Electronic Supplementary Material (ESI) for Dalton Transactions.

**Supporting information**

# Synthesis of quinolinyl-based pincer copper(II) complexes: An efficient catalyst system for Kumada coupling of alkyl chlorides and bromides with alkyl Grignard reagents

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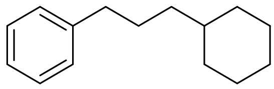
# Contents

## 1. Procedure for synthesis of ($^{Q}$NNN$^{Et2}$)CuX from Cu(I)X precursors

**Representative procedure: Synthesis of ($^{Q}$NNN$^{Et2}$)CuCl**. To an oven dried Schlenk flask were introduced ligand ($^{Q}$NNN$^{Et2}$)-H (0.1 g, 0.389 mmol) and CuCl (0.038 g, 0.387 mmol), and THF (10 mL) was added in to it. To the resultant reaction mixture, $Et_3N$ (0.071 mL, 0.506 mmol) was added and the reaction mixture was stirred at 70 °C for 3 h in a preheated oil bath. The reaction was cooled to room temperature and all the volatiles were evaporated. Product was then extracted with toluene (10 mL × 2), concentrated under vacuum and added $Et_2O$ (3 mL) to obtain crystalline compound **2**. Yield: 0.067 g, 49% (*Note*: Some white powder compound left in the flask after extraction with toluene, which might be the Cu(0) species). Analytical data is in good agreement with the same compound synthesized using $CuCl_2$.

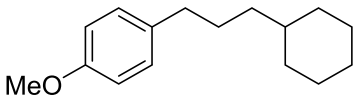
## 2. Characterization data of compounds

### (3-Cyclohexylpropyl)benzene (9aa)



The compound **9aa** was obtained as a colorless liquid. Yield: 0.026 g, 63%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.58-6.98 (m, 5H, Ar–H), 2.61 (t, $J$ = 7.6 Hz, 2H), 1.86-1.60 (m, 7H), 1.32-1.12 (m, 6H), 0.96-0.81 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 143.2 ($C_q$), 128.6 (2C, CH), 128.4 (2C, CH), 122.6 (CH), 37.8 (CH), 37.4 ($CH_2$), 36.5 ($CH_2$), 33.6 (2C, $CH_2$), 29.0 ($CH_2$), 26.9 ($CH_2$), 26.6 (2C, $CH_2$). The NMR spectral data is in accordance with the reported data.[S1]

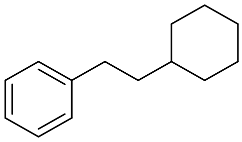
### 1-(3-Cyclohexylpropyl)-4-methoxybenzene (9ba)



The compound **9ba** was obtained as a colorless liquid. Yield: 0.042 g, 90%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.10 (d, $J$ = 7.9 Hz, 2H, Ar–H), 6.83 (d, $J$ = 8.5 Hz, 2H, Ar–H), 3.79 (s, 3H), 2.53 (t, $J$ = 7.9 Hz, 2H), 1.75-1.55 (m, 7H), 1.31-1.10 (m, 6H), 0.97-0.80 (m, 2H). $^{13}$C{$^1$H} NMR (100 MHz, $CDCl_3$): $\delta$ 157.7 ($C_q$), 132.2 ($C_q$), 129.4 (2C, CH), 113.8 (2C, CH), 52.3

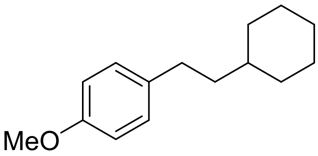
($CH_3$), 37.8 (CH), 37.3 ($CH_2$), 324 ($CH_2$), 33.6 (2C, $CH_2$), 29.2 ($CH_2$), 26.9 ($CH_2$), 26.6 (2C, $CH_2$). The NMR spectral data is in accordance with the reported data.[S2]

**(3-Cyclohexylethyl)benzene** (**9ca**)



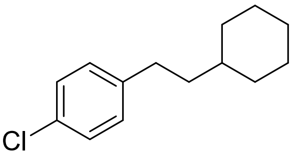
The compound **9ca** was obtained as a colorless liquid. Yield: 0.029 g, 76%. $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 7.36-7.07 (m, 5H, Ar–H), 2.66-2.56 (m, 2H), 1.89-1.59 (m, 6H), 1.58-1.44 (m, 2H), 1.40-1.11 (m, 5H), 1.03-0.81 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 143.4 ($C_q$), 128.5 (2C, CH), 128.4 (2C, CH), 122.6 (CH), 39.6 ($CH_2$), 37.5 (CH), 33.5 (2C, $CH_2$), 33.5 ($CH_2$), 26.9 ($CH_2$), 26.5 (2C, $CH_2$). The NMR spectral data is in accordance with the reported data.[S3]

**1-(2-Cyclohexylethyl)-4-methoxybenzene** (**9da**)



The compound **9da** was obtained as a colorless liquid. Yield: 0.036 g, 82%. $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.09 (d, $J$ = 8.0 Hz, 2H, Ar–H), 6.82 (d, $J$ = 7.6 Hz, 2H, Ar–H), 3.79 (s, 3H), 2.55 (t, $J$ = 8.0 Hz, 2H), 1.84-1.60 (m, 6H), 1.46 (q, $J$ = 7.1 Hz, 2H), 1.02-0.78 (m, 5H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$): $\delta$ 157.7 ($C_q$), 132.4 ($C_q$), 129.4 (2C, CH), 113.9 (2C, CH), 52.3 ($CH_3$), 39.8 ($CH_2$), 37.4 (CH), 33.5 (2C, $CH_2$), 32.5 ($CH_2$), 26.9 ($CH_2$), 26.5 (2C, $CH_2$). The NMR spectral data is in accordance with the reported data.[S3]

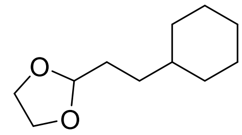
**1-Chloro-4-(2-cyclohexylethyl)benzene** (**8ea**)



The compound **9ea** was obtained as a light yellow liquid. Yield: 62% ($^1$H NMR yield, **9ea** and bicyclohexyl obtained as mixture). $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ 7.25-7.19 (m, 2H, Ar–H), 7.13-7.08 (m, 2H, Ar–H), 2.61-2.53 (m, 2H), 1.50-1.43 (m, 2H), 1.29-1.15 (m, 7H), 1.00-

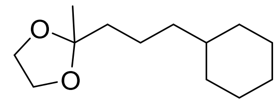
0.87 (m, 4H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): $\delta$ 141.8 ($C_q$), 131.3 ($C_q$), 129.9 (2C, CH), 128.5 (2C, CH), 43.6 (CH), 39.5 ($CH_2$), 33.5 (2C, $CH_2$), 32.8 ($CH_2$), 30.3 ($CH_2$), 26.5 (2C, $CH_2$). HRMS (ESI): *m/z* Calcd for $C_{14}H_{19}Cl$ $[M]^+$ 222.1170, found 222.1181.

**2-(2-Cyclohexylethyl)-1,3-dioxolane (9fa)**



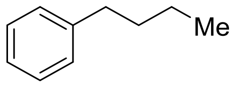
The compound **9fa** was obtained as a colorless liquid. Yield: 0.032 g, 82%. $^{1}H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.48 (t, $J$ = 4.9 Hz, 1H), 4.10 (dd, $J$ = 11.0, 4.9 Hz, 2H), 3.82-3.71 (m, 2H), 2.14-2.01 (m, 1H), 1.72-1.65 (m, 4H), 1.39-1.26 (m, 4H), 1.22-1.08 (m, 4H), 0.92-0.84 (m, 2H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 103.0 (CH), 67.1 (2C, $CH_2$), 37.7 (CH), 33.4 (2C, $CH_2$), 32.9 ($CH_2$), 31.7 ($CH_2$), 26.8 ($CH_2$), 26.5 (2C, $CH_2$). The NMR spectral data is in accordance with the reported data.[S4]

**2-(3-Cyclohexylpropyl)-2-methyl-1,3-dioxolane (9ga)**



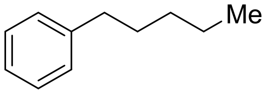
The compound **9ga** was obtained as a colorless liquid. Yield: 0.025 g, 58%. $^{1}H$ NMR (400 MHz, $CDCl_3$): $\delta$ 4.01-3.83 (m, 4H), 1.74-1.64 (m, 5H), 1.61 (d, $J$ = 6.1 Hz, 2H), 1.44-1.33 (m, 4H), 1.31 (s, 3H), 1.23-1.13 (m, 6H). $^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$): $\delta$ 110.4 ($C_q$), 64.8 (2C, $CH_2$), 39.7 ($CH_2$), 37.8 (CH), 37.8 ($CH_2$), 33.6 (2C, $CH_2$), 26.9 ($CH_2$), 26.6 (2C, $CH_2$), 23.9 ($CH_3$), 21.6 ($CH_2$). HRMS (ESI): *m/z* Calcd for $C_{13}H_{25}O_2$ $[M+H]^+$ 213.1849, found 213.1845.

***n*-Butylbenzene (9ab)**



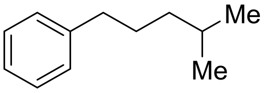
The compound **9ab** was obtained as a colorless liquid. Yield: 0.025 g, 93%. $^{1}H$ NMR (500 MHz, $CDCl_3$): $\delta$ 7.36-7.06 (m, 5H), 2.61 (t, $J$ = 7.8 Hz, 2H), 1.64-1.56 (m, 2H), 1.40-1.32 (m, 2H), 0.93 (t, $J$ = 7.2 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$): $\delta$ 143.1 ($C_q$), 128.6 (2C, CH), 128.4 (2C, CH), 122.6 (CH), 35.9 ($CH_2$), 33.9 ($CH_2$), 22.6 ($CH_2$), 14.1 ($CH_3$). The NMR spectral data is in accordance with the reported data.[S5]

***n*-Pentylbenzene** (**9ac**)



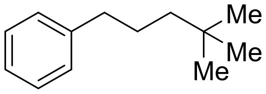
The compound **9ac** was obtained as a colorless liquid. Yield: 0.027 g, 92%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.30-7.13 (m, 5H), 2.60 (t, $J$ = 7.8 Hz, 2H), 1.62 (quin, $J$ = 7.3 Hz, 2H), 1.35-1.30 (m, 4H), 0.89 (t, $J$ = 6.5 Hz, 3H). $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 143.2 (C$_q$), 128.6 (2C, CH), 128.4 (2C, CH), 125.7 (CH), 36.2 (CH$_2$), 31.7 (CH$_2$), 31.4 (CH$_2$), 22.7 (CH$_2$), 14.2 (CH$_3$). The NMR spectral data is in accordance with the reported data.[S6]

**(4-Methylpentyl)benzene** (**9ad**)



The compound **9ad** was obtained as a colorless liquid. Yield: 0.029 g, 90%. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.52-6.94 (m, 5H, Ar–H), 2.58 (t, $J$ = 7.9 Hz, 2H), 1.65-1.54 (m, 3H), 1.27-1.19 (m, 2H), 0.87 (d, $J$ = 6.8 Hz, 6H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$): $\delta$ 143.2 (C$_q$), 128.6 (2C, CH), 128.4 (2C, CH), 125.8 (CH), 38.9 (CH$_2$), 36.4 (CH$_2$), 29.6 (CH$_2$), 28.1 (CH), 22.8 (2C, CH$_3$). The NMR spectral data is in accordance with the reported data.[S7]

**(4,4-Dimethylpentyl)benzene** (**9ae**)



The compound **9ae** was obtained as a colorless liquid. Yield: 0.032 g, 90%. $^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.36-7.12 (m, 5H, Ar–H), 2.59 (t, $J$ = 7.8 Hz, 2H), 1.64-1.56 (m, 2H), 1.28-1.22 (m, 2H), 0.88 (s, 9H). $^{13}$C{$^1$H} NMR (125 MHz, CDCl$_3$): $\delta$ 143.2 (C$_q$), 128.6 (2C, CH), 128.4 (2C, CH), 125.8 (CH), 44.1 (CH$_2$), 37.1 (CH$_2$), 30.5 (C$_q$), 29.6 (3C, CH$_3$), 26.9 (CH$_2$). The NMR spectral data is in accordance with the reported data.[S8]

## 3. X-ray structure determination

X-ray intensity data measurements of the complexes **2** and **3** were carried out on a Bruker D8 VENTURE Kappa Duo PHOTON II CPAD diffractometer with ($MoK_\alpha$= 0.71073Å) radiation at 100(2) K. The X-ray generator was operated at 50 kV and 1.4 mA. The X-ray data collection was monitored by the APEX3 program (Bruker, 2016).[S9] X-ray intensity data measurements of the complexes **4**.$(H_2O)_{0.5}$ and (**4**)$_n$ were carried out on a Bruker SMART APEX II CCD diffractometer with ($MoK_\alpha$= 0.71073Å) radiation at 150(2) K and 297(2) K respectively. The X-ray generator was operated at 50 kV and 30 mA. The X-ray data collection was monitored by APEX2 program (Bruker, 2006).[S10] For all the four complexes {**2**, **3**, **4**.$(H_2O)_{0.5}$ and (**4**)$_n$}, a preliminary set of cell constants and an orientation matrix were calculated from three sets of 12 frames (total 36 frames) and the data were collected with $\omega$ scan width of 0.5° at eight different settings of $\varphi$ and $2\theta$ keeping the sample-to-detector distance fixed at 5.00 cm for both compounds. All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2016). Using APEX3 (Bruker) program suite, the structure was solved with the ShelXS-97 (Sheldrick, 2008)[S11] structure solution program, using direct methods. The model was refined with version of ShelXL-2013 (Sheldrick, 2015)[S12] using Least Squares minimization. All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms.

