Supporting Information

Supracrystals of *N*-Heterocyclic Carbene-Coated Au Nanocrystals

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General Information

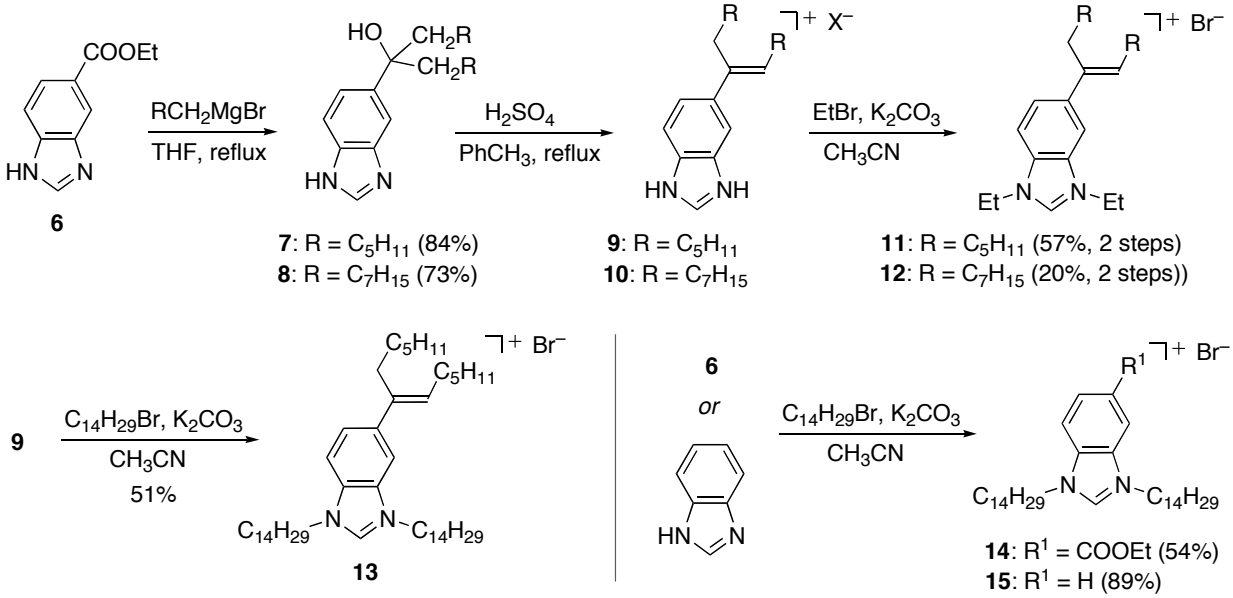
Reagents were purchased from commercial sources and used as received unless stated otherwise. 5-Ethoxycarbonyl benzimidazole (**6**) was prepared from benzimidazole-5-carboxylic acid according to a literature procedure.[1] THF was distilled from sodium-benzophenone ketyl under nitrogen atmosphere. Dichloromethane was distilled from CaH_2. Reactions involving organometallic species or air- or moisture-sensitive compounds were carried out under an atmosphere of argon by using standard Schlenk techniques. Purification by column chromatography were performed on silica gel (Kieselgel 60 Merck, granulometry 40–60 or 15–40 μm) or on Alumina (aluminium oxide 90 active neutral Merck, 63–200 μm). NMR spectra were recorded on Bruker Nanobay spectrometers 300 or 400 MHz. In $CDCl_3$ and CD_2Cl_2, proton chemical shifts (δ) are reported relative to the residual protonated solvent (δ = 7.26 and 5.32 ppm, respectively). ^{13}C chemical shifts (δ) are reported relative to the NMR solvent (CD_2Cl_2: δ = 54.00 ppm; $CDCl_3$: δ = 77.16 ppm). Coupling constants are reported in Hertz (Hz). The following abbreviations are used : s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, br = broad). Elemental analyses were performed at the "Institut de Chimie des Substances Naturelles" (service de microanalyse). HRMS were performed at the "Institut Parisien de Chimie Moléculaire" (UPMC-Univ Paris 6). XPS analyses were carried out at the "Laboratoire de Réactivité de Surface" (UPMC-Univ Paris 6).

[1] Barrow, J. C.; Coburn, C.; Selnick, H. G.; Ngo, P. L. "Preparation of 2-(pyridin-4-yl)acetamides as thrombin inhibitors" U. S. Patent 20020193398, December 19, 2002.

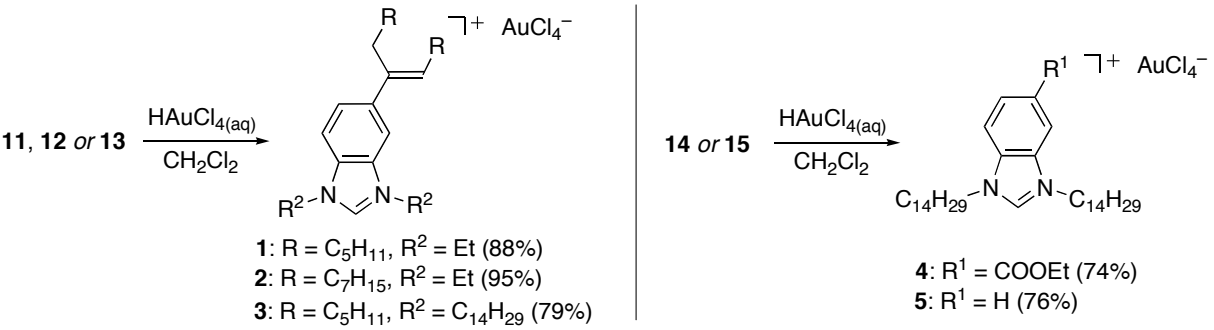
Synthesis of Chloroaurate(III) Benzimidazolium Salts (1–5) [NHC–H·$AuCl_4$]

Scheme S1: General synthetic scheme.

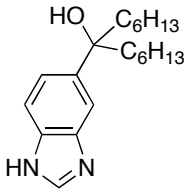
Benzimidazolium bromide salts :



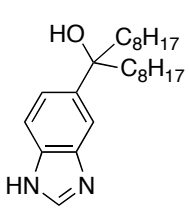
Benzimidazolium chloroaurate salts :



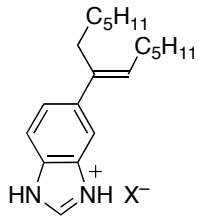
5-[1,1-Dihexyl-1-(hydroxy)methyl]benzimidazole (**7**).[2] To a solution of 5-ethoxycarbonyl benzimidazole (**6**) (2 g, 10.6 mmol) in THF (30 mL) was added dropwise at 0 °C a solution of hexylmagnesium bromide 2 M in Et_2O (18.6 mL, 37.2 mmol). The mixture was allowed to reflux for 5 h, after which it was cooled to 0 °C and quenched with $NH_4Cl_{(aq)}$ 10% (5 mL) and water (10 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (EtOAc:CH_2Cl_2 = 3:1) to give the title compound as a light brown oil (2.8 g, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.32 (s, 1H), 7.82 (s, 1H), 7.64 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 6.05 (br s, 2H), 1.94–1.77 (m, 4H), 1.35–1.08 (m, 16H), 0.78 (t, J = 6.6 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.17, 141.03, 137.22, 136.67, 120.75, 115.27, 112.10, 77.63, 43.40, 31.85, 29.82, 23.70, 22.69, 14.11.



5-[1,1-Dioctyl-1-(hydroxy)methyl]benzimidazole (**8**). To a solution of ester **6** (2 g, 10.6 mmol) in THF (30 mL) was added dropwise at 0 °C a solution of octylmagnesium bromide 2 M in Et_2O (18.6 mL, 37.2 mmol). The mixture was allowed to reflux for 5 h, after which it was cooled to 0 °C and quenched with $NH_4Cl_{(aq)}$ 10% (5 mL) and water (10 mL). The organic and aqueous layers were separated and the aqueous layer was extracted with Et_2O. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (EtOAc:CH_2Cl_2 = 3:1) to give the title compound as a light brown oil (2.9 g, 73%). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 8.07 (s, 1H), 7.80 (s, 1H), 7.60 (d, J = 8.5 Hz, 1H), 7.27 (dd, J = 8.5 and 1.5 Hz, 1H), 1.95–1.75 (m, 4H), 1.45–0.90 (m, 24H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.04, 140.87, 137.20, 136.54, 120.70, 115.46, 112.09, 77.60, 43.47, 31.96, 30.20, 29.64, 29.40, 23.72, 22.75, 14.20.

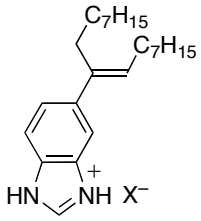


(E)-5-[1-(Hexyl)-hept-1-en-1-yl]benzimidazole (**9**) (protonated form). To a solution of alcohol **7** (0.95 g, 3 mmol) in toluene (20 mL) was added conc. H_2SO_4 (0.08 mL). The solution was allowed to reflux for 16 h, after which it was cooled to 20 °C and sat. $NaHCO_{3(aq)}$ (20 mL) was added. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (EtOAc:CH_2Cl_2 = 1:1) to give 0.8 g of the title compound as a light brown oil. (*E*)/(*Z*) ratio = 94:6. The nature of the counterion (X^-) could not be determined. ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.02 (br s, 2H), 9.94 (s, 1H), 7.88 (d, J = 8.7 Hz, 1H), 7.83 (s, 1H), 7.47 (dd, J = 8.7 and 1.3 Hz, 1H), 5.64 (t, J = 7.3 Hz, 1H), 2.28–2.20 (m, 2H), 2.16 (q, J = 7.3 Hz, 2H), 1.25–1.02 (m, 14H), 0.89 (t, J = 6.9 Hz, 3H), 0.80 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 143.64, 139.23, 139.02, 131.97, 130.29, 128.61, 126.32, 114.21, 111.71, 31.77, 31.69, 30.07, 29.51, 29.20, 28.84, 28.62, 22.65, 14.15, 14.12.

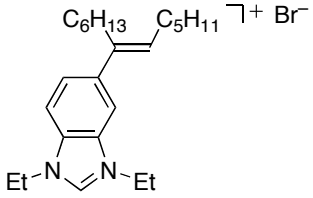


[2] The procedure was adapted from: (a) Cho, S. Y.; Grimsdale, A. C.; Jones, D. J.; Watkins, S. E.; Holmes, A. B. *J. Am. Chem. Soc.* **2007**, *129*, 11910-11911. (b) de Arriba, Á. L. F.; Simón, L.; Alcázar, V.; Cuellar, J.; Lozano-Martínez, P.; Morán, J. R. *Adv. Synth. Catal.* **2011**, *353*, 2681.

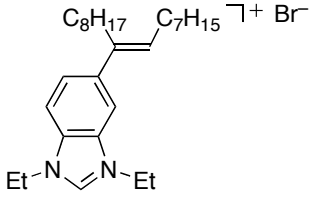
(E)-5-[1-(Octyl)-non-1-en-1-yl]benzimidazole (**10**) (protonated form). To a solution of alcohol **8** (1.12 g, 3 mmol) in toluene (20 mL) was added conc. H_2SO_4 (0.08 mL). The solution was allowed to reflux for 16 h, after which it was cooled to 20 °C and sat. $NaHCO_{3(aq)}$ (20 mL) was added. The organic phase was separated and the aqueous phase was extracted with EtOAc. The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The residue was purified by silica gel chromatography (EtOAc:CH_2Cl_2 = 1:1) to give 0.9 g of the title compound as a light brown oil. (*E*)/(*Z*) ratio = 94:6. The nature of the counterion (X^-) could not be determined. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.75 (br s, 2H), 9.55 (s, 1H), 7.85 (d, J = 8.7 Hz, 1H), 7.82 (s, 1H), 7.47 (d, J = 8.7 Hz, 1H), 5.65 (t, J = 7.2 Hz, 1H), 2.50–2.30 (m, 2H), 2.16 (q, J = 7.5 Hz, 2H), 1.50–1.06 (m, 22H), 0.90 (t, J = 6.8 Hz, 3H), 0.83 (t, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) 140.93, 140.51, 139.33, 137.57, 137.13, 129.26, 122.28, 115.31, 112.76, 32.02, 31.99, 30.41, 30.13, 29.75, 29.58, 29.42, 28.89, 28.82, 22.81, 22.78, 14.24, 14.21.



(E)-1,3-Diethyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium bromide (**11**). To a solution of alkene **9** (0.75 g, 2.5 mmol) in CH_3CN (10 mL) was added K_2CO_3 (0.35 g, 2.5 mmol) and EtBr (0.56 mL, 7.5 mmol). The mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure. The residue was taken off in CH_2Cl_2 and filtered through a short pad of Celite to remove the precipitate (KBr). The filtrate was concentrated under reduced pressure. The residue was washed with Et_2O and pentane and dried under vacuum to give the title compound as a light yellow solid (0.7 g, 52% from **7**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.10 (s, 1H), 7.62 (s, 2H), 7.53 (s, 1H), 5.70 (t, J = 7.2 Hz, 1H), 4.69–4.63 (m, 4H), 2.60–2.50 (m, 2H), 2.22 (q, J = 7.3 Hz, 2H), 1.78–1.73 (m, 6H), 1.25–1.07 (m, 14H), 0.90 (t, J = 6.4 Hz, 3H), 0.84 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.22, 141.37, 138.97, 132.82, 131.65, 129.93, 126.59, 112.57, 110.04, 43.14, 42.92, 31.78, 31.71, 30.22, 29.50, 29.23, 28.91, 28.61, 22.69, 15.10, 15.08, 14.18, 14.14. HRMS (ESI) *m/z* calcd for $C_{24}H_{39}N_2$ $[M–Br^-]^+$ 355.3113, found 355.3109. The (*E*) configuration of the major isomer was determined by NOESY experiments (see page S16).



(E)-1,3-Diethyl-5-[1-(octyl)-non-1-en-1-yl]benzimidazolium bromide (**12**). To a solution of alkene **10** (0.97 g, 2.7 mmol) in CH_3CN (10 mL) was added K_2CO_3 (0.37 g, 2.7 mmol) and EtBr (0.62 mL, 8.1 mmol). The mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure. The residue was taken off in CH_2Cl_2 and filtered through a short pad of Celite to remove the precipitate (KBr). The filtrate was concentrated under reduced pressure. The residue was washed with pentane and dried under vacuum to give the title compound as a white solid (0.3 g, 20% from **8**). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.45 (s, 1H), 7.61 (d, J = 8.8. Hz, 1H), 7.59 (d, J = 8.8. Hz, 1H), 7.51 (s, 1H), 5.69 (t, J = 7.2 Hz, 1H), 4.69–4.63 (m, 4H), 2.55–2.52 (m, 2H), 2.21 (q, J = 7.2 Hz, 2H), 1.75–1.70 (m, 6H), 1.25–1.12 (m, 22H), 0.92–0.79 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.07, 142.29, 138.96, 132.76, 131.63, 129.93, 126.44, 112.54, 110.01, 43.02, 42.81, 31.94, 30.19, 29.81, 29.55, 29.54, 29.47, 29.32, 28.93, 28.64, 22.77, 22.73, 15.10, 15.07, 14.21, 14.18. HRMS (ESI) *m/z* calcd for $C_{28}H_{47}N_2$ $[M–Br^-]^+$ 411.3739, found 411.3739.

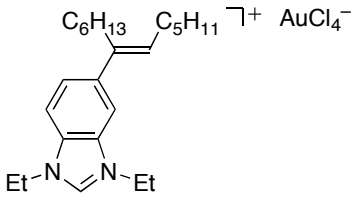


(E)-1,3-Ditetradecyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium bromide (**13**). A mixture of **9** (1.8 g, 6.1 mmol), K_2CO_3 (1.01 g, 7.32 mmol) and *n*-tetradecyl bromide (5.5 mL, 18.3 mmol) in CH_3CN (10 mL) was stirred at reflux for 24 h. The solvent was removed under reduced pressure. The residue was taken off in CH_2Cl_2 and filtered through a short pad of Celite to remove the precipitate (KBr). The filtrate was concentrated under reduced pressure. The residue was purified by chromatography on alumina (neutral, eluent : CH_2Cl_2) to give the title compound as a light yellow oil (2.4 g, 51%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 11.29 (s, 1H), 7.58 (d, J = 8.8 Hz, 1H), 7.53 (d, J = 8.8 Hz, 1H), 5.63 (t, J = 6.9 Hz, 1H), 4.70–4.40 (m, 4H), 2.55–2.40 (m, 2H), 2.15 (q, J = 7.5 Hz, 2H), 2.10–1.80 (m, 4H), 1.50–1.01 (m, 58H), 0.90–0.70 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.47, 142.13, 138.59, 132.23, 131.38, 129.75, 126.05, 112.61, 109.60, 47.53, 47.21, 31.64, 31.39, 31.33, 29.80, 29.41, 29.37, 29.34, 29.27, 29.15, 29.12, 29.08, 28.83, 28.51, 28.24, 26.32, 26.30, 22.40, 22.30, 13.82, 13.78, 13.74. HRMS (ESI) *m/z* calcd for $C_{48}H_{87}N_2$ $[M–Br^–]^+$ 691.6869, found 691.6871.

5-Ethoxycarbonyl-1,3-(ditetradecyl)benzimidazolium bromide (**14**). A mixture of ester **6** (1.9 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol) and *n*-tetradecyl bromide (9 mL, 30 mmol) in CH_3CN (10 mL) was stirred at reflux for 24 h. The solvent was removed under reduced pressure. The residue was taken off in CH_2Cl_2 and filtered through a short pad of Celite to remove the precipitate (KBr). The filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/pentane and dried under vaccum to give the title compound as white solid (3.6 g, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.82 (s, 1H), 8.38 (s, 1H), 8.33 (dd, J = 8.7 and 1.3 Hz, 1H), 7.75 (d, J = 8.7 Hz, 1H), 4.69–4.64 (m, 4H), 4.48 (q, J = 7.1 Hz, 2H), 2.13–2.02 (m, 4H), 1.47 (t, J = 7.1 Hz, 3H), 1.50–1.12 (m, 44H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.78, 145.20, 134.09, 131.34, 129.91, 128.21, 115.10, 113.11, 62.35, 48.17, 48.13, 32.04, 29.79, 29.76, 29.70, 29.62, 29.52, 29.50, 29.47, 29.16, 29.14, 26.69, 22.80, 14.45, 14.23. Anal. calcd for $(C_{38}H_{67}BrN_2O_2)\cdot(H_2O)_{0.5}$: C 67.83, H 10.19, N 4.16; found C 67.63, H 10.25, N 4.20. HRMS (ESI) *m/z* calcd for $C_{38}H_{67}N_2O_2$ $[M–Br^–]^+$ 583.5197, found 583.5193.

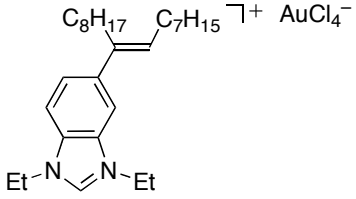
1,3-(Ditetradecyl)benzimidazolium bromide (**15**). A mixture of benzimidazole (1.18 g, 10 mmol), K_2CO_3 (1.38 g, 10 mmol) and *n*-tetradecyl bromide (9.0 mL, 30 mmol) in CH_3CN (10 mL) was stirred at reflux for 24 h. The solvent was removed under reduced pressure. The residue was taken off in CH_2Cl_2 and filtered through a short pad of Celite to remove the precipitate (KBr). The filtrate was concentrated under reduced pressure. The residue was recrystallized from CH_2Cl_2/pentane and dried under vacuum to give the title compound as a white solid (5.3 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 7.75–7.60 (m, 4H), 4.62 (t, J = 7.4 Hz, 4H), 2.14–1.98 (m, 4H), 1.48–1.13 (m, 44H), 0.87 (t, J = 6.7 Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 143.18, 131.50, 127.19, 113.18, 47.84, 32.06, 29.81, 29.78, 29.72, 29.71, 29.64, 29.52, 29.49, 29.19, 26.72, 22.83, 14.25. Anal. calcd for $(C_{35}H_{63}BrN_2)\cdot(H_2O)_{0.5}$: C 69.97, H 10.74, N 4.66; found C 69.90, H 10.84, N 4.69. HRMS (ESI) *m/z* calcd for $C_{35}H_{63}N_2$ $[M–Br^–]^+$ 511.4986, found 511.4983.

