Supplementary Information

Gold-Catalyzed Amination of *in situ* Formed Alkyl Gold Species with *p*-Quinonediimines as *N*-Sources

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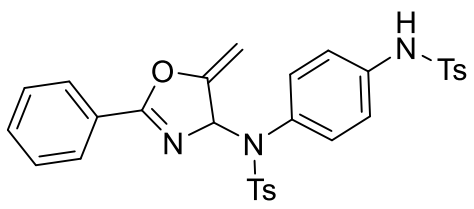
General Information

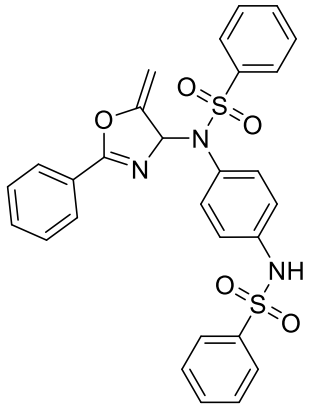
All reactions were carried out in oven-dried glassware. Solvents were dried by the standard methods. Gold catalyst $Me_3(OMe)$*t*BuXPhosAuNTf$_2$ and starting material *p*-quinonediimines **2** were prepared according to previously published procedure, and had physical and spectral properties identical to those earlier reported.[1,2] Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 MHz spectrometer; Chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

General Procedure for the Gold-Catalyzed Amination Reaction

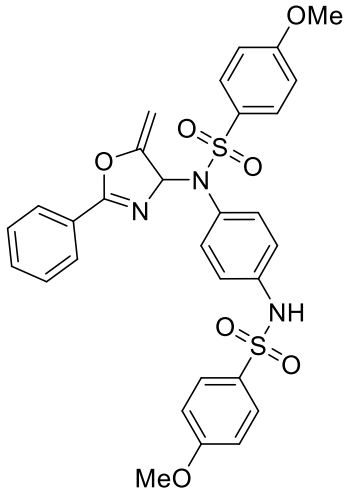
To a 10-mL oven-dried test tube containing a magnetic stirring bar, *p*-quinonediimines **2** (0.15 mmol, 1.5 equiv.), Et_3N (1.0 mg, 10 mol%), and $Me_3(OMe)$*t*BuXPhosAuNTf$_2$ (5.0 mg, 5.0 mol%) in DCE (1.0 mL), was added a solution of propargyl amides **1** (0.1 mmol, 1.0 equiv.) in DCE (1.0 mL) at room temperature under argon atmosphere. The resulting reaction mixture was stirred for 6 h under these conditions. When the reaction was completed (monitored by TLC), the solvent was evaporated in vacuo and the residue was purified by flash column chromatography on silica gel (hexanes/ethyl acetate = 6:1 to 3:1) to afford the pure products **3** in good to high yields.



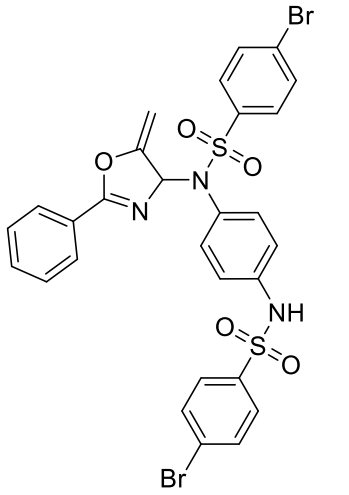
4-Methyl-*N*-(5-methylene-2-phenyl-4,5-dihydrooxazol-4-yl)-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3a). White solid, mp: 158-160 °C, 47.6 mg, 83% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.81 (d, *J* = 7.1 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 2.5 Hz, 1H), 6.88 – 6.81 (m, 5H), 4.99 (t, *J* = 2.8 Hz, 1H), 4.81 – 4.77 (m, 1H), 2.45 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.3, 156.1, 144.1, 143.9, 137.2, 136.5, 135.9, 133.2, 132.7, 131.7, 129.7, 129.4, 128.7, 128.49, 128.45, 127.3, 126.0, 121.0, 90.3, 81.2, 21.8, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{28}N_3O_5S_2$ $[M+H]^+$: 574.1465, found 574.1456.



***N*-(5-Methylene-2-phenyl-4,5-dihydrooxazol-4-yl)-*N*-(4-(phenylsulfonamido)phenyl)benzenesulfonamide (3b)**. White solid, mp: 85-87 °C, 48.5 mg, 78% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 (t, *J* = 7.9 Hz, 4H), 7.63 – 7.55 (m, 3H), 7.54 – 7.48 (m, 1H), 7.47 – 7.42 (m, 2H), 7.42 – 7.36 (m, 4H), 7.29 – 7.27 (m, 1H), 7.25 – 7.23 (m, 1H), 6.97 (t, *J* = 2.4 Hz, 1H), 6.84 (s, 4H), 4.99 (t, *J* = 2.9 Hz, 1H), 4.79 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 155.9, 139.3, 138.6, 137.3, 133.13, 133.10, 133.06, 132.7, 131.5, 129.0, 128.69, 128.67, 128.4, 128.3, 127.2, 125.8, 121.0, 90.4, 81.1; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}N_3O_5S_2$ $[M+H]^+$: 546.1152, found 546.1142.

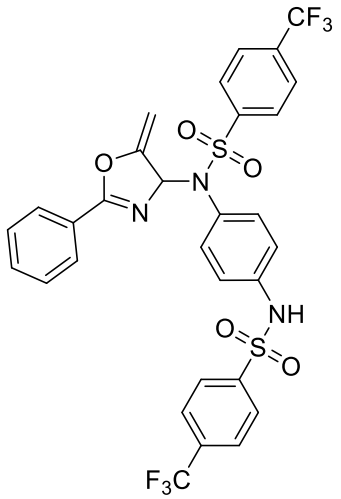


4-Methoxy-*N*-(4-((4-methoxyphenyl)sulfonamido)phenyl)-*N*-(5-methylene-2-phenyl-4,5-dihydrooxazol-4-yl)benzenesulfonamide (3c). White solid, mp: 109-111 °C, 51.4 mg, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 (d, *J* = 7.1 Hz, 2H), 7.66 (d, *J* = 8.9 Hz, 2H), 7.56 (d, *J* = 9.0 Hz, 2H), 7.53 – 7.48 (m, 1H), 7.42 – 7.36 (m, 2H), 7.09 (s, 1H), 6.95 (t, *J* = 2.5 Hz, 1H), 6.92 – 6.87 (m, 2H), 6.87 – 6.81 (m, 4H), 6.77 (d, *J* = 9.0 Hz, 2H), 4.97 (t, *J* = 2.8 Hz, 1H), 4.78 (t, *J* = 2.7 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.3, 163.3, 163.2, 156.1, 137.3, 133.1, 132.7, 131.7, 131.0, 130.6, 130.4, 129.5, 128.7, 128.4, 125.9, 120.8, 114.4, 114.2, 113.8, 90.3, 81.2, 55.7; HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{28}N_3O_7S_2$ $[M+H]^+$: 606.1363, found 606.1355.

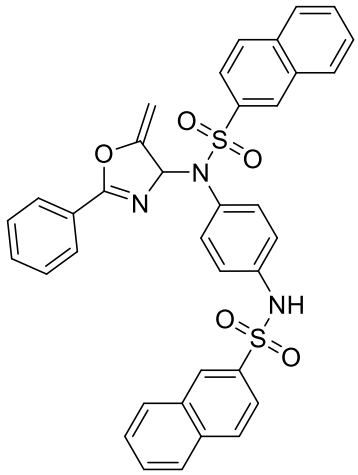


4-Bromo-*N*-(4-((4-bromophenyl)sulfonamido)phenyl)-*N*-(5-methylene-2-phenyl-4,5-dihydrooxazol-4-yl)benzenesulfonamide (3d). White solid, mp: 97-99 °C, 56.8 mg, 81% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.80 (d, *J* = 8.0 Hz, 2H), 7.66 –

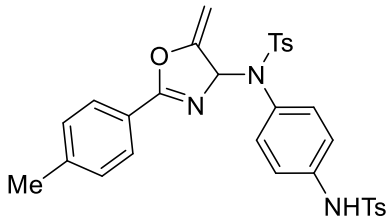
7.58 (m, 4H), 7.57 – 7.53 (m, 1H), 7.47 – 7.39 (m, 6H), 7.14 (s, 1H), 6.95 (s, 1H), 6.90 – 6.83 (m, 4H), 5.02 (t, J = 2.9 Hz, 1H), 4.81 (t, J = 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 155.7, 138.4, 137.7, 137.0, 133.1, 133.0, 132.4, 132.1, 131.7, 130.0, 128.8, 128.7, 128.5, 128.4, 128.2, 125.7, 121.2, 90.7, 81.3; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{21}NaBr_2N_3O_5S_2$ [M+Na]$^+$: 725.9161, found 725.9156.



***N*-(5-Methylene-2-phenyl-4,5-dihydrooxazol-4-yl)-4-(trifluoromethyl)-*N*-(4-((4-(trifluoromethyl)phenyl)sulfonamido)phenyl)benzenesulfonamide (3e)**. White solid, mp: 133-135 °C, 44.7 mg, 59% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, J = 8.2 Hz, 2H), 7.78 (d, J = 7.0 Hz, 2H), 7.73 (d, J = 8.3 Hz, 4H), 7.58 – 7.52 (m, 3H), 7.45 – 7.38 (m, 2H), 7.10 (s, 1H), 6.98 (t, J = 2.4 Hz, 1H), 6.89 (s, 4H), 5.03 (t, J = 2.9 Hz, 1H), 4.83 (t, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.8, 155.6, 143.0, 142.3, 136.9, 135.0 (q, J = 17.5 Hz), 134.7 (q, J = 275 Hz), 133.13, 133.06, 131.7, 128.9, 128.8, 128.4, 127.8, 126.2 (q, J = 3.4 Hz), 125.9 (q, J = 3.9 Hz), 125.6, 121.3, 90.9, 81.4.; ^{19}F NMR (376 MHz, $CDCl_3$) (δ, ppm) -63.57, -63.66; HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{22}F_6N_3O_5S_2$ [M+H]$^+$: 682.0900, found 682.0888.

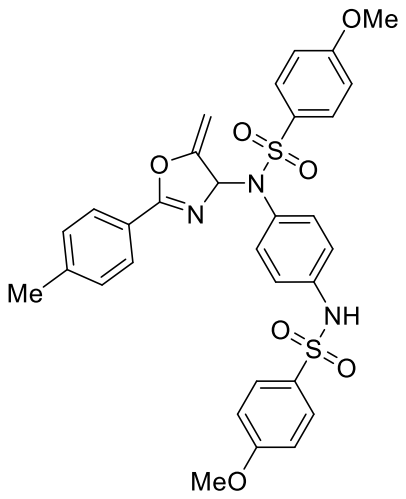


***N*-(5-Methylene-2-phenyl-4,5-dihydrooxazol-4-yl)-*N*-(4-(naphthalene-2-sulfonamido)phenyl)naphthalene-2-sulfonamide (3f)**. White solid, mp: 104-106 °C, 55.5 mg, 77% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.27 (s, 1H), 8.21 (s, 1H), 7.89 – 7.81 (m, 3H), 7.77 – 7.69 (m, 6H), 7.66 – 7.58 (m, 3H), 7.58 – 7.46 (m, 3H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.06 (s, 1H), 7.02 (t, *J* = 2.5 Hz, 1H), 6.85 (s, 4H), 4.95 (t, *J* = 2.9 Hz, 1H), 4.79 (t, *J* = 2.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 155.9, 137.2, 136.3, 135.8, 135.1, 135.0, 133.2, 132.7, 132.1, 132.0, 131.7, 129.9, 129.5, 129.4, 129.2, 129.0, 128.9, 128.8, 128.6, 128.4, 128.0, 128.0, 127.8, 127.4, 125.8, 123.6, 122.2, 120.9, 90.4, 81.4; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{27}NaN_3O_5S_2$ $[M+Na]^+$: 668.1284, found 668.1271.

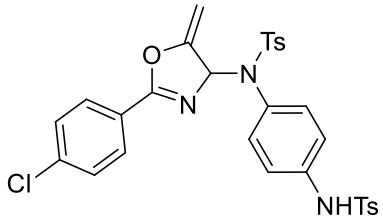


4-Methyl-*N*-(5-methylene-2-(*p*-tolyl)-4,5-dihydrooxazol-4-yl)-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3g). White solid, mp: 95-97 °C, 56.4 mg, 96% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.69 (d, *J* = 7.9 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.24 – 7.16 (m, 5H), 7.07 (d, *J* = 8.0 Hz, 2H), 6.94 (s, 1H), 6.87 – 6.81 (m, 4H), 4.96 (t, *J* = 2.8 Hz, 1H), 4.76 (t, *J* = 2.5 Hz, 1H), 2.44 (s, 3H), 2.39 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 156.1, 144.0, 143.8, 143.4, 137.2, 136.5, 135.8, 133.1, 131.6, 129.6, 129.4,

129.3, 128.4, 128.4, 127.2, 123.1, 121.0, 90.1, 81.2, 21.79, 21.75, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{30}N_3O_5S_2$ $[M+H]^+$: 588.1621, found 588.1612.

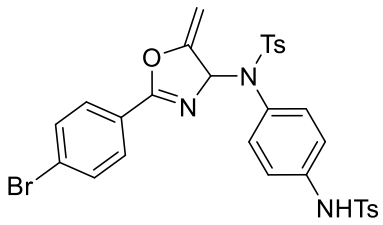


4-Methoxy-*N*-(4-((4-methoxyphenyl)sulfonamido)phenyl)-*N*-(5-methylene-2-(*p*-tolyl)-4,5-dihydrooxazol-4-yl)benzenesulfonamide (3h). White solid, mp: 98-100 °C, 57.6 mg, 93% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.71 – 7.67 (m, 4H), 7.54 (d, *J* = 8.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.97 – 6.84 (m, 5H), 6.83 – 6.72 (m, 4H), 6.44 (s, 1H), 4.97 (t, *J* = 2.7 Hz, 1H), 4.77 (t, *J* = 2.7 Hz, 1H), 3.89 (s, 3H), 3.83 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 163.3, 163.2, 156.2, 143.4, 137.2, 133.2, 131.9, 131.0, 130.6, 130.3, 129.5, 129.4, 128.4, 123.1, 120.9, 114.2, 113.8, 90.1, 81.2, 55.7, 21.8; HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{30}N_3O_7S_2$ $[M+H]^+$: 620.1520, found 620.1524.

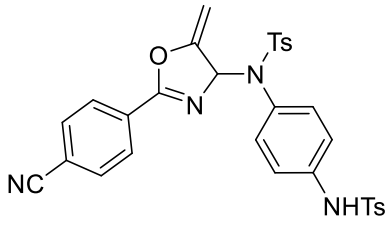


***N*-(2-(4-Chlorophenyl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3i)**. White solid, mp: 171-173 °C, 49.2 mg, 81% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.77 – 7.71 (m, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.40 – 7.36 (m, 2H), 7.25 – 7.21 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.95 (t, *J* = 2.4 Hz, 1H), 6.88 – 6.77 (m, 5H),

5.00 (t, J = 2.9 Hz, 1H), 4.80 (t, J = 2.6 Hz, 1H), 2.45 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.4, 156.0, 144.2, 143.9, 139.1, 137.3, 136.5, 136.0, 133.2, 131.6, 129.8, 129.6,7 129.4, 129.1, 128.4, 127.3, 124.4, 120.9, 90.6, 81.2 , 21.8, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{27}ClN_3O_5S_2$ $[M+H]^+$: 608.1075, found 608.1068.

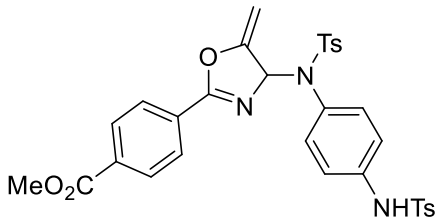


***N*-(2-(4-Bromophenyl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3j)**. White solid, mp: 87-89 °C, 56.6 mg, 87% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68 – 7.64 (m, 2H), 7.63 – 7.59 (m, 2H), 7.56 – 7.51 (m, 4H), 7.23 (d, J = 8.1 Hz, 2H), 7.16 (s, 1H), 7.10 (d, J = 8.1 Hz, 2H), 6.94 (m, J = 2.5 Hz, 1H), 6.84 (s, 4H), 4.99 (t, J = 2.9 Hz, 1H), 4.80 (t, J = 2.9 Hz, 1H), 2.44 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.5, 155.9, 144.2, 143.9, 137.3, 136.4, 135.9, 133.1, 132.0, 131.5, 129.9, 129.7, 129.4, 128.4, 127.6, 127.3, 24.8, 120.8, 90.6, 81.2, 21.8, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{30}H_{27}BrN_3O_5S_2$ $[M+H]^+$: 652.0570, found 652.0563.

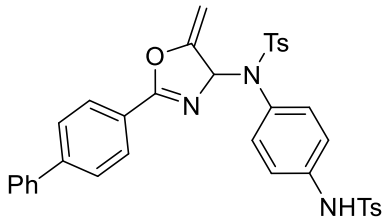


***N*-(2-(4-Cyanophenyl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3k)**. White solid, mp: 89-91 °C, 55.6 mg, 93% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.91 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.5 Hz, 2H), 7.60 – 7.56 (m, 4H), 7.25 – 7.21 (m, 3H), 7.15 (d, J = 8.0 Hz, 2H), 6.98 (t, J = 1.8 Hz, 1H), 6.88 – 6.78 (m, 4H), 5.03 (t, J = 3.0 Hz, 1H), 4.83 (t, J = 3.0 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) (δ,

ppm) 162.7, 155.6, 144.2, 144.1, 137.5, 136.3, 136.0, 133.0, 132.4, 131.2, 130.0, 129.7, 129.4, 129.0, 128.4, 127.3, 120.5, 118.0, 116.1, 91.3, 81.2, 21.8, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{27}N_4O_5S_2$ $[M+H]^+$: 599.1417, found 599.1412.

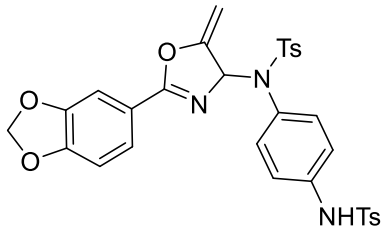


Methyl 4-(4-((4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)phenyl) sulfonamido)-5-methylene-4,5-dihydrooxazol-2-yl)benzoate (3l). White solid, mp: 95-96 °C, 53.6 mg, 85% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.06 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 7.00 – 6.96 (m, 1H), 6.91 – 6.81 (m, 5H), 5.02 (t, *J* = 2.9 Hz, 1H), 4.82 (t, *J* = 2.8 Hz, 1H), 3.94 (s, 3H), 2.45 (s, 3H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.3, 163.5, 155.9, 144.2, 144.0, 137.3, 136.4, 136.0, 133.7, 133.1, 129.8, 129.7, 129.4, 128.5, 128.4, 127.3, 120.9, 90.8, 81.2, 52.6, 21.8, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{30}N_3O_7S_2$ $[M+H]^+$: 632.1520, found 632.1514.

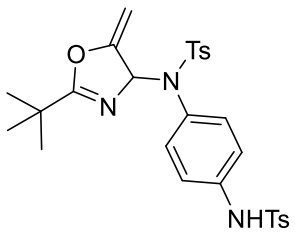


***N*-(2-([1,1'-Biphenyl]-4-yl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3m)**. White solid, mp: 87-89 °C, 59.7 mg, 92% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.90 (d, *J* = 8.3 Hz, 2H), 7.71 – 7.59 (m, 6H), 7.57 – 7.45 (m, 4H), 7.46 – 7.39 (m, 1H), 7.30 – 7.26 (m, 2H), 7.14 – 7.03 (m, 3H), 7.01 (t, *J* = 2.0 Hz, 1H), 6.89 (q, *J* = 9.0 Hz, 4H), 5.03 (t, *J* = 2.8 Hz, 1H), 4.82 (t, *J* = 2.6 Hz, 1H), 2.48 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, CDCl3) (δ, ppm) 164.2, 156.1, 145.5, 144.1, 143.9, 139.9, 137.3, 136.5, 135.9,

133.2, 131.7, 129.7, 129.3, 129.1, 129.0, 128.4, 128.4, 127.3, 127.3, 127.2, 124.7, 121.0, 90.3, 81.3, 21.8, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{36}H_{32}N_3O_5S_2$ $[M+H]^+$: 650.1778, found 650.1765.

