Supplementary Material (ESI) for Chemical Communications

Supporting Information

Construction of stereodefined 1,1,2,2-tetrasubstituted cyclopropanes by acid catalyzed reaction of aryldiazoacetates and α-substituted acroleins

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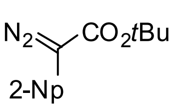
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, dq = double quartet, ddd= double double doublet, m = multiplet, br = broad, and app = apparent), coupling constants (Hz), and assignment. ^{13}C NMR spectra were measured on a JEOL JNM-FX400 (100 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard. High-resolution mass spectra (HRMS) were performed on Brucker microTOF. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF$_{254}$, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck, 230-400 mesh).

In experiments requiring dry solvent, propionitrile was purchased from Tokyo Chemical Industry Co., Ltd. and freshly distilled over calcium hydride prior to use. Dichloromethane was purchased from Kanto Chemical Co. Inc. as “Dehydrated”. Bistrifluoromethanesulfonimide was purchased from Fluka. α-Substituted acroleins were purchased or prepared according to the procedures[1-3] and used after distillation or column chromatography on silica gel. Aryldiazoacetates were synthesized according to the procedure[4] and purified by column chromatography on silica gel.

Preparation of *tert*-butyl aryldiazoacetates.

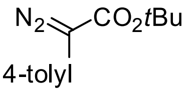
To a stirred solution of *tert*-butyl arylacetate (10 mmol) and *p*-acetamidobenzenesulfonyl azide (3.07 g, 12 mmol) in MeCN (20 mL) was added DBU (2.2 ml, 15 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the resulting mixture was quenched with 1N HCl, and extracted with hexane. The combined organic layers were washed with saturated aqueous $NaHCO_3$ and brine, and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and purified by flash column chromatography on silica gel (eluting with hexane/ethyl acetate = 50:1) to give the corresponding *tert*-butyl aryldiazoacetate.

All diazo compounds, except the following compounds have been previously reported.



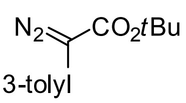
***tert*-Butyl 2-diazo-2-(2-naphthyl)acetate (Table 2, entry 6).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (1H, d, *J* = 2.0 Hz, Ar**H**), 7.83 (1H, d, *J* = 8.8 Hz, Ar**H**), 7.78 (2H, app d, *J* = 8.4 Hz, Ar**H**), 7.51 (1H, dd, *J* = 8.8, 2.0 Hz, Ar**H**), 7.39-7.50 (2H, m, Ar**H**), 1.59 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 133.6, 131.3, 128.5, 127.62, 127.57, 126.5, 125.6, 123.3, 122.5, 121.9, 82.2, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2075, 1695, 1368, 1327, 1267, 1250, 1144, 1125, 849, 808 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{16}N_2O_2$: *m/z* 291.1104 ([M + Na]$^+$), found: *m/z* 291.1092 ([M + Na]$^+$).



***tert*-Butyl 2-diazo-2-(4-tolyl)acetate (Table 2, entry 8).**

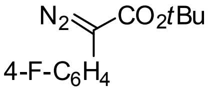
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.18 (2H, d, *J* = 8.4 Hz, Ar**H**), 2.33 (3H, s, C**H**$_3$), 1.54 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 135.4, 129.5, 124.1, 122.7, 81.9, 28.4, 21.0 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2079, 1697, 1514, 1368, 1346, 1287, 1246, 1142, 1007, 810 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{16}N_2O_2$: *m/z* 255.1104 ([M + Na]$^+$), found: *m/z* 255.1095 ([M + Na]$^+$).



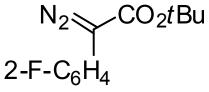
***tert*-Butyl 2-diazo-2-(4-tolyl)acetate (Table 2, entry 10).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (1H, s, Ar**H**), 7.23-7.26 (2H, m, Ar**H**), 6.95-7.00 (1H, m, Ar**H**), 2.35 (3H, s, C**H**$_3$), 1.55 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 138.6, 128.7, 126.4, 125.9, 124.6, 121.0, 81.9, 28.4, 21.6 (The resonance of the carbon that bears the diazo group was not detected);

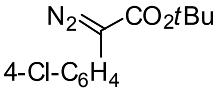
IR (neat) 2079, 1699, 1368, 1342, 1290, 1263, 1248, 1180, 1142, 779 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{16}N_2O_2$: *m/z* 255.1104 ([M + Na]$^+$), found: *m/z* 255.1096 ([M + Na]$^+$).



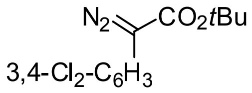
***tert*-Butyl 2-diazo-2-(4-fluorophenyl)acetate (Table 2, entry 12).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (2H, dd, *J* = 8.8 Hz, $^4J(^1H, ^{19}F)$ = 5.2 Hz, Ar**H**), 7.09 (2H, dd, *J* = 8.8 Hz, $^3J(^1H, ^{19}F)$ = 8.8 Hz, Ar**H**), 1.54 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 160.8 (d, $^1J(^{13}C, ^{19}F)$ = 246.9 Hz), 125.8 (d, $^3J(^{13}C, ^{19}F)$ = 7.4 Hz), 121.8 (d, $^4J(^{13}C, ^{19}F)$ = 3.3 Hz), 115.9 (d, $^2J(^{13}C, ^{19}F)$ = 17.4 Hz), 82.2, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2079, 1695, 1510, 1369, 1348, 1288, 1246, 1233, 1142, 1007, 831 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}FN_2O_2$: *m/z* 259.0853 ([M + Na]$^+$), found: *m/z* 259.0844 ([M + Na]$^+$).



***tert*-Butyl 2-diazo-2-(2-fluorophenyl)acetate (Table 2, entry 14).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.75 (1H, m, Ar**H**), 7.13-7.32 (2H, m, Ar**H**), 7.03-7.12 (1H, m, Ar**H**), 1.54 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 158.4 (d, $^1J(^{13}C, ^{19}F)$ = 248.6 Hz), 129.4 (d, $^4J(^{13}C, ^{19}F)$ = 1.7 Hz), 128.2 (d, $^3J(^{13}C, ^{19}F)$ = 9.0 Hz), 124.5 (d, $^3J(^{13}C, ^{19}F)$ = 4.1 Hz), 115.6 (d, $^2J(^{13}C, ^{19}F)$ = 21.4 Hz), 114.4 (d, $^2J(^{13}C, ^{19}F)$ = 12.3 Hz), 82.2, 28.3 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2092, 1697, 1497, 1369, 1348, 1288, 1246, 1144, 1107, 1009 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}FN_2O_2$: *m/z* 259.0853 ([M + Na]$^+$), found: *m/z* 259.0860 ([M + Na]$^+$).

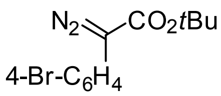


***tert*-Butyl 2-(4-chlorophenyl)-2-diazoacetate (Table 2, entry 15).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.33 (2H, d, *J* = 8.8 Hz, Ar**H**), 1.55 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 131.1, 129.0, 125.0, 124.8, 82.3, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2087, 1692, 1495, 1369, 1346, 1279, 1246, 1148, 1007, 829 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}ClN_2O_2$: *m/z* 275.0558 ([M + Na]$^+$), found: *m/z* 275.0547 ([M + Na]$^+$).



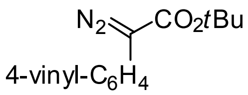
***tert*-Butyl 2-diazo-2-(3,4-dichlorophenyl)acetate (Table 2, entry 16).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (1H, d, *J* = 2.4 Hz, Ar**H**), 7.41 (1H, d, *J* = 8.8 Hz, Ar**H**), 7.25 (1H, dd, *J* = 8.8, 2.4 Hz, Ar**H**), 1.55 (9H, s, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 133.1, 130.5, 129.0, 126.7, 125.3, 122.6, 82.7, 28.3 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2083, 1697, 1477, 1369, 1346, 1281, 1244, 1146, 1042, 1028 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}Cl_2N_2O_2$: *m/z* 309.0168 ($[M + Na]^+$), found: *m/z* 309.0169 ($[M + Na]^+$).



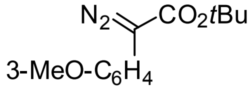
***tert*-Butyl 2-(4-bromophenyl)-2-diazoacetate (Table 2, entry 18).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.35 (2H, d, *J* = 8.8 Hz, Ar**H**), 1.54 (9H, s, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 131.9, 125.3, 119.0, 82.3, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2087, 1692, 1491, 1369, 1344, 1279, 1246, 1148, 1003, 829 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{13}BrN_2O_2$: *m/z* 319.0053 ($[M + Na]^+$), found: *m/z* 319.0053 ($[M + Na]^+$).



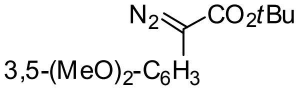
***tert*-Butyl 2-diazo-2-(4-vinylphenyl)acetate (Table 2, entry 19).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.45 (4H, br, Ar**H**), 6.68 (1H, dd, *J* = 18.0, 11.2 Hz, CH_2=C**H**), 5.73 (1H, d, *J* = 18.0 Hz, C**H**H=CH), 5.23 (1H, d, *J* = 11.2 Hz, CH**H**=CH), 1.55 (9H, s, $C(C\mathbf{H}_3)_3$) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 136.1, 134.8, 126.7, 125.3, 123.9, 113.5, 82.1, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2079, 1697, 1512, 1368, 1344, 1285, 1246, 1144, 1005, 841 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{14}H_{16}N_2O_2$: *m/z* 267.1104 ($[M + Na]^+$), found: *m/z* 267.1095 ($[M + Na]^+$).



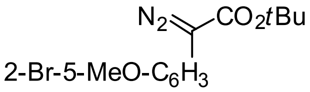
***tert*-Butyl 2-diazo-2-(3-methoxyphenyl)acetate (Table 2, entry 21).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (1H, dd, *J* = 8.4, 8.4 Hz, Ar**H**), 7.14 (1H, dd, *J* = 2.4, 2.4 Hz, Ar**H**), 6.97 (1H, ddd, *J* = 8.4, 1.2, 1.2 Hz, Ar**H**), 6.70 (1H, ddd, *J* = 8.4, 2.4, 1.2 Hz, Ar**H**), 3.81 (3H, s, $OC\mathbf{H}_3$), 1.55 (9H, s, $C(C\mathbf{H}_3)_3$) ; ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 160.0, 129.7, 127.6, 116.0, 111.3, 109.6, 82.0, 55.3, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2077, 1697, 1599, 1368, 1265, 1236, 1171, 1138, 1020, 687 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{16}N_2O_3$: *m/z* 271.1053 ([M + Na]$^+$), found: *m/z* 271.1042 ([M + Na]$^+$).



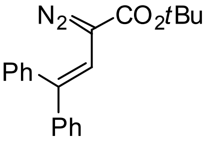
tert-Butyl 2-diazo-2-(3,5-dimethoxyphenyl)acetate (Table 2, entry 22).

^{1}H NMR (400 MHz, CDCl$_3$) δ 6.66 (2H, d, *J* = 2.0 Hz, Ar**H**), 6.27 (1H, t, *J* = 2.0 Hz, Ar**H**), 3.79 (6H, s, OC**H**$_3$), 1.55 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.3, 161.1, 128.3, 101.9, 97.9, 82.0, 55.3, 28.4 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2079, 1697, 1589, 1285, 1254, 1206, 1153, 1138, 1065, 1028 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{14}H_{18}N_2O_4$: *m/z* 301.1159 ([M + Na]$^+$), found: *m/z* 301.1150 ([M + Na]$^+$).



tert-Butyl 2-diazo-2-(2-bromo-5-methoxyphenyl)acetate (Table 2, entry 23).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.46 (1H, d, *J* = 8.8 Hz, Ar**H**), 7.07 (1H, d, *J* = 2.8 Hz, Ar**H**), 6.75 (1H, dd, *J* = 8.8, 2.8 Hz, Ar**H**), 3.80 (3H, s, OC**H**$_3$), 1.53 (9H, s, C(C**H**$_3$)$_3$) ; ^{13}C NMR (100 MHz, CDCl$_3$) δ 164.6, 158.9, 133.8, 126.9, 117.5, 116.2, 114.5, 82.1, 55.6, 28.3 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2089, 1694, 1470, 1368, 1288, 1234, 1173, 1144, 1026, 1009 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{15}BrN_2O_3$: *m/z* 349.0158 ([M + Na]$^+$), found: *m/z* 349.0158 ([M + Na]$^+$).



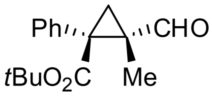
tert-Butyl 2-diazo-2-(2,2-diphenylvinyl)acetate (Table 2, entry 24).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.20-7.40 (10H, m, *J* = 8.8 Hz, Ar**H**), 6.27 (1H, s, Ph$_2$C=C**H**), 1.50 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 165.6, 142.0, 138.5, 135.9, 130.3, 128.4, 128.2, 127.8, 127.1, 126.9, 110.3, 82.1, 28.3 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2081, 1694, 1368, 1242, 1148, 1103, 908, 770, 758, 729 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{20}N_2O_2$: *m/z* 343.1417 ([M + Na]$^+$), found: *m/z* 343.1404 ([M + Na]$^+$).

General procedure for the diastereoselective cyclopropanation reaction.

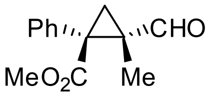
Method A: To a stirred solution of aryldiazoacetate (0.25 mmol) and α-substituted acrolein (0.30 mmol) in CH_2Cl_2 (1.0 mL) was added 1.0 M $TiCl_4$ in CH_2Cl_2 (50 µL, 0.050 mmol) dropwise at 0 °C under argon. The reaction mixture was stirred at the same temperature for 30 min. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 50:1~40:1) to give the corresponding cyclopropane.

Method B: To a stirred solution of aryldiazoacetate (0.25 mmol) and α-substituted acrolein (0.30 mmol) in propionitrile (1.0 mL) was added 0.52 M Tf_2NH in CH_2Cl_2 (98 µL, 0.050 mmol) dropwise at –78 °C under argon. The reaction mixture was stirred at the same temperature for 30 min. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 50:1~40:1) to give the corresponding cyclopropane.



***trans*-2-Formyl-2-methyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (Table 1, entry 1).**

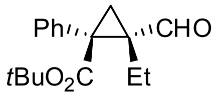
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (1H, s, C**H**O), 7.23-7.40 (5H, m, Ar**H**), 2.07 (1H, d, J = 5.6 Hz, C**H**H), 2.00 (1H, d, J = 5.6 Hz, CH**H**), 1.41 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 168.1, 135.2, 130.8, 128.3, 127.7, 82.1, 43.8, 37.0, 27.8, 22.5, 12.0; IR (neat) 2978, 1715, 1449, 1369, 1254, 1161, 1113, 959, 910, 847, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{20}O_3$: *m/z* 283.1305 ([M + Na]$^+$), found: *m/z* 283.1297 ([M + Na]$^+$).



***trans*-2-Formyl-2-methyl-1-phenylcyclopropanecarboxylic acid methyl ester (Table 1, entry 12).**

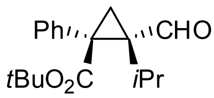
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (1H, s, C**H**O), 7.23-7.43 (5H, m, Ar**H**), 3.67 (3H, s, OC**H**$_3$), 2.17 (1H, d, J = 5.6 Hz, C**H**H), 2.08 (1H, d, J = 5.6 Hz, CH**H**), 1.40 (3H, s, C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 169.7, 134.5, 130.9, 128.5, 128.0, 52.8, 42.6, 37.5, 23.2, 12.0; IR (neat) 1710, 1495, 1449, 1435, 1310, 1260, 1211, 1109, 1082, 1065, 908 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{14}O_3$: *m/z* 241.0835 ([M +

Na]$^+$), found: *m/z* 241.0847 ([M + Na]$^+$).



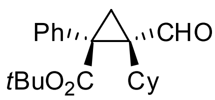
***trans*-2-Ethyl-2-formyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 1).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (1H, s, C**H**O), 7.23-7.37 (5H, m, Ar**H**), 2.09 (1H, d, *J* = 5.2 Hz, C**H**H), 1.94 (1H, d, *J* = 5.2 Hz, CH**H**), 1.94 (1H, dt, *J* = 7.2, 15.2 Hz, C**H**HCH$_3$), 1.76 (1H, dt, *J* = 7.2, 15.2 Hz, CH**H**CH$_3$), 1.37 (9H, s, C(C**H**$_3$)$_3$), 1.07 (3H, t, *J* = 7.2 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 168.4, 135.4, 130.8, 128.3, 127.6, 82.0, 43.9, 43.2, 27.8, 21.9, 19.7, 11.7; IR (neat) 2976, 1713, 1367, 1274, 1247, 1213, 1111, 959, 910, 750, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_3$: *m/z* 297.1461 ([M + Na]$^+$), found: *m/z* 297.1462 ([M + Na]$^+$).



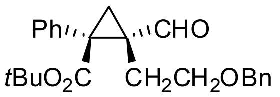
***trans*-2-Formyl-2-isopropyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 2).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (1H, d, *J* = 2.0 Hz, C**H**O), 7.21-7.36 (5H, m, Ar**H**), 1.97 (1H, d, *J* = 5.2 Hz, C**H**H), 1.94 (1H, d, *J* = 5.2 Hz, CH**H**), 1.66 (1H, m, C**H**(CH$_3$)$_2$), 1.44 (3H, d, *J* = 7.2 Hz, CH(C**H**$_3$)(CH$_3$)), 1.36 (9H, s, C(C**H**$_3$)$_3$), 1.18 (3H, d, *J* = 7.2 Hz, CH(CH$_3$)(C**H**$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 168.4, 135.6, 130.9, 128.2, 127.5, 81.9, 45.7, 45.4, 29.2, 27.7, 22.0, 19.5, 19.2; IR (neat) 2976, 1713, 1449, 1368, 1298, 1254, 1211, 1155, 847, 746, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{24}O_3$: *m/z* 311.1618 ([M + Na]$^+$), found: *m/z* 311.1614 ([M + Na]$^+$).



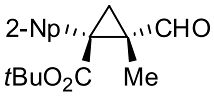
***trans*-2-Cyclohexyl-2-formyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 3).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (1H, d, *J* = 1.2 Hz, C**H**O), 7.20-7.35 (5H, m, Ar**H**), 2.10 (1H, m, Cy), 1.91-2.00 (1H, br, Cy), 1.96 (1H, d, *J* = 5.6 Hz, C**H**H), 1.94 (1H, d, *J* = 5.6 Hz, CH**H**), 1.75-1.85 (2H, m, Cy), 1.60-1.71 (3H, m, Cy), 1.09-1.40 (4H, m, Cy), 1.37 (1H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 168.4, 135.6, 131.0, 128.1, 127.5, 81.9, 45.1, 39.4, 29.6, 29.2, 27.7 (two peaks are overlapped), 27.0, 26.8, 26.1, 21.7; IR (neat) 2928, 2852, 1713, 1449, 1368, 1252, 1157, 1140, 847, 746, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{21}H_{28}O_3$: *m/z* 351.1931 ([M + Na]$^+$), found: *m/z* 351.1942 ([M + Na]$^+$).



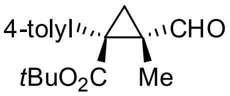
***trans*-2-((2-Benzyloxy)ethyl)-2-formyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 5).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (1H, s, C**H**O), 7.23-7.37 (10H, m, Ar**H**), 4.51 (2H, s, OC**H**$_2$Ph), 3.64-3.74 (1H, m, C**H**HOBn), 3.55-3.64 (1H, m, CH**H**OBn), 2.38-2.48 (1H, m, C**H**HCH$_2$OBn), 2.14 (1H, d, J = 5.2 Hz, C**H**H), 1.99 (1H, d, J = 5.2 Hz, CH**H**), 1.92-2.03 (1H, m, CH**H**CH$_2$OBn), 1.35 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 168.3, 138.4, 135.2, 130.9, 128.3, 128.2, 127.7, 127.6, 127.5, 82.2, 73.0, 68.1, 43.7, 39.7, 27.8, 26.6, 21.4; IR (neat) 2858, 1709, 1454, 1368, 1254, 1155, 1099, 912, 845, 737, 698 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{24}H_{28}O_4$: *m/z* 403.1880 ([M + Na]$^+$), found: *m/z* 403.1881 ([M + Na]$^+$).



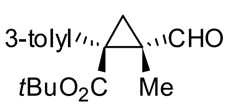
***trans*-2-Formyl-2-methyl-1-(2-naphthyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 6).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (1H, s, C**H**O), 7.74-7.87 (4H, m, Ar**H**), 7.45-7.52 (3H, m, Ar**H**), 2.16 (1H, d, J = 5.6 Hz, C**H**H), 2.13 (1H, d, J = 5.6 Hz, CH**H**), 1.46 (3H, s, C**H**$_3$), 1.37 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1, 168.0, 133.0, 132.9, 132.8, 129.3, 129.0, 128.0, 127.9, 127.8, 127.6, 126.3, 82.3, 44.0, 37.2, 27.9, 22.8, 12.0; IR (neat) 2976, 1711, 1368, 1242, 1159, 1111, 959, 914, 847, 816, 748 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{22}O_3$: *m/z* 333.1461 ([M + Na]$^+$), found: *m/z* 333.1461 ([M + Na]$^+$).



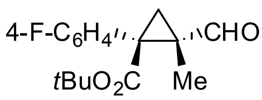
***trans*-2-Formyl-2-methyl-1-(4-tolyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 8).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (1H, s, C**H**O), 7.26 (2H, d, J = 8.0 Hz, Ar**H**), 7.09 (2H, d, J = 8.0 Hz, Ar**H**), 2.32 (3H, s, ArC**H**$_3$), 2.04 (1H, d, J = 5.6 Hz, C**H**H), 1.98 (1H, d, J = 5.6 Hz, CH**H**), 1.40 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 168.3, 137.5, 132.1, 130.6, 129.0, 82.0, 43.5, 36.9, 27.9, 22.6, 21.1, 12.1; IR (neat) 2978, 1713, 1514, 1456, 1317, 1159, 1105, 961, 912, 847 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_3$: *m/z* 297.1461 ([M + Na]$^+$), found: *m/z* 297.1449 ([M + Na]$^+$).



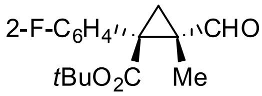
***trans*-2-Formyl-2-methyl-1-(3-tolyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 10).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (1H, s, C**HO**), 7.02-7.23 (4H, m, Ar**H**), 2.32 (3H, s, ArC**H**$_3$), 2.04 (1H, d, *J* = 5.6 Hz, C**H**H), 1.99 (1H, d, *J* = 5.6 Hz, CH**H**), 1.40 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.4, 168.2, 137.9, 135.0, 131.5, 128.5, 128.1, 127.9, 82.0, 43.8, 37.0, 27.9, 22.6, 21.3, 12.1; IR (neat) 2976, 1711, 1456, 1367, 1234, 1157, 1112, 959, 914, 849 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_3$: *m/z* 297.1461 ([M + Na]$^+$), found: *m/z* 297.1446 ([M + Na]$^+$).



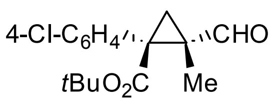
***trans*-1-(4-Fluorophenyl)-2-formyl-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 12).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (1H, s, C**HO**), 7.35 (2H, dd, *J* = 8.8 Hz, $^4J(^1H,\ ^{19}F)$ = 5.2 Hz, Ar**H**), 6.99 (2H, dd, *J* = 8.8 Hz, $^3J(^1H,\ ^{19}F)$ = 8.8 Hz, Ar**H**), 2.08 (1H, d, *J* = 5.6 Hz, C**H**H), 1.98 (1H, d, *J* = 5.6 Hz, CH**H**), 1.44 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 167.8, 162.1 (d, $^1J(^{13}C,\ ^{19}F)$ = 248.5 Hz), 132.4 (d, $^3J(^{13}C,\ ^{19}F)$ = 8.2 Hz), 131.0 (d, $^4J(^{13}C,\ ^{19}F)$ = 3.2 Hz), 115.2 (d, $^2J(^{13}C,\ ^{19}F)$ = 22.3 Hz), 82.3, 42.9, 37.1, 27.8, 22.6, 11.9; IR (neat) 2978, 1713, 1602, 1510, 1369, 1254, 1223, 1157, 959, 843 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}FO_3$: *m/z* 301.1210 ([M + Na]$^+$), found: *m/z* 301.1221 ([M + Na]$^+$).



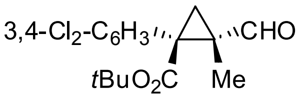
***trans*-1-(2-Fluorophenyl)-2-formyl-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 14).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (1H, s, C**HO**), 7.23-7.36 (2H, m, Ar**H**), 7.06-7.13 (1H, m, Ar**H**), 6.97-7.04 (1H, m, Ar**H**), 2.14 (1H, d, *J* = 5.2 Hz, C**H**H), 1.91 (1H, d, *J* = 5.2 Hz, CH**H**), 1.50 (3H, s, C**H**$_3$), 1.35 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 167.6, 161.8 (d, $^1J(^{13}C,\ ^{19}F)$ = 250.1 Hz), 131.7, 129.8 (d, $^3J(^{13}C,\ ^{19}F)$ = 8.3 Hz), 124.0 (d, $^3J(^{13}C,\ ^{19}F)$ = 3.3 Hz), 123.5 (d, $^2J(^{13}C,\ ^{19}F)$ = 14.0 Hz), 115.5 (d, $^2J(^{13}C,\ ^{19}F)$ = 22.3 Hz), 82.2, 38.2, 37.4, 27.8, 23.0, 11.3; IR (neat) 1715, 1495, 1452, 1368, 1256, 1229, 1207, 1161, 847, 758 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}FO_3$: *m/z* 301.1210 ([M + Na]$^+$), found: *m/z* 301.1205 ([M + Na]$^+$).



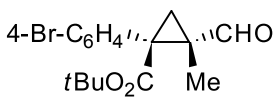
***trans*-1-(4-Chlorophenyl)-2-formyl-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 15).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (1H, s, C**HO**), 7.24-7.34 (4H, m, Ar**H**), 2.08 (1H, d, *J* = 5.6 Hz, C**H**H), 1.97 (1H, d, *J* = 5.6 Hz, CH**H**), 1.43 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.7, 167.6, 133.8, 133.7, 132.1, 128.5, 82.4, 43.1, 37.2, 27.8, 22.5, 11.9; IR (neat) 2978, 1713, 1493, 1369, 1254, 1159, 1094, 912, 833, 787 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}ClO_3$: *m/z* 317.0915 ([M + Na]$^+$), found: *m/z* 317.0907 ([M + Na]$^+$).



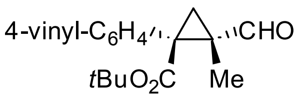
***trans*-1-(3,4-Difluorophenyl)-2-formyl-2-methylcyclopropane carboxylic acid *tert*-butyl ester (Table 2, entry 16).**

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.49 (1H, s, C**HO**), 7.49 (1H, d, *J* = 2.4 Hz, Ar**H**), 7.38 (1H, d, *J* = 8.0 Hz, Ar**H**), 7.21 (1H, dd, *J* = 8.0, 2.4 Hz, Ar**H**), 2.10 (1H, d, *J* = 5.6 Hz, C**H**H), 1.98 (1H, d, *J* = 5.6 Hz, CH**H**), 1.42 (3H, s, C**H**$_3$), 1.40 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.2, 167.1, 135.5, 132.6, 132.2, 130.3, 130.2, 82.8, 42.7, 37.5, 27.9, 22.5, 11.9; IR (neat) 1713, 1472, 1369, 1275, 1248, 1223, 1159, 1134, 1032, 912 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{18}Cl_2O_3$: *m/z* 351.0525 ([M + Na]$^+$), found: *m/z* 351.0513 ([M + Na]$^+$).



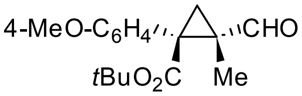
***trans*-1-(4-Bromophenyl)-2-formyl-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 18).**

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.45 (1H, s, C**HO**), 7.43 (2H, d, *J* = 8.8 Hz, Ar**H**), 7.25 (2H, d, *J* = 8.8 Hz, Ar**H**), 2.08 (1H, d, *J* = 6.0 Hz, C**H**H), 1.97 (1H, d, *J* = 6.0 Hz, CH**H**), 1.41 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.7, 167.5, 134.3, 132.5, 131.5, 121.9, 82.5, 43.1, 37.2, 27.8, 22.5, 11.9; IR (neat) 2976, 1713, 1395, 1368, 1254, 1157, 1074, 959, 845, 827 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{19}BrO_3$: *m/z* 361.0410 ([M + Na]$^+$), found: *m/z* 361.0415 ([M + Na]$^+$).



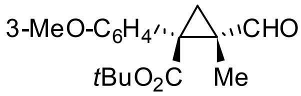
***trans*-2-Formyl-2-methyl-1-(4-vinylphenyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 19).**

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.44 (1H, s, C**HO**), 7.30-7.39 (4H, br, Ar**H**), 6.69 (1H, dd, *J* = 17.6, 11.2 Hz, CH$_2$C**H**), 5.75 (1H, d, *J* = 17.6 Hz, C**H**HCH), 5.26 (1H, d, *J* = 11.2 Hz, CH**H**CH), 2.07 (1H, d, *J* = 5.6 Hz, C**H**H), 1.99 (1H, d, *J* = 5.6 Hz, CH**H**), 1.41 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.2, 168.0, 137.0, 136.2, 134.6, 131.0, 126.1, 114.3, 82.2, 43.6, 37.1, 27.9, 22.6, 12.0; IR (neat) 1713, 1369, 1321, 1254, 1227, 1159, 1107, 961, 912, 845 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{22}O_3$: *m/z* 309.1461 ([M + Na]$^+$), found: *m/z* 309.1468 ([M + Na]$^+$).



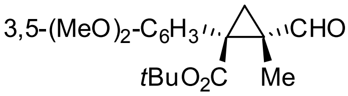
***trans*-2-Formyl-1-(4-methoxyphenyl)-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 20).**

^{1}H NMR (400 MHz, CDCl$_3$) (trans isomer) δ 8.46 (1H, s, C**H**O), 7.24-7.30 (2H, m, Ar**H**), 6.79-6.86 (2H, m, Ar**H**), 3.79 (3H, s, OC**H**$_3$), 2.04 (1H, d, *J* = 5.6 Hz, C**H**H), 1.97 (1H, d, *J* = 5.6 Hz, CH**H**), 1.39 (3H, s, C**H**$_3$), 1.38 (9H, s, C(C**H**$_3$)$_3$) / (cis isomer) δ 9.19 (1H, s, C**H**O), 7.28-7.32 (2H, m, Ar**H**), 6.82-6.90 (2H, m, Ar**H**), 3.81 (3H, m, OC**H**$_3$), 2.38 (1H, d, *J* = 5.6 Hz, C**H**H), 1.54 (1H, d, *J* = 5.6 Hz, CH**H**), 1.38 (9H, s, C(C**H**$_3$)$_3$), 0.93 (3H, s, C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) (mixture of two isomers) δ 200.62, 200.58, 168.3, 159.2, 159.0, 131.8, 131.7, 127.11, 127.07, 113.7, 113.6, 82.2, 82.0, 55.2, 43.8, 43.2, 38.6, 37.0, 27.9, 27.8, 23.9, 22.6, 14.2, 12.1; IR (neat) 1711, 1514, 1368, 1248, 1227, 1159, 1119, 1103, 1032, 912 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_4$: *m/z* 314.1444 ([M + Na]$^+$), found: *m/z* 314.1450 ([M + Na]$^+$).