**Table S1.** Selected bond lengths [Å] and angles [deg] for **2** and **3**

| Bond length (Å) | | Bond angles (°) | |
|---|---|---|---|
| Complex **2** | | | |
| Cu(1)–N(1) | 2.0690(10) | N(1)–Cu(1)–N(2) | 84.55(4) |
| Cu(1)–N(2) | 1.9086(10) | N(1)–Cu(1)–N(3) | 166.80(4) |
| Cu(1)–N(3) | 2.0093(10) | N(2)–Cu(1)–N(3) | 82.57(4) |
| Cu(1)–Cl(1) | 2.2105(3) | N(1)–Cu(1)–Cl(1) | 95.74(3) |
| | | N(2)–Cu(1)–Cl(1) | 172.07(3) |
| | | N(3)–Cu(1)–Cl(1) | 97.42(3) |
| Complex **3** | | | |
| Cu(1)–N(1) | 2.0691(12) | N(1)–Cu(1)–N(2) | 84.57(5) |
| Cu(1)–N(2) | 1.9097(12) | N(1)–Cu(1)–N(3) | 166.84(5) |
| Cu(1)–N(3) | 2.0128(12) | N(2)–Cu(1)–N(3) | 82.60(5) |
| Cu(1)–Br(1) | 2.3523(2) | N(1)–Cu(1)–Br(1) | 95.90(3) |
| | | N(2)–Cu(1)–Br(1) | 171.48(4) |
| | | N(3)–Cu(1)–Br(1) | 97.23(3) |

**Table S2.** Selected bond lengths [Å] and angles [deg] for **4**.$(H_2O)_{0.5}$ and (**4**)$_n$

| Bond length (Å) | | Bond angles (°) | |
|---|---|---|---|
| Complex **4**.$(H_2O)_{0.5}$ | | | |
| Cu(1)–N(1) | 2.0633(13) | N(1)–Cu(1)–N(2) | 83.99(6) |
| Cu(1)–N(2) | 1.9109(14) | N(1)–Cu(1)–N(3) | 162.42(6) |
| Cu(1)–N(3) | 2.0107(13) | N(2)–Cu(1)–N(3) | 82.51(6) |
| Cu(1)–O(1) | 1.9618(11) | N(1)–Cu(1)–O(1) | 99.01(5) |
| | | N(2)–Cu(1)–O(1) | 175.85(5) |
| | | N(3)–Cu(1)-O(1) | 95.08(5) |
| Complex (**4**)$_n$ | | | |
| Cu(1)–N(1) | 2.083(2) | N(1)–Cu(1)–N(2) | 82.89(9) |
| Cu(1)–N(2) | 1.926(2) | N(1)–Cu(1)–N(3) | 162.18(9) |
| Cu(1)–N(3) | 2.035(2) | N(2)–Cu(1)–N(3) | 81.50(9) |
| Cu(1)–O(1) | 1.9302(19) | N(1)–Cu(1)–O(1) | 99.12(9) |
| | | N(2)–Cu(1)–O(1) | 175.59(9) |
| | | N(3)–Cu(1)-O(1) | 95.89(9) |

**Table S3** Crystal data and structure refinement of complexes **2** and **3**

| | **2** | **3** |
|---|---|---|
| Empirical formula | $C_{15}H_{18}ClCuN_3O$ | $C_{15}H_{18}BrCuN_3O$ |
| Formula weight | 355.31 | 399.77 |
| Temperature, K | 100(2) K | 100(2) K |
| Cryst. Syst. | Monoclinic | Monoclinic |
| Space group | C2/c | C2/c |
| *a* (Å) | 14.5925(6) | 14.8335(5) |
| *b* (Å) | 13.2202(6) | 13.3212(4) |
| *c* (Å) | 16.1405(6) | 16.1662(5) |
| α (°) | 90 | 90 |
| β (°) | 101.955(2) | 101.8220(10) |
| γ (°) | 90 | 90 |
| V ($Å^3$) | 3046.2(2) | 3126.68(17) |
| Z | 8 | 8 |
| $\rho_{\text{cald.}}$ $Mg/m^3$ | 1.549 | 1.699 |
| $\varepsilon$ ($mm^{-1}$) | 1.611 | 3.954 |
| *F* (000) | 1464 | 1608 |
| Crystal size ($mm^3$) | 0.314x0.276x0.081 | 0.22x0.08x0.04 |
| $\theta$ (min, max) (°) | 2.304, 30.515 | 2.574, 30.503 |
| R(int) | 0.0230 | 0.0260 |
| Independent reflections | 4633 | 4765 |
| Completeness to θ (%) | 99.9 | 99.9 |
| Max. and min. transmission | 0.881, 0.632 | 0.858, 0.477 |
| Data/restraints/parameters | 4633/0/192 | 4765/0/192 |
| GOF on $F^2$ | 1.043 | 1.058 |
| R1, wR2 ($I>2\sigma(I)$) | 0.0228, 0.0582 | 0.0209, 0.0510 |
| R1, wR2 (all data) | 0.0259, 0.0598 | 0.0252, 0.0527 |
| CCDC No. | 1832852 | 1832854 |

**Table S4** Crystal data and structure refinement of complexes **4**.$(H_2O)_{0.5}$ and (**4**)$_n$

| | **4**.$(H_2O)_{0.5}$ | (**4**)$_n$ |
|---|---|---|
| Empirical formula | $C_{17}H_{22}CuN_3O_{3.5}$ | $C_{17}H_{21}CuN_3O_3$ |
| Formula weight | 387.91 | 378.92 |
| Temperature, K | 150(2) | 297(2) K |
| Cryst. Syst. | Monoclinic | Monoclinic |
| Space group | C2/c | $P2_1/n$ |
| *a* (Å) | 11.7397(4) | 13.750(3) |
| *b* (Å) | 13.8992(5) | 7.8669(17) |
| *c* (Å) | 21.0927(8) | 16.223(4) |
| α (°) | 90 | 90 |
| β (°) | 90.547(2) | 98.271(10) |
| γ (°) | 90 | 90 |
| V (Å$^3$) | 3441.6(2) | 1736.6(7) |
| Z | 8 | 2 |
| $\rho_{\text{cald.}}$ Mg/m$^3$ | 1.497 | 1.449 |
| $\varepsilon$ (mm$^{-1}$) | 1.293 | 1.277 |
| *F* (000) | 1616 | 788 |
| Crystal size (mm$^3$) | 0.43x0.31x0.21 | 0.42x0.32x0.22 |
| $\theta$ (min, max) (°) | 1.931, 27.992 | 1.817, 28.660 |
| R(int) | 0.0214 | 0.0592 |
| Independent reflections | 4129 | 4256 |
| Completeness to θ (%) | 99.9 | 98.6 |
| Max. and min. transmission | 0.773, 0.606 | 0.766, 0.616 |
| Data/restraints/parameters | 4129/0/228 | 4256/0/220 |
| GOF on F$^2$ | 1.070 | 1.050 |
| R1, wR2 ($I>2\sigma(I)$) | 0.0287, 0.0708 | 0.0470, 0.1163 |
| R1, wR2 (all data) | 0.0326, 0.0725 | 0.0633, 0.1253 |
| CCDC No. | 1832845 | 1832853 |

## 4. References

S1. J.-H. Liu, C.-T. Yang, X.-Y. Lu, Z.-Q. Zhang, L. Xu, M. Cui, X.-Y. Lu, B. Xiao, Y. Fu and L. Liu, *Chem. Eur. J.*, 2014, **20**, 15334-15338.

S2. T. Satoh, A. Kondo and J. Musashi, *Tetrahedron*, 2004, **60**, 5453-5460.

S3. J.-Y. Lee and G. C. Fu, *J. Am. Chem. Soc.*, 2003, **125**, 5616-5617.

S4. V. Phapale, E. Buñuel, M. García-Iglesias and D. Cárdenas, *Angew. Chem. Int. Ed.*, 2007, **46**, 8790-8795.

S5. F. Alonso, P. Riente and M. Yus, *Tetrahedron*, 2009, **65**, 10637-10643.

S6. M. Tobisu, R. Nakamura, Y. Kita and N. Chatani, *J. Am. Chem. Soc.*, 2009, **131**, 3174-3175.

S7. D. H. Burns, J. D. Miller, H.-K. Chan and M. O. Delaney, *J. Am. Chem. Soc.*, 1997, **119**, 2125-2133.

S8. C.-T. Yang, Z.-Q. Zhang, J. Liang, J.-H. Liu, X.-Y. Lu, H.-H. Chen and L. Liu, *J. Am. Chem. Soc.*, 2012, **134**, 11124-11127.

S9. APEX3, SAINT and SADABS, *Bruker AXS Inc.,* Madison, Wisconsin, USA, 2016.

S10. APEX2, SAINT and SADABS, *Bruker AXS Inc.,* Madison, Wisconsin, USA, 2006.

S11. G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112-122.

S12. G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3-8.

## 5. X-ray photoelectron spectra

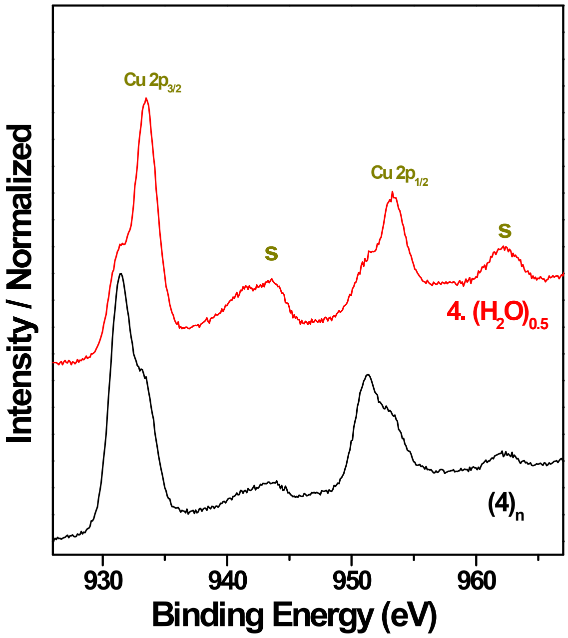


**Figure S1.** The X-ray photoelectron spectra of Cu 2p of the complexes **4.**$(H_2O)_{0.5}$ and (**4**)$_n$ with normalized intensities.

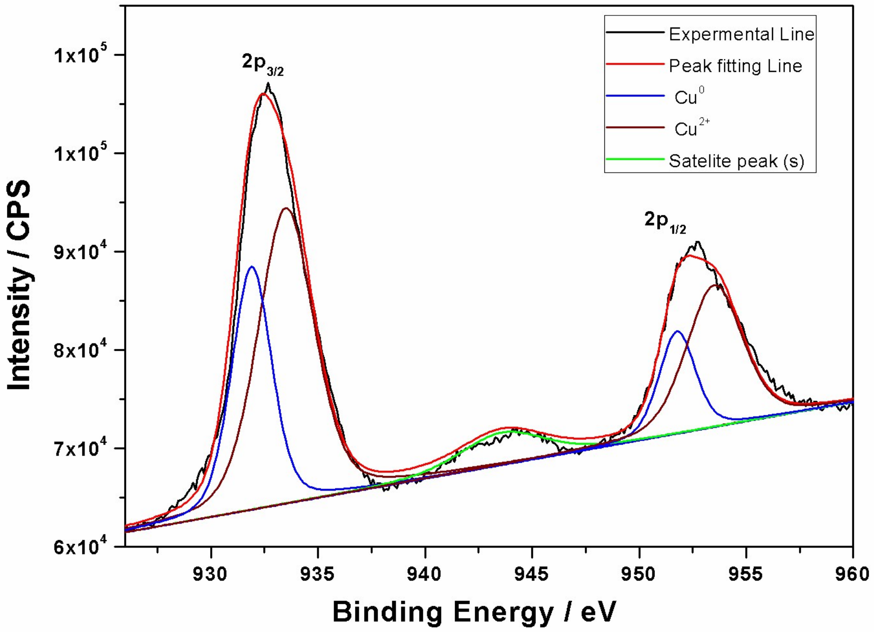
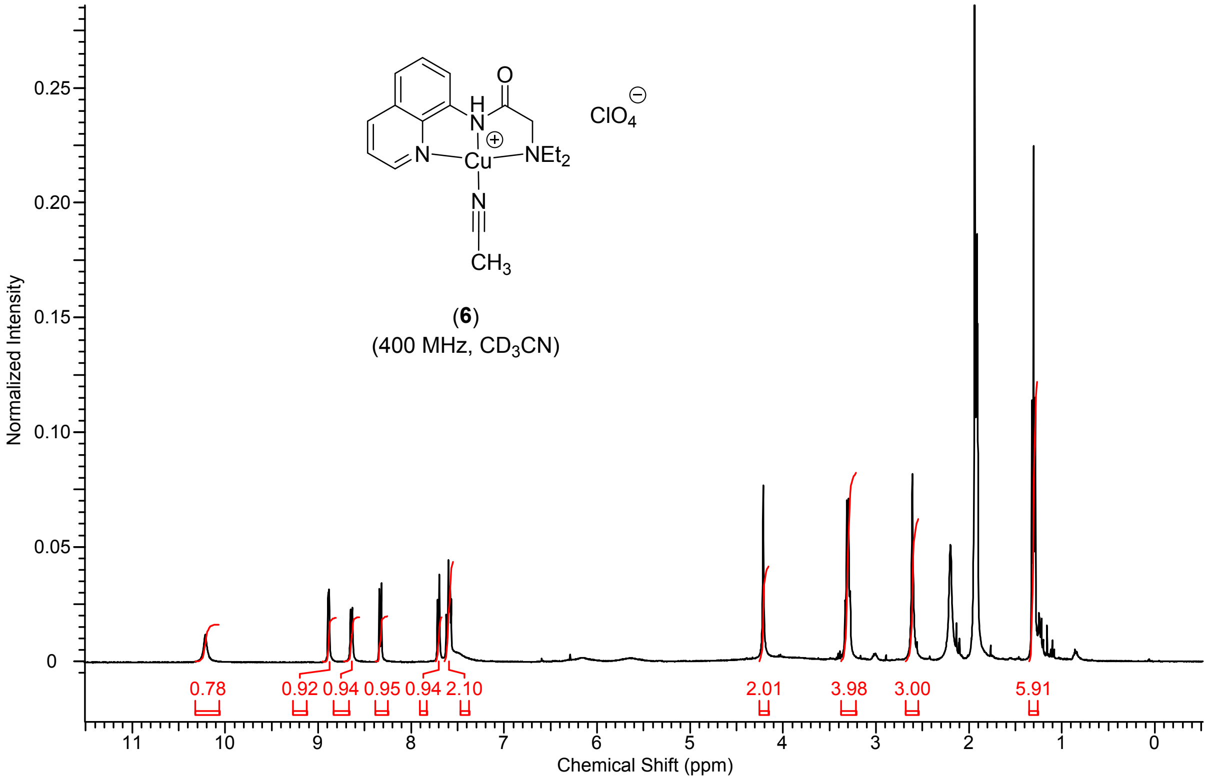
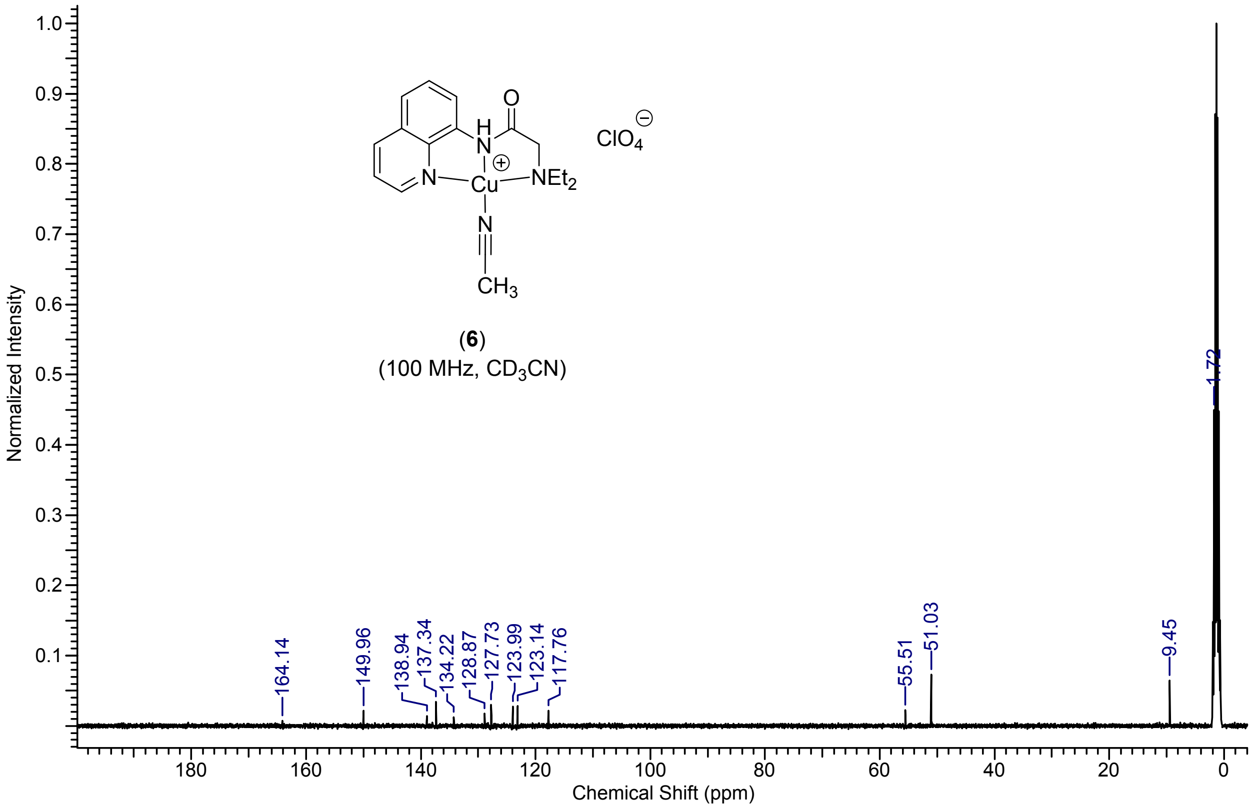
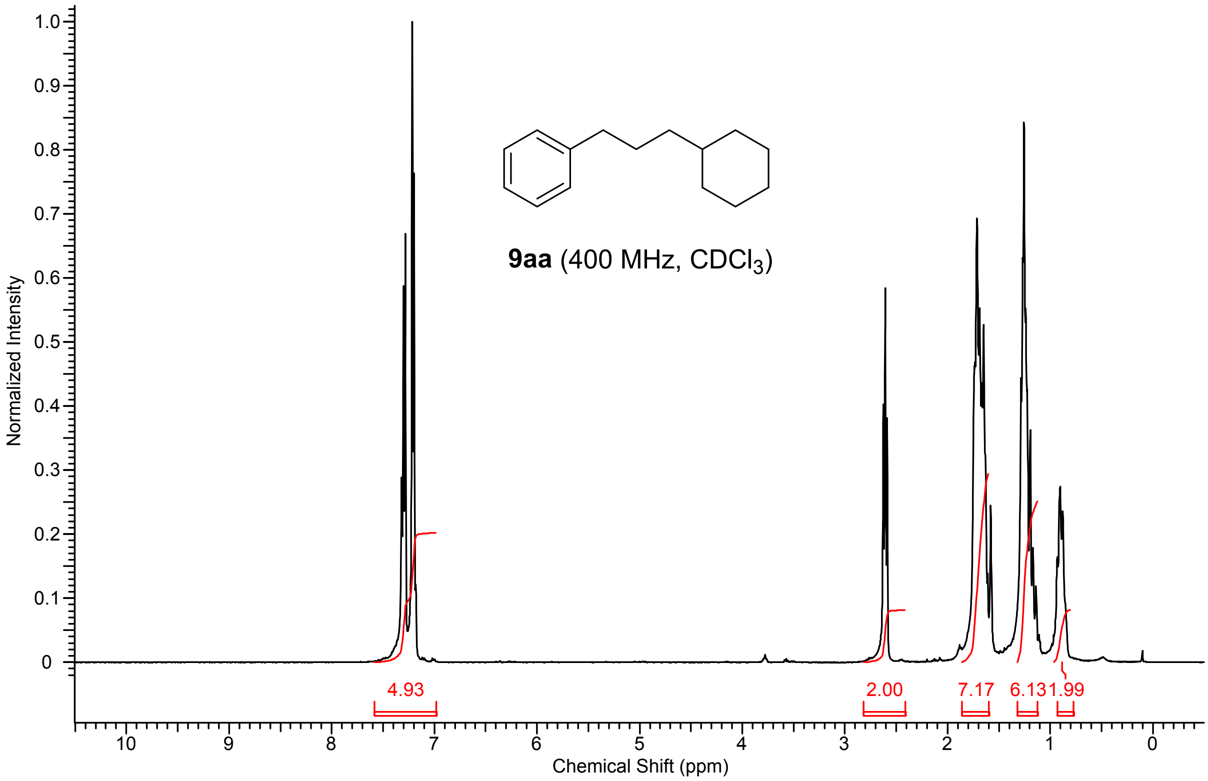