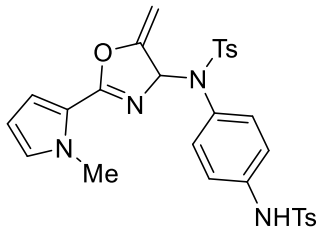


***N*-(2-(Benzo[*d*][1,3]dioxol-5-yl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3n)**. White solid, mp: 82-84 °C, 54.9 mg, 89% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (d, *J* = 8.3 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.38 – 7.34 (m, 1H), 7.26 – 7.21 (m, 3H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.94 – 6.91 (m, 1H), 6.86 – 6.77 (m, 6H), 6.03 (s, 2H), 4.95 (t, *J* = 2.8 Hz, 1H), 4.76 (t, *J* = 2.6 Hz, 1H), 2.45 (s, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.8, 156.2, 151.5, 148.0, 144.2, 143.8, 137.2, 136.6, 136.0, 133.2, 131.8, 129.7, 129.3, 128.4, 127.3, 124.0, 121.0, 119.8, 108.4, 108.3, 102.0, 90.0, 81.1, 21.8, 21.7; HRMS (TOF MS ESI$^{+)}$ calculated for $C_{31}H_{28}N_3O_7S_2$ $[M+H]^+$: 618.1363, found 618.1356.

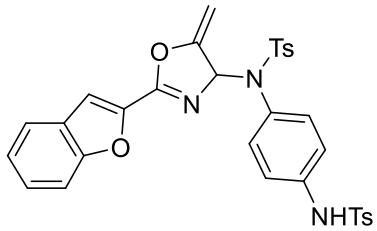


***N*-(2-(*tert*-Butyl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3o)**. White solid, mp: 76-78 °C, 44.3 mg, 80% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 – 7.60 (m, 4H), 7.32 (s, 1H), 7.20 (d, *J* = 8.1 Hz, 4H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.80 (d, *J* = 8.7 Hz, 2H), 6.73 (t, *J* = 2.3 Hz, 1H), 4.81 (t, *J* = 2.7 Hz, 1H), 4.66 (t, *J* = 2.5 Hz, 1H), 2.42 (s, 3H), 2.38 (s, 3H), 0.95 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 174.8, 156.7, 144.2, 143.8, 137.4, 136.6, 136.0, 133.5, 131.1, 129.8, 129.3, 128.3, 127.3, 120.3, 89.4, 80.5,

33.3, 27.0, 21.7, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{32}N_3O_5S_2$ $[M+H]^+$: 554.1778, found 554.1773.

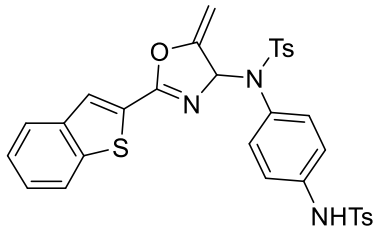


4-Methyl-*N*-(2-(1-methyl-1*H*-pyrrol-2-yl)-5-methylene-4,5-dihydrooxazol-4-yl)-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3p). White solid, mp: 73-75 °C, 43.2 mg, 75% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 6.85 – 6.80 (m, 6H), 6.66 (d, *J* = 3.5 Hz, 1H), 6.13 – 6.06 (m, 1H), 4.87 (t, *J* = 2.7 Hz, 1H), 4.66 (t, *J* = 2.5 Hz, 1H), 3.78 (s, 3H), 2.43 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 158.2, 154.7, 144.2, 143.7, 137.2, 136.7, 135.9, 133.0, 132.1, 129.8, 129.7, 129.1, 128.6, 127.3, 121.2, 118.8, 117.0, 108.5, 89.3, 81.6, 36.9, 21.74, 21.70; HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{29}N_4O_5S_2$ $[M+H]^+$: 577.1574, found 577.1566.



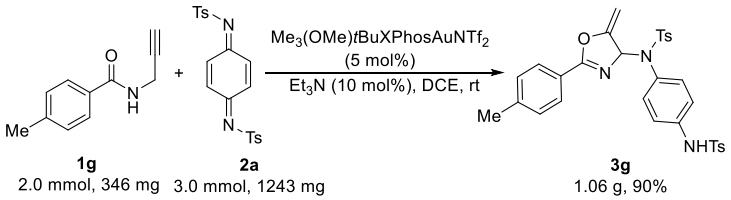
***N*-(2-(Benzofuran-2-yl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3q)**. White solid, mp: 97-99 °C, 50.3 mg, 82% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.66 – 7.61 (m, 3H), 7.56 (d, *J* = 8.4 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.44 (t, *J* = 8.1 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.26 – 7.22 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.99 (m, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.70 (s, 1H), 5.08 (t, *J* = 3.0 Hz, 1H), 4.90 (t, *J* = 3.0 Hz, 1H), 2.44 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 157.0, 156.1, 155.5, 144.2, 144.0, 137.3 136.6, 136.0, 133.3, 131.6, 129.7,

129.6, 128.3, 127.8, 127.3, 127.0, 124.2, 122.7, 121.1, 113.2, 112.4, 91.0, 81.1, 21.8, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{28}N_3O_6S_2$ $[M+H]^+$: 614.1414, found 614.1407.



***N*-(2-(Benzo[*b*]thiophen-2-yl)-5-methylene-4,5-dihydrooxazol-4-yl)-4-methyl-*N*-(4-((4-methylphenyl)sulfonamido)phenyl)benzenesulfonamide (3r)**. White solid, mp: 98-100 °C, 52.8 mg, 84% yield, ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.88 – 7.79 (m, 2H), 7.77 (s, 1H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.48 – 7.38 (m, 2H), 7.25 (d, *J* = 8.1 Hz, 3H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.96 (t, *J* = 2.4 Hz, 1H), 6.92 – 6.80 (m, 4H), 5.03 (t, *J* = 2.9 Hz, 1H), 4.84 (t, *J* = 2.7 Hz, 1H), 2.46 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.4, 156.0, 144.1, 143.9, 141.8, 138.9, 137.3, 136.4, 135.9, 133.2, 131.7, 129.6, 129.4, 129.1, 128.5, 128.3, 127.2, 127.1, 125.4, 125.3, 122.7, 121.1, 90.7, 81.3, 21.8, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{28}N_3O_5S_3$ $[M+H]^+$: 630.1186, found 630.1183.

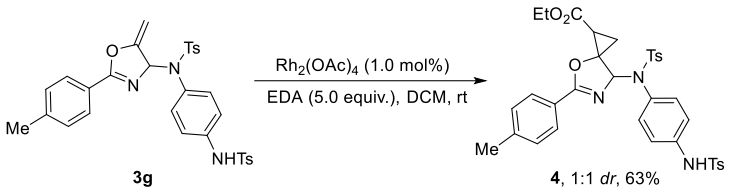
General Procedure for Scale Up



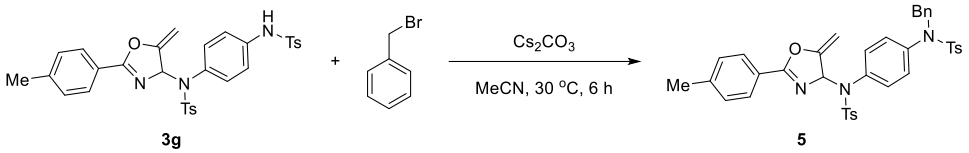
To a 50-mL oven-dried vial with a magnetic stirring bar, **2a** (1242 mg, 3.0 mmol), Et_3N (20.1 mg, 10 mol%), and Me_3(OMe)*t*BuXPhosAuNTf$_2$ (100 mg, 5.0 mol%) in DCE (10.0 mL), was added a solution of **1g** (346 mg, 2.0 mmol) in DCE (10.0 mL) at room temperature under argon atmosphere. The resulting reaction mixture was stirred for 6 h under these conditions. When the reaction was completed (monitored by TLC),

the solvent was evaporated in vacuo and the resulting residue was purified by flash column chromatography on silica gel (Hexanes : EtOAc = 3:1) to give 1.06 g pure product **3g** in 90% yield as white solid.

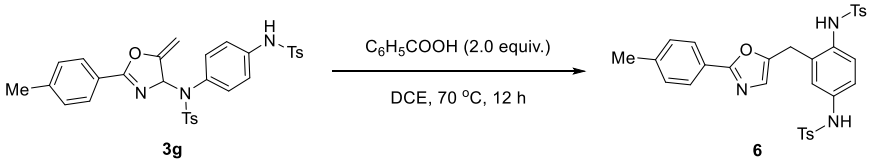
Synthetic Applications



Synthesis of 4: To a 10-mL oven-dried vial with a magnetic stirring bar, **3g** (29.4 mg, 0.1 mmol), and $Rh_2(OAc)_4$ (0.4 mg, 0.001 mmol, 1.0 mol%) in DCM (1.0 mL), was added a solution of ethyl diazoacetate (57 mg, 0.5 mmol, 5.0 equiv) in DCM (1.0 mL) at 0 °C *via* syringe pump in 1 h, and the resulting solution was stirred at room temperature for 2 h. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by flash column chromatography on silica gel (Hexanes : EtOAc = 5:1) to afford pure product **4** as yellow solid (42.4 mg, 63% yield, 1:1 *dr*), mp: 115-118 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.66 (s, 1H), 7.64 (s, 1H), 7.61 – 7.55 (m, 4H), 7.54 – 7.47 (m, 4H), 7.43 (s, 1H), 7.41 (s, 1H), 7.25 – 7.21 (m, 3H), 7.20 (d, J = 8.3 Hz, 3H), 7.16 (s, 2H), 7.13 (s, 2H), 7.04 (s, 2H), 7.00 (s, 2H), 6.98 (s, 1H), 6.96 (s, 1H), 6.86 (s, 2H), 6.84 (s, 2H), 6.34 (s, 2H), 4.15 (d, J = 7.2 Hz, 2H), 4.10 (d, J = 7.2 Hz, 2H), 2.45 (s, 3H), 2.41 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.27 – 2.23 (m, 1H), 2.22 – 2.19 (m, 1H), 2.09 (t, J = 7.1 Hz, 1H), 1.91 (t, J = 7.3 Hz, 1H), 1.84 (d, J = 6.8 Hz, 1H), 1.81 – 1.78 (m, 1H), 1.26 (d, J = 7.2 Hz, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.6, 168.2, 167.6, 166.8, 144.1, 143.9, 143.5, 143.2, 143.1, 137.2, 136.8, 136.6, 136.0, 135.9, 135.8, 133.0, 132.9, 132.4, 129.7, 129.7, 129.5, 129.4, 129.3, 129.0, 128.7, 128.5, 128.1, 127.3, 127.2, 127.1, 123.8, 123.7, 121.22, 121.19, 84.8, 72.0, 61.4, 61.2, 60.6, 28.0, 26.8, 21.8, 21.7, 21.6, 21.2, 16.0, 14.4, 14.3; HRMS (TOF MS ESI$^+$) calculated for $C_{35}H_{36}N_3O_7S_2$ $[M+H]^+$: 674.1989, found 674.1981.

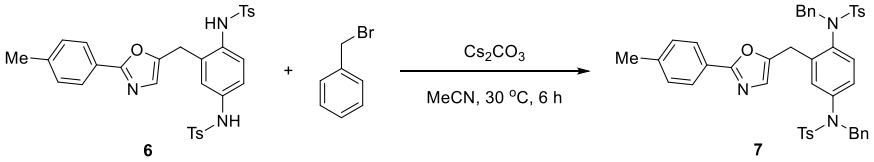


Synthesis of 5: To a 10-mL oven-dried vial with a magnetic stirring bar, **3g** (58.8 mg, 0.10 mmol, 1.0 equiv.), and Cs_2CO_3 (61.8 mg, 0.20 mmol, 2.0 equiv.) in MeCN (2.0 mL), was added BnBr (25.5 mg, 0. 15 mmol, 1.5 equiv.) at 30 °C, and the reaction mixture was stirred for 6 h under these conditions. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by column chromatography on silica gel (Hexanes : EtOAc = 3:1) to give 57.6 mg pure product **5** in 85% yield as white solid, mp: 96-98 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.72 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.19 – 7.12 (m, 5H), 7.09 – 7.04 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.90 (s, 1H), 6.85 (d, *J* = 8.3 Hz, 2H), 6.72 (d, *J* = 8.3 Hz, 2H), 4.99 (t, *J* = 2.9 Hz, 1H), 4.77 (t, *J* = 2.7 Hz, 1H), 4.69 (d, *J* = 14.1 Hz, 1H), 4.46 (d, *J* = 14.1 Hz, 1H), 2.42 (s, 6H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 156.2, 143.7, 143.6, 143.3, 139.3, 136.4, 135.6, 134.9, 134.6, 132.4, 129.4, 129.2, 129.0, 128.7, 128.5, 128.4, 128.3, 127.72, 127.68, 123.3, 90.1, 81.3, 54.6, 21.8, 21.7, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{38}H_{36}N_3O_5S_2$ $[M+H]^+$: 678.2091, found 678.2088.

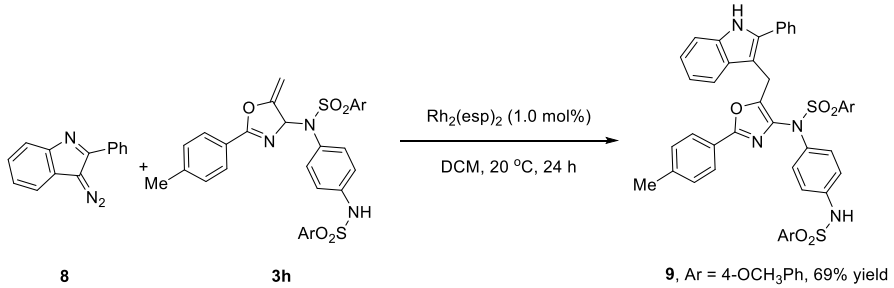


Synthesis of 6: To a 10-mL oven-dried vial with a magnetic stirring bar, **3g** (58.8 mg), benzoic acid (24.4 mg, 0.20 mmol, 2.0 equiv.), and DCE (1.0 mL) were added, and the reaction mixture was stirred for 12 h at 70 °C. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by column chromatography on silica gel (Hexanes : EtOAc = 2:1) to give 48.7 mg pure product **6** in 83% yield as white solid, mp: 70-72 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 (d, *J* = 4.3 Hz, 2H), 7.58 – 7.50 (m, 4H), 7.26 – 7.24 (m, 2H), 7.23 – 7.17 (m, 4H), 7.14 – 7.10 (m, 2H), 7.01 – 6.96 (m, 1H), 6.94 (s, 1H), 6.90 – 6.85 (m, 1H), 6.60 (s,

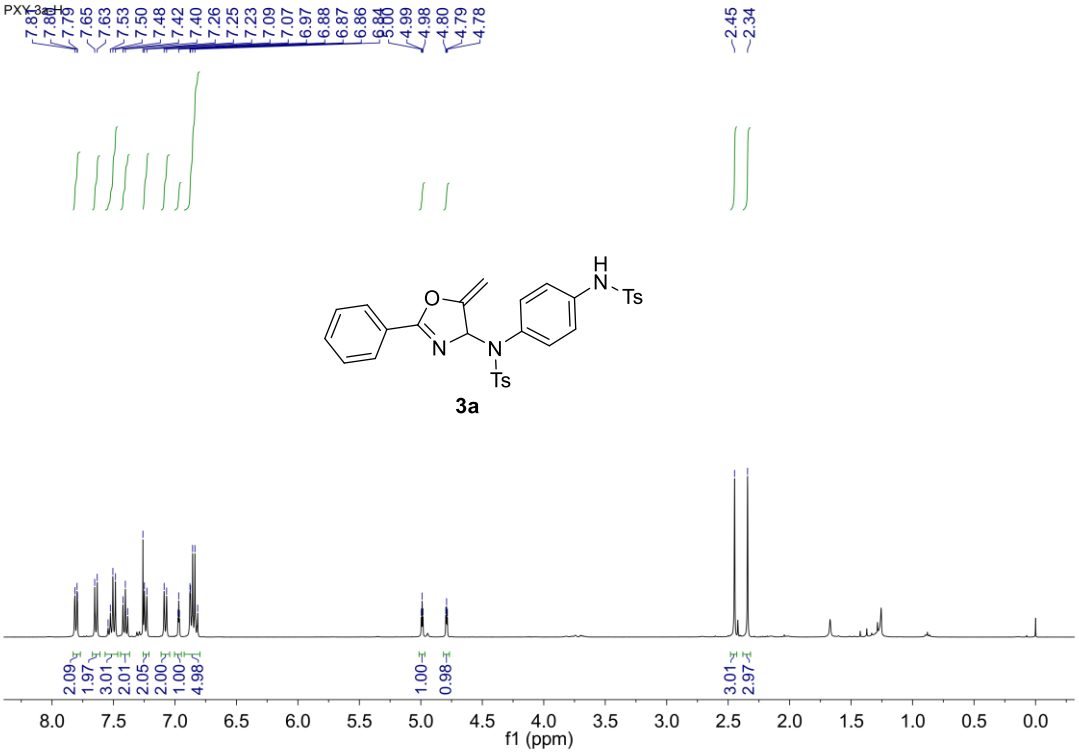
1H), 3.77 (s, 2H), 2.41 – 2.36 (m, 6H), 2.32 – 2.28 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.9, 149.1, 144.3, 144.2, 140.8, 136.4, 136.0, 135.9, 134.4, 131.0, 130.4, 129.9, 129.8, 129.6, 128.1, 127.3, 126.3, 125.1, 124.7, 122.7, 120.5, 28.0, 21.7, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{31}H_{30}N_3O_5S_2$ $[M+H]^+$: 588.1621, found 588.1612.



Synthesis of 7: To a 10-mL oven-dried vial with a magnetic stirring bar, **6** (48.7 mg), Cs_2CO_3 (52.5 mg, 0.17 mmol, 2.0 equiv.) in MeCN (1.0 mL), was added a solution of BnBr (42.5 mg, 0. 25 mmol, 3.0 equiv.), and the reaction mixture was stirred for 6 h at 30 °C. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by column chromatography on silica gel (Hexanes : EtOAc = 3:1) to give 58.9 mg pure product **7** in 92% yield as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 (d, *J* = 7.7 Hz, 2H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.30 – 7.26 (m, 3H), 7.23 – 7.13 (m, 6H), 7.13 – 7.08 (m, 3H), 7.08 – 7.04 (m, 2H), 7.02 – 6.98 (m, 2H), 6.84 (d, *J* = 11.9 Hz, 1H), 6.59 (s, 1H), 6.45 (d, *J* = 8.8 Hz, 1H), 6.16 (s, 1H), 5.04 (d, *J* = 13.2 Hz, 1H), 4.60 – 4.49 (m, 2H), 4.05 (d, *J* = 13.2 Hz, 1H), 3.87 – 3.70 (m, 2H), 2.46 (s, 3H), 2.42 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.2, 149.9, 144.7, 144.1, 140.5, 140.1, 139.2, 136.6, 135.5, 135.2, 135.1, 134.9, 129.8, 129.64, 129.58, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.8, 127.6, 126.2, 125.3, 125.1, 124.6, 56.2, 54.6, 27.1, 22.8, 21.8, 21.6; HRMS (TOF MS ESI$^+$) calculated for $C_{45}H_{42}N_3O_5S_2$ $[M+H]^+$: 768.2560, found 768.2551.



Synthesis of 9: To a 10-mL oven-dried vial with a magnetic stirring bar, **3h** (30.9 mg, 0.1 mmol, 1.0 equiv.), $Rh_2(esp)_2$ (0.5 mg, 1.0 mmol%) in DCM (1.0 mL), was added a solution of diazo compound **8** (54.8 mg, 0.25 mmol, 5.0 equiv.) in DCM (1.0 mL) at 0 ℃ *via* syringe pump in 2 hours, and the reaction mixture was stirred for 24 h at 20 ℃. When the reaction was completed (monitored by TLC), the crude reaction mixture was purified by column chromatography on silica gel (Hexanes : EtOAc = 4:1) to give 55.9 mg pure product **9** in 69% yield as yellow solid, mp: 180-183 ℃. ^{1}H NMR (400 MHz, DMSO) (δ, ppm) 11.34 (s, 1H), 10.31 (s, 1H), 7.71 – 7.66 (m, 4H), 7.59 – 7.55 (m, 4H), 7.51 – 7.47 (m, 2H), 7.44 – 7.39 (m, 1H), 7.35 – 7.32 (m, 1H), 7.31 – 7.26 (m, 3H), 7.12 – 7.09 (m, 3H), 7.08 – 7.06 (m, 1H), 7.06 – 7.02 (m, 3H), 7.02 – 6.98 (m, 2H), 6.73 (t, *J* = 7.0 Hz, 1H), 4.28 (s, 2H), 3.86 (s, 3H), 3.77 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, DMSO) (δ, ppm) 163.0, 162.5, 157.5, 151.9, 147.8, 140.8, 137.4, 135.8, 135.6, 134.9, 133.8, 132.4, 131.0, 130.6, 129.7, 129.1, 128.8, 128.4, 128.1, 125.5, 123.7, 121.7, 119.7, 118.8, 114.4, 114.1, 111.2, 105.2, 82.4, 55.7, 55.6, 21.0, 19.7; HRMS (TOF MS ESI$^+$) calculated for $C_{45}H_{39}N_4O_7S_2$ $[M+H]^+$: 811.2255, found 811.2246.