(E)-1,3-Diethyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**1**).[3] To a solution of



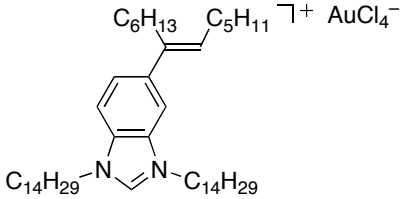
11 (0.18 g, 0.42 mmol) in CH_2Cl_2 (12 mL) was added under stirring a solution of $HAuCl_4{\cdot}3H_2O$ (0.15 g, 0.42 mmol) in water (12 mL). The mixture was stirred vigorously for 2 h at 20 °C. During the course of the reaction, the yellow color of the aqueous layer disappeared, while the organic phase became deep red. The organic layer was separated, concentrated and dried under vacuum to give the title compound as a blood red oil (0.256 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 7.68 (d, J = 8.8 Hz, 1H), 7.63 (dd, J = 8.8 and 1.2 Hz, 1H), 7.56 (s, 1H), 5.72 (t, J = 7.3 Hz, 1H), 4.58 (q, J = 7.4 Hz, 4H), 2.53 (t, J = 7.0 Hz, 2H), 2.20 (q, J = 7.4 Hz, 2H), 1.76–1.69 (m, 6H), 1.39–1.10 (m, 14H), 0.88 (t, J = 6.5, 3H), 0.82 (t, J = 6.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.35, 139.17, 138.81, 132.83, 131.69, 130.00, 126.90, 112.90, 110.14, 43.40, 43.15, 31.69, 31.61, 30.09, 29.37, 29.14, 28.82, 28.53, 22.59, 14.88, 14.83, 14.10, 14.08. HRMS (ESI) *m/z* calcd for $C_{24}H_{39}N_2$ $[M–AuCl_4^-]^+$ 355.3113, found 355. 3108.

(E)-1,3-Diethyl-5-[1-(octyl)-non-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**2**). To a solution of



12 (0.206 g, 0.42 mmol) in CH_2Cl_2 (12 mL) was added under stirring a solution of $HAuCl_4{\cdot}3H_2O$ (0.15 g, 0.42 mmol) in water (12 mL). The mixture was stirred vigorously for 2 h at 20 °C. During the course of the reaction, the yellow color of the aqueous layer disappeared, while the organic phase became deep red. The organic layer was separated, concentrated and dried under vacuum to give the title compound as a blood red oil (0.3 g, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.69 (d, J = 8.8 Hz, 1H), 7.61 (dd, J = 8.8 and 1.3 Hz, 1H), 7.55 (s, 1H), 5.71 (t, J = 7.3 Hz, 1H), 4.55 (q, J = 7.3 Hz, 4H), 2.52 (t, J = 7.0 Hz, 2H), 2.19 (q, J = 7.6 Hz, 2H), 1.71 (t, J = 7.6 Hz, 3H), 1.70 (t, J = 7.6 Hz, 3H), 1.50–1.10 (m, 22H), 0.84 (t, J = 6.4 Hz, 3H), 0.80 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.13, 138.93, 138.66, 132.61, 131.54, 129.87, 126.75, 112.85, 110.00, 43.29, 43.03, 31.70, 29.92, 29.56, 29.34, 29.31, 29.23, 29.10, 29.06, 28.72, 28.43, 22.54, 22.50, 14.73, 14.67, 14.01, 14.00. HRMS (ESI) *m/z* calcd for $C_{28}H_{47}N_2$ $[M–AuCl_4^-]^+$ 411.3739, found 411.3736.

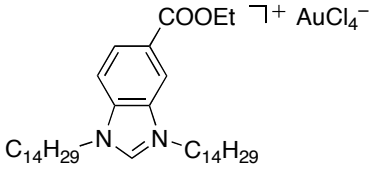
(E)-1,3-Ditetradecyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**3**). To a



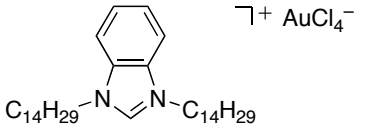
solution of **13** (0.94 g, 1.35 mmol) in CH_2Cl_2 (36 mL) was added under stirring a solution of $HAuCl_4{\cdot}3H_2O$ (0.53 g, 1.35 mmol) in water (36 mL). The mixture was stirred vigorously for 2 h at 20 °C. During the course of the reaction, the yellow color of the aqueous layer disappeared, while the organic phase became deep red. The organic layer was separated, concentrated and dried under vacuum to give the title compound as an orange oil (1.1 g, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.63 (d, J = 8.8 Hz, 1H), 7.53 (s, 1H), 5.73 (t, J = 7.3 Hz, 1H), 4.61–4.44 (m, 4H), 2.54 (t, J = 6.7 Hz, 2H), 2.21 (q, J = 7.3 Hz, 2H), 2.10–1.95 (m, 4H), 1.52–1.13 (m, 58H), 0.95–0.75 (m, 12H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.28, 139.79, 138.73, 132.83, 131.74, 130.04, 126.88, 112.94, 110.09, 48.21, 47.92, 31.92, 31.68, 31.60, 30.96, 30.08, 29.69, 29.68, 29.65, 29.64, 29.56, 29.43, 29.36, 29.15, 29.06, 28.82, 28.54, 26.69, 26.67, 22.68, 22.58, 22.57, 14.10, 14.06, 14.04. HRMS (ESI) *m/z* calcd for $C_{48}H_{87}N_2$ $[M–AuCl_4^-]^+$ 691.6869, found 691.6863.

[3] The procedure was adapted from: Serpell, C. J.; Cookson, J.; Thompson, A. L.; Brown, C. M.; Beer, P. D., *Dalton Trans.* **2013**, *42*, 1385.

5-Ethoxycarbonyl-1,3-(ditetradecyl)benzimidazolium tetrachloroaurate(III) (**4**). To a solution of **14** (0.37 g, 0.56 mmol) in CH_2Cl_2 (16 mL) was added under stirring a solution of $HAuCl_4 \cdot 3H_2O$ (0.2 g, 0.56 mmol) in water (16 mL). The mixture was stirred vigorously for 2 h at 20 °C. During the course of the reaction, the yellow color of the aqueous layer disappeared, while the organic phase became deep red. The organic layer was separated, concentrated and dried under vacuum to give the title compound as a red oil (0.38 g, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.77 (s, 1H), 8.39 (d, J = 1.6 Hz, 1H), 8.33 (dd, J = 8.8 and 1.6 Hz, 1H), 7.82 (d, J = 8.8 Hz, 1H), 4.57 (t, J = 7.5 Hz, 4H), 4.44 (q, J = 7.1 Hz, 2H), 2.11–2.02 (m, 4H), 1.40 (t, J = 7.1 Hz, 3H), 1.48–1.14 (m, 44H), 0.84 (t, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.67, 142.38, 134.10, 131.37, 130.12, 128.54, 115.30, 113.64, 62.17, 48.50, 48.45, 31.92, 29.70, 29.68, 29.66, 29.64, 29.56, 29.45, 29.43, 29.36, 29.08, 29.05, 26.76, 22.68, 14.37, 14.12. HRMS (ESI) *m/z* calcd for $C_{38}H_{67}N_2O_2$ $[M–AuCl_4^–]^+$ 583.5197, found 583.5191.

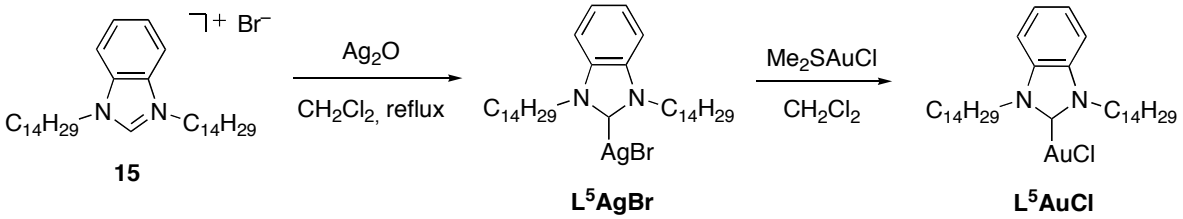


1,3-(Ditetradecyl)benzimidazolium tetrachloroaurate(III) (**5**). To a solution of **15** (0.25 g, 0.42 mmol) in CH_2Cl_2 (12 mL) was added under stirring a solution of $HAuCl_4 \cdot 3H_2O$ (0.15 g, 0.42 mmol) in water (12 mL). The mixture was stirred vigorously for 2 h at 20 °C. During the course of the reaction, the yellow color of the aqueous layer disappeared, while the organic phase became deep red. The organic layer was separated, concentrated and dried under vacuum to give the title compound as an orange solid (0.27g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.63 (s, 1H), 7.81–7.65 (m, 4H), 4.55 (t, J = 6.4 Hz, 4H), 2.20–2.00 (m, 4H), 1.51–1.15 (m, 44H), 0.87 (t, J = 6.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.53, 131.58, 127.82, 113.51, 48.36, 32.06, 29.83, 29.80, 29.75, 29.66, 29.61, 29.55, 29.50, 29.18, 26.82, 22.83, 14.25. Anal. calcd for $(C_{35}H_{63}AuCl_4N_2)\cdot(H_2O)$: C 48.39, H 7.54, N 3.22; found C 48.46, H 7.49, N 3.06. HRMS (ESI) *m/z* calcd for $C_{35}H_{63}N_2$ $[M–AuCl_4^–]^+$ 511.4986, found 511.4980.



Gold(I) complex **L^{5}AuCl**.

General scheme:



15 **L^{5}AgBr** **L^{5}AuCl**

L^{5}AgBr:[4] Ag_2O (0.278 g, 1.2 mmol) was added to a solution of **15** (0.592 g, 1.0 mmol) in CH_2Cl_2 (20 mL). The mixture was refluxed for 20 h, and filtered over celite. The filtrate was reduced to ca. 10 mL under reduced pressure. Pentane was added to the residual solution until precipitation of a white solid. The precipitate was isolated by filtration, washed with pentane and dried under vacuum to give the title compound as a white powder (0.546 g, 82%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.52 (dd, J = 6.2 and 3.1 Hz, 1H), 7.41 (dd, J = 6.2 and 3.1 Hz, 1H), 4.41 (t, J = 7.3 Hz, 2H), 1.98–1.78 (m, 2H), 1.42–1.12 (m, 22H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (400 MHz, CD_2Cl_2) δ 134.31, 124.44, 112.17, 50.16, 32.52, 30.84, 30.27, 30.24, 30.21, 30.14, 30.05, 29.94, 29.83, 27.42, 23.27, 14.45.

L^{5}AuCl: To a solution of **L^{5}AgBr** (0.51 g, 0.74 mmol) in CH_2Cl_2 (45 mL) was added [AuCl(SMe_2)] (0.215 g, 0.74 mmol). The resulting solution was stirred at 20 °C for 4 h. The grey precipitate formed (AgBr) was filtered off and the remaining clear solution was reduced to ca. 5 mL under reduced pressure. Hexane was added to the residual solution until precipitation of a white solid. The precipitate was isolated by filtration, washed with hexane and dried under vacuum to give the title compound as a white powder (0.515 g, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.50 (dd, J = 6.3 and 3.0 Hz, 1H), 7.42 (dd, J = 6.2 and 3.1 Hz, 1H), 4.47 (dd, J = 10.0 and 4.7 Hz, 2H), 2.16–1.83 (m, 2H), 1.44–1.13 (m, 22H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, CD_2Cl_2) δ 178.45, 133.54, 133.49, 124.60, 124.56, 111.91, 49.30, 49.17, 32.31, 30.29, 30.06, 30.03, 30.00, 29.93, 29.83, 29.74, 29.61, 27.13, 23.07, 14.25.

[4] The procedure was adapted from : Wang, H. M. J.; Lin, I. J. B. *Organometallics*, **1998**, *17*, 972.

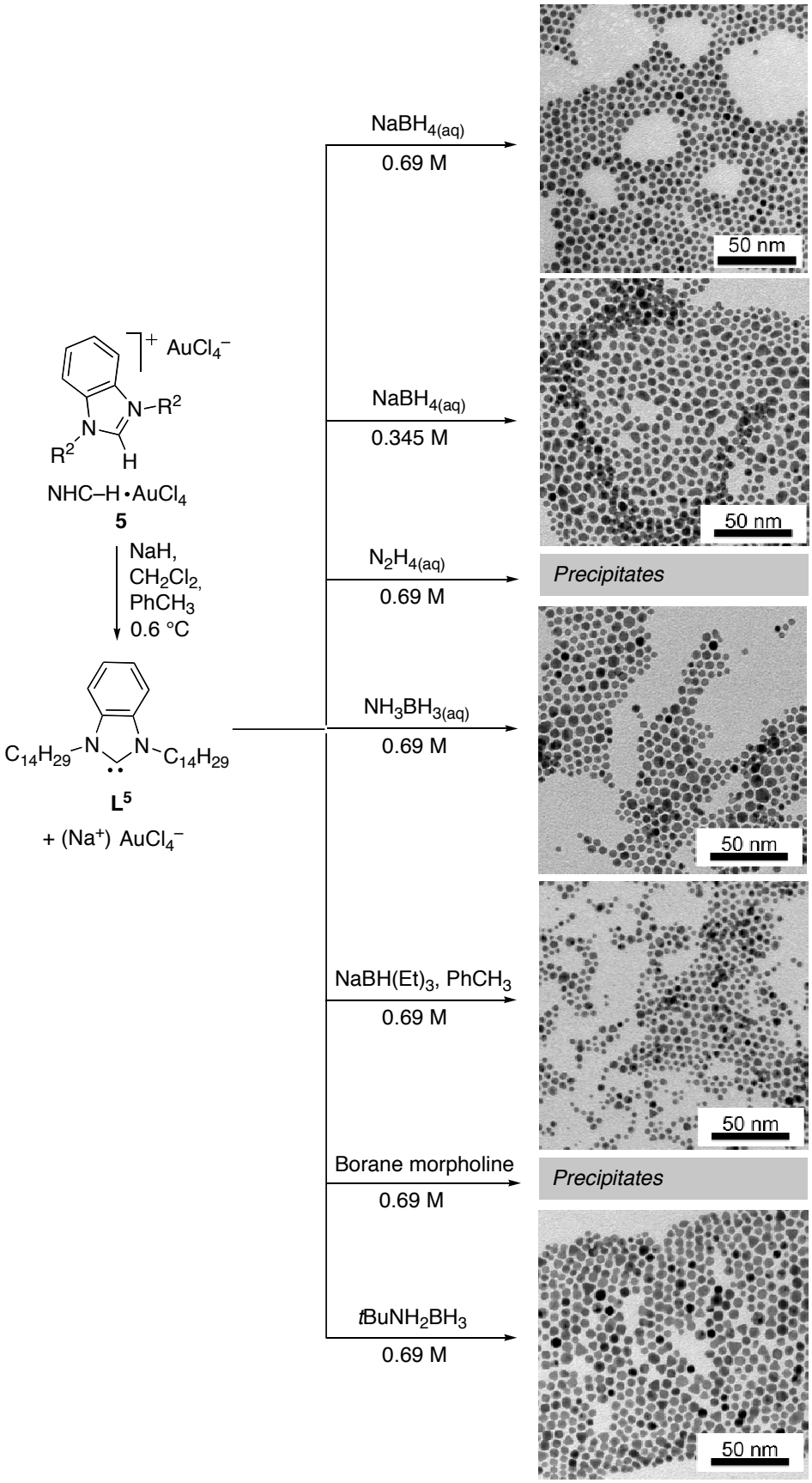


Figure S1. Different conditions tested (reduction step) with $\mathbf{L^5}$ and TEM images for the preparation $\mathbf{L^5}$-coated Au NCs. The reduction was performed at 0.6 °C.

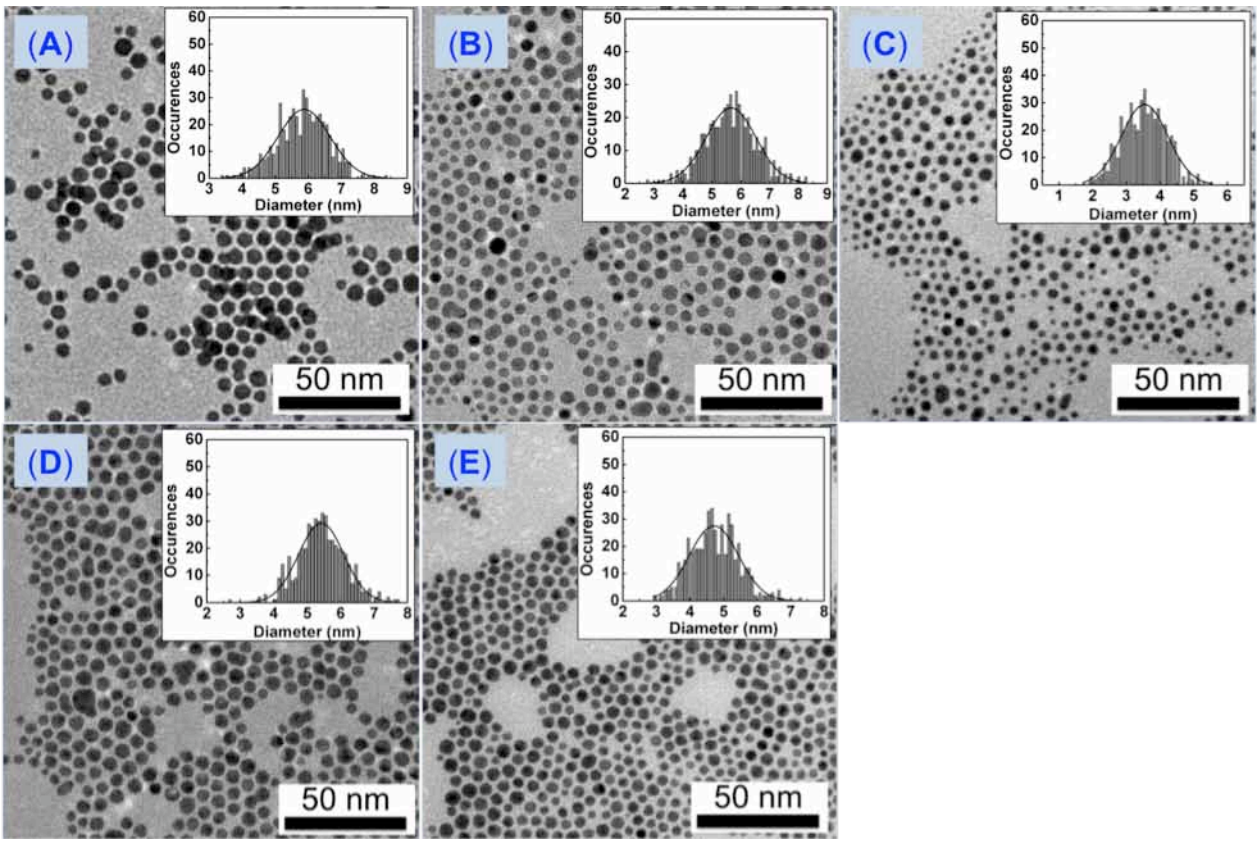


Figure S2. TEM images and size distributions (insets) of Au nanocrystals stabilized by $\mathbf{L^1}$ (**A**), $\mathbf{L^2}$ (**B**), $\mathbf{L^3}$ (**C**), $\mathbf{L^4}$ (**D**) and $\mathbf{L^5}$ (**E**), before size selection.

Table S1: Reproducibility: Average sizes and size distributions of different AuNCs batches.

