Supporting Information

Direct synthesis of N2-unprotected five-membered cyclic guanidines by regioselective [3+2] annulation of aziridines and cyanamides

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1. General Information

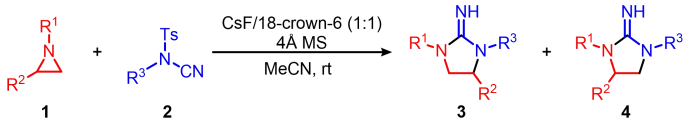
All reactions were performed in oven-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents were purified and dried according to standard methods prior to use. Organic solutions were concentrated under reduced pressure on a rotary evaporator or an oil pump. NMR spectra were recorded on a Bruker AM400 (400 MHz) spectrometer or Agilent DD2 (600 MHz) spectrometer. Chemical shifts are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR and chloroform-*d* (δ 77.16) for ^{13}C NMR. Data for ^1H NMR are recorded as follows: chemical shift (δ ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet), coupling constant (Hz) and integration. Data for ^{13}C NMR and ^{19}F NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectra (HRMS) were recorded on a Thermo Q-Exactive Spectrometer (ESI source). Reactions were monitored through thin layer chromatography (TLC) on silica gel-precoated glass plates. Flash column chromatography was performed using silica gel (300-400 mesh). CCDC-2129607 (**4aa**), CCDC 2129608 (**3ai**) and CCDC 2129609 (**4oh**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Aziridines **1** were synthesized employing literature procedure.[1]

N-tosyl-N-aryl cyanamides **2** were synthesized employing literature procedure.[2]

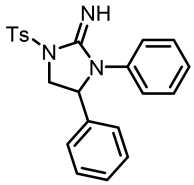
2. General Procedures and Analytical Data of the Products

2.1 General Procedures for [3+2] cycloaddition



In a 20 mL test tube was sequentially added aziridines **1** (0.20 mmol, 1 eq), N-tosyl-cyanamides **2** (0.24 mmol, 1.2 eq), CsF (0.40 mmol, 2.0 eq), 18-crown-6 (0.40 mmol, 2.0 eq), 4Å MS (100 mg) and MeCN (2.0 mL). The reaction mixture was stirred at room temperature. Upon complete consumption of **1** as monitored by TLC, the reaction mixture was concentrated under reduced pressure to obtain the crude product which was purified by flash column chromatography (hexane/EA) on silica gel to afford the pure products **3** or **4**.

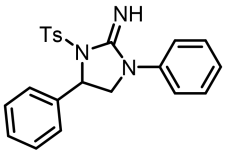
3,4-diphenyl-1-tosylimidazolidin-2-imine (3aa)



White solid (59 mg, 75% yield), purified by ethyl acetate:hexane = 1:6. m. p. 116-118 °C. ^1H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 2H), 7.31-7.18 (m, 9H), 7.03-7.02 (m, 3H), 4.98 (dd, *J* = 7.2 Hz, 5.2 Hz, 1H), 4.23-4.19 (m, 1H), 3.62 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 145.2, 139.0, 138.8, 133.9, 130.0, 129.0, 128.9, 128.4, 127.9, 126.3, 125.0, 123.5, 59.5, 52.3, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for

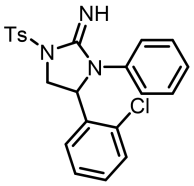
$C_{22}H_{22}N_3O_2S$ 392.1427, Found 392.1435.

1,4-diphenyl-3-tosylimidazolidin-2-imine (4aa)



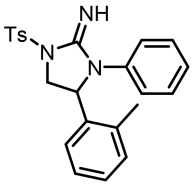
White solid (19 mg, 24% yield), purified by ethyl acetate:hexane = 1:6. m. p. 146-148 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.35-7.31 (m, 7H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.09 (t, *J* = 7.2 Hz, 1H), 5.19-5.18 (m, 1H), 4.10-4.07 (m, 1H), 3.60 (dd, *J* = 9.0 Hz, 3.6 Hz, 1H), 2.40 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.4, 144.9, 140.2, 139.9, 135.5, 129.8, 129.1, 129.0, 128.6, 127.8, 126.6, 124.3, 121.0, 58.4, 53.5, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{22}N_3O_2S$ 392.1427, Found 392.1433.

4-(2-chlorophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ba)



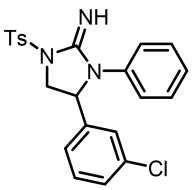
White solid (64 mg, 75% yield), purified by ethyl acetate:hexane = 1:3. m. p. 139-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.37-7.34 (m, 3H), 7.24-7.21 (m, 4H), 7.17-7.15 (m, 1H), 7.02-7.00 (m, 1H), 6.95-6.90 (m, 2H), 5.41 (dd, *J* = 8.4 Hz, 3.6 Hz, 1H), 4.23-4.19 (m, 1H), 3.70 (dd, *J* = 10.2 Hz, 3.6 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.5, 145.2, 139.0, 136.6, 134.0, 132.1, 130.1, 130.0, 129.3, 129.0, 127.7, 127.5, 127.1, 124.2, 121.3, 56.1, 50.9, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}N_3O_2S$ 426.1038, Found 426.1044.

3-phenyl-4-(*o*-tolyl)-1-tosylimidazolidin-2-imine (3ca)



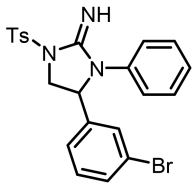
White solid (73 mg, 90% yield), purified by ethyl acetate:hexane = 1:2. m. p. 145-147 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.2 Hz, 2H), 7.29-7.25 (m, 4H), 7.21-7.18 (m, 2H), 7.10-7.08 (m, 2H), 7.01-6.98 (m, 1H), 6.88-6.83 (m, 2H), 5.20 (dd, *J* = 8.4 Hz, 4.8 Hz, 1H), 4.23-4.20 (m, 1H), 3.56 (dd, *J* = 9.0 Hz, 4.2 Hz, 1H), 2.43 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 145.2, 139.2, 137.0, 134.4, 134.1, 131.1, 130.0, 128.9, 127.9, 127.8, 126.8, 126.5, 124.4, 122.2, 59.1, 51.2, 21.7, 19.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1589.

4-(3-chlorophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3da)



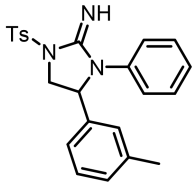
White solid (50 mg, 59% yield), purified by ethyl acetate:hexane = 1:7. m. p. 104-106 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 7.27-7.26 (m, 2H), 7.22-7.21 (m, 2H), 7.19-7.17 (m, 1H), 7.14-7.11 (m, 1H), 7.05-7.03 (m, 1H), 6.95-6.93 (m, 2H), 4.95 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H), 4.23-4.20 (m, 1H), 3.61 (dd, *J* = 10.2 Hz, 4.8 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.8, 145.4, 141.6, 138.8, 135.1, 133.9, 130.4, 130.1, 129.1, 128.7, 127.8, 126.4, 125.1, 124.5, 123.0, 59.0, 52.0, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}ClN_3O_2S$ 426.1038, Found 426.1042.

4-(3-bromophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ea)



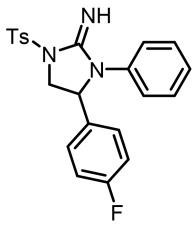
White solid (53 mg, 56% yield), purified by ethyl acetate:hexane = 1:7. m. p. 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.0 Hz, 2H), 7.35-7.31 (m, 3H), 7.27-7.21 (m, 4H), 7.13 (s, 1H), 7.08-7.04 (m, 2H), 6.98-6.96 (m, 1H), 4.95 (dd, *J* = 8.0 Hz, 4.8 Hz, 1H), 4.24-4.20 (m, 1H), 3.61 (dd, *J* = 10.0 Hz, 4.8 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.8, 145.4, 141.7, 138.7, 133.8, 131.6, 130.7, 130.1, 129.3, 129.1, 127.8, 125.2, 125.0, 123.2, 123.1, 58.9, 52.1, 21.9 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}{}^{79}BrN_3O_2S$ 470.0532, Found 470.0547.

3-phenyl-4-(*m*-tolyl)-1-tosylimidazolidin-2-imine (3fa)



White solid (60 mg, 74% yield), purified by ethyl acetate:hexane = 1:7. m. p. 116-117 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.32-7.26 (m, 4H), 7.23-7.19 (m, 2H), 7.09-7.00 (m, 3H), 6.83-6.81 (m, 2H), 4.94 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 4.22-4.18 (m, 1H), 3.63 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.45 (s, 3H), 2.21 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 145.1, 139.3, 139.0, 138.9, 134.0, 130.0, 129.2, 129.0 (3C), 127.9, 126.9, 124.9, 123.4, 123.2, 59.5, 52.4, 21.8, 21.5 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1592.

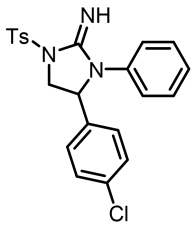
4-(4-fluorophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ga)



White solid (60 mg, 73% yield), purified by ethyl acetate:hexane = 1:6. m. p. 135-136 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.26-7.20 (m, 4H), 7.04-6.99 (m, 3H), 6.88-6.85 (m, 2H), 4.98-4.96 (m, 1H), 4.22-4.19 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 5.4 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 162.6 (d, *J* = 247.6 Hz), 151.0,

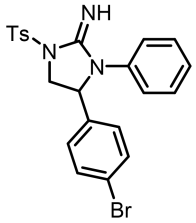
145.3, 138.8, 134.9 (d, J = 3.9 Hz), 134.1, 130.0, 129.1, 128.1 (d, J = 4.5 Hz), 127.9, 125.1, 123.3, 116.1 (d, J = 22.7 Hz), 58.9, 52.3, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.2 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}FN_3O_2S$ 410.1333, Found 410.1338.

4-(4-chlorophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ha)



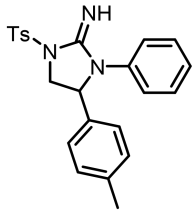
White solid (60 mg, 71% yield), purified by ethyl acetate:hexane = 1:7. m. p. 136-137 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, J = 7.8 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 7.26-7.20 (m, 4H), 7.13 (d, J = 8.4 Hz, 2H), 7.04-7.02 (m, 1H), 6.95 (d, J = 8.4 Hz, 2H), 4.96 (dd, J = 7.8 Hz, 5.4 Hz, 1H), 4.25-4.20 (m, 1H), 3.59 (dd, J = 9.6 Hz, 4.8 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 145.4, 138.8, 137.8, 134.3, 134.1, 130.1, 129.3, 129.1, 127.8, 127.6, 125.1, 123.0, 58.9, 52.2, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}ClN_3O_2S$ 426.1038, Found 426.1038.

4-(4-bromophenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ia)



White solid (70 mg, 75% yield), purified by ethyl acetate:hexane = 1:7. m. p. 143-146 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, J = 7.2 Hz, 2H), 7.29-7.28 (m, 4H), 7.26-7.25 (m, 2H), 7.23-7.21 (m, 2H), 7.05-7.02 (m, 1H), 6.89-6.88 (m, 2H), 4.95 (dd, J = 7.8 Hz, 5.4 Hz, 1H), 4.23-4.20 (m, 1H), 3.59 (dd, J = 9.6 Hz, 4.8 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.9, 145.4, 138.8, 138.4, 134.1, 132.3, 130.1, 129.1, 127.9, 127.8, 125.0, 123.0, 122.4, 59.0, 52.1, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}{}^{79}BrN_3O_2S$ 470.0532, Found 470.0536.

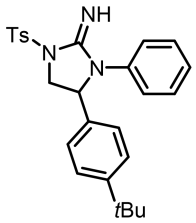
3-phenyl-4-(*p*-tolyl)-1-tosylimidazolidin-2-imine (3ja)



White solid (69 mg, 85% yield), purified by ethyl acetate:hexane = 1:6. m. p. 94-95 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 7.25-7.23 (m, 2H), 7.21-7.19 (m, 2H), 7.03-6.98 (m, 3H), 6.92-6.90 (m, 2H), 4.95 (dd, J = 7.8 Hz, 6.0 Hz, 1H), 4.20-4.17 (m, 1H), 3.59 (dd, J = 9.6 Hz, 5.4 Hz, 1H), 2.46 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 145.1, 139.0, 138.2, 136.0, 134.1, 130.0, 129.7, 129.0, 127.9, 126.3, 125.0, 123.4, 59.4, 52.4, 21.8, 21.2 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$

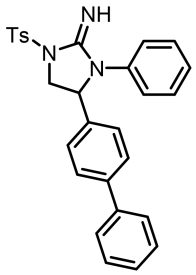
406.1584, Found 406.1599.

4-(4-(*tert*-butyl)phenyl)-3-phenyl-1-tosylimidazolidin-2-imine (3ka)



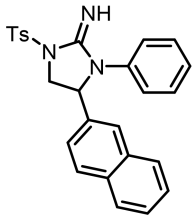
White solid (73 mg, 82% yield), purified by ethyl acetate:hexane = 1:8. m. p. 206-208 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.33-7.27 (m, 4H), 7.24-7.19 (m, 4H), 7.05-7.01 (m, 1H), 6.95 (d, *J* = 8.0 Hz, 2H), 4.97 (dd, *J* = 8.0 Hz, 5.2 Hz, 1H), 4.20-4.15 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.47 (s, 3H), 1.25 (s, 9H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.5, 151.3, 145.1, 139.1, 136.0, 134.2, 130.0, 129.0, 128.1, 125.99, 125.97, 124.9, 123.4, 59.3, 52.4, 34.7, 31.4, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{30}N_3O_2S$ 448.2053, Found 448.2066.

4-([1,1'-biphenyl]-4-yl)-3-phenyl-1-tosylimidazolidin-2-imine (3la)



White solid (74 mg, 79% yield), purified by ethyl acetate:hexane = 1:7. m. p. 209-211 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.42-7.39 (m, 4H), 7.35-7.27 (m, 5H), 7.23-7.21 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.04-7.01 (m, 1H), 5.03 (dd, *J* = 7.8 Hz, 4.8 Hz, 1H), 4.25-4.22 (m, 1H), 3.67 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 2.38 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 145.2, 141.3, 140.3, 139.0, 138.1, 134.1, 130.0, 129.01, 128.95, 127.9, 127.74, 127.72, 127.1, 126.7, 124.9, 123.2, 59.3, 52.4, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{28}H_{26}N_3O_2S$ 468.1740, Found 468.1745.

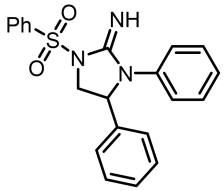
4-(naphthalen-2-yl)-3-phenyl-1-tosylimidazolidin-2-imine (3ma)



White solid (72 mg, 82% yield), purified by ethyl acetate:hexane = 1:8. m. p. 162-164 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78-7.76 (m, 1H), 7.73-7.69 (m, 3H), 7.60-7.58 (m, 1H), 7.46-7.44 (m, 2H), 7.41 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.20-7.17 (m, 2H), 7.15-7.12 (m, 3H), 7.00-6.97 (m, 1H), 5.13 (dd, *J* = 8.4 Hz, 4.8 Hz, 1H), 4.30 (dd, *J* = 9.6 Hz, 8.4 Hz, 1H), 3.75 (dd, *J* = 10.2 Hz, 4.8 Hz, 1H), 2.30 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.0, 145.2, 139.1, 136.7, 134.0, 133.2, 129.9, 129.4, 129.0, 128.1, 127.8, 127.7, 126.64, 126.55, 125.7, 124.8, 123.3, 122.8 (2C), 59.7, 52.2, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{24}N_3O_2S$ 442.1584, Found

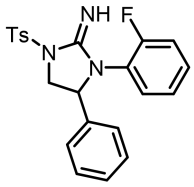
442.1585.

3,4-diphenyl-1-(phenylsulfonyl)imidazolidin-2-imine (3na)



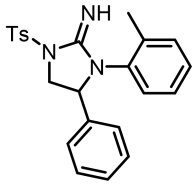
White solid (50 mg, 66% yield), purified by ethyl acetate:hexane = 1:7. m. p. 134-136 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 2H), 7.68-7.65 (m, 1H), 7.53 (t, *J* = 7.8 Hz, 2H), 7.26-7.24 (m, 2H), 7.21-7.17 (m, 5H), 7.02-7.01 (m, 3H), 4.99 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H), 4.25-4.22 (m, 1H), 3.64 (dd, *J* = 9.6 Hz, 5.4 Hz, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.1, 139.1, 138.9, 137.1, 134.1, 129.4, 129.2, 129.0, 128.5, 127.9, 126.3, 125.1, 123.5, 59.6, 52.4 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{21}H_{20}N_3O_2S$ 378.1271, Found 378.1286.

3-(2-fluorophenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ab)



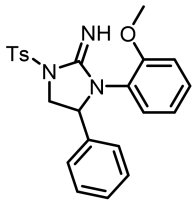
White solid (57 mg, 70% yield), purified by ethyl acetate:hexane = 1:2. m. p. 170-172 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.21-7.18 (m, 3H), 7.14-7.09 (m, 2H), 7.06-7.05 (m, 2H), 7.02-6.96 (m, 2H), 4.98-4.96 (m, 1H), 4.27-4.24 (m, 1H), 3.63-3.60 (m, 1H), 2.50 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4 (d, *J* = 252.2 Hz), 151.7, 145.3, 138.1, 133.9, 130.1, 129.8, 129.0, 128.9 (d, *J* = 7.6 Hz), 128.8, 128.0, 127.1, 125.7 (d, *J* = 10.6 Hz), 124.5 (d, *J* = 4.5 Hz), 116.7 (d, *J* = 19.6 Hz), 59.9, 52.6, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -119.0 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}FN_3O_2S$ 410.1333, Found 410.1348.

4-phenyl-3-(*o*-tolyl)-1-tosylimidazolidin-2-imine (3ac)



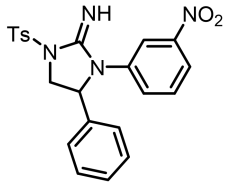
White solid (56 mg, 69% yield), purified by ethyl acetate:hexane = 1:3. m. p. 185-187 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.22-7.17 (m, 3H), 7.13-6.99 (m, 5H), 6.89-6.78 (m, 1H), 4.86-4.81 (m, 1H), 4.30-4.26 (m, 1H), 3.71-3.67 (m, 1H), 2.50 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6, 145.1, 138.2, 136.7, 136.4, 134.1, 131.4, 129.9, 128.9 (3C), 128.8, 128.2, 127.9, 127.3, 126.8, 60.5, 52.4, 21.8, 18.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1595.

3-(2-methoxyphenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ad)



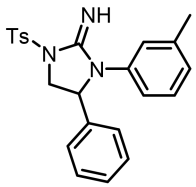
White solid (66 mg, 78% yield), purified by ethyl acetate:hexane = 1:2. m. p. 138-139 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.19-7.17 (m, 3H), 7.15-7.13 (m, 1H), 7.05-7.04 (m, 2H), 6.95-6.93 (m, 1H), 6.84-6.83 (m, 1H), 6.77-6.73 (m, 1H), 5.02-4.99 (m, 1H), 4.30-4.27 (m, 1H), 3.75 (s, 3H), 3.62-3.59 (m, 1H), 2.49 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.8, 153.0, 144.9, 138.9, 134.4, 131.1, 129.9, 129.2, 128.7, 128.5, 128.2, 127.3, 126.4, 120.9, 112.3, 59.7, 55.7, 52.7, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_3S$ 422.1533, Found 422.1549.

3-(3-nitrophenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ae)



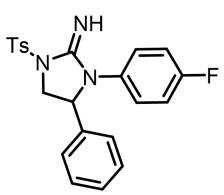
White solid (54 mg, 62% yield), purified by ethyl acetate:hexane = 1:7. m. p. 162-164 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.82 (d, *J* = 7.8 Hz, 1H), 7.76-7.75 (m, 3H), 7.36-7.31 (m, 3H), 7.24-7.19 (m, 3H), 7.01 (d, *J* = 7.8 Hz, 2H), 5.08 (dd, *J* = 7.8 Hz, 4.2 Hz, 1H), 4.23-4.20 (m, 1H), 3.66 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 148.5, 145.6, 140.3, 138.2, 133.6, 130.3, 129.5, 129.4, 128.8, 127.7, 127.5, 126.0, 118.6, 116.7, 58.7, 52.0, 21.8 pm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}N_4O_4S$ 437.1278, Found 437.1271.

4-phenyl-3-(*m*-tolyl)-1-tosylimidazolidin-2-imine (3af)



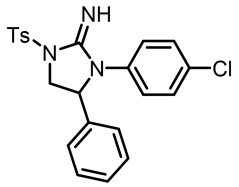
White solid (54 mg, 67% yield), purified by ethyl acetate:hexane = 1:7. m. p. 165-166 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 7.21-7.16 (m, 3H), 7.13 (s, 1H), 7.10-7.02 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 4.97 (dd, *J* = 8.0 Hz, 5.6 Hz, 1H), 4.24-4.19 (m, 1H), 3.62 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.46 (s, 3H), 2.23 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 145.2, 139.2, 138.9, 138.7, 134.1, 130.0, 129.1, 128.8, 128.4, 128.0, 126.4, 126.2, 124.4, 120.7, 59.8, 52.3, 21.8, 21.6 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1599.

3-(4-fluorophenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ag)



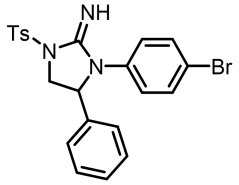
White solid (61 mg, 75% yield), purified by ethyl acetate:hexane = 1:9. m. p. 150-151 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.24-7.18 (m, 5H), 7.01 (d, *J* = 6.6 Hz, 2H), 6.90-6.87 (m, 2H), 4.91 (dd, *J* = 7.8 Hz, 6.0 Hz, 1H), 4.23-4.20 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0 (d, *J* = 247.6 Hz), 151.5 (d, *J* = 7.6 Hz), 145.3, 138.7, 134.9 (d, *J* = 3.0 Hz), 133.9, 130.1, 129.2, 128.6, 127.9, 126.5, 125.8, 115.8 (d, *J* = 22.7 Hz), 59.9, 52.2, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -116.9 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}FN_3O_2S$ 410.1333, Found 410.1339.

3-(4-chlorophenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ah)



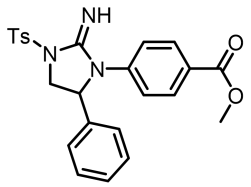
White solid (61 mg, 72% yield), purified by ethyl acetate:hexane = 1:13. m. p. 146-148 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.23-7.18 (m, 5H), 7.15-7.13 (m, 2H), 7.00-6.98 (m, 2H), 4.94 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H), 4.23-4.20 (m, 1H), 3.61 (dd, *J* = 10.2 Hz, 5.4 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 145.5, 138.6, 137.4, 133.8, 130.2, 129.2, 129.1, 128.7, 127.8, 126.3, 124.6, 116.7, 59.5, 52.2, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}ClN_3O_2S$ 426.1038, Found 426.1049.

3-(4-bromophenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3ai)



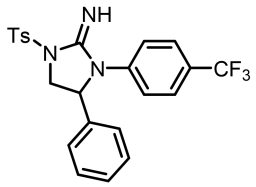
White solid (70 mg, 75% yield), purified by ethyl acetate:hexane = 1:15. m. p. 179-181 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.8 Hz, 2H), 7.31-7.29 (m, 4H), 7.24-7.17 (m, 5H), 6.99 (d, *J* = 7.2 Hz, 2H), 4.95 (dd, *J* = 8.4 Hz, 5.4 Hz, 1H), 4.21-4.18 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 4.8 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.7, 145.4, 138.7, 138.1, 133.8, 131.9, 130.1, 129.2, 128.6, 127.8, 126.2, 124.5, 117.7, 59.1, 52.2, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}{}^{79}BrN_3O_2S$ 470.0532, Found 470.0535.

methyl 4-(2-imino-5-phenyl-3-tosylimidazolidin-1-yl)benzoate (3aj)



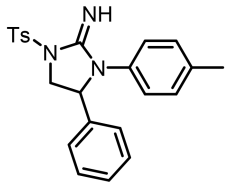
White solid (68 mg, 76% yield), purified by ethyl acetate:hexane = 1:7. m. p. 208-210 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.50-7.49 (m, 2H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.22-7.20 (m, 1H), 7.18-7.15 (m, 2H), 6.98 (d, *J* = 7.2 Hz, 2H), 5.06 (dd, *J* = 10.8 Hz, 3.6 Hz, 1H), 4.20-4.17 (m, 1H), 3.82 (s, 3H), 3.66 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 150.0, 145.4, 143.3, 138.9, 133.8, 130.3, 130.1, 129.3, 128.4, 127.6, 125.8, 125.0, 120.7, 58.6, 52.1, 52.0, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{24}N_3O_4S$ 450.1482, Found 450.1486.

4-phenyl-1-tosyl-3-(4-(trifluoromethyl)phenyl)imidazolidin-2-imine (3ak)



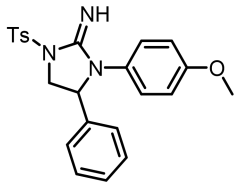
White solid (64 mg, 70% yield), purified by ethyl acetate:hexane = 1:13. m. p. 160-162 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.53-7.52 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.28-7.26 (m, 2H), 7.24-7.22 (m, 1H), 7.19-7.17 (m, 2H), 6.99 (d, *J* = 7.2 Hz, 2H), 5.03 (dd, *J* = 7.2 Hz, 3.6 Hz, 1H), 4.20-4.17 (m, 1H), 3.65 (dd, *J* = 10.2 Hz, 3.6 Hz, 1H), 2.44 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1 (q, *J* = 4.5 Hz), 145.5, 142.3, 138.8, 133.8, 130.2, 129.4, 128.6, 127.7, 126.5, 125.90, 125.86, 124.2 (q, *J* = 271.8 Hz), 121.5, 58.7, 52.2, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.3 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{20}F_3N_3O_2S$ 460.1301, Found 460.1310.

4-phenyl-3-(*p*-tolyl)-1-tosylimidazolidin-2-imine (3al)



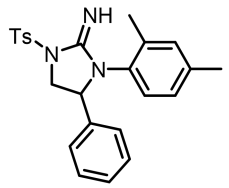
White solid (60 mg, 74% yield), purified by ethyl acetate:hexane = 1:9. m. p. 134-136 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.6 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.20-7.19 (m, 3H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.04-6.99 (m, 4H), 4.97-4.93 (m, 1H), 4.24-4.20 (m, 1H), 3.60 (dd, *J* = 9.6 Hz, 6.0 Hz, 1H), 2.46 (s, 3H), 2.21 (s. 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 145.1, 139.0, 136.1, 135.1, 134.0, 130.0, 129.7, 129.0, 128.4, 128.0, 126.5, 123.9, 59.8, 52.3, 21.8, 21.0 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1591.

3-(4-methoxyphenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3am)



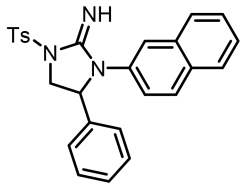
White solid (59 mg, 70% yield), purified by ethyl acetate:hexane = 1:4. m. p. 139-141 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 2H), 7.22-7.18 (m, 3H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.03 (d, *J* = 6.6 Hz, 2H), 6.73 (d, *J* = 9.0 Hz, 2H), 4.89-4.87 (m, 1H), 4.24-4.21 (m, 1H), 3.69 (s, 3H), 3.60 (dd, *J* = 9.6 Hz, 6.6 Hz, 1H), 2.47 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.4, 152.2, 145.1, 138.9, 134.1, 131.5, 130.0, 129.0, 128.5, 128.1, 126.8, 126.3, 114.4, 60.4, 55.5, 52.3, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_3S$ 422.1533, Found 422.1538.

3-(2,4-dimethylphenyl)-4-phenyl-1-tosylimidazolidin-2-imine (3an)



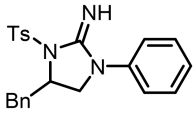
White solid (56 mg, 67% yield), purified by ethyl acetate:hexane = 1:3. m. p. 134-136 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.22-7.18 (m, 3H), 7.03-7.02 (m, 2H), 6.93 (s, 1H), 6.80-6.70 (m, 2H), 4.87-4.72 (m, 1H), 4.28-4.25 (m, 1H), 3.76-3.62 (m, 1H), 2.50 (s, 3H), 2.18 (s, 3H), 2.00 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.9, 145.1, 138.4, 137.7, 136.3, 134.1, 133.7, 132.1, 129.9, 128.84 (3C), 128.76, 128.2, 127.6, 127.4, 60.5, 52.4, 21.8, 21.0, 18.0 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{26}N_3O_2S$ 420.1740, Found 420.1747.

3-(naphthalen-2-yl)-4-phenyl-1-tosylimidazolidin-2-imine (3ao)



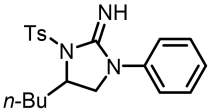
White solid (52 mg, 59% yield), purified by ethyl acetate:hexane = 1:8. m. p. 154-156 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.69 (d, *J* = 9.0 Hz, 2H), 7.62-7.53 (m, 3H), 7.38-7.35 (m, 2H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.19-7.16 (m, 3H), 7.08-7.07 (m, 2H), 5.11 (dd, *J* = 7.8 Hz, 5.4 Hz, 1H), 4.28-4.25 (m, 1H), 3.66 (dd, *J* = 9.6 Hz, 5.4 Hz, 1H), 2.46 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.3, 145.2, 139.0, 136.5, 134.1, 133.5, 131.0, 130.1, 129.1, 128.8, 128.5, 128.0, 127.7, 127.6, 126.4, 126.3, 125.6, 122.7, 120.9, 59.7, 52.4, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{24}N_3O_2S$ 442.1584, Found 442.1589.

4-benzyl-1-phenyl-3-tosylimidazolidin-2-imine (4oa)



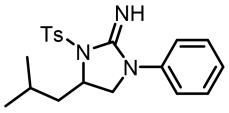
White solid (80 mg, 99% yield), purified by ethyl acetate:hexane = 1:3. m. p. 127-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.33-7.24 (m, 11H), 7.07-7.02 (m, 1H), 4.36-4.31 (m, 1H), 3.51-3.46 (m, 1H), 3.41-3.37 (m, 2H), 3.00 (dd, *J* = 13.6 Hz, 9.6 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.0, 145.1, 140.0, 136.0, 135.6, 130.2, 129.6, 128.9 (3C), 127.5, 127.3, 124.0, 120.6, 56.2, 49.0, 41.8, 21.7 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{24}N_3O_2S$ 406.1584, Found 406.1590.

4-butyl-1-phenyl-3-tosylimidazolidin-2-imine (4pa)



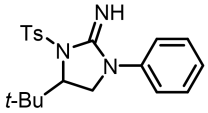
White solid (67 mg, 90% yield), purified by ethyl acetate:hexane = 1:3. m. p. 101-103 °C.^{1}H NMR (600 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.33-7.30 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 1H), 4.13-4.06 (m, 1H), 3.64-3.61 (m, 1H), 3.35 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 2.42 (s, 3H), 1.98-1.91 (m, 1H), 1.83-1.78 (m, 1H), 1.39-1.34 (m, 4H), 0.93-0.91 (m, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.3, 145.0, 140.2, 135.5, 130.1, 129.0, 127.6, 123.9, 120.5, 55.3, 50.1, 35.6, 26.8, 22.6, 21.7, 14.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{26}N_3O_2S$ 372.1740, Found 372.1749.

4-isobutyl-1-phenyl-3-tosylimidazolidin-2-imine (4qa)



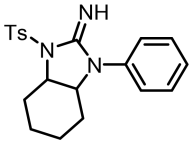
White solid (58 mg, 78% yield), purified by ethyl acetate:hexane = 1:2. m. p. 116-118 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.2 Hz, 2H), 7.33-7.31 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 1H), 4.14-4.10 (m, 1H), 3.62-3.60 (m, 1H), 3.32 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 2.42 (s, 3H), 1.94-1.90 (m, 1H), 1.75-1.62 (m, 2H), 1.00 (d, *J* = 6.6 Hz, 6H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.2, 145.0, 140.3, 135.5, 130.2, 129.0, 127.6, 123.9, 120.5, 54.1, 50.6, 45.0, 24.9, 23.4, 22.1, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{26}N_3O_2S$ 372.1740, Found 372.1747.

4-(*tert*-butyl)-1-phenyl-3-tosylimidazolidin-2-imine (4ra)



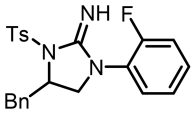
White solid (34 mg, 46% yield), purified by ethyl acetate:hexane = 1:3. m. p. 172-174 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.4 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.30-7.28 (m, 4H), 7.04 (t, *J* = 7.2 Hz, 1H), 3.91-3.89 (m, 1H), 3.43-3.42 (m, 1H), 3.35-3.32 (m, 1H), 2.41 (s, 3H), 1.01 (s, 9H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.4, 145.0, 139.9, 135.5, 130.1, 129.0, 127.7, 123.9, 120.4, 63.5, 48.0, 35.5, 25.8, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{26}N_3O_2S$ 372.1740, Found 372.1749.

1-phenyl-3-tosyloctahydro-2*H*-benzo[*d*]imidazol-2-imine (4sa)



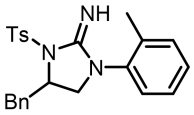
White solid (57 mg, 77% yield), purified by ethyl acetate:hexane = 1:2. m. p. 156-161 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.4 Hz, 2H), 7.38-7.35 (m, 4H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.13-7.12 (m, 2H), 3.31-3.26 (m, 1H), 2.96-2.93 (m, 1H), 2.72-2.70 (m, 1H), 2.47 (s, 3H), 1.94-1.89 (m, 2H), 1.78-1.70 (m, 2H), 1.38-1.33 (m, 2H), 1.16-1.10 (m, 1H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.4, 145.1, 138.8, 133.4, 130.0, 129.3, 128.2, 126.7, 126.3, 64.3, 62.9, 30.5, 28.7, 24.7, 23.8, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{24}N_3O_2S$ 370.1584, Found 370.1589

4-benzyl-1-(2-fluorophenyl)-3-tosylimidazolidin-2-imine (4ob)



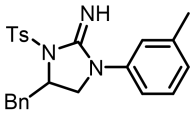
White solid (75 mg, 89% yield), purified by ethyl acetate:hexane = 1:2. m. p. 132-134 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.8 Hz, 2H), 7.35-7.30 (m, 4H), 7.28-7.25 (m, 3H), 7.17-7.15 (m, 1H), 7.07-7.03 (m, 3H), 4.39-4.35 (m, 1H), 3.46-3.43 (m, 1H), 3.34-3.32 (m, 2H), 3.09 (dd, *J* = 13.8 Hz, 9.0 Hz, 1H), 2.44 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.8 (d, *J* = 250.7 Hz), 151.2, 145.1, 136.0, 135.7, 130.1, 129.8, 128.9, 128.5, 128.3 (d, *J* = 7.6 Hz), 127.6, 127.3, 126.8 (d, *J* = 10.6 Hz), 124.6 (d, *J* = 3.0 Hz), 116.7 (d, *J* = 19.6 Hz), 57.3, 50.0, 41.5, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -120.4 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{23}FN_3O_2S$ 424.1490, Found 424.1498.

4-benzyl-1-(*o*-tolyl)-3-tosylimidazolidin-2-imine (4oc)



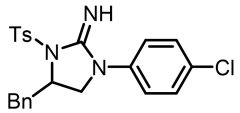
White solid (63 mg, 75% yield), purified by ethyl acetate:hexane = 1:2. m. p. 146-148 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.8 Hz, 2H), 7.35-7.31 (m, 4H), 7.29-7.25 (m, 3H), 7.16-7.11 (m, 3H), 6.76 (d, *J* = 6.6 Hz, 1H), 4.45-4.42 (m, 1H), 3.41-3.38 (m, 2H), 3.25 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 3.12 (dd, *J* = 13.8 Hz, 9.0 Hz, 1H), 2.45 (s, 3H), 1.94 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 151.7, 144.9, 137.4, 136.6, 136.1, 135.7, 131.4, 130.0, 129.9, 128.9, 128.1, 127.9, 127.3, 127.2, 127.1, 57.2, 50.5, 41.8, 21.8, 17.6 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{26}N_3O_2S$ 420.1740, Found 420.1757.

4-benzyl-1-(*m*-tolyl)-3-tosylimidazolidin-2-imine (4of)



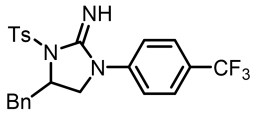
White solid (80 mg, 95% yield), purified by ethyl acetate:hexane = 1:2. m. p. 142-144 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.8 Hz, 2H), 7.32-7.30 (m, 4H), 7.26-7.24 (m, 3H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.09 (s, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 4.36-4.33 (m, 1H), 3.50-3.47 (m, 1H), 3.39-3.35 (m, 2H), 3.00 (dd, *J* = 13.8 Hz, 9.6 Hz, 1H), 2.42 (s, 3H), 2.28 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 150.1, 145.0, 139.9, 138.9, 136.2, 135.7, 130.1, 129.6, 128.9, 128.8, 127.6, 127.2, 125.0, 121.6, 118.0, 56.3, 49.2, 41.8, 21.7, 21.6 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{26}N_3O_2S$ 420.1740, Found 420.1758.

4-benzyl-1-(4-chlorophenyl)-3-tosylimidazolidin-2-imine (4oh)



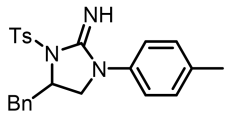
White solid (87 mg, 99% yield), purified by ethyl acetate:hexane = 1:4. m. p. 123-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.33-7.29 (m, 4H), 7.27-7.20 (m, 7H), 4.34-4.30 (m, 1H), 3.46-3.42 (m, 1H), 3.38-3.32 (m, 2H), 3.00 (dd, *J* = 13.6 Hz, 9.6 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 145.3, 138.5, 135.8, 135.4, 130.3, 129.6, 129.0, 128.8, 127.5 (2C), 127.4, 121.5, 56.1, 48.8, 41.8, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{23}ClN_3O_2S$ 440.1194, Found 440.1194.

4-benzyl-3-tosyl-1-(4-(trifluoromethyl)phenyl)imidazolidin-2-imine (4ok)



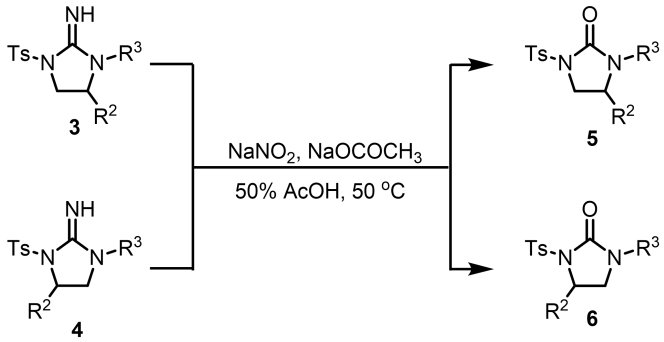
White solid (81 mg, 86% yield), purified by ethyl acetate:hexane = 1:8. m. p. 136-138 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.8 Hz, 2H), 7.51-7.48 (m, 4H), 7.33-7.29 (m, 4H), 7.26-7.23 (m, 3H), 4.35-4.32 (m, 1H), 3.49-3.46 (m, 1H), 3.41-3.35 (m, 2H), 2.99 (dd, *J* = 13.8 Hz, 9.6 Hz, 1H), 2.42 (s, 3H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 145.4, 143.2, 135.7, 135.4, 130.4, 129.6, 129.0, 127.5, 127.4, 126.0 (q, *J* = 3.0 Hz), 125.1 (q, *J* = 36.2 Hz), 124.3 (q, *J* = 270.3 Hz), 119.3, 56.0, 48.5, 41.9, 21.8 ppm; ^{19}F NMR (565 MHz, $CDCl_3$) δ -62.1 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{23}F_3N_3O_2S$ 474.1458, Found 474.1469.

4-benzyl-1-(*p*-tolyl)-3-tosylimidazolidin-2-imine (4ol)



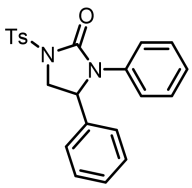
White solid (83 mg, 99% yield), purified by ethyl acetate:hexane = 1:2. m. p. 124-126 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.33-7.30 (m, 4H), 7.27-7.24 (m, 3H), 7.13 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.36-4.31 (m, 1H), 3.48-3.44 (m, 1H), 3.40-3.33 (m, 2H), 3.00 (dd, *J* = 13.2 Hz, 9.6 Hz, 1H), 2.42 (s, 3H), 2.27 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.4, 145.0, 137.2, 136.1, 135.6, 134.1, 130.1, 129.6, 129.5, 128.9, 127.6, 127.3, 121.1, 56.3, 49.3, 41.7, 21.8, 20.9 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{26}N_3O_2S$ 420.1740, Found 420.1753.

2.2 Procedure for the Transformation of Cyclic Guanidines to Ureas



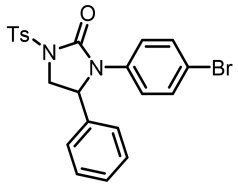
To a 25 mL oven dried round bottom flask with a magneton was added cyclic guanidine compounds **3** or **4** (0.2 mmol, 1 eq), sodium acetate (4.0 mmol, 20 eq) and 50% AcOH (4.0 mL). Then, sodium nitrite (5.0 mmol, 25 eq) was added within 1 h at room temperature. The reaction mixture was stirred at 50 °C for another 3-5 h. Upon complete consumption of the starting material (detected by TLC), the reaction mixture was then neutralized with saturated aqueous solution of $NaHCO_3$ and extracted with ethyl acetate. The ethyl acetate fraction was separated, washed with brine and dried over anhydrous Na_2SO_4. The volatile components were then removed under vacuum and the residue was further purified by column chromatography on silica gel to afford the urea products **5** or **6**.

3,4-diphenyl-1-tosylimidazolidin-2-one (5aa)



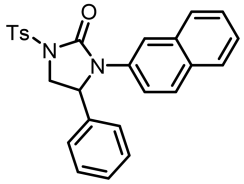
White solid (78 mg, 99% yield), purified by ethyl acetate:hexane = 1:5. m. p. 170-172 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.22-7.18 (m, 5H), 7.13-7.09 (m, 4H), 6.94 (t, *J* = 7.2 Hz, 1H), 5.12 (dd, *J* = 8.8 Hz, 5.2 Hz, 1H), 4.26-4.22 (m, 1H), 3.74 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.37 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 145.2, 138.5, 137.2, 134.9, 129.8, 129.4, 128.91, 128.87, 128.4, 126.2, 125.0, 121.3, 57.8, 50.4, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{21}N_2O_2S$ 393.1267, Found 393.1270.

3-(4-bromophenyl)-4-phenyl-1-tosylimidazolidin-2-one (5ai)



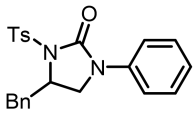
White solid (92 mg, 98% yield), purified by ethyl acetate:hexane = 1:5. m. p. 174-176 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.31-7.26 (m, 5H), 7.19-7.14 (m, 4H), 5.17 (dd, *J* = 8.8 Hz, 5.2 Hz, 1H), 4.34-4.30 (m, 1H), 3.80 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 145.4, 138.1, 136.3, 134.8, 131.9, 129.9, 129.6, 129.1, 128.4, 126.1, 122.6, 117.9, 57.6, 50.3, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{22}H_{20}Br^{79}N_2O_3S$ 471.0373, Found 471.0381.