PXY-3a-H
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7.42
7.40
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6.80
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4.78
2.45
2.34
O
N
H
N
Ts
N
Ts
3a
2.09
1.97
3.01
2.01
2.05
2.00
1.00
4.98
1.00
0.98
3.01
2.97
8.0
7.5
7.0
6.5
6.0
5.5
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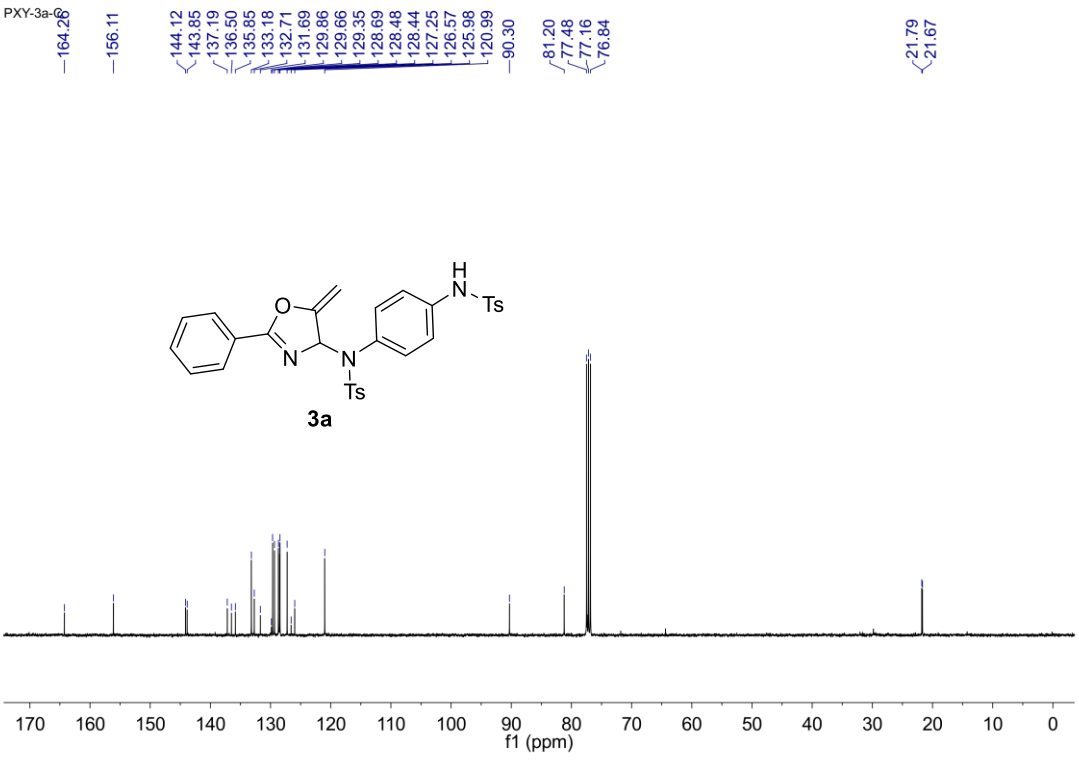
f1 (ppm)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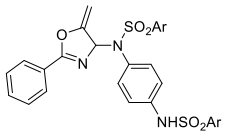
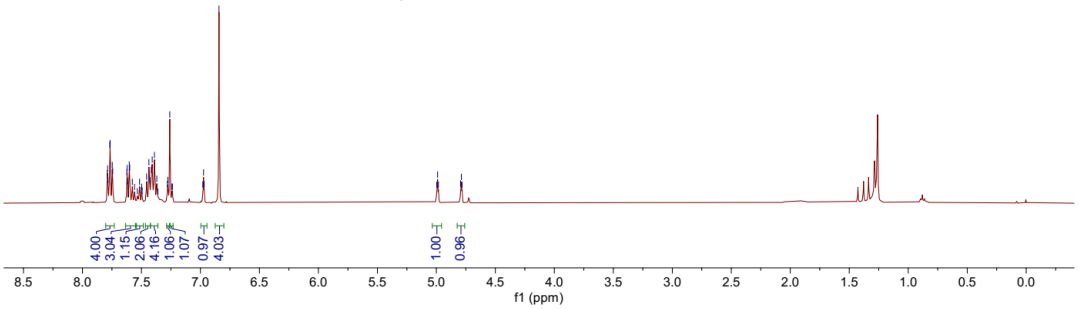
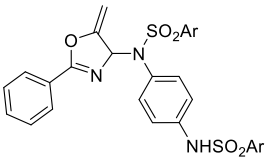
21.67
O
N
H
N
Ts
N
Ts
3a
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

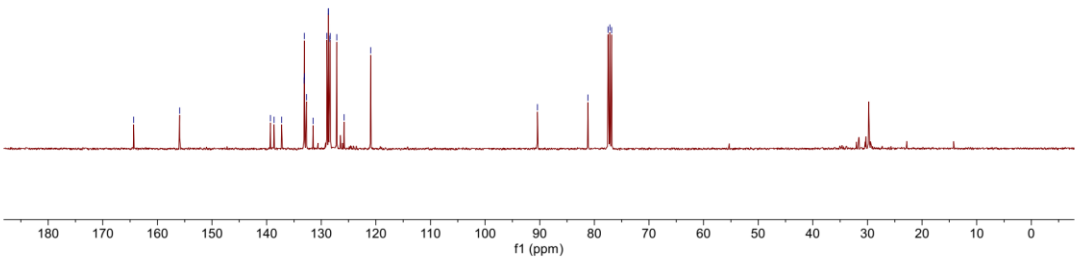


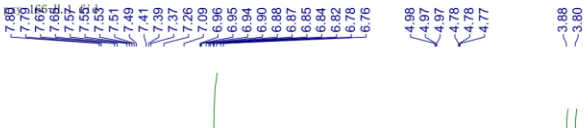
3b, Ar = Ph

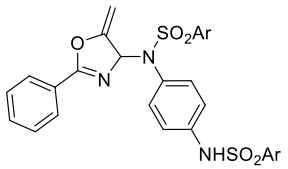




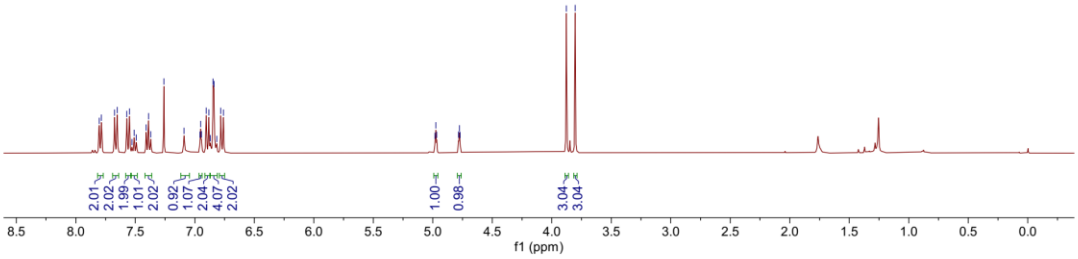
3b, Ar = Ph

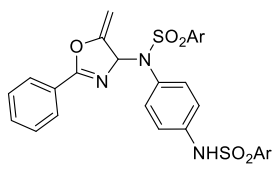




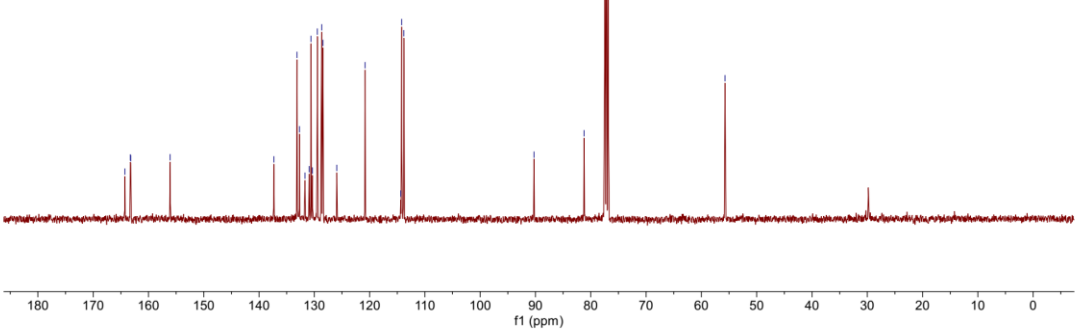


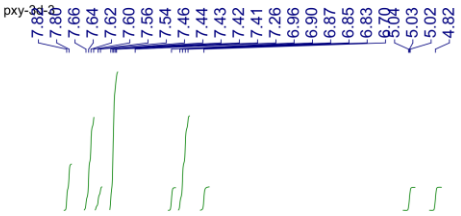
3c, Ar = 4-OMePh

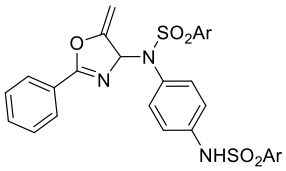




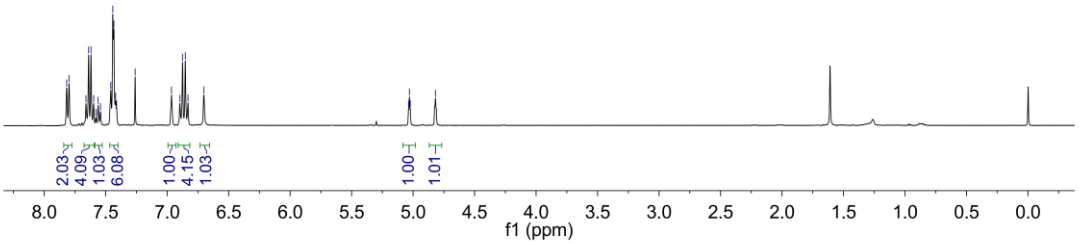
3c, Ar = 4-OMePh

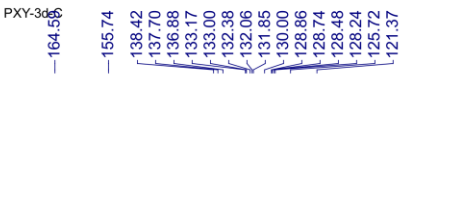




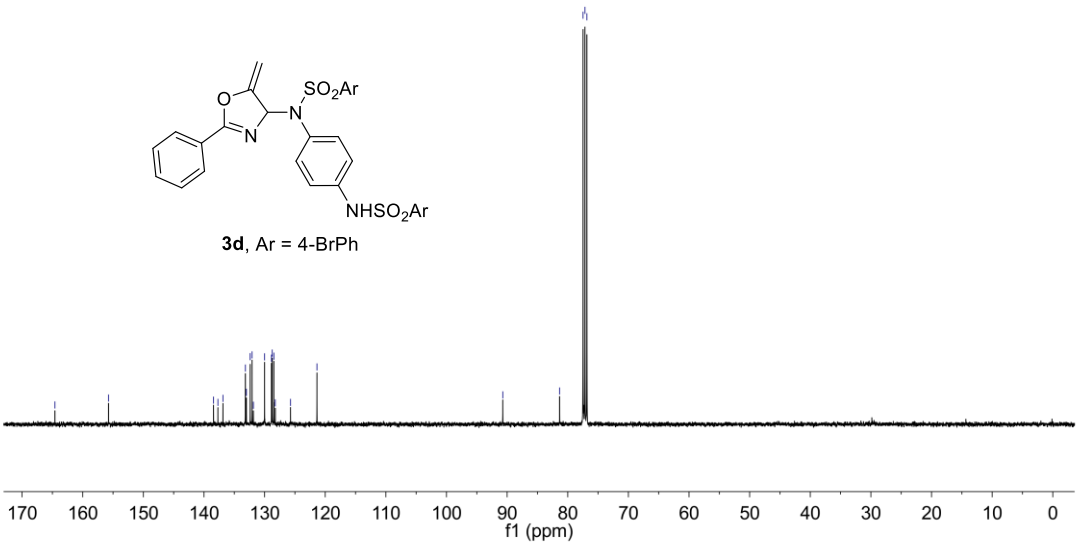


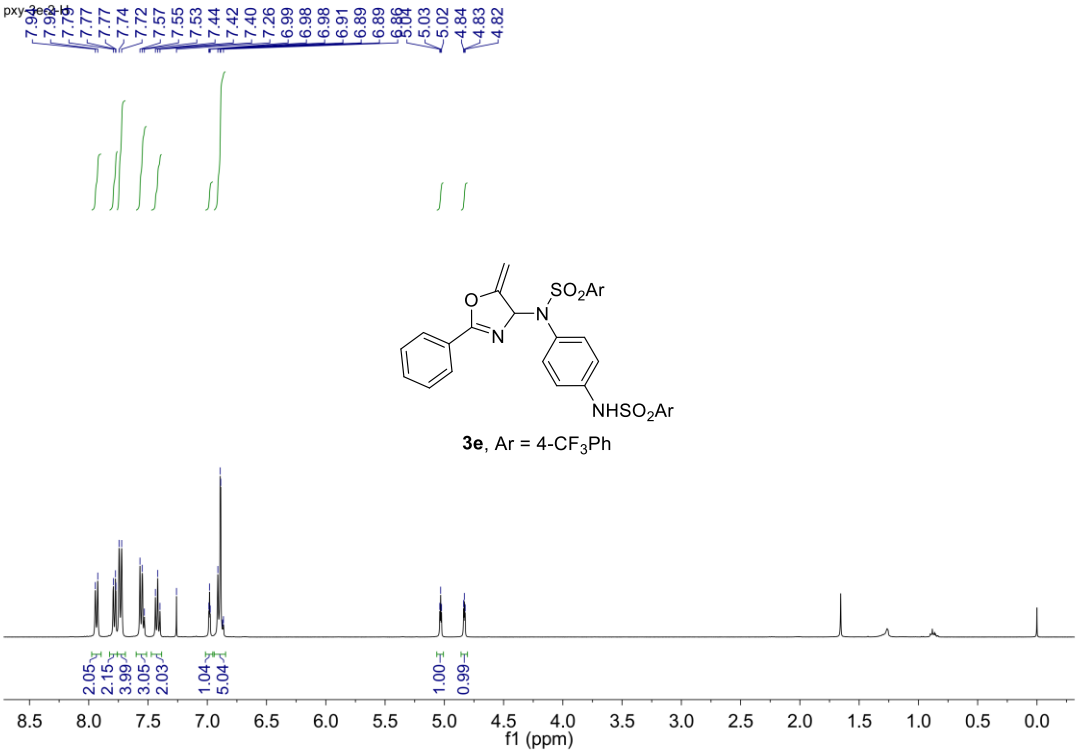
3d, Ar = 4-BrPh

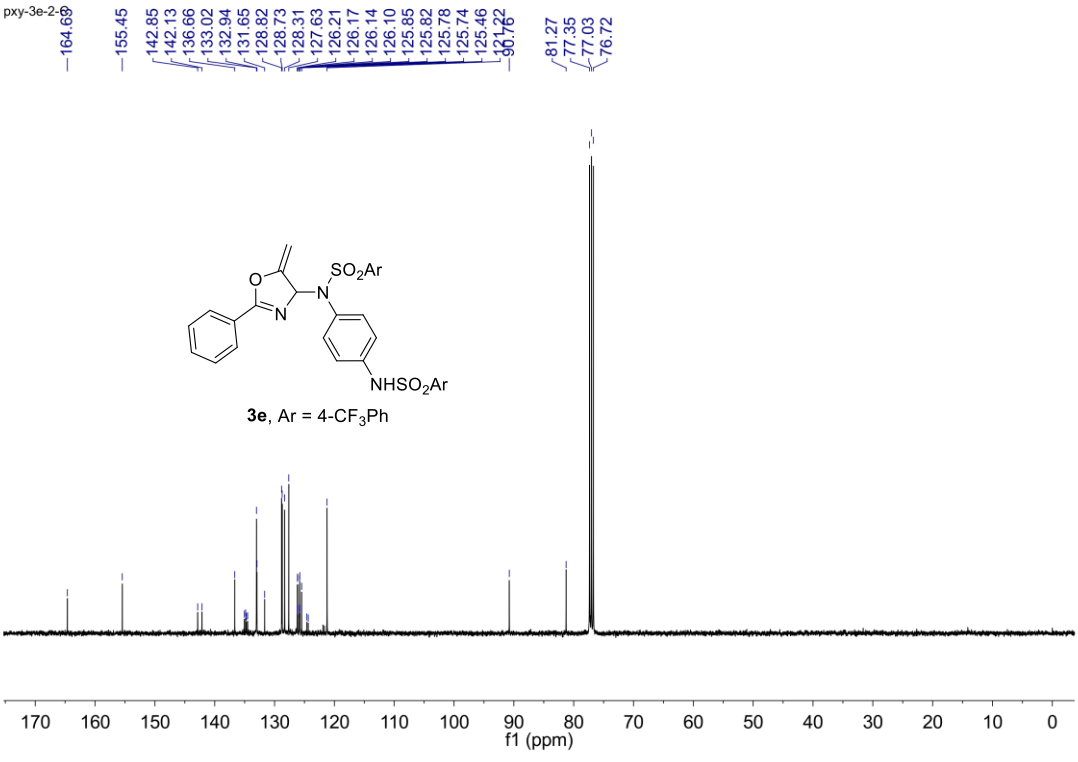


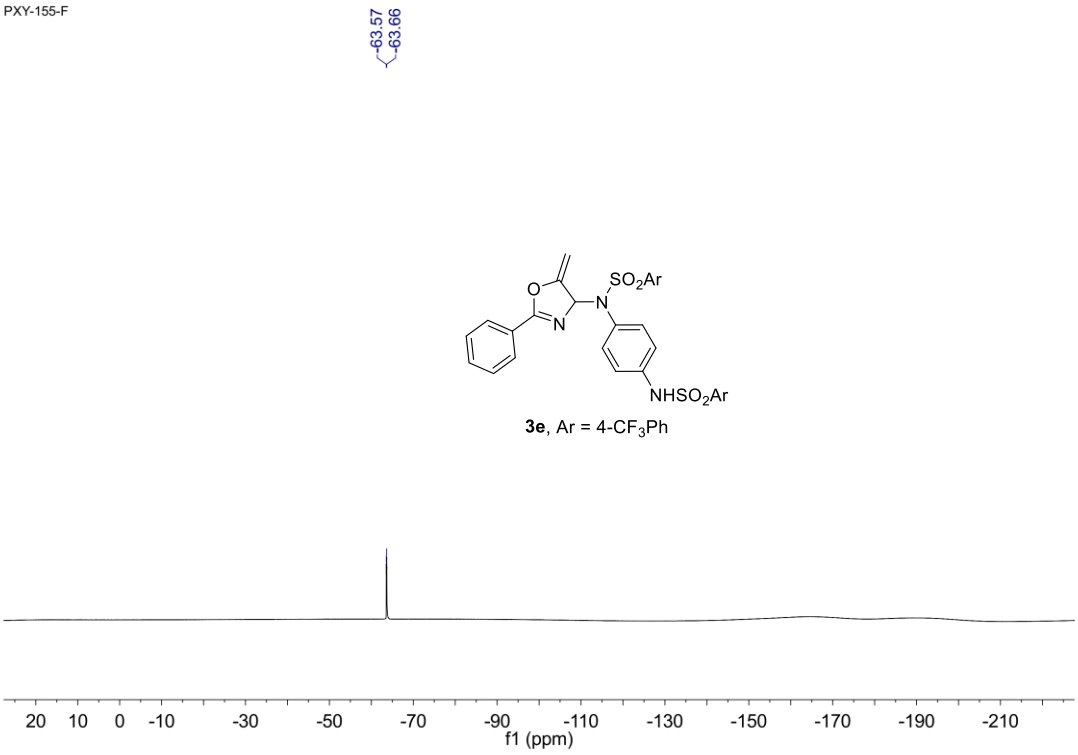


3d, Ar = 4-BrPh

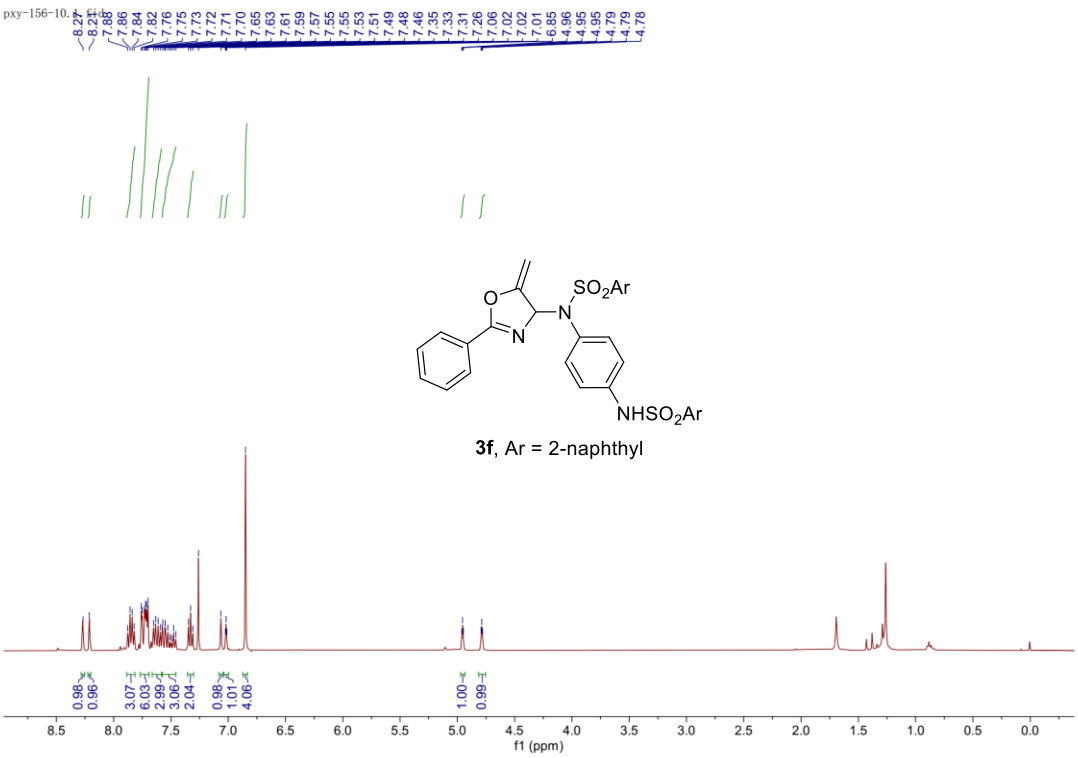



pxy-3e2-H
7.94
7.93
7.79
7.77
7.77
7.74
7.72
7.57
7.55
7.53
7.44
7.42
7.40
7.26
6.99
6.98
6.98
6.91
6.89
6.89
5.04
5.03
5.02
4.84
4.83
4.82
O
N
N
SO2Ar
NHSO2Ar
3e, Ar = 4-CF3Ph
2.05
2.15
3.99
3.05
2.03
1.04
5.04
1.00
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pxy-3e-2-C
164.69
155.45
142.85
142.13
136.66
133.02
132.94
131.65
128.82
128.73
128.31
127.63
126.21
126.17
126.14
126.10
125.85
125.82
125.78
125.74
125.46
121.22
90.76
81.27
77.35
77.03
76.72
O
N
N
SO2Ar
NHSO2Ar
3e, Ar = 4-CF3Ph
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

