Supporting Information

for

Copper(II) Triflate-Catalyzed Amination and Aziridination of 2-Alkyl Substituted 1,3-Dicarbonyl Compounds

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Control Experiment Procedure for Cu(II)-Catalyzed Aziridination of 5r to 2r (Scheme 2)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (0.6 mmol, 224 mg), and **5r** (0.5 mmol, 90 μL) was added. The reaction mixture was stirred for a further 3 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^1H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Cu(II)-Catalyzed Aziridination and Amination of 5r to 2r and 3r (Scheme 2)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (0.6 mmol, 224 mg), and **5r** (0.5 mmol, 90 μL) was added. The reaction mixture was stirred for a further 4 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^1H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave a mixture of the title compounds.

Control Experiment Procedure for Cu(II)-Catalyzed Aziridination of 3r to 2r (Scheme 2)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (0.6

mmol, 224 mg), and **3r** (0.5 mmol, 179 mg) was added. The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Cu(II)-Catalyzed Aziridination of 1g to 2g in the Presence of NH_2Ts (Scheme 3)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (1.5 mmol, 560 mg), H_2NTs (0.75 mmol, 128 mg) was added followed by **1g** (0.5 mmol, 81 μL). The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Cu(II)-Catalyzed Amination of 1g to 3g in the Presence of NH_2Ts (Scheme 3)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (0.6 mmol, 224 mg), H_2NTs (0.75 mmol, 128 mg) was added followed by **1g** (0.5 mmol, 81 μL). The reaction mixture stirred for a further 3 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Attempted Cu(II)-Catalyzed Amination of 5l (Scheme 4)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4 Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, $TsNH_2$ (0.6 mmol, 103 mg), and a solution of **5l** (0.5 mmol, 92 mg) in 0.5 mL of CH_2Cl_2 was added. The reaction mixture stirred for a further 4 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^1H NMR spectroscopy.

Control Experiment Procedure for Cu(II)-Catalyzed Amination of 5r to 3r (Scheme 4)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4 Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, $TsNH_2$ (0.6 mmol, 103 mg), and **5r** (0.5 mmol, 90 μL) was added. The reaction mixture stirred for a further 4 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^1H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Attempted Cu(II)-Catalyzed Amination of 5t (Scheme 4)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4 Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, $TsNH_2$ (0.6 mmol, 103 mg), and a solution of **5t** (0.5 mmol, 117 mg) in 0.5 mL of CH_2Cl_2 was added. The reaction mixture stirred for a further 7 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^1H NMR spectroscopy.

Control Experiment Procedure for Cu(II)-Catalyzed Amination of 1r to 3r in the Presence of BHT (Scheme 5, eq 1)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (1 mmol, 373 mg), BHT (0.75 mmol, 165 mg) was added followed by **1r** (0.5 mmol, 94 μL). The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Cu(II)-Catalyzed Amination of 5r to 3r in the Presence of BHT (Scheme 5, eq 1)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (1 mmol, 373 mg), BHT (0.75 mmol, 165 mg) was added followed by **5r** (0.5 mmol, 90 μL). The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Cu(II)-Catalyzed Aziridination of 3r to 2r in the Presence of BHT (Scheme 5, eq 2)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of, PhI=NTs (1 mmol, 373 mg), BHT (0.75 mmol, 165 mg or 1.5 mmol, 330 mg) was added followed by **3r** (0.5 mmol,

179 mg). The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy. Purification by flash column chromatography (4:1 *n*-hexanes/EtOAc as eluent) gave the title compound.

Control Experiment Procedure for Attempted Cu(II)-Catalyzed Aziridination of 3r in the Presence of TEMPO (Scheme 5, eq 2)

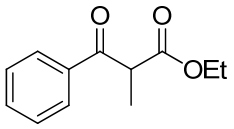
To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (1 mmol, 373 mg), TEMPO (0.75 mmol, 117 mg) was added followed by **3r** (0.5 mmol, 179 mg). The reaction mixture stirred for a further 18 h at room temperature. After that, the reaction was filtered through Celite, washed with EtOAc (50 mL), and evaporated to dryness. The crude mixture was then analyzed by ^{1}H NMR spectroscopy.

Control Experiment Procedure for Measuring the Deuterium Kinetic Isotope Effect for Cu(II)-Catalyzed Amination of 1g and d_5-1g to 3g and d_5-3g (Scheme 6)

To a mixture of $Cu(OTf)_2$ (0.05 mmol, 18.1 mg), 1,10-phen (0.05 mmol, 9.9 mg), and powdered 4Å MS (400 mg) was added 2 mL of CH_2Cl_2. After 1 h of stirring, PhI=NTs (0.6 mmol, 224 mg) was added followed by a solution of **1g** (0.5 mmol, 81 μL) and d_5-**1g** (0.5 mmol, 83 μL). After 2 h, the solution was assayed by GC-MS analysis.

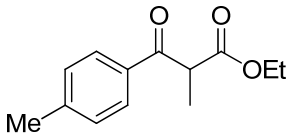
Spectroscopy Data

Ethyl 2-methyl-3-oxo-3-phenylpropanoate (1a)[S1]



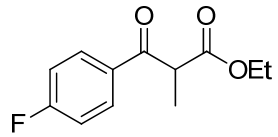
Pale yellow oil; ^{1}H NMR (400MHz): δ 7.98 (d, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (dd, J = 8.0, J = 7.2 Hz, 2H), 4.37 (q, J = 7.1 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 1.50 (d, J = 6.8 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): δ 195.9, 170.9, 135.9, 133.4, 128.7, 128.6, 61.4, 48.4, 14.0, 13.8; MS (ESI): *m/z* 207 $[M+H]^{+}$.

Ethyl 2-methyl-3-oxo-3-(*p*-tolyl)propanoate (1b)[S2]



Pale yellow oil; ^{1}H NMR: δ 7.88 (d, J = 7.8 Hz, 2H), 7.26 (d, J = 7.8 Hz, 2H), 4.37 (q, J = 7.1 Hz, 1H), 4.21-4.10 (m, 2H), 2.40 (s, 3H), 1.47 (d, J = 7.2 Hz, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 195.4, 170.9, 144.3, 133.4, 129.4, 128.7, 61.2, 48.1, 21.5, 13.9, 13.7; MS (ESI): *m/z* 221 $[M+H]^{+}$.

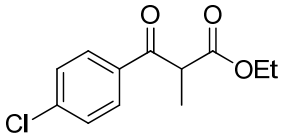
Ethyl 3-(4-fluorophenyl)-2-methyl-3-oxopropanoate (1c)



Pale yellow oil; ^{1}H NMR: δ 8.06-8.15 (m, 2H), 7.18-7.12 (m, 2H), 4.39 (q, J = 7.1 Hz, 1H), 4.15 (q, J = 7.2 Hz, 2H), 1.49 (d, J = 6.9 Hz, 3H), 1.17 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 194.2, 170.6, 167.5, 164.1, 132.3, 132.3, 131.3, 131.2, 116.0, 115.9, 115.6, 115.5, 61.3, 48.2, 13.8,

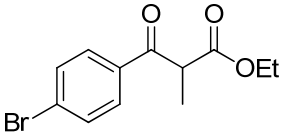
13.5; IR (NaCl, neat) *v*: 3078, 2986, 2940, 2909, 1728, 1682, 1597, 1504, 1226 cm^{-1}; HRMS (ESI): calcd. for $C_{12}H_{14}O_3F$ (M^++H): 225.0931, found: 225.0927.

Ethyl 3-(4-chlorophenyl)-2-methyl-3-oxopropanoate (1d)[S3]



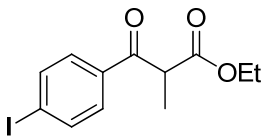
Pale yellow oil; ^{1}H NMR: δ 7.92 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 4.32 (q, J = 7.2 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.49 (d, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 194.6, 170.5, 139.9, 134.2, 130.0, 129.0, 61.4, 48.3, 13.9, 13.6; MS (ESI): *m/z* 241 $[M+H]^+$.

Ethyl 3-(4-bromophenyl)-2-methyl-3-oxopropanoate (1e)[S4]



Pale yellow oil; ^{1}H NMR: δ 7.85 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 7.8 Hz, 2H), 4.33 (q, J = 7.2 Hz, 1H), 4.14 (q, J = 7.2 Hz, 2H), 1.48 (d, J = 7.2 Hz, 3H), 1.17 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 194.7, 170.5, 134.6, 132.0, 130.1, 128.6, 61.4, 48.3, 14.0, 13.6; MS (ESI): *m/z* 285 $[M+H]^+$.

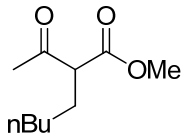
Ethyl 3-(4-iodophenyl)-2-methyl-3-oxopropanoate (1f)



Pale yellow oil; ^{1}H NMR: δ 7.79-7.52 (m, 2H), 7.64-7.60 (m, 2H), 4.21 (q, J = 7.1 Hz, 1H), 4.08 (q, J = 7.1 Hz, 2H), 1.41 (d, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 195.1,

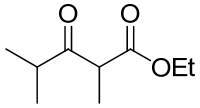
170.5, 138.0, 135.2, 130.0, 129.9, 101.6, 61.4, 48.2, 14.0, 13.6; IR (NaCl, neat) 3016, 2987, 2924, 2906, 1748, 1657, 1586; HRMS (ESI): calcd. for $C_{12}H_{14}O_3I$ (M^++H): 332.9988, found: 332.9998.

Methyl 2-acetylheptanoate (1j)[S5]



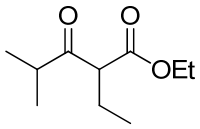
Pale yellow oil; ^{1}H NMR (400 MHz): δ 3.61 (s, 3H), 3.32 (t, J = 7.4 Hz, 1H), 2.10 (s, 3H), 1.73-1.70 (m, 2H), 1.18 (m, 6H), 0.76 (t, J = 3.2 Hz, 3H); ^{13}C NMR (100 MHz): δ 203.0, 170.2, 59.5, 52.1, 31.4, 28.6, 28.1, 27.0, 22.2, 13.8; MS (ESI): *m/z* 187 $[M+H]^+$.

Ethyl 2,4-dimethyl-3-oxopentanoate (1k)[S6]



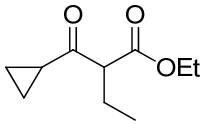
Pale yellow oil; ^{1}H NMR: δ 4.18 (q, J = 7.1 Hz, 2H), 3.69 (q, J = 7.1 Hz, 1H), 2.84 (m, J = 6.8 Hz, 1H), 1.33 (d, J = 7.2 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.12 (d, J = 6.6 Hz, 6H); ^{13}C NMR: δ 209.8, 170.5, 61.1, 50.7, 40.0, 18.4, 18.0, 14.0, 12.9; MS (ESI): *m/z* 173 $[M+H]^+$.

Ethyl 2-ethyl-4-methyl-3-oxopentanoate (1l)[S7]



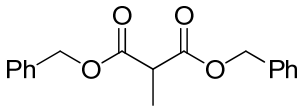
Pale yellow oil; ^{1}H NMR (400 MHz): δ 4.09 (q, J = 7.1 Hz, 2H), 3.48 (t, J = 7.2 Hz, 1H), 2.73 (m, J = 6.8 Hz, 1H), 1.81-1.77 (m, 2H), 1.18 (t, J = 7.2 Hz, 3H), 1.04-1.01 (m, 6H), 0.84 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz): δ 208.8, 169.5, 60.9, 58.3, 40.4, 21.5, 18.1, 17.8, 13.9, 11.8; MS (ESI): *m/z* 187 $[M+H]^+$.

Ethyl 2-(cyclopropanecarbonyl)butanoate (1m)



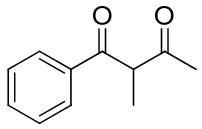
Pale yellow oil; ^{1}H NMR (400 MHz): δ 4.21 (q, J = 7.1 Hz, 2H), 3.47 (t, J = 7.4 Hz, 1H), 2.10-2.04 (m, 1H), 1.97-1.90 (m, 2H), 1.27 (t, J = 7.0 Hz, 3H) 1.10-106 (m, 2H), 0.97-0.91 (m, 5H); ^{13}C NMR: δ 205.5, 170.0, 61.6, 61.2, 21.6, 19.6, 14.2, 12.0, 11.7, 11.4; IR (neat, cm^{-1}) 2972, 2937, 2877, 1737, 1699, 1458, 1384; HRMS (ESI): calcd. for $C_{10}H_{16}O_3$ (M^++H): 185.1178, found: 185.1180.

Dibenzyl 2-methylmalonate (1p)[S8]



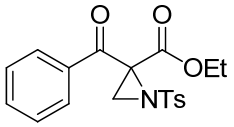
Pale yellow oil; ^{1}H NMR: δ 7.31-7.25 (m, 10H), 5.13 (s, 4 H), 3.53 (q, J = 7.2 Hz, 1H), 1.44 (d, J = 7.2 Hz, 3H); ^{13}C NMR: δ 169.7, 135.4, 128.5, 128.2, 128.0, 67.0, 46.1, 13.5; MS (ESI): *m/z* 299 $[M+H]^+$.

2-Methyl-1-phenylbutane-1,3-dione (1u)[S9]



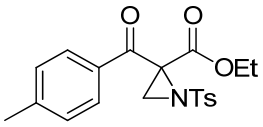
Pale yellow oil; ^{1}H NMR: δ 7.98 (d, J = 7.5 Hz, 2H), 7.58 (t, J = 7.2 Hz, 1H), 7.49-7.42 (m, 2H), 4.55 (q, J = 6.9 Hz, 1H), 2.16 (s, 3H), 1.43 (d, J = 7.2 Hz, 3H); ^{13}C NMR: δ 204.8, 197.4, 135.9, 133.6, 128.8, 128.6, 56.3, 28.1, 13.5; MS (ESI): *m/z* 177 $[M+H]^+$.

Ethyl 2-tosylaziridine-3-oxo-3-phenylpropanoate (2a)



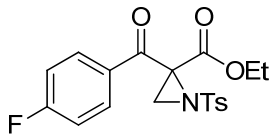
Pale yellow oil; ^{1}H NMR: δ 8.09 (d, J = 7.4 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.78 (t, J = 7.4 Hz, 1H), 7.58 (t, J = 7.7 Hz, 2H), 7.32 (d, J = 8.1 Hz, 2H), 4.31-4.19 (m, 2H), 3.36 (s, 1H), 2.93 (s, 1H), 2.45 (s, 3H), 1.14 (t, J = 8.0 Hz, 3H); ^{13}C NMR: δ 188.9, 164.9, 144.9, 136.3, 134.4, 134.0, 129.7, 129.6, 128.6, 127.9, 63.2, 53.7, 37.3, 21.7, 13.7; IR (NaCl, neat) v: 3067, 3021, 2986, 1751, 1734, 1690, 1597, 1448, 1341, 1217, 1165 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}NSO_5Na$ (M^++Na): 396.0882, found: 396.0892.

Ethyl 2-(4-methylbenzoyl)-1-tosylaziridine-2-carboxylate (2b)



Pale yellow oil; ^{1}H NMR: δ 7.99 (d, J = 8.1 Hz, 2H), 7.81 (d, J = 8.1 Hz, 2H), 7.31-7.21 (m, 4H), 4.31-4.19 (m, 2H), 3.33 (s, 1H), 2.92 (s, 1H), 2.42 (s, 6H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 188.4, 165.1, 145.2, 144.9, 136.4, 132.0, 129.9, 129.8, 129.6, 129.4, 129.3, 128.0, 127.1, 63.2, 53.9, 37.3, 21.9, 21.8, 21.7, 13.8; IR (NaCl, neat) v: 1734, 1684, 1607, 1341, 1215 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{22}NSO_5$ (M^++H): 388.1219, found: 388.1223.

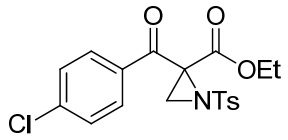
Ethyl 2-(4-fluorobenzoyl)-1-tosylaziridine-2-carboxylate (2c)



Pale yellow oil; ^{1}H NMR: δ 8.17-8.13 (m, 2H), 7.79 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.16-7.10 (m, 2H), 4.32-4.19 (m, 2H), 3.34 (s, 1H), 2.91 (s, 1H), 2.40 (s, 3H), 1.18 (t, J = 7.0 Hz, 3H); ^{13}C NMR: δ 187.5, 167.9, 164.8, 164.5, 145.0, 136.2, 132.6, 132.5, 130.9,

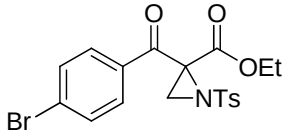
130.8, 129.8, 127.8, 115.9, 115.6, 63.3, 53.5, 37.4, 21.6, 13.7; IR (NaCl, neat) *v*: 3071, 3024, 2986, 1751, 1697, 1597, 1335, 1227, 1088 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}NSO_5F$ (M^++H): 392.0968, found: 392.0969.

Ethyl 2-(4-chlorobenzoyl)-1-tosylaziridine-2-carboxylate (2d)



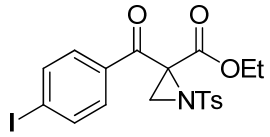
Pale yellow oil; ^{1}H NMR: δ 8.07 (d, J = 8.4 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.33-4.21 (m, 2H), 3.35 (s, 1H), 2.93 (s, 1H), 2.43 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 187.9, 164.8, 145.0, 140.6, 136.2, 132.8, 131.1, 129.8, 128.9, 127.8, 63.4, 53.4, 37.4, 21.6, 13.7. IR (NaCl, neat) *v*: 2982, 1753, 1732, 1692, 1589, 1402, 1339, 760 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}NSO_5SCl$ (M^++H): 408.0672, found: 408.0683.

Ethyl 2-(4-bromobenzoyl)-1-tosylaziridine-2-carboxylate (2e)



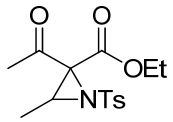
Pale yellow oil; ^{1}H NMR: δ 7.98 (d, J = 8.6 Hz, 2H), 7.79 (d, J = 8.3 Hz, 2H), 7.61 (d, J = 8.6 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 4.26 (q, J = 5.0 Hz, 2H), 3.34 (s, 1H), 2.92 (s, 1H), 2.42 (s, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR: δ 188.2, 164.7, 145.0, 136.1, 133.2, 131.9, 131.1, 129.8, 129.5, 127.8, 63.4, 53.3, 37.4, 21.6, 13.7. IR (NaCl, neat) *v*: 3019, 2399, 1748, 1694, 1339 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}NSO_5Br$ (M^++H): 452.0167, found: 452.0167.

Ethyl 2-(4-iodobenzoyl)-1-tosylaziridine-2-carboxylate (2f)



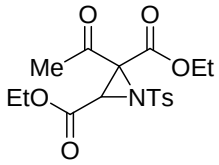
Pale yellow oil; ^{1}H NMR: δ 7.86-7.73 (m, 6H), 7.30 (d, J = 8.1 Hz, 2H), 4.31-4.20 (m, 2H), 3.33 (s, 1H), 2.92 (s, 1H), 2.41 (s, 3H), 1.20 (t, J = 7.1 Hz, 3H); ^{13}C NMR: δ 188.5, 164.7, 145.0, 137.9, 136.1, 133.7, 130.9, 129.8, 127.8, 102.5, 63.4, 53.3, 37.3, 21.7, 13.7. IR (NaCl, neat) v: 3019, 1734, 1684, 1935, 1395, 1213, 1165, 781 cm^{-1}; HRMS (ESI): calcd. for $C_{19}H_{19}NSO_5I$ (M^++H): 500.0029, found: 500.0047.

Ethyl 2-acetyl-3-methyl-1-tosylaziridine-2-carboxylate (2g)



Pale yellow oil, obtained as two diastereomers in a ratio of 1.8:1; ^{1}H NMR (400 MHz): δ 7.87 (d, J = 8.4 Hz, 3H), 7.37 (d, J = 8.0 Hz, 3H), 4.34-4.26 (m, 3H), 3.79 (q, J = 5.7 Hz, 1H, major), 3.70 (q, J = 5.6 Hz, 0.5H, minor), 2.45, (s, 1.5H, minor), 2.46 (s, 3H, major), 2.23 (s, 3H), 1.35-1.27 (m, 4.5H), 1.21 (t, J = 6.6 Hz, 4.5); ^{13}C NMR: δ 199.3, 196.0, 164.4, 164.0, 144.9, 144.8, 136.4, 136.0, 129.7, 129.6, 127.6, 63.1, 62.6, 59.9, 59.7, 45.1, 44.0, 29.6, 28.7, 21.6, 14.1, 13.9, 13.7, 13.0; IR (NaCl, neat) v: 3024, 2986, 2940, 1720, 1636, 1597, 1334, 1211, 1165, 1088 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{19}NSO_5$ (M^++H): 326.1062, found: 326.1058.

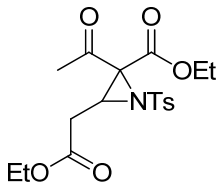
Diethyl 2-acetyl-1-tosylaziridine-2,3-dicarboxylate (2h)



Diastereomer 1: Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.90 (d, J = 8.0 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 4.34 (q, J = 3.2 Hz, 2H), 4.26 (s, 1H), 4.16 (q, J = 7.2 Hz, 2H), 2.47 (s, 3H), 2.29 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): δ 198.3, 164.4, 162.6, 145.5, 129.9, 127.9, 63.7, 62.7, 58.3, 45.5, 28.3, 21.7, 13.8, 13.7; IR (NaCl, neat) v: 3024, 2986, 2940, 1751, 1597, 1350, 1304, 1219, 1165, 1096 cm^{-1}; HRMS (ESI):calcd. for $C_{17}H_{22}NSO_7$ (M^++H): 384.1117, found: 384.1119.

Diastereomer 2: Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.89 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.28 (dq, J = 7.2 Hz, J = 0.8 Hz, 2H), 4.24 (s, 1H), 4.14 (q, J = 7.2 Hz, 2H), 2.53 (s, 3H), 2.44 (s, 3H), 1.29 (t, J = 7.0 Hz, 3H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR(100 MHz): δ 193.9, 164.0, 163.4, 145.3, 129.8, 127.9, 63.0, 62.4, 58.9, 44.9, 29.4, 21.7, 13.9; IR (NaCl, neat) v: 3024, 2986, 2940, 1751, 1597, 1350, 1304, 1219, 1165, 1096 cm^{-1}; HRMS (ESI):calcd. for $C_{17}H_{22}NSO_7$ (M^++H): 384.1117, found: 384.1119.

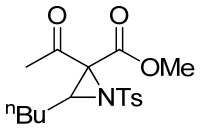
Ethyl 2-acetyl-3-(2-ethoxy-2-oxoethyl)-1-tosylaziridine-2-carboxylate (2i)



Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.80 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.29, (m, 3H), 4.14 (q, J = 7.1 Hz, 2H), 2.88-2.84 (m, 2H), 2.42 (s, 3H), 2.54 (s, 3H), 1.32 (t, J = 7.0 Hz, 3H), 1.26 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): δ 204.4, 174.8, 170.2, 143.2,

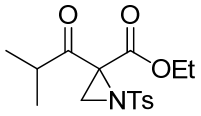
138.9, 129.4, 126.6, 83.0, 64.8, 63.0, 31.0, 28.2, 24.6, 21.5, 14.0, 13.6; IR (NaCl, neat) *v*: 3024, 2986, 2940, 1721, 1605, 1373, 1219, 1157, 1018 cm^{-1}; HRMS (ESI):calcd. for $C_{18}H_{24}NSO_7$ (M^++H): 398.1273, found: 398.1272.

Methyl 2-acetyl-3-butyl-1-tosylaziridine-2-carboxylate (2j)



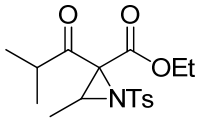
Colorless oil, obtained as two diastereomers in a ratio of 3.8:1; ^{1}H NMR (400 MHz): δ 7.87 (d, J = 8.0 Hz, 2.5H), 7.37 (d, J = 8.0 Hz, 2.5H), 3.84 (s, 3H, major),), 3.81 (s, 0.8H, minor), 3.68 (dd, J = 8.4 Hz, J = 4.8 Hz, 1H), 3.60 (dd, J = 7.4 Hz, J = 5.4 Hz, 0.3H, minor), 2.48 (s, 0.8H), 2.45 (s, 3H), 2.23 (s, 3H), 1.57-1.50 (m, 1.3H), 1.28-1.11 (m, 6.4 H), 0.83-0.76 (m, 3.7H); ^{13}C NMR: δ 199.3, 195.9, 164.6, 165.2, 144.9, 136.0, 135.7, 129.7, 127.9, 127.8, 59.8, 59.6, 53.6, 53.2, 49.6, 48.5, 29.6, 28.8, 28.2, 27.3, 21.9, 21.6, 13.7; IR (NaCl, neat) *v*: 3024, 2932, 2870, 1721, 1597, 1435, 1342, 1219, 1165 cm^{-1}; HRMS (ESI):calcd. for $C_{17}H_{24}NSO_5$ (M^++H): 354.1375, found: 354.1368.

Ethyl 2-isobutyryl-1-tosylaziridine-2-carboxylate (2k)



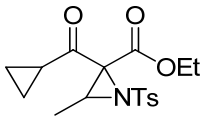
Pale yellow oil; ^{1}H NMR: δ 7.87 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.1 Hz, 2H), 4.33 (q, J = 7.2 Hz, 2H), 3.35 (s, 1H), 2.91-2.82 (m, 1H), 2.57 (s, 1H), 2.46 (s, 3H), 1.34 (t, J = 7.2 Hz, 3H), 1.08-1.02 (m, 6H); ^{13}C NMR: δ 204.9, 164.0, 145.1, 135.6, 129.7, 128.1, 63.0, 54.4, 36.3, 35.5, 21.7, 18.5, 17.5, 13.7; IR (NaCl, neat) *v*: 3466, 2978, 2936, 2876, 1746, 1717, 1597, 1468, 1020 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{22}NSO_5$ (M^++H): 340.1219, found: 340.1233.

Ethyl 2-isobutyryl-3-methyl-1-tosylaziridine-2-carboxylate (2l)



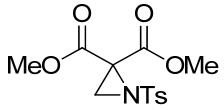
Brown oil, obtained as two diastereomers in a ratio of 1.7:1; major isomer: ^{1}H NMR (400 MHz): δ 7.86 (d, J = 8.0 Hz, 3.4H), 7.36 (d, J = 7.6 Hz, 3.4H), 4.33-4.27 (m, 3.4 H), 3.78 (q, J = 5.7 Hz, 1H, major), 3.72 (m, 0.7H, minor), 3.05 (m, 0.7H, minor), 2.94 (m, J = 6.8 Hz, 1H, major), 2.46 (s, 3H, major), 2.43(m, 2.1H, minor), 1.39-1.30 (m, 12H), 1.18-1.09 (m, 12H); ^{13}C NMR (100 MHz): δ 205.6, 203.2, 164.7, 164.3, 144.8, 144.7, 136.6, 136.1, 129.8, 129.7, 129.6, 127.7, 127.1, 63.0, 62.4, 59.3, 45.0, 43.5, 38.3, 31.0, 21.7, 18.6, 18.0, 17.8, 14.0, 13.9, 13.7, 13.5; IR (NaCl, neat) v: 2978, 2940, 2878, 1713, 1597, 1458, 1335, 1165 cm^{-1}; HRMS (ESI):calcd. for $C_{17}H_{24}NSO_5$ (M^++H): 354.1375, found: 354.1376.

Ethyl 2-(cyclopropanecarbonyl)-3-methyl-1-tosylaziridine-2-carboxylate (2m)



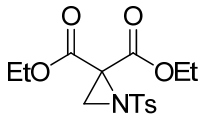
Pale yellow oil, obtained as two diastereomers in a ratio of 1.3:1; major isomer: ^{1}H NMR (400 MHz): δ 7.89 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 7.6 Hz, 2H), 4.34-4.26 (m, 2H), 3.78 (q, J = 5.6 Hz, 0.6H, major), 3.72 (m, 0.4H, minor), 2.45 (s, 3H), 2.28 (m, 0.6H, major), 2.18 (m, 0.4H, minor), 1.34-1.27 (m, 3H), 1.24-1.15 (m, 3H), 1.10-0.96 (m, 4H); ^{13}C NMR (100 MHz): δ 201.1, 198.6, 164.4, 164.2, 144.8, 136.3, 136.1, 129.7, 129.6, 127.7, 127.6, 62.9, 62.5, 60.6, 60.4, 44.7, 43.5, 21.9, 21.6, 19.1, 14.6, 14.1, 13.8, 13.7, 13.3, 12.9 ; IR (NaCl, neat) v: 3095, 3067, 3026, 2988, 2938, 2874, 1694, 1597, 1447, 1385, 1337 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{21}NSO_5$ (M^++H): 352.1219, found: 352.1223.

Dimethyl 1-tosylaziridine-2,2-dicarboxylate (2n)



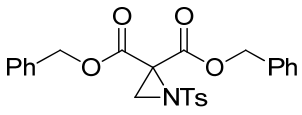
Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.87 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 3.83 (s, 6H), 3.00 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz): δ 164.2, 145.2, 135.2, 129.7, 128.2, 53.7, 49.8, 35.9, 21.7; IR (NaCl, neat) v: 3028, 2957, 1748, 1598 cm^{-1}; HRMS (ESI): calcd. for $C_{13}H_{16}NSO_6$ (M^++H): 314.0698, found: 314.0707.

