Supporting information for "Catalyst-Free Stereoselective Cyclopropanation of Electron Deficient Alkenes with Ethyl Diazoacetate"

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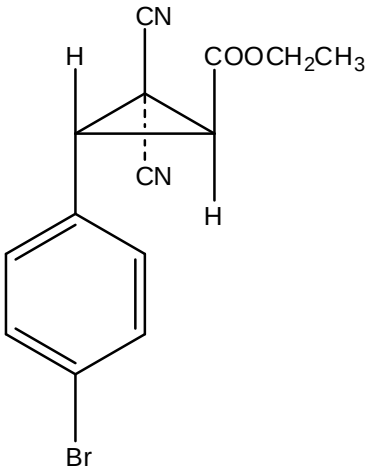
General: Unless otherwise mentioned all reactions were performed in open atmosphere in LR grade solvents. All the reagents and chemicals were purchased from Sigma-Aldrich Company and used without further any purification. Analytical thin layer chromatography was performed with E. Merck silica gel 60 F aluminium plates and visualized under UV 254 nm. ^{1}H NMR and ^{13}C NMR spectra were measured with Brucker 300, 500, and 600 MHz instruments. All the compounds were fully characterized by ^{1}H NMR, ^{13}C NMR, Mass-Spectroscopy, IR, and HRMS analysis.

General experimental procedure for cyclopropanation of arylidene-malononitrile or arylidene-ethyl cyanoacetate with EDA: In a 10 ml round bottom flask, the doubly activated alkene (1 mmol), ethyl diazoacetate (1.2 mmol), and acetonitrile (5 ml) were taken and the reaction mixture was stirred at room temperature until complete consumption of the alkene (TLC). Next the reaction mixture was concentrated to yield crude which was purified by silica-gel column chromatography using ethyl acetate-hexane (1:20) as eluent yielding the desired cyclopropananes.

General experimental procedure for one-pot, two-step, three-component reaction of aldehyde, malononitrile/ethyl cyanoacetate, and ethyl diazoacetate: In a 10 ml round bottom flask, aldehyde (1 mmol), malononitrile/ethyl cyanoacetate (1 mmol), acetonitrile (5 ml), and basic alumina (20 mg) was taken and the reaction mixture was stirred at ambient temperature until complete consumption of the aldehyde (TLC). Next ethyl diazoacetate (1.2 mmol) was added to it and the reaction mixture was further stirred at room temperature until complete consumption of the alkene (TLC). The desired cyclopropanes were further obtained as described above.

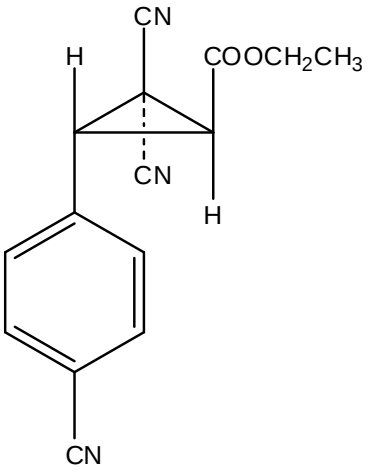
Characterization data for the synthesized cyclopropanes:

Ethyl 3-(4-bromophenyl)-2,2-dicyanocyclopropanecarboxylate (3a):



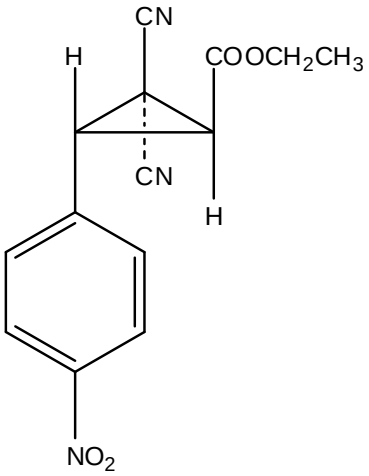
White solid; MP: 97 ^{0}C; ESIMS (*m/z*): 351 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3068, 2981, 2924, 2250, 1735, 1442, 1337, 1252; ^{1}H NMR ($CDCl_3$, 600MHz) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 3.09 (d, *J* = 7.9 Hz, 1H), 3.63 (d, *J* = 7.9 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.58 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 Hz) δ: 13.78, 14.03, 33.52, 37.67, 63.46, 111.27, 111.46, 124.24, 127.98, 129.83, 132.52, 164.57; HRMS calculated for $C_{15}H_{16}BrN_2O_3$: 351.0344; found: 351.0340.

Ethyl 2,2-dicyano-3-(4-cyanophenyl)cyclopropanecarboxylate (3b):



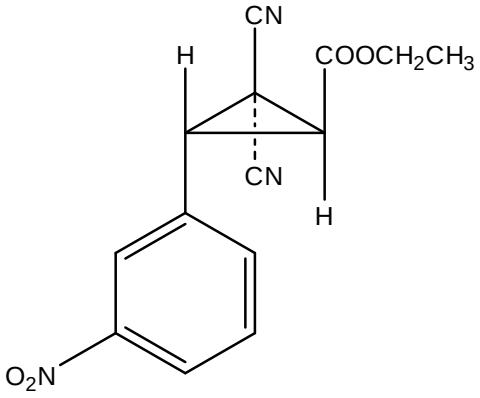
White solid; MP: 168 ^{0}C; ESIMS (*m/z*): 298 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3071, 3025, 2985, 2926, 2253, 2226, 1746, 1443, 1338, 1252, 1201, 1029; ^{1}H NMR ($CDCl_3$, 600 MHz) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 3.16 (d, *J* = 7.9 Hz, 1H), 3.72 (d, *J* = 7.9 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 7.9 Hz, 2H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ: 13.92, 13.99, 33.50, 37.39, 63.62, 110.89, 111.15, 113.95, 117.62, 129.19, 132.93, 134.09, 164.25; HRMS calculated for $C_{16}H_{16}N_3O_3$: 298.1191; found: 298.1185.

Ethyl 2,2-dicyano-3-(4-nitrophenyl)cyclopropanecarboxylate (3c):



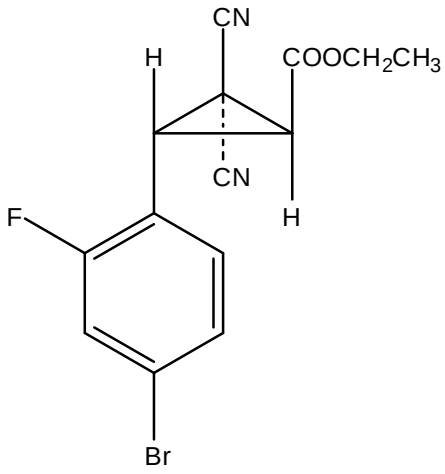
White solid; MP: 145 ^{0}C; ESIMS (*m/z*): 318 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3074, 2983, 2921, 2252, 1736, 1519, 1351; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 3.21 (d, *J* = 8.1 Hz, 1H), 3.77 (d, *J* = 8.1 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.53 (d, *J* = 8.7 Hz, 2H), 8.31 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.99, 33.57, 37.09, 63.71, 110.84, 111.10, 124.37, 129.52, 135.89, 148.60, 164.25; HRMS calculated for $C_{15}H_{16}N_3O_5$: 318.1090; found: 318.1080.

Ethyl 2,2-dicyano-3-(3-nitrophenyl)cyclopropanecarboxylate (3d):



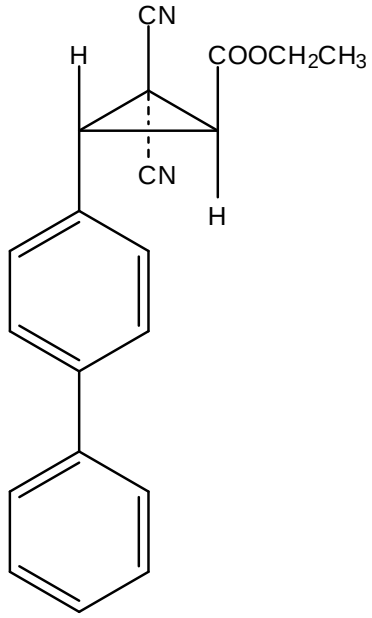
White solid; MP: 150 ^{0}C; ESIMS (*m/z*): 318 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3079, 3046, 2921, 2870, 2256, 1736, 1529, 1349, 1251, 1206; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 3.22 (d, *J* = 8.1 Hz, 1H), 3.79 (d, *J* = 8.1 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.66-7.71 (m, 2H), 8.20 (s, 1H), 8.31-8.33 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 150 Hz) δ: 13.93, 14.05, 33.49, 37.07, 63.77, 110.84, 111.16, 123.42, 124.83, 130.60, 131.19, 134.42, 148.53, 164.25; HRMS calculated for $C_{15}H_{16}N_3O_5$: 318.1090; found: 318.1081.

Ethyl 3-(4-bromo-2-fluorophenyl)-2,2-dicyanocyclopropanecarboxylate (3e):



White solid; MP: 104 ^{0}C; ESIMS (*m/z*): 369 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3073, 3028, 2997, 2249, 1745, 1490, 1408, 1270, 1028; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 3.11 (d, *J* = 8.1 Hz, 1H), 3.66 (d, *J* = 8.1 Hz, 1H), 4.36 (q, *J* = 7.2 Hz, 2H), 7.06-7.08 (m, 1H), 7.37-7.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.05, 14.00, 32.32, 33.18, 63.55, 110.91, 111.36, 116.21, 119.98, 120.17, 124.66, 124.73, 128.20, 128.23, 129.87, 129.90, 160.48, 162.51, 164.33; HRMS calculated for $C_{15}H_{15}BrFN_2O_3$: 369.0250; found: 369.0245.

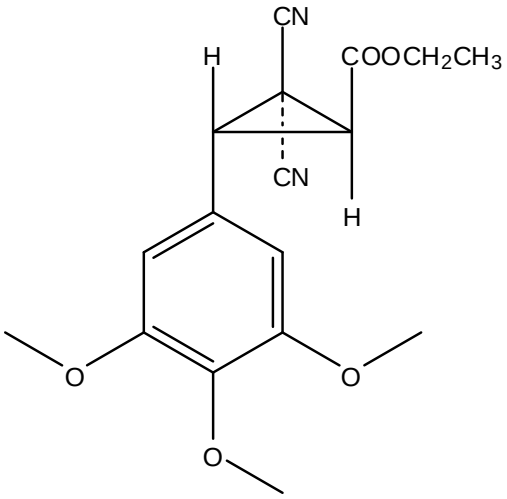
Ethyl 3-(biphenyl-4-yl)-2,2-dicyanocyclopropanecarboxylate (3f):



White solid; MP: 119 ^{0}C; ESIMS (*m/z*): 349 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3029, 2978, 2924, 2853, 2251, 1740, 1431, 1329, 1253, 1197; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 3.17 (d, *J* = 8.2 Hz, 1H), 3.72 (d, *J* = 8.2 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.37-7.40 (m, 3H), 7.45-

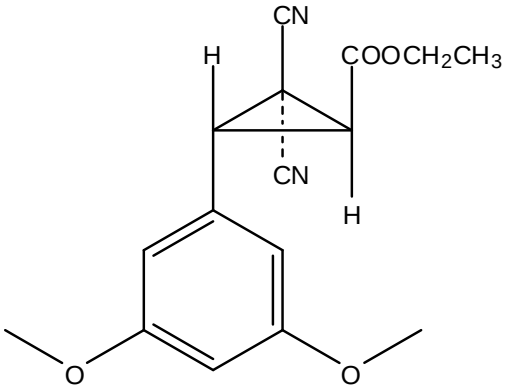
7.48 (m, 2H), 7.58 (d, *J* = 8.3Hz, 2H), 7.65 (d, *J* = 8.3Hz, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.71, 13.82, 33.34, 37.99, 63.13, 111.29, 111.45, 126.84, 127.64, 128.39, 128.65, 139.46, 142.54, 164.61; HRMS calculated for $C_{21}H_{21}N_2O_3$: 349.1552; found: 349.1548.

Ethyl 2,2-dicyano-3-(3,4,5-trimethoxyphenyl)cyclopropanecarboxylate (3g):



Oily compound; ESIMS (*m/z*): 353 (M+Na); IR (KBr, cm^{-1}): 2939, 2841, 2250, 1738, 1591, 1509, 1462, 1244, 1127; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 3.09 (d, *J* = 8.1 Hz, 1H), 3.63 (d, *J* = 8.1 Hz, 1H), 3.86 (s, 3H), 3.89 (s, 6H), 4.38 (q, *J* = 7.2 Hz, 2H), 6.49 (s, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.85, 14.03, 33.83, 38.74, 56.28, 60.88, 63.38, 105.30, 111.55, 111.78, 124.07, 139.18, 153.65, 164.76; HRMS calculated for $C_{17}H_{18}N_2NaO_5$: 353.1113; found: 353.1110.

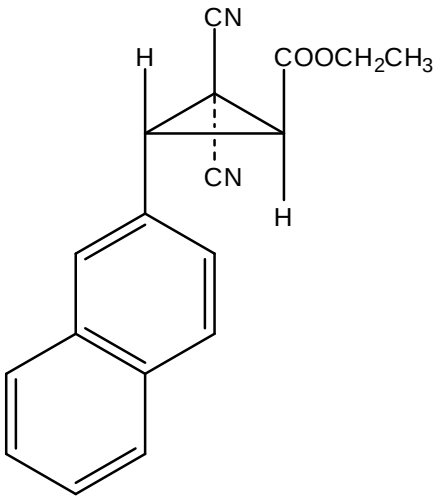
Ethyl 2,2-dicyano-3-(3,5-dimethoxyphenyl)cyclopropanecarboxylate (3h):



Oily compound; ESIMS (*m/z*): 347 (M+HCOOH+H); IR (KBr, cm^{-1}): 3019, 2922, 2850, 2250, 1739, 1599, 1461, 1426; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.37 (t, *J* = 7.2 Hz, 3H), 3.09 (d, *J* = 8.1 Hz, 1H), 3.61 (d, *J* = 8.1 Hz, 1H), 3.81 (s, 6H), 4.36 (q, *J* = 7.2 Hz, 2H), 6.42 (s, 2H), 6.48 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 Hz) δ: 13.76, 14.05, 33.54, 38.44, 55.49, 55.63, 63.35, 101.43, 105.71, 106.33, 111.58,

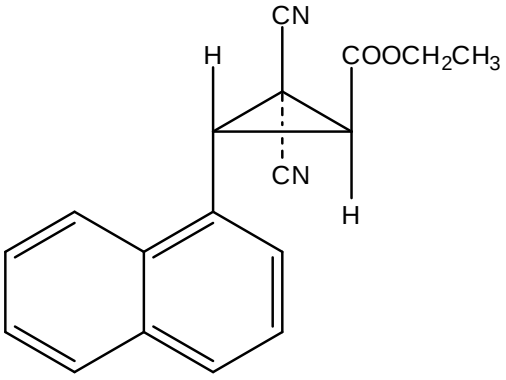
112.23, 136.09, 161.06, 161.27, 164.83; HRMS calculated for $C_{17}H_{19}N_2O_6$: 347.1243; found: 347.1239.