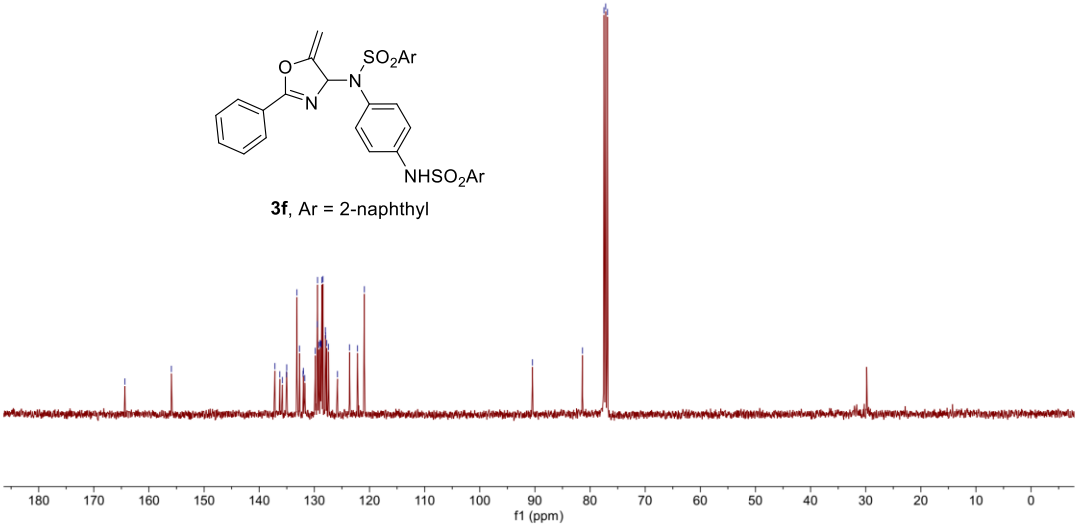


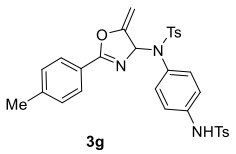
3e, Ar = 4-CF_3Ph



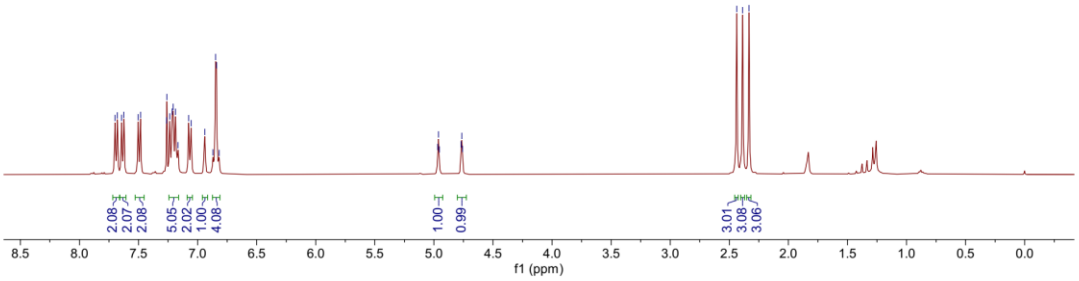
3f, Ar = 2-naphthyl

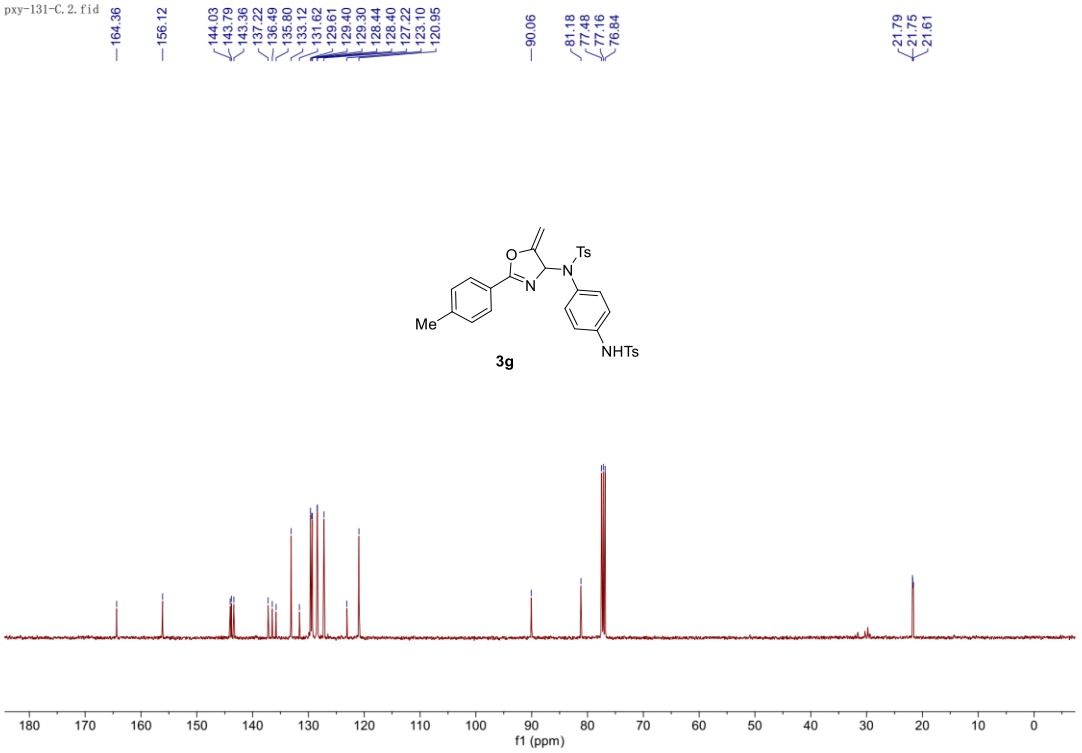
3f, Ar = 2-naphthyl

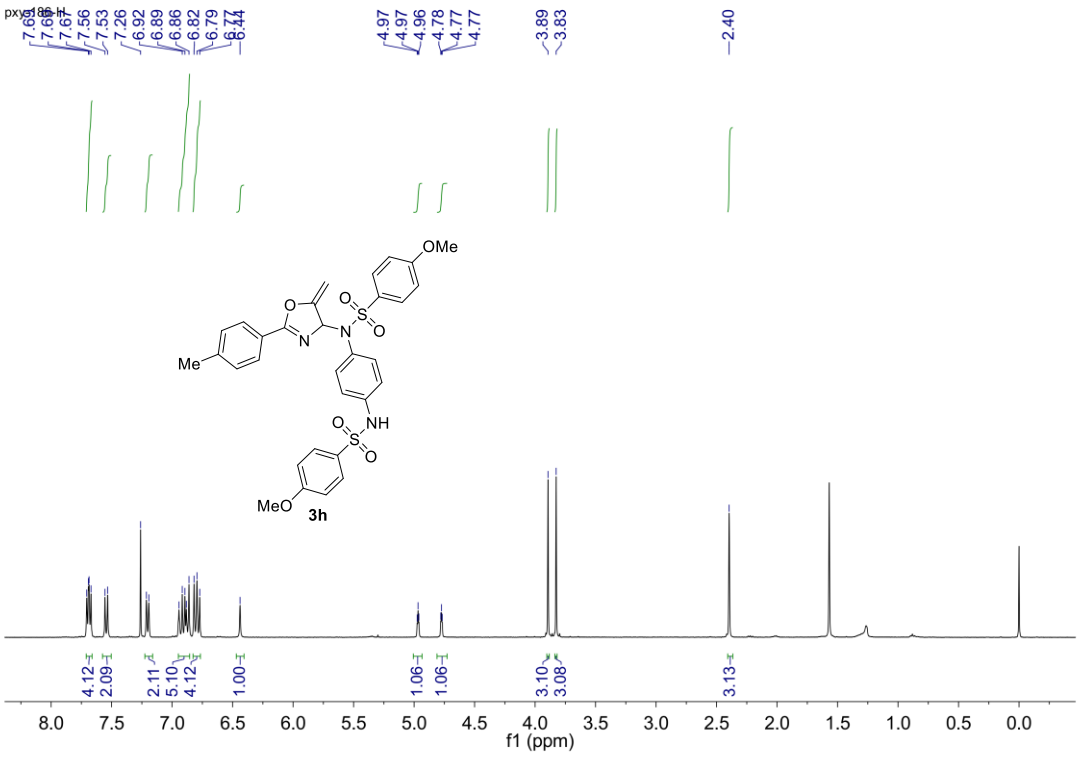


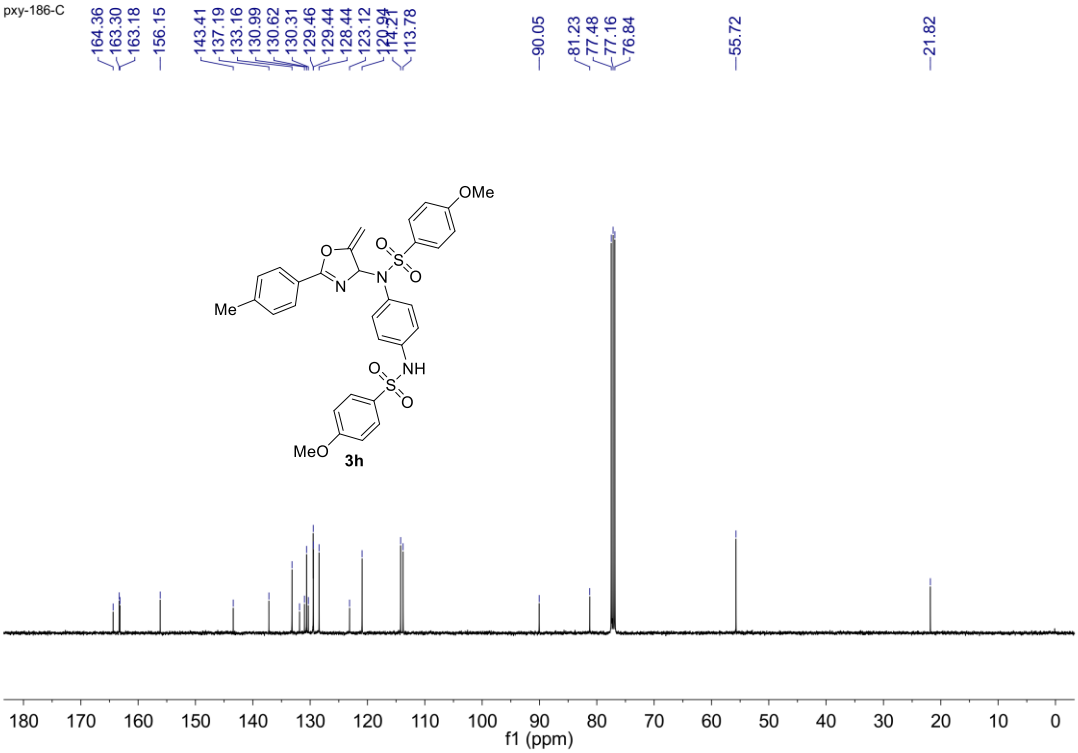


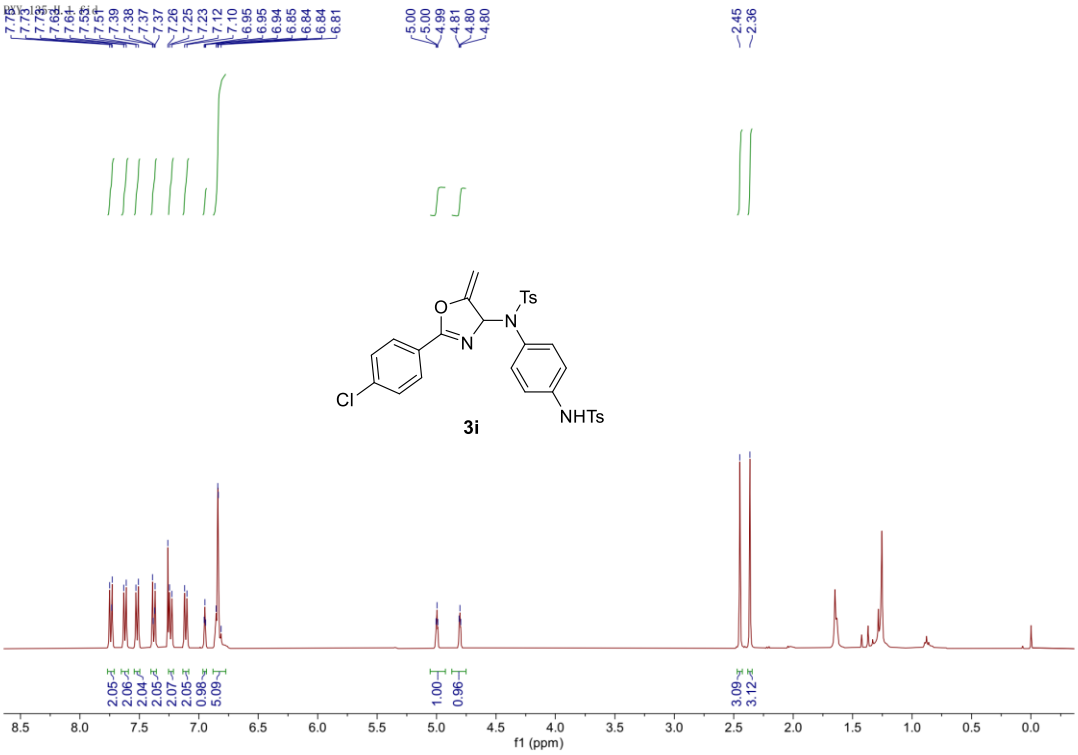
3g

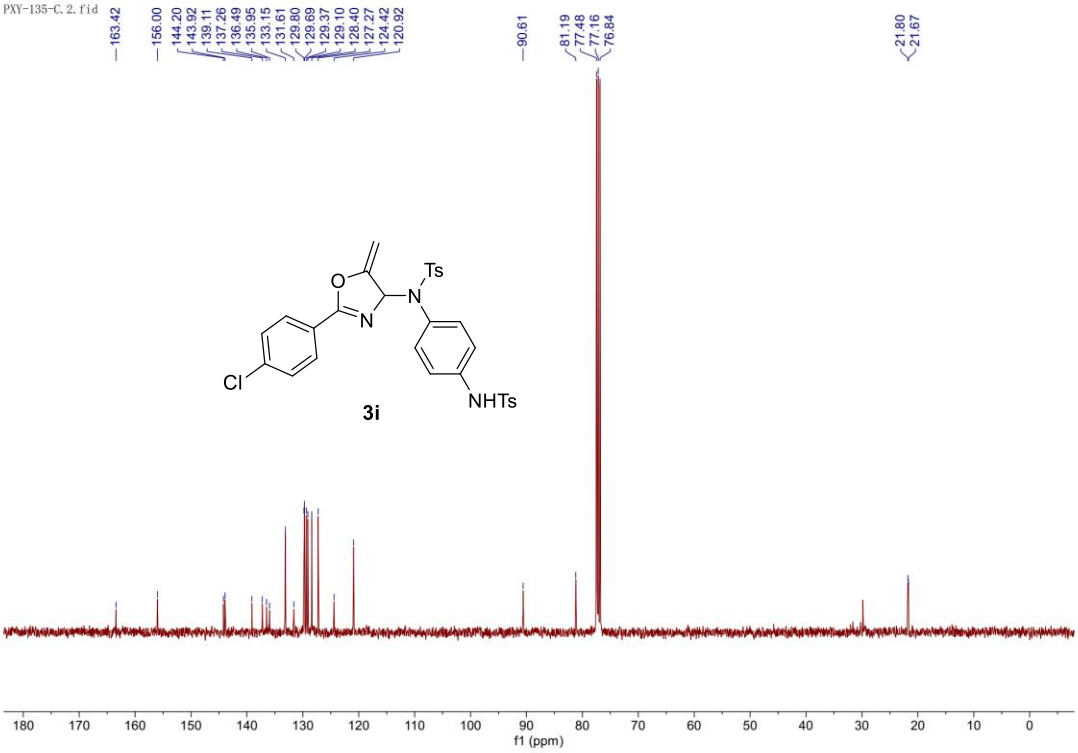


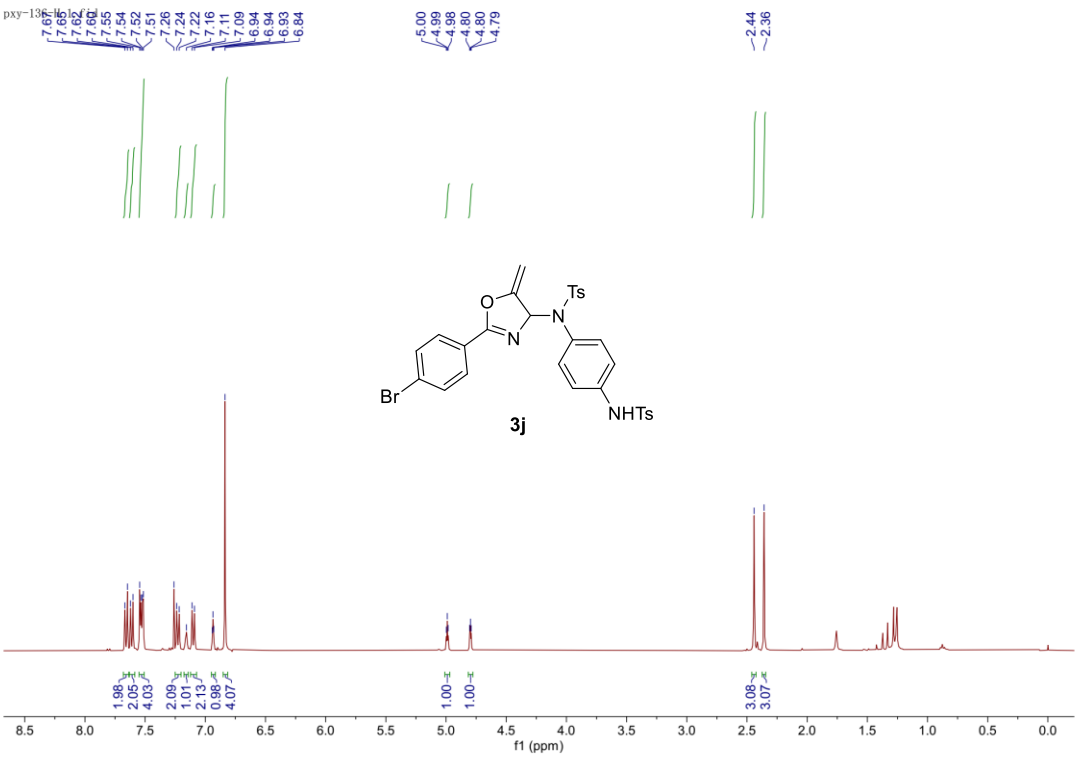

pxy-131-C.2.fid
164.36
156.12
144.03
143.79
143.36
137.22
136.49
135.80
133.12
131.62
129.61
129.40
129.30
128.44
128.40
127.22
123.10
120.95
90.06
81.18
77.48
77.16
76.84
21.79
21.75
21.61
Ts
N
O
N
Me
NHTs
3g
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

