

Reusable ammonium salt tagged NHC-copper(I) complexes: preparation and catalytic application in the three component click reactions

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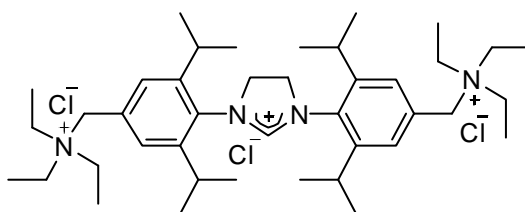
1. General Remarks

All the chemical and solvents were used as received without purification except MeOH, which was dried by distillation over magnesium powder and freshly distilled prior to use. 1,3-Bis(2,6-diisopropyl-4-(chloromethyl)phenyl)-4,5-dihydro-1H-imidazol-3-ium-chloride (**3**) was synthesized according to the reported procedure.¹ NMR spectra were recorded using a Bruker Avance TM III spectrometer operating at 400 MHz for ¹H and 100 MHz for ¹³C. Chemical shifts are given in ppm relative to TMS or to residual solvent proton resonances. High resolution mass spectra (HRMS) were obtained on a Bruker micrOTOF-QII spectrometer. All the reported yields in the catalytic studies are isolated yields and averaged by at least two runs.

2. preparation of carbene precursor and their copper complexes

1,3-bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**4a**)

10 mL triethylamine was added slowly to a MeOH solution (80 mL) of freshly synthesized intermediate **3** (2 g, 3.82 mmol) at room temperature, the reaction mixture was subsequently refluxed for 24 h. The solvent and excess tertiary amines were evaporated under the reduced pressure, and 100 mL of anhydrous ether was added to precipitate the product, and the resultant white powder was collected and washed with 10 mL of ether three times to give the corresponding ammonium salt tagged carbene precursor **4a** (2.61 g, 94%).

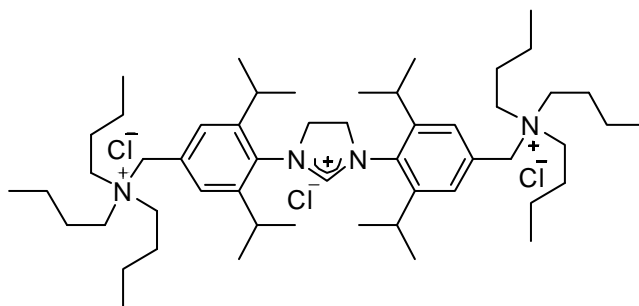


¹H NMR (D₂O): 1.23 (t, 12 H), 1.35-1.40 (m, 30 H), 3.07-3.14 (m, 4 H, *J* = 6.8 Hz), 3.16-3.25 (m, 12 H), 4.46 (s, 4 H), 4.59 (s, 4 H), 7.46 (s, 4 H); ¹H NMR (DMSO-*d*₆): 1.21 (d, 12 H, *J* = 6.8 Hz), 1.31-1.38 (m, 30 H, *J* = 6.8 Hz), 3.13 (t, 4 H, *J* = 6.4 Hz), 3.16-3.22 (m, 12 H, *J* = 7.2 Hz), 4.59 (d, 8 H, *J* = 10.4 Hz), 7.57 (s, 4H), 9.82 (s, 1 H); ¹³C NMR (D₂O): 7.0, 22.4, 24.2, 28.7, 52.6, 53.6, 59.8, 128.8, 130.5, 131.1, 147.7. HRMS *m/z* (ESI) calcd for C₄₁H₇₁N₄ [cation]³⁺ 206.5221, found 206.5226.

1,3-bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl)-4,5-dihydro-1H-imidazol-3-ium chloride (**4b**)

Imidazolium salts **3** (2 g, 3.82 mmol) was dissolved in 80 mL methanol, then 10 mL tributylamine was added to the solution, and the reaction mixture was refluxed for 24 h. The solvent and excess tributylamine were evaporated under reduced pressure, and 100 mL anhydrous ether was added to the residue, the mixture was vigorously stirred for 12 h. A filtration of the mixture afforded ligand **4b** as a white solid (3.14 g, 92%).

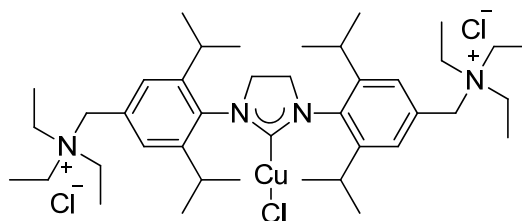
¹ V. Sashuk, D. Schoeps and H. Plenio, *Chem. Commun.*, 2009, 770-772.



^1H NMR (D_2O): 0.95 (t, 18 H, $J = 7.2$ Hz), 1.21 (d, 16 H, $J = 6.8$ Hz), 1.36 (d, 20 H, $J = 6.8$ Hz), 1.79 (s, 12 H), 3.08-3.14 (m, 16 H), 4.48 (s, 4 H), 4.58 (s, 4 H), 7.43 (s, 4 H); ^1H NMR ($\text{DMSO-}d_6$): 0.97 (t, 18 H), 1.21 (d, 16 H, $J = 6.8$ Hz), 1.28-1.37 (m, 20 H), 1.76 (s, 12 H), 3.15 (t, 16 H), 4.58 (s, 4 H), 4.65 (s, 4 H), 7.59 (s, 4 H), 9.89 (s, 1 H); ^{13}C NMR ($\text{DMSO-}d_6$): 13.6, 13.4, 23.3, 24.8, 28.2, 45.4, 53.8, 56.0, 57.9, 60.9, 125.4, 129.4, 131.0, 131.4, 146.8, 160.2. HRMS m/z (ESI) calcd for $\text{C}_{53}\text{H}_{95}\text{N}_4$ [cation] $^{3+}$ 262.5847, found 262.5853.

(1,3-bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) chloride (5a)

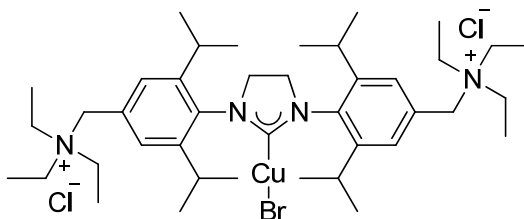
An oven-dried Schlenk flask was charged with **4a** (726 mg, 1.0 mmol), CuCl (109 mg, 1.1 mmol) and KO t -Bu (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **5a** was slowly precipitated and isolated as a yellow solid (584 mg, 74%).



^1H NMR (D_2O): 1.20-1.30 (m, 42 H), 3.10-3.16 (m, 16 H), 4.14 (s, 4 H), 4.36 (s, 4 H), 7.33 (s, 4 H); ^{13}C NMR (D_2O): 7.1, 22.7, 24.7, 28.3, 52.6, 53.5, 60.3, 128.6, 136.4, 148.7, 201.1. HRMS m/z (ESI) calcd for $\text{C}_{41}\text{H}_{70}\text{ClCuN}_4$ [cation] $^{2+}$ 358.2287, found 358.2295.

(1,3-bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) bromide dichloride (5b)

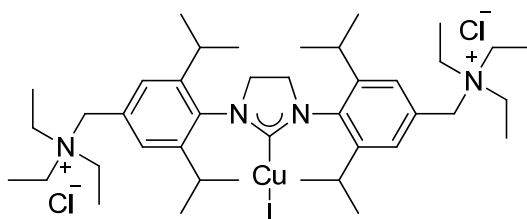
An oven-dried Schlenk flask was charged with **4a** (726 mg, 1.0 mmol), CuBr·SMe $_2$ (226 mg, 1.1 mmol) and KO t -Bu (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **5b** was slowly precipitated and isolated as a white solid (640 mg, 77%).



^1H NMR (D_2O): 1.16-1.20 (m, 24 H), 1.25 (t, 18 H, $J = 7$ Hz), 3.03-3.13 (m, 16 H), 4.10 (s, 4 H), 4.33 (s, 4 H), 7.30 (s, 4 H); ^{13}C NMR (D_2O): 7.0, 22.7, 24.6, 28.3, 52.6, 53.4, 60.3, 128.5, 136.4, 148.7, 201.3. HRMS m/z (ESI) calcd for $\text{C}_{41}\text{H}_{70}\text{BrCuN}_4$ [cation] $^{2+}$ 380.2034, found 380.2035.

(1,3-bis(2,6-diisopropyl-4-((triethylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) iodide dichloride (5c)

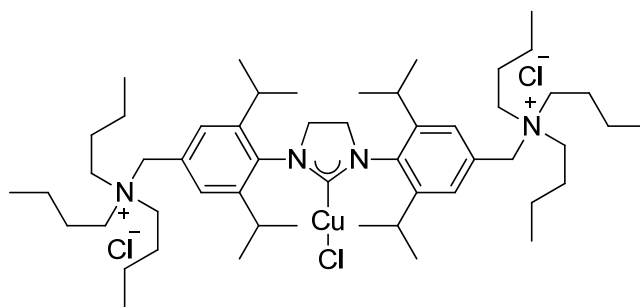
An oven-dried Schlenk flask was charged with **4a** (726 mg, 1.0 mmol), CuI (209 mg, 1.1 mmol) and KO t -Bu (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **5c** was slowly precipitated and isolated as a white solid (705 mg, 80%).



^1H NMR (D_2O): 1.10-1.15 (m, 24 H), 1.27 (t, 18 H, $J = 7$ Hz), 3.00-3.07 (m, 16 H), 3.98 (s, 4 H), 4.30 (s, 4 H), 7.21 (s, 4 H); ^{13}C NMR (D_2O): 7.0, 23.2, 24.6, 28.2, 52.3, 53.1, 59.8, 128.0, 137.2, 148.6, 201.4. HRMS m/z (ESI) calcd for $\text{C}_{41}\text{H}_{70}\text{ICuN}_4$ [cation] $^{2+}$ 404.1965, found 404.1950.

(1,3-bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) chloride (6a)

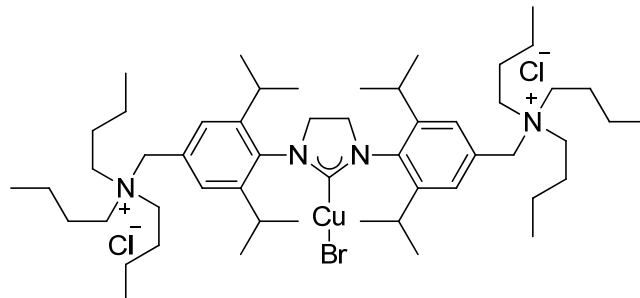
An oven-dried Schlenk flask was charged with **4b** (895 mg, 1.0 mmol), CuCl (109 mg, 1.1 mmol) and KO t -Bu (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **6a** was slowly precipitated and isolated as a yellow solid (680 mg, 71%).



^1H NMR (D_2O): 0.85 (d, 18 H, $J = 7.2$ Hz), 1.20-1.26 (m, 32 H), 1.68 (s, 12 H), 1.98 (s, 4 H), 3.11 (s, 16 H), 4.12 (s, 4 H), 4.38 (s, 4 H), 7.29 (s, 4 H); ^{13}C NMR ($\text{DMSO}-d_6$): 13.5, 19.3, 23.4, 24.9, 28.1, 53.7, 57.9, 61.5, 129.1, 131.1, 136.2, 147.1, 201.0. HRMS m/z (ESI) calcd for $\text{C}_{53}\text{H}_{94}\text{ClCuN}_4$ [cation] $^{2+}$ 442.3226, found 442.3224.

(1,3-bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) bromide dichloride (6b)

An oven-dried Schlenk flask was charged with **4b** (895 mg, 1.0 mmol), $\text{CuBr}\cdot\text{SMe}_2$ (226 mg, 1.1 mmol) and $\text{KO}t\text{-Bu}$ (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **6b** was slowly precipitated and isolated as a white solid (822 mg, 82%).

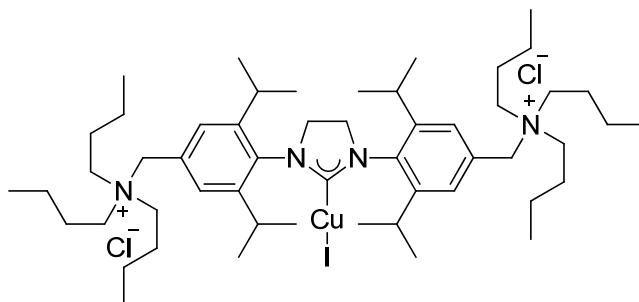


^1H NMR (D_2O): 0.82-0.88 (m, 18 H), 1.19-1.28 (m, 32 H), 1.69 (s, 12 H), 2.05 (s, 4 H), 3.03 (d, 16 H, $J = 4.8$ Hz), 4.13 (s, 4 H), 4.39 (d, 4 H, $J = 5.2$ Hz), 7.30 (s, 4 H); ^{13}C NMR ($\text{DMSO}-d_6$): 13.5, 19.4, 23.3, 25.0, 28.2, 53.7, 58.0, 61.2, 129.2, 131.1, 136.2, 147.1, 201.1. HRMS m/z (ESI) calcd for $\text{C}_{53}\text{H}_{94}\text{BrCuN}_4$ [cation] $^{2+}$ 464.2973, found 464.2977.

(1,3-bis(2,6-diisopropyl-4-((tributylammonio)methyl)phenyl)imidazolidin-2-yl)copper(I) iodide dichloride (6c)

An oven-dried Schlenk flask was charged with **4b** (895 mg, 1.0 mmol), CuI (209 mg, 1.1 mmol) and $\text{KO}t\text{-Bu}$ (135 mg, 1.0 mmol). The flask was evacuated and backfilled with argon three times before the addition of dried methanol (30 mL), then the mixture was refluxed for 12h. After the completion of reaction, the resultant reaction mixture was filtered through a plug of celite, and the filtrate was concentrated to about 10 mL under reduced pressure. Upon the addition of pentane to the crude reaction mixture, complex **6c** was slowly precipitated and isolated as a white solid (819

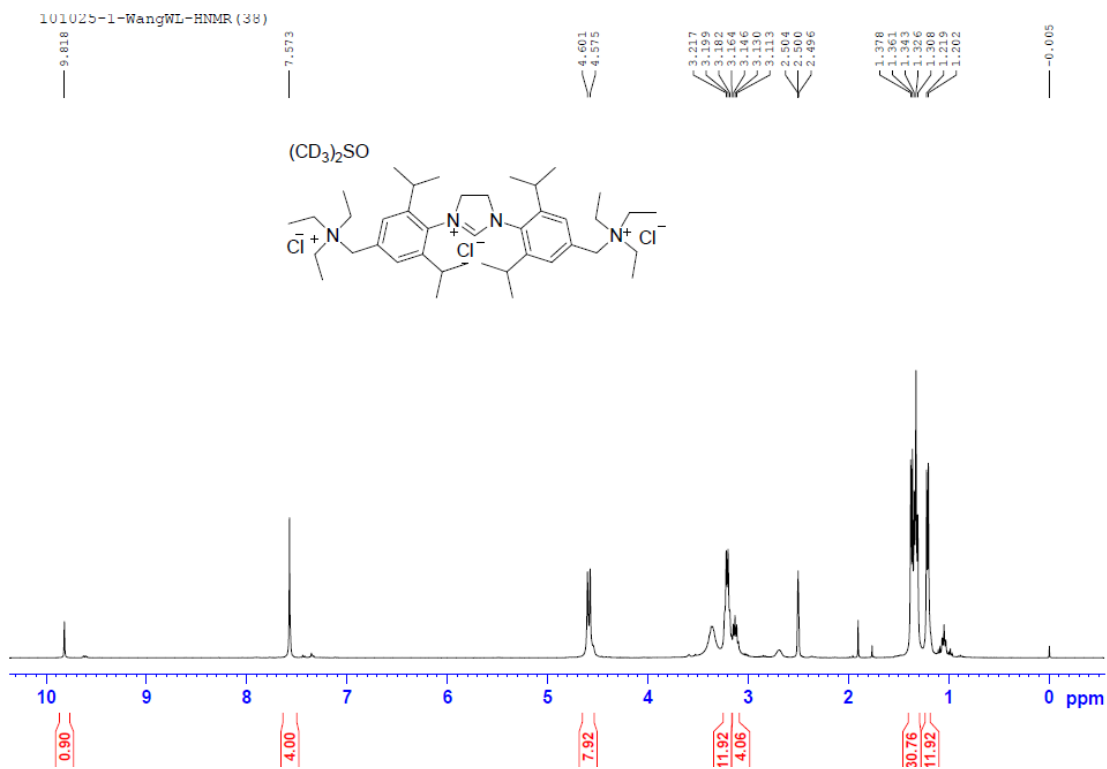
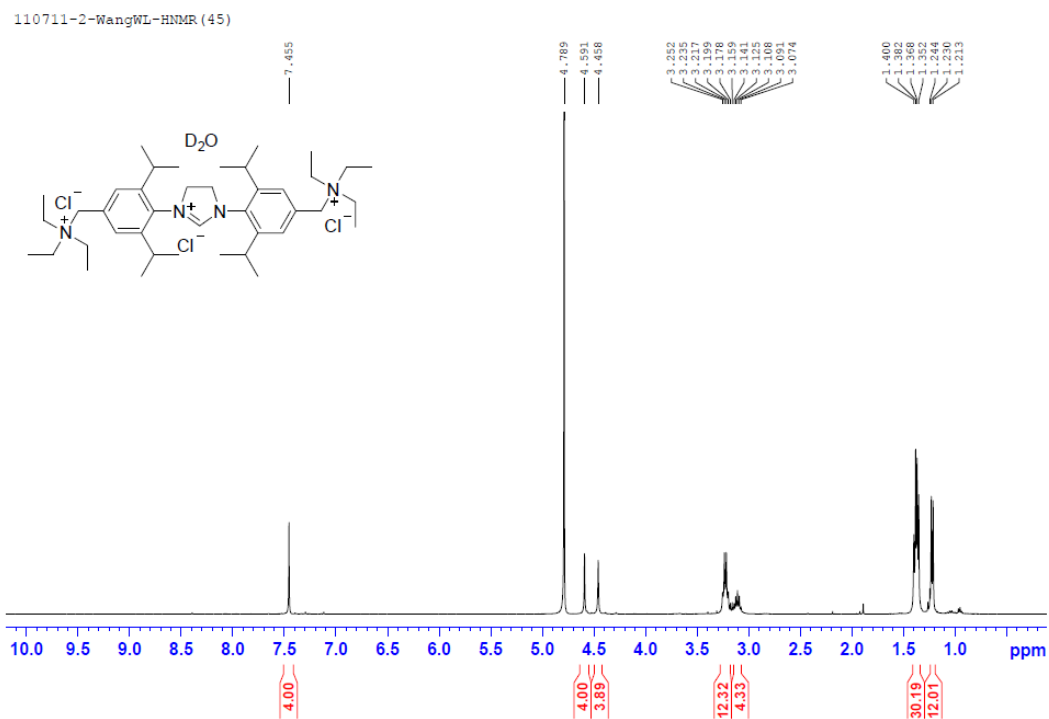
mg, 78%).



