Supporting Information

Tunable Room-Temperature Synthesis of Coinage Metal Chalcogenide Nanocrystals from *N*-Heterocyclic Carbene Synthons

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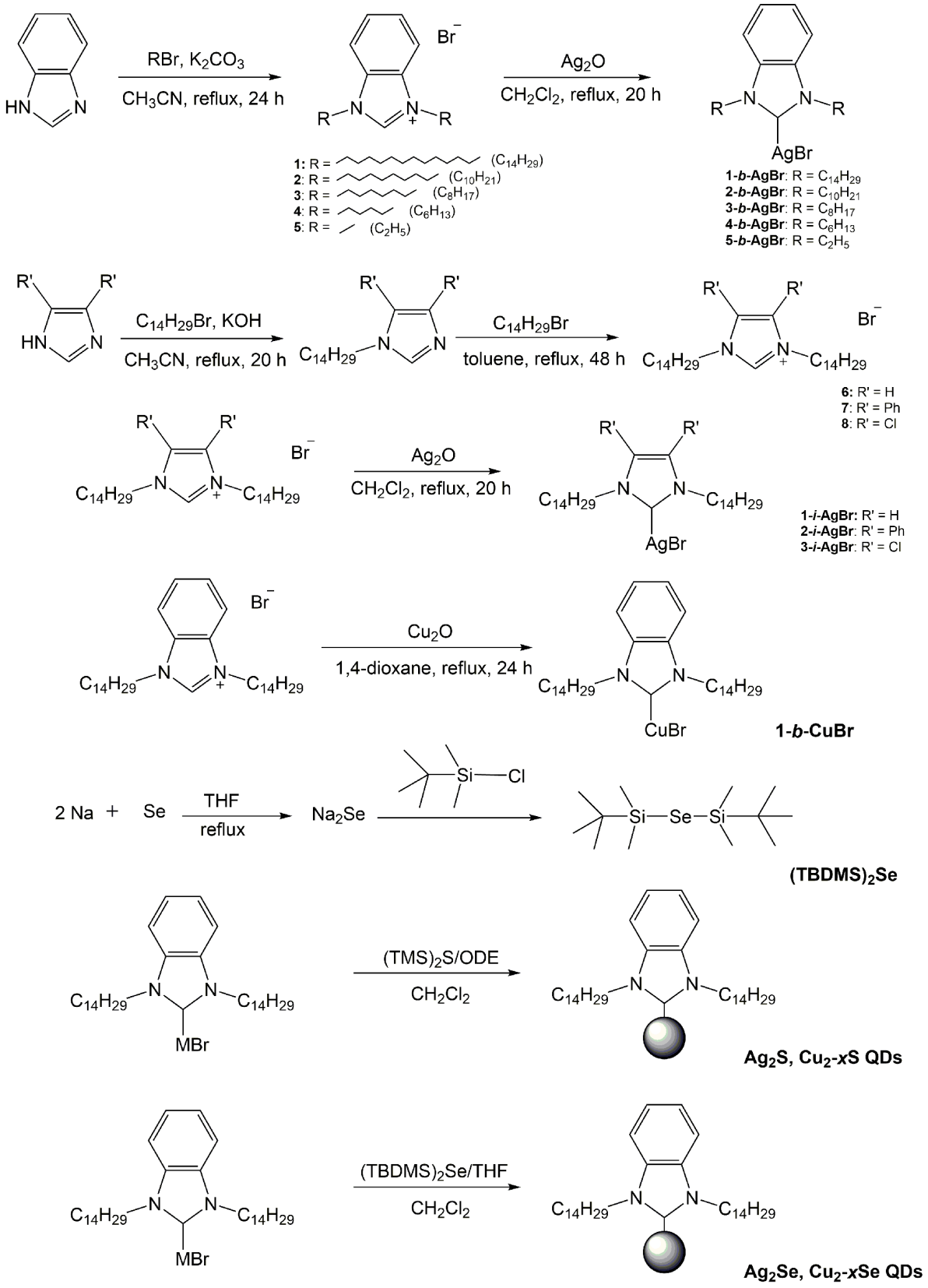
Table of Contents:

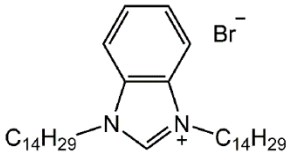
S1. General synthetic scheme



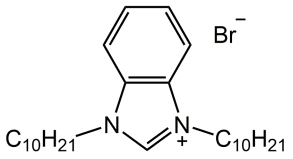
S2. Synthetic procedures

Benzimidazolium salts **1–5**, benzimidazole-based NHC-AgBr (**j-*b*-AgBr**, j = 1–5) and NHC-CuBr complexes, imidazole-based NHC-AgBr (**j-*i*-AgBr**, j = 1–3) complexes, and $(TBDMS)_2Se$ were synthesized according to modified literature procedures.[1-4] The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad.

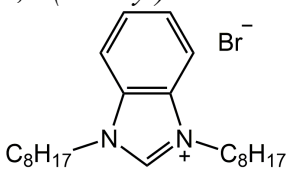
1,3-(Ditetradecyl)benzimidazolium bromide (**1**).[1] Benzimidazole (2.36 g, 20.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), *n*-tetradecyl bromide (18 mL, 60 mmol) and CH_3CN (20 mL) were added into a three-neck flask and stirred at reflux (~85 ˚C) for 24 h. After the reaction, the solvent was removed under reduced pressure, and the resulting solid was dissolved in CH_2Cl_2. The mixture was filtered to remove the KBr precipitate. The filtrate was then concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (6.8 g, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.71–7.63 (m, 4 H), 4.62 (t, J = 7.6 Hz, 4H), 2.10–2.00 (m, 4H), 1.45–1.2 (m, 44H), 0.87 (t, J = 7.1 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.06, 131.46, 127.18, 113.18, 47.82, 32.04, 29.79, 29.76, 29.70, 29.68, 29.62, 29.51, 29.47, 29.17, 22.81, 14.24.



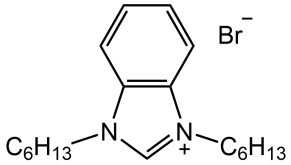
1,3-(Didecyl)benzimidazolium bromide (**2**). Benzimidazole (2.36 g, 20.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), *n*-decyl bromide (13 mL, 60 mmol) and CH_3CN (20 mL) were added into a three-neck flask and stirred at reflux (~85 ˚C) for 24 h. After the reaction, the solvent was removed under reduced pressure, followed by the dissolution in CH_2Cl_2. The mixture was filtered to remove the KBr precipitate. The filtrate was then concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (3.4 g, 35%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.56 (s, 1H), 7.71–7.65 (m, 4 H), 4.62 (t, J = 7.49 Hz, 4H), 2.08–2.02 (m, 4H), 1.43–1.23 (m, 28H), 0.86 (t, J = 6.64 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.94, 131.45, 127.19, 113.19, 47.82, 31.93, 29.66, 29.55, 29.48, 29.33, 29.15, 26.67, 22.75, 14.20.



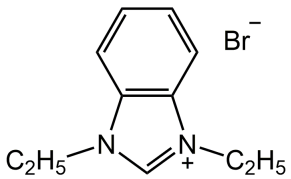
1,3-(Dioctyl)benzimidazolium bromide (**3**). Benzimidazole (2.36 g, 20.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), *n*-octyl bromide (12 mL, 60 mmol) and CH_3CN (20 mL) were added into a three-neck flask and stirred under reflux (~85 ˚C) for 24 h. After the reaction, the solvent was removed under reduced pressure, followed by the dissolution in CH_2Cl_2. The mixture was filtered to remove the KBr precipitate. The filtrate was then concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (2.5 g, 30%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.49 (s, 1H), 7.71–7.64 (m, 4 H), 4.62 (t, J = 7.52 Hz, 4H), 2.08–2.02 (m, 4H), 1.44–1.23 (m, 20H), 0.85 (t, J = 6.70 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.85, 131.43, 127.20, 113.19, 47.81, 31.76, 29.63, 29.12, 29.08, 26.65, 22.65, 14.13.



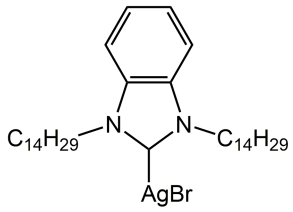
1,3-(Dihexyl)benzimidazolium bromide (**4**). Benzimidazole (2.36 g, 20.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), *n*-hexyl bromide (5.6 mL, 40 mmol) and CH_3CN (20 mL) were added into a three-neck flask and stirred under reflux (~85 ˚C) for 24 h. After the reaction, the solvent was removed under reduced pressure, followed by the dissolution in CH_2Cl_2. The mixture was filtered to remove the KBr precipitate. The filtrate was then concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (3.2 g, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.60 (s, 1H), 7.71–7.65 (m, 4 H), 4.62 (t, J = 7.52 Hz, 4H), 2.08–2.02 (m, 4H), 1.42–1.33 (m, 12H), 0.87 (t, J = 7.52 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.06, 131.46, 127.21, 113.18, 47.82, 31.27, 29.64, 26.35, 22.54, 14.06.



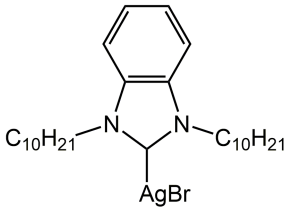
1,3-(Diethyl)benzimidazolium bromide (**5**). Benzimidazole (2.36 g, 20.0 mmol), K_2CO_3 (2.76 g, 20.0 mmol), *n*-ethyl bromide (3.0 mL, 40 mmol) and CH_3CN (20 mL) were added into a three-neck flask and stirred under reflux (~85 ˚C) for 24 h. After the reaction, the solvent was removed under reduced pressure, followed by the dissolution in CH_2Cl_2. The mixture was filtered to remove the KBr precipitate. The filtrate was then concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (3.3 g, 66%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 11.28 (s, 1H), 7.75–7.62 (m, 4 H), 4.67 (q, J = 7.34 Hz, 4H), 1.70 (t, J = 7.36 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.04, 131.22, 127.25, 113.17, 42.99, 14.98.



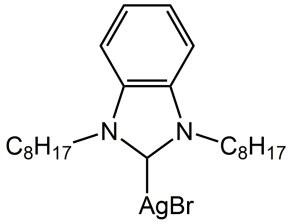
NHC-AgBr (**1-*b*-AgBr**).[1] Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **1** (1.2 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h, and excess Ag_2O was filtered away. The filtrate was concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a light brown solid (0.94 g, 74%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.51 (dd, J = 5.9 and 3.0 Hz, 2H), 7.43 (dd, J = 6.0 and 3.2 Hz, 2 H), 4.62 (t, J = 7.3 Hz, 4H), 2.10–1.9 (m, 4H), 1.4–1.1 (m, 44H), 0.87 (t, J = 6.7 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 134.27, 124.41, 112.14, 50.14, 32.50, 30.81, 30.26, 30.23, 30.20, 30.12, 30.04, 29.93, 29.81, 27.40, 23.27, 14.45.



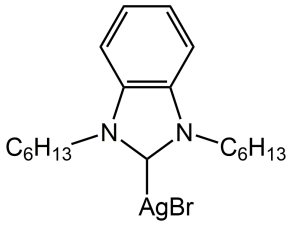
NHC-AgBr (**2-*b*-AgBr**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **2** (0.96 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h, and excess Ag_2O was filtered away. The filtrate was concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a white solid (0.65 g, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 6.2 and 3.1 Hz, 2H), 7.41 (dd, J = 6.1 and 3.1 Hz, 2 H), 4.39 (t, J = 7.3 Hz, 4H), 1.93–1.87 (m, 4H), 1.33–1.24 (m, 28H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.79, 124.12, 111.66, 49.76, 31.97, 30.50, 26.61, 29.57, 29.39, 29.37, 27.00, 22.80, 14.24.



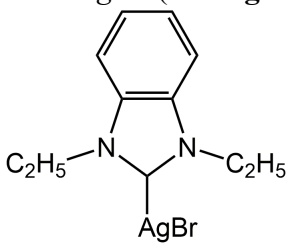
NHC-AgBr (**3-*b*-AgBr**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **3** (0.85 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h, and excess Ag_2O was filtered away. The filtrate was concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a light grey solid (0.62 g, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, J = 6.2 and 3.0 Hz, 2H), 7.41 (dd, J = 6.1 and 3.1 Hz, 2 H), 4.39 (t, J = 7.3 Hz, 4H), 1.93–1.87 (m, 4H), 1.36–1.24 (m, 20H), 0.86 (t, J = 6.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.797, 124.13, 111.67, 49.77, 31.86, 30.50, 29.33, 29.23, 27.00, 22.73, 14.20.



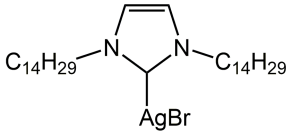
NHC-AgBr (**4-*b*-AgBr**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **4** (0.73 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h, and excess Ag_2O was filtered away. The filtrate was concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a light grey solid (0.47 g, 50%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 (dd, J = 6.5 and 3.4 Hz, 2H), 7.41 (dd, J = 6.2 and 3.4 Hz, 2 H), 4.39 (t, J = 7.3 Hz, 4H), 1.94–1.86 (m, 4H), 1.33–1.31 (m, 12H), 0.87 (t, J = 7.3 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.77, 124.14, 111.66, 49.76, 31.48, 30.45, 26.63, 22.60, 14.10.



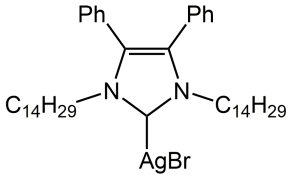
NHC-AgBr (**5-*b*-AgBr**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **5** (0.51 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h, and excess Ag_2O was filtered away. The filtrate was concentrated under reduced pressure. After, the residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to yield a light grey solid (0.33 g, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (dd, J = 6.1 and 3.1 Hz, 2H), 7.42 (dd, J = 6.1 and 3.1 Hz, 2 H), 4.47 (q, J = 7.3 Hz, 4H), 1.53 (t, J = 7.3 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 133.48, 124.24, 111.58, 44.74, 16.12.



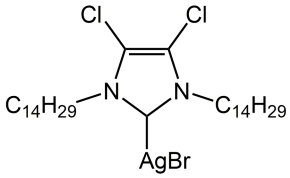
NHC-AgBr (**1-*i*-AgBr**).[3] Imidazole (2.0 g, 30 mmol), KOH (3.3 g, 60 mmol), *n*-tetradecyl bromide (9.0 mL, 30 mmol) and CH_3CN (17 mL) were added into a three-neck flask under nitrogen and stirred under reflux (~85 ˚C) for 20 h. After the reaction was finished, CH_3CN was removed under reduced pressure. The solid was then dissolved in CH_2Cl_2, washed with water (2 × 100 mL) and brine (100 mL), and dried by Na_2SO_4. An orange oil was obtained after the liquid was concentrated by vacuum. Subsequently, *n*-tetradecyl bromide (9.0 mL, 30 mmol) and toluene (20 mL) were added to the product under nitrogen, and the mixture was stirred under reflux for 48 h. The solvent was then evaporated to give a red oil (**6**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **6** (1.2 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h before filtering off excess Ag_2O. The CH_2Cl_2 was then removed under reduced pressure. An orange powder (**1-*i*-AgBr**, 0.26 g, 20%) was obtained after adding excess acetone to the organic residue, and drying under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.95 (s, 2H), 4.07 (t, J = 7.3 Hz, 4H), 1.82–1.77 (m, 4H), 1.29–1.25 (m, 44H), 0.88 (t, J = 6.8 Hz, 6H). ^{13}C



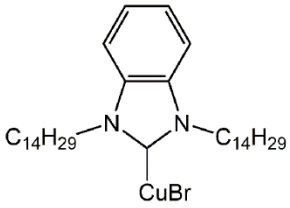
NMR (125 MHz, $CDCl_3$) δ 120.78, 52.28, 32.08, 31.63, 29.84, 29.81, 29.77, 29.68, 29.59, 29.51, 29.30, 26.63, 22.85, 14.28.

NHC-AgBr (**2-*i*-AgBr**). 

4,5-diphenylimidazole (3.3 g, 15 mmol), KOH (1.7 g, 30 mmol), *n*-tetradecyl bromide (4.5 mL, 15 mmol) and CH_3CN (9 mL) were added into a three-neck flask under nitrogen and stirred under reflux (~85 ˚C) for 20 h. After the reaction was finished, CH_3CN was removed under reduced pressure. The solid was then dissolved in CH_2Cl_2, washed with water (2 × 100 mL) and brine (100 mL), and dried by Na_2SO_4. A white solid was obtained after the liquid was concentrated by vacuum. Subsequently, *n*-tetradecyl bromide (4.5 mL, 15 mmol) and toluene (10 mL) were added to the product under nitrogen, and the mixture was stirred under reflux for 48 h. The solvent was then evaporated to give a white solid (**7**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **7** (1.4 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h before filtering excess Ag_2O. The CH_2Cl_2 was then removed under reduced pressure. A white solid (**2-*i*-AgBr**, 0.78 g, 49%) was obtained after adding excess acetone to the organic residue, and drying under vacuum. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.31 (m, 6H), 7.18–7.16 (m, 4H), 4.07–4.04 (t, 4H), 1.62–1.57 (m, 4H), 1.31–1.12 (m, 44H), 0.87 (t, J = 6.9 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.89, 130.55, 129.26, 128.89, 128.23, 50.01, 32.07, 31.77, 29.83, 29.80, 29.74, 29.62, 29.51, 29.44, 29.03, 26.53, 22.84, 14.27.

NHC-AgBr (**3-*i*-AgBr**). 

4,5-dichloroimidazole (2.0 g, 15 mmol), KOH (1.7 g, 30 mmol), *n*-tetradecyl bromide (4.5 mL, 15 mmol) and CH_3CN (9 mL) were added into a three-neck flask under nitrogen and stirred under reflux (~85 ˚C) for 20 h. After the reaction was finished, CH_3CN was removed under reduced pressure. The solid was then dissolved in CH_2Cl_2, washed with water (2 × 100 mL) and brine (100 mL), and dried by Na_2SO_4. An orange oil was obtained after the liquid was concentrated by vacuum. Subsequently, *n*-tetradecyl bromide (4.5 mL, 15 mmol) and toluene (10 mL) were added to the product under nitrogen, and the mixture was stirred under reflux for 48 h. The solvent was then evaporated to give a red oil (**8**). Ag_2O (0.56 g, 2.4 mmol) was added to a solution of **8** (1.2 g, 2.0 mmol) in dried CH_2Cl_2 (40 mL). The mixture was refluxed for 20 h before filtering off excess Ag_2O. The CH_2Cl_2 was then removed under reduced pressure. A pale grey powder (**3-*i*-AgBr**, 0.28 g, 20%) was obtained after adding excess acetone to the organic residue, and drying under vacuum. ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.13 (t, 4H), 1.82–1.77 (m, 4H), 1.32–1.25 (m, 44H), 0.88 (t, J = 7.1 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 117.17, 51.43, 32.07, 30.98, 29.83, 29.80, 29.76, 29.68, 29.56, 29.51, 29.27, 26.57, 22.84, 14.27.

