Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2011

PPh_3-Catalyzed Synthesis of Dicyano-2-Methylenebut-3-Enoates as Efficient Dienes in Catalytic Asymmetric Inverse-Electron-Demand Diels-Alder Reaction

Xianxing Jiang,[a,b] Dan Fu,[a] Xiaomei Shi,[a] Shoulei Wang,[a] and Rui Wang *[a,b]

[a] *Key Laboratory of Preclinical Study for New Drugs of Gansu Province, State Key Laboratory of Applied Organic Chemistry, Institute of Biochemistry and Molecular Biology, Lanzhou University, Lanzhou, China*

[b] *State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.*

E-mail: wangrui@lzu.edu.cn

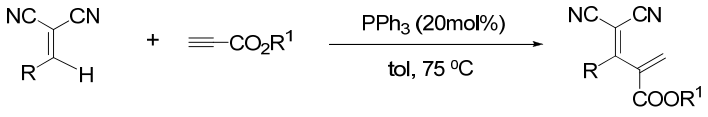
Supporting information

Contents

1.0 General Methods: All reactions were carried out under an argon atmosphere condition unless otherwise noted and solvents were dried according to established procedures. Reactions were monitored by thin layer chromatography (TLC), column chromatography purifications were carried out using silica gel GF254. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on Brucker 300 MHz spectrometer in $CDCl_3$ unless otherwise noted and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on Brucker 300 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as internal standard unless otherwise noted. Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). Infrared (IR) spectra were recorded on a FT-IR spectrometer. Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. HR-MS was measured with an APEX II 47e mass spectrometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. The ee values determination was carried out using chiral high-performance liquid chromatography (HPLC) with Daicel Chiracel chiral columns on Waters with a 2996 UV-detector and the dr values determined by 300 Hz ^{1}H NMR.

Materials: The catalysts were synthesized according to the literature procedures.[1]

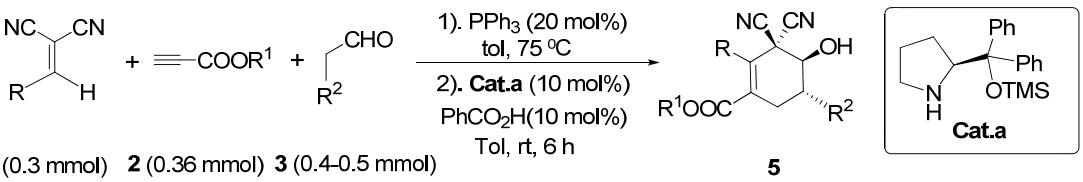
2.0 General procedure for synthesis of dicyano-2-methylenebut-3-enoates



1 (2.0 mmol) **2** (2.4 mmol) **3**

Arylidenemalononitrile (2.0 mmol), PPh_3 (20.0 mol%) were added to toluene (25 mL) in three-necked flask. The mixture was stirred at 75 °C under Argon. To this reaction mixture the solution of alkyl propiolate (2.4 mmol) in toluene (40 mL) was slowly added within 3 hours. Once the addition was finished, the reaction mixture was cooled down to room temperature. Then the mixture was directly subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1) to give the products.

3.0 General procedure for the PPh_3-catalyzed addition/asymmetric IEDDAR sequence



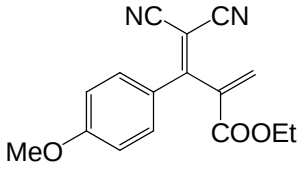
1 (0.3 mmol) **2** (0.36 mmol) **3** (0.4-0.5 mmol) **5**

This journal is © The Royal Society of Chemistry 2011

Arylidenemalononitrile (0.3 mmol), PPh_3 (20.0 mol%) were added to toluene (3 mL) in three-necked flask. The mixture was stirred at 75 °C under Argon. To this reaction mixture the solution of alkyl propiolate (0.36 mmol) in toluene (6 mL) was slowly added within 1.5 hours. The solution was stirred at room temperature for 1 h, and then was subjected to flash column chromatography on silica gel (petroleum ether/ethyl acetate = 15:1), affording the crude products were directly dissolved in a stirred solution of catalyst (10 mol %), and benzoic acid (10 mol %) in dry toluene (1.2 mL). Then alkyl aldehyde (0.4-0.5 mmol) was added. The solution was stirred at room temperature for a specified reaction time. After the reaction was completed (monitored by TLC), the resulting mixture was concentrated under reduced pressure and the residue was purified through column chromatography on silica gel (petroleum ether/ethyl acetate = 7:1) to give the optical pure products. The enantiomeric purity of the major diastereomer was determined by using HPLC.

4.0 Characterization data

Ethyl 4,4-dicyano-3-(4-methoxyphenyl)-2-methylenebut-3-enoate: 3a

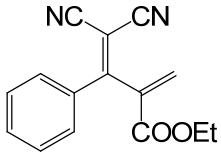


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.63(d, *J* = 9.0 Hz, 2 H), 6.99(d, *J* = 8.7 Hz, 2 H), 6.88(s, 1 H), 6.14(s, 1 H), 4.13-4.20(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 3.88(s, 3 H), 1.16(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.3, 163.6, 163.1, 138.1, 134.5, 131.3, 126.0, 114.6, 113.6, 113.2, 81.9, 62.1, 55.7, 13.9.

IR: ν 2982, 2227, 1725, 1603, 1511, 1462, 1424, 1370, 1308, 1268, 1179, 1025, 838, 812, 665 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{14}N_2O_3$+NH_4^+:300.1343; found: 300.1341, 0.7ppm.

Ethyl 4,4-dicyano-2-methylene-3-phenylbut-3-enoate: 3b

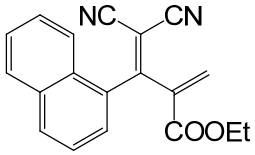


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.47-7.58(m, 5 H), 6.88(s, 1 H), 6.18(s, 1 H), 4.09-4.16(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 1.10(t, *J* =6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.6, 162.9, 137.9, 134.9, 133.9, 132.9, 129.1, 128.8, 112.8,112.7, 85.0, 62.1, 13.8.

IR: ν 2986, 2231, 1733, 1556, 1470, 1371, 1257, 1185, 1022, 911, 863, 810, 776, 701, 589 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{12}N_2O_2+NH_4^+$:270.1237; found: 270.1231, 2.2ppm.

Ethyl 4,4-dicyano-2-methylene-3-(naphthalen-1-yl)but-3-enoate: 3c

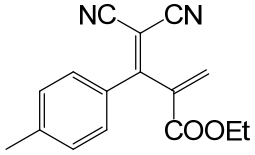


^{1}H NMR (300 MHz, $CDCl_3$): δ 8.02(d, *J* = 8.1 Hz, 1 H),7.90-7.93(m, 1 H),7.79-7.82(m, 1 H), 7.47-7.60(m, 4 H), 6.74(s, 1 H), 6.05(s, 1 H), 4.22-4.29(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.19(t, *J* = 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.3, 163.3, 139.0, 135.4, 133.8, 132.4, 132.3, 129.8, 128.9, 127.8, 127.7, 127.0, 124.8, 112.1, 112.0, 89.1, 62.4, 13.9.

IR: ν 2985, 2231, 1727, 1556, 1509, 1467, 1370, 1343, 1248, 1159, 1091, 1021, 864, 777, 738 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{19}H_{14}N_2O_2+NH_4^+$:320.1394; found: 320.1401, 2.2ppm.

Ethyl 4,4-dicyano-2-methylene-3-p-tolylbut-3-enoate: 3d

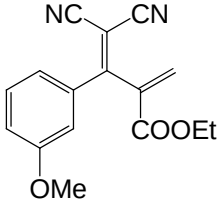


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.50(d, *J* = 8.4 Hz, 2 H), 7.30(d, *J* = 8.1 Hz, 2 H), 6.89(s, 1 H), 6.17(s, 1 H), 4.12-4.19(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 2.42(s, 3 H), 1.14(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.4, 163.1, 144.2, 138.0, 134.7, 130.4, 129.9, 128.9, 113.1, 112.9, 83.9, 62.1, 21.7, 13.8.

IR: ν 2985, 2228, 1729, 1608, 1550, 1448, 1410, 1258, 1184, 1022, 863, 820, 743, 666, 612 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{14}N_2O_2+NH_4^+$:284.1394; found: 284.1401, 2.5ppm.

Ethyl 4,4-dicyano-3-(3-methoxyphenyl)-2-methylenebut-3-enoate: 3e



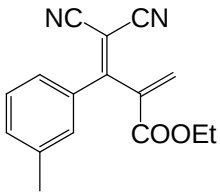
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.36-7.42(m, 1 H), 7.08-7.13(m, 3 H), 6.88(s, 1 H), 6.18(s, 1 H), 4.12-4.19(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 3.84(s, 3 H), 1.14(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.4, 162.9, 159.8, 137.9, 135,0, 134.7, 130.3, 121.2, 118.8, 113.8, 112.8, 112.6, 85.1,

62.1, 55.6, 13.8.

IR: ν 2983, 2230, 1728, 1561, 1428, 1329, 1268, 1235, 1183, 1095, 1020, 865, 791, 704, 562 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{14}N_2O_3+NH_4^+$:300.1343; found: 300.1347, 1.3ppm.

Ethyl 4,4-dicyano-2-methylene-3-m-tolylbut-3-enoate: 3f

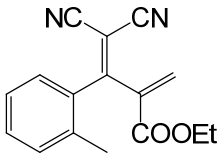


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.37(m, 4 H), 6.88(s, 1 H), 6.17(s, 1 H), 4.12-4.19(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 2.40(s, 3 H), 1.13(t, *J* =7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 170.8, 163.0, 139.1, 138.0, 134.6, 133.9, 133.7, 129.2, 129.0, 126.0, 112.8, 112.7, 84.8, 62.1, 21.3, 13.8.

IR: ν 2985, 2230, 1730, 1559, 1449, 1371, 1262, 1216, 1183, 1098, 1021, 864, 793, 706, 592 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{14}N_2O_2+NH_4^+$:284.1394; found: 284.1388, 2.1ppm.

Ethyl 4,4-dicyano-2-methylene-3-o-tolylbut-3-enoate: 3g

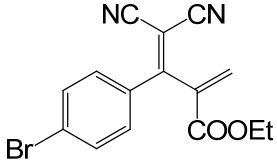


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.18-7.43(m, 4 H), 6.76(s, 1 H), 6.04(s, 1 H), 4.21-4.28(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 2.35(s, 3 H), 1.25(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 171.4, 163.1, 138.5, 136.3, 135.3, 134.3, 131.5, 131.4, 128.6, 126.2, 112.2, 111.9, 88.6, 62.3, 19.8, 13.9.

IR: ν 2985, 2232, 1729, 1560, 1454, 1391, 1252, 1158, 1115, 1022, 863, 767, 676, 593 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{14}N_2O_2+NH_4^+$:284.1394; found: 284.1400, 2.1ppm.

Ethyl 3-(4-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3h

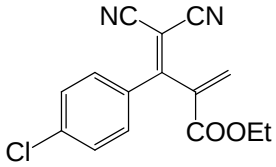


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.65(d, *J* = 8.7 Hz, 2 H), 7.45(d, *J* = 8.7 Hz, 2 H), 6.91 (s, 1 H), 6.22(s, 1 H), 4.12-4.19(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 1.15(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.3, 162.7, 137.5, 135.3, 132.7, 132.5, 130.2, 127.9, 112.5, 112.4, 85.5, 62.3, 13.8.

IR: ν 2924, 2854, 2231, 1729, 1582, 1485, 1401, 1331, 1253, 1184, 1074, 1014, 904, 830, 729 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}BrN_2O_2+NH_4^+$:348.0342; found: 348.0339, 0.9ppm.

Ethyl 3-(4-chlorophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3i

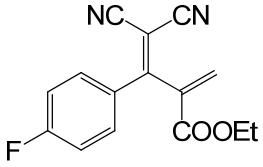


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.45-7.54(dd, *J* = 8.7 Hz, 18.0 Hz, 4 H), 6.90(s, 1 H), 6.22(s, 1 H), 4.12-4.19(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 1.15(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.1, 162.7, 139.3, 137.6, 135.2, 132.3, 130.1, 129.5, 112.6, 112.4, 85.5, 62.2, 13.8.

IR: ν 2985, 2231, 1729, 1590, 1490, 1404, 1254, 1184, 1096, 1018, 910, 834, 736, 650, 585 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}ClN_2O_2+NH_4^+$:304.0847; found: 304.0841, 2.0ppm.

Ethyl 4,4-dicyano-3-(4-fluorophenyl)-2-methylenebut-3-enoate: 3j

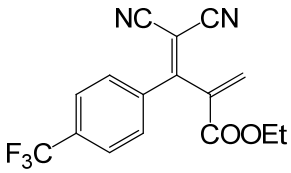


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.58-7.63(m, 2 H), 7.16-7.22(m, 2 H), 6.91(s, 1 H), 6.21(s, 1 H), 4.13-4.20(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.15(t, *J* = 6.9Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.2, 166.9, 163.5, 162.8, 158.4, 137.8, 135.0, 133.5, 133.4, 131.4, 131.3, 130.0, 117.4, 117.1, 116.8, 116.5, 112.7, 112.5, 85.0, 62.2, 13.8.

IR: ν 2986, 2231, 1729, 1599, 15081, 1472, 1410, 1245, 1163, 1106, 1020, 843, 749, 668, 528 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}FN_2O_2+NH_4^+$:288.1143; found: 288.1148, 1.7ppm.

Ethyl 4,4-dicyano-2-methylene-3-(4-(trifluoromethyl)phenyl)but-3-enoate: 3k



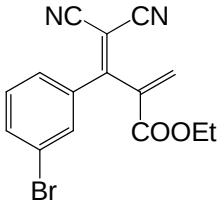
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.78 (d, *J* = 8.1 Hz, 2 H), 7.68 (d, *J* = 8.4 Hz, 2 H), 6.95 (s, 1 H), 6.27 (s, 1 H), 4.13-4.20 (dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.14 (t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 162.5, 137.4, 137.2, 135.4, 129.0, 126.2, 126.1, 112.0, 111.9, 87.3, 62.4,

13.8.

IR: ν 2988, 2234, 1732, 1564, 1449, 1410, 1326, 1257, 1132, 1069, 1019, 845, 698, 645, 599 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{16}H_{11}F_3N_2O_2+NH_4^+$:338.1111; found: 338.1103, 2.4ppm.

Ethyl 3-(3-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3l

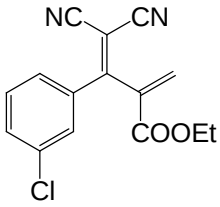


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.35-7.72(m, 4 H), 6.92(s, 1 H), 6.23(s, 1 H), 4.13-4.20(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 1.16(t, *J* =6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.9, 162.6, 137.4, 135.7, 135.6, 135.4, 131.3, 130.7, 127.3, 123.2, 112.2,112.1, 86.5, 62.3, 13.8.

IR: ν 2924, 2853, 2232, 1729 , 1559, 1470, 1407, 1249, 1183, 1075, 1021, 883, 792, 735, 688 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}BrN_2O_2+NH_4^+$:348.0342; found: 348.0336, 2.1ppm.

Ethyl 3-(3-chlorophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3m

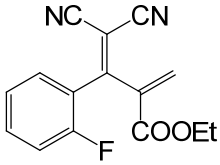


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.42-7.55(m, 4 H), 6.92(s, 1 H), 6.22(s, 1 H), 4.13-4.20(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.15(t, *J* =7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 162.6, 137.4, 135.5, 135.3, 132.6, 130.5, 128.5, 126.9, 112.2, 86.5, 62.3, 13.8.

IR: ν 2926, 2232, 1730, 1560, 1472, 1411, 1250, 1184, 1100, 1021, 883, 794, 752, 692, 593 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}ClN_2O_2+NH_4^+$:304.0847; found: 304.0854, 2.3ppm.

Ethyl 4,4-dicyano-3-(2-fluorophenyl)-2-methylenebut-3-enoate: 3n



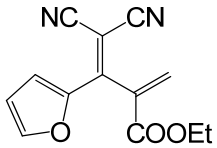
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.51-7.58(m, 1 H), 7.33-7.39(ddd, *J* = 1.8 Hz, 7.5 Hz, 1 H), 7.18-7.29(m, 2 H), 6.86(s, 1 H), 6.22(s, 1 H), 4.15-4.22(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.17(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 165.4, 162.5, 160.9, 157.5, 137.5, 134.9, 134.3,

130.0, 124.7, 122.7, 117.0, 116.7, 111.8, 89.1, 62.2, 13.8.

IR: ν 2924, 2234, 1730, 1612, 1581, 1450, 1371, 1254, 1184, 1108, 1021, 911, 811, 766, 675 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{11}FN_2O_2$+Na^+:293.0697; found: 293.0700, 1.0ppm.

Ethyl 4,4-dicyano-3-(furan-2-yl)-2-methylenebut-3-enoate: 3o

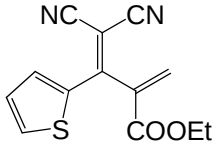


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.79 (d, *J* = 1.5 Hz, 1 H), 7.25 (d, *J* = 3.6 Hz, 1 H), 6.89(s, 1 H), 6.69-6.70(q, *J* = 1.5 Hz, 1 H), 6.12(s, 1 H), 4.24-4.31(dd, *J* = 7.2 Hz,14.1 Hz, 2 H), 1.27(t, *J* = 7.2Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.8, 153.0, 149.1, 148.7, 134.9, 134.3, 122.6, 114.3, 113.1, 113.0, 78.2, 62.3, 14.0.

IR: ν 3134, 2985, 2227, 1726, 1570, 1457, 1395, 1266, 1182, 1091, 1032, 852, 769, 668, 586 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{13}H_{10}N_2O_3$+NH_4^+:260.1030; found:260.1034, 1.5ppm.

Ethyl 4,4-dicyano-2-methylene-3-(thiophen-2-yl)but-3-enoate: 3p

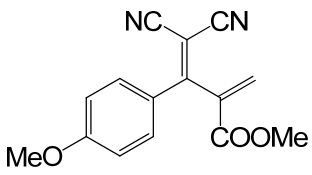


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.85-7.91(m, 2 H), 7.26-7.29(m, 1 H), 6.90(s, 1 H), 6.13(s, 1 H), 4.23-4.30(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 1.25(t, *J* = 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 162.8, 151.5, 138.7, 137.4, 136.4, 135.7, 134.1, 129.5, 113.6, 113.1, 79.3, 62.3, 14.0.

IR: ν 3108, 2985, 2225, 1725, 1537, 1410, 1322, 1257, 1156, 1064, 1021, 861, 730, 611, 570 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{13}H_{10}N_2O_2S$+NH_4^+:276.0801; found: 276.0802, 0.4ppm.

Methyl 4,4-dicyano-3-(4-methoxyphenyl)-2-methylenebut-3-enoate: 3q



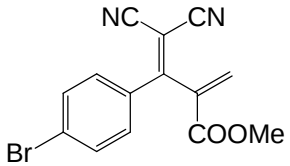
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.64(d, *J* = 9.0 Hz, 2 H), 6.99(d, *J* = 9.0 Hz, 2 H), 6.89(s, 1 H),

6.13 (s, 1 H), 3.88(s, 3 H), 3.74(s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 163.7, 137.8, 134.8, 131.4, 125.9, 115.1, 114.7, 113.5, 113.2, 82.1, 55.7, 53.0.

IR: ν 2955, 2219, 1730, 1604, 1512, 1436, 1258, 1180, 1122, 1028, 837, 784, 740, 664 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{15}H_{12}N_2O_3$+Na^+:291.0740; found: 291.0737, 1.0ppm.

Methyl 3-(4-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3r

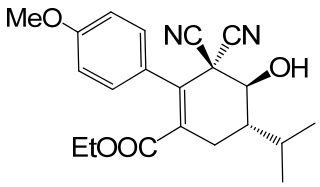


^{1}H NMR (300 MHz, $CDCl_3$): δ 7.66(d, *J* = 8.7Hz, 2 H), 7.46(d, *J* = 8.4Hz, 2 H), 6.92(s, 1 H), 6.21(s, 1 H), 3.73(s, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 169.0, 163.2, 137.2, 135.5, 133.1, 132.6, 131.8, 130.2, 112.5, 112.3, 85.7, 53.1.

IR: ν 2923, 2229, 1729, 1580, 1437, 1401, 1338, 1253, 1158, 1073, 1007, 900, 827, 726, 611 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{14}H_9BrN_2O_2$+NH_4^+:334.0186; found: 334.0177, 2.7ppm..

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarboxy late: 5a



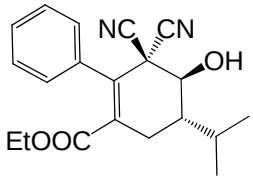
Colorless solid, $[\alpha]^{20}_D$= -9 (*c*=1.0, $CHCl_3$); mp 123 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.26-7.29(dd, *J* = 2.1 Hz, 6.6 Hz, 2 H), 6.91-6.93(dd, *J* = 1.8 Hz, 6.6 Hz, 2 H), 4.11-4.17(dd, *J* = 6.3 Hz, 11.4 Hz, 1 H), 3.88-3.95(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 3.83(s, 3 H), 3.25(d, *J* = 6.9 Hz, 1 H), 2.52-2.61(dd, *J* = 6.0 Hz, 5.7 Hz, 1 H), 2.34-2.44(m, 2 H), 2.09-2.20(m, 1 H), 1.03(d, *J* = 6.9 Hz, 3 H), 0.87-0.94(m, 6.o H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.5, 160.3, 136.4, 130.1, 129.9, 127.4, 114.2, 114.0, 113.0, 73.7, 61.4, 55.3, 48.5, 40.4, 26.3, 25.7, 20.0, 15.2, 13.6.

IR: ν 3462, 2963, 2253, 1716, 1663, 1608, 1512, 1465, 1371, 1290, 1252, 1179, 1107, 1027, 913, 833, 734 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}N_2O_4$+H^+: 369.1809; found: 369.1820, 3.0ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 217 nm.) Retention time: t_{major} =11.043 min, t_{minor} =20.611 min, ee = 97%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-phenylcyclohex-1-enecarboxylate: 5b



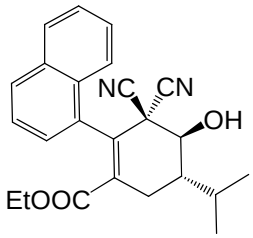
Colorless crystal, $[\alpha]^{20}_D$= -24 (*c*=1.0, $CHCl_3$); mp 156 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.33-7.41(m, 5 H), 4.14-4.20(dd, *J* = 6.9 Hz, 11.4 Hz, 1 H), 3.85-3.92(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 2.99(d, *J* = 4.8 Hz, 1 H), 2.56-2.64(dd, *J* = 6.0 Hz, 5.7 Hz, 1 H), 2.36-2.47(m, 2 H), 2.12-2.23(m, 1 H), 1.05(d, *J* = 6.9 Hz, 3 H), 0.96(d, *J* = 6.9 Hz, 3 H), 0.81(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.2, 136.4, 135.2, 130.4, 129.4, 128.7, 128.6, 114.0, 112.8, 73.8, 61.4, 48.3, 40.4, 26.3, 25.7, 20.0, 15.3, 13.4.

IR: ν 3463, 2966, 2254, 1714, 1662, 1467, 1371, 1281, 1259, 1106, 1020, 765, 705 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}N_2O_3$+NH_4^+:356.1969; found: 356.1979, 2.8ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 213 nm.) Retention time: t_{major} =7.337 min, t_{minor} =10.553 min, ee = 97%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(naphthalen-1-yl)cyclohex-1-enecarboxy late: 5c



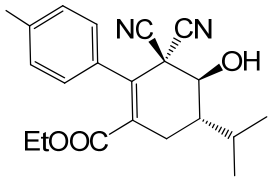
White solid, $[\alpha]^{20}_D$= -13 (*c*=1.0, $CHCl_3$); mp 131 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.01(d, *J* = 8.1 Hz, 1 H), 7.84-7.89(dd, *J* = 5.1 Hz, 12.6 Hz, 2 H), 7.43-7.55(m, 4 H), 4.23-4.29(dd, *J* = 6.6 Hz, 10.8 Hz, 1 H), 3.59-3.63(dd, *J* = 2.4 Hz, 7.2 Hz, 2 H), 3.24(d, *J* = 6.9 Hz, 1 H), 2.80-2.88(dd, *J* = 5.7 Hz, 5.4 Hz, 1 H), 2.31-2.53(m, 3 H), 1.09(d, *J* = 7.2 Hz, 3 H), 0.96(d, *J* = 6.6 Hz, 3 H), 0.33(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.7, 138.6, 133.5, 132.2, 131.4, 129.8, 128.4, 128.3, 126.7, 126.4, 125.4, 124.7, 114.1, 112.7, 74.4, 61.2, 48.8, 40.5, 26.4, 25.9, 20.1, 15.4, 12.8.

IR: ν 3463, 3059, 2964, 2255, 1712, 1655, 1508, 1467, 1371, 1261, 1138, 1094, 1019, 912, 778, 734 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{24}H_{24}N_2O_3$+NH_4^+:406.2125; found: 406.2130, 1.2ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel AS-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 221 nm.) Retention time: t_{major} =20.644 min, ee > 99%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-p-tolylcyclohex-1-enecarboxylate: 5d



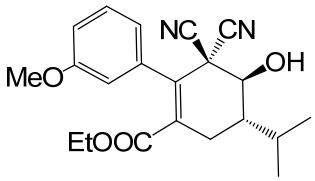
Colorless crystal, $[\alpha]^{20}_D$= -12 (*c*=1.0, $CHCl_3$); mp 154 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.18-7.25(m, 4 H), 4.12-4.17(dd, *J* = 3.6 Hz, 11.1 Hz, 1 H), 3.87-3.94(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 3.21(d, *J* = 5.4 Hz, 1 H), 2.53-2.61(dd, *J* = 6.0 Hz, 5.7 Hz, 1 H), 2.35-2.45(m, 5 H), 2.10-2.21(m, 1 H), 1.03(d, *J* = 6.9 Hz, 3 H), 0.94(d, *J* = 6.9 Hz, 3 H), 0.86(t, *J* = 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.4, 139.3, 136.2, 132.2, 130.4, 129.3, 128.5, 114.1, 112.9, 73.7, 61.4, 48.4, 40.4, 26.3, 25.7, 21.3, 20.0, 15.2, 13.4.

IR: ν 3430, 2968, 2249, 1718, 1666, 1510, 1464, 1394, 1370, 1279, 1255, 1108, 1055, 1017, 911, 821, 727 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}N_2O_3$+NH_4^+: 370.2125; found: 370.2128, 0.8ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 220 nm.) Retention time: t_{major} =7.002 min, ee > 99%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(3-methoxyphenyl)cyclohex-1-enecarbox ylate: 5e



Colorless solid, $[\alpha]^{20}_D$= -9 (*c*=1.0, $CHCl_3$); mp 112 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.27-7.34(dd, *J* = 8.1 Hz, 15.9 Hz, 1 H), 6.89-6.97(m, 3 H), 4.12-4.17(dd, *J* = 5.4 Hz, 11.1 Hz, 1 H), 3.88-3.95(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 3.81(s, 3 H), 3.27-3.29(d, *J* = 6.6 Hz, 1 H), 2.54-2.62(dd, *J* = 6.0 Hz, 6.0 Hz, 1 H), 2.35-2.46(m, 2 H), 2.11-2.21(m, 1 H), 1.03(d, *J* = 6.9 Hz, 3 H), 0.84-0.94(m, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.3, 159.5, 136.4, 130.1, 129.8, 121.0, 115.3, 114.1, 113.9, 113.0, 73.7, 61.5, 55.3, 48.1, 40.4, 26.3, 25.7, 20.0, 15.2, 13.4.

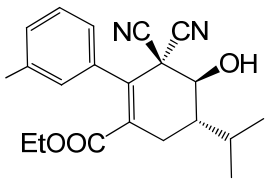
IR: ν 3463, 2963, 2254, 1716, 1657, 1581, 1466, 1427, 1371, 1287, 1261, 1209, 1104, 1031, 913,

797, 735 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}N_2O_4+NH_4^+$: 386.2074; found: 386.2072, 0.5ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 208 nm.) Retention time: t_{major} =11.019 min, ee > 99%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-m-tolylcyclohex-1-enecarboxylate: 5f



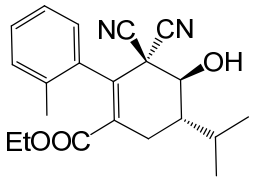
Colorless crystal, $[\alpha]^{20}_D$= -16 (*c*=1.0, $CHCl_3$); mp 128 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.28-7.32(m, 1 H), 7.12-7.26(m, 3 H), 4.60-4.62(d, *J* = 5.4 Hz, 0.6 H), 4.12-4.18(dd, *J* = 6.6 Hz, 11.1 Hz, 0.4 H), 3.86-3.94(dd, *J* = 7.2 Hz, 12.9 Hz, 2 H), 2.93-2.97(t, *J* = 6.6 Hz, 1 H), 2.37-2.70(m, 5.5 H), 2.15-2.22(m, 0.5 H), 1.78-1.84(m, 1 H), 1.02-1.08(m, 5 H), 0.93-0.96(d, *J* = 6.9 Hz, 1 H), 0.81-0.86(dt, *J* = 1.5 Hz, 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.5, 138.2, 136.2, 135.8, 135.2, 129.9, 129.2, 128.4, 125.7, 113.5, 113.2, 73.8, 70.6, 61.2, 48.2, 40.5, 29.1, 26.6, 25.7, 21.4, 20.3, 20.0, 15.3, 13.4.

IR: ν 3463, 2963, 2252, 1716, 1656, 1604, 1466, 1371, 1257, 1186, 1102, 1019, 714 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}N_2O_3+NH_4^+$: 370.2125; found: 370.2122, 0.8ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 215 nm.) Retention time: t_{major} =8.545 min, t_{minor} =9.853 min, ee = 96%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-o-tolylcyclohex-1-enecarboxylate: 5g



White solid, $[\alpha]^{20}_D$= -17 (*c*=1.0, $CHCl_3$); mp 134 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.21-2.28(m, 4 H), 4.61(d, *J* = 4.8 Hz, 1 H), 3.84-3.91(m, 2 H), 3.35-3.39(m, 1 H), 2.19-2.82 (cm, 6 H), 1.80-1.82(m, 1 H), 1.03-1.05(m, 5 H), 0.91-0.94(m, 1 H), 0.76-0.84(m, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.0, 137.2, 136.4, 135.2, 130.3, 129.2, 129.0, 128.5, 127.5, 125.8, 113.4, 113.3, 73.5, 70.3, 61.2, 46.5, 40.4, 29.2, 26.6, 20.3, 19.5, 15.3, 13.3.

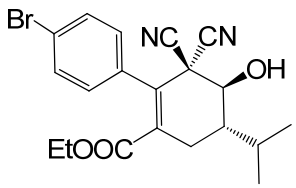
IR: ν 3467, 2965, 2230, 1714, 1655, 1583, 1463, 1371, 1280, 1258, 1231, 1108, 1034, 758, 730

cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{24}N_2O_3+NH_4^+$: 370.2125; found: 370.2119, 1.6ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel AD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 215 nm.) Retention time: t_{minor} =7.451 min, t_{major} =8.200 min, ee = 97%.

(4*S*,5*S*)-ethyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5h



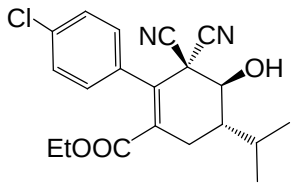
Colorless crystal, $[\alpha]^{20}_D$= -6 (*c*=1.0, $CHCl_3$); mp 151 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.55-7.58(dd, *J* = 2.1 Hz, 6.6 Hz, 2 H), 7.21-7.24(dd, *J* = 1.8 Hz, 6.6 Hz, 2 H), 4.11-4.17(dd, *J* = 6.9 Hz, 11.4 Hz, 1 H), 3.89-3.96(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 3.25(d, *J* = 6.9 Hz, 1 H), 2.56-2.64(dd, *J* = 5.7 Hz, 5.7 Hz, 1 H), 2.35-2.45(m, 2 H), 2.09-2.20(m, 1 H), 1.04(d, *J* = 6.9 Hz, 3 H), 0.88-0.94(m, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.8, 137.1, 134.0, 131.9, 130.4, 129.4, 123.9, 113.9, 112.7, 73.7, 61.7, 48.1, 40.4, 26.3, 25.6, 20.0, 15.2, 13.5.

IR: ν 3465, 2964, 2255, 1717, 1657, 1587, 1487, 1392, 1371, 1257, 1105, 1072, 1012, 912, 825, 733 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}BrN_2O_3+NH_4^+$: 434.1074; found: 434.1072, 0.5ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 216 nm.) Retention time: t_{major} =7.164 min, t_{minor} =10.085 min, ee = 95%.

(4*S*,5*S*)-ethyl 2-(4-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5i



Colorless crystal, $[\alpha]^{20}_D$= -10 (*c*=1.0, $CHCl_3$); mp 140 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.42(m, 2 H), 7.26-7.31(m, 2 H), 4.12-4.18(dd, *J* = 5.4 Hz, 11.4 Hz, 1 H), 3.89-3.96(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 3.19(d, *J* = 6.3 Hz, 1 H), 2.35-2.66(m, 3 H), 2.10-2.20(m, 1 H), 1.04(d, *J* = 7.2 Hz, 3 H), 0.87-0.94(m, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.9, 137.1, 135.7, 133.6, 130.2,

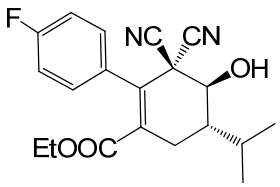
129.3, 129.0, 113.9, 112.7, 73.7, 61.7, 48.1, 40.4, 26.3, 25.6, 20.0, 15.2, 13.5.

IR: ν 3463, 2963, 2927, 2255, 1717, 1655, 1593, 1491, 1467, 1371, 1257, 1094, 1015, 912, 828, 732 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}ClN_2O_3+NH_4^+$: 390.1579; found: 390.1573, 1.5ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 220 nm.) Retention time: t_{major} =6.651 min, t_{minor} =8.576 min, ee = 97%.

(4S,5S)-ethyl 3,3-dicyano-2-(4-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5j



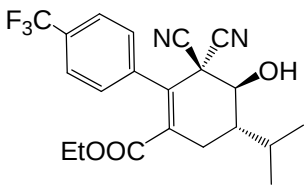
Colorless crystal, $[\alpha]^{20}_D$= -14 (*c*=1.0, $CHCl_3$); mp 140 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.30-7.36(m, 2 H), 7.07-7.14(m, 2 H), 4.62(d, *J* = 5.7 Hz, 0.4 H), 4.11-4.18(dd, *J* = 6.9 Hz, 11.4 Hz, 0.6 H), 3.88-3.95(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 3.24-3.29(m, 1 H), 2.34-2.71(m, 2.5 H), 2.11-2.20(m, 0.5 H), 1.75-1.85(m, 1 H), 1.02-1.06(m, 4 H),0.86-0.94(m, 5 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.2, 167.0, 137.2, 131.8, 131.7, 130.9, 130.8, 129.3, 127.8, 115.9, 115.6, 114.0, 112.7, 73.7, 70.3, 61.6, 61.4, 48.3, 46.1, 40.4, 29.0, 26.6, 26.3, 25.6, 20.3, 20.0, 15.2, 13.5.

IR: ν 3466, 2965, 2256, 1716, 1655, 1602, 1509, 1470, 1372, 1234, 1161, 1101, 1016, 913, 837, 734 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}FN_2O_3+NH_4^+$:374.1874; found: 374.1865, 2.4ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 208 nm.) Retention time: t_{major} =7.030 min, t_{minor} = 9.108 min, ee = 93%.

(4S,5S)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-(trifluoromethyl)phenyl)cyclohex-1-enecarboxylate: 5k



White solid, $[\alpha]^{20}_D$= -14 (*c*=1.0, $CHCl_3$); mp 140 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.71(d, *J* = 8.1 Hz, 2 H), 7.50(d, *J* = 8.1 Hz, 2 H), 4.15-4.21(dd, *J* = 6.9 Hz, 11.4 Hz, 1 H), 3.87-3.94(dd, *J* =

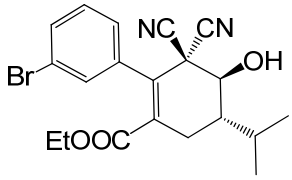
6.9 Hz, 14.1 Hz, 2 H), 3.16(d, *J* = 6.9 Hz, 1 H), 2.60-2.69(dd, *J* = 5.7 Hz, 5.7 Hz, 1 H), 2.36-2.48(m, 2 H), 2.12-2.23(m, 1 H), 1.05(d, *J* = 6.9 Hz, 3 H), 0.96(d, *J* = 6.9 Hz, 3 H), 0.82(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.5, 138.8, 137.4, 129.5, 129.4, 125.6, 125.5, 113.7, 112.5, 73.8, 61.7, 47.9, 40.4, 26.4, 25.7, 20.0, 15.2, 13.3.

IR: ν 3462, 2965, 2255, 1718, 1656, 1371, 1326, 1256, 1169, 1131, 1069, 1018, 838, 736 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{21}H_{21}F_3N_2O_3+NH_4^+$:424.1843; found: 424.1847, 0.9ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 0.5 mL/min, 215 nm.) Retention time: t_{major} =12.259 min, ee >99%.

(4S,5S)-ethyl 2-(3-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5l



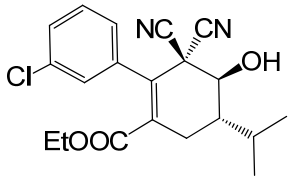
Pale yellow solid, $[\alpha]^{20}_D$= -11 (*c*=1.0, $CHCl_3$); mp 134 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.54-7.58(m, 1 H), 7.48-7.49(m, 1 H), 7.29-7.32(m, 2 H), 4.63-4.64(d, *J* = 5.4 Hz, 1 H), 3.91-3.98(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 2.85(t, *J* = 5.4 Hz, 1 H), 2.38-2.73(m, 2.5 H), 2.13-2.22(m, 0.5 H), 1.77-1.86(m, 1 H), 0.87-1.08(m, 9 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.8, 137.4, 132.5, 132.3, 131.8, 130.1, 129.0, 127.4, 122.5, 113.1, 112.5, 77.4, 77.0, 76.6, 73.8, 61.4, 47.9, 40.4, 29.1, 26.6, 25.7, 20.3, 15.3, 13.5.

IR: ν 3463, 2964, 2254, 1716, 1654, 1561, 1471, 1371, 1282, 1258, 1137, 1074, 788, 733, 704, 664 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}BrN_2O_3+NH_4^+$: 434.1071; found: 434.1060, 2.5ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 0.5 mL/min, 223 nm.) Retention time: t_{major} =14.406 min, t_{minor} =19.203 min, ee = 96%.

(4*S*,5*S*)-ethyl 2-(3-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5m



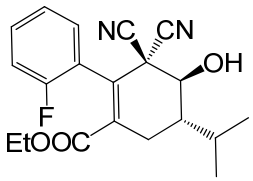
White solid, $[\alpha]^{20}_D$= -15 (*c*=1.0, $CHCl_3$); mp 105 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.23-7.39(m, 4 H), 4.62(br, 1 H), 3.90-3.97(dd, *J* = 6.9 Hz, 14.1 Hz, 2 H), 3.22(s, 1 H), 2.65-2.72(m, 2.5 H), 2.13-2.21(m, 0.5 H), 1.76-1.83(m, 1 H),1.02-1.07(m, 4 H) ,0.86-0.95(m, 5 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.0, 137.5, 134.4, 129.9, 129.6, 129.4, 129.0, 127.5, 127.0, 113.2, 113.0, 73.7, 70.4, 61.5, 47.9, 40.5, 29.1, 26.6, 20.3, 15.2, 13.5.

IR: ν 3461, 2962, 2928, 2250, 1719, 1655, 1565, 1471, 1371, 1283, 1259, 1136, 1087, 1017, 789, 706 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}ClN_2O_3+NH_4^+$:390.1579; found: 390.1571, 2.1ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 0.5 mL/min, 213 nm.) Retention time: t_{major} =14.118 min, ee >99%.

(4*S*,5*S*)-ethyl 3,3-dicyano-2-(2-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5n



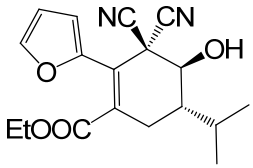
White solid, $[\alpha]^{20}_D$= -40 (*c*=1.0, $CHCl_3$); mp 134 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.38-7.44(m, 2 H), 7.11-7.24(m, 2 H), 4.63(d, *J* = 6.0 Hz, 0.4 H), 4.14-4.20(dd, *J* = 6.9 Hz, 11.4 Hz, 0.6 H), 3.90-3.97(dd, *J* = 7.2Hz, 14.4 Hz, 2 H), 3.29-3.39(dd, *J* = 6.9 Hz, 6.0 Hz, 1 H), 2.64-2.79(m, 1 H), 2.35-2.55(m, 1.5 H), 2.14-2.23(m, 0.5 H),1.81-1.85(m, 1 H), 1.02-1.06(m, 4 H), 0.85-0.94(m, 5 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.2, 158.0, 131.5, 131.4, 131.3, 124.4, 115.9, 115.6, 70.4, 61.6, 48.3, 40.4, 29.1, 26.3, 25.7, 20.3, 20.2, 20.0, 15.2, 13.4.

IR: ν 3468, 2966, 2254, 1715, 1657, 1613, 1490, 1448, 1371, 1261, 1136, 1104, 1021, 808, 763 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{21}FN_2O_3+NH_4^+$:374.1874; found: 374.1871, 0.3ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 212 nm.) Retention time: t_{major} =9.269 min, t_{minor} =11.573 min, ee =97%.

(4*S*,5*S*)-ethyl 3,3-dicyano-2-(furan-2-yl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5o



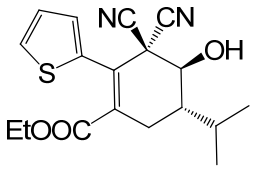
Colorless solid, $[\alpha]^{20}_D$= -23 (*c*=1.0, $CHCl_3$); mp 114 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47(d, *J* = 1.2 Hz, 1 H), 6.69-6.73(dd, *J* = 3.6 Hz, 9.0 Hz, 1 H), 6.46-6.49(m, 1 H), 4.62(d, *J* = 4.2 Hz, 1 H), 4.20-4.25(dd, *J* = 6.0 Hz, 6.9 Hz, 2 H), 3.49-3.57(dd, *J* = 7.2 Hz, 5.7 Hz, 1 H), 2.34-2.64(m, 2.5 H), 2.09-2.11(m, 0.5 H), 1.69-1.84(m, 1 H), 1.19-1.24(dt, *J* = 1.8 Hz, 6.9 Hz, 3 H), 0.98-1.04(m, 5 H), 0.88(d, *J* = 6.9 Hz, 1 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.5, 147.5, 143.6, 135.9, 135.1, 116.8, 113.5, 112.9, 111.6, 111.2, 73.9, 70.5, 61.9, 44.6, 40.5, 28.9, 27.1, 20.2, 14.0.

IR: ν 3466, 3154, 2966, 2256, 1723, 1652, 1472, 1371, 1284, 1250, 1162, 1020, 911, 743, 591 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{18}H_{20}N_2O_4$+NH_4^+:346.1761; found: 346.1750, 2.9ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 275 nm.) Retention time: t_{major} =12.100 min, ee>99%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(thiophen-2-yl)cyclohex-1-enecarboxylate: 5p



Pale yellow solid, $[\alpha]^{20}_D$= +35 (*c*=1.0, $CHCl_3$); mp 153 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.42-7.44(dd, *J* = 1.2 Hz, 5.1 Hz, 1 H), 7.18-7.20(dd, *J* = 0.9 Hz, 3.3 Hz, 1 H), 7.05-7.08(dd, *J* = 3.6 Hz, 5.1 Hz, 1 H), 4.12-4.18(dd, *J* = 6.9 Hz, 11.4 Hz, 1 H), 3.98-4.05(dd, *J* = 7.2 Hz, 14.1 Hz, 2 H), 3.26(d, *J* = 6.9 Hz, 1 H), 2.54-2.62(dd, *J* = 6.0 Hz, 5.7 Hz, 1 H), 2.35-2.45(m, 2 H), 2.09-2.19(m, 1 H), 0.99-1.03(m, 6 H), 0.93(d, *J* = 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.3, 139.3, 134.7, 129.1, 127.9, 127.3, 123.3, 114.1, 112.7, 73.6, 61.8, 48.6, 40.3, 26.7, 25.6, 20.0, 15.2, 13.6.

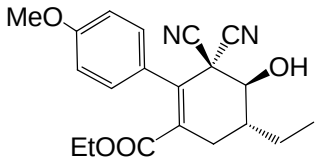
IR: ν 3471, 3108, 2965, 2254, 1725, 1650, 1464, 1435, 1370, 1260, 1196, 1095, 1016, 855, 713 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{18}H_{20}N_2O_3S$+NH_4^+:362.1533; found: 362.1537, 1.1ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane =

5/95, 1.0 mL/min, 225 nm.) Retention time: t_{major} =9.732 min, t_{minor} =18.197 min, ee = 97%.

(4*S*,5*R*)-ethyl 3,3-dicyano-5-ethyl-4-hydroxy-2-(4-methoxyphenyl)cyclohex-1-enecarboxylate: 5q



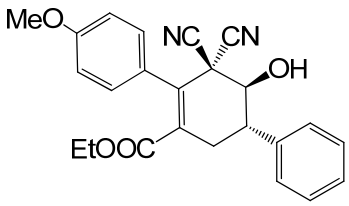
White solid, $[\alpha]^{20}_D$= -21 (*c*=1.0, $CHCl_3$); mp 102 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.25-7.31(m, 2 H), 6.90-6.95(m , 2 H), 4.02-4.07(dd, *J* = 2.7 Hz, 3.3 Hz, 1 H), 3.89-3.96(dd, *J* = 7.2 Hz, 14.4 Hz, 2 H), 3.83(s, 3 H), 3.18(br, 1 H), 2.75-2.83(dd, *J* = 5.4 Hz, 5.7 Hz, 1 H), 2.25-2.33(m, 1 H), 1.96-2.13(m, 2 H), 1.31-1.41(m, 1 H), 0.99-1.04(m, 3 H), 0.90(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.4, 160.3, 136.0, 130.3, 130.1, 127.4, 114.0, 112.9, 75.1, 61.4, 55.3, 48.1, 37.1, 31.6, 23.5, 13.6, 10.1.