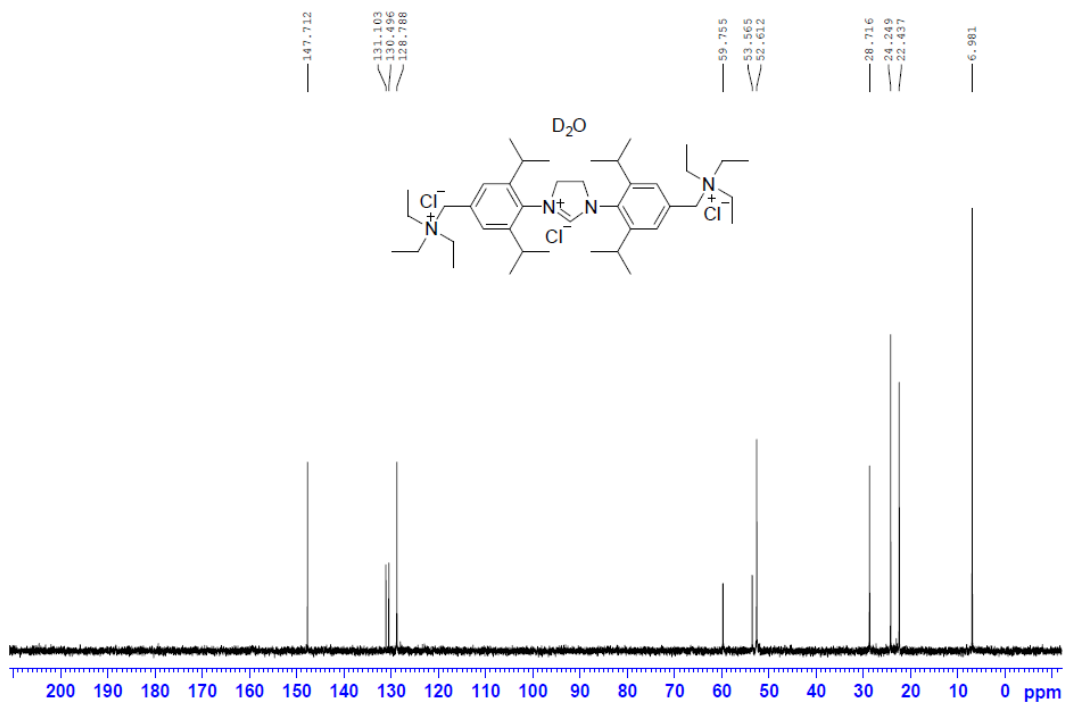
^1H NMR (D_2O): 0.83 (t, 18 H, $J = 7.2$ Hz), 1.18-1.24 (m, 32 H), 1.67 (s, 12 H), 1.93 (s, 4 H), 3.01 (s, 16 H), 4.12 (s, 4 H), 4.38 (s, 4 H), 7.29 (s, 4 H); ^{13}C NMR ($\text{DMSO-}d_6$): 13.5, 19.4, 23.4, 24.9, 28.1, 53.6, 57.9, 61.5, 129.1, 131.1, 136.2, 147.2, 201.1. HRMS m/z (ESI) calcd for $\text{C}_{53}\text{H}_{94}\text{ICuN}_4$ [cation] $^{2+}$ 488.2904, found 488.2909.

3. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ copies

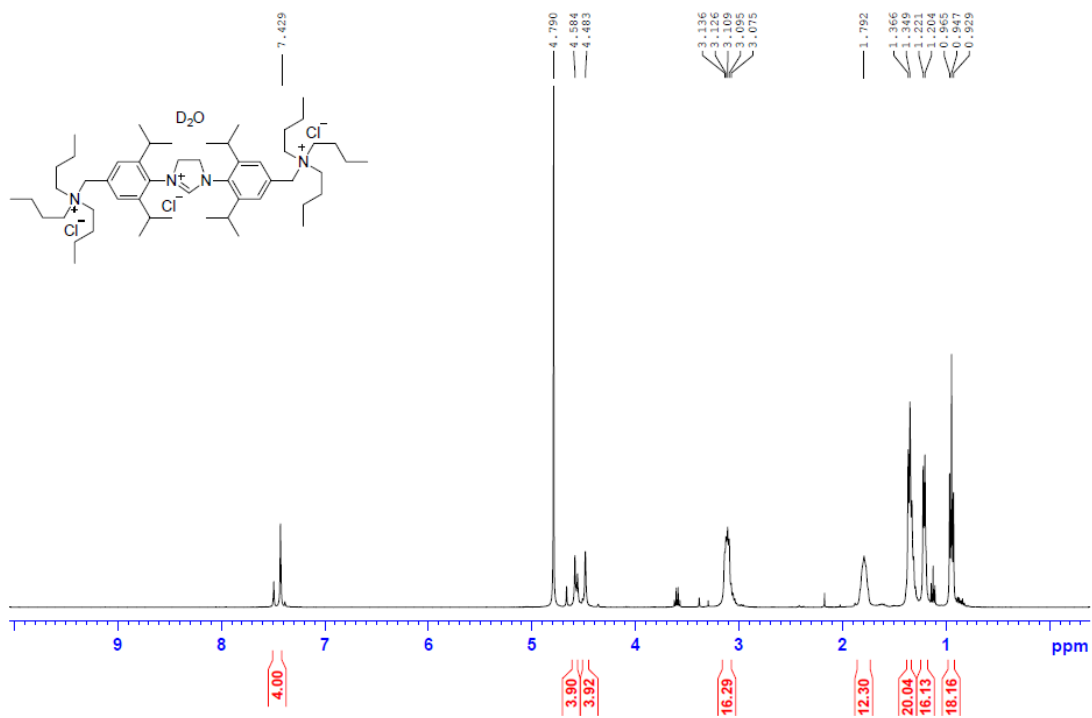
3.1 NMR copies of new compounds



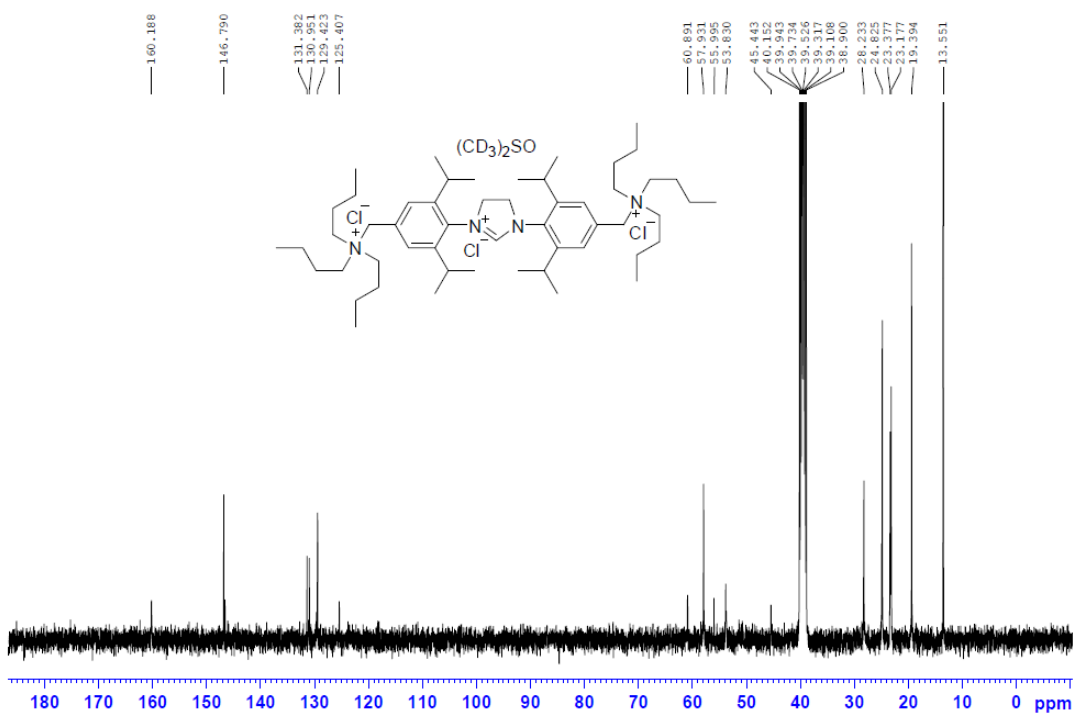
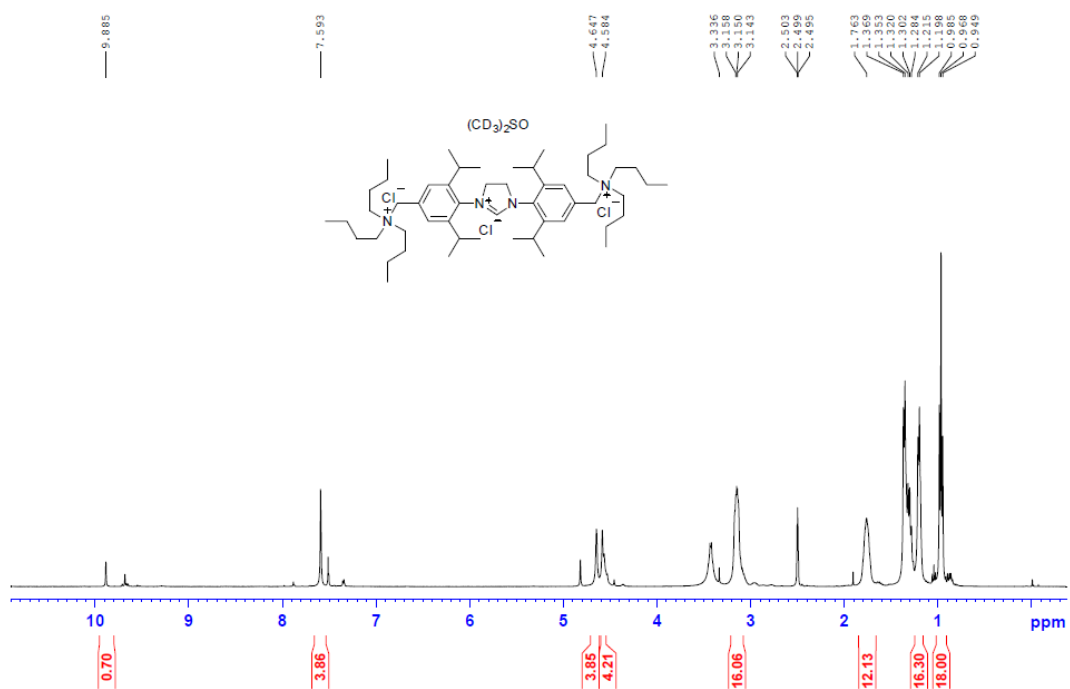
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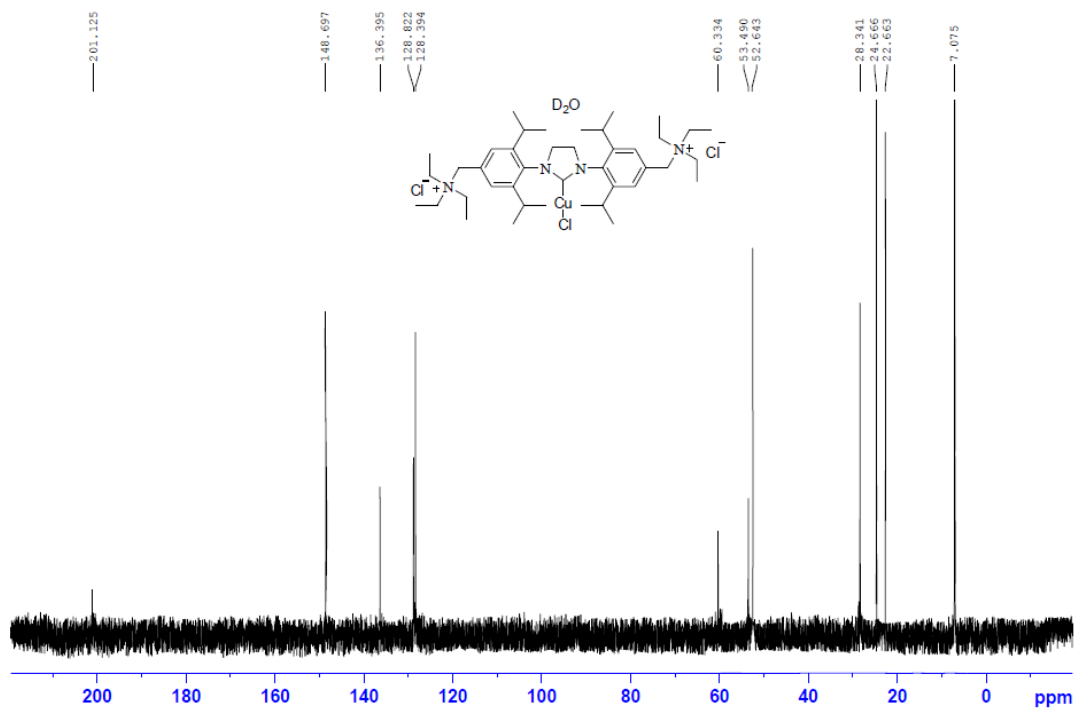
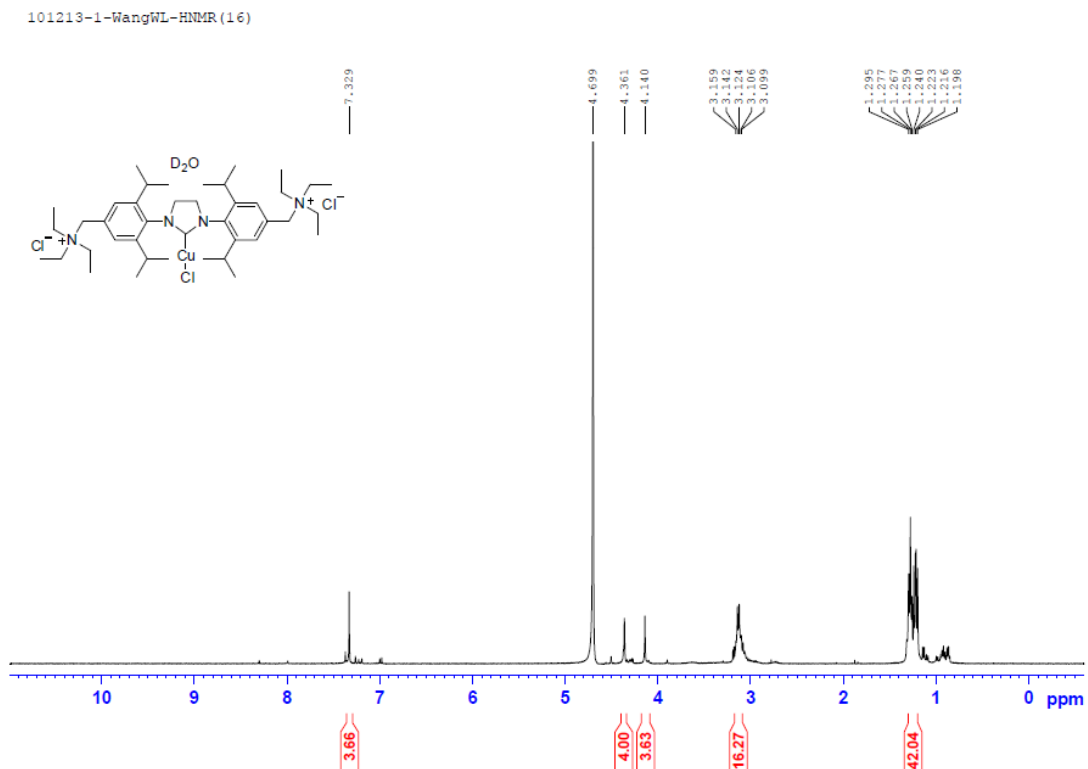


110118-ZXH-4-HNMR

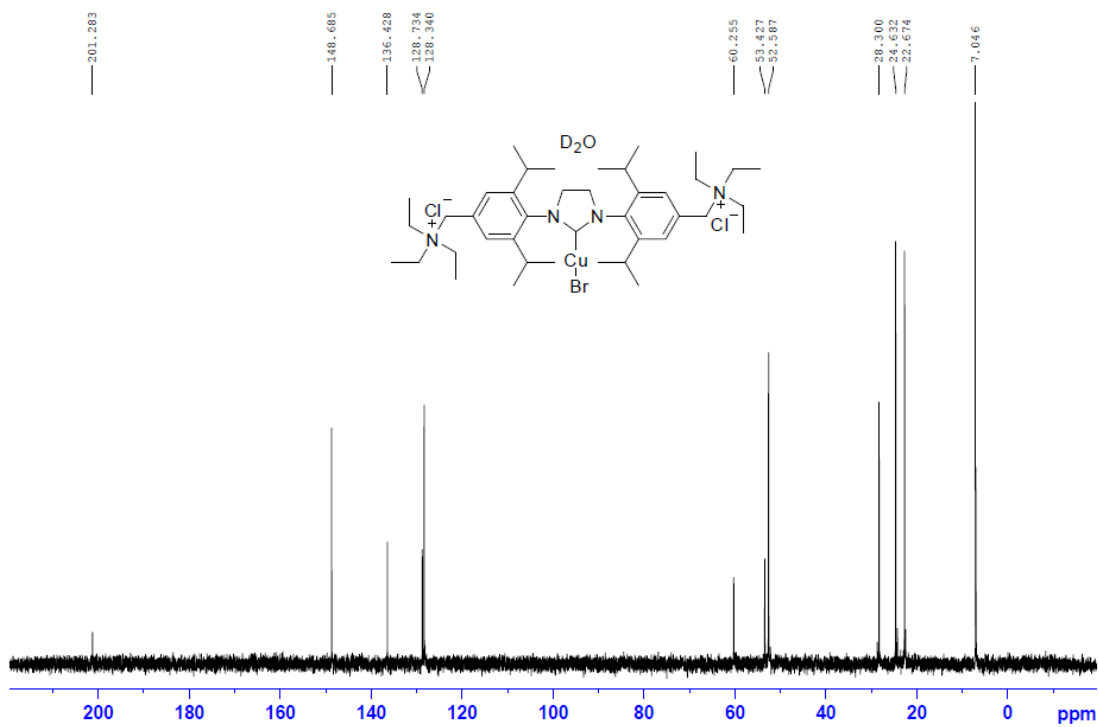
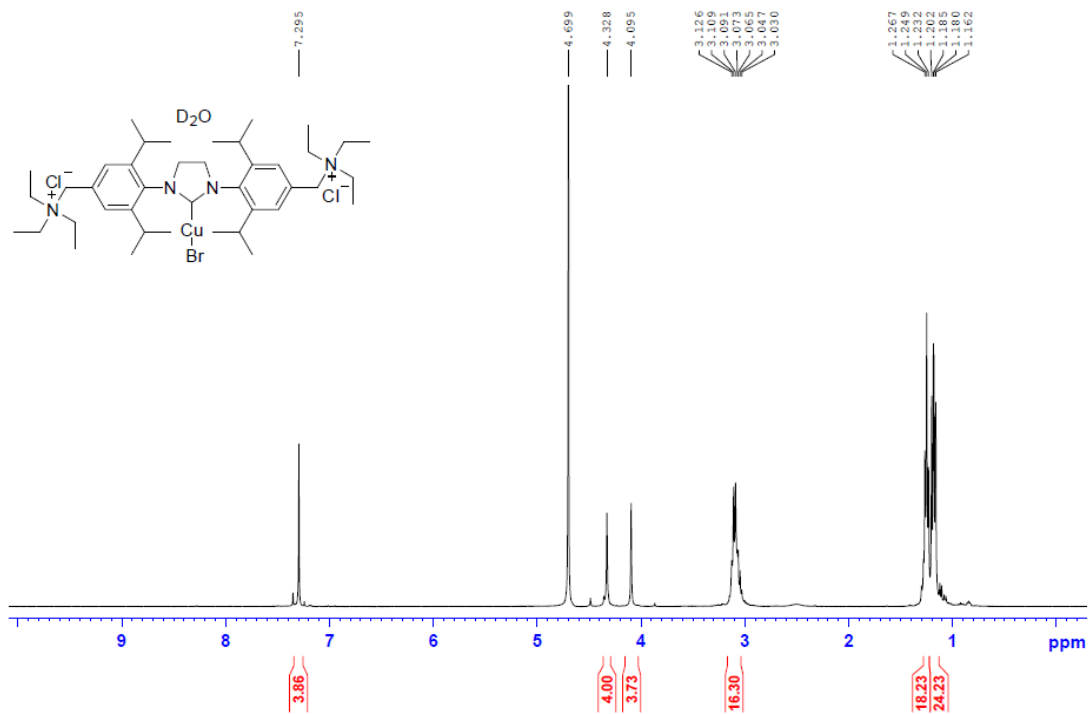