Ethyl 2,2-dicyano-3-(naphthalen-2-yl)cyclopropanecarboxylate (3i):



White solid; MP: 129 ^{0}C; ESIMS (*m/z*): 331 (M+H_2O+Na); IR (KBr, cm^{-1}): 3062, 3025, 2988, 2254, 1739, 1426, 1318, 1245, 1176; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.40 (t, *J* = 7.2 Hz, 3H), 3.28 (d, *J* = 8.1 Hz, 1H), 3.85 (d, *J* = 8.1 Hz, 1H), 4.38 (q, *J* = 7.2 Hz, 2H), 7.39 (dd, *J* = 8.5 & 1.8 Hz, 1H), 7.54-7.57 (m, 2H), 7.76 (s, 1H), 7.84-7.88 (m, 2H), 7.92 (d, *J* = 8.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.95, 14.07, 33.61, 38.66, 63.39, 111.60, 111.71, 124.98, 126.20, 127.09, 127.31, 127.84, 129.39, 132.93, 133.57, 164.89; HRMS calculated for $C_{18}H_{16}N_2NaO_3$: 331.1058; found: 331.1053.

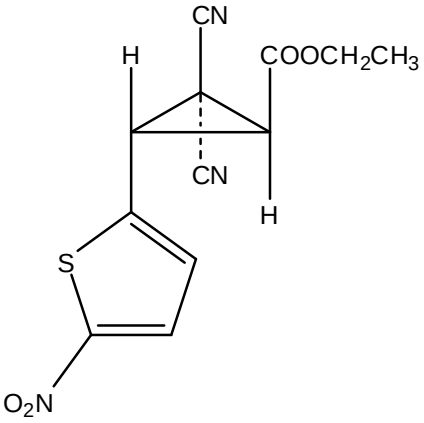
Ethyl 2,2-dicyano-3-(naphthalen-1-yl)cyclopropanecarboxylate (3j):



Brown solid; MP: 139 ^{0}C; ESIMS (*m/z*): 331 (M+H_2O+Na); IR (KBr, cm^{-1}): 3050, 3009, 2249, 1729, 1431, 1394, 1321, 1254; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.41 (t, *J* = 7.5 Hz, 3H), 3.31 (d, *J* = 8.3 Hz, 1H), 4.09 (d, *J* = 8.3 Hz, 1H), 4.39 (q, *J* = 7.5 Hz, 2H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.44-7.50 (m, 1H), 7.60-7.65 (m, 1H), 7.70-7.75 (m, 1H), 7.94 (d, J = 8.3 Hz, 2H), 8.05 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ: 13.69, 14.07, 33.64, 36.98, 63.40, 111.52, 111.77, 122.27, 124.92, 125.40,

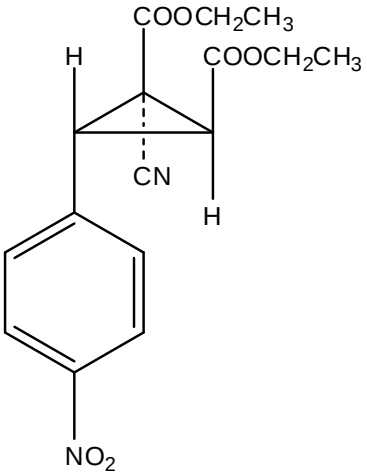
125.85, 126.87, 127.93, 129.21, 130.78, 131.93, 133.67, 164.97; HRMS calculated for $C_{18}H_{16}N_2NaO_3$: 331.1058; found: 331.1056.

Ethyl 2,2-dicyano-3-(5-nitrothiophen-2-yl)cyclopropanecarboxylate (3k):

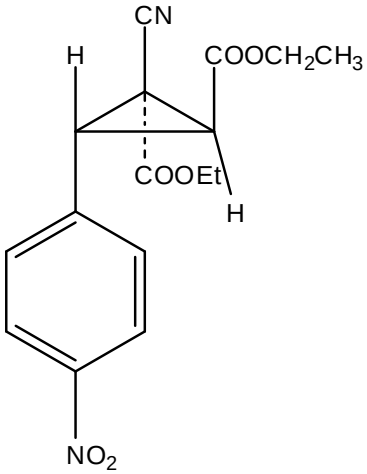


Brown solid; MP: 116 ^{0}C; ESIMS (*m/z*): 324 (M+CH_3OH+H); IR (KBr, cm^{-1}): 3101, 3037, 2252, 1724, 1507, 1418, 1344; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 1.39 (t, *J* = 7.2 Hz, 3H), 3.13 (d, *J* = 7.8 Hz, 1H), 3.78 (d, *J* = 7.8 Hz, 1H), 4.39 (q, *J* = 7.2 Hz, 2H), 7.08 (d, *J* = 4.2 Hz, 1H), 7.87 (d, *J* = 4.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 Hz) δ: 14.01, 14.90, 32.81, 34.77, 64.01, 110.19, 110.78, 127.76, 128.37, 138.41, 152.65, 163.54; HRMS calculated for $C_{13}H_{14}N_3O_5S$: 324.0654; found: 324.0649.

Diethyl 1-cyano-3-(4-nitrophenyl)cyclopropane-1,2-dicarboxylate (3l [major diastereomer; where nitrile is syn to aryl] **& 3l'**[minor diastereomer; where nitrile is anti to aryl]**):**



3l (major)

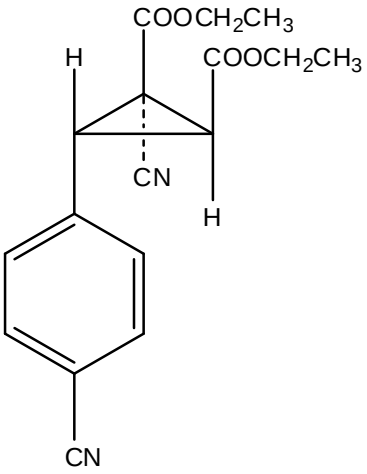


3l' (minor)

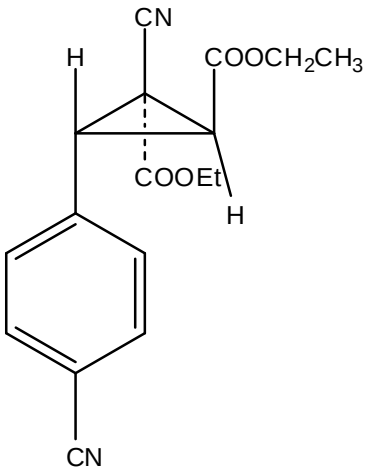
The mixture of **3l** and **3l'** was obtained in 10:1 ratio as semi-solid; ESIMS (*m/z*): 355 (M+Na); IR (KBr, cm^{-1}): 3082, 2986, 2937, 2247, 1741, 1603, 1524, 1349; ^{1}H NMR data assigned for **3l**: ($CDCl_3$, 500 MHz) δ: 1.30 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 3.15 (d, *J* = 8.4 Hz, 1H), 3.73 (d, *J* = 8.4 Hz, 1H), 4.23-4.37 (m, 4H), 7.50 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H); ^{1}H NMR data

assigned for **3l'**: ($CDCl_3$, 500 MHz) δ: 1.30 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 3.07 (d, *J* = 10.2 Hz, 1H), 3.48 (d, *J* = 10.2 Hz, 1H), 4.23-4.37 (m, 4H), 7.38 (d, *J* = 8.7 Hz, 2H), 8.27 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR for the mixture of **3l** and **3l'**($CDCl_3$, 125 Hz) δ: 13.66, 13.89, 13.94, 28.38, 29.59, 30.58, 31.81, 35.26, 35.66, 61.77, 62.50, 62.86, 63.84, 109.88, 114.36, 123.46, 124.01, 129.28, 130.34, 138.71, 144.95, 147.98, 148.57, 160.98, 163.22, 163.56, 164.59**;** HRMS calculated for $C_{16}H_{16}N_2NaO_6$: 355.0906; found: 355.0909.

Diethyl 1-cyano-3-(4-cyanophenyl)cyclopropane-1,2-dicarboxylate (3m [major diastereomer; where nitrile is syn to aryl] **& 3m'**[minor diastereomer; where nitrile is anti to aryl]**):**



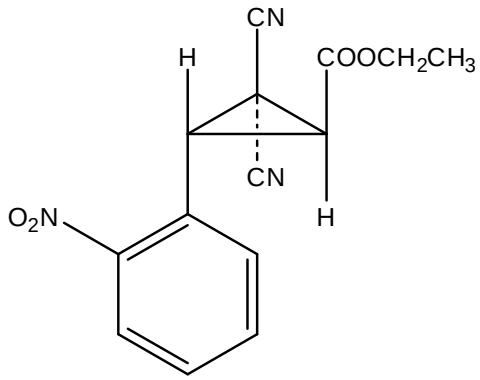
3m (major)



3m' (minor)

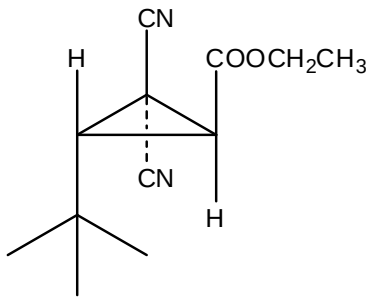
The mixture of **3m** and **3m'** was obtained in 10:1 ratio as semi-solid; ESIMS (*m/z*): 335 (M+Na); IR (KBr, cm^{-1}): 2986, 2231, 1739, 1607, 1270; ^{1}H NMR data assigned for **3m**: ($CDCl_3$, 500 MHz) δ: 1.30 (t, *J* = 7.2 Hz, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 3.16 (d, *J* = 8.4 Hz, 1H), 3.68 (d, *J* = 8.4 Hz, 1H), 4.22-4.36 (m, 4H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H); ^{1}H NMR data assigned for **3m'**: ($CDCl_3$, 500 MHz) δ: 1.30 (t, *J* = 7.2 Hz, 3H), 1.36 (t, *J* = 7.0 Hz, 3H), 3.05 (d, *J* = 10.3 Hz, 1H), 3.45 (d, *J* = 10.3 Hz, 1H), 4.23-4.37 (m, 4H), 7.32 (d, *J* = 8.7 Hz, 2H), 7.71 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR for the mixture of **3m** and **3m'**($CDCl_3$, 125 Hz) δ: 13.40, 13.66, 13.73, 25.82, 28.14, 33.99, 35.94, 35.26, 35.35, 61.46, 62.18, 62.57, 63.52**,** 109.31, 110.62, 117.60, 117.84, 127.35, 128.91, 131.72, 132.33, 135.49, 136.67, 141.53, 143.00, 160.86, 163.14, 163.72, 164.49**;** HRMS calculated for $C_{17}H_{16}N_2NaO_4$: 335.1008; found: 335.1008.

Ethyl 2,2-dicyano-3-(2-nitrophenyl)cyclopropanecarboxylate (3n):



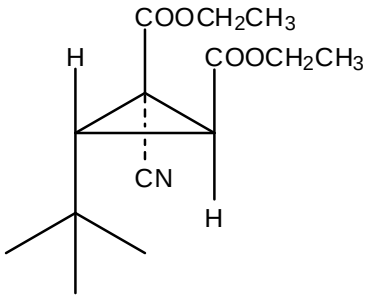
White solid; MP: 136 ^{0}C; ESIMS (*m/z*): 326 (M+H_2O+Na); IR (KBr, cm^{-1}): 3080, 2987, 2937, 2254, 1734, 1524, 1342, 1243, 1187; ^{1}H NMR ($CDCl_3$, 300MHz) δ: 1.38 (t, *J* = 7.2 Hz, 3H), 3.12 (d, *J* = 8.3 Hz, 1H), 4.07 (d, *J* = 8.3 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.66-7.80 (m, 2H), 8.31 (dd, *J* = 8.1 & 1.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 14.08, 14.23, 34.68, 36.80, 63.63, 111.10, 111.66, 125.53, 126.38, 130.83, 131.35, 134.67, 148.66, 164.43; HRMS calculated for $C_{14}H_{13}N_3NaO_5$: 326.0752; found: 326.0747.

Ethyl 3-tert-butyl-2,2-dicyanocyclopropanecarboxylate (3o):



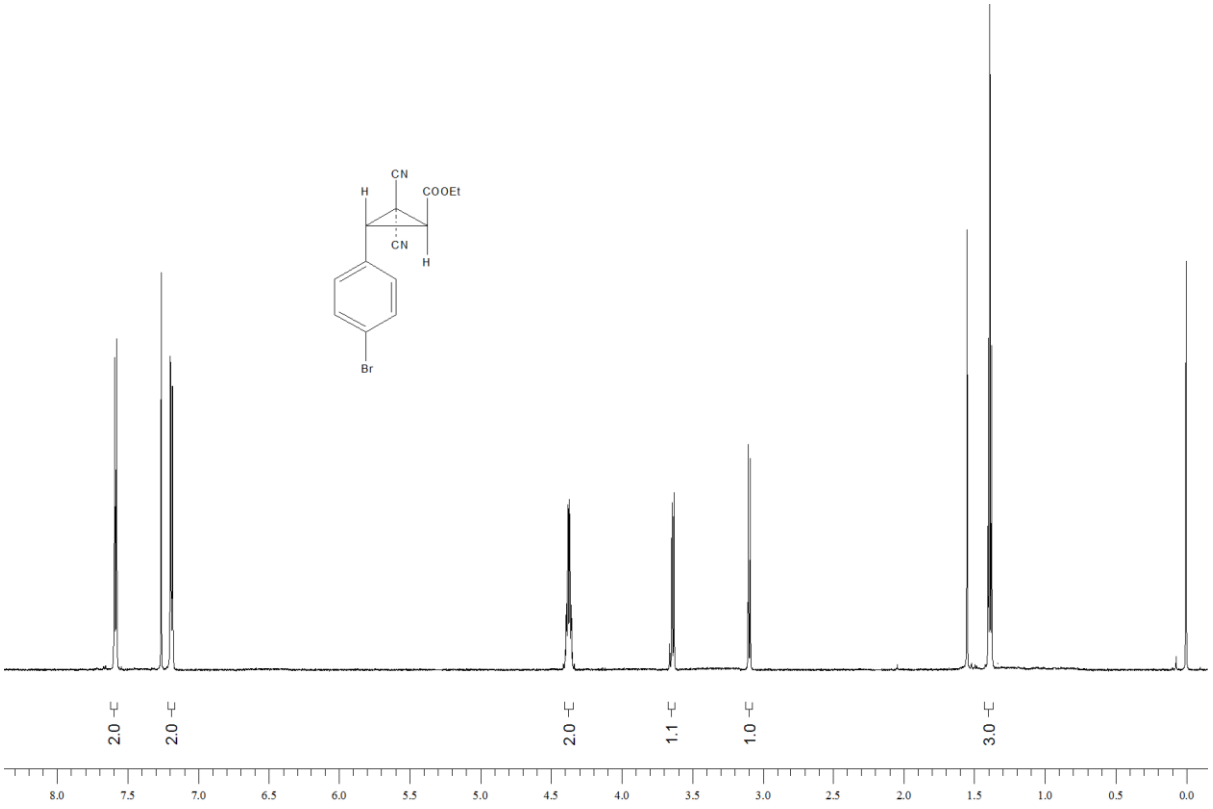
Oily compound; ESIMS (*m/z*): 239 (M+H_2O+H); IR (KBr, cm^{-1}): 2967, 2249, 1740, 1474, 1243; ^{1}H NMR ($CDCl_3$, 500MHz) δ: 1.16 (s, 9H), 1.35 (t, *J* = 7.2 Hz, 3H), 2.30 (d, *J* = 8.8 Hz, 1H), 2.67 (d, *J* = 8.8 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 8.77, 13.96, 27.91, 30.43, 32.54, 45.20, 62.97, 112.23, 112.81, 165.39; HRMS calculated for $C_{12}H_{19}N_2O_3$: 239.1395; found: 239.1390.