NCs Batch 2					
Entry	NHC Ligand	Before size selection		After size selection	
		d (nm)	σ (%)	d (nm)	σ (%)
1	$\mathbf{L^1}$	5.9	15.8	6.1	9.0
2	$\mathbf{L^2}$	5.6	19.2	5.8	10.9
3	$\mathbf{L^3}$	3.7	20.5	3.9	11.6
4	$\mathbf{L^4}$	5.3	17.2	5.2	10.9
5	$\mathbf{L^5}$	4.9	16.4	5.1	9.6

NCs Batch 3					
Entry	NHC Ligand	Before size selection		After size selection	
		d (nm)	σ (%)	d (nm)	σ (%)
1	$\mathbf{L^1}$	5.7	13.9	5.9	9.8
2	$\mathbf{L^2}$	5.5	21.4	5.7	11.6
3	$\mathbf{L^3}$	3.9	23.2	4.1	12.3
4	$\mathbf{L^4}$	5.4	16.8	5.3	11.2
5	$\mathbf{L^5}$	4.8	17.5	4.9	10.1

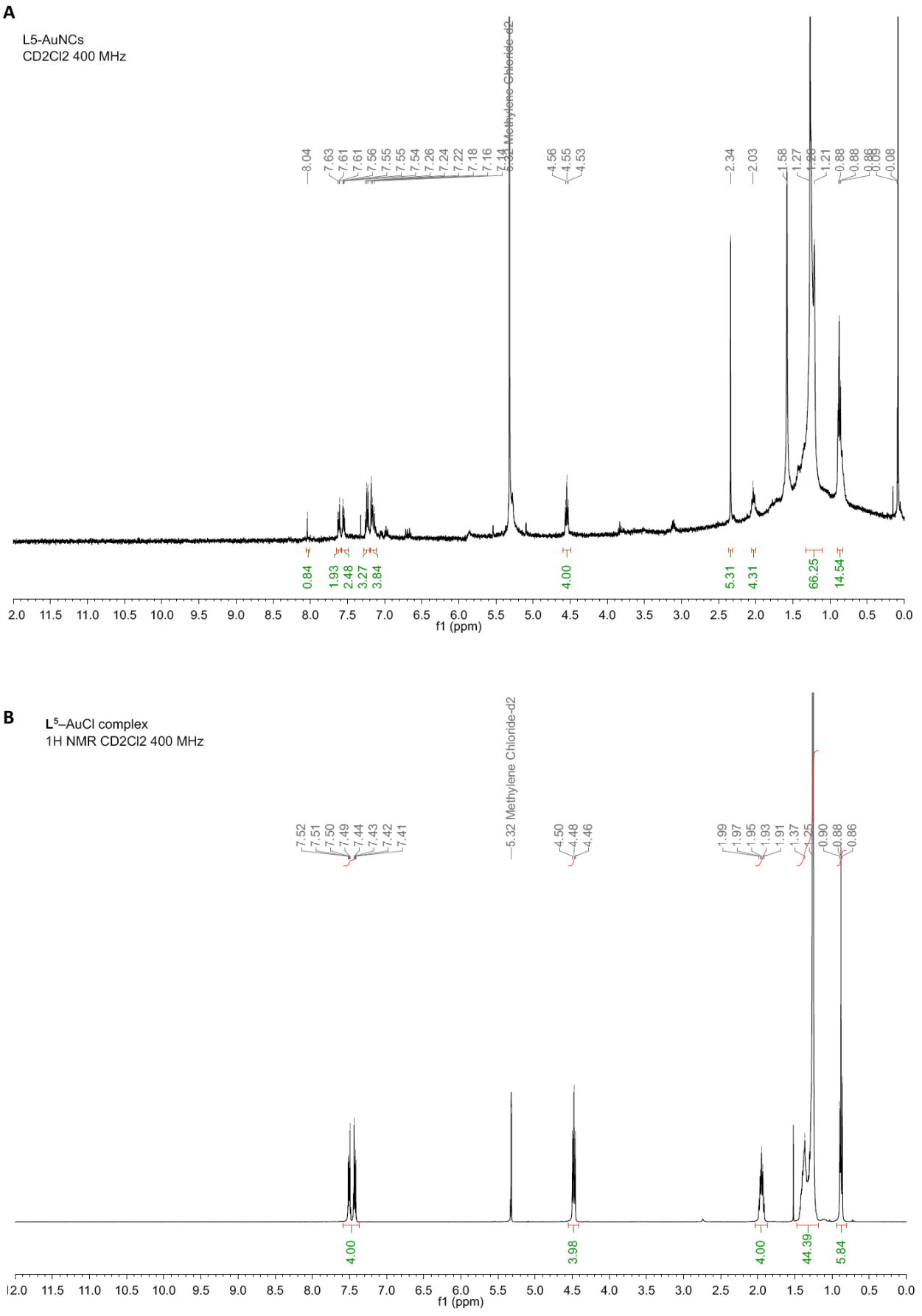


Figure S3. ^{1}H NMR spectra of **L^{5}**-coated AuNCs in CD_2Cl_2 (**A**) and **L^{5}**–AuCl (**B**).

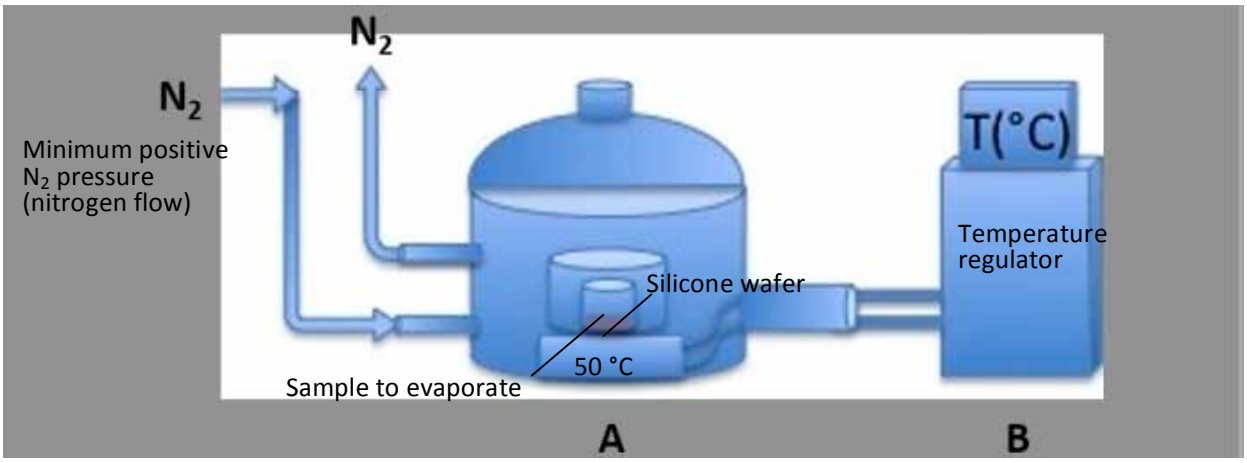


Figure S4. Evaporation device for Au supracrystals preparation.

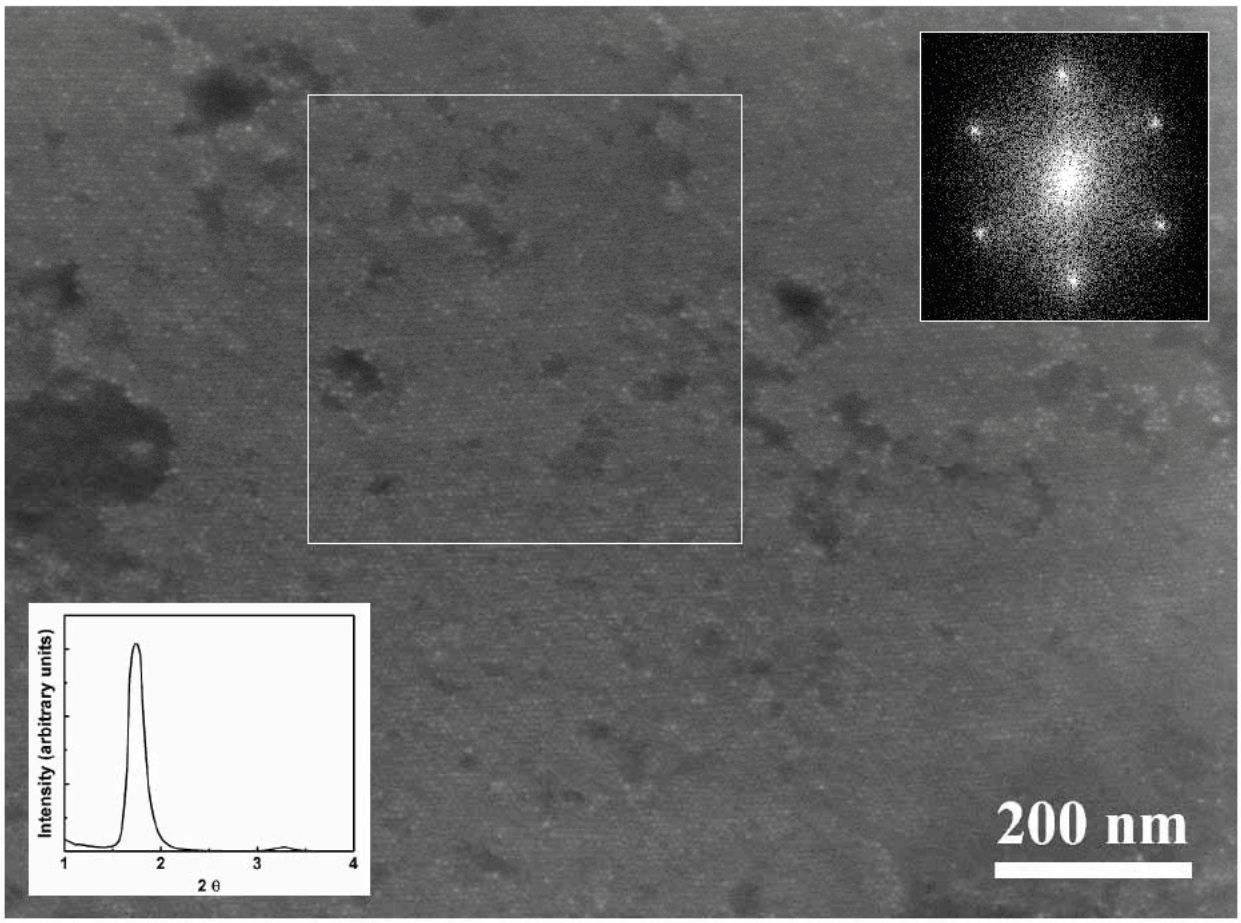
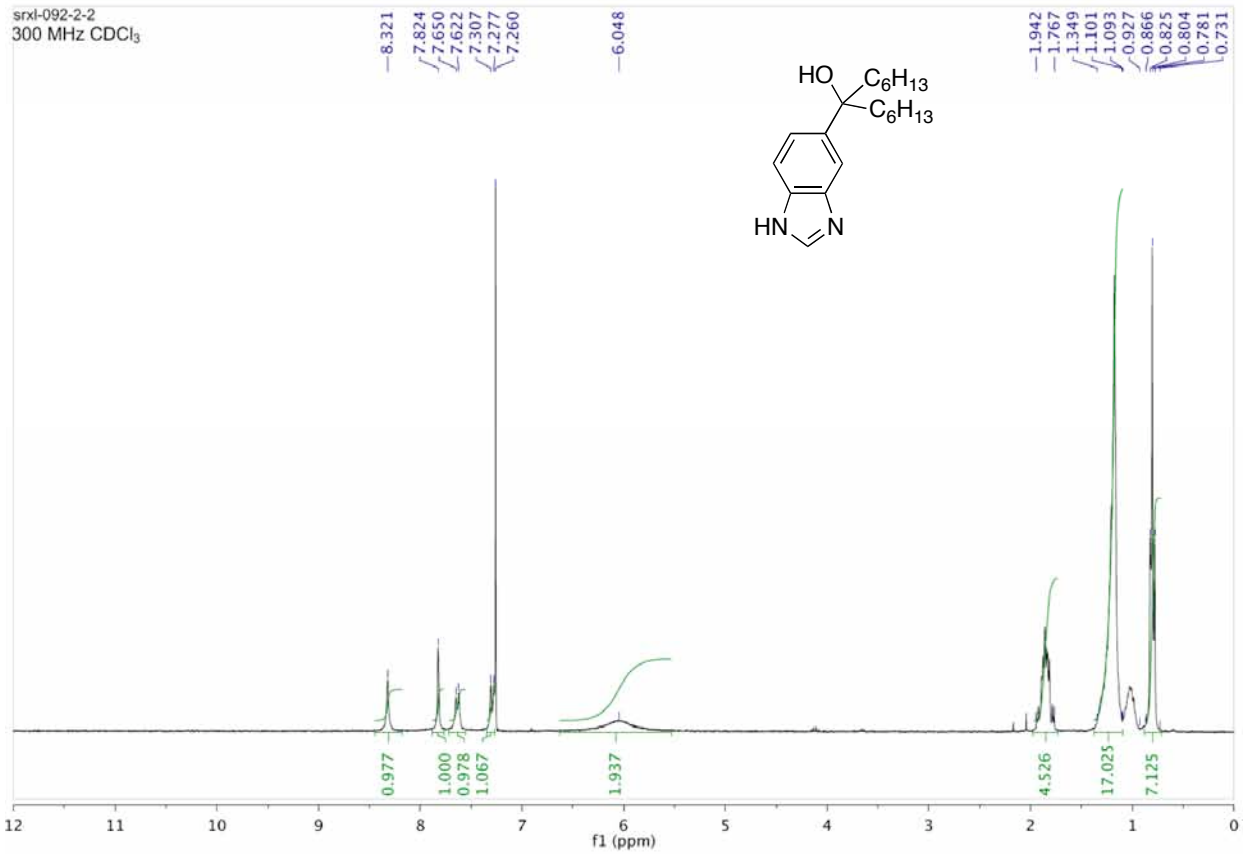
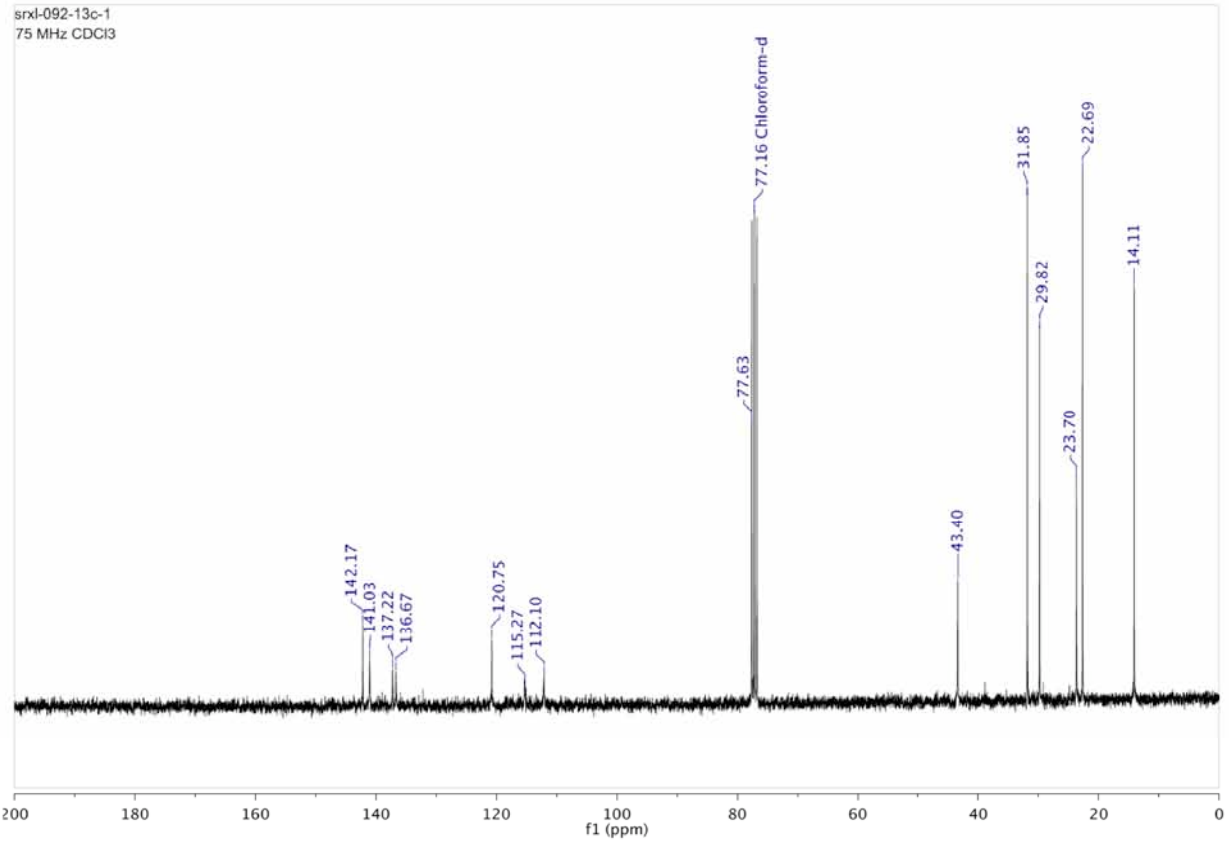


Figure S5. HRSEM image and SAXRD pattern of supracrystals made of $\mathbf{L}^4$-coated Au nanocrystals.