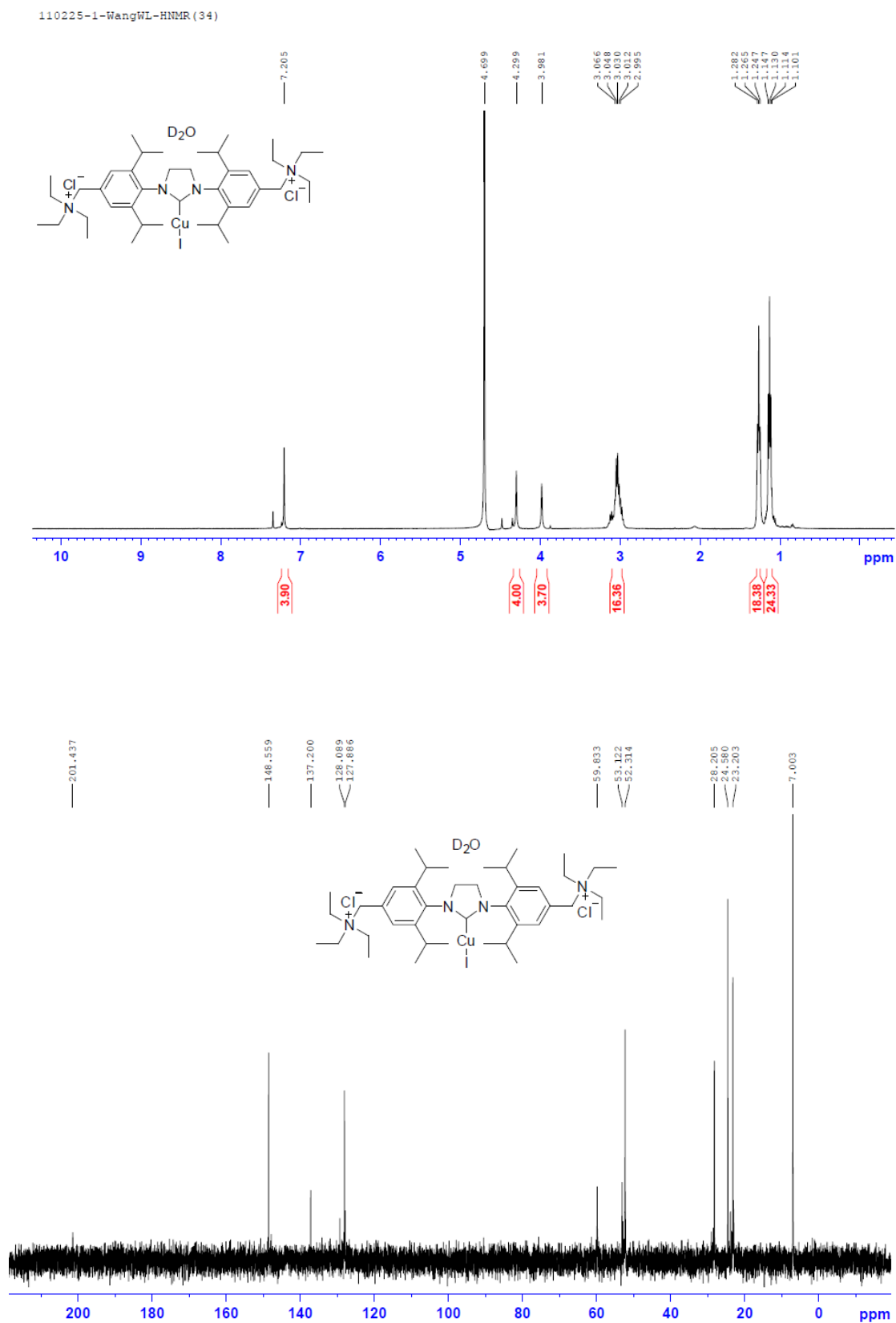
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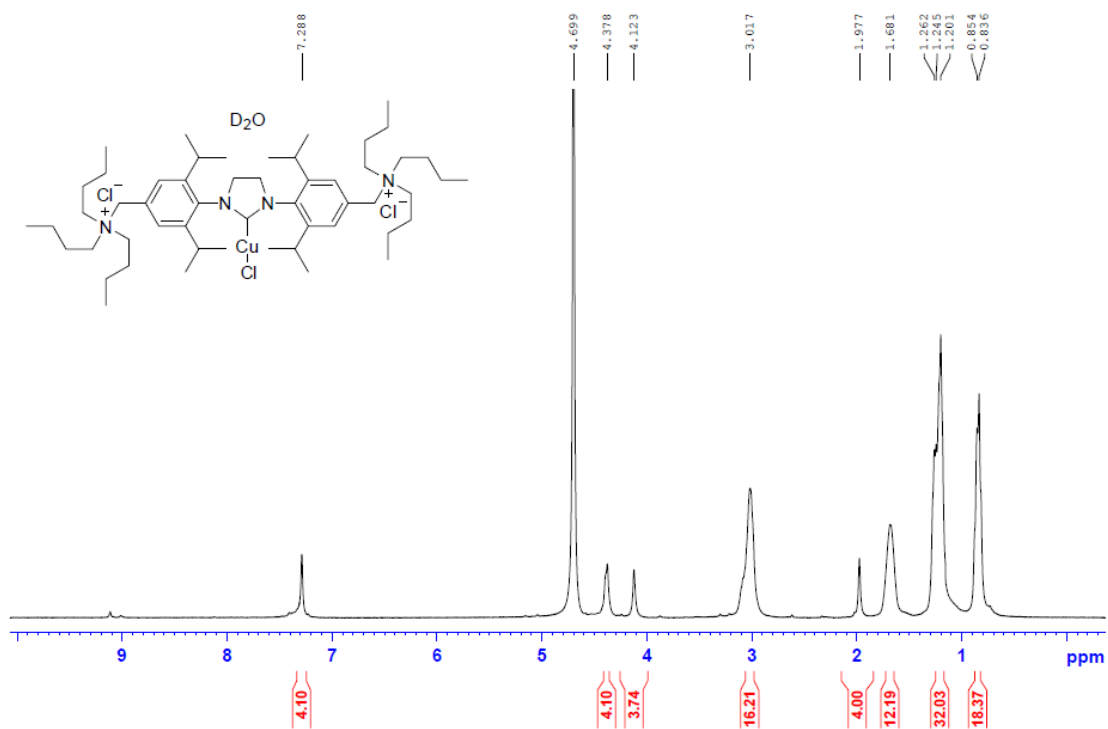


110225-2-WangWL-HNMR (36)

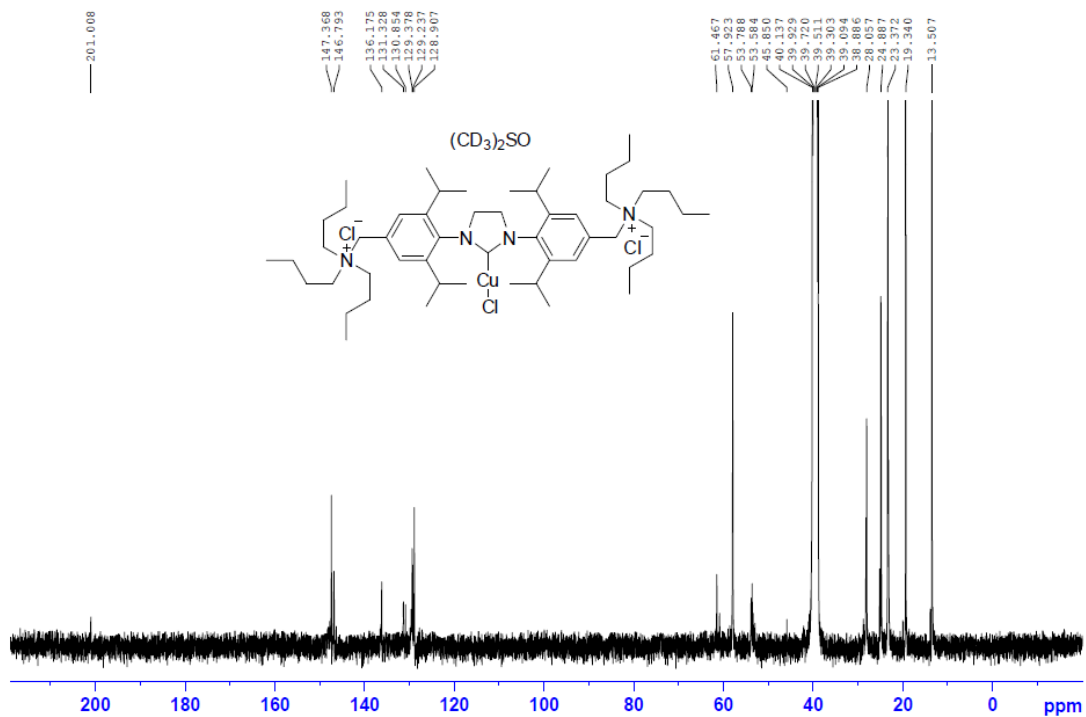




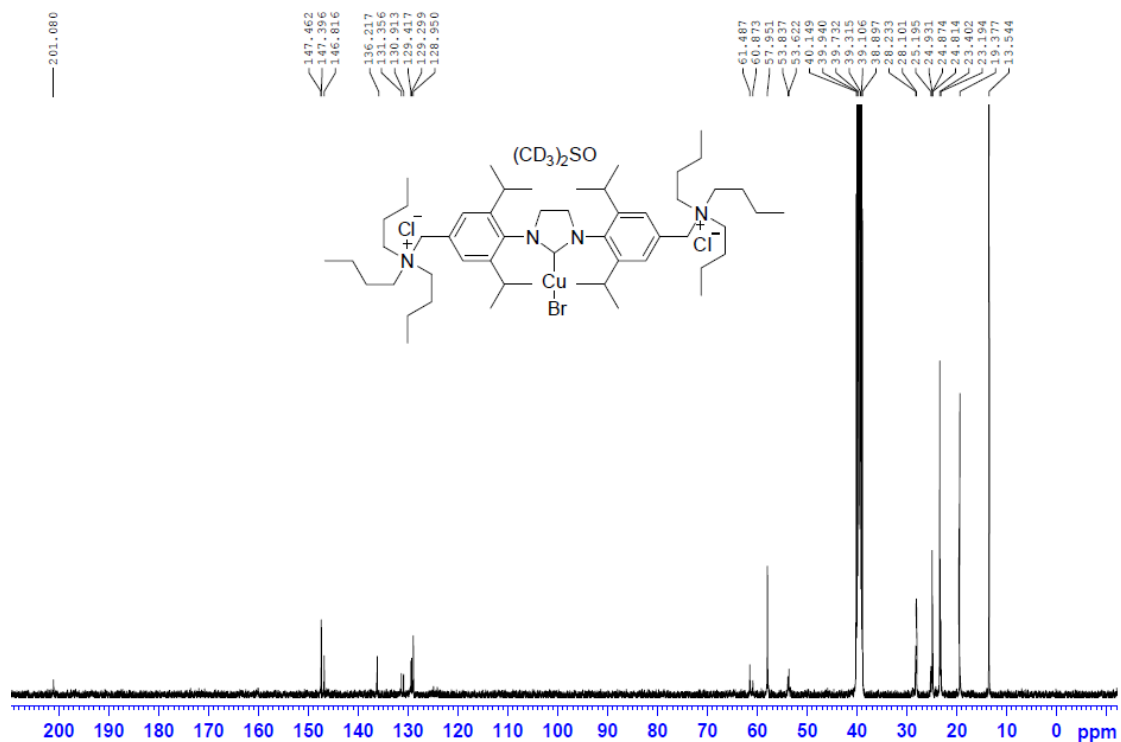
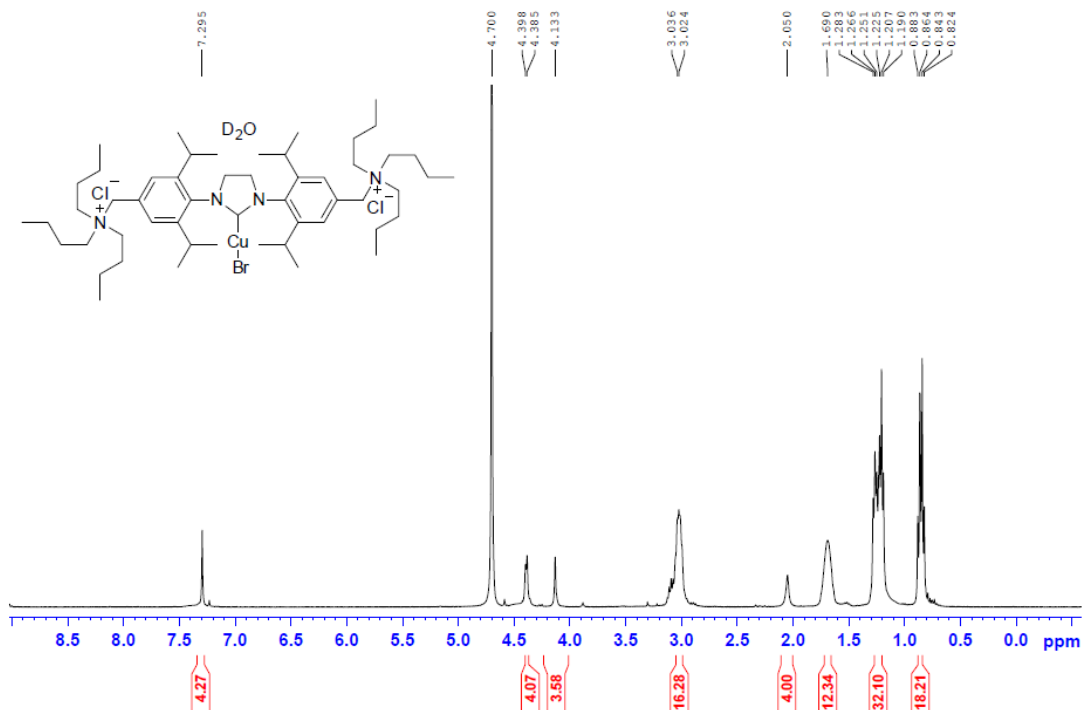
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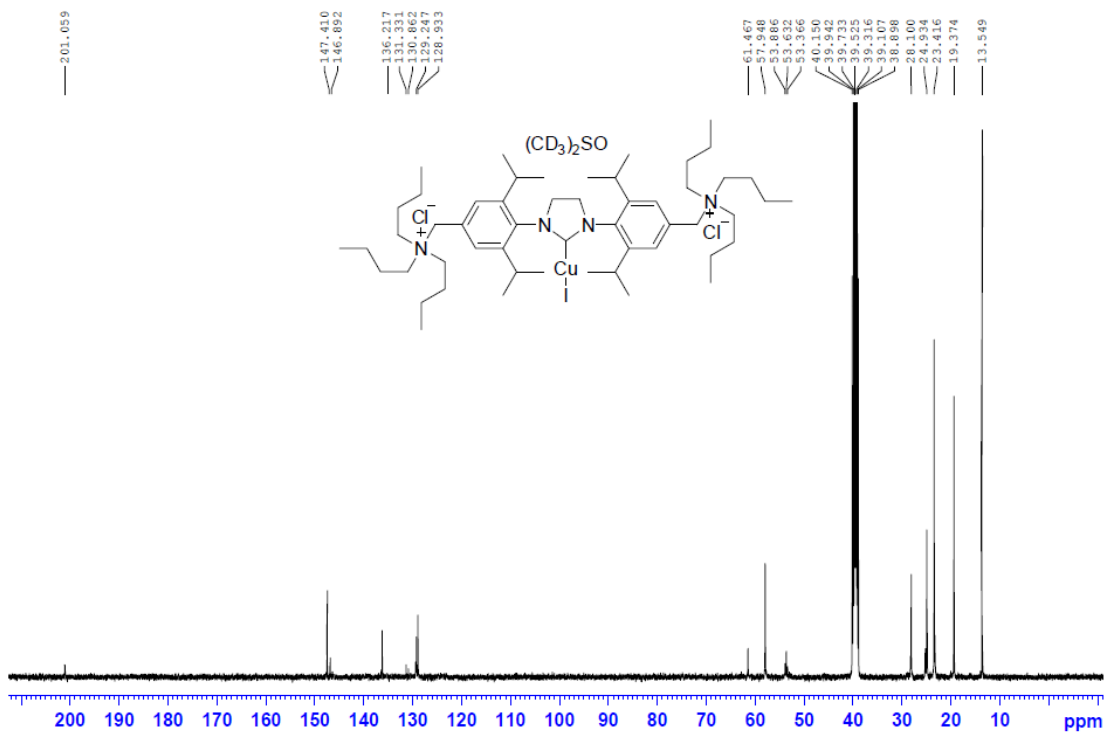
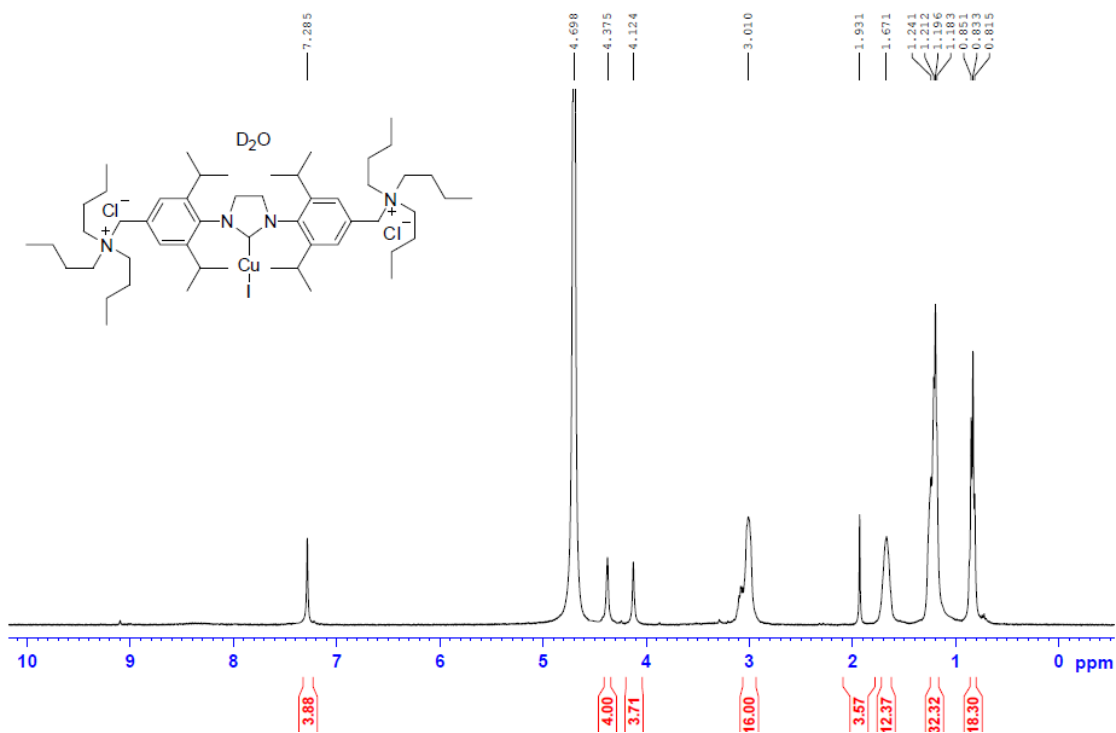
04-1-WangWL-CNMR