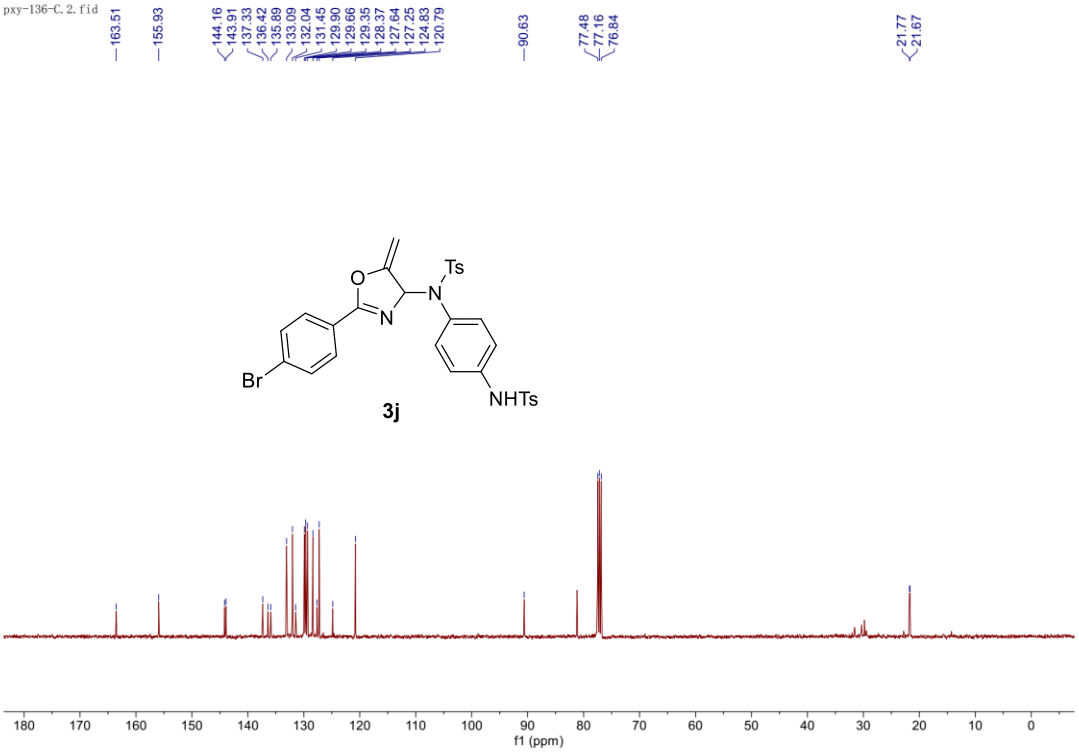

7.66
7.65
7.67
7.56
7.53
7.26
6.92
6.89
6.86
6.82
6.79
6.77
6.44
4.97
4.97
4.96
4.78
4.77
4.77
3.89
3.83
2.40
OMe
O
S
O
N
O
N
Me
NH
O
S
O
MeO
3h
4.12
2.09
2.11
5.10
4.12
1.00
1.06
1.06
3.10
3.08
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

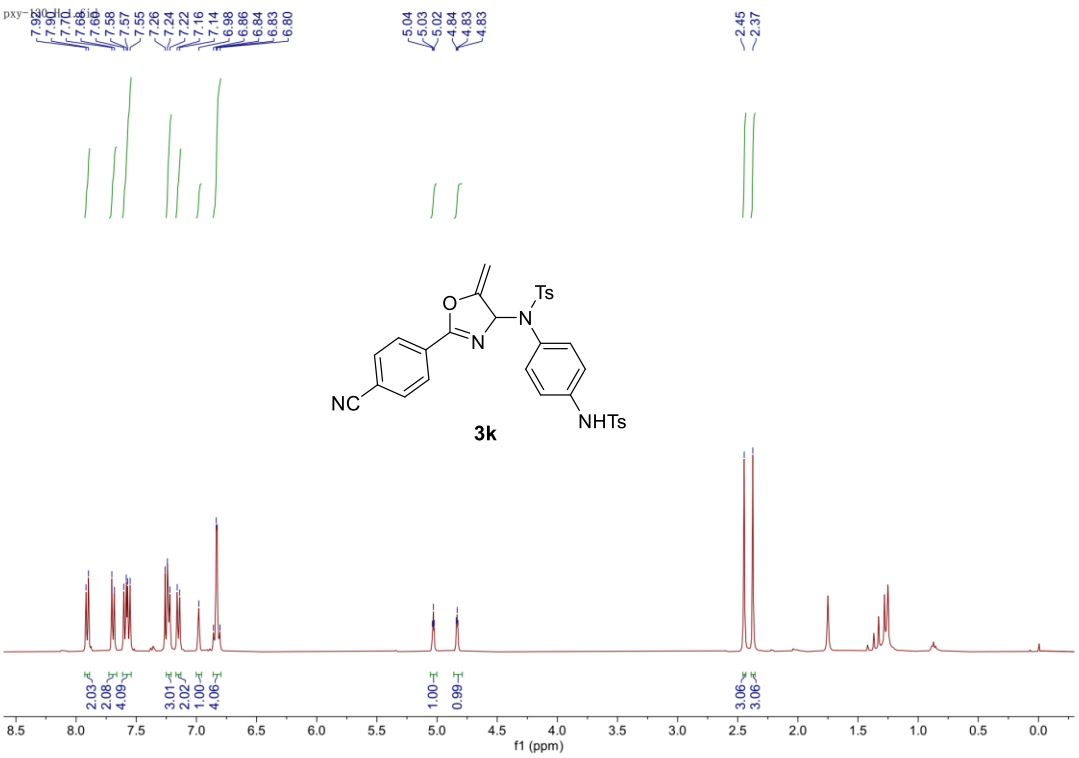

pxy-186-C
164.36
163.30
163.18
156.15
143.41
137.19
133.16
130.99
130.62
130.31
129.46
129.44
128.44
123.12
113.78
90.05
81.23
77.48
77.16
76.84
55.72
21.82
OMe
Me
NH
MeO
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

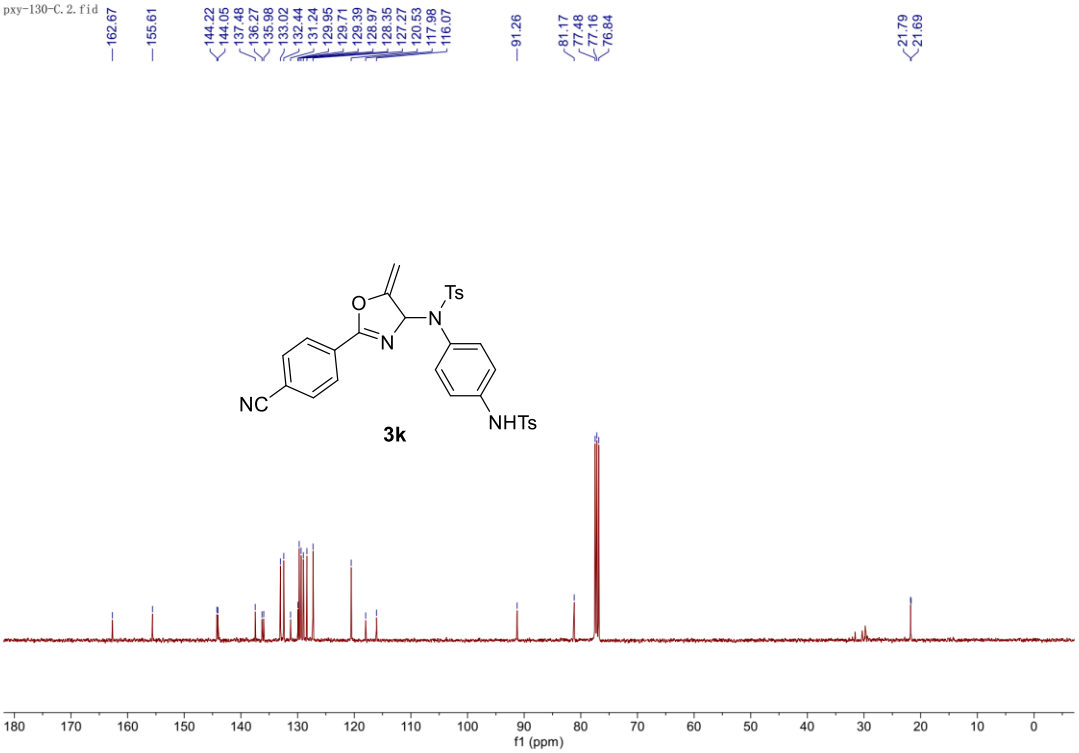

7.75
7.73
7.64
7.53
7.51
7.39
7.38
7.37
7.26
7.25
7.23
7.12
7.10
6.95
6.94
6.85
6.84
6.84
6.81
5.00
5.00
4.99
4.81
4.80
4.80
2.45
2.36
Ts
N
O
N
Cl
NHTs
3i
2.05
2.06
2.04
2.05
2.07
2.05
0.98
5.09
1.00
0.96
3.09
3.12
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

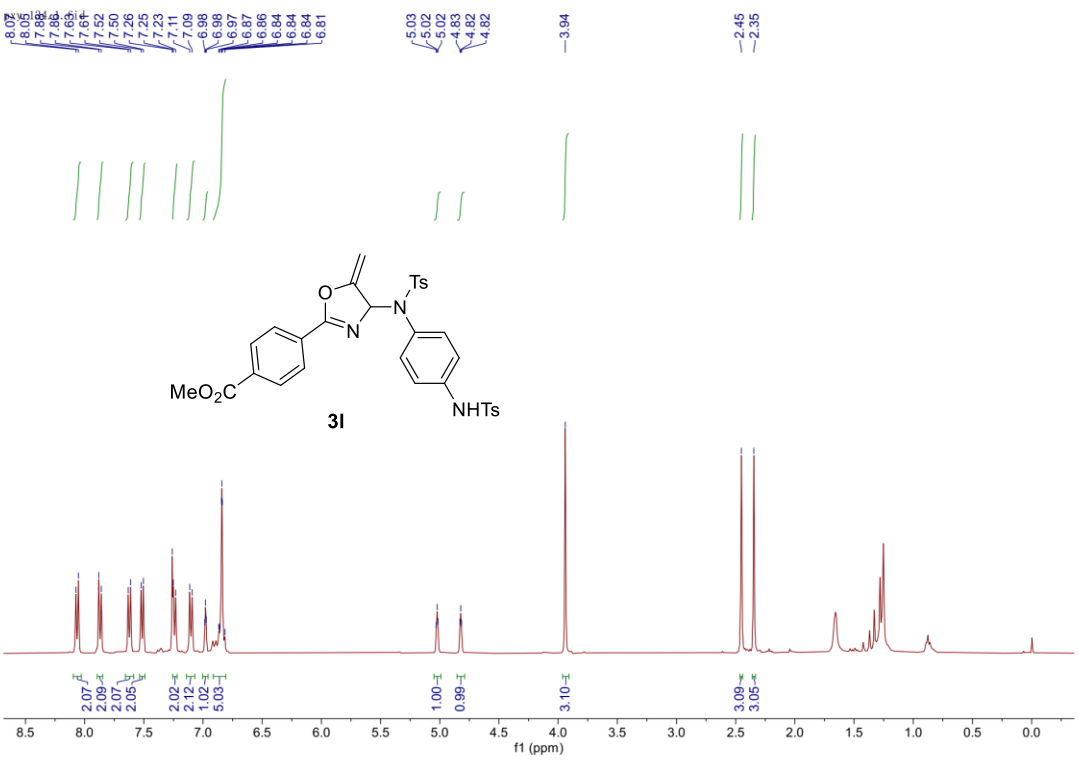

PXY-135-C.2.fid
163.42
156.00
144.20
143.92
139.11
137.26
136.49
135.95
133.15
131.61
129.80
129.69
129.37
129.10
128.40
127.27
124.42
120.92
90.61
81.19
77.48
77.16
76.84
21.80
21.67
Ts
N
O
N
Cl
NHTs
3i
f1 (ppm)

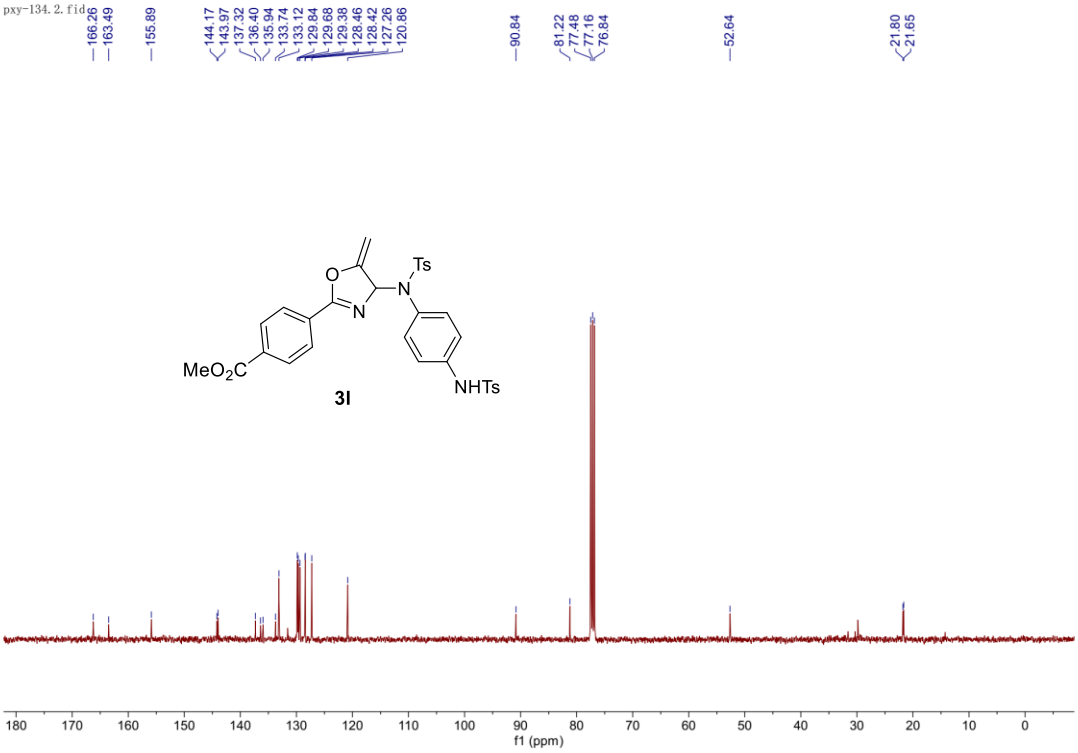

pxy-136-H.fid
7.67
7.65
7.62
7.60
7.55
7.54
7.52
7.51
7.26
7.24
7.22
7.16
7.11
7.09
6.94
6.94
6.93
6.84
5.00
4.99
4.98
4.80
4.80
4.79
2.44
2.36
Ts
N
O
N
Br
NHTs
3j
1.98
2.05
4.03
2.09
1.01
2.13
0.98
4.07
1.00
1.00
3.08
3.07
f1 (ppm)

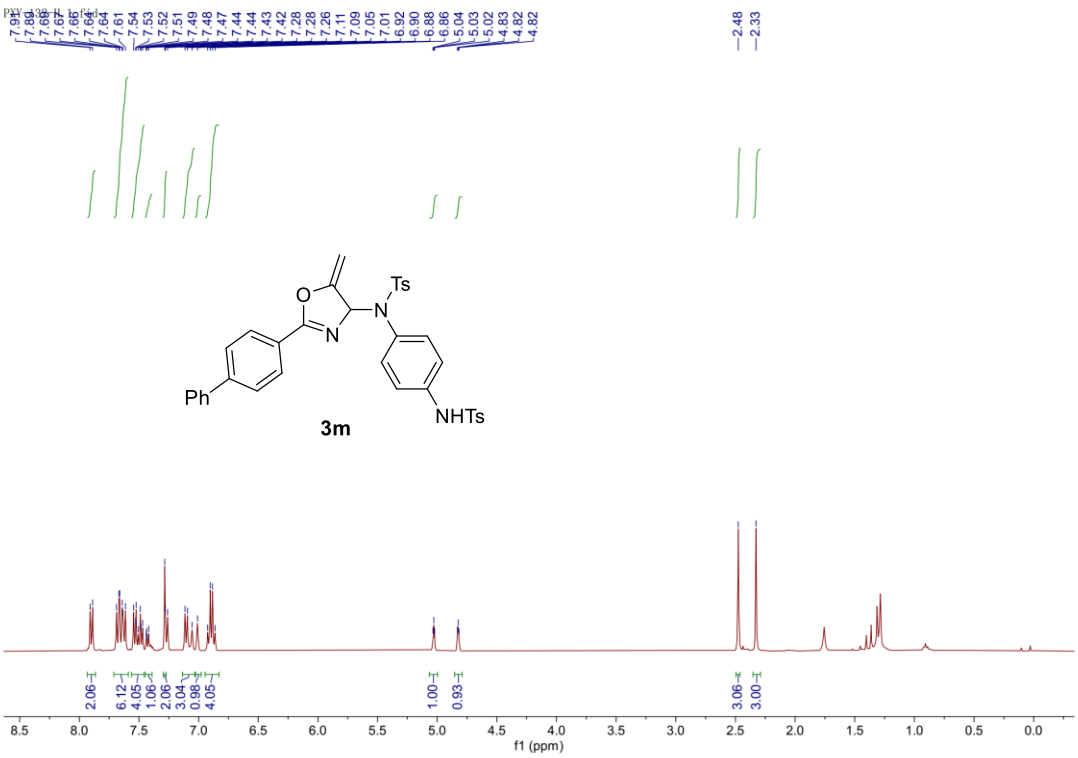

pxy-136-C.2.fid
163.51
155.93
144.16
143.91
137.33
136.42
135.89
133.09
132.04
131.45
129.90
129.66
129.35
128.37
127.64
127.25
124.83
120.79
90.63
77.48
77.16
76.84
21.77
21.67
Ts
N
O
N
Br
NHTs
3j
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

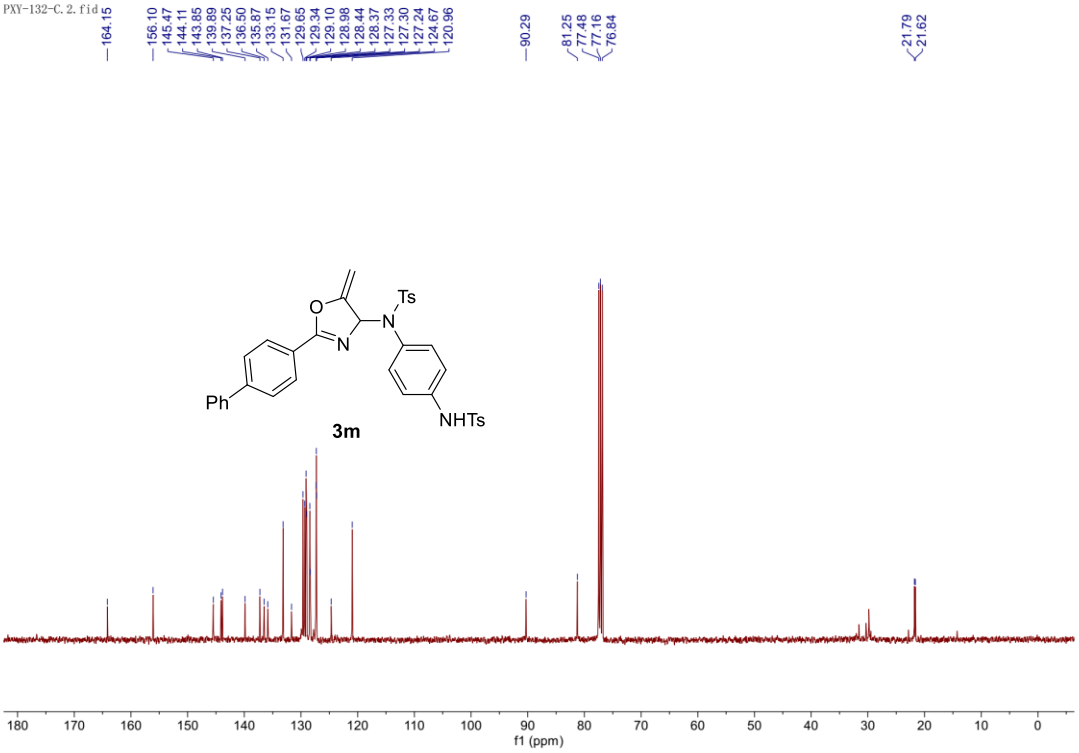

7.92
7.90
7.70
7.68
7.66
7.58
7.57
7.55
7.26
7.24
7.22
7.16
7.14
6.98
6.86
6.84
6.83
6.80
5.04
5.03
5.02
4.84
4.83
4.83
2.45
2.37
Ts
N
O
N
NC
NHTs
3k
2.03
2.08
4.09
3.01
2.02
1.00
4.06
1.00
0.99
3.06
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

