Supporting Information

Rhodium-Catalyzed C–C Bond Alkenylation and Arylation of *α*-Branched *N*-Sulfonyl Amines

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Table of Contents

1. General Information

Solvents

Anhydrous tetrahydrofuran, 1,4-dioxane and toluene were freshly distilled from sodium-benzophenone. Anhydrous 1,2-dimethoxyethane (DME) and 1,2-dichlorethane (DCE) were purchased from Energy Chemical (water ≤ 50 ppm by K.F.) and stored in glove box with 4 Å molecular sieves. Chloroform-d_1 and DMSO-d_6 were purchased from J&K Scientific Co., Ltd.

Chromatography

Thin layer chromatography (TLC) (250 μm thickness, F-254 indicator) and visualized by UV irradiation and staining with phosphomolybdic acid or iodine developing agents. Flash column chromatography was performed on 0.25 mm silica gel 60-F254, which was purchased from Yantai Jiangyou Co., China.

Spectroscopy and Instruments

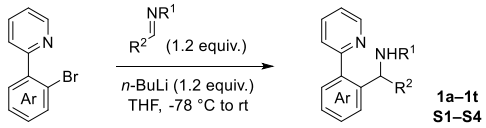
Proton nuclear magnetic resonance (^{1}H NMR) and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Bruker AVANCE NEO instrument (500 MHz and 600 MHz). Chemical shifts are reported in parts per million (ppm) referenced to the center peak of the residual solvent signal (^{1}H NMR: $CDCl_3$ = 7.26 ppm, DMSO-d_6 = 2.50 ppm; ^{13}C NMR: $CDCl_3$ = 77.00 ppm, DMSO-d_6 = 39.5 ppm). Peak multiplicities are reported as follows: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, coupling constants, *J*, were reported in Hertz unit (Hz). High-resolution mass spectra (HRMS) were recorded on a Waters Mass spectrometer using ESI-TOF (electrospray ionization-time of flight). X-ray crystallographic analyses were performed on Bruker D8 Venture.

Starting Materials

Dichloro(pentamethylcyclopentadienyl)rhodium(III) dimer and $RhCl_3 \cdot H_2O$ was purchased from Sinocompound Technology Co., Ltd. Silver carbonate and silver phosphate was purchased from J&K Scientific Co., Ltd. Other commercially available reagents were purchased from Energy Chemical and J&K Scientific Co., Ltd. All imines were synthesized following literature procedures[1] and diethoxydiarylsilanes were synthesized following literature procedures.[2] The $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$, $[Cp^*Rh(CH_3CN)_3](PF_6)_2$ and $[Cp^*Rh(CH_3CN)_3](BF_4)_2$ were synthesized following literature procedures.[3]

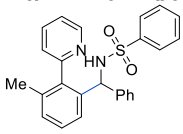
2. Experimental Procedures

2.1 Preparation of *α*-Branched Amines



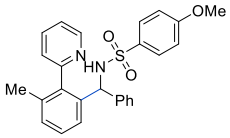
General procedure: The *α*-branched primary amines **1a–1t** and **S1–S4** were synthesized following this procedure. A 50 mL flame-dried flask was charged with stir bar, bromide[4] (3 mmol, 1.0 equiv.), and anhydrous THF (30 mL). *n*-BuLi solution (2.2 mL, 1.2 equiv., 1.6 M in hexane) was added dropwise to the reaction mixture at -78 °C. The mixture was stirred at -78 °C for 30 min, and then a solution of imine (3.6 mmol, 1.2 equiv.) in THF (10 mL) was added. The resulting reaction mixture was stirred -78 °C for 30 min, and then at room temperature for additional 2 hours. A saturated aqueous NH_4Cl solution (20 mL) was added at 0 °C. The mixture was extracted with ethyl acetate (30 mL), dried over Na_2SO_4, and then concentrated *in vacuo*. The residue was further purified by silica gel chromatography eluting with PE/EtOAc/CH_2Cl_2 (5:1:1, v/v/v) to afford the corresponding Ts-amine.

***N*-((3-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)benzenesulfonamide (S1)**



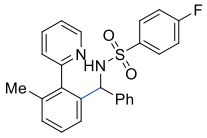
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) *δ* 8.63 (s, 1H), 8.47 (s, 1H), 7.70 (s, 1H), 7.60 (d, *J* = 6.9 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 3H), 7.35-7.29 (m, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 7.10-7.03 (m, 3H), 6.82 (s, 3H), 5.38 (s, 1H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) *δ* 157.4, 149.0, 141.2, 141.1, 139.0, 138.9, 135.9, 135.0, 131.6, 128.4, 128.3, 127.5, 127.5, 126.8, 126.4, 126.2, 124.7, 121.9, 57.2, 19.6. HRMS (ESI) *m/z* calcd. for $C_{25}H_{23}N_2O_2S$ $[M+H]^+$: 415.1475, found 415.1479.

4-methoxy-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)benzenesulfonamide (S2)



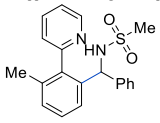
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) *δ* 8.63 (s, 1H), 8.35-8.20 (m, 1H), 7.70 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 6.9 Hz, 1H), 7.35-7.29 (m, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.11-7.05 (m, 3H), 6.92-6.88 (m, 2H), 6.83 (s, 2H), 5.33 (s, 1H), 3.79 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) *δ* 161.7, 157.4, 149.0, 141.3, 139.1, 138.9, 135.8, 135.0, 133.0, 128.4, 128.3, 127.5, 127.5, 126.9, 126.3, 124.8, 121.9, 113.6, 57.1, 55.4, 19.7. HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_2O_3S$ $[M+H]^+$: 445.1580, found 445.1585.

4-fluoro-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)benzenesulfonamide (S3)



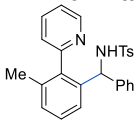
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) *δ* 8.65 (s, 1H), 8.51 (d, *J* = 8.6 Hz, 1H), 7.73 (s, 1H), 7.64 (s, 2H), 7.37-7.29 (m, 2H), 7.22-7.15 (m, 3H), 7.14 (d, *J* = 7.6 Hz, 1H), 7.12-7.07 (m, 3H), 6.83 (s, 2H), 5.37 (s, 1H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) *δ* 163.6 (d, *J* = 250.6 Hz), 157.3, 149.0, 140.9, 138.9, 138.7, 137.6 (d, *J* = 3.2 Hz), 135.9, 135.1, 129.2 (d, *J* = 9.3 Hz), 128.4, 127.6, 127.5, 126.9, 126.5, 124.7, 121.9, 115.3 (d, *J* = 22.3 Hz), 57.3, 19.6. HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}FN_2O_2S$ $[M+H]^+$: 433.1381, found 433.1384.

***N*-((3-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)methanesulfonamide (S4)**



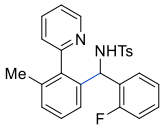
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) *δ* 8.68 (s, 1H), 8.03 (d, *J* = 9.0 Hz, 1H), 7.79 (s, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.42-7.31 (m, 2H), 7.25-7.20 (m, 3H), 7.19-7.13 (m, 1H), 7.07 (s, 2H), 5.42 (d, *J* = 9.0 Hz, 1H), 2.65 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) *δ* 157.5, 149.1, 141.9, 139.7, 139.2, 136.1, 135.3, 128.7, 128.0, 127.7, 126.7, 126.5, 124.9, 122.1, 56.8, 41.2, 19.8. HRMS (ESI) *m/z* calcd. for $C_{20}H_{21}N_2O_2S$ $[M+H]^+$: 353.1318, found 353.1319.

4-methyl-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(phenyl)methyl)benzenesulfonamide (1a)



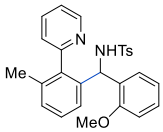
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.62 (s, 1H), 8.36 (s, 1H), 7.69 (s, 1H), 7.47 (d, J = 7.5 Hz, 2H), 7.37 (d, J = 6.8 Hz, 1H), 7.35-7.29 (m, 1H), 7.23-7.17 (m, 3H), 7.14 (d, J = 7.5 Hz, 1H), 7.10-7.05 (m, 3H), 6.82 (s, 2H), 5.35 (s, 1H), 2.32 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.4, 149.0, 141.9, 141.3, 139.2, 138.9, 138.4, 135.8, 135.0, 128.8, 128.3, 127.5, 127.5, 126.8, 126.3, 126.2, 124.7, 121.9, 57.1, 20.6, 19.7. HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_2O_2S$ [M+H]$^+$: 429.1631, found 429.1637.

***N*-((2-fluorophenyl)(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1b)**



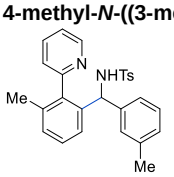
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.56 (s, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.67 (s, 1H), 7.46 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.8 Hz, 1H), 7.31-7.28 (m, 1H), 7.22 (t, J = 7.7 Hz, 1H), 7.18-7.15 (m, 3H), 7.15-7.09 (m, 1H), 6.93-6.88 (m, 2H), 6.80-6.74 (m, 1H), 5.72 (d, J = 8.0 Hz, 1H), 2.31 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 158.7 (d, J = 247.3 Hz), 157.1 , 149.0, 141.8, 139.0, 138.3, 137.8, 135.8, 135.2, 129.4 (d, J = 3.3 Hz), 128.6, 128.6 (d, J = 29.7 Hz), 128.5, 127.7 (d, J = 14.1 Hz), 127.2, 126.2, 124.7, 124.3, 123.4 (d, J = 3.4 Hz), 121.7, 114.5 (d, J = 21.8 Hz), 50.8, 20.6, 19.5. HRMS (ESI) *m/z* calcd. for $C_{26}H_{24}FN_2O_2S$ [M+H]$^+$: 447.1537, found 447.1539.

***N*-((2-methoxyphenyl)(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1c)**



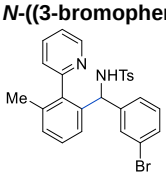
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.55 (s, 1H), 7.93 (s, 1H), 7.76-7.53 (m, 1H), 7.51 (d, J = 7.9 Hz, 1H), 7.48 (d, J = 8.0 Hz, 2H), 7.31-7.21 (m, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.14 (d, J = 7.5 Hz, 1H), 7.03 (td, J = 7.8, 1.7 Hz, 1H), 6.83 (d, J = 7.6 Hz, 1H), 6.64 (t, J = 7.5 Hz, 1H), 6.56 (d, J = 8.2 Hz, 1H), 5.81 (d, J = 7.8 Hz, 1H), 3.17 (s, 3H), 2.32 (s, 3H), 1.87 (s, 3H).^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.5, 155.4, 148.8, 141.5, 139.6, 139.1, 138.7, 135.4, 135.0, 128.7, 128.6, 128.4, 128.0, 127.8, 126.9, 126.3, 124.9, 124.4, 121.3, 119.3, 109.9, 54.4, 51.0, 20.6, 19.5. HRMS (ESI) *m/z* calcd. for $C_{27}H_{27}N_2O_3S$ [M+H]$^+$: 459.1737, found 459.1736.

4-methyl-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(m-tolyl)methyl)benzenesulfonamide (1d)



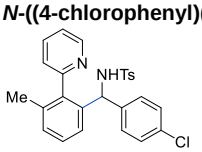
White solid. ^{1}H NMR (500 MHz, DMSO-d_6, 60 °C) δ 8.63 (d, J = 4.8 Hz, 1H), 8.29 (d, J = 7.4 Hz, 1H), 7.69 (s, 1H), 7.46 (d, J = 7.9 Hz, 2H), 7.42-7.29 (m, 2H), 7.24-7.12 (m, 4H), 6.94 (t, J = 7.6 Hz, 1H), 6.86 (d, J = 7.5 Hz, 1H), 6.68-6.39 (m, 2H), 5.32 (s, 1H), 2.31 (s, 3H), 2.07 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, 60 °C) δ 157.5, 149.0, 141.9, 141.0, 139.4, 138.9, 138.5, 136.5, 135.9, 135.1, 128.8, 128.4, 127.6, 127.5, 127.5, 127.0, 126.3, 124.9, 124.1, 121.9, 57.3, 20.7, 19.7. HRMS (ESI) *m/z* calcd. for $C_{27}H_{27}N_2O_2S$ [M+H]$^+$: 443.1788, found 443.1790.

***N*-((3-bromophenyl)(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1e)**



White solid. ^{1}H NMR (500 MHz, DMSO-d_6, 60 °C) δ 8.62 (d, J = 4.9 Hz, 1H), 8.44 (s, 1H), 7.71 (s, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.39-7.30 (m, 2H), 7.28-7.14 (m, 5H), 7.03 (t, J = 7.8 Hz, 1H), 6.93-6.75 (m, 2H), 5.33 (s, 1H), 2.32 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6, 60 °C) δ 157.2, 149.1, 143.8, 142.2, 138.9, 138.6, 138.1, 136.1, 135.3, 129.7, 129.5, 129.3, 129.0, 128.8, 127.8, 126.2, 125.9, 124.9, 124.7, 122.1, 121.0, 56.8, 20.7, 19.7. HRMS (ESI) *m/z* calcd. for $C_{26}H_{24}BrN_2O_2S$ [M+H]$^+$: 507.0736, found 507.0742.

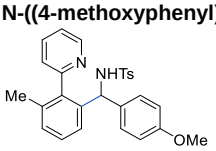
***N*-((4-chlorophenyl)(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1f)**



White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.17 (s, 1H), 7.97 (d, J = 8.4 Hz, 1H), 7.26 (s, 1H), 7.01 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.9 Hz, 1H), 6.89-6.85 (m, 1H), 6.78 (t, J = 7.7 Hz, 1H), 6.76-6.66 (m, 5H), 6.52-6.33 (m, 2H), 4.89 (s, 1H), 1.87 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (151

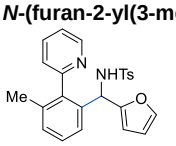
MHz, DMSO-d_6, 60 °C) δ 157.2, 149.0, 142.0, 140.3, 138.9, 138.7, 138.2, 135.9, 135.1, 131.2, 128.8, 128.6, 128.5, 127.7, 127.4, 126.2, 124.8, 121.9, 56.6, 20.6, 19.7. HRMS (ESI) *m/z* calcd. for $C_{26}H_{24}ClN_2O_2S$ $[M+H]^+$: 463.1242, found 463.1245.

N-((4-methoxyphenyl)(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1g)



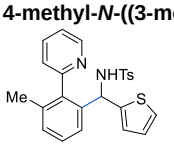
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.62 (s, 1H), 8.27 (s, 1H), 7.77-7.68 (m, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.42-7.34 (m, 1H), 7.34-7.29 (m, 1H), 7.24-7.15 (m, 3H), 7.13 (d, *J* = 7.5 Hz, 1H), 6.82-6.56 (m, 4H), 5.27 (s, 1H), 3.65 (s, 3H), 2.32 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.8, 157.5, 149.0, 141.8, 138.8, 138.4, 135.8, 134.9, 133.3, 129.0, 128.7, 128.1, 128.1, 127.5, 126.2, 125.4, 124.7, 121.8, 113.0, 56.6, 54.8, 20.6, 19.6. HRMS (ESI) *m/z* calcd. for $C_{27}H_{27}N_2O_3S$ $[M+H]^+$: 459.1737, found 459.1734.

***N*-(furan-2-yl(3-methyl-2-(pyridin-2-yl)phenyl)methyl)-4-methylbenzenesulfonamide (1h)**



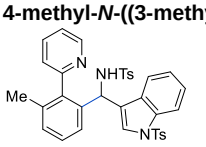
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.63 (m, 1H), 8.42 (d, *J* = 7.2 Hz, 1H), 7.77 (t, *J* = 7.3 Hz, 1H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.36-7.31 (m, 2H), 7.23-7.15 (m, 4H), 7.03 (s, 1H), 6.19-6.12 (m, 1H), 5.61 (d, *J* = 3.2 Hz, 1H), 5.32 (s, 1H), 2.32 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.1, 153.1, 149.0, 141.9, 141.8, 138.9, 138.3, 136.8, 135.8, 135.0, 128.7, 128.7, 127.5, 126.2, 124.8, 124.5, 121.9, 109.9, 107.3, 51.6, 20.6, 19.6. HRMS (ESI) *m/z* calcd. for $C_{26}H_{25}N_2O_2S$ $[M+H]^+$: 429.1631, found 429.1637.

4-methyl-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(thiophen-2-yl)methyl)benzenesulfonamide (1i)



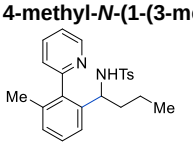
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.63 (s, 1H), 8.57 (d, *J* = 5.5 Hz, 1H), 7.75 (t, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.7 Hz, 1H), 7.36-7.31 (m, 1H), 7.25 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.23-7.14 (m, 4H), 6.98 (s, 1H), 6.75 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.37 (s, 1H), 5.48 (s, 1H), 2.32 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.1, 149.0, 145.5, 141.9, 138.9, 138.6, 138.2, 135.8, 134.9, 128.8, 128.6, 127.6, 126.3, 126.0, 125.3, 125.1, 124.6, 124.5, 121.9, 53.2, 20.6, 19.7. HRMS (ESI) *m/z* calcd. for $C_{24}H_{23}N_2O_2S_2$ $[M+H]^+$: 435.1195, found 435.1206.

4-methyl-*N*-((3-methyl-2-(pyridin-2-yl)phenyl)(1-tosyl-1H-indol-3-yl)methyl)benzenesulfonamide (1j)



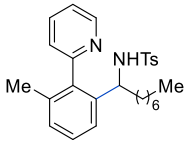
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.54 (s, 1H), 8.37 (d, *J* = 7.3 Hz, 1H), 7.74 (d, *J* = 8.4 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64-7.44 (m, 3H), 7.41-7.33 (m, 3H), 7.28-7.17 (m, 4H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.08-7.00 (m, 2H), 6.90 (s, 1H), 5.55 (d, *J* = 5.1 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 1.94 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 157.1, 149.0, 145.2, 142.0, 138.9, 138.2, 137.6, 135.8, 135.1, 134.1, 134.1, 129.9, 128.8, 128.7, 128.3, 127.6, 126.3, 126.2, 124.8, 124.6, 124.4, 123.3, 122.7, 121.9, 119.9, 112.6, 50.1, 20.7, 20.6, 19.6. HRMS (ESI) *m/z* calcd. for $C_{35}H_{32}N_3O_4S_2$ $[M+H]^+$: 622.1829, found 622.1857.

4-methyl-*N*-(1-(3-methyl-2-(pyridin-2-yl)phenyl)butyl)benzenesulfonamide (1k)



White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.75 (m, 1H), 7.52 (m, 2H), 7.35-7.26 (m, 1H), 7.21 (m, 1H), 7.06 (m, 4H), 7.00 (m, 1H), 6.28 (s, 1H), 4.04 (q, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 1.98 (s, 3H), 1.32-1.14 (m, 2H), 1.11-1.04 (m, 1H),, 0.90 (m, 1H), 0.54 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.8, 149.3, 142.5, 139.4, 138.4, 138.0, 136.3, 136.0, 129.0, 128.9, 128.0, 127.0, 125.5, 122.1, 56.8, 38.7, 21.4, 20.3, 19.0, 13.1. HRMS (ESI) *m/z* calcd. for $C_{23}H_{27}N_2O_2S$ $[M+H]^+$: 395.1793, found 395.1796.

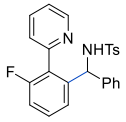
4-methyl-*N*-(1-(3-methyl-2-(pyridin-2-yl)phenyl)octyl)benzenesulfonamide (1l)



White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 4.9 Hz, 1H), 7.79-7.73 (m, 1H), 7.56-7.50 (m, 2H), 7.33-7.22 (m, 2H), 7.12-6.85 (m, 5H), 6.20 (s, 1H), 4.02 (q, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 1.99 (s, 3H), 1.33-1.12 (m, 4H), 1.10-0.96 (m, 5H), 0.88-0.85 (m, 3H), 0.83 (t, *J* = 7.3 Hz,

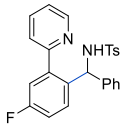
3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.3, 142.5, 139.5, 138.4, 138.0, 136.3, 136.1, 129.0, 129.0, 128.0, 127.0, 125.6, 122.1, 57.1, 36.6, 31.6, 28.9, 28.7, 25.9, 22.5, 21.4, 20.4, 14.0. HRMS (ESI) *m/z* calcd. for $C_{27}H_{35}N_2O_2S$ $[M+H]^+$: 451.2419, found 451.2423.

***N*-((3-fluoro-2-(pyridin-2-yl)phenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (1m)**



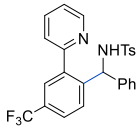
White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 5.0 Hz, 1H), 8.24 (d, *J* = 9.4 Hz, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.40-7.32 (m, 1H), 7.12-7.07 (m, 3H), 7.07-7.03 (m, 1H), 7.02-6.96 (m, 1H), 6.94-6.90 (m, 3H), 6.88-6.83 (m, 3H), 6.82-6.78 (m, 1H), 5.67 (d, *J* = 9.4 Hz, 1H), 2.35 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4 (d, *J* = 246.4 Hz), 153.0, 148.3, 142.5, 142.4, 140.1, 138.5, 136.1, 129.4 (d, *J* = 8.9 Hz), 129.1, 127.5, 127.1 (d, *J* = 15.3 Hz), 126.9, 126.7 (d, *J* = 3.7 Hz), 126.4, 126.2 (d, *J* = 3.2 Hz), 125.7, 122.5, 115.2 (d, *J* = 23.7 Hz), 60.8, 21.4. HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}FN_2O_2S$ $[M+H]^+$: 433.1381, found 433.1384.

***N*-((4-fluoro-2-(pyridin-2-yl)phenyl)(phenyl)methyl)-4-methylbenzenesulfonamide (1o)**



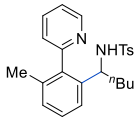
White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 1H), 8.59-8.52 (m, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.47 (td, *J* = 7.8, 1.8 Hz, 1H), 7.23-7.17 (m, 1H), 7.15-7.10 (m, 1H), 7.04 (d, *J* = 8.0 Hz, 2H), 7.02-6.91 (m, 6H), 6.88 (d, *J* = 7.9 Hz, 1H), 6.85-6.79 (m, 1H), 6.26 (d, *J* = 10.1 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1 (d, *J* = 246.1 Hz), 158.6 (d, *J* = 2.3 Hz), 147.6, 142.3, 141.6 (d, *J* = 3.0 Hz), 140.1, 138.2, 137.1, 128.9, 128.9, 128.0 (d, *J* = 14.2 Hz), 127.4, 127.0 (d, *J* = 3.2 Hz), 126.9, 126.2, 125.8, 124.6, 122.3, 115.3 (d, *J* = 24.8 Hz), 51.5, 21.4. HRMS (ESI) *m/z* calcd. for $C_{25}H_{22}FN_2O_2S$ $[M+H]^+$: 433.1381, found 433.1384.

4-methyl-*N*-(phenyl(2-(pyridin-2-yl)-4-(trifluoromethyl)phenyl)methyl)benzenesulfonamide (1p)



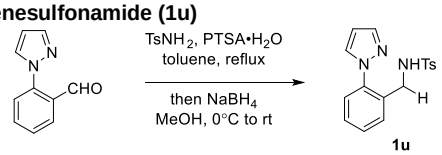
White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.8 Hz, 1H), 8.56-8.55 (m, 1H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.50 (td, *J* = 7.7, 1.8 Hz, 1H), 7.44 (s, 1H), 7.29-7.26 (m, 1H), 7.16-7.12 (m, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.95-6.90 (m, 6H), 5.78 (d, *J* = 9.6 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 158.4, 147.8, 143.4, 142.7, 139.9, 139.5, 138.4, 137.3, 131.5, 129.9 (q, *J* = 33.0 Hz), 129.1, 128.1 (q, *J* = 3.6 Hz), 127.6, 126.9, 126.6, 125.8, 124.7 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 270.5 Hz), 124.5, 122.6, 61.0, 21.2. HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}F_3N_2O_2S$ $[M+H]^+$: 483.1349, found 483.1362.

4-methyl-*N*-(1-(3-methyl-2-(pyridin-2-yl)phenyl)pentyl)benzenesulfonamide (1x)



White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 5.0 Hz, 1H), 7.76 (m, 1H), 7.53 (m, 2H), 7.31-7.29 (m, 1H), 7.23 (m, 1H), 7.07 (m, 4H), 7.00 (m, 1H), 6.29 (s, 1H), 4.05 (q, *J* = 7.5 Hz, 1H), 2.34 (s, 3H), 1.99 (s, 3H), 1.29-1.24 (m, 2H), 1.08-1.01 (m, 1H), 0.94-0.85 (m, 3H), 0.65 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.3, 142.5, 139.4, 138.4, 138.0, 136.3, 136.1, 129.0, 128.0, 127.0, 125.6, 125.6, 122.2, 57.3, 36.2, 28.0, 21.8, 21.4, 20.4, 13.7. HRMS (ESI) *m/z* calcd. for $C_{24}H_{29}N_2O_2S$ $[M+H]^+$: 409.1950, found 409.1957.

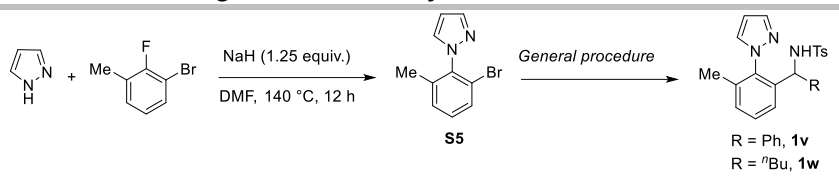
***N*-(2-(1*H*-pyrazol-1-yl)benzyl)-4-methylbenzenesulfonamide (1u)**



1u

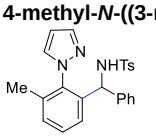
A 100 mL flame-dried flask was charged with stir bar, 2-(1*H*-pyrazol-1-yl)benzaldehyde[5] (1.7 g, 10.0 mmol, 1.0 equiv.), *p*-toluenesulfonamide (1.7 g, 10.0 mmol, 1.0 equiv.), PTSA·H_2O (190 mg, 1.0 mmol, 0.1 equiv.) and toluene (50 mL). The mixture was heated at reflux for 12 hours. After cooling to room temperature, toluene was removed *in vacuo* and methanol (20 mL) was added. The mixture reaction was added sodium borohydride (756 mg, 20.0 mmol, 2.0 equiv.) at 0 °C, and then at room temperature for 2 hours, 10 mL of water was added at 0 °C. The mixture was extracted with ethyl acetate (90 mL), dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was further purified by silica gel chromatography eluting with PE/EtOAc (8:1, v/v) to afford **1u**, a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69-7.65 (m, 2H), 7.62 (dd, *J* = 9.7, 2.2 Hz, 2H), 7.35-7.29 (m, 2H), 7.25-7.18 (m, 4H), 6.59 (t, *J* = 6.8 Hz, 1H), 6.42 (t, *J* = 2.2 Hz, 1H), 3.97 (d, *J* = 6.5 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 140.9, 139.5, 137.6, 132.4, 131.2, 130.3, 129.4, 128.9, 128.2, 127.0, 124.3, 107.2, 45.0, 21.5. HRMS (ESI) *m/z* calcd. for $C_{17}H_{18}N_3O_2S$ $[M+H]^+$: 328.1114, found 328.1122.



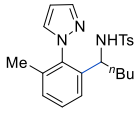
A 100 mL flame-dried flask was charged with stir bar, pyrazole (4.5 g, 6.6 mmol, 1.25 equiv.) and anhydrous DMF (20 mL). NaH (1.58 g, 6.6 mmol, 1.25 equiv.) was added to the reaction mixture at 0 °C. The mixture was stirred at 0 °C for 15 min, and then a solution of 1-bromo-2-fluoro-3-methylbenzene (10 g, 5.3 mmol, 1.0 equiv.) in anhydrous DMF (10 mL) was added. The resulting mixture was heated at 140 °C for 12 hours. After cooling to room temperature, 200 mL of water was added. The mixture was extracted with ethyl acetate (100 mL), dried over $MgSO_4$, and then concentrated *in vacuo*. The residue was further purified by silica gel chromatography eluting with PE/EtOAc (10:1, v/v) to afford bromide **S5**. Then, compounds **1v** and **1w** were synthesized from bromide **S5** following the above general procedure.

4-methyl-*N*-((3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)(phenyl)methyl)benzenesulfonamide (1v)



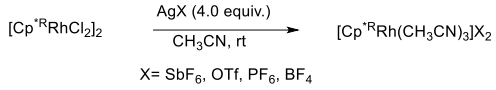
White solid. ^{1}H NMR (600 MHz, DMSO-d_6, 60 °C) δ 8.47 (d, J = 8.7 Hz, 1H), 7.73 (d, J = 1.8 Hz, 1H), 7.52 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 7.8 Hz, 1H), 7.31 (t, J = 7.7 Hz, 2H), 7.25-7.23 (m, 1H), 7.21 (d, J = 8.1 Hz, 2H), 7.17-7.12 (m, 3H), 6.91 (s, 2H), 6.41 (s, 1H), 5.24 (s, 1H), 2.34 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6, 60 °C) δ 142.0, 140.7, 139.7, 138.9, 138.1, 137.2, 135.4, 131.8, 129.0, 128.8, 128.6, 127.6, 126.8, 126.7, 126.3, 125.6, 105.6, 55.4, 20.6, 16.5. HRMS (ESI) *m/z* calcd. for $C_{24}H_{24}N_3O_2S$ $[M+H]^+$: 418.1584, found 418.1588.

4-methyl-*N*-(1-(3-methyl-2-(1*H*-pyrazol-1-yl)phenyl)pentyl)benzenesulfonamide (1w)



White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, J = 2.1 Hz, 1H), 7.55 (d, J = 8.0 Hz, 2H), 7.47 (s, 1H), 7.14-7.03 (m, 4H), 6.90 (s, 1H), 6.48 (t, J = 2.2 Hz, 1H), 6.08 (s, 1H), 3.95 (q, J = 7.8 Hz, 1H), 2.34 (s, 3H), 1.93 (s, 3H), 1.33-1.14 (m, 2H), 1.13-0.96 (m, 3H), 0.90-0.80 (m, 1H), 0.69 (t, J = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.6, 140.4, 139.1, 137.8, 137.3, 136.3, 132.3, 129.6, 129.1, 129.0, 127.0, 126.7, 106.4, 56.0, 35.7, 28.3, 21.8, 21.4, 17.3, 13.7. HRMS (ESI) *m/z* calcd. for $C_{22}H_{28}N_3O_2S$ $[M+H]^+$: 398.1902, found 398.1899.

2.2 Preparation of Rh(III) Catalysts



General procedure: To a suspension of $[Cp^{*R}RhCl_2]_2$ (0.5 mmol, 1.0 equiv.), which was synthesized accroding to the reference,[6] in dry CH_3CN (2 mL), a solution of Ag salt (2.0 mmol, 4.0 equiv.) in dry CH_3CN (3 mL) was added. The reaction mixture was stirred at room temperature for 3 hours. Then the precipitate was removed by filtration on celite, and the residue was washed with dry CH_3CN (15 mL). The filtrate was concentrated to 0.5 mL *in vacuo*. Et_2O (10 mL) was added to the solution, and a pale yellow solid precipitated out. The solid was collected by filtration, washed with Et_2O (15 mL), dried *in vacuo* to afford $[Cp^{*R}Rh(CH_3CN)_3]X_2$ in a quantitative yield.

$[Cp^{*}Rh(CH_3CN)_3](OTf)_2$

Pale yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.07 (s, 9H), 1.54 (s, 15H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 120.7 (q, J = 320 Hz), 118.1, 93.2, 8.3, 1.1. HRMS (ESI) *m/z* calcd. for $C_{12}H_{18}NRh$ $[M-2OTf-2CH_3CN]^{2+}$: 139.5242, found 139.5245.

$[Cp^{*H}Rh(CH_3CN)_3](SbF_6)_2$

Pale yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 5.84 (s, 1H), 2.06 (s, 9H), 1.61 (s, 6H), 1.53 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 118.1, 98.0, 97.9, 9.9, 8.1, 1.1. HRMS (ESI) *m/z* calcd. for $C_{11}H_{16}NRh$ $[M-2SbF_6-2CH_3CN]^{2+}$: 132.5163, found 132.5159.

$[Cp^{*iPr}Rh(CH_3CN)_3](SbF_6)_2$

Pale yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.67-2.62 (m, 1H), 2.07 (s, 9H), 1.61 (s, 6H), 1.54 (s, 6H), 1.30 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 118.1, 96.7, 93.7, 92.6, 24.1, 19.6, 9.0, 8.3, 1.1. HRMS (ESI) *m/z* calcd. for $C_{14}H_{22}NRh$ $[M-2SbF_6-2CH_3CN]^{2+}$: 153.5398, found 153.5399.

$[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$

Pale yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 2.27-2.19 (m, 1H), 2.07 (s, 9H), 1.87 (d, J = 12.2 Hz, 2H), 1.78 (d, J = 13.0 Hz, 2H), 1.70 (d, J = 13.0 Hz, 1H), 1.62 (s, 6H), 1.55-1.50 (m, 8H), 1.43-1.32 (m, 2H), 1.29-1.20 (m, 1H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 118.1, 96.9, 92.7, 92.2, 34.6, 29.4, 25.95, 25.2, 9.3, 8.4, 1.1. HRMS (ESI) *m/z* calcd. for $C_{17}H_{26}NRh$ $[M-2SbF_6-2CH_3CN]^{2+}$: 173.5555, found 173.5558.

$[Cp^{*CyP}Rh(CH_3CN)_3](SbF_6)_2$

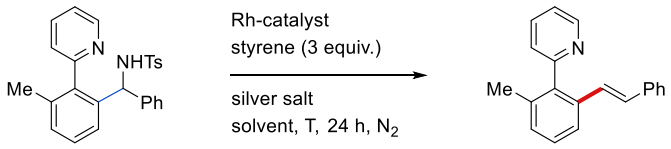
Pale yellow solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 2.78-2.72 (m, 1H), 2.10-2.03 (m, 10H), 1.82-1.64 (m, 6H), 1.61 (s, 6H), 1.54 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 118.1, 96.2, 93.0, 92.4, 34.1, 30.5, 26.4, 9.1, 8.3, 1.1. HRMS (ESI) *m/z* calcd. for $C_{16}H_{24}NRh$ [M-2SbF_6-2CH_3CN]$^{2+}$: 166.5476, found 166.5477.

[$Cp^{*Ph}Rh(CH_3CN)_3$](SbF_6)$_2$

Pale yellow solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.69 (d, J = 7.7 Hz, 2H), 7.63-7.55 (m, 3H), 2.07 (s, 9H), 1.65 (s, 6H), 1.59 (s, 6H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 129.9, 129.6, 129.1, 127.3, 118.1, 98.4, 92.3, 87.6, 9.4, 8.4, 1.1. HRMS (ESI) *m/z* calcd. for $C_{17}H_{20}NRh$ [M-2SbF_6-2CH_3CN]$^{2+}$: 170.5320, found 173.5326.

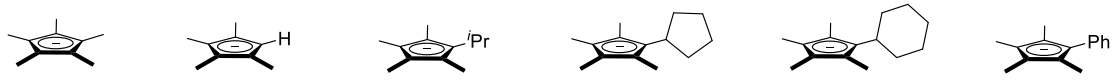
2.3 Condition Optimization

Table S1[a]



1a (1 equiv.) **2a**

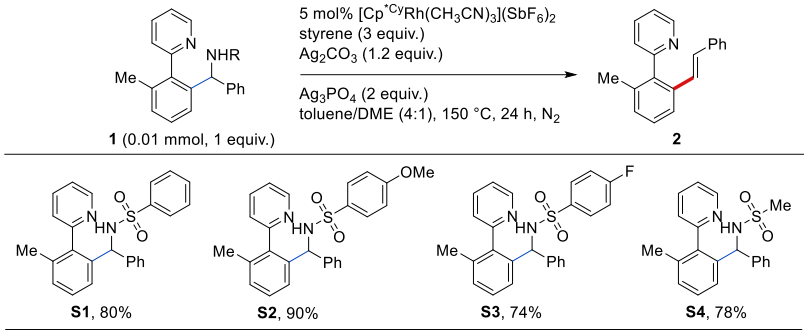
entry	Rh-catalyst	silver salt	solvent	T	yield
1	2.5 mol% $[Cp^*RhCl_2]_2$	no	DCE	130 °C	0%
2	2.5 mol% $[Cp^*RhCl_2]_2$	Ag_2CO_3 (2.2 equiv.)	DCE	130 °C	4%
3	2.5 mol% $[CpRhCl_2]_2$	Ag_2CO_3 (2.2 equiv.)	DCE	130 °C	trace
4	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	DCE	130 °C	12%
5	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	MeCN	130 °C	0%
6	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene	130 °C	30%
7	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	DME	130 °C	29%
8	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (1:1)	130 °C	37%
9	5 mol% $[Cp^*Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	52%
10	5 mol% $[Cp^*Rh(CH_3CN)_3](BF_4)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	36%
11	5 mol% $[Cp^*Rh(CH_3CN)_3](OTf)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	46%
12	5 mol% $[Cp^*Rh(CH_3CN)_3](PF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	41%
13	5 mol% $[Cp^{*H}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	40%
14	5 mol% $[Cp^{*iPr}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	47%
15	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	65%
16	5 mol% $[Cp^{*CyP}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	41%
17	5 mol% $[Cp^{*Ph}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (2.2 equiv.)	toluene/DME (4:1)	130 °C	50%
18	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)/Ag_3PO_4(2.0 equiv.)	toluene/DME (4:1)	130 °C	68%
19[b]	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)/Ag_3PO_4(2.0 equiv.)	toluene/DME (4:1)	130 °C	86%
20[b]	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)/Ag_3PO_4(2.0 equiv.)	toluene/DME (4:1)	150 °C	95%
21[b]	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)	toluene/DME (4:1)	150 °C	82%
22[b]	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_3PO_4 (2.0 equiv.)	toluene/DME (4:1)	150 °C	50%
23[c]	5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)/Ag_3PO_4(2.0 equiv.)	toluene/DME (4:1)	150 °C	96%
24[c]	2.5 mol% $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$	Ag_2CO_3 (1.2 equiv.)/Ag_3PO_4(2.0 equiv.)	toluene/DME (4:1)	150 °C	46%



Cp^* Cp^{*H} Cp^{*iPr} Cp^{*CyP} Cp^{*Cy} Cp^{*Ph}

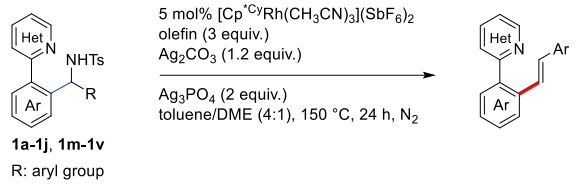
[a] 0.05 mmol **1a**, concentration was 0.05 M, the yields were detected by ^1H NMR using 1,1,2,2-tetrachloroethane as internal standard. [b] Concentration was 0.025 M. [c] 0.1 mmol **1a**, concentration was 0.025 M.

Table S2[a]

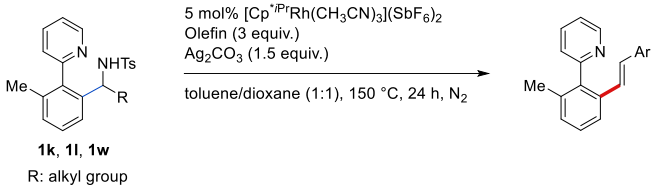


[a] 0.1 mmol **1**, concentration was 0.025 M, the yields were isolated yields.

2.4 Alkenylation of *α*-Branched Amine



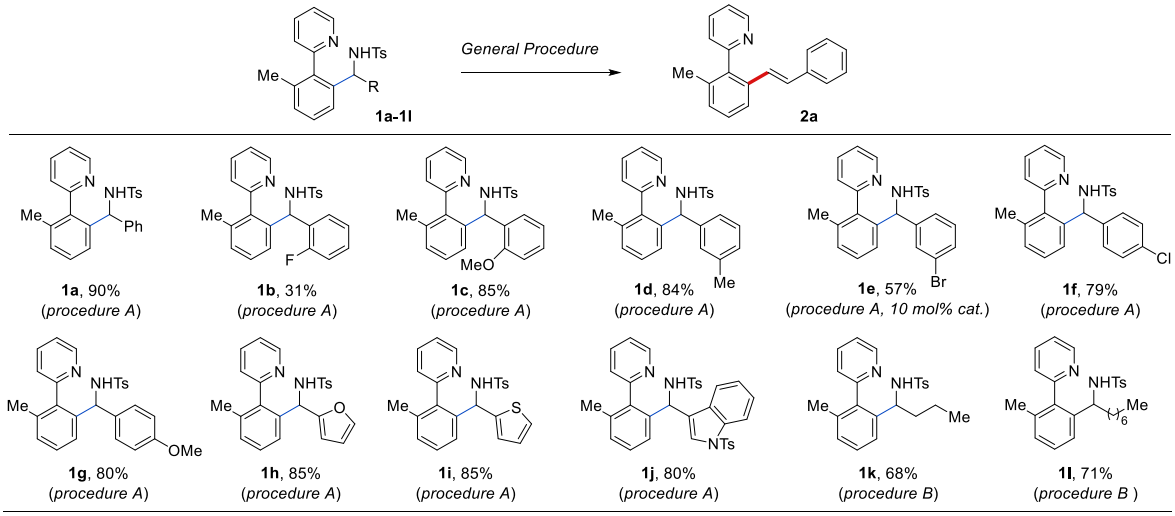
General procedure A: In an nitrogen-filled glove-box, an oven-dried 15 mL sealed tube was charged with a stir bar, *α*-branched primary amine (0.1 mmol, 1.0 equiv.), $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$ (4.4 mg, 5 mol %), Ag_2CO_3 (33 mg, 1.2 equiv.), and Ag_3PO_4 (83 mg, 2.0 equiv.). Then, toluene (3.2 mL), DME (0.8 mL), and olefin (0.3 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 150 °C for 24 hours. After cooling to room temperature, the mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (10 mL). The filtrate was concentrated *in vacuo* and the residue was purified by silica gel chromatography eluting with petroleum ether/acetone (15:1 to 10:1, v/v) to afford corresponding alkenylation product.



General procedure B: In an nitrogen-filled glove-box, an oven-dried 15 mL sealed tube was charged with a stir bar, *α*-branched primary amine **1x** (0.1 mmol, 1.0 equiv.) (or **1k**, **1l**, and **1v**), $[Cp^{*iPr}Rh(CH_3CN)_3](SbF_6)_2$ (4.2 mg, 5 mol %), Ag_2CO_3 (41.4 mg, 1.5 equiv.). Then, toluene (2 mL), dioxane (2 mL), and olefin (0.3 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 150 °C for 24 hours. After cooling to room temperature, the mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (10 mL). The filtrate was concentrated *in vacuo* and the residue was purified by silica gel chromatography eluting with petroleum ether/acetone (15:1 to 10:1, v/v) to afford corresponding alkenylation product.

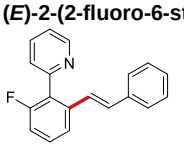
(*E*)-2-(2-methyl-6-styrylphenyl)pyridine (2a)[7]

Table S3



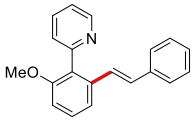
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.80-8.71 (m, 1H), 7.75 (td, J = 7.7, 1.8 Hz, 1H), 7.60 (d, J = 7.8 Hz, 1H), 7.33-7.17 (m, 9H), 6.94 (d, J = 16.2 Hz, 1H), 6.70 (d, J = 16.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.6, 139.6, 137.5, 136.1, 136.0, 129.7, 129.4, 128.5, 128.1, 127.4, 127.3, 126.4, 125.4, 123.0, 121.9, 20.3. HRMS (ESI) *m/z* calcd. for $C_{20}H_{18}N$ $[M+H]^+$: 272.1434, found 272.1432.

(*E*)-2-(2-fluoro-6-styrylphenyl)pyridine (S6)



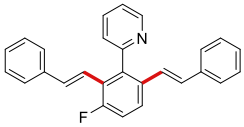
Pale yellow oil. (**Procedure A**, 21.2 mg, 77%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79-8.77 (m, 1H), 7.78 (td, J = 7.7, 1.8 Hz, 1H), 7.57 (d, J = 7.9 Hz, 1H), 7.44-7.19 (m, 8H), 7.10-7.05 (m, 1H), 7.03 (d, J = 16.2 Hz, 1H), 6.93 (d, J = 16.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 (d, J = 246.2 Hz), 153.5, 149.6, 138.6 (d, J = 3.1 Hz), 137.1, 136.1, 131.1, 129.6 (d, J = 9.5 Hz), 128.6, 127.8, 127.5 (d, J = 15.6 Hz), 126.6, 126.3 (d, J = 1.7 Hz), 125.9 (d, J = 3.8 Hz), 122.5, 121.4 (d, J = 3.2 Hz), 114.5 (d, J = 22.9 Hz). HRMS (ESI) *m/z* calcd. for $C_{19}H_{15}FN$ $[M+H]^+$: *m/z* 276.1183, found 276.1196.

(*E*)-2-(2-methoxy-6-styrylphenyl)pyridine (S7)[7]



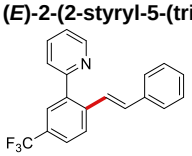
Pale yellow oil. (**Procedure A**, 24.1 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78-8.72 (m, 1H), 7.74 (td, J = 7.7, 1.9 Hz, 1H), 7.42-7.32 (m, 3H), 7.30-7.22 (m, 5H), 7.21-7.16 (m, 1H), 6.98 (d, J = 16.3 Hz, 1H), 6.93-6.89 (m, 1H), 6.76 (d, J = 16.3 Hz, 1H), 3.74 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.2, 156.3, 149.4, 137.5, 137.4, 135.8, 130.1, 129.2, 128.5, 127.4, 126.8, 126.5, 126.3, 121.8, 117.9, 110.0, 55.9. HRMS (ESI) *m/z* calcd. for $C_{20}H_{18}ON$ $[M+H]^+$: 288.1383, found 288.1378.

2-(3-fluoro-2,6-di((*E*)-styryl)phenyl)pyridine (S8)



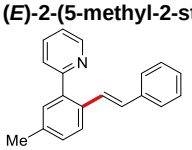
Pale yellow oil. (**Procedure A**, 25.3 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82-8.81 (m, 1H), 7.79 (td, J = 7.7, 1.8 Hz, 1H), 7.64 (dd, J = 8.7, 5.1 Hz, 1H), 7.37-7.19 (m, 13H), 7.01 (d, J = 16.6 Hz, 1H), 6.92 (d, J = 16.2 Hz, 1H), 6.68 (d, J = 16.2 Hz, 1H), 6.58 (d, J = 16.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.4 (d, J = 251.7 Hz), 157.6 (d, J = 3.1 Hz), 149.7, 140.5 (d, J = 3.3 Hz), 137.6, 137.3, 136.3, 135.0, 134.9, 132.8 (d, J = 4.2 Hz), 129.9 , 128.5, 128.5, 127.7, 127.5, 126.4, 126.4, 126.2, 125.5 (d, J = 8.8 Hz), 124.3 (d, J = 12.0 Hz), 122.4, 121.0, 116.2 (d, J = 23.5 Hz). HRMS (ESI) *m/z* calcd. for $C_{27}H_{21}FN$ $[M+H]^+$: 378.1653, found 378.1661.

(*E*)-2-(2-styryl-5-(trifluoromethyl)phenyl)pyridine (S9)[7]



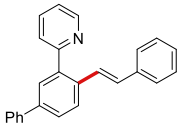
Pale yellow oil. (**Procedure A**, 26.6 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81-8.76 (m, 1H), 7.89-7.82 (m, 2H), 7.78 (td, J = 7.7, 1.8 Hz, 1H), 7.66 (dd, J = 8.2, 1.9 Hz, 1H), 7.50-7.46 (m, 1H), 7.42-7.38 (m, 2H), 7.36-7.30 (m, 3H), 7.29-7.21 (m, 2H), 7.13 (d, J = 16.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.5, 149.8, 139.8, 139.2, 136.9, 136.3, 132.2, 129.5 (q, J = 32.6 Hz), 128.7, 128.1, 127.3 (q, J = 3.3 Hz), 126.8, 126.7, 126.1, 125.2 (q, J = 3.3Hz), 125.0, 123.8 (q, J = 279.5), 122.5. HRMS (ESI) *m/z* calcd. for $C_{20}H_{15}F_3N$ $[M+H]^+$: 326.1151, found 326.1147.

(*E*)-2-(5-methyl-2-styrylphenyl)pyridine (S10)[7]



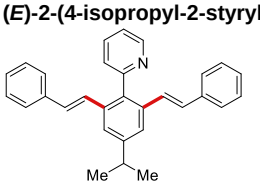
Pale yellow oil. (**Procedure A**, 1.2 equiv. styrene was used, 20.2 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.70 (m, 1H), 7.72 (td, J = 7.7, 1.9 Hz, 1H), 7.66 (d, J = 8.0 Hz, 1H), 7.46-7.43 (m, 1H), 7.40-7.35 (m, 3H), 7.33-7.16 (m, 6H), 7.02 (d, J = 16.2 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.5, 139.5, 137.7, 137.6, 135.9, 132.8, 130.7, 129.5, 129.2, 128.6, 127.4, 127.3, 126.5, 126.2, 125.1, 121.8, 21.1. HRMS (ESI) *m/z* calcd. for $C_{20}H_{18}N$ $[M+H]^+$: 272.1434, found 272.1432.

(*E*)-2-(4-styryl-[1,1'-biphenyl]-3-yl)pyridine (S11)[5]



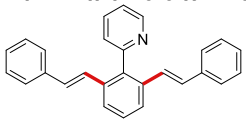
White solid. (**Procedure A**, 1.2 equiv. styrene was used, 27 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79-8.76 (m, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.79 (d, J = 2.0 Hz, 1H), 7.75 (td, J = 7.7, 1.8 Hz, 1H), 7.69-7.65 (m, 3H), 7.51-7.38 (m, 5H), 7.36-7.20 (m, 6H), 7.11 (d, J = 16.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.6, 140.4, 140.0, 137.5, 136.0, 134.7, 130.0, 128.9, 128.7, 128.6, 127.5, 127.4, 127.2, 127.0, 127.0, 126.7, 126.6, 125.1, 122.0.