NHC-CuBr (**1-*b*-CuBr**).[2] 

Cu_2O (0.34 g, 2.4 mmol) was added to a solution of **1** (1.2 g, 2.0 mmol) in dried 1,4-dioxane (40 mL). The mixture was refluxed for 20 h, and excess Cu_2O was then filtered off. The filtrate was concentrated under reduced pressure. The solid was isolated by filtration, and washed

with hexanes. After drying under vacuum, the title compound was obtained as a brown solid (0.9 g, 74%). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.48 (dd, J = 6.0 and 3.0 Hz, 2H), 7.40 (dd, J = 6.0 and 3.0 Hz, 2 H), 4.62 (t, J = 7.2 Hz, 4H), 2.10–1.9 (m, 4H), 1.4–1.1 (m, 44H), 0.87 (t, J = 6.8 Hz, 6H). ^{13}C NMR (125 MHz, CD_2Cl_2) δ 124.25, 111.94, 49.49, 32.50, 30.82, 30.26, 30.23, 30.20, 30.12, 30.04, 29.93, 29.78, 27.38, 23.27, 14.45.

$(TBDMS)_2Se$.[4] 0.62 g (27 mmol) Na, 1.07 g (13.0 mmol) Se powder, and 0.10 g (0.78 mmol) $C_{10}H_8$ were weighed into a three-neck Schlenk flask. 60 mL of dried THF was added. The solution was refluxed under a nitrogen atmosphere for 4 h, followed by cooling to room temperature. The dark solution was further cooled to 0 ˚C by an ice bath. 4.07 g (27.0 mmol) $(^{t}BuMe_2Si)_2Cl$ was added to the solution at 0 ˚C. The reaction mixture was allowed to stir with warming to room temperature overnight, and residual solids were filtered away. The filtrate was concentrated under reduced pressure and dried under vacuum. A reddish solid product was then obtained (3 g, 75%). ^{1}H NMR (400 MHz, C_6D_6) δ 1.01 (s, 9H), 0.37 (s, 6H). ^{13}C NMR (125 MHz, C_6D_6) δ 26.47, 19.40, 0.38.

Control experiment #1: Synthesis of Ag_2S QDs using oleate ligands under ambient conditions. Ag(oleate) was prepared by dissolving Ag_2O (115 mg, 0.500 mmol) with excess oleic acid (5 mL) at 100 ˚C for 2 h. A clear Ag(oleate) solution was obtained and subsequently diluted with 15 mL of CH_2Cl_2 to give a 50 mM Ag(oleate) stock solution. 0.5 mL of $(TMS)_2S$/ODE (0.1 M) was injected rapidly into 2 mL of the Ag(oleate) stock solution. The reaction mixture was allowed to stir at room temperature for 1 h before precipitation from excess acetone and redispersion in toluene.

Control experiment #2: Synthesis of Ag_2S nanocrystals using oleylamine under ambient conditions. AgBr(oleylamine) was prepared by dissolving AgBr (190 mg, 1.00 mmol) with excess oleylamine (5 mL) at 120 ˚C for 3 h. A clear AgBr(oleylamine) solution was obtained and subsequently diluted with 15 mL of toluene to give a 50 mM AgBr(oleylamine) stock solution. 0.5 mL of $(TMS)_2S$/ODE (0.1 M) was injected rapidly into 2 mL of the AgBr(oleylamine) stock solution. The reaction mixture was allowed to stir at room temperature for 1 h before precipitation from excess acetone and redispersion in toluene.

S3. Reaction kinetics monitored by UV-vis-NIR absorption and TEM analysis

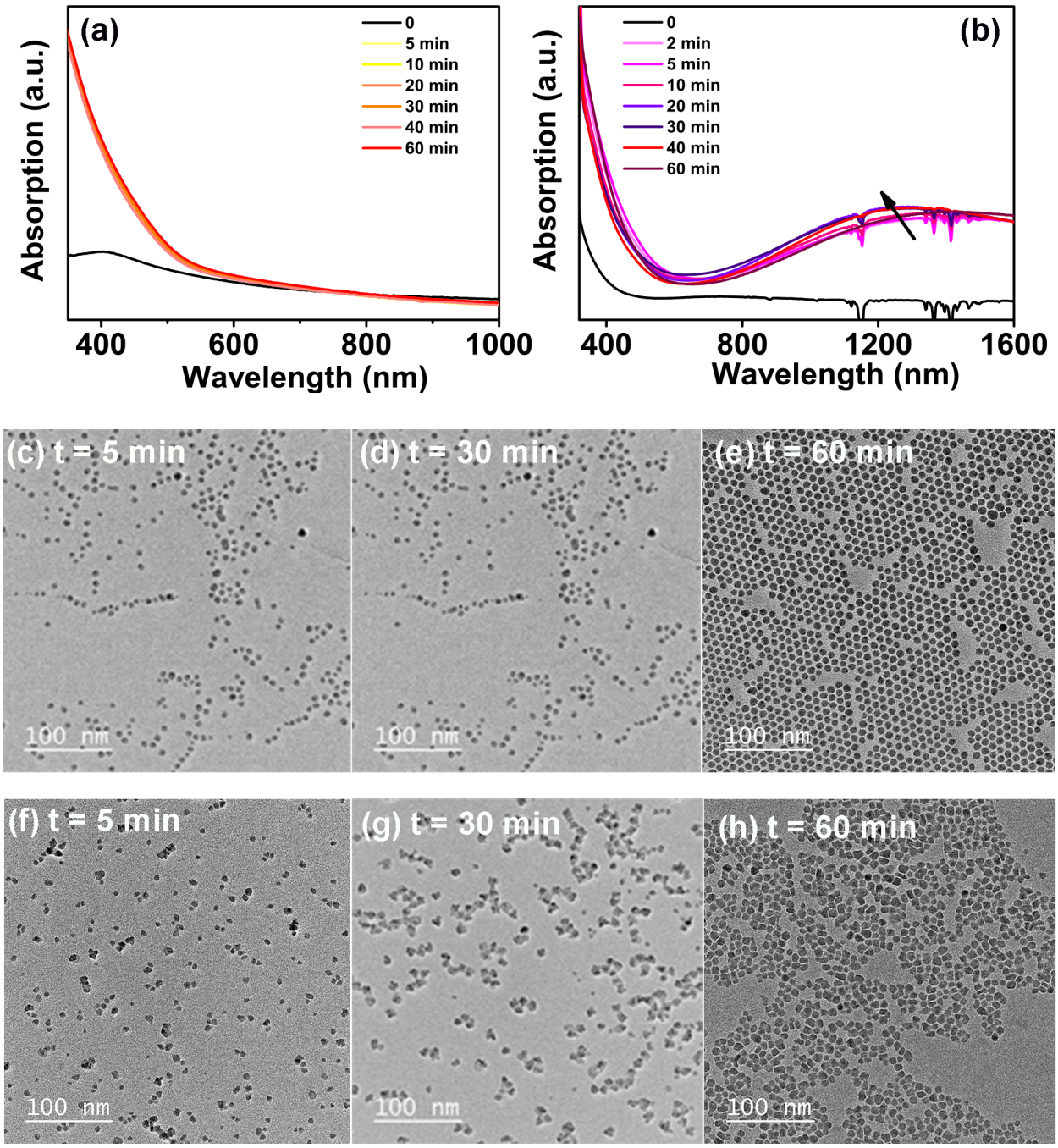


Figure S1. (a,b): UV-vis-NIR absorption spectra of in-situ reaction of Ag_2S QDs (from **1-*b*-AgBr**) and $Cu_{2-x}S$ (from **1-*b*-CuBr**), respectively. (c–e) TEM micrographs of Ag_2S QDs at various time points. Size analysis reveals d = 7.8 ± 0.8 nm (5 min), to 8.2 ± 0.7 nm (30 min), and 10.3 ± 0.6 nm (60 min) (300 counts for each). (f–h) TEM micrographs of $Cu_{2-x}S$ QDs at different time points. Size analysis presents d = 6.8 ± 1.0 nm (5 min), to 8.4 ± 1.2 nm (30 min), and 8.8 ± 0.8 nm (60 min) (300 counts for each).

S4. TEM micrographs of Ag_2S QDs prepared from oleate and oleylamine ligands

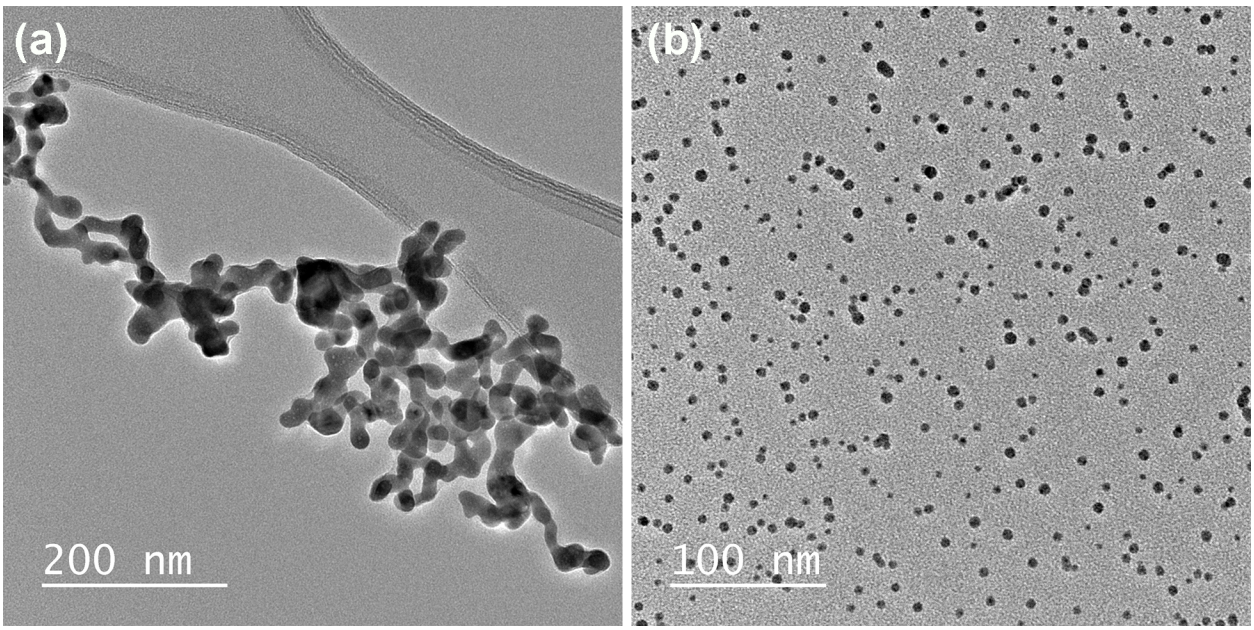


Figure S2. (a,b) TEM micrographs of Ag_2S QDs prepared from Ag(oleate), and AgBr(oleylamine) under ambient conditions, respectively.

S5. XRD data of Ag_2S from various NHC-AgBr complexes

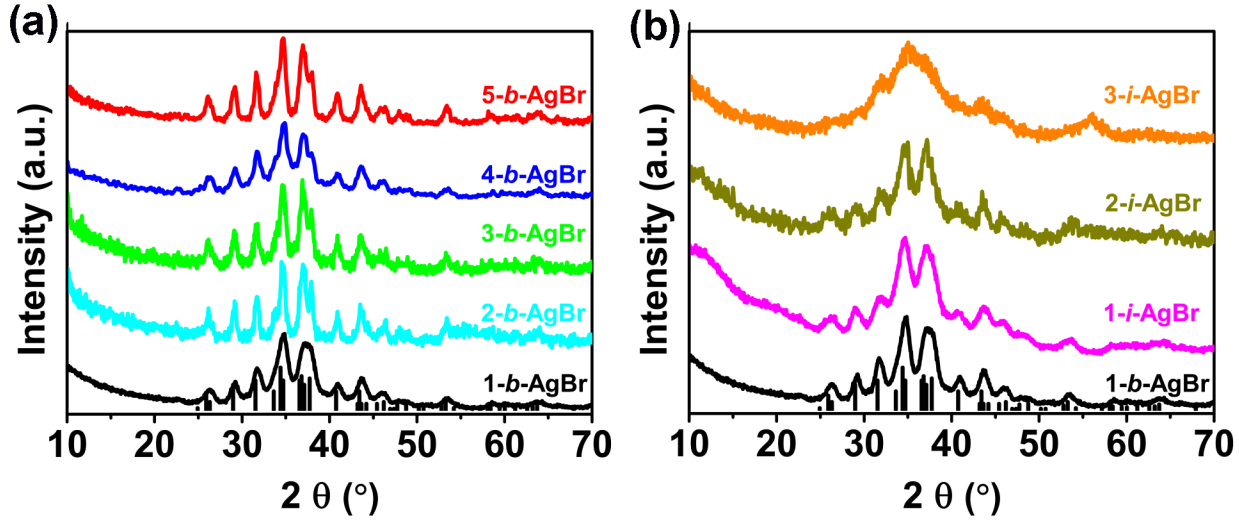


Figure S3. XRD patterns of the purified products prepared from different benzimidazole-based NHC-AgBr complexes (**j-*b*-AgBr**, j = 1–5) (a), and imidazole-based NHC-AgBr complexes (**j-*i*-AgBr**, j = 1–3) (b). All of the products are phase-pure monoclinic Ag_2S (PDF#00-014-0072).

S6. TEM micrographs of Ag_2S QDs prepared from various benzimidazole-based NHC-AgBr

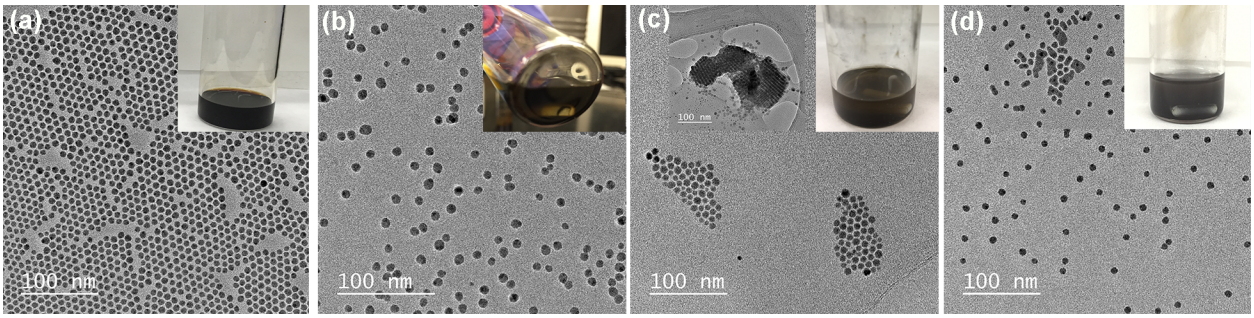


Figure S4. (a–d) TEM micrographs of Ag_2S QDs prepared from **1-*b*-AgBr** (10.3 ± 0.6 nm), **2-*b*-AgBr** (9.7 ± 0.6 nm), **3-*b*-AgBr** (9.2 ± 1.0 nm), and **4-*b*-AgBr** (9.6 ± 1.0 nm) complex, respectively. The insets on the upper right corner of each micrograph are photos of each solution mixture after a 1 h reaction. No precipitates were observed in the reaction using **1-*b*-AgBr** complex, while black solids were observed from solutions using **2-*b*-AgBr**, **3-*b*-AgBr**, and **4-*b*-AgBr** complex. More aggregates were observed as the length of *N*-alkyl chains decrease (from **2-*b*-AgBr**, **3-*b*-AgBr**, to **4-*b*-AgBr**). The insets on the upper left corner of (c) and (d) were representative TEM images of corresponding Ag_2S QDs, showing aggregates upon synthesized.

S7. High-resolution XPS spectra of NHC-AgBr, NHC-Ag_2S and NHC-$Cu_{2-x}S$ QDs

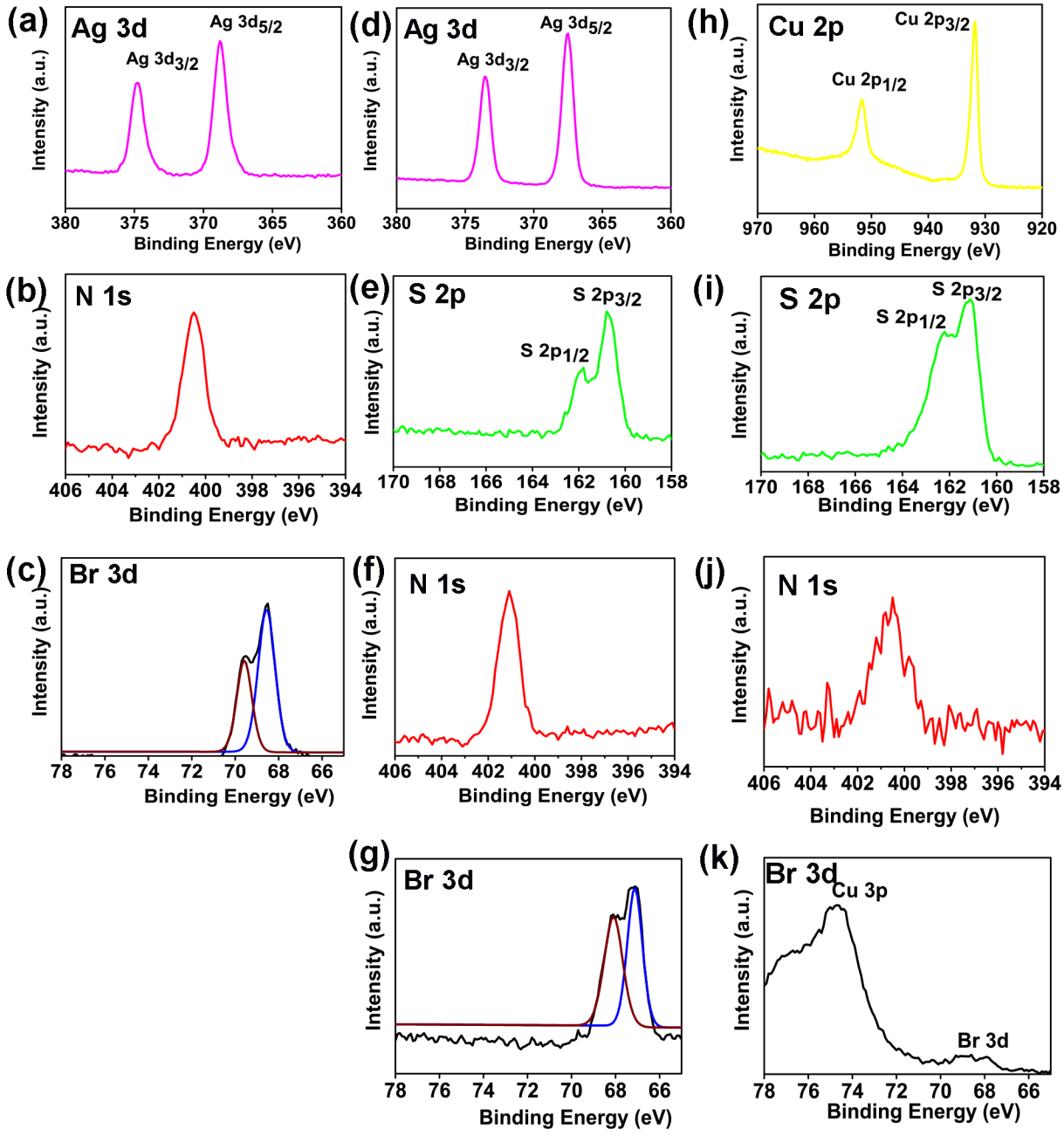


Figure S5. High-resolution XPS spectra of NHC-AgBr (**1-*b*-AgBr**, a–c), NHC-Ag_2S QDs (d–g), and NHC-$Cu_{2-x}S$ QDs (h–k). The absence of the strong Cu^{2+} satellite peaks (at 942 eV and 962 eV) in (h) proves that the oxidation state of $Cu_{2-x}S$ NCs is mostly Cu^{+}.