3-(naphthalen-2-yl)-4-phenyl-1-tosylimidazolidin-2-one (5ao)



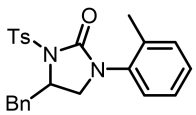
White solid (87 mg, 98% yield), purified by ethyl acetate:hexane = 1:5. m. p. 187-189 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 2H), 7.70-7.62 (m, 4H), 7.51 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.40-7.35 (m, 4H), 7.29-7.27 (m, 2H), 7.26-7.22 (m, 3H), 5.34 (dd, *J* = 9.2 Hz, 5.2 Hz, 1H), 4.40-4.35 (m, 1H), 3.87 (dd, *J* = 9.6 Hz, 5.2 Hz, 1H), 2.45 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 145.3, 138.5, 135.0, 134.8, 133.4, 130.8, 129.9, 129.5, 129.0, 128.8, 128.5, 127.8, 127.6, 126.5, 126.2, 125.7, 120.4, 119.1, 57.9, 50.4, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{23}N_2O_3S$ 443.1424, Found 443.1427.

4-benzyl-1-phenyl-3-tosylimidazolidin-2-one (6oa)



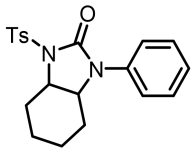
White solid (70 mg, 86% yield), purified by ethyl acetate:hexane = 1:6. m. p. 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.35-7.24 (m, 11H), 7.07 (t, *J* = 6.8 Hz, 1H), 4.69-4.65 (m, 1H), 3.82-3.77 (m, 1H), 3.60-3.50 (m, 2H), 2.88 (dd, *J* = 13.2 Hz, 10.0 Hz, 1H), 2.43 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 145.0, 138.4, 136.4, 135.6, 129.8, 129.6, 129.1, 129.0, 128.5, 127.4, 124.5, 118.9, 54.6, 47.3, 41.0, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{23}H_{23}N_2O_3S$ 407.1424, Found 407.1438.

4-benzyl-1-(*o*-tolyl)-3-tosylimidazolidin-2-one (6oc)



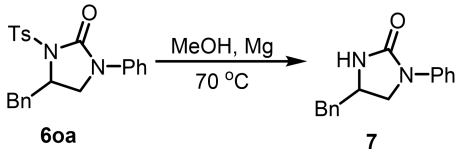
White solid (80 mg, 95% yield), purified by ethyl acetate:hexane = 1:5. m. p. 167-169 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.34-7.24 (m, 7H), 7.16-7.09 (m, 3H), 6.81 (d, *J* = 7.6 Hz, 1H), 4.73-4.67 (m, 1H), 3.73-3.68 (m, 1H), 3.48-3.38 (m, 2H), 3.06 (dd, *J* = 13.6 Hz, 9.2 Hz, 1H), 2.43 (s, 3H), 1.99 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 144.8, 136.4, 136.0, 135.8, 135.5, 131.3, 129.9, 129.7, 129.0, 128.4, 128.3, 127.4, 126.9, 126.6, 55.3, 49.3, 40.9, 21.8, 17.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{24}H_{25}N_2O_3S$ 421.1580, Found 421.1592.

1-phenyl-3-tosyloctahydro-2*H*-benzo[*d*]imidazol-2-one (6sa)



White solid (69 mg, 93% yield), purified by ethyl acetate:hexane = 1:4. m. p. 68-70 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 4H), 7.21-7.17 (m, 1H), 7.12-7.10 (m, 2H), 3.52-3.38 (m, 2H), 2.91-2.87 (m, 1H), 2.43 (s, 3H), 2.09-1.96 (m, 2H), 1.87-1.73 (m, 2H), 1.53-1.24 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 144.9, 136.4, 134.8, 129.7, 129.1, 128.7, 126.5, 124.6, 63.8, 62.4, 30.2, 28.5, 24.6, 23.8, 21.8 ppm; HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{20}H_{23}N_2O_3S$ 371.1424, Found 371.1430.

2.3 Procedure for the Deprotection of 6oa



6oa **7**

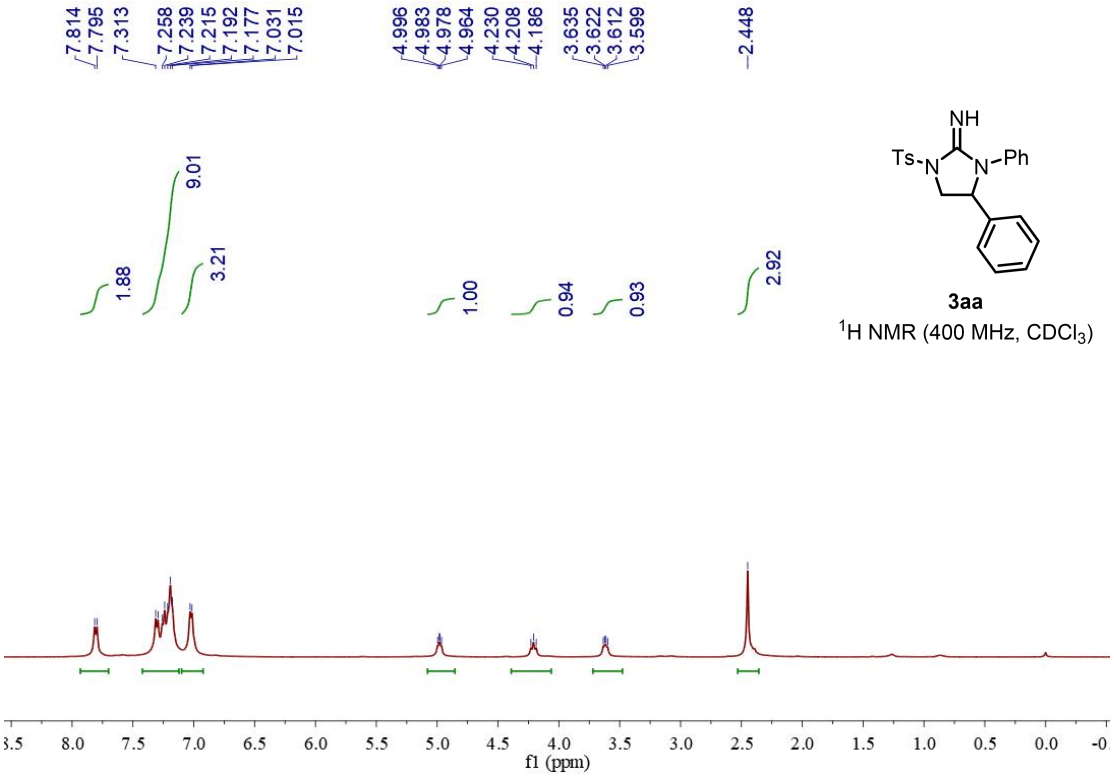
In a 20 mL reaction tube were added **6oa** (0.2 mmol), magnesium chips (3.0 mmol) and methanol (4.0 mL). The mixture was then stirred at 70 °C. Upon the complete consumption of **6op** detected by TLC, the reaction mixture was filtered through a celite pad and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate: hexane = 1:2), affording the desired product **7** as white solid (48 mg, 95% yield). m. p. 163-165 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.4 Hz, 2H), 7.36-7.32 (m, 4H), 7.29-7.27 (m, 1H), 7.23 (d, *J* = 7.2 Hz, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 5.08-4.83 (mz, 1H), 4.04-3.98 (m, 2H), 3.65-3.63 (m, 1H), 2.94-2.86 (m, 2H) ppm; ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.6, 140.1, 136.8, 129.2, 129.1, 129.0, 127.3, 122.9, 118.0, 50.7, 50.6, 42.5 ppm. HRMS (ESI) m/z: $[M + H]^+$ Calcd. for $C_{26}H_{17}N_2O$ 253.1335, Found 253.1340.

3. References.

[1] (a) Steiman, T. J.; Liu, J.; Mengiste, A. et al. Synthesis of β-Phenethylamines via Ni/Photoredox Cross-Electrophile Coupling of Aliphatic Aziridines and Aryl Iodides. *Journal of the American Chemical Society*, **2020**, *142* (16): 7598-7605; (b) Das, B. K.; Pradhan, S.; Punniyamurthy, T. Stereospecific Ring Opening and Cycloisomerization of Aziridines with Propargylamines: Synthesis of Functionalized Piperazines and Tetrahydropyrazines. *Organic Letters*, **2018**, *20* (15): 4444-4448; (c) Thakur, V. V.; Sudalai, A. N-Bromoamides as versatile catalysts for aziridination of olefins using chloramine-T. *Tetrahedron letters*, **2003**, *44* (5): 989-992.

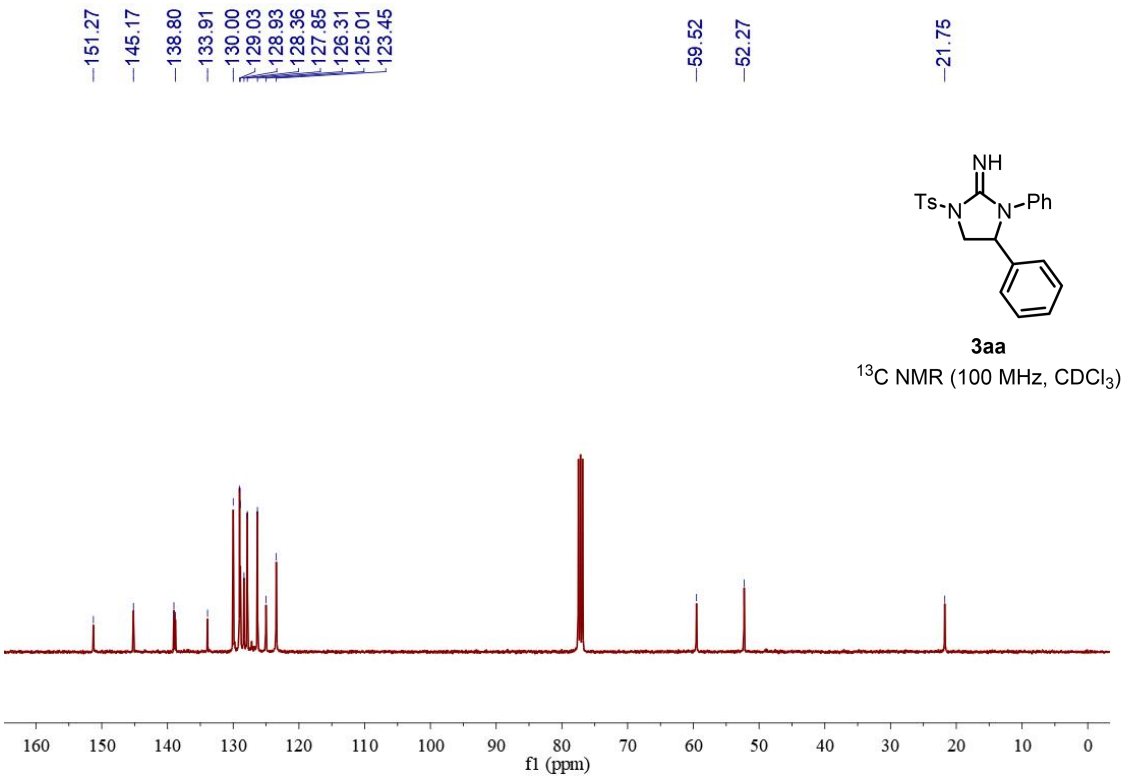
[2] (a) Ayres, J. N.; Williams, M. T. J.; Tizzard, G. J. et al. Synthesis and Reactivity of N-Allenyl Cyanamides. *Organic Letters*, **2018**, *20* (17): 5282-5285; (b) Anbarasan, P.; Neumann, H.; Beller, M. A General Rhodium-Catalyzed Cyanation of Aryl and Alkenyl Boronic Acids. *Angewandte Chemie International Edition*, **2011**, *50* (2): 519-522.

4. Copies of NMR Spectra



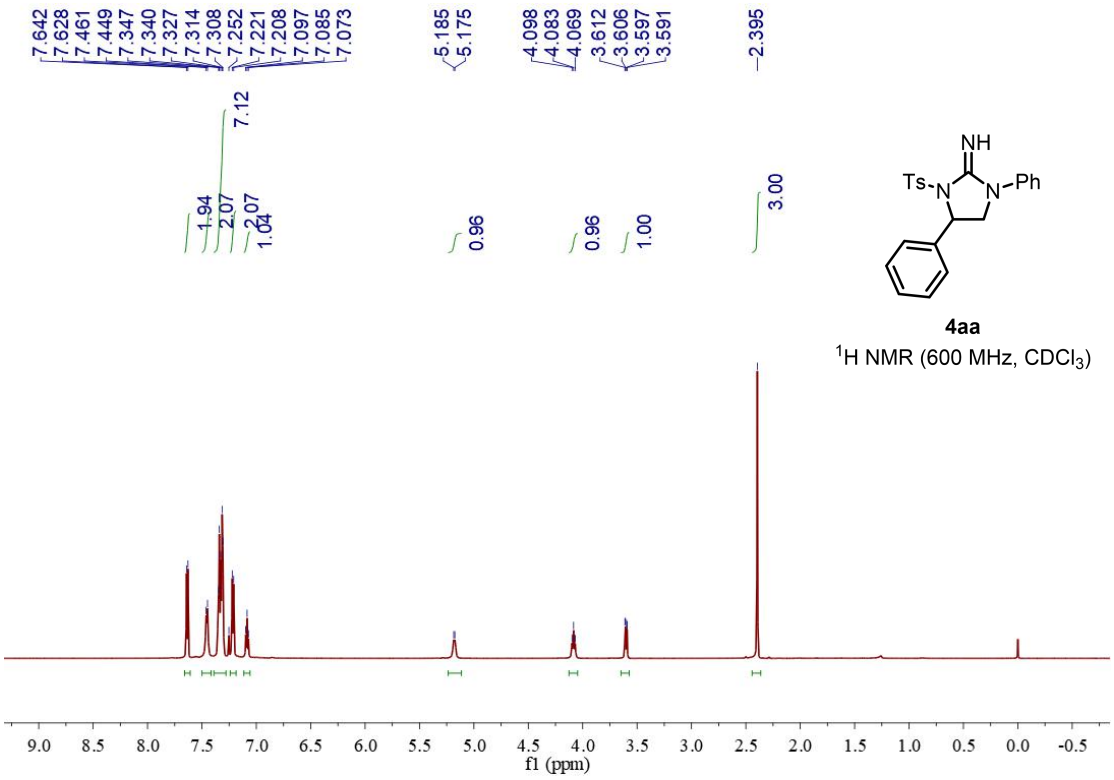
3aa

^{1}H NMR (400 MHz, $CDCl_3$)



3aa

^{13}C NMR (100 MHz, $CDCl_3$)



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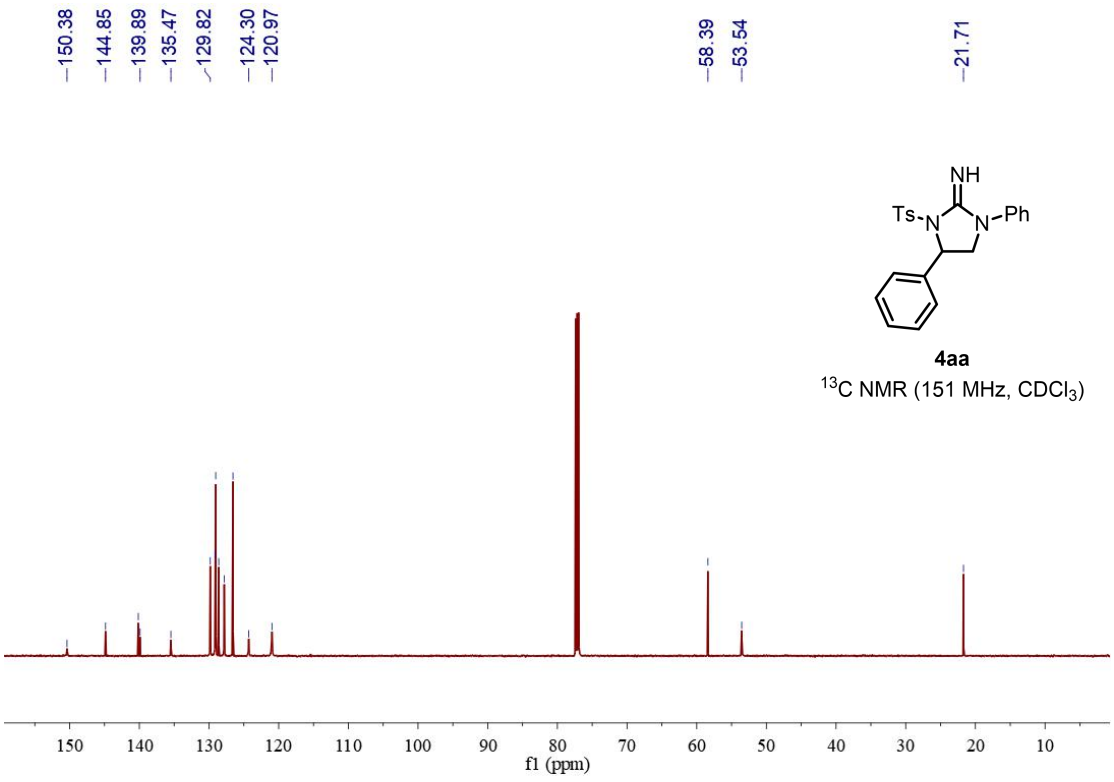
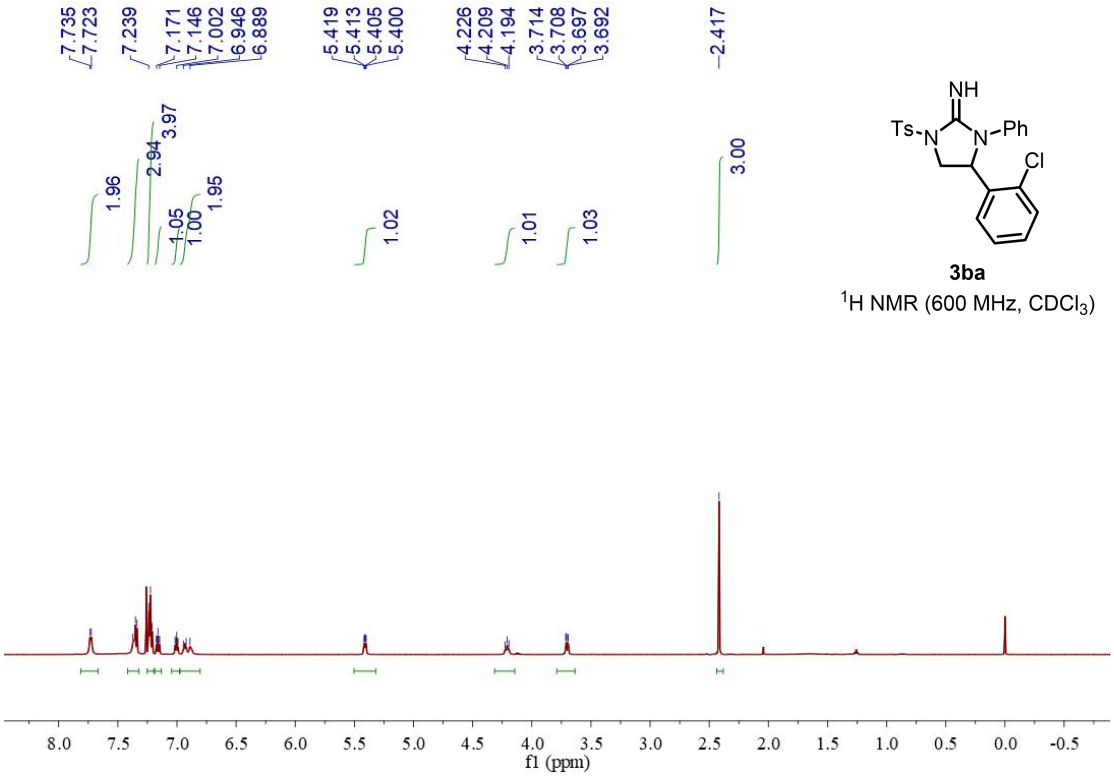
^{1}H NMR (600 MHz, $CDCl_3$)



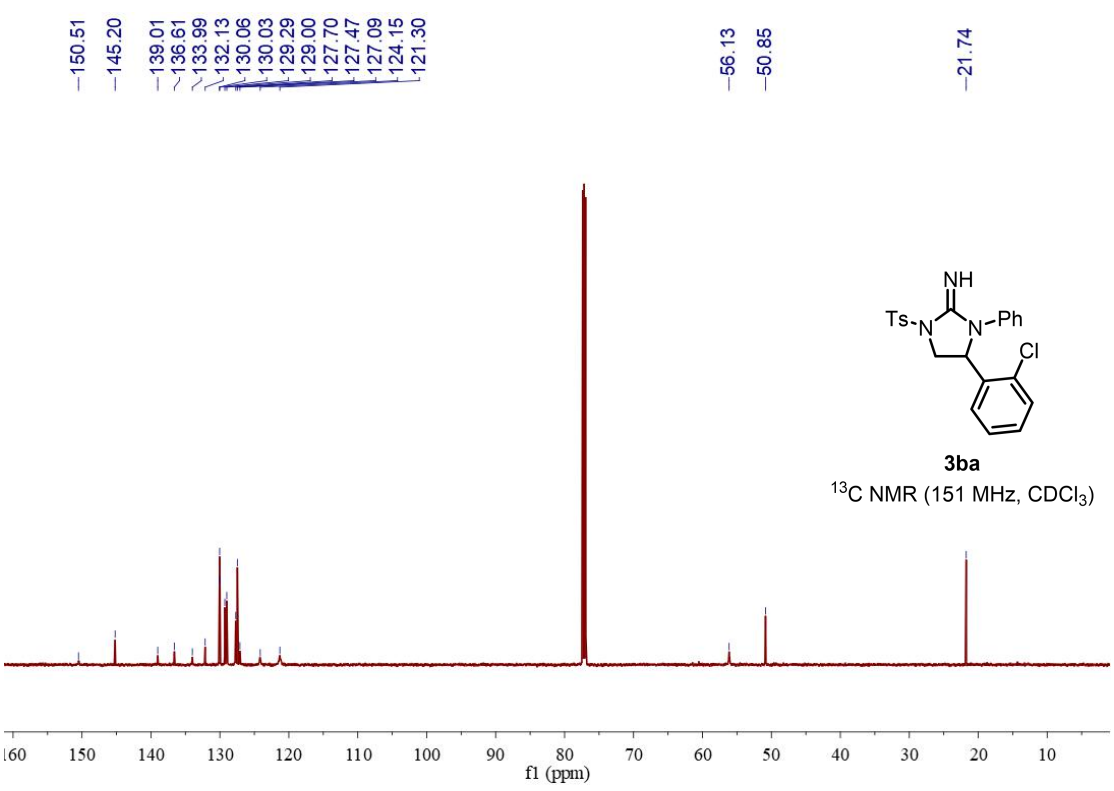
4aa

^{13}C NMR (151 MHz, $CDCl_3$)



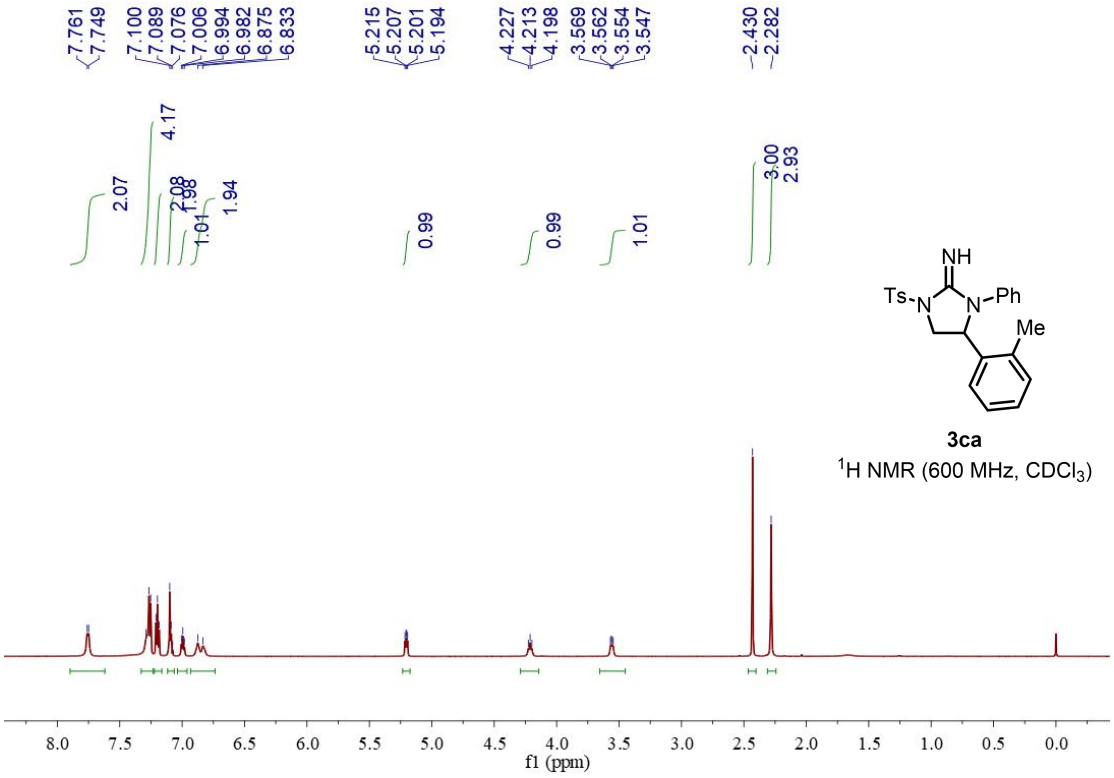
3ba

^{1}H NMR (600 MHz, $CDCl_3$)



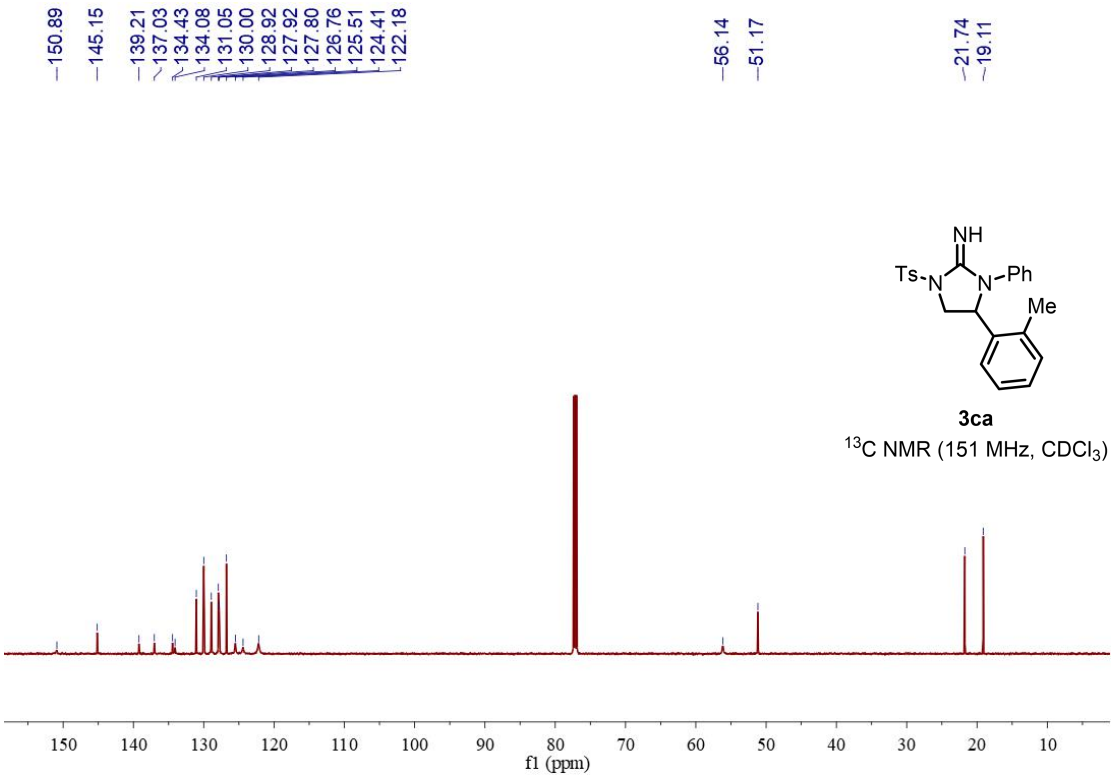
3ba

^{13}C NMR (151 MHz, $CDCl_3$)



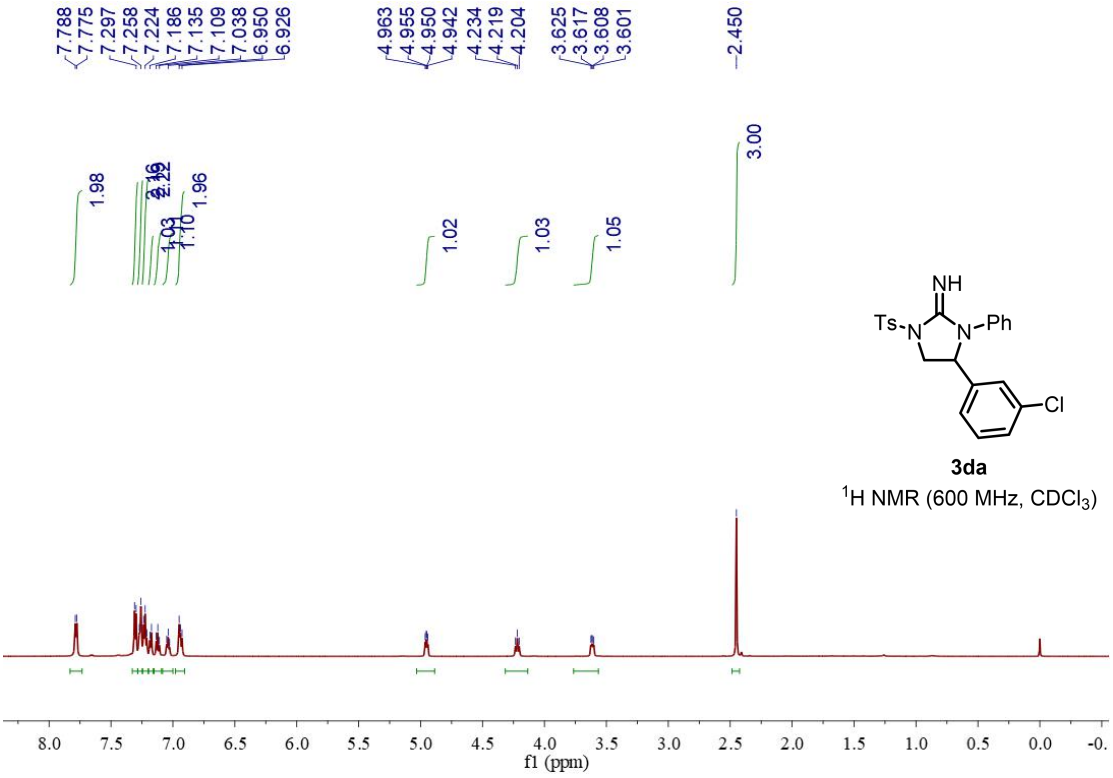
3ca

^{1}H NMR (600 MHz, $CDCl_3$)



3ca

^{13}C NMR (151 MHz, $CDCl_3$)



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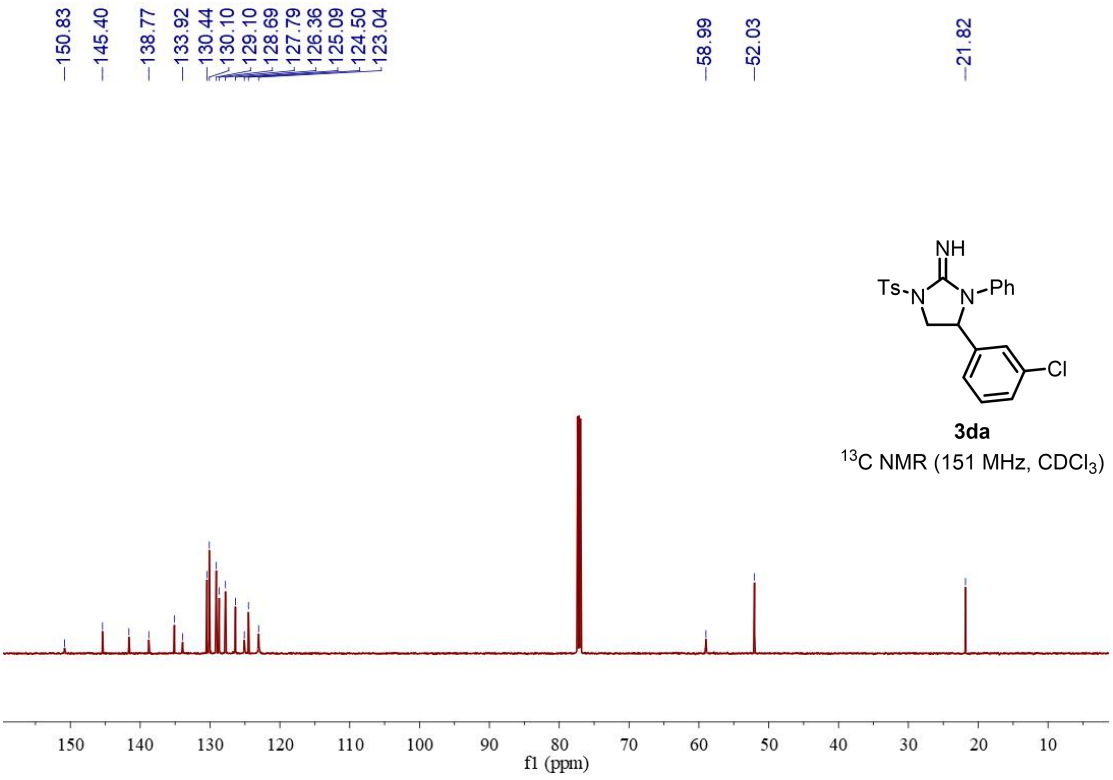
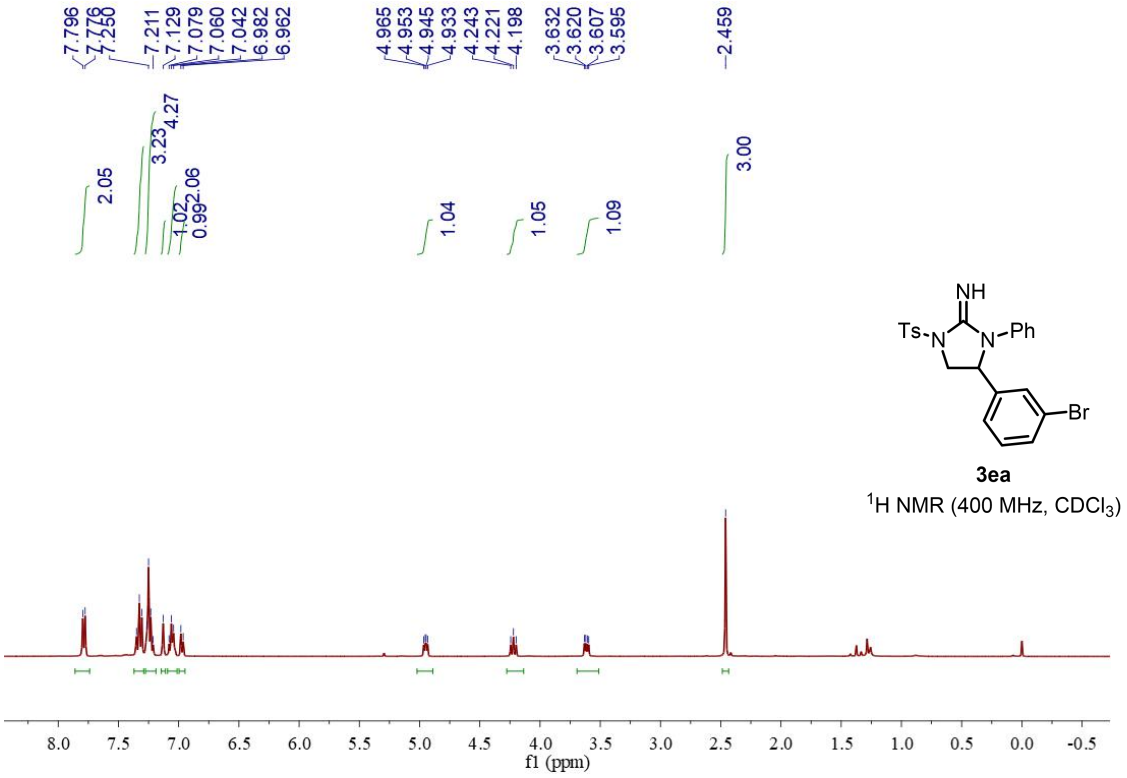
^{1}H NMR (600 MHz, $CDCl_3$)



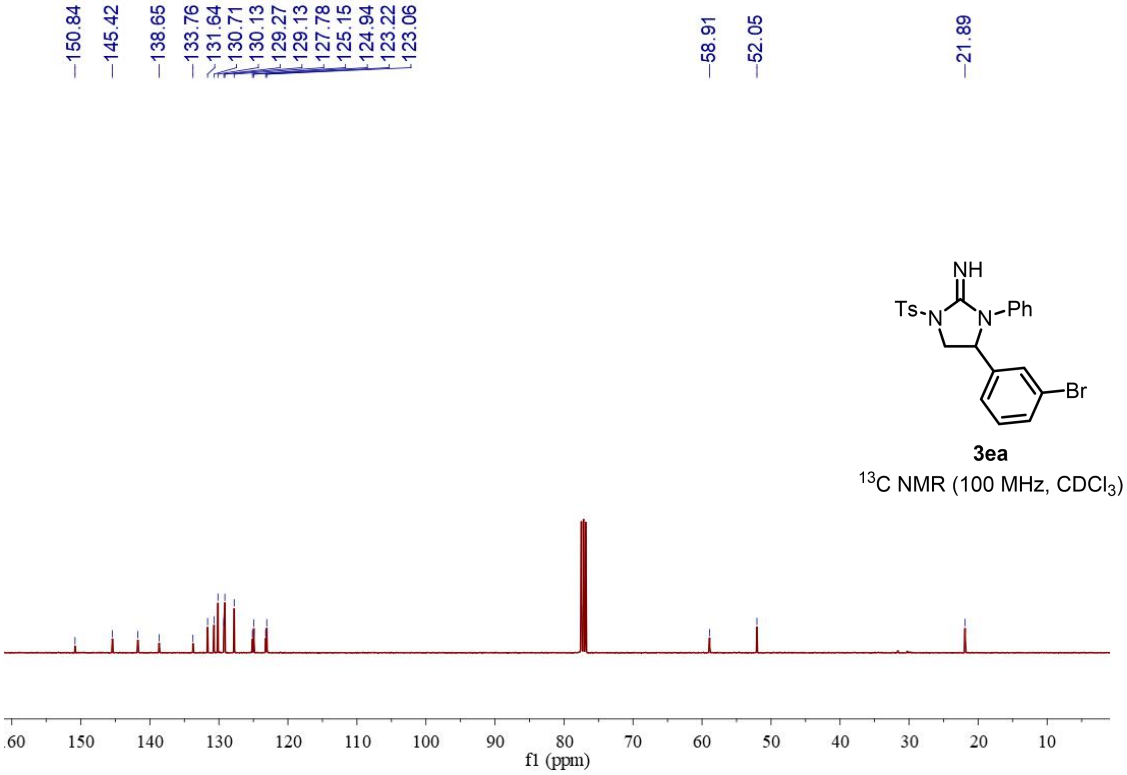
3da

^{13}C NMR (151 MHz, $CDCl_3$)



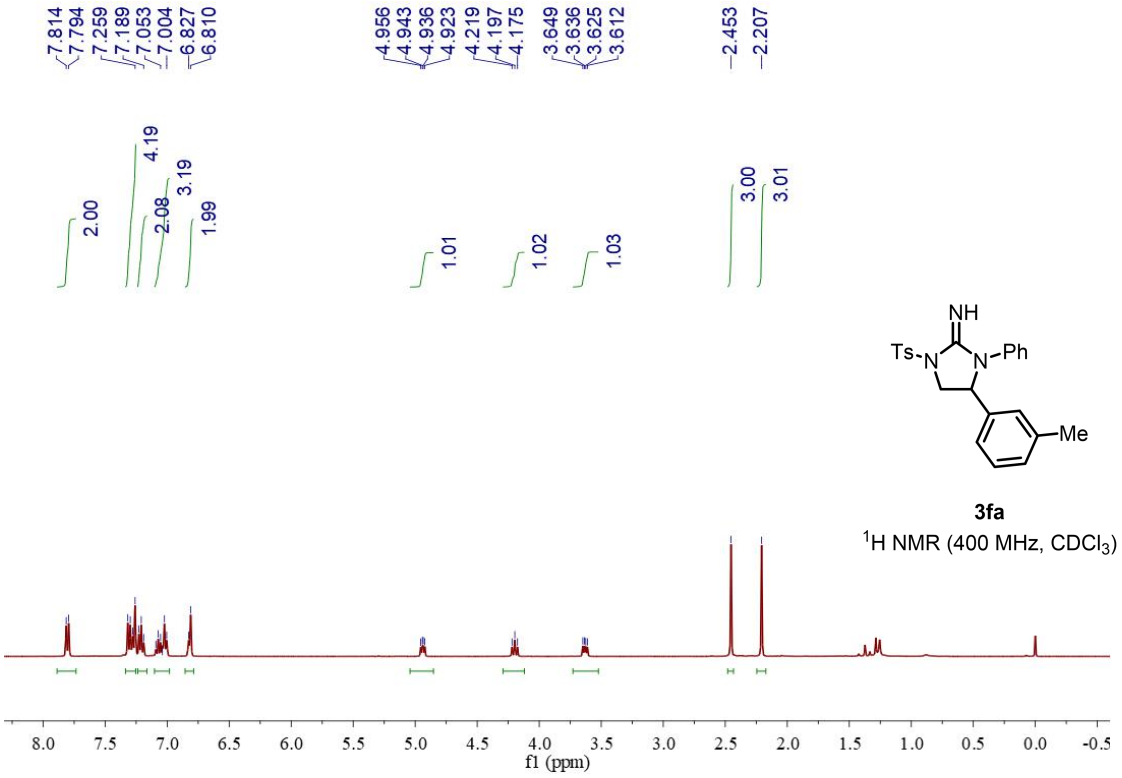
3ea

^{1}H NMR (400 MHz, $CDCl_3$)