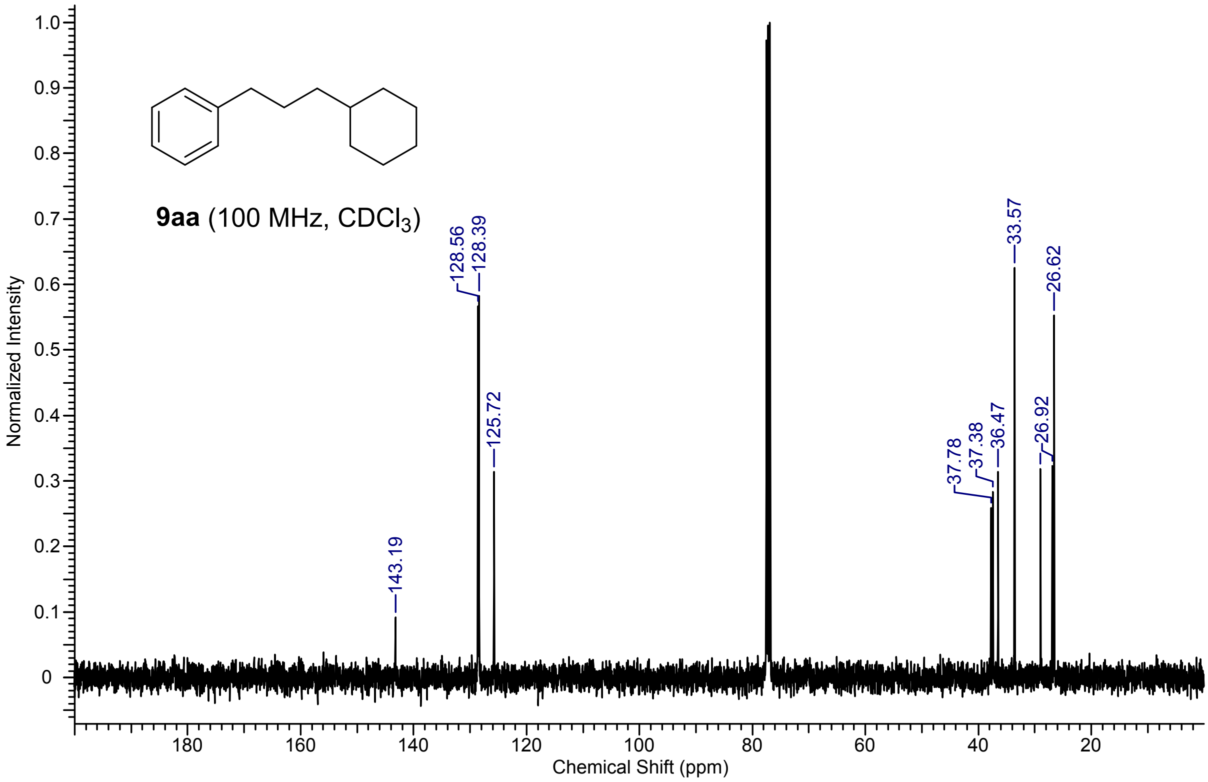
**Figure S2.** The X-ray photoelectron spectra of reaction mixture of **4** and Cu(0).

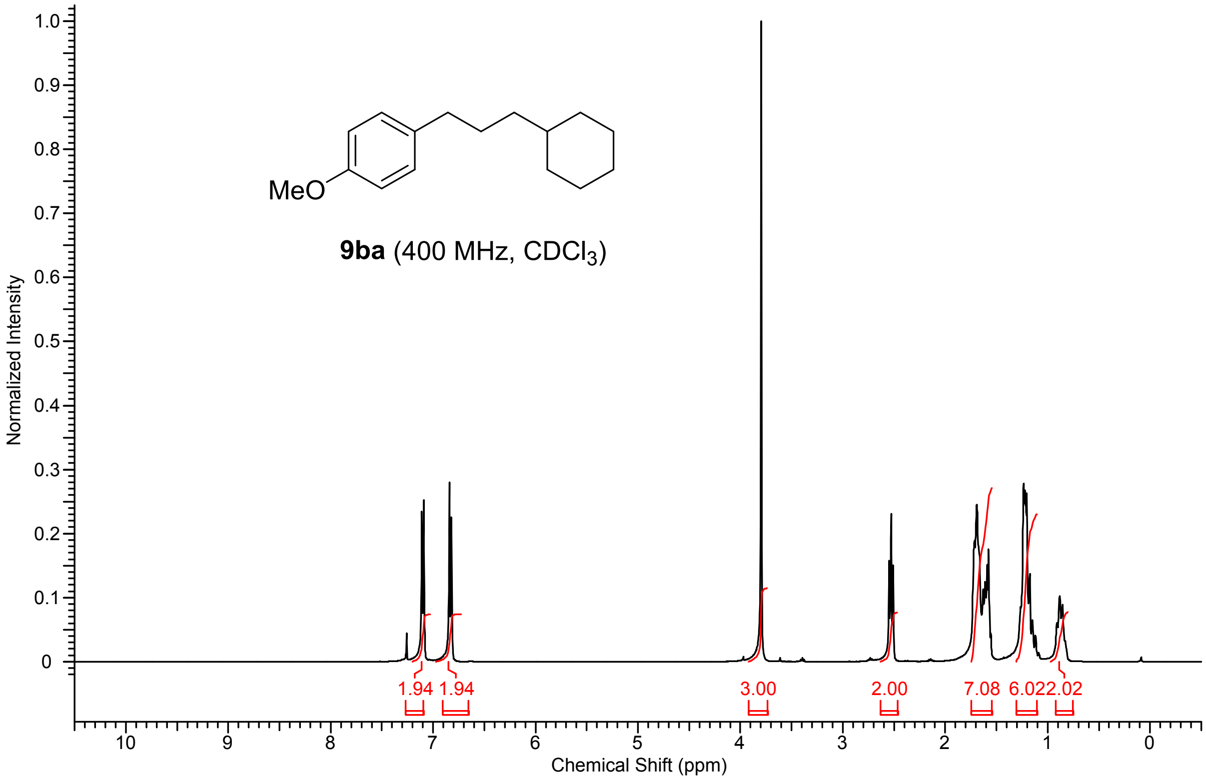
# 6. $^{1}$H and $^{13}$C NMR spectra of selected compounds



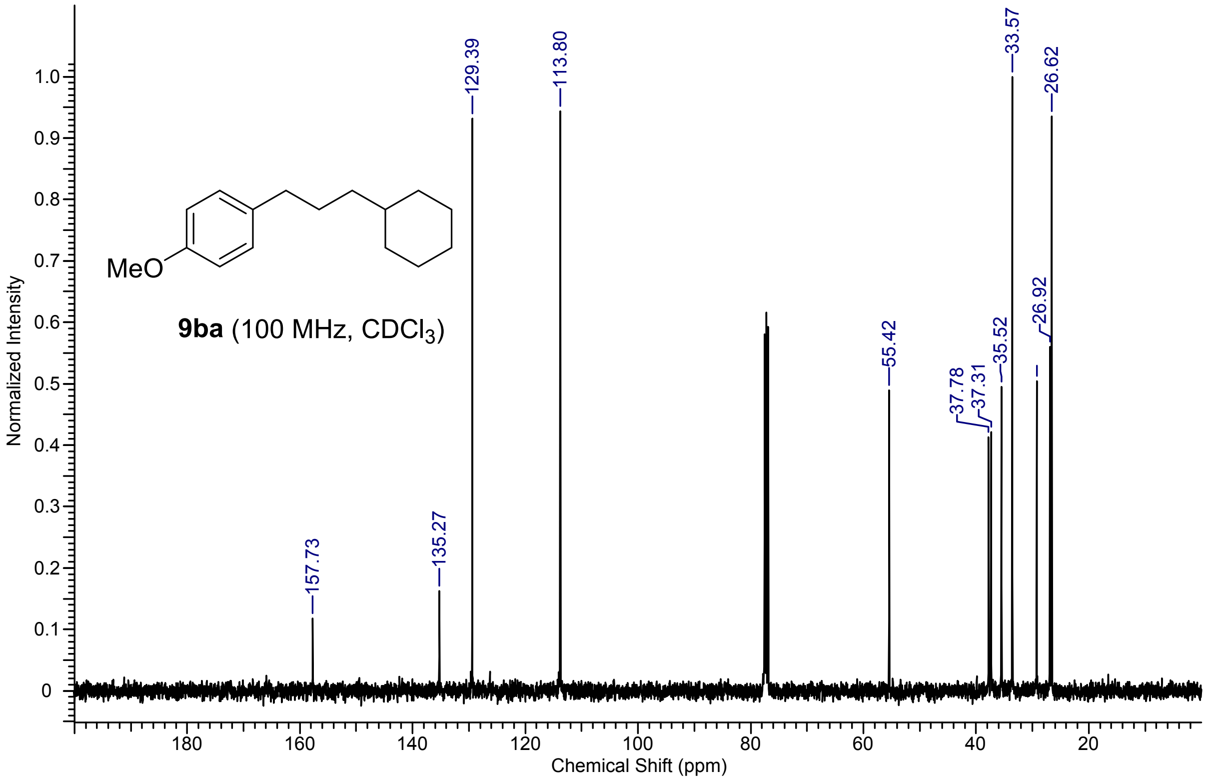



9aa (400 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.93
2.00
7.17
6.13
1.99
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

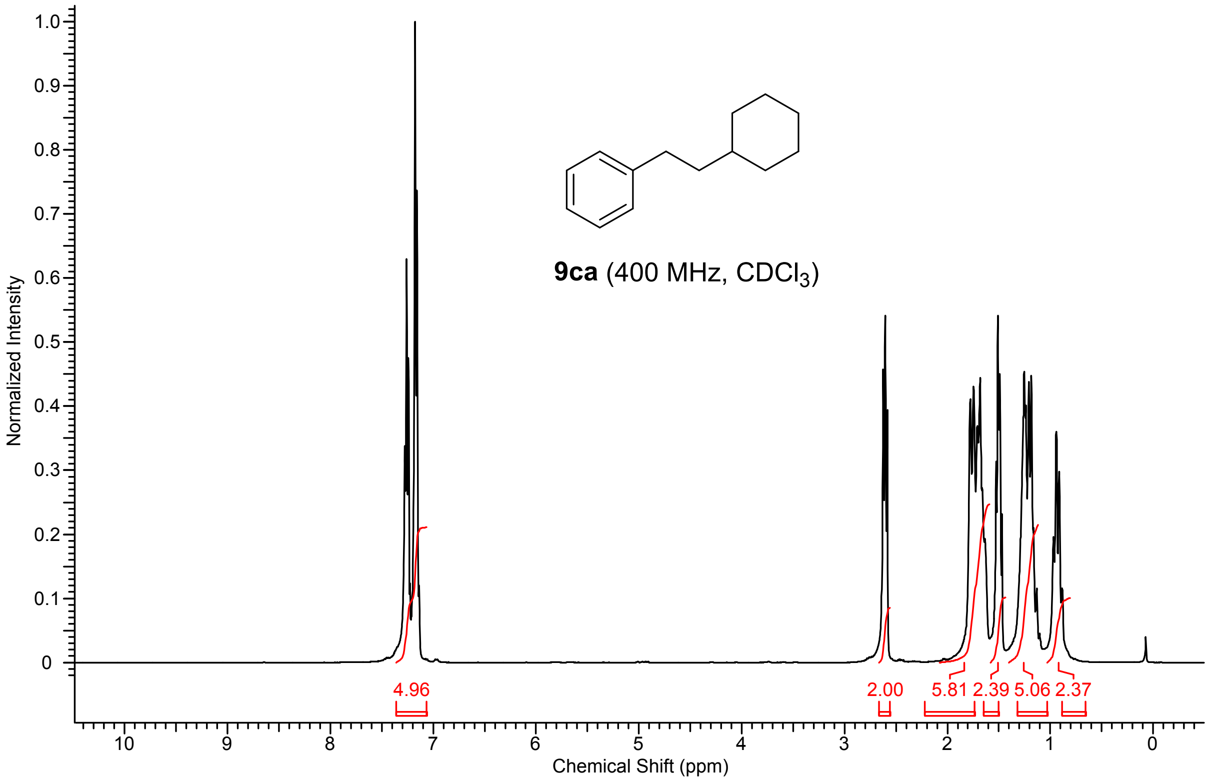

9aa (100 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
143.19
128.56
128.39
125.72
37.78
37.38
36.47
33.57
26.92
26.62
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

