Supporting Information

Stereoselective Synthesis of 3-Carboxy-4,5-dihydropyrroles via an Intramolecular Iminium Ion Cyclization Reaction

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General Consideration

Toluene and tetrahydrofuran (THF) were dried with Na and distilled. All other commercial reagents were used as received without additional purification. Melting point was uncorrected. Mass spectra and HPLC data was recorded on a LC/MS system with ELSD. The ^{1}H and ^{13}C NMR data were obtained on a 300 MHz NMR spectrometer with TMS as the internal standard and $CDCl_3$ as solvent unless otherwise stated. Multiplicities are indicated as the following: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; dd, doubled doublet; br, broad. Coupling constants (*J* values) where noted are quoted in Hertz. IR spectra were recorded on a FTIR spectrometer with only major peaks reported. High-resolution mass spectra (HRMS) were obtained with a time-of-flight (TOF) mass spectrometer (ESI).

Experimental Procedures and Compound Characterization

Preparation of (*E*)-methyl 2-((methylamino)methyl)-3-phenylacrylate 3a.[1] The solution of methyl 2-(acetoxy(phenyl)methyl)acrylate **1a** (4.0 g, 17.1 mmol) in THF (20 mL) was added dropwise over 15 min to a stirred solution of methylamine (30% in alcohol, 20 mL) in THF (80 mL) at 0 °C. The resulting solution was stirred for 30 min at 0 °C. The volatiles was removed *in vacuo* and saturated aqueous $NaHCO_3$ (20 mL) was added, extracted with EtOAc (3 x 20 mL). The combined EtOAc layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Petroleum ether/EtOAc = 1:1, v/v) afforded the desired product **3a** (3.154 g, 90% yield) as a pale yellow oil. ^{1}H NMR δ 7.83 (s, 1H), 7.48–7.37 (m, 5H), 3.84 (s, 3H), 3.57 (s, 2H), 2.44 (s, 3H), 1.93 (s, 1H); ^{13}C NMR δ 168.5, 142.0, 135.1, 130.6, 129.6, 128.9, 128.6, 52.1, 47.8, 36.2; MS (ESI): *m/z* 206.0 [M + H^+].

General procedure for the synthesis of (*E*)-methyl 2-(aminomethyl)-3-phenyl acrylate 3b-3d and 3f-3l. The solution of compound **1** (2.5 mmol) in THF (5 mL) was added dropwise over 15 min to a stirred solution of amine (5 mmol) and Et_3N (2.5 mmol) in THF (5 mL) at 0 °C. The resulting solution was stirred for 1-2 h at 0 °C. The volatiles was removed *in vacuo* and saturated aqueous $NaHCO_3$ (20 mL) was added, extracted with EtOAc (3 x 20 mL). The combined EtOAc layer was dried over

$MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Petroleum ether/EtOAc = 5:1~1:1, v/v) afforded the desired product **3**.

(*E*)-Methyl 2-((butylamino)methyl)-3-phenylacrylate 3b.[2] Pale yellow oil (488 mg, 79% yield); ^{1}H NMR δ 7.81 (s, 1H), 7.51–7.47 (m, 2H), 7.43–7.34 (m, 3H), 3.83 (s, 3H), 3.58 (s, 2H), 2.61 (t, 2H, J = 6.9), 1.54–1.42 (m, 2H), 1.40–1.28 (m, 2H), 0.90 (t, 3H, J = 7.5); ^{13}C NMR δ 168.7, 141.8, 135.3, 131.0, 129.7, 128.9, 128.6, 52.1, 49.4, 46.0, 32.2, 20.6, 14.1; MS (ESI): *m/z* 248.2 [M + H$^+$].

(*E*)-Methyl 2-((isopropylamino)methyl)-3-phenylacrylate 3c.[3] Colorless oil (391 mg, 67% yield); ^{1}H NMR δ 7.80 (s, 1H), 7.53–7.49 (m, 2H), 7.43–7.33 (m, 3H), 3.83 (s, 3H), 3.59 (s, 2H), 2.88–2.78 (m, 1H), 1.05 (d, 6H, J = 6.3); ^{13}C NMR δ 168.1, 141.3, 134.9, 130.7, 129.3, 128.6, 128.1, 51.6, 48.4, 43.6, 22.6; MS (ESI): *m/z* 234.1 [M + H$^+$].

(*E*)-Methyl 2-((benzylamino)methyl)-3-phenylacrylate 3d.[4] Pale yellow oil (549 mg, 78% yield); ^{1}H NMR δ 7.80 (s, 1H), 7.44–7.40 (m, 2H), 7.32–7.24 (m, 8H), 3.82 (s, 3H), 3.81 (s, 2H), 3.59 (s, 2H); ^{13}C NMR δ 168.7, 142.1, 142.0, 140.2, 135.2, 130.7, 129.8, 129.0, 128.6, 128.4, 127.1, 53.9, 52.2, 45.5; MS (ESI): *m/z* 282.1 [M + H$^+$].

(*E*)-Methyl 2-((butylamino)methyl)-3-(4-nitrophenyl)acrylate 3f. Yellow solid (490 mg, 67% yield); mp: 46–47 ^{o}C; ^{1}H NMR δ 8.26 (d, 2H, J = 8.7), 7.80 (s, 1H), 7.72 (d, 2H, J = 8.7), 3.86 (s, 3H), 3.51 (s, 2H), 2.63 (t, 2H, J = 6.9), 1.52–1.33 (m, 4H), 0.93 (t, 3H, J = 7.5); ^{13}C NMR δ 167.9, 147.7, 141.8, 139.1, 134.2, 130.6, 123.7, 52.4, 49.5, 46.1, 32.1, 20.5, 14.0; HRMS (ESI): calcd. for $C_{15}H_{24}N_2O_4$ [M + H]$^+$ 293.1496; found 293.1509.

(*E*)-Methyl 2-((butylamino)methyl)-3-(4-cyanophenyl)acrylate 3g. Pale yellow solid (408 mg, 60% yield); mp: 30–31 ^{o}C; ^{1}H NMR 7.78 (s, 1H), 7.70 (d, 2H, J = 8.7), 7.65 (d, 2H, J = 9.0), 3.85 (s, 3H), 3.52 (s, 2H), 2.64 (t, 2H, J = 6.9), 1.52–1.47 (m, 2H), 1.41–1.32 (m, 2H), 0.92 (t, 3H, J = 7.5); ^{13}C NMR δ 167.9, 139.8, 139.4, 133.7, 132.2, 130.2, 118.6, 112.2, 52.3, 49.4, 46.0, 32.0, 20.4, 14.0; HRMS (ESI): calcd. for $C_{16}H_{21}N_2O_2$ [M + H]$^+$ 273.1598; found 273.1607.

(*E*)-Methyl 2-((butylamino)methyl)-3-(4-chlorophenyl)acrylate 3h. Colorless oil (514 mg, 73% yield); ^{1}H NMR δ 7.74 (s, 1H), 7.46 (d, 2H, J = 9.0), 7.37 (d, 2H, J = 9.0), 3.83 (s, 3H), 3.53 (s, 2H), 2.62 (t, 2H, J = 6.3), 1.50–1.34 (m, 4H), 0.92 (t, 3H, J = 7.2); ^{13}C NMR δ 168.4, 140.5, 135.0, 133.7, 131.5, 131.1, 128.8, 52.2, 49.4, 46.0, 32.1, 20.5, 14.1; HRMS (ESI): calcd. for $C_{15}H_{21}ClNO_2$ $[M + H]^+$ 282.1255; found 282.1265.

(*E*)-Methyl 2-((butylamino)methyl)-3-*p*-tolylacrylate 3i. Colorless oil (536 mg, 82% yield); ^{1}H NMR δ 7.78 (s, 1H), 7.39 (d, 2H, J = 8.1), 7.20 (d, 2H, J = 8.1), 3.82 (s, 3H), 3.59 (s, 2H), 2.62 (t, J = 6.9, 2H), 2.38 (s, 3H), 1.52–1.42 (m, 2H), 1.39–1.29 (m, 2H), 0.91 (t, 3H, J = 7.5); ^{13}C NMR δ 168.8, 141.9, 139.1, 132.5, 130.2, 129.8, 129.3, 52.0, 49.4, 46.1, 32.2, 21.4, 20.6, 14.1. HRMS (ESI): calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802; found 262.1805.

(*E*)-Methyl 2-((butylamino)methyl)-3-*o*-tolylacrylate 3j. Colorless oil (477 mg, 73% yield); ^{1}H NMR δ 7.87 (s, 1H), 7.38–7.34 (m, 1H), 7.25–7.18 (m, 3H), 3.84 (s, 3H), 3.50 (s, 2H), 2.51 (t, 2H, J = 6.6), 2.30 (s, 3H), 1.42–1.25 (m, 4H), 0.87 (t, 3H, J = 6.9); ^{13}C NMR δ 168.5, 141.0, 136.9, 134.6, 131.5, 130.2, 129.1, 128.8, 125.9, 52.1, 48.9, 45.9, 32.1, 20.6, 20.1, 14.1; HRMS (ESI): calcd. for $C_{16}H_{24}NO_2$ $[M + H]^+$ 262.1802; found 262.1812.

(*E*)-Methyl 2-((butylamino)methyl)-3-(4-methoxyphenyl)acrylate 3k. Colorless oil (478 mg, 69% yield); ^{1}H NMR δ 7.76 (s, 1H), 7.49 (d, 2H, J = 8.7), 6.92 (d, 2H, J = 9.3), 3.84 (s, 3H), 3.82 (s, 3H), 3.60 (s, 2H), 2.64 (t, 2H, J = 6.9), 1.55–1.30 (m, 4H), 0.92 (t, 3H, J = 7.2); ^{13}C NMR δ 168.9, 160.3, 141.7, 131.6, 128.8, 127.8, 114.0, 55.3, 52.0, 49.4, 46.1, 32.1, 20.5, 14.0; HRMS (ESI): calcd. for $C_{16}H_{24}NO_3$ $[M + H]^+$ 278.1751; found 278.1764.

(*E*)-Methyl 2-((butylamino)methyl)-3-(2-methoxyphenyl)acrylate 3l. Colorless oil (444 mg, 64% yield); ^{1}H NMR δ 7.96 (s, 1H), 7.52 (d, 1H, J = 7.2), 7.32 (t, 1H, J = 7.5), 6.98 (t, 1H, J = 6.9), 6.91 (d, 1H, J = 8.4), 3.85 (s, 3H), 3.83 (s, 3H), 3.54 (s, 2H), 2.58 (t, 2H, J = 7.2), 1.47–1.31 (m, 4H), 0.89 (t, 3H, J = 7.5); ^{13}C NMR δ 168.7, 157.7, 137.9, 130.6, 130.5, 124.3, 120.4, 110.5, 55.5, 52.0, 49.1, 46.3, 32.1, 20.6, 14.1; HRMS (ESI): calcd. for $C_{16}H_{24}NO_3$ $[M + H]^+$ 278.1751; found 278.1764.

Preparation of (*E*)-methyl 3-phenyl-2-((phenylamino)methyl)acrylate 3e.[4,5] To a stirred solution of aniline (0.41 mL, 4.5 mmol) in H_2O (6 mL) was added methyl 2-(acetoxy(phenyl)methyl)acrylate **1a** (703 mg, 3 mmol). The resulting solution was stirred for the 5 h at 80 ^oC. The reaction mixture was extracted with EtOAc (2 x 15 mL). The combined EtOAc layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Petroleum ether/EtOAc = 30:1, v/v) afforded the desired product **3e** (489 mg, 61% yield) as a pale yellow oil. ^1H NMR δ 7.90 (s, 1H), 7.46–7.38 (m, 5H), 7.15 (t, 2H, J = 7.5), 6.73 (t, 1H, J = 7.5), 6.55 (d, 2H, J = 7.5), 4.14 (s, 2H), 3.84 (s, 3H).

General procedure for the synthesis of 4,5-dihydropyrrole 6. To a stirred solution of compound **3** (0.5 mmol) in toluene (2 mL) was added aldehyde (0.6 mmol). The resulting solution was heated in an azeotropic distillation apparatus for the corresponding time under N_2. The volatiles were removed *in vacuo*. Purification by flash column chromatography (Petroleum ether/EtOAc = 5:1~3:1, v/v) afforded the desired product **6**.

(4*R*,5*R*)-Methyl 1-methyl-4,5-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6a. White solid (116 mg, 79% yield); mp: 104–106 ^oC; ^1H NMR δ 7.38–7.27 (m, 6H), 7.25–7.15 (m, 5H), 4.32 (d, 1H, J = 7.5), 4.16 (d, 1H, J = 7.2), 3.54 (s, 3H), 2.77 (s, 3H); ^{13}C NMR δ 166.3, 152.3, 144.6, 140.7, 129.0, 128.5, 128.1, 127.4, 126.6, 101.9, 78.9, 57.5, 50.3, 35.3; IR (KBr) 2918, 1664, 1573, 1418, 1174, 1062, 754, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{20}NO_2$ $[M + H]^+$ 294.1489; found 294.1496.

(4*R*,5*R*)-Methyl 1-methyl-5-(4-nitrophenyl)-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6b. Yellow oil (105 mg, 62% yield); ^1H NMR δ 8.23 (d, 2H, J_1 = 6.6, J_2 = 2.1), 7.38–7.25 (m, 6H), 7.17–7.13 (m, 2H), 4.41 (d, 1H, J = 7.5), 4.08 (d, 1H, J = 7.5), 3.54 (s, 3H), 2.79 (s, 3H); ^{13}C NMR δ 165.9, 152.2, 147.9, 147.7, 143.6, 128.7, 127.4, 127.3, 127.0, 124.3, 102.8, 78.3, 57.8, 50.5, 35.8; IR (KBr) 2920, 1681, 1592, 1517, 1409, 1345, 1170, 1059, 759, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}N_2O_4$ $[M + H]^+$ 339.1339; found 339.1347.

(4*R*,5*R*)-Methyl 5-(4-cyanophenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6c. White solid (108 mg, 68% yield); mp: 107–108 ^oC; ^1H NMR δ 7.67

(d, 2H, J = 7.8), 7.37–7.24 (m, 6H), 7.15 (d, 2H, J = 7.5), 4.36 (d, 1H, J = 7.8), 4.07 (d, 1H, J = 7.8), 3.53 (s, 3H), 2.78 (s, 3H); ^{13}C NMR δ 166.0, 152.2, 146.0, 143.7, 132.9, 128.7, 127.4, 127.3, 127.0, 118.6, 112.0, 102.7, 78.6, 57.8, 50.5, 35.7; IR (KBr) 2943, 2230, 1686, 1590, 1396, 1159, 1064, 762, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{19}N_2O_2$ [M + H]$^+$ 319.1441; found 319.1449.

(4*R*,5*R*)-Methyl 5-(4-chlorophenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6d. White solid (87 mg, 53% yield); mp: 107–108 ^{o}C; ^{1}H NMR δ 7.36–7.22 (m, 5H), 7.16–7.12 (m, 5H), 4.27 (d, 1H, J = 7.8), 4.10 (d, 1H, J = 7.5), 3.53 (s, 3H), 2.75 (s, 3H); ^{13}C NMR δ 166.3, 152.3, 144.3, 139.3, 134.0, 129.2, 128.7, 128.1， 127.5, 126.8, 102.4, 78.5, 57.8, 50.5, 35.5; IR (KBr) 2943, 1668, 1593, 1410, 1182, 1061, 758, 705 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}ClNO_2$ [M + H]$^+$ 328.1099; found 328.1105.

(4*R*,5*R*)-Methyl 5-(3-chlorophenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6e. White solid (110 mg, 67% yield); mp: 70–71 ^{o}C; ^{1}H NMR δ 7.40–7.27 (m, 7H), 7.24–7.21 (m, 3H), 4.94 (d, 1H, J = 5.7), 4.10 (d, 1H, J = 5.4), 3.53 (s, 3H), 2.83 (s, 3H); ^{13}C NMR δ 166.4, 151.9, 144.3, 137.8, 133.2, 130.2, 129.2, 128.5, 127.6, 127.5, 126.8, 102.3, 74.1, 56.7, 50.5, 35.3; IR (KBr) 2947, 1662, 1588, 1410, 1182, 1063, 758, 704 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}ClNO_2$ [M + H]$^+$ 328.1099; found 328.1111.

(4*R*,5*R*)-Methyl 5-(2-chlorophenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6f. Pale yellow oil (118 mg, 72% yield); ^{1}H NMR δ 7.40 (s, 1H), 7.37–7.27 (m, 5H), 7.26–7.21 (m, 4H), 4.94 (d, 1H, J = 5.4), 4.10 (d, 1H, J = 5.1), 3.52 (s, 3H), 2.84 (s, 3H); ^{13}C NMR δ 166.3, 151.8, 144.3, 137.8, 133.1, 130.2, 129.1, 128.4, 127.6, 127.5, 127.4, 126.7, 102.3, 74.1, 56.7, 50.4, 35.3; IR (KBr) 2945, 1682, 1594, 1410, 1173, 1061, 758, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}ClNO_2$ [M + H]$^+$ 328.1099; found 328.1114.

(4*R*,5*R*)-Methyl 1-methyl-4-phenyl-5-*p*-tolyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6g. White solid (120 mg, 78% yield); mp: 90–92 ^{o}C; ^{1}H NMR δ 7.37–7.27 (m, 3H), 7.24–7.07 (m, 7H), 4.28 (d, 1H, J = 7.5), 4.15 (d, 1H, J = 7.2), 3.53 (s, 3H), 2.75 (s, 3H), 2.36 (s, 3H); ^{13}C NMR δ 166.5, 152.3, 144.8, 137.9, 137.8,

129.7, 128.6, 127.4, 126.7, 126.6, 101.9, 78.8, 57.5, 50.4, 35.3, 21.3; IR (KBr) 2945, 1667, 1588, 1414, 1178, 1061, 758, 703 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NO_2$ $[M + H]^+$ 308.1645; found 308.1657.

(4*R*,5*R*)-Methyl 1-methyl-4-phenyl-5-*m*-tolyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6h. Pale yellow oil (118 mg, 77% yield); ^1H NMR δ 7.38 (s, 1H), 7.32–7.27 (m, 3H), 7.23–7.11 (m, 4H), 7.02-6.97 (m, 2H), 4.28 (d, 1H, J = 7.5), 4.16 (d, 1H, J = 7.2), 3.53 (s, 3H), 2.77 (s, 3H), 2.35 (s, 3H); ^{13}C NMR δ 166.4, 152.3, 144.8, 140.7, 138.6, 128.84, 128.77, 128.5, 127.3, 127.1, 126.5, 123.7, 101.7, 78.8, 57.3, 50.3, 35.2, 21.5; IR (KBr) 2945, 1682, 1592, 1410, 1173, 1061, 756, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NO_2$ $[M + H]^+$ 308.1645; found 308.1650.

(4*R*,5*R*)-Methyl 1-methyl-4-phenyl-5-*o*-tolyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6i. Pale yellow oil (115 mg, 75% yield); ^1H NMR δ 7.39 (s, 1H), 7.31–7.26 (m, 3H), 7.23–7.13 (m, 6H), 4.66 (d, 1H, J = 7.2), 4.10 (d, 1H, J = 7.5), 3.52 (s, 3H), 2.79 (s, 3H), 2.02 (s, 3H); ^{13}C NMR δ 166.4, 152.1, 144.8, 138.4, 130.9, 128.6, 128.5, 128.4, 127.7, 127.4, 126.7, 126.6, 102.0, 57.3, 50.3, 35.4, 19.4; IR (KBr) 2945, 1682, 1592, 1412, 1173, 1061, 758, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NO_2$ $[M + H]^+$ 308.1645; found 308.1653.

(4*R*,5*R*)-Methyl 5-(4-methoxyphenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole -3-carboxylate 6j. White solid (126 mg, 78% yield); mp: 76–77 ^oC; ^1H NMR δ 7.37–7.26 (m, 3H), 7.24–7.12 (m, 5H), 6.90–6.87 (m, 2H), 4.26 (d, 1H, J = 7.8), 4.15 (d, 1H, J = 7.2), 3.82 (s, 3H), 3.54 (s, 3H), 2.74 (s, 3H); ^{13}C NMR δ 166.4, 159.5, 152.2, 144.7, 132.9, 128.5, 127.9, 127.4, 126.6, 114.3, 101.8, 78.5, 57.5, 55.3, 50.3, 35.2; IR (KBr) 2945, 1678, 1592, 1410, 1248, 1171, 1059, 758, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NO_3$ $[M + H]^+$ 324.1594; found 324.1602.

(4*R*,5*R*)-Methyl 5-(2-methoxyphenyl)-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole -3-carboxylate 6k. White solid (108 mg, 67% yield); mp: 74–75 ^oC; ^1H NMR δ 7.40 (s, 1H), 7.32–7.19 (m, 7H), 6.97 (t, 1H, J = 7.5), 6.89 (d, 1H, J = 8.1), 4.84 (d, 1H, J = 5.4), 4.06 (d, 1H, J = 5.4), 3.68 (s, 3H), 3.52 (s, 3H), 2.83 (s, 3H); ^{13}C NMR δ 166.7, 157.0, 152.1, 145.2, 128.8, 128.6, 128.2, 127.3, 126.6, 126.3, 120.8, 111.0, 101.7, 71.8, 56.2, 55.2, 50.2, 35.2; IR (KBr) 2943, 1662, 1576, 1412, 1242, 1165, 1059, 748,

696 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NO_3$ $[M + H]^+$ 324.1594; found 324.1609.

(4*R*,5*R*)-Methyl 1-methyl-4-phenyl-5-(thiophen-2-yl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6l. Pale yellow solid (109 mg, 73% yield); mp: 73–74 °C; ^{1}H NMR δ 7.32–7.27 (m, 4H), 7.24–7.17 (m, 3H), 6.95 (dd, 1H, J_1 = 5.1, J_2 = 3.9), 6.86 (dd, 1H, J_1 = 3.9, J_2 = 0.9), 4.55 (d, 1H, J = 7.5), 4.27 (d, 1H, J = 7.2), 3.55 (s, 3H), 2.79 (s, 3H); ^{13}C NMR δ 166.3, 151.6, 144.1, 143.9, 128.6, 127.4, 126.9, 125.7, 102.7, 74.5, 57.9, 50.5, 35.4; IR (KBr) 2943, 1670, 1589, 1414, 1178, 1057, 756, 716, 704 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{18}NO_2S$ $[M + H]^+$ 300.1053; found 300.1061.

(2*E*,2'*E*)-Dimethyl 2,2'-(methylazanediyl)bis(methylene)bis(3-phenylacrylate) 7a. Pale yellow oil (49 mg, 26% yield); ^{1}H NMR δ 7.84 (s, 2H), 7.64–7.61 (m, 4H), 7.32–7.29 (m, 6H), 3.76 (s, 6H), 3.45 (s, 4H), 2.20 (s, 3H); ^{13}C NMR δ 169.4, 143.0, 135.4, 130.6, 129.0, 128.5, 128.3, 52.8, 52.1, 41.6; IR (KBr) 2948, 1714, 1434, 1245, 1203, 1090, 767, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{26}NO_4$ $[M + H]^+$ 380.1856; found 380.1864.

(4*R*,5*S*)-methyl 5-cyclohexyl-1-methyl-4-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6o. White solid (83 mg, 56% yield); mp: 90–91 °C; ^{1}H NMR δ 7.30–7.24 (m, 3H), 7.21–7.13 (m, 3H), 4.01 (d, 1H, J = 4.8), 3.51 (s, 3H), 3.35 (t, 1H, J = 4.5), 2.91 (s, 3H), 1.78–1.15 (m, 11H); ^{13}C NMR δ 166.4, 151.7, 146.5, 128.4, 127.3, 126.2, 102.4, 78.9, 50.2, 48.4, 40.3, 35.3, 28.1, 26.6, 26.4, 26.1; IR (KBr) 2930, 1668, 1591, 1414, 1188, 1063, 759, 701 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{26}NO_2$ $[M + H]^+$ 300.1958; found 300.1964.

(4*R*,5*R*)-Methyl 1-butyl-4,5-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6p. White solid (126 mg, 75% yield); mp: 94–95 °C; ^{1}H NMR (DMSO-d_6) δ 7.69 (s, 1H), 7.42–7.20 (m, 8H), 7.12–7.08 (m, 2H), 4.45 (d, 1H, J = 5.7), 3.91 (d, 1H, J = 6.0), 3.41 (s, 3H), 3.28–3.18 (m, 1H), 2.88–2.80 (m, 1H), 1.42–1.17 (m, 4H), 0.81 (t, 3H, J = 7.5); ^{13}C NMR δ 166.5, 151.1, 145.0, 141.3, 129.0, 128.6, 128.1, 127.2, 126.6, 101.2, 76.6, 57.1, 50.3, 47.5, 30.3, 20.0, 13.7; IR (KBr) 2949, 1659, 1581, 1431, 1165, 1085, 762, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{26}NO_2$ $[M + H]^+$ 336.1958; found 336.1962.

(4*R*,5*R*)-Methyl 1-butyl-4-(4-nitrophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrrole-3-

carboxylate 6q. Yellow oil (126 mg, 66% yield); ^{1}H NMR δ 8.17 (d, 2H, J = 8.7), 7.50 (s, 1H), 7.38–7.30 (m, 5H), 7.27–7.17 (m, 2H), 4.42 (d, 1H, J = 6.9), 4.27 (d, 1H, J = 7.2), 3.53 (s, 3H), 3.12–3.02 (m, 1H), 2.98–2.90 (m, 1H), 1.54–1.42 (m, 2H), 1.34–1.20 (m, 2H), 0.88 (t, 3H, J = 7.2); ^{13}C NMR δ 166.0, 152.2, 151.6, 146.8, 140.3, 129.1, 128.5, 128.2, 126.6, 124.0, 100.3, 76.2, 57.1, 50.4, 47.4, 30.1, 19.9, 13.6; IR (KBr) 2927, 1670, 1581, 1526, 1425, 1348, 1168, 1080, 753, 701 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{25}N_2O_4$ [M + H]$^+$ 381.1809; found 381.1811.

(4*R*,5*R*)-Methyl 1-butyl-4-(4-cyanophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6r. Colorless oil (132 mg, 73% yield); ^{1}H NMR δ 7.60 (d, 2H, J = 8.7), 7.48 (s, 1H), 7.38–7.26 (m, 5H), 7.20–7.17 (m, 2H), 4.39 (d, 1H, J = 7.2), 4.21 (d, 1H, J = 7.5), 3.54 (s, 3H), 3.11–3.01 (m, 1H), 2.96–2.87 (m, 1H), 1.51–1.41 (m, 2H), 1.34–1.20 (m, 2H), 0.87 (t, 3H, J = 7.2); ^{13}C NMR δ 151.6, 150.2, 140.5, 132.6, 129.2, 128.6, 128.2, 126.7, 119.2, 110.6, 100.4, 76.3, 57.3, 50.5, 47.5, 30.3, 20.0, 13.8; IR (KBr) 2930, 2226, 1684, 1592, 1425, 1167, 1086, 762, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{25}N_2O_2$ [M + H]$^+$ 361.1911; found 361.1917.

(4*R*,5*R*)-Methyl 1-butyl-4-(4-chlorophenyl)-5-phenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6s. Colorless oil (146 mg, 79% yield); ^{1}H NMR δ 7.47 (s, 1H), 7.40–7.25 (m, 5H), 7.20–7.17 (m, 2H), 7.09 (d, 2H, J = 6.3), 4.38 (d, 1H, J = 7.2), 4.11 (d, 1H, J = 7.2), 3.54 (s, 3H), 3.11–3.00 (m, 1H), 2.95–2.85 (m, 1H), 1.48–1.40 (m, 2H), 1.32–1.24 (m, 2H), 0.87 (t, 3H, J = 7.2); ^{13}C NMR δ 166.4, 151.4, 143.5, 141.0, 132.3, 129.1, 128.8, 128.7, 128.3, 126.7, 100.9, 76.6, 56.6, 50.4, 47.5, 30.3, 20.0, 13.8; IR (KBr) 2930, 1684, 1592, 1425, 1169, 1088, 759, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{22}H_{25}ClNO_2$ [M + H]$^+$ 370.1568; found 370.1569.

(4*R*,5*R*)-Methyl 1-butyl-5-phenyl-4-*p*-tolyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6t. Colorless oil (146 mg, 84% yield); ^{1}H NMR δ 7.46 (s, 1H), 7.38–7.29 (m, 3H), 7.22–7.19 (m, 2H), 7.13–7.04 (m, 4H), 4.43 (d, 1H, J = 6.3), 4.10 (d, 1H, J = 6.6), 3.53 (s, 3H), 3.08–3.01 (m, 1H), 2.96–2.89 (m, 1H), 2.32 (s, 3H), 1.48–1.40 (m, 2H), 1.33–1.25 (m, 2H), 0.86 (t, 3H, J = 7.5); ^{13}C NMR δ 166.6, 151.1, 142.2, 141.5, 136.1, 129.4, 129.0, 128.1, 127.2, 126.6, 101.4, 76.7, 56.8, 50.4, 47.6, 30.3, 21.2, 20.0, 13.8; IR (KBr) 2930, 1684, 1592, 1425, 1167, 1084, 756, 701 cm^{-1}; HRMS (ESI): calcd.

for $C_{23}H_{28}NO_2$ [M + H]$^+$ 350.2115; found 350.2124.

(4*R*,5*R*)-Methyl 1-butyl-5-phenyl-4-*o*-tolyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6u. Colorless oil (132 mg, 75% yield); ^{1}H NMR δ 7.48 (s, 1H), 7.37–7.28 (m, 3H), 7.25–7.19 (m, 4H), 7.11–7.08 (m, 2H), 4.46 (d, 1H, J = 6.3), 4.42 (d, 1H, J = 6.3), 3.53 (s, 3H), 3.10–3.00 (m, 1H), 2.95–2.86 (m, 1H), 2.09 (s, 3H), 1.48–1.40 (m, 2H), 1.35–1.22 (m, 2H), 0.86 (t, 3H, J = 7.2); ^{13}C NMR δ 166.5, 151.0, 143.3, 141.6, 135.4, 130.1, 128.9, 128.1, 126.8, 126.6, 126.5, 126.2, 101.7, 76.6, 52.4, 50.3, 47.4, 30.3, 19.9, 19.8, 13.7; IR (KBr) 2954, 1682, 1592, 1425, 1167, 1084, 758, 702 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{28}NO_2$ [M + H]$^+$ 350.2115; found 350.2129.

(4*R*,5*R*)-Methyl 1-butyl-4-(4-methoxyphenyl)-5-phenyl-4,5-dihydro-1*H*-pyrrole -3-carboxylate 6v. Colorless oil (141 mg, 77% yield); ^{1}H NMR δ 7.45 (s, 1H), 7.37–7.30 (m, 3H), 7.22–7.18 (m, 2H), 7.08 (d, 2H, J = 8.4), 6.84 (d, 2H, J = 8.4), 4.41 (d, 1H, J = 6.6), 4.08 (d, 1H, J = 6.6), 3.79 (s, 3H), 3.54 (s, 3H), 3.09–3.03 (m, 1H), 2.97–2.87 (m, 1H), 1.49–1.41 (m, 2H), 1.33–1.24 (m, 2H), 0.86 (t, 3H, J = 7.2); ^{13}C NMR δ 166.4, 158.3, 150.9, 141.3, 137.2, 128.8, 128.1, 127.9, 126.5, 113.9, 101.3, 76.7, 56.3, 55.1, 50.1, 47.4, 30.2, 19.9, 13.6; IR (KBr) 2954, 1682, 1590, 1427, 1246, 1173, 1084, 760, 702 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{28}NO_3$ [M + H]$^+$ 366.2064; found 366.2065.

(4*R*,5*R*)-Methyl 1-butyl-4-(2-methoxyphenyl)-5-phenyl-4,5-dihydro-1*H*-pyrrole -3-carboxylate 6w. Pale yellow oil (120 mg, 66% yield); ^{1}H NMR δ 7.52 (s, 1H), 7.36–7.27 (m, 5H), 7.24–7.14 (m, 2H), 6.95–6.84 (m, 2H), 4.53 (d, 1H, J = 4.8), 4.36 (d, 1H, J = 4.8), 3.68 (s, 3H), 3.55 (s, 3H), 3.10–3.00 (m, 1H), 2.95–2.84 (m, 1H), 1.42–1.34 (m, 2H), 1.25–1.17 (m, 2H), 0.82 (t, 3H, J = 7.5); ^{13}C NMR δ 166.8, 157.0, 151.6, 141.7, 132.8, 128.5, 127.8, 127.7, 127.5, 126.6, 120.6, 110.6, 98.9, 75.6, 55.0, 50.3, 49.9, 47.3, 30.5, 19.8, 13.6; IR (KBr) 2954, 1682, 1592, 1427, 1244, 1167, 1082, 752, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{23}H_{28}NO_3$ [M + H]$^+$ 366.2064; found 366.2081.

(4*R*,5*R*)-Methyl 1-isopropyl-4,5-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6x. Colorless oil (80 mg, 50% yield); ^{1}H NMR δ 7.61 (s, 1H), 7.37–7.27 (m, 5H), 7.25–7.14 (m, 5H), 4.49 (d, 1H, J = 6.9), 4.07 (d, 1H, J = 6.6), 3.53 (s, 3H), 3.22–3.13

(m, 1H), 1.25 (d, 3H, J = 7.2), 1.10 (d, 3H, J = 6.3); ^{13}C NMR δ 166.6, 147.8, 145.2, 142.2, 129.0, 128.6, 128.0, 127.3, 126.6, 126.5, 101.8, 76.1, 57.0, 50.3, 48.1, 22.0, 21.5; IR (KBr) 2970, 1680, 1589, 1431, 1178, 1097, 760, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{24}NO_2$ [M + H]$^+$ 322.1802; found 322.1810.

(4*R*,5*S*)-Methyl 1-isopropyl-4,5-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 8x. Colorless oil (50 mg, 31% yield); ^{1}H NMR δ 7.71 (s, 1H), 7.48 (d, 2H, J = 7.2), 7.37–7.27 (m, 2H), 7.25–7.17 (m, 4H), 7.04 (br, 2H), 3.99 (d, 1H, J = 18.9), 3.74 (s, 3H), 3.33 (d, 1H, J = 18.6), 2.80 (br, 1H), 1.16–1.04 (m, 6H); ^{13}C NMR δ 168.3, 143.3, 140.5, 134.7, 134.4, 130.9, 129.4, 129.0, 128.4, 127.4, 127.0, 68.6, 52.1, 49.8, 45.2, 21.9, 21.8; IR (KBr) 2974, 1696, 1437, 1263, 1242, 1070, 771, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{21}H_{24}NO_2$ [M + H]$^+$ 322.1802; found 322.1810.

(4*R*,5*R*)-Methyl 1-benzyl-4,5-diphenyl-4,5-dihydro-1*H*-pyrrole-3-carboxylate 6y. Colorless oil (145 mg, 79% yield); ^{1}H NMR δ 7.49 (s, 1H), 7.37–7.29 (m, 6H), 7.23–7.13 (m, 7H), 7.08–7.04 (m, 2H), 4.35 (d, 1H, J = 7.2), 4.32 (d, 1H, J = 14.7), 4.16 (d, 1H, J = 7.2), 3.90 (d, 1H, J = 14.7), 3.52 (s, 3H); ^{13}C NMR δ 166.4, 150.9, 144.6, 140.8, 135.9, 129.0, 128.8, 128.4, 128.3, 128.1, 128.0, 127.3, 126.9, 126.5, 102.6, 75.9, 57.2, 52.0, 50.3; IR (KBr) 2943, 1670, 1576, 1431, 1170, 1072, 760, 698 cm^{-1}; HRMS (ESI): calcd. for $C_{25}H_{24}NO_2$ [M + H]$^+$ 370.1802; found 370.1811.

Preparation of methyl 1-methyl-4,5-diphenyl-1*H*-pyrrole-3-carboxylate 10a. To a stirred solution of compound **6a** (147 mg, 0.5 mmol) in CH_2Cl_2 (2 mL) was added DDQ (136 mg, 0.6 mmol). The resulting solution was stirred for the 2.5 h at room temperature, diluted with CH_2Cl_2 (10 mL). The resulting solution was washed with saturated aqueous $NaHCO_3$ (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Petroleum ether/EtOAc = 5:1, v/v) afforded the desired product **10a** (135 mg, 92% yield) as a white solid. mp: 167–168 ^{o}C; ^{1}H NMR δ 7.42 (s, 1H), 7.30–7.24 (m, 3H), 7.20–7.11 (m, 7H), 3.69 (s, 3H), 3.56 (s, 3H); ^{13}C NMR δ 165.1, 134.8, 133.3, 131.4, 131.0, 130.9, 128.34, 128.27, 127.7, 127.3, 126.2, 124.6, 113.1, 50.8, 35.4; IR (KBr) 2952, 1690, 1524, 1440, 1240, 1130, 767, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{18}NO_2$ [M + H]$^+$ 292.1332; found 292.1338.

Preparation of (3*R*,4*S*,5*R*)-methyl 1-methyl-4,5-diphenylpyrrolidine-3-carboxy

late 11a. To a stirred solution of compound **6a** (147 mg, 0.5 mmol) in CH_3CN (1 mL) was added AcOH (1 mL) and $NaBH(OAc)_3$ (318 mg, 1.5 mmol). The resulting solution was stirred for the 0.5 h at room temperature. The volatiles was removed *in vacuo* and saturated aqueous $NaHCO_3$ (10 mL) was added, extracted with EtOAc (3 x 10 mL). The combined EtOAc layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification by flash chromatography (Petroleum ether/EtOAc = 5:1, v/v) afforded the desired product **11a** (94 mg, 64% yield) as a white solid. mp: 69–70 ^{o}C; ^{1}H NMR δ 7.25–7.08 (m, 10H), 3.70 (s, 3H), 3.67 (d, 1H, J = 8.4), 3.58 (dd, 1H, J_1 = 8.4, J_2 = 7.5), 3.22–3.16 (m, 2H), 2.86 (t, 1H, J = 9.6), 2.18 (s, 3H); ^{13}C NMR δ 174.9, 141.3, 140.1, 128.5, 128.3, 128.1, 127.9, 127.6, 126.8, 80.1, 59.3, 57.6, 52.2, 49.5, 40.2; IR (KBr) 2948, 1728, 1454, 1236, 1196, 756, 700 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{22}NO_2$ $[M + H]^+$ 296.1645; found 296.1649.

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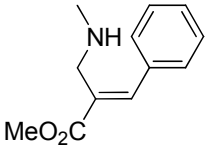
Spectra:



Chemical Formula: $C_{12}H_{15}NO_2$
Exact Mass: 205.11
Molecular Weight: 205.25

3a

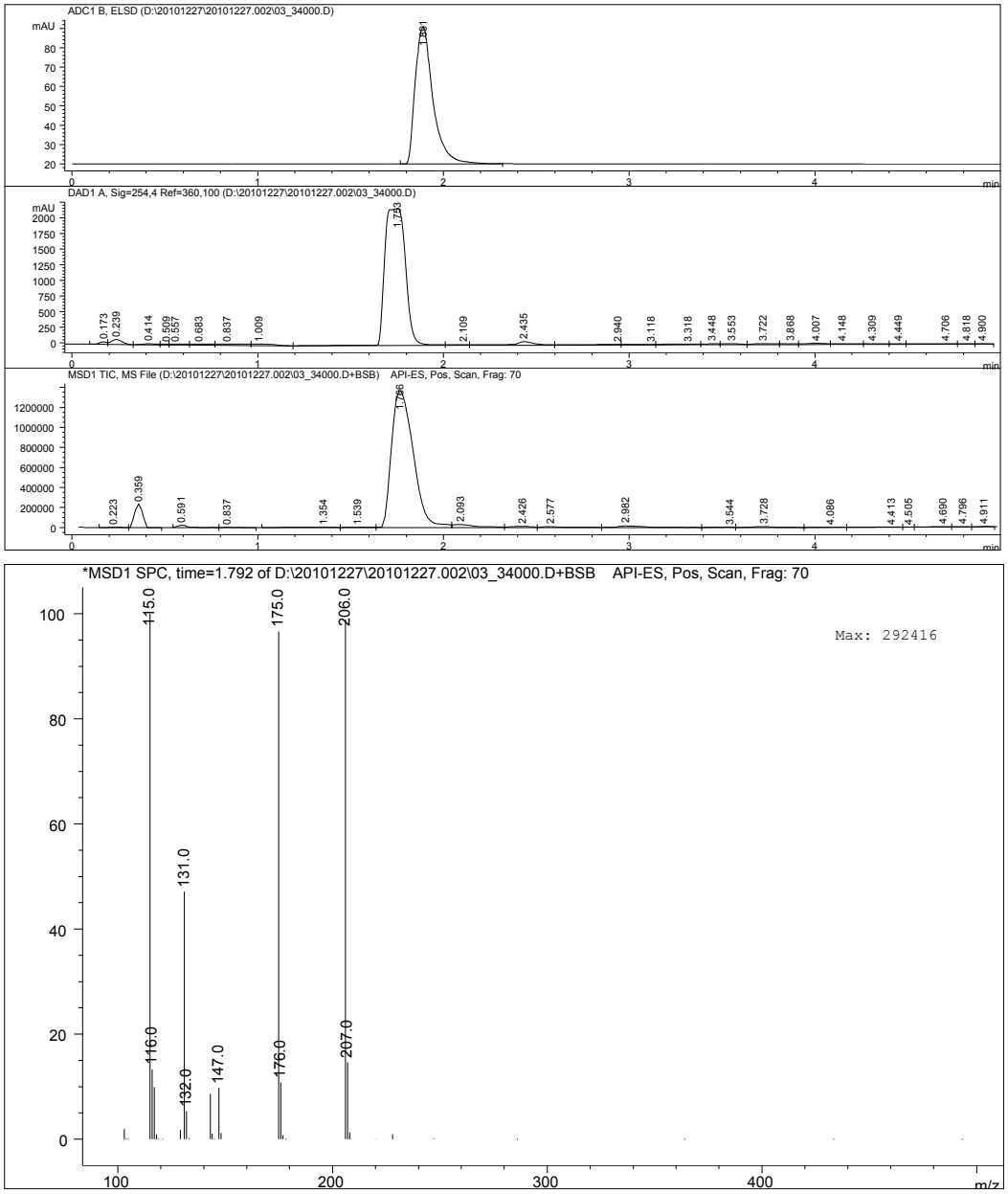


Fig. S-1: LC-MS-ELSD of compound **3a**

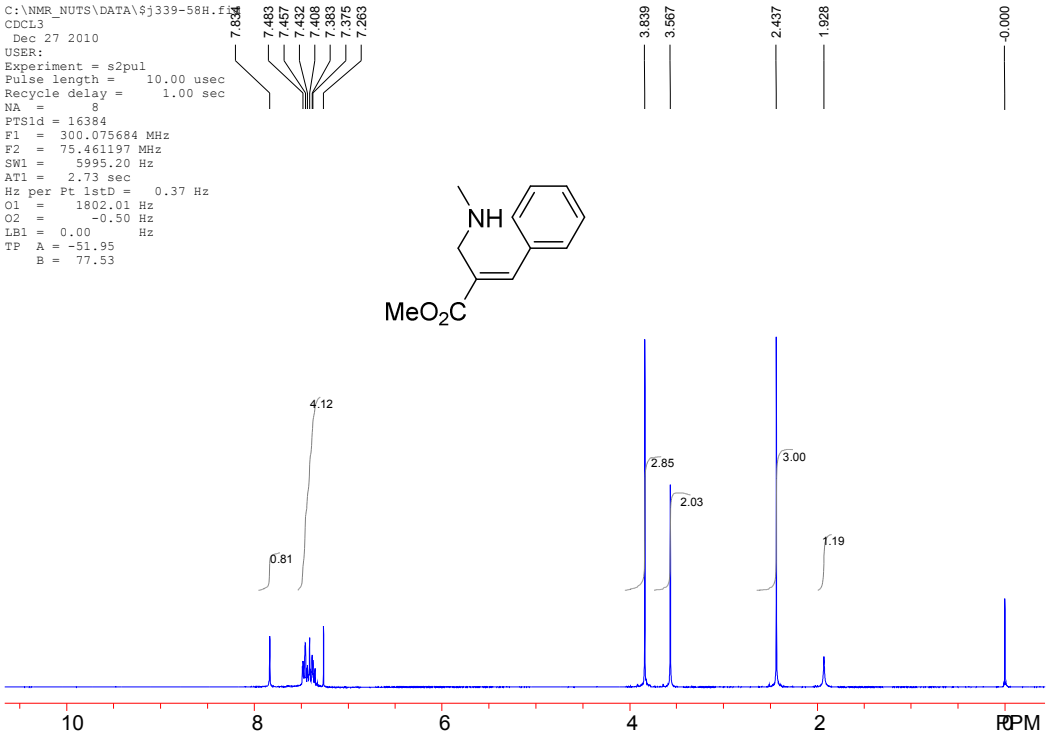


Fig. S-2: ^{1}H Spectra of compound **3a**

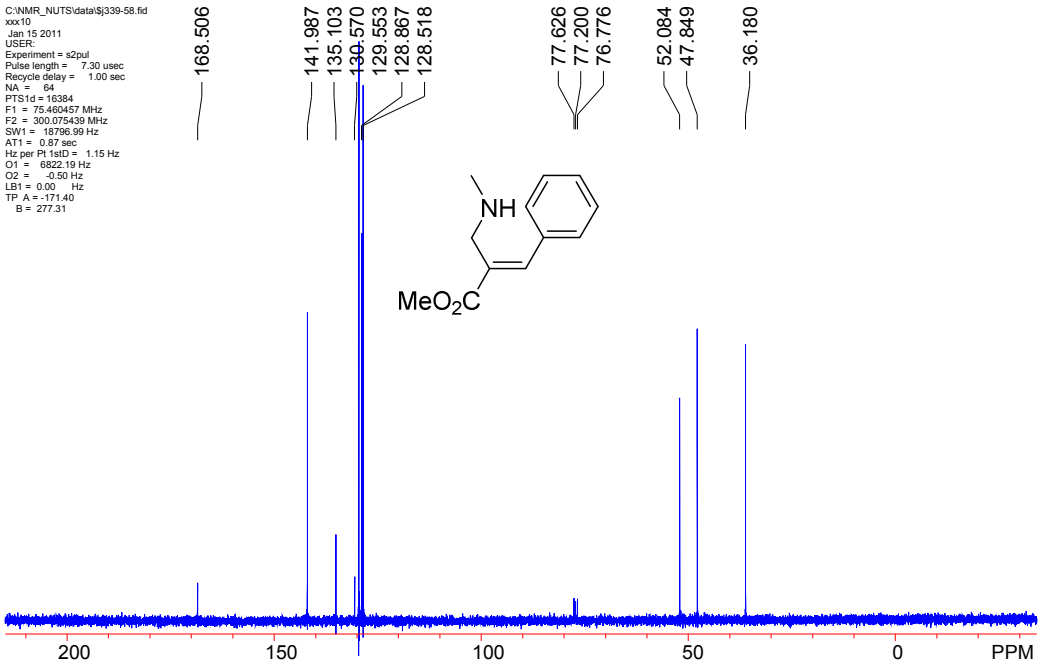
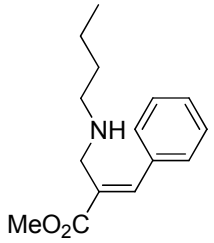


Fig. S-3: ^{13}C Spectra of compound **3a**



Chemical Formula: $C_{15}H_{21}NO_2$
Exact Mass: 247.16
Molecular Weight: 247.33

3b

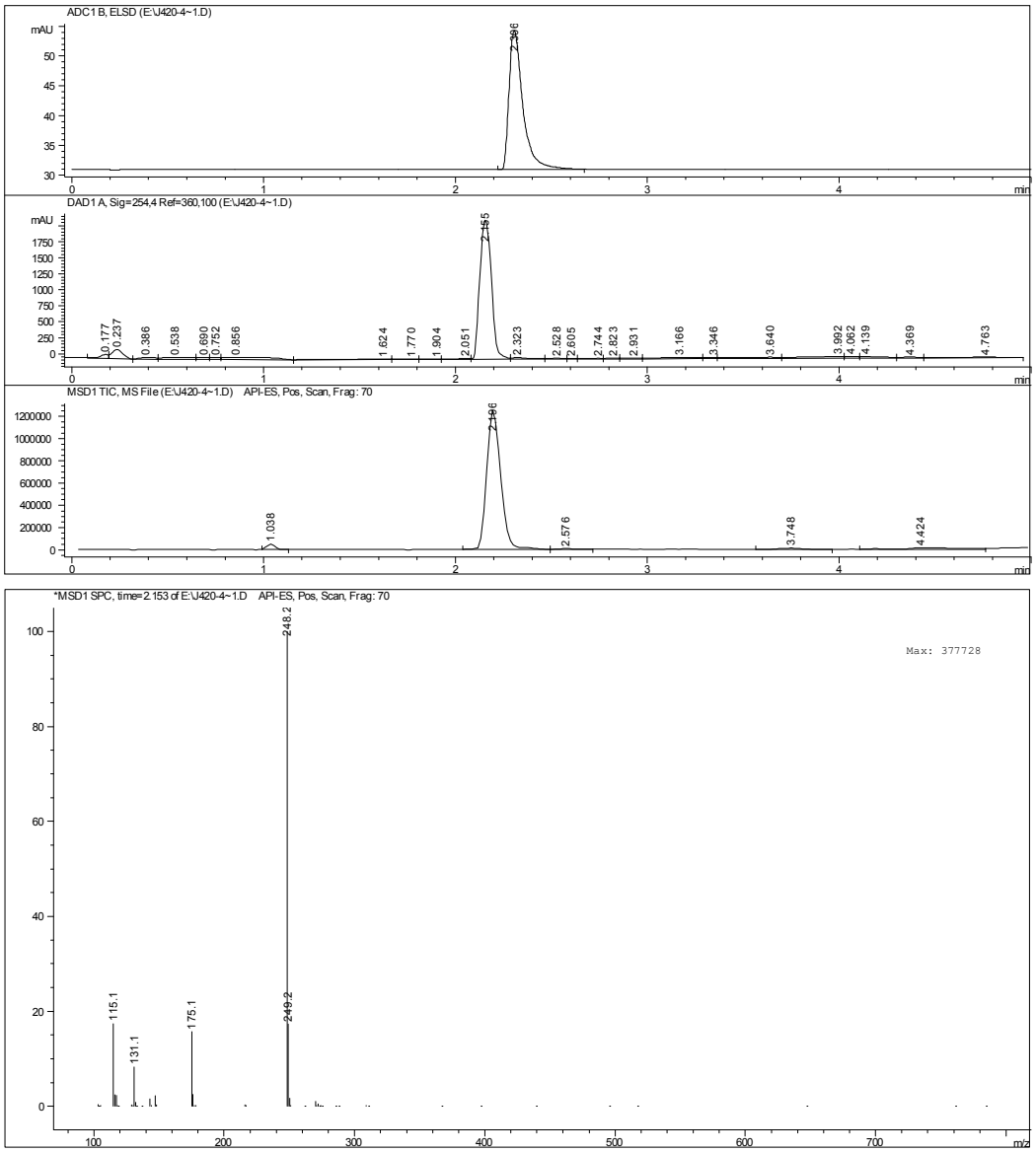


Fig. S-4: LC-MS-ELSD of compound **3b**

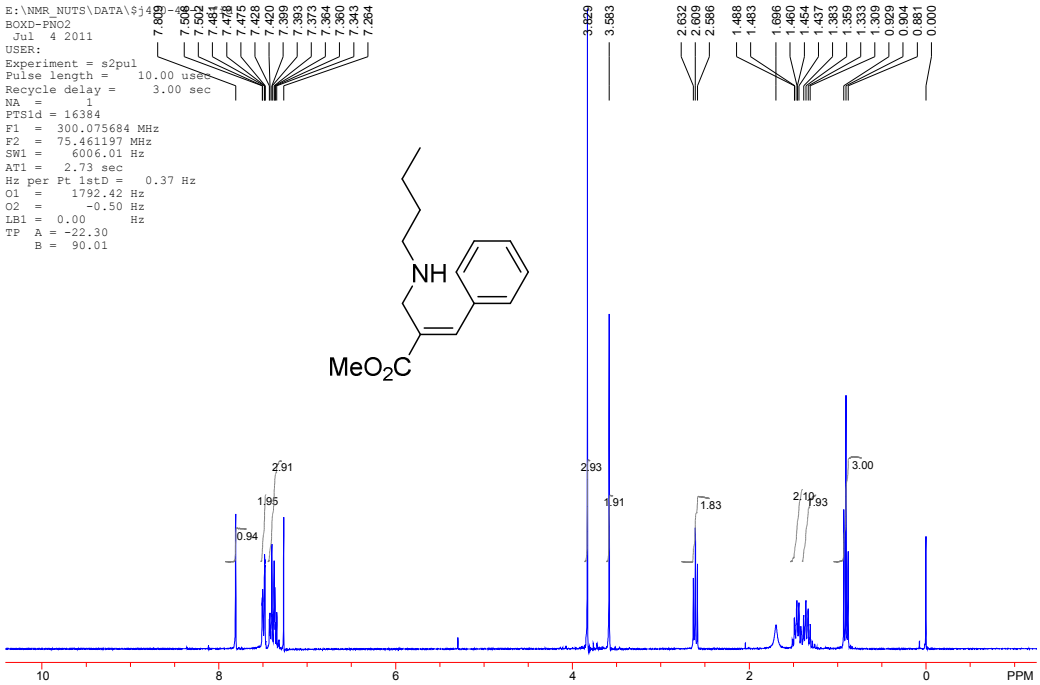


Fig. S-5: ^{1}H Spectra of compound **3b**

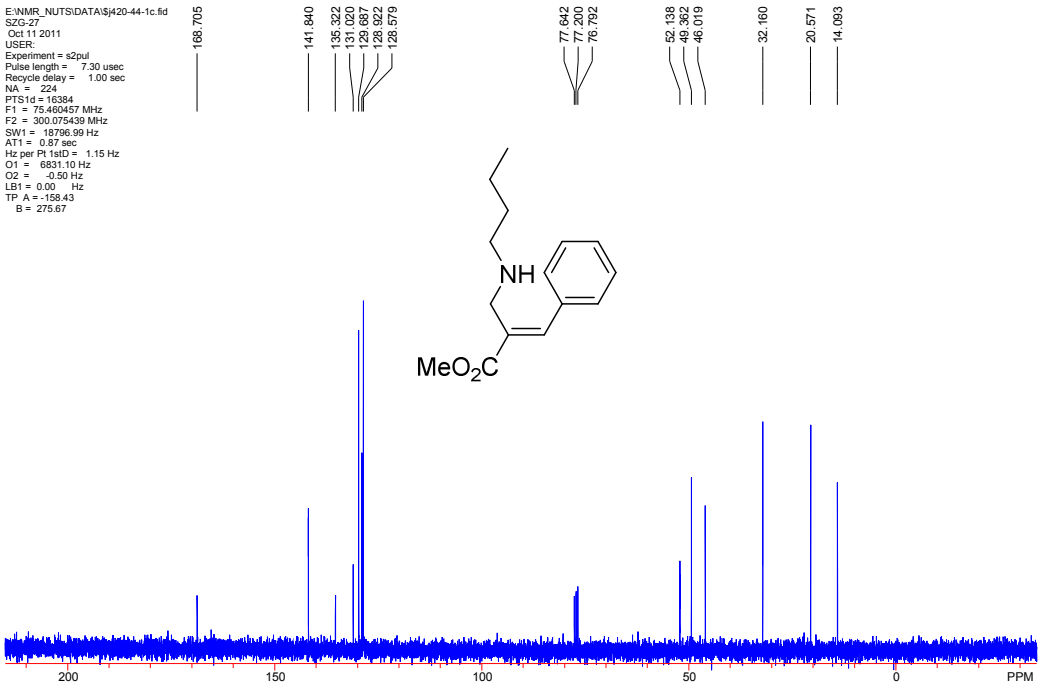
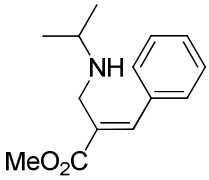


Fig. S-6: ^{13}C Spectra of compound **3b**



Chemical Formula: $C_{14}H_{19}NO_2$
Exact Mass: 233.14
Molecular Weight: 233.31

3c

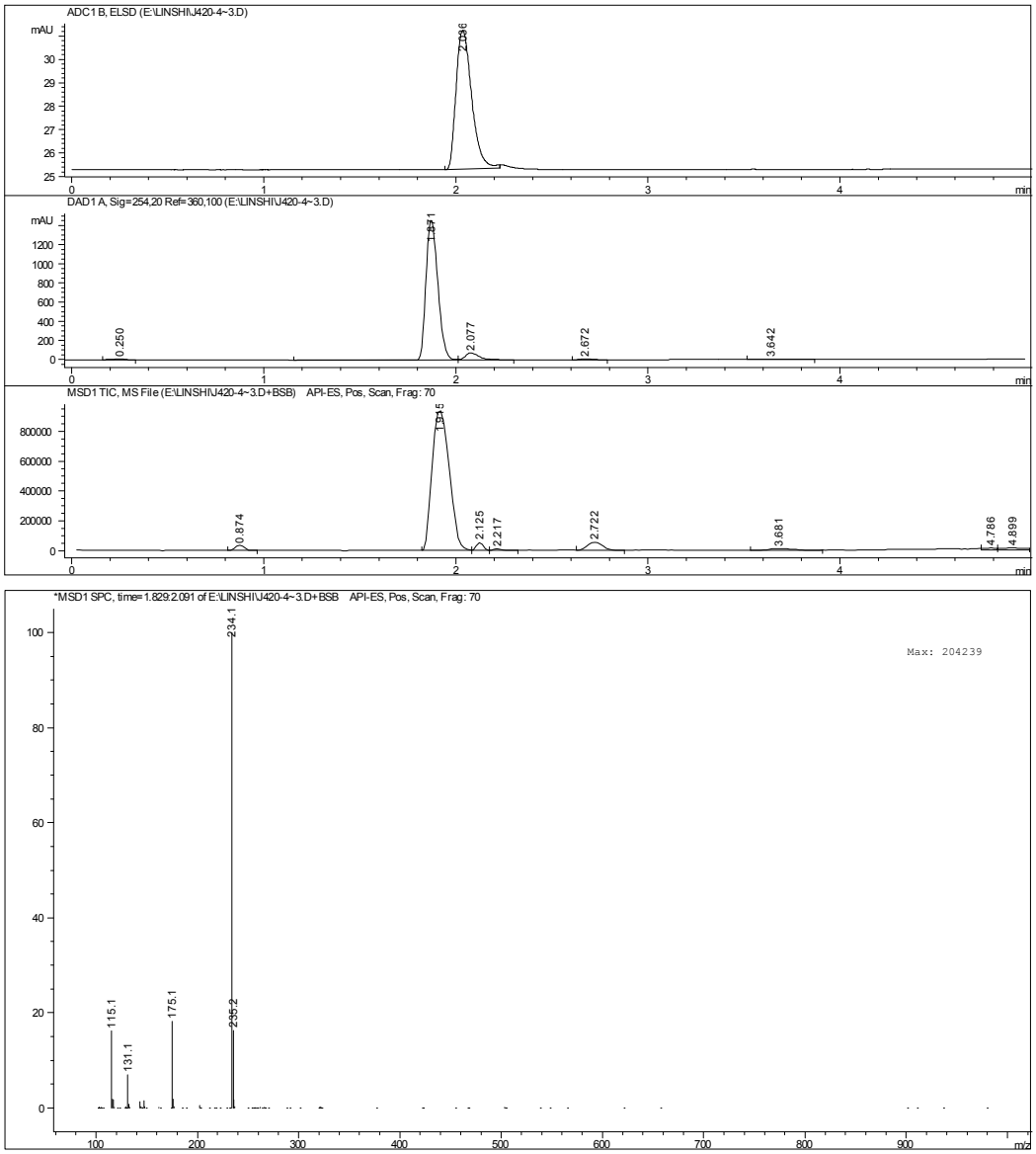


Fig. S-7: LC-MS-ELSD of compound **3c**

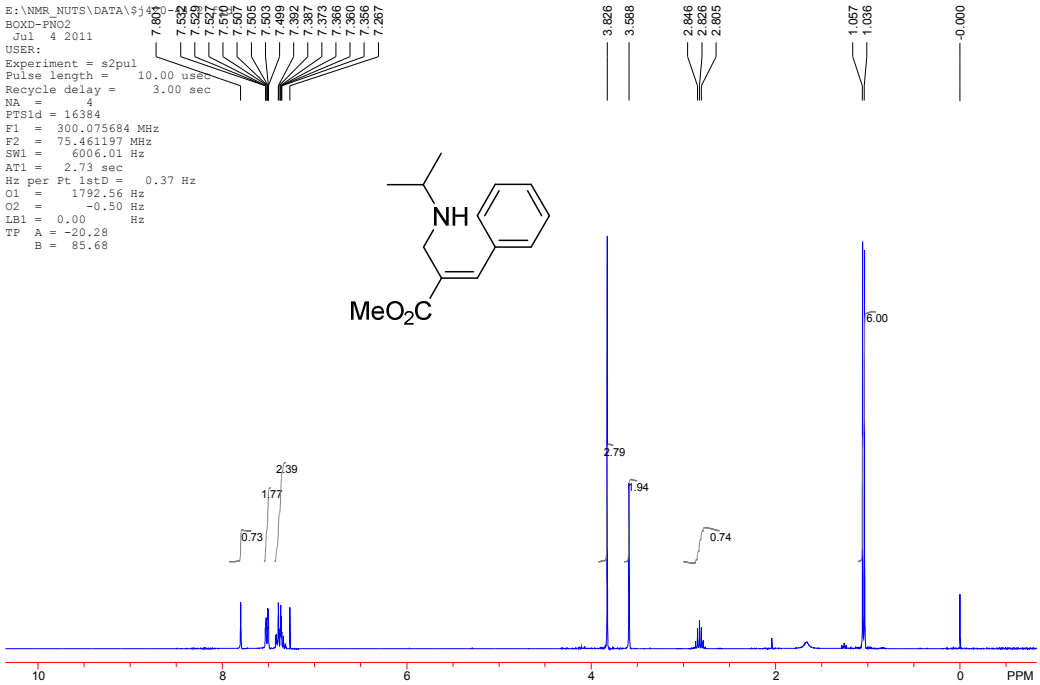


Fig. S-8: ^{1}H Spectra of compound **3c**

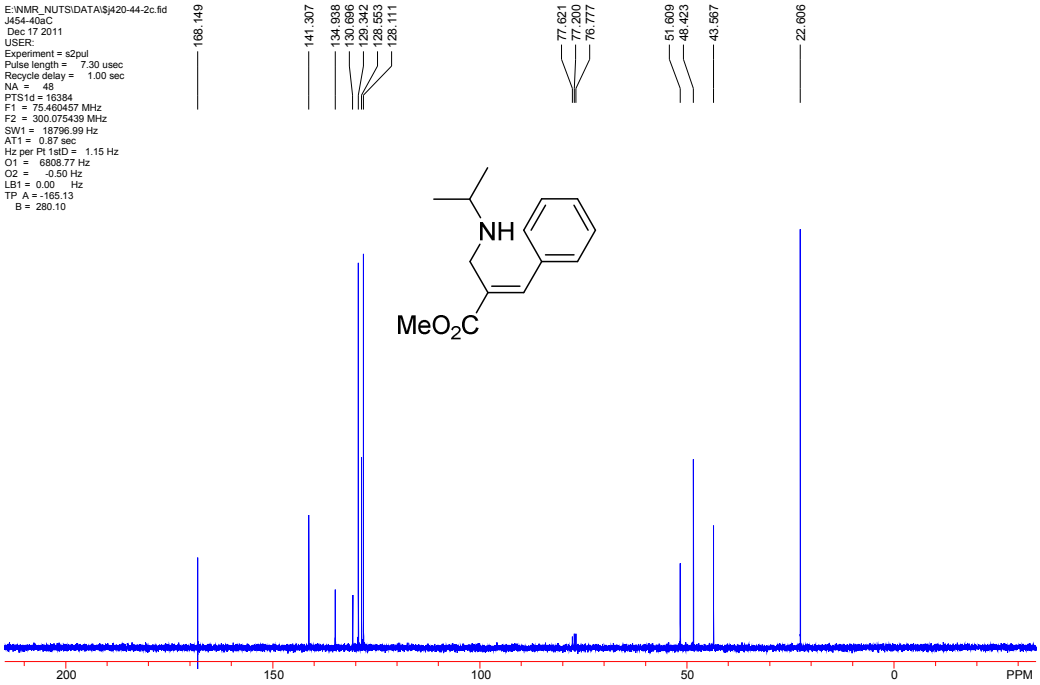
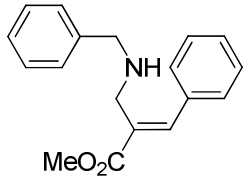


Fig. S-9: ^{13}C Spectra of compound **3c**



Chemical Formula: $C_{18}H_{19}NO_2$
Exact Mass: 281.14
Molecular Weight: 281.35

3d

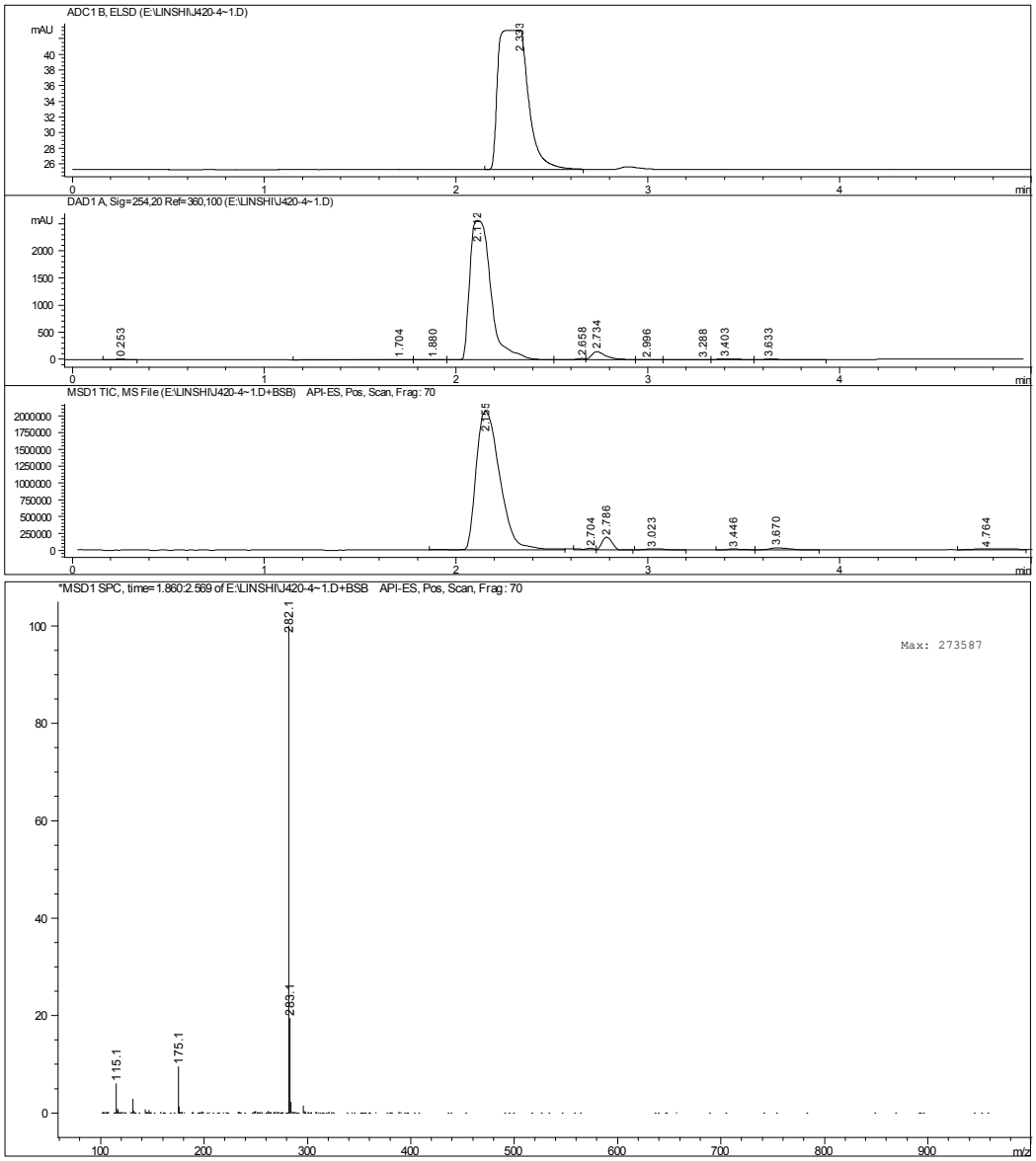


Fig. S-10: LC-MS-ELSD of compound **3d**

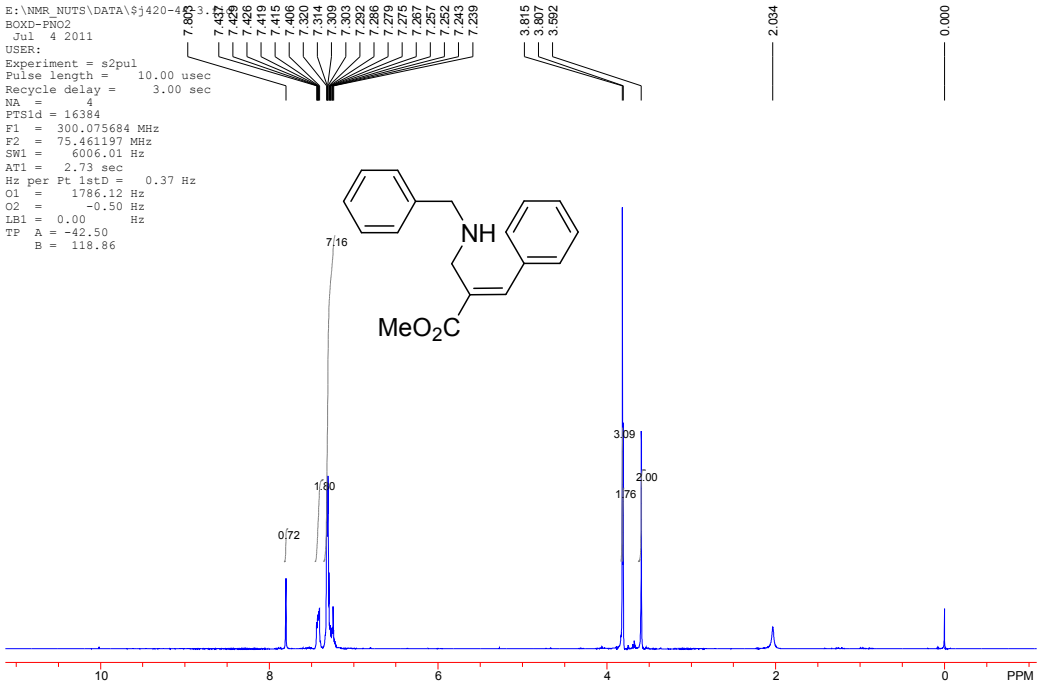


Fig. S-11: ^{1}H Spectra of compound **3d**

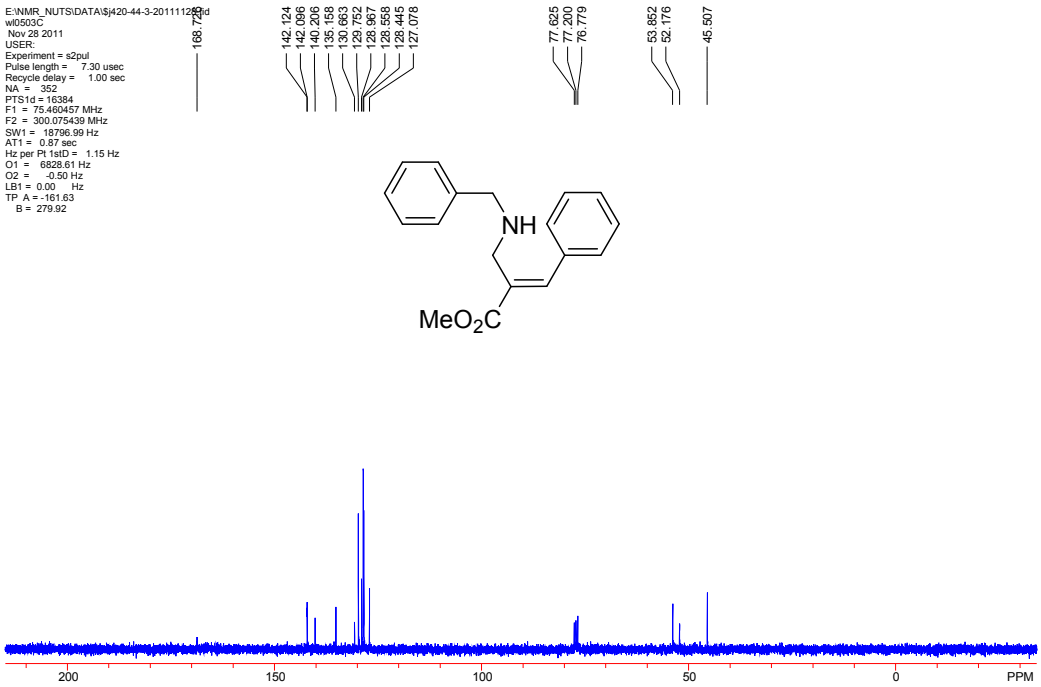
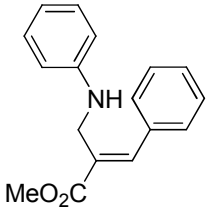


Fig. S-12: ^{13}C Spectra of compound **3d**



Chemical Formula: $C_{17}H_{17}NO_2$
Exact Mass: 267.13
Molecular Weight: 267.32

3e

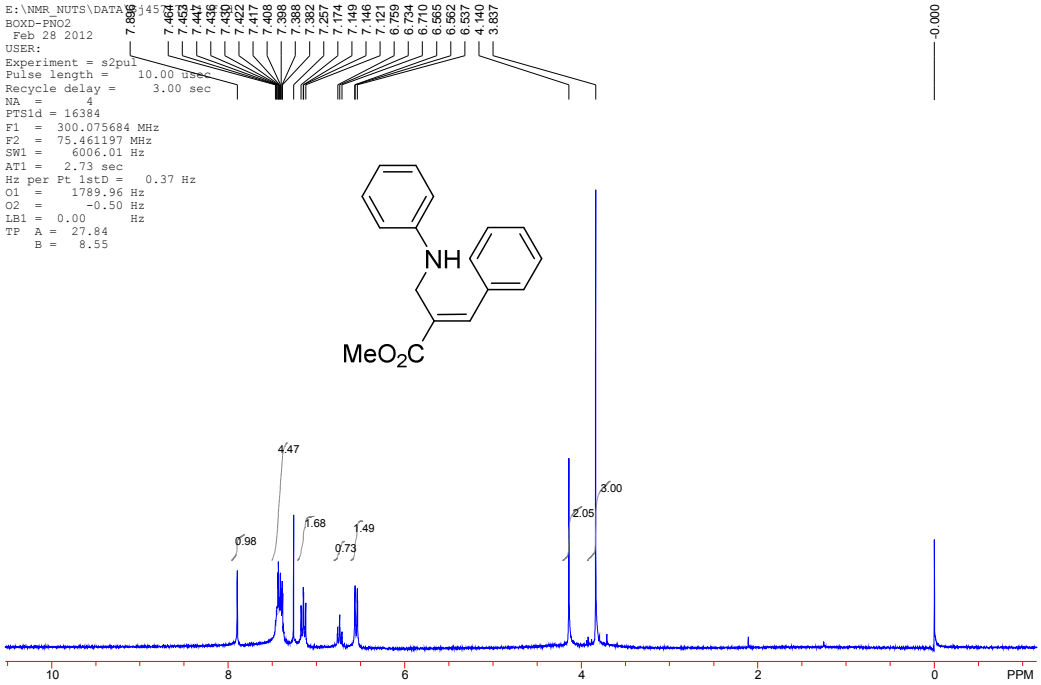
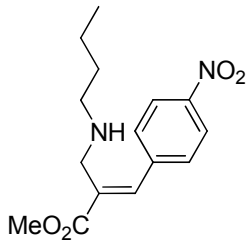


Fig. S-13: ^{1}H Spectra of compound **3e**



Chemical Formula: $C_{15}H_{20}N_2O_4$
Exact Mass: 292.14
Molecular Weight: 292.33

3f

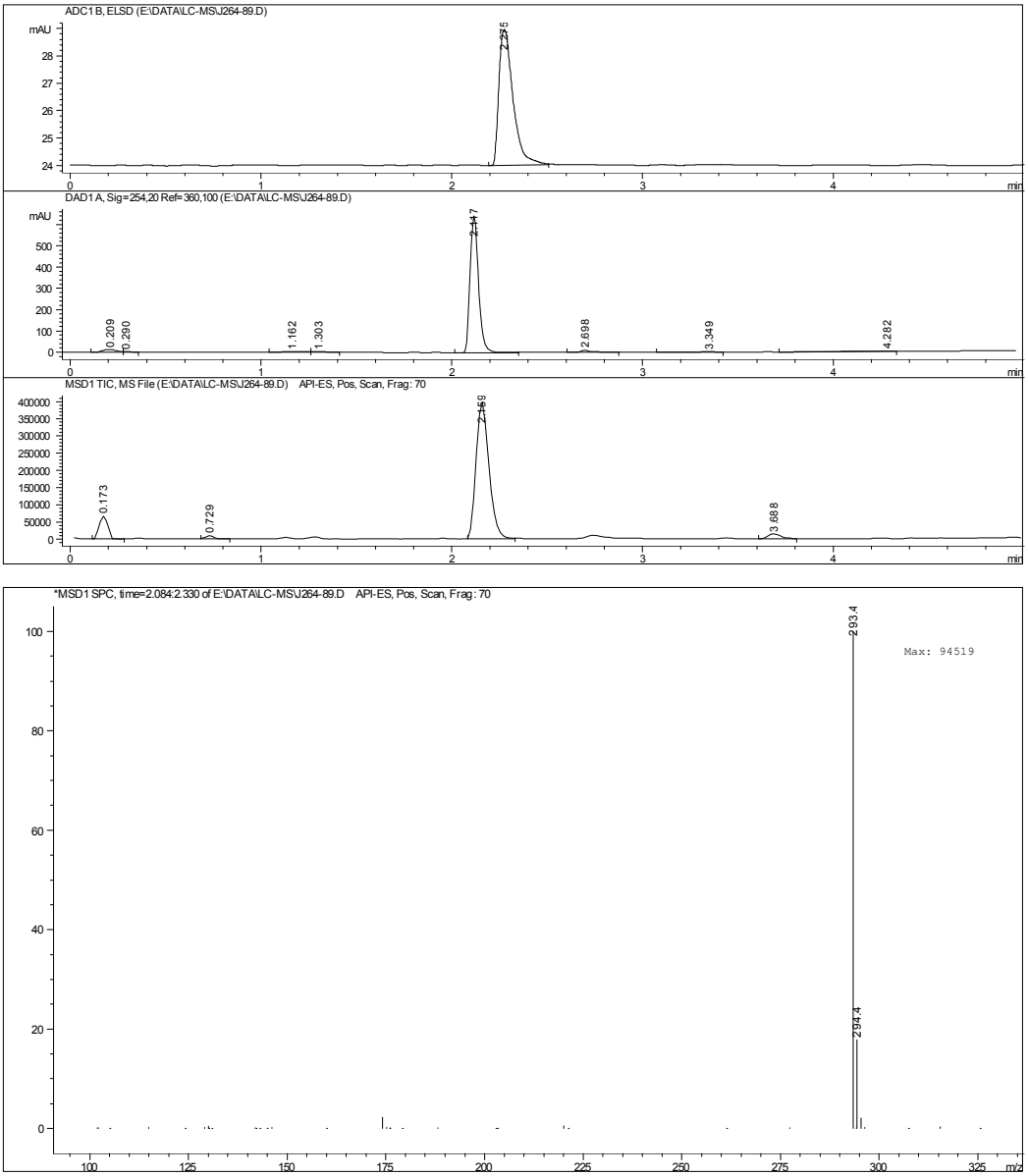


Fig. S-14: LC-MS-ELSD of compound **3f**

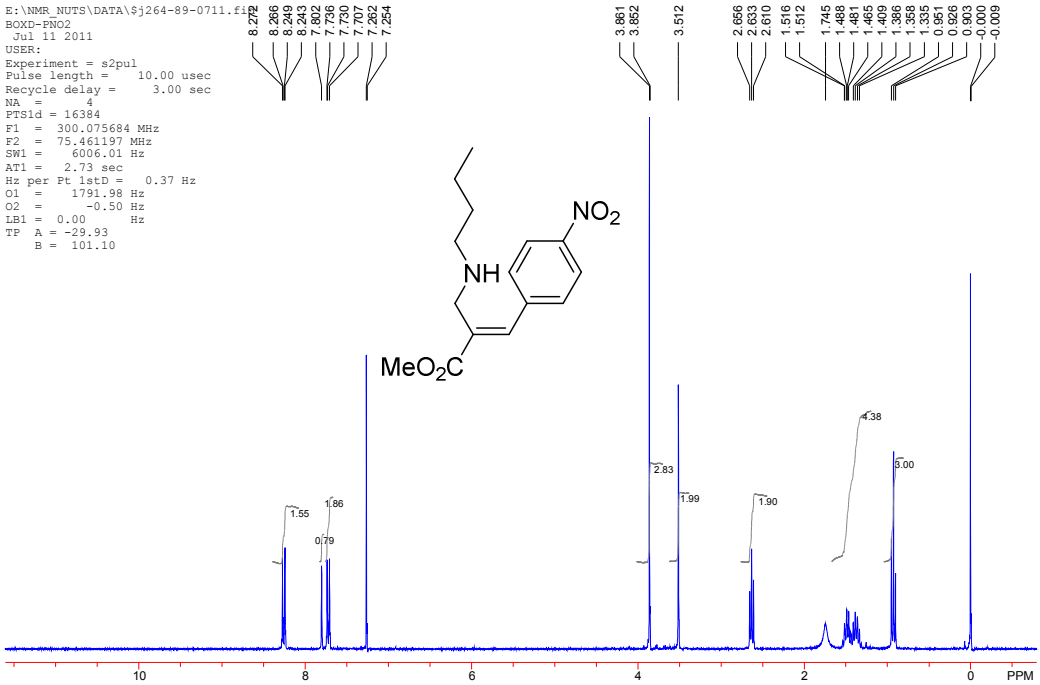


Fig. S-15: ^{1}H Spectra of compound **3f**

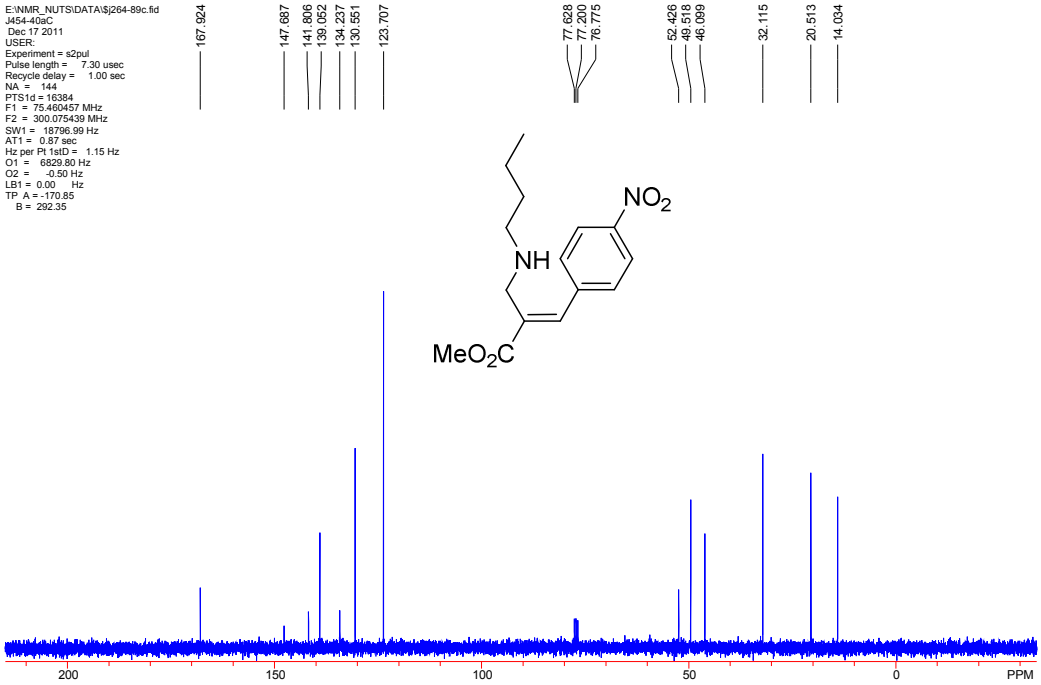
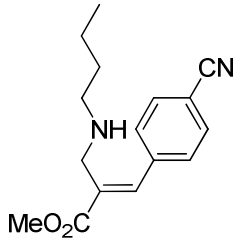


Fig. S-16: ^{13}C Spectra of compound **3f**



Chemical Formula: $C_{16}H_{20}N_2O_2$
Exact Mass: 272.15
Molecular Weight: 272.34

3g

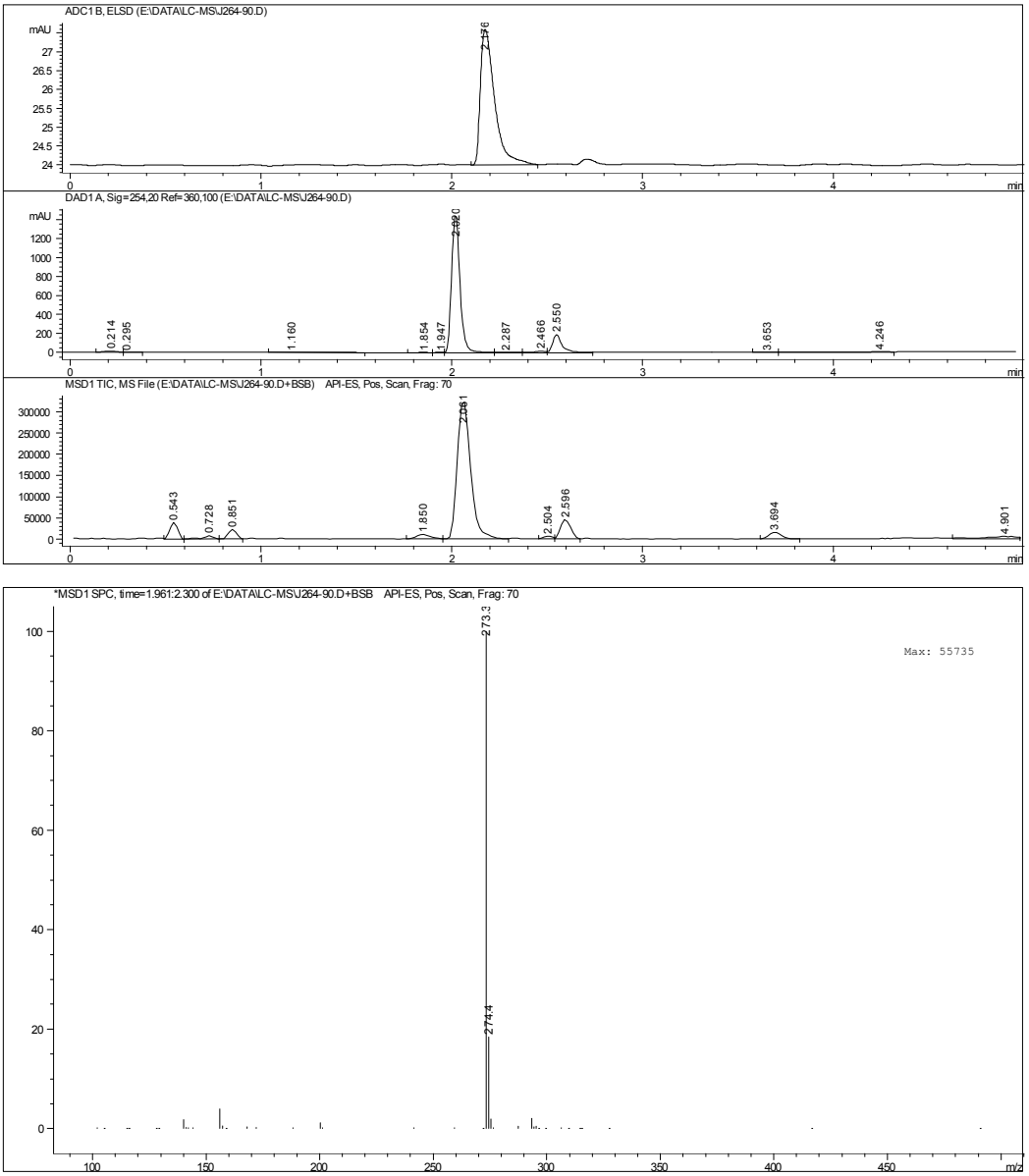


Fig. S-17: LC-MS-ELSD of compound **3g**

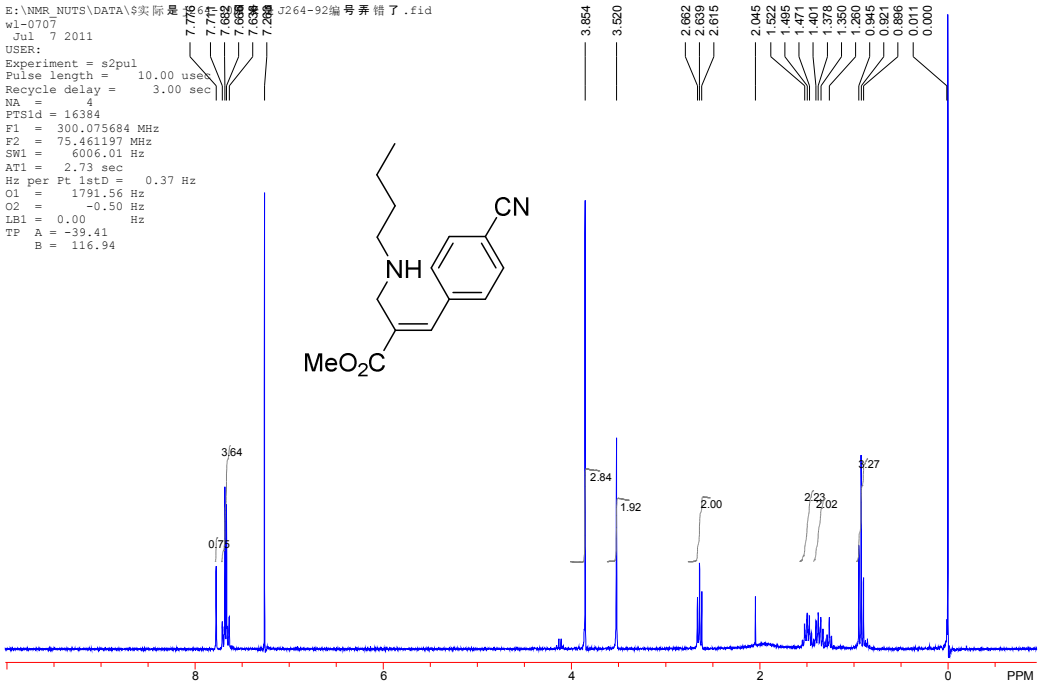


Fig. S-18: ^{1}H Spectra of compound **3g**

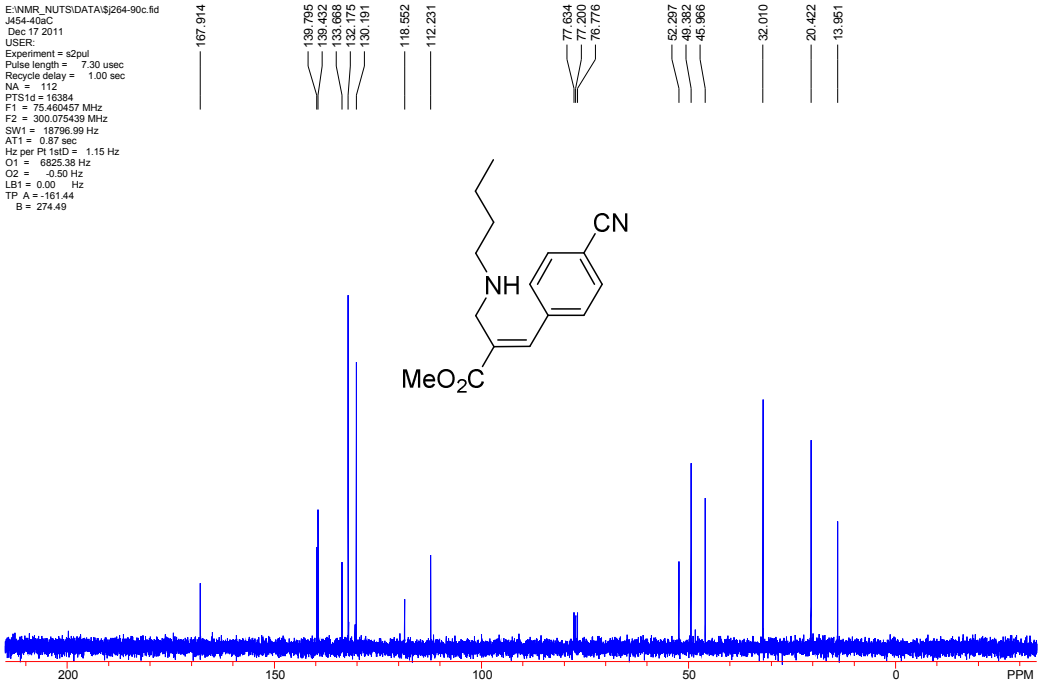
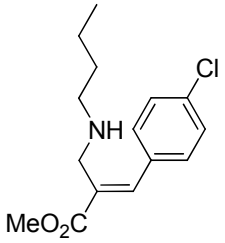


Fig. S-19: ^{13}C Spectra of compound **3g**



Chemical Formula: $C_{15}H_{20}ClNO_2$
Exact Mass: 281.12
Molecular Weight: 281.78

3h

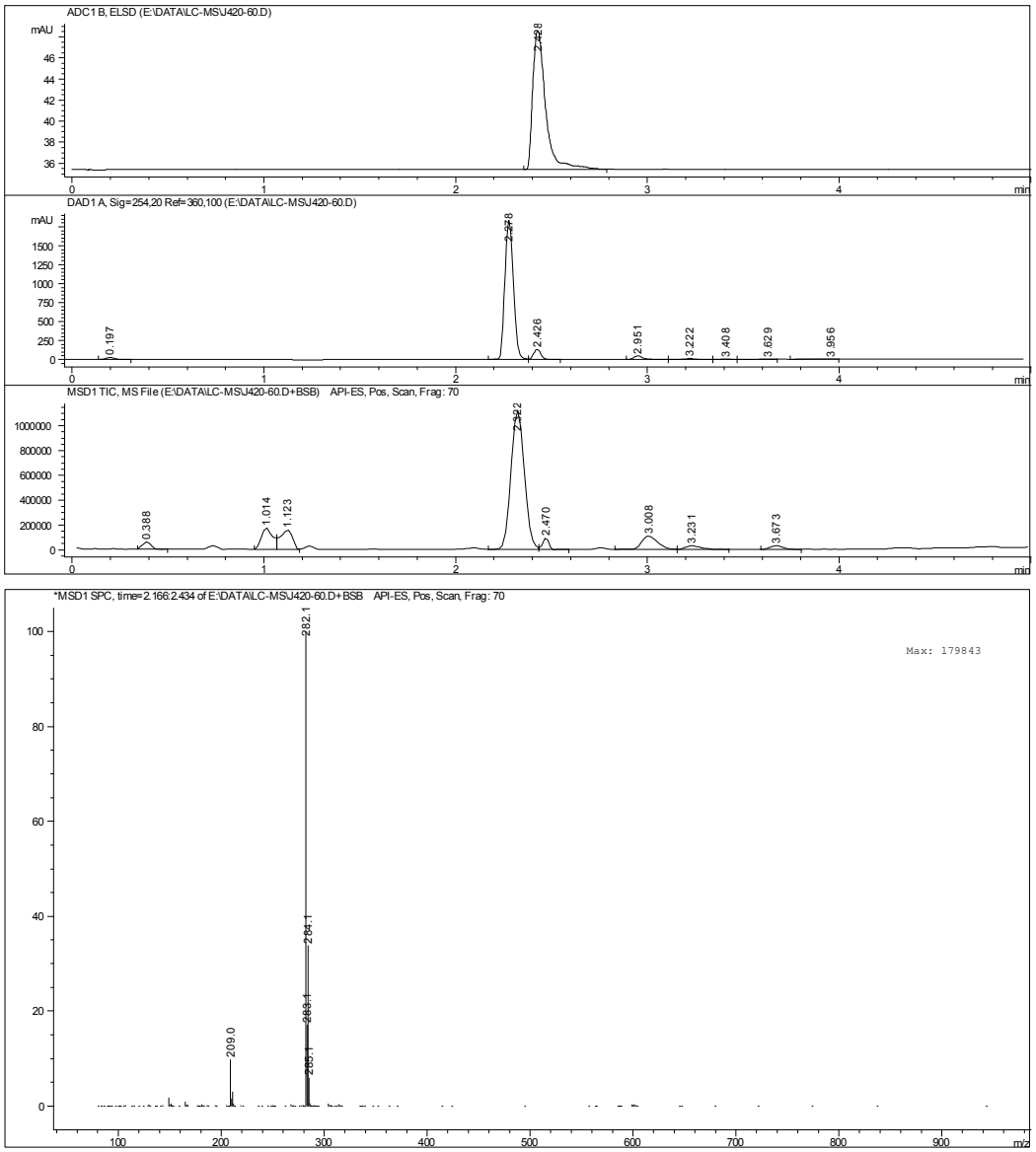


Fig. S-20: LC-MS-ELSD of compound **3h**

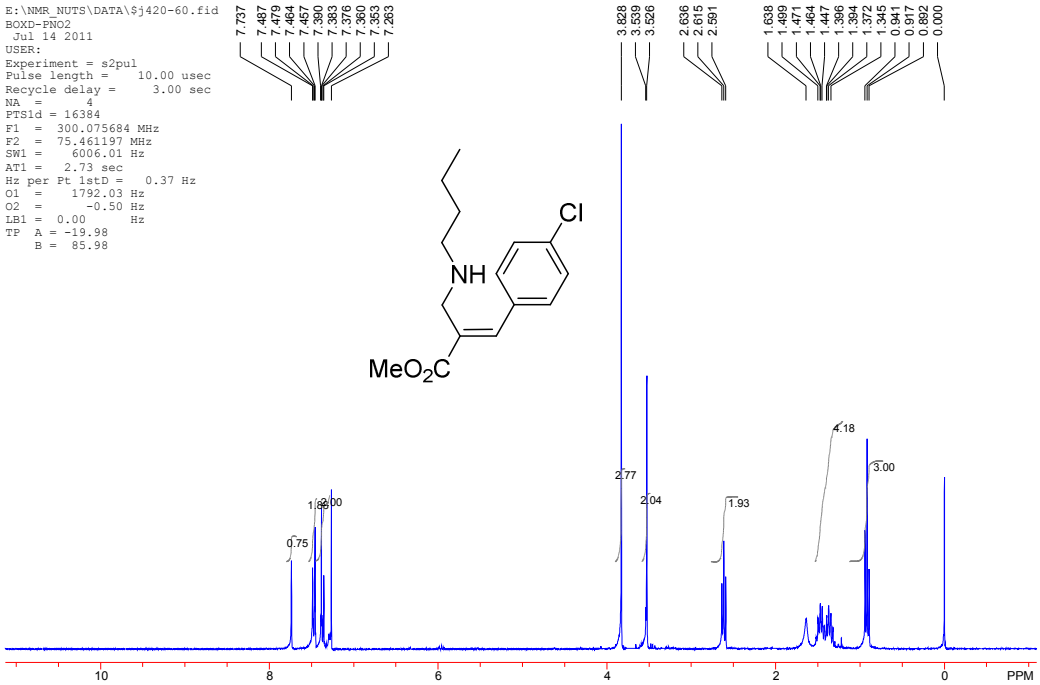


Fig. S-21: ^{1}H Spectra of compound **3h**

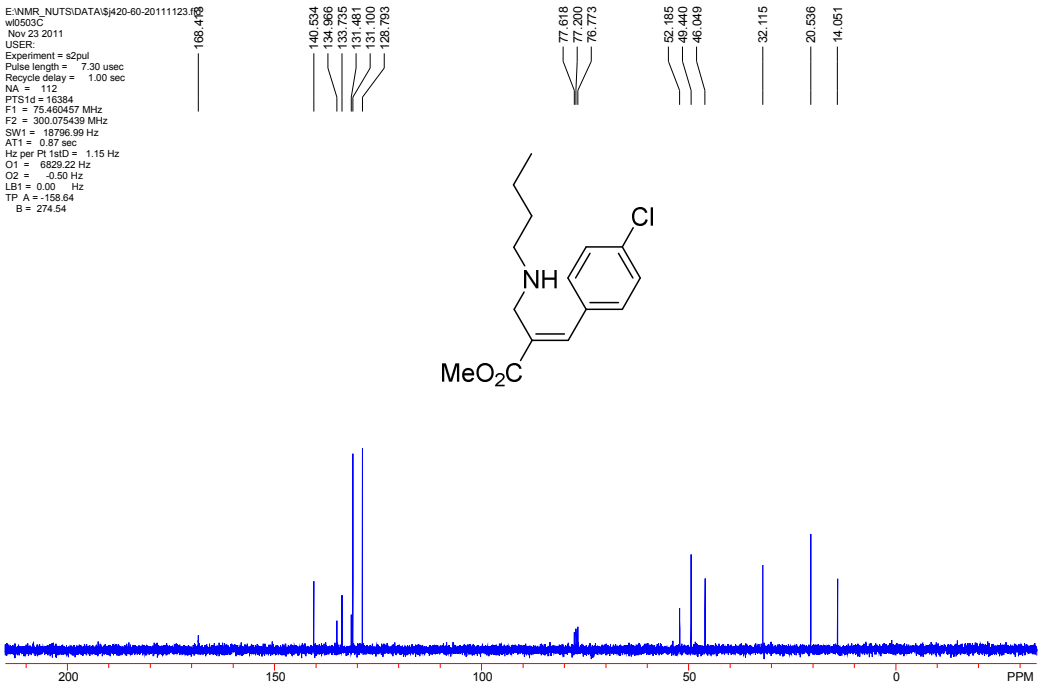
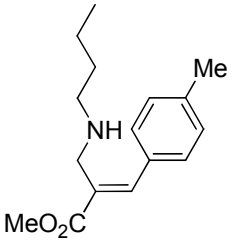


Fig. S-22: ^{13}C Spectra of compound **3h**



Chemical Formula: $C_{16}H_{23}NO_2$
Exact Mass: 261.17
Molecular Weight: 261.36

3i

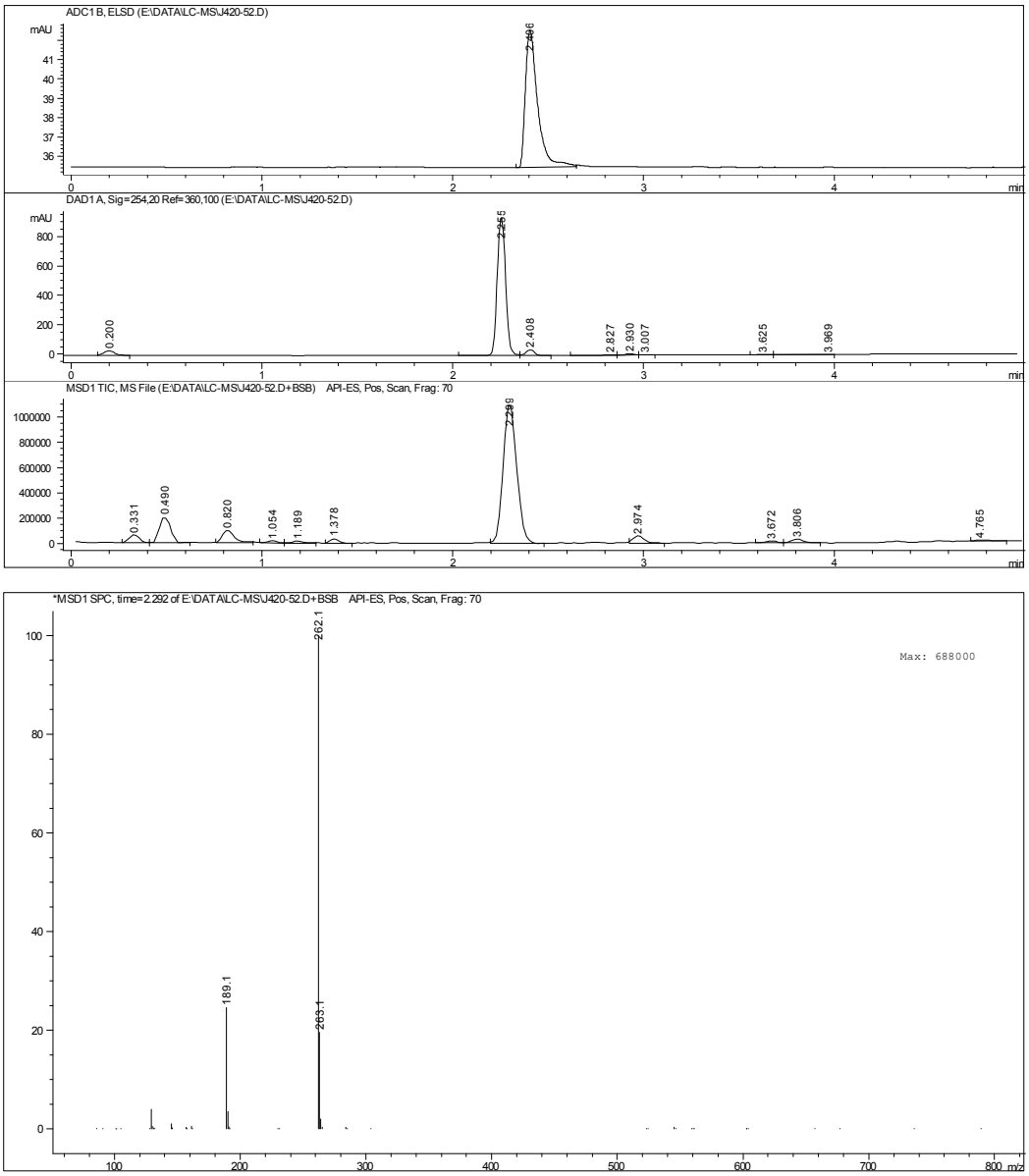


Fig. S-23: LC-MS-ELSD of compound **3i**

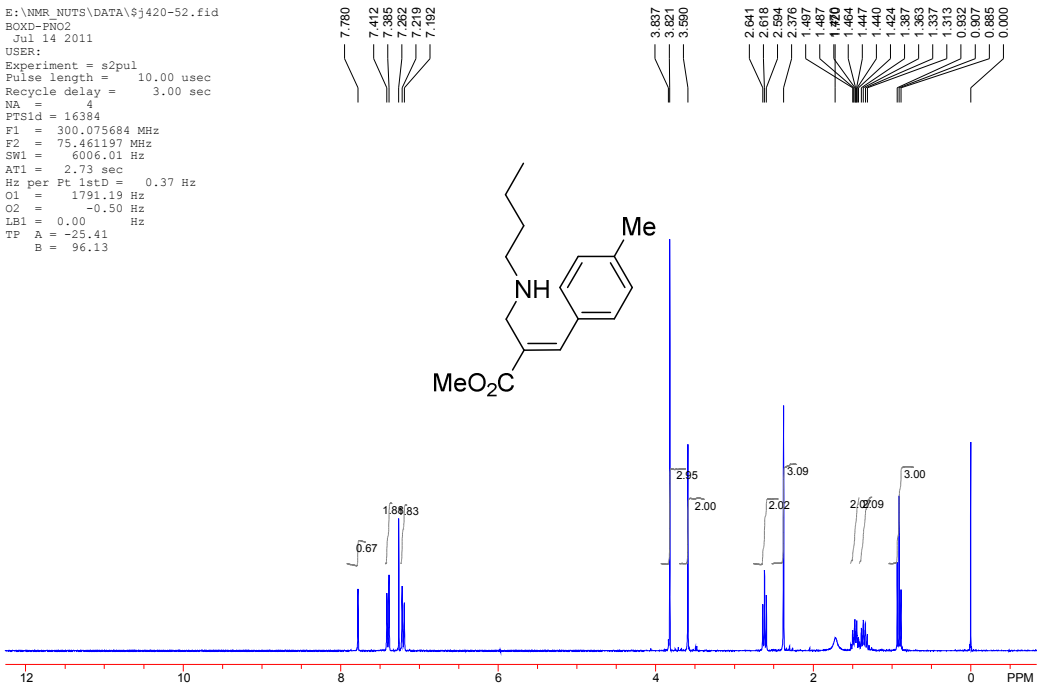


Fig. S-24: ^{1}H Spectra of compound **3i**

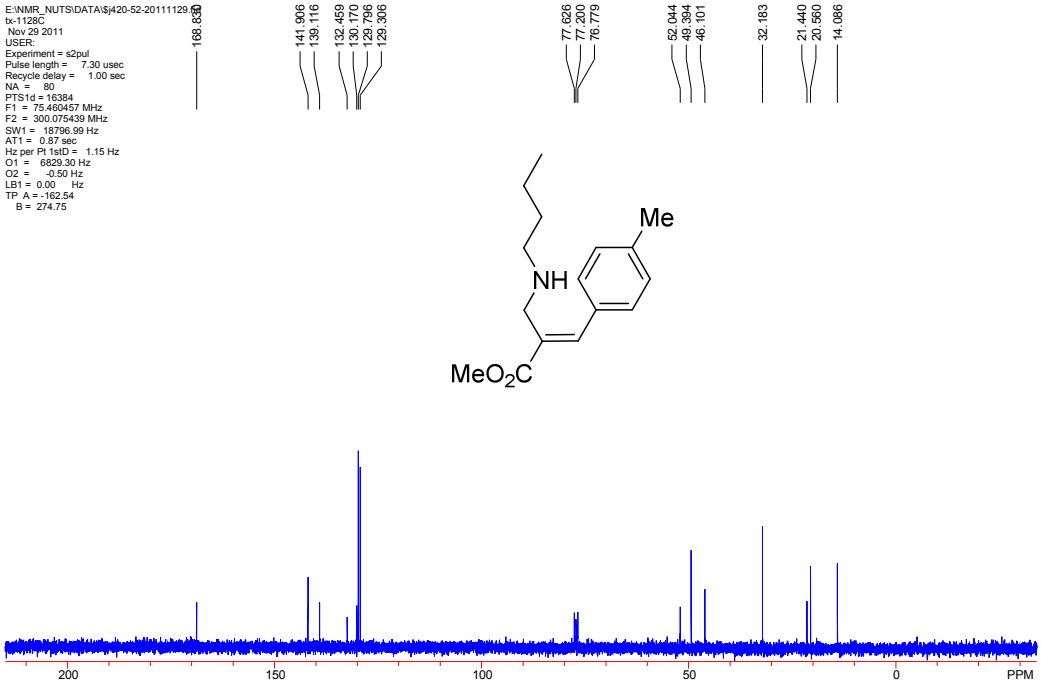
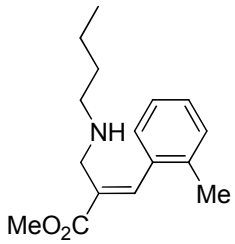


Fig. S-25: ^{13}C Spectra of compound **3i**



Chemical Formula: $C_{16}H_{23}NO_2$
Exact Mass: 261.17
Molecular Weight: 261.36

3j

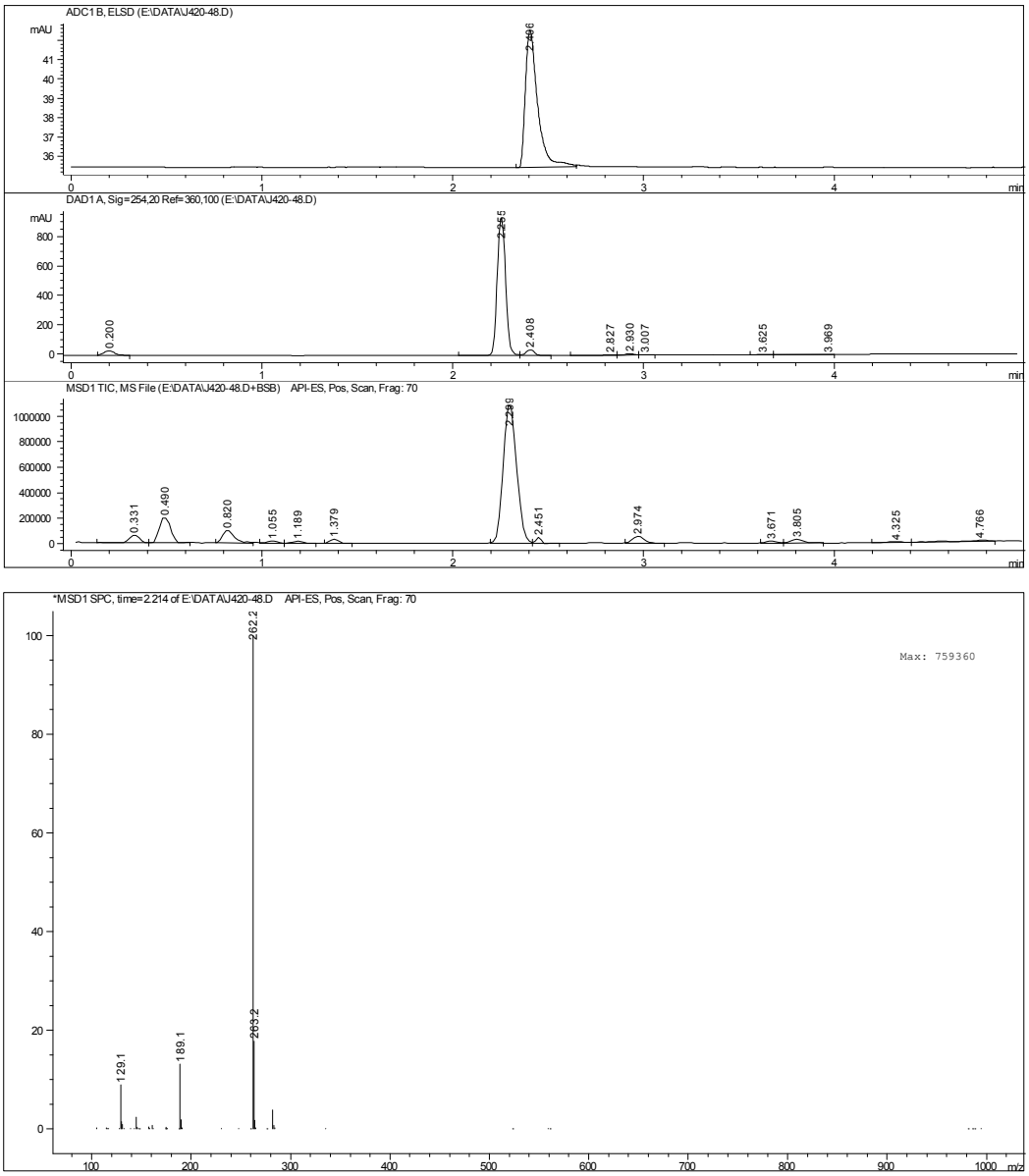


Fig. S-26: LC-MS-ELSD of compound **3j**

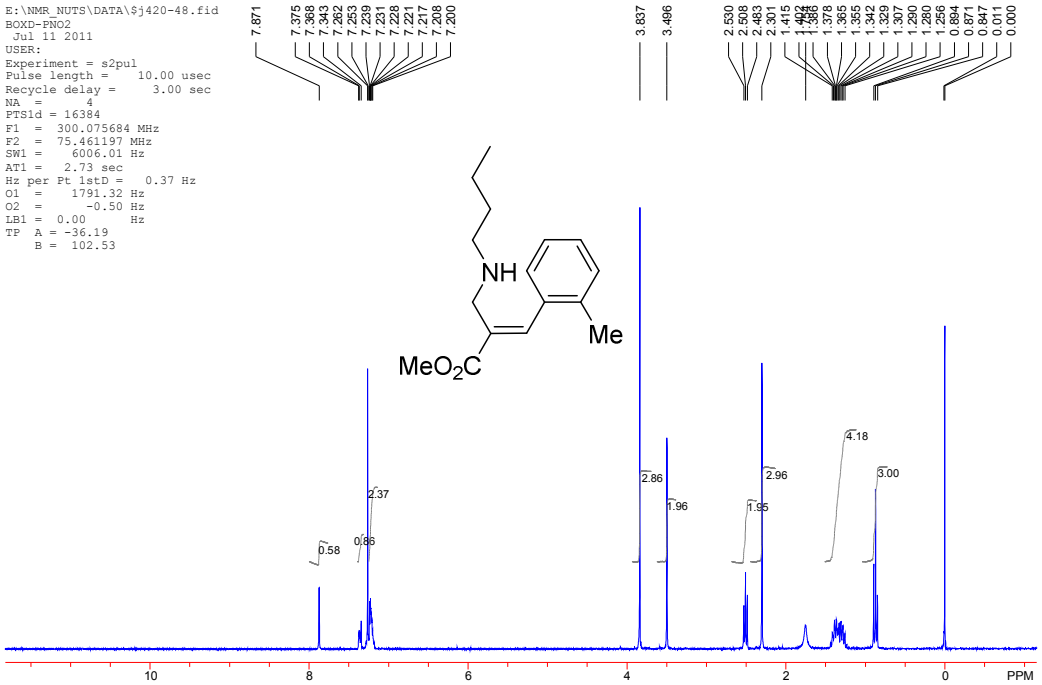


Fig. S-27: ^{1}H Spectra of compound **3j**

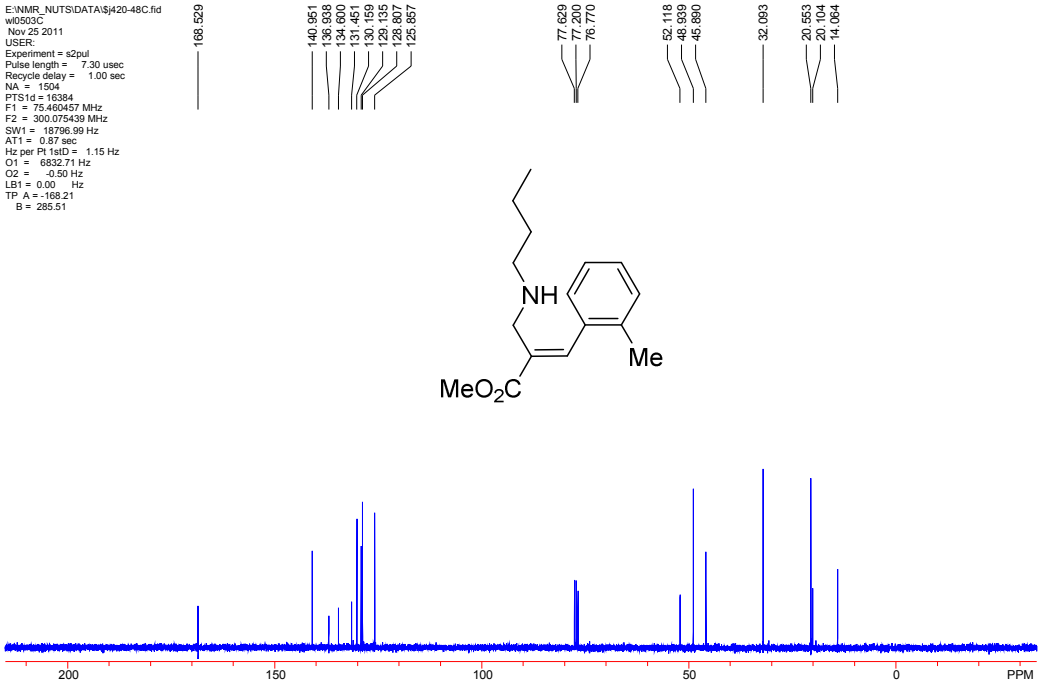
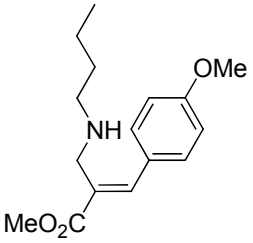


Fig. S-28: ^{13}C Spectra of compound **3j**



Chemical Formula: $C_{16}H_{23}NO_3$
Exact Mass: 277.17
Molecular Weight: 277.36

3k

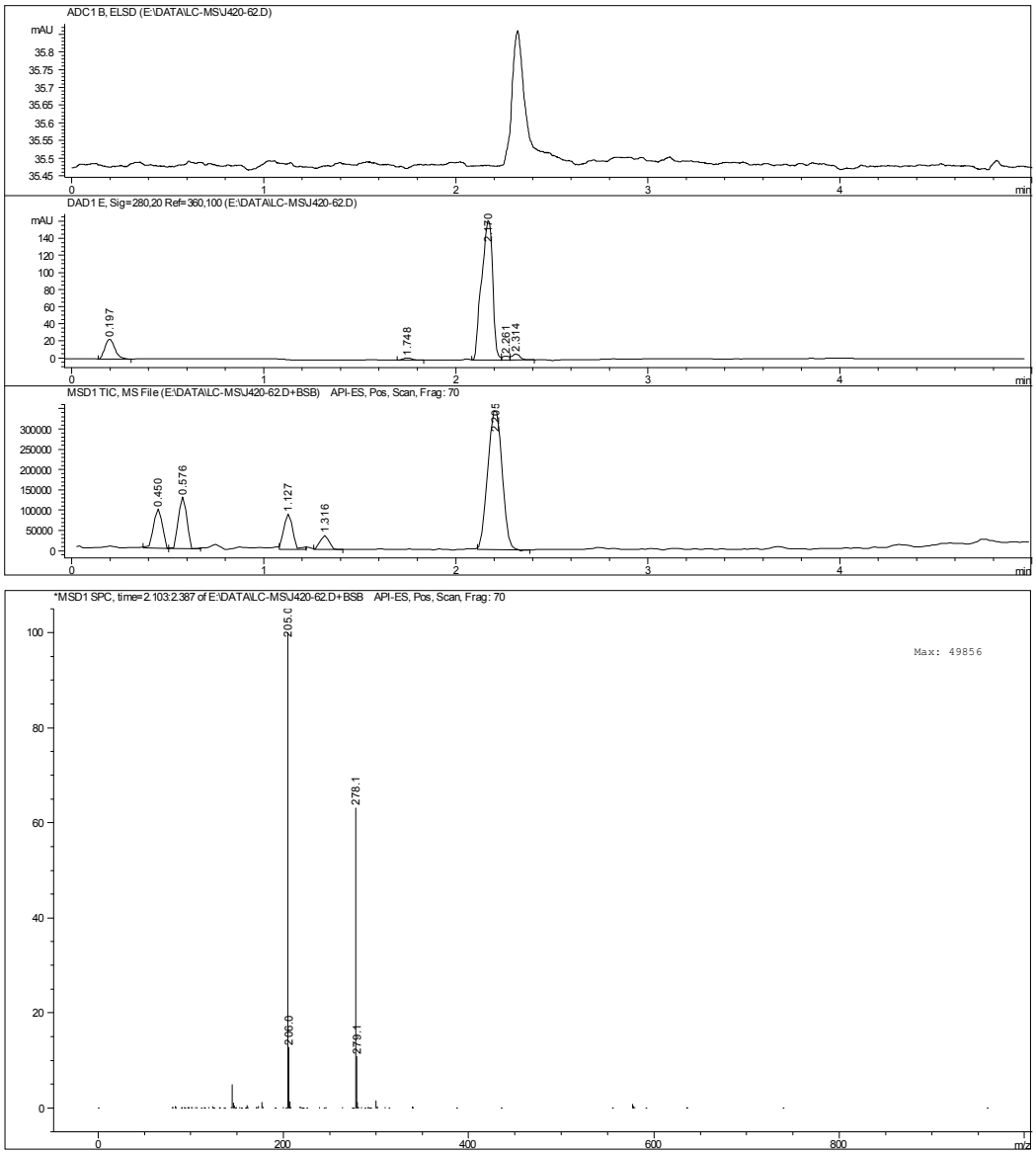


Fig. S-29: LC-MS-ELSD of compound **3k**

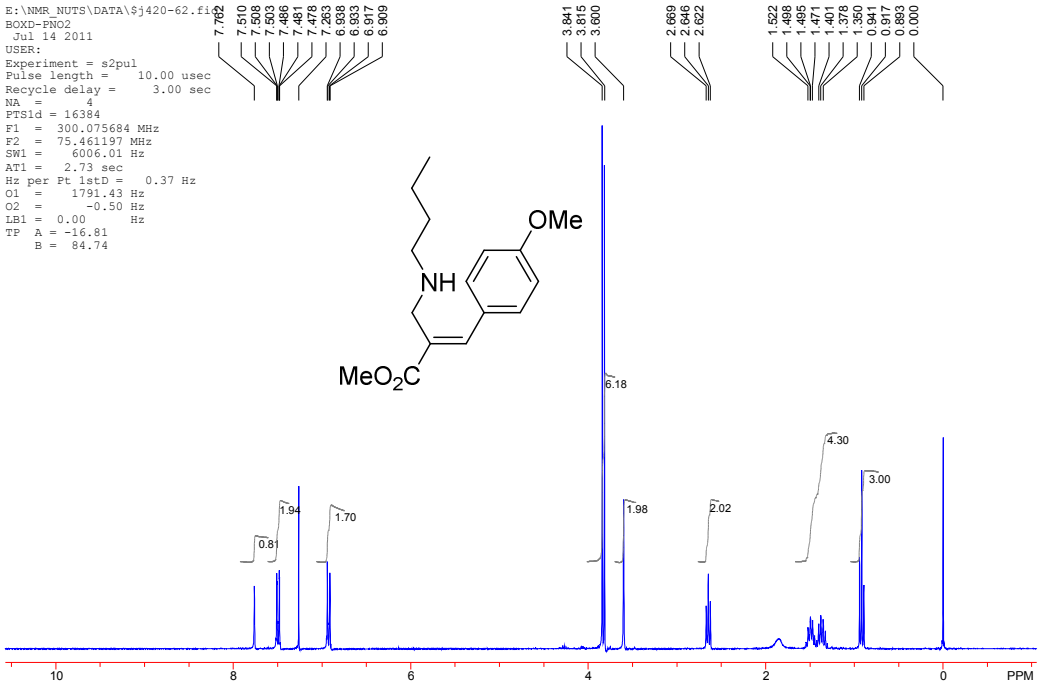


Fig. S-30: ^{1}H Spectra of compound **3k**

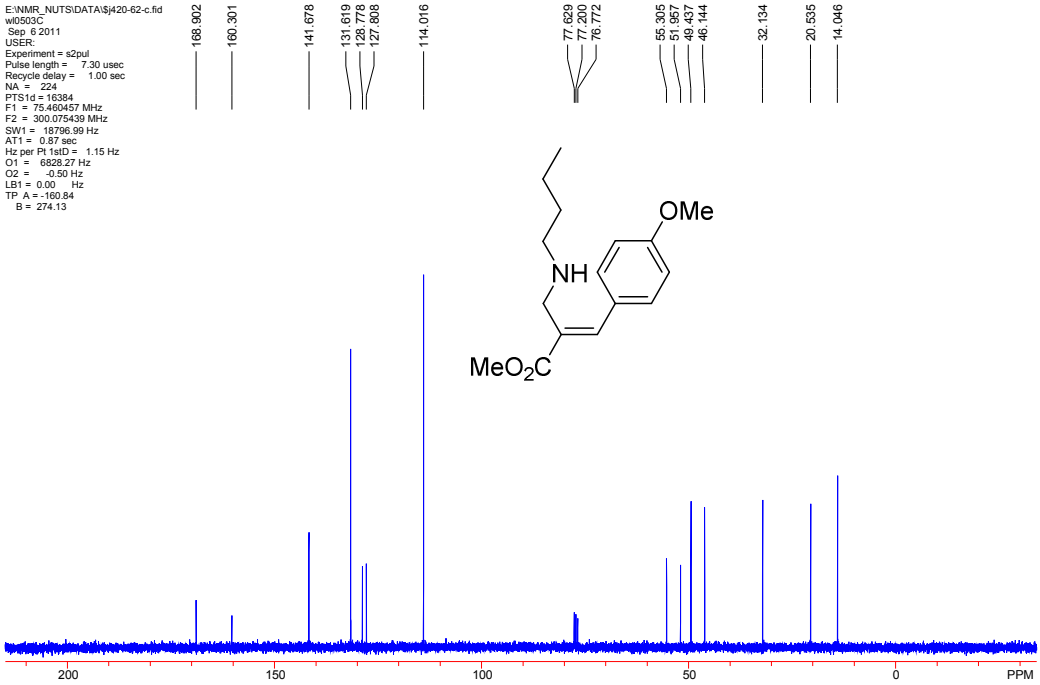
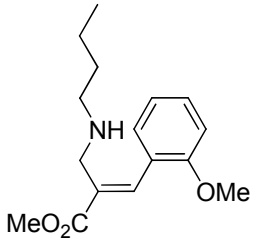


Fig. S-31: ^{13}C Spectra of compound **3k**



Chemical Formula: $C_{16}H_{23}NO_3$
Exact Mass: 277.17
Molecular Weight: 277.36

3l

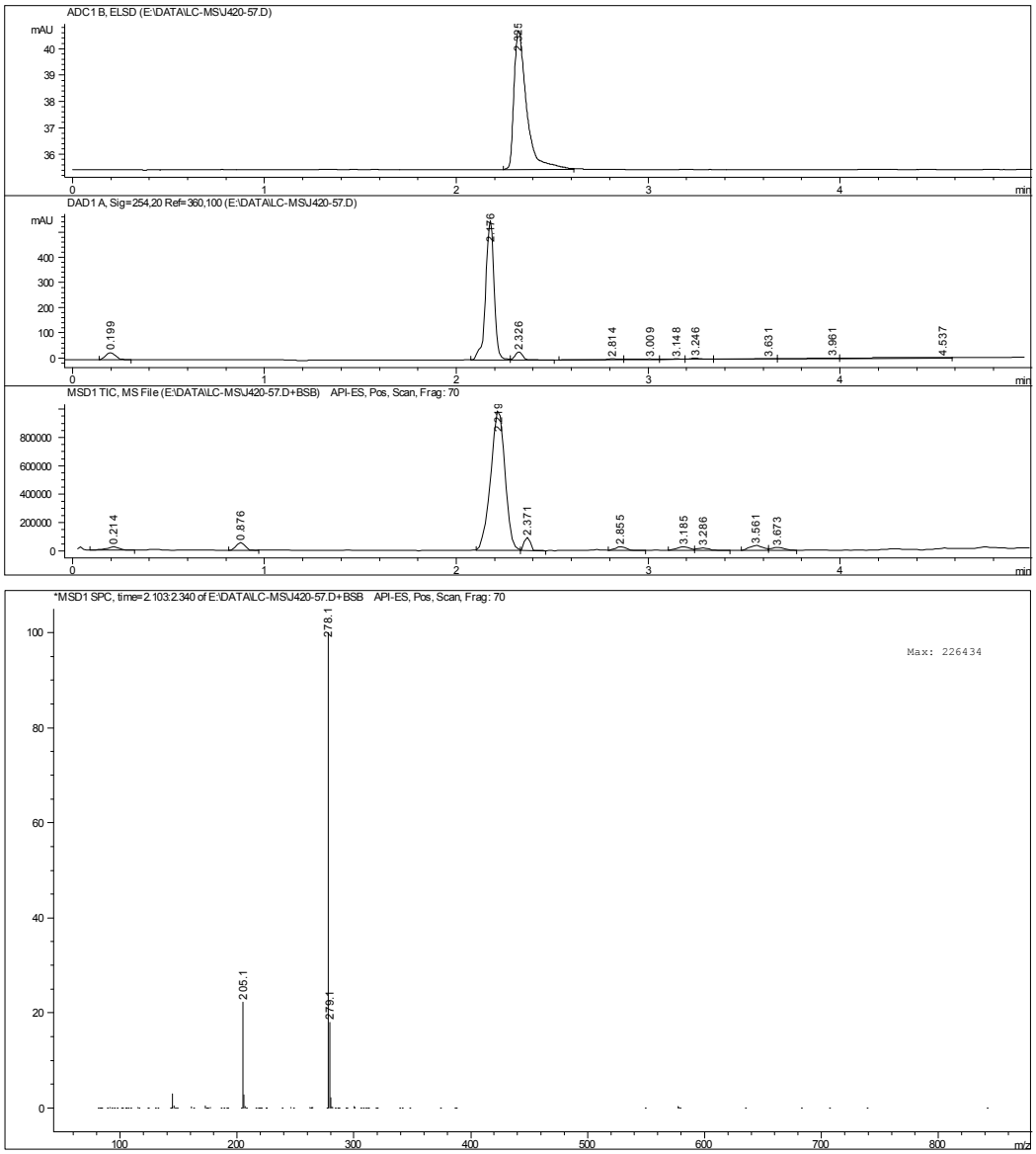


Fig. S-32: LC-MS-ELSD of compound **3l**

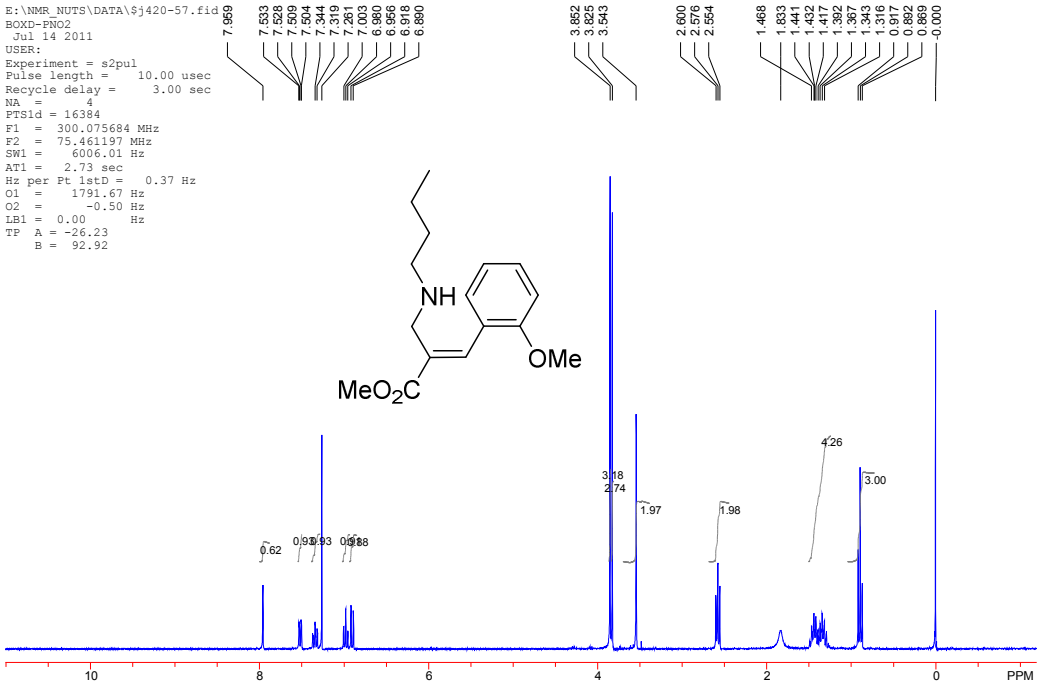


Fig. S-33: ^{1}H Spectra of compound **3l**

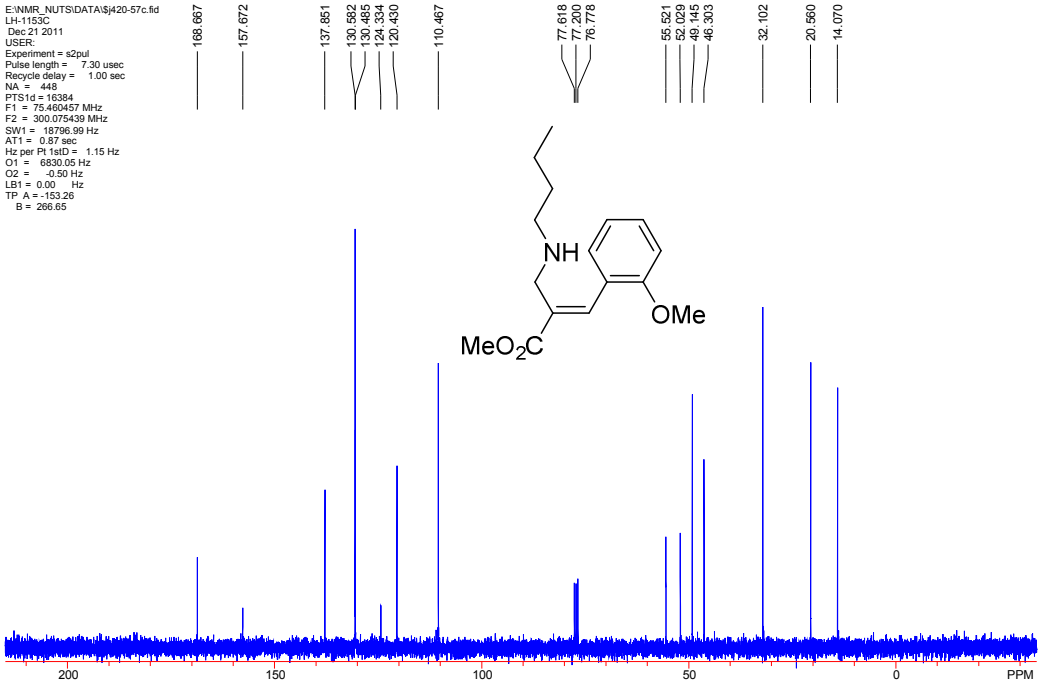
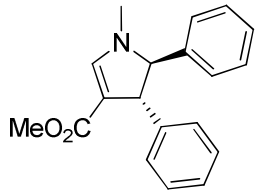


Fig. S-34: ^{13}C Spectra of compound **3l**



Chemical Formula: $C_{19}H_{19}NO_2$
Exact Mass: 293.14
Molecular Weight: 293.36

6a

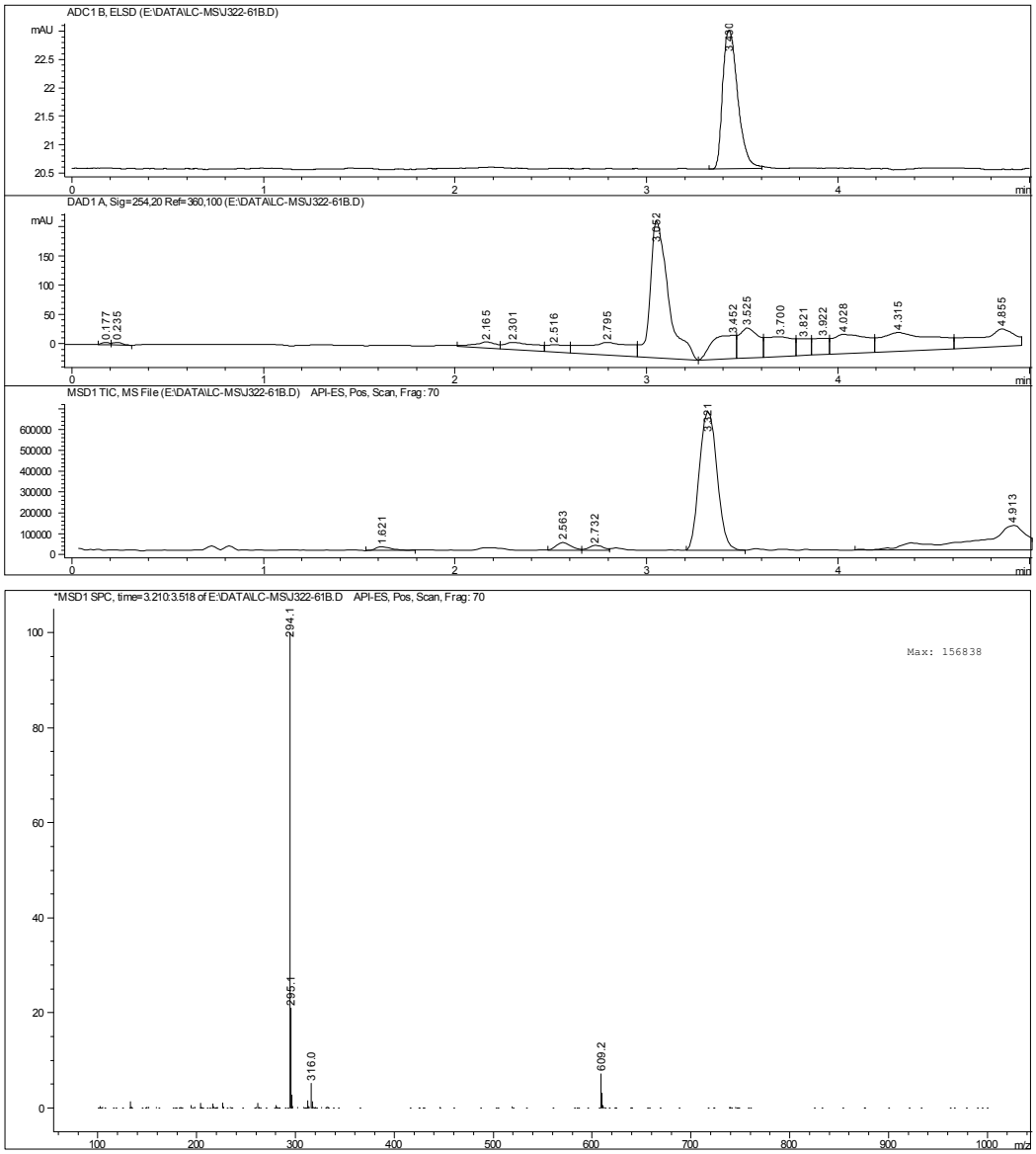


Fig. S-35: LC-MS-ELSD of compound **6a**

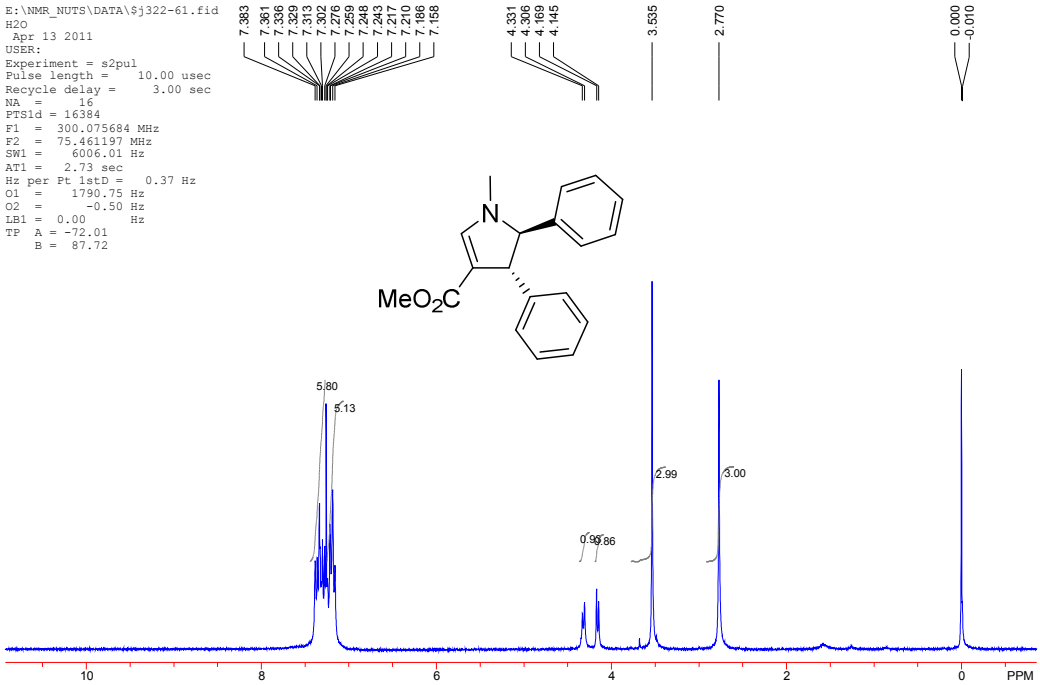


Fig. S-36: ^{1}H Spectra of compound **6a**

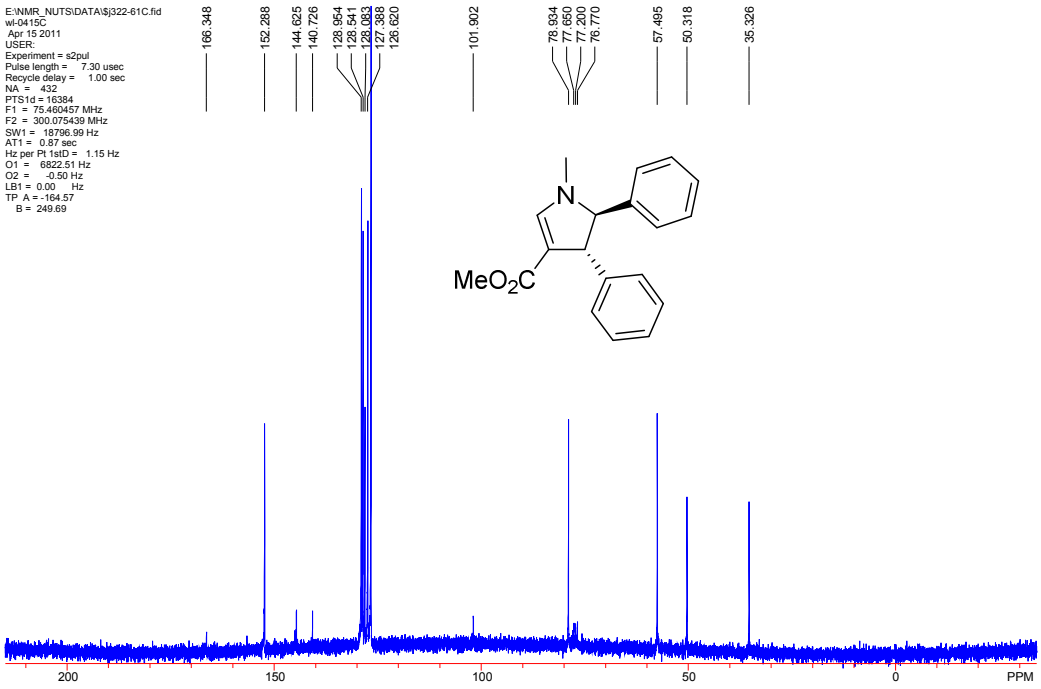
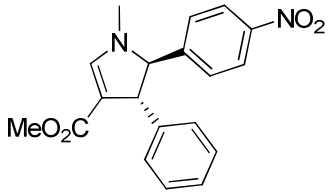


Fig. S-37: ^{13}C Spectra of compound **6a**



Chemical Formula: $C_{19}H_{18}N_2O_4$
Exact Mass: 338.13
Molecular Weight: 338.36

6b

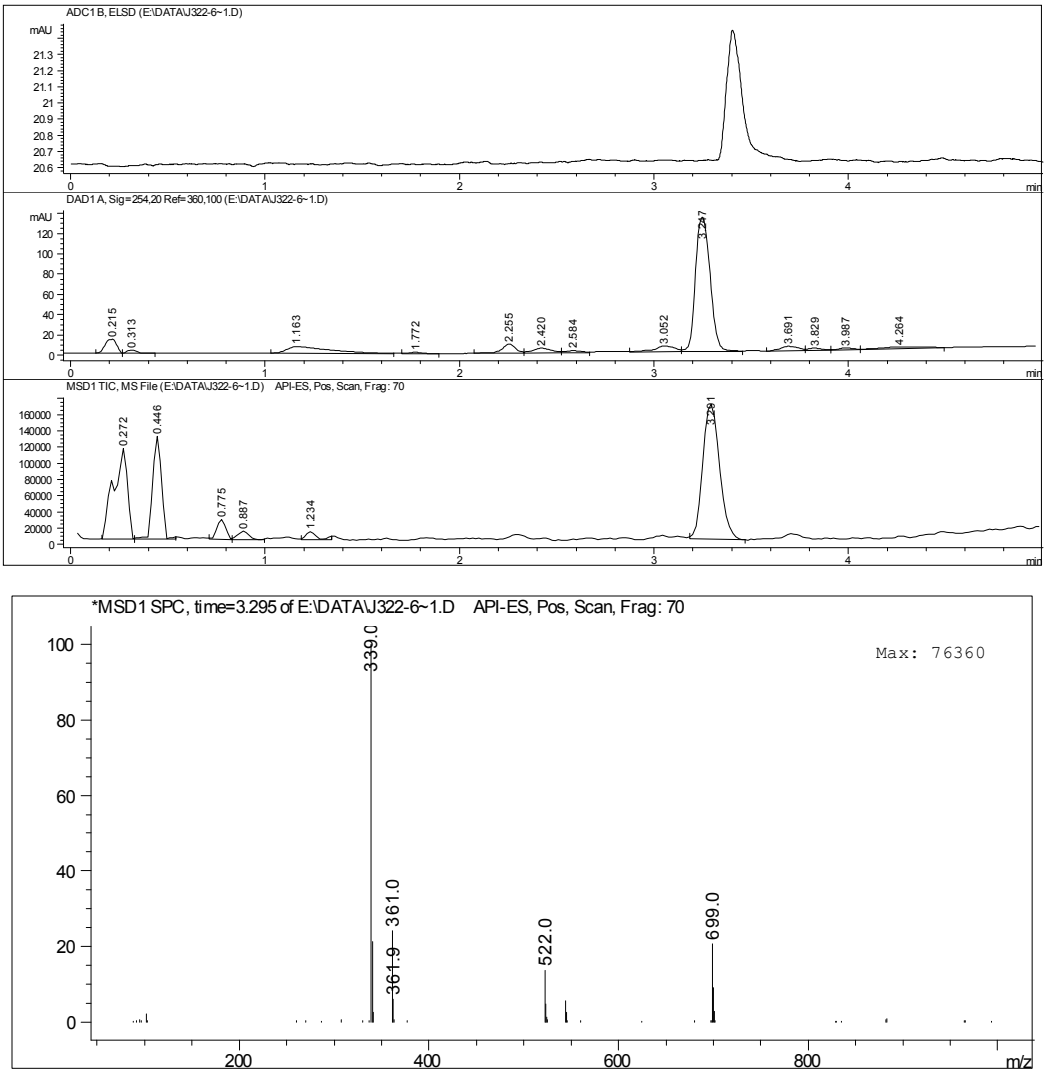


Fig. S-38: LC-MS-ELSD of compound **6b**

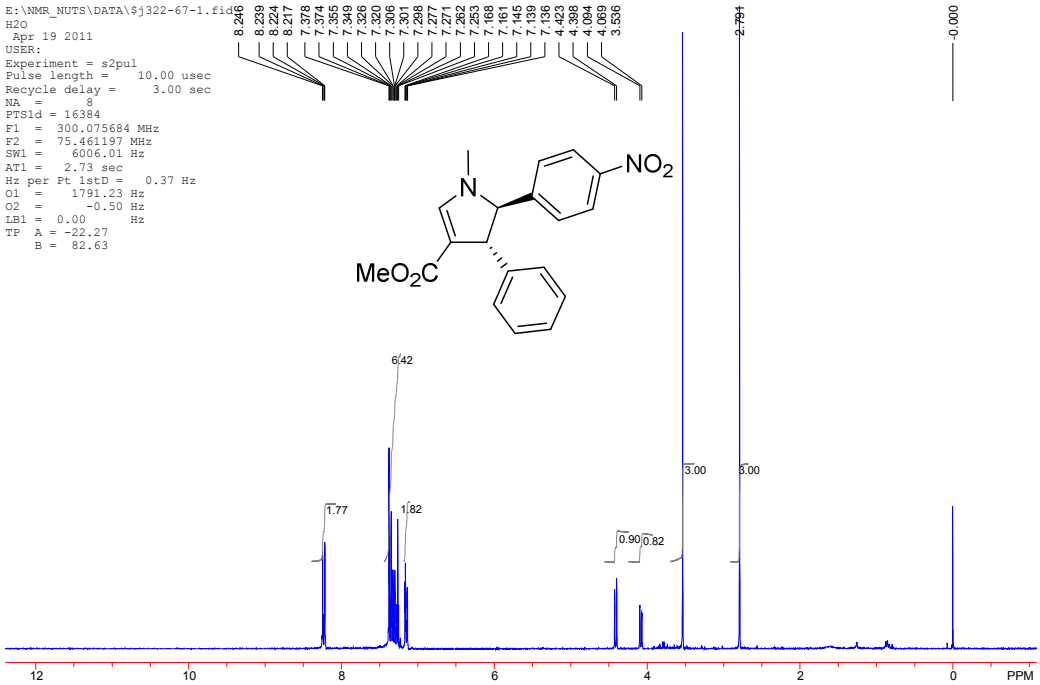


Fig. S-39: ^{1}H Spectra of compound **6b**

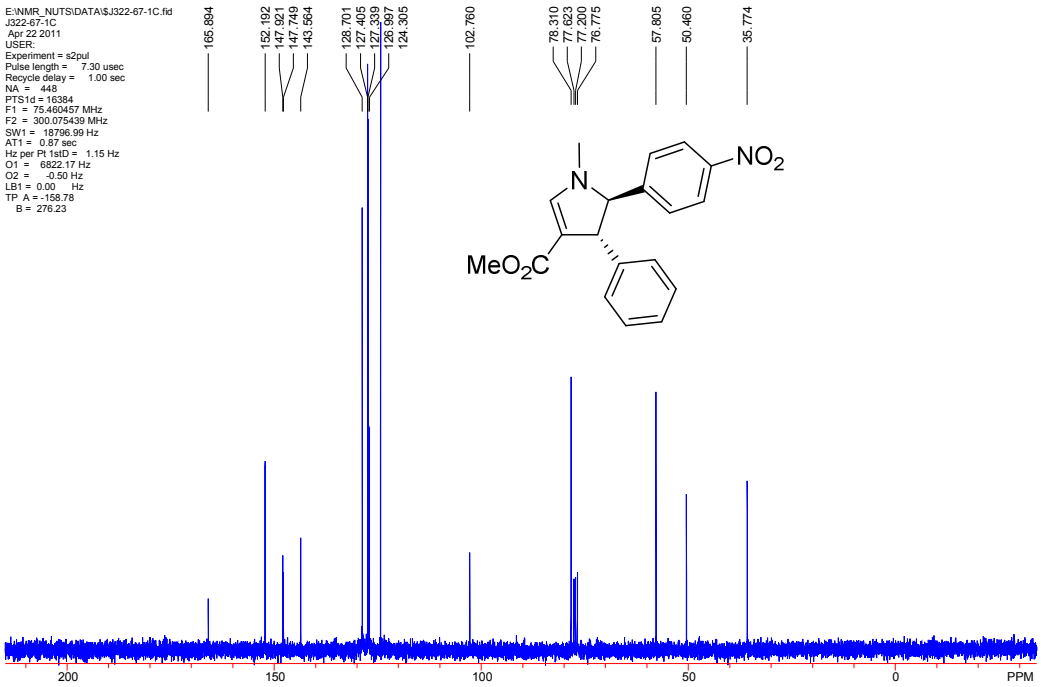
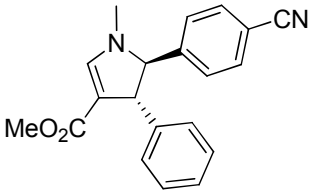


Fig. S-40: ^{13}C Spectra of compound **6b**



Chemical Formula: $C_{20}H_{18}N_2O_2$
Exact Mass: 318.14
Molecular Weight: 318.37

6c

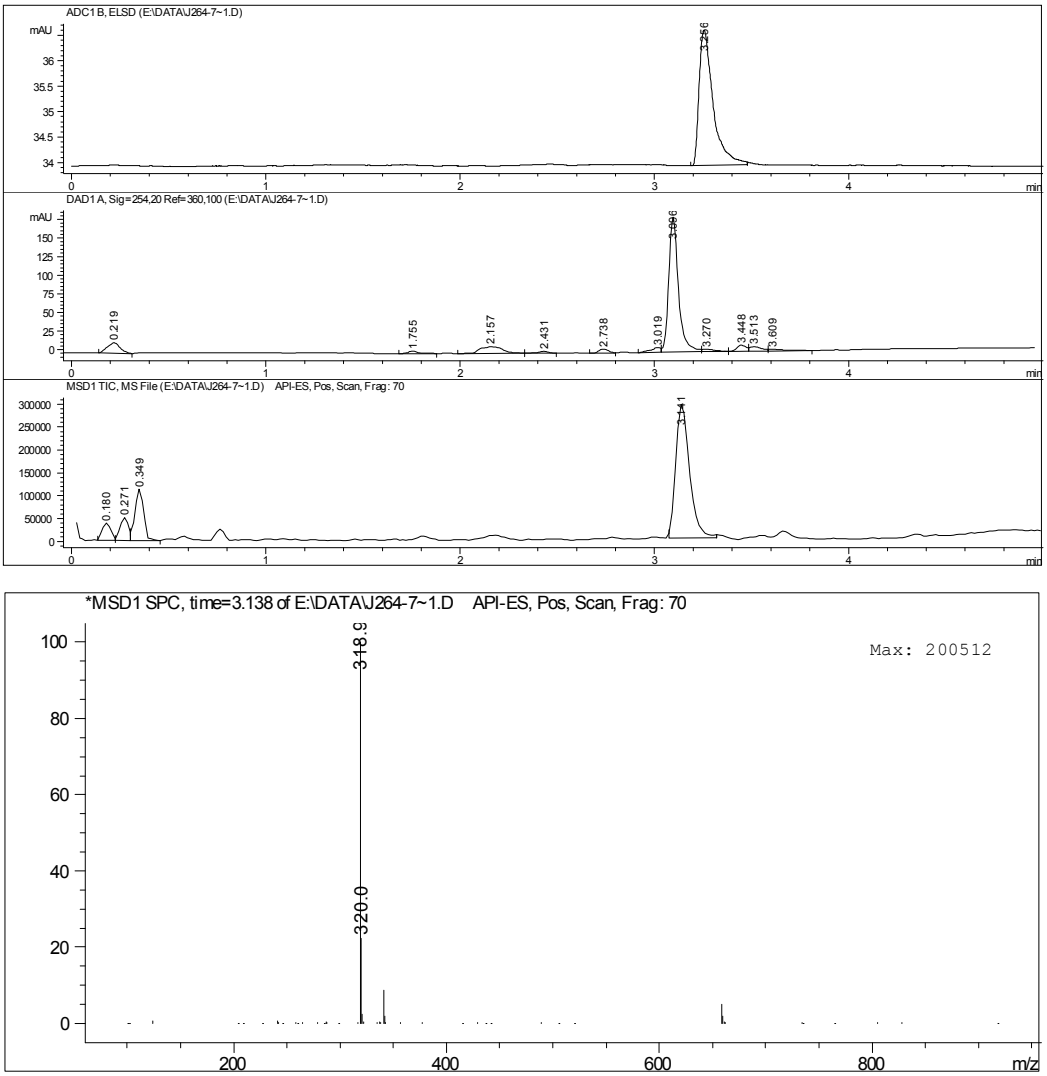


Fig. S-41: LC-MS-ELSD of compound **6c**

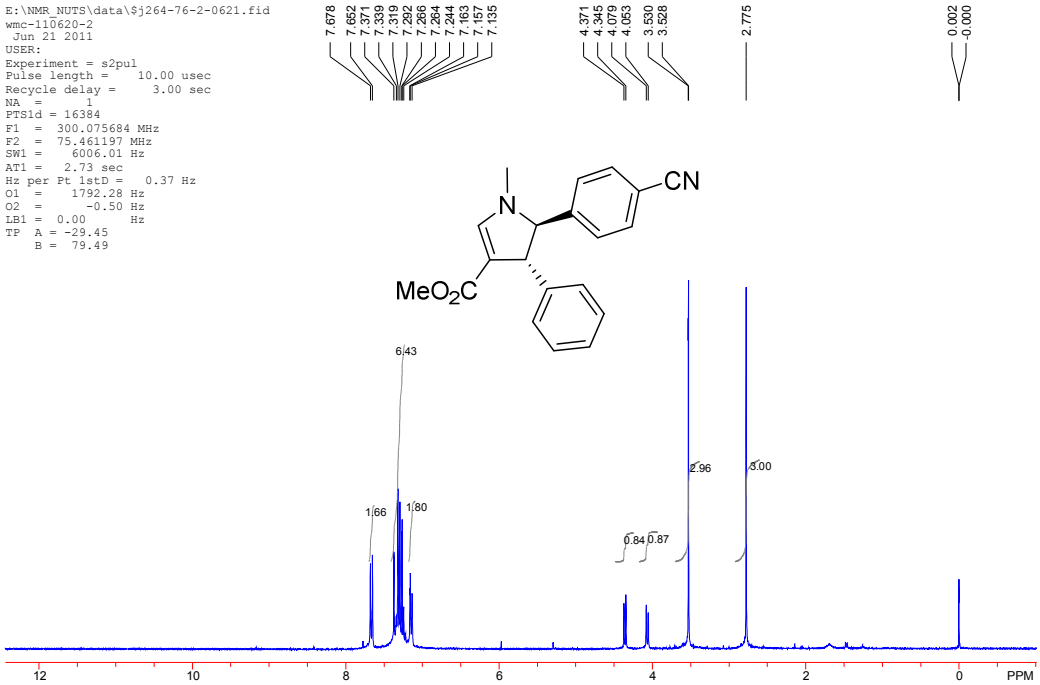


Fig. S-42: ^{1}H Spectra of compound **6c**

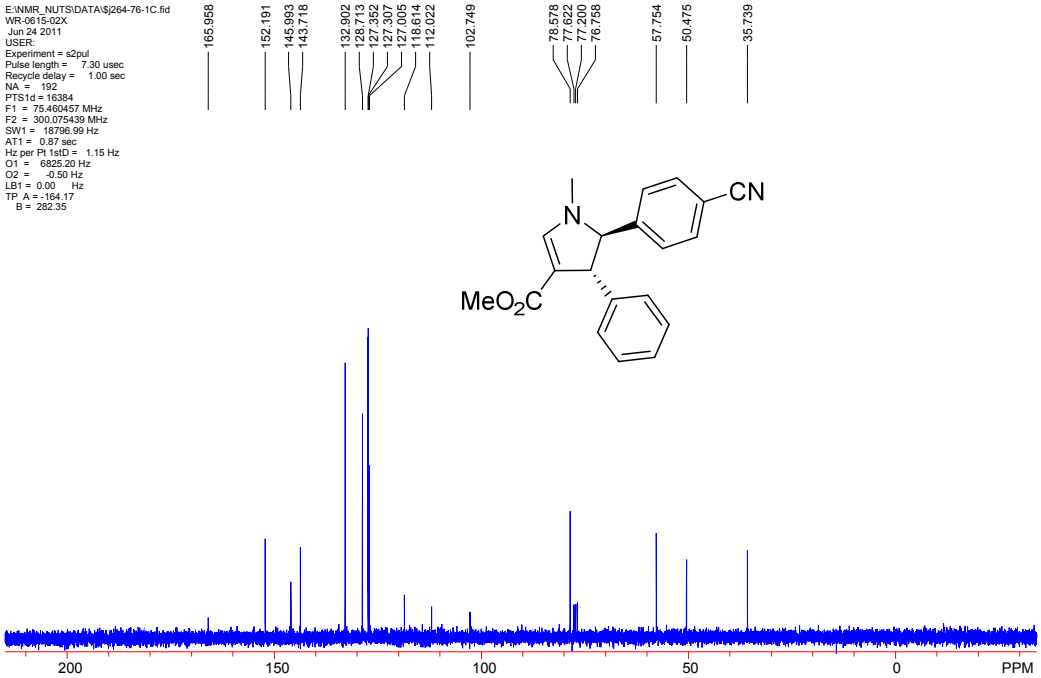
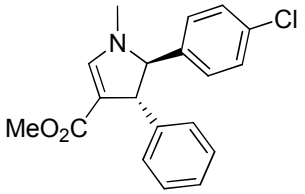


Fig. S-43: ^{13}C Spectra of compound **6c**



Chemical Formula: $C_{19}H_{18}ClNO_2$
Exact Mass: 327.10
Molecular Weight: 327.80

6d

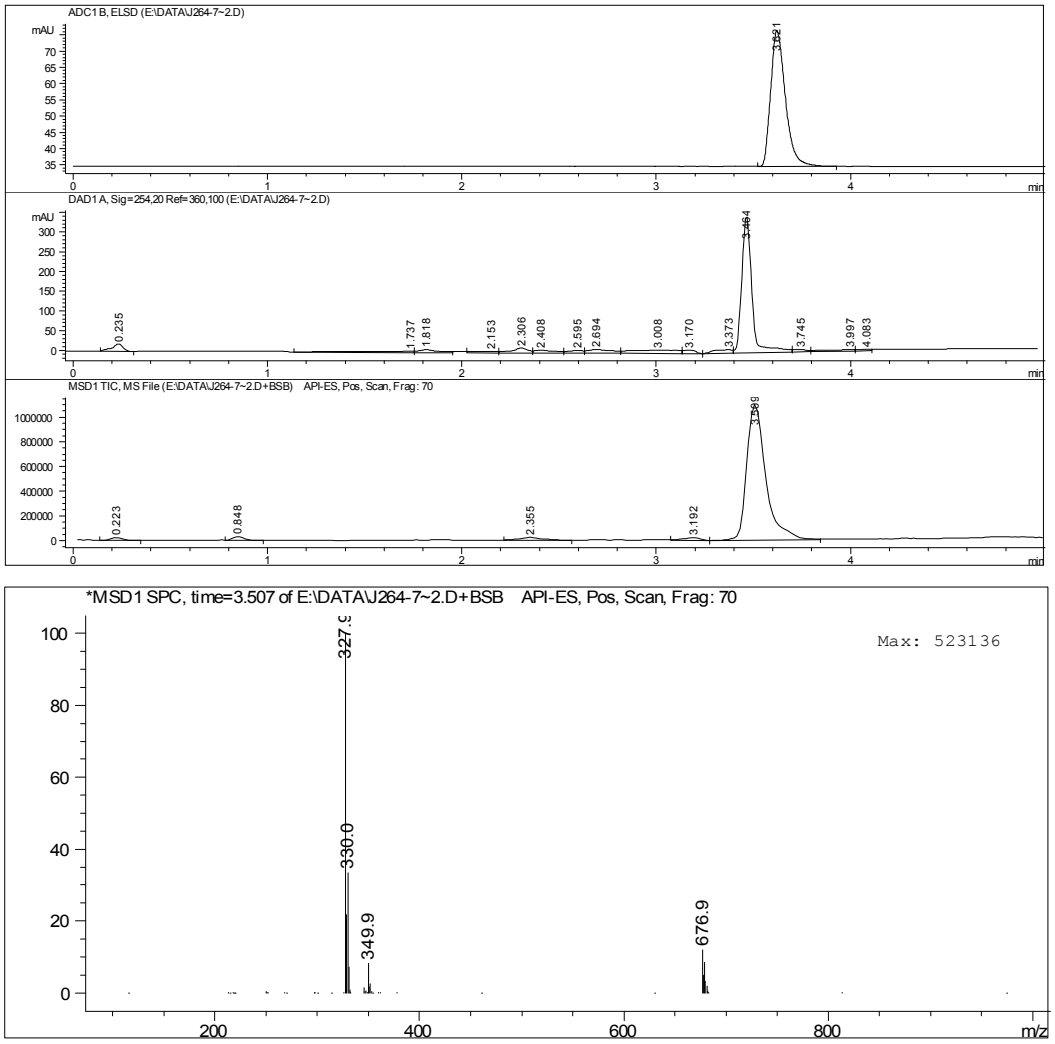


Fig. S-44: LC-MS-ELSD of compound **6d**

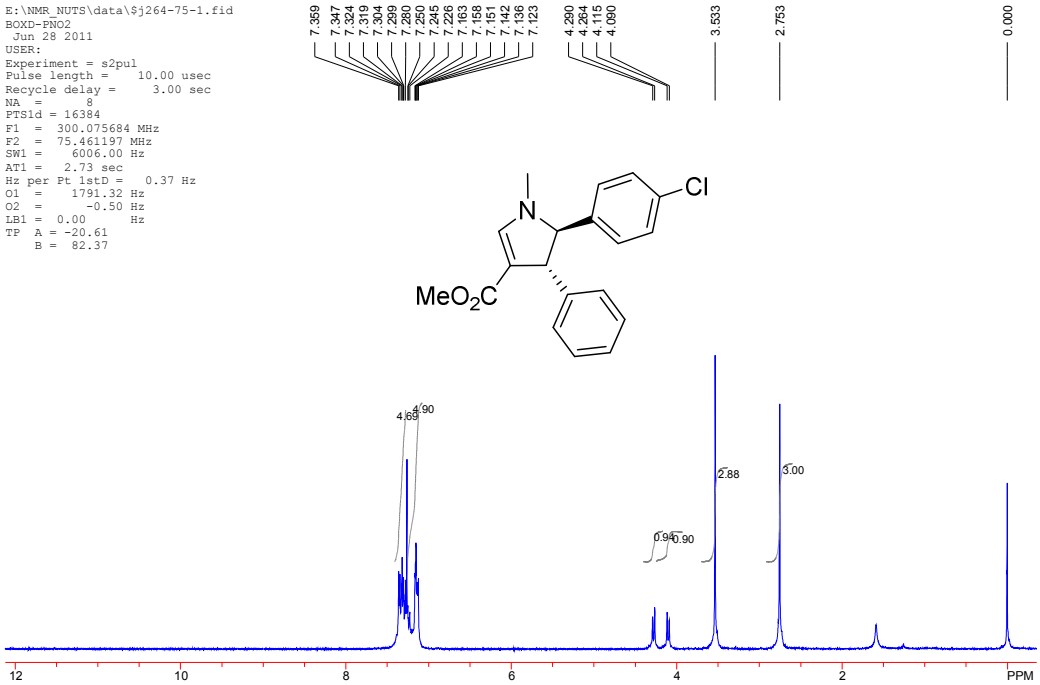


Fig. S-45: ^{1}H Spectra of compound **6d**

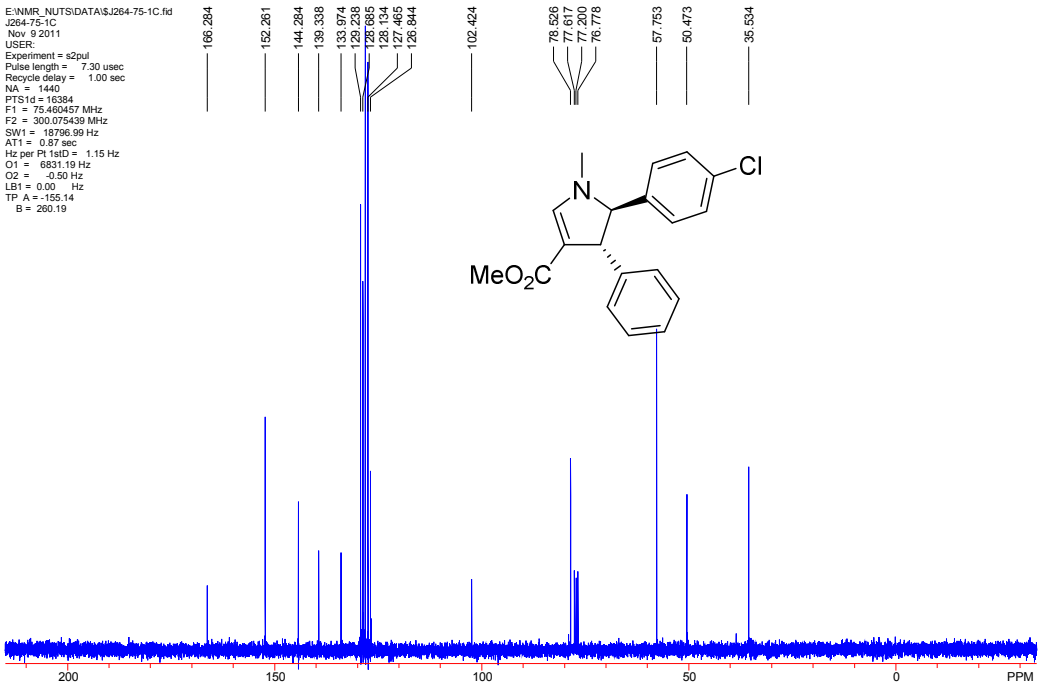
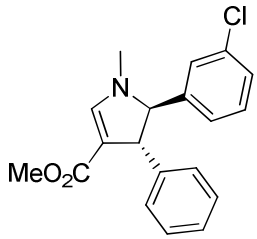


Fig. S-46: ^{13}C Spectra of compound **6d**



Chemical Formula: $C_{19}H_{18}ClNO_2$
Exact Mass: 327.10
Molecular Weight: 327.80

6e

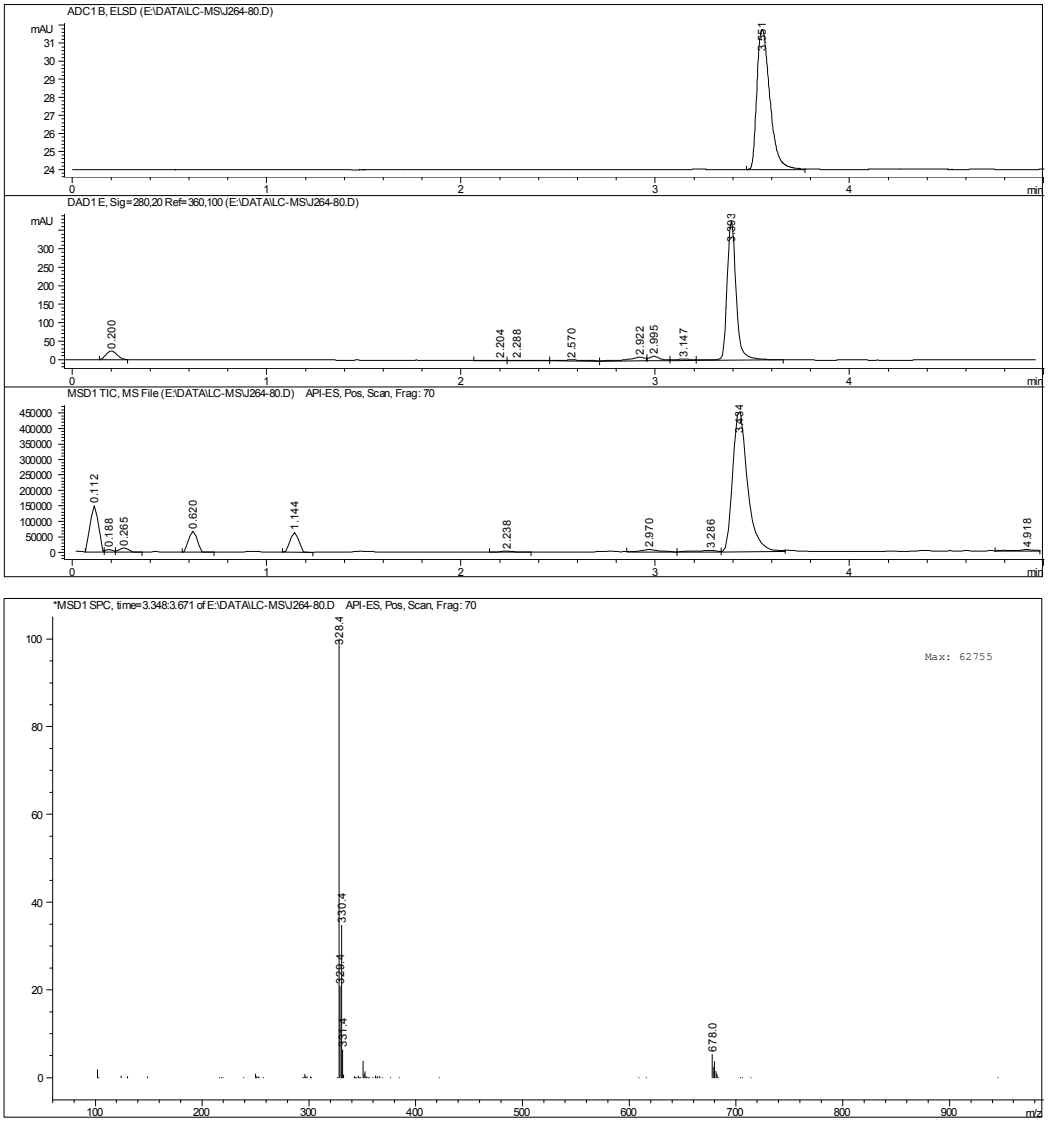


Fig. S-47: LC-MS-ELSD of compound **6e**

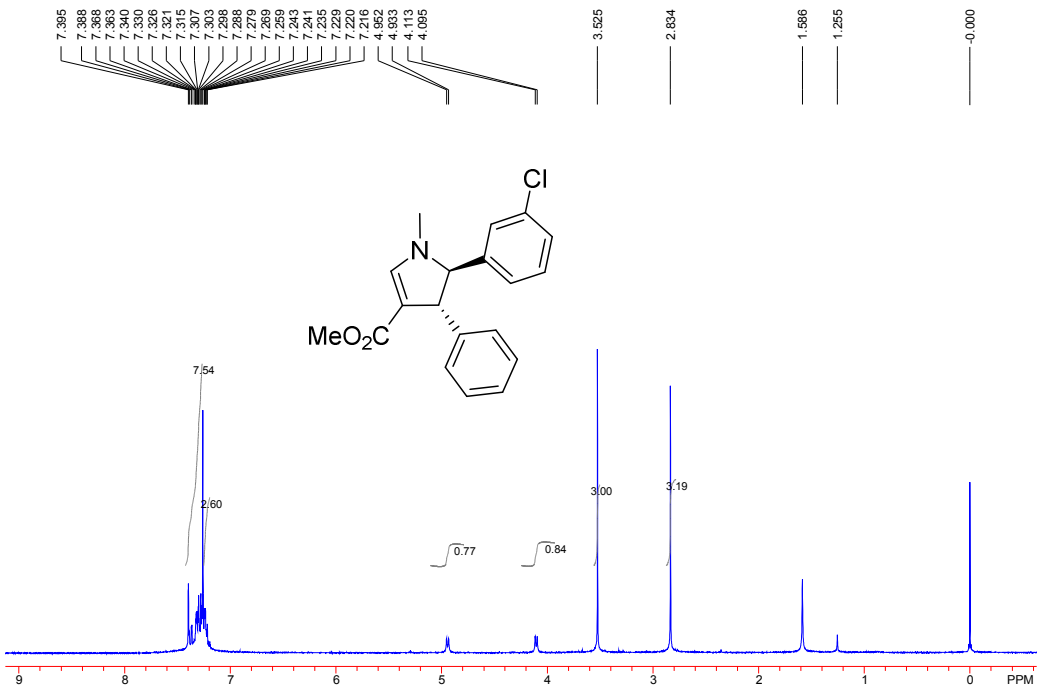


Fig. S-48: ^{1}H Spectra of compound **6e**

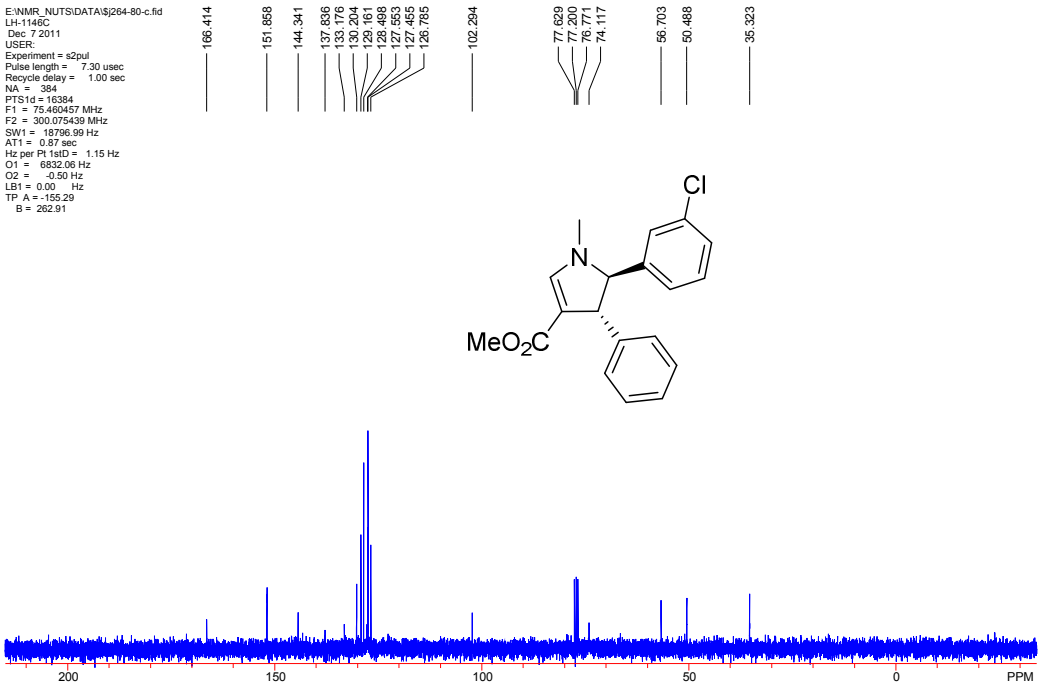
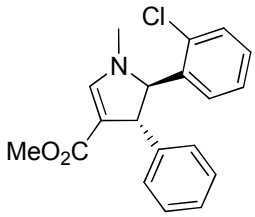


Fig. S-49: ^{13}C Spectra of compound **6e**



Chemical Formula: $C_{19}H_{18}ClNO_2$
Exact Mass: 327.10
Molecular Weight: 327.80

6f

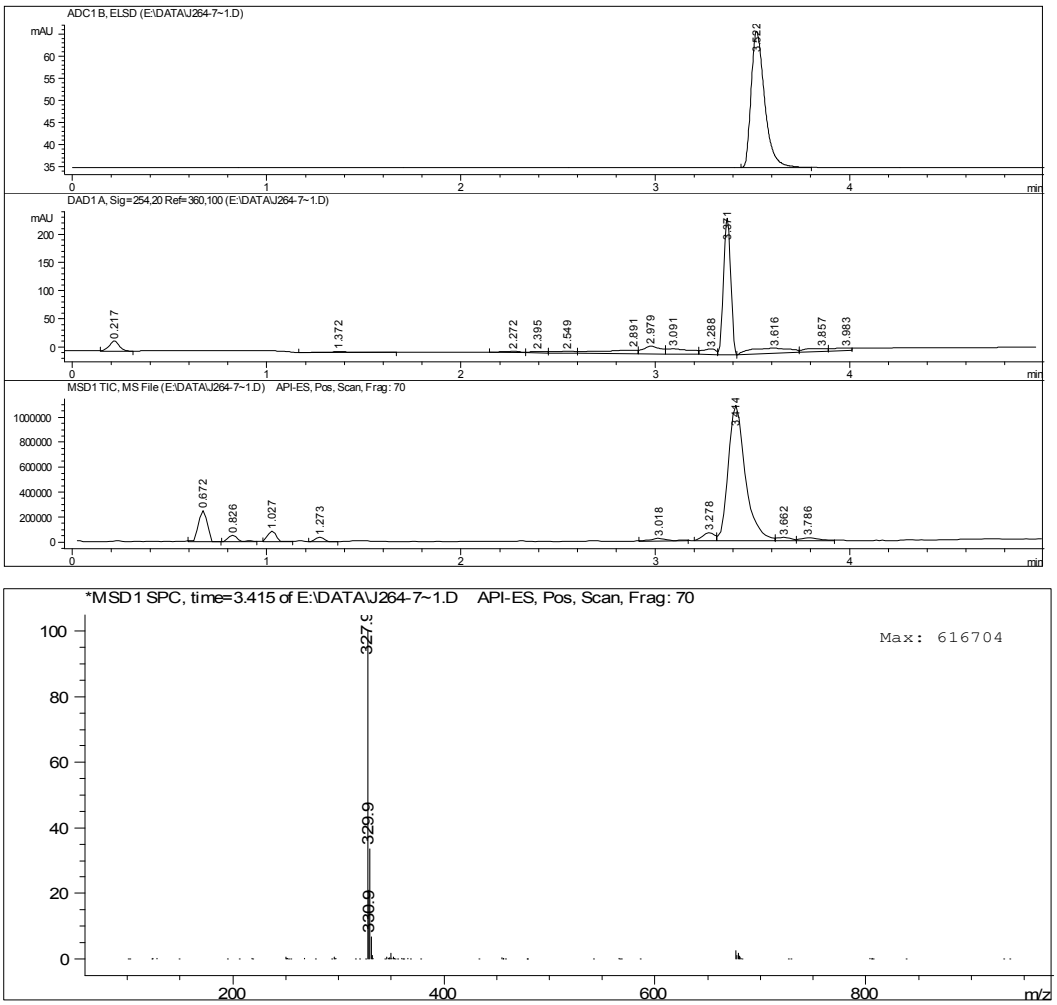


Fig. S-50: LC-MS-ELSD of compound **6f**

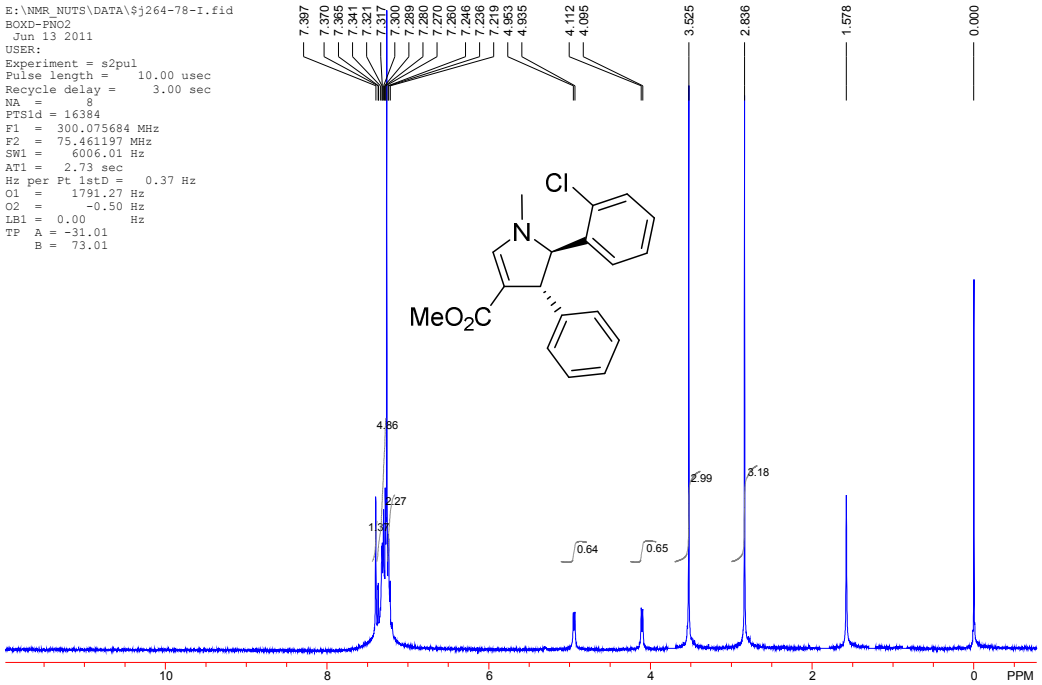


Fig. S-51: ^{1}H Spectra of compound **6f**

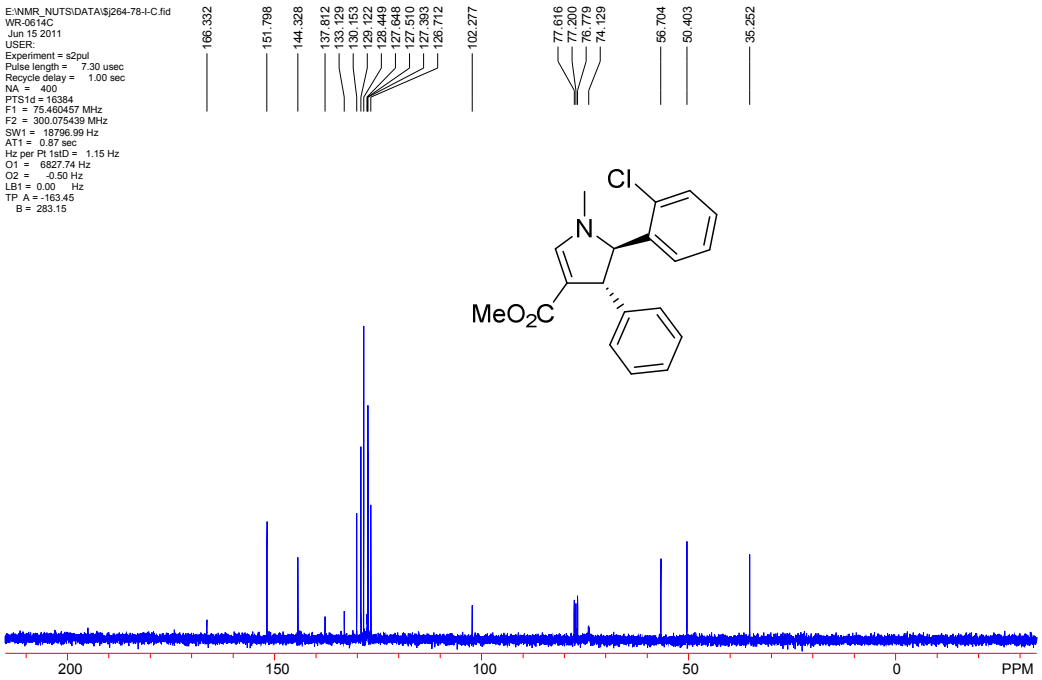
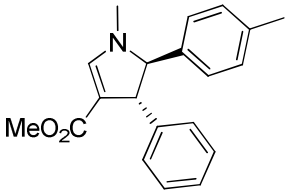


Fig. S-52: ^{13}C Spectra of compound **6f**



Chemical Formula: $C_{20}H_{21}NO_2$
Exact Mass: 307.16
Molecular Weight: 307.39

6g

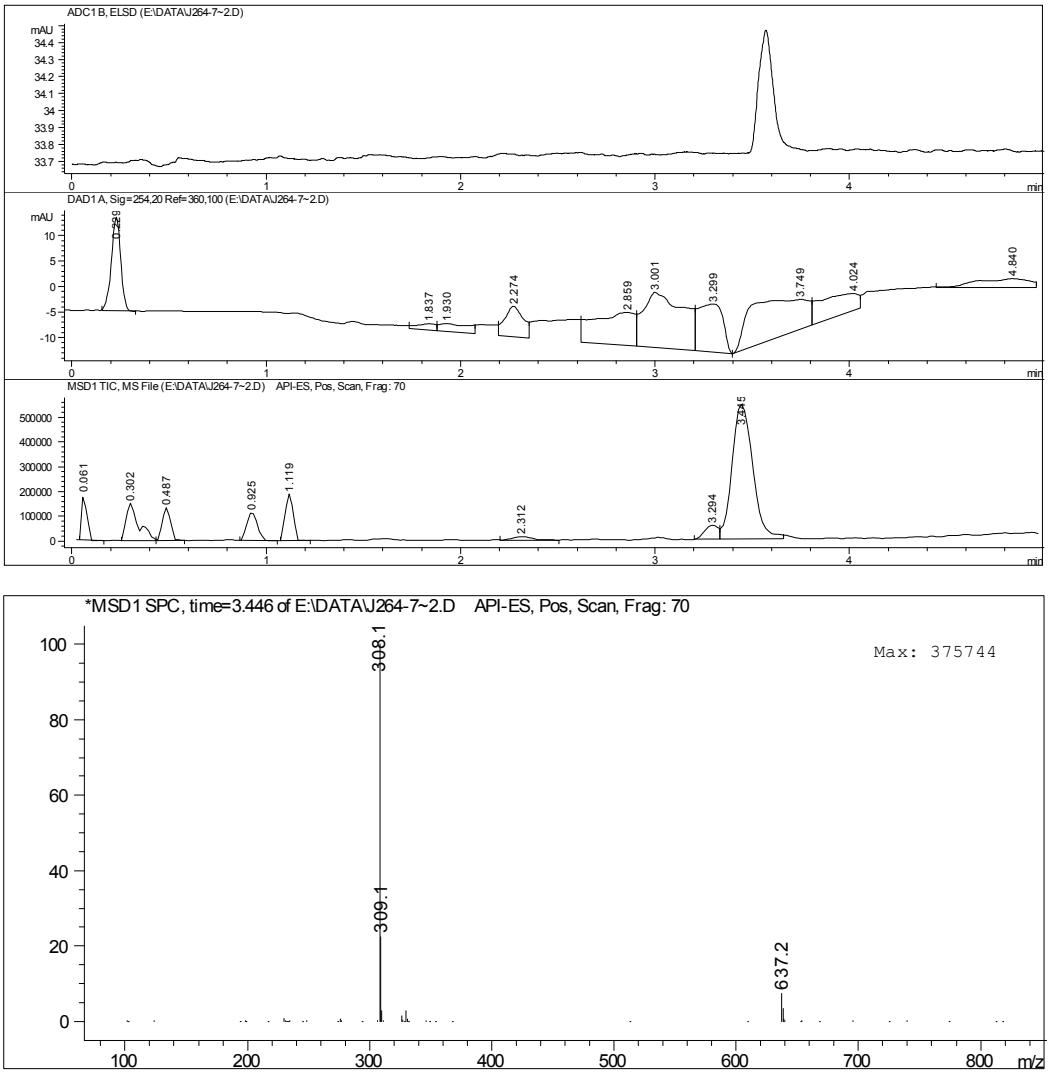


Fig. S-53: LC-MS-ELSD of compound **6g**

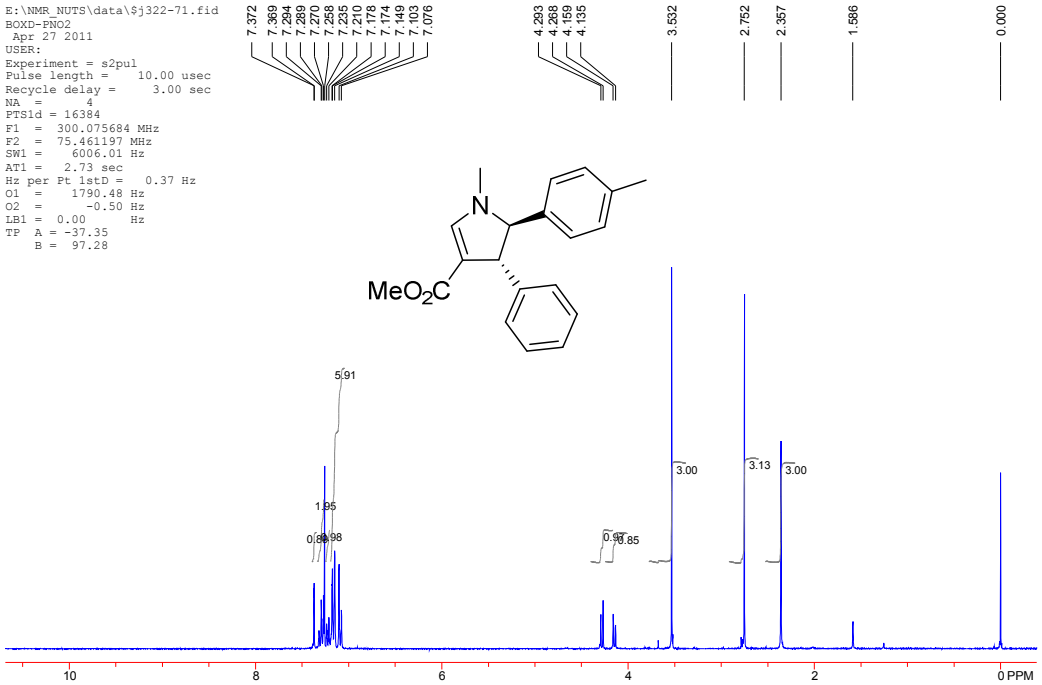


Fig. S-54: ^{1}H Spectra of compound **6g**

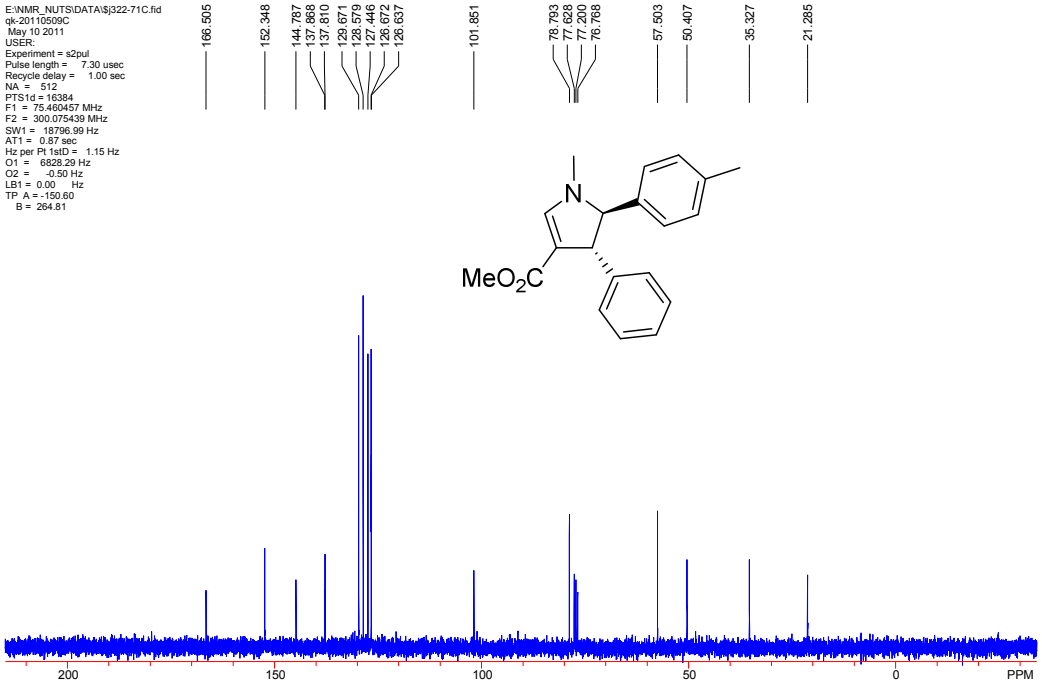
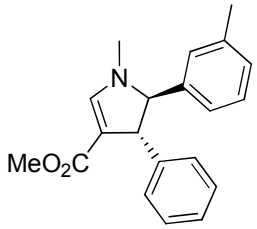


Fig. S-55: ^{13}C Spectra of compound **6g**



Chemical Formula: $C_{20}H_{21}NO_2$
Exact Mass: 307.16
Molecular Weight: 307.39

6h

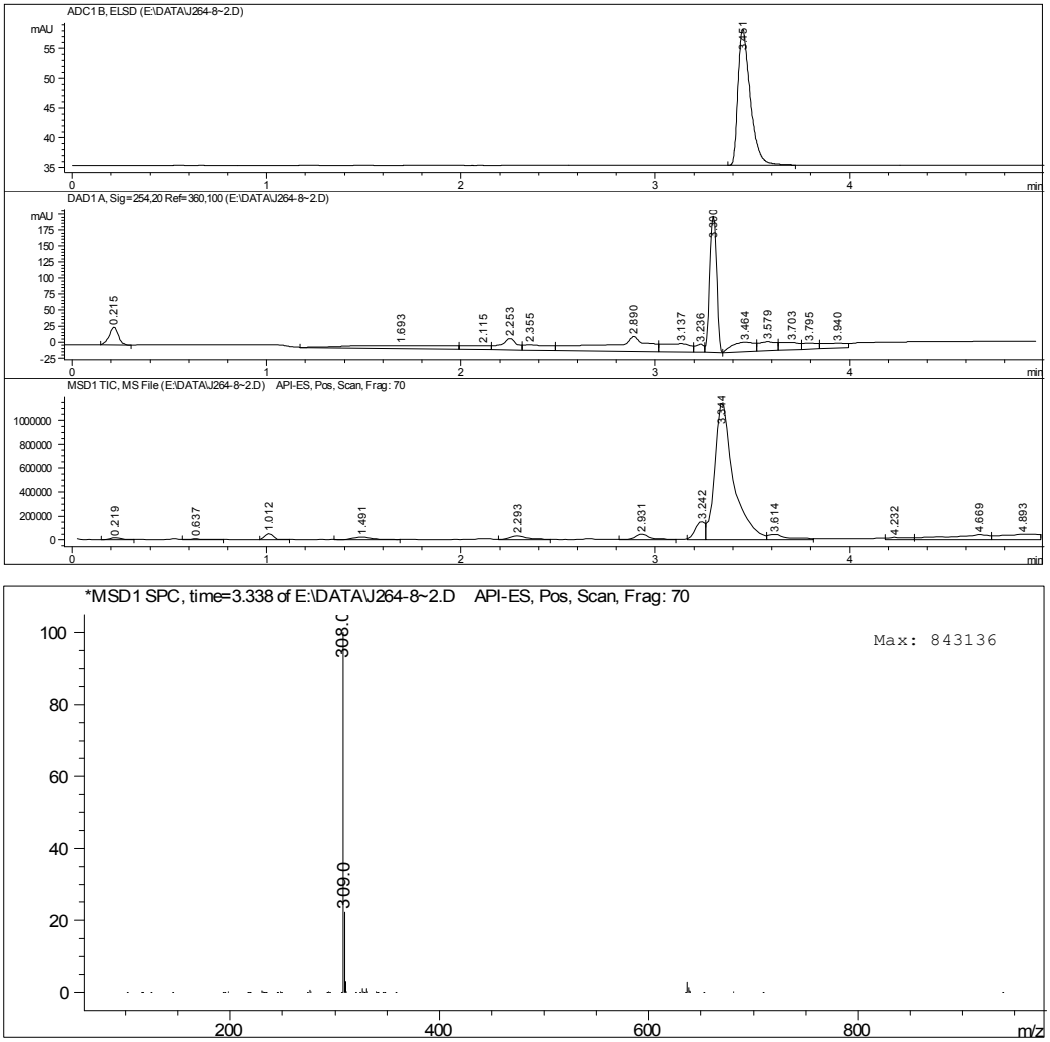


Fig. S-56: LC-MS-ELSD of compound **6h**

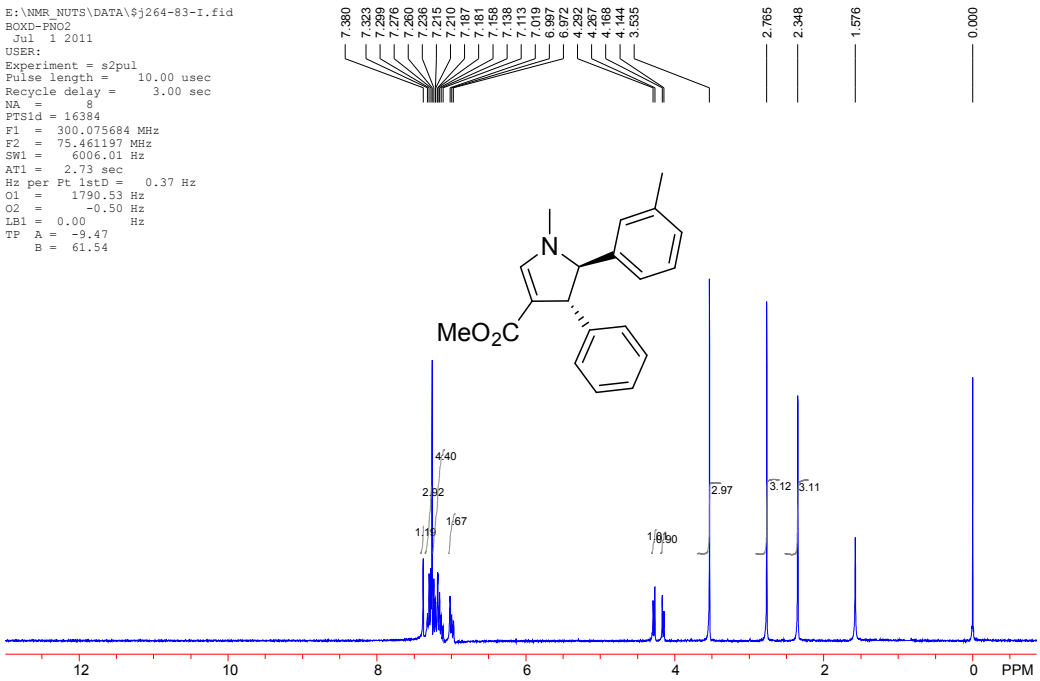


Fig. S-57: ^{1}H Spectra of compound **6h**

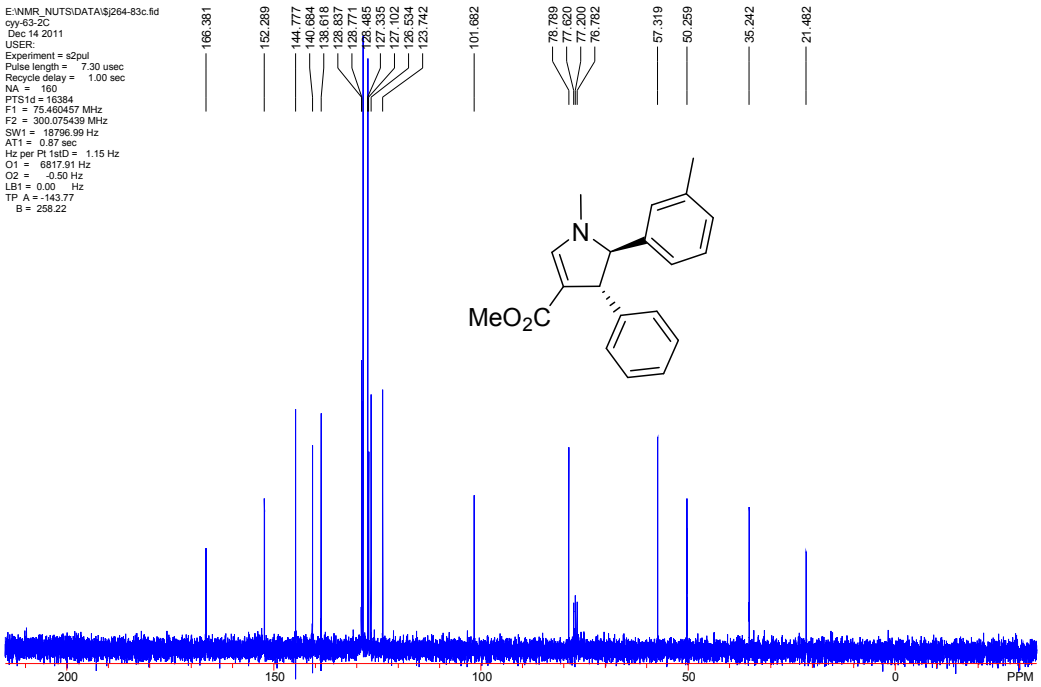
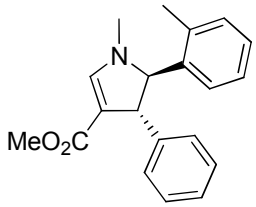
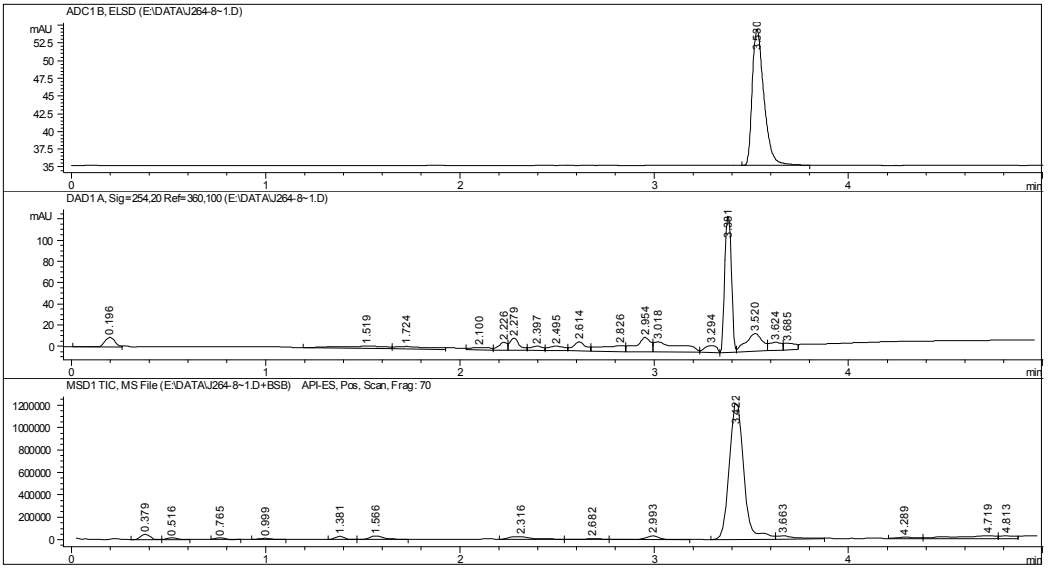


Fig. S-58: ^{13}C Spectra of compound **6h**



Chemical Formula: $C_{20}H_{21}NO_2$
Exact Mass: 307.16
Molecular Weight: 307.39

6i



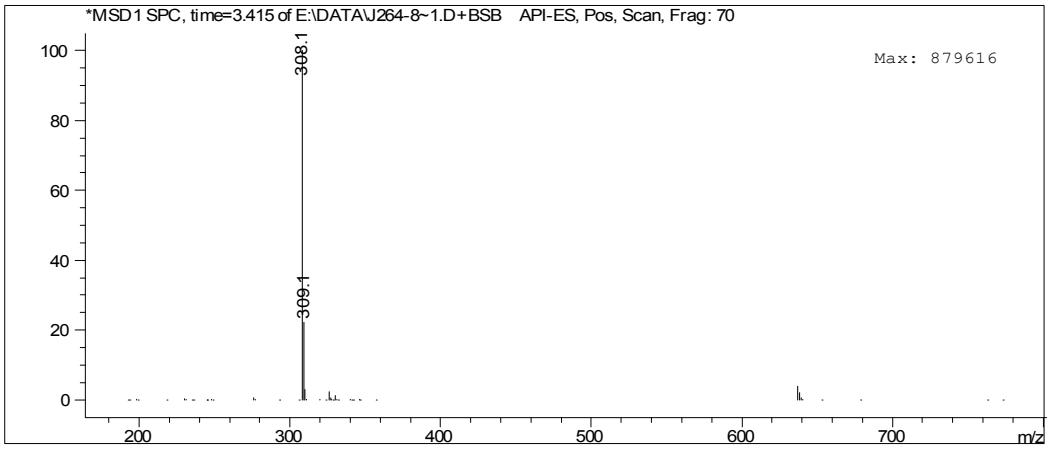


Fig. S-59: LC-MS-ELSD of compound **6i**

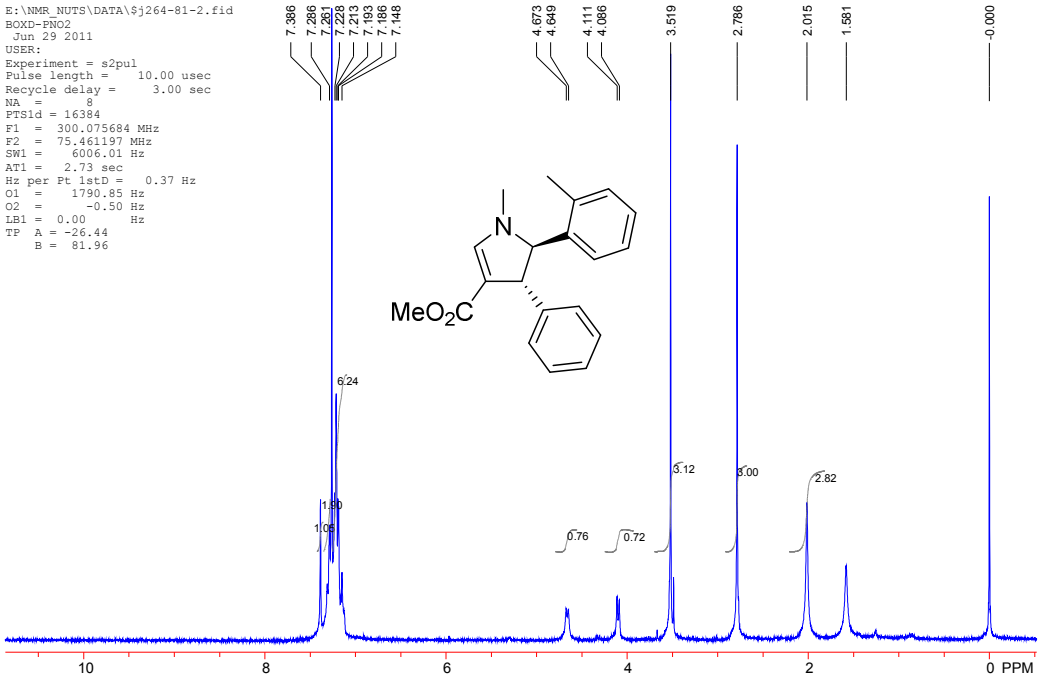


Fig. S-60: ^{1}H Spectra of compound **6i**

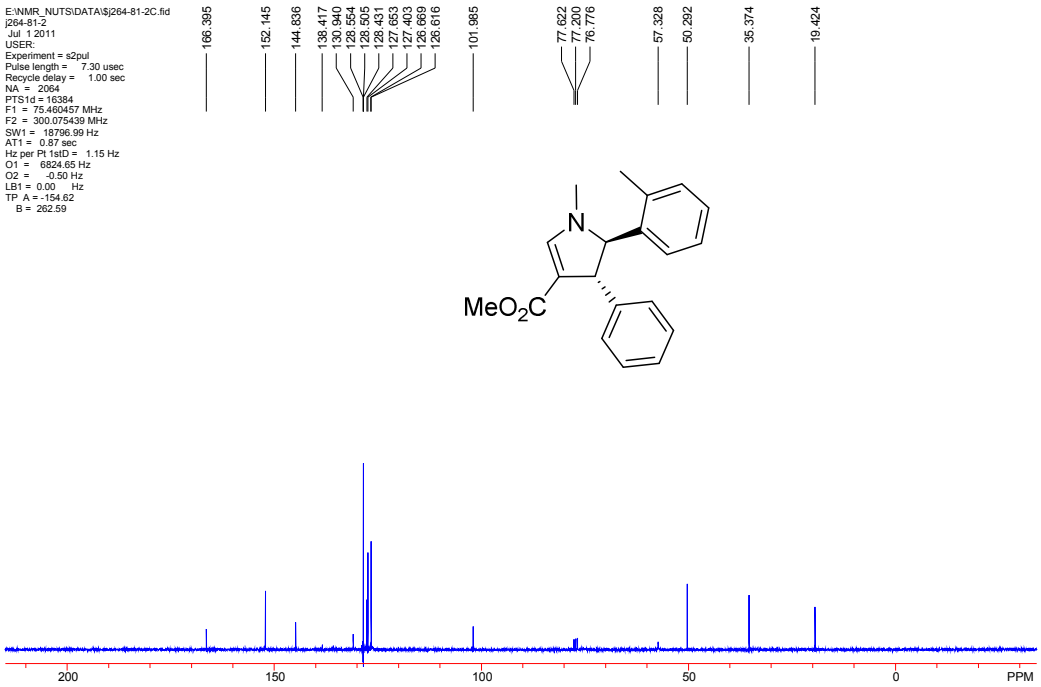
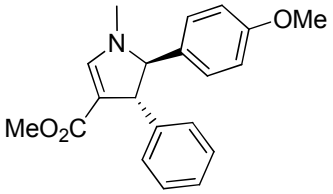
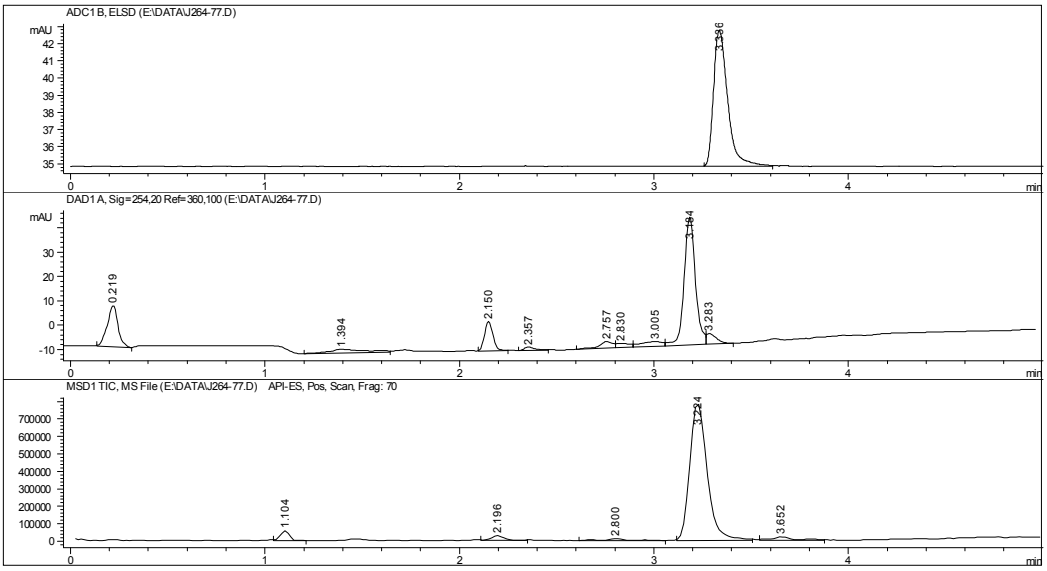


Fig. S-61: ^{13}C Spectra of compound **6i**



Chemical Formula: $C_{20}H_{21}NO_3$
Exact Mass: 323.15
Molecular Weight: 323.39

6j



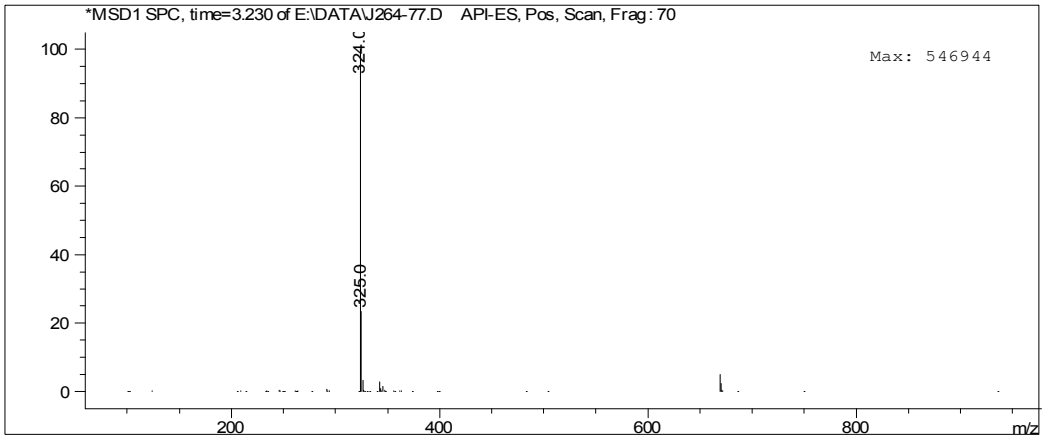


Fig. S-62: LC-MS-ELSD of compound **6j**

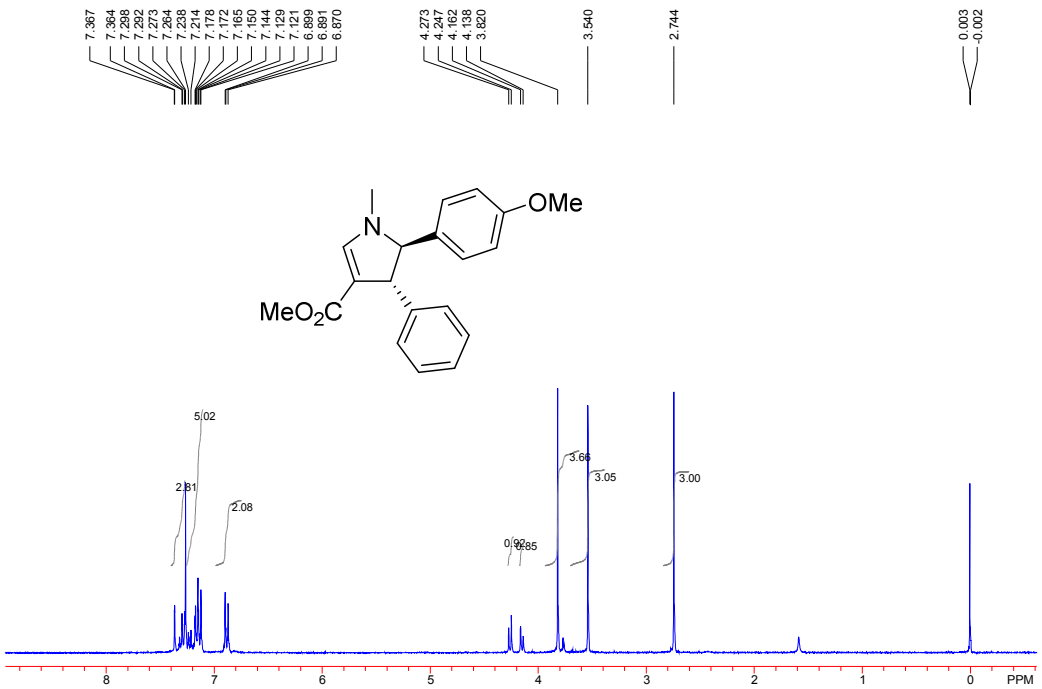


Fig. S-63: ^{1}H Spectra of compound **6j**

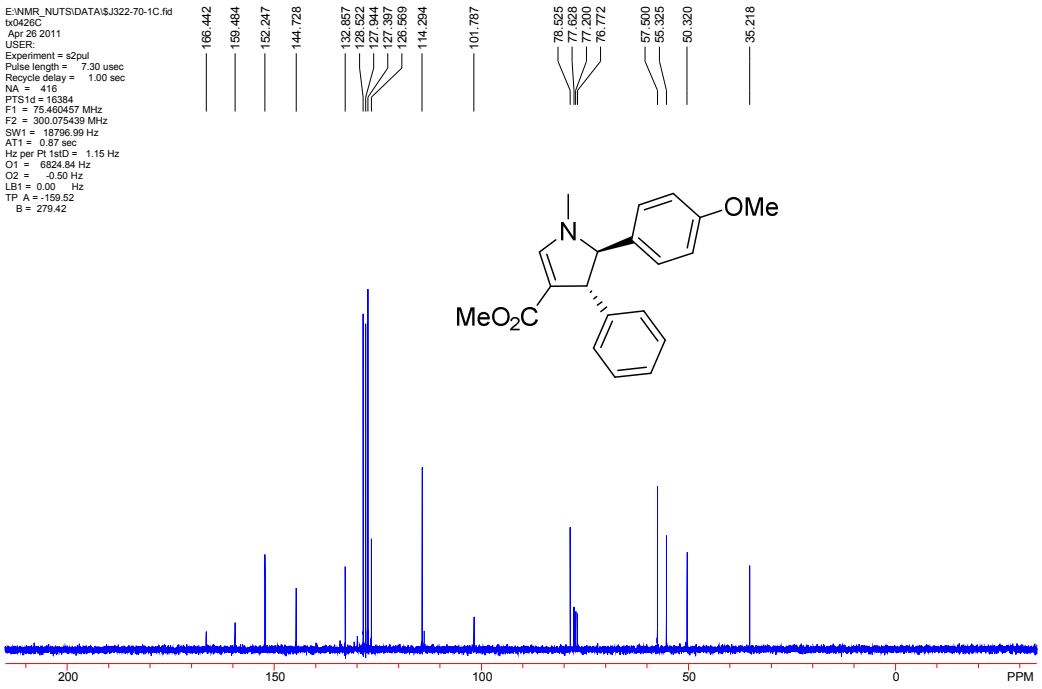
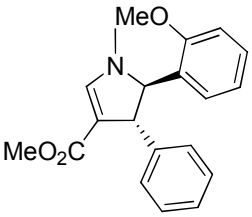


Fig. S-64: ^{13}C Spectra of compound **6j**



Chemical Formula: $C_{20}H_{21}NO_3$
Exact Mass: 323.15
Molecular Weight: 323.39

6k

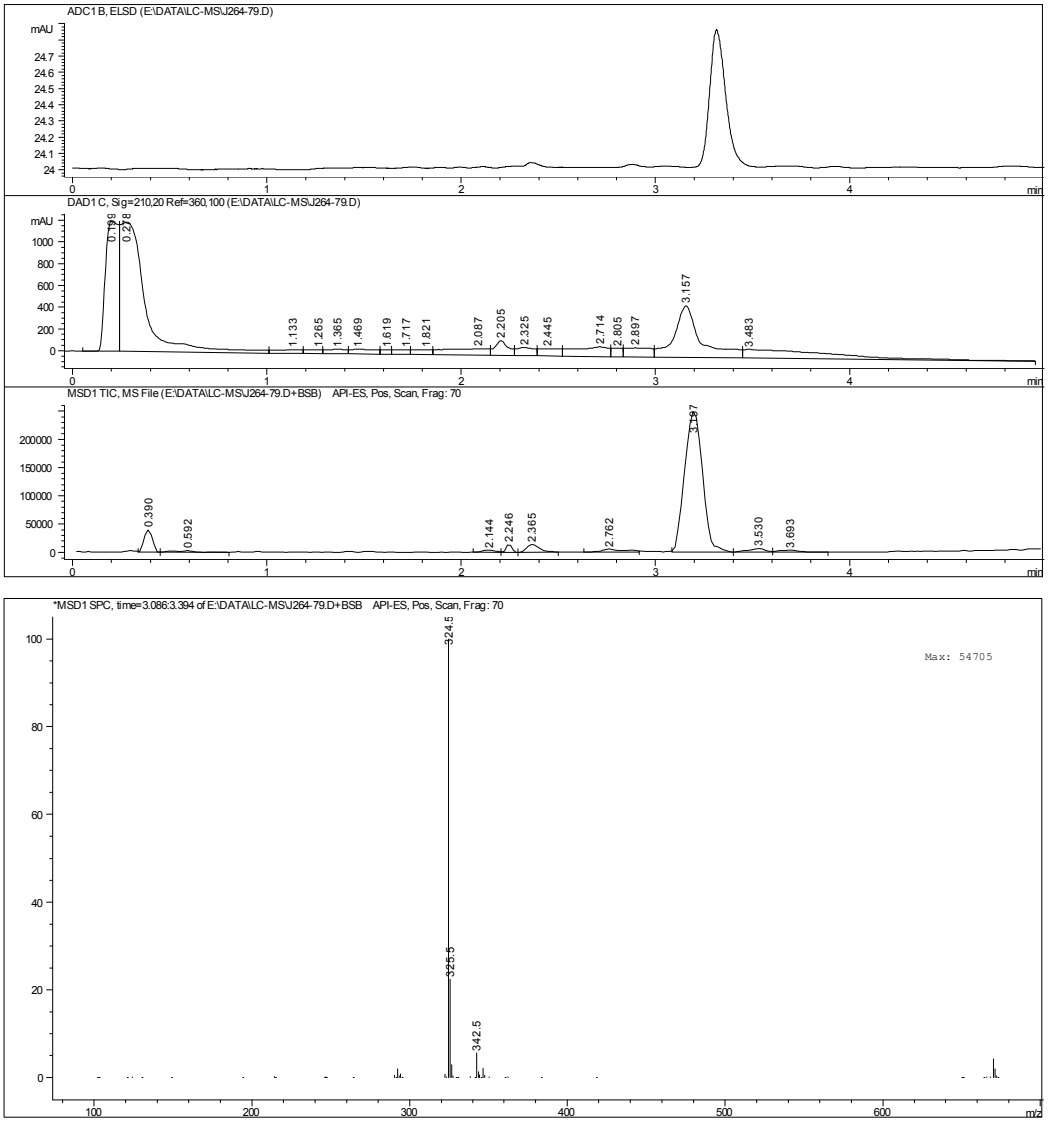


Fig. S-65: LC-MS-ELSD of compound **6k**

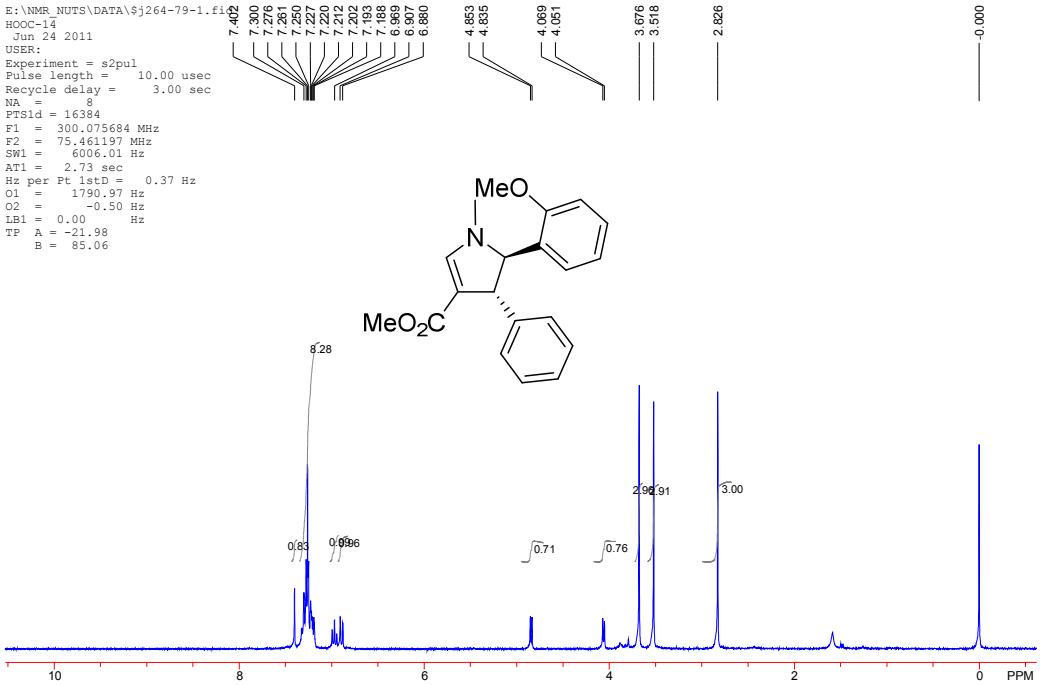


Fig. S-66: ^{1}H Spectra of compound **6k**

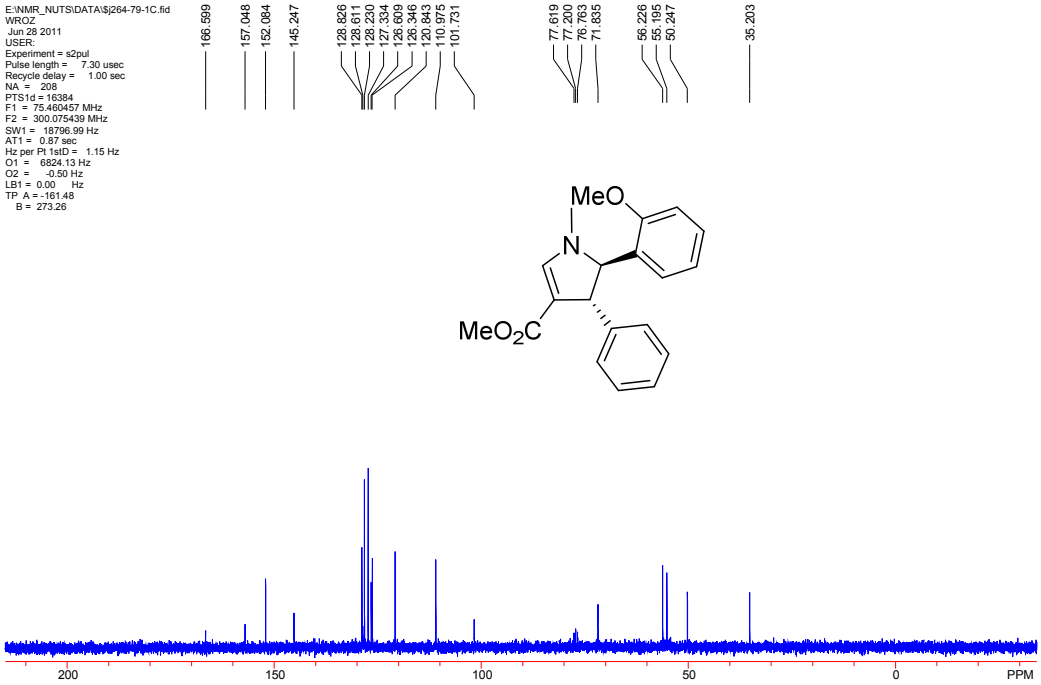
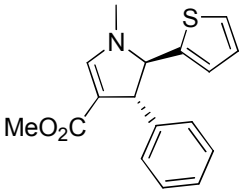


Fig. S-67: ^{13}C Spectra of compound **6k**



Chemical Formula: $C_{17}H_{17}NO_2S$
Exact Mass: 299.10
Molecular Weight: 299.39

6l

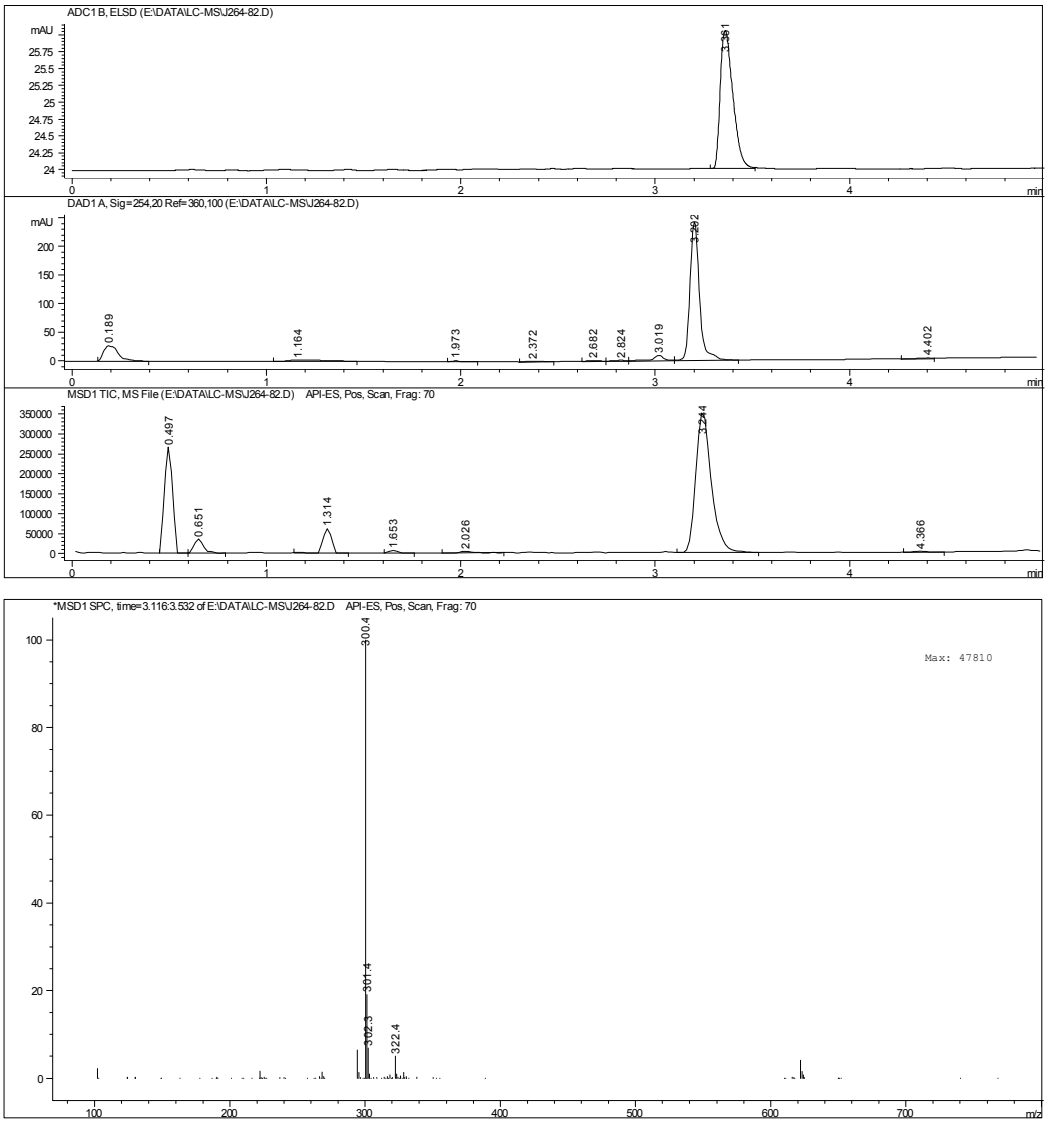


Fig. S-68: LC-MS-ELSD of compound **6l**

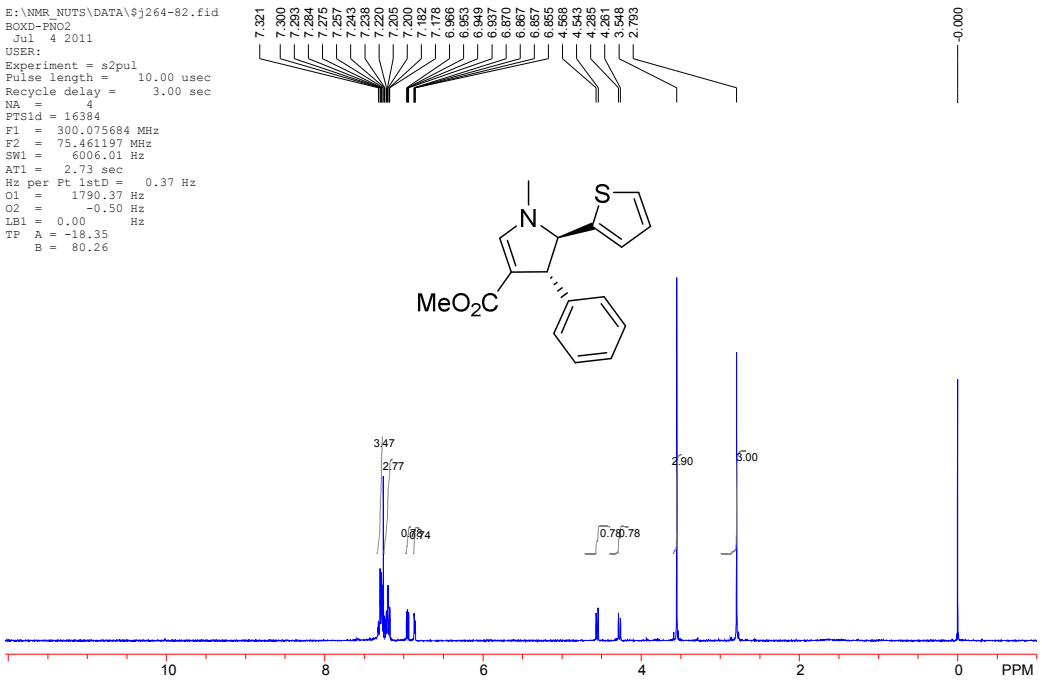


Fig. S-69: ^{1}H Spectra of compound **6l**

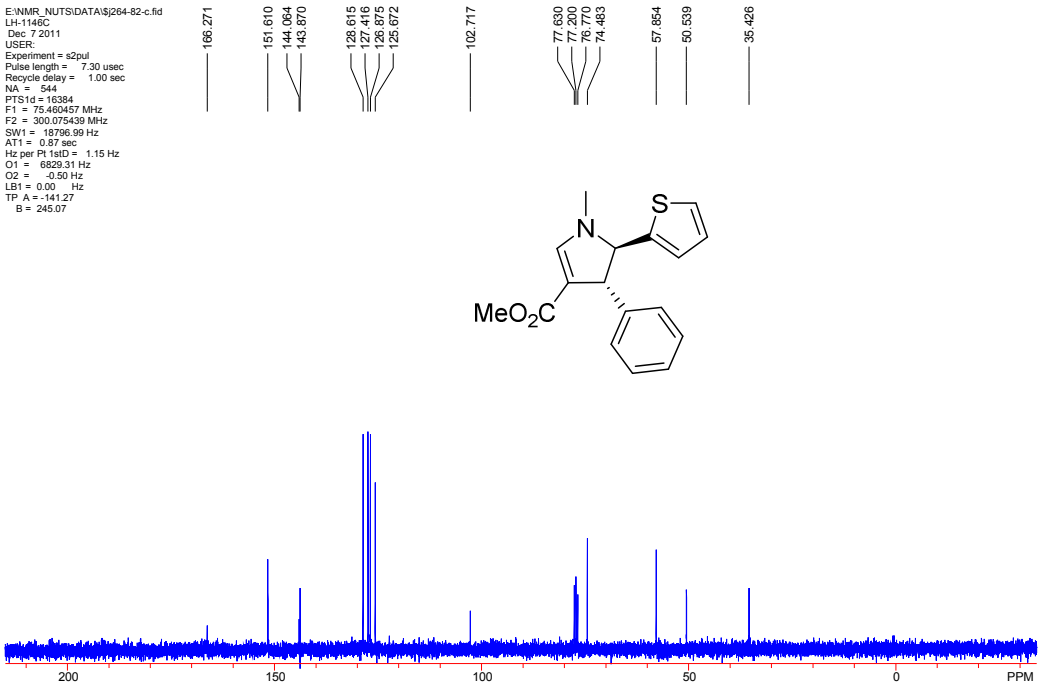
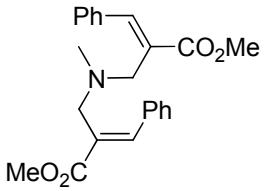


Fig. S-70: ^{13}C Spectra of compound **6l**



Chemical Formula: $C_{23}H_{25}NO_4$
Exact Mass: 379.18
Molecular Weight: 379.45

7a

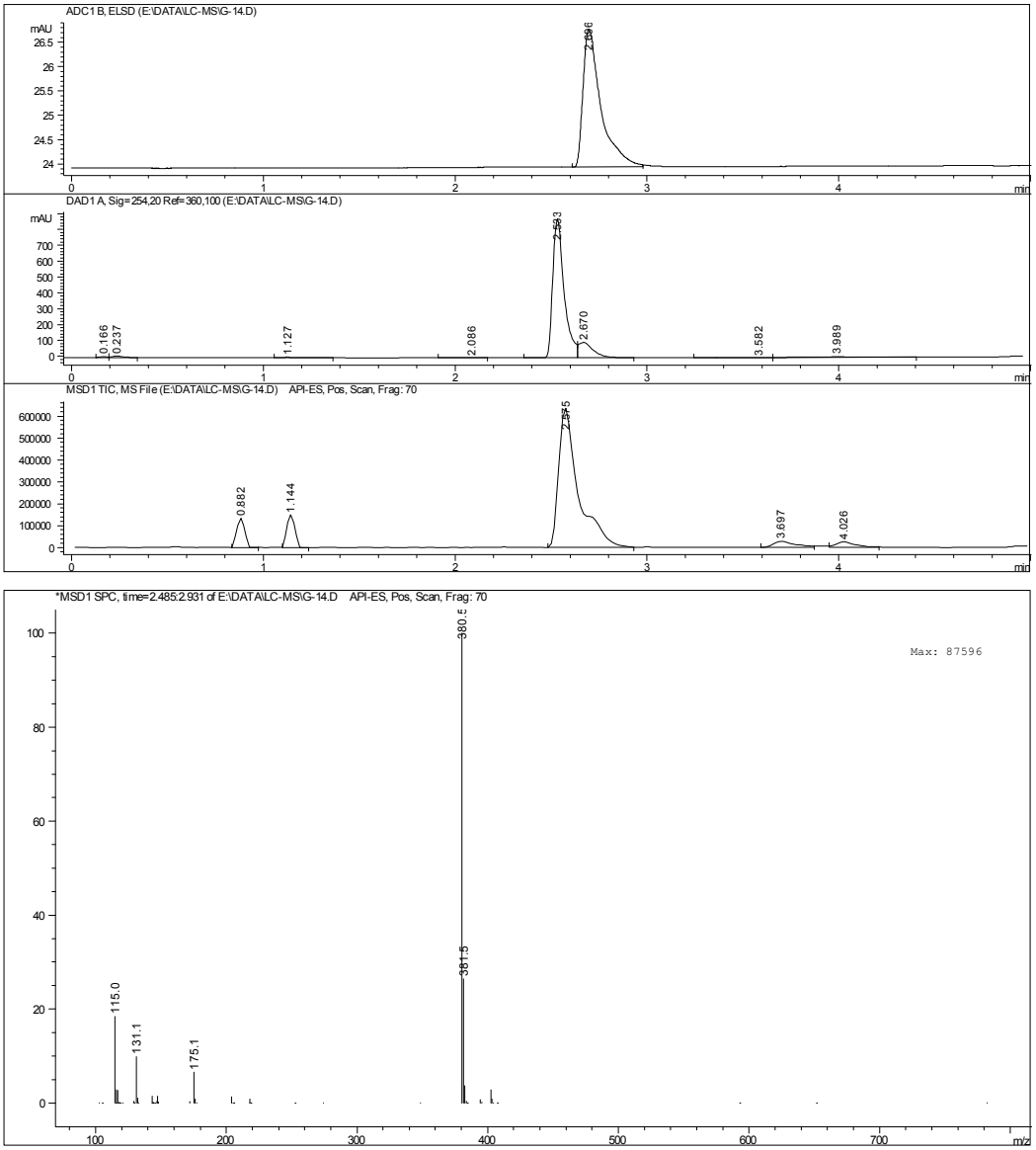


Fig. S-71: LC-MS-ELSD of compound **7a**

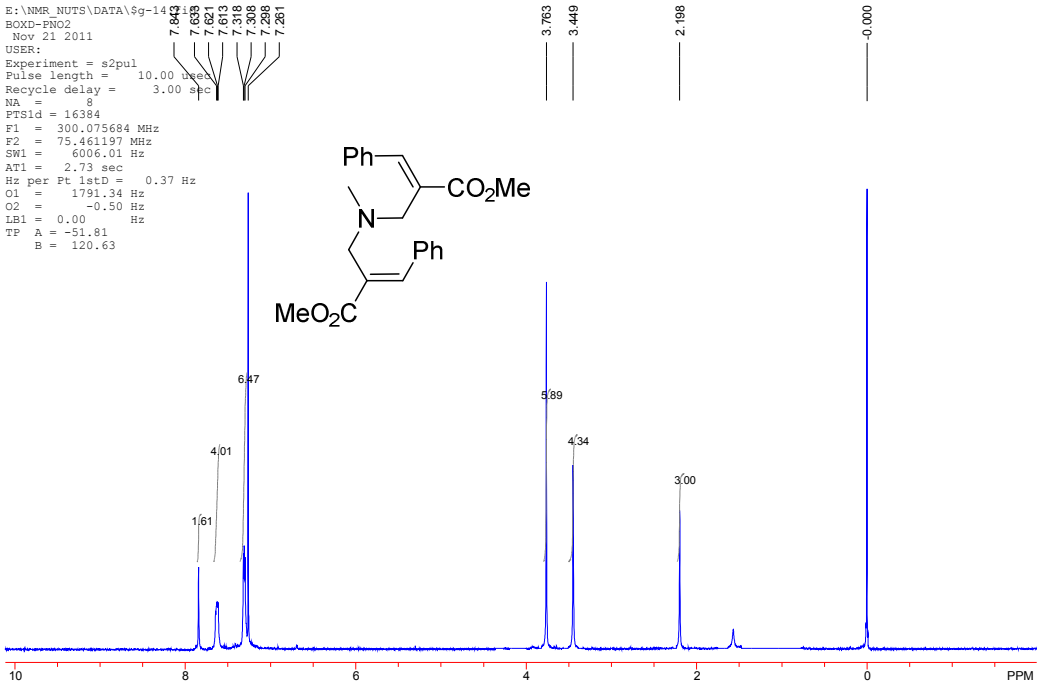


Fig. S-72: ^{1}H Spectra of compound **7a**

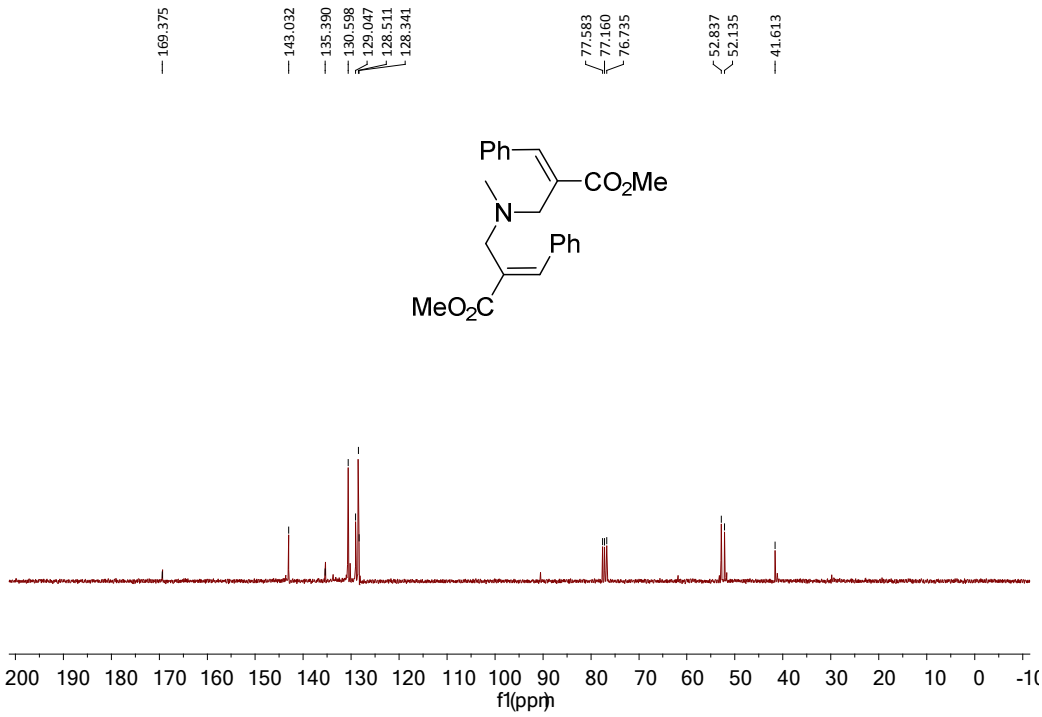
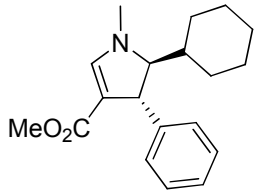


Fig. S-73: ^{13}C Spectra of compound **7a**



Chemical Formula: $C_{19}H_{25}NO_2$
Exact Mass: 299.19
Molecular Weight: 299.41

6o

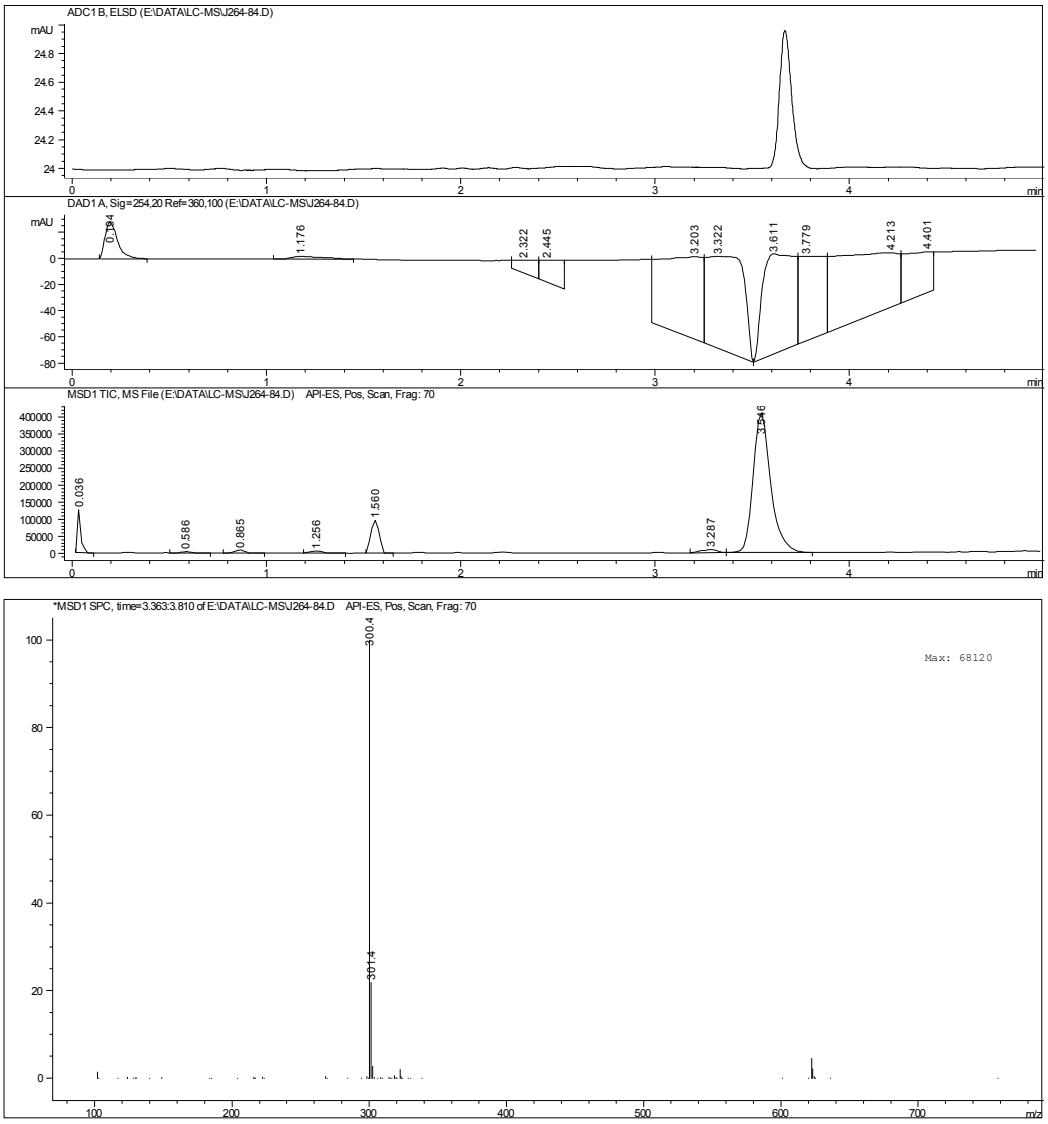


Fig. S-74: LC-MS-ELSD of compound **6o**

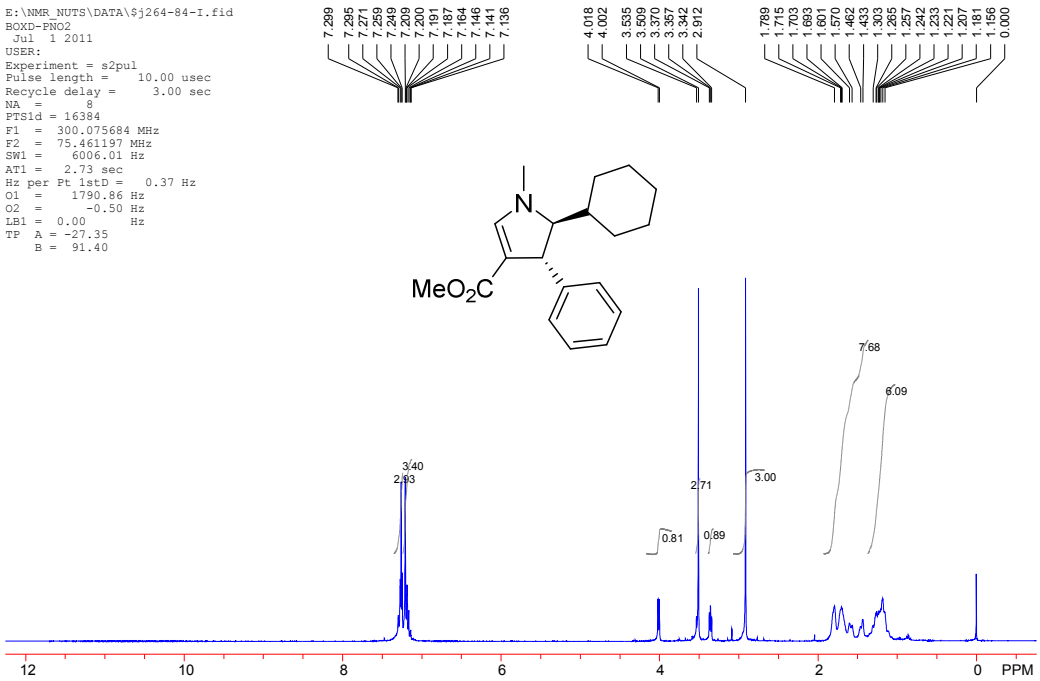


Fig. S-75: ^{1}H Spectra of compound **6o**

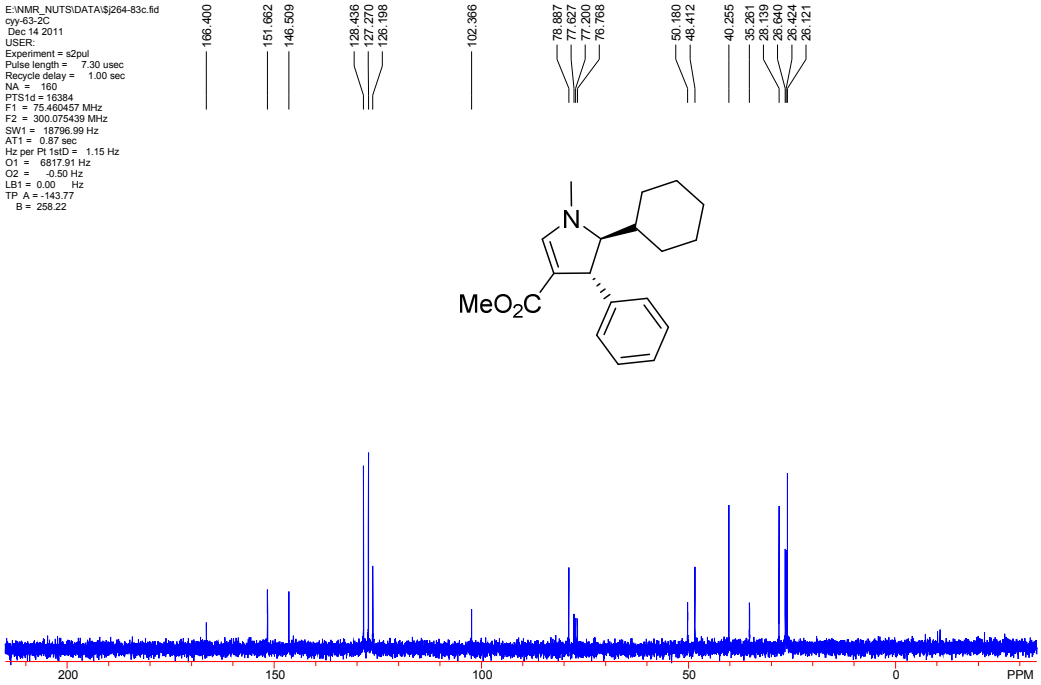
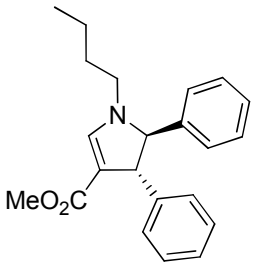


Fig. S-76: ^{13}C Spectra of compound **6o**



Chemical Formula: $C_{22}H_{25}NO_2$
Exact Mass: 335.19
Molecular Weight: 335.44

6p

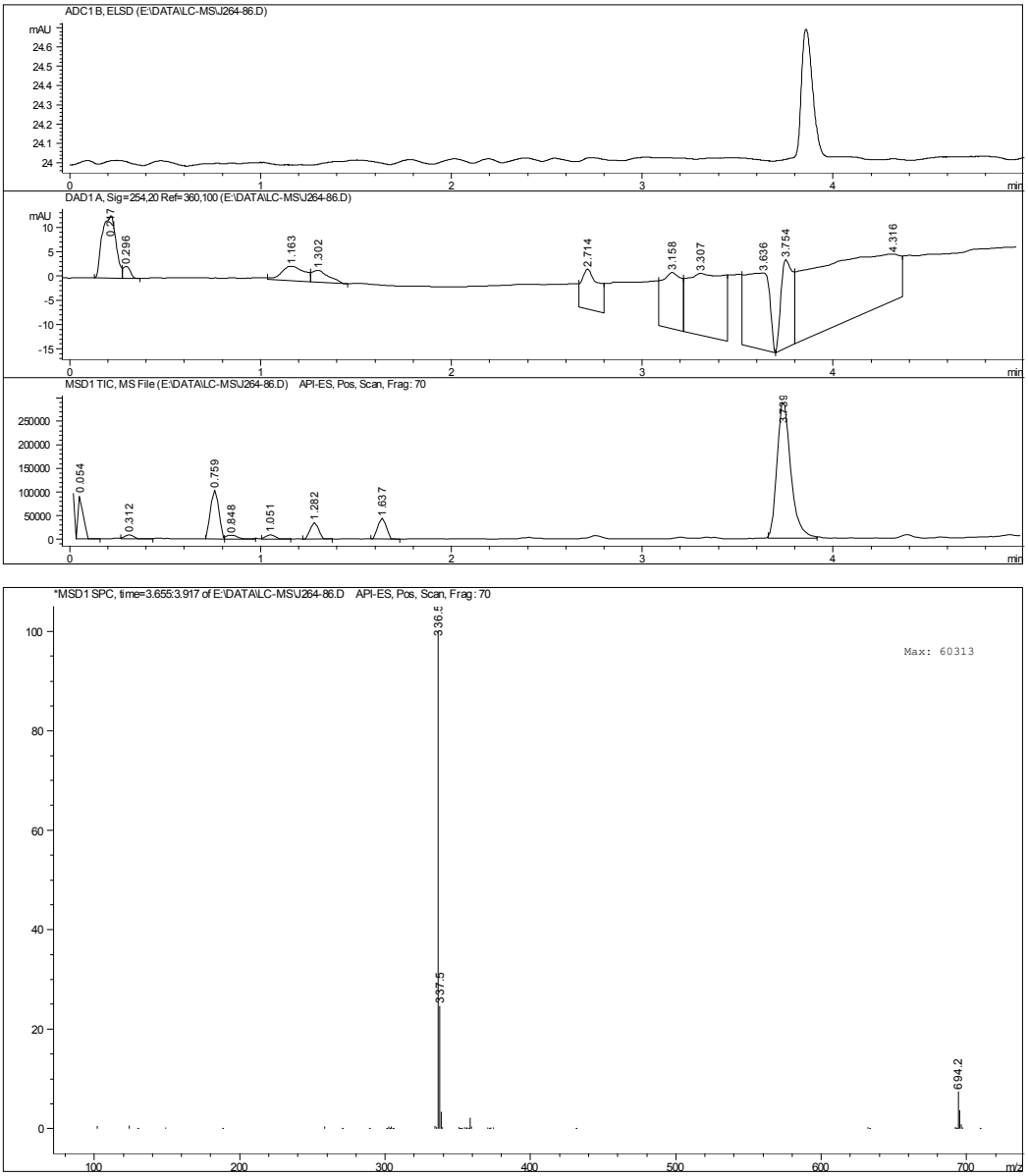


Fig. S-77: LC-MS-ELSD of compound **6p**

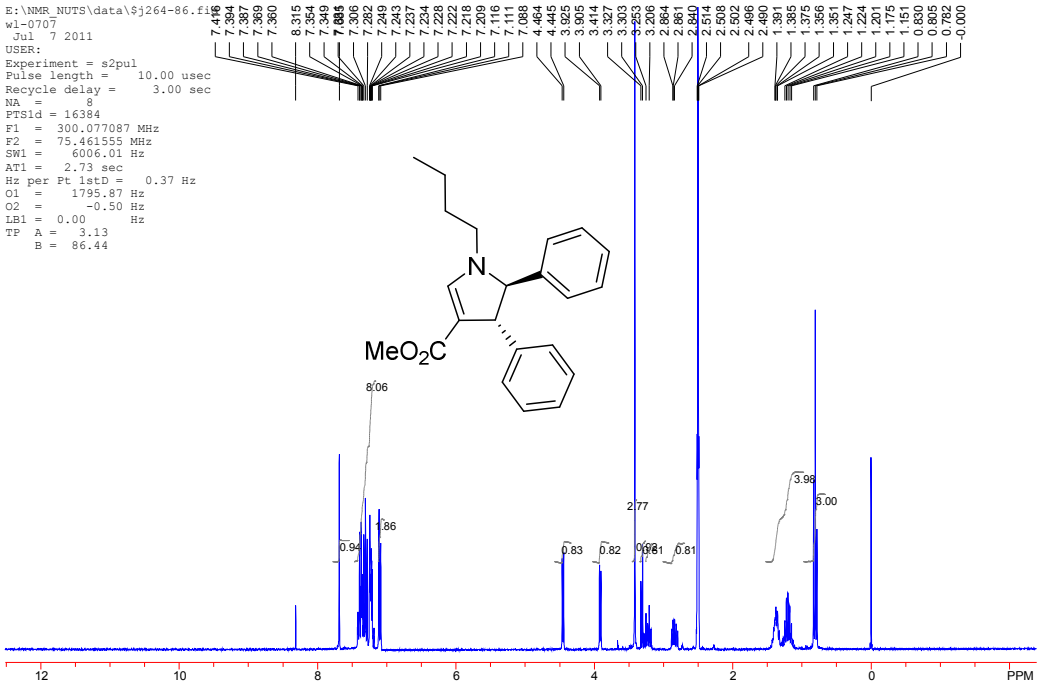


Fig. S-78: ^{1}H Spectra of compound **6p**

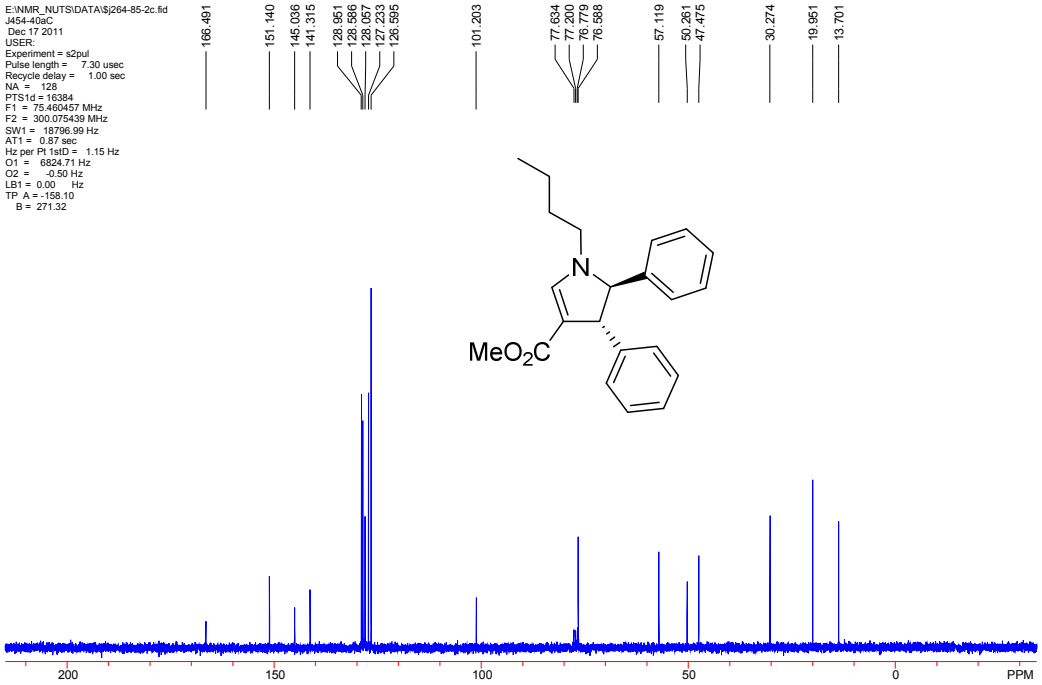
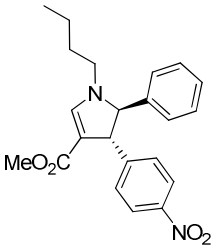
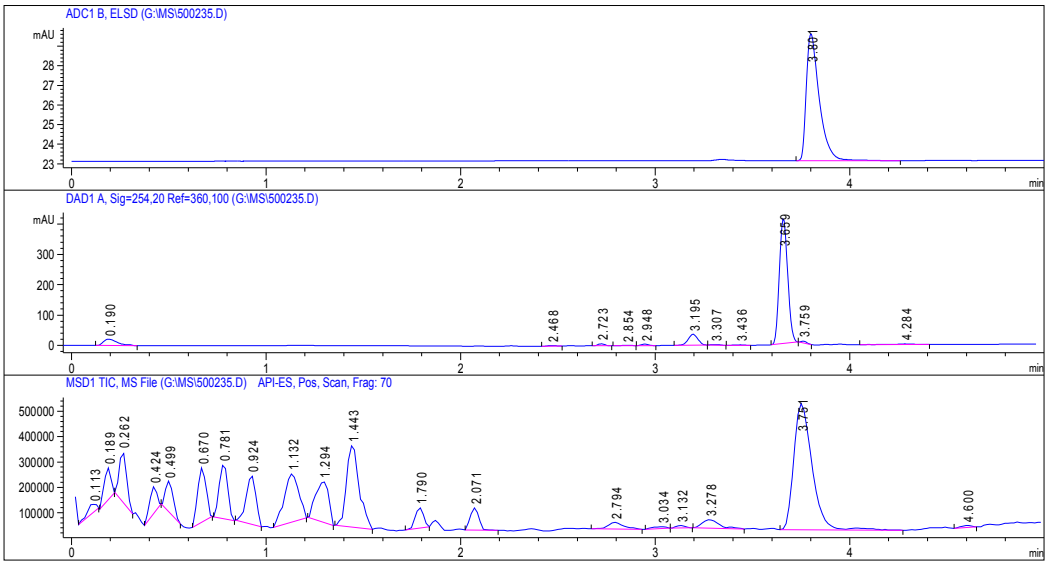


Fig. S-79: ^{13}C Spectra of compound **6p**



Chemical Formula: $C_{22}H_{24}N_2O_4$
Exact Mass: 380.17
Molecular Weight: 380.44

6q



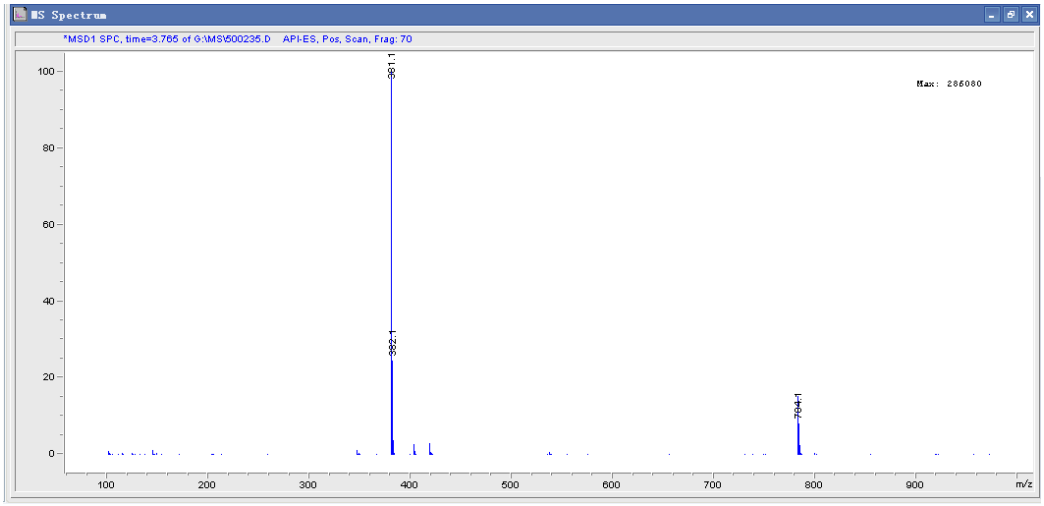


Fig. S-80: LC-MS-ELSD of compound **6q**

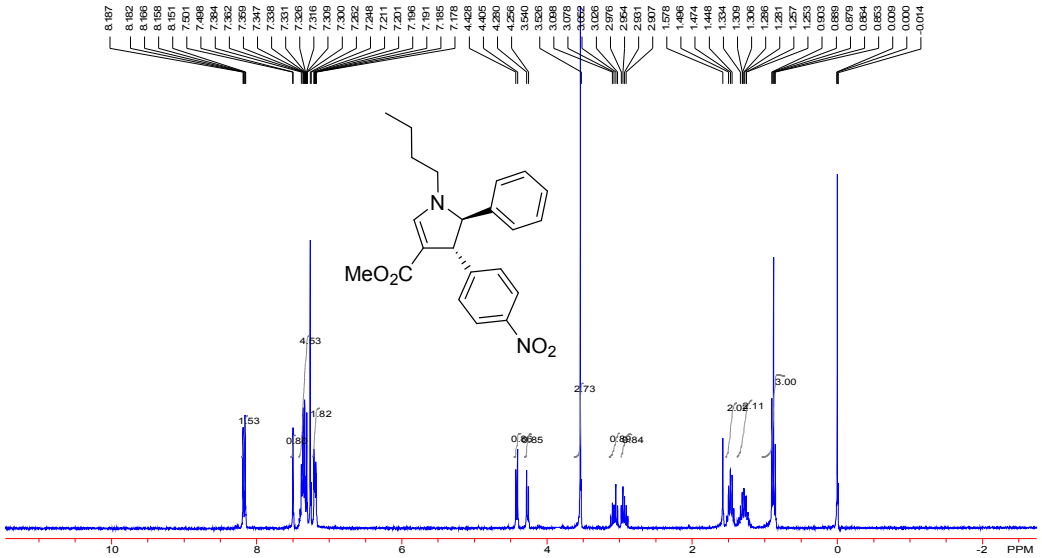


Fig. S-81: ^{1}H Spectra of compound **6q**

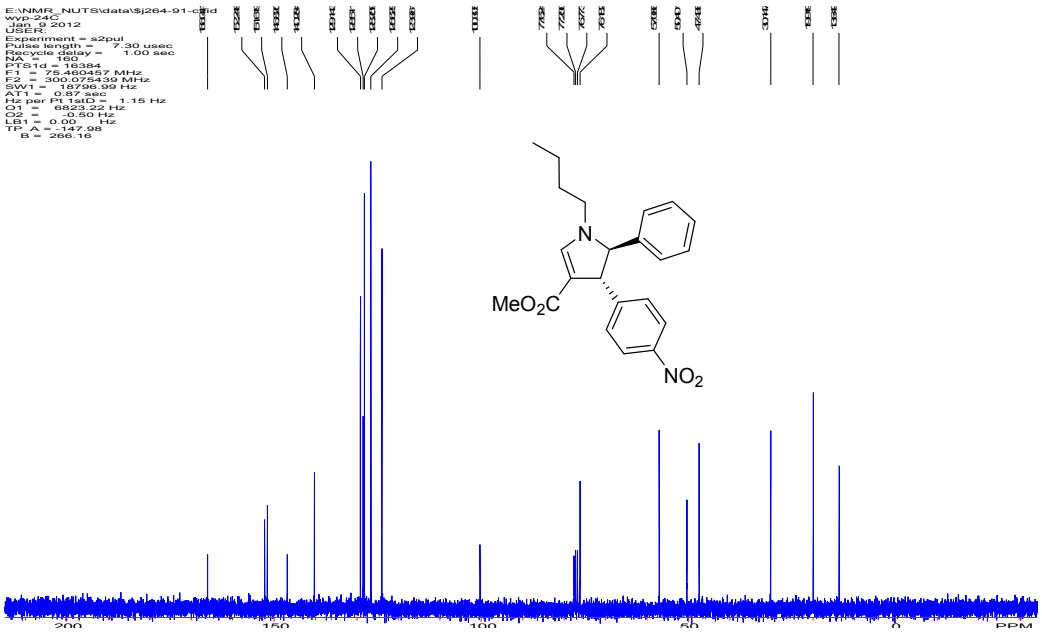
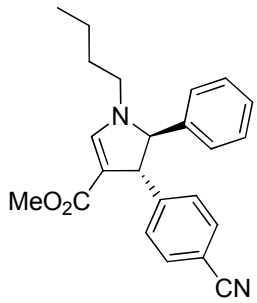


Fig. S-82: ^{13}C Spectra of compound **6q**



Chemical Formula: $C_{23}H_{24}N_2O_2$
Exact Mass: 360.18
Molecular Weight: 360.45

6r

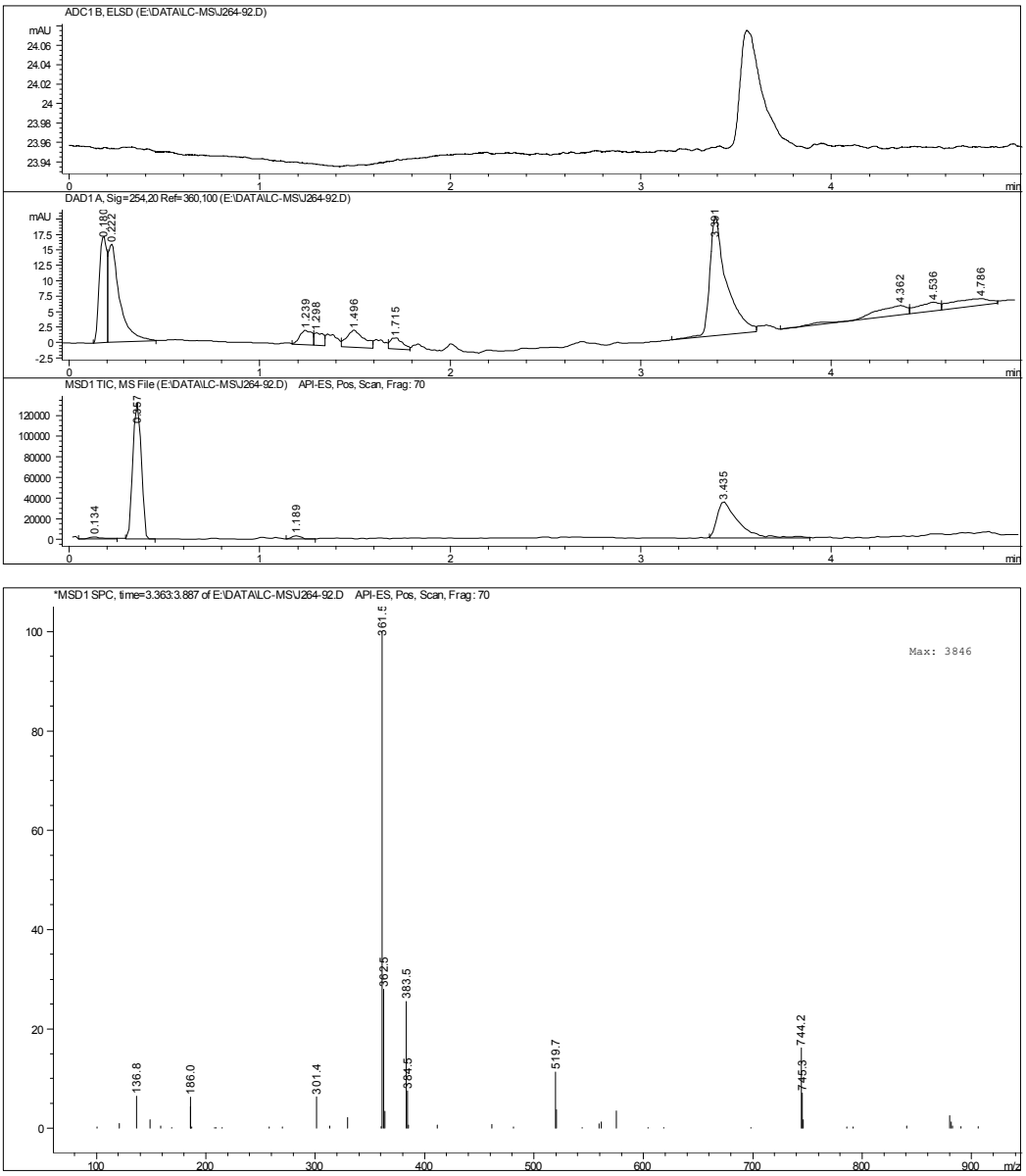


Fig. S-83: LC-MS-ELSD of compound **6r**

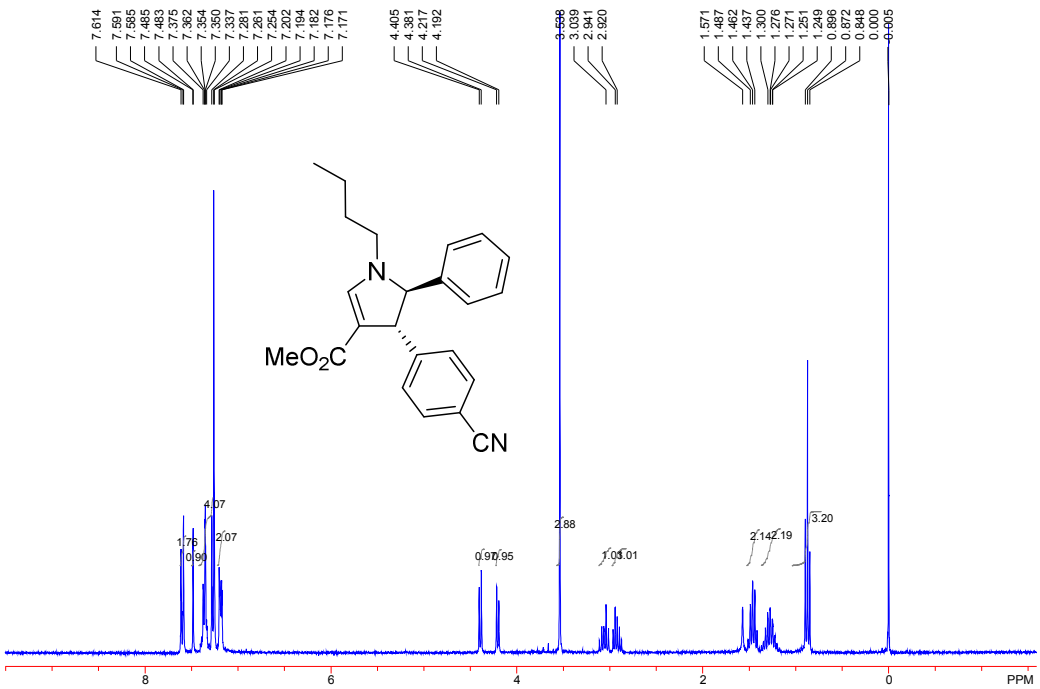


Fig. S-84: ^{1}H Spectra of compound **6r**

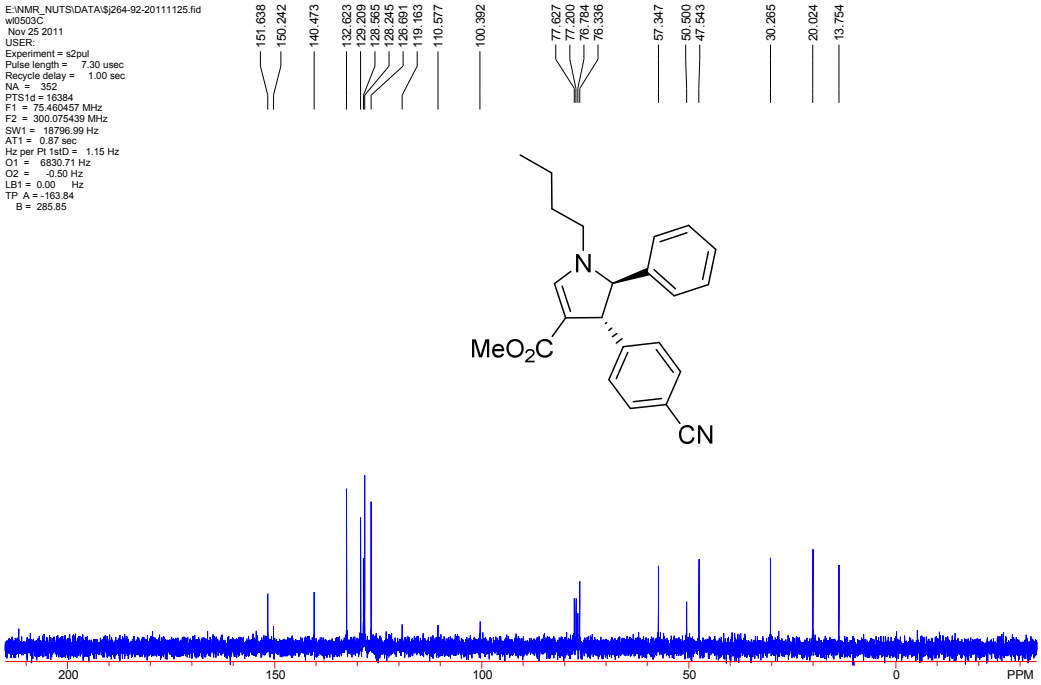
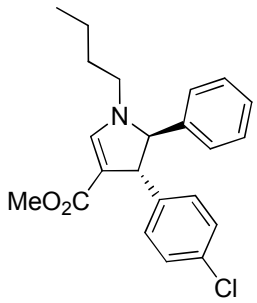


Fig. S-85: ^{13}C Spectra of compound **6r**



Chemical Formula: $C_{22}H_{24}ClNO_2$
Exact Mass: 369.15
Molecular Weight: 369.88

6s

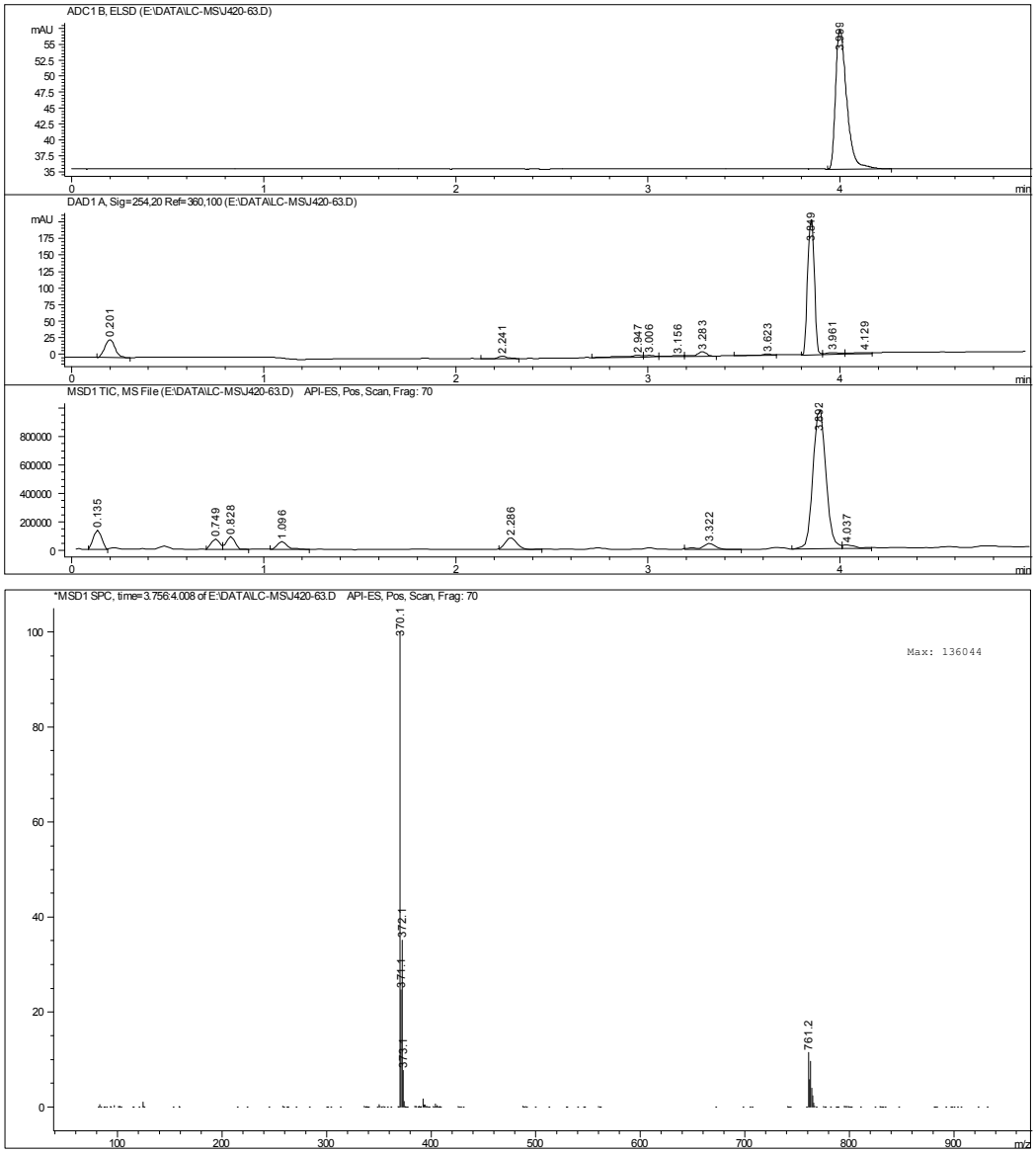


Fig. S-86: LC-MS-ELSD of compound **6s**

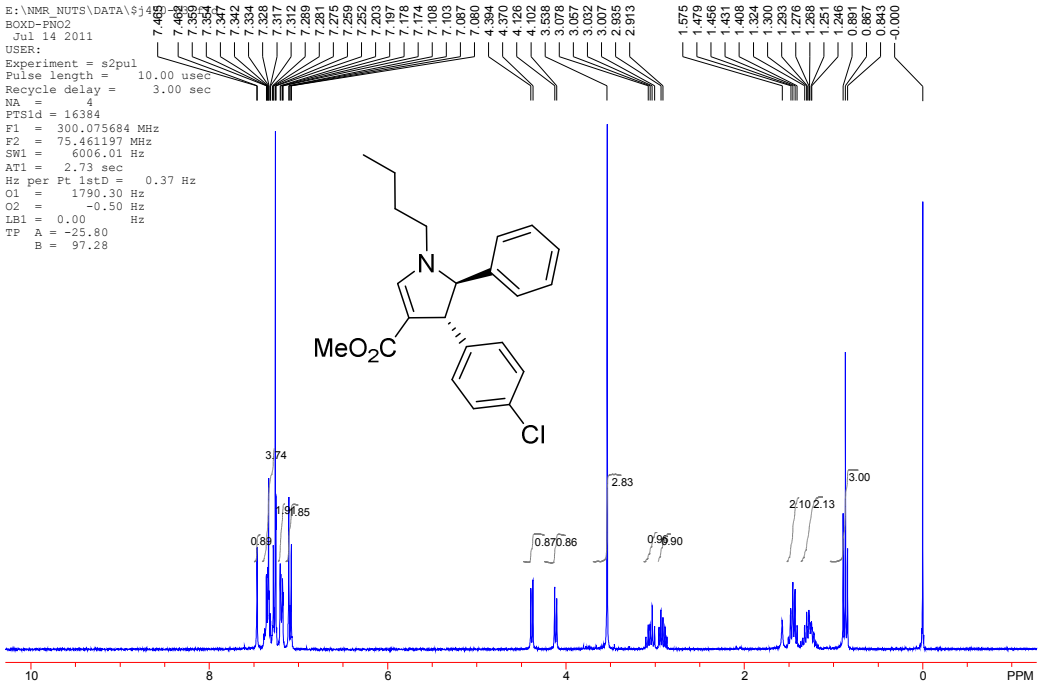


Fig. S-87: ^{1}H Spectra of compound **6s**

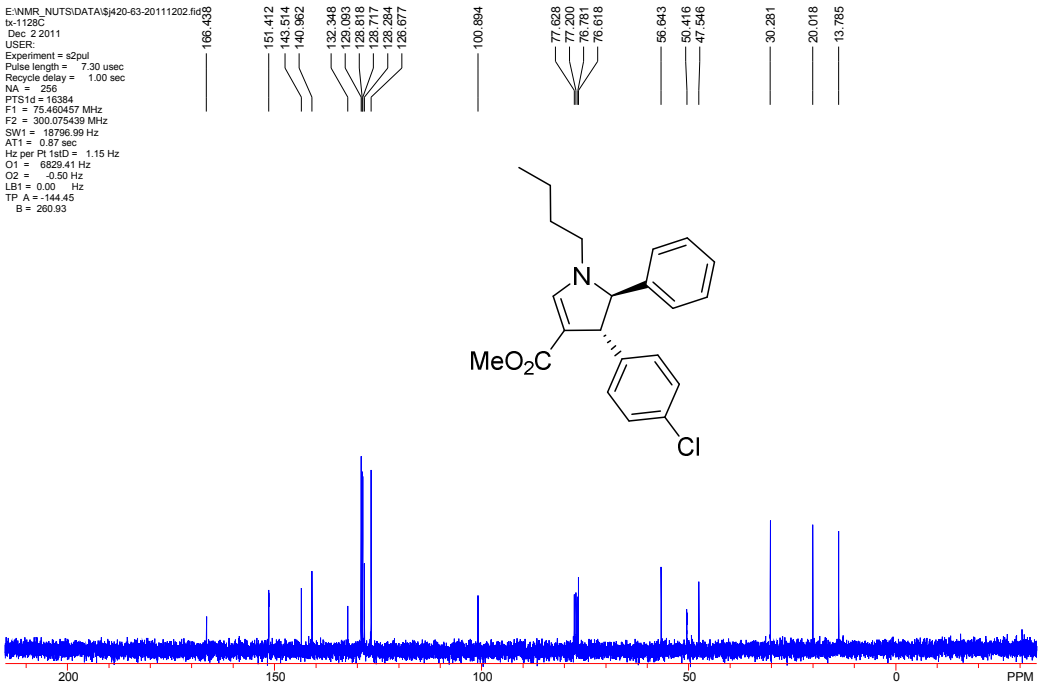
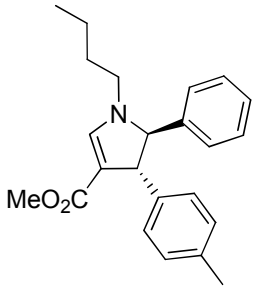


Fig. S-88: ^{13}C Spectra of compound **6s**



Chemical Formula: $C_{23}H_{27}NO_2$
Exact Mass: 349.20
Molecular Weight: 349.47

6t

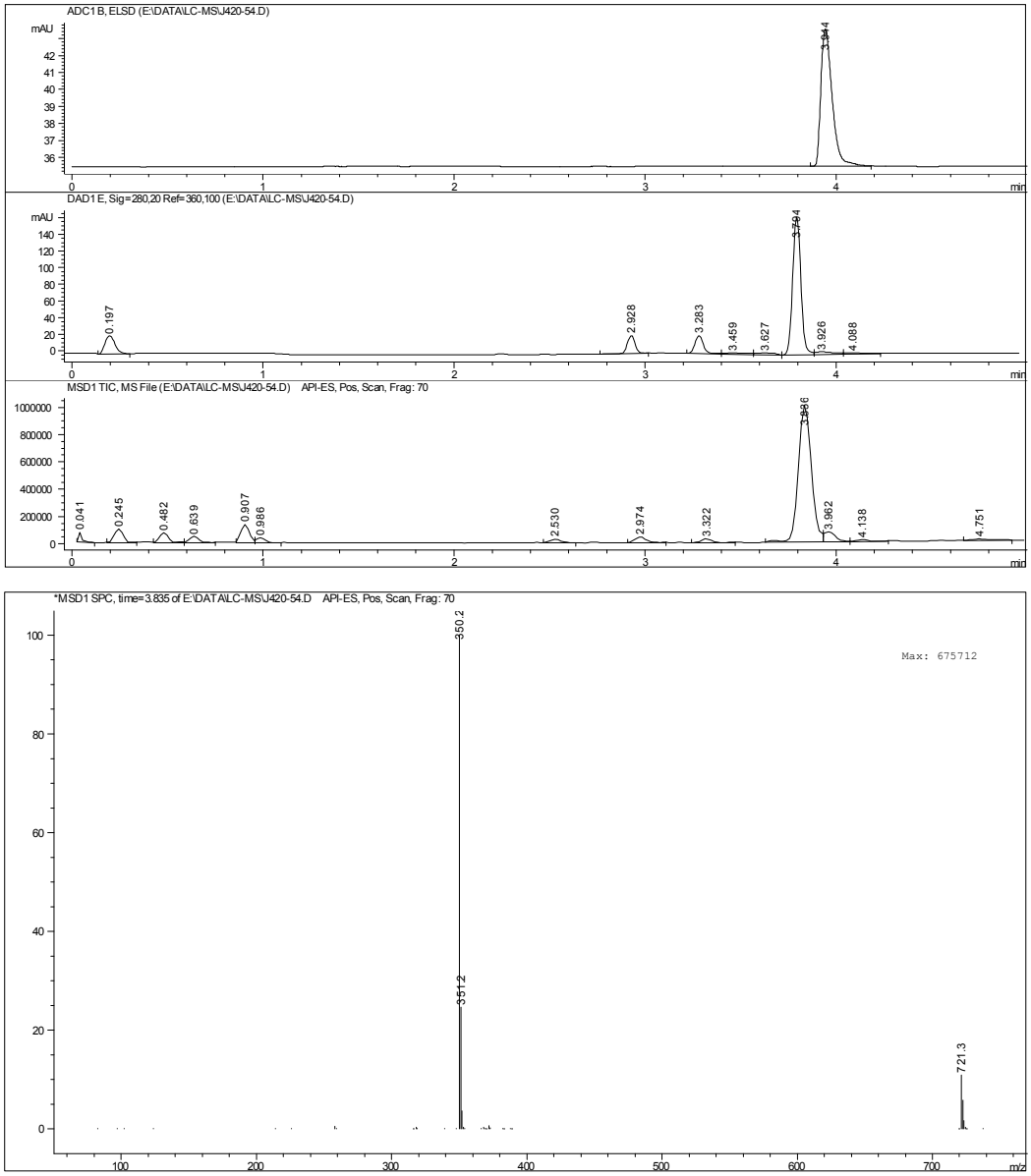


Fig. S-89: LC-MS-ELSD of compound **6t**

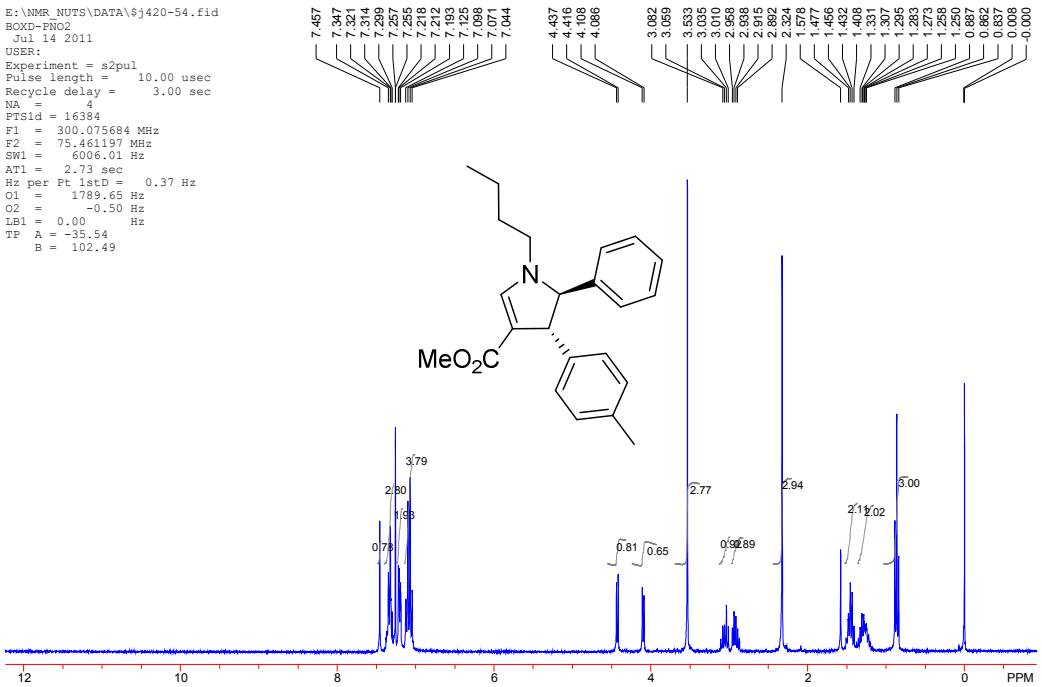


Fig. S-90: ^{1}H Spectra of compound **6t**

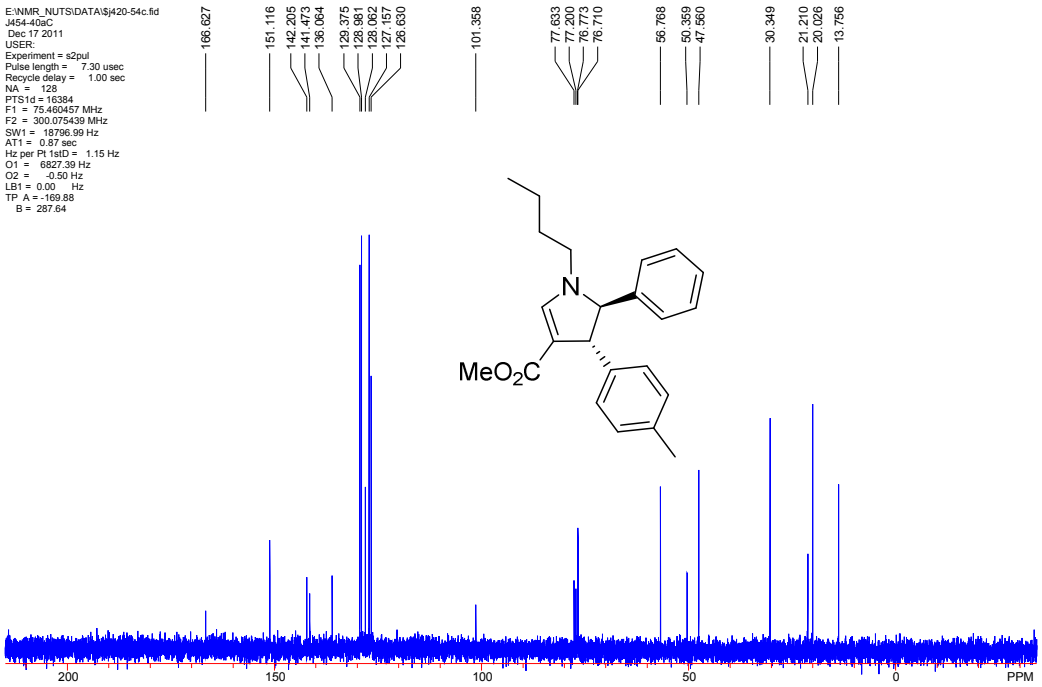
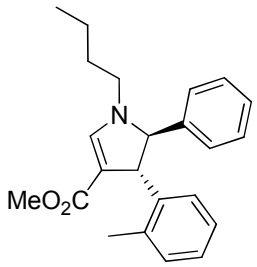


Fig. S-91: ^{13}C Spectra of compound **6t**



Chemical Formula: $C_{23}H_{27}NO_2$
Exact Mass: 349.20
Molecular Weight: 349.47

6u

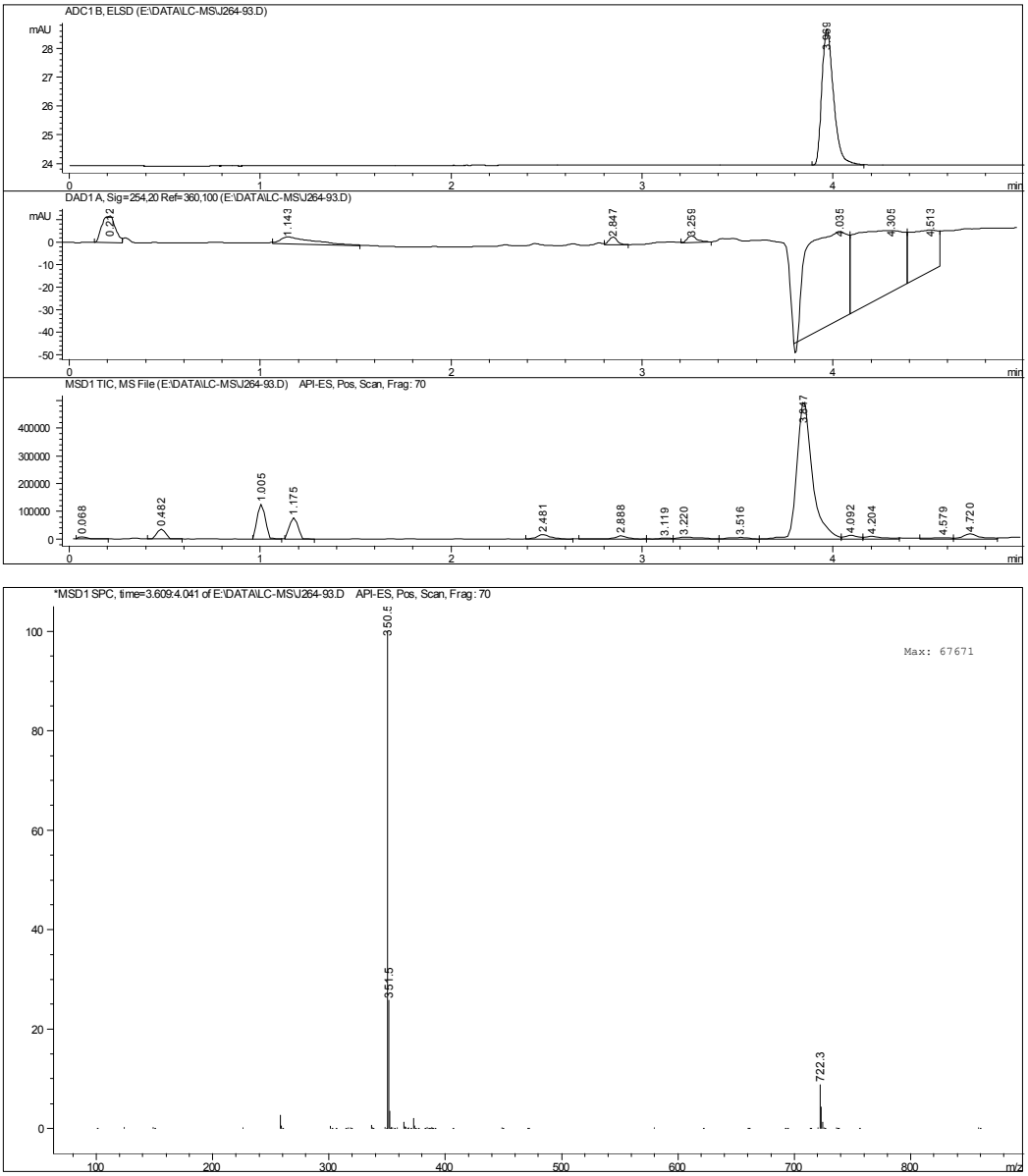


Fig. S-92: LC-MS-ELSD of compound **6u**

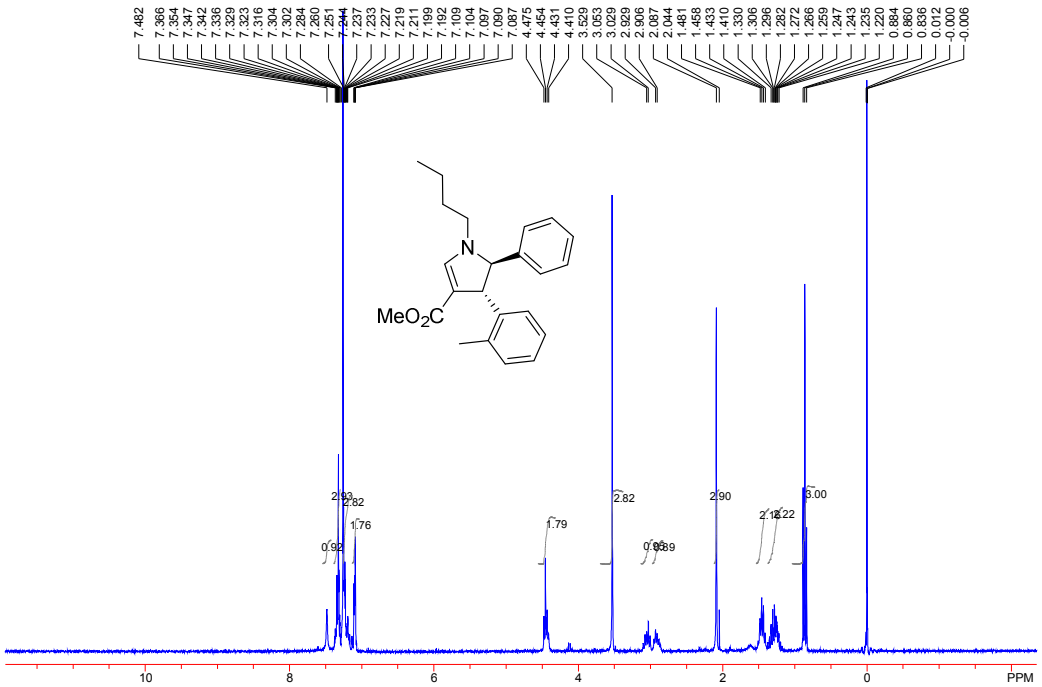


Fig. S-93: ^{1}H Spectra of compound **6u**

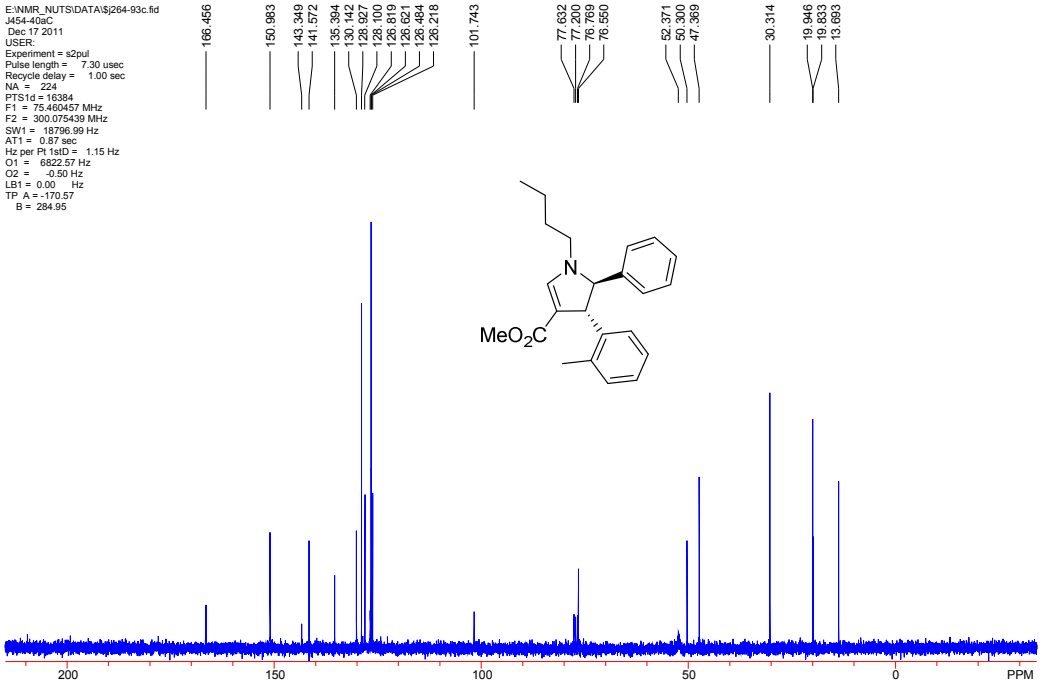
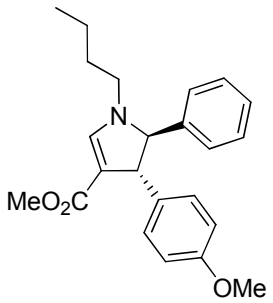


Fig. S-94: ^{13}C Spectra of compound **6u**



Chemical Formula: $C_{23}H_{27}NO_3$
Exact Mass: 365.20
Molecular Weight: 365.47

6v

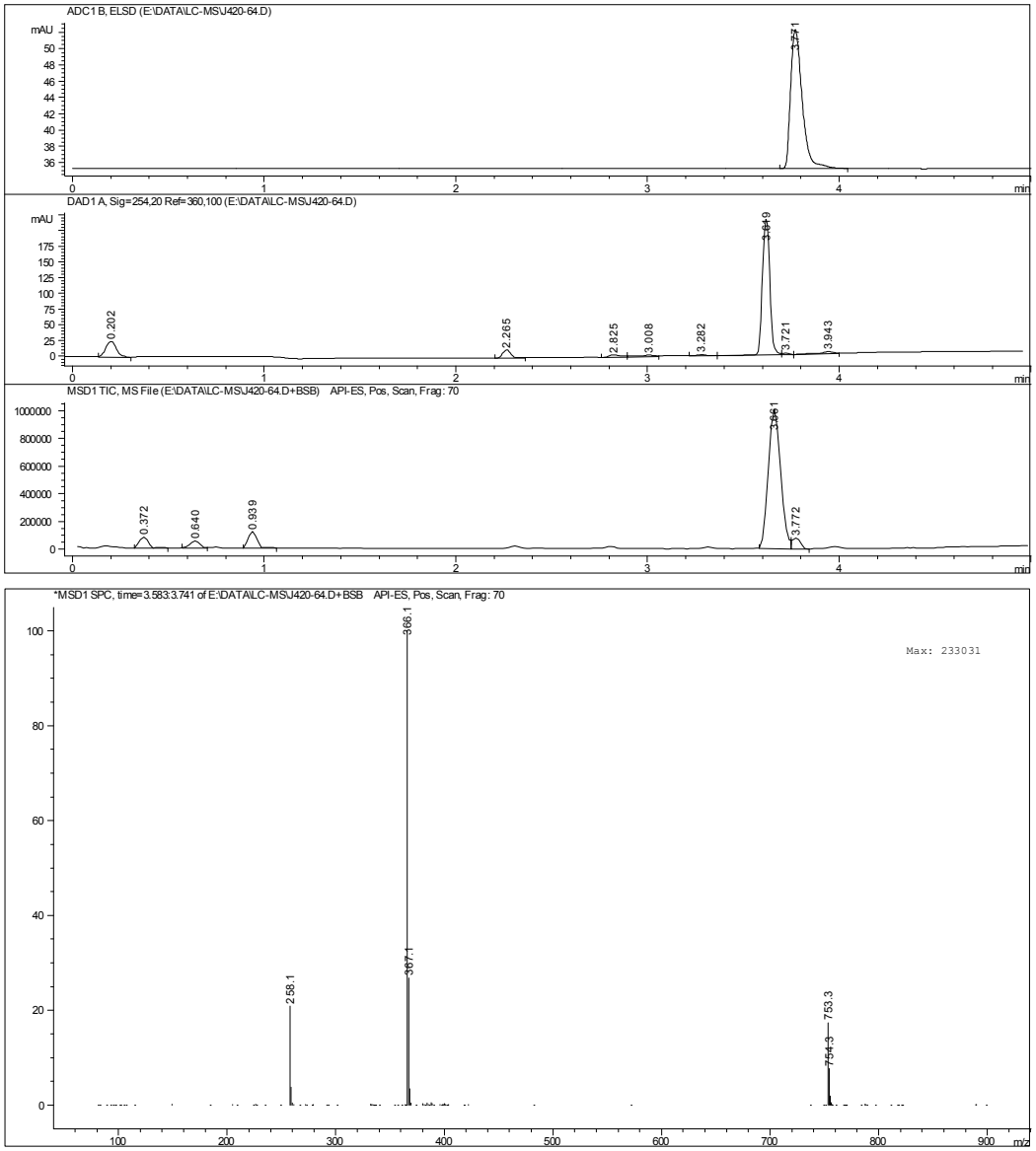


Fig. S-95: LC-MS-ELSD of compound **6v**

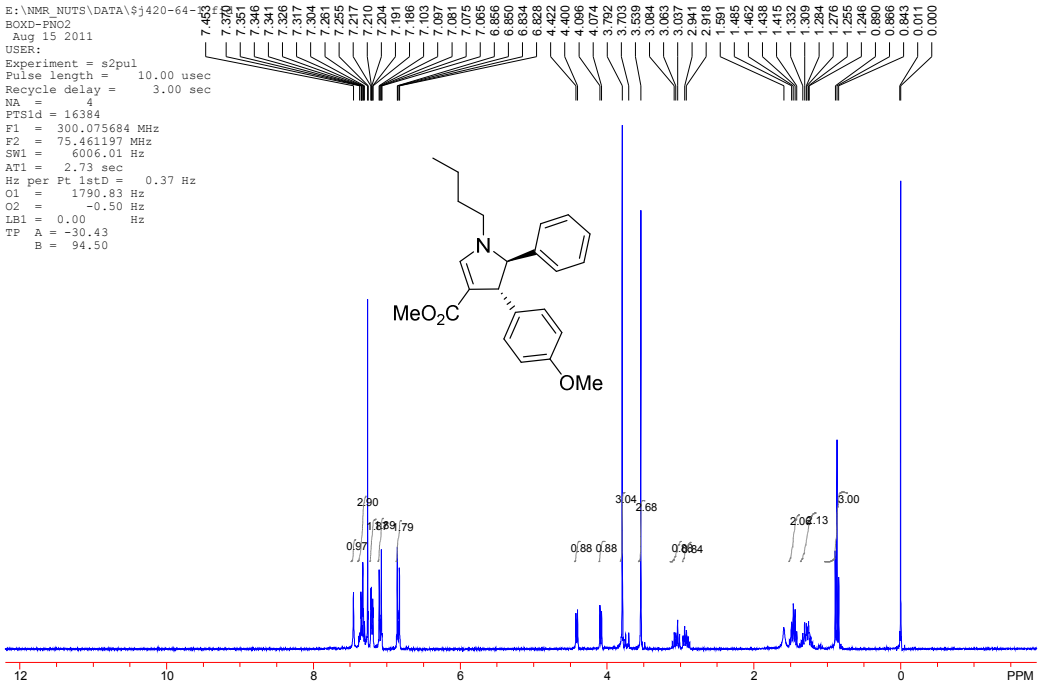


Fig. S-96: ^{1}H Spectra of compound **6v**

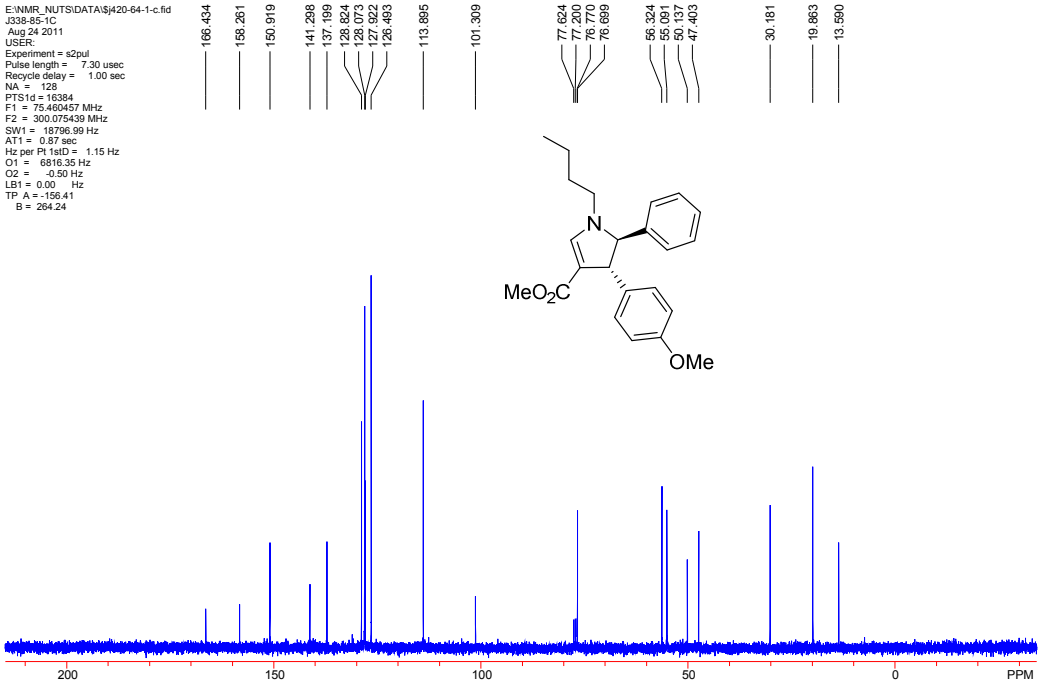
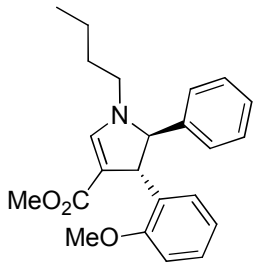


Fig. S-97: ^{13}C Spectra of compound **6v**



Chemical Formula: $C_{23}H_{27}NO_3$
Exact Mass: 365.20
Molecular Weight: 365.47

6w

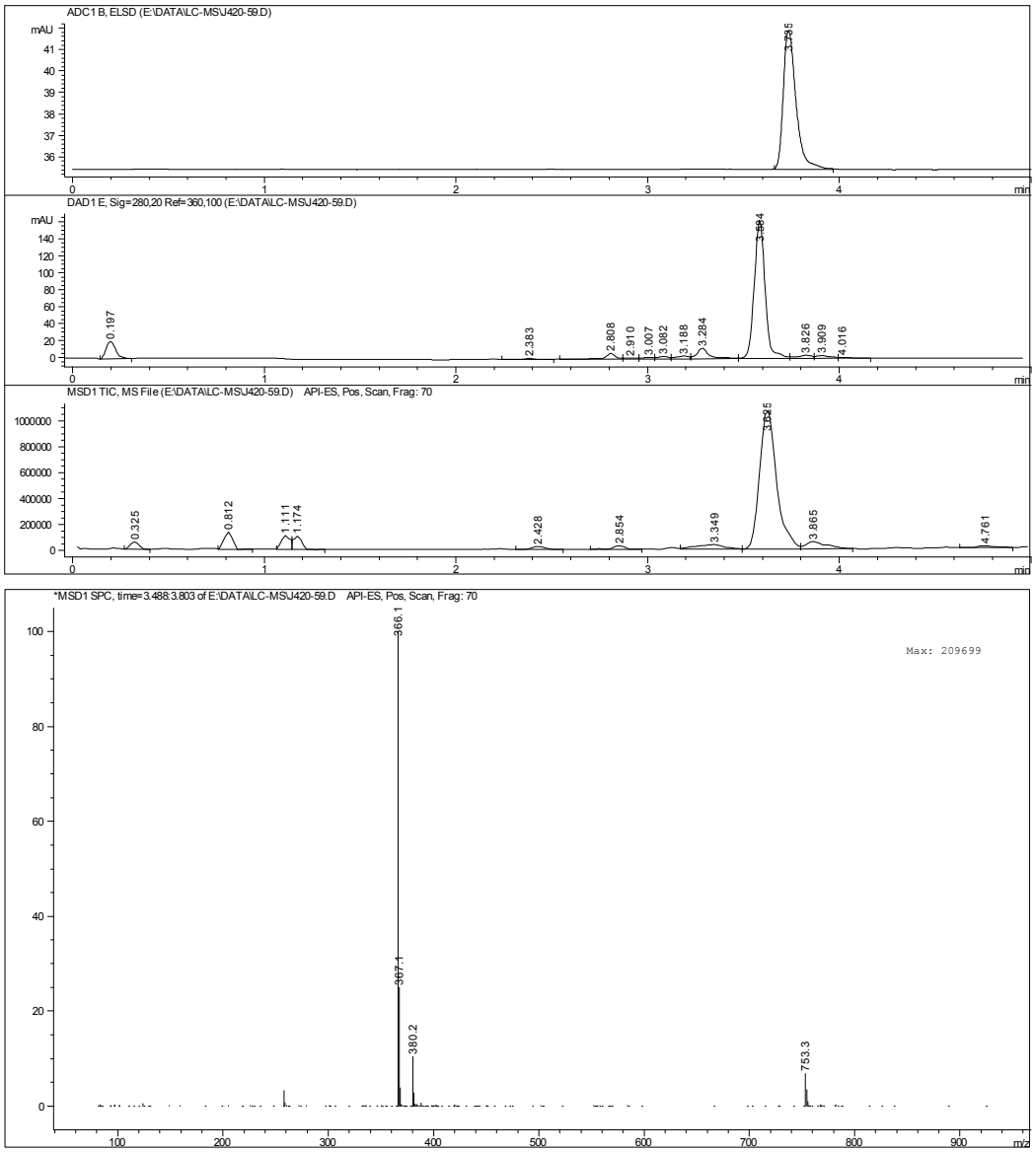


Fig. S-98: LC-MS-ELSD of compound **6w**

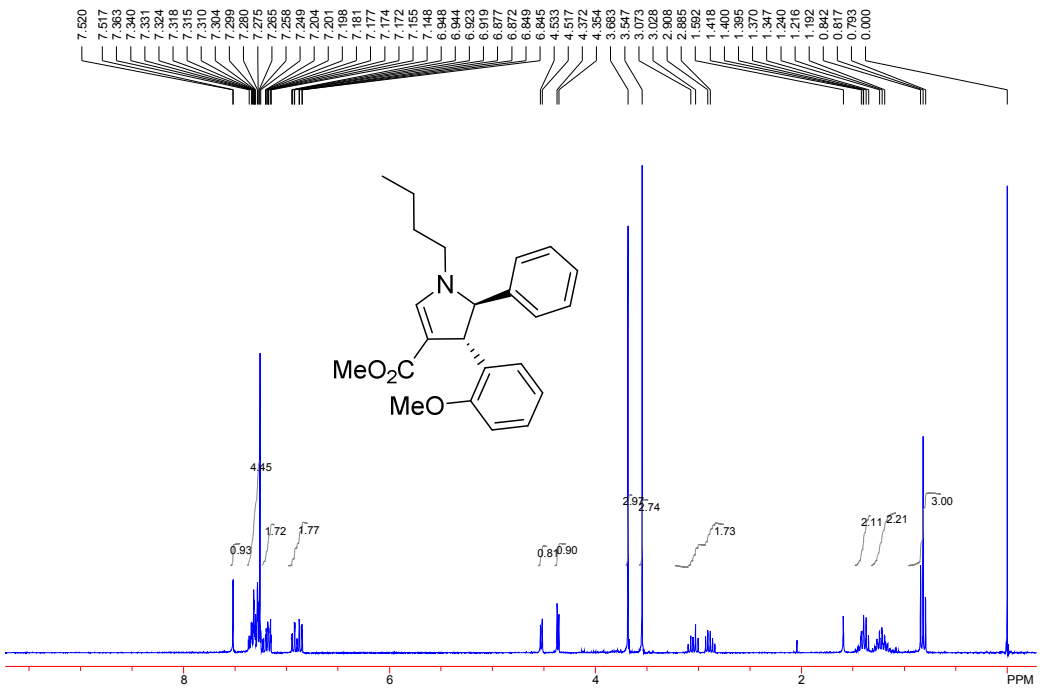


Fig. S-99: ^{1}H Spectra of compound **6w**

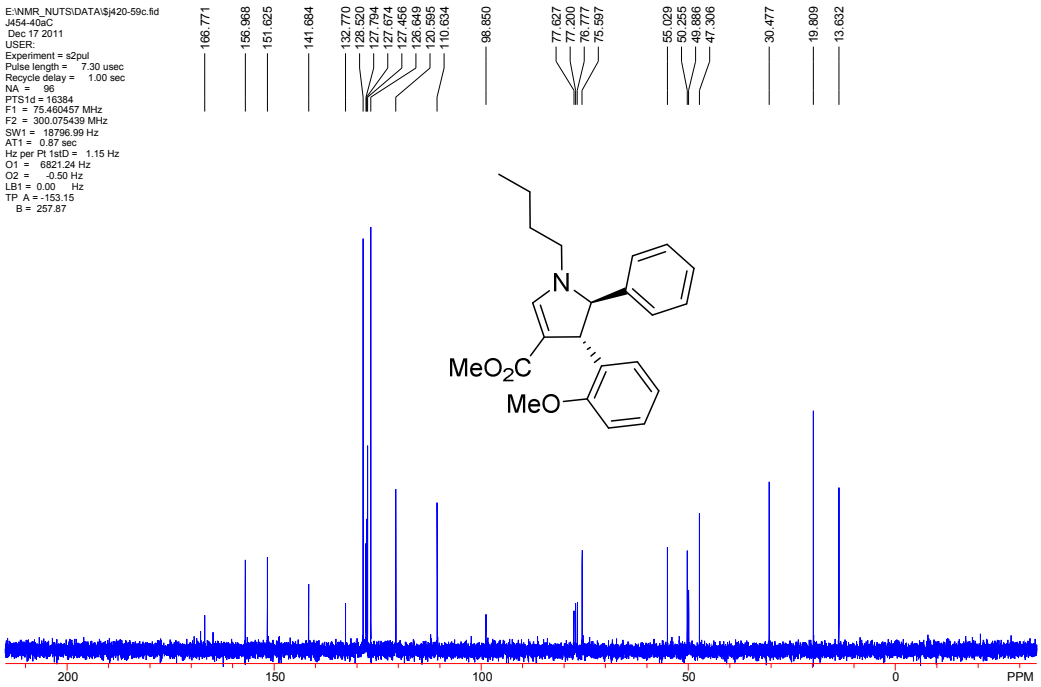
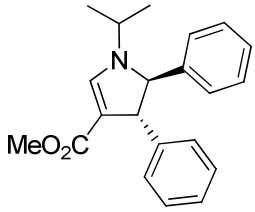


Fig. S-100: ^{13}C Spectra of compound **6w**



Chemical Formula: $C_{21}H_{23}NO_2$
Exact Mass: 321.17
Molecular Weight: 321.41

6x

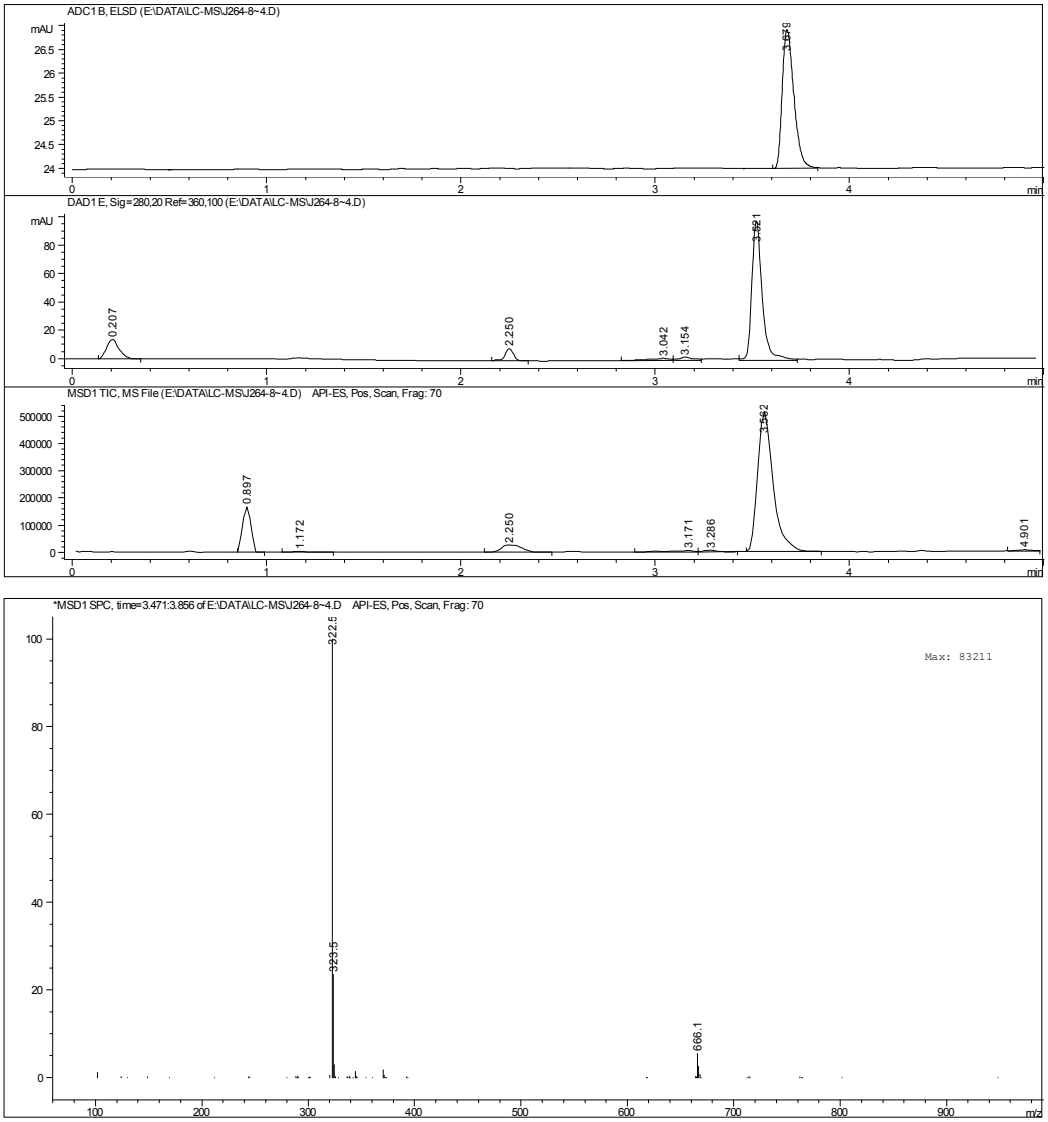


Fig. S-101: LC-MS-ELSD of compound **6x**

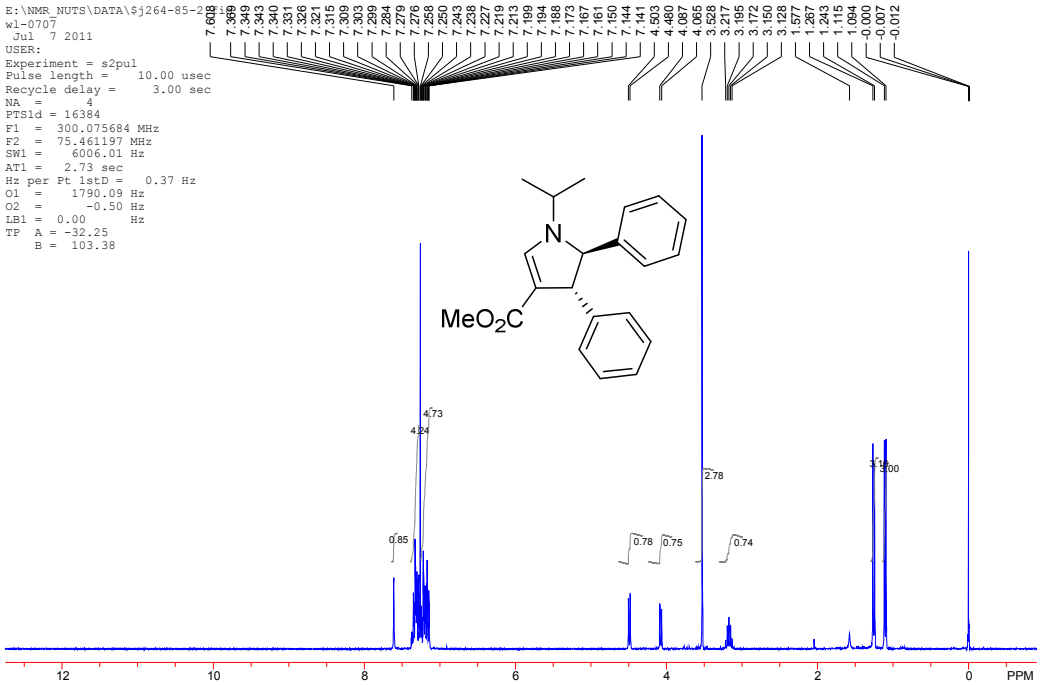


Fig. S-102: ^{1}H Spectra of compound **6x**

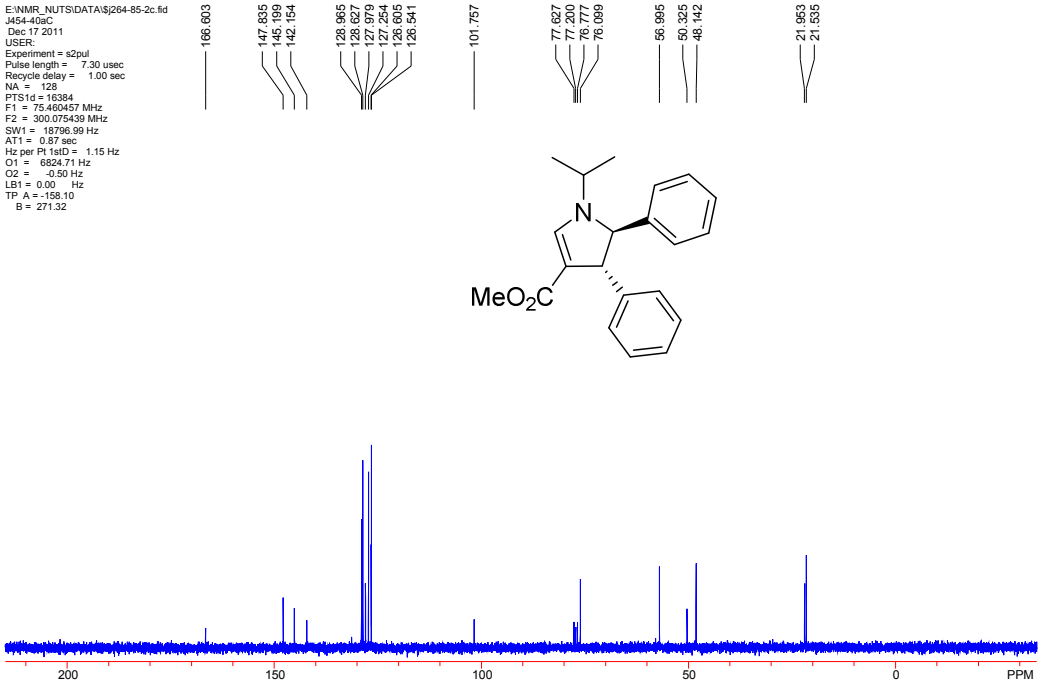
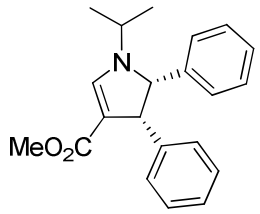


Fig. S-103: ^{13}C Spectra of compound **6x**



Chemical Formula: $C_{21}H_{23}NO_2$
Exact Mass: 321.17
Molecular Weight: 321.41

8x

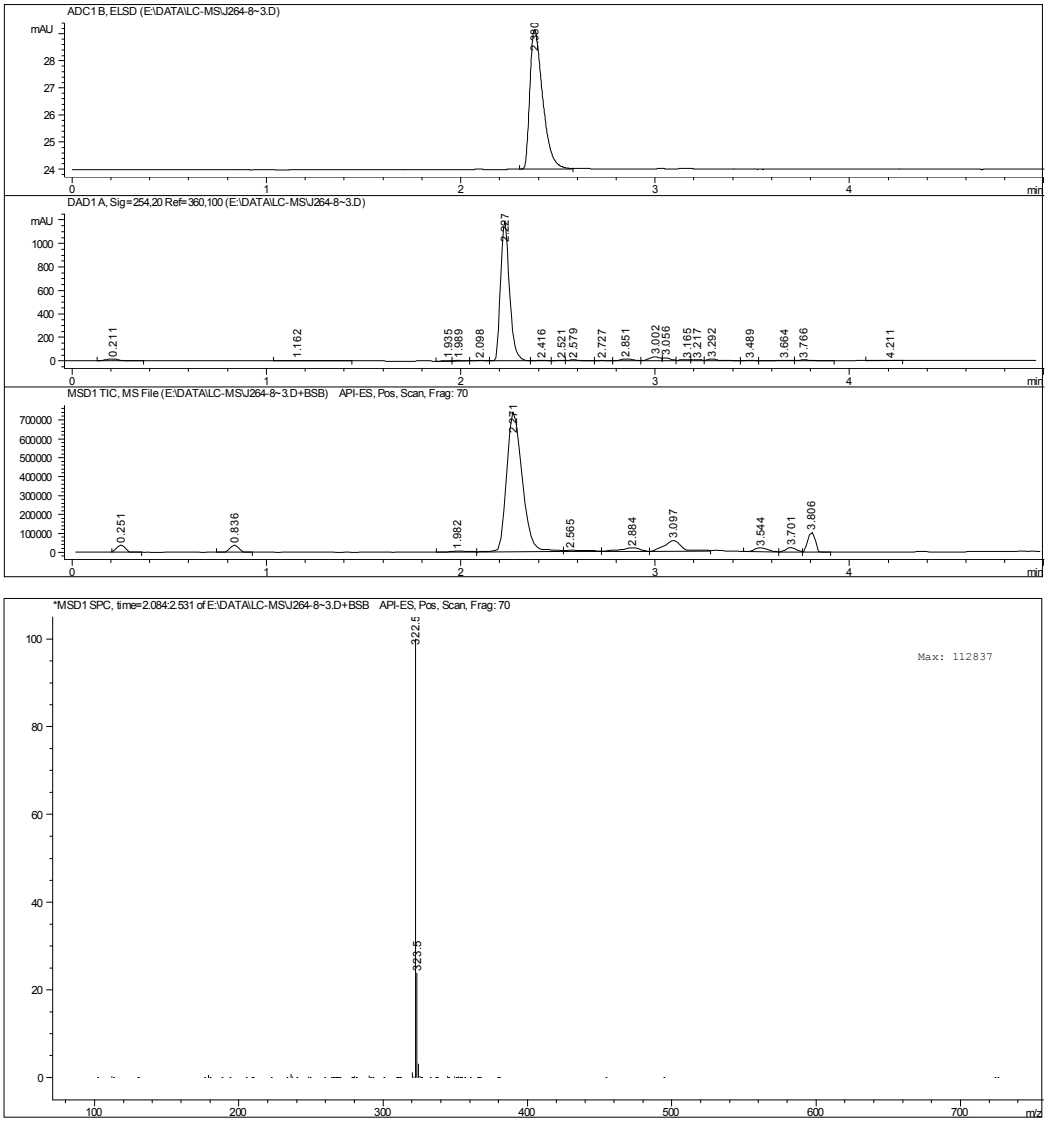


Fig. S-104: LC-MS-ELSD of compound **8x**

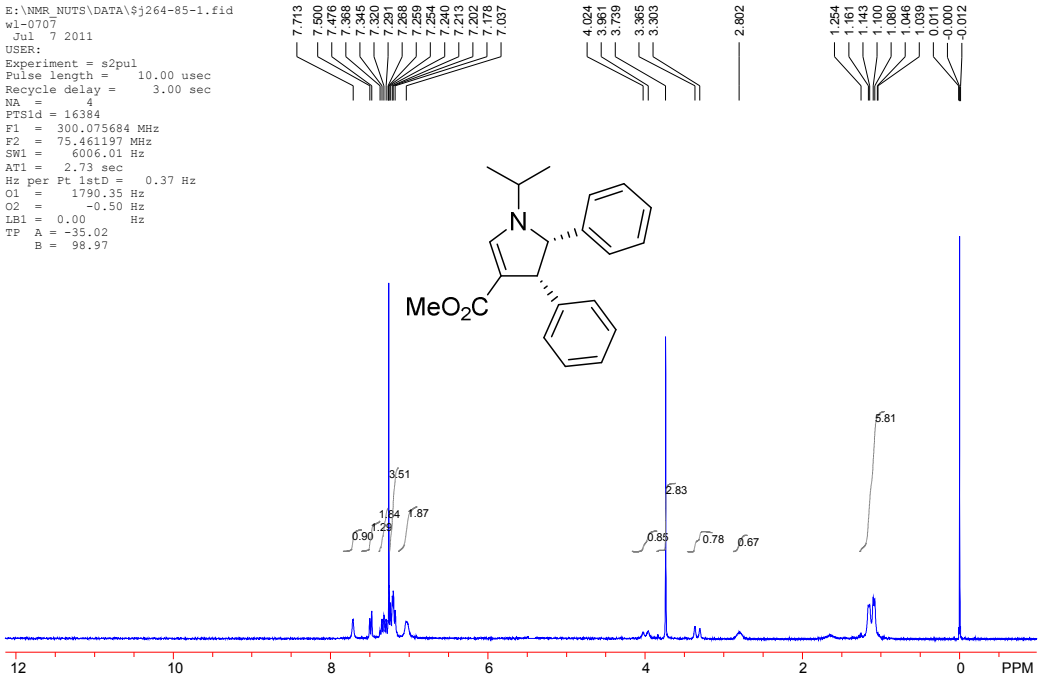


Fig. S-105: ^{1}H Spectra of compound **8x**

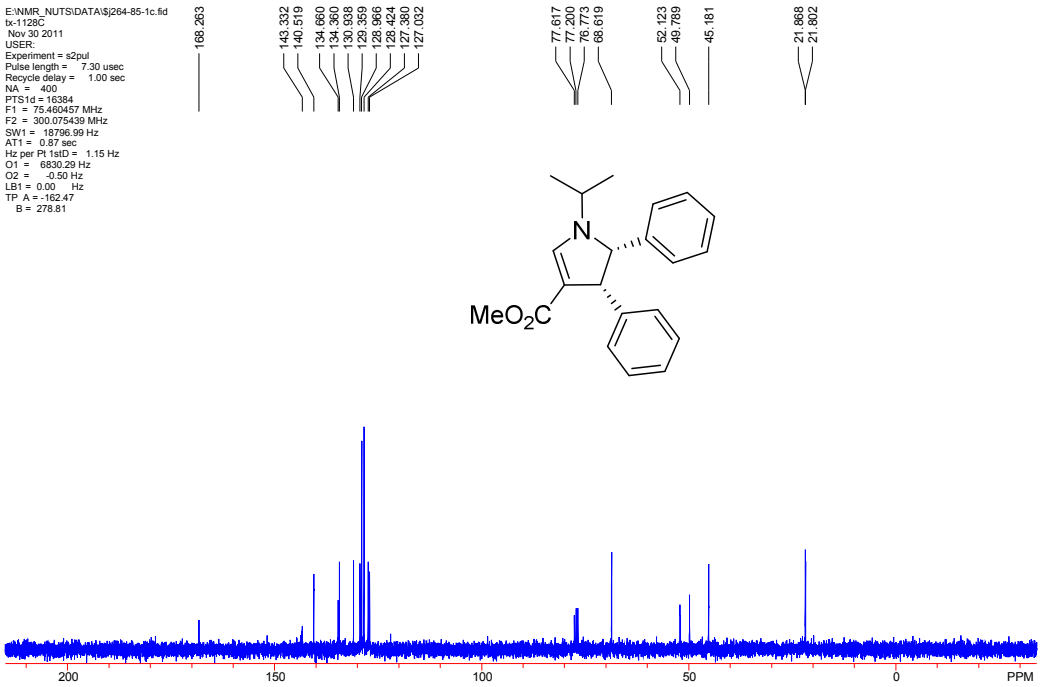
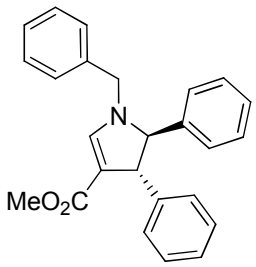


Fig. S-106: ^{13}C Spectra of compound **8x**



Chemical Formula: $C_{25}H_{23}NO_2$
Exact Mass: 369.17
Molecular Weight: 369.46

6y

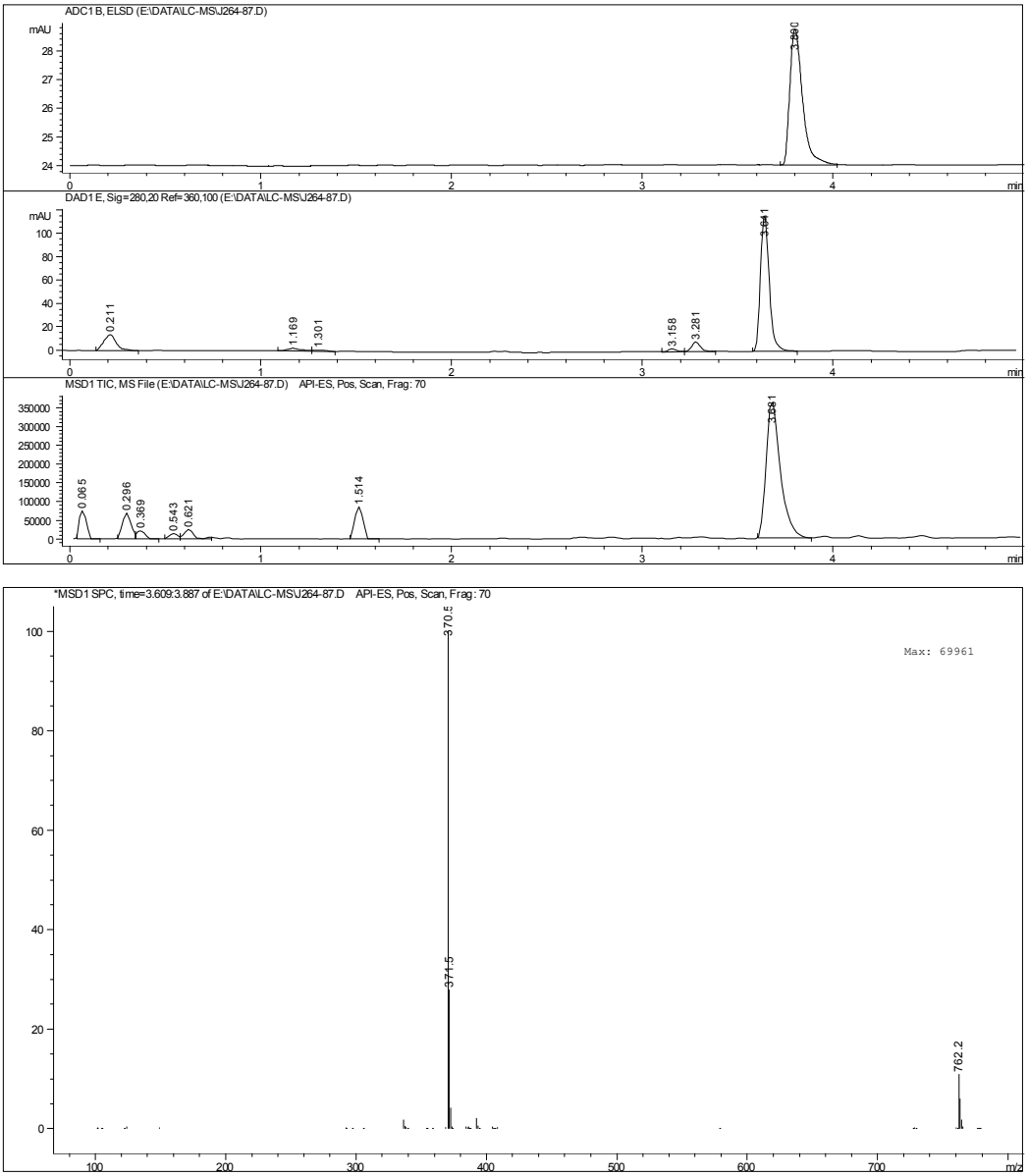


Fig. S-107: LC-MS-ELSD of compound **6y**

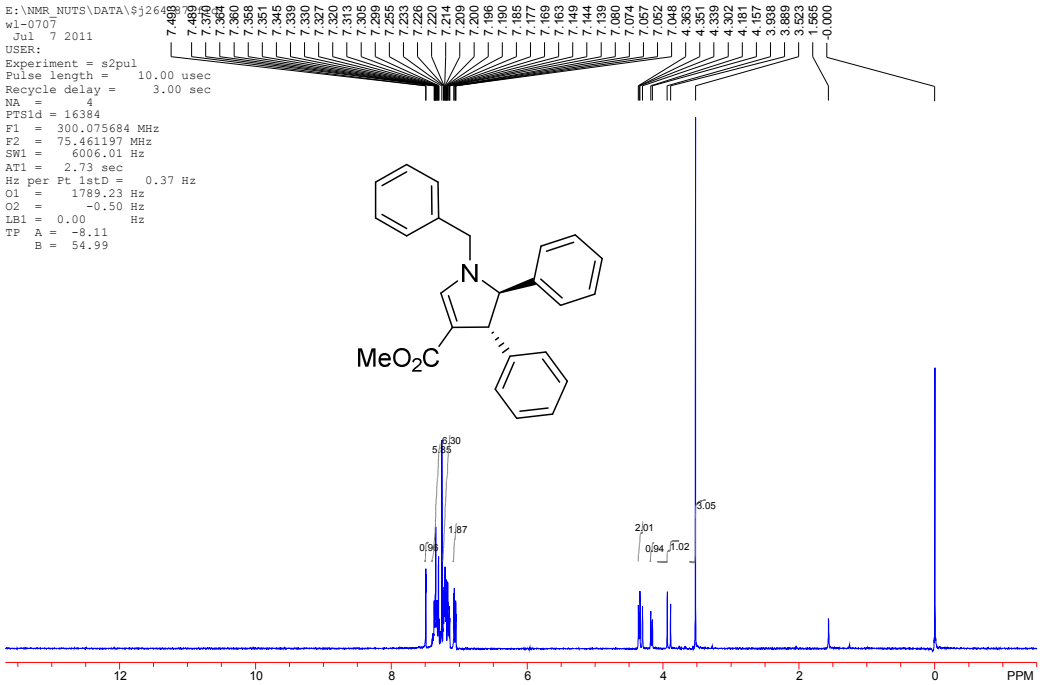


Fig. S-108: ^{1}H Spectra of compound **6y**

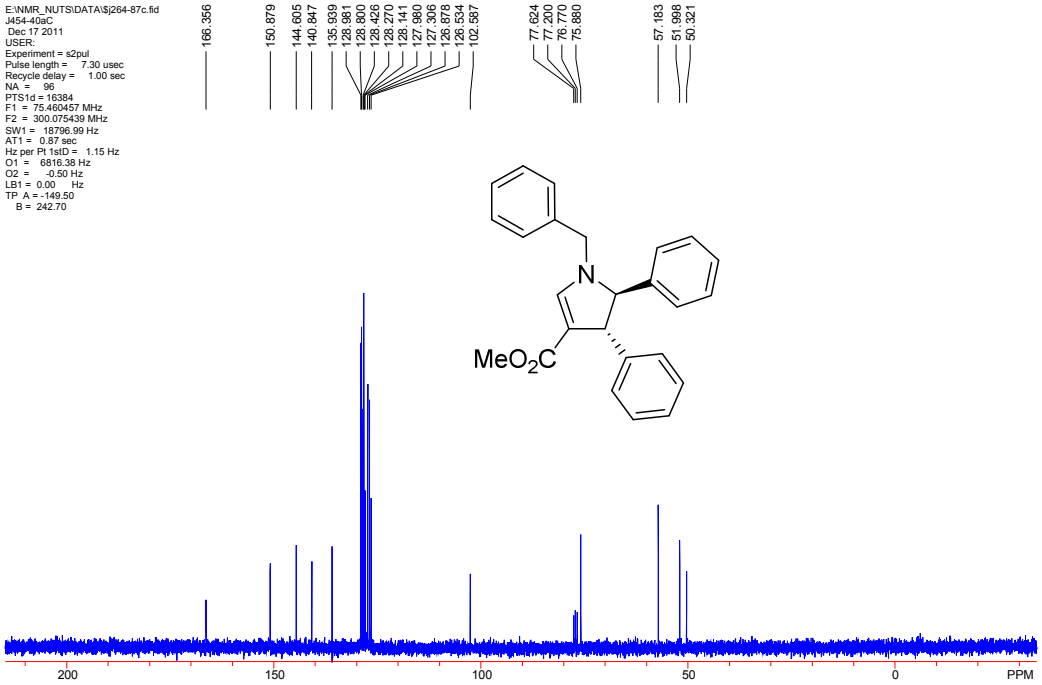
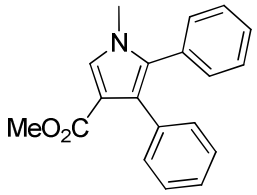


Fig. S-109: ^{13}C Spectra of compound **6y**



Chemical Formula: $C_{19}H_{17}NO_2$
Exact Mass: 291.13
Molecular Weight: 291.34

10a

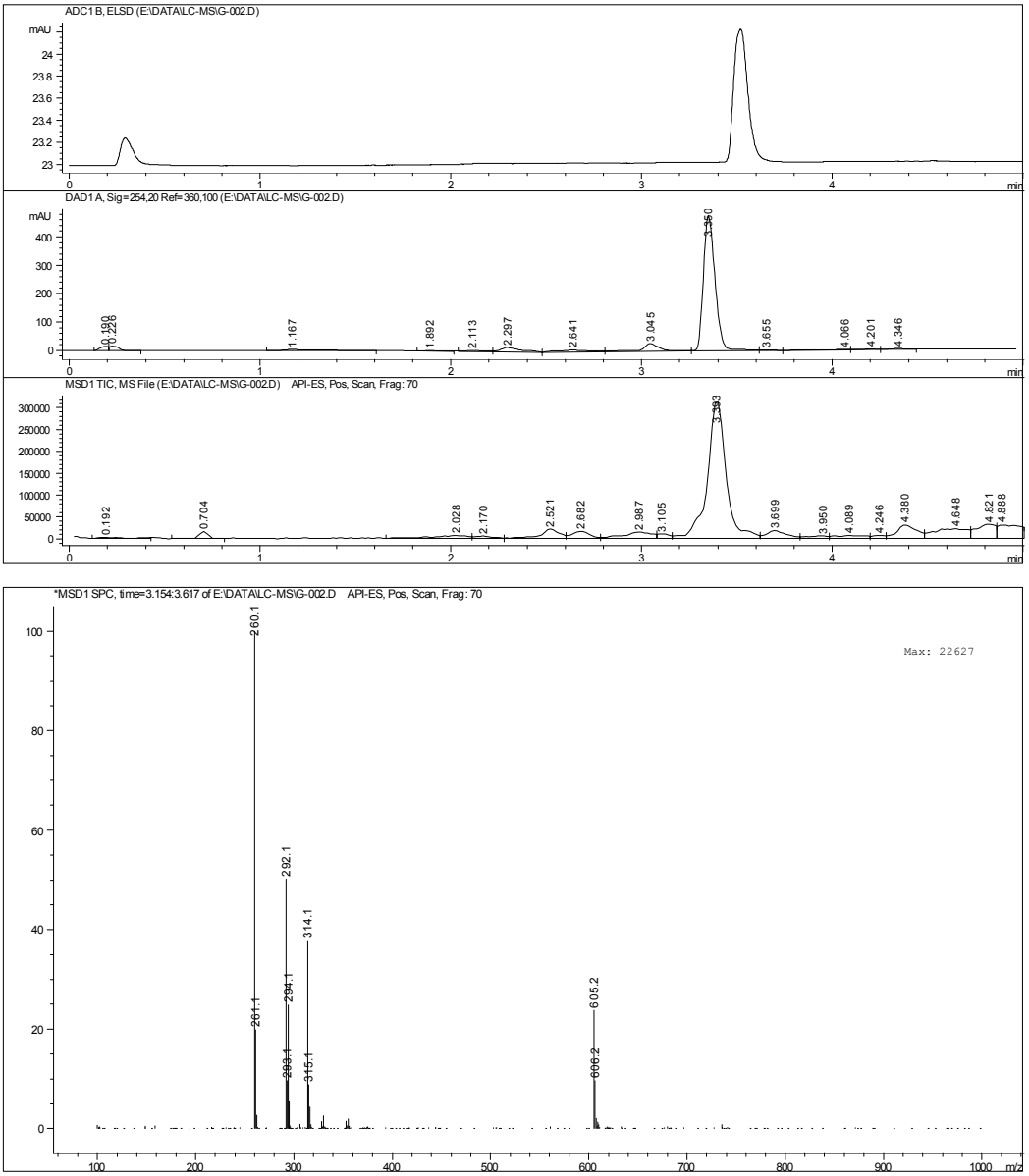


Fig. S-110: LC-MS-ELSD of compound **10a**

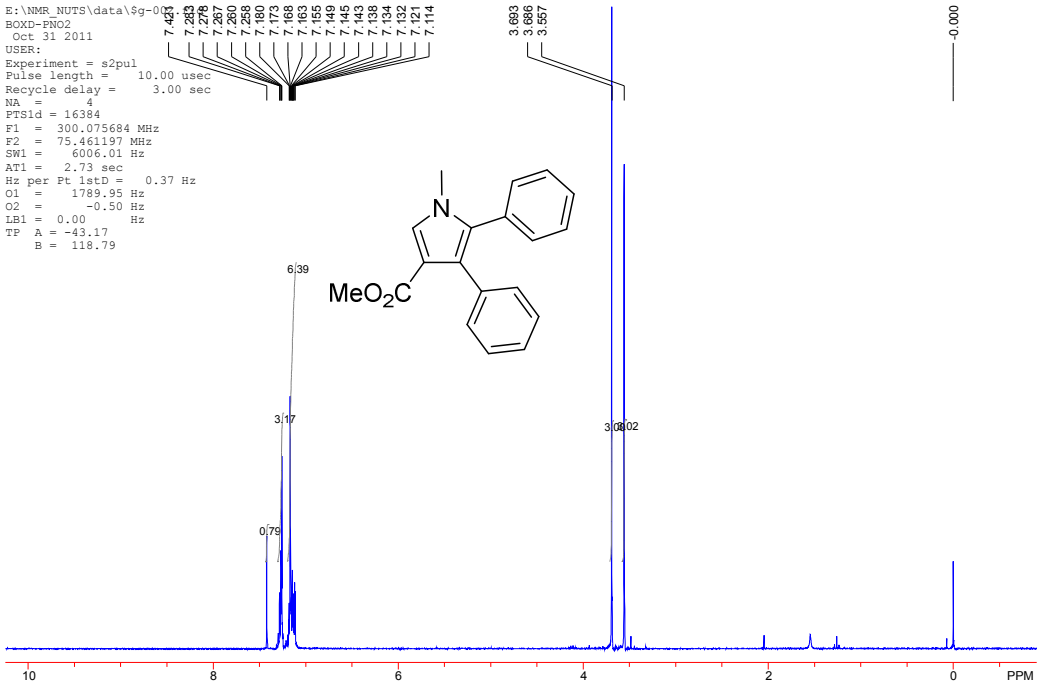


Fig. S-111: ^{1}H Spectra of compound **10a**

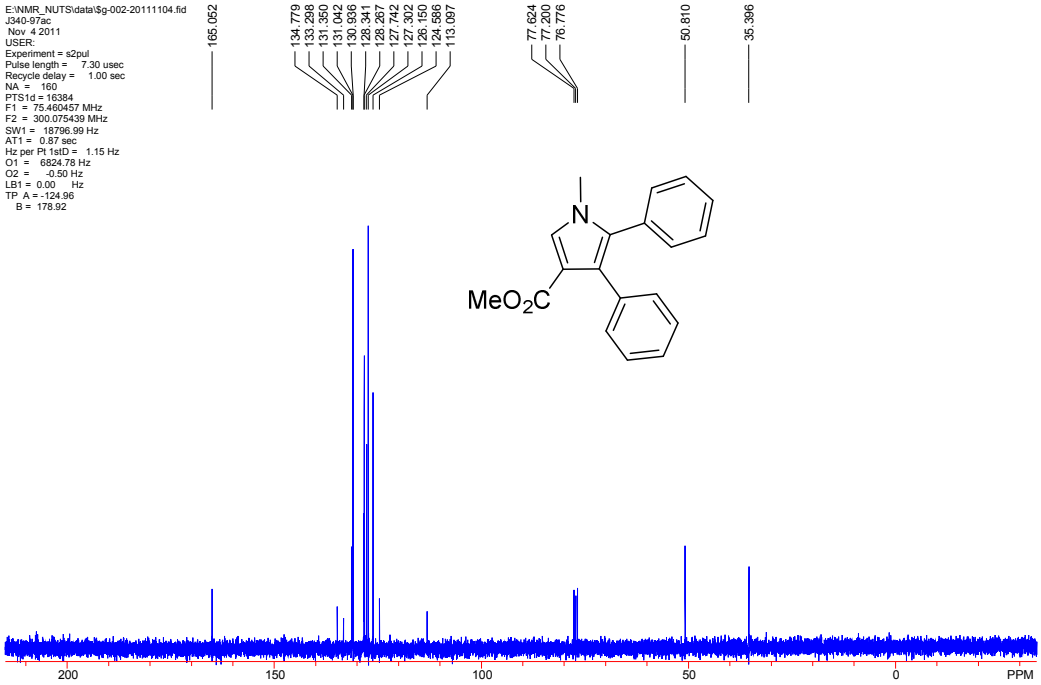
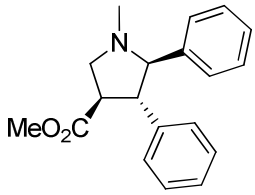


Fig. S-112: ^{13}C Spectra of compound **10a**



Chemical Formula: $C_{19}H_{21}NO_2$
Exact Mass: 295.16
Molecular Weight: 295.38

11a

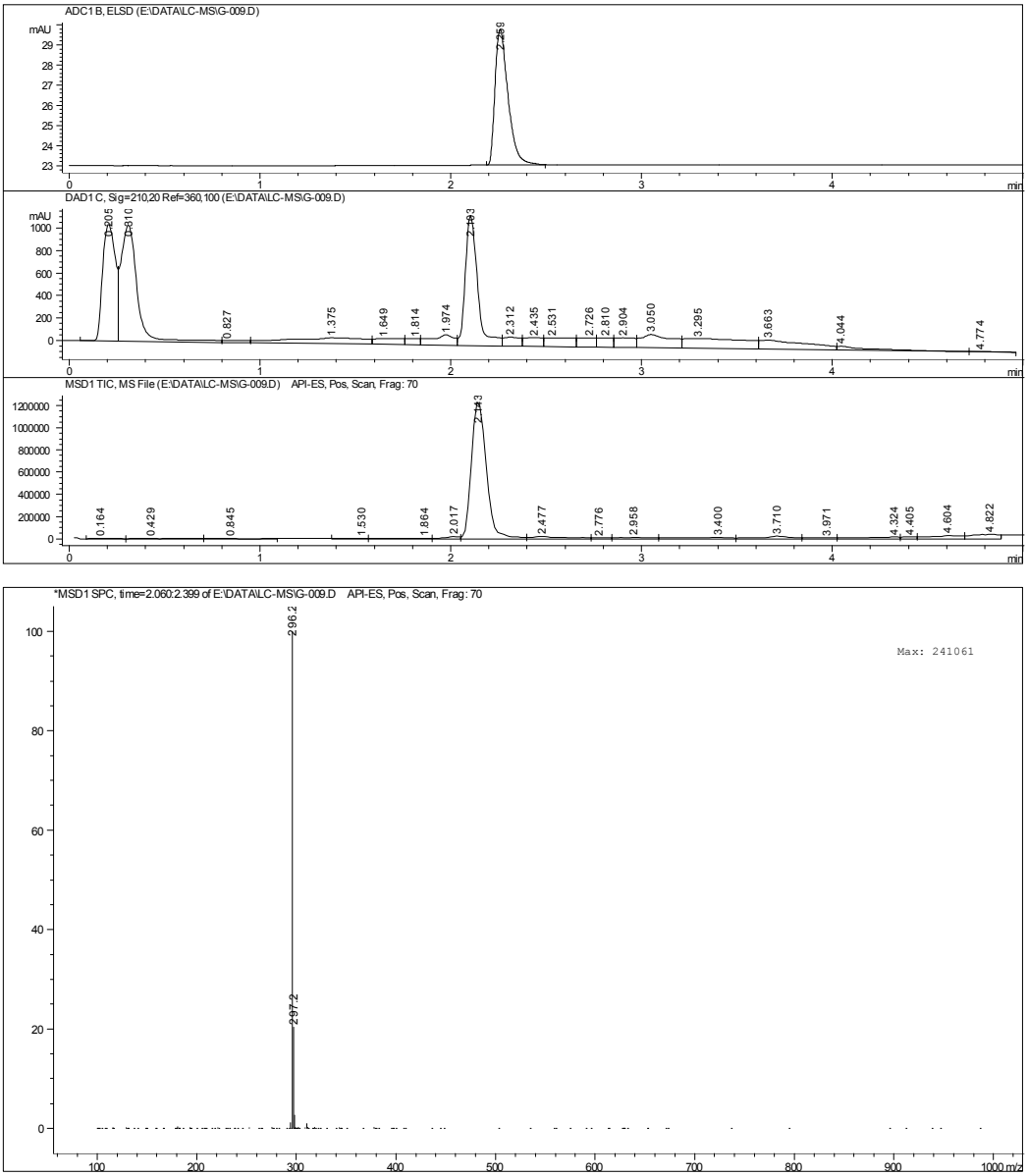


Fig. S-113: LC-MS-ELSD of compound **11a**

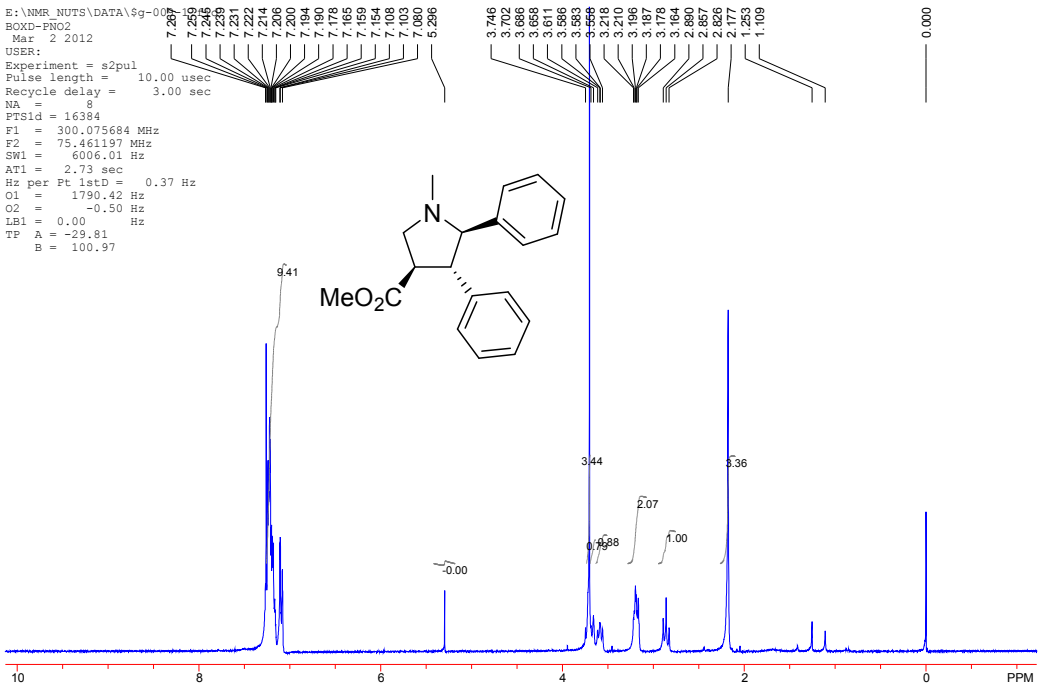


Fig. S-114: ^{1}H Spectra of compound **11a**

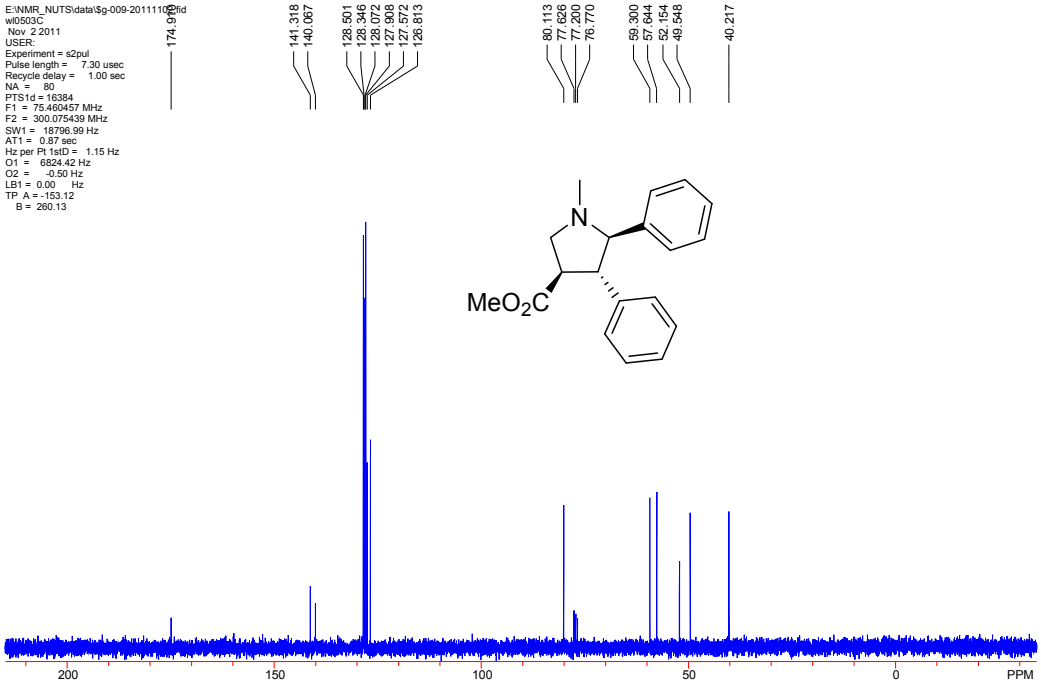


Fig. S-115: ^{13}C Spectra of compound **11a**