Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Palladium-Catalyzed Three-Component Tandem Cyclization of Buta-2,3-dien-1-ol, Aryl Iodides, and Imines: An Efficient Protocol for the Synthesis of Oxazolidine Derivatives

Yunlei Hou,[‡] Mingze Qin,[‡] Xiuxiu Yang, Qi Shen, Yanfang Zhao, Yajing Liu,* Ping Gong*[a]

Key Laboratory of Structure-Based Drug Design and Discovery (Shenyang Pharmaceutical University), Ministry of Education, 103 Wenhua Road,Shenhe District, Shenyang 110016, PR China

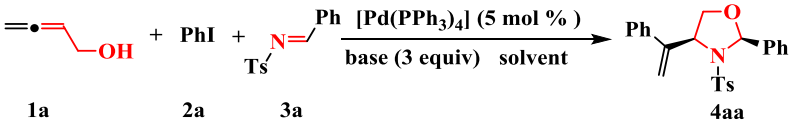
Contents

1. General Information

Unless otherwise noted, all reagents and solvents were obtained from commercial sources and used without further purification. Solvents were dried using standard methods and distilled before use. Reactions were monitored by thin-layer chromatography (TLC) on silica plates (F-254) and visualized under UV light. Melting points were obtained on a Büchi Melting Point B-540 apparatus and were uncorrected. All ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker ARX-400, 400 MHz spectrometers with TMS as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in hertz (Hz). HRMS analysis was performed on a Q-TOF mass analyzer using the ESI ionization method. Column chromatography was run on silica gel (200-300 mesh) from Qingdao Ocean Chemicals (Qingdao, Shandong, China).

2. General Procedure and Product Characterization

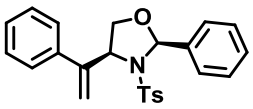
2.1 The Optimal Experimental Conditions



1a **2a** **3a** **4aa**

Under an atmosphere of nitrogen, buta-2,3-dien-1-ol **1a** (25 mg, 0.35 mmol) and iodobenzene **2a** (87 mg, 0.42 mmol, 1.2 equiv.) were added consecutively to a sealed tube charged with a mixture of CsF (148 mg, 1.0 mmol, 3.0 equiv.), [Pd(PPh$_3$)$_4$] (20mg, 0.018 mmol, 5 mol%), and imine **3a** (111 mg, 0.42 mmol, 1.2 equiv.) in dioxane (3 mL). The reaction mixture was stirred at 80 ℃ for 10 h and analyzed by TLC. After the reaction was complete, water (10 mL) was added, and the solution was extracted with dichloromethane; the organic phase was separated, washed with brine, dried ($MgSO_4$), filtered, and concentrated and the crude product was purified by column chromatography on silica gel with a mixture of ethyl acetate/petroleum (25:3, v/v) to afford the desired product **4aa**.

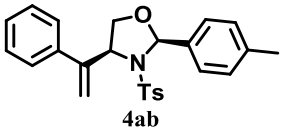
2.2 Product Characterization



4aa

***trans*-2-phenyl-4-(1-phenylvinyl)-3-tosyloxazolidine (4aa)**

Yield: 50% (72 mg), white solid, m.p.:120.6-121.5 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.90 (d, *J* = 8.2 Hz, 2H), 7.50 (t, *J* = 5.9 Hz, 4H), 7.44-7.25 (m, 8H), 6.19 (s, 1H), 5.39 (d, *J* = 6.4 Hz, 2H), 4.87 (t, *J* = 6.3 Hz, 1H), 4.00-3.85 (m, 1H), 3.53 (dd, *J* = 8.9, 5.5 Hz, 1H), 2.44 (s, 3H).^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.83, 144.78, 138.80, 138.49, 133.76, 130.55, 129.00, 128.90, 128.58, 128.35, 127.26, 126.84, 115.33, 92.16, 71.14, 62.33, 21.47.HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{23}NO_3S$ $[M + H]^+$: 406.1399.found $[M + H]^+$: 406.1387.

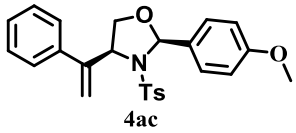


4ab

***trans*-4-(1-phenylvinyl)-2-(p-tolyl)-3-tosyloxazolidine (4ab)**

Yield: 55% (82 mg), white solid, m.p.:141.4-142.1 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.90 (d, *J* = 8.2 Hz, 2H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.29 (m, 7H), 7.21 (d, *J* = 7.9 Hz, 2H), 6.13 (s, 1H), 5.40 (d, *J* = 3.9 Hz, 2H), 4.86 (t, *J* = 6.2 Hz, 1H), 3.88 (dd, *J* = 8.8, 7.4 Hz, 1H), 3.53 (dd, *J* = 8.9, 5.4 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.96, 144.82, 138.90, 138.41, 135.62, 133.90, 130.62, 129.22, 129.00, 128.66, 128.44, 127.33, 126.90,

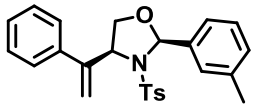
115.38, 92.29, 71.19, 62.36, 21.55, 21.24. HRMS (ESI-Q-TOF, m/z) calcd for $C_{25}H_{25}NO_3S$ $[M + H]^+$: 420.1555. found $[M + H]^+$: 420.1568.



4ac

***trans*-2-(4-methoxyphenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ac)**

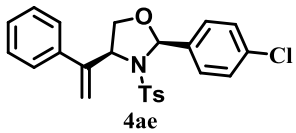
Yield: 52% (80 mg), white solid, m.p.:117.8-118.9 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.87 (d, J = 8.2 Hz, 2H), 7.48 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.6 Hz, 2H), 7.39 – 7.30 (m, 5H), 6.94 (d, J = 8.7 Hz, 2H), 6.07 (s, 1H), 5.41 (s, 2H), 4.88 – 4.83 (m, 1H), 3.84 (dd, J = 8.9, 7.4 Hz, 1H), 3.78 (s, 3H), 3.54 (dd, J = 8.9, 5.0 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 159.96, 146.10, 144.76, 138.95, 134.02, 130.59, 130.41, 129.00, 128.86, 128.62, 128.44, 126.93 (s, 5H), 115.41 (s, 2H), 113.99 (s, 5H), 92.31 (s, 2H), 71.08 (s, 2H), 62.29 (s, 2H), 55.61 (s, 2H), 21.55 (s, 2H). HRMS (ESI-Q-TOF, m/z) calcd for $C_{25}H_{25}NO_4S$ $[M + H]^+$: 436.1504. found $[M + H]^+$: 436.1548.



4ad

***trans*-4-(1-phenylvinyl)-2-(m-tolyl)-3-tosyloxazolidine (4ad)**

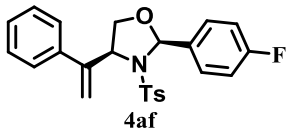
Yield: 45% (67 mg), white solid, m.p.:129.8-130.5 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.90 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 7.42 – 7.28 (m, 7H), 7.21 (d, J = 7.9 Hz, 2H), 6.13 (s, 1H), 5.40 (d, J = 3.1 Hz, 2H), 4.85 (t, J = 6.2 Hz, 1H), 3.92 – 3.82 (m, 1H), 3.52 (dd, J = 8.8, 5.4 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.97, 144.82, 138.91, 138.41, 135.62, 133.90, 130.62, 129.22, 129.00, 128.65, 128.44, 127.33, 126.90, 115.38, 92.30, 71.19, 62.36, 21.55, 21.24. HRMS (ESI-Q-TOF, m/z) calcd for $C_{25}H_{25}NO_3S$ $[M + H]^+$: 420.1555. found $[M + H]^+$: 420.1537.



4ae

***trans*-2-(4-chlorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ae)**

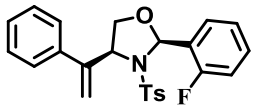
Yield: 51% (80 mg), white solid, m.p.:108.4-109.1 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.92 (d, J = 8.2 Hz, 2H), 7.45-7.50 (m, 6H), 7.31-7.36 (m, 5H), 6.20 (s, 1H), 5.37 (d, J = 9.2 Hz, 2H), 4.86 (t, J = 6.3 Hz, 1H), 3.88 (dd, J = 8.8, 7.5 Hz, 1H), 3.53 (dd, J = 9.0, 5.5 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.89, 144.99, 138.81, 137.70, 133.74, 133.68, 130.67, 129.26, 128.97, 128.72, 128.45, 127.02, 126.92, 115.51, 91.55, 71.24, 62.41, 21.56. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}ClNO_3S$ $[M + H]^+$: 440.1009. found $[M + H]^+$: 440.1043.



4af

***trans*-2-(4-fluorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4af)**

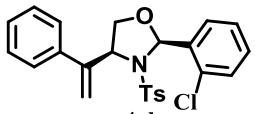
Yield: 48% (73 mg), white solid, m.p.:106.8-107.9 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.91 (d, J = 8.1 Hz, 2H), 7.48-7.54 (m, 4H), 7.30-7.35 (m, 5H), 7.22 (t, J = 8.8 Hz, 2H), 6.17 (s, 1H), 5.38 (d, J = 5.3 Hz, 2H), 4.87 (t, J = 6.0 Hz, 1H), 3.86 (t, J = 8.1 Hz, 1H), 3.55 (dd, J = 8.8, 5.2 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.89, 144.99, 138.81, 137.70, 133.71, 130.67, 130.05, 129.48, 129.26, 128.97, 128.72, 128.45, 128.21, 127.22, 127.02, 126.92, 115.51, 91.55, 71.24, 62.41, 21.56. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}FNO_3S$ $[M + H]^+$: 424.1304. found $[M + H]^+$: 424.1328.



4ag

***trans*-2-(2-fluorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ag)**

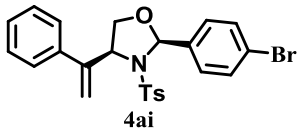
Yield: 30% (45 mg), white solid, m.p.:92.5-93.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.85 (d, J = 7.2 Hz, 2H), 7.59 – 7.36 (m, 8H), 7.22 (d, J = 7.4 Hz, 3H), 6.11 (s, 1H), 5.61 (s, 1H), 5.52 (s, 1H), 4.95 (s, 1H), 3.74 (d, J = 6.2 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 162.08, 159.61, 146.35, 145.04, 139.11, 133.50, 131.83, 130.69, 129.67, 129.00, 128.52, 127.29, 126.98, 125.33, 125.22, 124.70, 116.13, 115.99, 115.92, 87.32, 70.93, 62.11, 21.57. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}FNO_3S$ [M + H]$^+$: 424.1304. found [M + H]$^+$: 424.1332.



4ah

***trans*-2-(2-chlorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ah)**

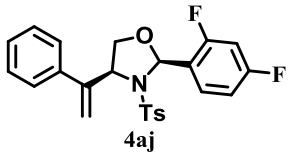
Yield: 28% (45 mg), white solid, m.p.:145.5-146.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.84 (d, J = 7.7 Hz, 2H), 7.51 (s, 4H), 7.46 (d, J = 7.0 Hz, 3H), 7.40 (d, J = 7.9 Hz, 4H), 6.13 (s, 1H), 5.70 (s, 1H), 5.55 (s, 1H), 4.93 (s, 1H), 3.73 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 146.39, 145.18, 139.31, 135.20, 133.45, 133.12, 131.34, 130.75, 130.04, 129.97, 129.70, 129.22, 128.98, 128.59, 128.47, 127.54, 126.96, 126.83, 116.65, 90.00, 70.71, 62.46, 21.58. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}ClNO_3S$ [M + H]$^+$: 440.1009. found [M + H]$^+$: 440.1021.



4ai

***trans*-2-(4-bromophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ai)**

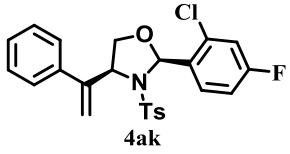
Yield: 54% (93 mg), white solid, m.p.:96.2-97.1 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.93 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.50 (d, J = 7.9 Hz, 3H), 7.44 (d, J = 8.2 Hz, 2H), 7.35 (br, 4H), 6.19 (s, 1H), 5.37 (d, J = 6.0 Hz, 2H), 4.86 (t, J = 6.0 Hz, 1H), 3.89 (t, J = 8.1 Hz, 1H), 3.53 (dd, J = 8.6, 5.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.89, 144.98, 138.81, 138.13, 133.68, 131.65, 130.67, 129.56, 128.97, 128.72, 128.44, 127.01, 122.41, 115.52, 91.60, 71.26, 62.42, 21.56. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}BrNO_3S$ [M + H]$^+$: 484.0504. found [M + H]$^+$: 484.0522.



4aj

***trans*-2-(2,4-difluorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4aj)**

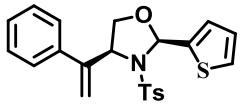
Yield: 25% (39 mg), white solid, m.p.:128.6-129.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.85 (d, J = 8.1 Hz, 2H), 7.52 (d, J = 7.8 Hz, 3H), 7.47 – 7.35 (m, 7H), 6.07 (s, 1H), 5.57 (s, 1H), 5.51 (s, 1H), 4.95 (s, 1H), 3.80 – 3.57 (m, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 146.31, 145.01, 143.65, 138.96, 137.97, 133.38, 130.62, 129.50, 128.92, 128.43, 127.21, 127.15, 126.88, 115.86, 104.44, 86.89, 70.88, 61.93, 21.48. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{21}F_2NO_3S$ [M + H]$^+$: 442.1210. found [M + H]$^+$: 442.1224.



4ak

***trans*-2-(2-chloro-4-fluorophenyl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4ak)**

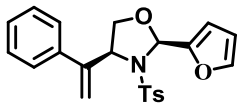
Yield: 18% (30 mg), white solid, m.p.:112.8-113.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.84 (d, J = 8.0 Hz, 2H), 7.52 (t, J = 7.8 Hz, 4H), 7.39-7.45 (m, 4H), 7.26 (d, J = 7.9 Hz, 2H), 6.09 (s, 1H), 5.67 (s, 1H), 5.55 (s, 1H), 4.94 (s, 1H), 3.75 (d, J = 3.8 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 163.78, 161.30, 146.49, 145.22, 139.26, 133.12, 133.12, 131.79, 131.79, 130.76, 129.73, 129.01, 128.99, 128.59, 128.50, 126.96, 117.35, 116.60, 115.05, 114.83, 114.02, 89.48, 70.79, 62.35, 21.57. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{21}ClFNO_3S$ [M + H]$^+$: 458.0915. found [M + H]$^+$: 458.0932.



4al

***trans*-4-(1-phenylvinyl)-2-(thiophen-2-yl)-3-tosyloxazolidine (4al)**

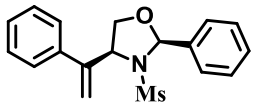
Yield: 47% (69 mg), white solid, m.p.:129.3-130.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.87 (d, J = 8.2 Hz, 2H), 7.61 – 7.56 (m, 1H), 7.48 (d, J = 8.1 Hz, 2H), 7.44 – 7.30 (m, 5H), 7.24 (d, J = 3.4 Hz, 1H), 7.04 (dd, J = 4.9, 3.7 Hz, 1H), 6.43 (s, 1H), 5.55 (s, 0H), 5.47 (s, 1H), 4.85 (t, J = 6.2 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.62 (dd, J = 8.9, 5.4 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.46, 144.91, 142.31, 138.85, 133.89, 130.61, 129.02, 128.59, 128.47, 127.85, 127.82, 127.20, 126.88, 115.58, 89.33, 71.43, 62.37, 21.50. HRMS (ESI-Q-TOF, m/z) calcd for $C_{22}H_{21}NO_3S_2$ [M + H]$^+$: 412.0963. found [M + H]$^+$: 412.0958.



4am

***trans*-2-(furan-2-yl)-4-(1-phenylvinyl)-3-tosyloxazolidine (4am)**

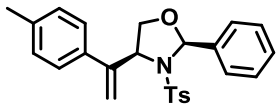
Yield: 43% (61 mg), white solid, m.p.:121.3-122.1 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.85 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 7.41 (t, J = 6.7 Hz, 3H), 7.38 – 7.32 (m, 3H), 6.47 (s, 2H), 6.20 (s, 1H), 5.58 (s, 1H), 5.46 (s, 1H), 4.81 (t, J = 6.5 Hz, 1H), 3.99 (t, J = 8.0 Hz, 1H), 3.61 (dd, J = 8.7, 5.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 150.68, 145.52, 144.19, 138.90, 133.92, 130.58, 129.71, 129.01, 128.95, 128.47, 127.11, 127.02, 126.94, 115.29, 110.98, 110.40, 86.45, 71.49, 61.99, 21.54. HRMS (ESI-Q-TOF, m/z) calcd for $C_{22}H_{21}NO_4S$ [M + H]$^+$: 396.1191. found [M + H]$^+$: 396.1179.



4an

***trans*-3-(methylsulfonyl)-2-phenyl-4-(1-phenylvinyl)oxazolidine (4an)**

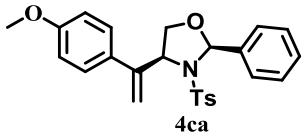
Yield: 45% (53 mg), white solid, m.p.:98.7-99.5 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.51 (d, J = 7.0 Hz, 2H), 7.47 (d, J = 6.8 Hz, 2H), 7.43 – 7.39 (m, 2H), 7.39 – 7.32 (m, 4H), 6.32 (s, 1H), 5.40 (s, 2H), 5.19 (t, J = 6.3 Hz, 1H), 4.37 (t, J = 8.1 Hz, 1H), 3.62 (dd, J = 8.7, 5.3 Hz, 1H), 3.26 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 146.13, 138.82, 128.95, 128.64, 128.44, 128.22, 127.26, 126.90, 126.77, 114.53, 91.94, 71.5, 61.73, 35.43. HRMS (ESI-Q-TOF, m/z) calcd for $C_{18}H_{19}NO_3S$ [M + H]$^+$: 330.1086. found [M + H]$^+$: 330.1077.



4ba

***trans*-2-phenyl-4-(1-(p-tolyl)vinyl)-3-tosyloxazolidine (4ba)**

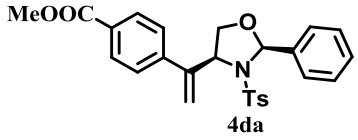
Yield: 55% (81 mg), white solid, m.p.:129.8-130.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.91 (d, J = 8.2 Hz, 2H), 7.49-7.51 (m, 4H), 7.44 – 7.33 (m, 3H), 7.26 (d, J = 8.1 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.19 (s, 1H), 5.35 (s, 2H), 4.85 (t, J = 6.3 Hz, 1H), 3.95 – 3.85 (m, 1H), 3.51 (dd, J = 8.8, 5.5 Hz, 1H), 2.45 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 145.68, 144.84, 138.59, 137.78, 135.98, 133.90, 130.62, 129.55, 129.07, 128.65, 127.34, 126.74, 114.50, 92.24, 71.26, 62.39, 21.55, 21.14. HRMS (ESI-Q-TOF, m/z) calcd for $C_{25}H_{25}NO_3S$ [M + H]$^+$: 420.1555. found [M + H]$^+$: 420.1548.



4ca

***trans*-4-(1-(4-methoxyphenyl)vinyl)-2-phenyl-3-tosyloxazolidine (4ca)**

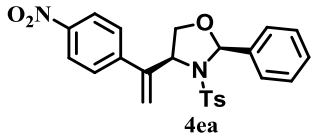
Yield: 53% (82 mg), white solid, m.p.:107.2-108.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.91 (d, J = 8.2 Hz, 2H), 7.50 (t, J = 7.3 Hz, 4H), 7.45 – 7.36 (m,3H), 7.31 (d, J = 8.7 Hz, 2H), 6.89 (d, J = 8.7 Hz,2H), 6.20 (s, 1H), 5.30 (s, 2H), 4.84 (t, J = 6.2 Hz, 1H), 3.91 (t, J = 8.1 Hz, 1H), 3.76 (s, 3H), 3.52 (dd, J = 8.8, 5.6 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 159.50, 145.24, 144.83, 138.62, 133.92, 131.15, 130.61, 129.06, 128.65, 128.21, 128.09, 127.35, 114.34, 92.24, 71.32, 62.43, 55.58, 21.55. HRMS (ESI-Q-TOF, m/z) calcd for $C_{25}H_{25}NO_4S$ $[M + H]^+$:436.1504. found $[M + H]^+$: 436.1531.



4da

***trans*-methyl 4-(1-(2-phenyl-3-tosyloxazolidin-4-yl)vinyl)benzoate (da)**

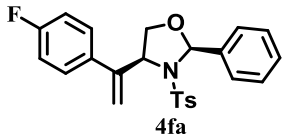
Yield: 40% (66 mg), white solid, m.p.:98.4-99.2 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.94 – 7.85 (m, 4H), 7.48-7.53 (m, 6H), 7.39 (d, J = 7.4 Hz, 3H), 6.20 (s, 1H), 5.52 (d, J = 4.8 Hz, 2H), 4.91 (t, J = 5.0 Hz,1H), 3.94 (t, J = 8.0 Hz, 1H), 3.86 (s, 3H), 3.56 (dd, J = 8.7, 5.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 166.36, 145.28, 144.91, 143.54, 138.49, 133.83, 130.64, 129.75, 129.39, 129.09, 128.67, 127.39, 127.30, 117.49, 92.21, 71.12, 62.18, 52.64, 21.55. HRMS (ESI-Q-TOF, m/z) calcd for $C_{26}H_{25}NO_5S$ $[M + H]^+$: 464.1453. found $[M + H]^+$: 464.1428.



4ea

***trans*-4-(1-(4-nitrophenyl)vinyl)-2-phenyl-3-tosyloxazolidine (4ea)**

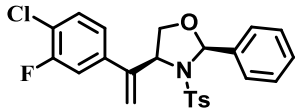
Yield: 38% (61 mg), white solid, m.p.:84.6-85.3 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 8.15 (d, J = 8.0 Hz, 2H), 7.92 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 8.1 Hz, 2H), 7.57 – 7.44 (m, 4H), 7.38 (d, J = 6.1 Hz, 3H), 6.20 (s, 1H), 5.58 (s, 2H), 4.93 (s, 1H), 3.95 (t, J = 7.6 Hz, 1H), 3.68 – 3.52 (m, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 147.32, 145.60, 144.97, 144.76, 138.43, 133.76, 130.65, 129.05, 128.72, 128.66, 128.59, 127.25, 123.93, 119.06, 92.19, 70.93, 62.19, 21.55. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}N_2O_5S$ $[M + H]^+$: 451.1249. found $[M + H]^+$: 451.1258.



4fa

***trans*-4-(1-(4-fluorophenyl)vinyl)-2-phenyl-3-tosyloxazolidine (4fa)**

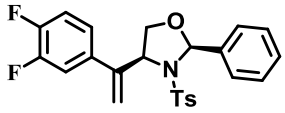
Yield: 46% (69 mg), white solid, m.p.:130.2-131.1 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.91 (d, J = 7.9 Hz, 2H), 7.49 (d, J = 7.9 Hz, 4H), 7.38-7.41 (m, 5H), 7.16 (t, J = 8.7 Hz, 2H), 6.18 (s, 1H), 5.38 (d, J = 16.1 Hz, 2H), 4.84 (t, J = 6.0 Hz, 1H), 3.90 (t, J = 8.1 Hz, 1H), 3.55 (dd, J = 8.5, 5.7 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 163.52, 161.09, 145.00, 144.87, 138.55, 135.32, 133.83, 130.62, 129.25, 129.17, 129.05, 128.70, 128.64, 127.31, 115.81, 115.59, 92.22, 71.04, 62.52, 21.55. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{22}FNO_3S$ $[M + H]^+$: 424.1304. found $[M + H]^+$: 424.1332.



4ga

***trans*-4-(1-(4-chloro-3-fluorophenyl)vinyl)-2-phenyl-3-tosyloxazolidine (4ga)**

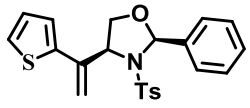
Yield: 33% (53 mg), white solid, m.p.:105.2-106.6 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.90 (d, *J* = 8.2 Hz, 2H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.43 (d, *J* = 5.7 Hz, 2H), 7.41 – 7.30 (m, 5H), 6.15 (s, 1H), 5.42 (d, *J* = 16.9 Hz, 2H), 4.85 (t, *J* = 6.2 Hz, 1H), 3.99 – 3.81 (m, 1H), 3.62 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 158.52, 156.06, 144.90, 144.20, 138.46, 136.83, 133.87, 130.59, 129.54, 129.02, 128.70, 128.57, 128.25, 128.18, 127.26, 120.03, 119.85, 117.58, 117.24, 117.04, 91.76 – 84.16, 70.76, 62.47, 21.55. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{21}ClFNO_3S$ $[M + H]^+$: 458.0915. found $[M + H]^+$: 458.0927.



4ha

***trans*-4-(1-(3,4-difluorophenyl)vinyl)-2-phenyl-3-tosyloxazolidine (4ha)**

Yield: 28% (44 mg), white solid, m.p.:111.9-112.8 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.91 (d, *J* = 8.2 Hz, 2H), 7.52 – 7.42 (m, 5H), 7.42 – 7.31 (m, 4H), 7.24 – 7.00 (m, 1H), 6.16 (s, 1H), 5.44 (d, *J* = 5.8 Hz, 2H), 4.86 (t, *J* = 6.2 Hz, 1H), 3.92 (dd, *J* = 8.9, 7.3 Hz, 1H), 3.60 (dd, *J* = 9.0, 5.4 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 150.92, 148.48, 144.89, 144.22, 138.50, 136.46, 133.85, 130.60, 129.04, 128.72, 128.61, 127.27, 124.25, 117.91, 117.74, 117.15, 116.57, 116.39, 92.17, 70.90, 62.32, 21.54. HRMS (ESI-Q-TOF, m/z) calcd for $C_{24}H_{21}F_2NO_3S$ $[M + H]^+$: 442.1210. found $[M + H]^+$: 442.1237.



4ia

***trans*-2-phenyl-4-(1-(thiophen-2-yl)vinyl)-3-tosyloxazolidine (4ia)**

Yield: 43% (63 mg), white solid, m.p.:121.3-122.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.85 (d, *J* = 7.8 Hz, 2H), 7.46-7.53 (m, 5H), 7.45 – 7.31 (m, 3H), 7.16 (s, 1H), 7.02 (s, 1H), 6.22 (s, 1H), 5.40 (s, 1H), 5.24 (s, 1H), 4.78 (t, *J* = 6.1 Hz, 1H), 4.15 (t, *J* = 7.8 Hz, 1H), 3.67 – 3.51 (m, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ_C 144.92, 141.71, 139.73, 138.41, 133.81, 130.64, 129.51, 129.34, 129.16, 128.77, 128.64, 128.41, 127.29, 126.16, 125.21, 124.13, 112.91, 92.14, 71.86, 62.03, 21.56. HRMS (ESI-Q-TOF, m/z) calcd for $C_{22}H_{21}NO_3S_2$ $[M + H]^+$: 412.0963. found $[M + H]^+$: 412.0988.

3. X-ray Crystallography of 4aa

A single-crystal of 4aa was obtained from EtOH/DCM solvent at room temperature. Diffraction data were collected on a Bruker SMART Apex-IICCD-based X-ray diffractometer with Mo-Kα. radiation (λ=0.71073). The empirical absorption correction was applied by using the SADABS program. The structure was solved using direct method, and refined by full-matrix least-squares on F^2 (G.M. Sheldrick, SHELXTL 97, program of crystal structure refinement, University of Gottingen, Germany, 1997). H-atoms were refined isotropically, while all other atoms were refined anisotropically. The crystallographic data were summarized in **Table S1** and the diagram was shown in **Figure S1**.

Table S1. Crystal data and structure refinement for 4aa.

Identification code	1

Empirical formula	C24H23NO3S
Formula weight	405.49
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 9.7939(15) Å a= 112.876(5)°.
	b = 10.1887(17) Å b= 93.064(5)°.
	c = 12.694(2) Å g = 111.984(4)°.
Volume	1052.5(3) Å3
Z	2
Density (calculated)	1.280 Mg/m3
Absorption coefficient	0.179 mm-1
F(000)	428
Crystal size	0.220 x 0.200 x 0.180 mm3
Theta range for data collection	1.790 to 24.779°.
Index ranges	-11<=h<=11, -11<=k<=11, -14<=l<=8
Reflections collected	6487
Independent reflections	3545 [R(int) = 0.0291]
Completeness to theta = 24.779°	98.0 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F2
Data / restraints / parameters	3545 / 0 / 269
Goodness-of-fit on F2	1.009
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1299

R indices (all data)	R1 = 0.0665, wR2 = 0.1468
Extinction coefficient	n/a
Largest diff. peak and hole	0.219 and -0.343 e.Å-3

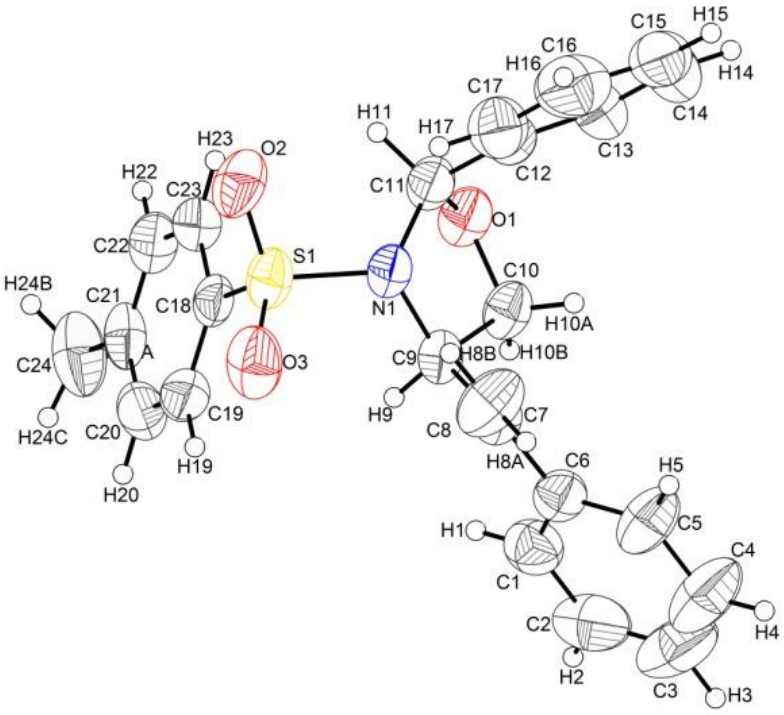
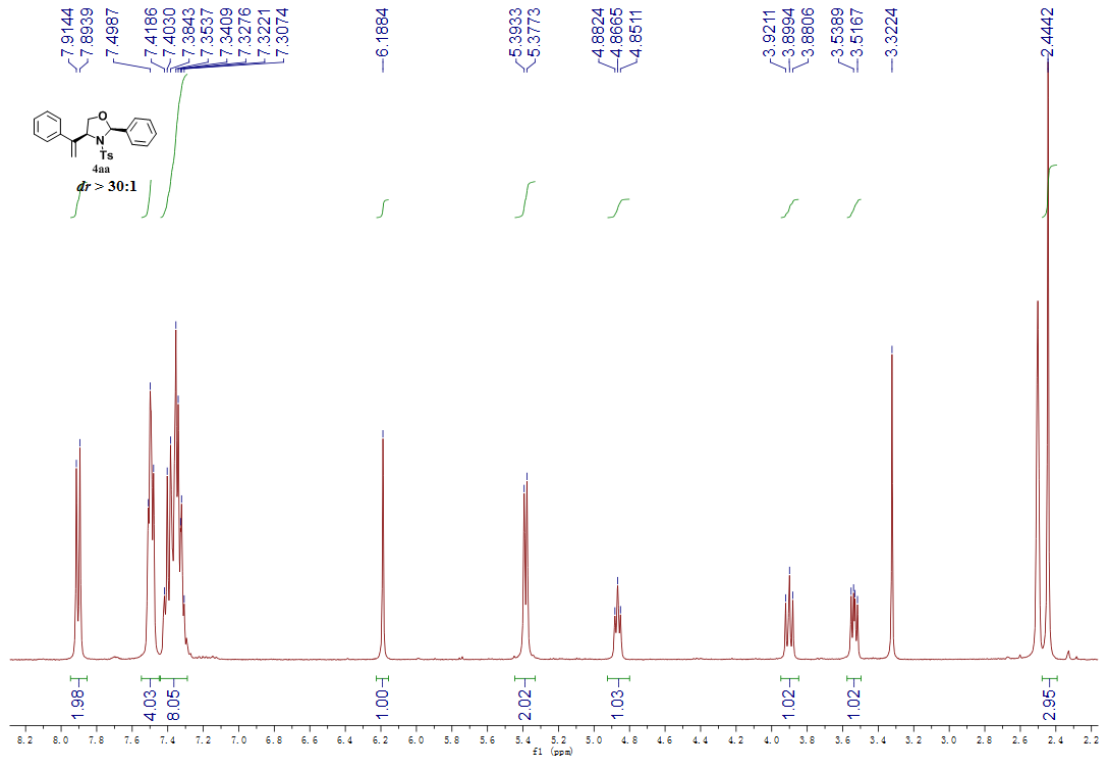
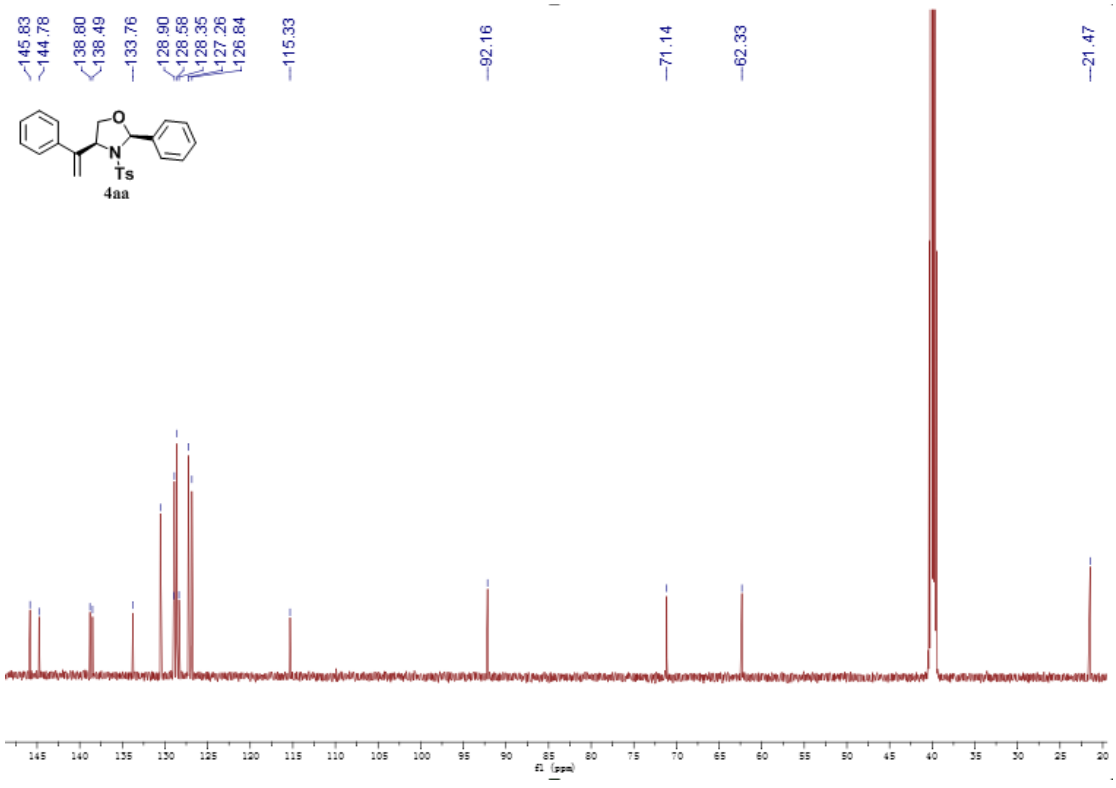
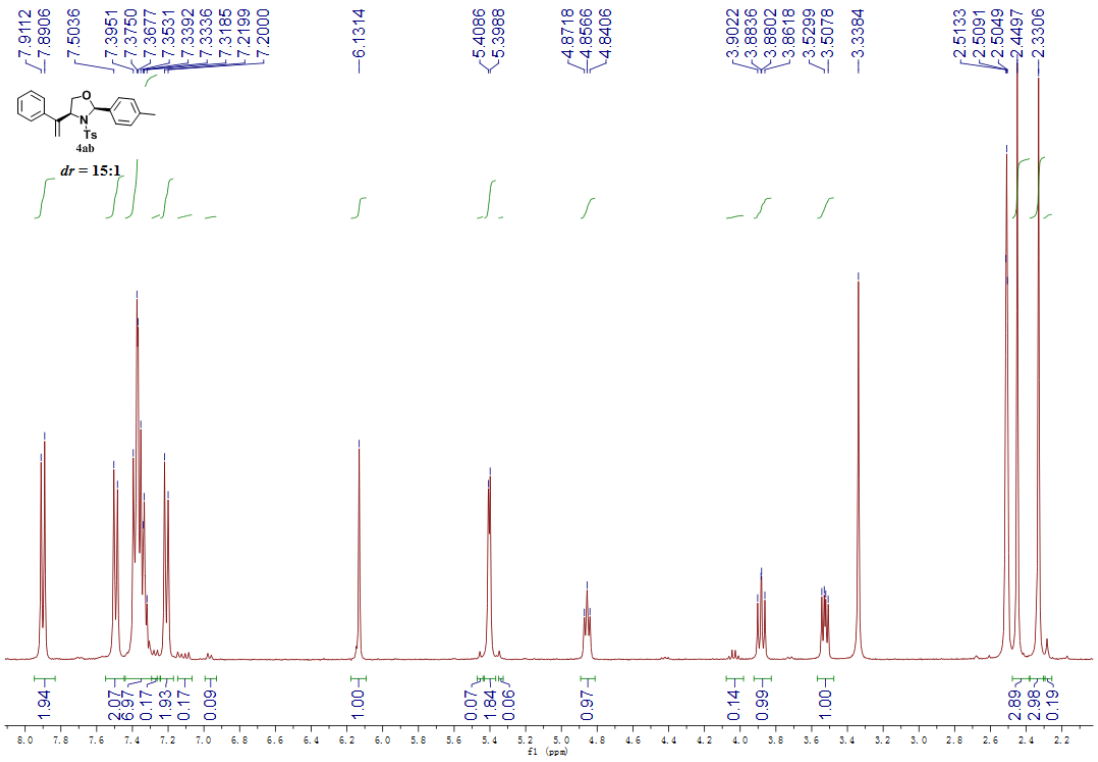


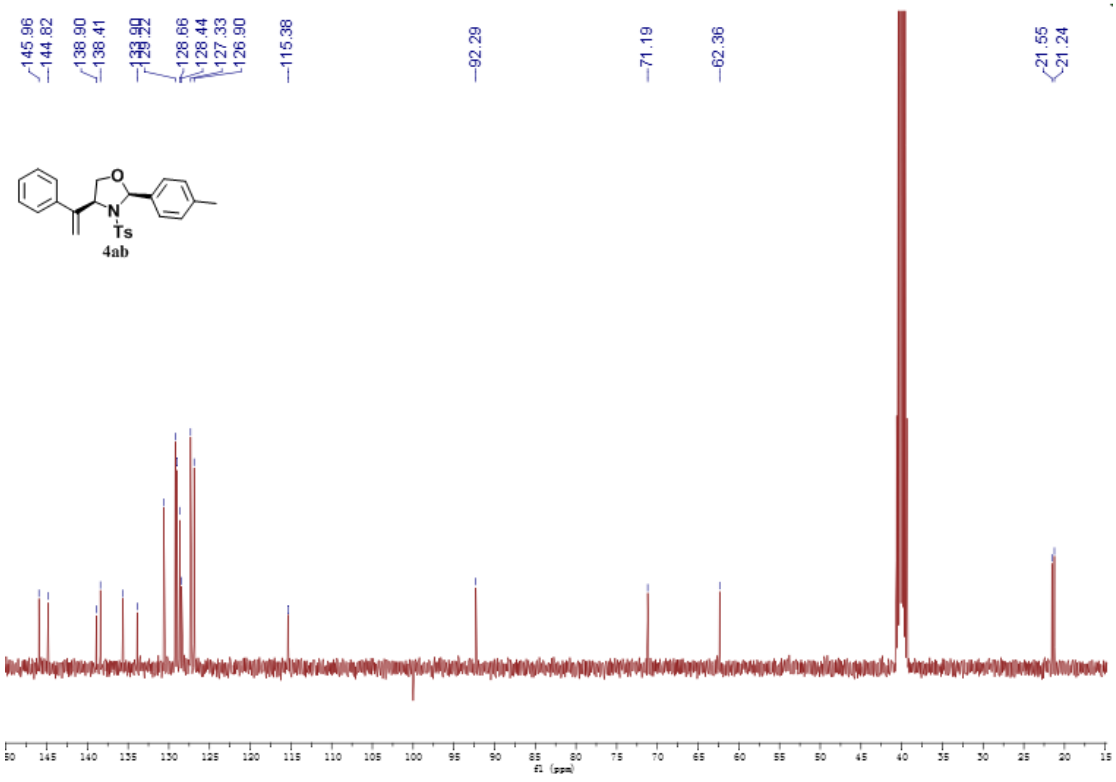
Figure S1. Molecular structure of 4aa.

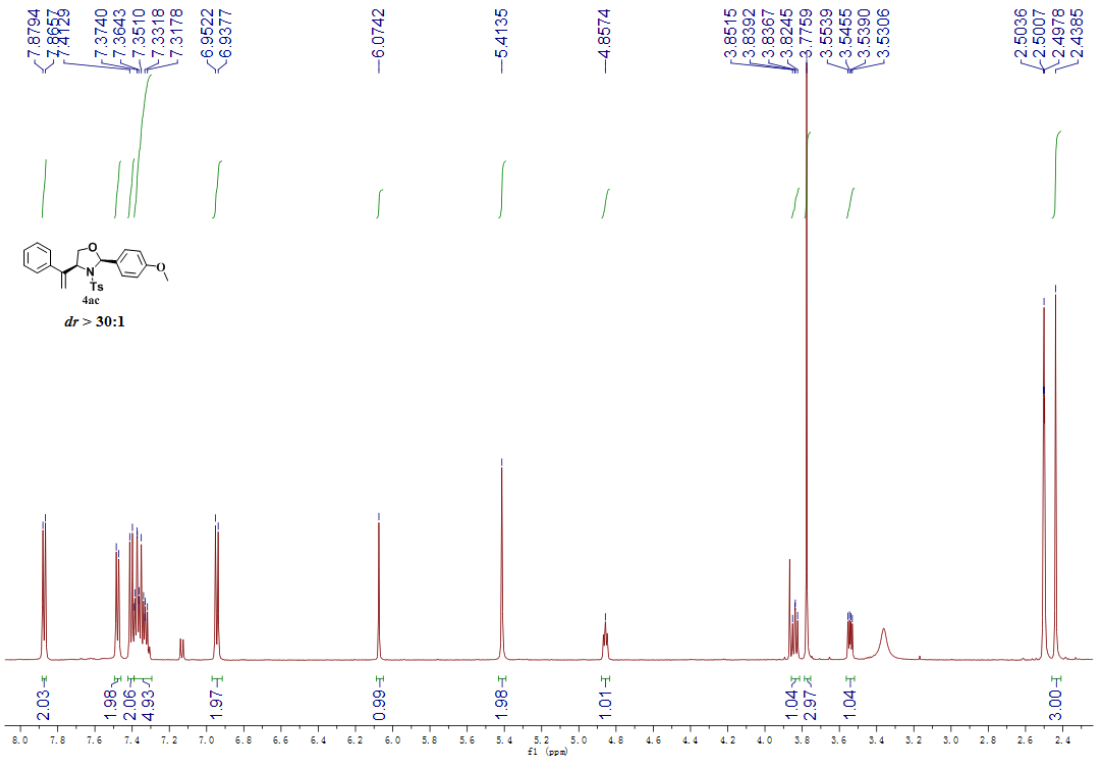
4. NMR Spectra of New Compounds

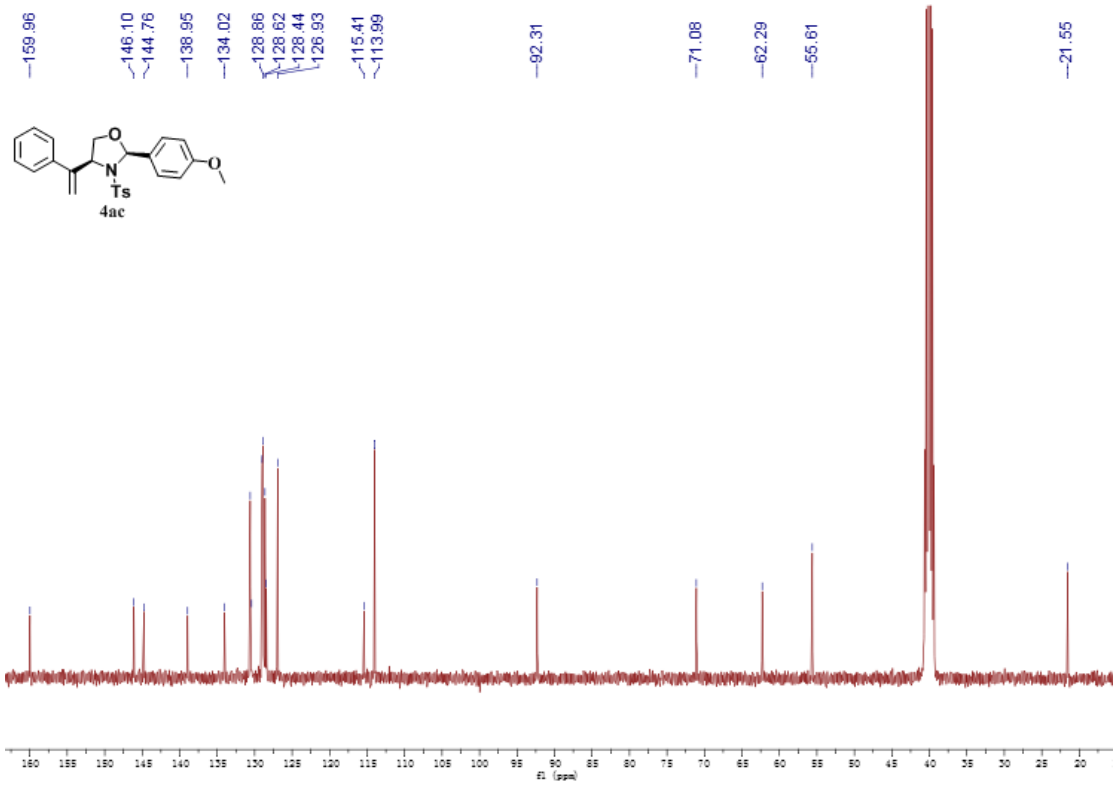


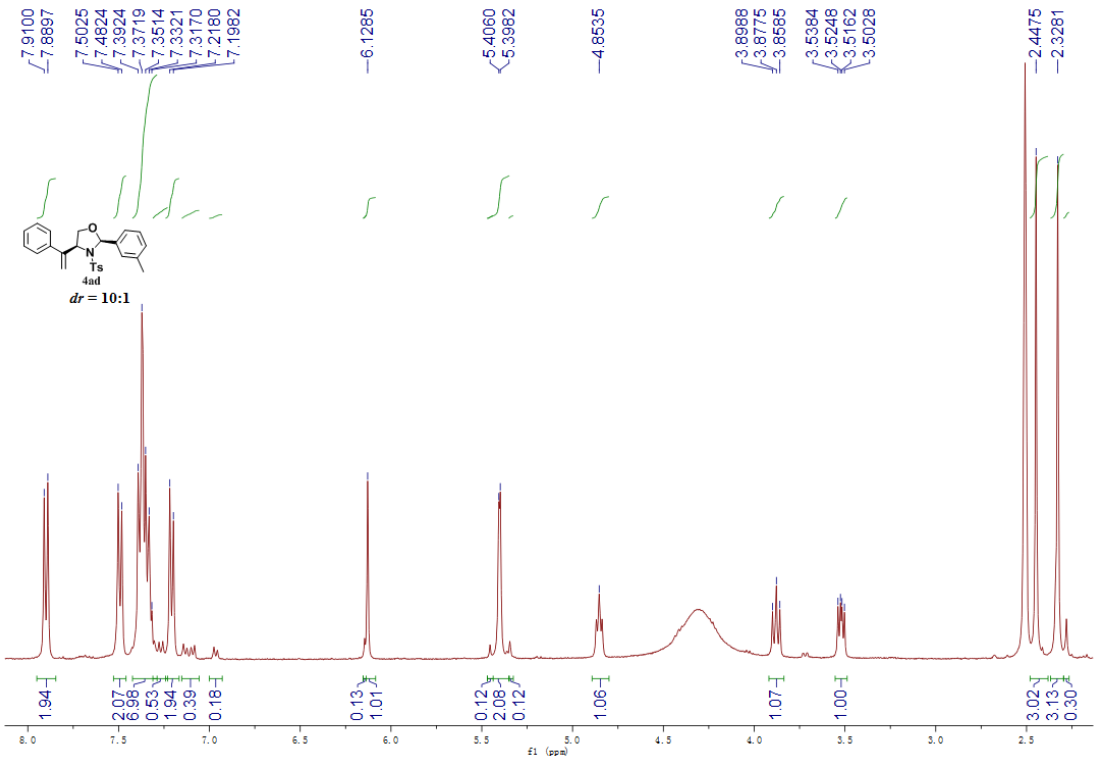


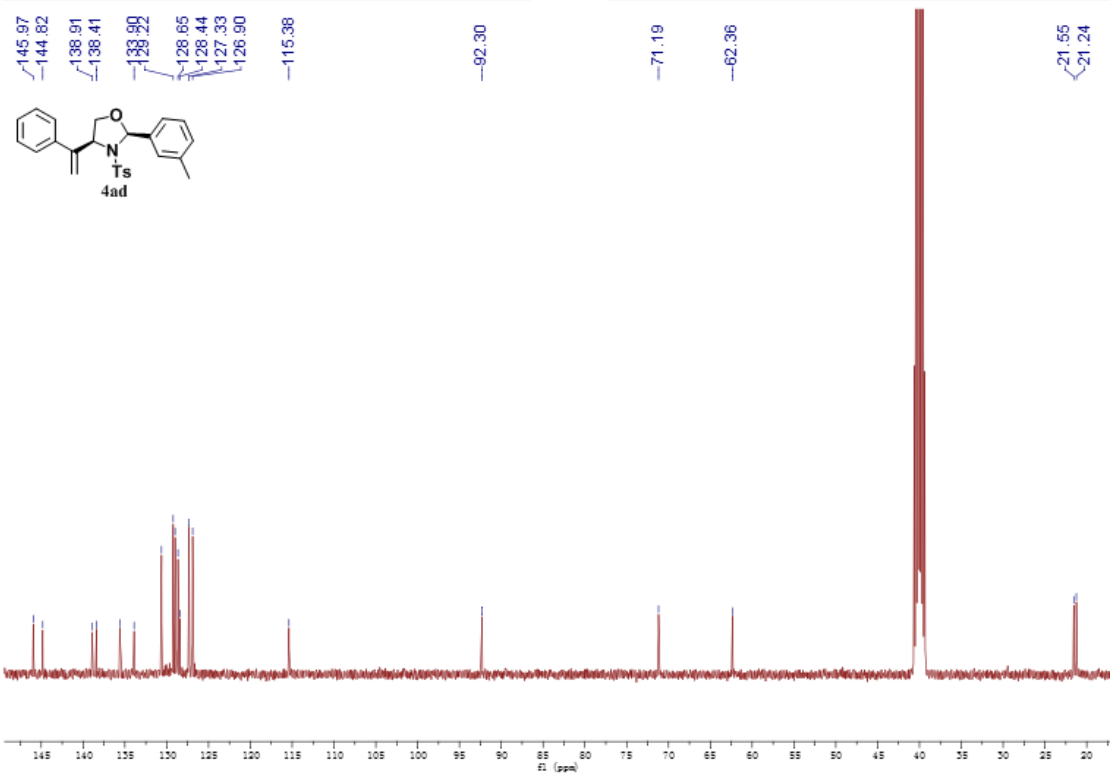

7.9112
7.8906
7.5036
7.3951
7.3750
7.3677
7.3531
7.3392
7.3336
7.3185
7.2199
7.2000
6.1314
5.4086
5.3988
4.8718
4.8566
4.8406
3.9022
3.8836
3.8802
3.8618
3.5299
3.5078
3.3384
2.5133
2.5091
2.5049
2.4497
2.3306
Ts
4ab
dr = 15:1
1.94
2.07
6.97
0.17
1.93
0.17
0.09
1.00
0.07
1.84
0.06
0.97
0.14
0.99
1.00
2.89
2.98
0.19
f1 (ppm)

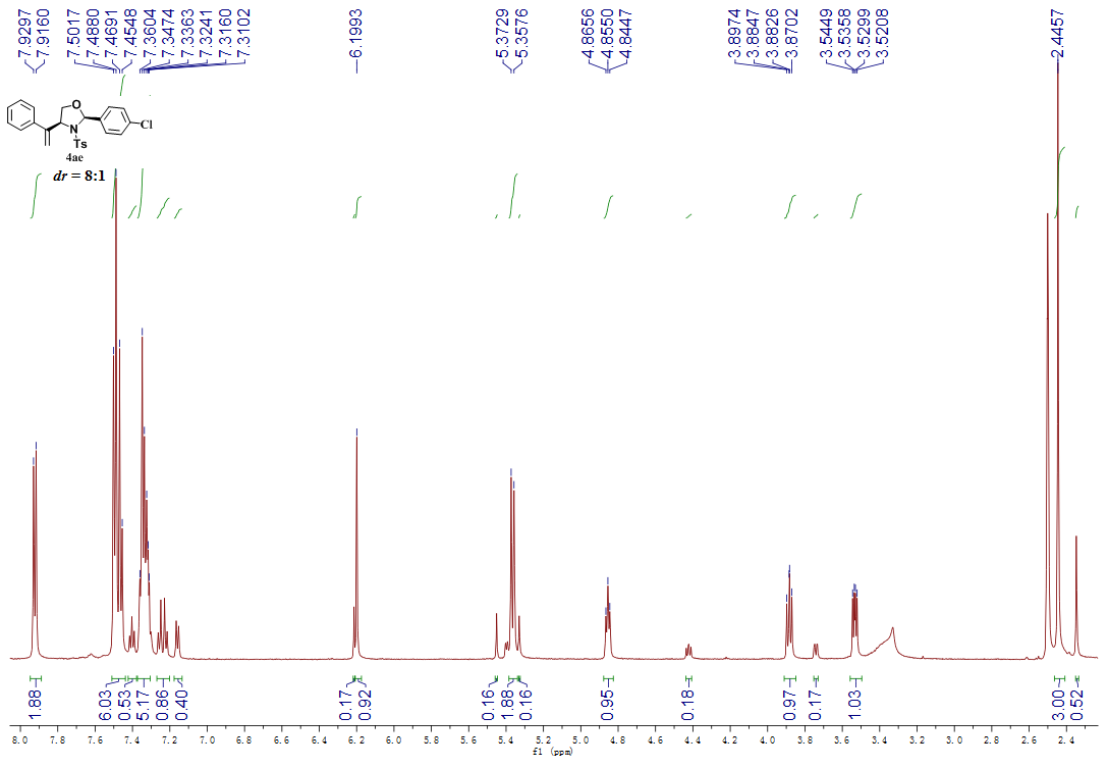

145.96
144.82
138.90
138.41
133.90
129.22
128.66
128.44
127.33
126.90
115.38
92.29
71.19
62.36
21.55
21.24
Ts
4ab
f1 (ppm)

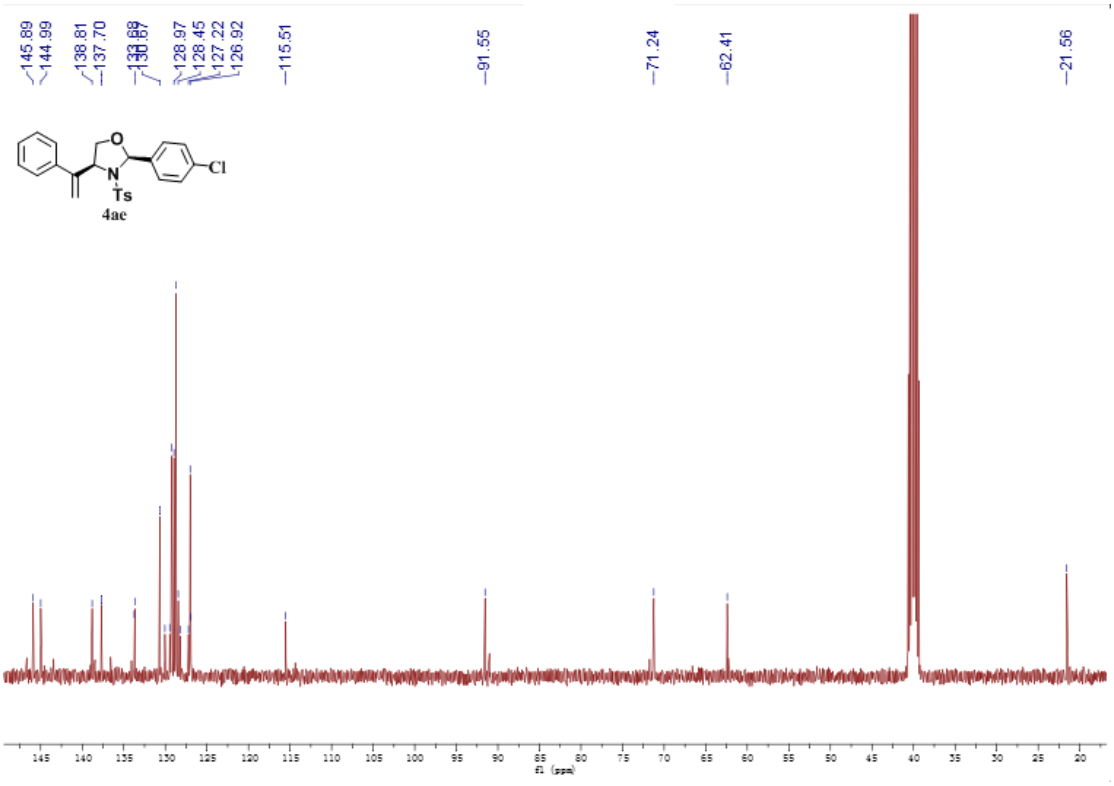

7.8794
7.8657
7.4129
7.3740
7.3643
7.3510
7.3318
7.3178
6.9522
6.9377
6.0742
5.4135
4.8574
3.8515
3.8392
3.8367
3.8245
3.7759
3.5539
3.5455
3.5390
3.5306
2.5036
2.5007
2.4978
2.4385
Ts
4ac
dr > 30:1
2.03
1.98
2.06
4.93
1.97
0.99
1.98
1.01
1.04
2.97
1.04
3.00
f1 (ppm)

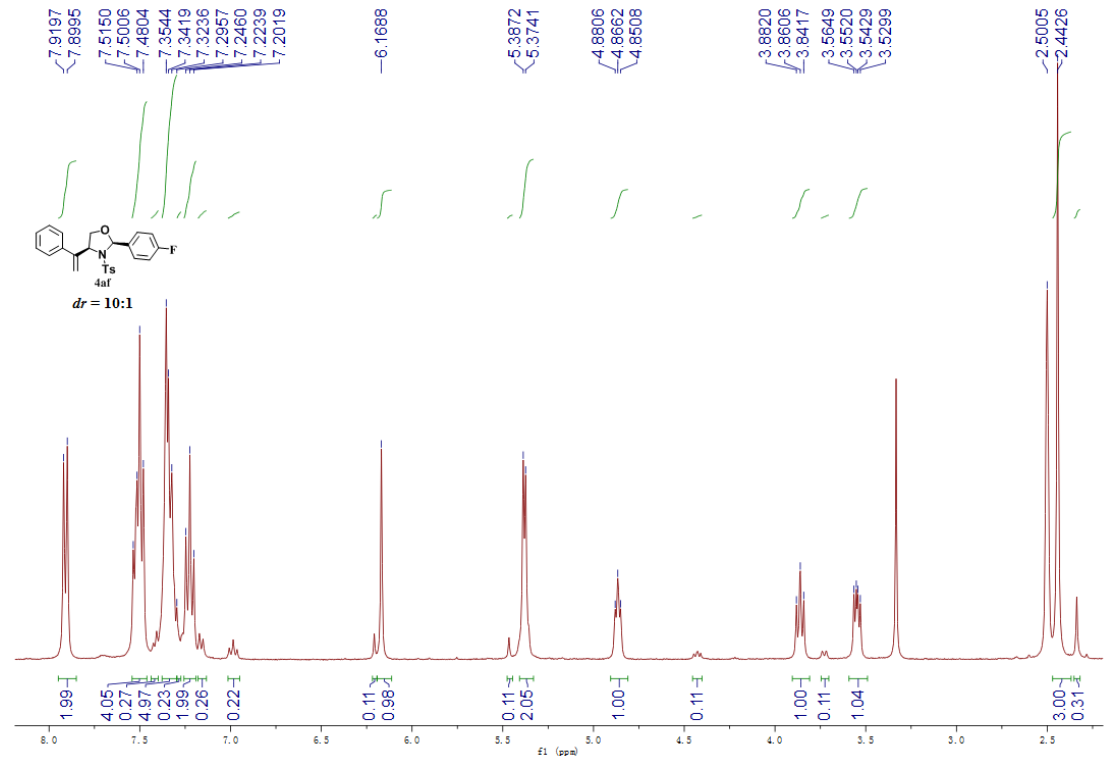

159.96
146.10
144.76
138.95
134.02
128.86
128.62
128.44
126.93
115.41
113.99
92.31
71.08
62.29
55.61
21.55
Ts
4ac
f1 (ppm)

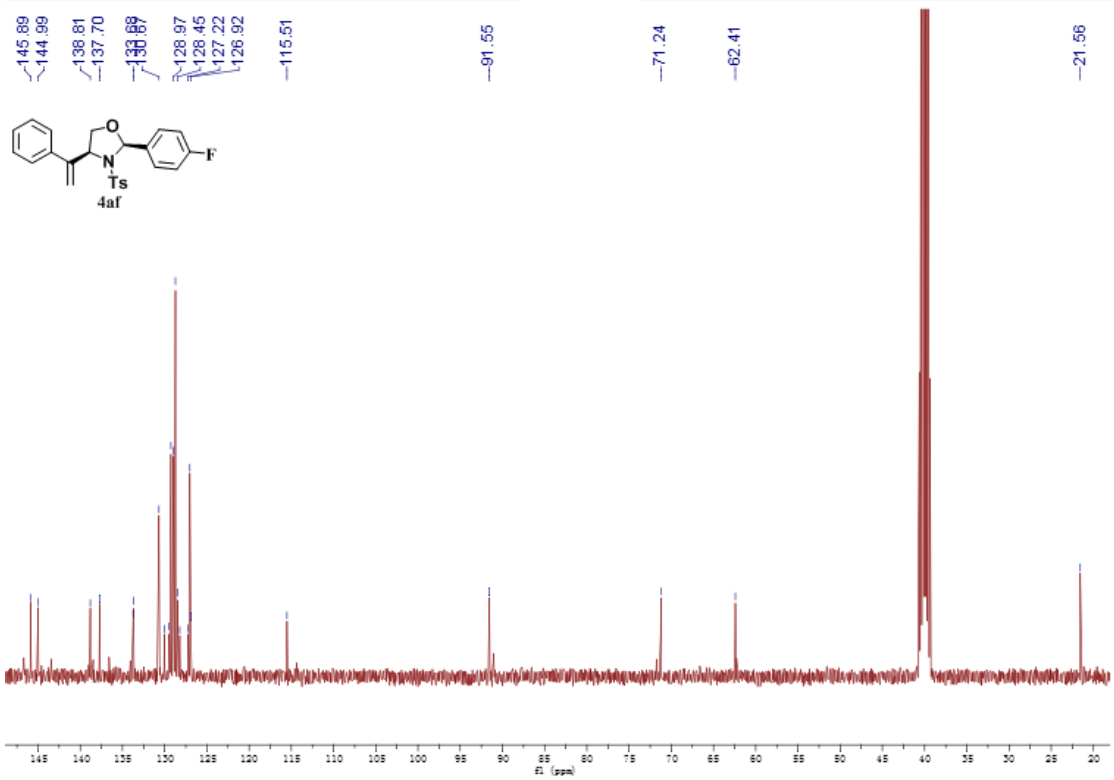

7.9100
7.8897
7.5025
7.4824
7.3924
7.3719
7.3514
7.3321
7.3170
7.2180
7.1982
6.1285
5.4060
5.3982
4.8535
3.8988
3.8775
3.8585
3.5384
3.5248
3.5162
3.5028
2.4475
2.3281
Ts
4ad
dr = 10:1
1.94
2.07
6.98
0.53
1.94
0.39
0.18
0.13
1.01
0.12
2.08
0.12
1.06
1.07
1.00
3.02
3.13
0.30
f1 (ppm)

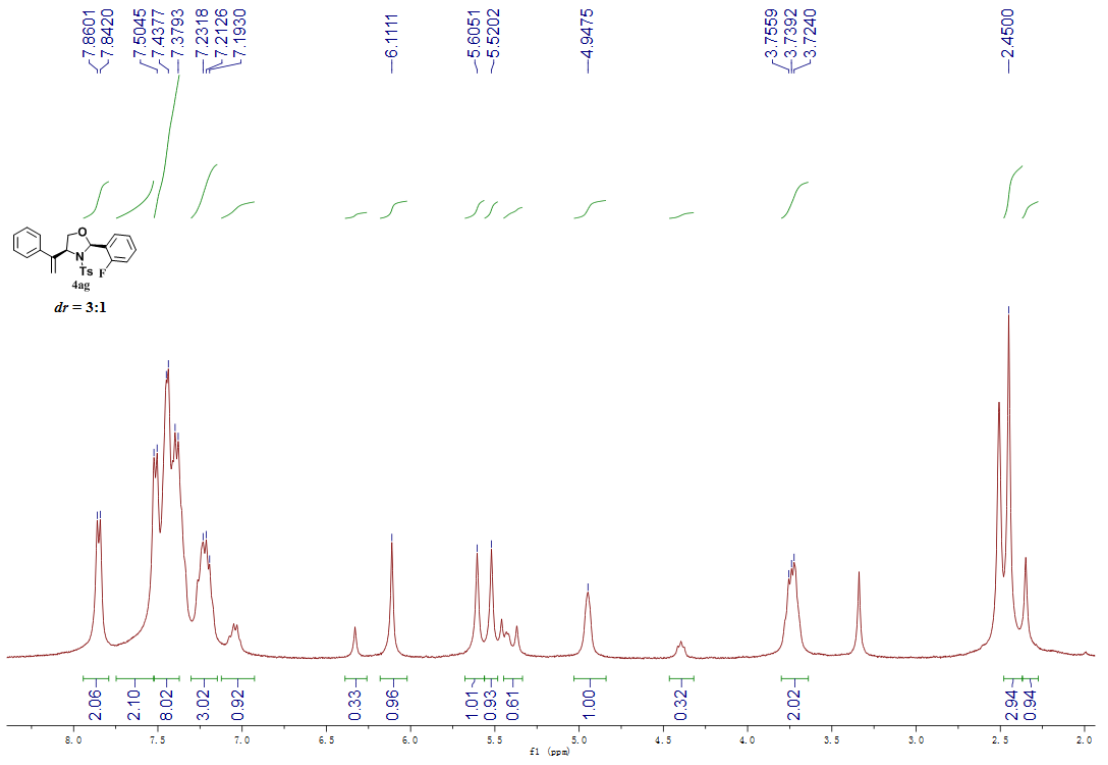

145.97
144.82
138.91
138.41
133.90
129.22
128.65
128.44
127.33
126.90
115.38
92.30
71.19
62.36
21.55
21.24
Ts
4ad
f1 (ppm)


7.9297
7.9160
7.5017
7.4880
7.4691
7.4548
7.3604
7.3474
7.3363
7.3241
7.3160
7.3102
6.1993
5.3729
5.3576
4.8656
4.8550
4.8447
3.8974
3.8847
3.8826
3.8702
3.5449
3.5358
3.5299
3.5208
2.4457
Cl
Ts
4ae
dr = 8:1
1.88
6.03
0.53
5.17
0.86
0.40
0.17
0.92
0.16
1.88
0.16
0.95
0.18
0.97
0.17
1.03
3.00
0.52
f1 (ppm)

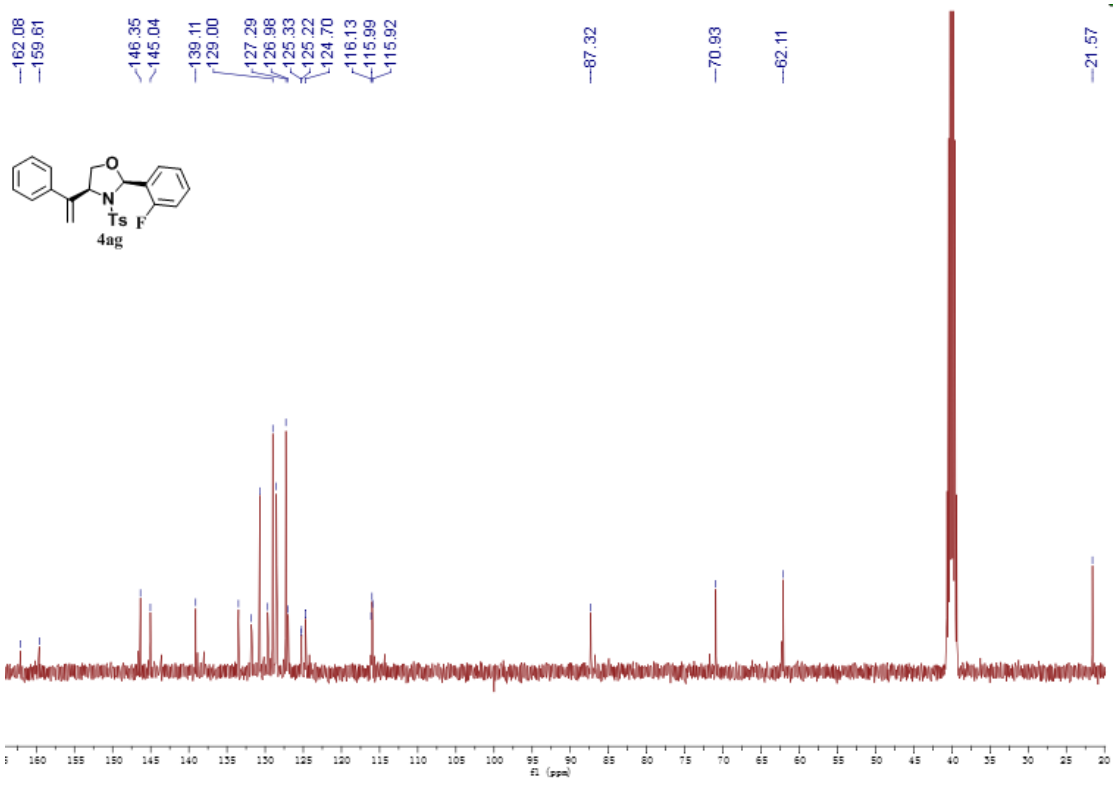

145.89
144.99
138.81
137.70
128.97
128.45
127.22
126.92
115.51
91.55
71.24
62.41
21.56
Cl
Ts
4ae
f1 (ppm)

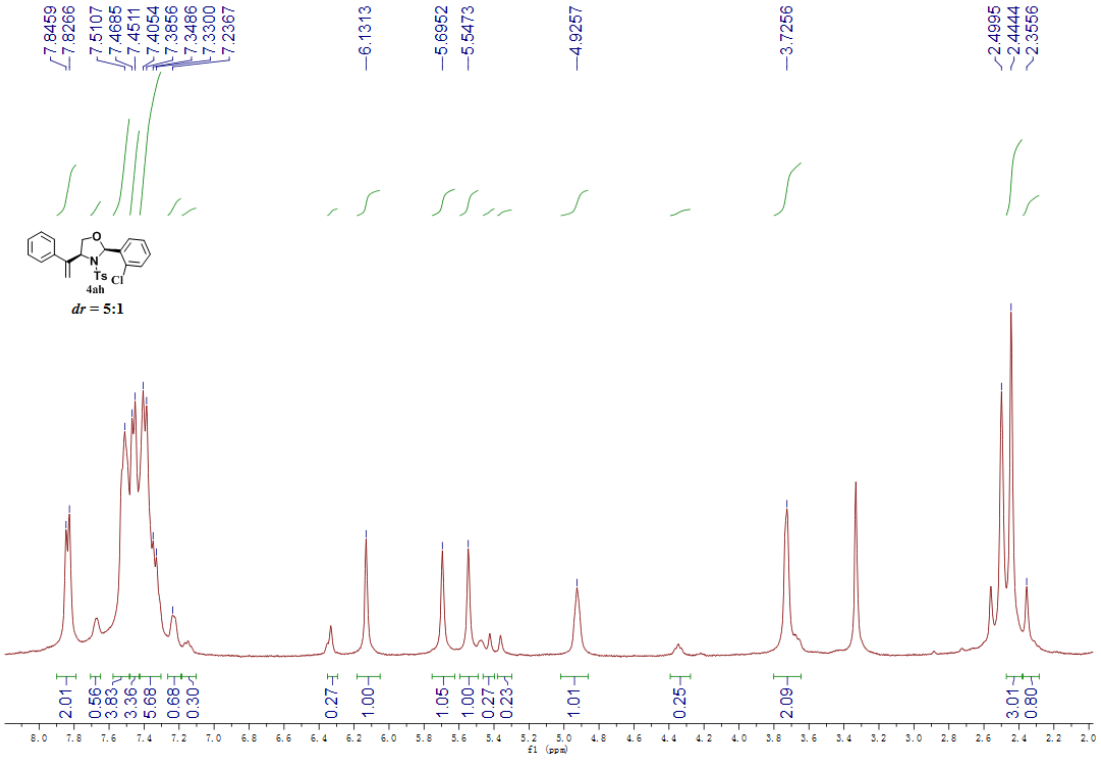

7.9197
7.8995
7.5150
7.5006
7.4804
7.3544
7.3419
7.3236
7.2957
7.2460
7.2239
7.2019
6.1688
5.3872
5.3741
4.8806
4.8662
4.8508
3.8820
3.8606
3.8417
3.5649
3.5520
3.5429
3.5299
2.5005
2.4426
Ts
4af
dr = 10:1
1.99
4.05
0.27
4.97
0.23
1.99
0.26
0.22
0.11
0.98
0.11
2.05
1.00
0.11
1.00
0.11
1.04
3.00
0.31
f1 (ppm)

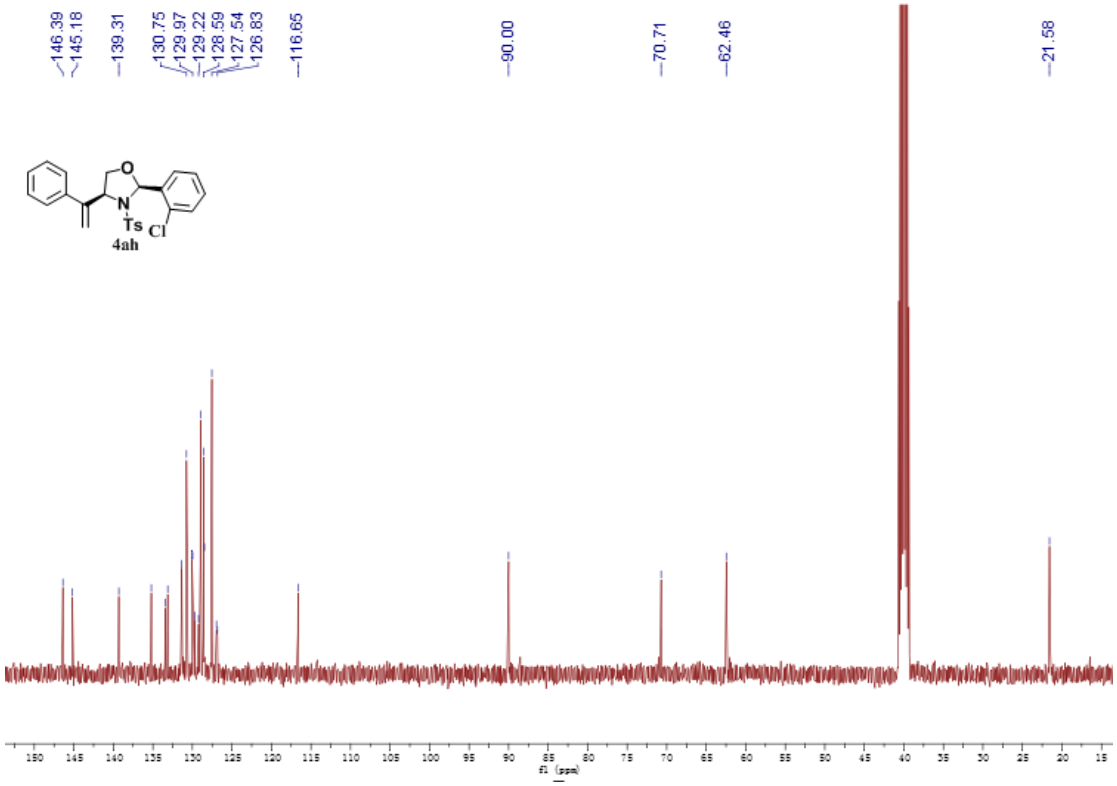

145.89
144.99
138.81
137.70
128.97
128.45
127.22
126.92
115.51
91.55
71.24
62.41
21.56
Ts
4af
f1 (ppm)

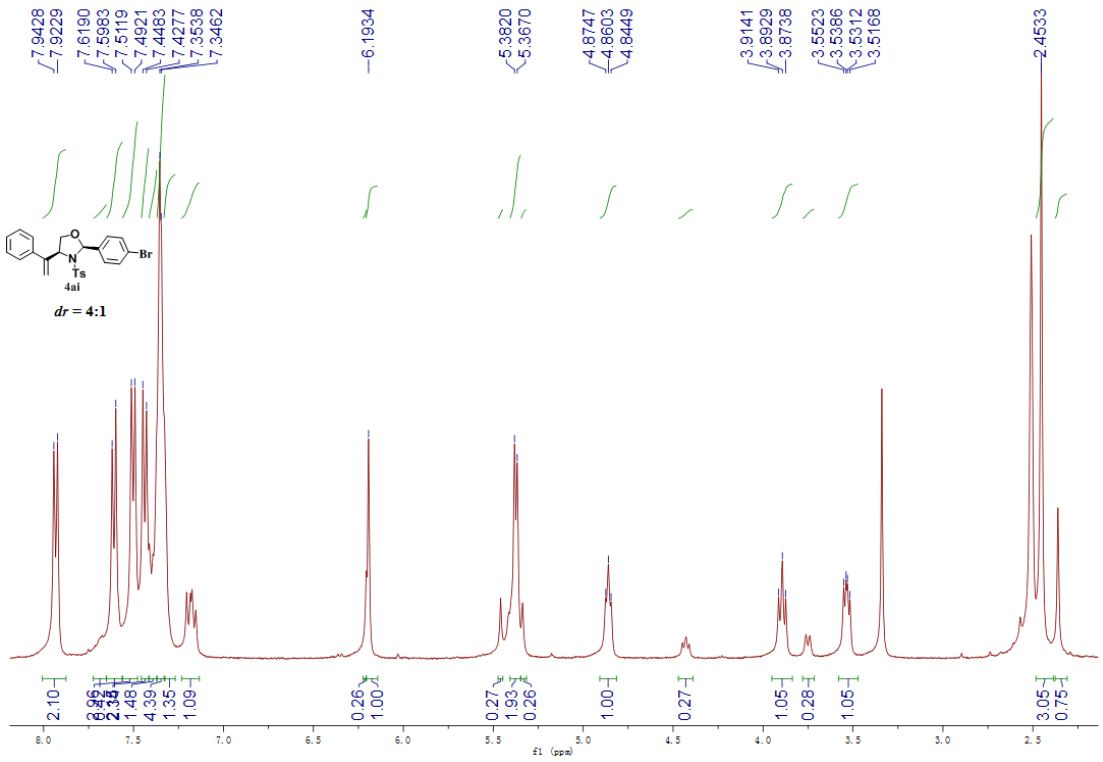

7.8601
7.8420
7.5045
7.4377
7.3793
7.2318
7.2126
7.1930
6.1111
5.6051
5.5202
4.9475
3.7559
3.7392
3.7240
2.4500
Ts F
4ag
2.06
2.10
8.02
3.02
0.92
0.33
0.96
1.01
0.93
0.61
1.00
0.32
2.02
2.94
0.94
f1 (ppm)

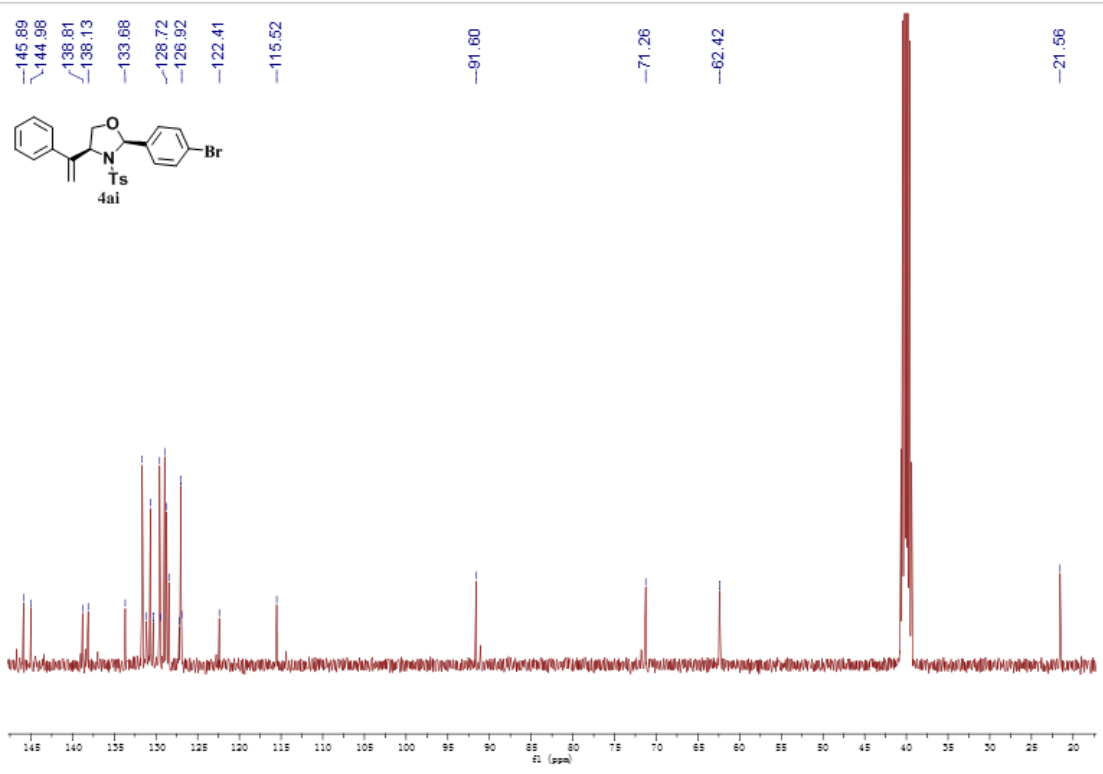
dr = 3:1

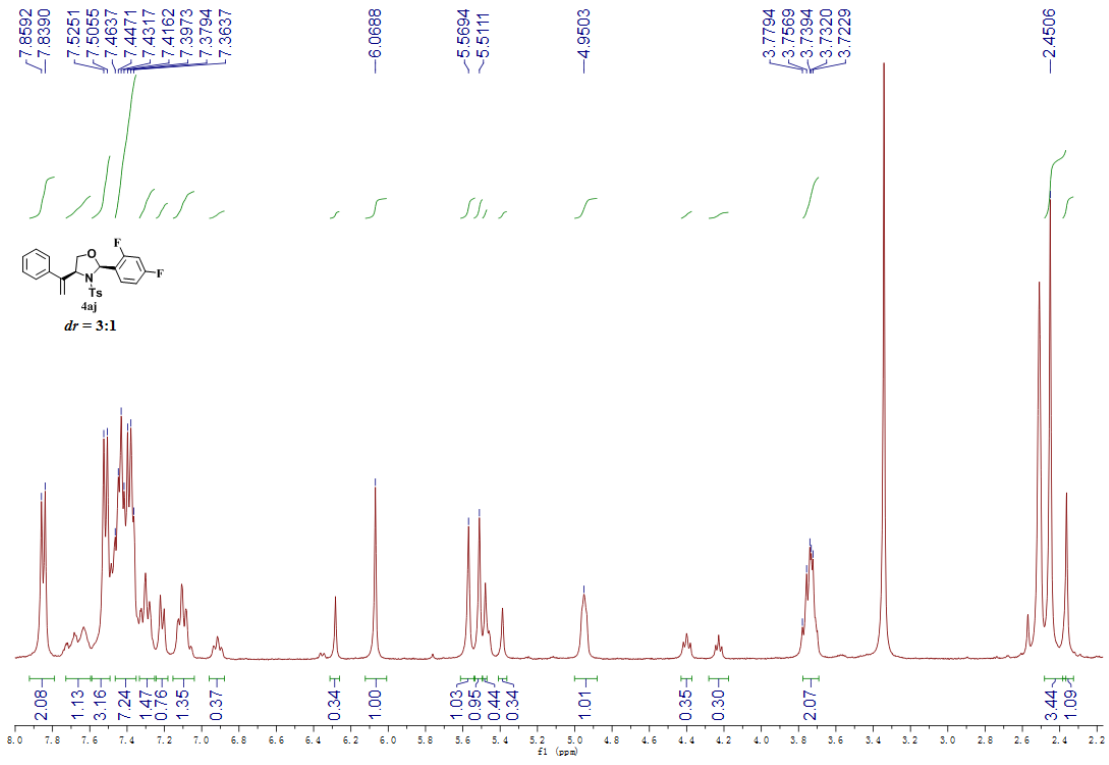

162.08
159.61
146.35
145.04
139.11
129.00
127.29
126.98
125.33
125.22
124.70
116.13
115.99
115.92
87.32
70.93
62.11
21.57
Ts F
4ag
f1 (ppm)

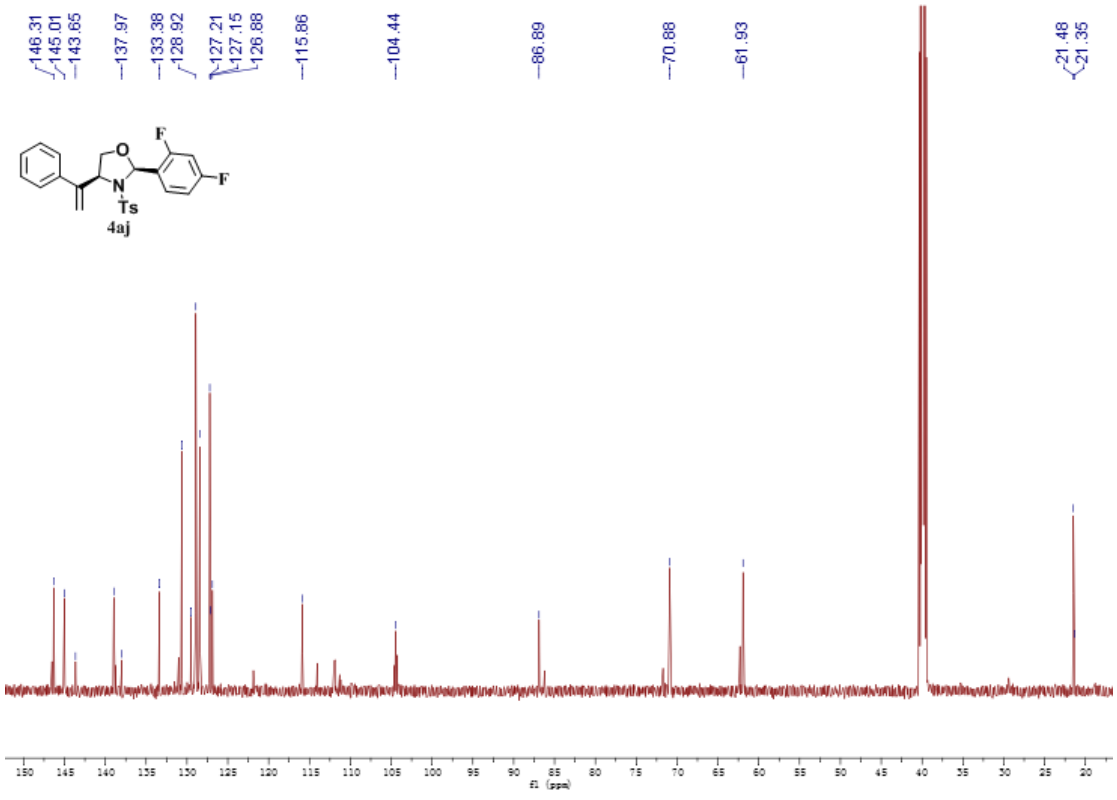

7.8459
7.8266
7.5107
7.4685
7.4511
7.4054
7.3856
7.3486
7.3300
7.2367
6.1313
5.6952
5.5473
4.9257
3.7256
2.4935
2.4444
2.3556
4ah
dr = 5:1
2.01
0.56
3.83
3.36
5.68
0.68
0.30
0.27
1.00
1.05
1.00
0.27
0.23
1.01
0.25
2.09
3.01
0.80
f1 (ppm)

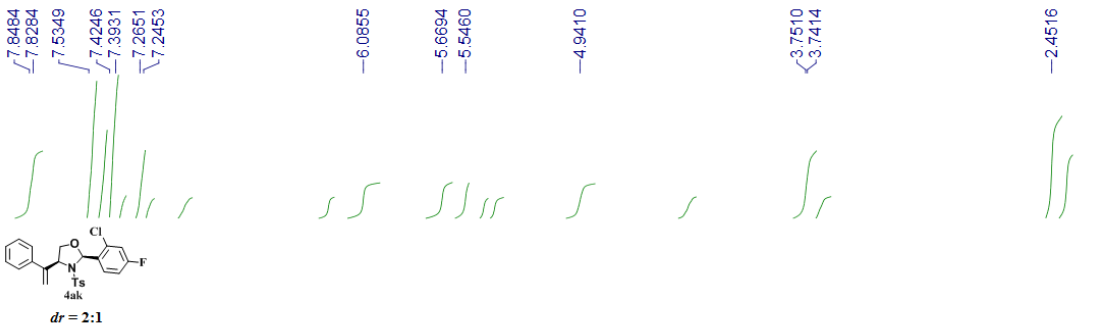

146.39
145.18
139.31
130.75
129.97
129.22
128.59
127.54
126.83
116.65
90.00
70.71
62.46
21.58
4ah
f1 (ppm)


7.9428
7.9229
7.6190
7.5983
7.5119
7.4921
7.4483
7.4277
7.3538
7.3462
6.1934
5.3820
5.3670
4.8747
4.8603
4.8449
3.9141
3.8929
3.8738
3.5523
3.5386
3.5312
3.5168
2.4533
Br
Ts
4ai
dr = 4:1
f1 (ppm)

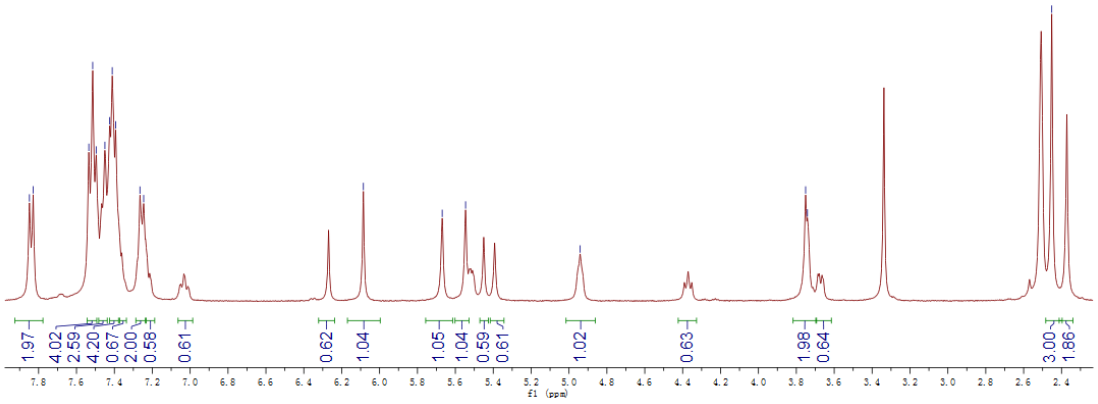

145.89
144.98
138.81
138.13
133.68
128.72
126.92
122.41
115.52
91.60
71.26
62.42
21.56
Br
Ts
4ai
f1 (ppm)

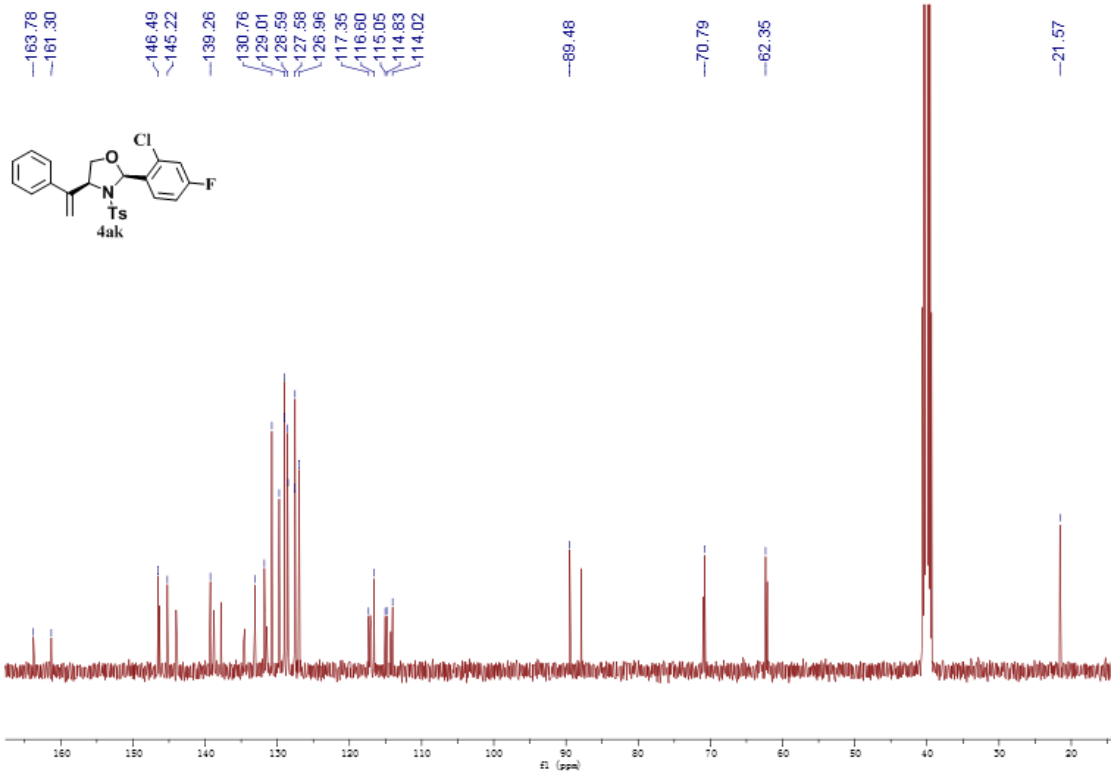

7.8592
7.8390
7.5251
7.5055
7.4637
7.4471
7.4317
7.4162
7.3973
7.3794
7.3637
6.0688
5.5694
5.5111
4.9503
3.7794
3.7569
3.7394
3.7320
3.7229
2.4506
F
F
O
N
Ts
4aj
dr = 3:1
2.08
1.13
3.16
7.24
1.47
0.76
1.35
0.37
0.34
1.00
1.03
0.95
0.44
0.34
1.01
0.35
0.30
2.07
3.44
1.09
f1 (ppm)

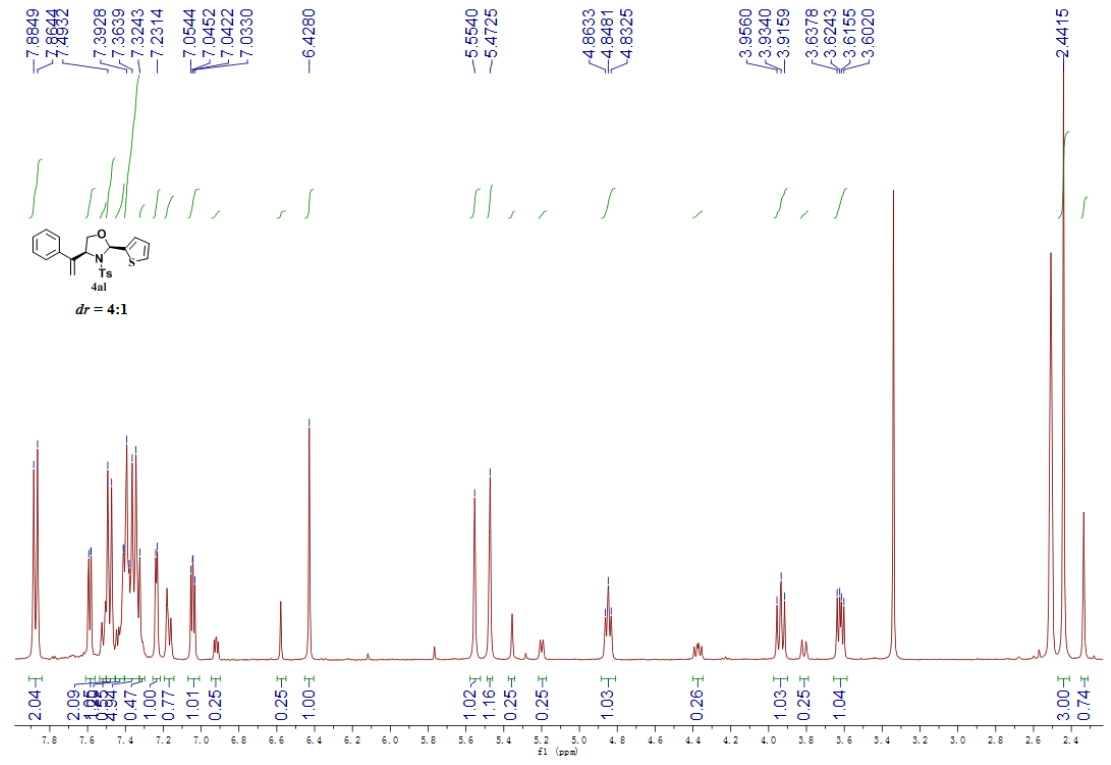

146.31
145.01
143.65
137.97
133.38
128.92
127.21
127.15
126.88
115.86
104.44
86.89
70.88
61.93
21.48
21.35
F
F
O
N
Ts
4aj
f1 (ppm)

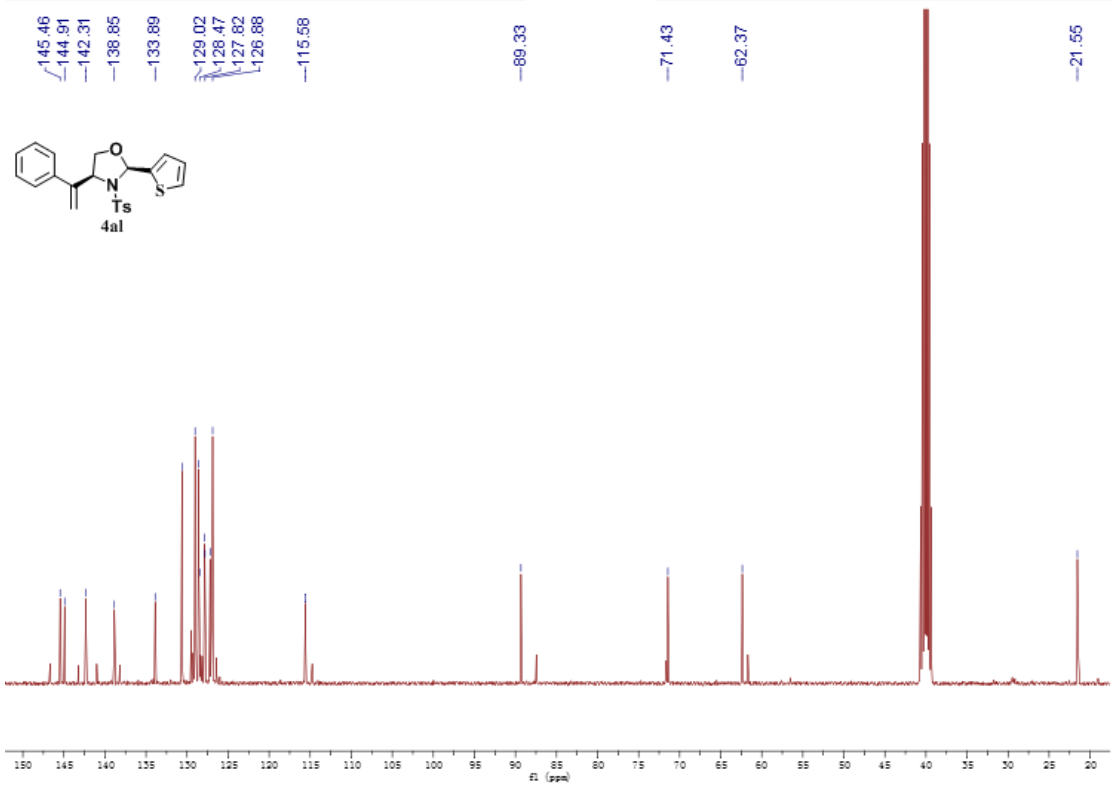

7.8484
7.8284
7.5349
7.4246
7.3931
7.2651
7.2453
6.0855
5.6694
5.5460
4.9410
3.7510
3.7414
2.4516
Cl
F
Ts
4ak

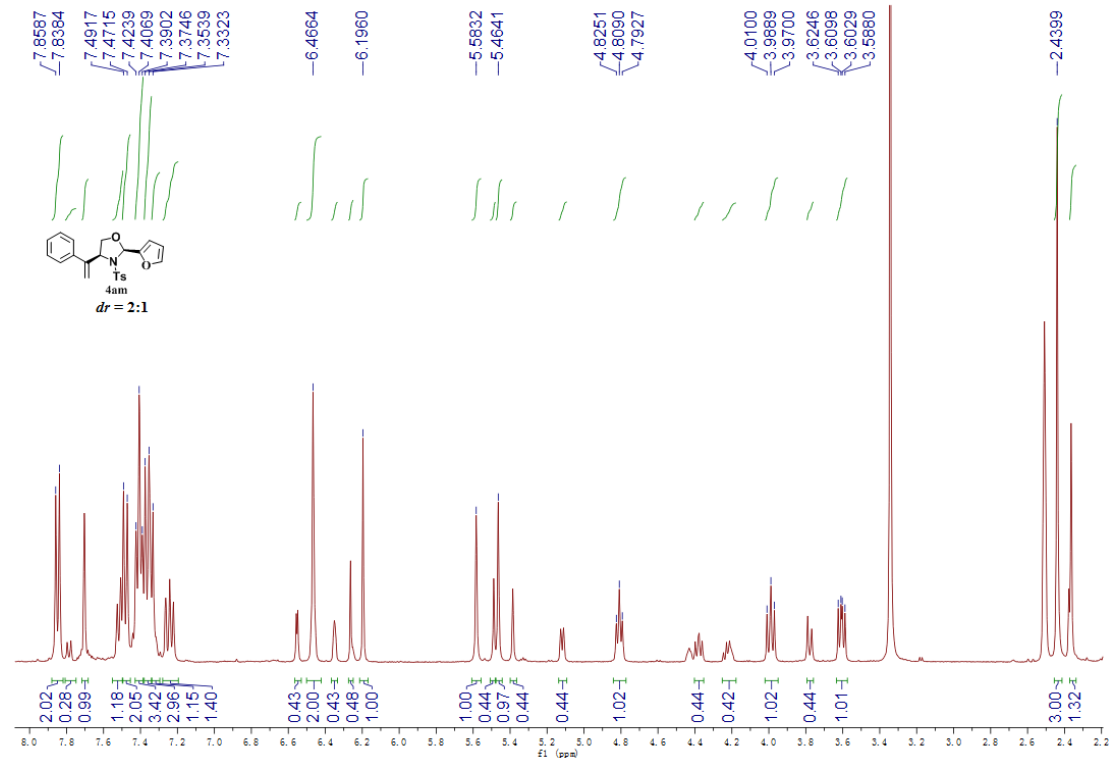
dr = 2:1

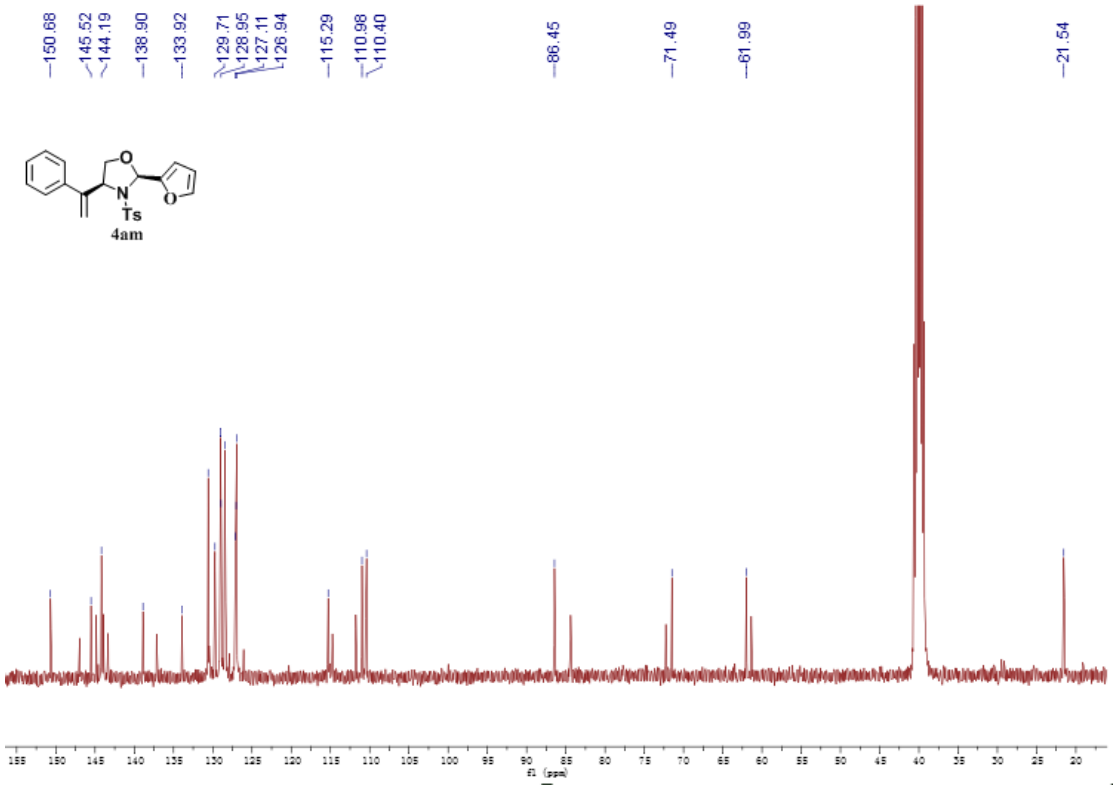

1.97
4.02
2.59
4.20
0.67
2.00
0.58
0.61
0.62
1.04
1.05
1.04
0.59
0.61
1.02
0.63
1.98
0.64
3.00
1.86
f1 (ppm)

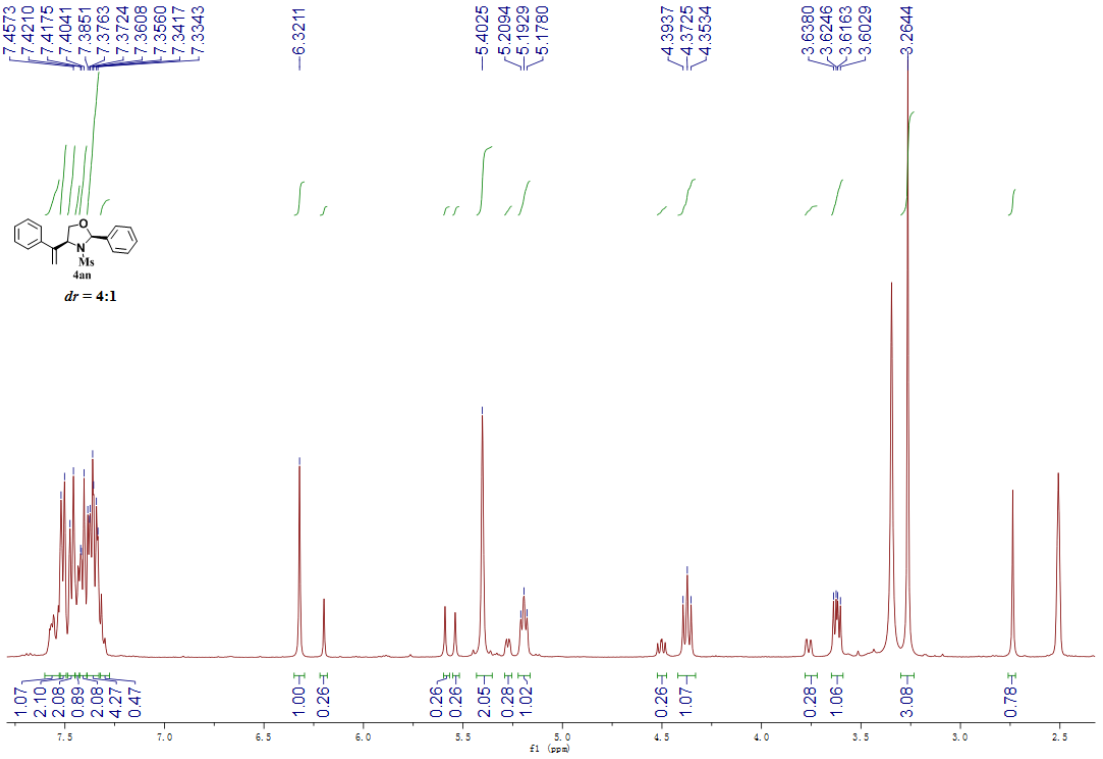

163.78
161.30
146.49
145.22
139.26
130.76
129.01
128.59
127.58
126.96
117.35
116.60
115.05
114.83
114.02
89.48
70.79
62.35
21.57
Cl
F
Ts
4ak
f1 (ppm)


7.8849
7.8644
7.8432
7.3928
7.3639
7.3243
7.2314
7.0544
7.0452
7.0422
7.0330
6.4280
5.5540
5.4725
4.8633
4.8481
4.8325
3.9560
3.9340
3.9159
3.6378
3.6243
3.6155
3.6020
2.4415
Ts
4al
dr = 4:1
f1 (ppm)

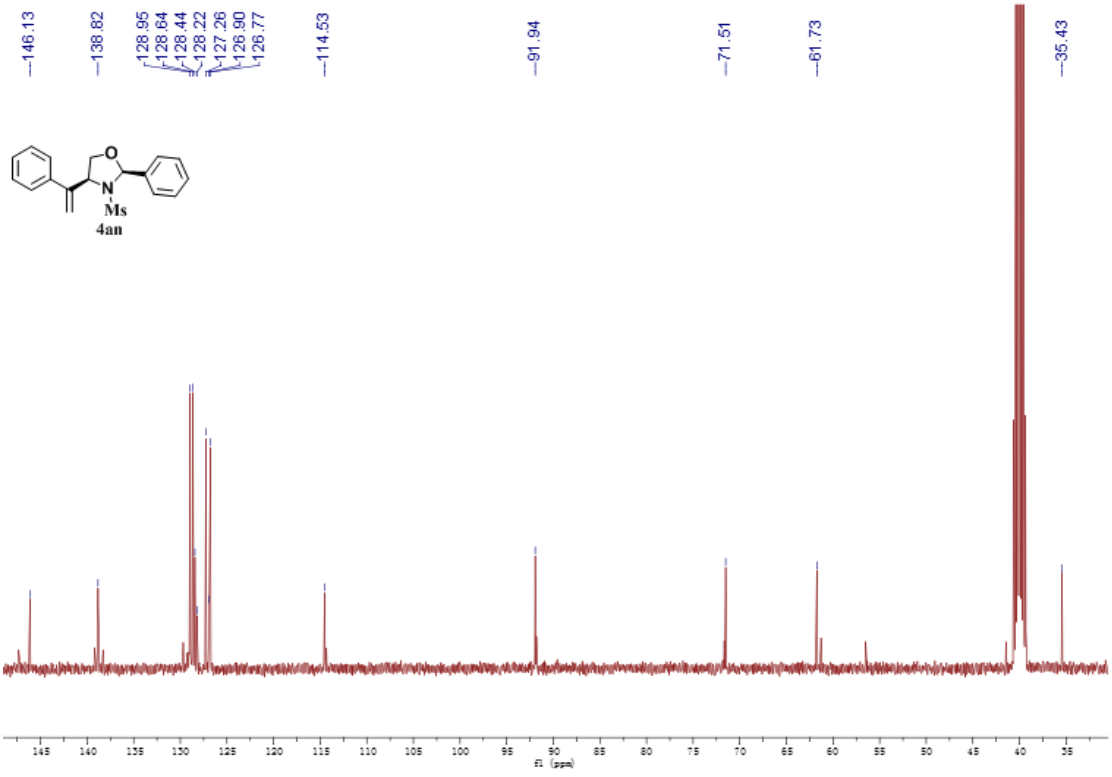

145.46
144.91
142.31
138.85
133.89
129.02
128.47
127.82
126.88
115.58
89.33
71.43
62.37
21.55
Ts
4al
f1 (ppm)

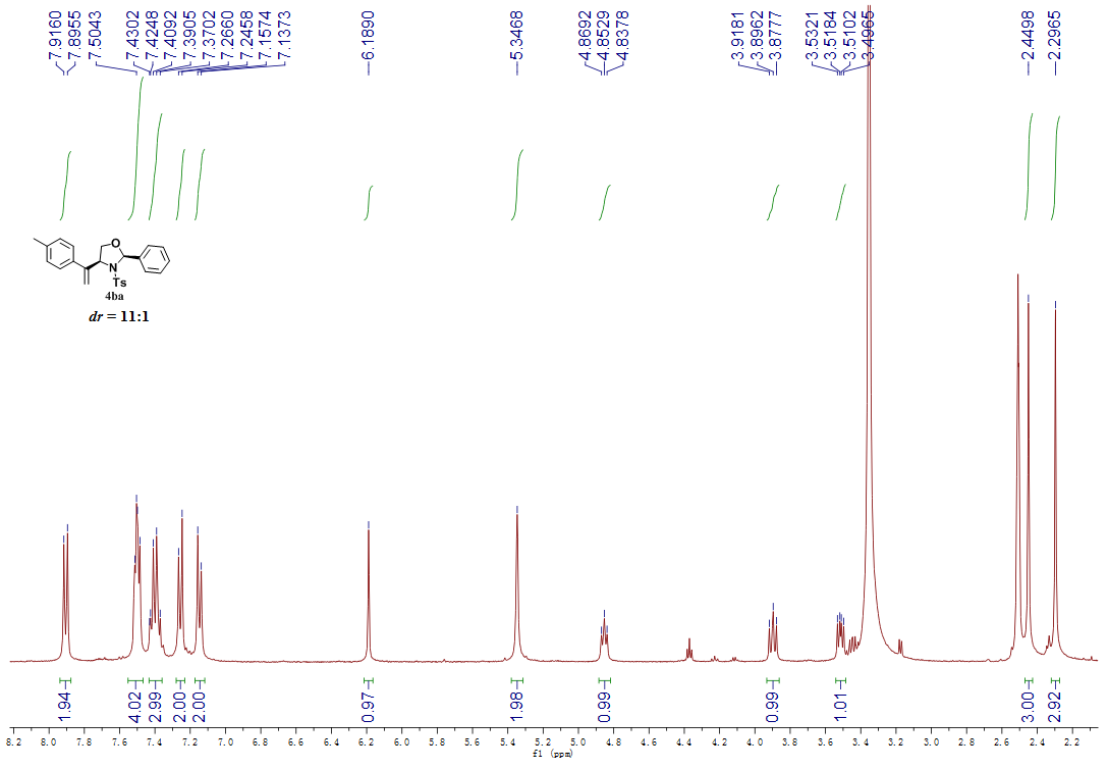

7.8587
7.8384
7.4917
7.4715
7.4239
7.4069
7.3902
7.3746
7.3539
7.3323
6.4664
6.1960
5.5832
5.4641
4.8251
4.8090
4.7927
4.0100
3.9889
3.9700
3.6246
3.6098
3.6029
3.5880
2.4399
Ts
4am
dr = 2:1
f1 (ppm)

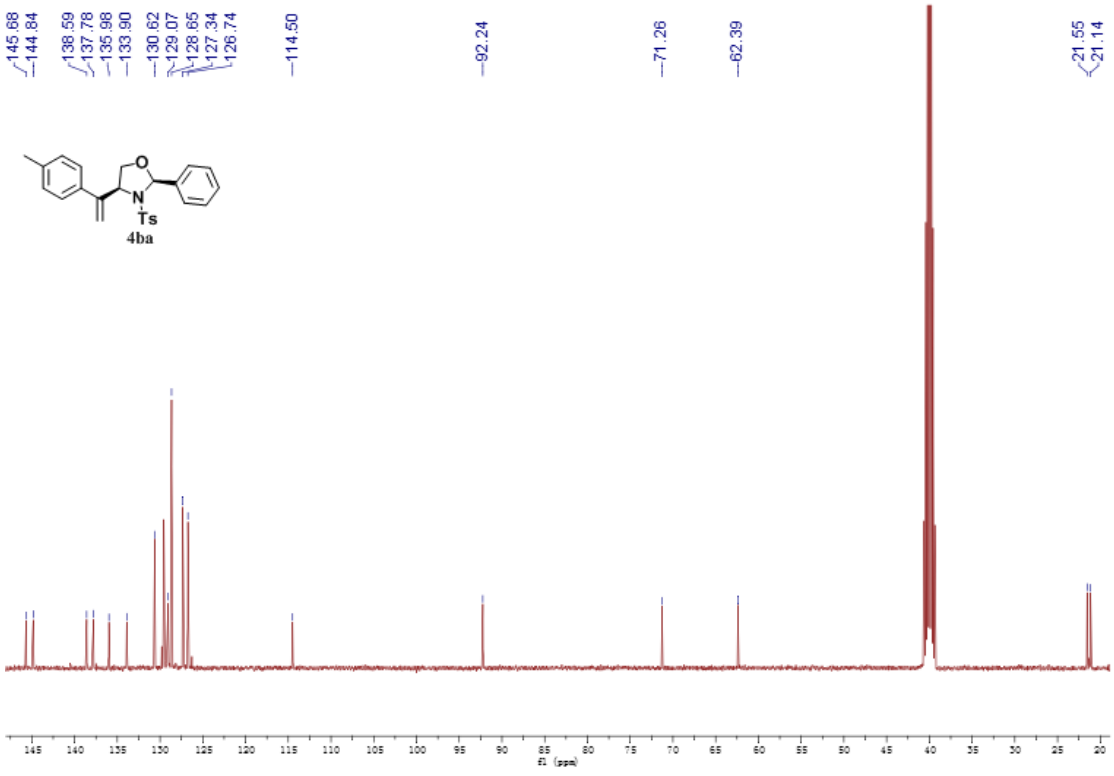

150.68
145.52
144.19
138.90
133.92
129.71
128.95
127.11
126.94
115.29
110.98
110.40
86.45
71.49
61.99
21.54
Ts
4am
f1 (ppm)

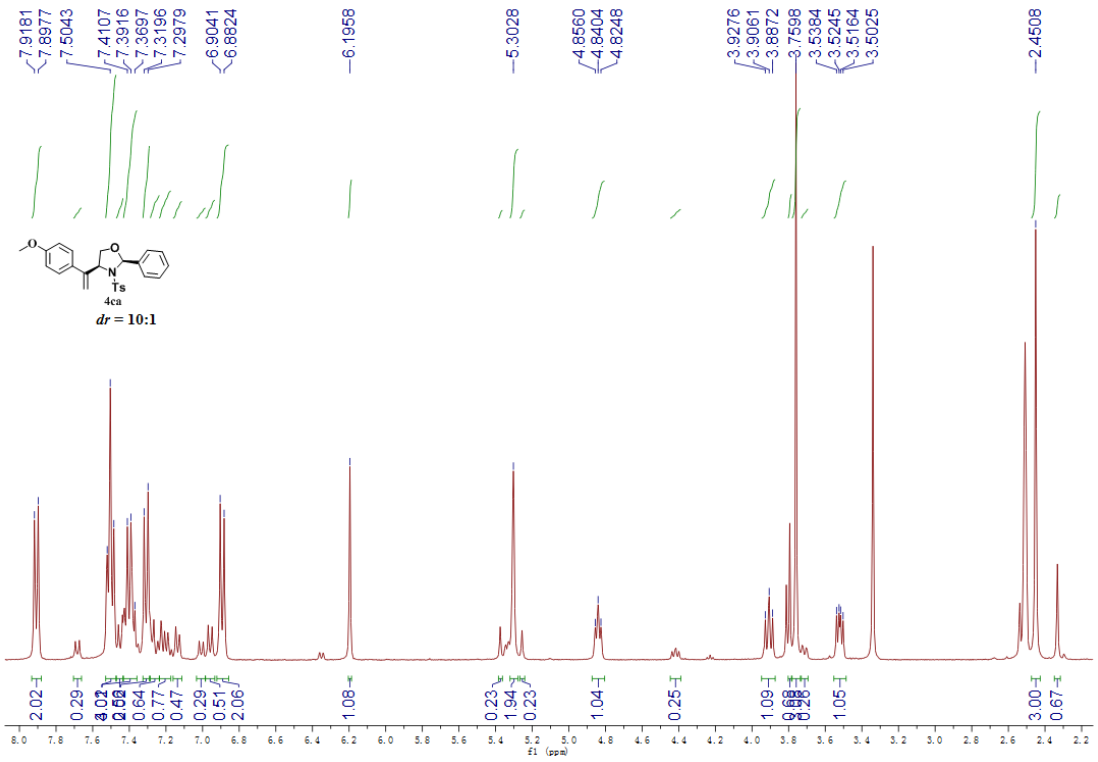

7.4573
7.4210
7.4175
7.4041
7.3851
7.3763
7.3724
7.3608
7.3560
7.3417
7.3343
6.3211
5.4025
5.2094
5.1929
5.1780
4.3937
4.3725
4.3534
3.6380
3.6246
3.6163
3.6029
3.2644
Ms
4an

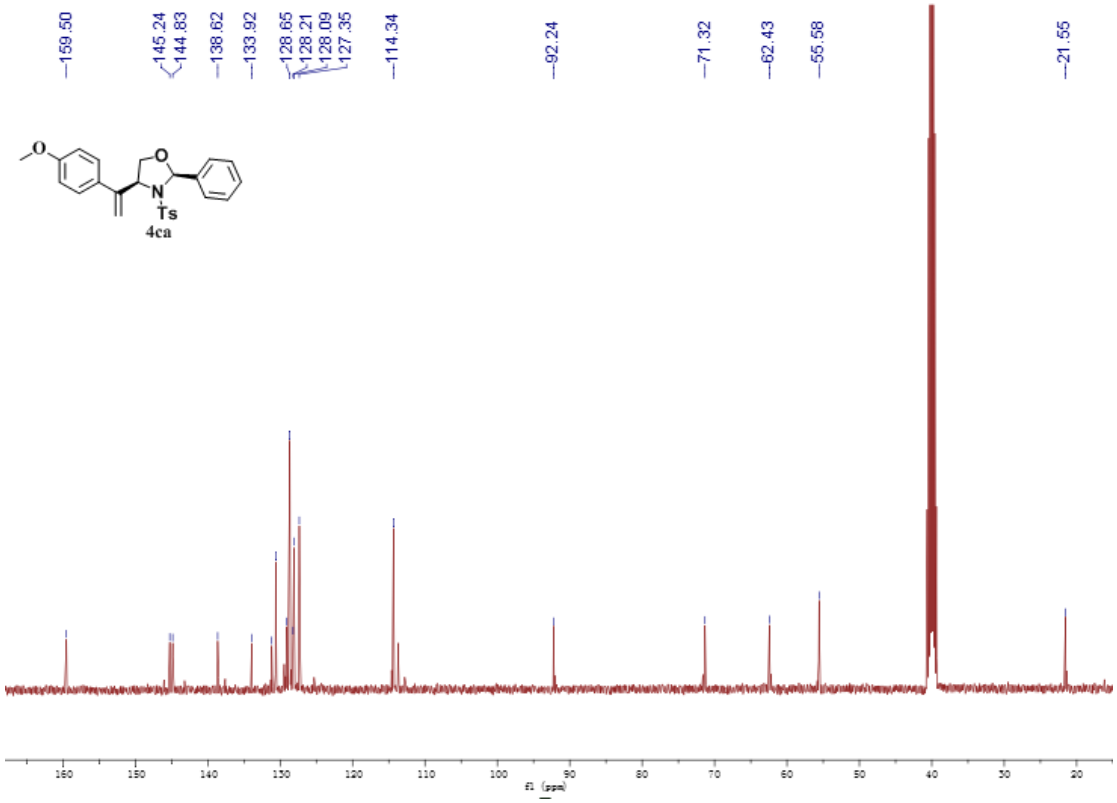
***dr* = 4:1**

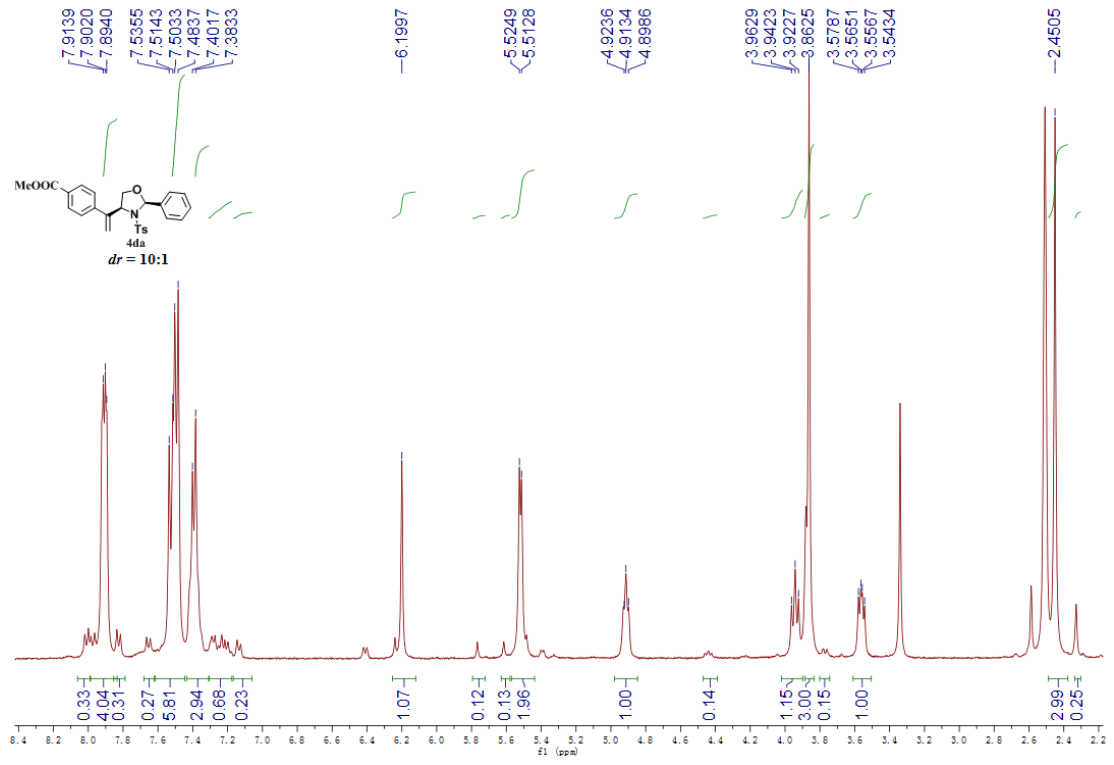

146.13
138.82
128.95
128.64
128.44
128.22
127.26
126.90
126.77
114.53
91.94
71.51
61.73
35.43
Ms
4an

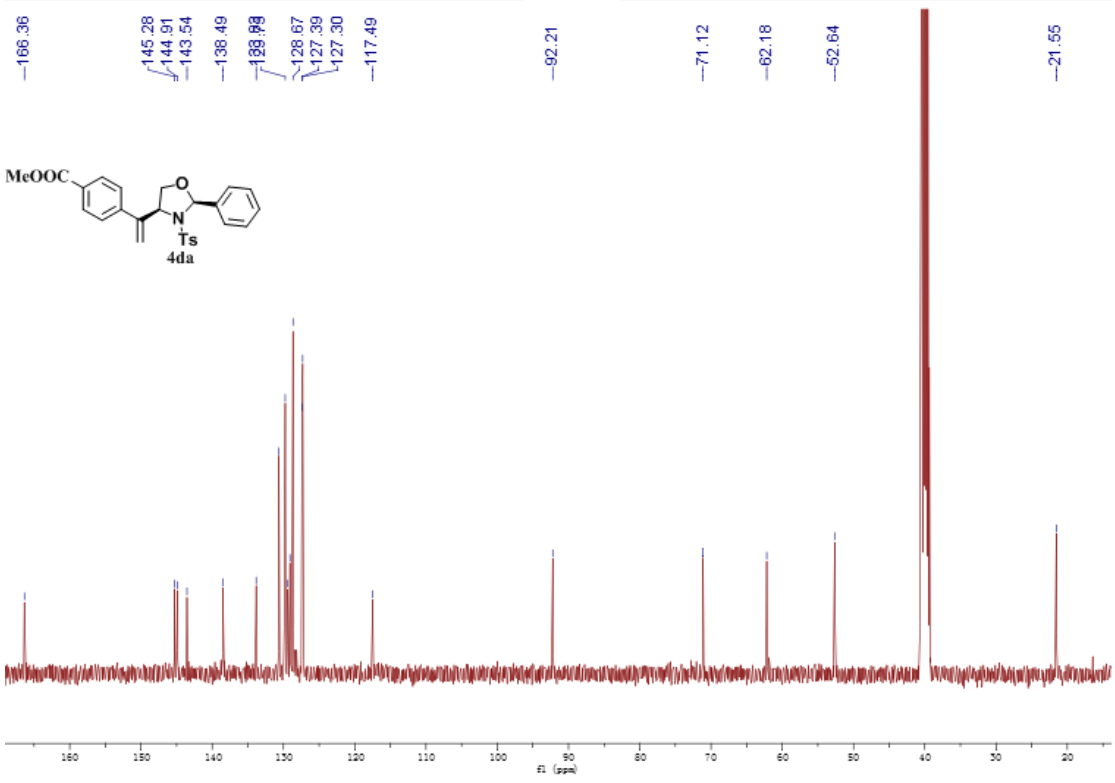

7.9160
7.8955
7.5043
7.4302
7.4248
7.4092
7.3905
7.3702
7.2660
7.2458
7.1574
7.1373
6.1890
5.3468
4.8692
4.8529
4.8378
3.9181
3.8962
3.8777
3.5321
3.5184
3.5102
3.4965
2.4498
2.2965
Ts
4ba
dr = 11:1
1.94
4.02
2.99
2.00
2.00
0.97
1.98
0.99
0.99
1.01
3.00
2.92
f1 (ppm)

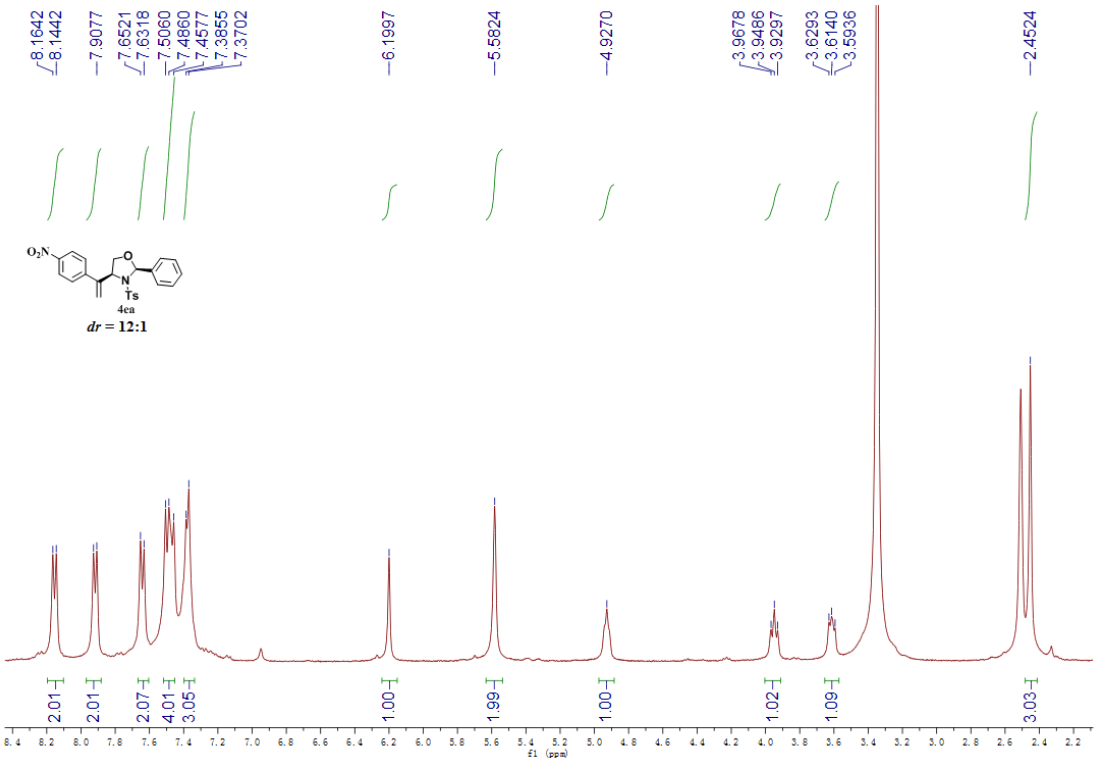

145.68
144.84
138.59
137.78
135.98
133.90
130.62
129.07
128.65
127.34
126.74
114.50
92.24
71.26
62.39
21.55
21.14
Ts
4ba
f1 (ppm)

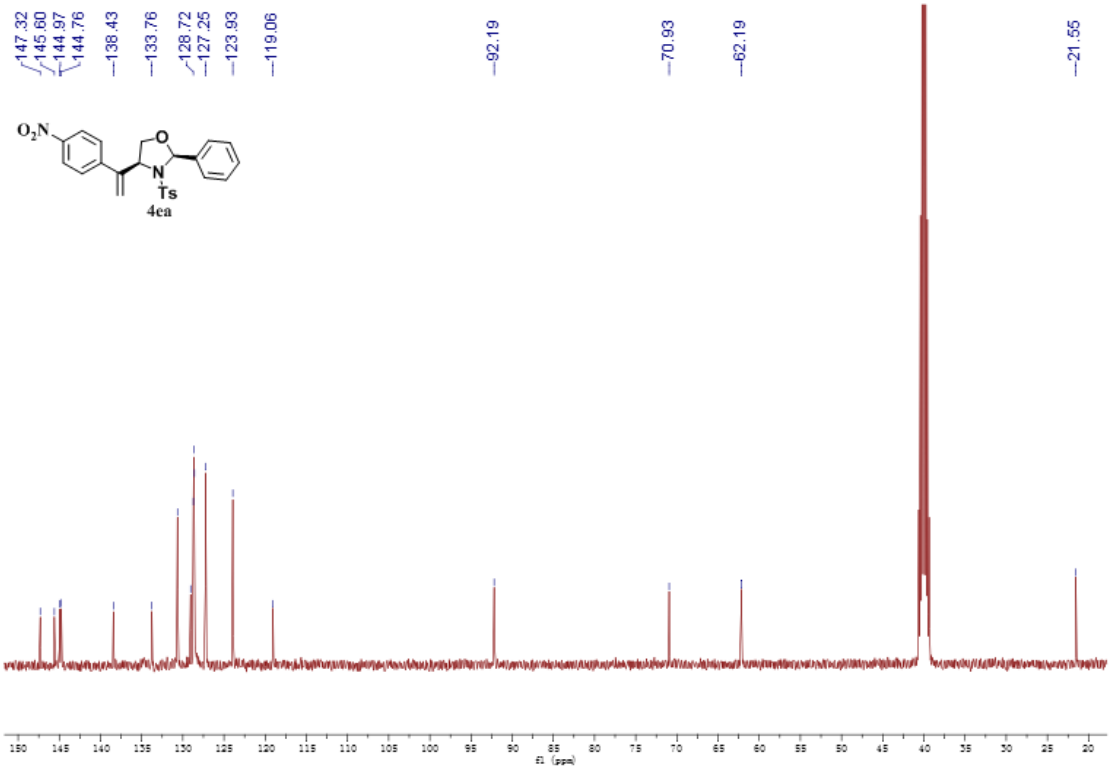

7.9181
7.8977
7.5043
7.4107
7.3916
7.3697
7.3196
7.2979
6.9041
6.8824
6.1958
5.3028
4.8560
4.8404
4.8248
3.9276
3.9061
3.8872
3.7598
3.5384
3.5245
3.5164
3.5025
2.4508
Ts
4ca
dr = 10:1
f1 (ppm)

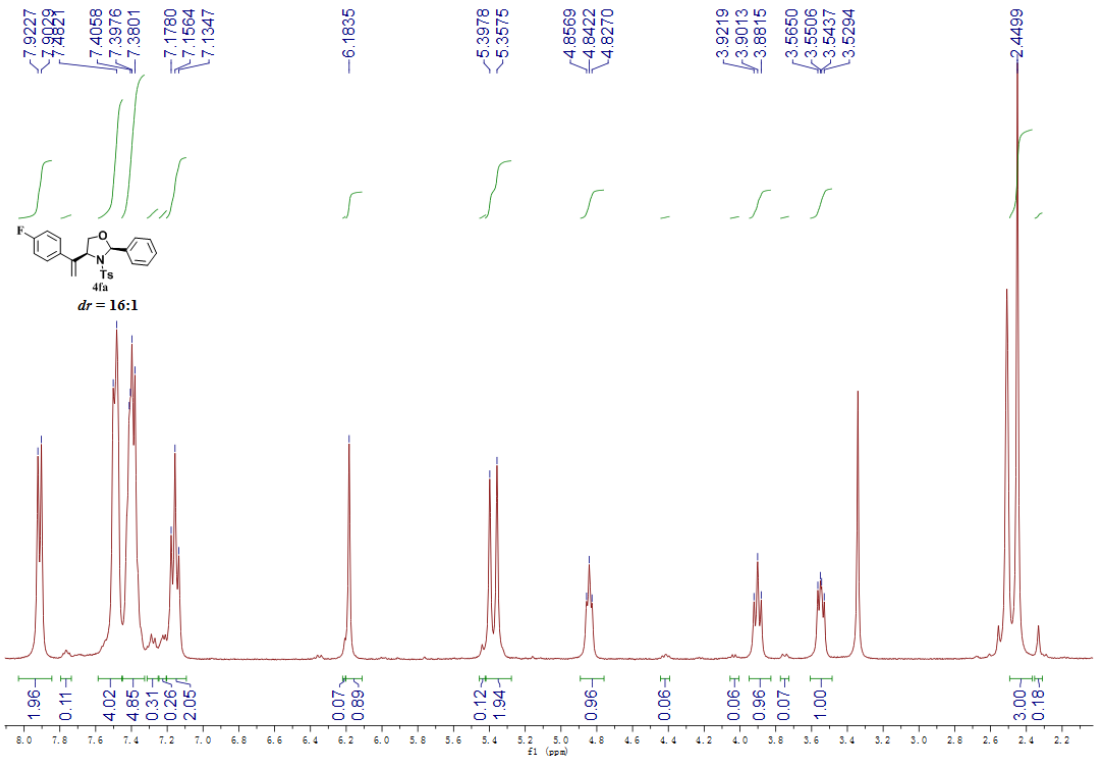

159.50
145.24
144.83
138.62
133.92
128.65
128.21
128.09
127.35
114.34
92.24
71.32
62.43
55.58
21.55
Ts
4ca
f1 (ppm)

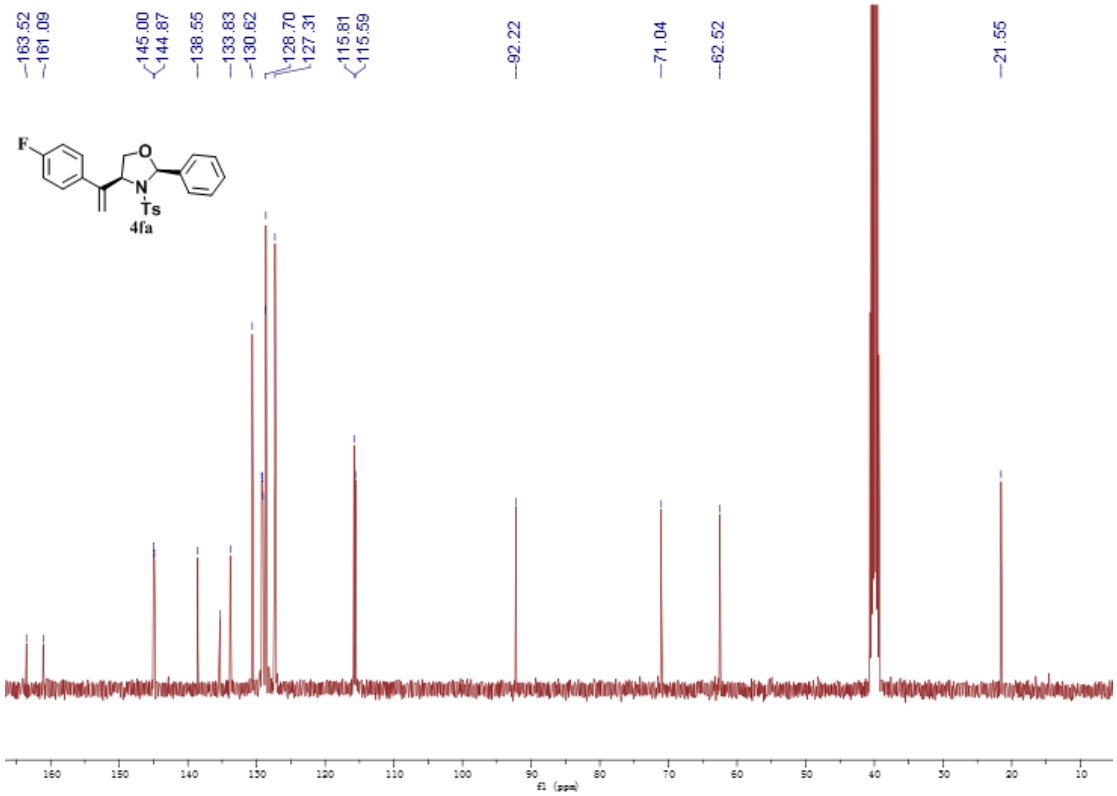

7.9139
7.9020
7.8940
7.5355
7.5143
7.5033
7.4837
7.4017
7.3833
6.1997
5.5249
5.5128
4.9236
4.9134
4.8986
3.9629
3.9423
3.9227
3.8625
3.5787
3.5651
3.5567
3.5434
2.4505
MeOOC
Ts
4da
dr = 10:1
0.33
4.04
0.31
0.27
5.81
2.94
0.68
0.23
1.07
0.12
0.13
1.96
1.00
0.14
1.15
3.00
0.15
1.00
2.99
0.25
f1 (ppm)