(*E*)-2-(4-isopropyl-2-styrylphenyl)pyridine (S12)[5]



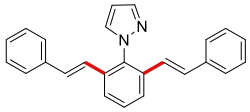
Pale yellow oil. (**Procedure A**, 29.8 mg, 74%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82-8.77 (m, 1H), 7.75 (td, J = 7.7, 1.8 Hz, 1H), 7.56 (s, 2H), 7.33-7.24 (m, 10H), 7.21-7.17 (m, 2H), 6.98 (d, J = 16.2 Hz, 2H), 6.78 (d, J = 16.2 Hz, 2H), 3.09-3.00 (m, 1H), 1.38 (d, J = 7.0 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.4, 149.5, 149.0, 137.5, 136.6, 136.4, 135.9, 129.8, 128.5, 127.5, 127.4, 126.5, 123.1, 121.9, 34.3, 24.0. HRMS (ESI) *m/z* calcd. for $C_{30}H_{28}N$ $[M+H]^+$: 402.2216, found 402.2234.

2-(2,6-di((*E*)-styryl)phenyl)pyridine (S13)[5]



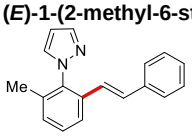
White solid. (**Procedure A**, 19.3 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83-8.77 (m, 1H), 7.77 (td, J = 7.7, 1.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 2H), 7.44 (t, J = 7.8 Hz, 1H), 7.37-7.28 (m, 2H), 7.29-7.23 (m, 8H), 7.24-7.14 (m, 2H), 6.98 (d, J = 16.2 Hz, 2H), 6.76 (d, J = 16.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.3, 149.6, 138.7, 137.5, 136.6, 136.1, 130.2, 128.6, 128.6, 127.6, 127.1, 126.6, 126.4, 124.9, 122.2.

(*E*)-1-(2-styrylphenyl)-1H-pyrazole (S14)[8]



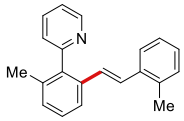
White solid. (**Procedure A**, 10.8 mg, 31%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.87-7.86 (m, 1H), 7.71 (d, J = 7.8 Hz, 2H), 7.56-7.55 (m, 1H), 7.49 (t, J = 7.8 Hz, 1H), 7.34-7.28 (m, 8H), 7.25-7.21 (m, 2H), 7.02 (d, J = 16.3 Hz, 2H), 6.54 (t, J = 2.1 Hz, 1H), 6.50 (d, J = 16.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.7, 137.0, 136.6, 136.2, 132.9, 131.6, 129.4, 128.6, 128.0, 126.7, 124.8, 123.1, 106.5. HRMS (ESI) calcd. for $[C_{25}H_{21}N_2]^+$ $(M+H)^+$: *m/z* 349.1699, found 349.1709.

(*E*)-1-(2-methyl-6-styrylphenyl)-1H-pyrazole (S15)[9]



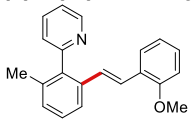
Colorless oil. (**Procedure A**, 15.5 mg, 60%; **Procedure B**, 10.4 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J = 1.8 Hz, 1H), 7.62 (dd, J = 7.9, 1.3 Hz, 1H), 7.50 (d, J = 2.3 Hz, 1H), 7.36 (t, J = 7.7 Hz, 1H), 7.33-7.24 (m, 4H), 7.25-7.18 (m, 2H), 6.97 (d, J = 16.3 Hz, 1H), 6.49 (t, J = 2.1 Hz, 1H), 6.43 (d, J = 16.3 Hz, 1H), 2.06 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.4, 138.1, 137.1, 136.7, 135.8, 131.9, 131.2, 129.7, 129.2, 128.6, 127.9, 126.7, 123.4, 123.4, 106.1, 17.4. HRMS (ESI) *m/z* calcd. for $C_{18}H_{17}N_2$ $[M+H]^+$: 261.1386, found 261.1385.

(*E*)-2-(2-methyl-6-(2-methylstyryl)phenyl)pyridine (2b)[10]



Pale yellow oil. (**Procedure A**, 23.9 mg, 84%; **Procedure B**, 18.3 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.76 (td, J = 7.7, 1.9 Hz, 1H), 7.61 (d, J = 7.7 Hz, 1H), 7.34 (t, J = 7.7 Hz, 1H), 7.31-7.25 (m, 2H), 7.25-7.19 (m, 2H), 7.16-7.05 (m, 4H), 6.61 (d, J = 16.0 Hz, 1H), 2.35 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.6, 139.6, 136.6, 136.4, 136.3, 136.2, 135.7, 130.2, 129.3, 128.6, 128.2, 127.8, 127.3, 126.0, 125.4, 125.3, 123.3, 121.8, 20.2, 19.9. HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}N$ $[M+H]^+$: 286.1590, found 286.1594.

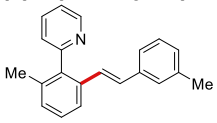
(*E*)-2-(2-(2-methoxystyryl)-6-methylphenyl)pyridine (2c)



Yellow oil. (**Procedure A**, 20.2 mg, 67%; **Procedure B**, 19.1 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76-8.75 (m, 1H), 7.75 (td, J = 7.7, 1.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.34-7.24 (m, 4H), 7.21-7.14 (m, 3H), 6.87-6.80 (m, 2H), 6.71 (d, J = 16.3 Hz, 1H), 3.79 (s, 3H), 2.08 (s, 3H).

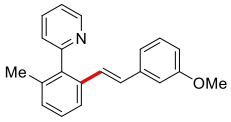
^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 156.8, 149.5, 139.5, 136.5, 136.2, 136.0, 129.1, 128.4, 128.1, 127.7, 126.7, 126.5, 125.5, 124.5, 123.0, 121.7, 120.5, 110.8, 55.4, 20.3. HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539, found 302.1540.

(*E*)-2-(2-methyl-6-(3-methylstyryl)phenyl)pyridine (2d)



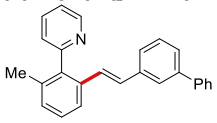
Yellow oil. (**Procedure A**, 23.8 mg, 84%; **Procedure B**, 22.6 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.75 (td, *J* = 7.7, 1.9 Hz, 1H), 7.59 (d, *J* = 7.7 Hz, 1H), 7.32-7.24 (m, 3H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.16-7.11 (m, 1H), 7.07-7.03 (m, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.90 (d, *J* = 16.2 Hz, 1H), 6.68 (d, *J* = 16.2 Hz, 1H), 2.29 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.6, 139.5, 138.0, 137.5, 136.4, 136.1, 136.1 129.9, 129.3, 128.4, 128.2, 128.1, 127.4, 127.1, 125.4, 123.4, 123.0, 121.8, 21.3, 20.3. HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}N$ $[M+H]^+$: 286.1590, found 286.1595.

(*E*)-2-(2-(3-methoxystyryl)-6-methylphenyl)pyridine (2e)



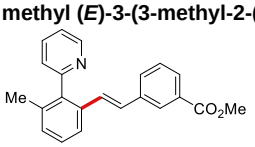
Pale yellow oil. (**Procedure A**, 17.8 mg, 59%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76-8.75 (m, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.59 (d, *J* = 7.8 Hz, 1H), 7.33-7.25 (m, 3H), 7.22-7.15 (m, 2H), 6.93-6.82 (m, 2H), 6.80-6.65 (m, 3H), 3.76 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.7, 159.0, 149.6, 139.6, 139.0, 136.4, 136.1, 135.9, 129.6, 129.5, 129.4, 128.2, 127.7, 125.4, 123.0, 121.9, 119.1, 112.8, 112.0, 55.1, 20.3. HRMS (ESI) *m/z* calcd. for $C_{21}H_{20}NO$ $[M+H]^+$: 302.1539, found 302.1538.

(*E*)-2-(2-(2-([1,1'-biphenyl]-3-yl)vinyl)-6-methylphenyl)pyridine (2f)



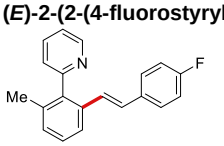
Yellow oil. (**Procedure A**, 28.9 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76-8.75 (m, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.55-7.50 (m, 2H), 7.47-7.38 (m, 4H), 7.36-7.19 (m, 7H), 6.99 (d, *J* = 16.1 Hz, 1H), 6.76 (d, *J* = 16.1 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0, 149.6, 141.5, 141.0, 139.6, 138.0, 136.4, 136.1, 136.0, 129.7, 129.5, 128.9, 128.7, 128.2, 127.8, 127.3, 127.1, 126.3, 125.7, 125.4, 125.0, 123.1, 121.9, 20.3. HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}N$ $[M+H]^+$: 348.1747, found 348,1748.

methyl (*E*)-3-(3-methyl-2-(pyridin-2-yl)styryl)benzoate (2g)



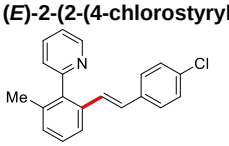
Yellow oil. (**Procedure A**, 25.9 mg, 79%; **Procedure B**, 22.2 mg, 67%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78-8.76 (m, 1H), 7.92 (t, *J* = 1.8 Hz, 1H), 7.86-7.82 (m, 1H), 7.78 (td, *J* = 7.7, 1.9 Hz, 1H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.35-7.25 (m, 4H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 16.2 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 3.89 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.9, 158.9, 149.6, 139.7, 137.9, 136.4, 136.2, 135.6, 130.4, 130.3, 129.7, 128.8, 128.5, 128.3, 128.2, 127.9, 125.4, 123.1, 121.9, 52.1, 20.2. HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489, found 330.1496.

(*E*)-2-(2-(4-fluorostyryl)-6-methylphenyl)pyridine (2h)[10]



Yellow oil. (**Procedure A**, 25.3 mg, 87%; **Procedure B**, 24.4 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.35-7.24 (m, 3H), 7.23-7.15 (m, 3H), 6.97-6.85 (m, 3H), 6.60 (d, *J* = 16.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.1 (d, *J* = 246.4 Hz), 159.0, 149.6, 139.6, 136.4, 136.1, 135.8, 133.7 (d, *J* = 3.3 Hz), 129.4, 128.5, 128.2, 127.9 (d, *J* = 8.0 Hz), 127.0 (d, *J* = 2.3 Hz), 125.4, 122.9, 121.9, 115.4 (d, *J* = 20.8 Hz), 20.3. HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}NF$ $[M+H]^+$: 290.1340, found 290.1342.

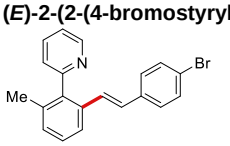
(*E*)-2-(2-(4-chlorostyryl)-6-methylphenyl)pyridine (2i)[10]



Yellow oil. (**Procedure A**, 25.6 mg, 84%; **Procedure B**, 23.9 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.77 (td, *J* = 7.6, 1.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.35-7.28 (m, 2H), 7.28-7.23 (m, 1H), 7.24-7.18 (m, 3H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.88 (d, *J* = 16.2 Hz, 1H),

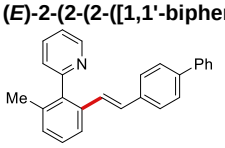
6.66 (d, *J* = 16.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.0, 149.7, 139.7, 136.5, 136.2, 136.1, 135.7, 133.0, 129.7, 128.7, 128.5, 128.2, 127.9, 127.6, 125.4, 123.0, 122.0, 20.3. HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}NCl$ $[M+H]^+$: 306.1044, found 306.1042.

(*E*)-2-(2-(4-bromostyryl)-6-methylphenyl)pyridine (2j)[10]



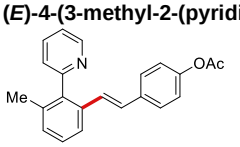
Yellow oil. (**Procedure A**, 30.6 mg, 87%; **Procedure B**, 30.1 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.77-8.75 (m, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.5 Hz, 2H), 7.33-7.28 (m, 2H), 7.27-7.23 (m, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.5 Hz, 2H), 6.86 (d, *J* = 16.2 Hz, 1H), 6.67 (d, *J* = 16.2 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 158.8, 149.5, 139.5, 136.3, 136.0, 135.4, 131.4, 129.5, 128.3, 128.0, 127.8, 127.7, 125.2, 122.8, 121.8, 120.9, 20.1. HRMS (ESI) *m/z* calcd. for $C_{20}H_{17}BrN$ $[M+H]^+$: 350.0539, found 350.0536.

(*E*)-2-(2-(2-([1,1'-biphenyl]-4-yl)vinyl)-6-methylphenyl)pyridine (2k)



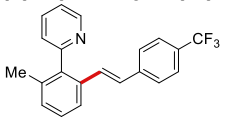
Foam solid. (**Procedure A**, 25.2 mg, 73%; **Procedure B**, 26.4 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.80-8.78 (m, 1H), 7.79 (td, *J* = 7.6, 1.8 Hz, 1H), 7.64 (d, *J* = 7.8 Hz, 1H), 7.59-7.54 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.45-7.40 (m, 2H), 7.37-7.28 (m, 6H), 7.23 (d, *J* = 7.5 Hz, 1H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.76 (d, *J* = 16.2 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.1, 149.6, 140.6, 140.1, 139.6, 136.6, 136.4, 136.1, 136.0, 129.4, 129.2, 128.7, 128.2, 127.4, 127.2, 127.2, 126.9, 126.8, 125.4, 123.0, 121.9, 20.3. HRMS (ESI) *m/z* calcd. for $C_{26}H_{22}N$ $[M+H]^+$: 348.1747, found 348.1748.

(*E*)-4-(3-methyl-2-(pyridin-2-yl)styryl)phenyl acetate (2l)



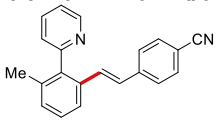
Yellow oil. (**Procedure A**, 24.3 mg, 74%; **Procedure B**, 24.1 mg, 73%).^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.77-8.75 (m, 1H), 7.76 (td, *J* = 7.7, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.32-7.20 (m, 6H), 6.97 (d, *J* = 8.7 Hz, 2H), 6.91 (d, *J* = 16.1 Hz, 1H), 6.64 (d, *J* = 16.1 Hz, 1H), 2.27 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 169.4, 159.0, 149.8, 149.6, 139.6, 136.4, 136.2, 135.8, 135.4, 129.5, 128.7, 128.1, 127.6, 127.3, 125.4, 123.0, 121.9, 121.6, 21.1, 20.2. HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}NO_2$ $[M+H]^+$: 330.1489, found 330.1489.

(*E*)-2-(2-methyl-6-(4-(trifluoromethyl)styryl)phenyl)pyridine (2m)[10]



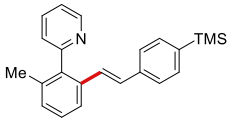
Pale yellow oil. (**Procedure A**, 29.6 mg, 87%; **Procedure B**, 29.2 mg, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.78-8.76 (m, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.34-7.29 (m, 4H), 7.29-7.21 (m, 2H), 6.95 (d, *J* = 16.2 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 158.8, 149.7, 141.0, 139.9, 136.5, 136.2, 135.3, 130.0, 129.8, 129.0 (q, *J* = 32.7 Hz), 128.3, 128.2, 126.5, 125.4 (q, *J* = 3.5 Hz), 125.4, 124.2 (q, *J* = 272.0 Hz), 123.1, 122.0, 20.2. HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}NF_3$ $[M+H]^+$: 340.1308, found 340.1313.

(*E*)-4-(3-methyl-2-(pyridin-2-yl)styryl)benzonitrile (2n)



Yellow oil. (**Procedure A**, 22.4 mg, 76%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.78-8.77 (m, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.38-7.21 (m, 6H), 6.92 (d, *J* = 16.2 Hz, 1H), 6.81 (d, *J* = 16.2 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 158.7, 149.7, 142.0, 140.1, 136.6, 136.2, 135.0, 132.3, 131.0, 130.3, 128.3 127.7, 126.8, 125.3, 123.1, 122.1, 119.0, 110.3, 20.2. HRMS (ESI) *m/z* calcd. for $C_{21}H_{17}N_2$ $[M+H]^+$: 297.1386, found 297.1382.

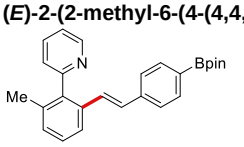
(*E*)-2-(2-methyl-6-(4-(trimethylsilyl)styryl)phenyl)pyridine (2o)



Yellow oil. (**Procedure A**, 28.4 mg, 83%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.76-8.75 (m, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.60 (d, *J* = 7.8 Hz,

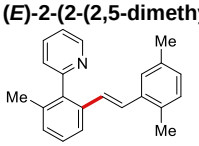
1H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.33-7.18 (m, 6H), 6.93 (d, *J* = 16.2 Hz, 1H), 6.72 (d, *J* = 16.2 Hz, 1H), 2.09 (s, 3H), 0.23 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.1, 149.6, 139.7, 139.6, 137.9, 136.4, 136.1, 136.0, 133.5, 129.7, 129.4, 128.1, 127.6, 125.7, 125.4, 123.0, 121.8, 20.2, -1.2. HRMS (ESI) *m/z* calcd. for $C_{23}H_{26}NSi$ $[M+H]^+$: 344.1829, found 344.1827.

(*E*)-2-(2-methyl-6-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)styryl)phenyl)pyridine (2p)



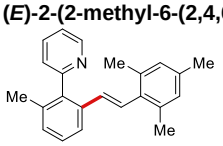
Pale yellow oil. (**Procedure A**, 15.7 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.76-8.75 (m, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.33-7.20 (m, 6H), 6.94 (d, *J* = 16.1 Hz, 1H), 6.74 (d, *J* = 16.2 Hz, 1H), 2.10 (s, 3H), 1.32 (s, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.0, 149.6, 140.2, 139.7, 136.4, 136.1, 135.9, 135.0, 129.8, 129.6, 128.4, 128.2, 125.7, 125.4, 123.1, 121.9, 83.7, 24.8, 20.3. HRMS (ESI) *m/z* calcd. for $C_{26}H_{29}BNO_2$ $[M+H]^+$: 398.2286, found 398.2287.

(*E*)-2-(2-(2,5-dimethylstyryl)-6-methylphenyl)pyridine (2q)



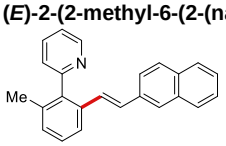
Pale yellow oil. (**Procedure A**, 26.1 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.75-8.74 (m, 1H), 7.74 (td, *J* = 7.7, 1.9 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33-7.19 (m, 4H), 7.07 (d, *J* = 16.0 Hz, 1H), 7.03-6.97 (m, 2H), 6.91 (d, *J* = 7.4 Hz, 1H), 6.58 (d, *J* = 16.1 Hz, 1H), 2.27 (s, 3H), 2.22 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.2, 149.6, 139.5, 136.5, 136.4, 136.4, 136.2, 135.3, 132.7, 130.1, 129.3, 128.5, 128.1, 128.1, 126.2, 125.4, 123.4, 121.8, 20.9, 20.2, 19.4. HRMS (ESI) *m/z* calcd. for $C_{22}H_{22}N$ $[M+H]^+$: 300.1747, found 300.1748.

(*E*)-2-(2-methyl-6-(2,4,6-trimethylstyryl)phenyl)pyridine (2r)



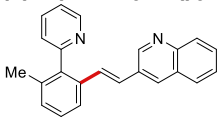
Colorless oil. (**Procedure A**, 13.6 mg, 44%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.70-8.68 (m, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.63 (d, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.7 Hz, 1H), 7.27-7.18 (m, 3H), 6.92 (d, *J* = 16.6 Hz, 1H), 6.80 (s, 2H), 6.18 (d, *J* = 16.6 Hz, 1H), 2.23 (s, 3H), 2.15 (s, 6H), 2.08 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 149.6, 139.4, 136.4, 136.3, 136.1, 136.1, 134.3, 132.3, 129.1, 128.5, 128.2, 127.9, 125.1, 122.8, 121.8, 20.9, 20.2. HRMS (ESI) *m/z* calcd. for $C_{23}H_{24}N$ $[M+H]^+$: 314.1903, found 314.1901.

(*E*)-2-(2-methyl-6-(2-(naphthalen-2-yl)vinyl)phenyl)pyridine (2s)[10]



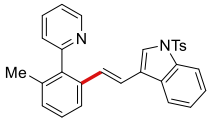
Pale yellow oil. (26.7 mg, 83%).^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.82-8.75 (m, 1H), 7.79-7.72 (m, 3H), 7.70-7.63 (m, 3H), 7.45-7.26 (m, 6H), 7.25-7.20 (m, 1H), 7.10 (d, *J* = 16.2 Hz, 1H), 6.82 (d, *J* = 16.2 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 159.1, 149.6, 139.7, 136.4, 136.1, 136.0, 135.0, 133.5, 132.8, 129.9, 129.5, 128.2, 128.1, 127.9, 127.6, 127.6, 126.6, 126.2, 125.8, 125.4, 123.4, 123.0, 121.9, 20.3. HRMS (ESI) *m/z* calcd. for $C_{24}H_{20}N$ $[M+H]^+$: 322.1590, found 322.1587.

(*E*)-3-(3-methyl-2-(pyridin-2-yl)styryl)quinoline (2t)



White foam solid. (**Procedure A**, 26.9 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.83 (d, *J* = 2.2 Hz, 1H), 8.81-8.76 (m, 1H), 8.02 (d, *J* = 8.4 Hz, 1H), 7.91 (d, *J* = 2.2 Hz, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 1H), 7.68-7.61 (m, 2H), 7.53-7.47 (m, 1H), 7.38-7.25 (m, 4H), 7.08 (d, *J* = 16.3 Hz, 1H), 6.91 (d, *J* = 16.3 Hz, 1H), 2.12 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) *δ* 158.8, 149.8, 149.2, 147.3, 139.9, 136.6, 136.3, 135.4, 132.5, 130.5, 130.0, 129.6, 129.2, 129.1, 128.3, 128.0, 127.7, 126.9, 126.2, 125.4, 122.9, 122.1, 20.3. HRMS (ESI) *m/z* calcd. for $C_{23}H_{19}N_2$ $[M+H]^+$: 323.1543, found 323.1549.

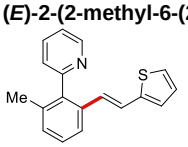
(*E*)-3-(3-methyl-2-(pyridin-2-yl)styryl)-1-tosyl-1H-indole (2u)



White foam solid. (**Procedure A**, 30.2 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$) *δ* 8.79-8.78 (m, 1H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.79 (td, *J* = 7.7, 1.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 7.8 Hz, 1H), 7.50 (s, 1H), 7.35-7.12 (m, 9H), 6.99 (d, *J* = 16.2 Hz, 1H), 6.78 (d, *J* = 16.2 Hz, 1H),

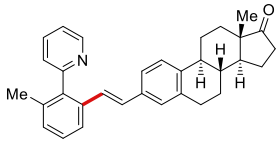
2.32 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.1, 149.8, 145.0, 139.5, 136.4, 136.3, 135.9, 135.5, 135.0, 129.9, 129.4, 128.9, 128.4, 128.2, 126.8, 125.4, 124.8, 124.0, 123.3, 122.4, 121.9, 121.0, 120.3, 120.2, 113.7, 21.5, 20.3. HRMS (ESI) *m/z* calcd. for $C_{29}H_{25}N_2O_2S$ $[M+H]^+$: 465.1631, found 465.1632.

(*E*)-2-(2-methyl-6-(2-(thiophen-2-yl)vinyl)phenyl)pyridine (2v)

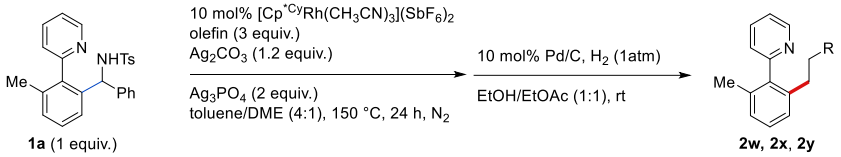


Yellow oil. (**Procedure A**, 16.8 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.77 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.33-7.23 (m, 3H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.09-7.02 (m, 2H), 6.91 (d, *J* = 3.3 Hz, 2H), 6.51 (d, *J* = 16.0 Hz, 1H), 2.09 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.9, 149.6, 143.1, 139.4, 136.4, 136.1, 135.6, 129.4, 128.2, 127.4, 127.0, 125.7, 125.4, 124.2, 122.7, 122.7, 121.9, 20.3. HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NS$ $[M+H]^+$: 278.0998, found 278.0990.

(13*S*)-13-methyl-3-((*E*)-3-methyl-2-(pyridin-2-yl)styryl)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (2z)



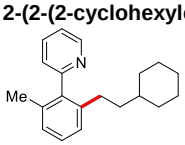
White foam solid. (**Procedure A**, 39.4 mg, 88%; **Procedure B**, 30.5 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77-8.75 (m, 1H), 7.75 (td, *J* = 7.6, 1.8 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.33-7.25 (m, 3H), 7.20 (s, 2H), 7.06 (s, 1H), 6.99 (s, 1H), 6.88 (d, *J* = 16.2 Hz, 1H), 6.65 (d, *J* = 16.2 Hz, 1H), 2.86 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.50 (dd, *J* = 19.0, 8.6 Hz, 1H), 2.42-2.33 (m, 1H), 2.31-2.22 (m, 1H), 2.20-1.90 (m, 7H), 1.64-1.41 (m, 6H), 0.89 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 220.8, 159.1, 149.6, 139.5, 139.2, 136.6, 136.4, 136.2, 136.1, 135.2, 129.6, 129.3, 128.1, 127.3, 126.8, 125.5, 125.4, 123.7, 123.0, 121.8 , 50.5, 47.9, 44.4, 38.1, 35.8, 31.5, 29.3, 26.4, 25.7, 21.6, 20.3, 13.8. HRMS (ESI) *m/z* calcd. for $C_{32}H_{34}NO$ $[M+H]^+$: 448.2635, found 448.2640.



1a (1 equiv.) **2w, 2x, 2y**

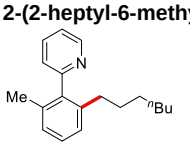
Step 1: the alkenylation was conducted following the **general procedure A** with 10 mol% Rh-catalyst.
Step 2: a 5 mL flame-dried flask was charged with the alkenylation product and 10 mg Pd/C (10 wt%). The reaction flask was evacuated and backfilled with H_2 through a H_2 balloon followed by addition of ethanol (0.5 mL) and ethyl acetate (0.5 mL). The reaction mixture was stirred at room temperature for 12 hours. The reaction mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (10 mL). The residue was concentrated *in vacuo* and afforded **2w**, **2x**, **2y** in quantitative yield.

2-(2-(2-cyclohexylethyl)-6-methylphenyl)pyridine (2w)



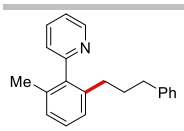
Colorless oil. (18.9 mg, 67%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.72-8.71 (m, 1H), 7.75 (td, *J* = 7.7, 1.8 Hz, 1H), 7.28-7.20 (m, 3H), 7.13-7.07 (m, 2H), 2.32 (t, 2H), 2.02 (s, 3H), 1.63-1.52 (m, 3H), 1.51-1.43 (m, 2H), 1.36-1.20 (m, 2H), 1.17-0.99 (m, 4H), 0.75-0.64 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 149.5, 141.1, 140.1, 136.0, 135.8, 127.9, 127.4, 126.6, 124.7, 121.6, 39.2, 37.5, 33.0, 30.8, 26.6, 26.2, 20.3. HRMS (ESI) *m/z* calcd. for $C_{20}H_{26}N$ $[M+H]^+$: 280.2060, found 280.2062.

2-(2-heptyl-6-methylphenyl)pyridine (2x)



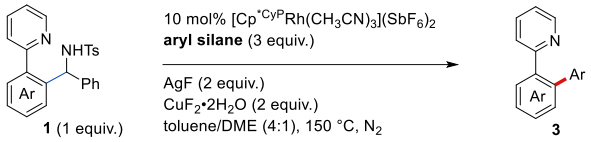
Colorless oil. (12.4 mg, 46%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.65-8.63 (m, 1H), 7.67 (td, *J* = 7.6, 1.8 Hz, 1H), 7.21-7.13 (m, 3H), 7.07-7.01 (m, 2H), 2.24 (t, *J* = 8.0 Hz, 2H), 1.95 (s, 3H), 1.42-1.24 (m, 2H), 1.18-1.01 (m, 8H), 0.76 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 149.5, 140.7, 140.1, 136.0, 135.8, 127.9, 127.4, 126.6, 124.7, 121.6, 33.4, 31.6, 31.1, 29.4, 28.9, 22.6, 20.3, 14.1. HRMS (ESI) *m/z* calcd. for $C_{19}H_{26}N$ $[M+H]^+$: 268.2060, found 268.2069.

2-(2-methyl-6-(3-phenylpropyl)phenyl)pyridine (2y)



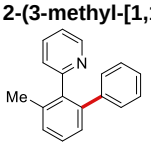
Colorless oil. (11.8 mg, 41%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.69-8.68 (m, 1H), 7.70 (td, J = 7.6, 1.8 Hz, 1H), 7.25-7.18 (m, 5H), 7.15-7.09 (m, 3H), 7.04-7.00 (m, 2H), 2.47 (t, J = 7.6 Hz, 2H), 2.37 (t, J = 8.0 Hz, 2H), 2.02 (s, 3H), 1.83-1.66 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 149.5, 142.2, 140.2, 140.1, 136.0, 135.9, 128.3, 128.1, 127.9, 127.6, 126.6, 125.5, 124.6, 121.6, 35.6, 33.1, 32.5, 20.3. HRMS (ESI) *m/z* calcd. for $C_{21}H_{22}N$ $[M+H]^+$: 288.1747, found 288.1753.

2.5 Arylation of *α*-Branched Amine



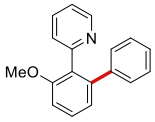
General procedure: In an nitrogen-filled glove-box, an oven-dried 15 mL sealed tube was charged with a stir bar, α-branched primary amine (0.1 mmol, 1.0 equiv.), $[Cp^{*CyP}Rh(CH_3CN)_3](SbF_6)_2$ (8.8 mg, 10 mol %), AgF (25 mg, 2.0 equiv.), $CuF_2{\cdot}2H_2O$ (28 mg, 2.0 equiv.). toluene (3.2 mL), DME (0.8 mL) and aryl silane (0.3 mmol, 3.0 equiv.). The mixture was stirred at 150 °C for 24 hours. After cooling to room temperature, the reaction mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (10 mL). The filtrate was concentrated *in vacuo* and the residue was purified by silica gel chromatography eluting with petroleum ether/acetone (20:1 to 10:1, v/v) to afford corresponding arylation product.

2-(3-methyl-[1,1'-biphenyl]-2-yl)pyridine (3a)[11]



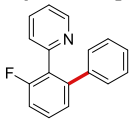
White foam solid, (13.7 mg, 56%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, J = 4.8 Hz, 1H), 7.44 (td, J = 7.7, 1.8 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.32-7.24 (m, 2H), 7.16-7.04 (m, 6H), 6.88 (d, J = 7.8 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 148.8, 141.6, 141.2, 139.3, 136.7, 135.7, 129.6, 129.4, 128.0, 127.6, 126.2, 125.6, 121.3, 20.5. HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}N$ $[M+H]^+$: 246.1277, found 246.1286.

2-(3-methoxy-[1,1'-biphenyl]-2-yl)pyridine (3b)[12]



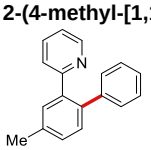
White foam solid, (13.2 mg, 51%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60-8.55 (m, 1H), 7.48 (td, J = 7.7, 1.8 Hz, 1H), 7.43 (t, J = 8.0 Hz, 1H), 7.15-7.11 (m, 3H), 7.10-7.05 (m, 4H), 7.03-7.00 (m, 2H), 3.79 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 157.2, 156.8, 148.8, 142.8, 141.0, 135.5, 129.6, 129.2, 127.6, 126.3, 126.3, 122.5, 121.3, 110.1, 55.8. HRMS (ESI) *m/z* calcd. for $C_{18}H_{16}NO$ $[M+H]^+$: 262.1226, found 262.1233.

2-(3-fluoro-[1,1'-biphenyl]-2-yl)pyridine (3c)[11]



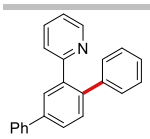
White foam solid, (11.5 mg, 46%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60-8.58 (m, 1H), 7.53 (td, J = 7.7, 1.8 Hz, 1H), 7.46-7.41 (m, 1H), 7.26-7.24 (m, 1H), 7.20-7.16 (m, 4H), 7.16-7.12 (m, 1H), 7.11-7.06 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.3 (d, J = 247.4 Hz), 154.2, 149.2, 143.4, 140.0, 135.7, 129.6 (d, J = 8.8 Hz), 129.5, 127.9, 127.7 (d, J = 14.6 Hz), 126.9, 126.2, 125.9 (d, J = 3.2 Hz), 122.0, 114.7 (d, J = 22.9 Hz). HRMS (ESI) *m/z* calcd. for $C_{17}H_{13}NF$ $[M+H]^+$: 250.1027, found 250.1033.

2-(4-methyl-[1,1'-biphenyl]-2-yl)pyridine (3d)[12]



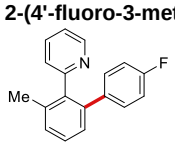
White foam solid, (11.8 mg, 48%).^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, J = 4.7 Hz, 1H), 7.53 (s, 1H), 7.39-7.31 (m, 2H), 7.30-7.20 (m, 4H), 7.16-7.07 (m, 3H), 6.86 (d, J = 7.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.3, 149.3, 141.3, 139.2, 137.8, 137.4, 135.1, 131.0, 130.4, 129.7, 129.3, 128.0, 126.5, 125.5, 121.3, 21.1. HRMS (ESI) *m/z* calcd. for $C_{18}H_{15}N$ $[M+H]^+$: 246.1277, found 246.1290.

2-([1,1':4',1''-terphenyl]-2'-yl)pyridine (3e)[13]



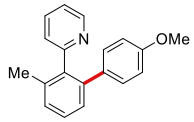
White foam solid, (15.8 mg, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (d, J = 4.6 Hz, 1H), 7.94 (s, 1H), 7.71 (d, J = 7.8 Hz, 3H), 7.52 (d, J = 7.9 Hz, 1H), 7.48-7.33 (m, 4H), 7.26-7.19 (m, 5H), 7.15-7.10 (m, 1H), 6.94 (d, J = 7.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.2, 149.4, 140.9, 140.5, 140.5, 139.8, 139.6, 135.3, 131.0, 129.7, 129.3, 128.7, 128.1, 127.4, 127.2, 127.1, 126.8, 125.5, 121.5. HRMS (ESI) *m/z* calcd. for $C_{23}H_{17}N$ $[M+H]^+$: 308.1434, found 308.1446.

2-(4'-fluoro-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (3f)[11]



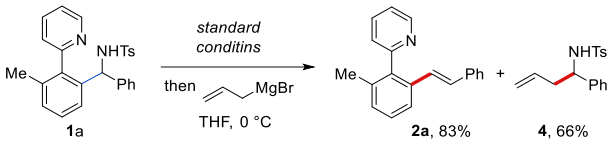
White foam solid, (12.8 mg, 47%).^{1}H NMR (600 MHz, $CDCl_3$) δ 8.64-8.61 (m, 1H), 7.48 (td, J = 7.7, 1.8 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.29 (d, J = 7.2 Hz, 1H), 7.24 (d, J = 7.5 Hz, 1H), 7.13-7.08 (m, 1H), 7.05-7.01 (m, 2H), 6.88 (dt, J = 7.8, 1.1 Hz, 1H), 6.85-6.79 (m, 2H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5 (d, J = 245.4 Hz), 159.4, 148.9, 140.2, 139.4, 137.6, 136.8, 135.8, 131.1 (d, J = 7.7 Hz), 129.5, 128.1, 127.5, 125.5, 121.4, 114.5 (d, J = 21.7 Hz). HRMS (ESI) *m/z* calcd. for $C_{18}H_{15}NF$ $[M+H]^+$: 264.1183, found 264.1196.

2-(4'-methoxy-3-methyl-[1,1'-biphenyl]-2-yl)pyridine (3g)[11]



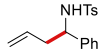
White foam solid. (14.6 mg, 53%). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66-8.62 (m, 1H), 7.47 (td, J = 7.7, 1.8 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 7.28-7.23 (m, 2H), 7.13-7.08 (m, 1H), 6.98 (d, J = 8.7 Hz, 2H), 6.88 (d, J = 7.8 Hz, 1H), 6.67 (d, J = 8.7 Hz, 2H), 3.73 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 158.0, 148.8, 140.8, 139.3, 136.7, 135.8, 134.1, 130.7, 129.1, 128.0, 127.6, 125.6, 121.2, 113.1, 55.1, 20.5. HRMS (ESI) *m/z* calcd. for $C_{19}H_{18}NO$ $[M+H]^+$: 276.1383, found 276.1389.

2.6 One-Pot Protocol for Divergent Synthesis



In an nitrogen-filled glove-box, an oven-dried 15 mL sealed tube was charged with a stir bar, *α*-branched primary amine **1a** (0.1 mmol, 1.0 equiv.), $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$ (4.4 mg, 5 mol %), Ag_2CO_3 (33 mg, 1.2 equiv.), and Ag_3PO_4 (83 mg, 2.0 equiv.). Then, toluene (3.2 mL), DME (0.8 mL), and styrene (0.3 mmol, 3.0 equiv.) were added. The reaction mixture was stirred at 150 °C for 24 hours. After cooling to room temperature, the solvent was removed *in vacuo* and the residue was dissolved in THF (3 mL). The Allylmagnesium bromide solution (0.15 mL, 1.5 equiv., 1.0 M in diethyl ether) was added dropwise at 0 °C. The reaction mixture was stirred at this temperature for 2 hours. Then, the mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (10 mL). The filtrate was concentrated *in vacuo* and the residue was purified by silica gel chromatography eluting with petroleum ether/acetone (15:1 to 10:1, v/v) to afford **2a** (22.4 mg, 83%) and **4** (20.6 mg, 68%).

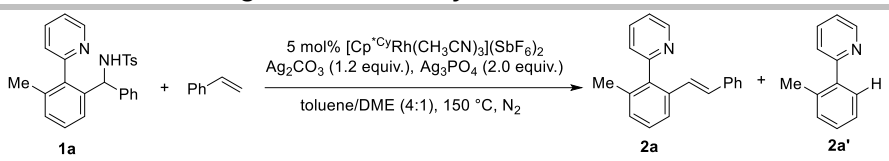
4-methyl-N-(1-phenylbut-3-en-1-yl)benzenesulfonamide (4)[14]



White solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, J = 8.2 Hz, 2H), 7.21-7.12 (m, 5H), 7.07 (m, 2H), 5.56-5.45 (m, 1H), 5.09-5.03 (m, 2H), 4.80 (d, J = 6.4 Hz, 1H), 4.38 (q, J = 6.6 Hz, 1H), 2.50-2.40 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.1, 140.3, 137.4, 133.0, 129.3, 128.4, 127.4, 127.1, 126.5, 119.4, 57.0, 41.9, 21.5.

2.7 Mechanism Study

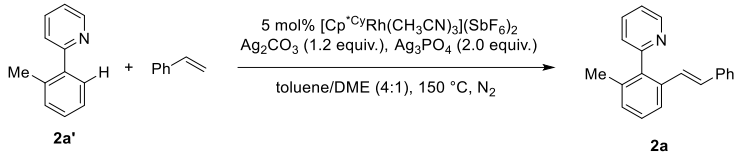
Table S4. Reaction Monitoring



Entry	Time (min)	**1a** (%)	**2a** (%)	**2a'** (%)
1	10	78	15	4
2	20	68	21	10
3	40	60	30	8.5
4	60	38	40	6
5	80	34	50	5.6
6	100	30	56	3.7
7	120	28	64	0
8	140	19	79	0
9	160	9	85	0

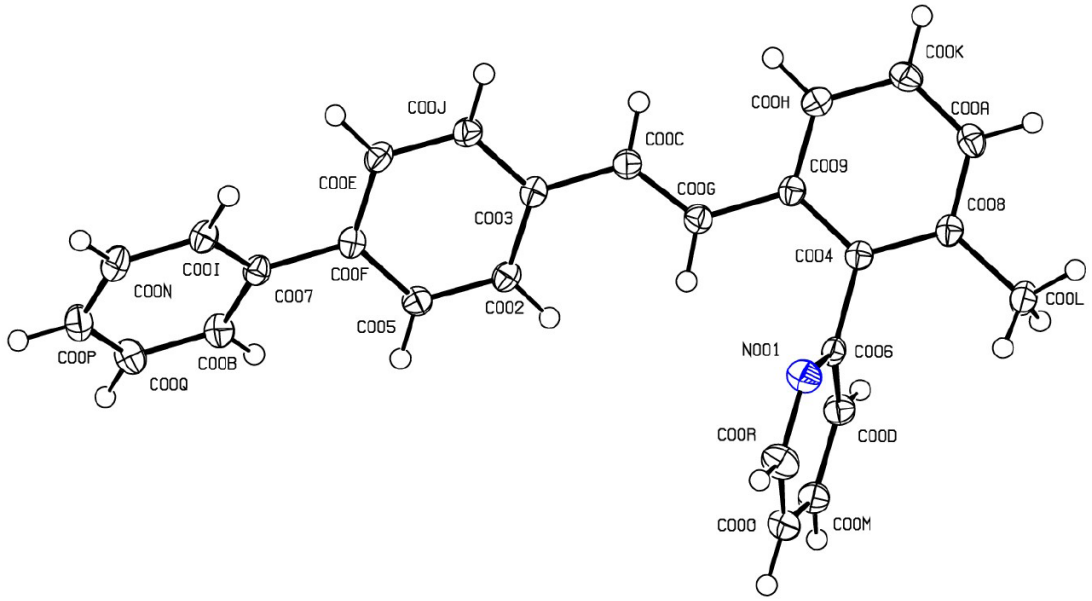
In an nitrogen-filled glove-box, an oven-dried 4 mL vial was charged with a stir bar, **1a** (21.4 mg, 0.05 mmol), $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$ (2.2 mg, 5 mol %), Ag_2CO_3 (16.5 mg, 0.06 mmol) and Ag_3PO_4 (41.5 mg, 0.1 mmol), toluene (1.6 mL), DME (0.4 mL) and styrene (18 μL, 0.15 mmol). The mixture was stirred at 150 °C for the specific time (as shown in the above table **S4**). Then the mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (5 mL). The filtrate was concentrated *in vacuo*. The remaining substrate **1a** and yields of **2a** and **2a'** were detected by ^1H NMR by using 1,1,2,2-tetrachloroethane as the standard.

Alkenylation of 2a' *via* C–H bond cleavage



In an nitrogen-filled glove-box, an oven-dried 4 mL vial was charged with a stir bar, **2a'** (21.4 mg, 0.05 mmol), $[Cp^{*Cy}Rh(CH_3CN)_3](SbF_6)_2$ (2.2 mg, 5 mol %), Ag_2CO_3 (16.5 mg, 0.06 mmol) and Ag_3PO_4 (41.5 mg, 0.1 mmol), toluene (1.6 mL), DME (0.4 mL) and styrene (18 μL, 0.15 mmol). Set up five reactions individually at the same time. The reaction mixture was heated at 150 °C for 100 minutes. Then, the mixture was filtered through a pad of celite and eluted with CH_2Cl_2 (5 mL). The filtrate was concentrated *in vacuo*. A quantitative yield of **2a** was measured by using ^1H NMR with 1,1,2,2-tetrachloroethane as the standard.