S8. FT-IR spectra and TGA traces of NHCAgBr, NHC-Ag_2S, and NHC-$Cu_{2-x}S$ QDs

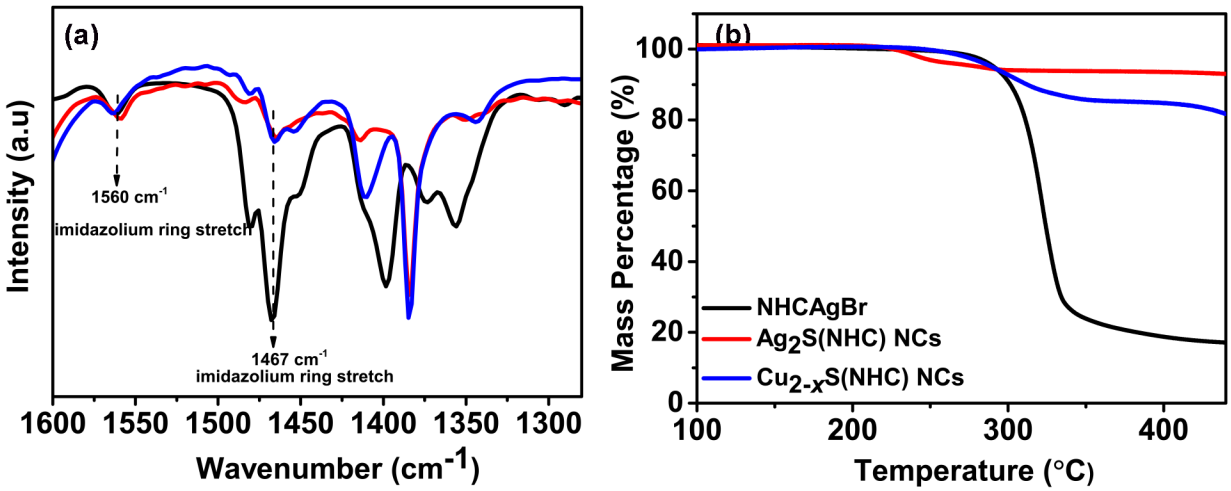


Figure S6. (a) FT-IR spectra and (b) TGA traces of NHC-AgBr (**1-*b*-AgBr**), NHC-Ag_2S, and NHC-$Cu_{2-x}S$ QDs.

S9. Calculations of NHC ligands on the surface of Ag_2S QDs

The number of NHC ligands per QD can be calculated based on the mass loss from TGA and the mean radius of QDs obtained from TEM analysis. The calculations are performed below:

NHC molecular weight (**1** minus proton and bromine): m_{NHC} = 510.49 g/mol

m_{Ag2S} = 247.7 g/mol; Density ρ_{Ag2S} = 7.23 g/cm^3

d_{Ag2S} = 10 nm

Assuming each ligand is binding to X number of Ag_2S units, we can solve for the ratio of NHC:Ag_2S. Define $X=\frac{N_{NHC}}{N_{Ag2S}}$ where N is the number of atoms.

For Ag_2S QDs, since the mass percentage of NHC ligands is 10%, we have:

$$0.073 = \frac{X * m_{NHC}}{(X * m_{NHC} + m_{Ag2S})}$$

$$X = \frac{N_{NHC}}{N_{Ag2S}} = 0.038$$

# of NHC ligands per Ag_2S QD = V*density*(Avogardro's number) *(ratio NHC:Ag_2S)/m_{Ag2S} =

$$\frac{\frac{4}{3}*Pi*r^3*7.23*6.02*10^{23}*0.038}{247.7} = 346 \text{ NHC/1-}Ag_2S \text{ QD}$$

Here we assume a smooth, spherical Ag_2S QD.

S10. ^{1}H NMR and ^{13}C NMR spectra of the benzimidazolium salt, NHC-AgBr, NHC-CuBr complexes and $(TBDMS)_2Se$

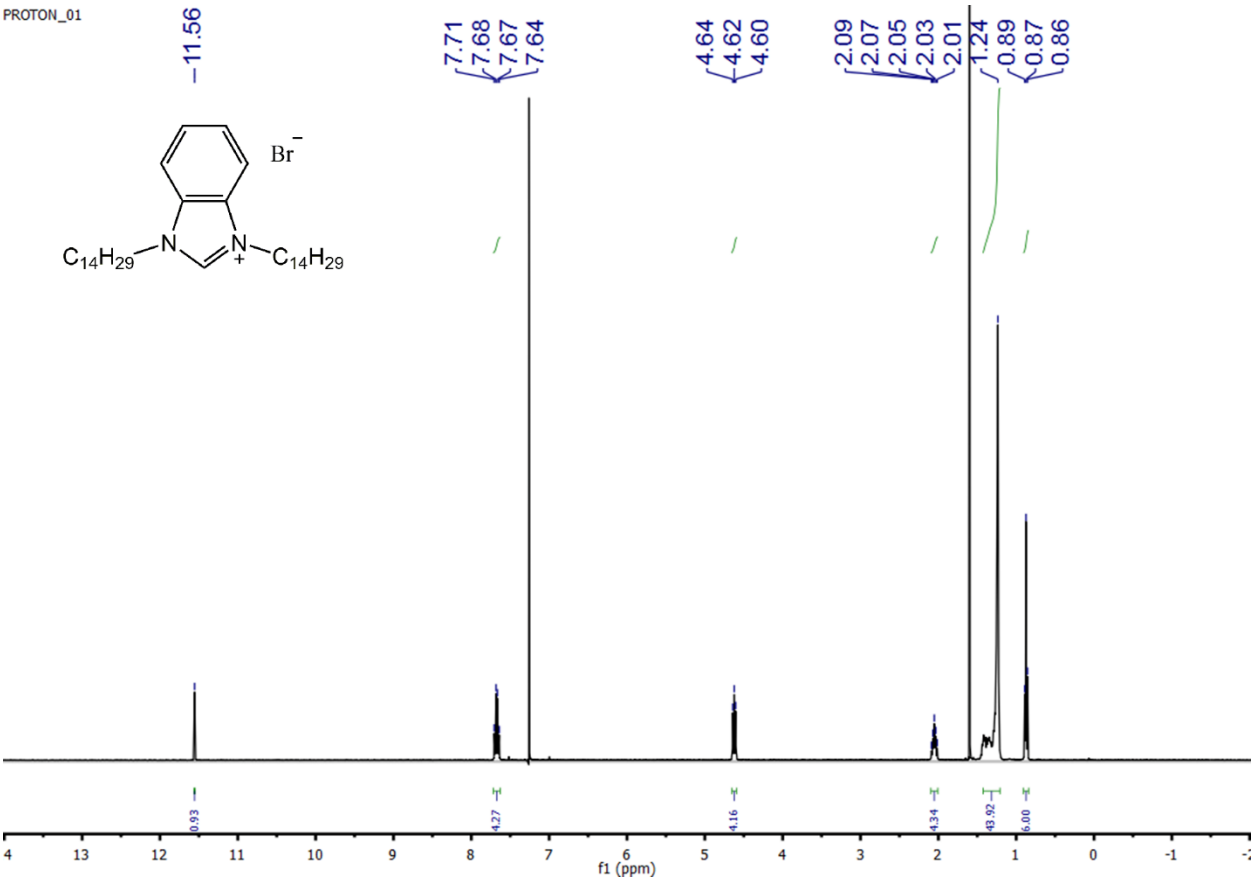


Figure S7. ^{1}H NMR spectrum of **1** in $CDCl_3$.

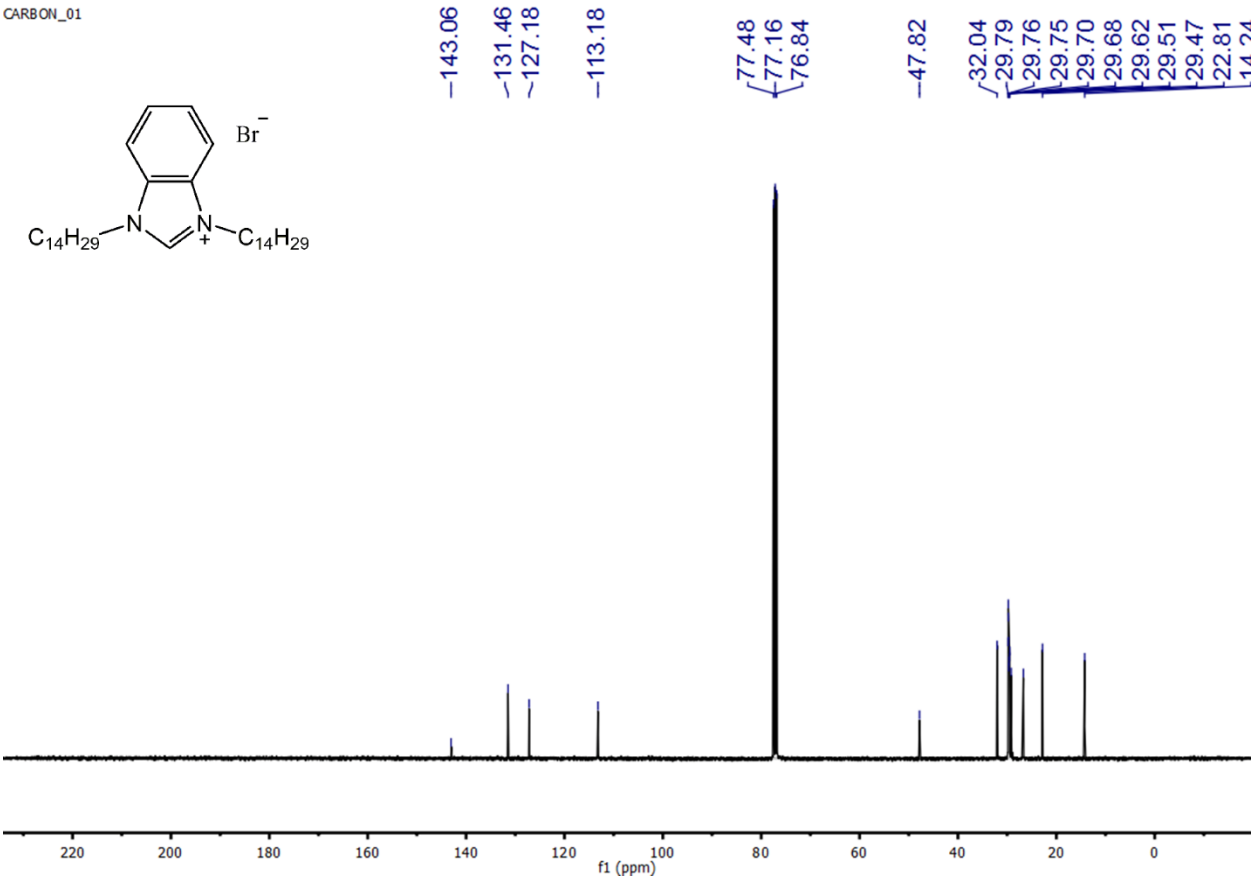


Figure S8. ^{13}C NMR spectrum of **1** in $CDCl_3$.

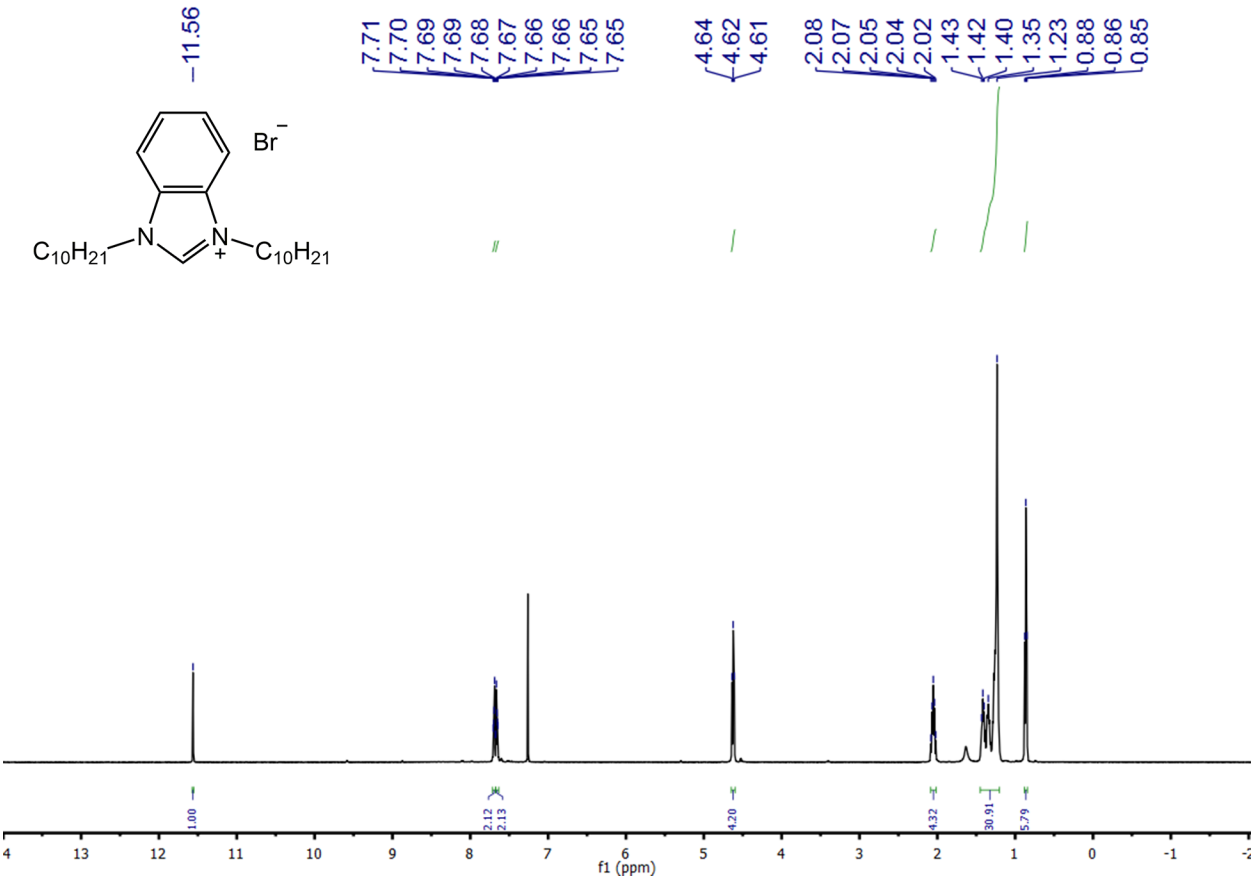


Figure S9. ^{1}H NMR spectrum of **2** in $CDCl_3$.

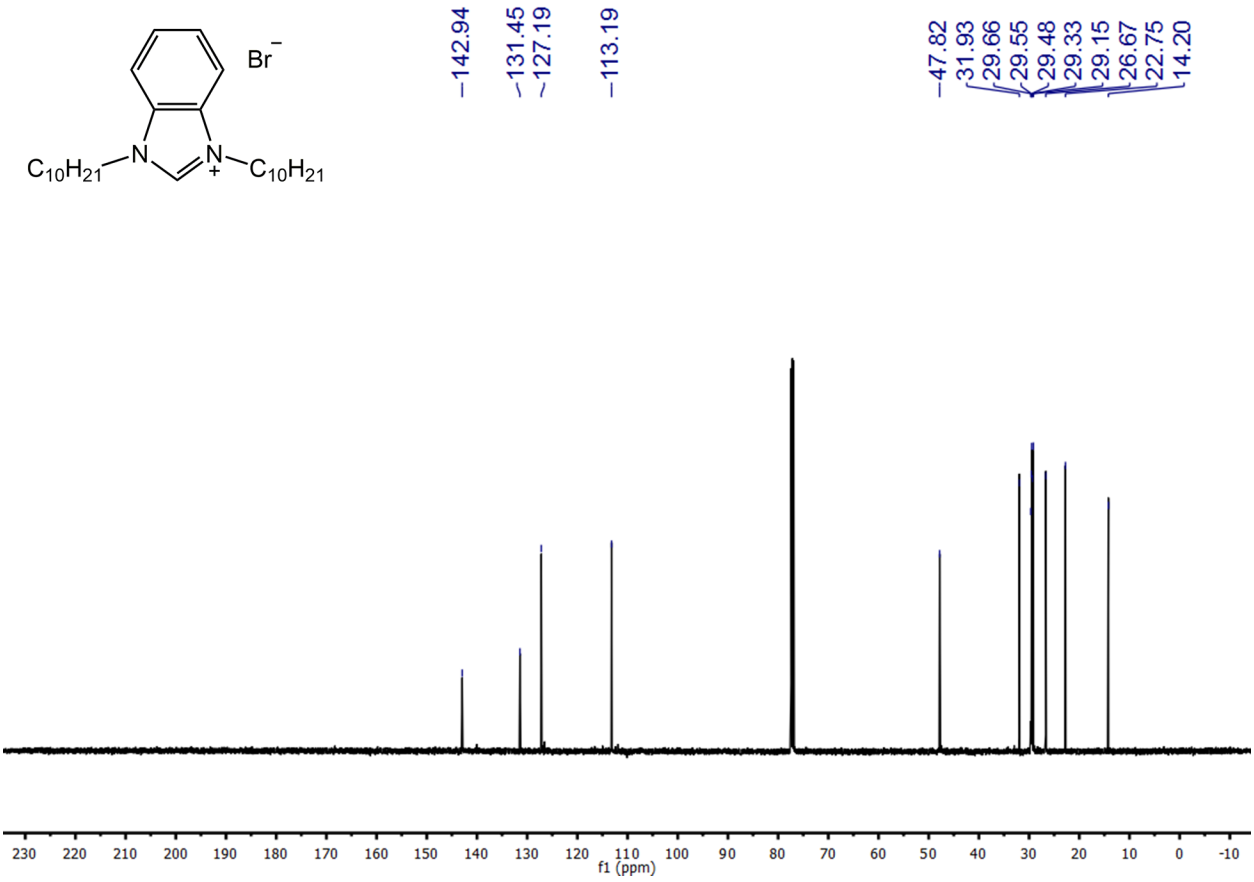


Figure S10. ^{13}C NMR spectrum of **2** in $CDCl_3$.

