. N.; Day, A. R. *J. Org. Chem.* **1963**, *28*, 736–740.
(46) Kuznetsov, L. I.; Kolodyazhnyi, Y. V.; Vlotskaya, O. A.; Chikina, N. L.; Kuz′menko, V. V.; Garnovskii, A. D. *Koord. Khim.* **1982**, *8*, 445–453.
(47) Kinoshita, A.; Takei, Y.; Goto, S. *Jpn. Kokai Tokkyo Koho* **1988**, JP63184760, CAN, 110:31371.
(48) Bostai, B.; Novák, Z.; Bényei, A. C.; Kotschy, A. *Org. Lett.* **2007**, *9*, 3437–3439.
(49) Pozharskii, A. F.; Kuz′menko, V. V.; Foces-Foces, C.; Llamas-Saiz, A. L.; Claramunt, R. M.; Sanz, D.; Elguero, J. *J. Chem. Soc., Perkin Trans. 2* **1994**, 841–846.
(50) Legault, C.; Charette, A. B. *J. Org. Chem.* **2003**, *68*, 7119–7122.