A SIMPLE, EFFICIENT AND GREEN PROCEDURE FOR KNOEVENAGEL CONDENSATION IN HYDROXYL-FUNCTIONALIZED IONIC LIQUIDS

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Supporting Information

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General information

Commercially available reagents were purchased from Adamas Reagent Co., Ltd (Adamas-Beta, China) and used as supplied unless stated otherwise. Solvents were purified and dried by the standard procedures and distilled prior to use. Diethyl ether is dried over sodium and then purified by distillation from lithium aluminum hydride under an inert nitrogen atmosphere. All other commercially available reagents were used as purchased, unless otherwise noted. Reaction progress was

monitored by thin layer chromatography (TLC) on aluminum backed silica gel plates, visualized with UV light. NMR spectra were acquired using a Bruker ARX 400 FT NMR plus spectrometer at 25 ℃. ^{1}H NMR spectra were referenced to the residual peaks of D_2O (4.33 ppm), or DMSO-d_6 (2.50 ppm). The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet and m = multiplet. ^{13}C NMR spectra were referenced to the residual peak of the solvent used in the measurement (DMSO-d_6 = 39.52 ppm). Infrared spectra were obtained as thin films on KBr plates and were recorded on a Nicolet NEXUS-670 FTIR spectrometer. All mass spectra of ILs (diluted solution in acetonitrile) were recorded using Agilent 1100 LC/MSD Electrospray mass spectrometer. Elemental analyses were performed on a Vario EL Ⅲ instrument. The melting points of the synthesized ILs were measured by DSC, using a TA Instruments Modulated DSC 2910. Melting points of all the condensation products determined using a heating stage with microscope and are uncorrected.

General procedures for the synthesis of ionic liquids

1-[2(2-Hydroxyethoxy)ethyl]-1,5-diazabicyclo[4.3.0]non-5-ene chloride (**3a**):

2-(2-Chloroethoxy)ethanol (1.11 g, 10 mmol) was added to a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (1.24 g, 10 mmol) dissolved in ethyl ester (20 mL). The mixture was stirred at 80 ℃ for 24 hours under N_2 atmosphere. The reaction was monitored by TLC. Upon completion, the solvent was evaporated under reduced pressure and the residue was washed with diethyl ether to give the product. The product was dried in vacuum for 24 hours at 100 ℃.

1-(3-Hydroxypropyl)-1,5-diazabicyclo[4.3.0]non-5-ene bromide (3b):

3-Bromo-1-propanol (1.38 g, 10 mmol) was added to a solution of 1,5-diazabicyclo[4.3.0]non-5-ene (1.24 g, 10 mmol) dissolved in ethyl ester (20 mL). The mixture was stirred at room temperature for 24 hours under N_2 atmosphere. The reaction was monitored by TLC. Upon completion, the solvent was evaporated under reduced pressure and the residue was washed with diethyl ether to give the product. The product was dried in vacuum for 24 hours at 100 ℃.

1-[2(2-Hydroxyethoxy)ethyl]-1,8-diazabicyclo[5.4.0]und-7-ecene chloride (3c) was prepared as the procedure of **3a**.

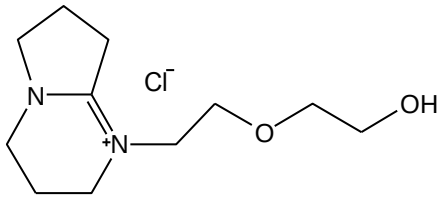
1-(3-Hydroxypropyl)-1,8-diazabicyclo[5.4.0]und-7-ecene bromide (3d) was prepared as the procedure of **3b**.

General procedures for the Knoevenagel condensation

A round bottom flask was charged with aryl aldehyde (10 mmol), active methylene compounds (10 mmol) and ionic liquid (2 mmol). The reaction mixture was stirred and monitored by TLC. Upon completion, water was added and the mixture was stirred. The mixture was allowed to stand to separate into two layers, affording the product and ionic liquid. The separated solid product was suction-filtered and further purified by crystallization from hot ethanol. The filtrate containing the ionic liquid was then evaporated under reduced pressure, and the ionic liquid was reused directly for the next run.

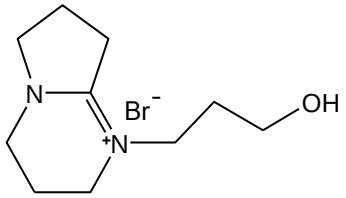
Characterization data for ionic liquids

1-[2(2-Hydroxyethoxy)ethyl]-1,5-diazabicyclo[4.3.0]non-5-ene chloride (**3a**)



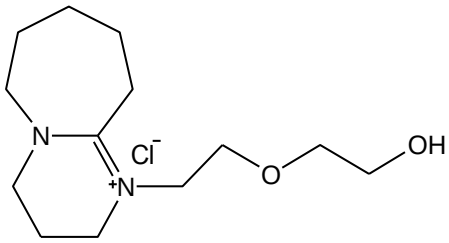
Yield: 97%, colorless oil. ^{1}H NMR (400 MHz, D_2O) δ: 3.62 (t, *J* = 4.0 Hz, 2H), 3.56-3.58 (m, 4H), 3.47-3.51 (m, 4H), 3.35 (t, *J* = 8.0 Hz, 2H), 3.26 (t, *J* = 4.0 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 1.89-2.03 (m, 4H); ^{13}C NMR (100 MHz, D_2O) δ: 165.08, 72.00, 67.16, 60.26, 54.06, 52.22, 44.46, 41.91, 30.24, 18.55, 17.86; IR (KBr): 3324, 2944, 1670, 1449, 1313, 1109, 1061; MS (ESI) for the cation of $[C_{11}H_{21}O_2N_2]Cl$: m/z= 213.1. Anal. Calcd for $C_{11}H_{21}N_2O_2Cl$: C, 53.17; H, 8.51; N, 11.26. Found: C, 53.24; H, 8.59; N, 11.15.

1-(3-Hydroxypropyl)-1,5-diazabicyclo[4.3.0]non-5-ene bromide (3b):



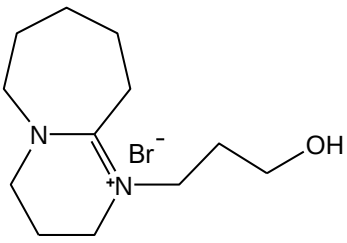
Yield: 99%, white solid, mp 39.8 ℃. ^{1}H NMR (400 MHz, D_2O) δ: 3.58 (t, *J* = 8.0 Hz, 2H), 3.52 (t, *J* = 8.0 Hz, 2H), 3.38 (t, *J* = 8.0 Hz, 2H), 3.31 (t, *J* = 8.0 Hz, 2H), 3.26 (t, *J* = 8.0 Hz, 2H), 2.89 (t, *J* = 8.0 Hz, 2H), 1.99-2.10 (m, 2H), 1.93-1.97 (m, 2H), 1.75-1.80 (m, 2H); ^{13}C-NMR (100 MHz, D_2O) δ: 164.41, 58.34, 53.94, 49.55, 43.88, 42.01, 29.96, 29.01, 18.53, 17.79; IR (KBr): 3318, 2949, 1677, 1447, 1315, 1101, 1060; MS (ESI) for the cation of $[C_{10}H_{19}ON_2]$Br: m/z=183.1. Anal. Calcd for $C_{10}H_{19}N_2OBr$: C, 45.63; H, 7.28; N, 10.65. Found: C, 45.62; H, 7.33; N, 10.54.

1-[2(2-Hydroxyethoxy)ethyl]-1,8-diazabicyclo[5.4.0]und-7-ecene chloride (3c)



Yield 95%, colorless oil. ^{1}H NMR (400 MHz, D_2O) δ: 3.57-3.63 (m, 4H), 3.50 (t, *J* = 4.0 Hz, 2H), 3.38-3.44 (m, 4H), 3.18 (t, *J* = 8.0 Hz, 4.0 Hz, 2H), 2.73-2.78 (m, 2H), 2.50 (t, *J* = 8.0 Hz, 2H), 1.92-1.96 (m, 2H), 1.54-1.59 (m, 6H); ^{13}C NMR (100 MHz, D_2O) δ: 167.06, 72.10, 67.77, 60.49, 54.84, 52.80, 48.84, 46.87, 32.59, 27.63, 25.29, 22.54, 19.65; IR (KBr): 3325, 2939, 1622, 1445, 1321, 1116, 1069; MS (ESI) for the cation of $[C_{13}H_{25}O_2N_2]$Cl: m/z= 241.1. Anal. Calcd for $C_{13}H_{25}N_2O_2Cl$: C, 56.41; H, 9.10; N, 10.12. Found: C, 56.51; H, 9.04; N, 10.07.

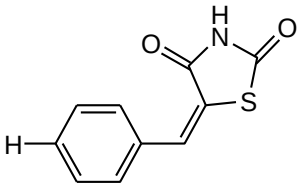
1-(3-Hydroxypropyl)-1,8-diazabicyclo[5.4.0]und-7-ecene bromide (3d).



Yield 99%, white solid, mp 39.8 ℃. ^{1}H NMR (400 MHz, D_2O) δ: 3.62 (t, *J* = 4.0 Hz, 2H), 3.56-3.58 (m, 4H), 3.47-3.51 (m, 4H), 3.35 (t, *J* = 8.0 Hz, 2H), 3.26 (t, *J* = 8.0 Hz, 2H), 2.90 (t, *J* = 8.0 Hz, 2H), 1.89-2.03 (m, 6H); ^{13}C NMR (100 MHz, D_2O) δ: 166.40, 58.43, 54.84, 50.48, 48.80, 46.87, 32.88, 30.29, 27.69, 25.59, 22.57, 19.65; IR (KBr): 3327, 2951, 1665, 1446, 1310, 1109, 1061; MS (ESI) for the cation of $[C_{12}H_{23}ON_2]Br$: m/z= 211.2. Anal. Calcd for $C_{12}H_{23}N_2OBr$: C, 49.49; H, 7.96; N, 9.62. Found: C, 49.45; H, 8.07; N, 9.59.

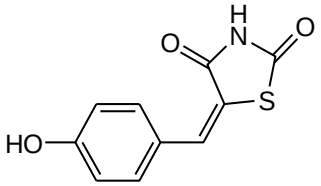
Characterization data for 5-arylidine-2,4-thiazolidinediones

5-Benzylidene-2,4-thiazolidinedione (6a) [1]



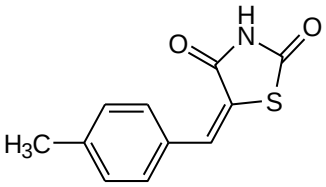
Yield 95%, white solid, mp 240-242 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.65 (s, 1H, NH), 7.81 (s, 1H, CH), 7.62 (m, 2H, ArH), 7.56 (m, 3H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.32, 167.75, 133.49, 132.26, 130.89, 130.47, 129.71, 123.92.

5-(4-Hydroxybenzylidene)-2,4-thiazolidinedione (6b) [2]



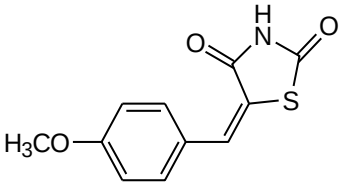
Yield 90%, white solid, mp 281-284 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.49 (s, 1H, NH), 10.34 (s, 1H, OH), 7.74 (s, 1H, CH), 7.47 (m, 2H, ArH), 6.92 (m, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.53, 167.97, 160.35, 132.87, 124.39, 119.45, 116.80.

5-(4-Methylbenzylidene)-2,4-thiazolidinedione (6c) [1]



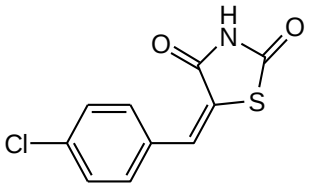
Yield 90%, white solid, mp 224-227 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.59 (s, 1H, NH), 7.77 (s, 1H, CH), 7.51 (d, J = 8.0 Hz, 2H, ArH), 7.37 (d, J = 8.0 Hz, 2H, ArH), 2.37 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.33, 167.84, 141.18, 132.34, 130.73, 130.54, 130.41, 122.76, 21.89.