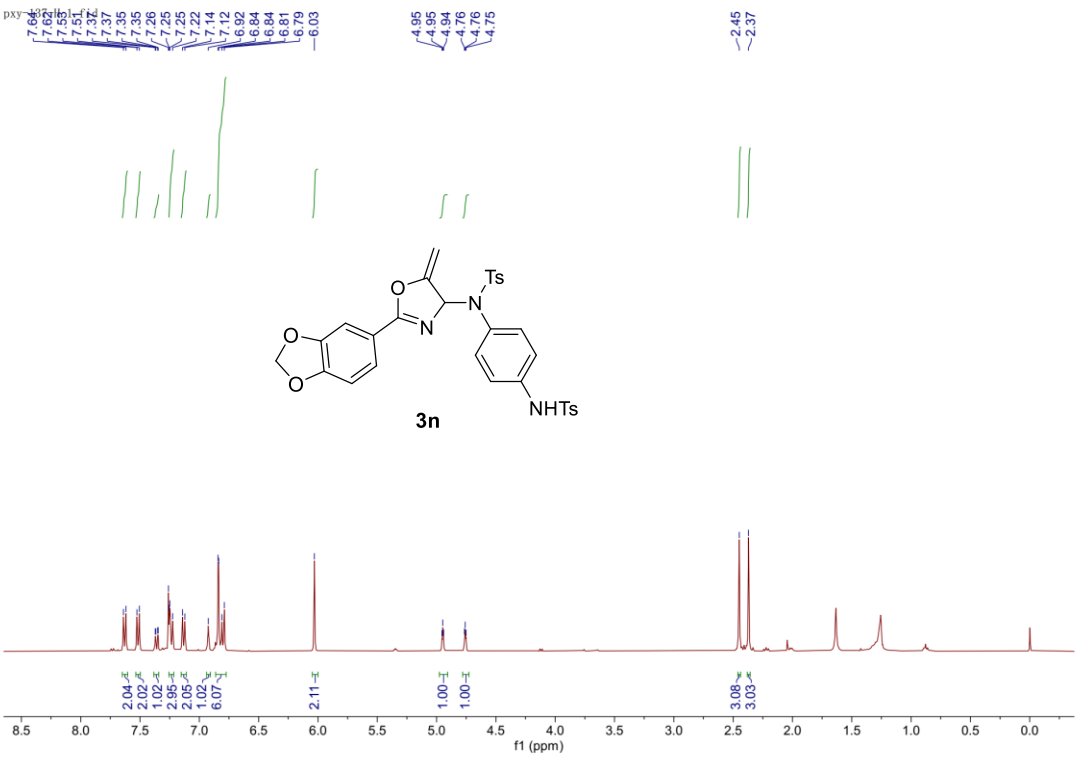

pxy-130-C.2.fid
162.67
155.61
144.22
144.05
137.48
136.27
135.98
133.02
132.44
131.24
129.95
129.71
129.39
128.97
128.35
127.27
120.53
117.98
116.07
91.26
81.17
77.48
77.16
76.84
21.79
21.69
Ts
N
O
N
NC
NHTs
3k
f1 (ppm)

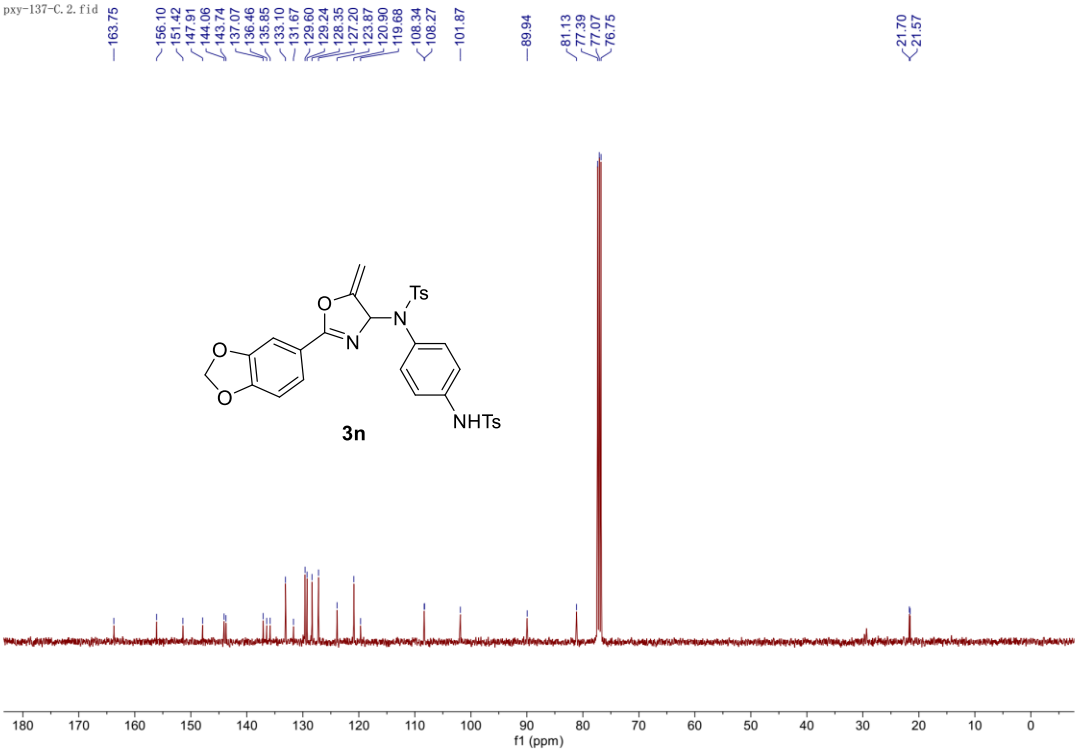

8.07
8.05
7.88
7.86
7.65
7.61
7.52
7.50
7.26
7.25
7.23
7.11
7.09
6.98
6.97
6.87
6.86
6.84
6.84
6.84
6.81
5.03
5.02
5.02
4.83
4.82
4.82
3.94
2.45
2.35
Ts
N
O
N
MeO2C
NHTs
3l
2.07
2.09
2.07
2.05
2.02
2.12
1.02
5.03
1.00
0.99
3.10
3.09
3.05
f1 (ppm)

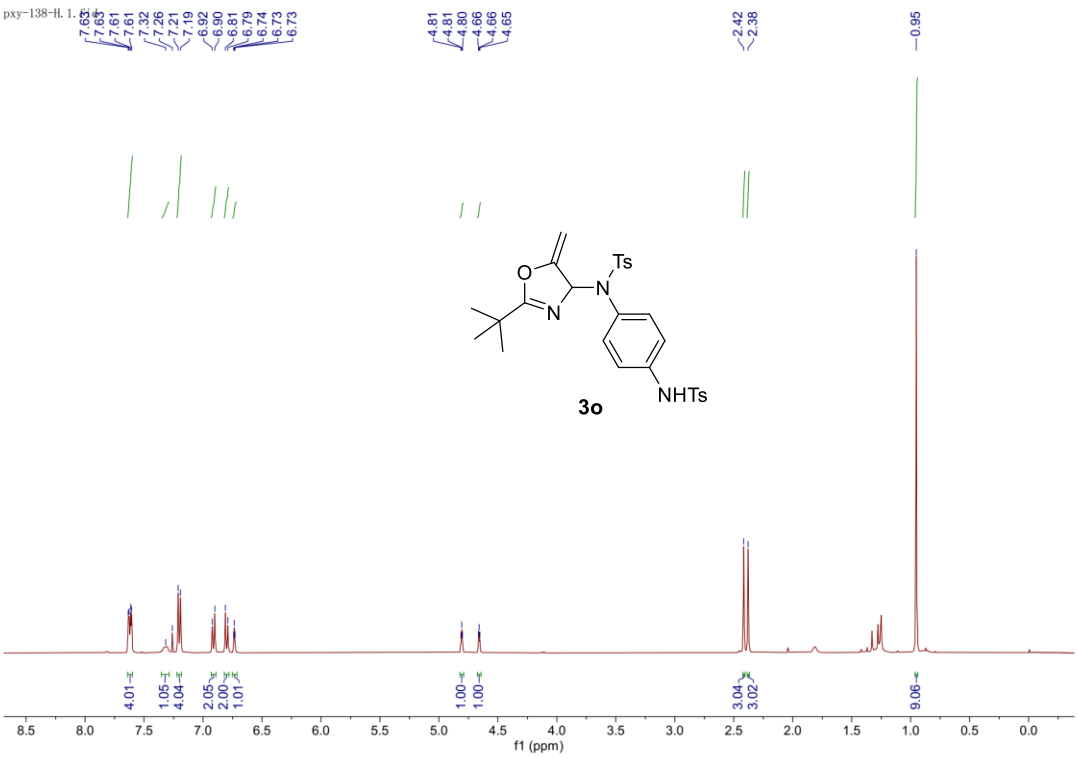

pxy-134.2.fid
166.26
163.49
155.89
144.17
143.97
137.32
136.40
135.94
133.74
133.12
129.84
129.68
129.38
128.46
128.42
127.26
120.86
90.84
81.22
77.48
77.16
76.84
52.64
21.80
21.65
Ts
N
O
N
MeO2C
NHTs
3l
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

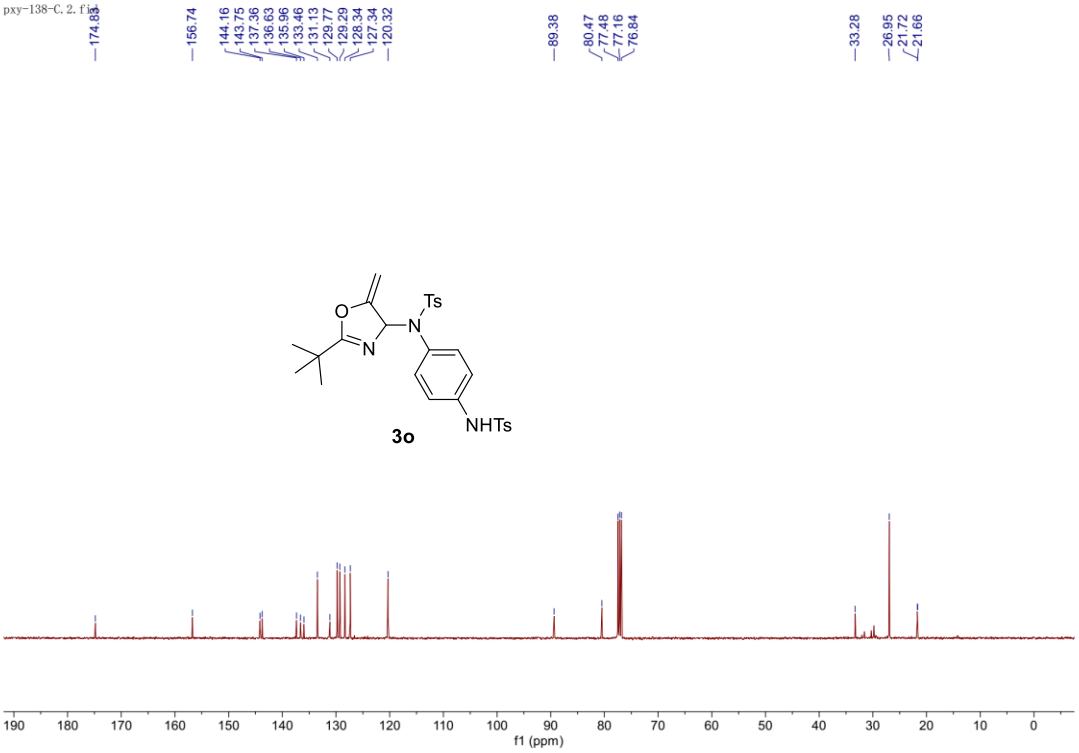

7.91
7.89
7.68
7.67
7.66
7.64
7.64
7.61
7.54
7.53
7.52
7.51
7.49
7.48
7.47
7.44
7.44
7.43
7.42
7.28
7.28
7.26
7.11
7.09
7.05
7.01
6.92
6.90
6.88
6.86
5.04
5.03
5.02
4.83
4.82
4.82
2.48
2.33
Ts
N
O
N
Ph
NHTs
3m
2.06
6.12
4.05
1.06
2.06
3.04
0.98
4.05
1.00
0.93
3.06
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

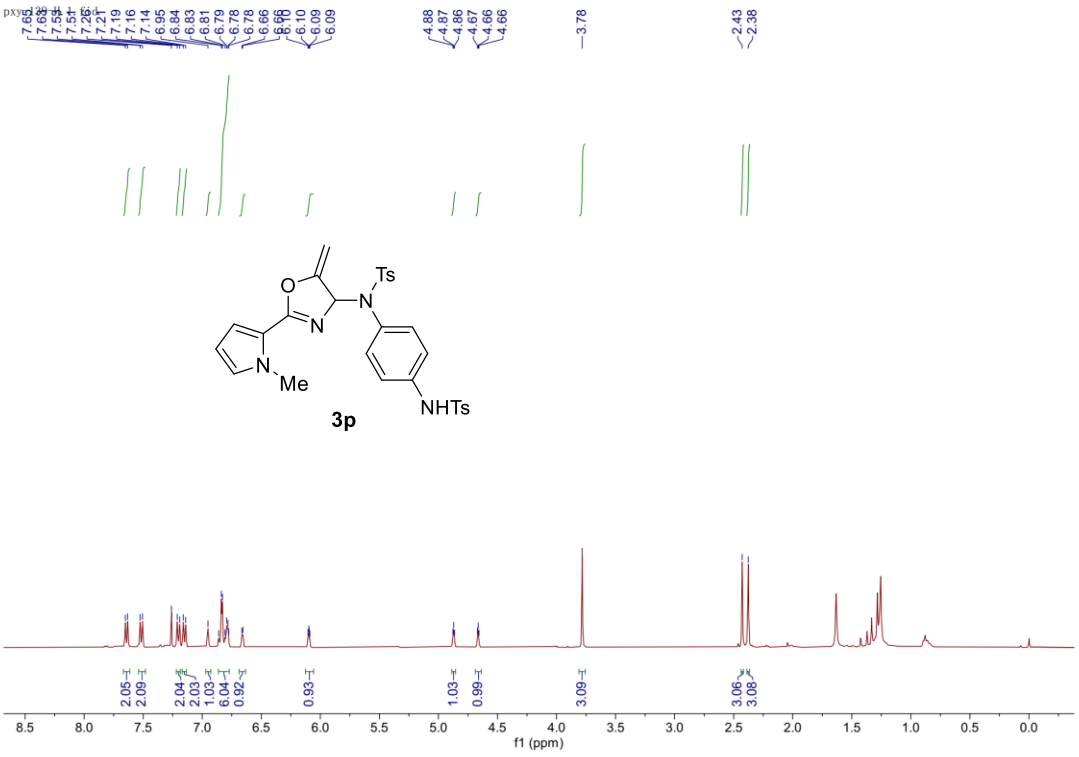

PXY-132-C.2.fid
164.15
156.10
145.47
144.11
143.85
139.89
137.25
136.50
135.87
133.15
131.67
129.65
129.34
129.10
128.98
128.44
128.37
127.33
127.30
127.24
124.67
120.96
90.29
81.25
77.48
77.16
76.84
21.79
21.62
Ts
N
O
N
Ph
NHTs
3m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

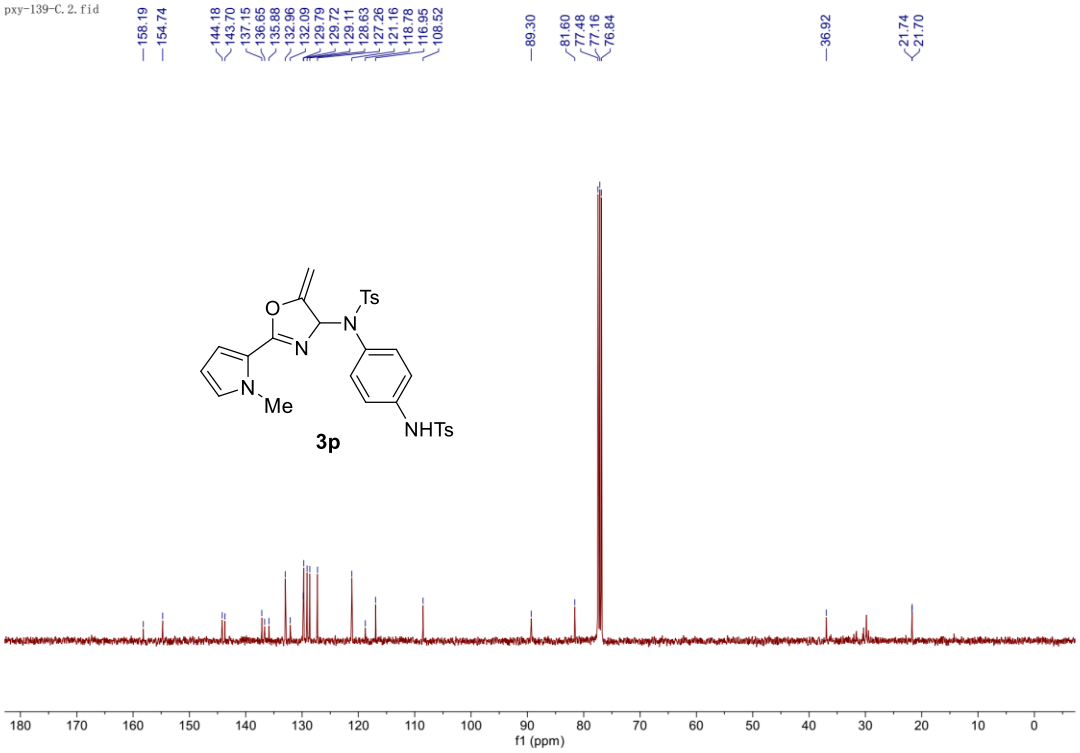

7.64
7.62
7.53
7.51
7.37
7.35
7.26
7.25
7.22
7.14
7.12
6.92
6.84
6.84
6.81
6.79
6.03
4.95
4.95
4.94
4.76
4.76
4.75
2.45
2.37
Ts
N
O
O
O
N
NHTs
3n
2.04
2.02
1.02
2.95
2.05
1.02
6.07
2.11
1.00
1.00
3.08
3.03
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

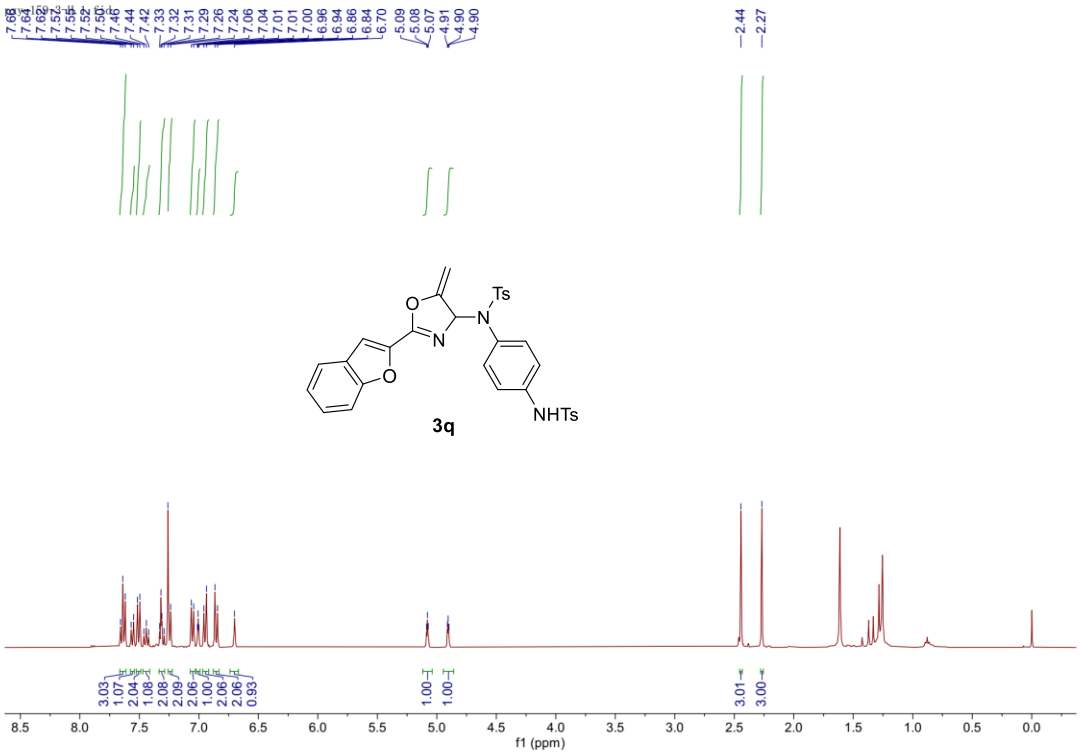

pxy-137-C.2.fid
163.75
156.10
151.42
147.91
144.06
143.74
137.07
136.46
135.85
133.10
131.67
129.60
129.24
128.35
127.20
123.87
120.90
119.68
108.34
108.27
101.87
89.94
81.13
77.39
77.07
76.75
21.70
21.57
Ts
N
O
O
O
N
NHTs
3n
f1 (ppm)