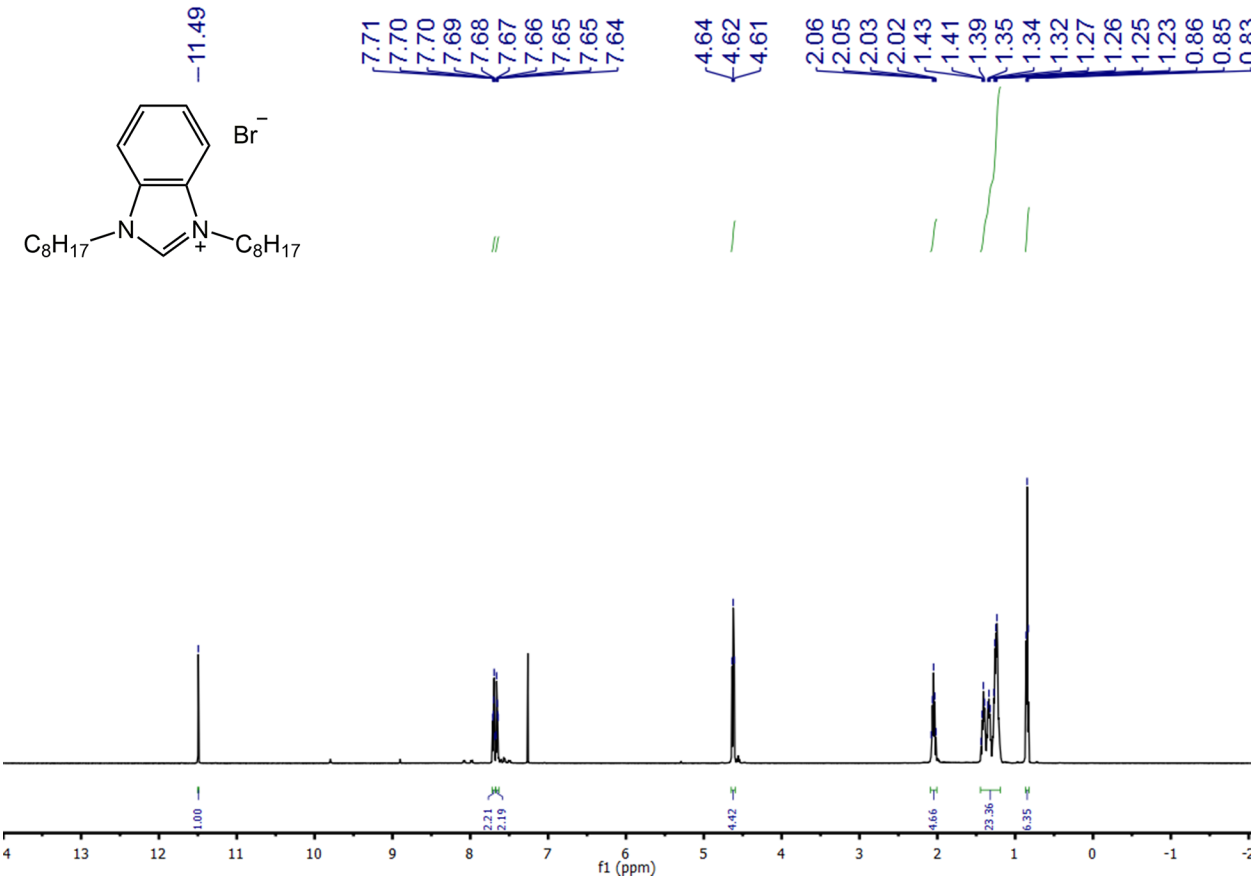


Figure S11. ^{1}H NMR spectrum of **3** in $CDCl_3$.

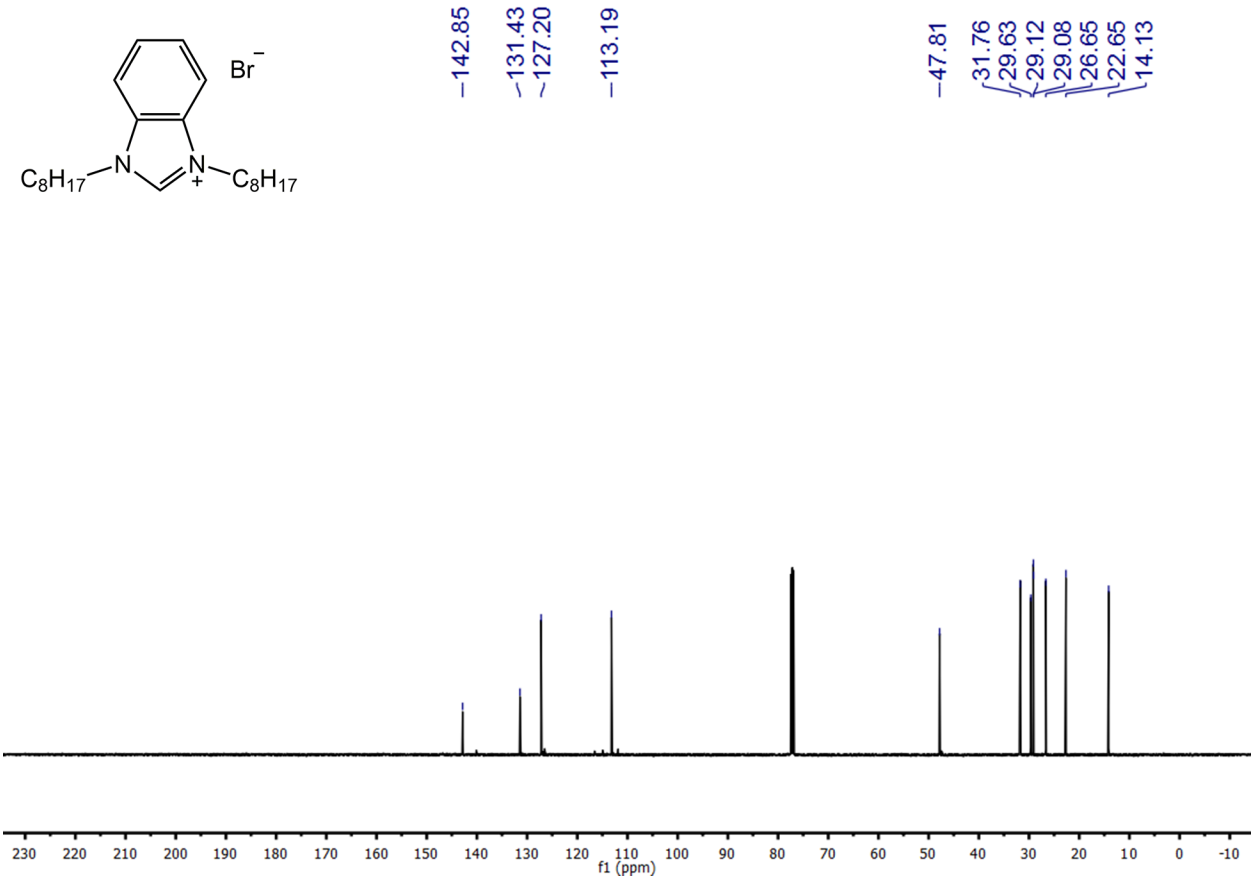


Figure S12. ^{13}C NMR spectrum of **3** in $CDCl_3$.

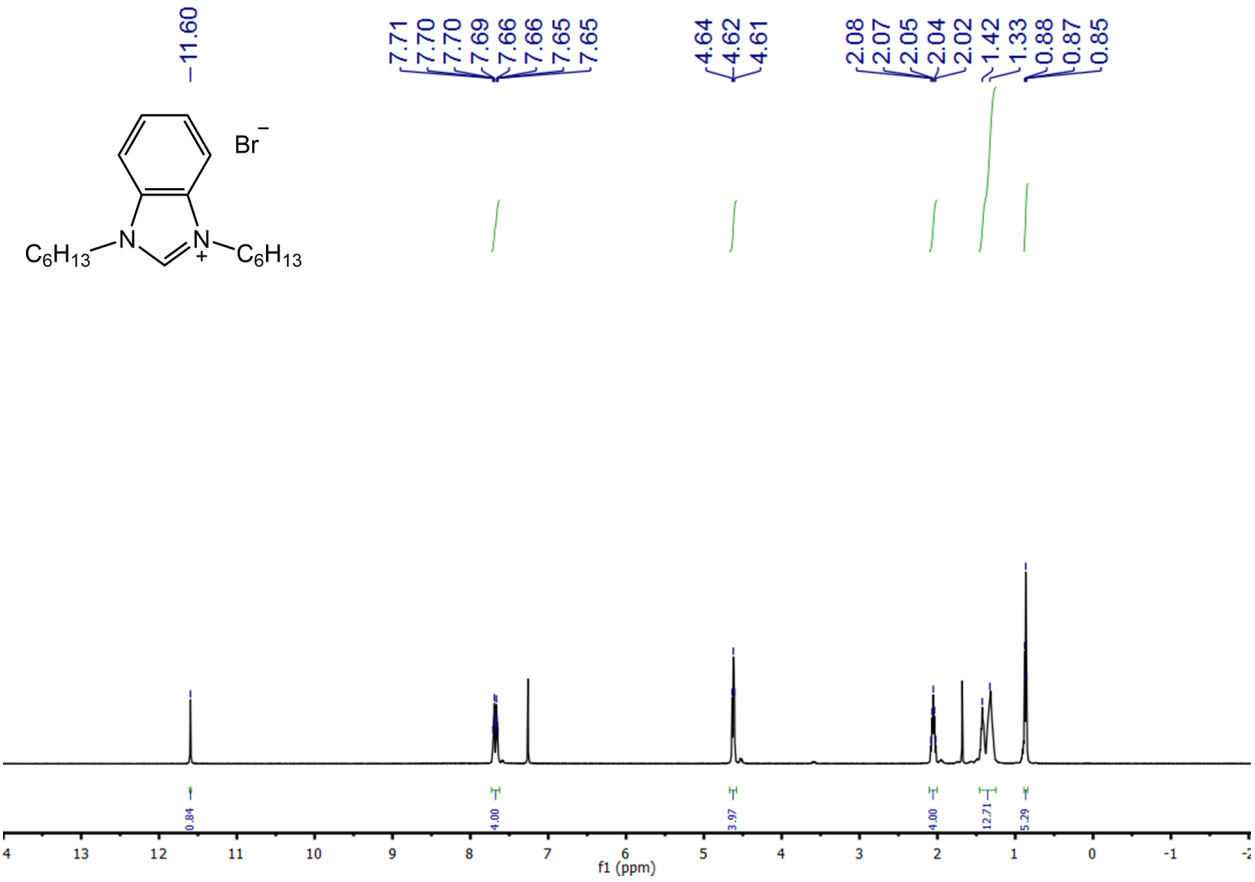


Figure S13. ^{1}H NMR spectrum of **4** in $CDCl_3$.

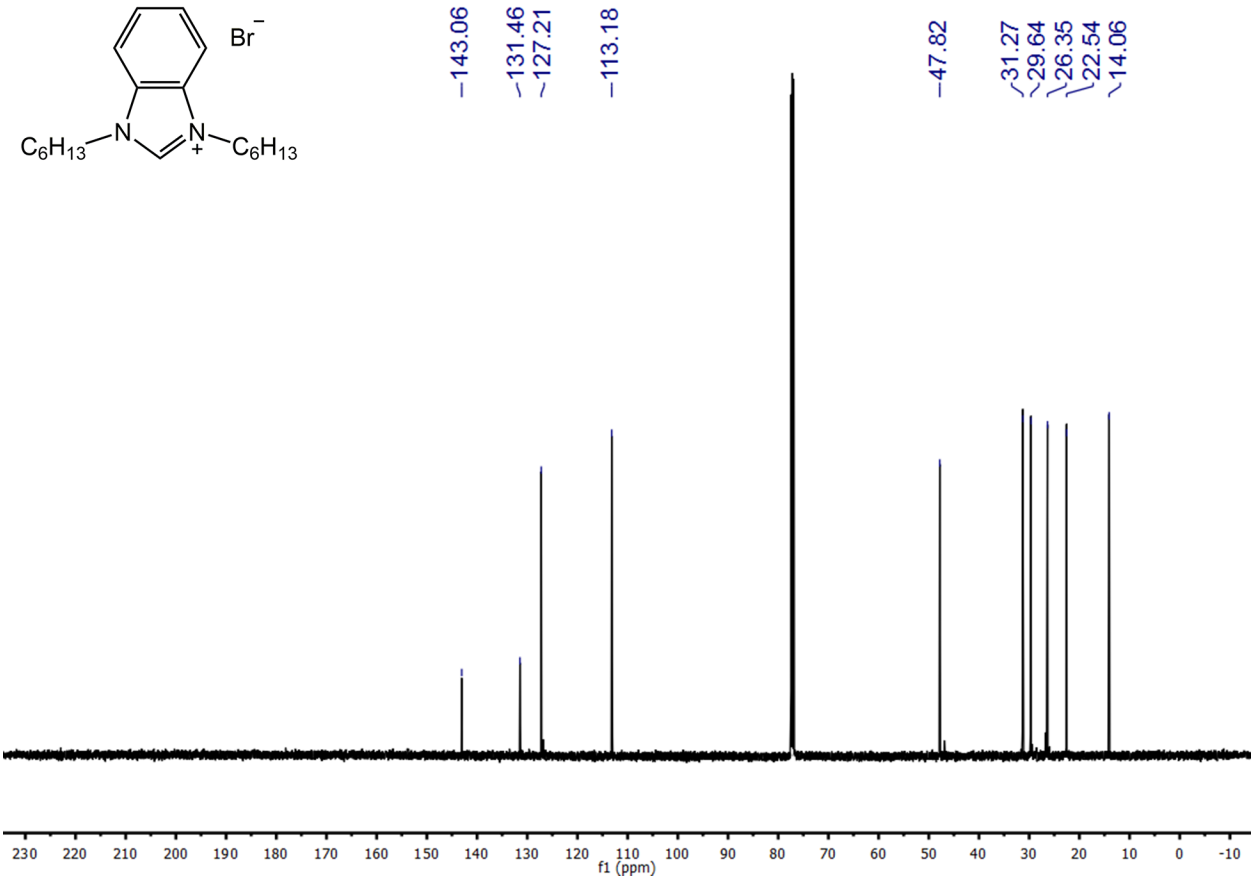


Figure S14. ^{13}C NMR spectrum of **4** in $CDCl_3$.

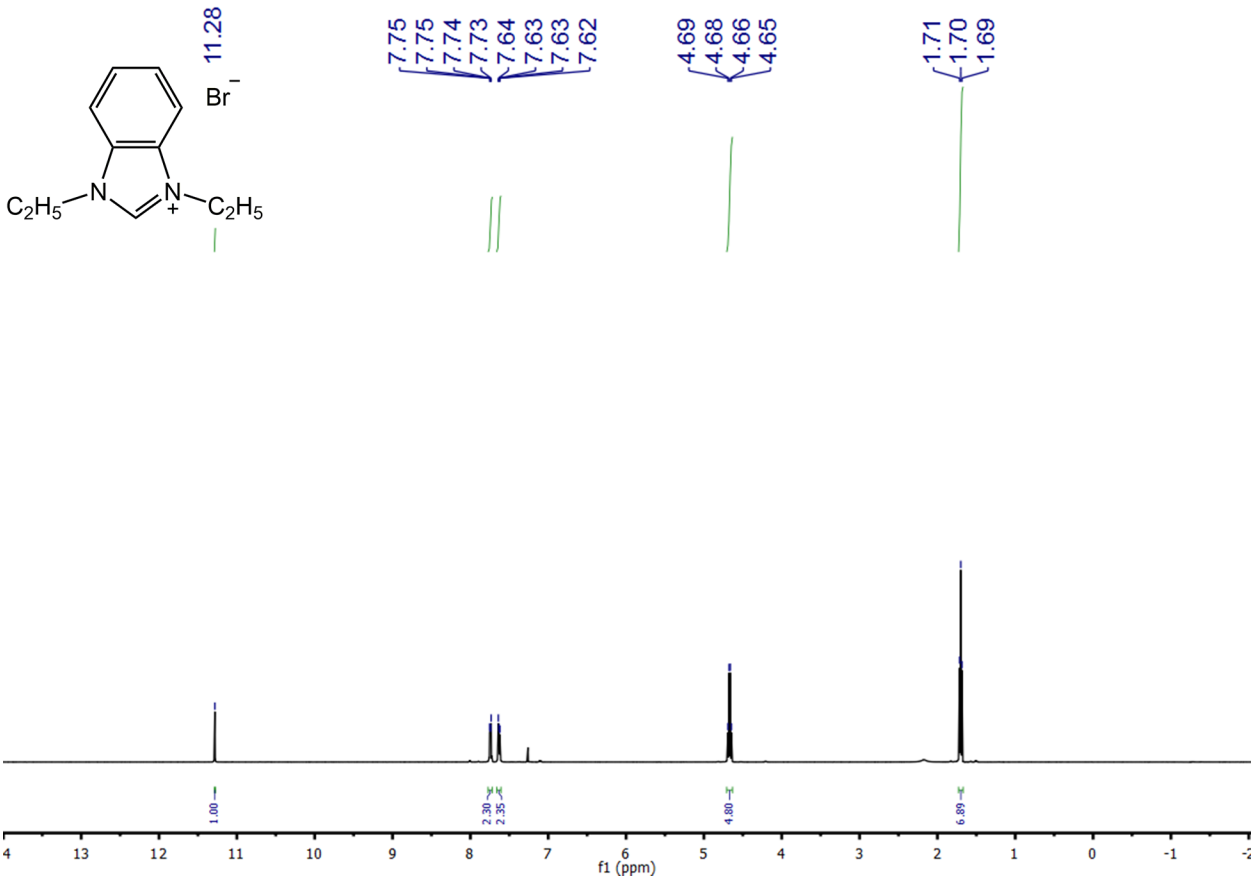


Figure S15. ^{1}H NMR spectrum of **5** in $CDCl_3$.

