Supporting Information

Phosphine-catalyzed [3 + 2] annulation of 2-aminoacrylates with allenoates and mechanistic studies

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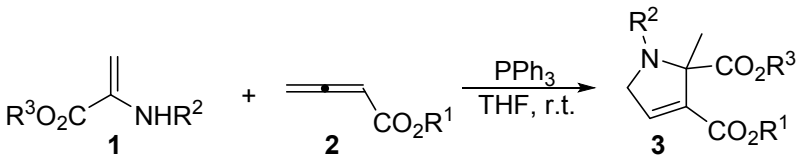
1. General remarks

Melting points were determined on a digital melting point apparatus, and temperatures were uncorrected. ^{1}H NMR spectra were recorded on a Varian Mercury-300 and 400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard; coupling constants *J* are given in Hz. ^{13}C NMR spectra were recorded on a Varian Mercury-300 and 400 spectrophotometers (75 or 100 MHz) with complete proton decoupling spectrophotometers ($CDCl_3$: 77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. Flash column chromatography was performed using 300-400 mesh silica gel. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. Mass spectra were recorded by EI, ESI, MALDI and HRMS was measured on a HP-5989 instrument.

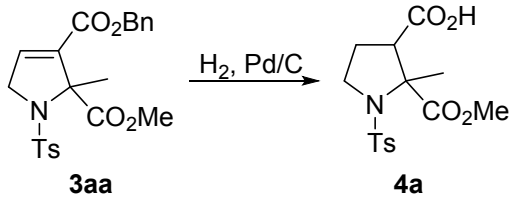
2. General procedure

General Procedure for the Synthesis of **3**



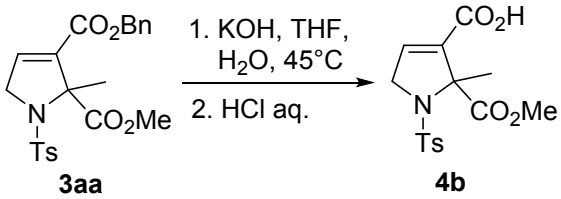
To a 20 mL flame-dried tube was charged with 2-aminoacrylates **1** (0.1 mmol, 1.0 equiv), PPh_3 (0.01 mmol, 0.1 equiv) and allenoates **2** (0.12 mmol, 1.2 equiv). Then, 2.5 mL tetrahydrofuran was added into the tube under argon atmosphere. The reaction mixture was stirred at room temperature for 4 h. The solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2) to give the corresponding crude product **3**.

General Procedure for the Synthesis of **4a**



In a 50 mL round-bottom flask, 3-pyrroline **3aa** (1.0 mmol) was added to Pd/C (0.2 mmol) in MeOH (10.0 mL) under H_2 atmosphere for 20 hours at room temperature. After completion of reaction as indicated by TLC, the solid was filtered out. Subsequently, the solvent was concentrated under reduced pressure, and the residue was purified directly by flash column chromatography (Petroleum ether /ethyl acetate = 4:1-2:1) to give the corresponding product **4a**.

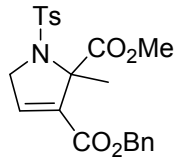
General Procedure for the Synthesis of **4b**



A mixture of 3-pyrroline **3aa** (1.0 mmol, 1.0 equiv) and potassium hydroxide (20.0 mmol, 20.0 equiv) in THF/H_2O (20 mL, v:v = 1:1) was stirred at 45 ^oC for 12 hours. Then Aqueous hydrochloric acid solution (HCl:H_2O = 1:2) was added to keep pH of the solution at 5-6. The

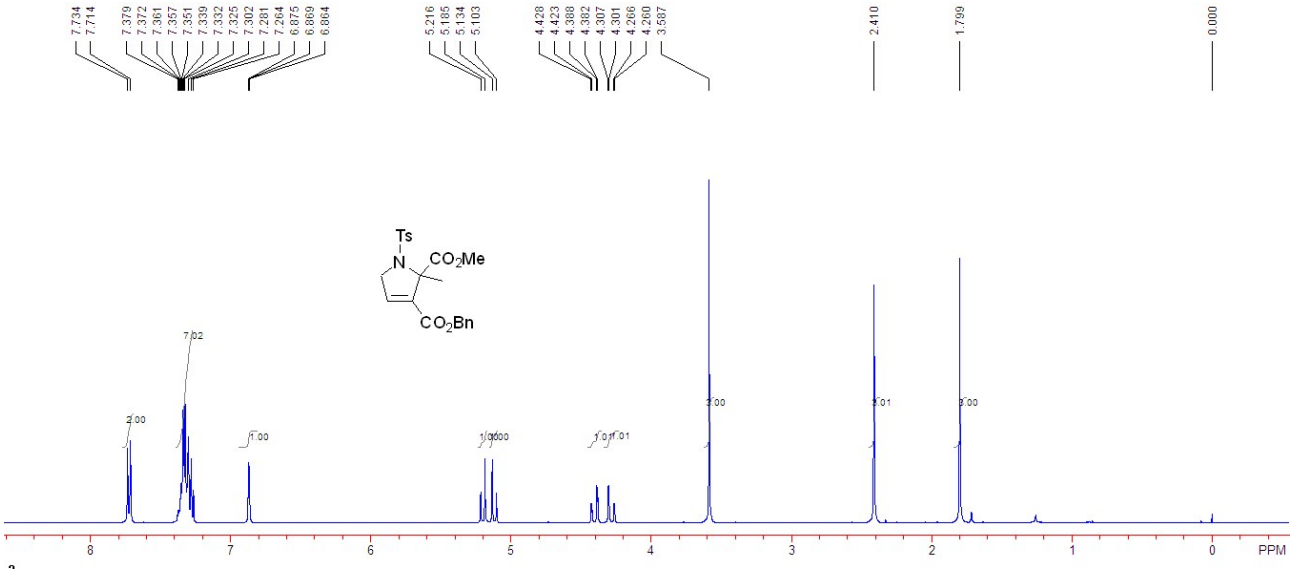
aqueous layer was extracted with ether and the combined organic phase was washed with brine, dried over Na_2SO_4. The solvent was concentrated under vacuum to provide crude product, which was purified directly by flash column chromatography (Petroleum ether /ethyl acetate = 100:1-2:1) to give the corresponding product **4b**.

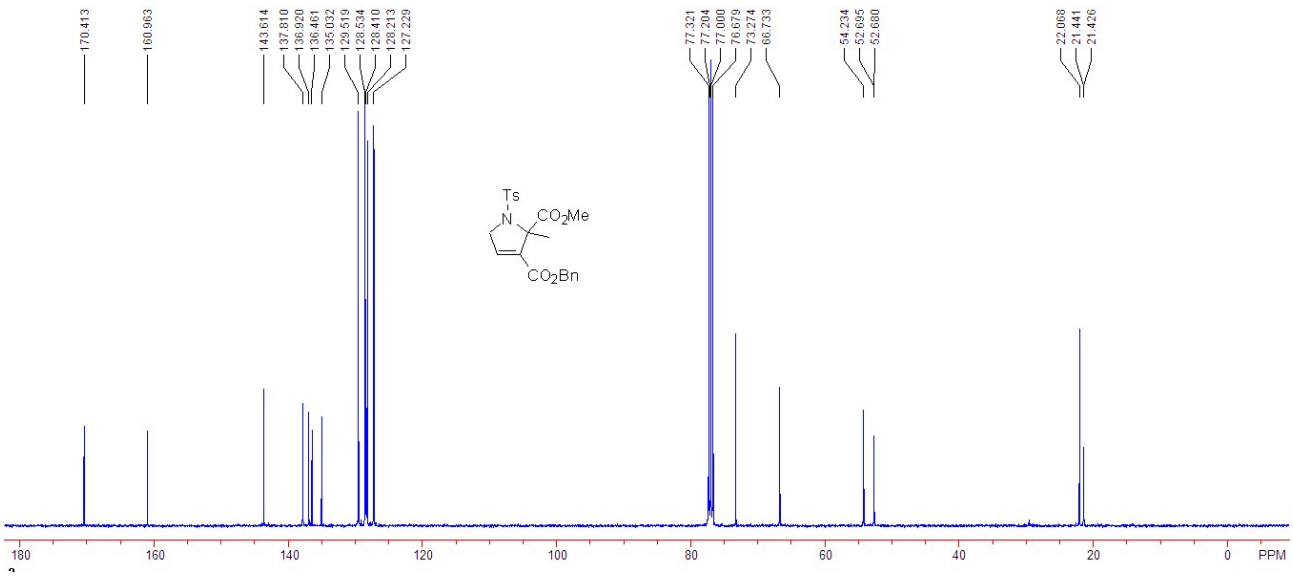
3. Characterization and spectra charts for compounds 3, 4a and 4b.

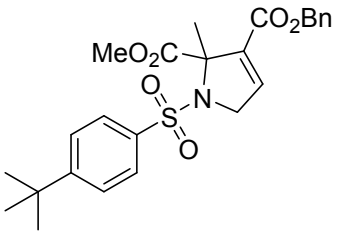


3-benzyl 2-methyl 2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3aa)

A yellow oil, 39.5 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.38-7.30 (m, 5H), 7.27 (d, *J* = 6.8 Hz, 2H), 6.87 (t, *J* = 2.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.41 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.27 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.59 (s, 3H), 2.41 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 161.0, 143.6, 137.8, 136.9, 136.5, 135.0, 129.5, 128.5, 128.4, 128.2, 127.2, 73.3, 66.7, 54.2, 52.7, 22.1, 21.4 (d, *J* = 1.5 Hz); IR (neat): ν 2938, 1751, 1720, 1456, 1346, 1250, 1158, 1104, 1054, 737, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{27}N_2O_6S^+$ $(M+NH_4)^+$ requires 447.1584, Found: 447.1596.

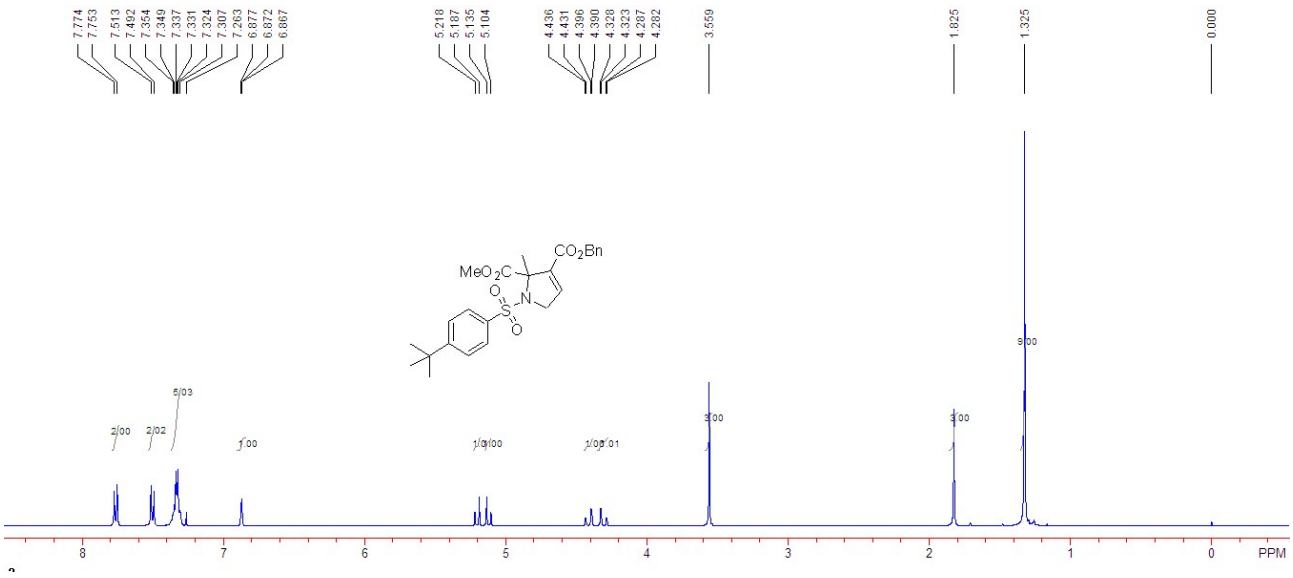


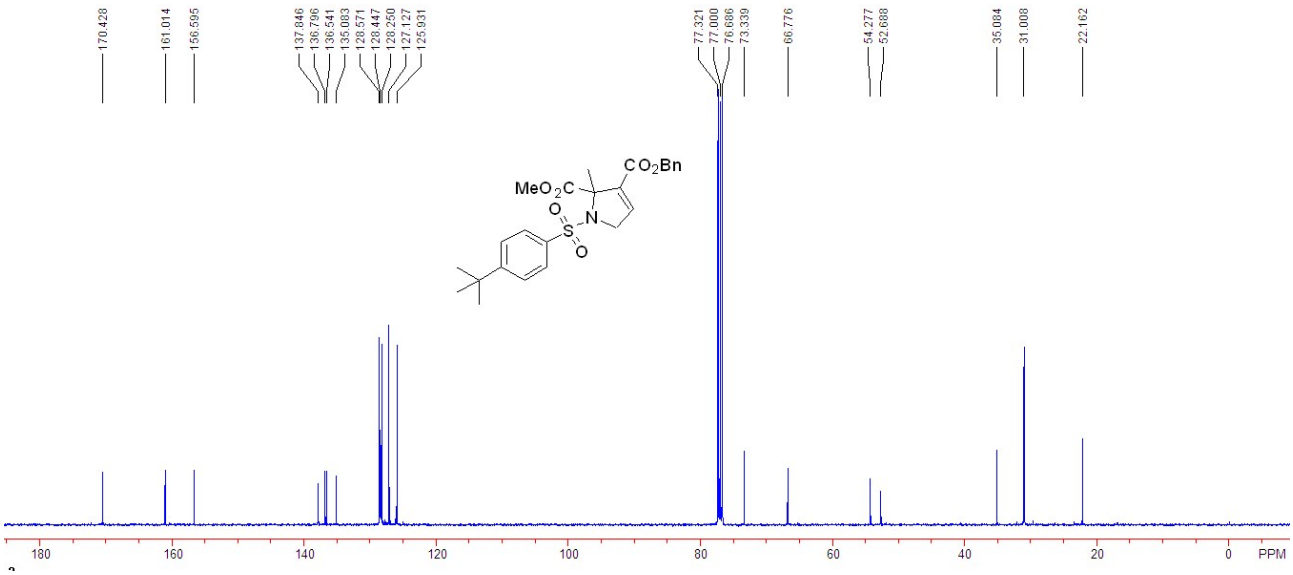


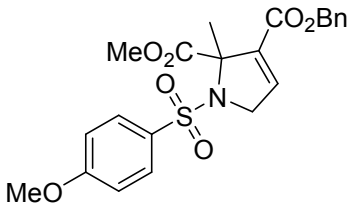


3-benzyl-2-methyl-1-((4-(tert-butyl)phenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ba)

A yellow oil, 42.4 mg, 90% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.4 Hz, 2H), 7.35-7.31 (m, 5H), 6.87 (t, *J* = 2.0 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.42 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.31 (dd, *J* = 2.0, 2.0 Hz, 1H), 3.56 (s, 3H), 1.83 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 161.0, 156.6, 137.8, 136.8, 136.5, 135.1, 128.6, 128.4, 128.3, 127.1, 125.9, 73.3, 66.8, 54.3, 52.7, 35.1, 31.0, 22.2; IR (neat): ν 2972, 2832, 1751, 1720, 1566, 1423, 1350, 1267, 1168, 1102, 1066, 846, 737, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{25}H_{33}N_2O_6S^+$ $(M+NH_4)^+$ requires 489.2054, Found: 489.2062.



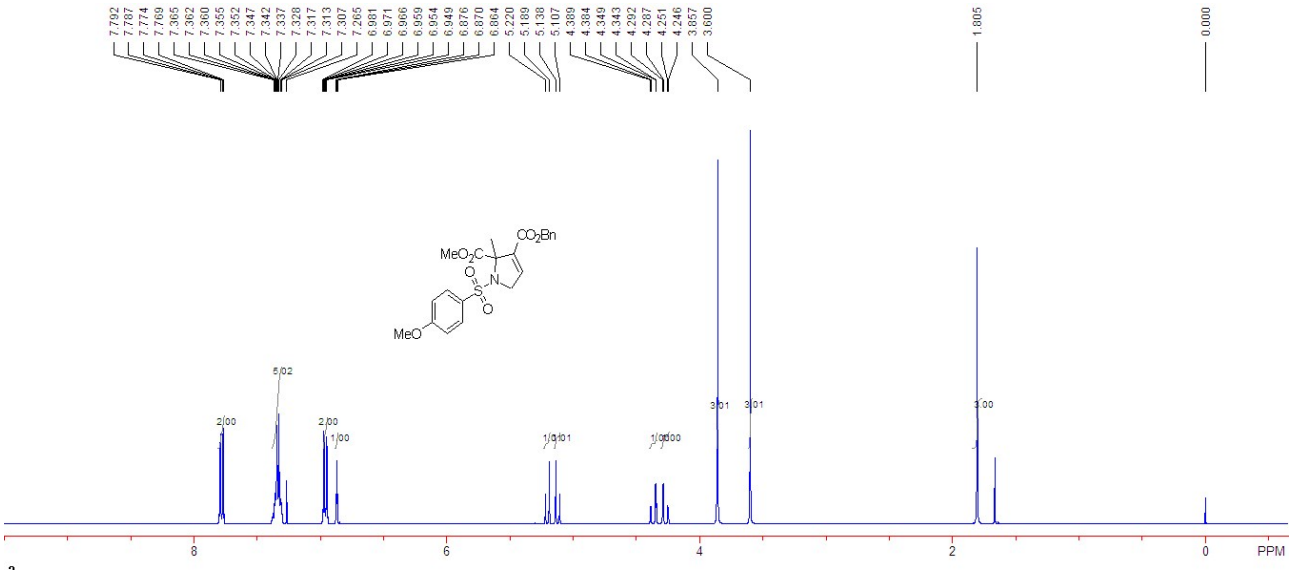


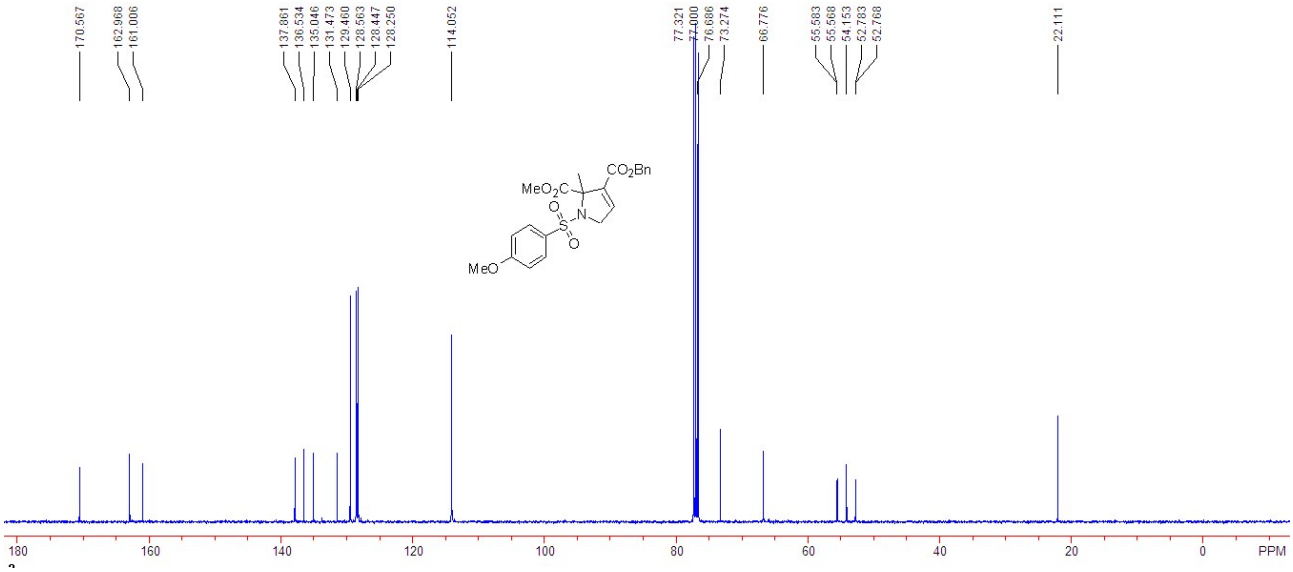


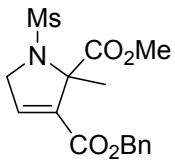
3-benzyl-2-methyl-1-((4-methoxyphenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ca)

A yellow oil, 41.0 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (td, *J* = 2.0, 8.4 Hz, 2H), 7.50 (td, *J* = 2.0, 8.4 Hz, 2H), 7.37-7.31 (m, 5H), 6.87 (t, *J* = 2.4 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.37 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.27 (dd, *J* = 2.0, 2.0 Hz, 1H), 3.86 (s, 3H), 3.60 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.6, 163.0, 161.0, 137.9,

136.5, 135.0, 131.5, 129.5, 128.6, 128.4, 128.3, 114.1, 73.3, 66.8, 55.6 (d, J = 1.5 Hz), 54.2, 52.8 (d, J = 1.5 Hz); IR (neat): ν 2978, 2913, 2215, 2038, 1752, 1720, 1576, 1499, 1346, 1248, 1156, 1104, 830, 815, 799, 676 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{23}NNaO_7S^+$ $(M+Na)^+$ requires 468.1087, Found:468.1092.

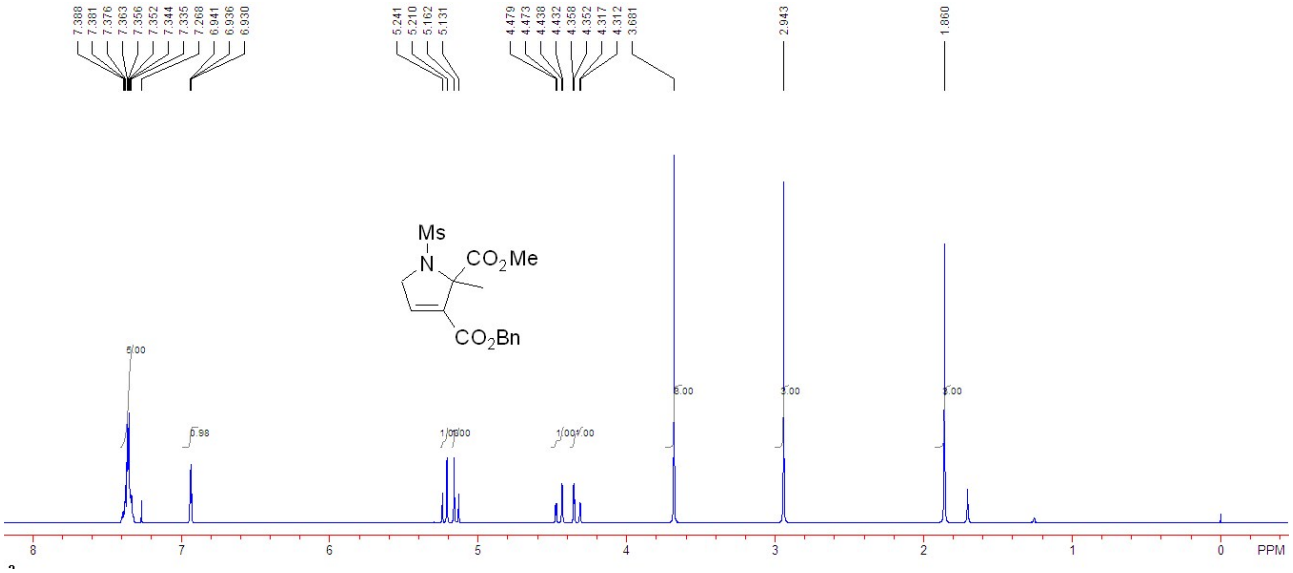


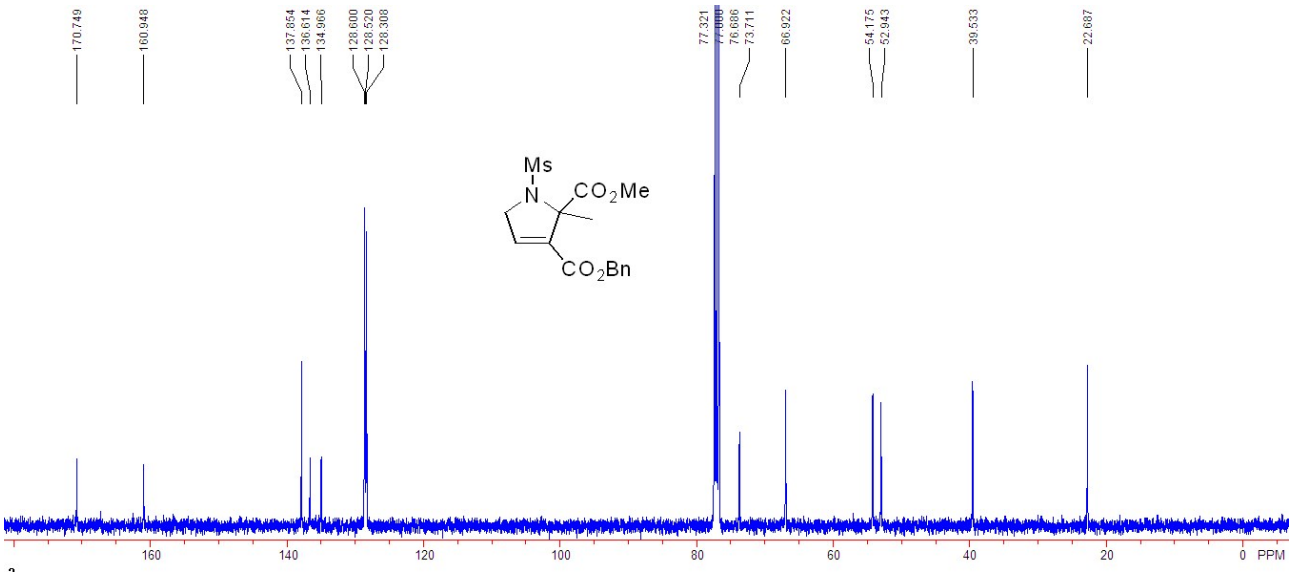


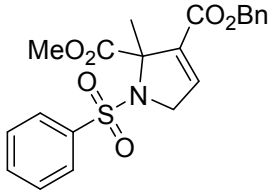


3-benzyl 2-methyl 2-methyl-1-(methylsulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3da)

A yellow oil, 26.5 mg, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.40-7.34 (m, 5H), 6.94 (t, *J* = 2.0 Hz, 1H), 5.23 (d, *J* = 12.4 Hz, 1H), 5.15 (d, *J* = 12.4 Hz, 1H), 4.46 (dd, *J* = 2.4, 2.4 Hz, 1H), 4.34 (dd, *J* = 2.4, 2.0 Hz, 1H), 3.68 (s, 3H), 2.94 (s, 3H), 1.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.7, 160.9, 137.9, 136.6, 135.0, 128.6, 128.5, 128.3, 73.7, 66.9, 54.2, 52.9, 39.5, 22.7; IR (neat): ν 2988, 2900, 2215, 2121, 2088, 1761, 1743, 1405, 1394, 1250, 1065, 1057, 1028, 892, 668, 679 cm^{-1}; HRMS (ESI) Calcd. For $C_{16}H_{23}N_2O_6S^+$ $(M+NH_4)^+$ requires 371.1271, Found: 371.1281.