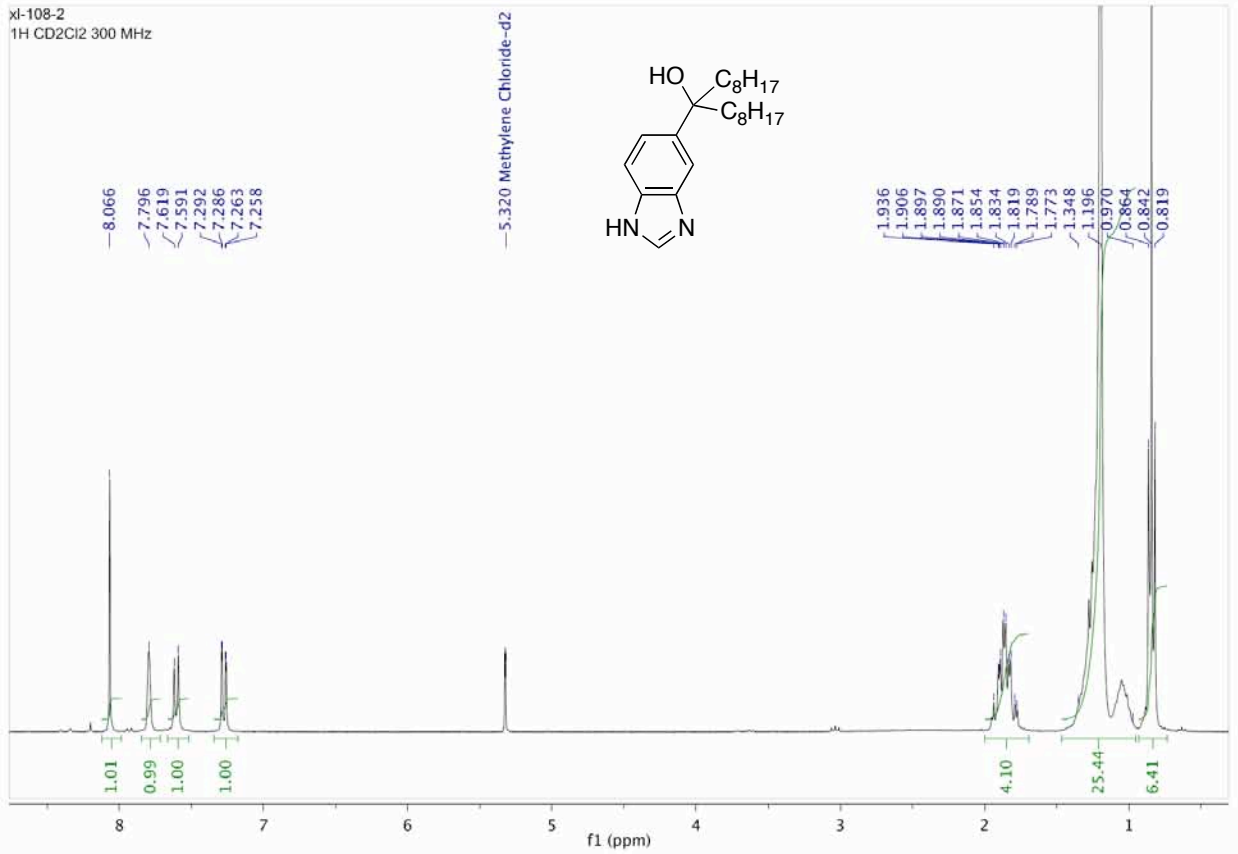
^{1}H and ^{13}C spectra of new compounds

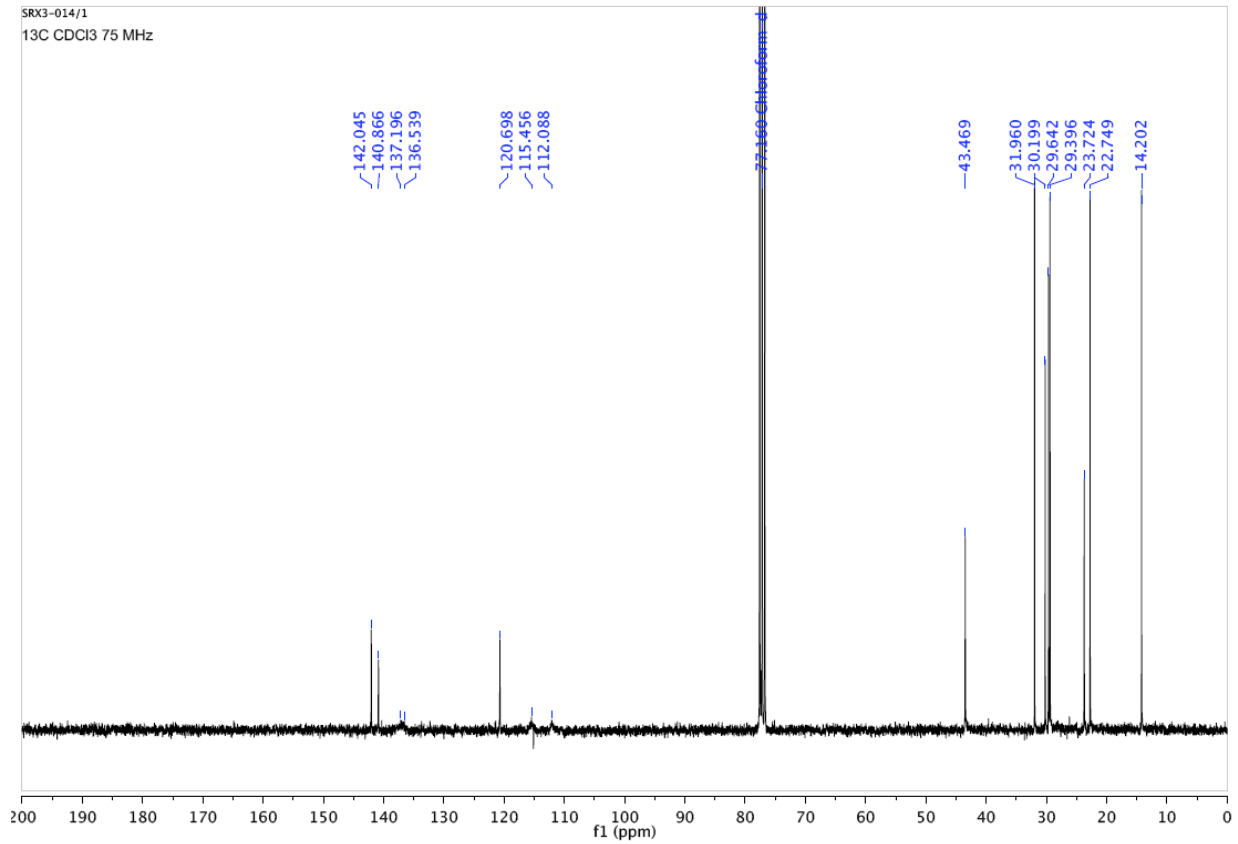
5-[1,1-Dihexyl-1-(hydroxy)methyl]benzimidazole (**7**)



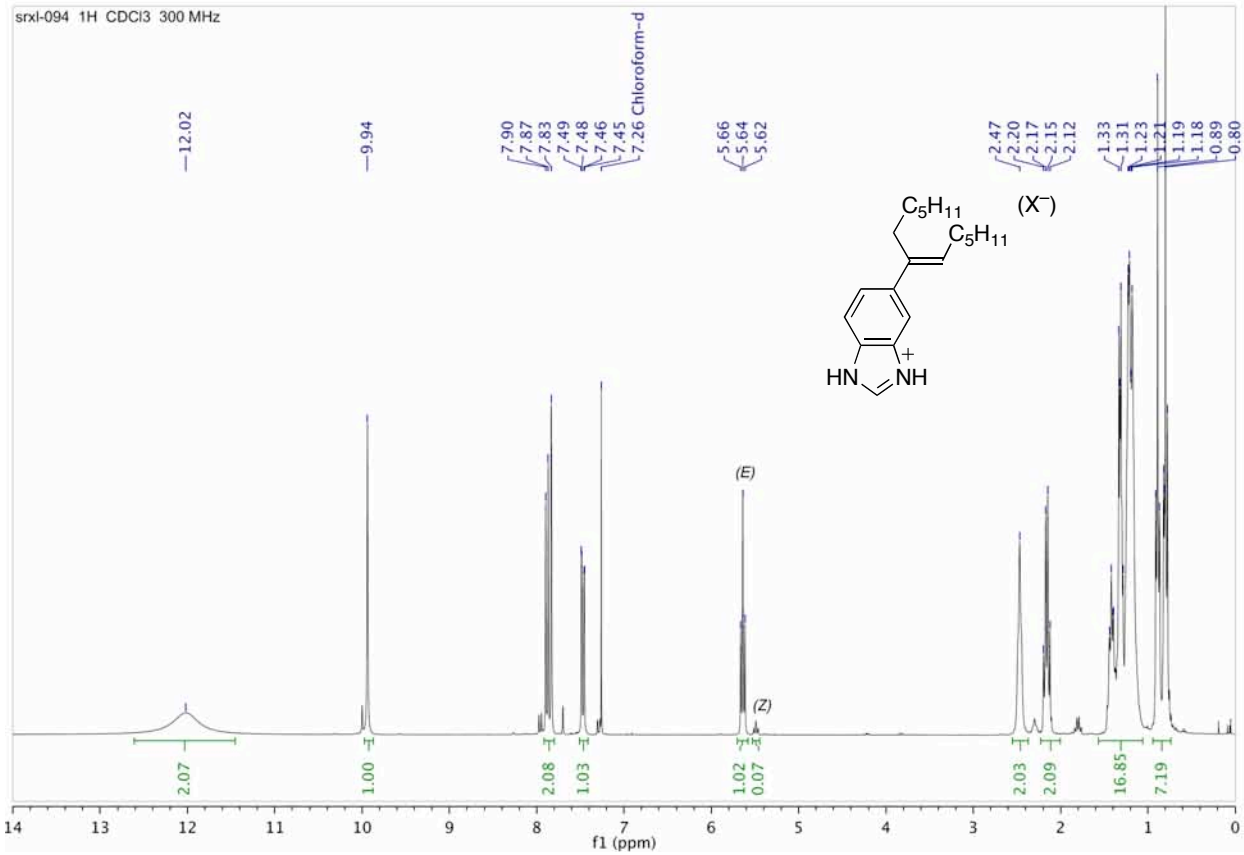


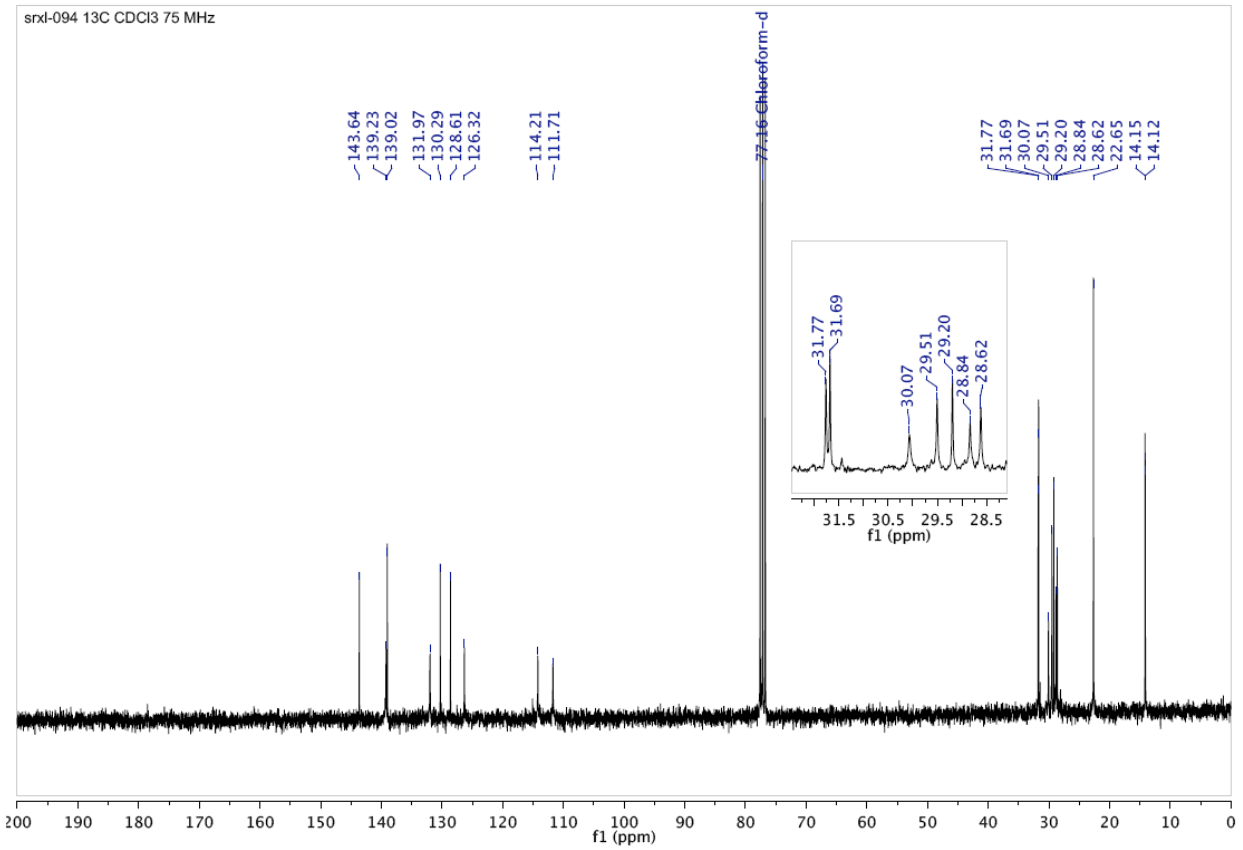
5-[1,1-Dioctyl-1-(hydroxy)methyl]benzimidazole (**8**)





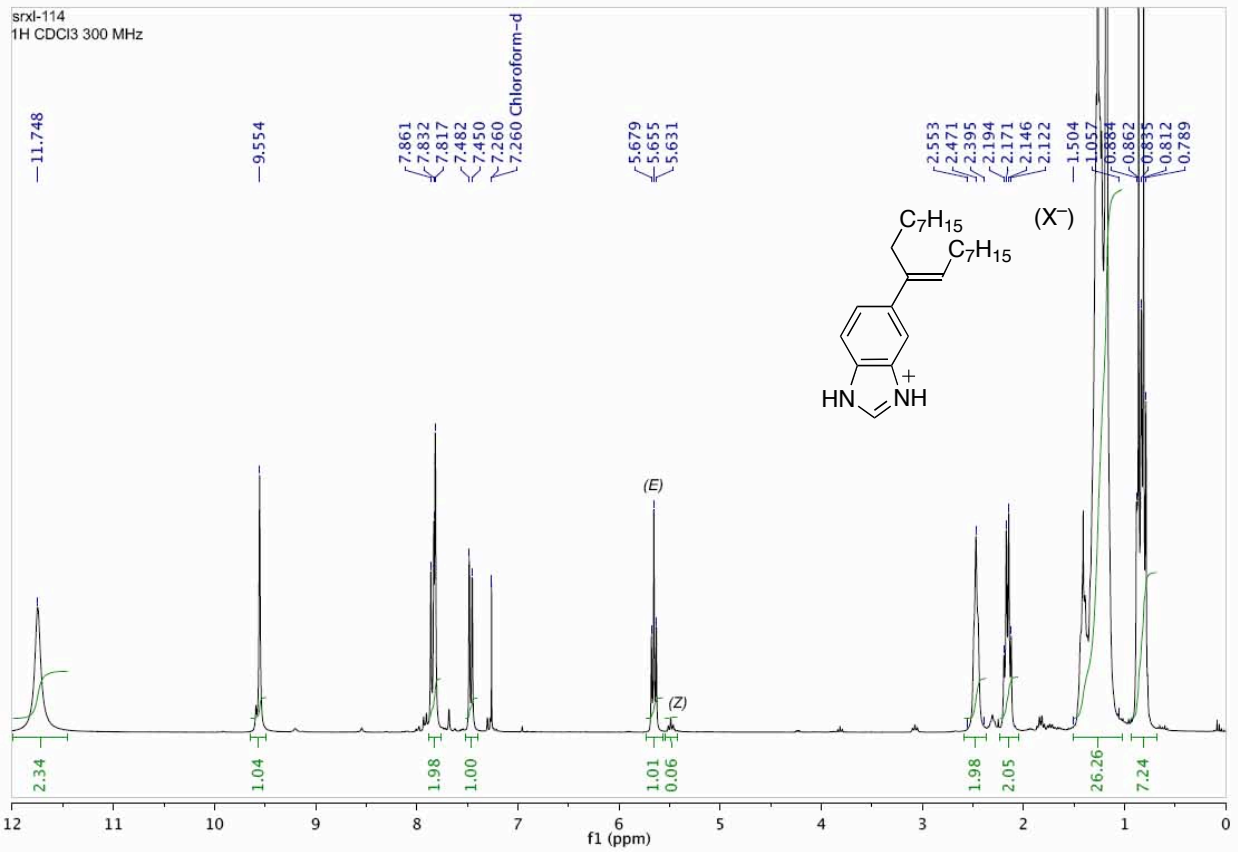
(E)-5-[1-(Hexyl)-hept-1-en-1-yl]benzimidazole (**9**)

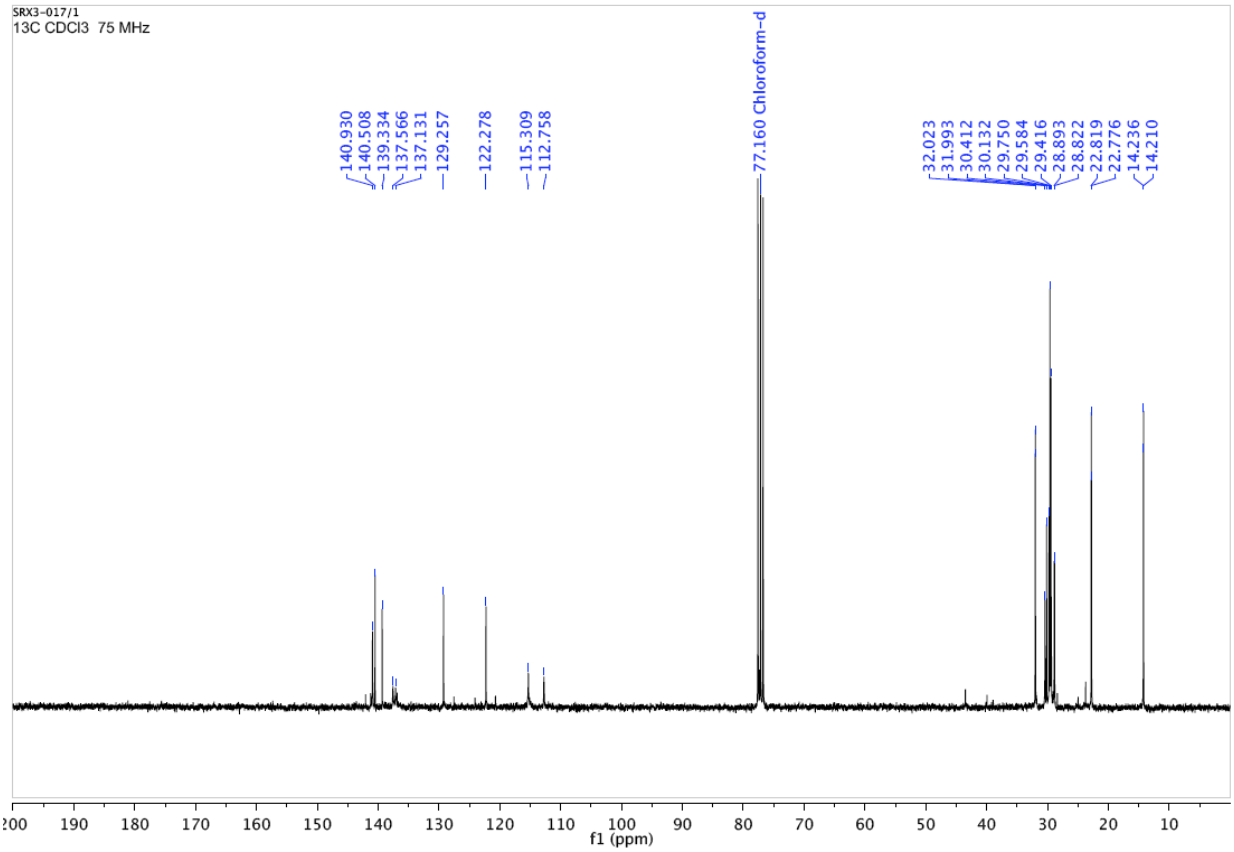




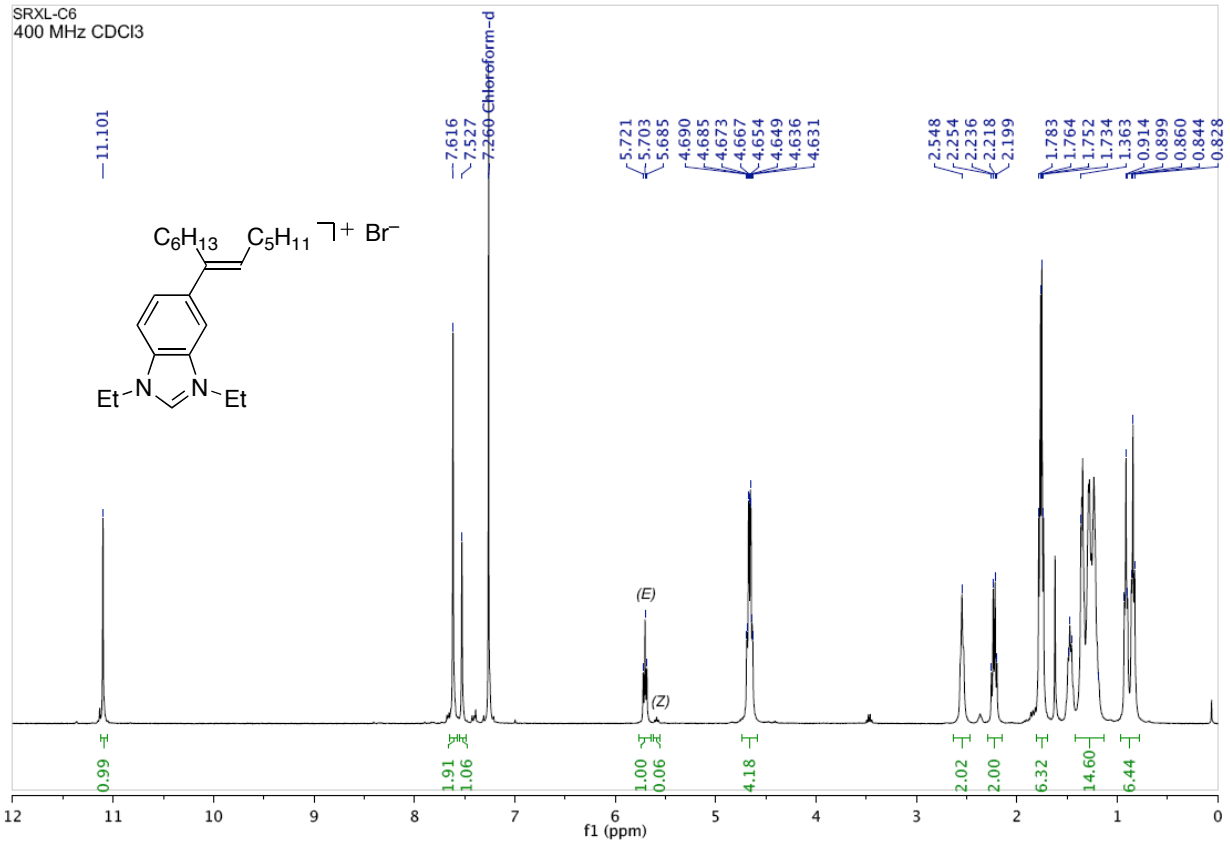
(E)-5-[1-(Octyl)-non-1-en-1-yl]benzimidazole (**10**)