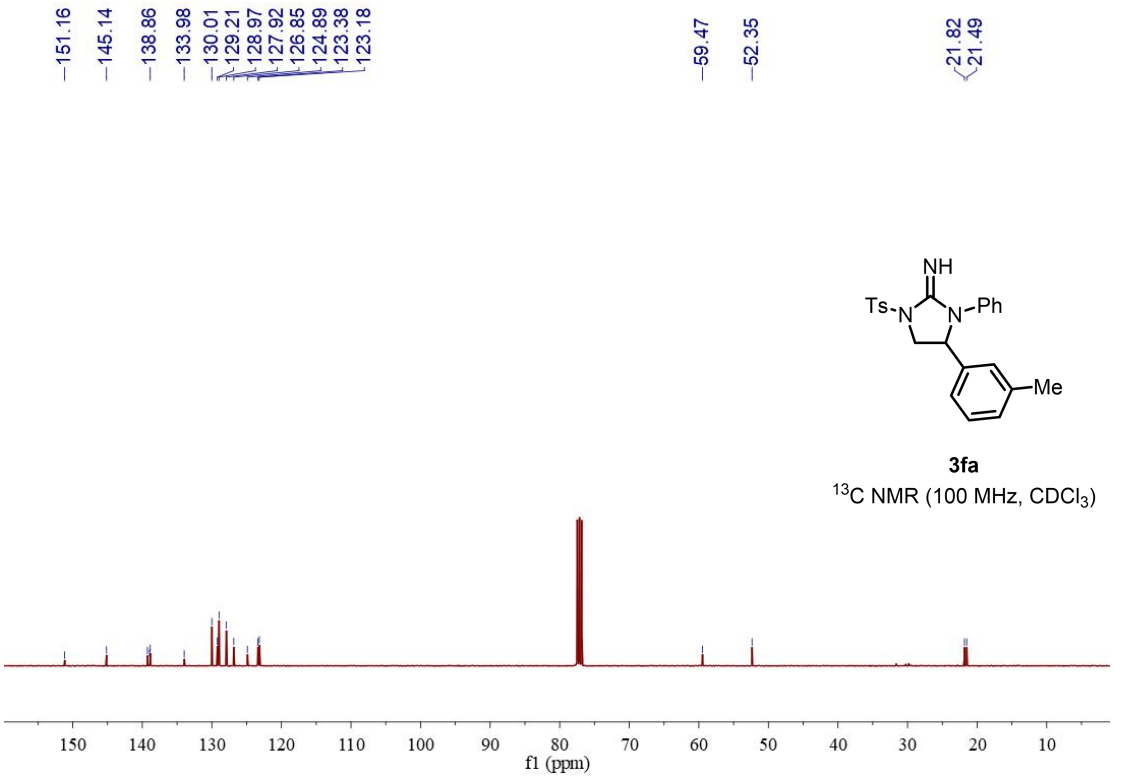
3ea

^{13}C NMR (100 MHz, $CDCl_3$)



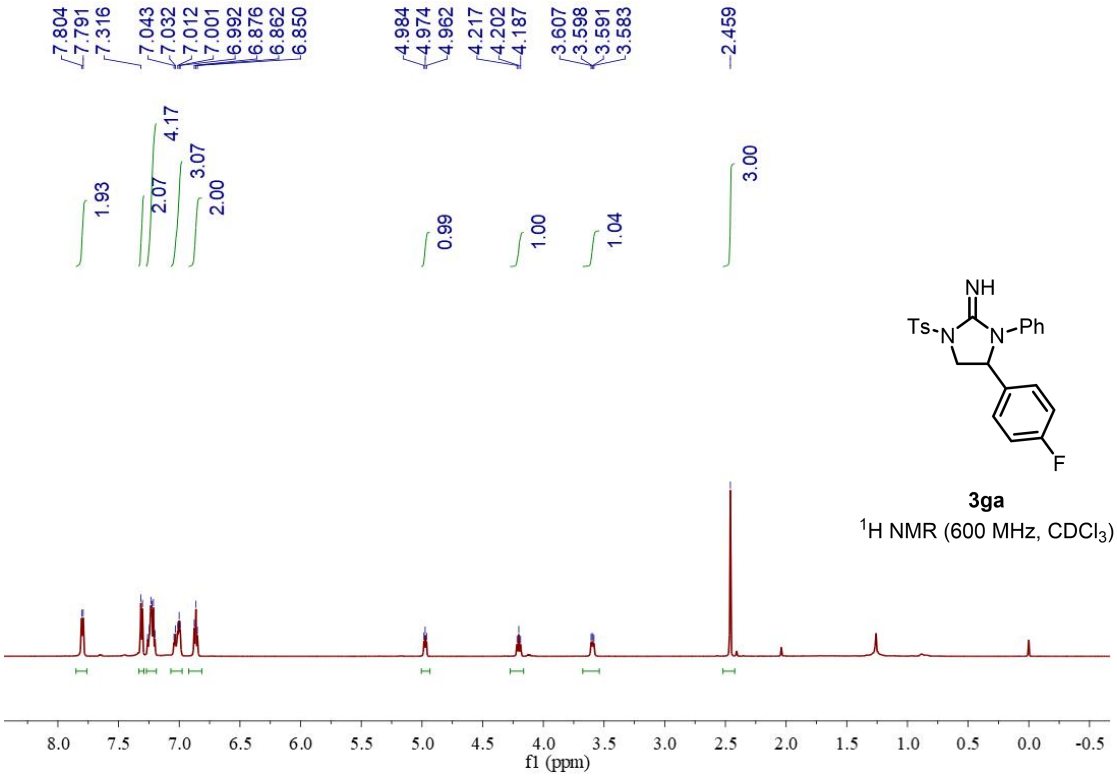
3fa

^{1}H NMR (400 MHz, $CDCl_3$)



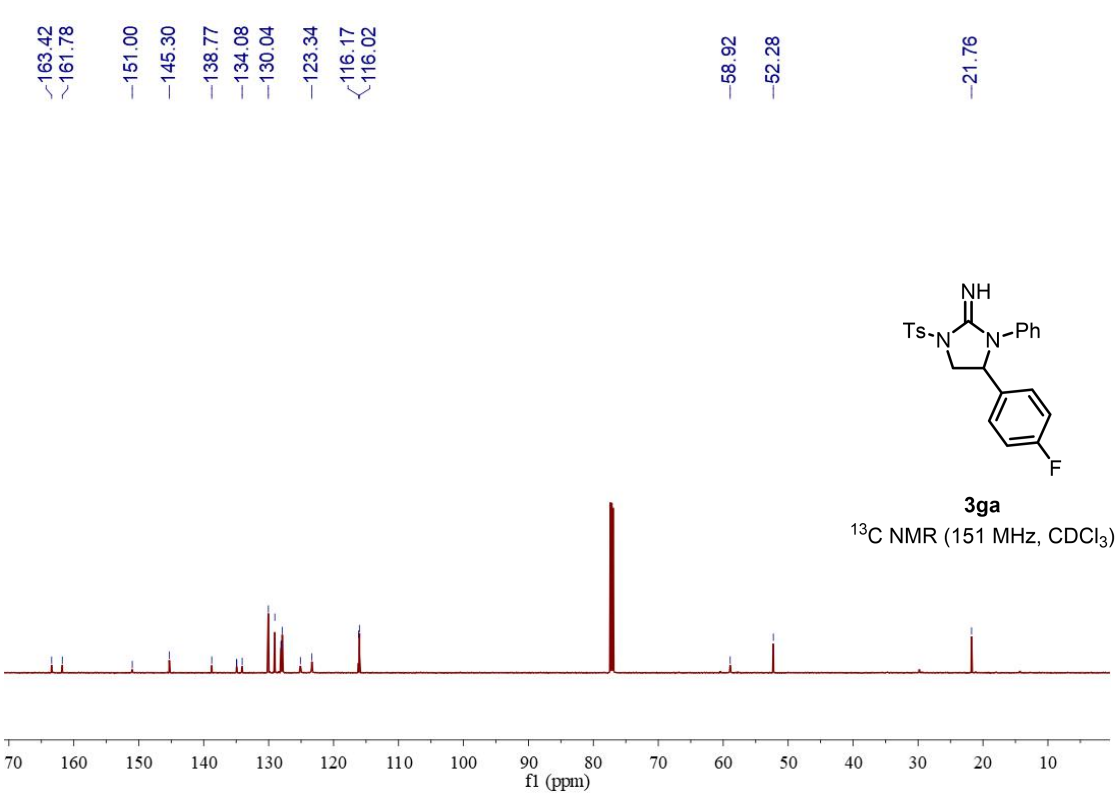
3fa

^{13}C NMR (100 MHz, $CDCl_3$)



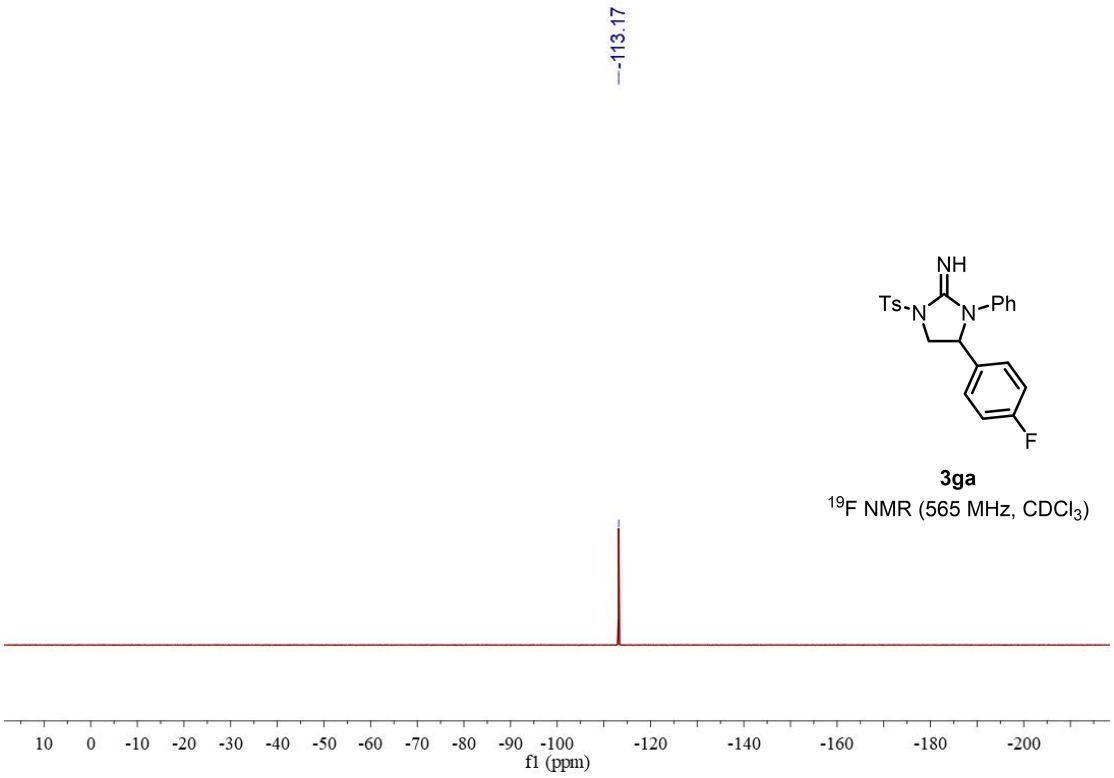
3ga

^{1}H NMR (600 MHz, $CDCl_3$)



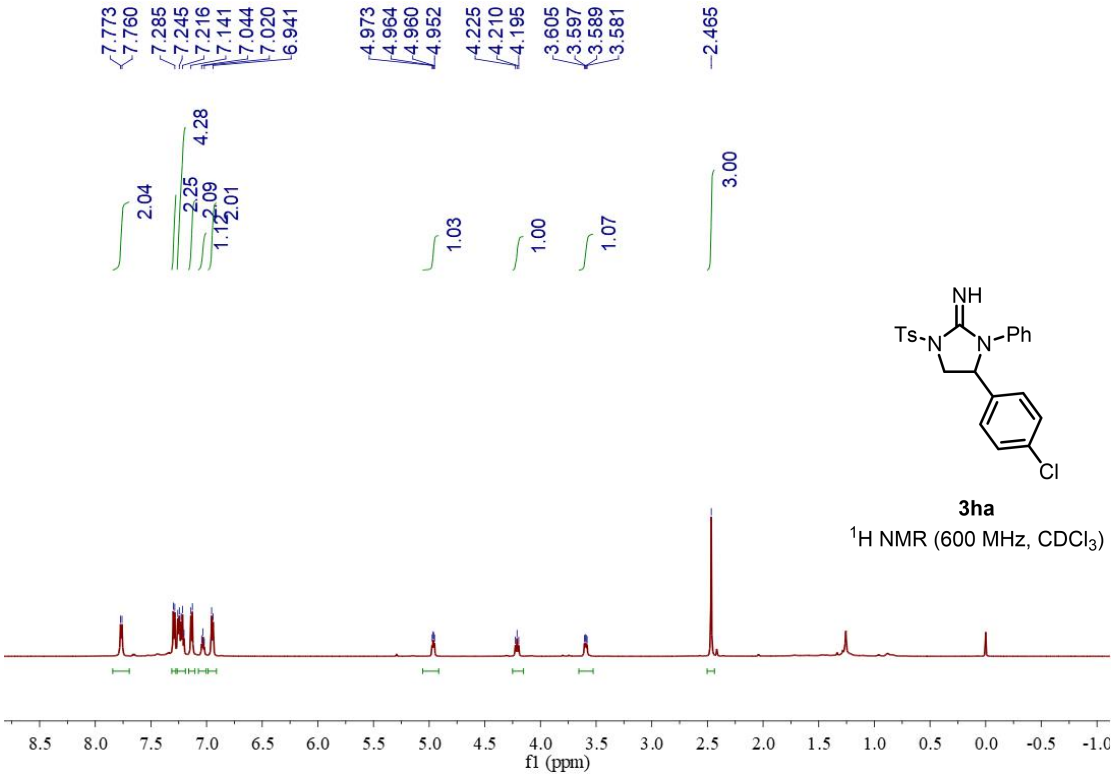
3ga

^{13}C NMR (151 MHz, $CDCl_3$)



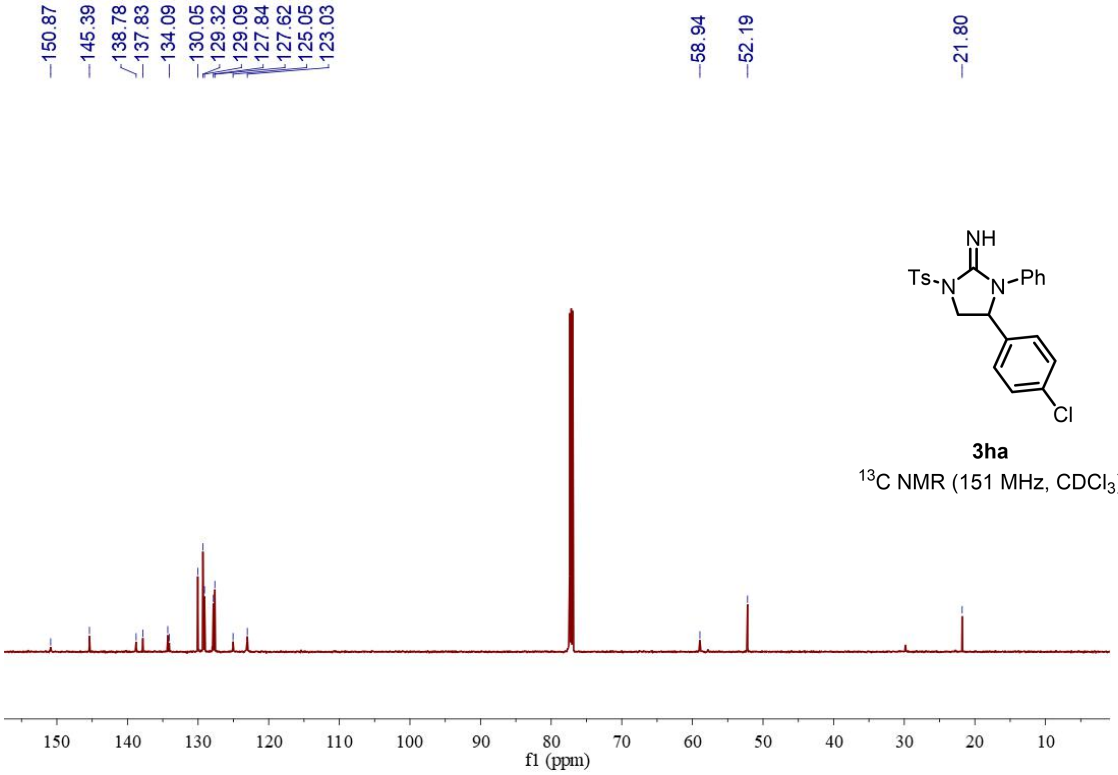
3ga

^{19}F NMR (565 MHz, $CDCl_3$)



3ha

^{1}H NMR (600 MHz, $CDCl_3$)



3ha

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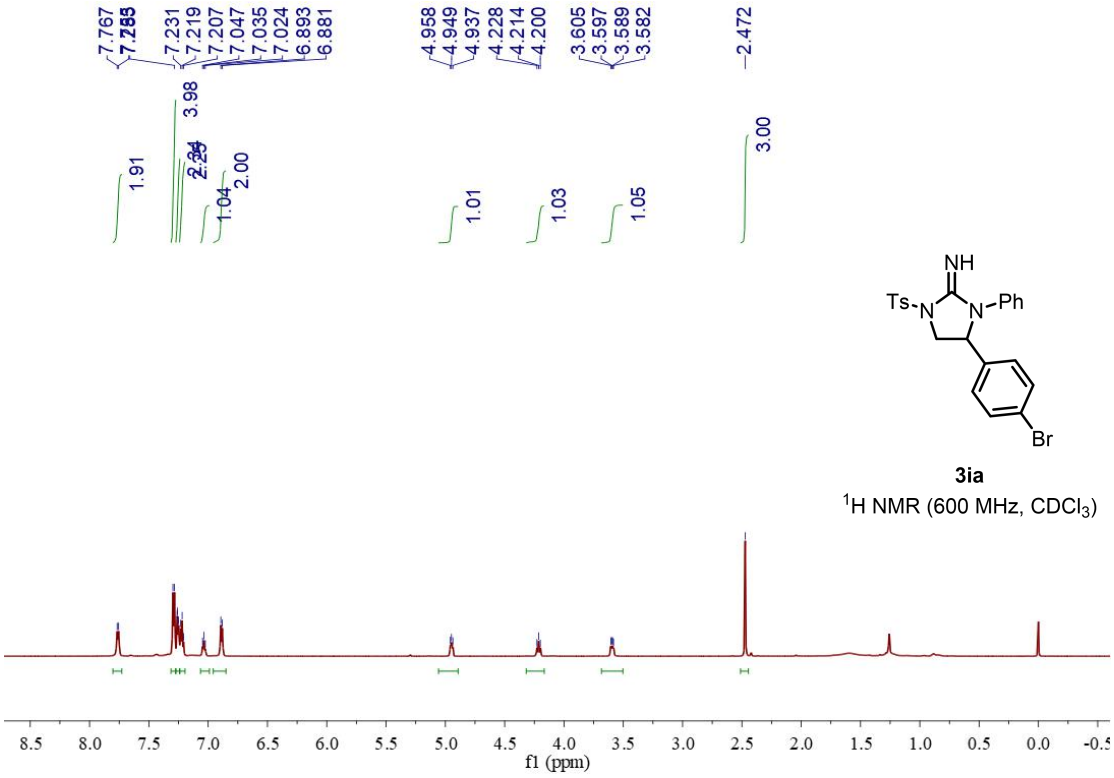
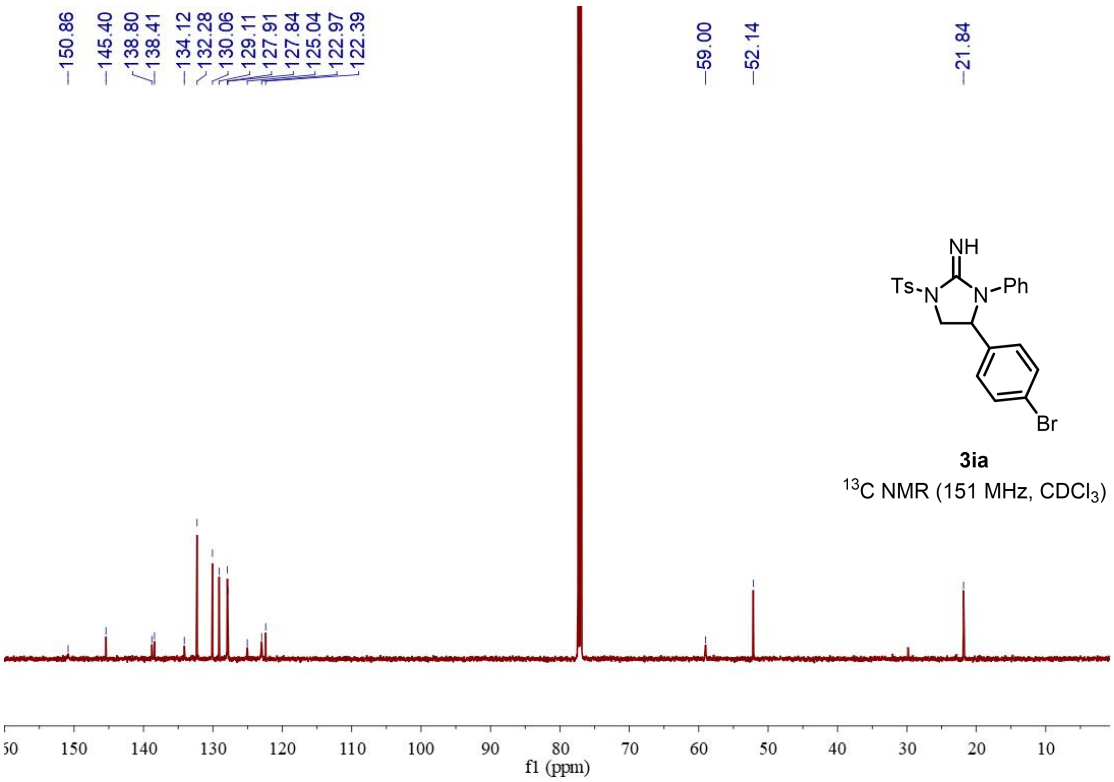


3ia

^{1}H NMR (600 MHz, $CDCl_3$)



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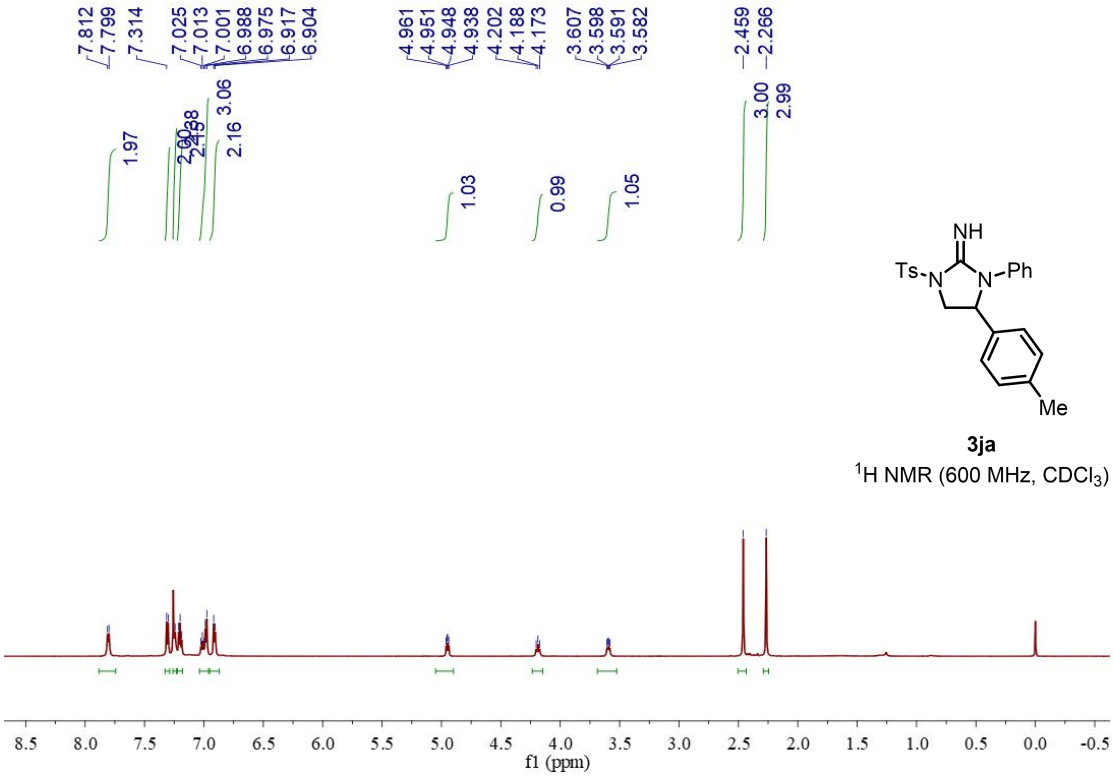
^{13}C NMR (151 MHz, $CDCl_3$)



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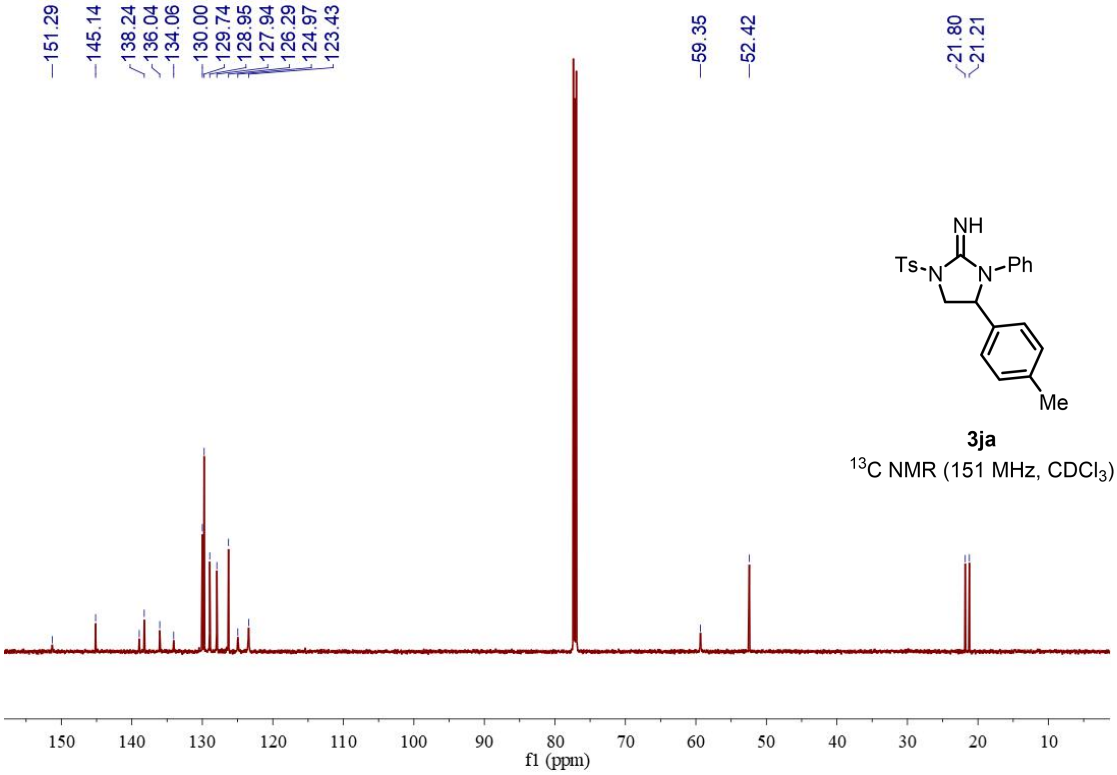

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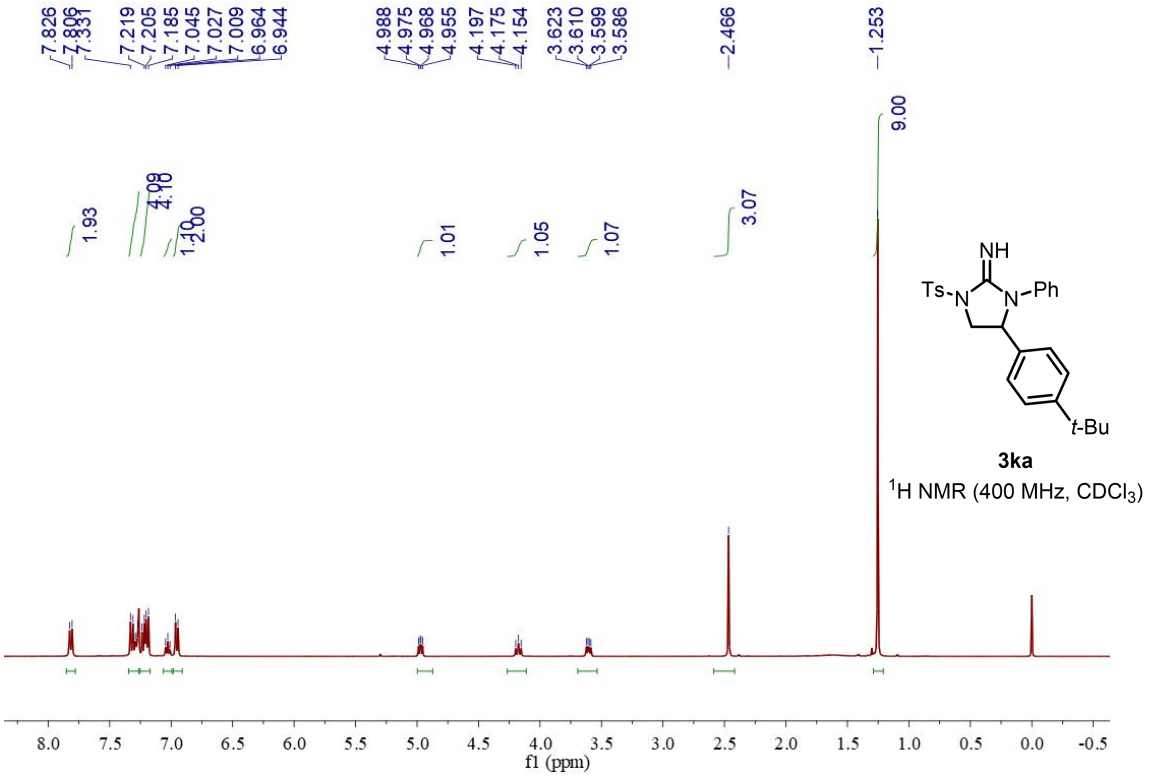

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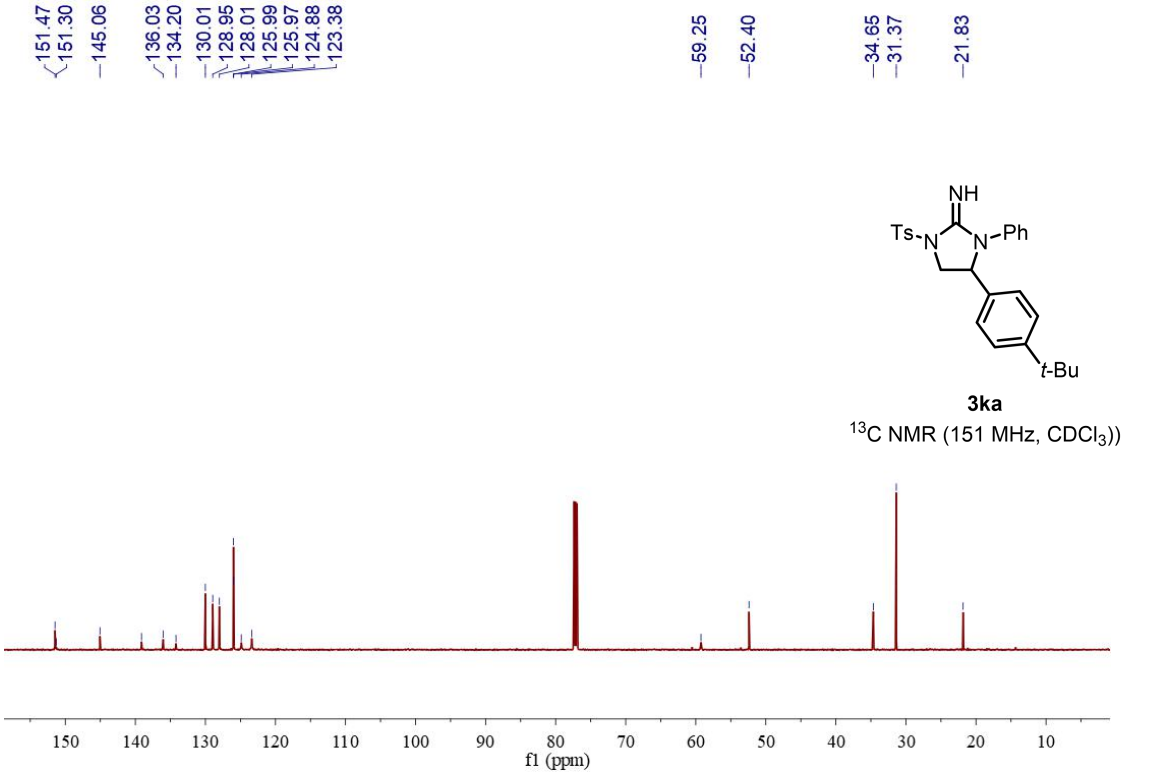

3ka

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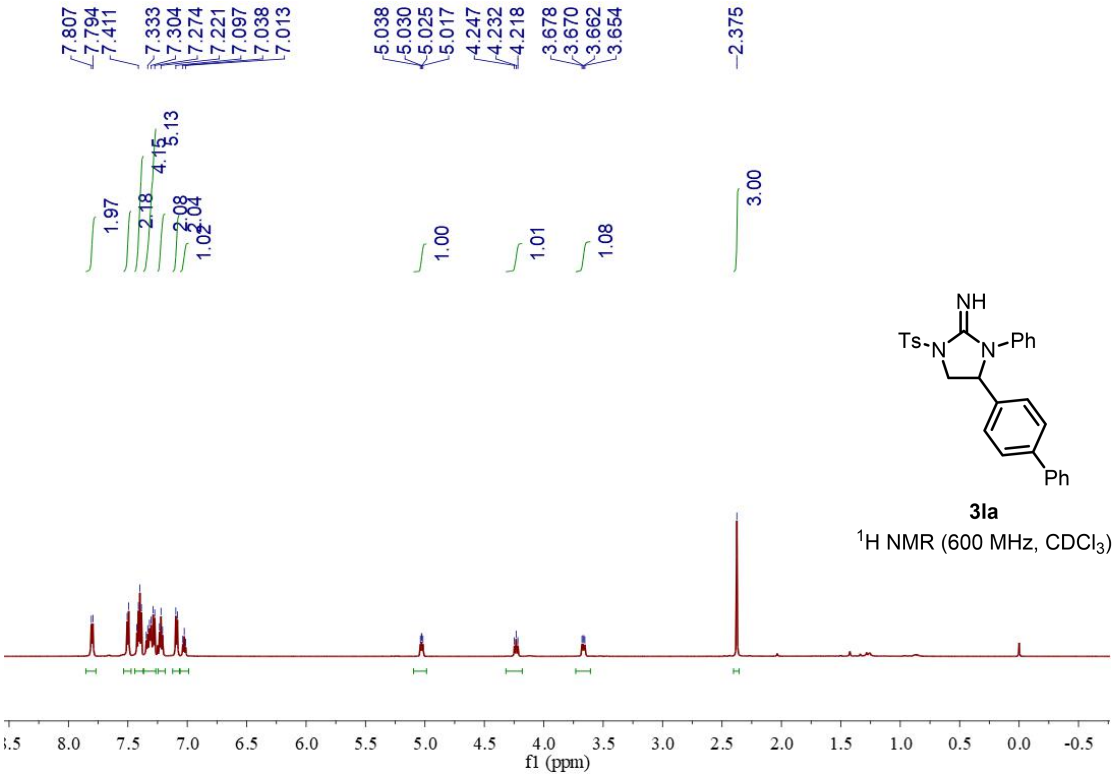
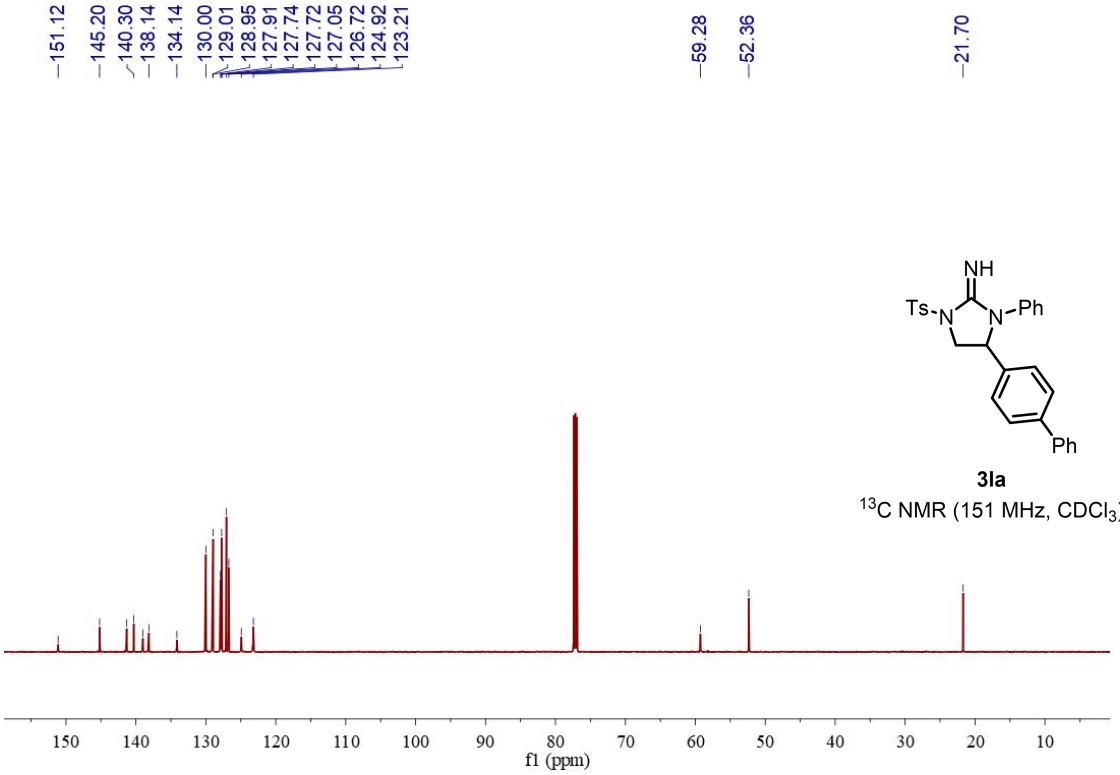


3la

^{1}H NMR (600 MHz, $CDCl_3$)



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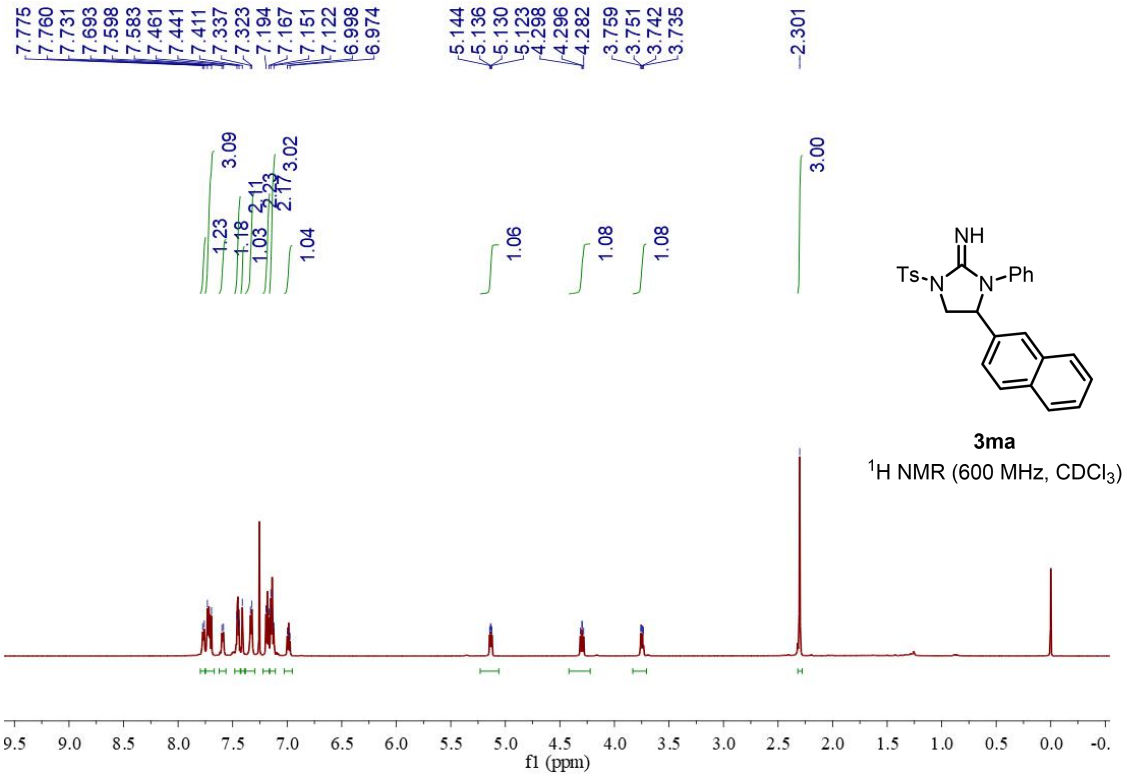

3ma

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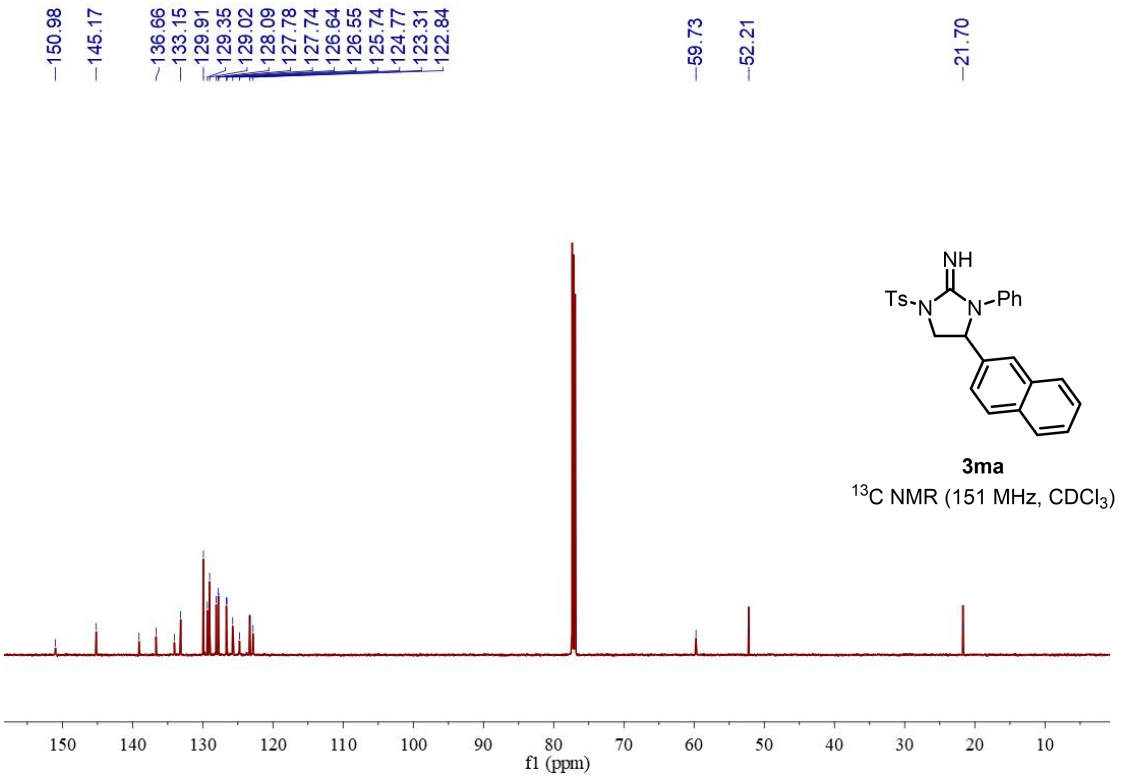