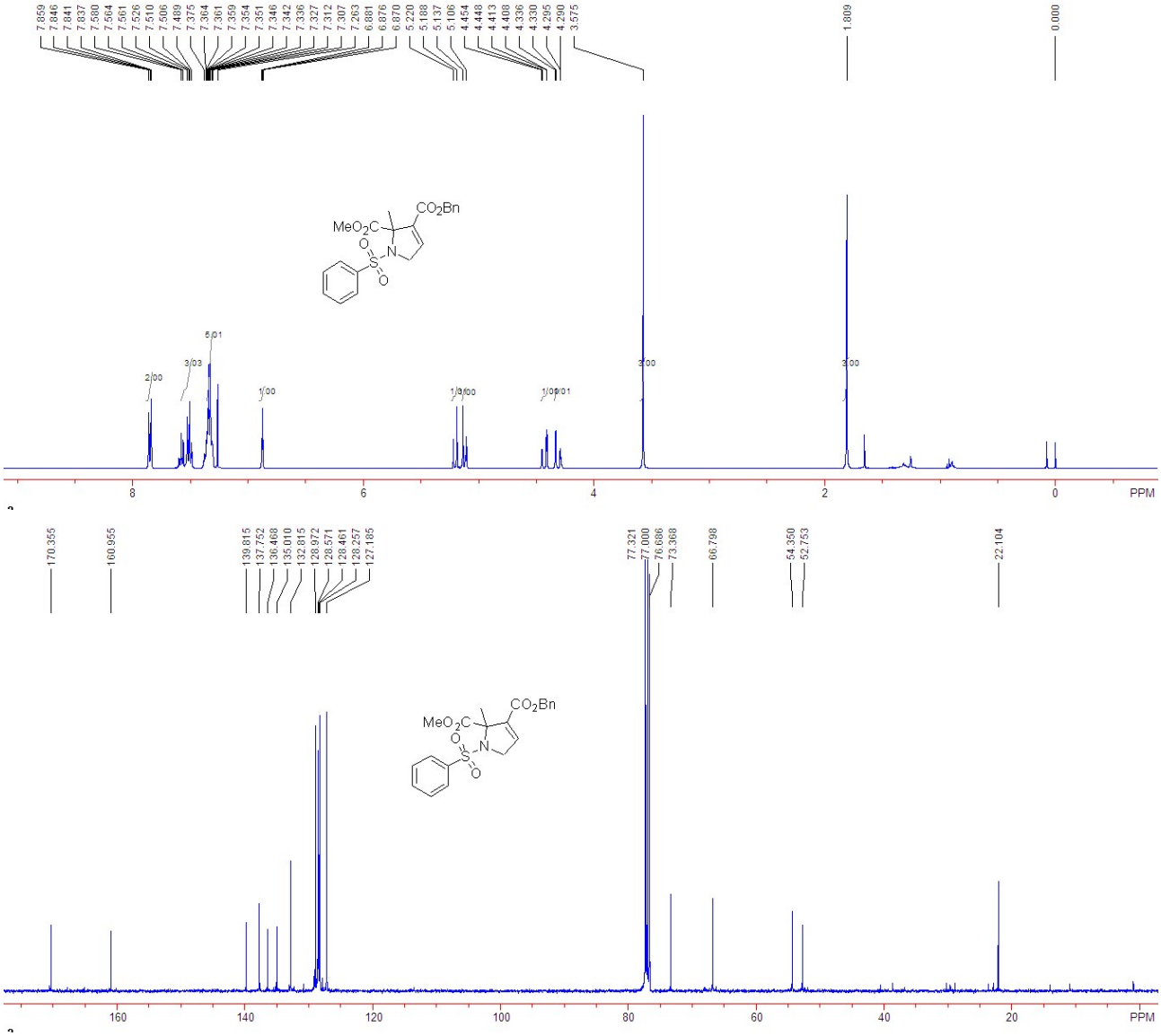


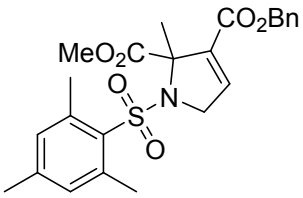




3-benzyl-2-methyl-2-methyl-1-(phenylsulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ea)

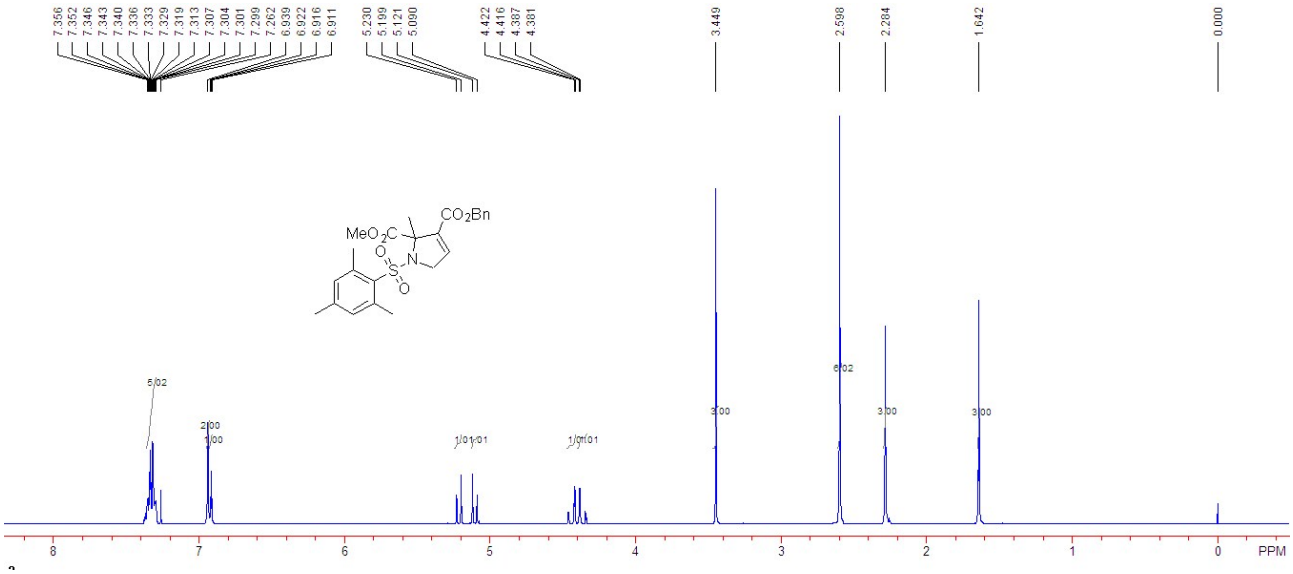
A yellow oil, 29.1 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.58-7.49 (m, 1H), 7.38-7.31 (m, 5H), 6.88 (t, *J* = 2.0 Hz, 1H), 5.20 (d, *J* = 12.8 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.43 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.27 (dd, *J* = 2.0, 2.4 Hz, 1H), 3.58 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 161.0, 139.8, 137.8, 136.5, 135.0, 132.8, 129.0, 128.6, 128.5, 128.3, 127.2, 73.4, 66.8, 54.4, 52.8, 22.1; IR (neat): ν 2946, 1751, 1720, 1447, 1347, 1253, 1161, 1106, 1054, 754, 722, 692 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{25}N_2O_6S^+$ $(M+NH_4)^+$ requires 433.1428, Found: 433.1439.

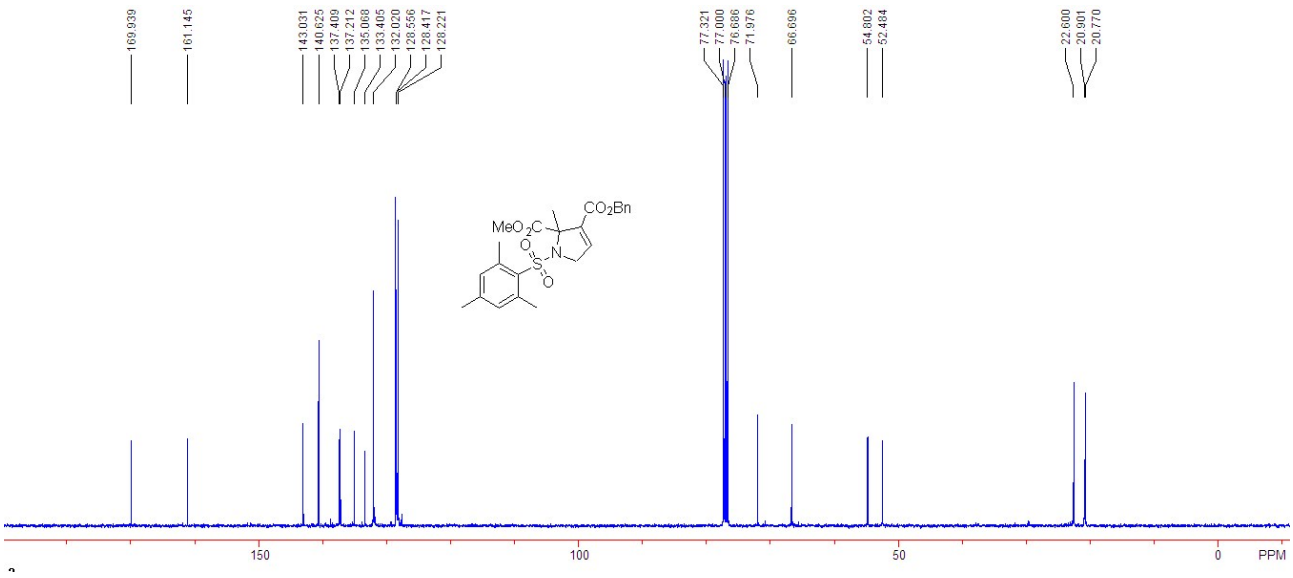


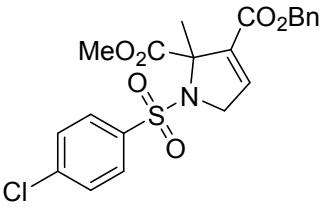


3-benzyl 2-methyl 1-(mesitylsulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3fa)

A yellow oil, 38.0 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.36-7.30 (m, 5H), 6.94 (s, 2H), 6.92 (t, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 4.44 (dd, *J* = 2.0, 2.4 Hz, 1H), 4.37 (dd, *J* = 2.4, 2.4 Hz, 1H), 3.45 (s, 3H), 2.60 (s, 6H), 2.28 (s, 3H), 1.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.9, 161.1, 143.0, 140.6, 137.4, 137.2, 135.1, 133.4, 132.0, 128.6, 128.4, 128.2, 72.0, 66.7, 54.8, 52.5, 22.6, 20.9, 20.8; IR (neat): ν 2954, 1745, 1715, 1313, 1247, 1153, 1081, 1046, 851, 699, 675 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{31}N_2O_6S^+$ $(M+NH_4)^+$ requires 475.1897, Found: 475.1909.

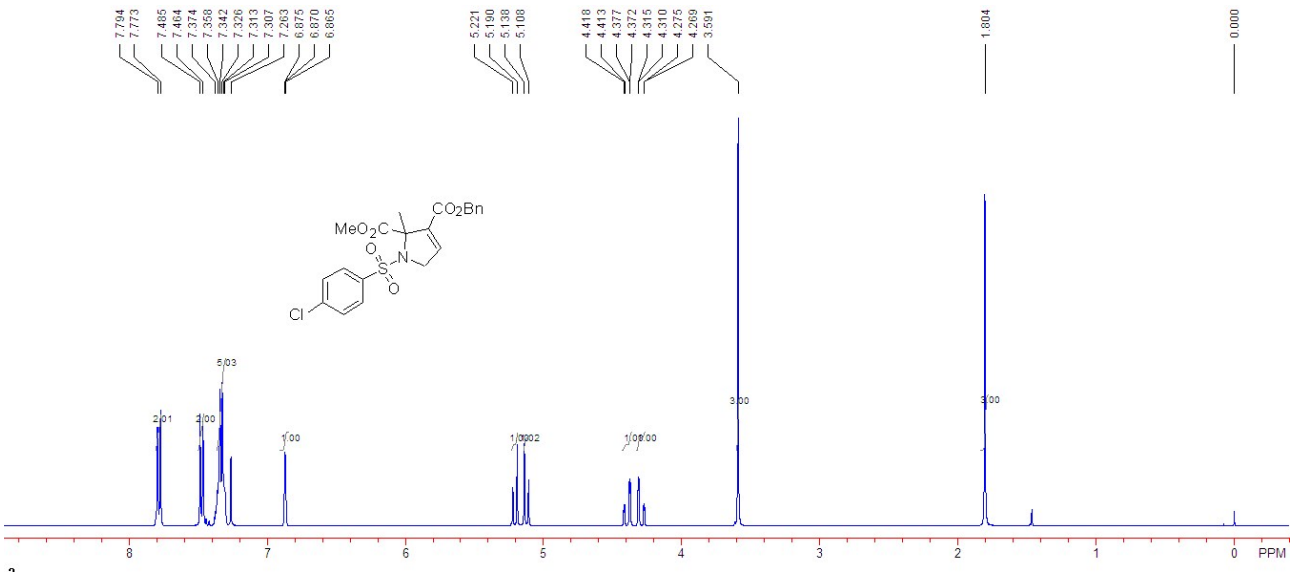


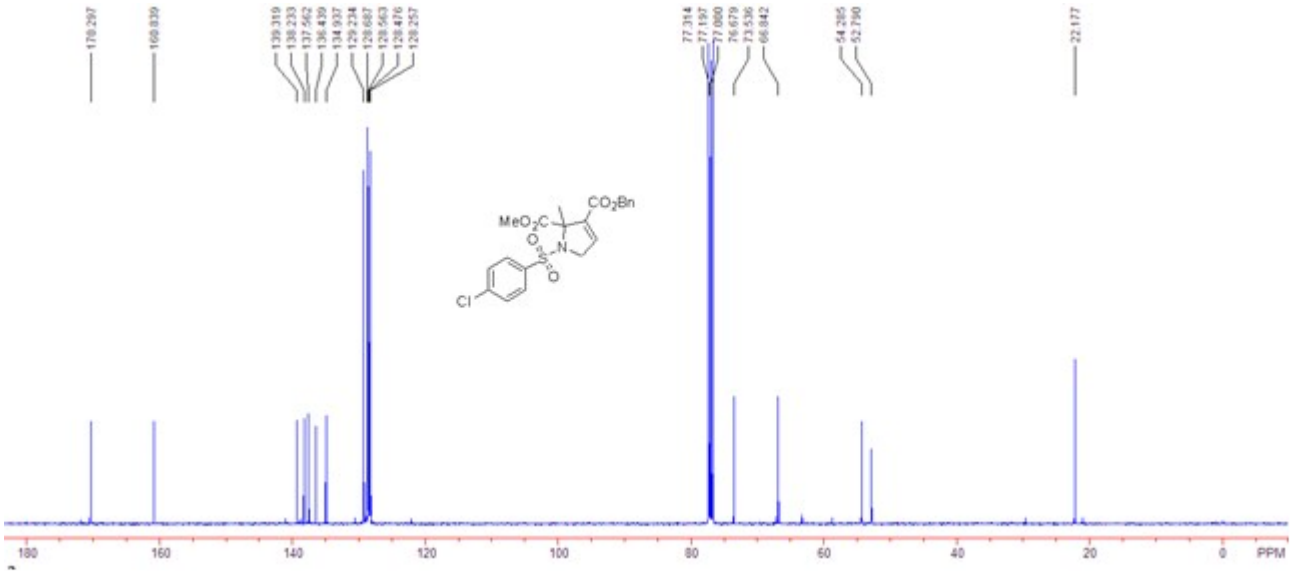


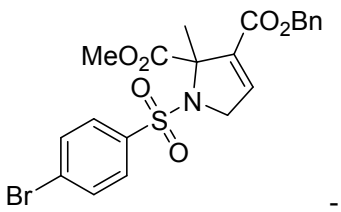


3-benzyl-2-methyl-1-((4-chlorophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ga)

A yellow oil, 42.7 mg, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.37-7.31 (m, 5H), 6.87 (t, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.0 Hz, 1H), 4.40 (dd, *J* = 2.0, 2.0 Hz, 1H), 4.30 (dd, *J* = 2.0, 2.4 Hz, 1H), 3.59 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.3, 160.8, 139.3, 138.2, 137.6, 136.4, 134.9, 129.2, 128.7, 128.6, 128.5, 128.3, 73.5, 66.8, 54.3, 52.8, 22.2; IR (neat): ν 2943, 1750, 1720, 1348, 1265, 1161, 1108, 1090, 1054, 1102, 758, 698 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{24}ClN_2O_6S^+$ $(M+NH_4)^+$ requires 467.1038, Found: 467.1049.



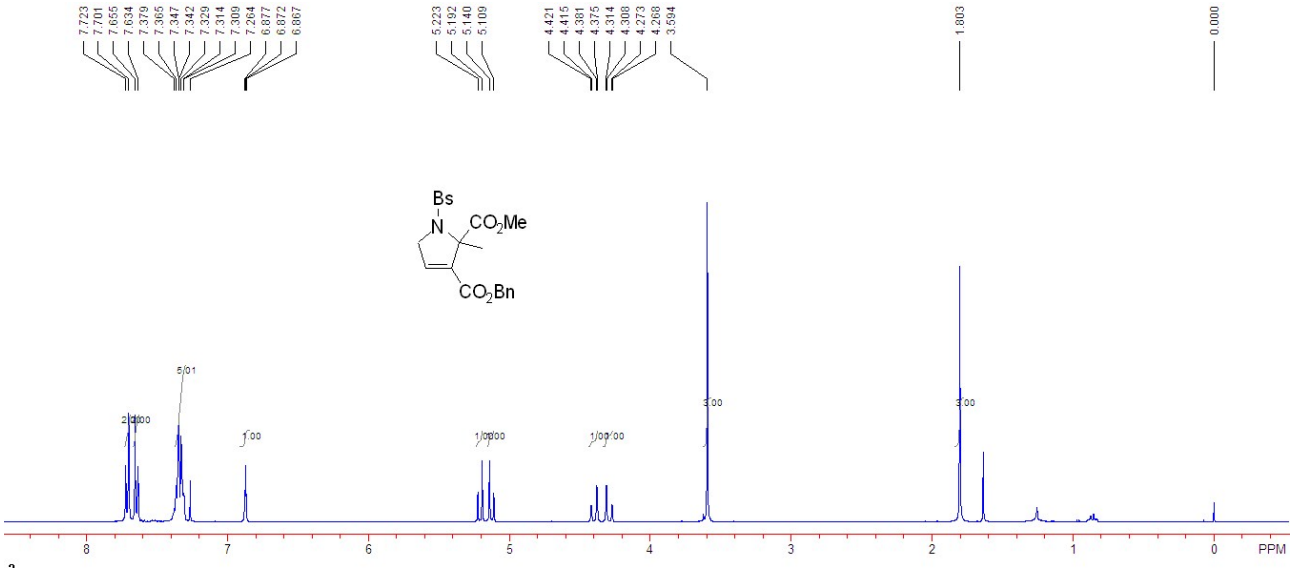


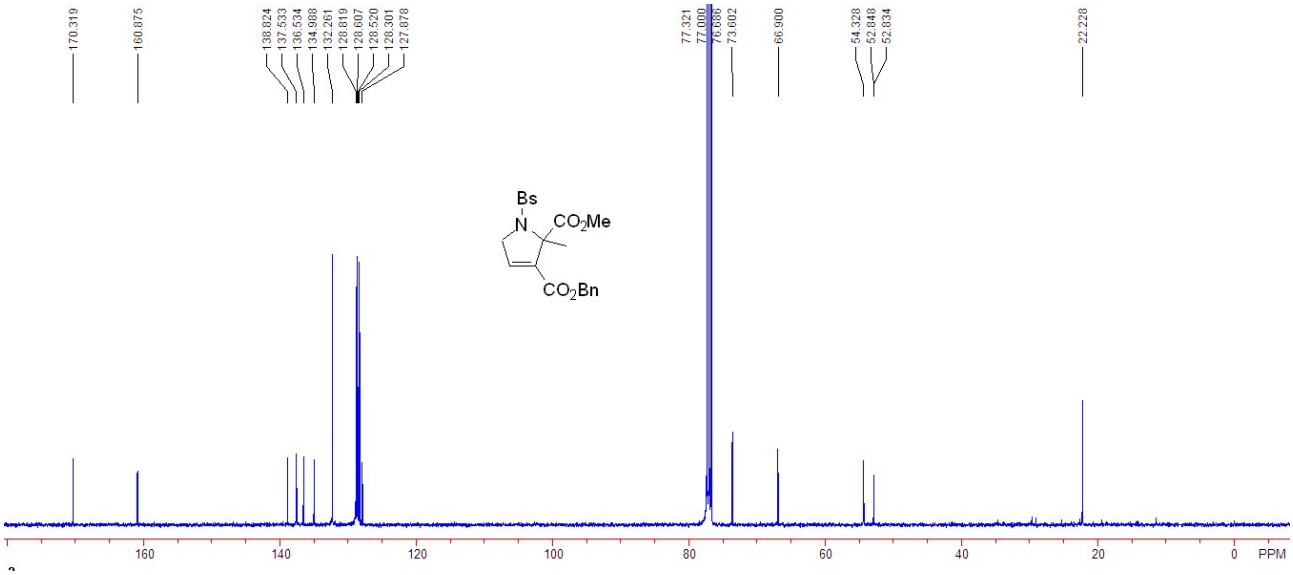


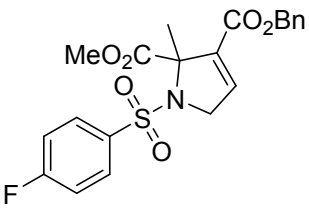
3-benzyl-2-methyl-1-((4-bromophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ha)

A yellow oil, 34.6 mg, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.71 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.38-7.31 (m, 5H), 6.87 (t, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.12 (d, *J* = 12.4 Hz, 1H), 4.40 (dd, *J* = 2.4, 16.0 Hz, 1H), 4.29 (dd, *J* = 2.4, 16.0 Hz, 1H), 3.59 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.3, 160.9, 138.8, 137.5, 136.5, 135.0, 132.3,

128.8, 128.6, 128.5, 128.3, 127.9, 73.6, 66.9, 54.3, 52.8 (d, J = 1.4 Hz), 22.2; IR (neat): ν 2988, 1750, 1721, 1267, 1261, 1161, 1108, 1067, 1052, 739, 678, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{24}BrN_2O_6S^+$ $(M+NH_4)^+$ requires 511.0533, Found: 511.0536.



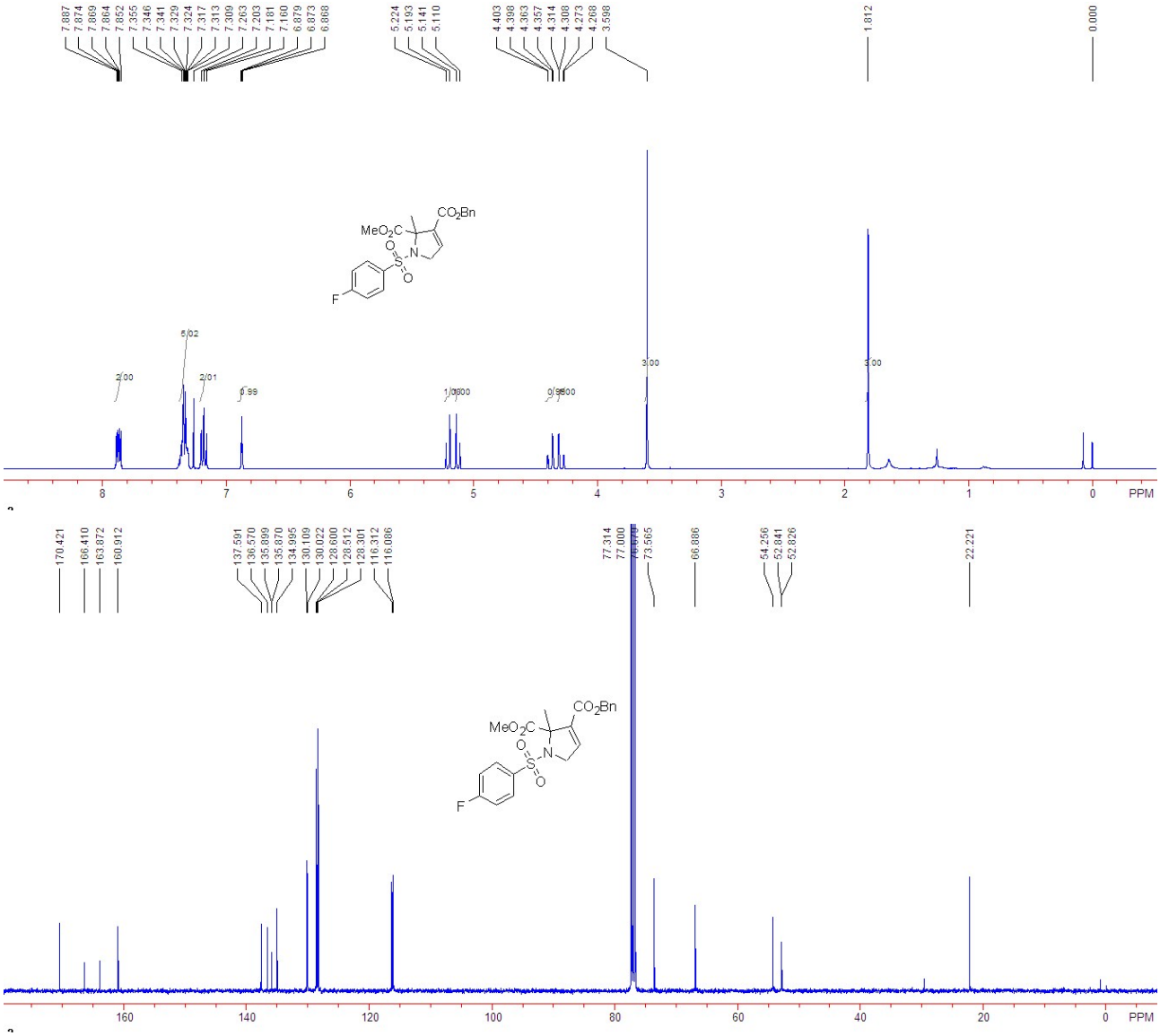


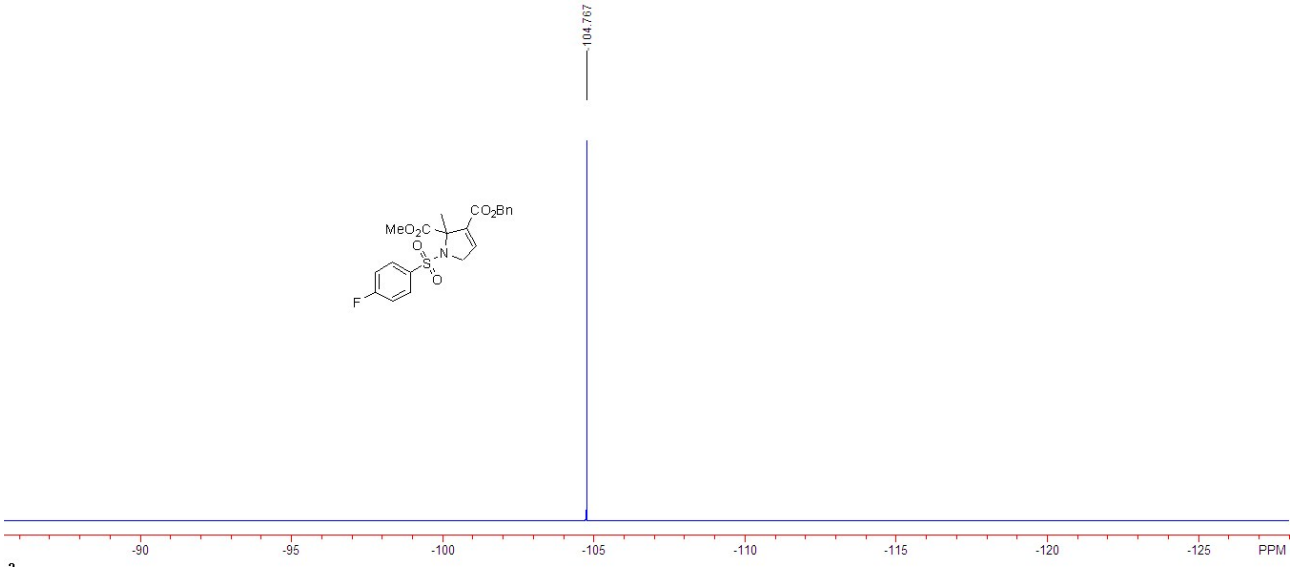


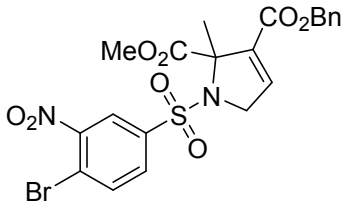
3-benzyl-2-methyl-1-((4-fluorophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ia)

A yellow oil, 26.0 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.89-7.85 (m, 2H), 7.36-7.31 (m, 5H), 7.18 (t, J = 8.8 Hz, 2H), 6.87 (t, J = 2.4 Hz, 1H), 5.21 (d, J = 12.4 Hz, 1H), 5.13 (d, J

= 12.4 Hz, 1H), 4.38 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.29 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.60 (s, 3H), 1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 165.4 (d, *J* = 253.8 Hz), 160.9, 137.6, 136.6, 135.9 (d, *J* = 2.9 Hz), 135.0, 130.1 (d, *J* = 8.7 Hz), 128.6, 128.5, 128.3, 116.2 (d, *J* = 22.6 Hz), 73.6, 66.9, 54.3, 52.8 (d, *J* = 1.5 Hz), 22.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ -104.77; IR (neat): ν 2988, 2901, 1749, 1721, 1349, 1250, 1165, 1155, 1107, 1056, 677, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{24}FN_2O_6S^+$ $(M+NH_4)^+$ requires 451.1334, Found: 451.1342.

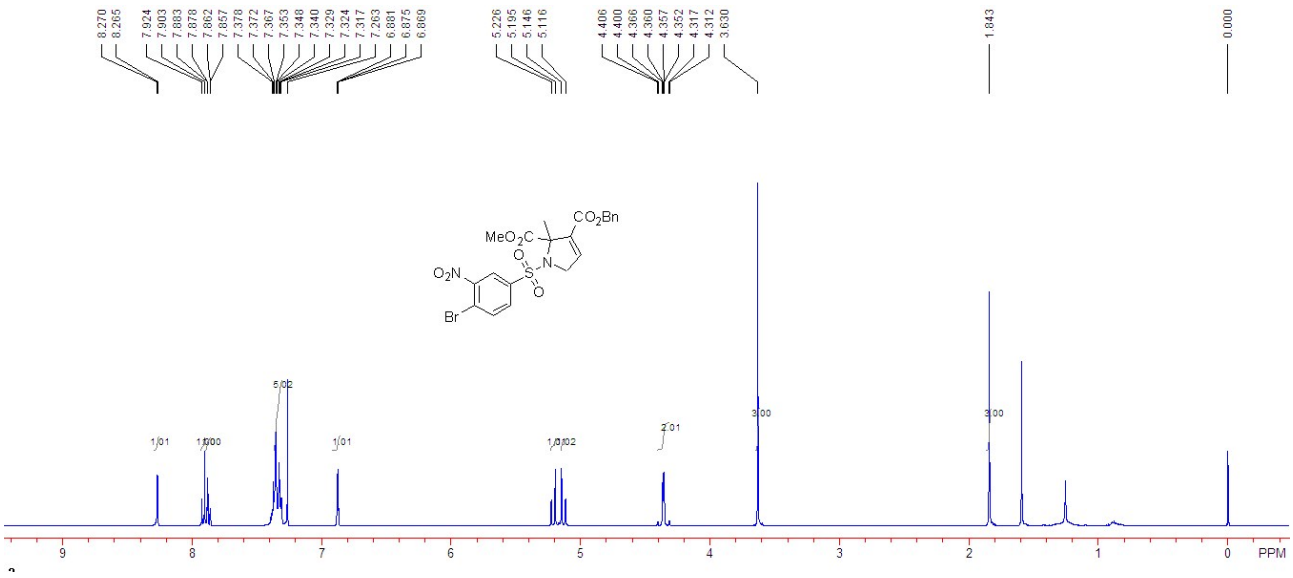


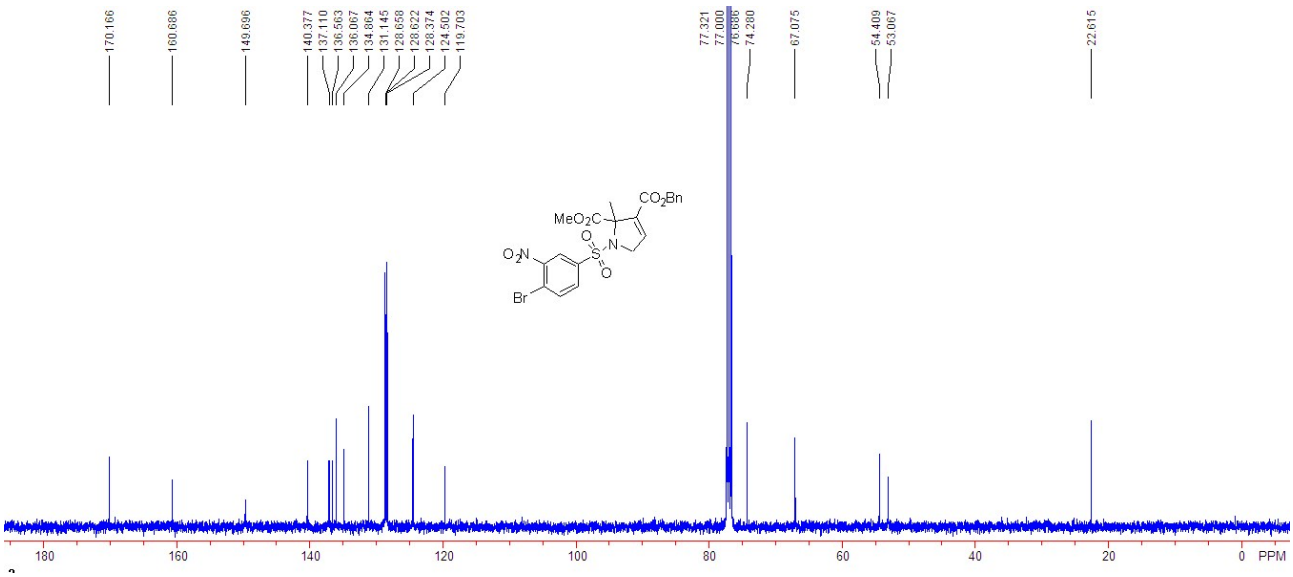


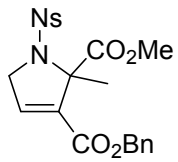


3-benzyl-2-methyl-1-((4-bromo-3-nitrophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ja)

A yellow oil, 34.5 mg, 64% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.27 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.38-7.32 (m, 5H), 6.88 (t, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.38 (dd, *J* = 2.4, 16.0 Hz, 1H), 4.33 (dd, *J* = 2.0, 16.0 Hz, 1H), 3.63 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.2, 160.7, 150.0, 140.4, 137.1, 136.6, 136.1, 134.9, 131.1, 128.7, 128.6, 128.4, 124.5, 119.7, 74.3, 67.1, 54.4, 53.1, 22.6; IR (neat): ν 2917, 1721, 1540, 1354, 1267, 1169, 1152, 1108, 1055, 1032, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{23}BrN_3O_8S^+$ $(M+NH_4)^+$ requires 556.0384, Found: 556.0364.



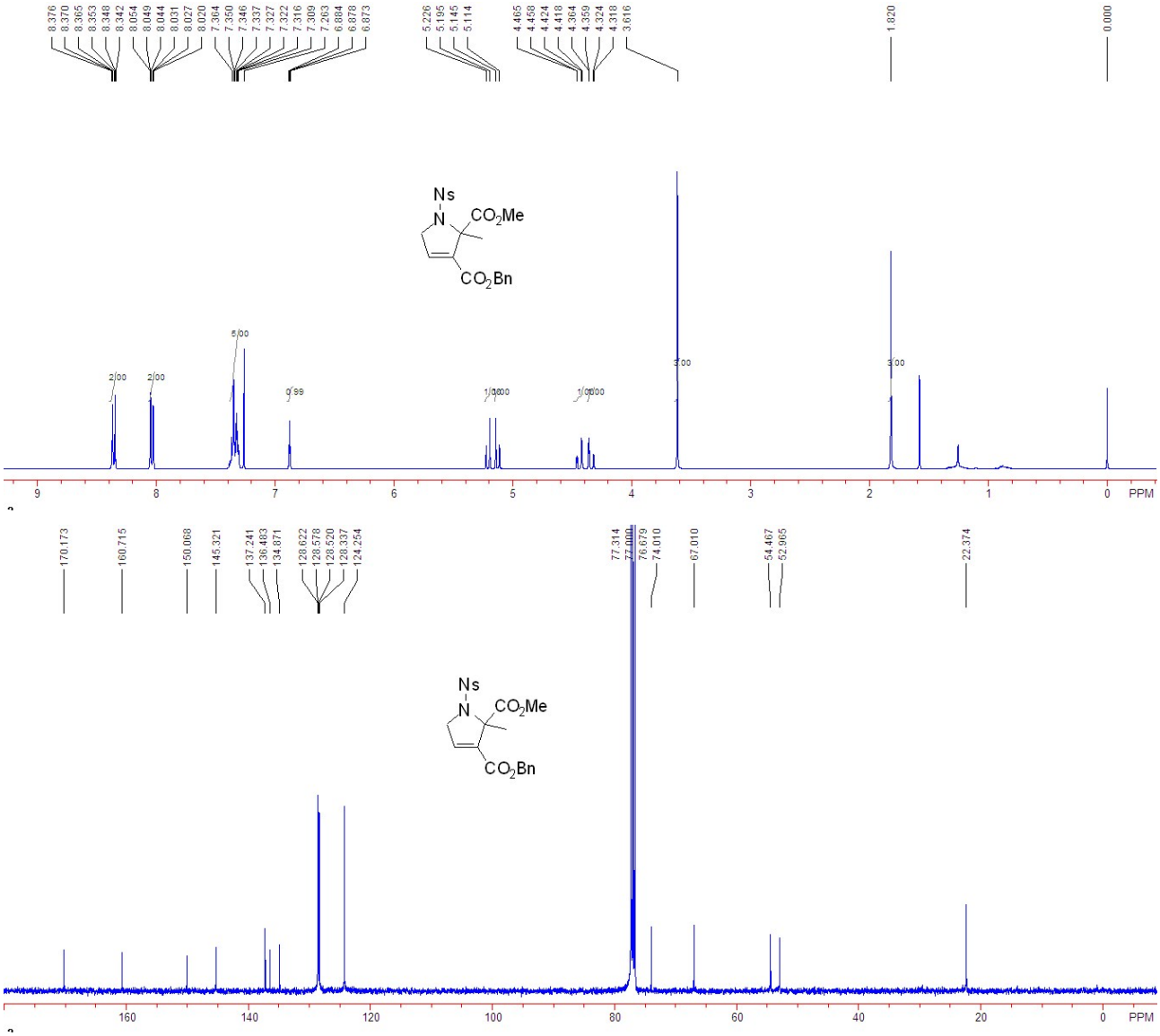


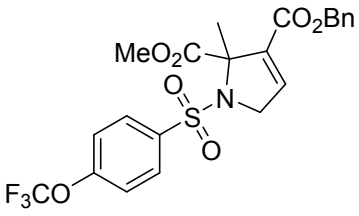


3-benzyl-2-methyl-1-((4-bromo-3-nitrophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ka)

A yellow oil, 27.6 mg, 60% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.36 (td, *J* = 2.0, 8.8 Hz, 2H), 8.04 (td, *J* = 2.0, 8.8 Hz, 2H), 7.36-7.31 (m, 5H), 6.88 (t, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 4.44 (dd, *J* = 2.4, 16.0 Hz, 1H), 4.34 (dd, *J* = 2.4, 16.0 Hz, 1H), 3.62 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.2, 160.7, 150.1, 145.3, 137.2, 136.5, 134.9, 128.62, 128.58, 128.5, 128.3, 124.3, 74.0, 67.0, 54.5, 53.0, 22.4; IR (neat): ν 2988, 2900,

1750, 1722, 1532, 1351, 1252, 1163, 1109, 1066, 1056, 737, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{24}N_3O_8S^+$ $(M+NH_4)^+$ requires 478.1279, Found: 478.1281.

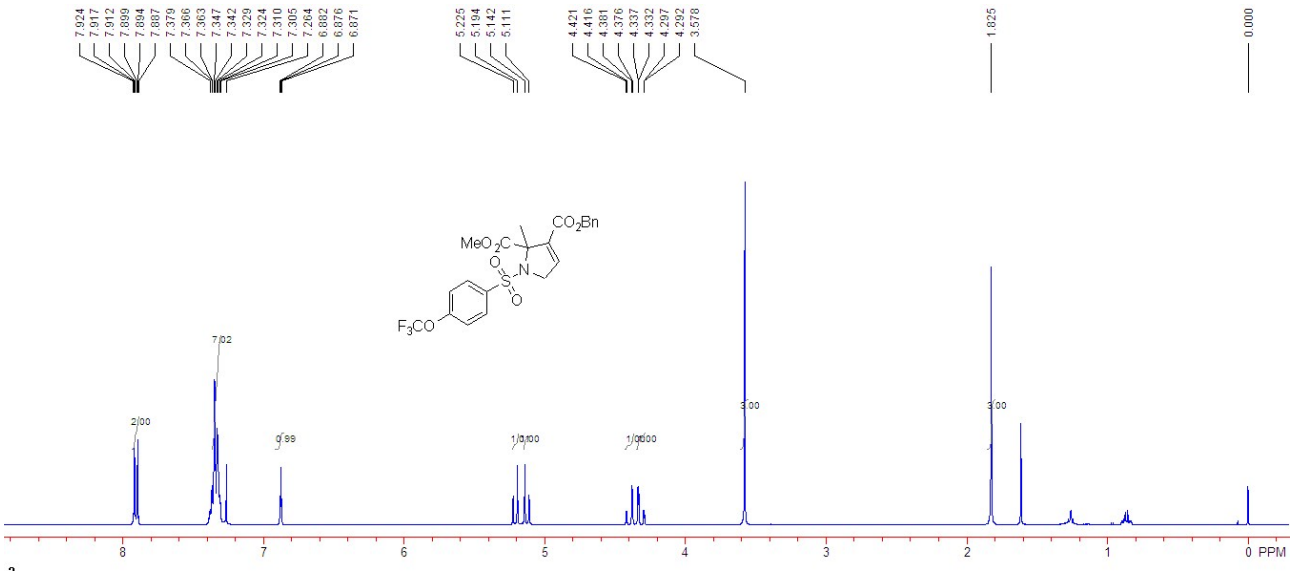


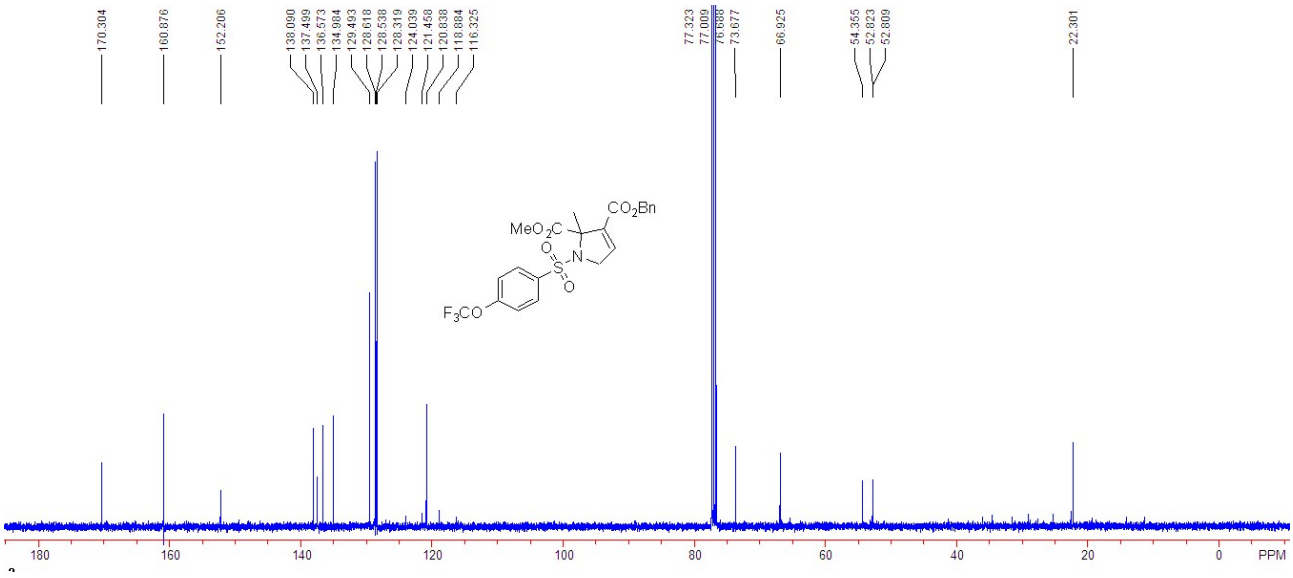


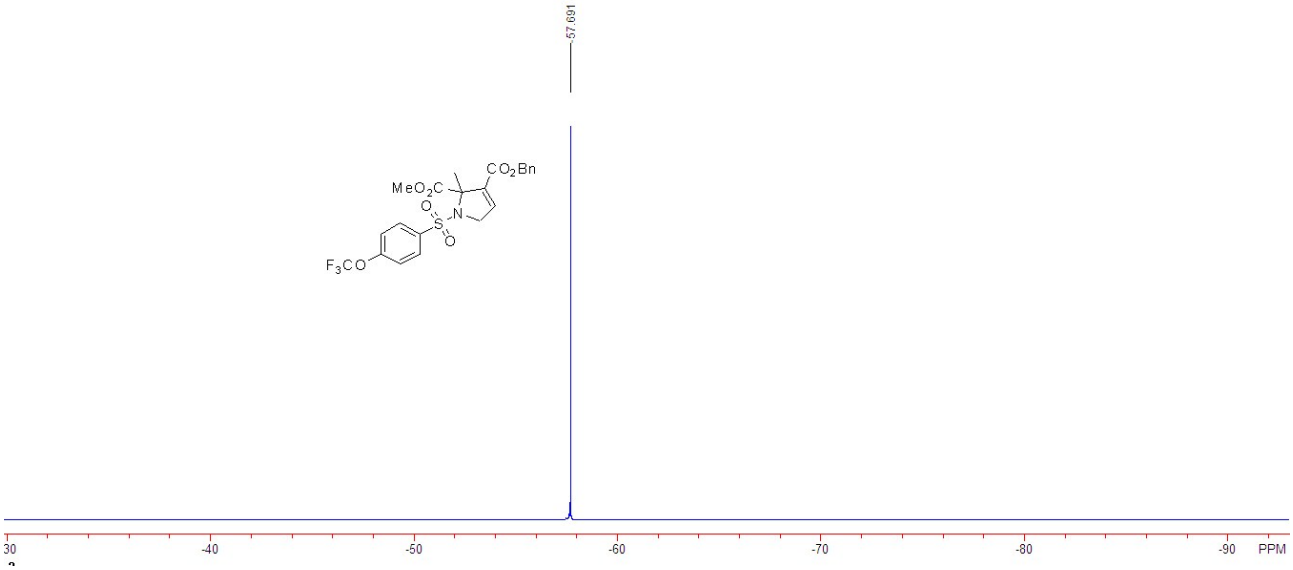
3-benzyl-2-methyl-2-methyl-1-((4-(trifluoromethoxy)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3la)

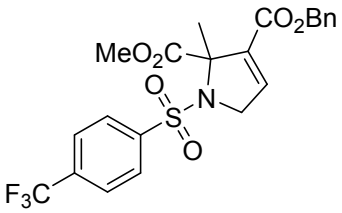
A yellow oil, 21.0 mg, 42% yield; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.91 (td, J = 2.8, 9.2 Hz, 2H), 7.38-7.31 (m, 7H), 6.88 (t, J = 2.4 Hz, 1H), 5.17 (d, J = 12.4 Hz, 1H), 5.13 (d, J = 12.4 Hz,

1H), 4.40 (dd, J = 2.0, 16.0 Hz, 1H), 4.31 (dd, J = 2.0, 16.0 Hz, 1H), 3.58 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.3, 160.9, 152.2, 138.1, 137.5, 136.6, 135.0, 129.5, 128.6 128.5, 128.3, 120.8, 120.2 (q, J = 258.1 Hz), 73.7, 66.9, 54.4, 52.8 (d, J = 1.4 Hz), 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -57.69; IR (neat): ν 2954, 1752, 1721, 1596, 1499, 1325, 1266, 1104, 1125, 1108, 1062, 714 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}FN_2O_7S^+$ $(M+NH_4)^+$ requires 517.1251, Found: 517.1259.





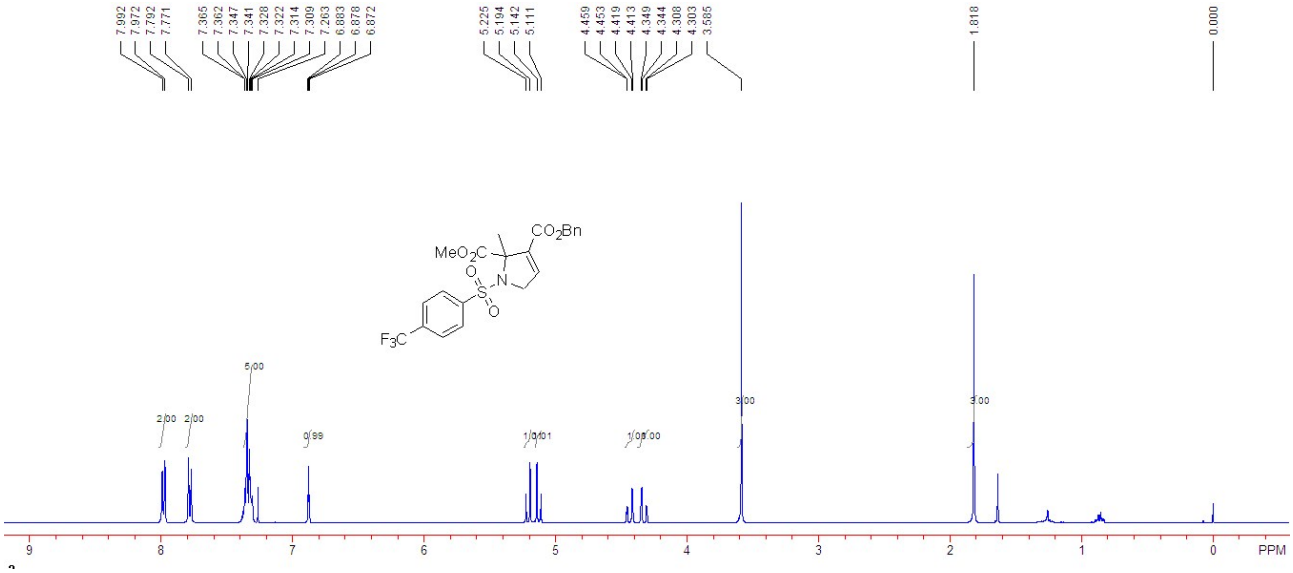


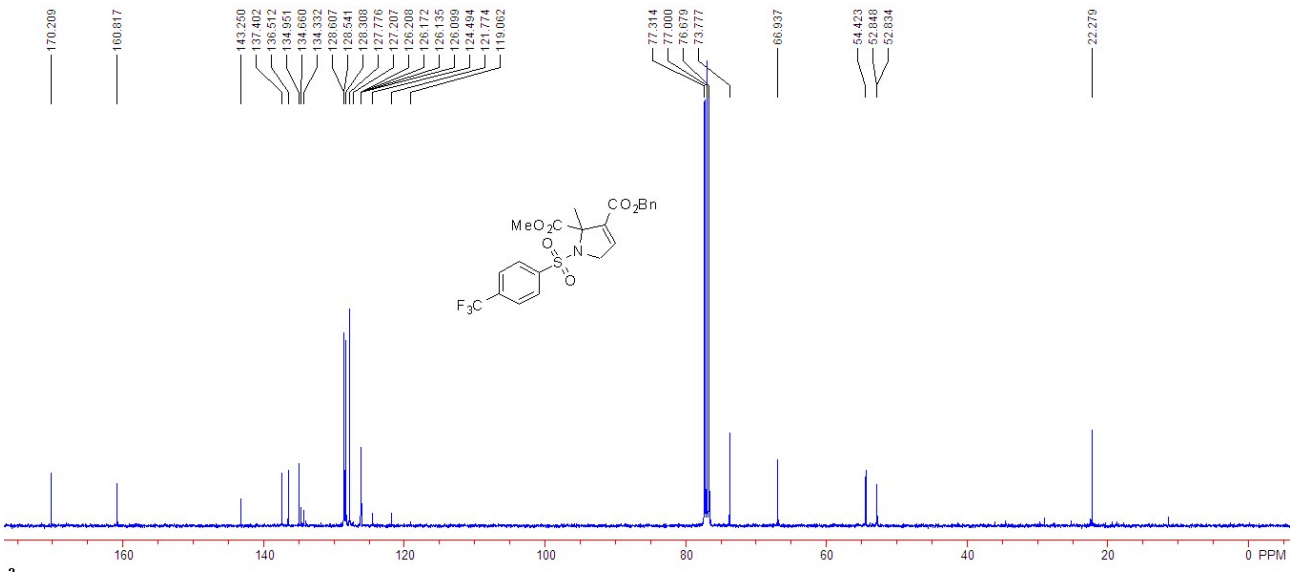


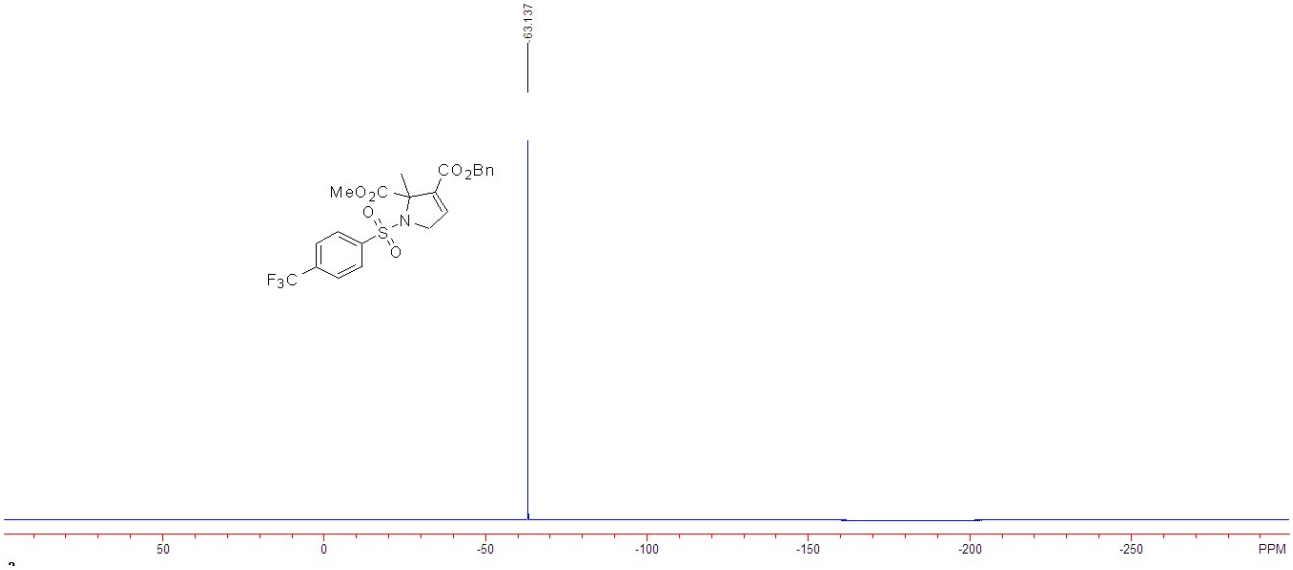
3-benzyl-2-methyl-2-methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ma)

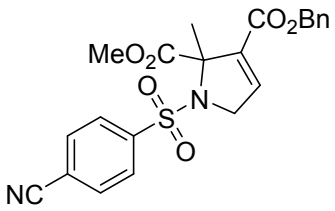
A yellow oil, 27.1 mg, 56% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.98 (d, J = 8.0 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.37-7.31 (m, 5H), 6.88 (t, J = 2.0 Hz, 1H), 5.21 (d, J = 12.4 Hz, 1H), 5.13 (d, J = 12.4 Hz, 1H), 4.44 (dd, J = 2.4, 16.0 Hz, 1H), 4.33 (dd, J = 2.0, 16.4 Hz, 1H), 3.59 (s, 3H),

1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.2, 160.8, 143.3, 137.4, 136.5, 135.0, 134.5 (d, J = 32.8 Hz), 128.6, 128.5, 128.3, 127.8, 126.2 (q, J = 3.6 Hz), 123.1 (q, J = 271.2 Hz), 73.8, 66.9, 54.4, 52.8 (d, J = 1.4 Hz), 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.14; IR (neat): ν 2954, 1752, 1721, 1350, 1323, 1266, 1164, 1125, 1108, 1062, 714 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}FN_2O_6S^+$ $(M+NH_4)^+$ requires 501.1302, Found: 501.1312.





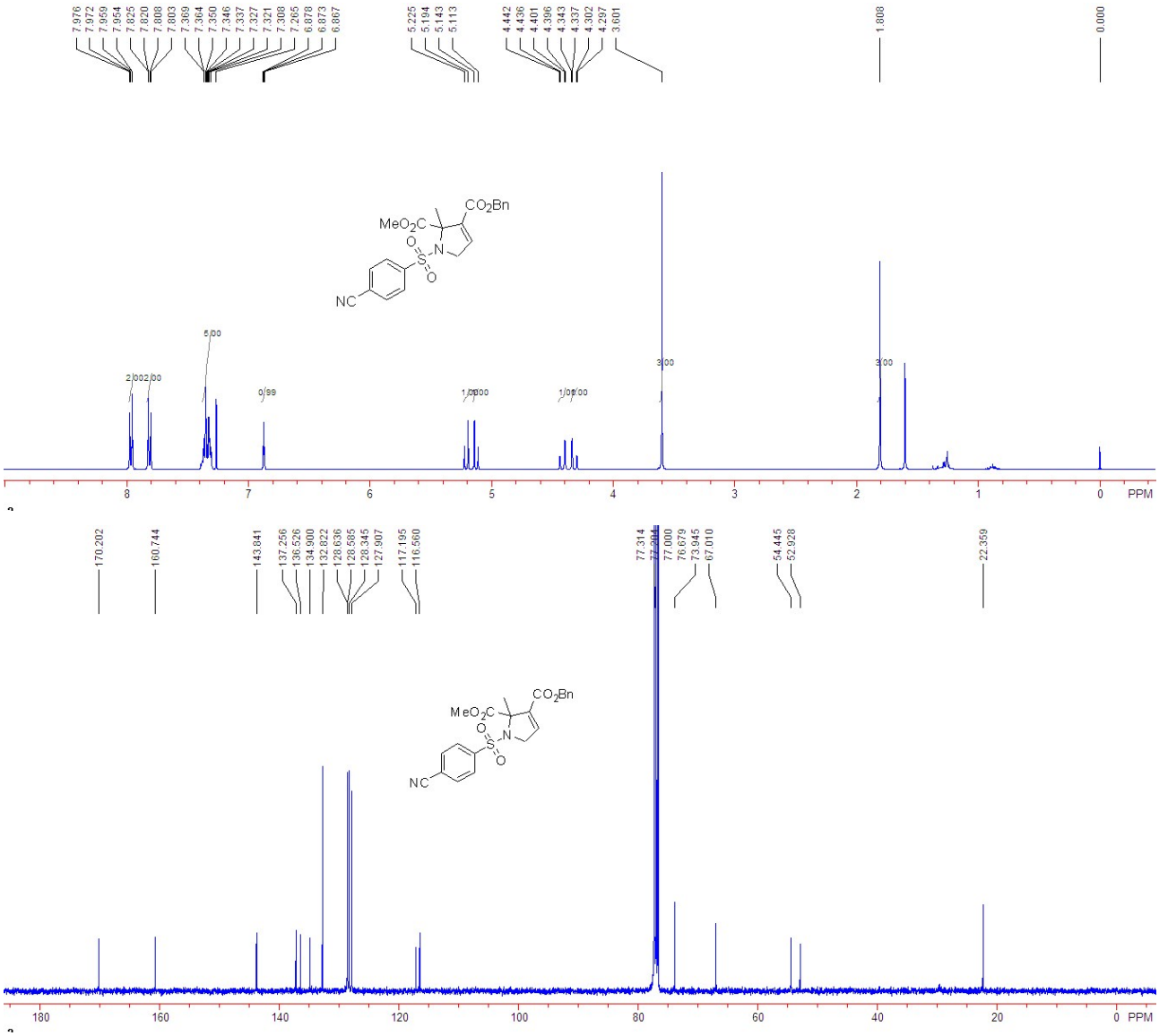


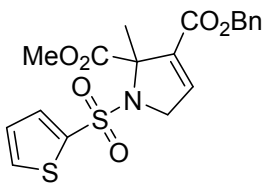


3-benzyl-2-methyl-1-((4-cyanophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3na)

A yellow oil, 24.2 mg, 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.81 (d, *J* = 8.8 Hz, 2H), 7.37-7.31 (m, 5H), 6.87 (t, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 4.42 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.32 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.60 (s, 3H),

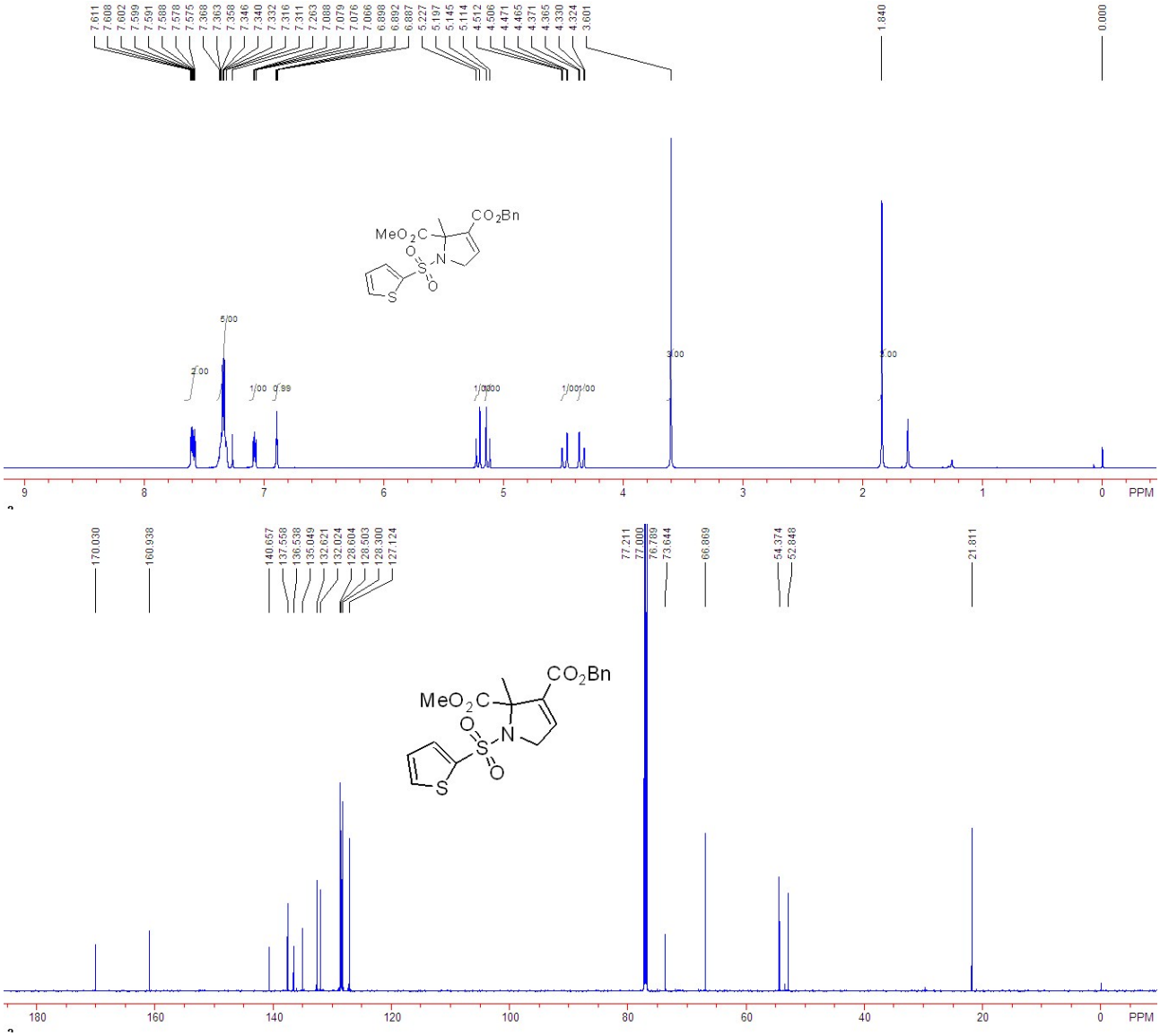
1.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.2, 160.7, 143.8, 137.3, 136.5, 134.9, 132.8, 128.64, 128.59, 128.3, 127.9, 117.2, 116.6, 73.9, 67.0, 54.4, 52.9, 22.4; IR (neat): ν 2988, 2901, 1750, 1721, 1641, 1455, 1394, 1350, 1266, 1161, 1108, 1054, 840, 749, 668 cm^{-1}; HRMS (ESI) Calcd. For $C_{22}H_{24}N_2O_6S^+$ $(M+NH_4)^+$ requires 458.1380, Found: 458.1382.

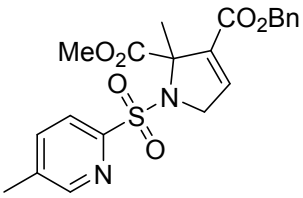




3-benzyl-2-methyl-2-methyl-1-(thiophen-2-ylsulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3oa)

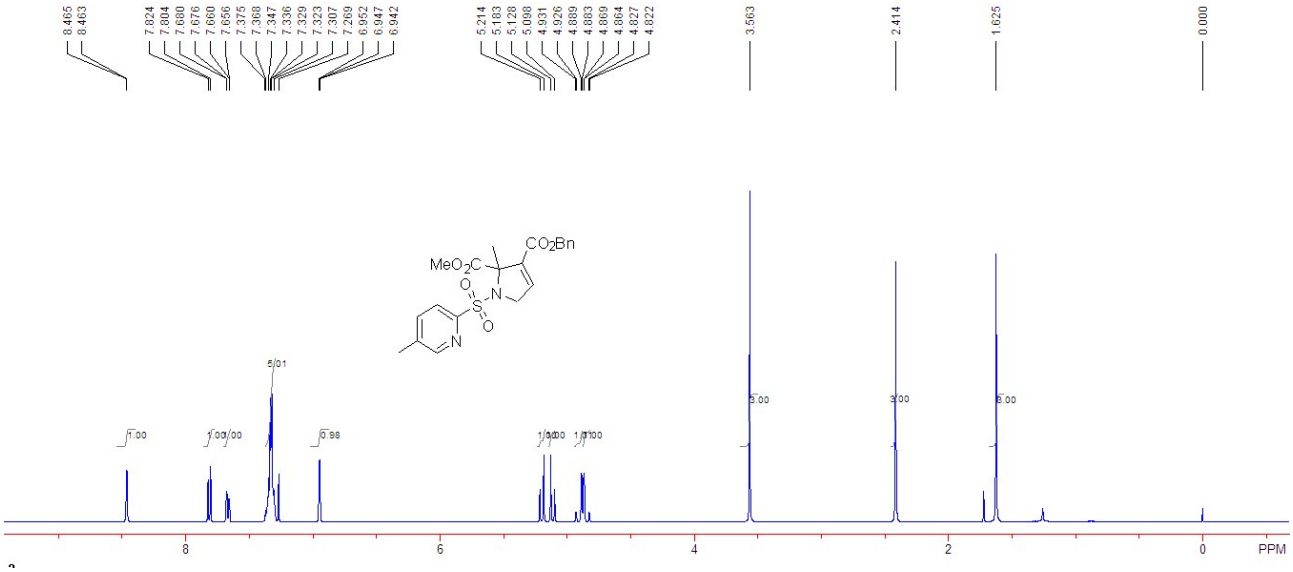
A yellow oil, 21.1 mg, 50% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.61-7.58 (m, 2H), 7.37-7.31 (m, 5H), 7.08 (dd, *J* = 3.6, 4.8 Hz, 1H), 6.89 (t, *J* = 2.4 Hz, 1H), 5.21 (d, *J* = 12.0 Hz, 1H), 5.13 (d, *J* = 12.4 Hz, 1H), 4.49 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.35 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.60 (s, 3H), 1.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.0, 160.9, 140.7, 137.6, 136.5, 135.0, 132.6, 132.0, 128.6, 128.5, 128.3, 127.1, 73.6, 66.9, 54.3, 52.8, 21.8; IR (neat): ν 2943, 1750, 1720, 1468, 1365, 1261, 1108, 1090, 1054, 1102, 758, 698 cm^{-1}; HRMS (ESI) Calcd. For $C_{19}H_{23}N_2O_6S_2^+$ $(M+NH_4)^+$ requires 439.5210, Found: 439.5212.

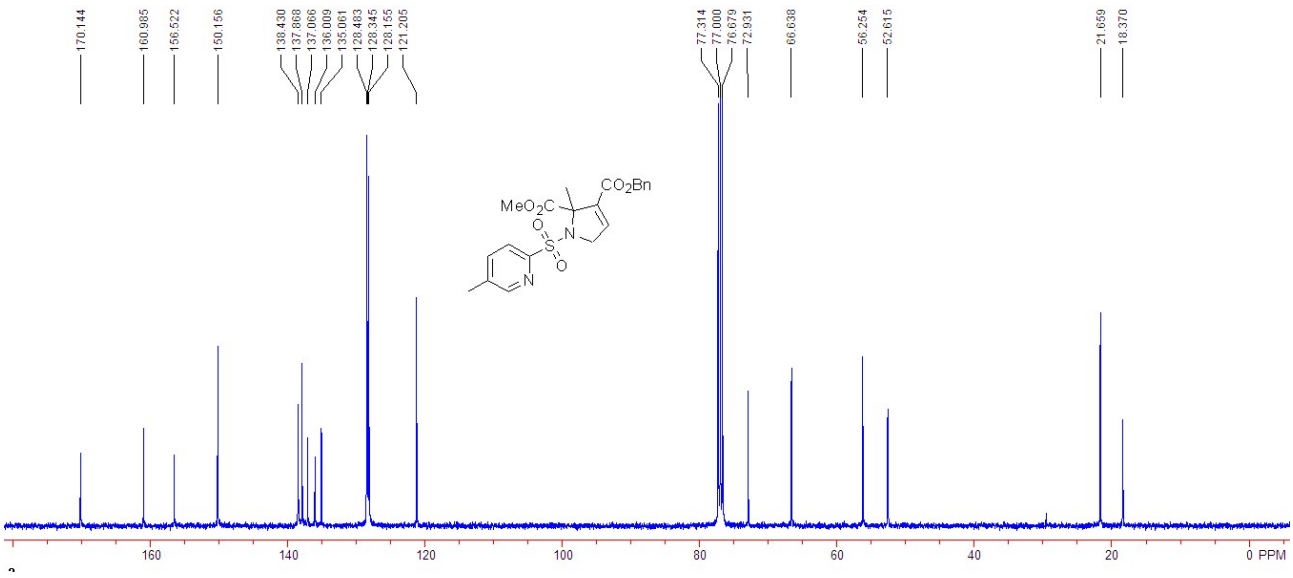


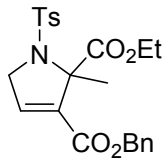


3-benzyl-2-methyl-2-methyl-1-((5-methylpyridin-2-yl)sulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3pa)

A yellow oil, 34.4 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.46 (d, *J* = 0.8 Hz, 1H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.67 (dd, *J* = 1.6, 8.0 Hz, 1H), 7.38-7.31 (m, 5H), 6.95 (t, *J* = 2.0 Hz, 1H), 5.20 (d, *J* = 12.4 Hz, 1H), 5.11 (d, *J* = 12.0 Hz, 1H), 4.91 (dd, *J* = 2.0, 16.8 Hz, 1H), 4.85 (dd, *J* = 2.0, 16.8 Hz, 1H), 3.56 (s, 3H), 2.41 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.1, 161.0, 156.5, 150.2, 138.4, 137.9, 137.1, 136.0, 135.1, 128.5, 128.3, 128.2, 121.2, 72.9, 66.6, 56.3, 52.6, 21.7, 18.4; IR (neat): ν 2943, 1750, 1720, 1488, 1465, 1261, 1108, 1090, 1054, 1102, 758, 698 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{23}N_2O_6S^+$ $(M+H)^+$ requires 431.1271, Found: 431.1280.

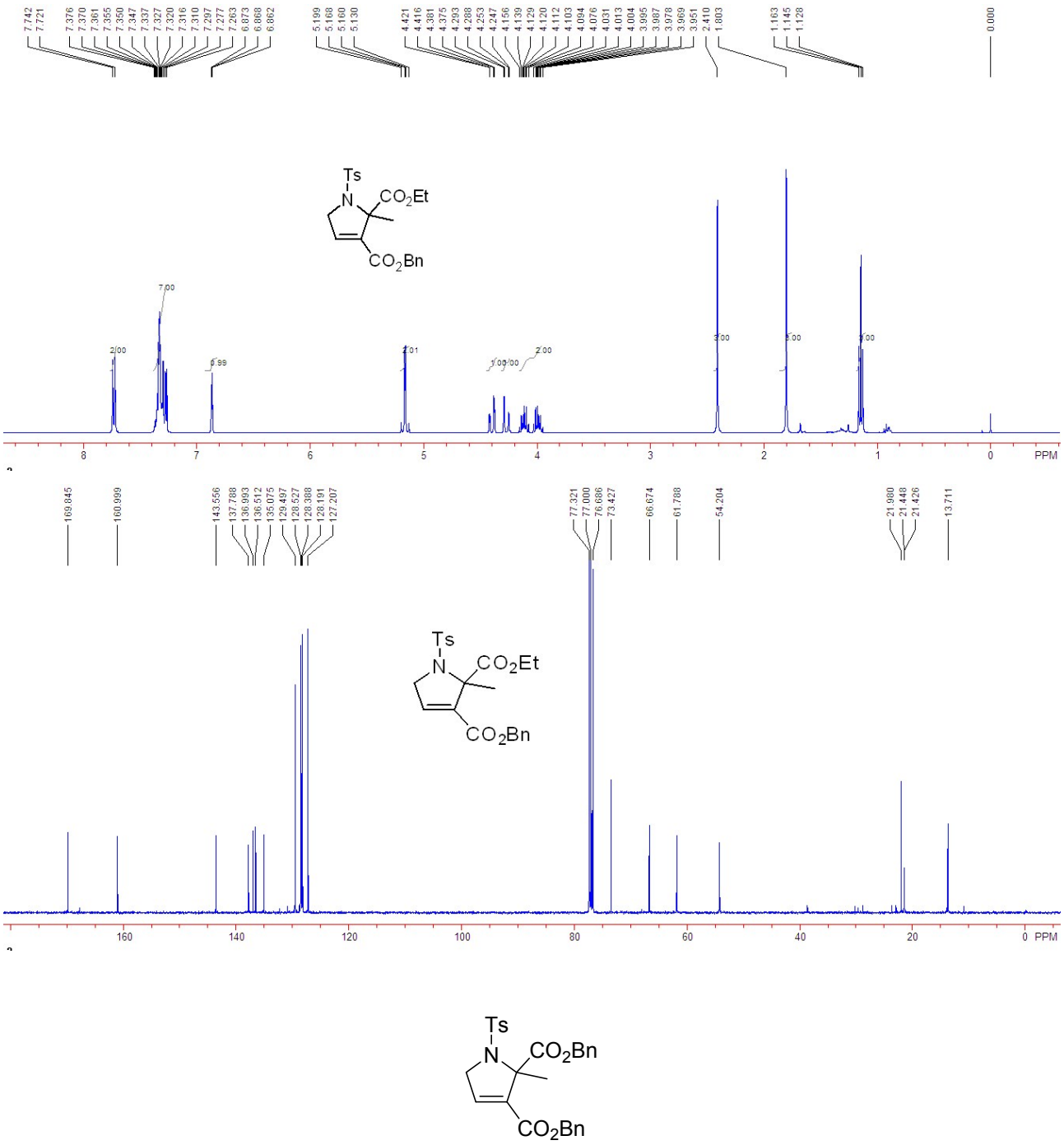






3-benzyl-2-ethyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3qa)

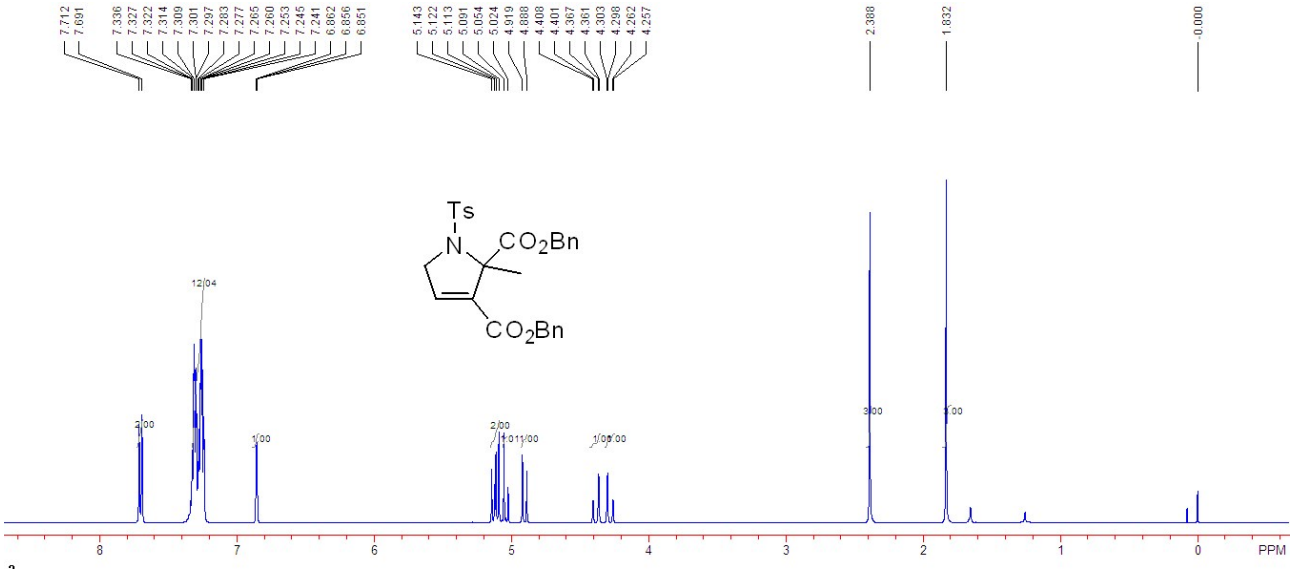
A yellow oil, 38.1 mg, 86% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.36-7.31 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 2.4 Hz, 1H), 5.18 (d, *J* = 12.4 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 4.40 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.27 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.16-3.95 (m, 2H), 2.41 (s, 3H), 1.80 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.8, 161.0, 143.6, 137.8, 137.0, 136.5, 135.1, 129.5, 128.5, 128.4, 128.2, 127.2, 73.4, 66.7, 61.8, 54.2, 22.0, 21.4 (d, *J* = 2.2 Hz), 13.7; IR (neat): ν 2936, 1747, 1720, 1346, 1249, 1158, 1103, 1054, 815, 738, 699, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{23}H_{29}N_2O_6S^+$ $(M+NH_4)^+$ requires 461.1741, Found: 461.1750.

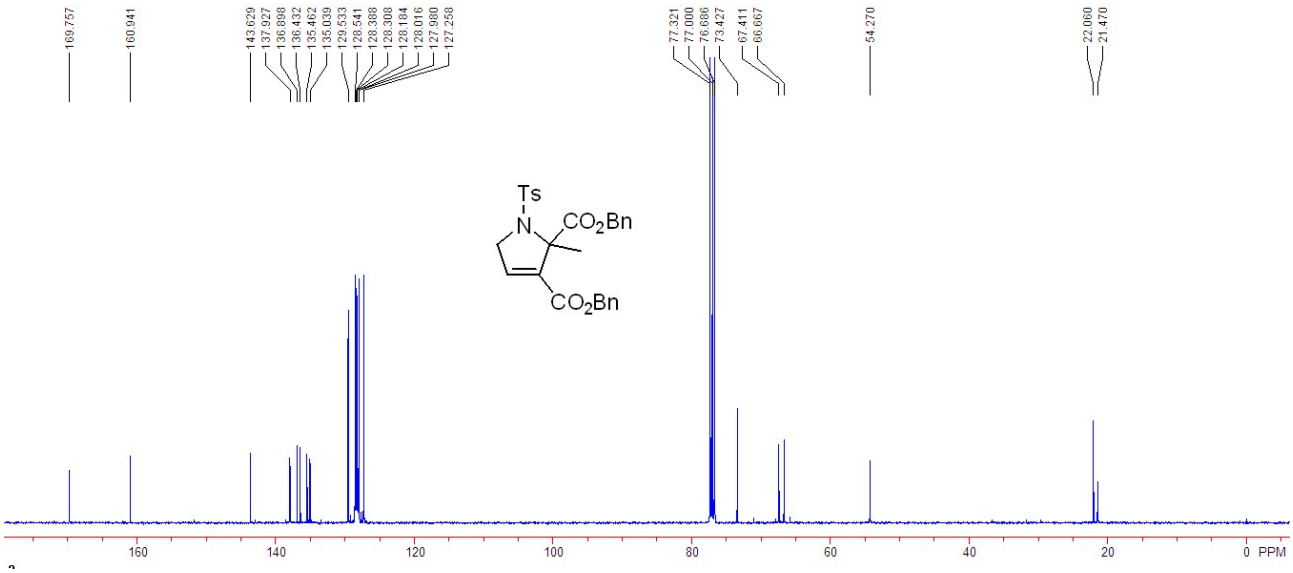


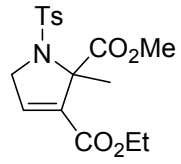
dibenzyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ra)

A yellow oil, 47.5 mg, 94% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.70 (d, *J* = 8.4 Hz, 2H), 7.34-7.24 (m, 10H), 7.29 (d, *J* = 8.0 Hz, 2H), 6.86 (t, *J* = 2.4 Hz, 1H), 5.13 (d, *J* = 12.0 Hz, 1H), 5.11 (d, *J* = 12.4 Hz, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 4.90 (d, *J* = 12.4 Hz, 1H), 4.38 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.28 (dd, *J* = 2.0, 16.4 Hz, 1H), 2.39 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.8, 160.9, 143.6, 137.9, 136.9, 136.4, 135.5, 135.0, 129.5, 128.5, 128.4, 128.3, 128.2, 128.02, 127.98, 127.3, 73.4, 67.4, 66.7, 54.3, 22.1, 21.5; IR (neat): ν 2949, 1751, 1721, 1456,

1347, 1266, 1159, 1106, 1054, 747, 697, 669 cm^{-1}; HRMS (ESI) Calcd. For $C_{28}H_{31}N_2O_6S^+$ $(M+NH_4)^+$ requires 523.1897, Found: 523.1907.



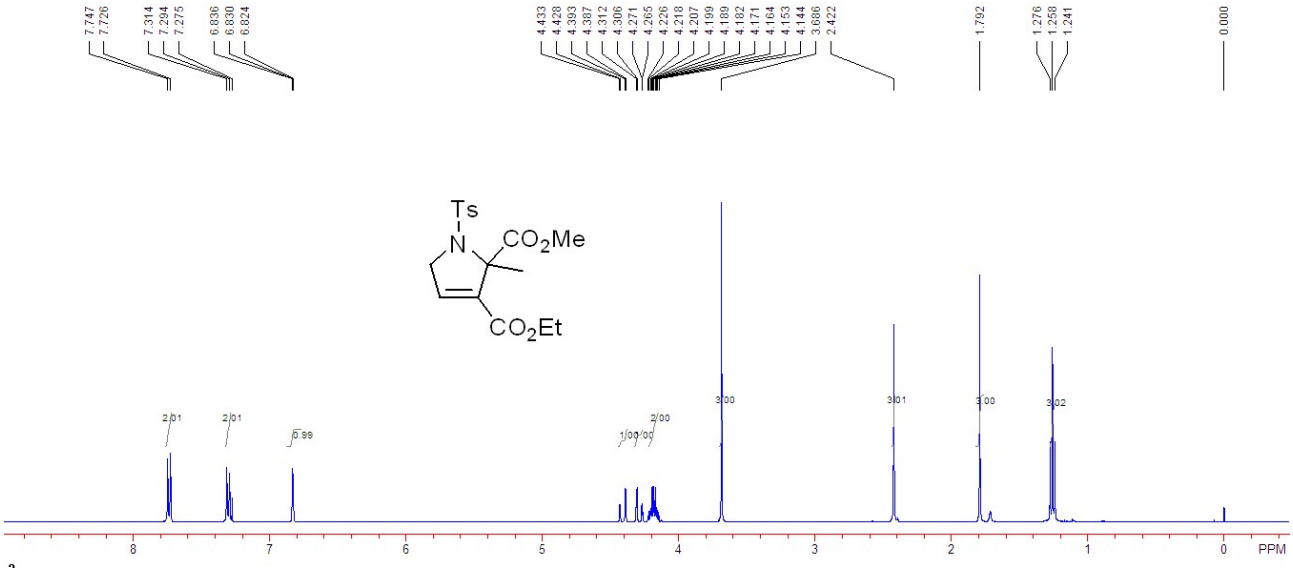


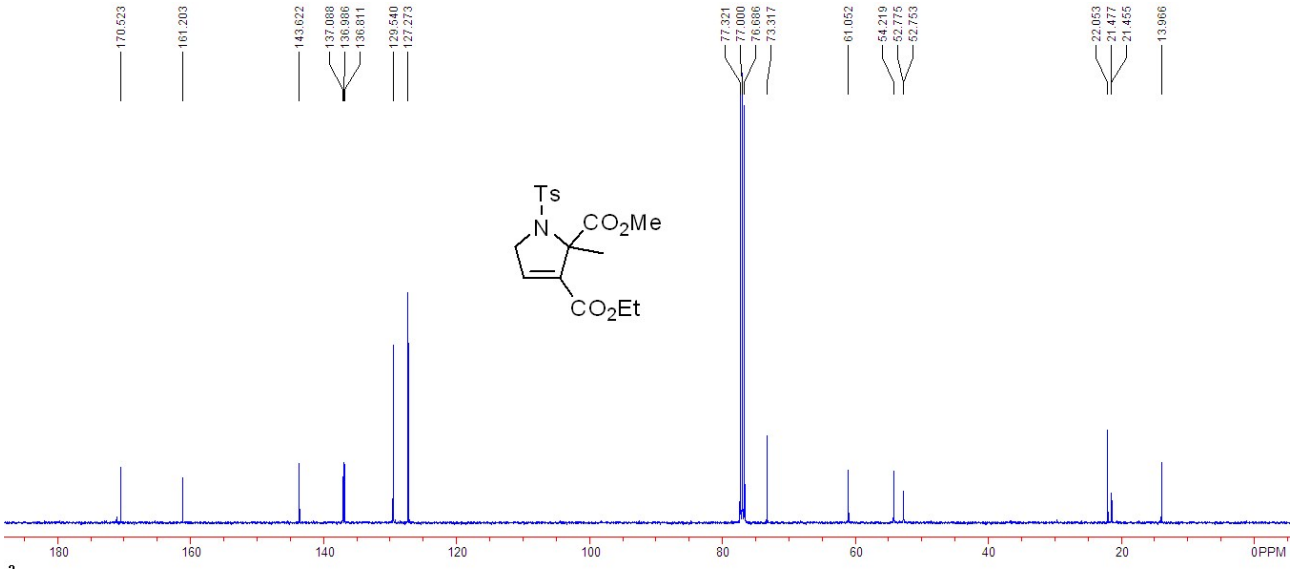


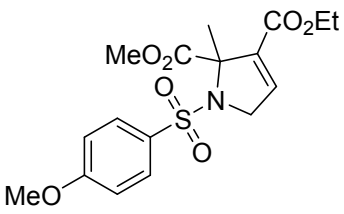
3-ethyl-2-methyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ab)

A yellow oil, 33.8 mg, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 2.4 Hz, 1H), 4.41 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.29 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.23-4.14 (m, 2H), 3.69 (s, 3H), 2.42 (s, 3H), 1.79 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.5, 161.2, 143.6, 137.1, 137.0, 136.8, 129.5, 127.3, 73.3,

61.1, 54.2, 52.8, 22.1, 21.5 (d, J = 2.2 Hz), 14.0; IR (neat): ν 2972, 1750, 1718, 1344, 1317, 1252, 1157, 1102, 1057, 1016, 815, 752, 708, 670 cm^{-1}; HRMS (ESI) Calcd. For $C_{17}H_{25}N_2O_6S^+$ $(M+NH_4)^+$ requires 385.1428, Found: 385.1440.

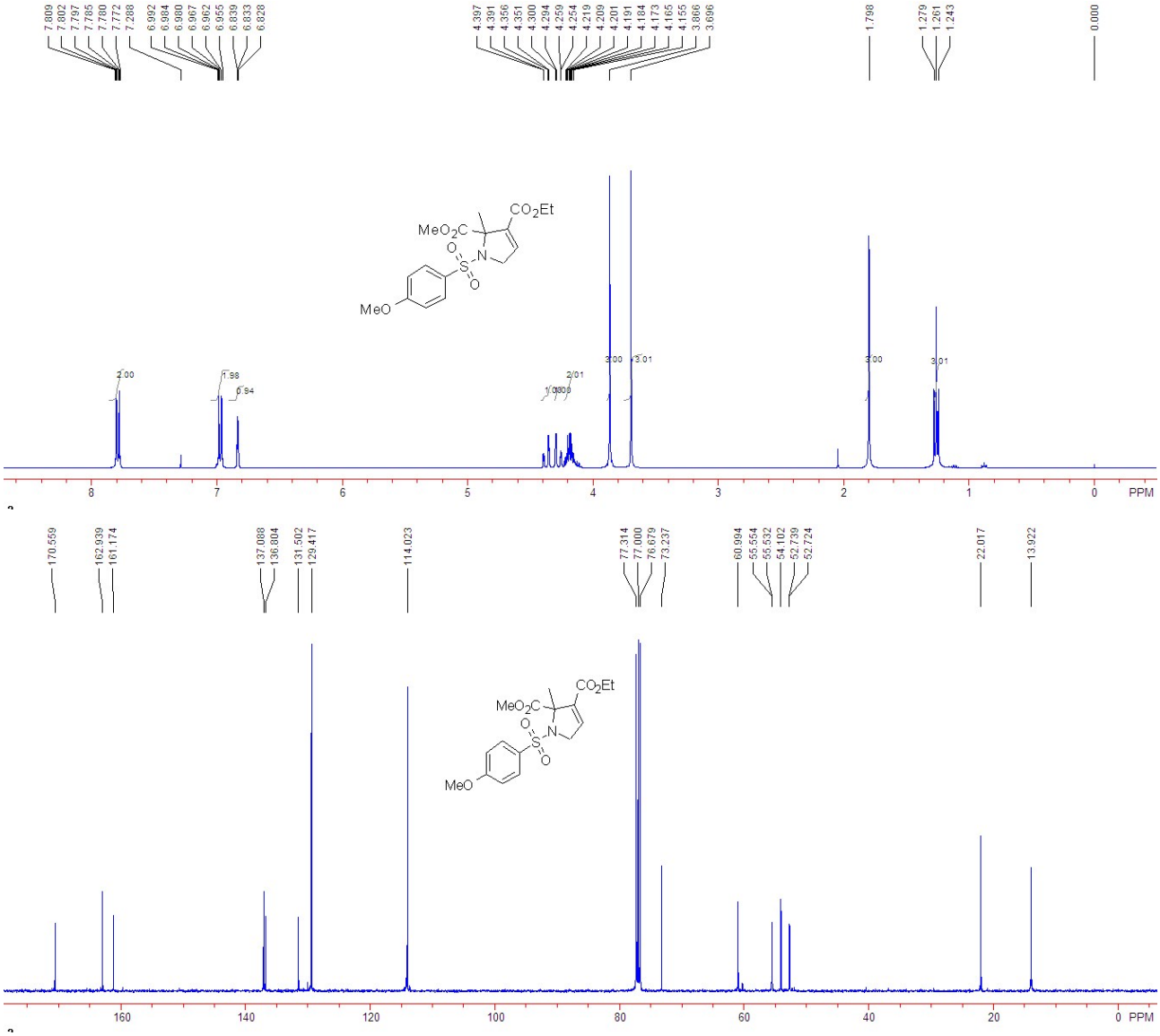


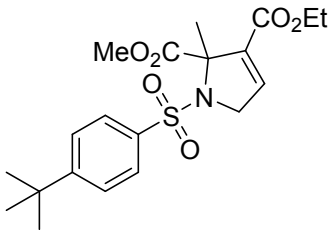




3-ethyl-2-methyl-1-((4-methoxyphenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3bb)

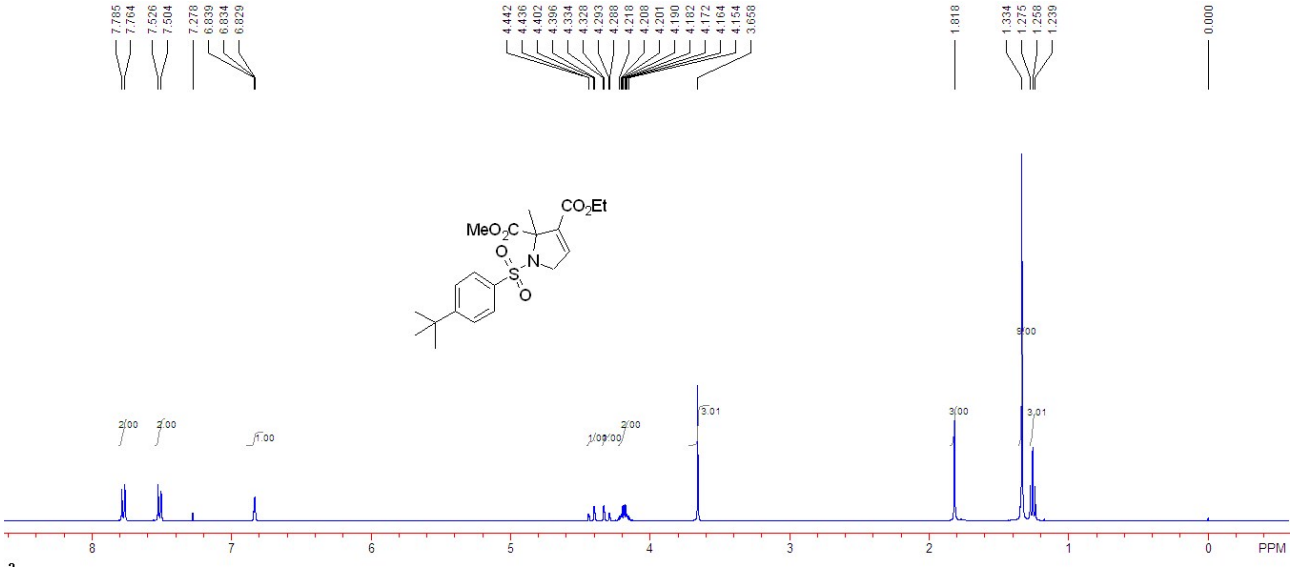
A yellow oil, 32.6 mg, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.79 (td, *J* = 2.0, 8.8 Hz, 2H), 6.97 (td, *J* = 2.0, 8.8 Hz, 2H), 6.83 (t, *J* = 2.4 Hz, 1H), 4.37 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.28 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.22-4.16 (m, 2H), 3.87 (s, 3H), 3.70 (s, 3H), 1.80 (s, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.6, 162.9, 161.2, 137.1, 136.8, 131.5, 129.4, 114.0, 73.2, 61.0, 55.5 (d, *J* = 2.2 Hz), 54.1, 52.7 (d, *J* = 1.5 Hz), 22.0, 13.9; IR (neat): ν 2945, 1752, 1720, 1596, 1499, 1346, 1260, 1156, 1104, 830, 815, 799, 676 cm^{-1}; HRMS (ESI) Calcd. For $C_{17}H_{22}NO_7S^+$ $(M+H)^+$ requires 384.1111, Found: 384.1117.

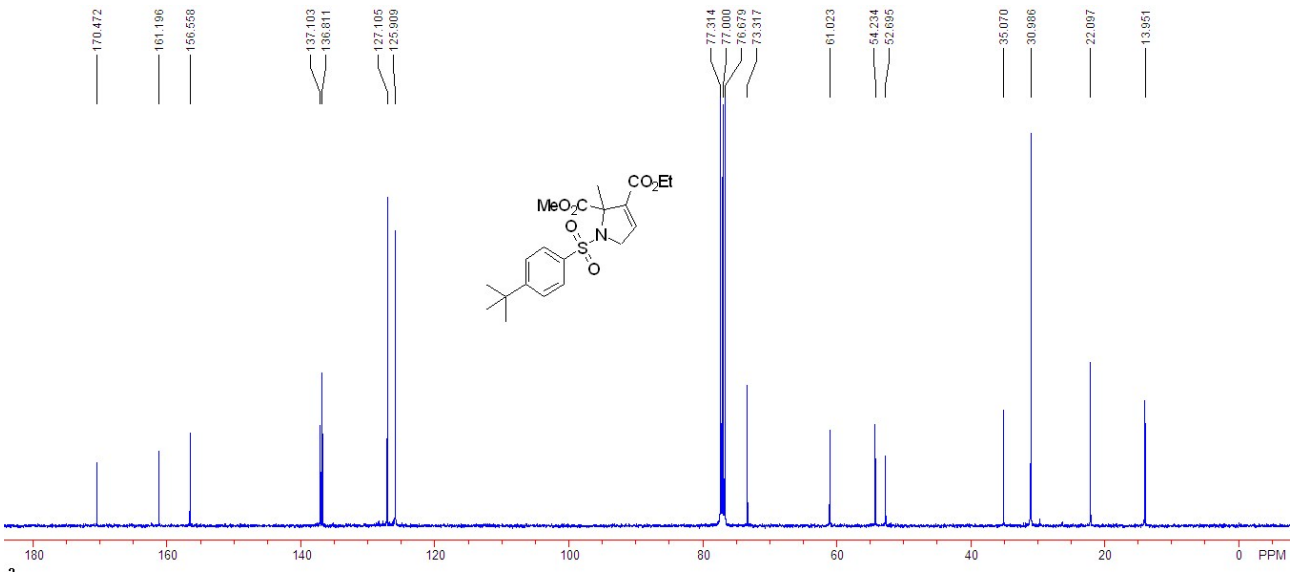


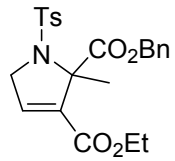


3-ethyl-2-methyl-1-((4-(tert-butyl)phenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3cb)

A yellow oil, 30.3 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 6.83 (t, *J* = 2.0 Hz, 1H), 4.42 (dd, *J* = 2.4, 16.0 Hz, 1H), 4.31 (dd, *J* = 2.4, 16.0 Hz, 1H), 4.22-4.15 (m, 2H), 3.66 (s, 3H), 1.82 (s, 3H), 1.33 (s, 9H), 1.26 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.5, 161.2, 156.6, 136.8, 127.1, 125.9, 73.3, 61.0, 54.2, 54.1, 52.7, 35.1, 31.0, 22.1, 14.0; IR (neat): ν 2972, 2862, 1752, 1721, 1590, 1453, 1346, 1267, 1163, 1116, 1102, 1089, 1059, 846, 747 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{31}N_2O_6S^+$ $(M+NH_4)^+$ requires 427.1897, Found: 427.1900.

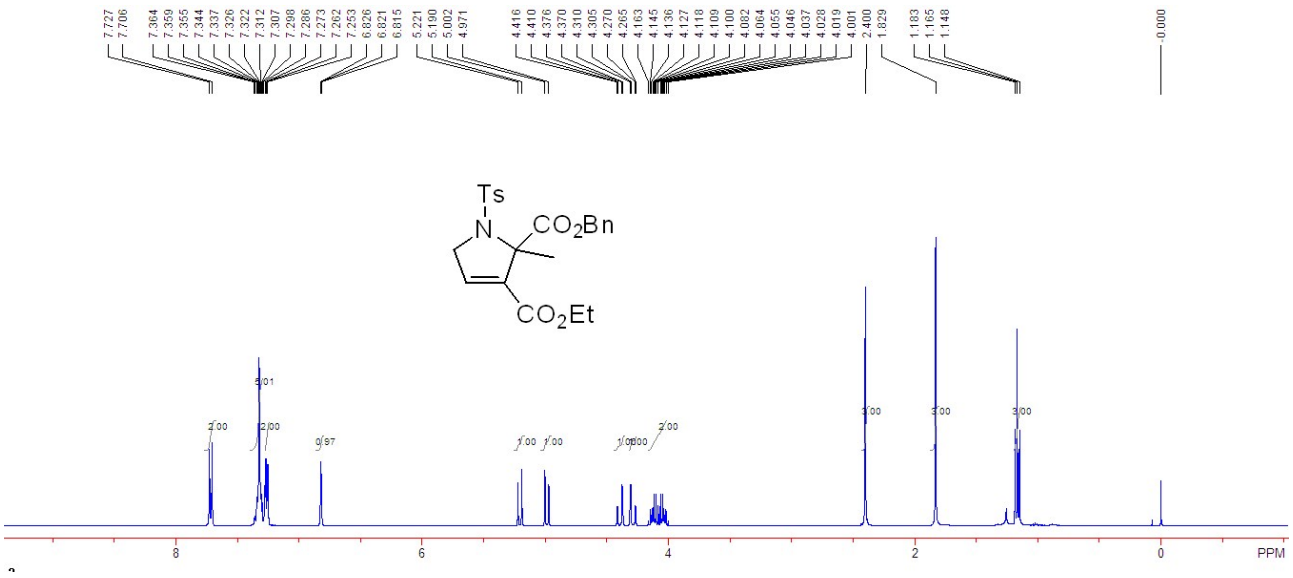


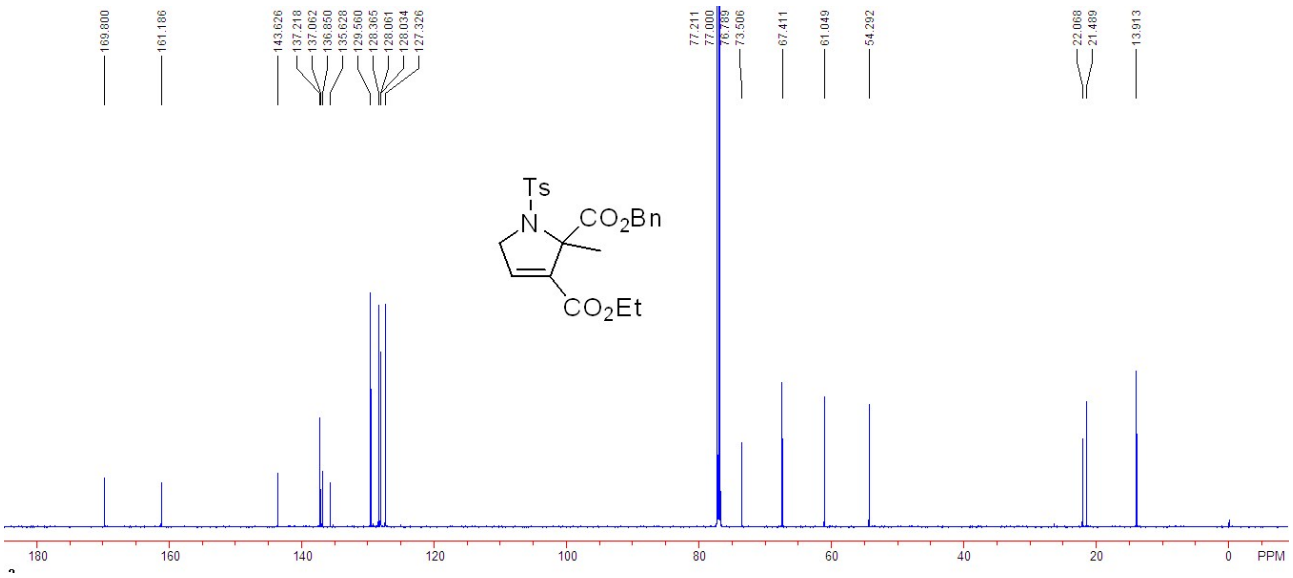


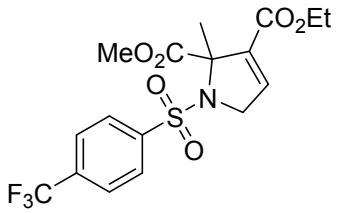


2-benzyl-3-ethyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3db)

A yellow oil, 35.5 mg, 80% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.72 (d, *J* = 8.4 Hz, 2H), 7.36-7.29 (m, 5H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.82 (t, *J* = 2.0 Hz, 1H), 5.21 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.39 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.29 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.16-4.00 (m, 2H), 2.40 (s, 3H), 1.83 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.8, 161.2, 143.6, 137.2, 137.1, 136.9, 135.6, 129.6, 128.4, 128.1, 128.0, 127.3, 73.5, 67.4, 61.0, 54.3, 22.1, 21.5, 13.9; IR (neat): ν 2974, 2927, 2854, 1752, 1720, 1644, 1592, 1456, 1346, 1254, 1105, 1058, 815, 749, 698, 671 cm^{-1}; HRMS (ESI) Calcd. For $C_{23}H_{29}N_2O_6S^+$ $(M+NH_4)^+$ requires 461.1741, Found: 461.1749.



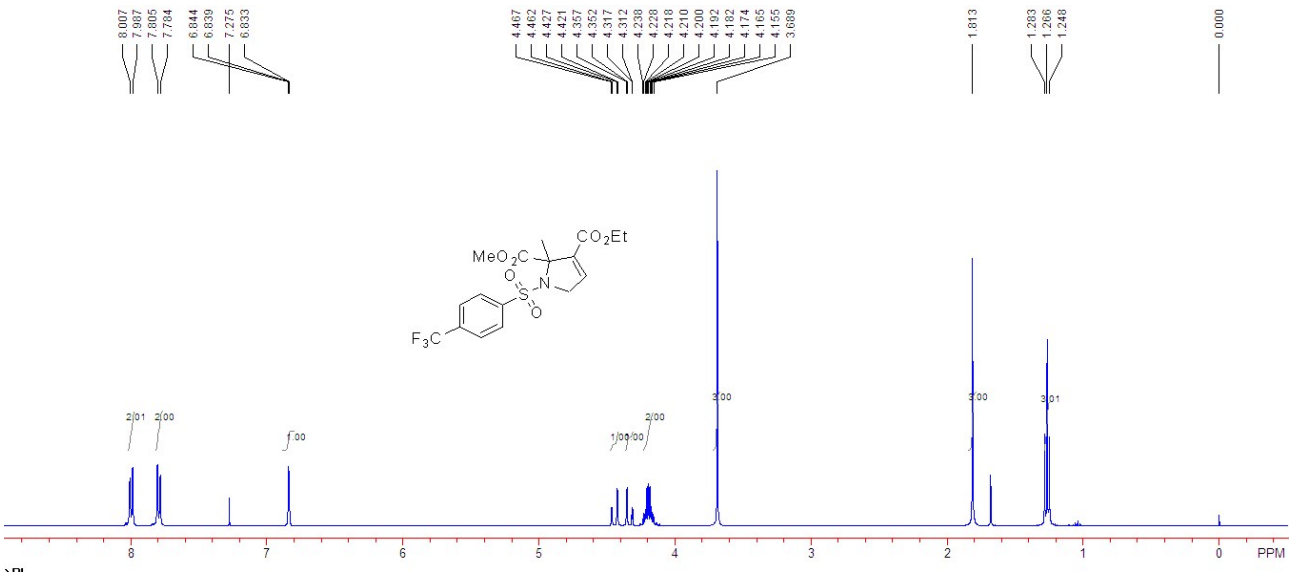




3-ethyl-2-methyl-2-methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3eb)

A yellow oil, 35.0 mg, 83% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.00 (d, J = 8.0 Hz, 2H), 7.79 (d, J = 8.4 Hz, 2H), 6.84 (t, J = 2.4 Hz, 1H), 4.44 (dd, J = 2.0, 16.0 Hz, 1H), 4.33 (dd, J = 2.0, 16.0 Hz, 1H), 4.24-4.16 (m, 2H), 3.69 (s, 3H), 1.81 (s, 3H), 1.27 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.3, 161.0, 143.3, 136.8, 136.7, 134.5 (q, J = 33.5 Hz), 127.8, 126.1 (q, J =

3.7 Hz), 123.1 (q, J = 271.3 Hz), 73.8, 61.2, 54.4, 52.9 (d, J = 2.2 Hz), 22.2, 14.0; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.14; IR (neat): ν 3108, 2995, 2948, 1751, 1720, 1647, 1605, 1461, 1351, 1404, 1351, 1321, 1253, 1164, 1105, 1014, 845, 747, 713 cm^{-1}; HRMS (ESI) Calcd. For $C_{17}H_{22}F_3N_2O_6S^+$ $(M+NH_4)^+$ requires 439.1145, Found: 439.1155.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7.784
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6.839
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6.633
4.467
4.462
4.427
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4.352
4.317
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4.238
4.228
4.218
4.210
4.200
4.192
4.182
4.174
4.165
4.155
3.689
1.813
1.283
1.266
1.248
0.000
MeO2C
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2.00
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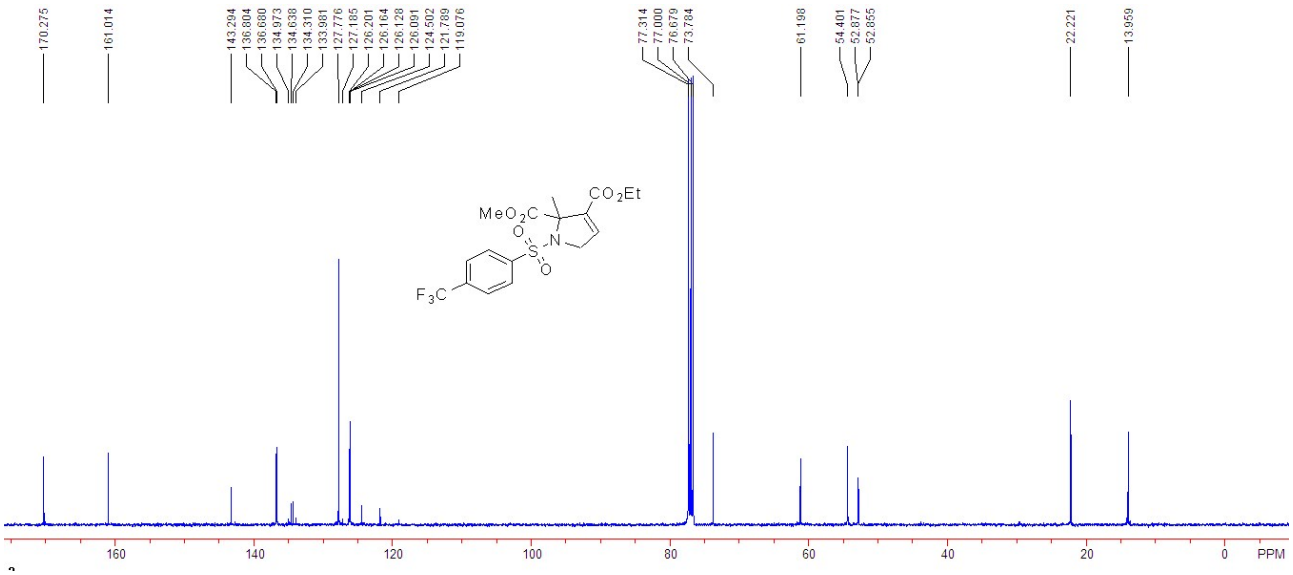
PPM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77.000
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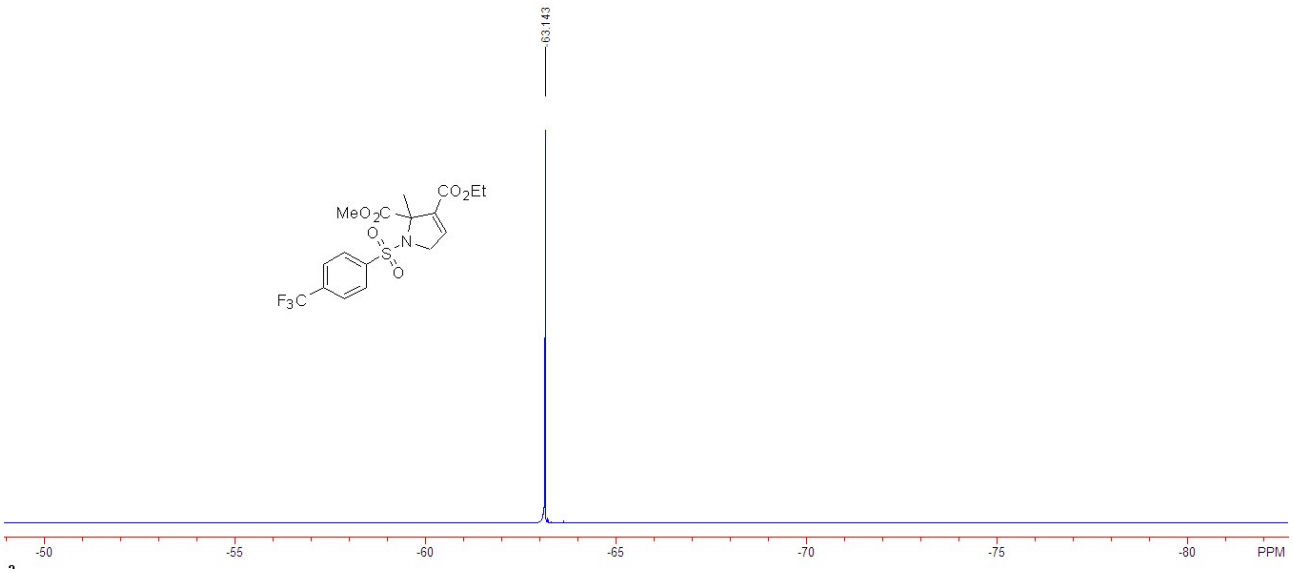
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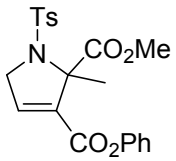
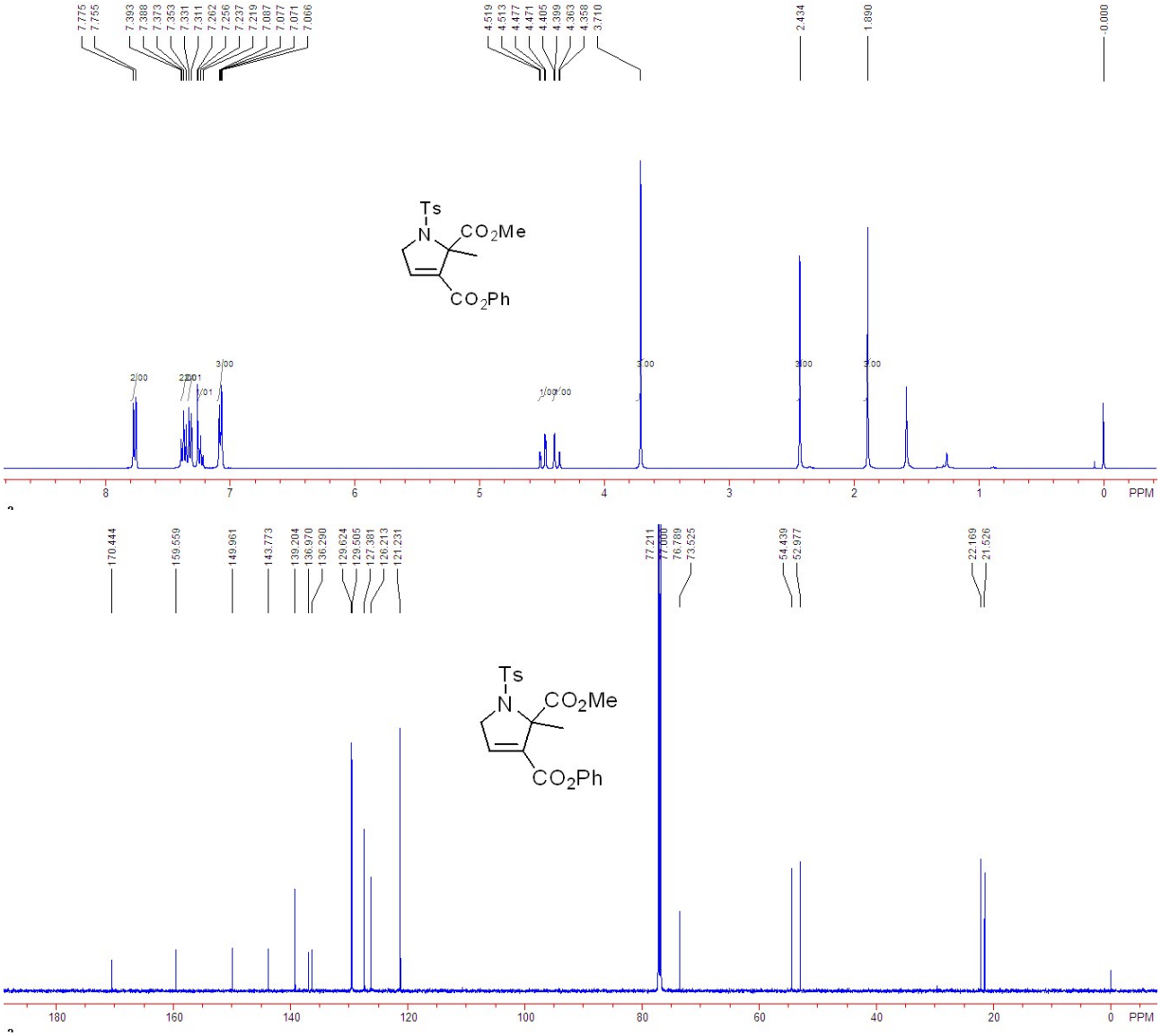
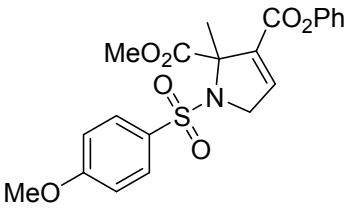
F3C
PPM



2-methyl-3-phenyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ac)

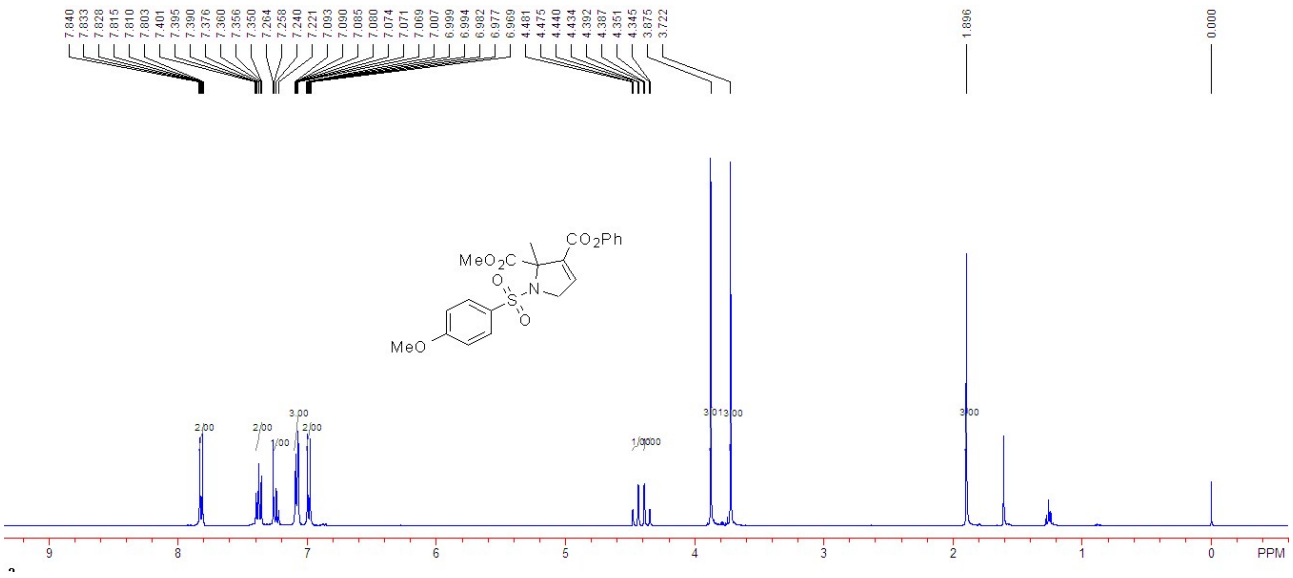
A yellow oil, 34.6 mg, 79% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.39-7.37 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09-7.07 (m, 3H), 4.50 (dd, *J* = 2.4, 16.8 Hz, 1H), 4.38 (dd, *J* = 2.4, 16.8 Hz, 1H), 3.71 (s, 3H), 2.43 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 159.6, 149.7, 143.8, 139.2, 137.0, 136.3, 129.6, 129.5, 127.4, 126.2, 121.2, 73.5, 54.4, 53.0, 22.2, 21.5; IR (neat): ν 3369, 3267, 2945, 2924, 1740, 1642, 1587, 1491, 1451, 1344, 1252, 1192, 1161, 1099, 1038, 815, 738, 689, 672 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}NNaO_6S^+$ $(M+Na)^+$ requires 438.0982, Found: 438.0986.

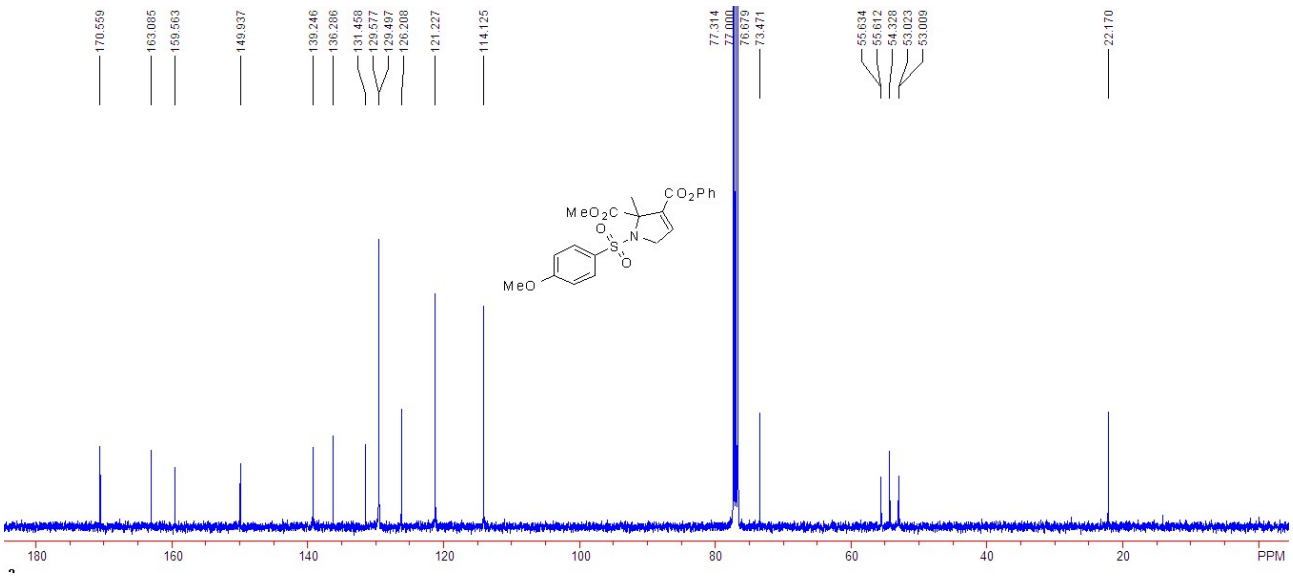


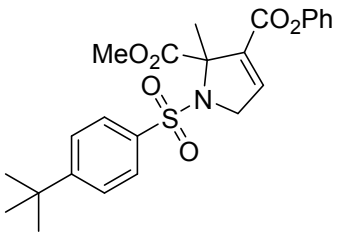


2-methyl-3-phenyl-1-((4-methoxyphenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3bc)

A yellow oil, 32.2 mg, 71% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (td, *J* = 9.2, 2.0 Hz, 2H), 7.40-7.35 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09-7.07 (m, 3H), 6.99 (td, *J* = 8.8, 2.0 Hz, 2H), 4.46 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.37 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.88 (s, 3H), 2.72 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.6, 163.1, 159.6, 150.0, 139.2, 136.3, 131.5, 129.6, 129.5, 126.2, 121.2, 114.1, 73.5, 55.6 (d, *J* = 2.2 Hz), 54.3, 53.0 (d, *J* = 1.4 Hz), 22.2; IR (neat): ν 3100, 2945, 2835, 1748, 1596, 1498, 1357, 1255, 1188, 1154, 1096, 1031, 833, 741, 676 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{21}NNaO_7S^+$ $(M+Na)^+$ requires 454.0931, Found: 454.0933.



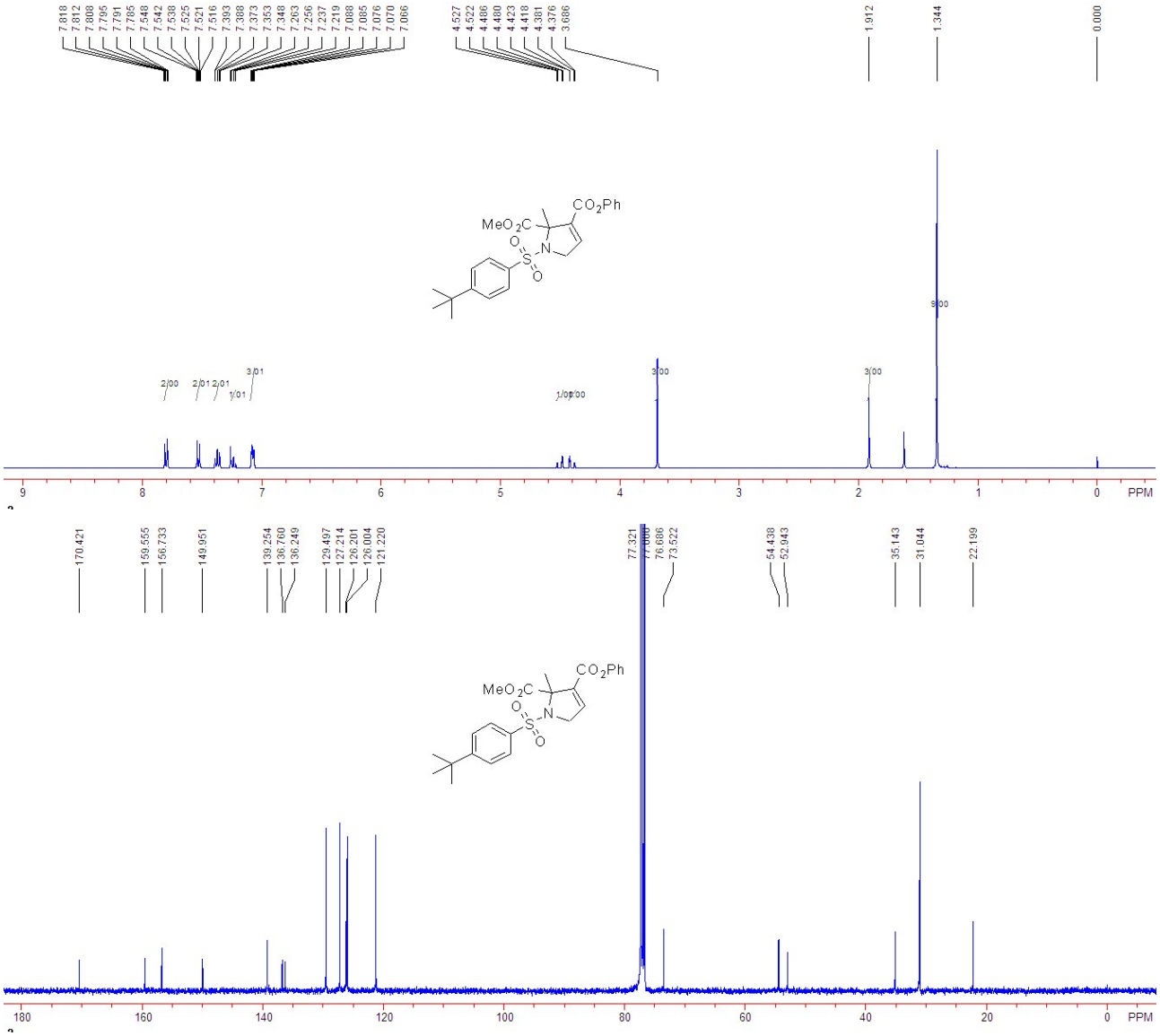


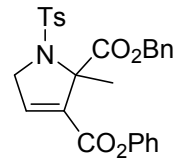


2-methyl-3-phenyl-1-((4-(tert-butyl)phenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3cc)

A yellow oil, 33.9 mg, 74% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.80 (td, *J* = 8.4, 2.4 Hz, 2H), 7.53 (td, *J* = 8.4, 2.4 Hz, 2H), 7.39-7.35 (m, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.09-7.07 (m, 3H), 4.50 (dd, *J* = 2.0, 16.8 Hz, 1H), 4.40 (dd, *J* = 2.0, 16.8 Hz, 1H), 3.69 (s, 3H), 1.91 (s, 3H), 1.34 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.4, 159.6, 156.7, 150.0, 139.3, 136.8, 136.2, 129.5,

127.2, 126.2, 126.0, 121.2, 73.5, 54.4, 52.9, 35.1, 31.0, 22.2; IR (neat): ν 2970, 2850, 1751, 1720, 1562, 1403, 1350, 1267, 1168, 1130, 1102, 1089, 846, 737, 676 cm^{-1}; HRMS (ESI) Calcd. For $C_{24}H_{31}N_2O_6S^+$ $(M+NH_4)^+$ requires 475.1897, Found: 475.1904.

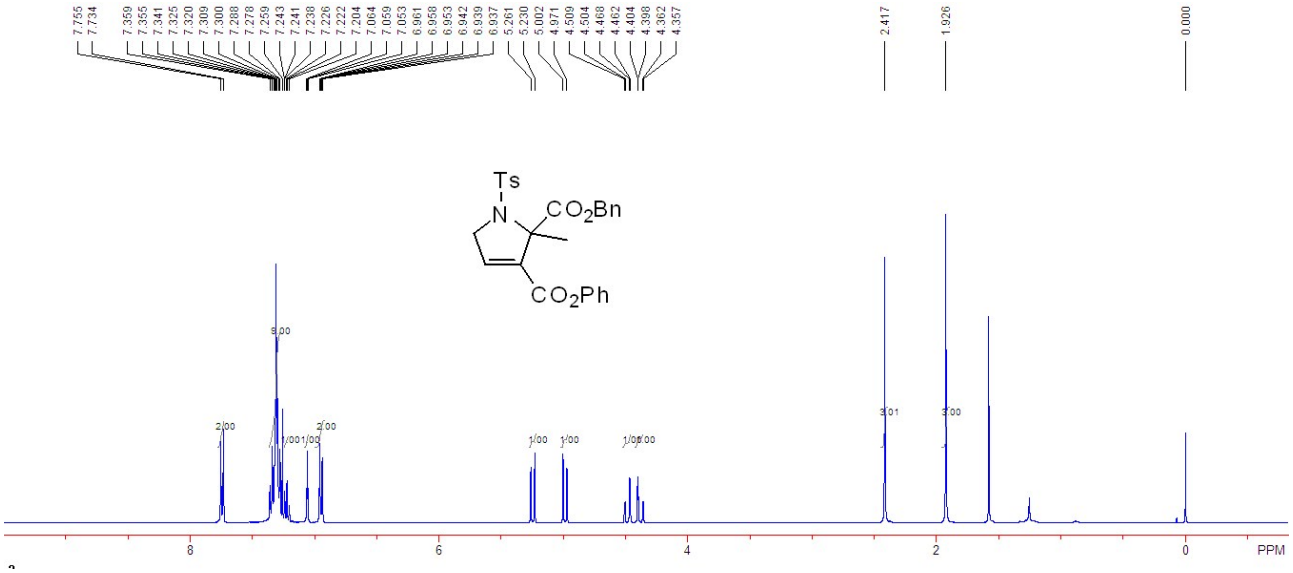


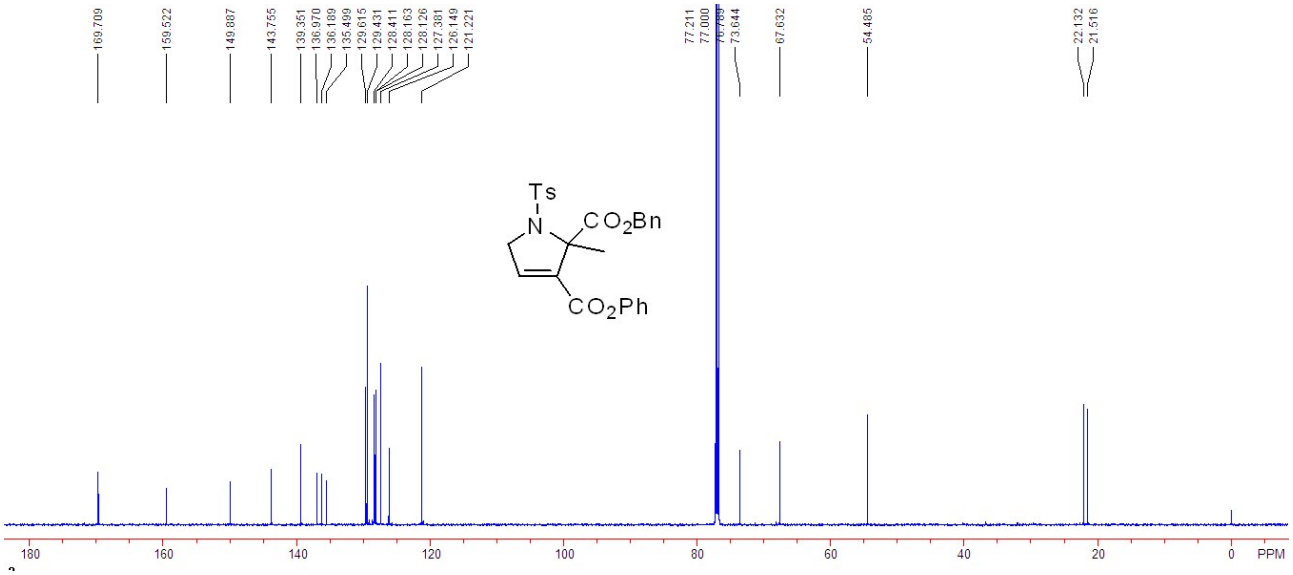


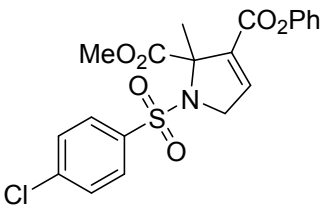
2-benzyl 3-phenyl 2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3dc)

A yellow oil, 39.3 mg, 80% yield; ^1H NMR (400 MHz, $CDCl_3$, TMS) δ 7.74 (d, *J* = 8.4 Hz, 2H), 7.36-7.28 (m, 9H), 7.24-7.20 (m, 1H), 7.06 (t, *J* = 2.0 Hz, 1H), 6.95 (td, *J* = 7.6, 1.2 Hz, 2H), 5.25 (d, *J* = 12.4 Hz, 1H), 4.99 (d, *J* = 12.4 Hz, 1H), 4.49 (dd, *J* = 2.0, 16.4 Hz, 1H), 4.38 (dd, *J* = 2.0,

16.4 Hz, 1H), 2.42 (s, 3H), 1.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 169.7, 159.5, 149.9, 143.8, 139.4, 137.0, 136.2, 135.5, 129.6, 129.4, 128.4, 128.2, 128.1, 127.4, 126.1, 121.2, 73.6, 67.6, 54.5, 22.1, 21.5; IR (neat): ν 3058, 3029, 2924, 1737, 1634, 1590, 1491, 1348, 1248, 1191, 1160, 1101, 1036, 815, 739, 690 cm^{-1}; HRMS (ESI) Calcd. For $C_{27}H_{29}N_2O_6S^+$ $(M+NH_4)^+$ requires 509.1741, Found: 509.1745.

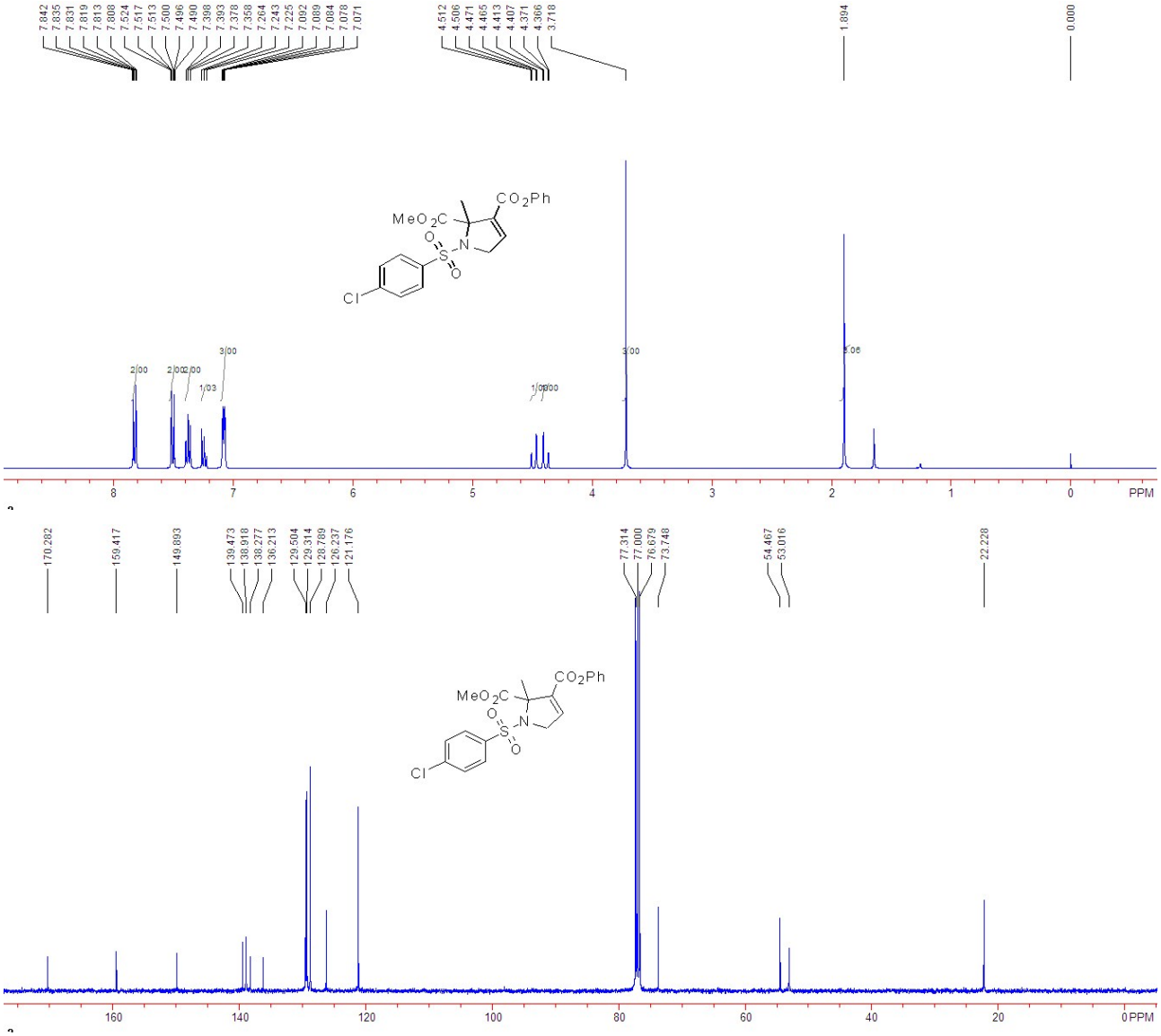


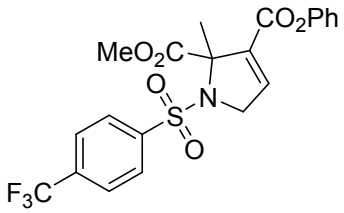




2-methyl-3-phenyl-1-((4-chlorophenyl)sulfonyl)-2-methyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ec)

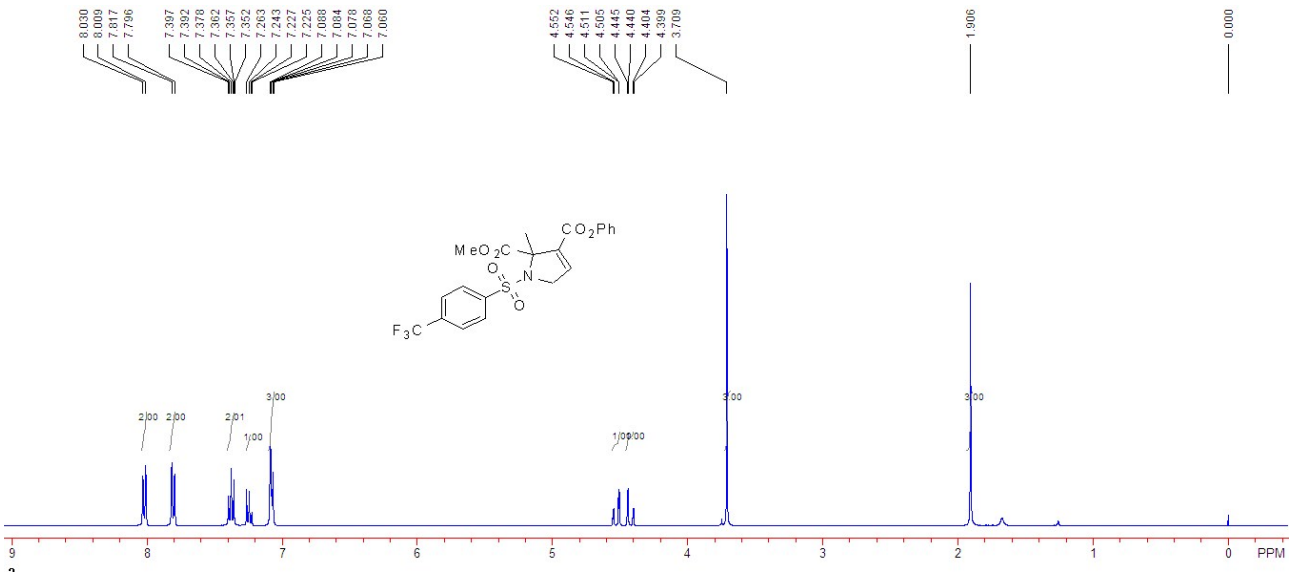
A yellow oil, 36.6 mg, 84% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.82 (td, *J* = 8.8, 2.4 Hz, 2H), 7.51 (td, *J* = 8.4, 2.4 Hz, 2H), 7.40-7.36 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09-7.07 (m, 3H), 4.49 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.39 (dd, *J* = 2.4, 16.4 Hz, 1H), 3.72 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.3, 159.4, 150.0, 139.5, 138.9, 138.3, 136.2, 129.5, 129.3, 128.8, 126.2, 121.2, 73.7, 54.5, 53.0, 22.2; IR (neat): ν 2943, 1751, 1720, 1448, 1340, 1265, 1161, 1108, 1069, 1036, 1102, 758, 696 cm^{-1}; HRMS (ESI) Calcd. For $C_{20}H_{22}ClN_2O_6S^+$ $(M+NH_4)^+$ requires 453.0882, Found: 453.0887.

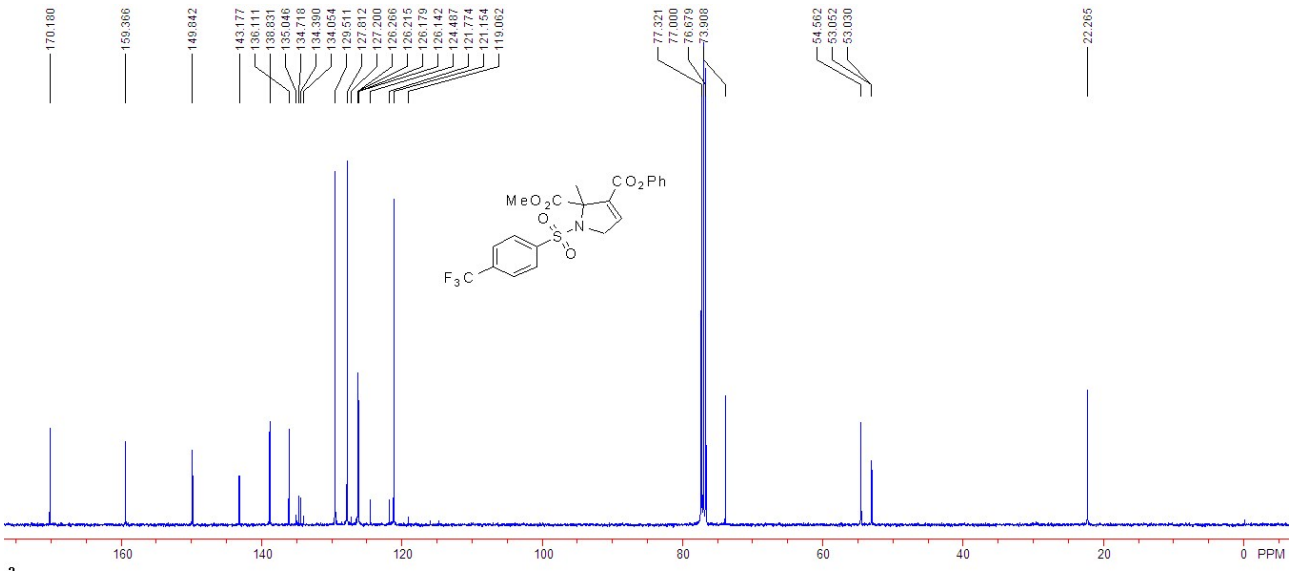


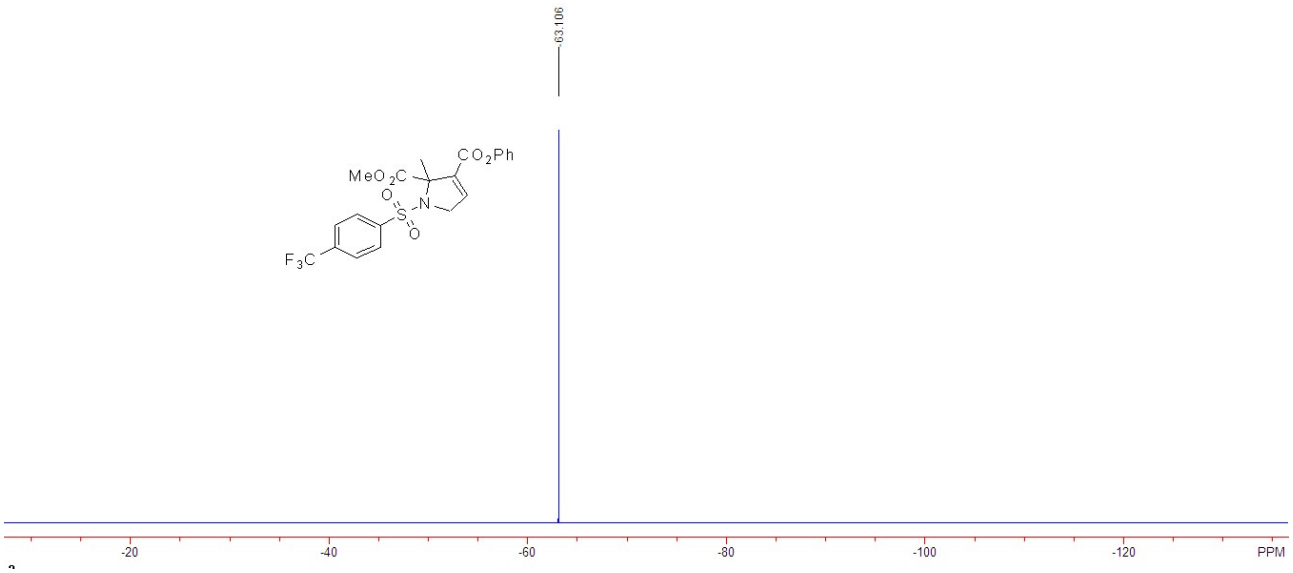


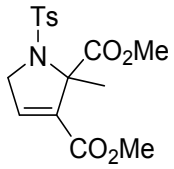
2-methyl-3-phenyl-2-methyl-1-((4-(trifluoromethyl)phenyl)sulfonyl)-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3fc)

A yellow oil, 40.8 mg, 87% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.81 (d, *J* = 8.4 Hz, 2H), 7.40-7.35 (m, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.09-7.06 (m, 3H), 4.53 (dd, *J* = 2.4, 16.4 Hz, 1H), 4.42 (dd, *J* = 2.0, 16.4 Hz, 1H), 3.71 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.2, 159.4, 149.8, 143.2, 138.8, 136.1, 134.6 (q, *J* = 32.8 Hz), 129.5, 127.8, 126.3, 126.2 (q, *J* = 3.7 Hz), 123.1 (q, *J* = 271.2 Hz), 121.2, 73.9, 54.6, 53.0 (d, *J* = 2.2 Hz), 22.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -63.11; IR (neat): ν 2966, 1750, 1721, 1346, 1323, 1260, 1164, 1125, 1108, 1062, 824, 714, 676 cm^{-1}; HRMS (ESI) Calcd. For $C_{21}H_{22}F_3N_2O_6S^+$ $(M+NH_4)^+$ requires 487.4302, Found: 487.4312.


8.030
8.009
7.817
7.796
7.397
7.392
7.378
7.362
7.357
7.352
7.263
7.243
7.227
7.225
7.088
7.084
7.078
7.068
7.060
4.552
4.546
4.511
4.505
4.445
4.440
4.404
4.399
3.709
1.906
0.000
CO2Ph
MeO2C
O
S
N
O
F3C
2.00
2.00
2.01
1.00
3.00
1.09
1.00
3.00
3.00
9
8
7
6
5
4
3
2
1
0
PPM

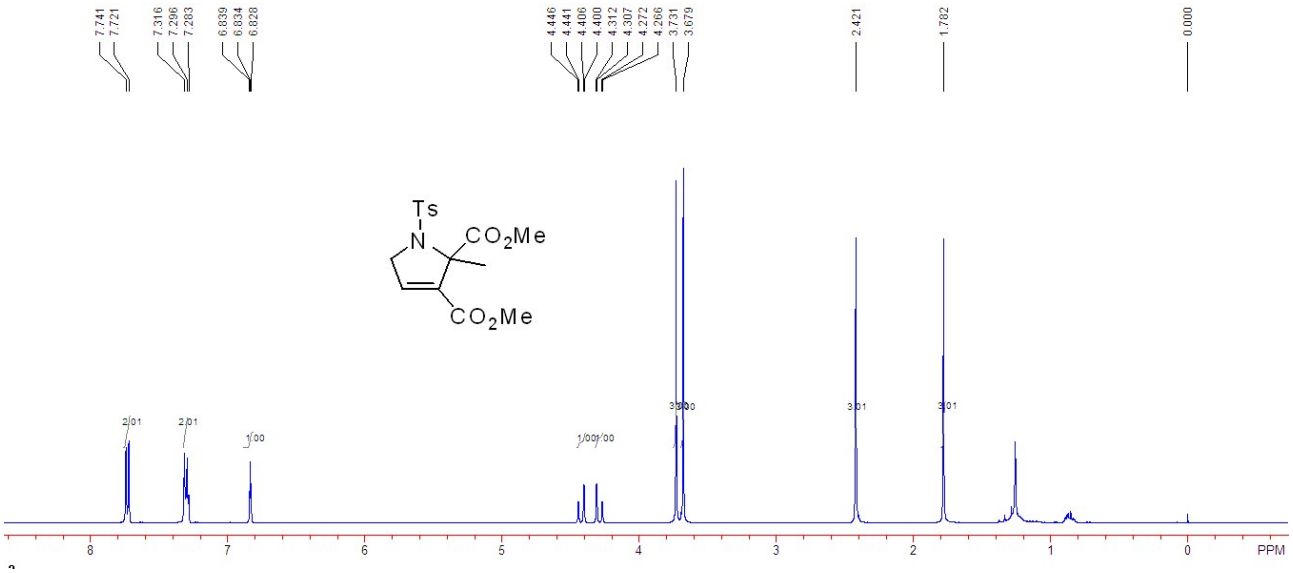

170.180
159.366
149.842
143.177
136.111
135.046
134.718
134.390
134.054
129.511
127.812
127.200
126.266
126.215
126.179
126.142
124.487
121.774
121.154
119.062
77.321
77.000
76.679
73.908
54.562
53.052
53.030
22.265
CO2Ph
MeO2C
O
S
N
O
F3C
160
140
120
100
80
60
40
20
0
PPM

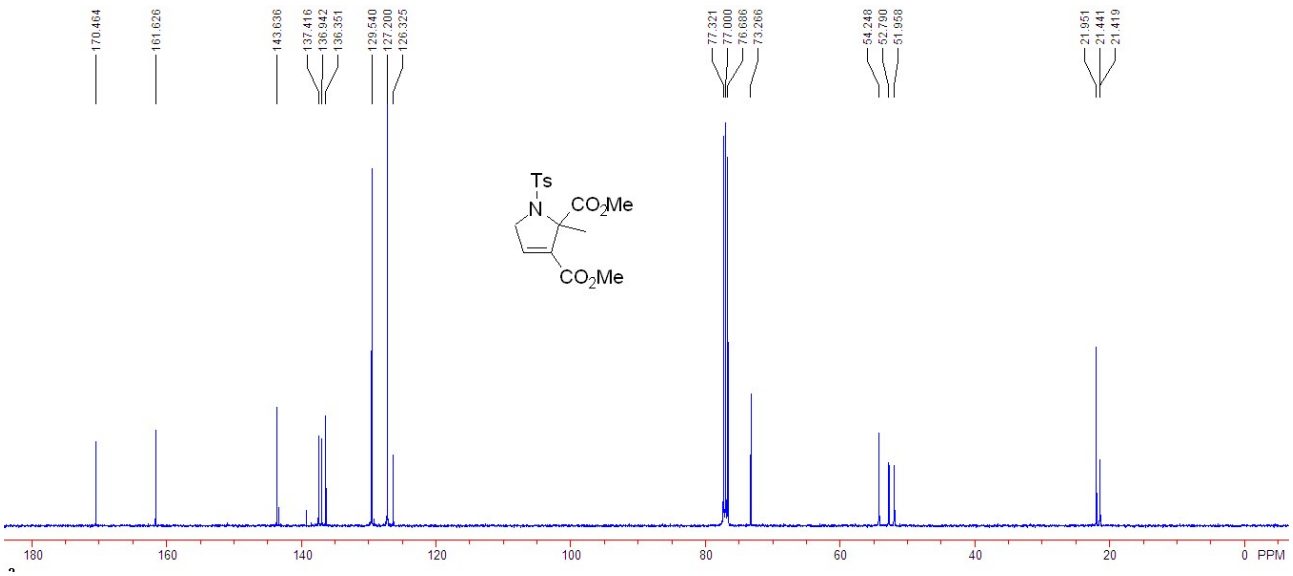

63.106
CO2Ph
MeO2C
O
S
N
O
F3C
-20
-40
-60
-80
-100
-120
PPM

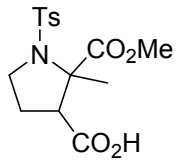


dimethyl-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-2,3-dicarboxylate (3ad)

A yellow oil, 31.1 mg, 88% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.73 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 2.4 Hz, 1H), 4.42 (dd, *J* = 2.0, 16.0 Hz, 1H), 4.29 (dd, *J* = 2.0, 16.0 Hz, 1H), 3.73 (s, 3H), 3.68 (s, 3H), 2.42 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.5, 161.6, 143.6, 137.4, 136.9, 136.4, 129.5, 127.2, 73.3, 54.2, 52.8, 52.0, 22.0, 21.4 (d, *J* = 2.2 Hz); IR (neat): ν 2933, 1752, 1720, 1446, 1342, 1260, 1161, 1108, 1069, 1040, 1102, 814, 758, 696 cm^{-1}; HRMS (ESI) Calcd. For $C_{16}H_{19}NNaO_6S^+$ $(M+Na)^+$ requires 376.0825, Found: 376.0831.

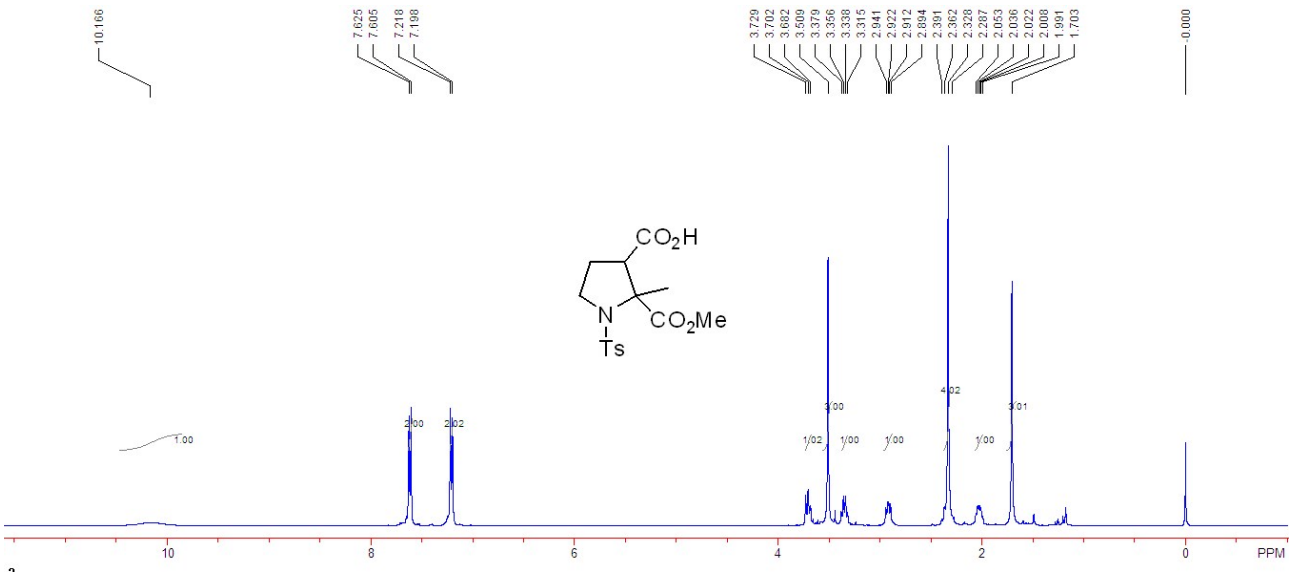


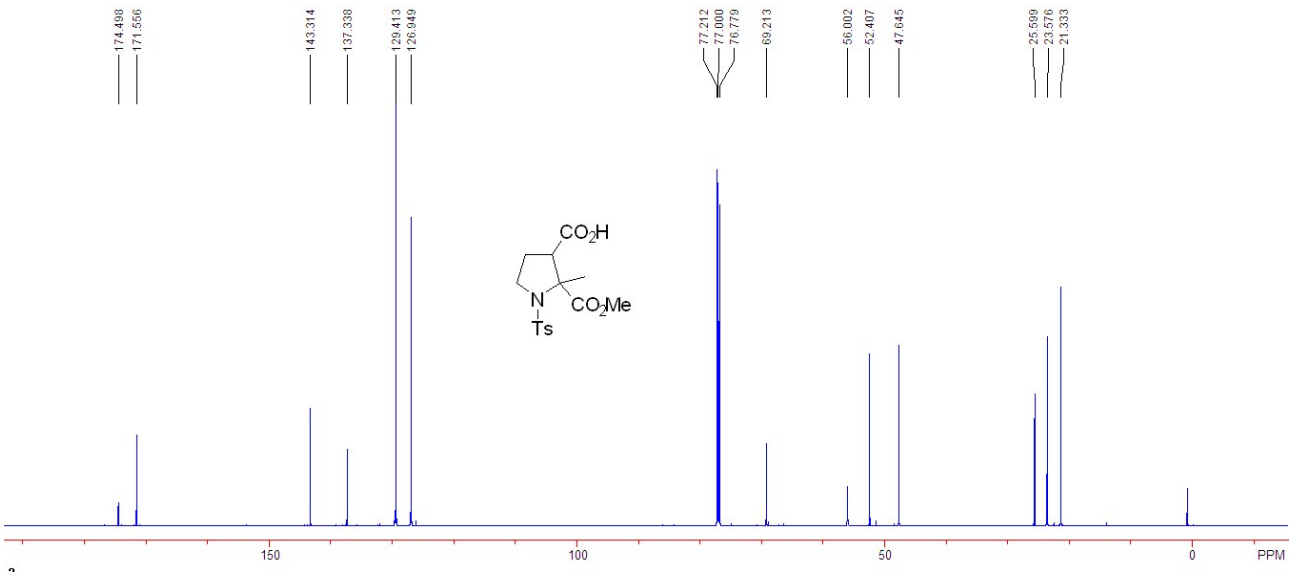


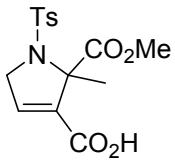


2-(methoxycarbonyl)-2-methyl-1-tosylpyrrolidine-3-carboxylic acid (4a)

A yellow oil, 341.4 mg, 100% yield; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.17 (s, 1H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 3.73-3.68 (m, 1H), 3.51 (s, 3H), 3.35 (dd, *J* = 9.2, 16.4 Hz, 1H), 2.92 (dd, *J* = 7.6, 11.6 Hz, 1H), 2.39-2.29 (m, 1H), 2.33 (s, 3H), 2.06-2.00 (m, 1H), 1.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 174.5, 171.6, 143.3, 137.3, 129.4, 126.9, 69.2, 56.0, 52.4, 47.6, 25.6, 23.6, 21.3; IR (neat): ν 3380, 2900, 1762, 1728, 1446, 1342, 1220, 1161, 1108, 1140, 1102, 814, 758, 696 cm^{-1}; HRMS (ESI) Calcd. For $C_{15}H_{19}NNaO_6S^+$ $(M+Na)^+$ requires 364.0825, Found: 364.0824.



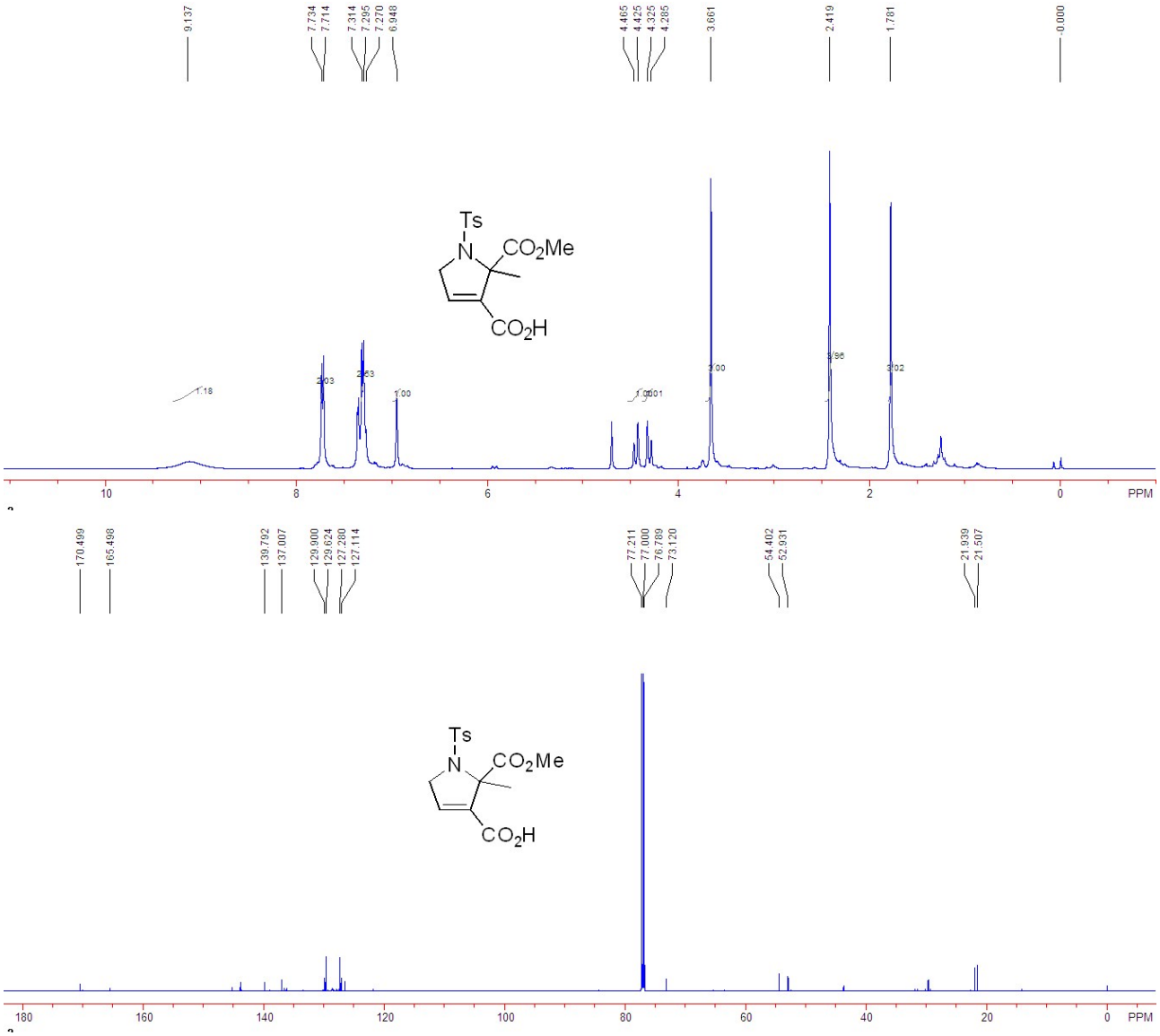




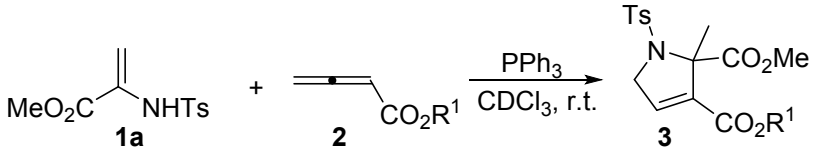
2-(methoxycarbonyl)-2-methyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylic acid (4b)

A yellow oil, 162.9 mg, 48% yield (this compound contains some impurities due to the high polarity acetic acid); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 9.14 (s, 1H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.30 (d, *J* = 7.6 Hz, 2H), 6.95 (s, 1H), 4.45 (d, *J* = 16.0 Hz, 1H), 4.30 (d, *J* = 16.0 Hz, 1H), 3.66 (s, 1H), 2.42 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ 170.5, 165.5, 139.8, 137.0, 129.9, 129.6, 127.3, 127.1, 73.1, 54.4, 52.9, 21.9, 21.5; IR (neat): ν 3250, 2920, 1752, 1730, 1632,

1382, 1260, 1167, 1108, 1069, 1048, 1102, 814, 798, 696 cm^{-1}; HRMS (ESI) Calcd. For $C_{15}H_{17}NNaO_6S^+$ $(M+Na)^+$ requires 362.0669, Found: 362.0666.

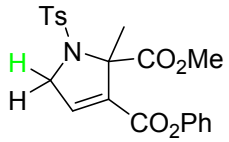


4. Time-dependent NMR studies



To a NMR tube was charged with 2-aminoacrylate **1a** (0.10 mmol, 1.0 equiv) and allenoate **2** (0.12 mmol, 1.2 equiv). Then, 0.5 mL $CDCl_3$ was added into the NMR tube. Finally, PPh_3 (0.03 mmol, 0.3 equiv) was added into the NMR tube. The sample was introduced into the NMR spectrometer at room temperature, and the reaction was monitored at the same temperature.

Spectra were recorded every 2 minutes for 16 minutes. Each spectrum was then analyzed to calculate the yield of product **3**. The yield of product **3** was calculated by the relevant CH integral ratio of characteristic peaks (colored green, blue and red of S1~S6) and the methyl of *p*-toluenesulfonyl group. Fig. S1, S2, S3 were the crude spectra of 2-aminoacrylate **1a** reacting with allenoates **2c**, **2b**, **2a**, respectively. In Fig. S1, the signal peak at 0.00 ppm was the internal standard of $CDCl_3$ (TMS) and signal peaks at 4.24 ppm~4.33 ppm were the characteristic peaks of the CH colored green in **3**. In Fig. S2, the signal peak at 0.00 ppm was the internal standard of $CDCl_3$ (TMS) and signal peaks at 6.70 ppm~6.80 ppm were the characteristic peaks of the CH colored blue in **3**. In Fig. S3, the signal peak at 0.00 ppm was the internal standard of $CDCl_3$ (TMS) and signal peaks at 4.20 ppm~4.33 ppm were the characteristic peaks of the CH colored red in **3**.



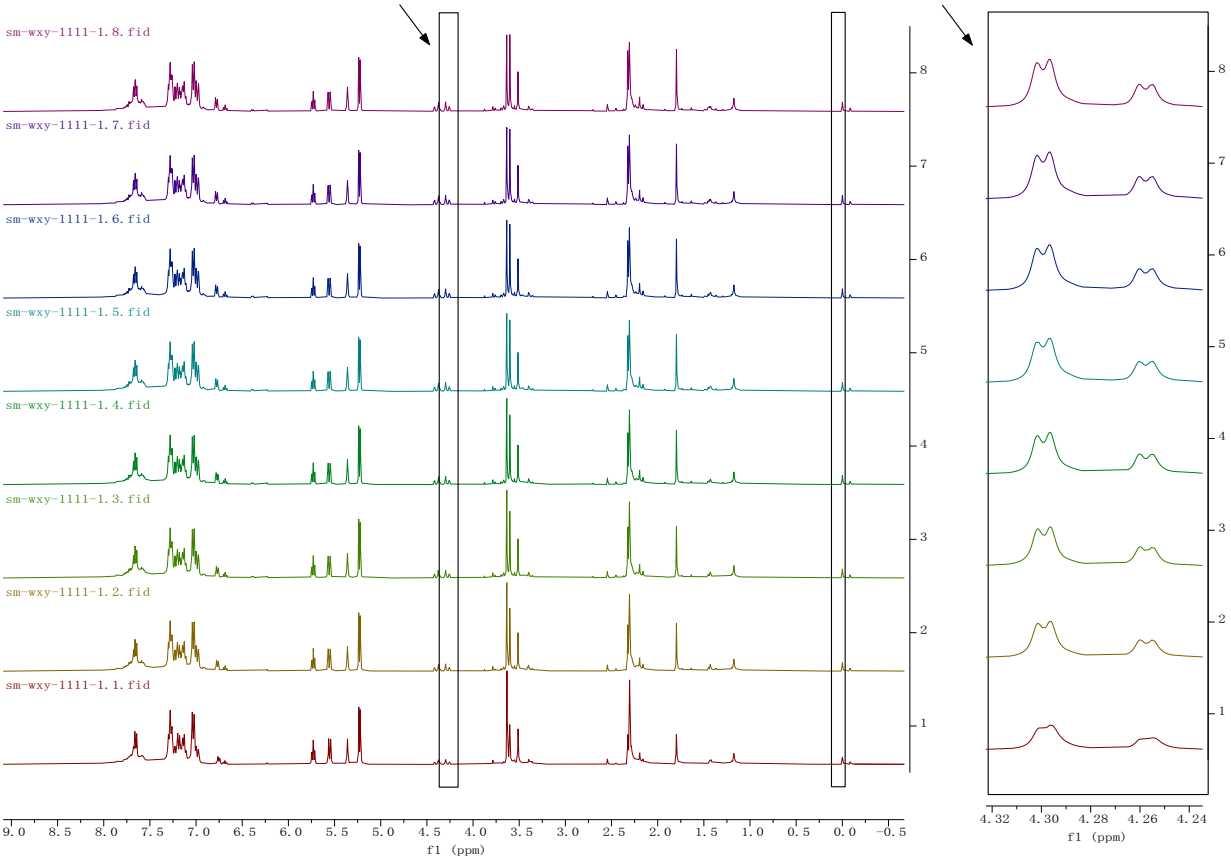

sm-wxy-1111-1.8.fid
sm-wxy-1111-1.7.fid
sm-wxy-1111-1.6.fid
sm-wxy-1111-1.5.fid
sm-wxy-1111-1.4.fid
sm-wxy-1111-1.3.fid
sm-wxy-1111-1.2.fid
sm-wxy-1111-1.1.fid
f1 (ppm)
f1 (ppm)

Fig. S1

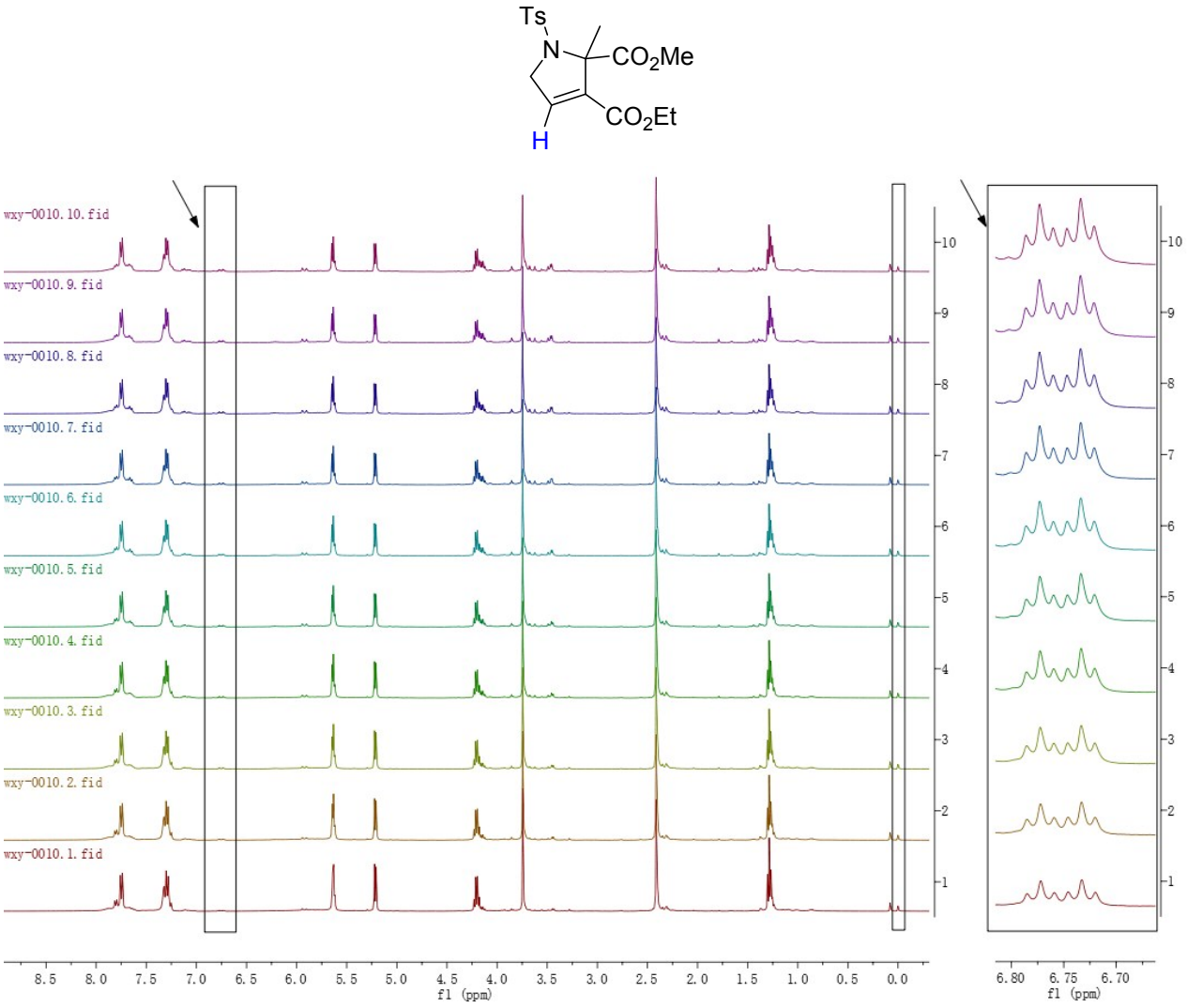

Ts
N
CO2Me
CO2Et
H
wxy-0010.10.fid
wxy-0010.9.fid
wxy-0010.8.fid
wxy-0010.7.fid
wxy-0010.6.fid
wxy-0010.5.fid
wxy-0010.4.fid
wxy-0010.3.fid
wxy-0010.2.fid
wxy-0010.1.fid
f1 (ppm)
f1 (ppm)

Fig. S2

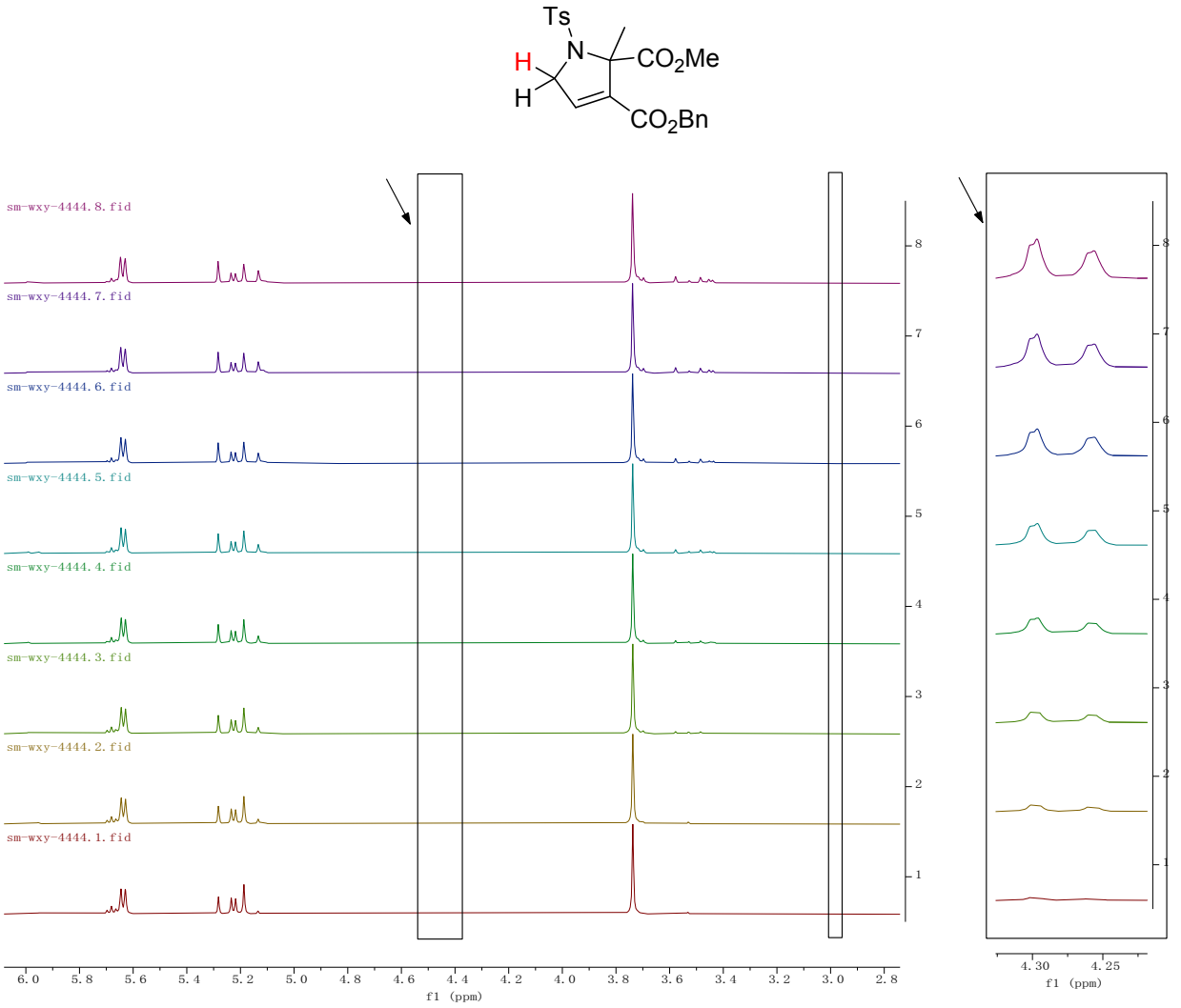
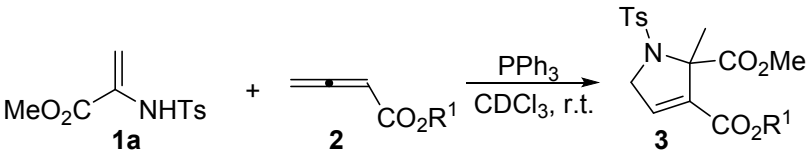


Fig. S3



To a NMR tube was charged with 2-aminoacrylate **1a** (0.10 mmol, 1.0 equiv) and allenoate **2** (0.12 mmol, 1.2 equiv). Then, 0.5 mL $CDCl_3$ was added into the NMR tube. Finally, PPh_3 (0.01 mmol, 0.1 equiv) was added into the NMR tube. The sample was introduced into the NMR spectrometer at room temperature and the reaction was monitored at the same temperature.

Spectra were recorded every 2 minutes for 16 minutes. Each spectrum was then analyzed to calculate the yield of product **3**. Fig. S4, S5, S6 were the crude spectra of 2-aminoacrylate **1a** reacting with allenoates **2c**, **2b**, **2a**, respectively. In Fig. S4, the signal peak at 0.00 ppm was the

internal standard of $CDCl_3$ (TMS) and signal peaks at 4.26 ppm~4.33 ppm were the characteristic peaks of the CH colored green in **3**. In Fig. S5, the signal peak at 0.00 ppm was the internal standard of $CDCl_3$ (TMS) and signal peaks at 6.60 ppm~6.75 ppm were the characteristic peaks of the CH colored blue in **3**. In Fig. S6, the signal peak at 0.00 ppm was the internal standard of $CDCl_3$ (TMS) and signal peaks at 4.22 ppm~4.33 ppm were the characteristic peaks of the CH colored red in **3**.

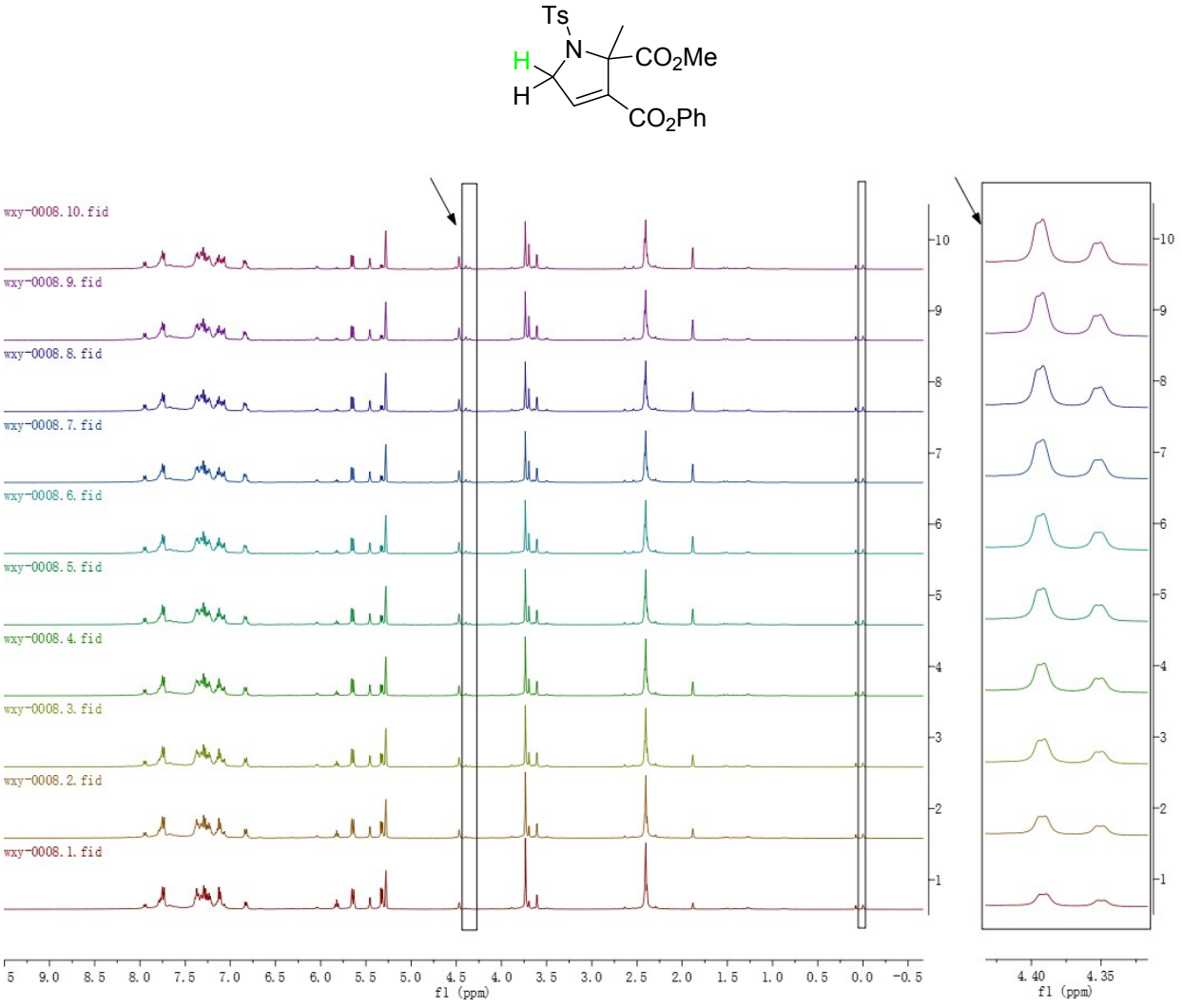
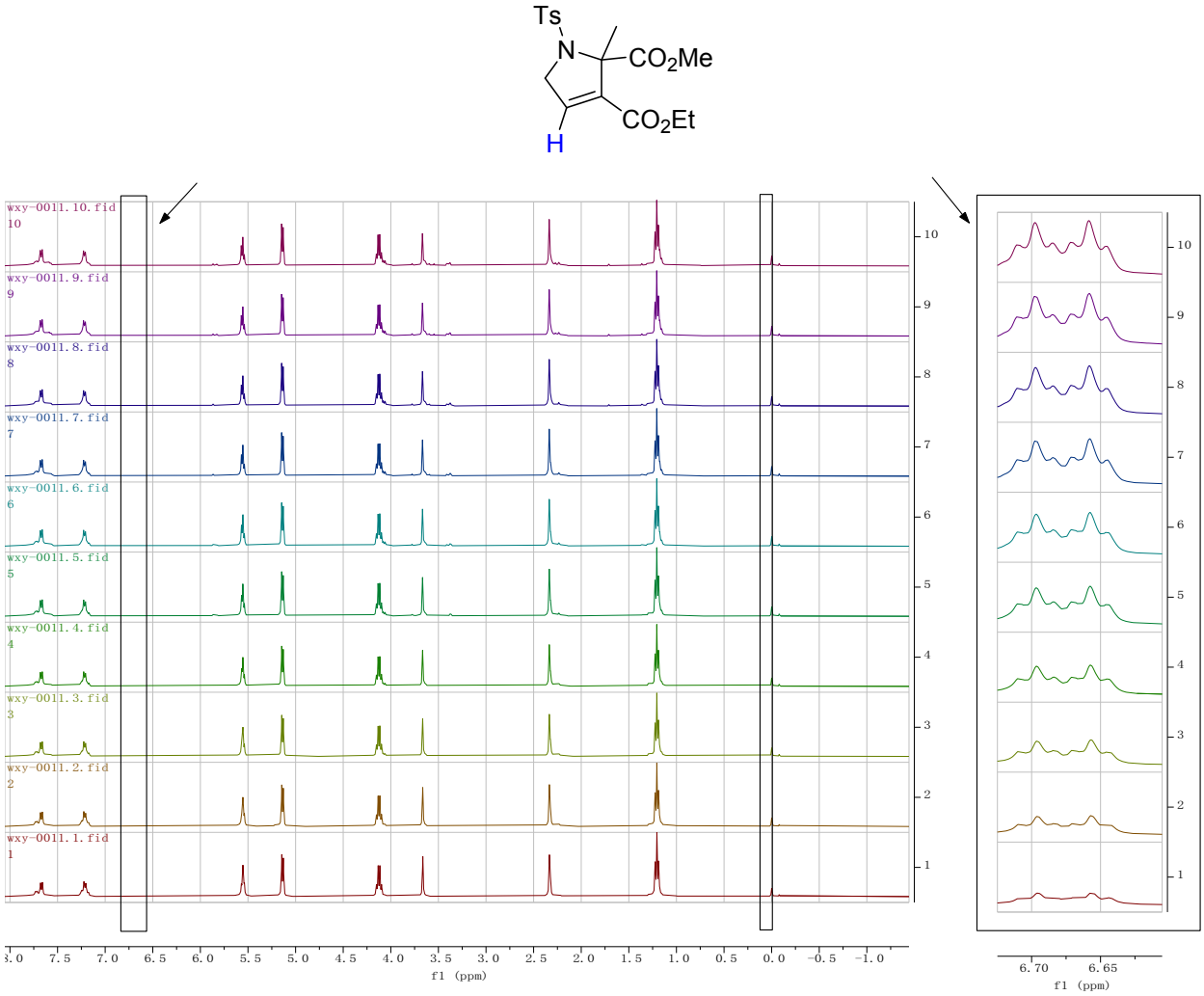


Fig. S4


Ts
N
CO2Me
CO2Et
H
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wxy-0011.9.fid
wxy-0011.8.fid
wxy-0011.7.fid
wxy-0011.6.fid
wxy-0011.5.fid
wxy-0011.4.fid
wxy-0011.3.fid
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f1 (ppm)
6.70
6.65
f1 (ppm)

Fig. S5

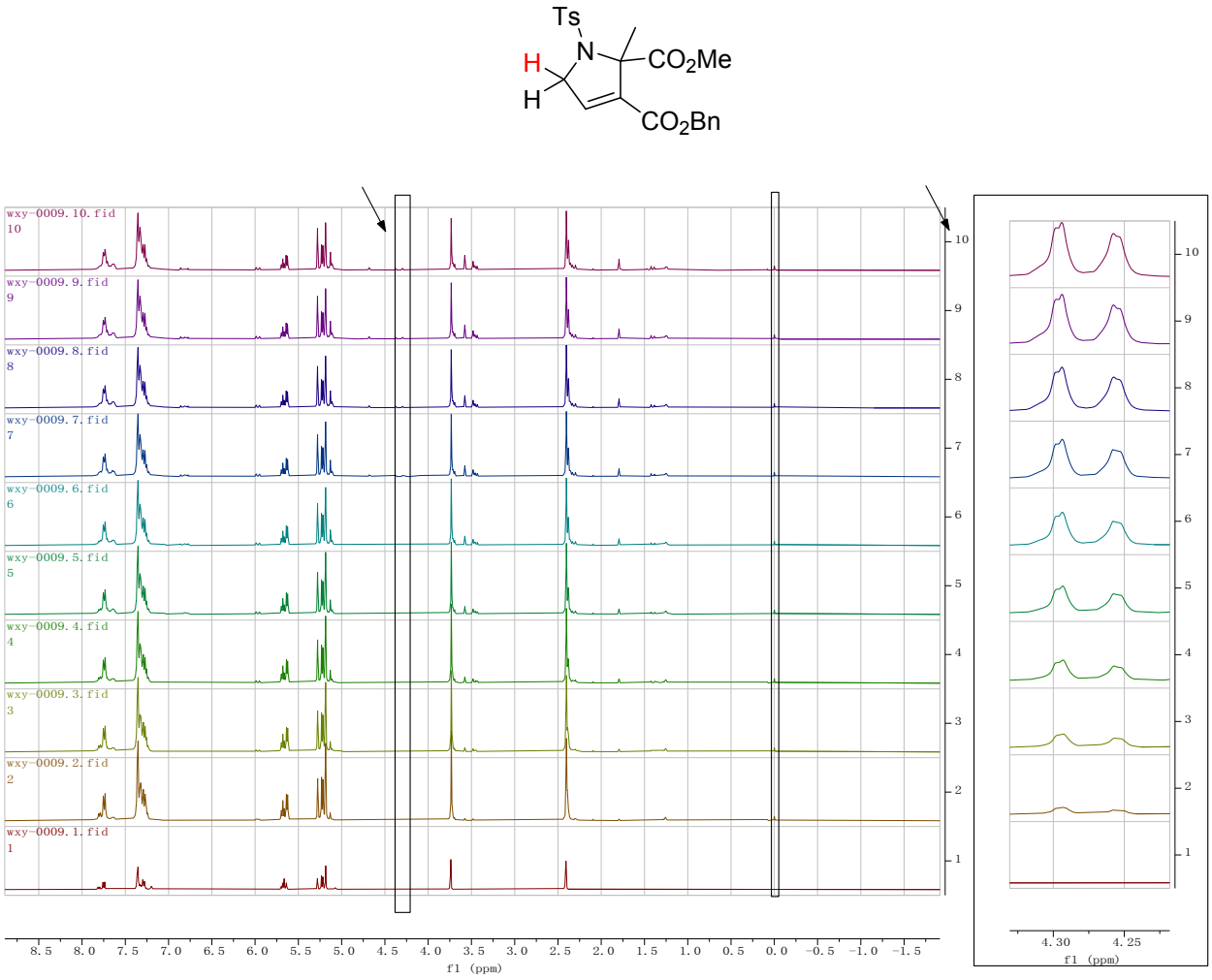
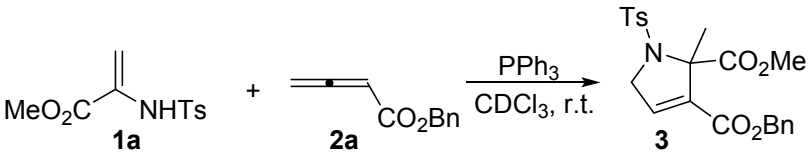

Ts
N
H
H
CO2Me
CO2Bn
wxy-0009.10.fid
10
wxy-0009.9.fid
9
wxy-0009.8.fid
8
wxy-0009.7.fid
7
wxy-0009.6.fid
6
wxy-0009.5.fid
5
wxy-0009.4.fid
4
wxy-0009.3.fid
3
wxy-0009.2.fid
2
wxy-0009.1.fid
1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5
f1 (ppm)
4.30
4.25
f1 (ppm)

Fig. S6

In order to study the reaction mechanism, we did 5 sets of controlled experiments as follows：



1: To a NMR tube was charged with PPh_3 (0.03 mmol, 0.3 equiv). After 18 min, the sample was introduced into the NMR spectrometer at room temperature, and the reaction was monitored at the same temperature.

2: To a NMR tube was charged with 2-aminoacrylate **1a** (0.10 mmol, 1.0 equiv). Then, 0.5 mL $CDCl_3$ was added into the NMR tube. Finally, PPh_3 (0.03 mmol, 0.3 equiv) was added into the NMR tube. After 18 min, the sample was introduced into the NMR spectrometer at room temperature, and the reaction was monitored at the same temperature.

3: To a NMR tube was charged with allenoate **2a** (0.12 mmol, 1.2 equiv). Then, 0.5 mL CDCl3 was added into the NMR tube. Finally, PPh_3 (0.03 mmol, 0.3 equiv) was added into the NMR tube. After 18 min, the sample was introduced into the NMR spectrometer at room temperature, and the reaction was monitored at the same temperature.

4: To a NMR tube was charged with 2-aminoacrylate **1a** (0.10 mmol, 1.0 equiv) and allenoate **2a** (0.12 mmol, 1.2 equiv). Then, 0.5 mL $CDCl_3$ was added into the NMR tube. Finally, PPh_3 (0.03 mmol, 0.3 equiv) was added into the NMR tube. After reacted for 18 min, the sample was introduced into the NMR spectrometer, and the reaction was monitored at the same temperature.

5: To a NMR tube was charged with 2-aminoacrylate **1a** (0.10 mmol, 1.0 equiv) and allenoate **2a** (0.12 mmol, 1.2 equiv). Then, 0.5 mL $CDCl_3$ was added into the NMR tube. Finally, PPh_3 (0.03 mmol, 0.3 equiv) was added into the NMR tube. After reacted for 600 min, the sample was introduced into the NMR spectrometer at room temperature, and the reaction was monitored at the same temperature.

According to phosphine spectra of 5 sets of controlled experiments (show in Fig. S7), we conclude that the catalyst is bound in substrates to generate an active zwitterionic intermediate during the reaction,

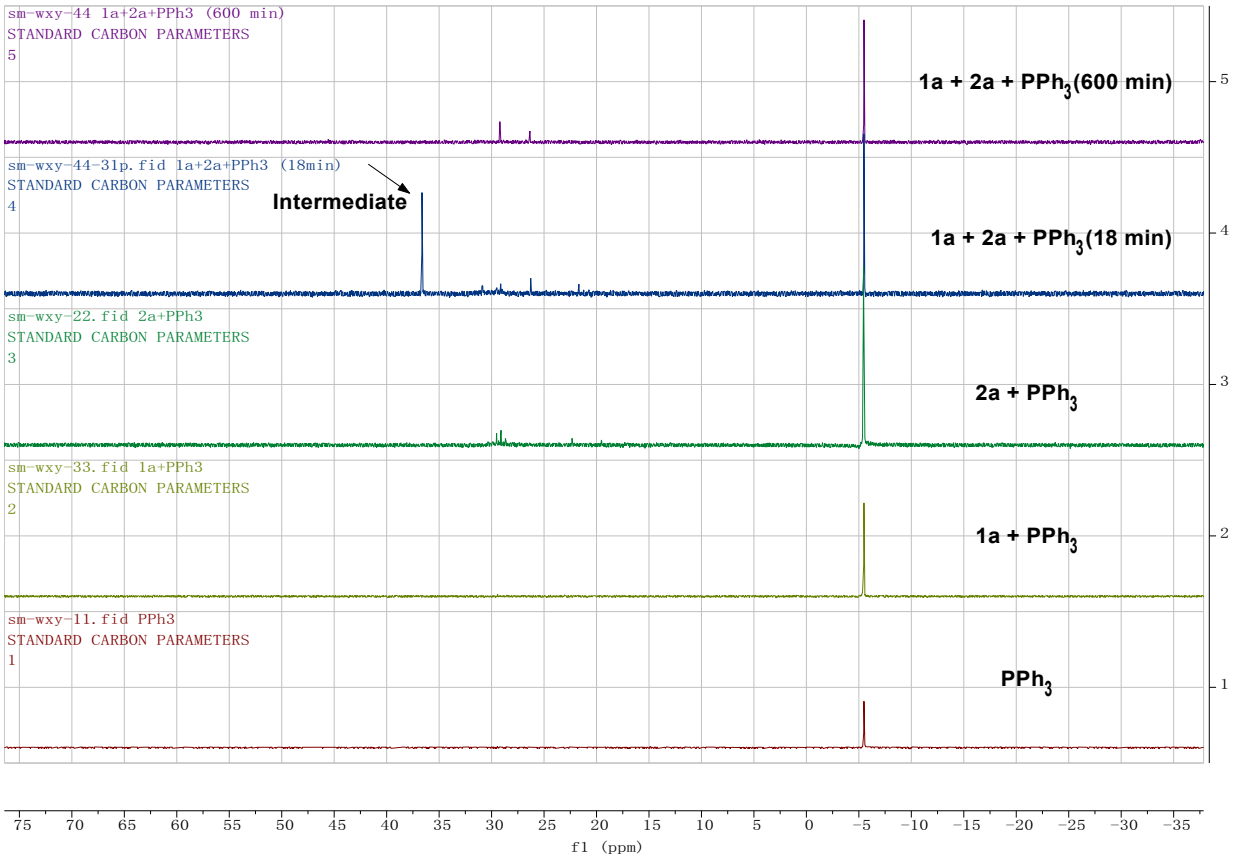
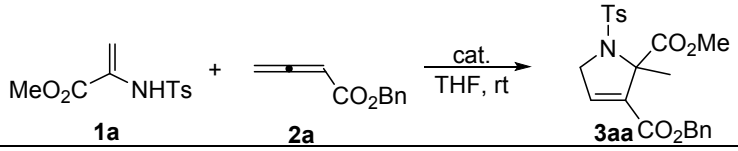
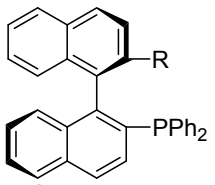

sm-wxy-44 1a+2a+PPh3 (600 min)
STANDARD CARBON PARAMETERS
5
1a + 2a + PPh3(600 min)
sm-wxy-44-31p.fid 1a+2a+PPh3 (18min)
STANDARD CARBON PARAMETERS
4
Intermediate
1a + 2a + PPh3(18 min)
sm-wxy-22.fid 2a+PPh3
STANDARD CARBON PARAMETERS
3
2a + PPh3
sm-wxy-33.fid 1a+PPh3
STANDARD CARBON PARAMETERS
2
1a + PPh3
sm-wxy-11.fid PPh3
STANDARD CARBON PARAMETERS
1
PPh3
f1 (ppm)

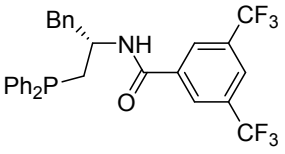
Fig. S7

5. Screening of chiral phosphine catalysts on the annulation of 1a and 2a or 2c.

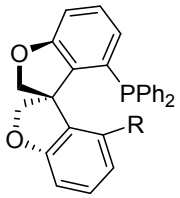




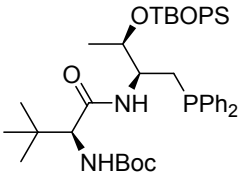
CP1: R = OH, NR
CP2: R = OMe, NR
CP3: R= PPh_2, NR



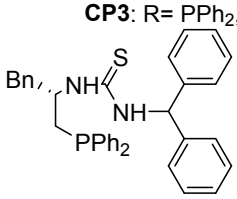
CP4: [b] yield: 82%, [c] ee: 43%



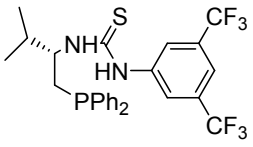
CP5: R = PPh_2, NR
CP6: R = OH, NR



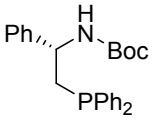
CP7: yield: 77%, ee: 15%



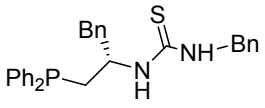
CP8: 42%, rac



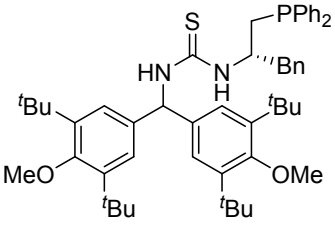
CP9: NR



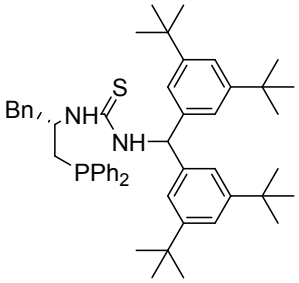
CP10: NR



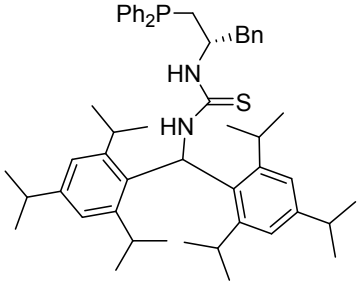
CP11: yield: 88%, ee: 36%



CP12: yield: 82%, ee: 12%

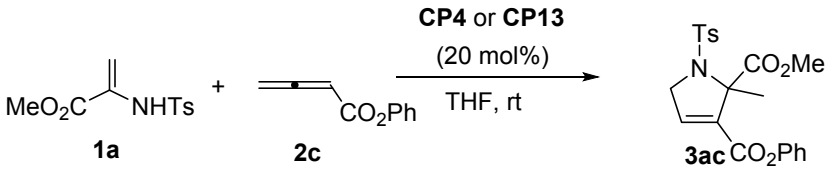


CP13: yield: 92%, ee: 52%

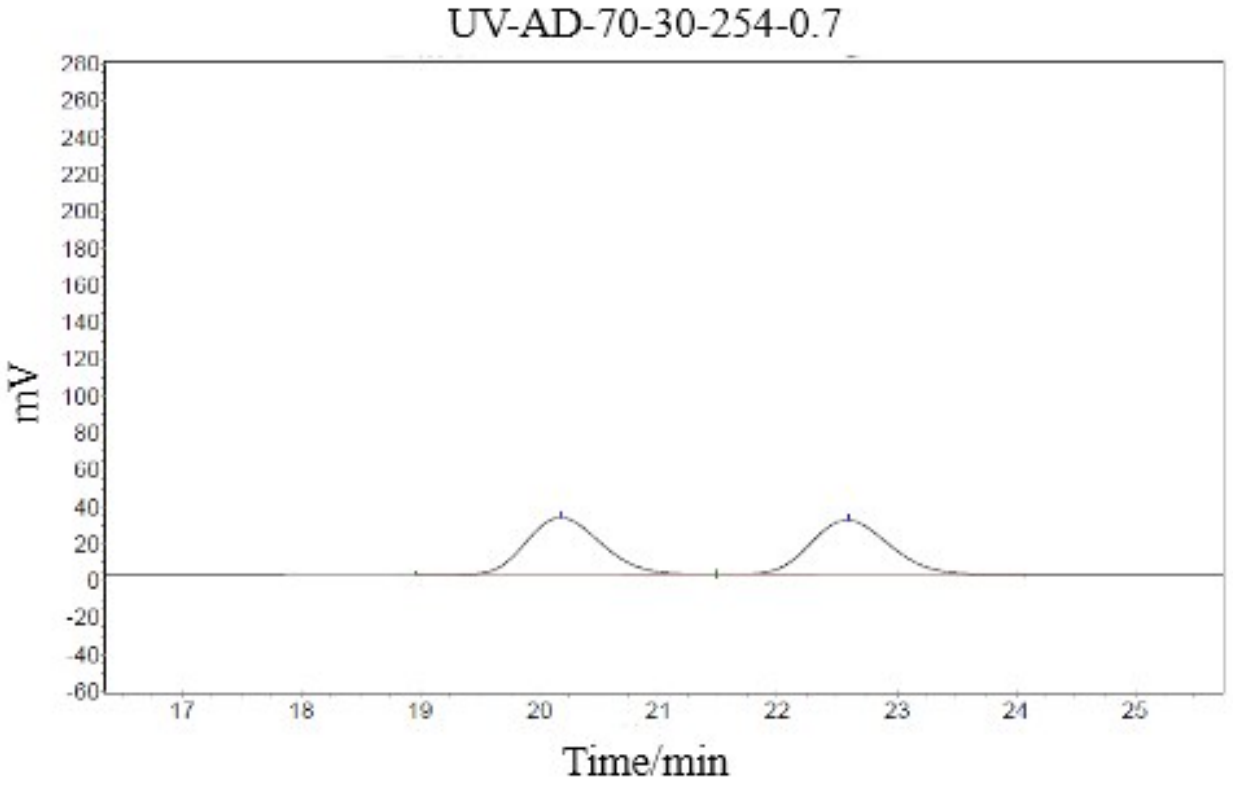


CP14: yield: 77%, ee: 26%

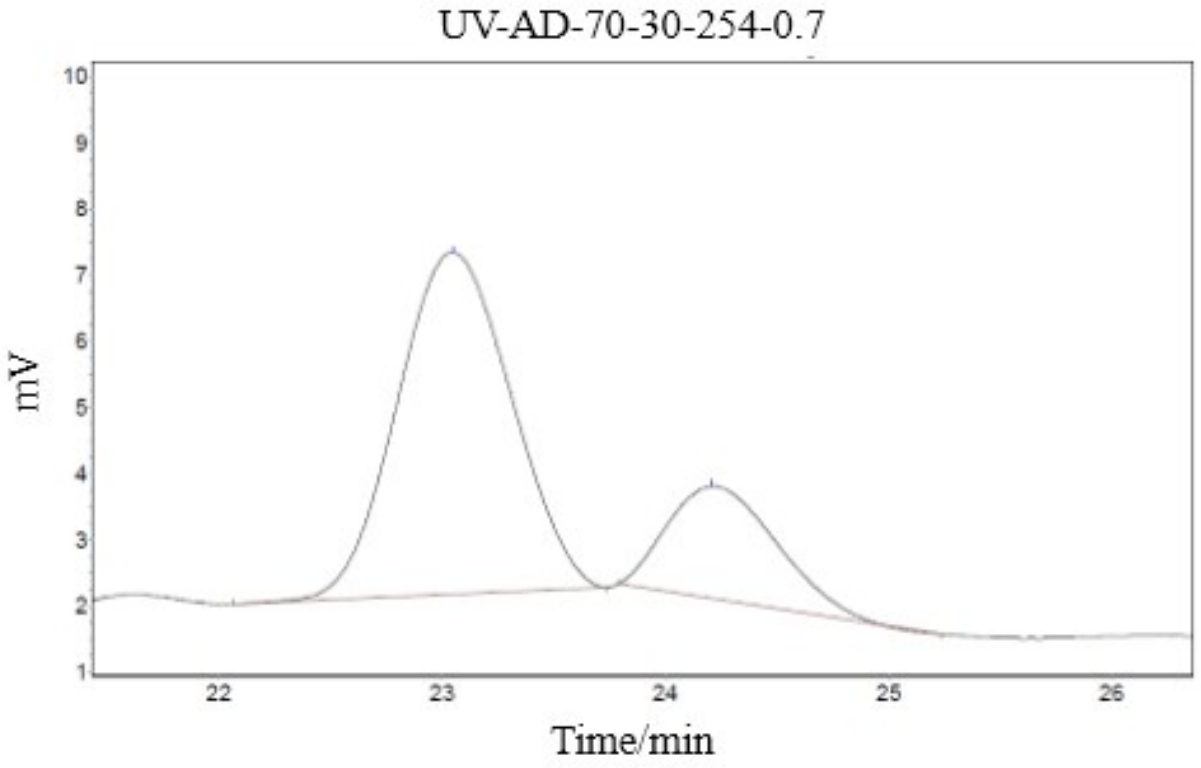
[a] All reactions were carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (20 mol%) and 2 mL THF at room temperature. [b] Yield of isolated **3aa.** [c] Determined by HPLC analysis on a chiral stationary phase.



80-90% yield
10-20% *ee*



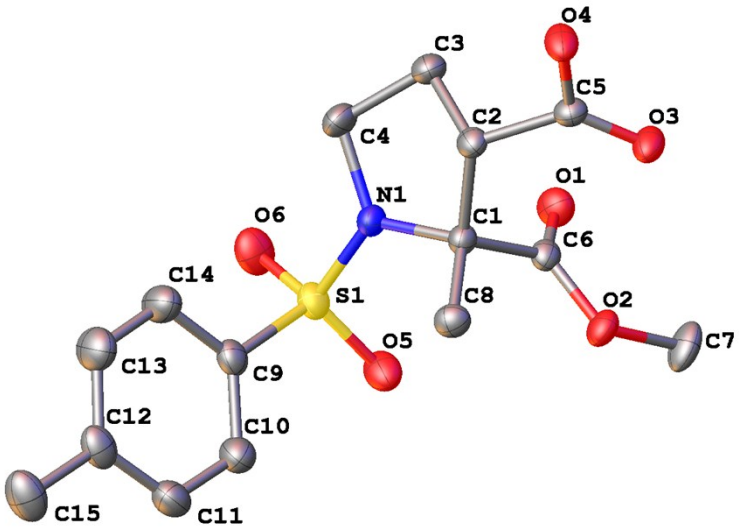
NO.	Ret. time/min	Height/mV	Area/mV*min	Rel. area%
1	20.182	30780.984	1340940.750	49.9401
2	22.590	29399.578	1344155.125	50.0599
Total		60180.563	2685095.875	100.0000



NO.	Ret. time/min	Height/mV	Area/mV*min	Rel. area%
1	23.048	5165.604	182775.797	76.0270
2	24.212	1692.318	57633.203	23.9730
Total		6857.922	240409.000	100.0000

A yellow oil Translation: a Chiralcel AD-H column [λ = 254 nm; eluent: Hexane/Isopropanol = 70/30; Flow rate: 0.70 mL/min; t_1 = 27.37 min, t_2 = 31.36 min; ee% = 52%

6. X-ray data of 4a.



The crystal data of **4a** have been deposited in CCDC with number 1938505. Empirical Formula: $C_{15}H_{19}NO_6S$; Formula Weight: 341.37; Crystal Color, colorless; Crystal Dimensions: 0.12 x 0.08 x 0.06 mm^3; Crystal System: Orthorhombic; Lattice Parameters: a = 13.3705(2)Å, b = 7.27390(10)Å, c = 31.8622(5)Å, $\alpha = 90^o$, $\beta = 90^o$, $\gamma = 90^o$, V = 1811.2(4)$Å^3$; Space group: Pbca; Z = 8; D_{calc} = 1.463 g/cm^3; F_{000} = 3098.78(8); Final R indices [I>2sigma(I)] R1 = 0.0331, wR2 = 0.0861.

7. References.

1. X. Y. Chen, R. C. Lin, and S. Ye, *Chem. Commun*. 2012, **48**, 1317.
2. L. J. Yang, S. Wang, J. Nie, S. Li, and J. A. Ma, *Org. Lett*. 2013, **15**, 5214.
3. H. Z. Gui, Y. Wei, and M. Shi, *Org. Biomol. Chem*. 2018, **16**, 9218.