3. X-Ray Crystallographic Data

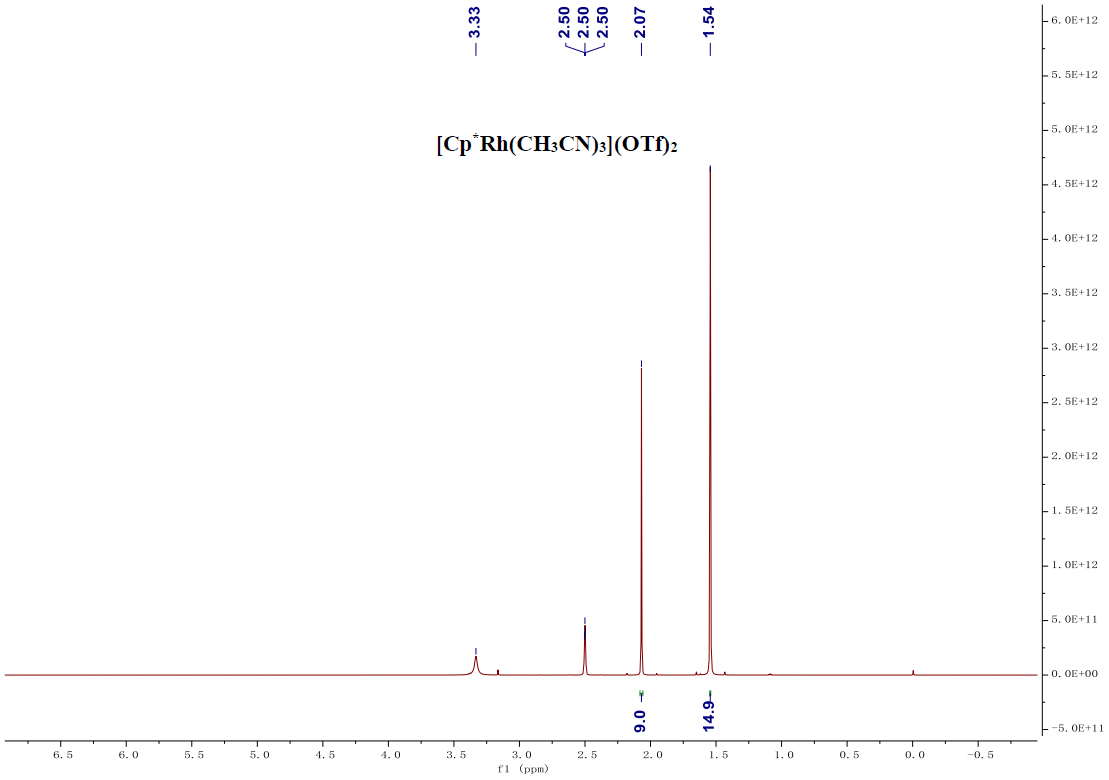


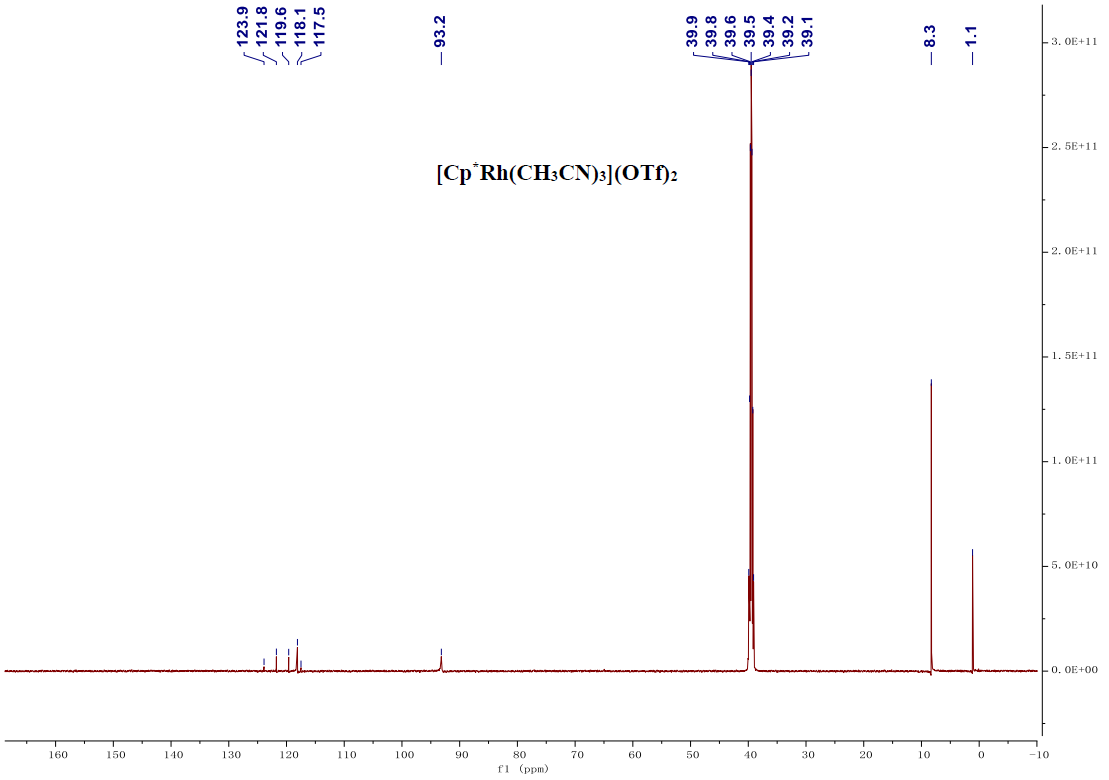
Crystal data and structure refinement for compound 2k

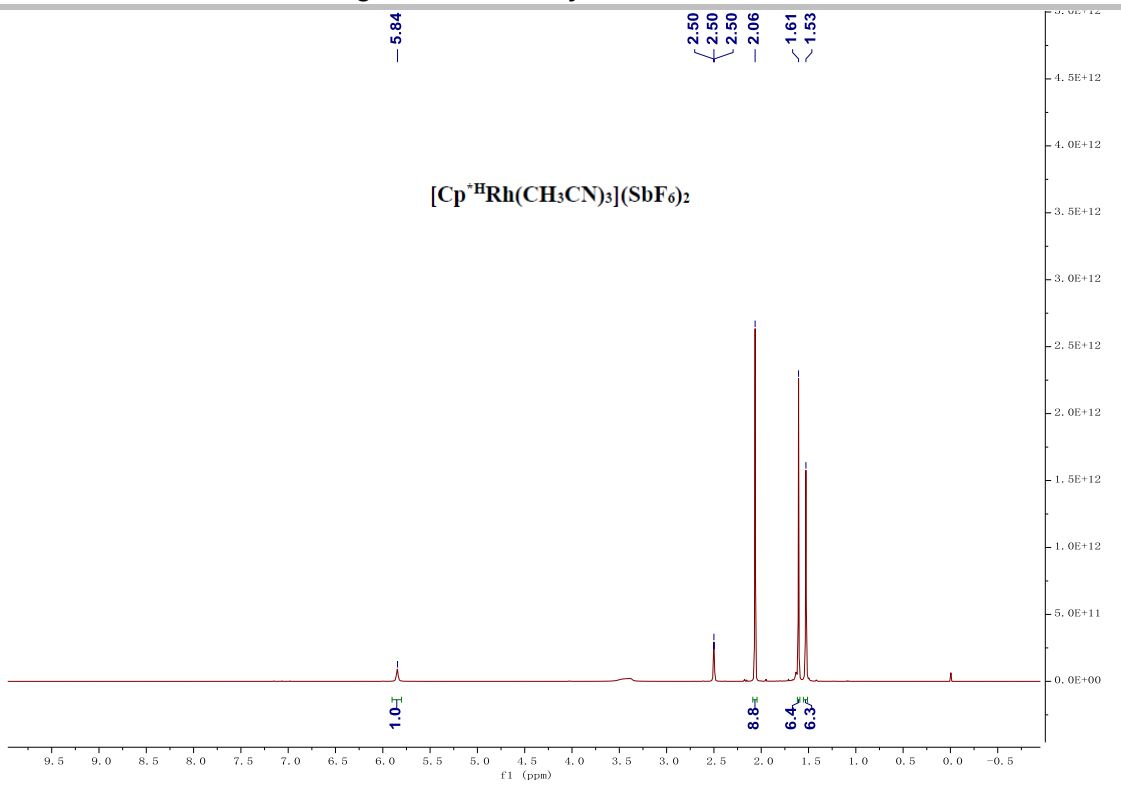
CCDC	1968169
Empirical formula	$C_{26}H_{21}N$
Formula weight	347.44
Temperature/K	100.0
Crystal system	triclinic
Space group	P -1
a/Å	9.0336(5)
b/Å	10.5141(5)
c/Å	12.1297(7)
α/°	110.415(2)
β/°	95.345(2)
γ/°	114.138(2)
Volume/Å3	947.12(9)
Z	2
ρ_{calc}g/cm3	1.218
μ/mm^{-1}	0.070
F(000)	368
Crystal size/mm^3	0.077 × 0.355 × 0.448
Radiation	MoKa (λ = 0.71073)
2Θ range for data collection/°	4.584 to 56.632
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 13, -16 ≤l ≤ 16
Reflections collected	36207
Refinement method	Full-matrix least-squares on shelXL
Independent reflections	4665 [Rint = 0.0278, Rsigma = 0.0156]

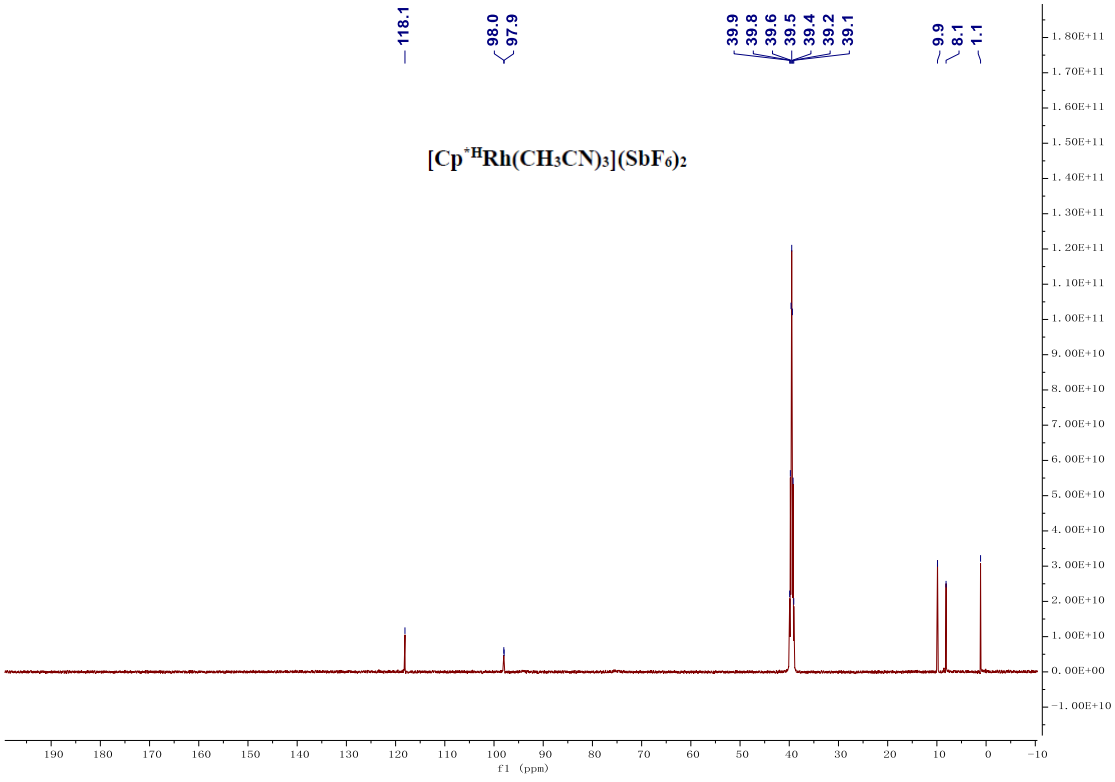
Data/restraints/parameters	4665/0/245
Goodness-of-fit on F^2	1.047
Final R indexes [I>=2σ (I)]	R1 = 0.0392, wR2 = 0.1031
Final R indexes [all data]	R1 = 0.0431, wR2 = 0.1064
Largest diff. peak/hole / e $Å^{-3}$	0.036/-0.184

4. NMR Spectra






5.84
2.50
2.50
2.50
2.06
1.61
1.53
[Cp*HRh(CH3CN)3](SbF6)2
1.0
8.8
6.4
6.3
f1 (ppm)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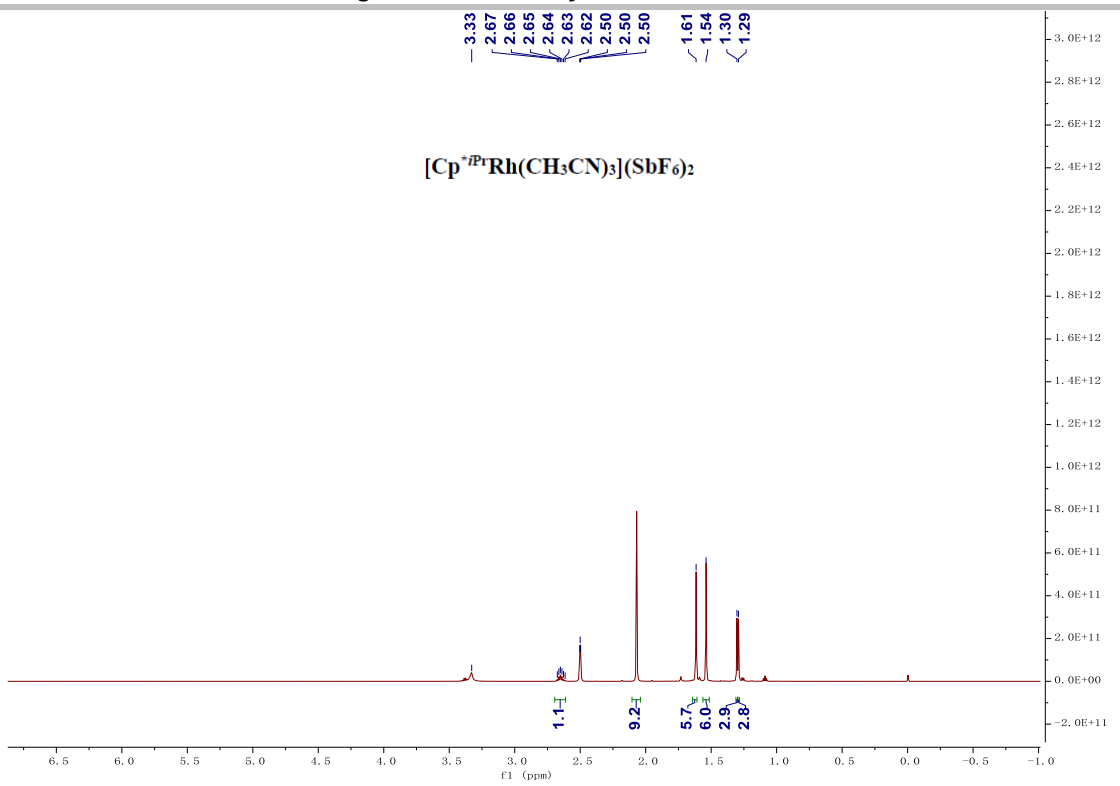
98.0
97.9
39.9
39.8
39.6
39.5
39.4
39.2
39.1
9.9
8.1
1.1
[Cp*HRh(CH3CN)3](SbF6)2
f1 (ppm)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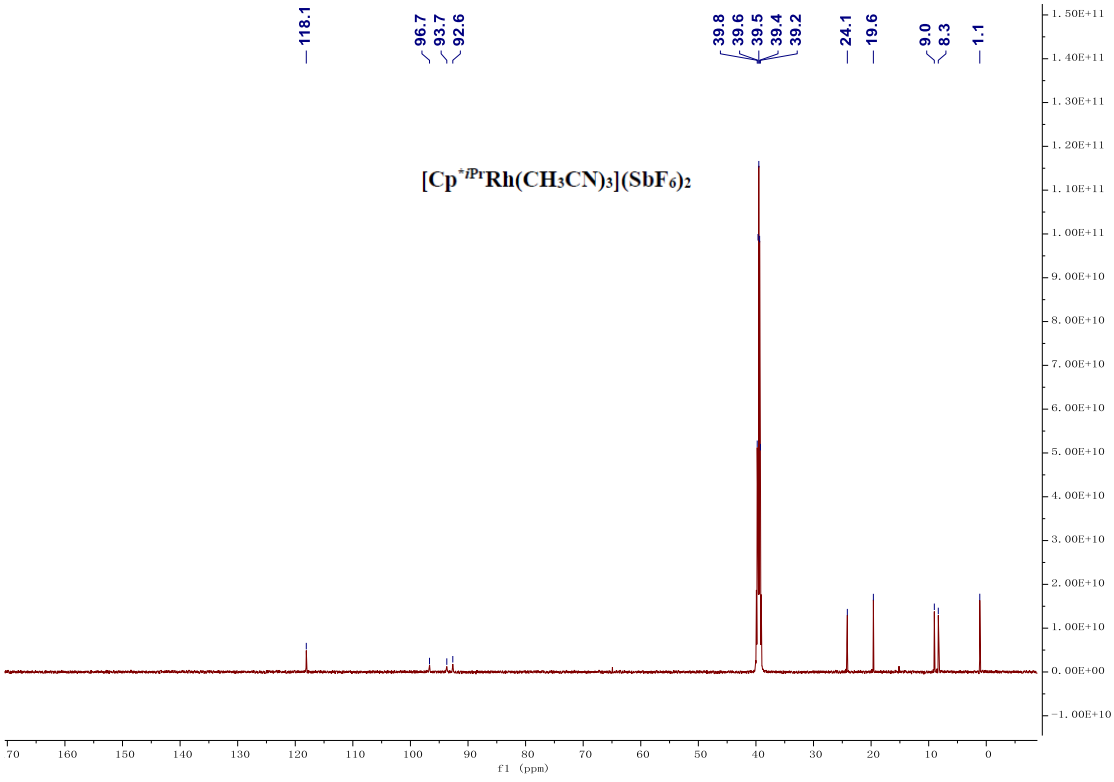
2.67
2.66
2.65
2.64
2.63
2.62
2.50
2.50
2.50
1.61
1.54
1.30
1.29
[Cp*iPrRh(CH3CN)3](SbF6)2
1.1
9.2
5.7
6.0
2.9
2.8
f1 (ppm)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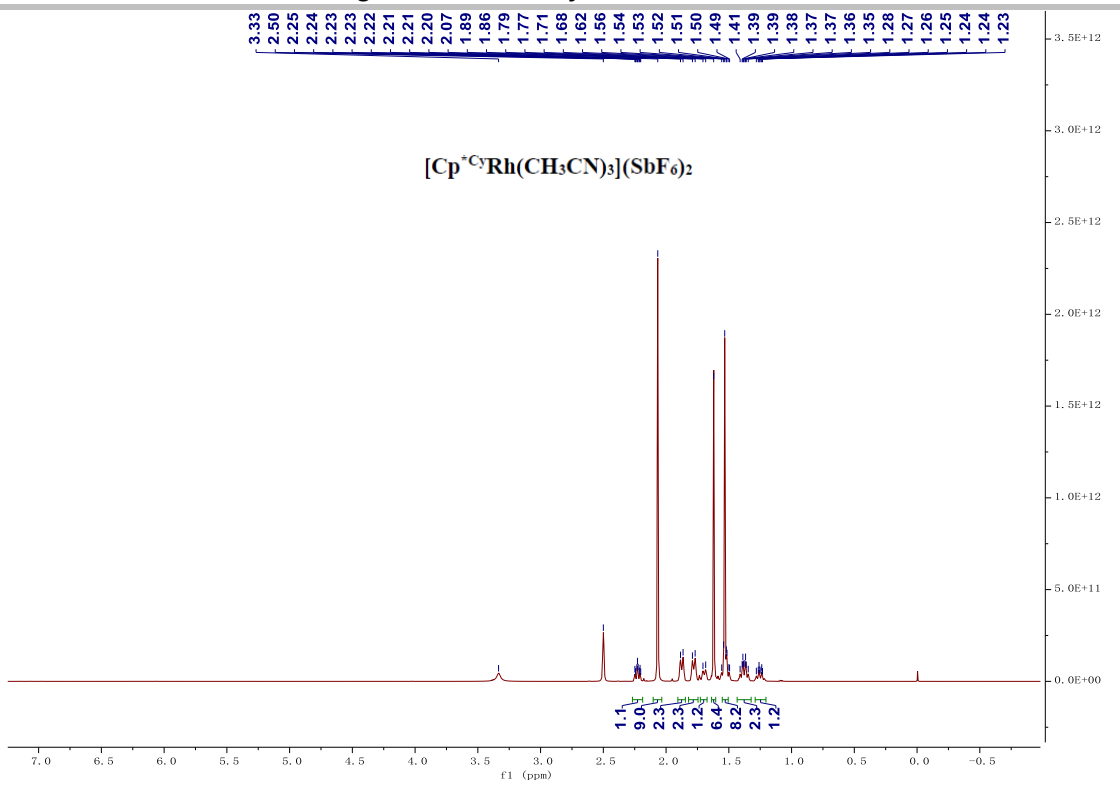
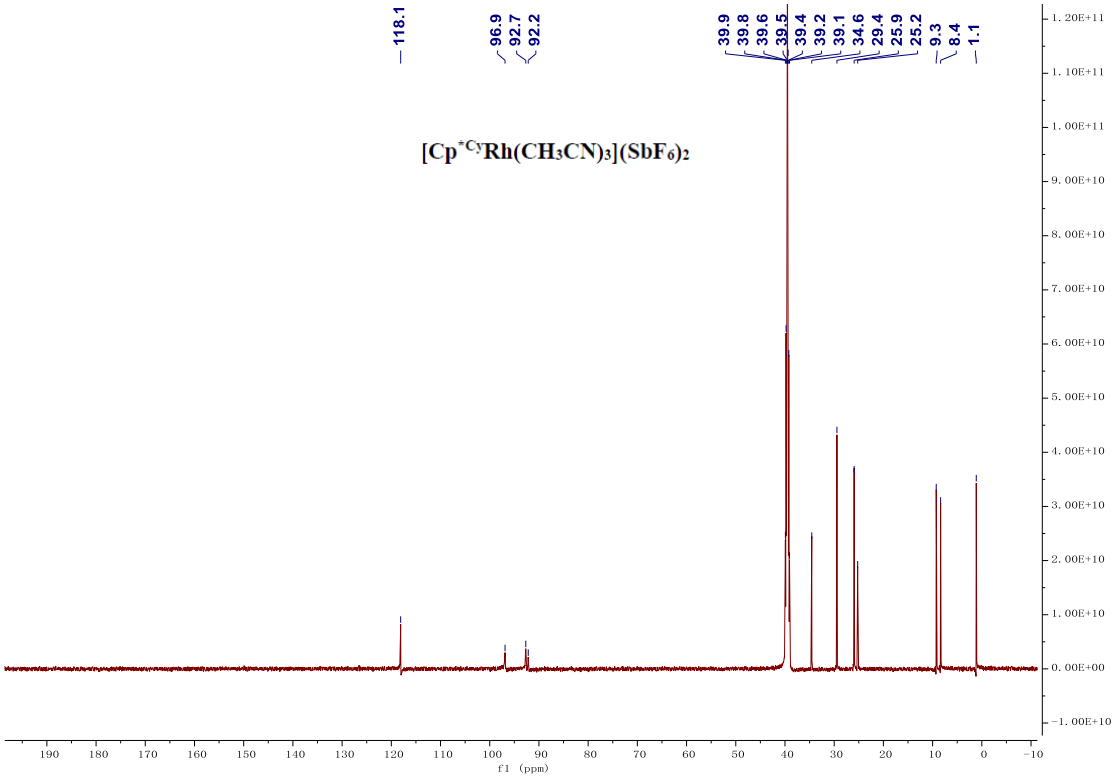
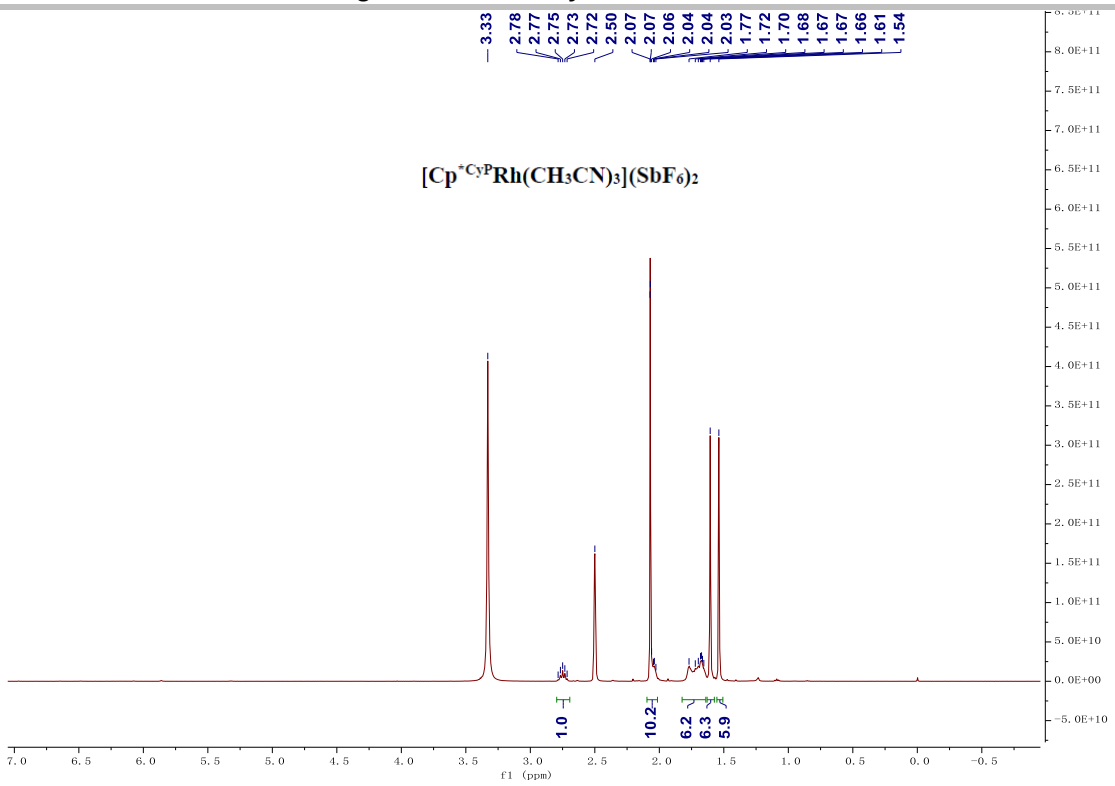
93.7
92.6
39.8
39.6
39.5
39.4
39.2
24.1
19.6
9.0
8.3
1.1
[Cp*iPrRh(CH3CN)3](SbF6)2
f1 (ppm)


3.33 2.50 2.25 2.24 2.23 2.23 2.22 2.21 2.21 2.20 2.07 1.89 1.86 1.79 1.77 1.71 1.68 1.62 1.56 1.54 1.53 1.52 1.51 1.50 1.49 1.41 1.39 1.39 1.38 1.37 1.37 1.36 1.35 1.28 1.27 1.26 1.25 1.24 1.24 1.23
[Cp*CyRh(CH3CN)3](SbF6)2
1.1 9.0 2.3 2.3 1.2 6.4 8.2 2.3 1.2
f1 (ppm)


118.1
96.9 92.7 92.2
39.9 39.8 39.6 39.5 39.4 39.2 39.1 34.6 29.4 25.9 25.2 9.3 8.4 1.1
[Cp*CyRh(CH3CN)3](SbF6)2
f1 (ppm)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2.50
2.07
2.07
2.06
2.04
2.04
2.03
1.77
1.72
1.70
1.68
1.67
1.67
1.66
1.61
1.54
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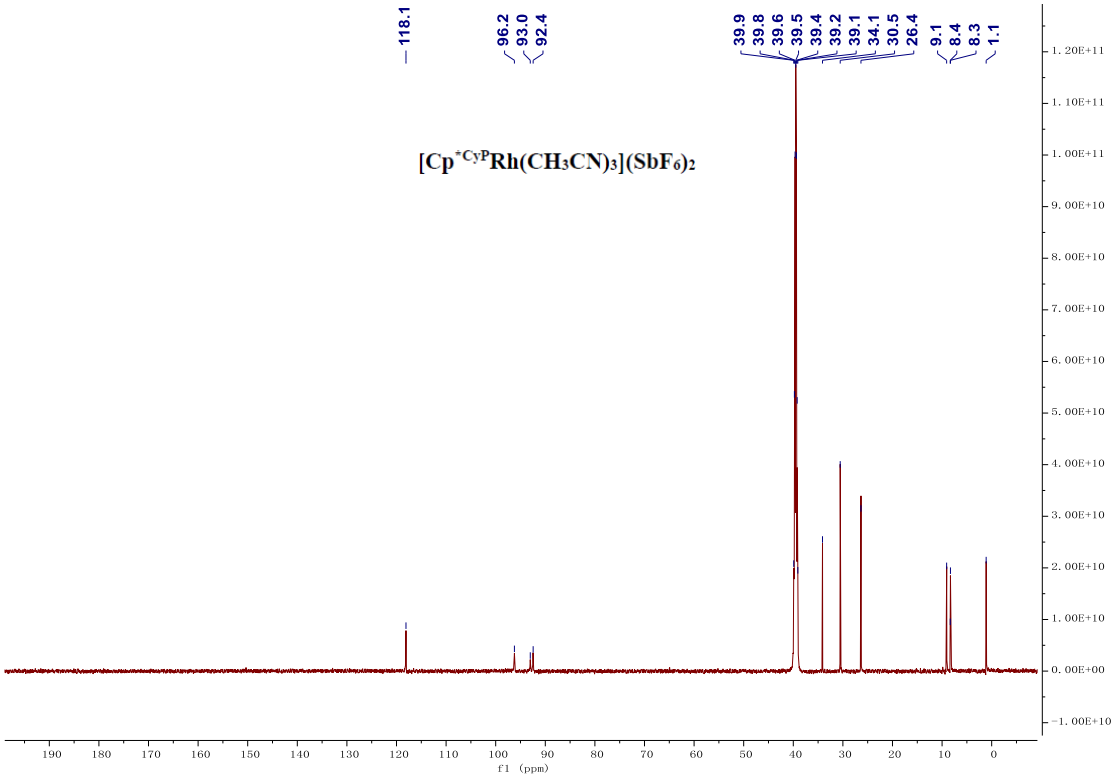
10.2
6.2
6.3
5.9
f1 (ppm)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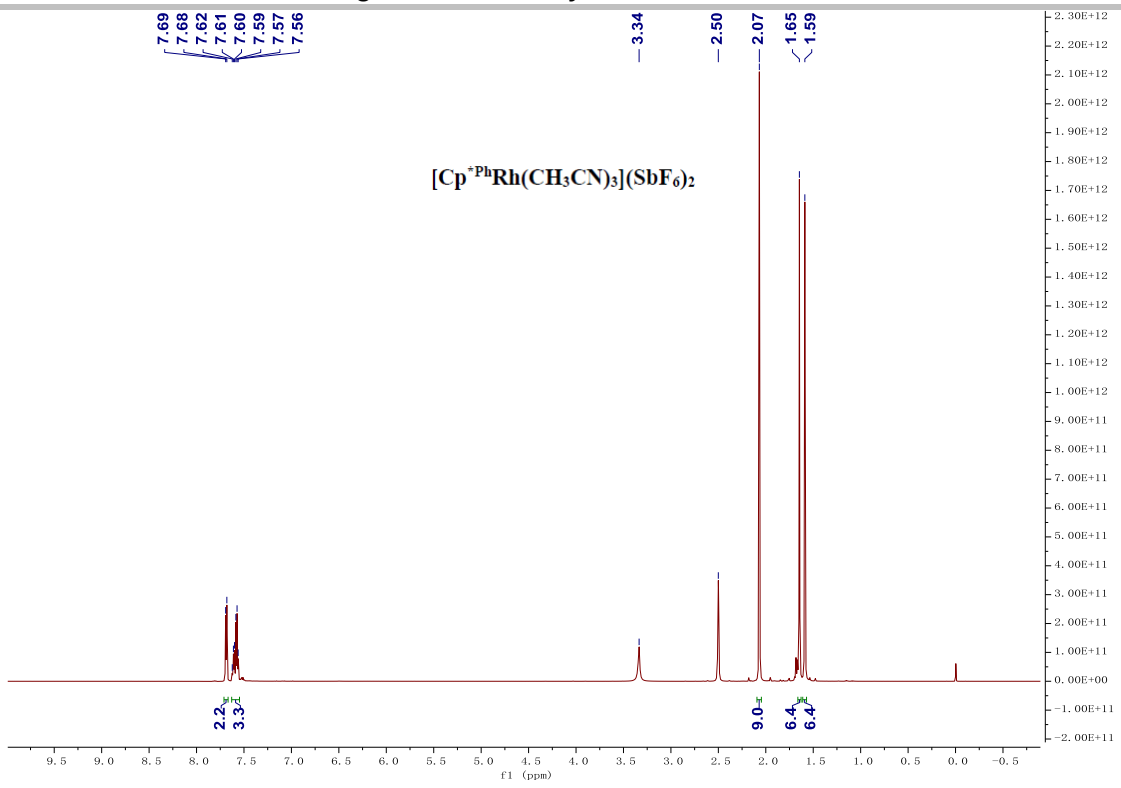
39.9
39.8
39.6
39.5
39.4
39.2
39.1
34.1
30.5
26.4
9.1
8.4
8.3
1.1
[Cp*CyPRh(CH3CN)3](SbF6)2
f1 (ppm)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7.62
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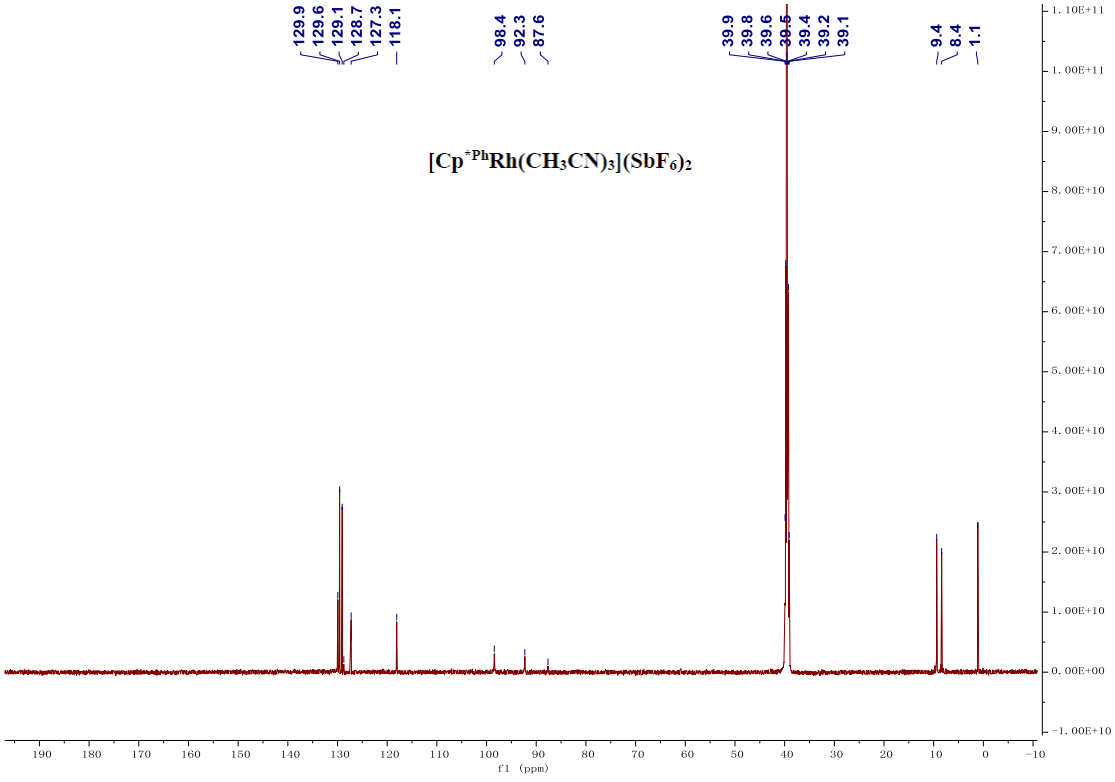
7.60
7.59
7.57
7.56
3.34
2.50
2.07
1.65
1.59
[Cp*PhRh(CH3CN)3](SbF6)2
2.2
3.3
9.0
6.4
6.4
f1 (ppm)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129.6
129.1
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127.3
118.1
98.4
92.3
87.6
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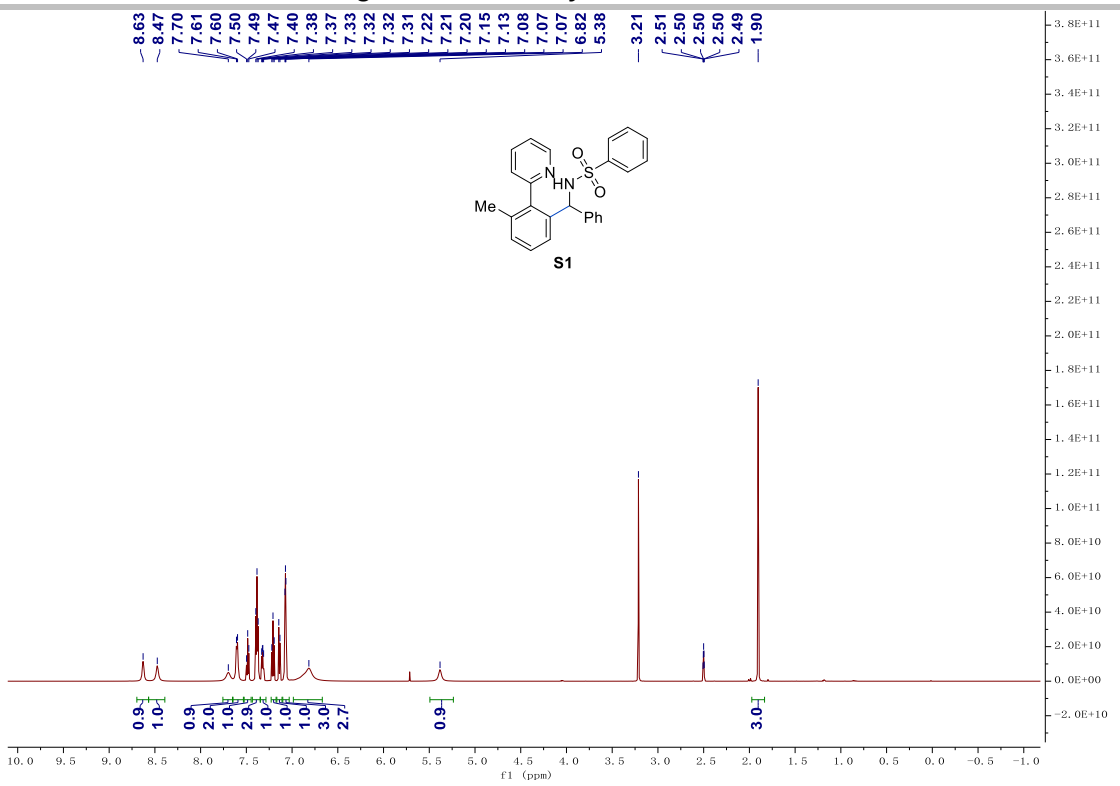
39.8
39.6
39.5
39.4
39.2
39.1
9.4
8.4
1.1
[Cp*PhRh(CH3CN)3](SbF6)2
f1 (ppm)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7.33
7.32
7.32
7.31
7.22
7.21
7.20
7.15
7.13
7.08
7.07
7.07
6.82
5.38
3.21
2.51
2.50
2.50
2.50
2.49
1.90
Me
Ph
S1
0.9
1.0
0.9
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2.9
1.0
1.0
1.0
3.0
2.7
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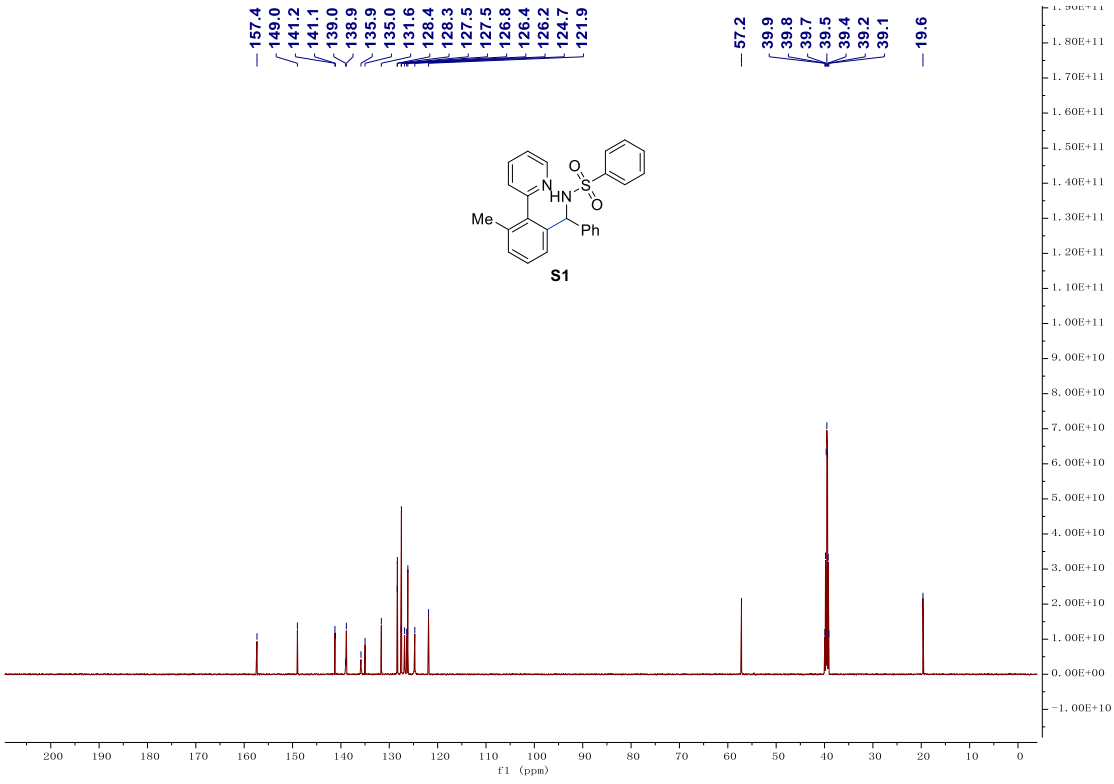
3.0
f1 (ppm)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126.8
126.4
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124.7
121.9
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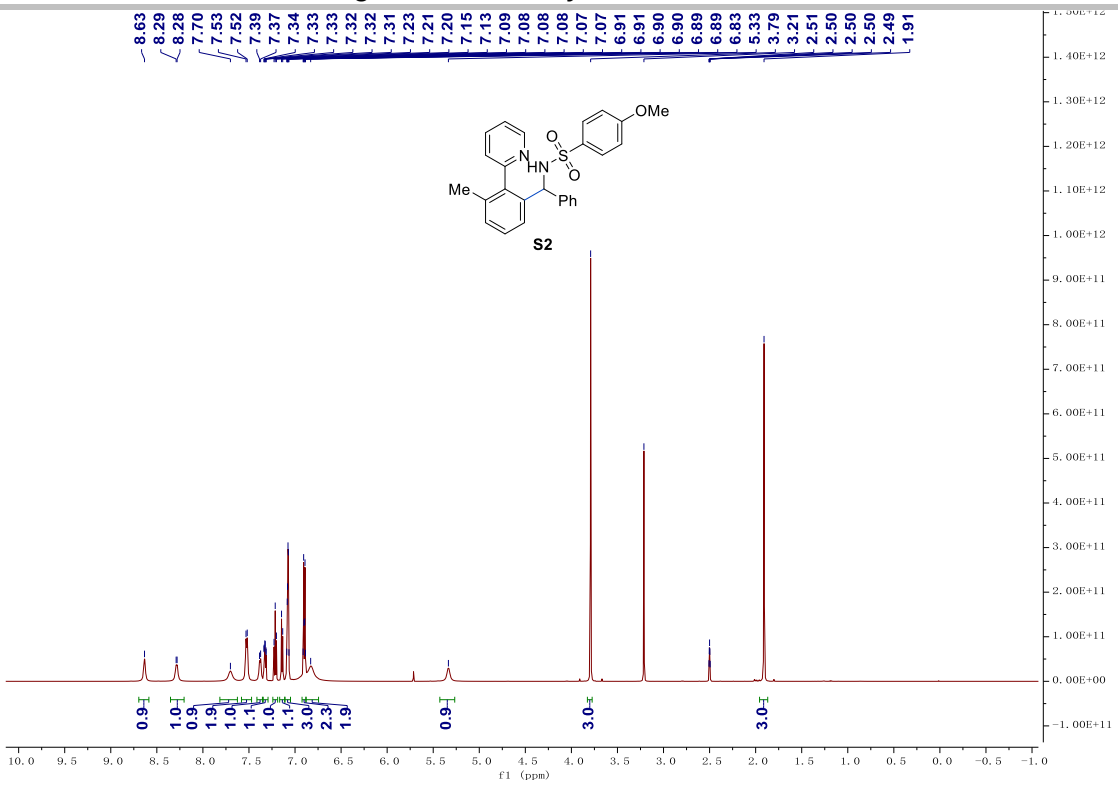
19.6
Me
Ph
S1
f1 (ppm)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7.31
7.23
7.21
7.20
7.15
7.13
7.09
7.08
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7.08
7.07
7.07
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6.91
6.90
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6.89
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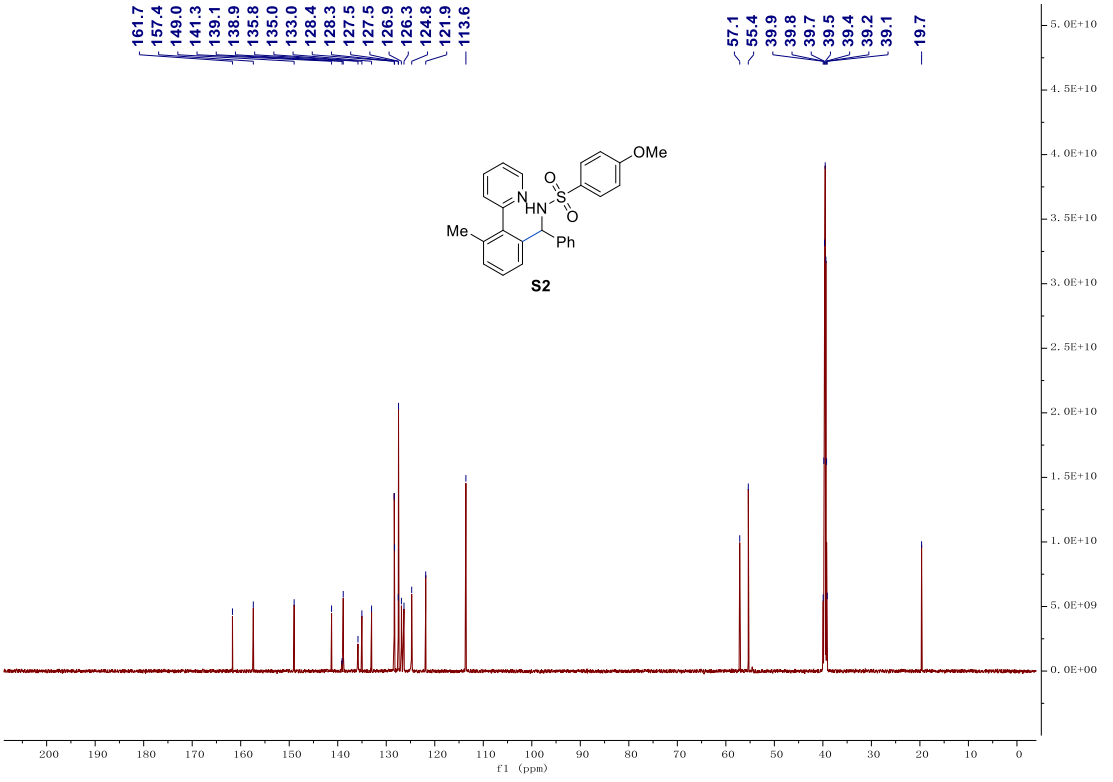
2.50
2.50
2.50
2.49
1.91
OMe
O
S
O
N
HN
Me
Ph
S2
0.9
1.0
0.9
1.9
1.0
1.1
1.0
1.1
3.0
2.3
1.9
0.9
3.0
3.0
f1 (ppm)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135.0
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128.4
128.3
127.5
127.5
126.9
126.3
124.8
121.9
113.6
57.1
55.4
39.9
39.8
39.7
39.5
39.4
39.2
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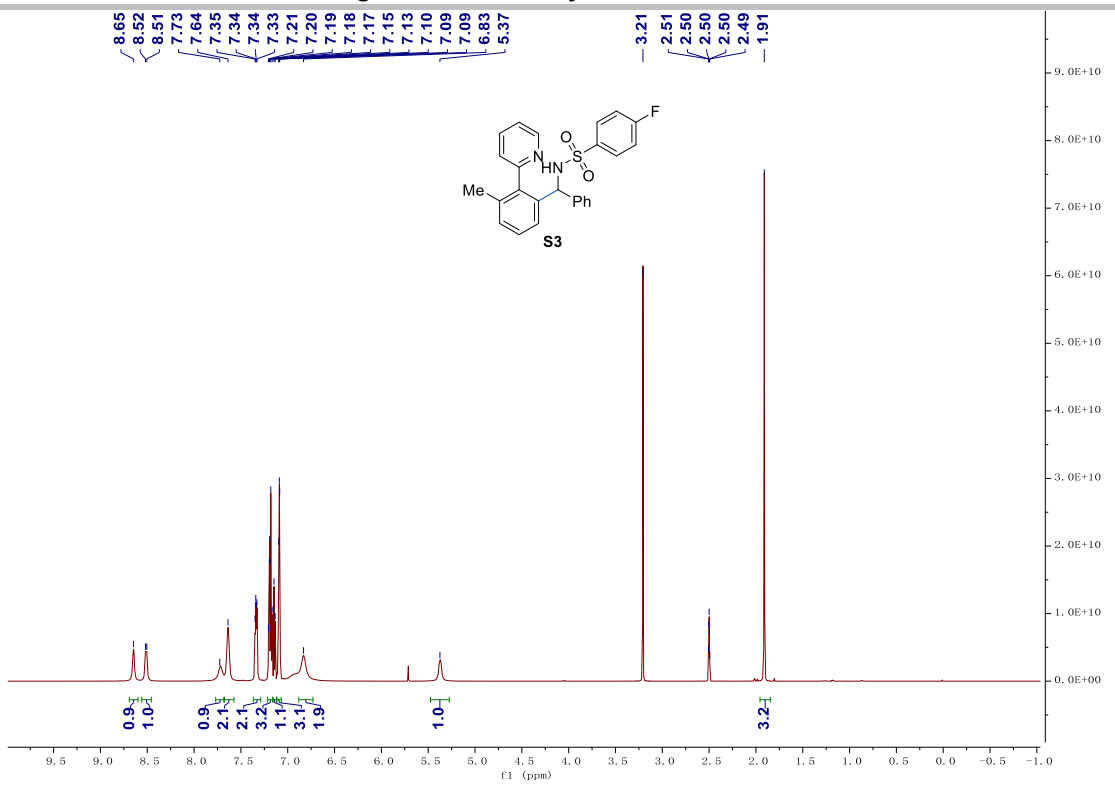
S
O
N
HN
Me
Ph
S2
f1 (ppm)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7.18
7.17
7.15
7.13
7.10
7.09
7.09
6.83
5.37
3.21
2.51
2.50
2.50
2.50
2.49
1.91
F
O
S
O
N
HN
Me
Ph
S3
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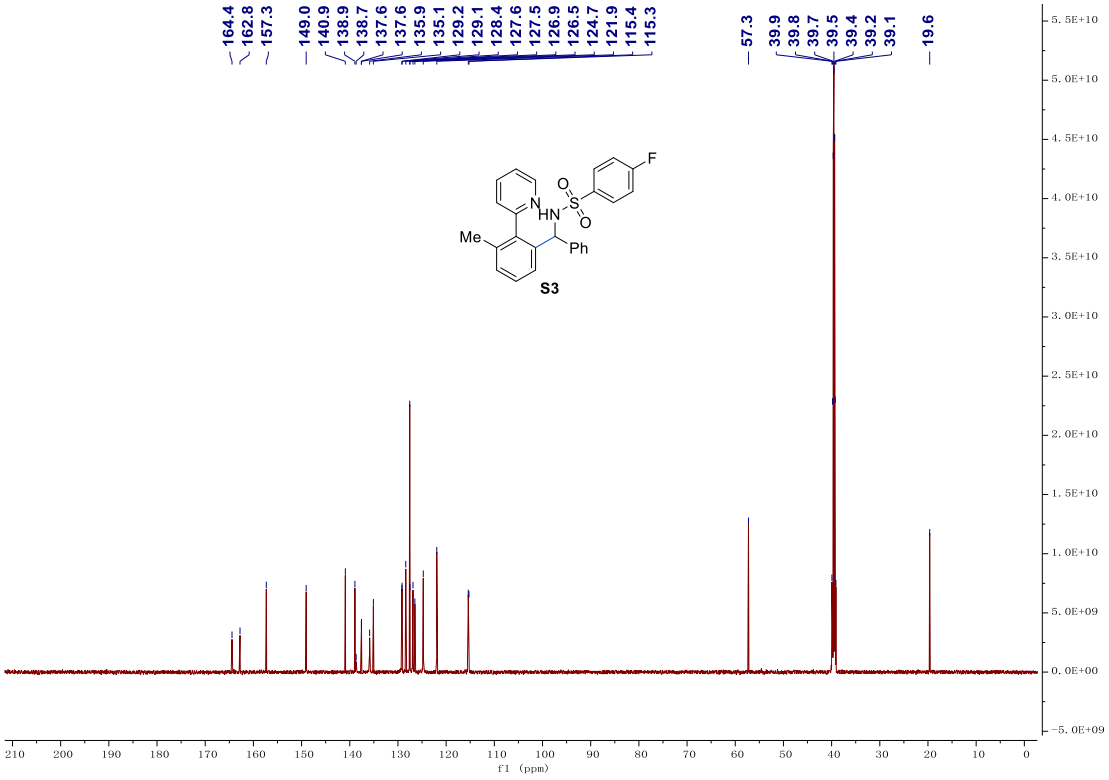
0.9
2.1
2.1
3.2
1.1
3.1
1.9
1.0
3.2
f1 (ppm)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135.1
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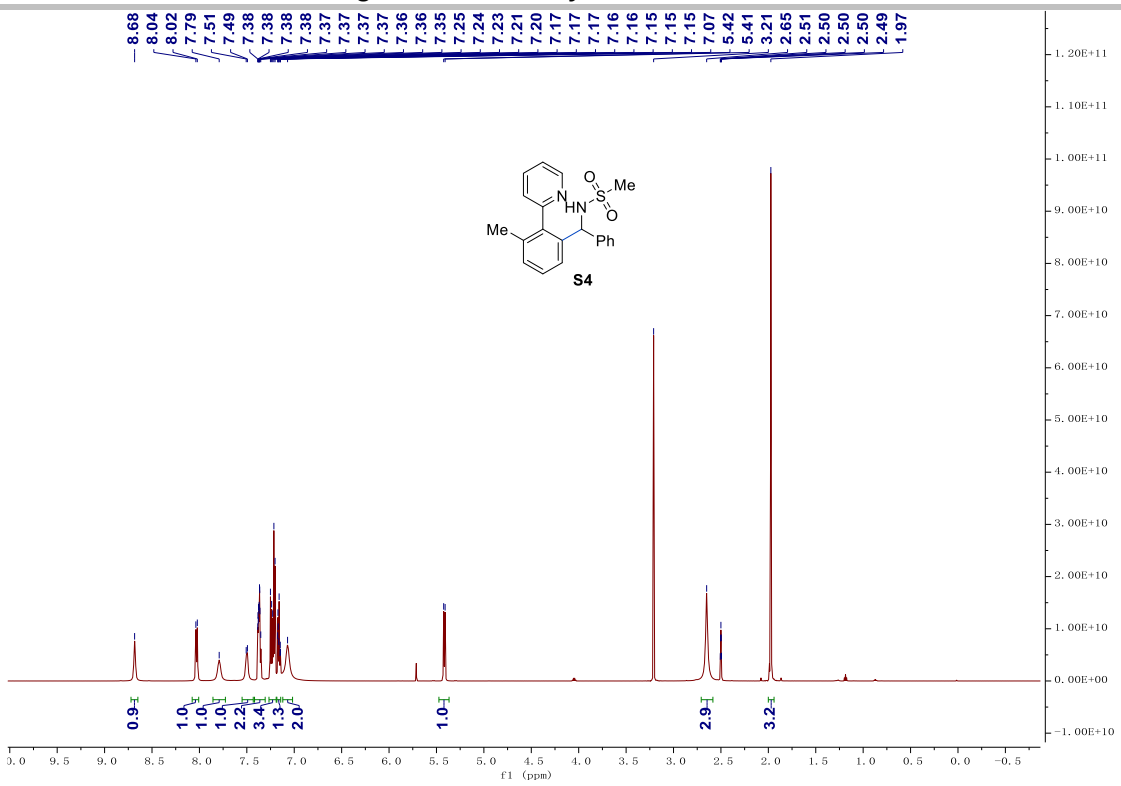
129.1
128.4
127.6
127.5
126.9
126.5
124.7
121.9
115.4
115.3
57.3
39.9
39.8
39.7
39.5
39.4
39.2
39.1
19.6
F
O
S
O
N
HN
Me
Ph
S3
f1 (ppm)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7.37
7.36
7.36
7.35
7.25
7.24
7.23
7.21
7.20
7.17
7.17
7.17
7.16
7.16
7.15
7.15
7.15
7.07
5.42
5.41
3.21
2.65
2.51
2.50
2.50
2.50
2.49
1.97
Me
HN
O
S
O
Me
Ph
S4
0.9
1.0
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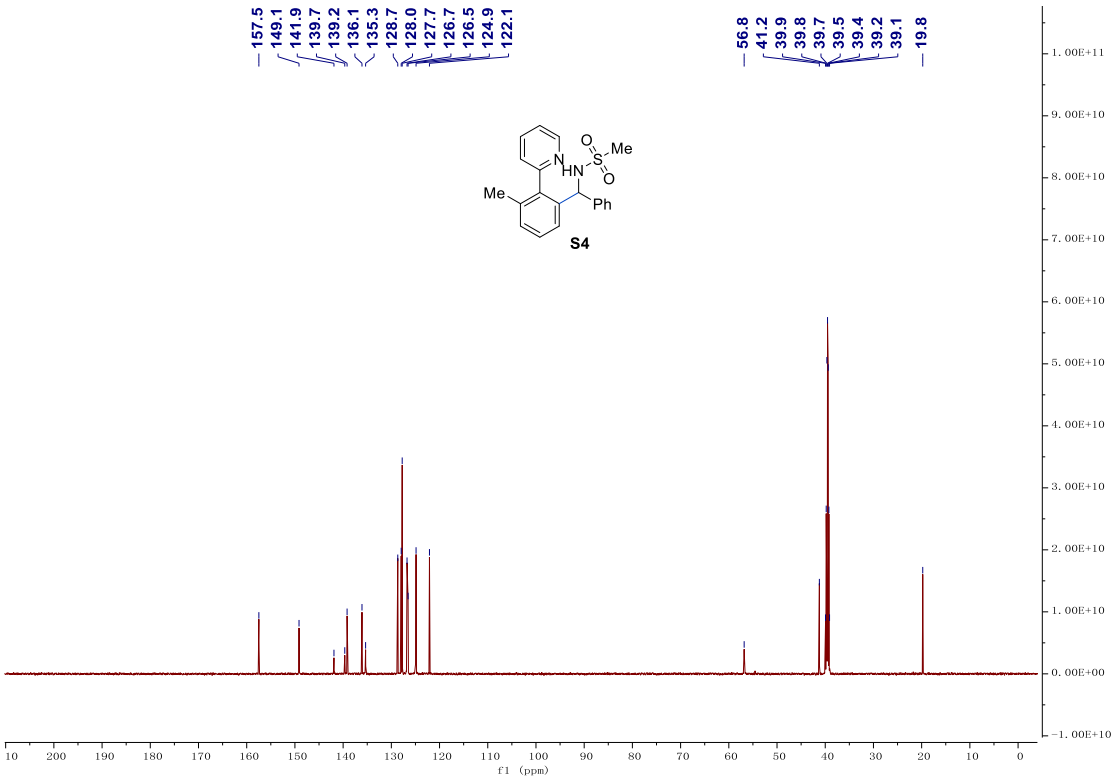
1.0
2.2
3.4
1.3
2.0
1.0
2.9
3.2
f1 (ppm)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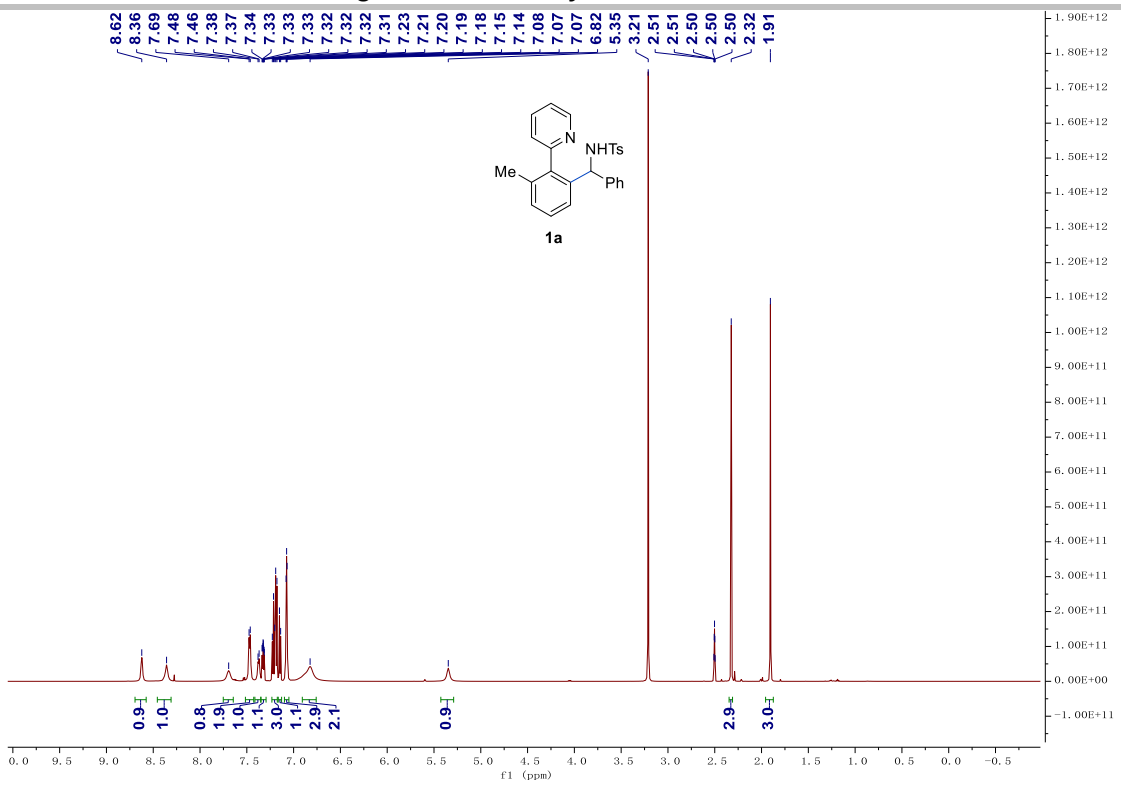
135.3
128.7
128.0
127.7
126.7
126.5
124.9
122.1
56.8
41.2
39.9
39.8
39.7
39.5
39.4
39.2
39.1
19.8
Me
HN
O
S
O
Me
Ph
S4
f1 (ppm)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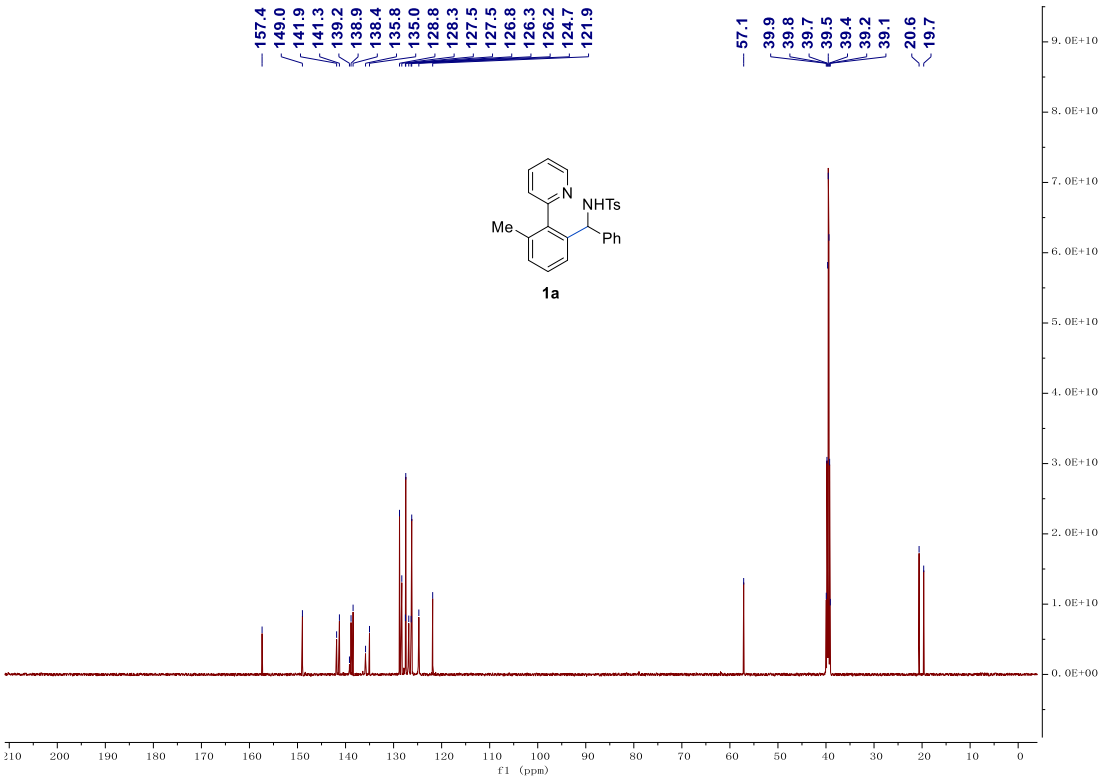
7.31
7.23
7.21
7.20
7.19
7.18
7.15
7.14
7.08
7.07
7.07
6.82
5.35
3.21
2.51
2.51
2.50
2.50
2.50
2.32
1.91
N
NHTs
Me
Ph
1a
0.9
1.0
0.8
1.9
1.0
1.1
3.0
1.1
2.9
2.1
0.9
2.9
3.0
f1 (ppm)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135.8
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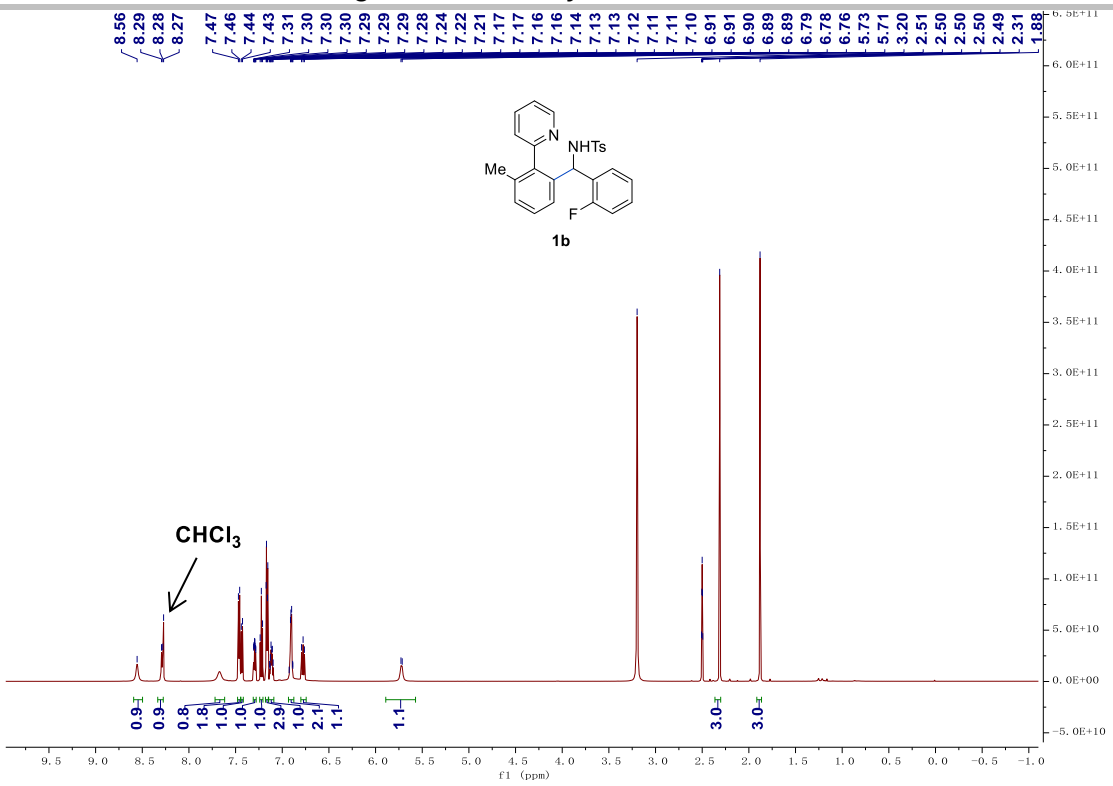
128.8
128.3
127.5
127.5
126.8
126.3
126.2
124.7
121.9
57.1
39.9
39.8
39.7
39.5
39.4
39.2
39.1
20.6
19.7
N
NHTs
Me
Ph
1a
f1 (ppm)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N
NHTs
Me
F
1b
CHCl3
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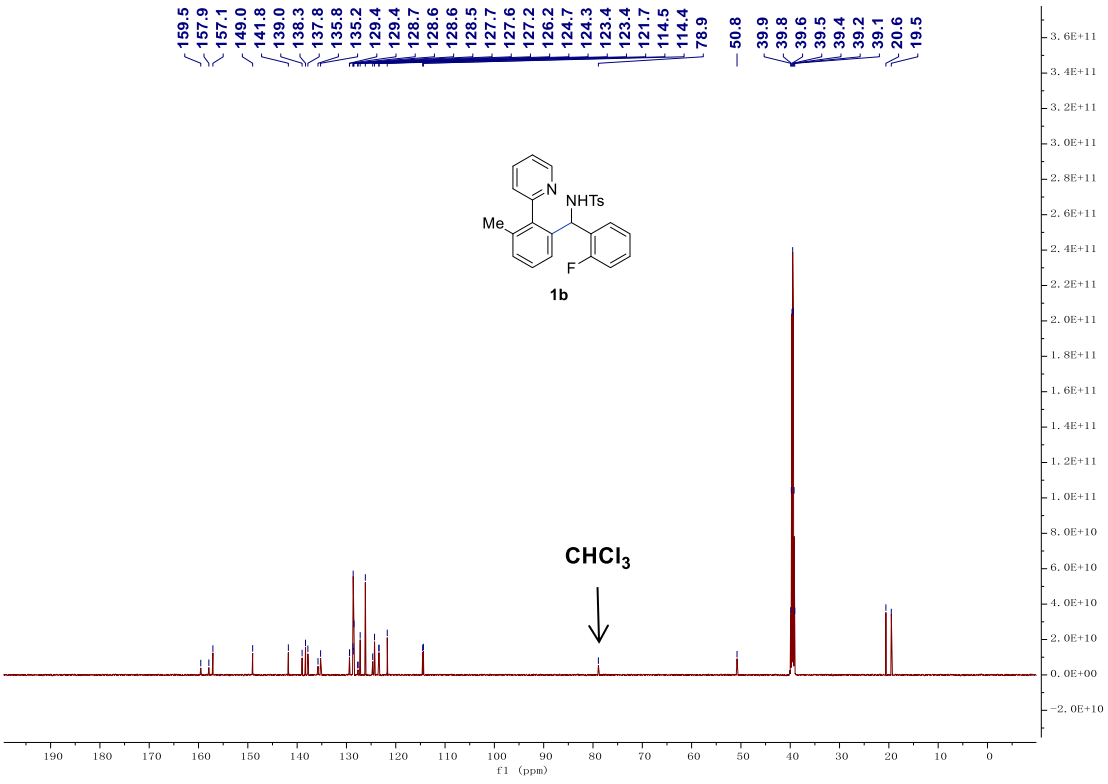
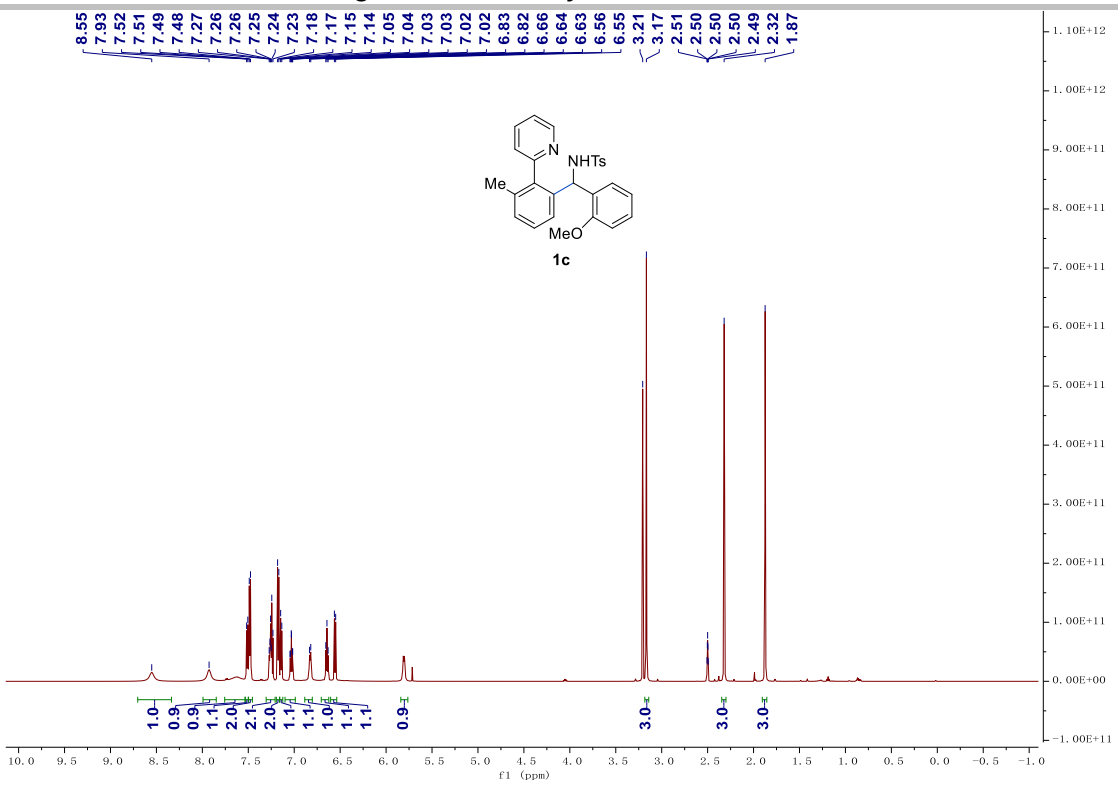
f1 (ppm)