3ma

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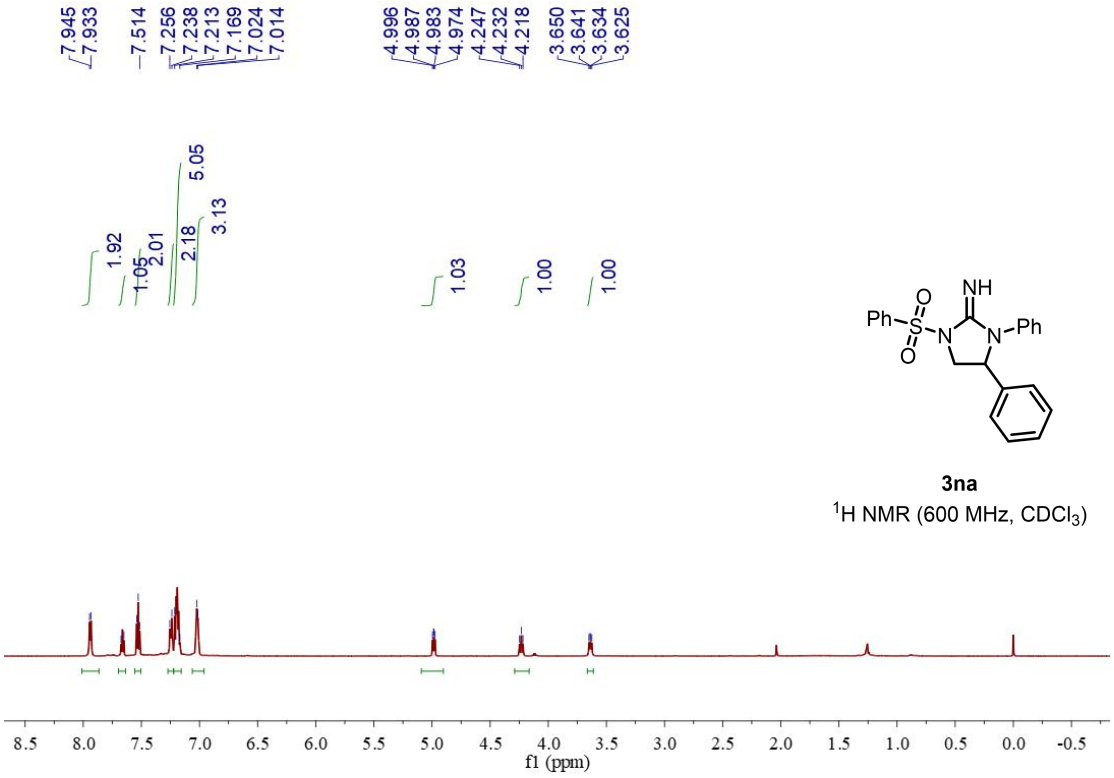

3na

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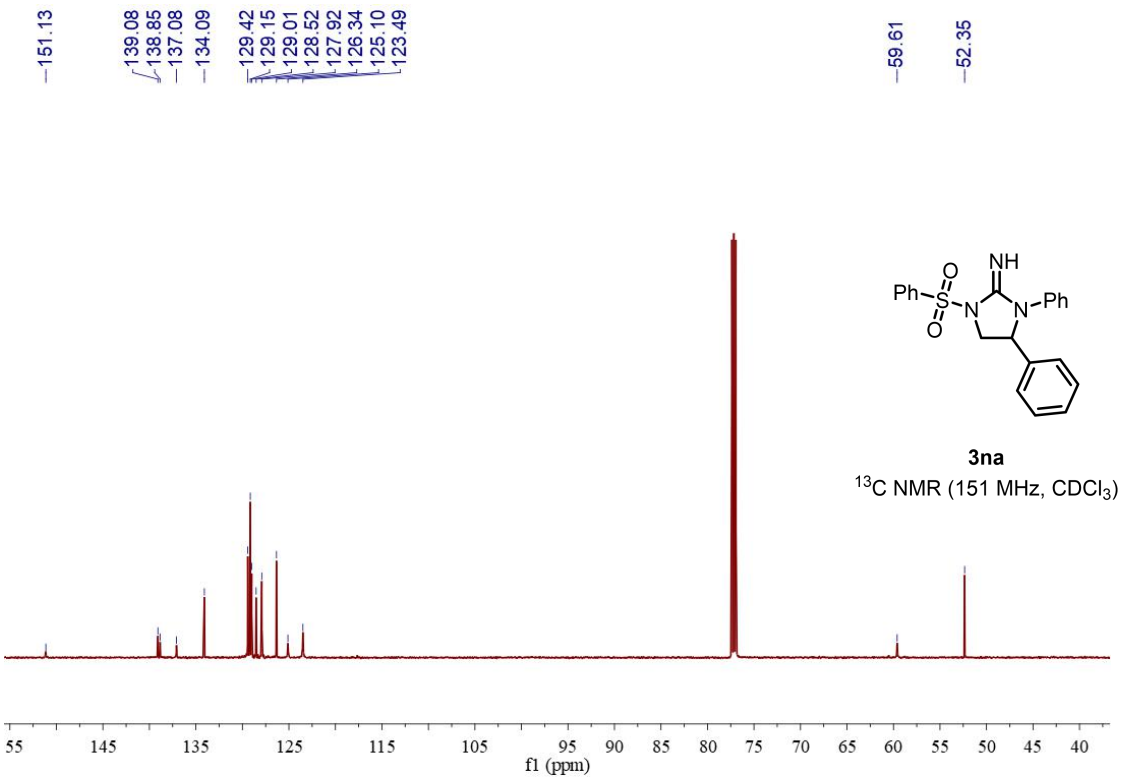
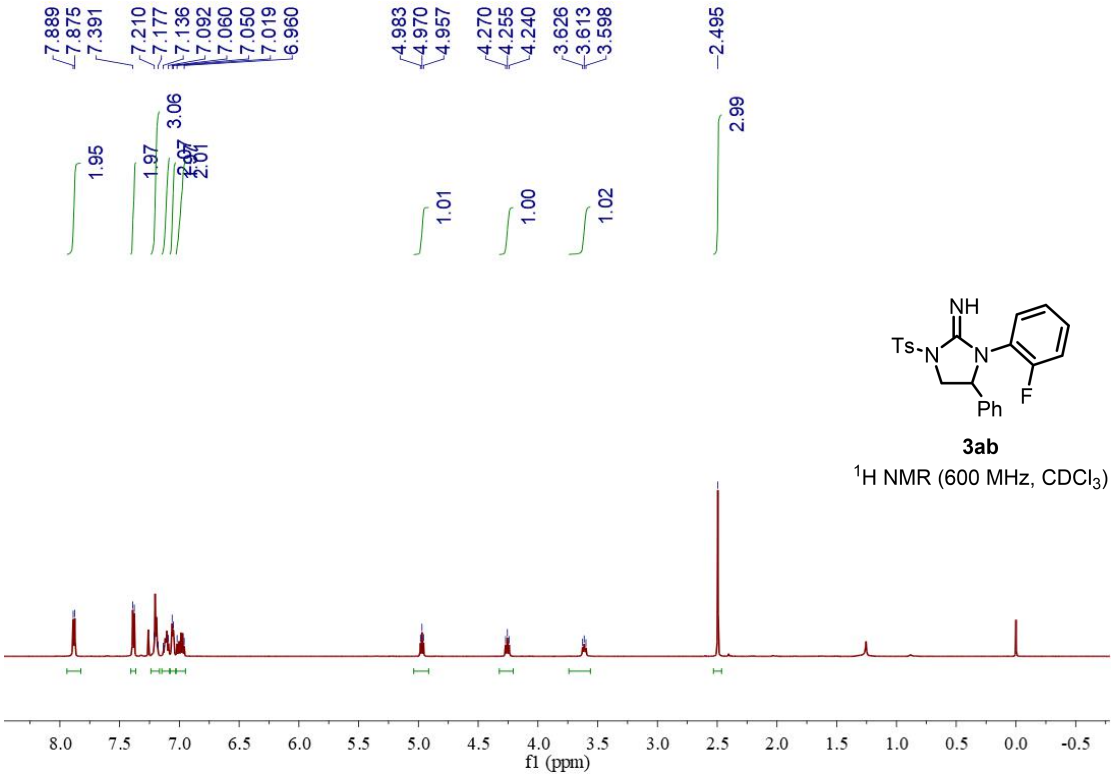


3na

^{13}C NMR (151 MHz, $CDCl_3$)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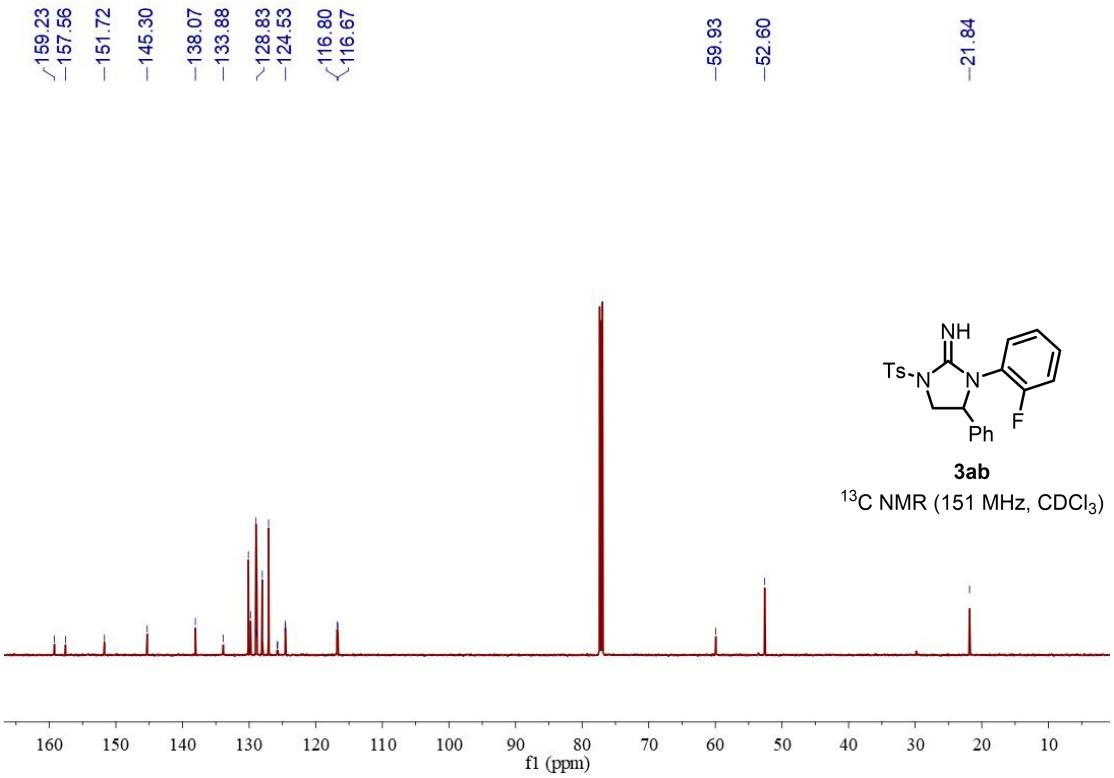
7.177
7.136
7.092
7.060
7.050
7.019
6.960
4.983
4.970
4.957
4.270
4.255
4.240
3.626
3.613
3.598
2.495
1.95
1.97
3.06
2.07
2.01
1.01
1.00
1.02
2.99
NH
Ts
N
N
Ph
F
3ab
1H NMR (600 MHz, CDCl3)
f1 (ppm)


159.23
157.56
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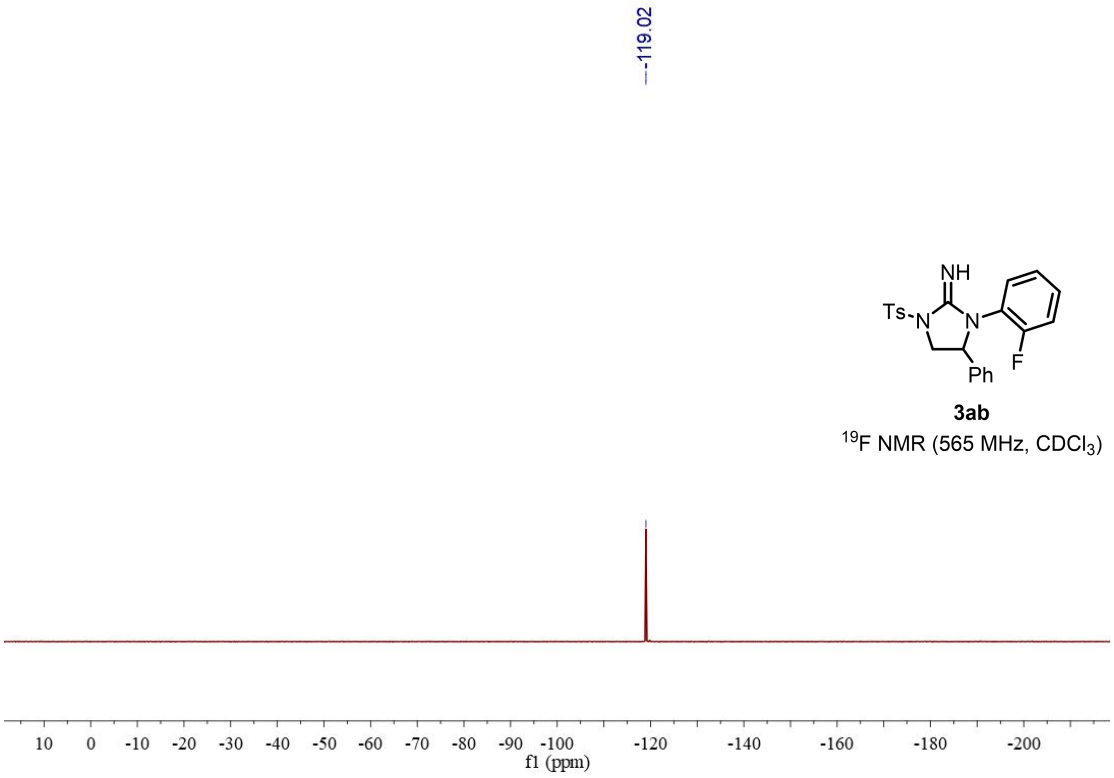
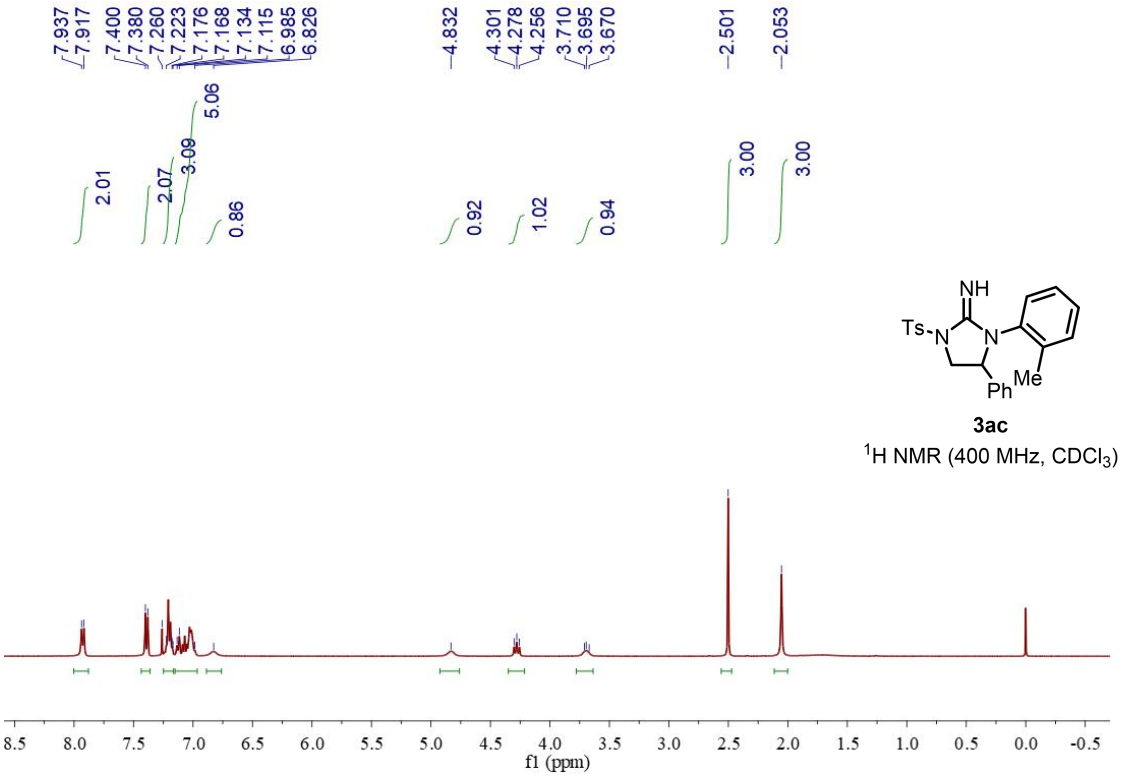
145.30
138.07
133.88
128.83
124.53
116.80
116.67
59.93
52.60
21.84
NH
Ts
N
N
Ph
F
3ab
13C NMR (151 MHz, CDCl3)
f1 (ppm)



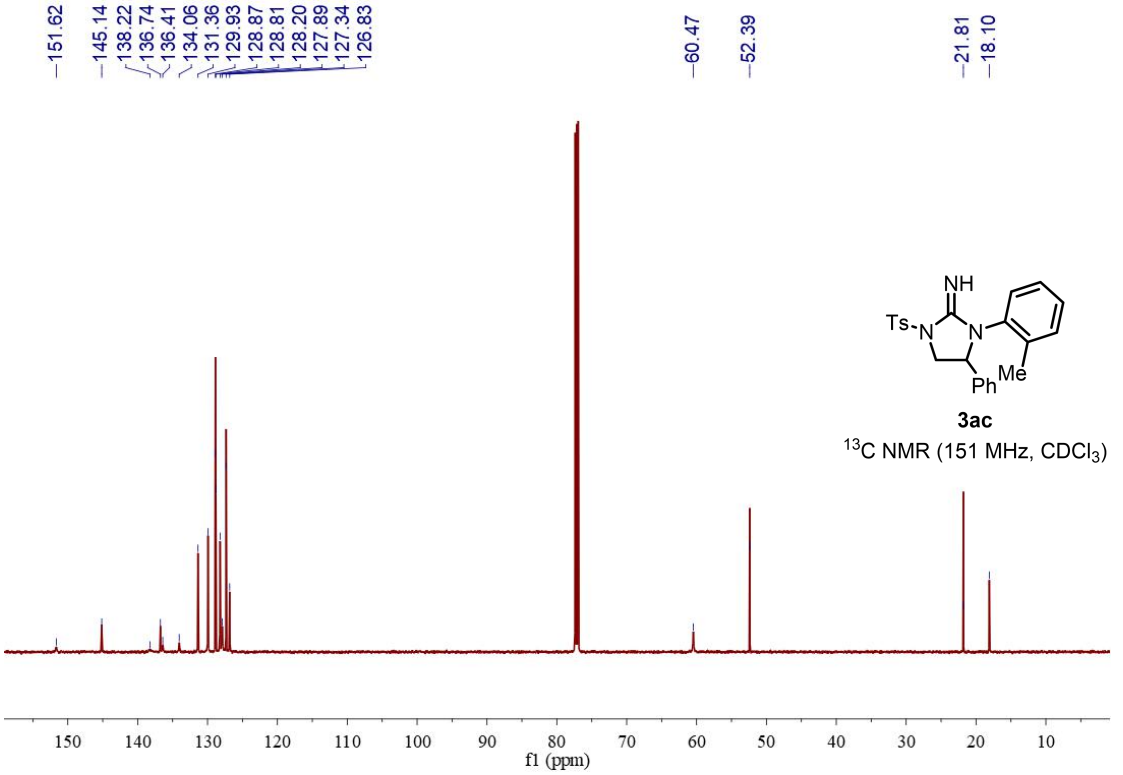
3ab

^{19}F NMR (565 MHz, $CDCl_3$)



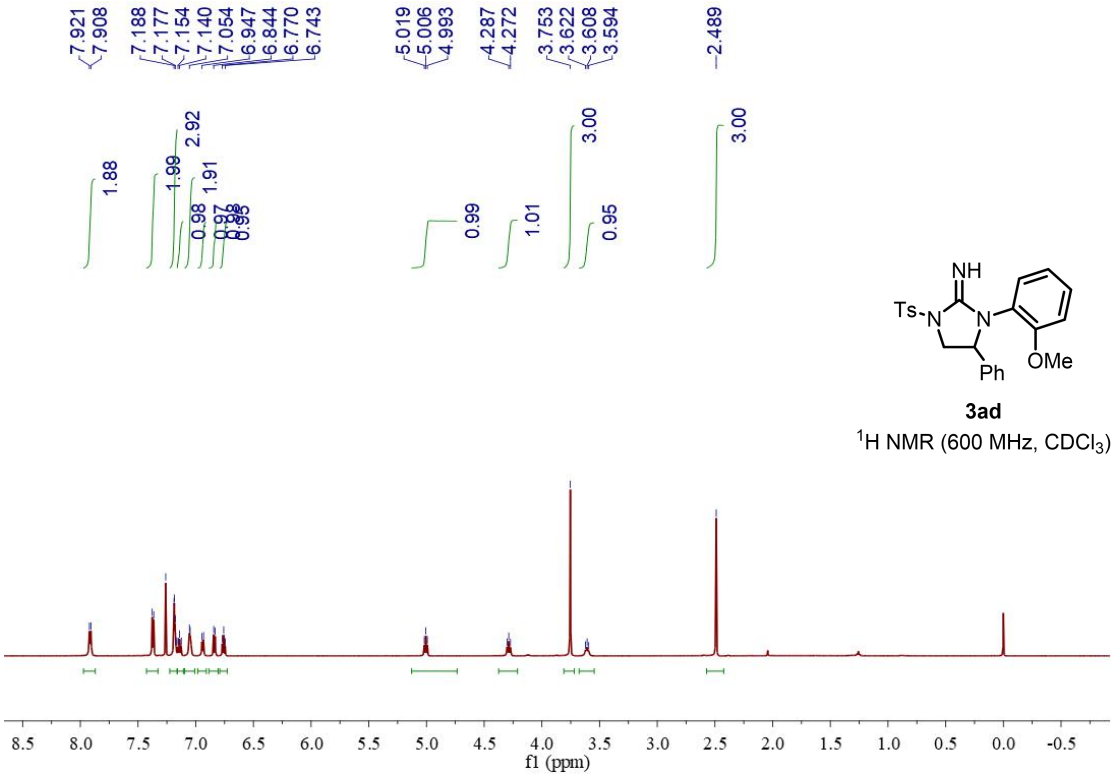
3ac

^{1}H NMR (400 MHz, $CDCl_3$)



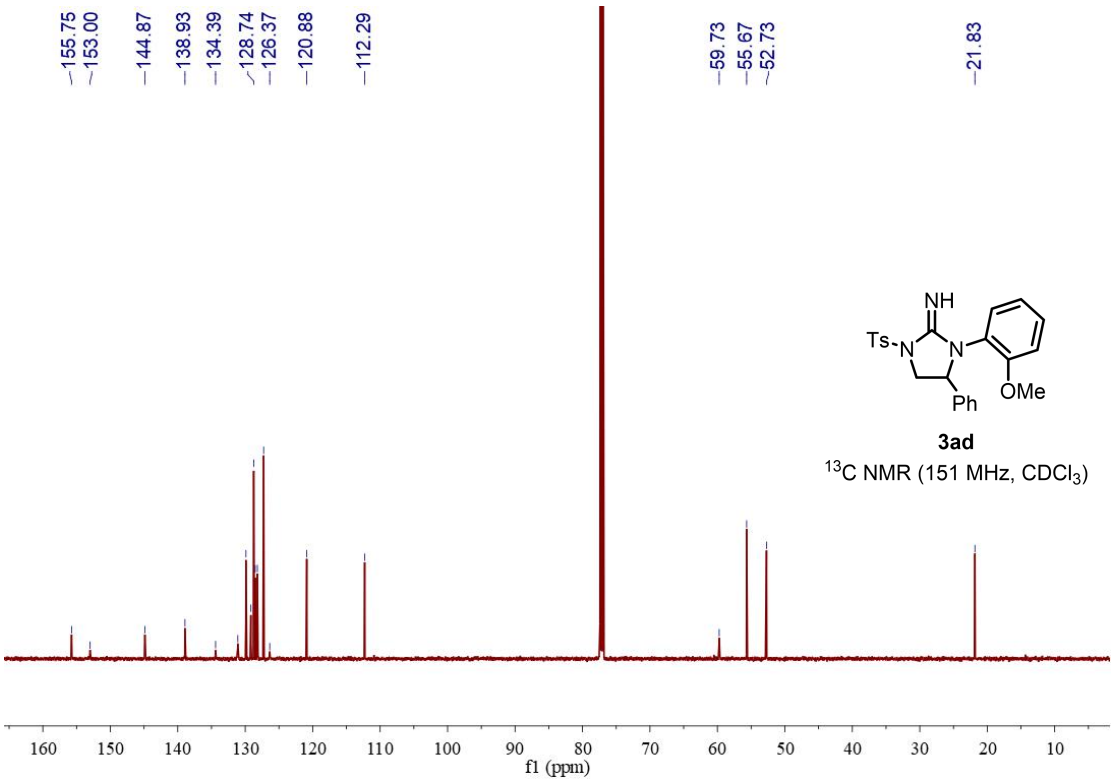
3ac

^{13}C NMR (151 MHz, $CDCl_3$)



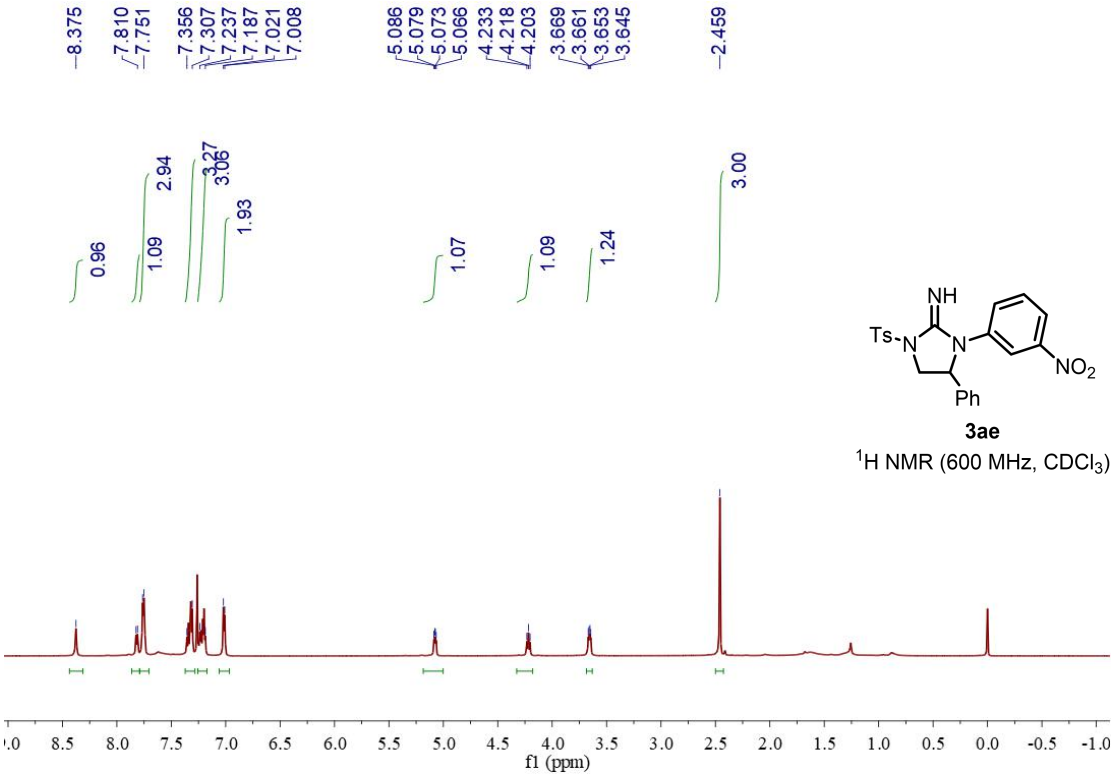
3ad

^{1}H NMR (600 MHz, $CDCl_3$)



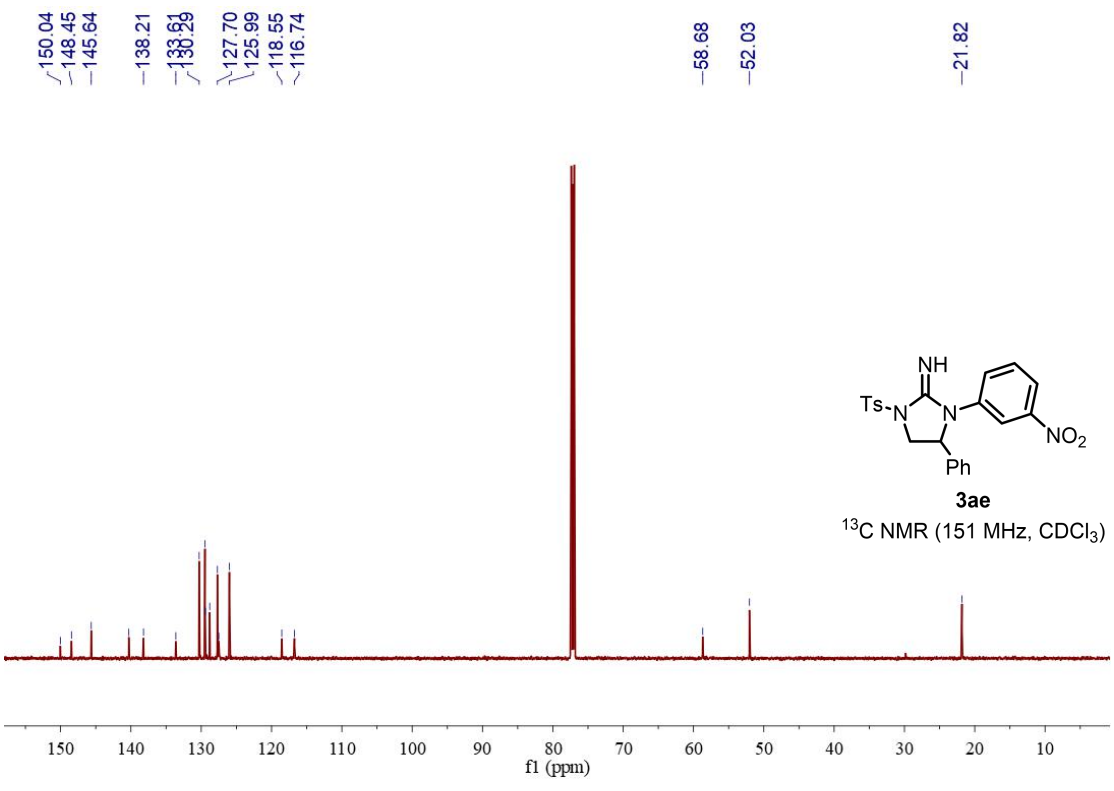
3ad

^{13}C NMR (151 MHz, $CDCl_3$)



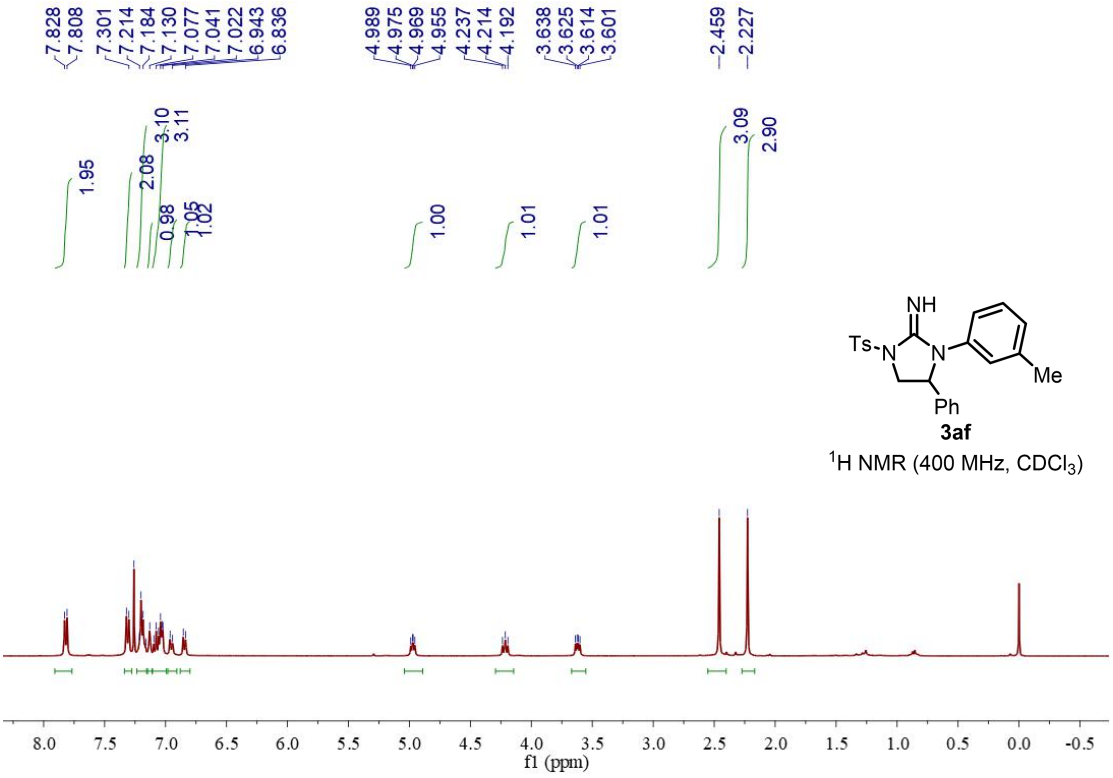
3ae

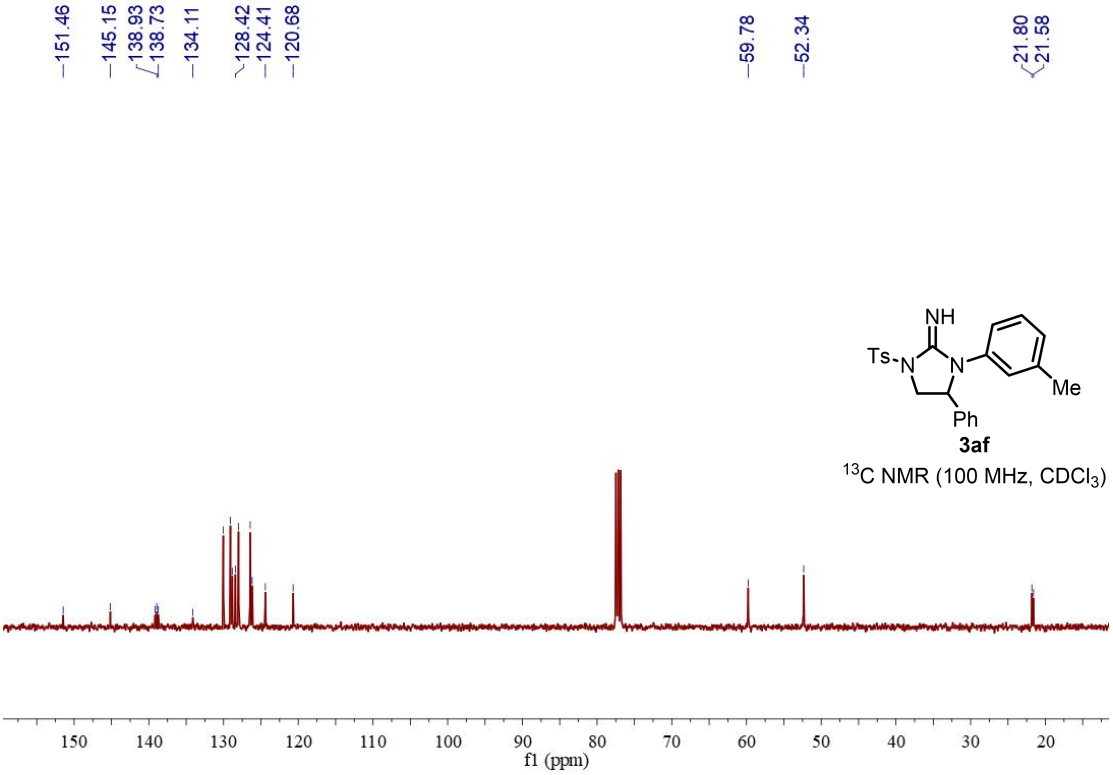
^{1}H NMR (600 MHz, $CDCl_3$)

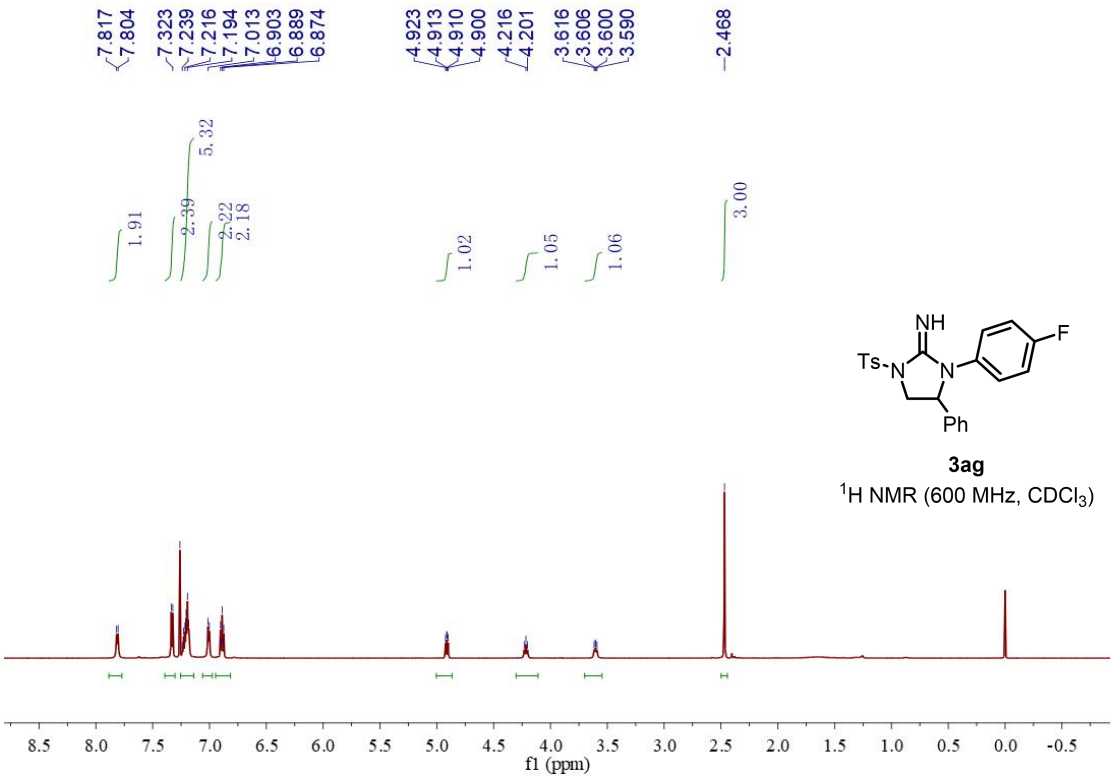


3ae

^{13}C NMR (151 MHz, $CDCl_3$)

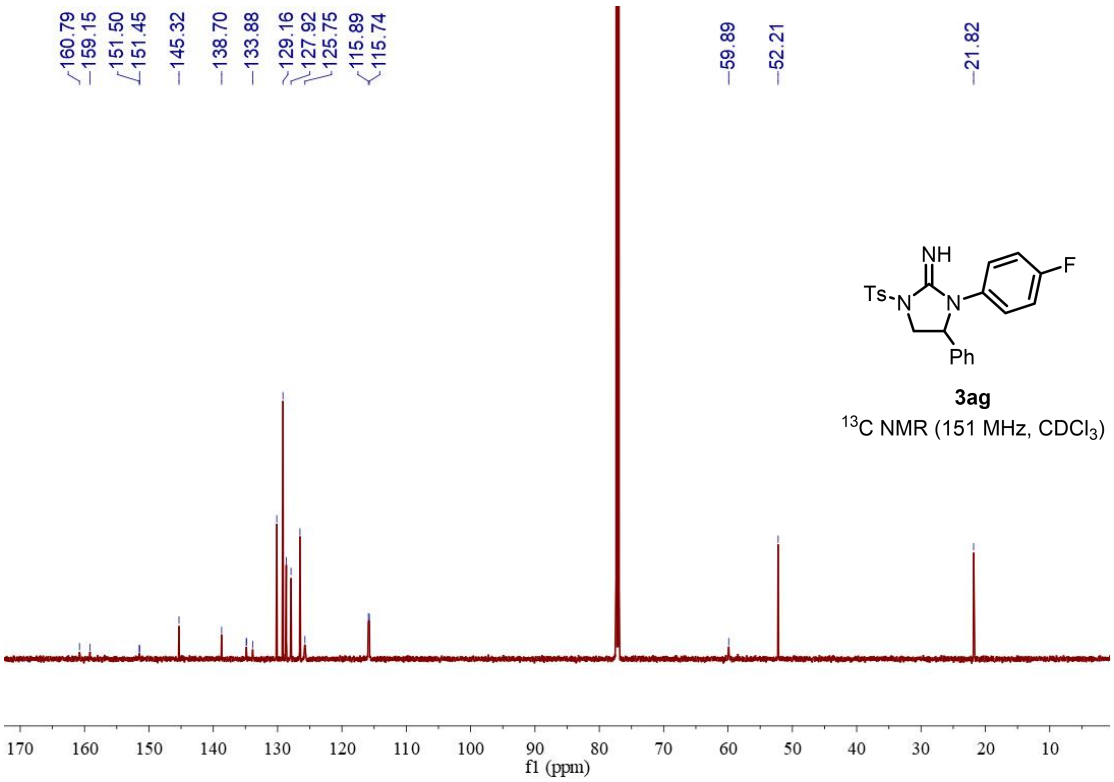

7.828
7.808
7.301
7.214
7.184
7.130
7.077
7.041
7.022
6.943
6.836
4.989
4.975
4.969
4.955
4.237
4.214
4.192
3.638
3.625
3.614
3.601
2.459
2.227
1.95
2.08
3.10
3.11
0.98
1.05
1.02
1.00
1.01
1.01
3.09
2.90
NH
Ts
N
N
Me
Ph
3af
1H NMR (400 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