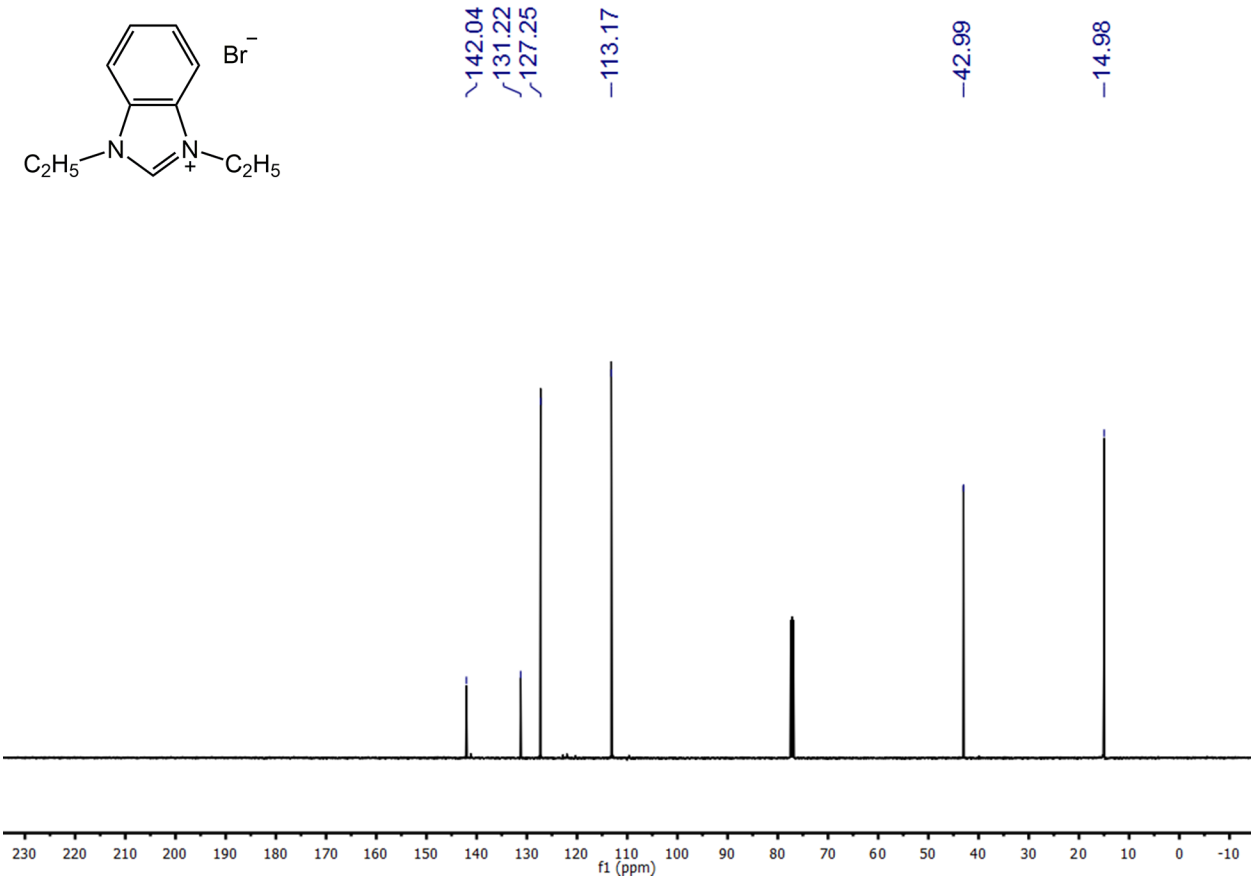


Figure S16. ^{13}C NMR spectrum of **5** in $CDCl_3$.

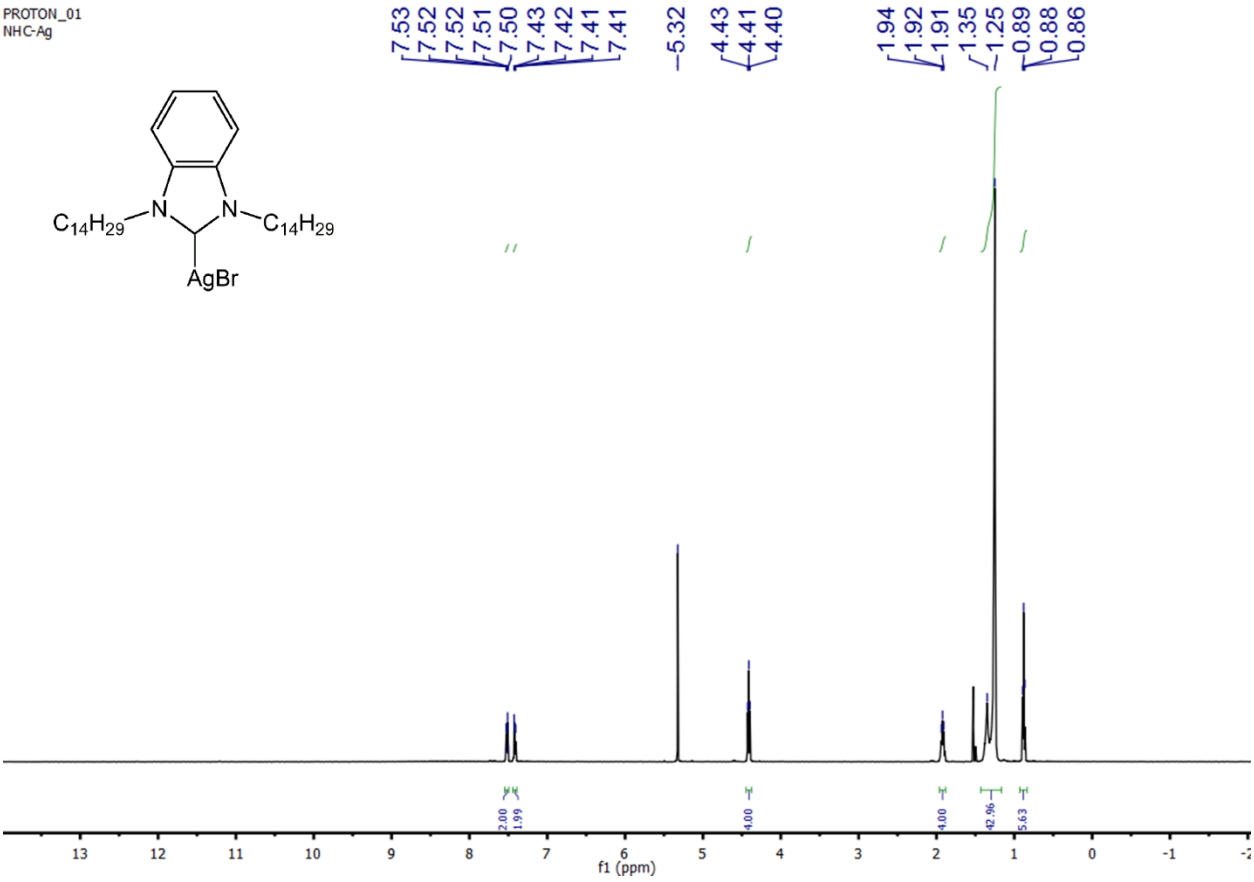


Figure S17. ^{1}H NMR spectrum of **1-*b*-AgBr** in CD_2Cl_2.

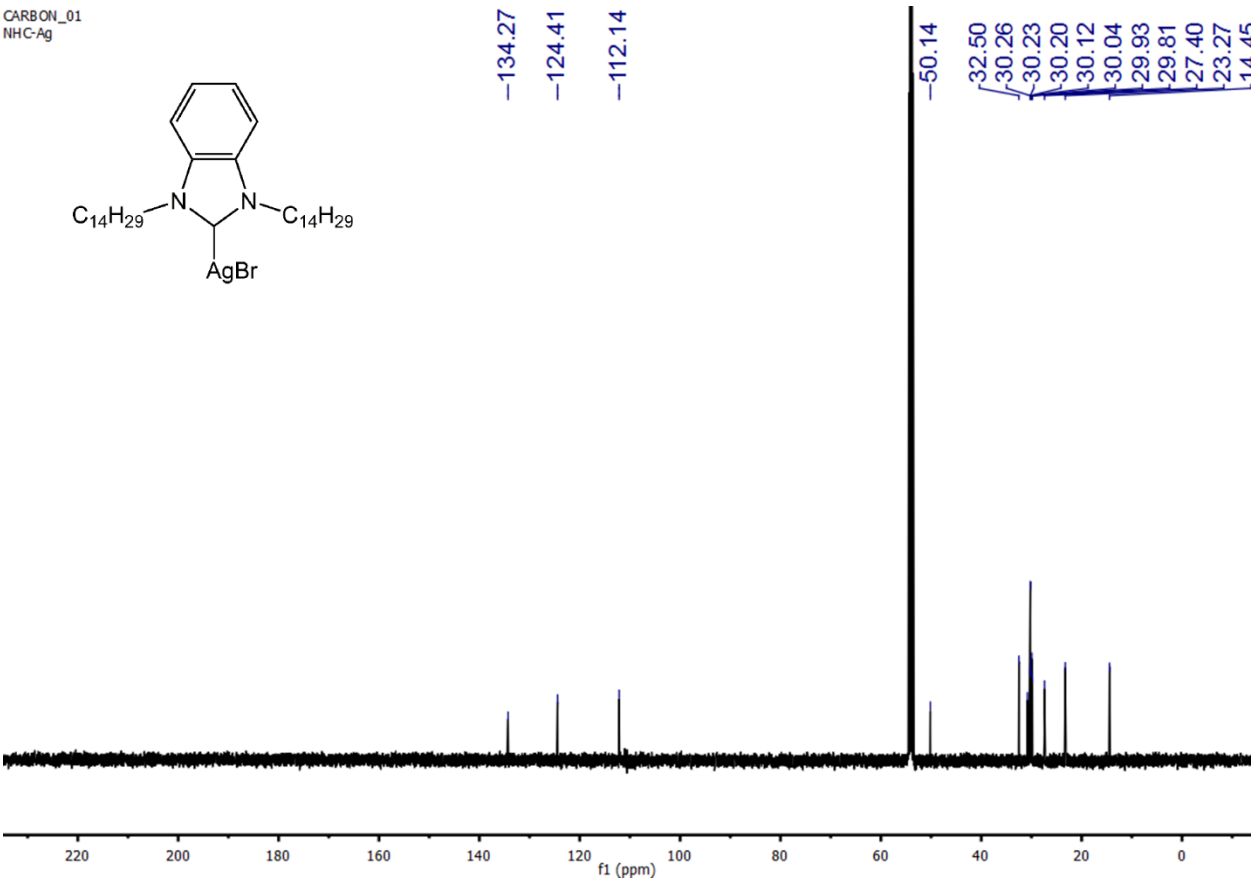


Figure S18. ^{13}C NMR spectrum of **1-*b*-AgBr** in CD_2Cl_2.

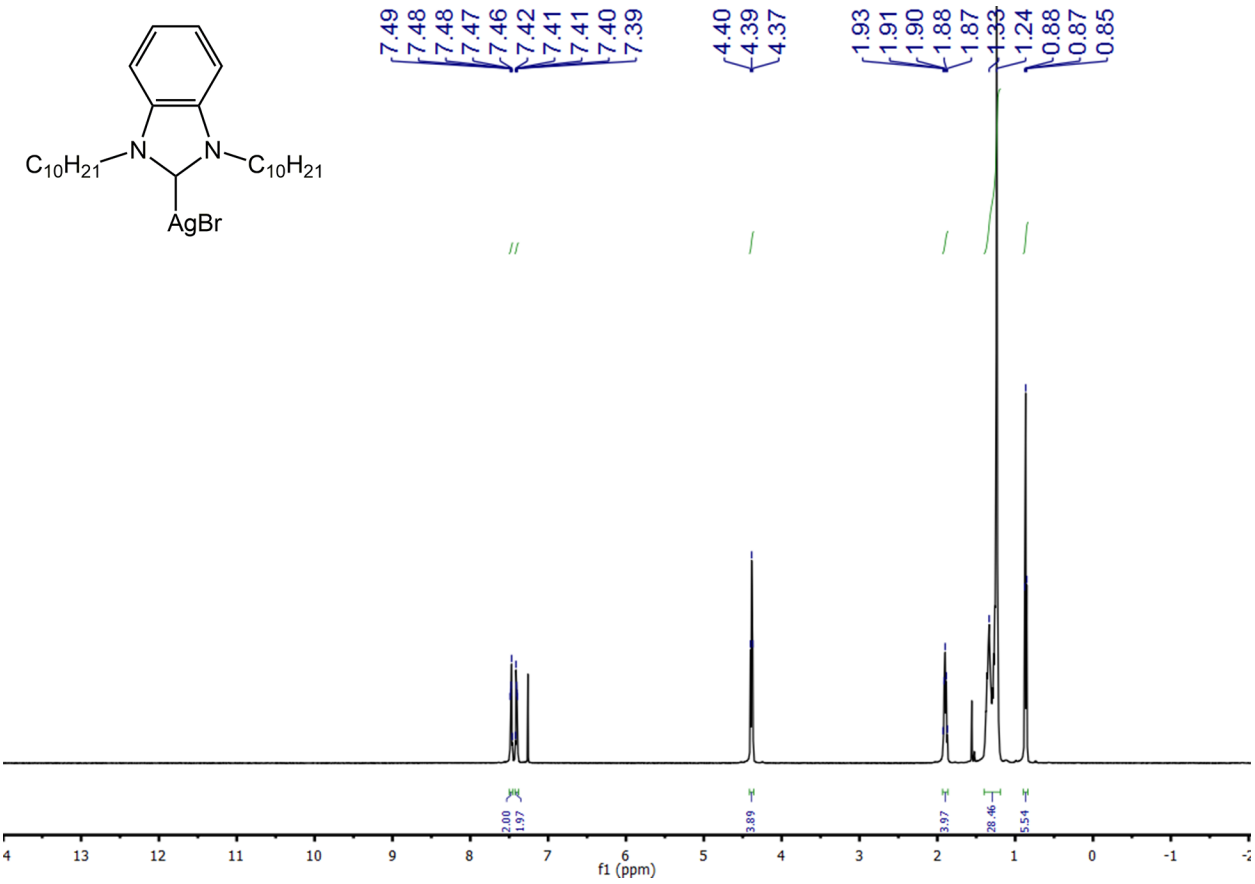


Figure S19. ^{1}H NMR spectrum of **2-*b*-AgBr** in $CDCl_3$.

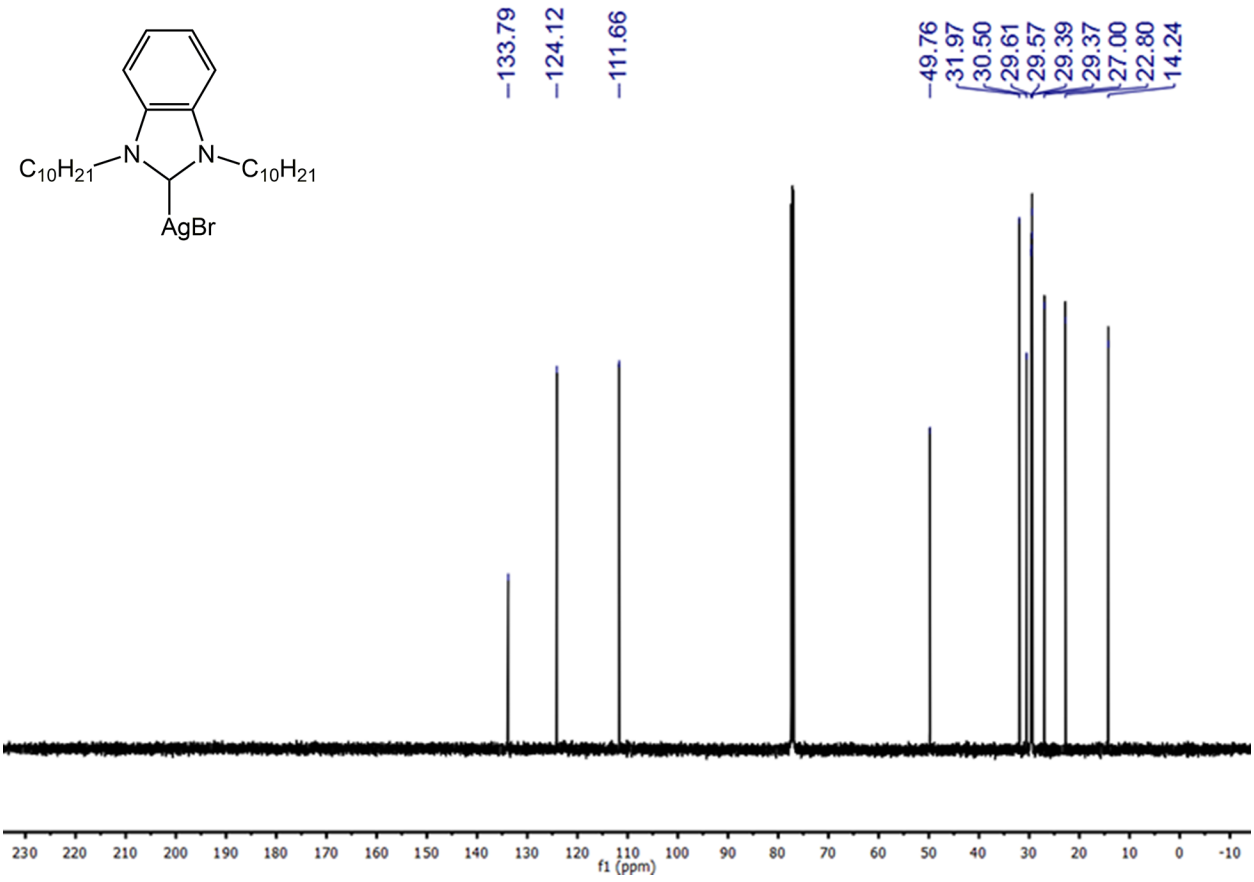


Figure S20. ^{13}C NMR spectrum of **2-*b*-AgBr** in $CDCl_3$.

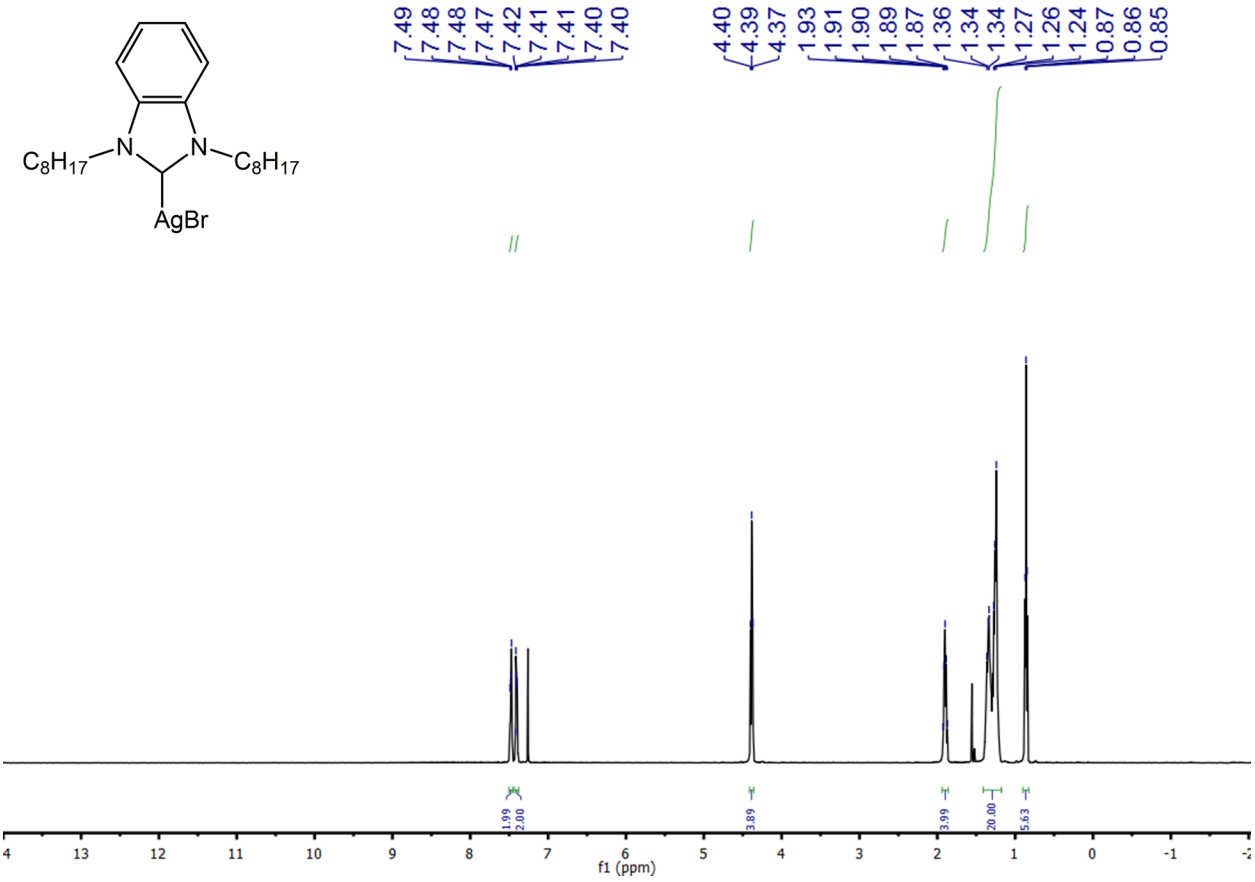


Figure S21. ^{1}H NMR spectrum of **3-*b*-AgBr** in $CDCl_3$.

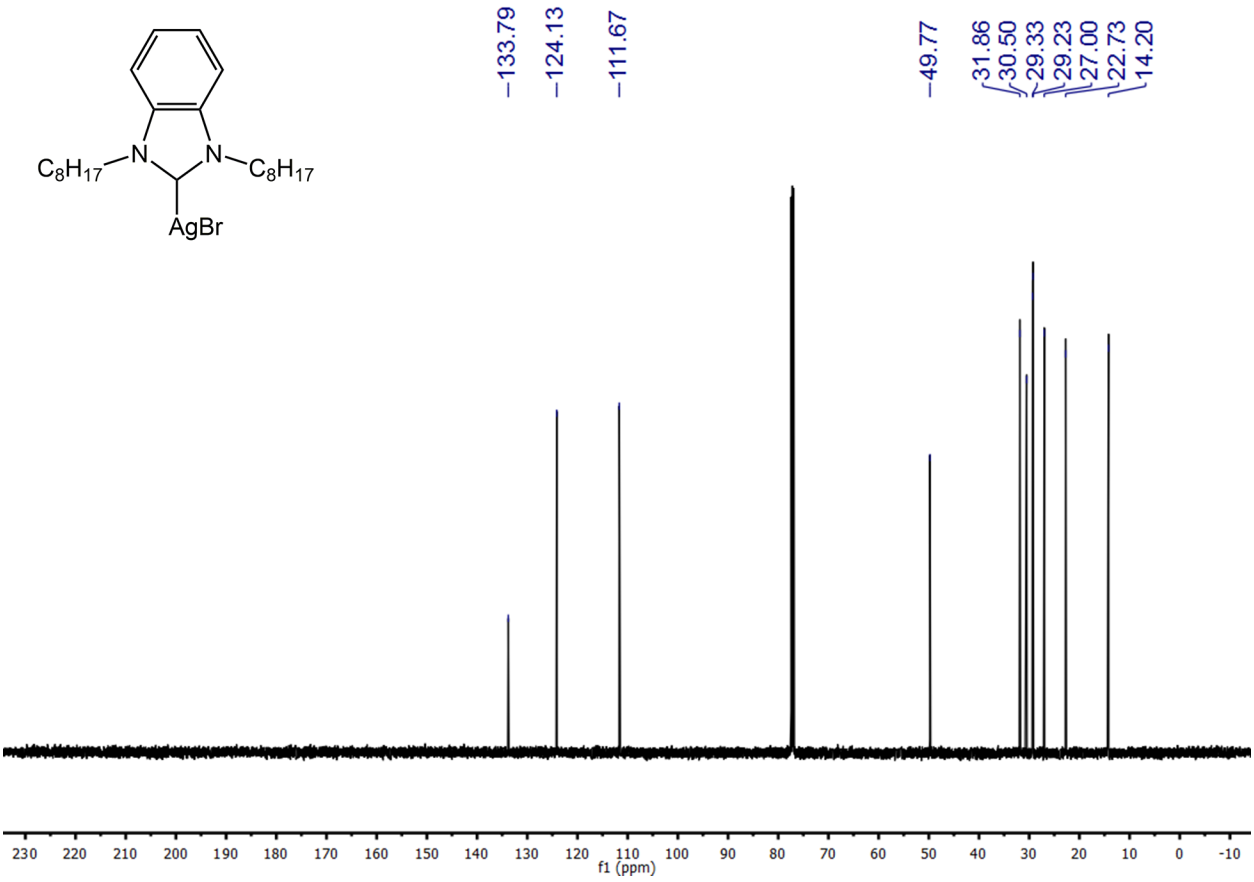


Figure S22. ^{13}C NMR spectrum of **3-*b*-AgBr** in $CDCl_3$.

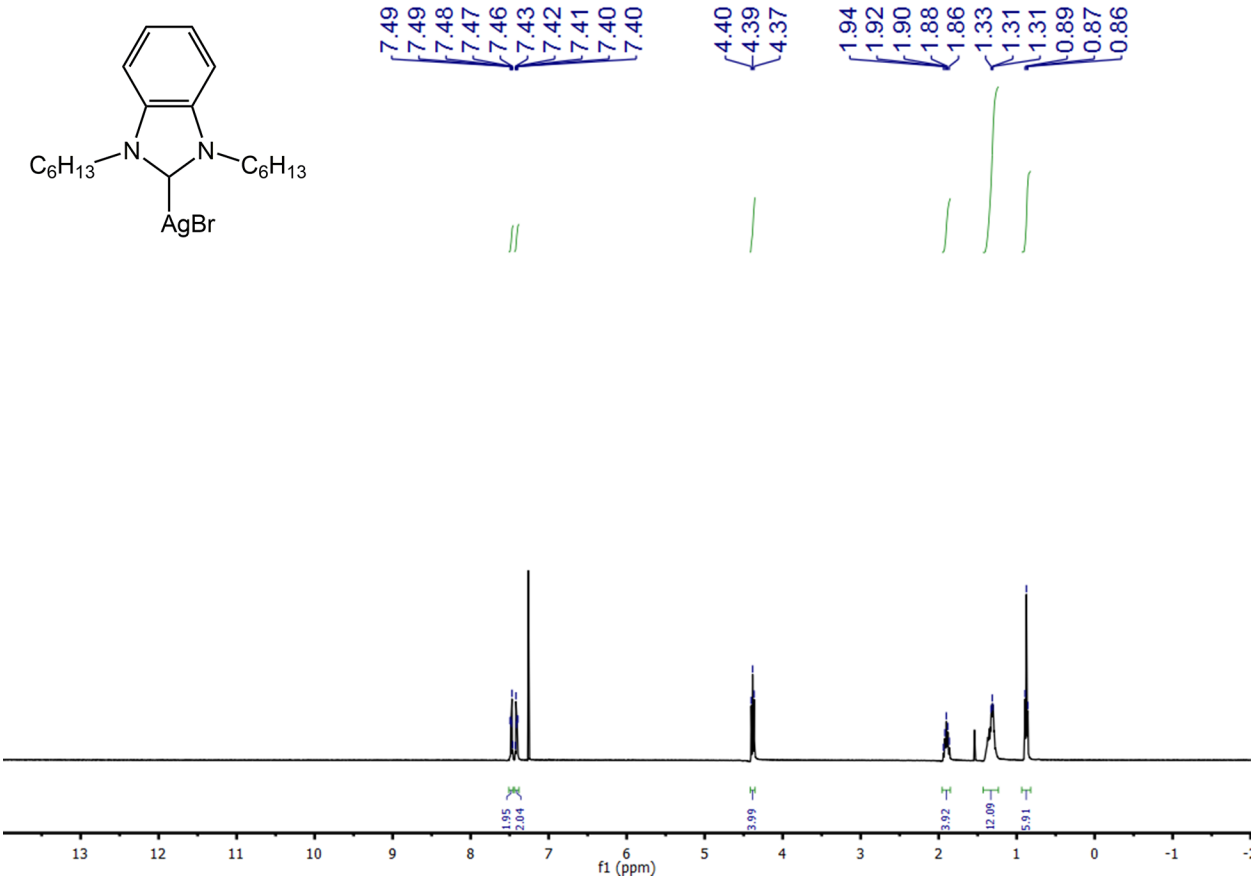


Figure S23. ^{1}H NMR spectrum of **4-*b*-AgBr** in $CDCl_3$.

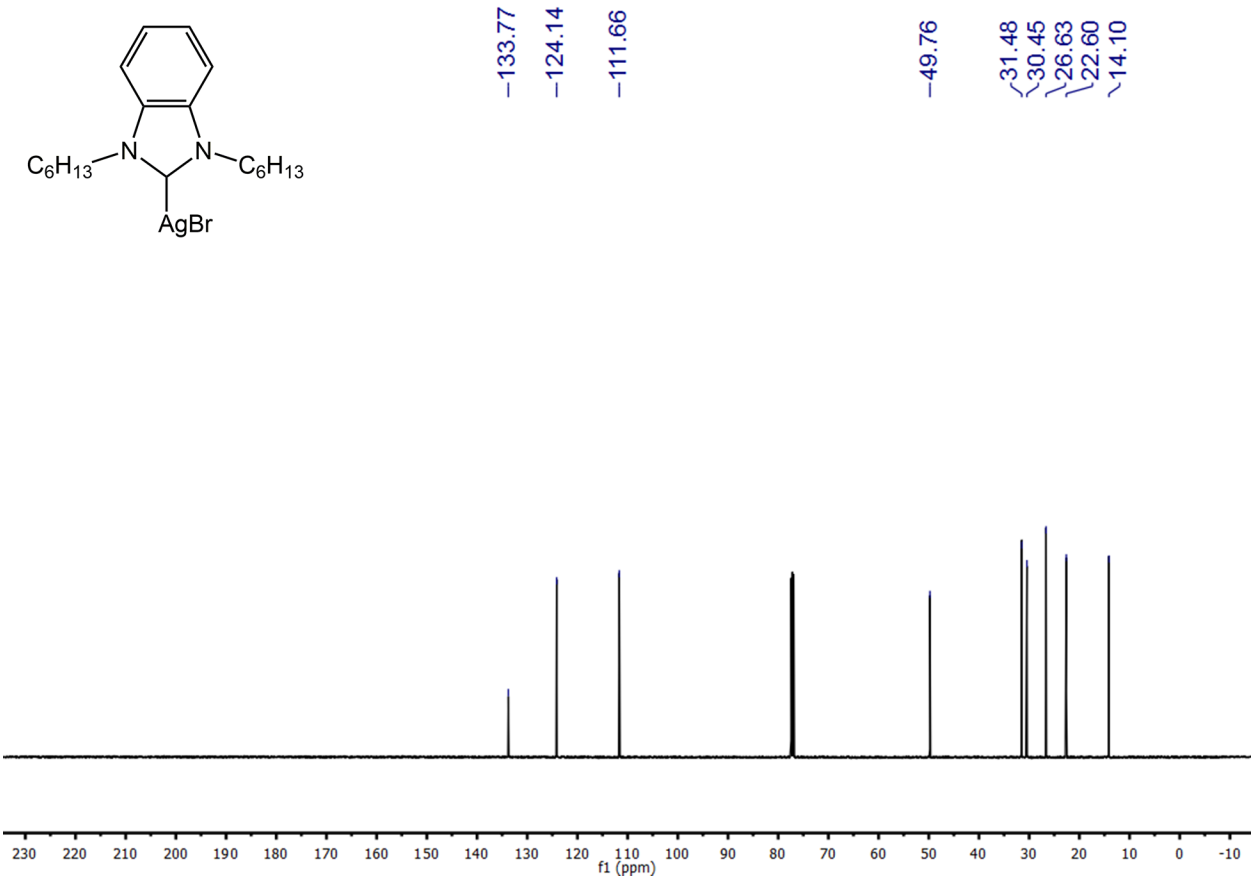


Figure S24. ^{13}C NMR spectrum of **4-*b*-AgBr** in $CDCl_3$.

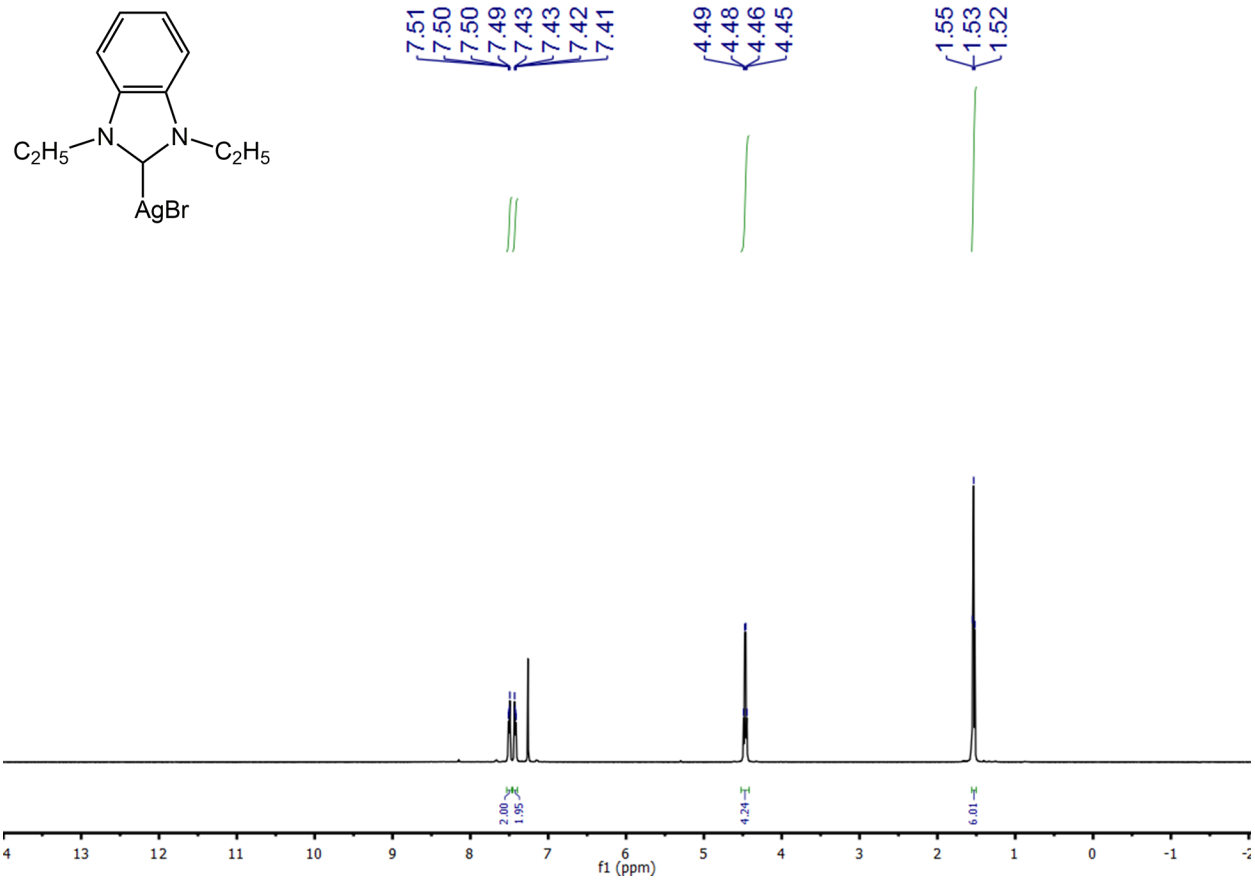


Figure S25. ^{1}H NMR spectrum of **5-*b*-AgBr** in $CDCl_3$.

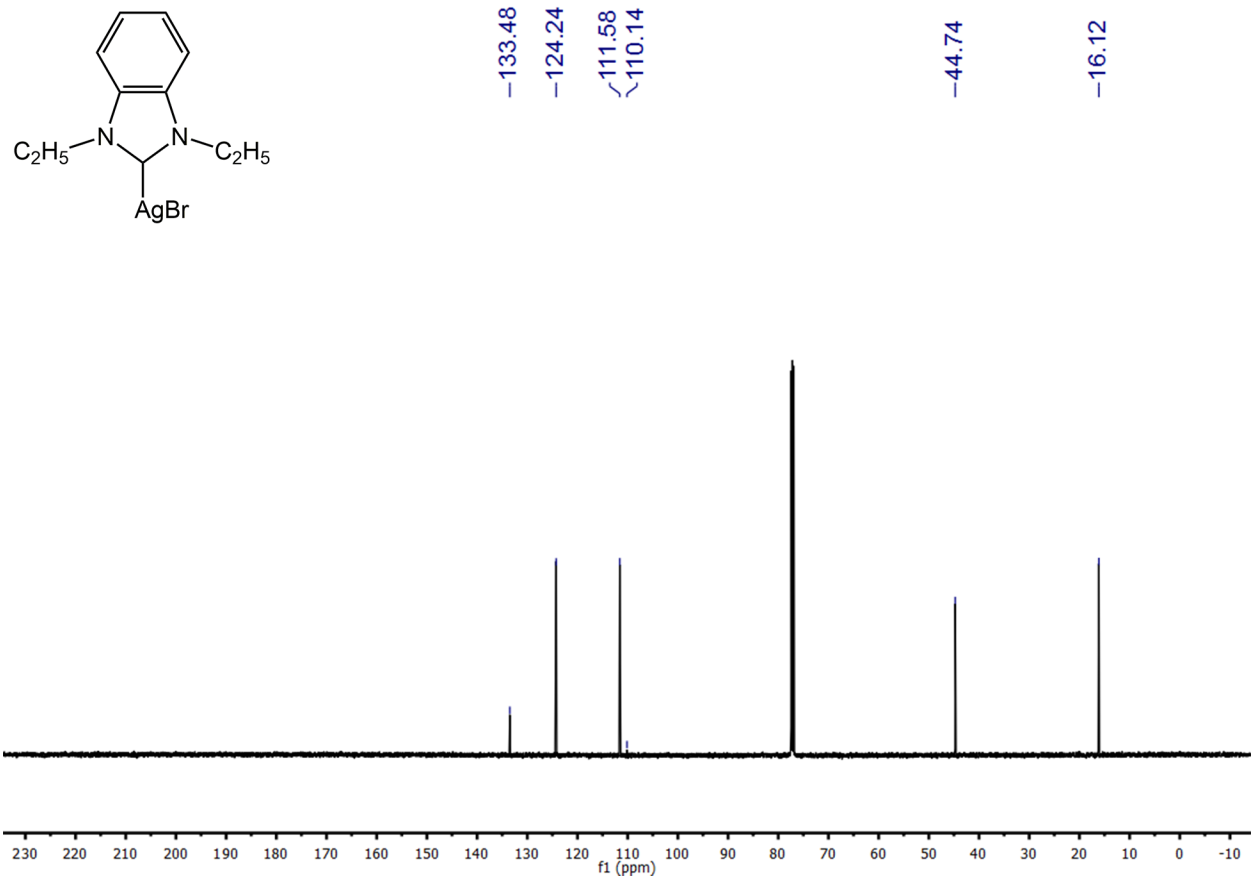


Figure S26. ^{13}C NMR spectrum of 5-***b*-AgBr** in $CDCl_3$.

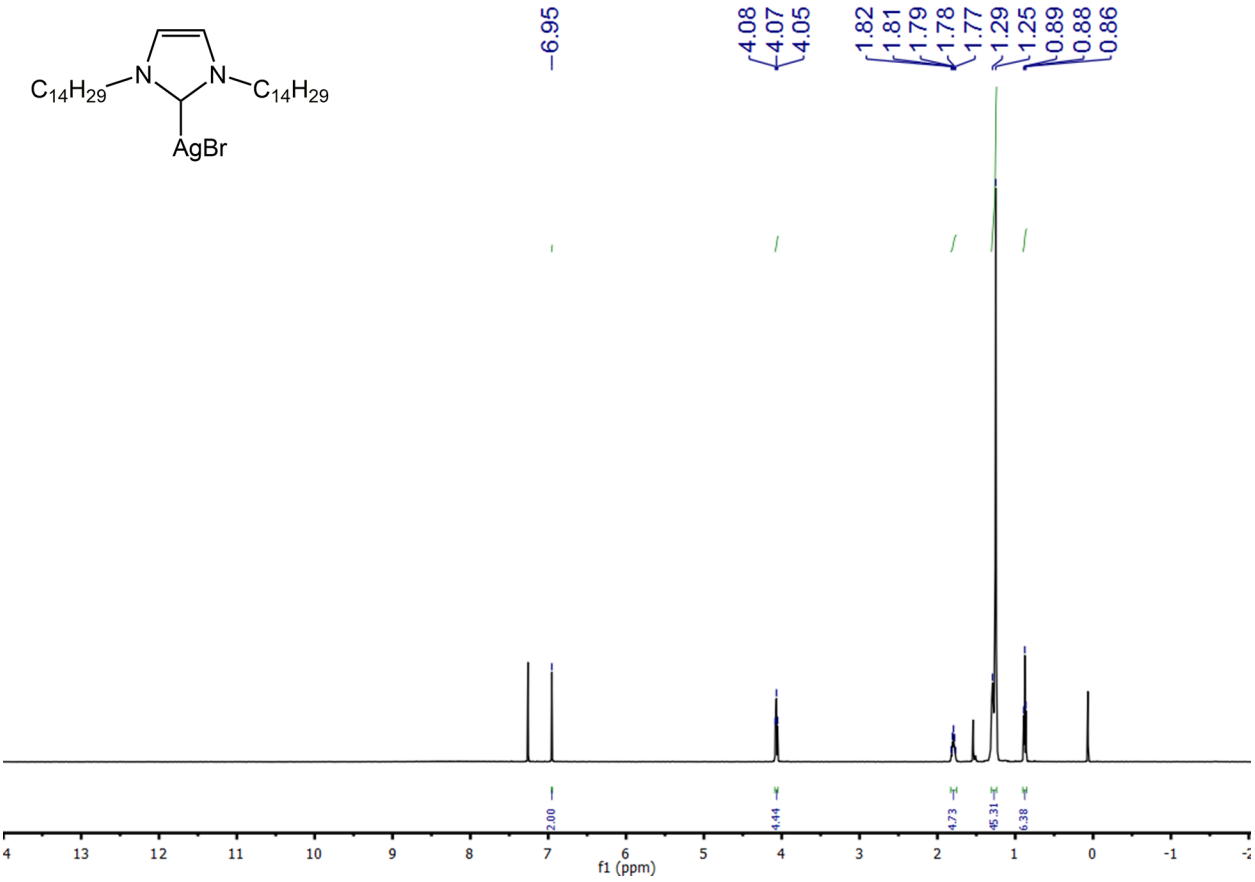


Figure S27. ^{1}H NMR spectrum of **1-*i*-AgBr** in $CDCl_3$.

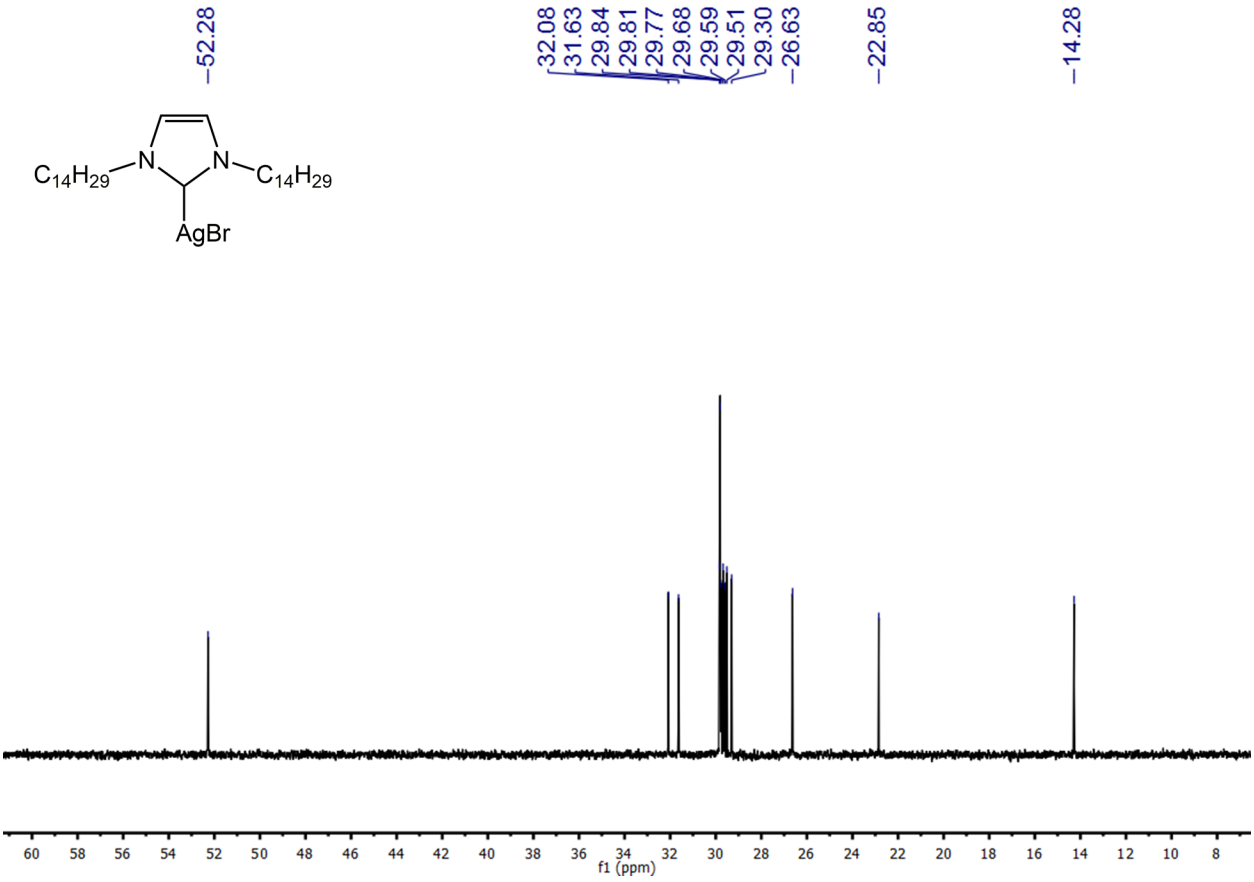


Figure S28. ^{13}C NMR spectrum of **1-*i*-AgBr** in $CDCl_3$.

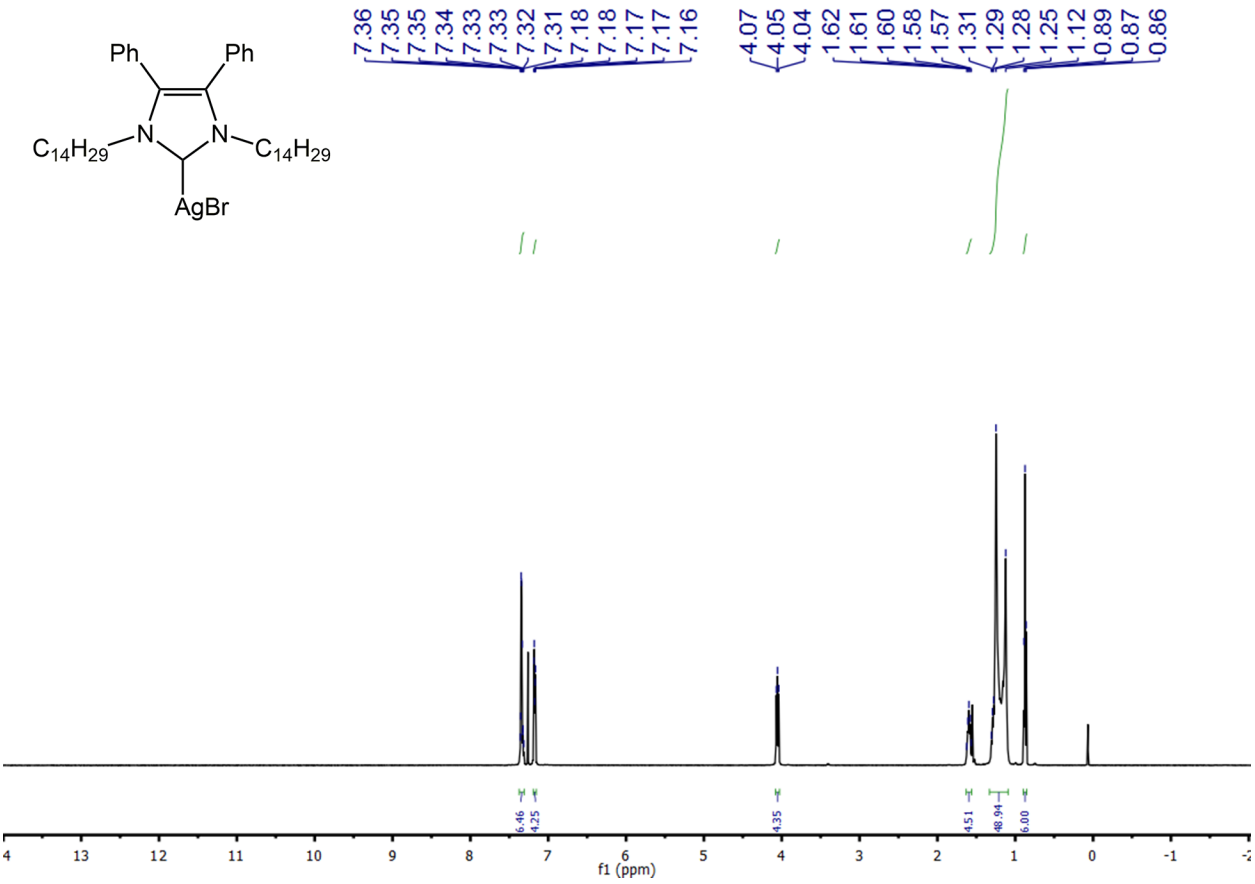


Figure S29. ^{1}H NMR spectrum of **2-*i*-AgBr** in $CDCl_3$.

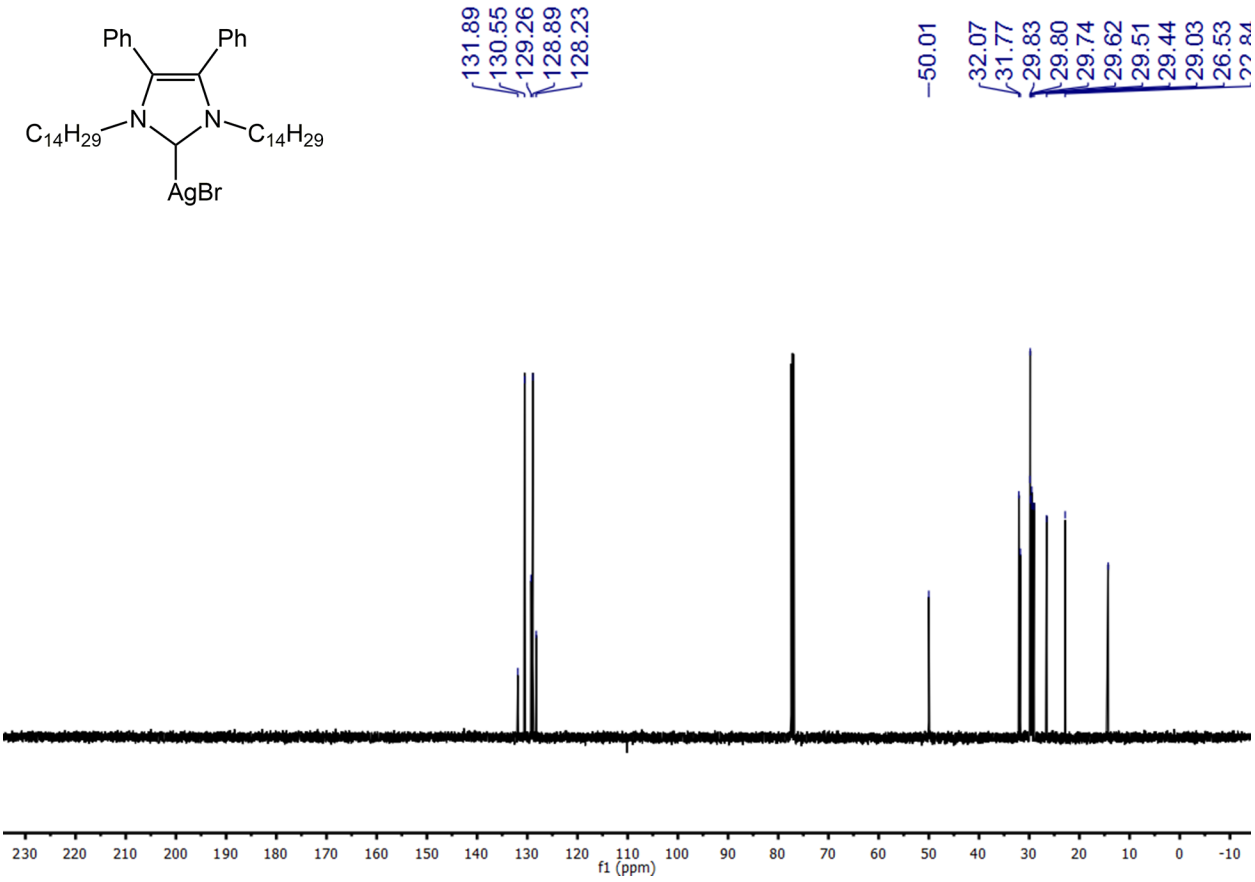


Figure S30. ^{13}C NMR spectrum of **2-*i*-AgBr** in $CDCl_3$.

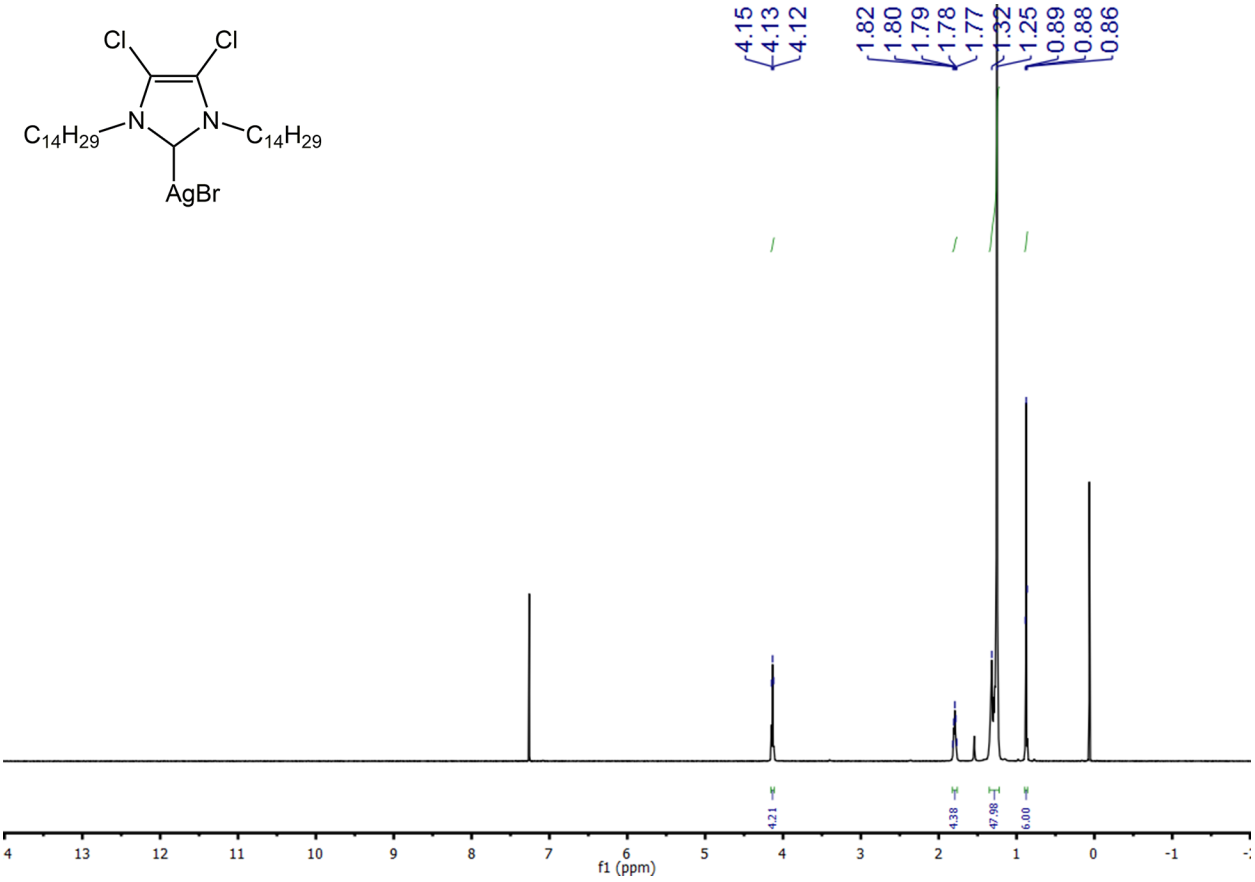


Figure S31. ^{1}H NMR spectrum of **3-*i*-AgBr** in $CDCl_3$.

