

Facile syntheses of N-heterocyclic carbene precursors through Cu(II)- or Ag(I)-catalyzed amination of N-alkynyl formamidines

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General Information:

Unless otherwise stated, all reactions and manipulations were performed using standard Schlenk techniques. All solvents were purified by distillation using standard methods. Commercially available reagents were used without further purification. NMR spectra were recorded by using a Bruker 400 MHz spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (^1H NMR CDCl_3 : 7.26 ppm; ^{13}C NMR CDCl_3 : 77.0 ppm). Mass spectra were recorded on the HP-5989 instrument by EI/ESI methods. X-ray diffraction analysis was performed by using a Bruker Smart-1000 X-ray diffractometer.

Synthesis of 1a-1d, 2a-2c:

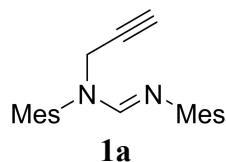
Procedure A:

NaH (60% suspension in mineral oil, 1.5 eq.) was added into a stirred solution of formimidamide (1.0 eq.) in dried DMF at 0 °C under N_2 . The mixture was then warmed to room temperature and stirred for 1 h. Bromoalkynes (1.1~1.2 eq.) was added drop wise to the mixture. After the addition was completed, the reaction mixture was stirred for an additional 4 h. When the reaction was completed (monitored by TLC), the reaction was quenched with water and the mixture was extracted for three times with EtOAc. The combined organic layer was washed with H_2O , saturated NaCl aqueous solution and dried with anhydrous Na_2SO_4 . The organic layer was concentrated under reduced pressure to afford the desired product.

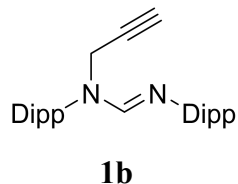
Procedure B:

A Schlenk tube was charged with formamidine (1.0 eq.), KI (2.0 eq.), K_2CO_3 (2.0 eq.), evacuated, and backfilled with N_2 . Then the solvent DMF was added under N_2 atmosphere. Then 1-bromo-2-butyne (1.1 eq.) was added into the solution. The mixture was reflux at 100 °C for 8 h. When the reaction was completed (monitored by TLC), the reaction was quenched

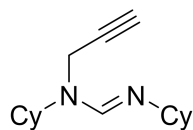
with water and the mixture was extracted for three times with EtOAc. The organic layer was dried over Na₂SO₄, and concentrated in vacuum to get crude product.



Following the procedure **A**, *N,N'*-dimesitylformimidamide (1.0 g, 3.57 mmol), bromopropyne (467 mg, 3.92 mmol), NaH (214 mg, 5.36 mmol) afford the product **1a** as pure brown oil (1.1 g, 96%). ¹H NMR (400 MHz, CDCl₃) δ = 7.18 (s, 1H, NCHN), 6.93 (s, 2H, ArH), 6.84 (s, 2H, ArH), 4.56 (s, 2H, NCH₂), 2.29 (s, 9H, ArCH₃), 2.24 (s, 3H, ArCH₃), 2.20 (s, 1H, CCH), 2.18 (s, 6H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 151.5 (NCN), 146.7 (ArC), 138.3 (ArC), 137.7 (ArC), 137.2 (ArC), 131.3 (ArC), 129.3 (ArC), 129.1 (ArC), 128.4 (ArC), 79.4 (CHC), 71.9 (CHC), 36.8 (NCH₂), 20.9 (ArCH₃), 20.6 (ArCH₃), 18.5 (ArCH₃), 18.2 (ArCH₃).

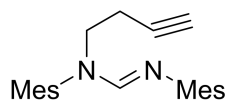


Following the procedure **A**, *N,N'*-bis(2,6-diisopropylphenyl)formimidamide (500 mg, 1.37 mmol), bromopropyne (194.4 mg, 1.64 mmol), NaH (82.4 mg, 2.05 mmol) afford the product **1b** as pure brown solid (581 mg, 98%). ¹H NMR (400 MHz, CDCl₃) δ = 7.33 (t, *J* = 7.6 Hz, 1H, ArH), 7.21 (s, 1H, NCHN), 7.19 (d, *J* = 7.6 Hz, 2H, ArH), 7.08 (d, *J* = 7.6 Hz, 2H, ArH), 6.99 (t, *J* = 8.0 Hz, 1H, ArH), 4.56 (d, *J* = 2.0 Hz, 2H, NCH₂), 3.31-3.20 (m, 4H, ArCH(CH₃)₂), 2.21 (s, 1H, CCH), 1.30 (d, *J* = 6.8 Hz, 6H, CH₃), 1.19 (d, *J* = 6.8 Hz, 12H, CH₃), 1.14 (d, *J* = 6.8 Hz, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 150.1 (NCHN), 148.6 (ArC), 146.7 (ArC), 139.8 (ArC), 137.7 (ArC), 129.0 (ArC), 124.1 (ArC), 122.8 (ArC), 122.6 (ArC), 78.9 (CHC), 72.3 (CHC), 53.4 (ArCH₂), 38.6 (NCH₂), 28.5 (CH₃), 27.8 (CH₃), 24.9 (CH₃), 24.5 (CH₃), 23.6 (CH₃).



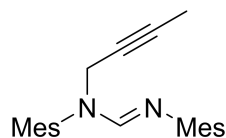
1c

Following the procedure **A**, *N,N'*-dicyclohexylformimidamide (2 g, 9.60 mmol), bromopropyne (1.86 mg, 15.8 mmol), NaH (345 mg, 14.4 mmol) afford the product **1c** as pale brown oil (1.04 g, 44%). ¹H NMR (400 MHz, CDCl₃) δ = 7.45 (s, 1H, NCHN), 4.04 (d, *J* = 2.5 Hz, 2H, NCH₂), 3.31-3.16 (m, 1H, NCyH), 2.93-2.80 (m, 1H, NCyH), 2.13-2.08 (m, *J* = 2.4 Hz, 1H, CCH), 1.93-1.02 (m, 22H, CyH). ¹³C NMR (100 MHz, CDCl₃) δ = 149.73 (NCHN), 81.08 (CHC), 77.21 (CHC), 69.93 (NCyC), 64.38 (NCyC), 58.10 (NCH₂), 35.55 (CyC), 34.48 (CyC), 32.69 (CyC), 31.54 (CyC), 29.21 (CyC), 25.55 (CyC), 25.31 (CyC), 25.13 (CyC), 24.86 (CyC), 24.57 (CyC).



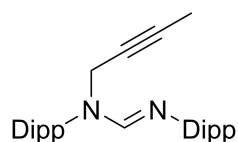
1d

Following the procedure **B**, *N,N'*-dimesitylformimidamide (1.0 g, 3.57 mmol), KI (1.07 g, 7.13 mmol), K₂CO₃ (985 mg, 7.13 mmol), 4-bromo-1-butyne (475 mg, 3.57 mmol) in DMF refluxing 18 h afford the product **1d** as colorless oil (350 mg, 31%). ¹H NMR (400 MHz, CDCl₃) δ = 7.12 (s, 1H, NCHN), 6.91 (s, 2H, ArH), 6.82 (s, 2H, ArH), 3.91 (t, *J* = 7.6 Hz, 2H, CH₂), 2.75-2.70 (m, 2H, CH₂), 2.28 (s, 3H, ArCH₃), 2.24 (s, 6H, ArCH₃), 2.23 (s, 4H, ArCH₃), 2.14 (s, 6H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 152.2 (NCHN), 146.9 (ArC), 139.1 (ArC), 137.3 (ArC), 136.3 (ArC), 131.2 (ArC), 129.4 (ArC), 129.0 (ArC), 128.4 (ArC), 81.9 (CHC), 69.4 (CHC), 47.6 (NCH₂), 20.8 (CH₃), 20.6 (CH₃), 18.6 (CH₃), 18.3 (CH₃), 17.5 (CH₃).



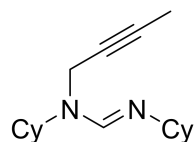
2a

Following the procedure **A**, *N,N'*-dimesitylformimidamide (3.00 g, 10.70 mmol), 1-bromo-2-butyne (1.70 g, 12.84 mmol), NaH (642 mg, 16.05 mmol) afford the product **2a** as pare brown oil (3.90 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ = 7.13 (s, 1H, NCHN), 6.90 (s, 2H, ArH), 6.81 (s, 2H, ArH), 4.46 (d, *J* = 2.0 Hz, 2H, NCH₂), 2.27 (s, 9H, ArCH₃), 2.22 (s, 3H, ArCH₃), 2.16 (s, 6H, ArCH₃), 1.76 (s, 3H, CCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 151.5 (NCHN), 146.9 (ArC), 138.6 (ArC), 137.4 (ArC), 137.1 (ArC), 131.1 (ArC), 129.1 (ArC), 129.1 (ArC), 128.3 (ArC), 79.3 (CHC), 74.5 (CHC), 37.2 (NCH₂), 20.8 (CH₃), 20.6 (CH₃), 18.4 (CH₃), 18.1 (CH₃).



2b

Following the procedure **A**, *N,N'*-bis (2,6-diisopropylphenyl) formimidamide (3.00 g, 8.22 mmol), 1-bromo-2-butyne (1.30 g, 9.86 mmol), NaH (494 mg, 12.33 mmol) afford the product **2b** as pare brown solid (3.36 g, 98%). ¹H NMR (400 MHz, CDCl₃) δ = 7.37 -7.31 (m, 1H), 7.20 (d, *J* = 6.2 Hz, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.01 (dd, *J* = 8.2, 7.0 Hz, 1H), 4.50 (d, *J* = 2.3 Hz, 2H, NCH₂), 3.36-3.23 (m, 4H, ArCH(CH₃)₂), 1.79 (d, *J* = 2.3 Hz, 3H, CCH₃), 1.32 (d, *J* = 6.8 Hz, 6H, ArCHCH₃), 1.21 (d, *J* = 6.9 Hz, 12H, ArCHCH₃), 1.16 (d, *J* = 6.9 Hz, 6H, ArCHCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 150.1 (NCHN), 148.4 (ArC), 146.9 (ArC), 139.8 (ArC), 138.1 (ArC), 128.8 (ArC), 124.1 (ArC), 122.6 (ArC), 79.80 (CHC), 74.2 (CHC), 39.2 (NCH₂), 28.6 (CH₃), 27.7 (CH₃), 24.9 (CH₃), 24.4 (CH₃), 23.6 (CH₃).



2c

Following the procedure **C**, *N,N'*-dicyclohexylformimidamide (1.5 g, 7.20 mmol), KI (2.39 g, 14.4 mmol), K₂CO₃ (1.99 g, 14.4 mmol), 1-bromo-2-butyne (1.05 g, 7.92 mmol)

afford the product **2c** as pure brown oil (1.43 g, 77%). ¹H NMR (400 MHz, CDCl₃) δ = 7.41 (s, 1H, NCHN), 3.95 (d, *J* = 2.4 Hz, 2H, NCH₂), 3.27-3.21 (m, 1H, NCyH), 2.84-2.79 (m, 1H, NCyH), 1.83-1.77 (m, 4H, CyH), 1.75 (s, 3H, CCH₃), 1.72-1.69 (m, 2H, CyH), 1.61-1.54 (m, 3H, CyH), 1.43-1.22 (m, 8H, CyH), 1.13-1.08 (m, 3H, CyH); ¹³C NMR (100 MHz, CDCl₃) δ = 150.5 (NCHN), 64.8 (CHC), 58.2 (CHC), 35.9 (NCH₂), 33.7 (CyC), 31.9 (CyC), 25.9 (CyC), 25.6 (CyC), 25.6 (CyC), 25.4 (CyC).

Synthesis of complexes 3~9:

Procedure C: A Schlenk tube was charged with formamidine (1.0 eq.) and Cu(OTf)₂ (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at 80 °C for 2 h. When the reaction was completed (monitored by TLC), the reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried with Na₂SO₄, and concentrated in vacuum, and purified through column chromatography on silica gel to afford the product.

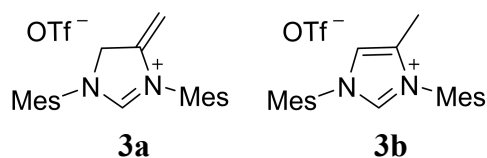
Procedure D: A Schlenk tube was charged with formamidine (1.0 eq.) and AgOTf (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at 80 °C for 2 h. When the reaction was completed (monitored by TLC), the reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried with Na₂SO₄, and concentrated in vacuum and purified through column chromatography on silica gel to afford the product.

Procedure E: A Schlenk tube was charged with formamidine (1.0 eq.) and AgOTf (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at room temperature for 2 h. When the reaction was completed (monitored by TLC), the reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried with Na₂SO₄, and concentrated in vacuum and purified through column chromatography on silica gel to afford the product.

Procedure F: A Schlenk tube was charged with formamidine (1.0 eq.), AgOTf (0.1 eq.), HOTf (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at room temperature for 3 h, and 80 °C for 4 h. The reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried over Na₂SO₄, and concentrated in vacuum to afford the product in the NMR yield.

Procedure G: A Schlenk tube was charged with formamidine (1.0 eq.), Cu(OTf)₂ (0.1 eq.), HOTf (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at room temperature for 3 h, and 80 °C for 4 h. The reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried over Na₂SO₄, and concentrated in vacuum to afford the product in the NMR yield.

Procedure H: A Schlenk tube was charged with formamidine (1.0 eq.), HOTf (1.0 eq.), evacuated, and backfilled with N₂. Dried DCE was successively added. The mixture was then stirred at room temperature for 3 h, and 80 °C for 4 h. The reaction was quenched with water and the mixture was filtered. The filtration was extracted by DCM for three times. The organic layer was dried over Na₂SO₄, and concentrated in vacuum to afford the product in the NMR yield.



Following the procedure C, **1a** (100 mg, 0.314 mmol) and Cu(OTf)₂ (113.6 mg, 0.314 mmol) afford the product **3a** as pale yellow oil (108 mg, 73%). Mp: 215-216 °C; ¹H NMR (400 MHz, CDCl₃) δ = 9.18 (s, 1H, NCHN), 7.02 (s, 2H, ArH), 6.98 (s, 2H, ArH), 5.06 (m, 2H, NCH₂), 4.97 (d, *J* = 2.4 Hz, 1H, CCH₂), 4.53 (d, *J* = 3.2 Hz, 1H, CCH₂), 2.33 (s, 9H, ArCH₃), 2.31 (s, 3H, ArCH₃), 2.26 (s, 6H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 160.6 (NCHN), 141.2 (ArC), 141.0 (ArC), 140.2 (ArC), 135.4 (ArC), 134.6 (ArC), 130.1 (ArC),

129.7 (ArC), 126.4 (CCH₂), 120.4 (q, J_{C-F} =319 Hz), 94.8 (CCH), 55.4 (NCH₂), 21.1 (CH₃), 21.0 (CH₃), 17.5 (CH₃), 17.3 (CH₃), 17.2 (CH₃); IR (KBr): ν (cm⁻¹) 3017, 2922, 2852, 1672, 1618, 1483, 1462, 1257, 1153, 1030, 854, 637; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₂₂H₂₇N₂⁺:319.2174, found: 319.2252.

Following the procedure **D**, **1a** (100 mg, 0.314 mmol) and AgOTf (81 mg, 0.314 mmol) afford the product **3a** in a 39% NMR yield.

Following the procedure **F**, **1a** (50 mg, 0.157 mmol), AgOTf (4 mg, 0.015 mmol), and HOTf (0.023 ml, 0.157 mmol) afford the product **3b** in a 90% NMR yield. Our data are in full agreement with those reported in the literature.¹ ¹H NMR (400 MHz, CDCl₃) δ = 9.20 (s, 1H, NCHN), 7.30 (s, 1H, NCH), 7.06 (d, J = 17.4 Hz, 4H, ArH), 2.36 (d, J = 8.0 Hz, 6H, CH₃), 2.15 (d, J = 9.3 Hz, 9H, CH₃), 2.08 (s, 6H, CH₃).

Following the procedure **G**, **1a** (50 mg, 0.157 mmol), Cu(OTf)₂ (5 mg, 0.015 mmol), and HOTf (0.023 ml, 0.157 mmol) afford the product **3a** and **3b** in a 62% and 28% NMR yield.

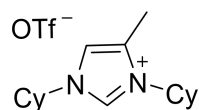


Following the procedure **C**, **1b** (100 mg, 0.248 mmol) and Cu(OTf)₂ (89 mg, 0.248 mmol) afford the product **4a** as pale yellow solid (96 mg, 70%). Mp: 155-156 °C; ¹H NMR (400 MHz, CDCl₃) δ = 9.21 (s, 1H, NCHN), 7.57-7.49 (m, 2H, ArH), 7.34 (d, J = 8.0 Hz, 2H, ArH), 7.30 (d, J = 7.6 Hz, 2H, ArH), 5.20 (d, J = 3.2 Hz, 2H, NCH₂), 5.16 (d, J = 2.8 Hz, 1H, CCH₂), 4.58 (d, J = 3.6 Hz, 1H, CCH₂), 2.90-2.80 (m, 4H, ArCH(CH₃)₂), 1.38 (d, J = 6.8 Hz, 6H, CH₃), 1.29 (d, J = 6.8 Hz, 12H, CH₃), 1.28 (d, J = 7.2 Hz, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 160.1 (NCHN), 146.2 (ArC), 145.7 (ArC), 141.9 (ArC), 132.0 (ArC), 131.8 (ArC), 128.9 (ArC), 125.8 (ArC), 125.1 (ArC), 125.0 (CCH₂), 96.3 (CCH), 57.8 (NCH₂), 29.4 (ArCH), 29.3 (ArCH), 24.8 (CH₃), 24.5 (CH₃), 23.9 (CH₃), 23.7 (CH₃); IR (KBr): ν (cm⁻¹) 3070, 2964, 2872, 1612, 1465, 1329, 1282, 1253, 1156, 1030, 806, 637; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₂₈H₃₉N₂⁺:403.3113, found: 403.3109.

Following the procedure **D**, **1b** (100 mg, 0.248 mmol) and AgOTf (64 mg, 0.248 mmol) afford the product **4a** in a 33% NMR yield.