151.46
145.15
138.93
138.73
134.11
128.42
124.41
120.68
59.78
52.34
21.80
21.58
NH
Ts
N
N
Me
Ph
3af
13C NMR (100 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)



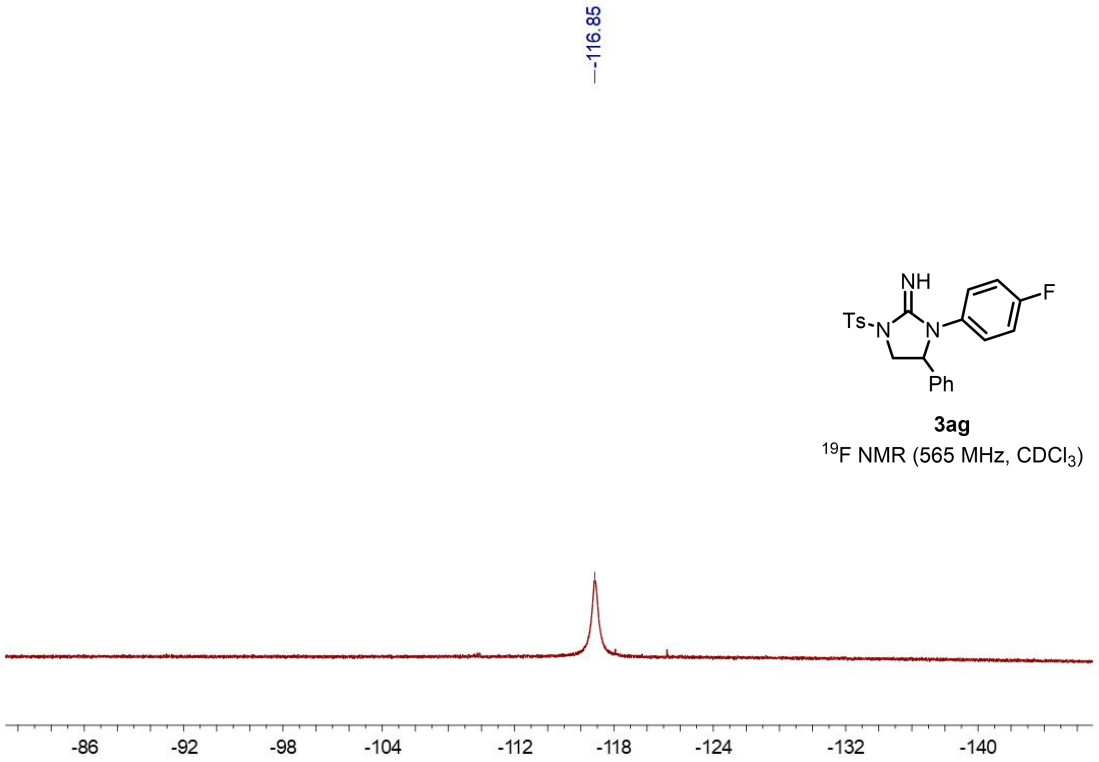
3ag

^{1}H NMR (600 MHz, $CDCl_3$)



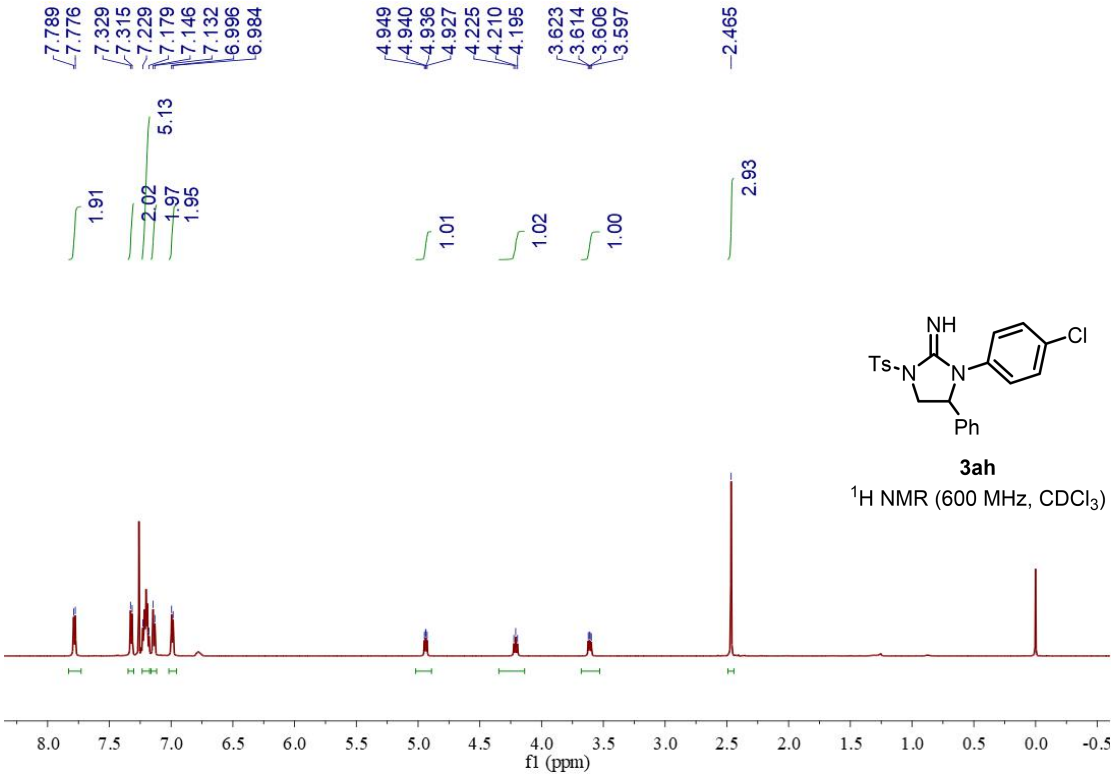
3ag

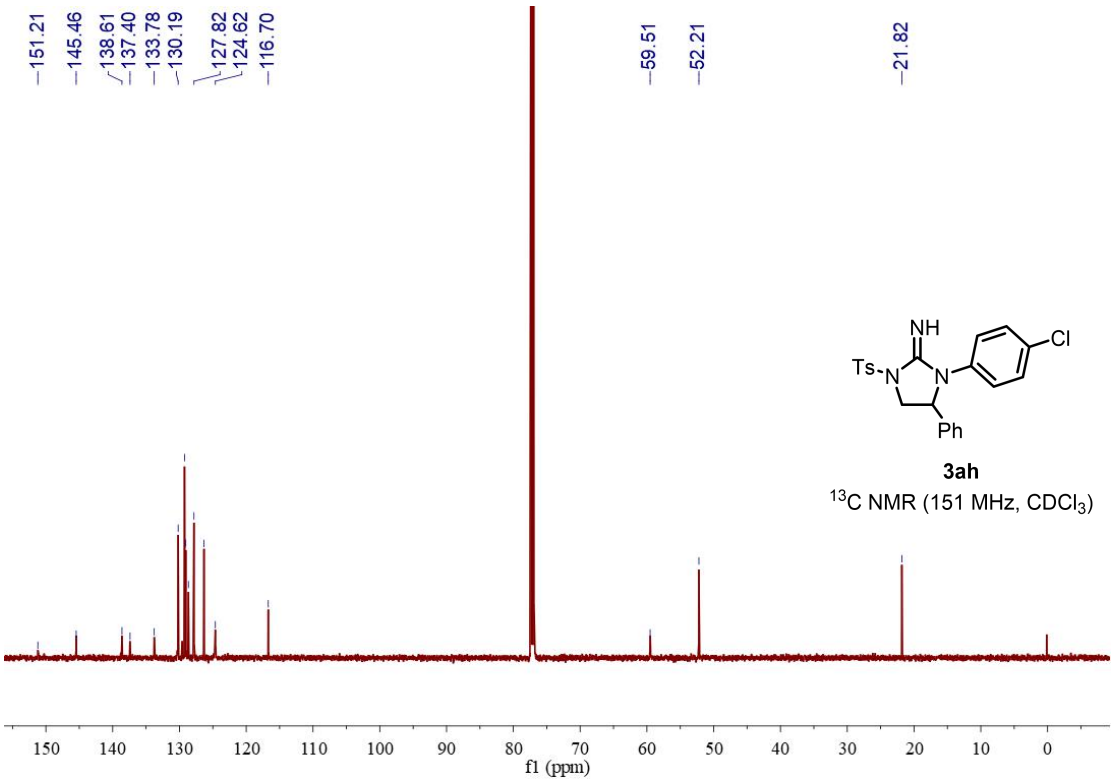
^{13}C NMR (151 MHz, $CDCl_3$)

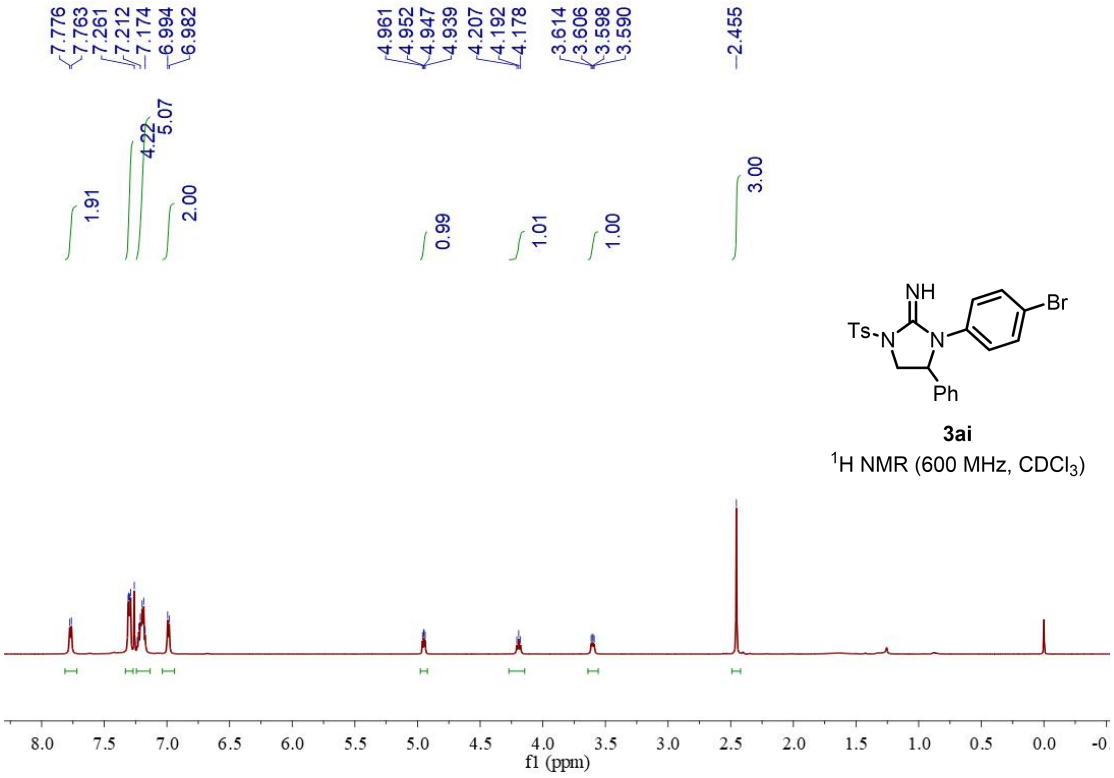


3ag

^{19}F NMR (565 MHz, $CDCl_3$)

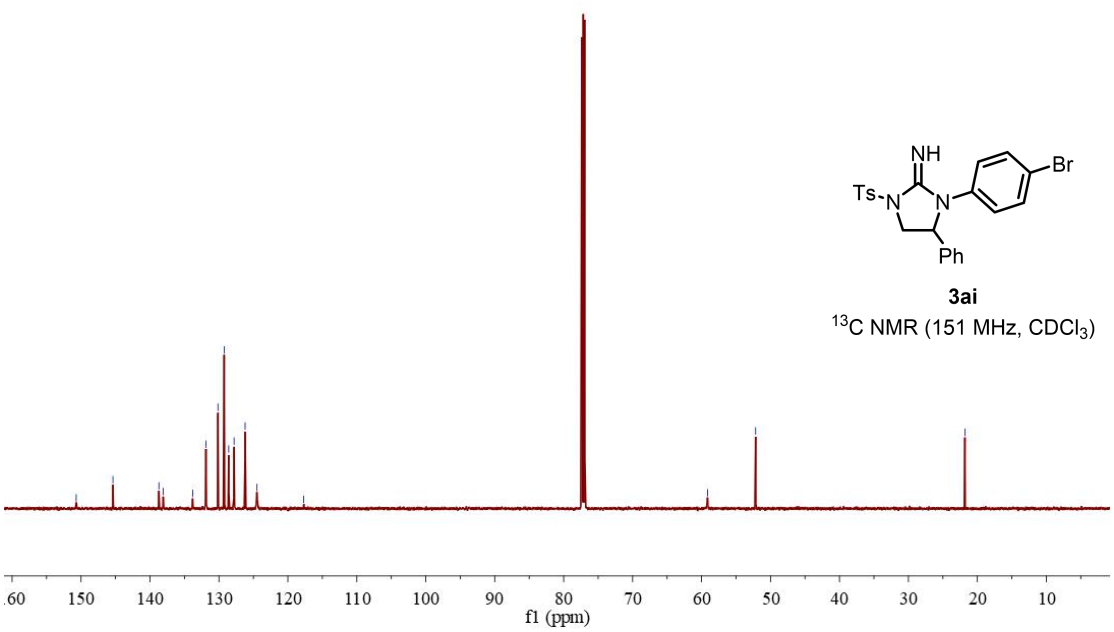

7.789
7.776
7.329
7.315
7.229
7.179
7.146
7.132
6.996
6.984
4.949
4.940
4.936
4.927
4.225
4.210
4.195
3.623
3.614
3.606
3.597
2.465
5.13
2.93
1.91
2.02
1.97
1.95
1.01
1.02
1.00
NH
Cl
Ts
N
N
Ph
3ah
1H NMR (600 MHz, CDCl3)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


151.21
145.46
138.61
137.40
133.78
130.19
127.82
124.62
116.70
59.51
52.21
21.82
NH
Cl
Ts
N
N
Ph
3ah
13C NMR (151 MHz, CDCl3)
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



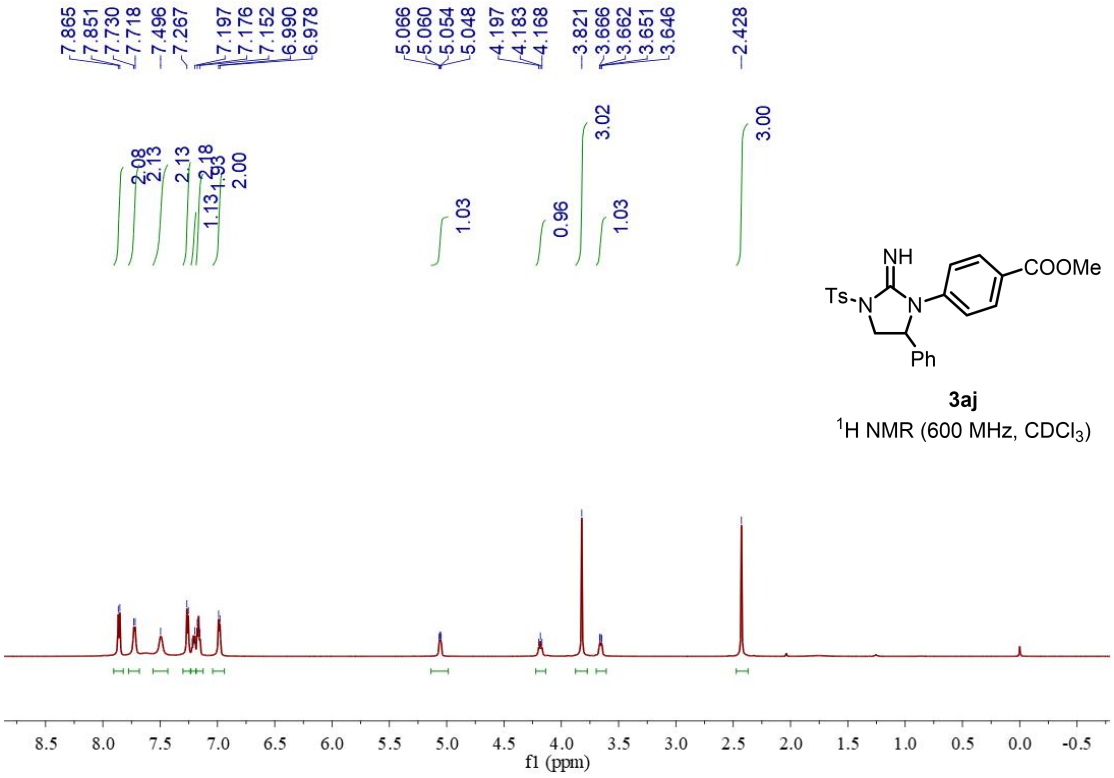
3ai

^{1}H NMR (600 MHz, $CDCl_3$)



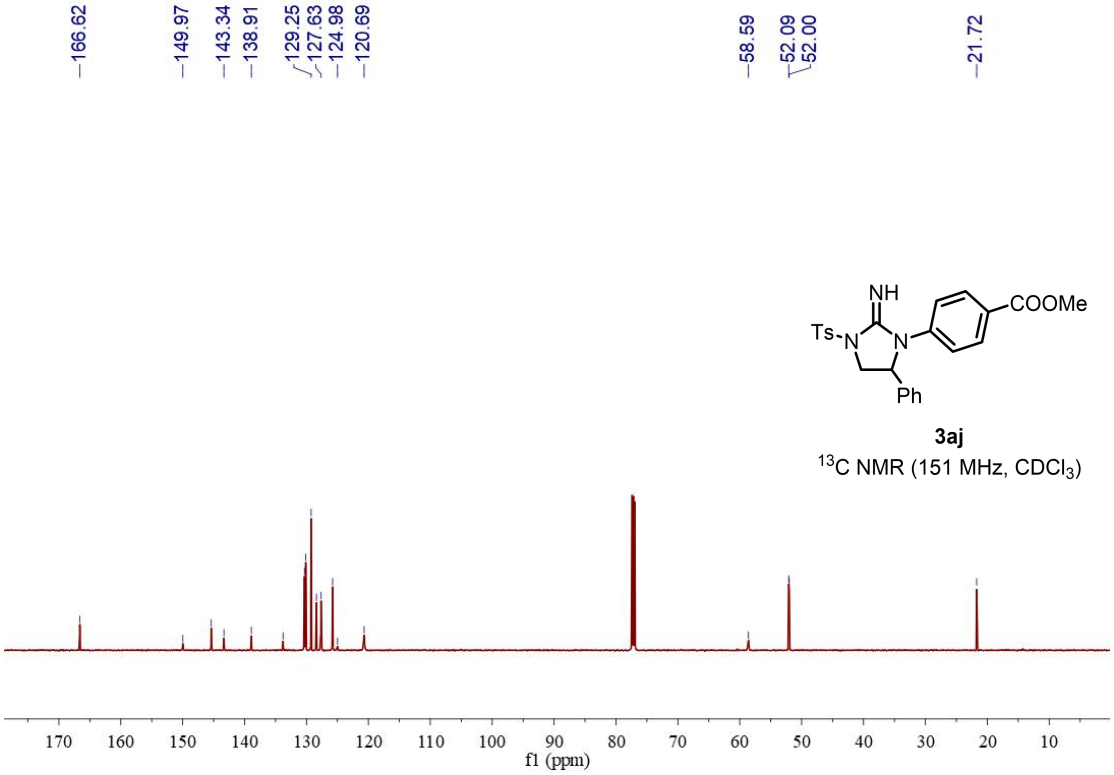
3ai

^{13}C NMR (151 MHz, $CDCl_3$)



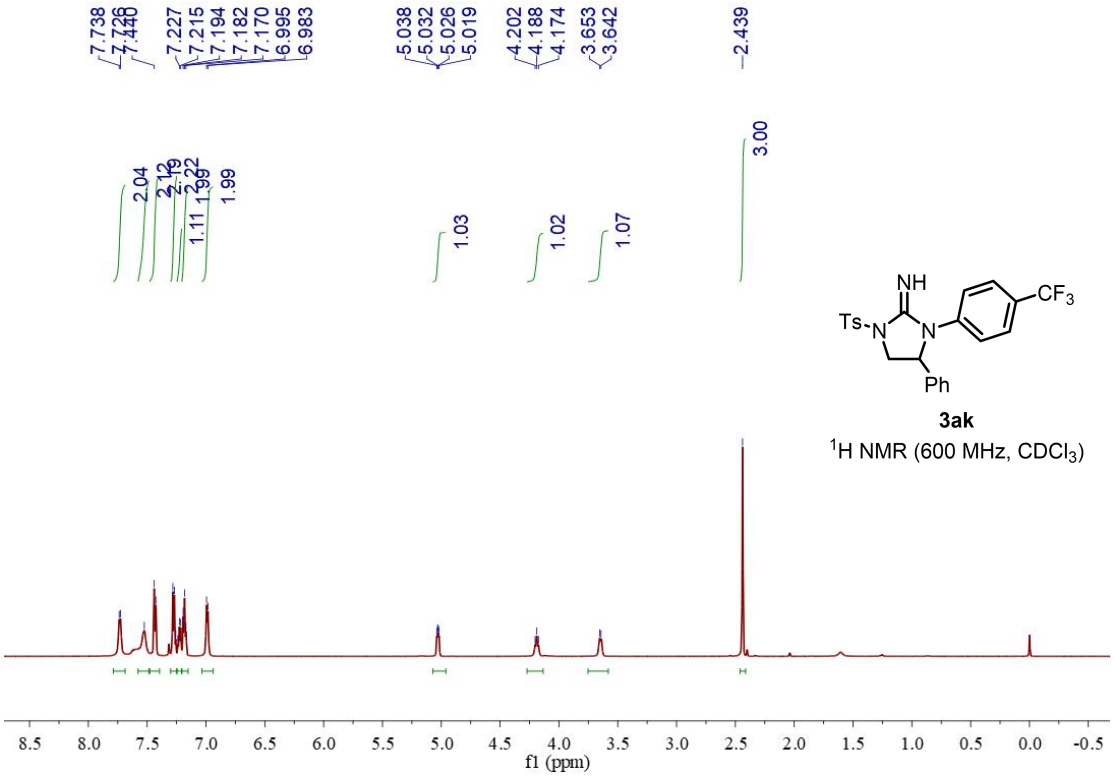
3aj

^{1}H NMR (600 MHz, $CDCl_3$)



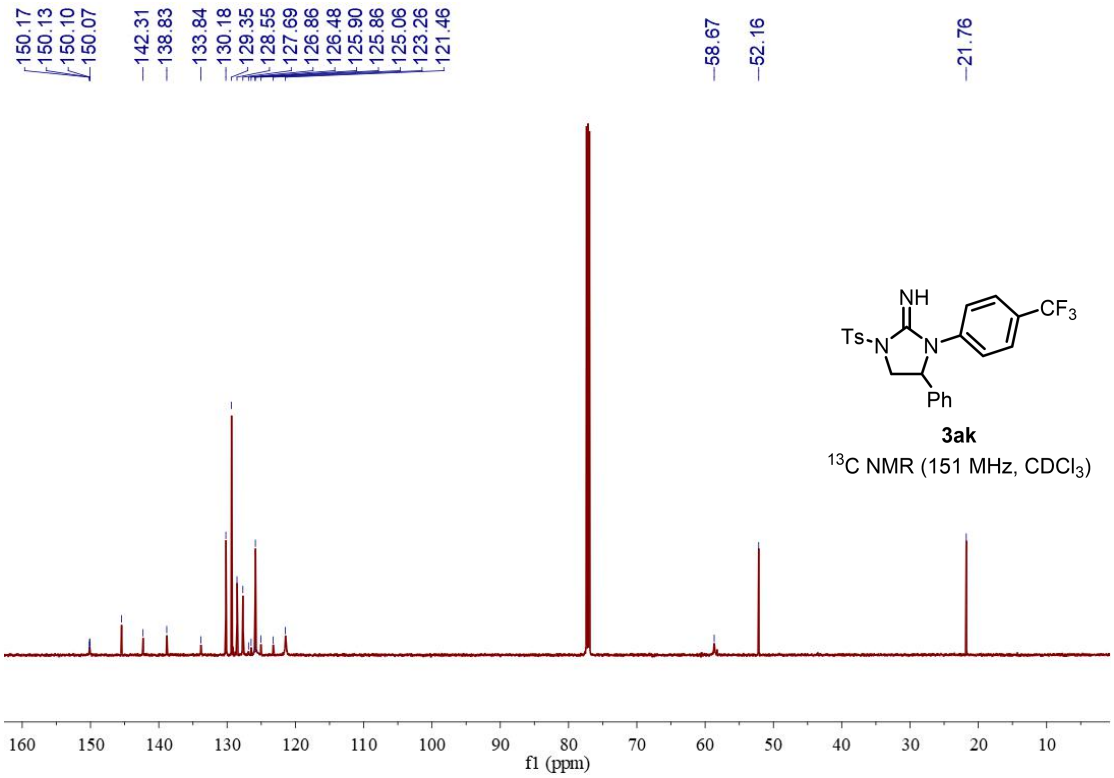
3aj

^{13}C NMR (151 MHz, $CDCl_3$)



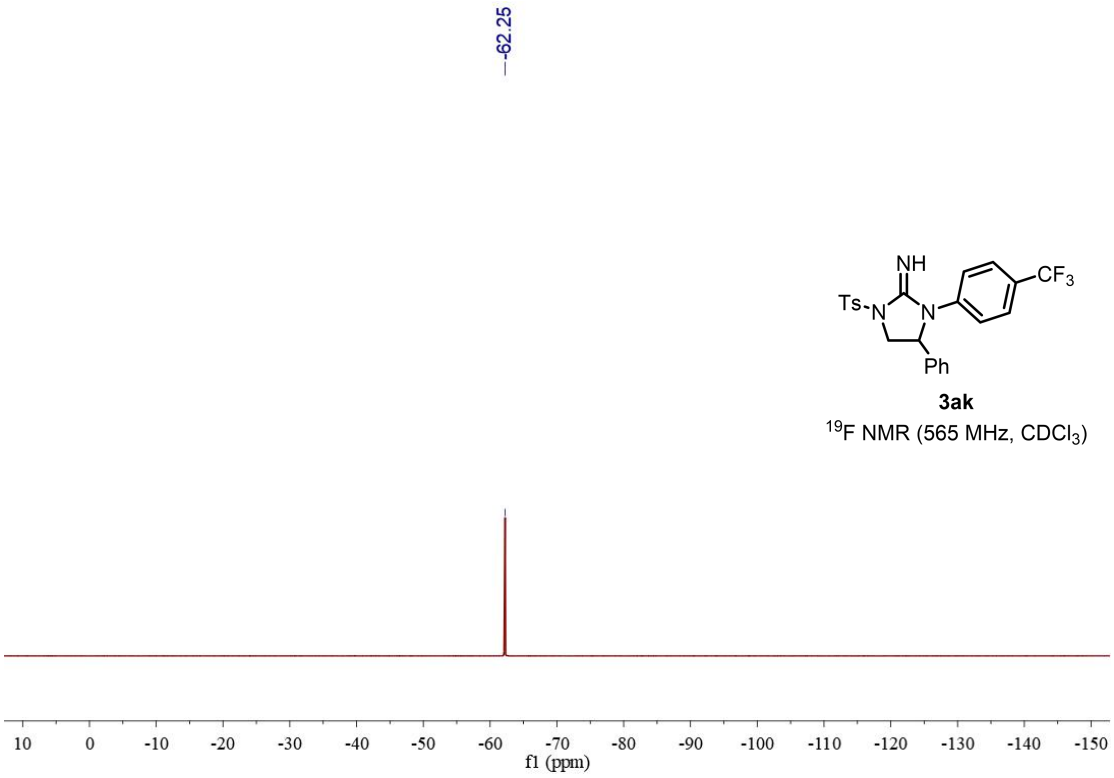
3ak

^{1}H NMR (600 MHz, $CDCl_3$)



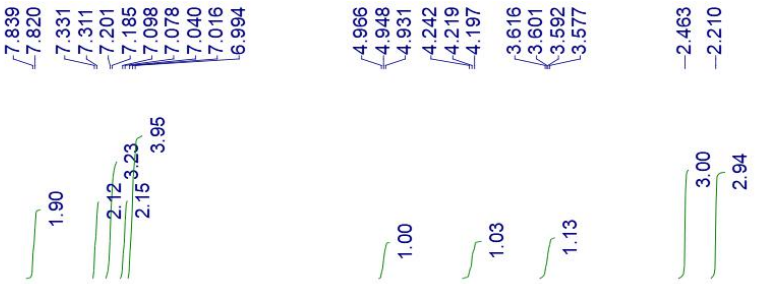
3ak

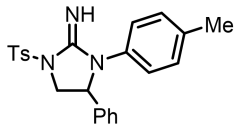
^{13}C NMR (151 MHz, $CDCl_3$)



3ak

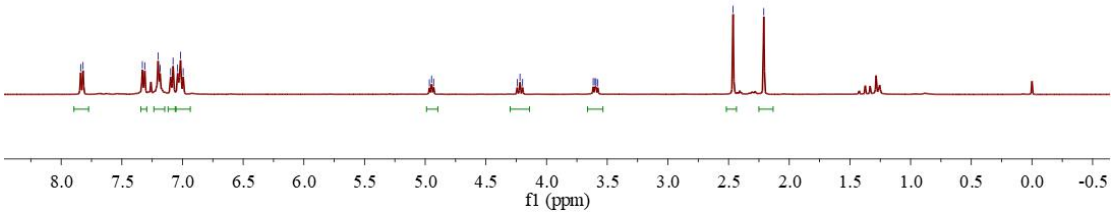
^{19}F NMR (565 MHz, $CDCl_3$)

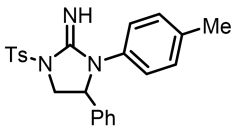




3al

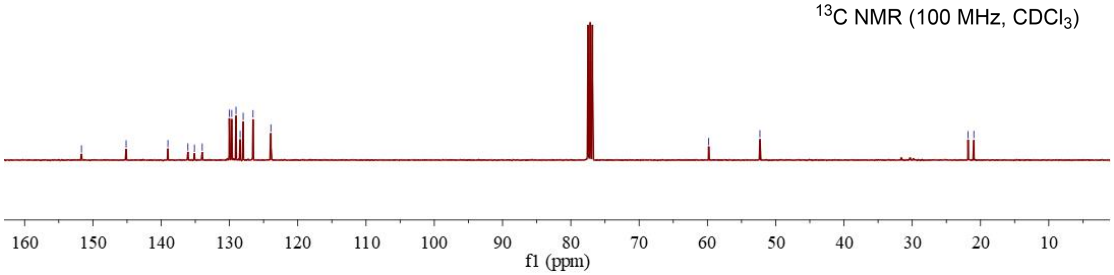
^{1}H NMR (400 MHz, $CDCl_3$)

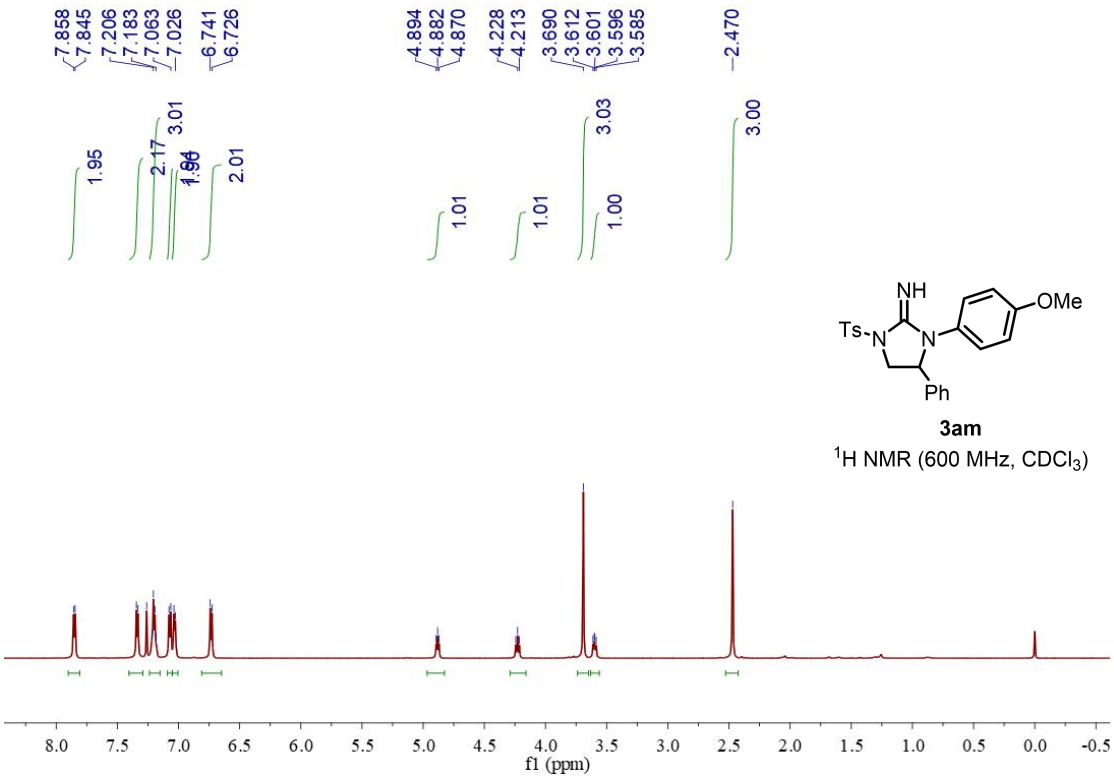




3al

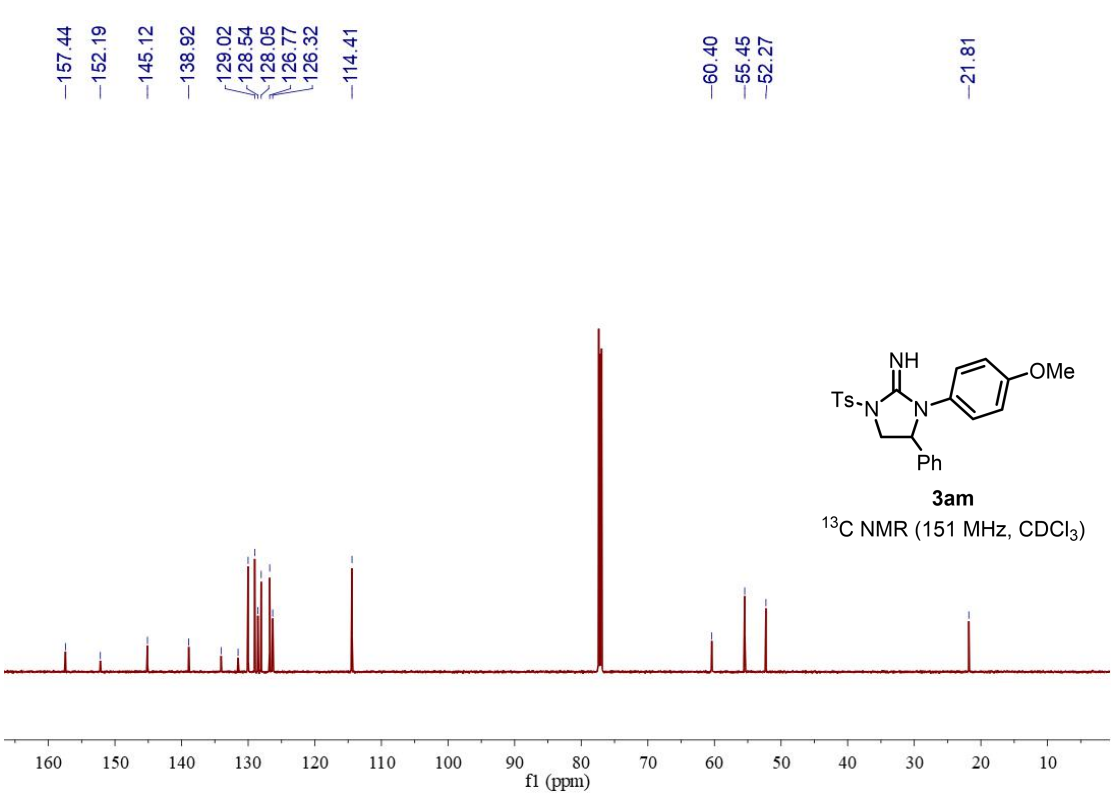
^{13}C NMR (100 MHz, $CDCl_3$)





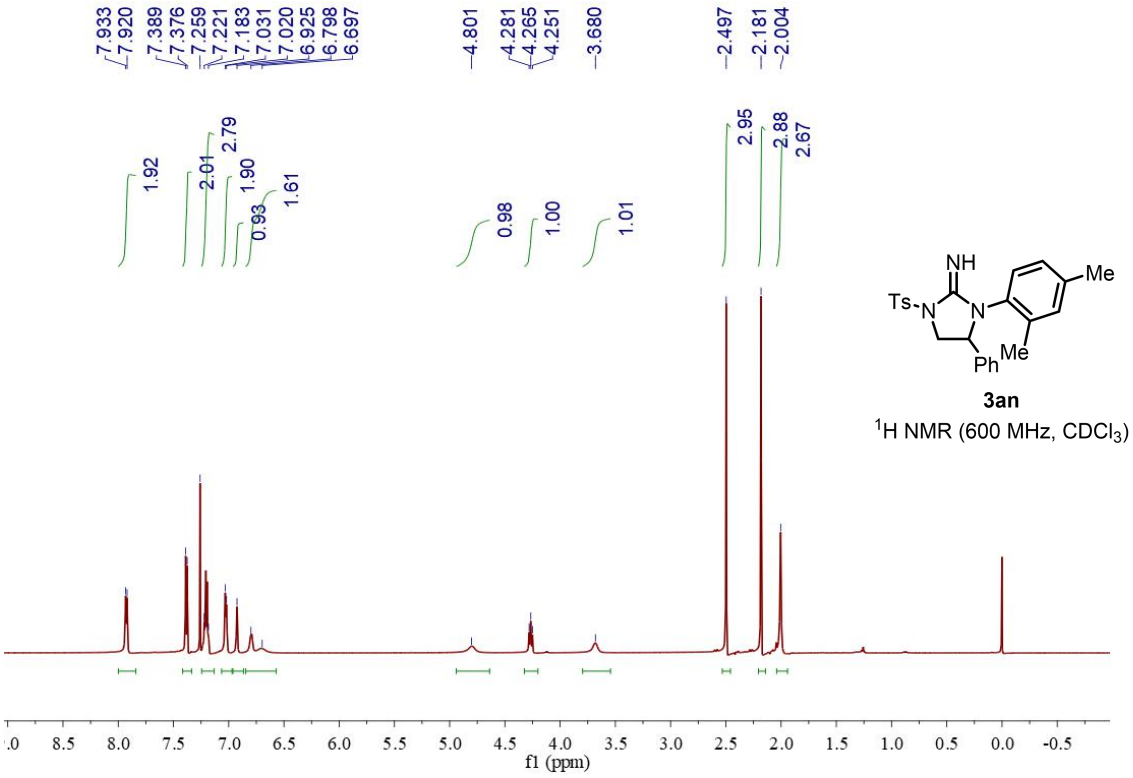
3am

^{1}H NMR (600 MHz, $CDCl_3$)



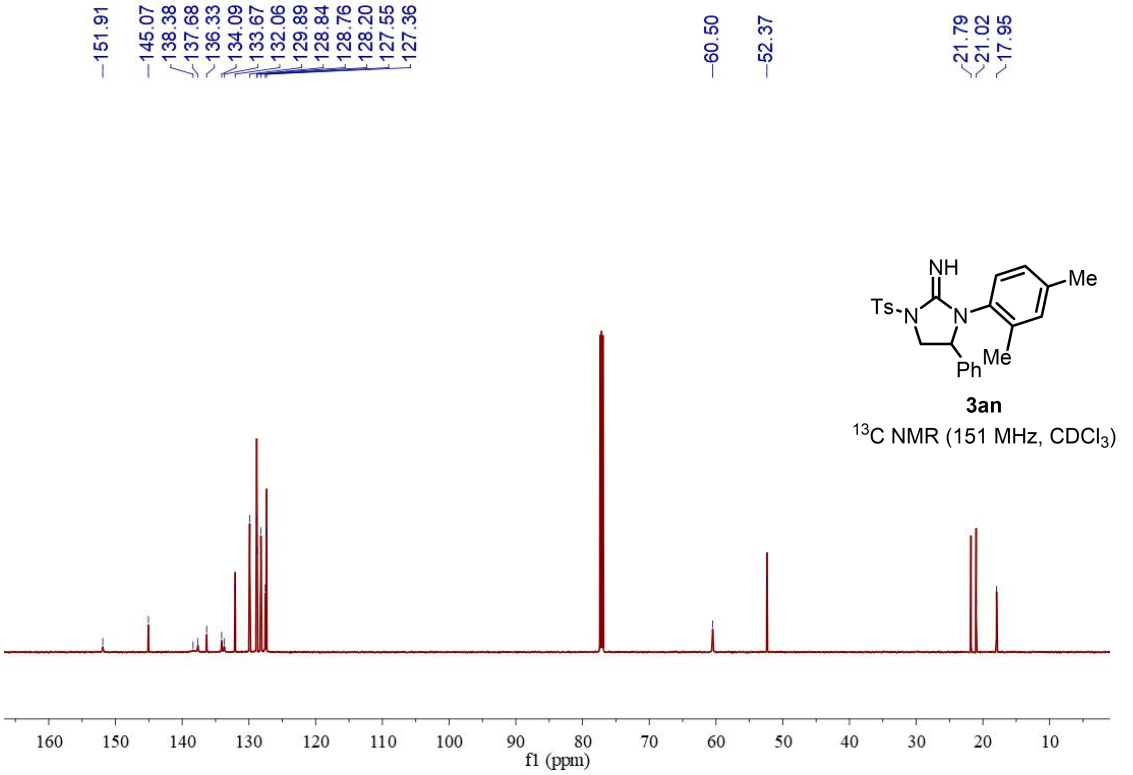
3am

^{13}C NMR (151 MHz, $CDCl_3$)