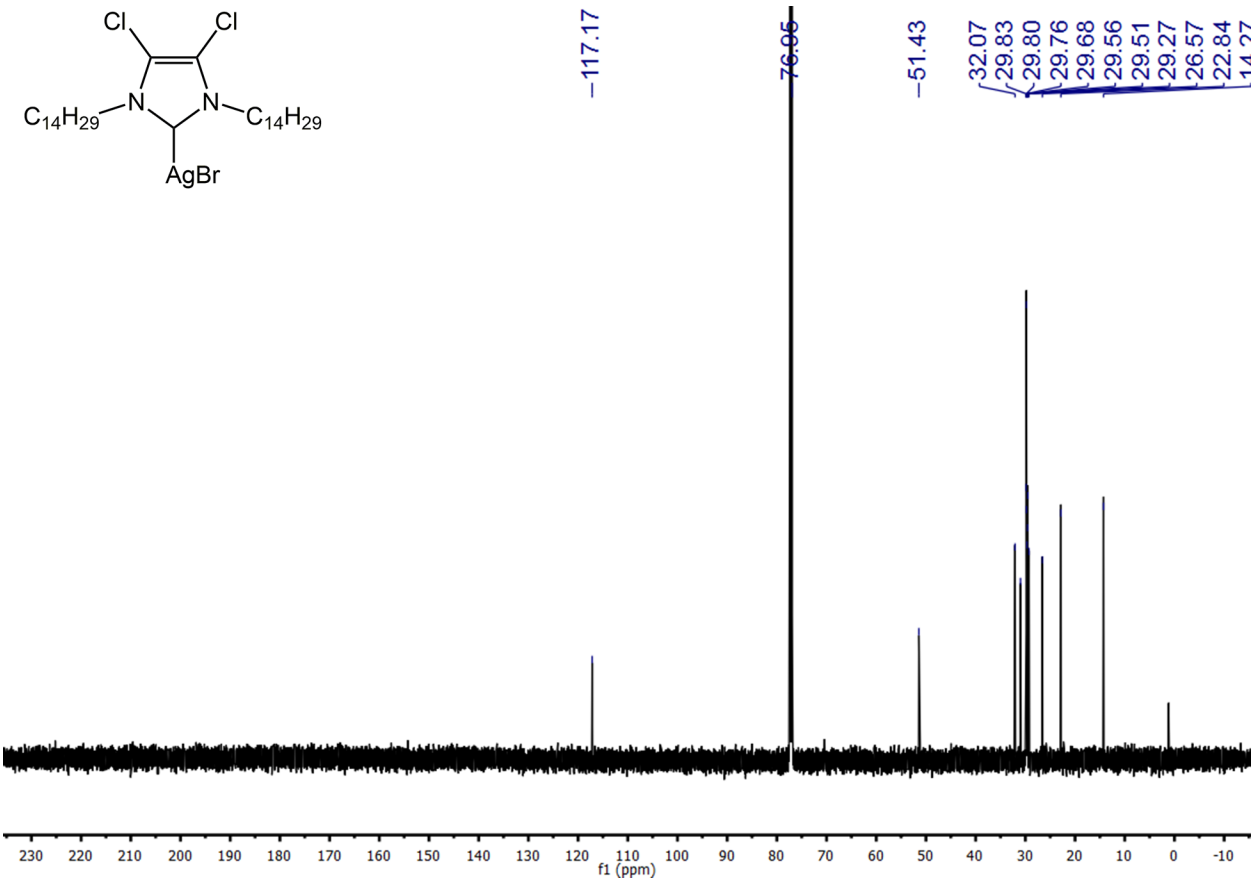


Figure S32. ^{13}C NMR spectrum of **3-*i*-AgBr** in $CDCl_3$.

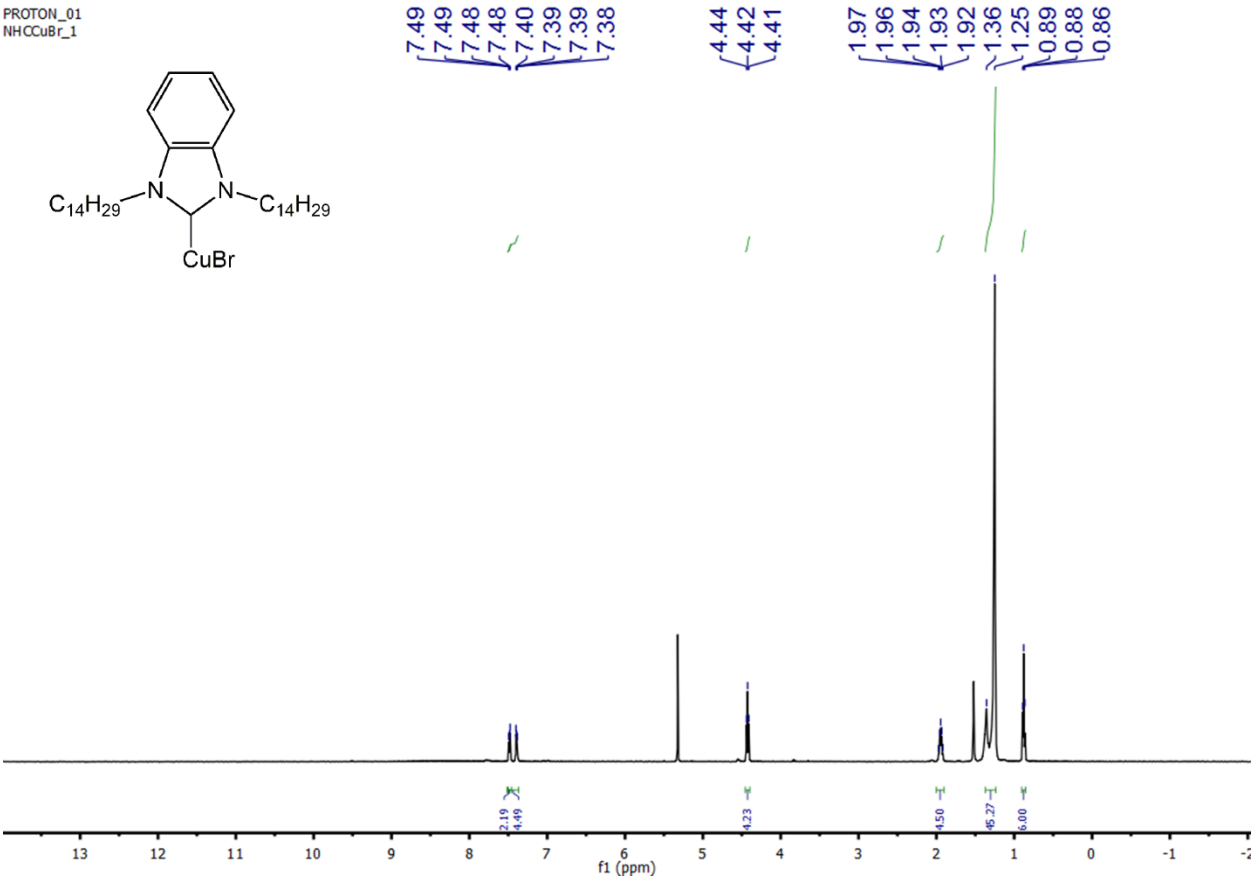


Figure S33. ^{1}H NMR spectrum of **1-*b*-CuBr** in CD_2Cl_2.

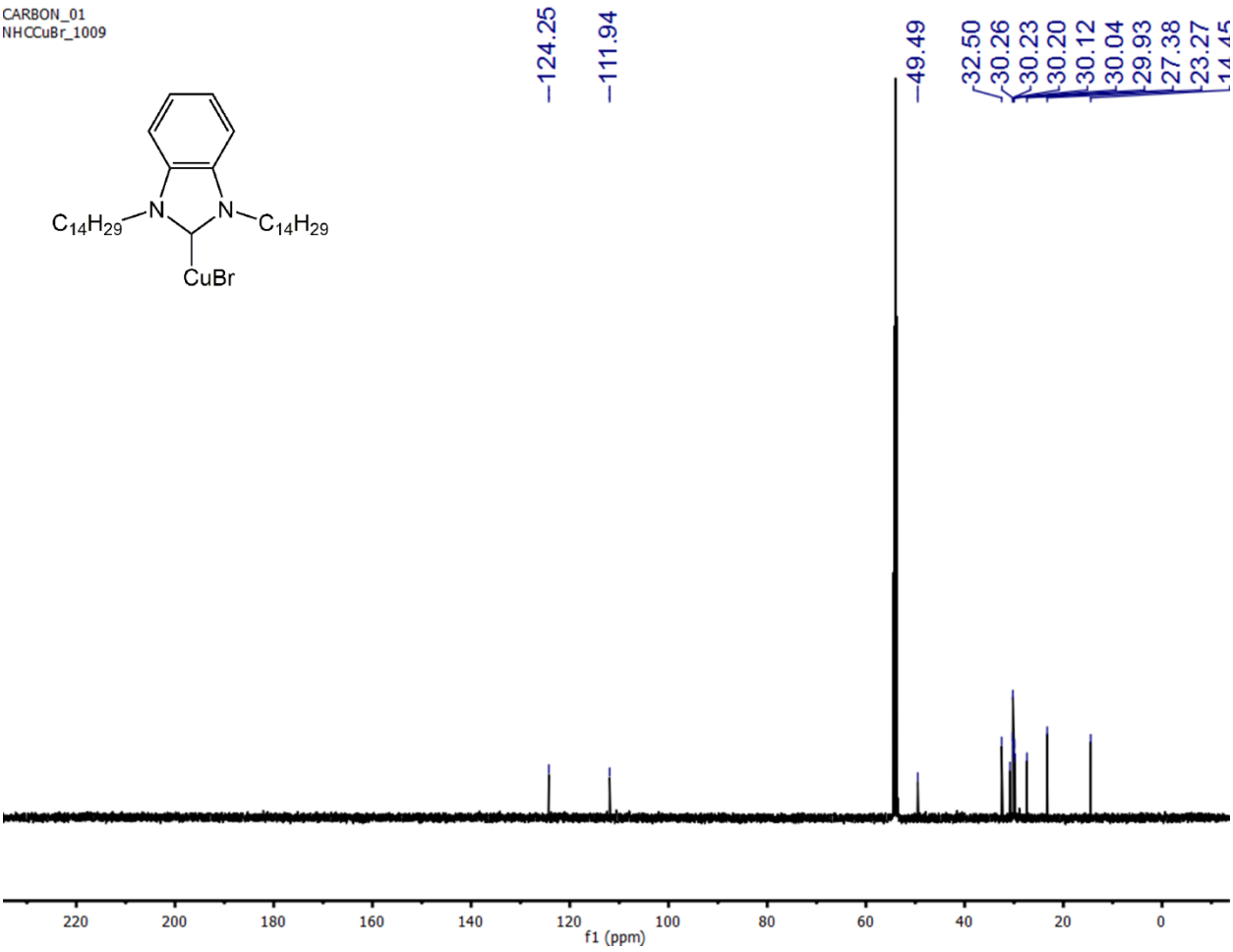


Figure S34. ^{13}C NMR spectrum of **1-*b*-CuBr** in CD_2Cl_2.

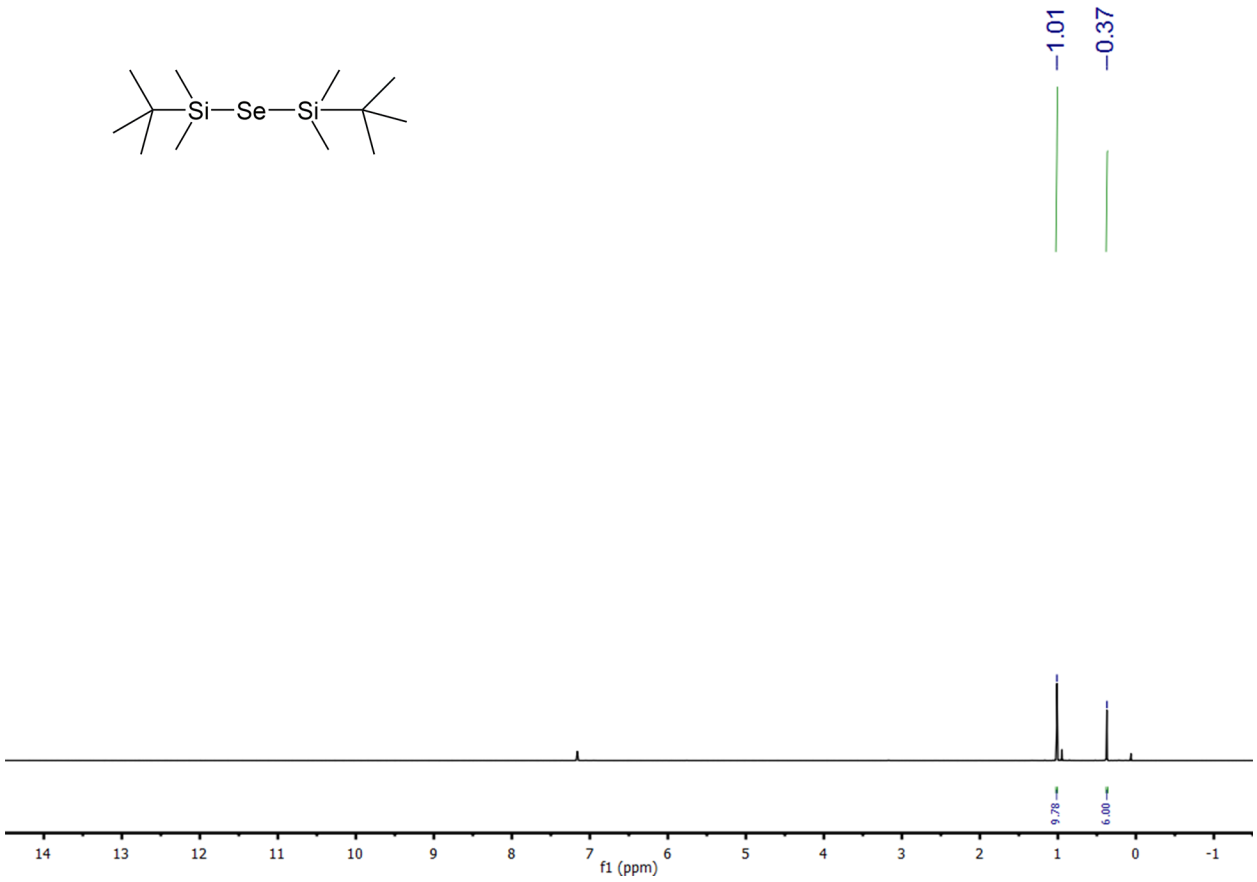


Figure S35. ^{1}H NMR spectrum of $(TBDMS)_2Se$ in C_6D_6.

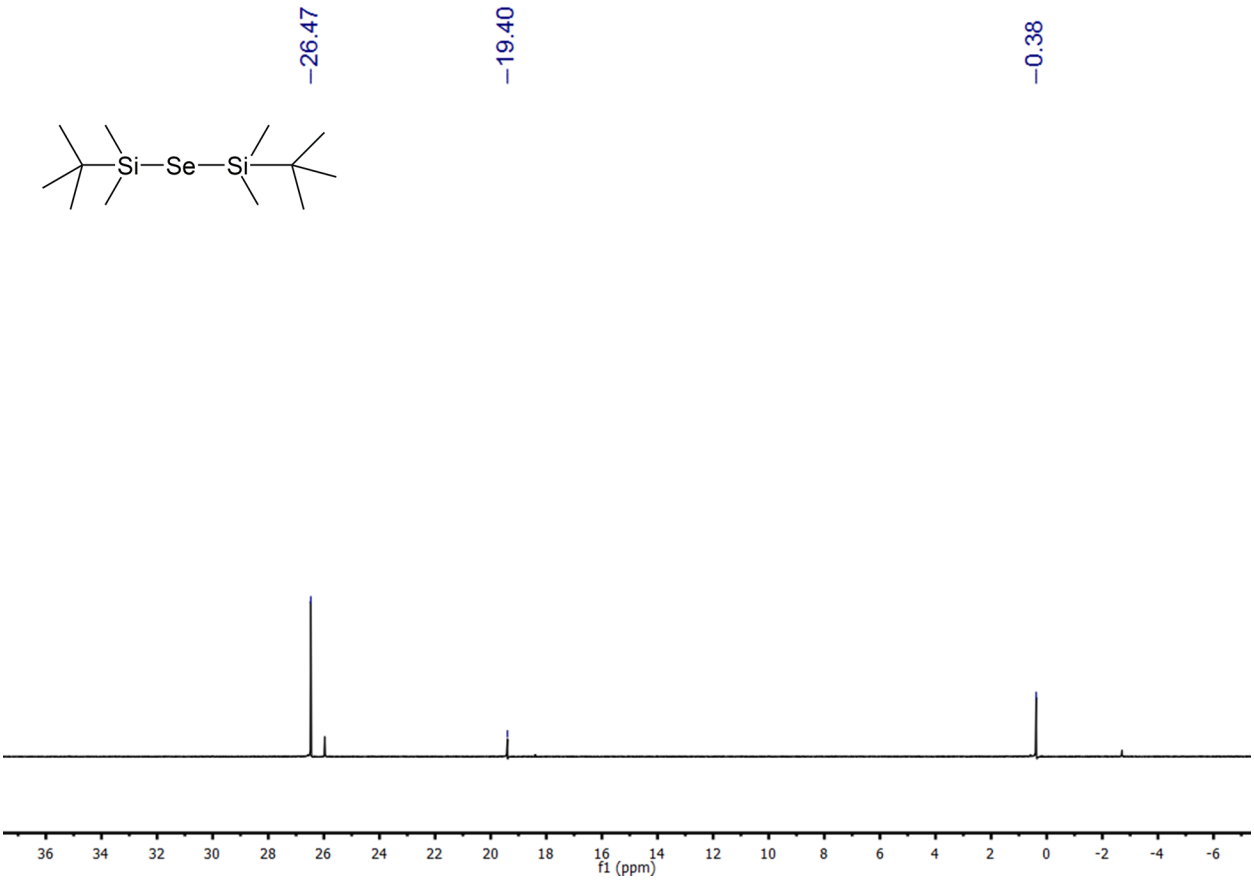


Figure S36. ^{13}C NMR spectrum of $(TBDMS)_2Se$ in C_6D_6.

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