159.5 157.9 157.1 149.0 141.8 139.0 138.3 137.8 135.8 135.2 129.4 129.4 128.7 128.6 128.6 128.5 127.7 127.6 127.2 126.2 124.7 124.3 123.4 123.4 121.7 114.5 114.4 78.9 50.8 39.9 39.8 39.6 39.5 39.4 39.2 39.1 20.6 19.5
N
NHTs
Me
F
1b
CHCl3
f1 (ppm)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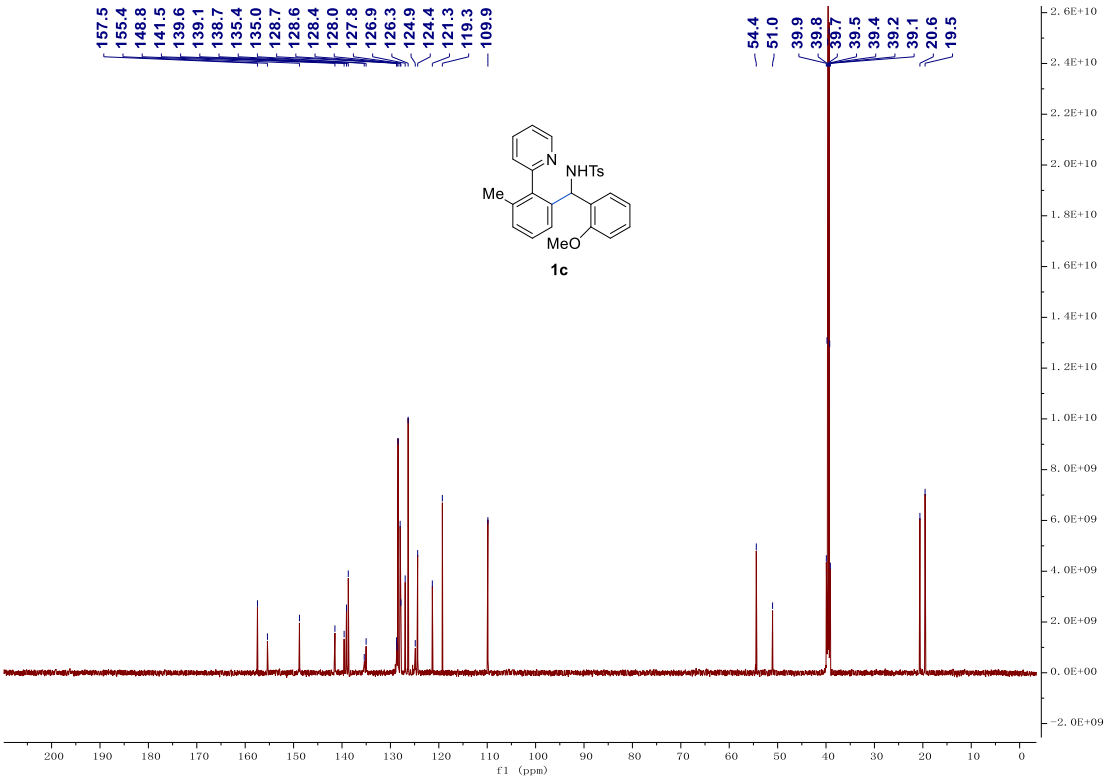
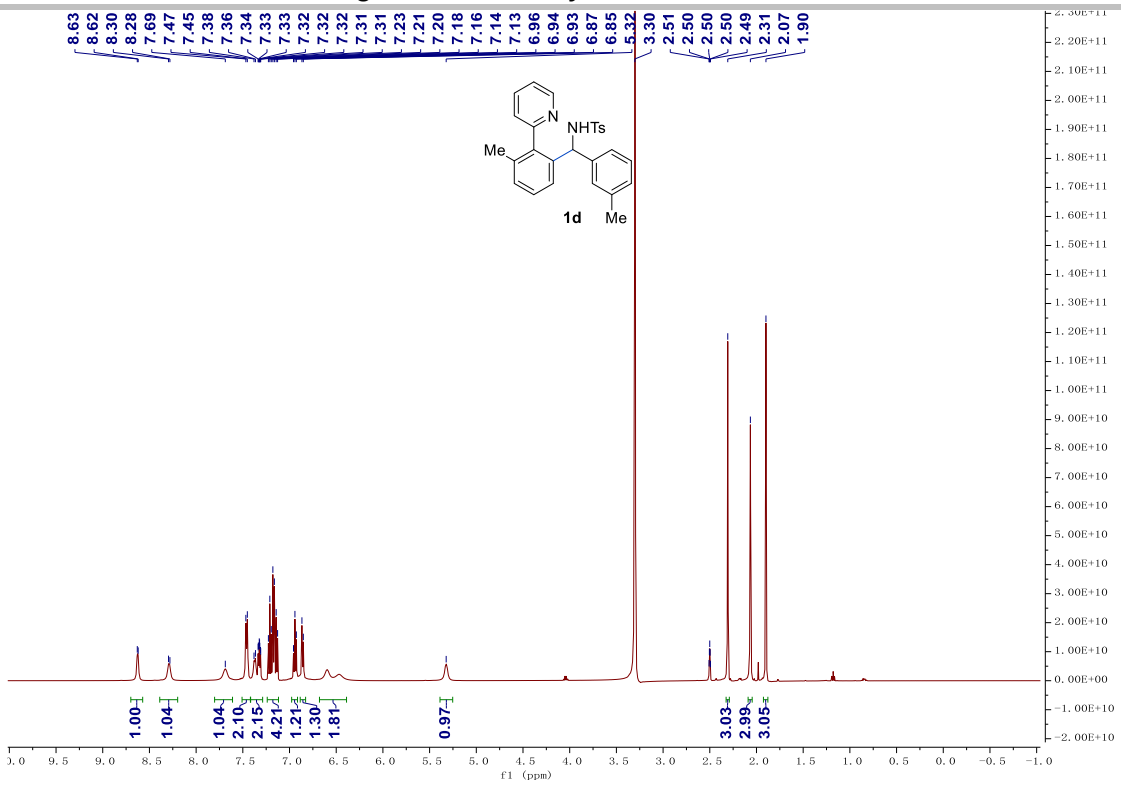
N
NHTs
Me
MeO
1c
1.0 0.9 0.9 1.1 2.0 2.1 2.0 1.1 1.1 1.0 1.1 1.1 0.9 3.0 3.0 3.0
f1 (ppm)


157.5 155.4 148.8 141.5 139.6 139.1 138.7 135.4 135.0 128.7 128.6 128.4 128.0 127.8 126.9 126.3 124.9 124.4 121.3 119.3 109.9
54.4 51.0 39.9 39.8 39.7 39.5 39.4 39.2 39.1 20.6 19.5
N
NHTs
Me
MeO
1c
f1 (ppm)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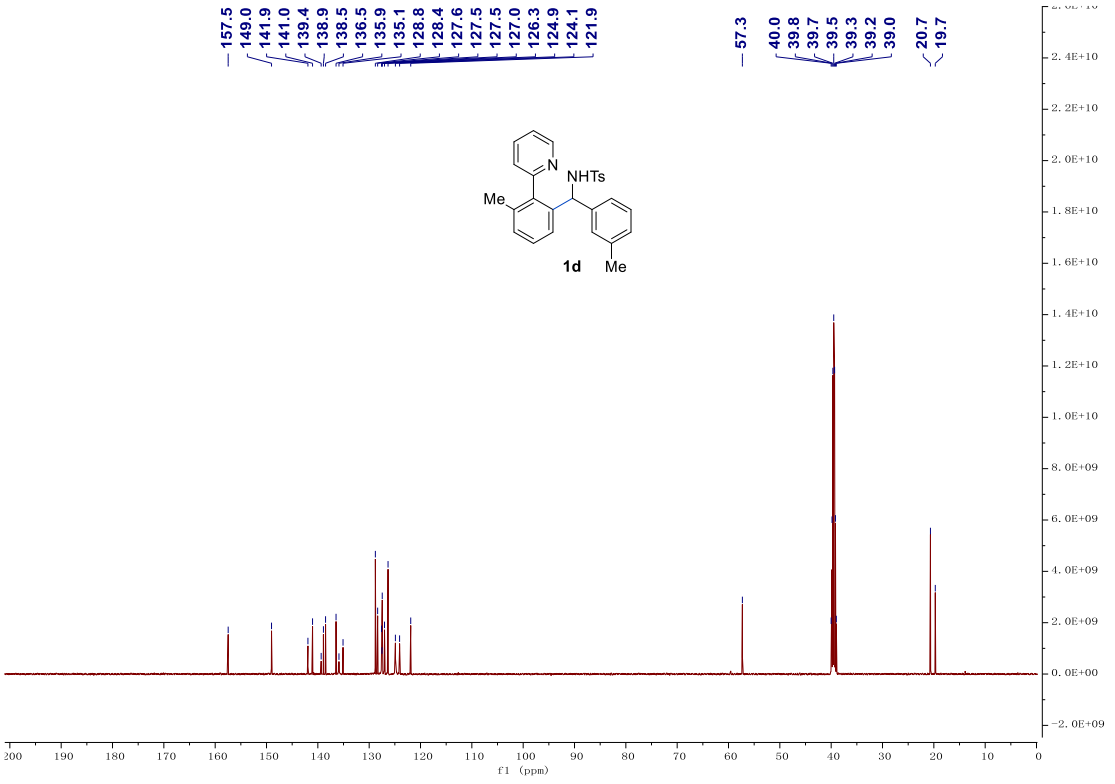
N
NHTs
Me
1d
Me
1.00 1.04 1.04 2.10 2.15 4.21 1.21 1.30 1.81 0.97 3.03 2.99 3.05
f1 (ppm)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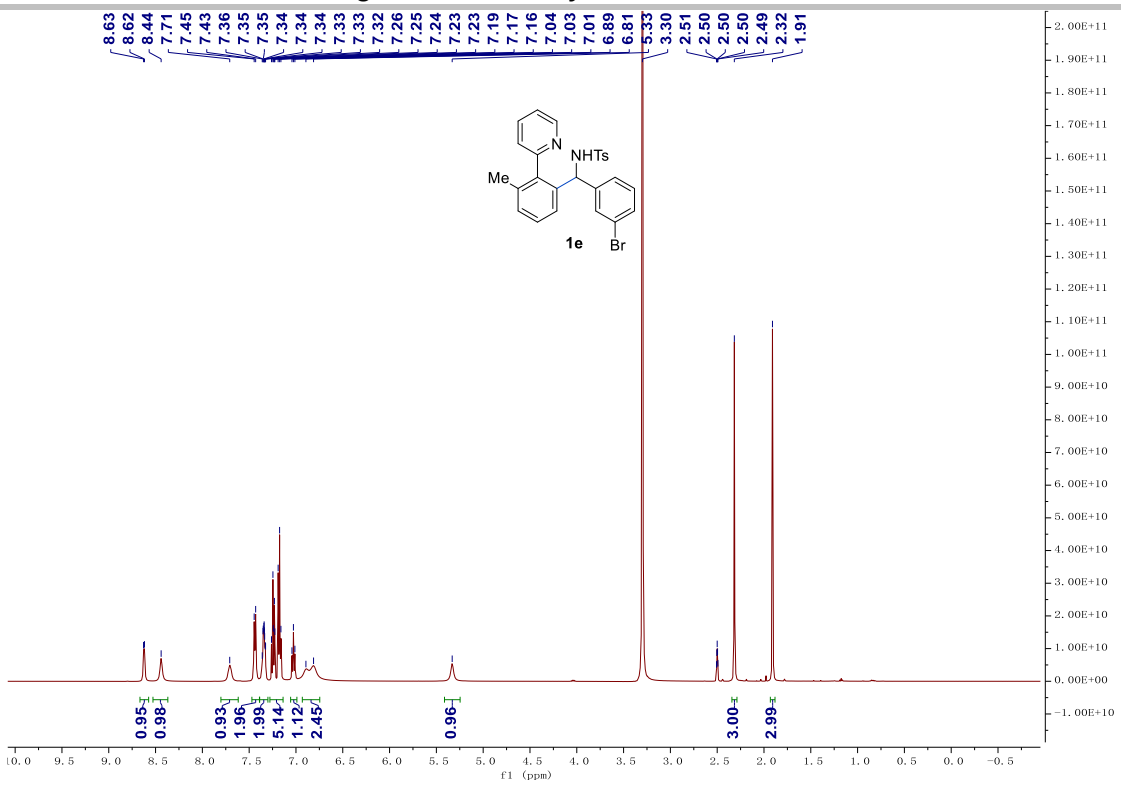
57.3 40.0 39.8 39.7 39.5 39.3 39.2 39.0 20.7 19.7
N
NHTs
Me
1d
Me
f1 (ppm)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7.33
7.32
7.26
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7.23
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7.17
7.16
7.04
7.03
7.01
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6.81
5.33
3.30
2.51
2.50
2.50
2.50
2.49
2.32
1.91
N
NHTs
Me
1e
Br
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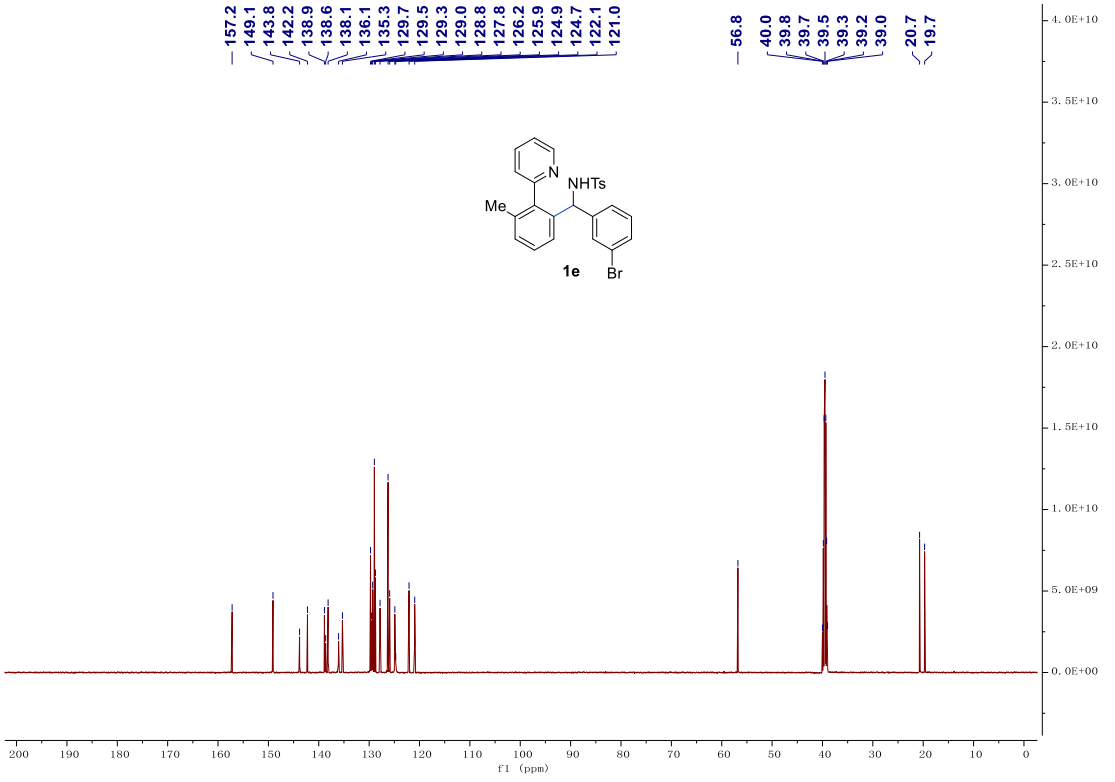
0.98
0.93
1.96
1.99
5.14
1.12
2.45
0.96
3.00
2.99
f1 (ppm)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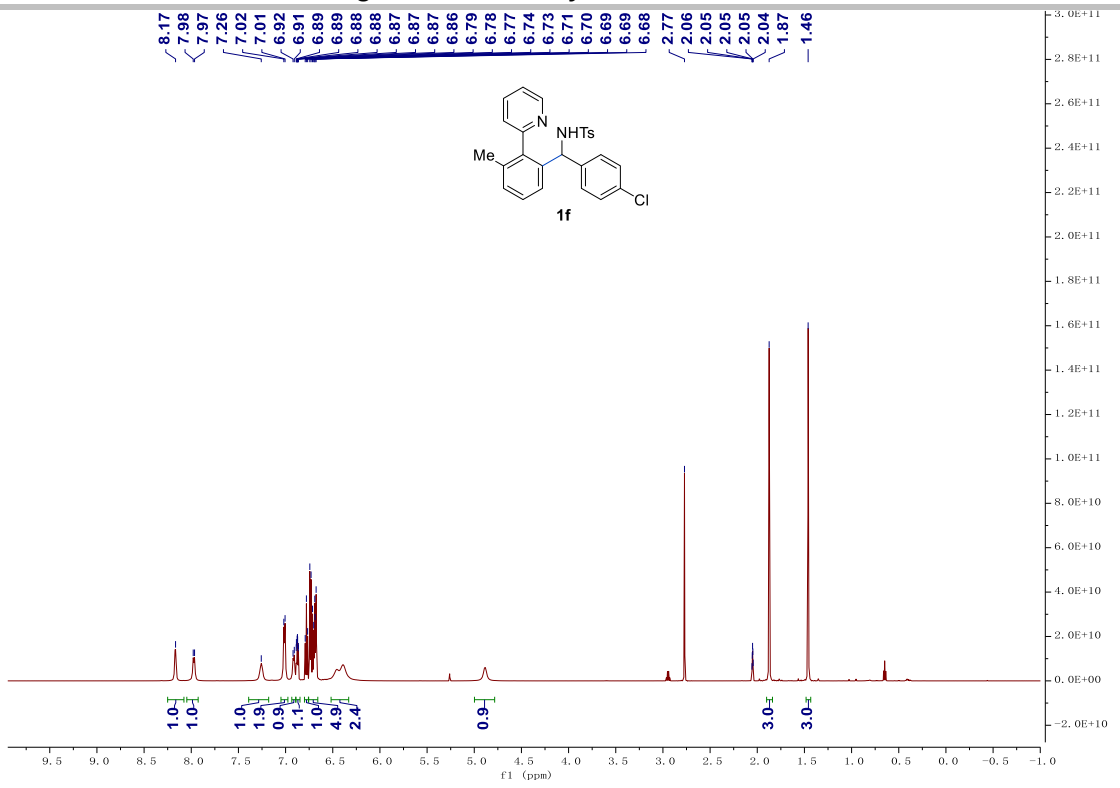
138.1
136.1
135.3
129.7
129.5
129.3
129.0
128.8
127.8
126.2
125.9
124.9
124.7
122.1
121.0
56.8
40.0
39.8
39.7
39.5
39.3
39.2
39.0
20.7
19.7
N
NHTs
Me
1e
Br
f1 (ppm)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6.89
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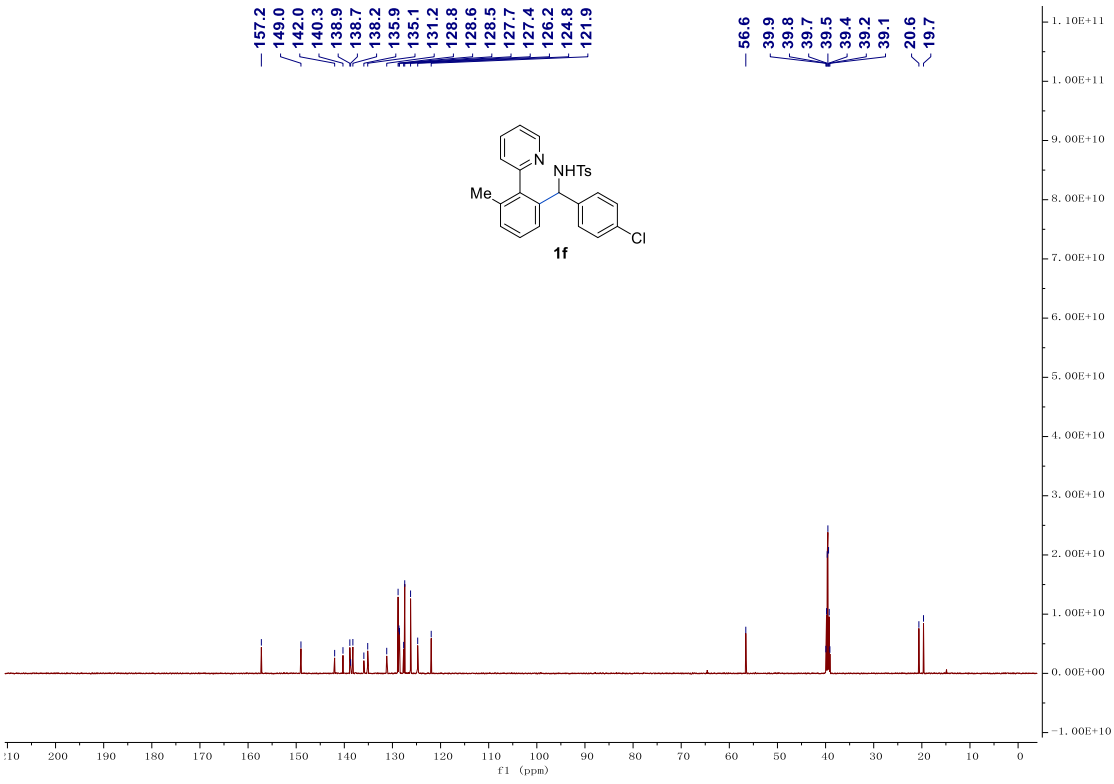
6.87
6.87
6.87
6.86
6.79
6.78
6.77
6.74
6.73
6.71
6.70
6.69
6.69
6.68
2.77
2.06
2.05
2.05
2.05
2.04
1.87
1.46
N
NHTs
Me
Cl
1f
1.0
1.0
1.0
1.9
0.9
1.1
1.0
4.9
2.4
0.9
3.0
3.0
f1 (ppm)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135.1
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128.8
128.6
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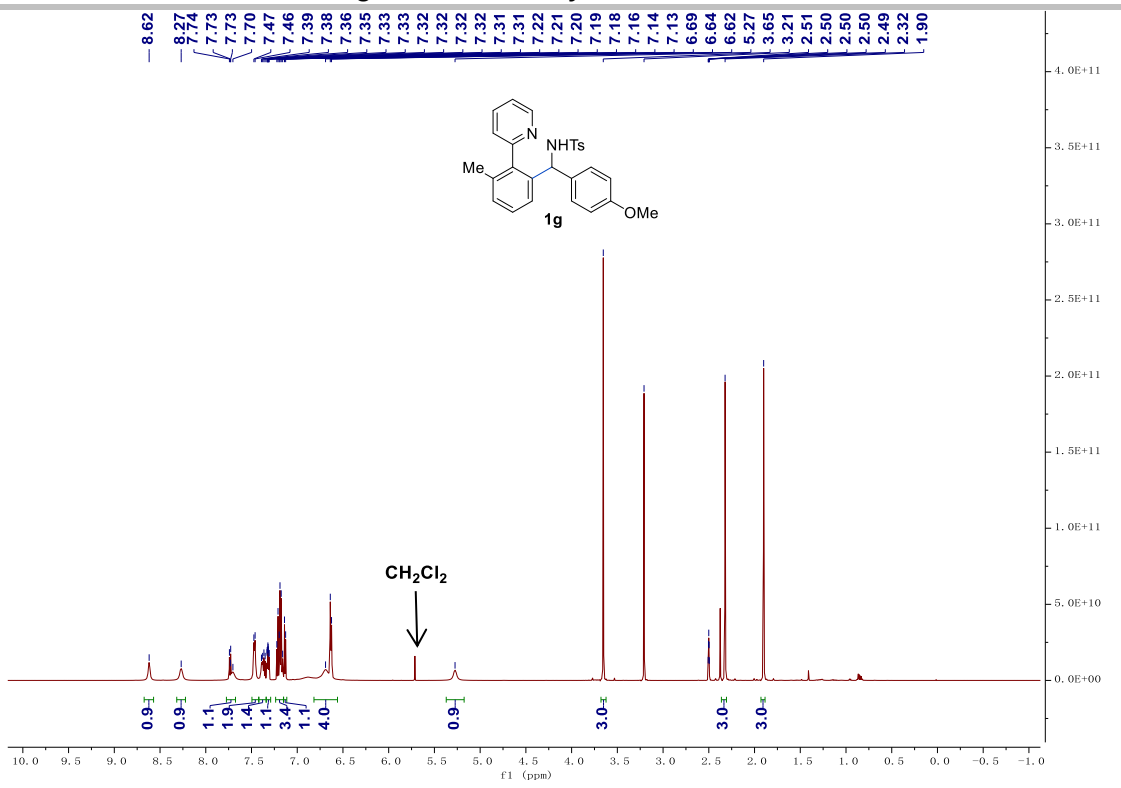
127.7
127.4
126.2
124.8
121.9
56.6
39.9
39.8
39.7
39.5
39.4
39.2
39.1
20.6
19.7
N
NHTs
Me
Cl
1f
f1 (ppm)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7.33
7.32
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7.32
7.32
7.31
7.31
7.22
7.21
7.20
7.19
7.18
7.16
7.14
7.13
6.69
6.64
6.62
5.27
3.65
3.21
2.51
2.50
2.50
2.50
2.49
2.32
1.90
N
NHTs
Me
OMe
1g
CH2Cl2
0.9
0.9
1.1
1.9
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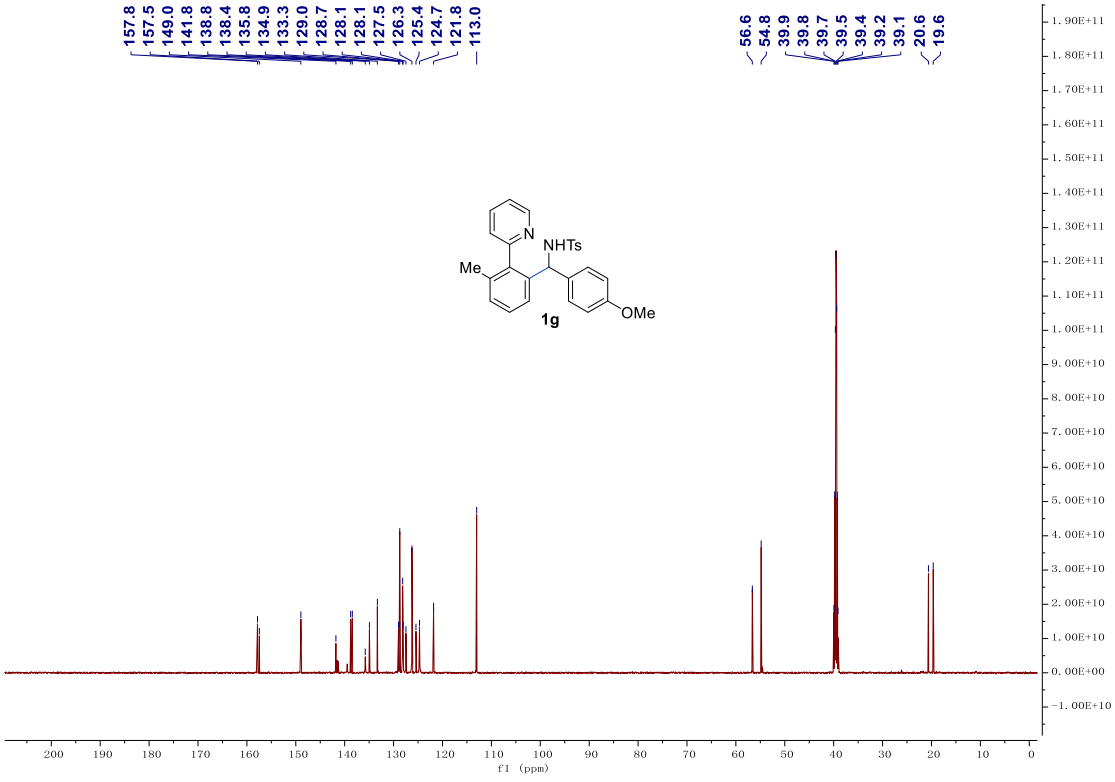
1.1
3.4
1.1
4.0
0.9
3.0
3.0
3.0
f1 (ppm)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128.1
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127.5
126.3
125.4
124.7
121.8
113.0
56.6
54.8
39.9
39.8
39.7
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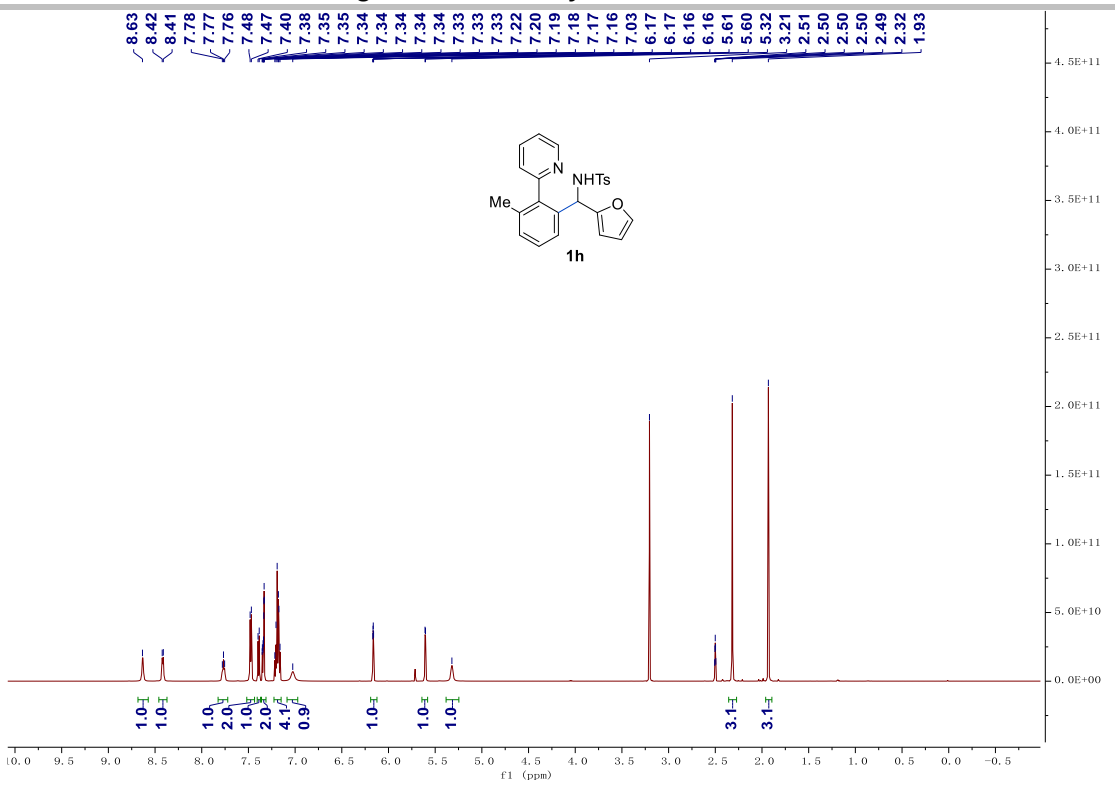
39.2
39.1
20.6
19.6
N
NHTs
Me
OMe
1g
f1 (ppm)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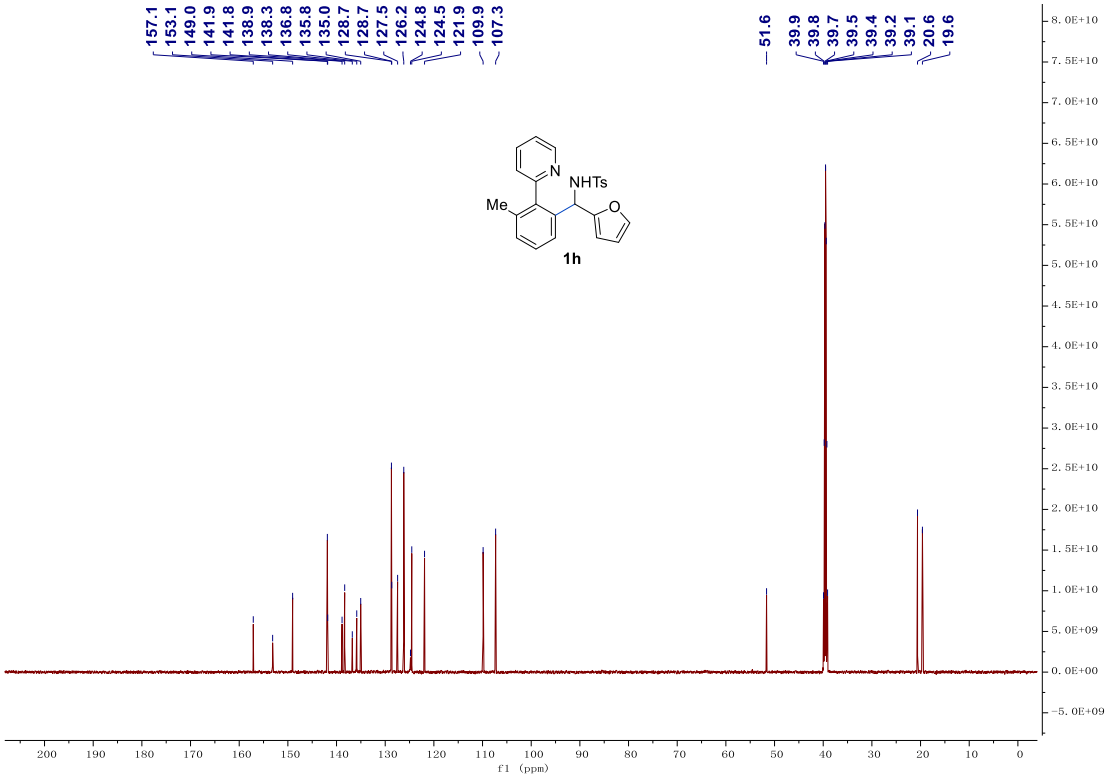
N
NHTs
Me
O
1h
1.0 1.0 1.0 2.0 1.0 2.0 4.1 0.9 1.0 1.0 1.0 3.1 3.1
f1 (ppm)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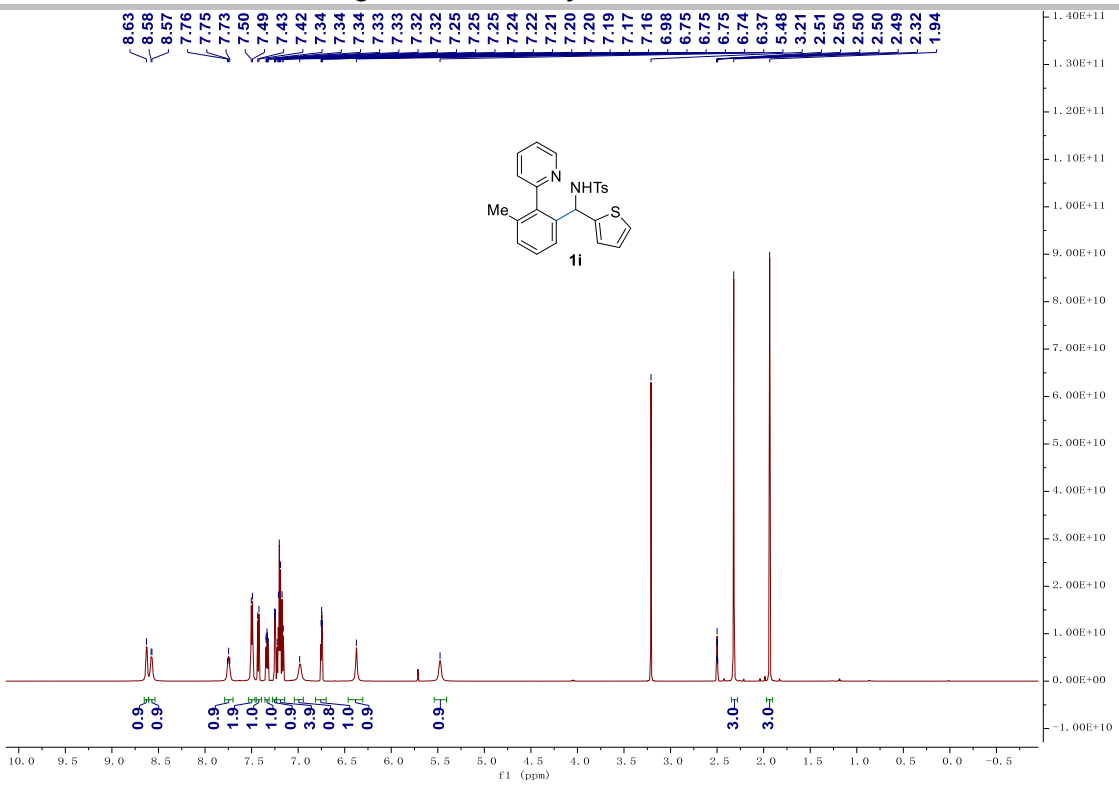
N
NHTs
Me
O
1h
f1 (ppm)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7.32
7.32
7.25
7.25
7.25
7.24
7.22
7.21
7.20
7.20
7.19
7.17
7.16
6.98
6.75
6.75
6.74
6.37
5.48
3.21
2.51
2.50
2.50
2.50
2.49
2.32
1.94
N
NHTs
Me
S
1i
0.9
0.9
0.9
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1.0
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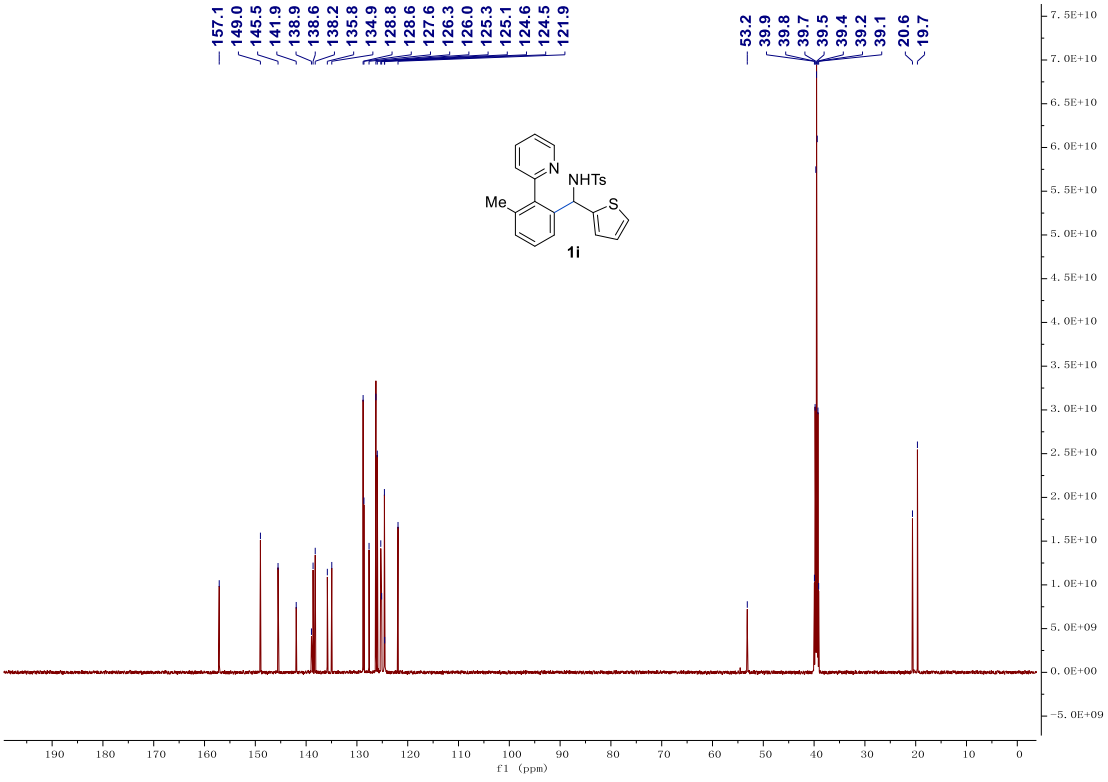
0.9
3.9
0.8
1.0
0.9
0.9
3.0
3.0
f1 (ppm)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126.3
126.0
125.3
125.1
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121.9
53.2
39.9
39.8
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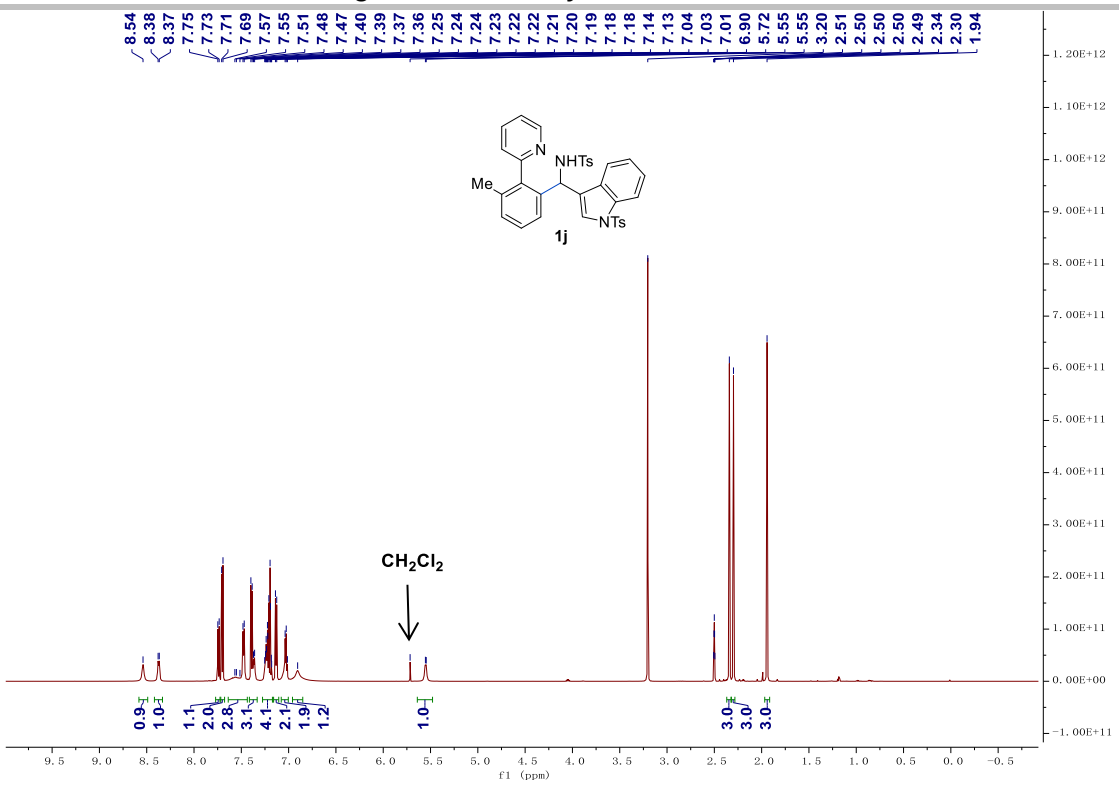
20.6
19.7
N
NHTs
Me
S
1i
f1 (ppm)