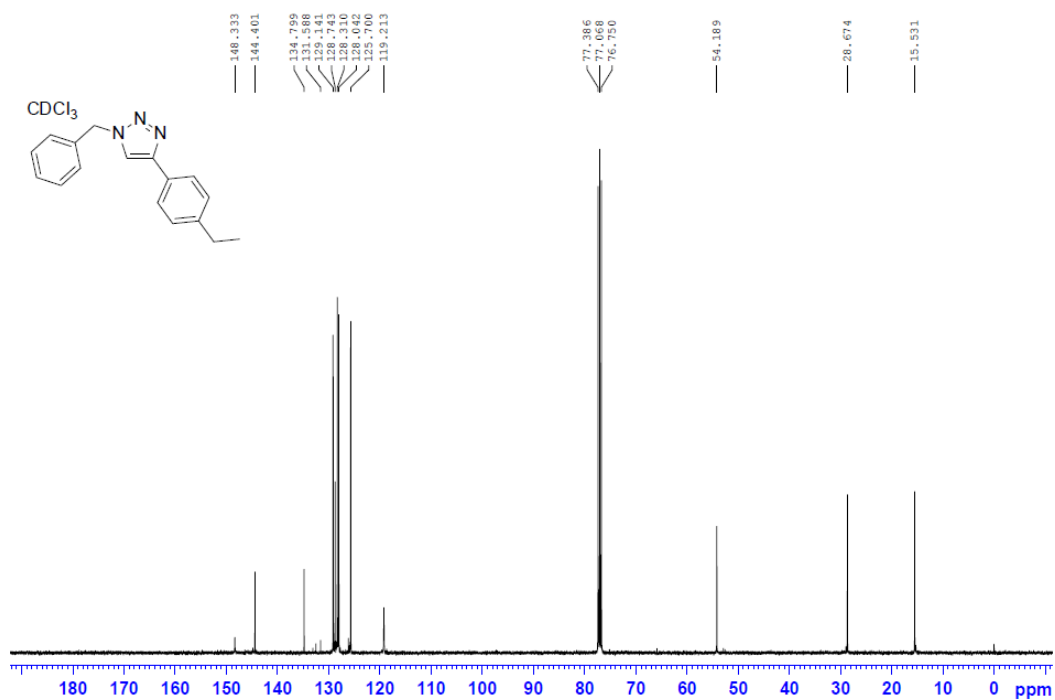
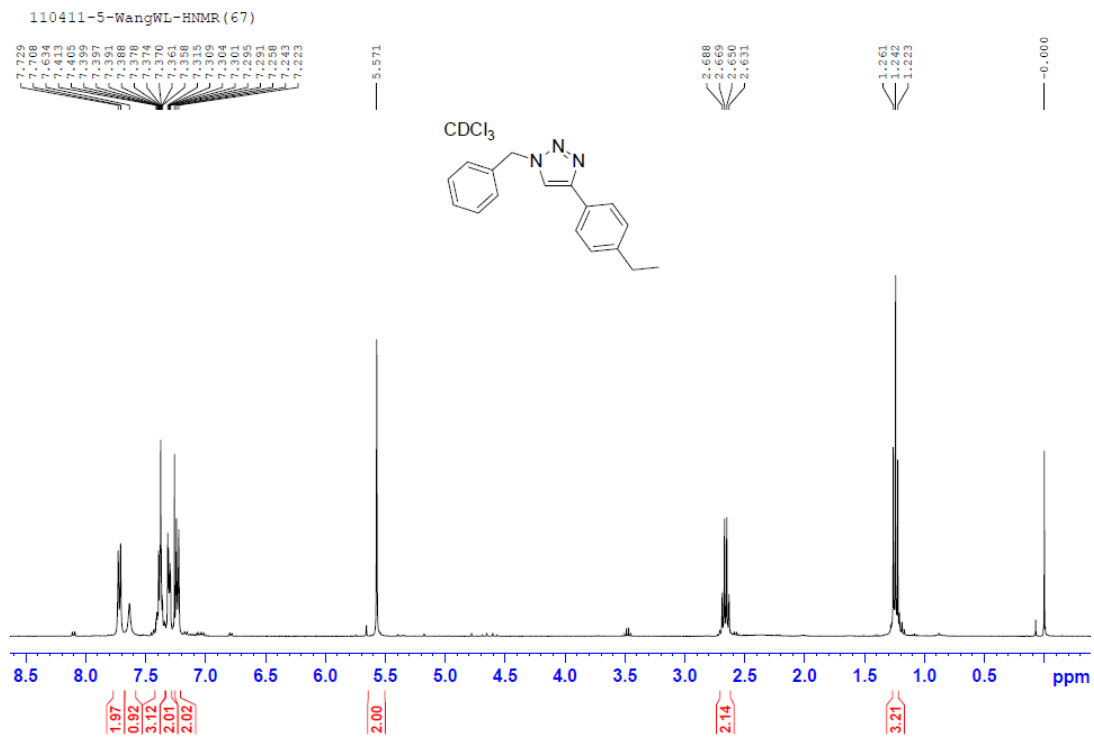


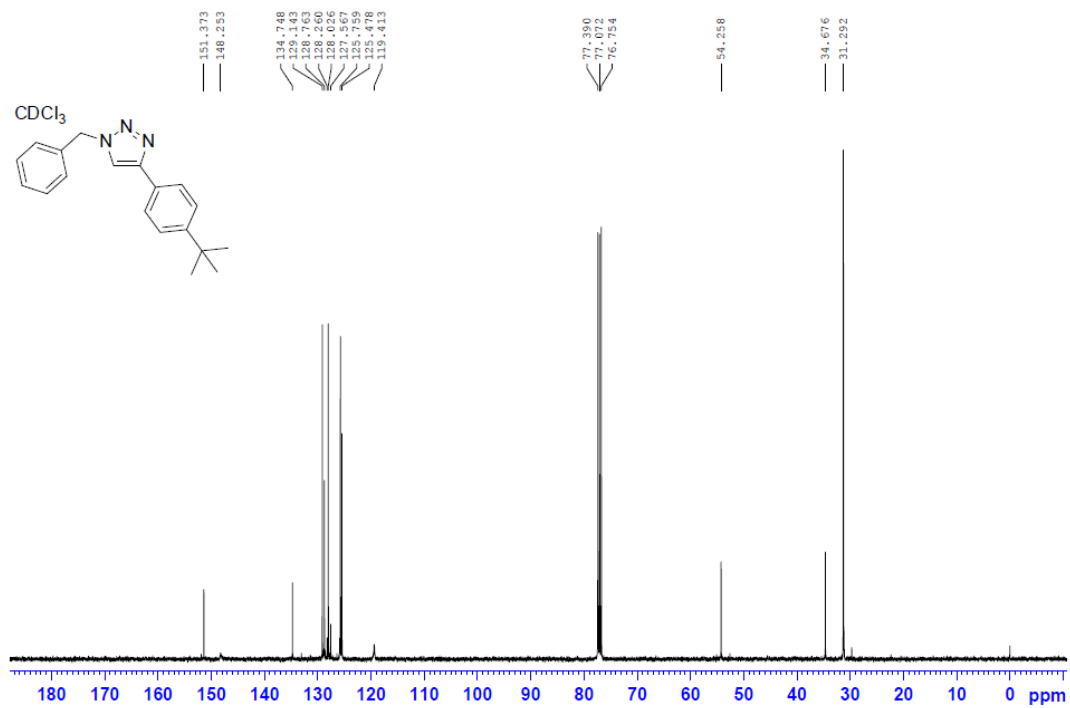
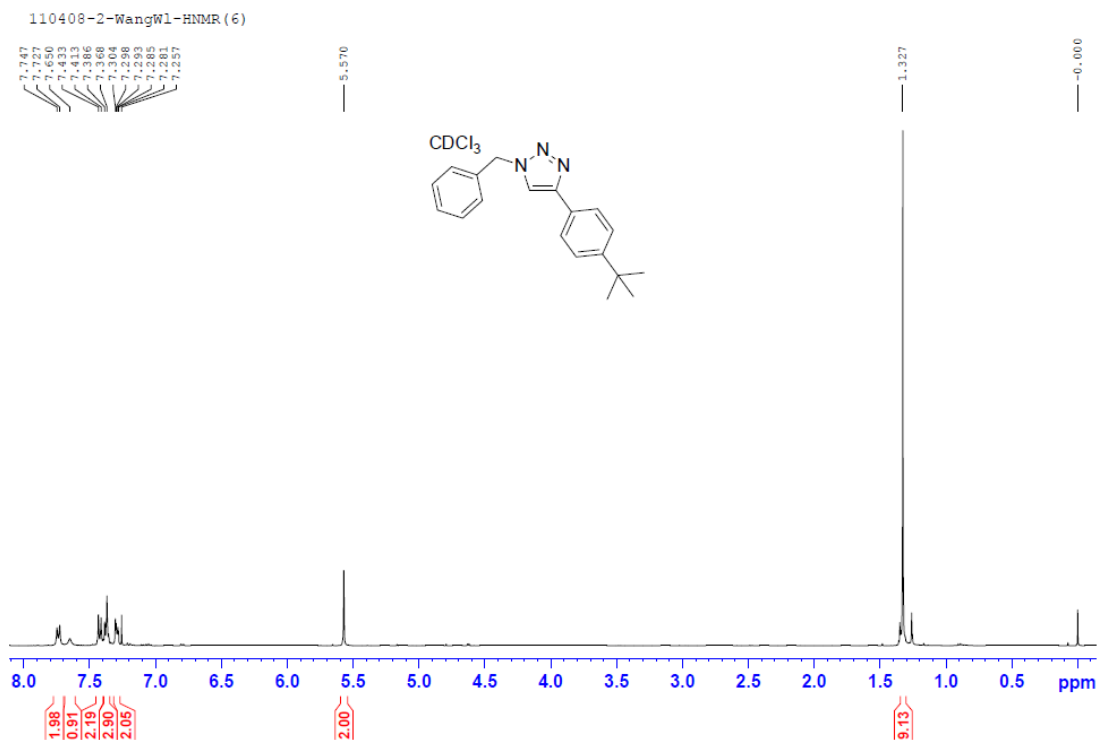
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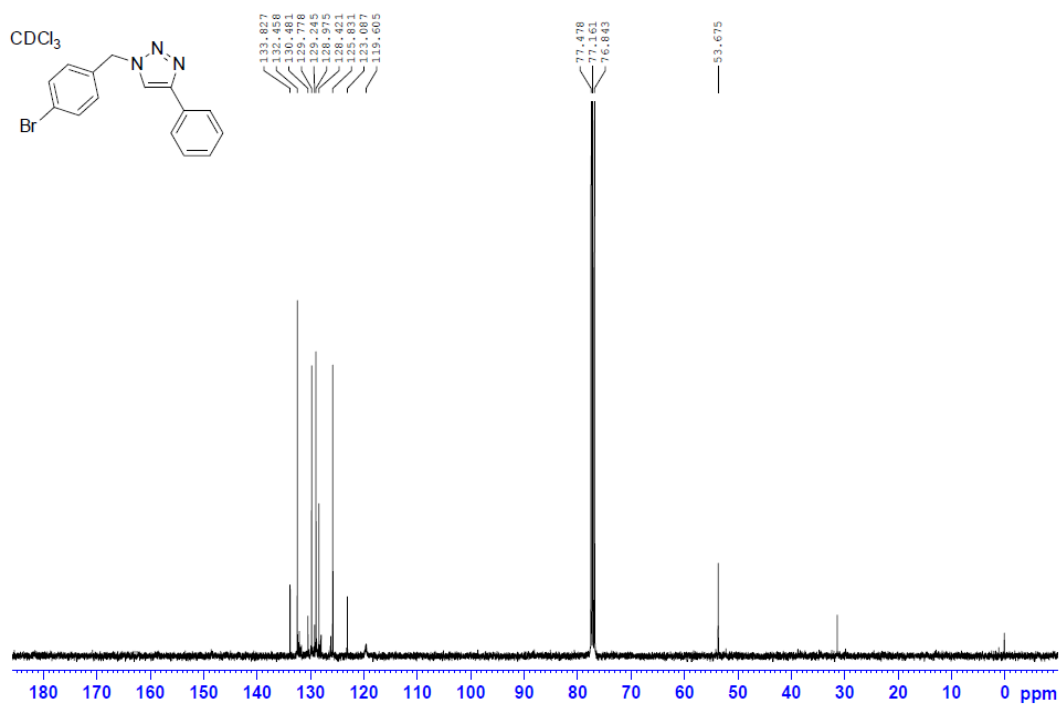
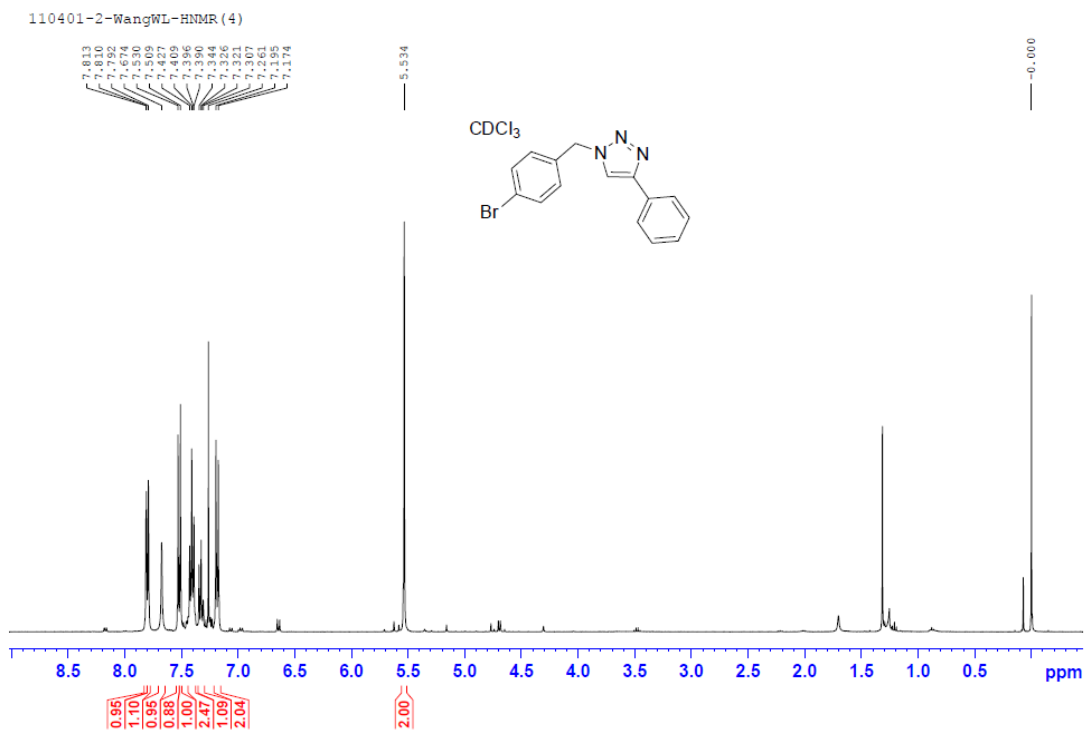