***trans*-2-Formyl-1-(3-methoxyphenyl)-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 21).**

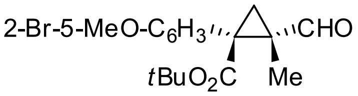
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.43 (1H, s, C**H**O), 7.20 (1H, dd, *J* = 8.0, 8.0 Hz, Ar**H**), 6.96 (1H, ddd, *J* = 8.0, 0.8, 0.8 Hz, Ar**H**), 6.93 (1H, dd, *J* = 1.6, 0.8 Hz, Ar**H**), 6.80 (1H, ddd, *J* = 8.0, 1.6, 0.8 Hz, Ar**H**), 3.79 (3H, s, OC**H**$_3$), 2.04 (1H, d, *J* = 5.2 Hz, C**H**H), 1.99 (1H, d, *J* = 5.2 Hz, CH**H**), 1.40 (3H, s, C**H**$_3$), 1.39 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.1, 167.9, 159.4, 136.6, 129.2, 123.2, 116.3, 113.5, 82.1, 55.2, 43.8, 37.1, 27.9, 22.6, 12.0; IR (neat) 1711, 1599, 1368, 1317, 1288, 1240, 1157, 1113, 1042, 847 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{22}O_4$: *m/z* 314.1444 ([M + Na]$^+$), found: *m/z* 314.1443 ([M + Na]$^+$).



***trans*-2-Formyl-1-(3,5-methoxyphenyl)-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 22).**

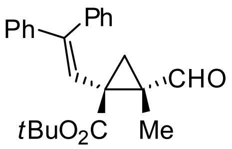
^{1}H NMR (400 MHz, CDCl$_3$) δ 8.45 (1H, s, C**H**O), 6.54 (2H, d, *J* = 2.4 Hz, Ar**H**), 6.36 (1H, t, *J* = 2.4 Hz, Ar**H**), 3.76 (3H, s, OC**H**$_3$), 2.02 (1H, d, *J* = 5.2 Hz, C**H**H), 1.98 (1H, d, *J* = 5.2 Hz, CH**H**), 1.40 (3H, s, C**H**$_3$), 1.39 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 200.2, 167.9, 160.5, 137.3, 108.9, 100.1, 82.2, 55.3, 44.0, 37.1, 27.9, 22.7, 12.1; IR (neat) 1711, 1595, 1458, 1425, 1368, 1244, 1206, 1155, 1043, 847 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{24}O_5$: *m/z* 343.1522 ([M + Na]$^+$), found: *m/z*

343.1516 ([M + Na]$^+$).



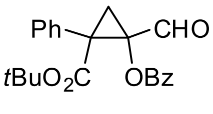
***trans*-2-Formyl-1-(2-bromo-5-methoxyphenyl)-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 23).**

^{1}H NMR (400 MHz, CDCl$_3$) (major rotamer) δ 8.59 (1H, s, C**H**O), 7.40 (1H, d, *J* = 7.2 Hz, Ar**H**), 6.92 (1H, d, *J* = 3.2 Hz, Ar**H**), 6.70 (1H, d, *J* = 7.2, 3.2 Hz, Ar**H**), 3.80 (3H, s, OC**H**$_3$), 2.11 (1H, d, *J* = 5.2 Hz, C**H**H), 1.94 (1H, d, *J* = 5.2 Hz, CH**H**), 1.37 (9H, s, C(C**H**$_3$)$_3$) / (minor rotamer) δ 8.65 (1H, s, C**H**O), 7.43 (1H, d, *J* = 9.2 Hz, Ar**H**), 6.71 (1H, dd, *J* = 9.2, 3.2 Hz, Ar**H**), 6.66 (1H, d, *J* = 3.2 Hz, Ar**H**), 3.73 (3H, s, OC**H**$_3$), 2.37 (1H, d, *J* = 5.6 Hz, C**H**H), 1.91 (1H, d, *J* = 5.6 Hz, CH**H**), 1.62 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) (mixture of two rotamers) δ 199.9, 198.0, 167.5, 167.4, 158.8, 158.3, 137.6, 137.5, 133.7, 133.5, 119.6, 117.9, 115.7, 114.2, 82.3, 82.2, 55.5, 55.4, 44.1, 43.1, 39.5, 39.3, 27.80, 27.75, 26.1, 25.0, 11.4, 11.2; IR (neat) 1715, 1470, 1368, 1290, 1248, 1236, 1209, 1159, 1038, 1016 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{21}BrO_4$: *m/z* 391.0515 ([M + Na]$^+$), found: *m/z* 391.0509 ([M + Na]$^+$).



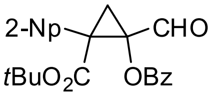
***trans*-2-Formyl-1-(2,2-diphenylvinyl)-2-methylcyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 24).**

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.54 (1H, s, C**H**O), 7.18-7.41 (8H, m, Ar**H**), 7.05-7.14 [(2H, m, Ar**H**), (1H, s, Ph$_2$C=C**H**)], 3.04 (1H, dd, *J* = 18.0, 2.0 Hz, C**H**H), 2.75 (1H, dd, *J* = 18.0, 2.0 Hz, CH**H**), 1.53 (9H, s, C(C**H**$_3$)$_3$), 1.02 (3H, s, C**H**$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 202.9, 163.9, 146.4, 141.9, 141.6, 135.1, 128.8, 128.7, 128.35, 128.31, 127.3, 127.2, 81.2, 66.0, 60.6, 42.0, 28.2, 20.3; IR (neat) 1709, 1368, 1281, 1256, 1163, 1136, 1078, 758, 745, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{24}H_{26}O_3$: *m/z* 385.1786 ([M + Na]$^+$), found: *m/z* 385.1774 ([M + Na]$^+$).



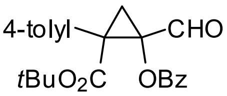
2-Benzoyloxy-2-formyl-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (major isomer) (Table 2, entry 25).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.75 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 7.45-7.98 (8H, m, Ar**H**), 2.70 (1H, d, *J* = 6.8 Hz, C**H**H), 2.39 (1H, d, *J* = 6.8 Hz, CH**H**), 1.24 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) δ 192.2, 166.0, 165.8, 133.9, 133.6, 130.7, 130.0, 128.9, 128.5, 128.4, 128.2, 82.5, 69.0, 44.5, 27.5, 22.3; IR (neat) 1722, 1369, 1310, 1271, 1236, 1155, 1088, 1067, 1024, 708 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{22}H_{22}O_5$: *m/z* 389.1359 ([M + Na]$^+$), found: *m/z* 389.1365 ([M + Na]$^+$).



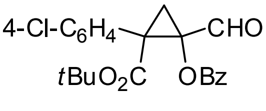
2-Benzoyloxy-2-formyl-1-(2-naphthyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 26).

^{1}H NMR (400 MHz, $CDCl_3$) (major isomer) δ 8.74 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 7.45-7.97 (8H, m, Ar**H**), 7.16-7.24 (2H, m, Ar**H**), 2.79 (1H, d, *J* = 6.8 Hz, C**H**H), 2.53 (1H, d, *J* = 6.8 Hz, CH**H**), 1.24 (9H, s, C(C**H**$_3$)$_3$) / (minor isomer) δ 9.67 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 7.45-7.97 (8H, m, Ar**H**), 7.37-7.45 (2H, m, Ar**H**), 2.92 (1H, d, *J* = 6.8 Hz, C**H**H), 2.17 (1H, d, *J* = 6.8 Hz, CH**H**), 1.40 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (mixture of two isomers) δ 194.0, 192.0, 167.1, 166.0, 165.8, 165.6, 133.7, 133.5, 133.05, 133.01, 131.7, 131.0, 130.3, 130.0, 129.7, 129.6, 129.0, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.9, 127.7, 127.6, 126.5, 126.3, 126.2, 83.1, 82.7, 69.1, 68.2, 45.9, 44.6, 27.8, 27.5, 24.9, 22.5; IR (neat) 1721, 1269, 1246, 1175, 1155, 1090, 1067, 750, 733, 708 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{26}H_{24}O_5$: *m/z* 439.1520 ([M + Na]$^+$), found: *m/z* 439.1516 ([M + Na]$^+$).



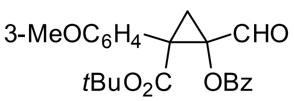
2-Benzoyloxy-2-formyl-1-(4-tolyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 27)

^{1}H NMR (400 MHz, $CDCl_3$) (major isomer) δ 8.75 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 7.12-7.70 (7H, m, Ar**H**), 2.66 (1H, d, *J* = 6.8 Hz, C**H**H), 2.38 (1H, d, *J* = 6.8 Hz, CH**H**), 2.35 (3H, s, C**H**$_3$), 1.25 (9H, s, C(C**H**$_3$)$_3$) / (minor isomer) δ 9.60 (1H, s, C**H**O), 7.12-7.70 (9H, m, Ar**H**), 2.78 (1H, d, *J* = 6.8 Hz, C**H**H), 2.01 (1H, d, *J* = 6.8 Hz, CH**H**), 1.41 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) (mixture of two isomers) δ 194.0, 192.4, 167.3, 166.2, 165.7, 165.6, 138.0, 137.9, 133.6, 133.5, 130.8, 130.5, 130.4, 130.04, 130.00, 129.7, 129.2, 129.1, 128.9, 128.6, 128.5, 128.3, 82.8, 82.4, 69.0, 68.2, 45.6, 44.1, 27.8, 27.5, 24.6, 22.3, 21.18, 21.15; IR (neat) 1720, 1369, 1306, 1269, 1238, 1157, 1094, 1067, 1024, 710 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{24}O_5$: *m/z* 403.1516 ([M + Na]$^+$), found: *m/z* 403.1518 ([M + Na]$^+$).



2-Benzoyloxy-2-formyl-1-(4-chlorophenyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 28)

^{1}H NMR (400 MHz, $CDCl_3$) (major isomer) δ 8.85 (1H, s, C**H**O), 8.07-8.12 (2H, m, Ar**H**), 7.31-7.68 (7H, m, Ar**H**), 2.69 (1H, d, *J* = 6.8 Hz, C**H**H), 2.34 (1H, d, *J* = 6.8 Hz, CH**H**), 1.23 (9H, s, C(C**H**$_3$)$_3$) / (minor isomer) δ 9.61 (1H, s, C**H**O), 7.31-7.68 (9H, m, Ar**H**), 2.81 (1H, d, *J* = 6.8 Hz, C**H**H), 2.00 (1H, d, *J* = 6.8 Hz, CH**H**), 1.41 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) (mixture of two isomers) δ 193.6, 192.1, 166.7, 166.0, 165.7, 165.5, 134.4, 134.1, 133.8, 133.7, 132.5, 132.1, 132.0, 131.9, 130.0, 129.7, 128.7, 128.6, 128.6, 128.5, 128.4, 128.3, 83.3, 82.8, 69.0, 68.0, 45.1, 44.0, 27.8, 27.5, 24.6, 22.4; IR (neat) 1726, 1314, 1271, 1238, 1159, 1092, 1015, 912, 835, 743 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{22}H_{21}ClO_5$: *m/z* 423.0970 ([M + Na]$^+$), found: *m/z* 423.0974 ([M + Na]$^+$).

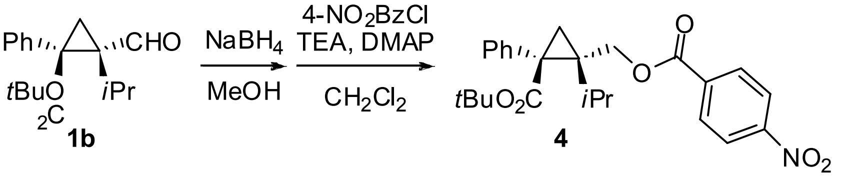


2-Benzoyloxy-2-formyl-1-(3-methoxyphenyl)cyclopropanecarboxylic acid *tert*-butyl ester (Table 2, entry 29)

^{1}H NMR (400 MHz, CDCl$_3$) (major isomer) δ 8.73 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 6.80-7.70 (7H, m, Ar**H**), 3.83 (3H, s, OC**H**$_3$), 2.67 (1H, d, *J* = 6.8 Hz, C**H**H), 2.38 (1H, d, *J* = 6.8 Hz, CH**H**), 1.26 (9H, s, C(C**H**$_3$)$_3$) / (minor isomer) δ 9.62 (1H, s, C**H**O), 8.05-8.15 (2H, m, Ar**H**), 6.80-7.70 (7H, m, Ar**H**), 2.76 (1H, d, *J* = 6.8 Hz, C**H**H), 2.03 (1H, d, *J* = 6.8 Hz, CH**H**), 1.42 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, CDCl$_3$) (mixture of two isomers) δ 194.0, 192.1, 165.9, 165.7, 159.5, 159.4, 135.4, 134.6, 133.61, 133.57, 130.04, 130.00, 129.7, 129.4, 129.1, 128.9, 128.5, 128.3, 122.95, 122.89, 116.2, 116.0, 114.6, 114.2, 114.0, 113.4, 84.4, 82.9, 82.5, 81.5, 69.0, 68.1, 45.1, 55.3, 44.4, 28.5, 27.8, 27.54, 27.50, 24.6, 22.4; IR (neat) 1722, 1271, 1244, 1153, 1105, 1090, 1167, 1034, 1026, 708 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{24}O_6$: *m/z* 419.1465 ([M + Na]$^+$), found: *m/z* 419.1464 ([M + Na]$^+$).

Determination of the relative stereochemistry (Scheme 1).

The relative stereochemistry was determined unambiguously by the X-ray crystallographic analysis after the derivatization of the cyclopropanecarboxaldehyde **1b** to the corresponding 4-nitrobenzoyl ester **4**. Stereochemistries of other products were tentatively assigned by comparing the ^{1}H NMR spectrum of these cyclopropanes with **1b**.



trans-2-Isopropyl-2-(4-nitrobenzoyloxymethyl)-1-phenylcyclopropanecarboxylic acid *tert*-butyl ester (4).

To a stirred solution of **1b** (22.3 mg, 0.077 mmol) in methanol (5 mL) was added $NaBH_4$ (8.7 mg, 0.23 mmol) at 0 °C. The reaction mixture was stirred at the same temperature for 1 h. The mixture was quenched with 1 N HCl and extracted with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated. The residue was used to the next step without further purification.

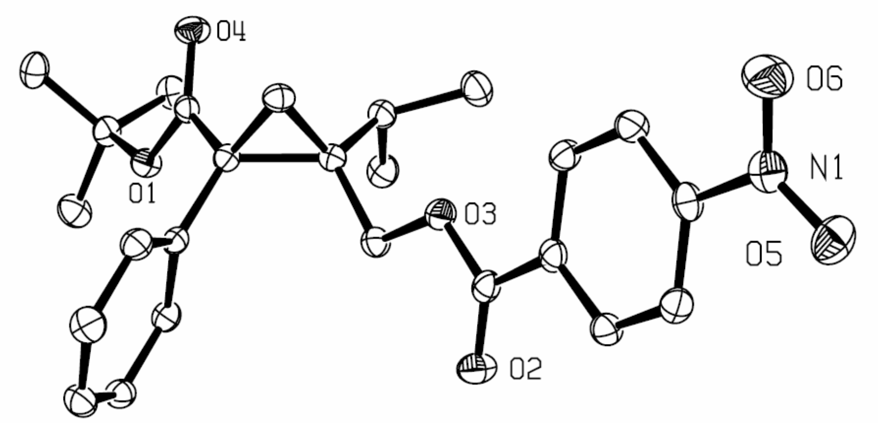
To a stirred solution of this residue in CH_2Cl_2 (5mL) was added Et_3N (21 μL, 0.15 mmol), DMAP (1.8 mg, 0.015 mmol) and 4-nitrobenzoyl chloride (22.3 mg, 0.12 mmol) at room temperature. The reaction mixture was stirred overnight at the same temperature. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 30:1) to give the ester **4** (83% yield in 2 steps).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (2H, d, J = 9.2 Hz, Ar**H**), 8.06 (2H, d, J = 9.2 Hz, Ar**H**), 7.35-7.48 (2H, m, Ar**H**), 7.17-7.24 (3H, m, Ar**H**), 4.12 (1H, d, J = 12.4 Hz, OC**H**H), 4.08 (1H, d, J = 12.4 Hz, OCH**H**), 1.76 (1H, app quint, J = 7.2 Hz, C**H**$(CH_3)_2$), 1.68 (1H, d, J = 5.2 Hz, C**H**H), 1.41 (1H, d, J = 5.2 Hz, CH**H**), 1.39 (9H, s, $C(C\mathbf{H}_3)_3$), 1.28 (3H, d, J = 6.8 Hz, $CH(C\mathbf{H}_3)(CH_3)$), 1.17 (3H, d, J = 7.2 Hz, $CH(CH_3)(C\mathbf{H}_3)$) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 164.1, 150.5, 136.7, 135.5, 131.1, 130.5, 127.8, 127.7, 127.3, 123.5, 81.3, 65.6, 43.2, 36.1, 31.0, 27.8, 21.0, 20.4, 20.3 ppm; IR (neat) 1717, 1530, 1368, 1348, 1269, 1246, 1159, 1116, 1101, 719 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{29}NO_6$: *m/z* 462.1887 ($[M + Na]^+$), found: *m/z* 462.1883 ($[M + Na]^+$).

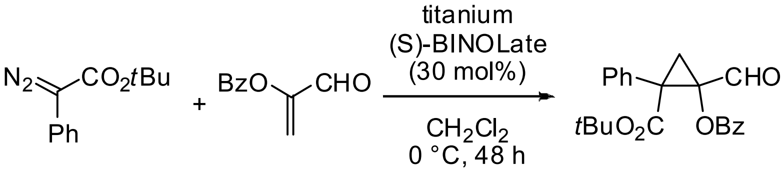
The product was recrystallized from hexane/ether. The single crystal was mounted on a glass capillary. Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated MoK*α* radiation (λ = 0.71069 Å) to a maximam 2*θ* value of 55°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[5] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined by using the riding model. The crystallographic data were summarized in the following table.

Empirical Formula	$C_{25}H_{29}O_6N$
Formula Weight	439.51
Crystal System	monoclinic
Lattice Parameters	a = 11.040(3) Å
	b = 7.235(2) Å
	c = 28.628(7) Å
	β = 91.016(12) °
	V = 2286.3(11) $Å^3$
Space Group	$P2_1/n$ (#14)
Z value	4
Dcalc	1.277 g/cm^3
T, °C	25
μ(MoKα)	0.909 cm^{-1}
No. of Reflections Measured	Total: 21055
No. Observations (All reflections)	5179
No. Variables	290
R (All reflections)	0.0701
R_w (All reflections)	0.1576
Goodness of Fit	1.070

Ortep diagram of 4.



Titanium-BINOLate catalyzed asymmetric cyclopropanation reaction (Scheme 2).



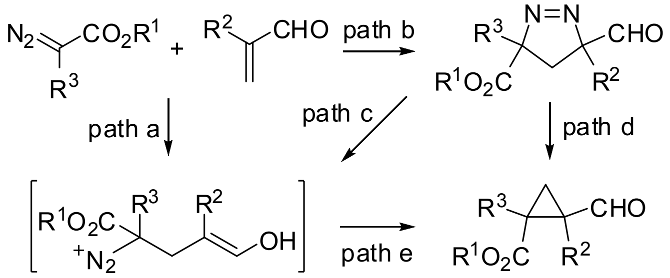
To a stirred solution of (*S*)-BINOL (42.9 mg, 0.15 mmol) in CH_2Cl_2 (1.0 mL) was added $Ti(O\textit{i}Pr)_4$ (22.2 μL, 0.075 mmol) at room temperature under argon atmosphere. The mixture was then stirred for 1 h at the same temperature to afford the orange colored solution of Ti(IV)/(*S*)-BINOL complex.

To the catalyst solution prepared as above were added a solution of α-benzoyloxyacrolein (52.9 mg, 0.30 mmol) and *tert*-butyl phenyldiazoacetate (54.6 mg, 0.25 mmol) in CH_2Cl_2 (1.0 mL) dropwise at 0 °C. The reaction mixture was stirred at the same temperature for 48 h. The mixture was quenched with aqueous $NaHCO_3$, extracted with ethyl acetate and dried over Na_2SO_4. After concentration under reduced pressure, the residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 30:1) to give the cyclopropane.

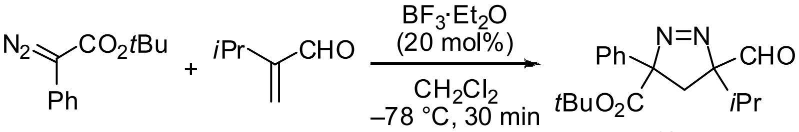
The enantiomeric purity was determined by HPLC analysis (Daicel Chiralpak AD-H, hexane/2-propanol = 100/1, flow rate = 0.5 mL/min, retention time; 36.0 min (major) and 52.5 min (minor)).

Mechanistic Study of the acid catalyzed cyclopropanation reaction.

The possible courses of cyclopropanation can be delineated as below. At the first stage of the reaction, diazoacetate and α,β-unsaturated aldehyde would react in two different manners. One possibility is that diazoacetate adds to the β-positon of activated aldehyde (Michael addition, path a) to give the diazonium intermediate and that intermediate closes the ring spontaneously to generate cyclopropane and nitrogen. Another possibility is that 1,3-dipolar cycloaddition reaction initially takes place to give 1-pyrazoline (path b). The initially formed 1-pyrazoline ring is then opened by the action of acid catalysts to yield cyclopropane (path c→e).[6] Thermal or light driven ring contraction of 1-pyrazoline (path d) is also known. However, such a process seems to be unlikely under our reaction conditions. Hence, our concern is that the reaction takes place whether via direct Michael addition of diazoacetate (path a→e) or via 1,3-dipolar cycloaddition (path b→c→e).

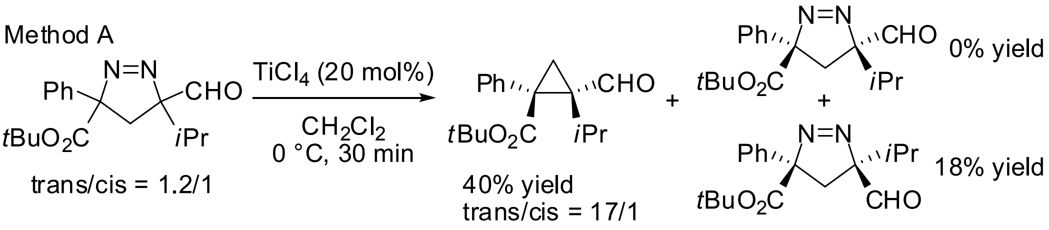


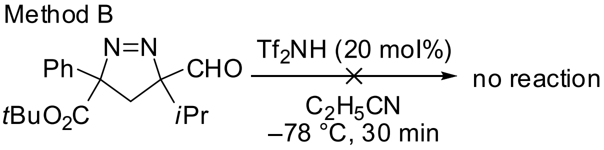
According to this line, an intriguing phenomenon was observed when the cyclopropanation of α-isopropylacrolein and *tert*-butyl phenyldiazoacetate was conducted in the presence of 20 mol% $BF_3 \cdot Et_2O$ at –78 °C in CH_2Cl_2. The reaction proceeded smoothly, however the resulting compound was not the expected cyclopropane but 1-pyrazoline, as a mixture of diastereomers (for experimental procedure, see below).



5 71% yield
trans/cis = 1/0.71

This observation actually led us to the assumption that this cyclopropanation reaction might be intervening acid catalyzed 1,3-dipolar cycloaddition and denitrogenation of the resulting 1-pyrazoline (path b→c→e). To identify the course of the reactions catalyzed by $TiCl_4$ and Tf_2NH, 1-pyrazoline was re-subjected to the standard reaction conditions (Method A and Method B).



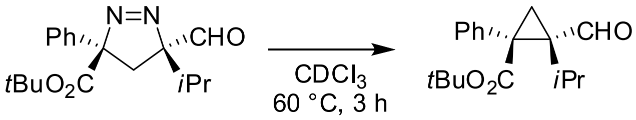


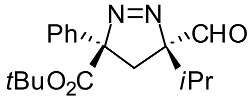
As shown above, each method led to totally different results. In Method B, the possibility of 1,3-dipolar cycloaddition pathway (path b→c→e) was easily excluded due to the disability of Tf_2NH to activate the 1-pyrazoline ring under the reaction condition. Rather weird is the result obtained by Method A. Starting from mixtures of trans and cis isomers of 1-pyrazoline, *trans*-cyclopropane and *cis*-1-pyrazoline were isolated as two major products. This observation clearly indicated the existence of the ring opening process of 1-pyrazoline. However, since we never observed the remaining cis-1-pyrazolines in $TiCl_4$ catalyzed cyclopropanation reaction of aryldiazoacetates and α-substituted acroleins, at this moment, we are speculating that Michael-initiated ring closure is also operative in this case.

BF_3·Et_2O catalyzed 1,3-dipolar cycloaddtion reaction of *tert*-butyl phenyldiazoacetate and α-isopropyl acrolein.

To a stirred solution of *tert*-butyl phenyldiazoacetate (152.8 mg, 0.70 mmol) and α-isopropyl acrolein (66.3 mg, 0.30 mmol) in CH_2Cl_2 (2.8 mL) was added BF_3·OEt_2 (18 μL, 0.14 mmol) at –78 °C under argon. The reaction mixture was stirred at the same temperature for 1 h. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel (eluting with hexane/ethyl acetate = 40:1 ~ 20:1) to give1-pyrazline **5** (71% yield, trans/cis = 1.2/1).

One isomer could be obtained in analytically pure form by further purification by column chromatography on silica gel. Heating $CDCl_3$ solution of this isomer at 60 °C for 3 h resulted in the formation of *trans*-cyclopropane. From this observation, the stereochemistry of this isomer was determined to be *trans*.





trans-5-Formyl-5-isopropyl-3-phenyl-1-pyrazoline-3-carboxylic acid _tert_-butyl ester.

^{1}H NMR (400 MHz, CDCl$_3$) δ 9.92 (1H, s, C**H**O), 7.26-7.43 (5H, m, Ar**H**), 2.96 (1H, app sept, *J* = 6.8 Hz, C**H**(CH$_3$)$_2$), 2.40 (1H, d, *J* = 14.0 Hz, C**H**H), 2.34 (1H, d, *J* = 14.0 Hz, CH**H**), 1.43 (9H, s, C(C**H**$_3$)$_3$), 0.99 (3H, d, *J* = 6.8 Hz, CH(C**H**$_3$)(CH$_3$)), 0.84 (3H, d, *J* = 6.8 Hz, CH(CH$_3$)(C**H**$_3$)); ^{13}C NMR (100 MHz, CDCl$_3$) δ 196.1, 168.8, 138.9, 128.7, 128.1, 125.7, 111.3, 104.1, 83.3, 31.2, 27.8, 27.0, 17.4, 16.4; IR (neat) 2974, 1726, 1468, 1393, 1369, 1273, 1258, 1153, 1113, 843 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{24}N_2O_3$: *m/z* 339.1679 ([M + Na]$^+$), found: *m/z* 339.1683 ([M + Na]$^+$).

References.