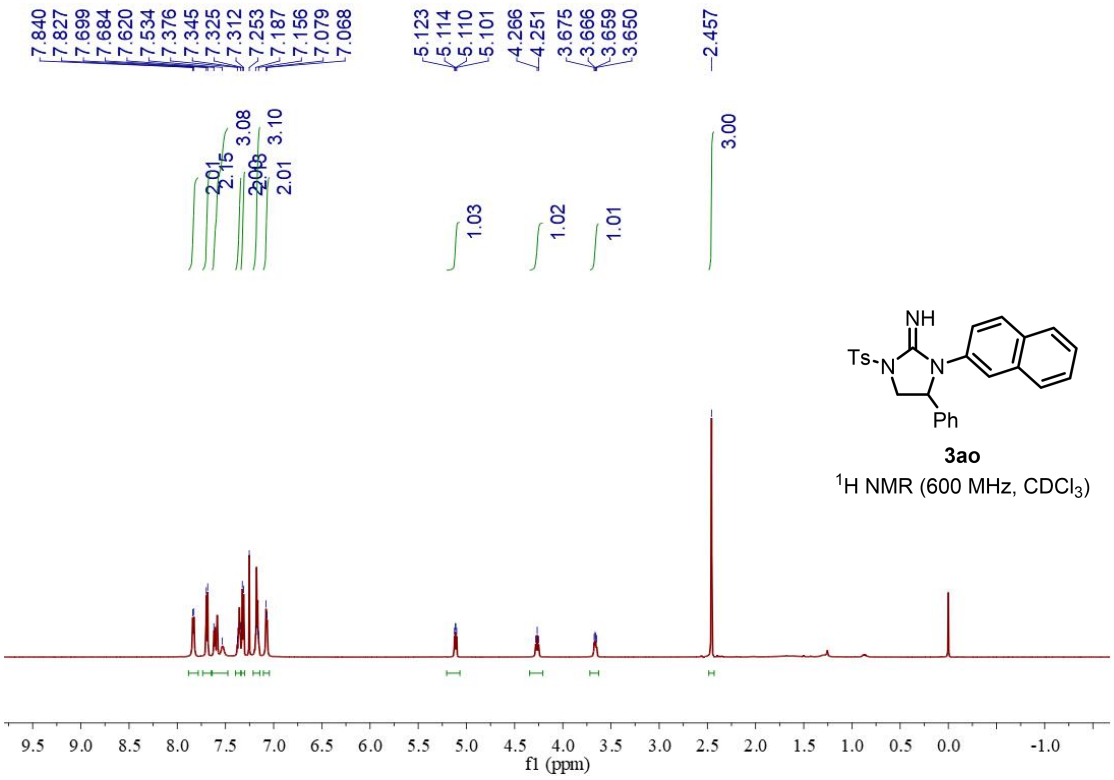
3an

^{1}H NMR (600 MHz, $CDCl_3$)



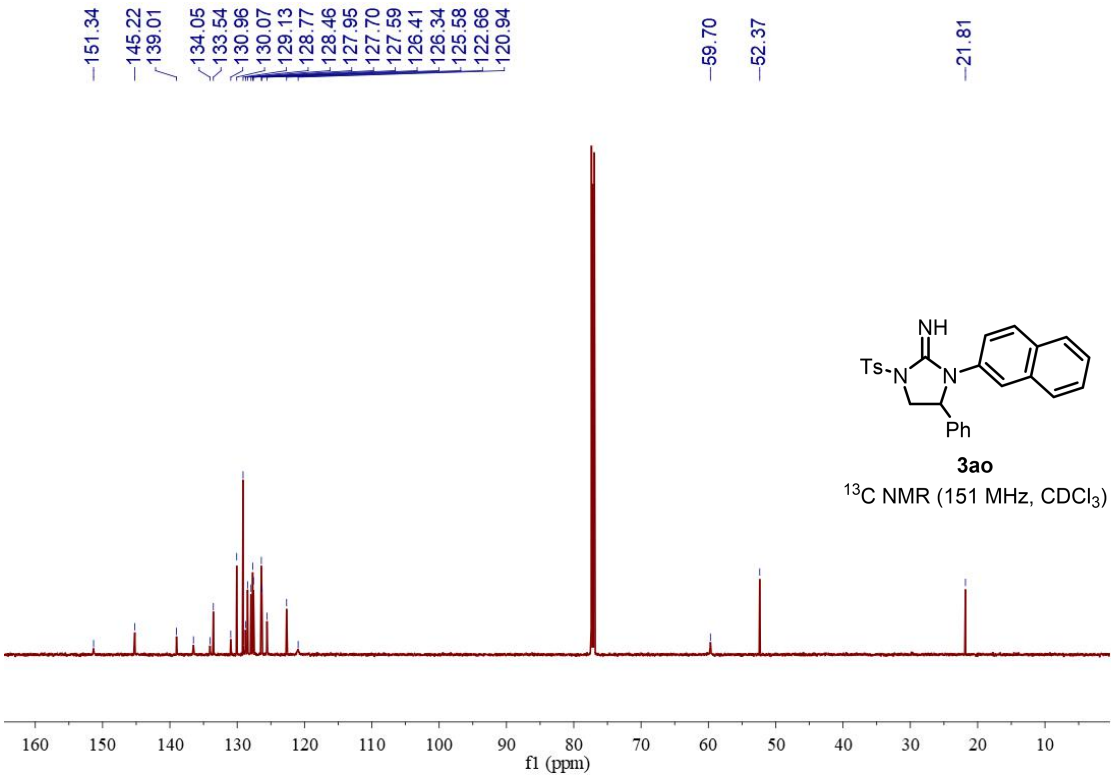
3an

^{13}C NMR (151 MHz, $CDCl_3$)



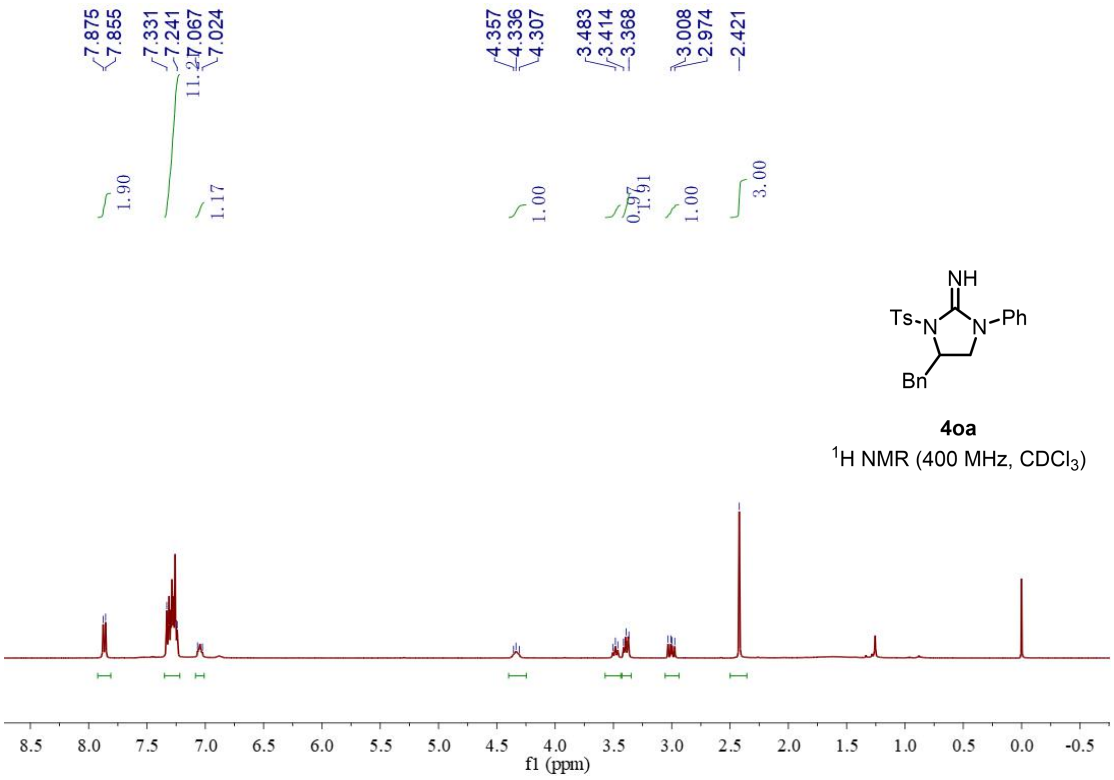
3ao

^{1}H NMR (600 MHz, $CDCl_3$)



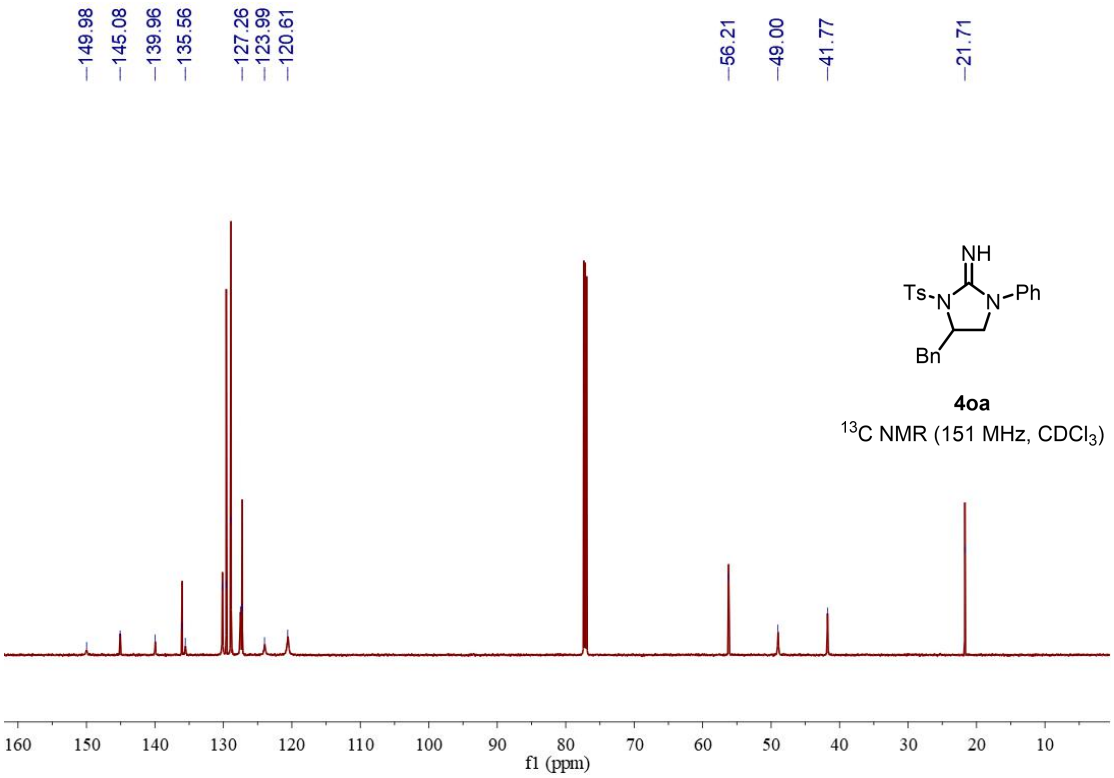
3ao

^{13}C NMR (151 MHz, $CDCl_3$)



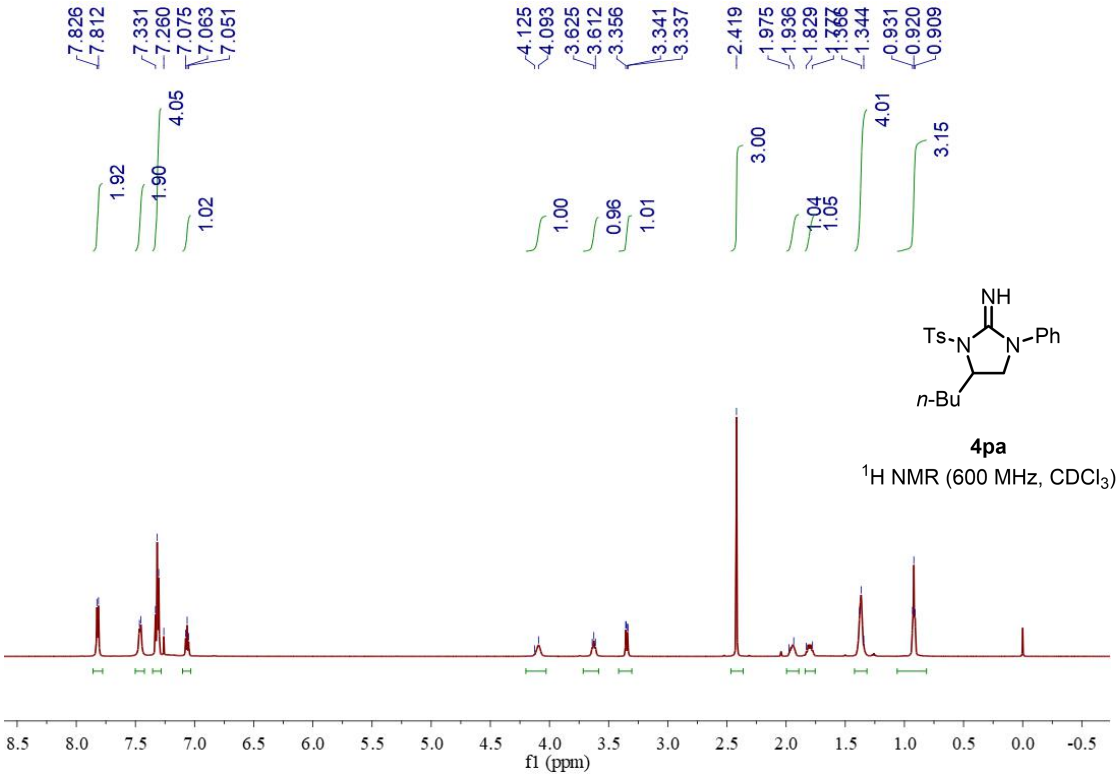
4oa

^{1}H NMR (400 MHz, $CDCl_3$)



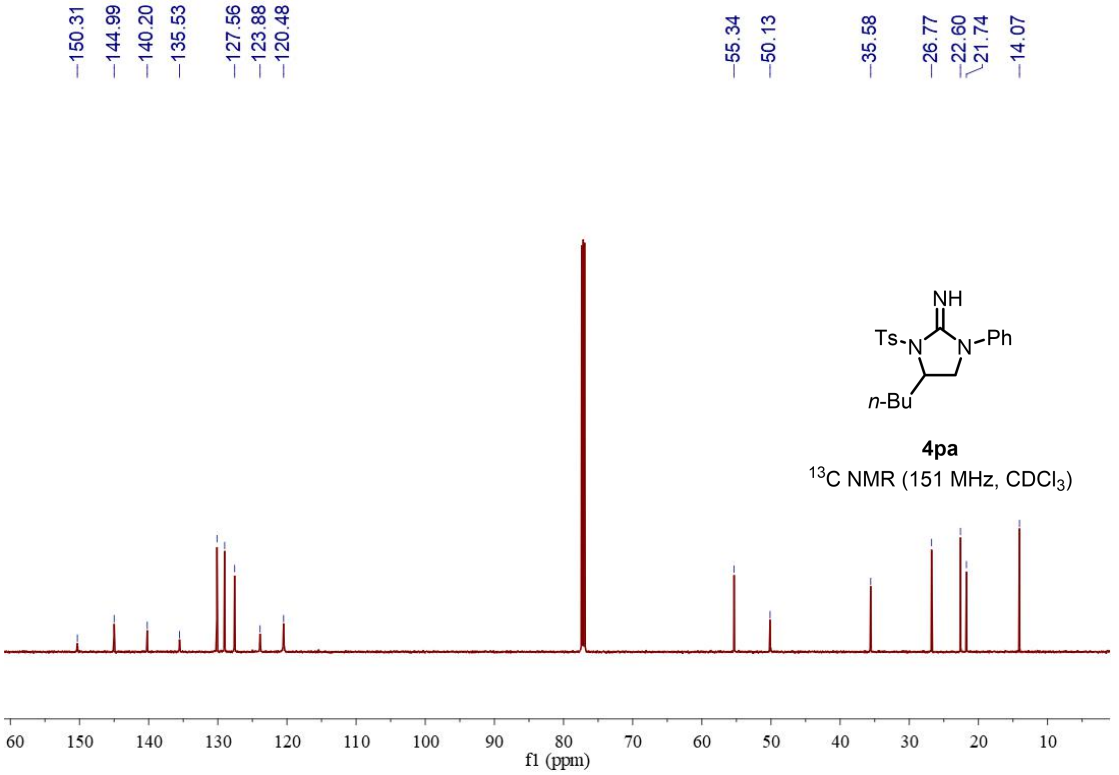
4oa

^{13}C NMR (151 MHz, $CDCl_3$)



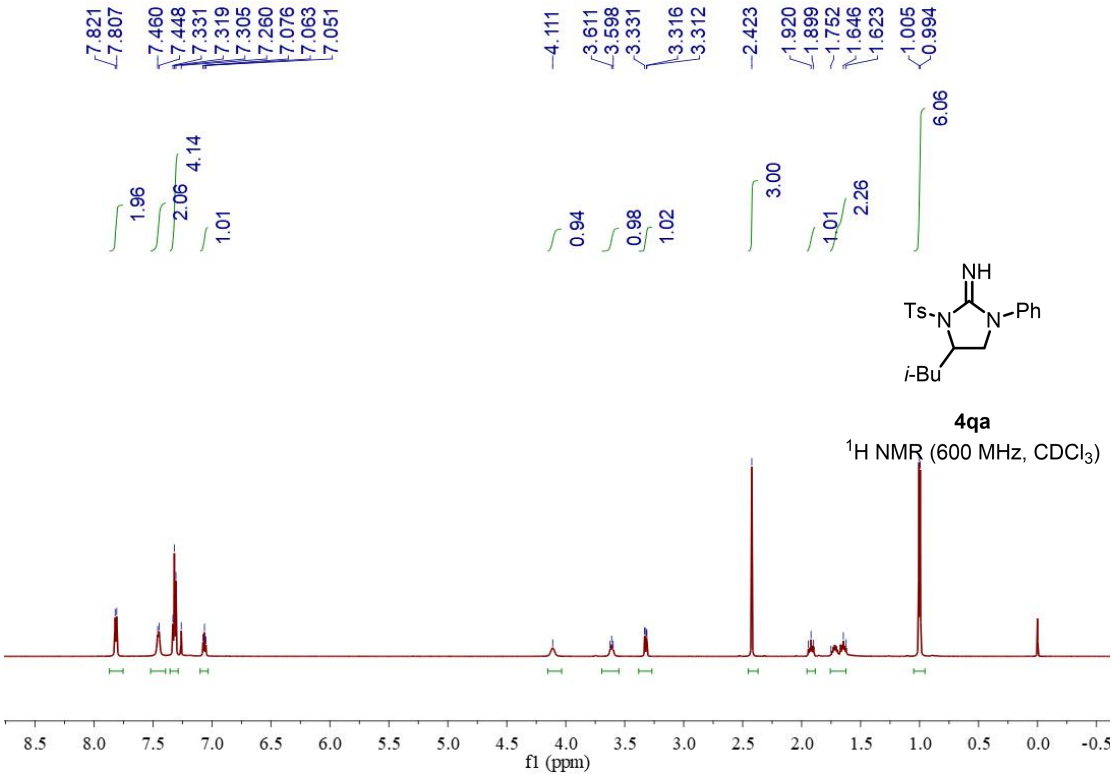
4pa

^{1}H NMR (600 MHz, $CDCl_3$)



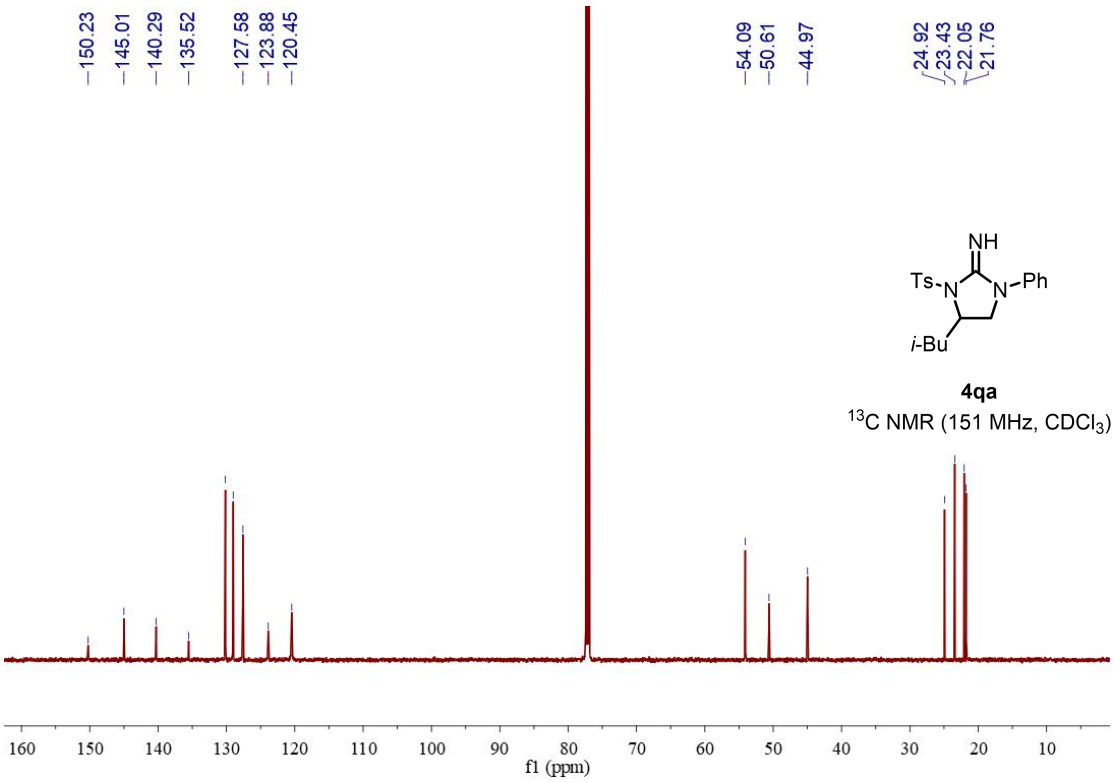
4pa

^{13}C NMR (151 MHz, $CDCl_3$)



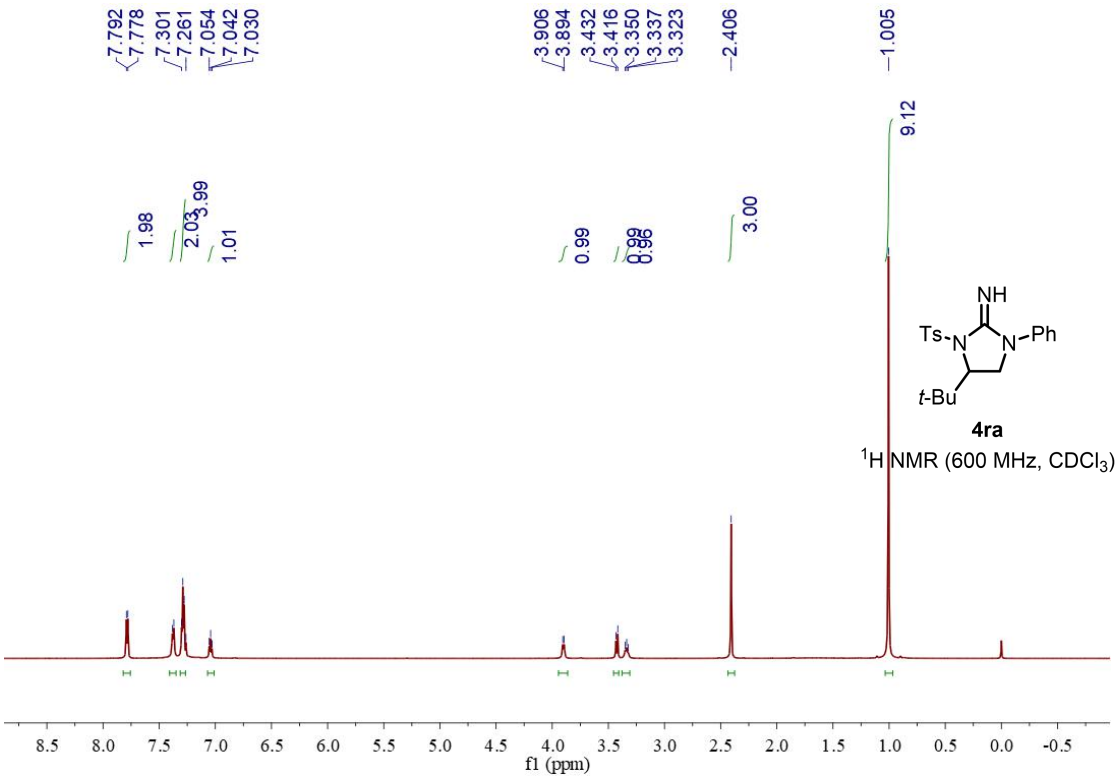
4qa

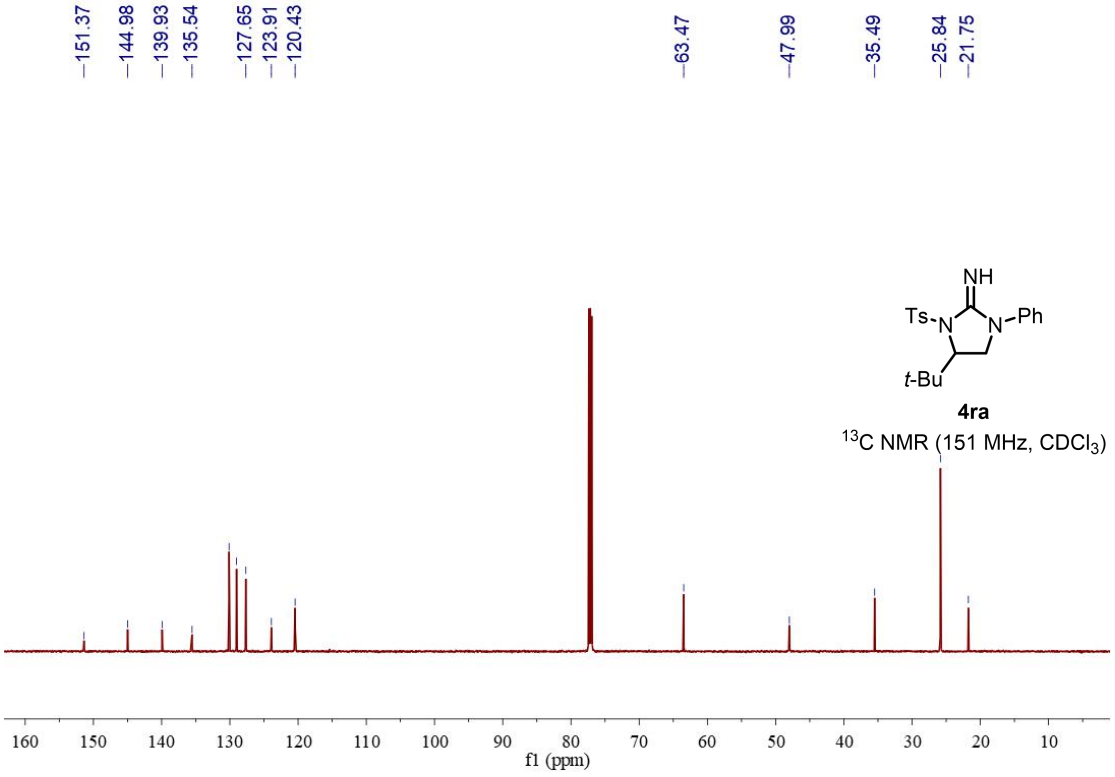
^{1}H NMR (600 MHz, $CDCl_3$)

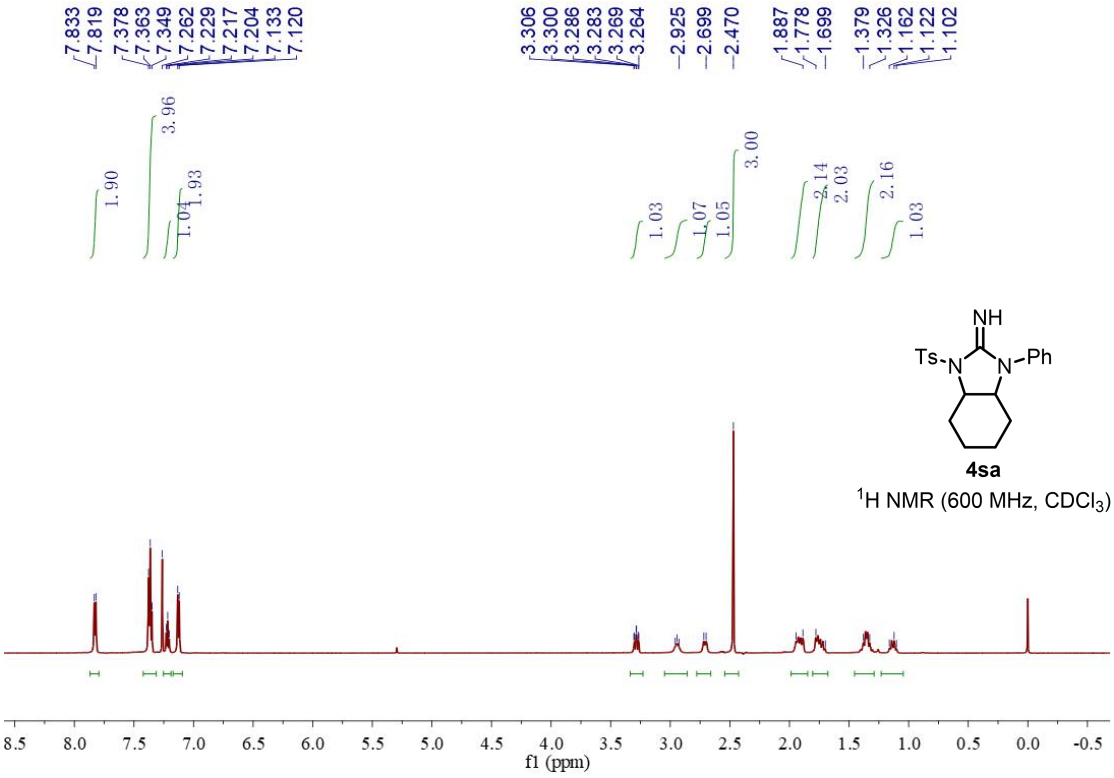


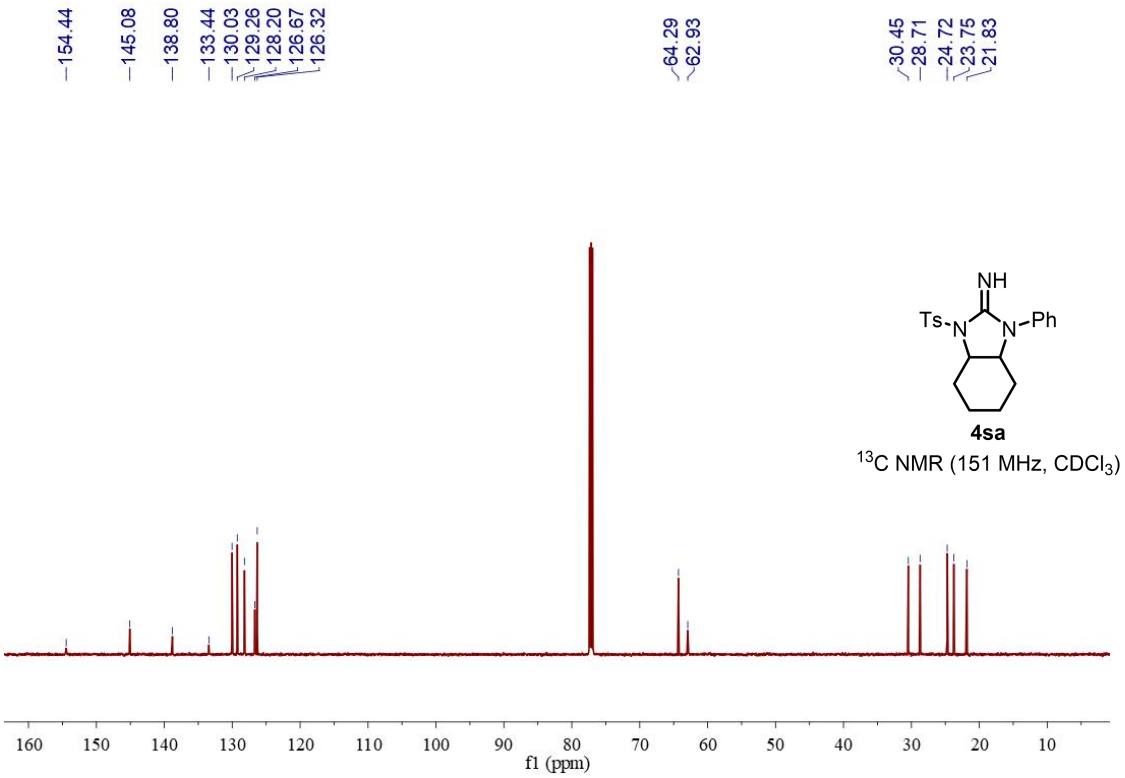
4qa

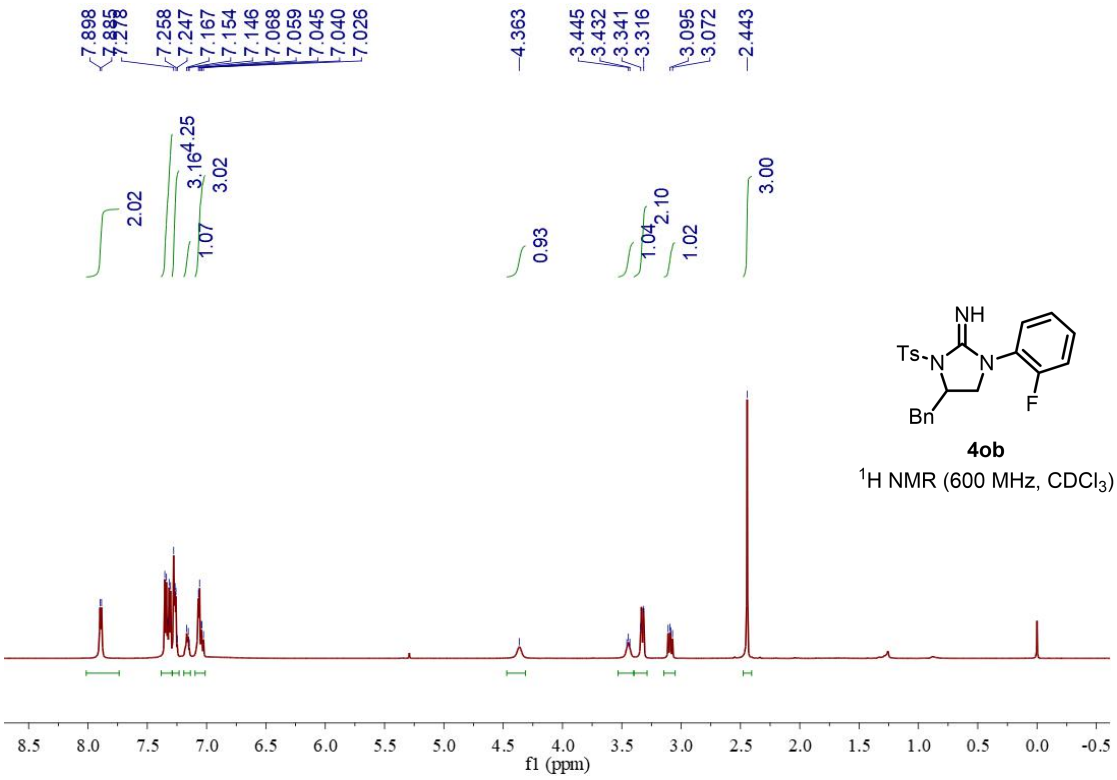
^{13}C NMR (151 MHz, $CDCl_3$)


7.792
7.778
7.301
7.261
7.054
7.042
7.030
3.906
3.894
3.432
3.416
3.350
3.337
3.323
2.406
1.005
9.12
1.98
2.03
3.99
1.01
0.99
3.00
NH
Ts
N
N
Ph
t-Bu
4ra
1H NMR (600 MHz, CDCl3)
f1 (ppm)


151.37
144.98
139.93
135.54
127.65
123.91
120.43
63.47
47.99
35.49
25.84
21.75
NH
Ts
N
N
Ph
t-Bu
4ra
13C NMR (151 MHz, CDCl3)
f1 (ppm)

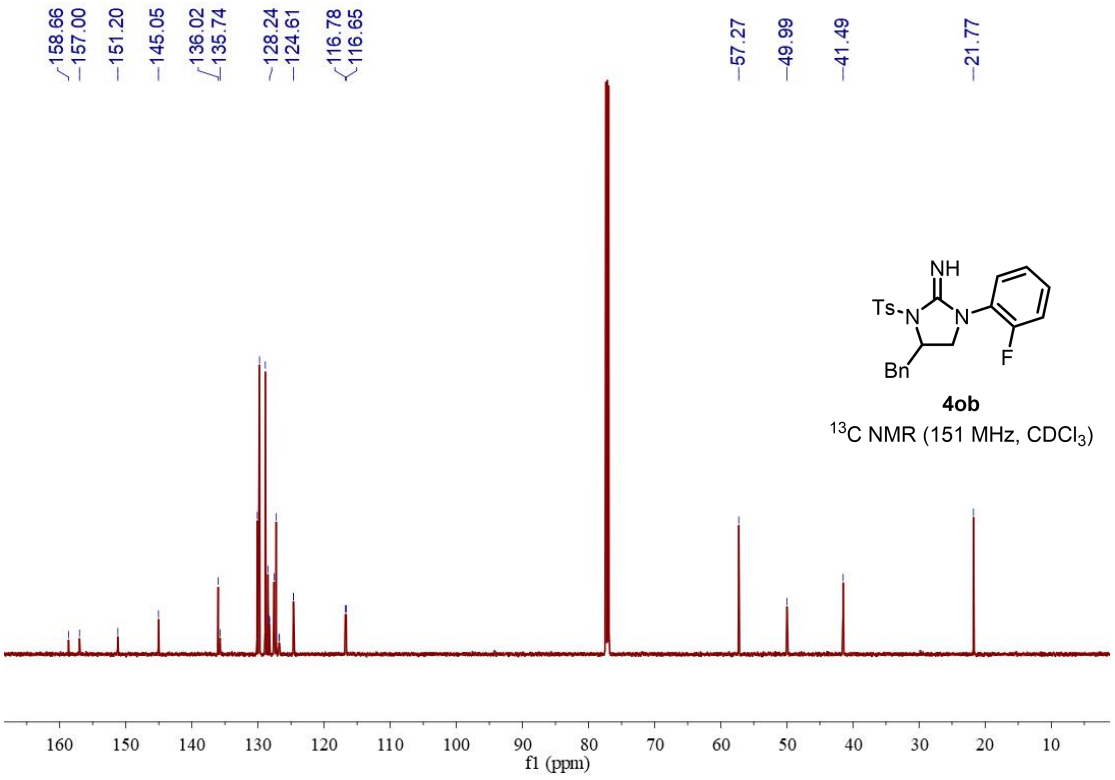

7.833
7.819
7.378
7.363
7.349
7.262
7.229
7.217
7.204
7.133
7.120
3.306
3.300
3.286
3.283
3.269
3.264
2.925
2.699
2.470
1.887
1.778
1.699
1.379
1.326
1.162
1.122
1.102
1.90
3.96
1.04
1.93
1.03
1.07
1.05
3.00
2.14
2.03
2.16
1.03
NH
Ts
N
N
Ph
4sa
^{1}H NMR (600 MHz, CDCl$_3$)
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


154.44
145.08
138.80
133.44
130.03
129.26
128.20
126.67
126.32
64.29
62.93
30.45
28.71
24.72
23.75
21.83
NH
Ts
N
N
Ph
4sa
^{13}C NMR (151 MHz, CDCl$_3$)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)



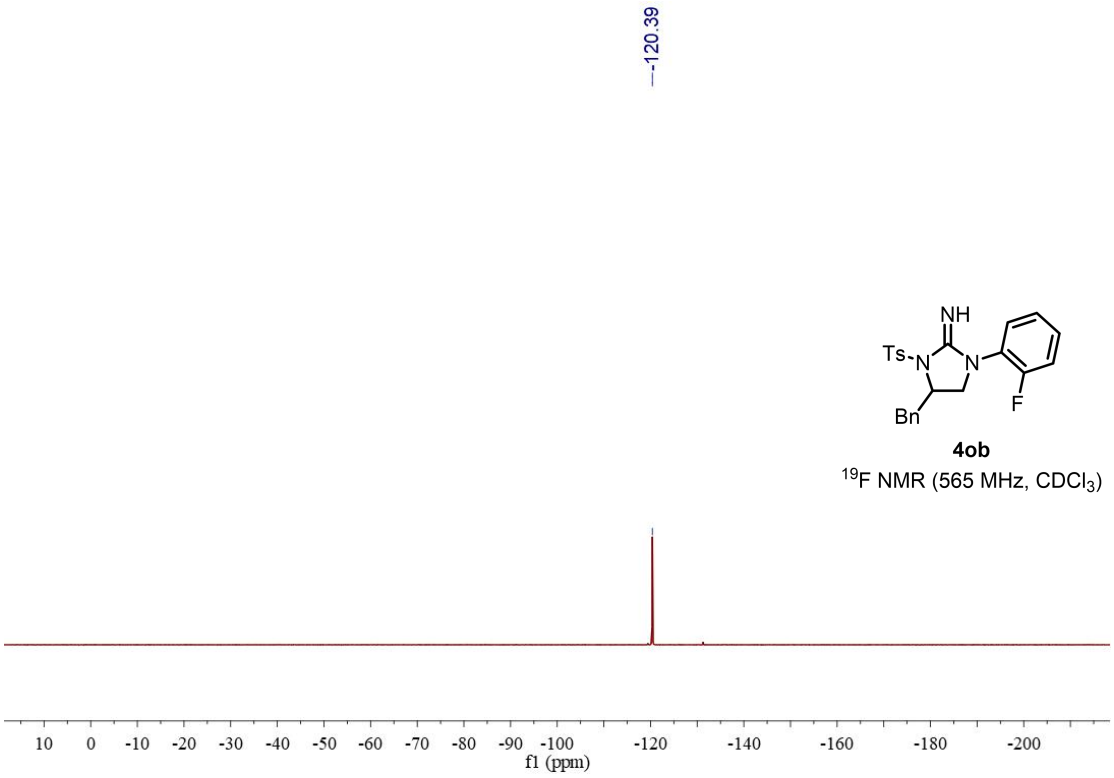
4ob

^{1}H NMR (600 MHz, $CDCl_3$)