Diethyl 3-tert-butyl-1-cyanocyclopropane-1,2-dicarboxylate (3p):

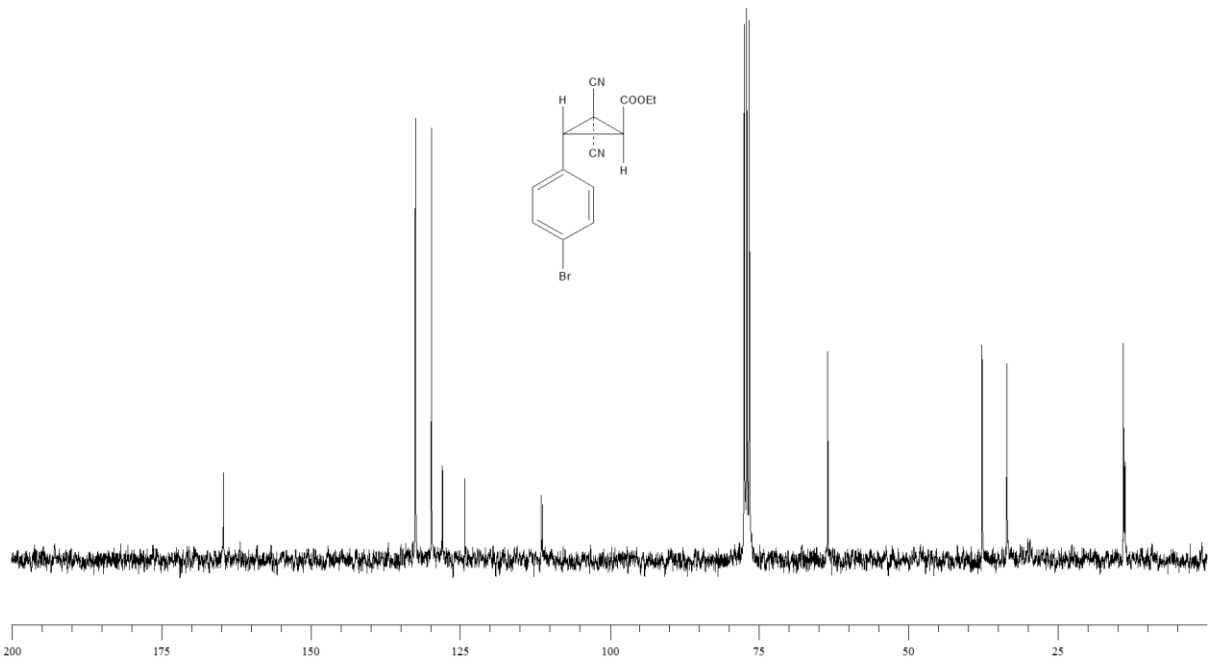


White solid; MP 47 ^{0}C; ESIMS (*m/z*): 290 (M +Na); IR (KBr, cm^{-1}): 2967, 2243, 1739, 1470, 1369, 1290; ^{1}H NMR ($CDCl_3$, 300MHz) δ: 1.14 (s, 9H), 1.24-1.35 (m, 6H), 2.32 (d, *J* = 9.1 Hz, 1H), 2.64 (d, *J* = 9.1 Hz, 1H), 4.13-4.30 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ: 13.92, 13.96, 22.93, 26.12, 29.95, 34.42, 43.23, 61.84, 63.22, 116.37, 164.72, 166.11; HRMS calculated for $C_{14}H_{21}NNaO_4$: 290.1368; found: 290.1360.

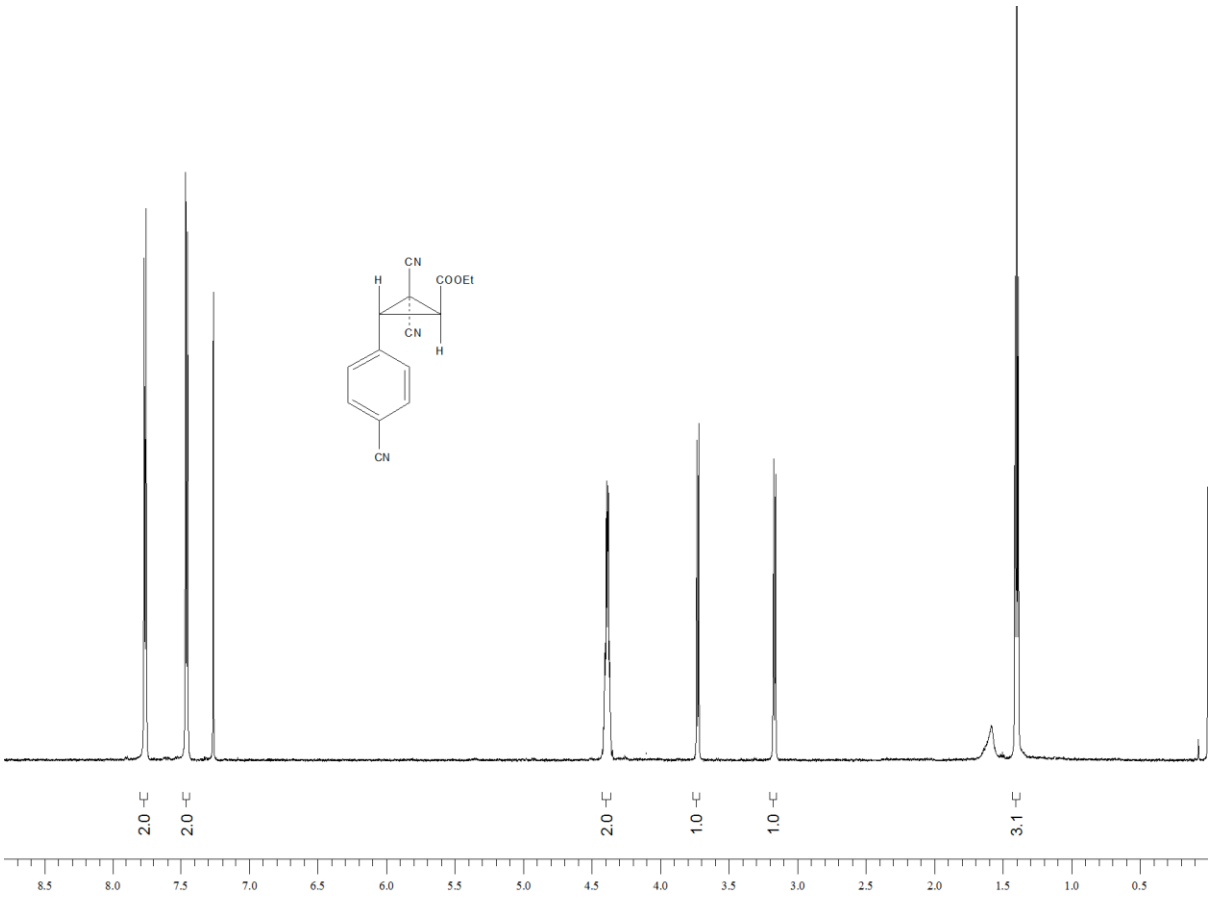
1H NMR of 3a:



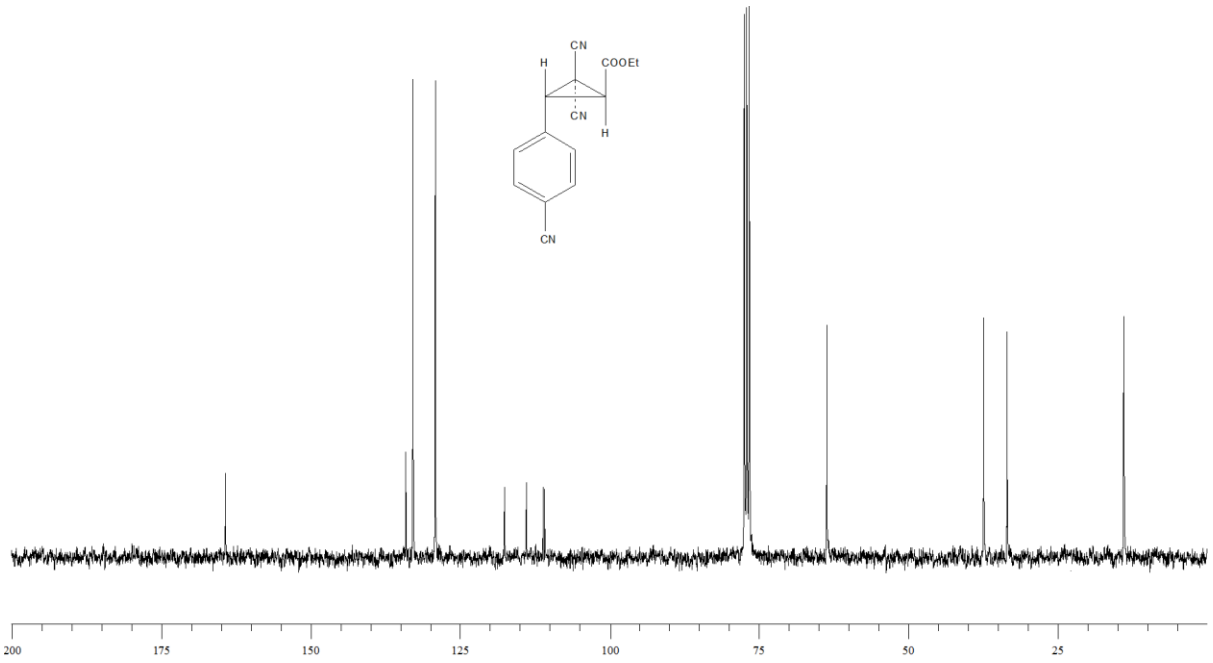
13C NMR of 3a:



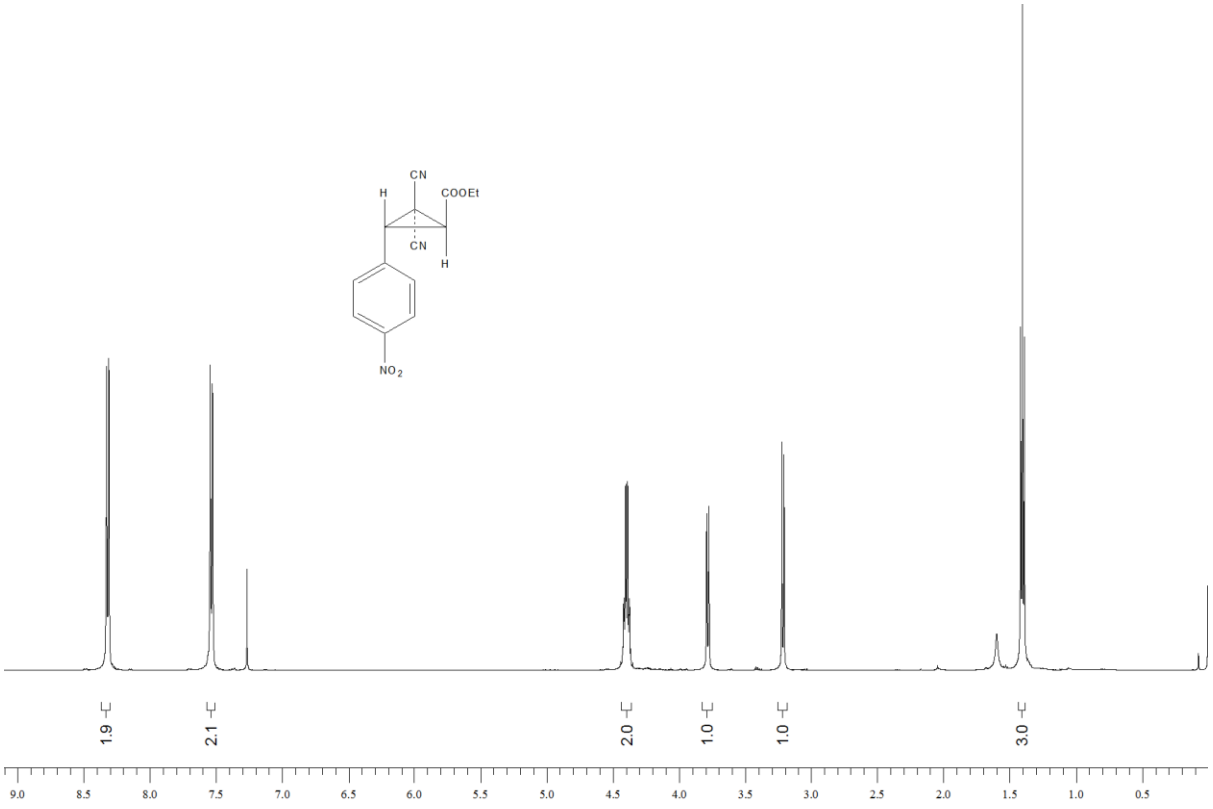
1H NMR of 3b:



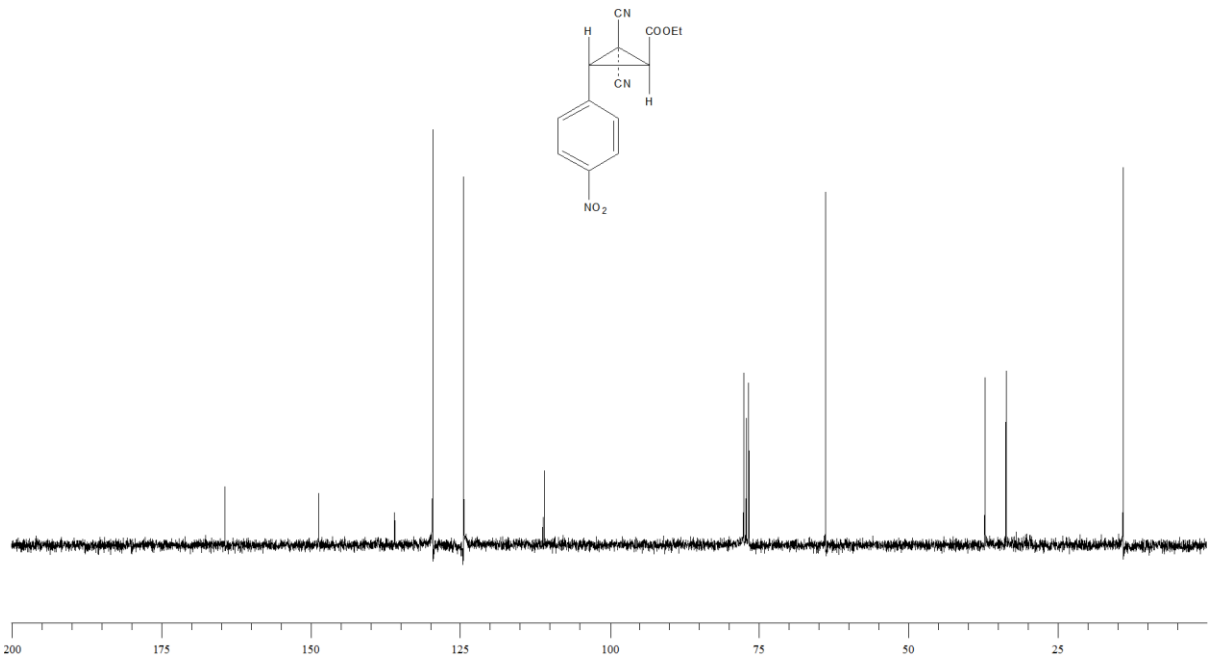
13C NMR of 3b:



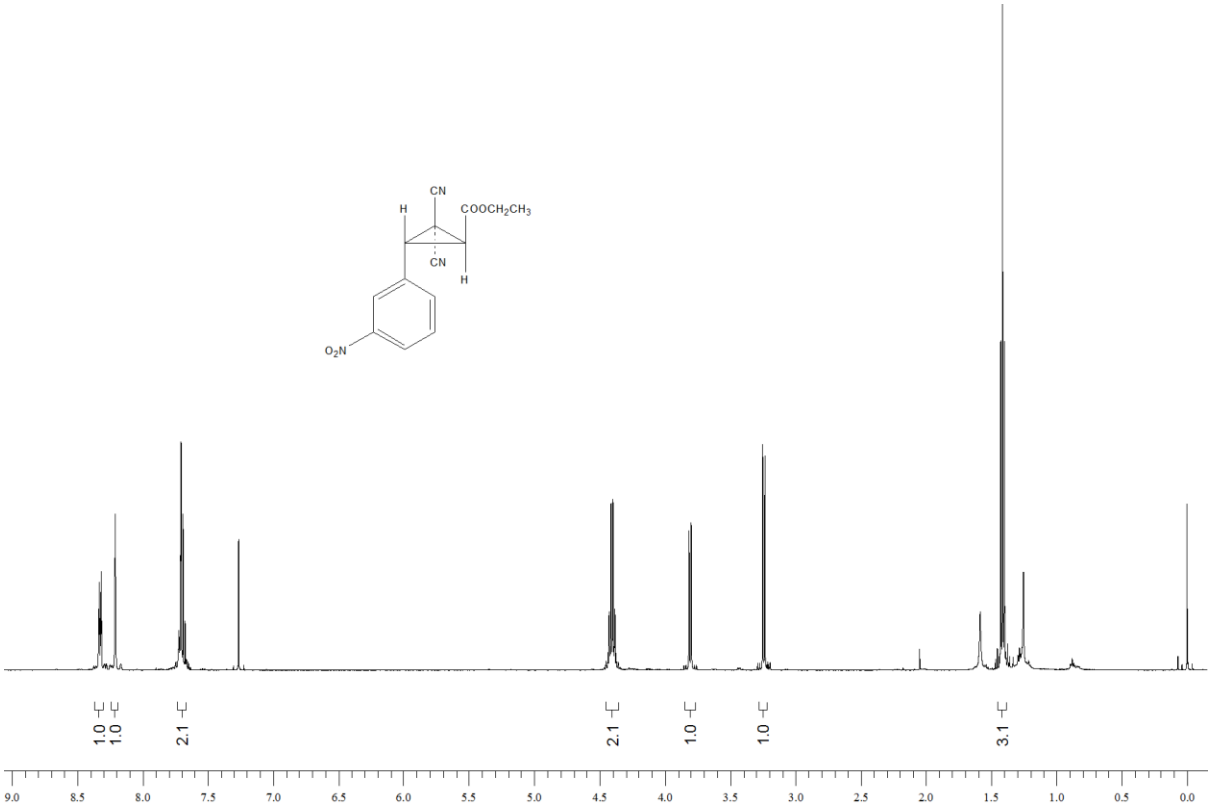
1H NMR of 3c:



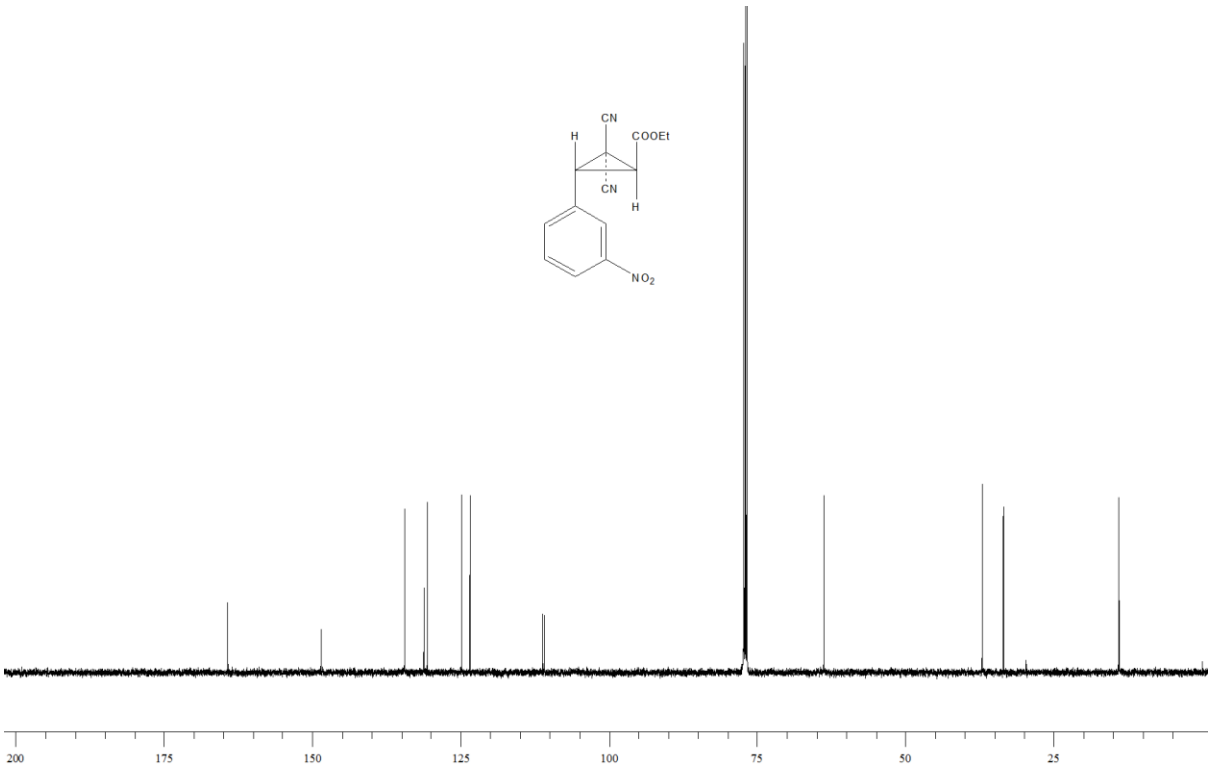
13C NMR of 3c:



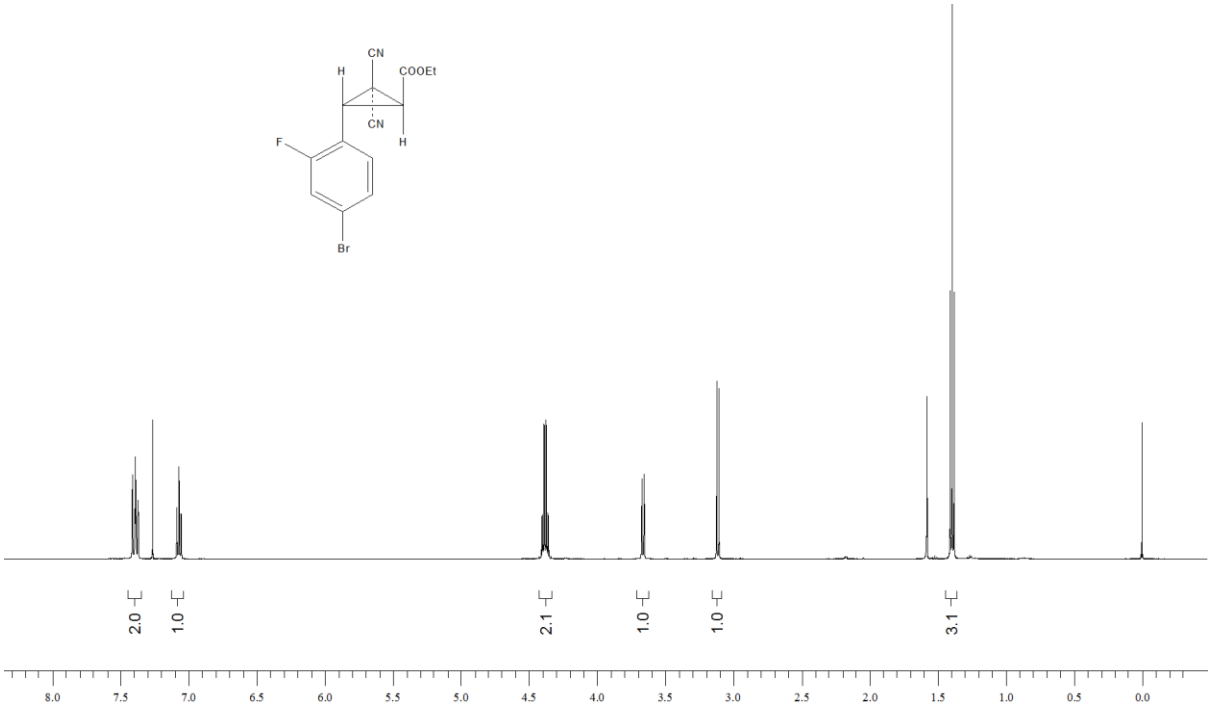
1H NMR of 3d:



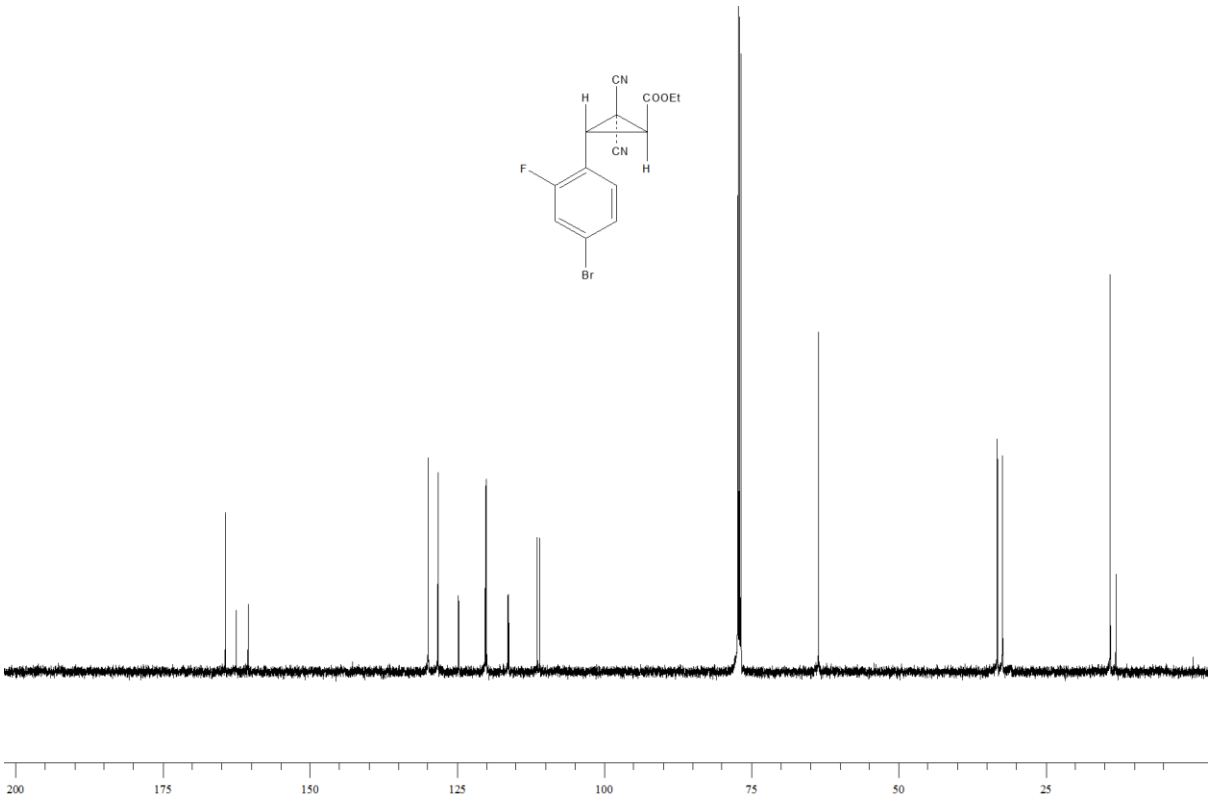
13C NMR of 3d:



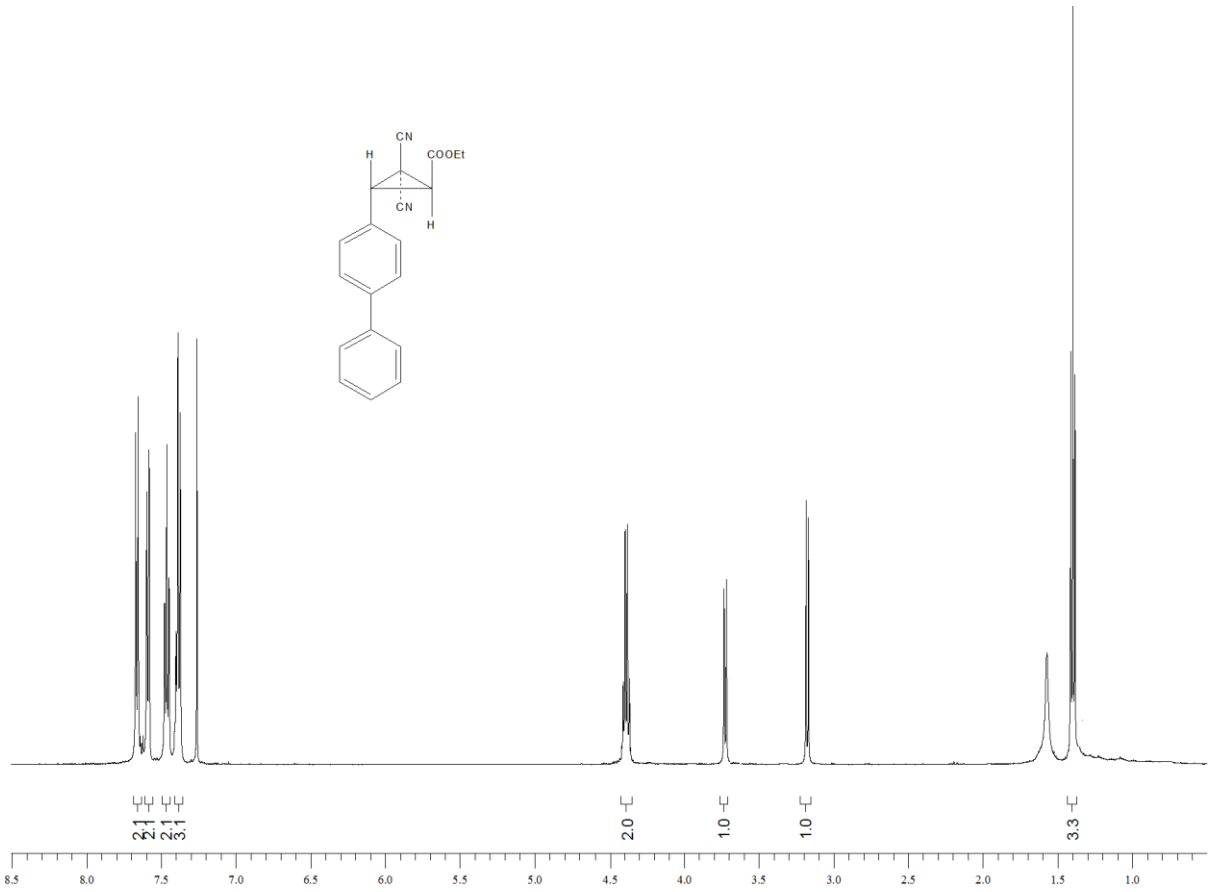
1H NMR of 3e:



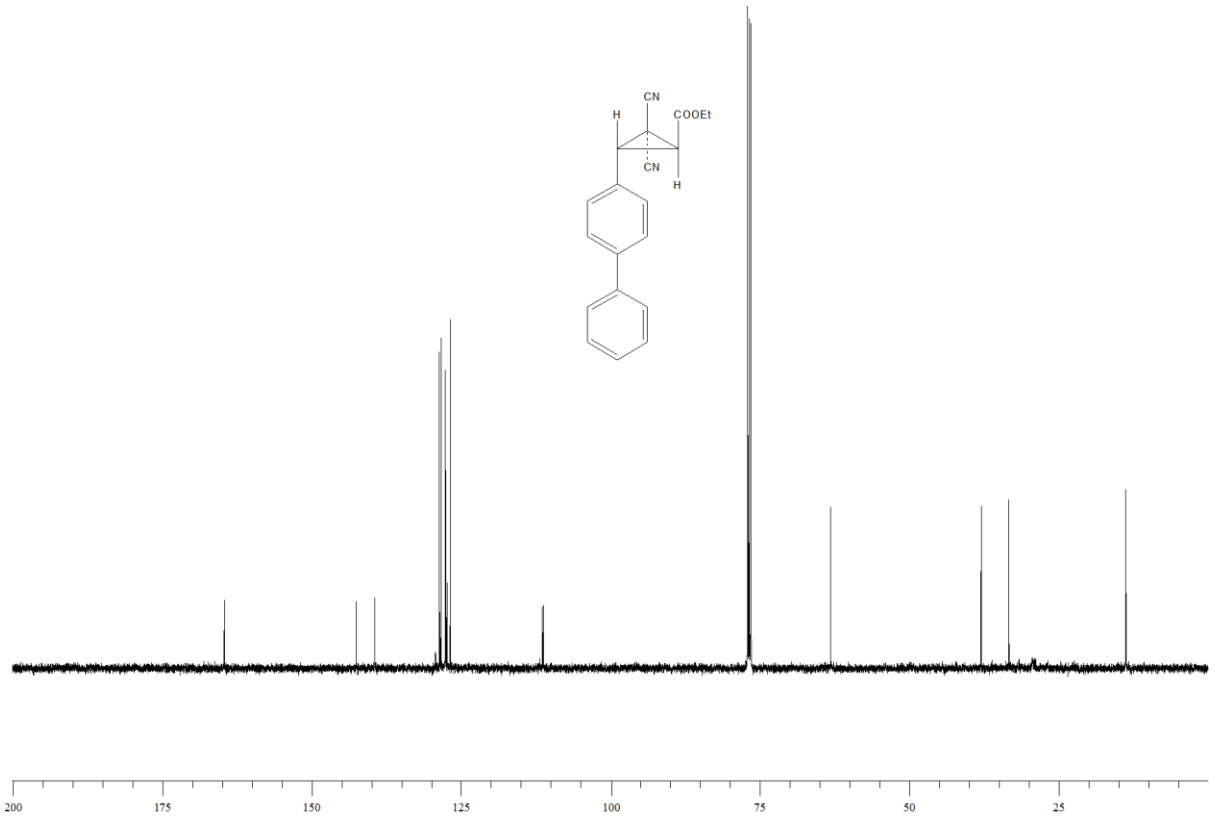
13C NMR of 3e:



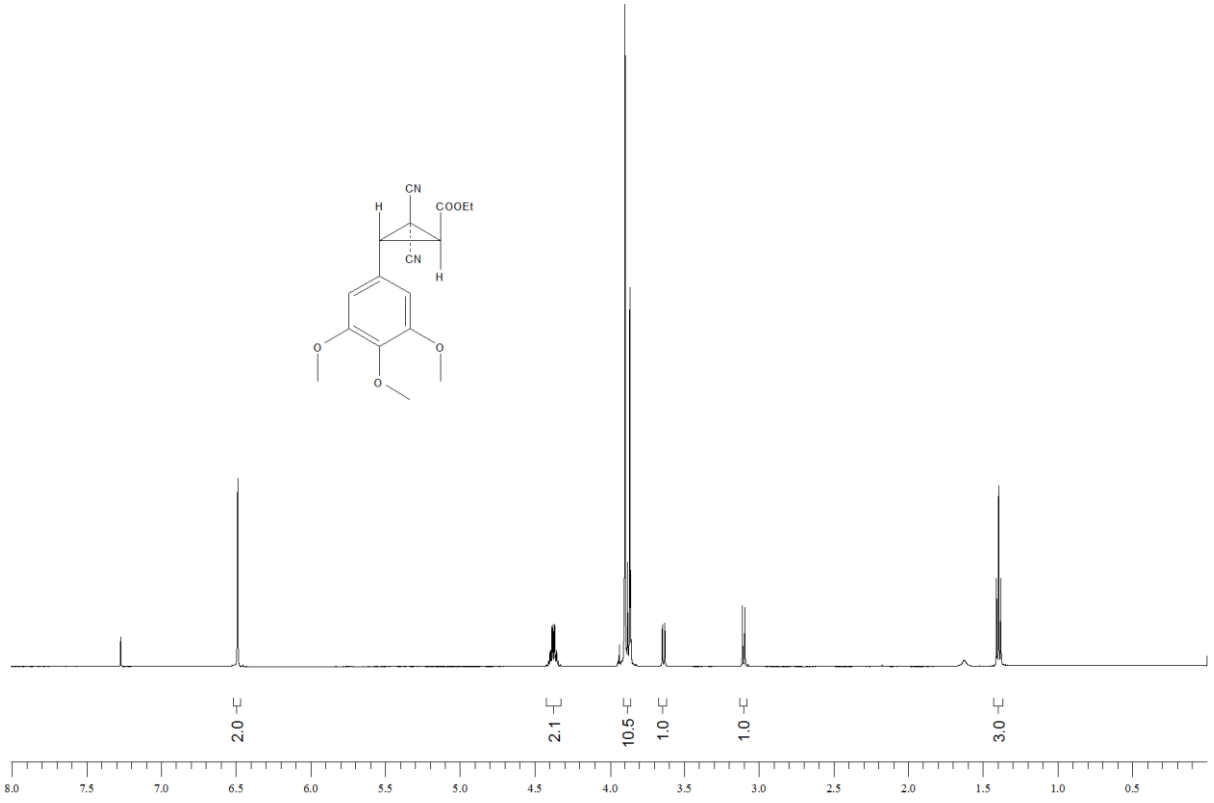
1H NMR of 3f:



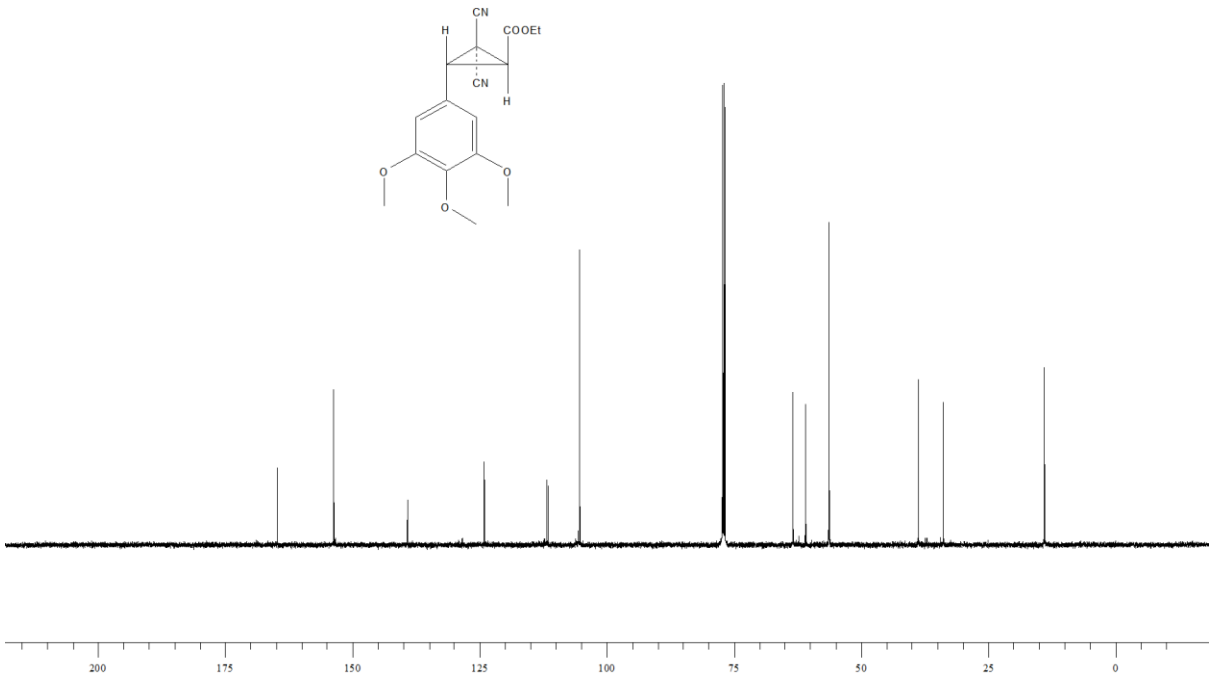
13C NMR of 3f:



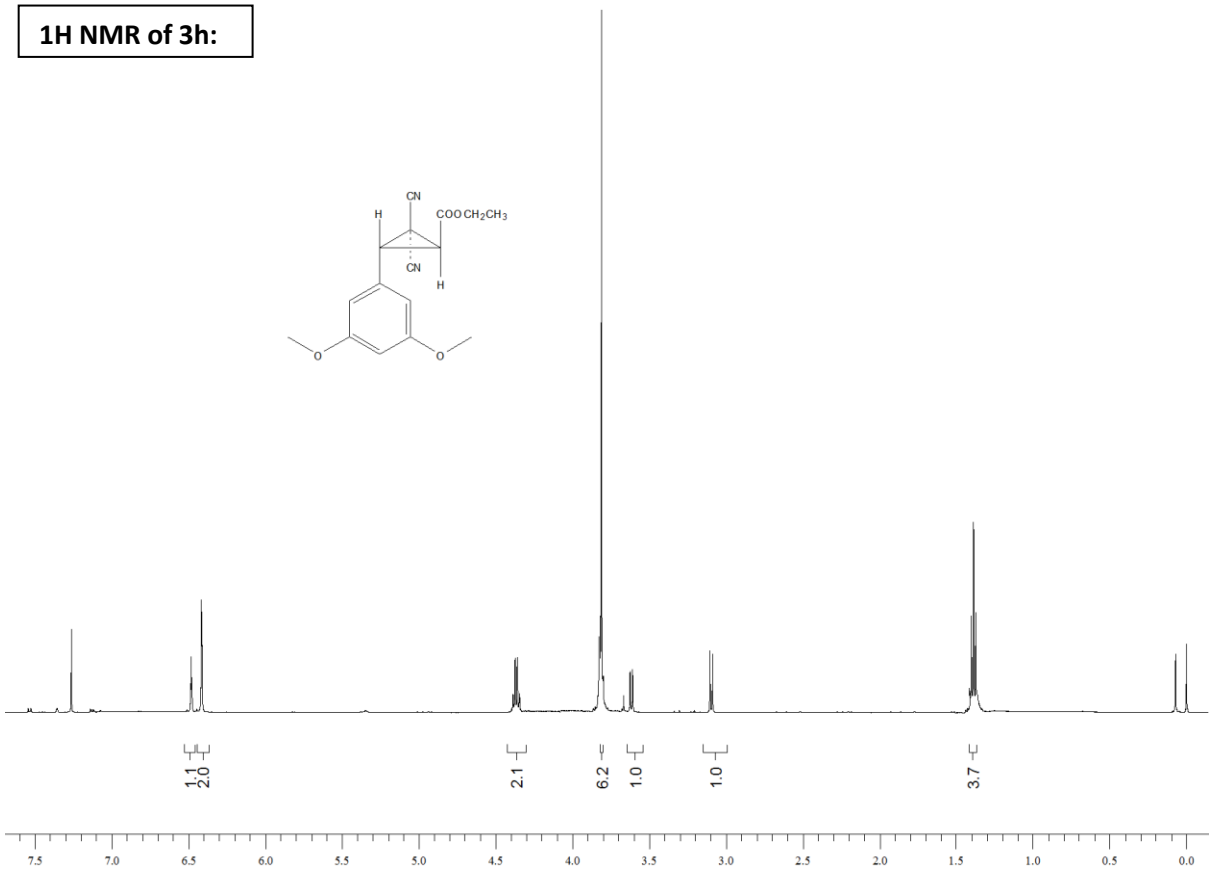
1H NMR of 3g:



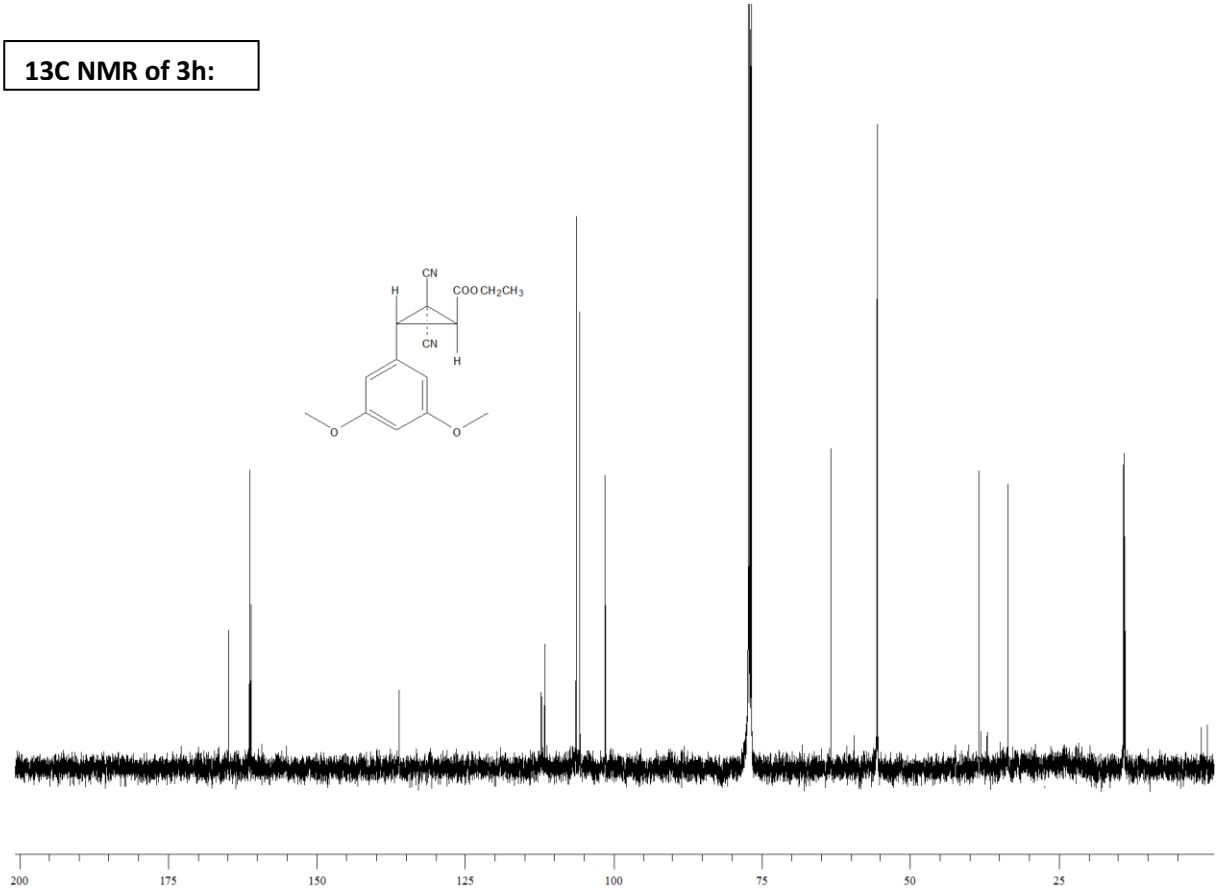
13C NMR of 3g:



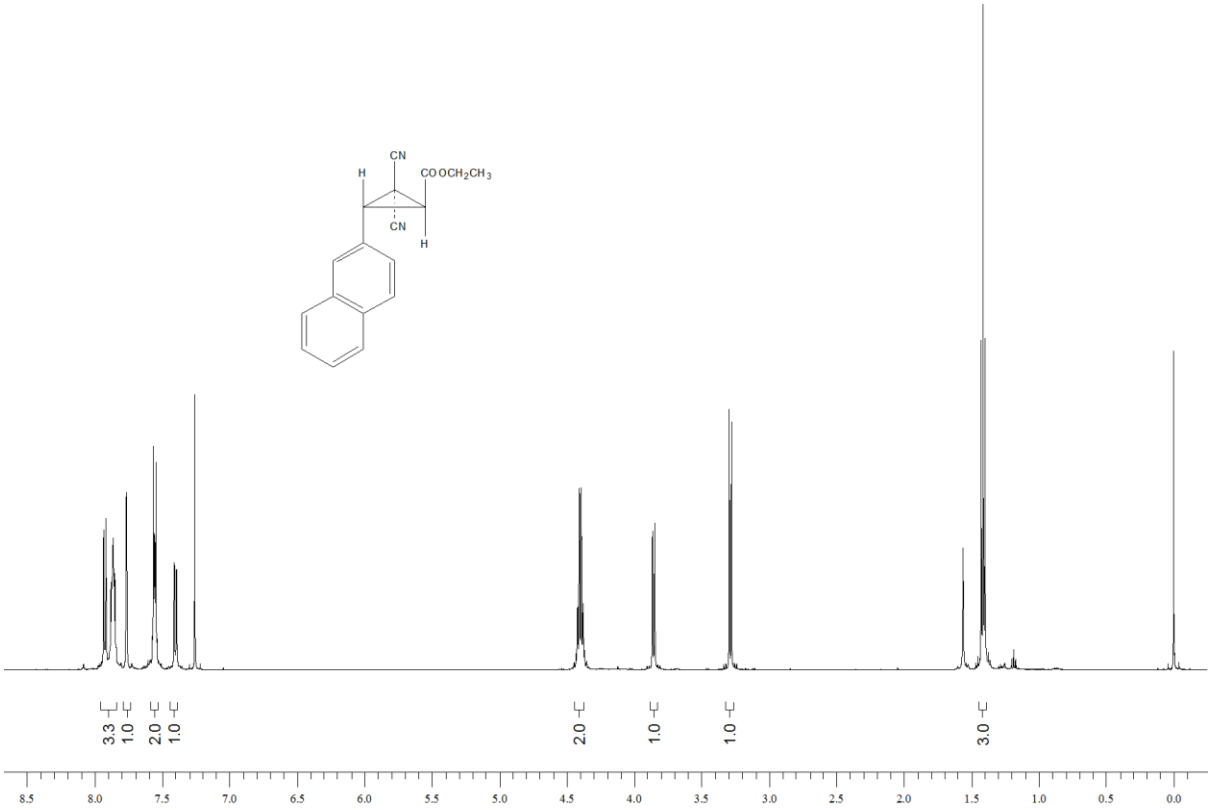
1H NMR of 3h:



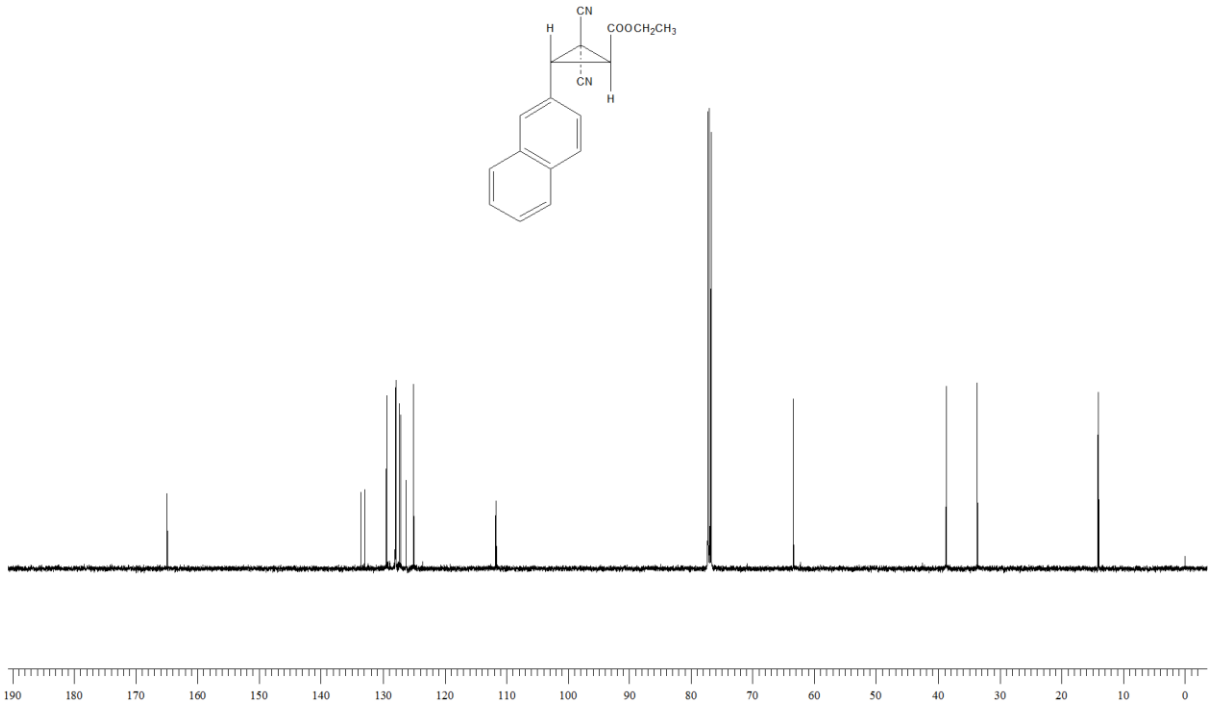
13C NMR of 3h:



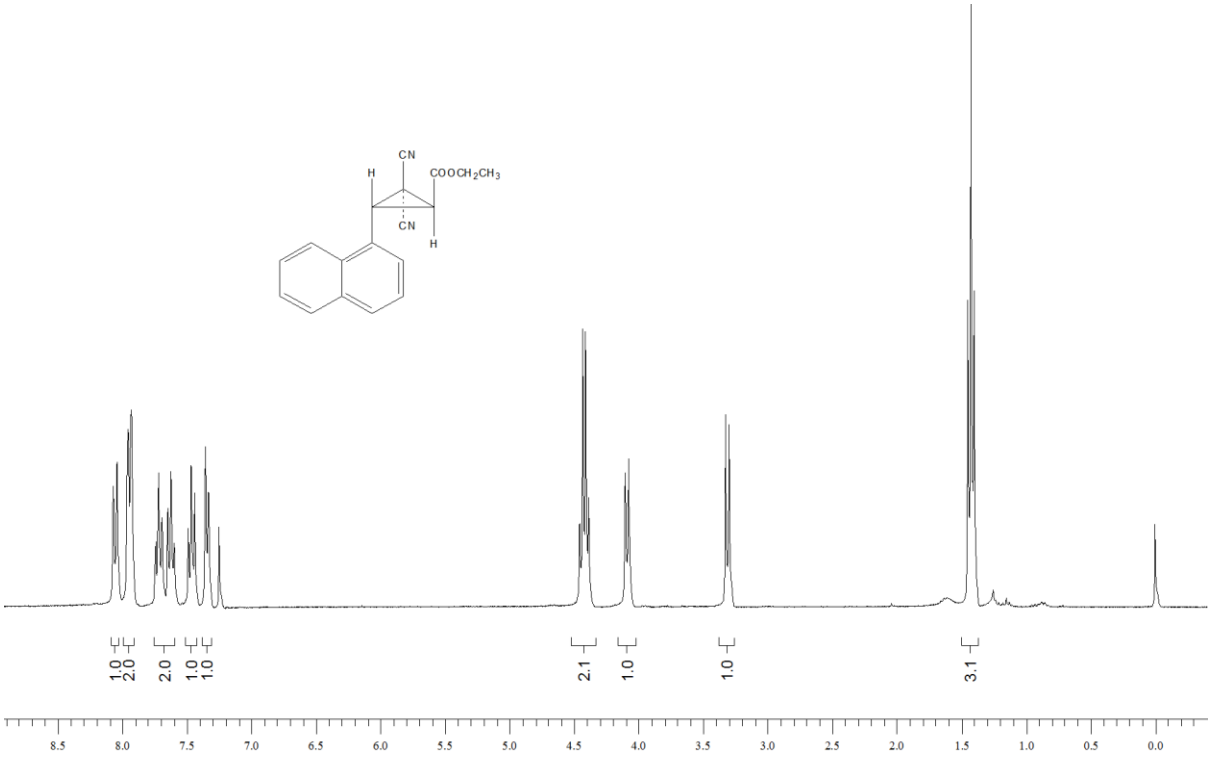
1H NMR of 3i:



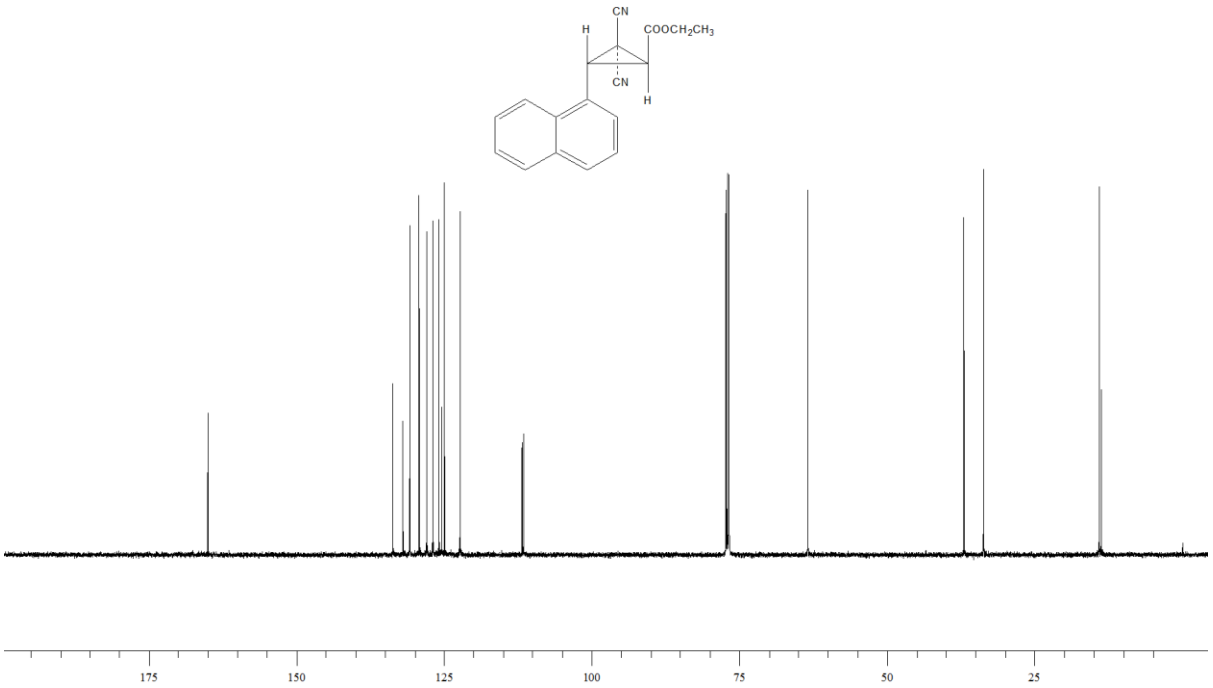
13C NMR of 3i:



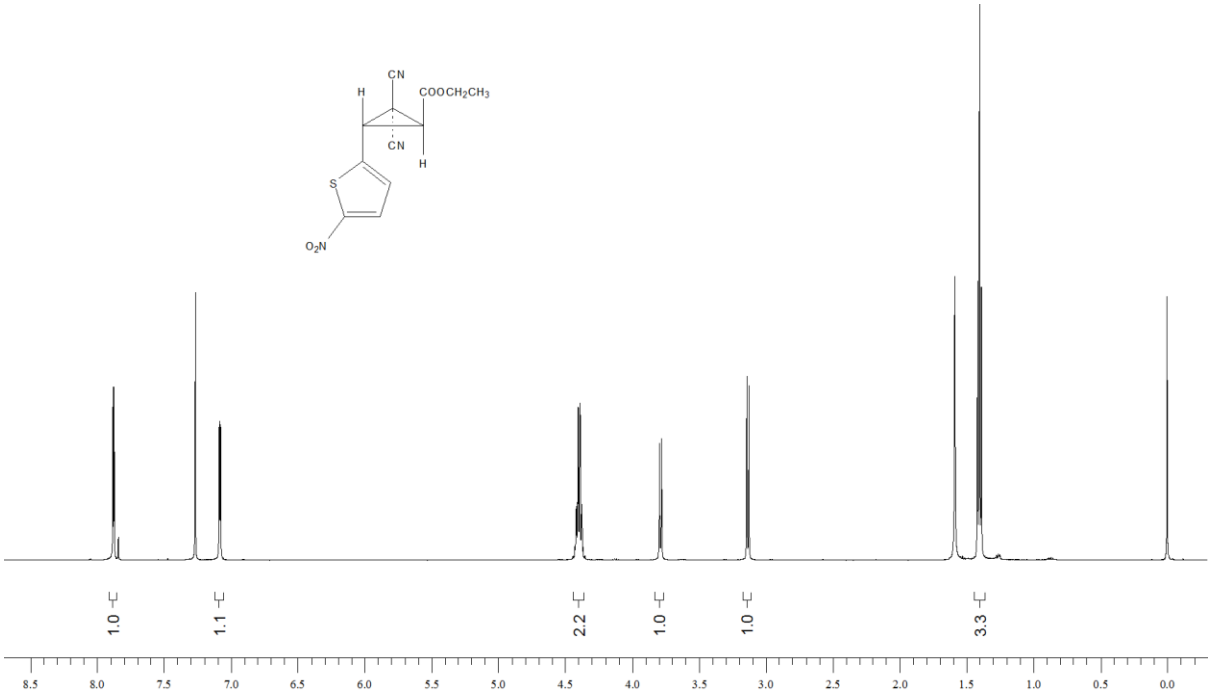
1H NMR of 3j:



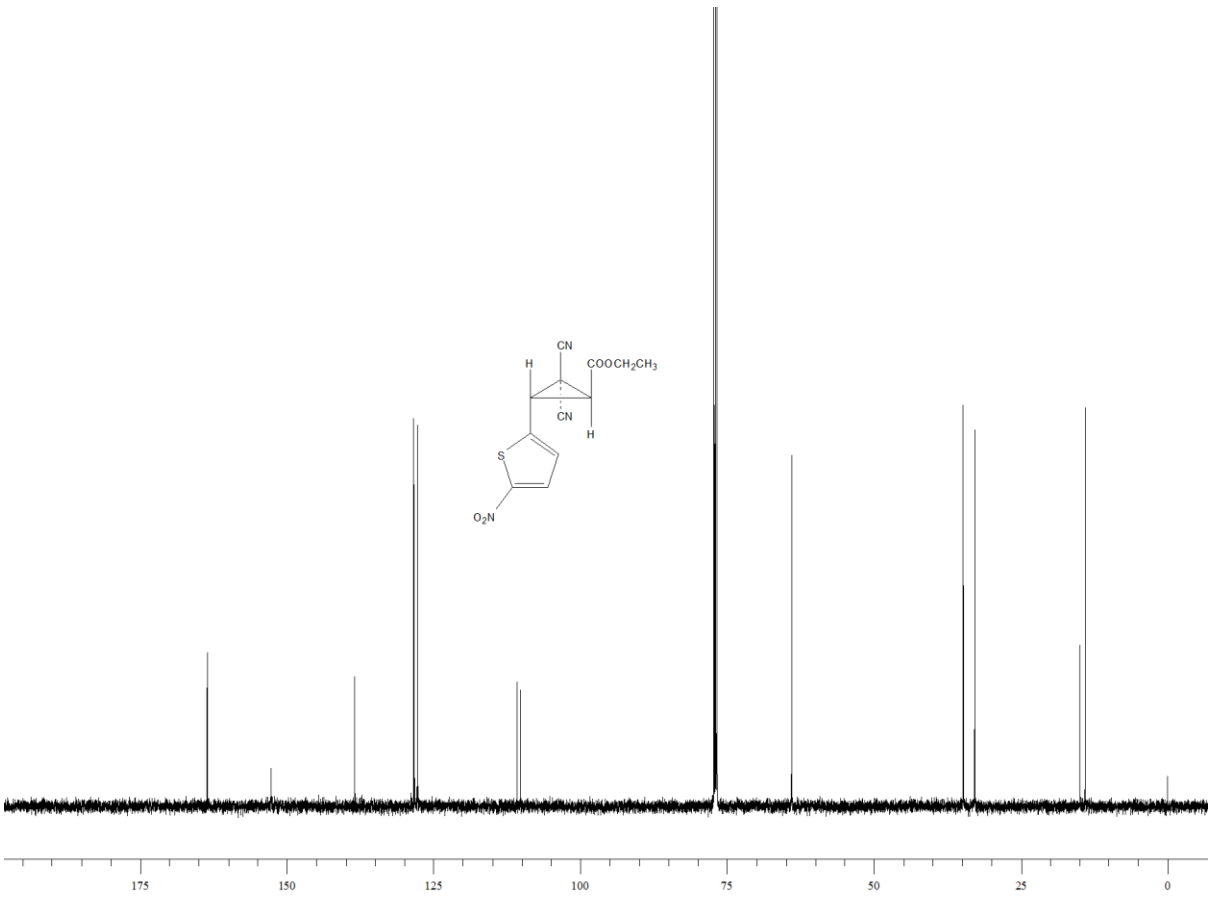
13C NMR of 3j:



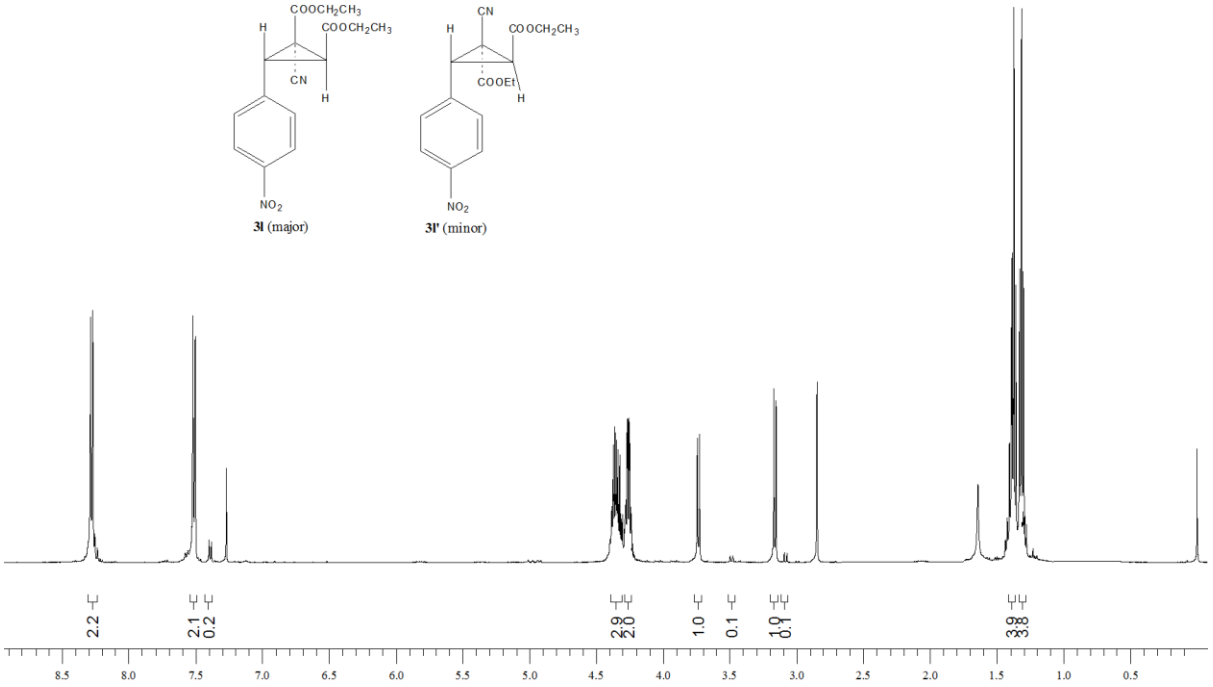
1H NMR of 3k:



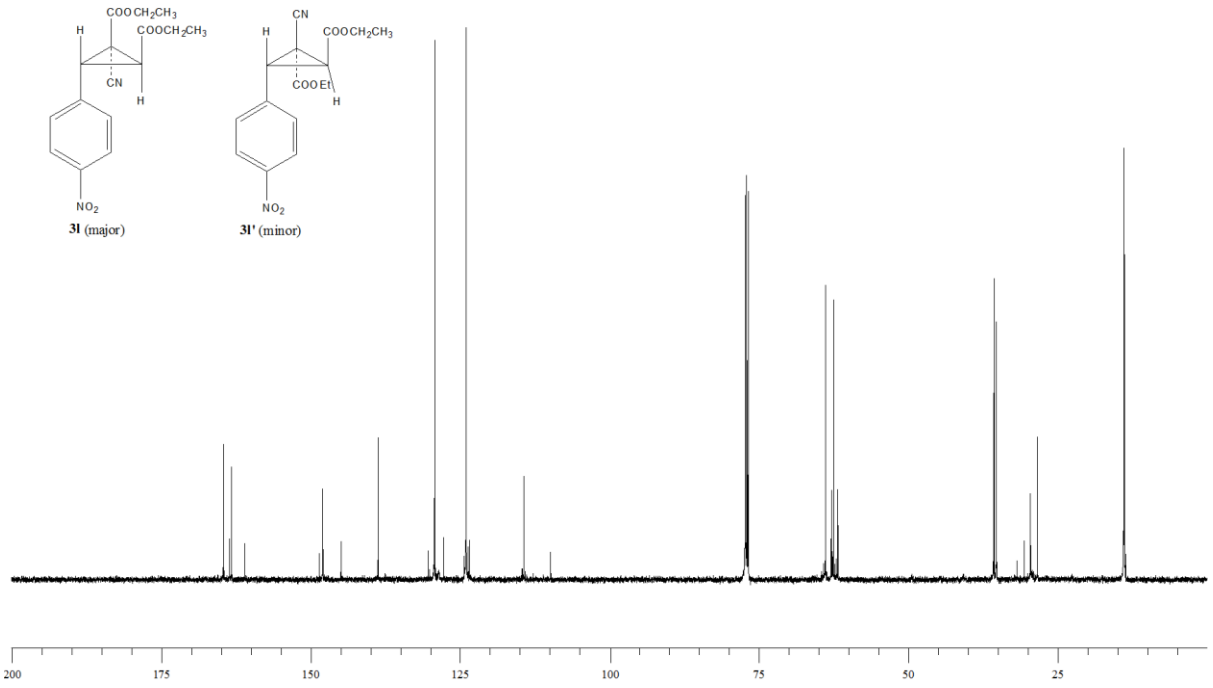
13C NMR of 3k:



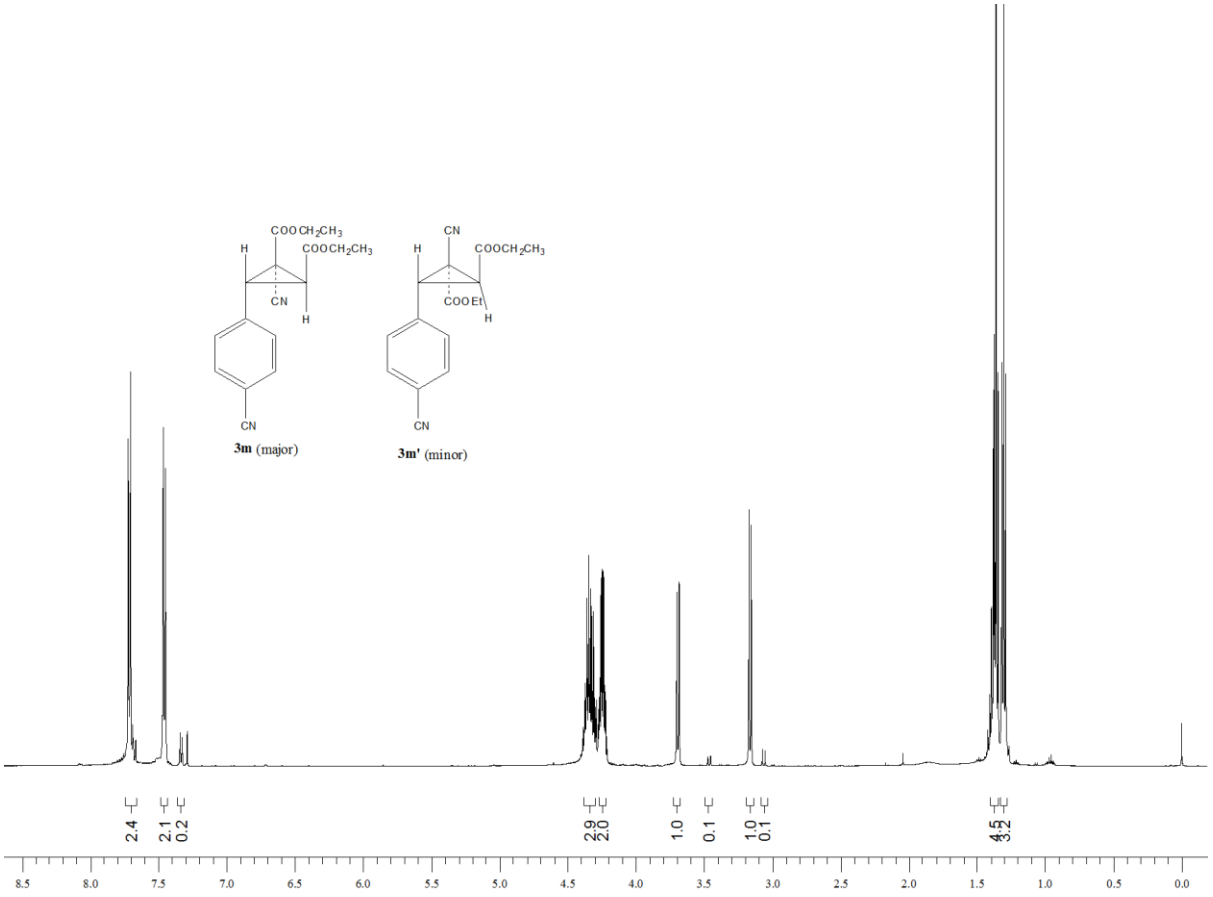
1H NMR for the mixture of 3l & 3l':



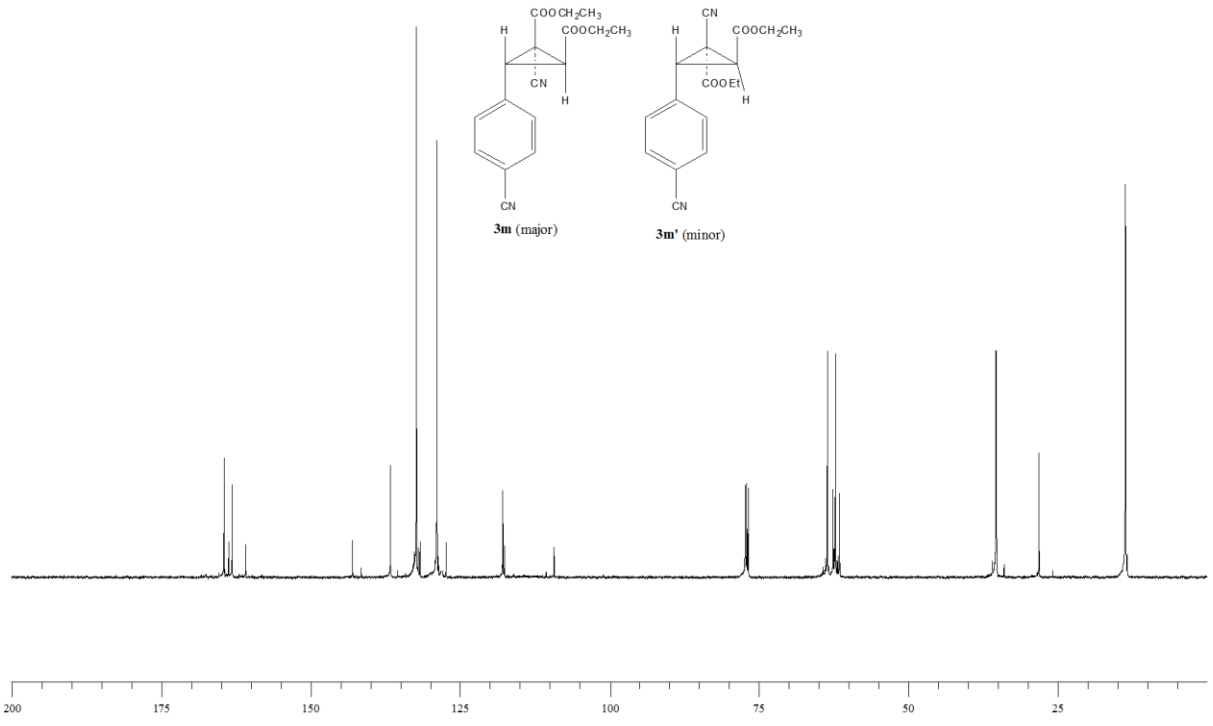
13C NMR of 3l & 3l':