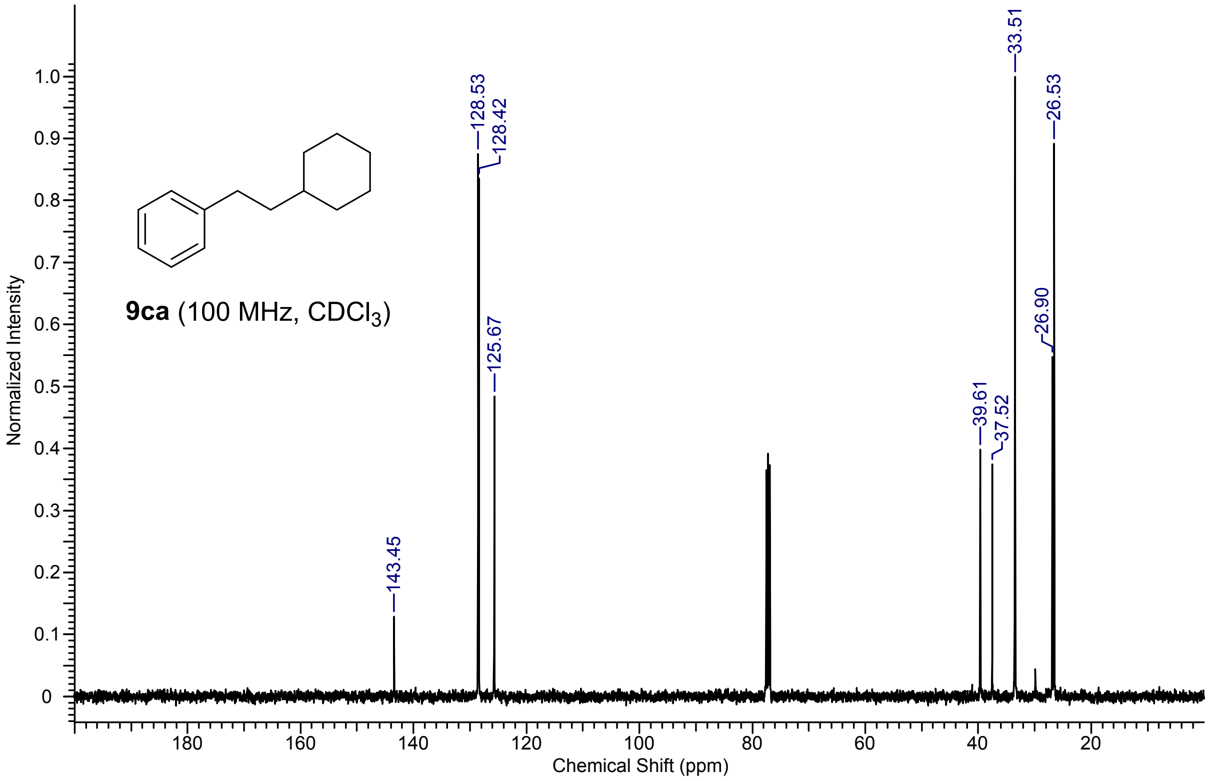


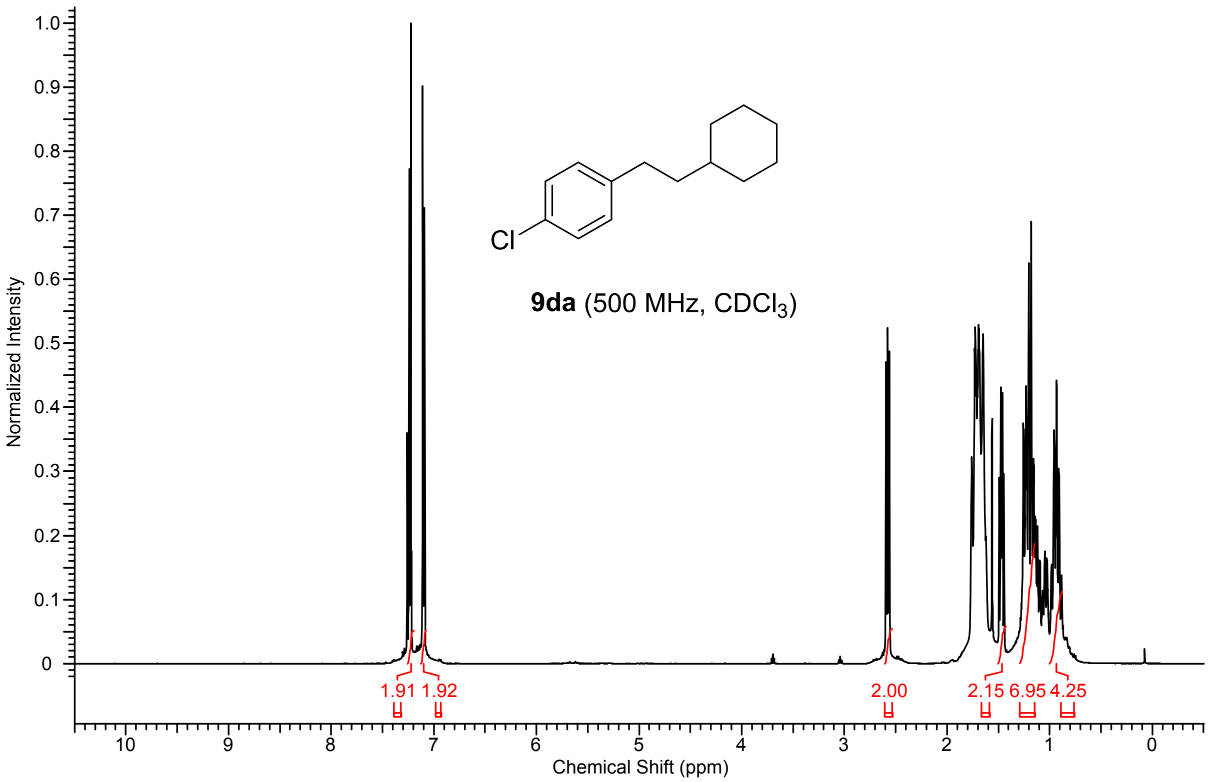
**9ba** (400 MHz, $CDCl_3$)

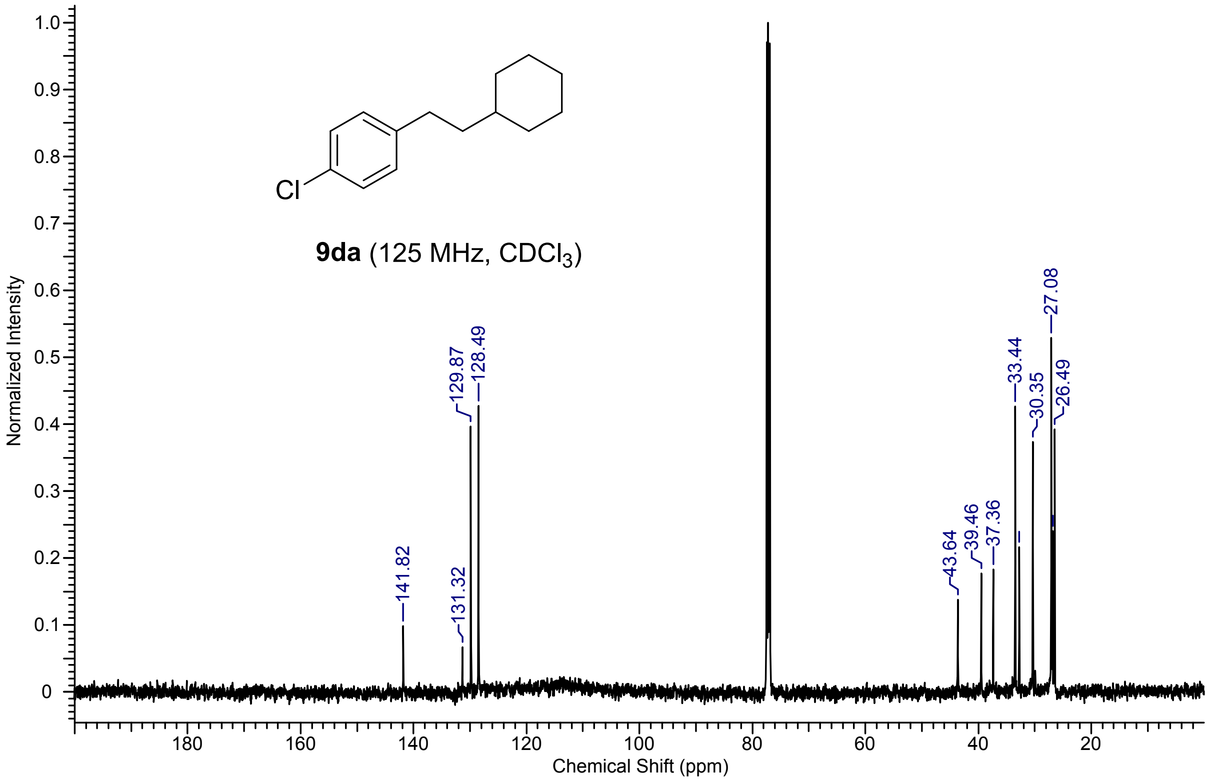


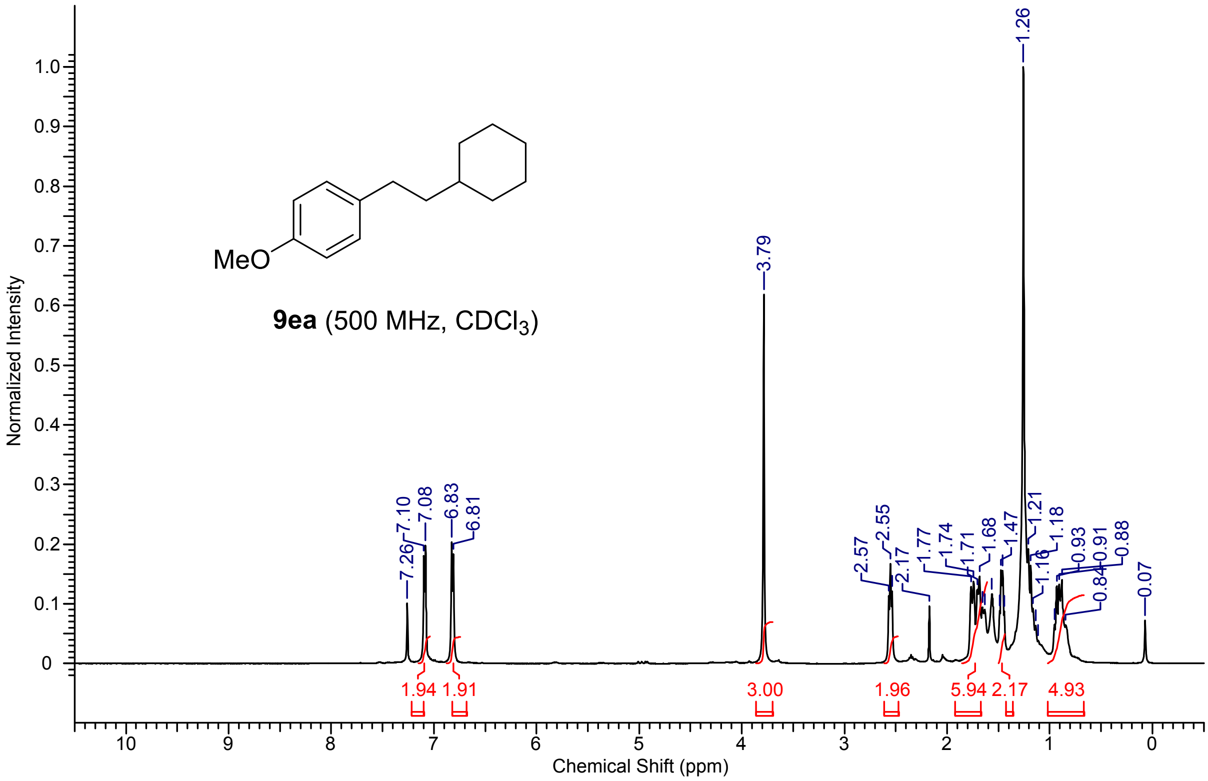
**9ba** (100 MHz, $CDCl_3$)

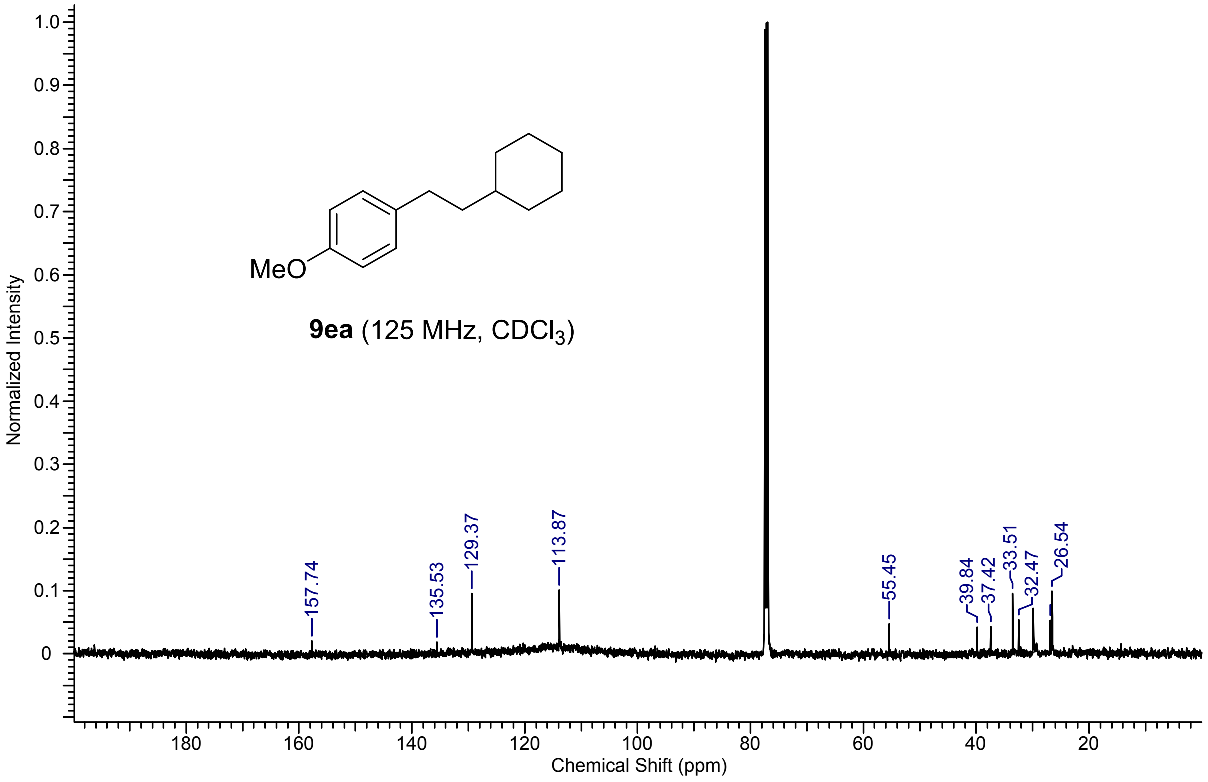

9ca (400 MHz, CDCl$_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.96
2.00
5.81
2.39
5.06
2.37
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