IR: ν 3463, 2969, 2253, 1716, 1656, 1608, 1512, 1464, 1371, 1293, 1251, 1180, 1105, 1028, 832, 735 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}N_2O_4$+NH_4^+: 372.1918; found: 372.1928, 2.7ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 216 nm.) Retention time: t_{major} =13.859 min, t_{minor} =22.268 min, ee =92%.

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-2-(4-methoxyphenyl)-5-phenylcyclohex-1-enecarboxy late: 5r



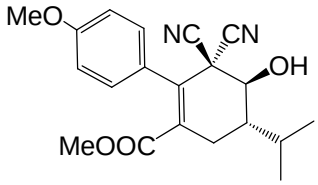
White solid, $[\alpha]^{20}_D$= -7 (*c*=1.0, $CHCl_3$); mp 154 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.33-7.43(m, 7 H), 6.94-6.97(dd, *J* = 1.8 Hz, 6.6 Hz, 2 H), 4.52(d, *J* = 11.1Hz, 1 H), 3.89-3.96(dd, *J* = 7.2 Hz, 14.1Hz, 2 H), 3.84(s, 3 H), 3.27-3.37(m, 1 H), 2.79-3.00(m, 2 H), 2.46(br, 1 H), 0.91(t, *J* = 7.2 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 166.8, 160.4, 137.1, 135.8, 130.8, 130.2, 129.6, 128.6, 128.1, 127.1, 114.0, 113.5, 112.5, 74.4, 61.5, 55.3, 47.3, 44.0, 34.6, 13.6.

IR: ν 3452, 2954, 2841, 2255, 1723, 1655, 1607, 1512, 1436, 1289, 1252, 1181, 1114, 1029, 912, 830, 733, 702 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{24}H_{22}N_2O_4$+NH_4^+: 420.1918; found: 420.1909, 2.1ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OJ-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 222 nm.) Retention time: t_{major} =13.101 min, ee>99%.

(4*S*,5*S*)-methyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarboxylate: 5s



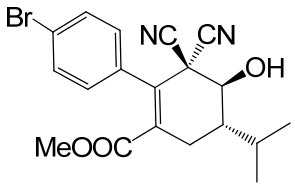
Colorless solid, $[\alpha]^{20}_{D}$= -6 (*c*=1.0, $CHCl_3$); mp 130 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.24-7.29(m, 2 H), 6.90-6.94(m, 2 H), 4.60(s, 1 H), 3.83(s, 3 H), 3.48(s, 3 H), 3.14(br, 1 H), 2.34-2.68(m, 2.5 H), 1.72-1.85(m, 1.5 H), 1.01-1.06(m, 6 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 168.1, 160.1, 136.2, 129.9, 128.7, 127.9, 114.0, 113.5, 113.3, 73.7, 70.5, 55.2, 52.2, 46.2, 40.5, 29.0, 26.7, 20.3, 15.2.

IR: ν 3468, 2962, 2255, 1721, 1654, 1608, 1512, 1437, 1370, 1289, 1253, 1181, 1030, 972, 913, 831, 734 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{20}H_{22}N_2O_4+H^+$: 355.1652; found: 355.1646, 1.7ppm.

Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 224 nm.) Retention time: t_{major} =11.699 min, t_{minor} =25.162 min, ee =93%.

(4*S*,5*S*)-methyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5t



Colorless solid, $[\alpha]^{20}_{D}$= -8 (*c*=1.0, $CHCl_3$); mp 141 °C. **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.54-7.58(m, 2 H), 7.19-7.24(m, 2 H), 4.16(d, *J* = 11.1 Hz, 1 H), 3.49(s, 3 H), 3.05(br, 1 H), 2.35-2.64(m, 3 H), 2.10-2.21(m, 1 H), 1.04(d, *J* = 7.2 Hz, 3 H), 0.95(d, *J* = 6.9 Hz, 3 H); **^{13}C NMR** (75 MHz, $CDCl_3$): δ 167.1, 136.7, 133.9, 132.0, 130.1, 129.8, 124.0, 113.8, 112.6, 73.7, 52.4, 48.0, 40.3, 26.4, 25.6, 20.0, 15.2.

IR: ν 3467, 2961, 2255, 1724, 1654, 1587, 1487, 1435, 1393, 1256, 1107, 1071, 1010, 911, 818, 731 cm^{-1}.

HRMS-ESI (*m/z*): calcd for $C_{19}H_{19}BrN_2O_3+H^+$: 403.0652; found: 403.0642, 2.5ppm.

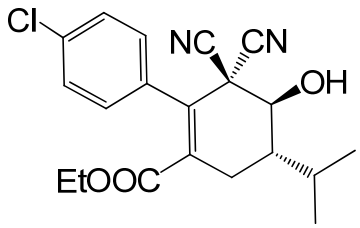
Major diastereomer: ee was determined by HPLC analysis (Chiralcel OD-H, *i*-PrOH/ Hexane = 5/95, 1.0 mL/min, 218 nm.) Retention time: t_{major} =7.921 min, t_{minor} =12.481 min, ee = 96%.

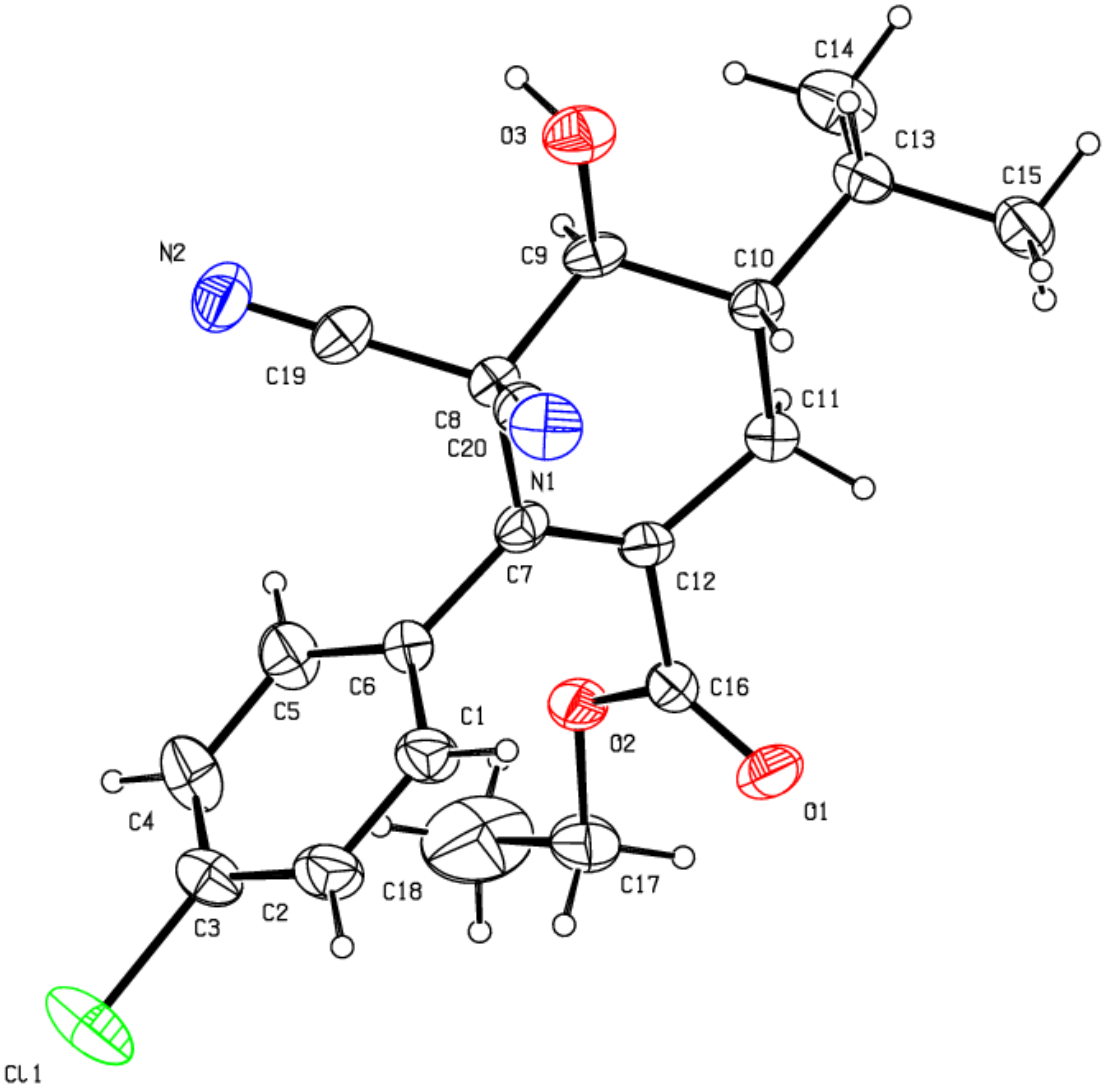
5.0 References.

(1). Marigo, M.; Wabnitz, T. C.; Fielenbach, D.; Jøgensen, K. A. *Angew. Chem. Int. Ed*. **2005**, *44*, 794.

6.0 X-Ray structure of 5i

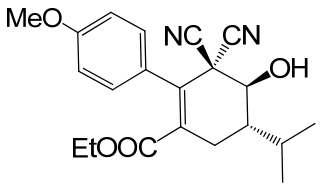
(4*S*,5*S*)-ethyl 2-(4-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5i (CCDC 825720).

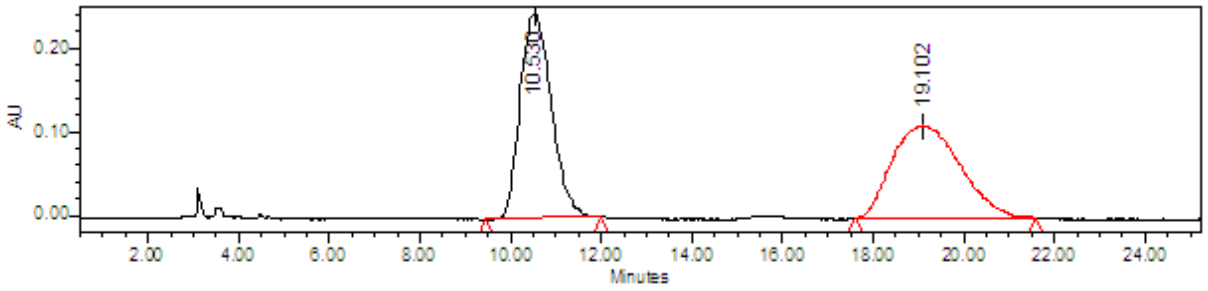




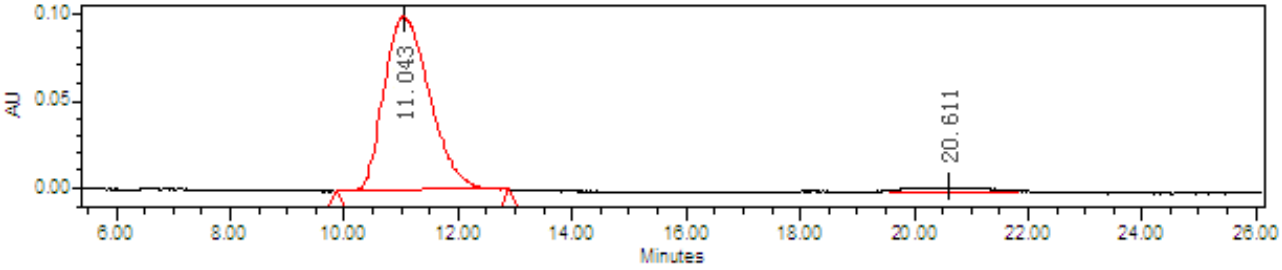
7.0. Copies of HPLC spectra of racemic/chiral products

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarboxy late: 5a



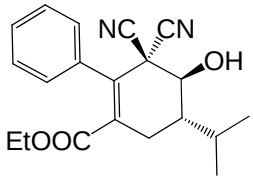


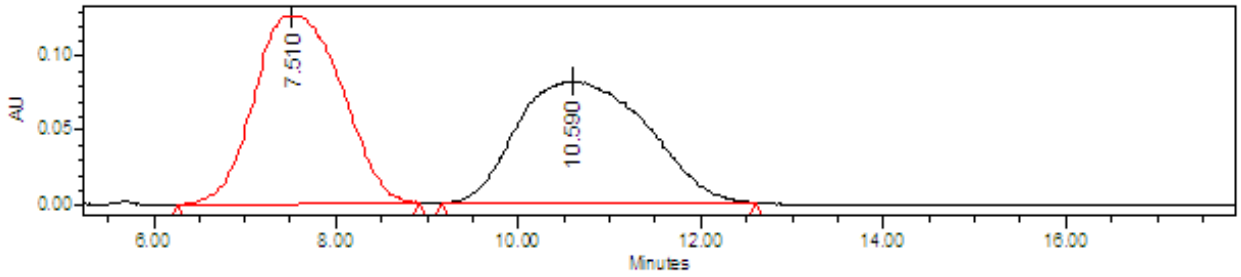
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	10.530	50.35	bb	Unknown
2	19.102	49.65	bb	Unknown



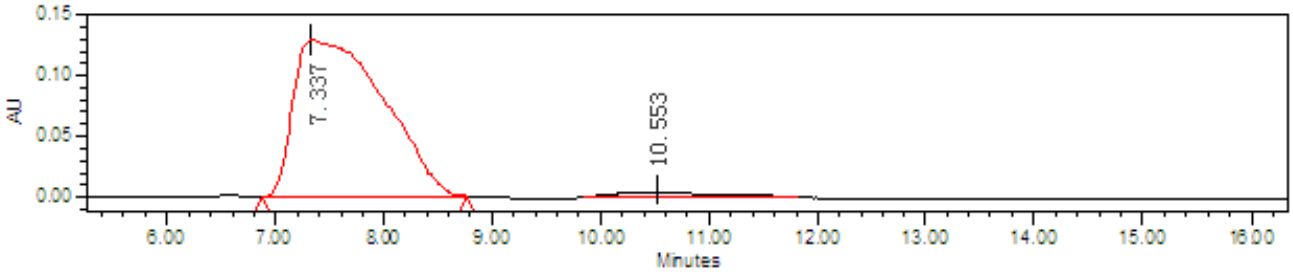
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	11.043	98.34	bb	Unknown
2	20.611	1.66	bb	Unknown

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-phenylcyclohex-1-enecarboxylate: 5b





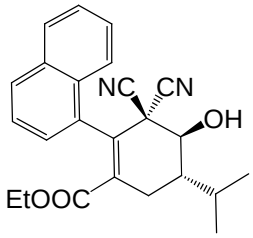
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.510	50.82	bb	Unknown
2	10.590	49.18	bb	Unknown

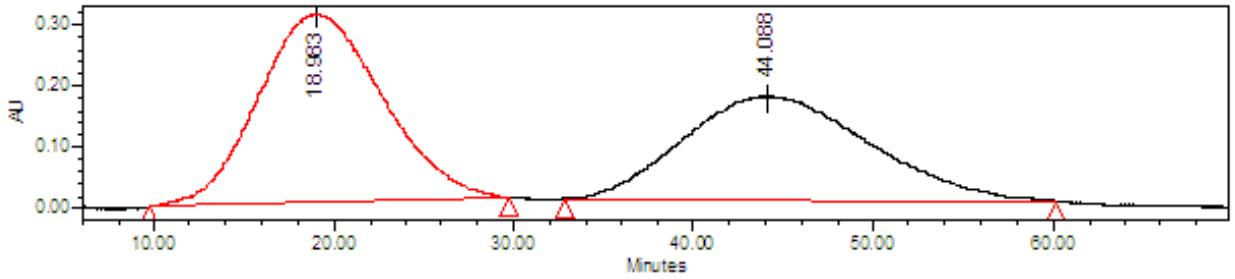


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.337	98.41	bb	Unknown
2	10.553	1.59	bb	Unknown

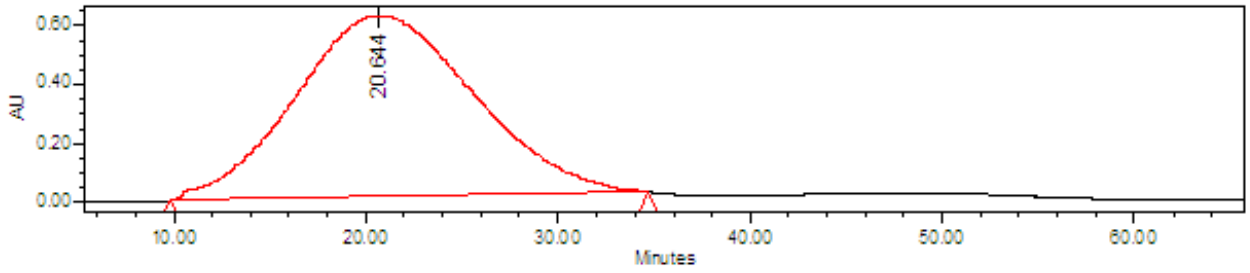
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(naphthalen-1-yl)cyclohex-1-enecarboxy

late: 5c



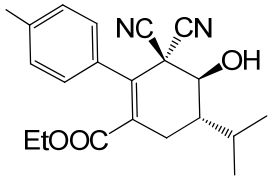


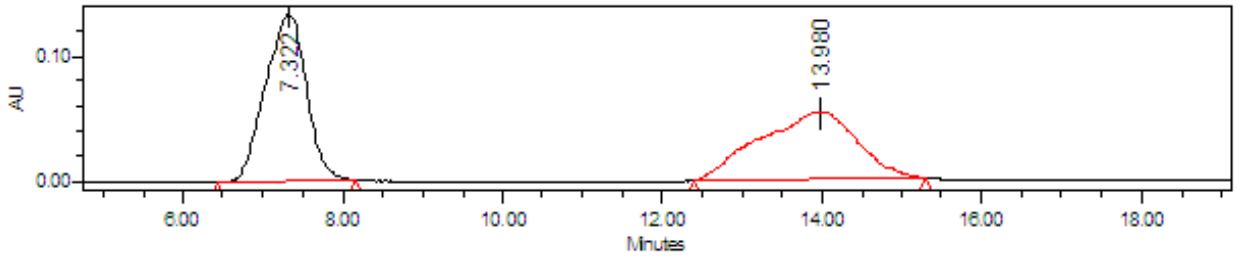
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	18.983	54.89	bb	Unknown
2	44.088	45.11	bb	Unknown



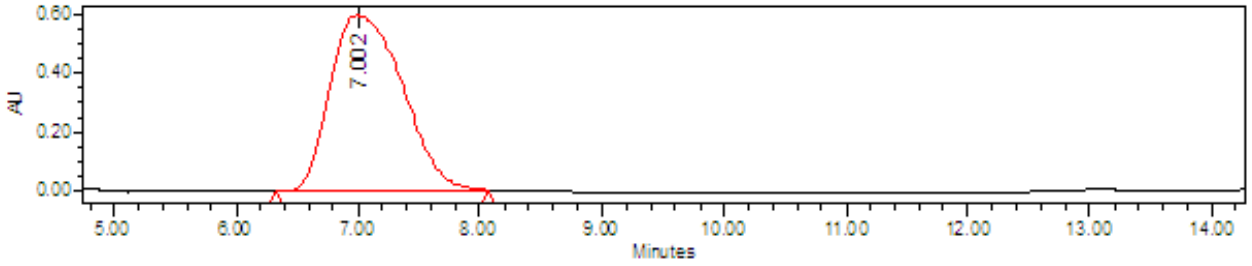
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	20.644	100.00	bb	Unknown
2				

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-p-tolylcyclohex-1-enecarboxylate: 5d





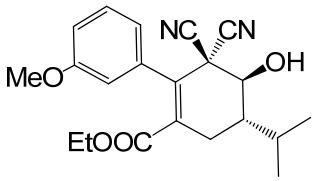
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.322	50.65	bb	Unknown
2	13.980	49.35	bb	Unknown

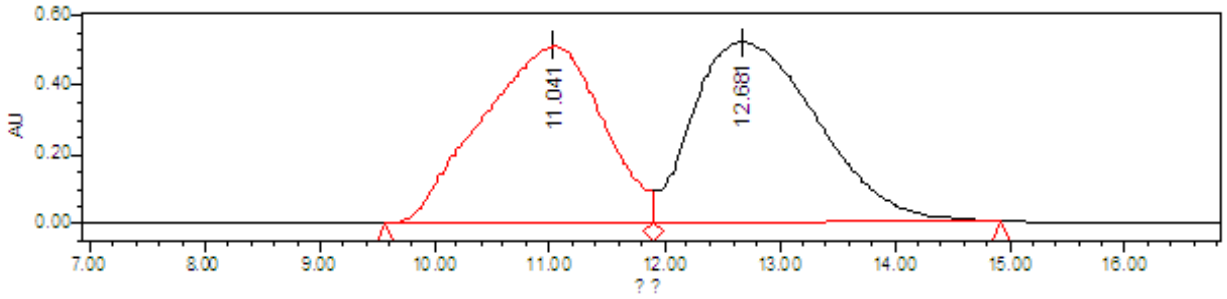


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.002	100.00	bb	Unknown
2				

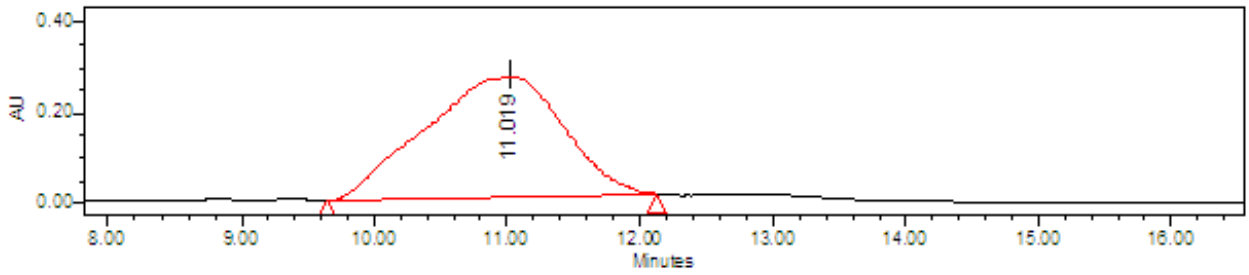
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(3-methoxyphenyl)cyclohex-1-enecarbox

ylate: 5e



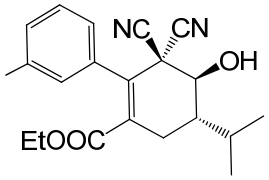


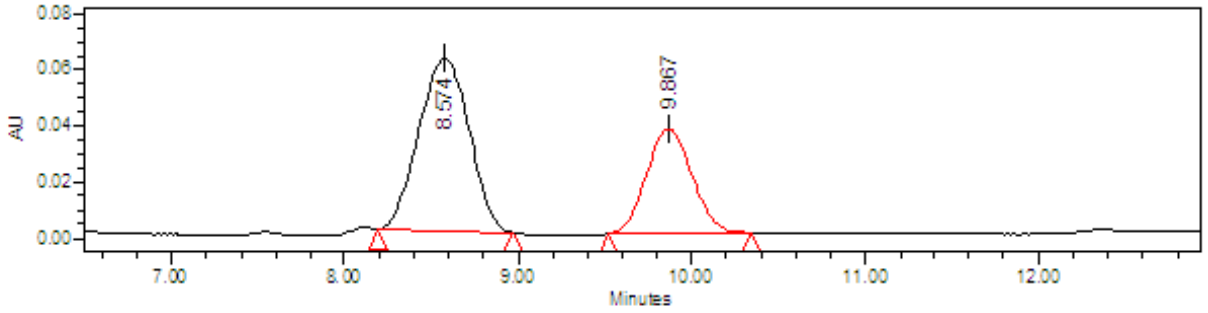
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	11.041	48.69	bb	Unknown
2	12.681	51.31	bb	Unknown



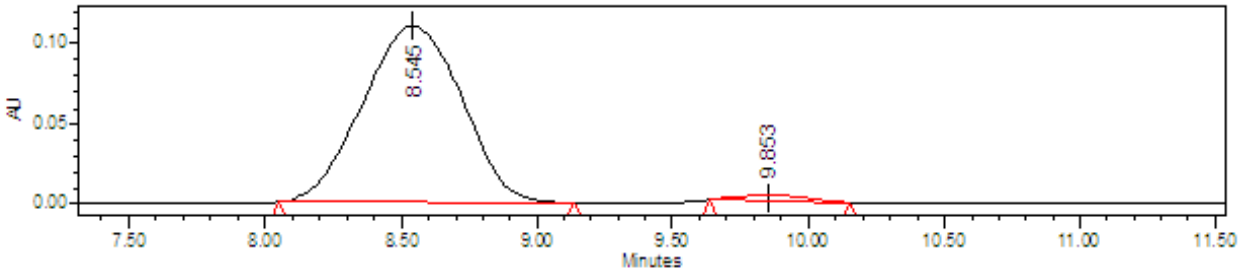
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	11.019	100.00	bb	Unknown
2				

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-m-tolylcyclohex-1-enecarboxylate: 5f



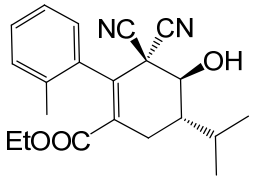


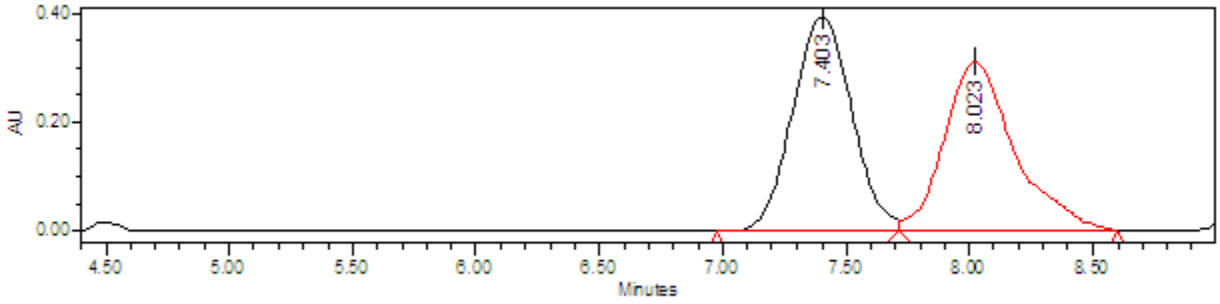
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	8.574	64.51	bb	Unknown
2	9.867	35.49	bb	Unknown



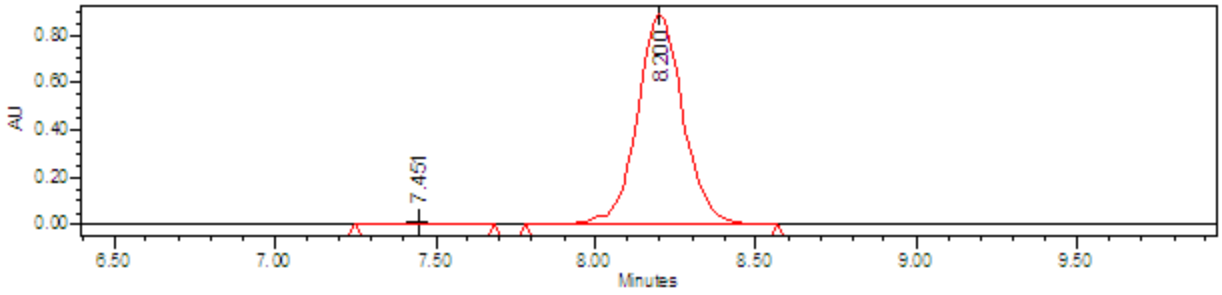
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	8.545	98.15	bb	Unknown
2	9.853	1.85	bb	Unknown

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-o-tolylcyclohex-1-enecarboxylate: 5g





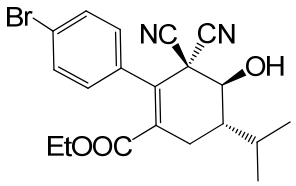
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.403	51.93	bb	Unknown
2	8.023	48.07	bb	Unknown

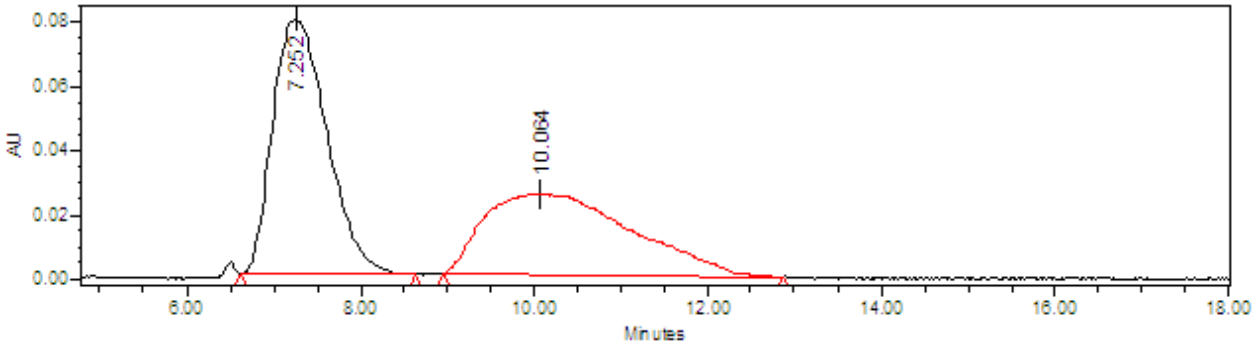


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.451	1.38	bb	Unknown
2	8.200	98.62	bb	Unknown

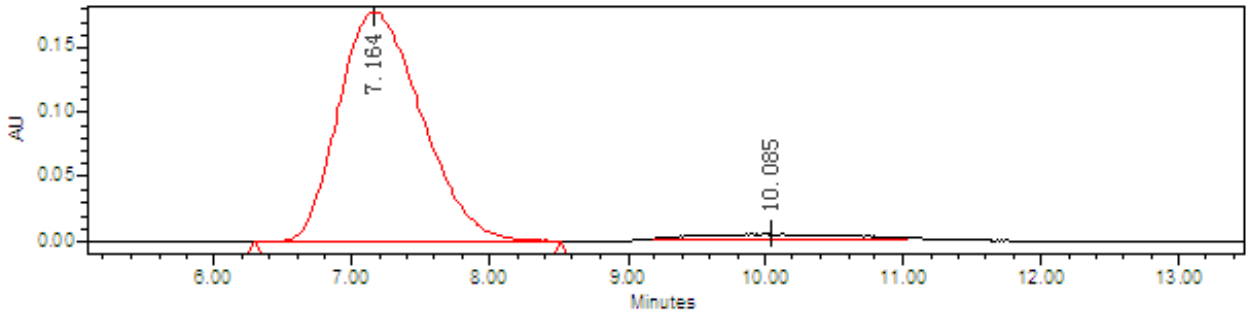
(4*S*,5*S*)-ethyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5h





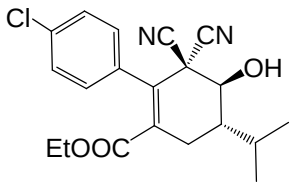
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.252	53.86	bb	Unknown
2	10.064	46.14	bb	Unknown

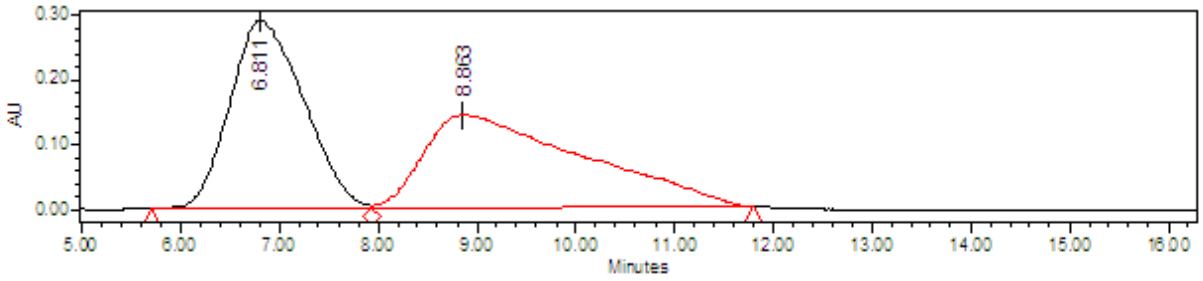


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.164	97.37	bb	Unknown
2	10.085	2.63	bb	Unknown

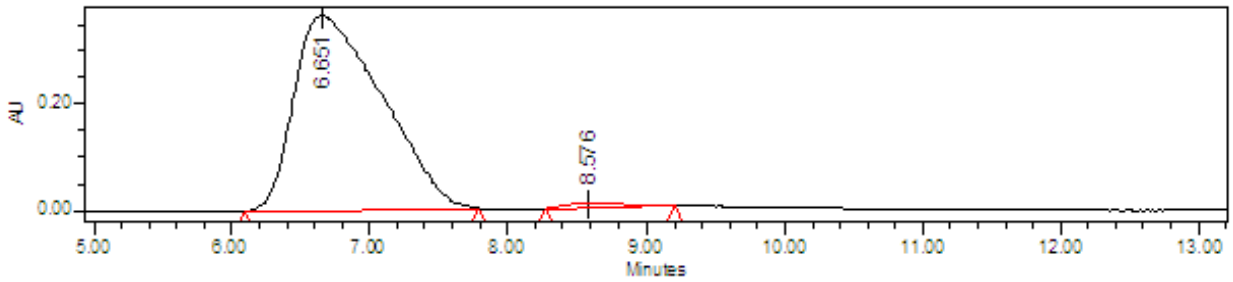
(4*S*,5*S*)-ethyl 2-(4-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5i





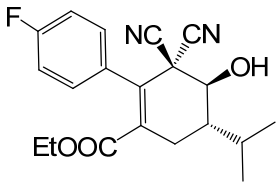
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	6.811	48.44	bb	Unknown
2	8.863	51.56	bb	Unknown

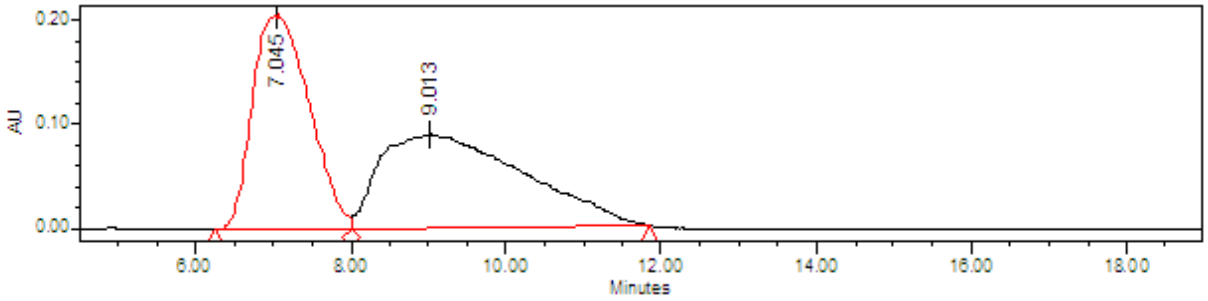


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	6.651	98.65	bb	Unknown
2	8.576	1.35	bb	Unknown

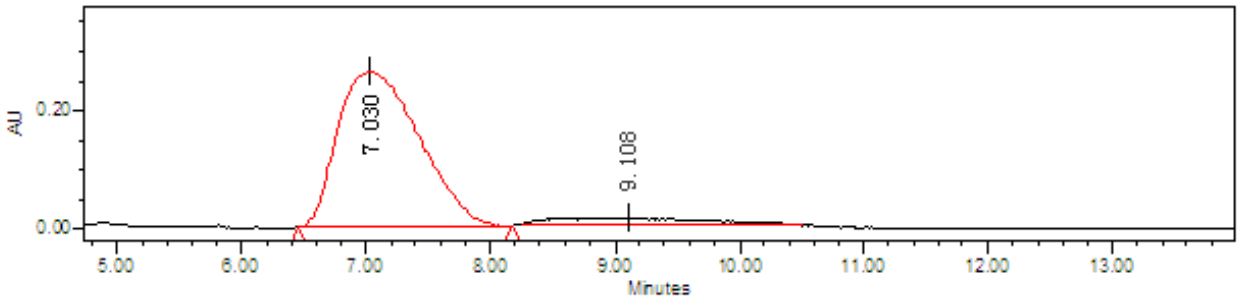
(4S,5S)-ethyl 3,3-dicyano-2-(4-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5j





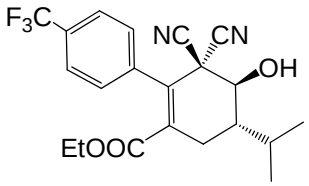
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.045	47.62	bb	Unknown
2	9.013	52.38	bb	Unknown

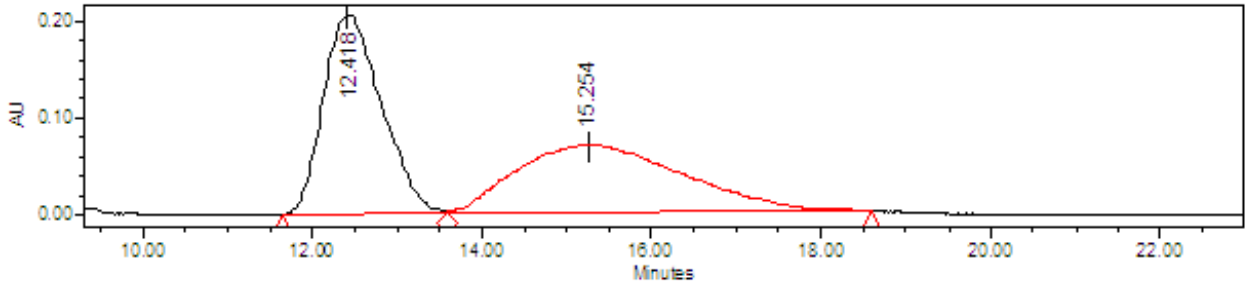


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.030	96.43	bb	Unknown
2	9.108	3.57	bb	Unknown

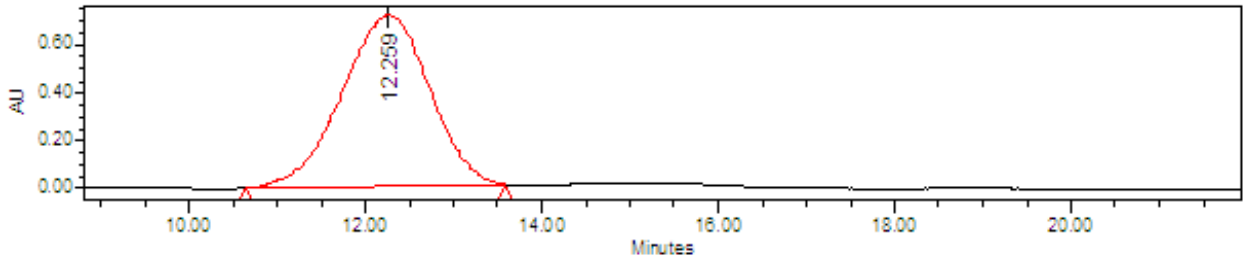
(4S,5S)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-(trifluoromethyl)phenyl)cyclohex-1-en

ecarboxylate: 5k





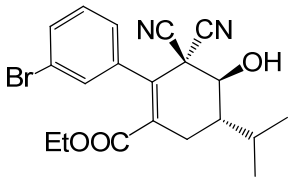
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	12.418	50.58	bb	Unknown
2	15.254	49.42	bb	Unknown

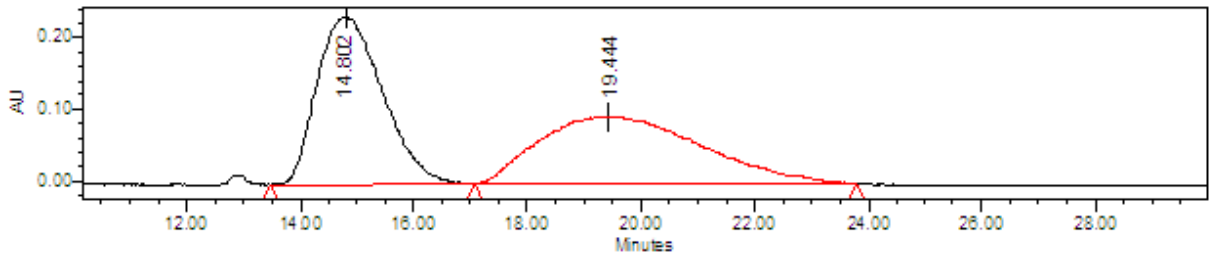


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	12.259	100.00	bb	Unknown
2				

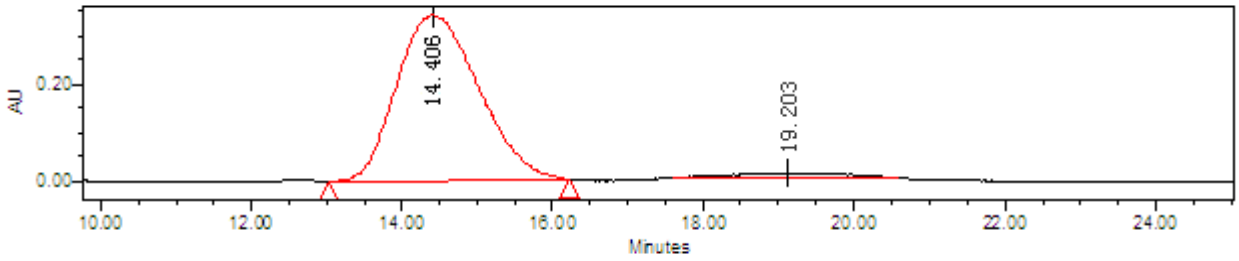
(4S,5S)-ethyl 2-(3-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5l





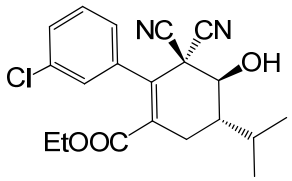
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	14.802	50.42	bb	Unknown
2	19.444	49.58	bb	Unknown

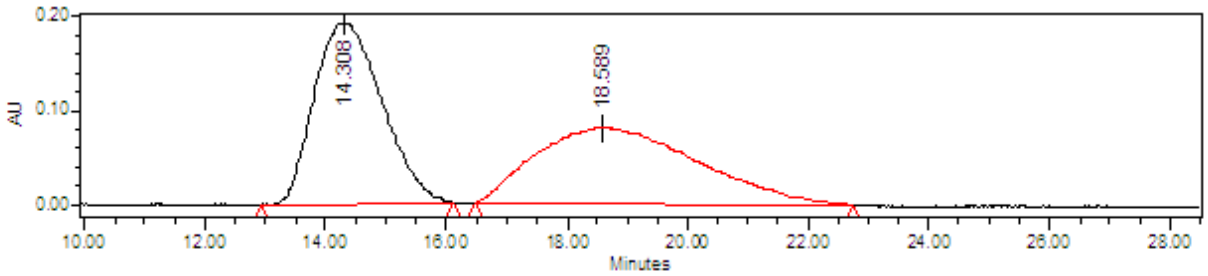


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	14.406	98.22	bb	Unknown
2	19.203	1.78	bb	Unknown

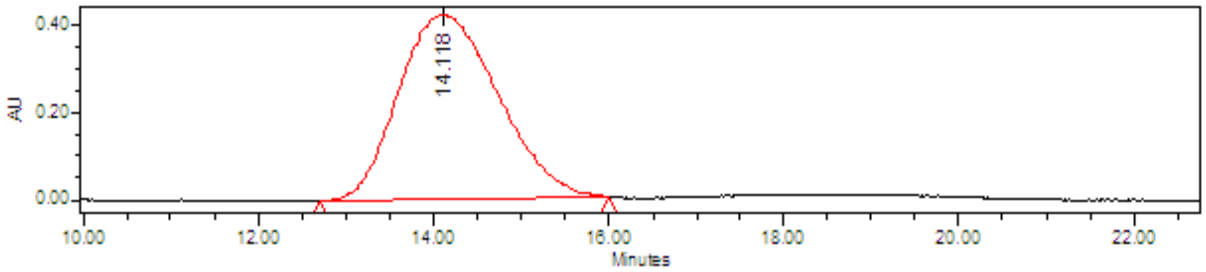
(4*S*,5*S*)-ethyl 2-(3-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5m





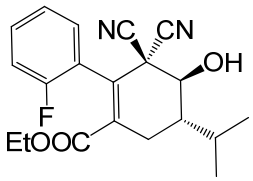
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	14.308	50.21	bb	Unknown
2	18.589	49.79	bb	Unknown

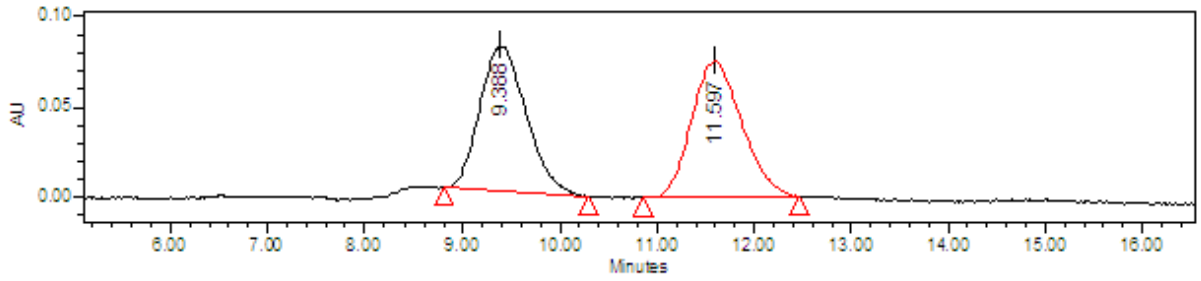


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	14.118	100.00	bb	Unknown
2				

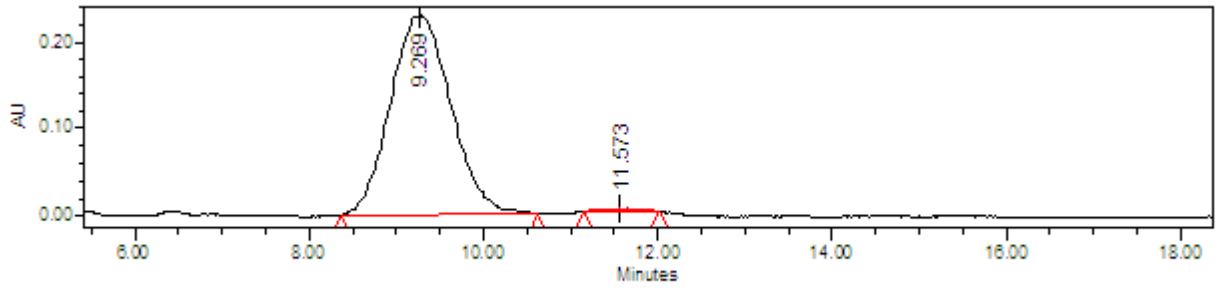
(4*S*,5*S*)-ethyl 3,3-dicyano-2-(2-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5n