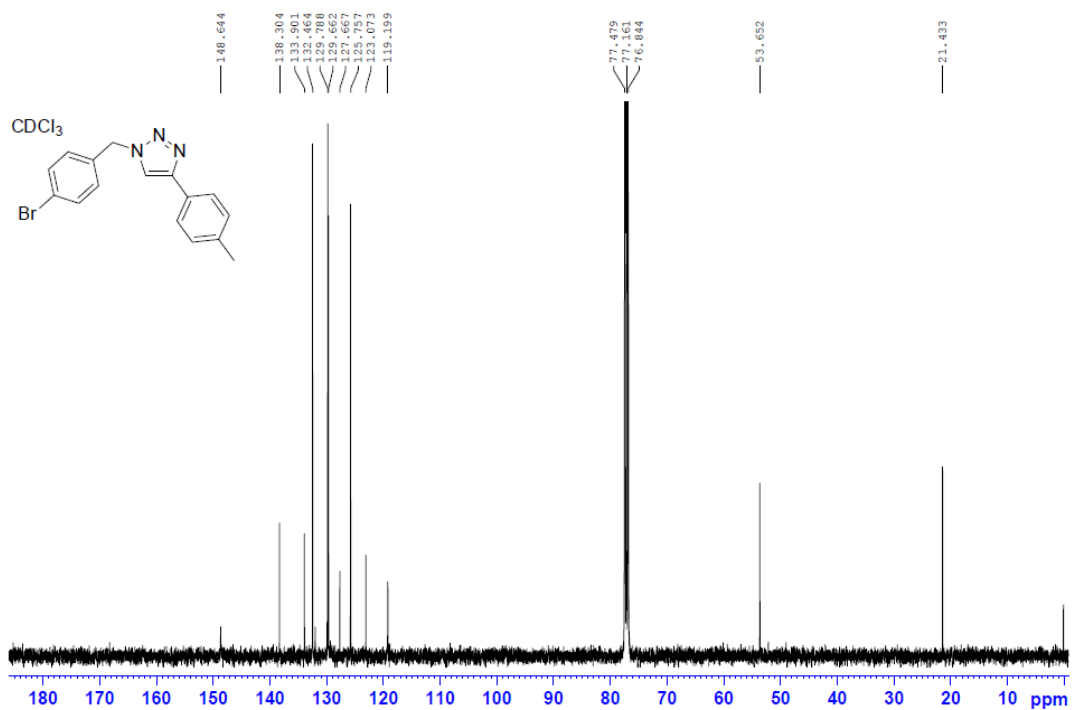
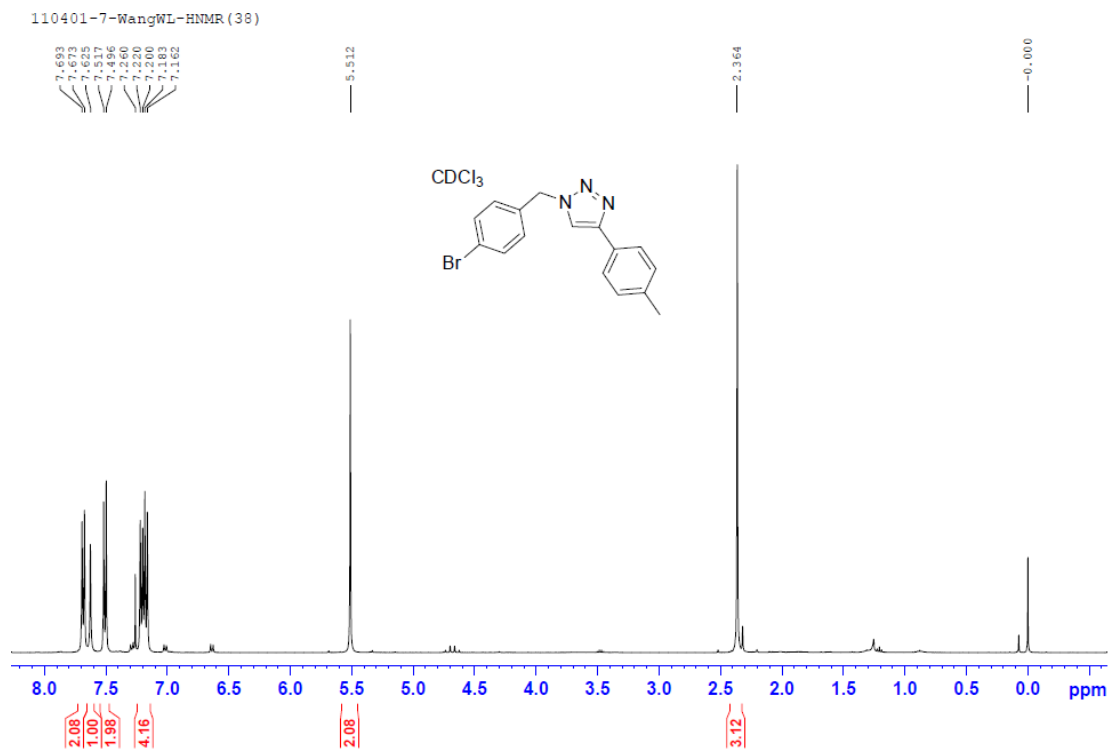
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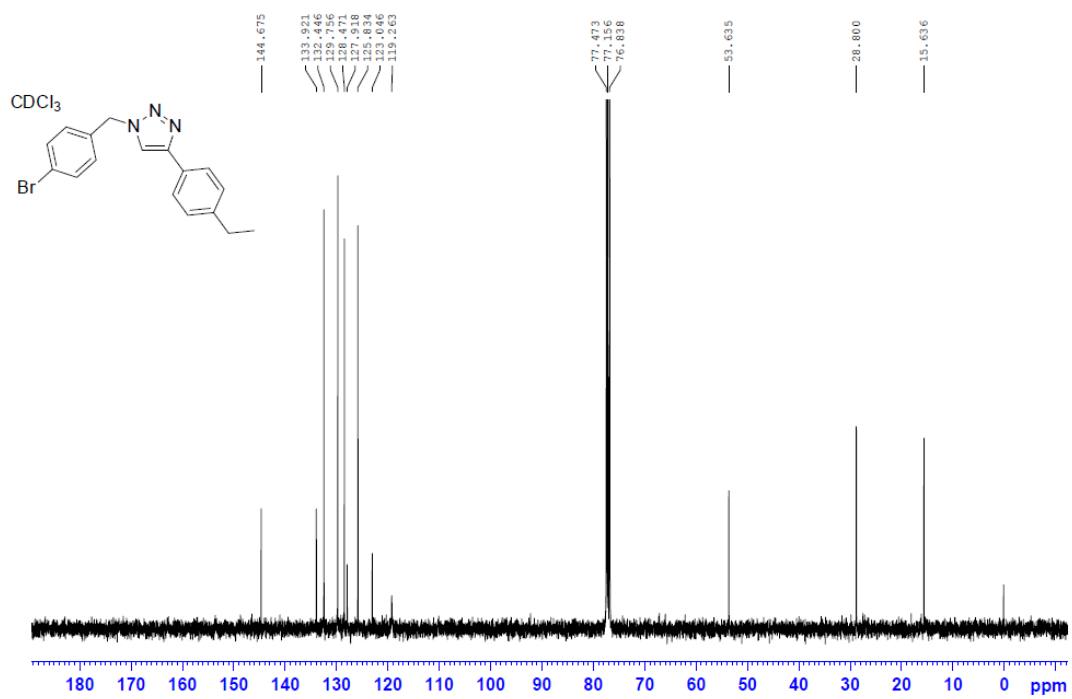
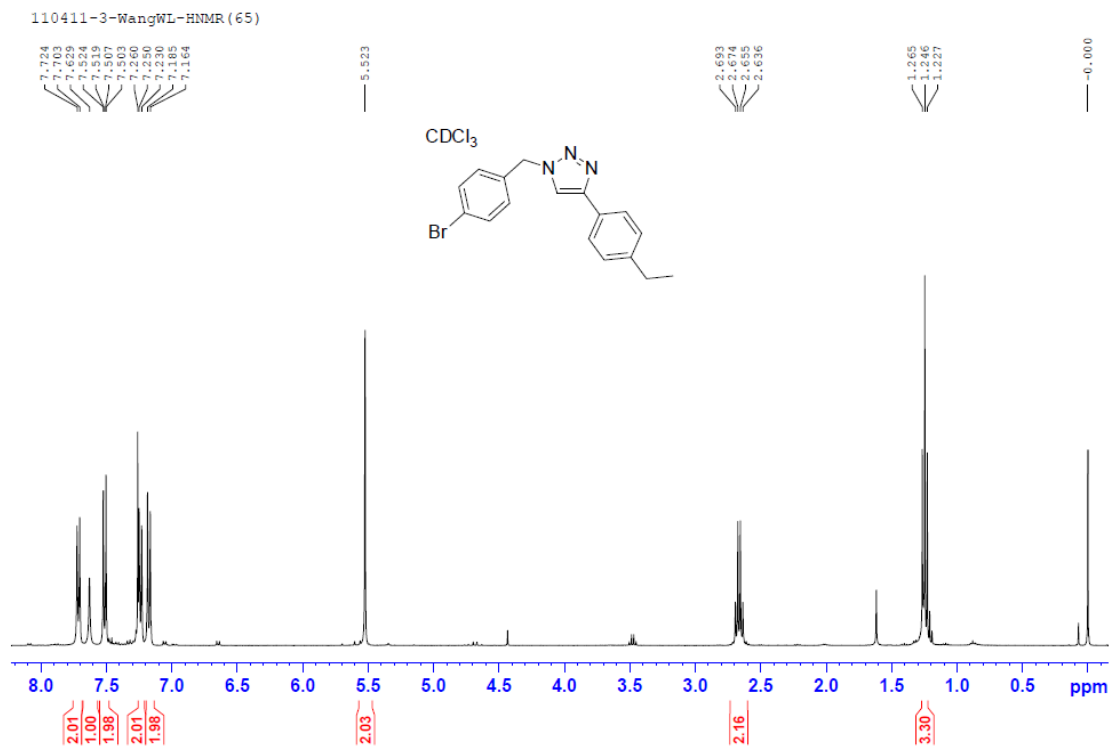


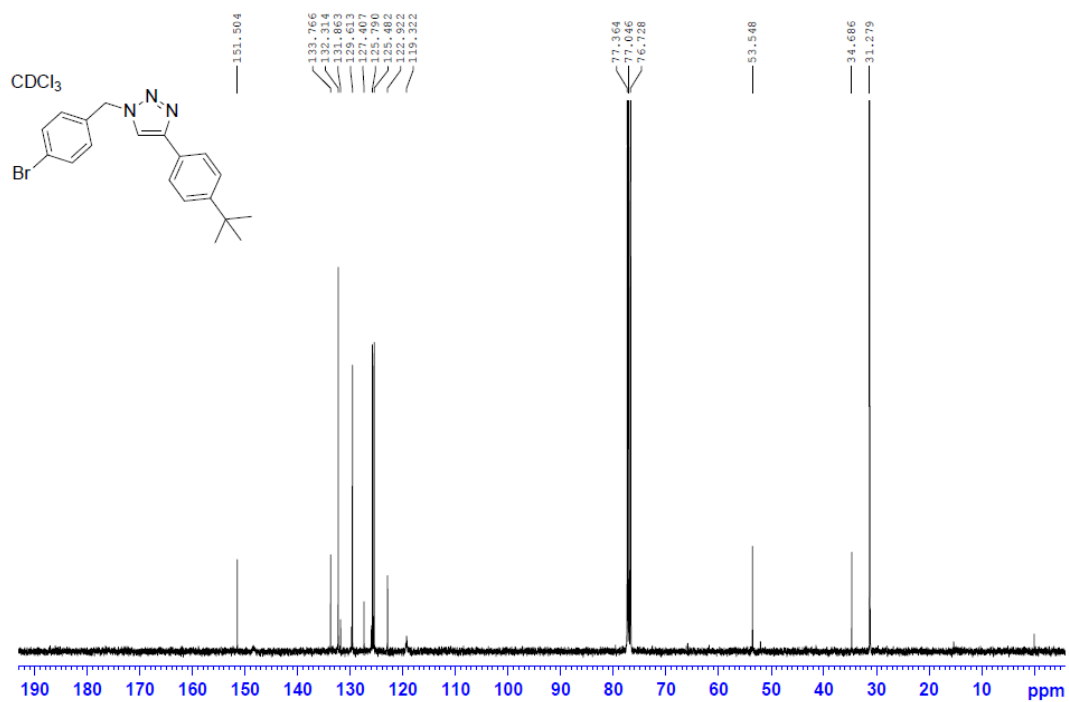
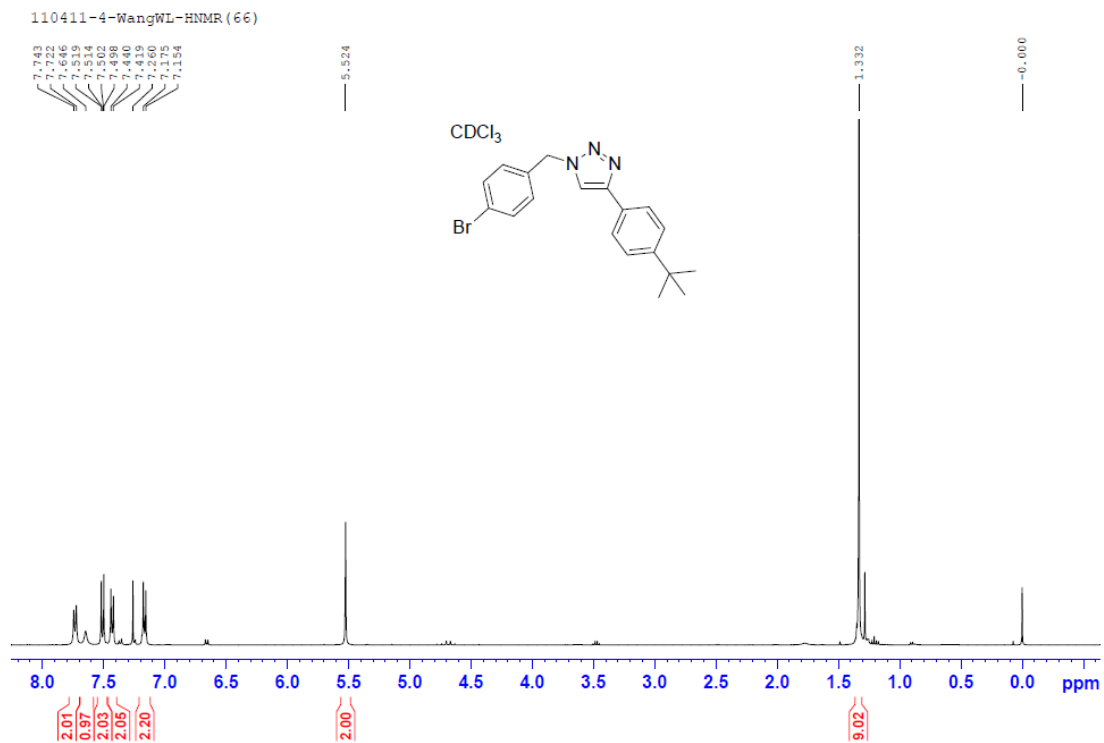


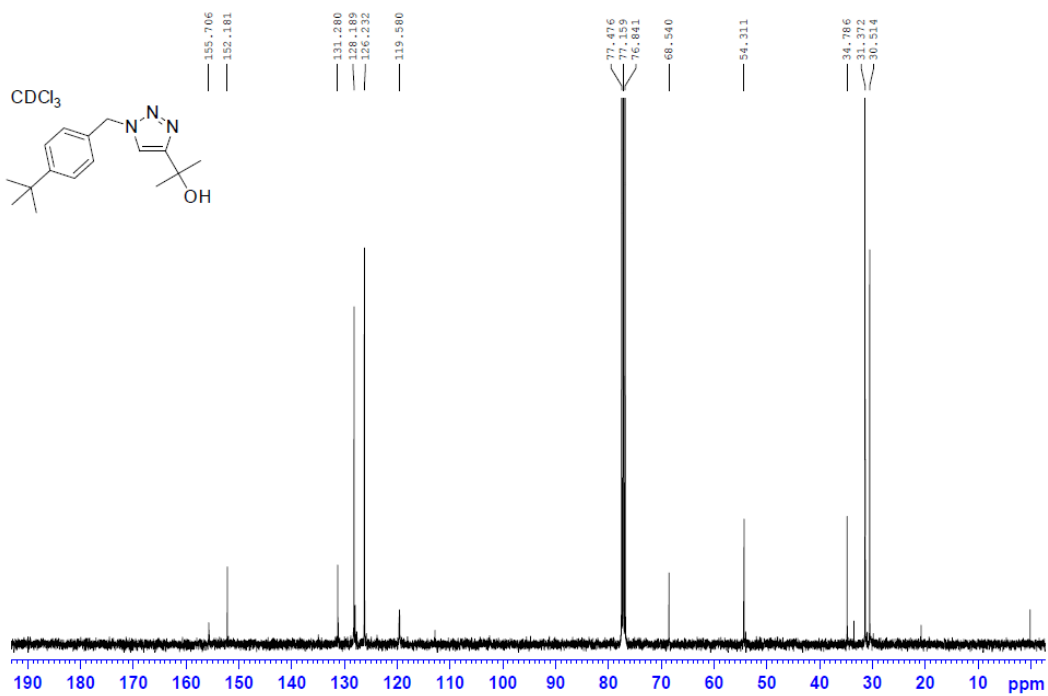
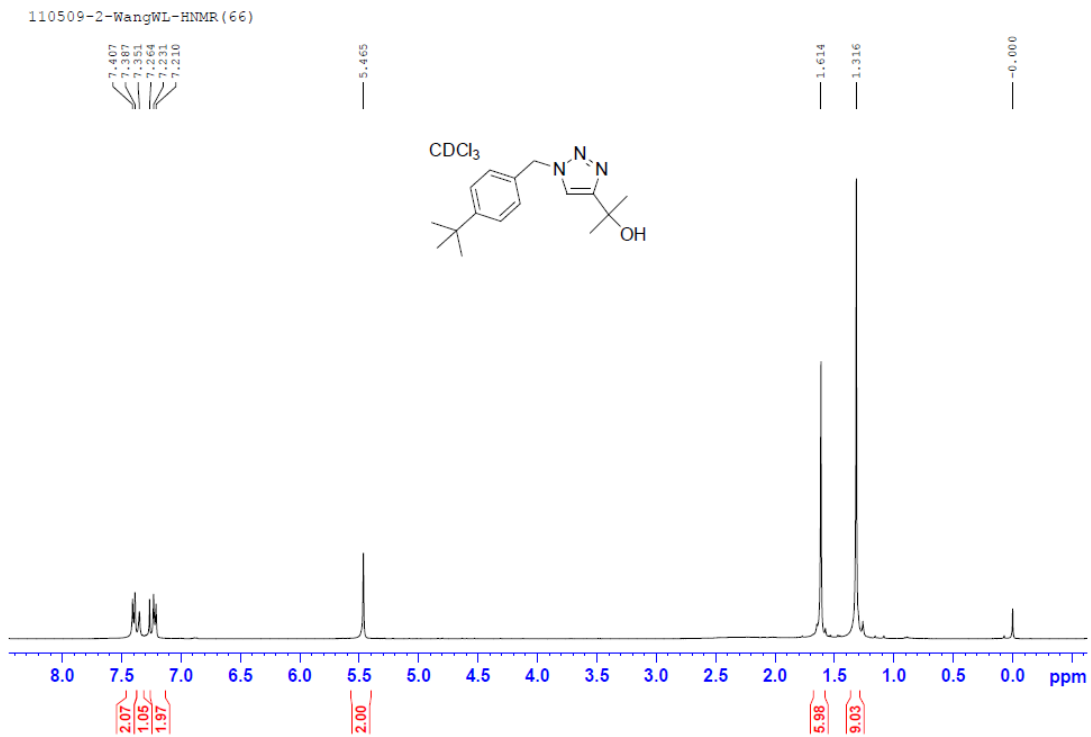


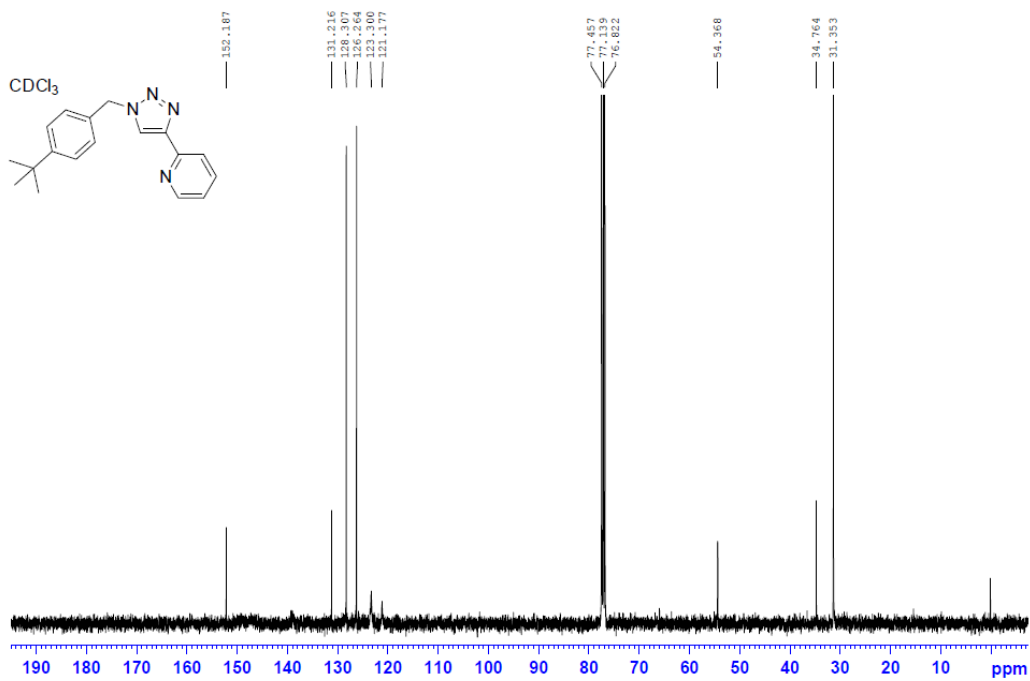
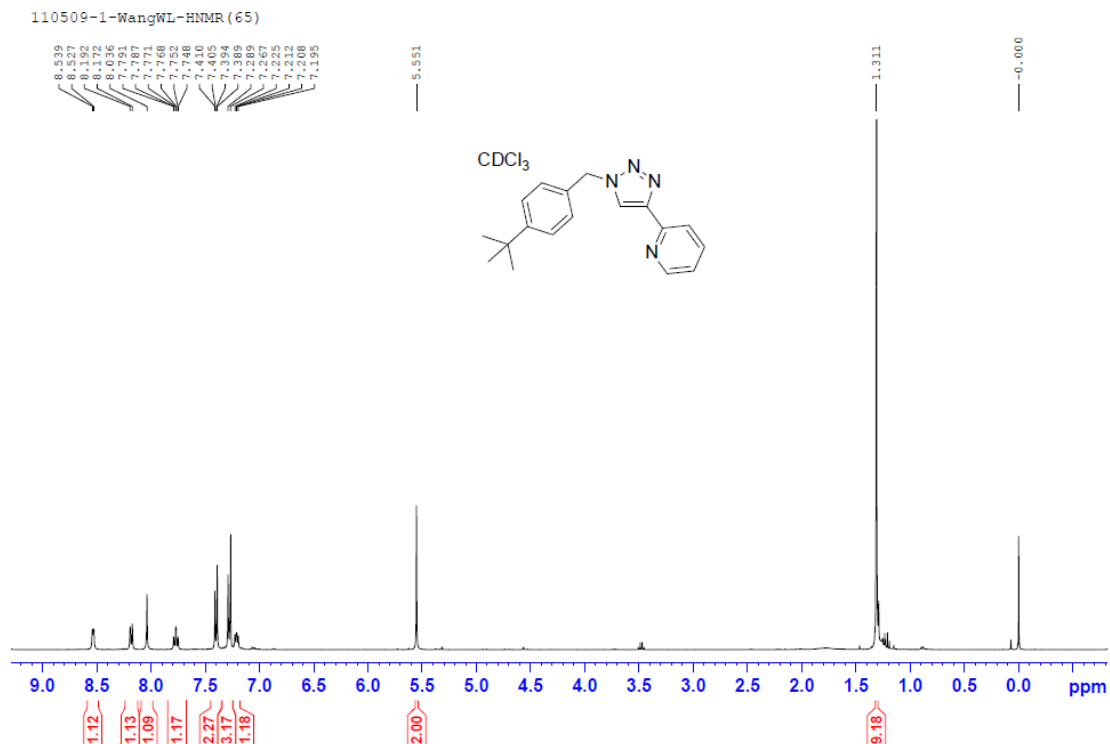


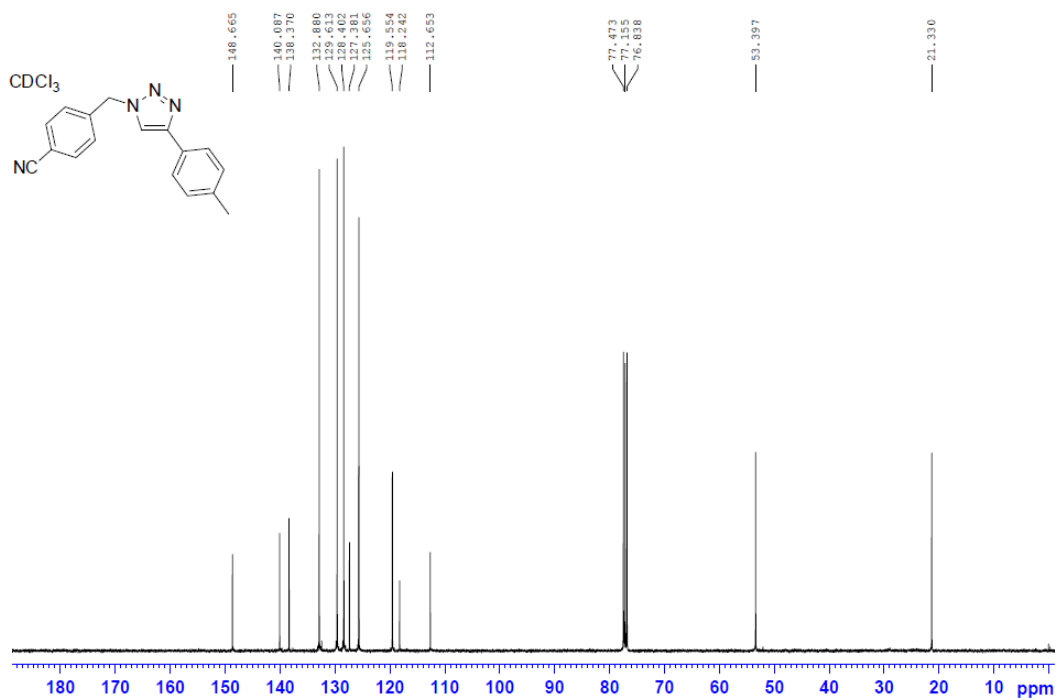
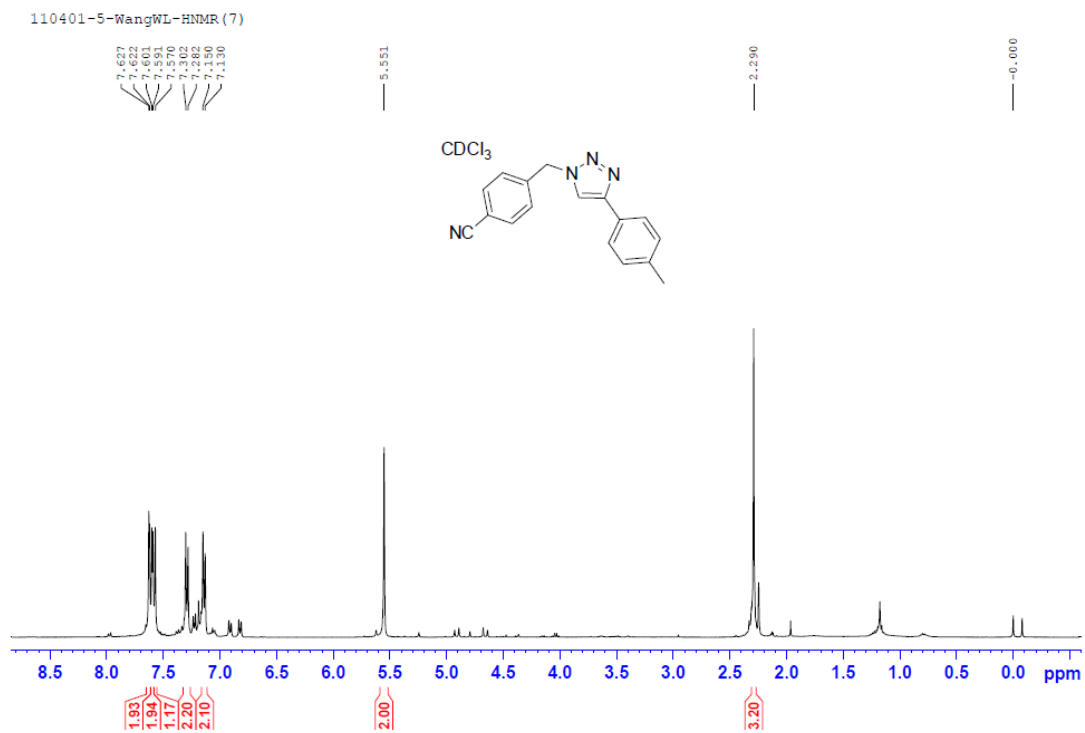


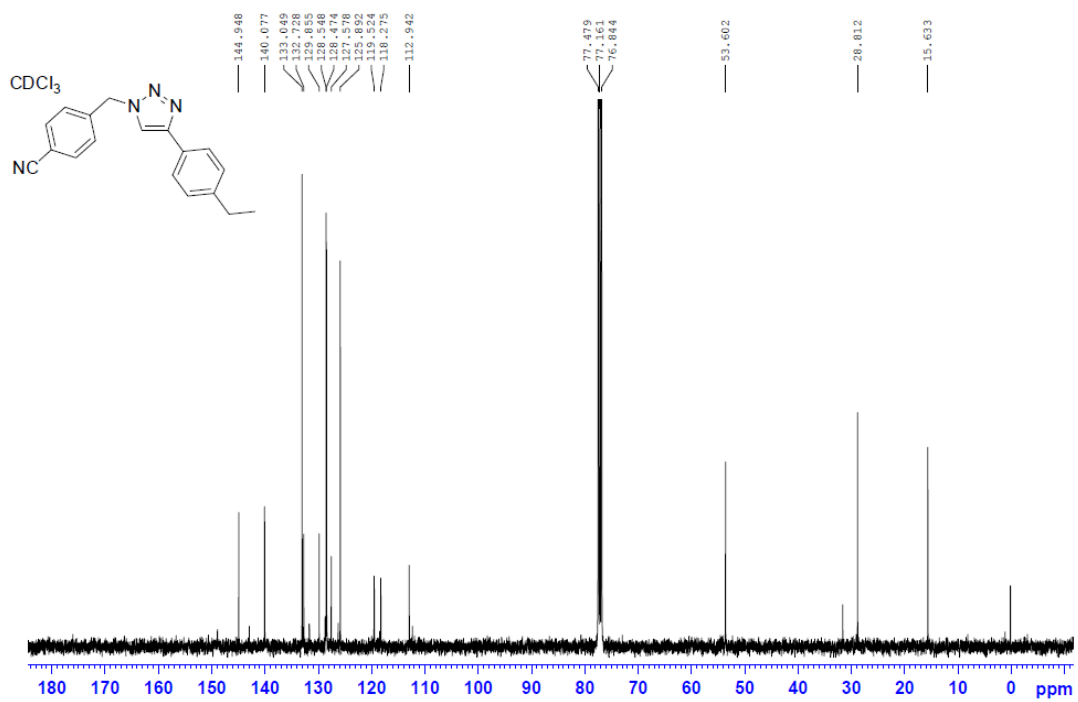
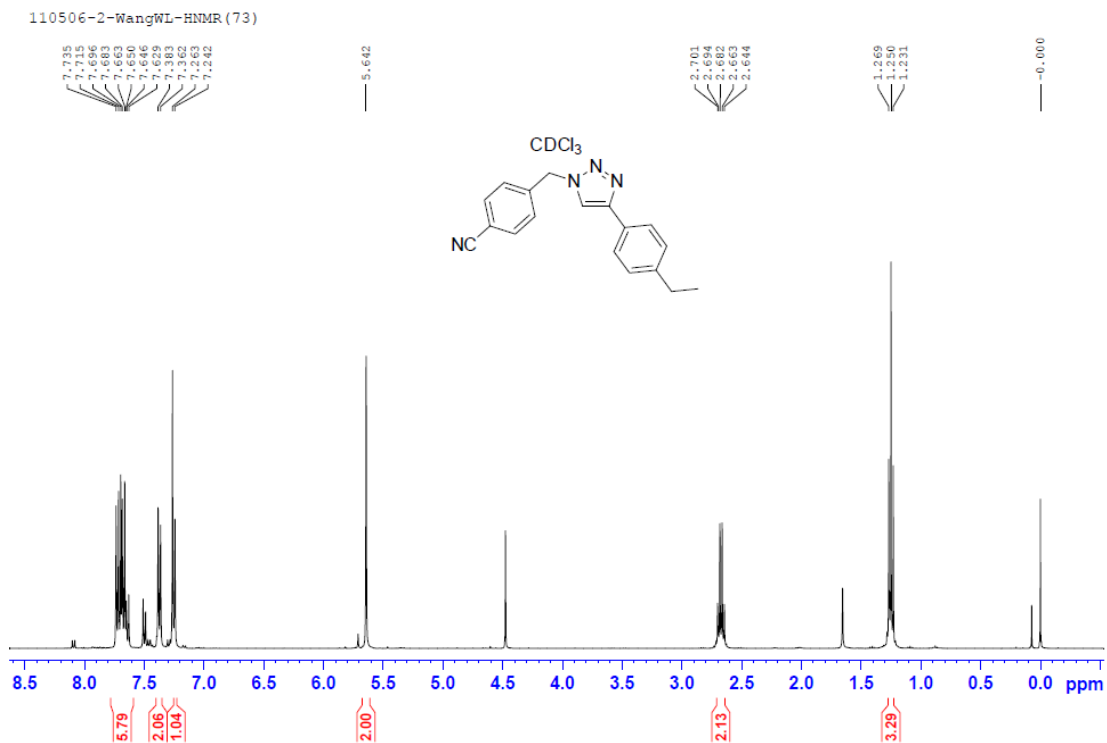


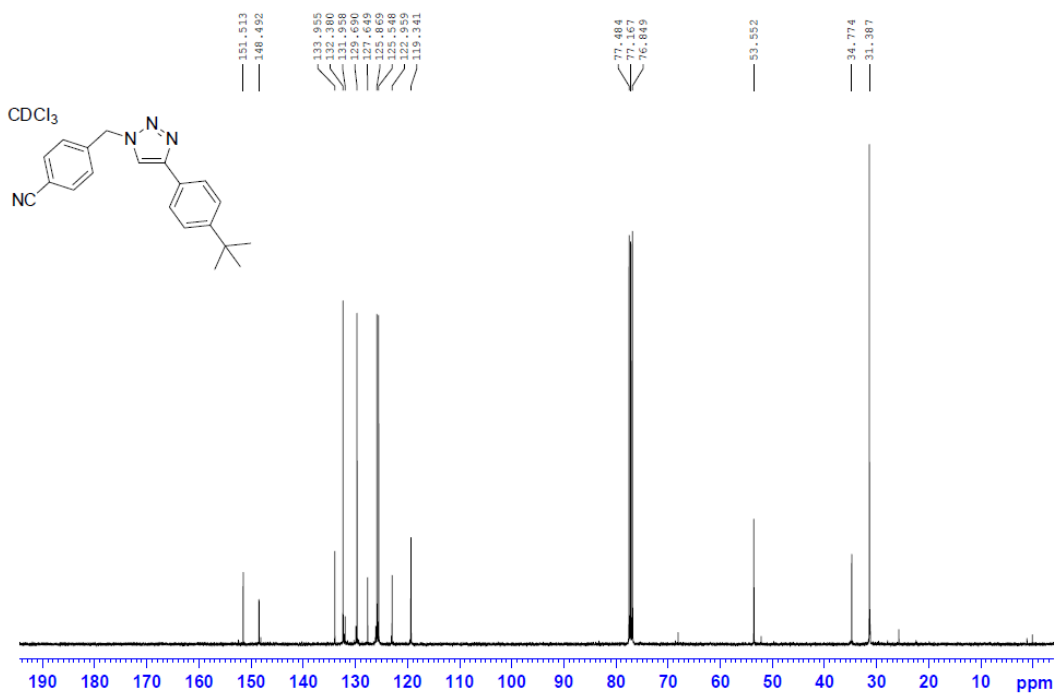
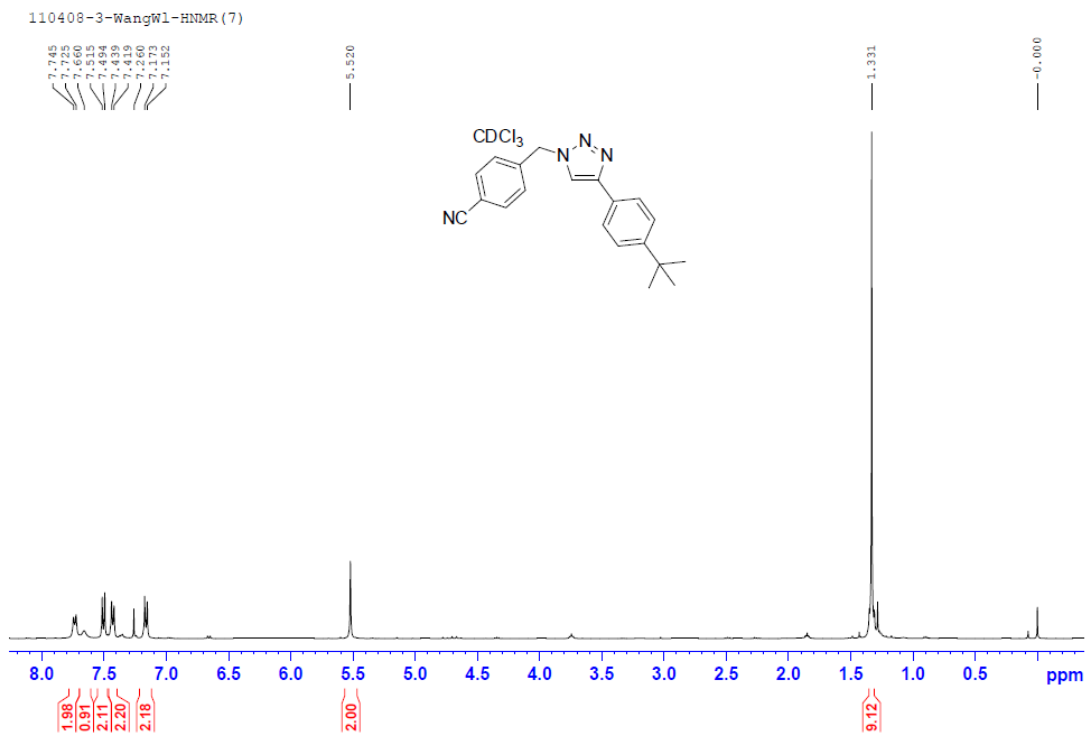