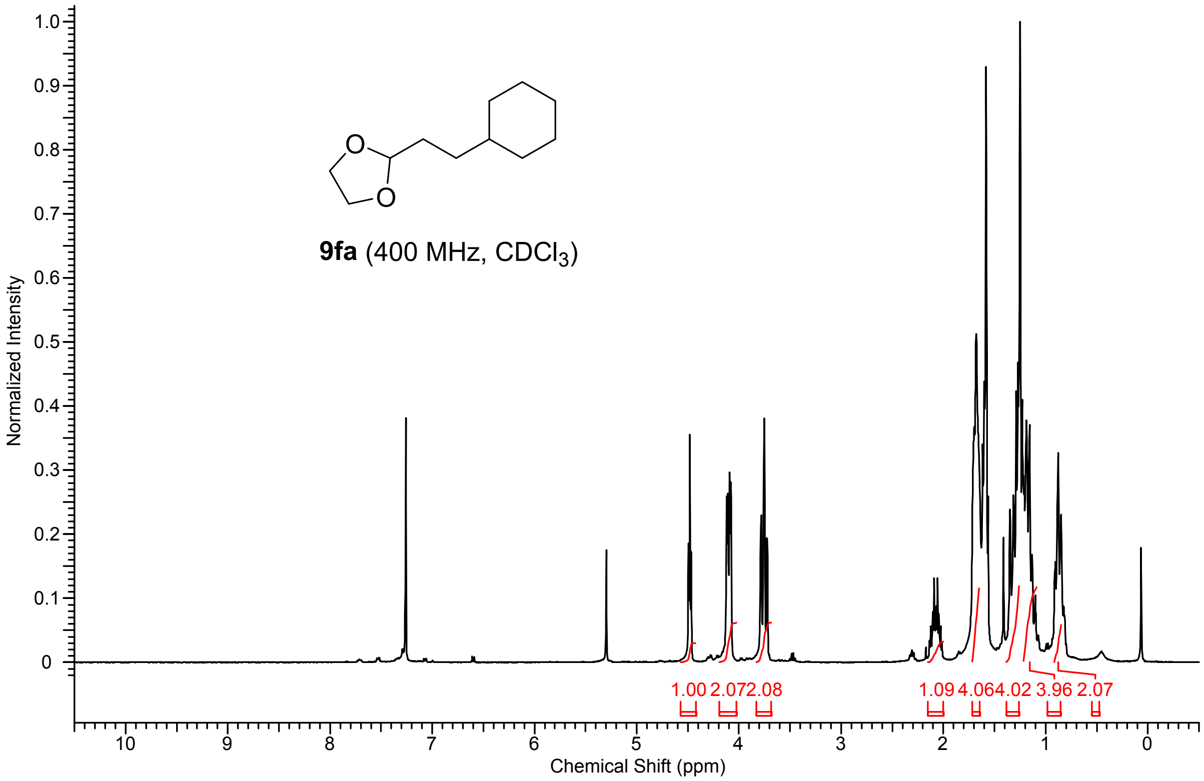

9ca (100 MHz, CDCl$_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
143.45
128.53
128.42
125.67
39.61
37.52
33.51
26.90
26.53
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

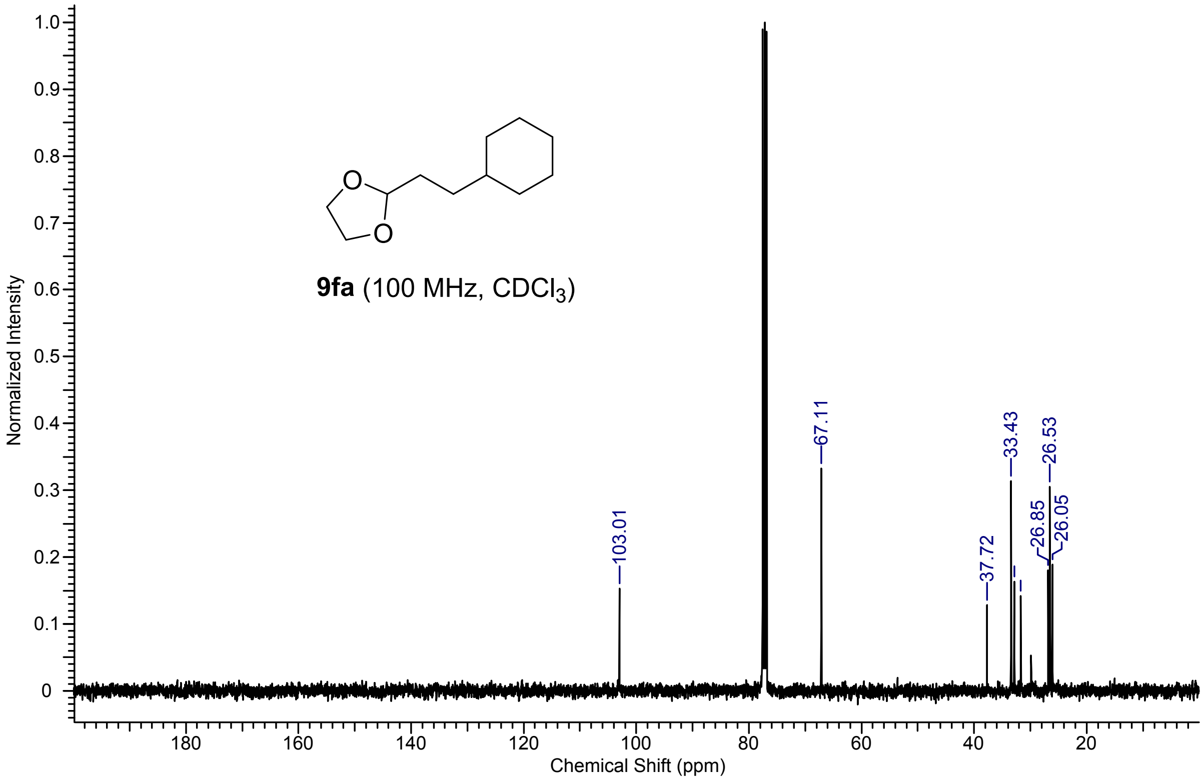

Cl
9da (500 MHz, CDCl$_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.91
1.92
2.00
2.15
6.95
4.25
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

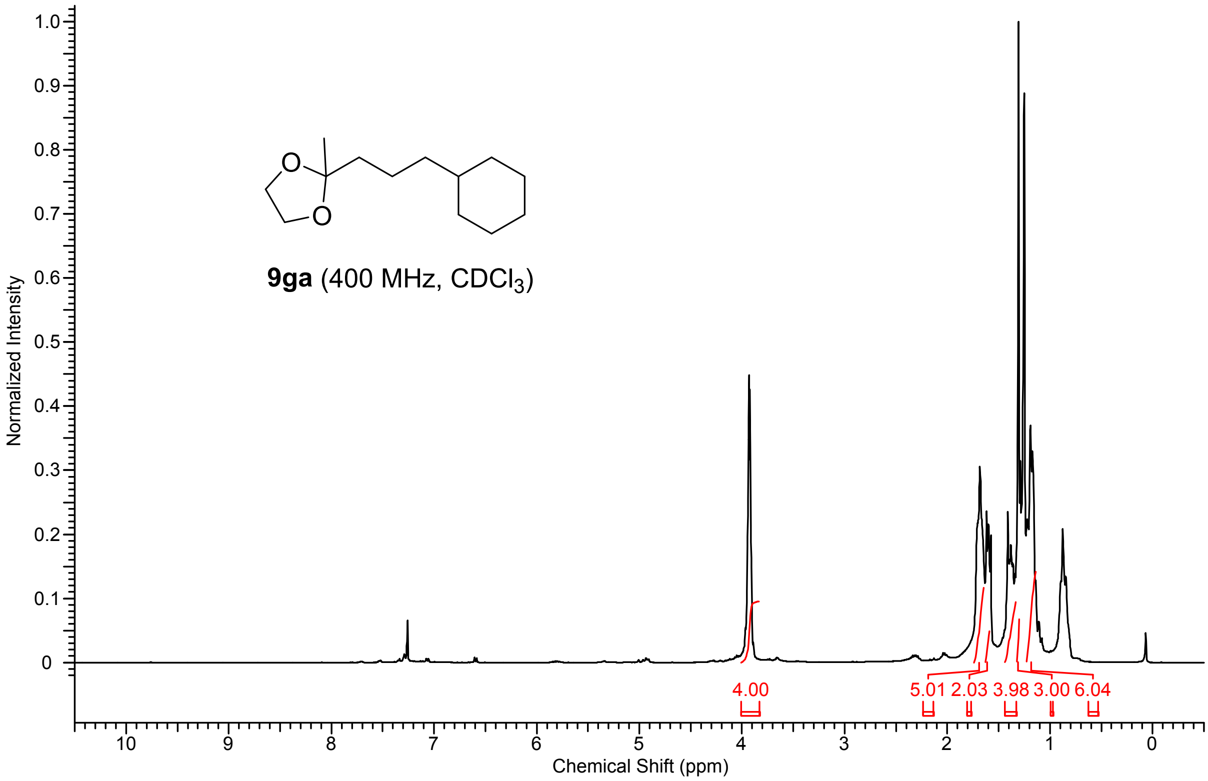

Cl
9da (125 MHz, CDCl$_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
141.82
131.32
129.87
128.49
43.64
39.46
37.36
33.44
30.35
27.08
26.49
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

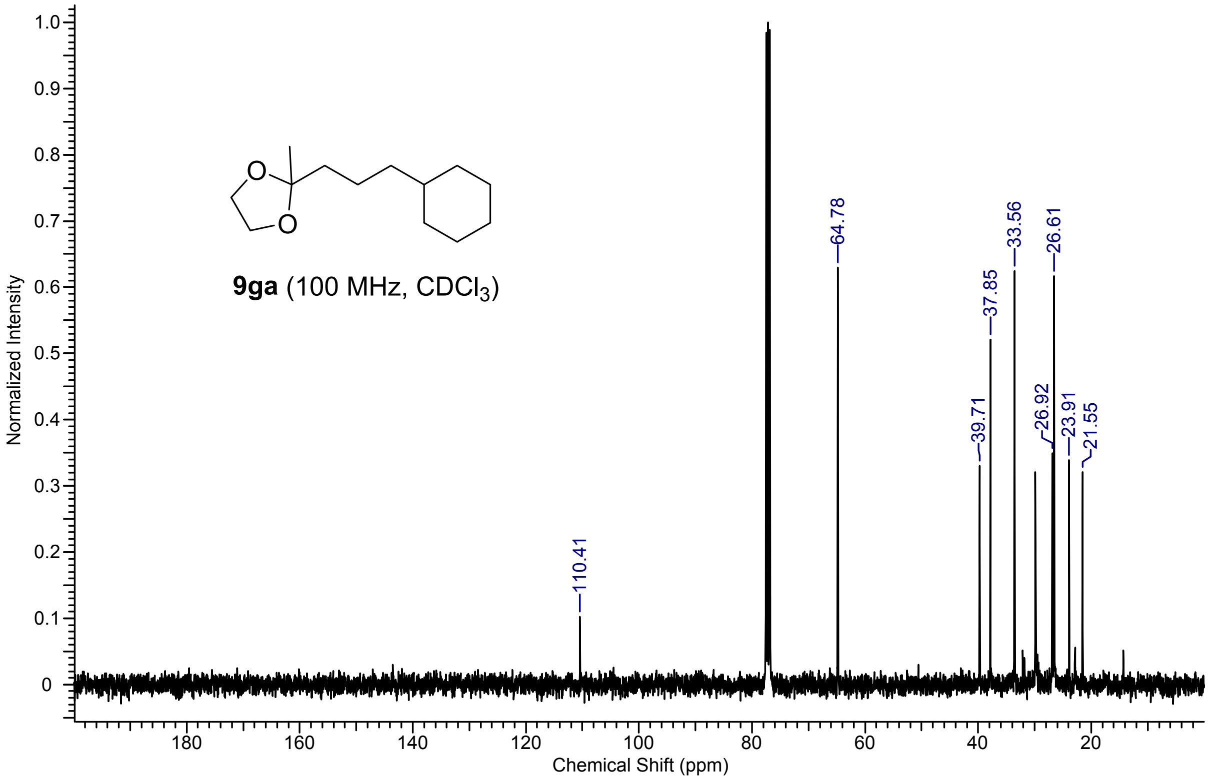

MeO
9ea (500 MHz, CDCl$_3$)
Normalized Intensity
Chemical Shift (ppm)
7.26
7.10
7.08
6.83
6.81
3.79
2.57
2.55
2.17
1.77
1.74
1.71
1.68
1.47
1.26
1.21
1.18
1.16
0.93
0.91
0.88
0.84
0.07
1.94
1.91
3.00
1.96
5.94
2.17
4.93

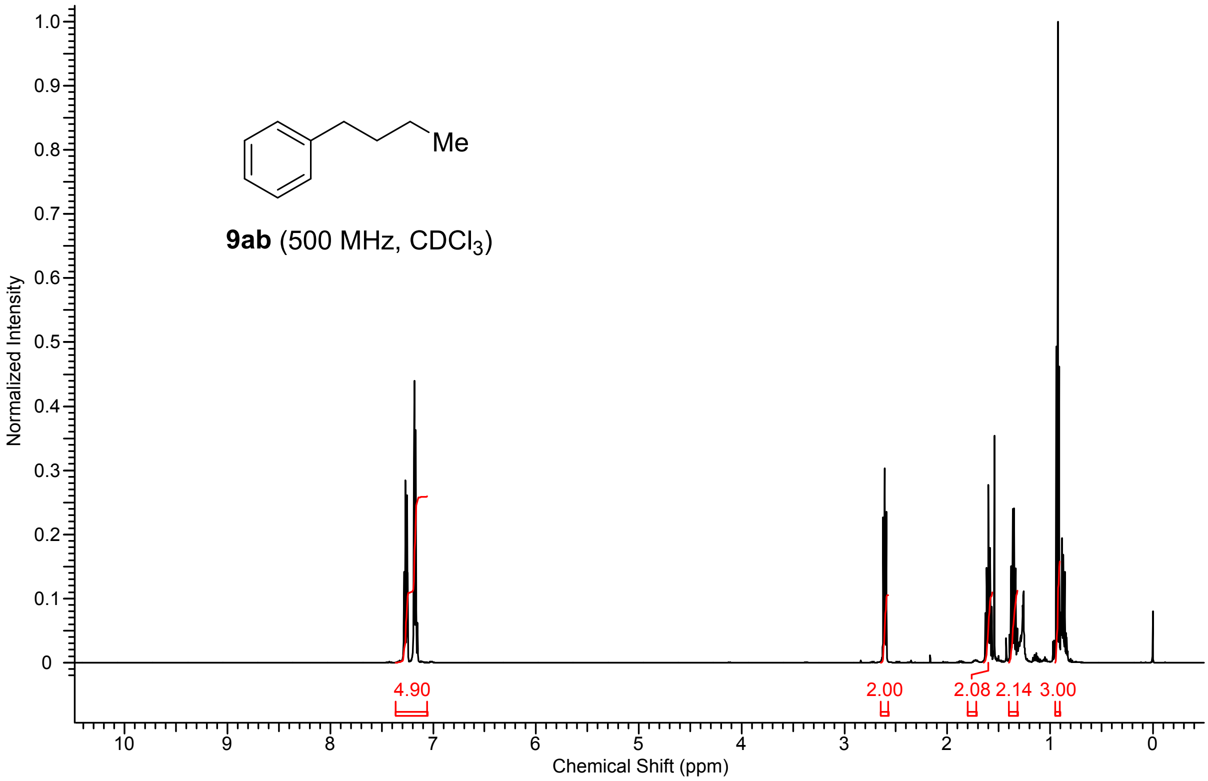

MeO
9ea (125 MHz, CDCl$_3$)
Normalized Intensity
Chemical Shift (ppm)
157.74
135.53
129.37
113.87
55.45
39.84
37.42
33.51
32.47
26.54

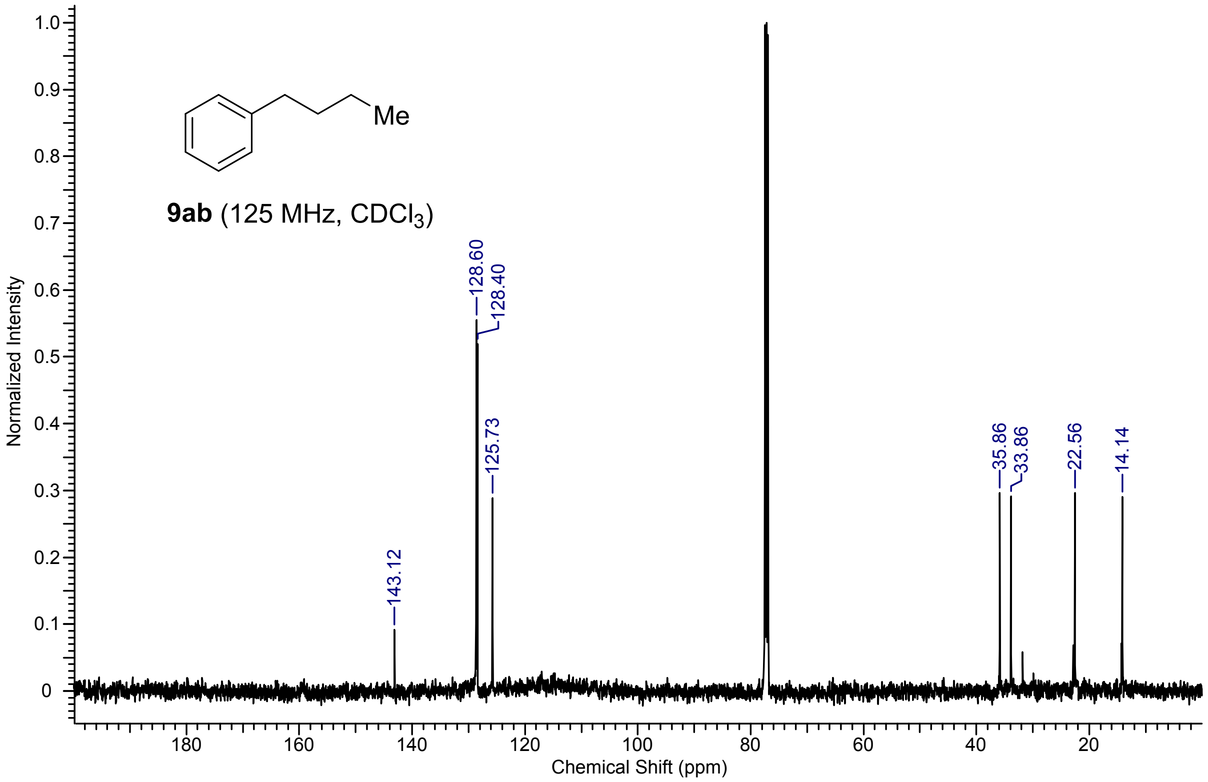

9fa (400 MHz, CDCl3)
O
O
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.00
2.07
2.08
1.09
4.06
4.02
3.96
2.07
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

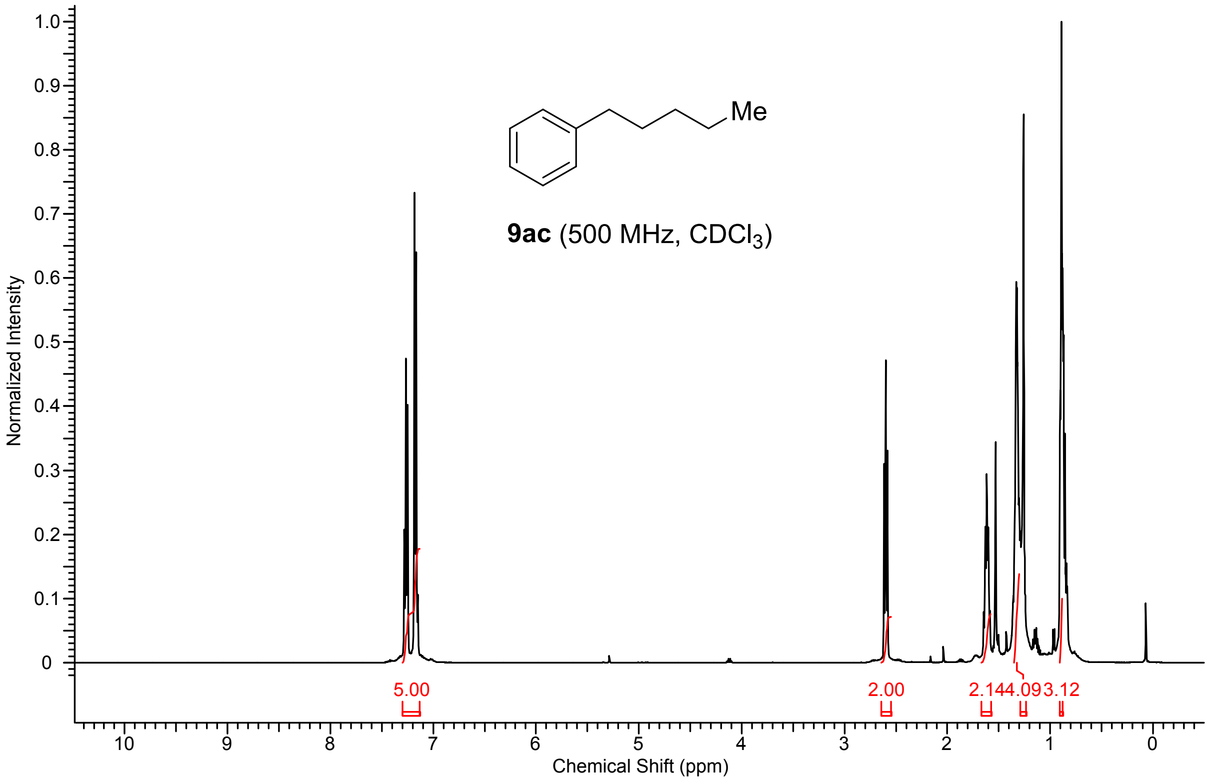

9fa (100 MHz, CDCl3)
O
O
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
103.01
67.11
37.72
33.43
26.85
26.53
26.05
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

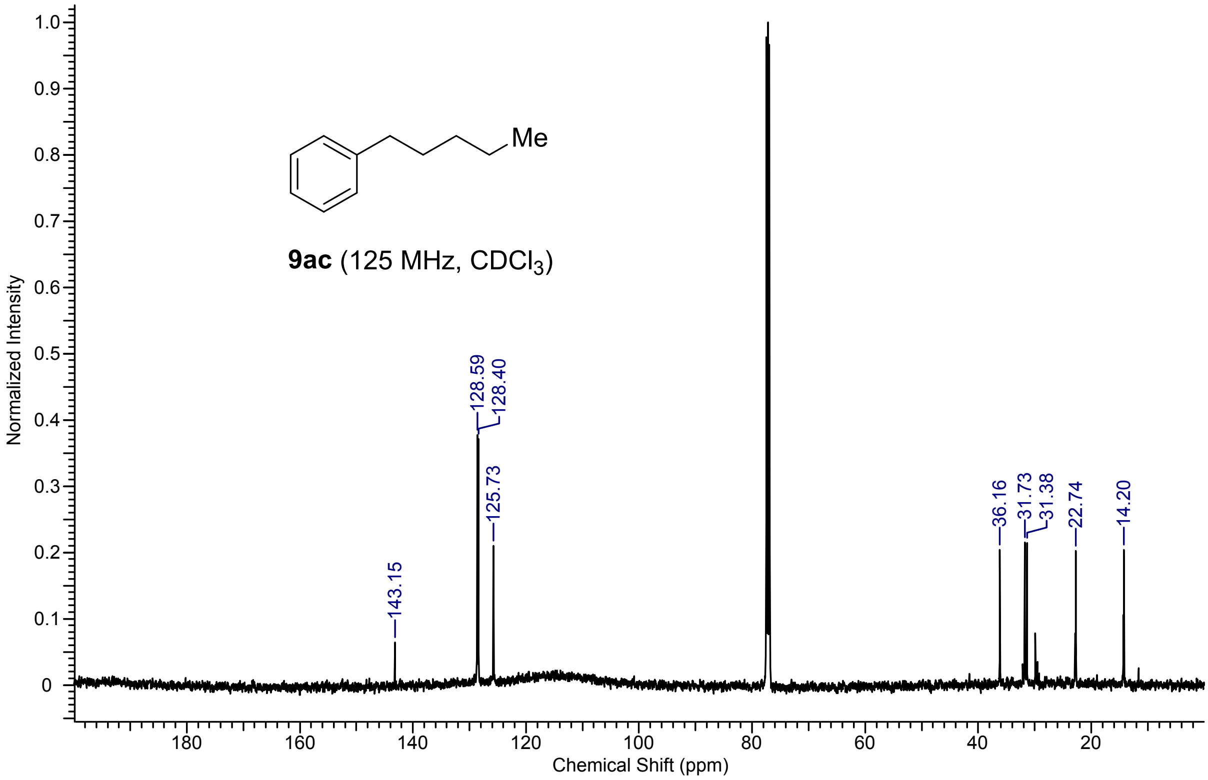

9ga (400 MHz, CDCl3)
O
O
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.00
5.01
2.03
3.98
3.00
6.04
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

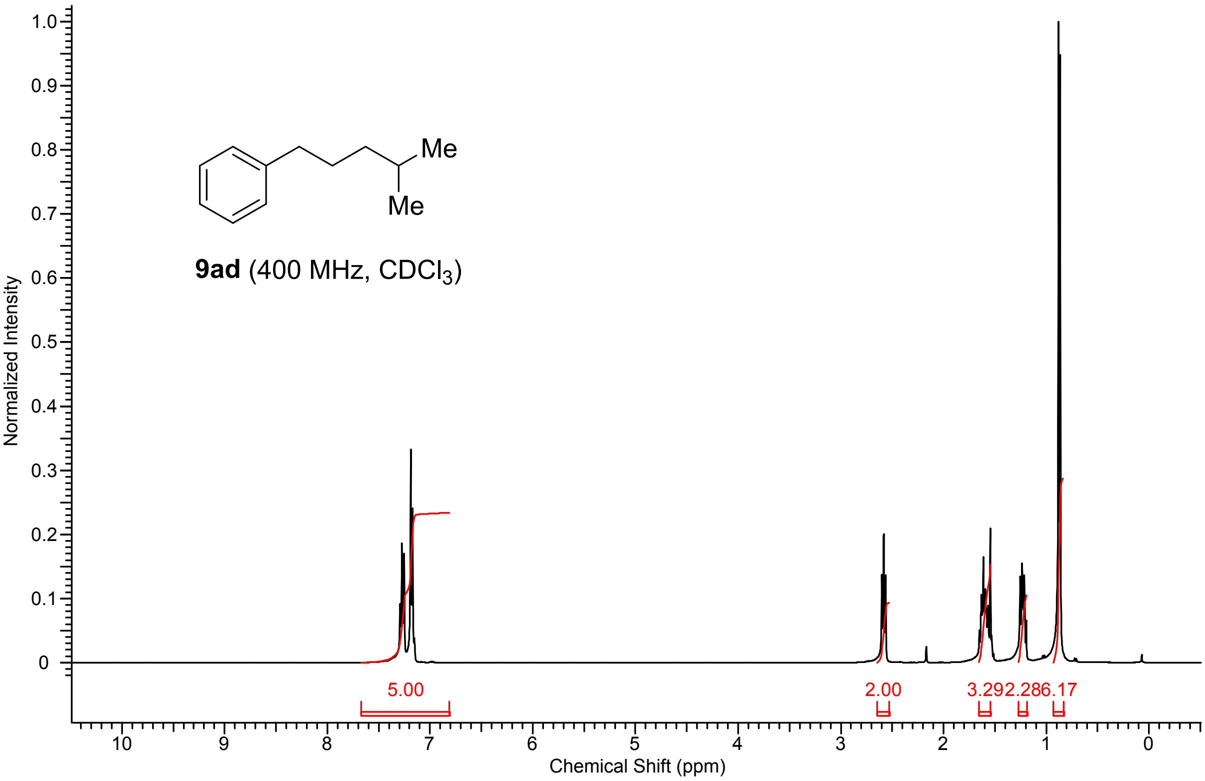

9ga (100 MHz, CDCl3)
O
O
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
110.41
64.78
39.71
37.85
33.56
26.92
26.61
23.91
21.55
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

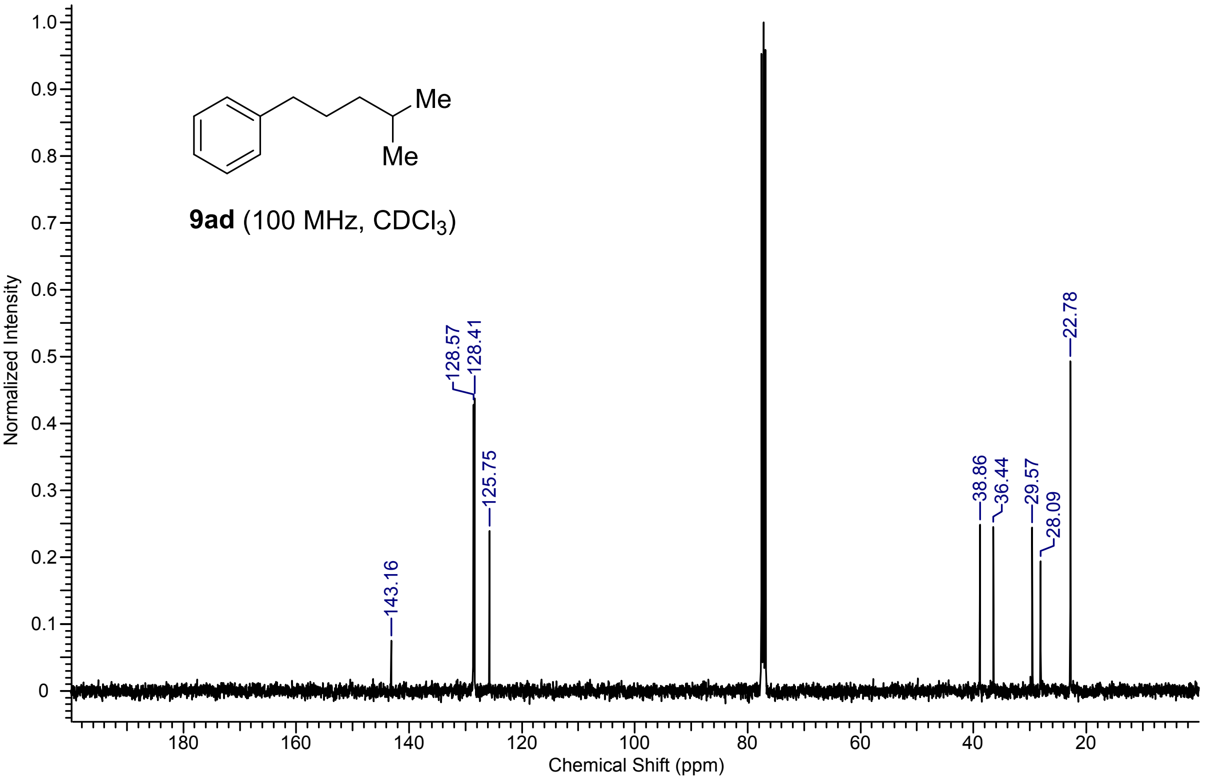

Me
**9ab** (500 MHz, $CDCl_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.90
2.00
2.08
2.14
3.00
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

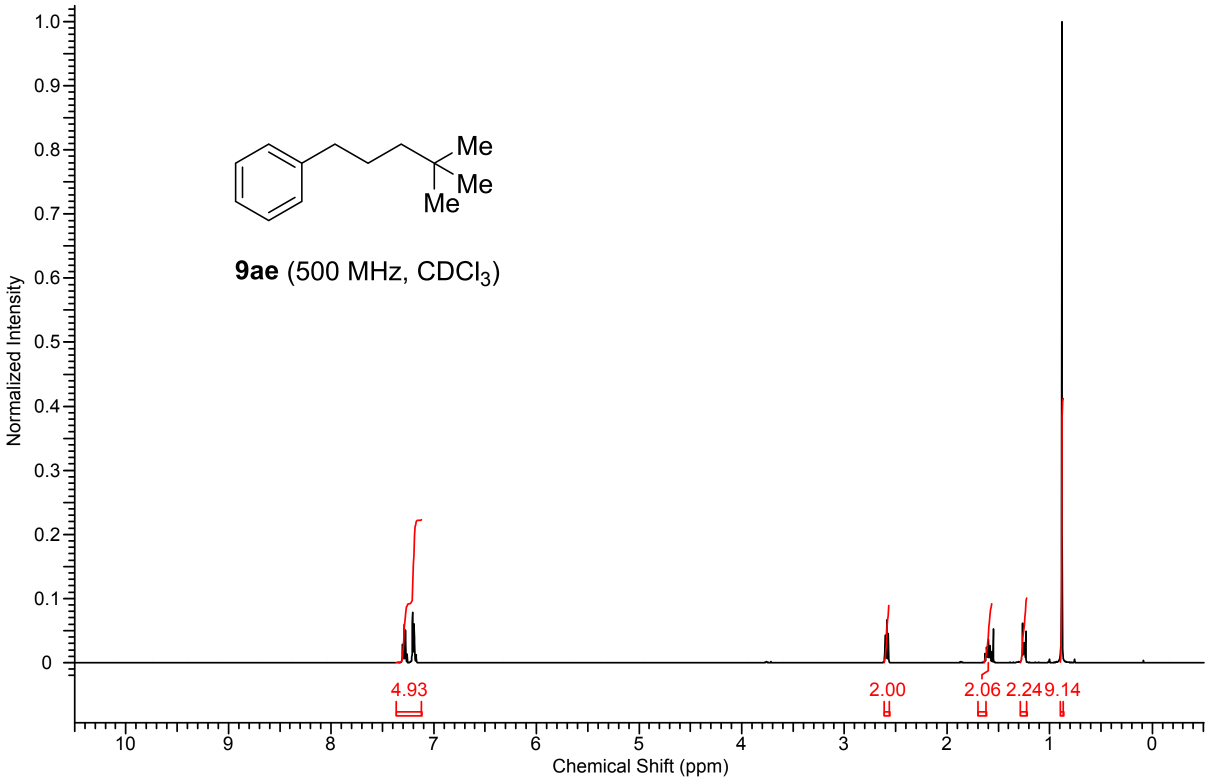

Me
**9ab** (125 MHz, $CDCl_3$)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
143.12
128.60
128.40
125.73
35.86
33.86
22.56
14.14
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

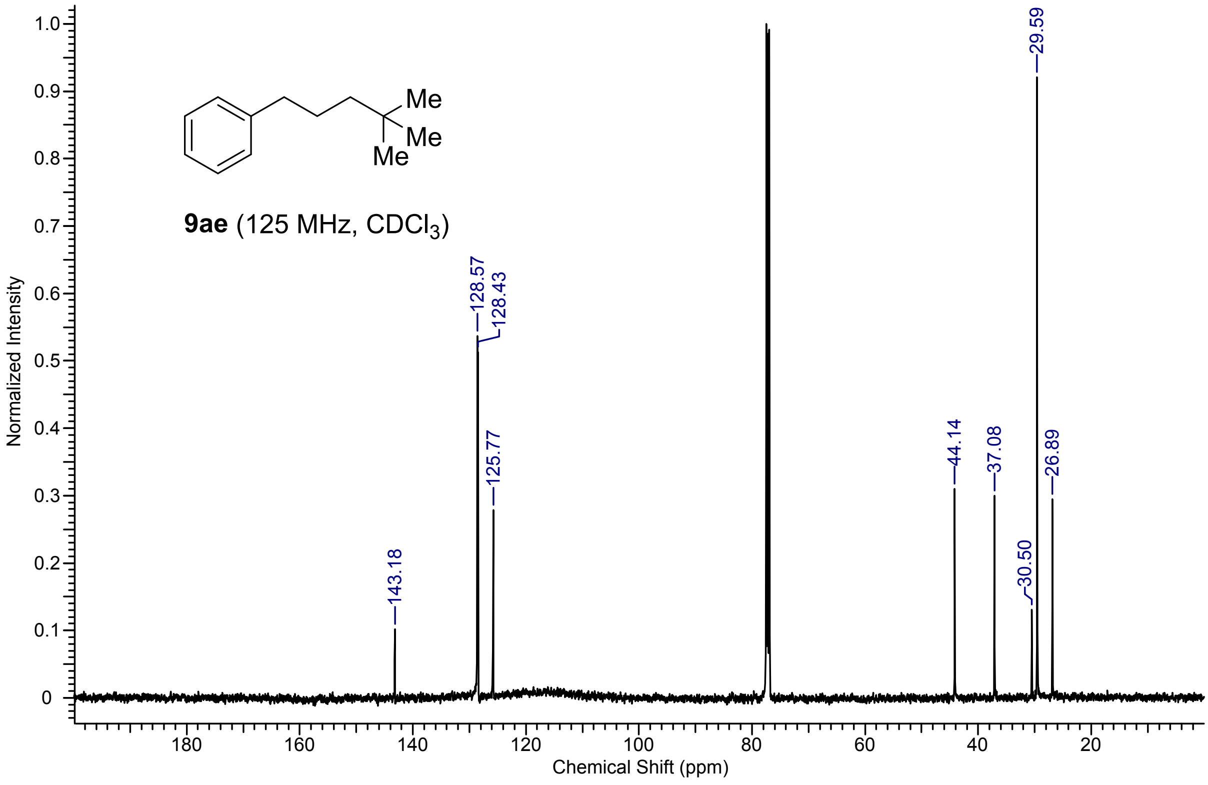

**9ac** (500 MHz, $CDCl_3$)


**9ac** (125 MHz, $CDCl_3$)


Me
Me
9ad (400 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
5.00
2.00
3.29
2.28
6.17
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

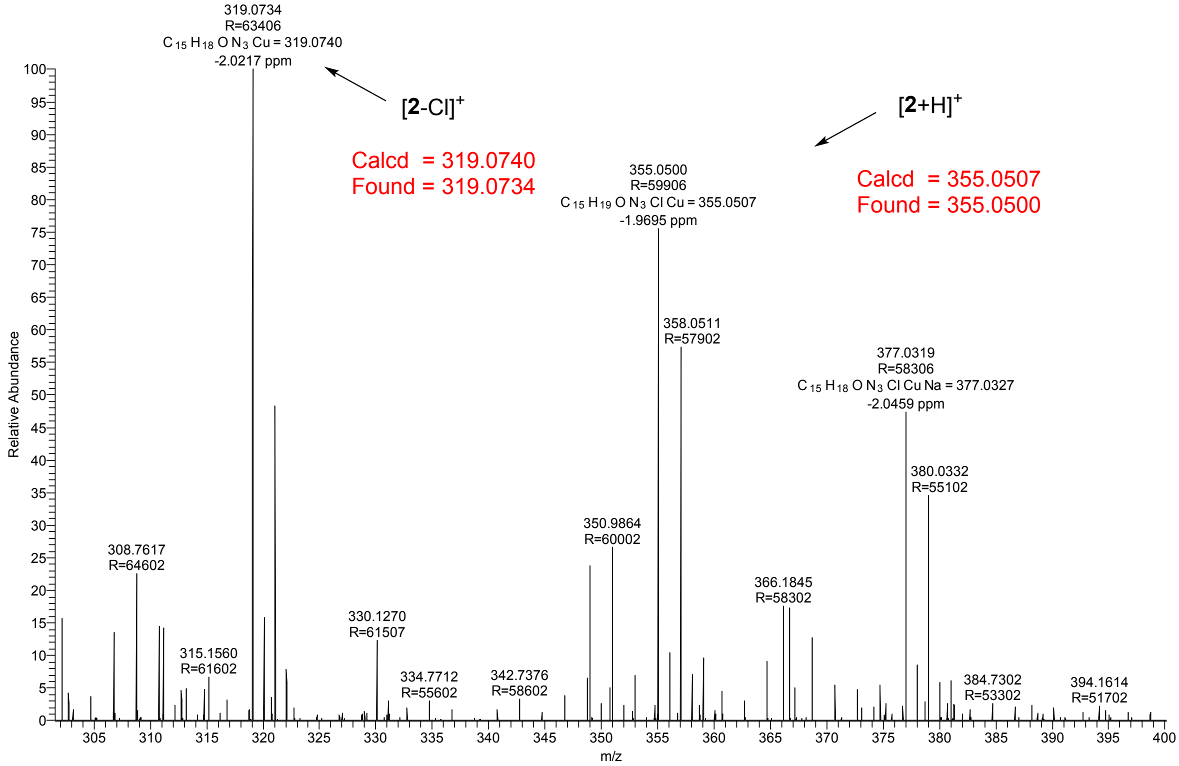

Me
Me
9ad (100 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
143.16
128.57
128.41
125.75
38.86
36.44
29.57
28.09
22.78
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)


Me
Me
Me
9ae (500 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.93
2.00
2.06
2.24
9.14
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

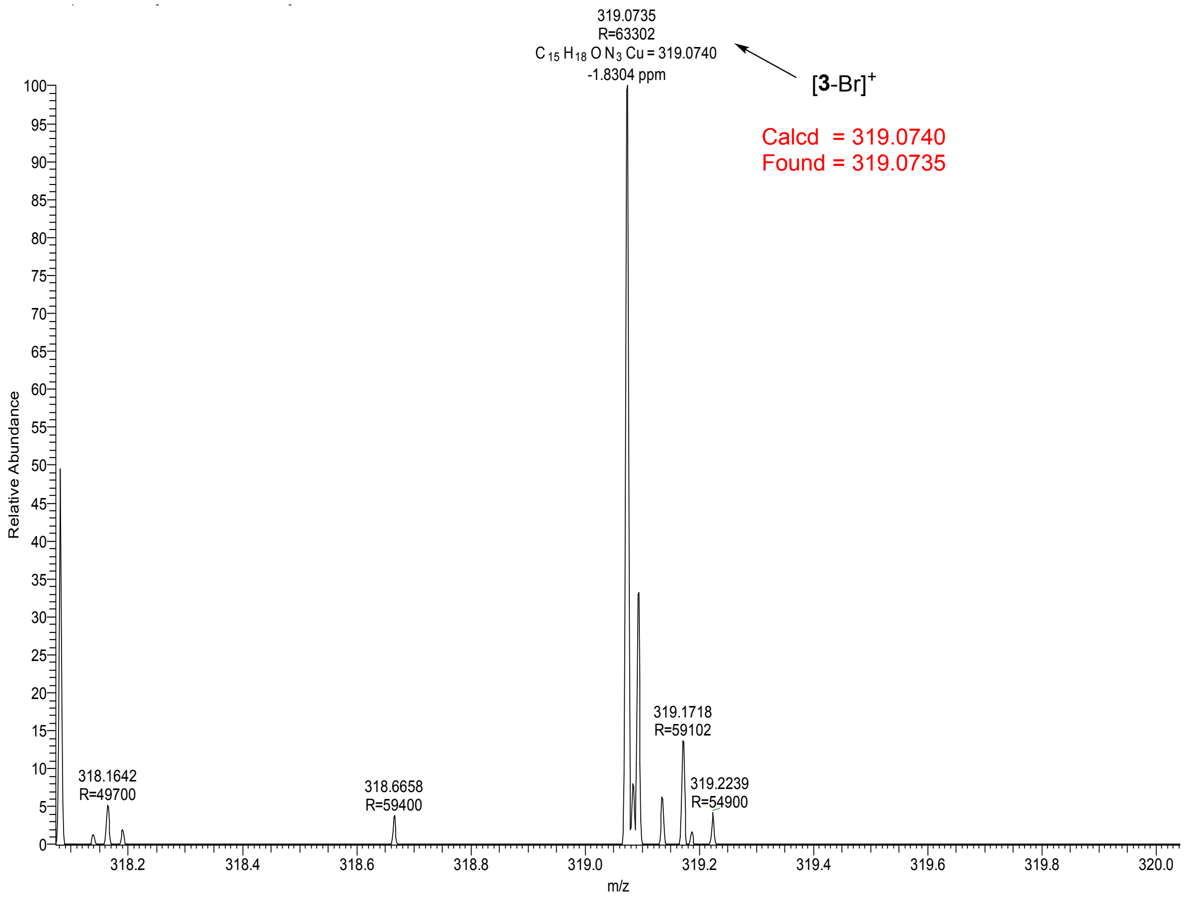

Me
Me
Me
9ae (125 MHz, CDCl3)
Normalized Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
143.18
128.57
128.43
125.77
44.14
37.08
30.50
29.59
26.89
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)

## 7. HRMS and MALDI of copper complexes

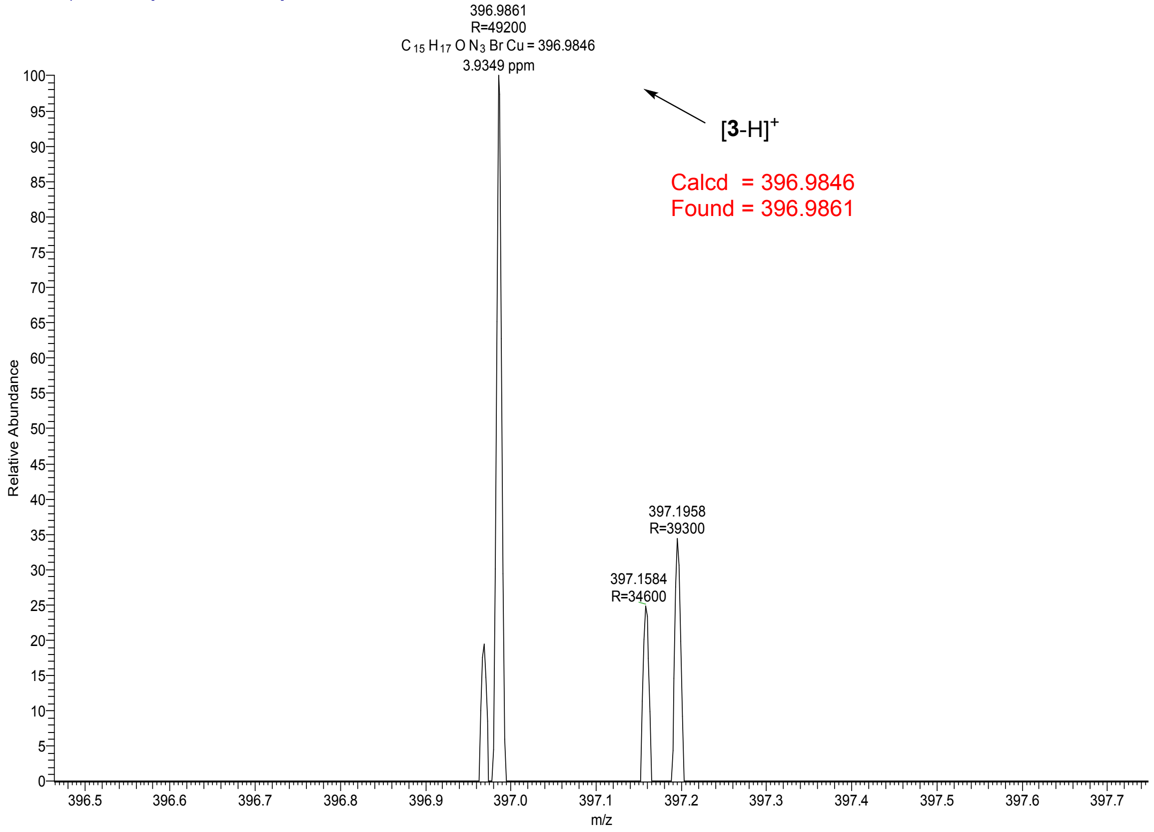
### ($^{Q}$NNN$^{Et2}$)CuCl (**2**)



## $(^{Q}NNN^{Et2})$CuBr (**3**)

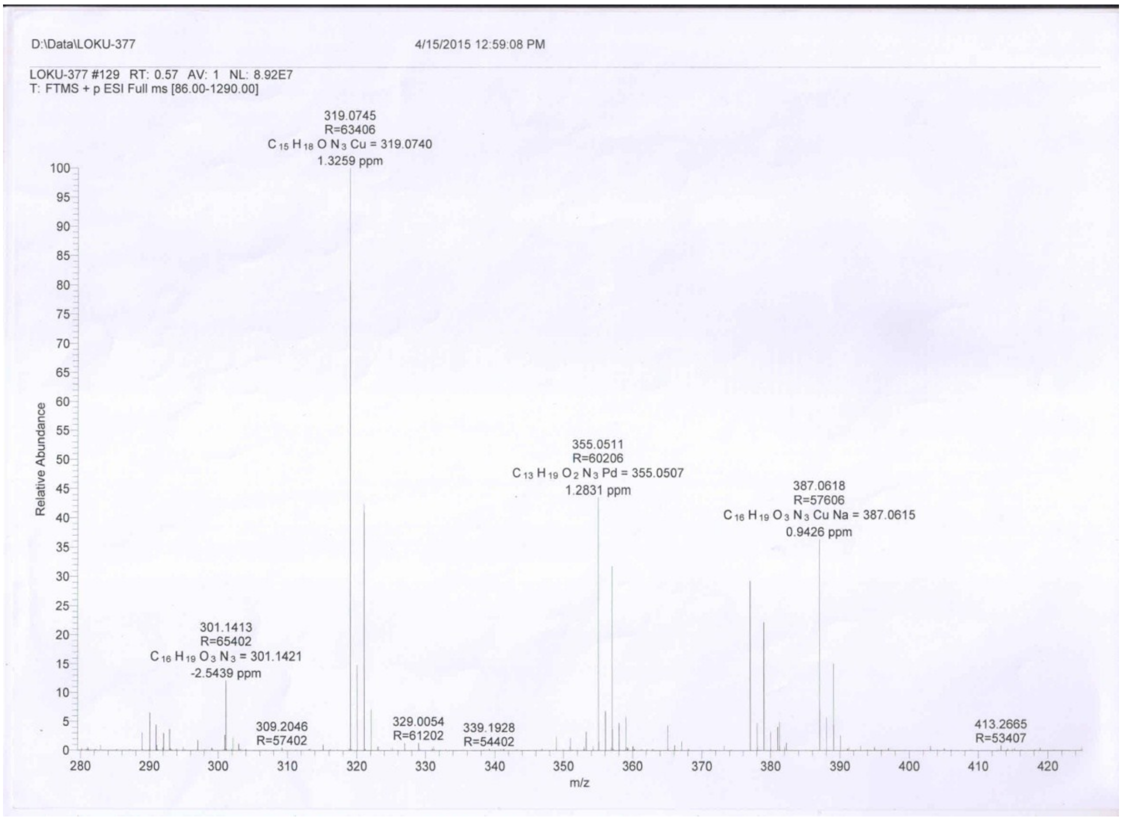


## [**3**-H]$^+$

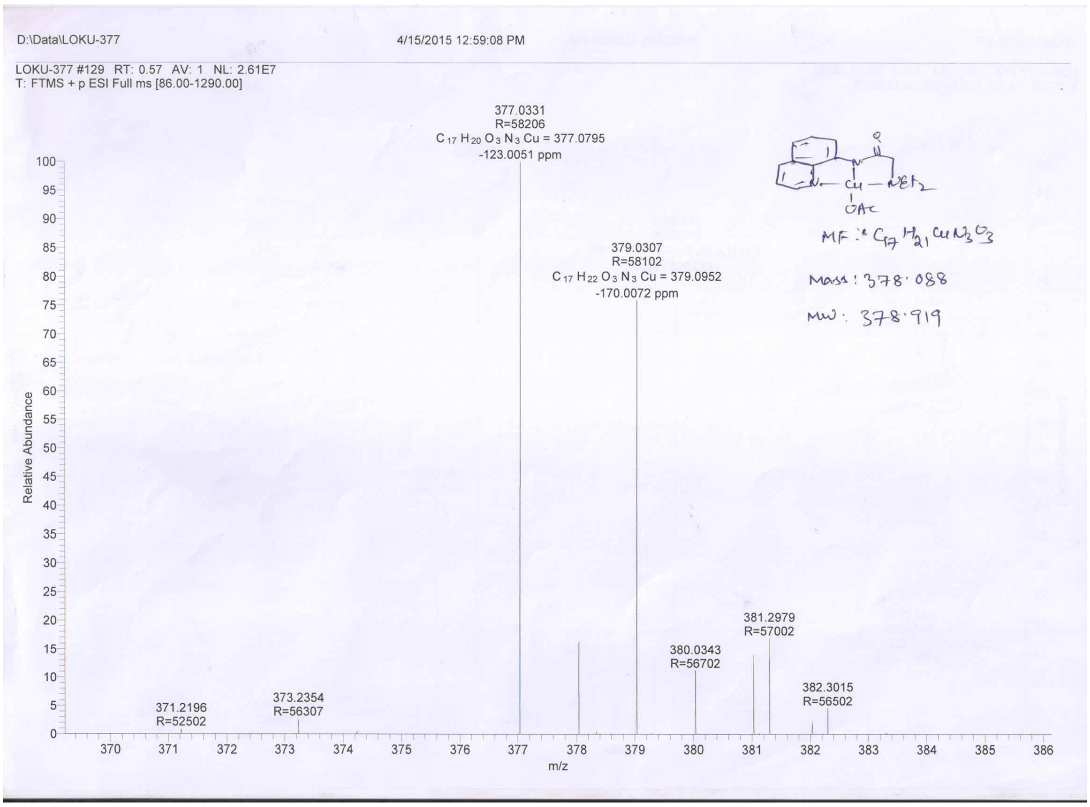


HRMS of ($^{Q}$NNN$^{Et2}$)Cu(OAc).$(H_2O)_{0.5}$ [**4**.$(H_2O)_{0.5}$]:

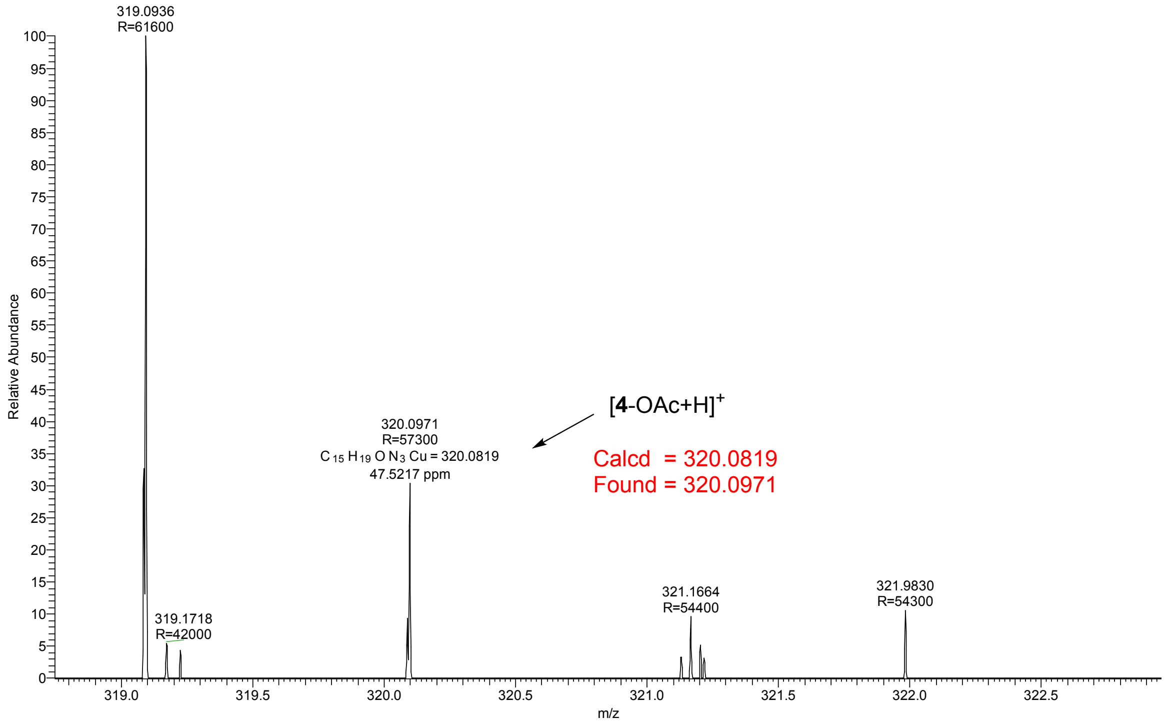
[**4**-OAc]$^+$



[**4**+H]$^+$



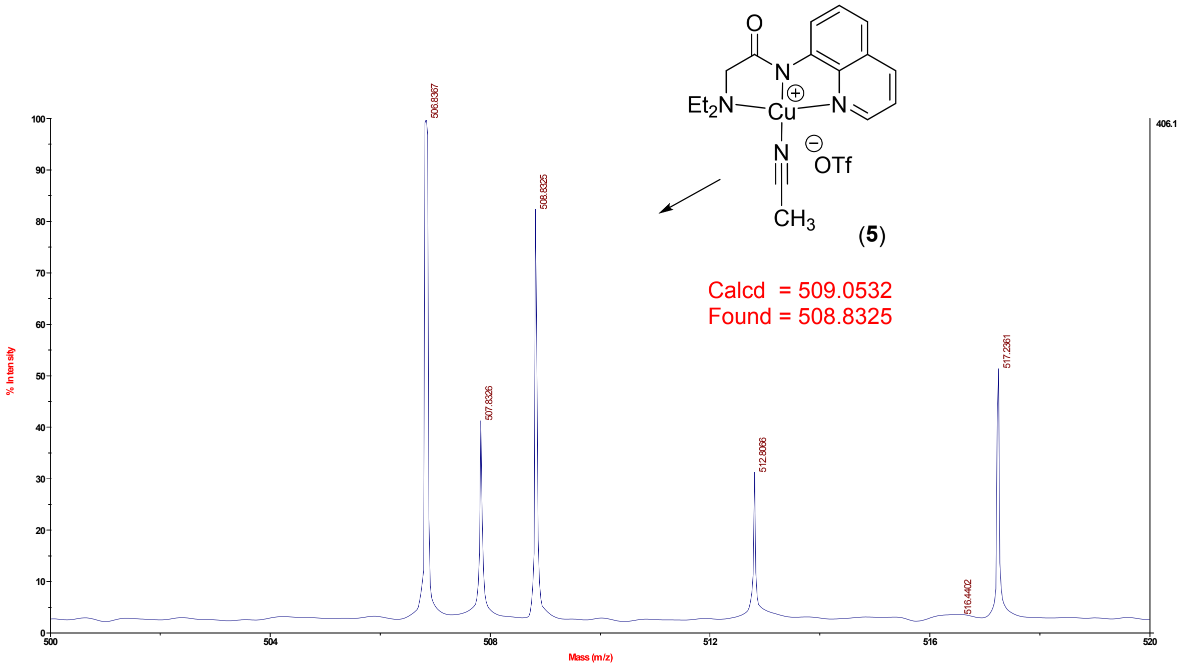
# HRMS of $[(^{Q}NNN^{Et2})Cu(OAc)]_n$ $[(\mathbf{4})_n]$



$[\mathbf{4}\text{-OAc+H}]^+$

Calcd = 320.0819
Found = 320.0971

## MALDI-TOF-MS of the complex [($^{Q}$NNN$^{Et2}$)Cu(MeCN)]OTf (**5**)



## [**5**–($CH_3CN$+OTf)]$^+$