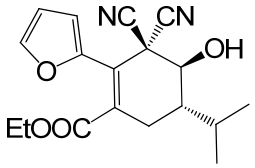


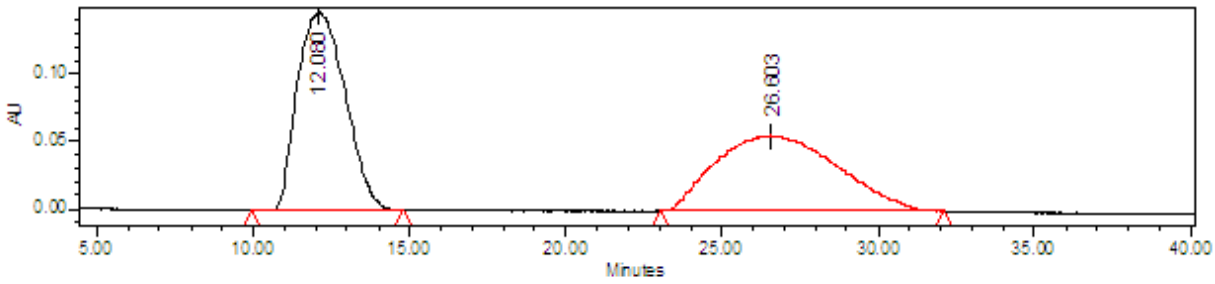
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	9.388	49.67	bb	Unknown
2	11.597	50.33	bb	Unknown



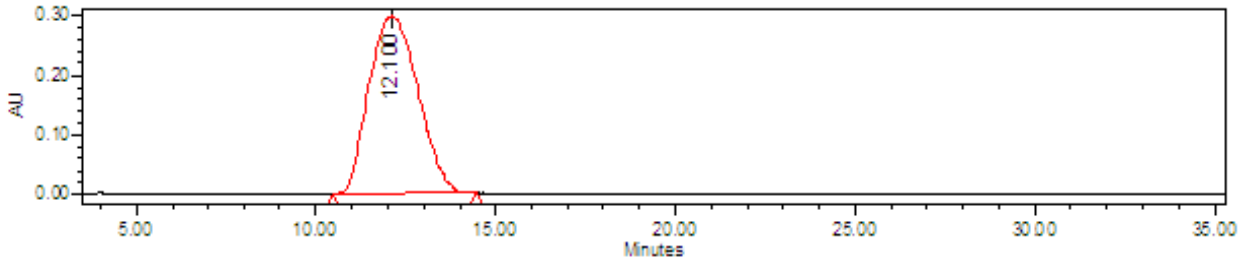
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	9.269	98.69	bb	Unknown
2	11.573	1.31	bb	Unknown

(4*S*,5*S*)-ethyl 3,3-dicyano-2-(furan-2-yl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5o





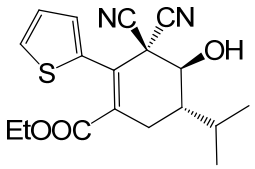
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	12.080	50.00	bb	Unknown
2	26.603	50.00	bb	Unknown

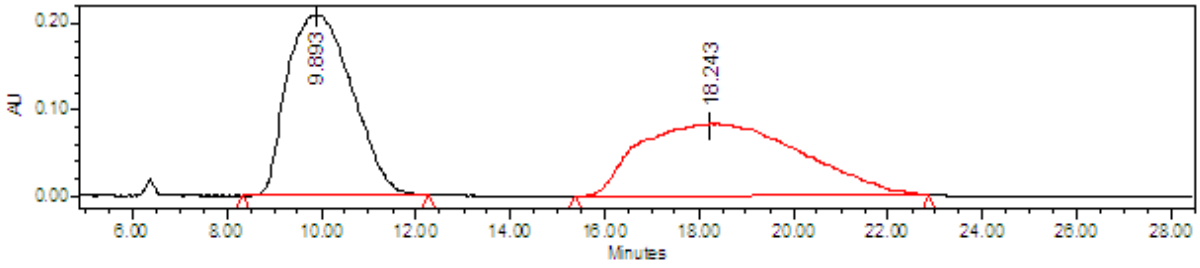


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	12.100	100.00	bb	Unknown
2				

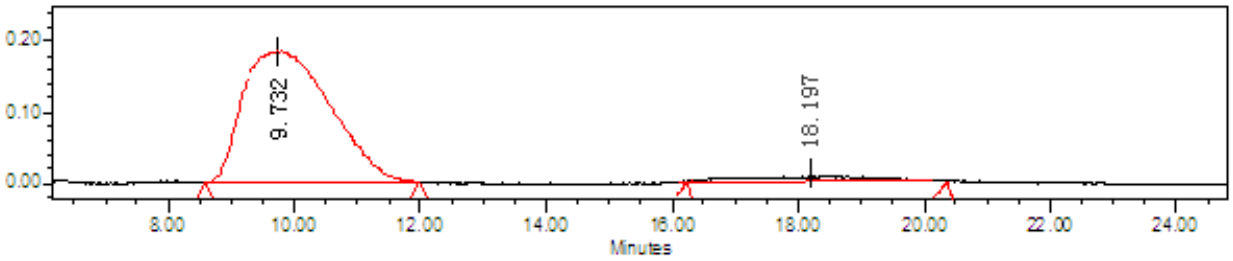
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(thiophen-2-yl)cyclohex-1-enecarboxylate:

5p





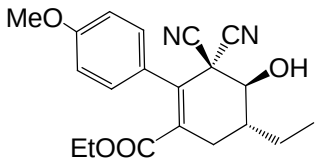
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	9.893	50.07	bb	Unknown
2	18.243	49.93	bb	Unknown

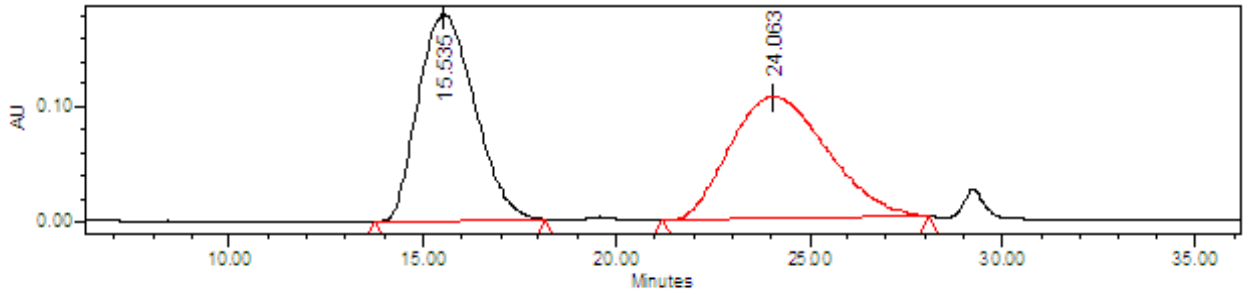


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	9.735	98.66	bb	Unknown
2	18.197	1.34	bb	Unknown

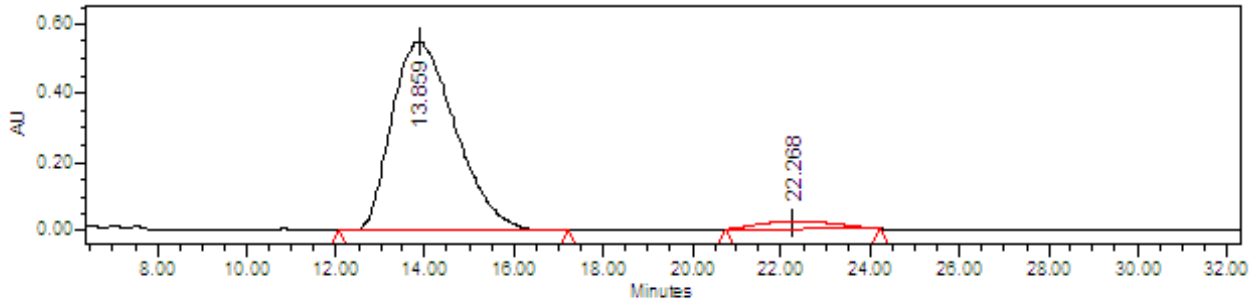
(4*S*,5*R*)-ethyl 3,3-dicyano-5-ethyl-4-hydroxy-2-(4-methoxyphenyl)cyclohex-1-enecarboxylate:

5q





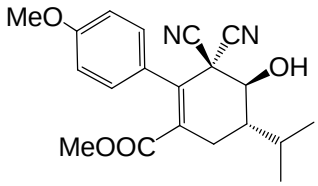
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	15.535	49.61	bb	Unknown
2	24.063	50.39	bb	Unknown

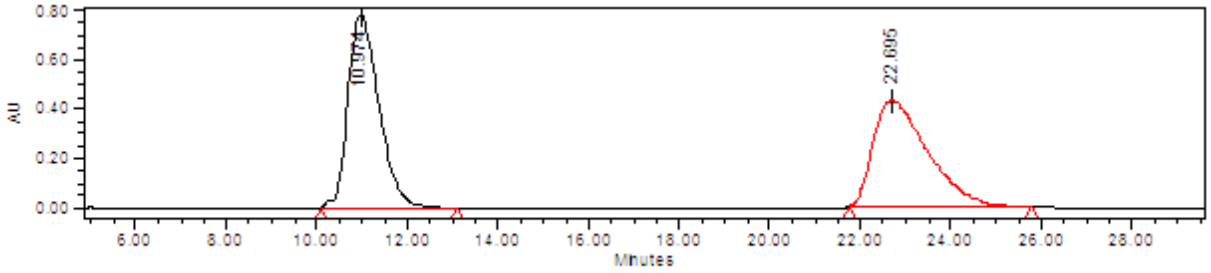


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	13.859	95.98	bb	Unknown
2	22.268	4.02	bb	Unknown

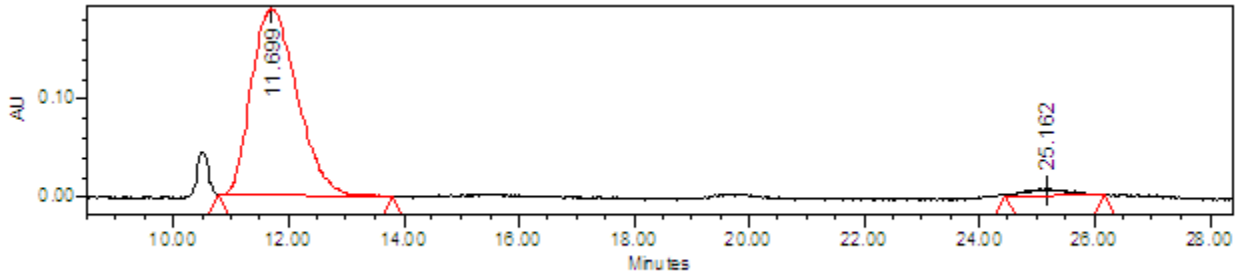
(4*S*,5*S*)-methyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarbo

xylate: 5s





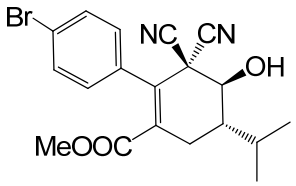
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	10.974	50.53	bb	Unknown
2	22.695	49.47	bb	Unknown

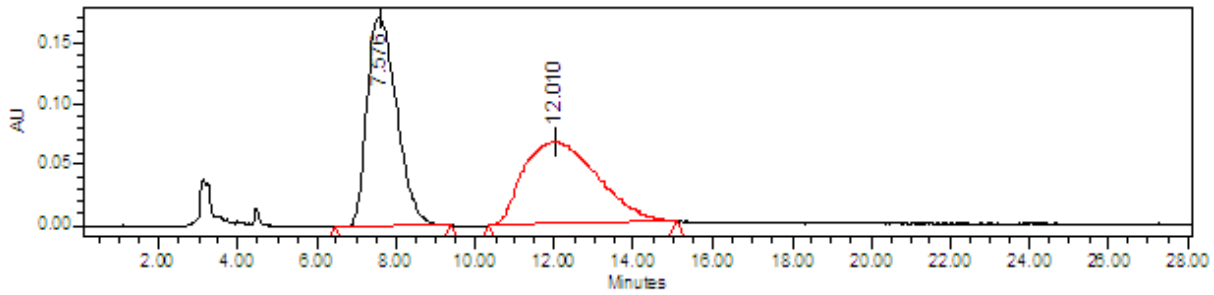


Entry	Retention Time	Area (%)	Int Type	Peak Type
1	11.699	96.51	bb	Unknown
2	25.162	3.49	bb	Unknown

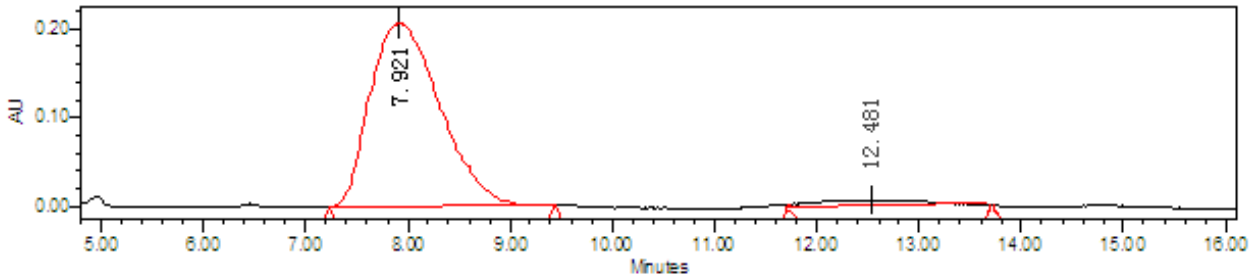
(4*S*,5*S*)-methyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxy

late: 5t





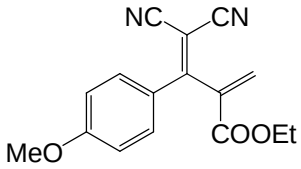
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.576	50.50	bb	Unknown
2	12.010	49.50	bb	Unknown

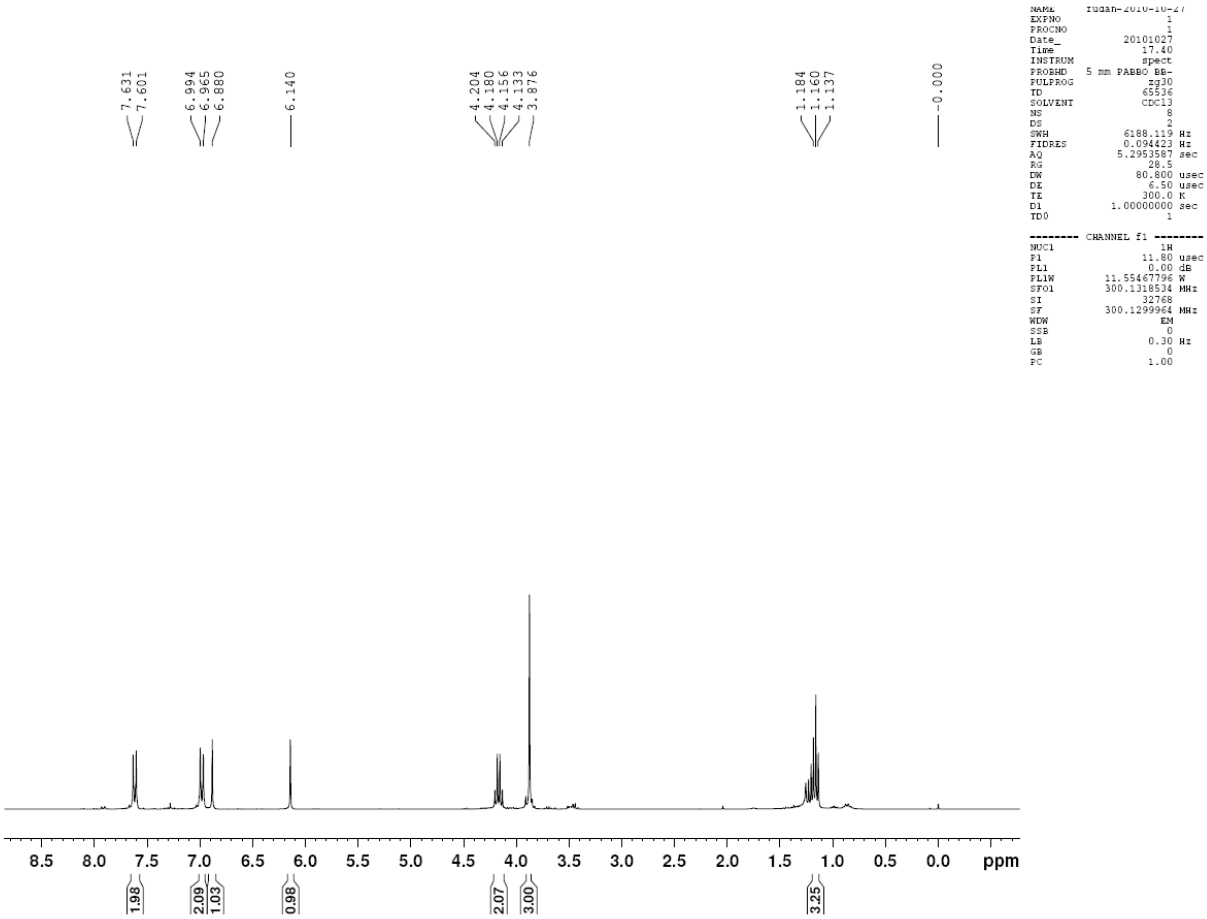


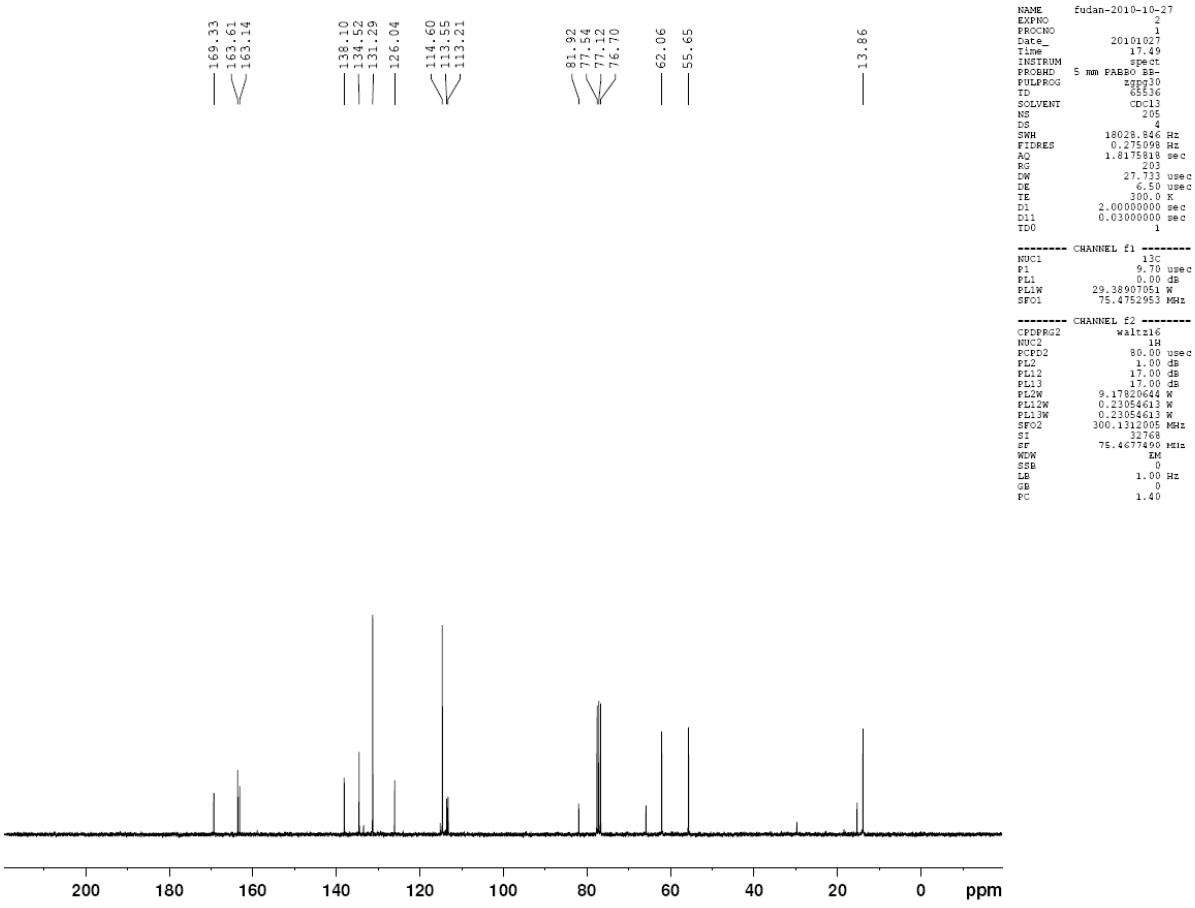
Entry	Retention Time	Area (%)	Int Type	Peak Type
1	7.921	97.89	bb	Unknown
2	12.481	2.11	bb	Unknown

8.0 Copies of NMR spectra of products

Ethyl 4,4-dicyano-3-(4-methoxyphenyl)-2-methylenebut-3-enoate: 3a

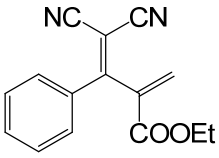


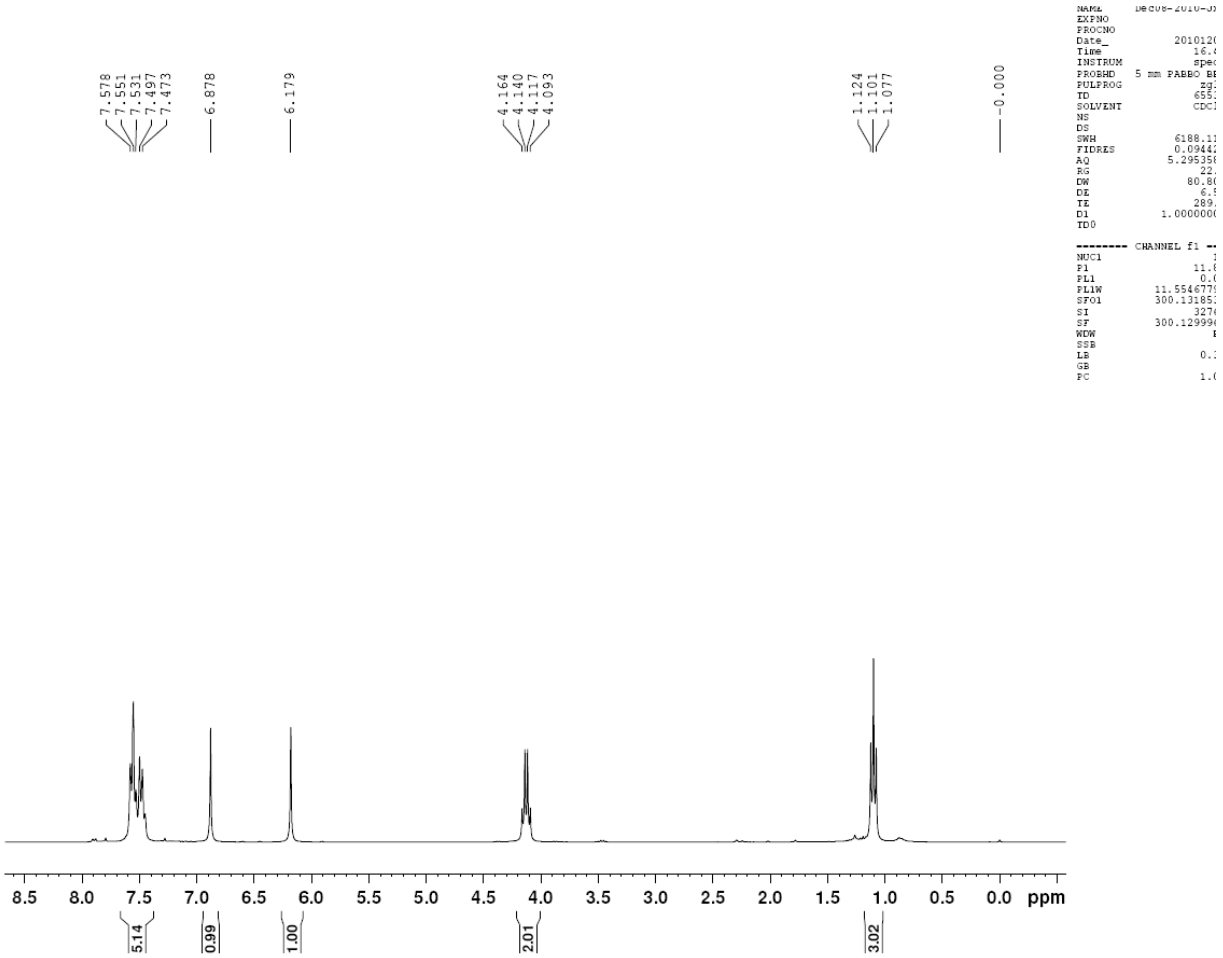


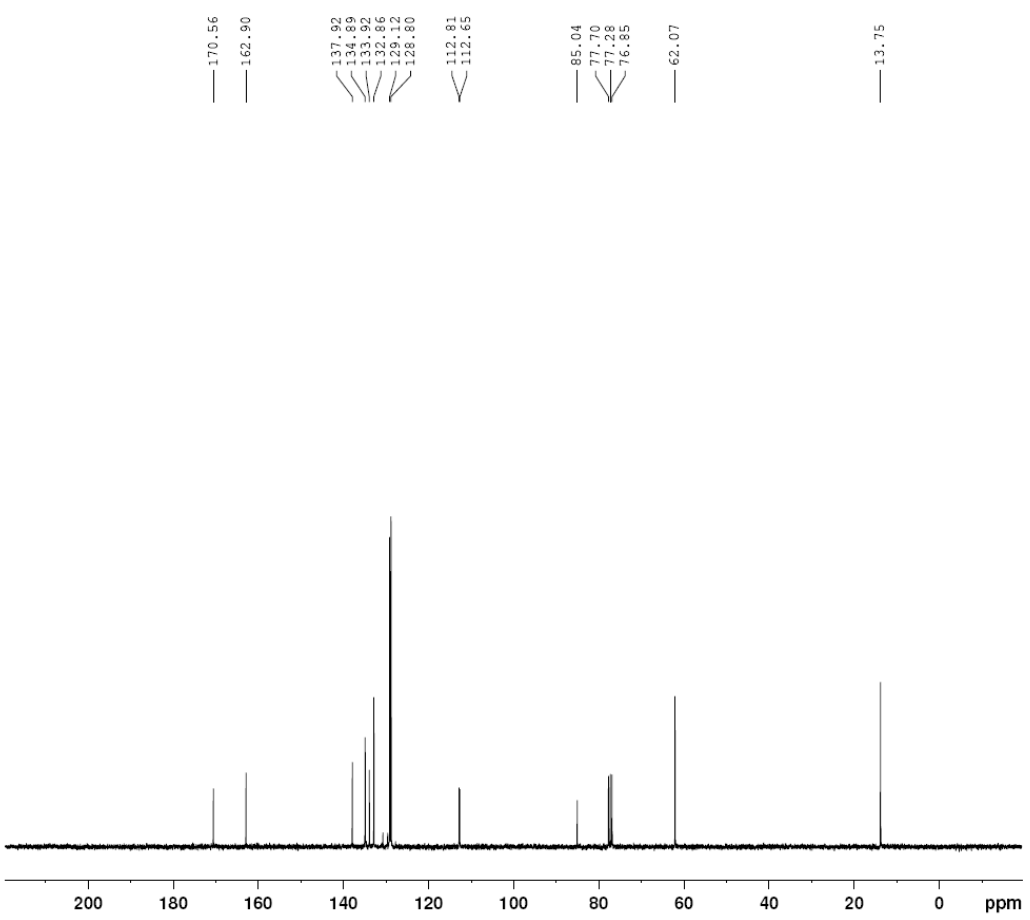



```
NAME        fudan-2010-10-27
EXPNO                     2
PROCNO                    1
Date_              20101027
Time                  17.49
INSTRUM               spect
PROBHD   5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                     205
DS                       4
SWH             18028.846 Hz
FIDRES          0.275098 Hz
AQ              1.8175818 sec
RG                     203
DW                27.733 usec
DE                 6.50 usec
TE                300.0 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.70 usec
PL1                   0.00 dB
PL1W          29.38907051 W
SFO1          75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2             waltz16
NUC2                   1H
PCPD2                80.00 usec
PL2                   1.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
PL2W           9.17820644 W
PL12W          0.23054613 W
PL13W          0.23054613 W
SFO2          300.1312005 MHz
SI                   32768
SF             75.4677490 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

Ethyl 4,4-dicyano-2-methylene-3-phenylbut-3-enoate: 3b

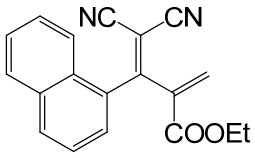


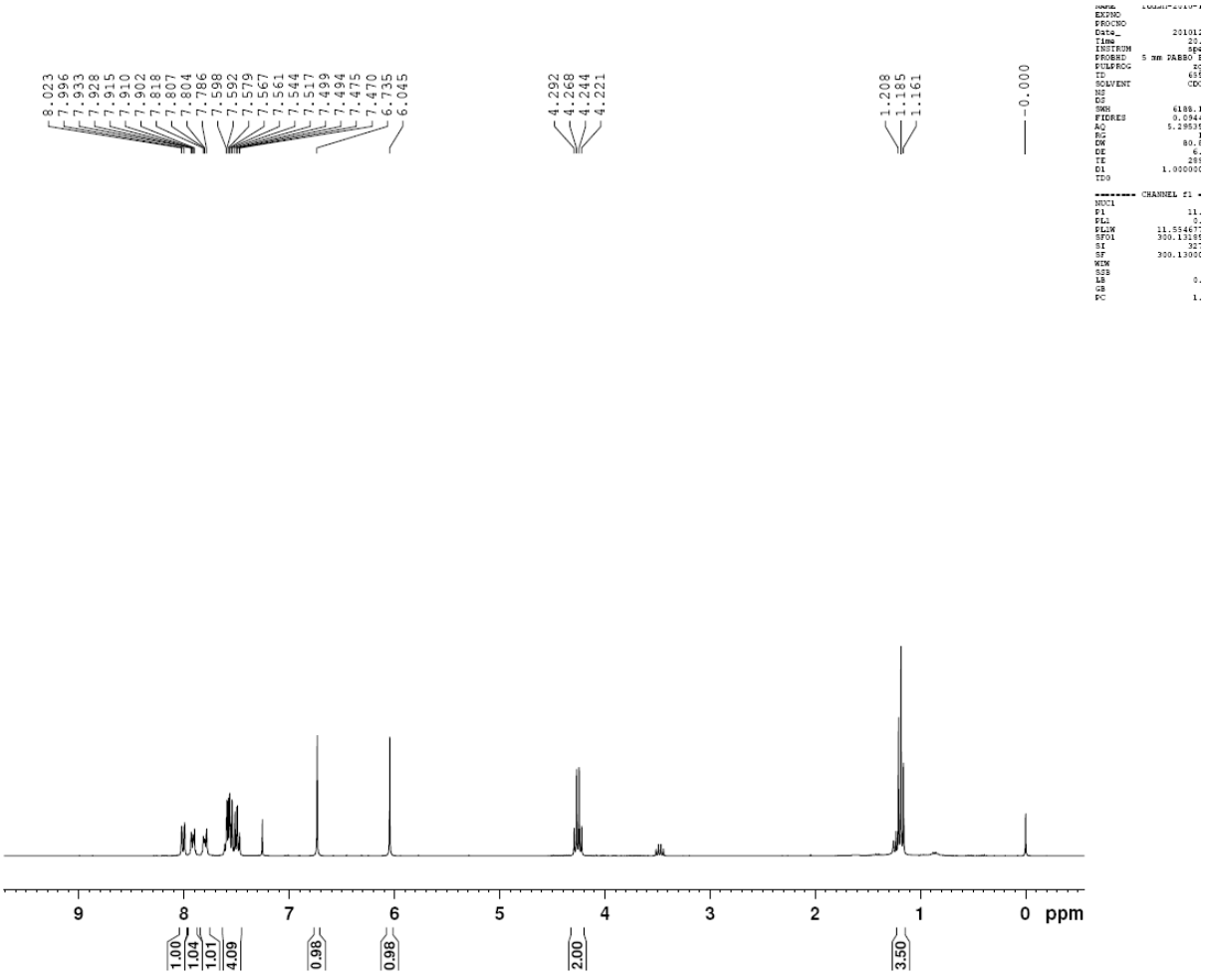


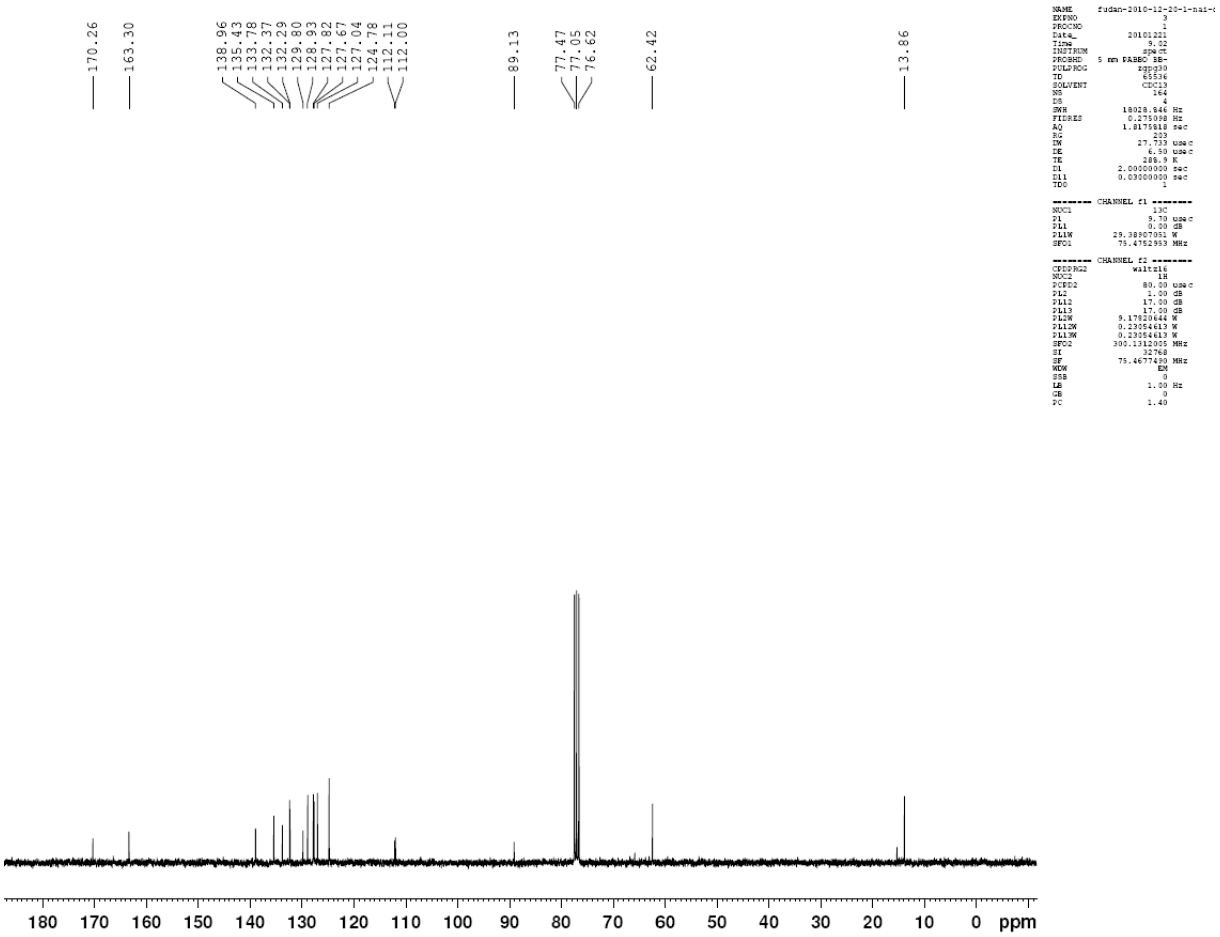