Following the procedure **F**, **1a** (47 mg, 0.116 mmol), AgOTf (3 mg, 0.011 mmol), and HOTf (18 mg, 0.116 mmol) afford the product **4b** as pale yellow solid in the yield 95%. Mp: 299-301 °C; ¹H NMR (400 MHz, CDCl₃) δ = 9.10 (d, *J* = 1.6 Hz, 1H, NCHN), 7.61 – 7.55 (m, 2H, ArH), 7.55 – 7.50 (m, 1H, NCH), 7.35 (d, *J* = 7.9 Hz, 2H, ArH), 7.30 (d, *J* = 7.8 Hz, 2H, ArH), 2.42 – 2.34 (m, 2H, ArCH(CH₃)₂), 2.30 – 2.22 (m, 2H, ArCH(CH₃)₂), 2.18 (s, 3H, CH₃), 1.29 – 1.22 (m, 13H, CH₃), 1.19 – 1.13 (m, 12H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 145.2 (NCHN), 144.9 (NCH), 137.4 (ArC), 133.9 (ArC), 132.3 (ArC), 131.9 (ArC), 129.8 (ArC), 127.3 (ArC), 124.9 (ArC), 124.5 (ArC), 122.7 (ArC), 120.5 (q, *J*_{C-F}=319 Hz), 29.03 (ArCH), 28.97 (ArCH), 24.70 (CH₃), 24.36 (CH₃), 23.75 (CH₃), 23.06 (CH₃), 9.37 (CH₃); IR (KBr): ν (cm⁻¹) 3085, 2965, 2872, 1637, 1538, 1465, 1329, 1254, 1153, 1030, 806, 776, 637; HRMS (ESI): *m/z* [M-OTf]⁺ calcd. for C₂₈H₃₉N₂⁺:403.3108, found: 403.3105.

Following the procedure **G**, **1a** (56 mg, 0.138 mmol), Cu(OTf)₂ (5 mg, 0.013 mmol), and HOTf (21 mg, 0.138 mmol) afford the product **4b** in a 75% NMR yield.



5

Following the procedure **C**, **1c** (100 mg, 0.407 mmol) and Cu(OTf)₂ (147 mg, 0.407 mmol) afford the product **5** in a 98% NMR yield. ¹H NMR (400 MHz, CDCl₃) δ = 9.06 (s, 1H, NCHN), 7.15 (s, 1H, NCH), 4.43-4.29 (m, 1H, NCyH), 4.05-3.91 (m, 1H, NCyH), 2.34 (s, 3H, CH₃), 2.20-1.15 (m, 22H, CyH); ¹³C NMR (100 MHz, CDCl₃) δ = 132.51 (NCHN), 130.52 (NCCH₃), 120.5 (q, *J*_{C-F}=319 Hz), 117.01 (NCH), 59.74 (NCyC), 57.62 (NCyC), 43.51 (CyC), 33.16 (CyC), 32.92 (CyC), 25.23 (CyC), 24.75 (CyC), 24.42 (CyC), 24.28 (CyC), 9.29 (CCH₃); IR (KBr): ν (cm⁻¹) 2935, 2859, 1645, 1555, 1454, 1262, 1157, 1029, 845, 635; HRMS (ESI): *m/z* [M-OTf]⁺ calcd. for C₁₆H₂₇N₂⁺:247.2169, found:247.2168.

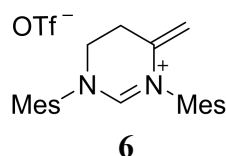
Following the procedure **D**, **1c** (100 mg, 0.407 mmol) and AgOTf (104 mg, 0.407 mmol) afford the product **5** as pale yellow oil (65 mg, 40%).

Following the procedure **E**, **1c** (100 mg, 0.407 mmol) and AgOTf (104 mg, 0.407 mmol) afford the product **5** as pale yellow oil (105 mg, 65%).

Following the procedure **F**, **1c** (47 mg, 0.194 mmol) and AgOTf (5 mg, 0.019 mmol), HOTf (29 mg, 0.194 mmol) afford the product **5** in a 83% NMR yield.

Following the procedure **G**, **1c** (47 mg, 0.193 mmol), Cu(OTf)₂ (7 mg, 0.019 mmol), and HOTf (29 mg, 0.193 mmol) afford the product **5** in a 85% NMR yield.

Following the procedure **H**, **1c** (30 mg, 0.121 mmol) and HOTf (18 mg, 0.121 mmol) afford the product **5** in a 86% NMR yield.

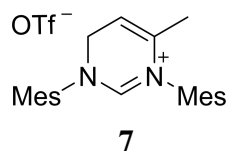


Following the procedure **C**, **1d** (70 mg, 0.210 mmol) and Cu(OTf)₂ (77 mg, 0.210 mmol) afford the product **6** as pale yellow oil (70 mg, 69%). ¹H NMR (400 MHz, CDCl₃) δ = 7.90 (s, 1H, NCHN), 6.96 (s, 2H, ArH), 6.92 (s, 2H, ArH), 4.97 (s, 1H, CCH₂), 4.52 (s, 1H, CCH₂), 3.99 (s, 2H, CH₂), 3.23 (s, 2H, CH₂), 2.27 (s, 9H, ArCH₃), 2.24 (s, 3H, ArCH₃), 2.19 (s, 6H, ArCH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 152.6 (NCHN), 141.1 (ArC), 140.8 (ArC), 135.8 (CCH₂), 135.0 (ArC), 134.9 (ArC), 133.6 (ArC), 132.7 (ArC), 130.2 (ArC), 130.1 (ArC), 120.5 (q, J_{C-F}=319 Hz), 105.1 (CCH₂), 47.9 (NCH₂), 25.2 (NCH₂CH₂), 21.0 (CH₃), 20.9 (CH₃), 17.6 (CH₃), 17.2 (CH₃); IR (KBr): ν (cm⁻¹) 2920, 2850, 1659, 1639, 1480, 1372, 1333, 1261, 1145, 1030, 854, 637; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₂₃H₂₉N₂⁺:333.2325, found: 333.2325.

Following the procedure **D**, **1d** (100 mg, 0.301 mmol) and AgOTf (78 mg, 0.301 mmol) afford the product **6** in a 83% NMR yield.

Following the procedure **F**, **1d** (65 mg, 0.194 mmol) and AgOTf (5 mg, 0.019 mmol), HOTf (29 mg, 0.194 mmol) afford the product **6** in a 44% NMR yield.

Following the procedure **G**, **1d** (46 mg, 0.138 mmol) and Cu(OTf)₂ (5 mg, 0.013 mmol), HOTf (21 mg, 0.138 mmol) afford the product **6** in a 17% NMR yield.

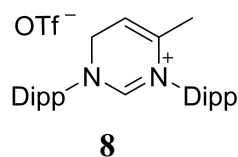


Following the procedure **C**, **2a** (100 mg, 0.301 mmol) and Cu(OTf)₂ (109 mg, 0.301 mmol) afford the product **7** as pale yellow solid (113mg, 78%). Mp: 169-171 °C; ¹H NMR (400 MHz, CDCl₃) δ = 7.88 (s, 1H, NCHN), 6.99 (s, 4H, ArH), 5.53 (s, 1H, CCH), 4.60 (s, 2H, NCH₂), 2.40 (s, 6H, ArCH₃), 2.32 (s, 6H, ArCH₃), 2.31 (s, 3H, ArCH₃), 2.29 (s, 3H, ArCH₃), 1.61 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 154.3 (NCHN), 141.2 (ArC), 141.0 (ArC), 135.2 (ArC), 134.6 (ArC), 133.4 (ArC), 132.0 (ArC), 131.8 (ArC), 130.4 (ArC), 130.0 (ArC), 120.6 (q, J_{C-F}=319 Hz), 105.2 (NCH₂CH), 49.0 (NCH₂), 21.0 (ArCH₃), 20.9 (ArCH₃), 17.7 (ArCH₃), 17.3 (ArCH₃), 17.1 (CCH₃); IR (KBr): ν (cm⁻¹) 3038, 2923, 2856, 1706, 1635, 1442, 1339, 1259, 1148, 1029, 856, 636, 572; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₂₃H₂₉N₂⁺: 333.2331, found: 333.2339.

Following the procedure **D**, **2a** (100 mg, 0.301 mmol) and AgOTf (78 mg, 0.301 mmol) afford the product **7** as pale yellow solid (105 mg, 72%).

Following the procedure **F**, **2a** (52 mg, 0.155 mmol), AgOTf (4 mg, 0.015 mmol), and HOTf (23 mg, 0.155 mmol) afford the product **7** in a 82% NMR yield.

Following the procedure **G**, **2a** (46 mg, 0.138 mmol), Cu(OTf)₂ (5 mg, 0.013 mmol), and HOTf (21 mg, 0.138 mmol) afford the product **7** in a 15% NMR yield.



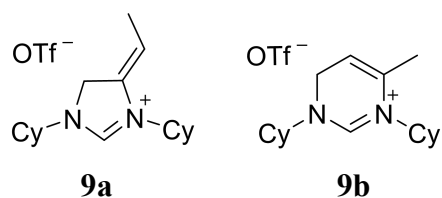
Following the procedure **C**, **2b** (100 mg, 0.240 mmol) and Cu(OTf)₂ (87 mg, 0.240 mmol) afford the product **8** as pale yellow solid (85 mg, 62%). Mp: 238-239 °C; ¹H NMR (400 MHz, CDCl₃) δ = 7.54 (s, 1H, NCHN), 7.50 (d, J = 8.0 Hz, 1H, ArH), 7.47 (d, J = 8.4 Hz, 1H, ArH), 7.30 (d, J = 2.0 Hz, 2H, ArH), 7.28 (d, J = 1.6 Hz, 2H, ArH), 5.80 (s, 1H, CCH), 4.72 (s, 2H, NCH₂), 3.20-3.07 (m, 4H, ArCH(CH₃)₂), 1.65 (s, 3H, CH₃), 1.41 (d, J = 6.8 Hz, 6H, CH₃), 1.37 (d, J = 6.8 Hz, 6H, CH₃), 1.27 (d, J = 7.2 Hz, 6H, CH₃), 1.25 (d, J = 7.2 Hz, 6H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 152.6 (NCHN), 146.1 (ArC), 144.7 (ArC), 133.7 (ArC), 132.0 (ArC), 131.8 (ArC), 131.1 (ArC), 125.8 (ArC), 125.3 (ArC), 120.7 (q,

J_{C-F} =319 Hz), 106.3 (NCH₂CH), 51.7 (NCH₂), 28.9 (ArCH), 28.8 (ArCH), 25.3 (CH₃), 25.0 (CH₃), 24.8 (CH₃), 23.3 (CH₃), 17.7 (CH₃); IR (KBr): ν (cm⁻¹) 3068, 2965, 2873, 1708, 1632, 1465, 1392, 1325, 1258, 1150, 1032, 806, 757, 637; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₂₉H₄₁N₂⁺: 417.3270, found: 417.3272.

Following the procedure **D**, **2b** (50 mg, 0.120 mmol) and AgOTf (31 mg, 0.120 mmol) afford the product **8** in a 91% NMR yield.

Following the procedure **F**, **2b** (49 mg, 0.116 mmol), AgOTf (3 mg, 0.011 mmol), and HOTf (18 mg, 0.116 mmol) afford the product **8** in a 82% NMR yield.

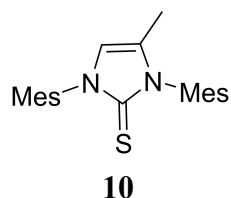
Following the procedure **G**, **2b** (57 mg, 0.138 mmol), Cu(OTf)₂ (5 mg, 0.013 mmol), and HOTf (21 mg, 0.138 mmol) afford the product **8** in a 73% NMR yield.



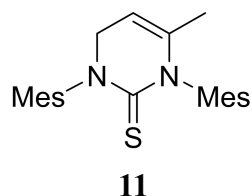
Following the procedure **D**, **2c** (100 mg, 0.384 mmol) and AgOTf (139 mg, 0.384 mmol) afford the product **9a** as pale yellow oil (55 mg, 35%). ¹H NMR (400 MHz, CDCl₃) δ = 8.80 (s, 1H, NCHN), 5.06-5.00 (m, 1H, NCyH), 4.52 (t, J =3.2 Hz, 2H, NCH₂), 3.97-3.95 (m, 1H, CCH), 3.83-3.77 (m, 1H, NCyH), 2.13-2.09 (m, 2H, CyH), 2.00-1.95 (m, 4H, CH₃), 1.89-1.75 (m, 5H, CyH), 1.72-1.63 (m, 4H, CyH), 1.45-1.40 (m, 4H, CyH), 1.34-1.25 (m, 4H, CyH); ¹³C NMR (100 MHz, CDCl₃) δ = 150.2 (NCHN), 132.2 (NCH₂CH), 120.5 (q, J_{C-F} =319 Hz), 103.2 (NCCH₃), 64.5 (NCyC), 58.6 (NCyC), 40.8 (NCH₂), 32.2 (CyC), 29.2 (CyC), 25.4 (CyC), 24.5 (CyC), 24.3 (CyC), 23.9 (CyC), 17.2 (CCH₃); IR (KBr): ν (cm⁻¹) 2834, 2858, 1709, 1641, 1452, 1352, 1256, 1154, 1030, 894, 638; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₁₇H₂₉N₂⁺: 261.2325, found: 261.2325.

Following the procedure **E**, **2c** (100 mg, 0.384 mmol) and AgOTf (99 mg, 0.384 mmol) afford the product **9b** as pale yellow oil (83 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ = 8.12 (s, 1H, NCHN), 4.94 (s, 1H, CCH), 4.03 (s, 2H, NCH₂), 3.80 (t, J = 11.6 Hz, 1H, NCyH), 3.42 (t, J = 12.0 Hz, 1H, NCyH), 1.87 (s, 3H, CH₃), 1.80-1.71 (m, 9H, CyH), 1.66-1.64 (m, 2H, CyH), 1.52-1.35 (m, 6H, CyH), 1.24-1.15 (m, 3H, CyH); ¹³C NMR (100 MHz, CDCl₃) δ = 155.5 (NCHN), 132.1 (NCCH₂), 120.5 (q, J_{C-F} = 318 Hz), 103.5 (CCH), 58.4 (NCyC), 57.5

(NCyC), 51.7 (NCH₂), 33.6 (CyC), 32.4 (CyC), 30.7 (CyC), 25.2 (CyC), 24.5 (CyC), 24.4 (CyC), 24.3 (CyC), 10.9 (CCH₃); IR (KBr): ν (cm⁻¹) 2936, 2859, 1709, 1643, 1454, 1355, 1311, 1258, 1157, 1032, 870, 636; HRMS (ESI): m/z [M-OTf]⁺ calcd. for C₁₇H₂₉N₂⁺:261.2325, found: 261.2324.

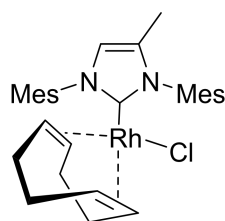


A Schlenk tube was charged with **3** (50 mg, 0.106 mmol), ^tBuOK (15.7 mg, 0.14 mmol), S₈ (7 mg, 0.212 mmol), evacuated and backfilled with N₂. Dried THF was successively added. The mixture was then stirred at room temperature for 2 h. When the reaction was completed (monitored by TLC), the solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EA = 10:1) to give the product **10** as pale yellow powder (19 mg, 49%). Mp: 252-253 °C; ¹H NMR (400 MHz, CDCl₃) δ = 7.00 (d, J = 12.1 Hz, 4H, ArH), 6.53 (s, 1H, NCH), 2.33 (d, J = 5.9 Hz, 6H, CH₃), 2.12 (d, J = 11.7 Hz, 12H, CH₃), 1.91 (d, J = 1.1 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ = 162.5 (SC), 139.1 (ArC), 138.9 (ArC), 135.8 (ArC), 135.6 (ArC), 133.6 (ArC), 131.6 (ArC), 129.3 (ArC), 129.1 (ArC), 126.2 (NCH), 114.1 (NCCH₃), 29.6 (CH₃), 21.1 (CH₃), 21.1 (CH₃), 17.8 (CH₃), 17.6 (CH₃), 10.4 (CH₃); IR (KBr): ν (cm⁻¹) 2917, 2853, 1674, 1486, 1397, 1357, 1199, 1035, 1009, 860, 758, 637; HRMS (ESI): m/z [M + Na]⁺ calcd. for C₂₂H₂₆N₂NaS⁺: 373.1709, found: 373.1707.



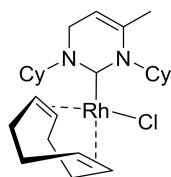
KHMDS (1.0 M in hexane, 0.124 mL, 0.124 mmol) was added drop wise to a solution of **7a** (50 mg, 0.103 mmol) and S₈ (5mg, 0.206 mmol) in THF (2 mL) at -78 °C. After 30 minutes, the mixture was warmed to room temperature, and stirred for 2 h. The solvent was

evacuated in vacuum, and the residue was purified by column chromatography on silica gel (PE/EA = 10:1) to give the product **11** as pale yellow powder (33 mg, 79%). Mp: 202-203 °C; ¹H NMR (400 MHz, CDCl₃) δ = 6.92 (s, 2H, ArH), 6.89 (s, 2H, ArH), 4.93-4.92 (m, 1H, CCH), 4.17 (dd, *J* = 3.2 Hz, 2.0 Hz, 2H, NCH₂), 2.32 (s, 6H, ArCH₃), 2.28 (s, 3H, ArCH₃), 2.27 (s, 3H, ArCH₃), 2.26 (s, 6H, ArCH₃), 1.43 (s, 3H, CH₃); ¹³C NMR (100 MHz, CDCl₃) δ = 176.7 (NCHN), 140.7 (ArC), 137.3 (ArC), 137.2 (ArC), 136.9 (ArC), 136.1 (ArC), 134.1 (ArC), 134.0 (ArC), 129.6 (ArC), 128.8 (ArC), 97.3 (NCH₂CH), 48.3 (NCH₂), 21.1 (CH₃), 21.0 (CH₃), 20.2 (CH₃), 17.8 (CH₃), 17.2 (CH₃); IR (KBr): ν (cm⁻¹) 2915, 2853, 1702, 1490, 1449, 1355, 1314, 1278, 1225, 1046, 849, 732; HRMS(ESI): *m/z* [M+H]⁺ calcd. for C₂₃H₂₉N₂S⁺:365.2051, found: 365.2047.