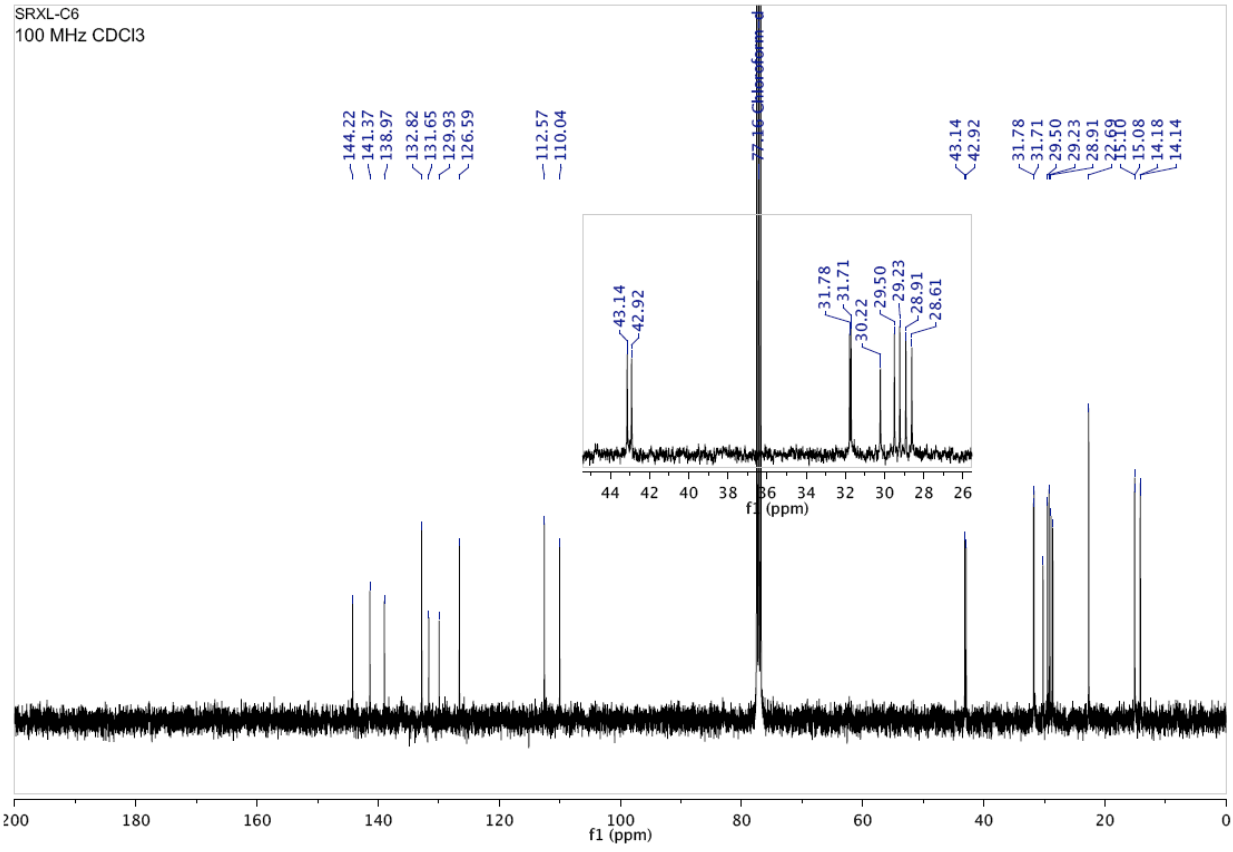
(E)-5-[1-(Hexyl)-hept-1-en-1-yl]benzimidazole (**10**)

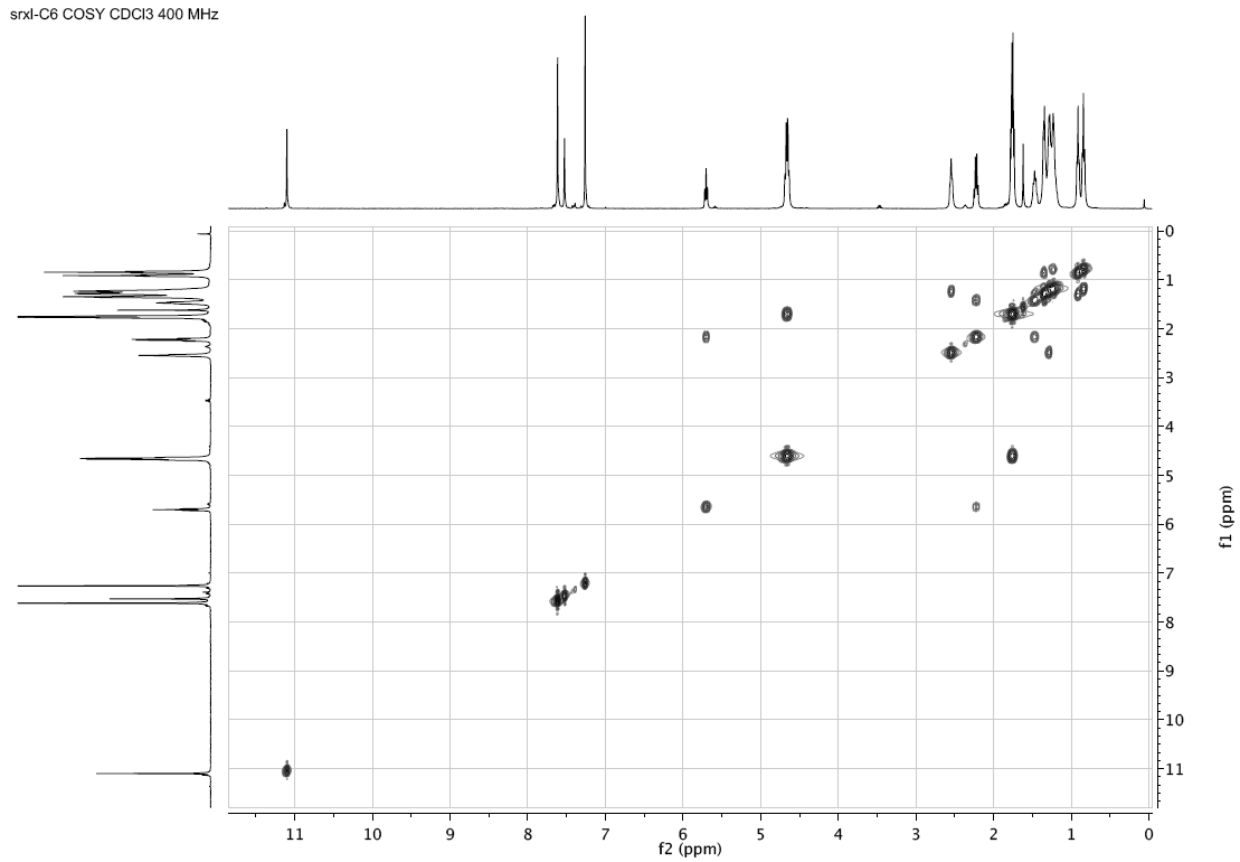




(E)-1,3-Diethyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium bromide (**11**)



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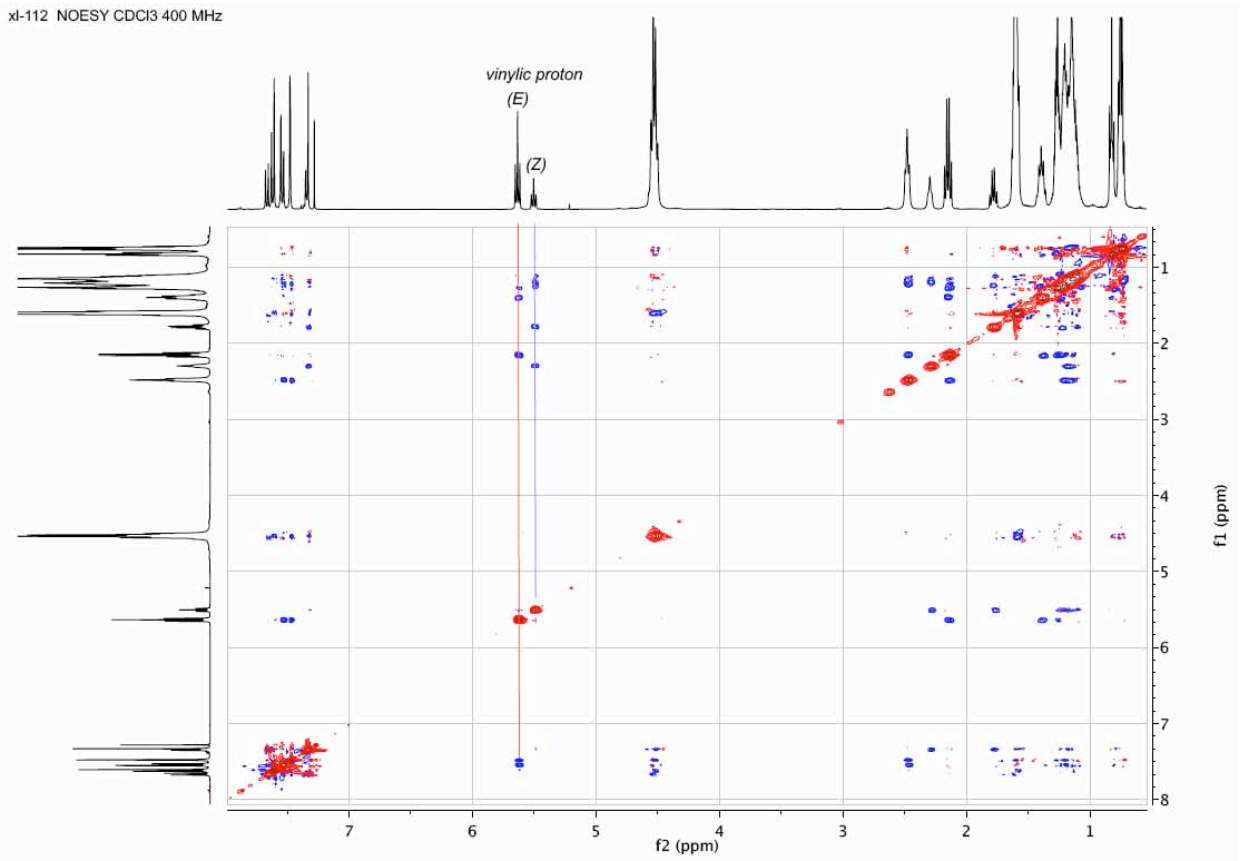
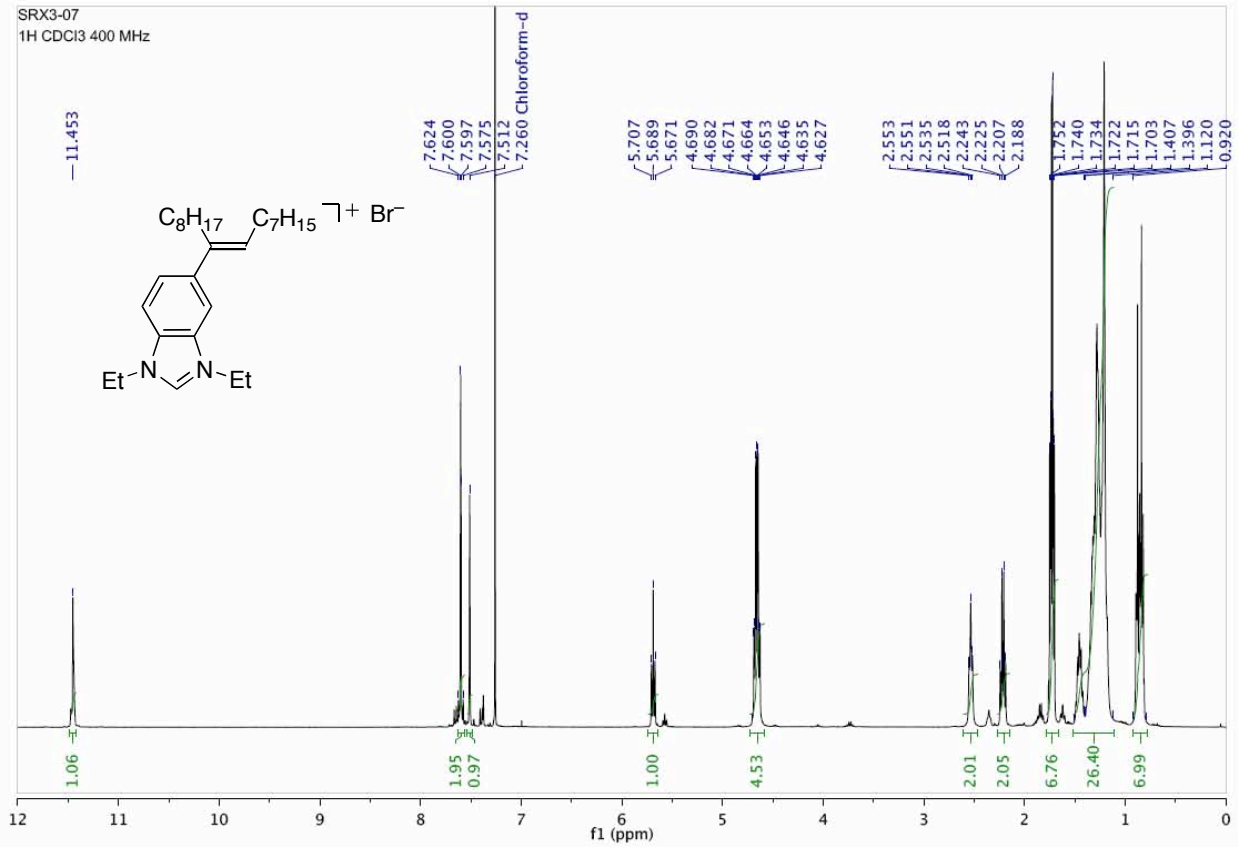
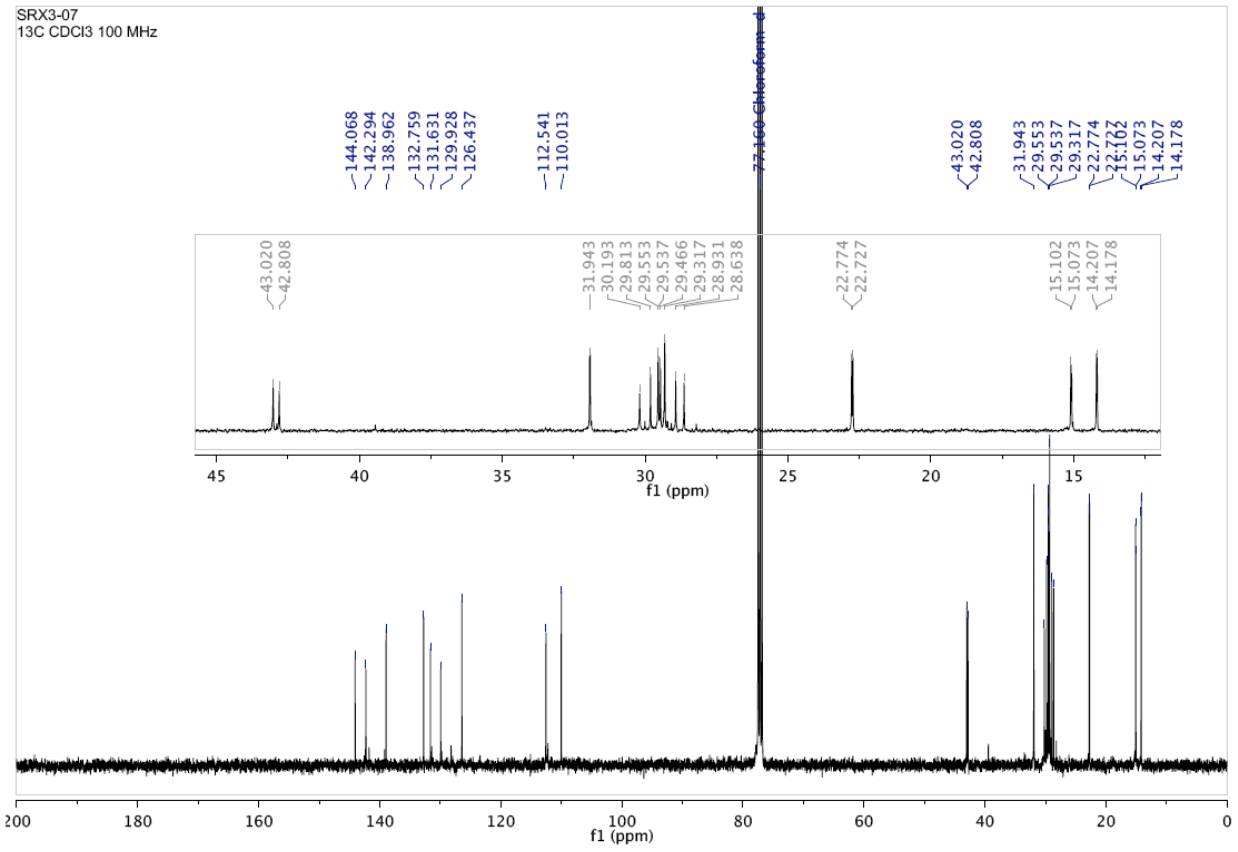
f2 (ppm)
f1 (ppm)

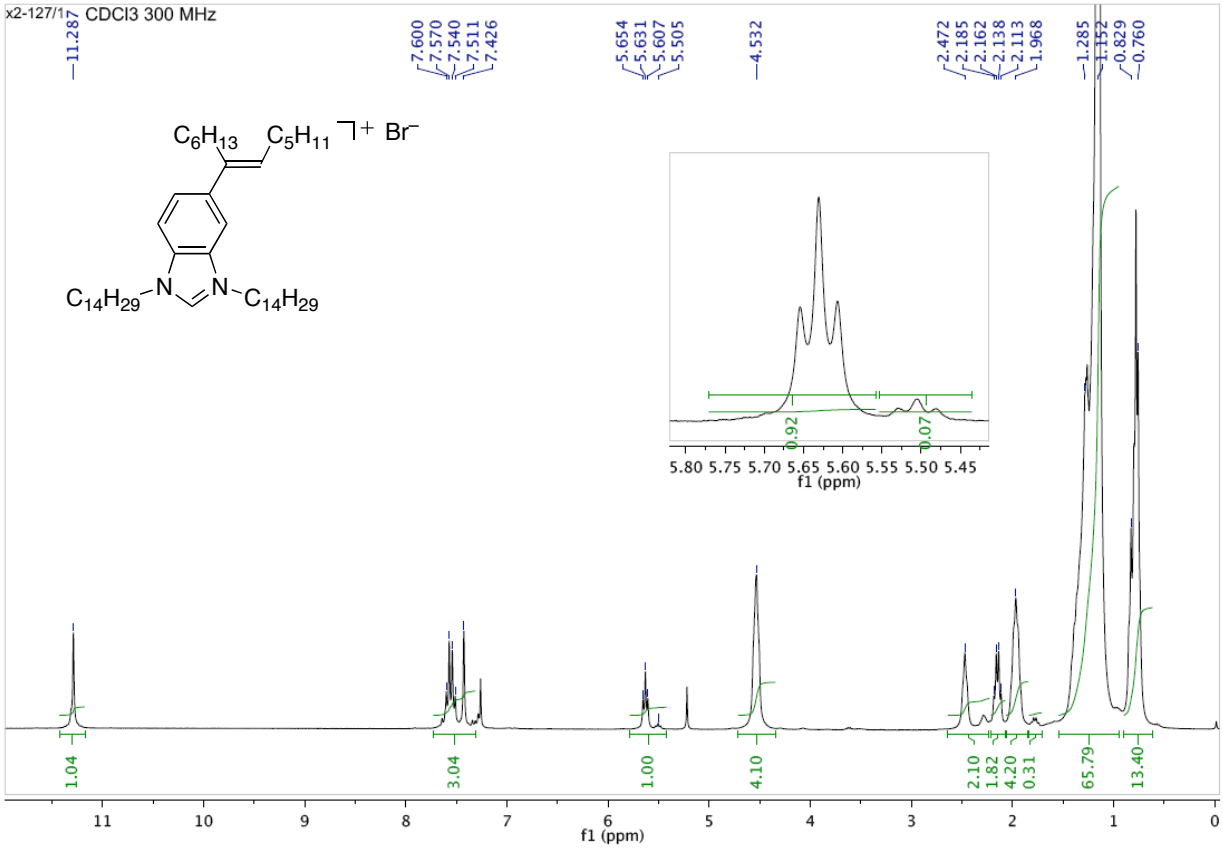

xl-112 NOESY CDCl3 400 MHz
vinylic proton
(E)
(Z)
f2 (ppm)
f1 (ppm)

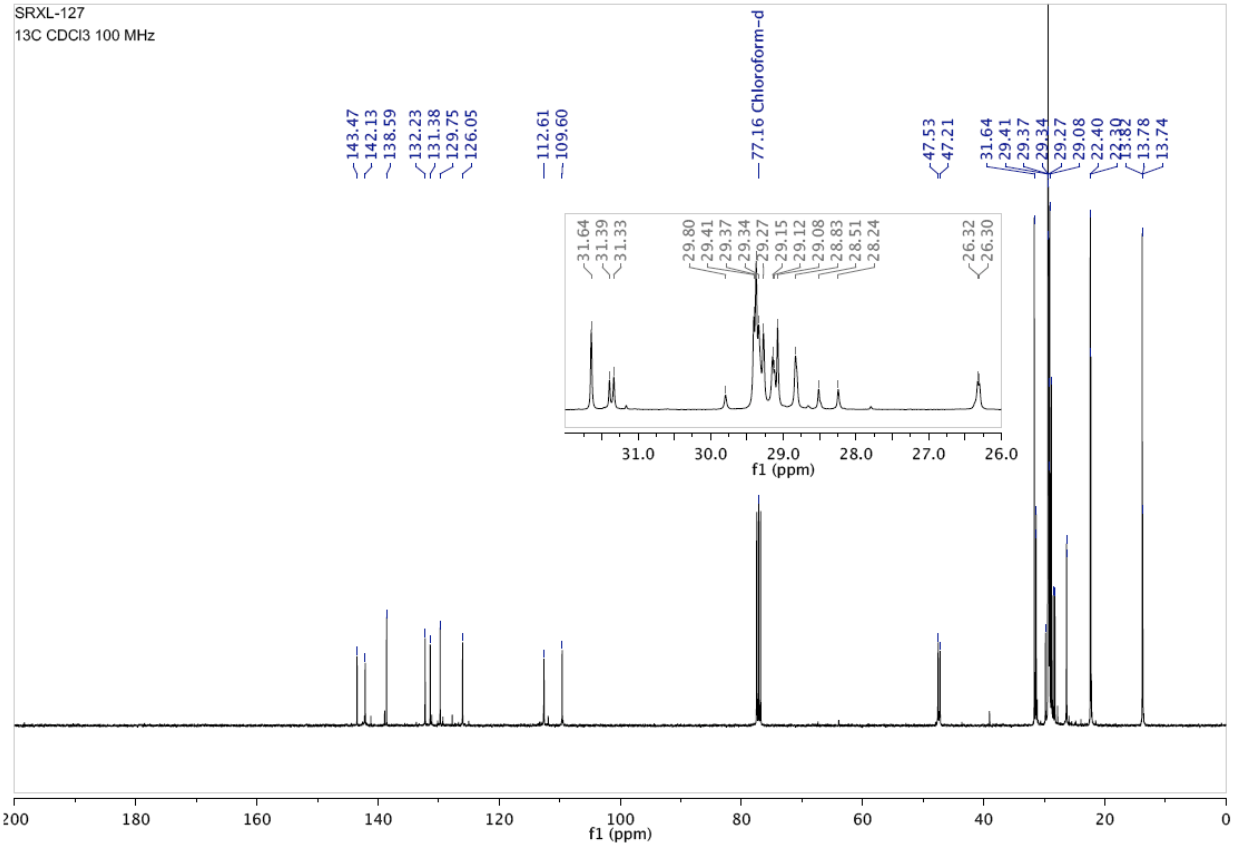
(E)-1,3-Diethyl-5-[1-(octyl)-non-1-en-1-yl]benzimidazolium bromide (**12**)



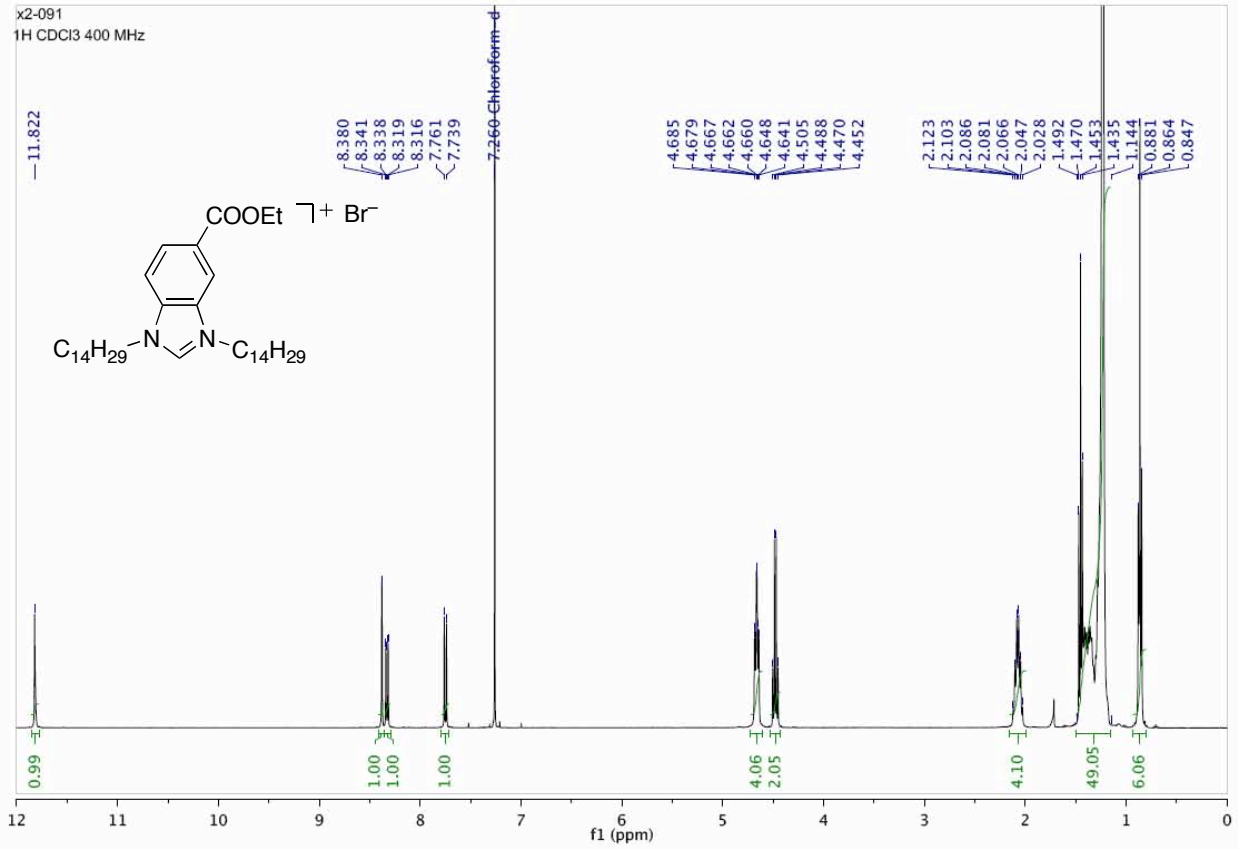


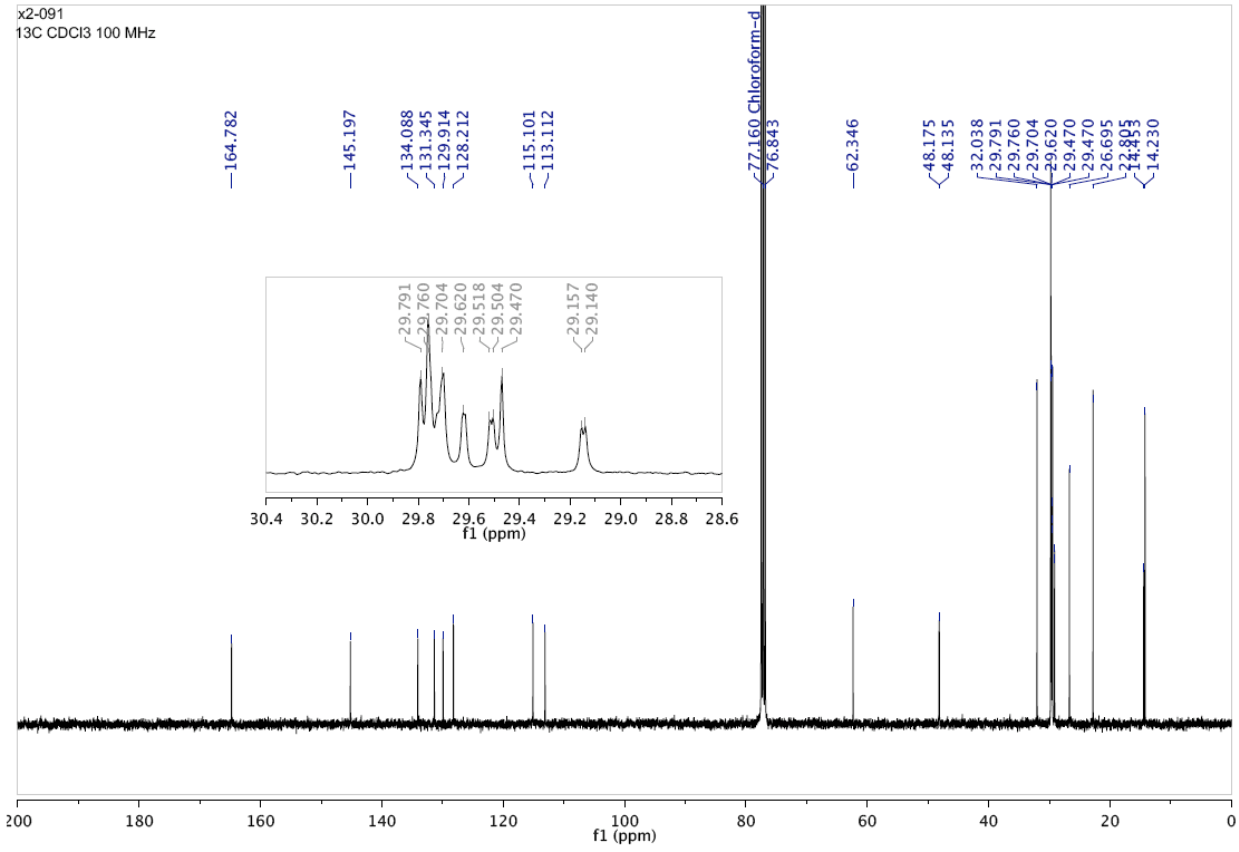
(E)-1,3-Ditetradecyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium bromide (**13**)



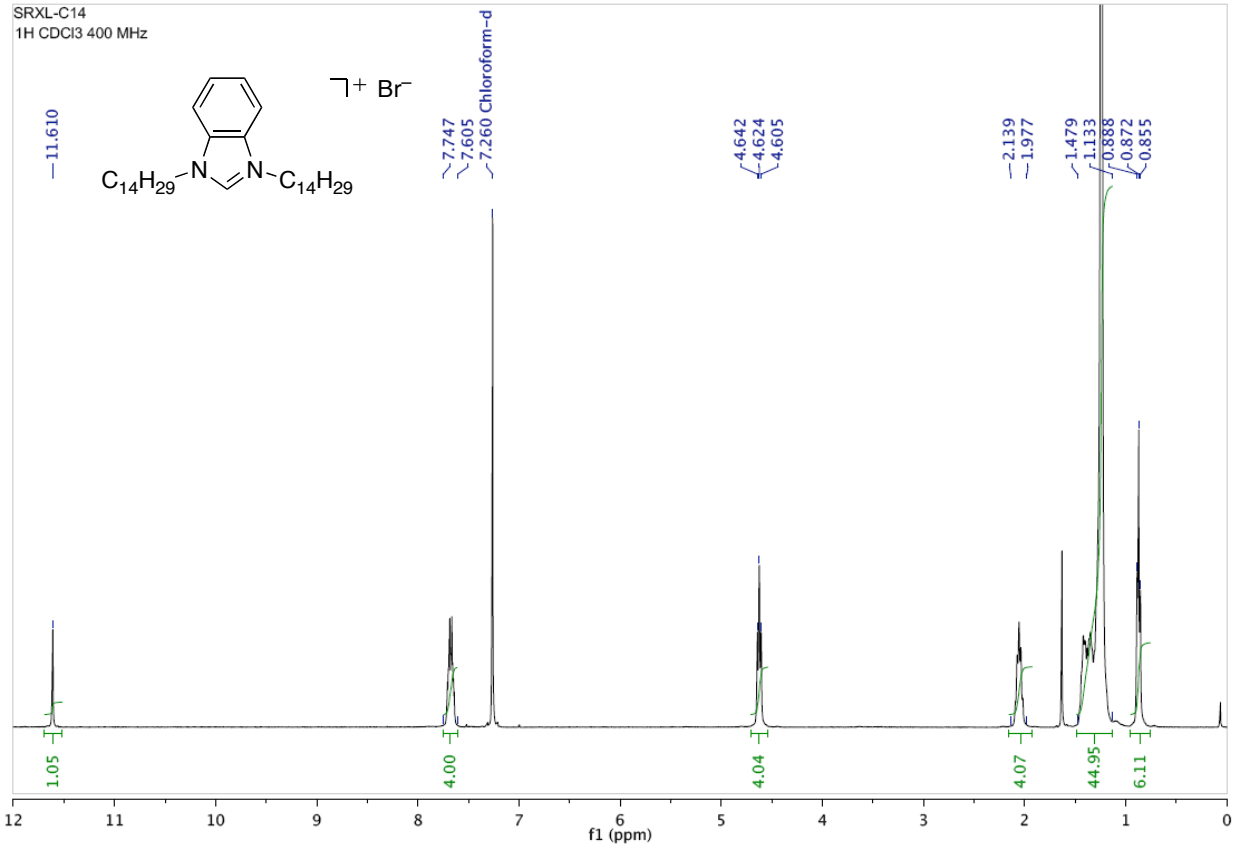


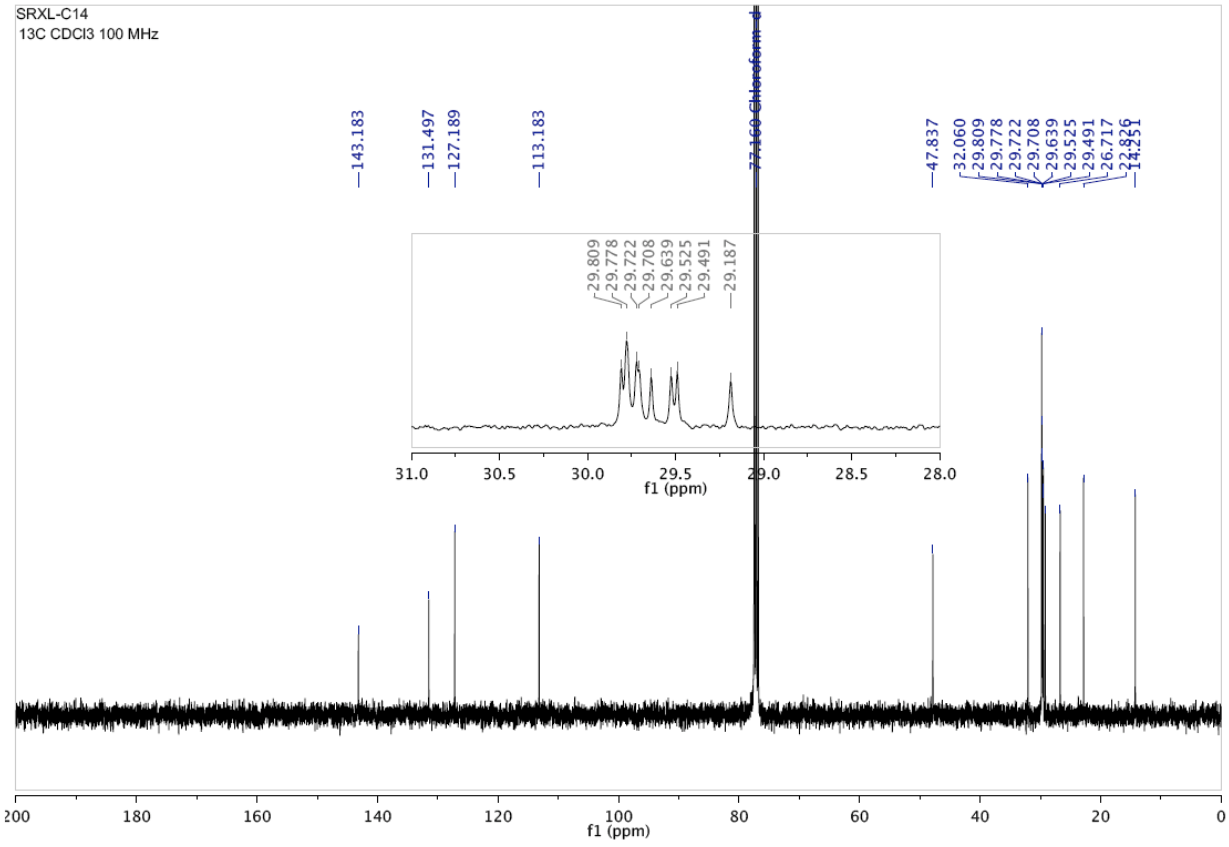
5-Ethoxycarbonyl-1,3-(ditetradecyl)benzimidazolium bromide (**14**)