```
NAME          Dec08-2010-Jxx1
EXPNO                      2
PROCNO                     1
Date_               20101208
Time                   16.48
INSTRUM                spect
PROBHD     5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                        87
DS                         4
SWH              18028.846 Hz
FIDRES               0.275098 Hz
AQ                1.8175818 sec
RG                       203
DW                  27.733 usec
DE                    6.50 usec
TE                   290.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                     13C
P1                    9.70 usec
PL1                   0.00 dB
PL1W            29.38907051 W
SFO1             75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                80.00 usec
PL2                   1.00 dB
PL12                 17.00 dB
PL13                 17.00 dB
PL2W            9.17820644 W
PL12W           0.23054613 W
PL13W           0.23054613 W
SFO2             300.1312005 MHz
SI                    32768
SF               75.4677490 MHz
WDW                      EM
SSB                       0
LB                    1.00 Hz
GB                        0
PC                    1.40
```

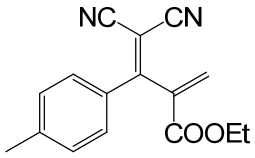
Ethyl 4,4-dicyano-2-methylene-3-(naphthalen-1-yl)but-3-enoate: 3c

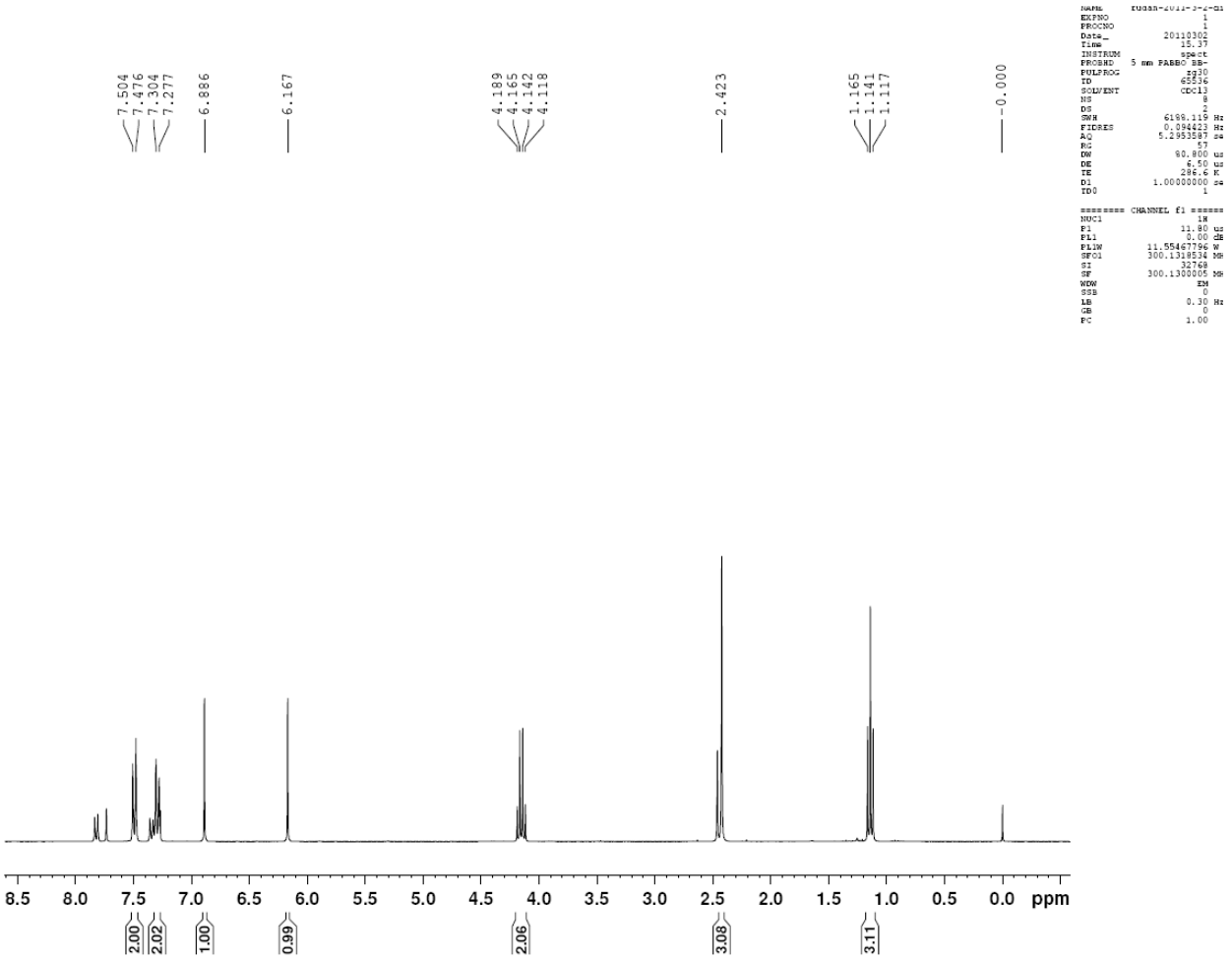


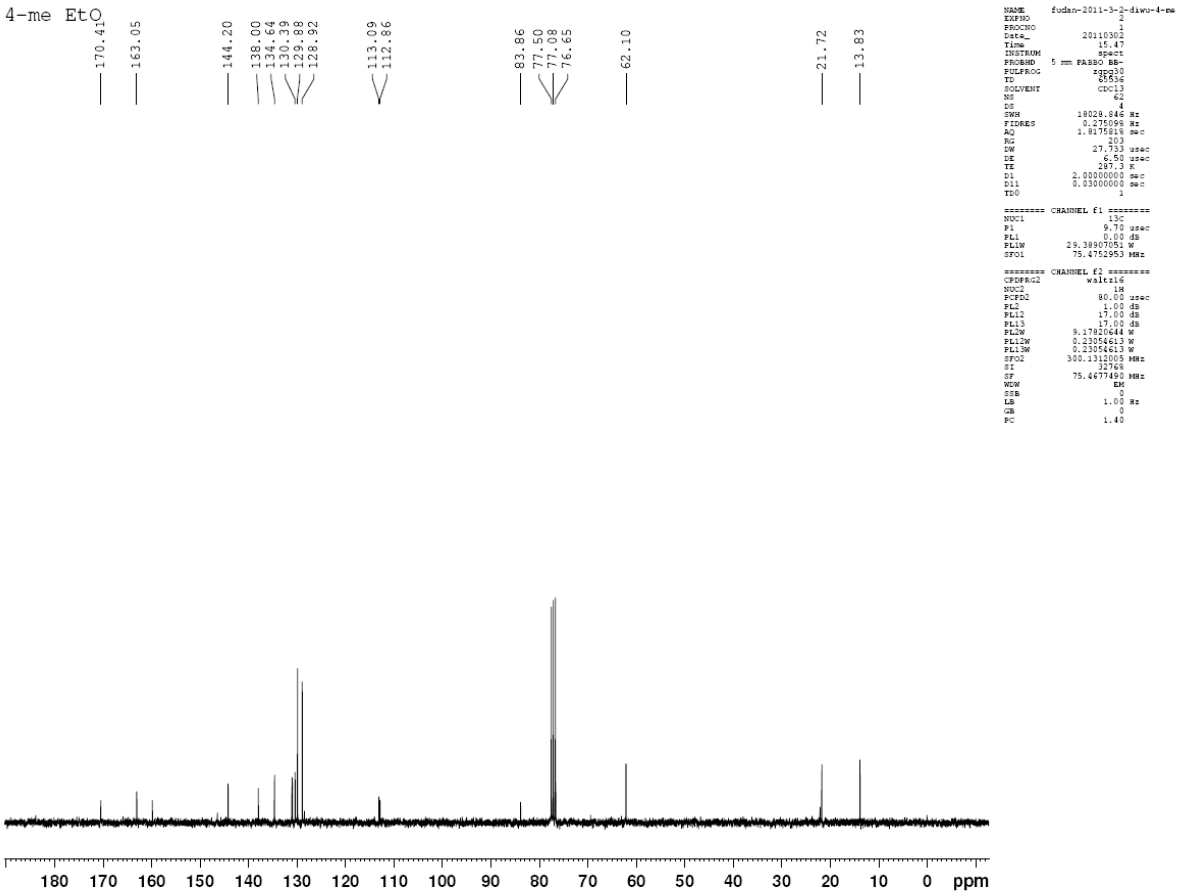



170.26
163.30
138.96
135.43
133.78
132.37
132.29
129.80
128.93
127.82
127.67
127.04
124.78
112.11
112.00
89.13
77.47
77.05
76.62
62.42
13.86
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

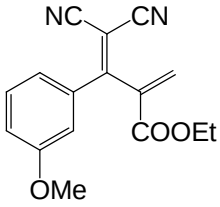
Ethyl 4,4-dicyano-2-methylene-3-p-tolylbut-3-enoate: 3d

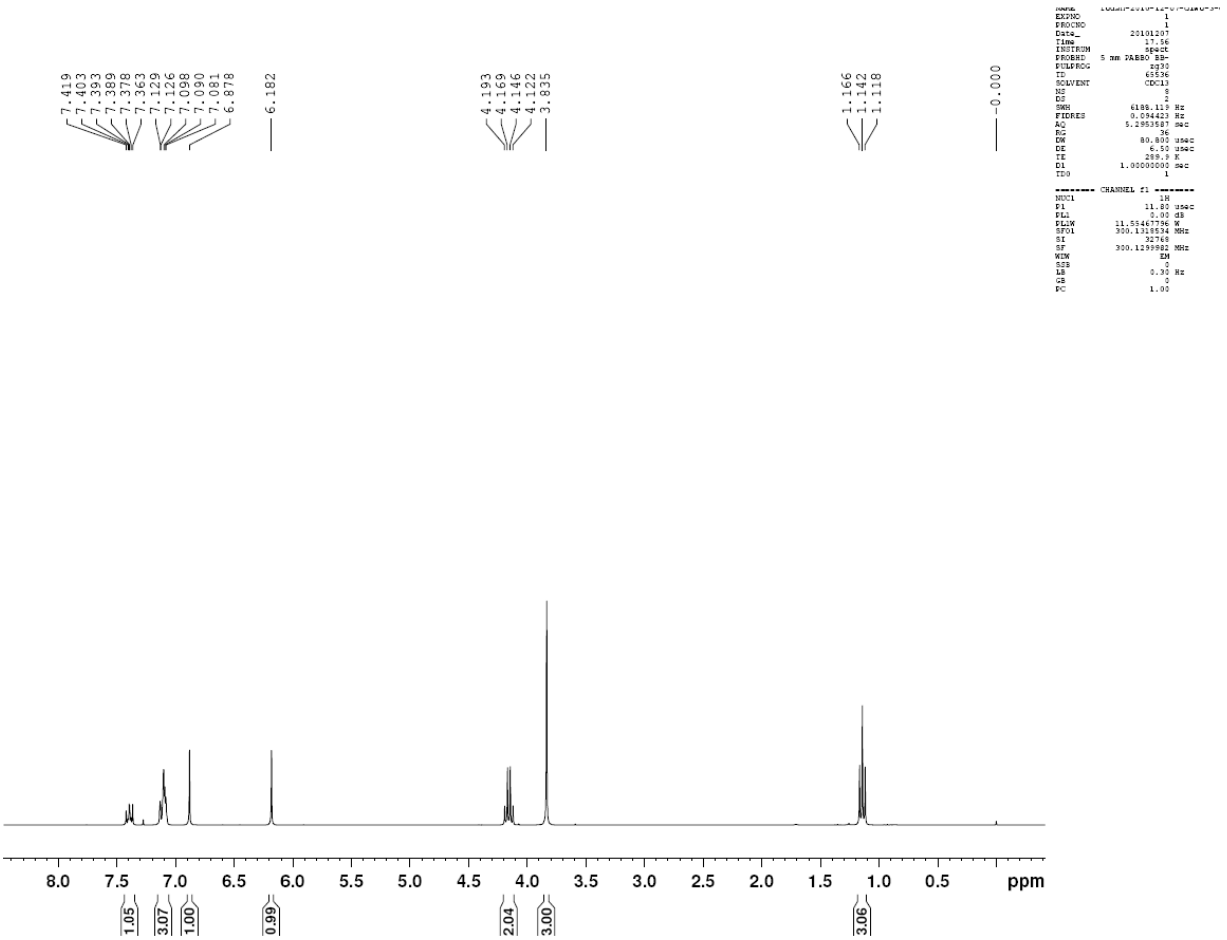


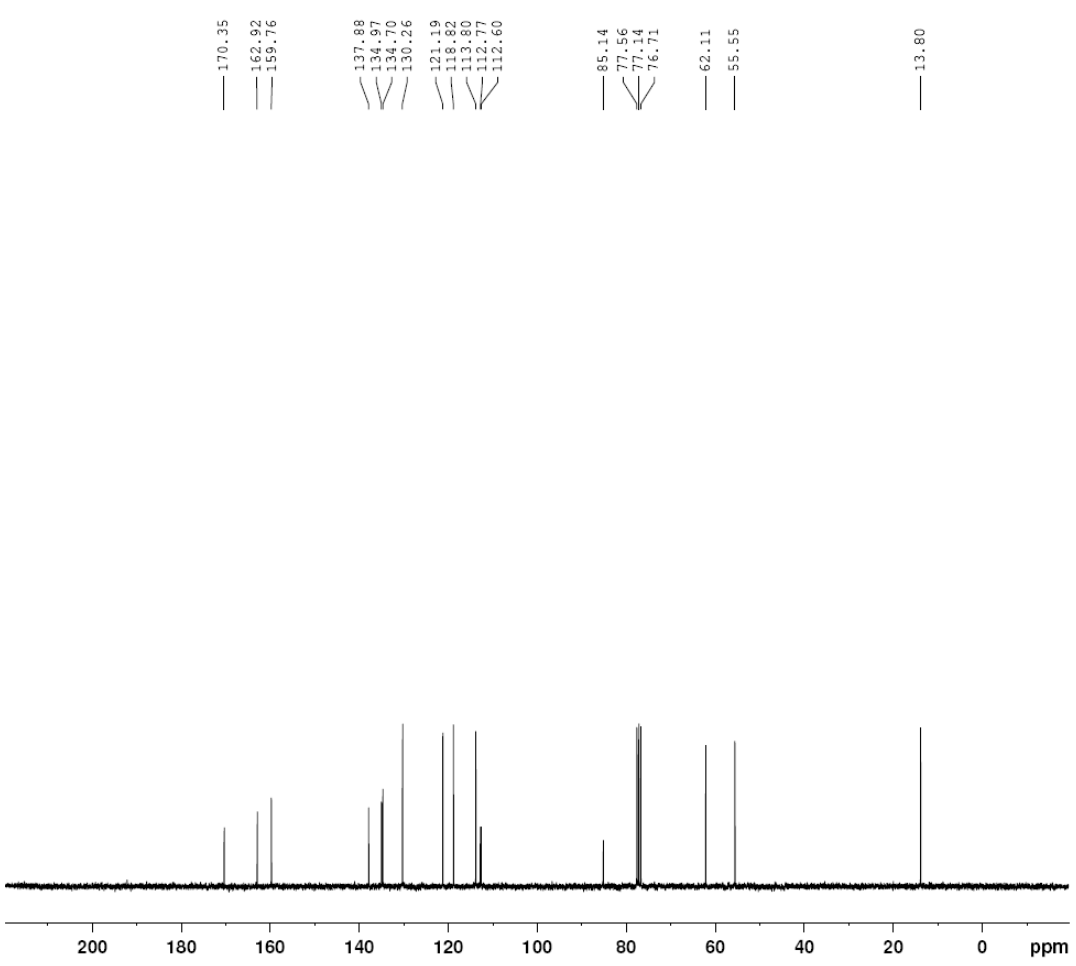



4-me EtO
170.41
163.05
144.20
138.00
134.64
130.39
129.88
128.92
113.09
112.86
83.86
77.50
77.08
76.65
62.10
21.72
13.83
NAME fudan-2011-3-2-diwu-4-me
EXPNO 2
PROCNO 1
Date_ 20110302
Time 15.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 62
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175819 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 287.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17920644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

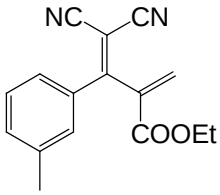
Ethyl 4,4-dicyano-3-(3-methoxyphenyl)-2-methylenebut-3-enoate: 3e

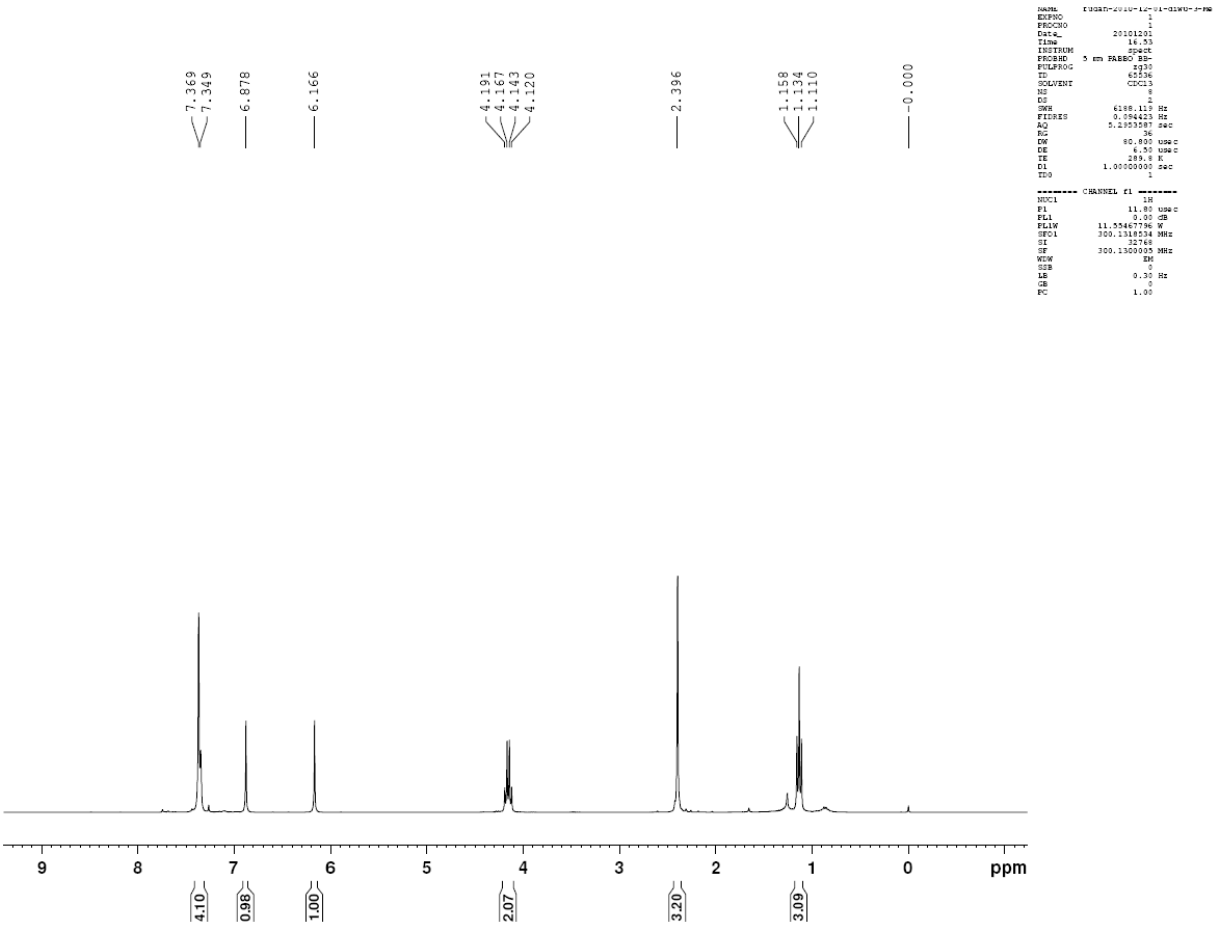


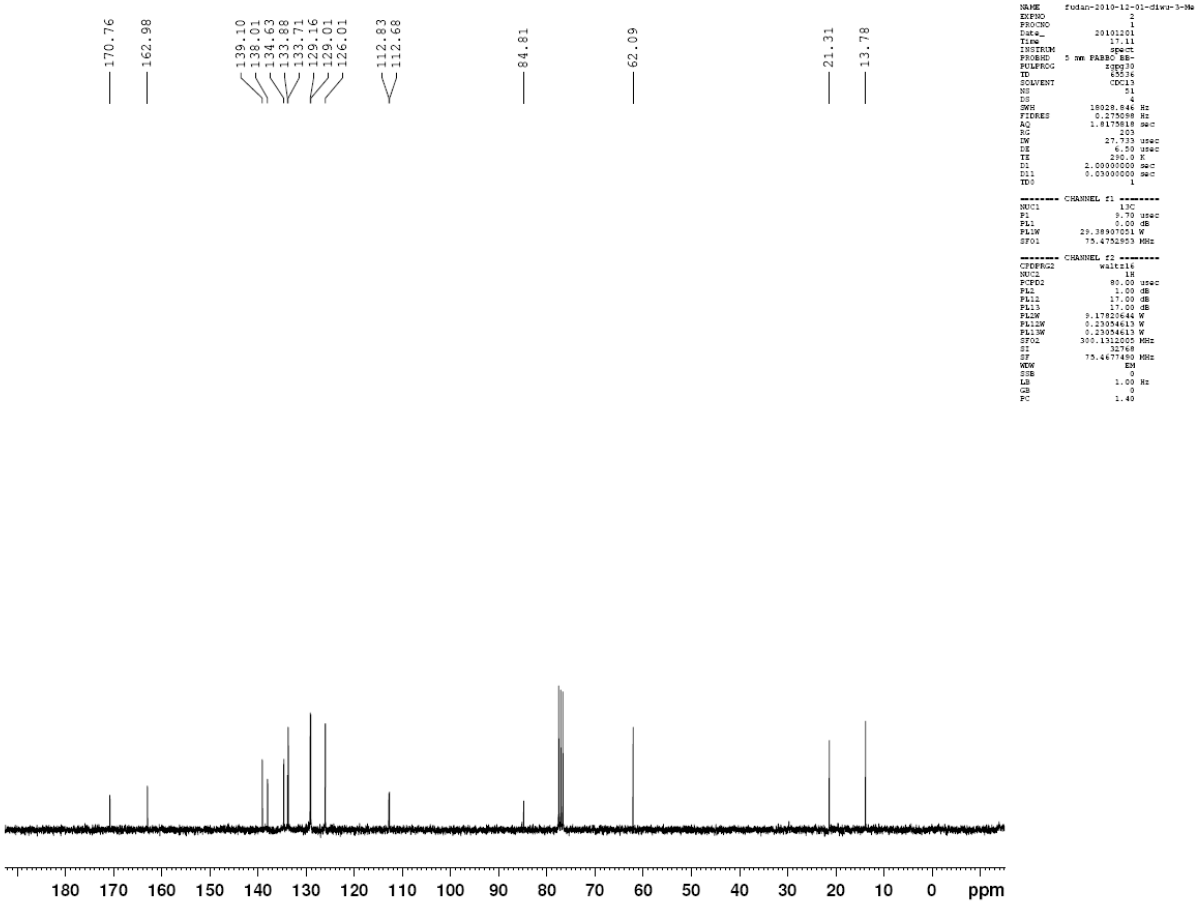



170.35
162.92
159.76
137.88
134.97
134.70
130.26
121.19
118.82
113.80
112.77
112.60
85.14
77.56
77.14
76.71
62.11
55.55
13.80
200
180
160
140
120
100
80
60
40
20
0
ppm

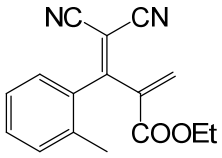
Ethyl 4,4-dicyano-2-methylene-3-m-tolylbut-3-enoate: 3f

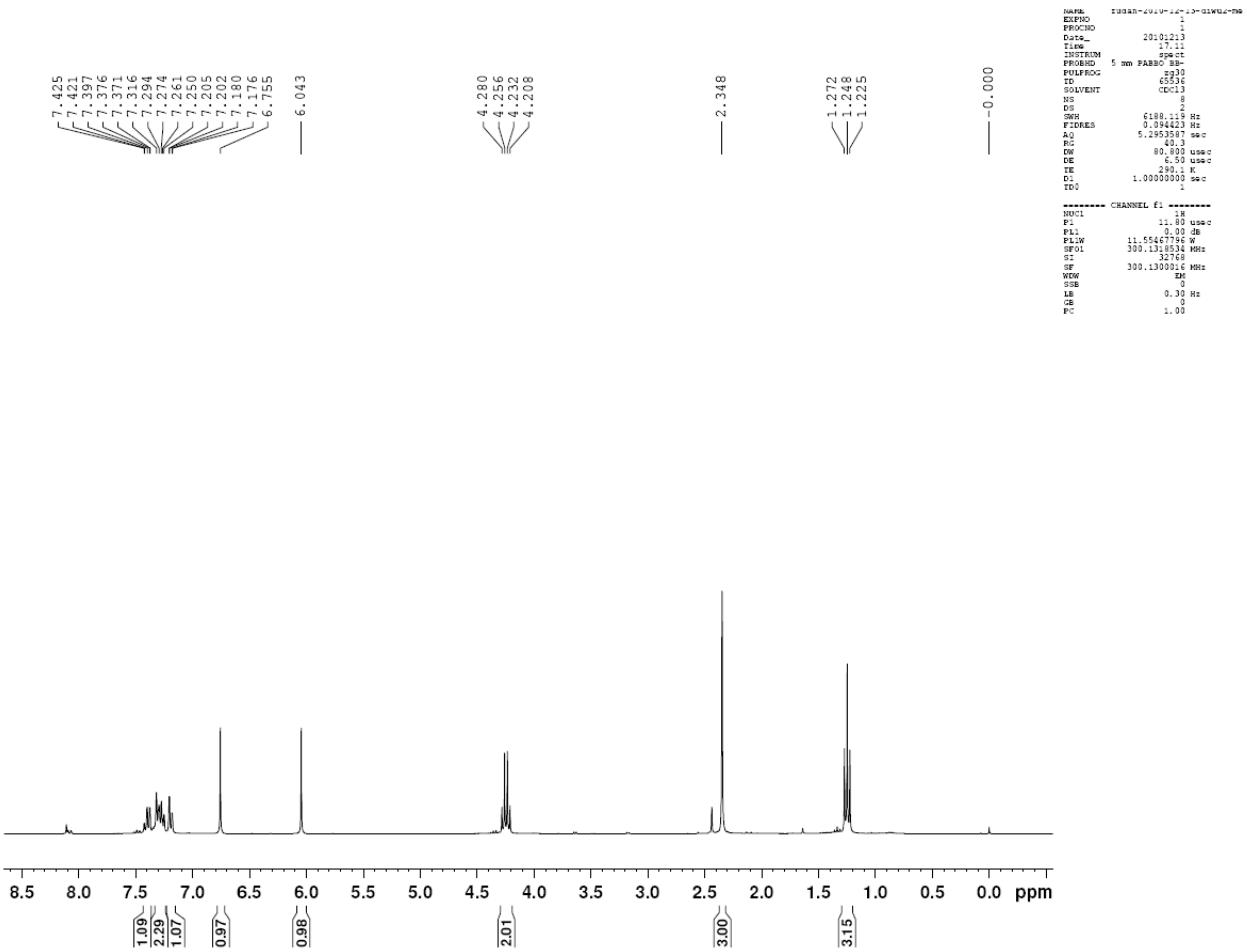


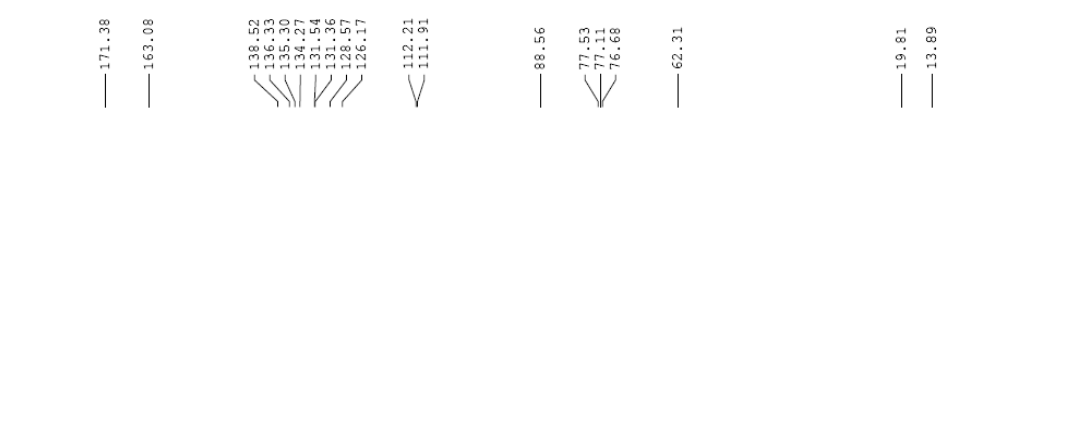



170.76
162.98
139.10
138.01
134.63
133.88
133.71
129.16
129.01
126.01
112.83
112.68
84.81
62.09
21.31
13.78
NAME fudan-2010-12-01-diwu-3-Me
EXPNO 2
PROCNO 1
Date_ 20101201
Time 17.11
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 51
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752853 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL1 1.00 dB
PL11 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

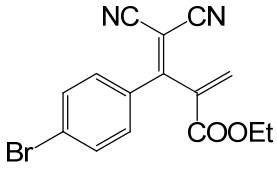
Ethyl 4,4-dicyano-2-methylene-3-o-tolylbut-3-enoate: 3g

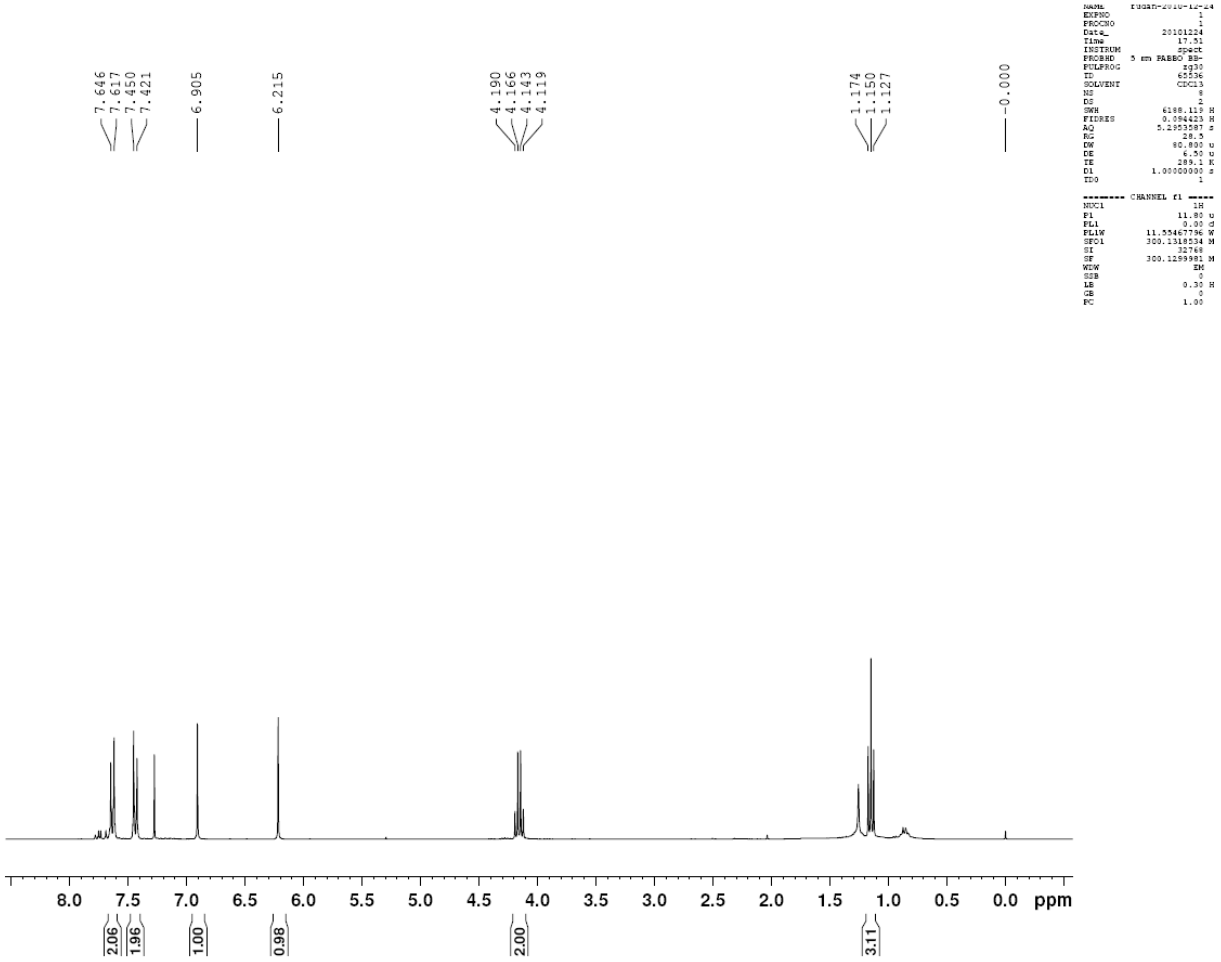


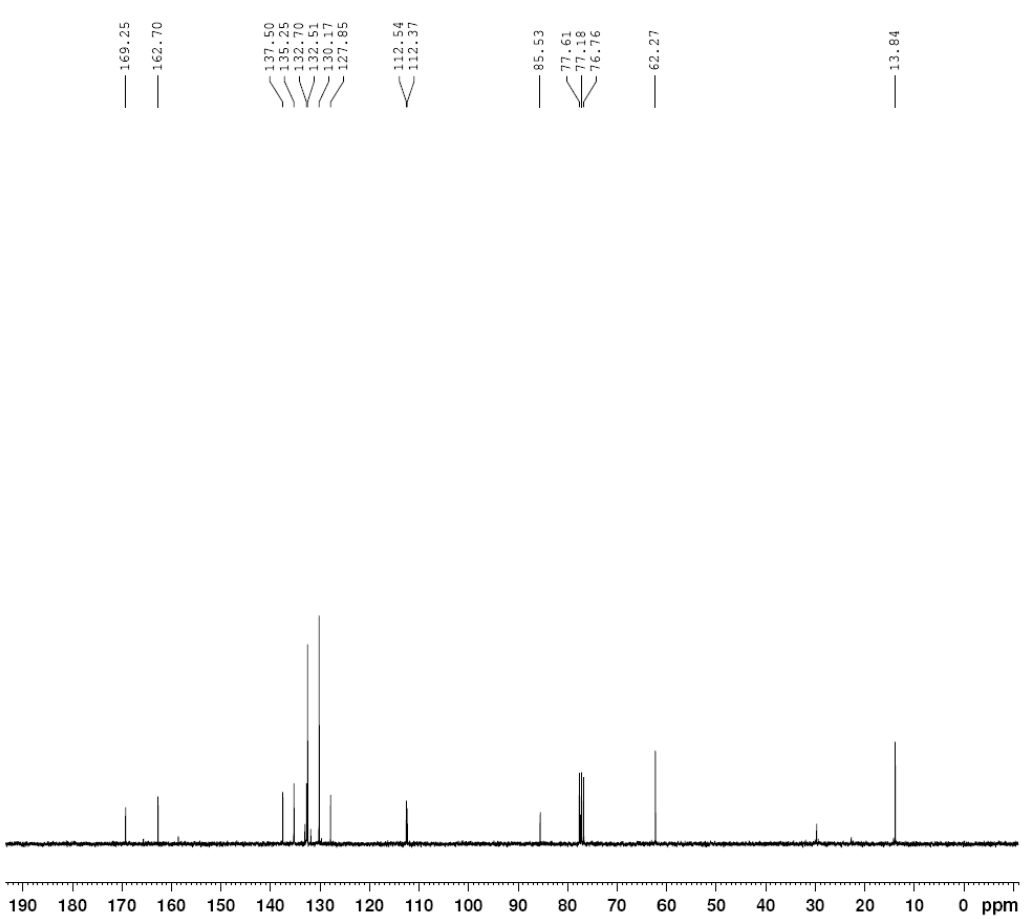



171.38
163.08
138.52
136.33
135.30
134.27
131.54
131.36
128.57
126.17
112.21
111.91
88.56
77.53
77.11
76.68
62.31
19.81
13.89
NAME fudan-2010-12-13-diwu2-
EXPNO 2
PROCNO 1
Date_ 20101213
Time 17.16
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 70
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17826644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

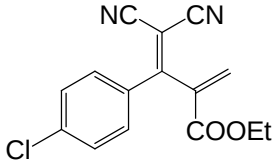
Ethyl 3-(4-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3h

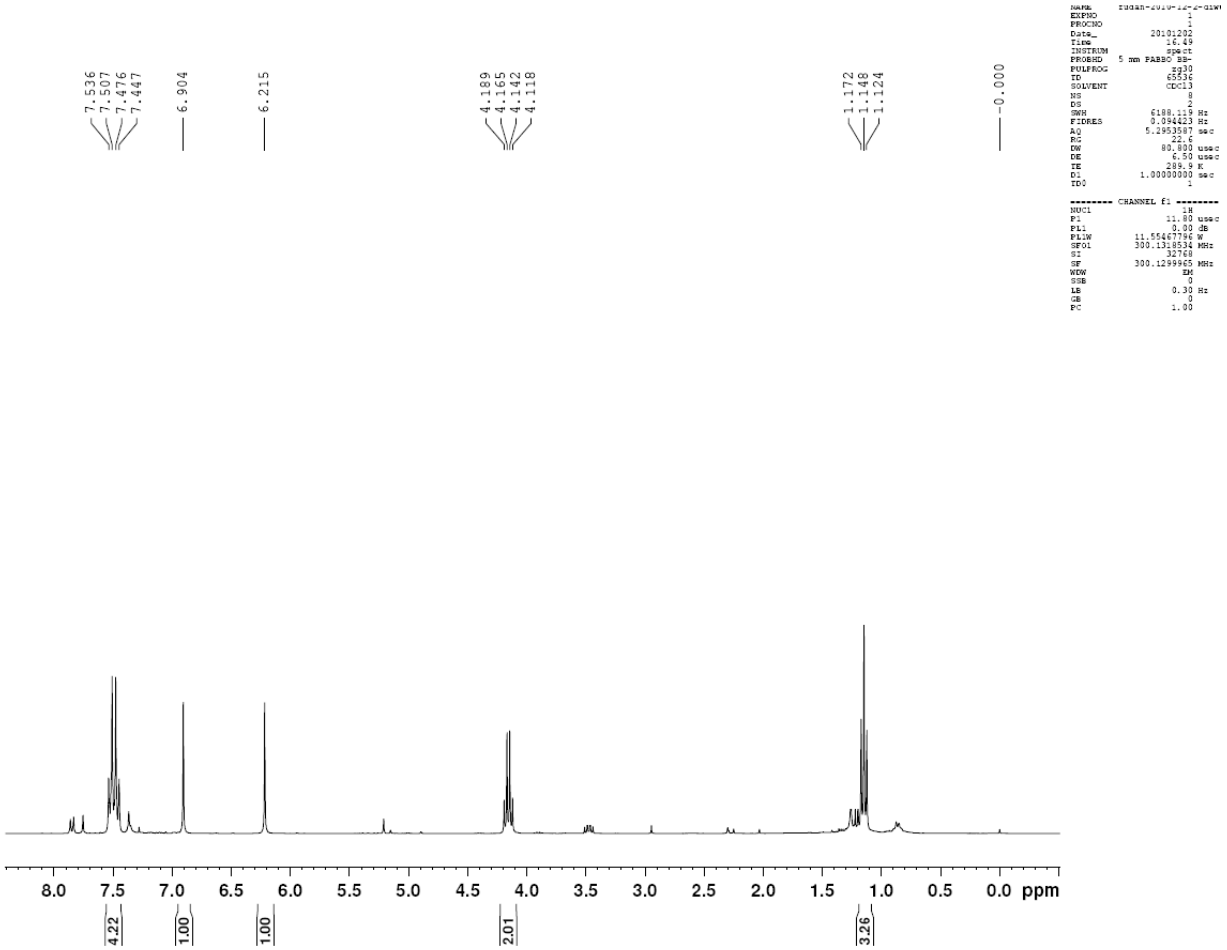


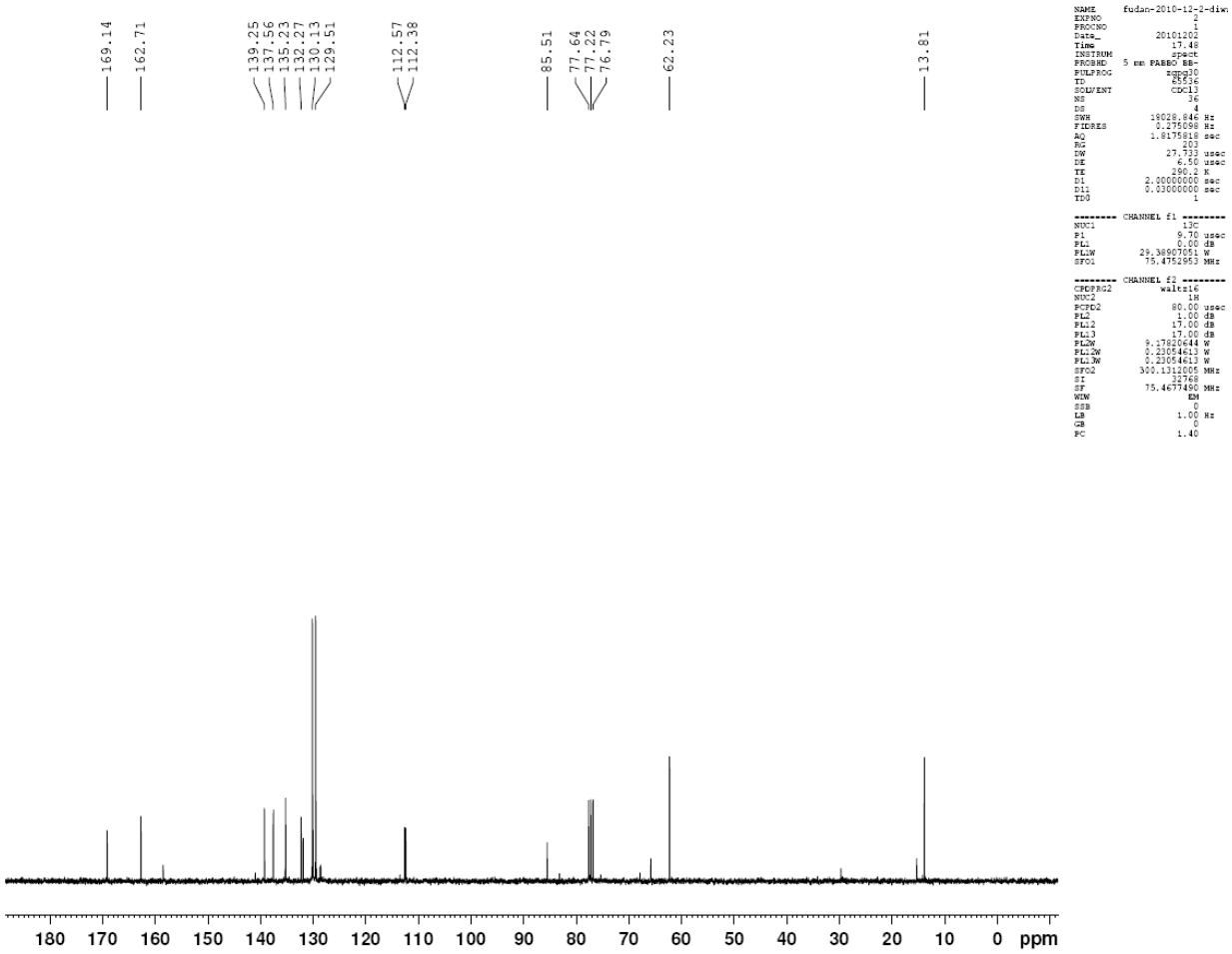



169.25
162.70
137.50
135.25
132.70
132.51
130.17
127.85
112.54
112.37
85.53
77.61
77.18
76.76
62.27
13.84
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

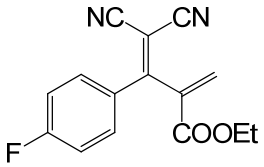
Ethyl 3-(4-chlorophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3i

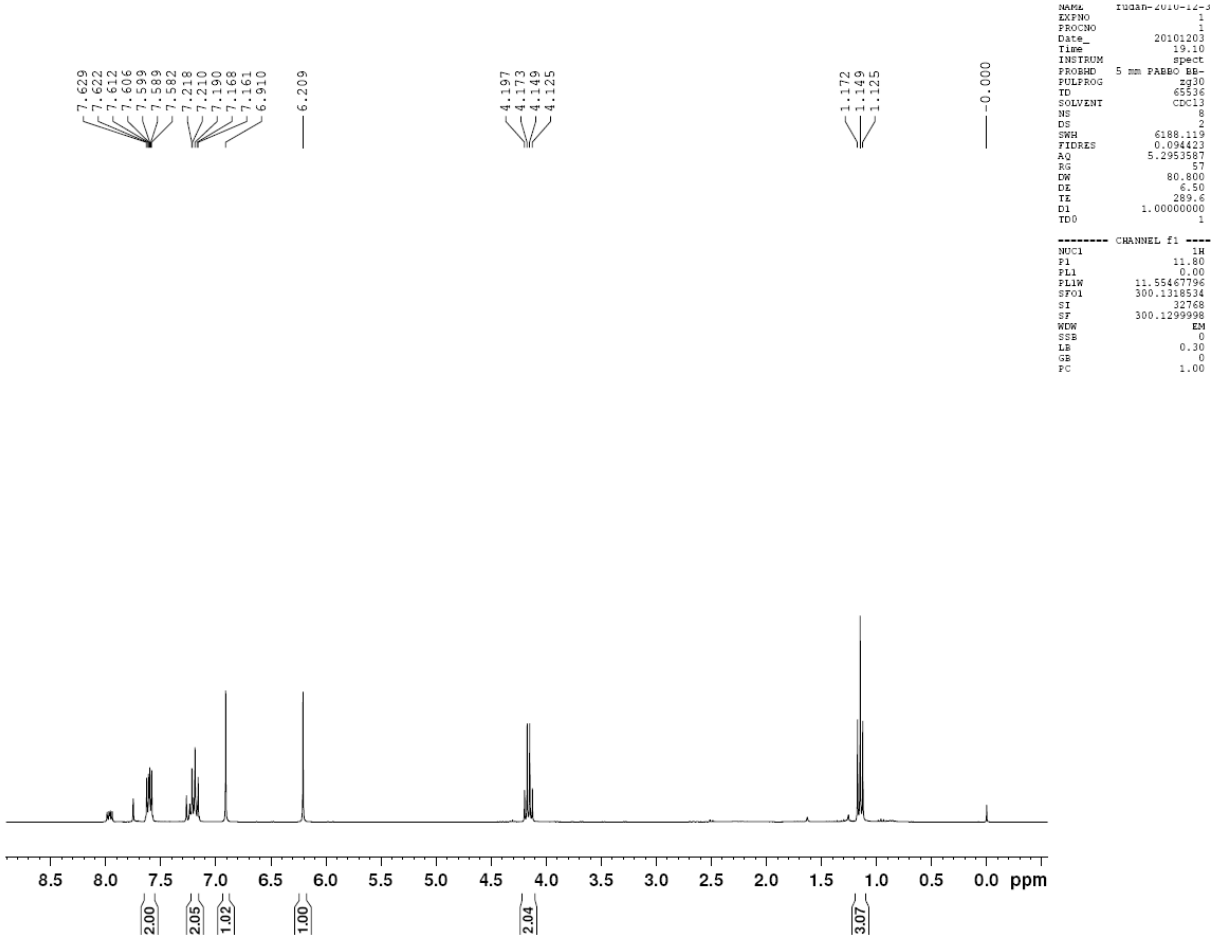


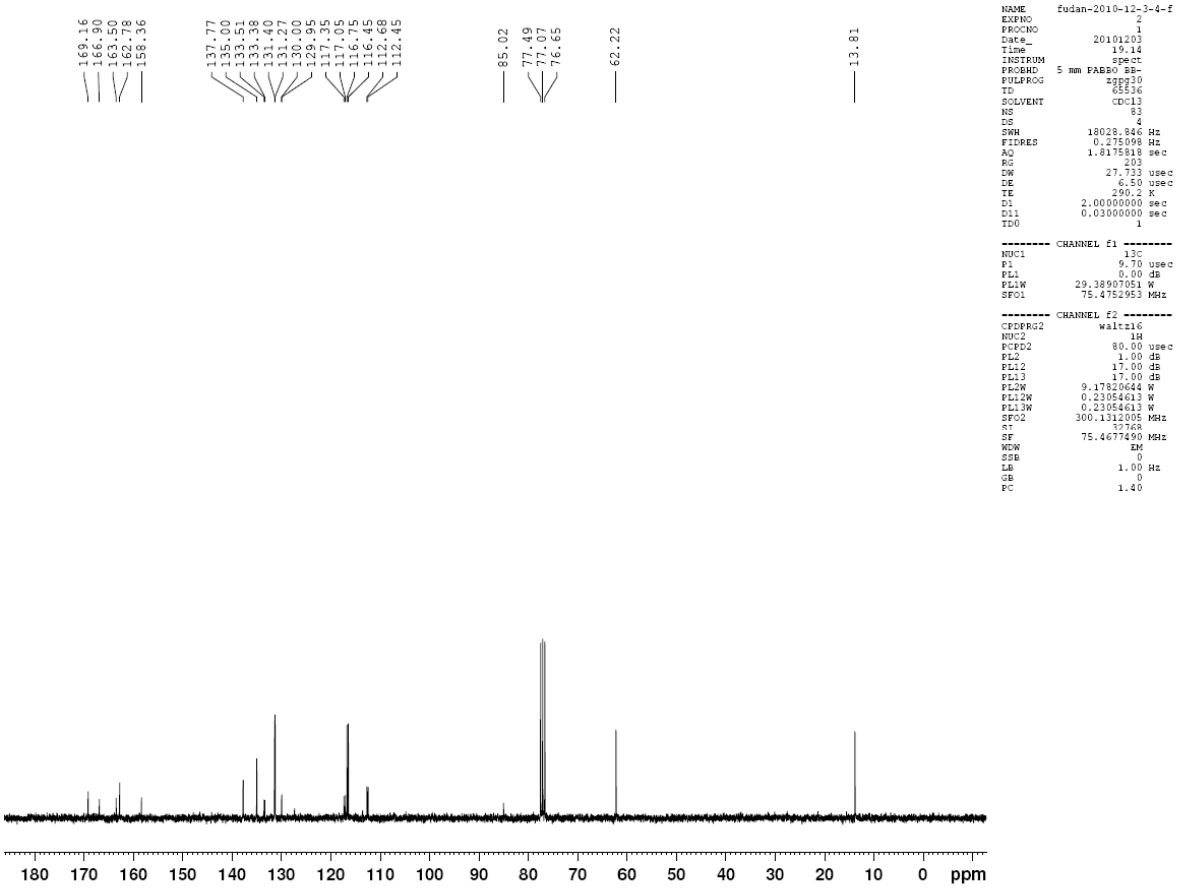



169.14
162.71
139.25
137.56
135.23
132.27
130.13
129.51
112.57
112.38
85.51
77.64
77.22
76.79
62.23
13.81
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Ethyl 4,4-dicyano-3-(4-fluorophenyl)-2-methylenebut-3-enoate: 3j

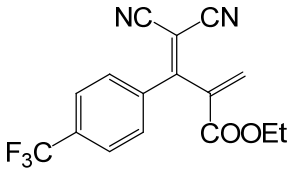


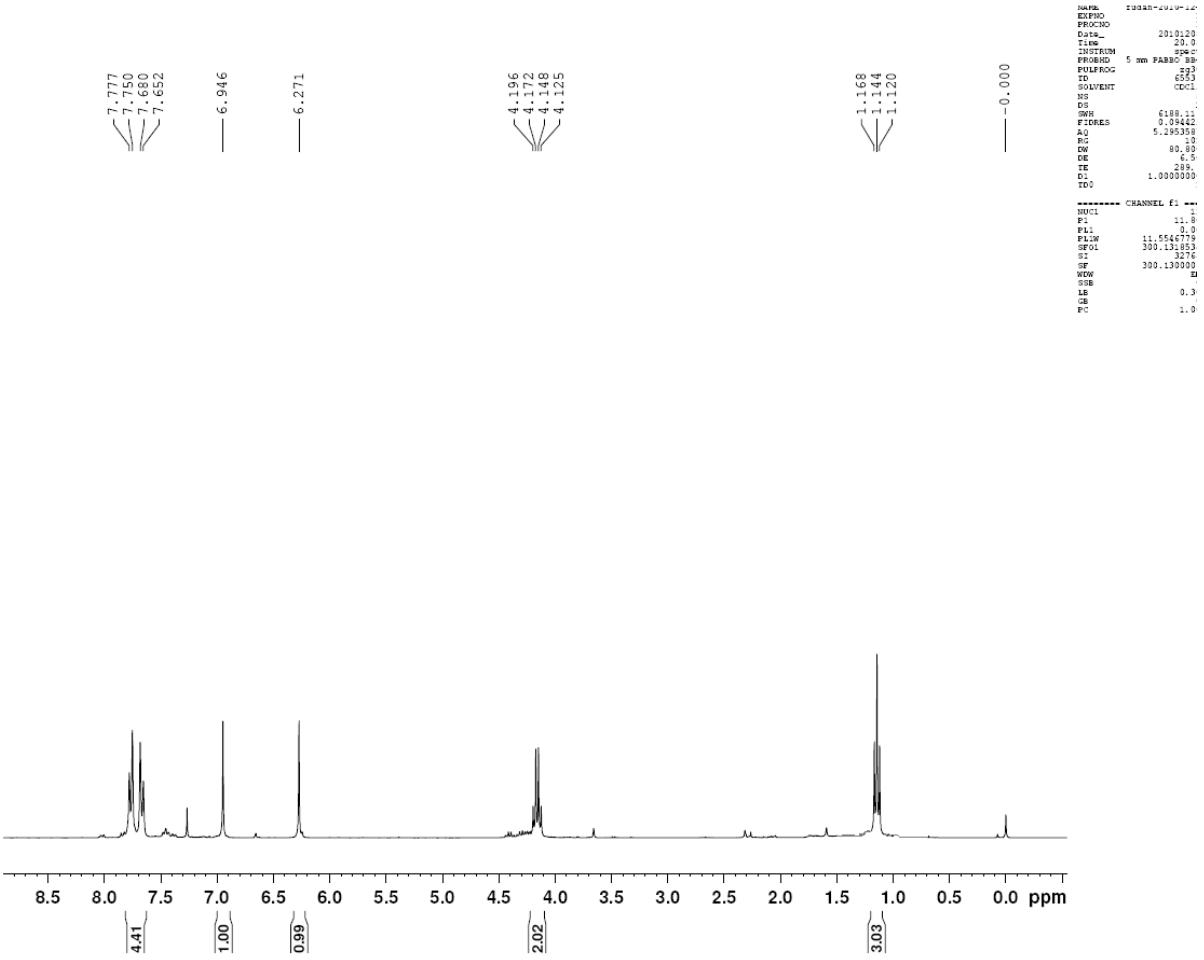


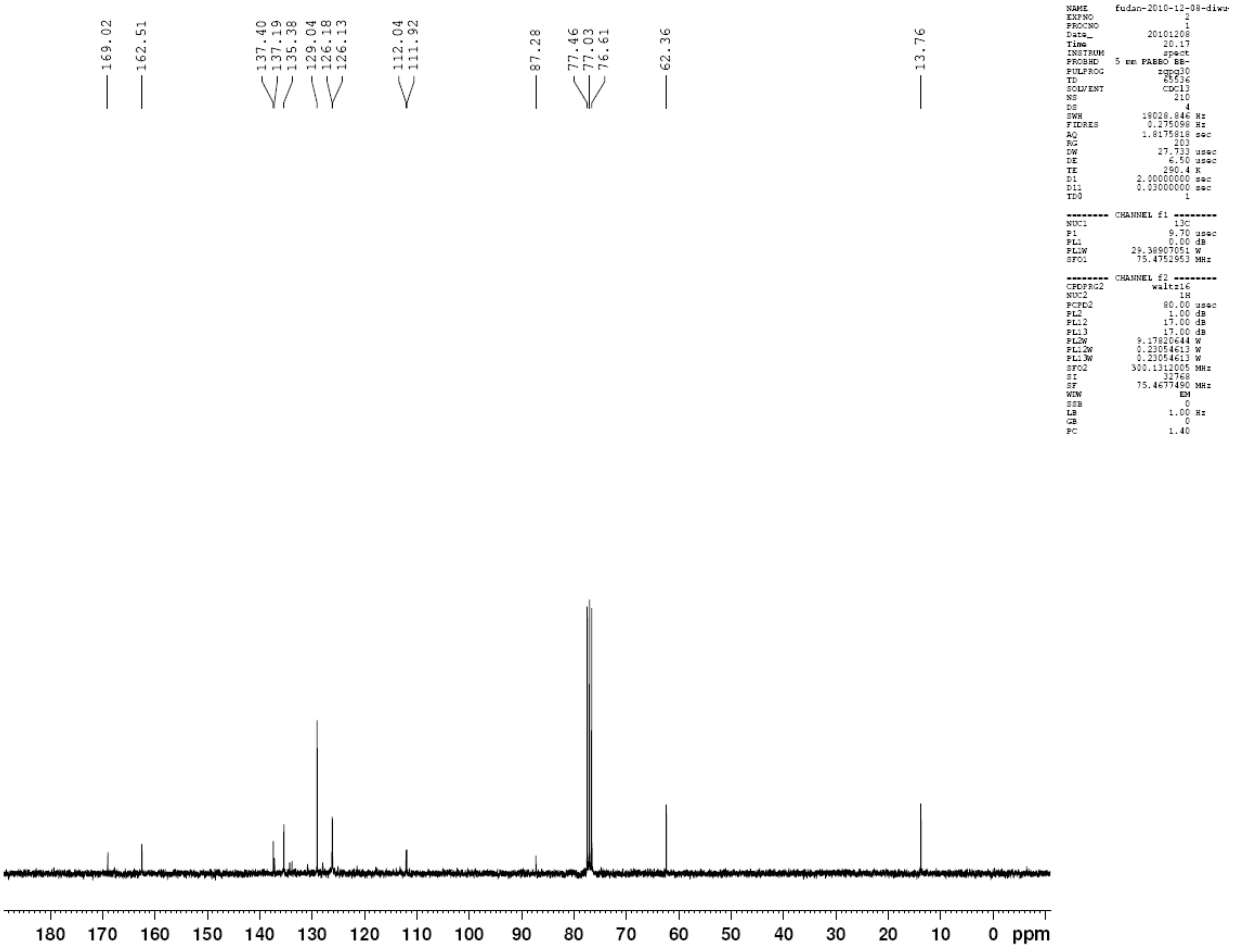


NAME	fudan-2010-12-3-4-f
EXPNO	2
PROCNO	1
Date_	20101203
Time	19.14
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	83
DS	4
SWH	18028.846 Hz
FIDRES	0.275098 Hz
AQ	1.8175818 sec
RG	203
DW	27.733 usec
DE	6.50 usec
TE	290.2 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
--------- CHANNEL f1 ---------	
NUC1	13C
P1	9.70 usec
PL1	0.00 dB
PL1W	29.38907051 W
SFO1	75.4752953 MHz
--------- CHANNEL f2 ---------	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	17.00 dB
PL13	17.00 dB
PL2W	9.17820644 W
PL12W	0.23054613 W
PL13W	0.23054613 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677490 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

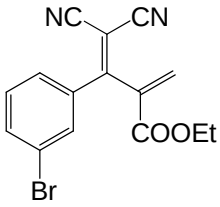
Ethyl 4,4-dicyano-2-methylene-3-(4-(trifluoromethyl)phenyl)but-3-enoate: 3k

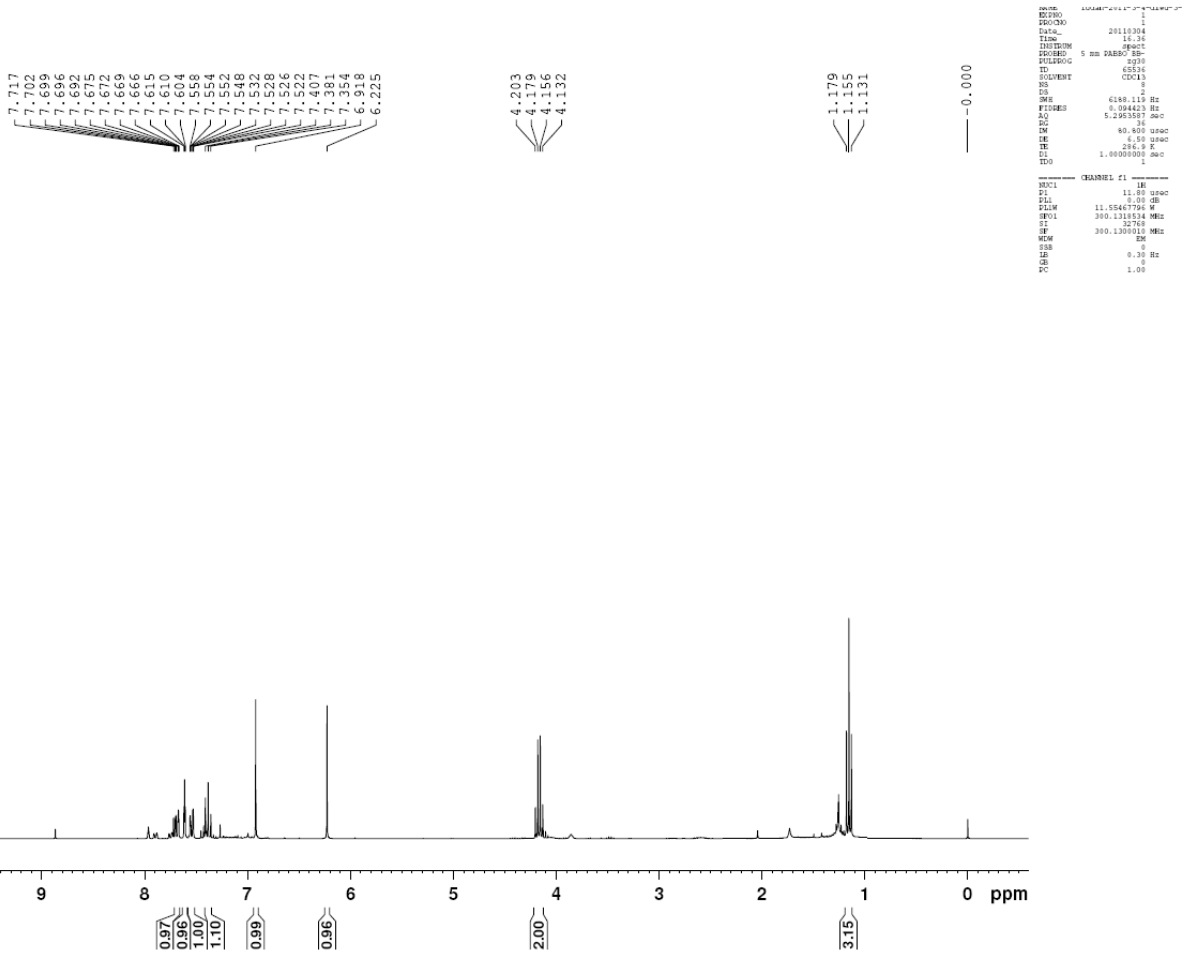


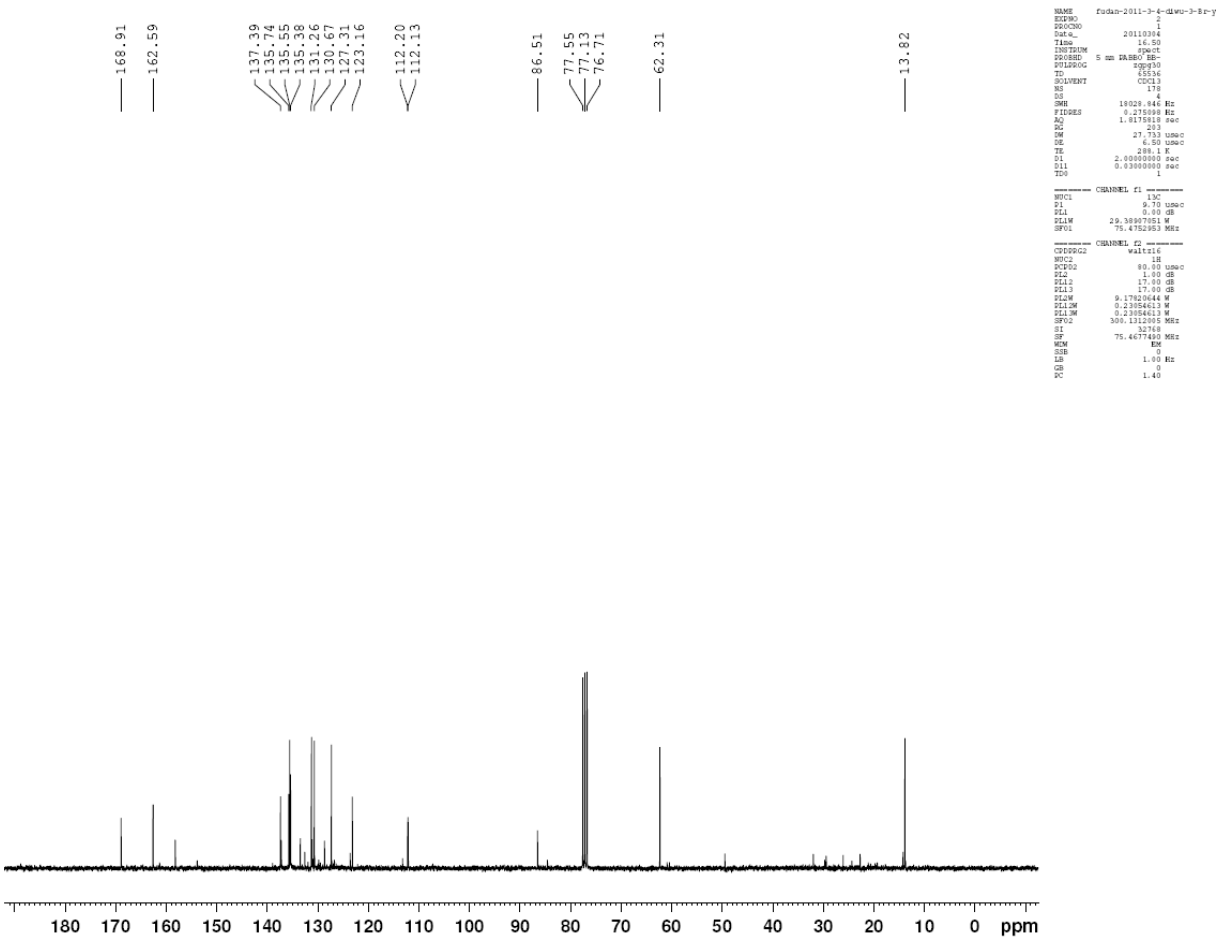



169.02
162.51
137.40
137.19
135.38
129.04
126.18
126.13
112.04
111.92
87.28
77.46
77.03
76.61
62.36
13.76
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

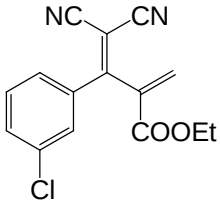
Ethyl 3-(3-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3l

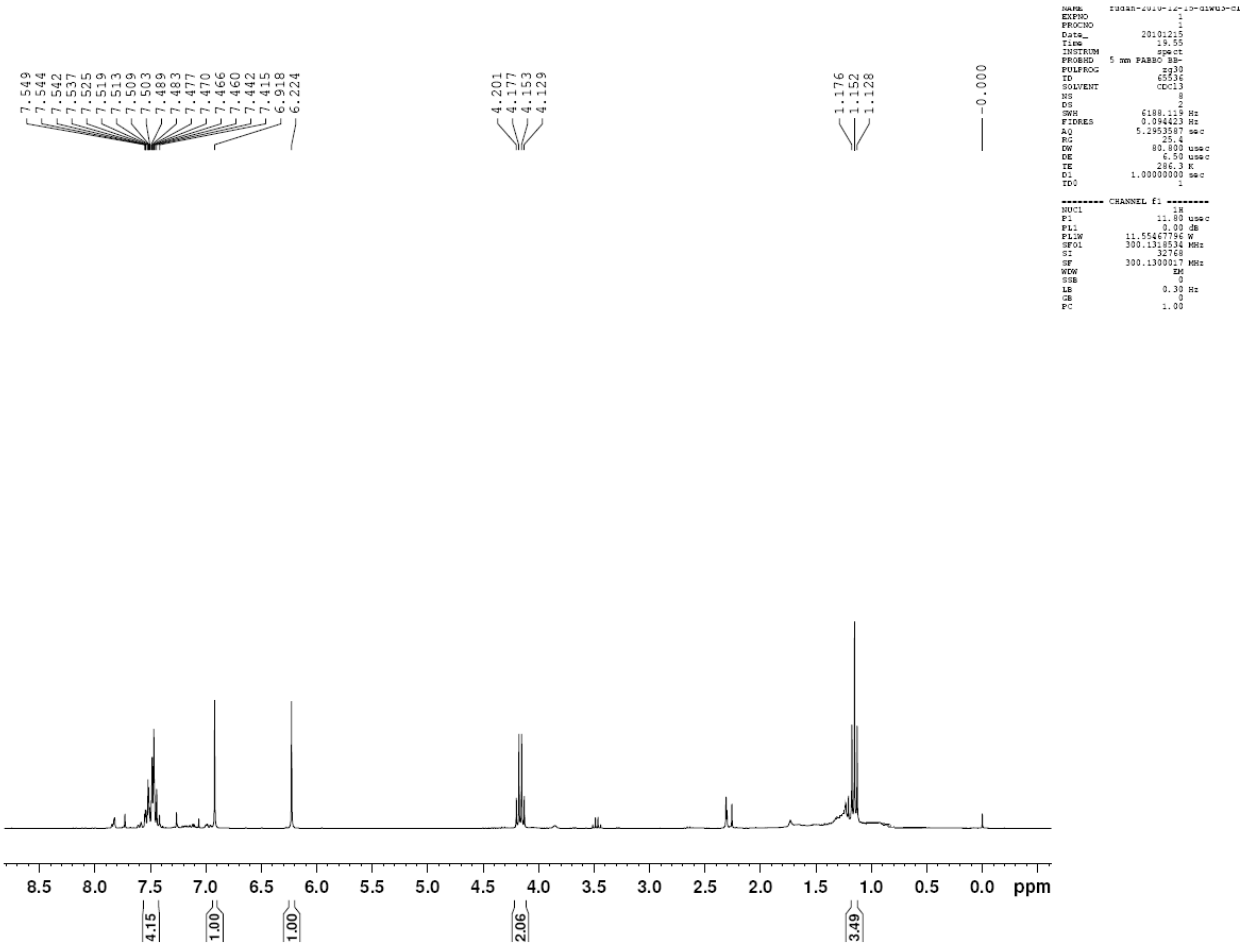


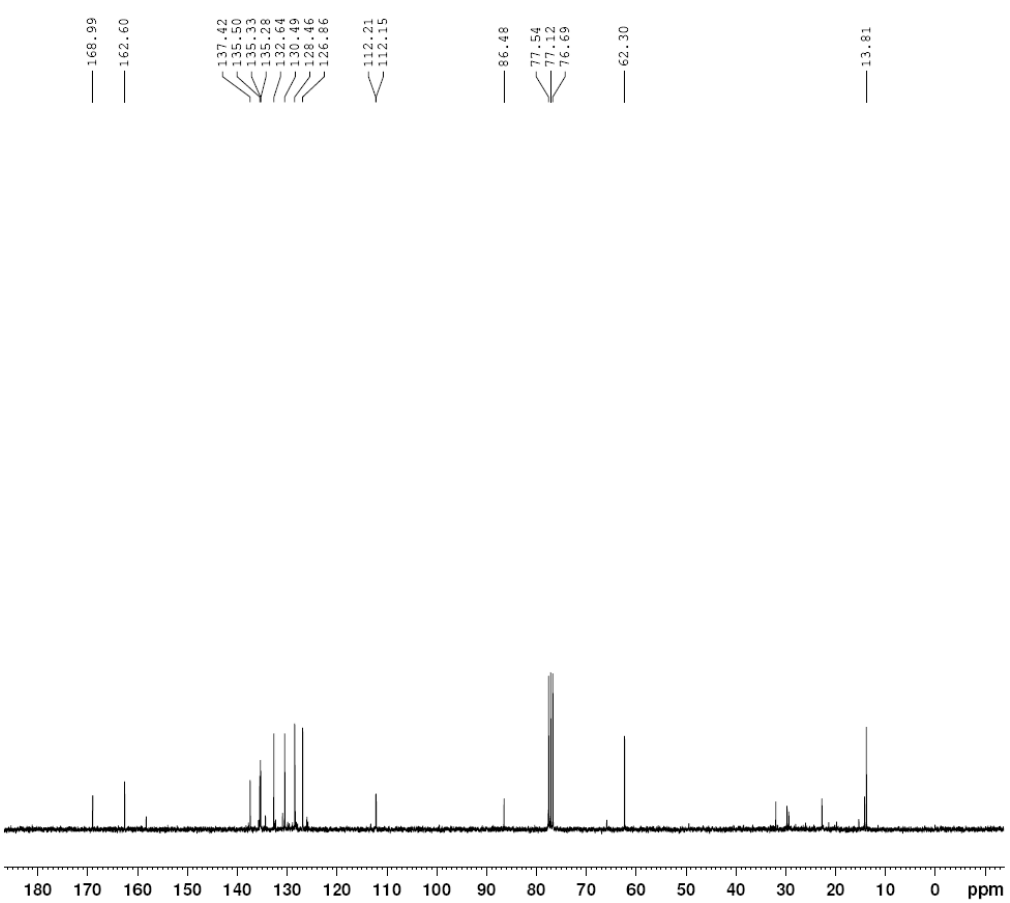



168.91
162.59
137.39
135.74
135.55
135.38
131.26
130.67
127.31
123.16
112.20
112.13
86.51
77.55
77.13
76.71
62.31
13.82
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Ethyl 3-(3-chlorophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3m

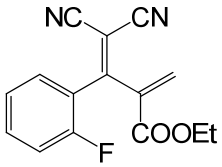


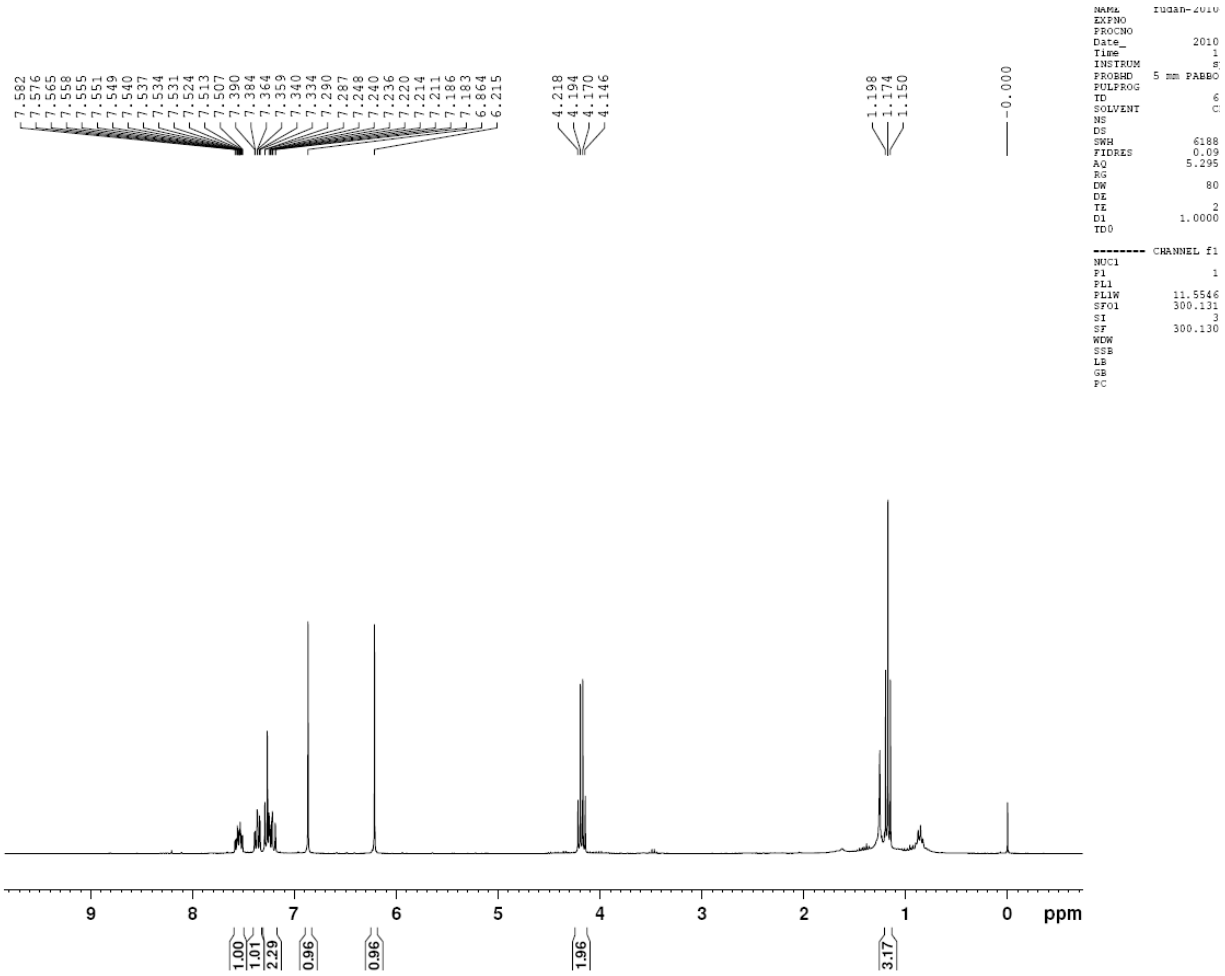


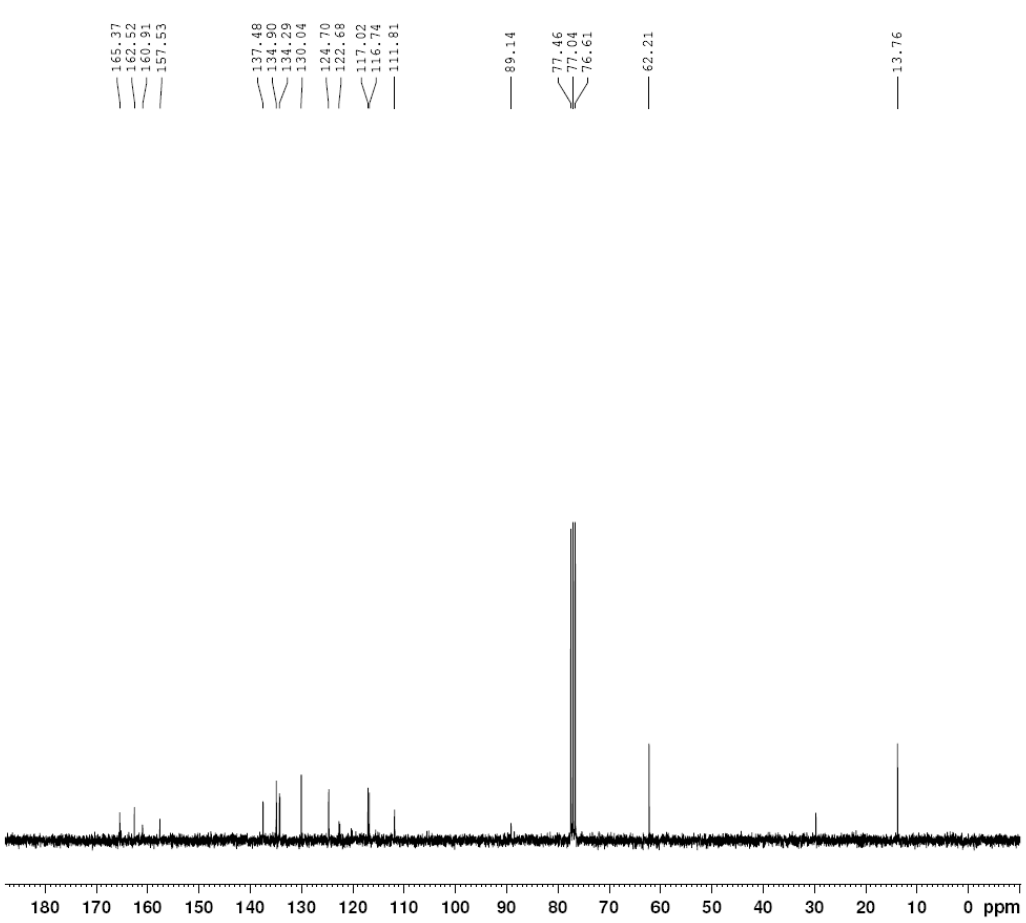



```
NAME        fudan-2010-12-15-diwa3-c1
EXPNO                              2
PROCNO                             1
Date_                       20101215
Time                           19.59
INSTRUM                         spect
PROBHD     5 mm PABBO BB/
PULPROG                     zgpg30
TD                              65536
SOLVENT                         CDCl3
NS                                112
DS                                  4
SWH                       18028.846 Hz
FIDRES                     0.275098 Hz
AQ                         1.8175818 sec
RG                               203
DW                          27.733 usec
DE                           6.50 usec
TE                          286.7 K
D1                      2.00000000 sec
D11                     0.03000000 sec
TD0                                1

======== CHANNEL f1 ========
NUC1                             13C
P1                              9.70 usec
PL1                             0.00 dB
PL1W                   29.38907051 W
SFO1                   75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                              1H
PCPD2                          80.00 usec
PL2                             1.00 dB
PL12                           17.00 dB
PL13                           17.00 dB
PL2W                    9.17820644 W
PL12W                   0.23054613 W
PL13W                   0.23054613 W
SFO2                   300.1312005 MHz
SI                           32768
SF                     75.4677490 MHz
WDW                             EM
SSB                              0
LB                              1.00 Hz
GB                               0
PC                              1.40
```

Ethyl 4,4-dicyano-3-(2-fluorophenyl)-2-methylenebut-3-enoate: 3n

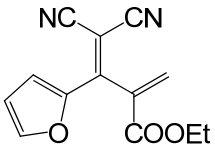


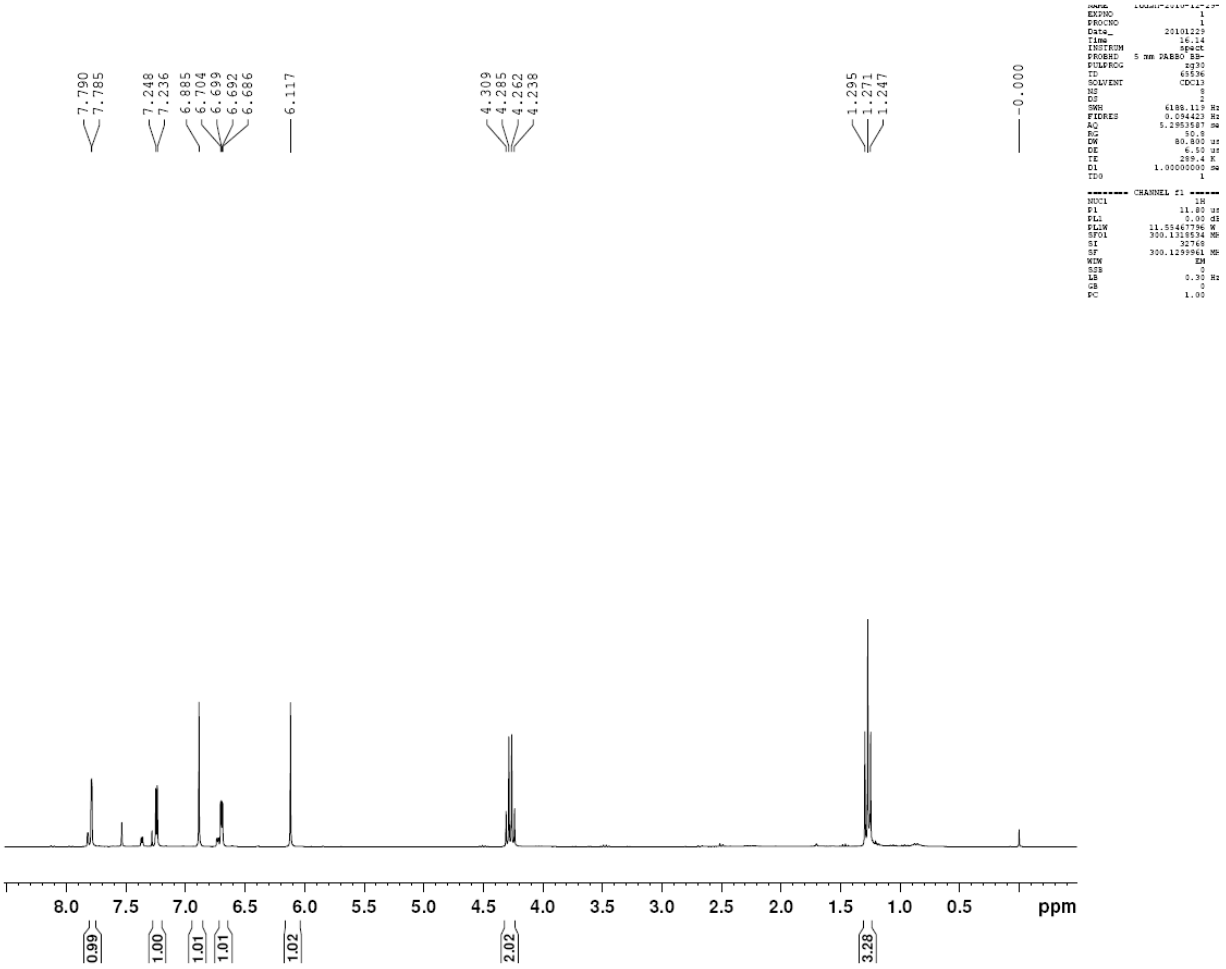


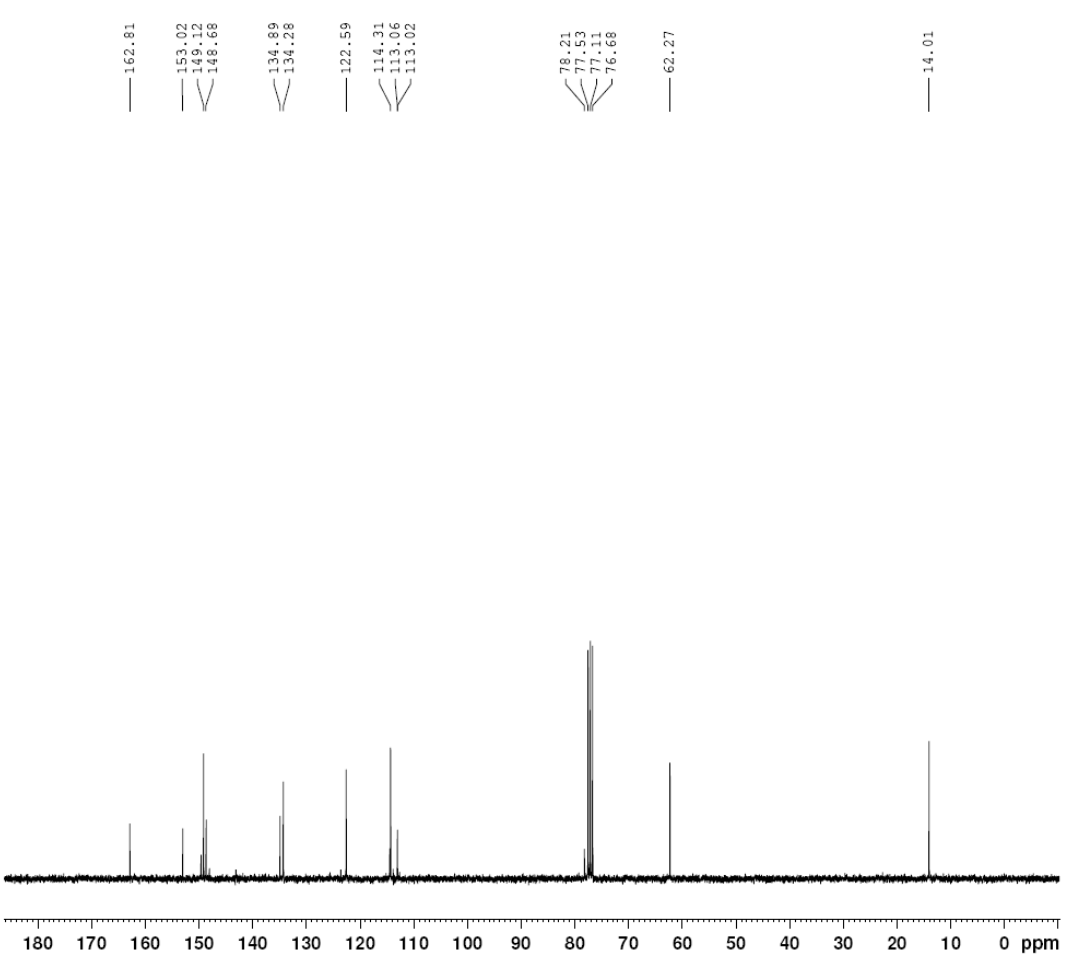


NAME	fudan-2010-12-2-2-f
EXPNO	2
PROCNO	1
Date_	20101202
Time	17.36
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	120
DS	4
SWH	18028.846 Hz
FIDRES	0.275098 Hz
AQ	1.8175818 sec
RG	203
DW	27.733 usec
DE	6.50 usec
TE	290.1 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
-------- CHANNEL f1 --------	
NUC1	13C
P1	9.70 usec
PL1	0.00 dB
PL1W	29.38907051 W
SFO1	75.4752953 MHz
-------- CHANNEL f2 --------	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.00 dB
PL12	17.00 dB
PL13	17.00 dB
PL2W	9.17820644 W
PL12W	0.23054613 W
PL13W	0.23054613 W
SFO2	300.1312005 MHz
SI	32768
SF	75.4677490 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

Ethyl 4,4-dicyano-3-(furan-2-yl)-2-methylenebut-3-enoate: 3o





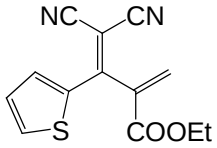


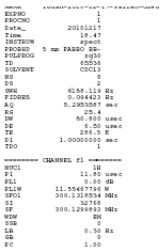
NAME fudan-2010-12-29-diwa-
EXPNO 2
PROCNO 1
Date_ 20101229
Time 16.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 107
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

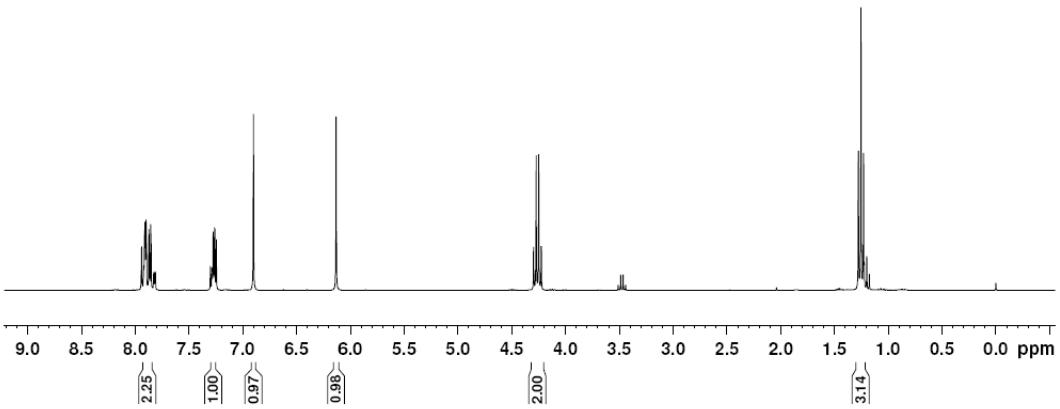
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz

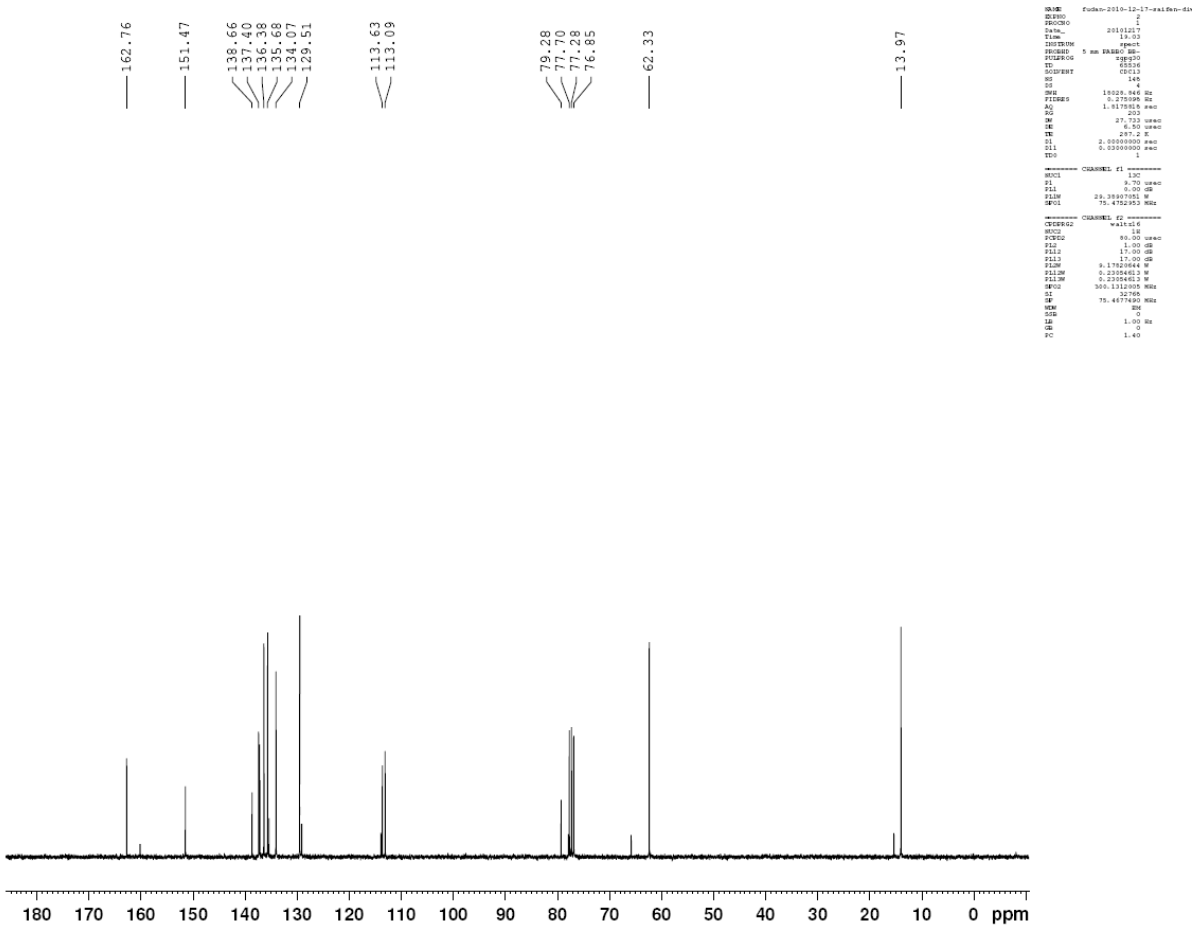
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17620644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

Ethyl 4,4-dicyano-2-methylene-3-(thiophen-2-yl)but-3-enoate: 3p

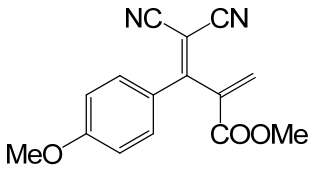


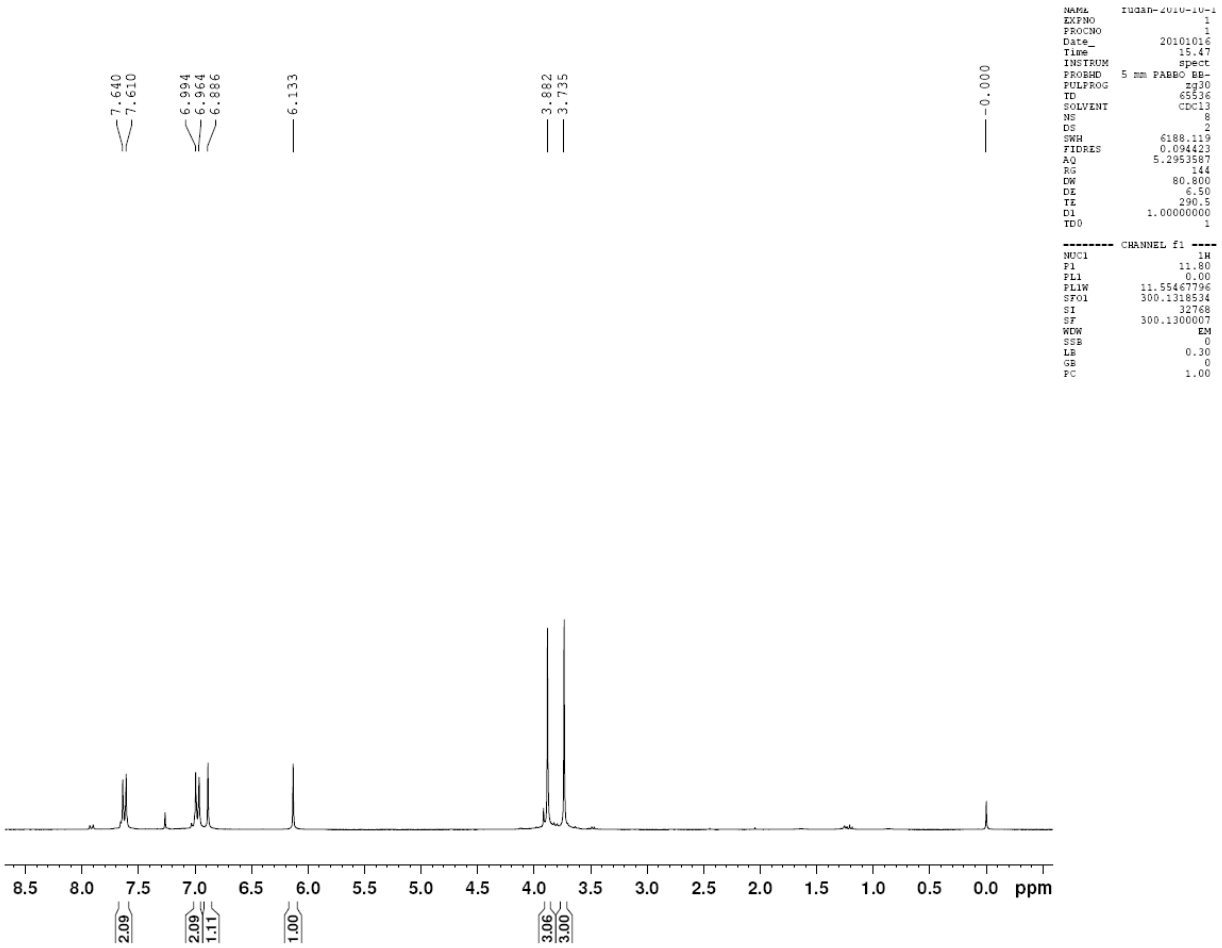


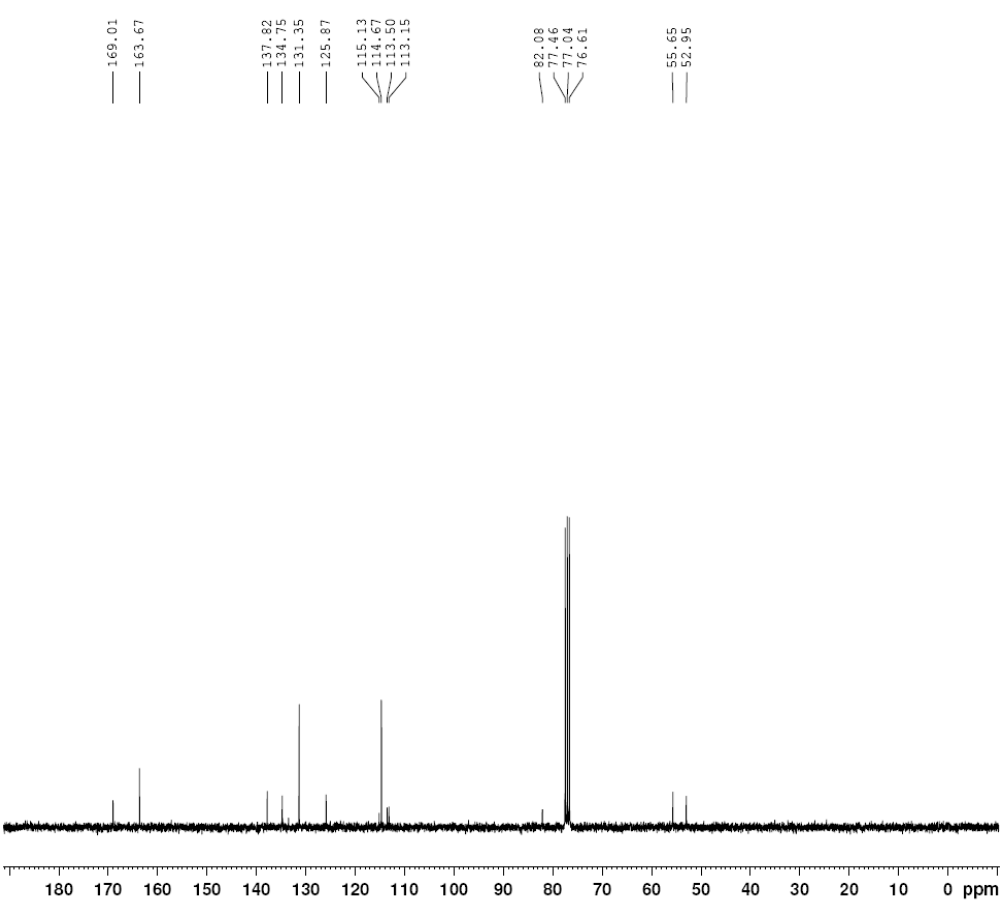



162.76
151.47
138.66
137.40
136.38
135.68
134.07
129.51
113.63
113.09
79.28
77.70
77.28
76.85
62.33
13.97
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Methyl 4,4-dicyano-3-(4-methoxyphenyl)-2-methylenebut-3-enoate: 3q

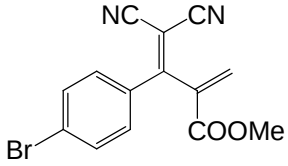


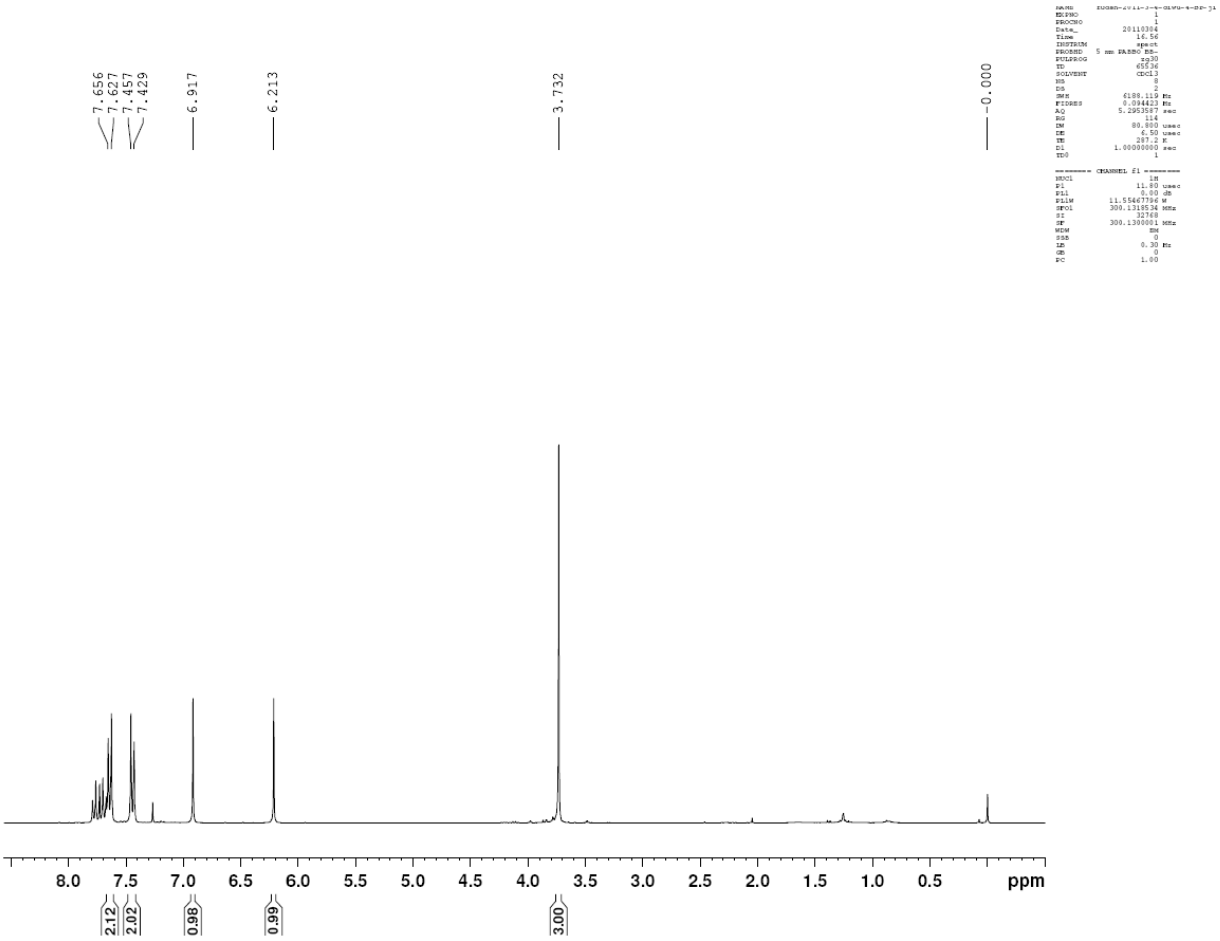


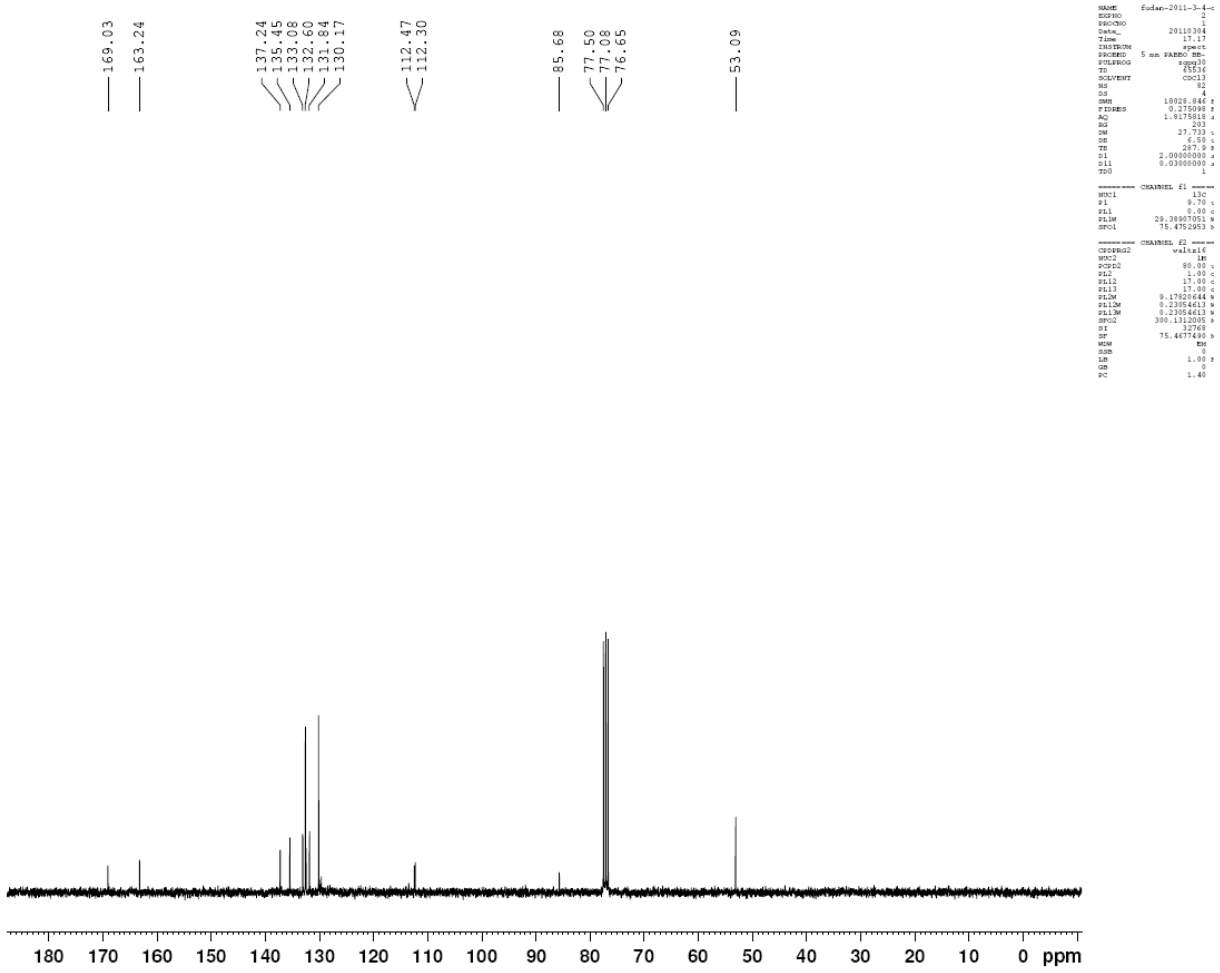



```
NAME          fudan-2010-10-16
EXPNO                        2
PROCNO                       1
Date_                 20101016
Time                     15.52
INSTRUM                  spect
PROBHD     5 mm PABBO BB-
PULPROG                 zgpg30
TD                       65536
SOLVENT                  CDCl3
NS                         151
DS                           4
SWH                  18028.846 Hz
FIDRES                0.275098 Hz
AQ                    1.817581 sec
RG                         203
DW                      27.733 usec
DE                        6.50 usec
TE                       290.9 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                          1

======== CHANNEL f1 ========
NUC1                       13c
P1                        9.70 usec
PL1                       0.00 dB
PL1W               29.38907051 W
SFO1                75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2                 waltz16
NUC2                        1H
PCPD2                    80.00 usec
PL2                       1.00 dB
PL12                     17.00 dB
PL13                     17.00 dB
PL2W                9.17820644 W
PL12W               0.23054613 W
PL13W               0.23054613 W
SFO2               300.1312005 MHz
SI                       32768
SF                  75.4677490 MHz
WDW                         EM
SSB                          0
LB                        1.00 Hz
GB                           0
PC                        1.40
```

Methyl 3-(4-bromophenyl)-4,4-dicyano-2-methylenebut-3-enoate: 3r

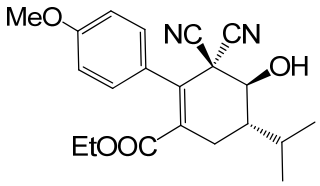


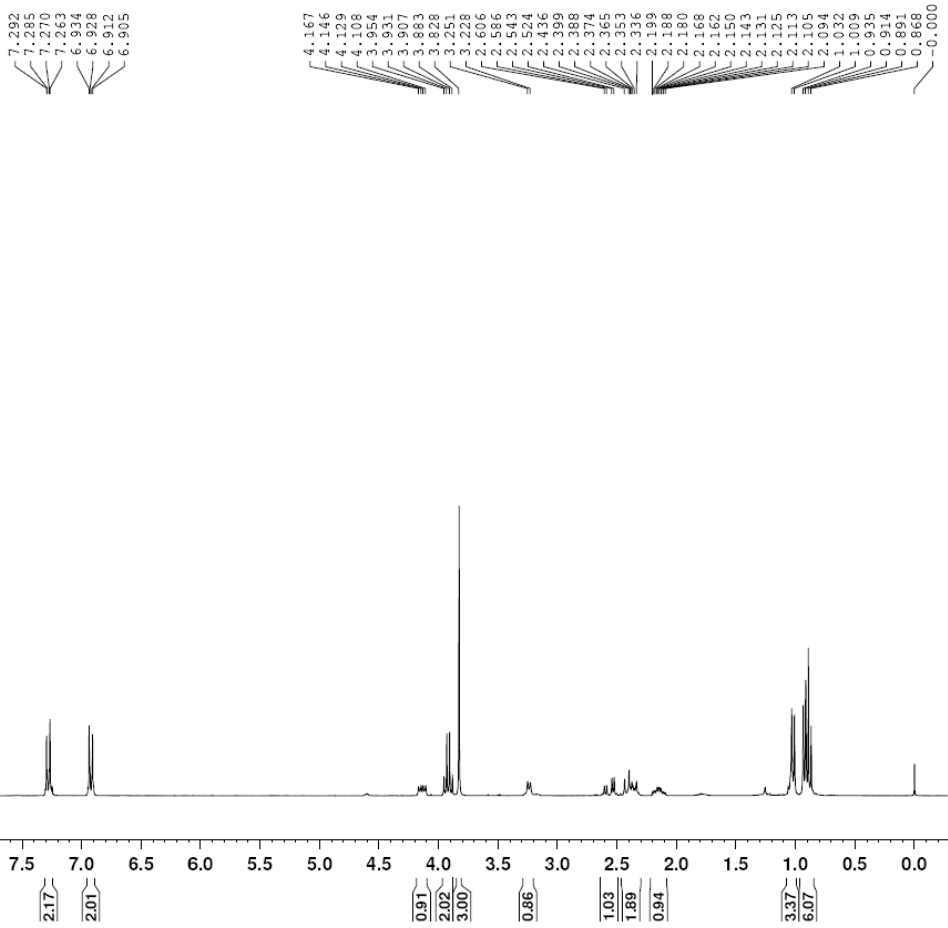


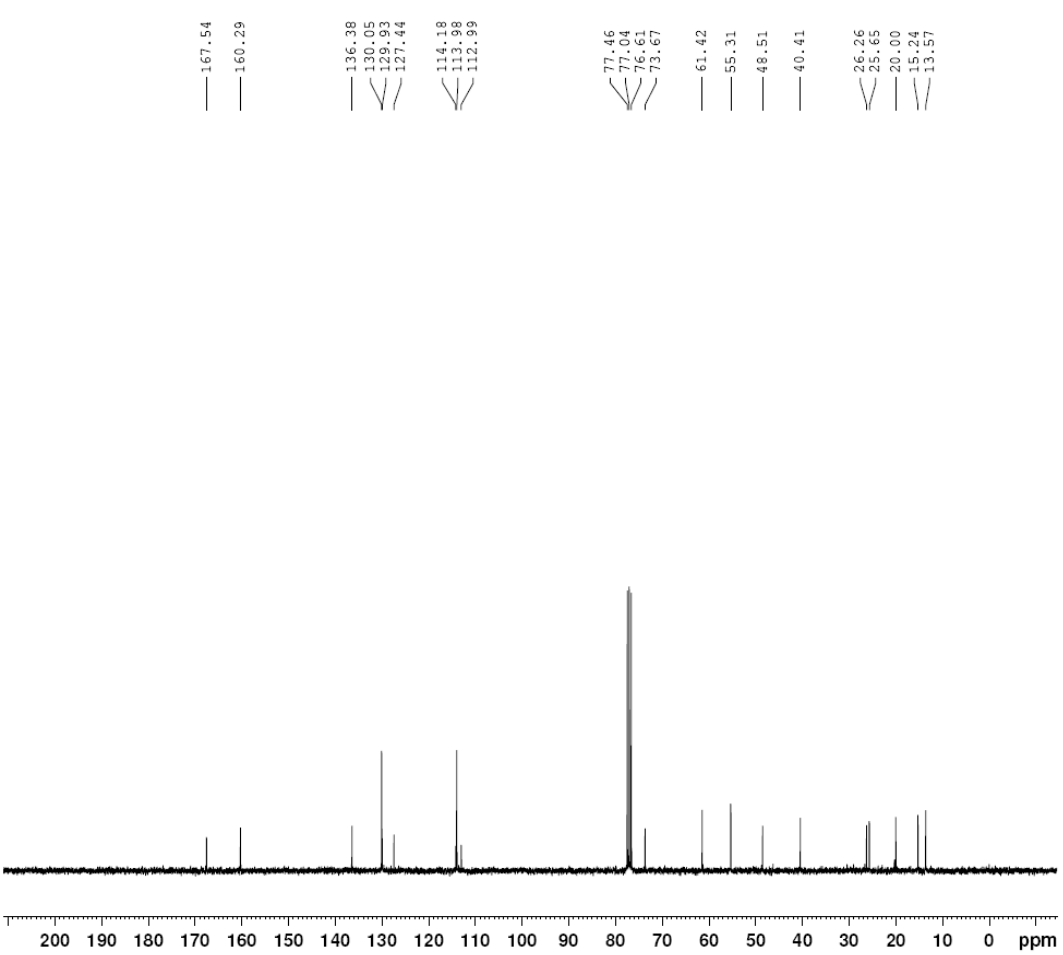

169.03
163.24
137.24
135.45
133.08
132.60
131.84
130.17
112.47
112.30
85.68
77.50
77.08
76.65
53.09
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarboxy

late: 5a

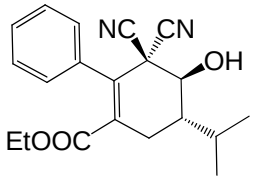


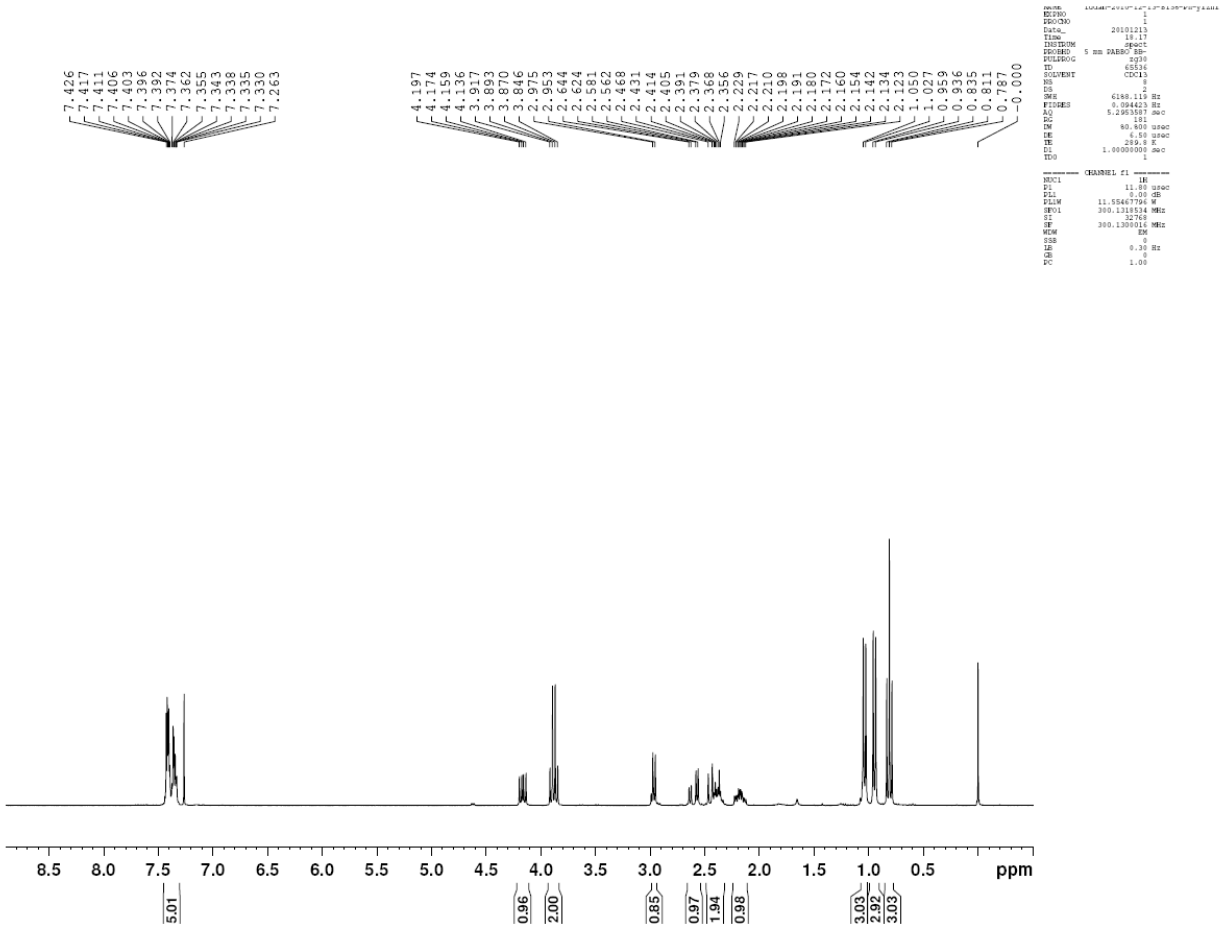


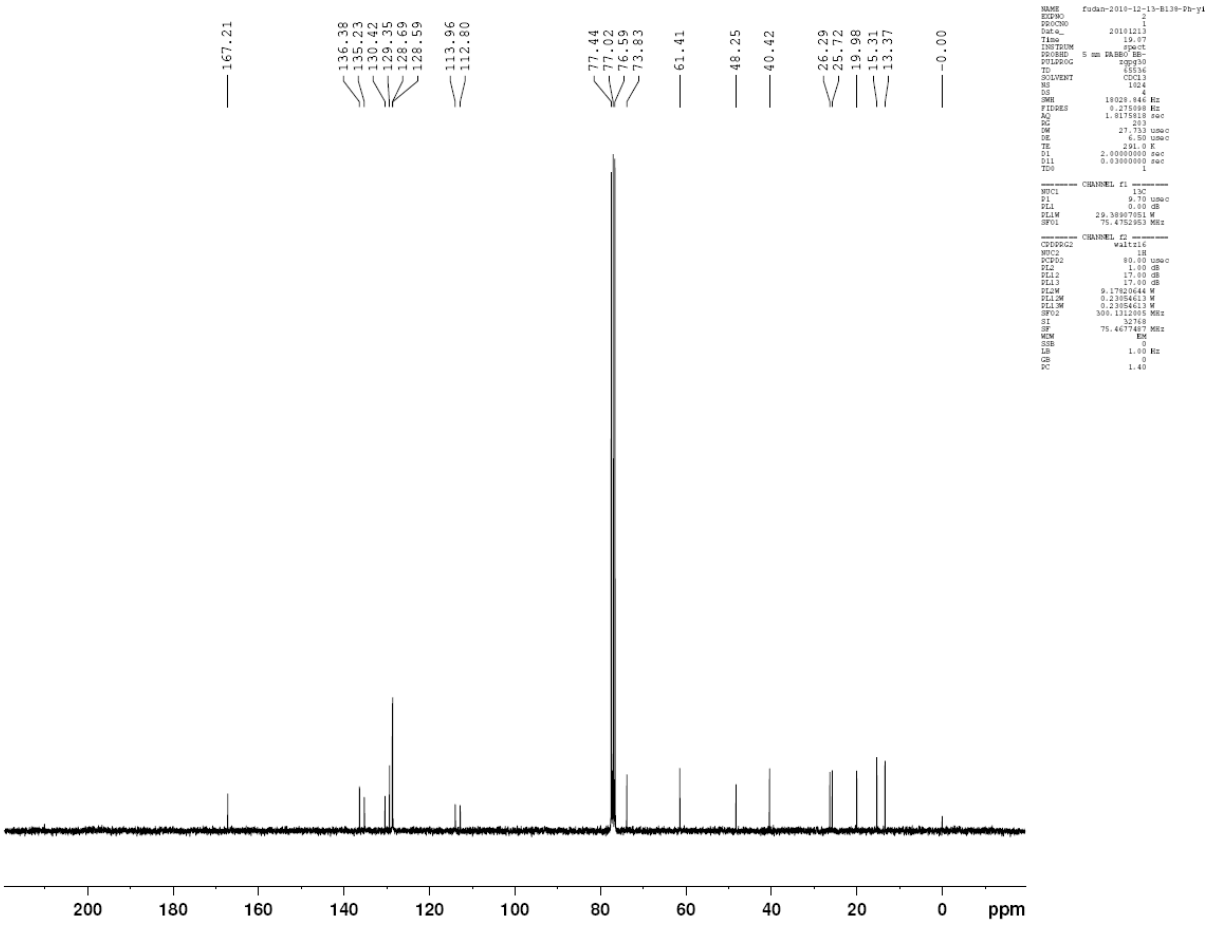



```
NAME                fudan-2010-11-29-B
EXPNO                            2
PROCNO                           1
Date_                     20101129
Time                         16.48
INSTRUM                      spect
PROBHD     5 mm PABBO BB-
PULPROG                   zgpg30
TD                            65536
SOLVENT                     CDCl3
NS                              191
DS                                4
SWH                       18028.846 Hz
FIDRES                        0.275098 Hz
AQ                        1.8175818 sec
RG                              203
DW                           27.733 use
DE                            6.50 use
TE                          290.7 K
D1                        2.00000000 sec
D11                       0.03000000 sec
TD0                              1

======== CHANNEL f1 =======
NUC1                           13C
P1                            9.70 use
PL1                           0.00 dB
PL1W                  29.38907051 W
SFO1                  75.4752953 MHz

======== CHANNEL f2 =======
CPDPRG2                    waltz16
NUC2                           1H
PCPD2                        80.00 use
PL2                           1.00 dB
PL12                         17.00 dB
PL13                         17.00 dB
PL2W                   9.17820644 W
PL12W                  0.23054613 W
PL13W                  0.23054613 W
SFO2                  300.1312805 MHz
SI                            32768
SF                    75.4677490 MHz
WDW                            EM
SSB                               0
LB                            1.00 Hz
GB                                0
PC                            1.40
```

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-phenylcyclohex-1-enecarboxylate: 5b

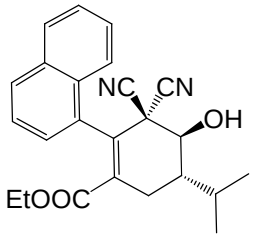


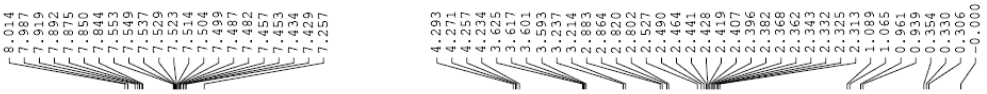


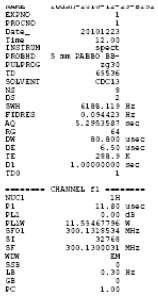

167.21
136.38
135.23
130.42
129.35
128.69
128.59
113.96
112.80
77.44
77.02
76.59
73.83
61.41
48.25
40.42
26.29
25.72
19.98
15.31
13.37
0.00
200
180
160
140
120
100
80
60
40
20
0
ppm

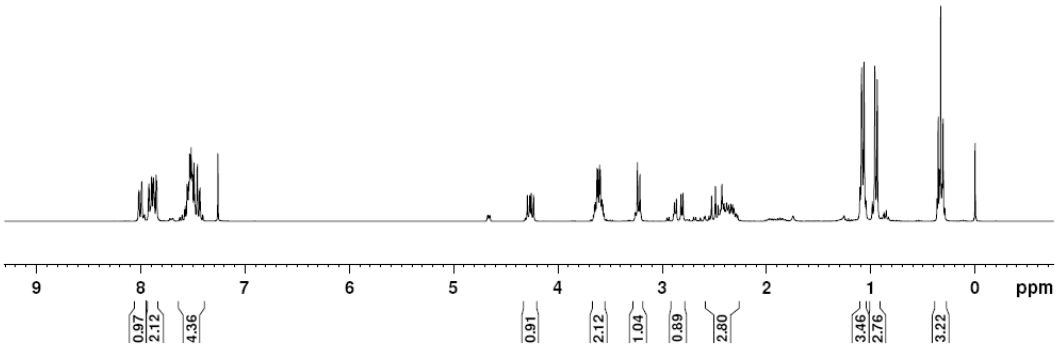
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(naphthalen-1-yl)cyclohex-1-enecarboxy

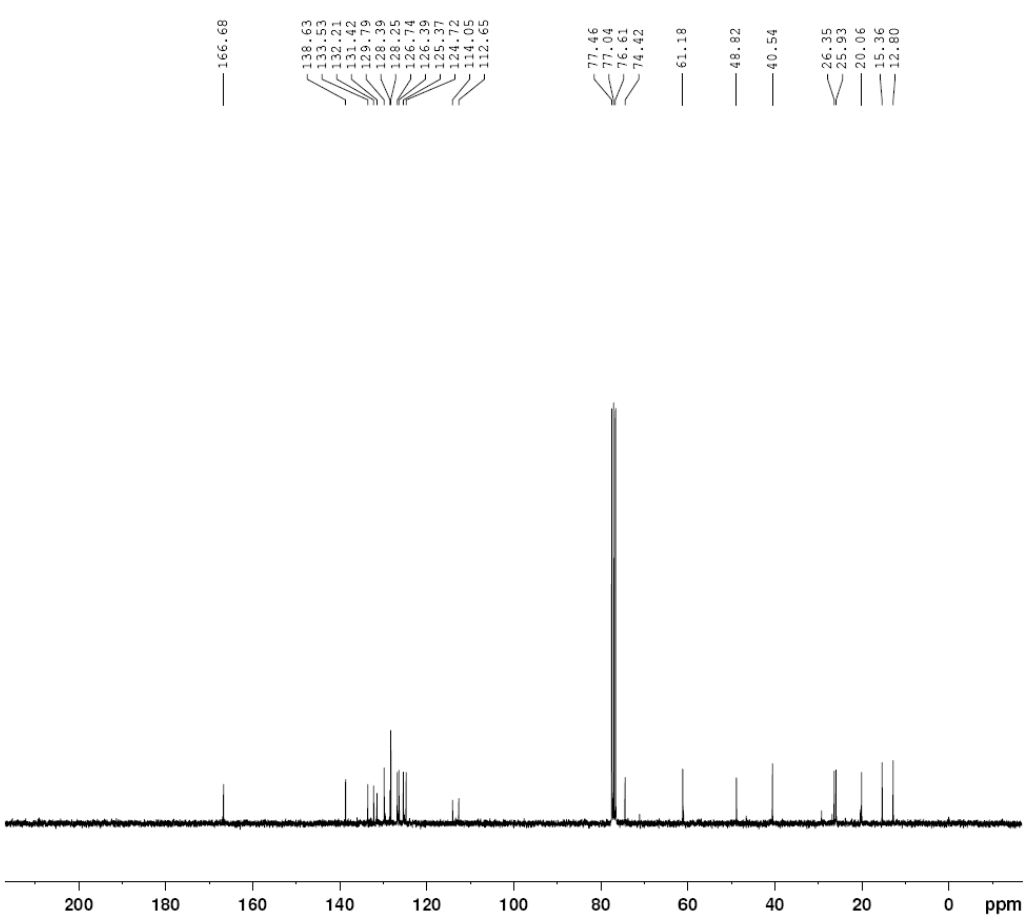
late: 5c



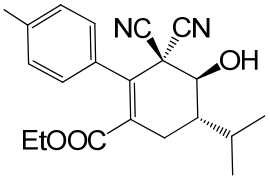


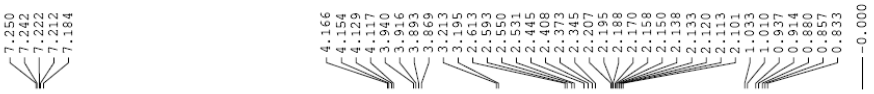


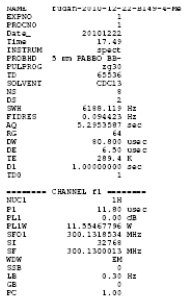


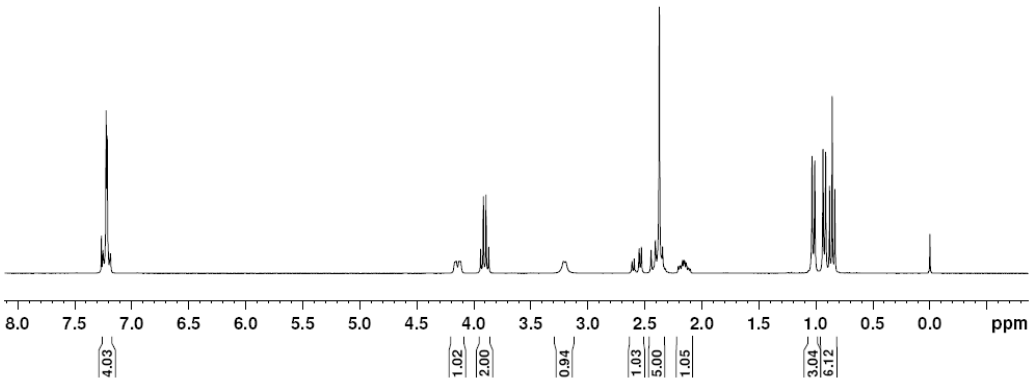

166.68
138.63
133.53
132.21
131.42
129.79
128.39
128.25
126.74
126.39
125.37
124.72
114.05
112.65
77.46
77.04
76.61
74.42
61.18
48.82
40.54
26.35
25.93
20.06
15.36
12.80
200
180
160
140
120
100
80
60
40
20
0
ppm

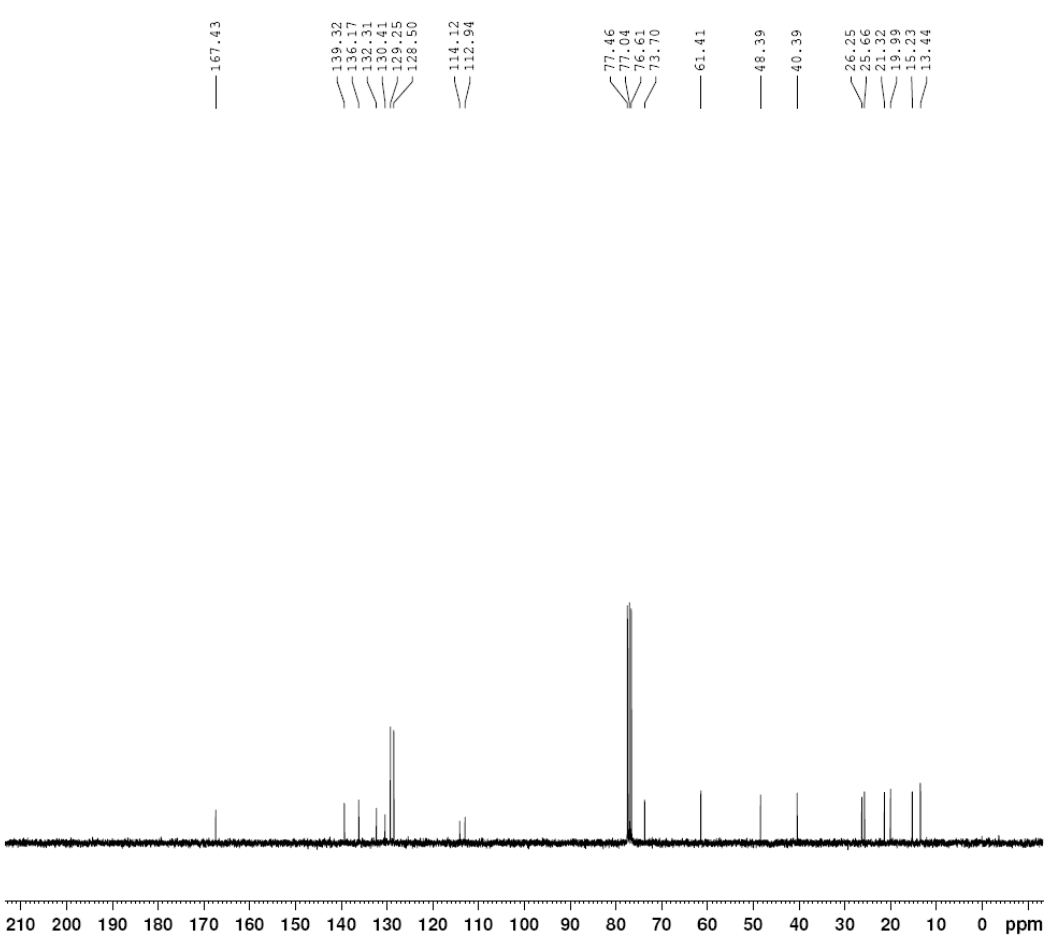
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-p-tolylcyclohex-1-enecarboxylate: 5d





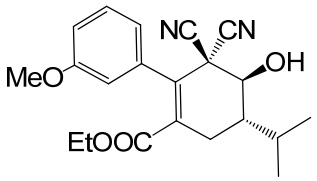


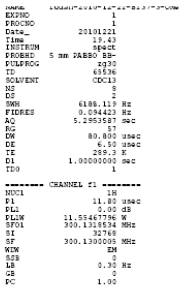


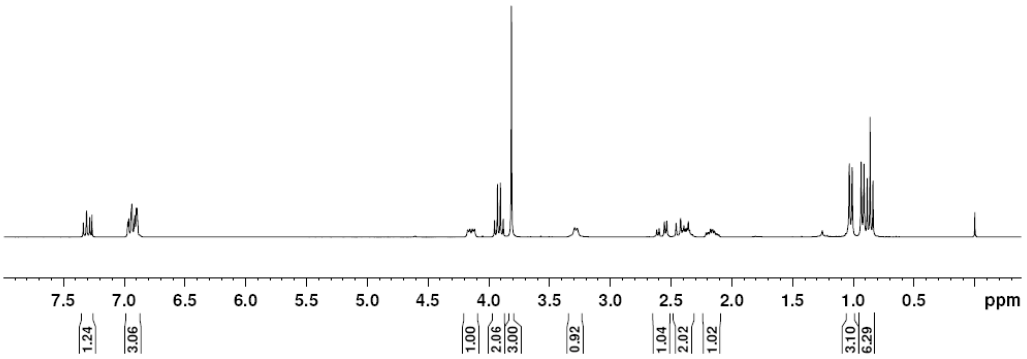

167.43
139.32
136.17
132.31
130.41
129.25
128.50
114.12
112.94
77.46
77.04
76.61
73.70
61.41
48.39
40.39
26.25
25.66
21.32
19.99
13.23
13.44
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

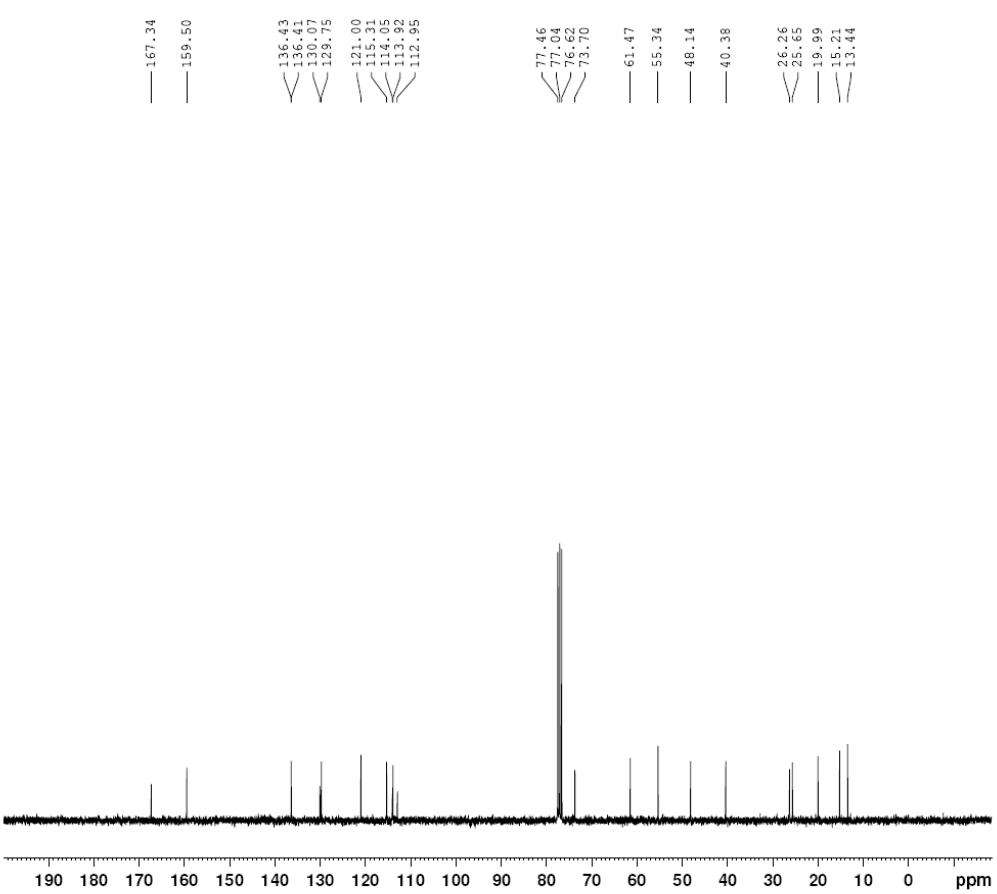
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(3-methoxyphenyl)cyclohex-1-enecarbox

ylate: 5e

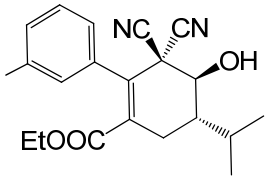


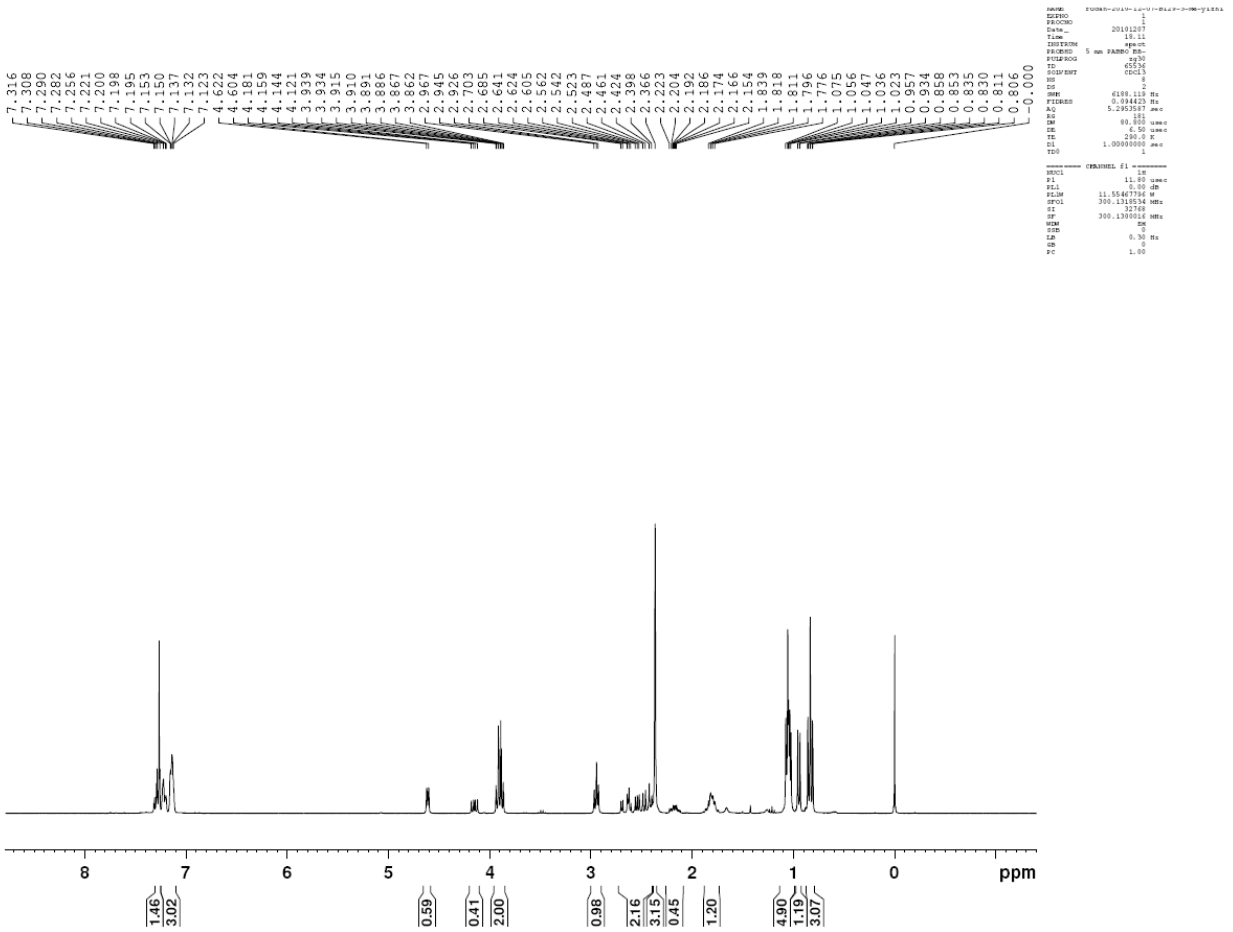


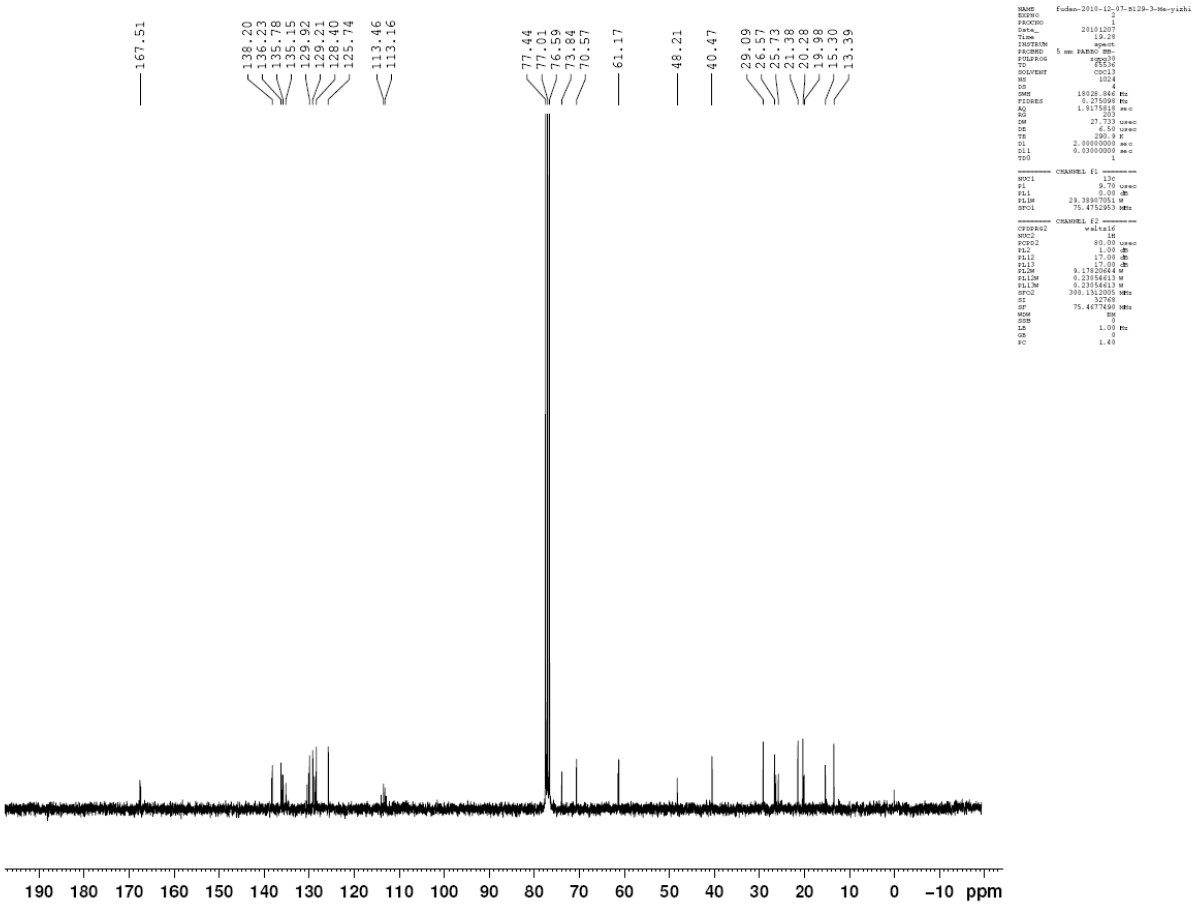



167.34
159.50
136.43
136.41
130.07
129.75
121.00
115.31
114.05
113.92
112.95
77.46
77.04
76.62
73.70
61.47
55.34
48.14
40.38
26.26
25.65
19.99
15.21
13.44
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

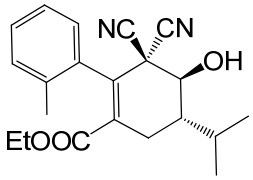
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-m-tolylcyclohex-1-enecarboxylate: 5f

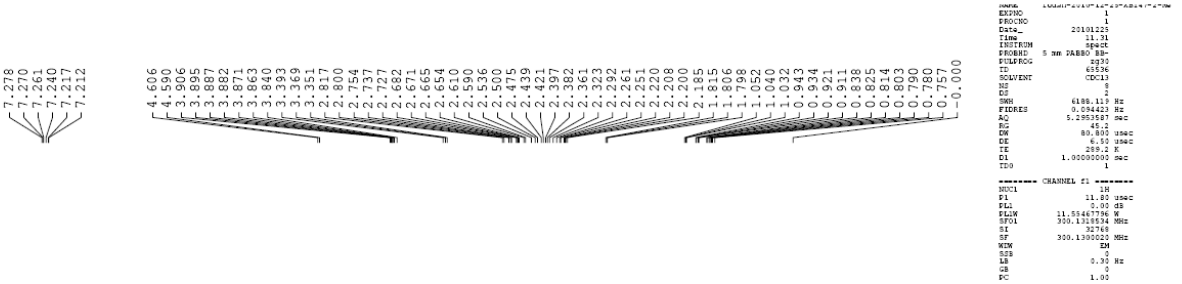


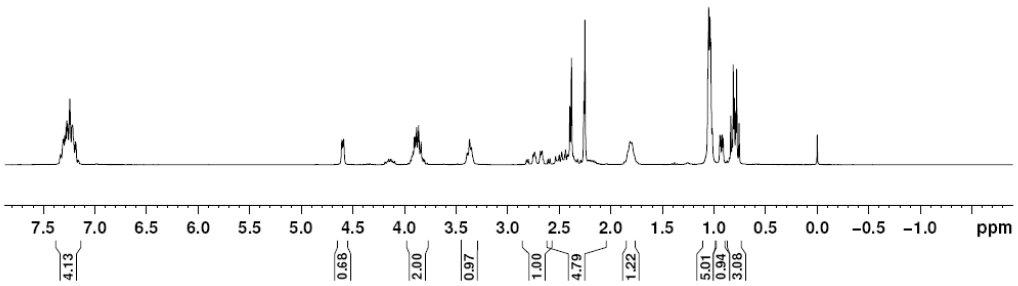


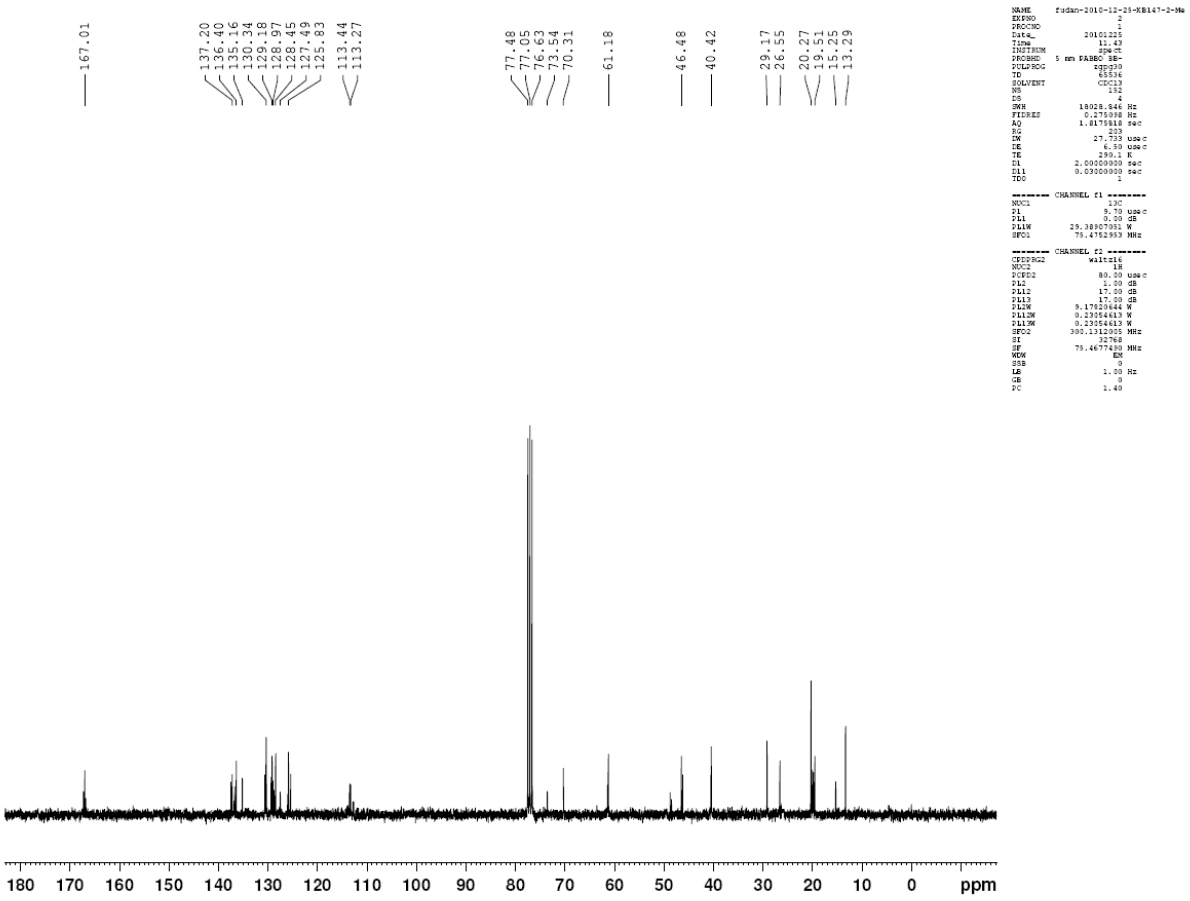

167.51
138.20
136.23
135.78
135.15
129.92
129.21
128.40
125.74
113.46
113.16
77.44
77.01
76.59
73.84
70.57
61.17
48.21
40.47
29.09
26.57
25.73
21.38
20.28
19.98
15.30
13.39
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 ppm

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-o-tolylcyclohex-1-enecarboxylate: 5g

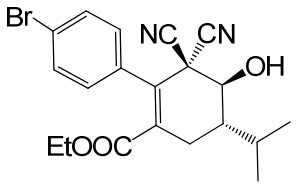


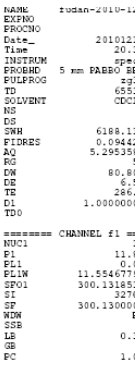


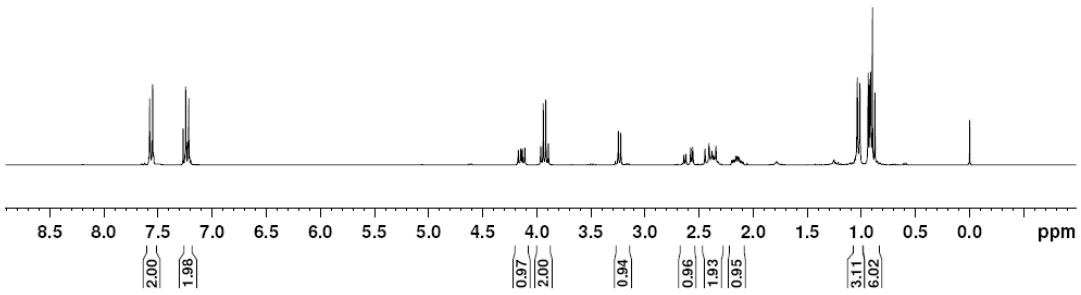


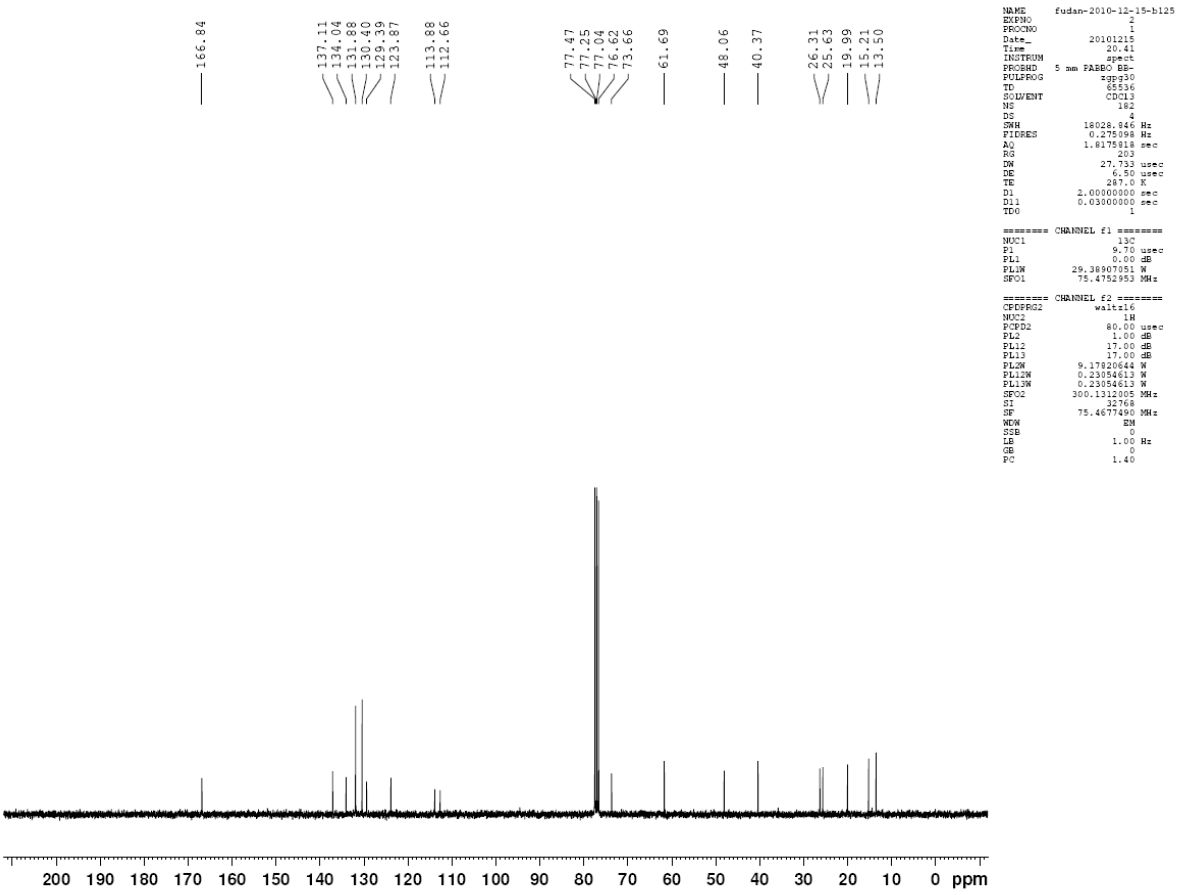

167.01
137.20
136.40
135.16
130.34
129.18
128.97
128.45
127.49
125.83
113.44
113.27
77.48
77.05
76.63
73.54
70.31
61.18
46.48
40.42
29.17
26.55
20.27
19.51
15.25
13.29
NAME fudan-2010-12-25-XB147-2-Me
EXPNO 2
PROCNO 1
Date_ 20101225
Time 11.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 152
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(4*S*,5*S*)-ethyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5h



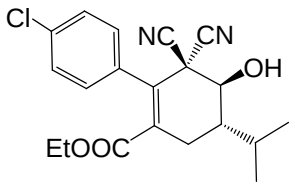


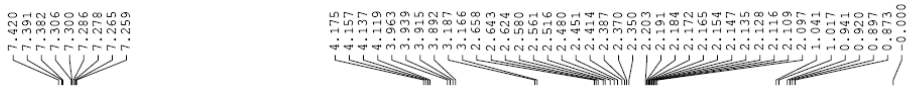


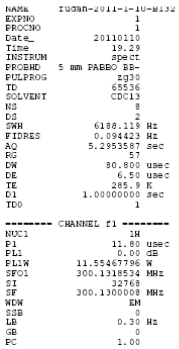

166.84
137.11
134.04
131.88
130.40
129.39
123.87
113.88
112.66
77.47
77.25
77.04
76.62
73.66
61.69
48.06
40.37
26.31
25.63
19.99
15.21
13.50
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

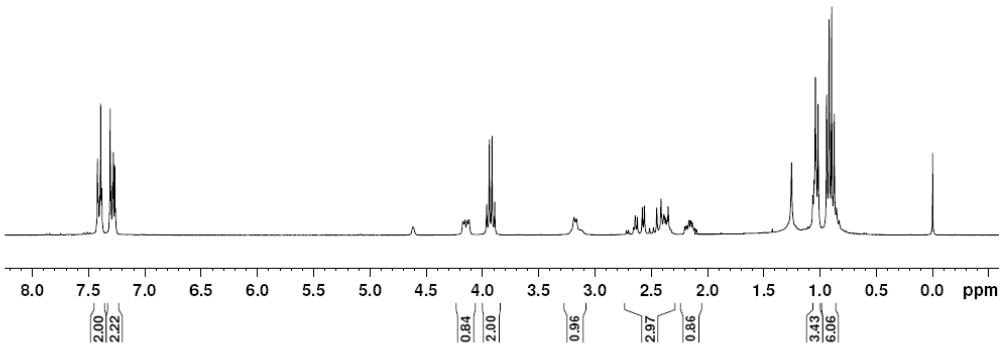
(4*S*,5*S*)-ethyl 2-(4-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

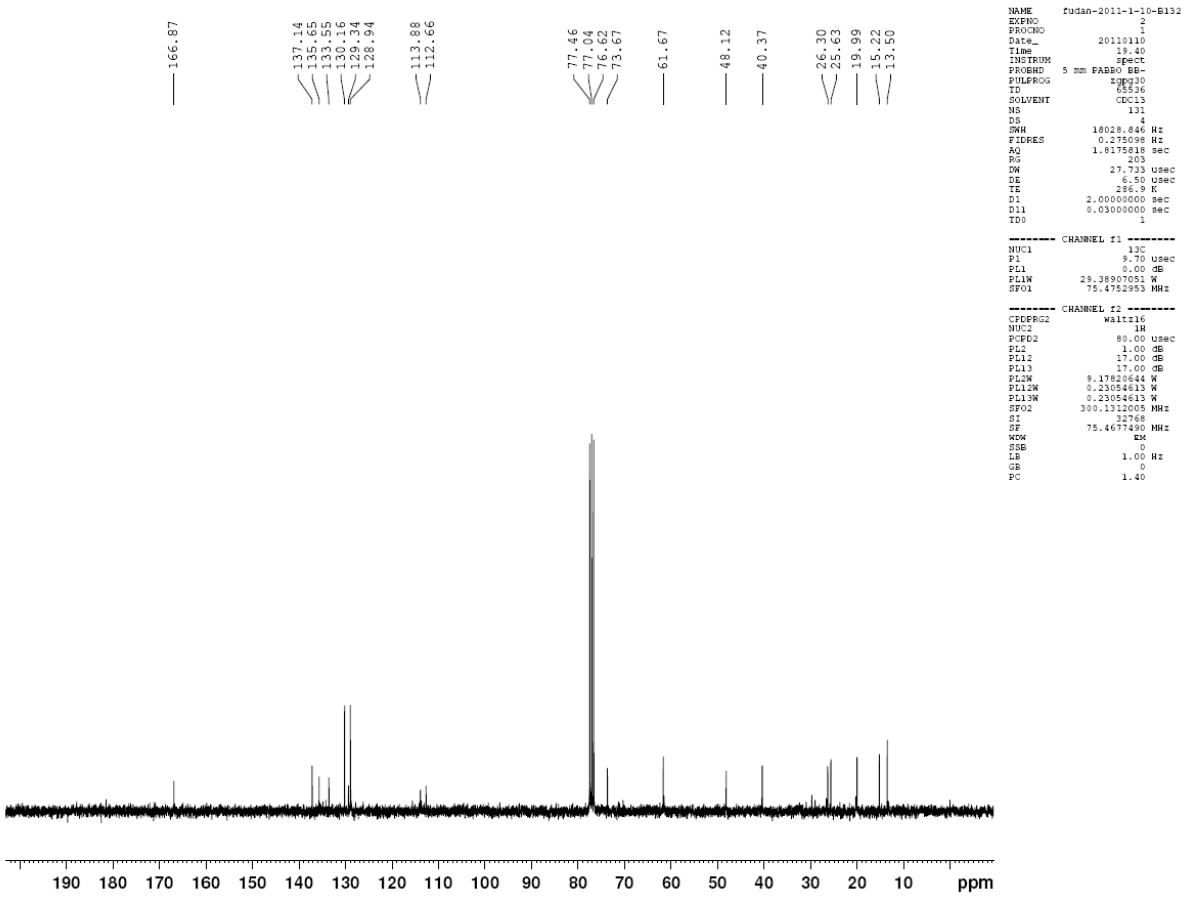
te: 5i





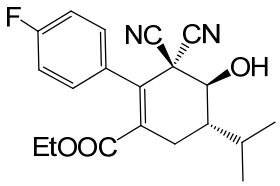


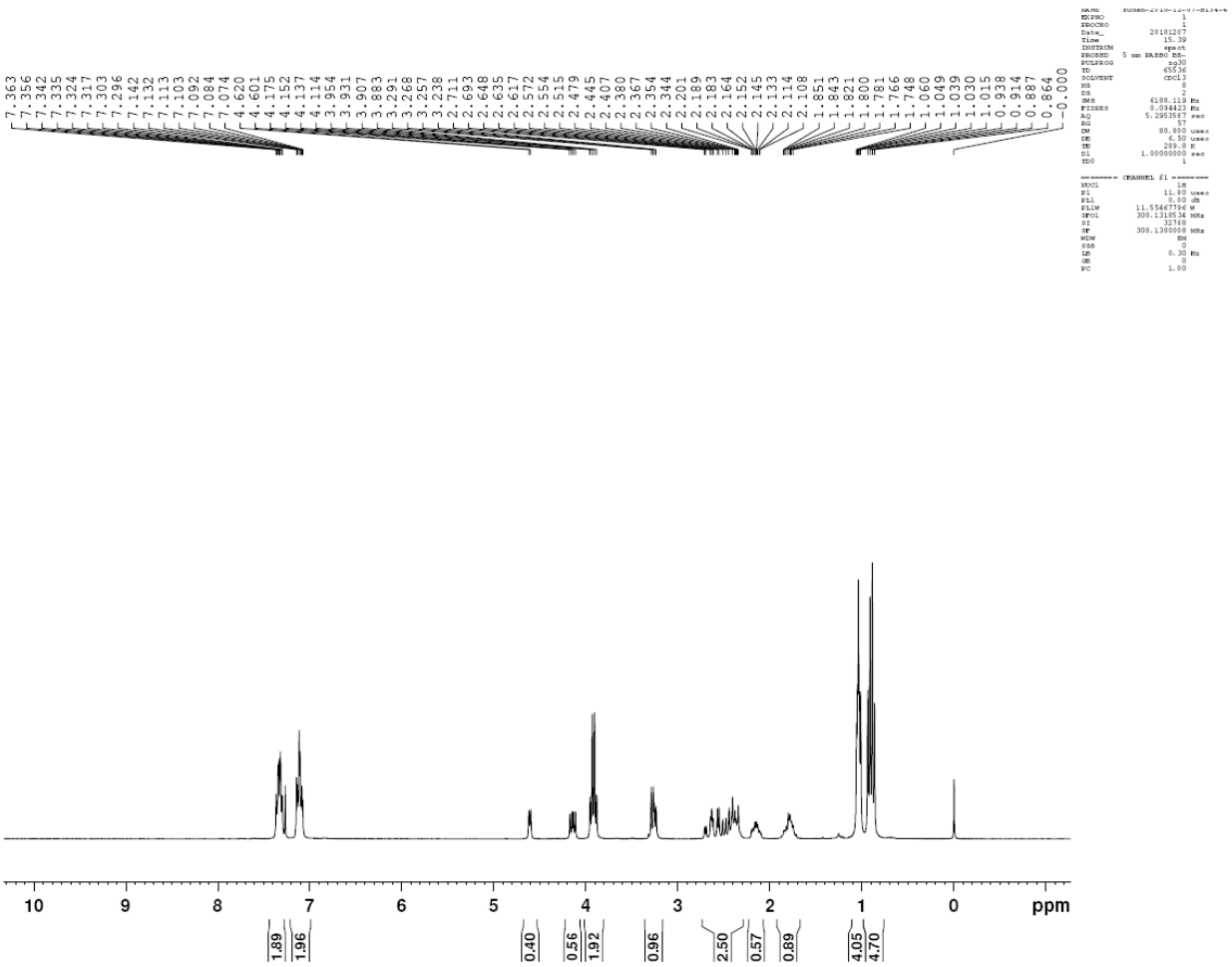


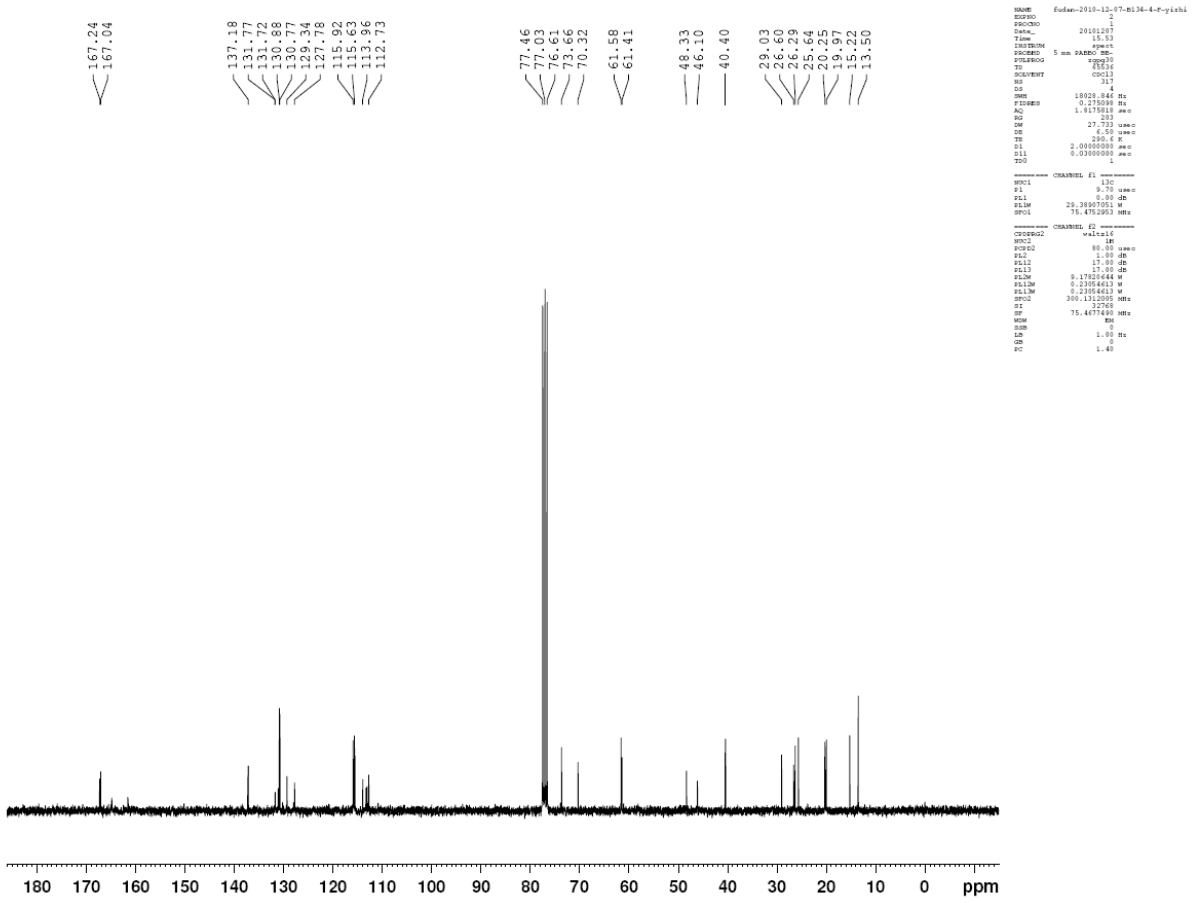

166.87
137.14
135.65
133.55
130.16
129.34
128.94
113.88
112.66
77.46
77.04
76.62
73.67
61.67
48.12
40.37
26.30
25.63
19.99
15.22
13.50
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
NAME fudan-2011-1-10-B132
EXPNO 2
PROCNO 1
Date_ 20110110
Time 19.40
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 131
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 286.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
CHANNEL f1
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
CHANNEL f2
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

(4S,5S)-ethyl 3,3-dicyano-2-(4-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5j

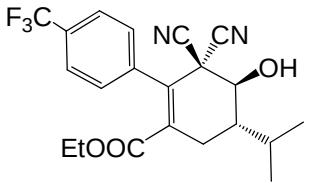


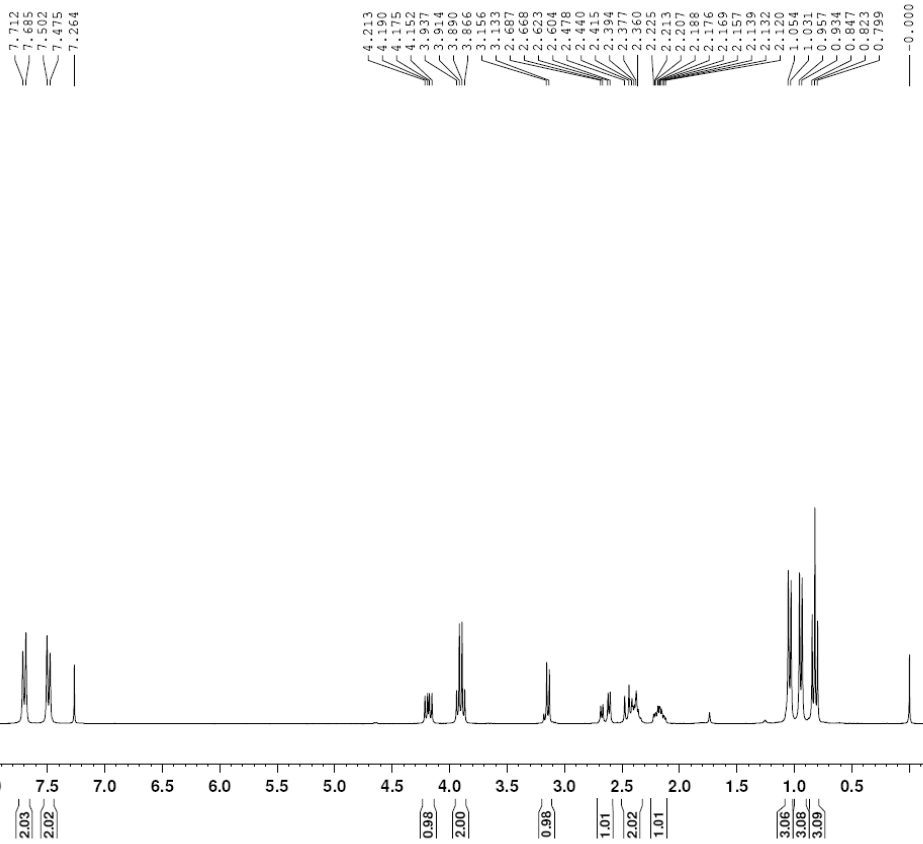


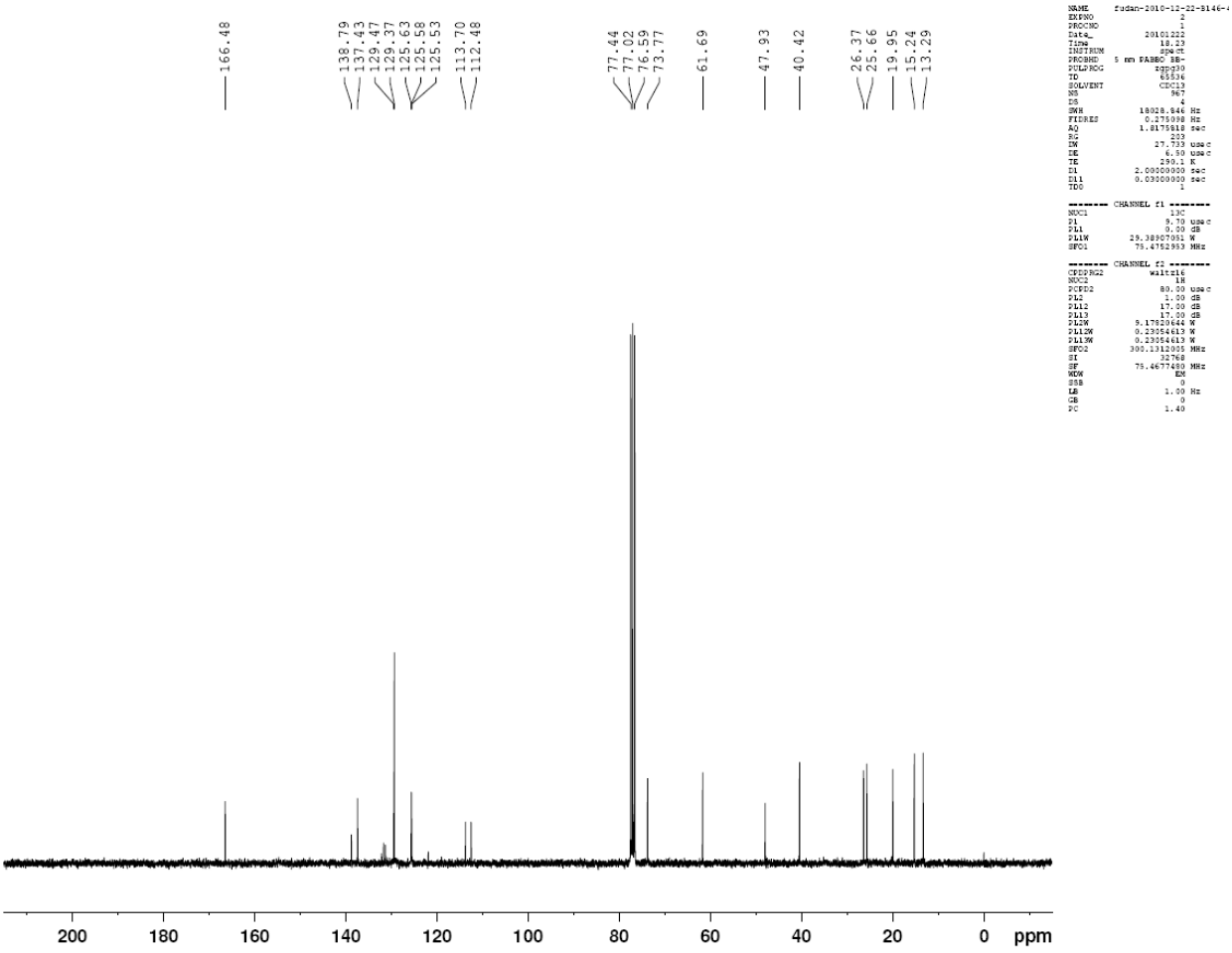

167.24
167.04
137.18
131.77
131.72
130.88
130.77
129.34
127.78
115.92
115.63
113.96
112.73
77.46
77.03
76.61
73.66
70.32
61.58
61.41
48.33
46.10
40.40
29.03
26.60
26.29
25.64
20.25
19.97
15.22
13.50
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(4S,5S)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-(trifluoromethyl)phenyl)cyclohex-1-en