12

KHMDS (1.0 M in hexane, 0.39 mL, 0.39 mmol) was added drop wise to a solution of **3** (50 mg, 0.106 mmol) and [Rh(cod)Cl]₂ (27.1 mg, 0.05 mmol) in THF (3 mL) at -78 °C. After 30 minutes, the mixture was warmed to room temperature and stirred for 2 h. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EA = 25:1) to give the product as an orange product (28 mg, 43%). ¹H NMR (400 MHz, CDCl₃) δ = 7.07 (s, 2H, ArH), 7.02 (s, 1H, ArH), 6.99 (s, 1H, ArH), 6.69 (s, 1H, NCH), 4.45 (d, *J* = 11.6 Hz, 2H, CHCH), 3.31 (d, *J* = 13.6 Hz, 2H, CHCH), 2.42 (s, 2H), 2.38 (m, 4H), 2.33 (d, *J* = 8.4 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 3H), 1.87 (s, 3H), 1.82 (s, 3H), 1.55 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 183.0 (d, *J* = 51.9 Hz, NCRh), 165.5 (ArC), 163.9 (ArC), 138.4 (ArC), 138.0 (ArC), 137.5 (ArC), 136.4 (ArC), 134.5 (ArC), 134.0 (ArC), 131.0 (ArC), 129.6 (CHCH), 128.4 (CHCH), 125.6 (ArC), 120.4 (NCCH₃), 95.8 (NCH), 67.5, 54.3, 33.0, 32.4, 28.4, 21.2, 21.1, 18.8, 17.6, 9.7; IR (KBr): ν (cm⁻¹) 2921, 2852, 1678, 1608, 1482, 1377, 1282, 1154, 1031, 851, 657; HRMS (EI): *m/z* [M]⁺ calcd. for C₃₀H₃₈N₂ClRh⁺:564.1773, found: 564.1777.



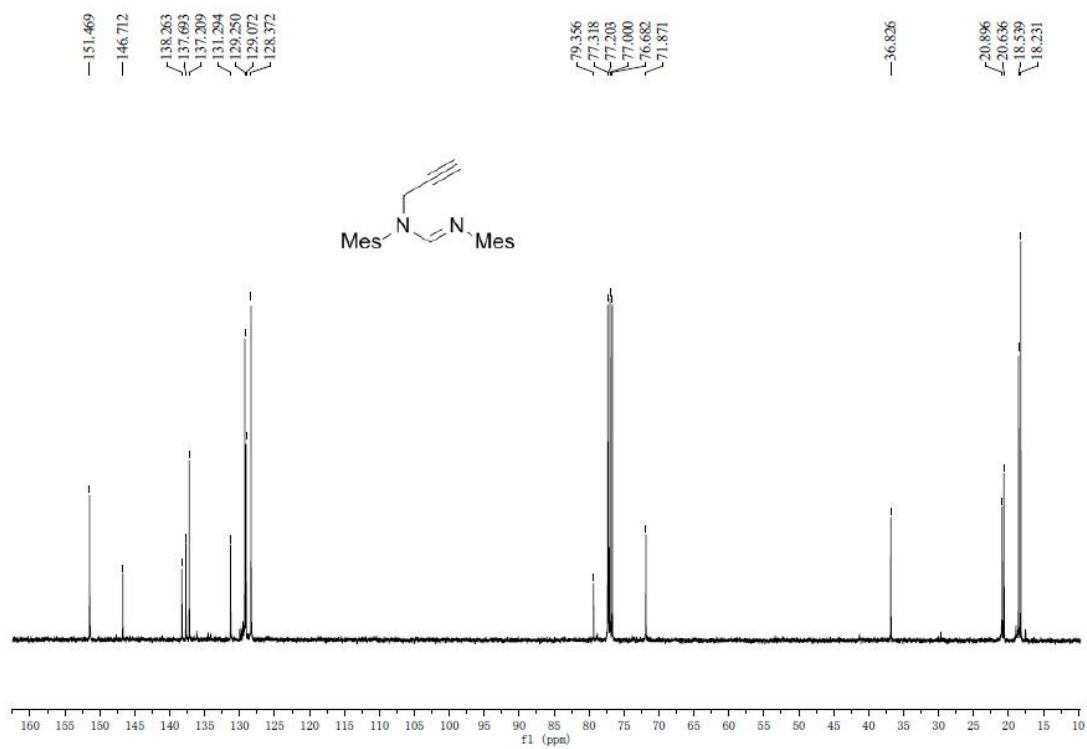
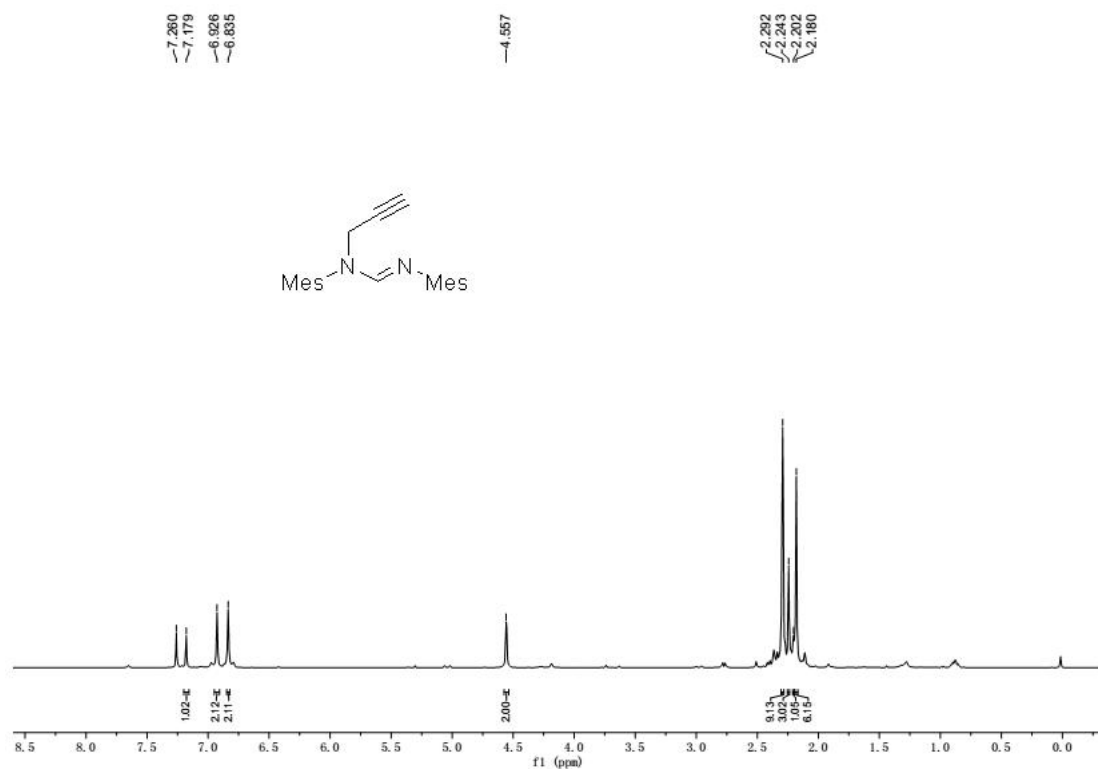
13

KHMDS (1.0 M in hexane, 0.39 mL, 0.39 mmol) was added drop wise to a solution of **9b** (140 mg, 0.34 mmol) and $[\text{Rh}(\text{cod})\text{Cl}]_2$ (92 mg, 0.17 mmol) in THF (5 mL) at $-78\text{ }^\circ\text{C}$. After 30 minutes, the mixture was warmed to room temperature and stirred for 2 h. The solvent was evacuated in vacuo, and the residue was purified by column chromatography on silica gel (PE/EA = 25:1) to give the product **13** as an orange product (30 mg, 17%). ^1H NMR (400 MHz, CDCl_3) δ = 6.41-6.34 (m, 1H, NCyH), 6.30-6.23 (m, 1H, NCyH), 4.91 (s, 2H, CHCH), 4.59 (m, 1H, CCH), 3.53-3.51 (m, 2H, NCH₂), 3.37 (m, 2H, CHCH), 2.40-2.31 (m, 5H), 2.21-2.10 (m, 2H), 1.97-1.94 (m, 3H), 1.91 (s, 3H, CH₃), 1.88-1.82 (m, 5H), 1.79-1.73 (m, 3H), 1.67-1.55 (m, 7H), 1.37-1.30 (m, 1H), 1.16-1.08 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ = 211.3 (d, J = 46.1 Hz, NCRh), 134.9 (CHCH), 102.6 (NCCH₃), 96.1 (NCH₂C), 68.3 (NCyC), 67.3 (NCyC), 65.1 (NCH₂), 39.46, 34.07, 33.16, 32.38, 31.89, 30.84, 30.65, 29.67, 29.33, 29.29, 29.18, 29.00, 28.59, 27.61, 27.18, 26.85, 26.13, 25.94, 22.66, 21.58, 14.08; IR (KBr): ν (cm^{-1}) 2923, 2851, 1694, 1658, 1497, 1449, 1358, 1261, 1089, 1022, 800, 641; HRMS(ESI): m/z $[\text{M}-\text{Cl}+\text{CH}_3\text{CN}]^+$ calcd. for $\text{C}_{27}\text{H}_{43}\text{N}_3^+$: 512.2507, found: 512.2500.

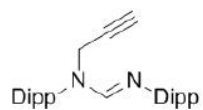
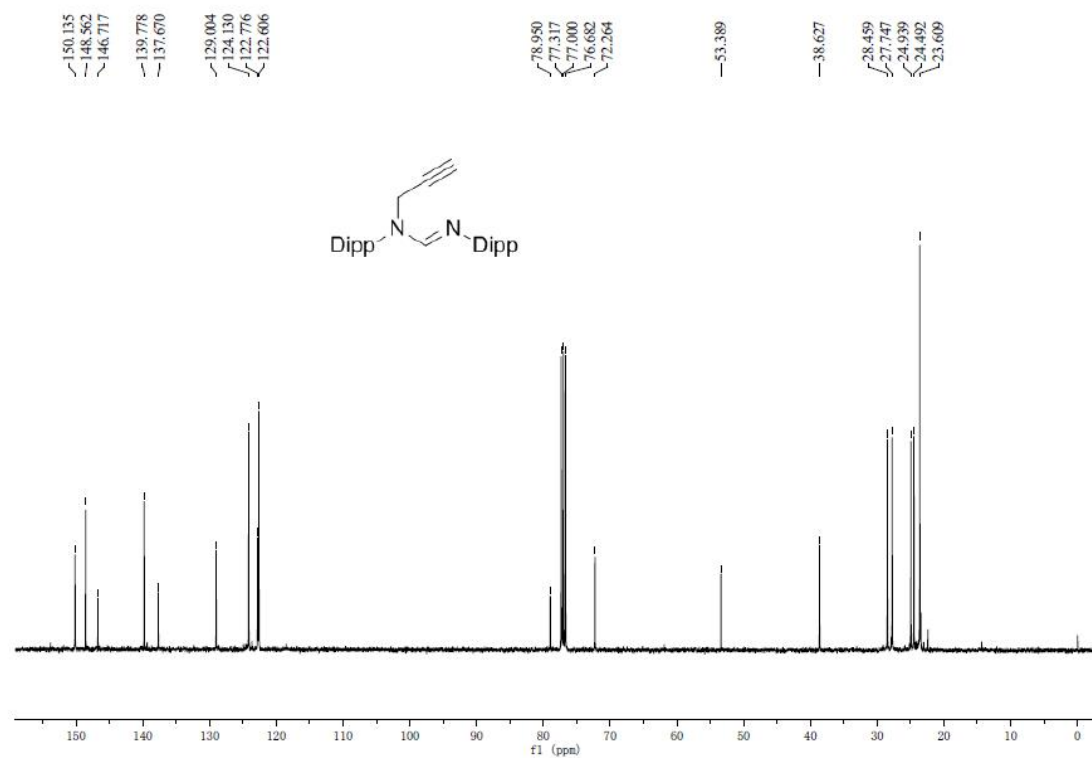
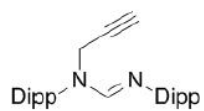
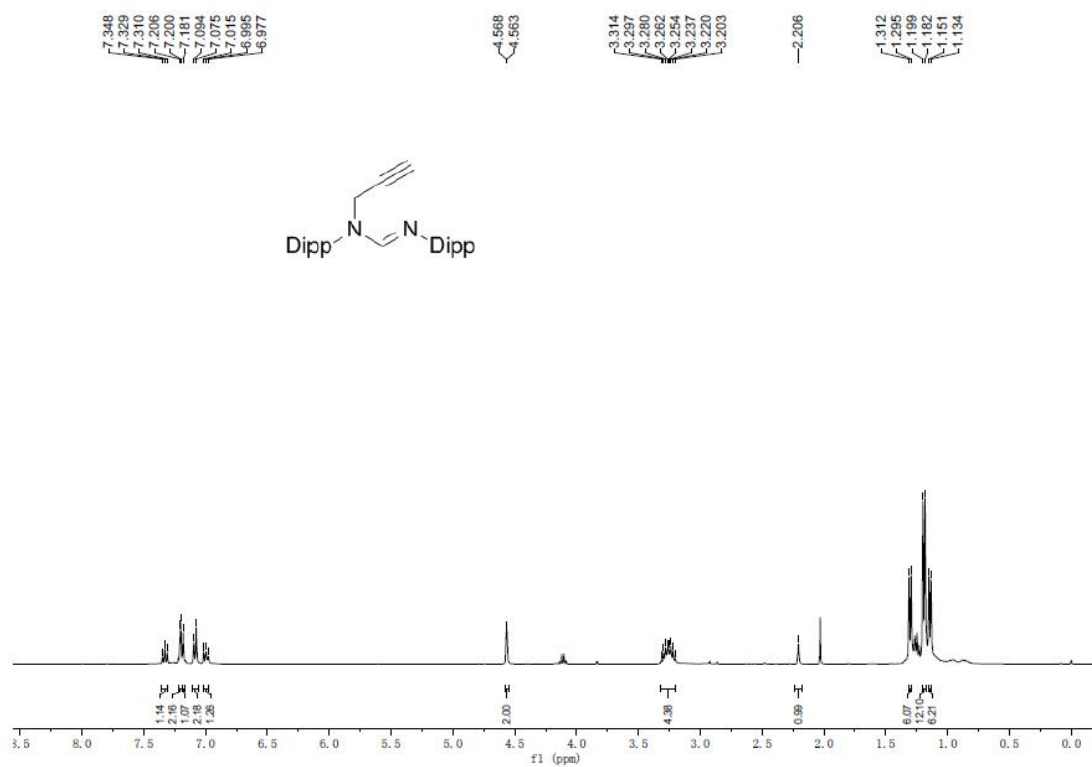
Reference:

1. S. Urban, M. Tursky, R. Fröhlich and F. Glorius, *Dalton Trans.*, 2009, 6934.

**NMR spectra:
compound 1a**

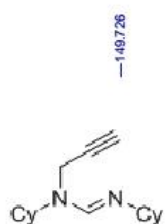
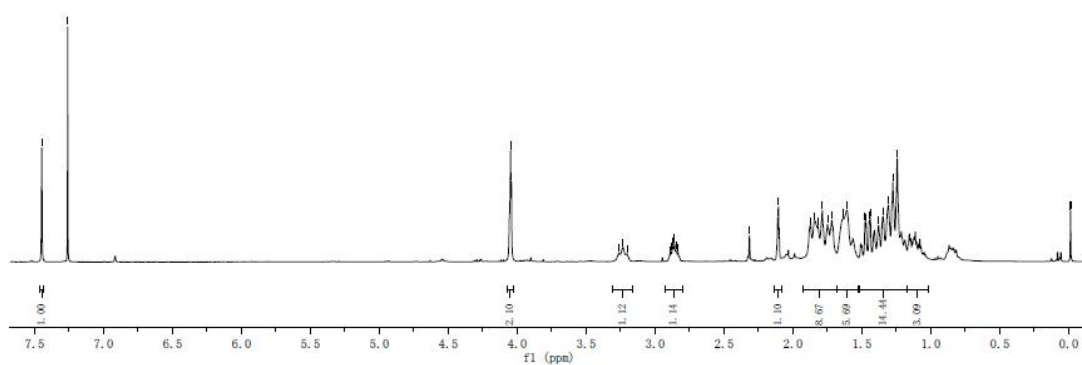
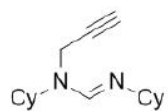