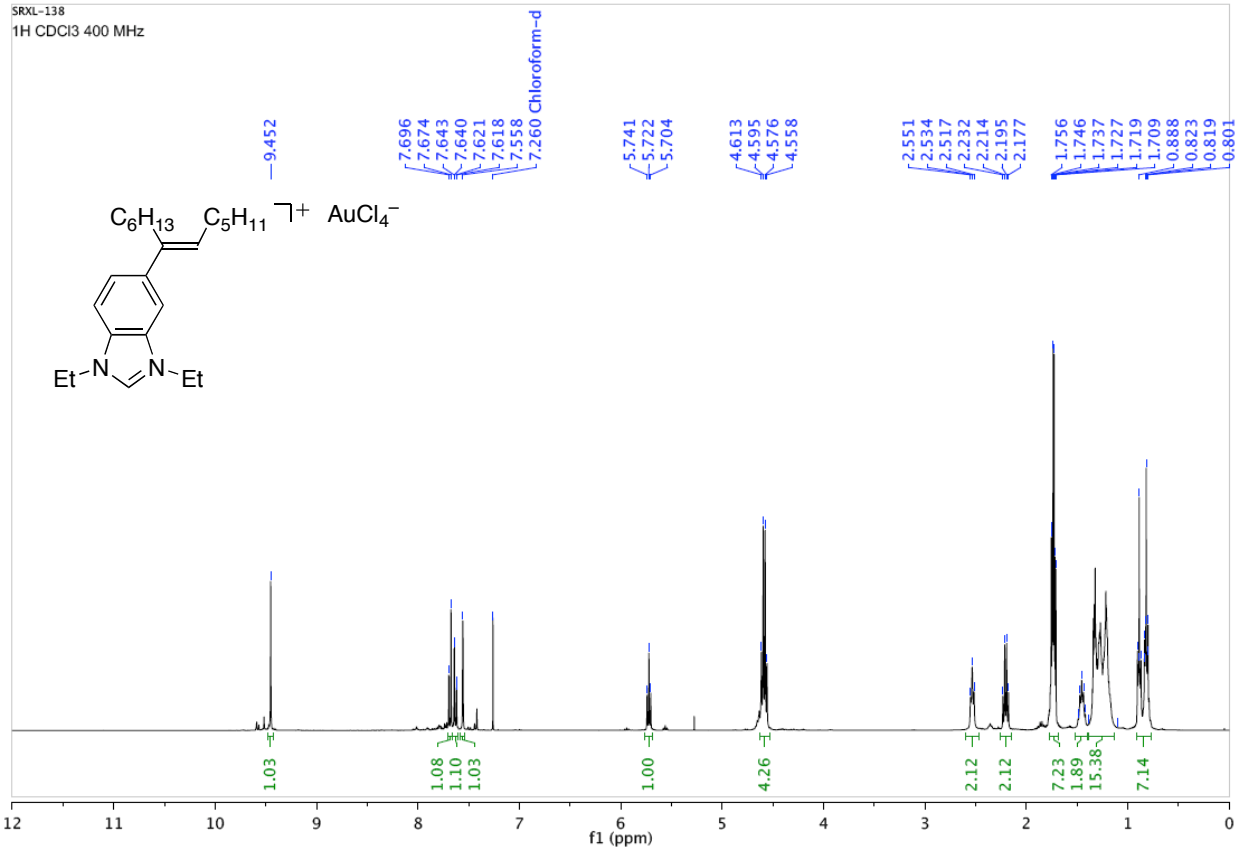


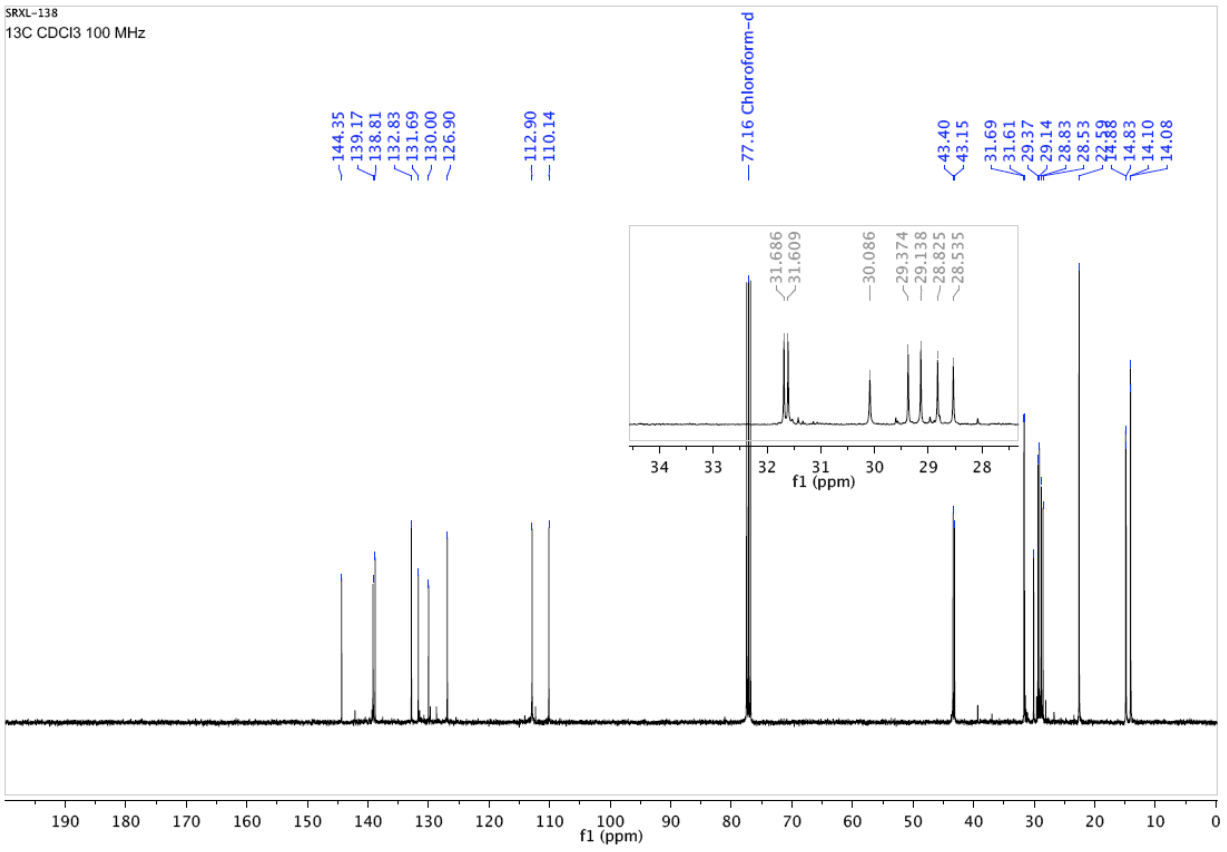
1,3-(Ditetradecyl)benzimidazolium bromide (**15**)



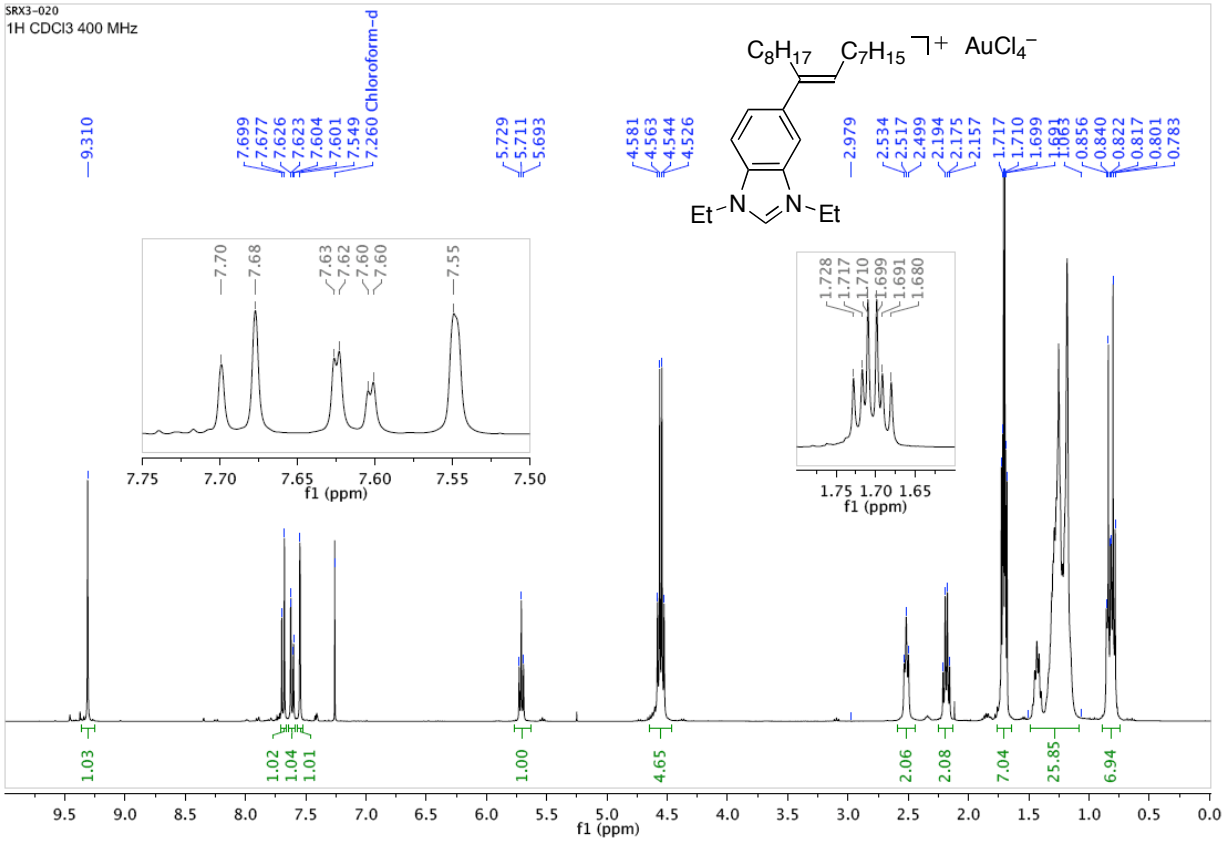


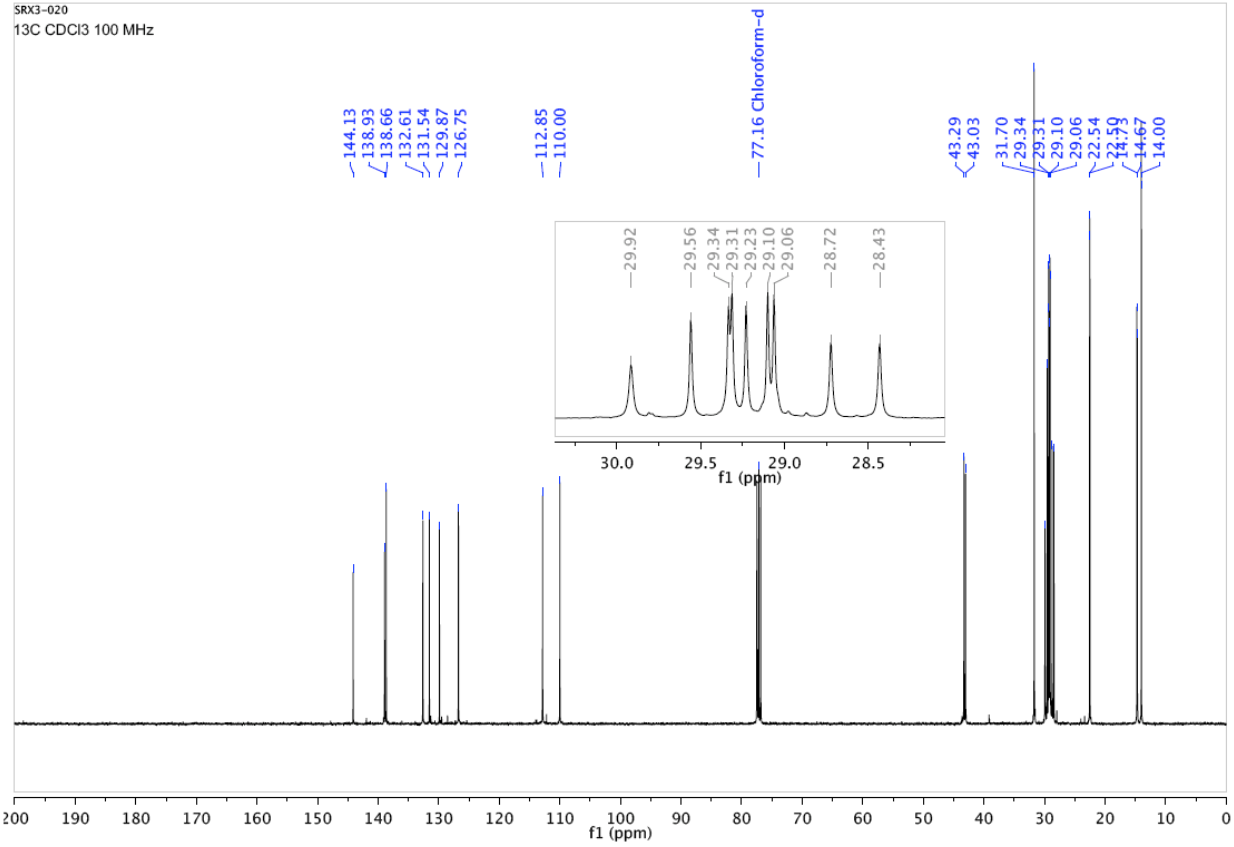
(E)-1,3-Diethyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**1**)



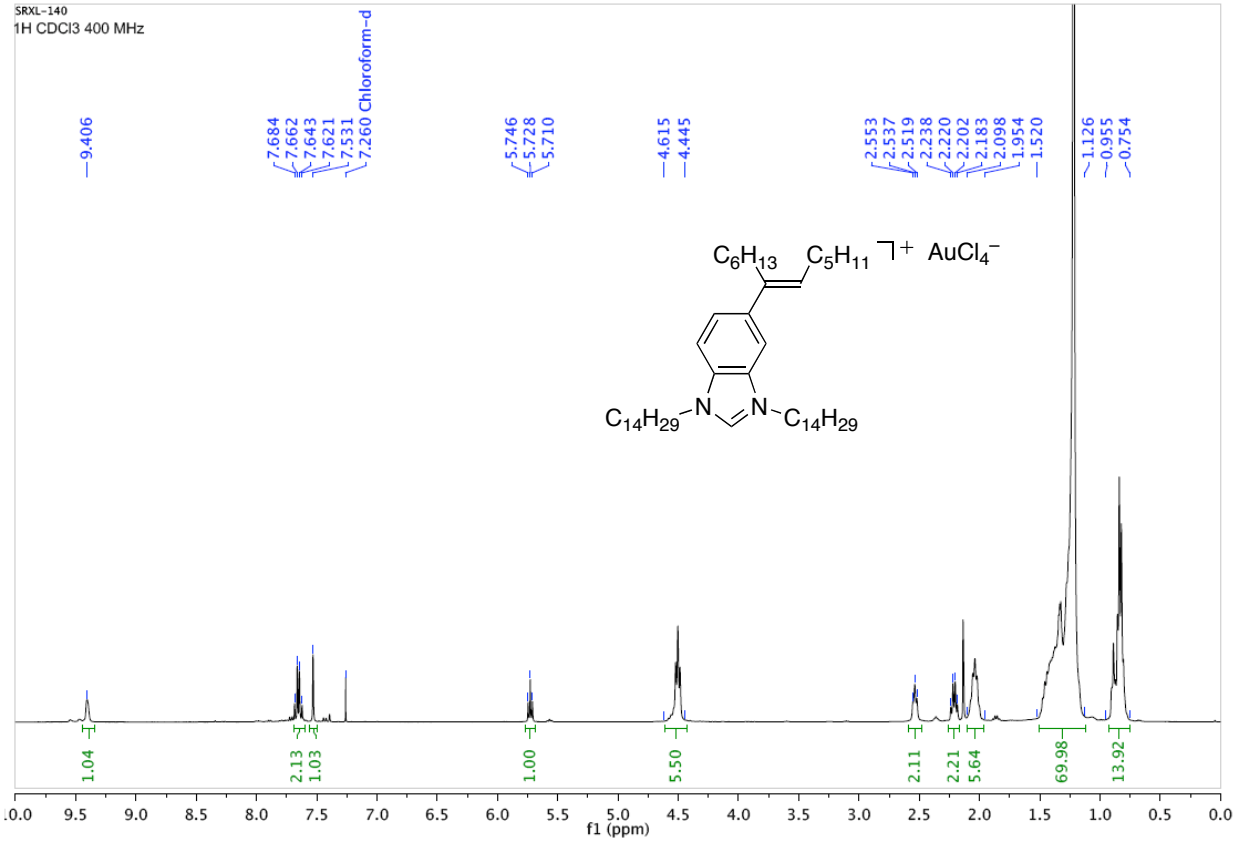


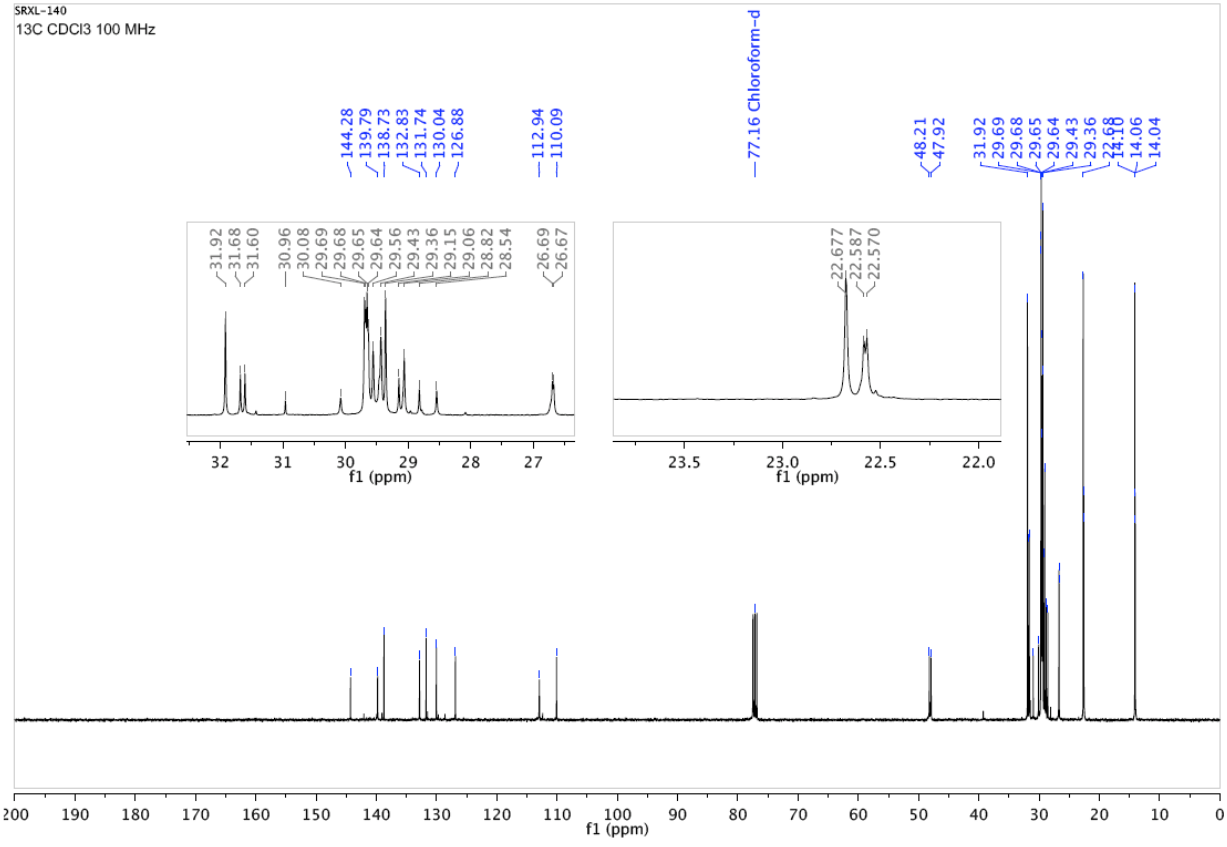
(E)-1,3-Diethyl-5-[1-(octyl)-non-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**2**)