8.54 8.38 8.37 7.75 7.73 7.71 7.69 7.57 7.55 7.51 7.48 7.47 7.40 7.39 7.37 7.36 7.25 7.24 7.24 7.23 7.22 7.22 7.21 7.20 7.19 7.18 7.18 7.14 7.13 7.04 7.03 7.01 6.90 5.72 5.55 5.55 3.20 2.51 2.50 2.50 2.50 2.49 2.34 2.30 1.94
N
NHTs
Me
NTs
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CH2Cl2
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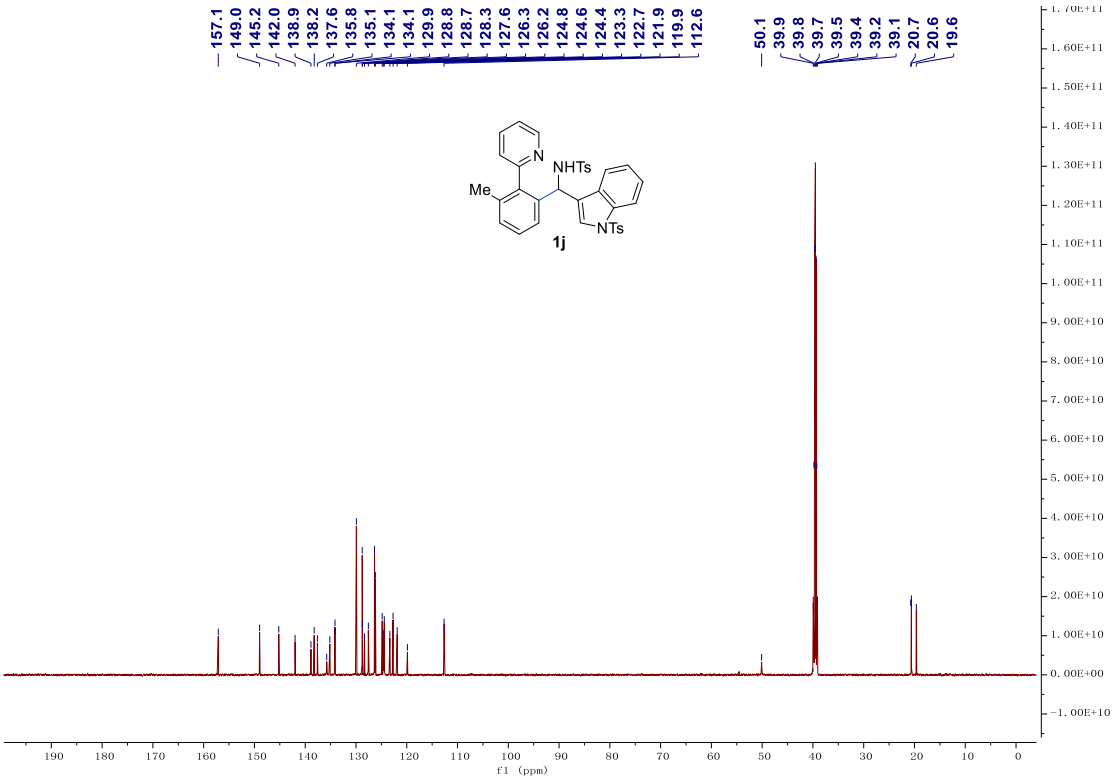
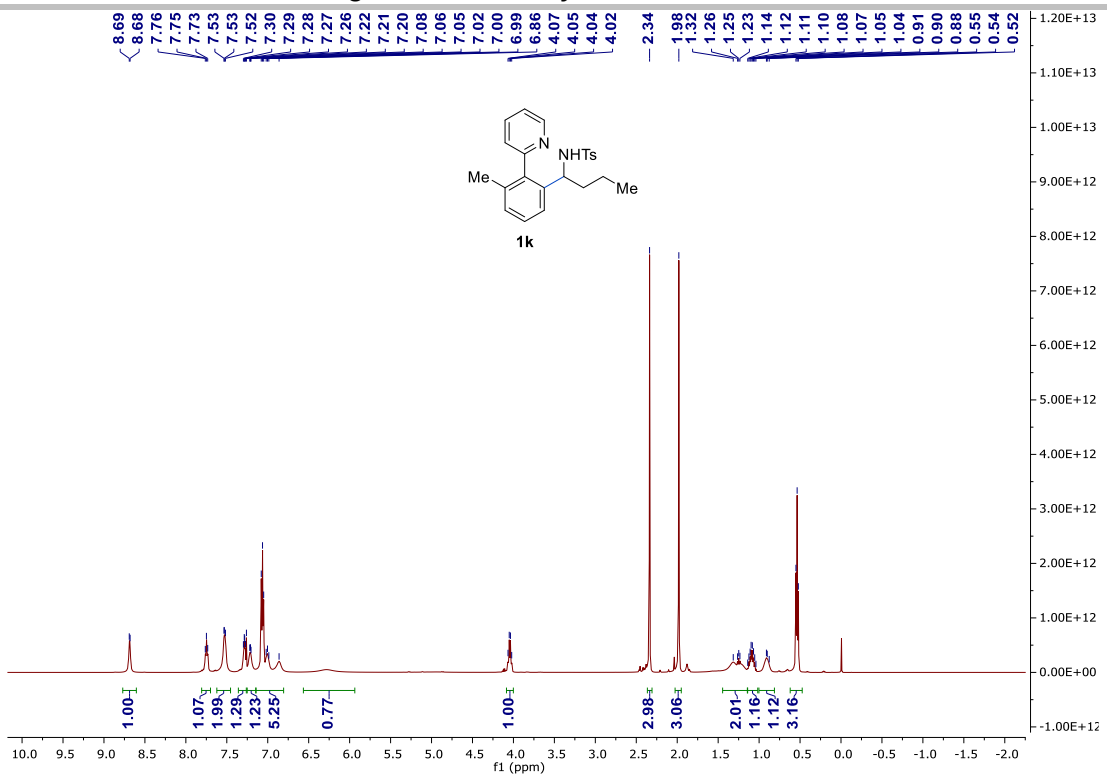
f1 (ppm)


157.1 149.0 145.2 142.0 138.9 138.2 137.6 135.8 135.1 134.1 134.1 129.9 128.8 128.7 128.3 127.6 126.3 126.2 124.8 124.6 124.4 123.3 122.7 121.9 119.9 112.6
50.1 39.9 39.8 39.7 39.5 39.4 39.2 39.1 20.7 20.6 19.6
N
NHTs
Me
NTs
1j
f1 (ppm)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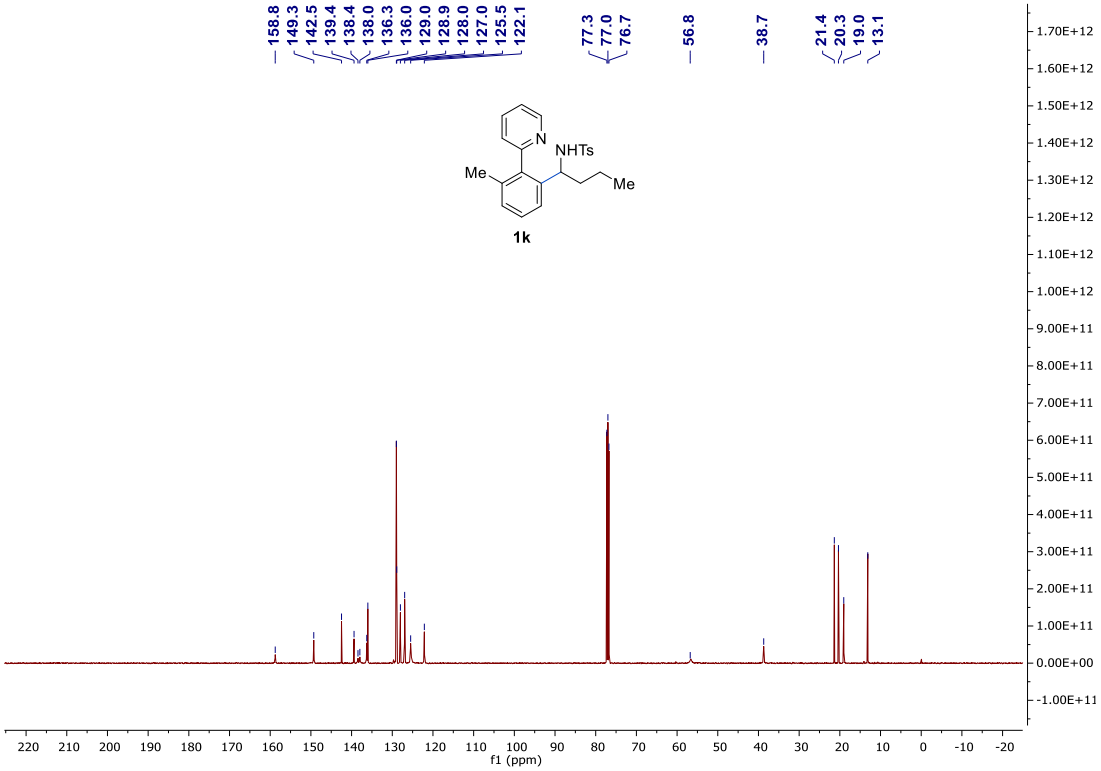
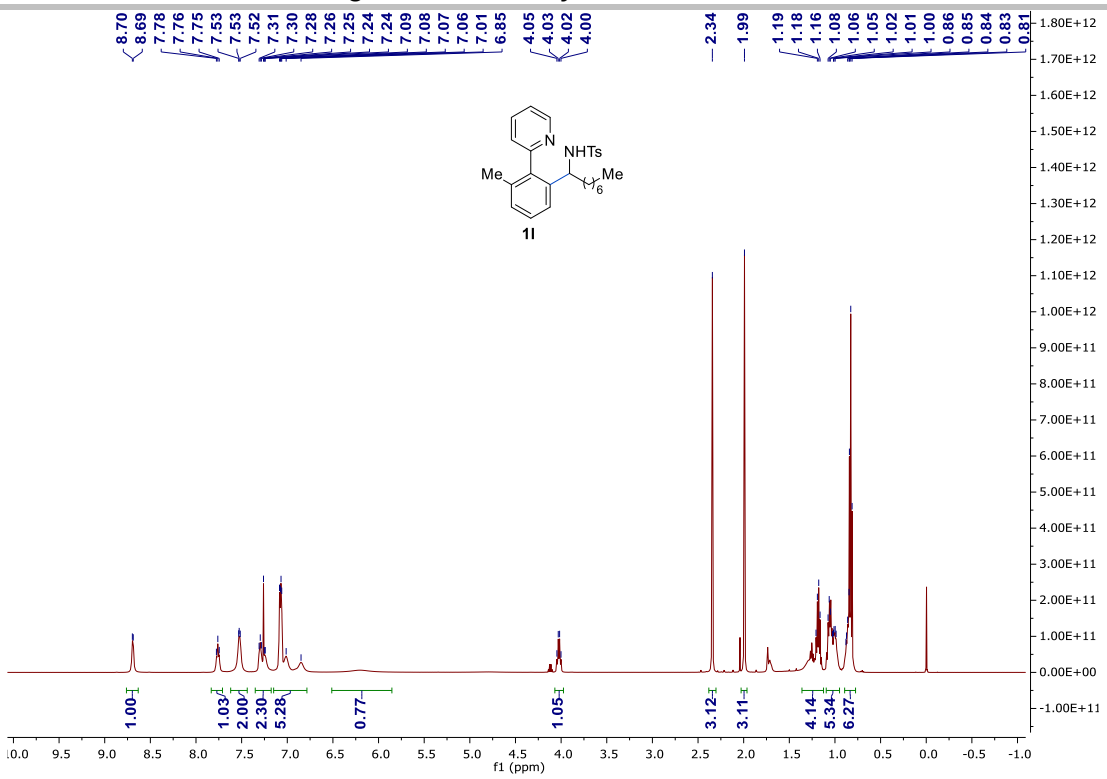
N
NHTs
Me
Me
1k
1.00 1.07 1.99 1.29 1.23 5.25 0.77 1.00 2.98 3.06 2.01 1.16 1.12 3.16
f1 (ppm)


158.8 149.3 142.5 139.4 138.4 138.0 136.3 136.0 129.0 128.9 128.0 127.0 125.5 122.1 77.3 77.0 76.7 56.8 38.7 21.4 20.3 19.0 13.1
N
NHTs
Me
Me
1k
f1 (ppm)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4.02
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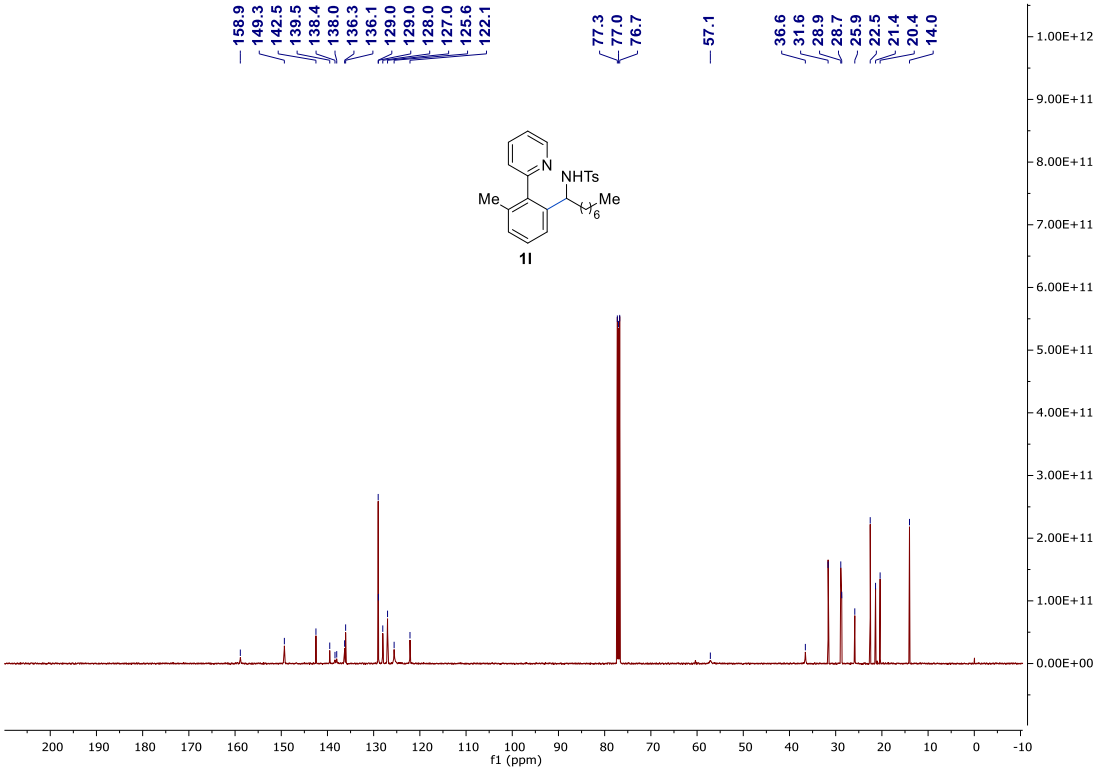
2.34
1.99
1.19
1.18
1.16
1.08
1.06
1.05
1.02
1.01
1.00
0.86
0.85
0.84
0.83
0.81
N
NHTs
Me
Me
6
1l
1.00
1.03
2.00
2.30
5.28
0.77
1.05
3.12
3.11
4.14
5.34
6.27
f1 (ppm)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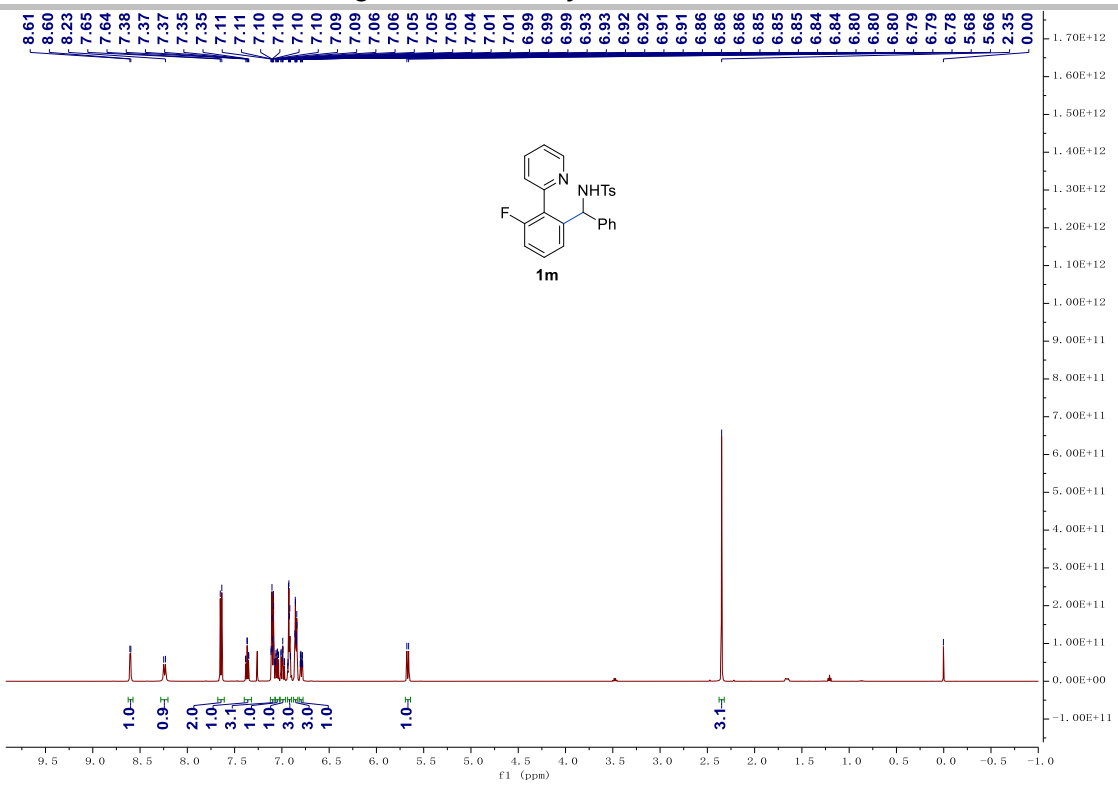
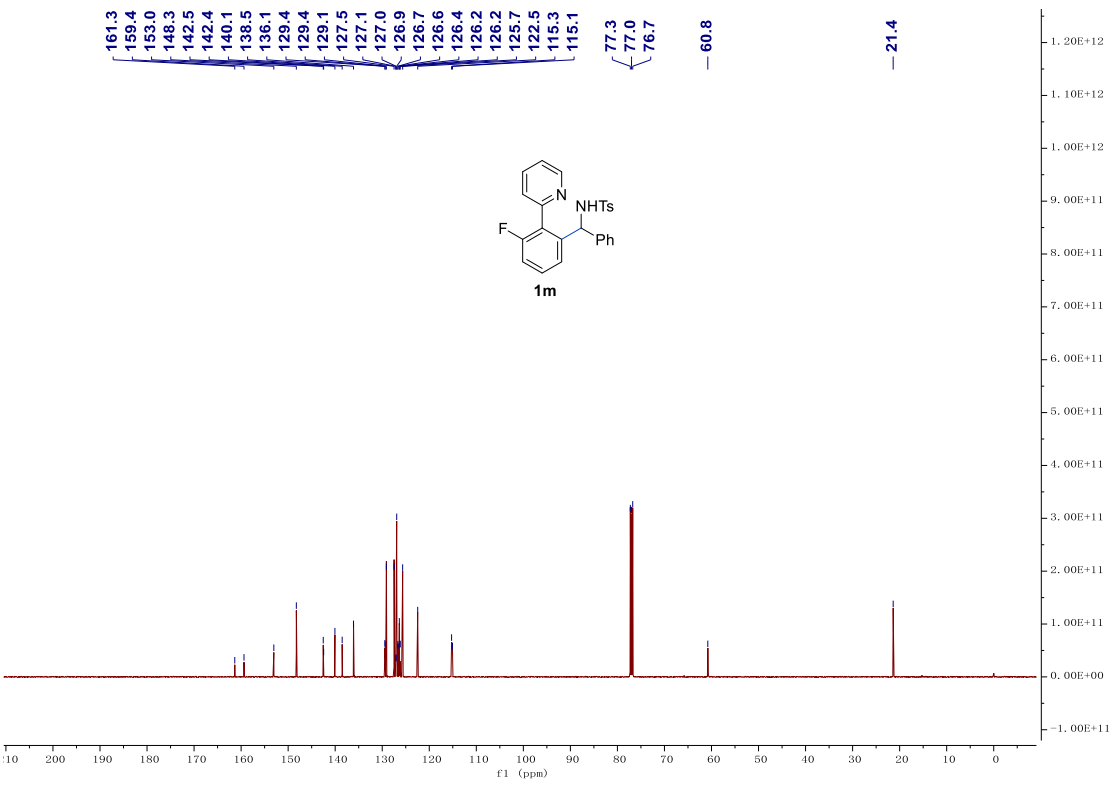
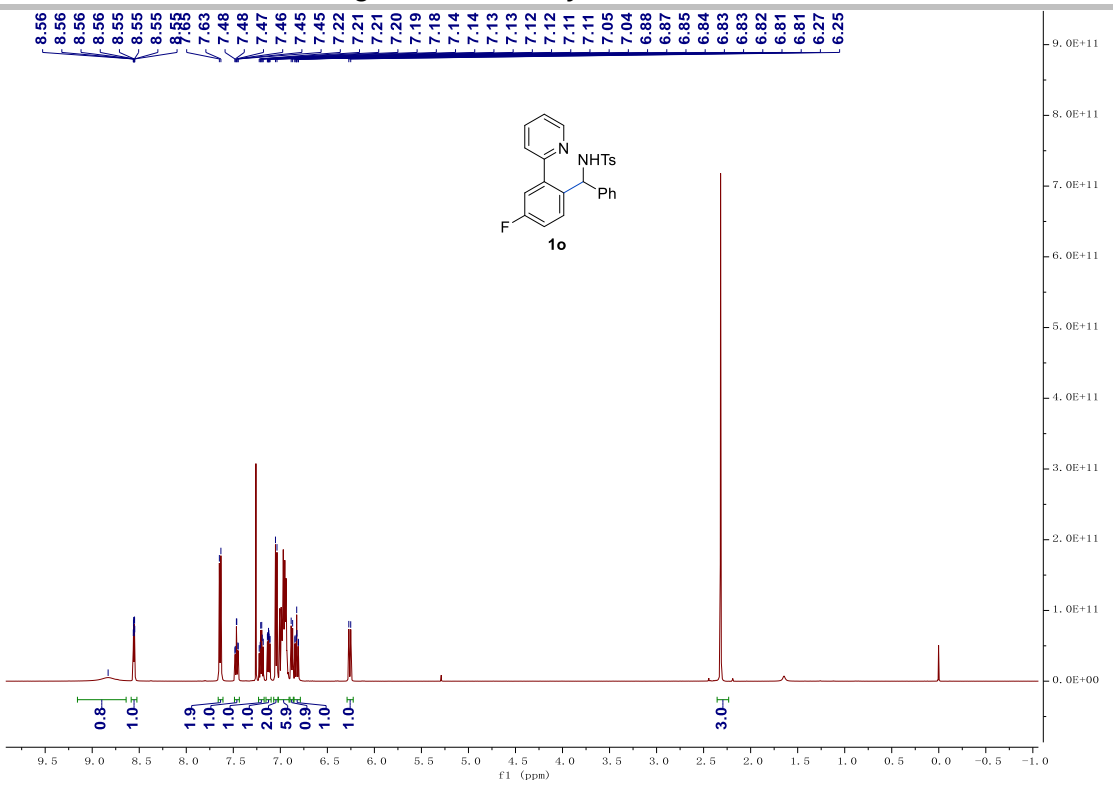
149.3
142.5
139.5
138.4
138.0
136.3
136.1
129.0
129.0
128.0
127.0
125.6
122.1
77.3
77.0
76.7
57.1
36.6
31.6
28.9
28.7
25.9
22.5
21.4
20.4
14.0
N
NHTs
Me
Me
6
1l
f1 (ppm)


8.61 8.60 8.23 7.65 7.64 7.38 7.37 7.37 7.35 7.35 7.11 7.11 7.10 7.10 7.10 7.10 7.09 7.09 7.06 7.06 7.05 7.05 7.05 7.04 7.01 7.01 6.99 6.99 6.93 6.93 6.92 6.92 6.91 6.91 6.86 6.86 6.85 6.85 6.84 6.84 6.80 6.80 6.80 6.79 6.79 6.78 5.68 5.66 2.35 0.00
N
NHTs
F
Ph
1m
1.0 0.9 2.0 1.0 3.1 1.0 1.0 3.0 3.0 1.0 1.0 3.1
f1 (ppm)


161.3 159.4 153.0 148.3 142.5 142.4 140.1 138.5 136.1 129.4 129.4 129.1 127.5 127.1 127.0 126.9 126.7 126.6 126.4 126.2 126.2 125.7 122.5 115.3 115.1
77.3 77.0 76.7
60.8
21.4
N
NHTs
F
Ph
1m
f1 (ppm)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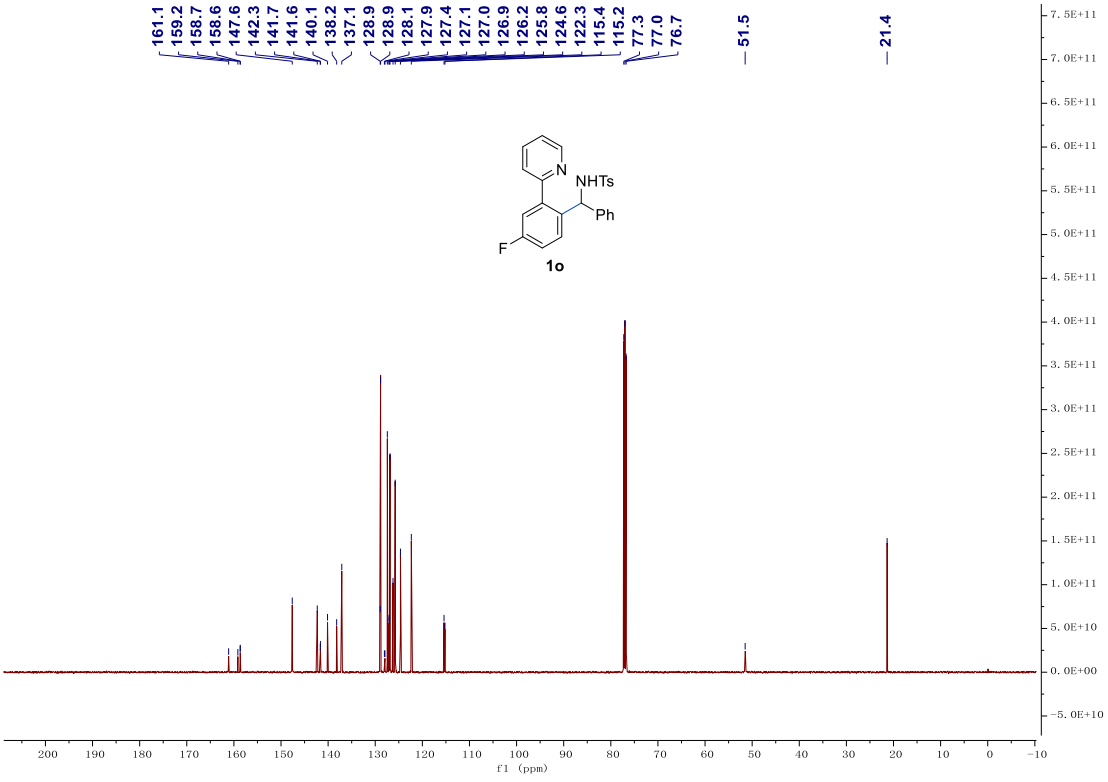
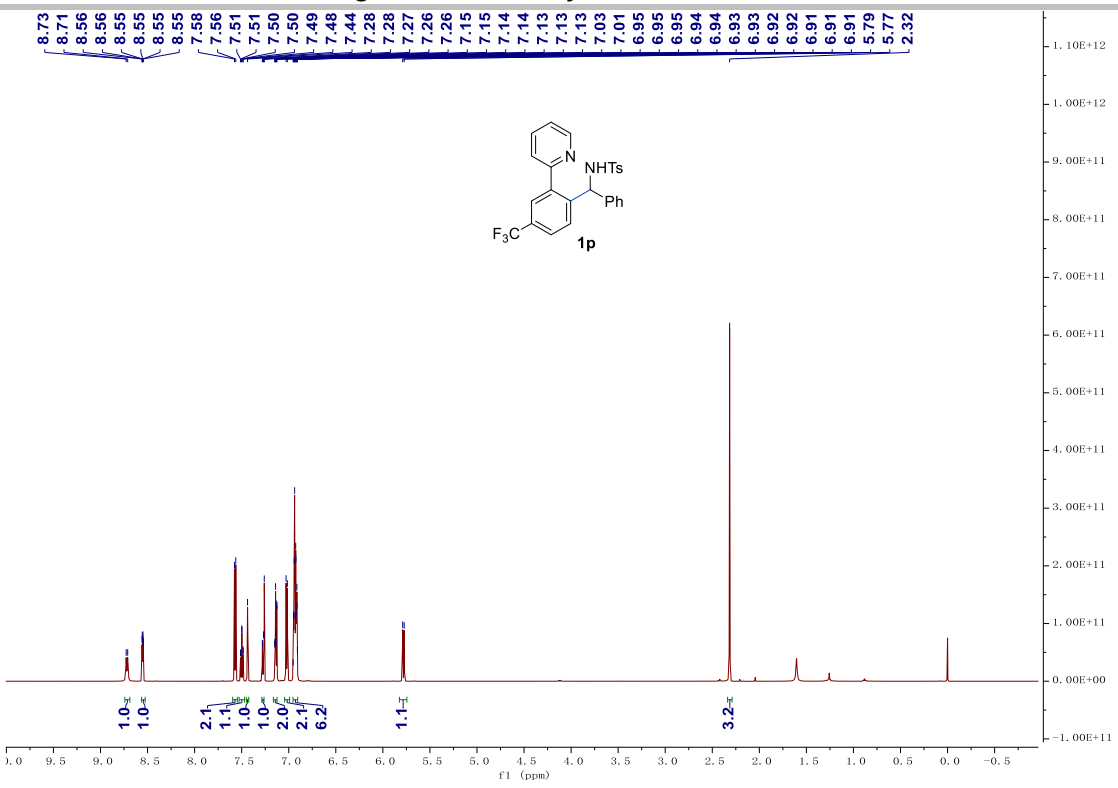
N
NHTs
Ph
F
1o
0.8 1.0 1.9 1.0 1.0 1.0 2.0 5.9 0.9 1.0 1.0 3.0
f1 (ppm)


161.1 159.2 158.7 158.6 147.6 142.3 141.7 141.6 140.1 138.2 137.1 128.9 128.9 128.1 127.9 127.4 127.1 127.0 126.9 126.2 125.8 124.6 122.3 115.4 115.2 77.3 77.0 76.7 51.5 21.4
N
NHTs
Ph
F
1o
f1 (ppm)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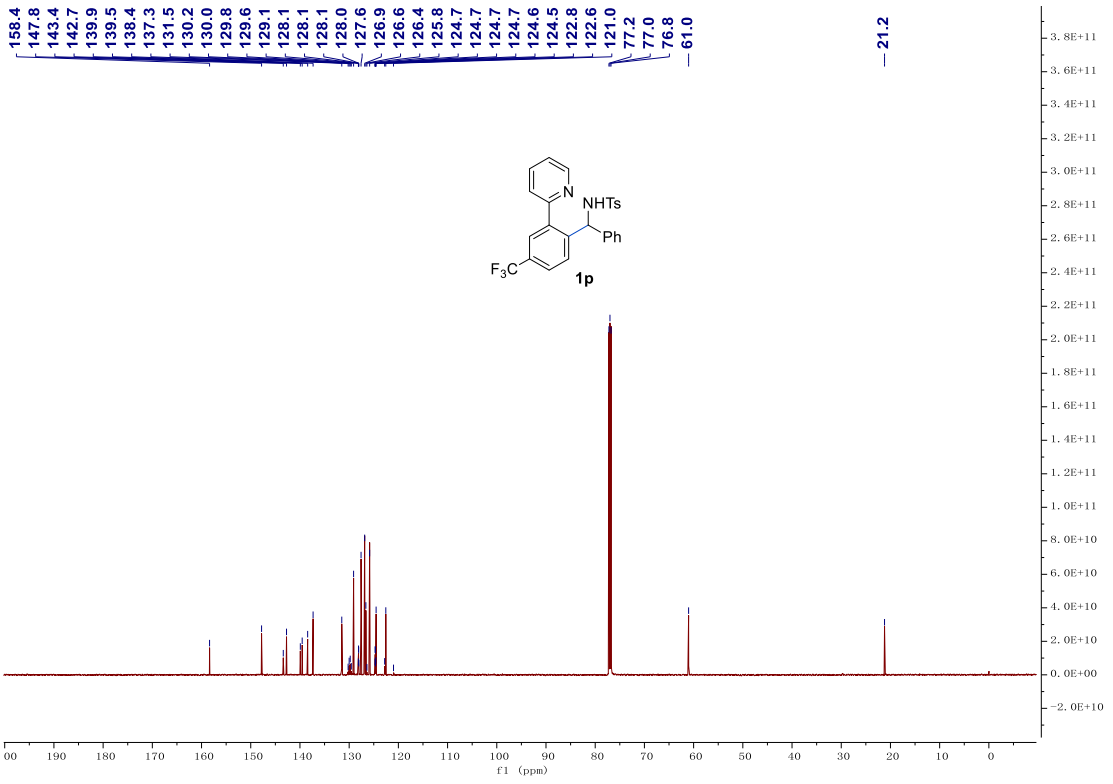
N
NHTs
Ph
F3C
1p
1.0 1.0 2.1 1.1 1.0 1.0 2.0 2.1 6.2 1.1 3.2
f1 (ppm)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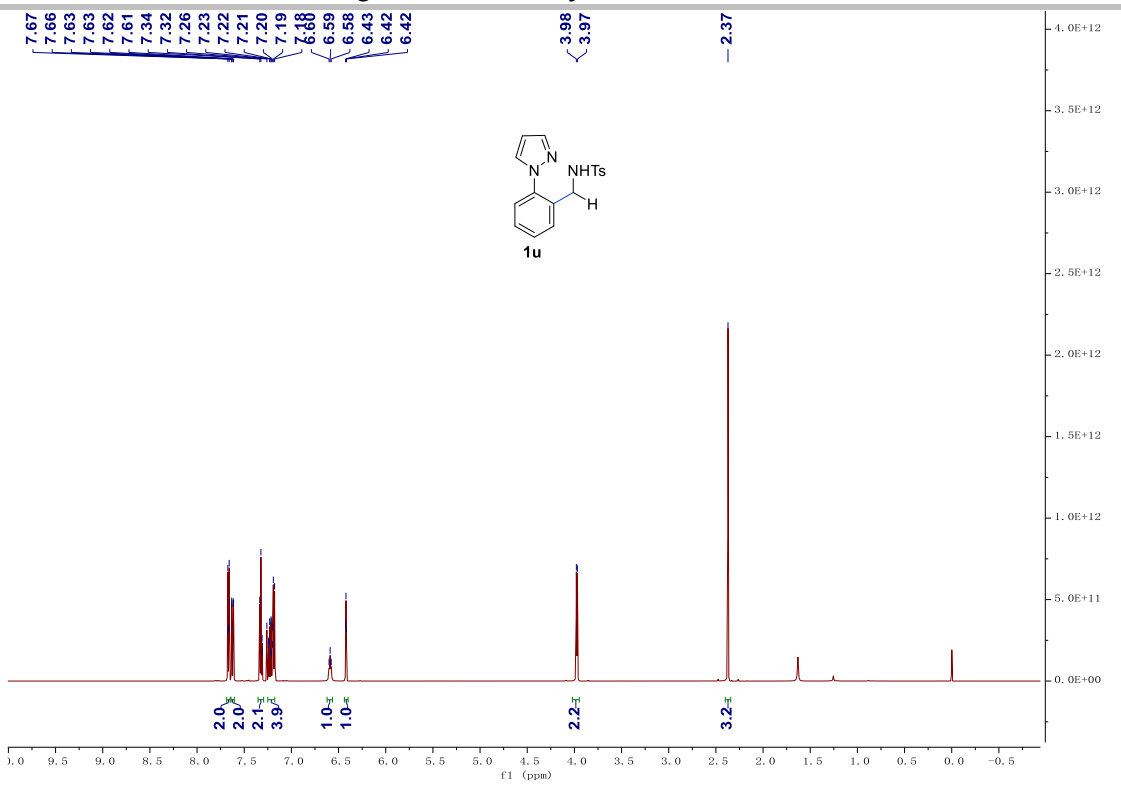
N
NHTs
Ph
F3C
1p
f1 (ppm)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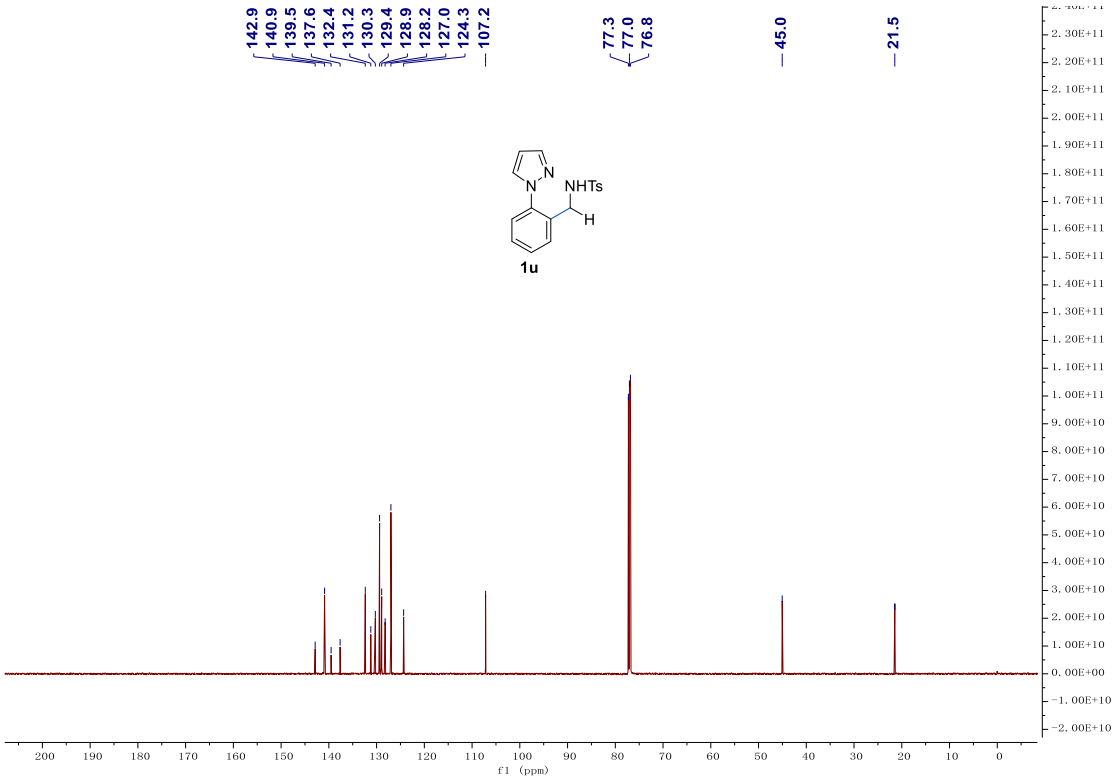
7.66
7.63
7.63
7.62
7.61
7.34
7.32
7.26
7.23
7.22
7.21
7.20
7.19
6.60
6.59
6.58
6.43
6.42
6.42
3.98
3.97
2.37
NHTs
H
1u
2.0
2.0
2.1
3.9
1.0
1.0
2.2
3.2
f1 (ppm)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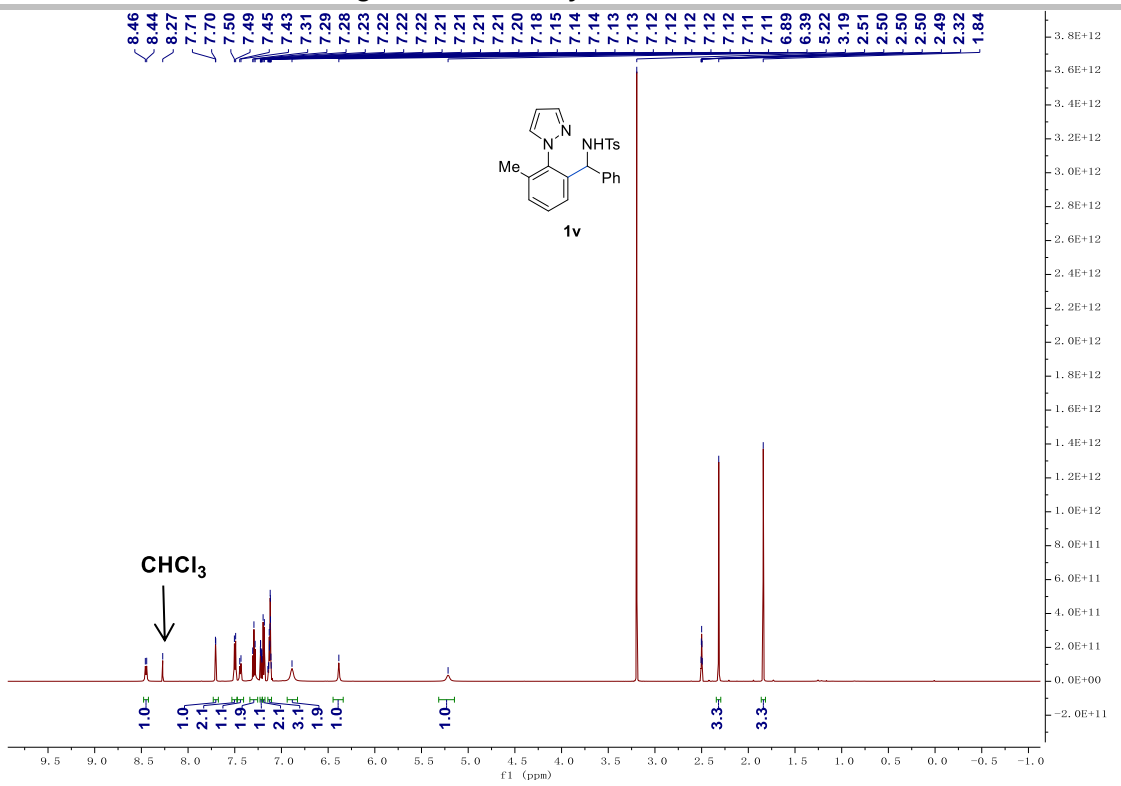
140.9
139.5
137.6
132.4
131.2
130.3
129.4
128.9
128.2
127.0
124.3
107.2
77.3
77.0
76.8
45.0
21.5
NHTs
H
1u
f1 (ppm)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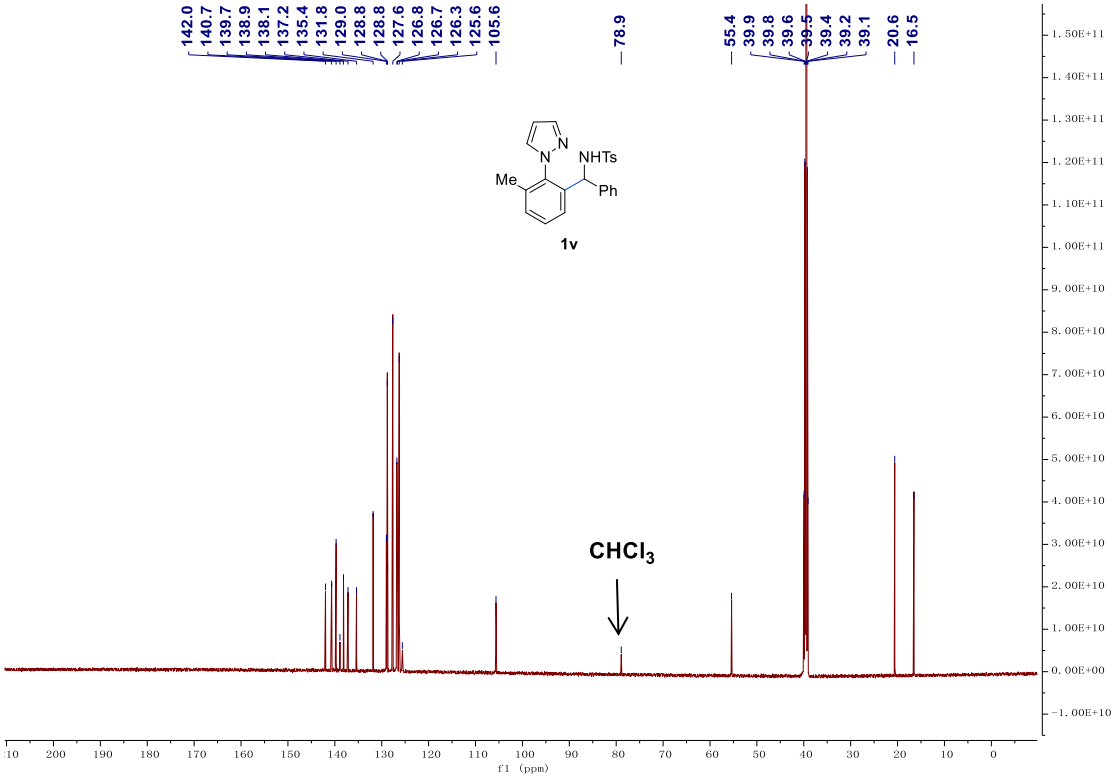
8.44
8.27
7.71
7.70
7.50
7.49
7.45
7.43
7.31
7.29
7.28
7.23
7.22
7.22
7.22
7.21
7.21
7.21
7.21
7.20
7.18
7.15
7.14
7.14
7.13
7.13
7.12
7.12
7.12
7.12
7.12
7.11
7.11
6.89
6.39
5.22
3.19
2.51
2.50
2.50
2.50
2.49
2.32
1.84
N
N
NHTs
Me
Ph
1v
CHCl3
1.0
1.0
2.1
1.1
1.9
1.1
2.1
3.1
1.9
1.0
1.0
3.3
3.3
f1 (ppm)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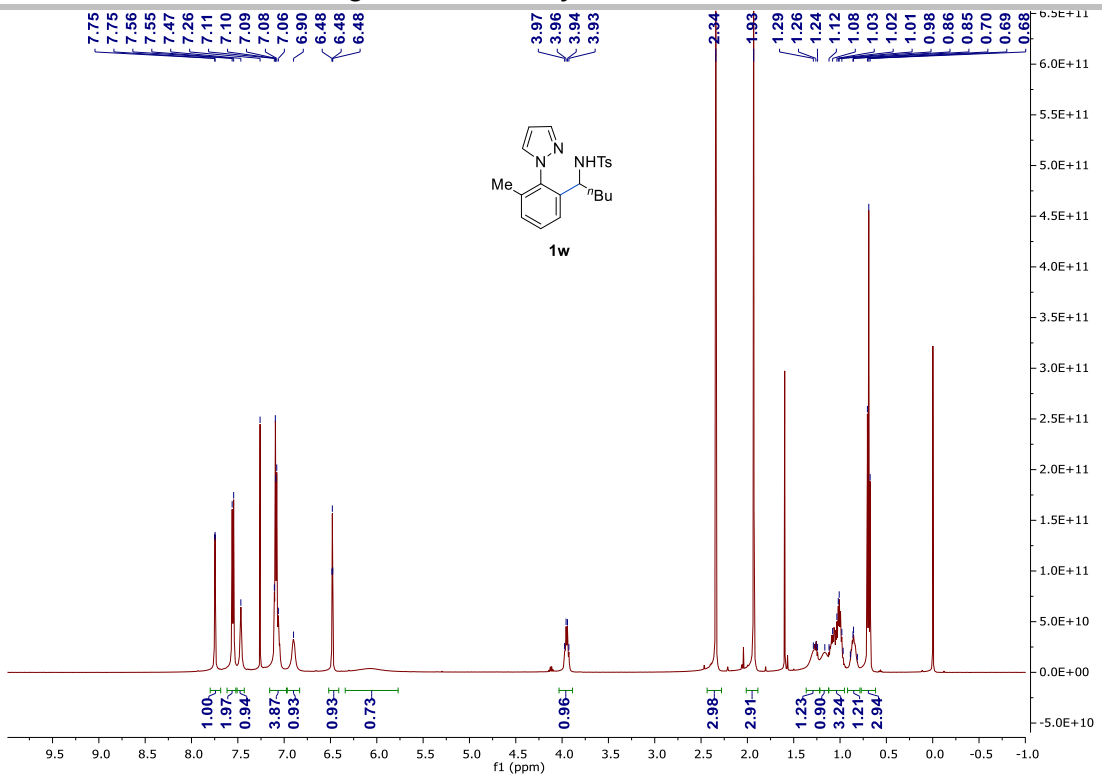
140.7
139.7
138.9
138.1
137.2
135.4
131.8
129.0
128.8
128.8
127.6
126.8
126.7
126.3
125.6
105.6
78.9
55.4
39.9
39.8
39.6
39.5
39.4
39.2
39.1
20.6
16.5
N
N
NHTs
Me
Ph
1v
CHCl3
f1 (ppm)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7.75
7.56
7.55
7.47
7.26
7.11
7.10
7.09
7.08
7.06
6.90
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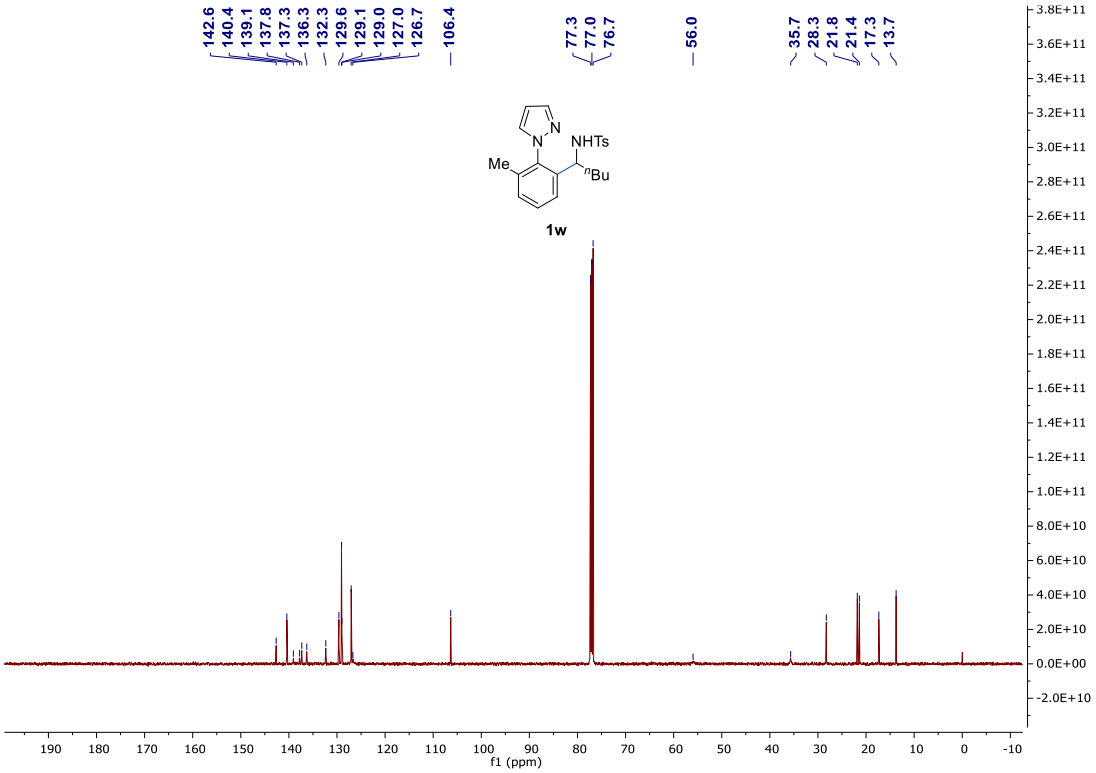
6.48
6.48
3.97
3.96
3.94
3.93
2.34
1.93
1.29
1.26
1.24
1.12
1.08
1.03
1.02
1.01
0.98
0.86
0.85
0.70
0.69
0.68
NHTs
Me
nBu
1w
1.00
1.97
0.94
3.87
0.93
0.93
0.73
0.96
2.98
2.91
1.23
0.90
3.24
1.21
2.94
f1 (ppm)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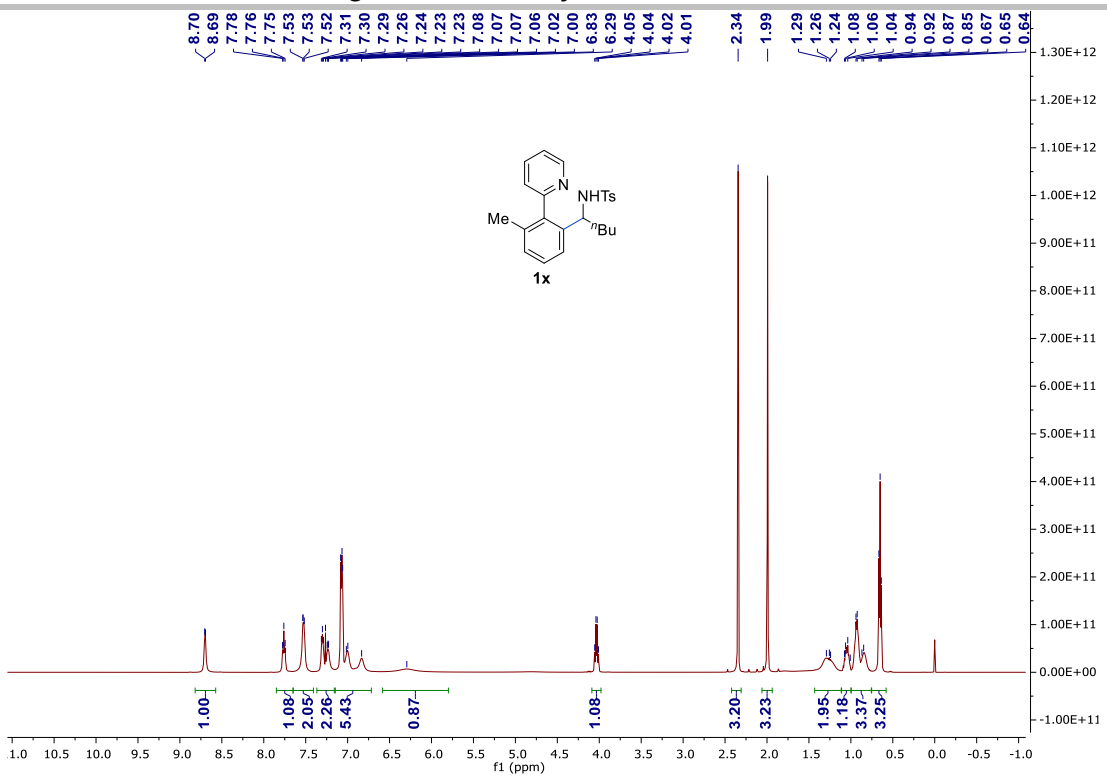
140.4
139.1
137.8
137.3
136.3
132.3
129.6
129.1
129.0
127.0
126.7
106.4
77.3
77.0
76.7
56.0
35.7
28.3
21.8
21.4
17.3
13.7
NHTs
Me
nBu
1w
f1 (ppm)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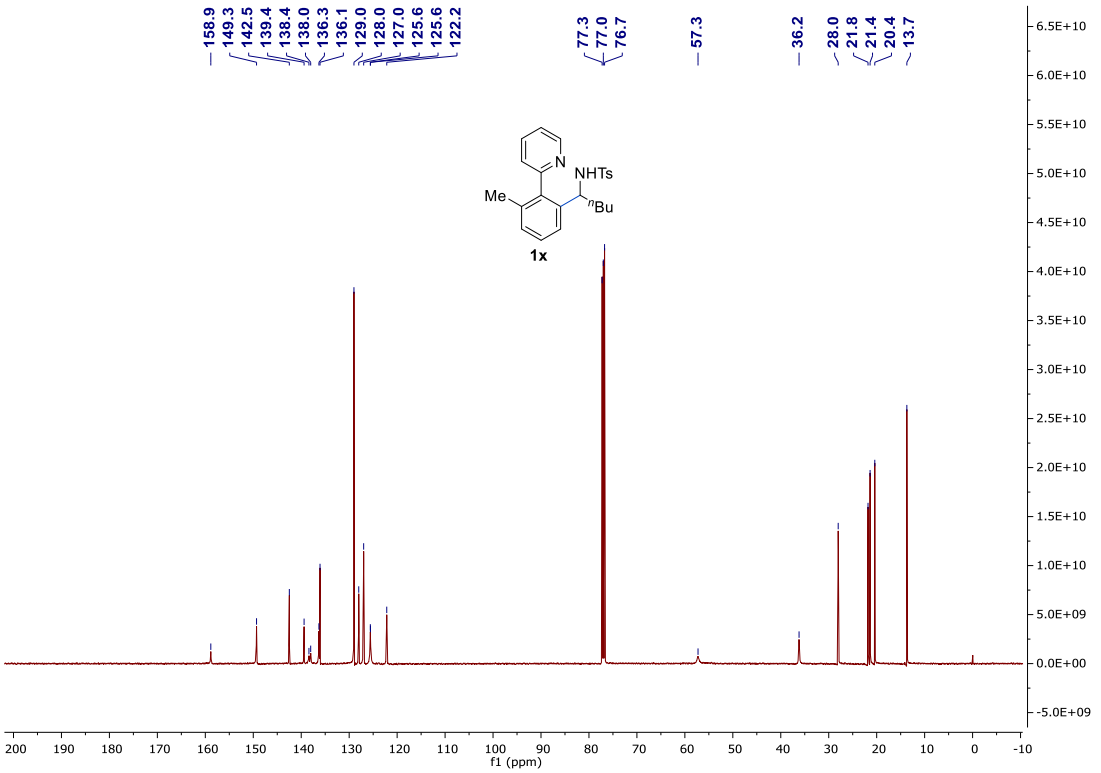
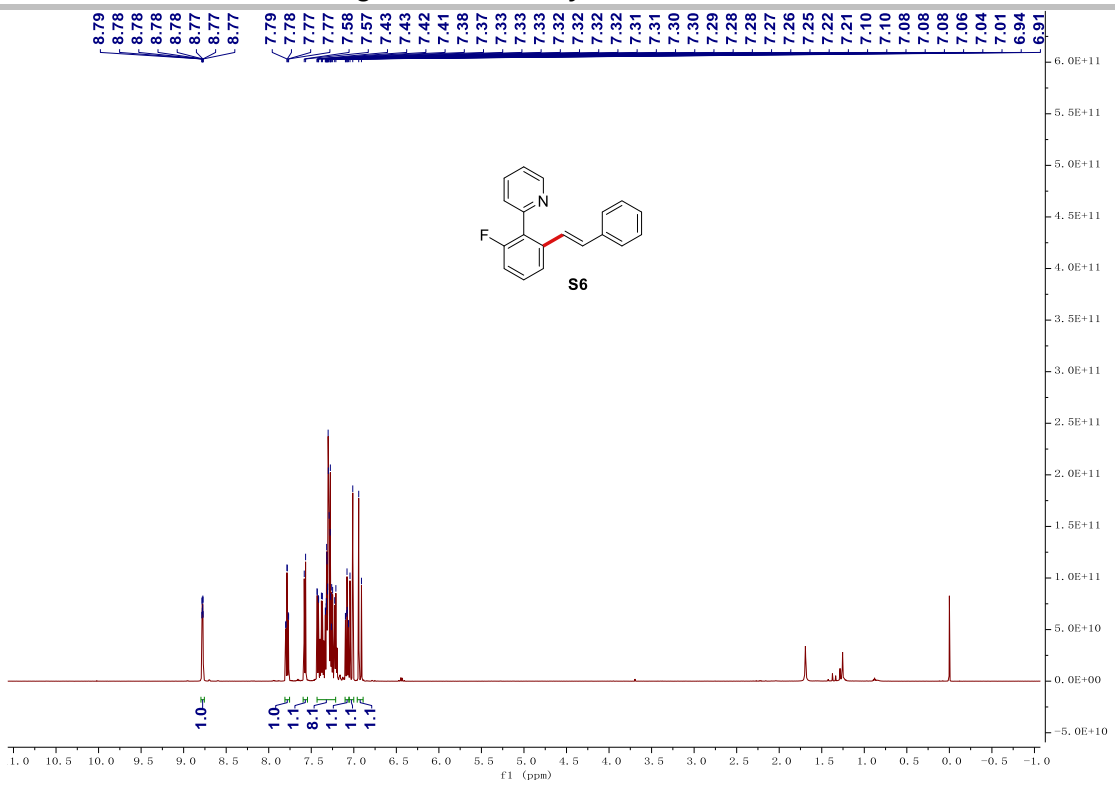
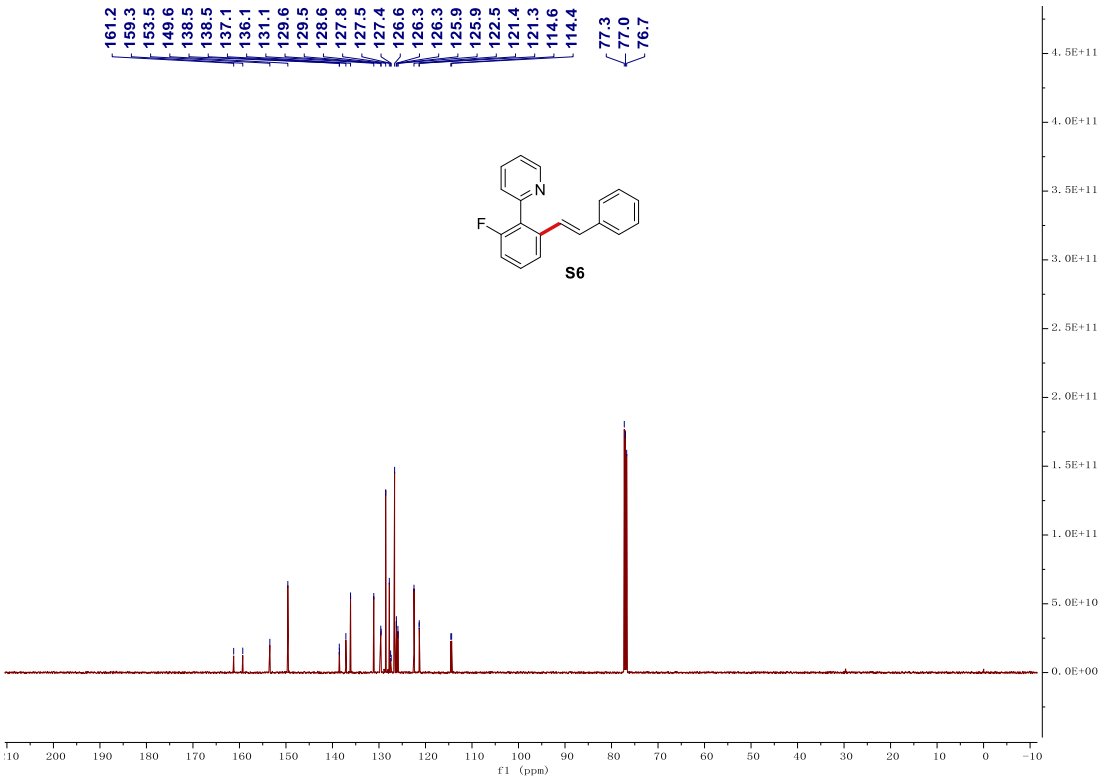
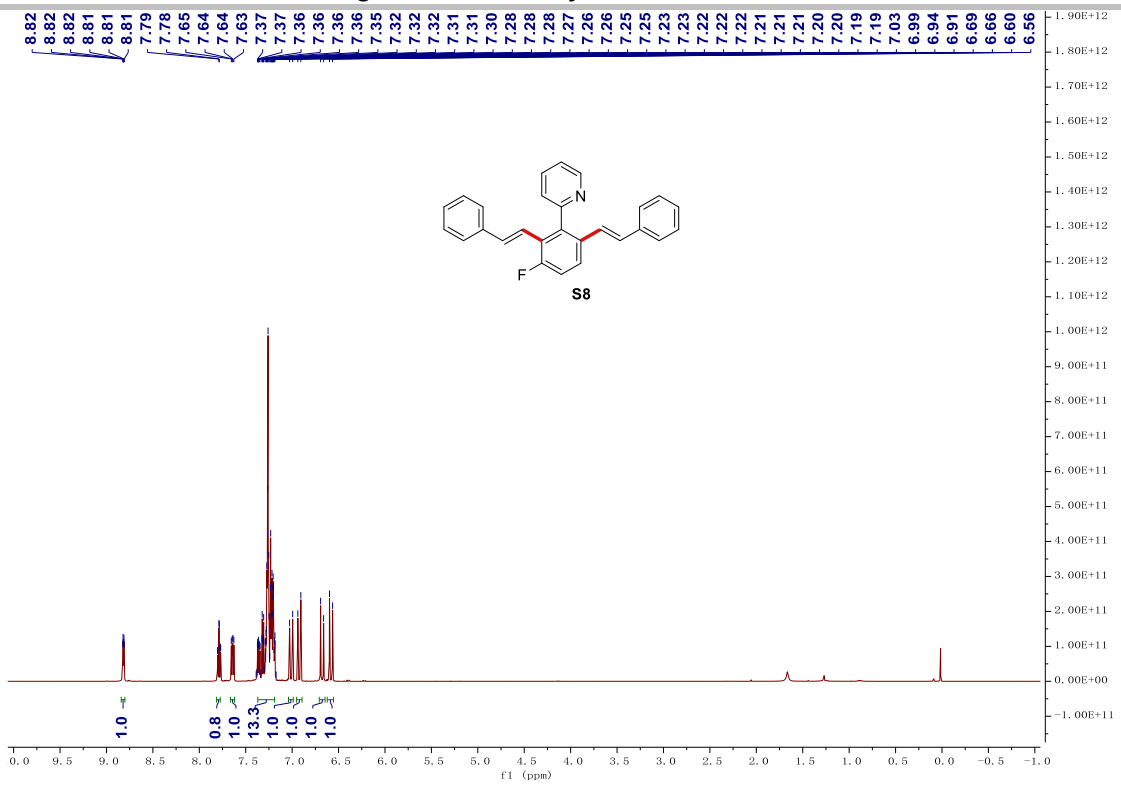
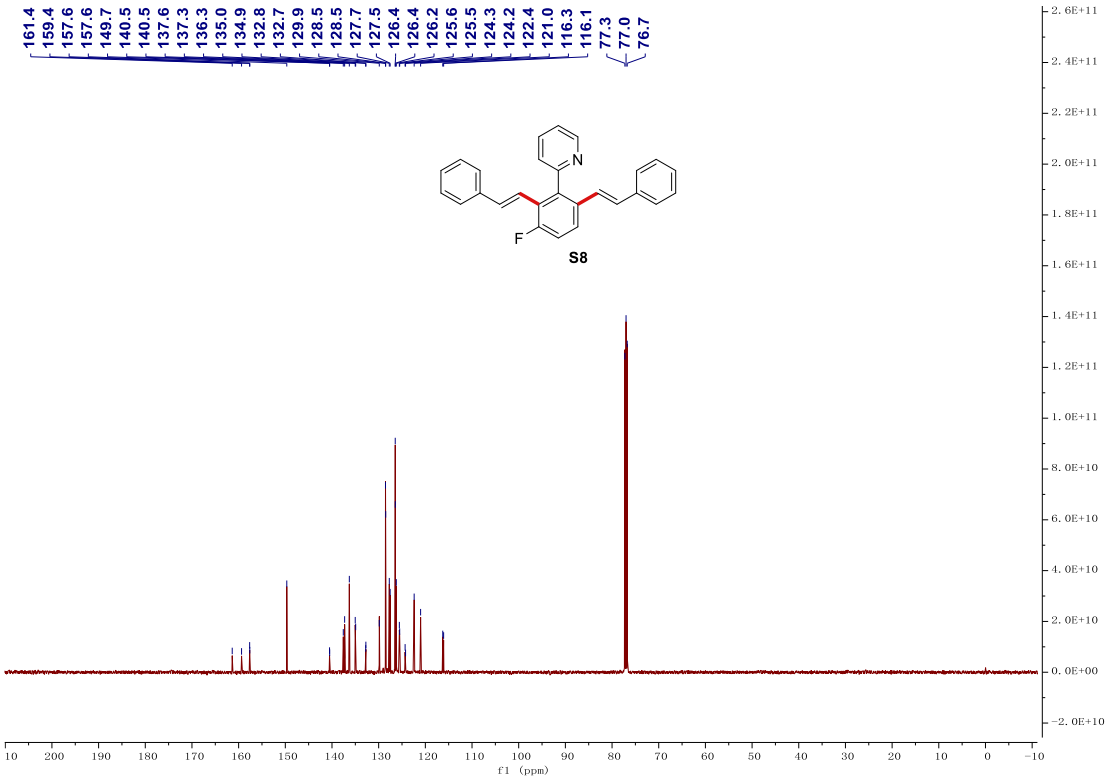
8.69
7.78
7.76
7.75
7.53
7.53
7.52
7.31
7.30
7.29
7.26
7.24
7.23
7.23
7.08
7.07
7.07
7.06
7.02
7.00
6.83
6.29
4.05
4.04
4.02
4.01
2.34
1.99
1.29
1.26
1.24
1.08
1.06
1.04
0.94
0.92
0.87
0.85
0.67
0.65
0.64
N
NHTs
Me
nBu
1x
1.00
1.08
2.05
2.26
5.43
0.87
1.08
3.20
3.23
1.95
1.18
3.37
3.25
f1 (ppm)

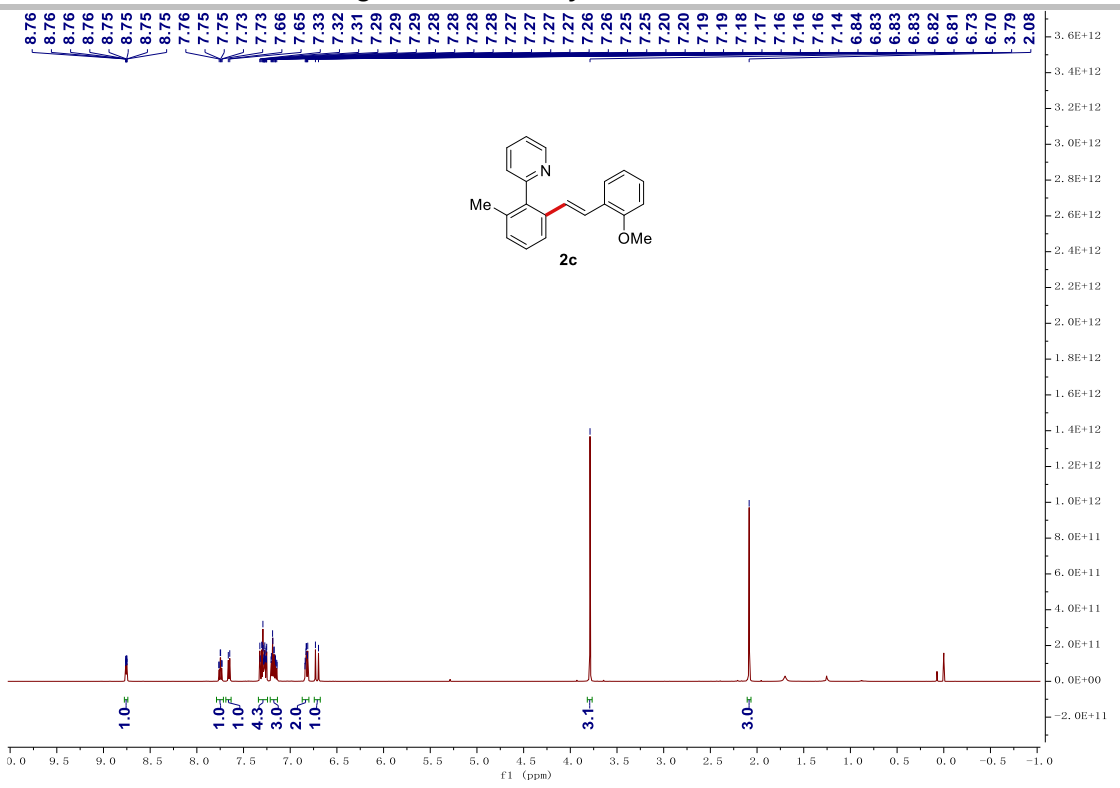

158.9
149.3
142.5
139.4
138.4
138.0
136.3
136.1
129.0
128.0
127.0
125.6
125.6
122.2
77.3
77.0
76.7
57.3
36.2
28.0
21.8
21.4
20.4
13.7
N
NHTs
Me
nBu
1x
f1 (ppm)


8.79 8.78 8.78 8.78 8.78 8.77 8.77 8.77
7.79 7.78 7.77 7.77 7.58 7.57 7.43 7.43 7.42 7.41 7.38 7.37 7.33 7.33 7.33 7.32 7.32 7.32 7.32 7.31 7.31 7.30 7.30 7.29 7.28 7.28 7.27 7.26 7.25 7.22 7.21 7.10 7.10 7.08 7.08 7.08 7.06 7.04 7.01 6.94 6.91
N
F
S6
1.0 1.0 1.1 8.1 1.1 1.1 1.1
f1 (ppm)


161.2 159.3 153.5 149.6 138.5 138.5 137.1 136.1 131.1 129.6 129.5 128.6 127.8 127.5 127.4 126.6 126.3 126.3 125.9 125.9 122.5 121.4 121.3 114.6 114.4
77.3 77.0 76.7
N
F
S6
f1 (ppm)


8.82 8.82 8.82 8.81 8.81 8.81 7.79 7.78 7.65 7.64 7.64 7.63 7.37 7.37 7.36 7.36 7.36 7.36 7.35 7.32 7.32 7.31 7.31 7.30 7.28 7.28 7.28 7.27 7.26 7.26 7.25 7.25 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.21 7.20 7.20 7.19 7.19 7.03 6.99 6.94 6.91 6.69 6.66 6.60 6.56
N
F
S8
1.0 0.8 1.0 13.3 1.0 1.0 1.0 1.0
f1 (ppm)


161.4 159.4 157.6 157.6 149.7 140.5 140.5 137.6 137.3 136.3 135.0 134.9 132.8 132.7 129.9 128.5 128.5 127.7 127.5 126.4 126.4 126.2 125.6 125.5 124.3 124.2 122.4 121.0 116.3 116.1 77.3 77.0 76.7
N
F
S8
f1 (ppm)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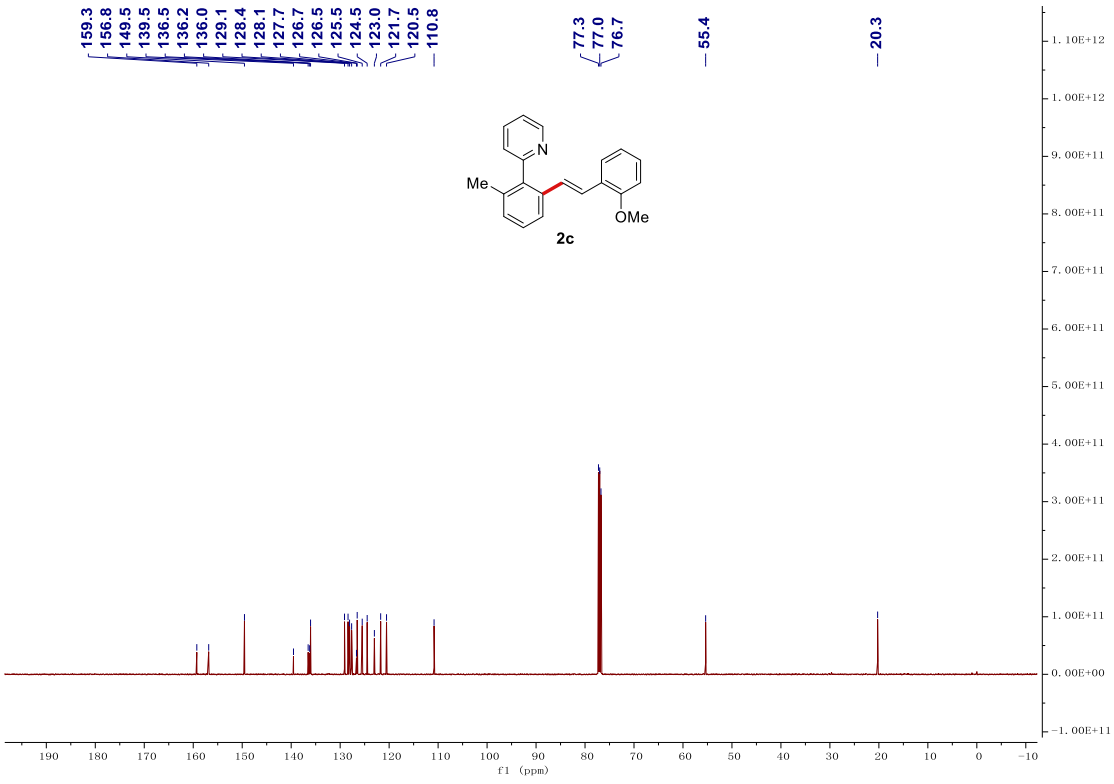
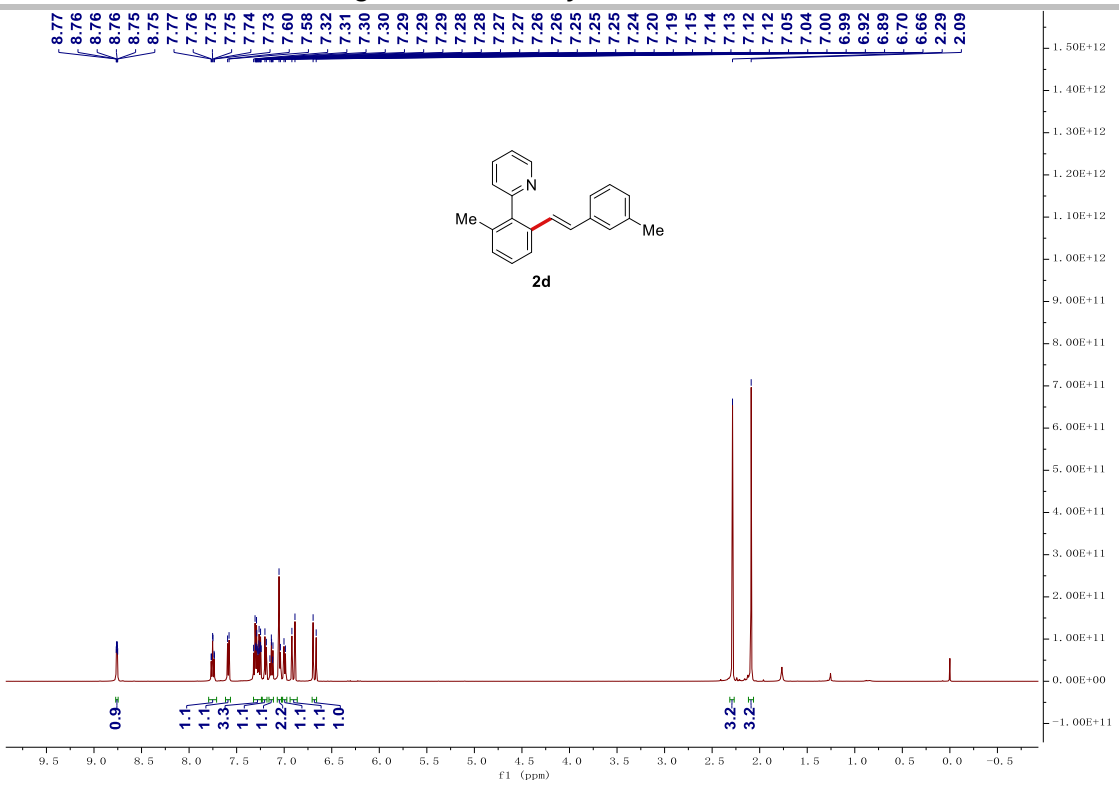
N
Me
OMe
2c
1.0 1.0 1.0 4.3 3.0 2.0 1.0 3.1 3.0
f1 (ppm)


159.3 156.8 149.5 139.5 136.5 136.2 136.0 129.1 128.4 128.1 127.7 126.7 126.5 125.5 124.5 123.0 121.7 120.5 110.8
77.3 77.0 76.7
55.4
20.3
N
Me
OMe
2c
f1 (ppm)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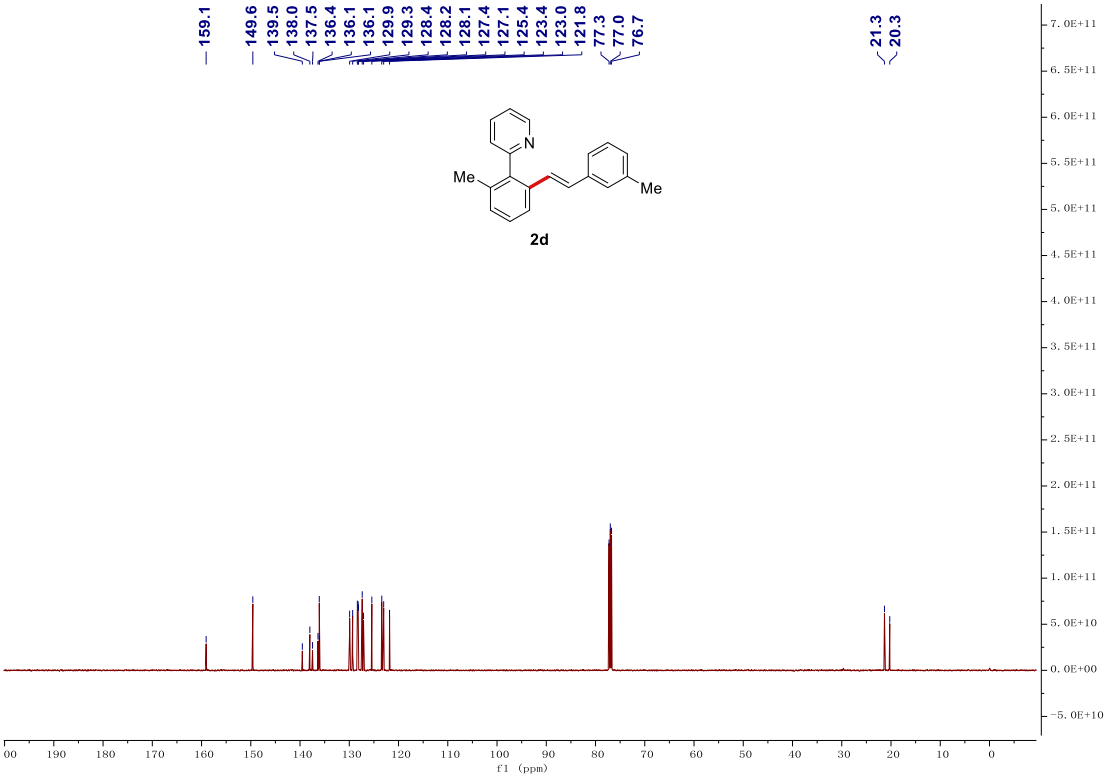
N
Me
Me
2d
0.9 1.1 1.1 3.3 1.1 1.1 2.2 1.1 1.1 1.0 3.2 3.2
f1 (ppm)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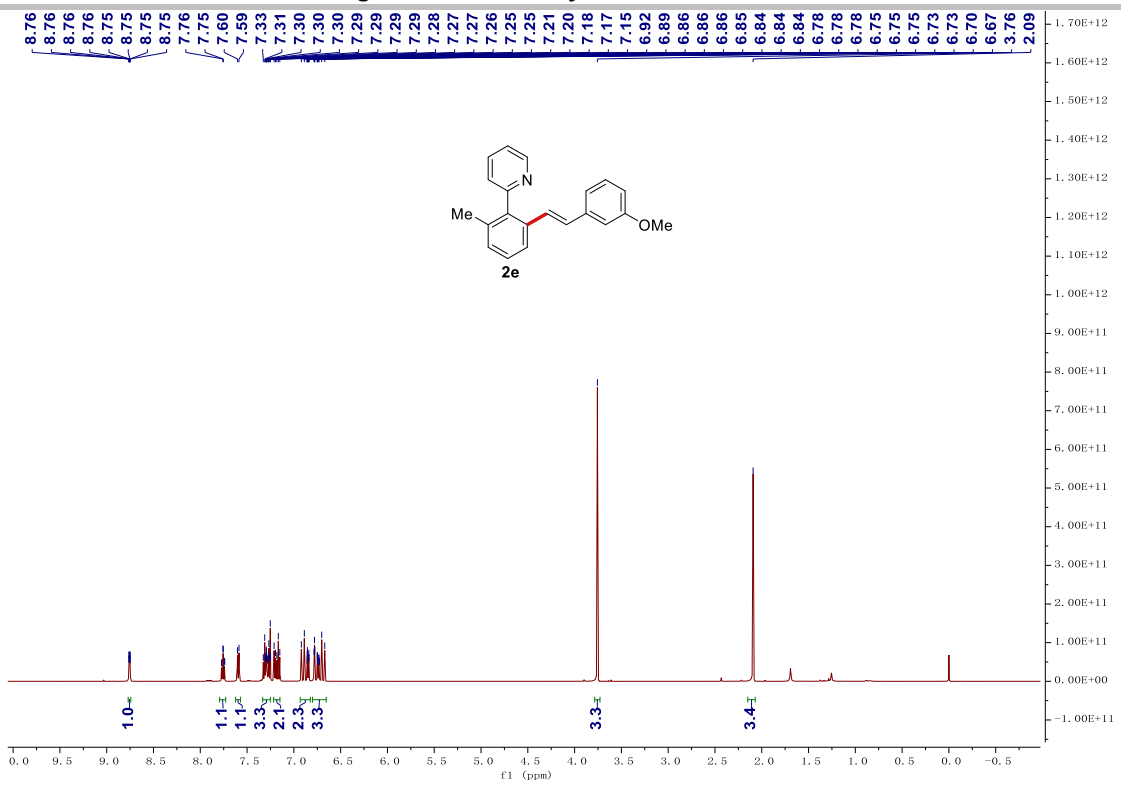
N
Me
Me
2d
f1 (ppm)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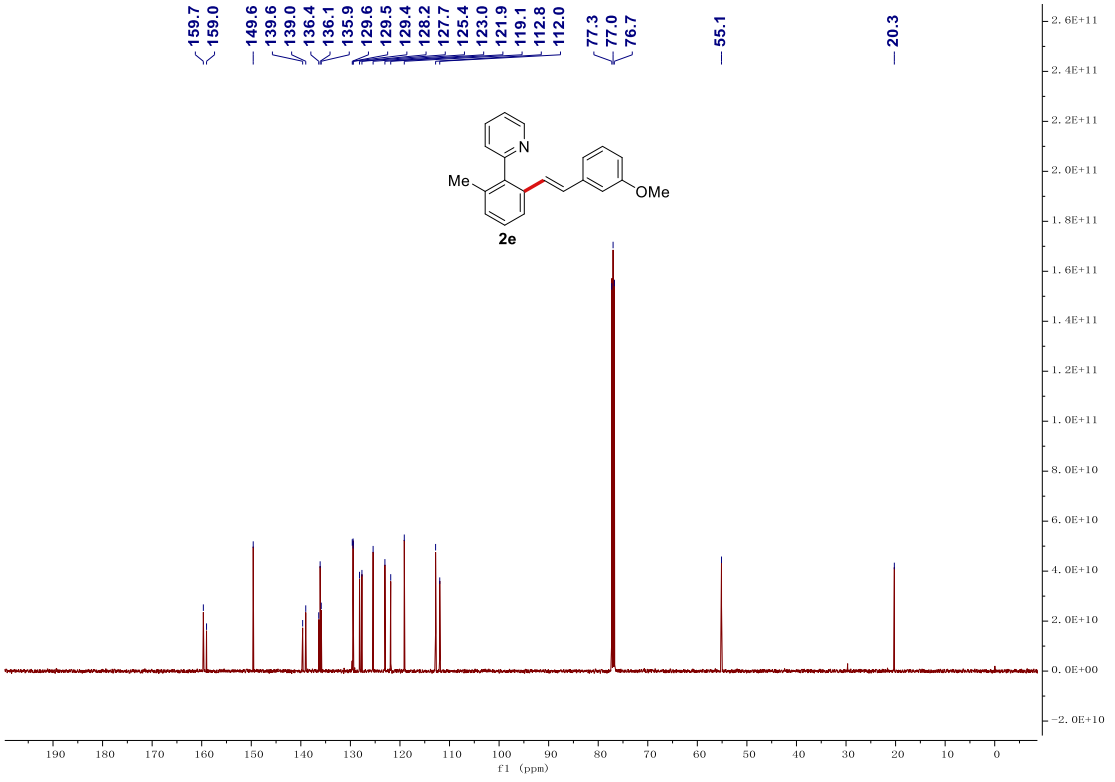
N
Me
OMe
2e
1.0 1.1 1.1 3.3 2.1 2.3 3.3 3.3 3.4
f1 (ppm)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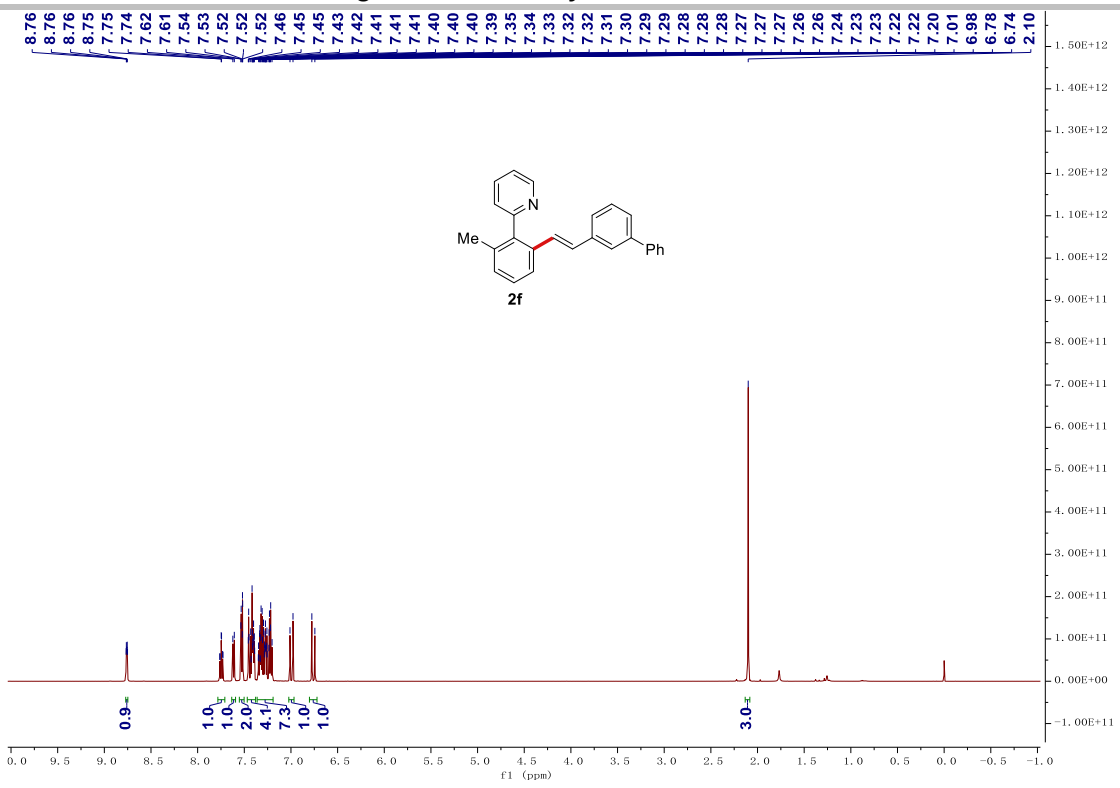
N
Me
OMe
2e
f1 (ppm)


8.76 8.76 8.76 8.75 7.75 7.74 7.62 7.61 7.54 7.53 7.52 7.52 7.52 7.46 7.45 7.45 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.35 7.34 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.24 7.23 7.23 7.22 7.22 7.20 7.01 6.98 6.78 6.74 2.10
N
Me
Ph
2f
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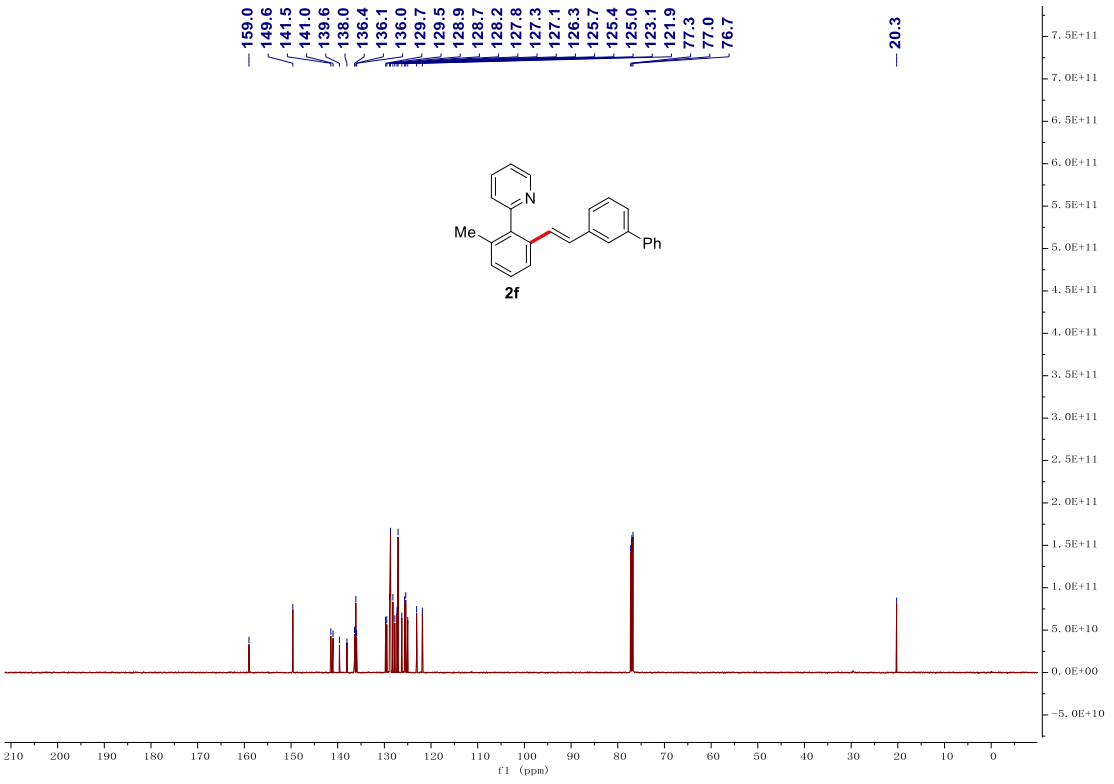
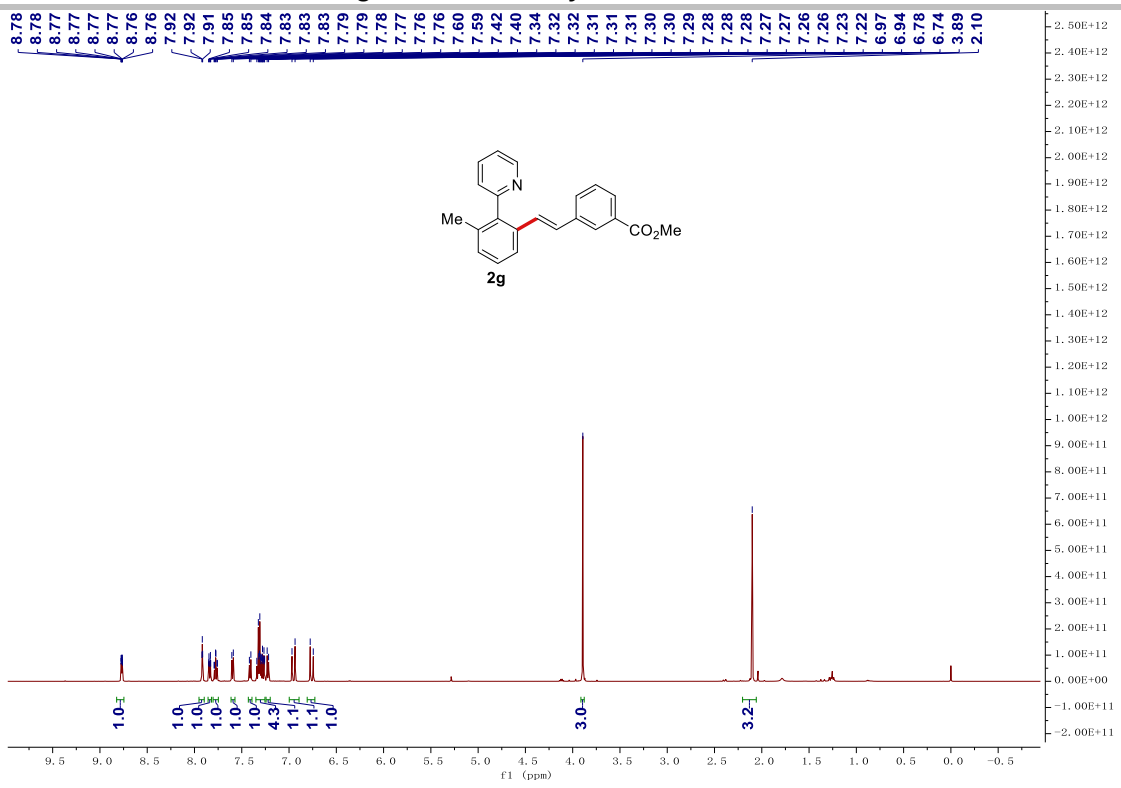
1.0
1.0
2.0
4.1
7.3
1.0
1.0
3.0
f1 (ppm)


159.0 149.6 141.5 141.0 139.6 138.0 136.4 136.1 136.0 129.7 129.5 128.9 128.7 128.2 127.8 127.3 127.1 126.3 125.7 125.4 125.0 123.1 121.9 77.3 77.0 76.7
20.3
N
Me
Ph
2f
f1 (ppm)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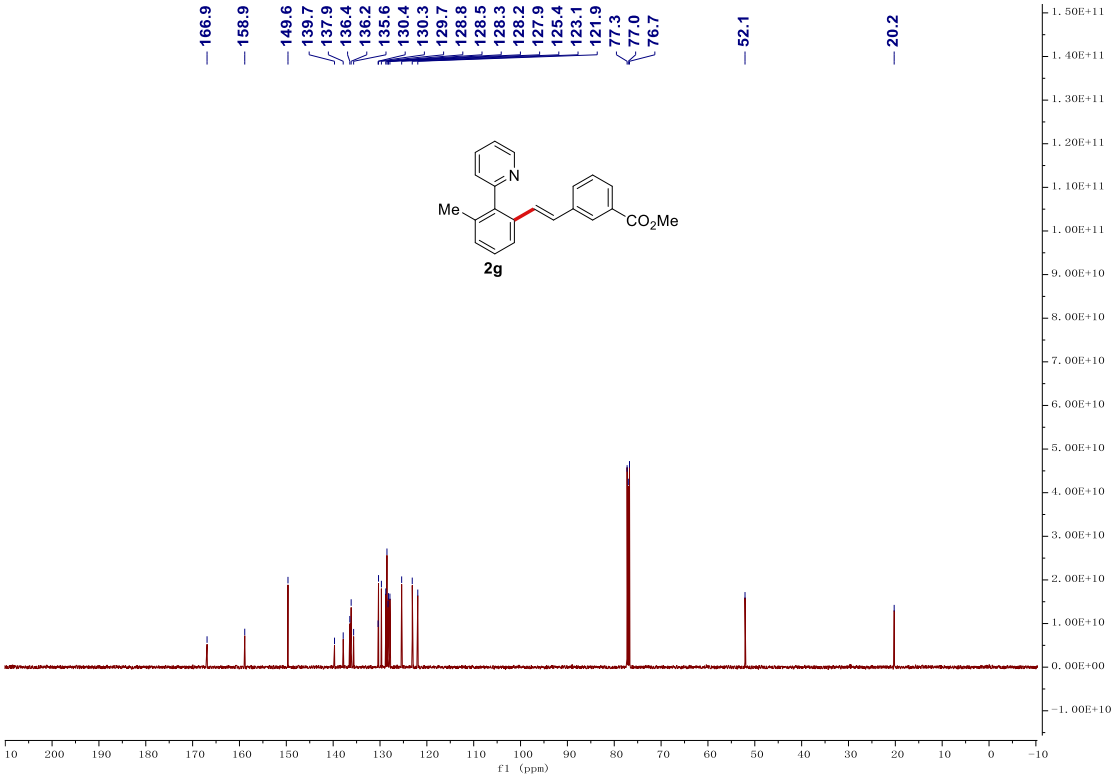
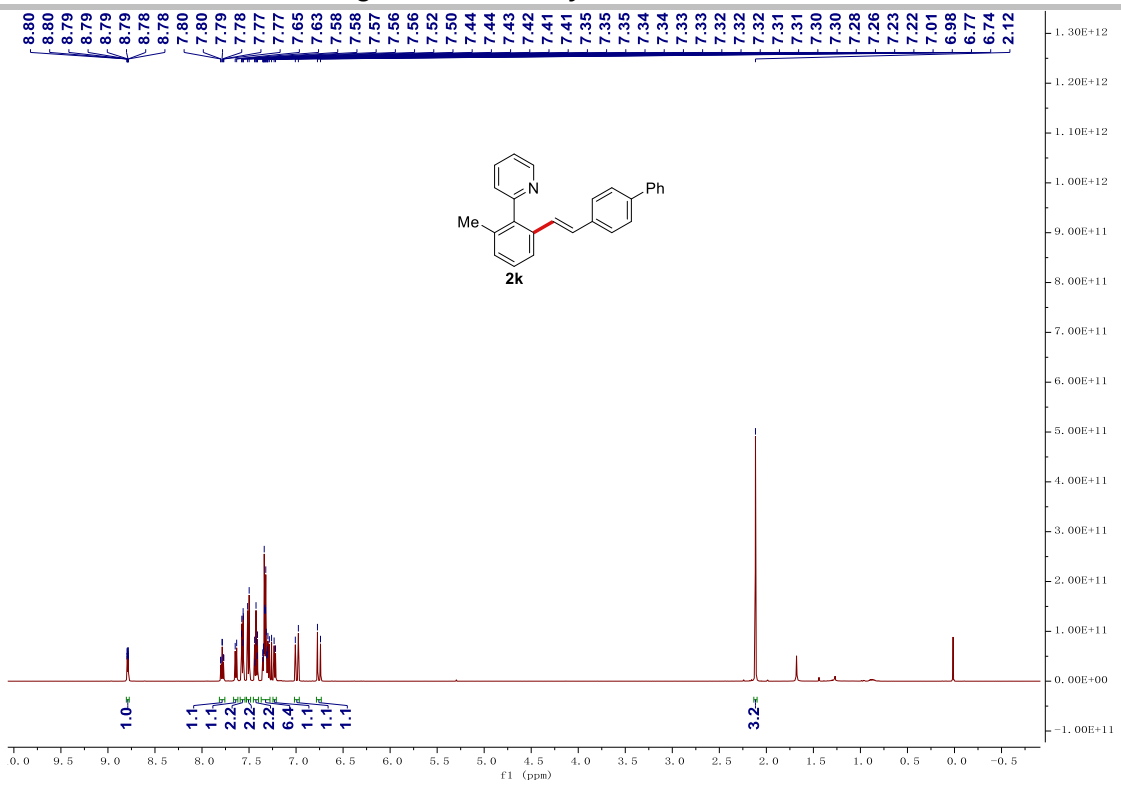
N
Me
CO2Me
2g
1.0 1.0 1.0 1.0 1.0 1.0 4.3 1.1 1.1 1.0 3.0 3.2
f1 (ppm)


166.9 158.9 149.6 139.7 137.9 136.4 136.2 135.6 130.4 130.3 129.7 128.8 128.5 128.3 128.2 127.9 125.4 123.1 121.9 77.3 77.0 76.7 52.1 20.2
N
Me
CO2Me
2g
f1 (ppm)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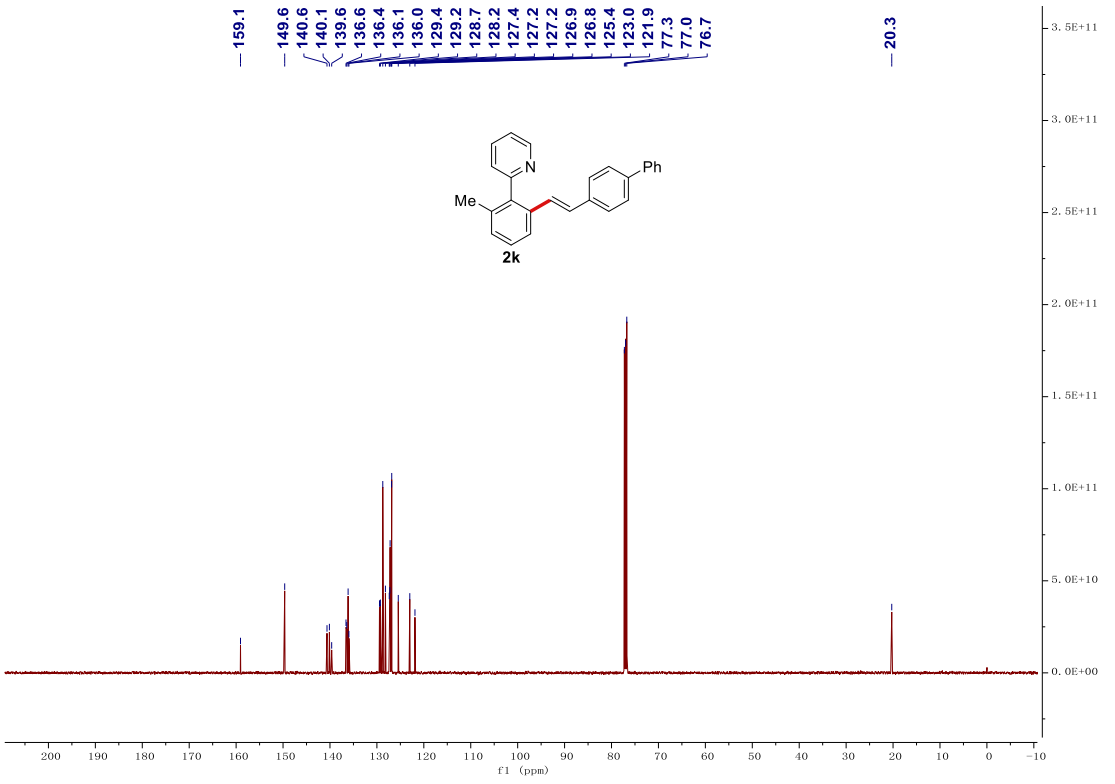
N
Ph
Me
2k
1.0
1.1
1.1
2.2
2.2
2.2
6.4
1.1
1.1
1.1
3.2
f1 (ppm)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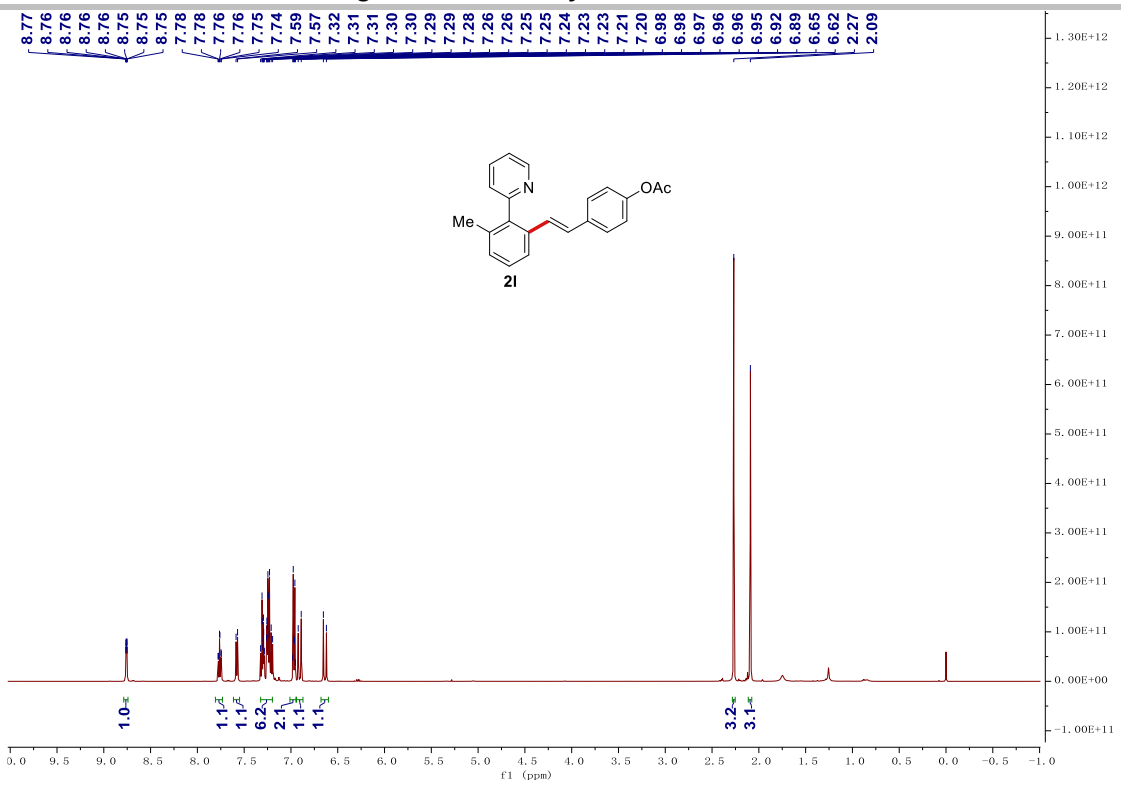
140.6
140.1
139.6
136.6
136.4
136.1
136.0
129.4
129.2
128.7
128.2
127.4
127.2
127.2
126.9
126.8
125.4
123.0
121.9
77.3
77.0
76.7
20.3
N
Ph
Me
2k
f1 (ppm)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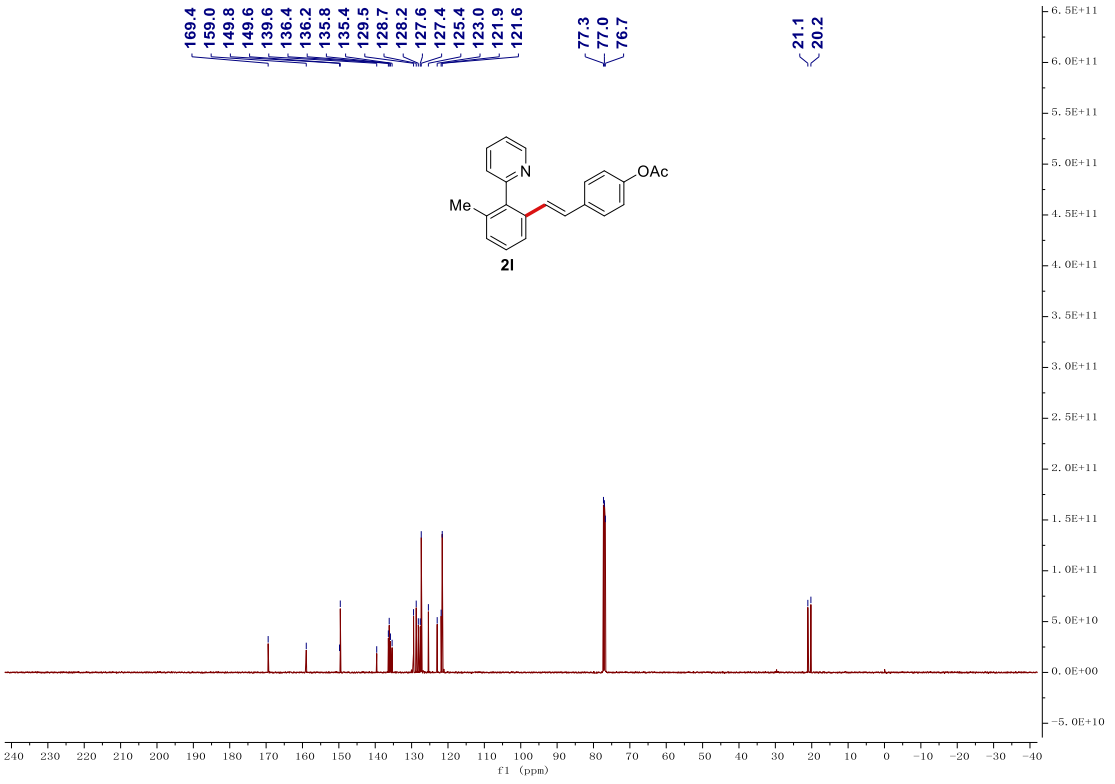
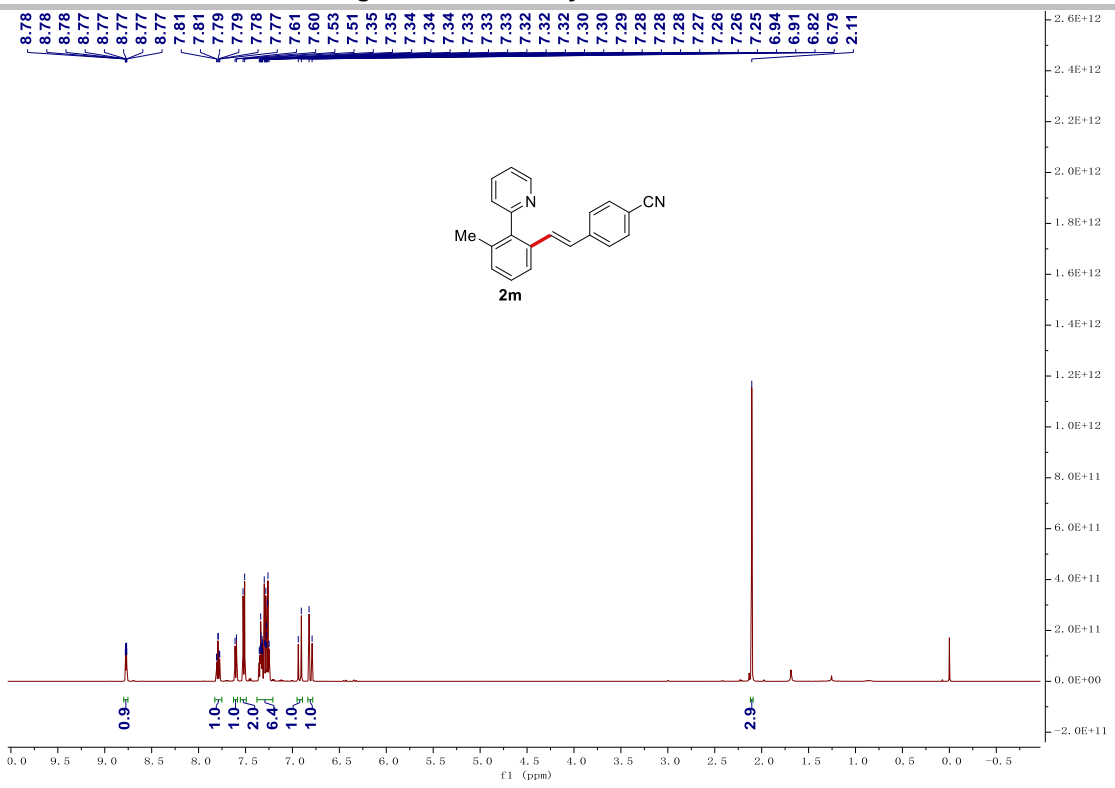
N
OAc
Me
2l
1.0 1.1 1.1 6.2 2.1 1.1 1.1 3.2 3.1
f1 (ppm)


169.4 159.0 149.8 149.6 139.6 136.4 136.2 135.8 135.4 129.5 128.7 128.2 127.6 127.4 125.4 123.0 121.9 121.6
77.3 77.0 76.7
21.1 20.2
N
OAc
Me
2l
f1 (ppm)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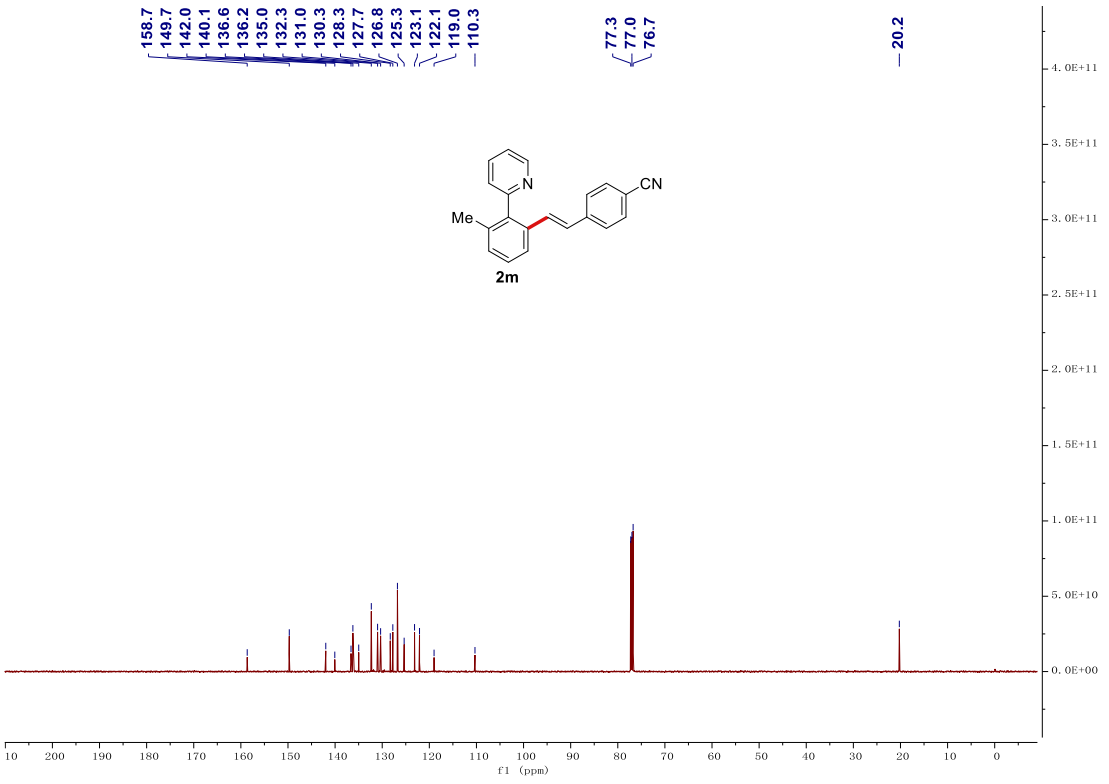
N
CN
Me
2m
0.9 1.0 1.0 2.0 6.4 1.0 1.0 2.9
f1 (ppm)


158.7 149.7 142.0 140.1 136.6 136.2 135.0 132.3 131.0 130.3 128.3 127.7 126.8 125.3 123.1 122.1 119.0 110.3
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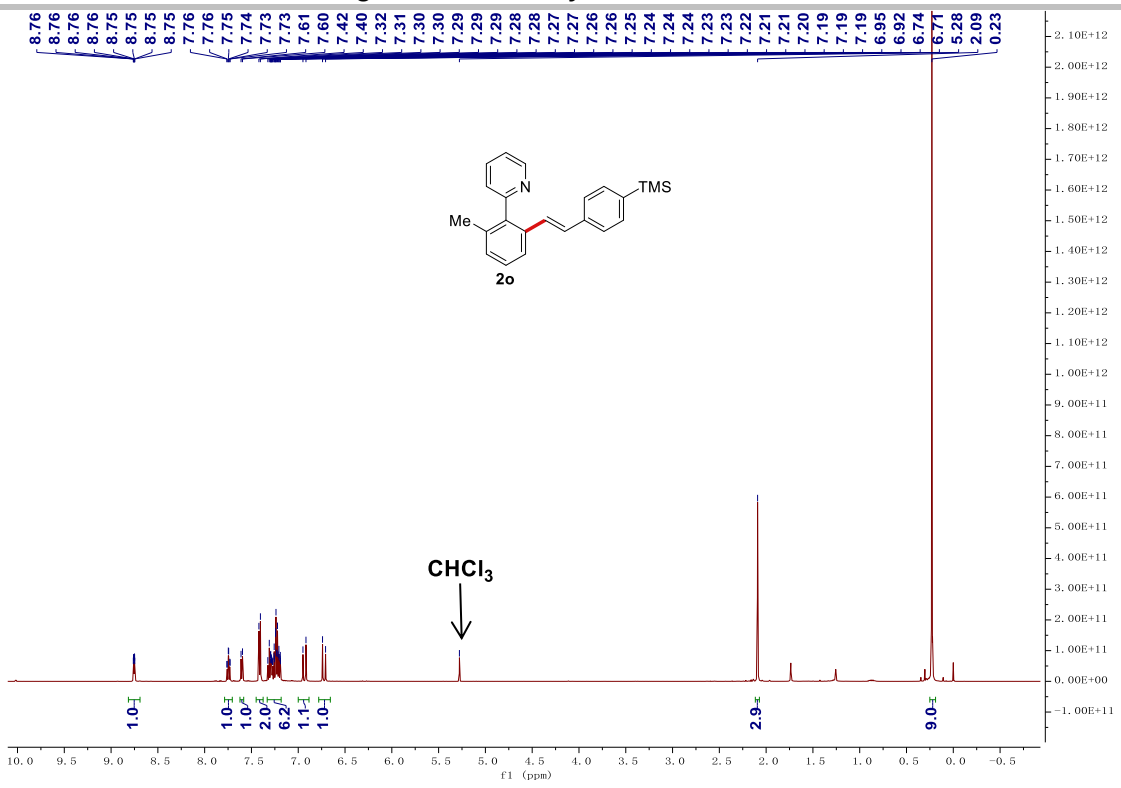
20.2
N
CN
Me
2m
f1 (ppm)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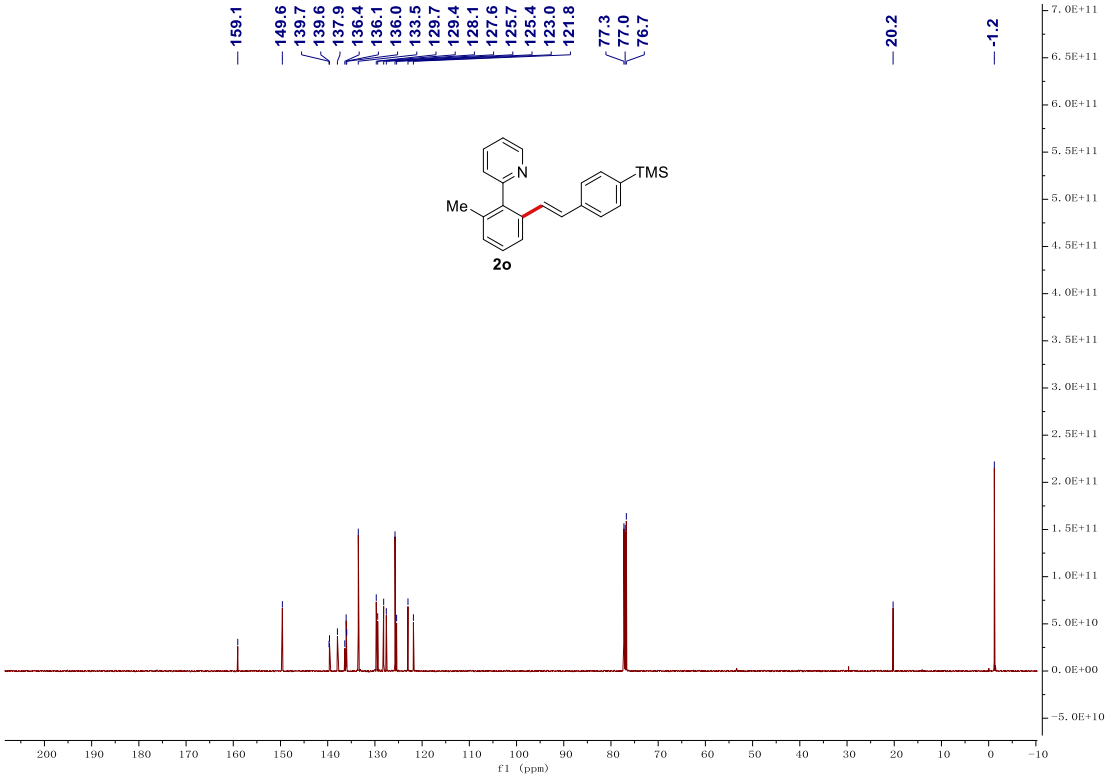
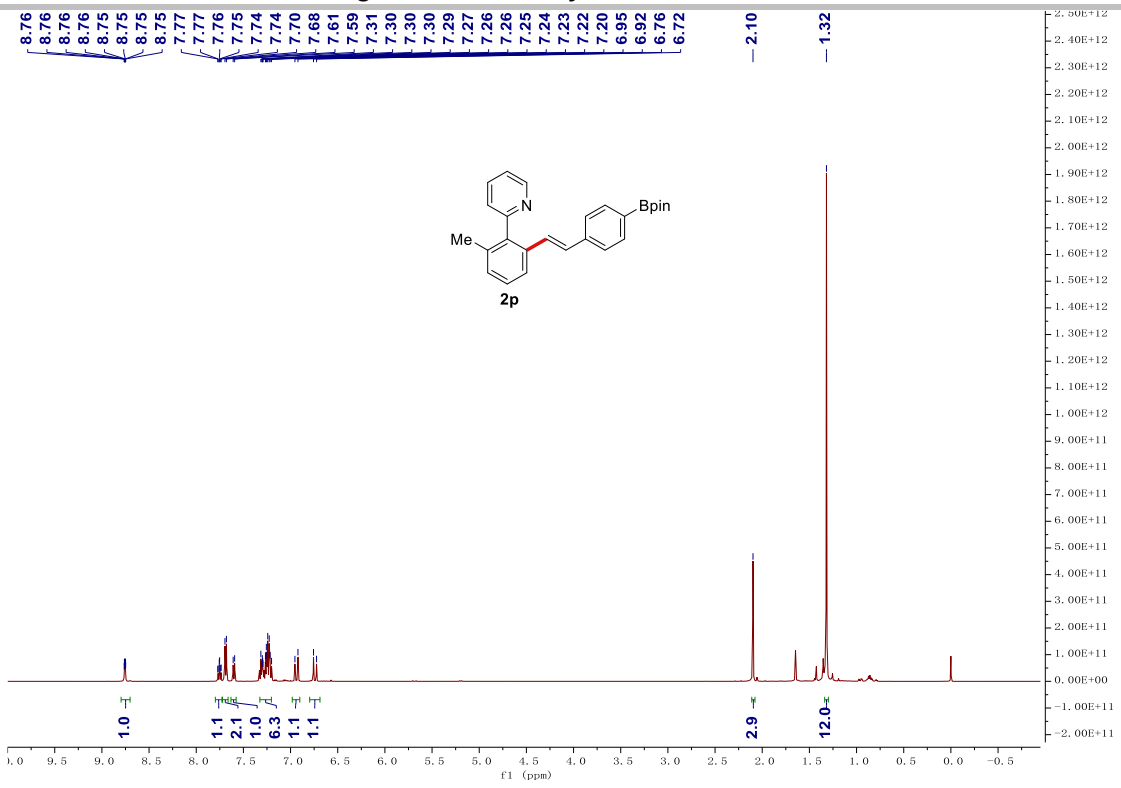
N
TMS
Me
2o
CHCl3
1.0 1.0 1.0 2.0 6.2 1.1 1.0 2.9 9.0
f1 (ppm)