compound 1b

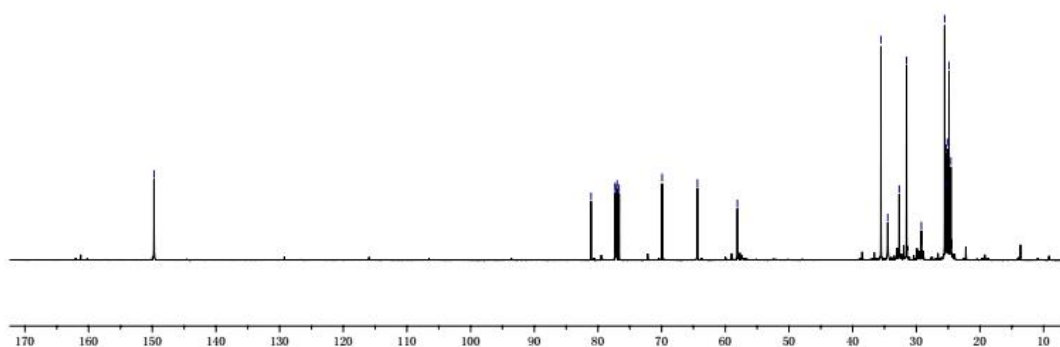


compound 1c

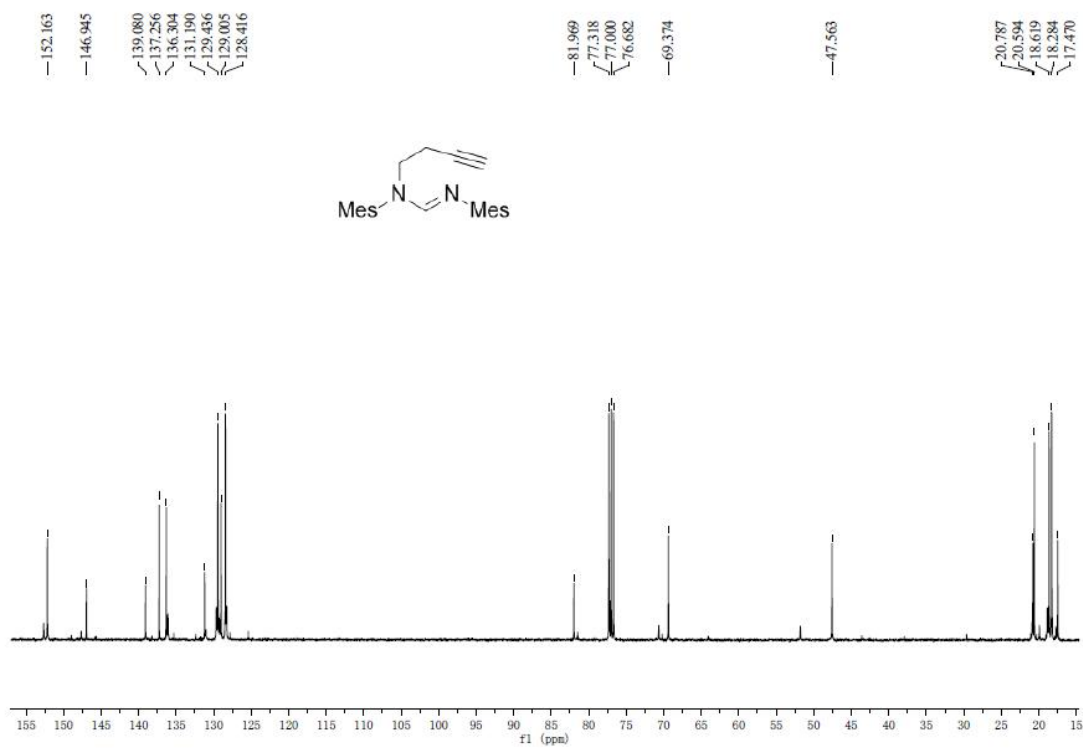
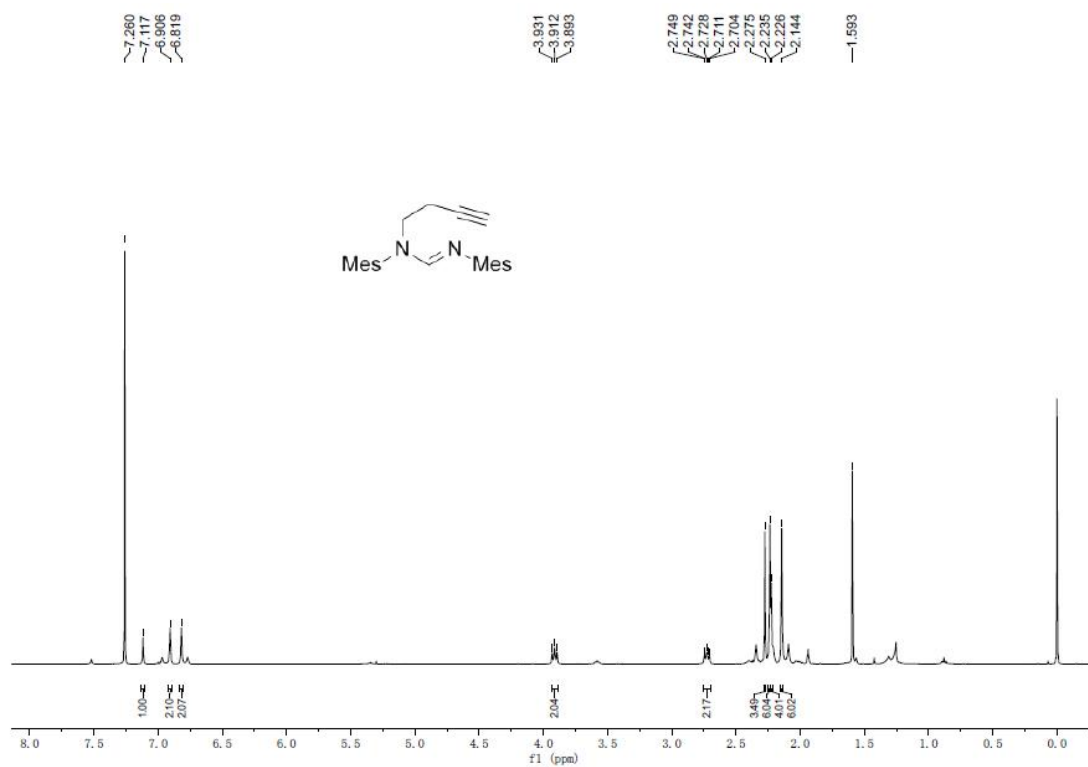
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1.632
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1.014
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24.573



compound 1d

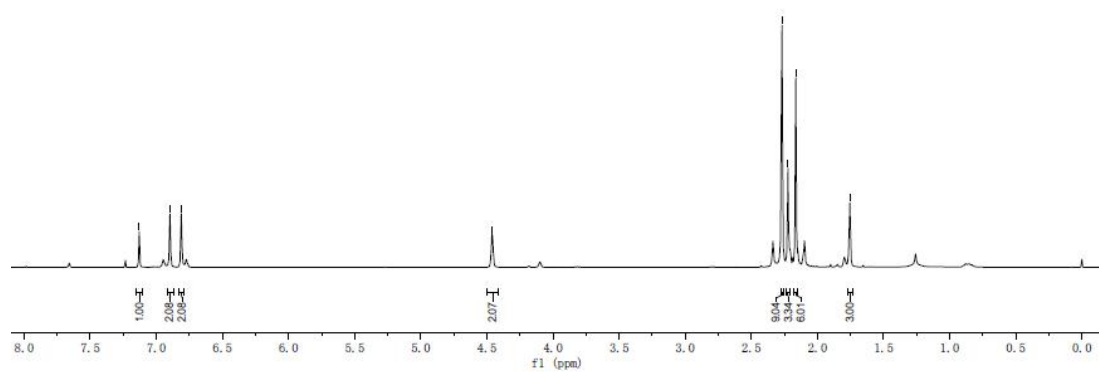
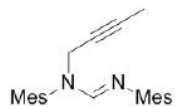


compound 2a

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4.457

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2.164
1.755



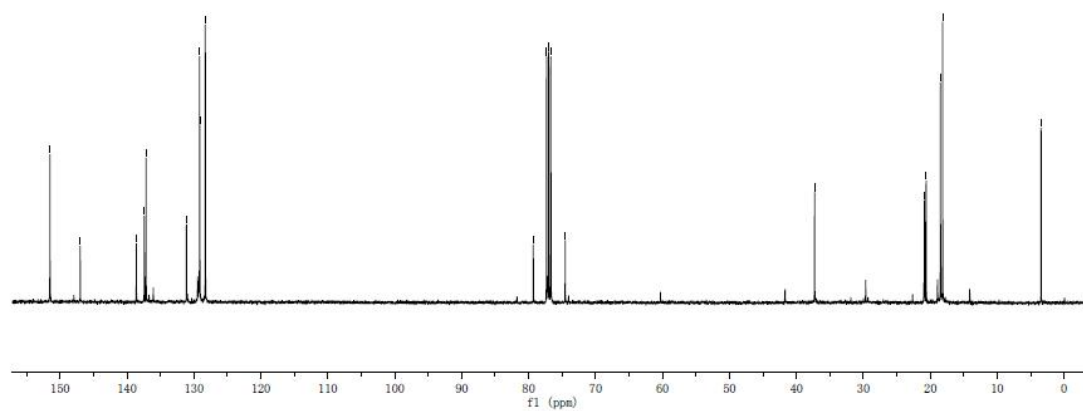
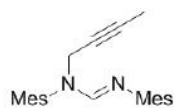
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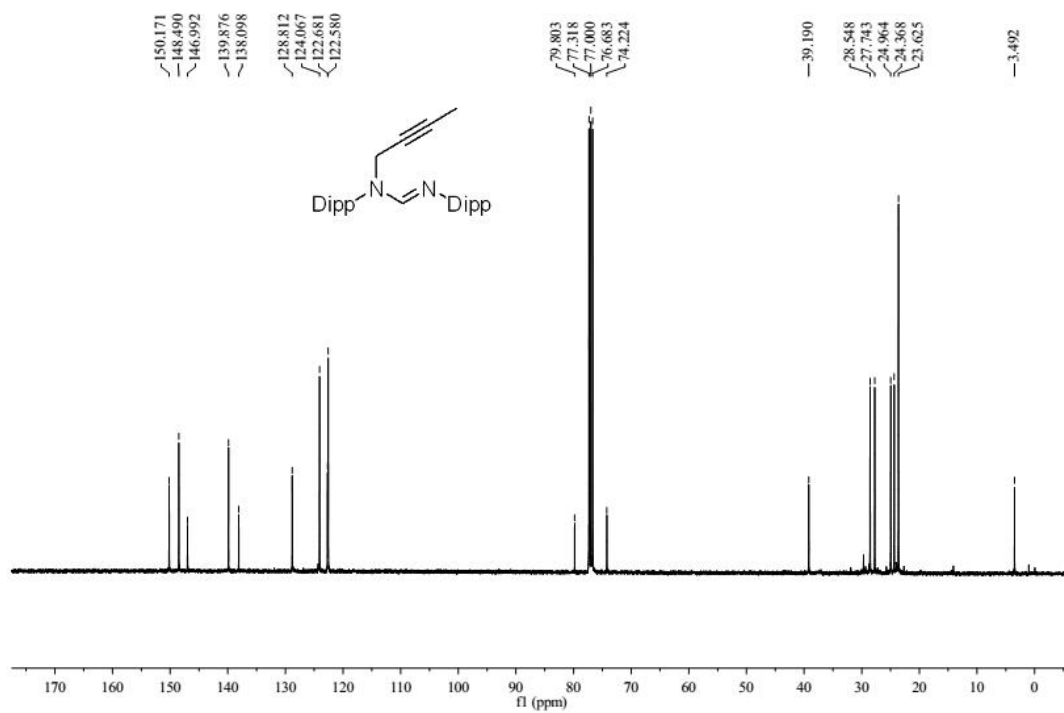
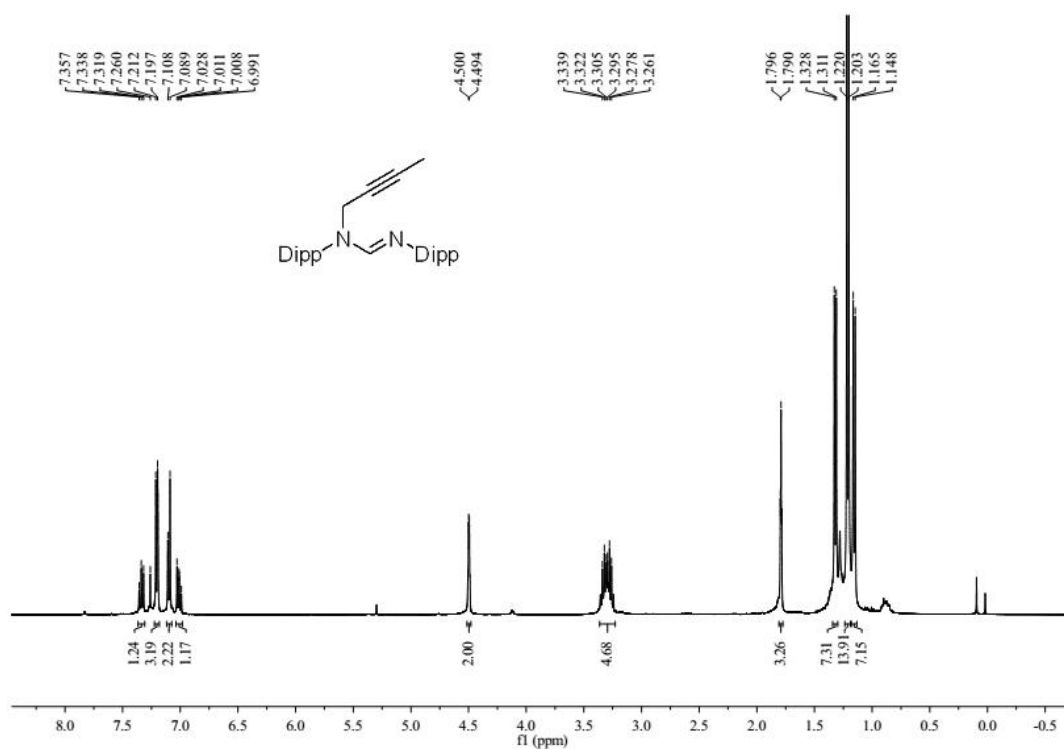
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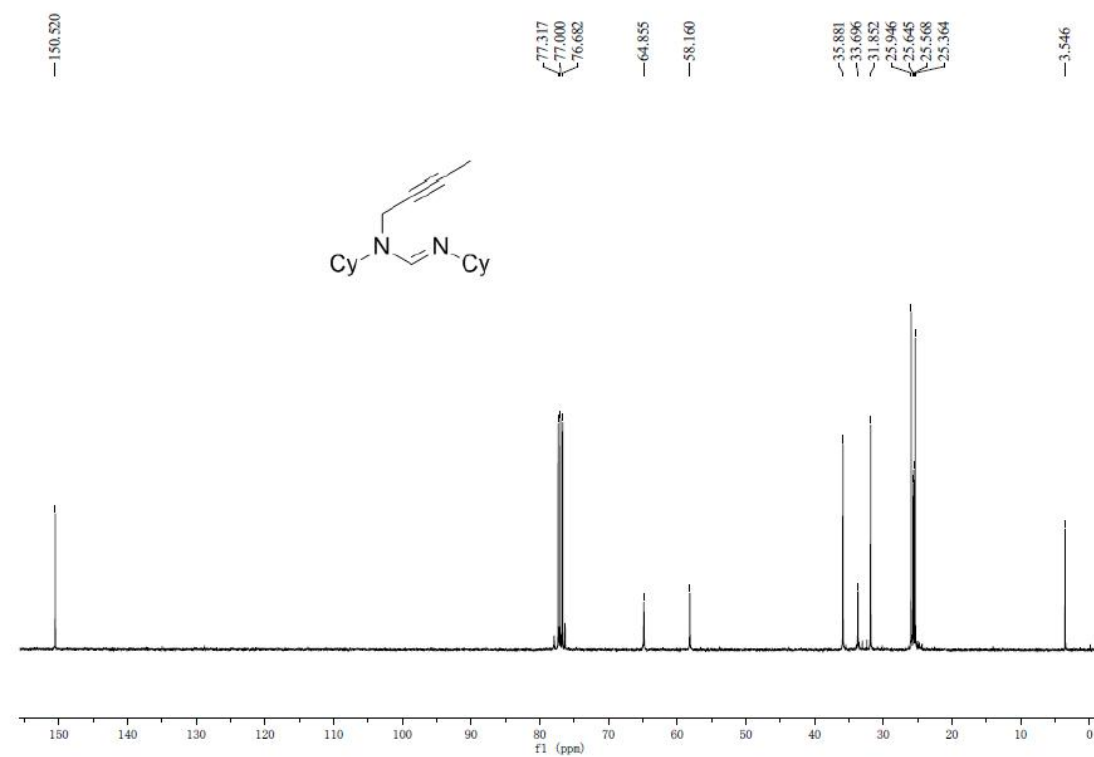
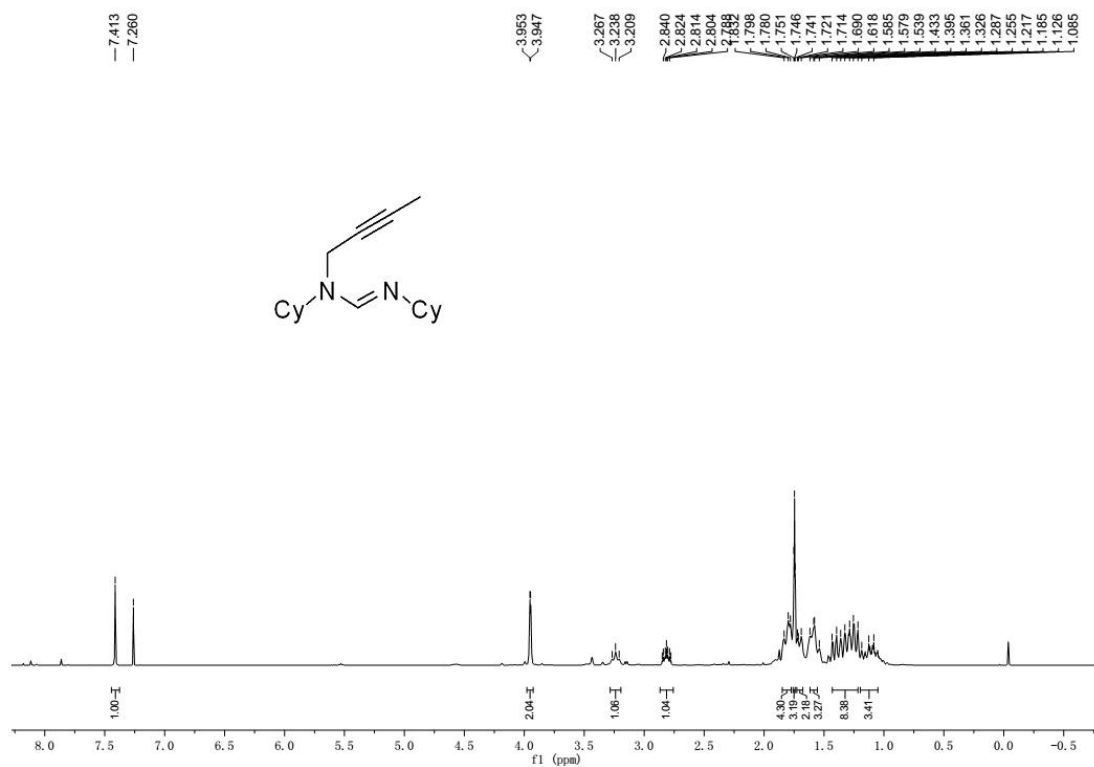
3.443