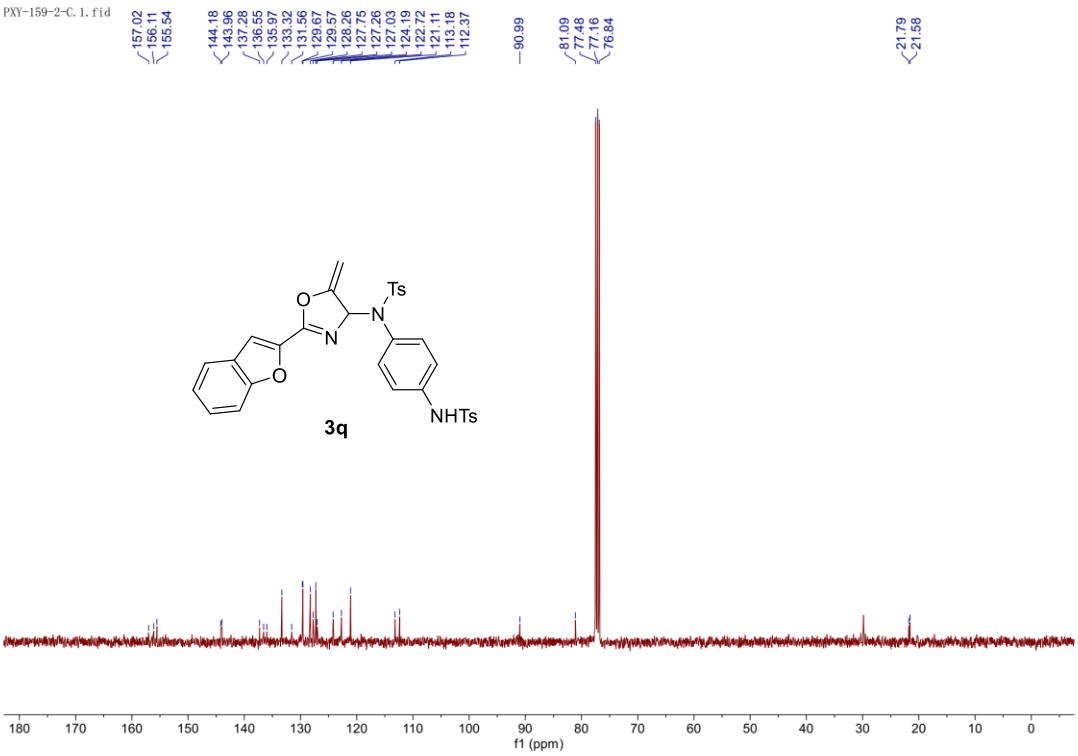

pxy-138-H.1.fid
7.63
7.63
7.61
7.61
7.32
7.26
7.21
7.19
6.92
6.90
6.81
6.79
6.74
6.73
6.73
4.81
4.81
4.80
4.66
4.66
4.65
2.42
2.38
0.95
Ts
N
O
N
NHTs
3o
4.01
1.05
4.04
2.05
2.00
1.01
1.00
1.00
3.04
3.02
9.06
f1 (ppm)

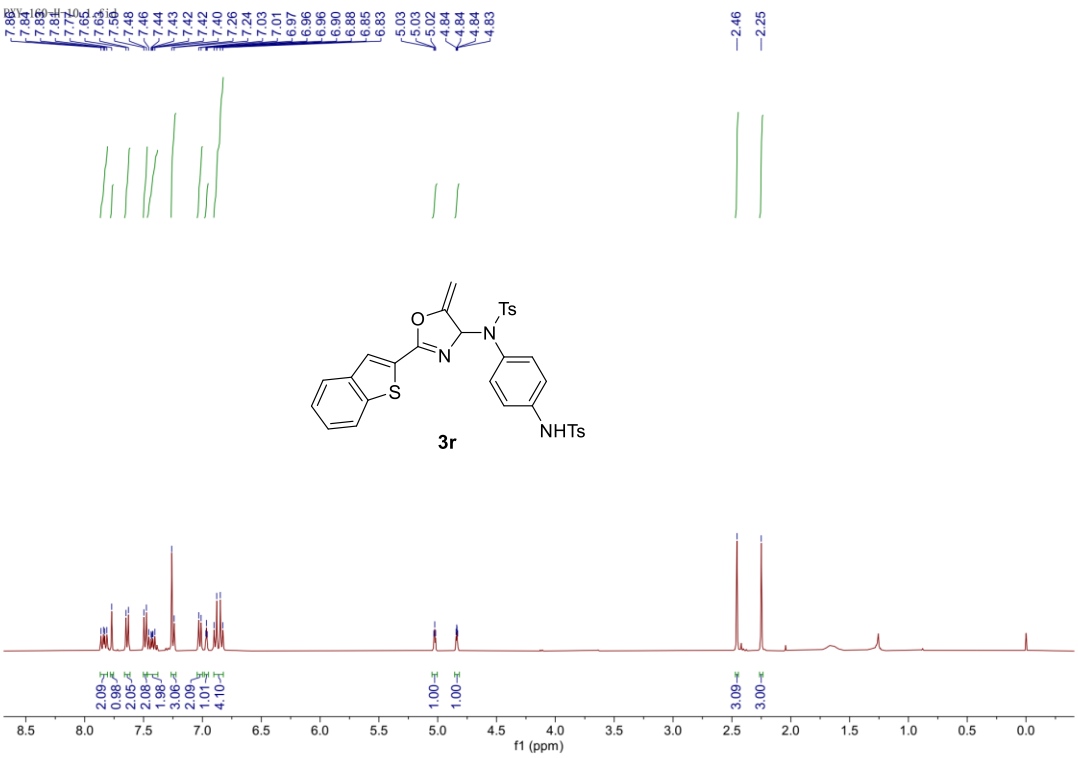

pxy-138-C. 2. fid
174.83
156.74
144.16
143.75
137.36
136.63
135.96
133.46
131.13
129.77
129.29
128.34
127.34
120.32
89.38
80.47
77.48
77.16
76.84
33.28
26.95
21.72
21.66
Ts
N
O
N
NHTs
3o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

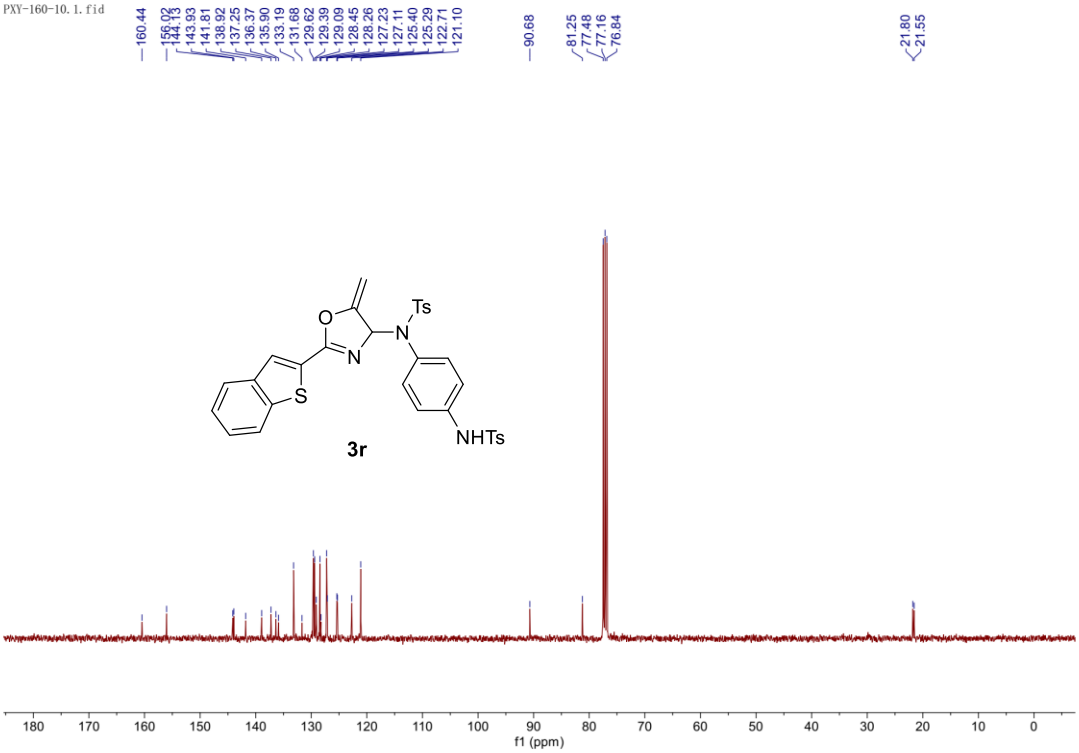

7.61
7.63
7.53
7.51
7.26
7.21
7.19
7.16
7.14
6.95
6.84
6.83
6.81
6.79
6.78
6.78
6.66
6.10
6.09
6.09
4.88
4.87
4.86
4.67
4.66
4.66
3.78
2.43
2.38
Ts
N
O
N
N
Me
NHTs
3p
2.05
2.09
2.04
2.03
1.03
6.04
0.92
0.93
1.03
0.99
3.09
3.06
3.08
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

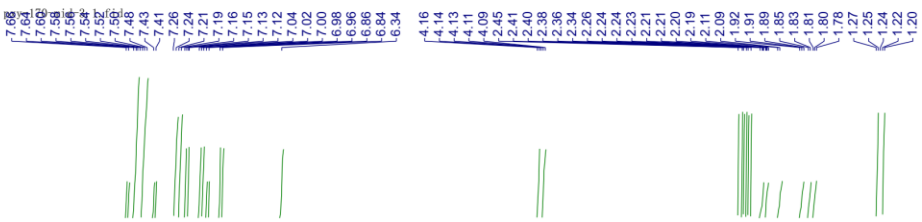

pxy-139-C.2.fid
158.19
154.74
144.18
143.70
137.15
136.65
135.88
132.96
132.09
129.79
129.72
129.11
128.63
127.26
121.16
118.78
116.95
108.52
89.30
81.60
77.48
77.16
76.84
36.92
21.74
21.70
Ts
N
O
N
N
Me
NHTs
3p
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

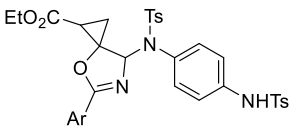

7.68
7.64
7.62
7.52
7.50
7.46
7.44
7.42
7.33
7.32
7.31
7.29
7.26
7.24
7.06
7.04
7.01
7.01
7.00
6.96
6.94
6.86
6.84
6.70
5.09
5.08
5.07
4.91
4.90
4.90
2.44
2.27
Ts
N
O
N
O
NHTs
3q
3.03
1.07
2.04
1.08
2.08
2.09
2.06
1.00
1.06
2.06
0.93
1.00
1.00
3.01
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


PXY-159-2-C.1.fid
157.02
156.11
155.54
144.18
143.96
137.28
136.55
135.97
133.32
131.56
129.67
129.57
128.26
127.75
127.26
127.03
124.19
122.72
121.11
113.18
112.37
90.99
81.09
77.48
77.16
76.84
21.79
21.58
Ts
N
O
N
O
NHTs
3q
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

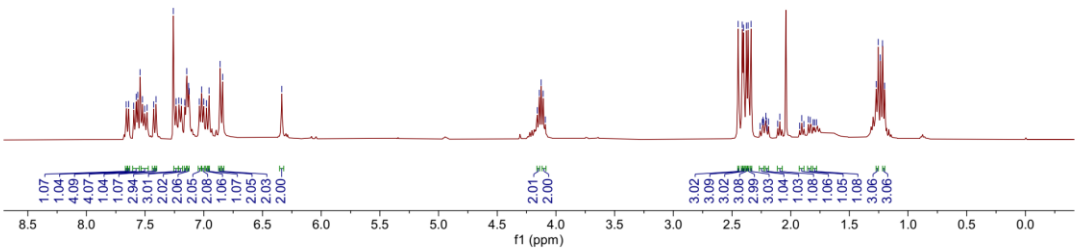

7.85
7.84
7.82
7.81
7.77
7.65
7.63
7.56
7.48
7.46
7.44
7.43
7.42
7.40
7.26
7.24
7.03
7.01
6.97
6.96
6.96
6.90
6.88
6.85
6.83
5.03
5.03
5.02
4.84
4.84
4.84
4.83
2.46
2.25
Ts
N
O
N
S
NHTs
3r
2.09
0.98
2.05
2.08
1.98
3.06
2.09
1.01
4.10
1.00
1.00
3.09
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