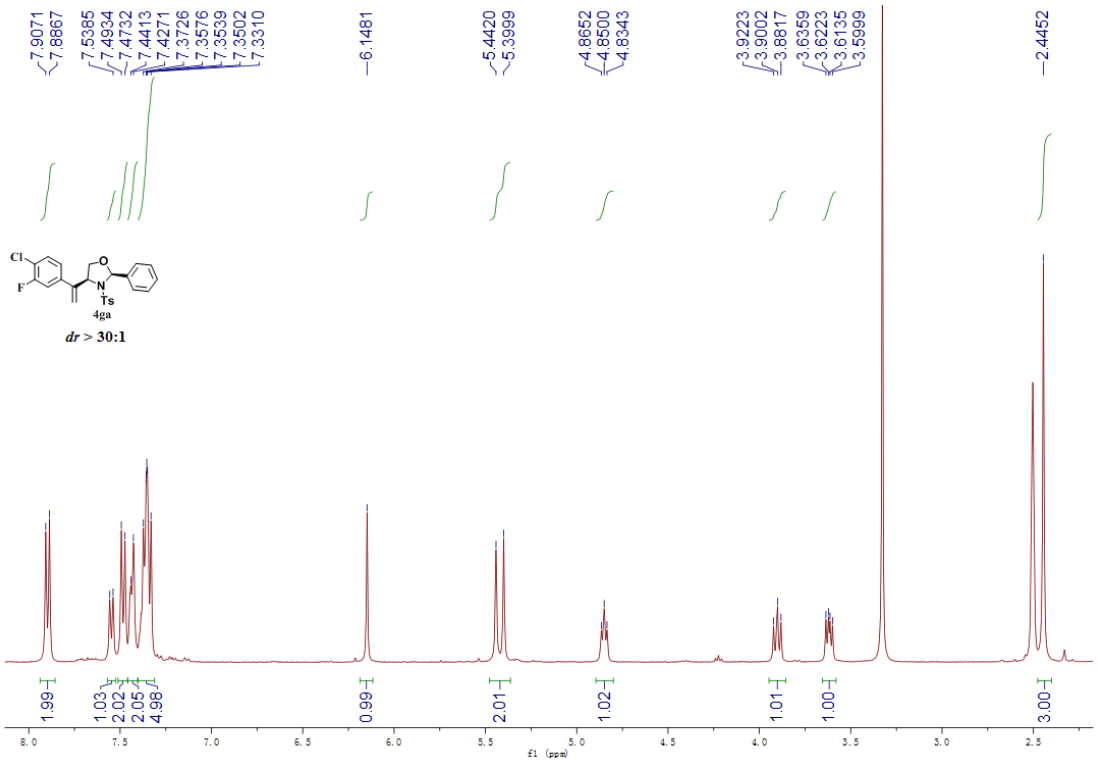

166.36
145.28
144.91
143.54
138.49
128.67
127.39
127.30
117.49
92.21
71.12
62.18
52.64
21.55
MeOOC
Ts
4da
f1 (ppm)

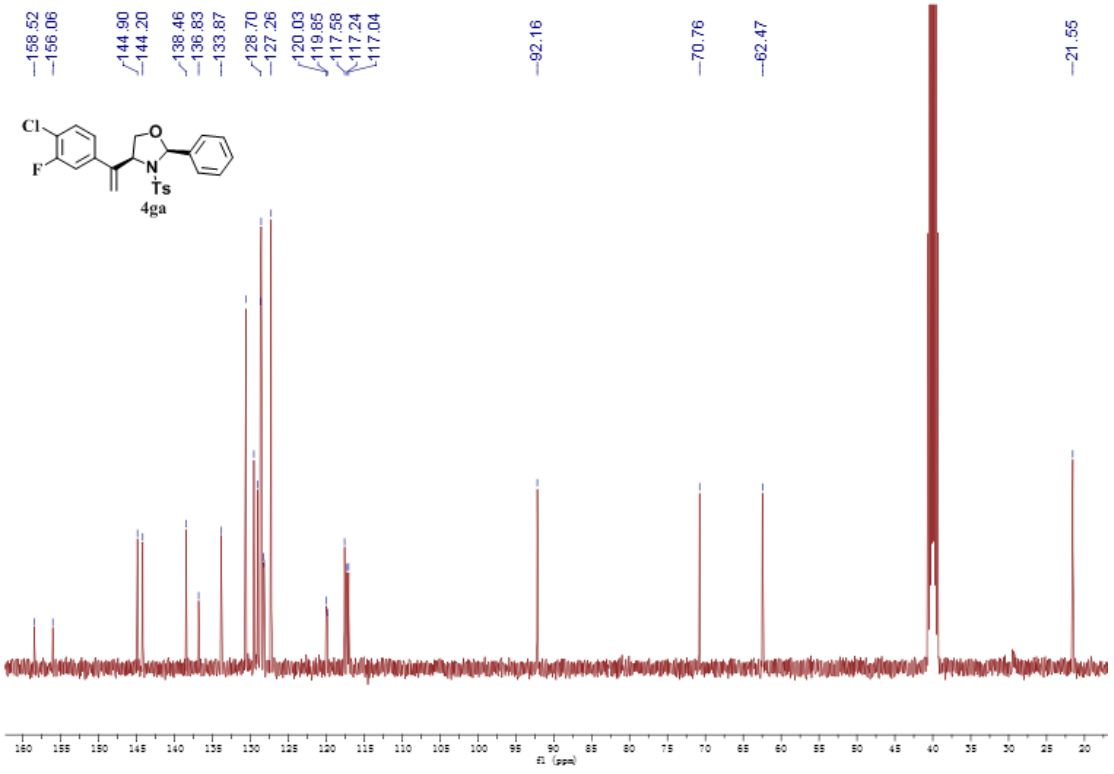

8.1642
8.1442
7.9077
7.6521
7.6318
7.5060
7.4860
7.4577
7.3855
7.3702
6.1997
5.5824
4.9270
3.9678
3.9486
3.9297
3.6293
3.6140
3.5936
2.4524
Ts
4ea
dr = 12:1
2.01
2.01
2.07
4.01
3.05
1.00
1.99
1.00
1.02
1.09
3.03
f1 (ppm)

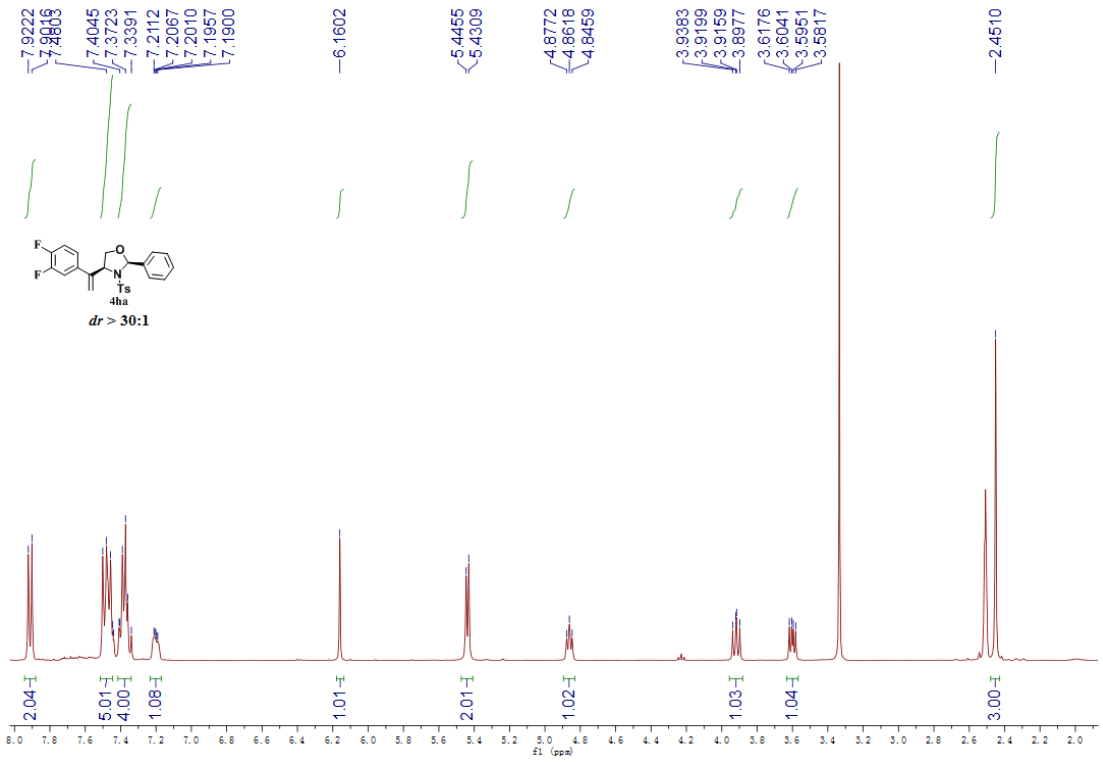

147.32
145.60
144.97
144.76
138.43
133.76
128.72
127.25
123.93
119.06
92.19
70.93
62.19
21.55
Ts
4ea
f1 (ppm)

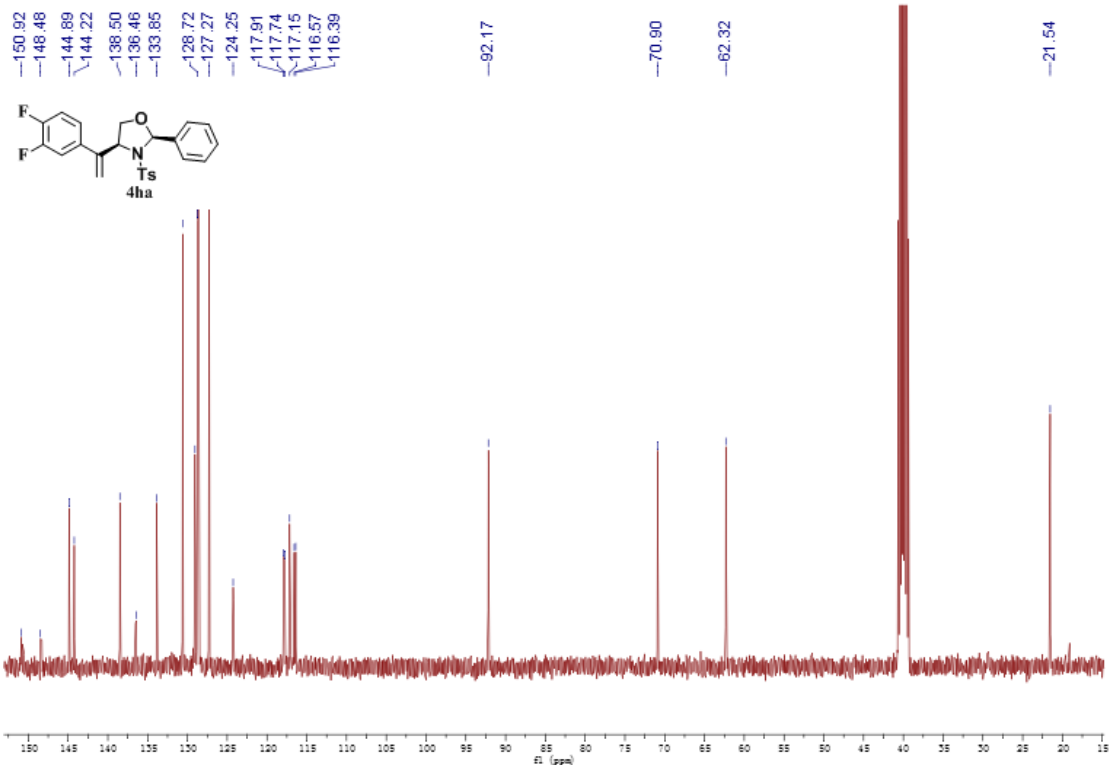

7.9227
7.9029
7.4058
7.3976
7.3801
7.1780
7.1564
7.1347
6.1835
5.3978
5.3575
4.8569
4.8422
4.8270
3.9219
3.9013
3.8815
3.5650
3.5506
3.5437
3.5294
2.4499
F
O
N
Ts
4fa
dr = 16:1
1.96
0.11
4.02
4.85
0.31
0.26
2.05
0.07
0.89
0.12
1.94
0.96
0.06
0.06
0.96
0.07
1.00
3.00
0.18
f1 (ppm)

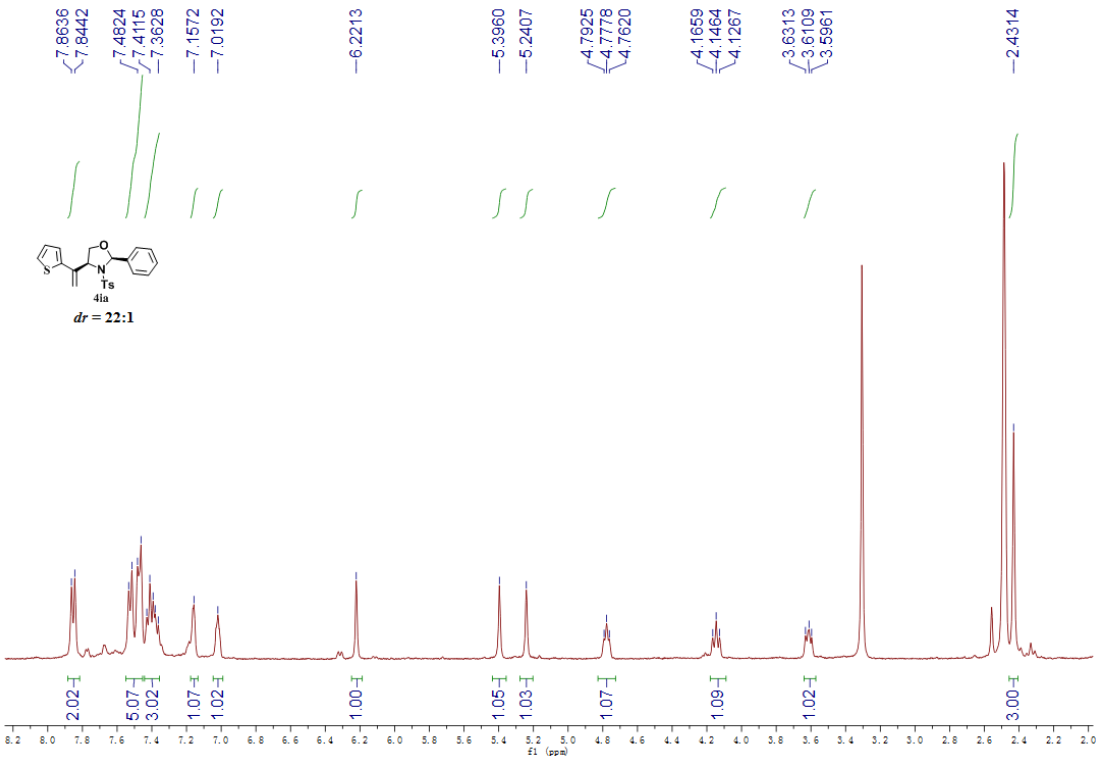

163.52
161.09
145.00
144.87
138.55
133.83
130.62
128.70
127.31
115.81
115.59
92.22
71.04
62.52
21.55
F
O
N
Ts
4fa
f1 (ppm)

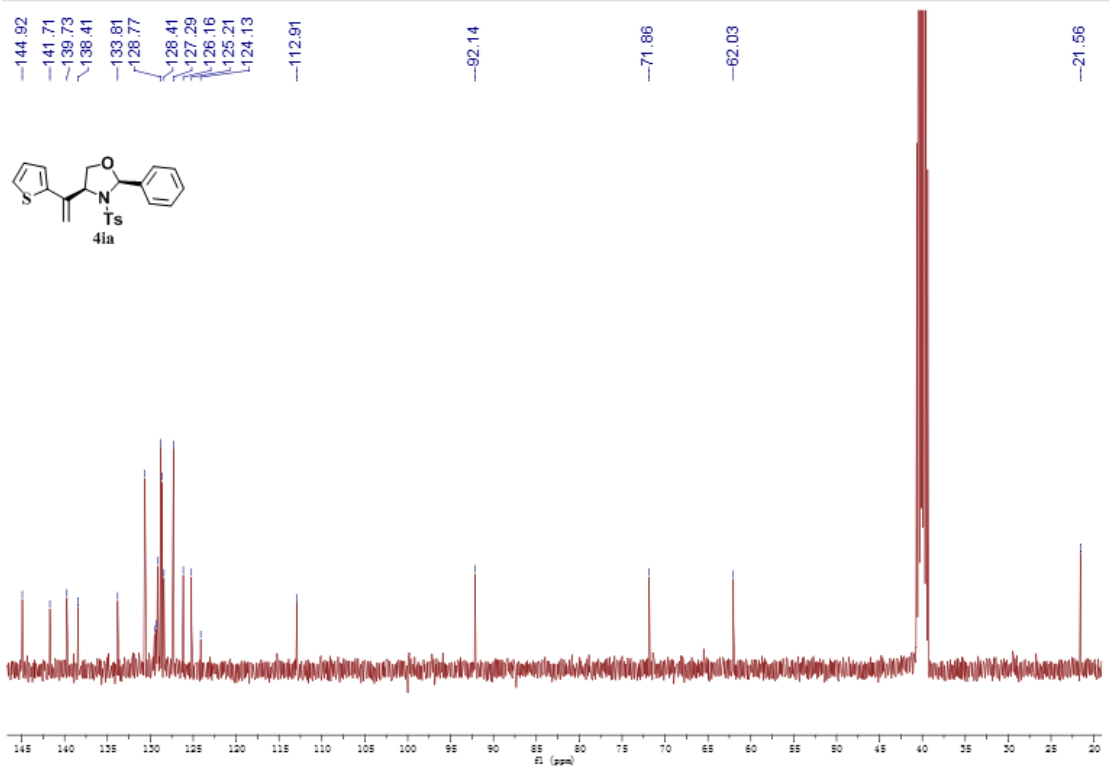

7.9071
7.8867
7.5385
7.4934
7.4732
7.4413
7.4271
7.3726
7.3576
7.3539
7.3502
7.3310
6.1481
5.4420
5.3999
4.8652
4.8500
4.8343
3.9223
3.9002
3.8817
3.6359
3.6223
3.6135
3.5999
2.4452
Cl
F
O
N
Ts
4ga
dr > 30:1
1.99
1.03
2.02
2.05
4.98
0.99
2.01
1.02
1.01
1.00
3.00
f1 (ppm)


158.52
156.06
144.90
144.20
138.46
136.83
133.87
128.70
127.26
120.03
119.85
117.58
117.24
117.04
92.16
70.76
62.47
21.55
Cl
F
O
N
Ts
4ga
f1 (ppm)


7.9222
7.9016
7.4803
7.4045
7.3723
7.3391
7.2112
7.2067
7.2010
7.1957
7.1900
6.1602
5.4455
5.4309
4.8772
4.8618
4.8459
3.9383
3.9199
3.9159
3.8977
3.6176
3.6041
3.5951
3.5817
2.4510
F
F
O
N
Ts
4ha
dr > 30:1
2.04
5.01
4.00
1.08
1.01
2.01
1.02
1.03
1.04
3.00
f1 (ppm)


150.92
148.48
144.89
144.22
138.50
136.46
133.85
128.72
127.27
124.25
117.91
117.74
117.15
116.57
116.39
92.17
70.90
62.32
21.54
F
F
O
N
Ts
4ha
f1 (ppm)


7.8636
7.8442
7.4824
7.4115
7.3628
7.1572
7.0192
6.2213
5.3960
5.2407
4.7925
4.7778
4.7620
4.1659
4.1464
4.1267
3.6313
3.6109
3.5961
2.4314
Ts
4ia
dr = 22:1
2.02
5.07
3.02
1.07
1.02
1.00
1.05
1.03
1.07
1.09
1.02
3.00
f1 (ppm)


144.92
141.71
139.73
138.41
133.81
128.77
128.41
127.29
126.16
125.21
124.13
112.91
92.14
71.86
62.03
21.56
Ts
4ia
f1 (ppm)