compound 2b

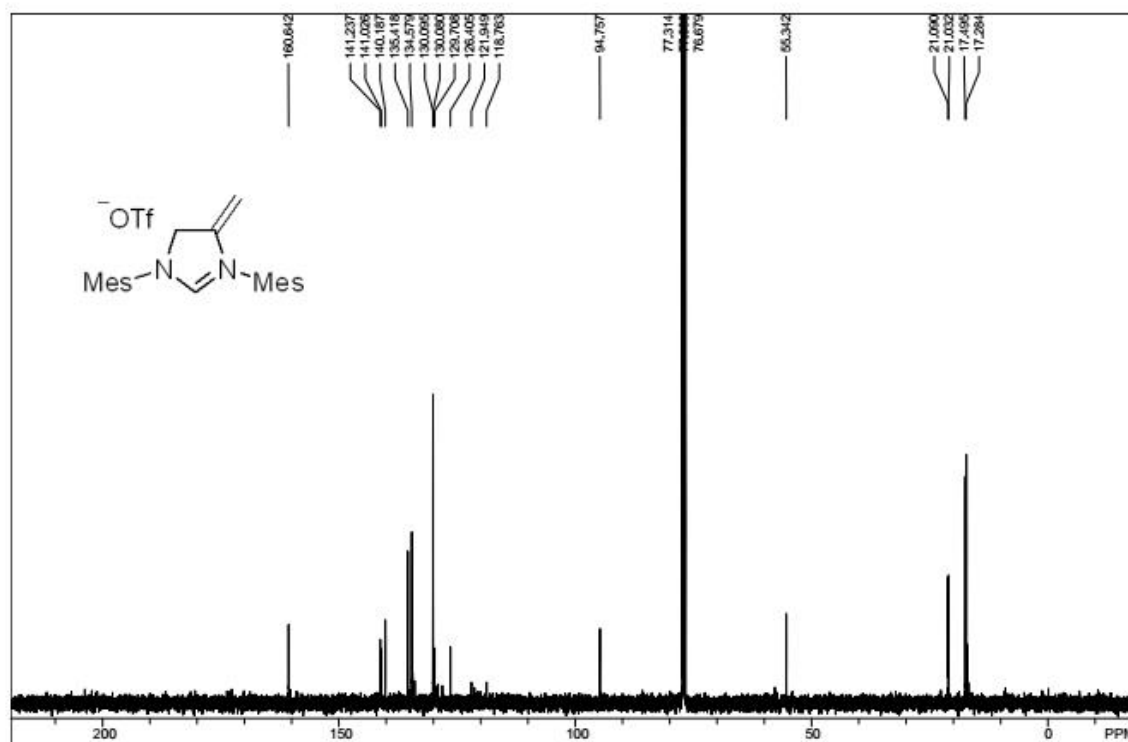
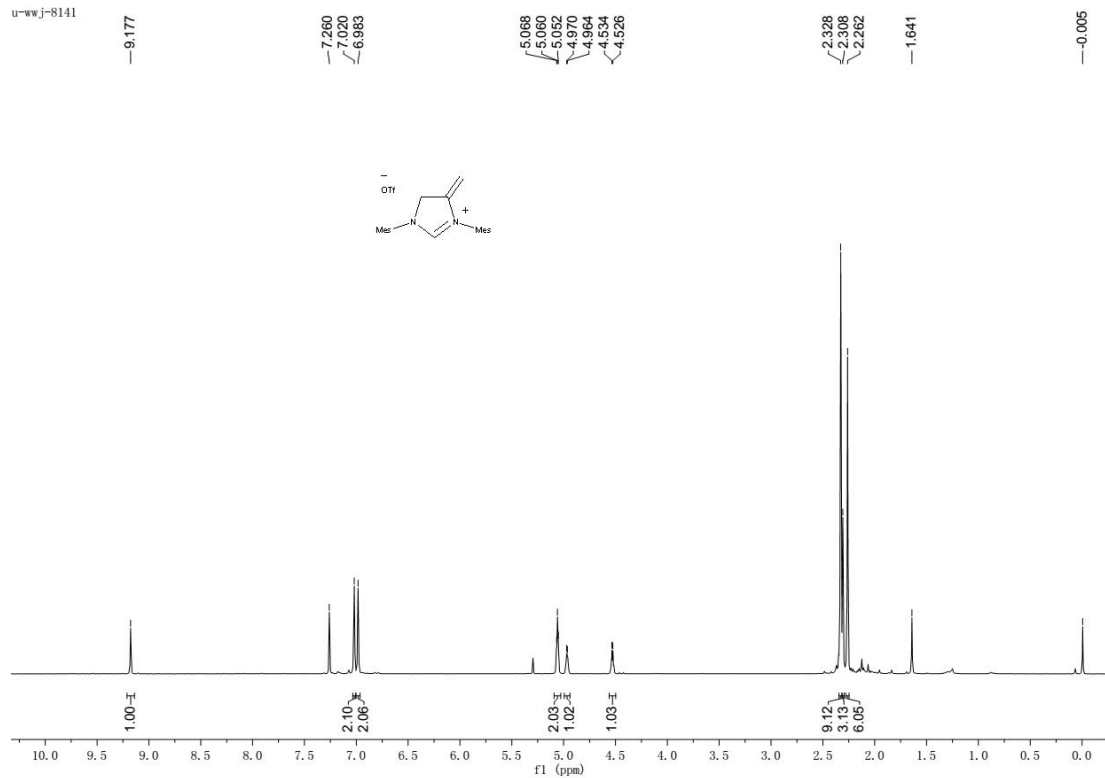


compound 2c

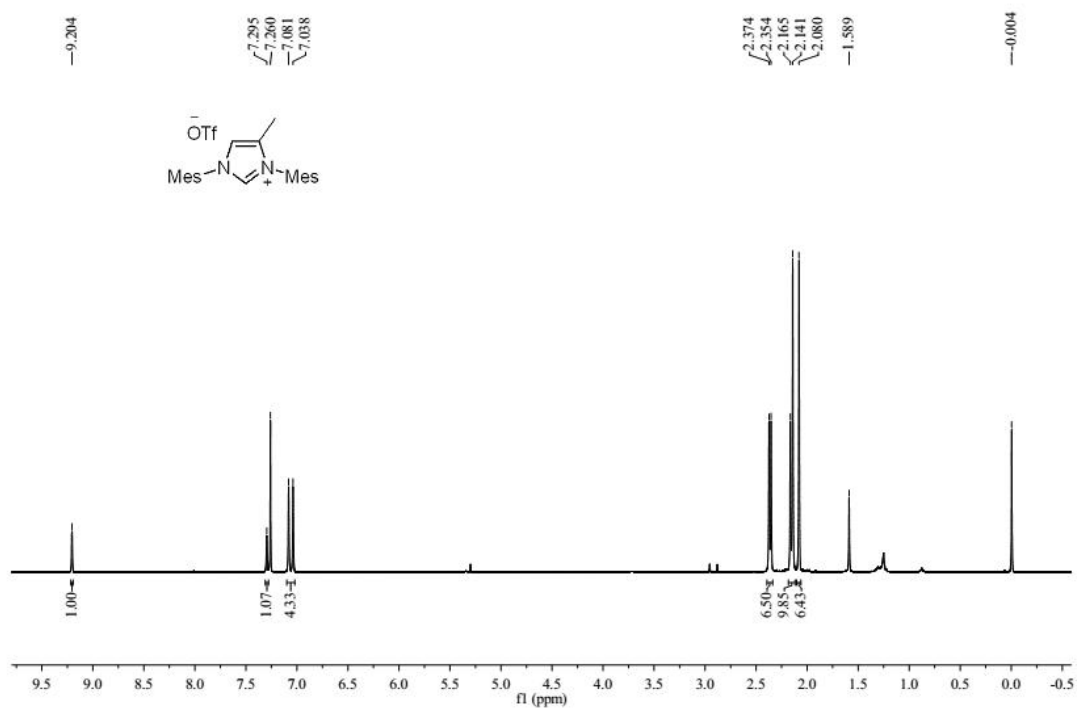


compound 3a

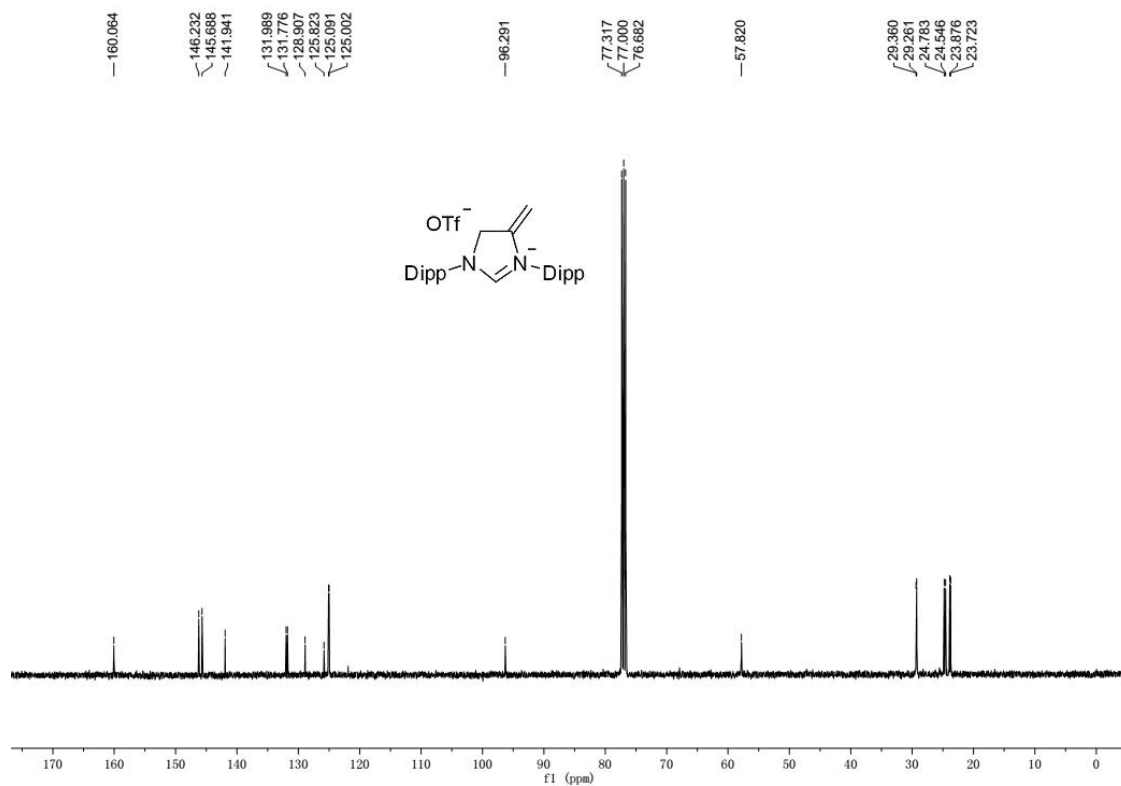
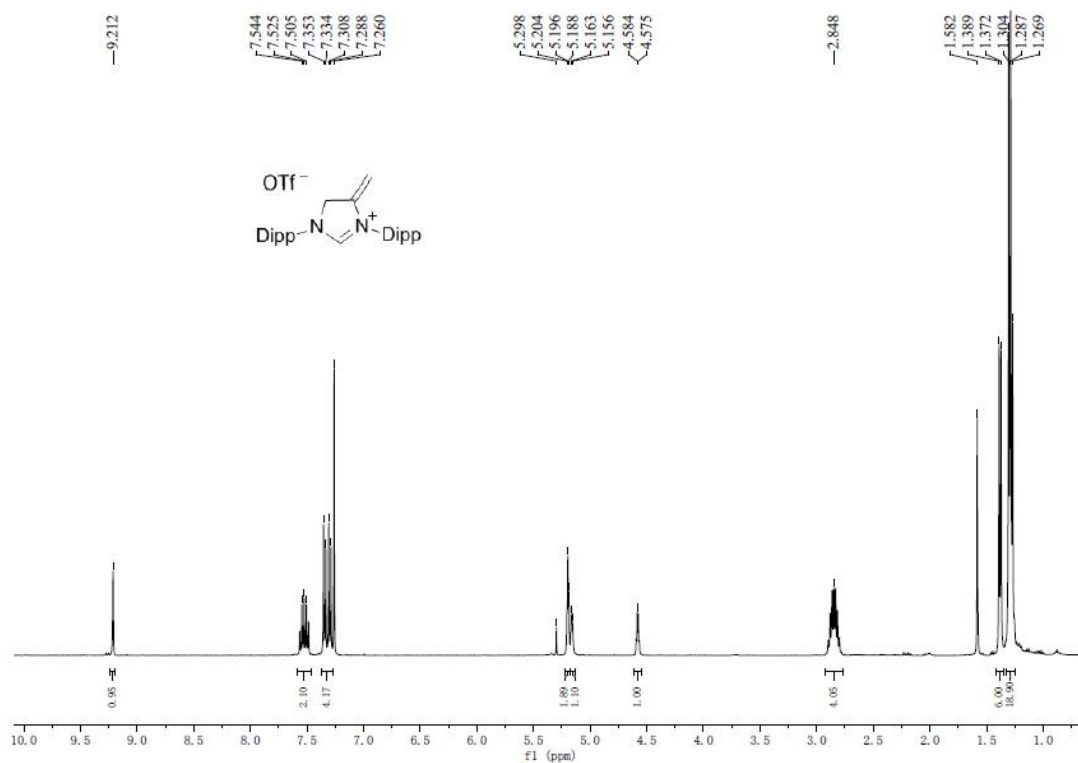
u-wwj-8141



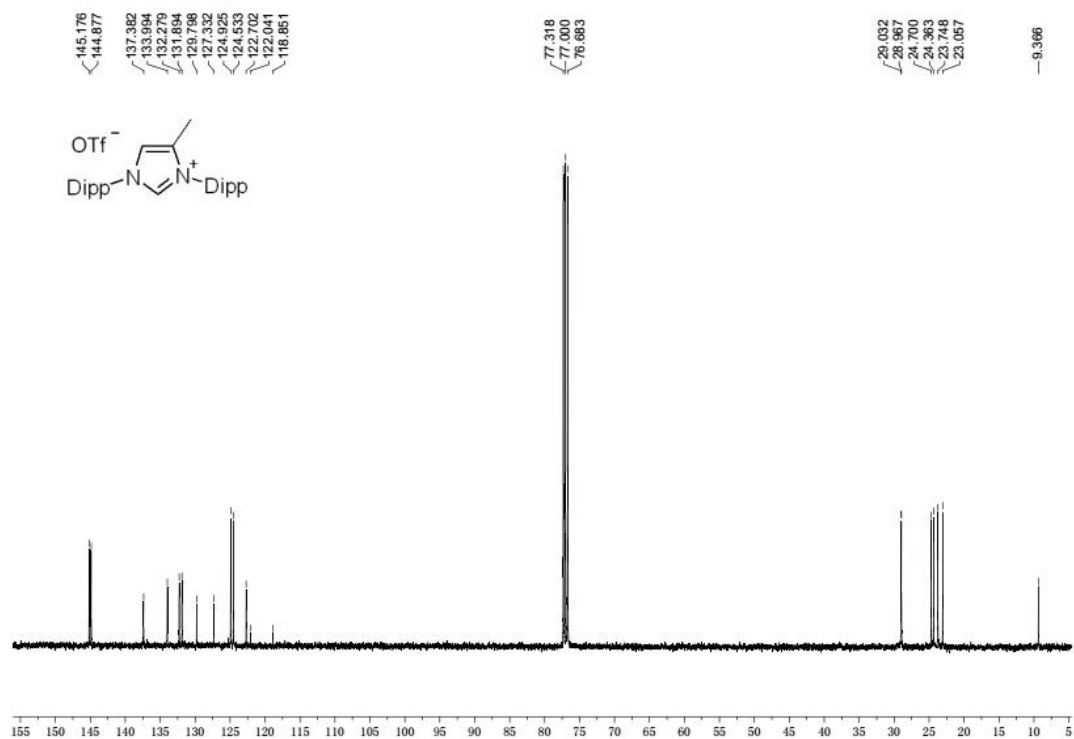
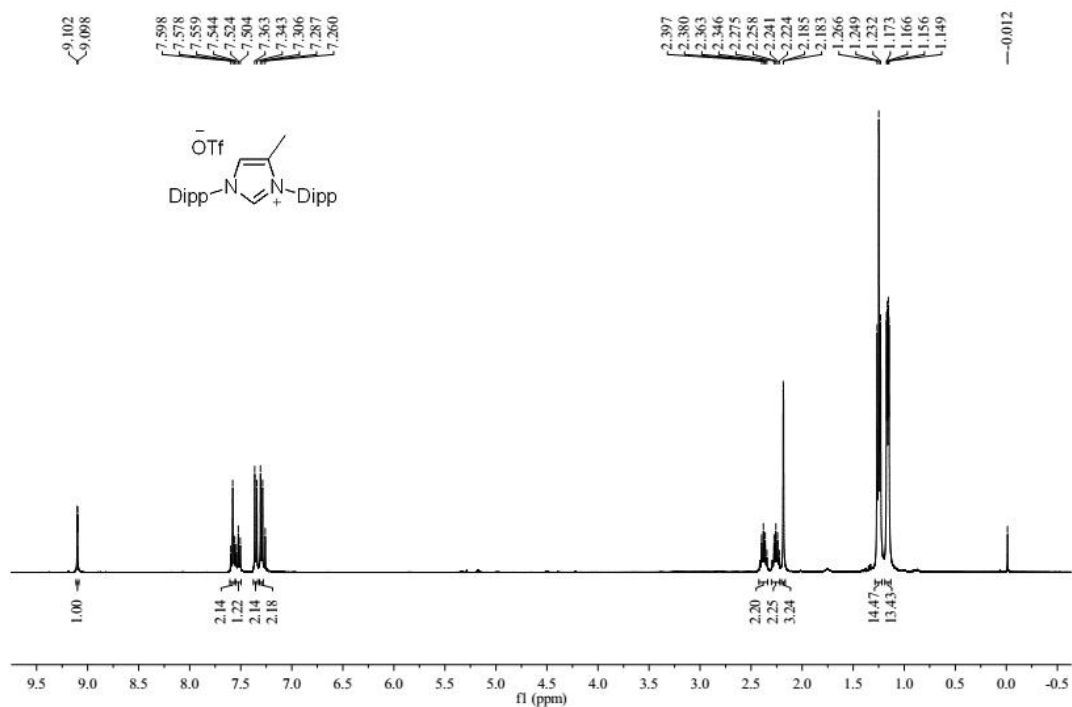
compound 3b



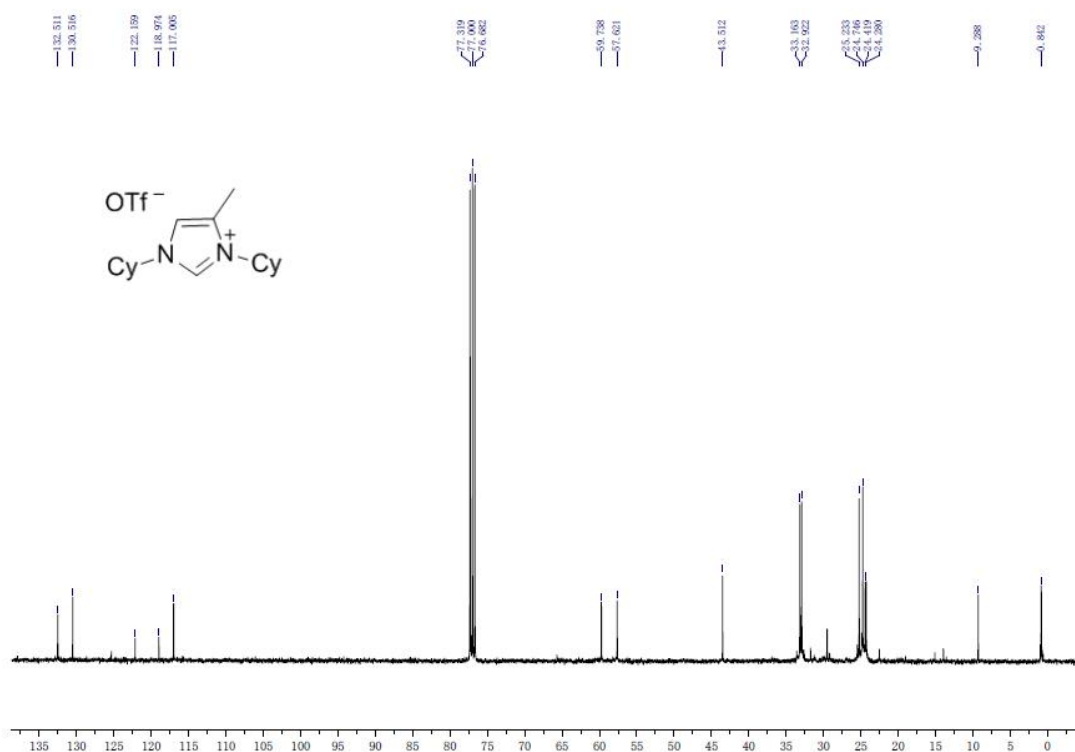
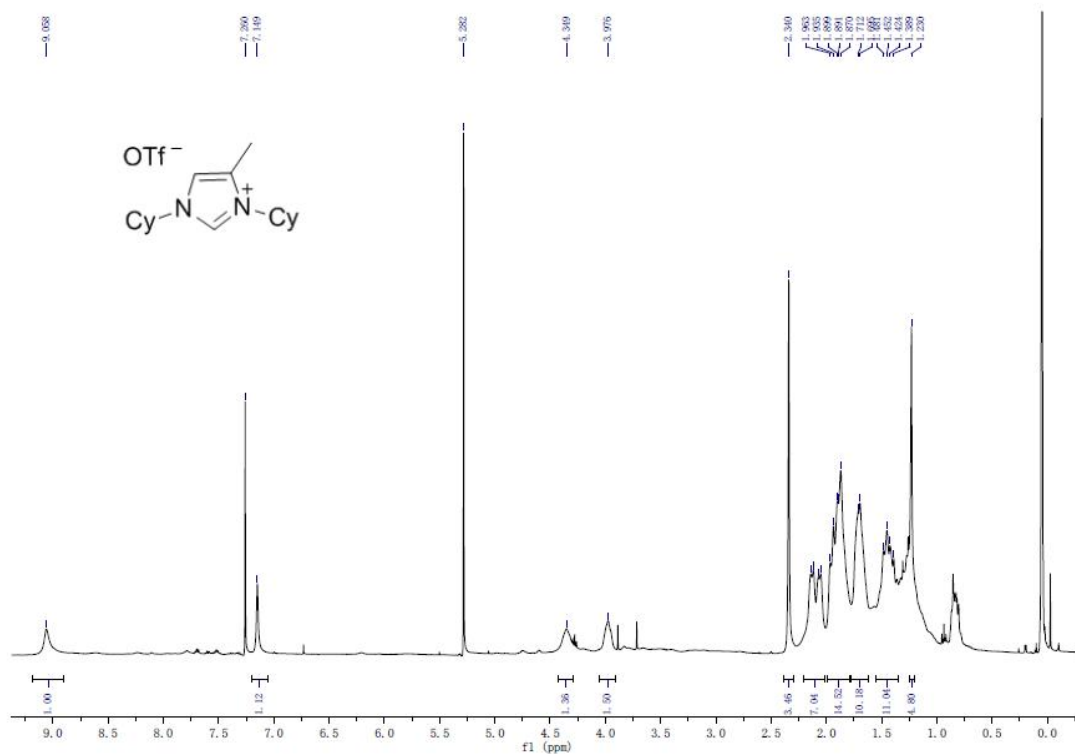
compound 4a



compound 4b

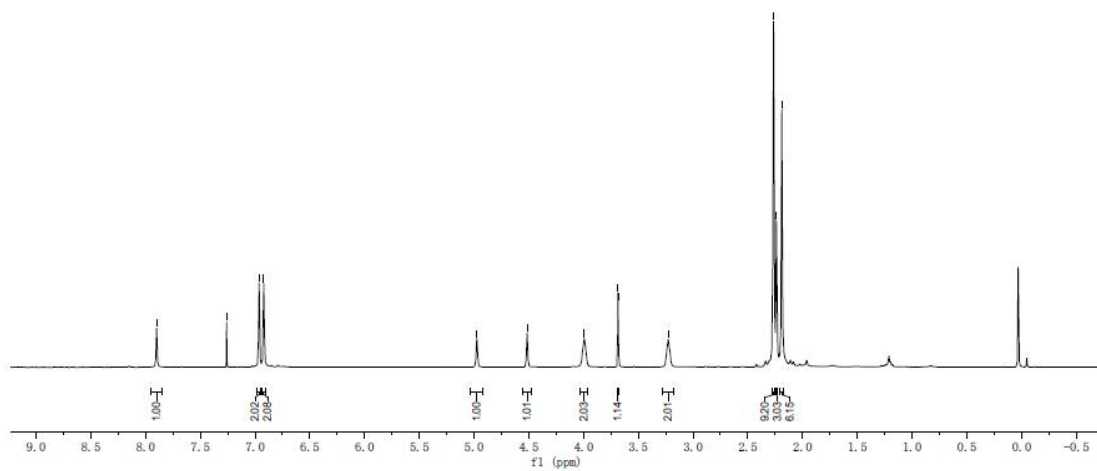
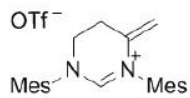


compound 5

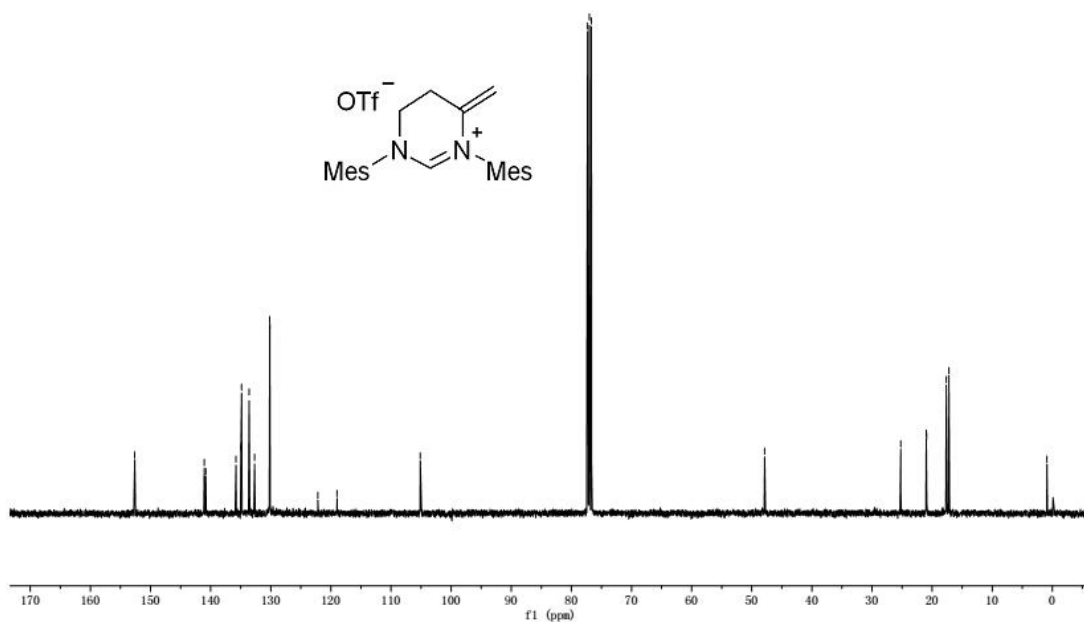
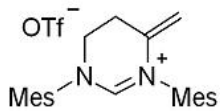


compound 6

7.899, 7.260, 6.983, 6.920, 4.974, 4.515, 3.994, 3.686, 3.682, 3.226, 2.265, 2.239, 2.190

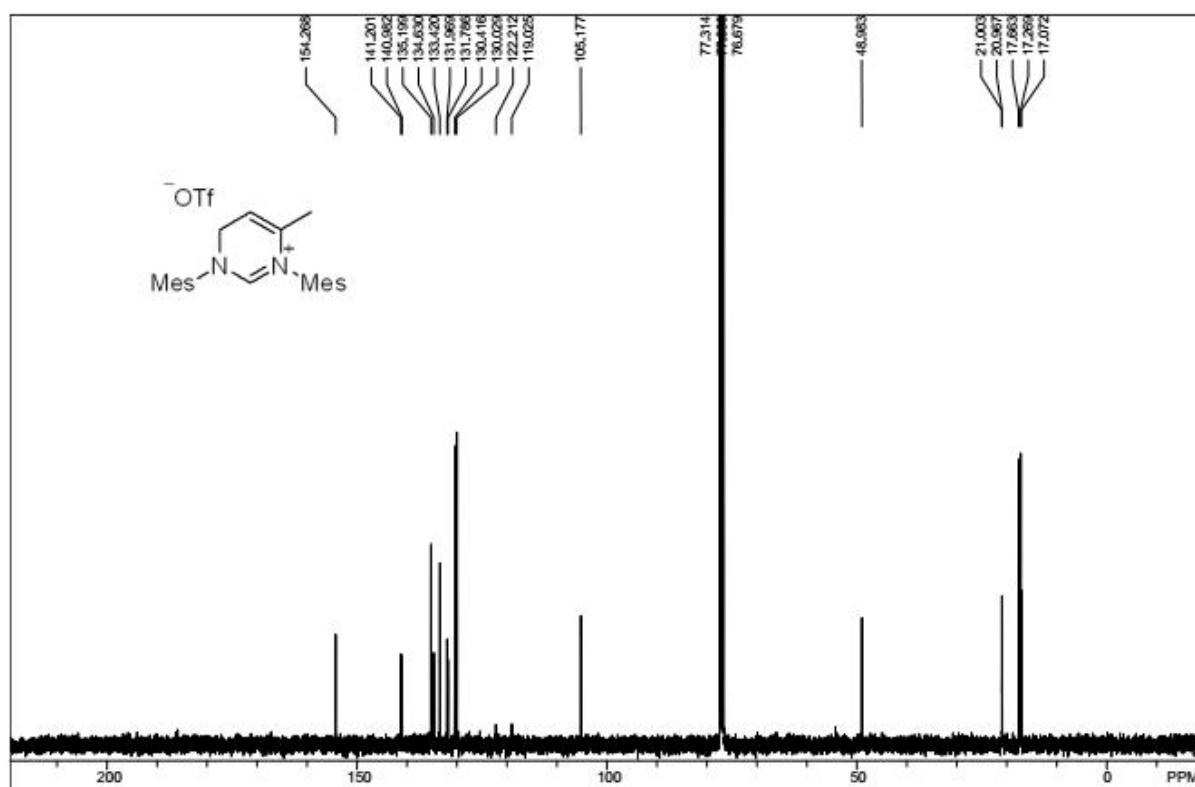
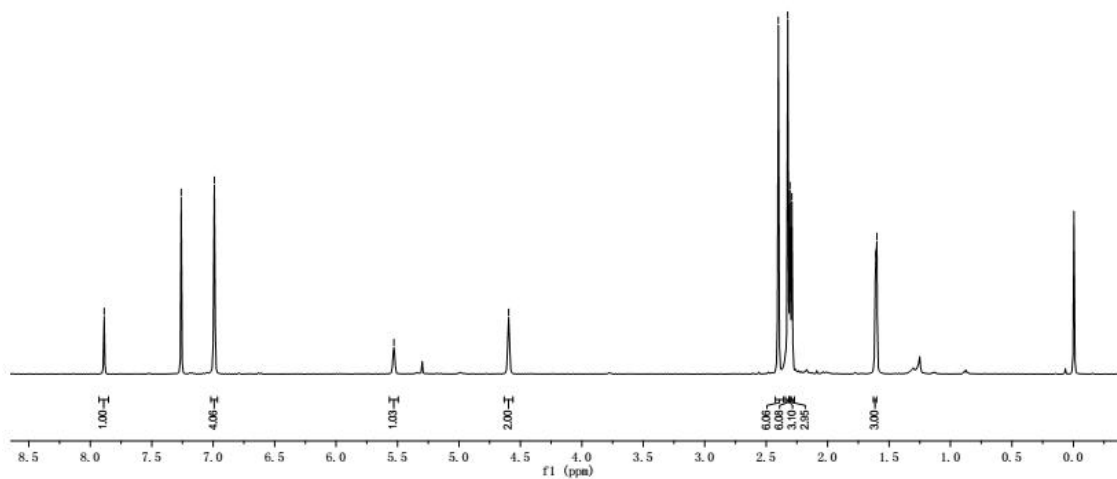
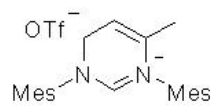


152.634, 141.057, 140.808, 135.789, 134.983, 134.850, 133.606, 132.691, 130.178, 130.152, 122.161, 118.974, 105.131, 77.318, 77.000, 76.682, 47.850, 25.217, 20.978, 20.916, 17.648, 17.207, -0.902

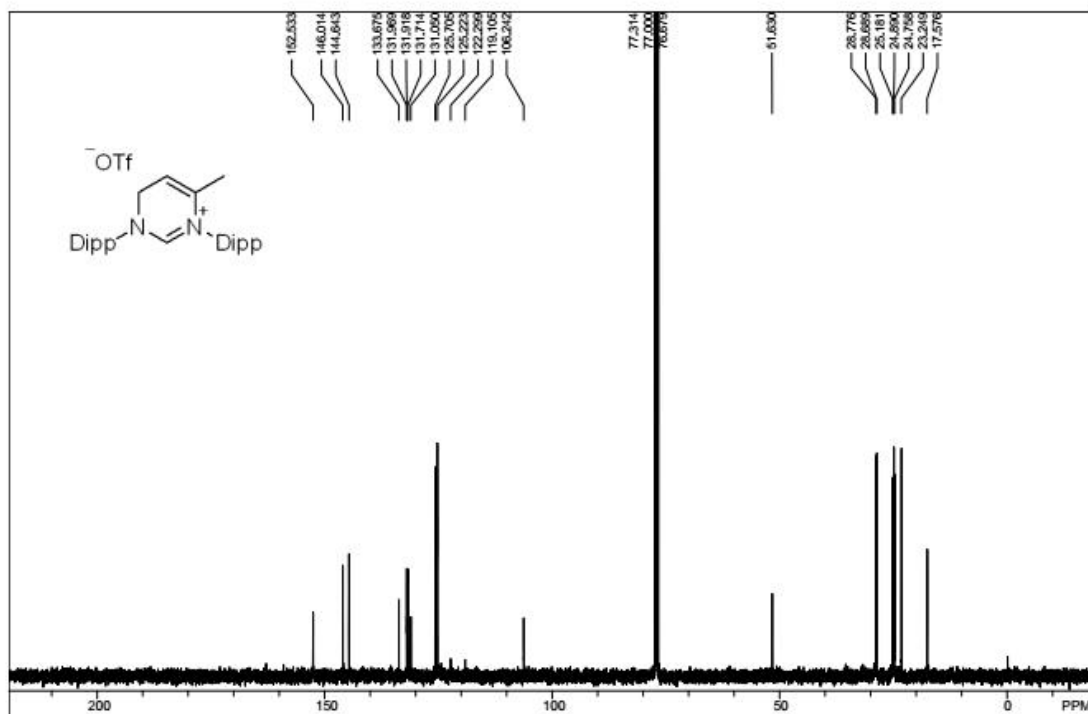
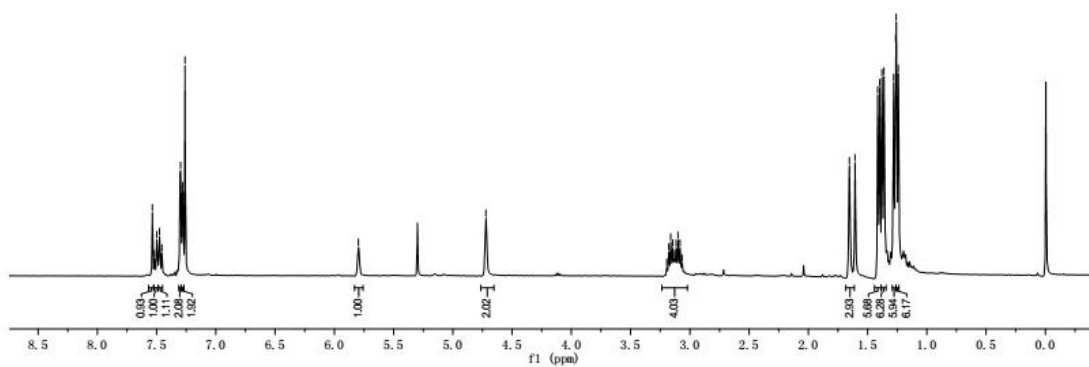
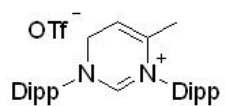
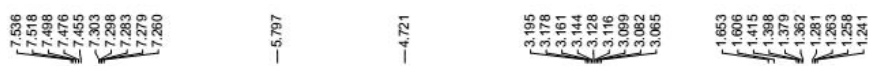


compound 7

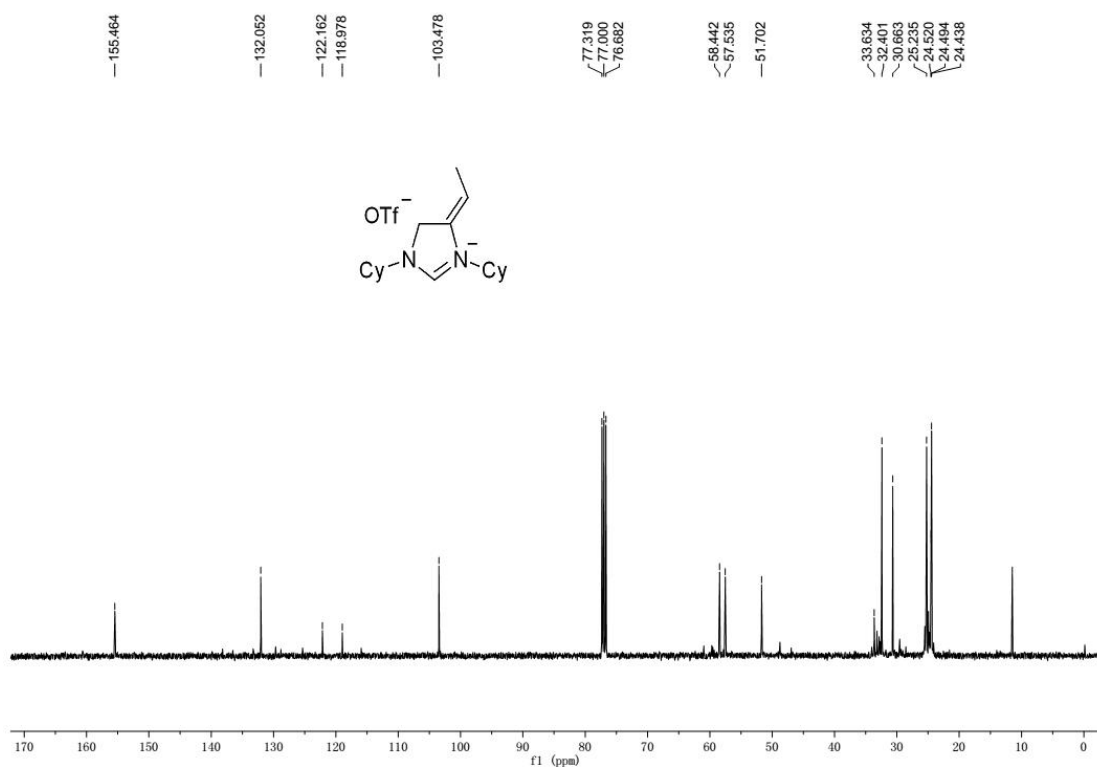
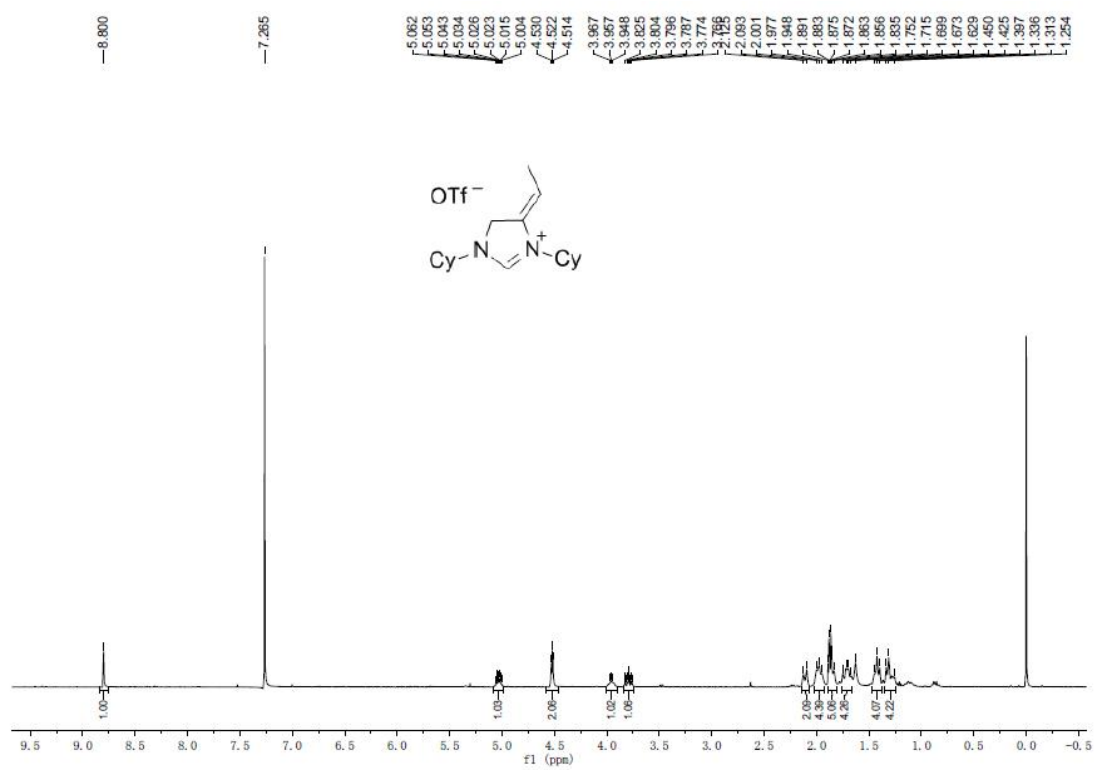
δ 7.887
 δ 7.280
 δ 6.991
 δ 5.530
 δ 4.596
 δ 2.402
 δ 2.324
 δ 2.307
 δ 2.291
 δ 1.608
 δ 1.600



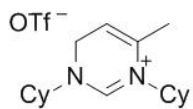
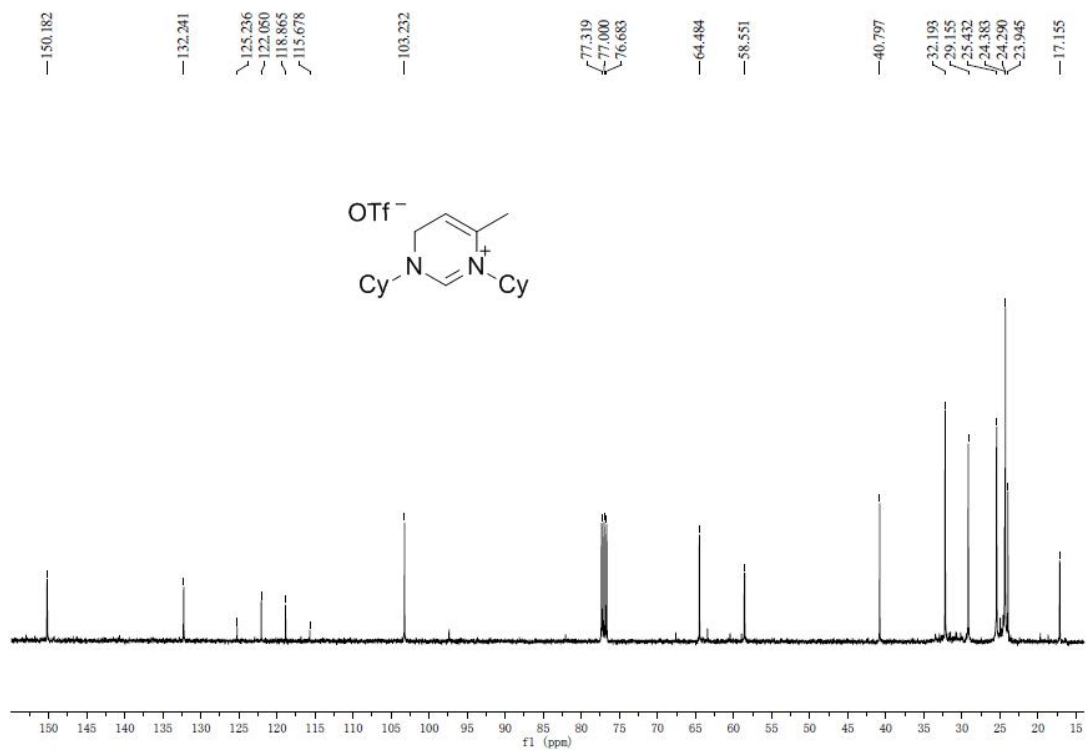
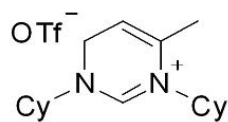
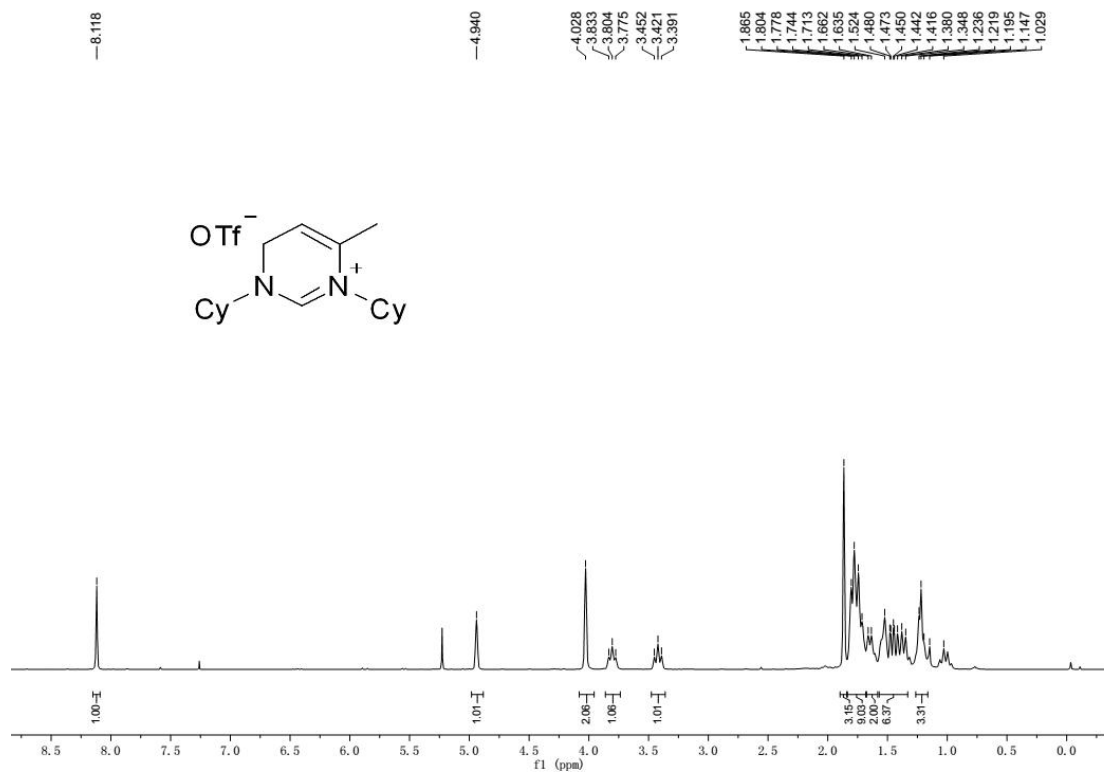
compound 8



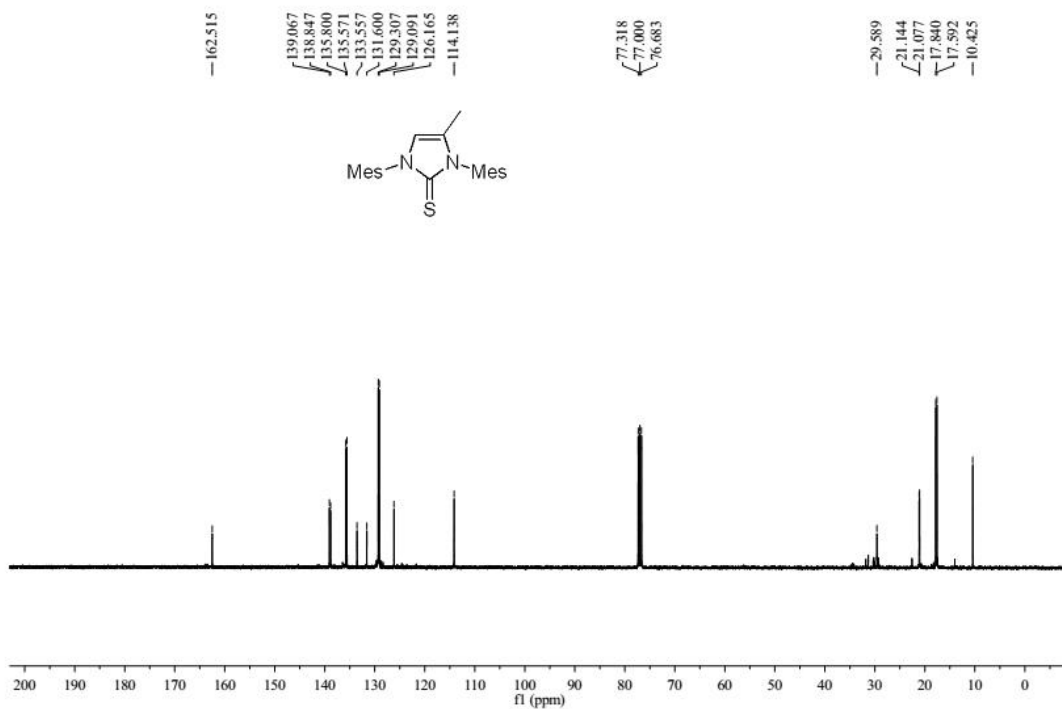
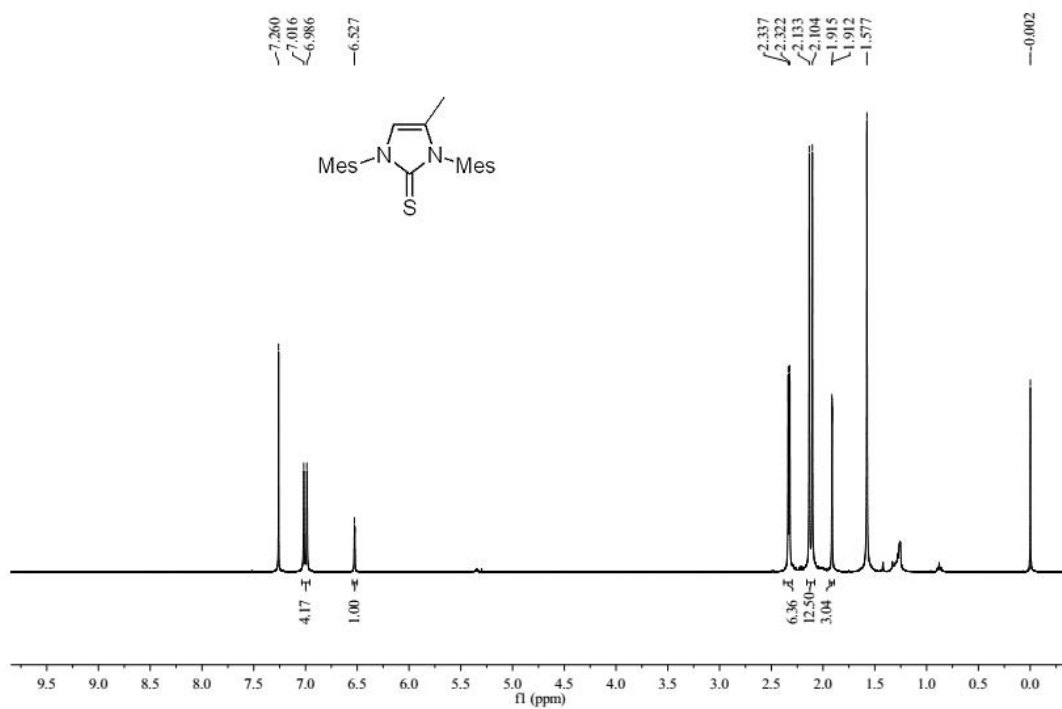
compound 9a