159.1 149.6 139.7 139.6 137.9 136.4 136.1 136.0 133.5 129.7 129.4 128.1 127.6 125.7 125.4 123.0 121.8 77.3 77.0 76.7 20.2 -1.2
N
TMS
Me
2o
f1 (ppm)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8.76
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7.74
7.70
7.68
7.61
7.59
7.31
7.30
7.30
7.30
7.29
7.27
7.26
7.26
7.25
7.24
7.23
7.22
7.20
6.95
6.92
6.76
6.72
2.10
1.32
N
Bpin
Me
2p
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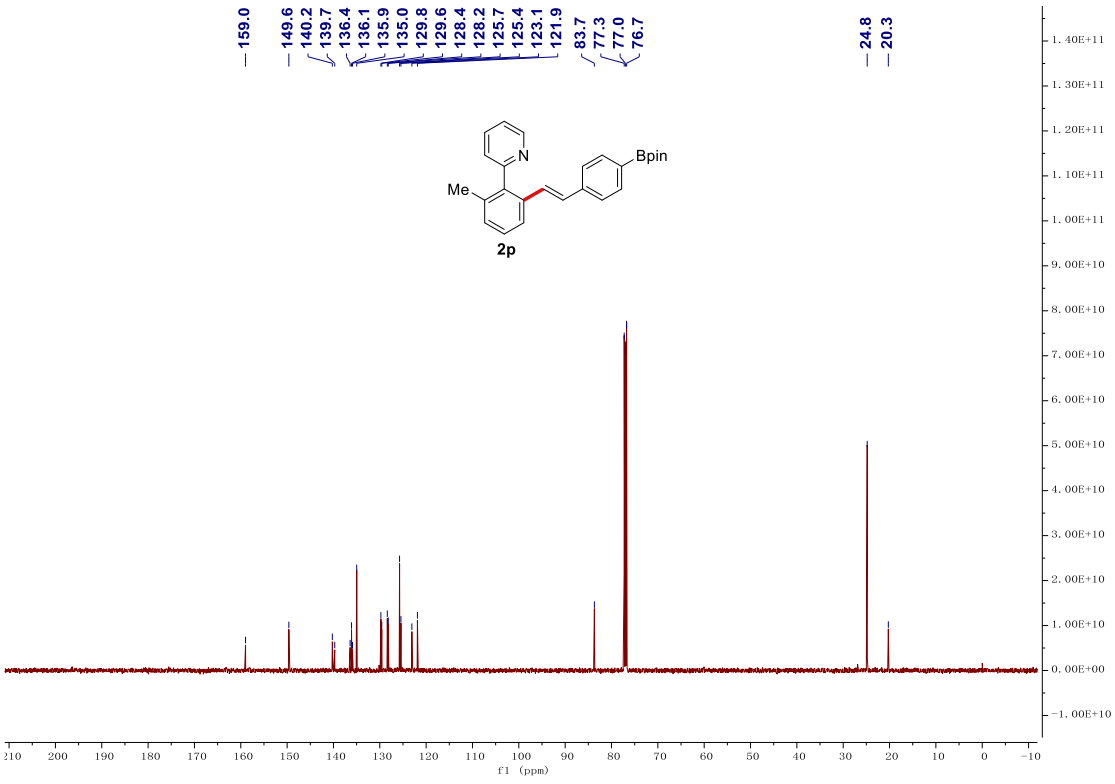
1.1
2.1
1.0
6.3
1.1
1.1
2.9
12.0
f1 (ppm)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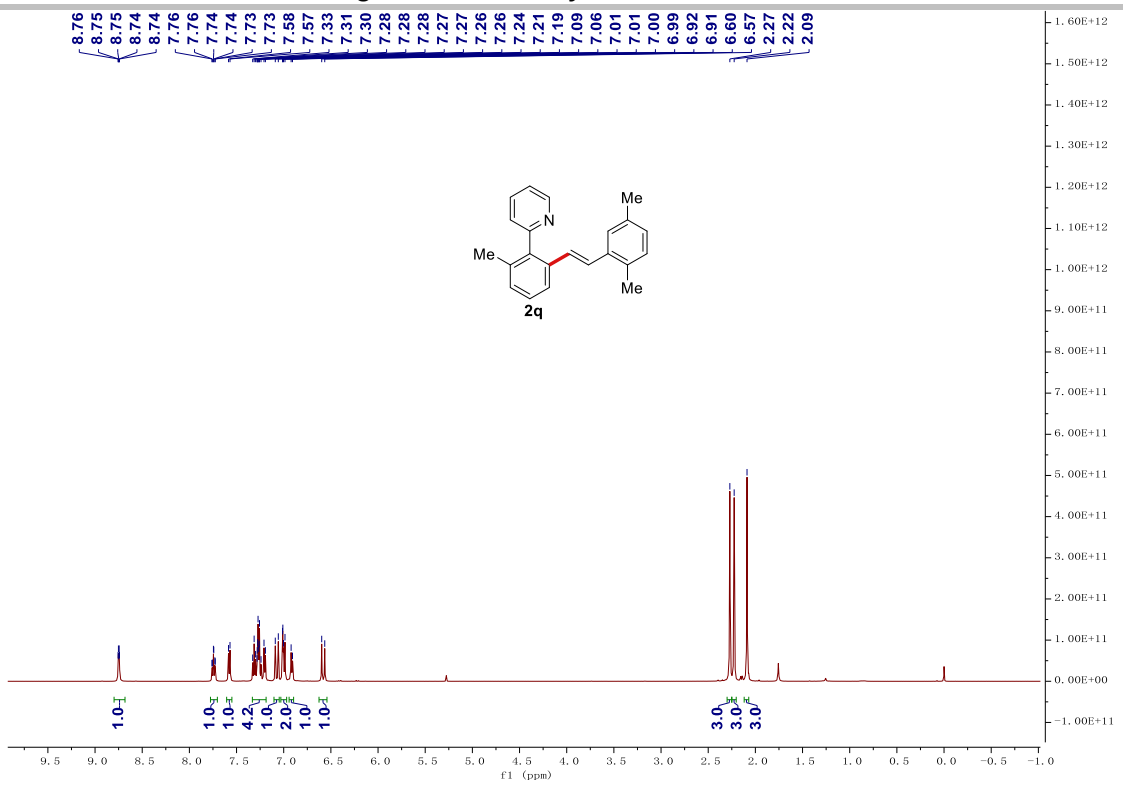
149.6
140.2
139.7
136.4
136.1
135.9
135.0
129.8
129.6
128.4
128.2
125.7
125.4
123.1
121.9
83.7
77.3
77.0
76.7
24.8
20.3
N
Bpin
Me
2p
f1 (ppm)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8.75
8.75
8.74
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7.74
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7.73
7.73
7.58
7.57
7.33
7.31
7.30
7.28
7.28
7.28
7.27
7.27
7.26
7.26
7.24
7.21
7.19
7.09
7.06
7.01
7.01
7.00
6.99
6.92
6.91
6.60
6.57
2.27
2.22
2.09
Me
N
Me
Me
2q
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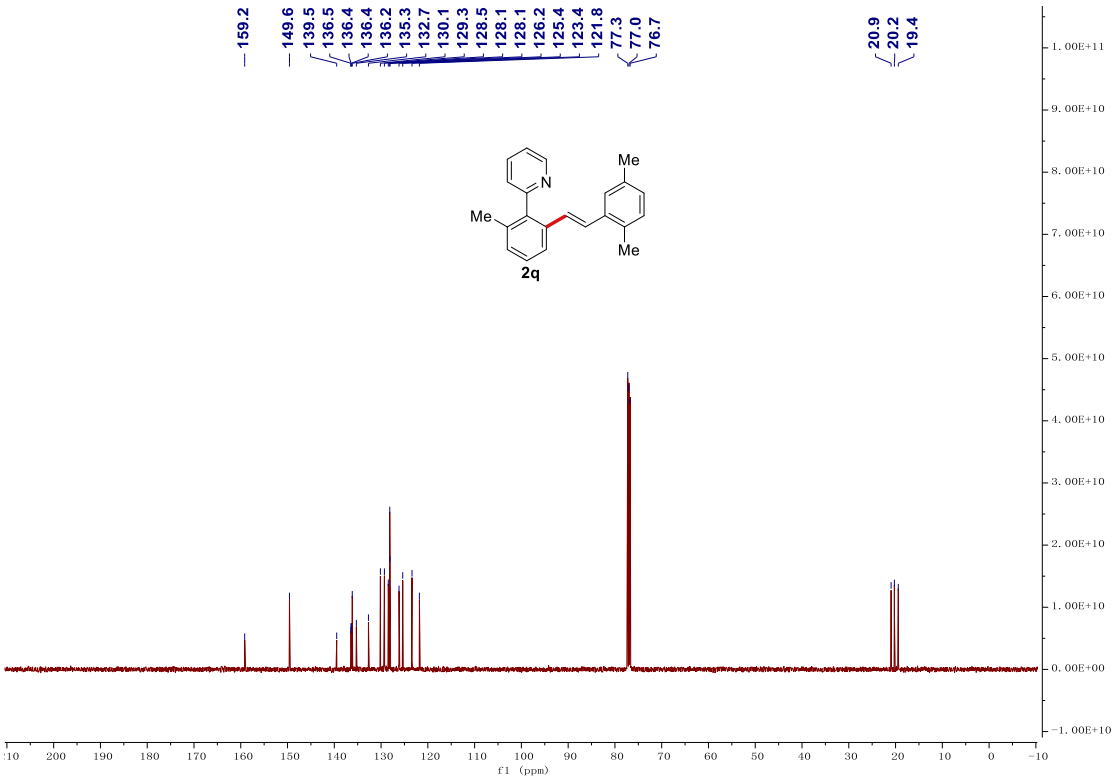
1.0
1.0
4.2
1.0
2.0
1.0
1.0
3.0
3.0
3.0
f1 (ppm)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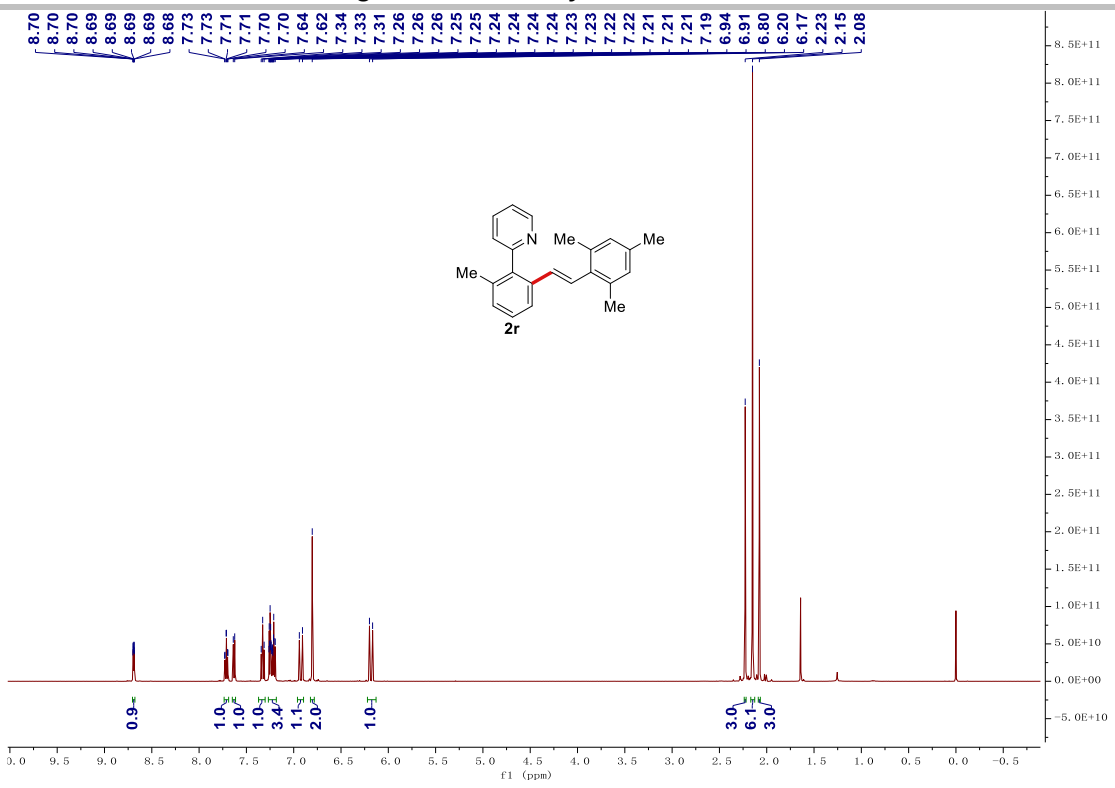
139.5
136.5
136.4
136.4
136.2
135.3
132.7
130.1
129.3
128.5
128.1
128.1
126.2
125.4
123.4
121.8
77.3
77.0
76.7
20.9
20.2
19.4
Me
N
Me
Me
2q
f1 (ppm)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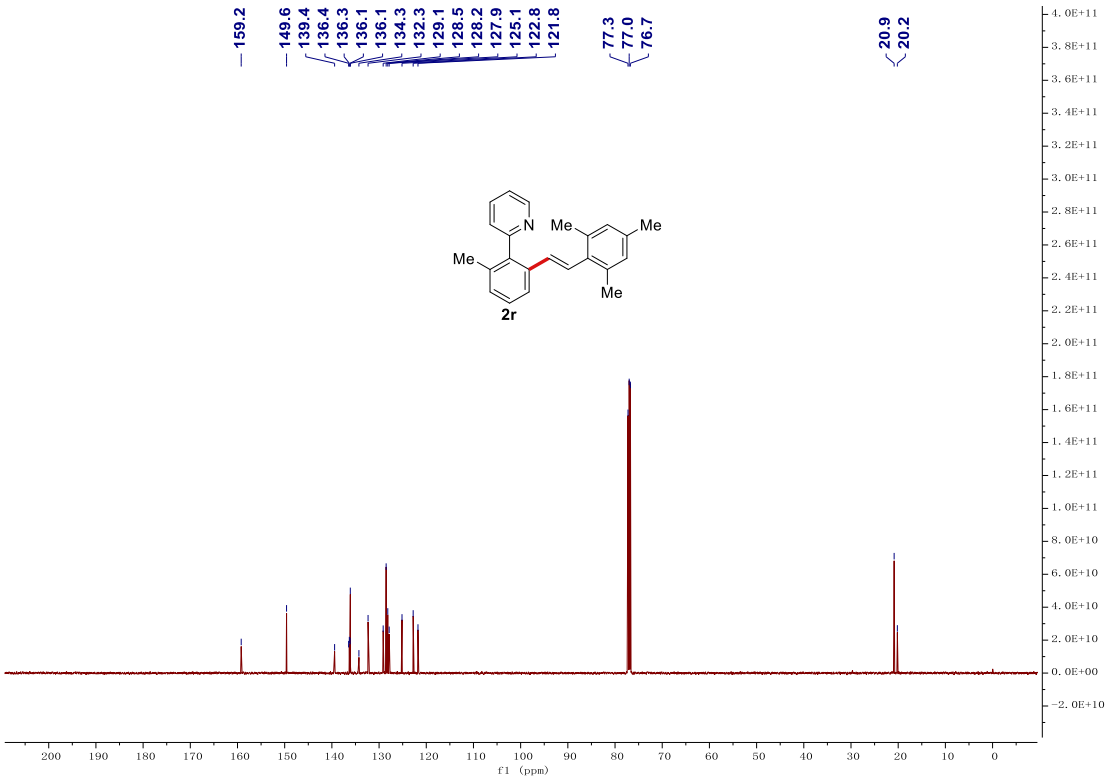
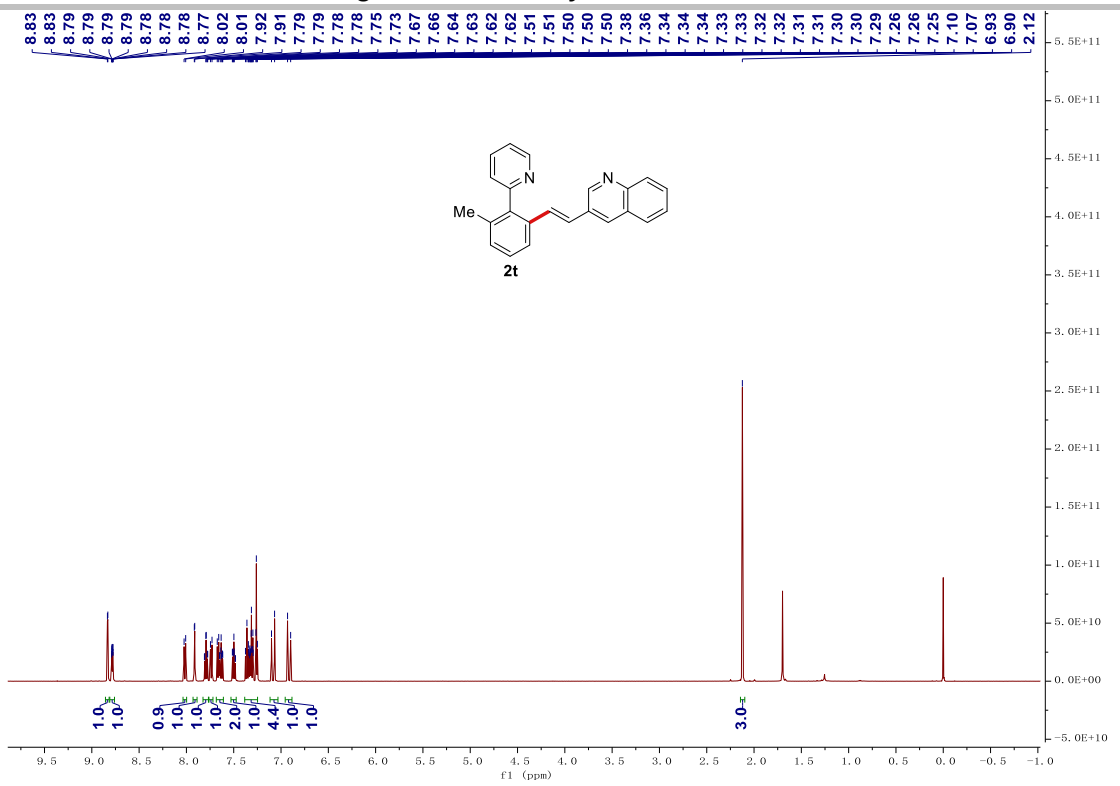
N
Me
Me
Me
Me
2r
0.9 1.0 1.0 1.0 3.4 1.1 2.0 1.0 3.0 6.1 3.0
f1 (ppm)


159.2 149.6 139.4 136.4 136.3 136.1 136.1 134.3 132.3 129.1 128.5 128.2 127.9 125.1 122.8 121.8 77.3 77.0 76.7 20.9 20.2
N
Me
Me
Me
Me
2r
f1 (ppm)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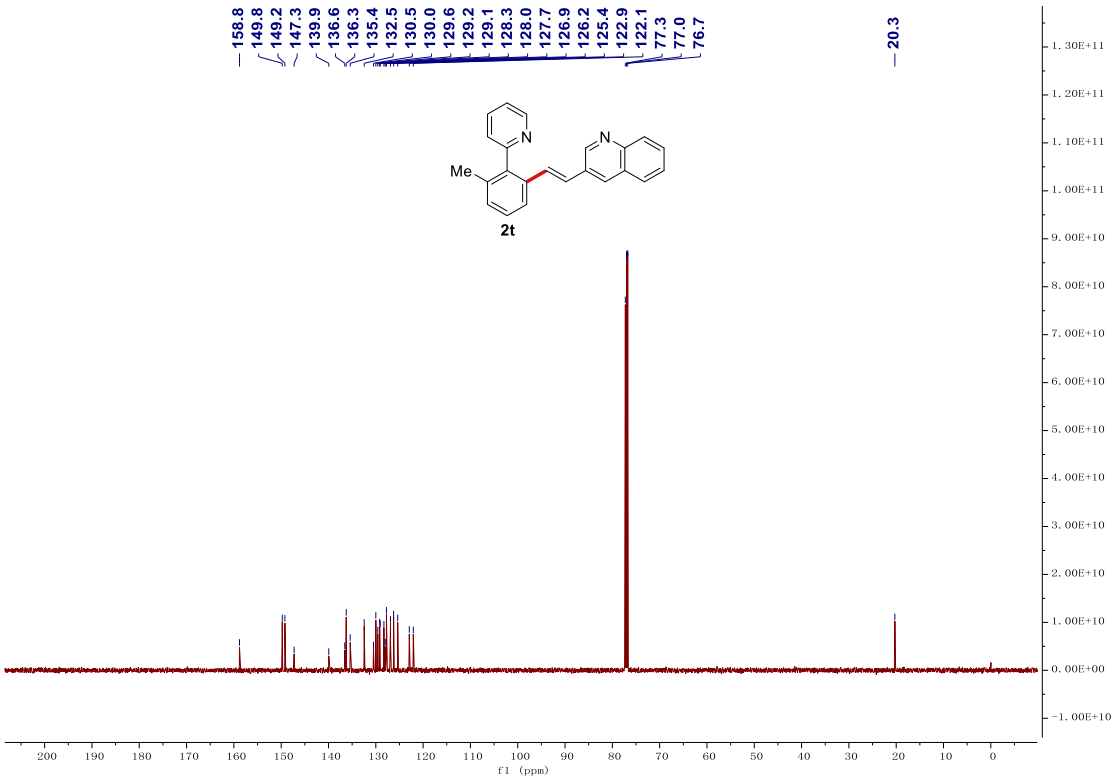
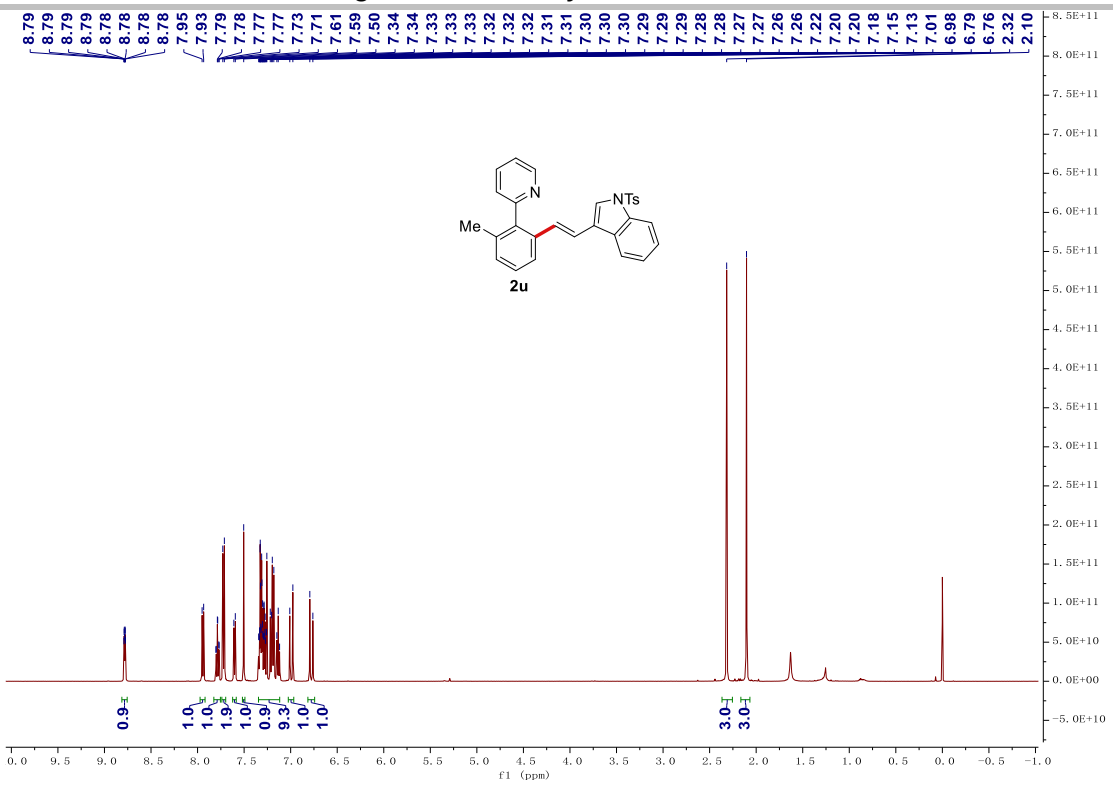
N
N
Me
2t
1.0 1.0 0.9 1.0 1.0 1.0 2.0 1.0 4.4 1.0 1.0 3.0
f1 (ppm)


158.8 149.8 149.2 147.3 139.9 136.6 136.3 135.4 132.5 130.5 130.0 129.6 129.2 129.1 128.3 128.0 127.7 126.9 126.2 125.4 122.9 122.1 77.3 77.0 76.7
20.3
N
N
Me
2t
f1 (ppm)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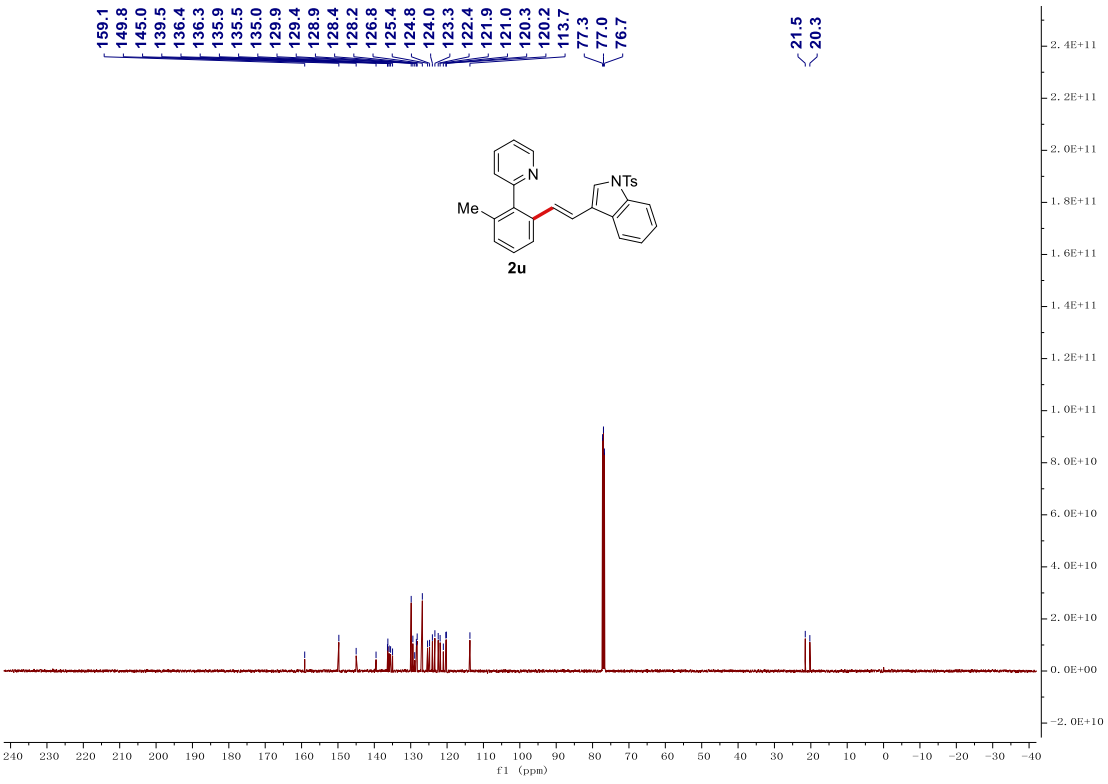
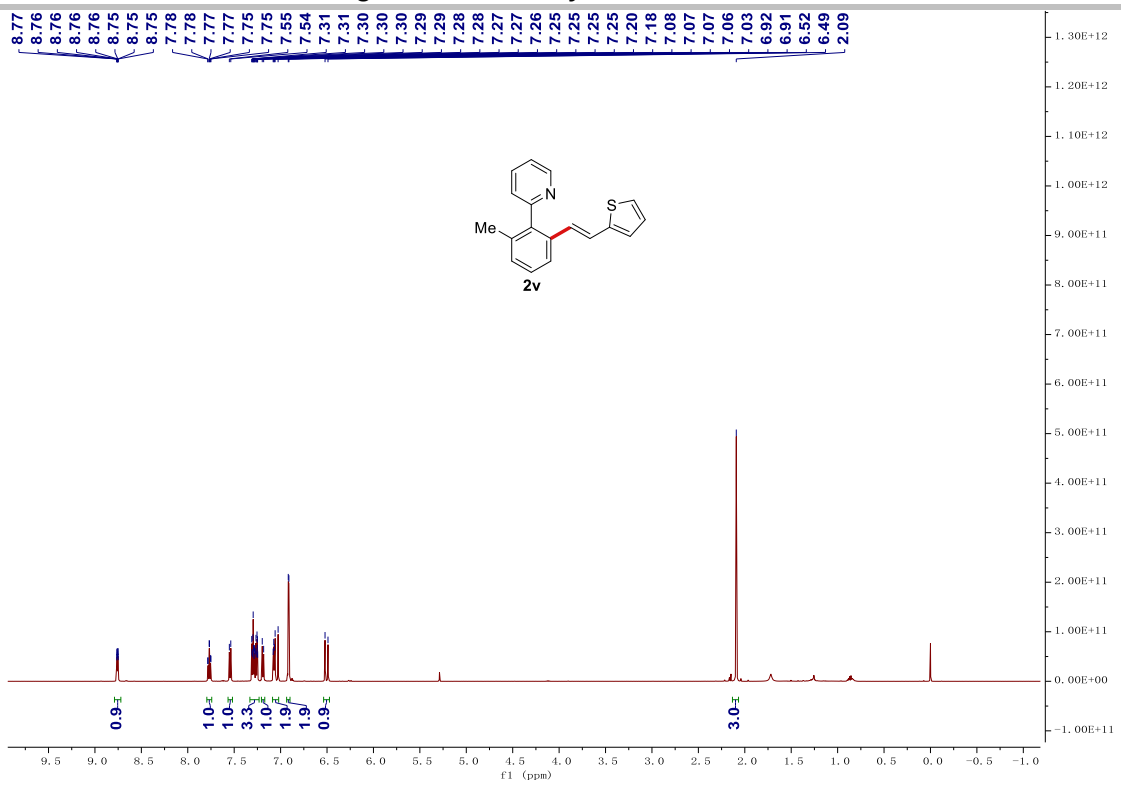
N
NTs
Me
2u
0.9 1.0 1.0 1.9 1.0 0.9 9.3 1.0 1.0 3.0 3.0
f1 (ppm)


159.1 149.8 145.0 139.5 136.4 136.3 135.9 135.5 135.0 129.9 129.4 128.9 128.4 128.2 126.8 125.4 124.8 124.0 123.3 122.4 121.9 121.0 120.3 120.2 113.7 77.3 77.0 76.7 21.5 20.3
N
NTs
Me
2u
f1 (ppm)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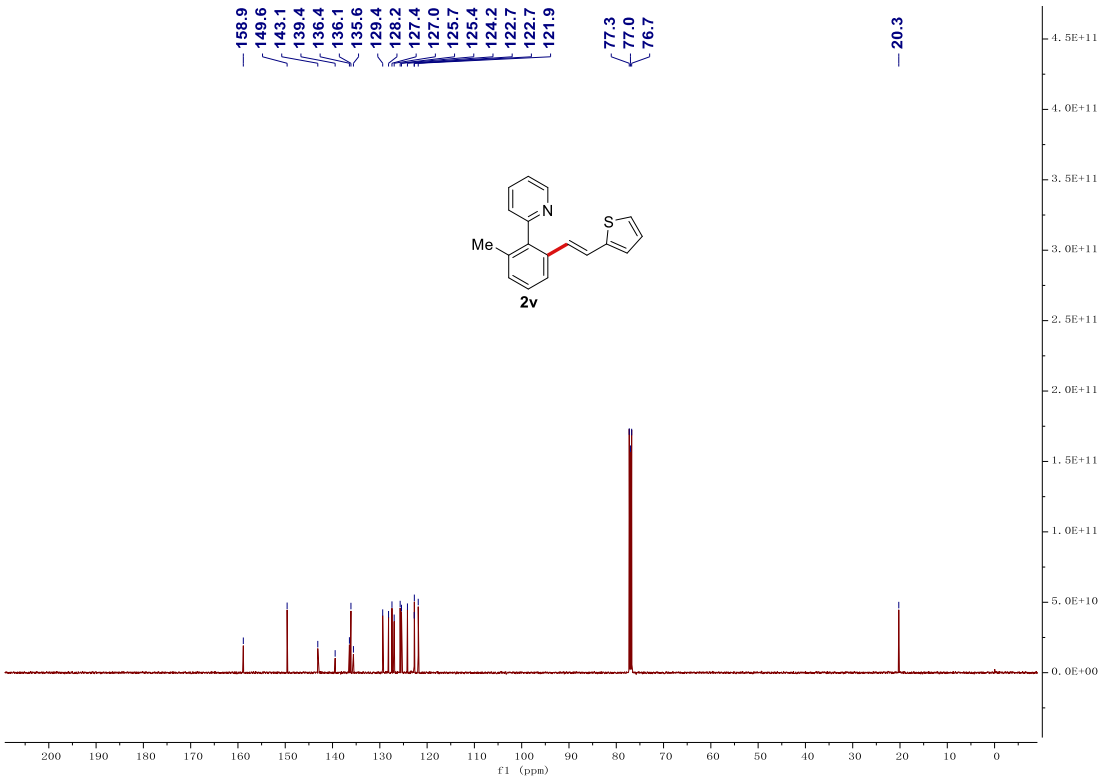
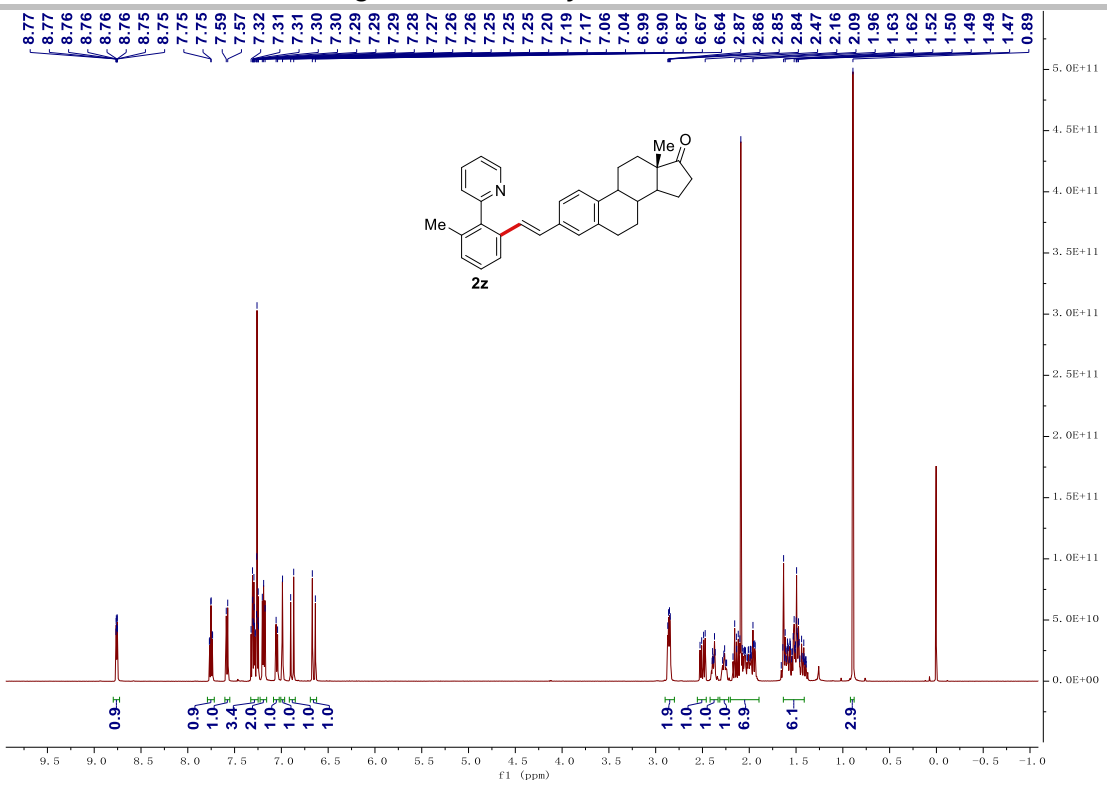
N
S
Me
2v
0.9 1.0 1.0 3.3 1.0 1.9 1.9 0.9 3.0
f1 (ppm)


158.9 149.6 143.1 139.4 136.4 136.1 135.6 129.4 128.2 127.4 127.0 125.7 125.4 124.2 122.7 122.7 121.9
77.3 77.0 76.7
20.3
N
S
Me
2v
f1 (ppm)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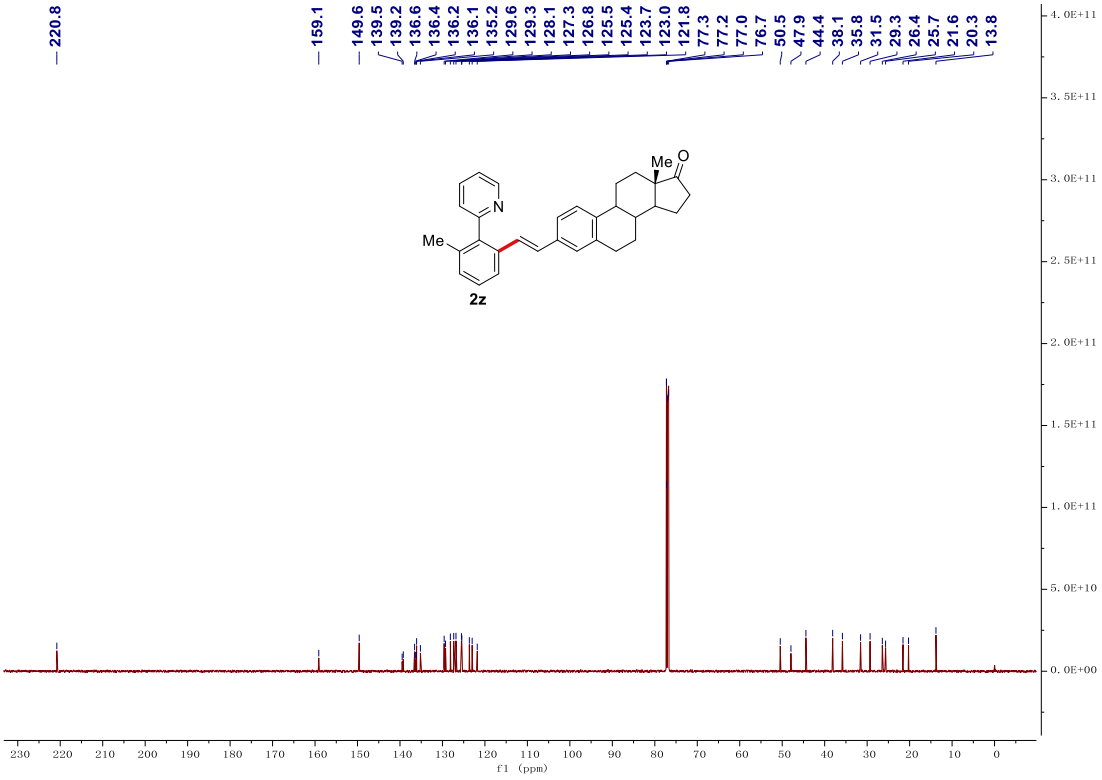
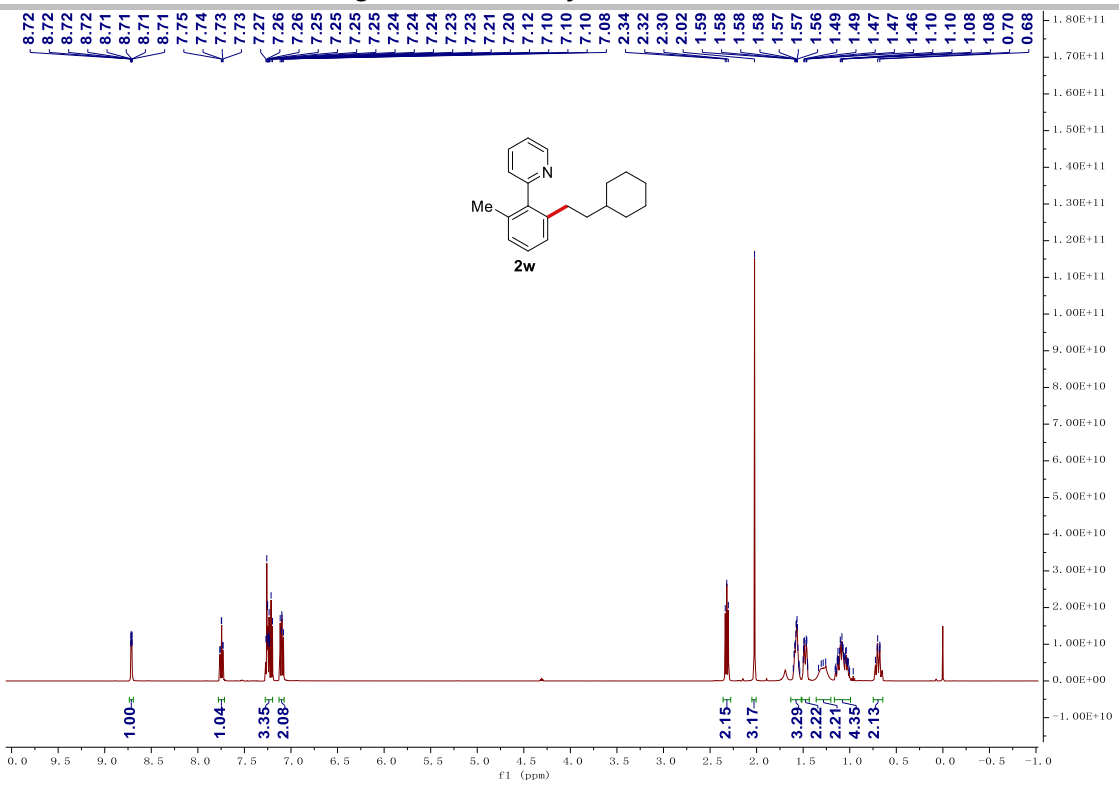
Me
O
N
Me
2z
0.9 0.9 1.0 3.4 2.0 1.0 1.0 1.0 1.0 1.9 1.0 1.0 1.0 6.9 6.1 2.9
f1 (ppm)


220.8
159.1
149.6 139.5 139.2 136.6 136.4 136.2 136.1 135.2 129.6 129.3 128.1 127.3 126.8 125.5 125.4 123.7 123.0 121.8 77.3 77.2 77.0 76.7 50.5 47.9 44.4 38.1 35.8 31.5 29.3 26.4 25.7 21.6 20.3 13.8
Me
O
N
Me
2z
f1 (ppm)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N
Me
2w
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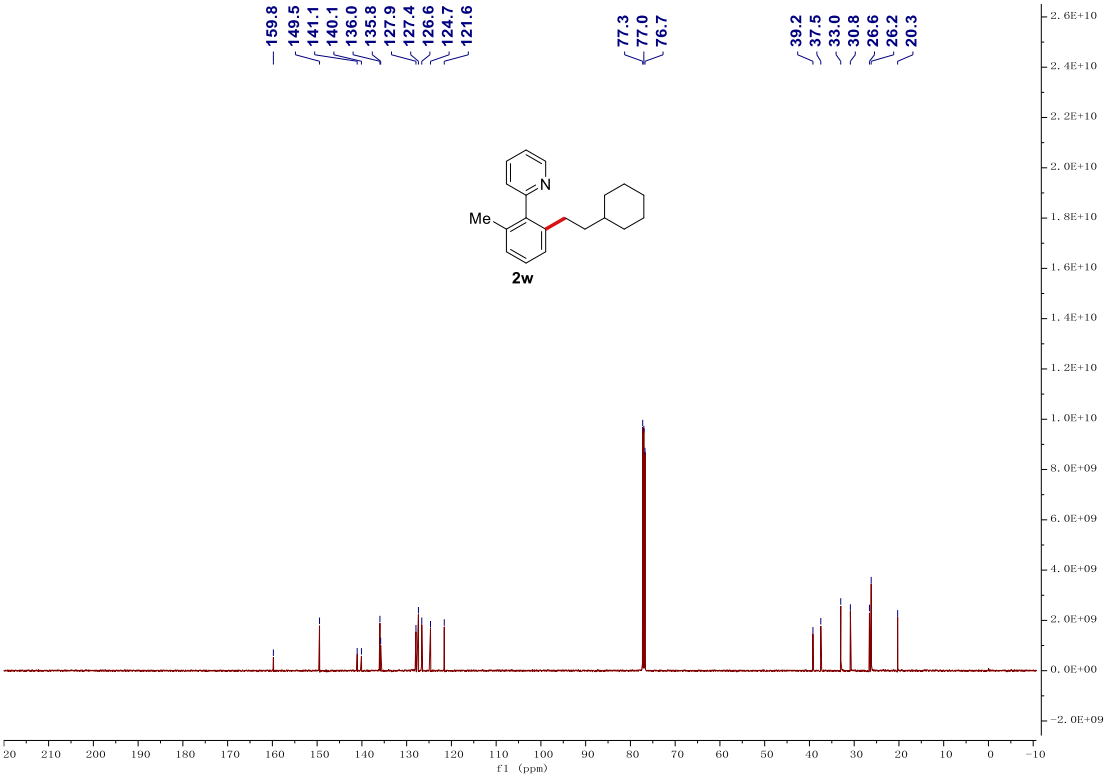
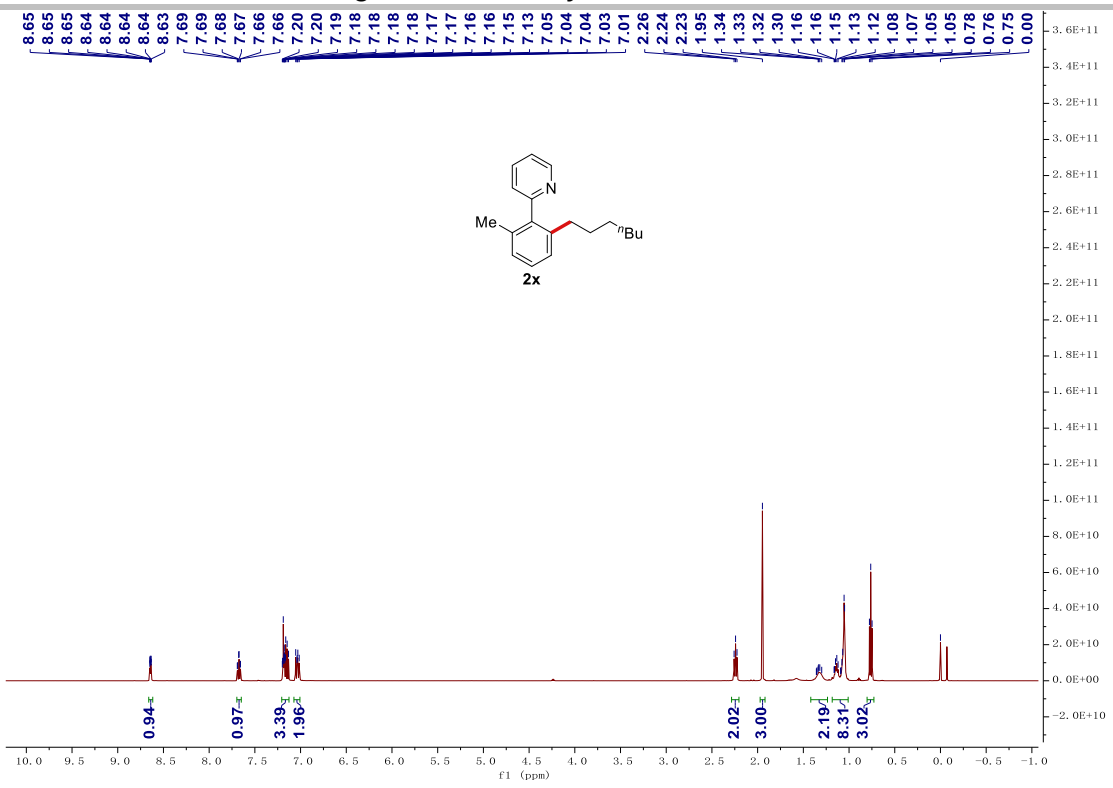
f1 (ppm)


159.8 149.5 141.1 140.1 136.0 135.8 127.9 127.4 126.6 124.7 121.6
77.3 77.0 76.7
39.2 37.5 33.0 30.8 26.6 26.2 20.3
N
Me
2w
f1 (ppm)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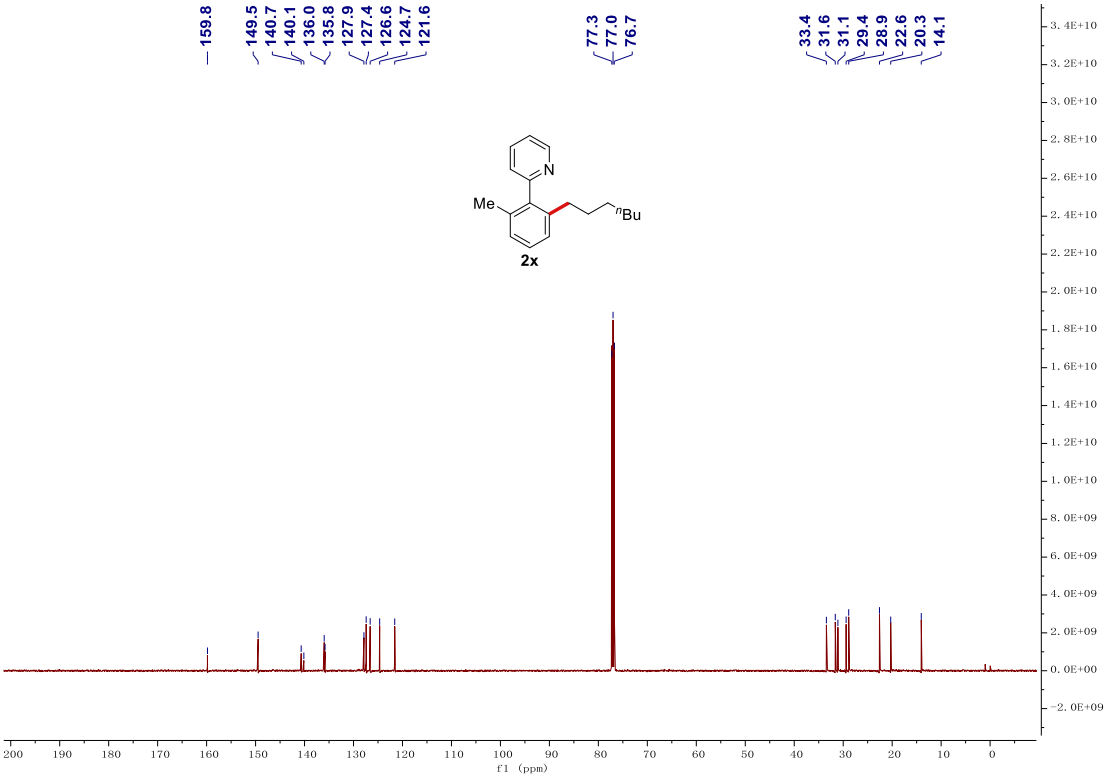
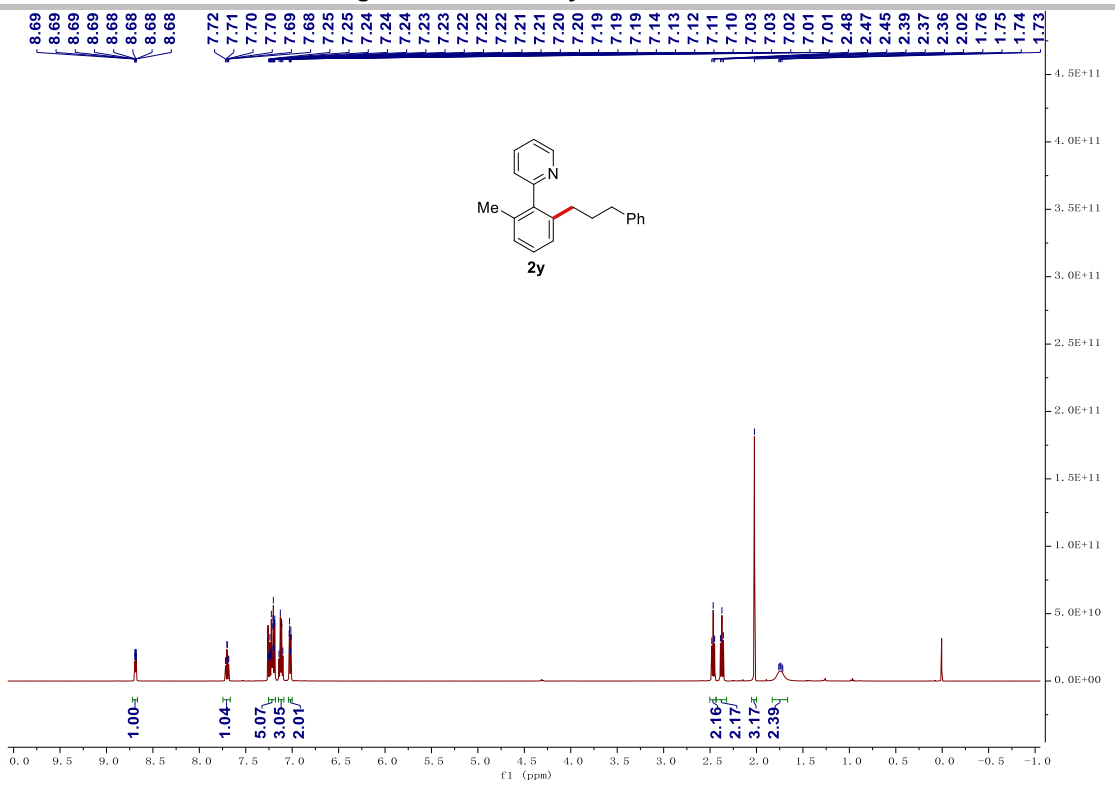
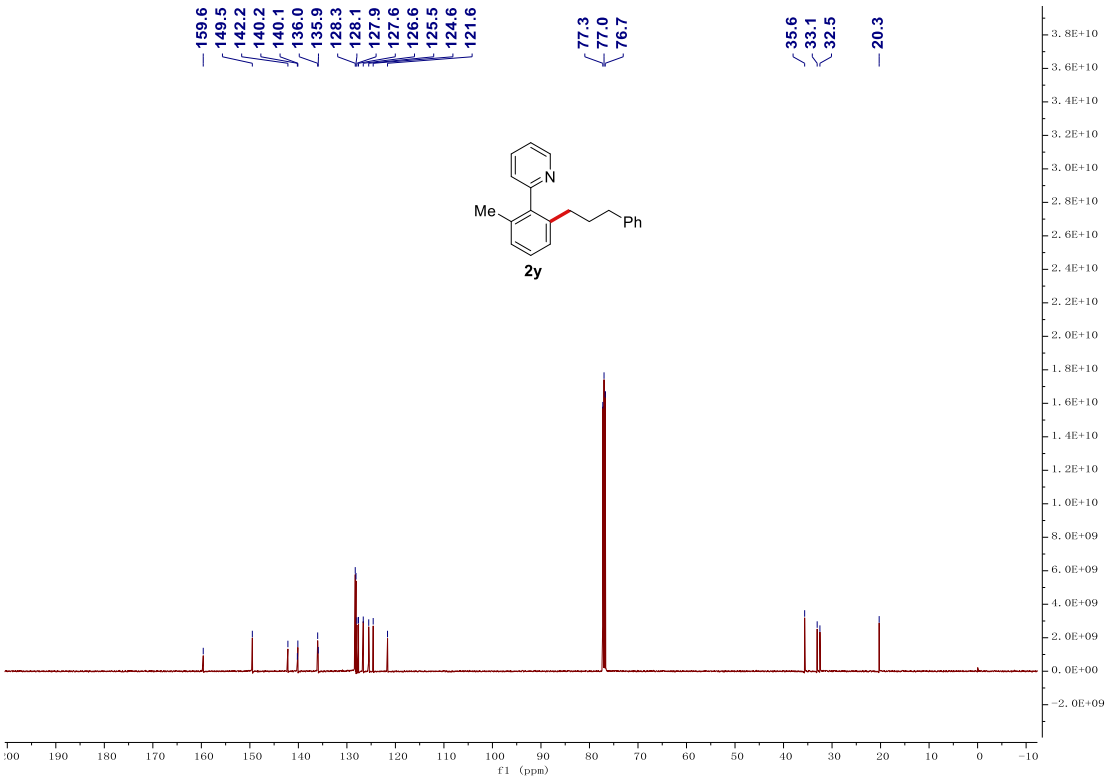
N
Me
nBu
2x
0.94 0.97 3.39 1.98 2.02 3.00 2.19 8.31 3.02
f1 (ppm)


159.8 149.5 140.7 140.1 136.0 135.8 127.9 127.4 126.6 124.7 121.6
77.3 77.0 76.7
33.4 31.6 31.1 29.4 28.9 22.6 20.3 14.1
N
Me
nBu
2x
f1 (ppm)


8.69 8.69 8.69 8.69 8.68 8.68 8.68 8.68
7.72 7.71 7.70 7.70 7.69 7.68 7.25 7.25 7.24 7.24 7.24 7.23 7.23 7.22 7.22 7.22 7.21 7.21 7.20 7.20 7.19 7.19 7.19 7.14 7.13 7.12 7.11 7.10 7.03 7.03 7.02 7.01 7.01 2.48 2.47 2.45 2.39 2.37 2.36 2.02 1.76 1.75 1.74 1.73
N
Me
Ph
2y
1.00 1.04 5.07 3.05 2.01 2.16 2.17 3.17 2.39
f1 (ppm)


159.6 149.5 142.2 140.2 140.1 136.0 135.9 128.3 128.1 127.9 127.6 126.6 125.5 124.6 121.6
77.3 77.0 76.7
35.6 33.1 32.5
20.3
N
Me
Ph
2y
f1 (ppm)

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