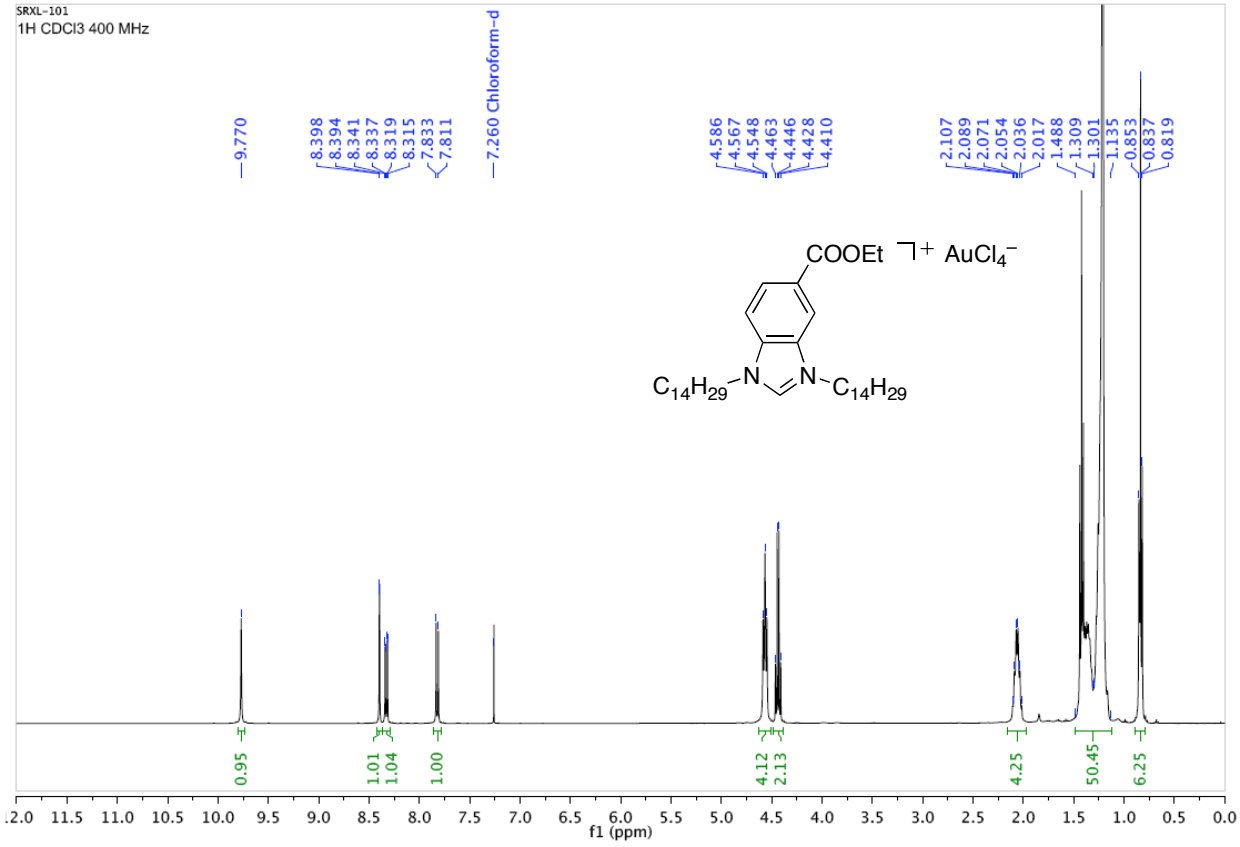


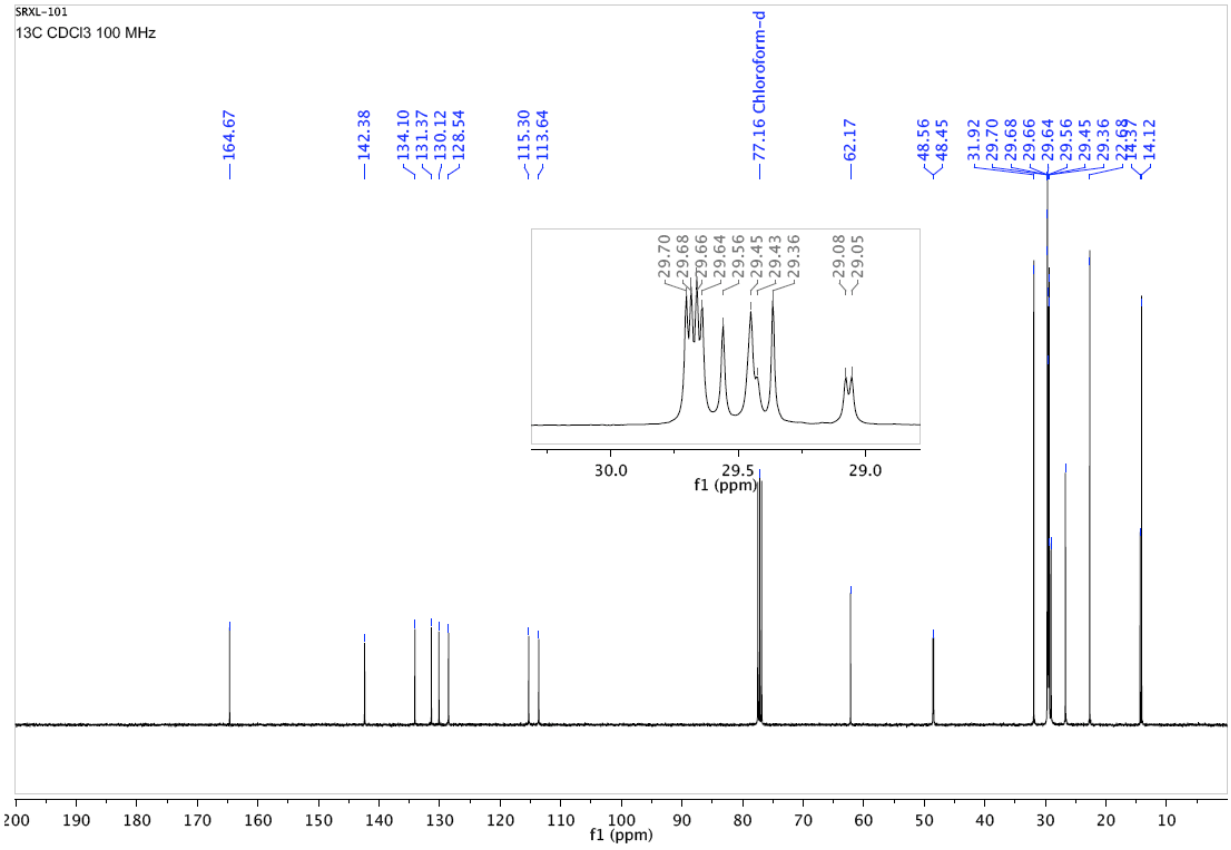
(E)-1,3-Ditetradecyl-5-[1-(hexyl)-hept-1-en-1-yl]benzimidazolium tetrachloroaurate(III) (**3**)



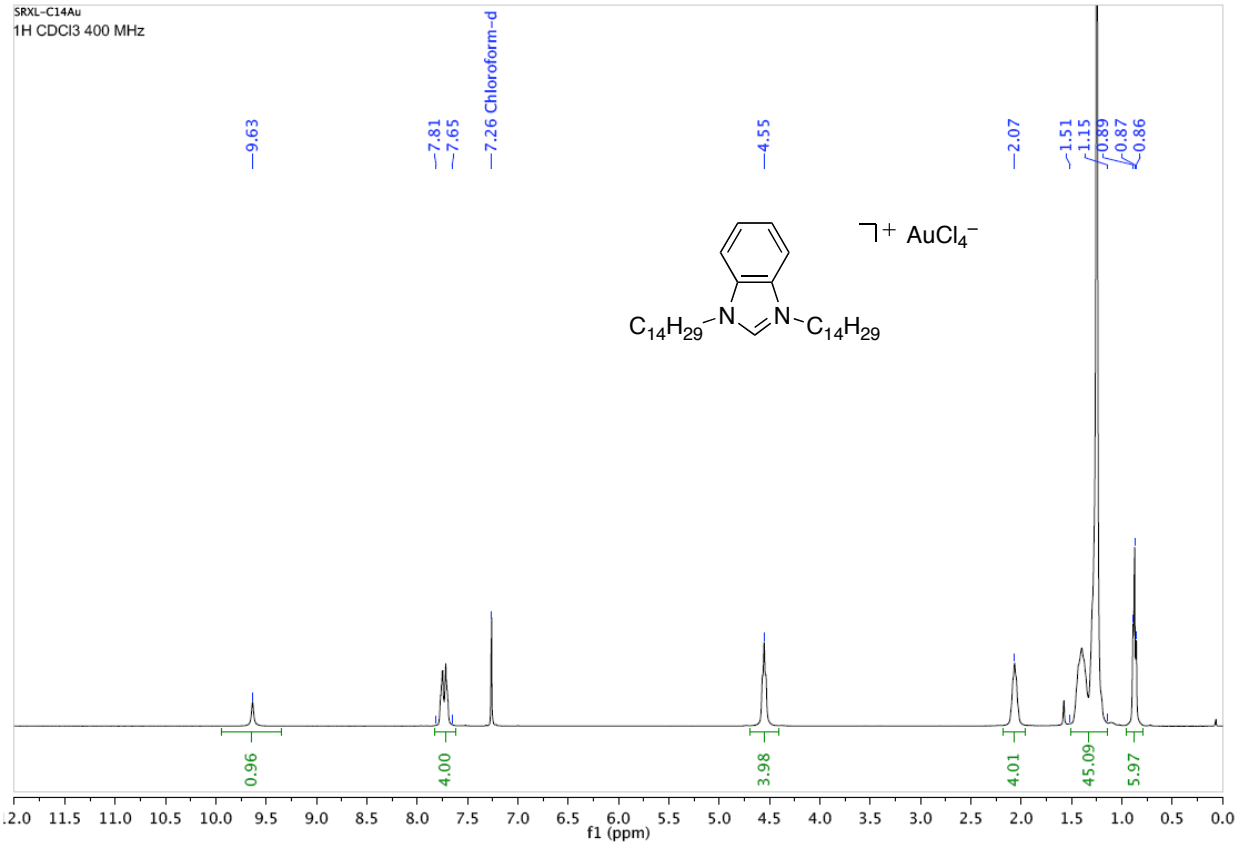


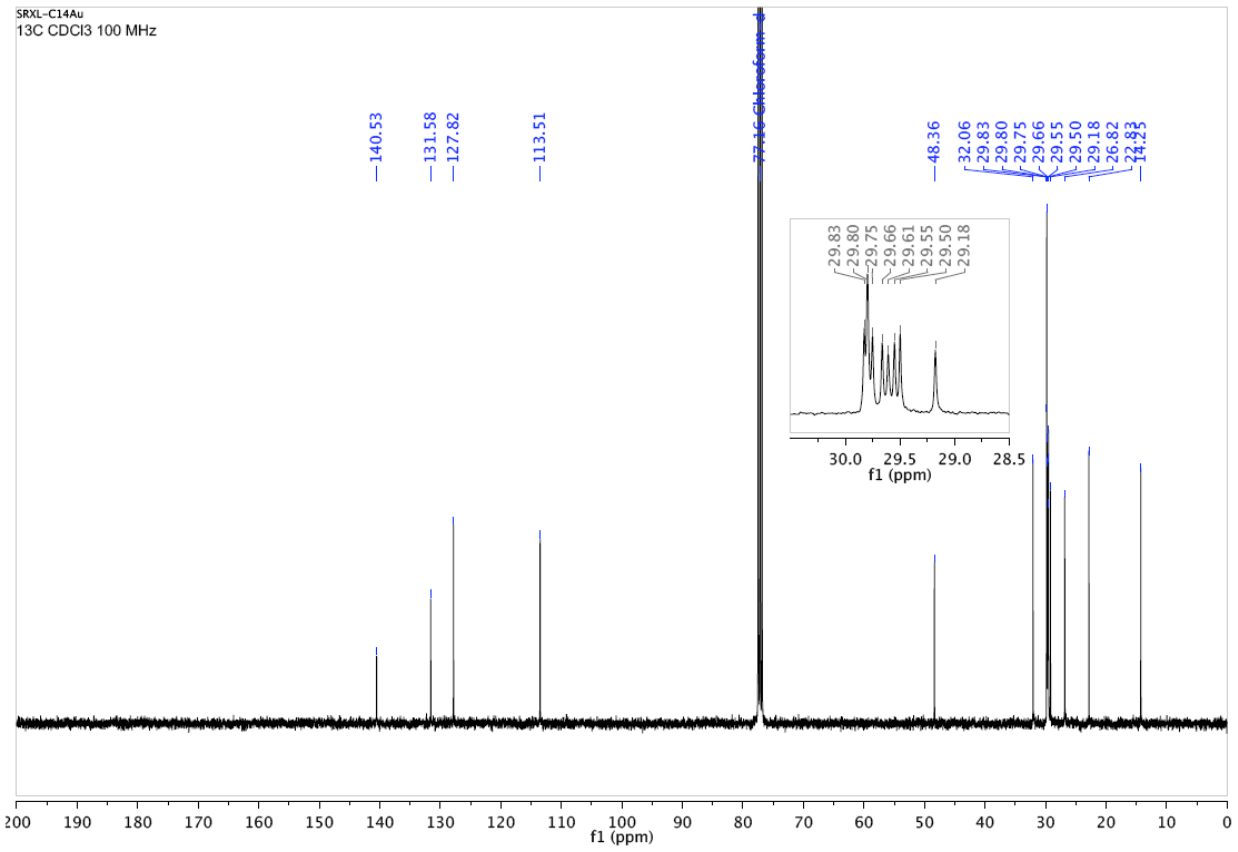
5-Ethoxycarbonyl-1,3-(ditetradecyl)benzimidazolium tetrachloroaurate(III) (**4**)



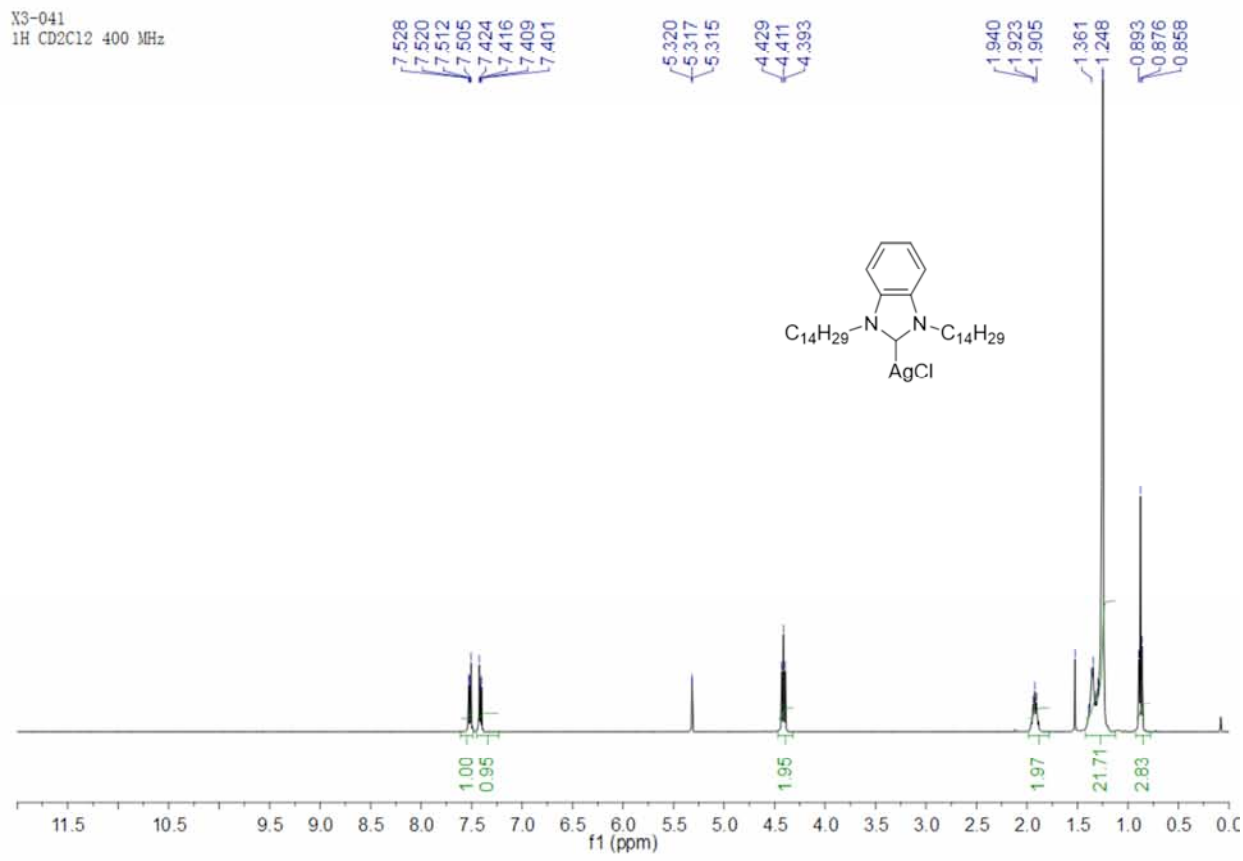


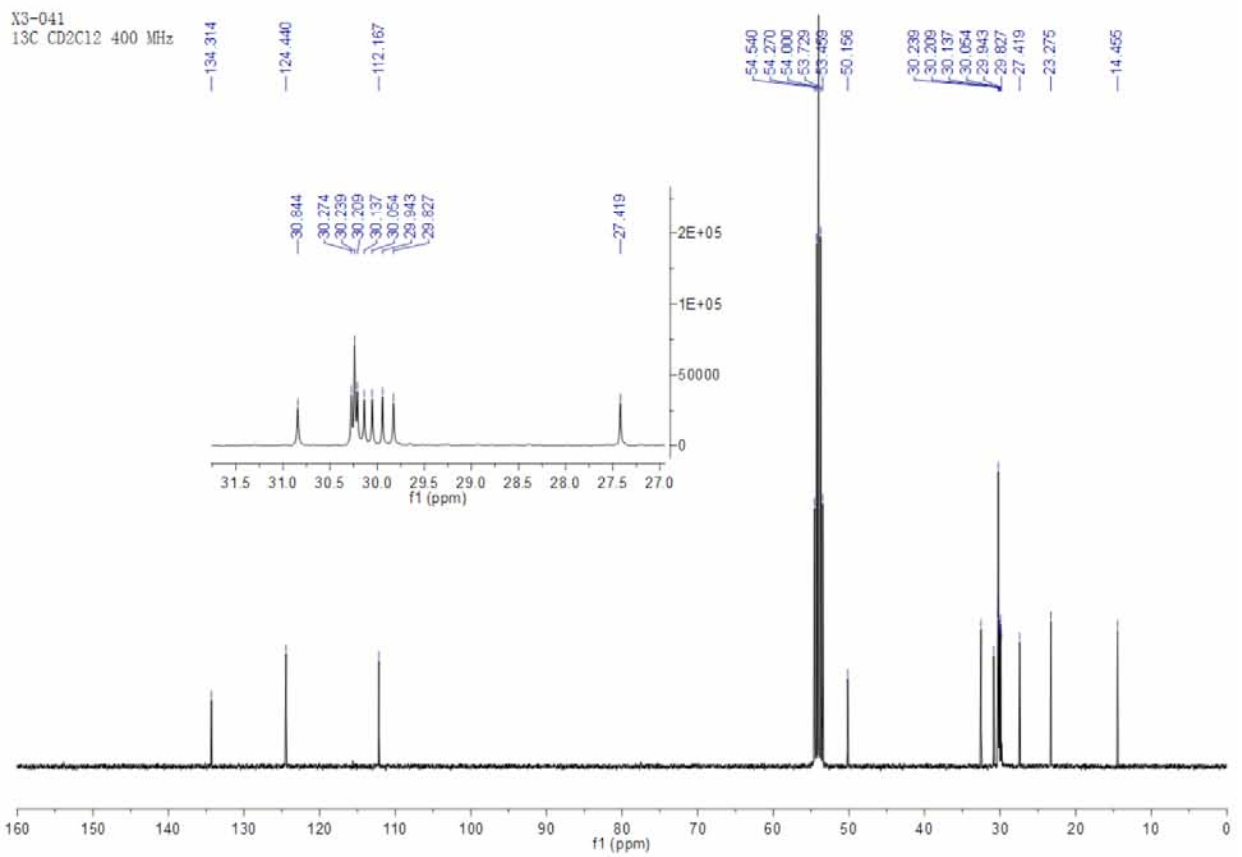
1,3-(Ditetradecyl)benzimidazolium tetrachloroaurate(III) (**5**)





Silver(I) complex **L^{5}AgBr**





Gold(I) complex **L^{5}AuCl**