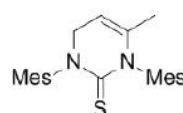
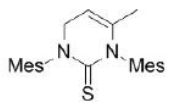
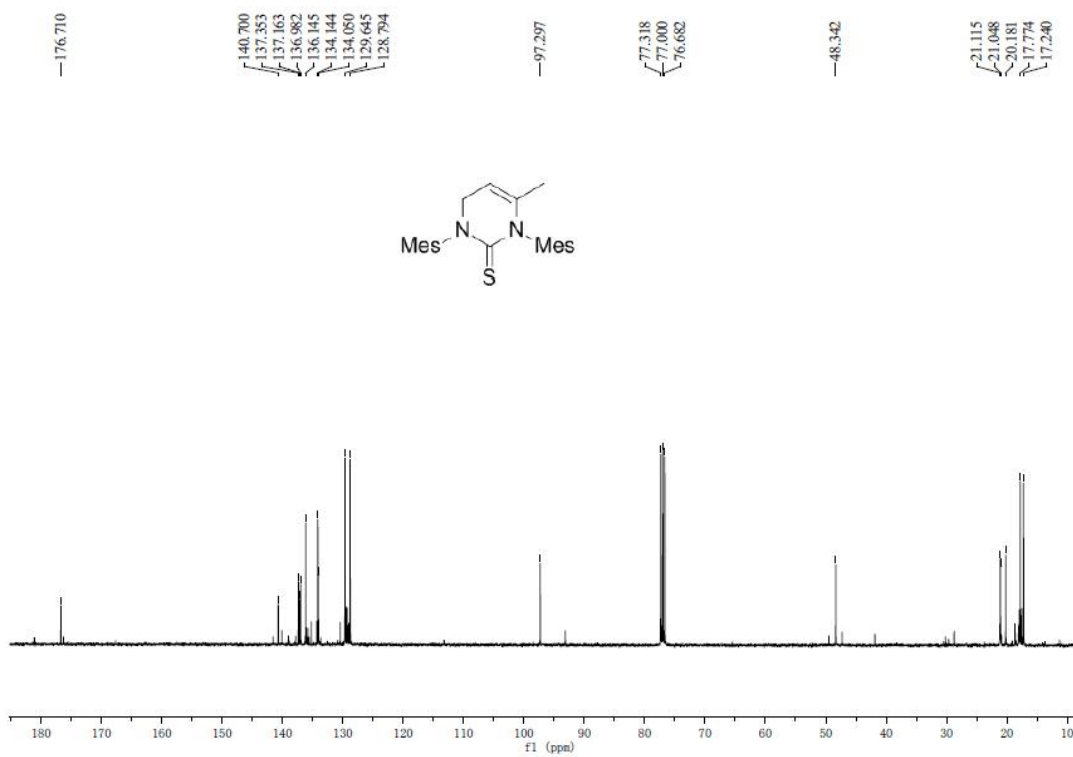
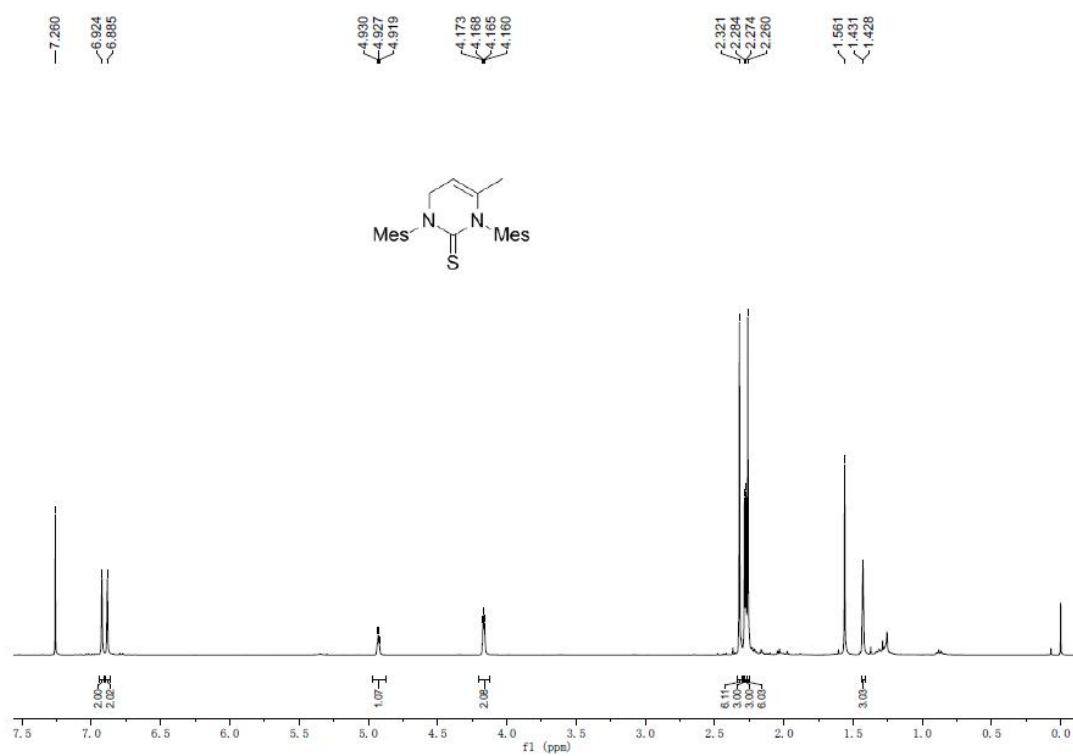
compound 9b



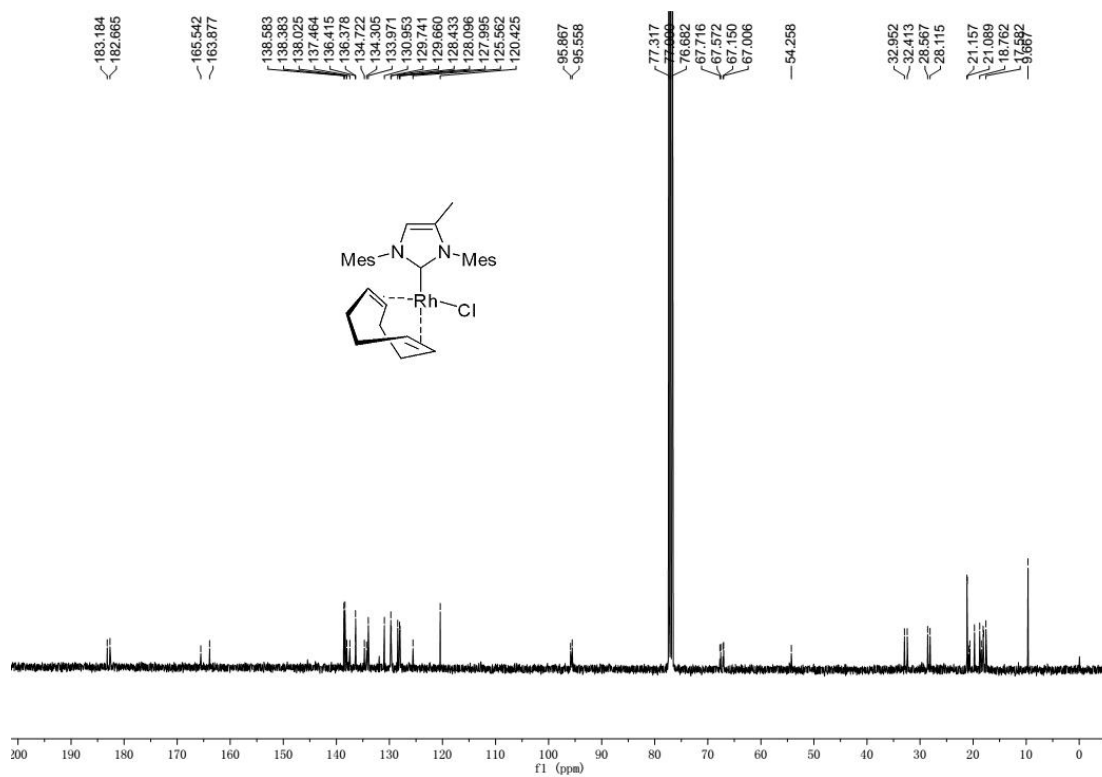
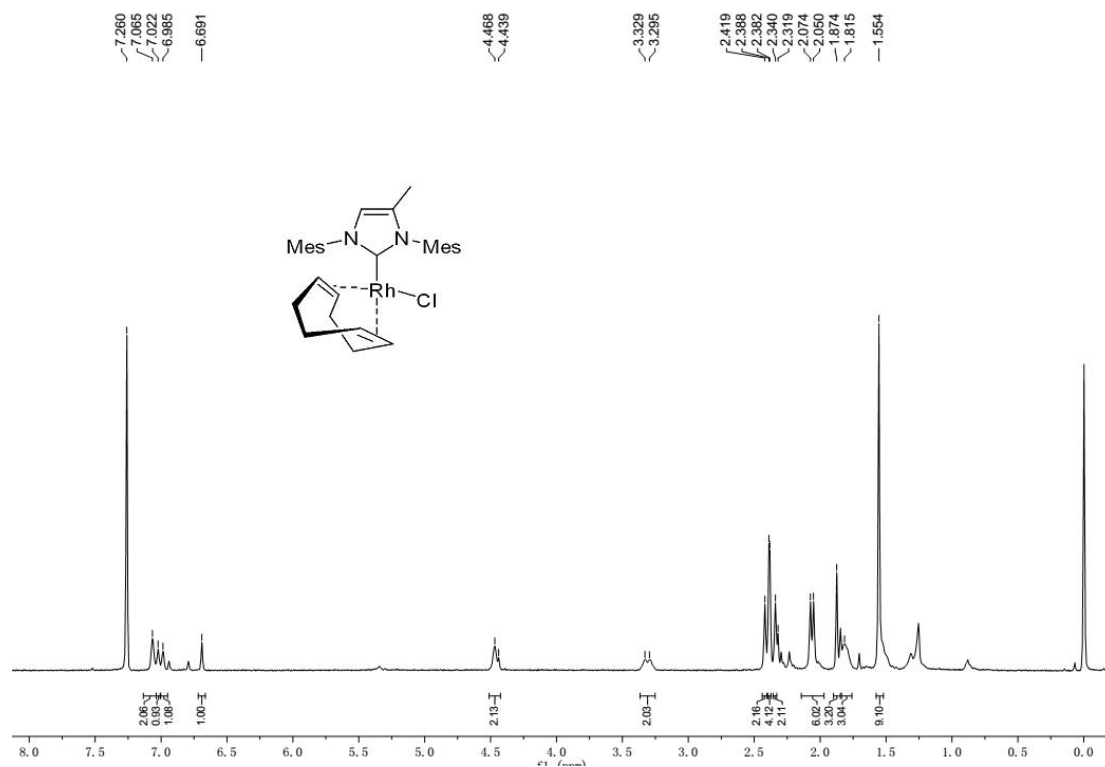
compound 10



compound 11

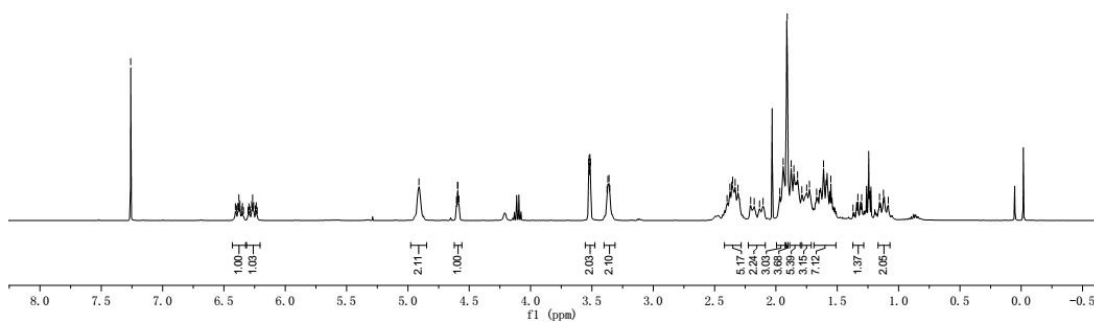
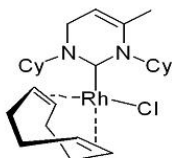


compound 12



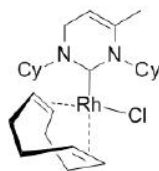
compound 13

7.260, 6.407, 6.399, 6.387, 6.378, 6.370, 6.358, 6.349, 6.344, 6.304, 6.296, 6.288, 6.274, 6.266, 6.258, 6.244, 6.236, 6.229, 4.910, 4.604, 4.596, 4.594, 4.585, 3.526, 3.523, 3.519, 3.515, 3.512, 3.376, 3.370, 3.361, 3.355, 2.398, 2.375, 2.352, 2.333, 2.310, 2.206, 2.178, 2.133, 2.104, 1.989, 1.941, 1.908, 1.876, 1.854, 1.824, 1.788, 1.749, 1.627, 1.609, 1.592, 1.552, 1.371, 1.332, 1.301, 1.156, 1.124, 1.084

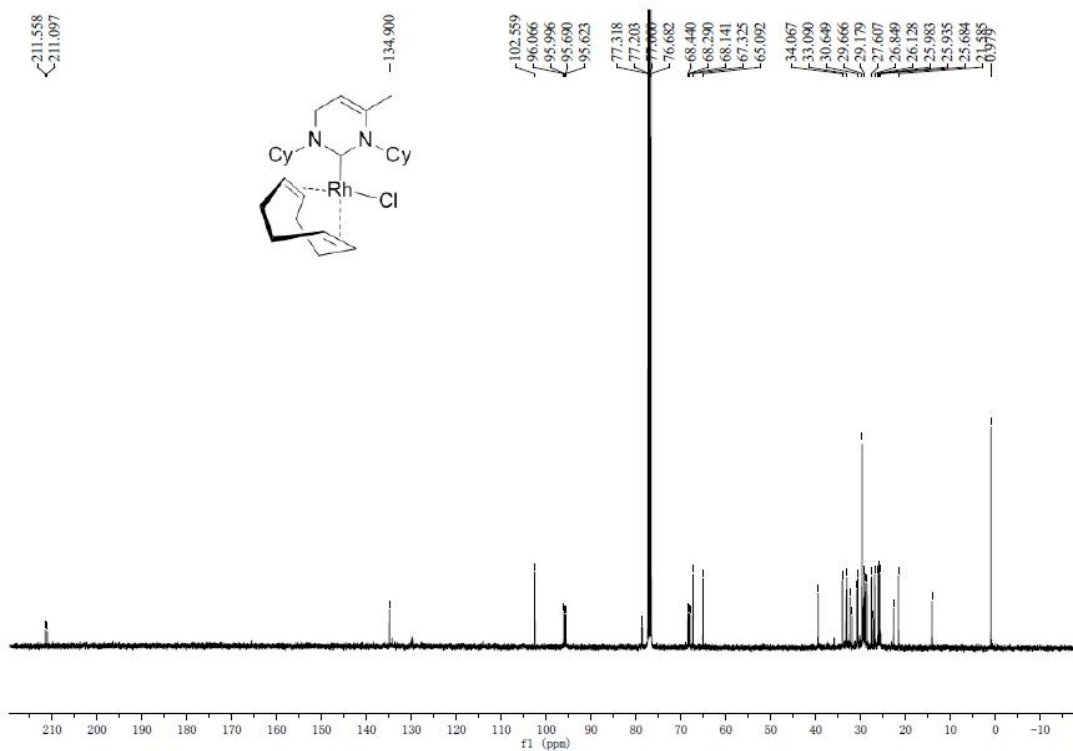


211.558, 211.097

134.900



102.559, 96.066, 95.996, 95.690, 95.623, 77.318, 77.203, 77.000, 76.682, 68.440, 68.290, 68.141, 67.325, 65.092, 34.067, 33.090, 30.649, 29.666, 29.179, 27.607, 26.849, 26.128, 25.983, 25.935, 25.684, 21.585, 0.978



X-Ray Crystallography: Each crystal was mounted on a glass fiber. Crystallographic measurements were made on a Bruker Smart Apex 100 CCD area detector using graphite monochromated Mo-K α radiation ($\lambda_{\text{Mo-K}\alpha} = 0.71073 \text{ \AA}$). The structures were solved by direct methods (SHELXS-97) and refined on F² by full-matrix least squares (SHELX-97) using all unique data. All the calculations were carried out with the SHELXTL18 program.

Key details of the crystal and structure refinement data are summarized in Table S1-S2. Further crystallographic details may be found in the respective CIF files, which were deposited at the Cambridge Crystallographic Data Centre, Cambridge, UK [CCDC 1507982 (**7**) and 1507983 (**3a**)].

Table S1

	3a	7
Identification code	a40411ba	mo_40408b
Formula	C ₃₀ H ₄₁ Cl ₂ F ₃ N ₂ O ₃ S	C ₂₄ H ₂₉ F ₃ N ₂ O ₃ S
Formula weight	637.61	482.55
T, K	293(2)	213(2)
crystal system	Orthorhombic	Monoclinic
space group	P b c a	P 21/c
a, Å	20.338(7)	15.879(3)
b, Å	16.179(5)	9.6304(17)
c, Å	21.087(7)	17.698(3)
α, deg	90	90
β, deg	90	111.401(3)
γ, deg	90	90
Volume, Å ³	6938(4)	2519.7(8)
Z	8	4
Dcalc, Mg / m ³	1.221	1.272
absorption coefficient, mm ⁻¹	0.294	0.177
F(000)	2688	1016
crystal size, mm	0.600 x 0.150 x 0.100	0.450 x 0.200 x 0.050
2θ range, deg	1.876 to 25.006	2.350 to 25.007
reflections	25983/6084	14464/4411
collected /unique data / restraints/ parameters	[R(int) = 0.0964] 6084 / 0 / 382	[R(int) = 0.00.0367] 4411 / 34 / 329
goodness of fit on F ²	0.911	1.034
final R indices [I > 2σ(I)]a	R1 = 0.0730, wR2 = 0.1881	R1 = 0.0510, wR2 = 0.1553
R indices (all data)	R1 = 0.1718, wR2 = 0.2294	R1 = 0.0795, wR2 = 0.1776
lgst diff peak and hole, e/Å ³	0.508 and -0.339	0.281 and -0.266