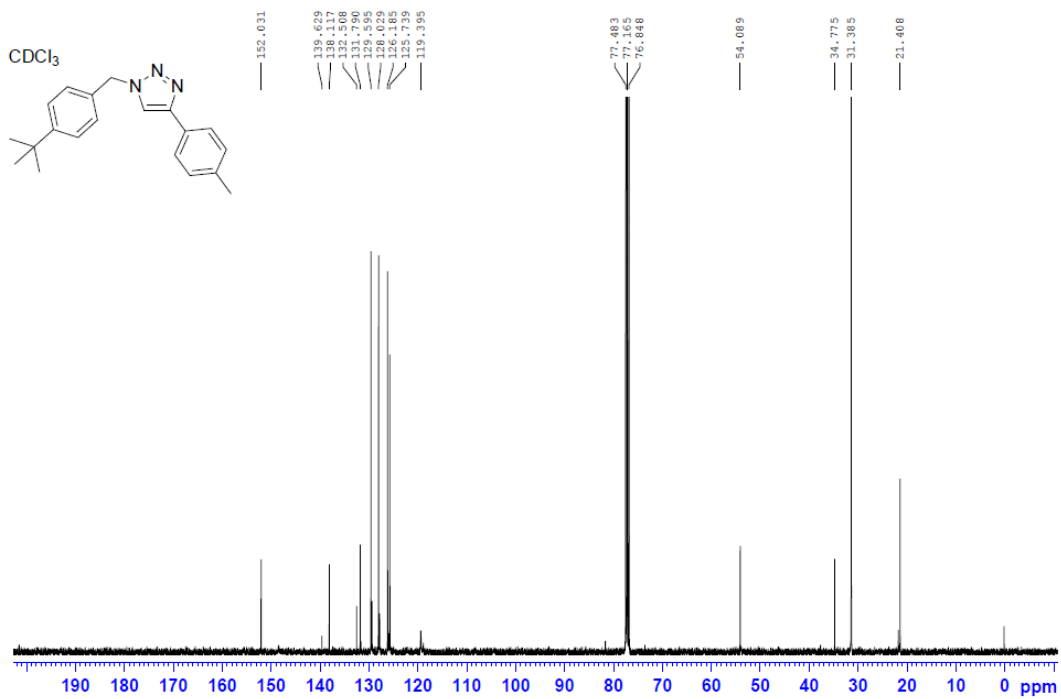
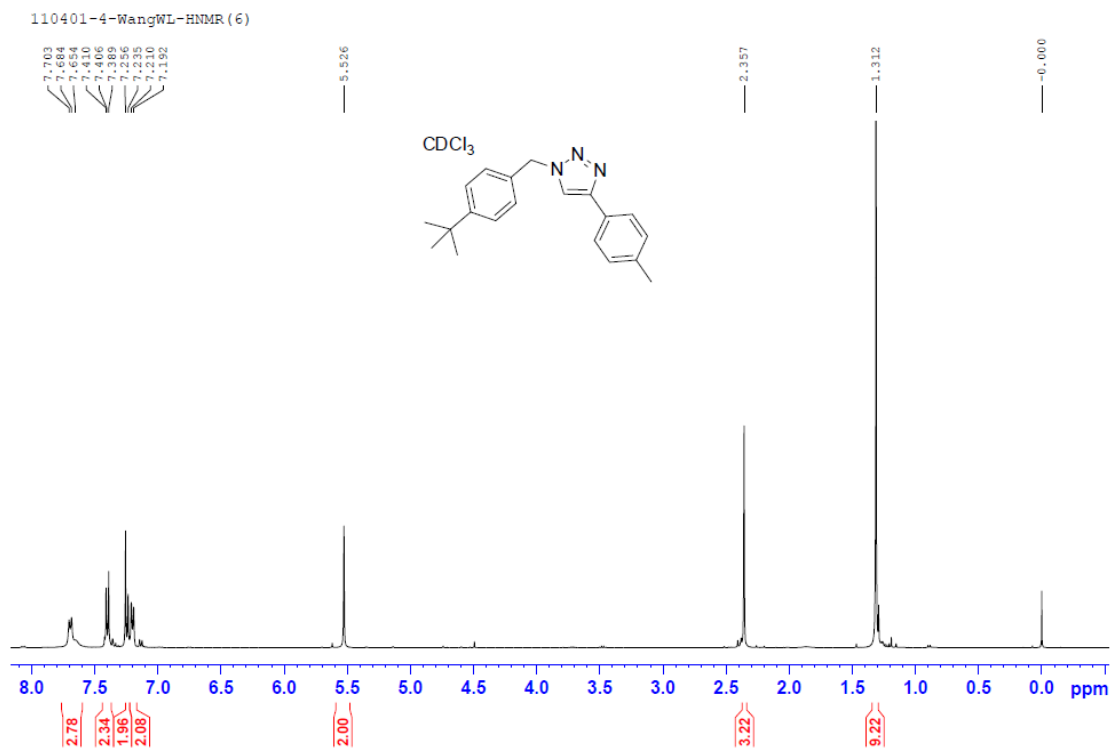


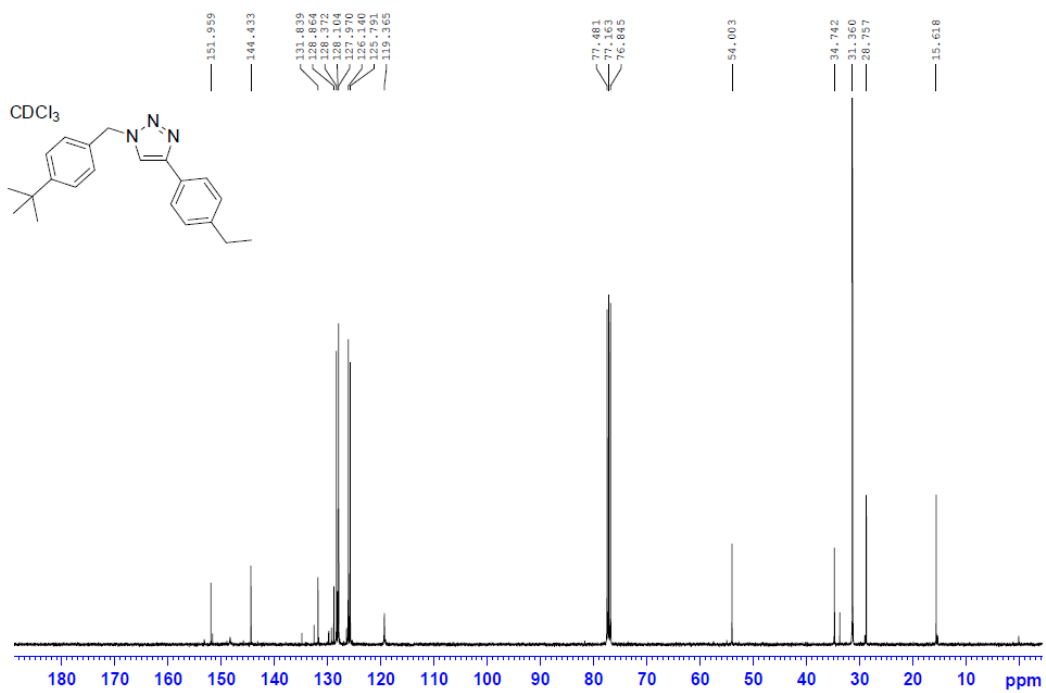
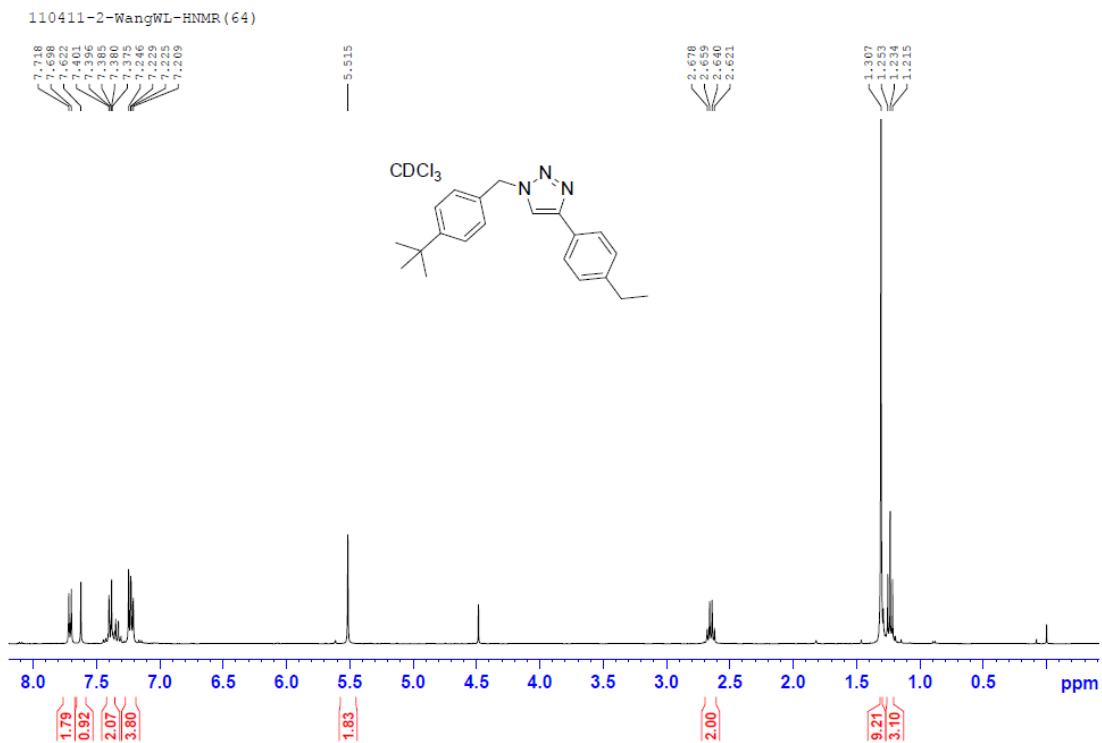


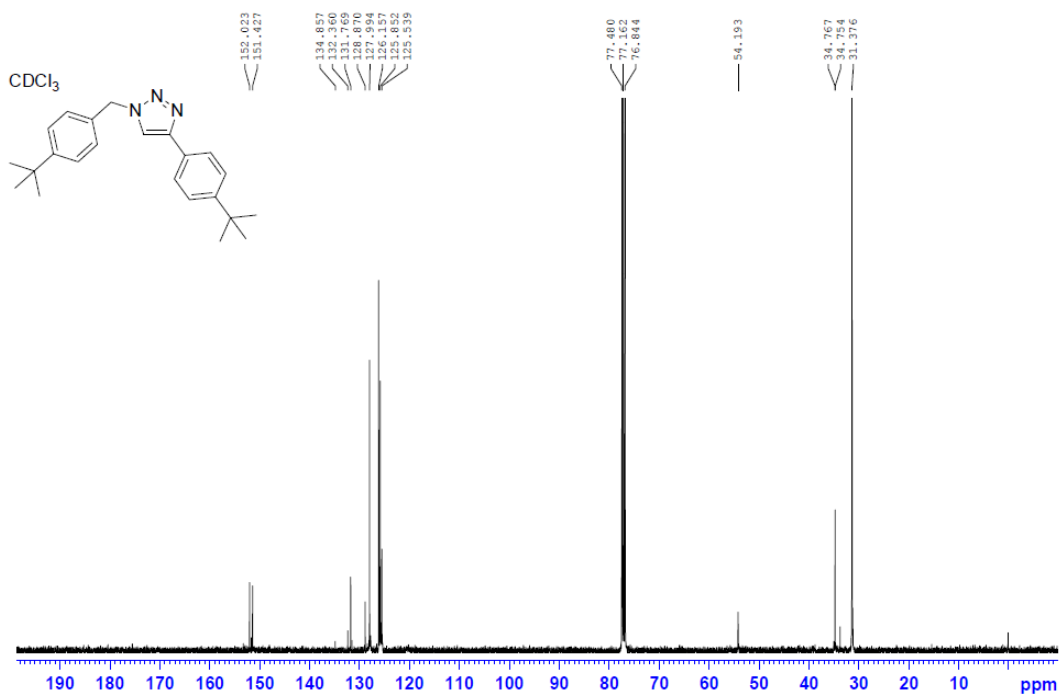
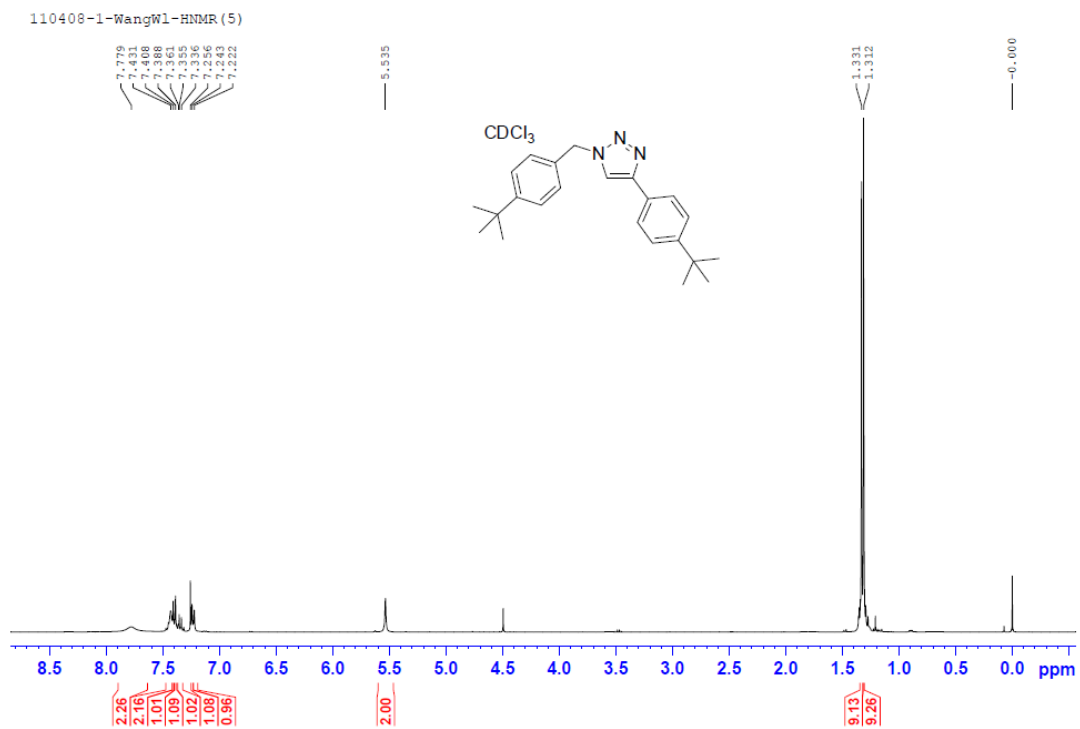


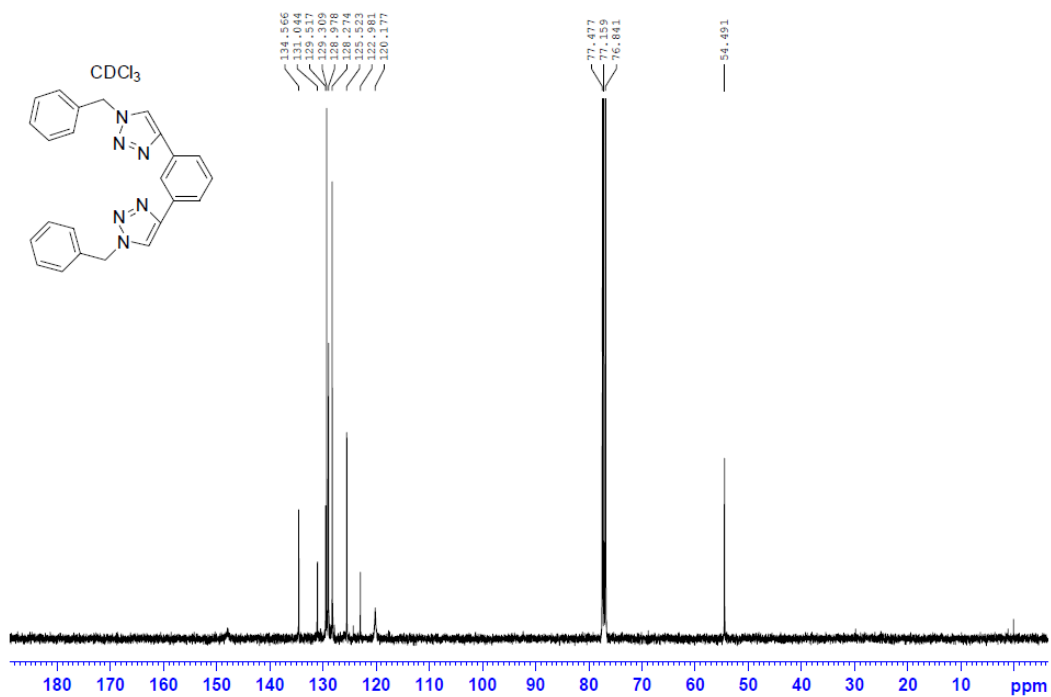
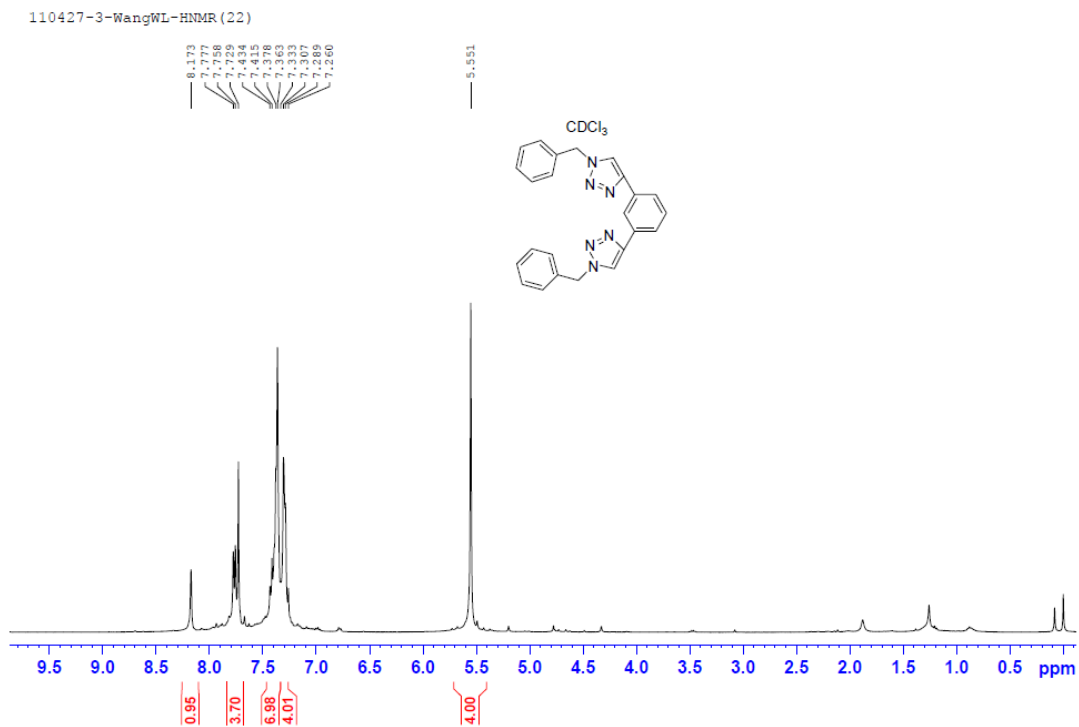




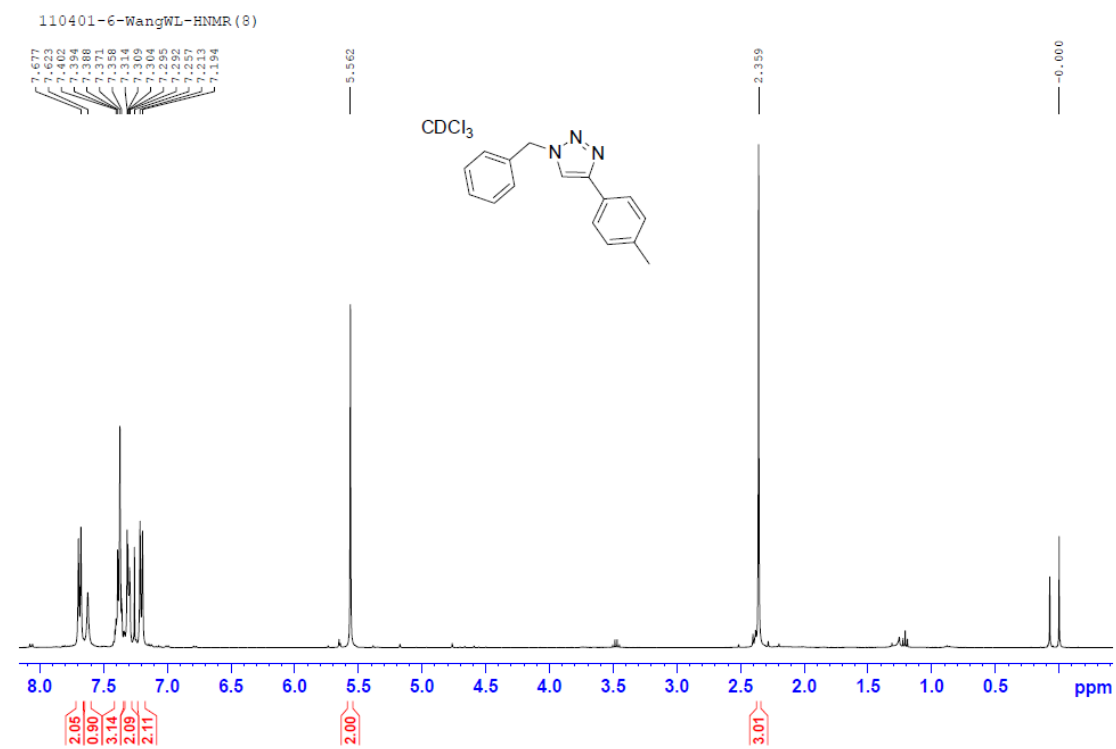
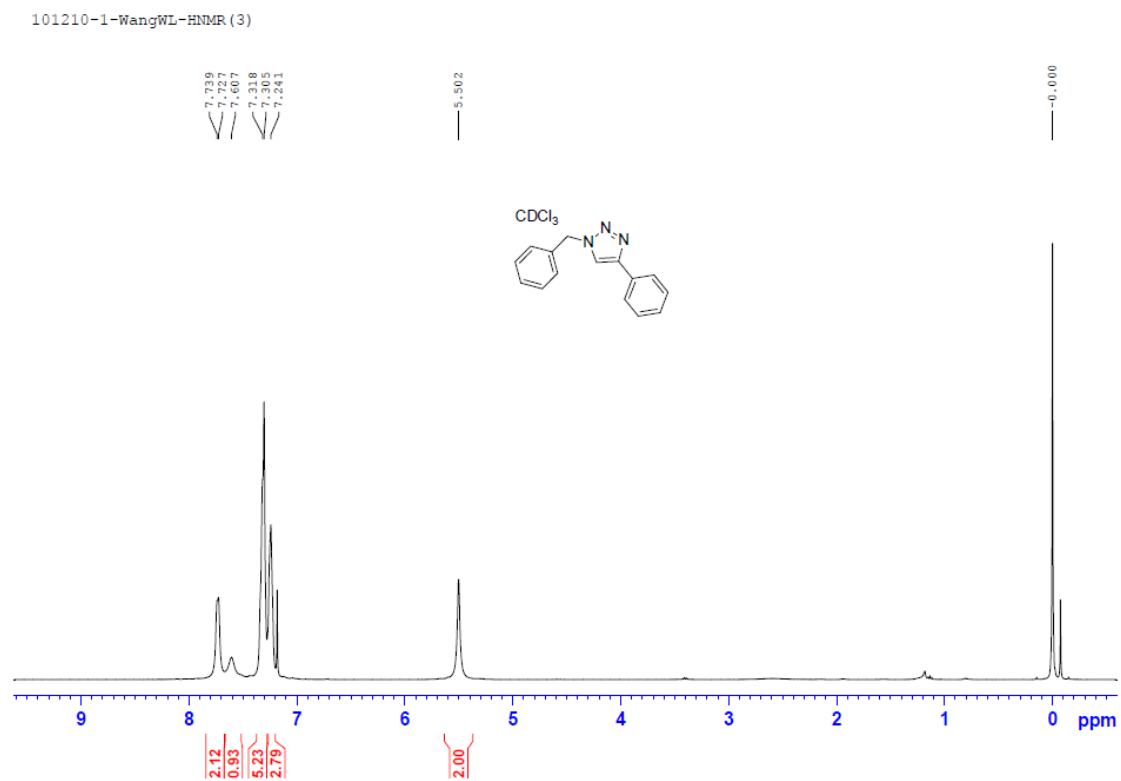


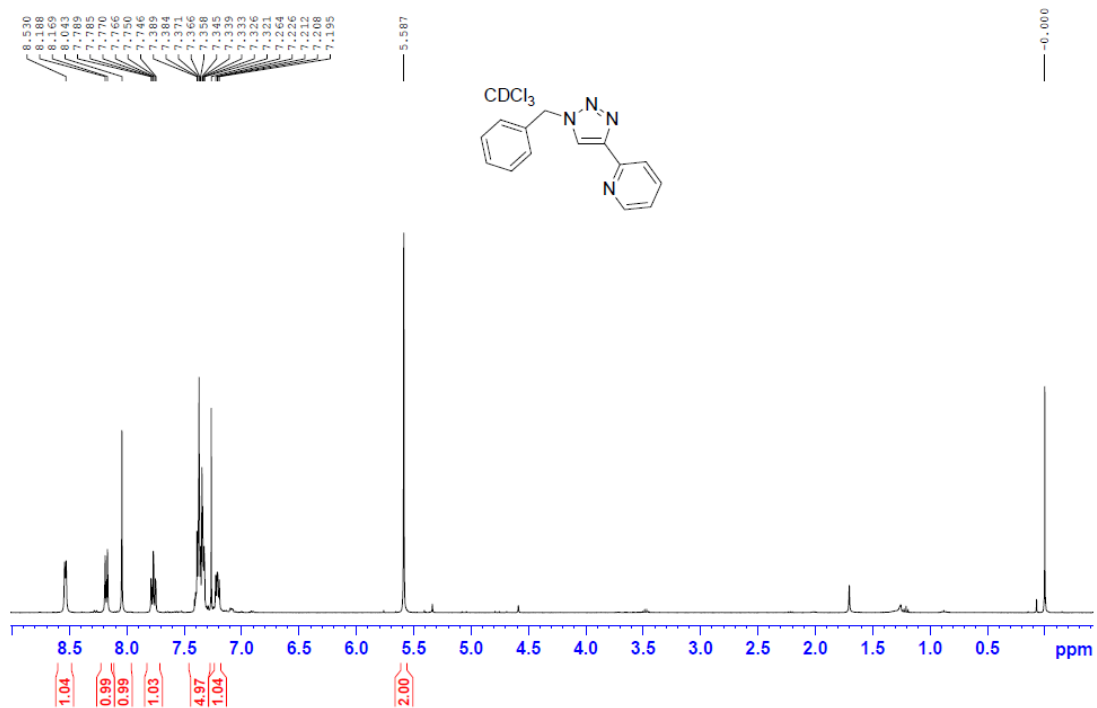




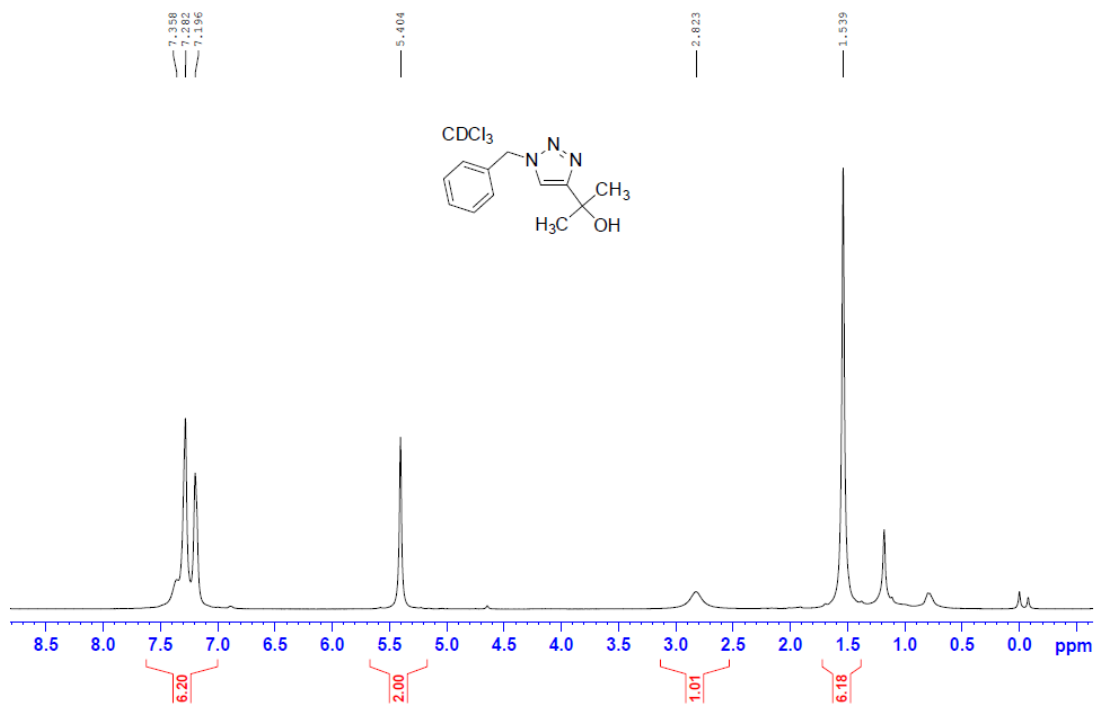


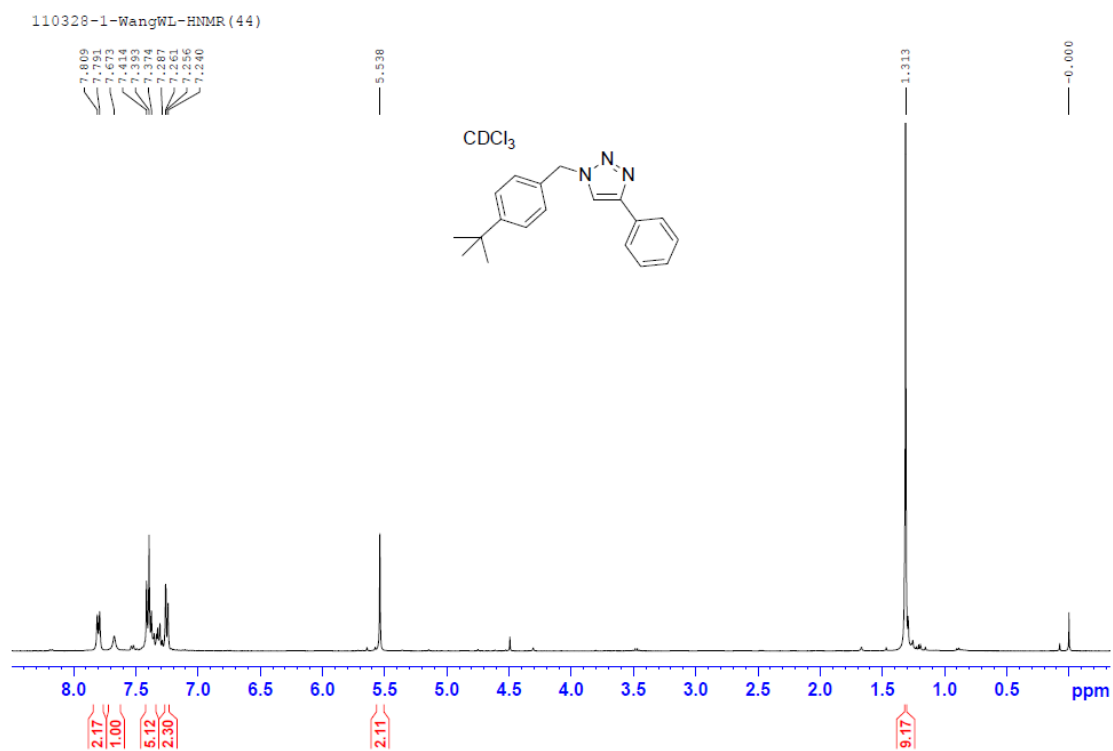
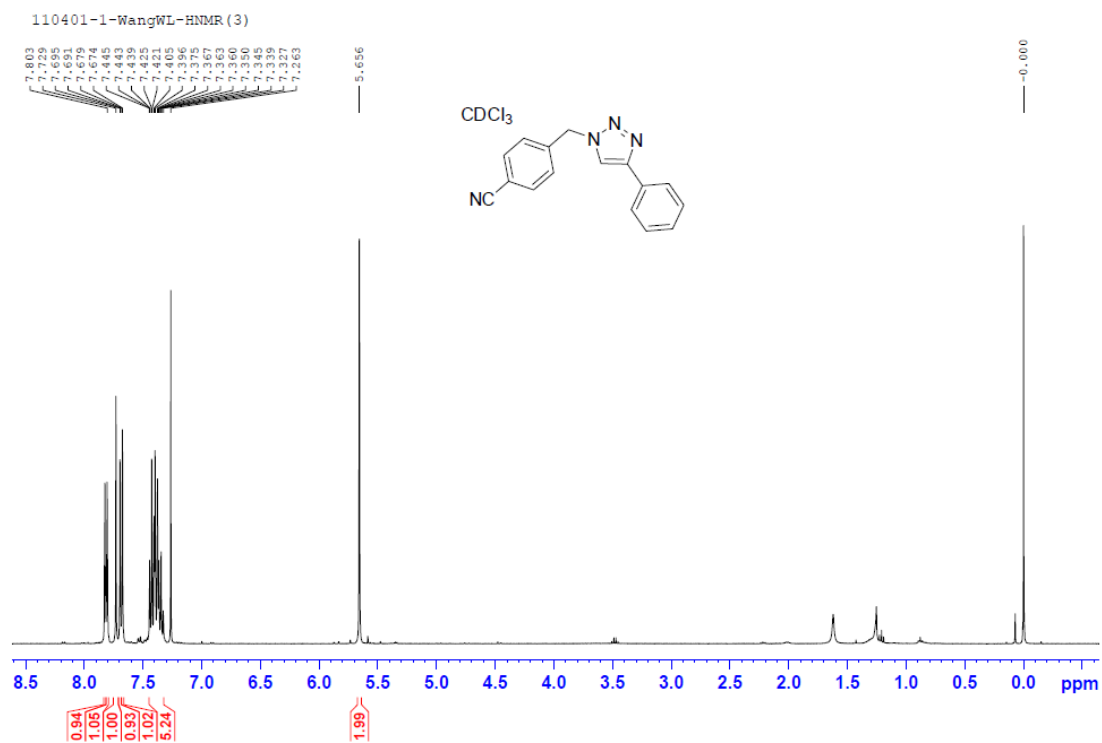
3.2 NMR copies of known compounds

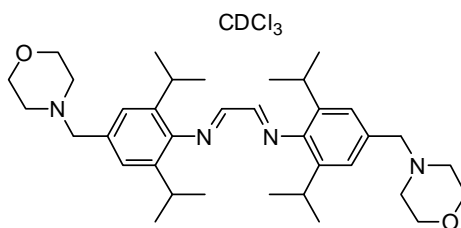




110411-7-WangWL-HNMR (69)







100809-4-WangWL-HNMR (27)