Diethyl 1-tosylaziridine-2,2-dicarboxylate (2o)



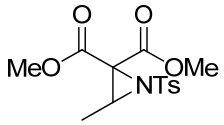
Pale yellow solid; mp = 85-88°C; ^{1}H NMR (400 MHz): δ 7.89 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.30 (q, J = 7.1 Hz, 4H), 2.99 (s, 2H), 2.46 (s, 3H), 1.32 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz): δ 163.8, 145.1, 135.4, 129.7, 128.1, 63.0, 50.1, 35.9, 21.7, 13.8; IR (NaCl, neat) v: 3019, 1746, 1599 cm^{-1}; HRMS (ESI):calcd. for $C_{15}H_{20}NSO_6$ (M^++H): 342.1011, found: 342.1011.

Dibenzyl 1-tosylaziridine-2,2-dicarboxylate (2p)



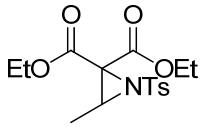
Colorless oil; ^{1}H NMR: δ 7.82 (d, J = 8.4 Hz, 2H), 7.33-7.23 (m, 12H), 5.20 (s, 4H), 3.02 (s, 2H), 2.41 (s, 3H); ^{13}C NMR: δ 163.6, 145.0, 135.3, 134.5, 129.7, 128.6, 128.5, 128.4, 128.2, 68.6, 50.1, 35.8, 21.7; IR (NaCl, neat) v: 3017, 1751, 1636, 1605, 1342, 1219, 1165, 1088 cm^{-1}; HRMS (ESI): calcd. for $C_{25}H_{24}NSO_6$ (M^++H): 466.1324, found: 466.1322.

Dimethyl 3-methyl-1-tosylaziridine-2,2-dicarboxylate (2q)



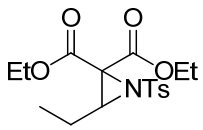
Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.87 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H), 3.78 (m, 4H), 2.44 (s, 3H), 1.26 (d, J = 5.6 Hz, 3H); ^{13}C NMR (100 MHz): δ 164.0, 163.9, 144.7, 136.1, 129.7, 127.7, 55.2, 53.7, 53.3, 44.0, 21.6, 13.3; IR (NaCl, neat) v: 3019, 2955, 2399, 1748, 1437, 1339, 1092 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{18}NO_6S$ (M^++H): 328.0855, found: 328.0859.

Diethyl 3-methyl-1-tosylaziridine-2,2-dicarboxylate (2r)



Pale yellow solid; mp = 101-105^{o}C; ^{1}H NMR (400 MHz): δ 7.88 (d, J = 8.4 Hz, 2H); 7.34 (d, J = 8.0 Hz, 2H), 4.36-4.21 (m, 4H), 3.78 (q, J = 5.7 Hz, 1H), 2.44 (s, 3H), 1.32 (t, J = 7.2 Hz, 3 H), 1.28 (t, J = 7.0 Hz, 6H); ^{13}C NMR (100 MHz): δ 163.6, 163.4, 144.6, 136.4, 129.6, 127.7, 63.0, 62.5, 55.5, 43.9, 21.6, 14.0, 13.7, 13.3; IR (NaCl, neat) v: 3420, 3021, 1746, 1636, 1339, 1092 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{21}NO_6SNa$ (M^++Na): 378.0987, found: 378.0981.

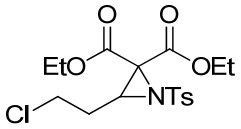
Diethyl 3-ethyl-1-tosylaziridine-2,2-dicarboxylate (2s)



Pale yellow solid; mp = 64-66^{o}C; ^{1}H NMR: δ 7.84 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.32-4.16 (m, 4H), 3.60 (dd, J = 8.1, J = 5.4 Hz, 1H), 2.44 (s, 3H), 1.62-1.48 (m, 1H),

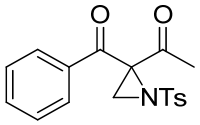
1.29-1.18 (m, 7 H), 0.92 (t, J = 7.5 Hz, 3H); ^{13}C NMR: δ 163.6, 163.4, 144.6, 136.2, 129.6, 127.8, 63.0, 62.4, 55.6, 49.6, 21.6, 21.5, 14.0, 13.7, 10.9; IR (NaCl, neat) v: 3011, 1645, 1339, 1094 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{24}NO_6S$ (M^++H): 370.1324, found: 370.1328.

Diethyl 3-(2-chloroethyl)-1-tosylaziridine-2,2-dicarboxylate (2t)



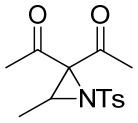
Pale yellow oil; ^{1}H NMR (400 MHz): δ 7.90 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 4.37-4.22 (m, 4H), 3.85 (dd, J = 6.2 Hz, J = 3.5 Hz, 1H), 3.55-3.50 (m, 1H), 3.42-3.37 (m, 1H), 2.45 (s, 3H), 2.11-2.06 (m, 1H), 1.79-1.73 (m, 1H), 1.35-1.25 (m, 6H); ^{13}C NMR (100 MHz): δ 163.4, 163.0, 145.0, 135.7, 129.7, 129.6, 128.0, 126.9, 63.2, 62.8, 55.1, 45.6, 41.1, 31.0, 21.7, 14.0, 13.7; IR (NaCl, neat) v: 3024, 2983, 2940, 2907, 1748, 1597, 1445, 1369 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{22}NO_6NaSCl$ (M^++Na): 426.0754, found: 426.0768.

1-(2-Benzoyl-1-tosylaziridin-2-yl)ethanone (2u)



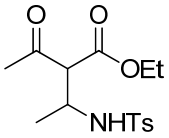
Pale yellow oil; ^{1}H NMR: δ 7.91 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 8.3 Hz, 2H), 7.70 (t, J = 8.3 Hz, 1H), 7.58 (d, J = 7.4 Hz, 2H), 7.45 (d, J = 7.9 Hz, 2H), 3.16 (s, 1H), 2.92 (s, 1H), 2.45 (s, 3H), 2.31 (s, 3H); ^{13}C NMR: δ 199.7, 189.9, 145.2, 135.2, 134.7, 134.2, 129.8, 129.7, 128.7, 128.5, 128.2, 71.7, 71.1, 59.4, 35.4, 26.7, 21.7, 19.3, 13.9; IR (NaCl, neat) v: 3019, 1715, 1690, 1215, 758 cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{17}NSO_4Na$ (M^++Na): 366.0776, found: 366.0779.

1,1'-(3-Methyl-1-tosylaziridine-2,2-diyl)diethanone (2v)



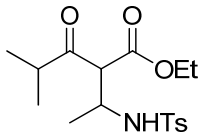
Pale yellow oil; ^{1}H NMR: δ 7.86 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 3.69 (q, J = 5.8, 1H), 2.46 (s, 3H), 2.43 (s, 3H), 2.38 (s, 3H), 1.17 (d, J = 5.7, 3H); ^{13}C NMR: δ 202.0, 197.3, 145.1, 135.9, 129.8, 127.6, 64.8, 44.7, 30.1, 29.2, 21.6, 13.8; IR (NaCl, neat) v: 3067, 3024, 2930, 1707, 1674, 1599, 1358, 1335, 1219, 1165, 1088; HRMS (ESI): calcd. for $C_{14}H_{17}NSO_4Na$ (M^++Na): 318.0776, found: 318.0786.

Ethyl 2-acetyl-3-(4-methylphenylsulfonamido)butanoate (3g)



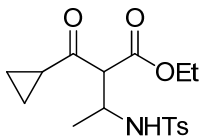
Reaction time = 3 h; white solid, obtained as two diastereomers in a ratio of 1:1; mp = 80-83^{o}C; ^{1}H NMR: δ 7.75 (d, J = 8.1 Hz, 4H), 7.30 (d, J = 7.2 Hz, 4H) 5.59 (d, J = 9.9 Hz, 1H), 5.47 (d, J = 9.6 Hz, 1H), 4.22-3.94 (m, 6H), 3.61 (d, J = 5.4 Hz, 1H), 3.58 (d, J = 4.8 Hz, 1H), 2.42 (s, 6H), 2.20 (s, 3H), 2.16 (s, 3H), 1.29-1.22 (m, 6H), 1.10 (t, J = 6.9 Hz, 6H); ^{13}C NMR: δ 202.4, 201.7, 168.6, 167.8, 143.5, 143.4, 138.1, 129.7, 127.0, 63.8, 63,6, 61,8, 61.7, 49.1, 49.0, 30.1, 29.4, 21.5, 19.6, 19.3, 14.0; IR (NaCl, neat) v: 3066, 3032, 3010, 2988, 2941, 1701, 1627, 1590, 1497, 1417; HRMS (ESI): calcd. for $C_{15}H_{22}NO_5S$ (M^++H): 328.1219, found: 328.1227.

Ethyl 4-methyl-2-(1-(4-methylphenylsulfonamido)ethyl)-3-oxopentanoate (3l)



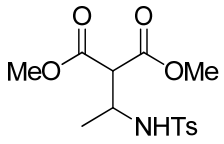
Reaction time = 4 h; white solid, obtained as two diastereomers in a ratio of 1:1; mp = 92-95°C; ^{1}H NMR: δ 7.74 (d, *J* = 7.2 Hz, 4H), 7.29 (d, *J* = 6.9 Hz, 4H), 5.66 (d, *J* = 9.6 Hz, 1H), 5.44 (d, *J* = 9.3 Hz, 1H), 4.19-3.93 (m, 6H), 3.84 (d, *J* = 5.7 Hz, 1H), 3.80 (d, *J* = 4.2 Hz, 1H), 2.78-2.63 (m, 2H), 2.41 (s, 6H), 1.26-1.18 (m, 6H), 1.12-1.08 (m, 12H), 1.02 (t, *J* = 6.6 Hz, 6H); ^{13}C NMR: δ 209.1, 207.6, 168.3, 167.8, 143.4, 143.3, 138.4, 138.1, 129.7, 129.6, 127.0, 127.0, 61.7, 61.7, 61.0, 59.9, 49.5, 49.1, 41.7, 40.6, 21.5, 19.6, 19.4, 18.0, 17.7, 17.4, 13.9; IR (NaCl, neat) *v*: 3024, 2978, 2940, 1736, 1713, 1636, 1597, 1335, 1219, 1165, 1096 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{26}NO_5S$ (M^++H): 356.1532, found: 356.1559.

Ethyl 2-(cyclopropanecarbonyl)-3-(4-methylphenylsulfonamido)butanoate (3m)



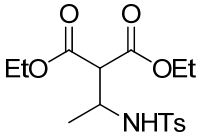
Reaction time = 0.5 h; white solid, obtained as two diastereomers in a ratio of 1:1; mp = 82-84°C; ^{1}H NMR (400 MHz): *δ* 7.74 (d, *J* = 7.2 Hz, 4H), 7.29 (d, *J* = 9.6 Hz, 4H), 5.50-5.47 (m, 2H), 4.19-4.06 (m, 6H), 3.78 (d, *J* = 4.8 Hz, 1H), 3.73 (d, *J* = 5.2 Hz, 1H), 2.42 (s, 6H), 1.98-1.96 (m, 2H), 1.27-1.22 (m, 6H), 1.13 (t, *J* = 6.8 Hz, 6H), 1.05-0.88 (m, 8H); ^{13}C NMR (100 MHz): *δ* 204.7 203.8, 168.6, 167.9, 143.3, 143.3, 138.3, 138.3, 129.7, 127.0, 64.0, 63.3, 61.7, 61.7, 49.1, 49.1, 21.5, 21.4, 20.7, 19.9, 19.3, 14.0, 14.0, 12.4, 12.3, 12.2; IR (NaCl, neat) *v*: 3067, 3026, 2984, 2940, 1686, 1599, 1447, 1420, 1387 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{24}NO_5S$ (M^++H): 354.1375, found: 354.1378.

Dimethyl 2-(1-(4-methylphenylsulfonamido)ethyl)malonate (3q)



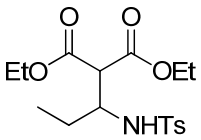
Reaction time = 4 h; white solid; mp = 125-128^{o}C; ^{1}H NMR: δ 7.75 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.58 (d, *J* = 9.8 Hz, 1H), 4.04-3.97 (m, 1H), 3.72 (s, 3H), 3.59 (s, 3H), 3.54 (d, *J* = 4.8 Hz, 1H), 2.41 (s, 3H), 1.17 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR: δ 168.1, 167.5, 143.3, 138.2, 129.6, 127.0, 56.4, 52.6, 49.2, 21.5, 19.6; IR (NaCl, neat) *v*: 3472, 3028, 2955, 1734, 1599, 1437, 1339, 1161, 1092 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{19}NO_5SNa$ (M^++Na): 352.0831, found: 352.0848.

Diethyl 2-(1-(4-methylphenylsulfonamido)ethyl)malonate (3r)



Reaction time = 4 h; colorless oil; ^{1}H NMR: δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.49 (d, *J* = 9.9 Hz, 1H), 4.25-3.93 (m, 5H), 3.47 (d, *J* = 4.7 Hz, 1H), 2.42 (s, 3H), 1.29-1.16 (m, 9H); ^{13}C NMR: δ 167.8, 167.2, 143.3, 138.4, 129.6, 127.0, 61.8, 61.7, 56.5, 49.2, 21.5, 19.6, 14.0, 13.9; IR (NaCl, neat) *v*: 3442, 3028, 1722, 1636, 1418, 1341, 1094 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{24}NO_6S$ (M^++H): 358.1342, found: 358.1313.

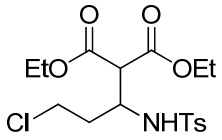
Diethyl 2-(1-(4-methylphenylsulfonamido)propyl)malonate (3s)



Reaction time = 5 h; colorless oil; ^{1}H NMR: *δ* 7.74 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 5.60 (d, *J* = 9.6 Hz, 1H), 4.22-4.13 (m, 2H), 4.07-3.91 (m, 2H), 3.84-3.78 (m, 1H), 3.56

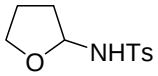
(d, J = 4.2 Hz, 1H), 2.41 (s, 3H), 1.65-1.52 (m, 2H), 1.26 (t, J = 7.1 Hz, 3H), 1.19 (t, J = 7.2 Hz, 3H), 0.79 (t, J = 7.4 Hz, 3H); ^{13}C NMR: δ 168.0, 167.4, 143.1, 138.6, 129.5, 126.9, 61.8, 61.6, 55.1, 54.4, 26.9, 21.4, 14.0, 13.9, 10.7; IR (NaCl, neat) v: 3021, 2984, 1724, 1638, 1422, 1373, 1337, 1094 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{25}NO_6SNa$ (M^++Na): 394.1300, found: 394.1303.

Diethyl 2-(3-chloro-1-(4-methylphenylsulfonamido)propyl)malonate (3t)



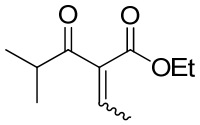
Reaction time = 7 h; white solid; mp = 75-79^{o}C; ^{1}H NMR: δ 7.73 (d, J = 8.2 Hz, 2H), 7.26 (d, J = 8.2 Hz, 2H), 5.72 (d, J = 9.9 Hz, 1H), 4.21-3.97 (m, 5H), 3.59 (d, J = 4.2 Hz, 1H), 3.63-3.43 (m, 1H), 3.39-3.33 (m, 1H), 2.38 (s, 3H), 2.18-2.10 (m, 1H), 1.99-1.93 (m, 1H), 1.28-1.19 (m, 6H); ^{13}C NMR: δ 167.6, 167.1, 143.5, 138.1, 129.6, 126.9, 61.9, 61.8, 55.0, 50.9, 41.0, 36.1, 21.4, 14.1, 13.9, 13.8; IR (NaCl, neat) v: 3345, 3030, 2984, 2940, 1716, 1634, 1599, 1495, 1094 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{25}NO_6SCl$ (M^++H): 406.1091, found: 406.1103.

Tetrahydro-*N*-tosylfuran-2-amine (4)[S10]



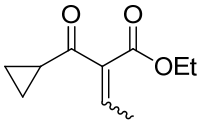
Colorless oil; ^{1}H NMR (400 MHz): δ 7.80 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 5.63 (d, J = 8.7 Hz, 1H), 5.32-5.37 (m, 1H), 3.66-3.71 (m, 2H), 2.42 (s, 3H), 2.12-2.17 (m, 1H), 1.77-1.91 (m, 3H); ^{13}C NMR (100 MHz): δ 143.3, 138.5, 129.5, 127.1, 85.0, 67.2, 32.7, 24.0, 21.6; MS (ESI) m/z 242 [M+H]$^+$.

Ethyl 2-ethylidene-4-methyl-3-oxopentanoate (5l)[S11]



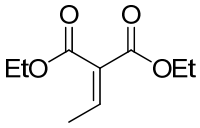
Colorless oil; ^{1}H NMR: δ 7.04 (q, *J* = 7.3 Hz, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 2.95 (m, *J* = 7.0 Hz, 1H), 1.84 (d, *J* = 7.5 Hz, 3H), 1.29 (t, *J* = 7.2, 3H), 1.13 (d, *J* = 6.9 Hz, 6H); ^{13}C NMR: δ 207.8, 164.5, 143.3, 136.3, 61.0, 40.6, 17.8, 15.4, 14.1; MS (ESI): *m/z* 185 $[M+H]^+$.

Ethyl 2-(cyclopropanecarbonyl)but-2-enoate (5m)



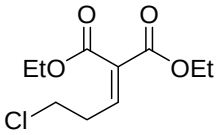
The alkene was found to rapidly decompose in solution over a 30 min period after flash column chromatography. The ^{1}H and ^{13}C NMR spectra of **5m** containing these unknown decomposition products is provided as Figure S44 (*vide infra*). Colorless oil, IR (NaCl, neat) *v*: 2965, 2934, 2853, 1730, 1701, 1446, 1386, 1248 cm^{-1}; HRMS (ESI): calcd. for $C_{10}H_{15}O_3$ $(M^+ + H)$: 183.1021, found: 183.1024.

Diethyl 2-ethylidenemalonate (5r)[S12]



Colorless oil; ^{1}H NMR (400 MHz): δ 6.92 (q, *J* = 7.2 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 4.14 (q, *J* = 7.2 Hz, 2H), 1.86 (d, *J* = 7.2 Hz, 3H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz): δ 165.1, 163.7, 144.3, 129.6, 60.9, 15.2, 14.0, 13.9. MS (ESI): *m/z* 187 $[M+H]^+$.

Diethyl 2-(3-chloropropylidene)malonate (5t)



Colorless oil; ^{1}H NMR: δ 7.02 (t, *J* = 7.5 Hz, 1H), 4.36-4.17 (m, 4H), 3.64 (t, *J* = 6.6 Hz, 2H), 2.81 (q, *J* = 6.9 Hz, 2H), 1.36-1.25 (m, 6H); ^{13}C NMR δ 164.8, 163.6, 144.4, 130.8, 61.4, 61.3, 42.2, 32.4, 14.1, 14.0; IR (NaCl, neat) *v*: 3019, 2986, 2967, 2938, 2872, 2399, 1726, 1715, 1645, 1520, 1476, 1445, 1377, 1265 cm^{-1}; HRMS (ESI): calcd. for $C_{10}H_{15}O_4ClNa$ (M^++Na): 257.0557, found: 257.0549.

^{1}H and ^{13}C NMR Spectra

Figure S1. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-methyl-3-oxo-3-phenylpropanoate (**1a**)

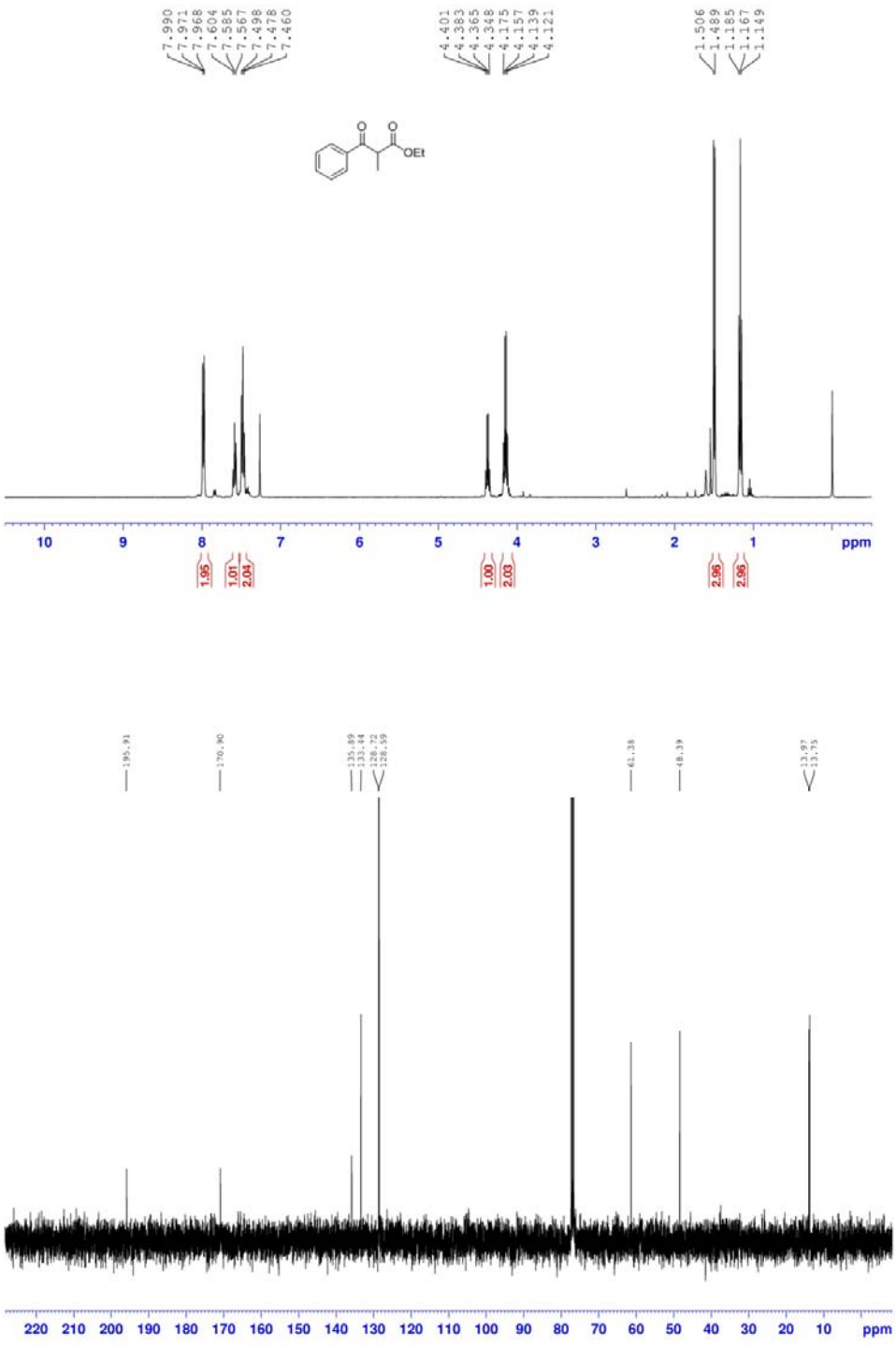


Figure S2. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-methyl-3-oxo-3-(p-tolyl)propanoate (**1b**)

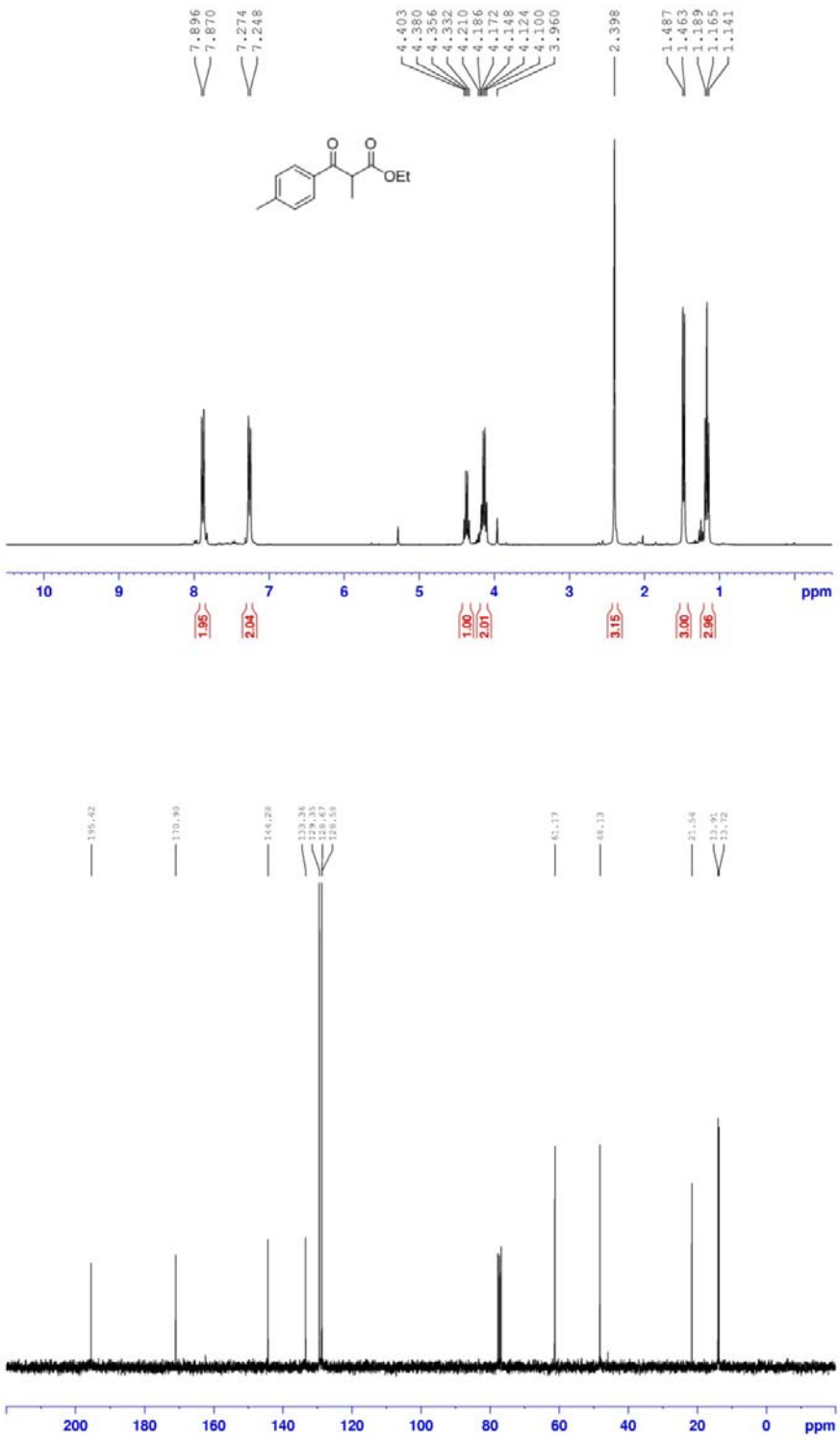


Figure S3. ^{1}H and ^{13}C NMR Spectra of Ethyl 3-(4-fluorophenyl)-2-methyl-3-oxopropanoate (**1c**)

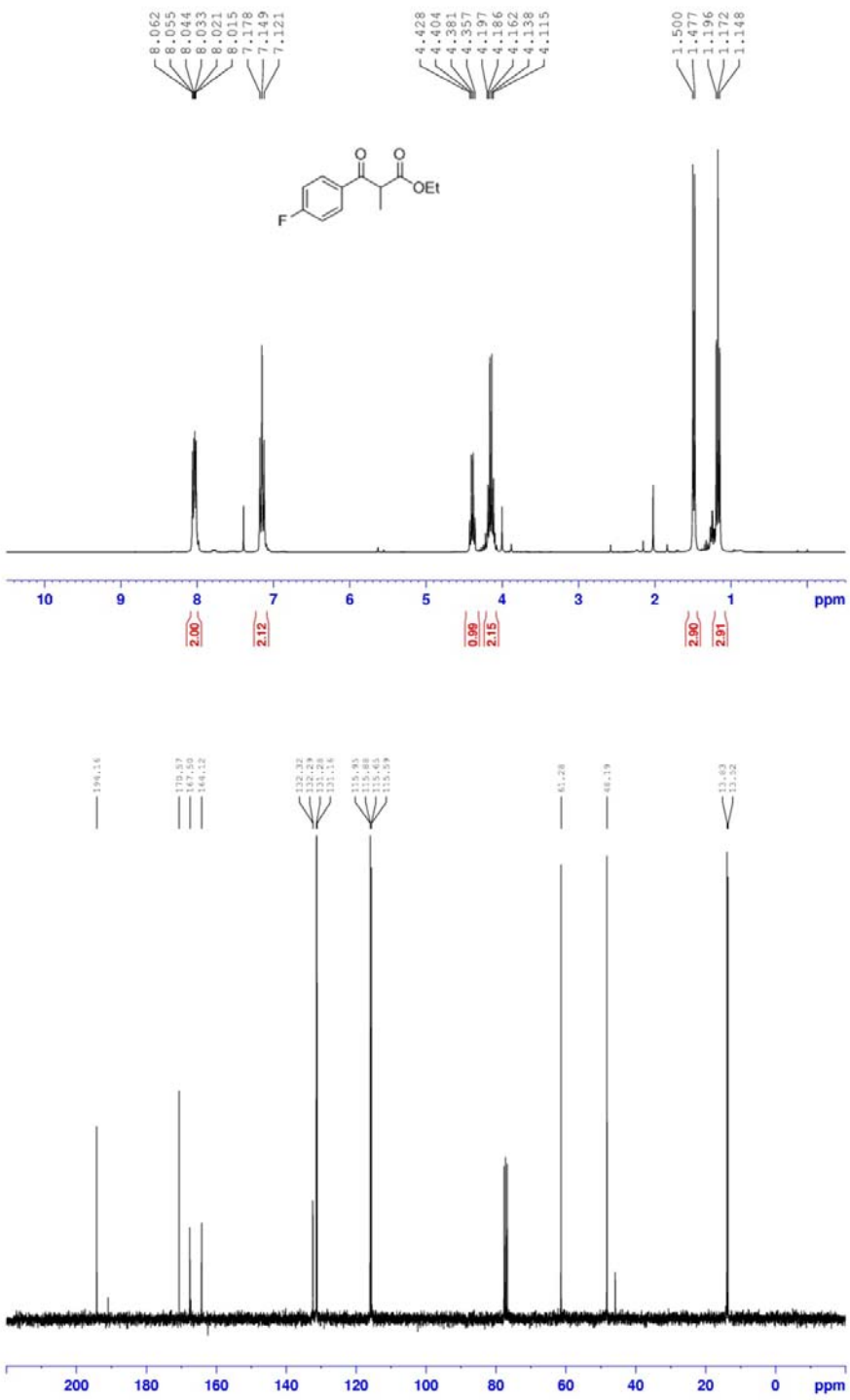


Figure S4. ^{1}H and ^{13}C NMR Spectra of Ethyl 3-(4-chlorophenyl)-2-methyl-3-oxopropanoate (**1d**)