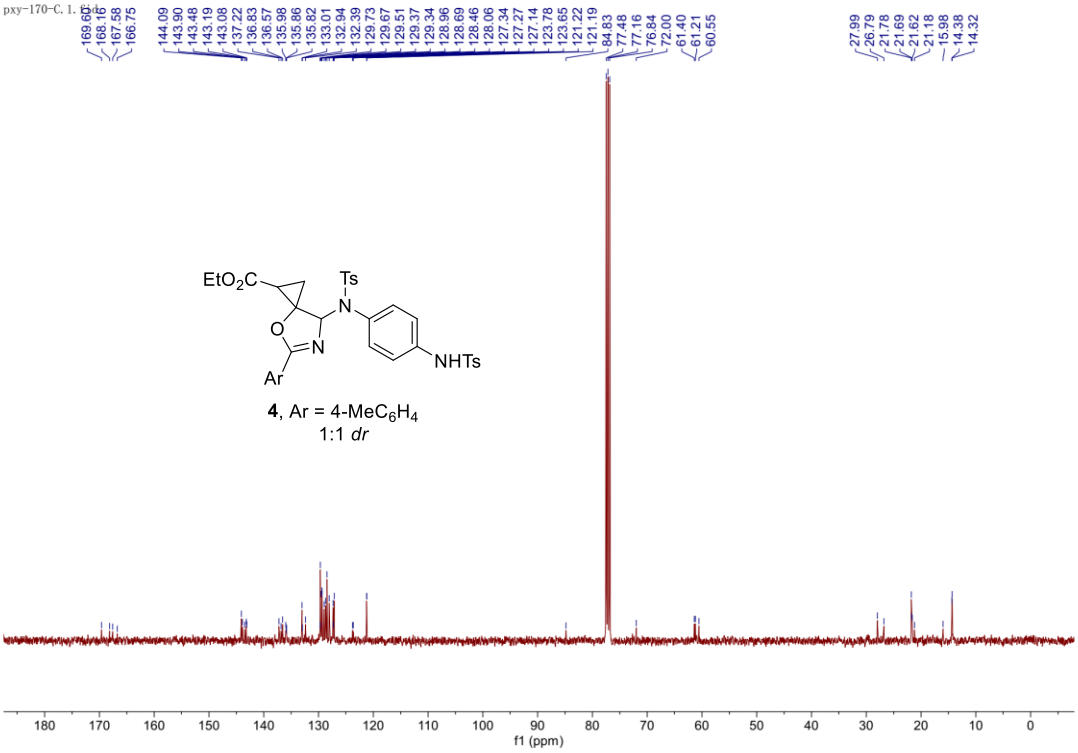


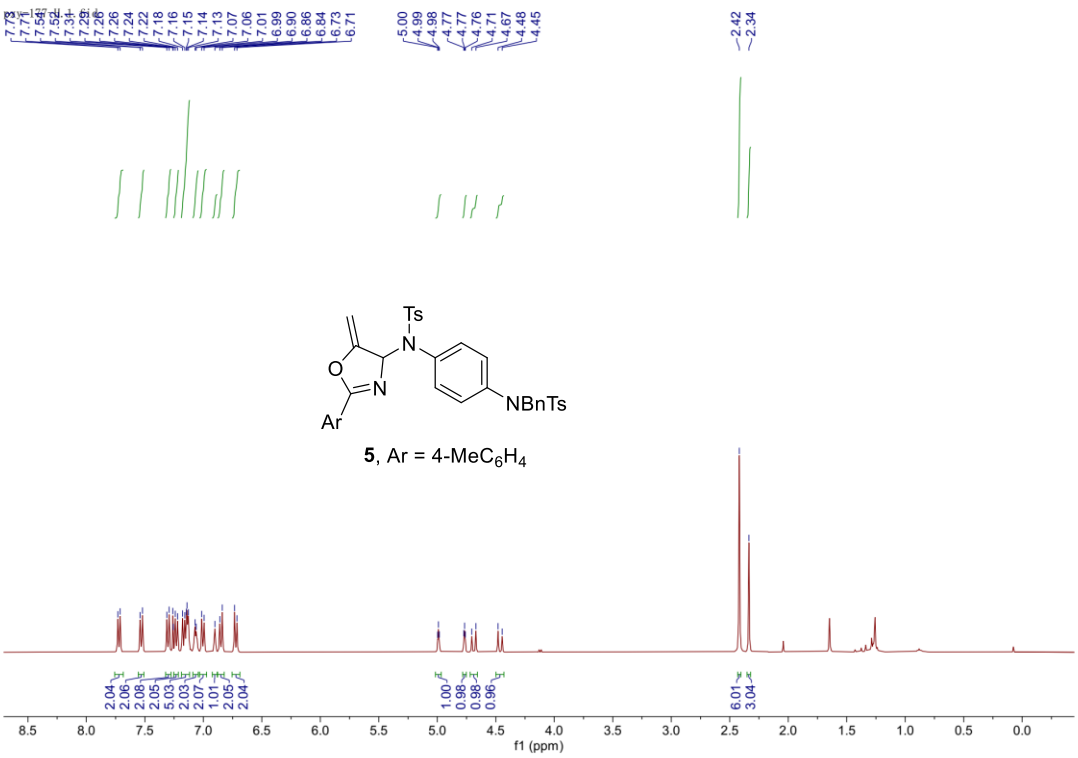


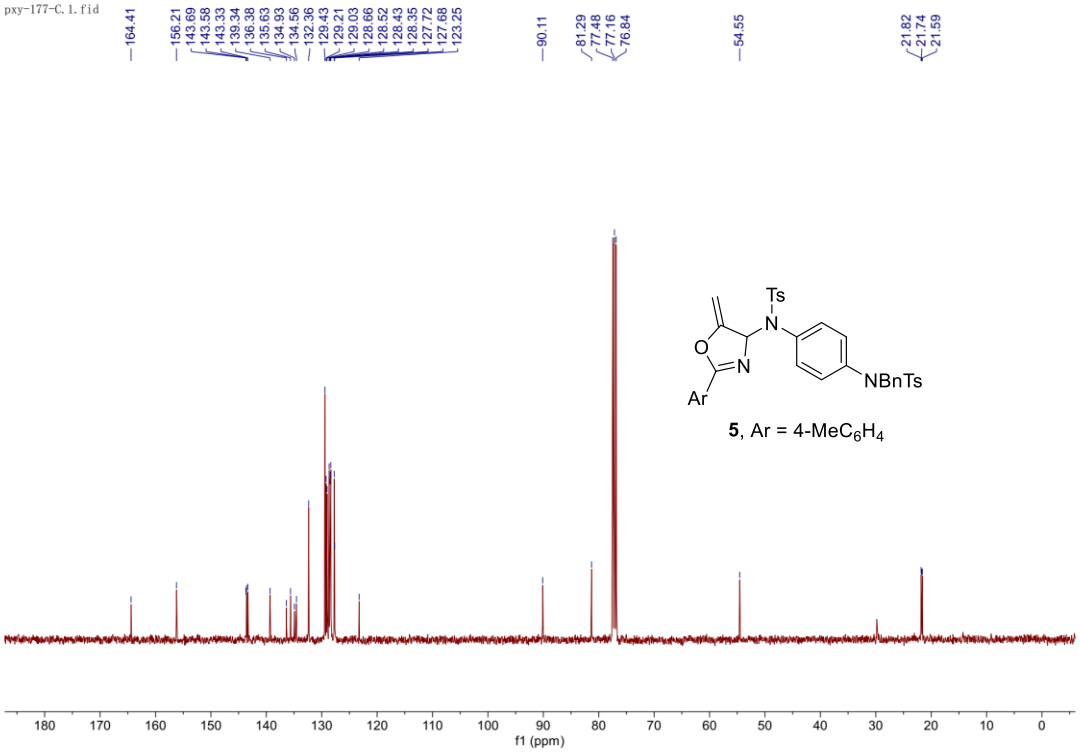


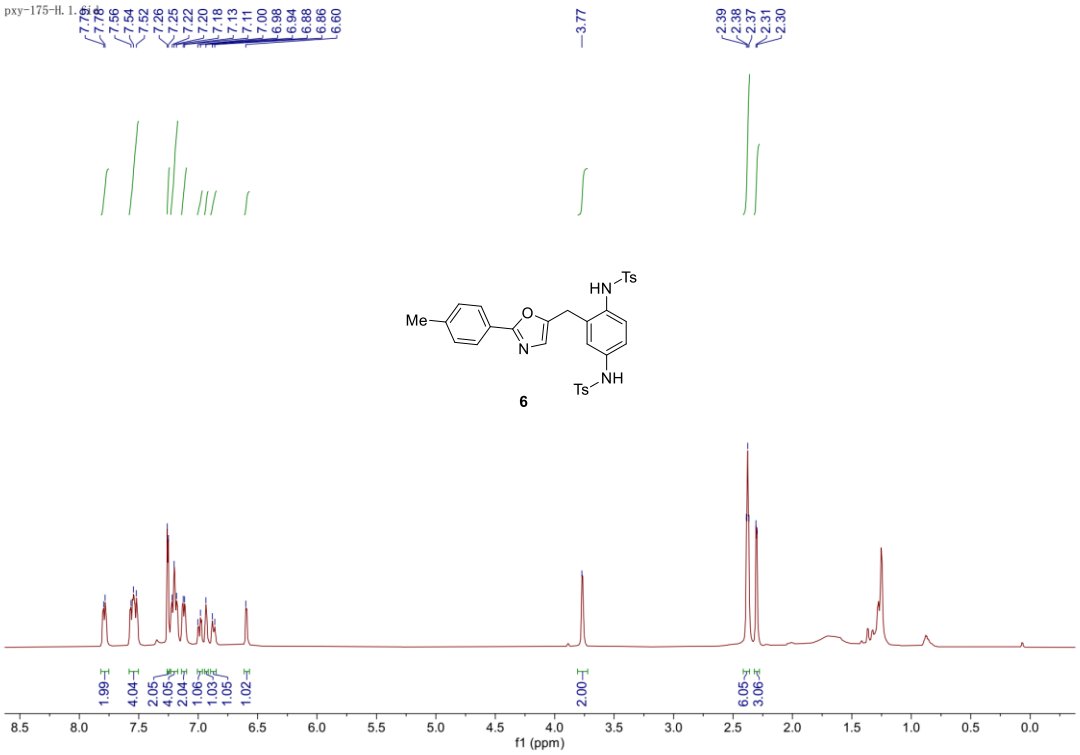
4, Ar = 4-MeC_6H_4
1:1 *dr*

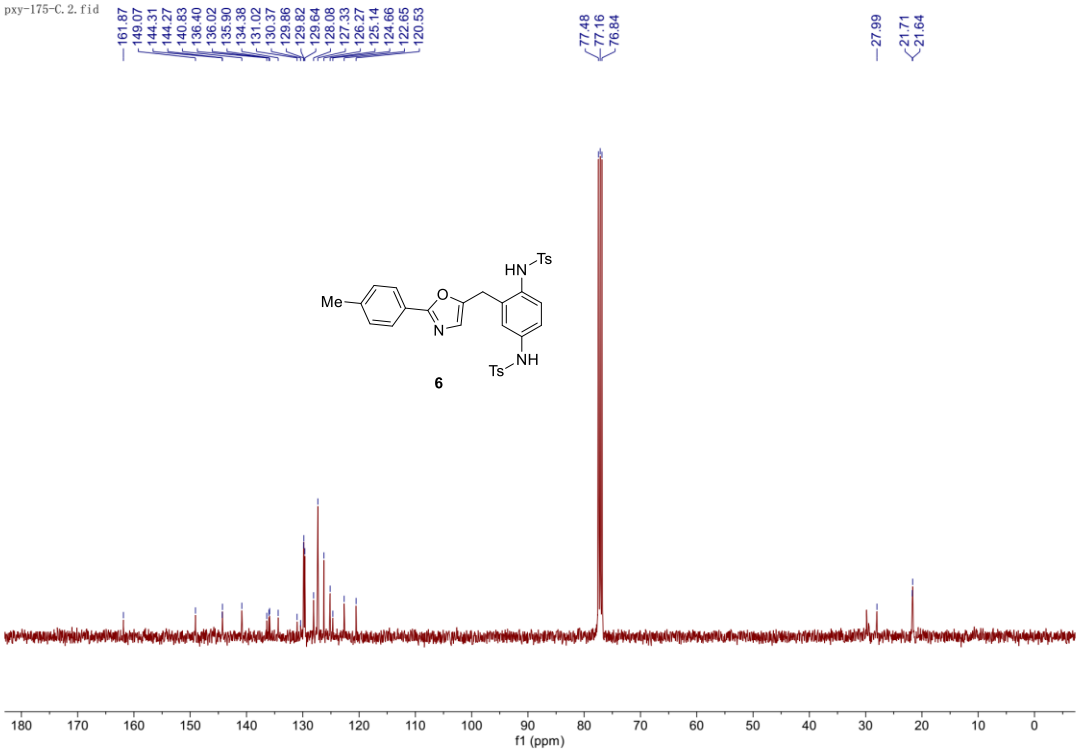


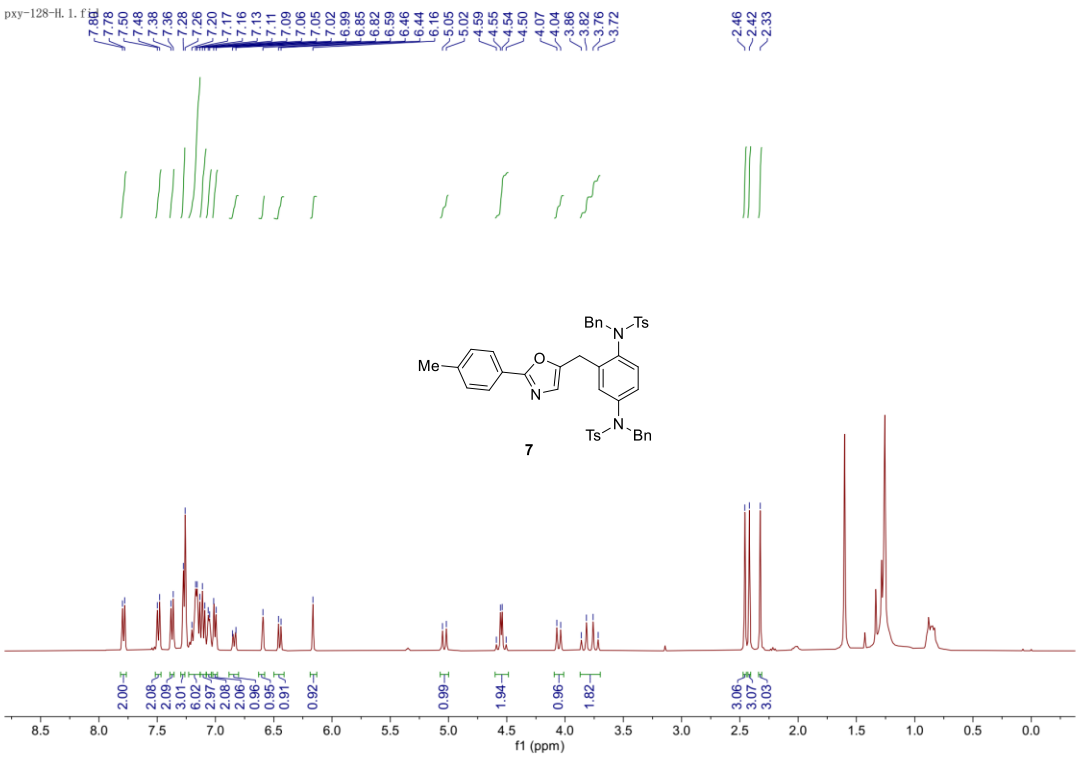

EtO2C
Ts
N
O
N
Ar
NHTs
4, Ar = 4-MeC6H4
1:1 dr
f1 (ppm)

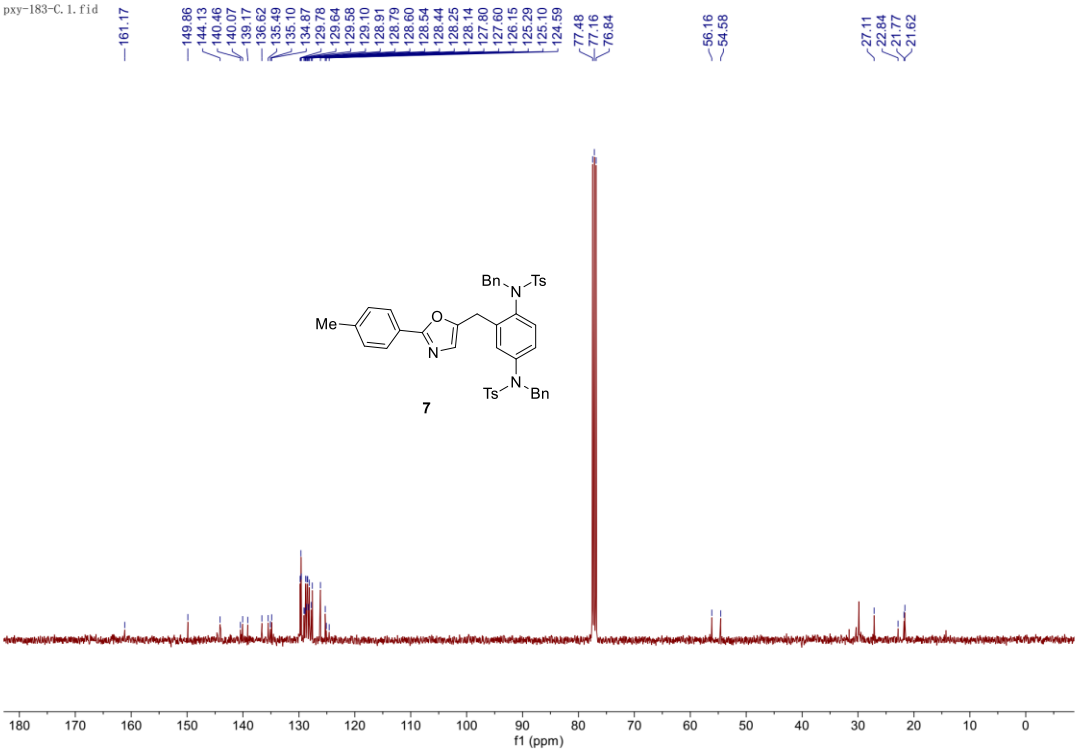

Ts
N
O
N
Ar
NBnTs
5, Ar = 4-MeC6H4
f1 (ppm)

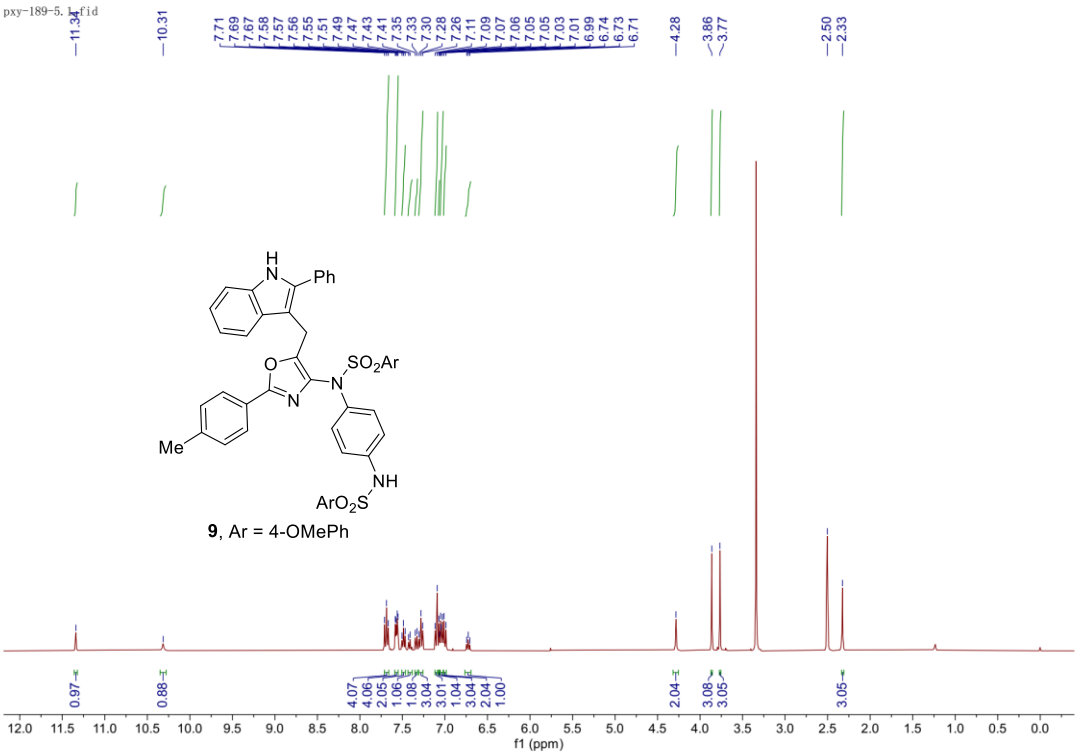

pxy-177-C.1.fid
164.41
156.21
143.69
143.58
143.33
139.34
136.38
135.63
134.93
134.56
132.36
129.43
129.21
129.03
128.66
128.52
128.43
128.35
127.72
127.68
123.25
90.11
81.29
77.48
77.16
76.84
54.55
21.82
21.74
21.59
Ts
N
O
N
Ar
NBnTs
5, Ar = 4-MeC6H4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

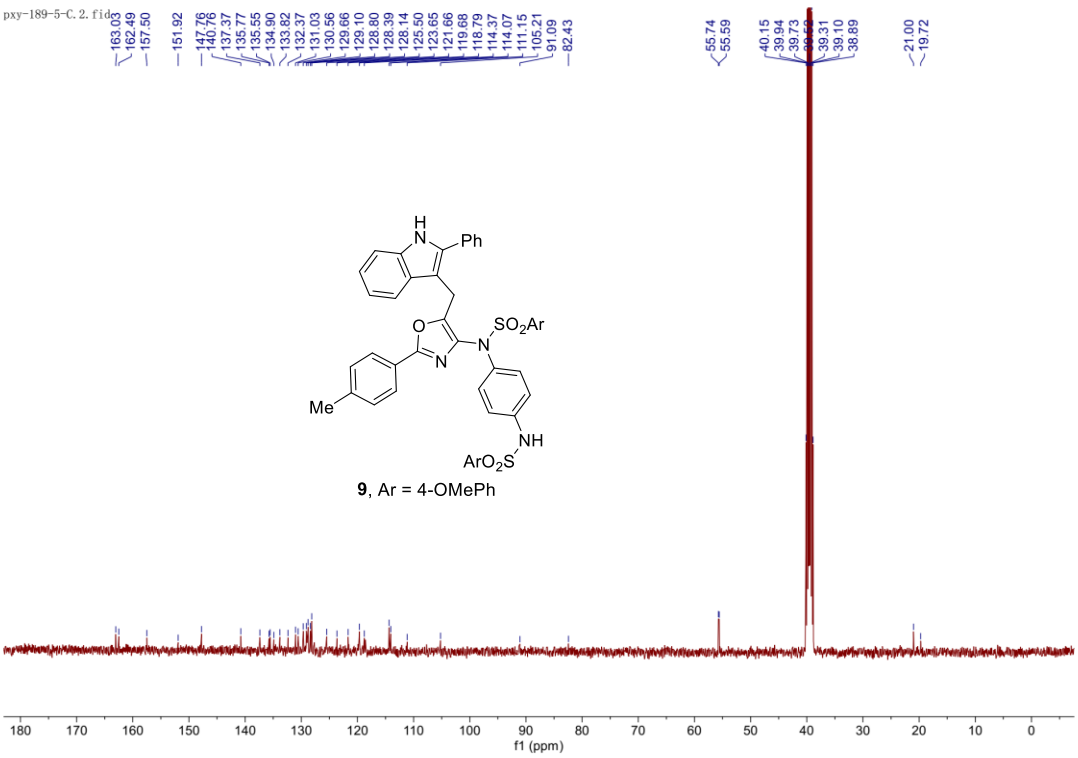

pxy-175-H.1.fid
7.79
7.78
7.56
7.54
7.52
7.26
7.25
7.22
7.20
7.18
7.13
7.11
7.00
6.98
6.94
6.88
6.86
6.60
3.77
2.39
2.38
2.37
2.31
2.30
HN
Ts
Me
O
N
NH
Ts
6
1.99
4.04
2.05
4.05
2.04
1.06
1.03
1.05
1.02
2.00
6.05
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pxy-175-C.2.fid
161.87
149.07
144.31
144.27
140.83
136.40
136.02
135.90
134.38
131.02
130.37
129.86
129.82
129.64
128.08
127.33
126.27
125.14
124.66
122.65
120.53
77.48
77.16
76.84
27.99
21.71
21.64
HN
Ts
Me
O
N
Ts
NH
6
f1 (ppm)


pxy-128-H.1.fid
7.80
7.78
7.50
7.48
7.38
7.36
7.28
7.26
7.20
7.17
7.16
7.13
7.11
7.09
7.06
7.05
7.02
6.99
6.85
6.82
6.59
6.46
6.44
6.16
5.05
5.02
4.59
4.55
4.54
4.50
4.07
4.04
3.86
3.82
3.76
3.72
2.46
2.42
2.33
Bn
N
Ts
Me
O
N
Ts
N
Bn
7
2.00
2.08
2.09
3.01
6.02
2.97
2.08
2.06
0.96
0.95
0.91
0.92
0.99
1.94
0.96
1.82
3.06
3.07
3.03
f1 (ppm)

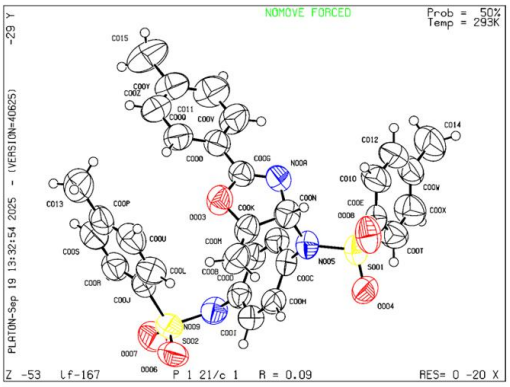

pxy-183-C.1.fid
161.17
149.86
144.13
140.46
140.07
139.17
136.62
135.49
135.10
134.87
129.78
129.64
129.58
129.10
128.91
128.79
128.60
128.54
128.44
128.25
128.14
127.80
127.60
126.15
125.29
125.10
124.59
77.48
77.16
76.84
56.16
54.58
27.11
22.84
21.77
21.62
Bn
N
Ts
Me
O
N
Ts
N
Bn
7
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

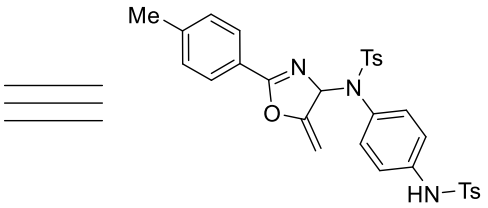

pxy-189-5.1.fid
11.34
10.31
7.71
7.69
7.67
7.58
7.57
7.56
7.55
7.51
7.49
7.47
7.43
7.41
7.35
7.33
7.30
7.28
7.26
7.11
7.09
7.07
7.06
7.05
7.05
7.03
7.01
6.99
6.74
6.73
6.71
4.28
3.86
3.77
2.50
2.33
H
N
Ph
O
N
SO2Ar
N
Me
NH
ArO2S
9, Ar = 4-OMePh
0.97
0.88
4.07
4.06
2.05
1.06
1.08
3.04
3.01
1.04
3.04
2.04
1.00
2.04
3.08
3.05
3.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


pxy-189-5-C.2.fid
163.03
162.49
157.50
151.92
147.76
140.76
137.37
135.77
135.55
134.90
133.82
132.37
131.03
130.56
129.66
129.10
128.80
128.39
128.14
125.50
123.65
121.66
119.68
118.79
114.37
114.07
111.15
105.21
91.09
82.43
55.74
55.59
40.15
39.94
39.73
39.52
39.31
39.10
38.89
21.00
19.72
H
N
Ph
O
N
SO2Ar
N
Me
NH
ArO2S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

9, Ar = 4-OMePh

Single-Crystal X-ray Diffraction of 3g





3g
CCDC 2490309

```
Bond precision:   C-C = 0.0094 A          Wavelength=1.54184

Cell:             a=15.9606(11)     b=10.2207(10)     c=18.4680(13)
                  alpha=90          beta=93.322(7)    gamma=90
Temperature:      293 K

                  Calculated                Reported
Volume            3007.6(4)                 3007.6(4)
Space group       P 21/c                    P 1 21/c 1
Hall group        -P 2ybc                   -P 2ybc
Moiety formula    C31 H29 N3 O5 S2          C31 H29 N3 O5 S2
Sum formula       C31 H29 N3 O5 S2          C31 H29 N3 O5 S2
Mr                587.69                    587.69
Dx,g cm-3         1.298                     1.298
Z                 4                         4
Mu (mm-1)         1.966                     1.966
F000              1232.0                    1232.0
F000'             1238.10
h,k,lmax          19,12,23                  19,12,22
Nref              6113                      5680
Tmin,Tmax         0.954,0.981               0.755,1.000
Tmin'             0.943

Correction method= # Reported T Limits: Tmin=0.755 Tmax=1.000
AbsCorr = MULTI-SCAN


Data completeness= 0.929          Theta(max)= 74.019

R(reflections)= 0.0890( 2490)                wR2(reflections)=
                                             0.3396( 5680)
S = 0.984                  Npar= 373
```

References

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2 Y. Wang, K. Ji, S. Lan and L. Zhang, *Angew. Chem. Int. Ed.*, 2012, **51**, 1915-1918.