5-(4-Methoxybenzylidene)-2,4-thiazolidinedione (6d): [2]



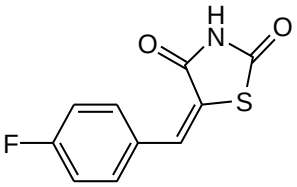
Yield 82%, white solid, mp 217-220 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.53 (s, 1H, NH), 7.74 (s, 1H, CH), 7.54 (d, J = 8.0 Hz, 2H, ArH), 7.08 (d, J = 8.0 Hz, 2H, ArH), 2.09 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.41, 167.87, 161.43, 132.54, 132.29, 125.94, 120.65, 115.34, 55.82.

5-(4-Chlorobenzylidene)-2,4-thiazolidinedione (6e): [3]



Yield 83%, yellow solid, mp 223-224 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.68 (s, 1H, NH), 7.78 (s, 1H, CH), 7.58-7.63 (m, 4H, ArH). ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.08, 167.66, 135.45, 132.39, 132.08, 129.83, 124.77.

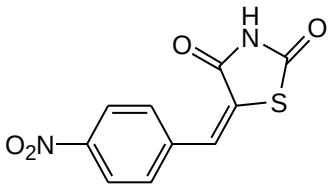
5-(4-Fluorobenzylidene)-2,4-thiazolidinedione (6f): [4]



Yield 93%, white solid, mp 221-224 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.69 (s, 1H, NH), 7.81 (s, 1H, CH), 7.63-7.65 (m, 4H, ArH); ^{13}C NMR (100 MHz,

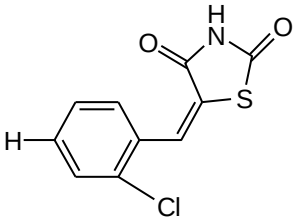
DMSO-d_6) δ: 168.22, 167.69, 161.71, 132.97, 132.88, 131.17, 130.20, 123.71, 117.07, 116.85.

5-(4-Nitrobenzylidene)-2,4-thiazolidinedione (6g): [1]



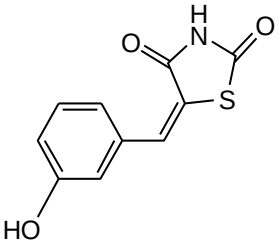
Yield 85%, white solid, mp 259-262 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.74 (s, 1H, NH), 7.81 (s, 1H, CH), 7.65 (d, J = 8.0 Hz, 2H, ArH), 7.62 (d, 2H, J = 8.0 Hz, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.17, 167.64, 135.47, 132.42, 132.10, 130.85, 129.87, 124.91.

5-(2-Chlorobenzylidene)-2,4-thiazolidinedione (6h): [1]



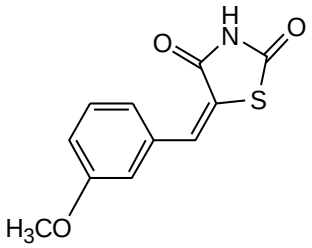
Yield 77%, yellow solid, mp 289-230 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.79 (s, 1H, NH), 7.93 (s, 1H, CH), 7.58 (d, J = 8.0 Hz, 2H, ArH), 7.52-7.56 (m, 2H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.10, 167.45, 134.92, 132.32, 131.48, 130.82, 129.35, 128.59, 127.75, 127.16.

5-(3-Hydroxylbenzylidene)-2,4-thiazolidinedione (6i): [3]



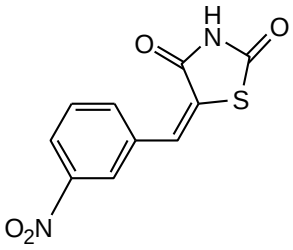
Yield 93%, white solid, mp 250-251 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.61 (s, 1H, NH), 9.86 (s, 1H, OH), 7.69 (s, 1H, CH), 7.33 (t, J = 8.0 Hz, 1H, ArH), 7.03 (d, J = 8.0 Hz, 2H, ArH), 6.98 (s, 1H, ArH), 6.88 (d, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.42, 167.79, 158.32, 134.65, 132.46, 130.83, 123.74, 121.78, 118.20, 116.38.

5-(3-Methoxybenzylidene)-2,4-thiazolidinedione (6j): [3]



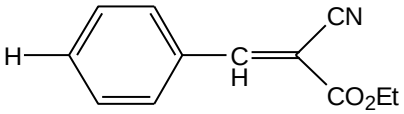
Yield 84%, white solid, mp 186-188 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.64 (s, 1H, NH), 7.76 (s, 1H, CH), 7.45 (t, J = 8.0 Hz, 1H, ArH), 7.14 (s, 1H, ArH), 7.05 (d, J = 8.0 Hz, 1H, ArH), 3.80 (s, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 168.30, 167.73, 160.08, 134.86, 132.22, 130.89, 122.32, 116.76, 115.78, 55.82.

5-(4-Nitrobenzylidene)-2,4-thiazolidinedione (6k): [3]



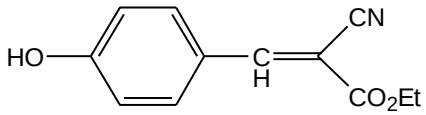
Yield 87%, white solid, mp 180-182 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.80 (s, 1H, NH), 8.42 (s, 1H, CH), 8.27 (d, J = 8.0 Hz, 1H, ArH), 7.99 (t, J = 8.0 Hz, 1H, ArH), 7.93 (s, 1H, ArH), 7.81 (t, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 167.74, 167.47, 148.67, 135.88, 135.20, 131.33, 129.82, 127.05, 124.90, 124.79.

Ethyl (*E*)-2-cyano-3-phenyl-2-propenoate (8a):[5]



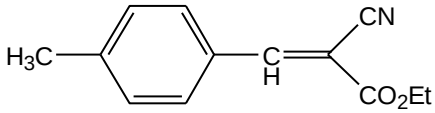
Yield 98%, white solid, mp 49-50 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.41 (s, 1H, CH), 8.05 (d, J = 8.0 Hz, 2H, ArH), 7.58-7.65 (m, 3H, ArH), 4.30-4.35 (m, 2H, CH_2), 1.31 (t, J = 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.25, 155.56, 133.87, 131.74, 131.19, 129.79, 116.05, 103.08, 62.85, 14.61.

Ethyl (*E*)-2-cyano-3-(4-hydroxylphenyl)-2-propenoate (8b):[5]



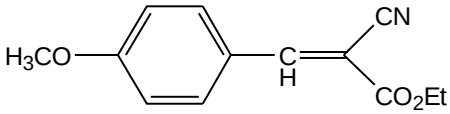
Yield 96%, white solid, mp 168-170 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 10.86 (s, 1H, OH), 8.25 (s, 1H, CH), 8.00 (d, J = 8.0 Hz, 2H, ArH), 6.95 (d, J = 8.0 Hz, 2H, ArH), 4.27-4.32 (m, 2H, CH_2), 1.30 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 163.35, 163.08, 155.16, 134.53, 123.25, 116.94, 97.31, 61.82, 14.30.

Ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate (8c):[6]



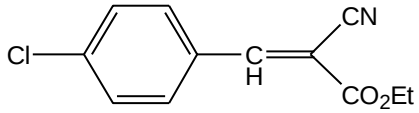
Yield 91%, white solid, mp 90-92 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.37 (s, 1H, CH), 7.98 (d, J = 8.0 Hz, 2H, ArH), 7.41 (d, J = 8.0 Hz, 2H, ArH), 4.29-4.35 (m, 2H, CH_2), 2.41(s, 3H, CH_3), 1.31 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.00, 154.16, 138.48, 132.91, 130.71, 129.95, 115.76, 103.65, 63.05, 14.31.

Ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (8d):[5]



Yield 88%, white solid, mp 80-82 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.32 (d, J = 8.0 Hz, 1H, CH), 8.07 (d, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 4.28-4.33 (m, 2H, CH_2), 3.87 (s, 3H, CH_3), 1.31 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 162.43, 155.46, 144.90, 131.36, 130.45, 129.15, 116.25, 101.54, 62.41, 21.60, 14.61.

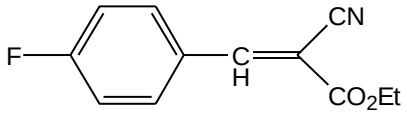
Ethyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate (8e):[5]



Yield 92%, yellow solid, mp 91-92 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.42 (s, 1H, CH), 8.07 (d, J = 8.0 Hz, 2H, ArH), 7.68 (d, J = 8.0 Hz, 2H, ArH), 4.30-4.36 (m, 2H, CH_2), 1.32 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ:

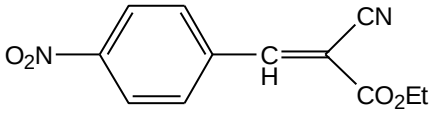
162.0, 154.21, 138.44, 132.83, 130.81, 129.88, 115.78, 103.62, 62.80, 14.31.

Ethyl (*E*)-2-cyano-3-(4-fluorophenyl)-2-propenoate (8f):[7]



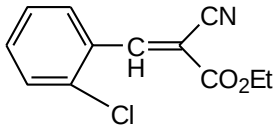
Yield 96%, white solid, mp 94-95 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.43 (s, 1H, CH), 8.15-8.19 (m, 2H, ArH), 7.48 (t, J = 8.0 Hz, 2H, ArH), 4.30-4.36 (m, 2H, CH_2), 1.32 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 166.39, 163.78, 162.13, 154.45, 133.57, 128.21, 117.22, 117.00, 115.57, 102.68, 62.86, 14.30.

Ethyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate (8g):[5]



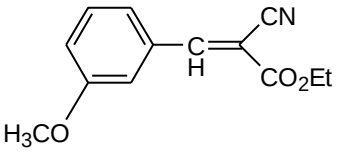
Yield 91%, white solid, mp 170-172 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.58 (s, 1H, CH), 8.41 (d, J = 8.0 Hz, 2H, ArH), 8.25 (d, J = 8.0 Hz, 2H, ArH), 4.34-4.39 (m, 2H, CH_2), 1.33 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.75, 153.12, 149.79, 137.84, 132.14, 124.53, 115.27, 107.30, 62.79, 14.28.

Ethyl (*E*)-2-cyano-3-(2-chlorophenyl)-2-propenoate (8h):[8]



Yield 80%, yellow solid, mp 46-48 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.53 (s, 1H, CH), 8.11 (d, J = 8.0 Hz, 2H, ArH), 7.56-7.63 (m, 3H, ArH), 4.32-4.38(m, 2H, CH_2), 1.32 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.59, 151.02, 135.17, 134.68, 130.74, 130.23, 130.03, 128.40, 115.11, 107.16, 62.81, 13.93.

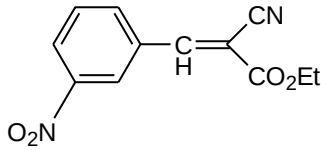
Ethyl (*E*)-2-cyano-3-(3-methoxyphenyl)-2-propenoate (8i):[8]



Yield 83%, white solid, mp 52-54 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.31

(s, 1H, CH), 8.08 (d, J = 8.0 Hz, 2H, ArH), 7.14 (d, J = 8.0 Hz, 2H, ArH), 4.28-4.33 (m, 2H, CH_2), 3.88 (s, 3H, CH_3), 1.32 (t, J = 8.0 Hz, 3H, CH_3); ^{13}C NMR (100 MHz, DMSO-d_6) δ: 164.01, 162.72, 154.79, 133.90, 124.36, 116.58, 115.42, 99.00, 62.41, 56.09, 14.32.

Ethyl (*E*)-2-cyano-3-(3-nitrophenyl)-2-propenoate (8j):[5]



Yield 89%, white solid, mp 130-131 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ: 8.94 (s, 1H, CH), 8.62 (s, 1H, OH), 8.44 (d, J = 8.0 Hz, 2H, ArH), 7.90 (t, J = 8.0 Hz, 2H, ArH), 4.33-4.39(m, 2H, CH_2), 1.34 (t, J = 8.0 Hz, 3H, CH_3);^{13}C NMR (100 MHz, DMSO-d_6) δ: 161.77, 153.30, 148.53, 136.93, 133.31, 131.46, 127.58, 125.42, 115.45, 105.95, 63.14, 14.31.