ecarboxylate: 5k

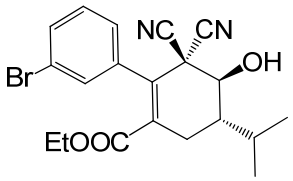


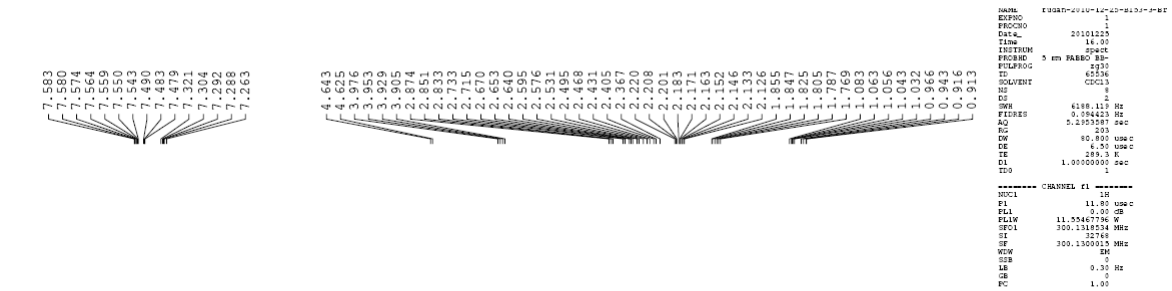


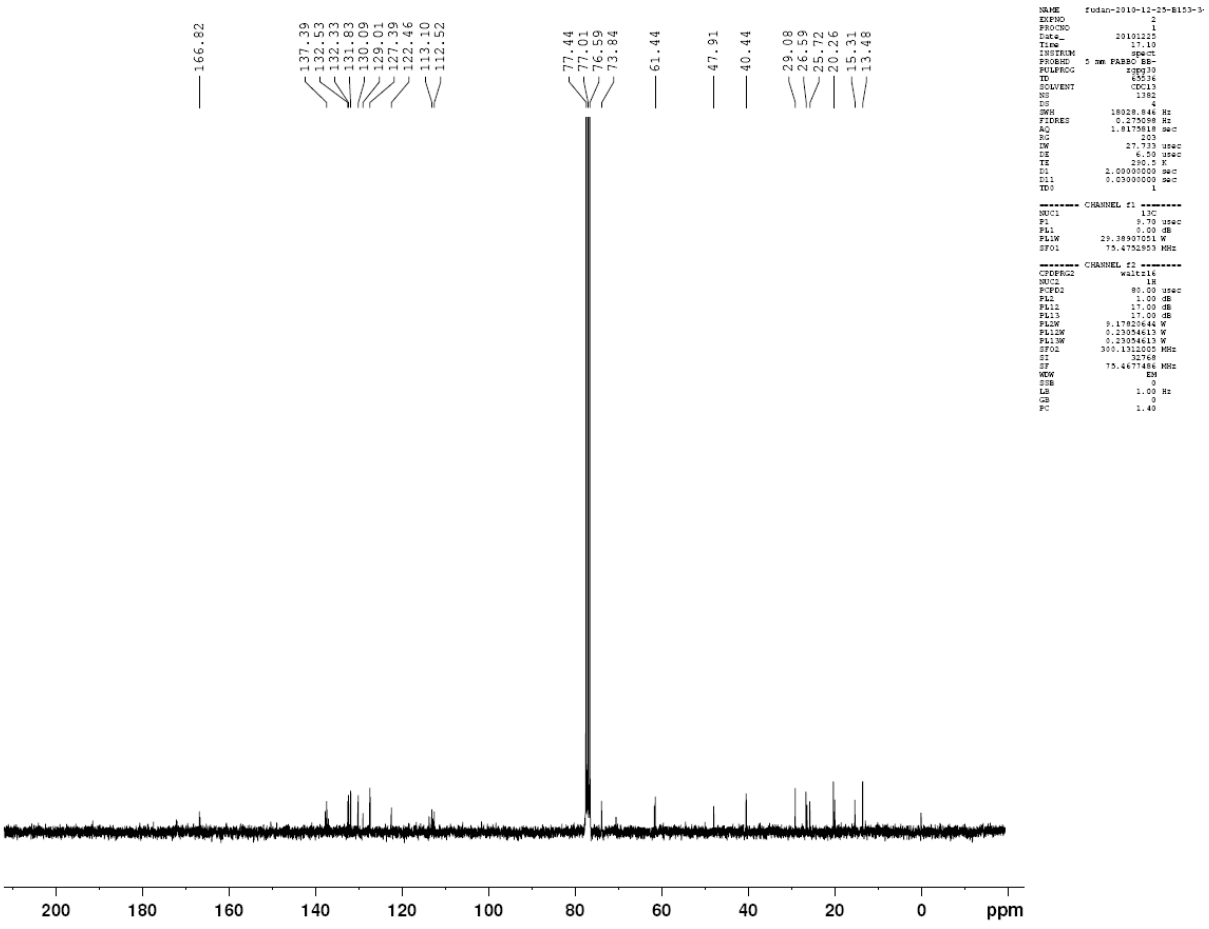

166.48
138.79
137.43
129.47
129.37
125.63
125.58
125.53
113.70
112.48
77.44
77.02
76.59
73.77
61.69
47.93
40.42
26.37
25.66
19.95
15.24
13.29
200
180
160
140
120
100
80
60
40
20
0
ppm

(4S,5S)-ethyl 2-(3-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

te: 5l

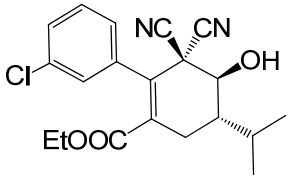


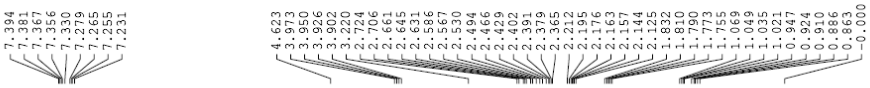


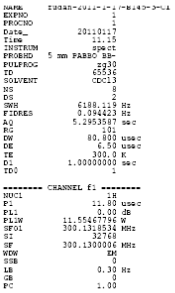

166.82
137.39
132.53
132.33
131.83
130.09
129.01
127.39
122.46
113.10
112.52
77.44
77.01
76.59
73.84
61.44
47.91
40.44
29.08
26.59
25.72
20.26
15.31
13.48
200
180
160
140
120
100
80
60
40
20
0
ppm

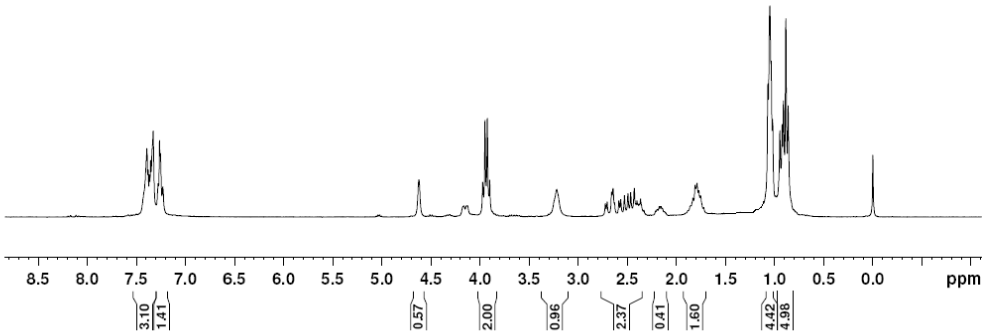
(4*S*,5*S*)-ethyl 2-(3-chlorophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

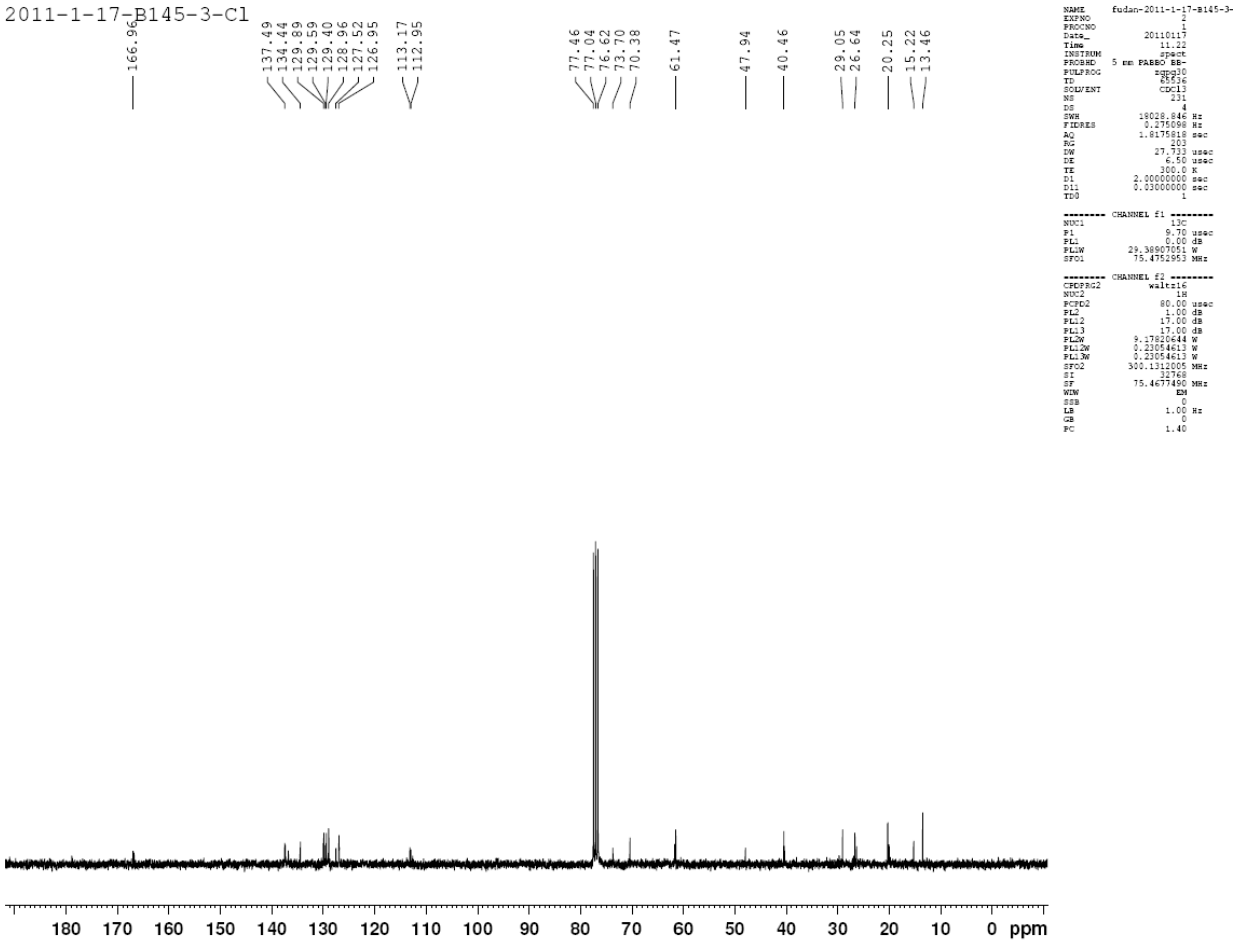
te: 5m





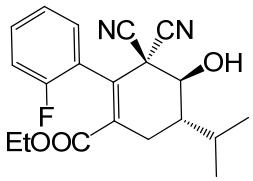


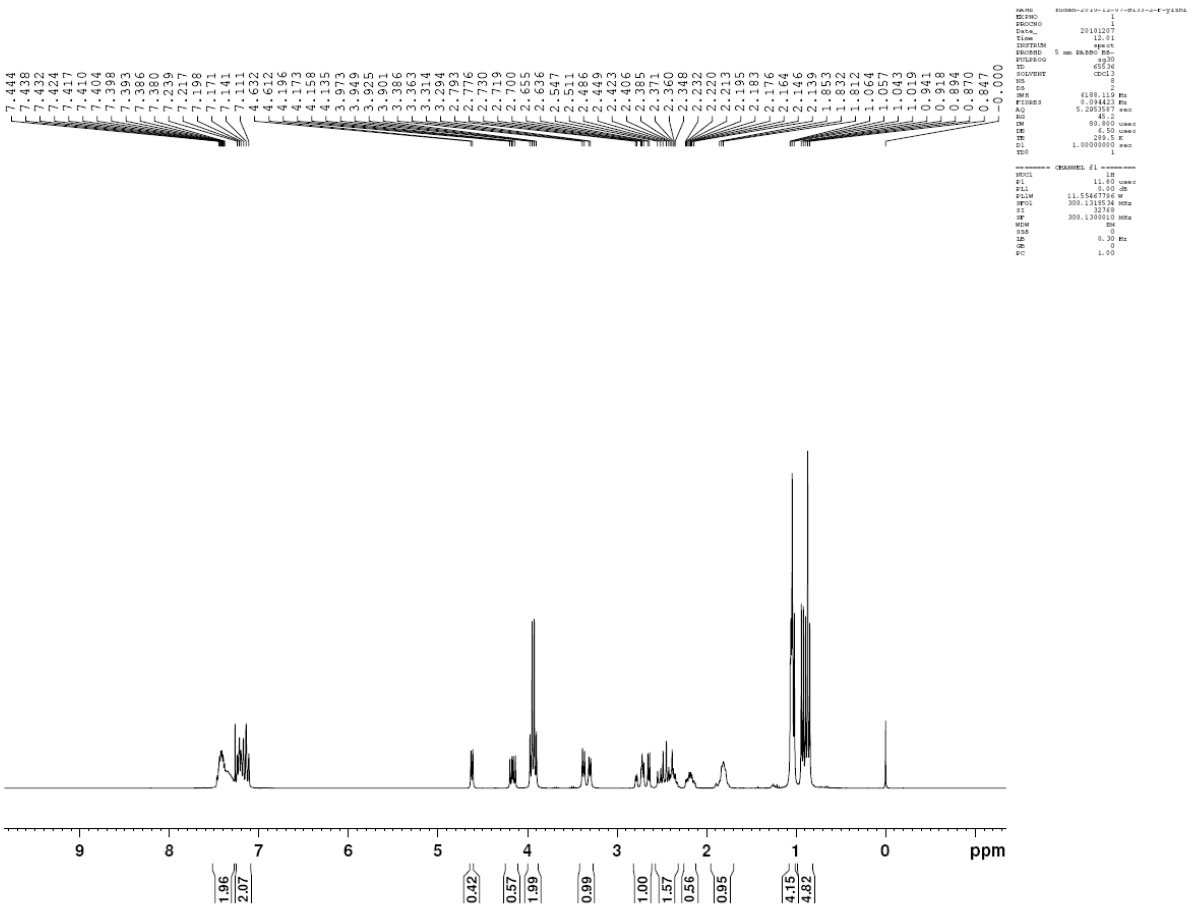


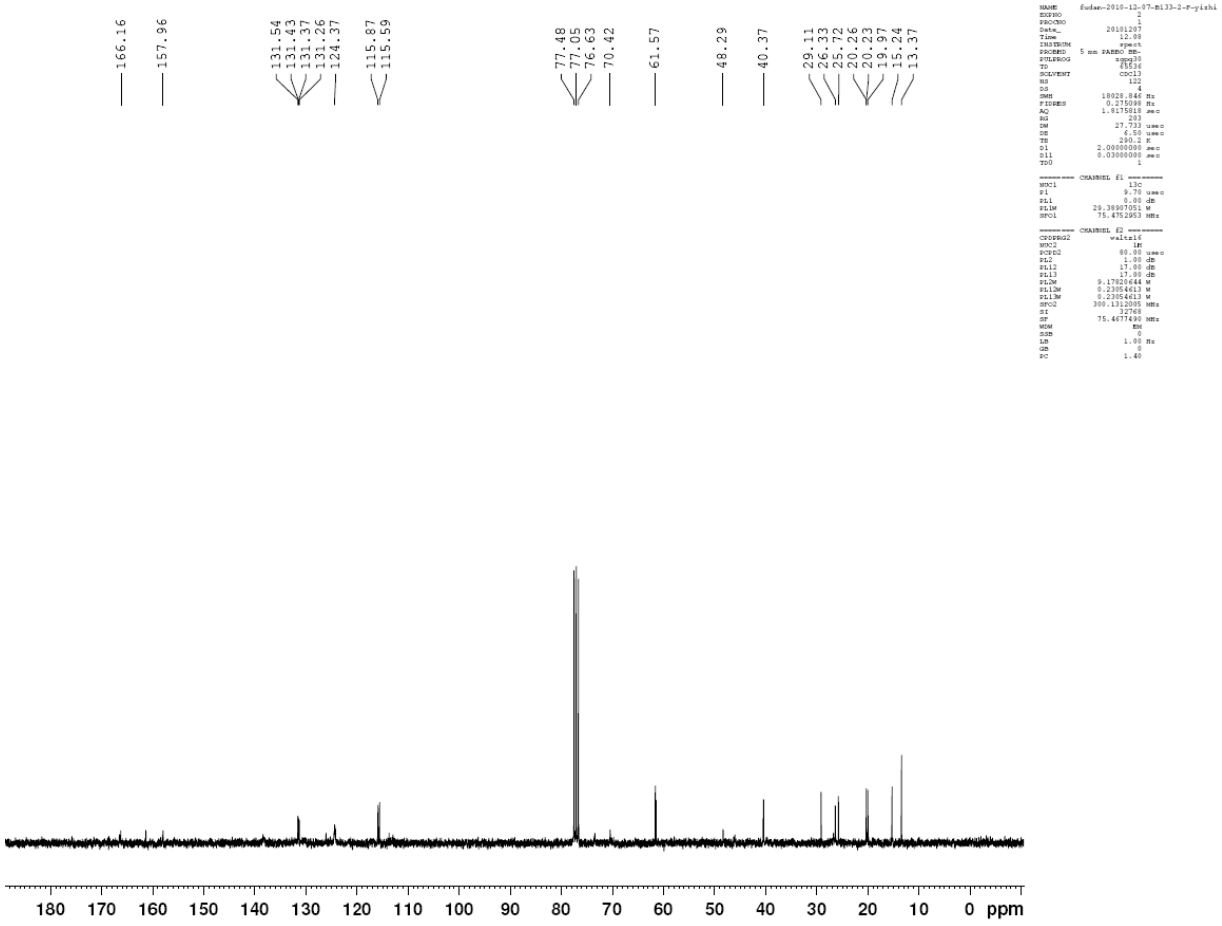

2011-1-17-B145-3-Cl
166.96
137.49
134.44
129.89
129.59
129.40
128.96
127.52
126.95
113.17
112.95
77.46
77.04
76.62
73.70
70.38
61.47
47.94
40.46
29.05
26.64
20.25
15.22
13.46
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

(4*S*,5*S*)-ethyl 3,3-dicyano-2-(2-fluorophenyl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxyla

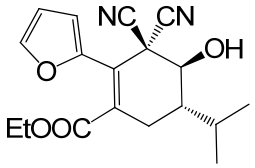
te: 5n

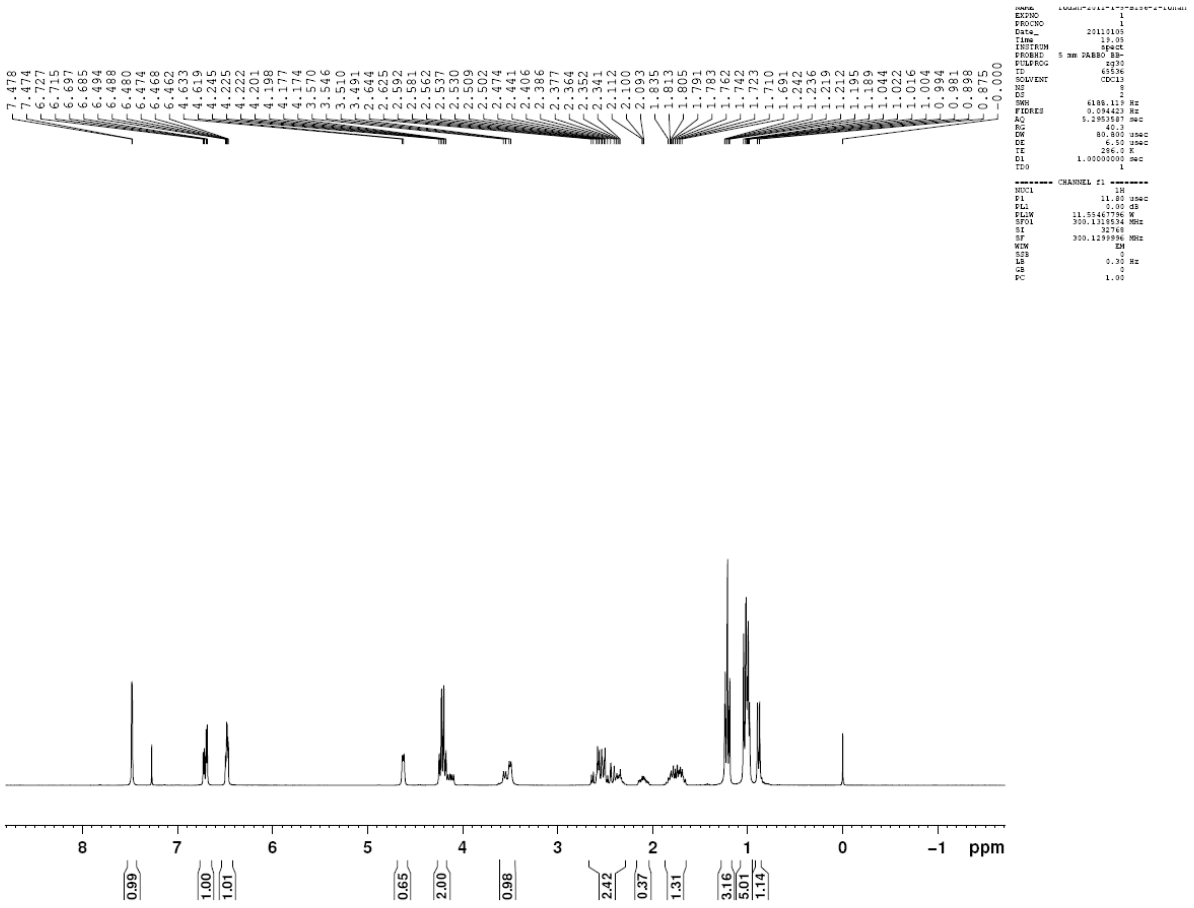


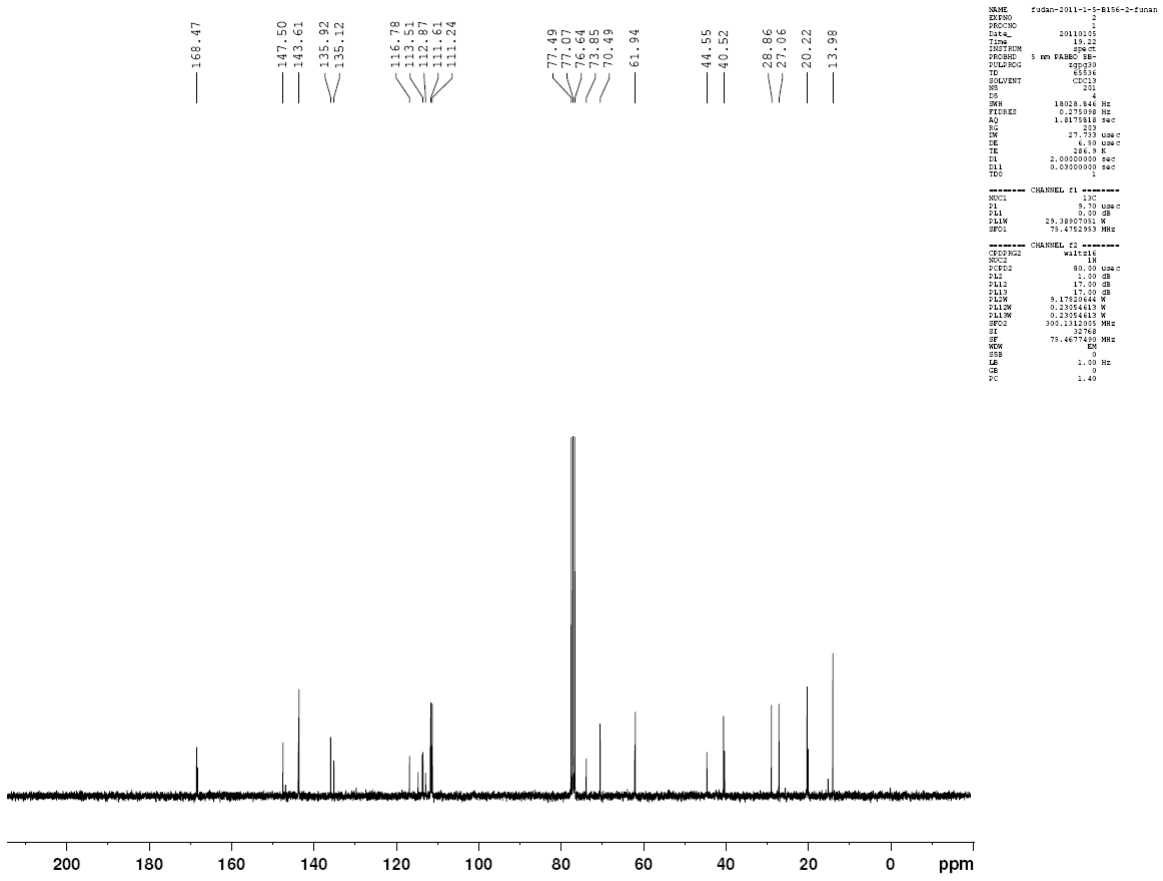



166.16
157.96
131.54
131.43
131.37
131.26
124.37
115.87
115.59
77.48
77.05
76.63
70.42
61.57
48.29
40.37
29.11
26.33
25.72
20.26
20.23
19.97
15.24
13.37
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

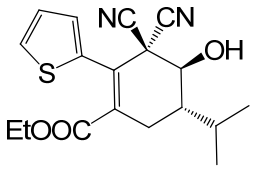
(4*S*,5*S*)-ethyl 3,3-dicyano-2-(furan-2-yl)-4-hydroxy-5-isopropylcyclohex-1-enecarboxylate: 5o

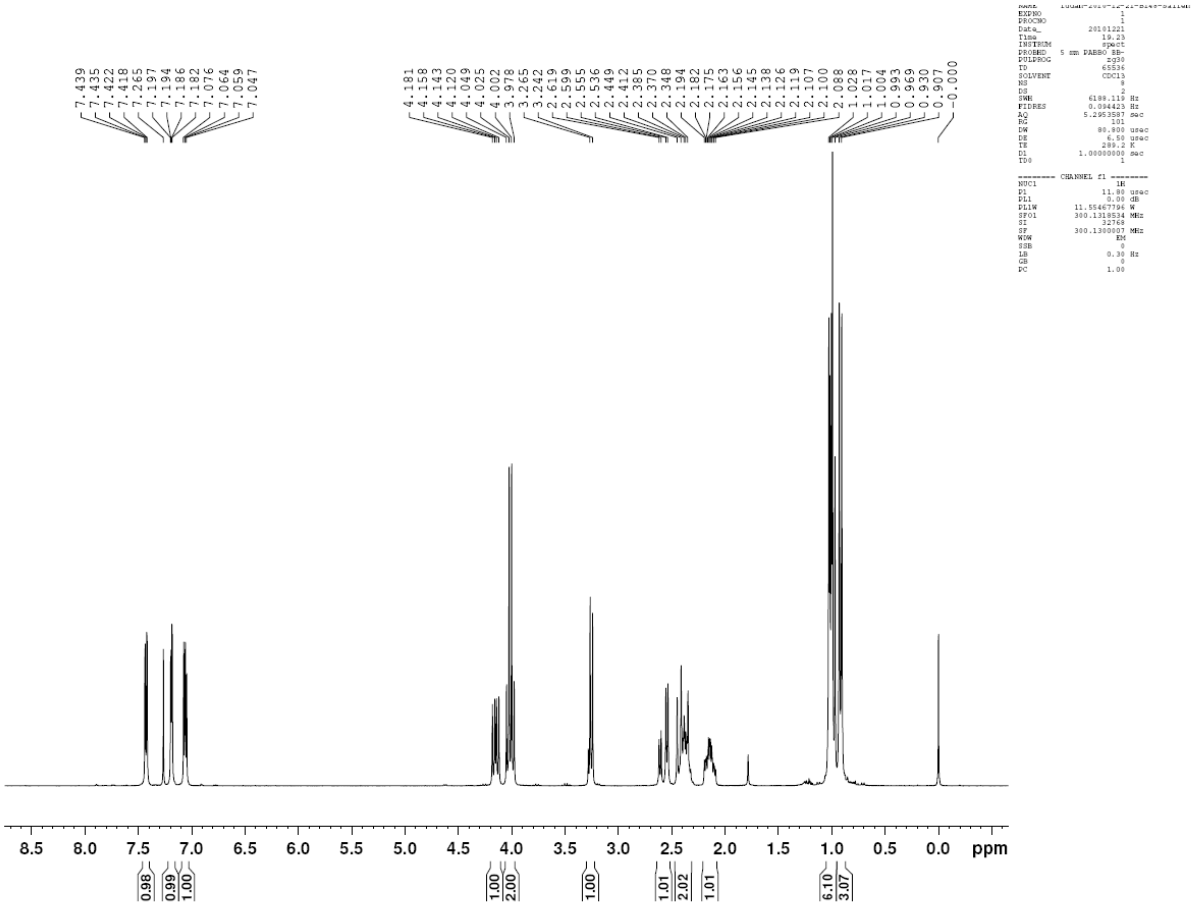


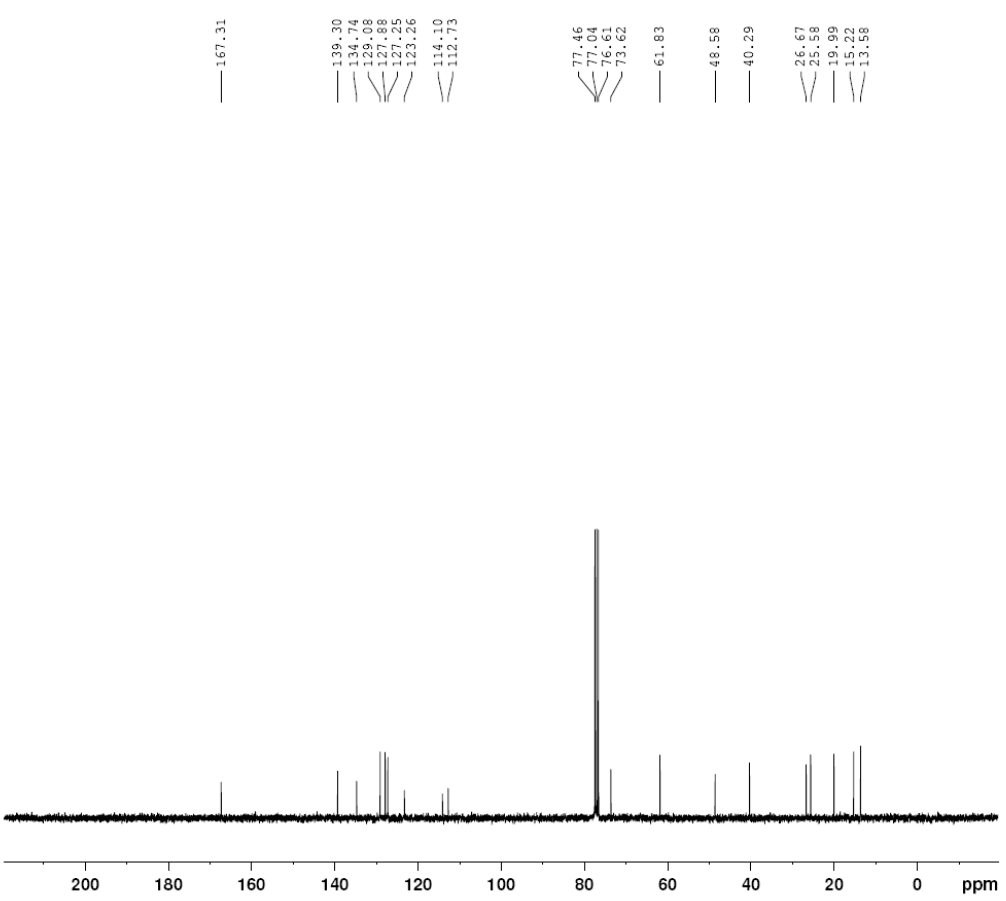



168.47
147.50
143.61
135.92
135.12
116.78
113.51
112.87
111.61
111.24
77.49
77.07
76.64
73.85
70.49
61.94
44.55
40.52
28.86
27.06
20.22
13.98
NAME fudan-2011-1-5-B156-2-funan
EXPNO 2
PROCNO 1
Date_ 20110105
Time 19.22
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 201
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 286.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752993 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17920444 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm

(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(thiophen-2-yl)cyclohex-1-enecarboxylate: 5p

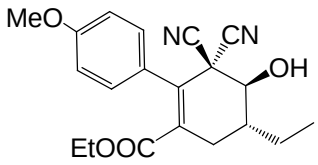


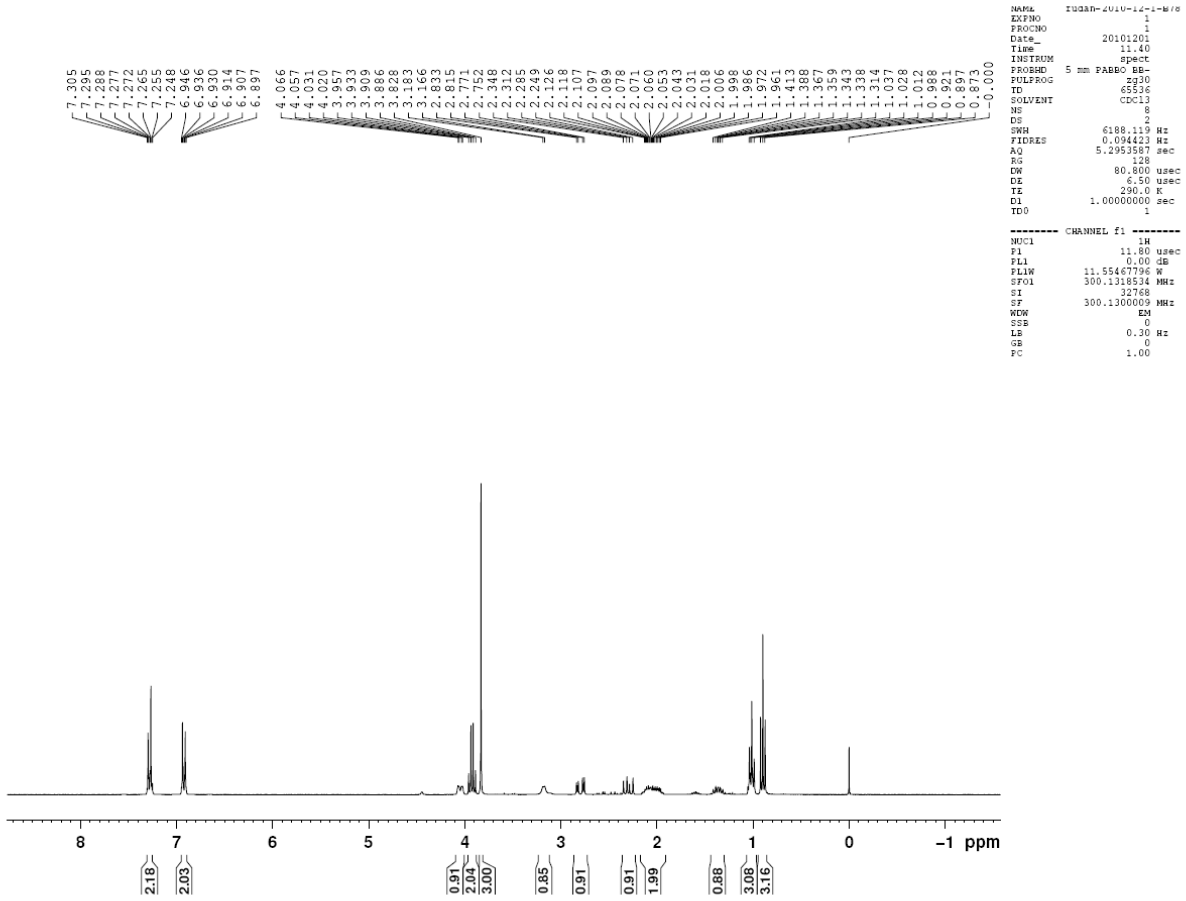


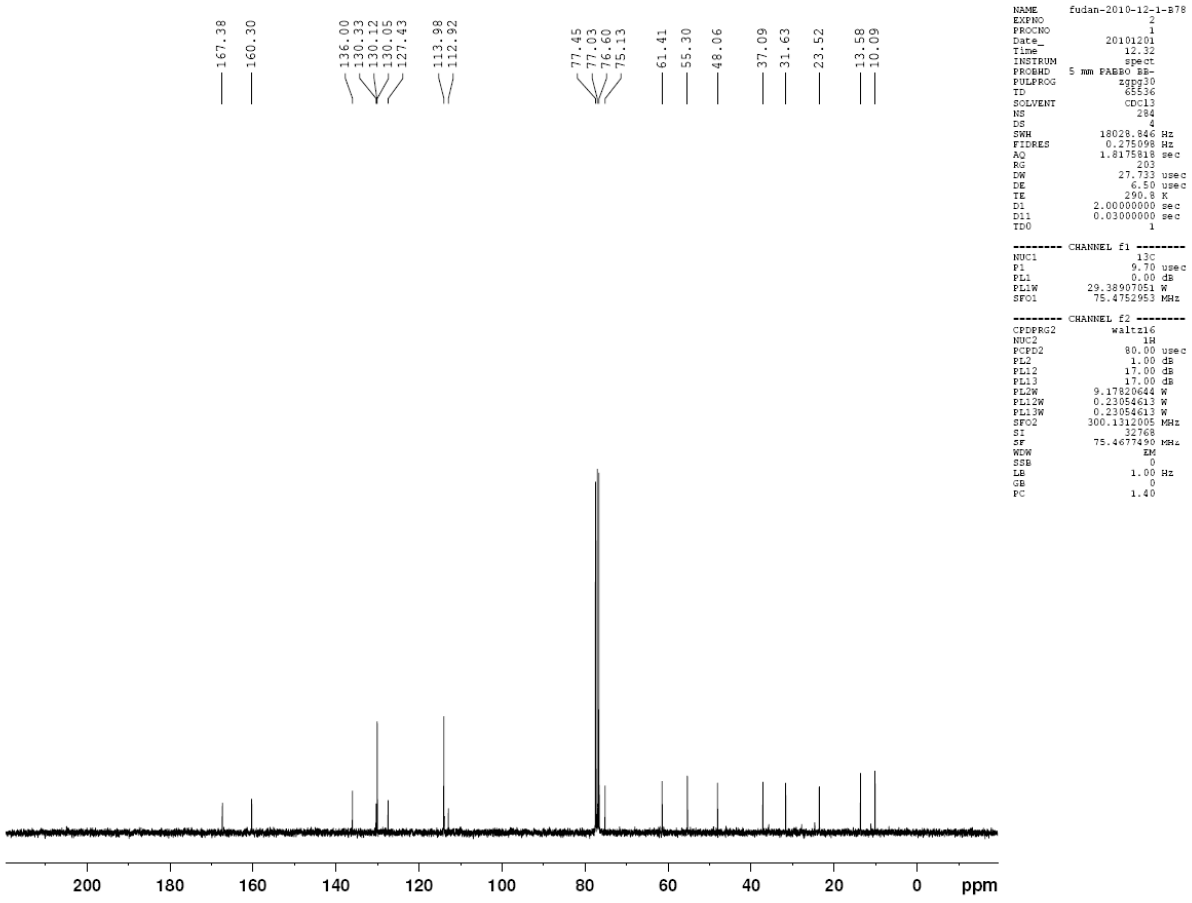

167.31
139.30
134.74
129.08
127.88
127.25
123.26
114.10
112.73
77.46
77.04
76.61
73.62
61.83
48.58
40.29
26.67
25.58
19.99
15.22
13.58
200
180
160
140
120
100
80
60
40
20
0
ppm

(4*S*,5*R*)-ethyl 3,3-dicyano-5-ethyl-4-hydroxy-2-(4-methoxyphenyl)cyclohex-1-enecarboxylate:

5q

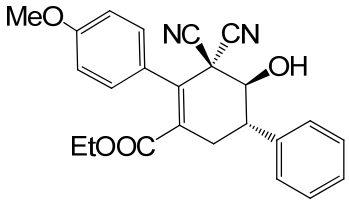


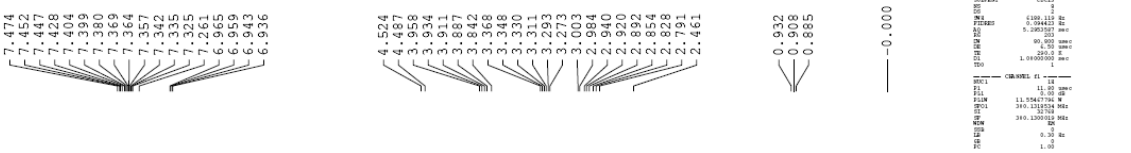


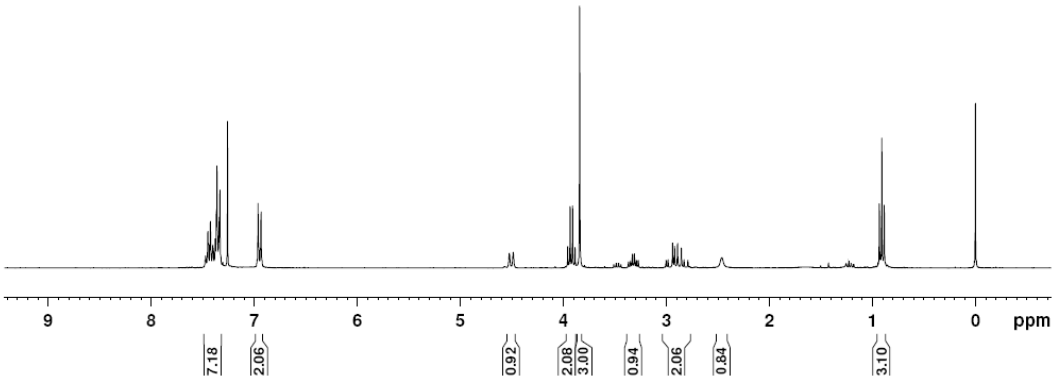

167.38
160.30
136.00
130.33
130.12
130.05
127.43
113.98
112.92
77.45
77.03
76.60
75.13
61.41
55.30
48.06
37.09
31.63
23.52
13.58
10.09
200
180
160
140
120
100
80
60
40
20
0
ppm
NAME fudan-2010-12-1-B78
EXPNO 2
PROCNO 1
Date_ 20101201
Time 12.32
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 284
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
-------- CHANNEL f1 --------
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
-------- CHANNEL f2 --------
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

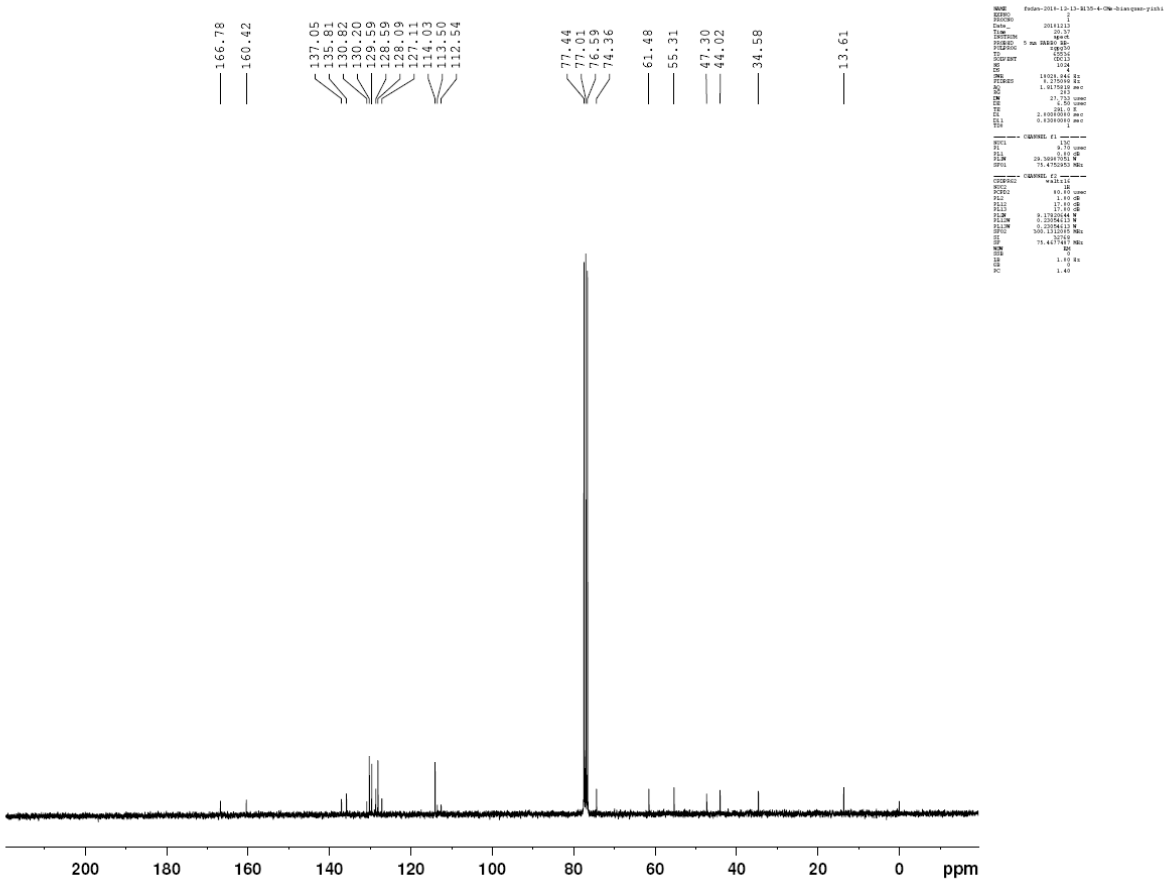
(4*S*,5*S*)-ethyl 3,3-dicyano-4-hydroxy-2-(4-methoxyphenyl)-5-phenylcyclohex-1-enecarboxy

late: 5r



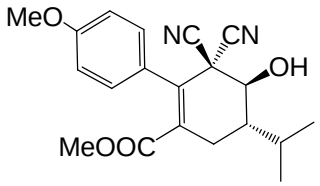


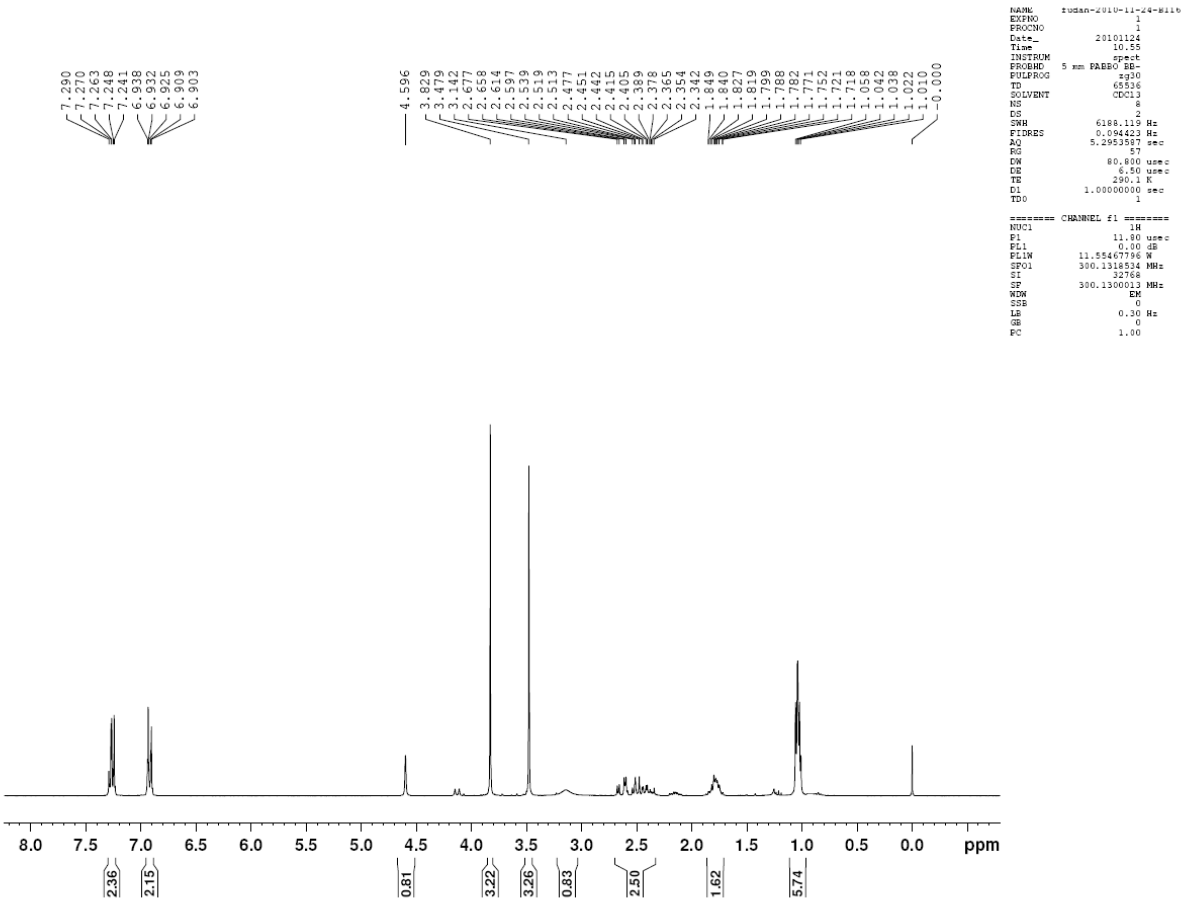


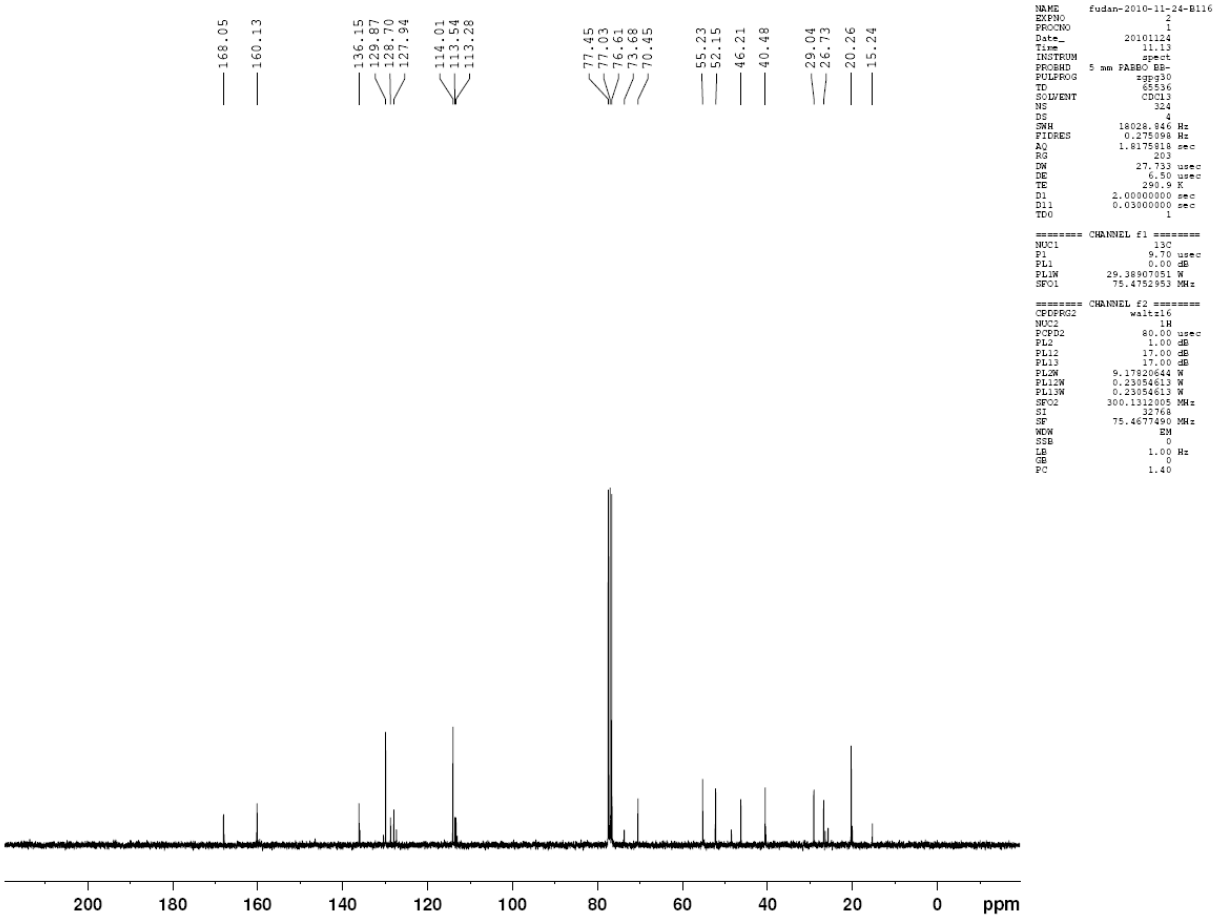

166.78
160.42
137.05
135.81
130.82
130.20
129.59
129.09
128.09
127.11
114.03
113.50
112.54
77.44
77.01
76.59
74.36
61.48
55.31
47.30
44.02
34.58
13.61
200
180
160
140
120
100
80
60
40
20
0
ppm

(4*S*,5*S*)-methyl 3,3-dicyano-4-hydroxy-5-isopropyl-2-(4-methoxyphenyl)cyclohex-1-enecarbo

xylate: 5s

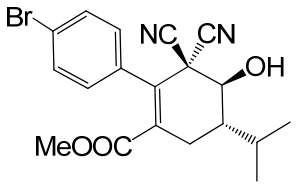


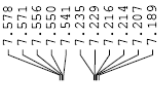


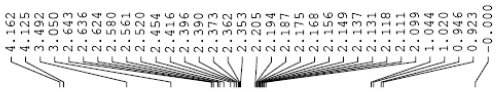

168.05
160.13
136.15
129.87
128.70
127.94
114.01
113.54
113.28
77.45
77.03
76.61
73.68
70.45
55.23
52.15
46.21
40.48
29.04
26.73
20.26
15.24
200
180
160
140
120
100
80
60
40
20
0
ppm
NAME fudan-2010-11-24-B116
EXPNO 2
PROCNO 1
Date_ 20101124
Time 11.13
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 324
DS 4
SWH 18028.846 Hz
FIDRES 0.275098 Hz
AQ 1.8175818 sec
RG 203
DW 27.733 usec
DE 6.50 usec
TE 290.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.70 usec
PL1 0.00 dB
PL1W 29.38907051 W
SFO1 75.4752953 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 1.00 dB
PL12 17.00 dB
PL13 17.00 dB
PL2W 9.17820644 W
PL12W 0.23054613 W
PL13W 0.23054613 W
SFO2 300.1312005 MHz
SI 32768
SF 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

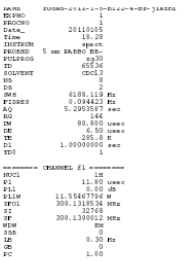
(4*S*,5*S*)-methyl 2-(4-bromophenyl)-3,3-dicyano-4-hydroxy-5-isopropylcyclohex-1-enecarboxy

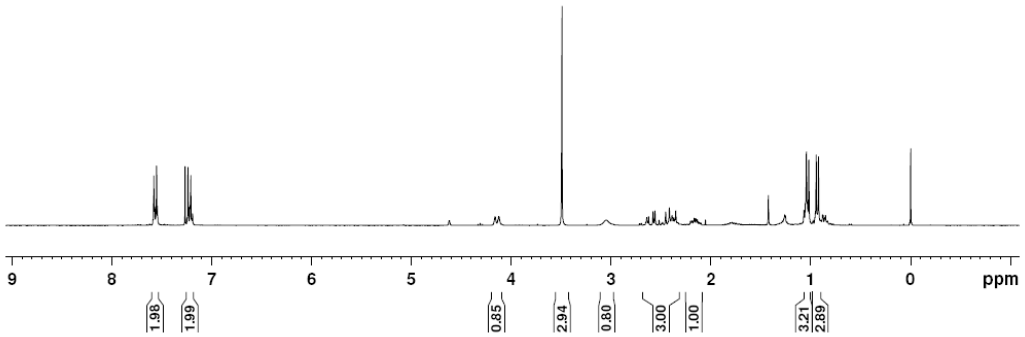
late: 5t

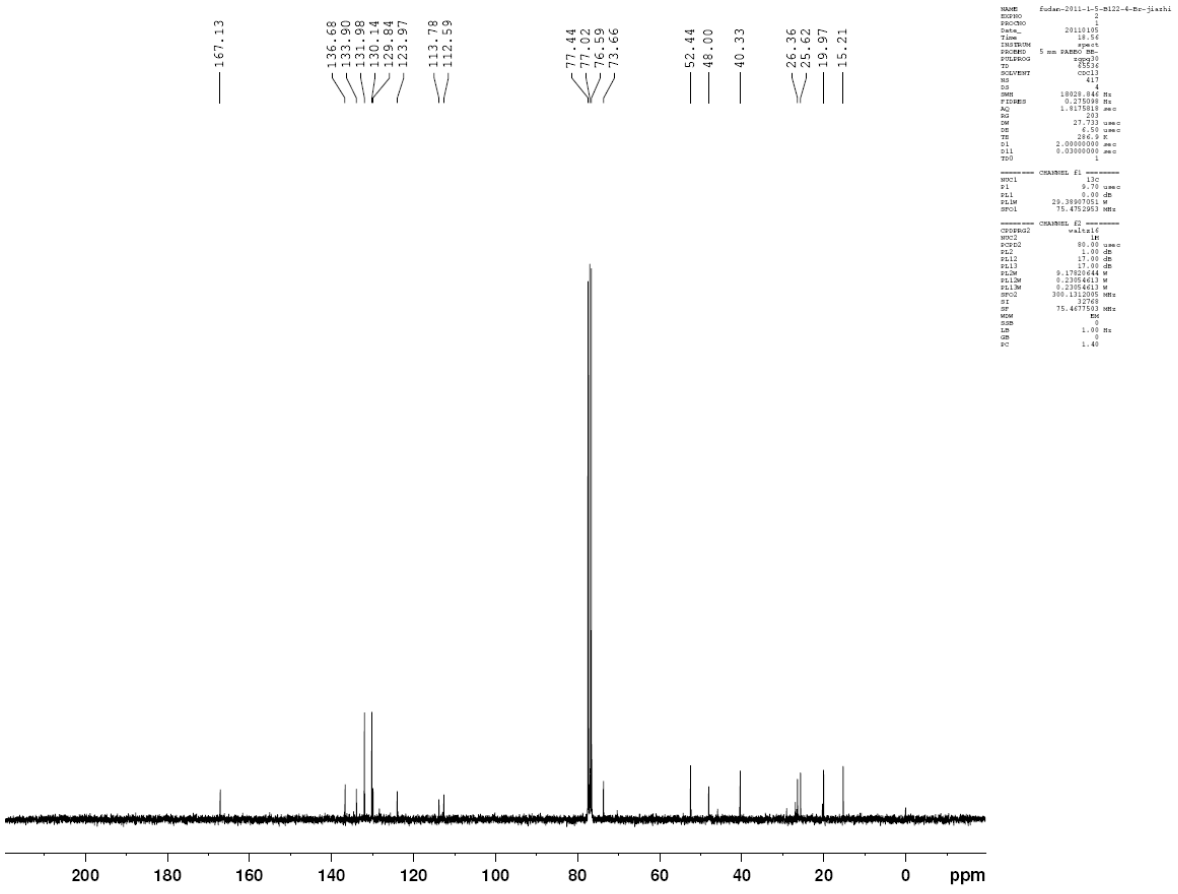











167.13
136.68
133.90
131.98
130.14
129.84
123.97
113.78
112.59
77.44
77.02
76.59
73.66
52.44
48.00
40.33
26.36
25.62
19.97
15.21
200
180
160
140
120
100
80
60
40
20
0
ppm