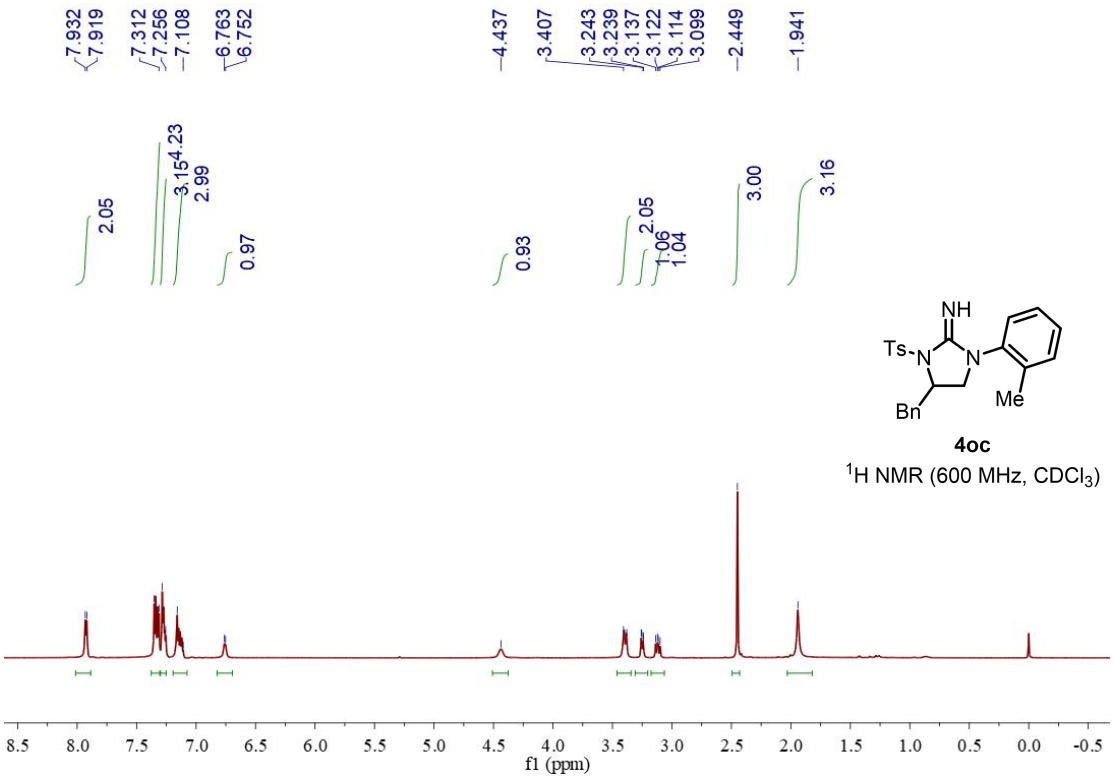
4ob

^{13}C NMR (151 MHz, $CDCl_3$)



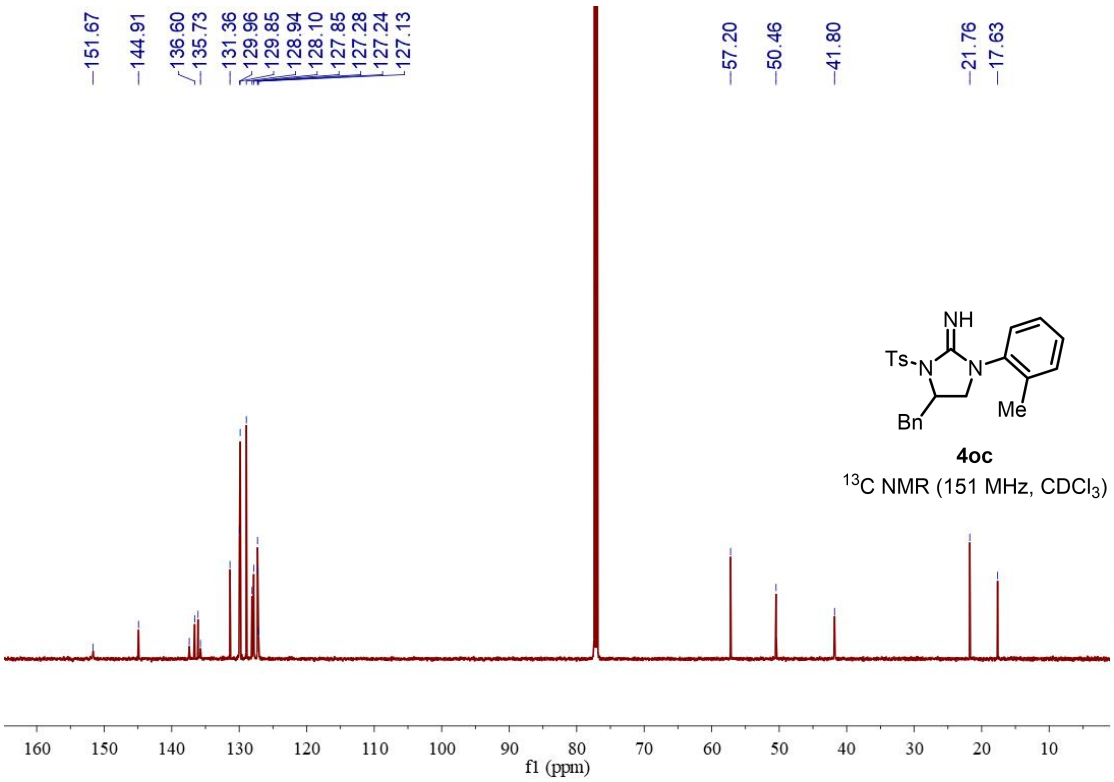
4ob

^{19}F NMR (565 MHz, $CDCl_3$)



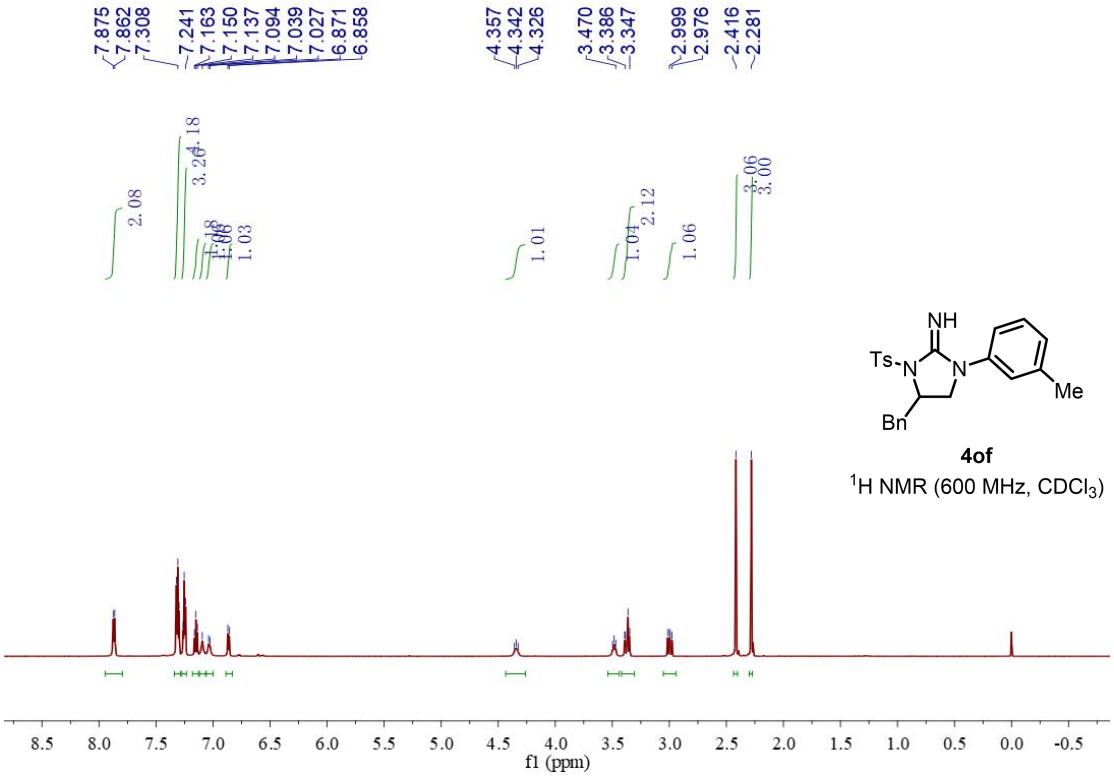
4oc

^{1}H NMR (600 MHz, $CDCl_3$)



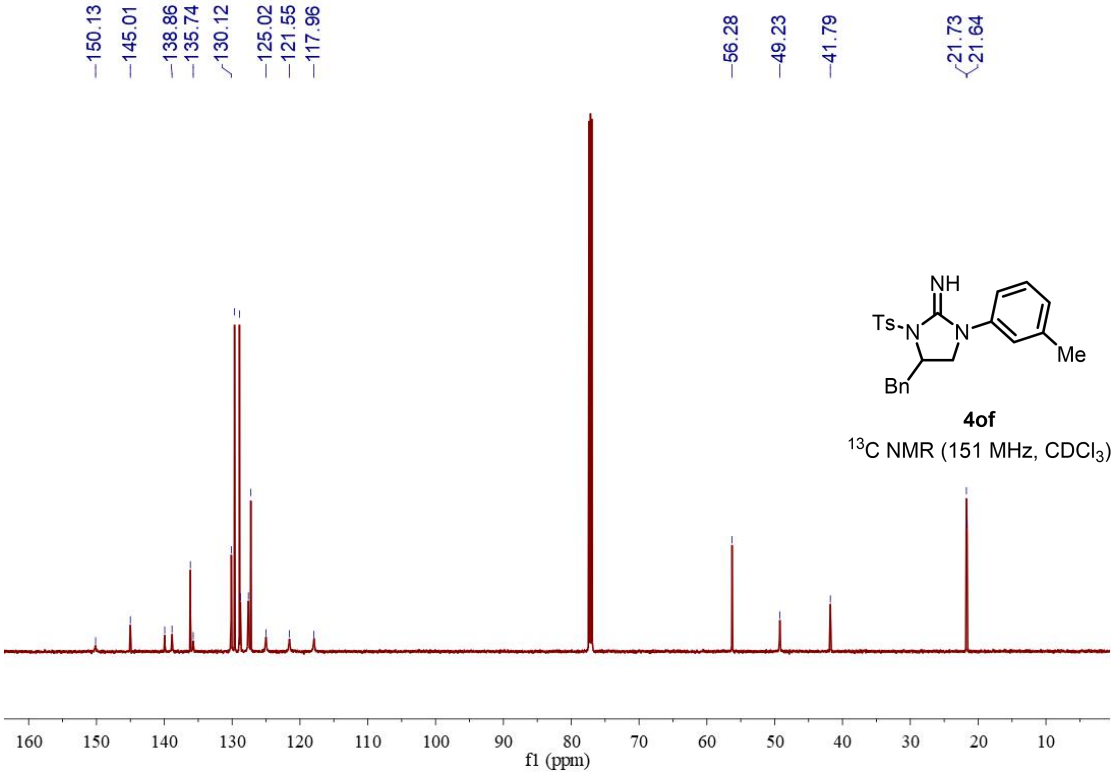
4oc

^{13}C NMR (151 MHz, $CDCl_3$)



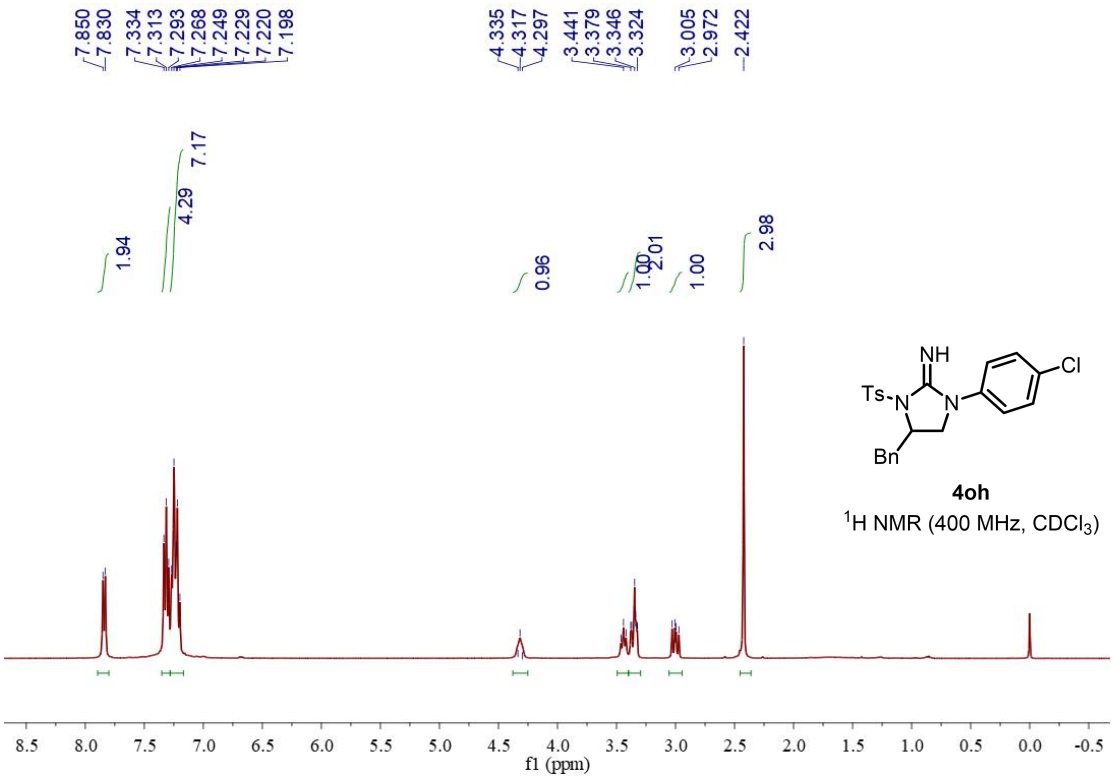
4of

^{1}H NMR (600 MHz, $CDCl_3$)



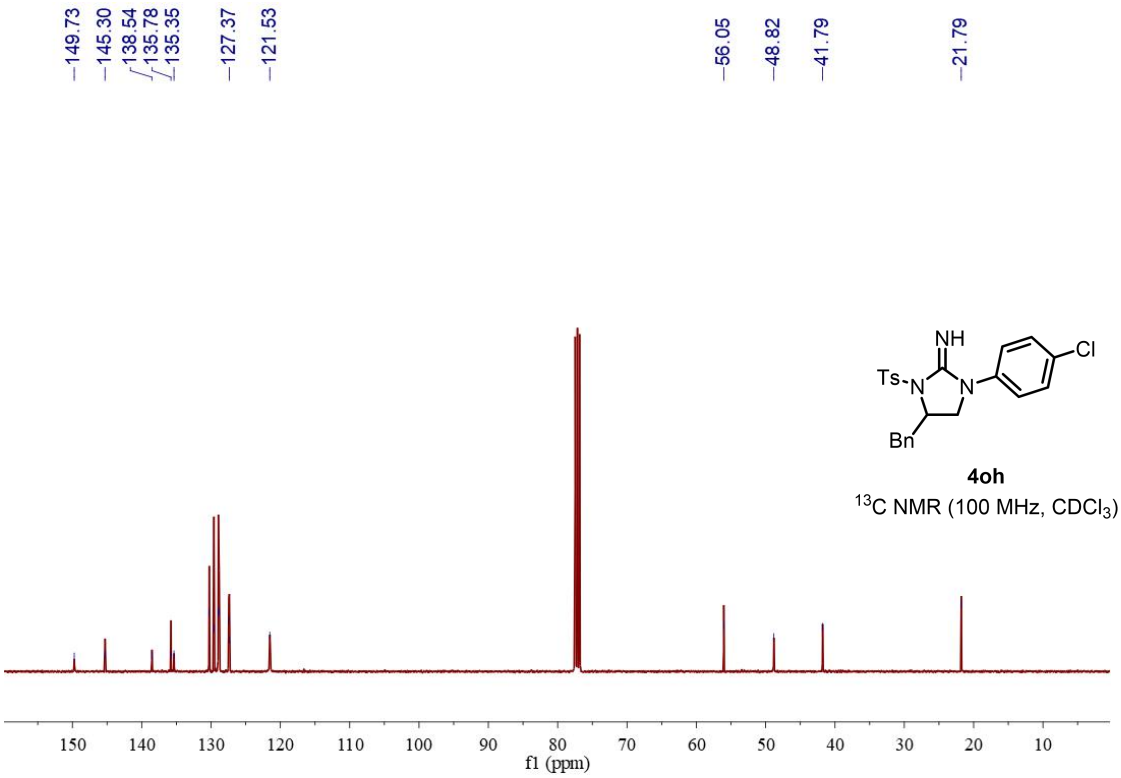
4of

^{13}C NMR (151 MHz, $CDCl_3$)



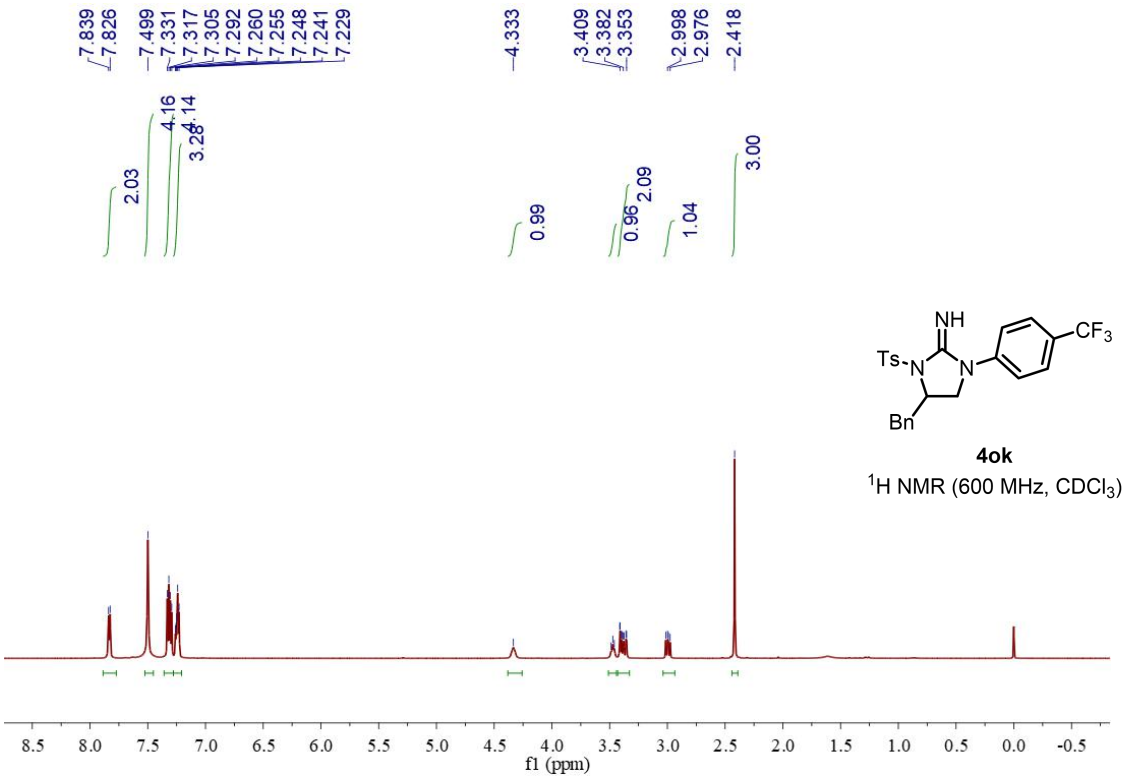
4oh

^{1}H NMR (400 MHz, $CDCl_3$)



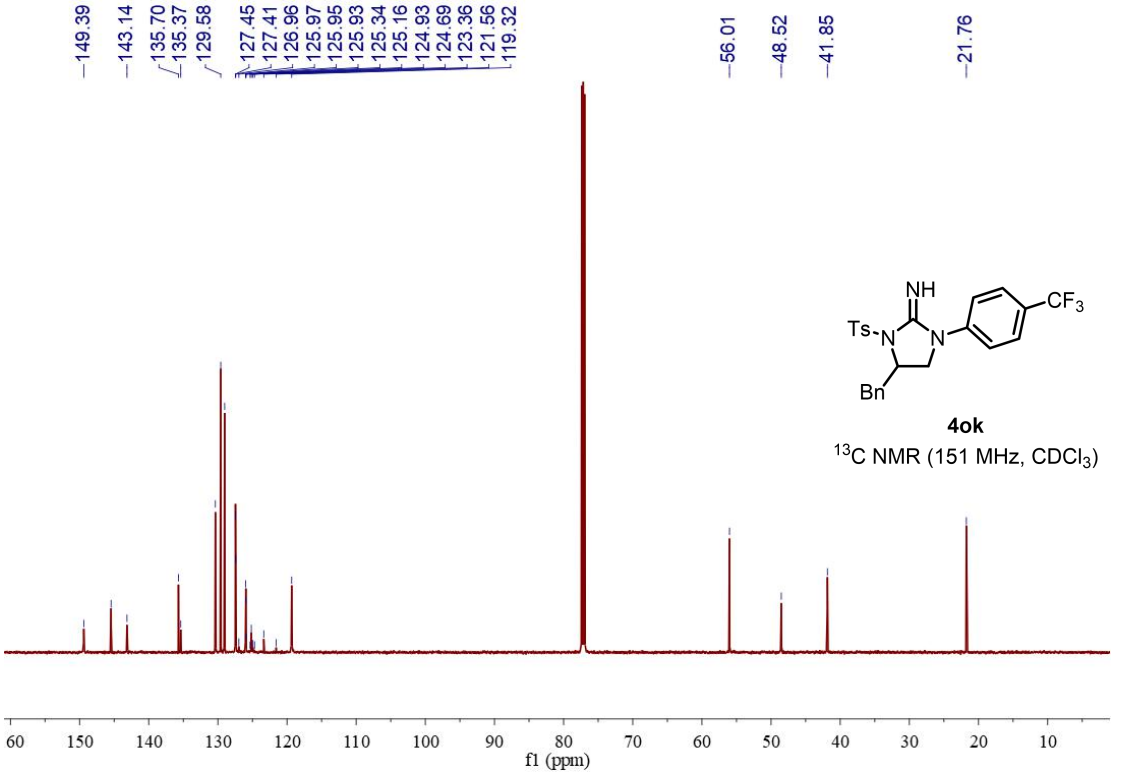
4oh

^{13}C NMR (100 MHz, $CDCl_3$)



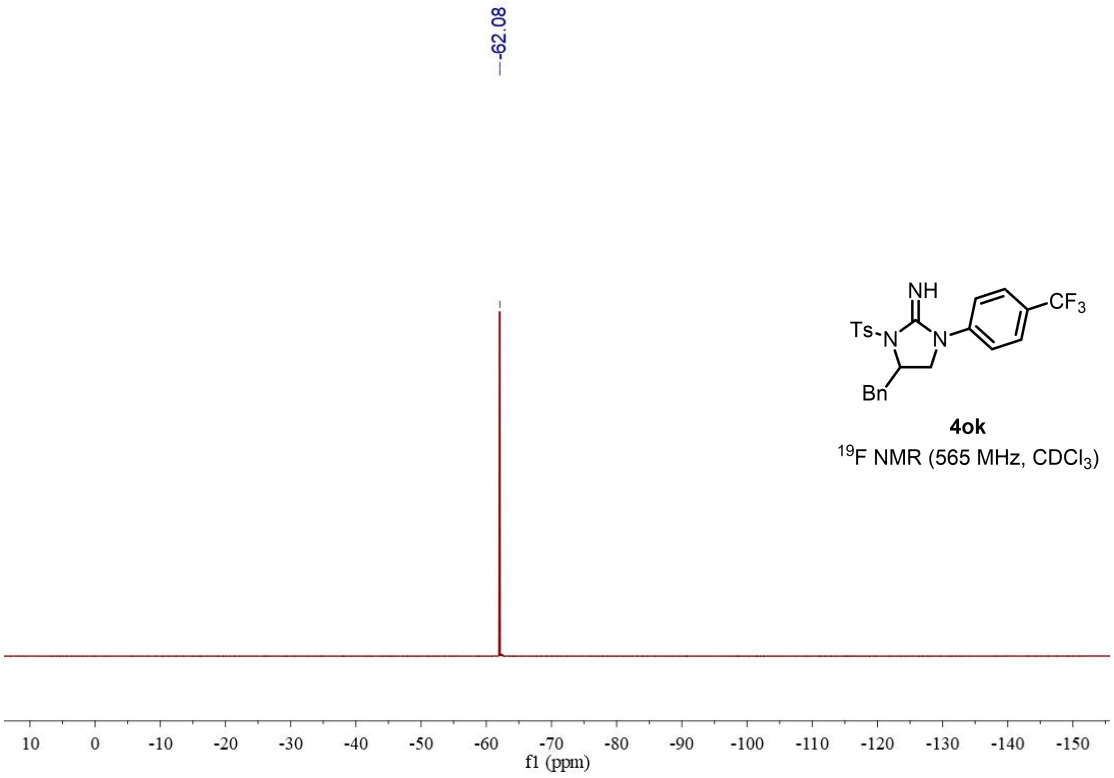
4ok

^{1}H NMR (600 MHz, $CDCl_3$)



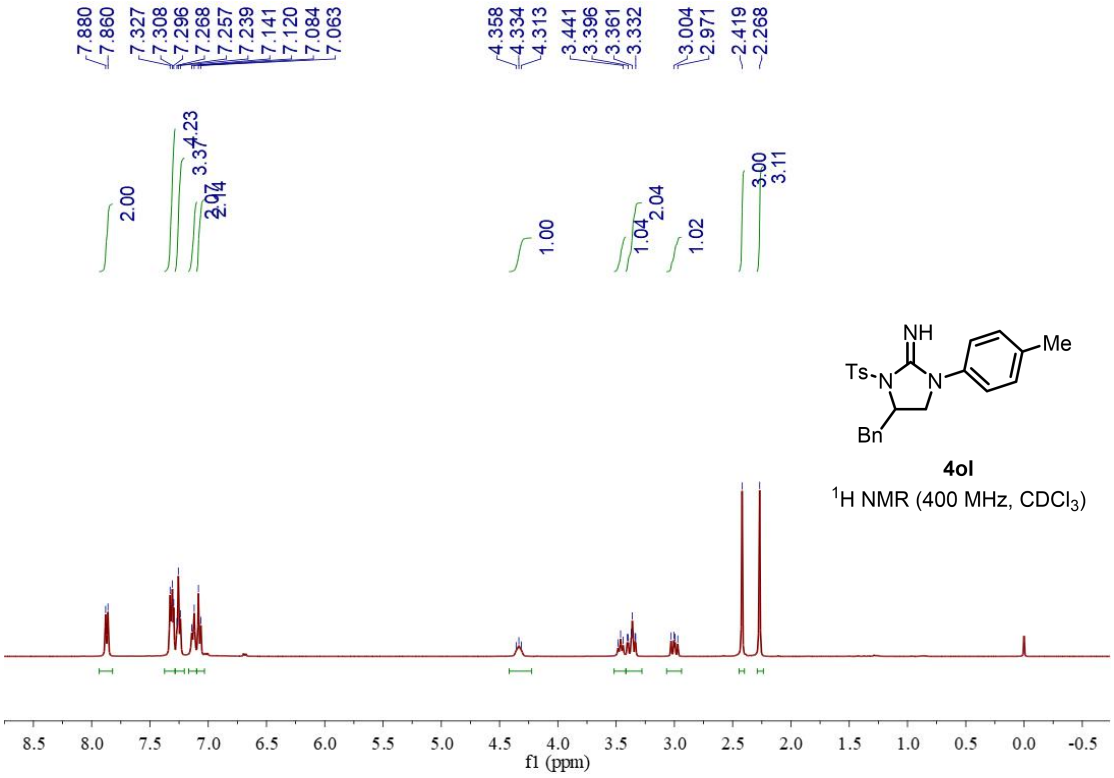
4ok

^{13}C NMR (151 MHz, $CDCl_3$)



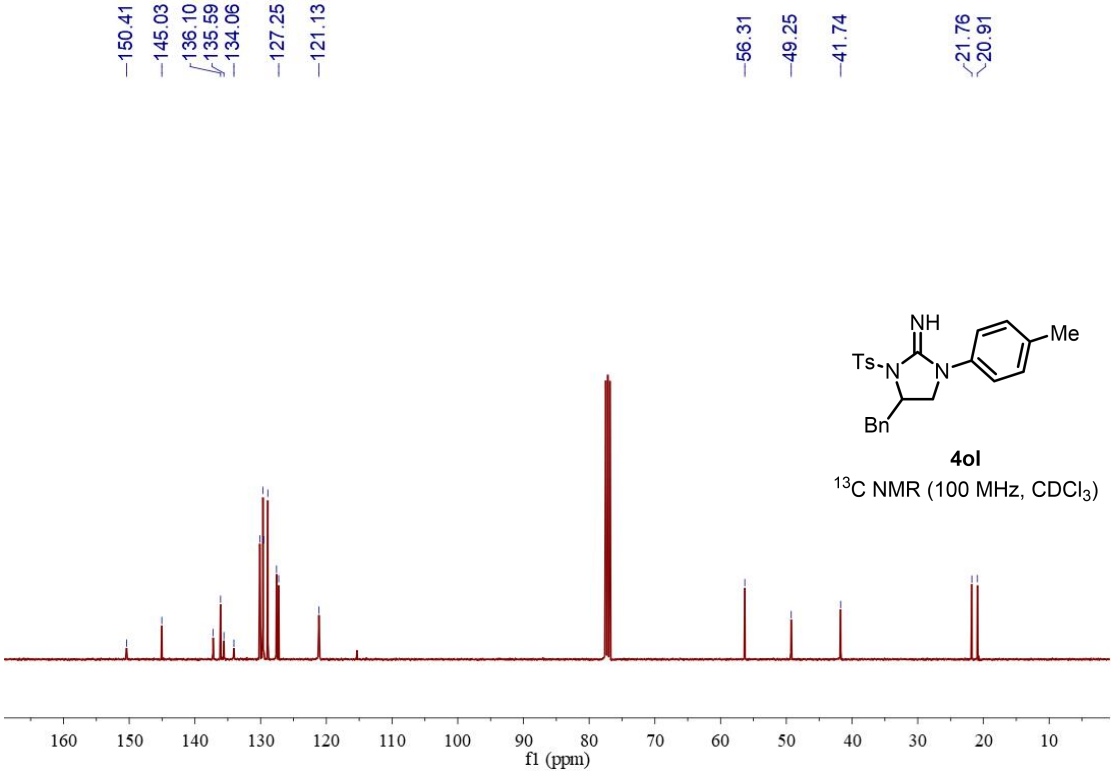
4ok

^{19}F NMR (565 MHz, $CDCl_3$)



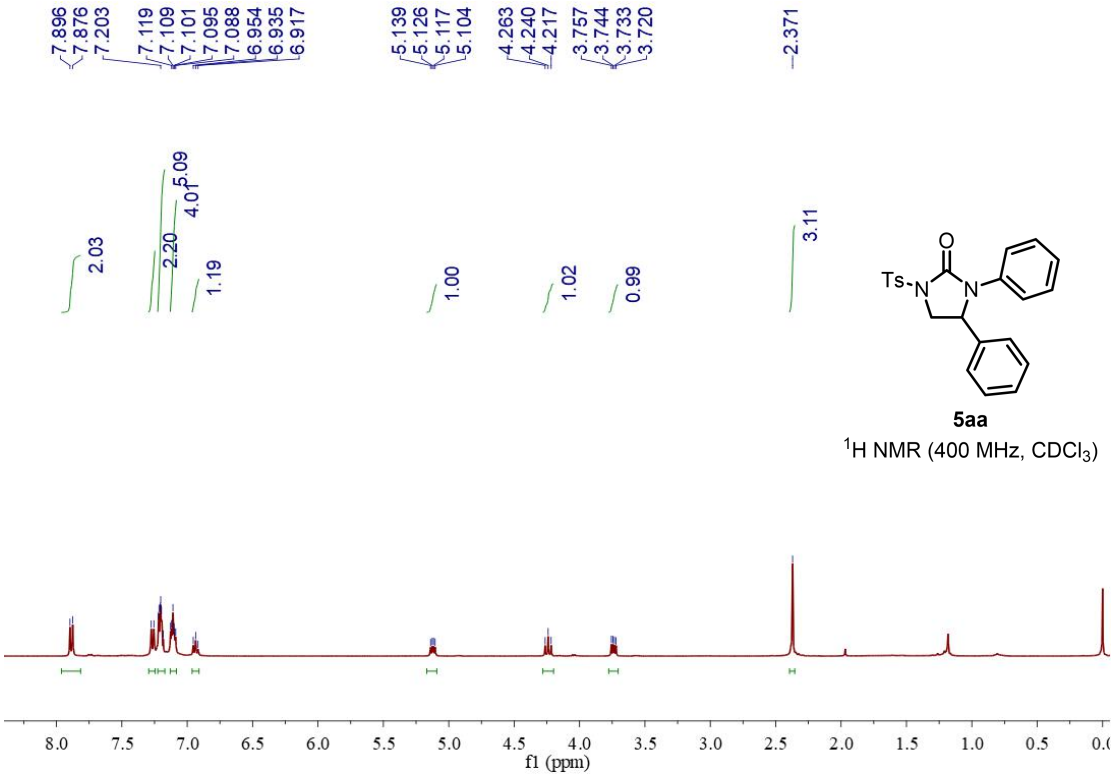
4ol

^{1}H NMR (400 MHz, $CDCl_3$)



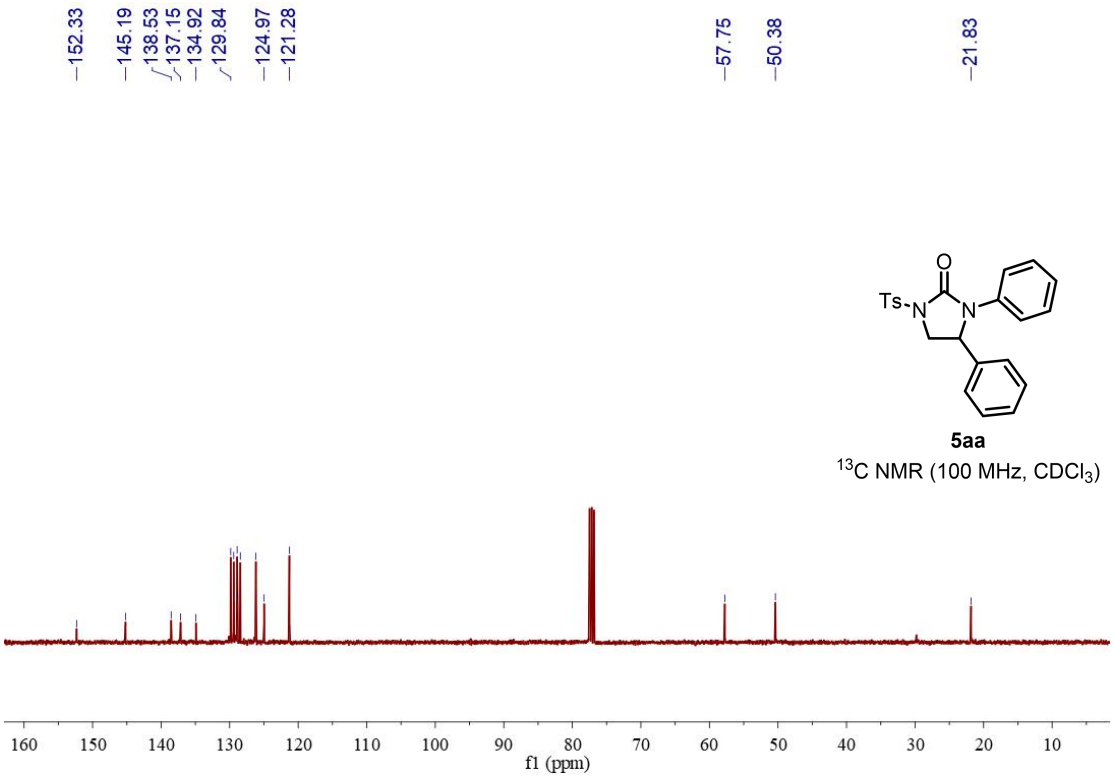
4ol

^{13}C NMR (100 MHz, $CDCl_3$)



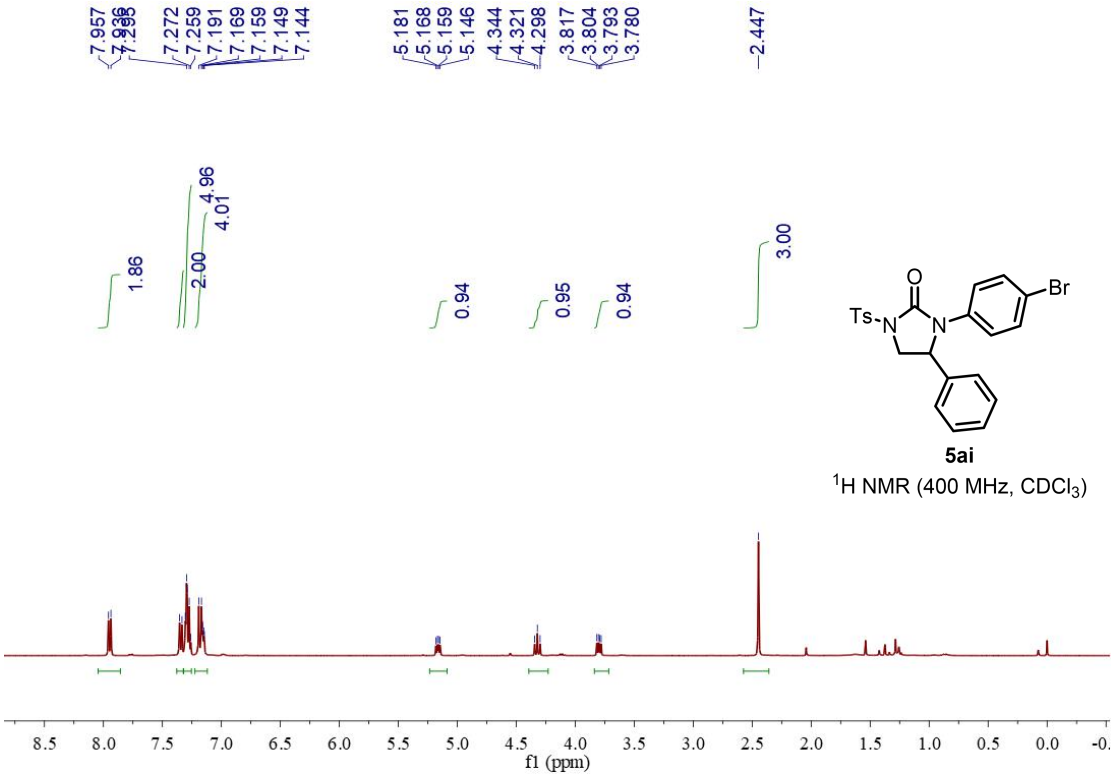
5aa

^{1}H NMR (400 MHz, $CDCl_3$)



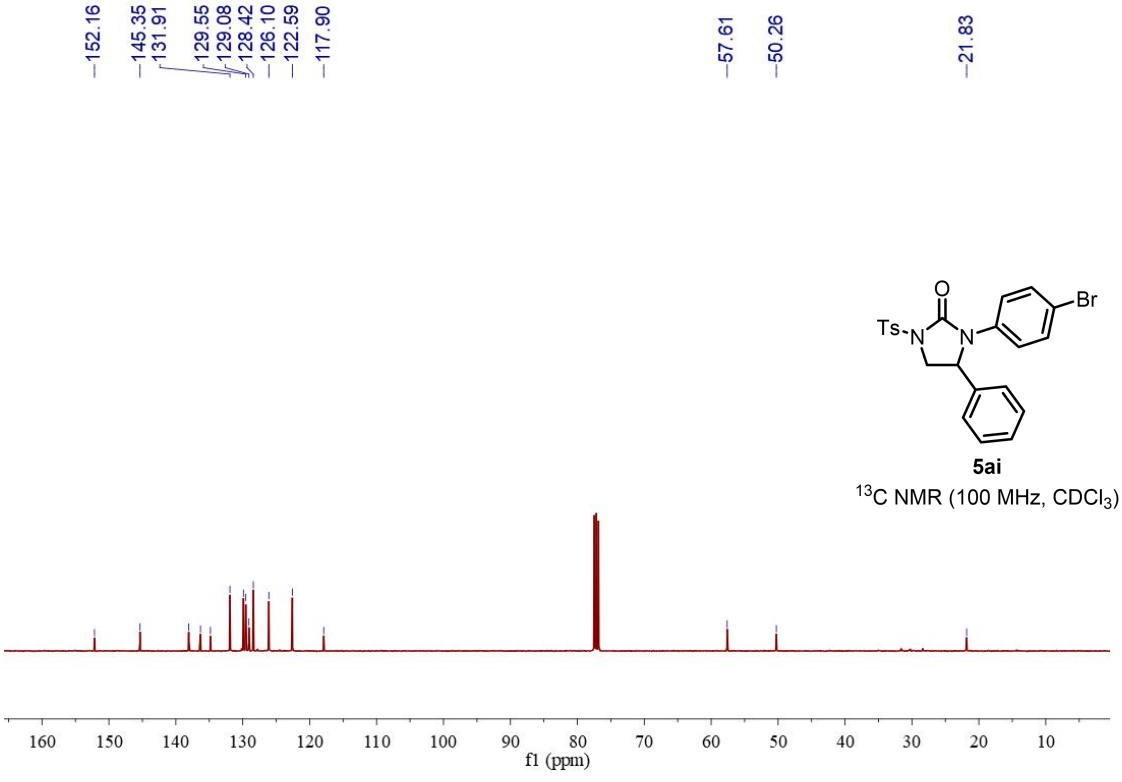
5aa

^{13}C NMR (100 MHz, $CDCl_3$)



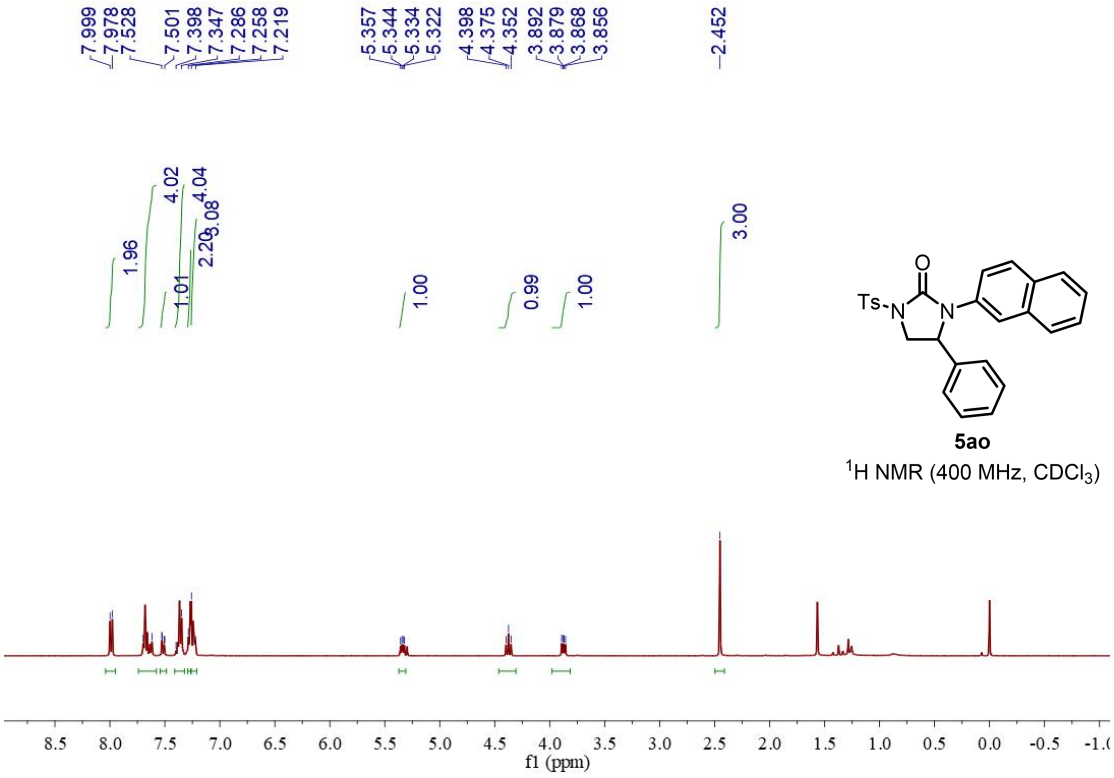
5ai

^{1}H NMR (400 MHz, $CDCl_3$)



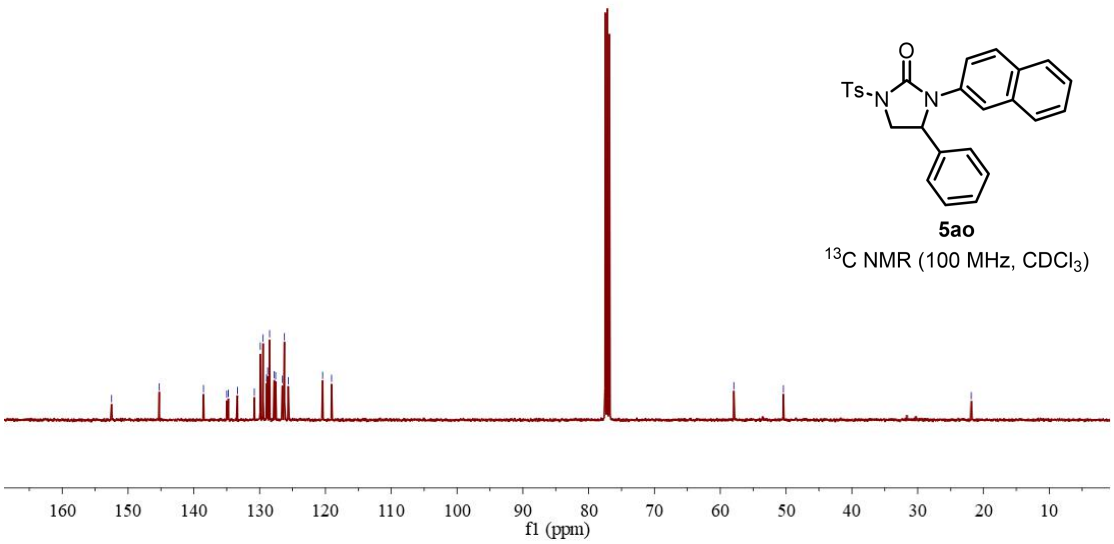
5ai

^{13}C NMR (100 MHz, $CDCl_3$)



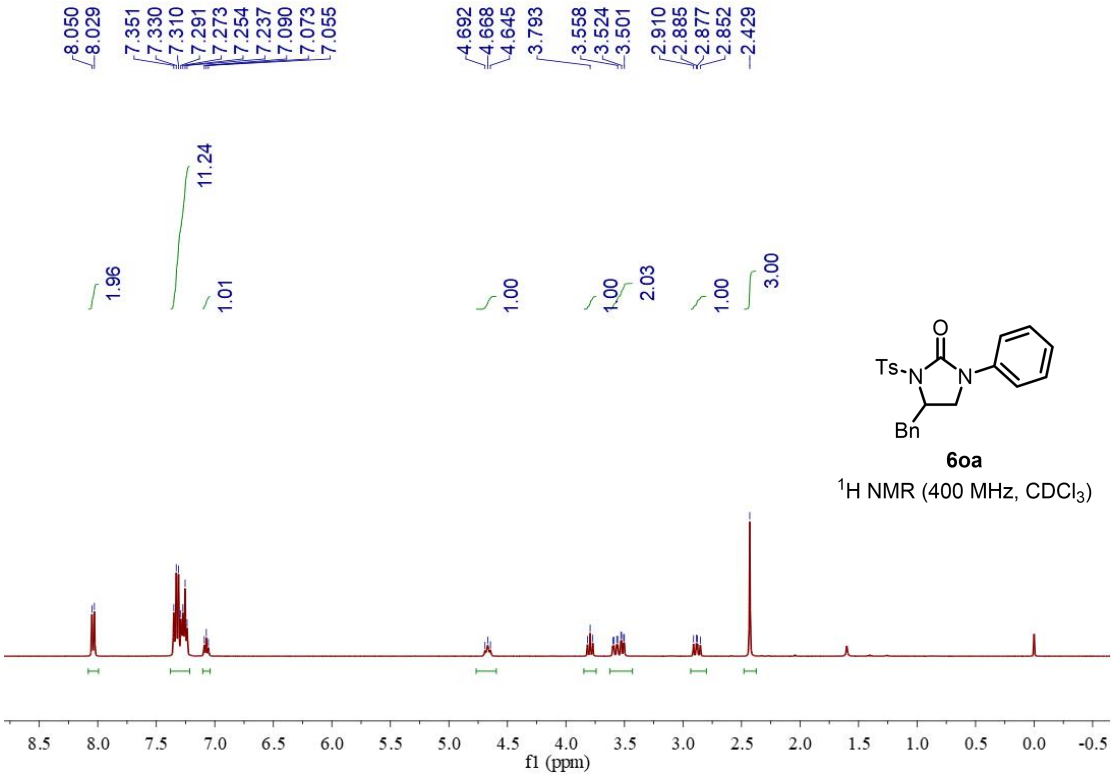
5ao

^{1}H NMR (400 MHz, $CDCl_3$)



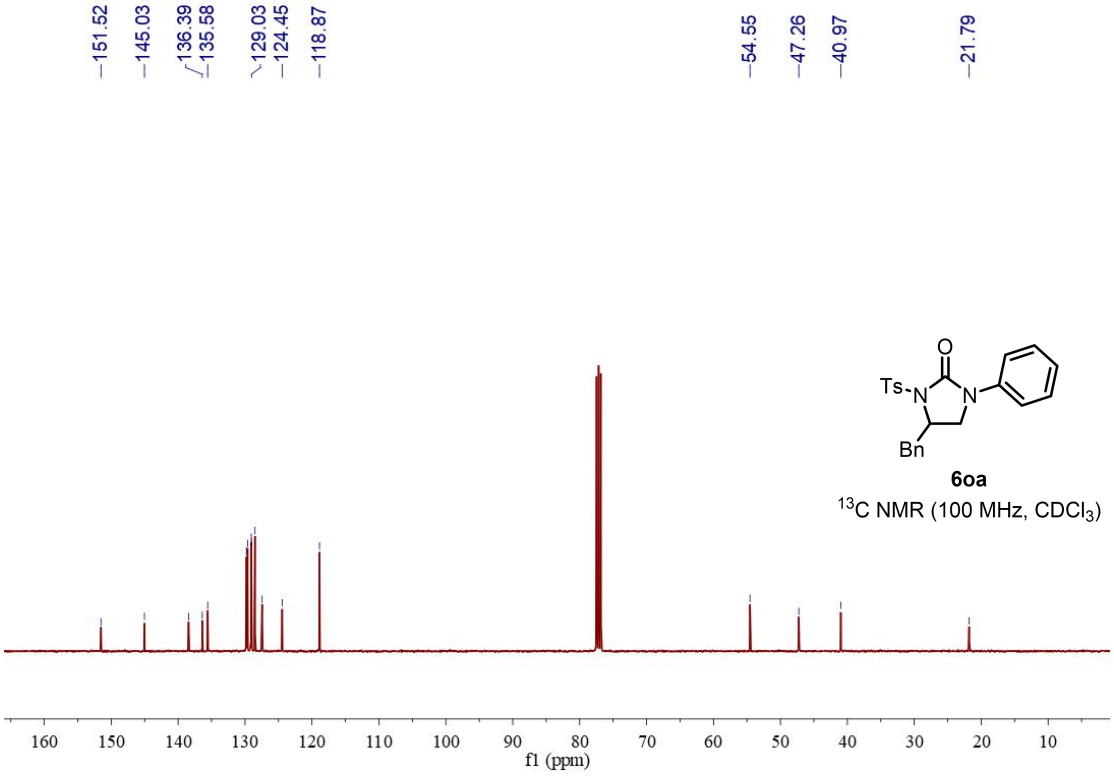
5ao

^{13}C NMR (100 MHz, $CDCl_3$)



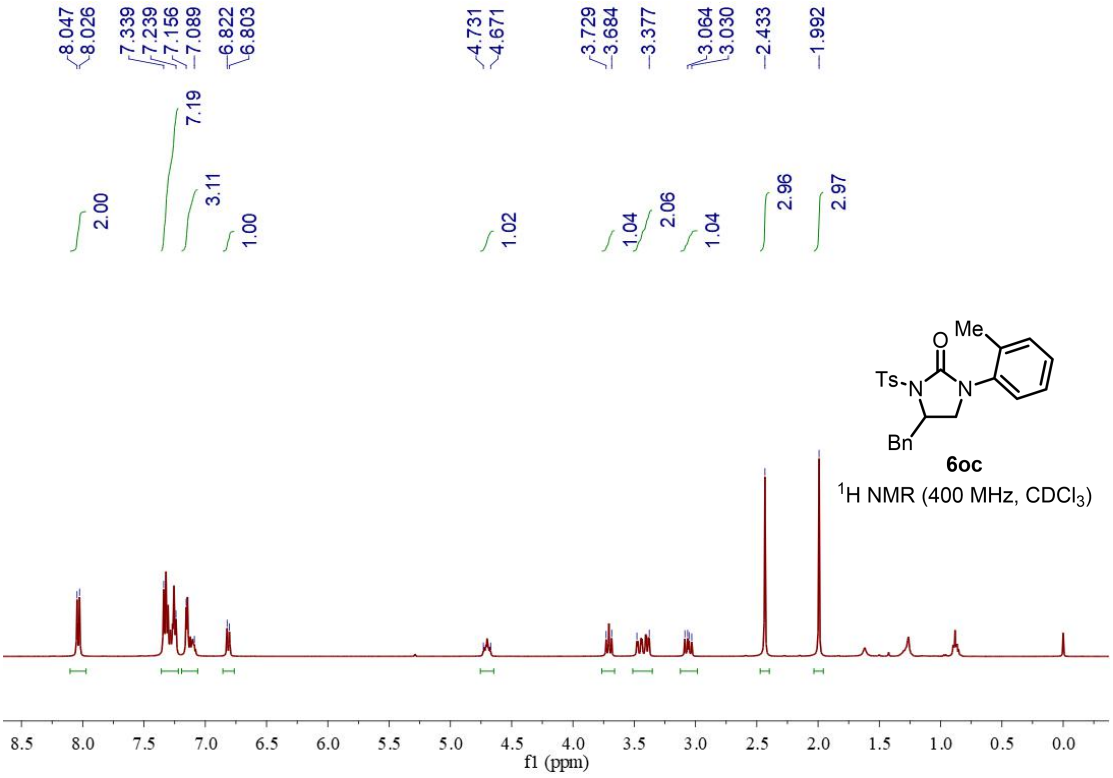
6oa

^{1}H NMR (400 MHz, $CDCl_3$)



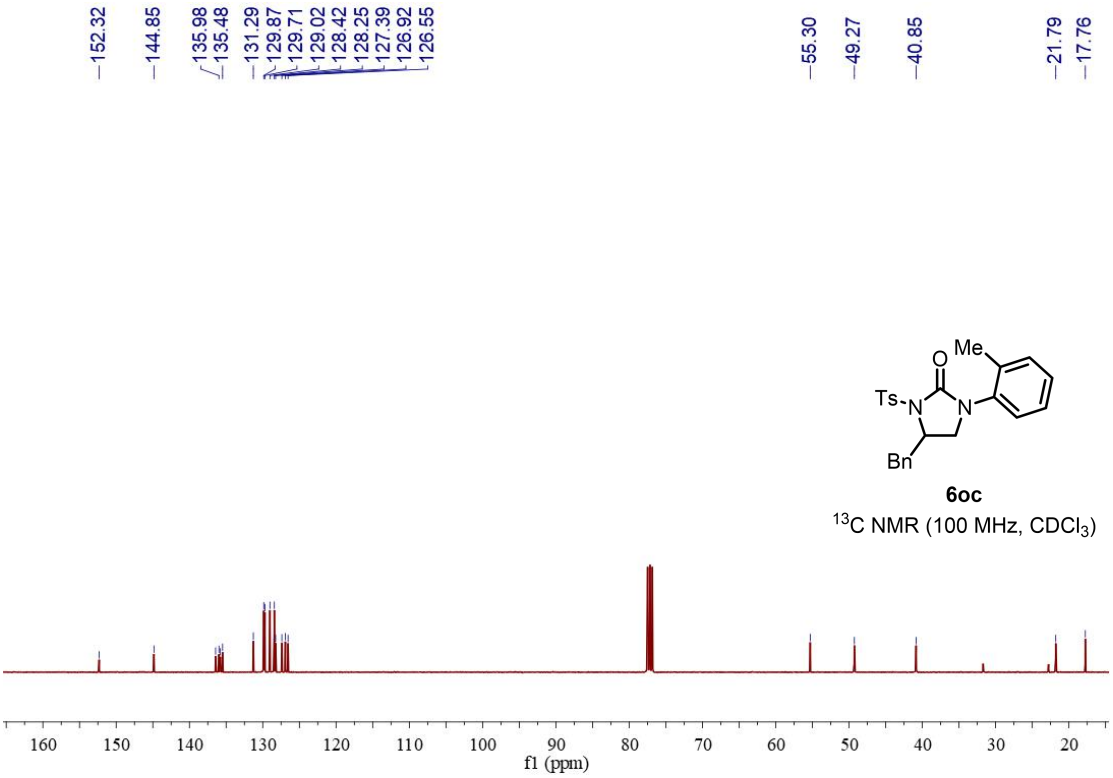
6oa

^{13}C NMR (100 MHz, $CDCl_3$)



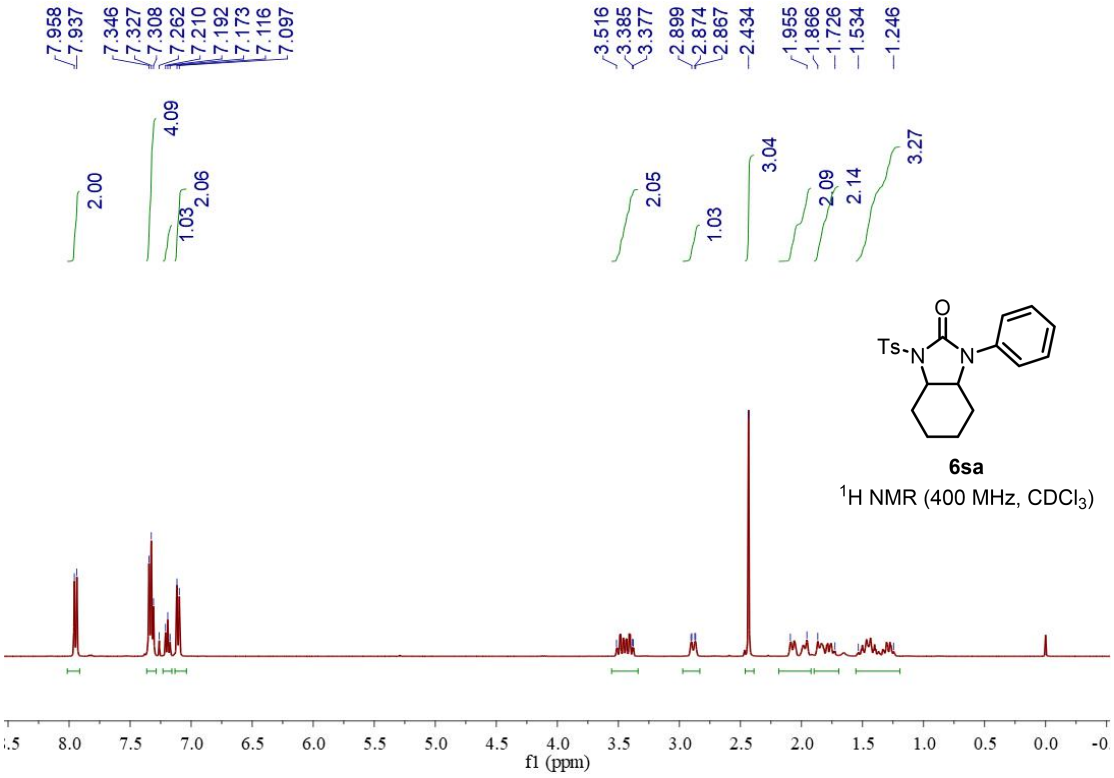
6oc

^{1}H NMR (400 MHz, $CDCl_3$)



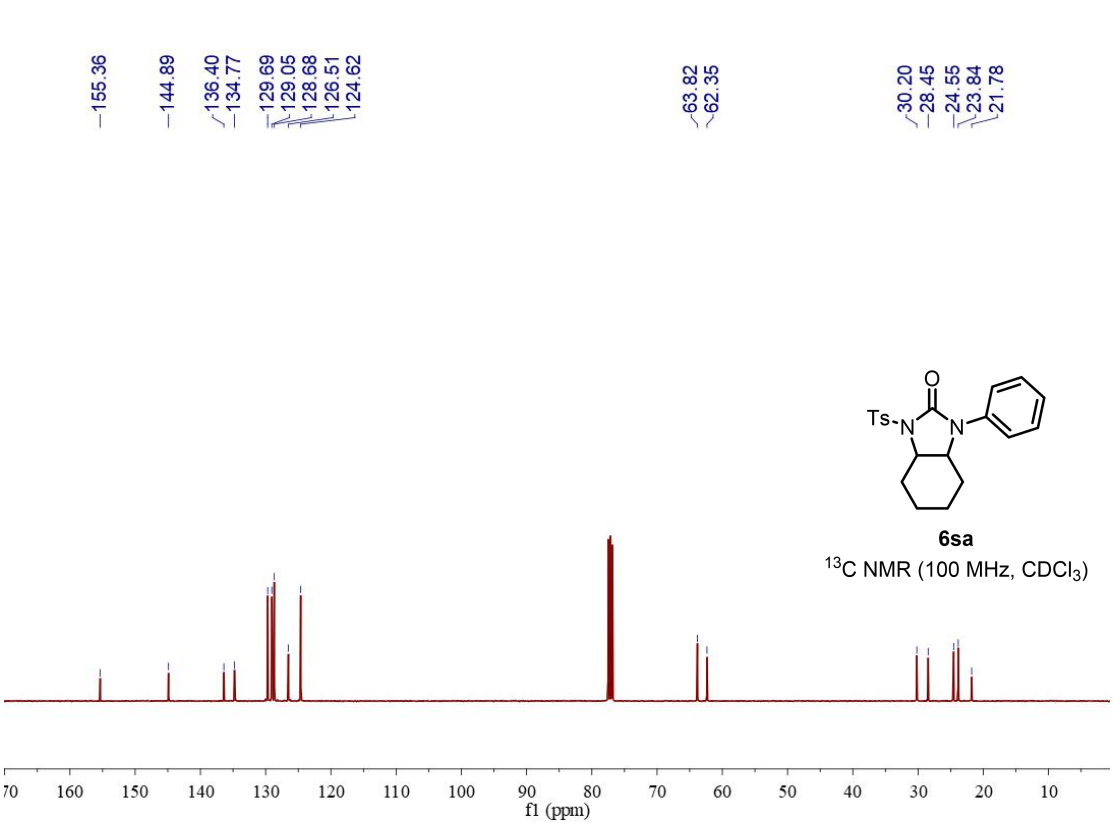
6oc

^{13}C NMR (100 MHz, $CDCl_3$)



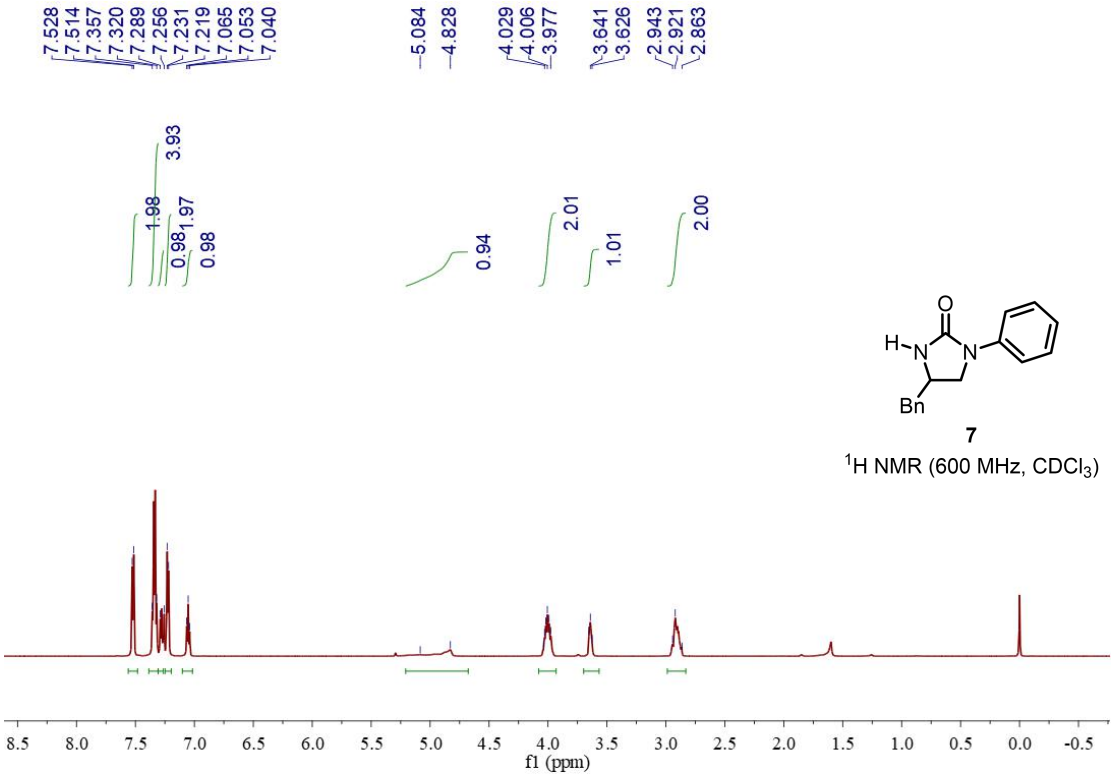
6sa

^{1}H NMR (400 MHz, $CDCl_3$)



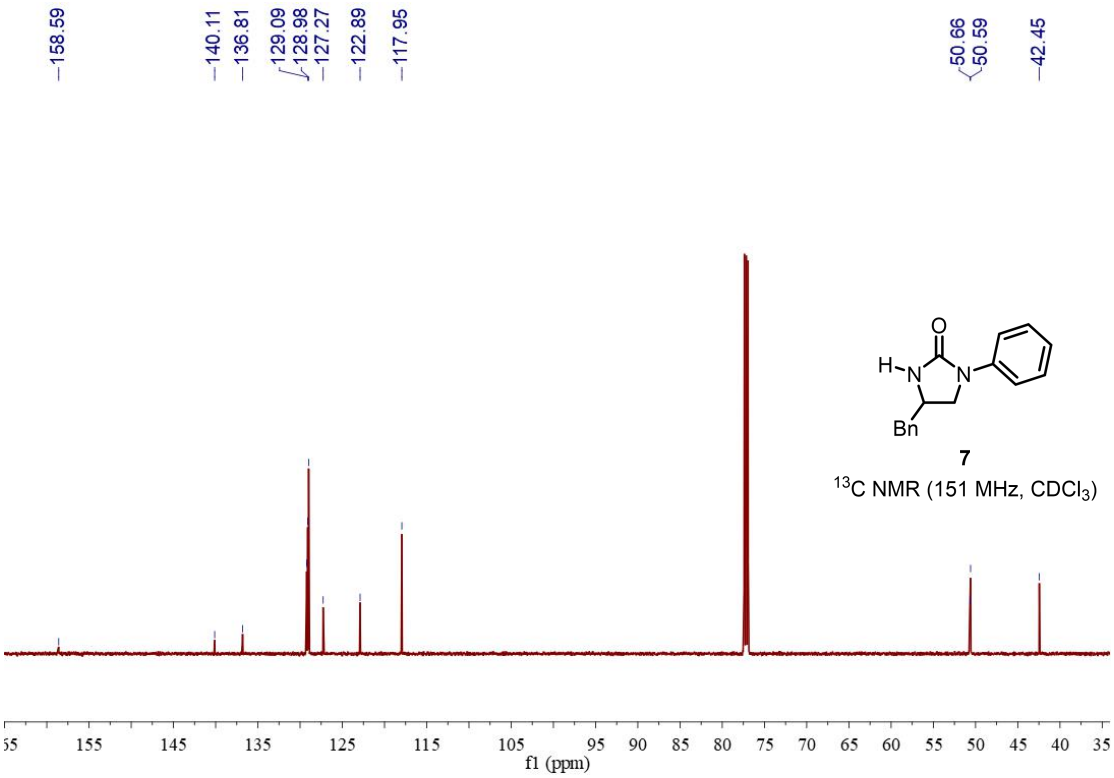
6sa

^{13}C NMR (100 MHz, $CDCl_3$)



7

^{1}H NMR (600 MHz, $CDCl_3$)



7

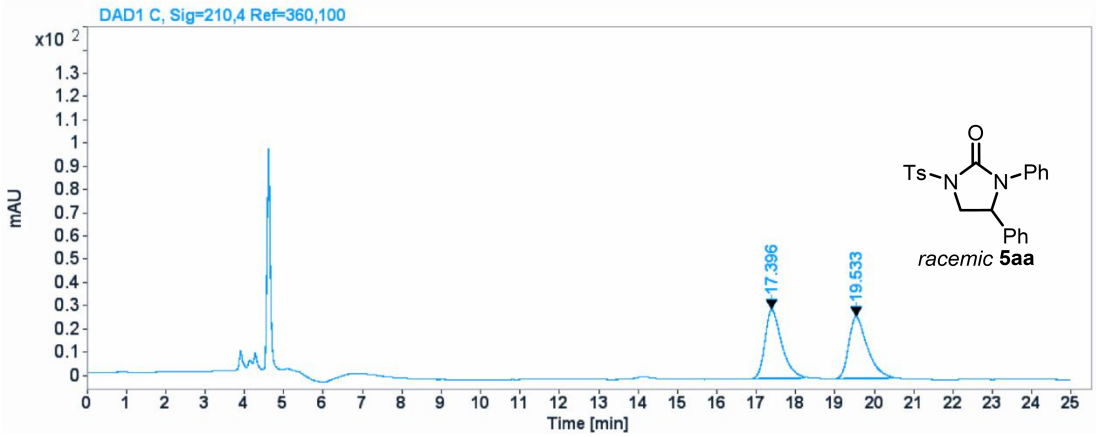
^{13}C NMR (151 MHz, $CDCl_3$)

5. HPLC Chromatograms

HPLC chromatogram of 5aa

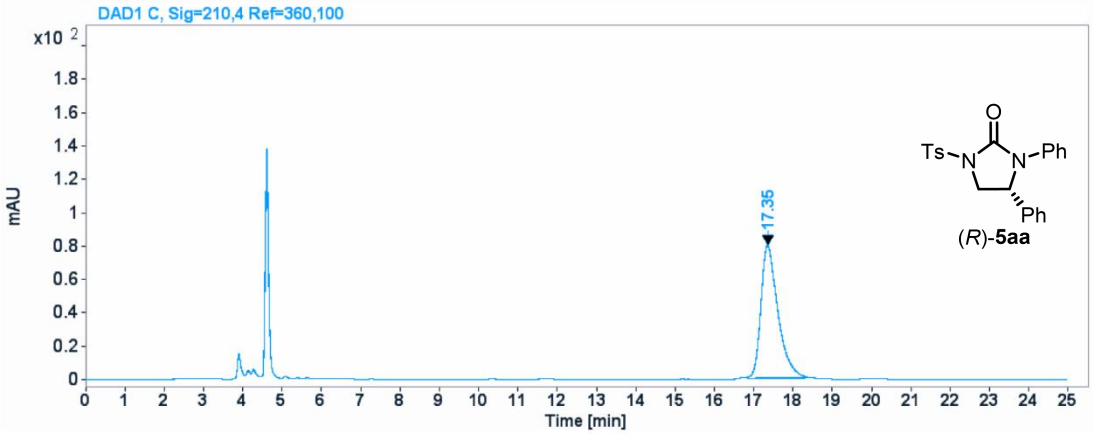
Enantiomeric excess was determined by HPLC with a Chiralpak® IB column (*n*-hexane/*i*-propanol = 75/25, 1.0 mL/min, 210 nm, 25 °C);

$t_r(R)$ = 17.396 min, $t_r(S)$ = 19.533 min; >99% ee.



Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
17.396	0.441	870.360	29.589	50.1209
19.533	0.484	866.160	26.465	49.8791
	Sum	1736.5195		



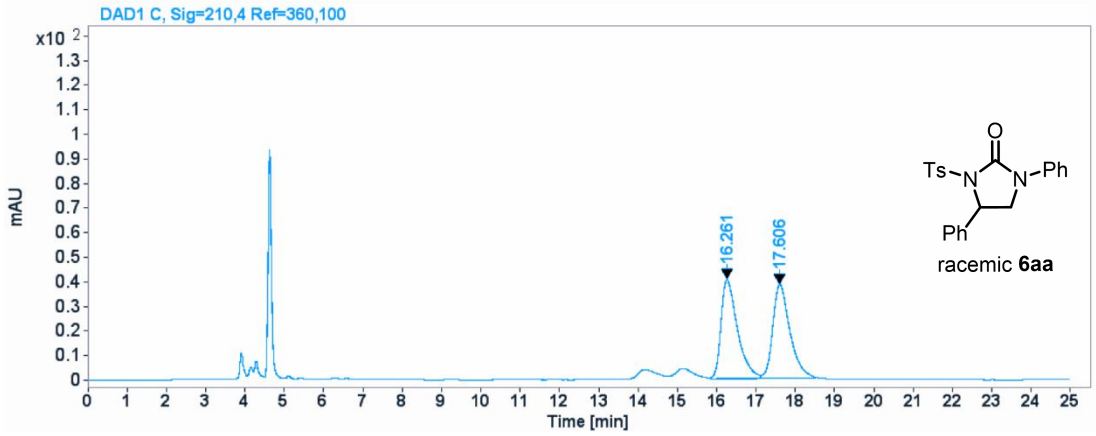
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
17.350	0.448	2415.292	80.088	100.0000
	Sum	2415.2915		

HPLC chromatogram of 6aa

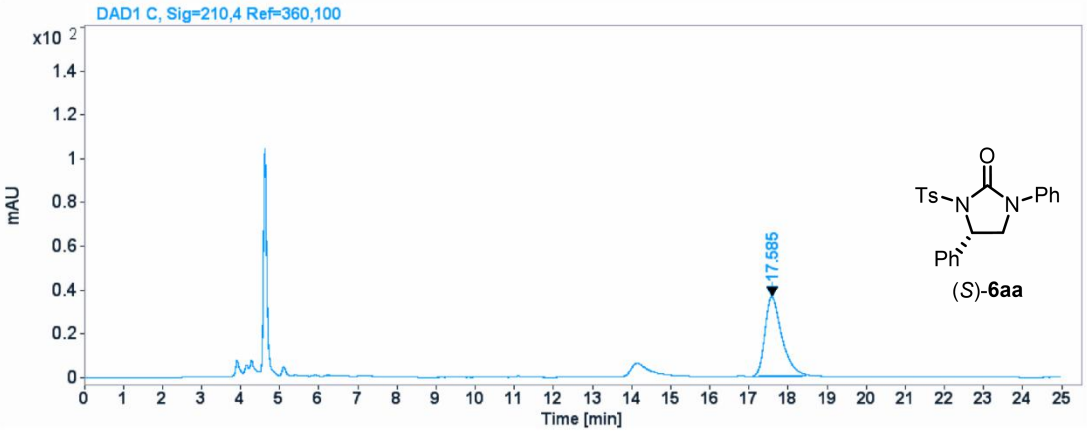
Enantiomeric excess was determined by HPLC with a Chiralpak® IB column (*n*-hexane/*i*-propanol = 75/25, 1.0 mL/min, 210 nm, 25 °C);

$t_r(R)$ = 16.261 min, $t_r(S)$ = 17.606 min; >99% ee.



Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
16.261	0.428	1160.281	40.313	50.1472
17.606	0.452	1153.468	38.274	49.8528
	Sum	2313.7491		



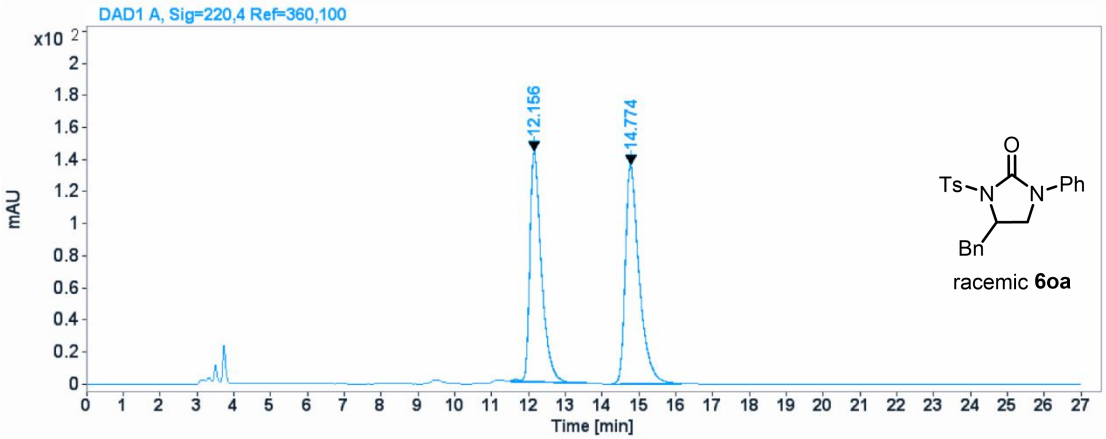
Signal: DAD1 C, Sig=210,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
17.585	0.447	1079.166	36.126	100.0000
	Sum	1079.1663		

HPLC chromatogram of 6oa

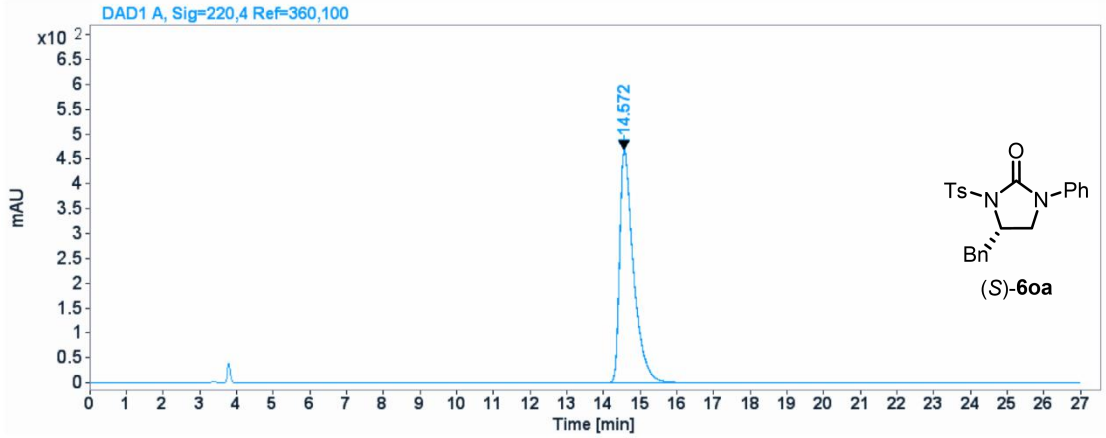
Enantiomeric excess was determined by HPLC with a Chiralpak® IB column (*n*-hexane/*i*-propanol = 80/20, 1.0 mL/min, 220 nm, 25 °C);

$t_r(R)$ = 12.156 min, $t_r(S)$ = 14.774 min; >99% ee.



Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
12.156	0.323	3138.951	143.761	46.8087
14.774	0.387	3566.966	136.394	53.1913
	Sum	6705.9170		



Signal: DAD1 A, Sig=220,4 Ref=360,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%
14.572	0.387	12224.776	467.296	100.0000
	Sum	12224.7764		

6. Single-Crystal X-Ray Diffraction Data

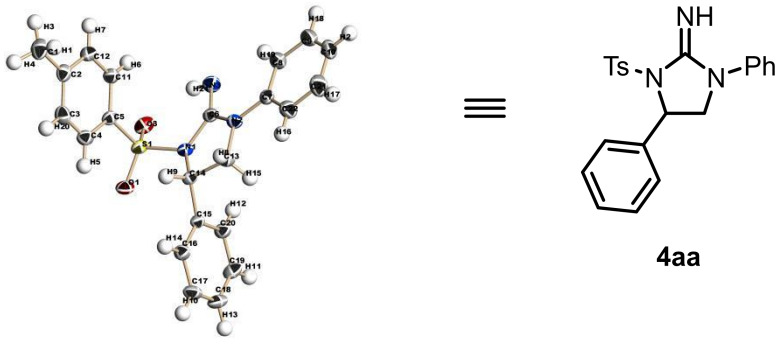


Fig S-1. ORTEP drawing of **4aa (**CCDC 2129607**)** with 50% ellipsoid probability

Identification code	**4aa**	
Empirical formula	$C_{22}H_{21}N_3O_2S$	
Formula weight	391.48 g/mol	
Temperature	276(2) K	
Wavelength	1.54178 Å	
Crystal system, space group	Monoclinic, P 1 21/n 1	
Unit cell dimensions	a = 8.6347(16) Å	α = 90°
	b = 6.1566(11) Å	β =95.175(7)°
	c = 35.983(7) Å	γ = 90°
Volume	1905.1(6) $Å^3$	
Z	4	
Absorption coefficient	1.698 mm^{-1}	
F(000)	824	
Theta range for data collection	2.47 to 65.49°	
imiting indices	-8<=h<=10, -7<=k<=7, -42<=l<=42	
Absorption correction	Multi-Scan	
Data / parameters	3183/258	
Goodness-of-fit on F^2	1.096	
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1052	
R indices (all data)	R1 = 0.0521, wR2 = 0.1107	
Largest diff. peak and hole	0.337 and -0.419 $eÅ^{-3}$	

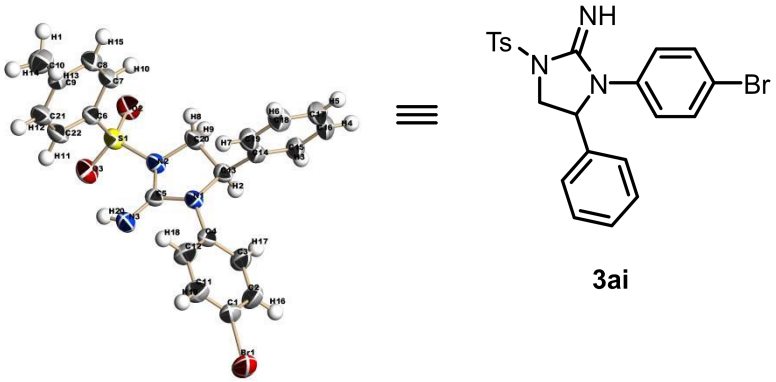


Fig S-1. ORTEP drawing of **3ai (**CCDC 2129608**)** with 50% ellipsoid probability

Identification code	**3ai**	
Empirical formula	$C_{22}H_{20}BrN_3O_2S$	
Formula weight	470.38 g/mol	
Temperature	301(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Triclinic, P -1	
Unit cell dimensions	a = 8.4289(7) Å	α = 102.292(3)°
	b = 8.9127(7) Å	β =92.181(4)°
	c = 14.3601(13) Å	γ = 93.615(3)°
Volume	1050.50(15) $Å^3$	
Z	2	
Absorption coefficient	2.079 mm^{-1}	
F(000)	480	
Theta range for data collection	2.35 to 28.34°	
Limiting indices	-11<=h<=11, -11<=k<=11, -19<=l<=19	
Absorption correction	Multi-Scan	
Data / parameters	5229/267	
Goodness-of-fit on F^2	1.033	
Final R indices [I>2sigma(I)]	R1 = 0.0346, wR2 = 0.0869	
R indices (all data)	R1 = 0.0460, wR2 = 0.0941	
Largest diff. peak and hole	0.434 and -0.577 $eÅ^{-3}$	

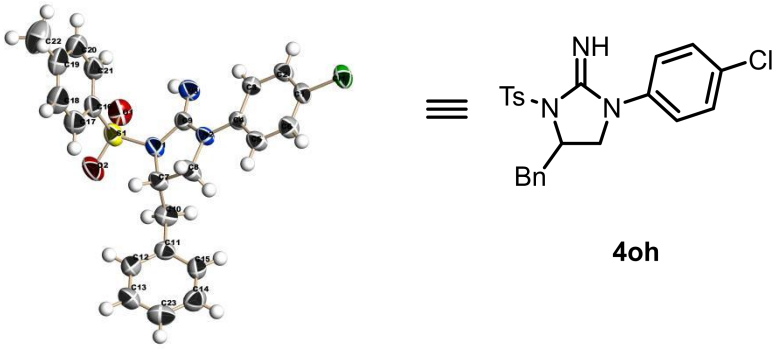


Fig S-1. ORTEP drawing of **4oh (**CCDC 2129609**)** with 50% ellipsoid probability

Identification code	**4oh**	
Empirical formula	$C_{23}H_{22}ClN_3O_2S$	
Formula weight	439.94 g/mol	
Temperature	306(2) K	
Wavelength	0.71073 Å	
Crystal system, space group	Monoclinic, P 1 21/n 1	
Unit cell dimensions	a = 13.4605(8) Å	α = 90°
	b = 8.4799(5) Å	β =102.521(2)°
	c = 19.7332(12) Å	γ = 90°
Volume	2198.9(2) $Å^3$	
Z	4	
Absorption coefficient	0.293 mm^{-1}	
F(000)	920	
Theta range for data collection	2.62 to 26.53°	
Limiting indices	-16<=h<=16, -10<=k<=10, -24<=l<=24	
Absorption correction	Multi-Scan	
Data / parameters	4540/275	
Goodness-of-fit on F^2	1.009	
Final R indices [I>2sigma(I)]	R1 = 0.0635, wR2 = 0.1352	
R indices (all data)	R1 = 0.1273, wR2 = 0.1715	
Largest diff. peak and hole	0.210 and -0.322 $eÅ^{-3}$	