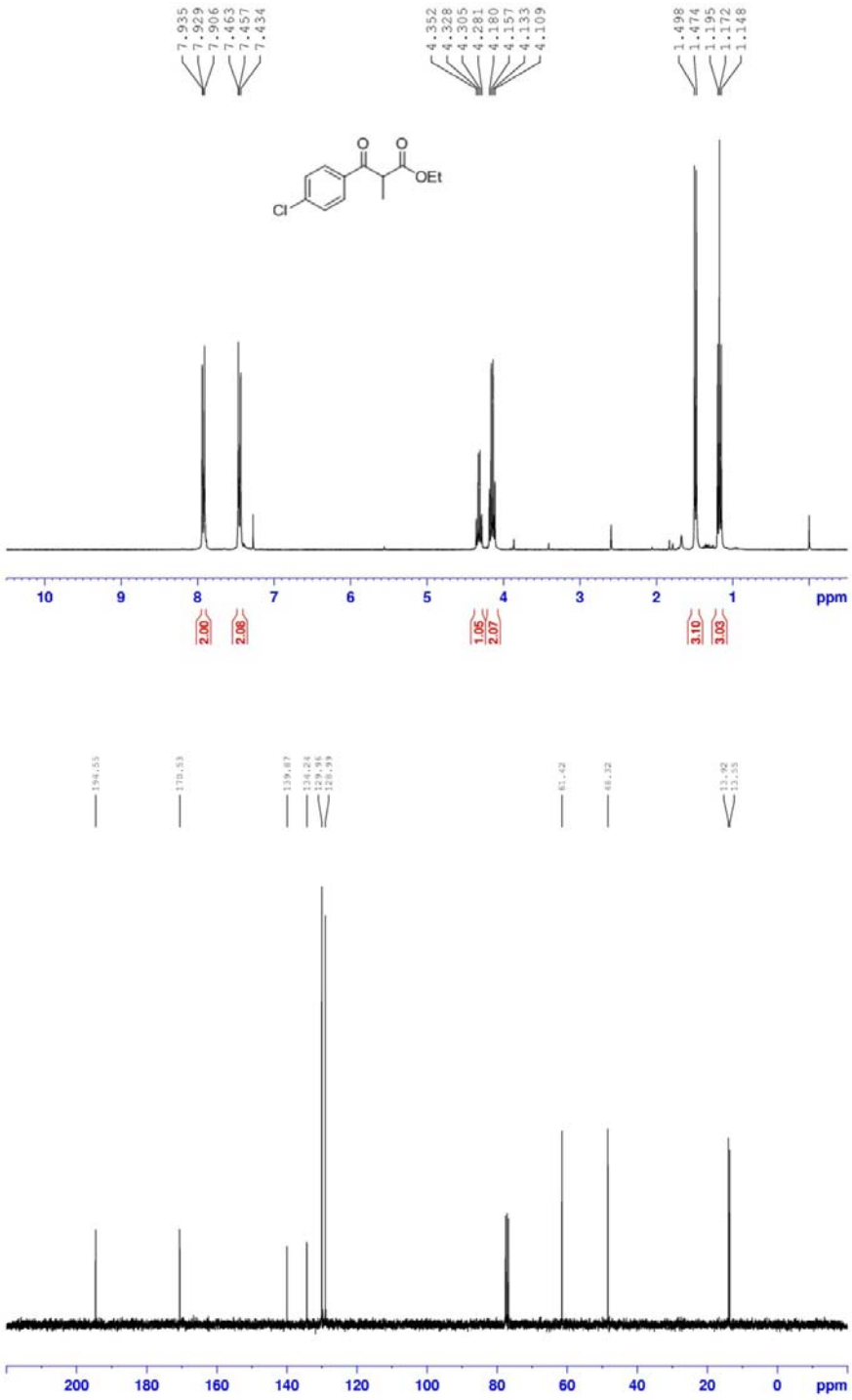


Figure S5. ^{1}H and ^{13}C NMR Spectra of Ethyl 3-(4-bromophenyl)-2-methyl-3-oxopropanoate (**1e**)

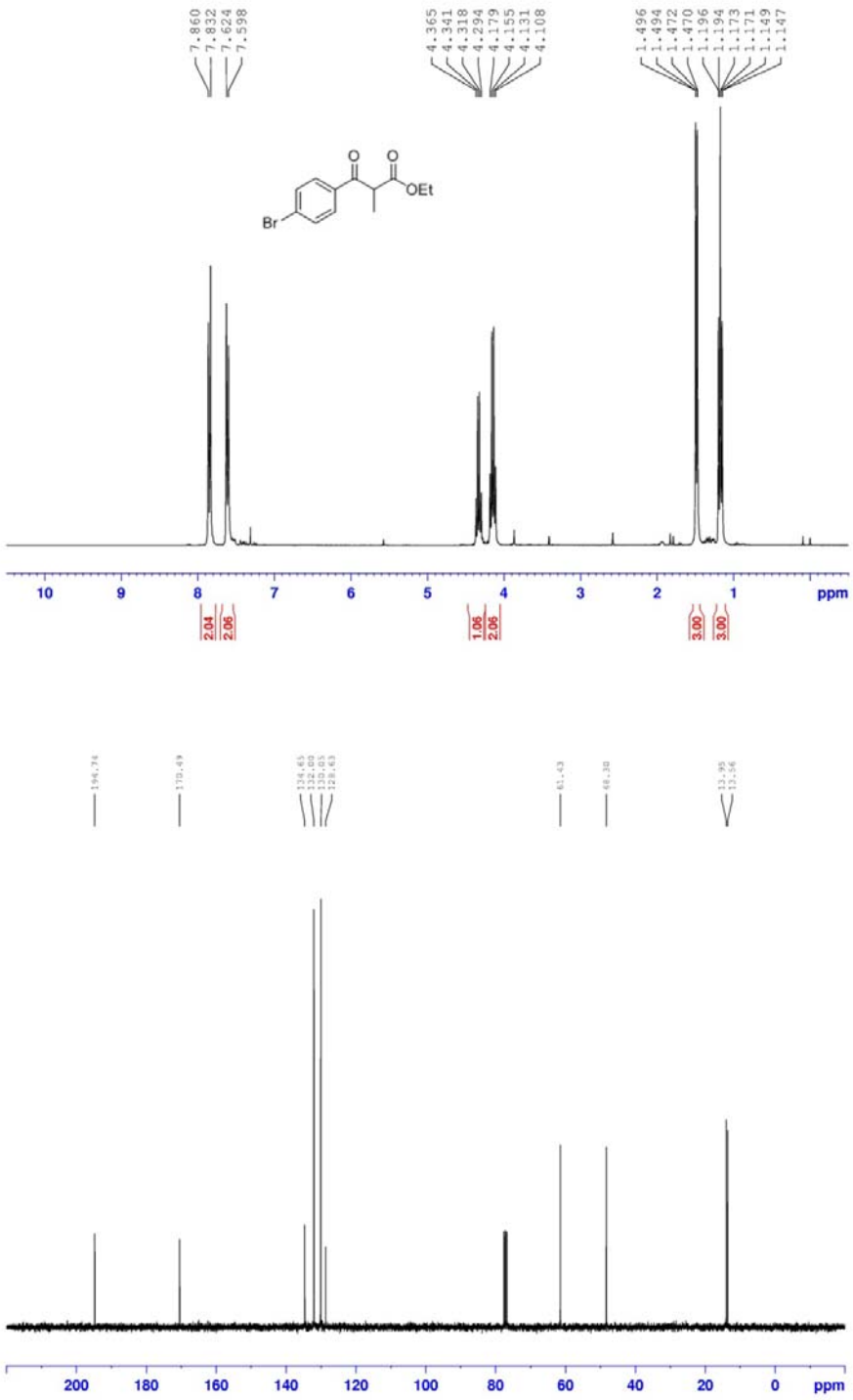


Figure S6. ^{1}H and ^{13}C NMR Spectra of Ethyl 3-(4-iodophenyl)-2-methyl-3-oxopropanoate (**1f**)

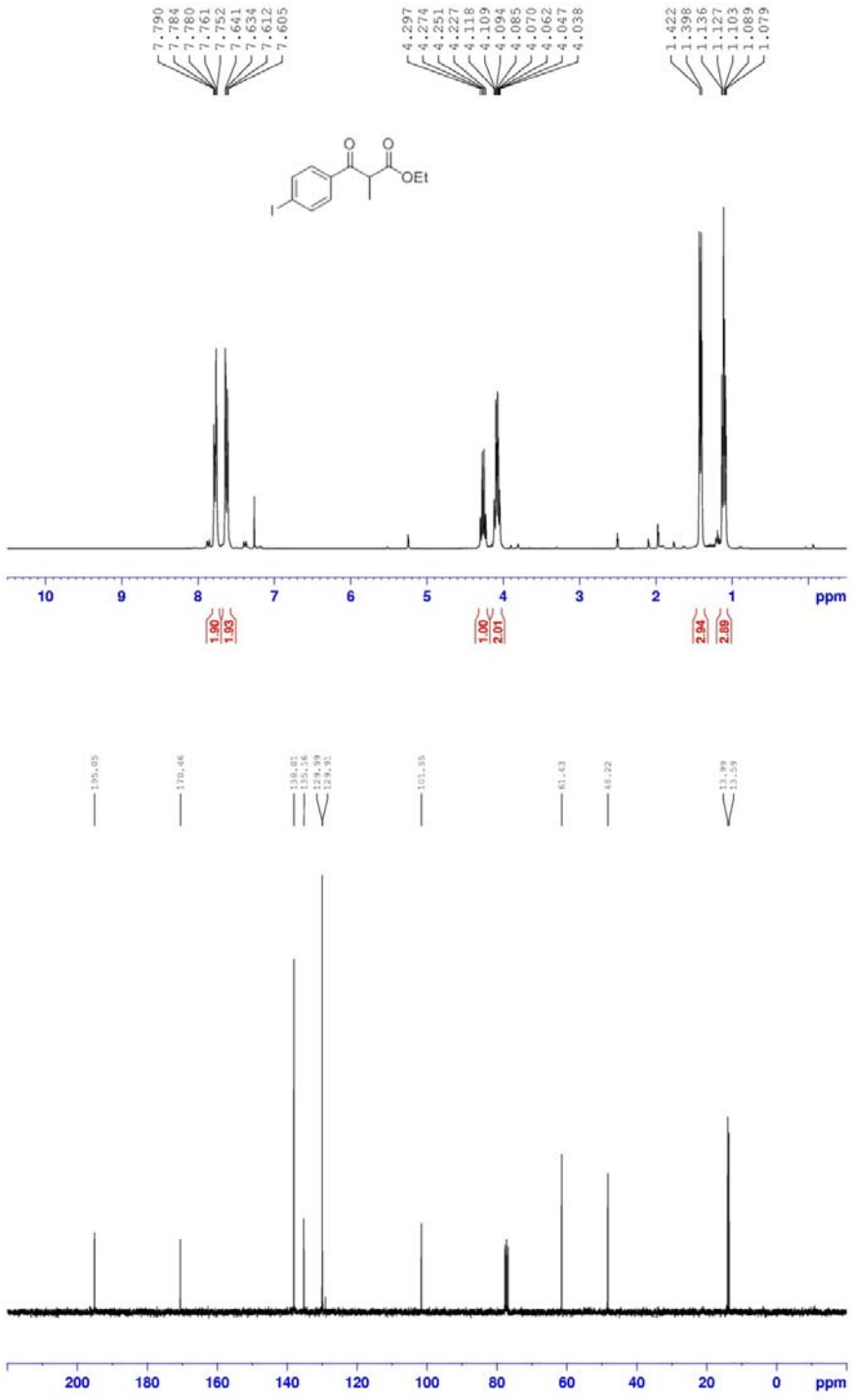


Figure S7. ^{1}H and ^{13}C NMR Spectra of Methyl 2-acetylheptanoate (**1j**)

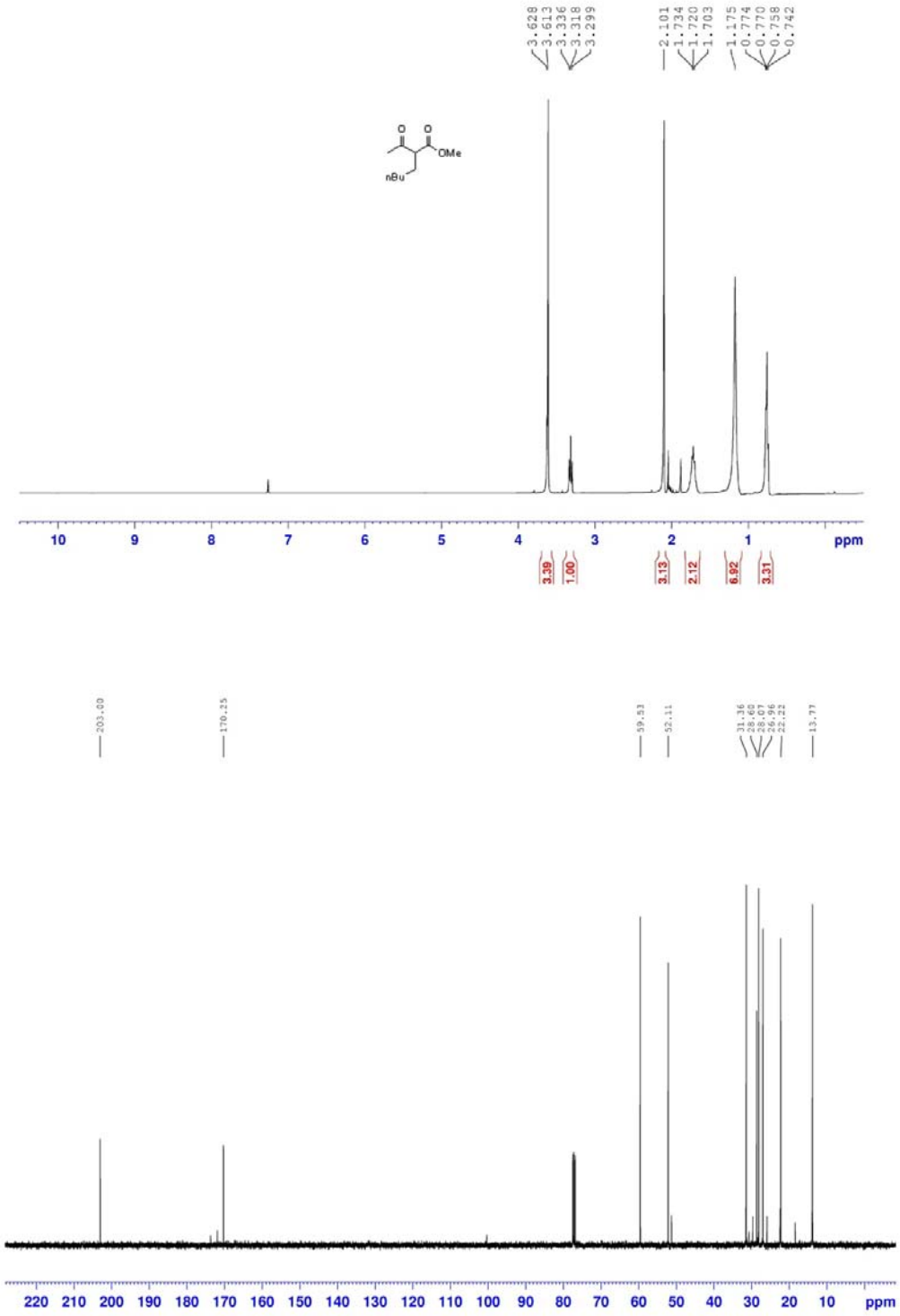


Figure S8. ^{1}H and ^{13}C NMR Spectra of Ethyl 2,4-dimethyl-3-oxopentanoate (**1k**)

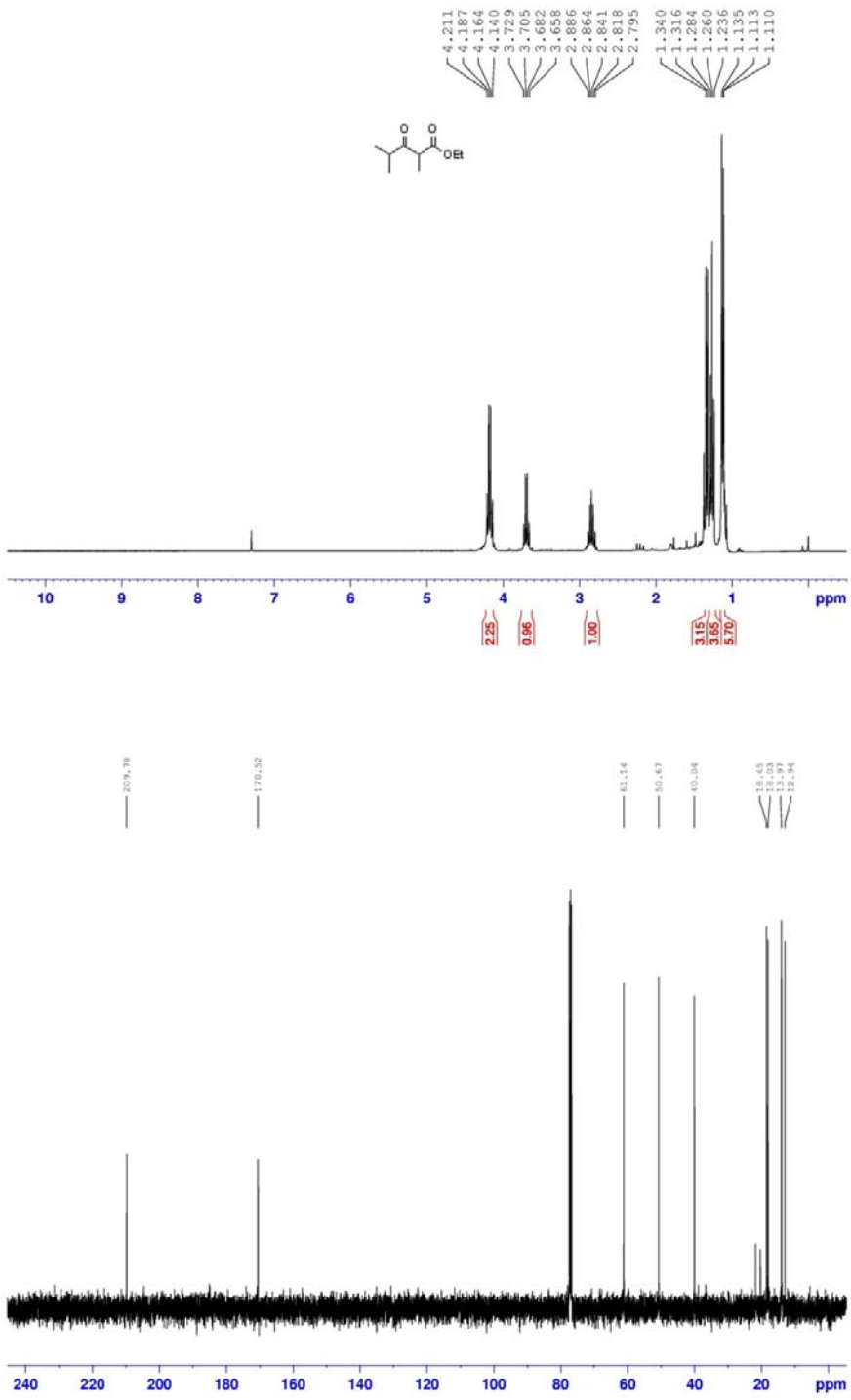


Figure S9. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-ethyl-4-methyl-3-oxopentanoate (**1l**)

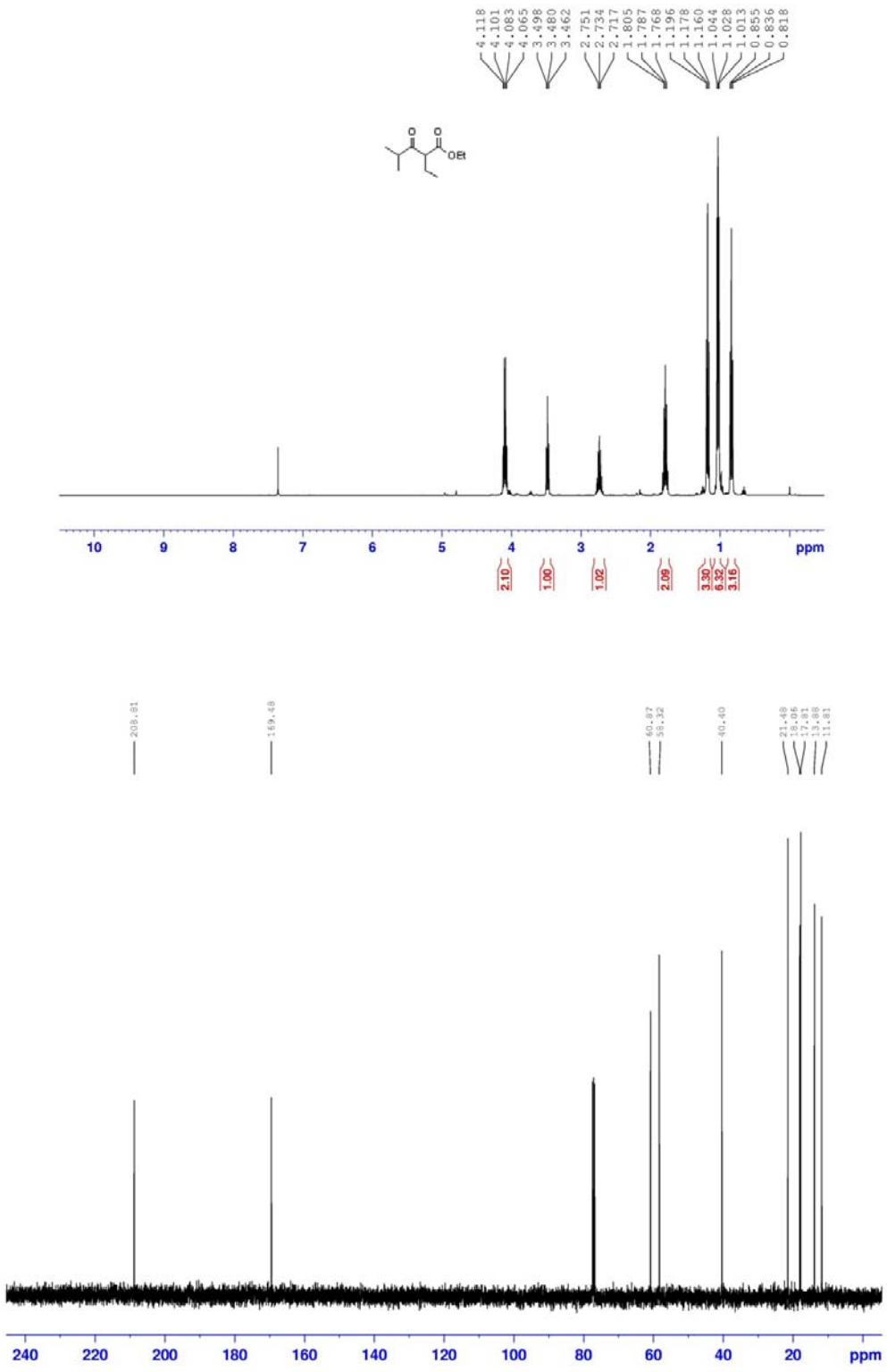


Figure S10. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(cyclopropanecarbonyl)butanoate (**1m**)

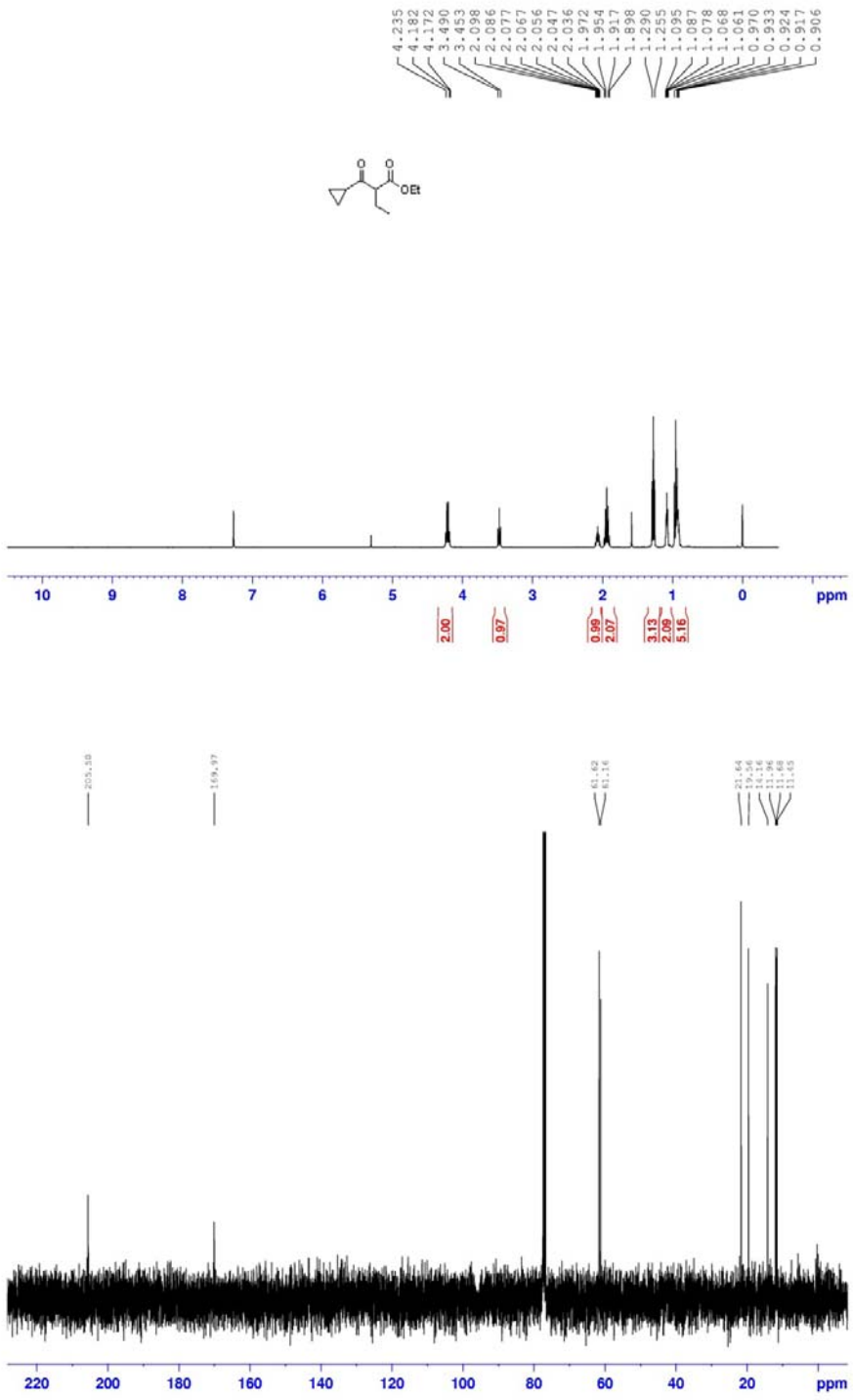


Figure S11. ^{1}H and ^{13}C NMR Spectra of Dibenzyl 2-methylmalonate (**1p**)

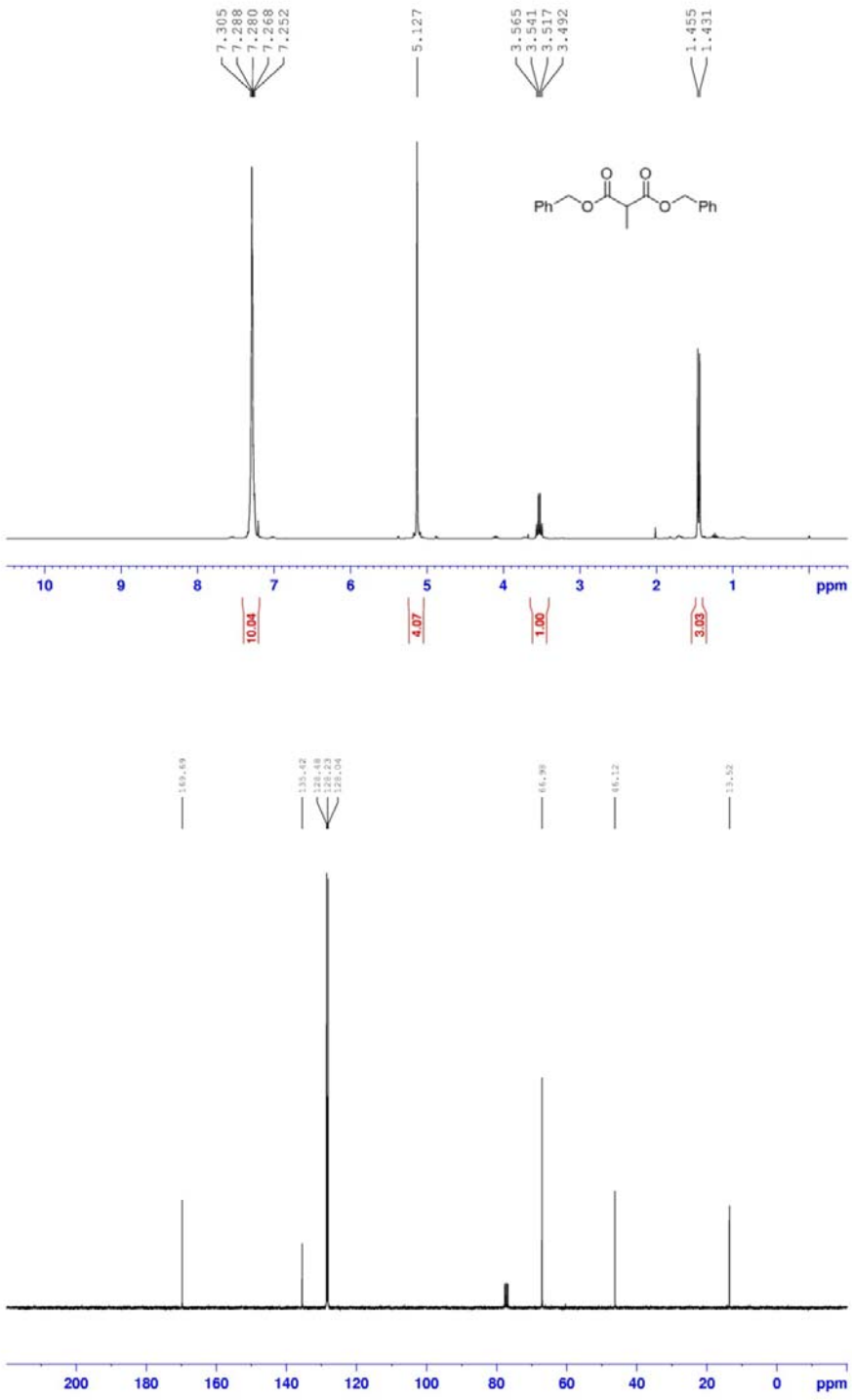


Figure S12. ^{1}H and ^{13}C NMR Spectra of 2-Methyl-1-phenylbutane-1,3-dione (**1u**)

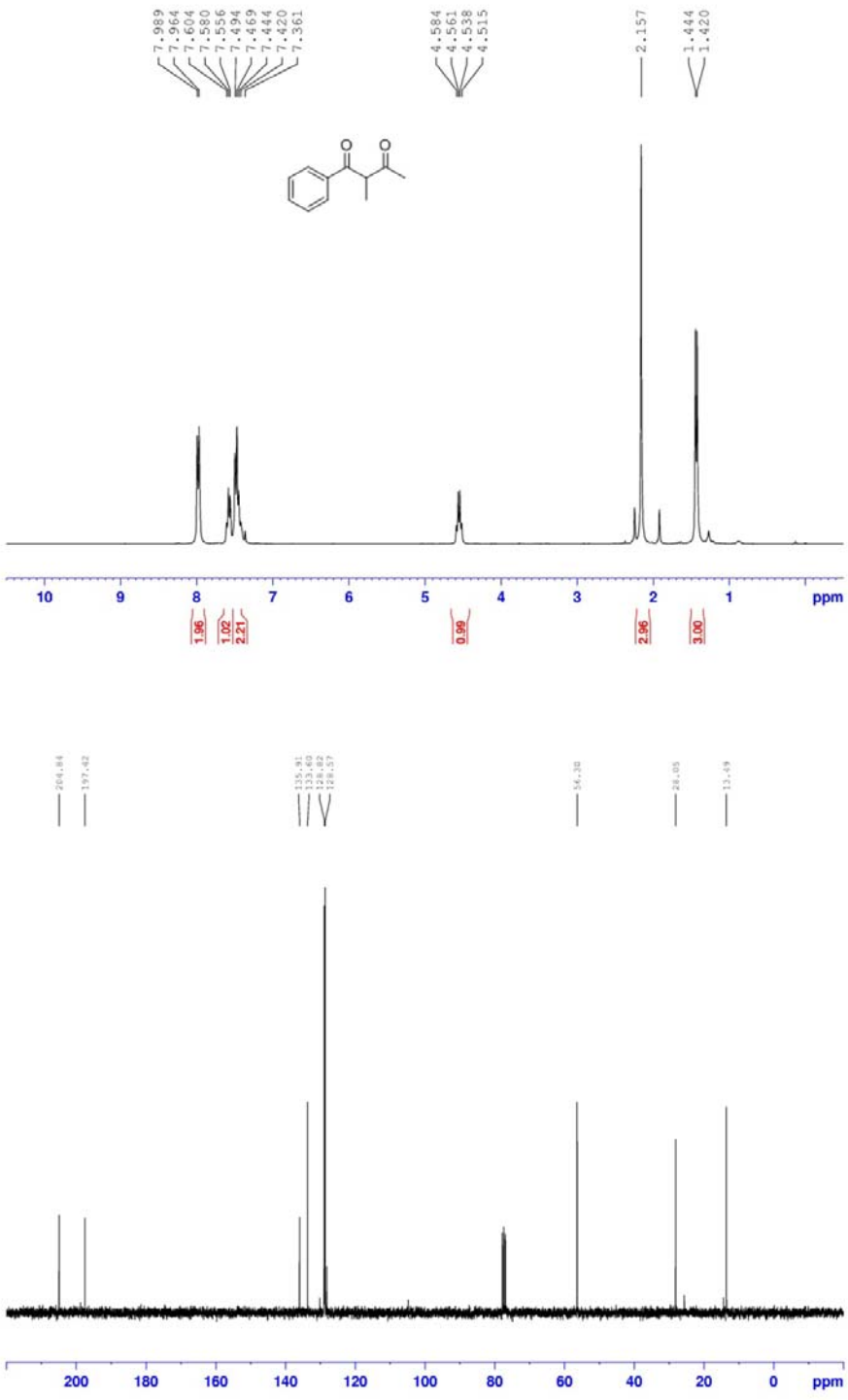


Figure S13. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-tosylaziridine-3-oxo-3-phenylpropanoate (**2a**)

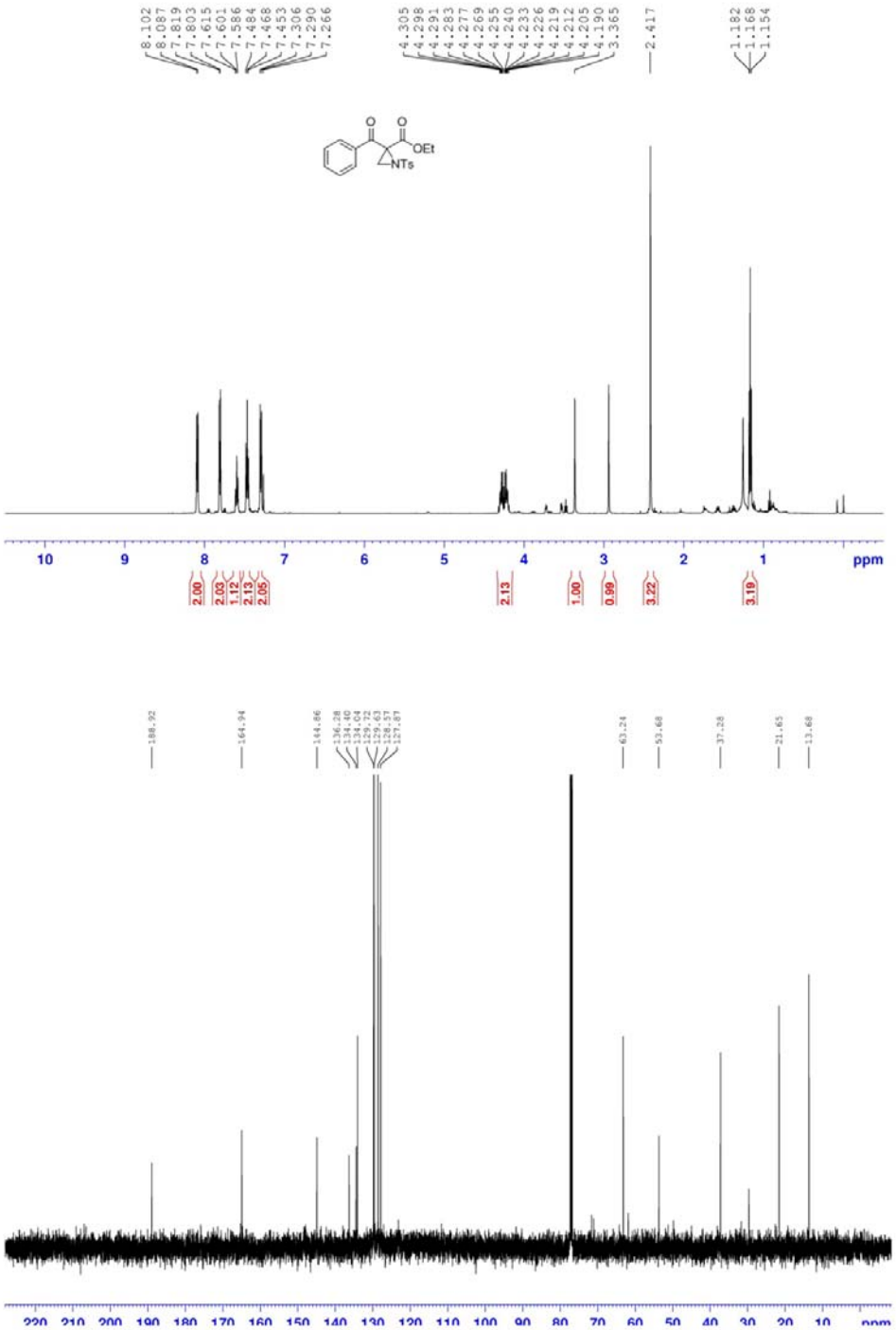


Figure S14. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(4-methylbenzoyl)-1-tosylaziridine-2-carboxylate (**2b**)

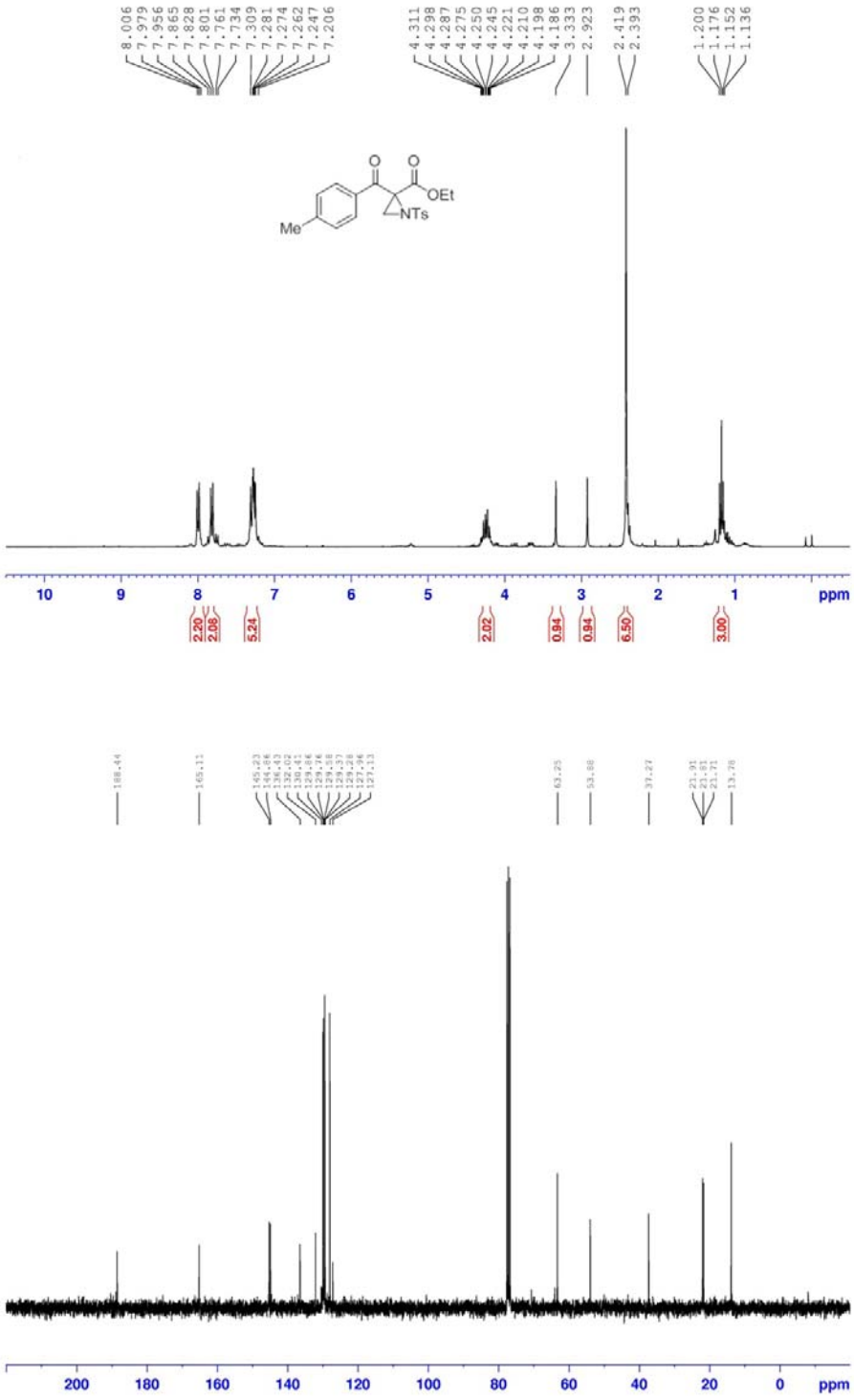


Figure S15. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(4-fluorobenzoyl)-1-tosylaziridine-2-carboxylate (**2c**)

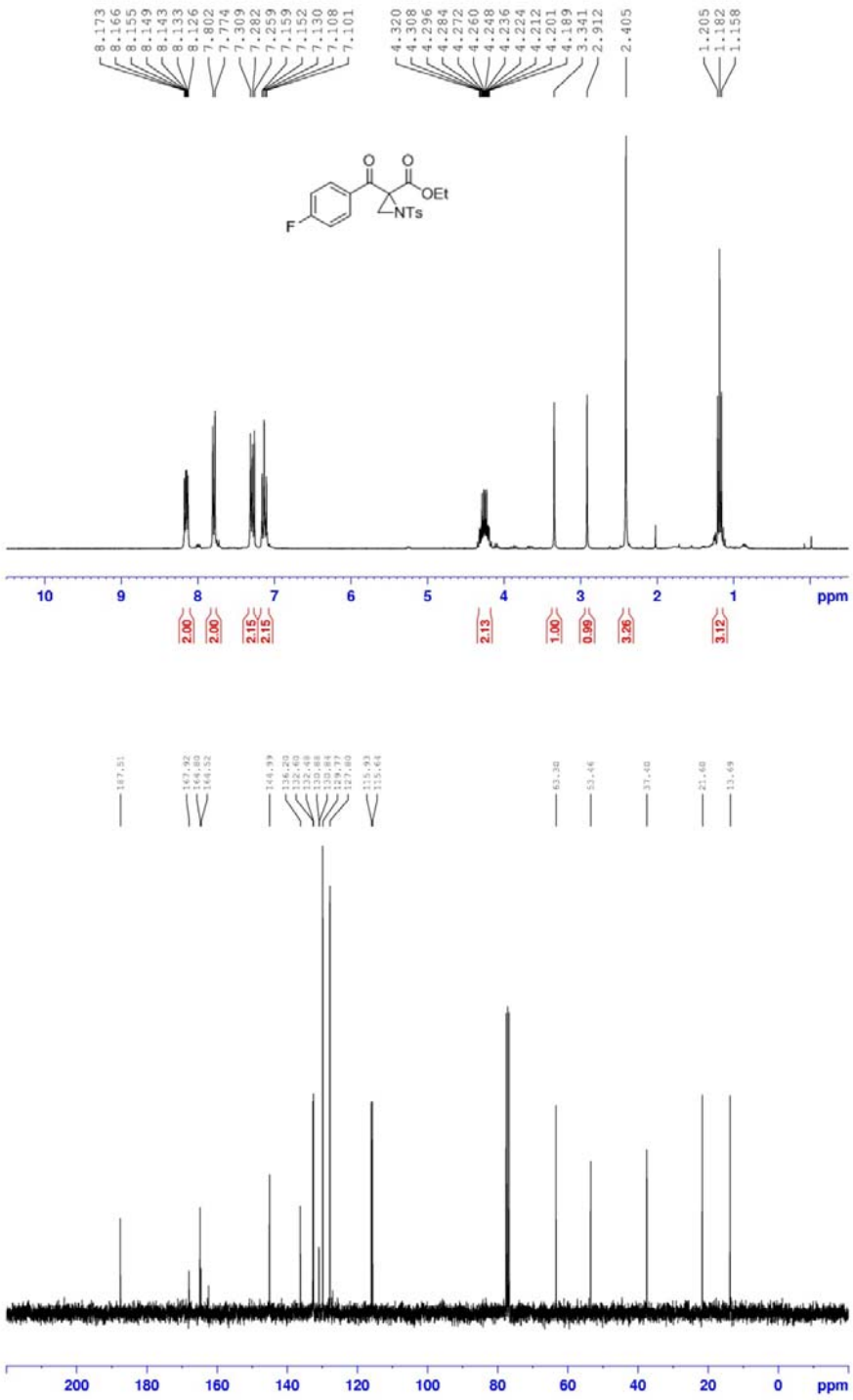


Figure S16. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(4-chlorobenzoyl)-1-tosylaziridine-2-carboxylate (**2d**)

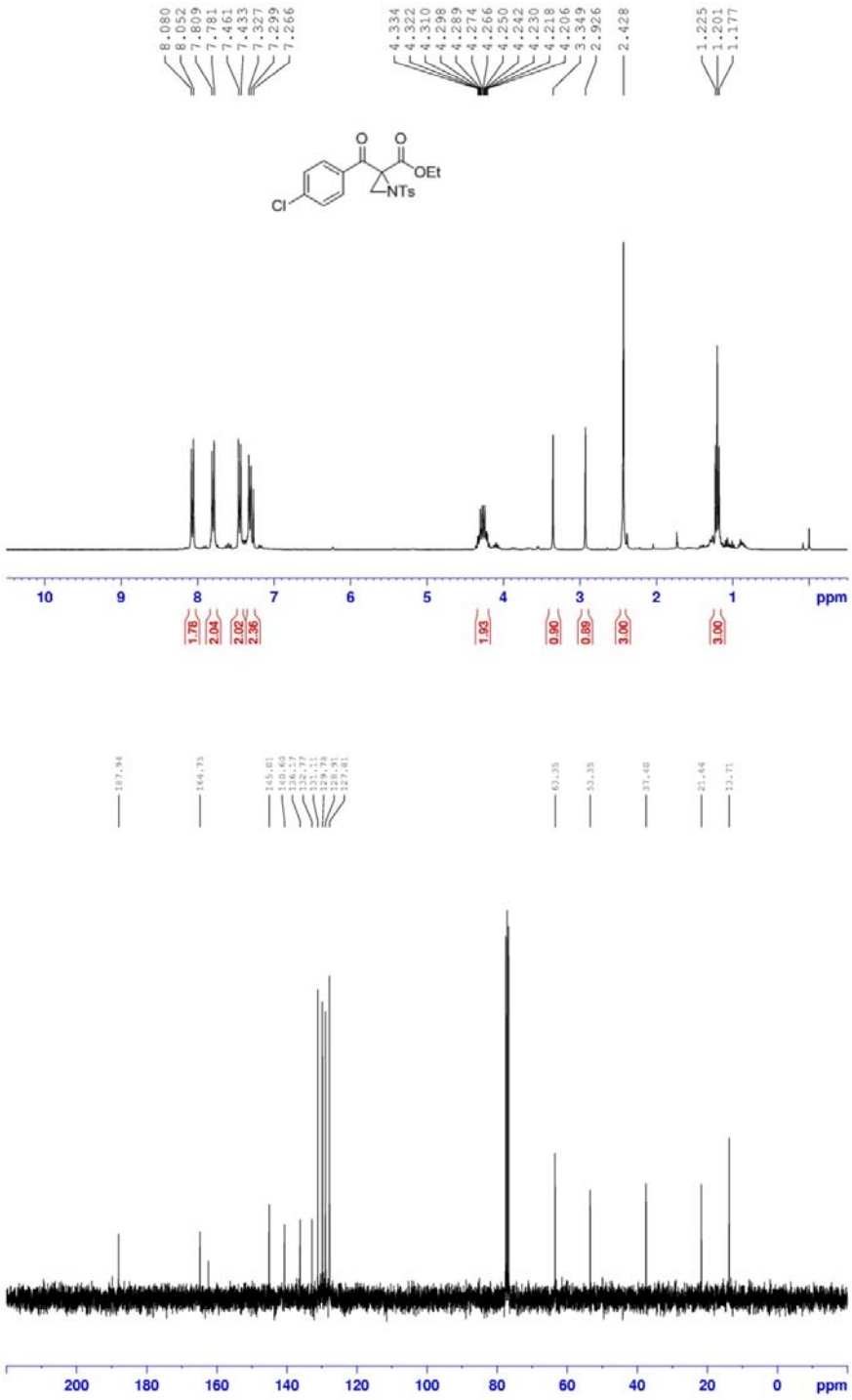


Figure S17. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(4-bromobenzoyl)-1-tosylaziridine-2-carboxylate (**2e**)

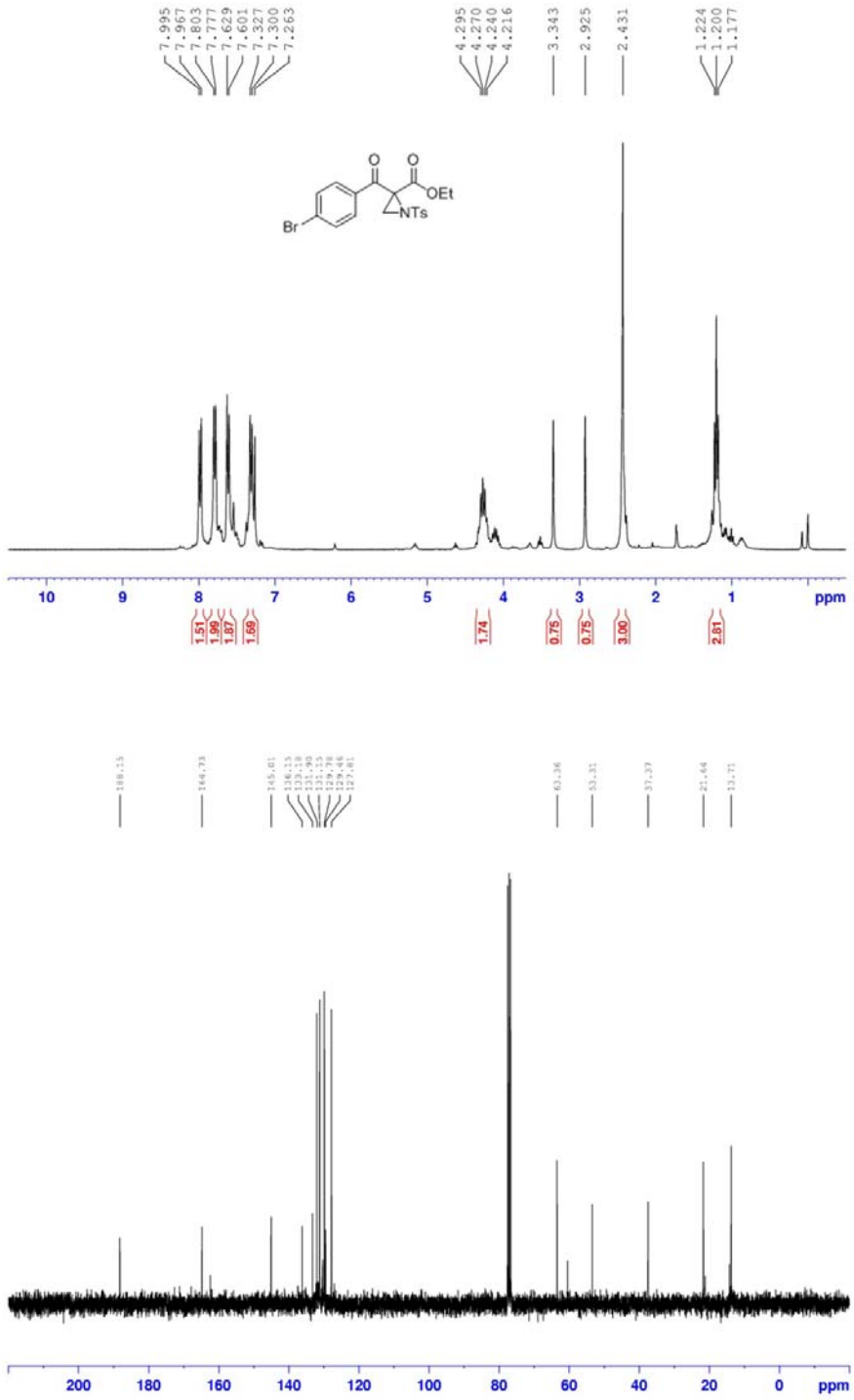


Figure S18. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(4-iodobenzoyl)-1-tosylaziridine-2-carboxylate (**2f**)

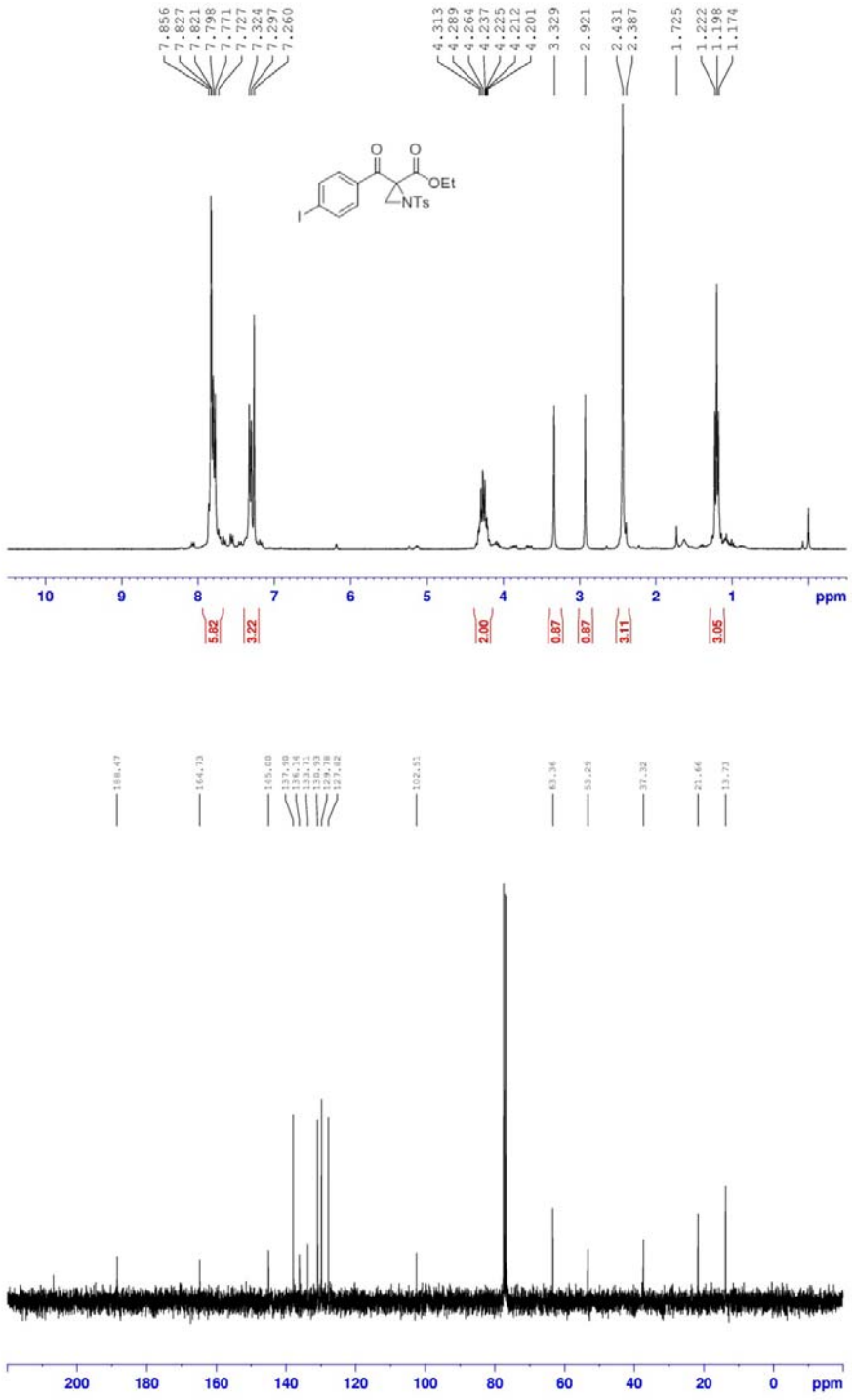


Figure S19. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-acetyl-3-methyl-1-tosylaziridine-2-carboxylate (**2g**)

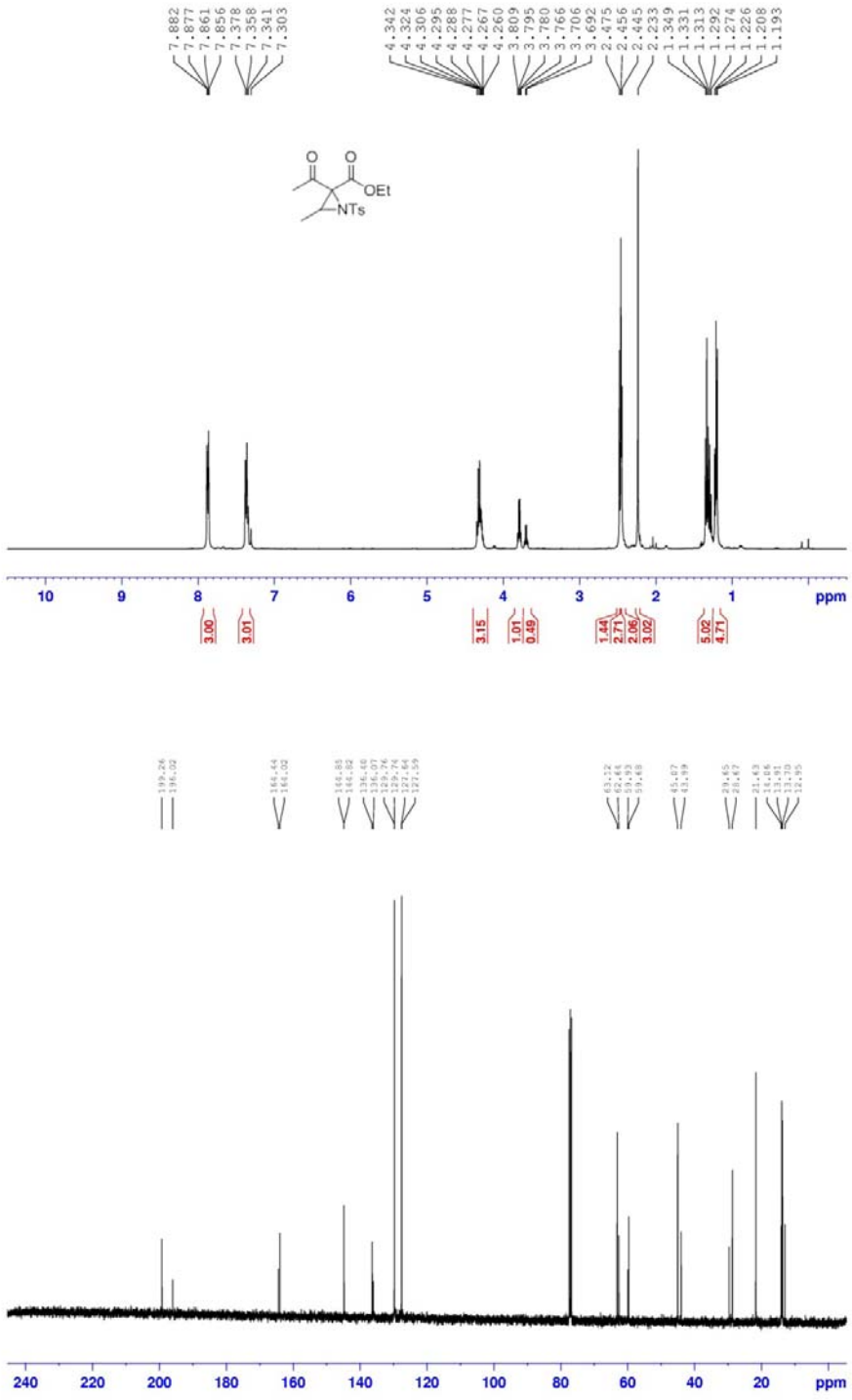
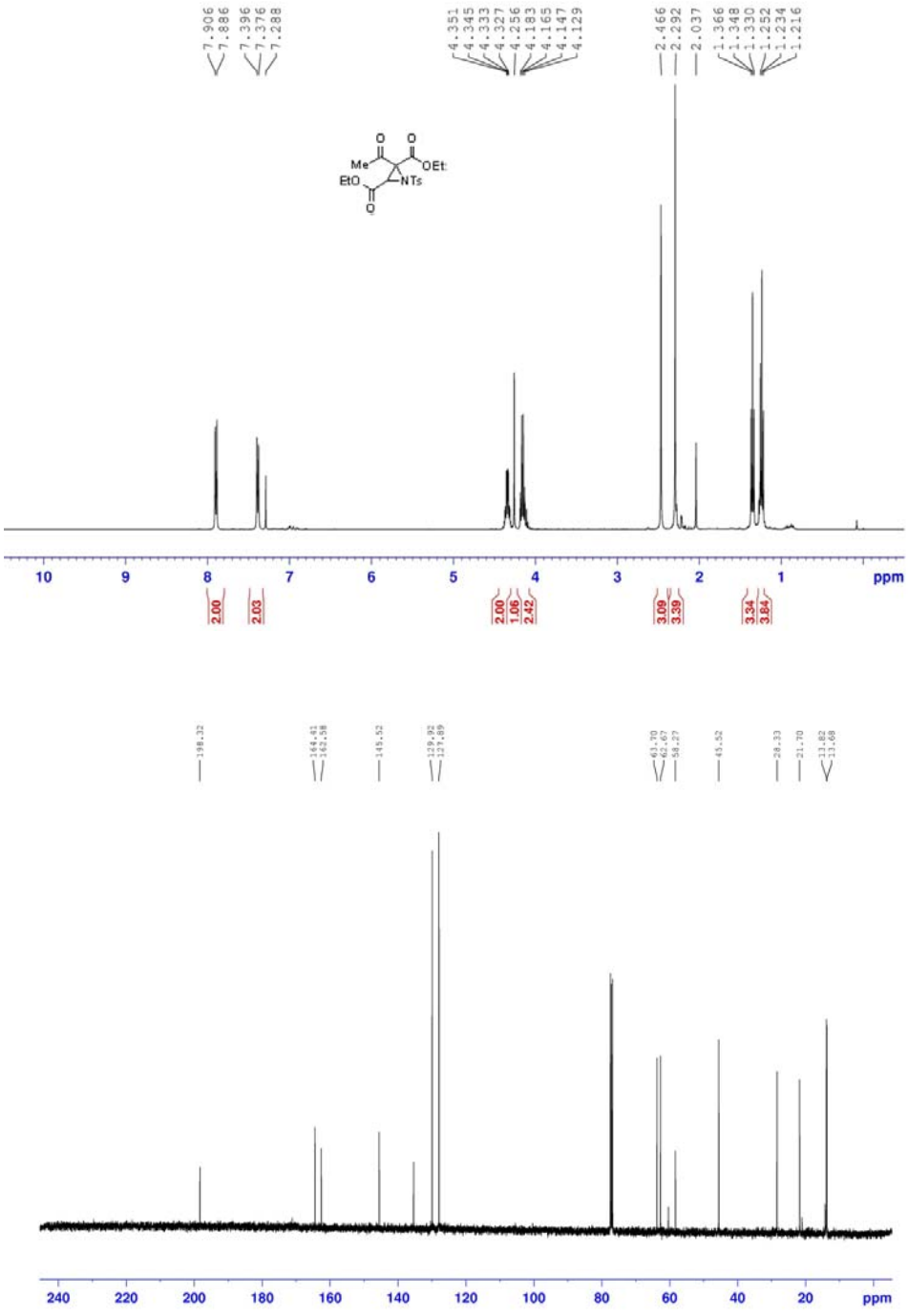


Figure S20. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-acetyl-1-tosylaziridine-2,3-dicarboxylate (**2h**)

Diastereomer 1



Diastereomer 2

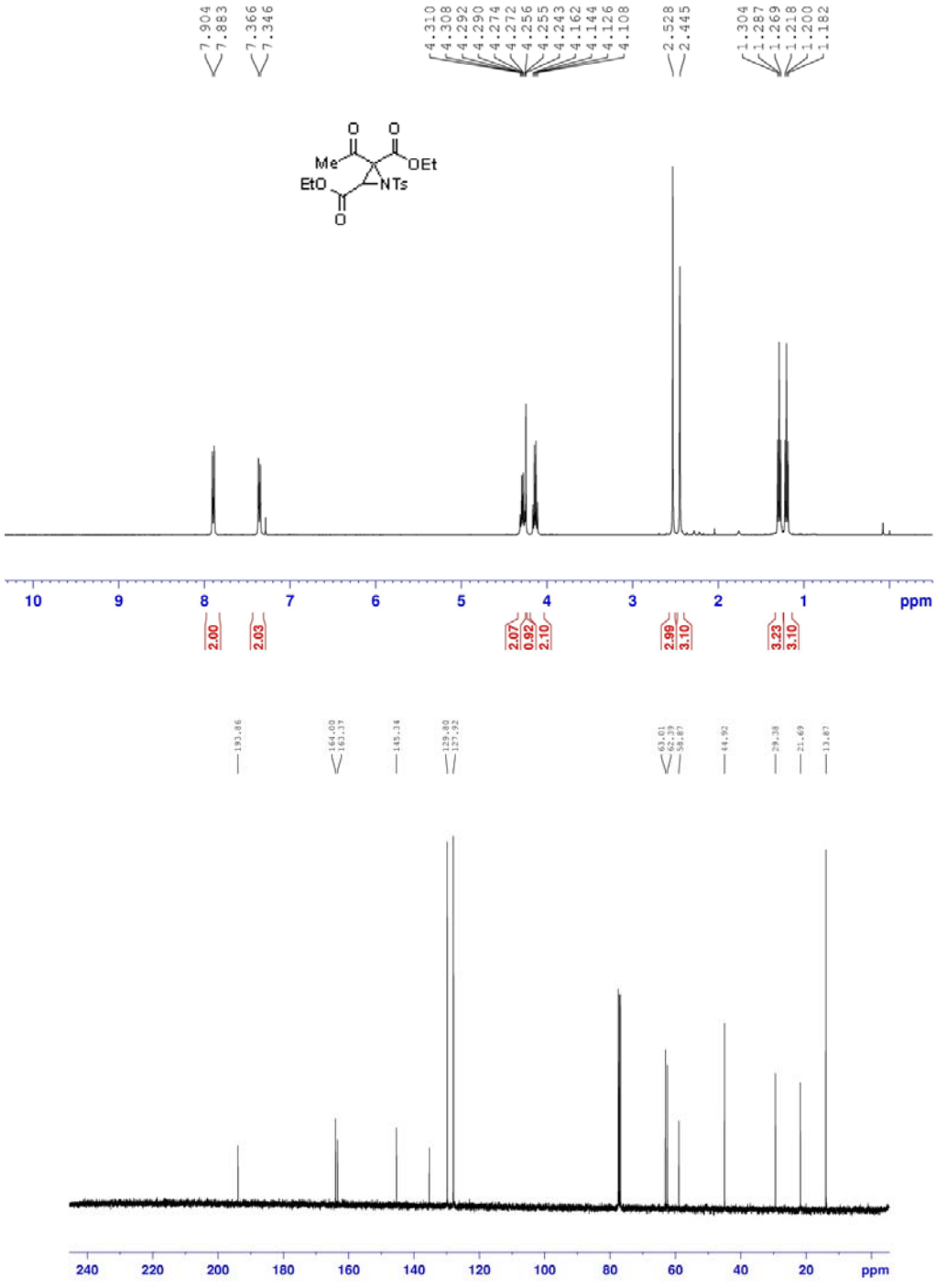


Figure S21. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-acetyl-3-(2-ethoxy-2-oxoethyl)-1-tosylaziridine-2-carboxylate (**2i**)

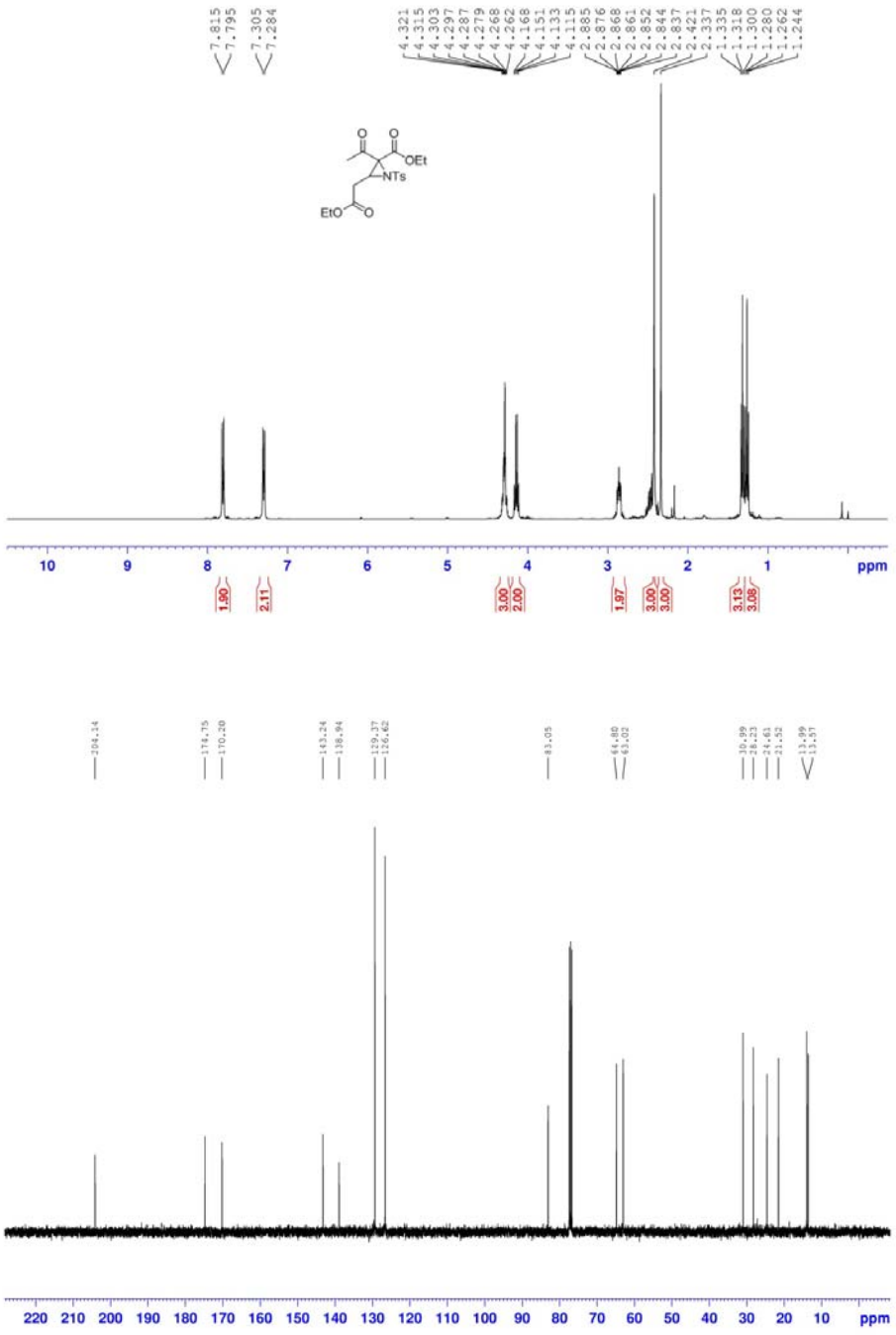


Figure S22. ^{1}H and ^{13}C NMR Spectra of Methyl 2-acetyl-3-butyl-1-tosylaziridine-2-carboxylate (**2j**)

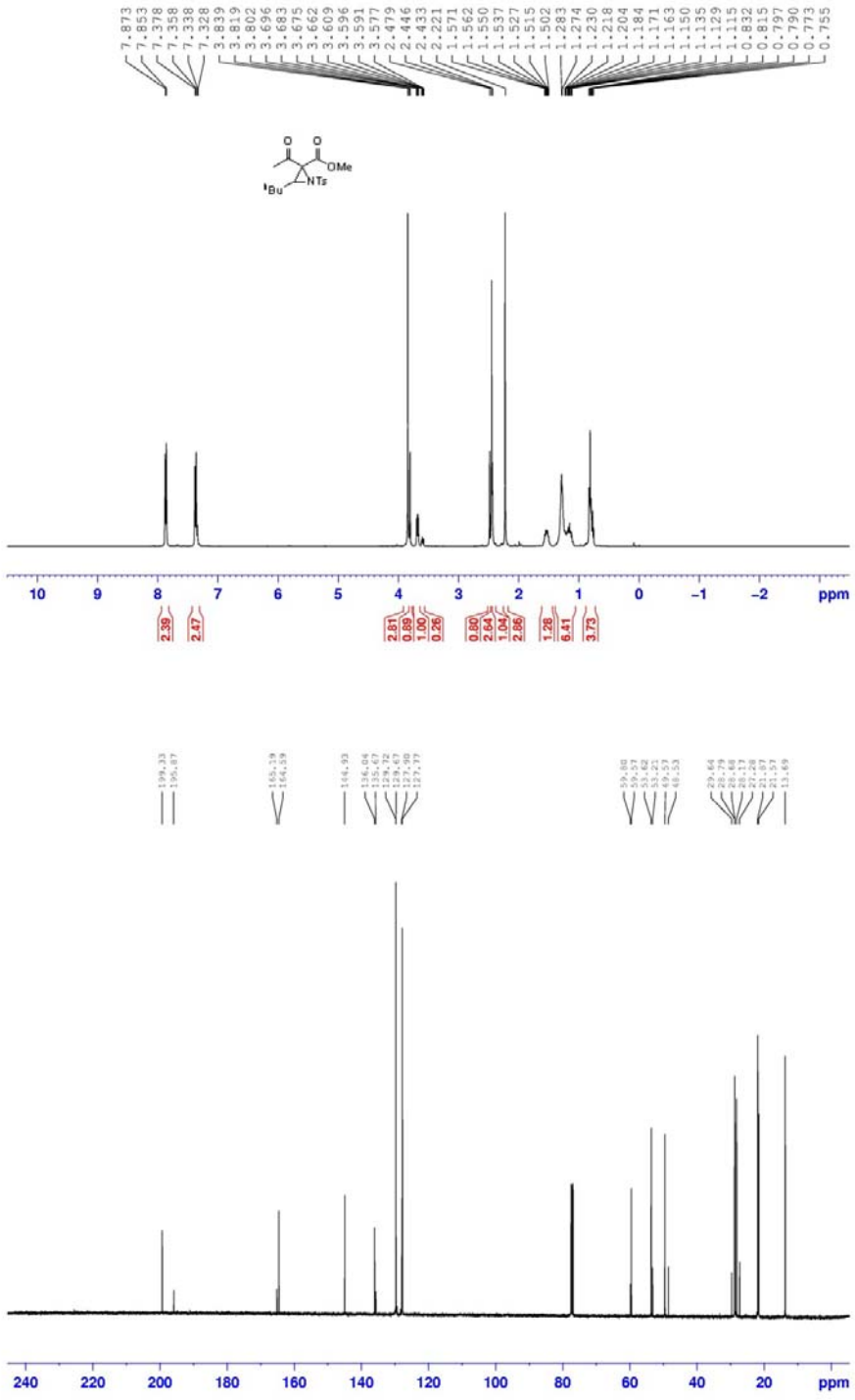


Figure S23. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-isobutyryl-1-tosylaziridine-2-carboxylate (**2k**)

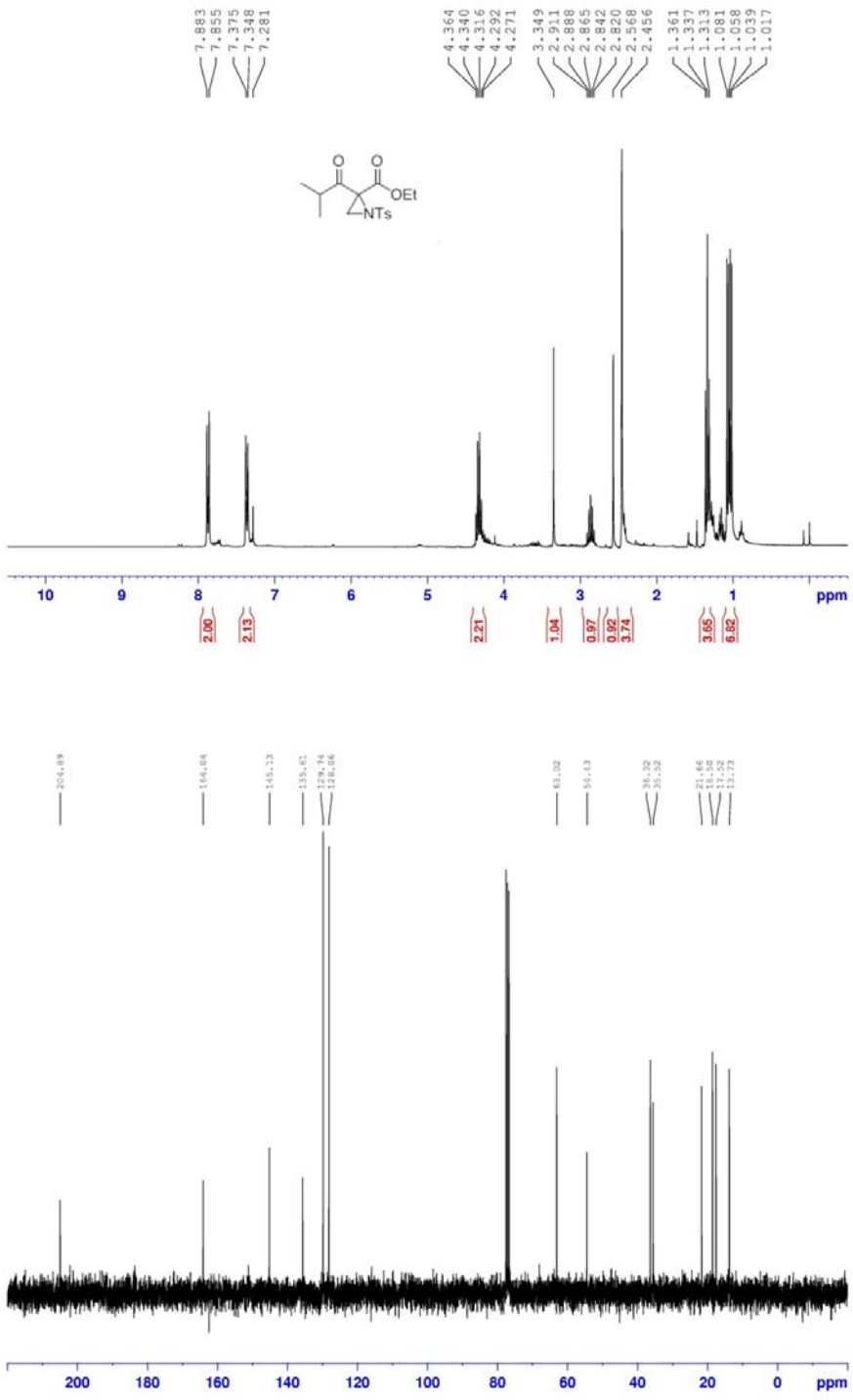


Figure S24. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-isobutyryl-3-methyl-1-tosylaziridine-2-carboxylate (**2l**)

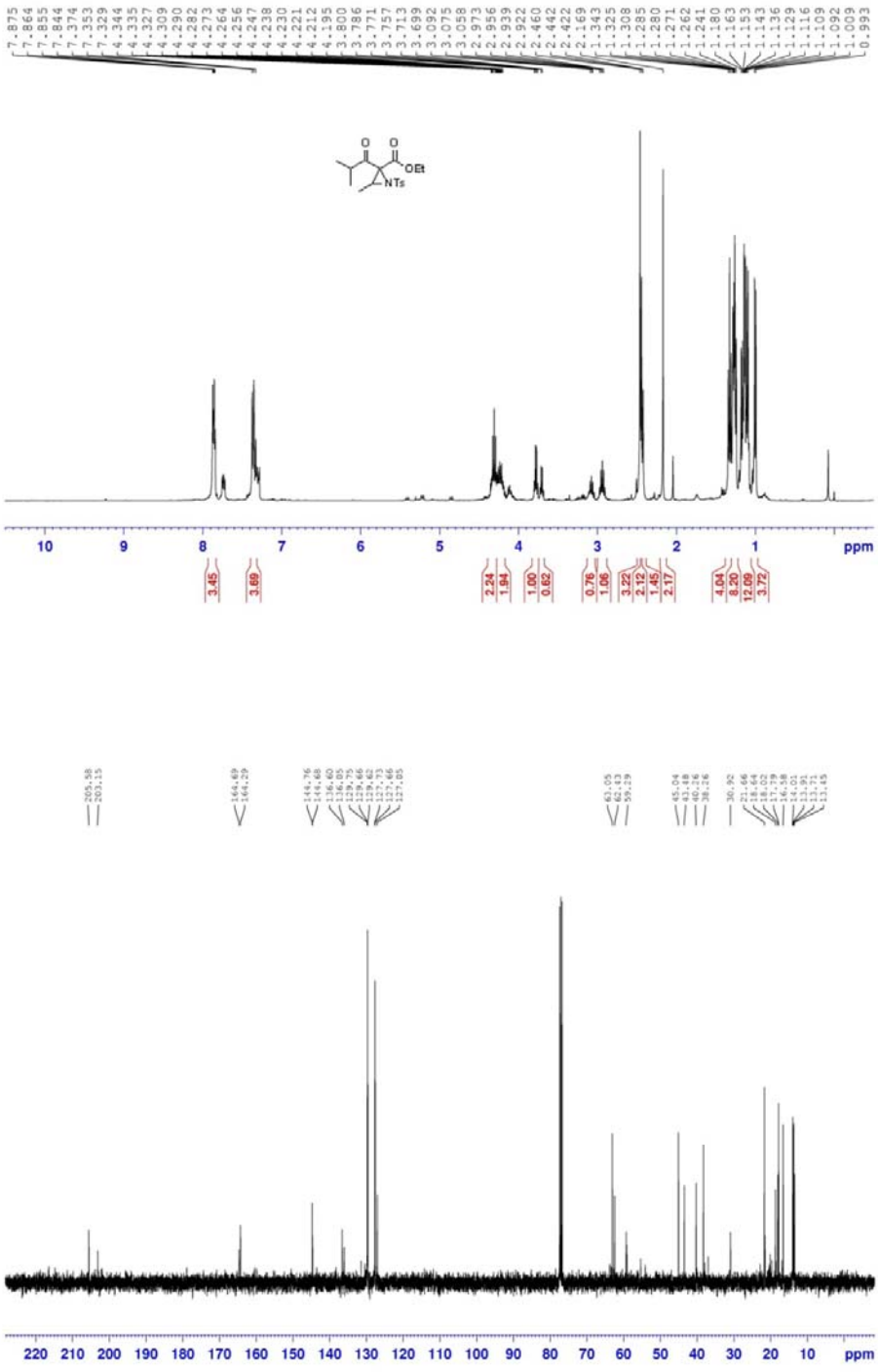


Figure S25. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(cyclopropanecarbonyl)-3-methyl-1-tosylaziridine-2-carboxylate (**2m**)

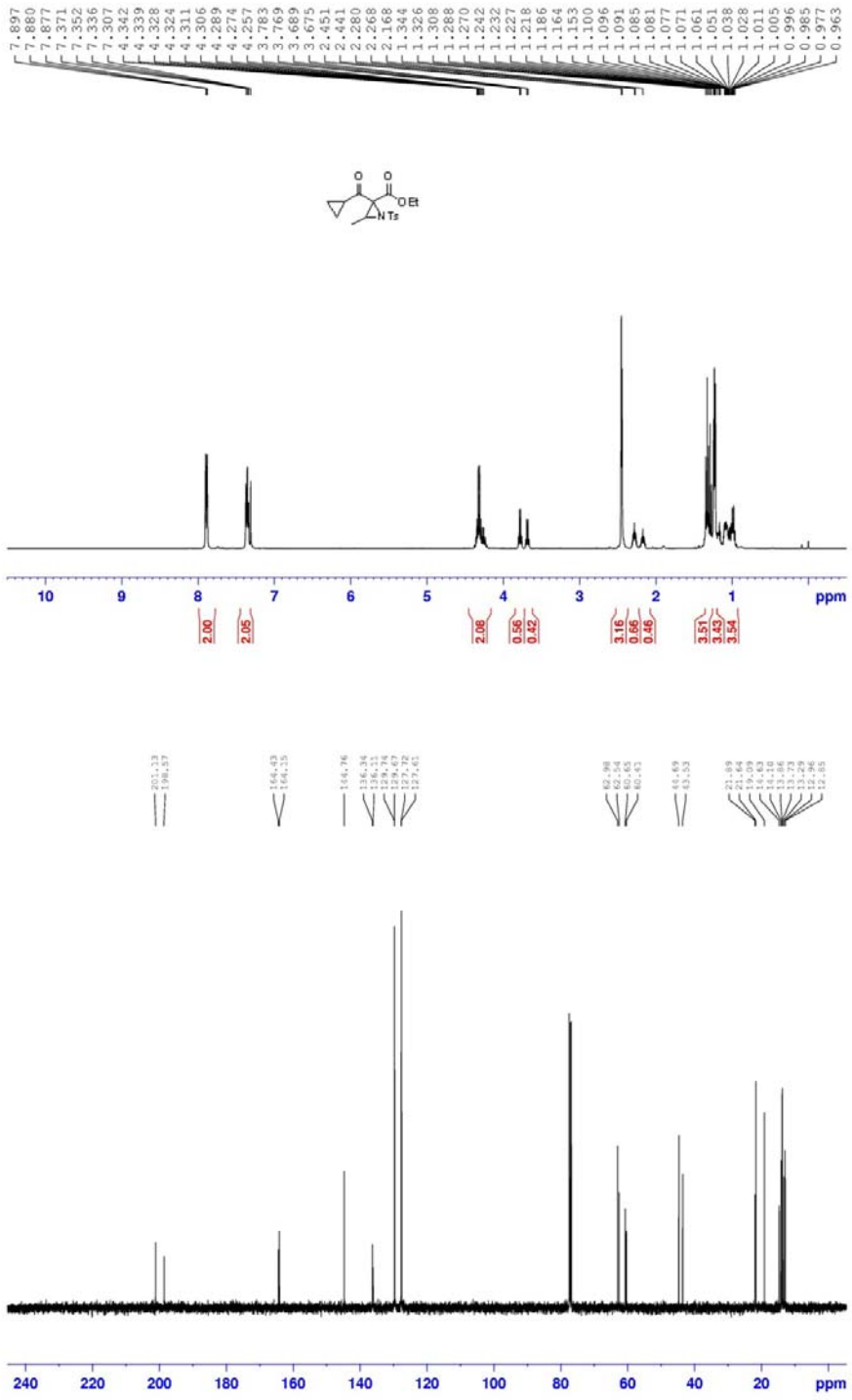


Figure S26. ^{1}H and ^{13}C NMR Spectra of Dimethyl 1-tosylaziridine-2,2-dicarboxylate (**2n**)

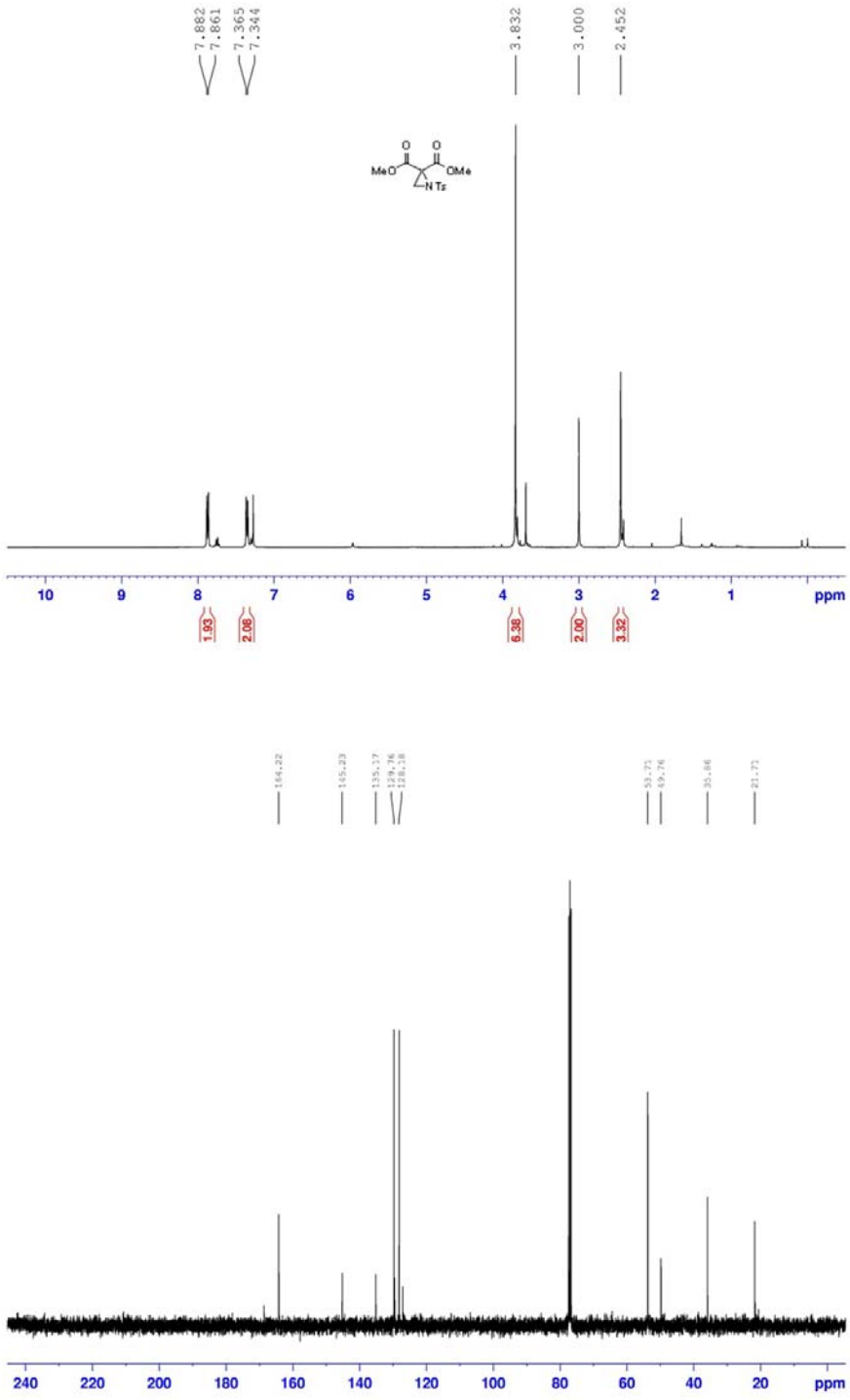


Figure S27. ^{1}H and ^{13}C NMR Spectra of Diethyl 1-tosylaziridine-2,2-dicarboxylate (**2o**)

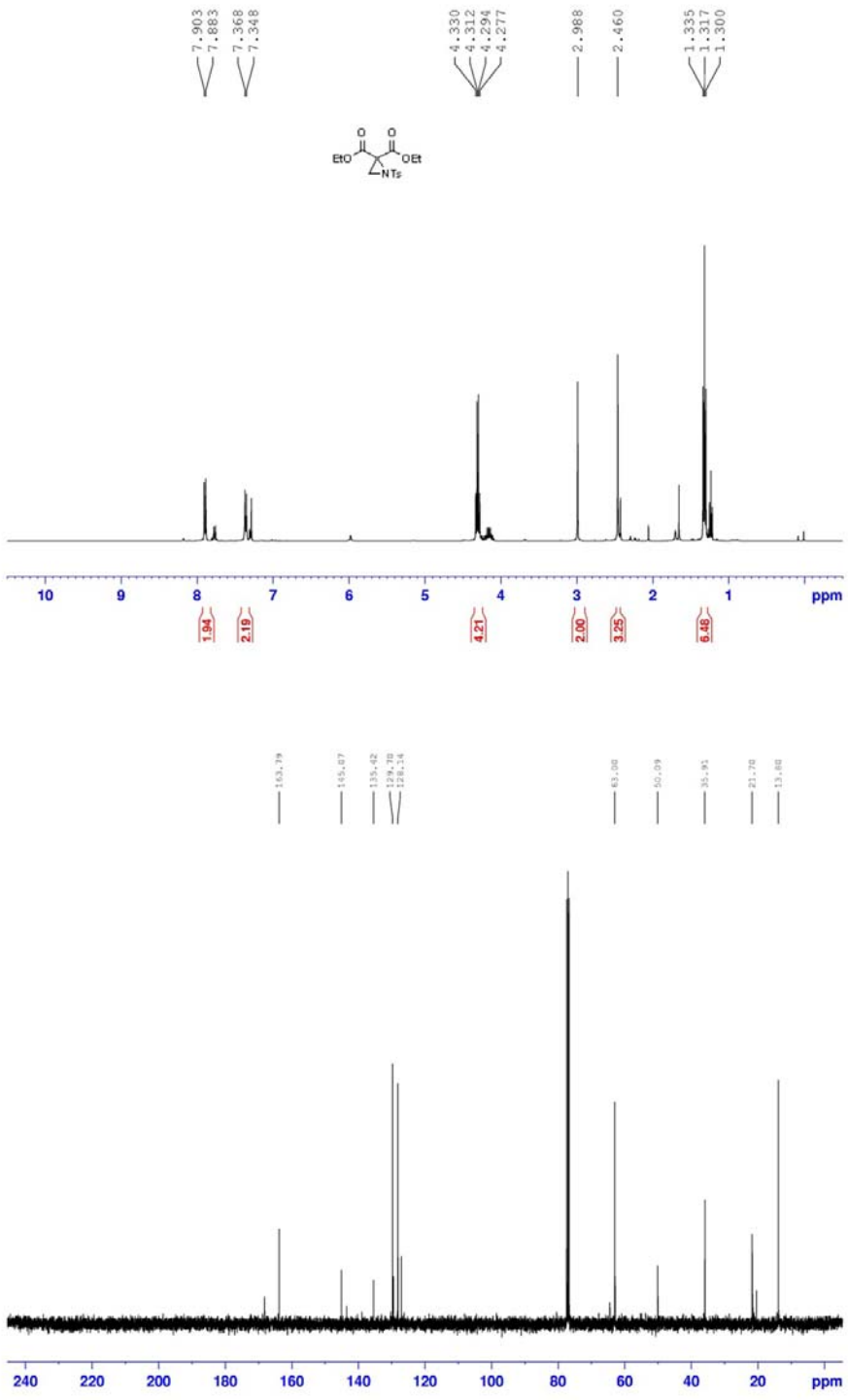


Figure S28. ^{1}H and ^{13}C NMR Spectra of Dibenzyl 1-tosylaziridine-2,2-dicarboxylate (**2p**)

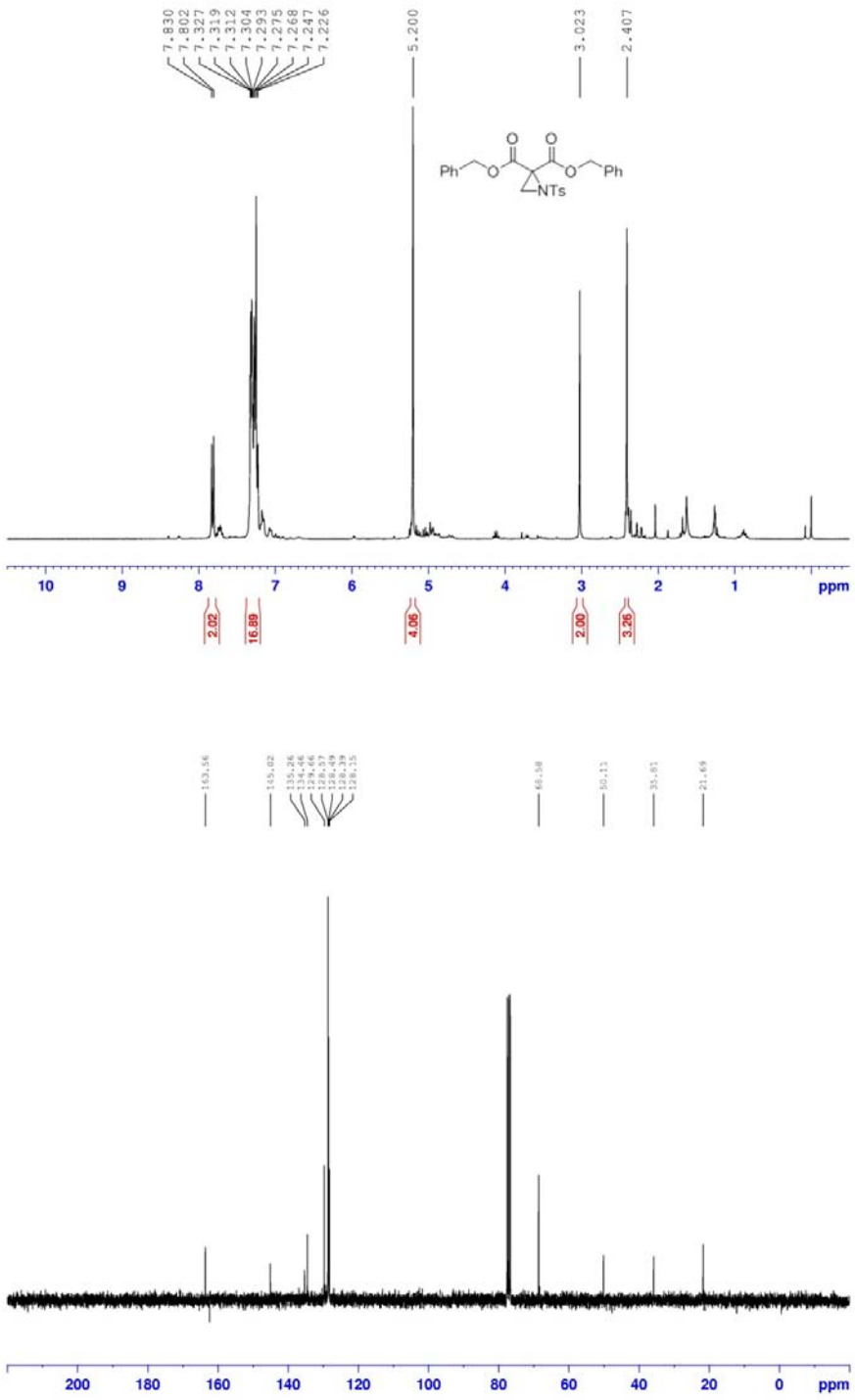


Figure S29. ^{1}H and ^{13}C NMR Spectra of Dimethyl 3-methyl-1-tosylaziridine-2,2-dicarboxylate (**2q**)

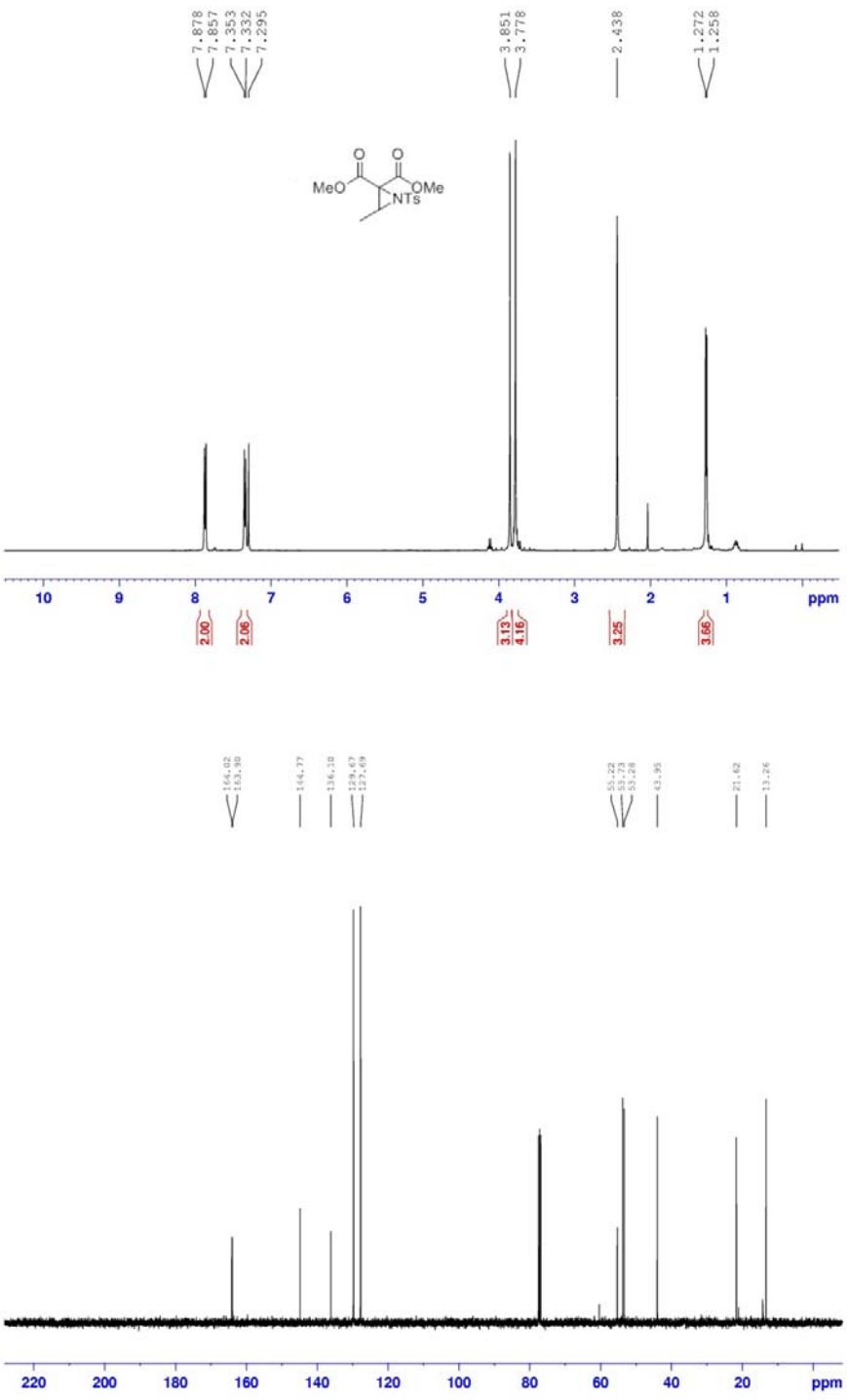


Figure S30. ^{1}H and ^{13}C NMR Spectra of Diethyl 3-methyl-1-tosylaziridine-2,2-dicarboxylate (**2r**)

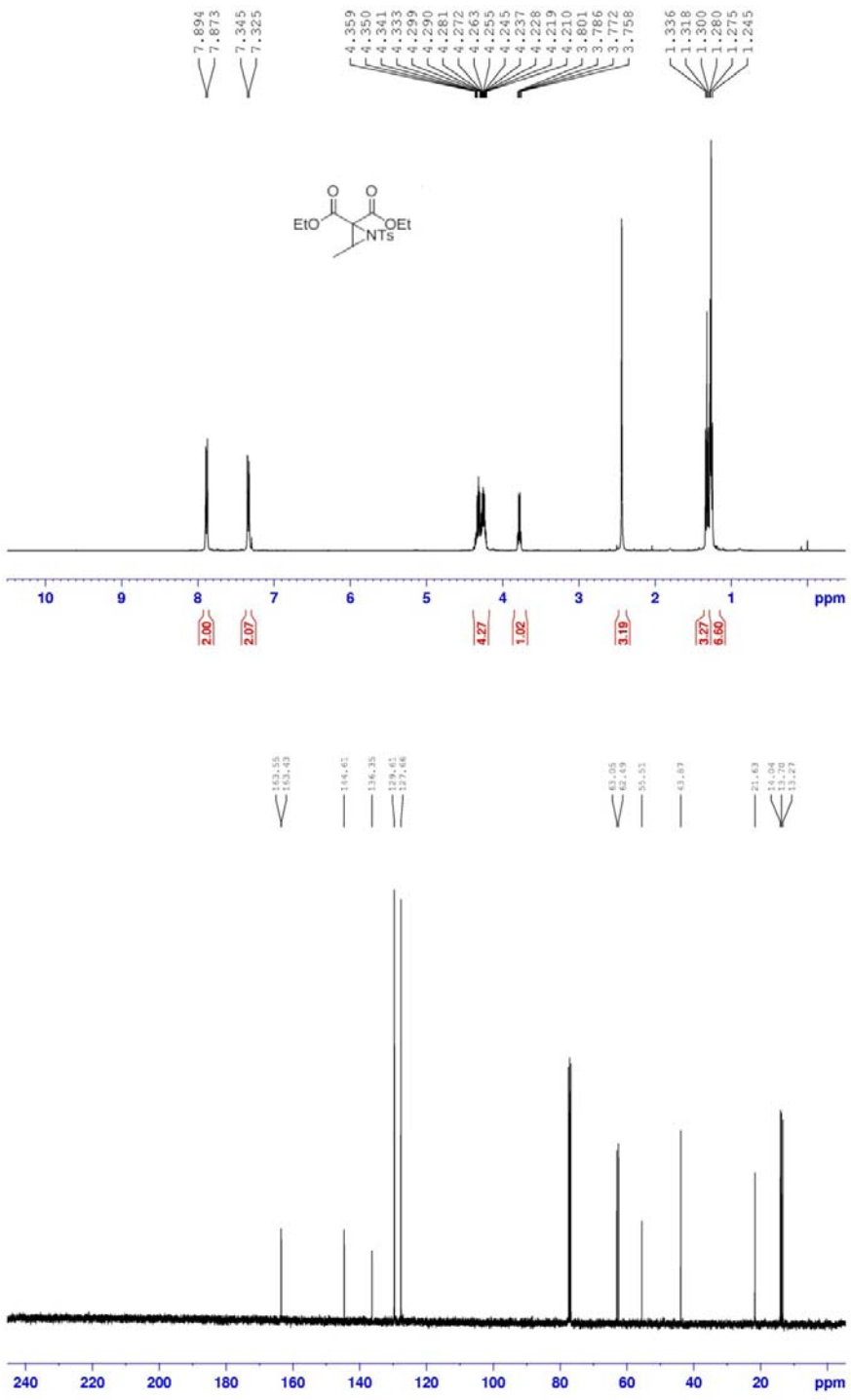


Figure S31. ^{1}H and ^{13}C NMR Spectra of Diethyl 3-ethyl-1-tosylaziridine-2,2-dicarboxylate (**2s**)

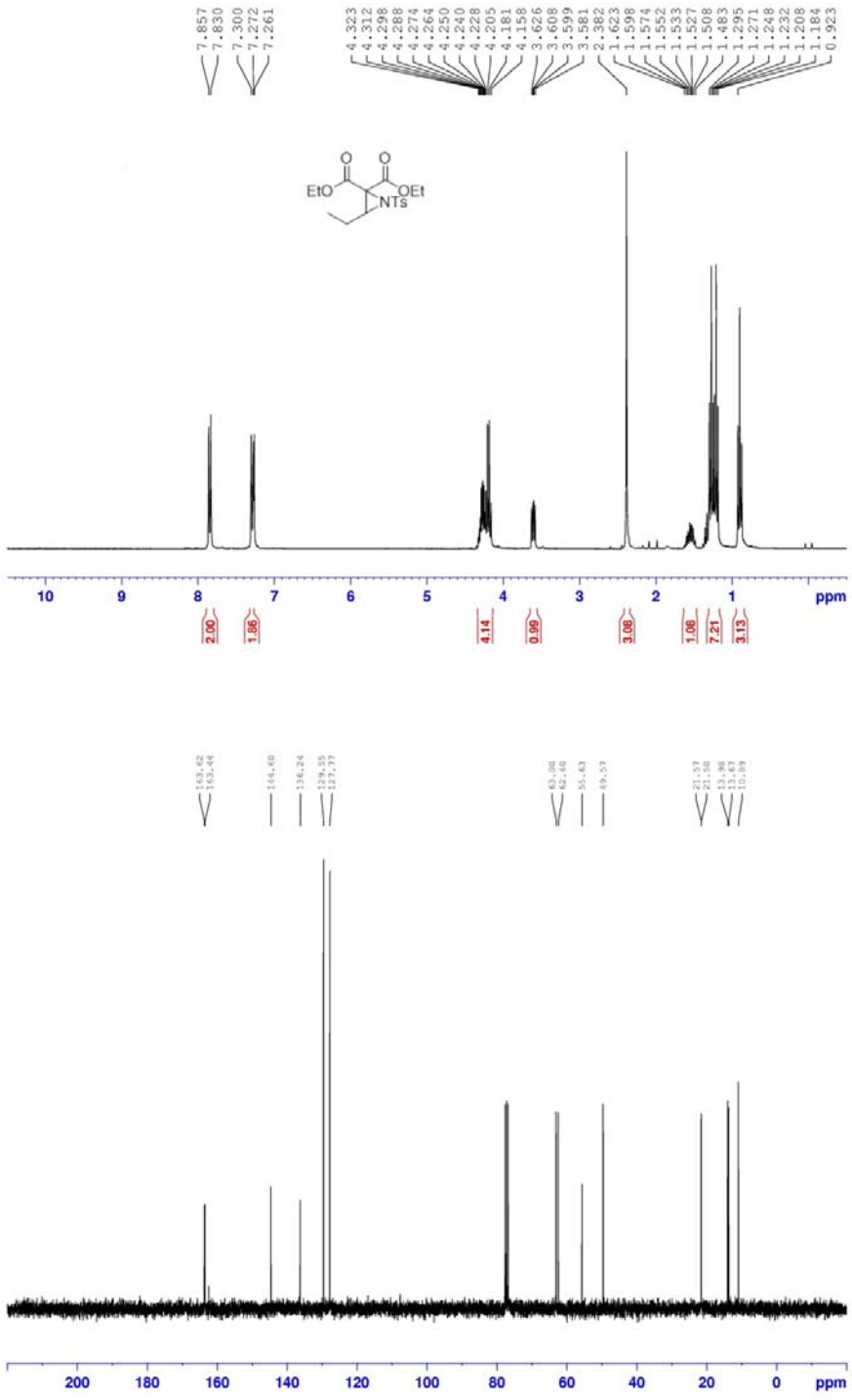


Figure S32. ^{1}H and ^{13}C NMR Spectra of Diethyl 3-(2-chloroethyl)-1-tosylaziridine-2,2-dicarboxylate (**2t**)

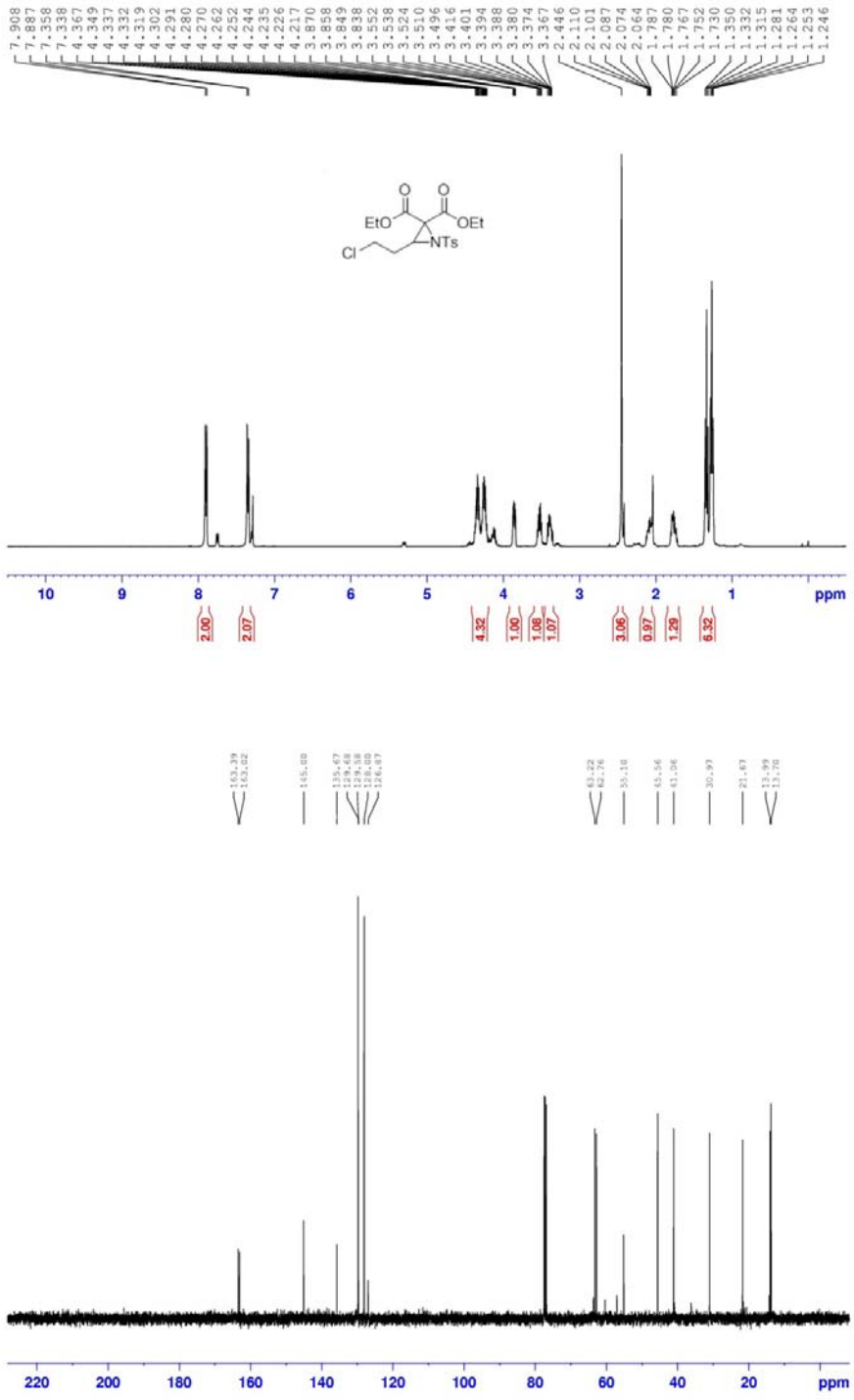


Figure S33. ^{1}H and ^{13}C NMR Spectra of 1-(2-Benzoyl-1-tosylaziridin-2-yl)ethanone (**2u**)

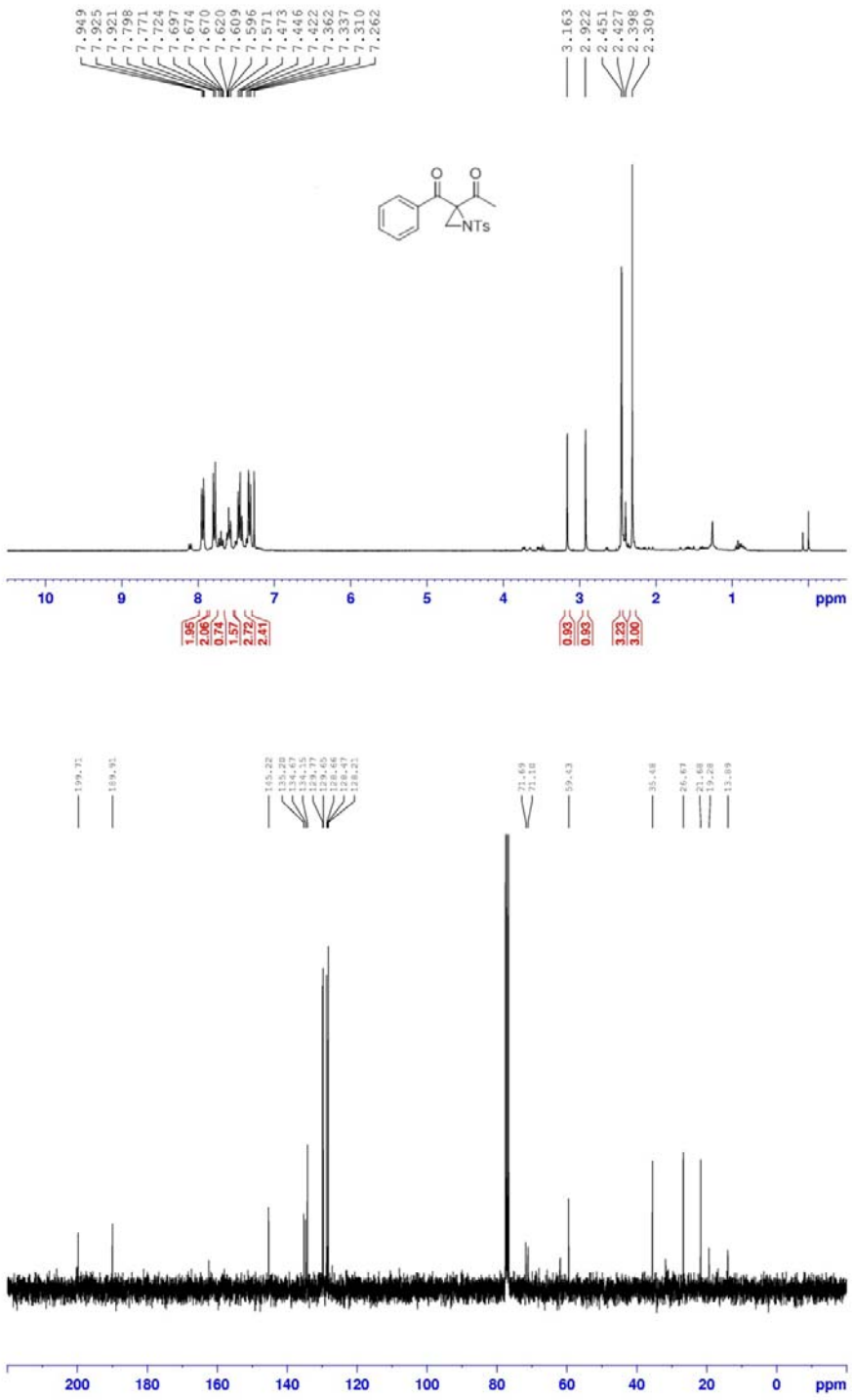


Figure S34. ^{1}H and ^{13}C NMR Spectra of 1,1'-(3-Methyl-1-tosylaziridine-2,2-diyl)diethanone (**2v**)

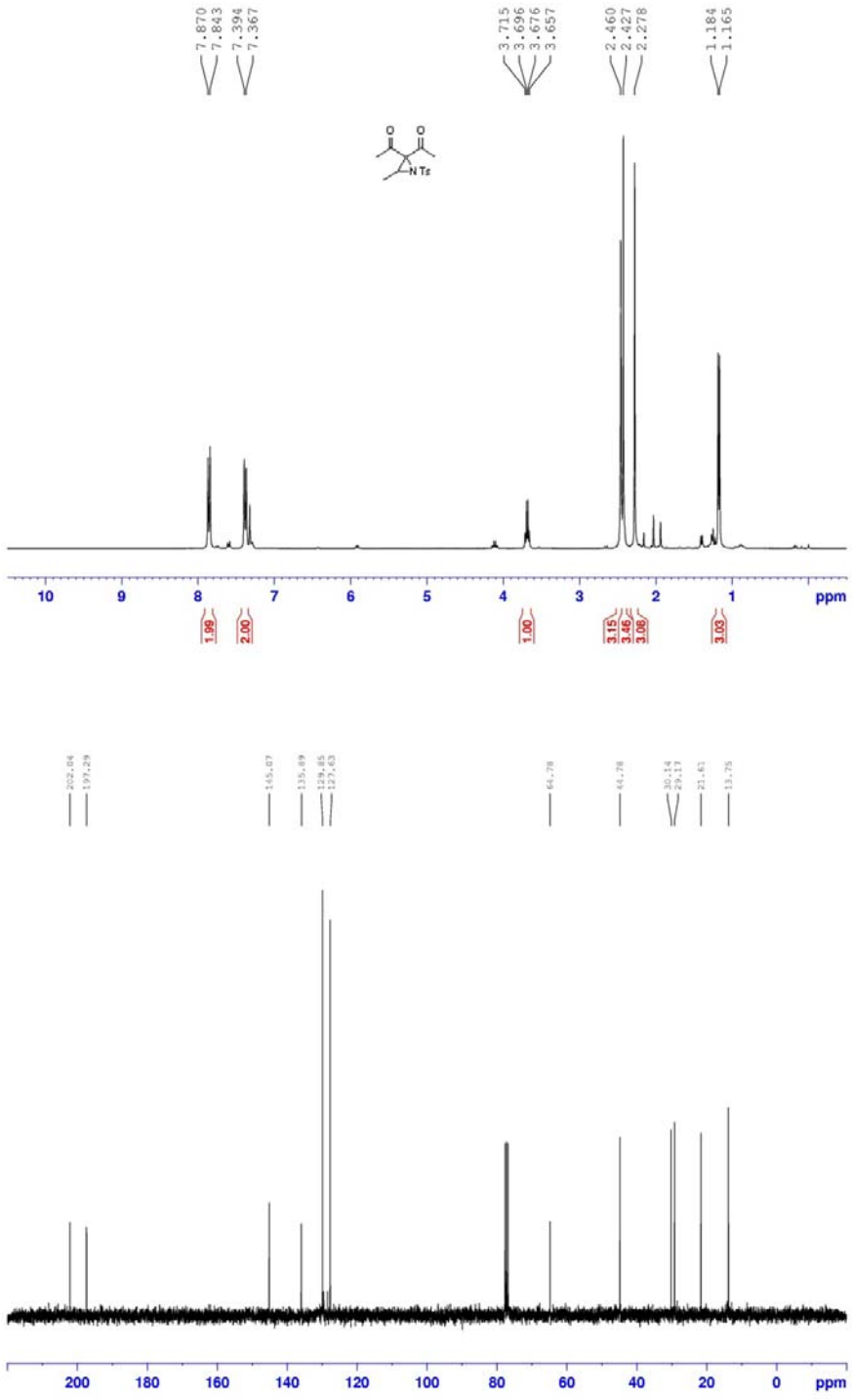


Figure S35. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-acetyl-3-(4-methylphenylsulfonamido) butanoate (**3g**)

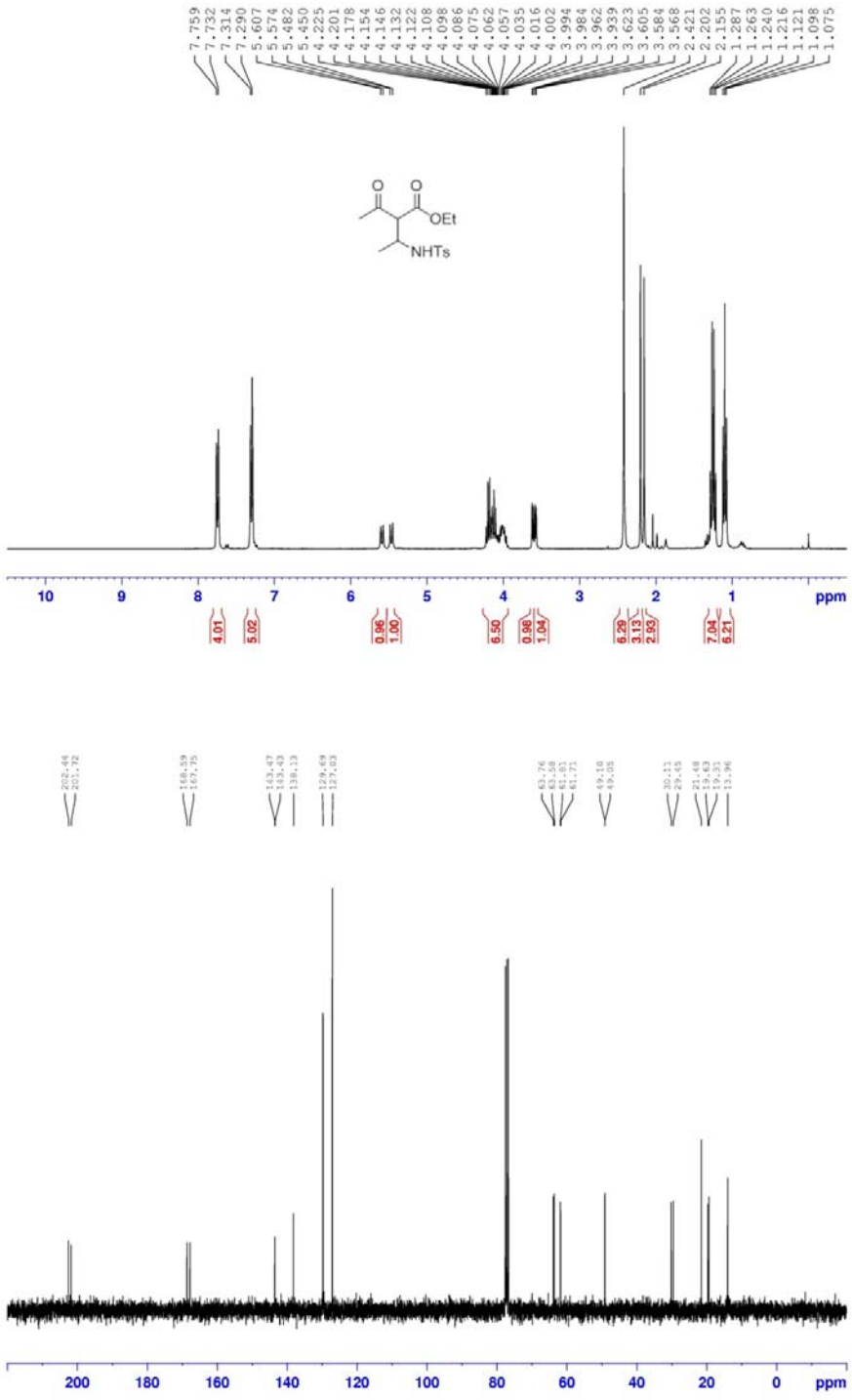


Figure S36. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-acetyl-3-(4-methylphenylsulfonamido) butanoate (**3l**)

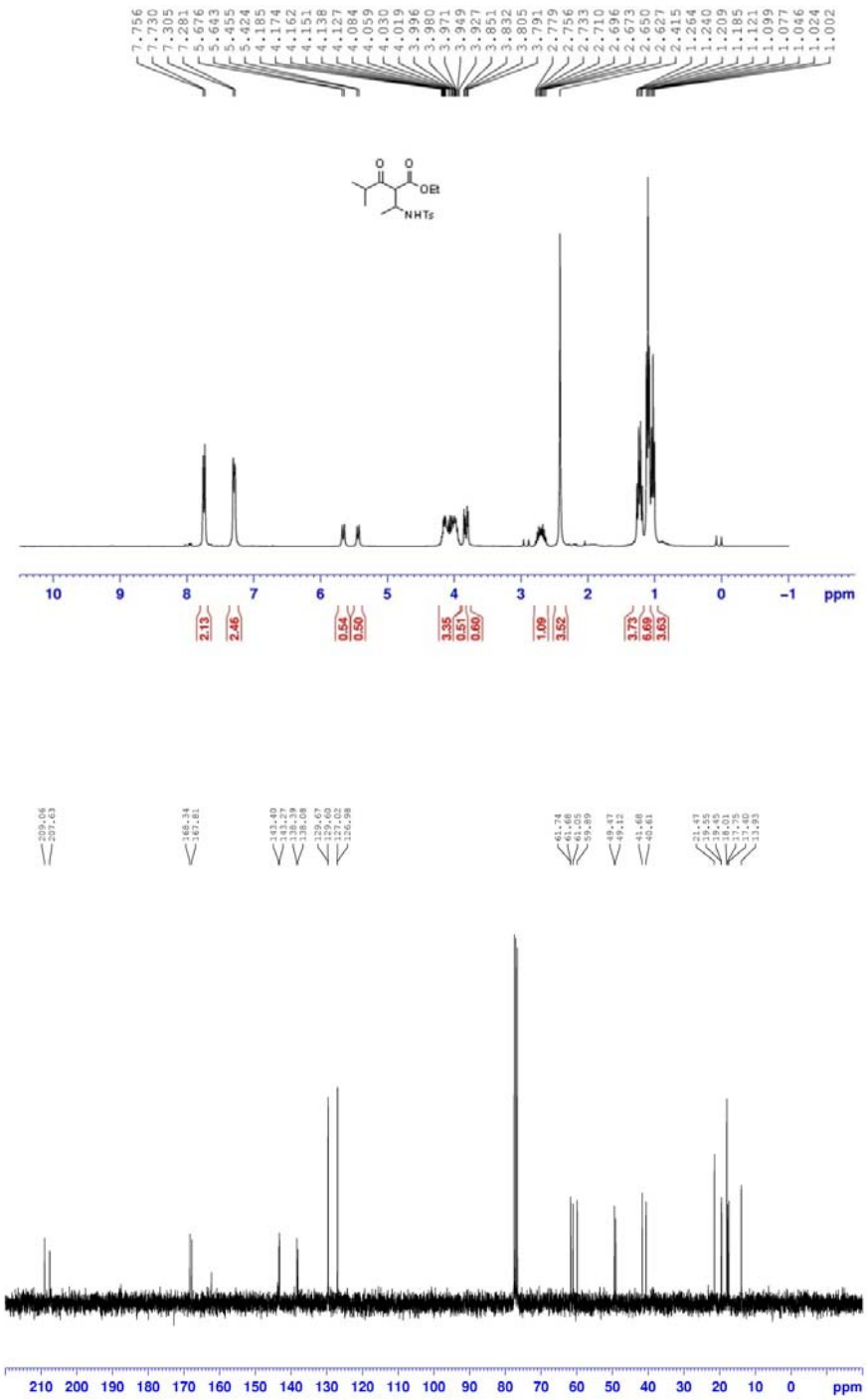


Figure S37. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-(cyclopropanecarbonyl)-3-(4-methylphenylsulfonamido)butanoate (**3m**)

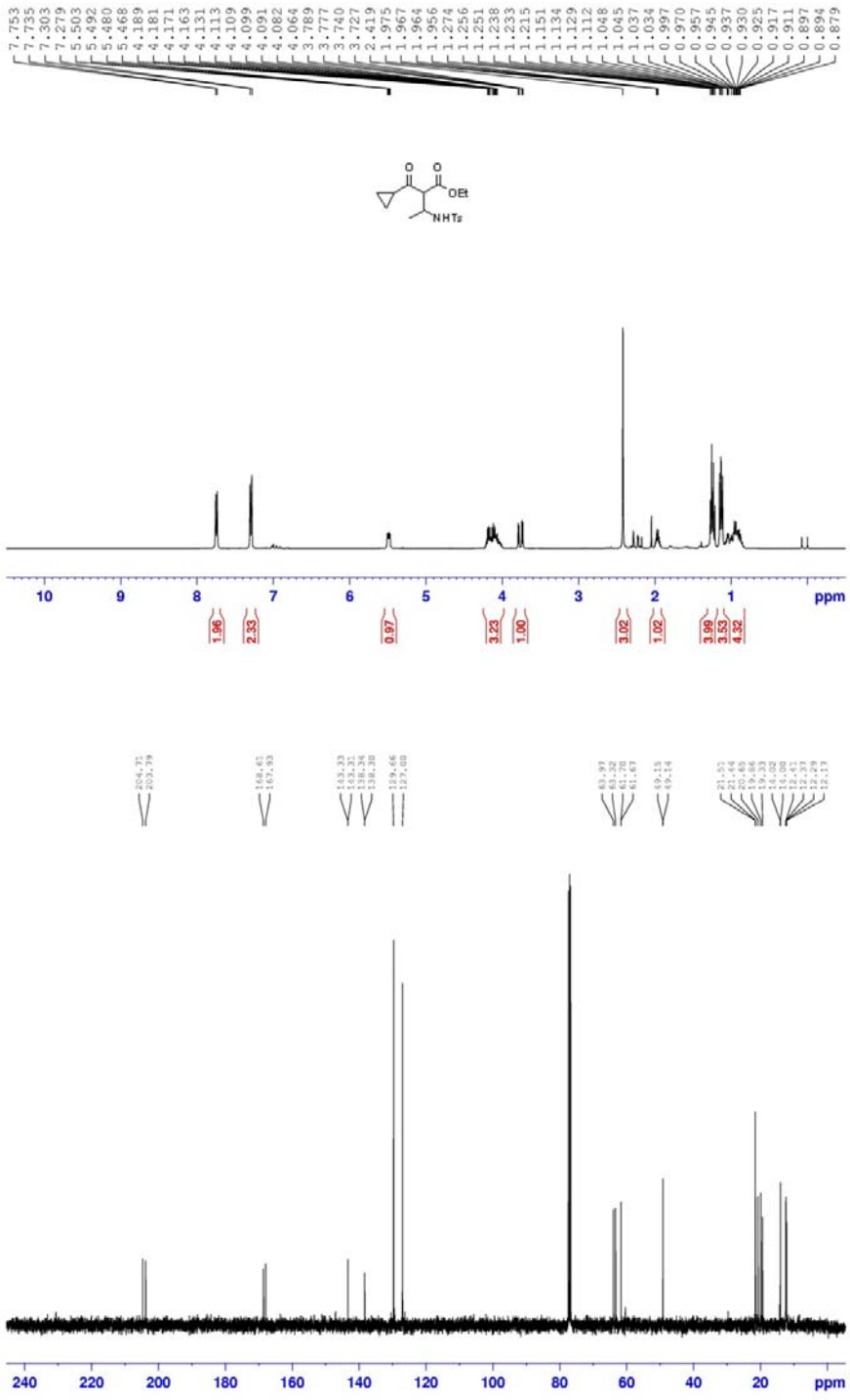


Figure S38. ^{1}H and ^{13}C NMR Spectra of Dimethyl 2-(1-(4-methylphenylsulfonamido)ethyl) malonate (**3q**)

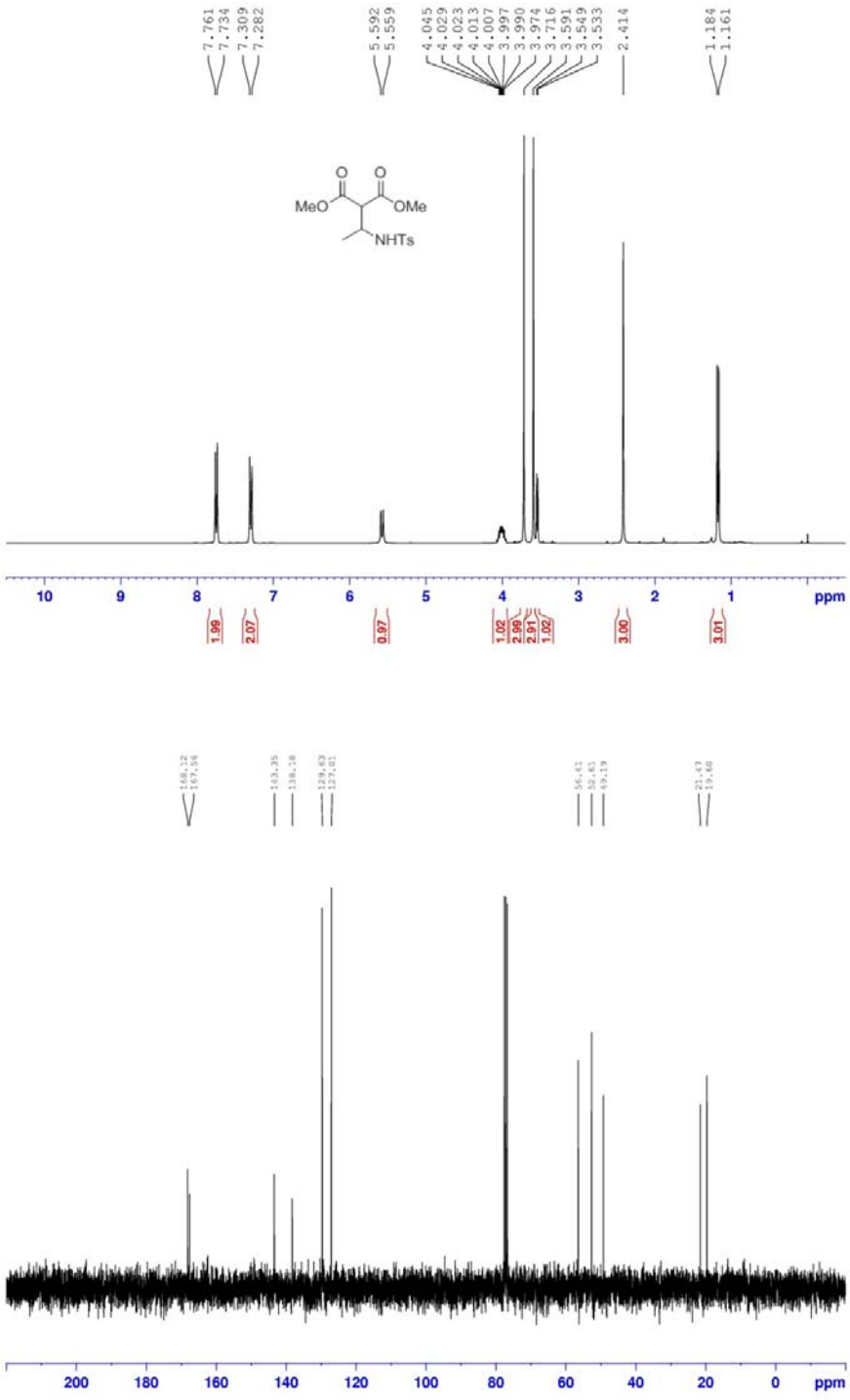


Figure S39. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-(1-(4 methylphenylsulfonamido)ethyl) malonate (**3r**)

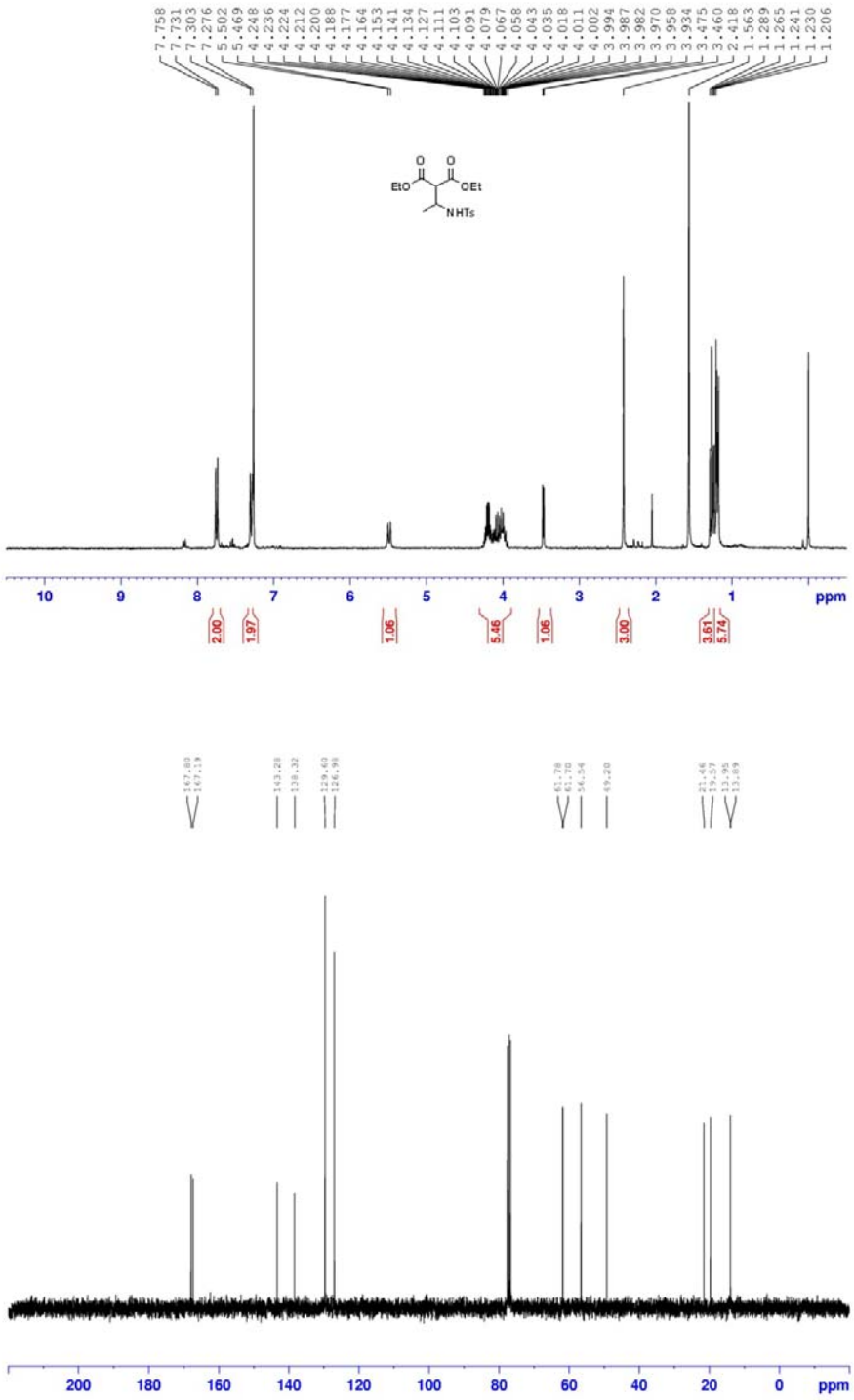


Figure S40. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-(1-(4-methylphenylsulfonamido)propyl) malonate (**3s**)

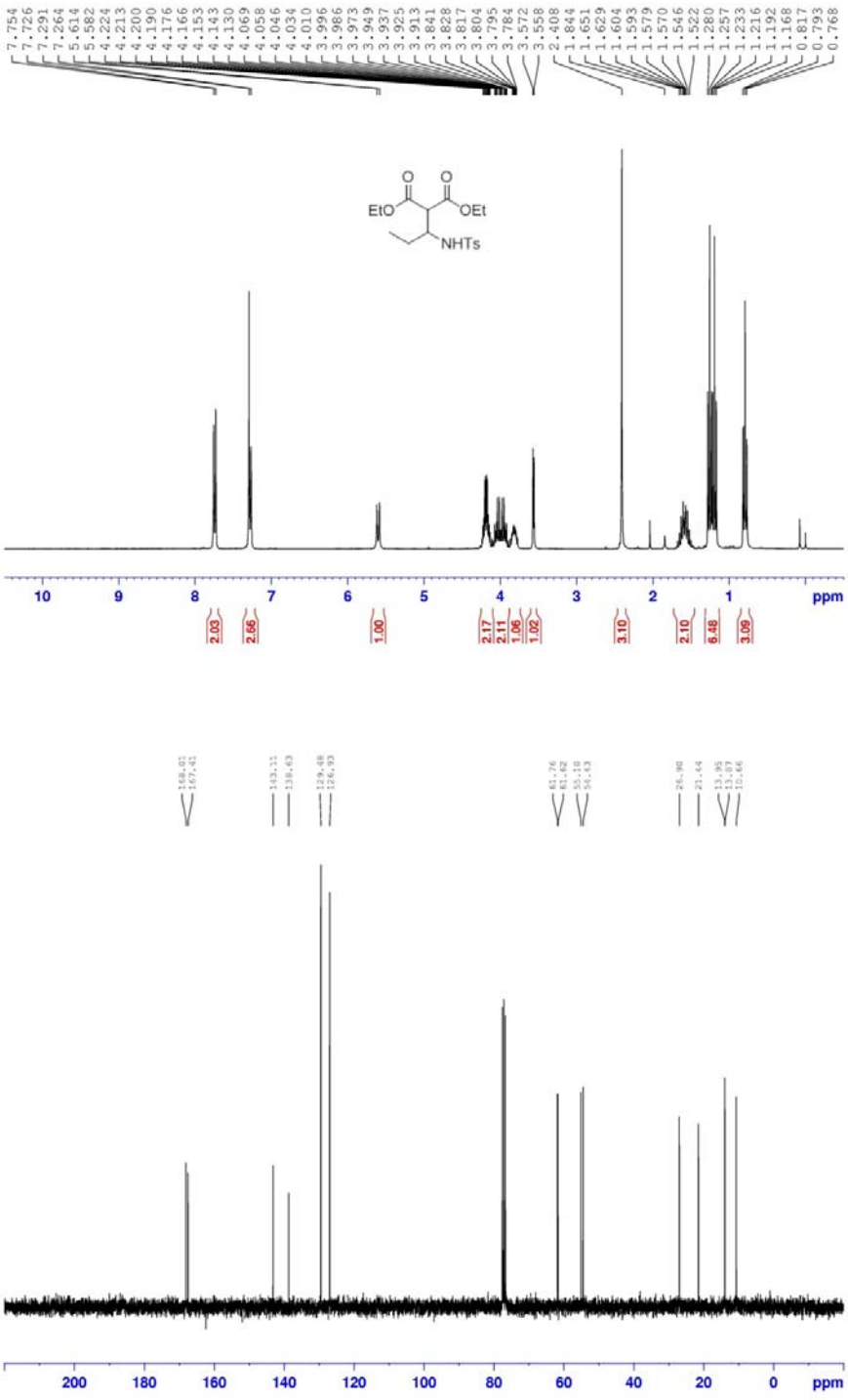


Figure S41. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-(3-chloro-1-(4-methylphenylsulfonamido) propyl)malonate (**3t**)

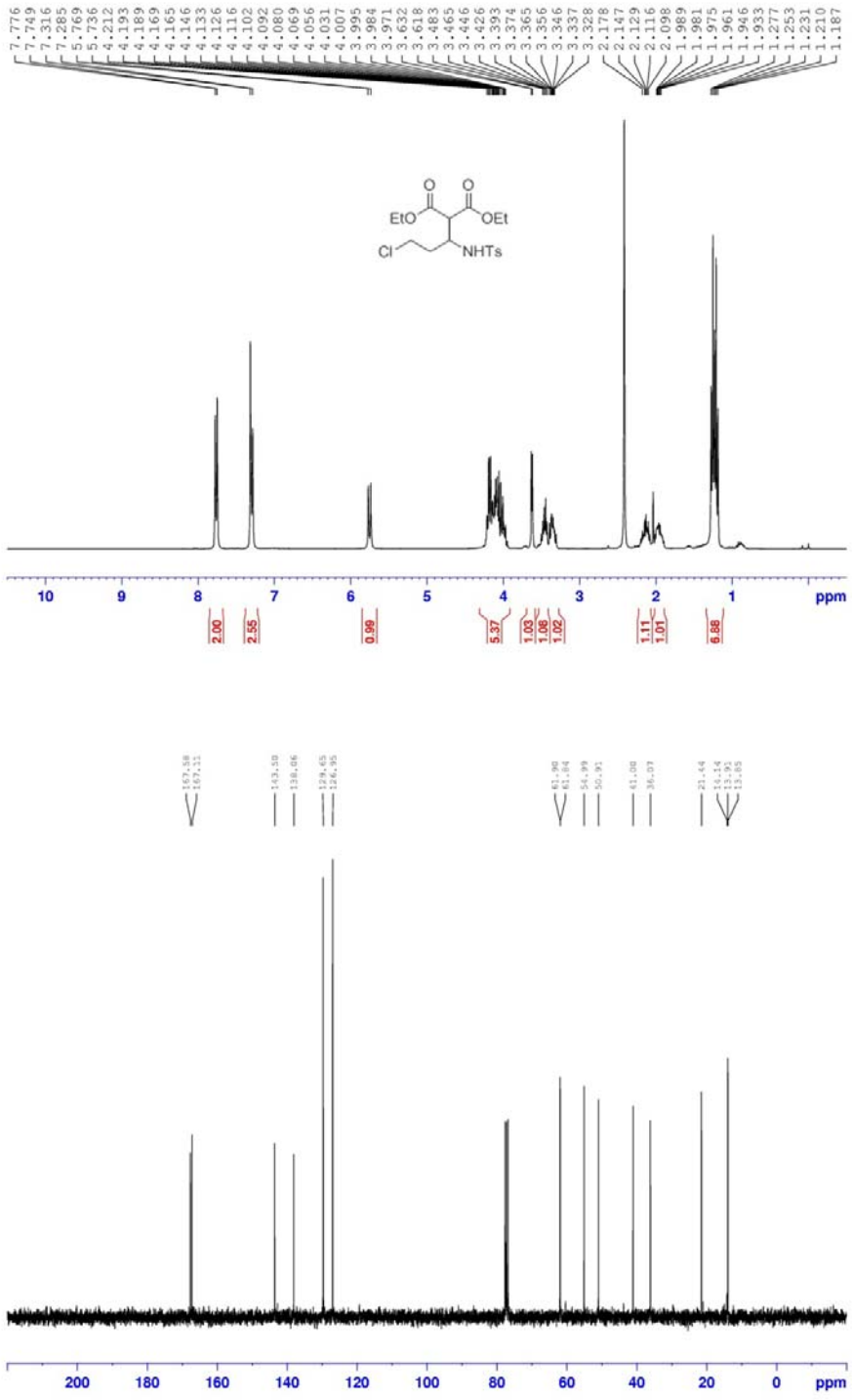


Figure S42. ^{1}H and ^{13}C NMR Spectra of Tetrahydro-*N*-tosylfuran-2-amine (**4**)

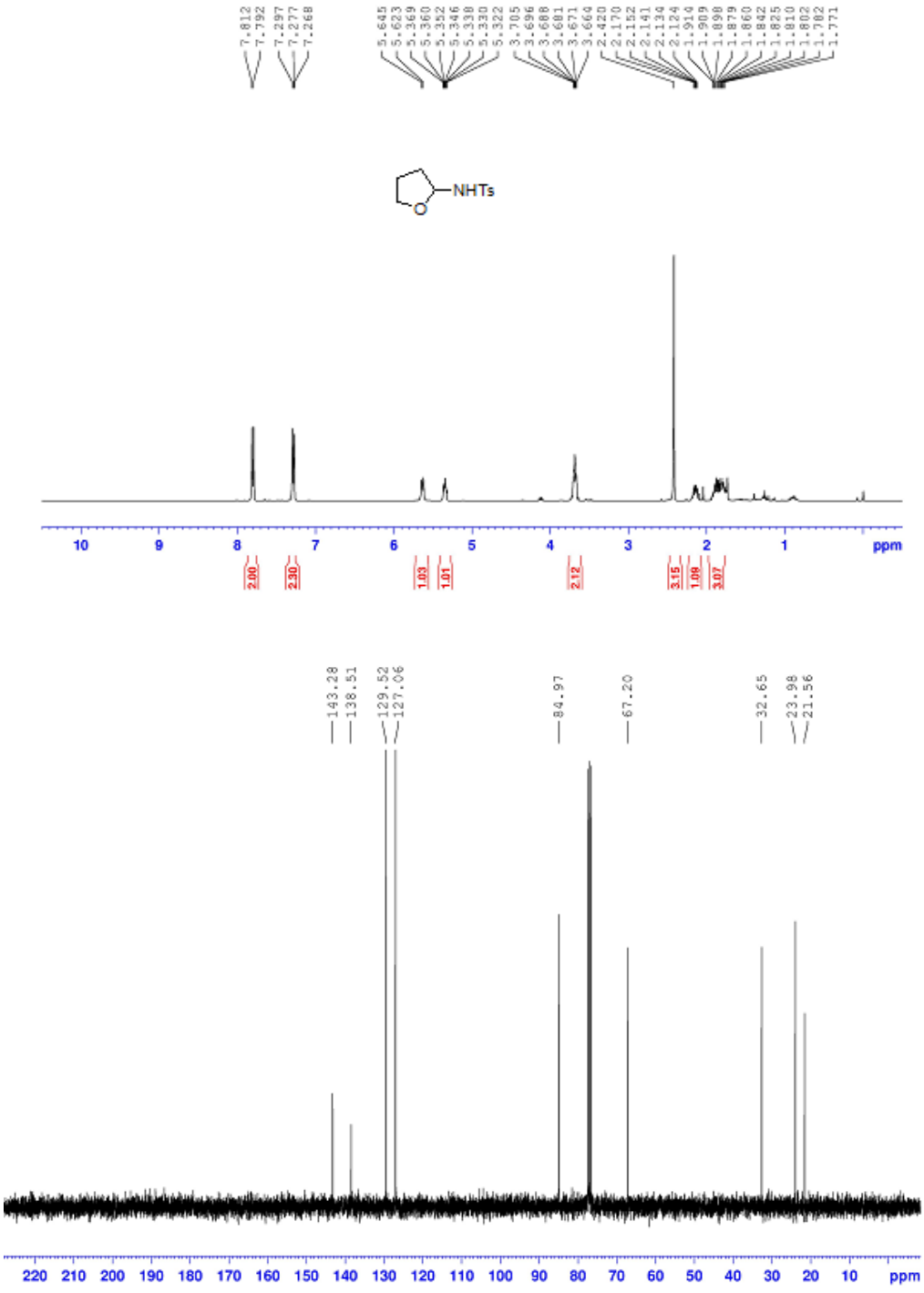


Figure S43. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-ethylidene-4-methyl-3-oxopentanoate (**5l**)

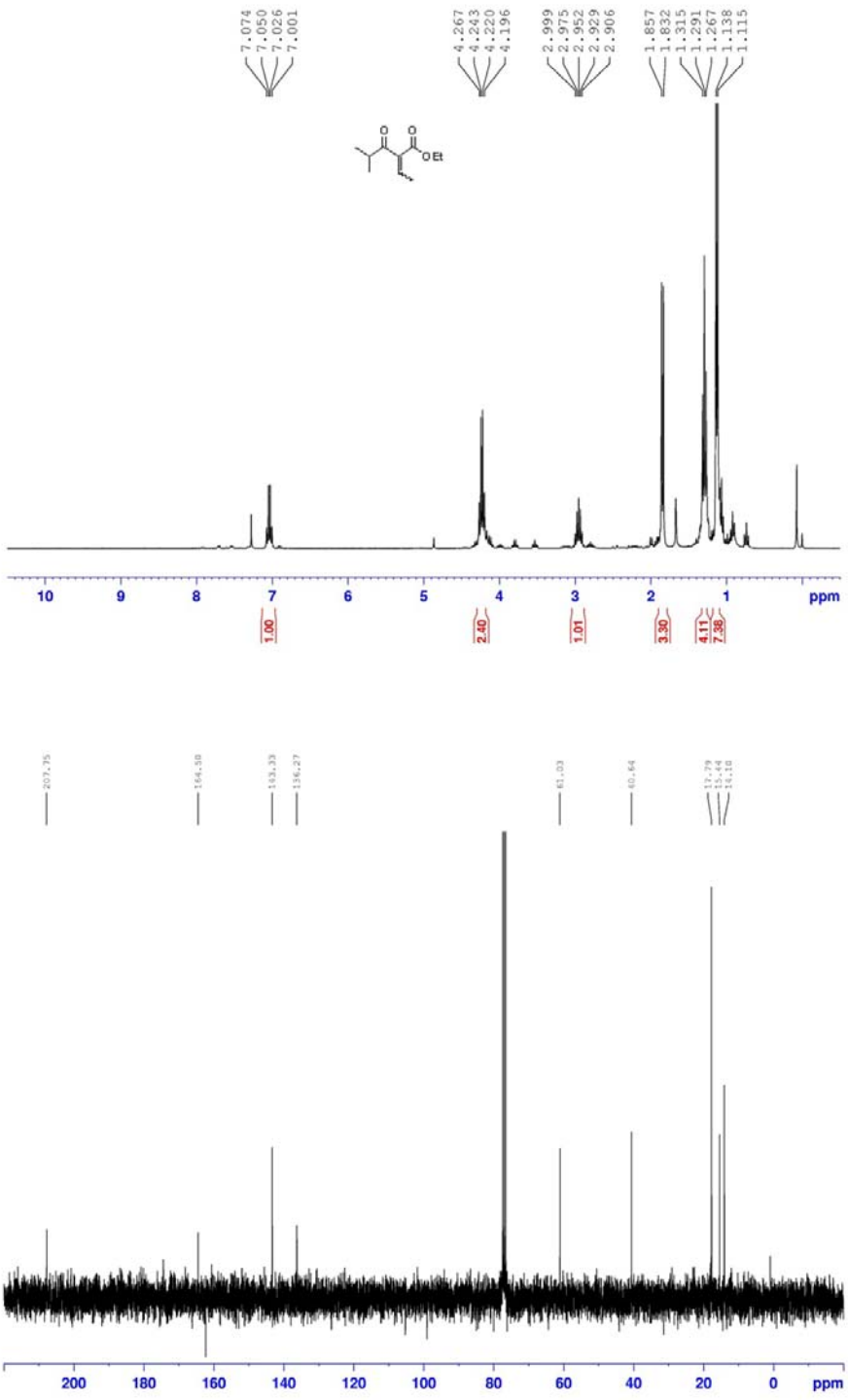


Figure S44. ^{1}H and ^{13}C NMR Spectra of Ethyl 2-methyl-3-oxo-3-phenylpropanoate (**5m**)

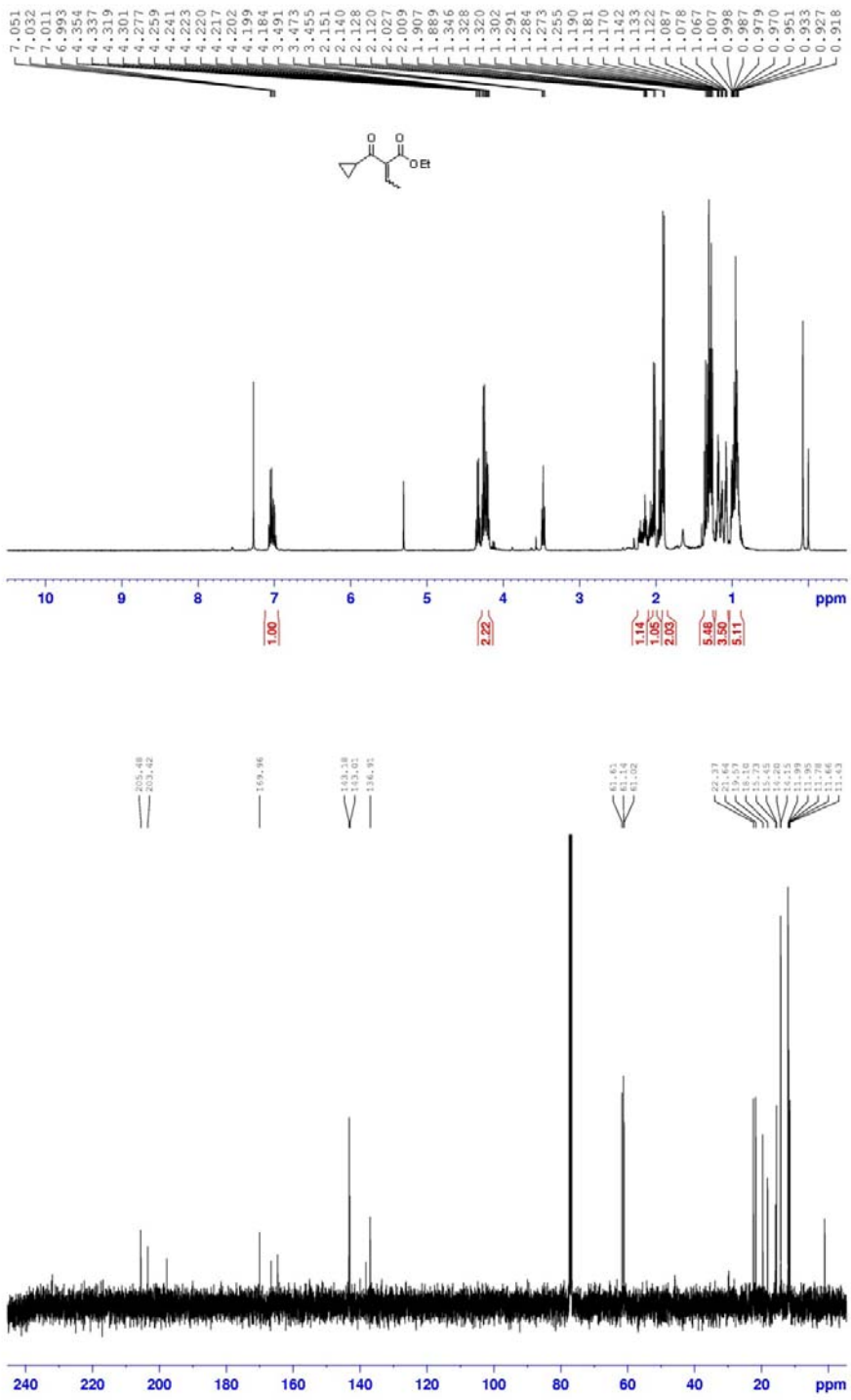


Figure S45. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-ethylidenemalonate (**5r**)

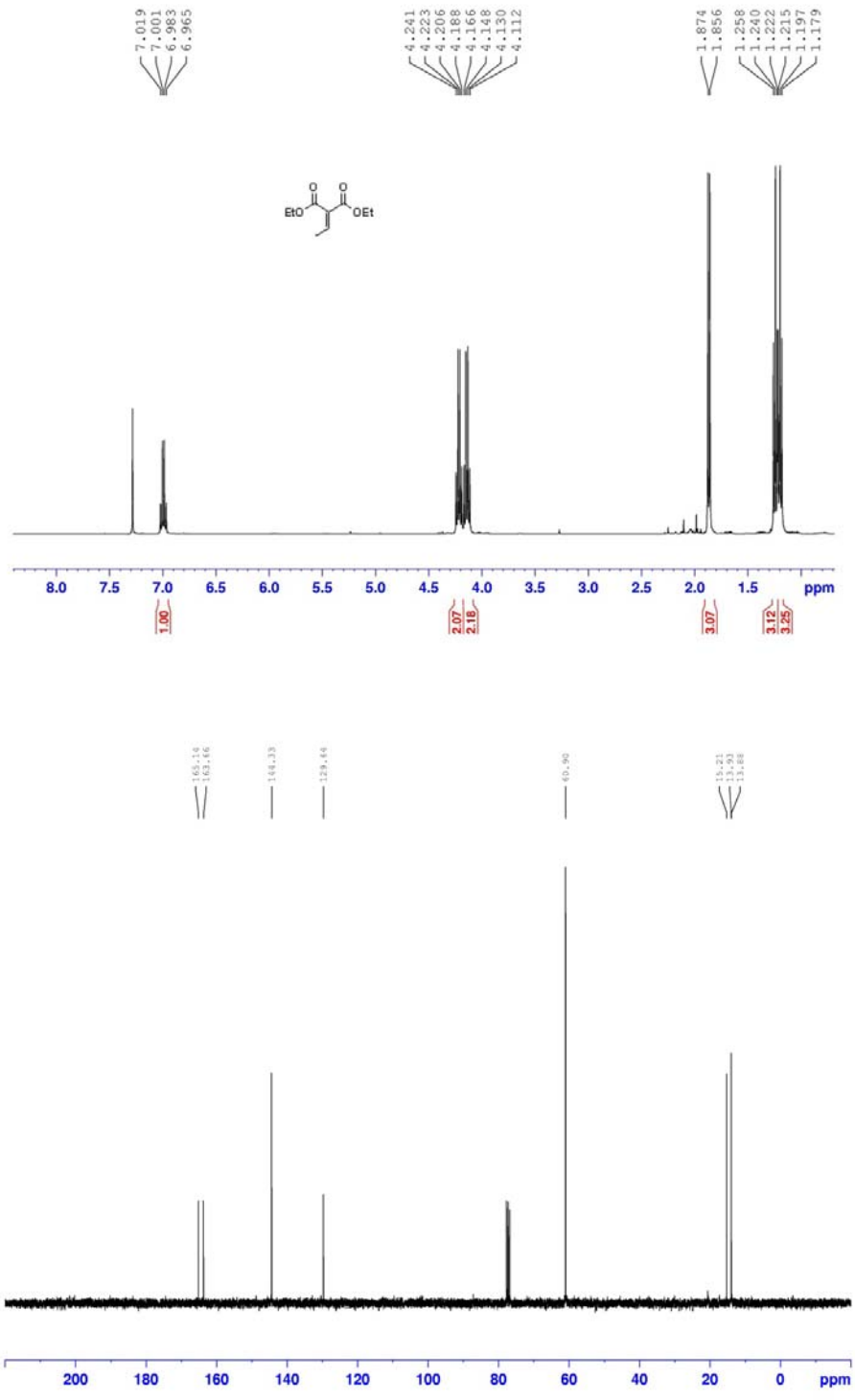


Figure S46. ^{1}H and ^{13}C NMR Spectra of Diethyl 2-(3-chloropropylidene)malonate (**5t**)

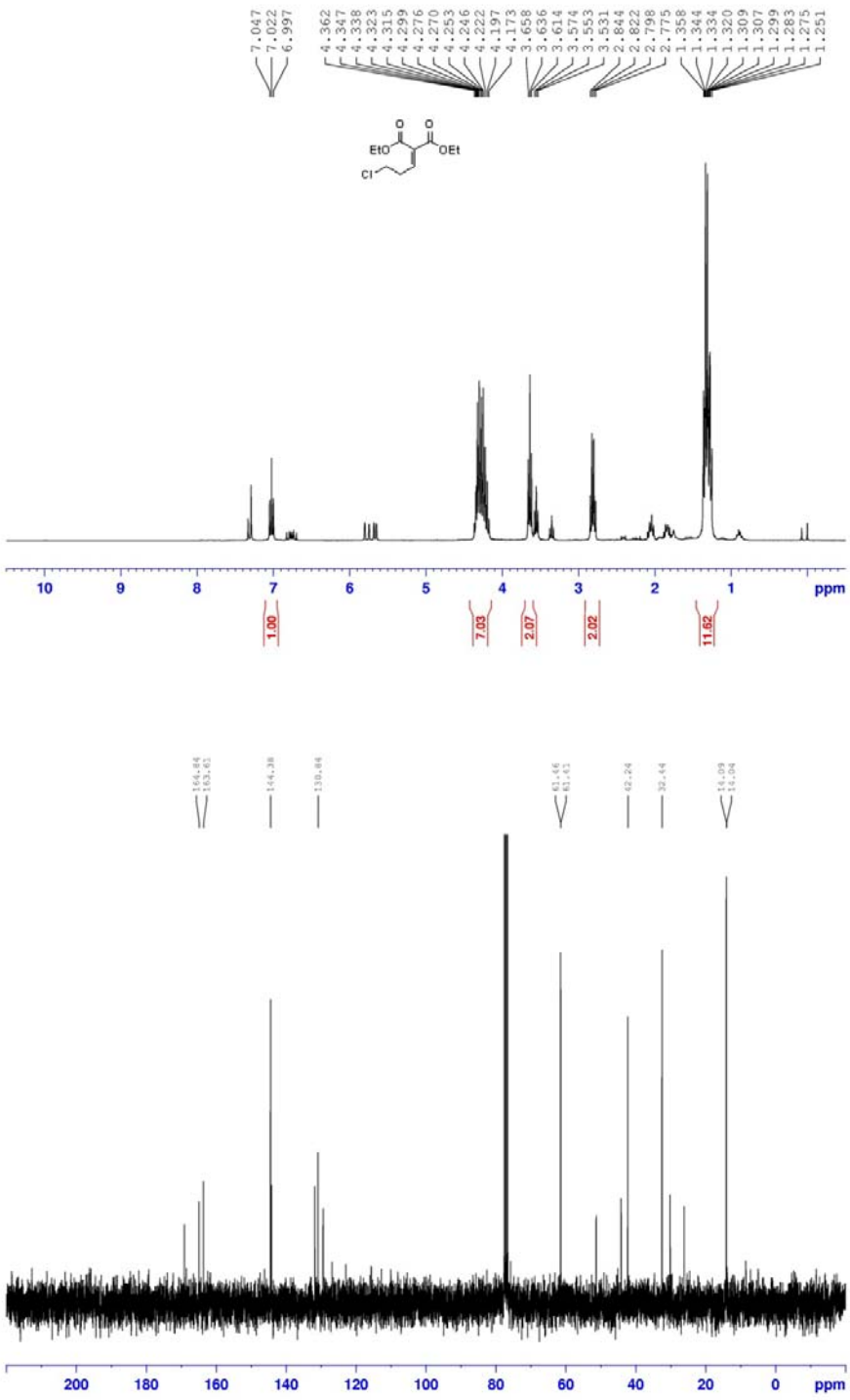
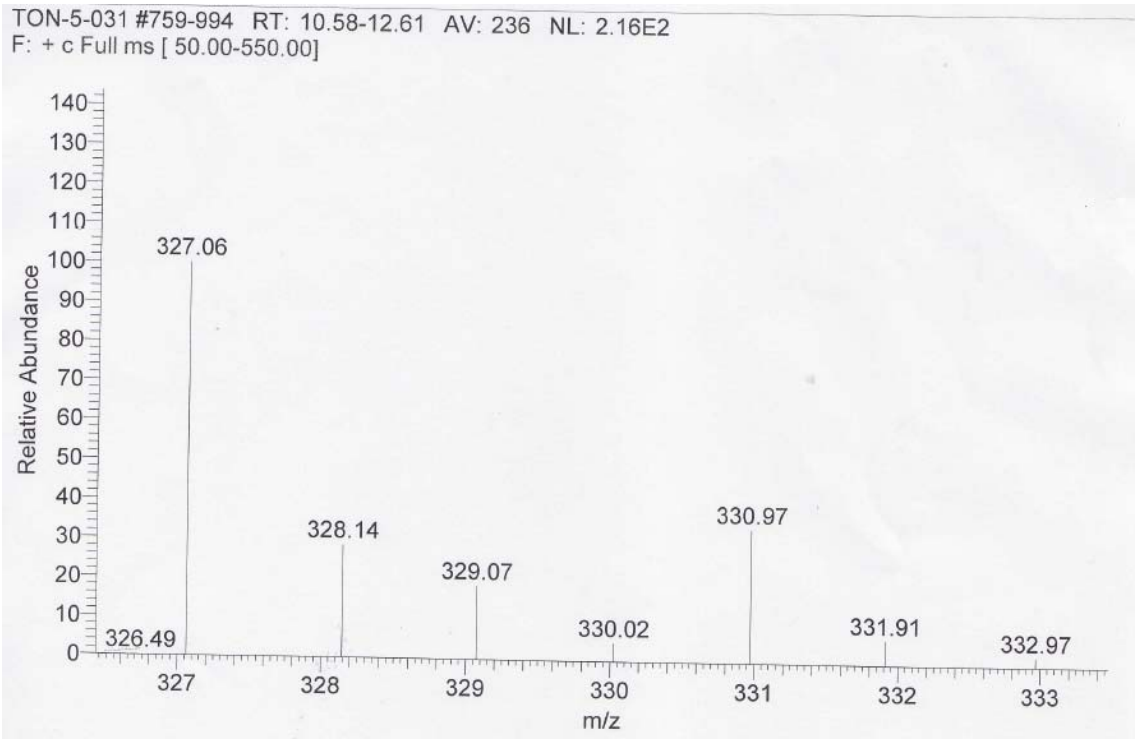


Figure S47. Mass Spectrum of Kinetic Isotope Experiment Studies



References

S1. Smith, A. M. R.; Rzepa, H. S.; White, A. J. P.; Billen, D.; Hii, K. K. *J. Org. Chem.* **2010**, *75*, 3085.

S2. Katritzky, A. R.; Wang, Z.; Wang, M.; Wilkerson, C. R.; Hall, C. D.; Akhmedov, N. G. *J. Org. Chem.* **2004**, *69*, 6617.

S3. Fishman, N; Zuffanti, Z. *J. Am. Chem. Soc.* **1951**, *73*, 4466.

S4. Yamada, T.; Nagata, T.; Sugi, K. D.; Yorozu, K.; Ikeno, T.; Ohtsuka, Y.; Miyazaki, D.; Mukaiyama, T. *Chem. Eur. J.* **2003**, *9*, 4485.

S5. Madsen, U.; Braeuner-Osborne, H.; Frydenvang, K.; Hvene, L.; Johansen, T. N.; Nielsen, B.; Sanchez, C.; Stensboel, T. B.; Bischoff, F.; Krogsgaard-Larsen, P. *J. Med. Chem.* **2001**, *44*, 1051.

S6. Chan, Y.; Balle, J.; Kevin Sparrow, J.; Boyd, P. D. W.; Brimble, M. A.; Barker, D. *Tetrahedron* **2010**, *66*, 7179.

S7. Kurts, A. L.; Dem'yanov, P. I.; Macias, A.; Beletskaya, I. P.; Reutov, O. A**.** *Tetrahedron* **1971**, *27*, 4769.

S8. Xu, Q.; Ye, X.; Zhai, H.; Cheng, B. *Org. Lett.* **2009**, *11*, 4136.

S9. Sato, K.; Yamazoe, S.; Yamamoto, R.; Ohata, S.; Tarui, A.; Omote, M.; Kumadaki, I.; Ando, A. *Org. Lett.* **2008**, *10*, 2405.

S10. He, L.; Yu, J.; Zhang, J.; Yu, X.-Q. *Org. Lett.* **2007**, *9*, 2277.

S11. Antonioletti, R.; Bovicelli, P.; Malancona, S. *Tetrahedron* **2002**, *58*, 589.

S12. Liu, H.; Auchus, R.; Walsh, C. T. *J. Am. Chem. Soc.* **1984**, *106*, 5335.