Spectral data of all the products

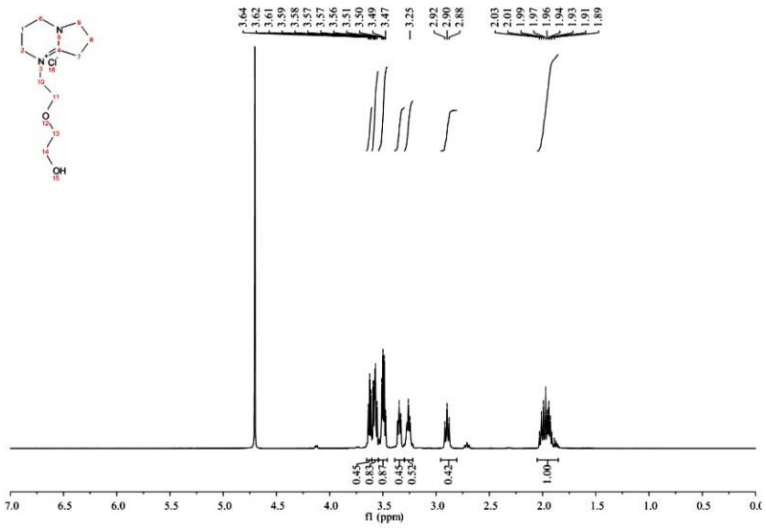


Figure S1. ^{1}H NMR of 1-[2(2-hydroxyethoxy)ethyl]-1,5-diazabicyclo[4.3.0]non-5-ene chloride **(3a)**

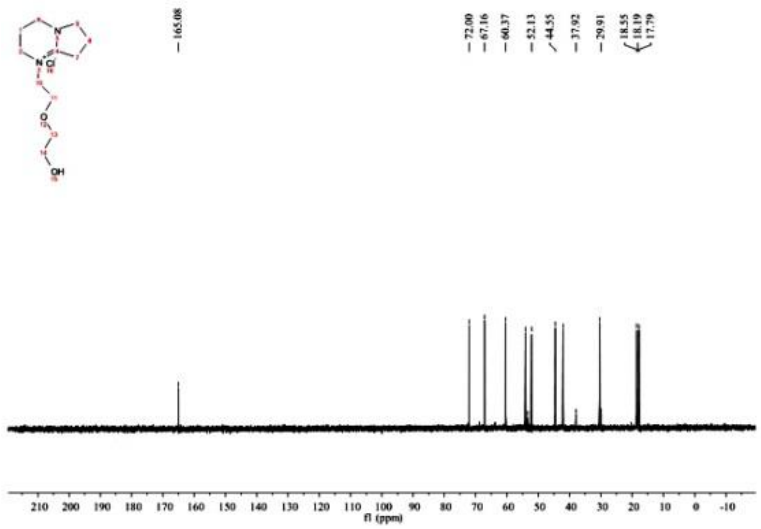


Figure S2. ^{13}C NMR of 1-[2(2-hydroxyethoxy)ethyl]-1,5-diazabicyclo[4.3.0]non-5-ene chloride **(3a)**

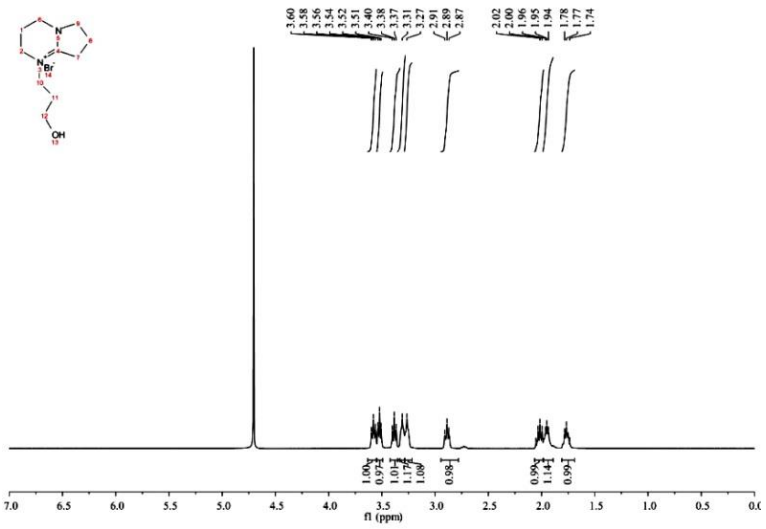


Figure S3. ^{1}H NMR of 1-(3-hydroxypropyl)-1,5-diazabicyclo[4.3.0]non-5-ene bromide **(3b)**

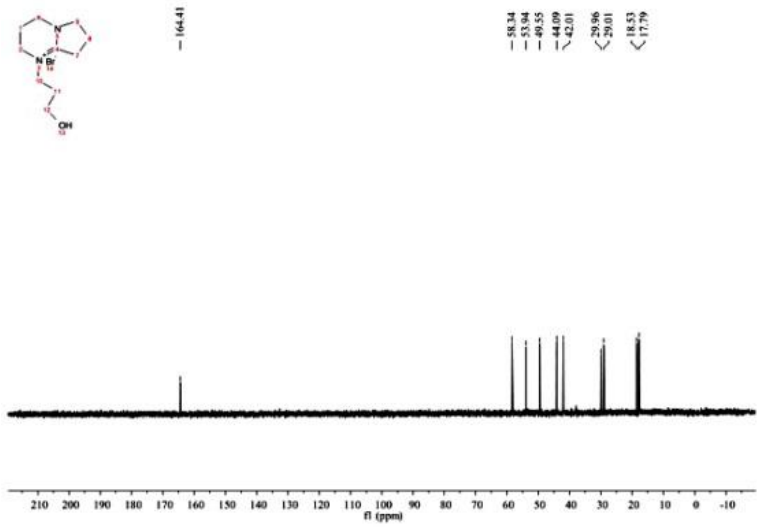


Figure S4. ^{13}C NMR of 1-(3-hydroxypropyl)-1,5-diazabicyclo[4.3.0]non-5-ene bromide **(3b)**

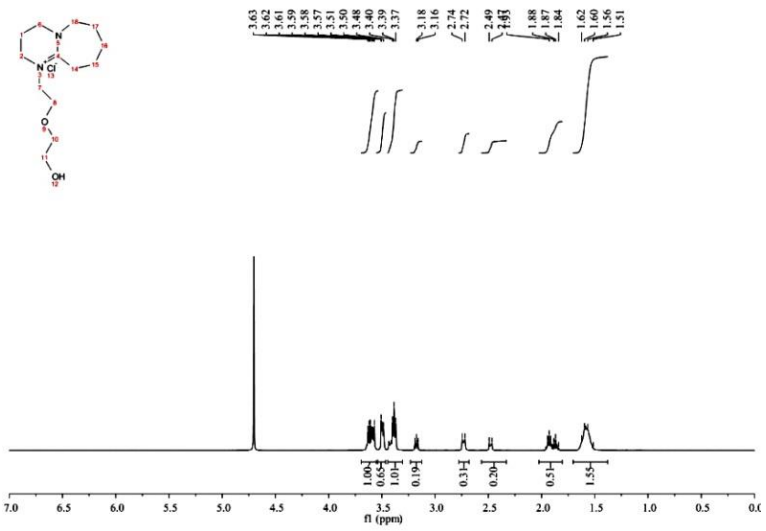


Figure S5. ^{1}H NMR of

1-[2(2-hydroxyethoxy)ethyl]-1,8-diazabicyclo[5.4.0]und-7-ecene chloride **(3c)**

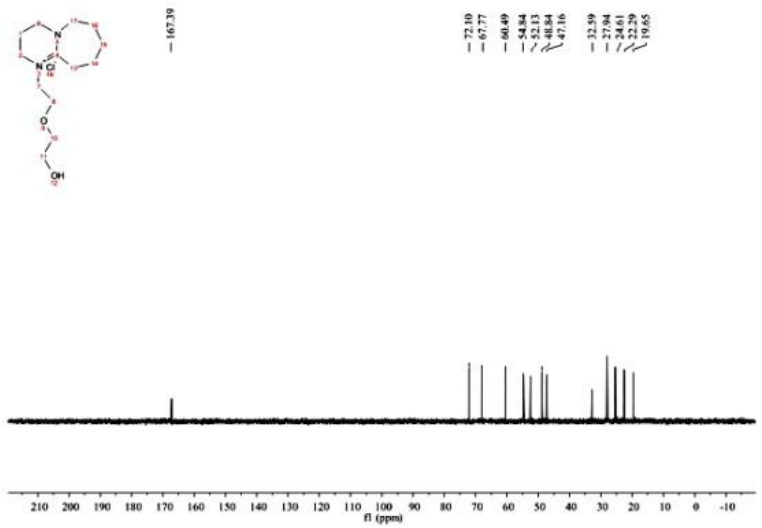


Figure S6. ^{13}C NMR of

1-[2(2-hydroxyethoxy)ethyl]-1,8-diazabicyclo[5.4.0]und-7-ecene chloride **(3c)**

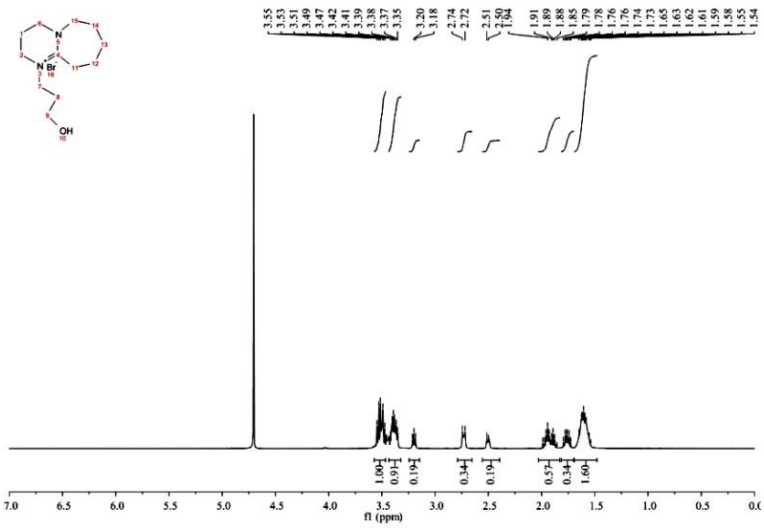


Figure S7. ^{1}H NMR of 1-(3-hydroxypropyl)-1,8-diazabicyclo[5.4.0]und-7-ecene

bromide **(3d)**

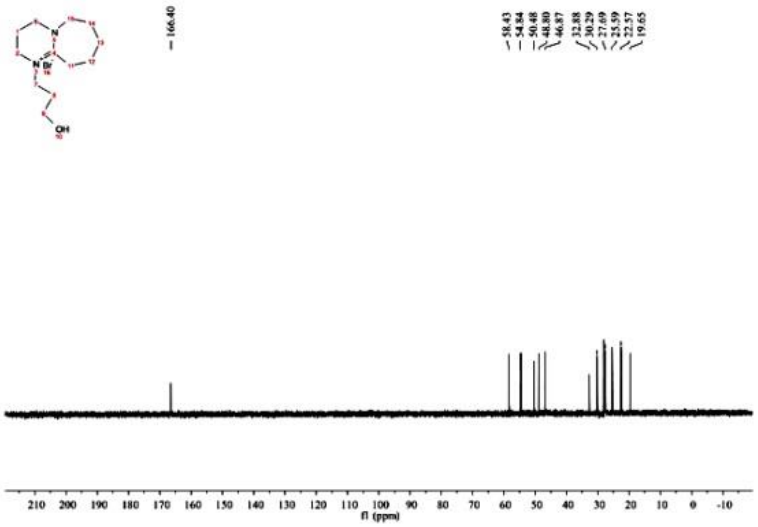


Figure S8. ^{13}C NMR of 1-(3-hydroxypropyl)-1,8-diazabicyclo[5.4.0]und-7-ecene bromide **(3d)**

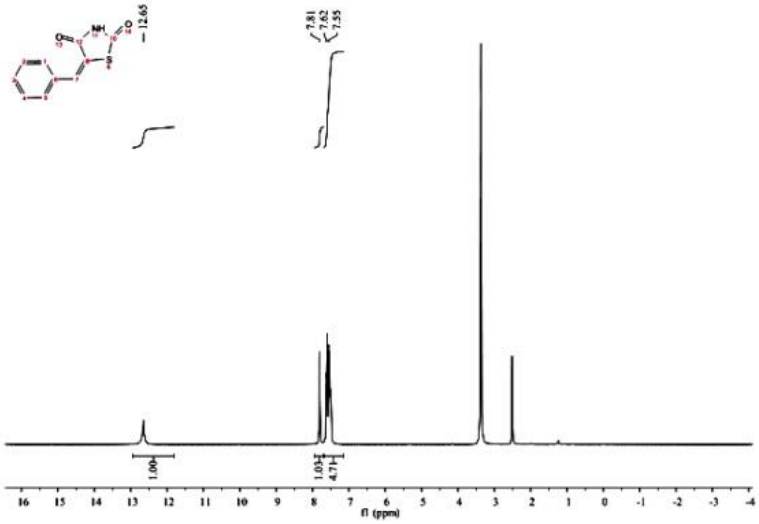


Figure S9. ^{1}H NMR of 5-benzylidene-2,4-thiazolidinedione **(6a)**

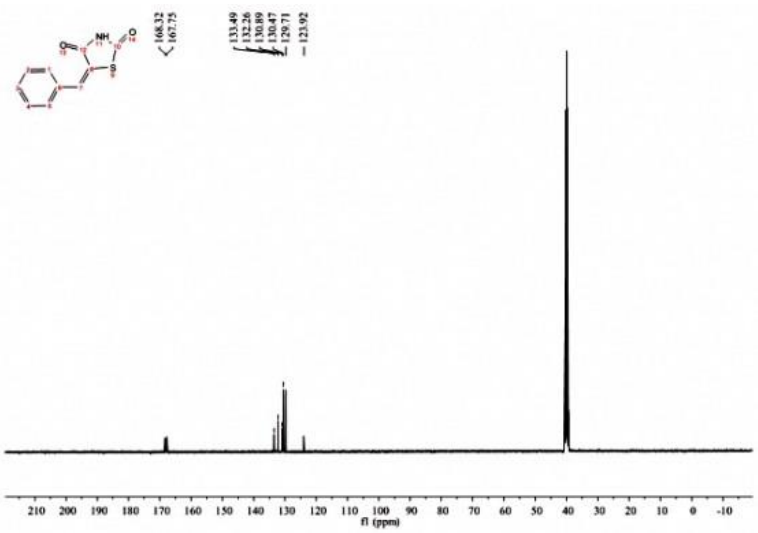


Figure S10. ^{13}C NMR of 5-benzylidene-2,4-thiazolidinedione **(6a)**

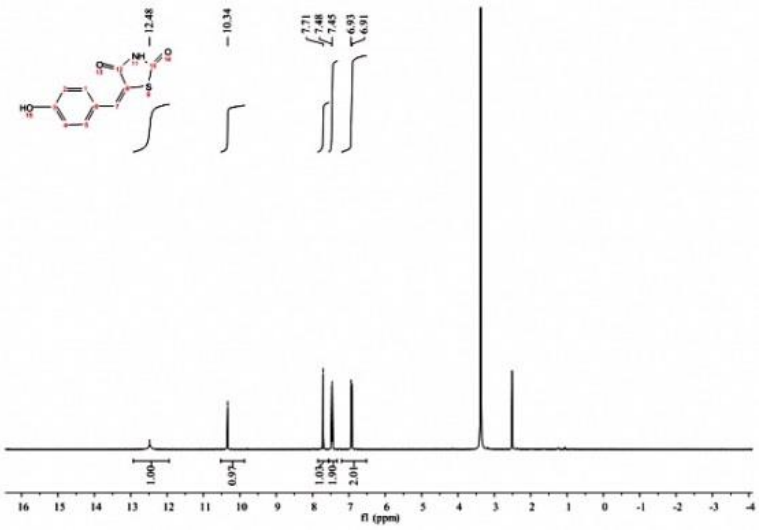


Figure S11. ^{1}H NMR of 5-(4-hydroxybenzylidene)-2,4-thiazolidinedione **(6b)**

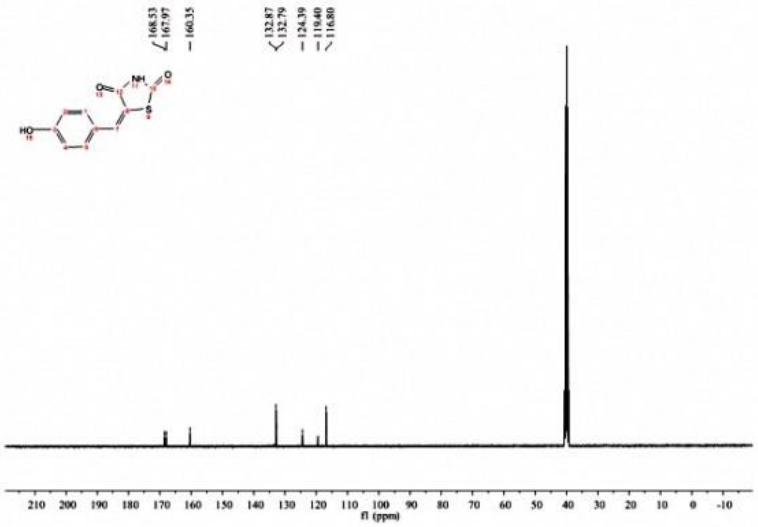


Figure S12. ^{13}C NMR of 5-(4-hydroxybenzylidene)-2,4-thiazolidinedione **(6b)**

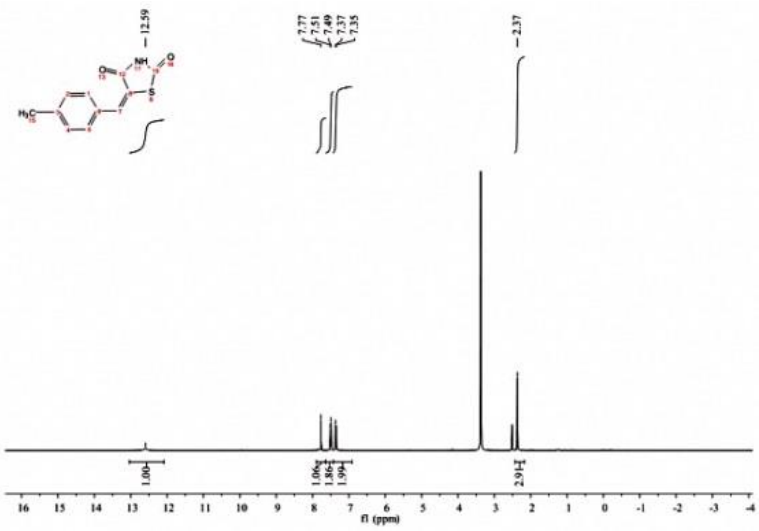


Figure S13. ^{1}H NMR of 5-(4-methylbenzylidene)-2,4-thiazolidinedione **(6c)**

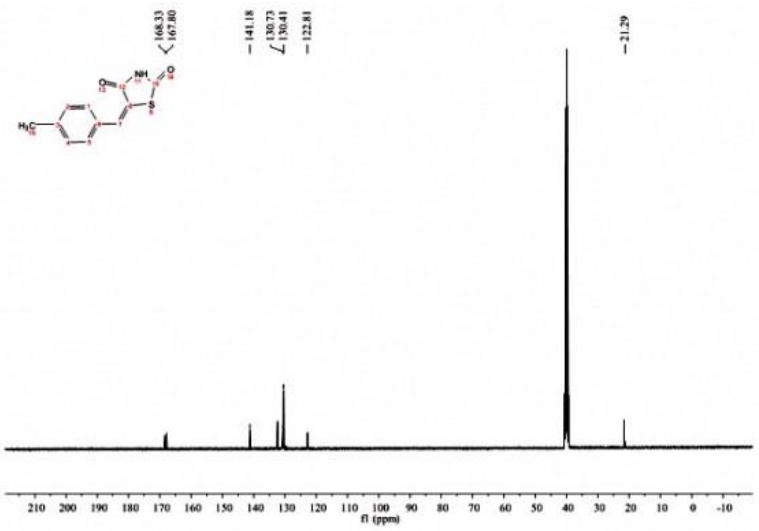


Figure S14. ^{13}C NMR of 5-(4-methylbenzylidene)-2,4-thiazolidinedione **(6c)**

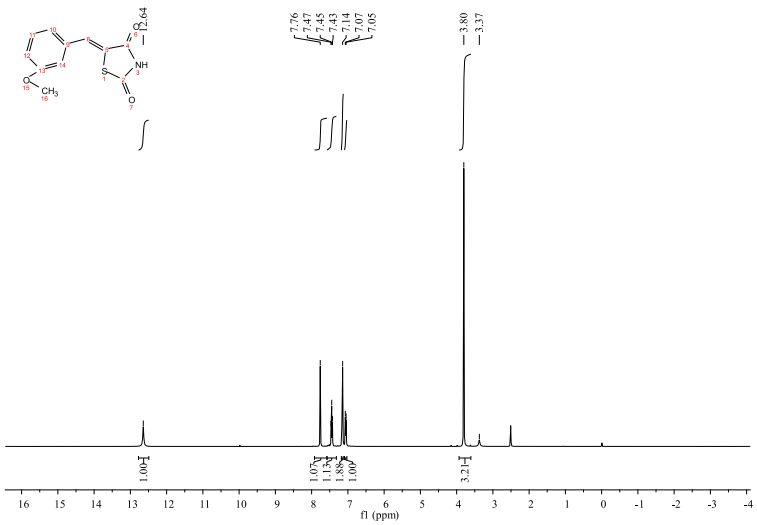


Figure S15. ^{1}H NMR of 5-(4-methoxybenzylidene)-2,4-thiazolidinedione **(6d)**

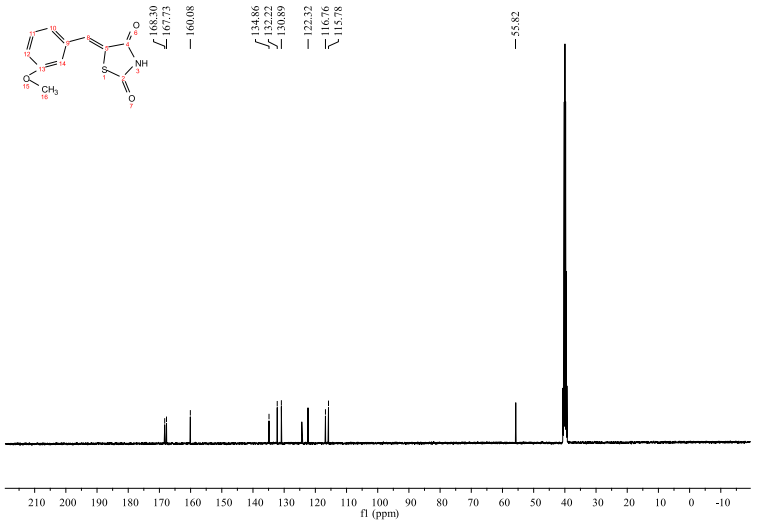


Figure S16. ^{13}C NMR of 5-(4-methoxybenzylidene)-2,4-thiazolidinedione **(6d)**

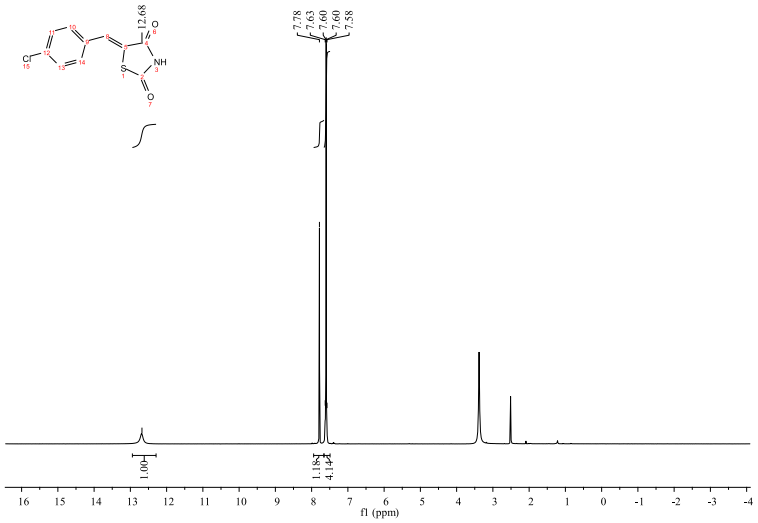


Figure S17. ^{1}H NMR of 5-(4-chlorobenzylidene)-2,4-thiazolidinedione **(6e)**

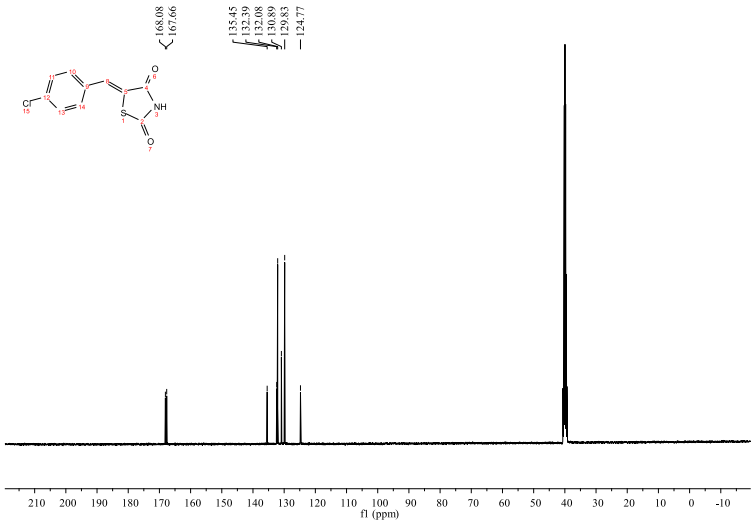


Figure S18. ^{13}C NMR of 5-(4-chlorobenzylidene)-2,4-thiazolidinedione **(6e)**

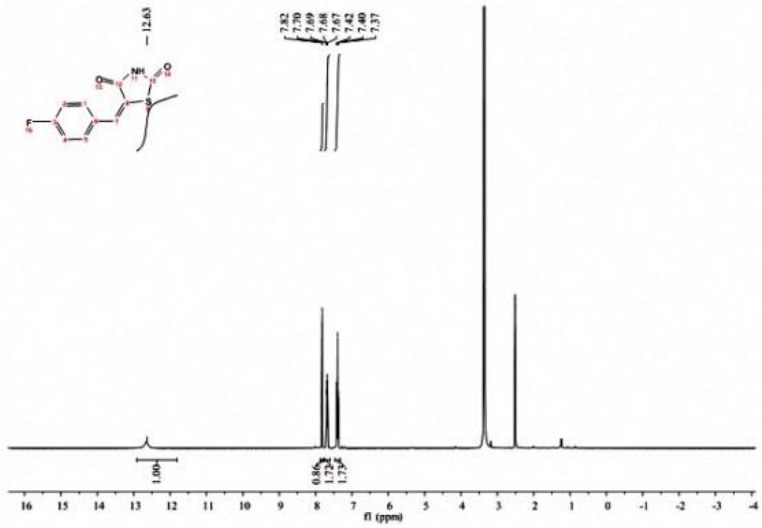


Figure S19. ^{1}H NMR of 5-(4-fluorobenzylidene)-2,4-thiazolidinedione **(6f)**

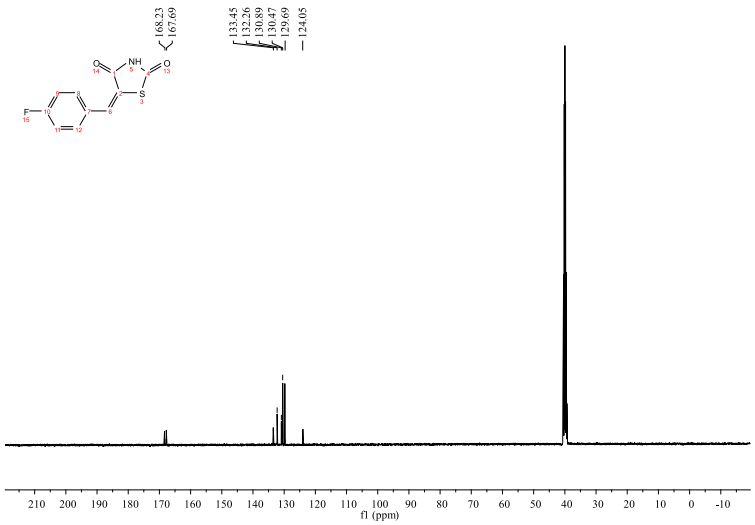


Figure S20. ^{13}C NMR of 5-(4-fluorobenzylidene)-2,4-thiazolidinedione **(6f)**

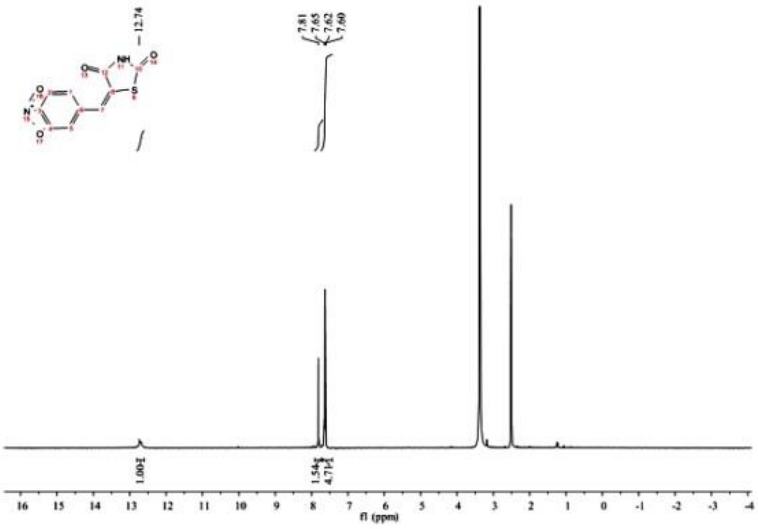


Figure S21. ^{1}H NMR of 5-(4-Nitrobenzylidene)-2,4-thiazolidinedione **(6g)**

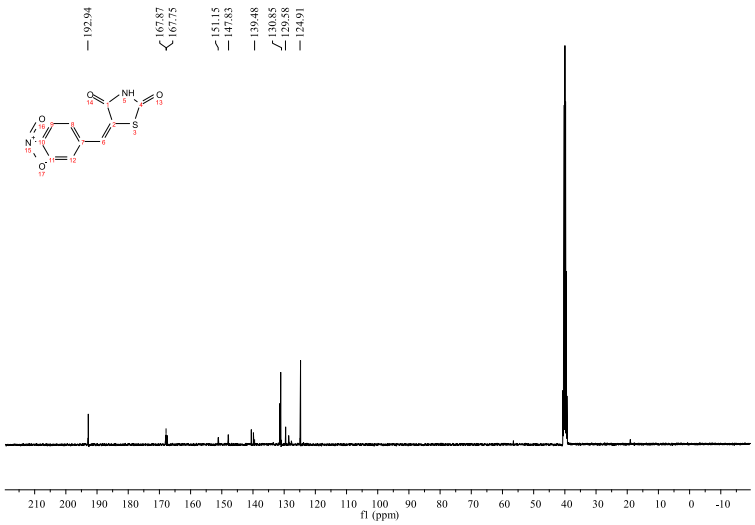


Figure S22. ^{13}C NMR of 5-(4-Nitrobenzylidene)-2,4-thiazolidinedione **(6g)**

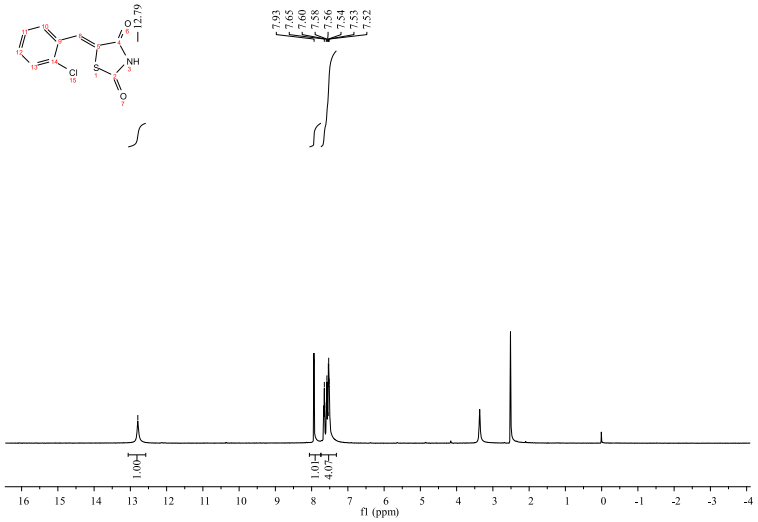


Figure S23. ^{1}H NMR of 5-(2-chlorobenzylidene)-2,4-thiazolidinedione **(6h)**

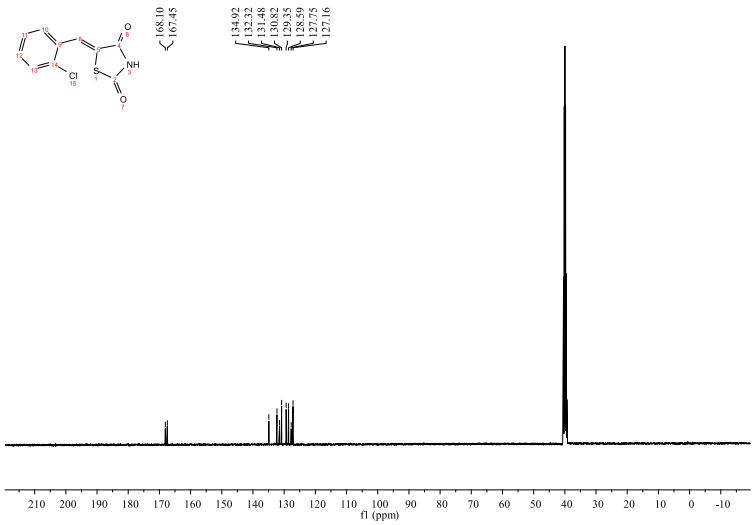


Figure S24. ^{13}C NMR of 5-(2-chlorobenzylidene)-2,4-thiazolidinedione **(6h)**

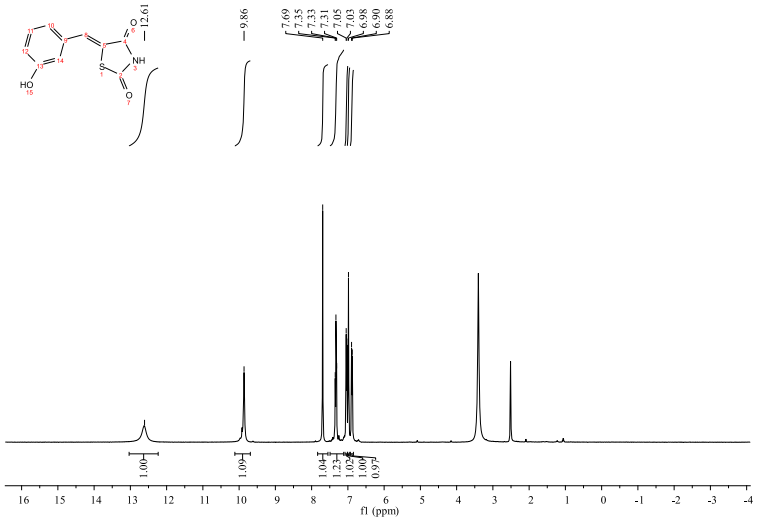


Figure S25. ^{1}H NMR of 5-(3-hydroxylbenzylidene)-2,4-thiazolidinedione **(6i)**

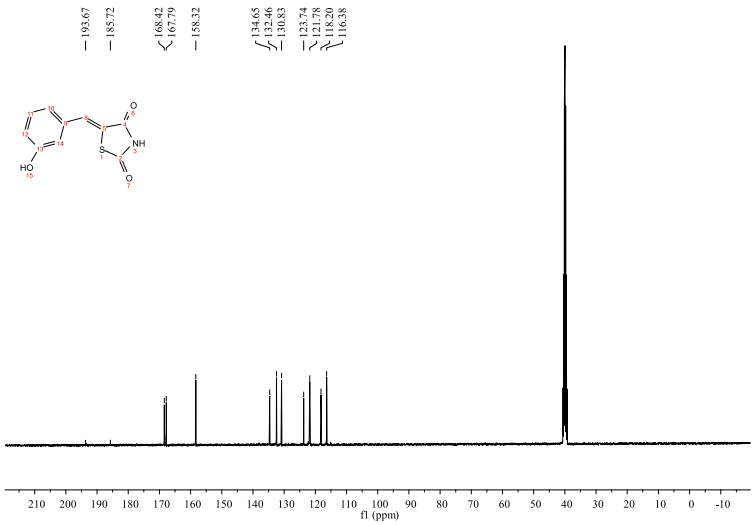


Figure S26. ^{13}C NMR of 5-(3-hydroxylbenzylidene)-2,4-thiazolidinedione **(6i)**

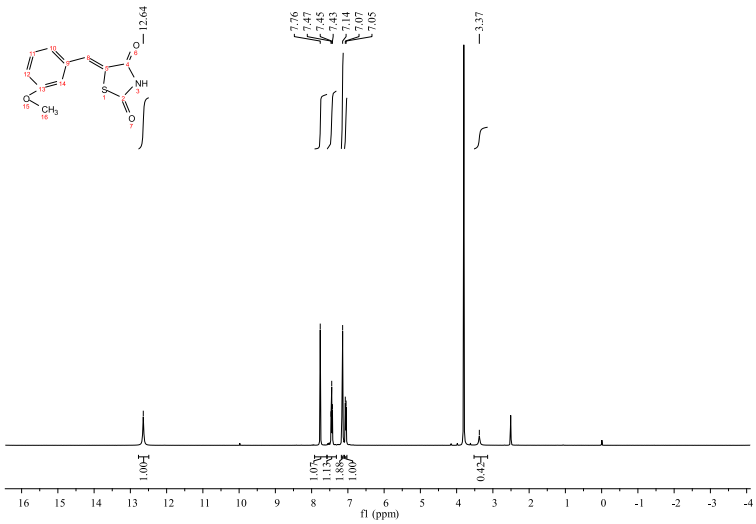


Figure S27. ^{1}H NMR of 5-(3-methoxybenzylidene)-2,4-thiazolidinedione **(6j)**

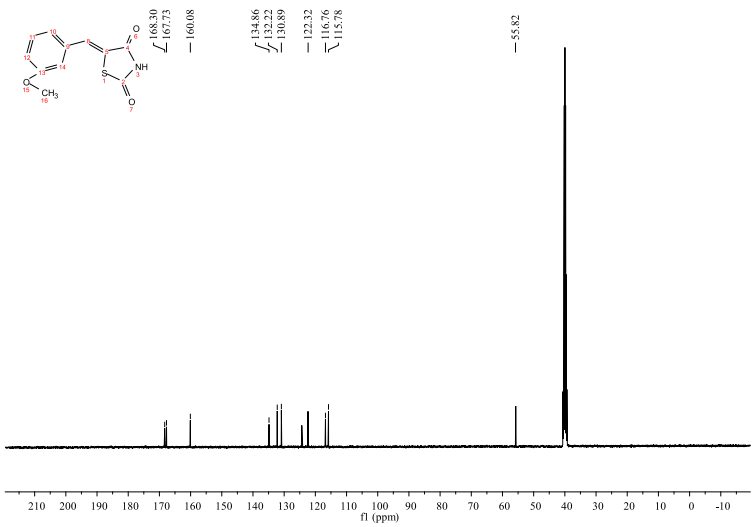


Figure S28. ^{13}C NMR of 5-(3-methoxybenzylidene)-2,4-thiazolidinedione **(6j)**

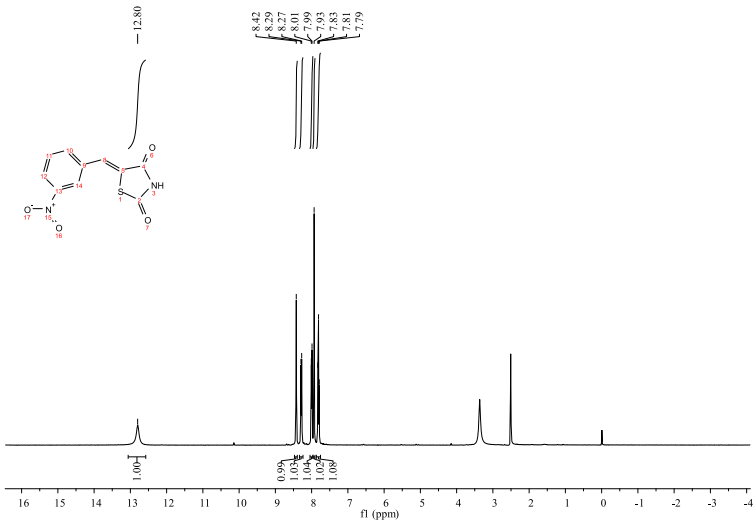


Figure S29. ^{1}H NMR of 5-(3-nitrobenzylidene)-2,4-thiazolidinedione **(6k)**

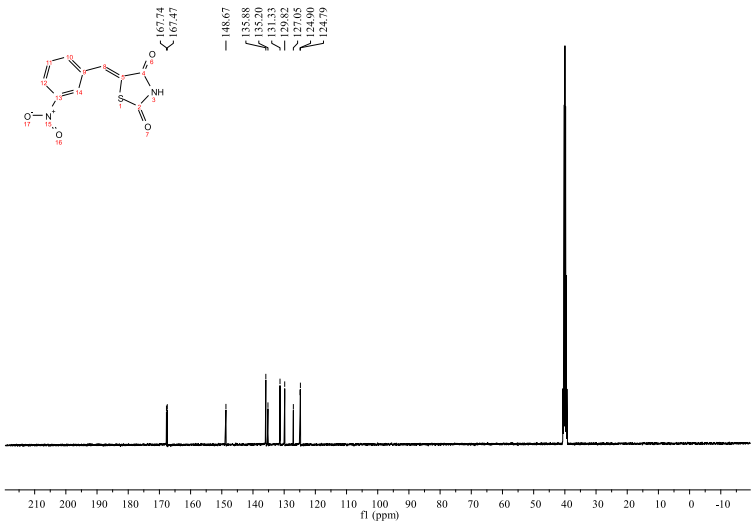


Figure S30. ^{13}C NMR of 5-(3-nitrobenzylidene)-2,4-thiazolidinedione **(6k)**

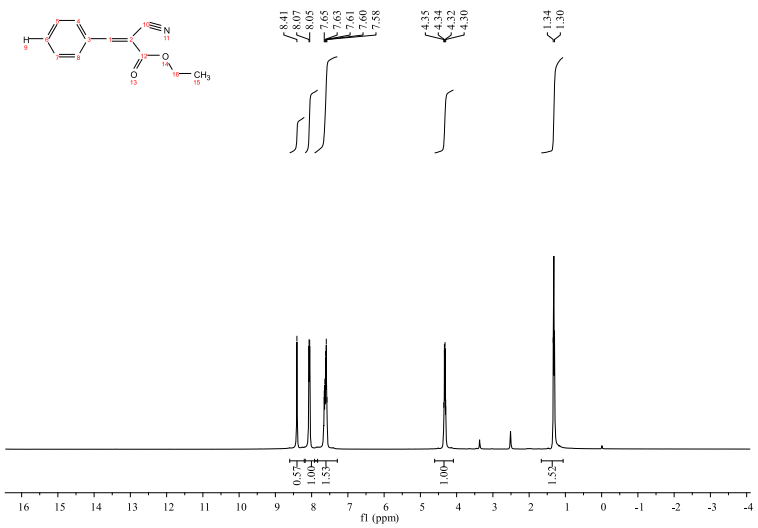


Figure S31. ^{1}H NMR of ethyl (*E*)-2-cyano-3-phenyl-2-propenoate **(8a)**

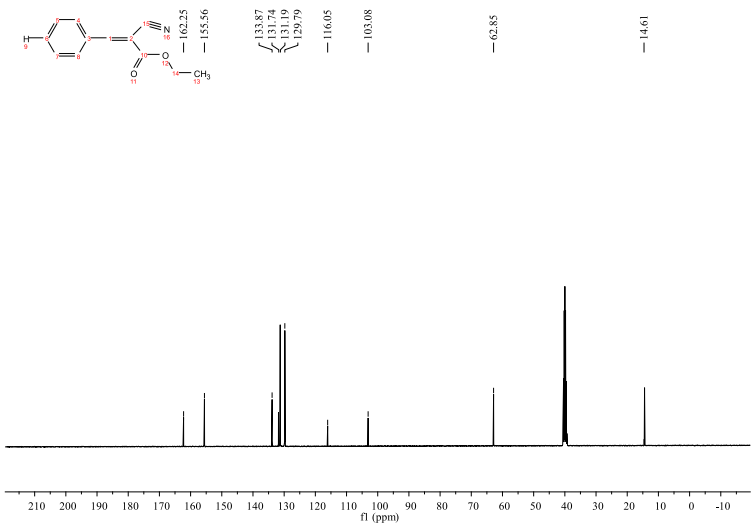


Figure S32. ^{13}C NMR of ethyl (*E*)-2-cyano-3-phenyl-2-propenoate **(8a)**

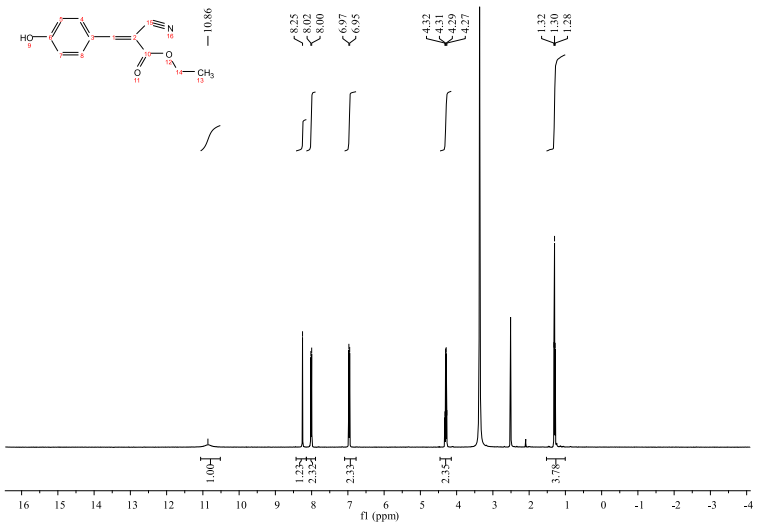


Figure S33. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-hydroxylphenyl)-2-propenoate **(8b)**

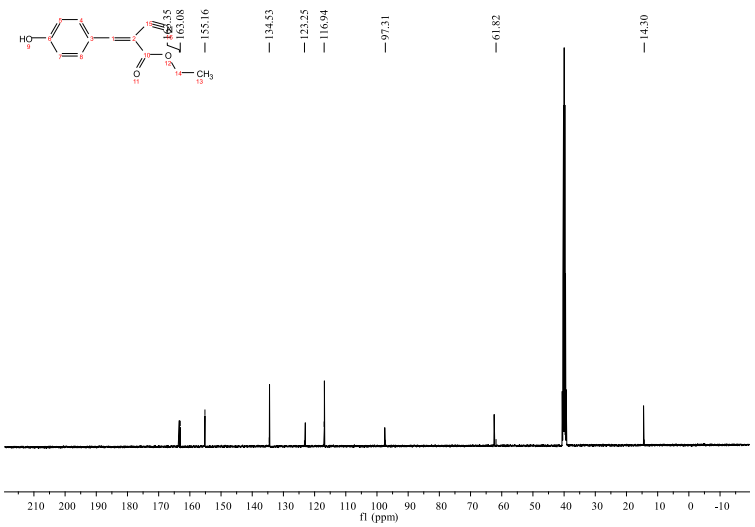


Figure S34. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-hydroxylphenyl)-2-propenoate **(8b)**

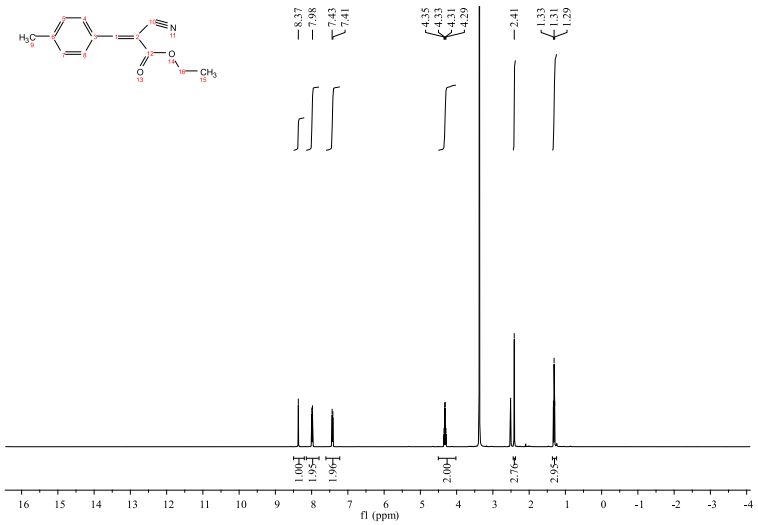


Figure S35. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate **(8c)**

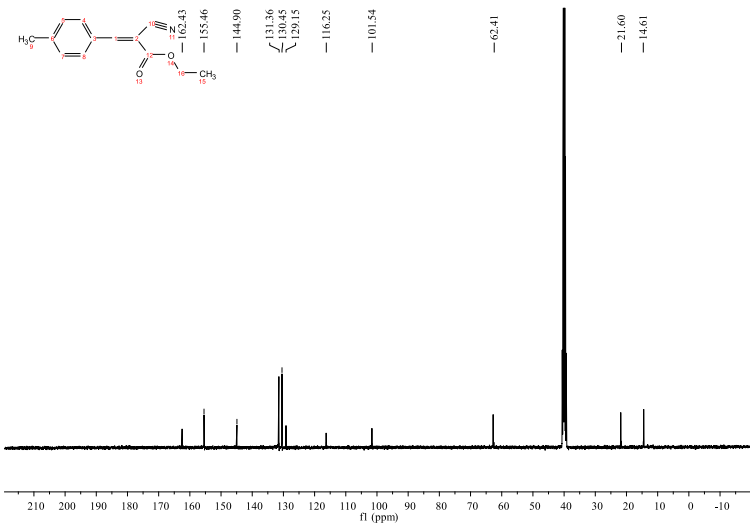


Figure S36. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-methylphenyl)-2-propenoate **(8c)**

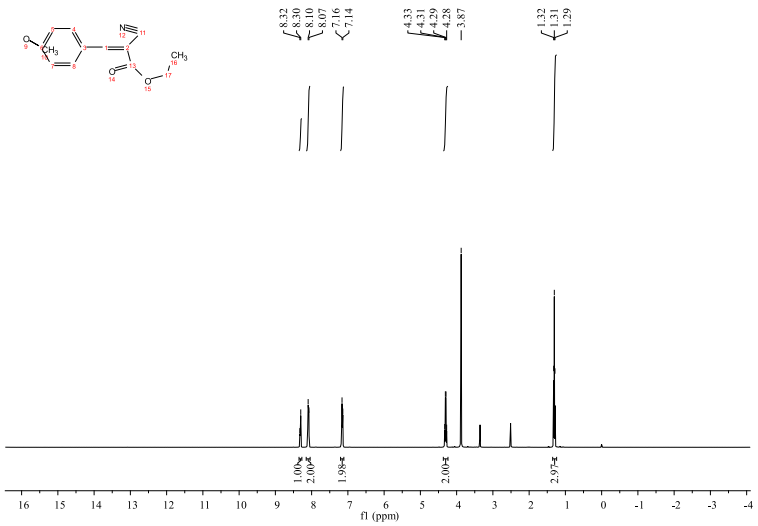


Figure S37. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate **(8d)**

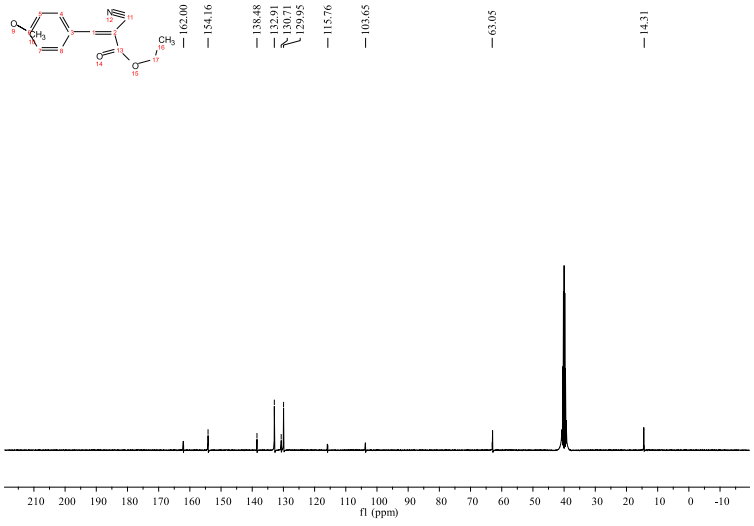


Figure S38. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-methoxyphenyl)-2-propenoate **(8d)**

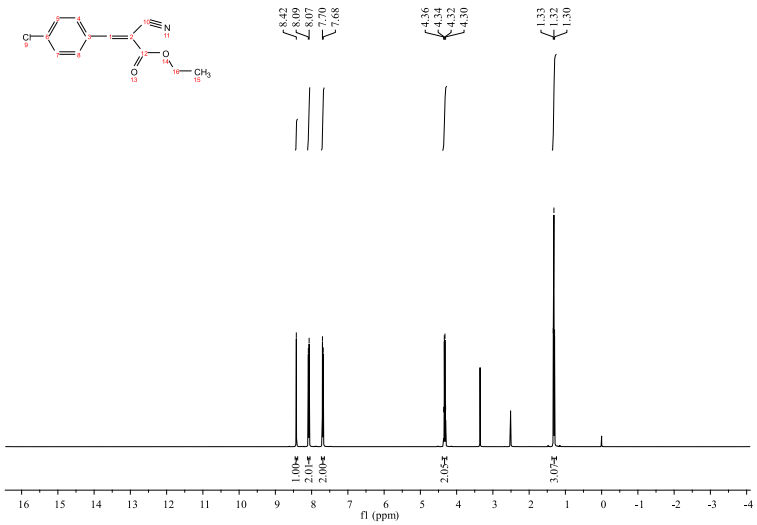


Figure S39. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate **(8e)**

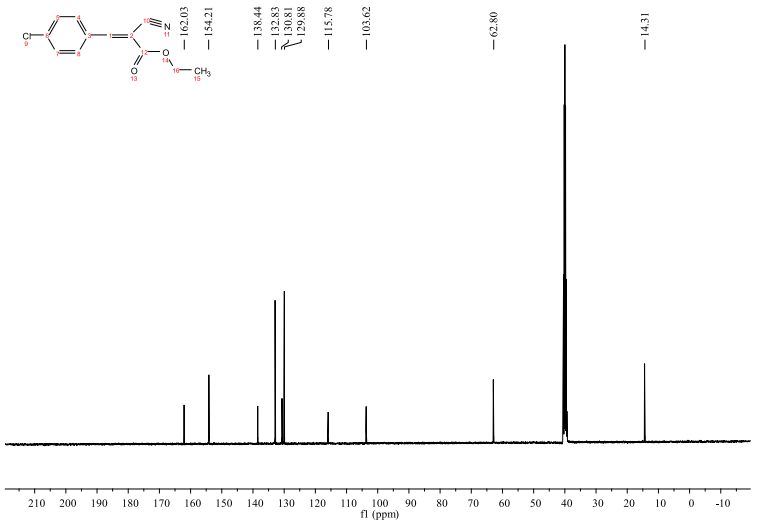


Figure S40. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-chlorophenyl)-2-propenoate **(8e)**

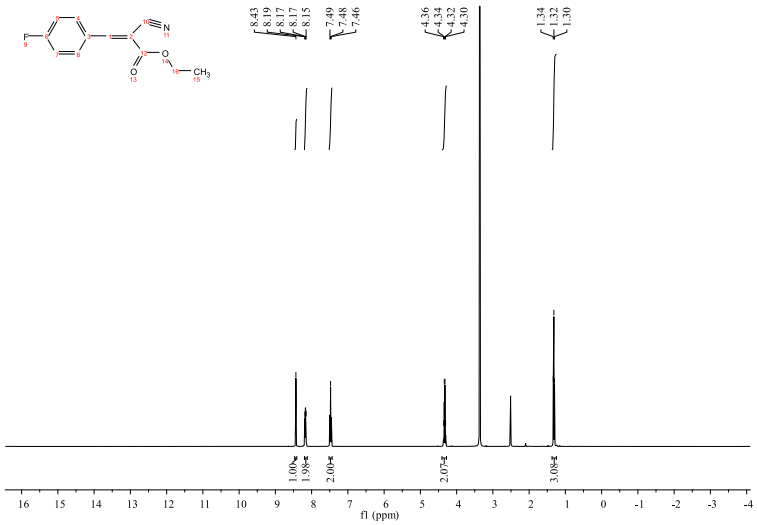


Figure S41. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-fluorophenyl)-2-propenoate **(8f)**

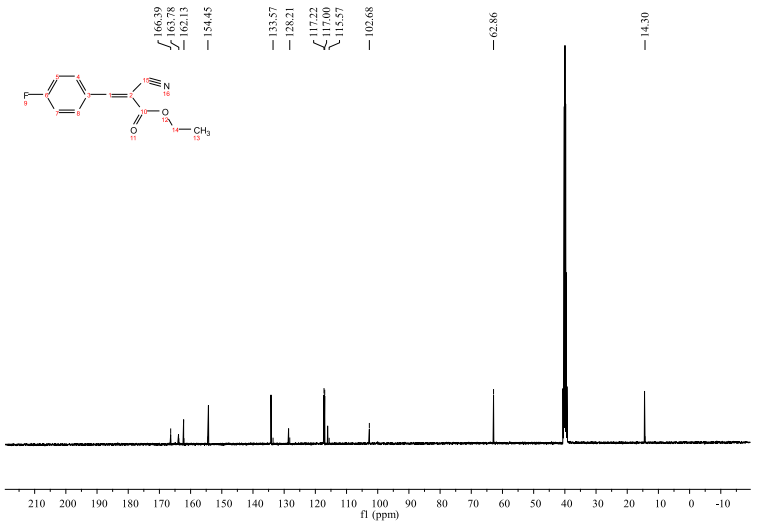


Figure S42. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-fluorophenyl)-2-propenoate **(8f)**

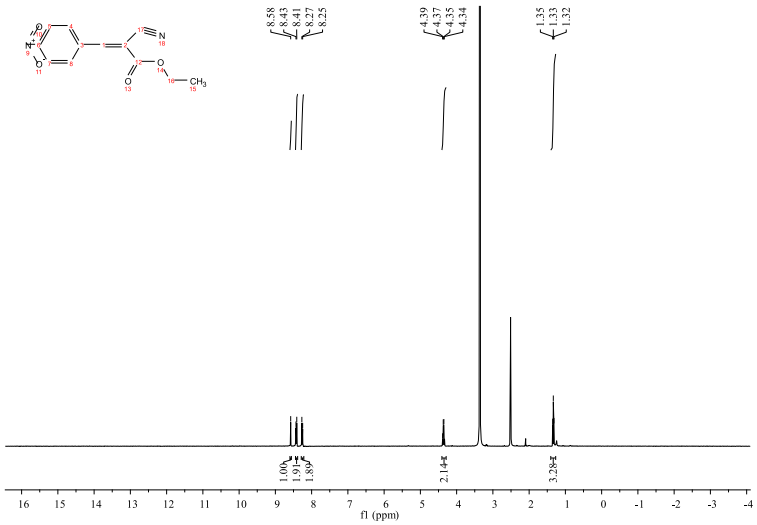


Figure S43. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate **(8g)**

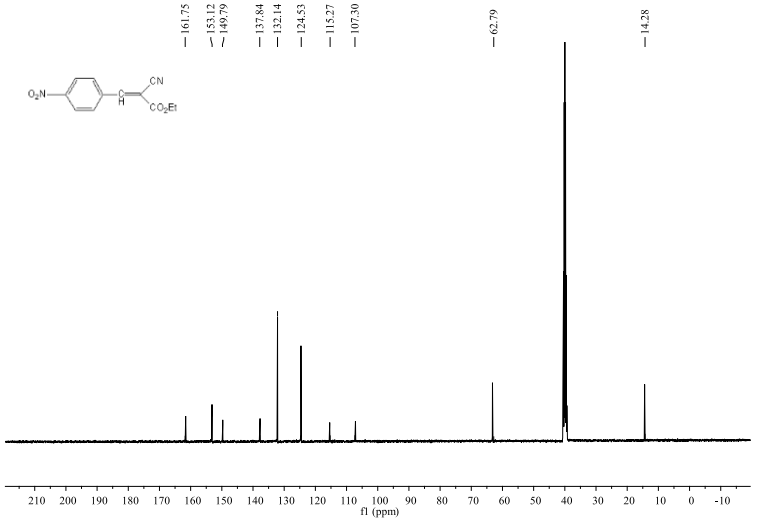


Figure S44. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(4-nitrophenyl)-2-propenoate **(8g)**

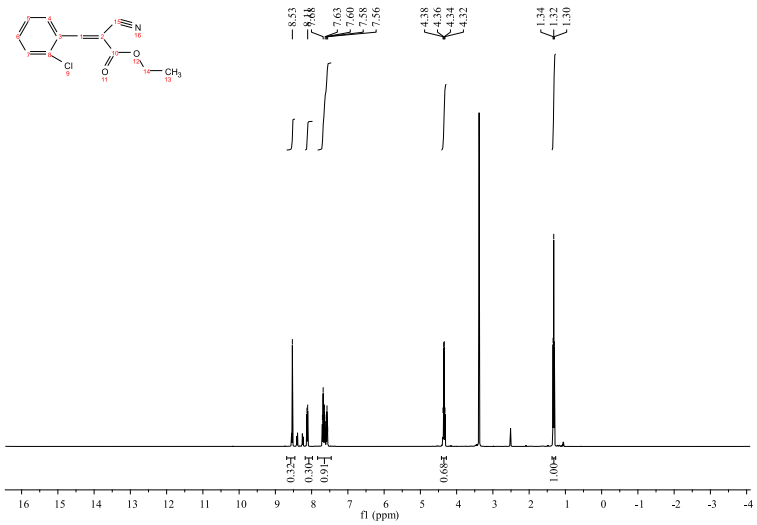


Figure S45. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(2-chlorophenyl)-2-propenoate **(8h)**

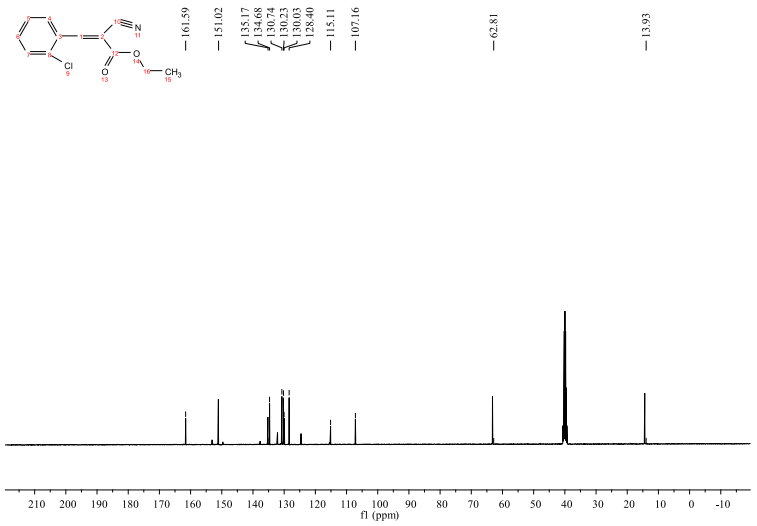


Figure S46. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(2-chlorophenyl)-2-propenoate **(8h)**

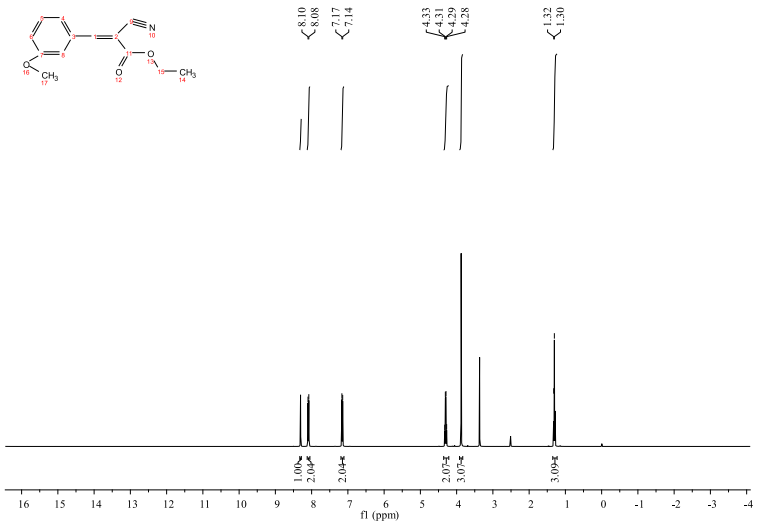


Figure S47. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(3-methoxyphenyl)-2-propenoate **(8i)**

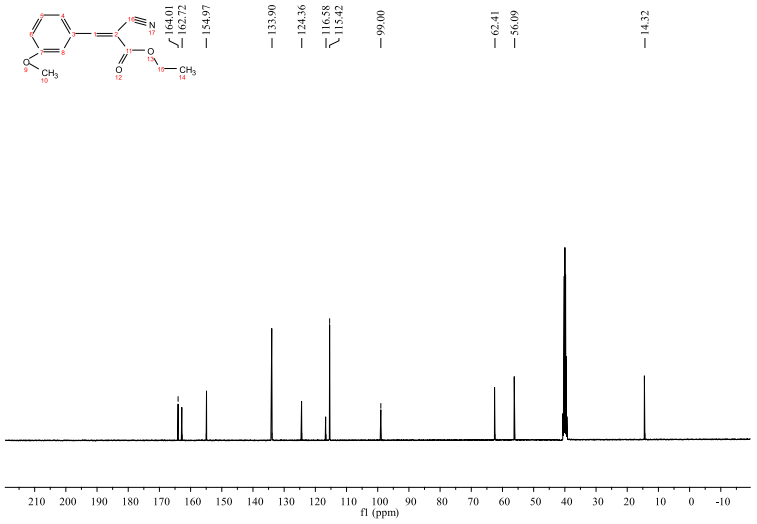


Figure S48. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(3-methoxyphenyl)-2-propenoate **(8i)**

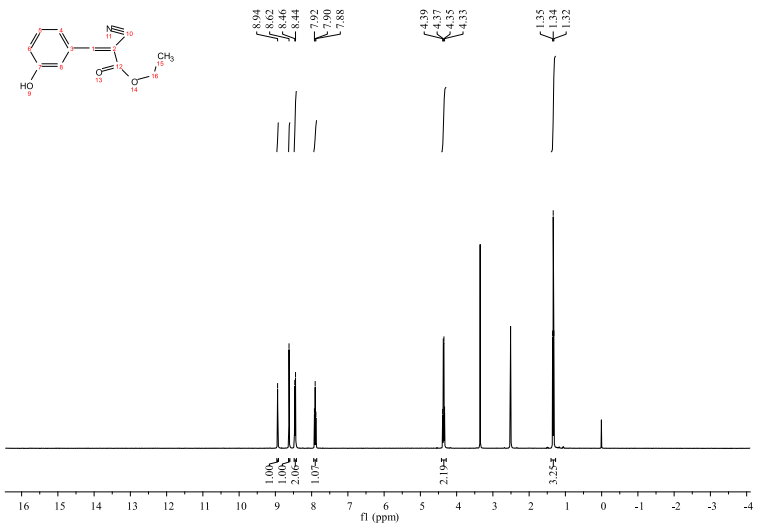


Figure S49. ^{1}H NMR of ethyl (*E*)-2-cyano-3-(3-nitrophenyl)-2-propenoate **(8j)**

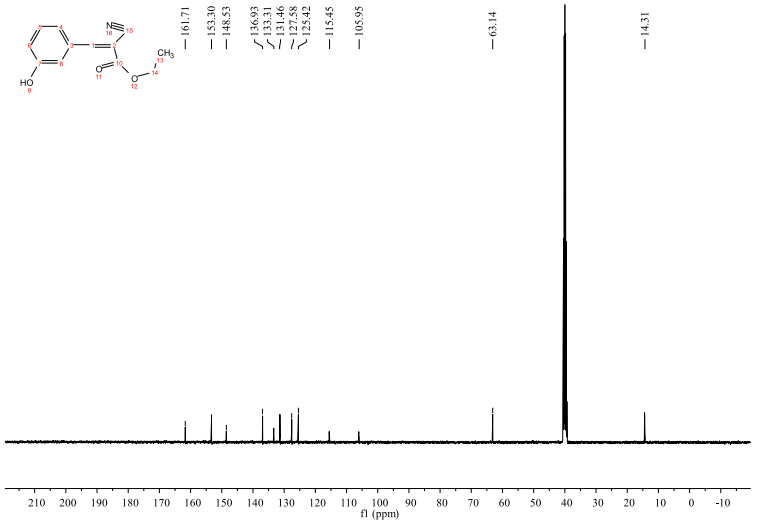


Figure S50. ^{13}C NMR of ethyl (*E*)-2-cyano-3-(3-nitrophenyl)-2-propenoate **(8j)**

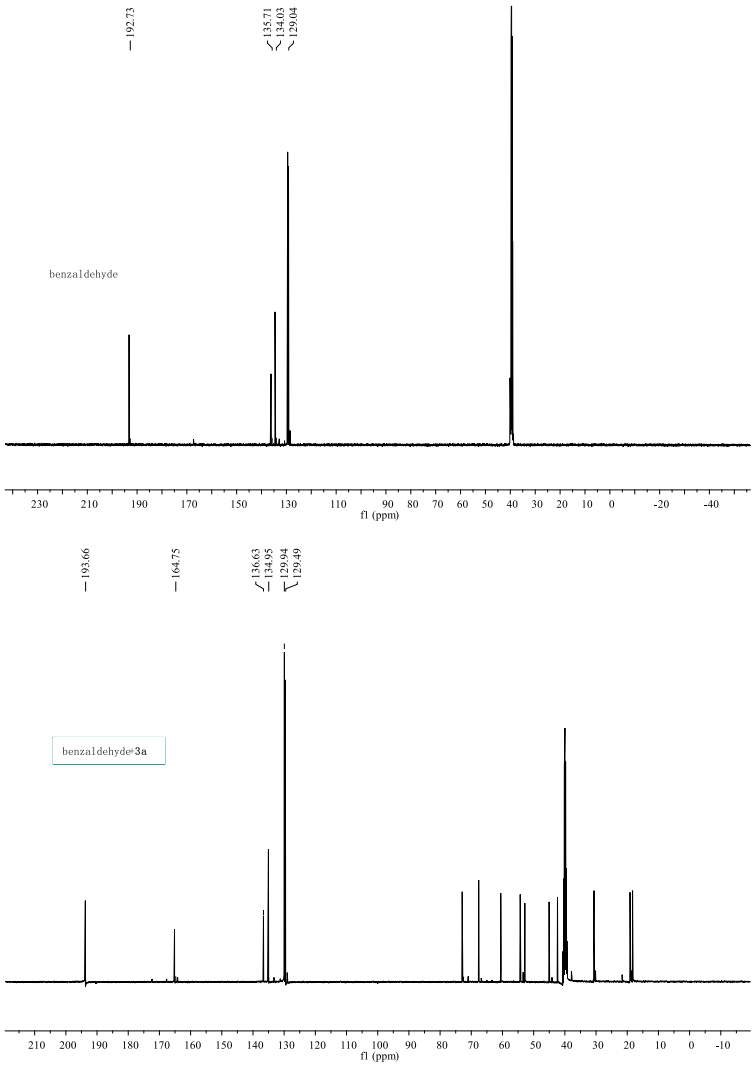


Figure S51. ^{13}C NMR of benzaldehyde and benzaldehyde-**3a** adduct

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