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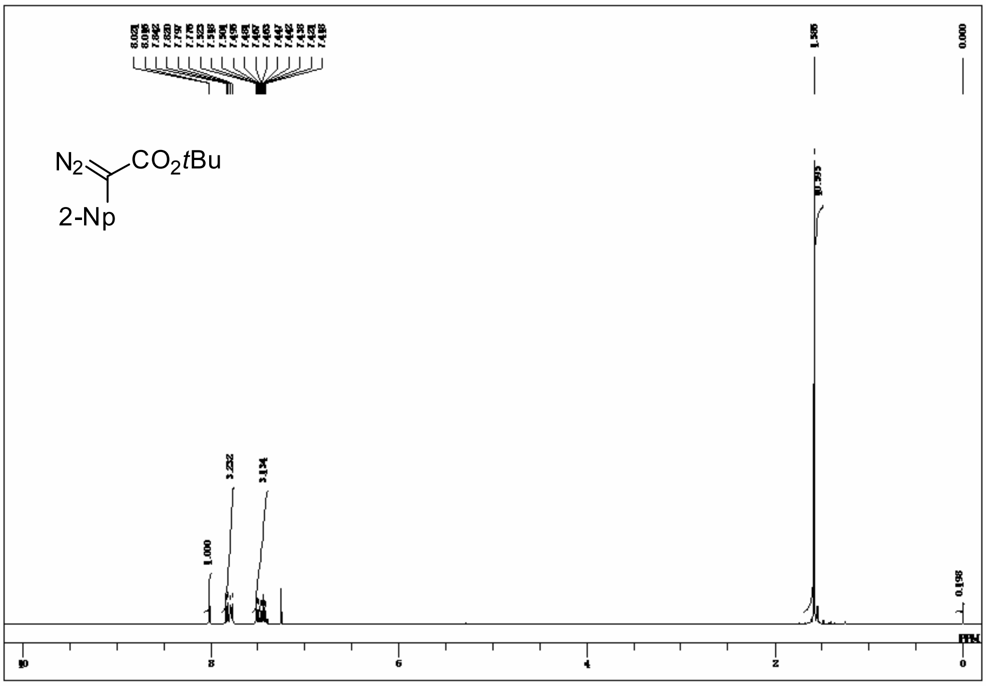
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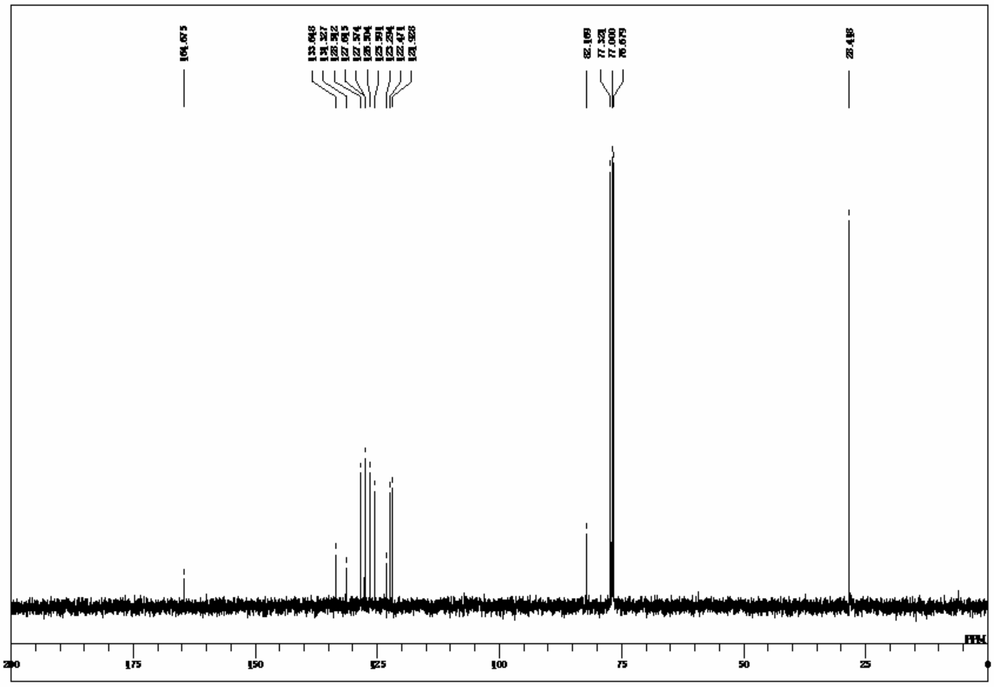
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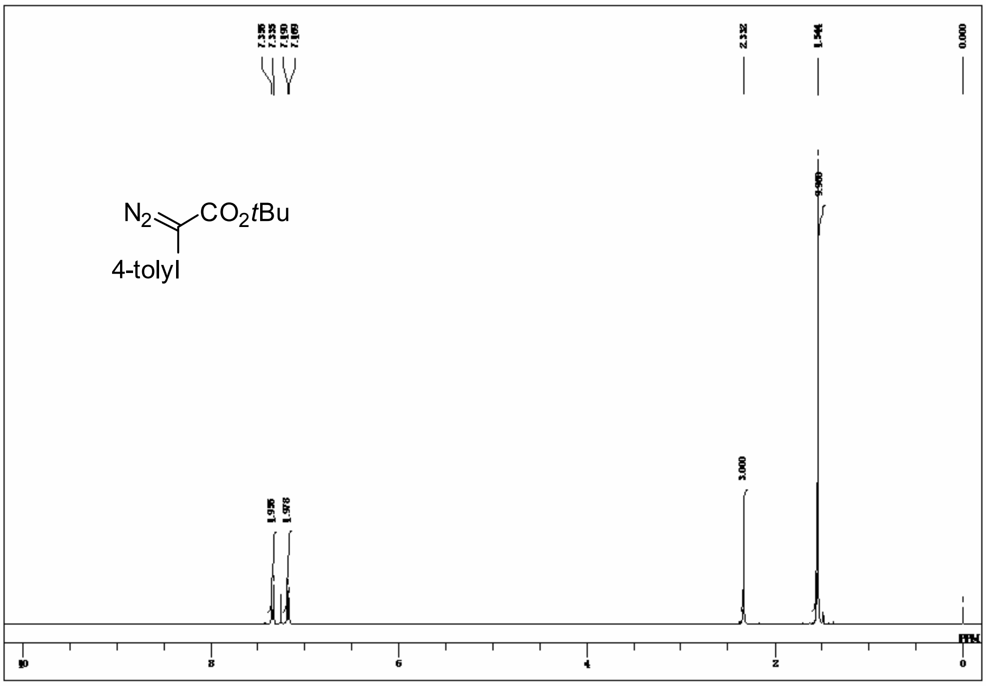
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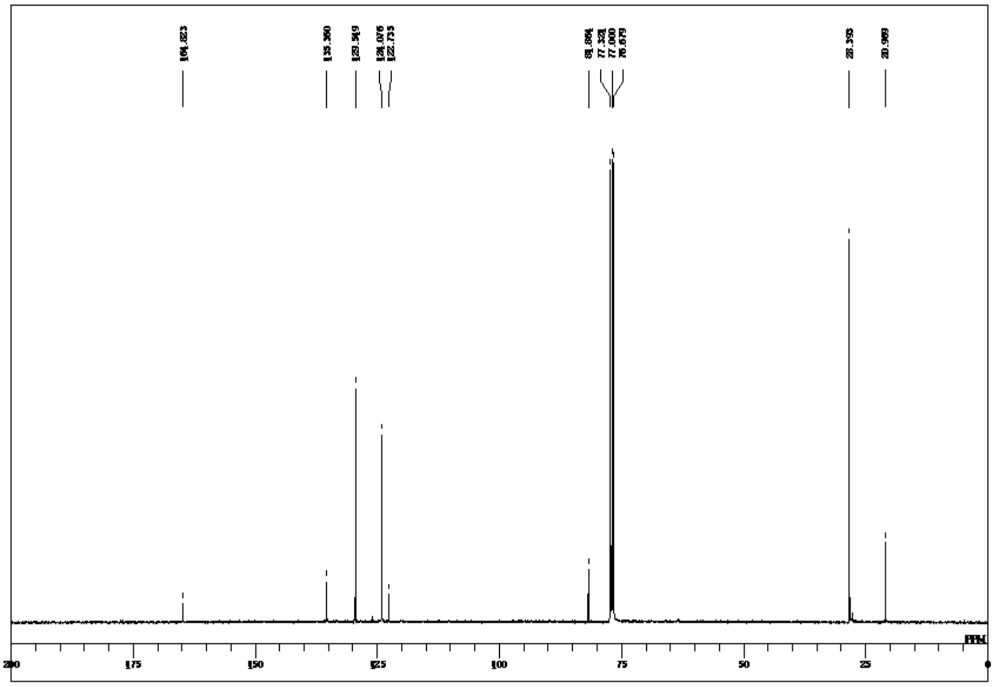
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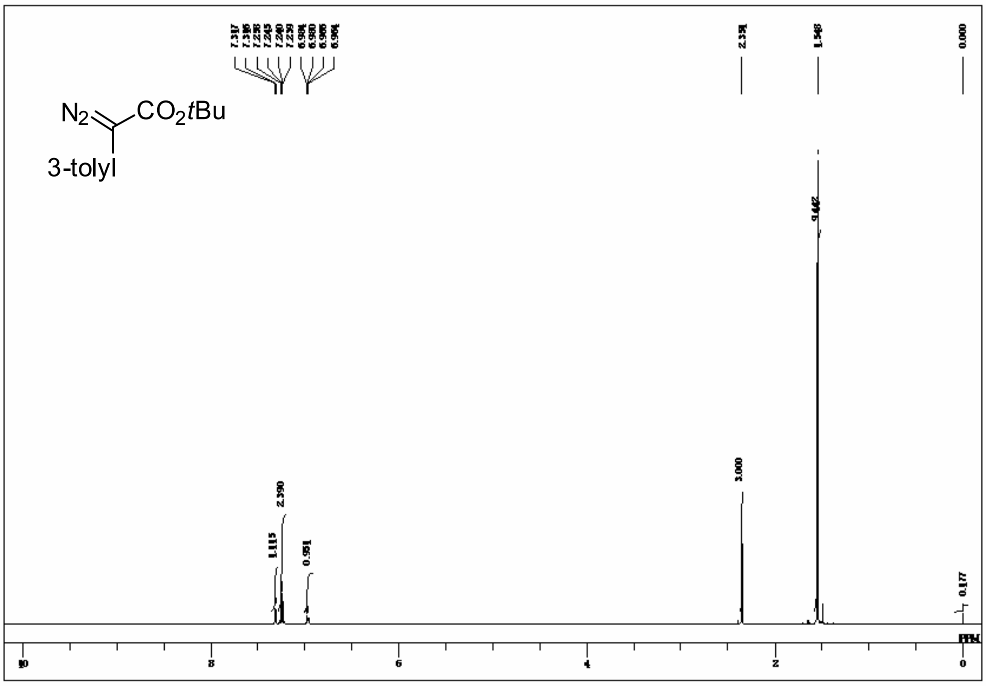
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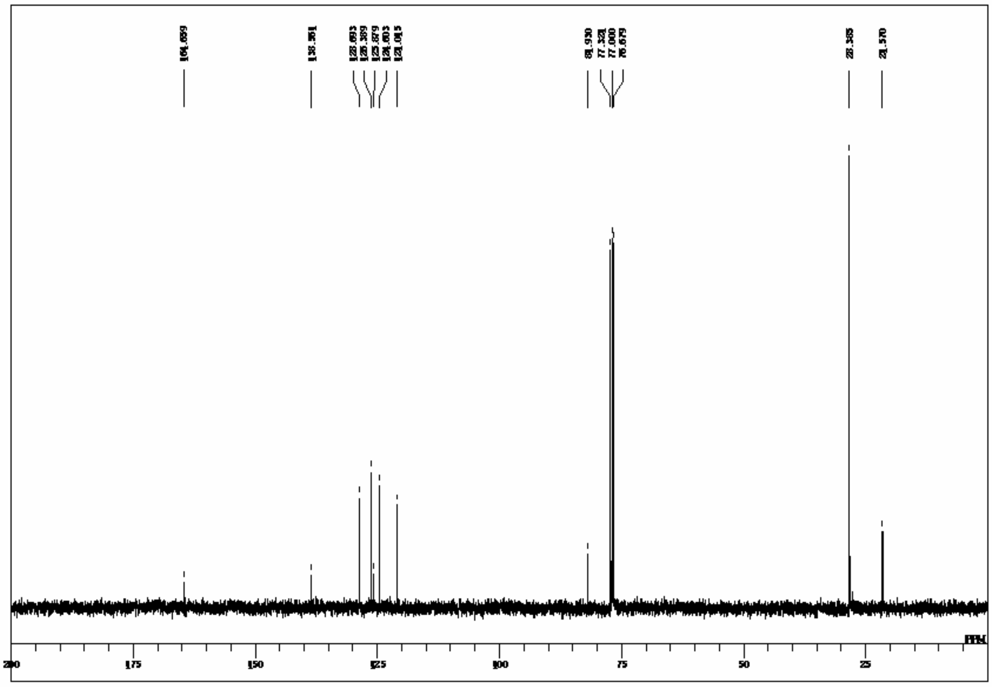
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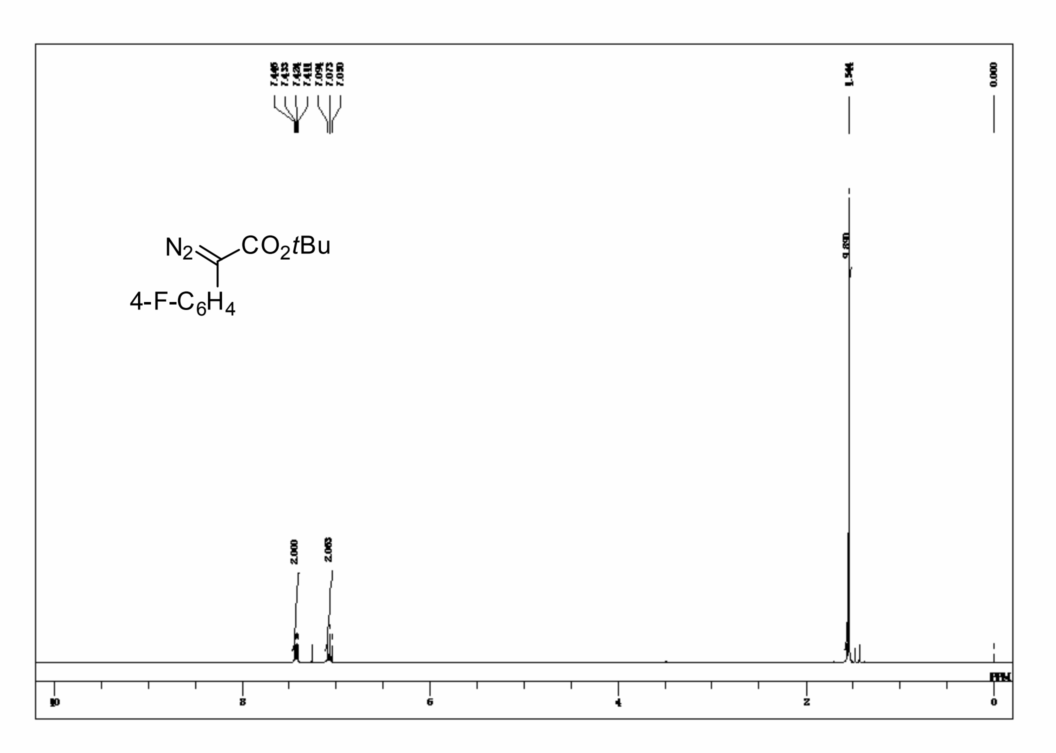
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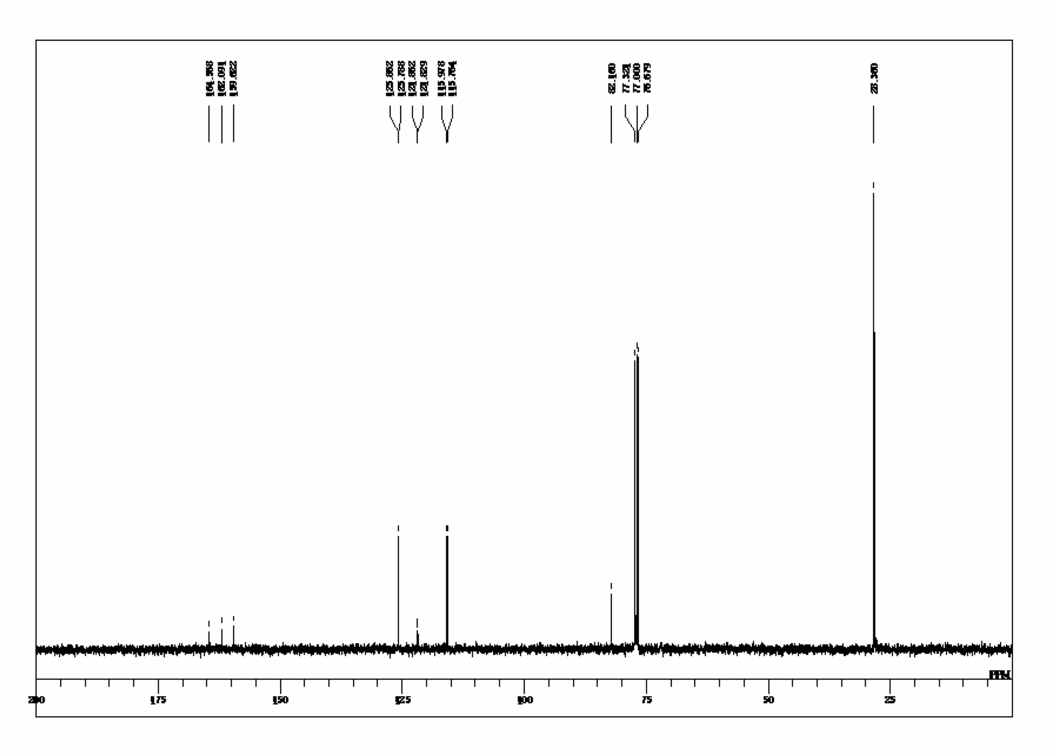
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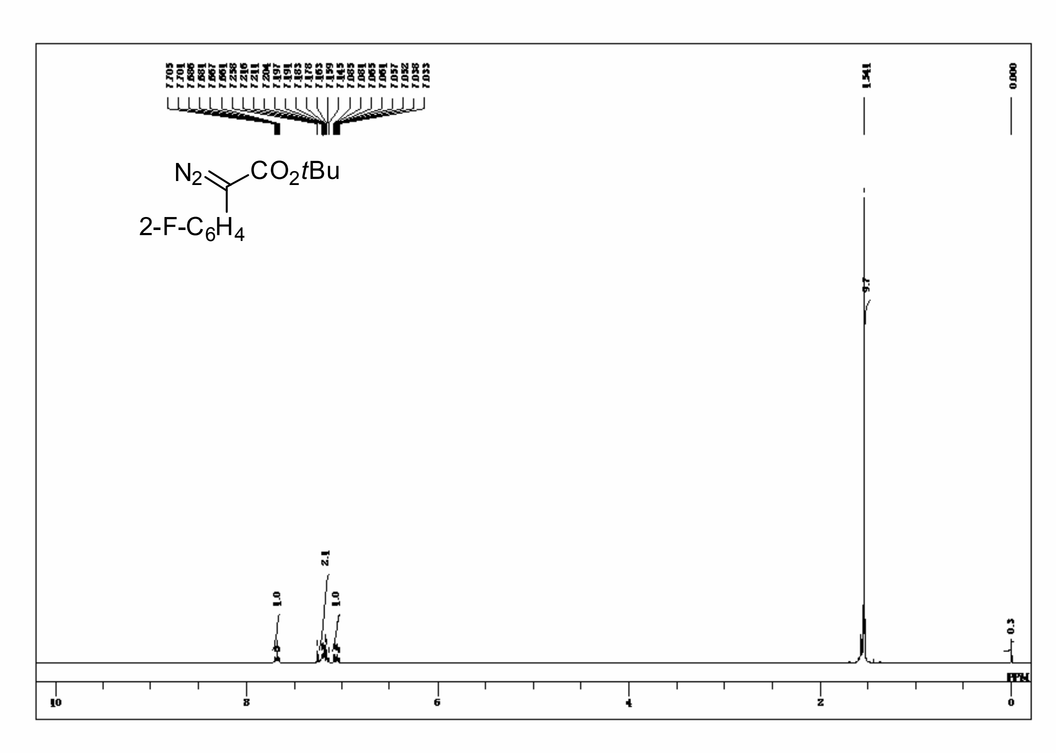
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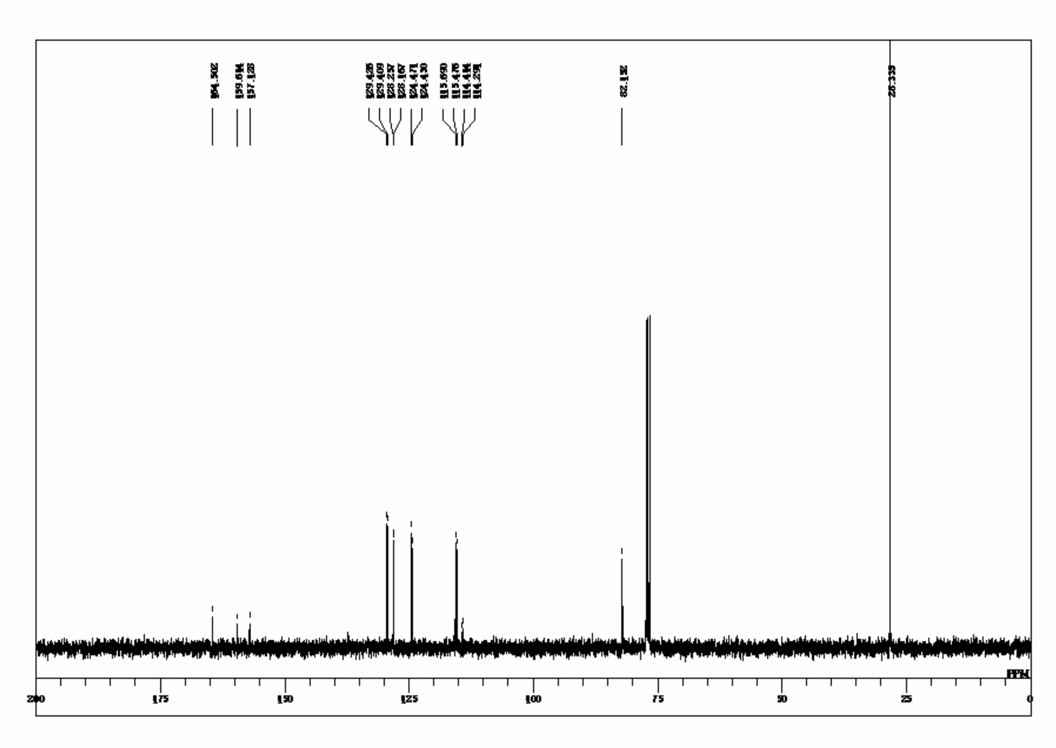
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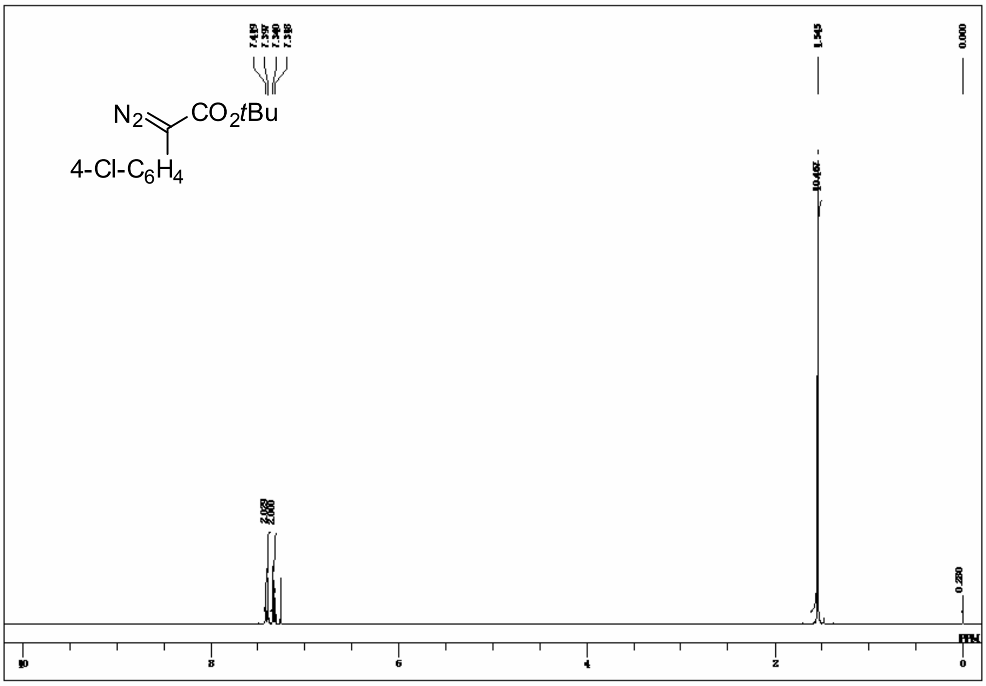
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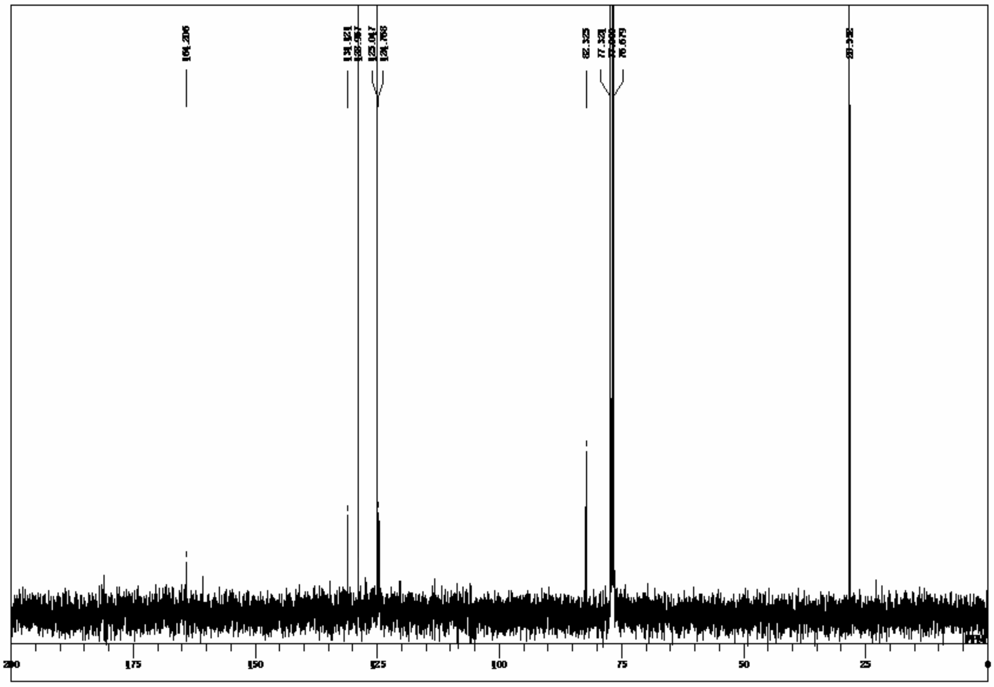
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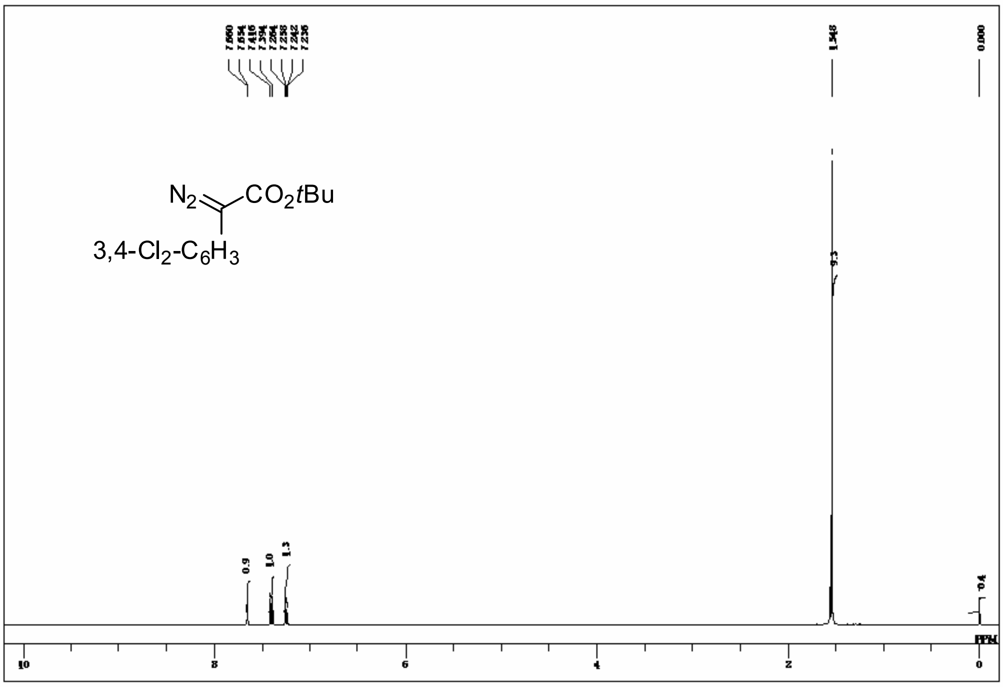
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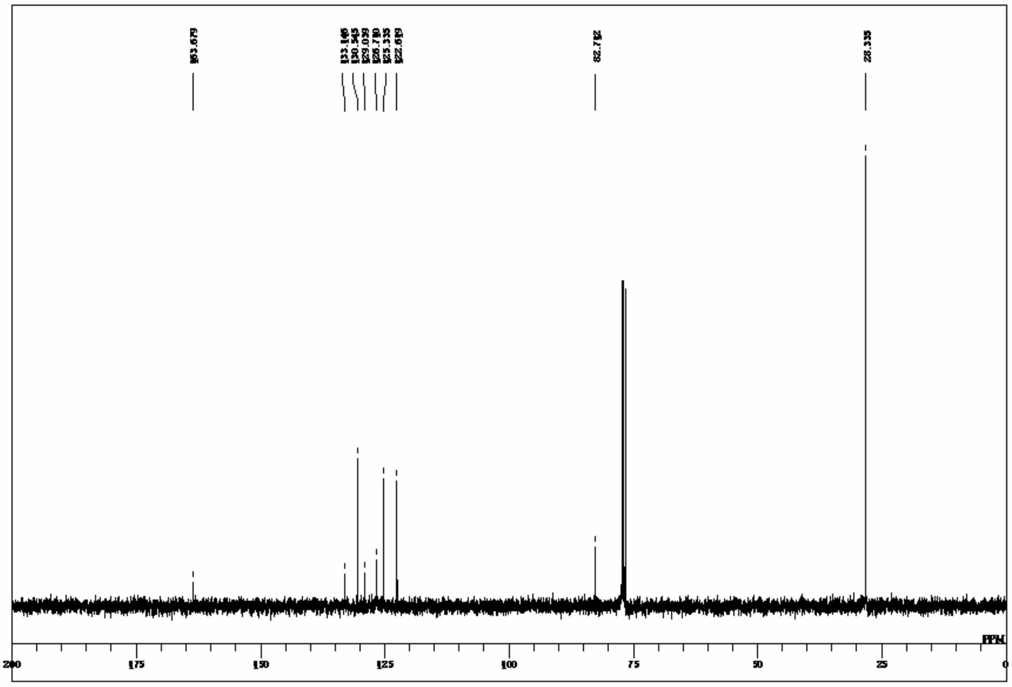
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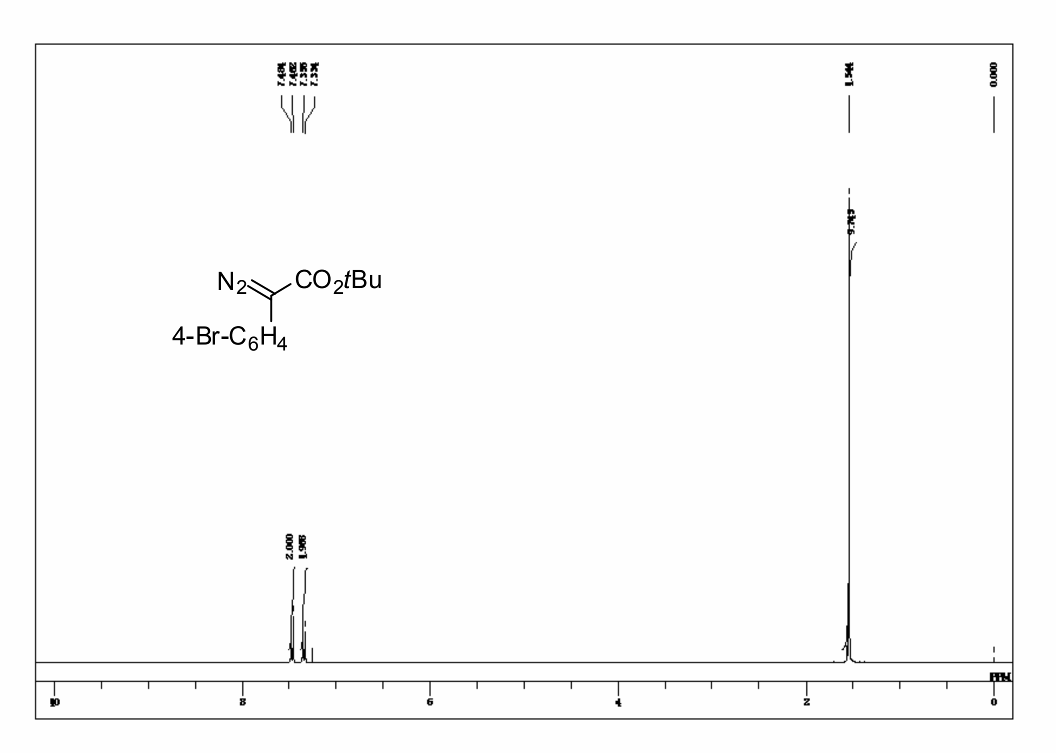
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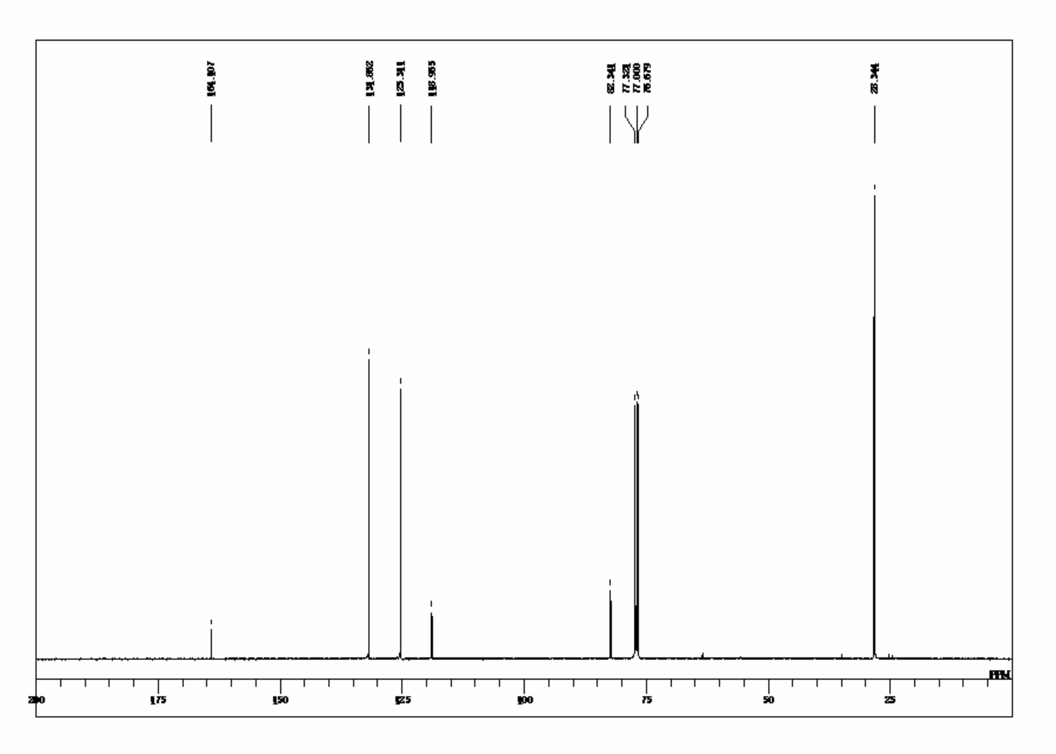
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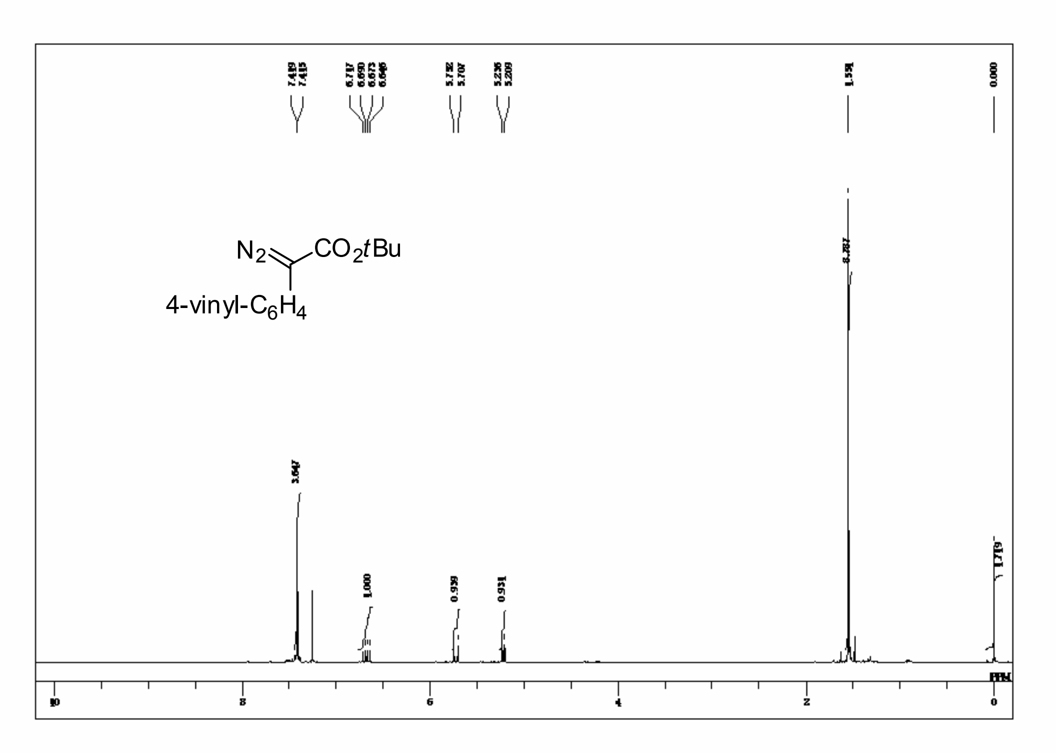
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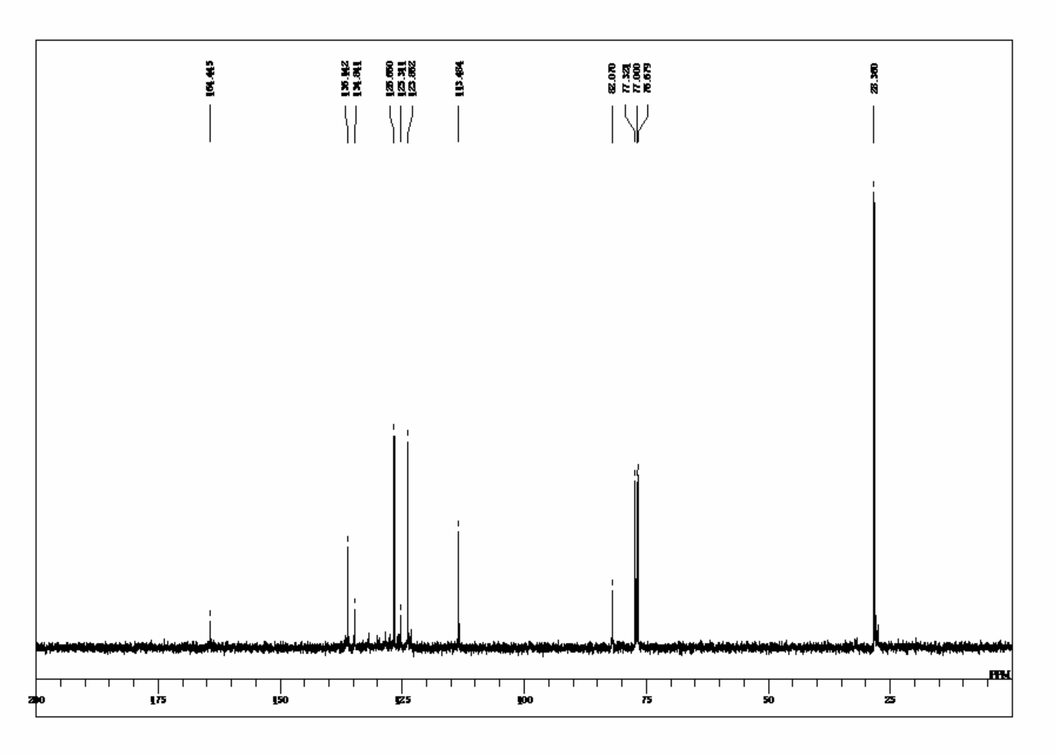
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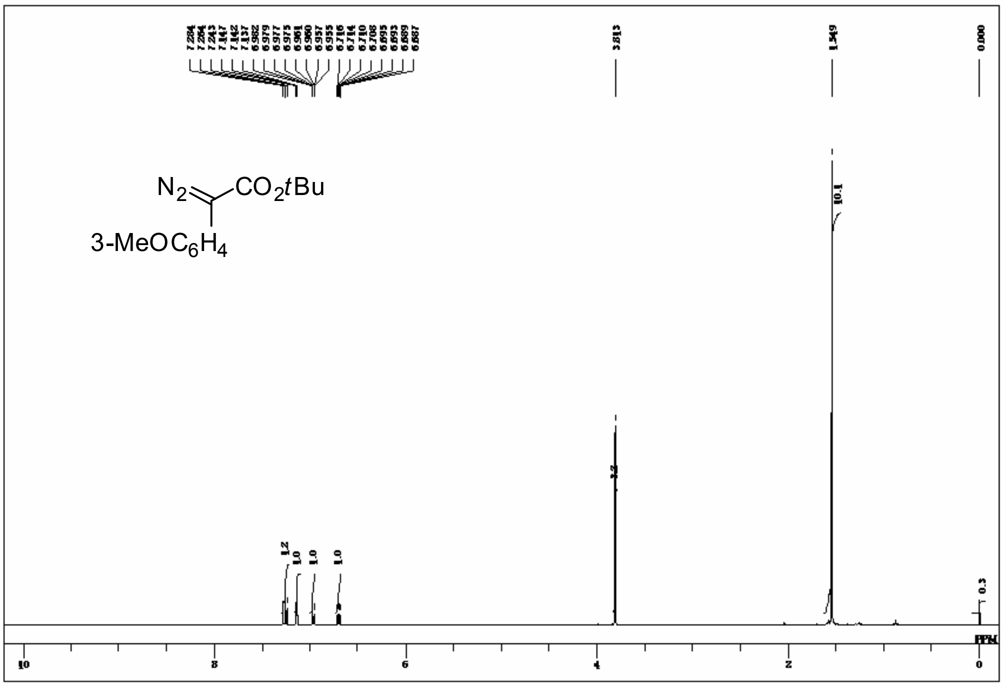
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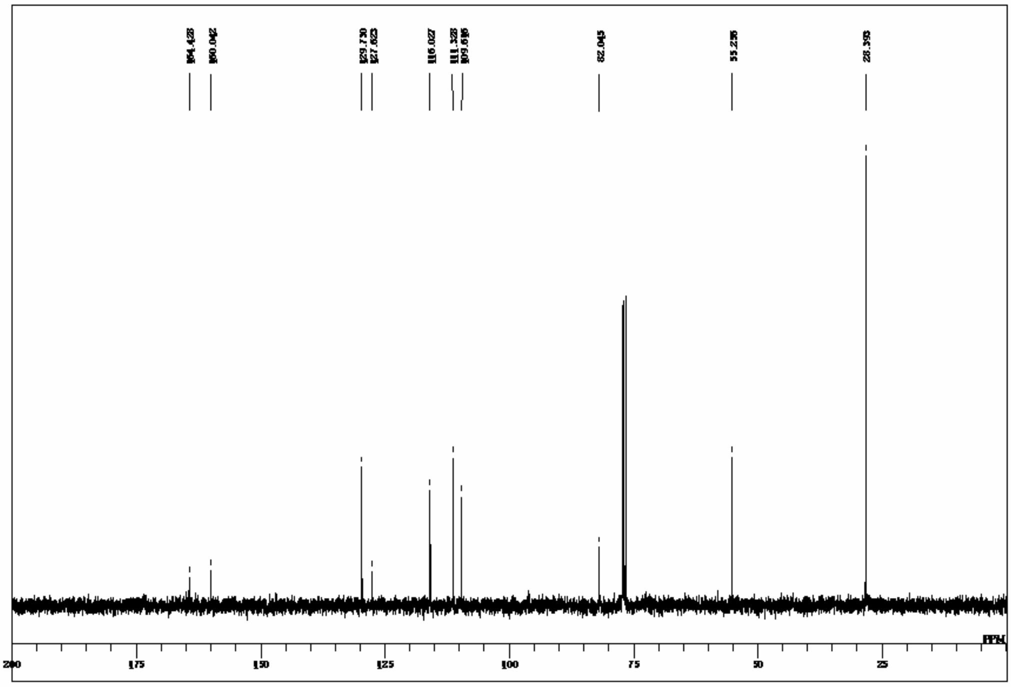
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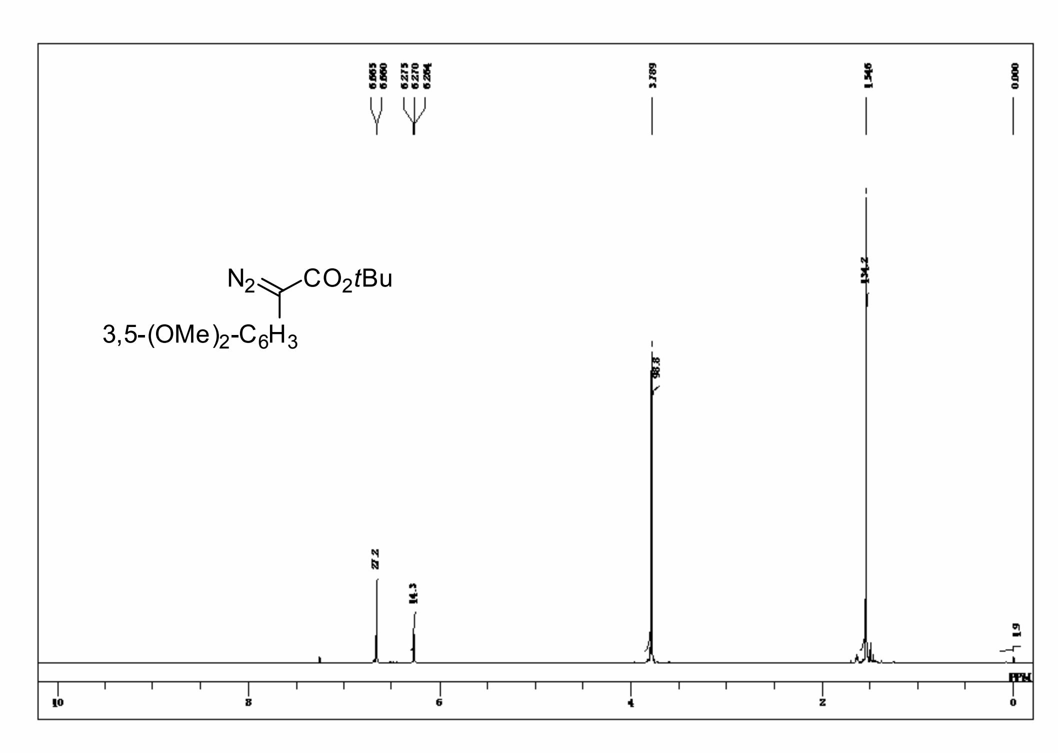
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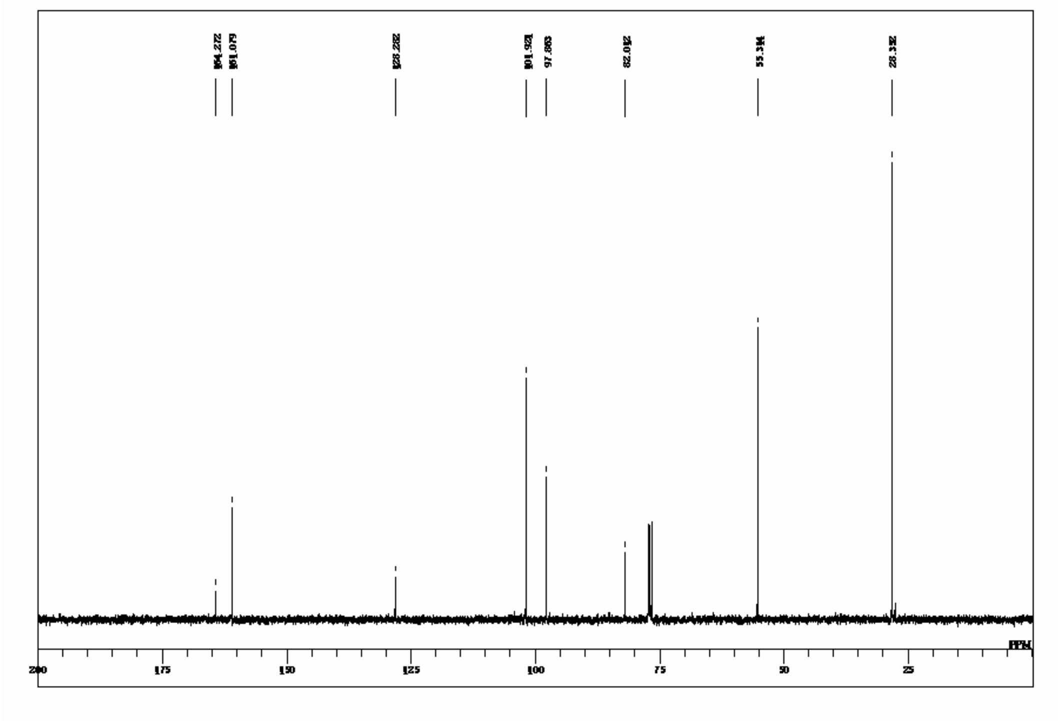
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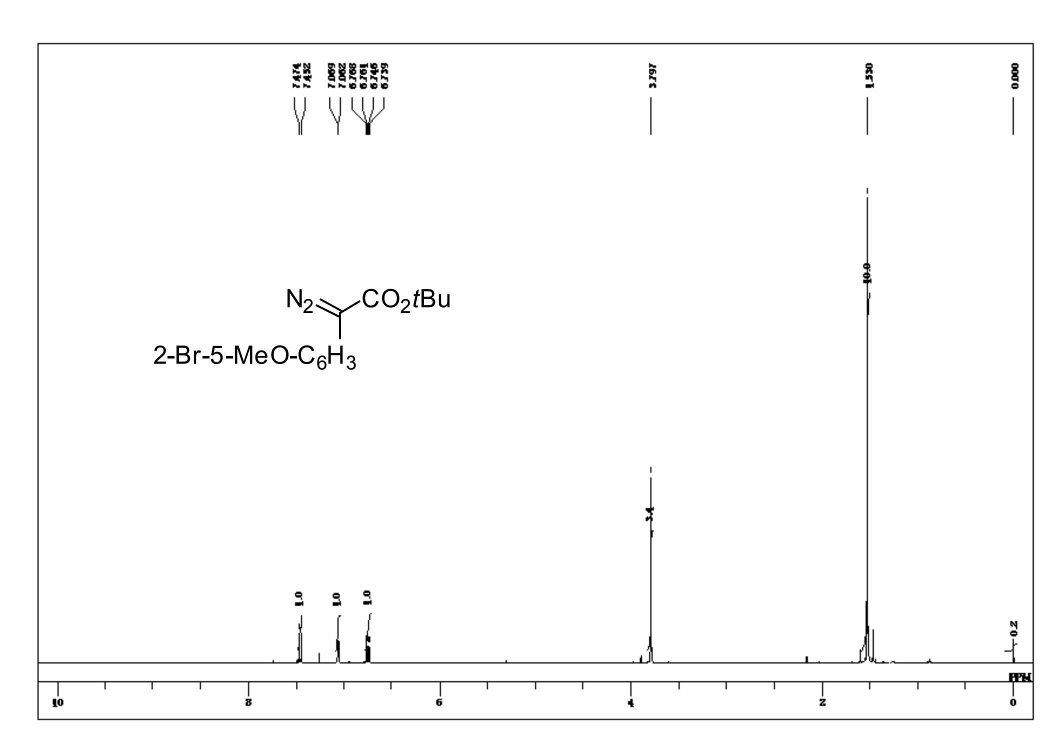
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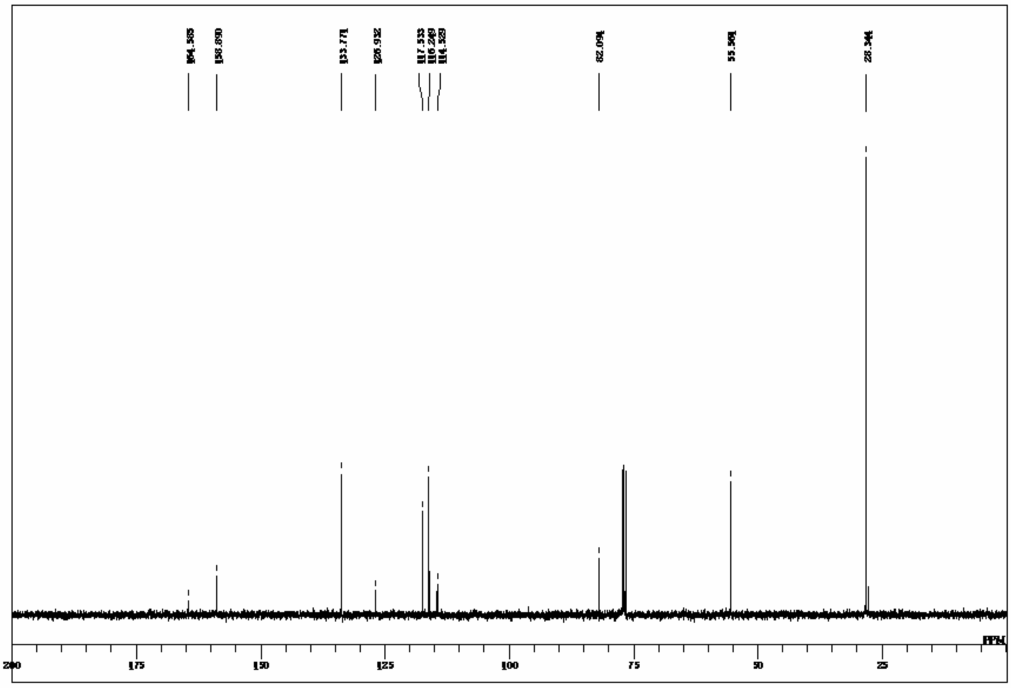
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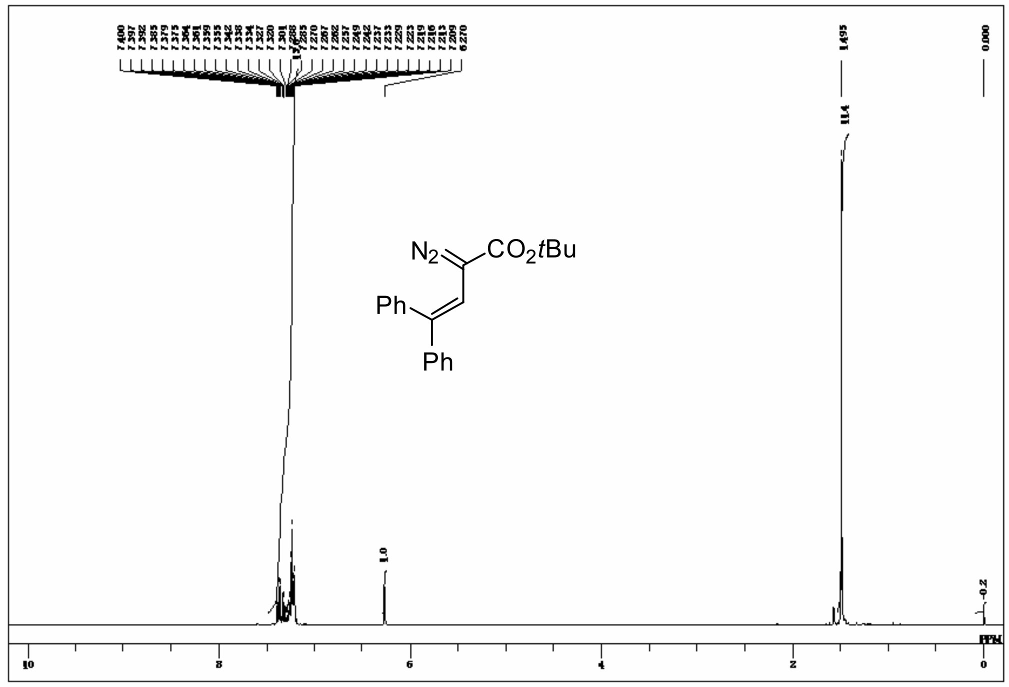
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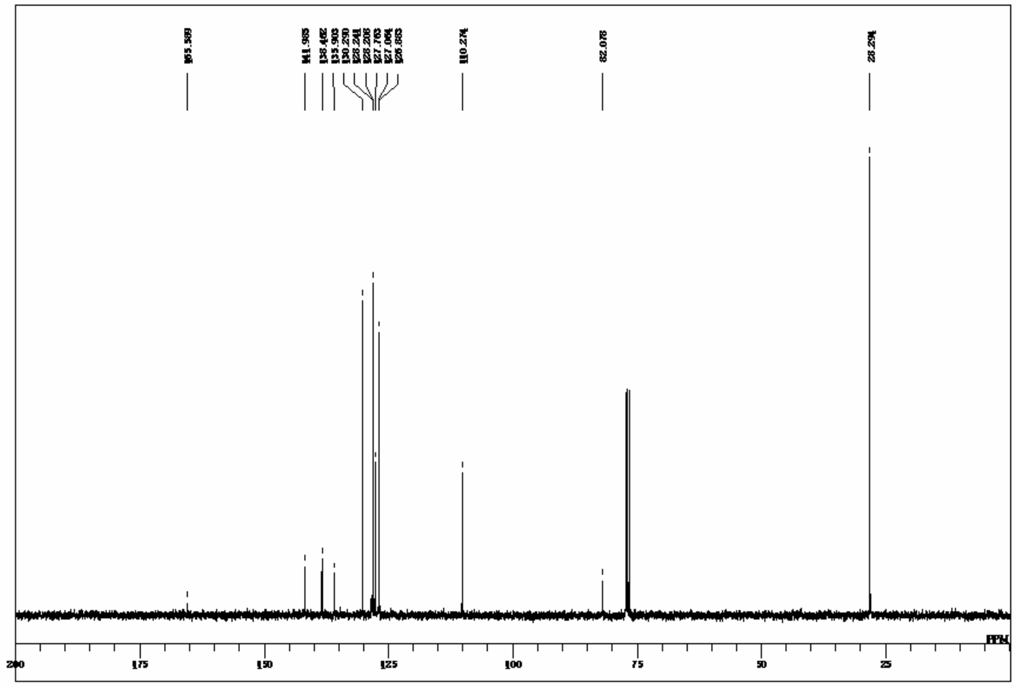
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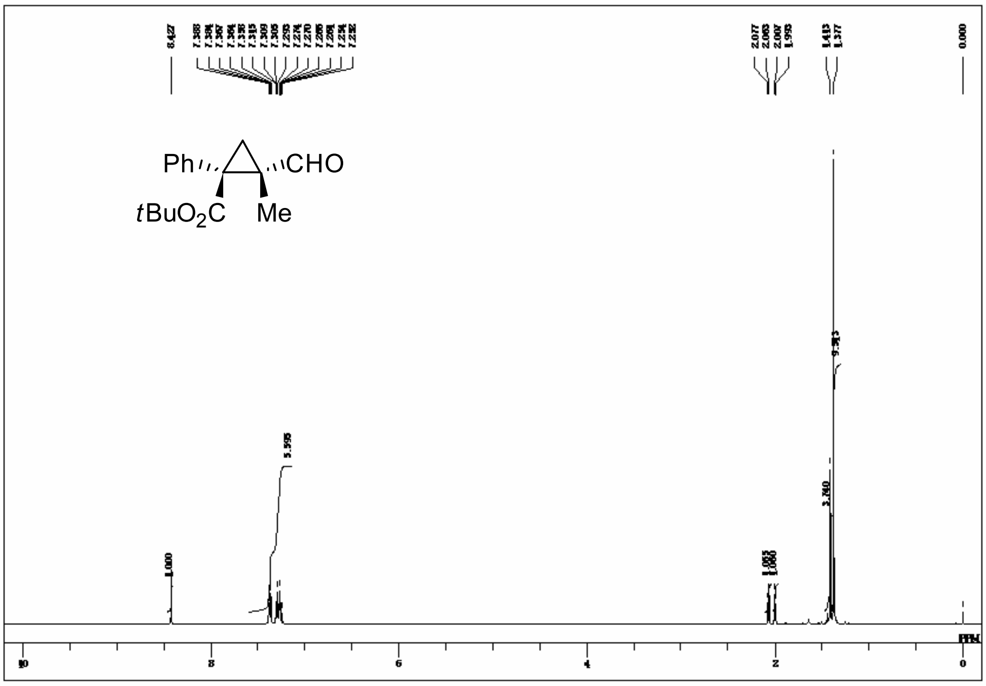
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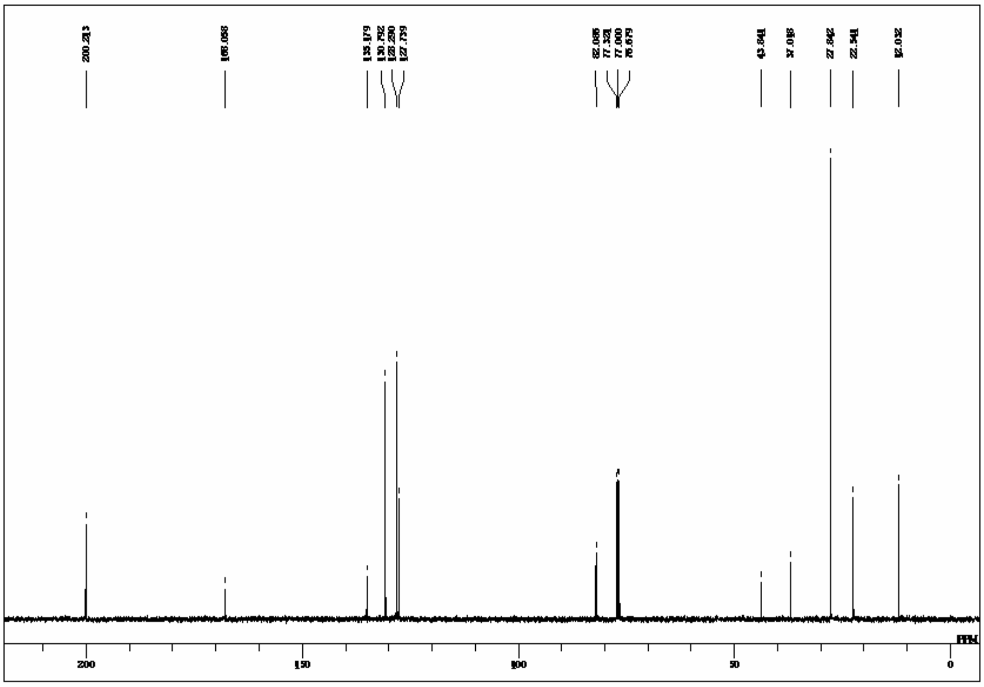
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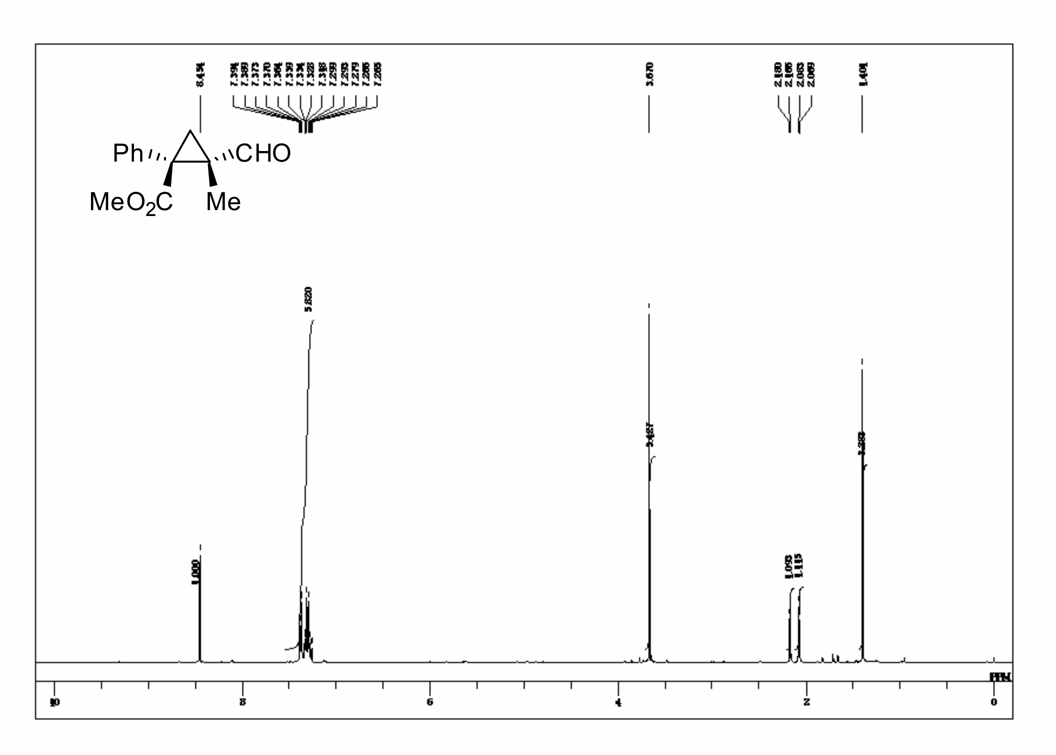
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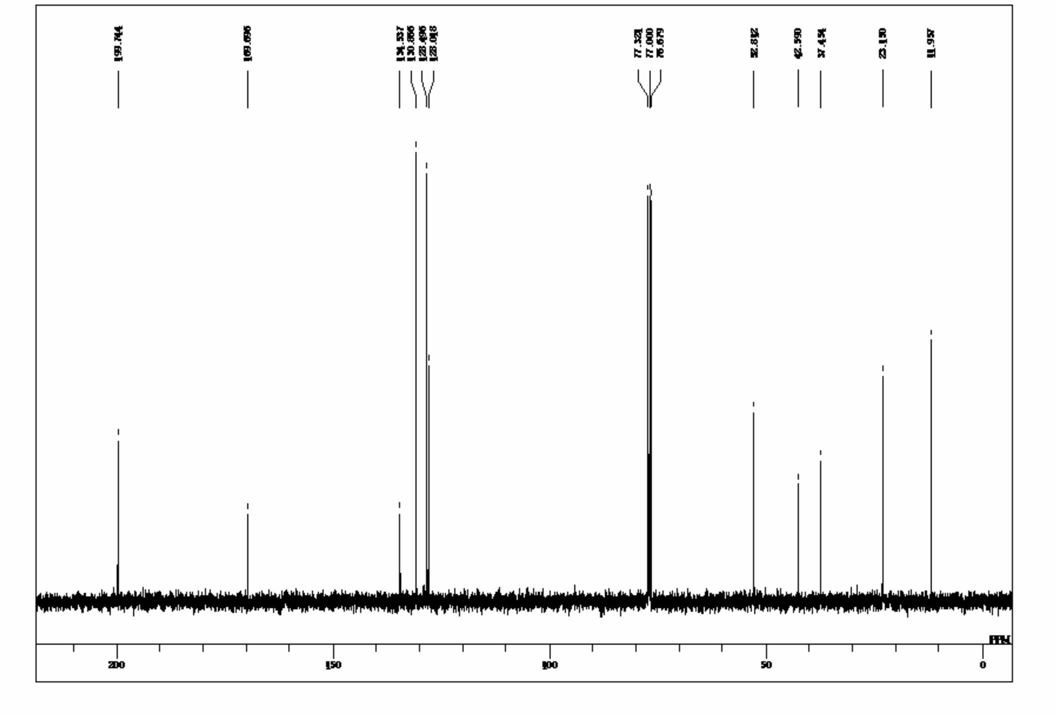
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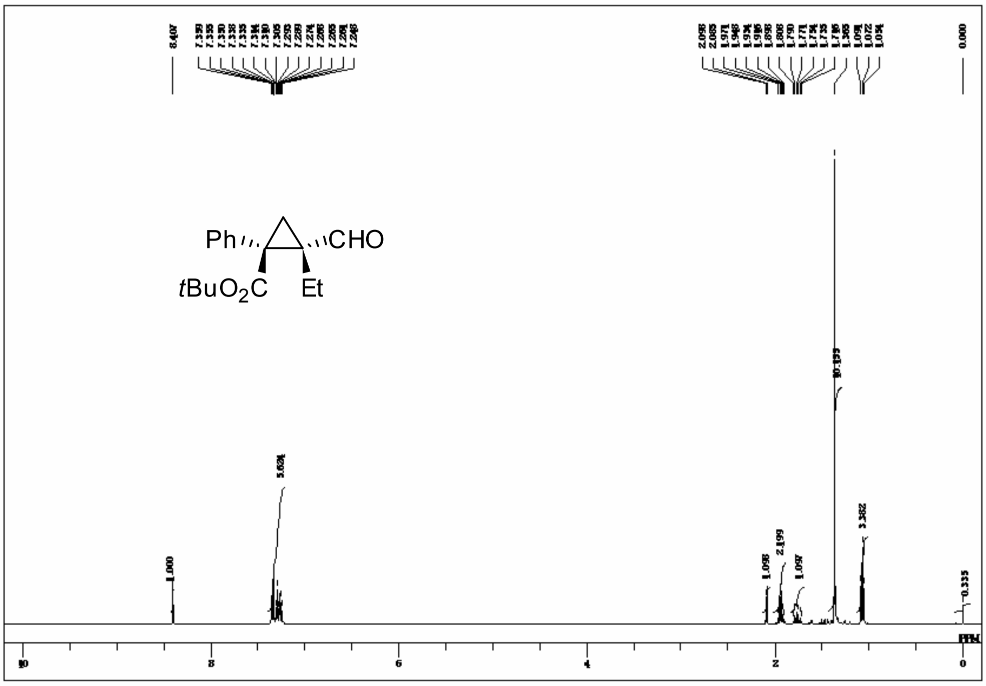
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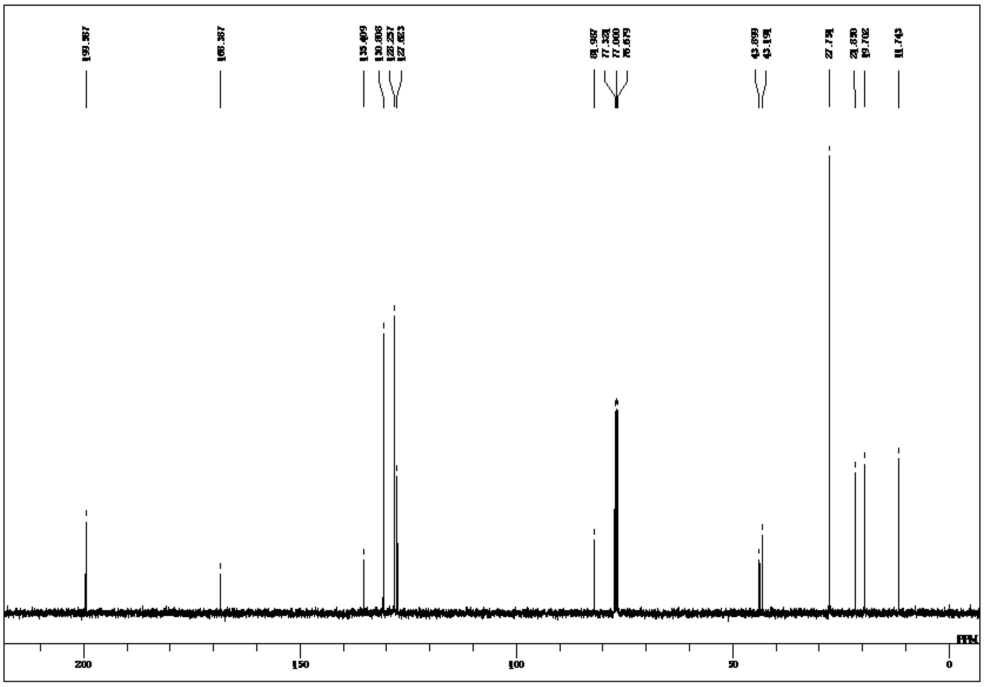
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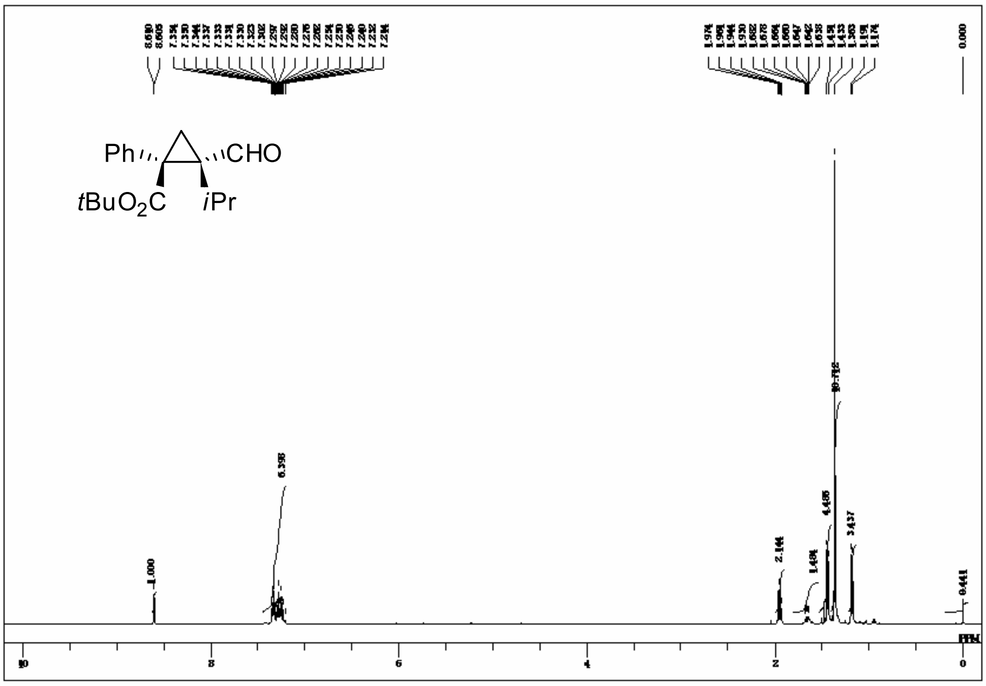
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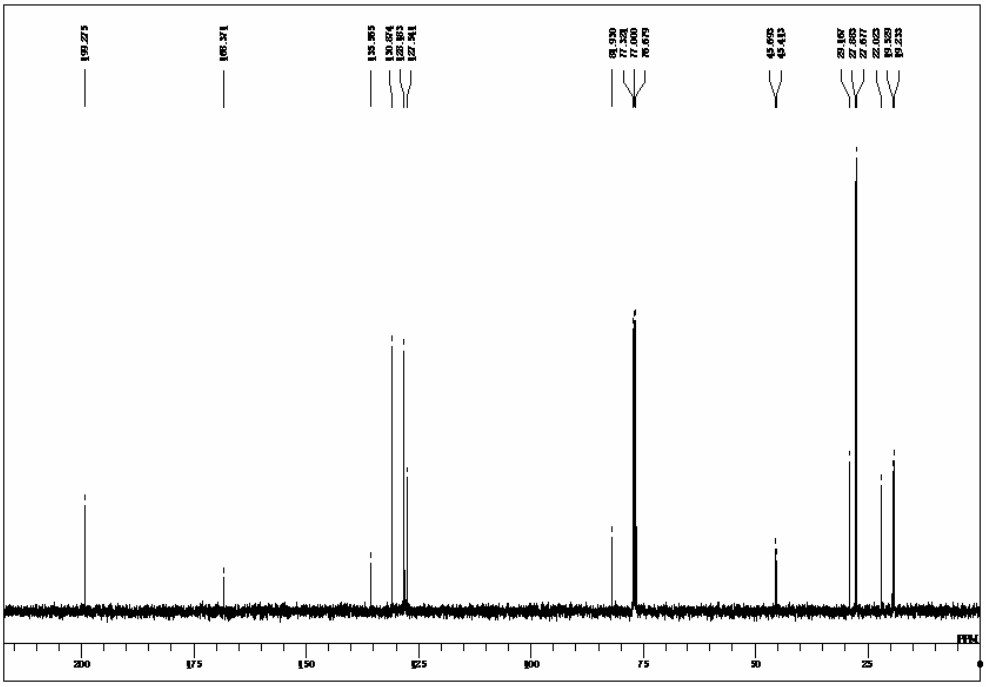
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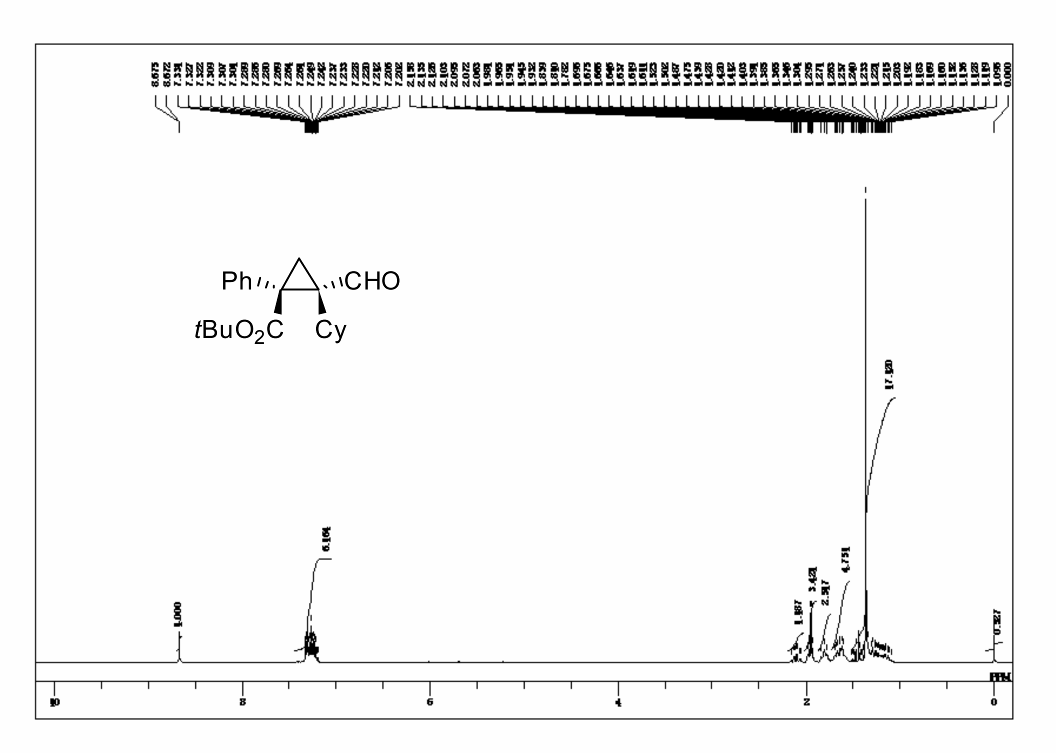
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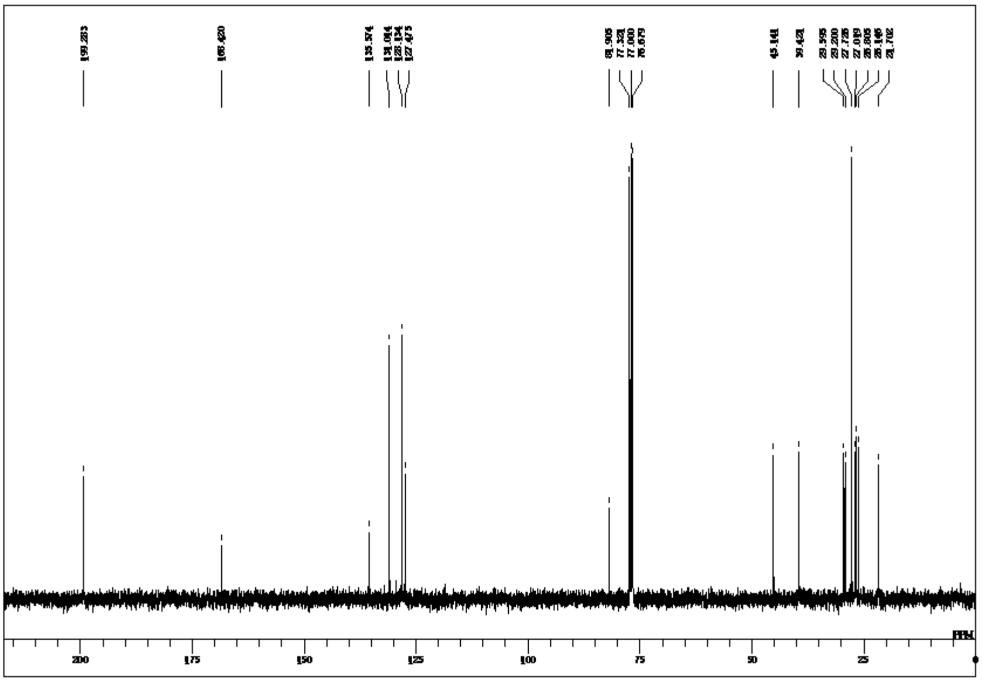
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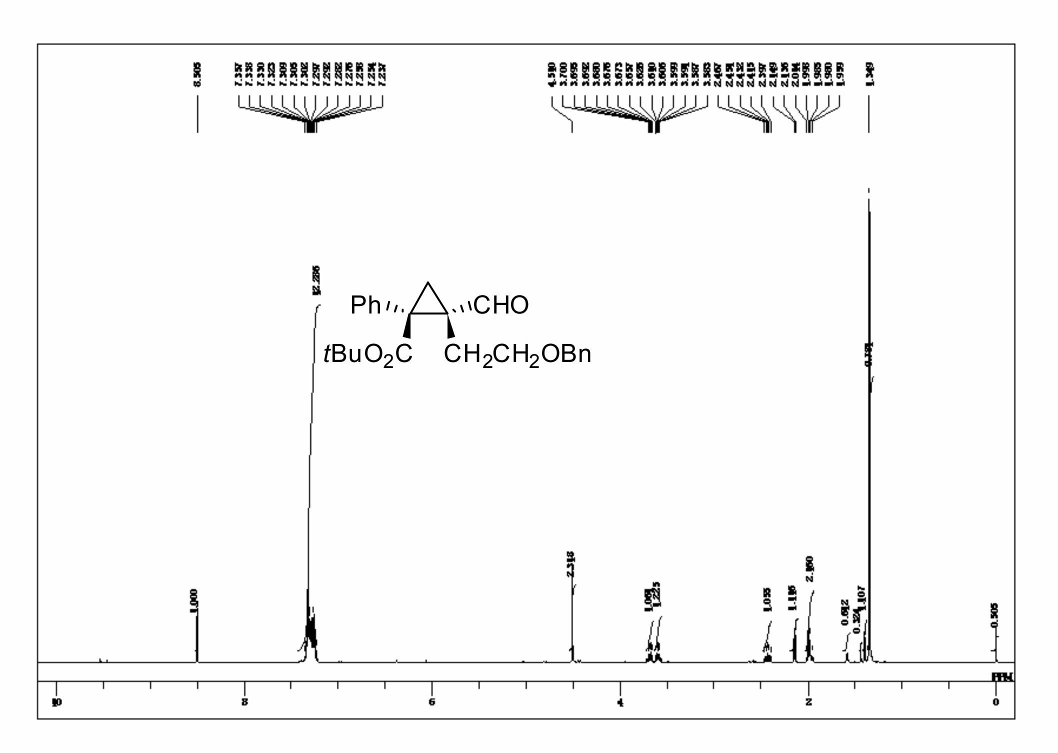
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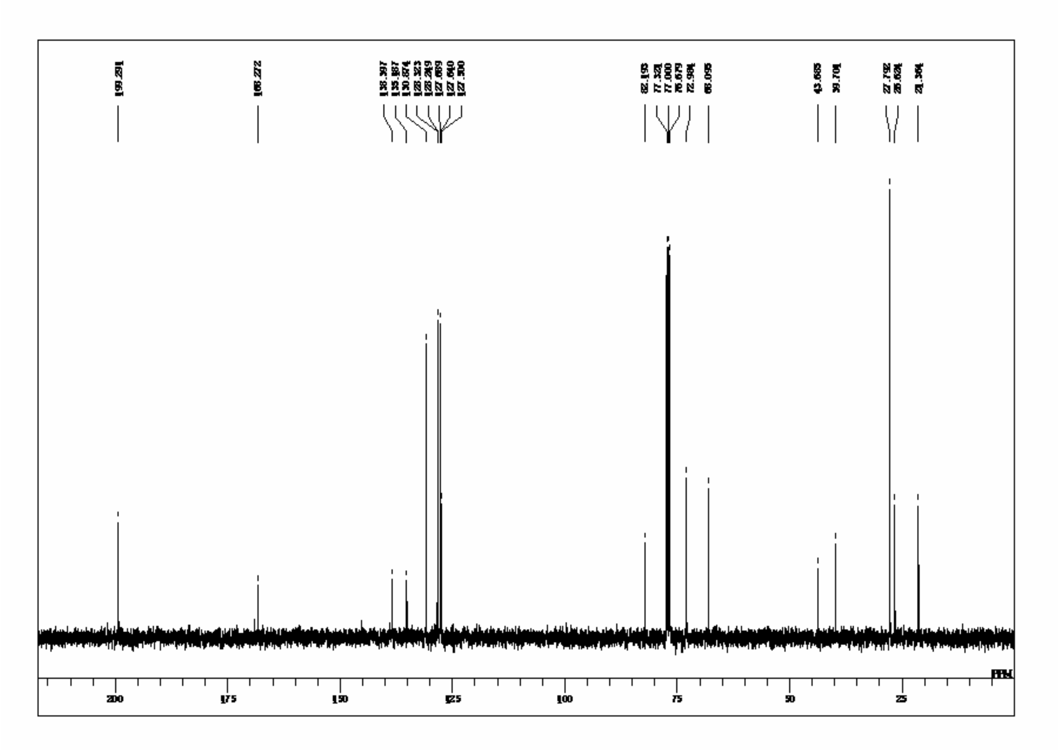
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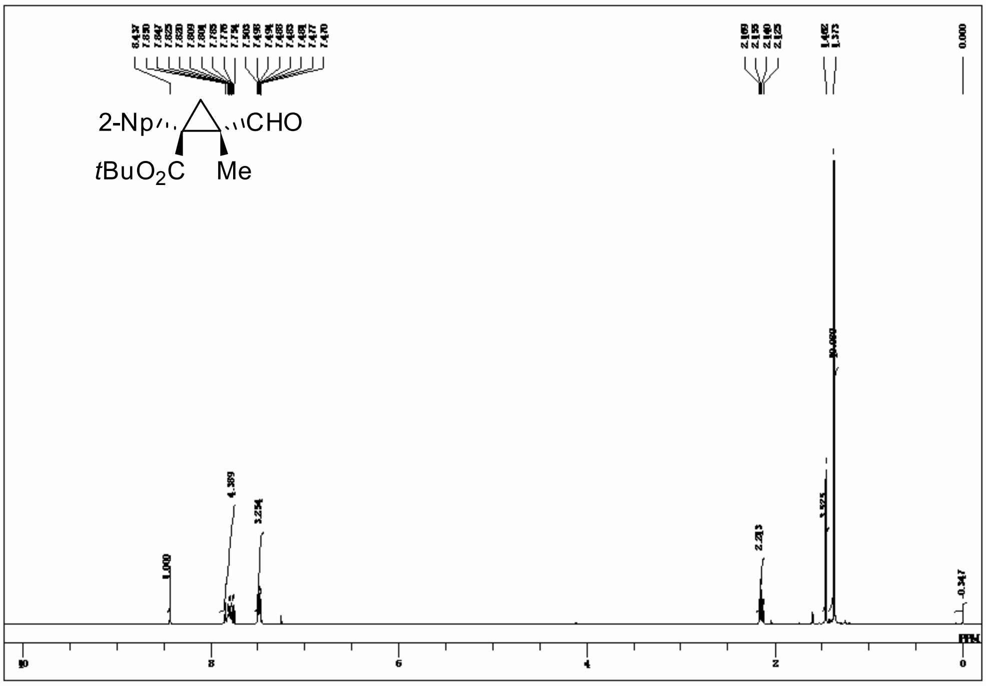
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7.481
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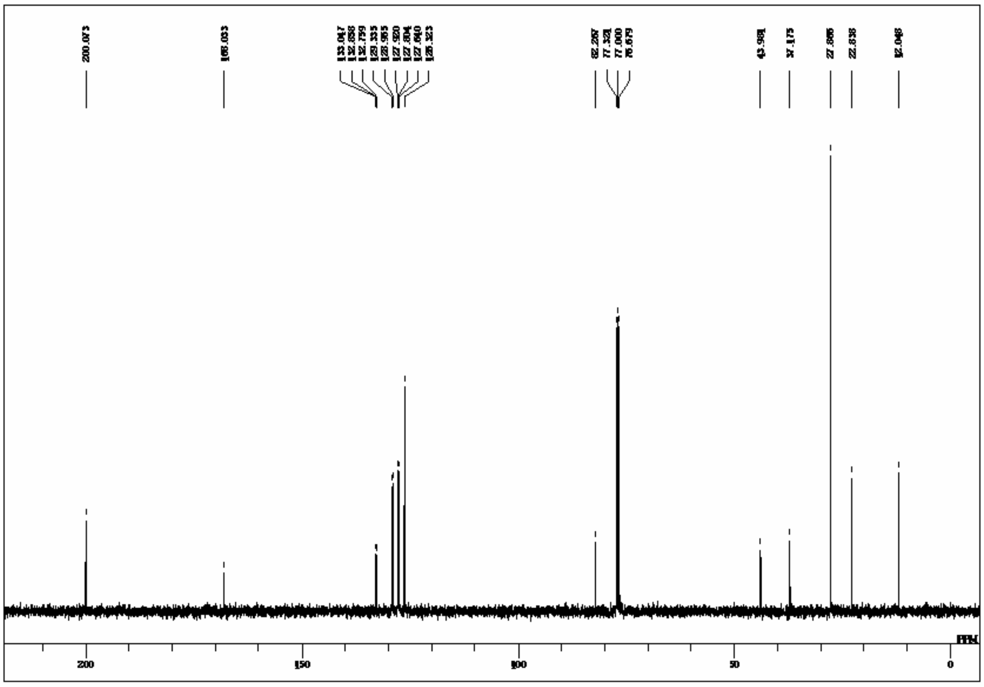
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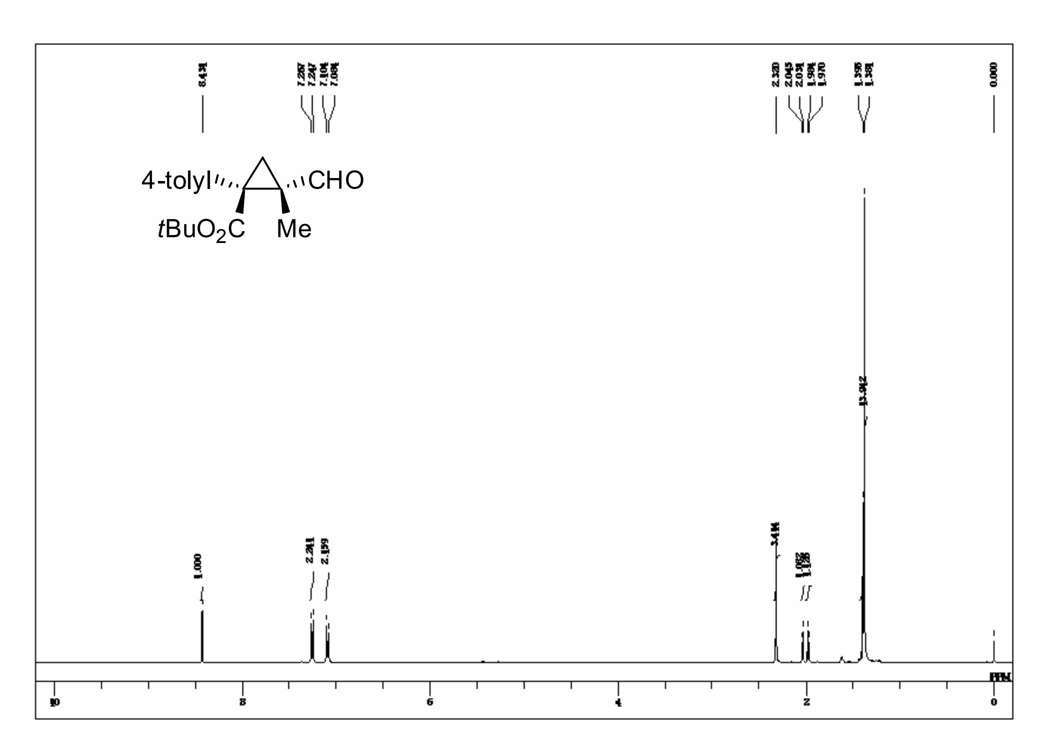
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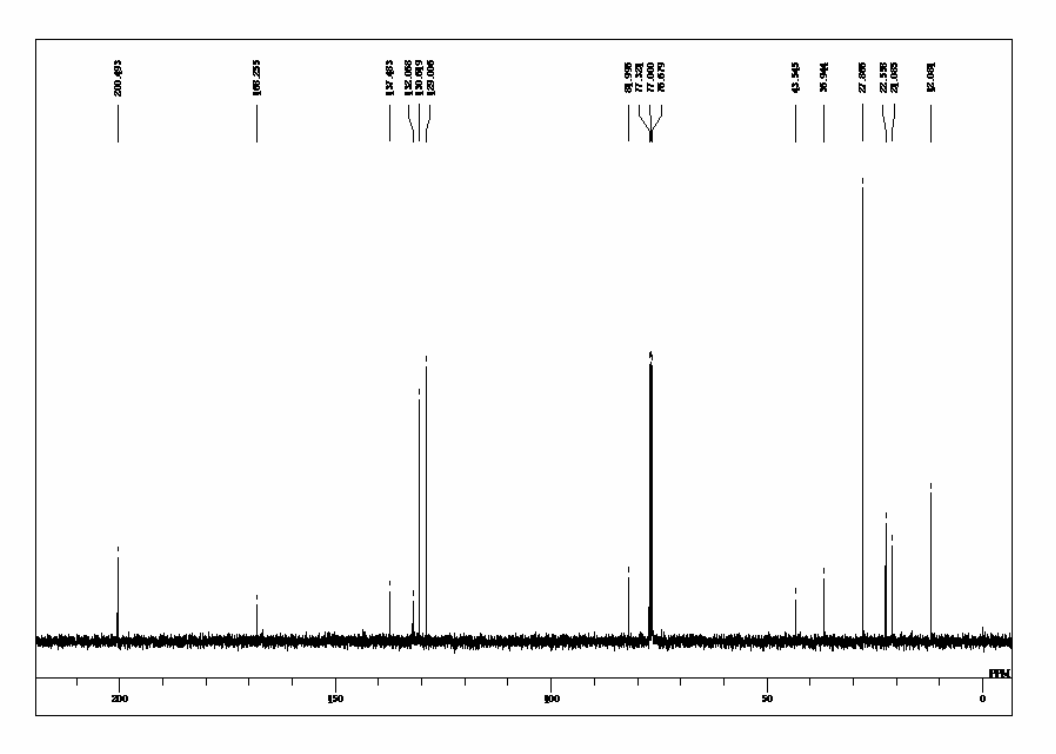
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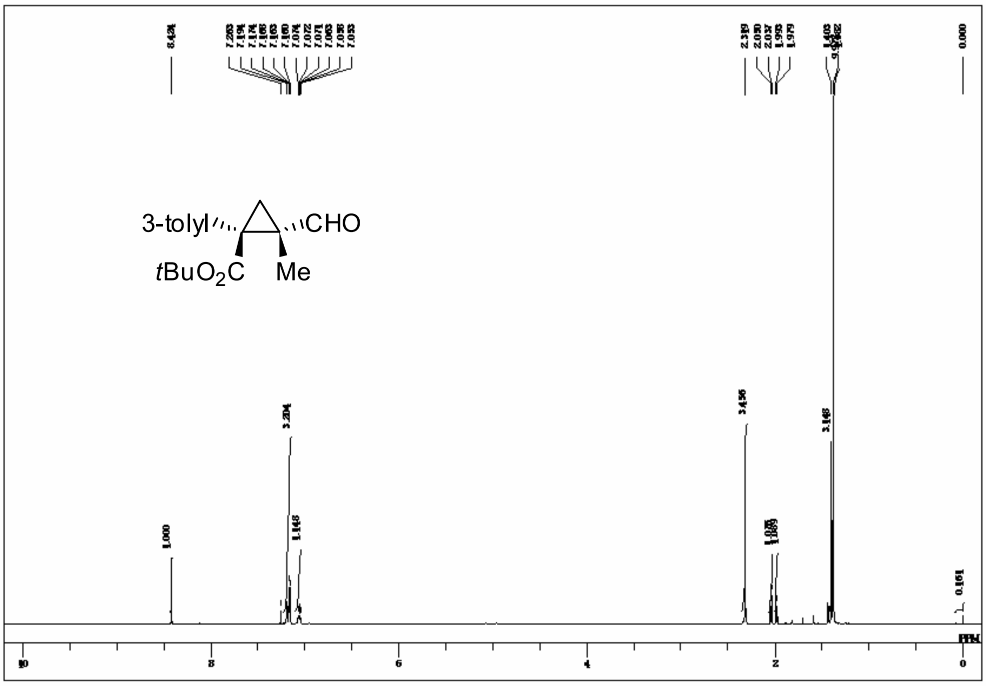
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1.403
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Me
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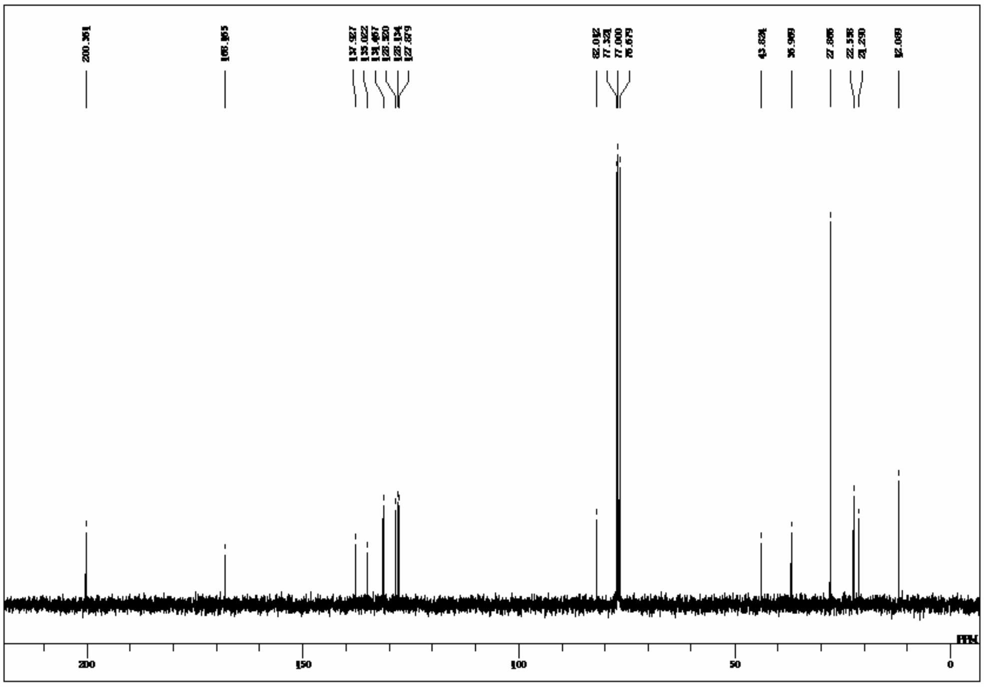
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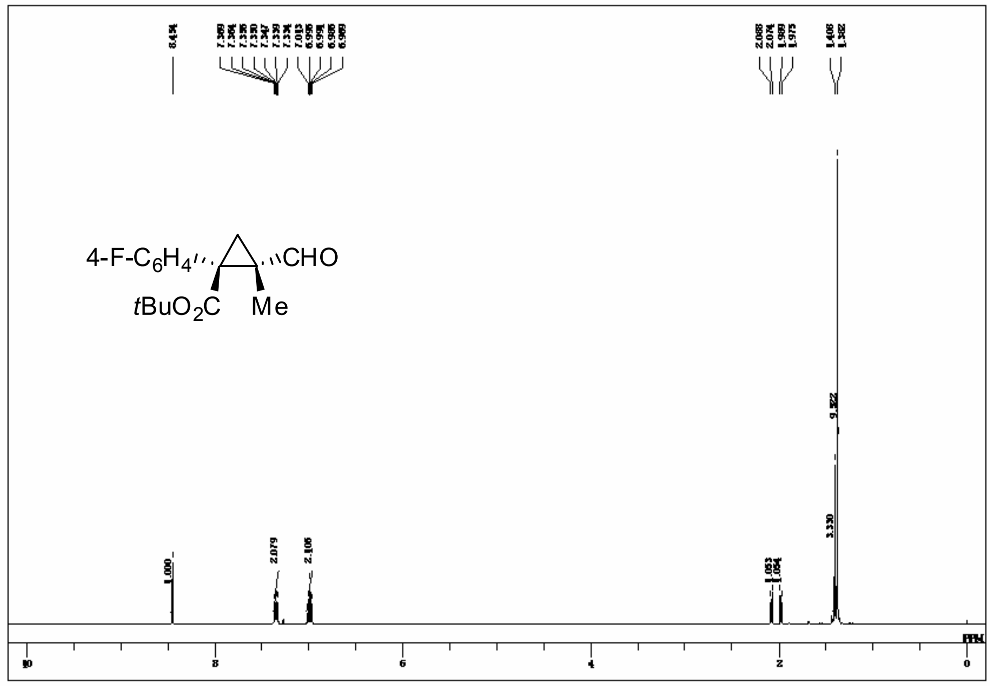
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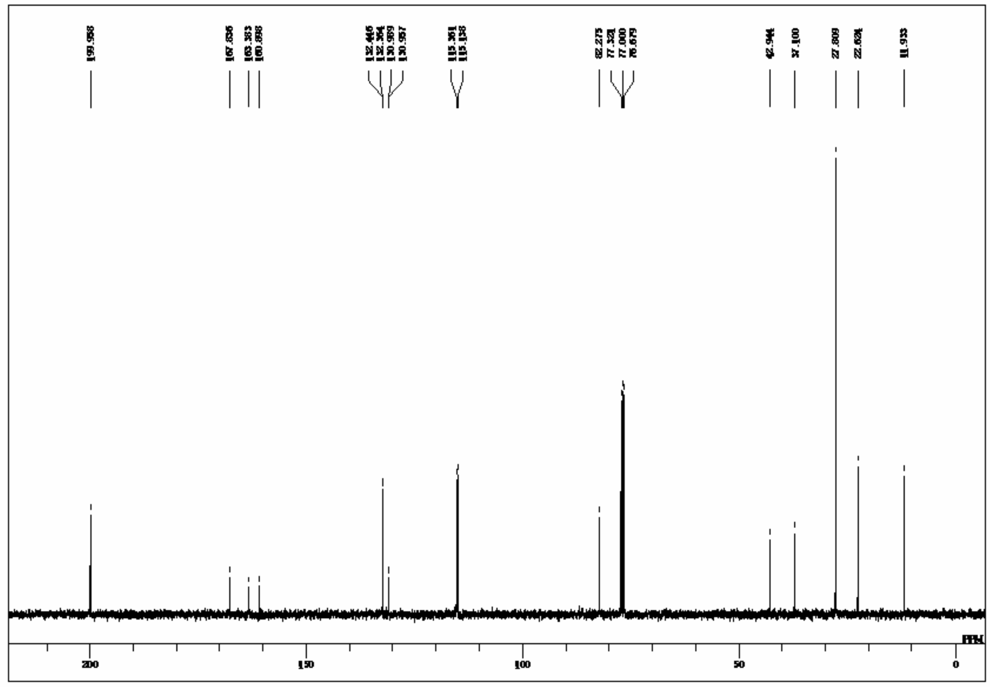
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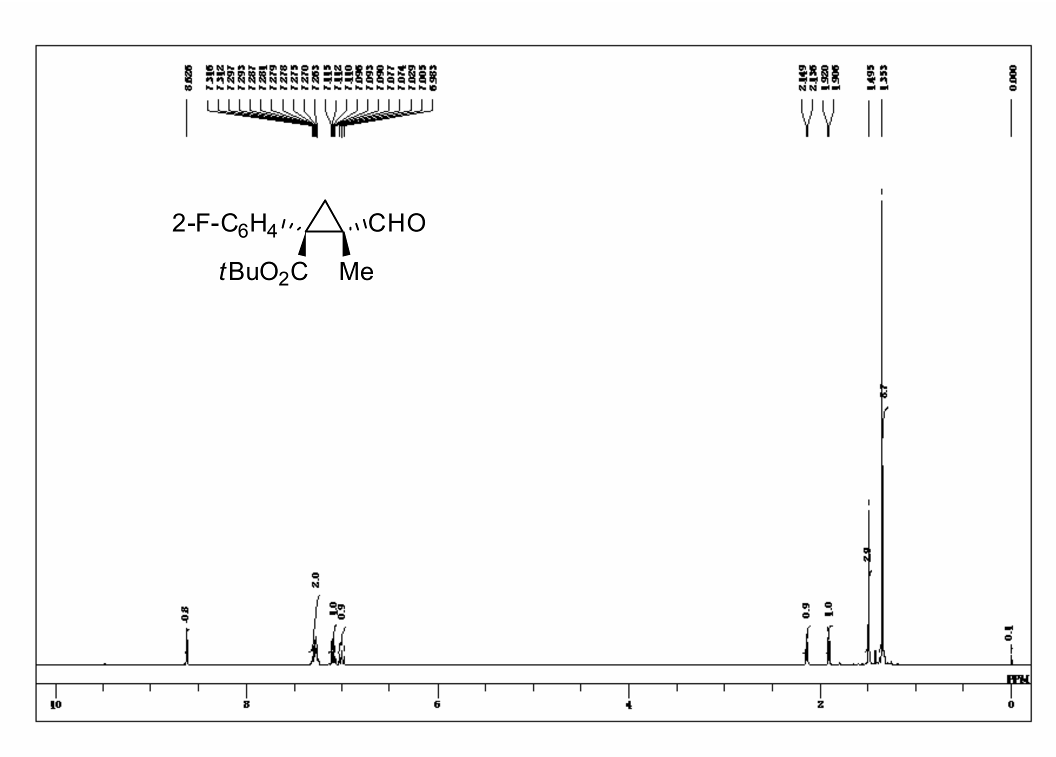
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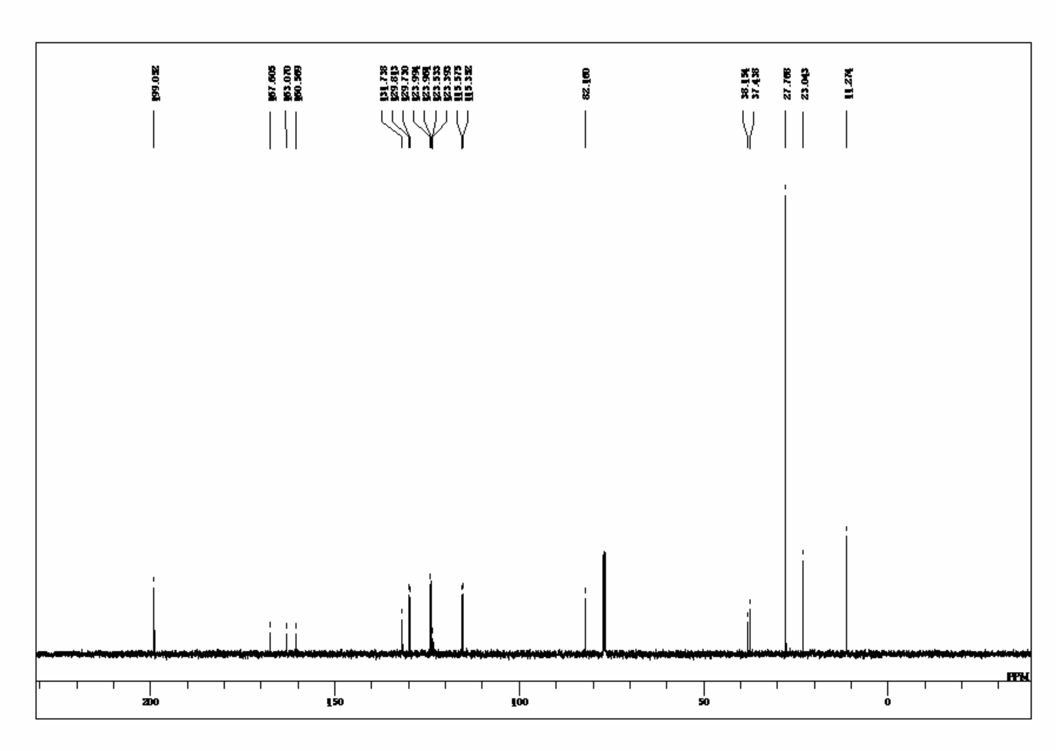
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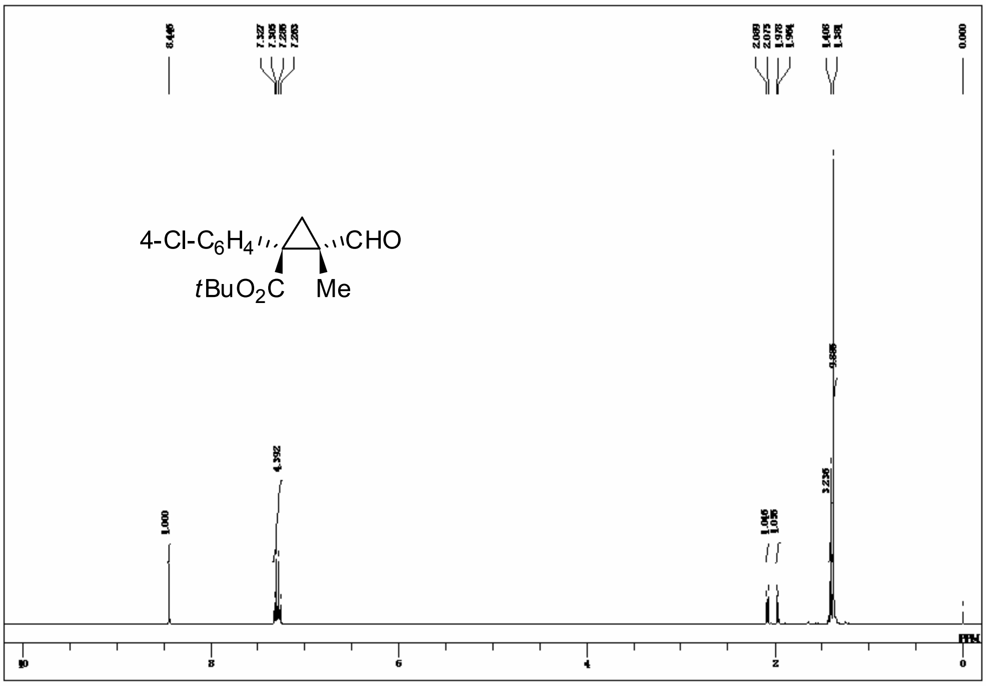
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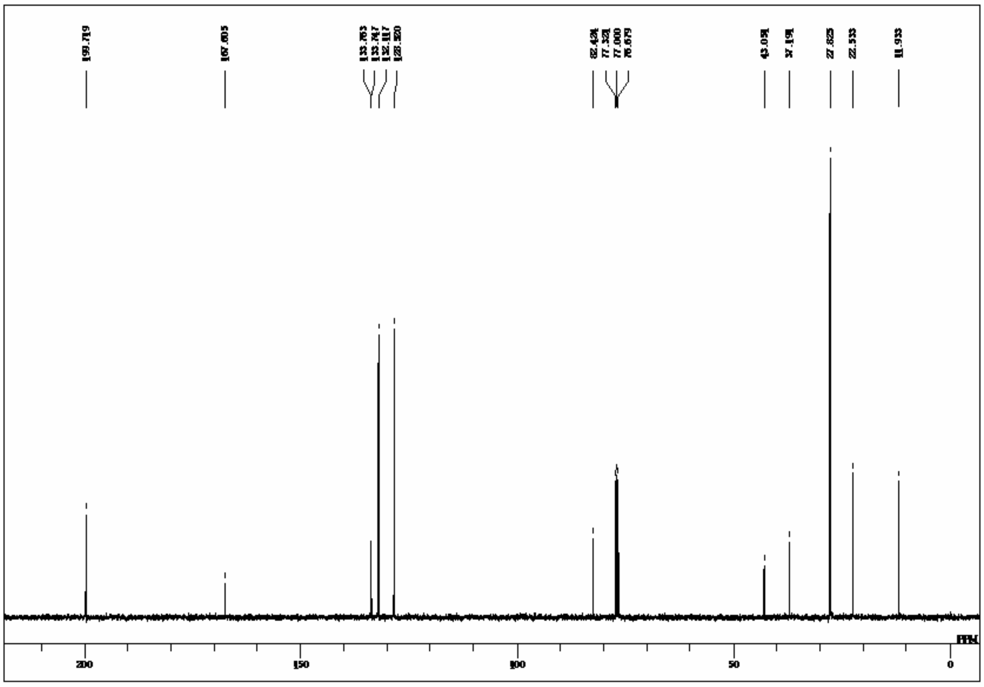
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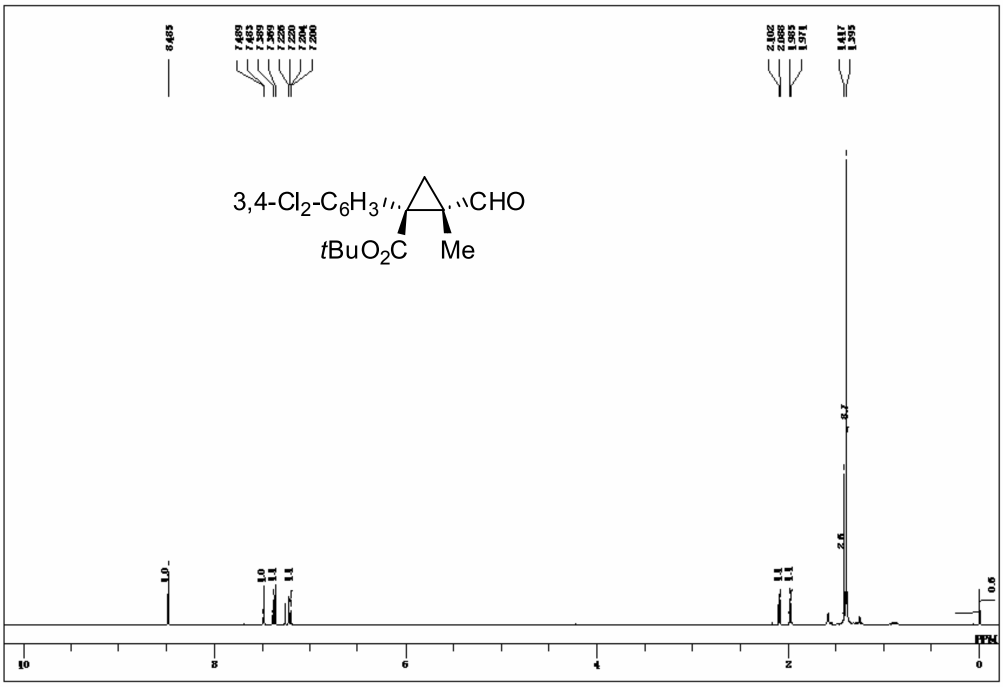
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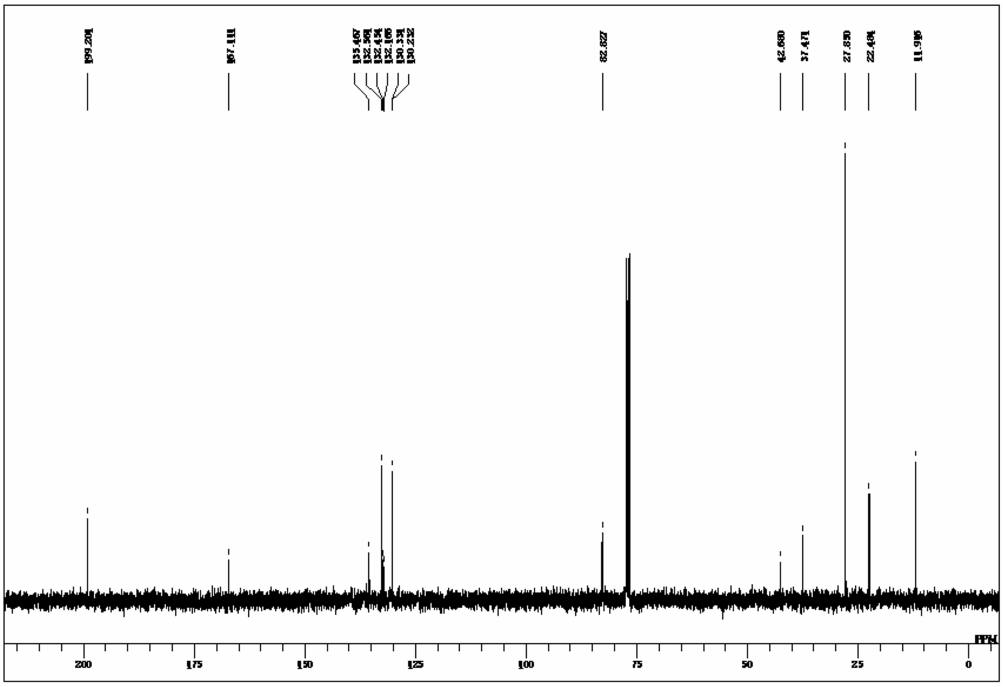
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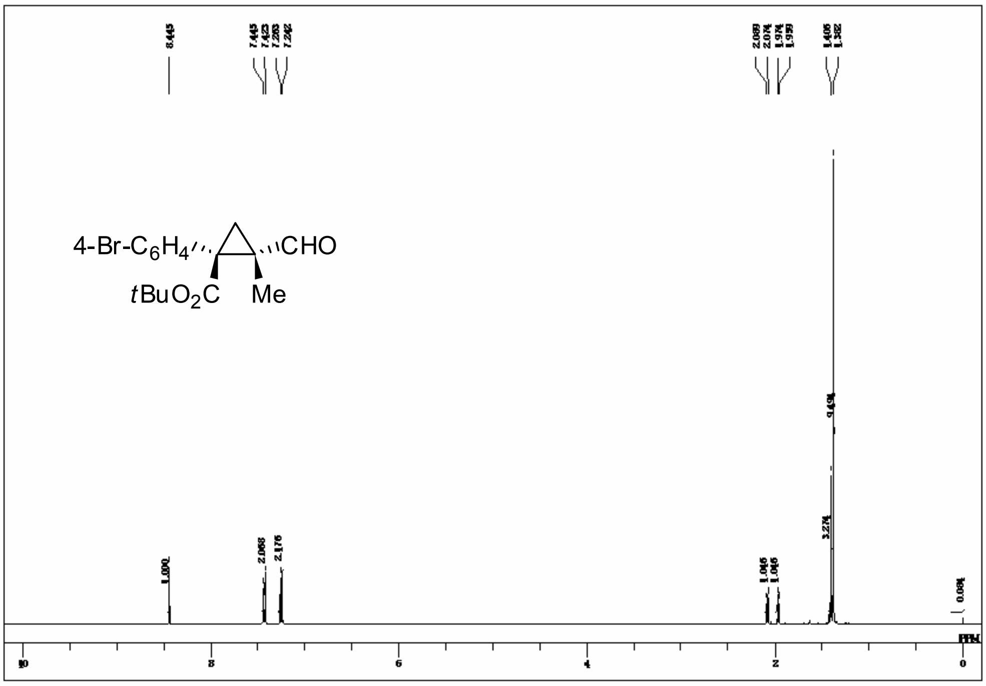
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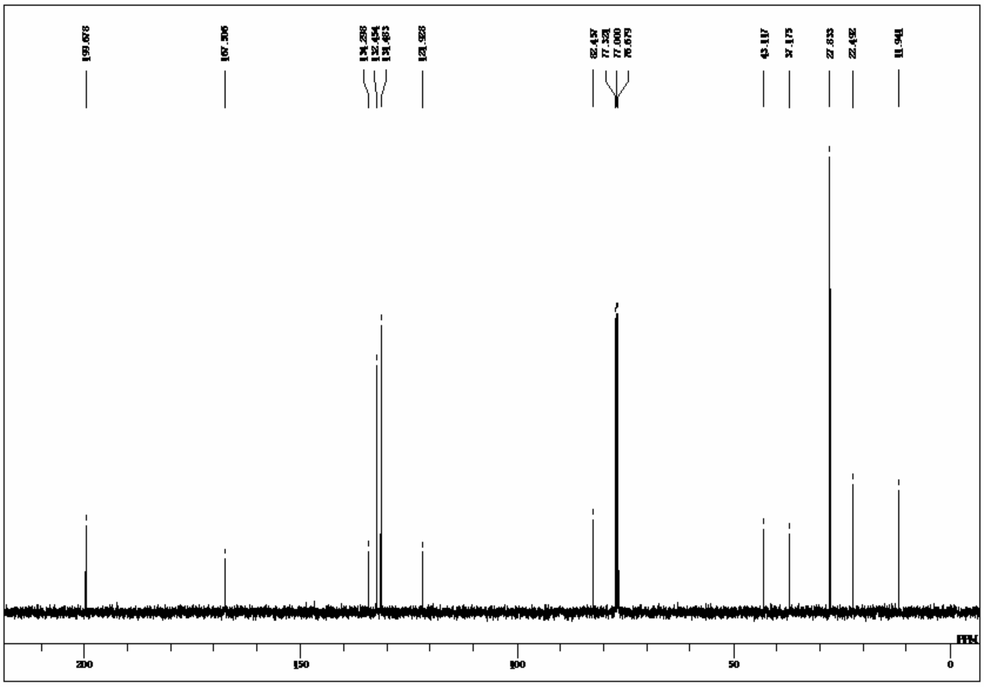
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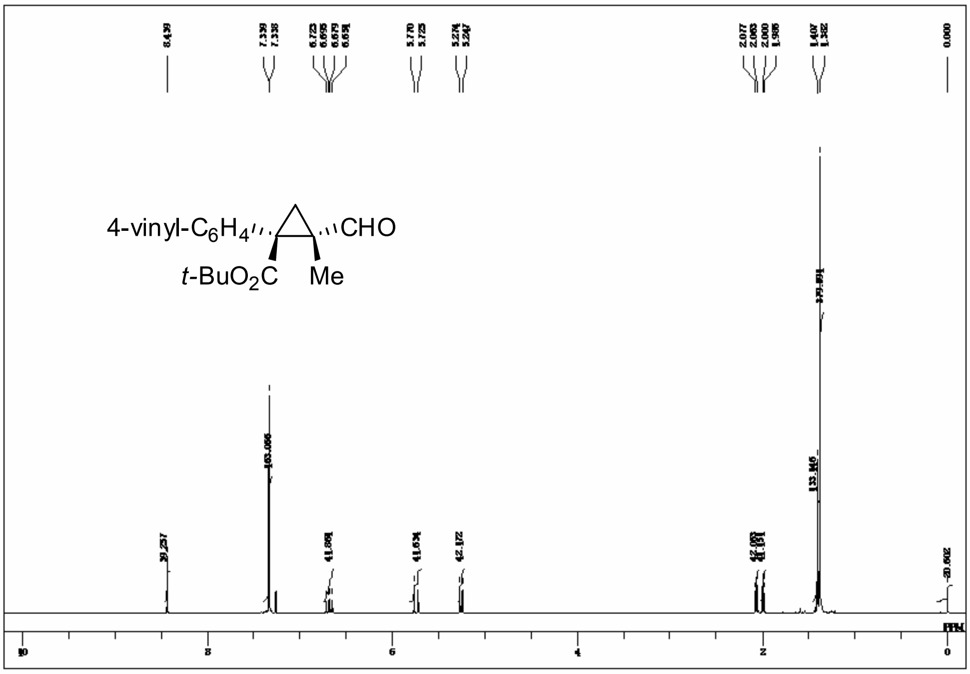
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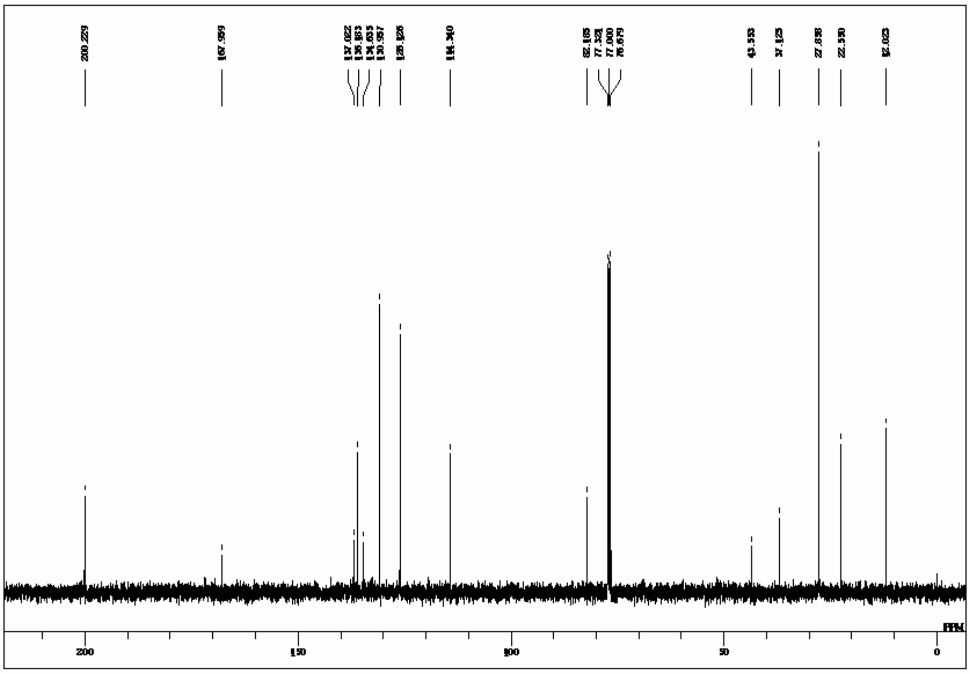
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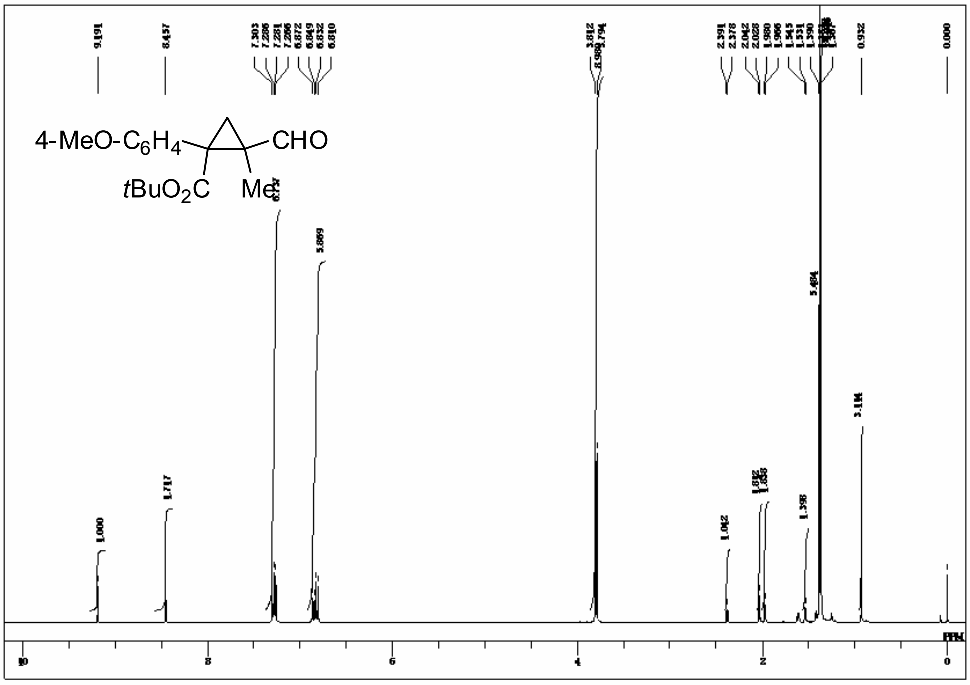
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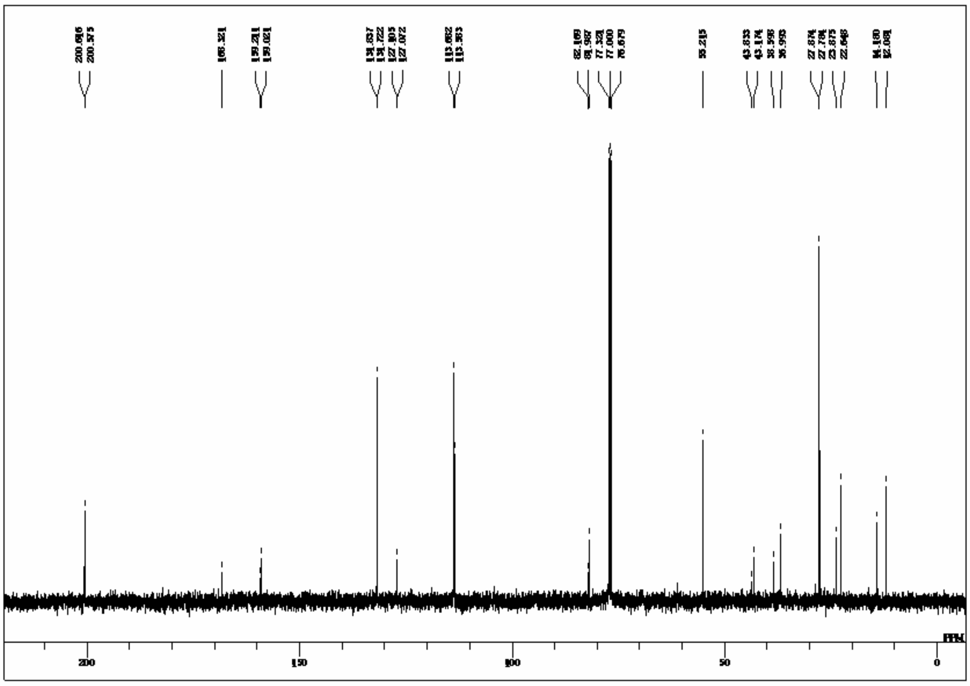
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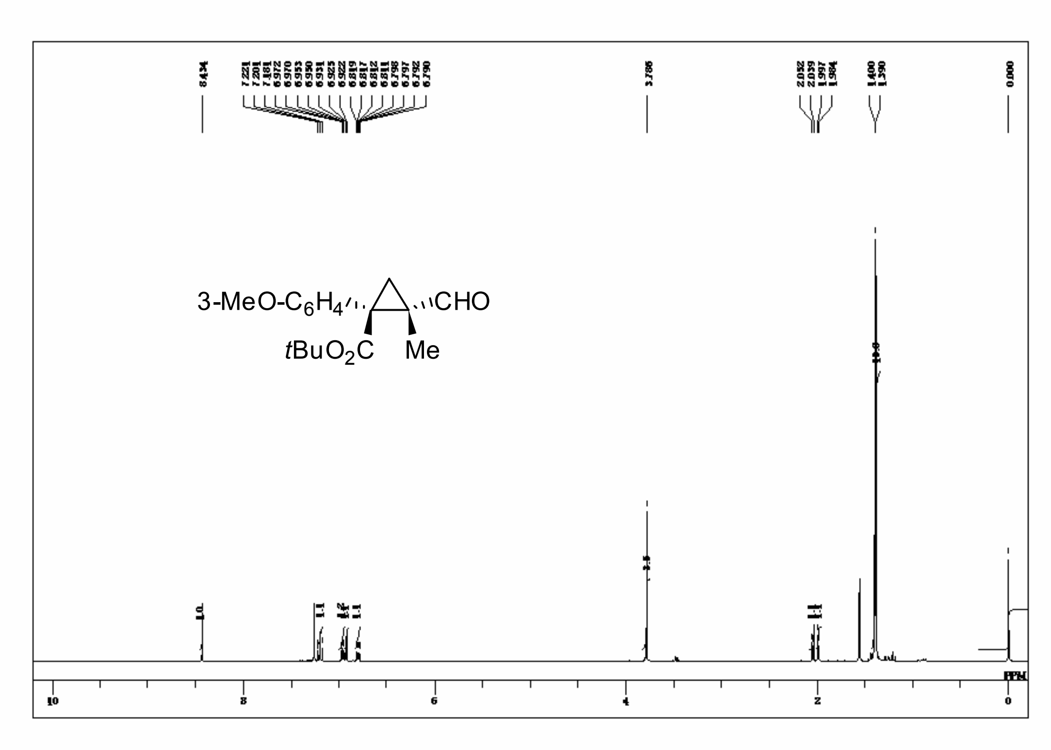
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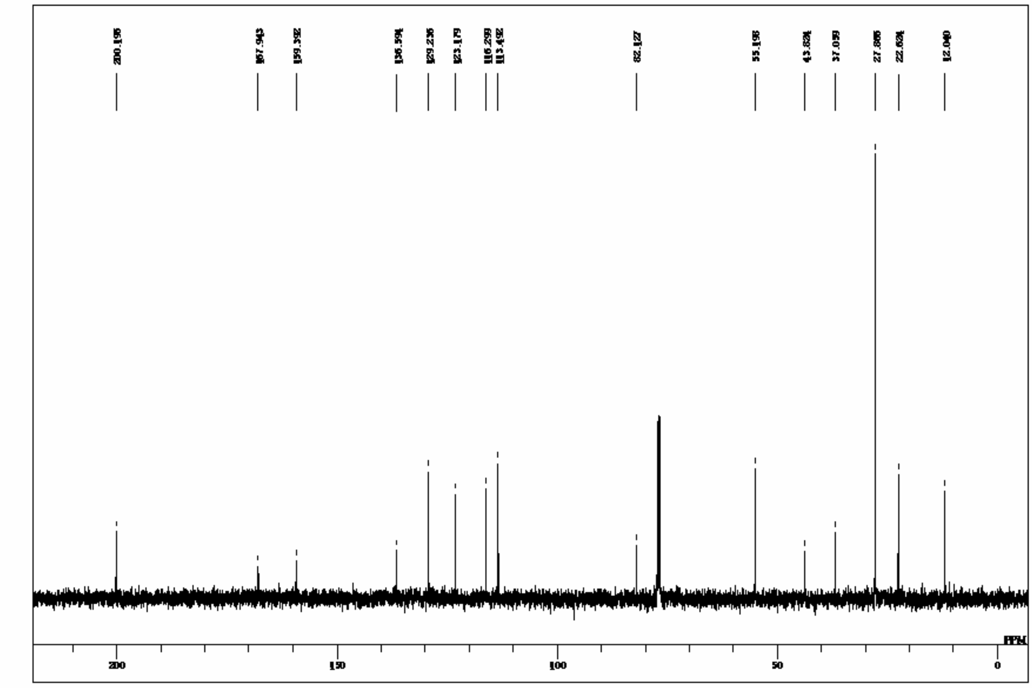
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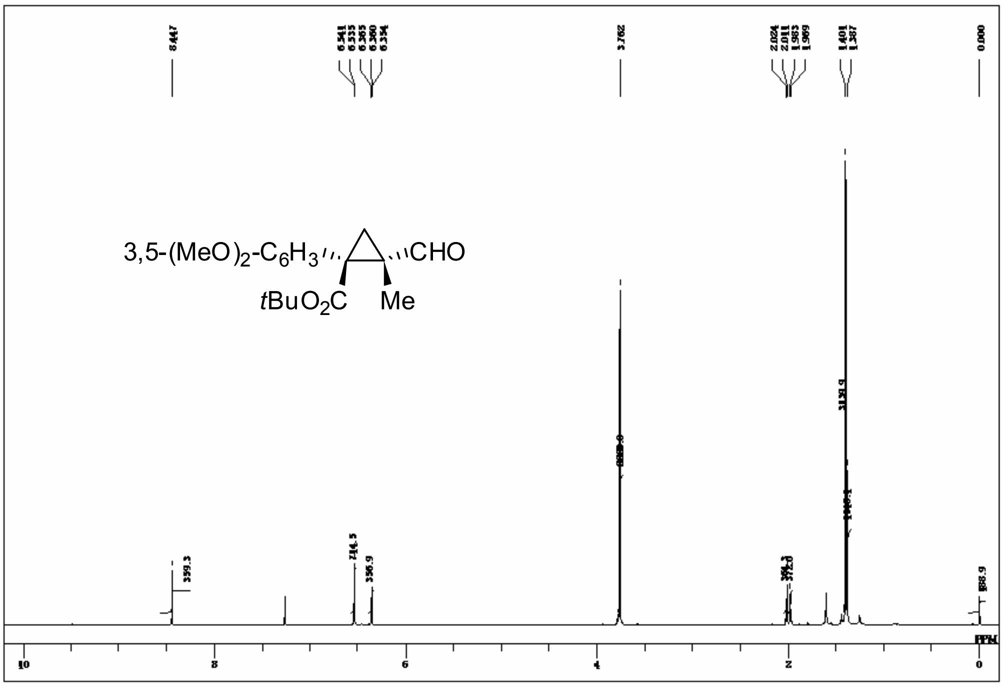
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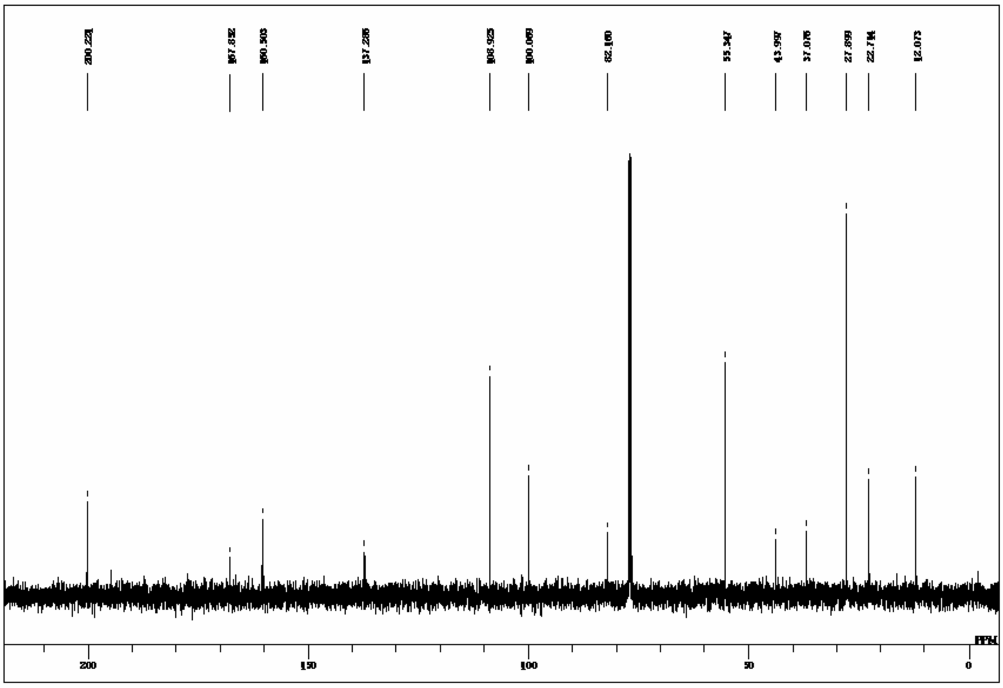
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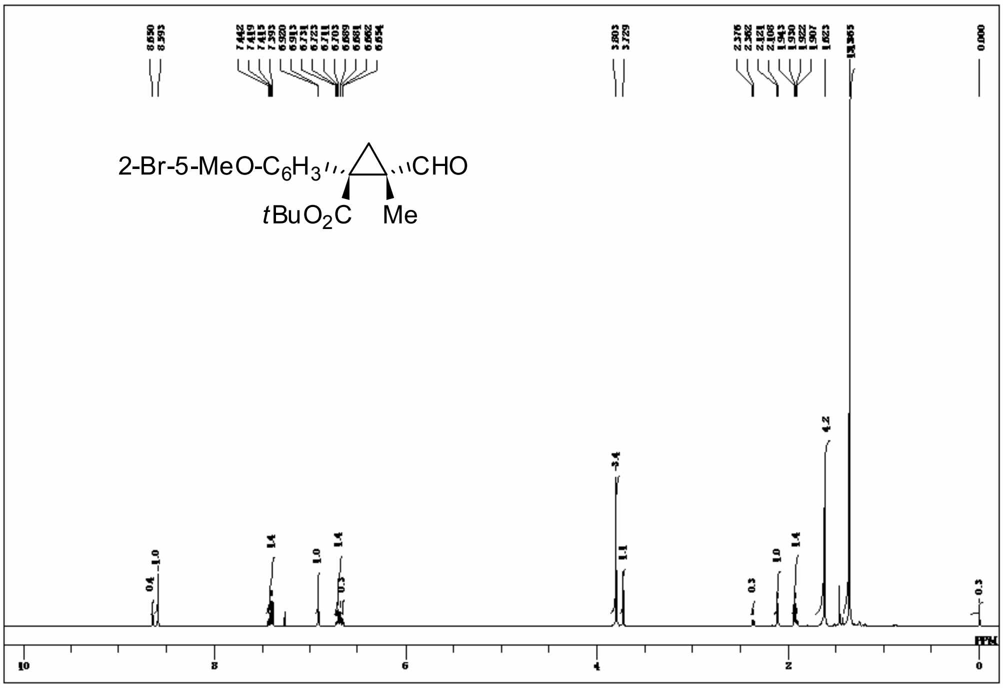
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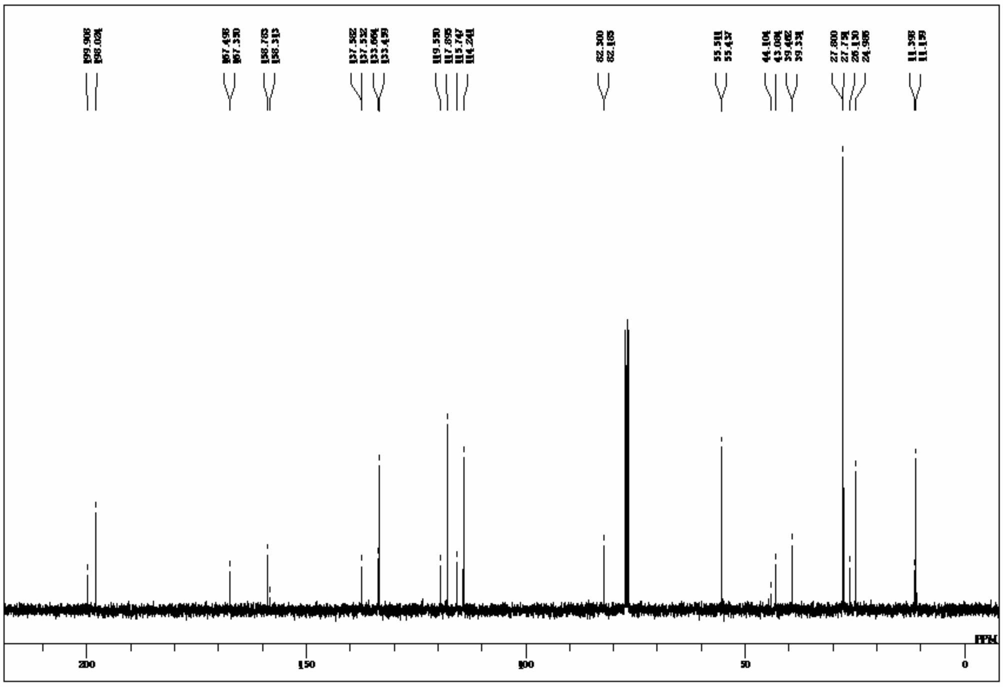
2-Br-5-MeO-C6H3
CHO
tBuO2C
Me
0.4
1.0
1.4
1.0
1.4
0.3
3.4
1.1
0.3
1.0
1.4
4.2
0.3
PPM
10
8
6
4
2
0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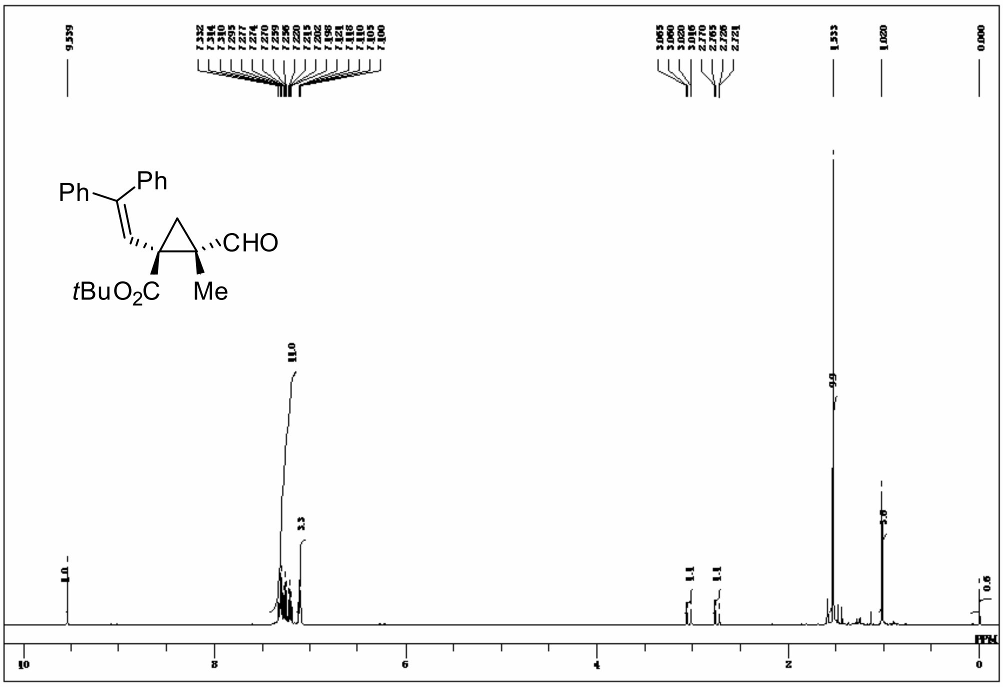
198.024
167.498
167.330
158.783
158.313
137.582
137.532
133.664
133.459
119.550
117.895
115.747
114.241
82.300
82.185
55.511
55.437
44.104
43.084
39.462
39.351
27.800
27.791
26.130
24.986
11.398
11.159
PPM
200
150
100
50
0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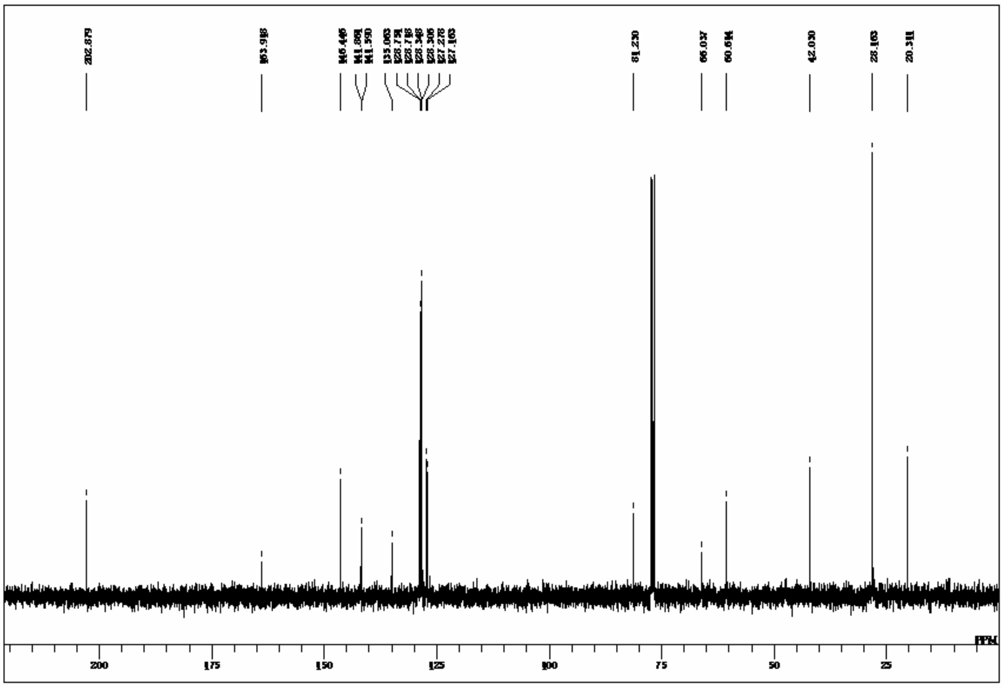
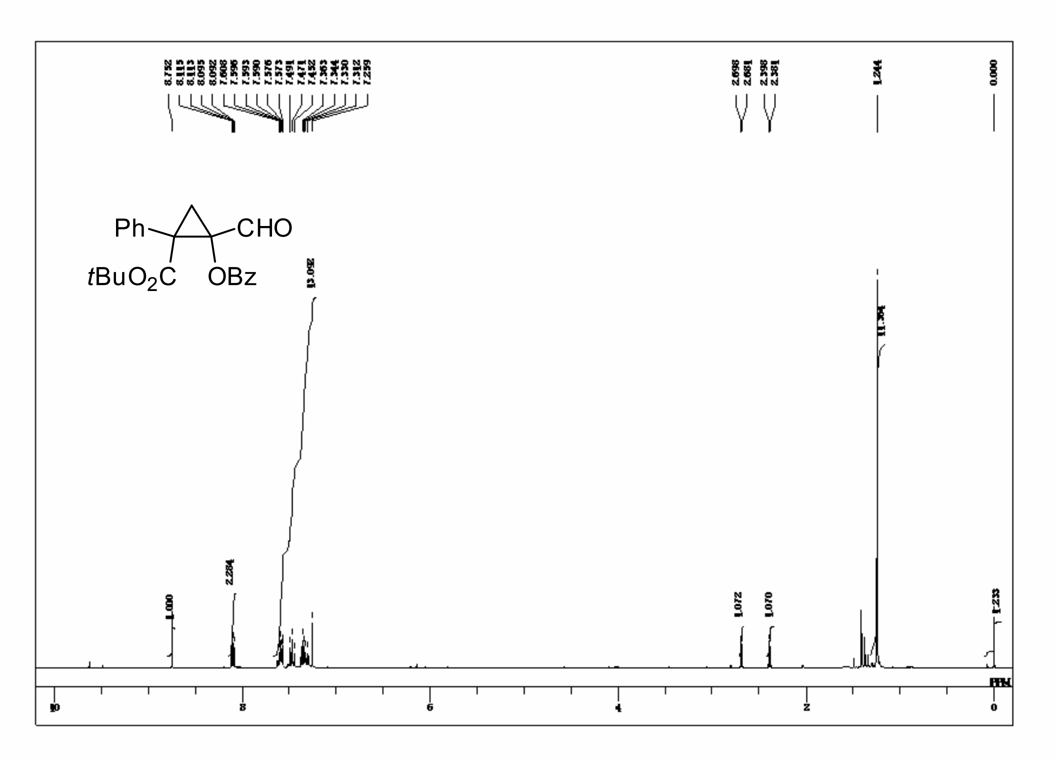
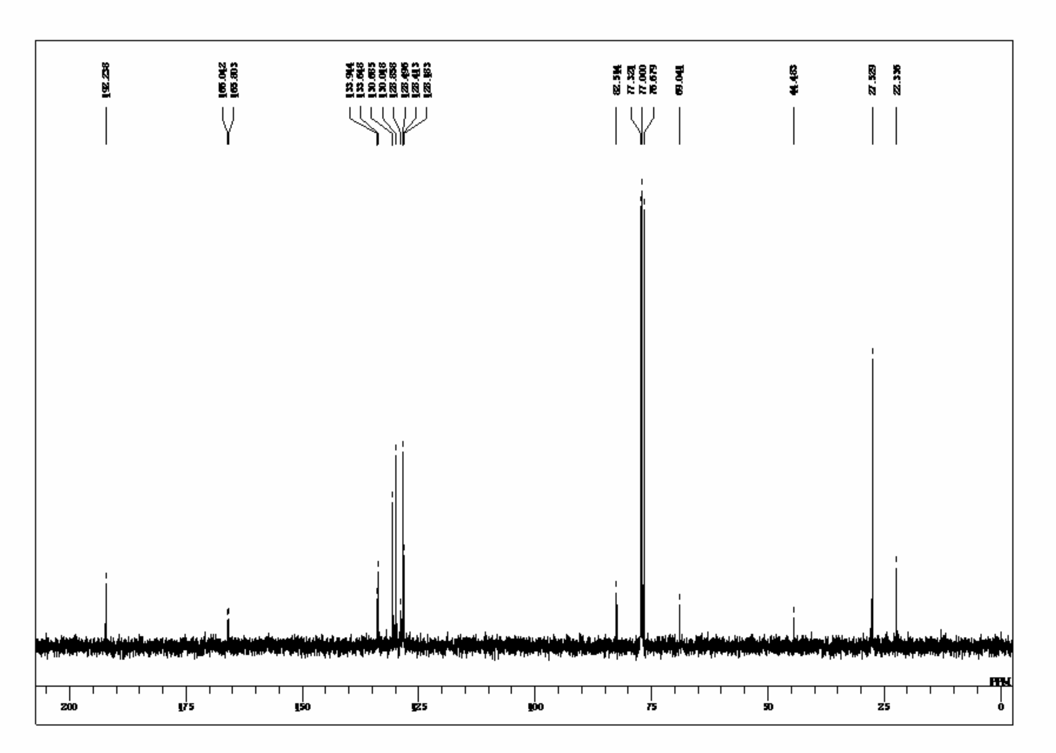
7.314
7.310
7.295
7.277
7.274
7.270
7.259
7.256
7.220
7.215
7.202
7.198
7.121
7.118
7.110
7.105
7.100
3.065
3.060
3.020
3.016
2.770
2.765
2.726
2.721
1.533
1.020
0.000
Ph
Ph
CHO
tBuO2C
Me
1.0
11.0
3.3
1.1
1.1
9.9
3.0
0.6
10
8
6
4
2
0
PPM


202.879
163.918
146.446
141.891
141.590
135.063
128.751
128.718
128.348
128.306
127.276
127.163
81.230
66.037
60.614
42.030
28.163
20.311
200
175
150
125
100
75
50
25
PPM


8.732
8.115
8.113
8.095
8.092
7.608
7.596
7.593
7.590
7.576
7.573
7.491
7.471
7.452
7.363
7.344
7.330
7.312
7.299
2.698
2.681
2.398
2.381
1.244
0.000
Ph
CHO
tBuO2C
OBz
13.092
11.304
2.284
1.000
1.072
1.070
1.233
10
8
6
4
2
0
PPM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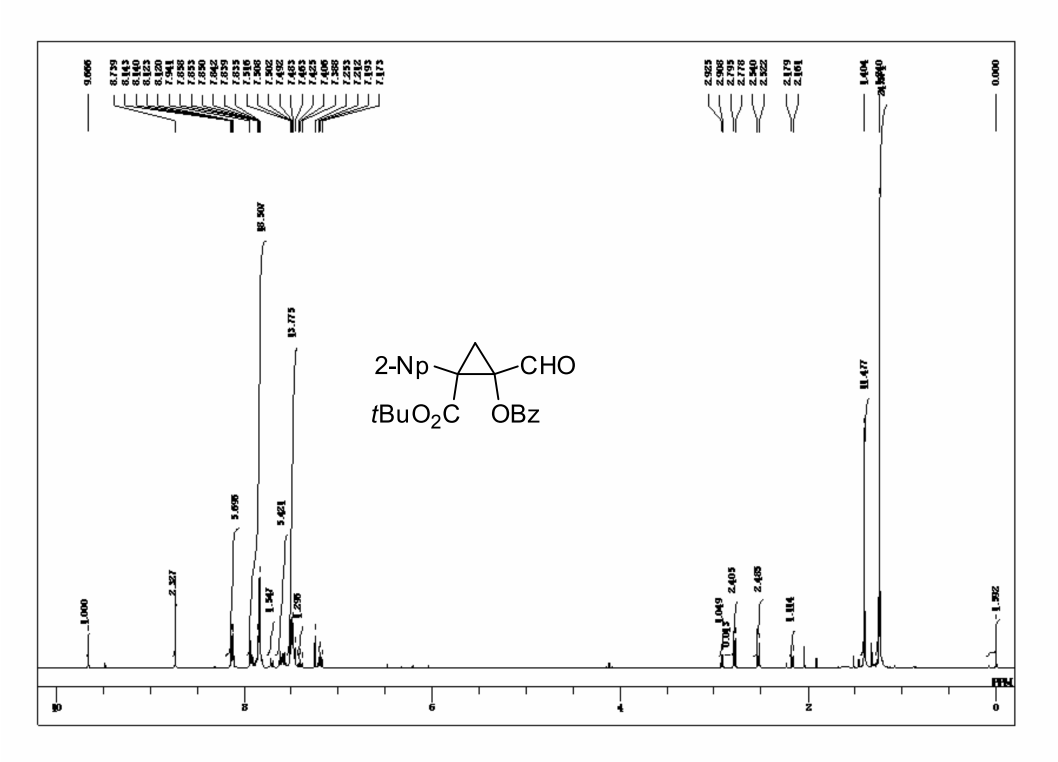
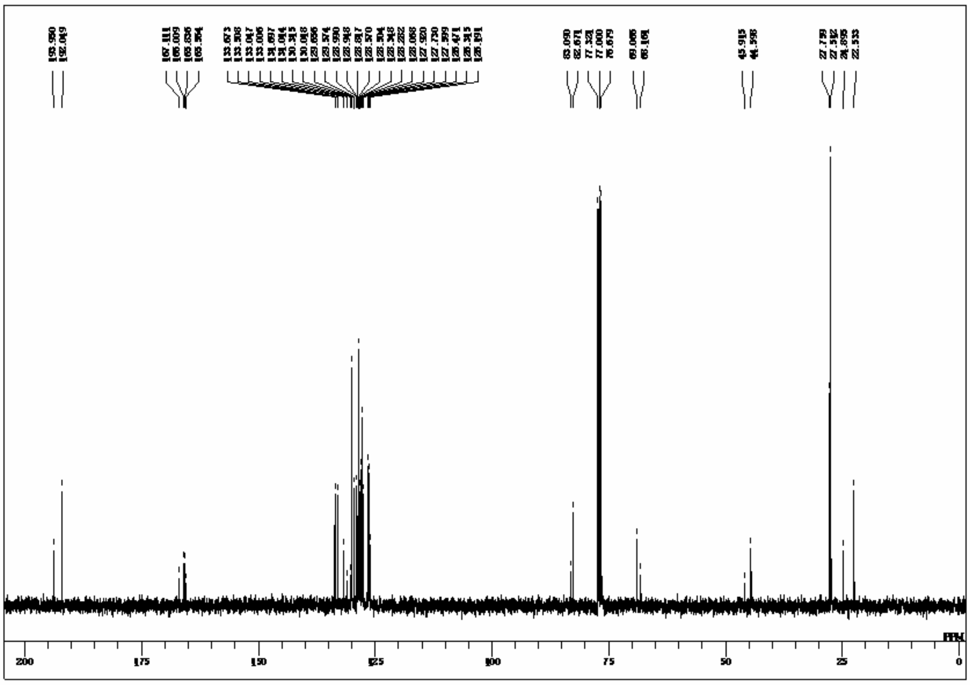
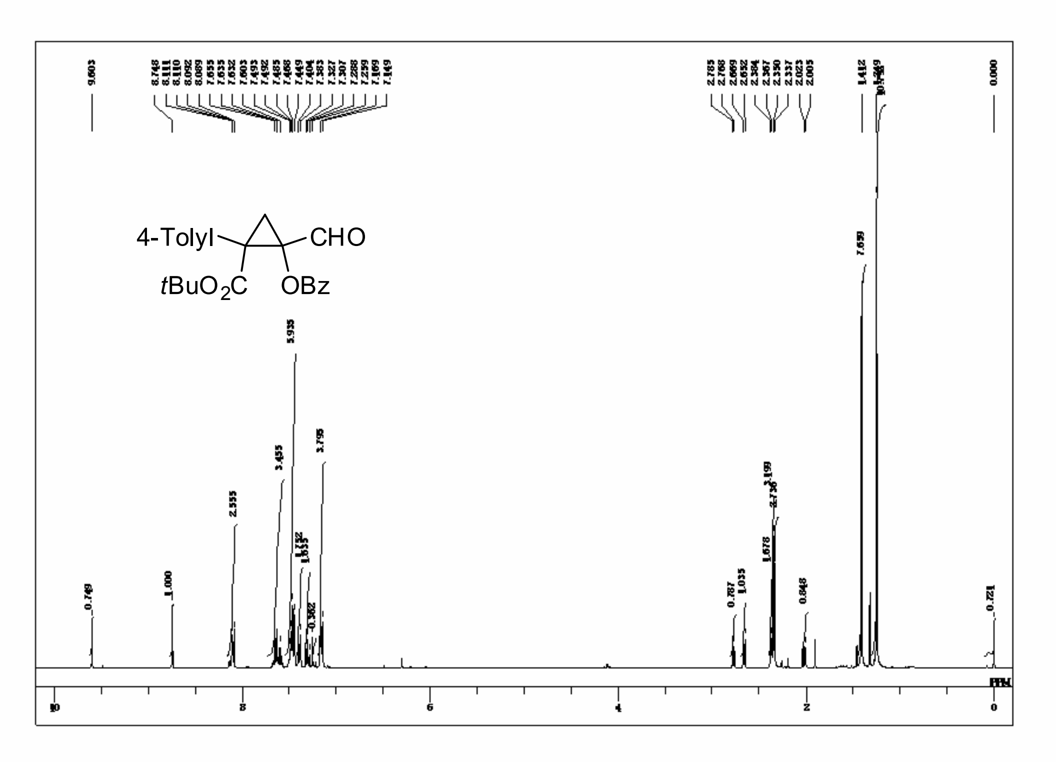
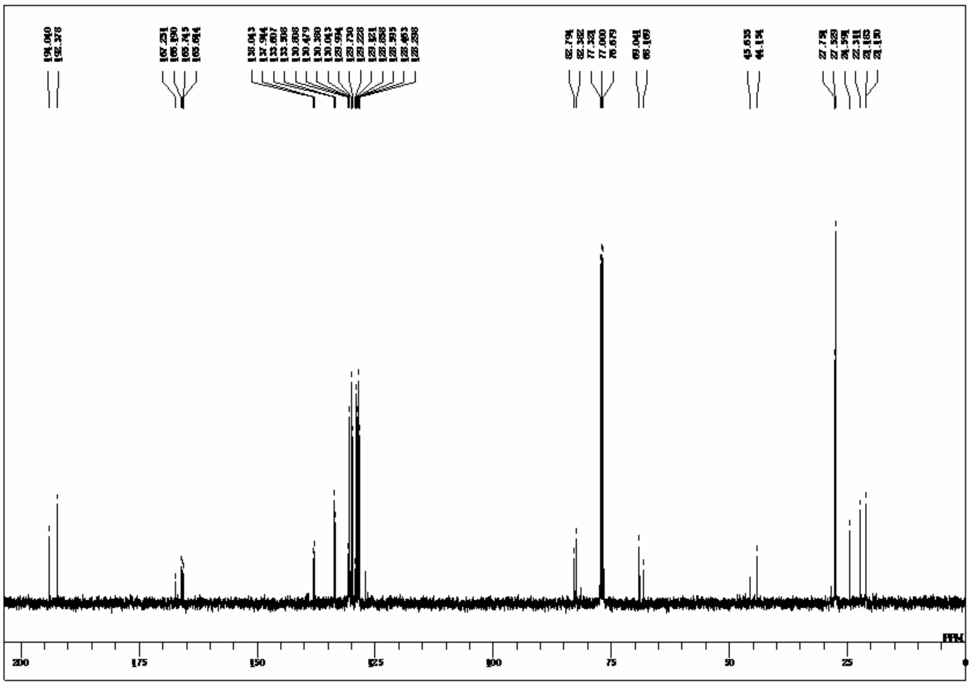
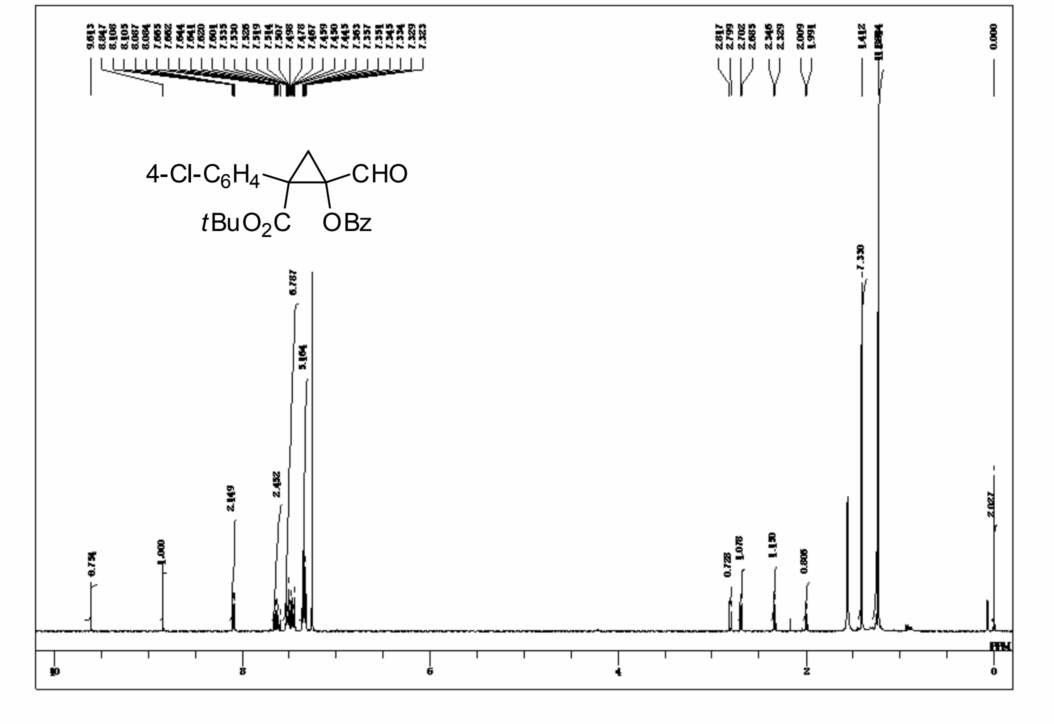
165.042
163.803
133.944
133.648
130.635
130.048
128.858
128.495
128.413
128.183
82.514
77.321
77.000
76.679
69.041
44.453
27.523
22.335
200
175
150
125
100
75
50
25
0
PPM

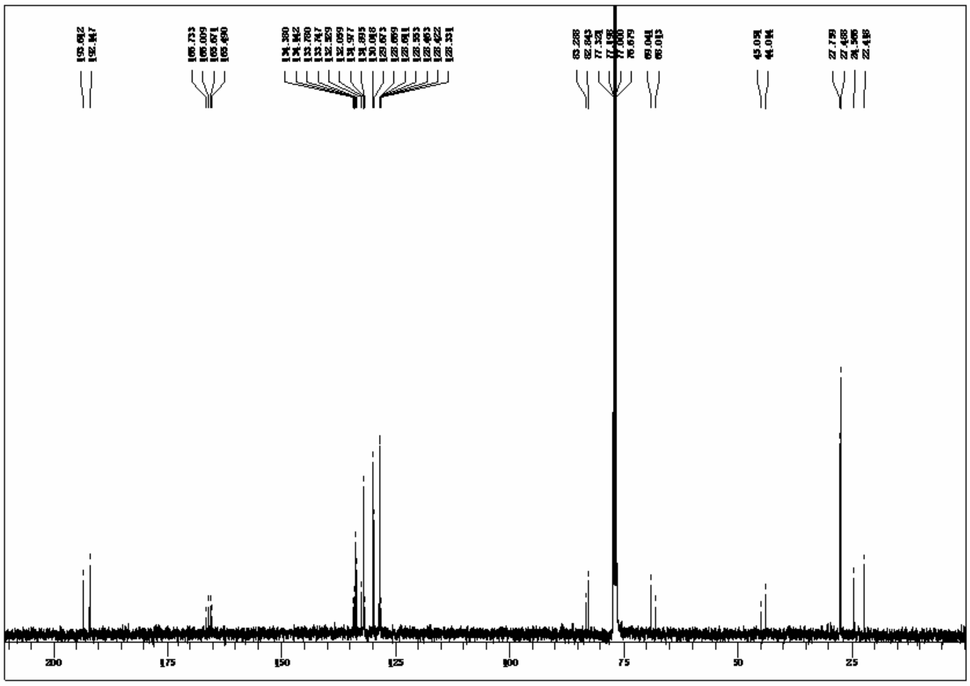

2-Np
CHO
tBuO2C
OBz
PPM
10
8
6
4
2
0

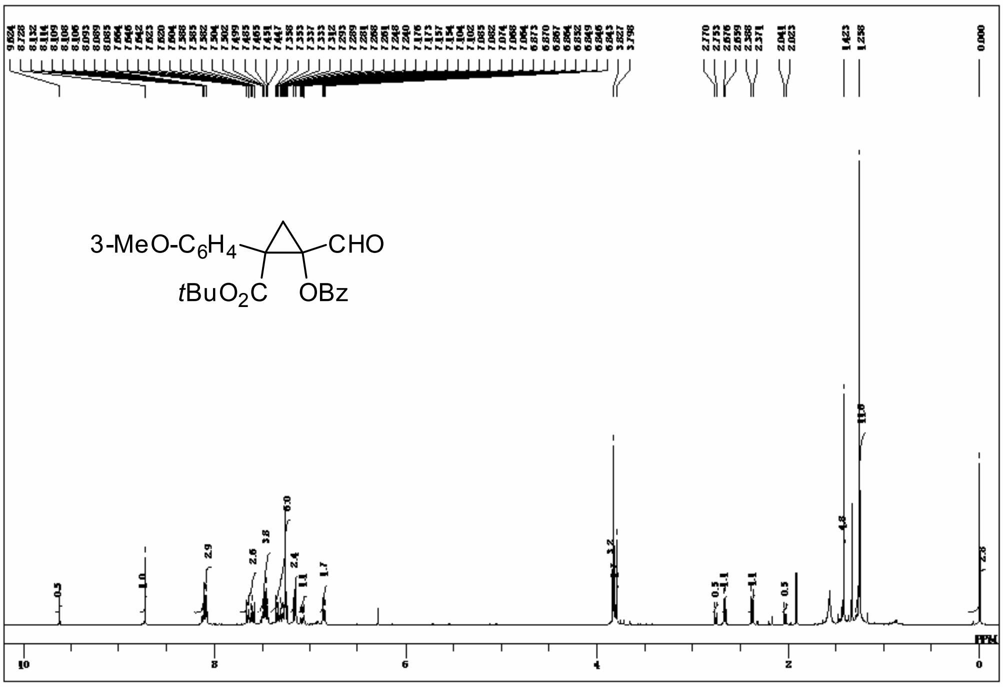

PPM
200
175
150
125
100
75
50
25
0

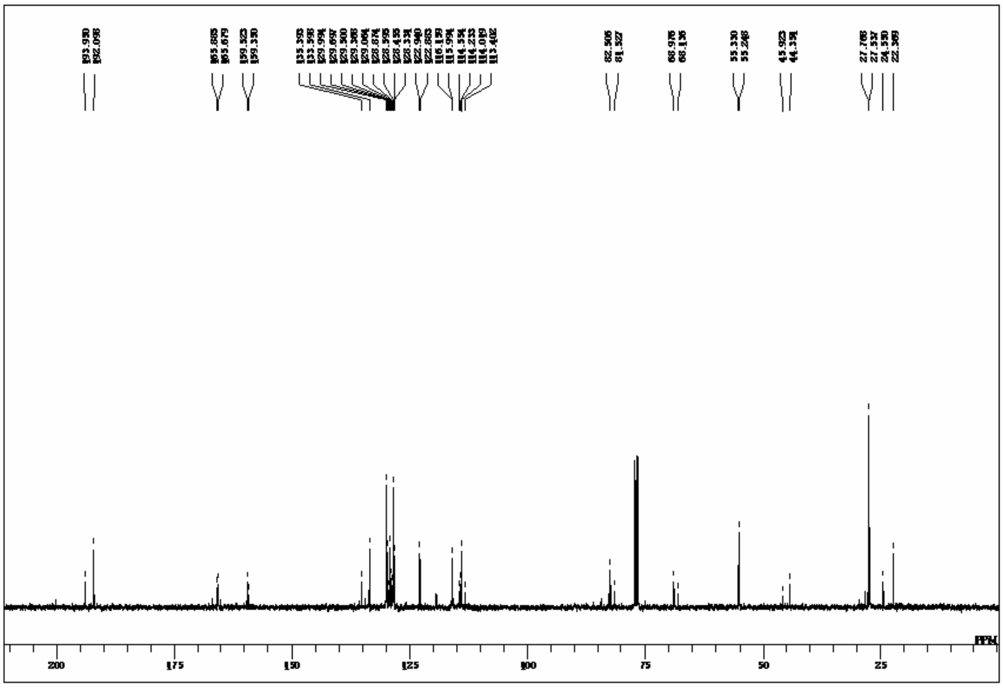

4-Tolyl
CHO
tBuO2C
OBz
PPM
10
8
6
4
2
0

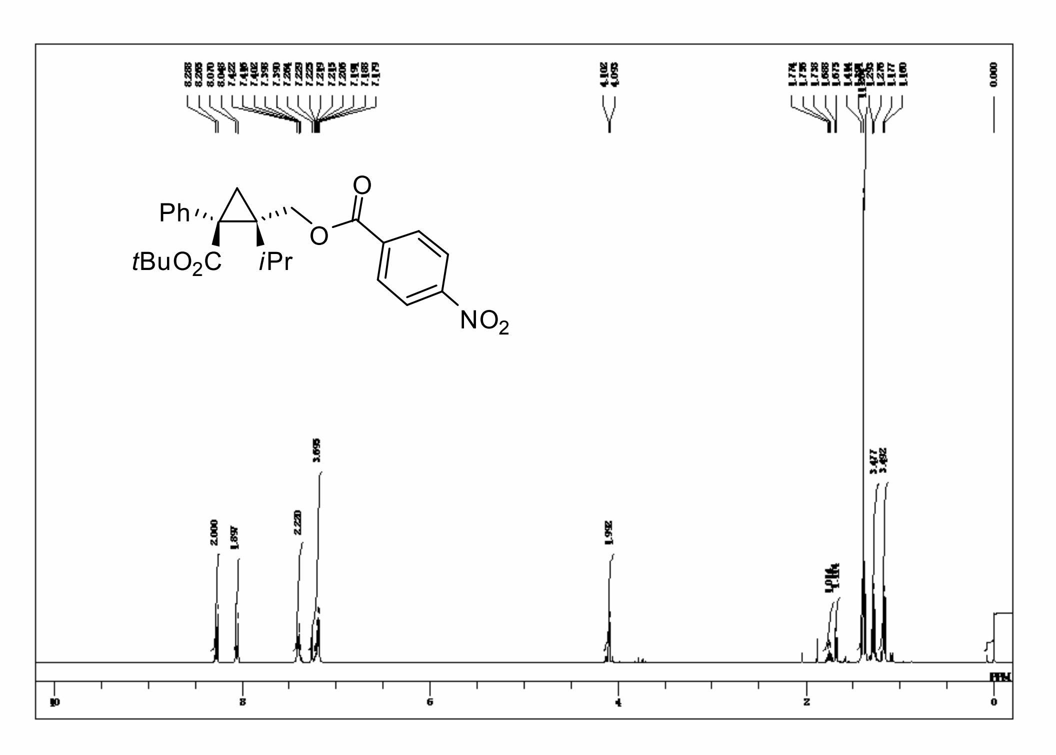

PPM
200
175
150
125
100
75
50
25
0

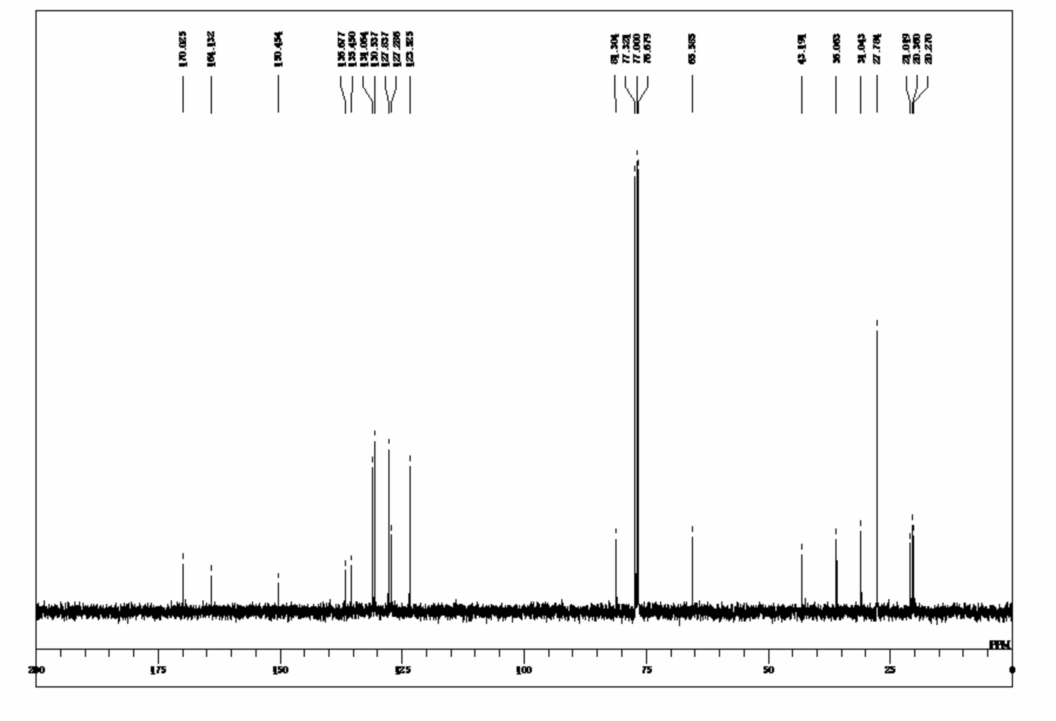

4-Cl-C6H4
CHO
tBuO2C
OBz
9.613
8.847
8.108
7.330
2.817
2.799
2.702
2.683
2.346
2.329
2.009
1.991
1.412
0.000
0.754
1.000
2.149
2.432
6.787
5.164
0.728
1.078
1.150
0.808
2.027
PPM
10
8
6
4
2
0


200
175
150
125
100
75
50
25


9.624 8.728 8.132 8.114 8.109 8.108 8.106 8.093 8.089 8.085 7.664 7.646 7.642 7.623 7.620 7.604 7.588 7.585 7.582 7.504 7.502 7.499 7.485 7.465 7.451 7.447 7.358 7.353 7.337 7.333 7.312 7.293 7.289 7.281 7.268 7.261 7.248 7.240 7.176 7.173 7.157 7.154 7.104 7.102 7.085 7.082 7.074 7.068 7.064 6.873 6.870 6.867 6.864 6.852 6.849 6.846 6.843 3.827 3.798
2.770 2.753 2.676 2.659 2.388 2.371 2.041 2.023 1.423 1.238 0.000
3-MeO-C6H4
CHO
tBuO2C
OBz
0.5
1.0
2.9
2.6
3.8
6.0
2.4
1.1
1.7
3.2
0.5
1.1
1.1
0.5
4.8
11.6
2.8
10
8
6
4
2
0
PPM


193.950 192.098 165.885 165.679 159.523 159.330 135.395 133.558 129.994 129.697 129.500 129.368 129.004 128.874 128.595 128.455 128.331 122.940 122.885 116.159 115.994 114.554 114.233 114.019 113.402 82.506 81.527 68.976 68.136 55.330 55.248 45.923 44.391 27.768 27.537 24.530 22.369
200
175
150
125
100
75
50
25
PPM


8.288
8.265
8.070
8.046
7.422
7.418
7.402
7.398
7.390
7.234
7.233
7.225
7.219
7.215
7.206
7.191
7.185
7.179
4.102
4.095
1.774
1.756
1.738
1.688
1.675
1.414
1.295
1.276
1.177
1.160
0.000
Ph
tBuO2C
iPr
O
O
NO2
2.000
1.897
2.220
3.695
1.992
1.014
1.104
3.477
3.492
10
8
6
4
2
0
PPM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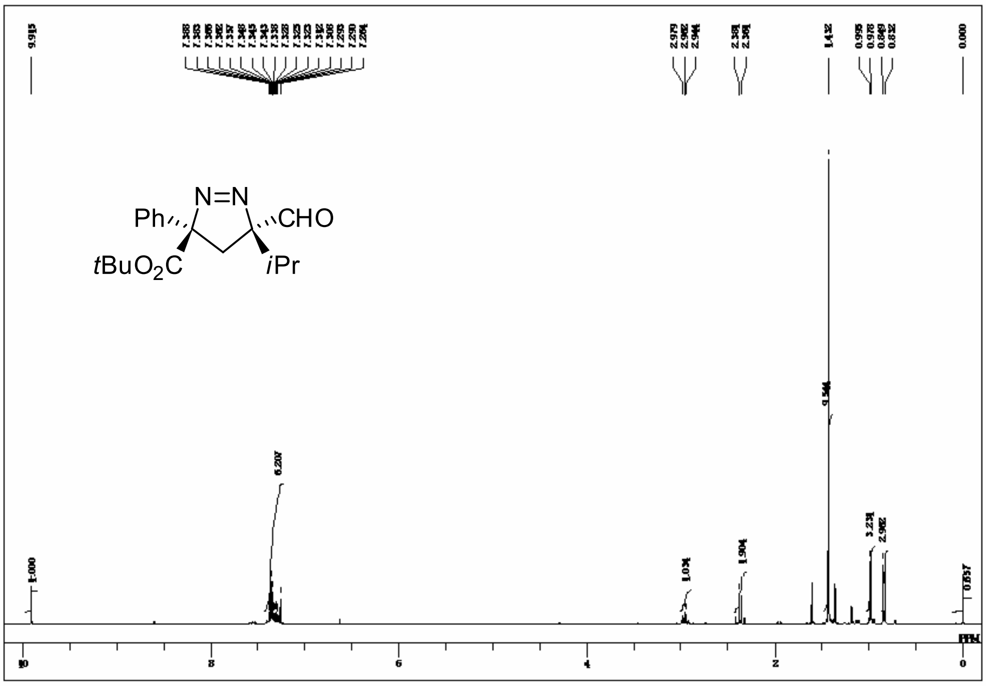
164.132
150.454
136.677
135.450
131.064
130.537
127.837
127.286
123.325
81.304
77.321
77.000
76.679
65.583
43.191
36.063
31.043
27.784
21.019
20.380
20.270
200
175
150
125
100
75
50
25
0
PPM


N=N
Ph
CHO
tBuO2C
iPr
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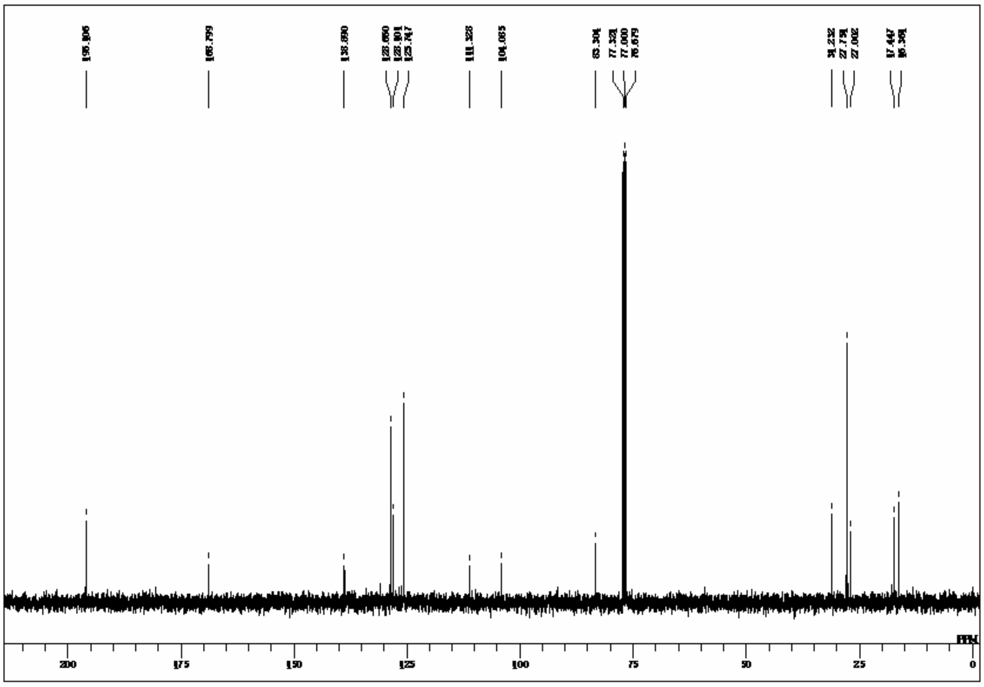
2.962
2.944
1.432
0.995
0.978
0.849
0.832
0.000
1.000
6.207
1.034
1.904
9.566
3.231
2.982
0.557
10
8
6
4
2
0
PPM


138.890
125.747
111.328
104.085
83.304
77.321
77.000
76.679
27.751
27.002
17.447
200
175
150
125
100
75
50
25
0
PPM