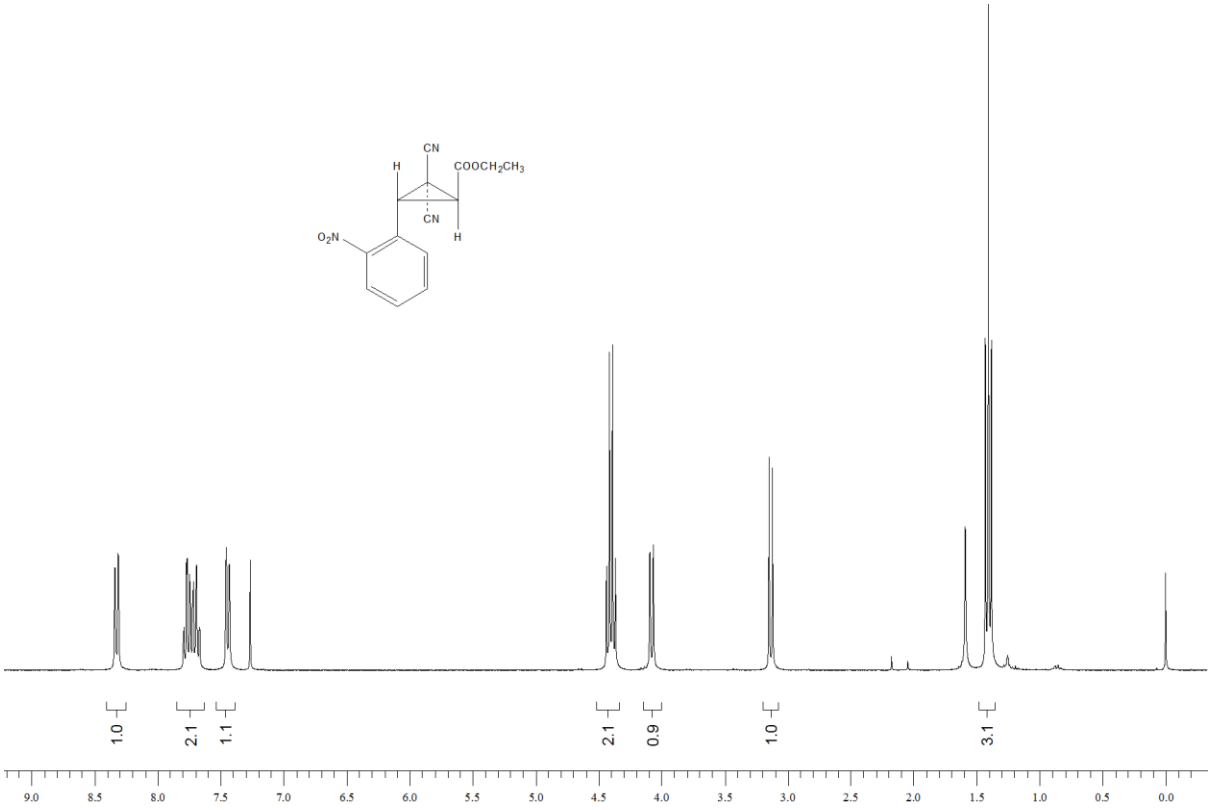
1H NMR for the mixture of 3m & 3m':



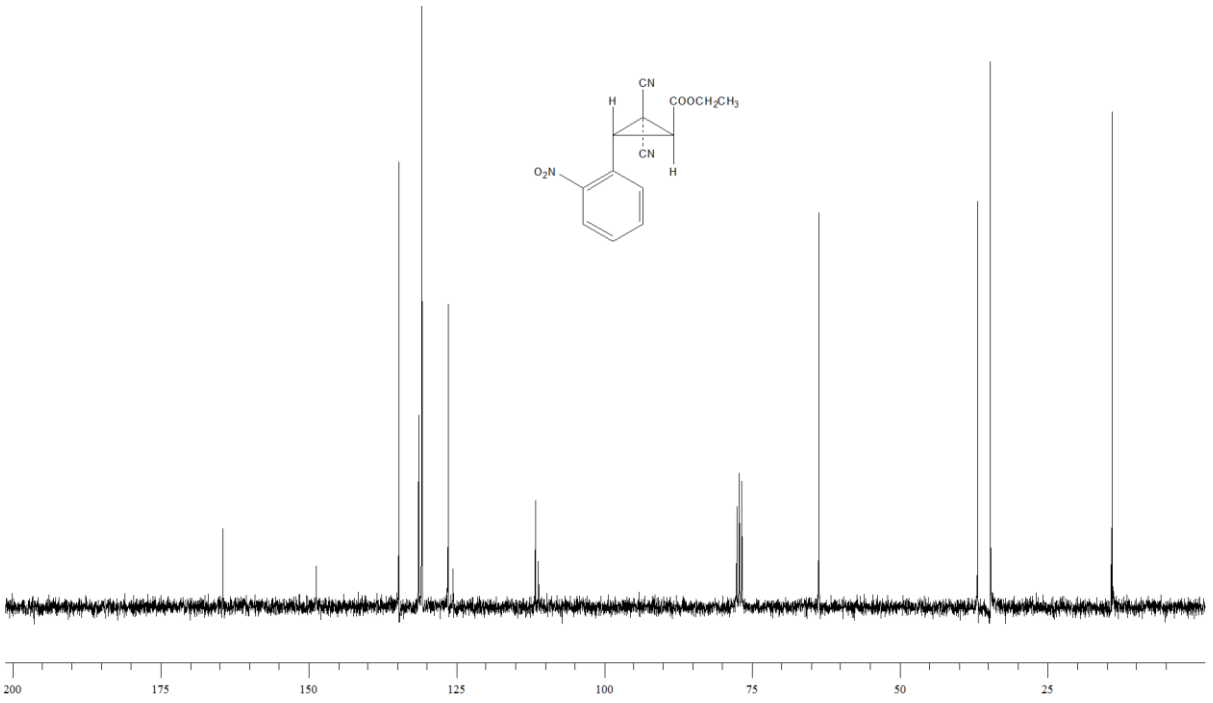
13C NMR for the mixture of 3m & 3m':



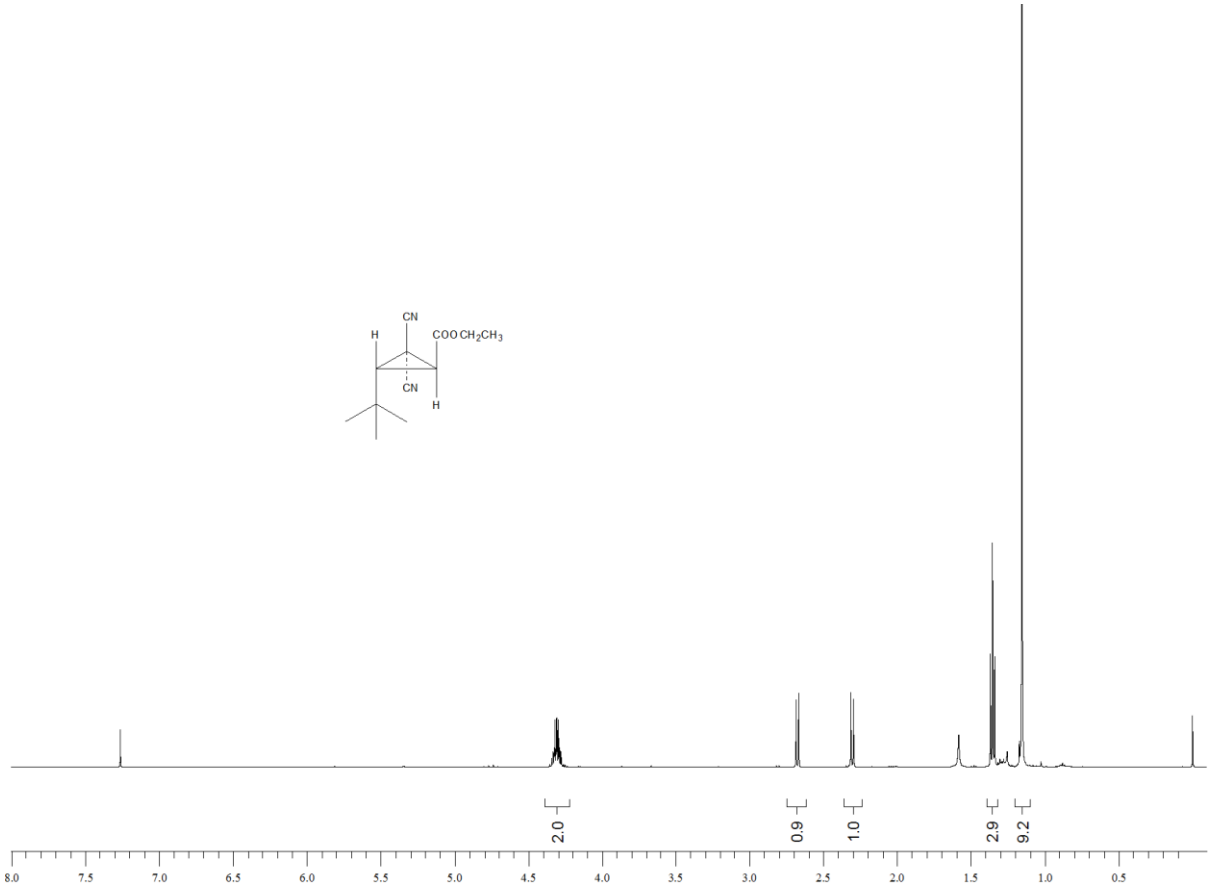
1H NMR of 3n:



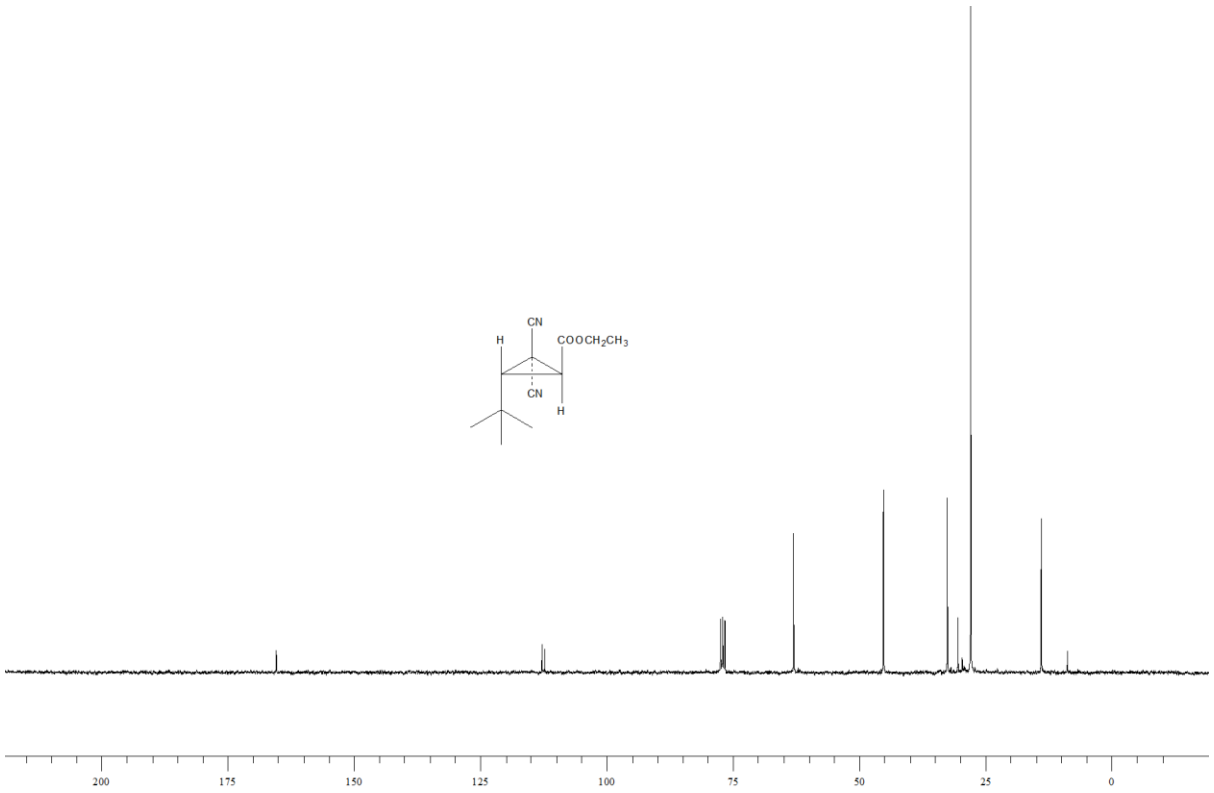
13C NMR of 3n:



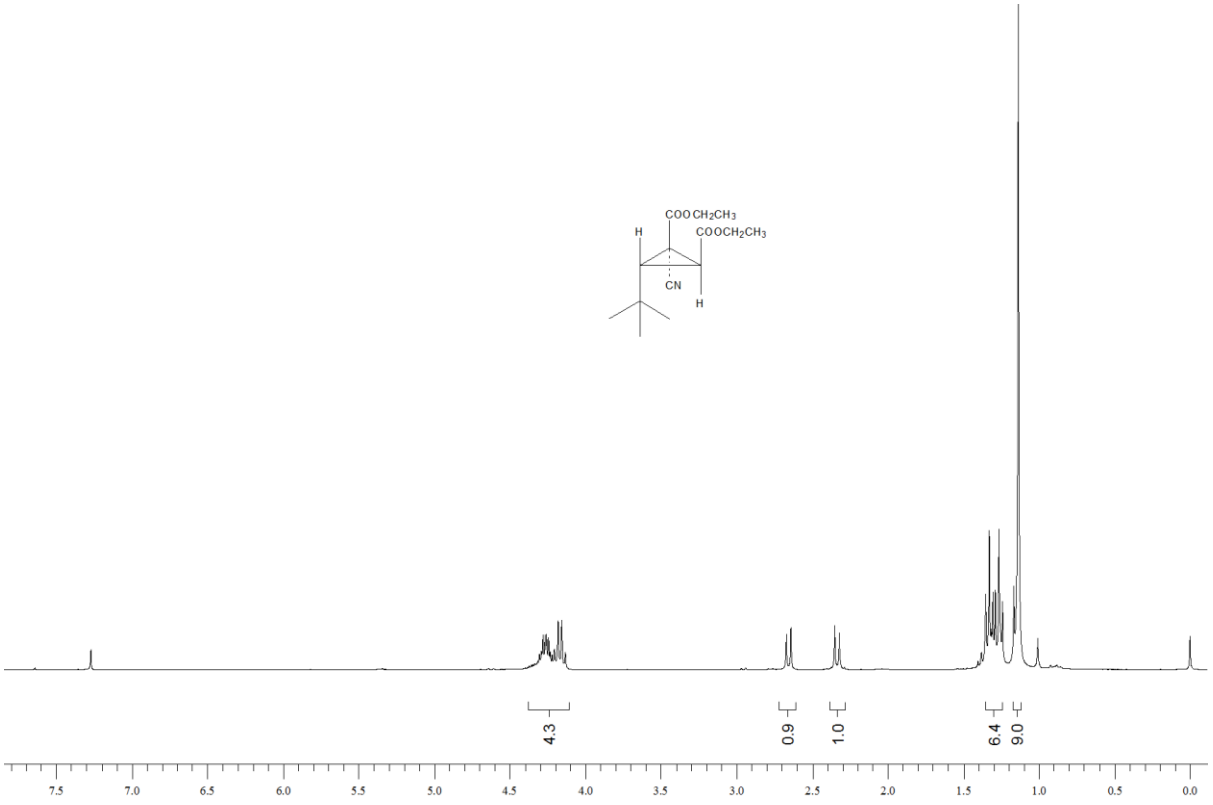
1H NMR of 3o:



13C NMR of 3o:



1H NMR of 3p:



13C NMR of 3p: