Supporting Information

Stereoselective Construction of Seven-Membered Rings with an All-Carbon Quaternary Center by Direct Tiffeneau-Demjanov-type Ring Expansion

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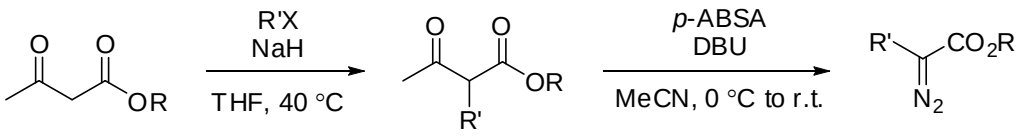
General Information. Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from tetramethylsilane as an internal standard, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = double-doublet, ddd= double-double-doublet, dt=double-triplet, 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. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. 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).

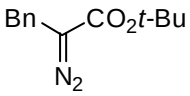
In experiments requiring dry solvent, dichloromethane was purchased from Kanto Chemical Co. Inc. as “Dehydrated” and further purified by passing through neutral alumina under nitrogen atmosphere. Simple ketones were purchased and used after distillation or column chromatography on silica gel.

·Preparation of α-alkyldiazoacetates (1).[1]

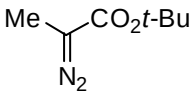


To a stirred suspension of NaH (60 % dispersion in mineral oil, 1.04 g, 26 mmol) in THF (20 mL), acetoacetate (20 mmol) was added dropwise at room temperature under Ar atmosphere. After the formation of a clear solution, the corresponding alkyl halide (22 mmol) was added dropwise, and the mixture was stirred at 40 °C for 10 h. The resulting mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography to afford the corresponding α-alkyl-β-ketoesters.

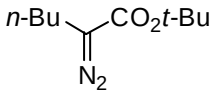
To a stirred solution of thus-formed α-alkyl-β-ketoester (5 mmol) and *p*-acetamidobenzenesulfonyl azide (*p*-ABSA) (1.92 g, 7.5 mmol) in MeCN (10 mL) was added DBU (2.2 ml, 15 mmol) at 0 °C. The reaction mixture was then allowed to warm to room temperature. After stirring for 12 h, the resulting mixture 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 to give the corresponding α-alkyldiazoacetates.



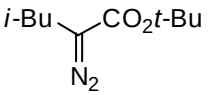
***tert*-Butyl 2-diazo-3-phenylpropanoate.**
Previously reported in the literature.[2a]



***tert*-Butyl 2-diazopropanoate.**
Previously reported in the literature.[2b]

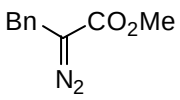


***tert*-Butyl 2-diazohexanoate.**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.25 (2H, t, *J* = 7.2 Hz, N_2=CC**H**$_2$), 1.30-1.54 (4H, m, CH_2C**H**$_2$C**H**$_2CH_3$), 1.47 (9H, s, C(C**H**$_3$)$_3$), 0.93 (3H, t, *J* = 7.2 Hz, CH_2C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 80.8, 29.6, 28.3, 22.6, 21.8, 13.6 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2961, 2932, 2075, 1686, 1368, 1339, 1308, 1175, 1128, 739 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{10}H_{18}N_2O_2$: *m/z* 221.1260 ([M + Na]$^+$), found: *m/z* 221.1245 ([M + Na]$^+$).

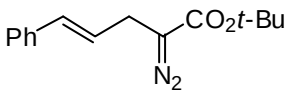


***tert*-Butyl 2-diazo-4-methylpentanoate.**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (2H, d, *J* = 7.2 Hz, N_2=CC**H**$_2$), 1.80 (1H, m, C**H**(CH)$_3$), 1.48 (9H, s, C(C**H**$_3$)$_3$), 0.95 (6H, d, *J* = 6.8 Hz,

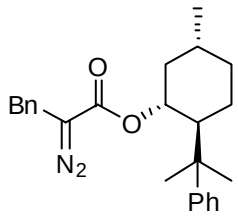
$CH_2C\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 80.8, 32.2, 28.3, 27.9, 21.8 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2961, 2077, 1686, 1456, 1368, 1352, 1325, 1130, 1067, 739 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{10}H_{18}N_2O_2$: *m/z* 221.1260 ($[M + Na]^+$), found: *m/z* 221.1261 ($[M + Na]^+$).



Methyl 2-diazo-3-phenylpropanoate.
Previously reported in the literature.[2a]

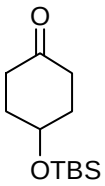


***tert*-Butyl (*E*)-2-diazo-5-phenylpent-4-enoate.**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.42 (5H, m, Ar**H**), 6.49 (1H, d, *J* = 15.6 Hz, PhC**H**=CH), 6.19 (1H, dt, *J* = 15.6, 6.8 Hz, PhCH=C**H**), 3.16 (2H, dd, *J* = 6.8, 1.6 Hz, N_2=CC$\mathbf{H}_2$), 1.49 (9H, s, C($C\mathbf{H}_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 136.8, 132.5, 128.5, 127.5, 126.3, 124.3, 81.3, 28.4, 26.8 (The resonance of the carbon that bears the diazo group was not detected); IR (neat) 2978, 2077, 1684, 1368, 1337, 1157, 1111, 964, 739, 692 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{15}H_{18}N_2O_2$: *m/z* 281.1260 ($[M + Na]^+$), found: *m/z* 281.1255 ($[M + Na]^+$).

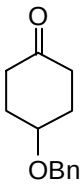


(1*R*,2*S*,5*R*)-8-Phenylmentyl 2-diazo-3-phenylpropanoate (10).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00-7.40 (9H, m, Ar**H**), 4.96 (1H, app dt, *J* = 10.8, 4.8 Hz, OC**H**), 3.47 (2H, br, PhC$\mathbf{H}_2$), 2.00 (1H, m, Cy), 1.87 (1H, m, Cy), 1.71 (1H, m, Cy), 1.64 (1H, m, Cy), 1.47 (1H, m, Cy), 0.75-1.40 (3H, m, Cy), 1.32 (3H, s, C(Ph)($C\mathbf{H}_3$)(CH_3)), 1.22 (3H, s, C(Ph)(CH_3)($C\mathbf{H}_3$)), 0.86 (3H, d, *J* = 6.8 Hz, CHC$\mathbf{H}_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 151.4, 137.4, 128.6, 128.3, 127.8, 126.9 125.2, 125.0, 77.2, 74.5, 50.8, 42.2, 39.6, 34.5, 31.3, 29.2, 28.1, 26.6, 24.6, 21.7; IR (neat) 2955, 2920, 2081, 1678, 1360, 1296, 1173, 1103, 980, 698 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{30}N_2O_2$: *m/z* 413.2199 ($[M + Na]^+$), found: *m/z* 413.2209 ($[M + Na]^+$); $[\alpha]_D^{28} = -7.1$ (*c* = 1.0, $CHCl_3$).

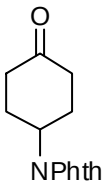
·Preparation of functionalized cyclohexanones.



4-(*tert*-Butyldimethylsilyloxy)cyclohexanone (6 (R^3 = H, R^4 = TBS)).
Prepared according to the literature.[3a]

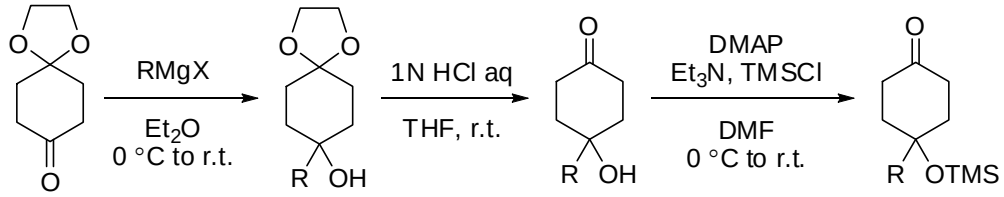


4-(Benzyloxy)cyclohexanone (6 (R^3 = H, R^4 = Bn)).
Prepared according to the literature.[3b]

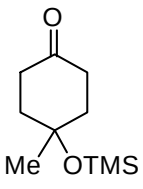


4-(*N*-Phthaloylamino)cyclohexanone (4 (R^3 = Nphth)).
Prepared according to the literature.[3c]

4-Alkyl-4-(trimethylsilyloxy)cyclohexanone.

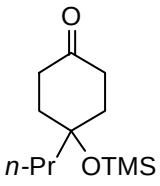


(Step1 & 2)
Prepared according to the literature.[3d]
(Step 3)[3e]
A solution of the cyclohexanone (5 mmol), DMAP (61 mg, 0.5 mmol), and Et_3N (1.0 mL, 7.5 mmol) in DMF (10 mL) was cooled to 0 °C and TMSCl (767 μL, 6.0 mmol) was added dropwise. The resulting suspension was stirred for 2 h at room temperature and then quenched with saturated aqueous NH_4Cl solution and extracted with Et_2O. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography to afford the corresponding silyl-protected cyclohexanone.

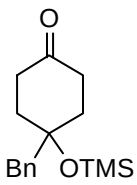


4-Methyl-4-(trimethylsilyloxy)cyclohexanone (6 (R^3 = Me, R^4 = TMS)).
^{1}H NMR (400 MHz, $CDCl_3$) 2.68 (2H, dt, *J* = 14.4, 5.6 Hz, *c*-Hex), 2.18 (2H, m, *c*-Hex), 1.98 (2H, m, *c*-Hex), 1.73 (2H, dt, J = 14.0, 4.8 Hz, *c*-Hex), 1.37 (3H, s, C**H**$_3$), 0.17 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.5, 71.4, 39.8, 37.3, 29.2, 2.3; IR (neat) 2959, 1717, 1250, 1132, 1051, 1005, 864,

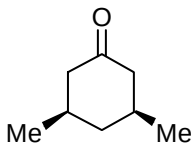
839, 804, 752 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{10}H_{20}O_2Si$: *m/z* 223.1125 ([M + Na]$^+$), found: *m/z* 223.1121 ([M + Na]$^+$).



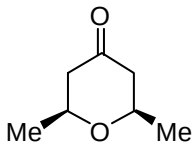
4-Propyl-4-(trimethylsilyloxy)cyclohexanone (6 (R^3 =*n*-Pr, R^4 = TMS)). ^{1}H NMR (400 MHz, $CDCl_3$) 2.67 (2H, dt, *J* = 14.0, 6.0 Hz, *c*-Hex), 2.20 (2H, m, R), 1.94 (2H, m, R), 1.74 (2H, dt, J = 13.2, 4.4 Hz, *c*-Hex), 1.58 (2H, m, R), 1.39 (2H, m, R), 0.94 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$), 0.16 (9H, s, $OSi(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.6, 74.1, 44.4, 37.33, 37.26, 17.1, 14.5, 2.4; IR (neat) 2959, 1717, 1250, 1138, 1123, 1049, 1009, 839, 808, 752 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{12}H_{24}O_2Si$: *m/z* 251.1438 ([M + Na]$^+$), found: *m/z* 251.1435 ([M + Na]$^+$).



4-Benzyl-4-(trimethylsilyloxy)cyclohexanone (6 (R^3 = Bn, R^4 = TMS)). ^{1}H NMR (400 MHz, $CDCl_3$) 7.15-7.31 (5H, m, Ar**H**), 3.00 (2H, s, $PhC\mathbf{H}_2$), 2.64 (2H, dt, *J* = 14.0, 6.4 Hz, *c*-Hex), 2.19 (2H, m, *c*-Hex), 1.94 (2H, m, *c*-Hex), 1.77 (2H, dt, *J* = 13.6, 4.4 Hz, *c*-Hex), 0.22 (9H, s, $OSi(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.8, 137.1, 130.4, 128.1, 126.6, 74.7, 49.0, 37.2, 36.5, 2.6; IR (neat) 2953, 1713, 1250, 1115, 1051, 1005, 881, 835, 752, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{24}O_2Si$: *m/z* 299.1438 ([M + Na]$^+$), found: *m/z* 299.1438 ([M + Na]$^+$).

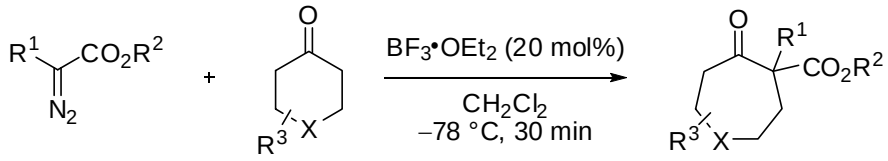


***cis*-3,5-Dimethylcyclohexanone (8 (X = CH_2)).** Previously reported, and prepared according to the procedure therein.[3f]

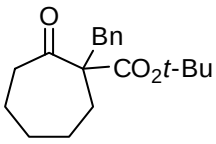


***cis*-2,6-Dimethyltetrahydropyran-4-one (8 (X = O)).** Previously reported, and prepared according to the procedure therein.[3g]

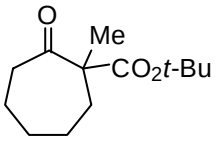
·General procedure for the diastereoselective ring expansion of functionalized cyclohexanones with α-alkyldiazoacetates.



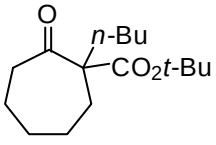
To a stirred solution of alkyldiazoacetate (0.20 mmol) and cyclohexanone derivative (0.21 mmol) in dichloromethane (1.0 mL) was added $BF_3{\cdot}OEt_2$ (5.1 μL, 0.040 mmol) at –78 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 30 min. The mixture was quenched with 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 = 80:1~60:1) to give the corresponding cycloheptanone.



***tert*-Butyl 1-benzyl-2-oxocycloheptanecarboxylate (3a).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.27 (5H, m, Ar**H**), 3.29 (1H, d, *J* = 14.0 Hz, PhC**H**H), 2.98 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.62 (1H, ddd, *J* = 12.8, 8.4, 3.2 Hz, *c*-Hep), 2.30 (1H, ddd, *J* = 12.8, 10.0, 3.6 Hz, *c*-Hep), 2.00 (1H, ddd, *J* = 14.4, 8.8, 0.8 Hz, *c*-Hep), 1.18-1.82 (7H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 171.0, 137.1, 130.7, 128.0, 126.6, 81.9, 64.6, 42.3, 40.6, 31.9, 29.9, 27.9, 25.4, 24.4; IR (neat) 2932, 1726, 1709, 1454, 1368, 1254, 1240, 1142, 847, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{19}H_{26}O_3$: *m/z* 325.1774 ([M + Na]$^+$), found: *m/z* 325.1767 ([M + Na]$^+$).

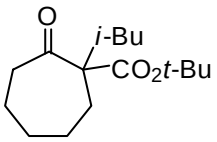


***tert*-Butyl 1-methyl-2-oxocycloheptanecarboxylate (3b).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.74 (1H, ddd, *J* = 12.8, 10.8, 3.2 Hz, *c*-Hep), 2.47 (1H, ddd, *J* = 12.8, 8.8, 2.8 Hz, *c*-Hep), 2.10 (1H, ddd, *J* = 14.4, 9.2, 0.8 Hz, *c*-Hep), 1.22-1.89 (7H, m, *c*-Hep), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.30 (3H, s, C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 172.8, 81.5, 59.3, 42.1, 35.5, 30.1, 27.8, 25.7, 24.7, 21.5; IR (neat) 2978, 2931, 1734, 1705, 1456, 1369, 1242, 1146, 1105, 849 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{13}H_{22}O_3$: *m/z* 249.1461 ([M + Na]$^+$), found: *m/z* 249.1452 ([M + Na]$^+$).

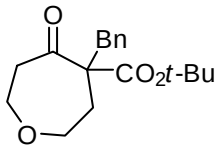


***tert*-Butyl 1-butyl-2-oxocycloheptanecarboxylate (3c).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (1H, ddd, *J* = 12.8, 9.2, 3.6 Hz, *c*-Hep), 2.47 (1H, ddd, *J* = 12.8, 8.8, 2.8 Hz, *c*-Hep), 2.08 (1H, m, *c*-Hep), 1.92 (1H, m, *c*-Hep), 1.15-1.82 (12H, m, *c*-Hep and C_3**H**$_6$$CH_3$), 1.45 (9H, s, C(C**H**$_3$)$_3$), 0.90 (3H, t, *J* = 6.8 Hz, C_3H_6C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.8, 81.4, 63.3, 42.0, 35.0, 32.7, 29.9, 27.9, 26.6, 25.5, 24.8, 23.2, 13.9; IR (neat) 2955, 2932, 2862, 1709, 1456, 1368, 1244, 1217, 1142, 849 cm^{-1}; HRMS (ESI) exact

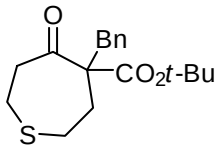
mass calcd. for $C_{16}H_{28}O_3$: *m/z* 291.1931 ($[M + Na]^+$), found: *m/z* 291.1920 ($[M + Na]^+$).



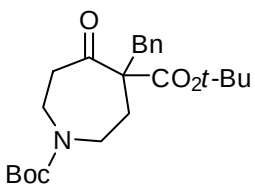
***tert*-Butyl 1-isobutyl-2-oxocycloheptanecarboxylate (3d).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.63 (1H, ddd, *J* = 12.8, 10.0, 4.0 Hz, *c*-Hep), 2.45 (1H, ddd, *J* = 11.6, 8.0, 3.6 Hz, *c*-Hep), 2.08 (1H, m, *c*-Hep), 2.14 (1H, m, *c*-Hep), 1.91 (1H, app dd, *J* = 14.4, 6.8 Hz, *c*-Hep), 1.20-1.80 (11H, m, *c*-Hep and $C_3\mathbf{H}_5(CH_3)_2$), 1.46 (9H, s, $C(C\mathbf{H}_3)_3$), 0.91 (3H, d, *J* = 6.4 Hz, $CH(C\mathbf{H}_3)(CH_3)$), 0.88 (3H, d, *J* = 6.4 Hz, $CH(CH_3)(C\mathbf{H}_3)$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.7, 172.0, 81.5, 63.4, 43.2, 41.5, 32.7, 29.8, 27.9, 25.7, 24.71, 24.66, 24.64, 23.9; IR (neat) 2955, 2932, 2868, 1707, 1456, 1368, 1231, 1140, 939, 847 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{16}H_{28}O_3$: *m/z* 291.1931 ($[M + Na]^+$), found: *m/z* 291.1919 ($[M + Na]^+$).



***tert*-Butyl 4-benzyl-5-oxooxepane-4-carboxylate (3e).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.30 (5H, m, Ar**H**), 3.62-3.84 (4H, m, $C\mathbf{H}_2OC\mathbf{H}_2$), 3.24 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.10 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.83 (1H, ddd, *J* = 14.8, 6.8, 3.6 Hz, $OCH_2C\mathbf{H}_2$), 2.60 (1H, ddd, *J* = 12.8, 10.0, 3.6 Hz, $OCH_2C\mathbf{H}_2$), 2.07 (1H, ddd, *J* = 15.6, 5.2, 2.0 Hz, $OCH_2C\mathbf{H}_2$), 1.84 (1H, ddd, *J* = 15.2, 10.0, 3.2 Hz, $OCH_2C\mathbf{H}_2$), 1.43 (9H, s, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.4, 170.5, 136.3, 130.7, 128.1, 126.8, 82.6, 68.1, 65.7, 63.8, 45.8, 41.4, 34.4, 27.9; IR (neat) 2974, 2872, 1705, 1358, 1254, 1146, 1105, 843, 739, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{24}O_4$: *m/z* 327.1567 ($[M + Na]^+$), found: *m/z* 322.1570 ($[M + Na]^+$).

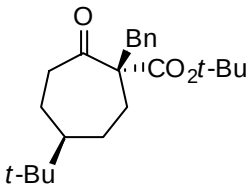


***tert*-Butyl 4-benzyl-5-oxothiepane-4-carboxylate (3f).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.30 (3H, m, Ar**H**), 7.10-7.16 (2H, m, Ar**H**), 3.36 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.11 (1H, ddd, *J* = 13.2, 7.6, 3.6 Hz, $SCH_2C\mathbf{H}_2$), 2.97 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.64-2.94 (4H, m, $C\mathbf{H}_2SC\mathbf{H}_2$), 2.53 (1H, m, $SCH_2C\mathbf{H}_2$), 2.41 (1H, ddd, *J* = 14.8, 6.4, 2.0 Hz, $SCH_2C\mathbf{H}_2$), 1.86 (1H, ddd, *J* = 14.8, 11.2, 2.8 Hz, $SCH_2C\mathbf{H}_2$), 1.41 (9H, s, $C(C\mathbf{H}_3)_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.9, 170.3, 136.4, 130.6, 128.0, 126.8, 82.6, 64.5, 44.3, 41.4, 36.4, 28.3, 27.9, 26.0; IR (neat) 2974, 2930, 1707, 1369, 1271, 1260, 1148, 1123, 843, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{18}H_{24}O_3S$: *m/z* 343.1338 ($[M + Na]^+$), found: *m/z* 343.1346 ($[M + Na]^+$).

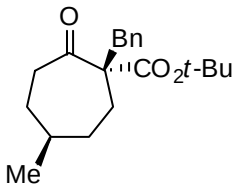


Di-*tert*-butyl 4-benzyl-5-oxoazepane-1,4-dicarboxylate (3g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17-7.30 (3H, m, Ar**H**), 7.10-7.16 (2H, m, Ar**H**), 3.80 (1H, br, NC**H**H), 3.29 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.15 (1H, br, NC**H**H), 2.97 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.64-2.88 (2H, m, $NC\mathbf{H}_2$), 2.07 (1H, ddd, *J* = 15.2, 4.8, 2.4 Hz, $NCH_2C\mathbf{H}H$), 1.20-1.64 (3H, m, $NCH_2C\mathbf{H}_2$), 1.44 (9H, s, $C(C\mathbf{H}_3)_3$), 1.41 (9H, s, $C(C\mathbf{H}_3)_3$);

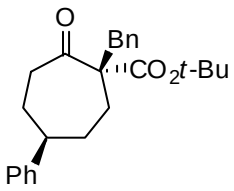
^{13}C NMR (100 MHz, $CDCl_3$) δ 206.1, 170.3, 154.6, 136.4, 130.6, 128.0, 126.8, 82.6, 80.0, 65.8, 64.0, 42.3, 41.7, 34.2, 28.4, 27.9, 15.2; IR (neat) 2974, 2932, 1695, 1412, 1368, 1242, 1150, 1115, 1086, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{33}NO_5$: *m/z* 426.2251 ([M + Na]$^+$), found: *m/z* 426.2249 ([M + Na]$^+$).



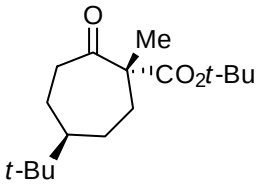
***tert*-Butyl *trans*-1-benzyl-5-*tert*-butyl-2-oxocycloheptanecarboxylate (5a).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.28 (5H, m, Ar**H**), 3.42 (1H, d, *J* = 14.0 Hz, PhC**H**H), 2.81 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.64 (1H, ddd, *J* = 12.8, 11.2, 2.8 Hz, *c*-Hep), 2.42 (1H, ddd, *J* = 10.8, 6.0, 0.8 Hz, *c*-Hep), 1.91-2.12 (3H, m, *c*-Hep), 1.83 (1H, m, *c*-Hep), 1.17-1.45 (2H, m, *c*-Hep), 1.39 (9H, s, C(C**H**$_3$)$_3$), 0.83 (9H, s, C(C**H**$_3$)$_3$), 0.66 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 170.5, 137.5, 130.5, 128.0, 126.5, 82.0, 65.0, 52.5, 39.9, 38.1, 33.2, 29.4, 28.5, 27.8, 27.6, 24.4; IR (neat) 2959, 2866, 1711, 1454, 1368, 1246, 1150, 84, 733, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{34}O_3$: *m/z* 381.2400 ([M + Na]$^+$), found: *m/z* 381.2408 ([M + Na]$^+$).



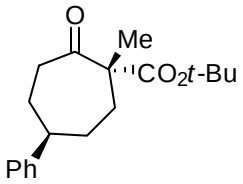
***tert*-Butyl *trans*-1-benzyl-5-methyl-2-oxocycloheptanecarboxylate (5b).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11-7.30 (5H, m, Ar**H**), 3.43 (1H, d, *J* = 14.4 Hz, PhC**H**H), 2.83 (1H, d, *J* = 14.4 Hz, PhCH**H**), 2.68 (1H, ddd, *J* = 12.8, 11.6, 2.8 Hz, *c*-Hep), 2.37 (1H, ddd, *J* = 11.2, 6.8, 2.4 Hz, *c*-Hep), 1.94-2.09 (2H, m, *c*-Hep), 1.89 (1H, m, *c*-Hep), 1.13-1.74 (3H, m, *c*-Hep), 1.39 (9H, s, C(C**H**$_3$)$_3$), 0.88 (3H, d, *J* = 6.4 Hz, C**H**$_3$), 0.87 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 170.4, 137.4, 130.5, 128.0, 126.5, 81.9, 65.1, 39.9, 38.3, 36.7, 35.0, 31.8, 29.0, 27.8, 22.5; IR (neat) 2953, 2928, 1454, 1368, 1279, 1246, 1142, 845, 737, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{28}O_3$: *m/z* 339.1931 ([M + Na]$^+$), found: *m/z* 339.1923 ([M + Na]$^+$).



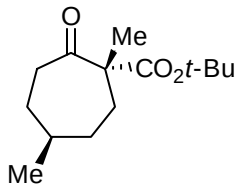
***tert*-Butyl *trans*-1-benzyl-2-oxo-5-phenylcycloheptanecarboxylate (5c).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07-7.31 (10H, m, Ar**H**), 3.48 (1H, d, *J* = 14.4 Hz, PhC**H**H), 2.92 (1H, d, *J* = 14.4 Hz, PhCH**H**), 2.83 (1H, ddd, *J* = 13.6, 11.6, 2.8 Hz, *c*-Hep), 2.72 (1H, app ddt, *J* = 12.0, 3.2, 2.8 Hz, *c*-Hep), 2.51 (1H, ddd, *J* = 11.2, 6.4, 2.4 Hz, *c*-Hep), 2.00-2.26 (3H, m, *c*-Hep), 1.86 (1H, m, *c*-Hep), 1.68 (1H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$), 1.30 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.4, 170.3, 146.5, 137.4, 130.6, 128.5, 128.1, 126.7, 126.6, 126.3, 82.2, 65.1, 49.0, 40.2, 38.1, 35.1, 31.1, 29.6, 27.9; IR (neat) 2976, 2930, 1707, 1452, 1368, 1252, 1148, 758, 739, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{30}O_3$: *m/z* 401.2087 ([M + Na]$^+$), found: *m/z* 401.2098 ([M + Na]$^+$).



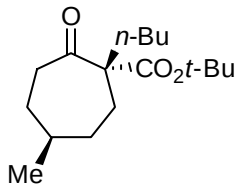
***tert*-Butyl *trans*-5-*tert*-butyl-1-methyl-2-oxocycloheptanecarboxylate (5d).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.77 (1H, m, *c*-Hep), 2.46 (1H, m, *c*-Hep), 2.14 (1H, m, *c*-Hep), 1.84-2.06 (3H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$), 1.29 (3H, s, C**H**$_3$), 1.23 (2H, m, *c*-Hep), 0.85 (9H, s, C(C**H**$_3$)$_3$), 0.84 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 172.7, 81.6, 59.4, 52.5, 40.7, 34.8, 33.3, 28.1, 27.8, 27.7, 25.0, 19.9; IR (neat) 2959, 2938, 2868, 1732, 1692, 1368, 1258, 1234, 1152, 1109 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{30}O_3$: *m/z* 305.2087 ([M + Na]$^+$), found: *m/z* 305.2082 ([M + Na]$^+$).



***tert*-Butyl *trans*-1-methyl-2-oxo-5-phenylcycloheptanecarboxylate (5e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23-7.33 (2H, m, Ar**H**), 7.11-7.22 (3H, m, Ar**H**), 2.96 (1H, ddd, *J* = 13.6, 11.6, 2.4 Hz, *c*-Hep), 2.74 (1H, m, *c*-Hep), 2.54 (1H, ddd, *J* = 11.2, 6.8, 2.0 Hz, *c*-Hep), 2.35 (1H, m, *c*-Hep), 1.92-2.12 (3H, m, *c*-Hep), 1.63 (1H, m, *c*-Hep), 1.46 (1H, m, *c*-Hep), 1.45 (9H, s, C(C**H**$_3$)$_3$), 1.36 (3H, s, C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 172.5, 146.6, 128.5, 126.6, 126.4, 81.8, 59.6, 49.1, 41.0, 34.8, 34.7, 31.7, 27.8, 19.9; IR (neat) 2978, 2936, 2866, 1736, 1707, 1369, 1254, 1152, 1107, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{19}H_{26}O_3$: *m/z* 325.1774 ([M + Na]$^+$), found: *m/z* 325.1765 ([M + Na]$^+$).

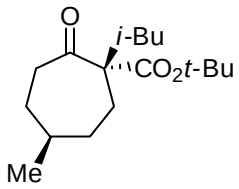


***tert*-Butyl *trans*-1,5-dimethyl-2-oxocycloheptanecarboxylate (5f).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.81 (1H, ddd, *J* = 13.2, 12.0, 2.4 Hz, *c*-Hep), 2.42 (1H, ddd, *J* = 11.6, 7.2, 2.0 Hz, *c*-Hep), 2.19 (1H, dd, *J* = 15.2, 11.6 Hz, *c*-Hep), 1.60-1.95 (4H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$), 1.29 (3H, s, C**H**$_3$), 1.14 (1H, m, *c*-Hep), 0.98 (1H, m, *c*-Hep), 0.91 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.6, 172.7, 81.6, 59.6, 40.8, 36.9, 34.8, 34.2, 32.4, 27.8, 22.7, 20.0; IR (neat) 2951, 2932, 1736, 1711, 1458, 1369, 1281, 1248, 1148, 1107 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{14}H_{24}O_3$: *m/z* 263.1618 ([M + Na]$^+$), found: *m/z* 263.1609 ([M + Na]$^+$).

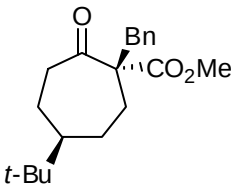


***tert*-Butyl *trans*-1-butyl-5-methyl-2-oxocycloheptanecarboxylate (5g).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (1H, app dt, *J* = 12.0, 2.8 Hz, *c*-Hep), 2.37 (1H, ddd, *J* = 12.0, 7.2, 2.8 Hz, *c*-Hep), 1.80-2.20 (4H, m, *c*-Hep), 1.56-1.76 (2H, m, *c*-Hep), 1.13-1.50 (6H, m, *c*-Hep and/or *n*-Bu), 1.42 (9H, s, C(C**H**$_3$)$_3$), 0.90 (3H, t, *J* = 6.4 Hz, C_3H_6C**H**$_3$), 0.90 (1H, m, *c*-Hep) 0.89 (3H, d, *J* = 7.6 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 171.6, 81.5, 63.6, 40.2, 36.7, 34.8, 33.1, 32.2, 30.2, 27.9, 26.7, 23.2, 22.5, 13.9; IR (neat) 2955, 2928, 2872, 1711,

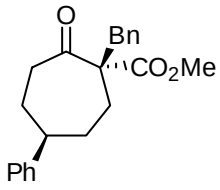
1456, 1368, 1269, 1244, 1215, 1142 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{30}O_3$: *m/z* 305.2087 ($[M + Na]^+$), found: *m/z* 305.2090 ($[M + Na]^+$).



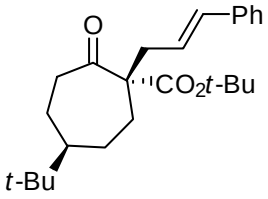
tert-Butyl _trans_-1-isobutyl-5-methyl-2-oxocycloheptanecarboxylate (5h).
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.66 (1H, ddd, *J* = 13.2, 11.6, 2.8 Hz, *c*-Hep), 2.34 (1H, ddd, *J* = 11.2, 6.8, 2.4 Hz, *c*-Hep), 2.16 (1H, dd, *J* = 15.2, 10.8 Hz, *c*-Hep), 1.95-2.07 (2H, m, *c*-Hep), 1.87 (1H, m, *c*-Hep), 1.56-1.77 (3H, m, *c*-Hep), 1.12-1.49 (3H, m, *c*-Hep), 1.43 (9H, s, C(C**H**$_3$)$_3$), 0.80-1.00 (2H, m, *c*-Hep), 0.92 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 0.90 (6H, app d, *J* = 6.4 Hz, CH(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 171.7, 81.7, 63.7, 41.1, 39.8, 36.7, 35.0, 31.9, 29.9, 27.8, 24.8, 24.5, 23.8, 22.5; IR (neat) 2955, 2928, 2870, 1709, 1456, 1368, 1234, 1140, 1126, 845 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{30}O_3$: *m/z* 305.2087 ($[M + Na]^+$), found: *m/z* 305.2091 ($[M + Na]^+$).



Methyl _trans_-1-benzyl-5-_tert_-butyl-2-oxocycloheptanecarboxylate (5i).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18-7.30 (3H, m, Ar**H**), 7.02-7.12 (2H, m, Ar**H**), 3.67 (3H, s, OC**H**$_3$), 3.51 (1H, d, *J* = 14.2 Hz, PhC**H**H), 2.80 (1H, d, *J* = 14.2 Hz, PhCH**H**), 2.64 (1H, ddd, *J* = 12.4, 11.2, 2.4 Hz, *c*-Hep), 2.43 (1H, ddd, *J* = 10.8, 6.0, 1.6 Hz, *c*-Hep), 1.94-2.16 (3H, m, *c*-Hep), 1.87 (1H, m, *c*-Hep), 1.16-1.37 (2H, m, *c*-Hep), 0.84 (9H, s, C(C**H**$_3$)$_3$), 0.72 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 171.6, 137.1, 130.2, 128.2, 126.7, 64.6, 52.4, 40.1, 38.2, 33.2, 28.83, 28.80, 28.6, 27.6, 24.3; IR (neat) 2955, 1732, 1711, 1454, 1441, 1240, 1196, 1175, 737, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{28}O_3$: *m/z* 339.1931 ($[M + Na]^+$), found: *m/z* 339.1921 ($[M + Na]^+$).

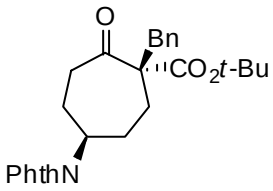


Methyl _trans_-1-benzyl-2-oxo-5-phenylcycloheptanecarboxylate (5j).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15-7.34 (6H, m, Ar**H**), 7.03-7.15 (4H, m, Ar**H**), 3.71 (3H, s, OC**H**$_3$), 3.57 (1H, d, *J* = 14.4 Hz, PhC**H**H), 2.87 (1H, d, *J* = 14.4 Hz, PhCH**H**), 2.83 (1H, ddd, *J* = 13.6, 11.2, 2.4 Hz, *c*-Hep), 2.73 (1H, app ddt, *J* = 12.4, 4.8, 2.4 Hz, *c*-Hep), 2.52 (1H, ddd, *J* = 11.2, 6.8, 2.4 Hz, *c*-Hep), 2.04-2.31 (3H, m, *c*-Hep), 1.92 (1H, m, *c*-Hep), 1.70 (1H, m, *c*-Hep), 1.38 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.2, 171.4, 146.3, 137.0, 130.2, 128.5, 128.3, 126.8, 126.6, 126.4, 64.8, 52.5, 48.9, 40.4, 38.2, 35.0, 31.0, 28.9; IR (neat) 2949, 1728, 1709, 1493, 1452, 1234, 1196, 1173, 739, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{22}H_{24}O_3$: *m/z* 359.1618 ($[M + Na]^+$), found: *m/z* 359.1618 ($[M + Na]^+$).



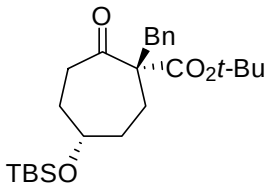
***tert*-Butyl *trans*-1-(*trans*-cinnamyl)-5-*tert*-butyl-2-oxocycloheptanecarboxylate (5k).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.40 (5H, m, Ar**H**), 6.41 (1H, d, *J* = 15.6 Hz, Ph-C**H**=CH), 6.20 (1H, ddd, J = 15.6, 8.4, 6.8 Hz, Ph-CH=C**H**), 2.94 (1H, ddd, *J* = 14.4, 6.8, 1.2 Hz, Ph-C=C-C**H**H), 2.65 (1H, ddd, *J* = 12.8, 11.6, 2.4 Hz, *c*-Hep), 2.44 (1H, ddd, *J* = 11.2, 6.4, 2.0 Hz, *c*-Hep), 2.36 (1H, ddd, *J* = 14.4, 8.8, 1.2 Hz, Ph-C=C-CH**H**), 2.10 (2H, m, *c*-Hep), 1.84-2.03 (2H, m, *c*-Hep), 1.40 (9H, s, C(C**H**$_3$)$_3$), 1.17-1.35 (2H, m, *c*-Hep), 0.84 (9H, s, C(C**H**$_3$)$_3$), 0.78 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.2, 170.9, 137.4, 133.2, 128.4, 127.1, 126.1, 126.0, 81.8, 63.8, 52.5, 40.3, 37.2, 33.3, 30.8, 28.4, 27.9, 27.6, 24.7; IR (neat) 2963, 1709, 1368, 1246, 1152, 1130, 1113, 966, 743, 692 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{36}O_3$: *m/z* 407.2557 ([M + Na]$^+$), found: *m/z* 407.2562 ([M + Na]$^+$).



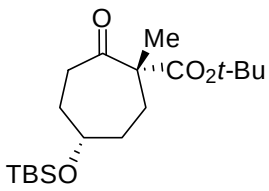
***tert*-Butyl *trans*-1-benzyl-2-oxo-5-(*N*-phthaloylamino)cycloheptanecarboxylate (5l).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, m, Phth), 7.71 (2H, m, Phth), 7.12-7.40 (5H, m, Ar**H**), 4.30 (1H, m, C**H**NPhth), 3.54 (1H, d, *J* = 14.0 Hz, PhC**H**H), 2.92 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.76 (1H, ddd, *J* = 14.0, 11.6, 2.4 Hz, *c*-Hep), 2.49 (1H, ddd, *J* = 11.6, 6.4, 2.4 Hz, *c*-Hep), 2.35 (1H, ddd, *J* = 26.0, 13.6, 2.8 Hz, *c*-Hep), 2.10-2.22 (3H, m, *c*-Hep), 1.95 (1H, m, *c*-Hep), 1.75 (1H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 169.9, 167.8, 137.1, 134.0, 131.8, 130.5, 128.1, 126.6, 123.2, 82.4, 65.1, 53.3, 38.0, 37.9, 29.7, 28.5, 27.9, 27.8; IR (neat) 2976, 2932, 1707, 1393, 1371, 1248, 1146, 1084, 719, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{27}H_{29}NO_5$: *m/z* 470.1938 ([M + Na]$^+$), found: *m/z* 470.1950 ([M + Na]$^+$).



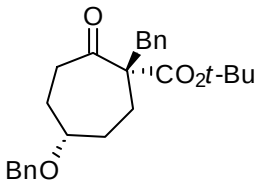
***tert*-Butyl *cis*-1-benzyl-5-(*tert*-butyldimethylsilyloxy)-2-oxocycloheptanecarboxylate (7a).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.37 (5H, m, Ar**H**), 3.82 (1H, m, C**H**OTBS), 3.29 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.00 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.83 (1H, app dt, *J* = 12.0, 2.4 Hz, *c*-Hep), 2.47 (1H, app dd, *J* = 15.6, 10.0 Hz, *c*-Hep), 2.71 (1H, ddd, *J* = 12.0, 8.4, 2.8 Hz, *c*-Hep), 1.53-1.83 (4H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$), 0.87 (9H, s, SiC(C**H**$_3$)$_3$), 0.016 (3H, Si(C**H**$_3$)(CH$_3$)), 0.013 (3H, Si(CH$_3$)(C**H**$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 170.8, 137.2, 130.7, 128.0, 126.5, 82.0, 69.2, 64.5, 39.8, 36.7, 34.5, 32.0, 27.8, 25.7, 23.9, 18.0, -4.83, -4.85; IR (neat) 2953, 2930, 1732, 1709, 1369, 1252, 1152, 1080, 839, 775 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{40}O_4Si$: *m/z* 455.2588 ([M + Na]$^+$), found: *m/z* 455.2587 ([M + Na]$^+$).



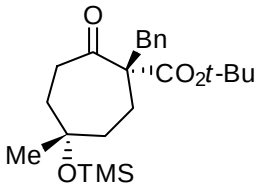
***tert*-Butyl *cis*-5-(*tert*-butyldimethylsilyloxy)-1-methyl-2-oxocycloheptanecarboxylate (7b).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 (1H, m, C**H**OTBS), 3.14 (1H, app dt, *J* = 12.0, 2.4 Hz, *c*-Hep), 2.66 (1H, dd, *J* = 14.8, 10.4 Hz, *c*-Hep), 2.27 (1H, ddd, *J* = 12.4, 8.0, 2.4 Hz, *c*-Hep), 1.78-2.00 (2H, m, *c*-Hep), 1.47 (1H, m, *c*-Hep), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.28 (3H, s, C**H**$_3$), 1.14 (1H, m, *c*-Hep), 0.91 (9H, s, SiC(C**H**$_3$)$_3$), 0.91 (1H, m, *c*-Hep), 0.05 (6H, Si(C**H**$_3$)$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.1, 172.6, 81.6, 68.2, 59.1, 36.3, 34.5, 32.1, 27.8, 27.6, 25.7, 20.4, 18.0, -4.8, -4.9; IR (neat) 2930, 1736, 1705, 1369, 1252, 1159, 1128, 1080, 835, 773 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{19}H_{36}O_4Si$: *m/z* 379.2275 ([M + Na]$^+$), found: *m/z* 379.2276 ([M + Na]$^+$).



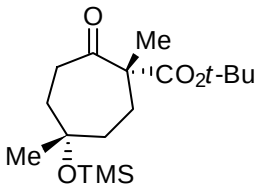
***tert*-Butyl *cis*-1-benzyl-5-(benzyloxy)-2-oxocycloheptanecarboxylate (7c).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.38 (5H, m, Ar**H**), 4.51 (1H, d, *J* = 12.0 Hz, PhC**H**HO), 4.44 (1H, d, *J* = 12.0 Hz, PhCH**H**O), 3.46 (1H, m, C**H**OBn), 3.25 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.04 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.82 (1H, ddd, *J* = 13.2, 10.8, 2.4 Hz, *c*-Hep), 2.37 (1H, app dd, *J* = 15.2, 8.8 Hz, *c*-Hep), 2.17 (1H, ddd, *J* = 12.0, 8.8, 3.2 Hz, *c*-Hep), 1.88-2.00 (2H, m, *c*-Hep), 1.88-2.0 (2H, m, *c*-Hep), 1.79 (1H, m, *c*-Hep), 1.64 (1H, m, *c*-Hep), 1.40-1.60 (2H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.3, 170.8, 138.6, 136.9, 130.6, 128.4, 128.1, 127.5, 127.4, 126.6, 82.2, 76.2, 70.0, 64.4, 40.3, 37.5, 30.8, 28.4, 27.9, 25.1; IR (neat) 2976, 2932, 2866, 1707, 1454, 1368, 1248, 1150, 1070, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{26}H_{32}O_4$: *m/z* 431.2193 ([M + Na]$^+$), found: *m/z* 431.2191 ([M + Na]$^+$).



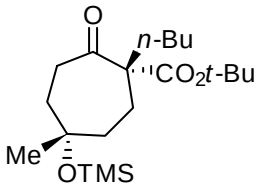
***tert*-Butyl *cis*-1-benzyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (7d).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.35 (5H, m, Ar**H**), 3.39 (1H, d, *J* = 14.4 Hz, PhC**H**H), 2.97 (1H, dt, *J* = 12.4, 2.0 Hz, *c*-Hep), 2.87 (1H, d, *J* = 14.4 Hz, PhCH**H**), 2.59 (1H, m, *c*-Hep), 2.18 (1H, ddd, *J* = 11.6, 7.2, 2.0 Hz, *c*-Hep), 1.84 (1H, ddt, *J* = 14.4, 7.6, 2.0 Hz, *c*-Hep), 1.04-1.70 (4H, m, *c*-Hep), 1.40 (9H, s, C(C**H**$_3$)$_3$), 1.20 (3H, s, C**H**$_3$), 0.11 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.4, 170.5, 137.6, 130.6, 128.0, 126.5, 81.9, 73.9, 65.0, 41.0, 38.6, 37.4, 37.0, 30.9, 27.8, 23.9, 2.4 ; IR (neat) 2967, 1707, 1248, 1146, 1084, 1045, 1005, 856, 843, 704 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{36}O_4Si$: *m/z* 427.2275 ([M + Na]$^+$), found: *m/z* 427.2277 ([M + Na]$^+$).



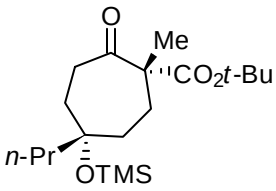
***tert*-Butyl *cis*-1,5-dimethyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (7e).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.17 (1H, ddd, *J* = 12.8, 12.0, 2.0 Hz, *c*-Hep), 2.69 (1H, app dd, *J* = 15.2, 10.4 Hz, *c*-Hep), 2.21 (1H, ddd, *J* = 12.0, 7.6, 2.0 Hz, *c*-Hep), 1.85 (1H, m, *c*-Hep), 1.76 (1H, m, *c*-Hep), 1.20-1.55 (3H, m, *c*-Hep), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.28 (3H, s, C**H**$_3$), 1.26 (3H, s, C**H**$_3$), 0.15 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.4, 172.6, 81.5, 73.6, 59.4, 40.6, 37.9, 37.1, 31.1, 28.9, 27.8, 19.7, 2.3; IR (neat) 2970, 1738, 1709, 1250, 1146, 1130, 1092, 1049, 1032, 839 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{32}O_4Si$: *m/z* 351.1962 ([M + Na]$^+$), found: *m/z* 351.1967 ([M + Na]$^+$).



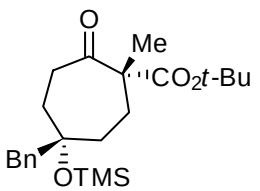
***tert*-Butyl *cis*-1-butyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (7f).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.96 (1H, app dt, *J* = 12.4, 2.4 Hz, *c*-Hep), 2.62 (1H, app dd, *J* = 15.2, 11.2 Hz, *c*-Hep), 2.17 (1H, ddd, *J* = 12.0, 7.6, 2.0 Hz, *c*-Hep), 2.00 (1H, m, *c*-Hep), 1.84 (1H, m, *c*-Hep), 1.10-1.89 (9H, m, *c*-Hep and *n*-Bu), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.24 (3H, s, C**H**$_3$), 0.90 (3H, t, *J* = 6.8 Hz, CH_2C**H**$_3$), 0.14 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.2, 171.5, 81.4, 74.0, 63.3, 40.8, 37.8, 37.0, 33.4, 30.9, 27.9, 26.8, 25.3, 23.3, 13.9, 2.4; IR (neat) 2959, 1711, 1250, 1171, 1144, 1128, 1096, 1045, 1003, 839 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{38}O_4Si$: *m/z* 393.2432 ([M + Na]$^+$), found: *m/z* 393.2440 ([M + Na]$^+$).



***tert*-Butyl *cis*-1-methyl-2-oxo-5-propyl-5-(trimethylsilyloxy)cycloheptanecarboxylate (7g).**

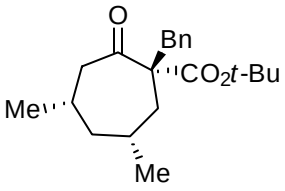
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.13 (1H, app dt, *J* = 12.4, 2.0 Hz, *c*-Hep), 2.63 (1H, app dd, *J* = 12.8, 10.8 Hz, *c*-Hep), 2.23 (1H, ddd, *J* = 12.4, 7.6, 2.0 Hz, *c*-Hep), 1.15-1.82 (9H, m, *c*-Hep and *n*-Pr), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.27 (3H, s, C**H**$_3$), 0.89 (3H, t, *J* = 7.6 Hz, CH_2C**H**$_3$), 0.15 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.3, 172.6, 81.6, 76.5, 59.2, 46.2, 37.9, 37.0, 35.7, 29.0, 27.8, 19.9, 17.1, 14.6, 2.4; IR (neat) 2959, 1738, 1709, 1250, 1171, 1146, 1126, 1094, 1078, 837 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{19}H_{36}O_4Si$: *m/z* 379.2275 ([M + Na]$^+$), found: *m/z* 379.2268 ([M + Na]$^+$).



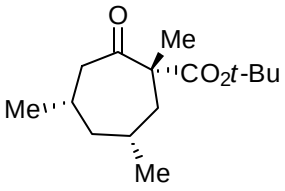
***tert*-Butyl *cis*-5-benzyl-1-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (7h).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.31 (5H, m, Ar**H**), 3.13 (1H, app

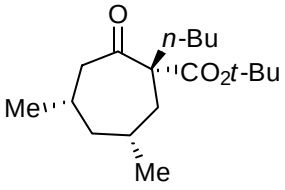
dt, J = 12.4, 2.4 Hz, *c*-Hep), 2.85 (2H, s, PhC**H**$_2$), 2.62 (1H, app dd, J = 15.2, 10.8 Hz, *c*-Hep), 2.26 (1H, ddd, J = 12.4, 8.0, 2.0 Hz, *c*-Hep), 1.70-1.95 (2H, m, *c*-Hep), 1.13-1.60 (4H, m, *c*-Hep), 1.43 (9H, s, C(C**H**$_3$)$_3$), 1.17 (3H, s, C**H**$_3$), 0.19 (9H, s, OSi(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.9, 172.5, 137.0, 130.5, 128.0, 126.6, 81.6, 77.2, 59.1, 50.5, 37.3, 37.0, 35.4, 29.1, 27.8, 20.0, 2.6; IR (neat) 2951, 1736, 1705, 1369, 1252, 1155, 1126, 1082, 837, 754 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{23}H_{36}O_4Si$: *m/z* 427.2275 ([M + Na]$^+$), found: *m/z* 427.2281 ([M + Na]$^+$).



***tert*-Butyl *cis*-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (9a).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.40 (5H, m, Ar**H**), 3.38 (1H, d, J = 14.0 Hz, PhC**H**H), 2.88 (1H, d, J = 14.0 Hz, PhCH**H**), 2.50 (1H, dd, J = 12.0, 11.2 Hz, *c*-Hep), 2.31 (1H, ddd, J = 10.8, 2.4, 1.6 Hz, *c*-Hep), 1.94 (1H, dd, J = 15.6, 10.0 Hz, *c*-Hep), 1.10-1.88 (5H, m, *c*-Hep), 1.41 (9H, s, C(C**H**$_3$)$_3$), 1.00 (3H, d, J = 7.2 Hz, CHC**H**$_3$), 0.94 (1H, m, *c*-Hep), 0.88 (3H, d, J = 6.8 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.0, 170.5, 137.5, 130.6, 128.0, 126.5, 82.0, 64.5, 48.7, 48.6, 38.2, 37.8, 35.0, 29.1, 27.8, 24.8, 23.5; IR (neat) 2955, 1711, 1456, 1368, 1260, 1242, 1146, 1045, 737, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{21}H_{30}O_3$: *m/z* 353.2087 ([M + Na]$^+$), found: *m/z* 353.2088 ([M + Na]$^+$).

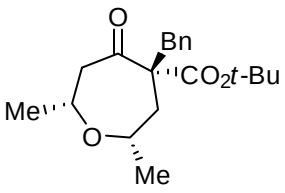


***tert*-Butyl *cis*-1,4,6-trimethyl-2-oxocycloheptanecarboxylate (9b).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.65 (1H, app t, J = 11.2 Hz, *c*-Hep), 2.31 (1H, app dt, J = 11.2, 1.6 Hz, *c*-Hep), 2.09 (1H, dd, J = 14.8, 10.4 Hz, *c*-Hep), 1.20-1.80 (4H, m, *c*-Hep), 1.42 (9H, s, C(C**H**$_3$)$_3$), 1.29 (3H, s, C**H**$_3$), 1.14 (1H, m, *c*-Hep), 1.01 (3H, d, J = 6.4 Hz, CHC**H**$_3$), 0.97 (3H, d, J = 6.8 Hz, CHC**H**$_3$), 0.96 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.0, 172.6, 81.6, 58.9, 49.5, 48.7, 43.4, 34.5, 29.6, 27.8, 25.4, 23.8, 19.9; IR (neat) 2955, 1736, 1709, 1458, 1369, 1265, 1238, 1165, 1136, 1109 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{15}H_{26}O_3$: *m/z* 277.1774 ([M + Na]$^+$), found: *m/z* 277.1766 ([M + Na]$^+$).

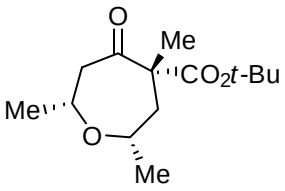


***tert*-Butyl *cis*-1-butyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (9c).**
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.47 (1H, t, J = 11.6 Hz, *c*-Hep), 2.27 (1H, app dt, J = 10.0, 1.6 Hz, *c*-Hep), 1.94-2.10 (2H, m, *c*-Hep and/or *n*-Bu), 1.15-1.84 (9H, m, *c*-Hep and/or *n*-Bu), 1.42 (9H, s, C(C**H**$_3$)$_3$), 0.99 (3H, d, J = 6.8 Hz, CHC**H**$_3$), 0.96 (3H, d, J = 6.8 Hz, CHC**H**$_3$), 0.94 (1H, m, *c*-Hep), 0.91 (3H, t, J = 7.6 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.9, 171.6, 81.5, 62.8, 49.0, 48.7, 39.4, 34.8, 32.8, 29.4, 27.8, 26.7, 25.4, 23.5, 23.2, 13.9; IR (neat) 2955, 2928, 2870, 1709, 1458, 1368, 1256, 1136, 1047, 841 cm^{-1}; HRMS (ESI) exact mass

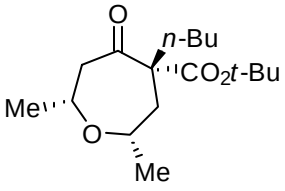
calcd. for $C_{18}H_{32}O_3$: *m/z* 319.2244 ([M + Na]$^+$), found: *m/z* 319.2238 ([M + Na]$^+$).



***tert*-Butyl *cis*-4-benzyl-2,7-dimethyl-5-oxooxepane-4-carboxylate (9d).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16-7.30 (5H, m, Ar**H**), 3.54 (1H, m, **H**COCH), 3.24 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.14 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.87 (1H, m, HCOC**H**), 2.83 (1H, dd, *J* = 11.6, 10.4 Hz, OCHC**H**$_2$), 2.51 (1H, dd, *J* = 11.6, 0.8 Hz, OCHC**H**$_2$), 2.25 (1H, dd, *J* = 16.4, 8.8 Hz, OCHC**H**$_2$), 1.94 (1H, app d, *J* = 15.6 Hz, OCHC**H**$_2$), 1.43 (9H, s, C(C**H**$_3$)$_3$), 1.24 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 1.06 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.8, 170.4, 137.0, 130.8, 128.2, 126.8, 82.4, 74.6, 73.0, 63.7, 52.6, 39.0, 37.9, 27.8, 23.6, 22.9; IR (neat) 2976, 1711, 1369, 1267, 1244, 1152, 1138, 1103, 843, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{20}H_{28}O_4$: *m/z* 355.1880 ([M + Na]$^+$), found: *m/z* 355.1885 ([M + Na]$^+$).

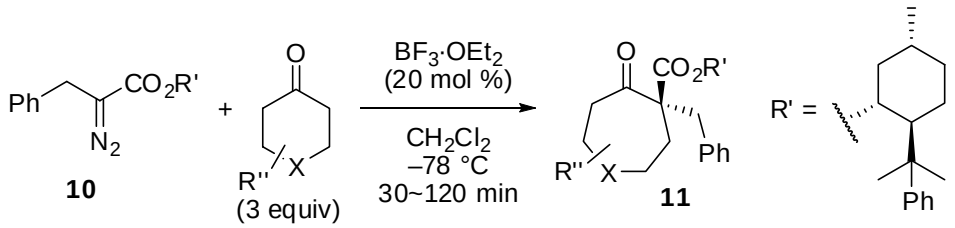


***tert*-Butyl *cis*-2,4,7-trimethyl-5-oxooxepane-4-carboxylate (9e).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.60 (1H, m, **H**COCH), 3.35 (1H, m, HCOC**H**), 2.98 (1H, dd, *J* = 12.0, 10.4 Hz, OCHC**H**$_2$), 2.52 (1H, dd, *J* = 12.0, 1.2 Hz, OCHC**H**$_2$), 2.38 (1H, dd, *J* = 15.6, 8.8 Hz, OCHC**H**$_2$), 1.72 (1H, app d, *J* = 15.6 Hz, OCHC**H**$_2$), 1.43 (9H, s, C(C**H**$_3$)$_3$), 1.32 (3H, s, C**H**$_3$), 1.27 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 1.25 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.8, 172.0, 82.0, 74.4, 72.9, 58.2, 53.2, 42.8, 27.8, 24.2, 23.2, 20.5; IR (neat) 2934, 2870, 2976, 1736, 1711, 1369, 1269, 1240, 1161, 1130 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{14}H_{24}O_4$: *m/z* 279.1567 ([M + Na]$^+$), found: *m/z* 279.1557 ([M + Na]$^+$).

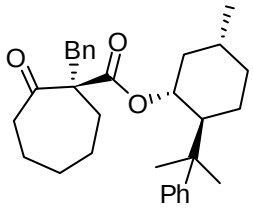


***tert*-Butyl *cis*-4-butyl-2,7-dimethyl-5-oxooxepane-4-carboxylate (9f).** ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.62 (1H, m, **H**COCH), 3.26 (1H, m, HCOC**H**), 2.77 (1H, dd, *J* = 11.6, 10.4 Hz, OCHC**H**$_2$), 2.47 (1H, dd, *J* = 12.0, 1.2 Hz, OCHC**H**$_2$), 2.34 (1H, dd, *J* = 16.0, 8.8 Hz, OCHC**H**$_2$), 1.98 (1H, m, *n*-Bu), 1.78 (1H, app d, *J* = 15.6 Hz, OCHC**H**$_2$), 1.16-1,62 (5H, m, *n*-Bu), 1.44 (9H, s, C(C**H**$_3$)$_3$), 1.26 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 1.23 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 0.91 (3H, t, *J* = 6.8 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.5, 171.2, 81.9, 74.8, 73.1, 62.1, 52.7, 38.9, 34.0, 27.9, 26.6, 24.1, 23.2, 22.9, 13.9; IR (neat) 2972, 2932, 2864, 1736, 1711, 1369, 1240, 1153, 1134, 1105 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{17}H_{30}O_4$: *m/z* 321.2036 ([M + Na]$^+$), found: *m/z* 321.2031 ([M + Na]$^+$).

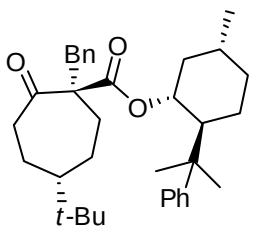
·General procedure for the asymmetric ring expansion of functionalized cyclohexanones with (–)-phenylmenthyl α-benzyldiazoacetate.



To a stirred solution of (–)-phenylmenthyl α-benzyldiazoacetate (78.1 mg, 0.20 mmol) and the corresponding cyclohexanone derivative (0.60 mmol) in dichloromethane (1.0 mL) was added $BF_3{\cdot}OEt_2$ (5.1 μL, 0.040 mmol) at –78 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature until all consumption of the diazo compound (30-120 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 = 80:1~60:1) to give the corresponding cycloheptanone.

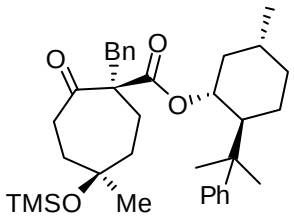


(1*R*,2*S*,5*R*)-8-Phenylmenthyl (*R*)-1-benzyl-2-oxocycloheptanecarboxylate (11a).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.40 (10H, m, Ar**H**), 4.89 (1H, app dt, *J* = 10.8, 4.0 Hz, OC**H**), 3.18 (1H, d, *J* = 13.6 Hz, PhC**H**H), 2.84 (1H, d, *J* = 13.6 Hz, PhCH**H**), 2.50 (1H, m, Cy), 2.16 (1H, m, Cy), 1.91-2.02 (2H, m, Cy), 0.67-1.89 (14H, m, Cy), 1.32 (3H, s, C(Ph)(C**H**$_3$)(CH$_3$)), 1.24 (3H, s, C(Ph)(CH$_3$)(C**H**$_3$)), 0.85 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.1, 172.1, 150.8, 136.6, 130.9, 128.1, 128.0, 126.6, 125.6, 125.4, 76.8, 63.7, 49.9, 43.6, 41.5, 40.5, 40.1, 34.4, 31.5, 31.3, 30.4, 29.1, 27.3, 25.5, 25.0, 24.5, 21.7; IR (neat) 2949, 2926, 2862, 1722, 1709, 1454, 1231, 1213, 1198, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{31}H_{40}O_3$: *m/z* 483.2870 ([M + Na]$^+$), found: *m/z* 483.2877 ([M + Na]$^+$); $[\alpha]_D^{28}$ = –4.8 (*c* = 1.0, $CHCl_3$).



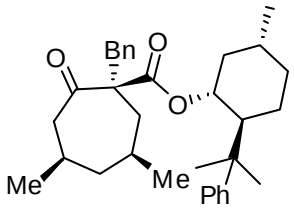
(1*R*,2*S*,5*R*)-8-Phenylmenthyl (1*R*,5*S*)-1-benzyl-5-*tert*-butyl-2-oxocycloheptanecarboxylate (11b).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09-7.39 (10H, m, Ar**H**), 4.86 (1H, app dt, *J* = 10.4, 4.4 Hz, OC**H**), 3.10 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.05 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.62 (1H, m, Cy), 1.77-2.12 (5H, m, Cy), 0.64-1.70 (9H, m, Cy), 1.30 (3H, s, C(Ph)(C**H**$_3$)(CH$_3$)), 1.22 (3H, s, C(Ph)(CH$_3$)(C**H**$_3$)), 0.82 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$), 0.76 (9H, s, CH(C**H**$_3$)$_3$), 0.39 (1H, m, Cy); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.9, 171.6, 150.5, 137.2, 130.9, 128.1, 128.0, 126.5, 125.6, 125.4, 76.7, 63.7, 52.1, 49.8, 41.3, 41.1, 40.2, 38.0, 34.3, 33.1, 31.2, 30.3, 29.7, 28.1, 27.5, 27.3, 24.8, 24.4, 21.7; IR (neat) 2955, 2926, 1726, 1709, 1454, 1229,

1206, 1175, 908, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{35}H_{48}O_3$: *m/z* 539.3496 ([M + Na]$^+$), found: *m/z* 539.3485 ([M + Na]$^+$); $[\alpha]_D^{28}$ = 47.8 (*c* = 1.0, $CHCl_3$).



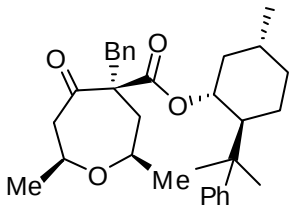
(1*R*,2*S*,5*R*)-8-Phenylmenthyl (1*R*,5*S*)-1-benzyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (11c).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12-7.32 (10H, m, Ar**H**), 4.88 (1H, app dt, *J* = 10.8, 4.4 Hz, OC**H**), 3.19 (1H, d, *J* = 14.0 Hz, PhC**H**H), 3.07 (1H, d, *J* = 14.0 Hz, PhCH**H**), 3.04 (1H, m, Cy), 2.53 (1H, dd, *J* = 14.8, 10.8 Hz, Cy), 2.22 (1H, m, Cy), 1.67-1.90 (4H, m, Cy), 0.77-1.60 (8H, m, Cy), 1.27 (3H, s, C(Ph)(C**H**$_3$)(CH$_3$)), 1.23 (3H, s, C(Ph)(CH$_3$)(C**H**$_3$)), 1.13 (3H, s, C**H**$_3$), 0.81 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 0.67 (1H, m, Cy), 0.10 (9H, s, Si(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.5, 171.8, 150.3, 137.3, 131.0, 128.04, 128.00, 126.5, 125.7, 125.4, 76.5, 73.7, 63.8, 50.3, 41.5, 40.6, 40.3, 38.6, 37.8, 37.7, 34.3, 31.3, 30.8, 30.6, 27.4, 25.2, 23.5, 21.7, 2.4; IR (neat) 2955, 2924, 1730, 1707, 1250, 1209, 1047, 1007, 839, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{35}H_{50}O_4Si$: *m/z* 585.3371 ([M + Na]$^+$), found: *m/z* 585.3377 ([M + Na]$^+$); $[\alpha]_D^{30}$ = 25.2 (*c* = 1.0, $CHCl_3$).



(1*R*,2*S*,5*R*)-8-Phenylmenthyl (1*R*,4*R*,6*S*)-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (11d).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06-7.44 (10H, m, Ar**H**), 4.87 (1H, app dt, *J* = 10.8, 4.4 Hz, OC**H**), 3.20 (1H, d, *J* = 14.0 Hz, PhC**H**H), 2.98 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.37 (1H, m, Cy), 0.55-2.01 (15H, m, Cy), 1.31 (3H, s, C(Ph)(C**H**$_3$)(CH$_3$)), 1.23 (3H, s, C(Ph)(CH$_3$)(C**H**$_3$)), 0.99 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$), 0.84 (3H, d, *J* = 6.4 Hz, CHC**H**$_3$), 0.73 (3H, d, *J* = 6.0 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.9, 171.7, 150.5, 137.3, 131.1, 128.1, 127.9, 126.6, 125.6, 125.5, 76.8, 63.3, 49.9, 49.8, 48.5, 41.2, 40.2, 38.7, 38.1, 34.7, 34.3, 31.3, 29.9, 29.5, 27.3, 24.6, 24.3, 23.7, 21.7; IR (neat) 2953, 2924, 1726, 1707, 1495, 1456, 1236, 1213, 764, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{33}H_{44}O_3$: *m/z* 511.3183 ([M + Na]$^+$), found: *m/z* 511.3178 ([M + Na]$^+$); $[\alpha]_D^{27}$ = 37.5 (*c* = 1.0, $CHCl_3$).

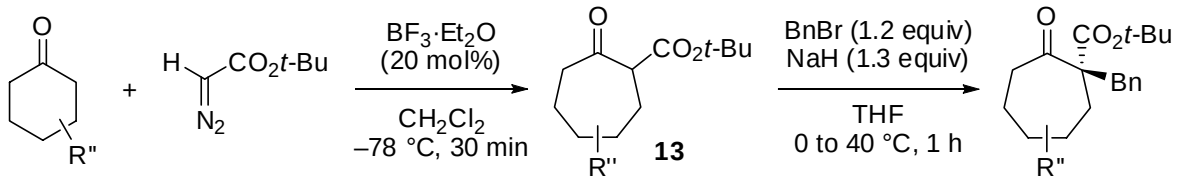


(1*R*,2*S*,5*R*)-8-Phenylmenthyl (2*R*,4*S*,7*S*)- 4-benzyl-2,7-dimethyl-5-oxooxepane-4-carboxylate (11e).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13-7.37 (10H, m, Ar**H**), 4.90 (1H, app dt, *J* = 10.4, 4.4 Hz, OC**H**), 3.48 (1H, d, *J* = 13.6 Hz, PhC**H**H), 3.41 (1H, m, **H**COCH), 2.85 (1H, dd, *J* = 12.0, 10.4 Hz, HCOC**H**), 2.77 (1H, d, *J* = 13.6 Hz, PhCH**H**), 2.55 (1H, d, *J* = 11.2 Hz, Cy), 2.44 (1H, m, Cy), 2.10 (1H, dd, *J* = 16.0, 8.0 Hz, Cy), 1.95 (1H, d, *J* = 16.4 Hz, Cy), 1.93 (1H, m, Cy), 1.86 (1H, m, Cy), 0.68-1.59 (6H, m,

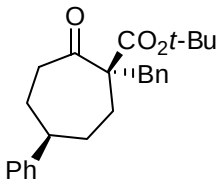
Cy), 1.31 (3H, s, C(Ph)(C**H**$_3$)(CH$_3$)), 1.24 (3H, s, C(Ph)(CH$_3$)(C**H**$_3$)), 1.22 (3H, d, J = 6.4 Hz, CHC**H**$_3$), 0.89 (3H, d, J = 6.4 Hz, CHC**H**$_3$), 0.85 (3H, d, J = 6.4 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6, 171.6, 150.4, 136.8, 131.2, 128.2, 128.1, 126.9, 125.6, 125.5, 76.9, 74.2, 73.2, 62.8, 53.5, 49.9, 41.4, 40.2, 38.8, 38.5, 34.3, 31.3, 29.3, 27.2, 24.8, 23.2, 23.0, 21.7; IR (neat) 2968, 2928, 1726, 1707, 1234, 1209, 1123, 1101, 1094, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{32}H_{42}O_4$: *m/z* 513.2975 ($[M + Na]^+$), found: *m/z* 513.2986 ($[M + Na]^+$); $[\alpha]_D^{28}$ = 55.8 (*c* = 1.0, $CHCl_3$).

·Preparation of the diastereomeric cycloheptanone via alkylation of pre-formed *t*-butyl 2-oxocycloheptanecarboxylate derivatives for the unambiguous determination of diastereoselectivity.



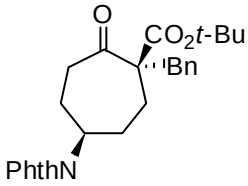
To a stirred solution of alkyldiazoacetate (0.20 mmol) and cyclohexanone derivative (0.21 mmol) in dichloromethane (1.0 mL) was added $BF_3{\cdot}OEt_2$ (5.1 μL, 0.040 mmol) at –78 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 30 min. The mixture was quenched with 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 = 80:1~60:1) to give the corresponding cycloheptanone **13**.

To a stirred suspension of NaH (60 % dispersion in mineral oil, 47 mg, 1.17 mmol) in THF (4 mL), the solution of the corresponding cycloheptanone **13** (0.90 mmol) in THF (4 mL) was added dropwise at 0 °C under Ar atmosphere. After the mixture became clear, BnBr (128 μL, 1.08 mmol) was added dropwise, and the mixture was stirred at 40 °C for 1 h. The resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography to afford the alkylated cycloheptanone.



***tert*-Butyl *cis*-1-benzyl-2-oxo-5-phenylcycloheptanecarboxylate (*epi*-5c).**

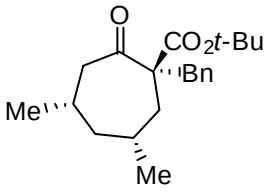
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08-7.33 (10H, m, Ar**H**), 3.25 (1H, d, *J* = 13.2 Hz, PhC**H**H), 3.15 (1H, d, *J* = 13.2 Hz, PhCH**H**), 2.63 (1H, m, *c*-Hep), 2.51 (1H, m, *c*-Hep), 2.27 (1H, m, *c*-Hep), 2.13 (1H, m, *c*-Hep), 1.74-2.17 (5H, m, *c*-Hep), 1.50 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.7, 171.5, 147.3, 136.3, 130.7, 128.5, 128.1, 126.8, 126.5, 126.2, 82.2, 64.3, 47.8, 43.3, 43.2, 33.4, 33.2, 31.1, 28.1; IR (neat) 2974, 2932, 1726, 1701, 1452, 1368, 1242, 1148, 760, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{25}H_{30}O_3$: *m/z* 401.2087 ([M + Na]$^+$), found: *m/z* 401.2073 ([M + Na]$^+$).



***tert*-butyl *cis*-1-benzyl-2-oxo-5-(*N*-phthaloylamino)cycloheptanecarboxylate (*epi*-5l).**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, m, Phth), 7.71 (2H, m, Phth), 7.20-7.38 (3H, m, Ar**H**), 7.08-7.18 (2H, m, Ar**H**), 4.08 (1H, m,

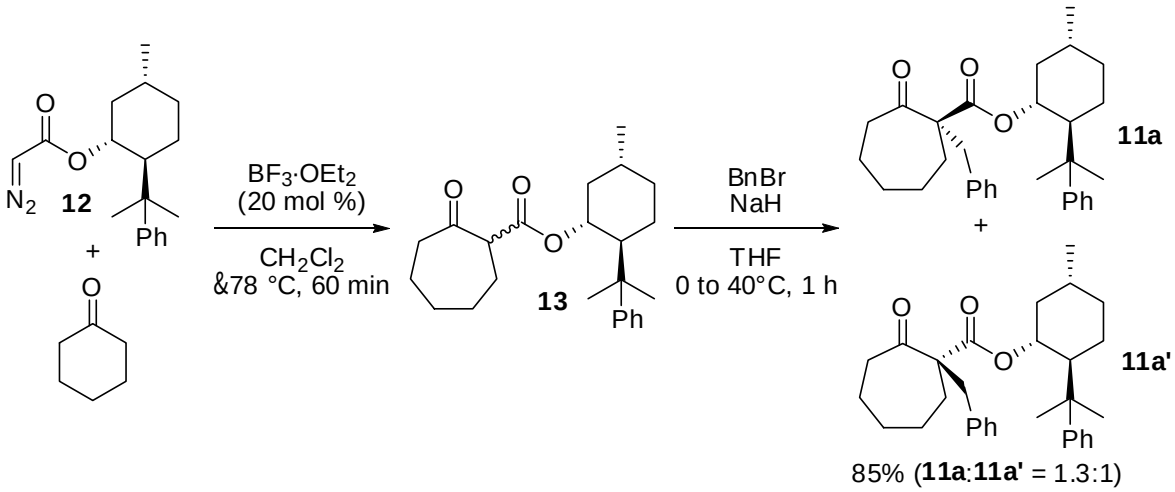
C**H**NPhth), 3.32 (1H, d, *J* = 13.2 Hz, PhC**H**H), 3.09 (1H, d, *J* = 13.2 Hz, PhCH**H**), 2.76 (1H, app q, *J* = 12.8 Hz, *c*-Hep), 2.50-2.68 (2H, m, *c*-Hep), 2.05-2.24 (2H, m, *c*-Hep), 1.62-1.85 (3H, m, *c*-Hep), 1.57 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.9, 171.5, 167.8, 136.0, 133.9, 131.8, 130.7, 128.2, 126.9, 123.2, 82.9, 64.0, 52.9, 43.3, 41.9, 32.0, 29.0, 27.9, 27.2; IR (neat) 2976, 2934, 1705, 1395, 1371, 1244, 1148, 910, 718, 702 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{27}H_{29}NO_5$: *m/z* 470.1938 ([M + Na]$^+$), found: *m/z* 470.1944 ([M + Na]$^+$).



***tert*-Butyl *trans*-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (*epi*-9a).**

^{1}H NMR (400 MHz, $CDCl_3$) 7.11-7.28 (5H, m, Ar**H**), 3.17 (1H, d, *J* = 13.6 Hz, PhC**H**H), 3.07 (1H, d, *J* = 13.6 Hz, PhCH**H**), 2.46 (1H, m, *c*-Hep), 2.07 (1H, dd, *J* = 13.2, 11.2 Hz, *c*-Hep), 1.78-1.96 (3H, m, *c*-Hep), 1.64 (1H, m, *c*-Hep), 1.43 (9H, s, C(C**H**$_3$)$_3$), 1.40 (1H, m, *c*-Hep), 0.93 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$), 0.92 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$), 0.83 (1H, m, *c*-Hep); ^{13}C NMR (100 MHz, $CDCl_3$) δ 209.8, 171.4, 136.4, 130.7, 128.0, 126.7, 81.8, 64.0, 51.7, 47.4, 43.2, 42.3, 30.9, 30.6, 28.0, 24.6, 23.9; IR (neat) 2955, 2928, 1728, 1697, 1454, 1368, 1246, 1148, 847, 700 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{21}H_{30}O_3$: *m/z* 353.2087 ([M + Na]$^+$), found: *m/z* 353.2088 ([M + Na]$^+$).

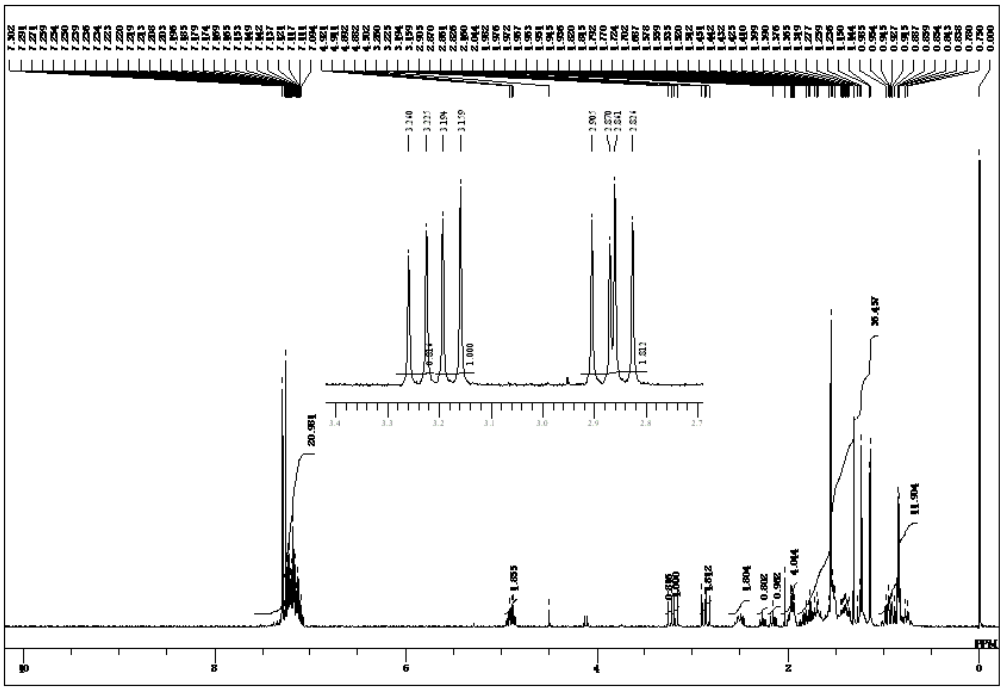
·Preparation of the diastereomeric mixture of (1*R*,2*S*,5*R*)-8-phenylmenthyl 1-benzyl-2-oxocycloheptanecarboxylate (11a and 11a') via alkylation of pre-formed (1*R*,2*S*,5*R*)-8-phenylmenthyl 2-oxocycloheptanecarboxylate.



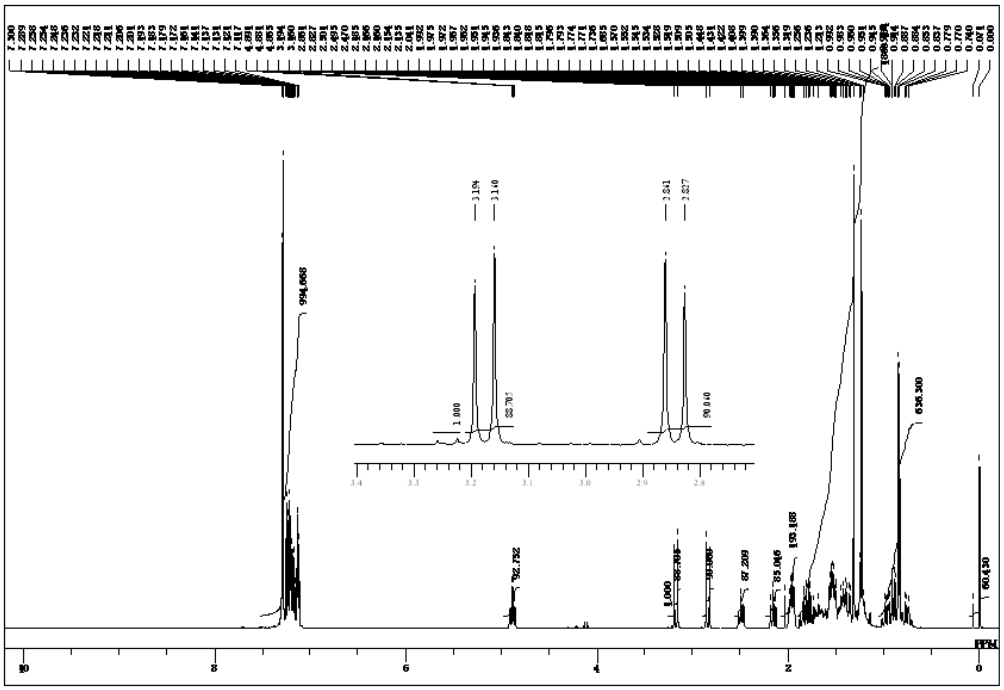
To a stirred solution of (1*R*,2*S*,5*R*)-phenylmenthyl diazoacetate **12**[5] (45.1 mg, 0.15 mmol) and cyclohexanone (46.6 μL, 0.45 mmol) in dichloromethane (1.5 mL) was added $BF_3{\cdot}OEt_2$ (3.8 μL, 0.030 mmol) at –78 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 1 h. The mixture was quenched with aqueous $NaHCO_3$ and extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to give a crude mixture of **13**.

To a stirred suspension of NaH (60 % dispersion in mineral oil, 7.8 mg, 0.195 mmol) in THF (1 mL), a solution of thus-prepared crude mixture of **13** in THF (2 mL) was added dropwise at 0 °C under Ar atmosphere. After the formation of clear reaction solution, benzyl bromide (21.4 μL, 0.18 mmol) was added dropwise, and the mixture was then stirred at 40 °C for 1 h. The resulting mixture was quenched with saturated aqueous NH_4Cl solution and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography to afford the alkylated compound **11a** and **11a'** as a mixture of diastereomers.

·^{1}H NMR spectra of the diasteremeric mixture of **11a** and **11a'** (1.3:1)

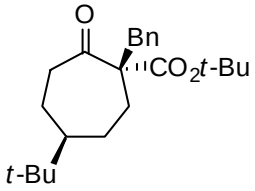


·^{1}H NMR spectra of **11a** prepared according to the ring expansion of cyclohexanone with (–)-phenylmenthyl α-benzyldiazoacetate.



·Determination of the relative configuration by X-ray crystallographic analysis.

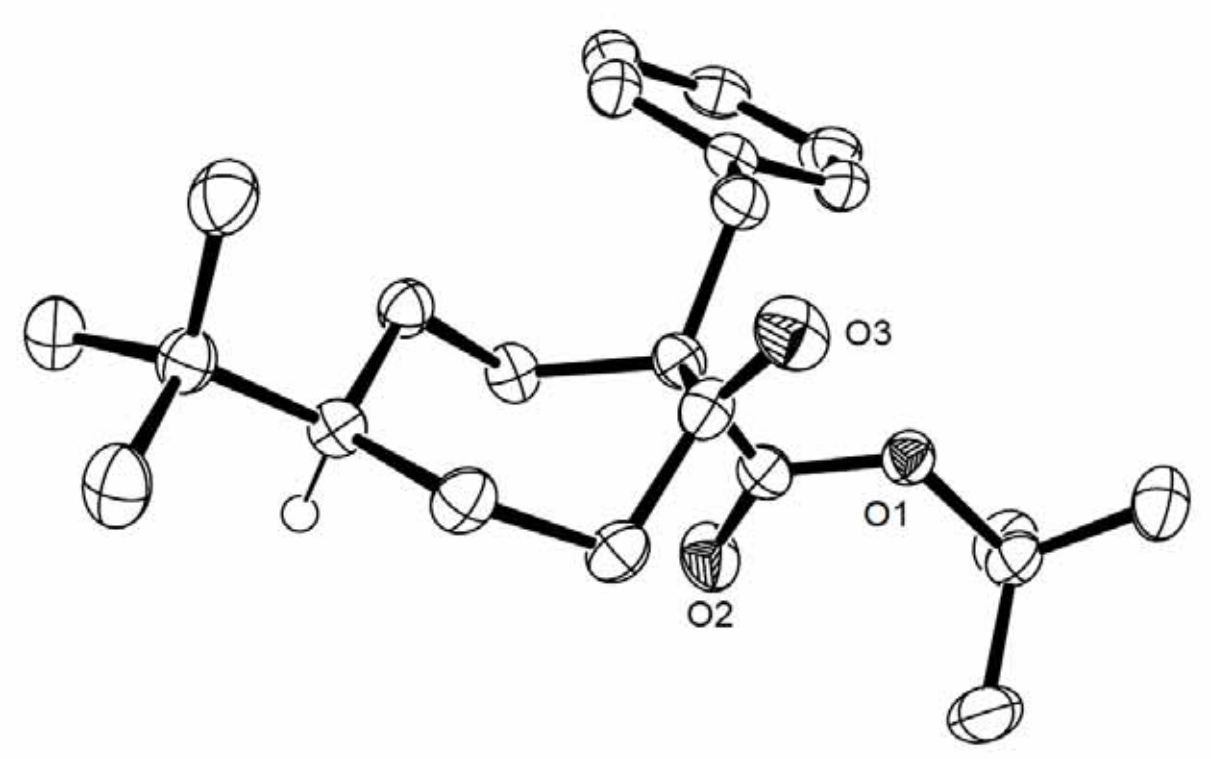
***tert*-Butyl *trans*-1-benzyl-5-*tert*-butyl-2-oxocycloheptanecarboxylate (5a).**



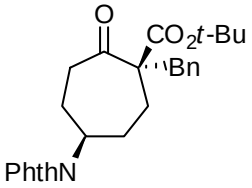
The product **5a** was recrystallized from hexane/CH_2Cl_2. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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	$C_{23}H_{34}O_3$
formula weight	358.52
crystal system	orthorhombic
space group	Pbca (#61)
a, Å	11.5213(2)
b, Å	16.0501(3)
c, Å	22.5320(4)
V , Å^3	4166.58(13)
Z	8
D_{calc}, g/cm^3	1.143
T, °C	–150
μ (CuKα), cm^{-1}	5.774
no. of reflns meased	37529
no. of reflns obsd	3808
no. of reflns variable	236
R (All reflections)	0.0453
R_w (All reflections)	0.1107
Goodness of Fit	1.077

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 693726). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


O3
O1
O2

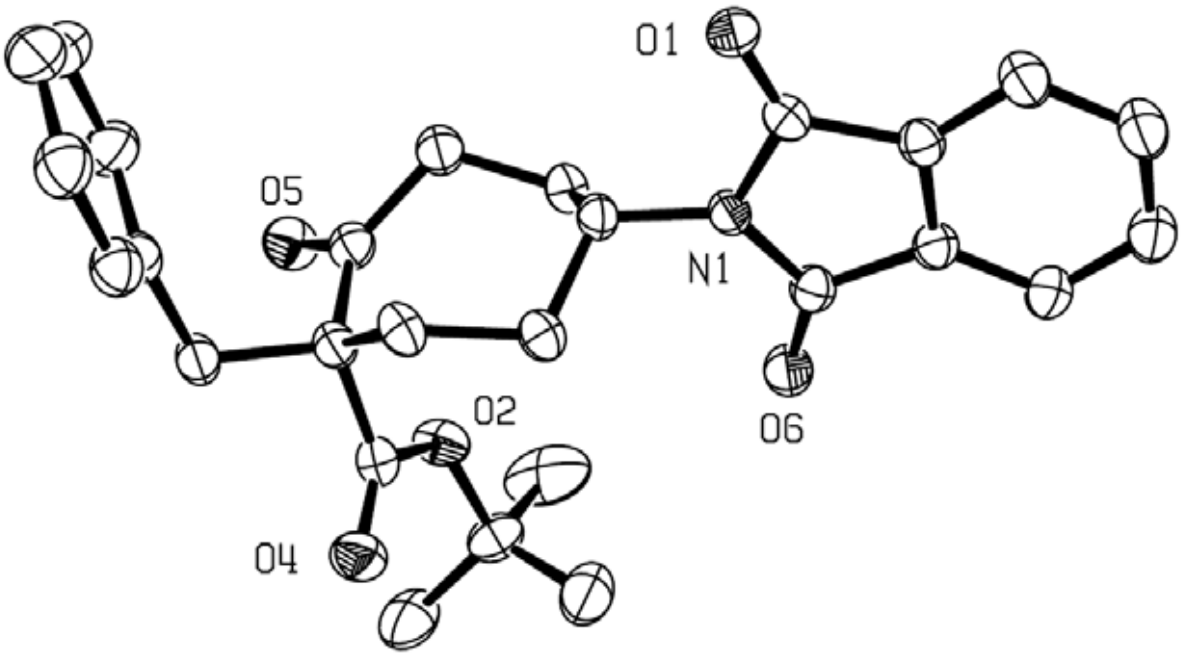
***tert*-Butyl *cis*-1-benzyl-2-oxo-5-(*N*-phthaloylamino)cycloheptanecarboxylate (5l').**



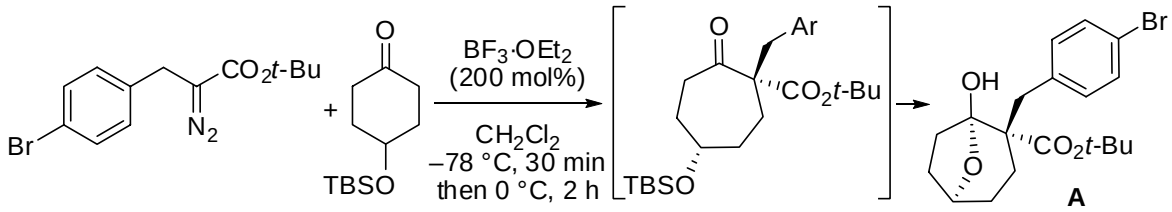
The product was recrystallized from hexane/CH_2Cl_2. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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	$C_{27}H_{29}O_5N$
formula weight	447.53
crystal system	monoclinic
space group	P21/c (#14)
a, Å	12.9192(2)
b, Å	7.97322(14)
c, Å	23.6874(4)
β, °	99.3190(9)
V , Å^3	2407.78(8)
Z	4
D_{calc}, g/cm^3	1.234
T, °C	–150
μ (CuKα), cm^{-1}	6.891
no. of reflns meased	23608
no. of reflns obsd	4408
no. of reflns variable	299
R (All reflections)	0.0541
R_w (All reflections)	0.1914
Goodness of Fit	1.449

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 695856). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


O1
O5
N1
O2
O6
O4

***tert*-Butyl *cis*-1-(4-bromobenzyl)-5-(*tert*-butyldimethylsilyloxy)-2-oxocycloheptanecarboxylate (4-bromobenzyl analog of 7a).**



To a stirred solution of *tert*-butyl 4-bromobenzyldiazoacetate (62.2 mg, 0.20 mmol) and 4-(*tert*-butyldimethylsilyloxy)cyclohexanone (42.9 mg, 0.21 mmol) in dichloromethane (1.0 mL) was added $BF_3{\cdot}OEt_2$ (50.7 μL, 0.40 mmol) at –78 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 30 min and then warmed up to 0 °C. After stirring for 2 h at the same temperature to remove the TBS moiety, 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 to give the bicyclic compound **A**.

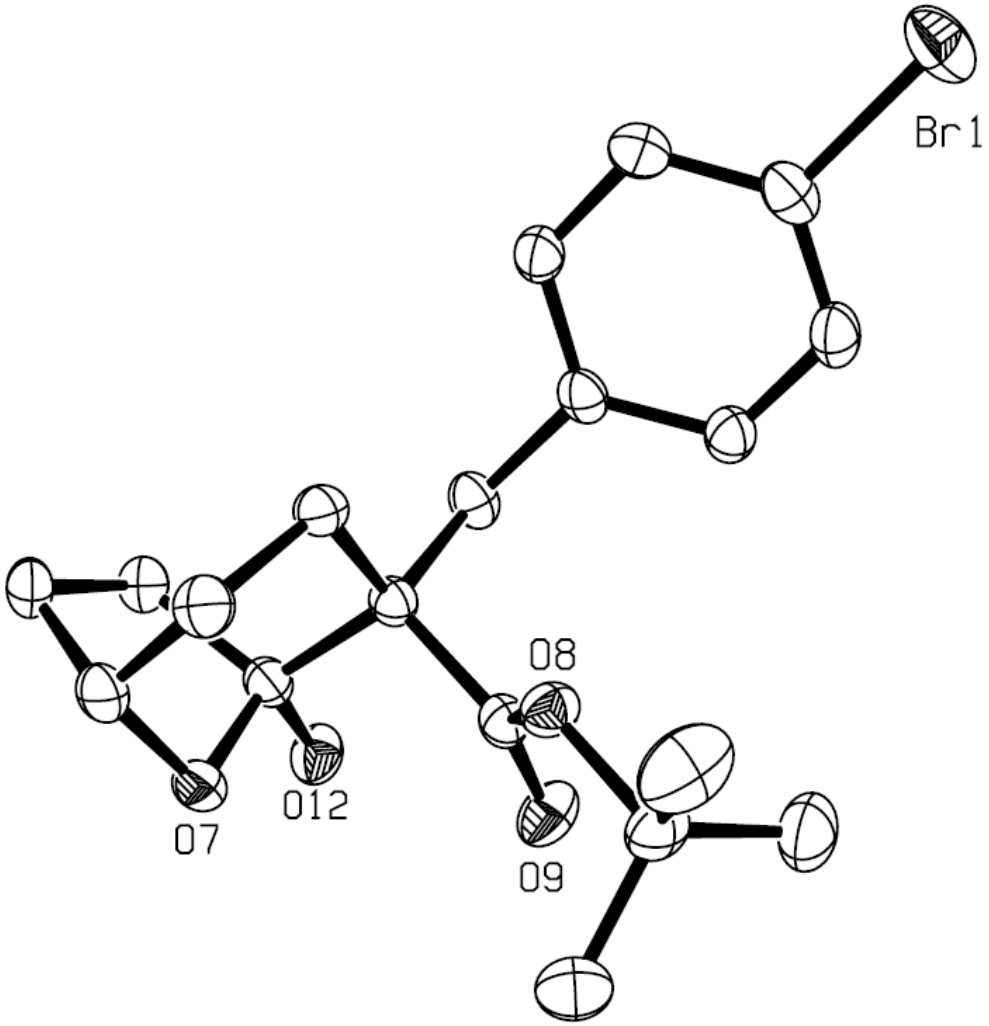
^{1}H NMR (400 MHz, $CDCl_3$) 7.38 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.00 (2H, d, *J* = 8.4 Hz, Ar**H**), 6.28 (1H, s, O**H**), 4.49 (1H, m, C**H**OH), 3.28 (1H, d, *J* = 13.6 Hz, PhC**H**H), 2.56 (1H, d, *J* = 13.6 Hz, PhCH**H**), 2.16-2.29 (2H, m, *c*-Hep), 1.73-1.97 (3H, m, *c*-Hep), 1.20-1.66 (3H, m, *c*-Hep), 1.36 (9H, s, C(C**H**$_3$)$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 135.1, 131.9, 131.0, 120.6, 107.1, 83.0, 76.7, 55.2, 41.1, 31.5, 29.3, 28.2, 27.9, 26.4; IR (neat) 3402, 2957, 1684, 1155, 1148, 1121, 1053, 1013, 974, 841 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{19}H_{25}BrO_4$: *m/z* 419.0828 ([M + Na]$^+$), found: *m/z* 419.0833 ([M + Na]$^+$).

The product **A** was recrystallized from hexane/CH_2Cl_2. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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.

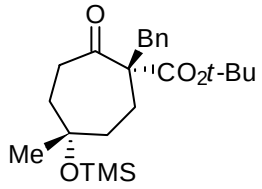
empirical formula	$C_{19}H_{25}BrO_4$
formula weight	397.31
crystal system	monoclinic
space group	C2/c (#15)
a, Å	43.1526(8)
b, Å	11.2187(2)
c, Å	31.5156(6)
β, °	131.9164(7)
V , Å^3	11353.1(4)
Z	24
D_{calc}, g/cm^3	1.395

T, °C	–150
μ (CuKα), cm^{-1}	31.192
no. of reflns meased	62505
no. of reflns obsd	10366
no. of reflns variable	650
R (All reflections)	0.0404
R_w (All reflections)	0.0870
Goodness of Fit	1.094

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 699469). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.



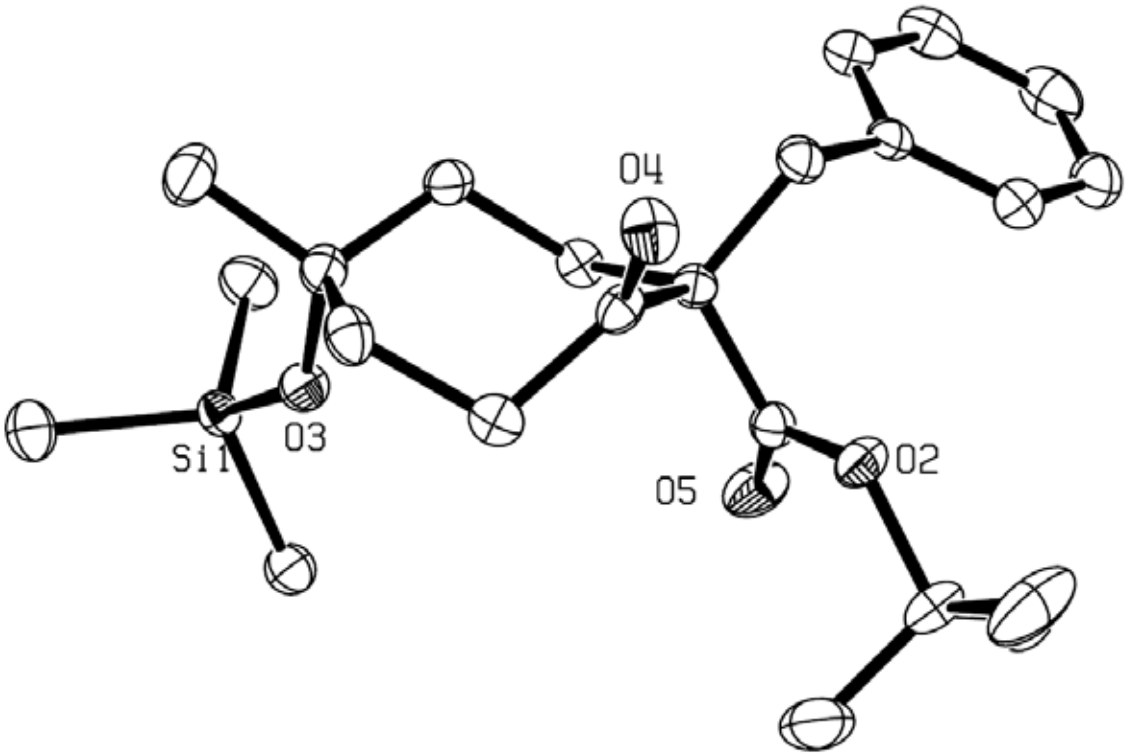
***tert*-Butyl *cis*-1-benzyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (7d).**



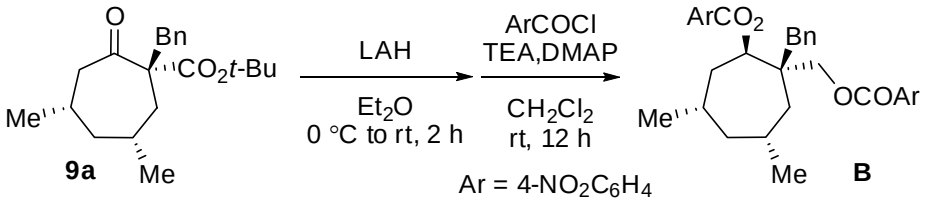
The product **7d** was recrystallized from hexane/CH_2Cl_2. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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	$C_{23}H_{36}O_4Si$
formula weight	404.62
crystal system	monoclinic
space group	P21/n (#14)
a, Å	11.5821(2)
b, Å	10.12751(19)
c, Å	20.1127(4)
β, °	98.0019(11)
V , Å^3	2336.22(8)
Z	4
D_{calc}, g/cm^3	1.150
T, °C	–150
μ (CuKα), cm^{-1}	10.761
no. of reflns meased	22681
no. of reflns obsd	4243
no. of reflns variable	254
R (All reflections)	0.0559
R_w (All reflections)	0.1146
Goodness of Fit	1.082

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 699702). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.


O4
Si1
O3
O5
O2

***tert*-Butyl *cis*-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (9a).**



To a stirred solution of *tert*-butyl *cis*-1-benzyl-4,6-dimethyl-2-oxocycloheptanecarboxylate (181.8 mg, 0.55 mmol) in Et_2O (5 mL), LAH (41.7 mg, 1.1 mmol) was added at 0 °C. The suspension was warmed up to room temperature and stirred for 2 h. The reaction mixture was slowly quenched with 15% NaOH (41 μL), H_2O (41 μL), and 15 % NaOH (123 μL). After stirring for 5 min, the residue was filtrated through the celite pad and the solvent was evaporated. The crude material was used in the next step without further purification.

To a stirred solution of the crude material (ca. 0.55 mmol) in CH_2Cl_2, DMAP (33.6 mg, 0.28 mmol), TEA (383 μL, 2.8 mmol), and *p*-nitrobenzoyl chloride (408 mg, 2.2. mmol) were added at room temperature and the reaction mixture was stirred for 12 h at the same temperature. The reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4 and evaporated. The residue was purified by flash column chromatography to afford the compound **B**.

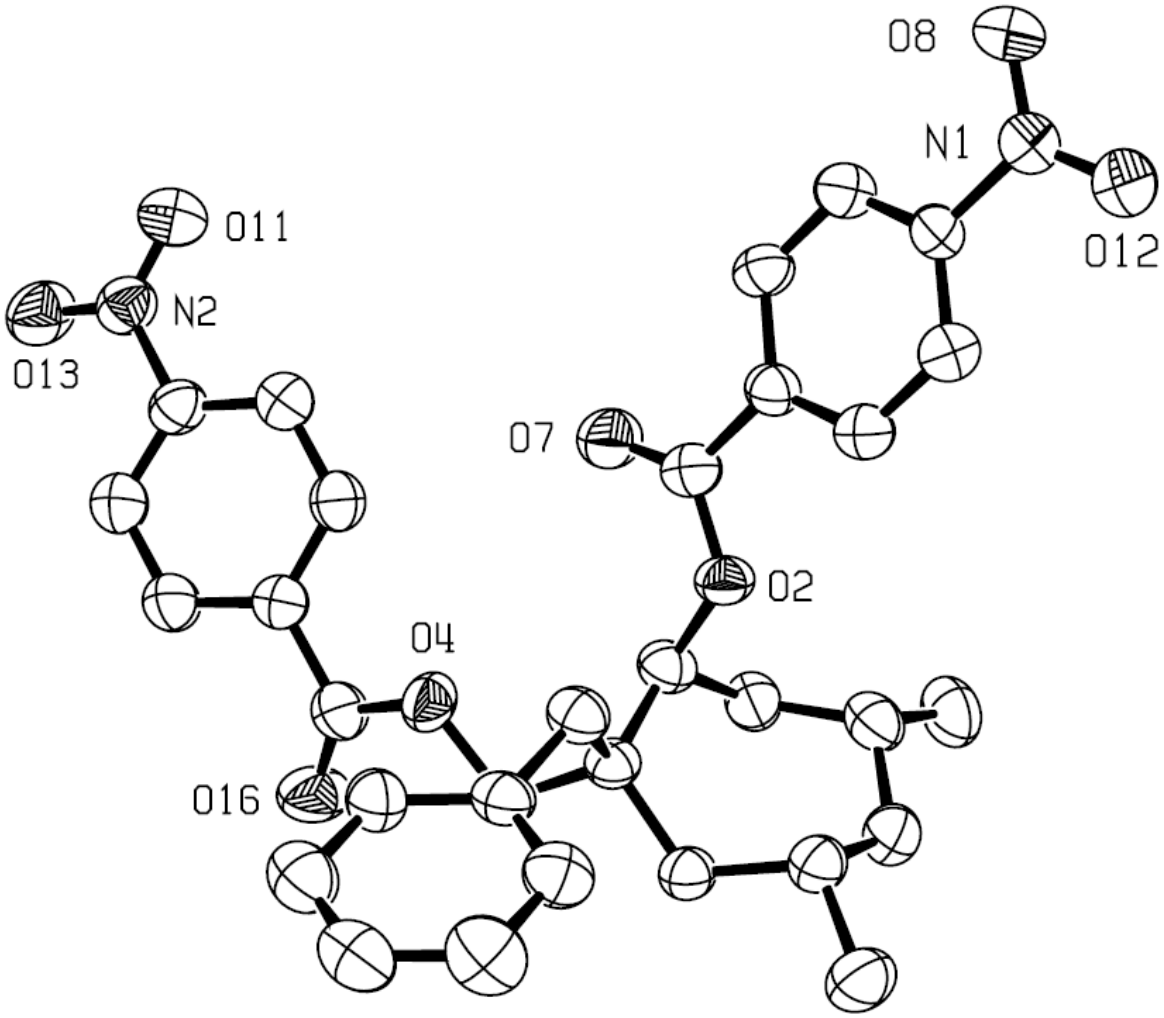
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06-8.38 (8H, m, Ar**H**), 7.10-7.40 (8H, m, Ar**H**), 5.63 (1H, dd, *J* = 9.2, 2.0 Hz, OC**H**), 4.08 (2H, s, OC**H**$_2$), 3.03 (2H, s, PhC**H**$_2$), 2.31 (1H, m, *c*-Hep), 1.94-2.20 (2H, m, *c*-Hep), 1.81 (1H, dd, *J* = 14.0, 4.4 Hz, *c*-Hep), 0.8-1.28 (3H, m, *c*-Hep), 1.06 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$), 1.03 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 163.7, 150.7, 150.6, 136.9, 135.6, 135.2, 130.7, 130.6, 128.4, 126.7, 123.70, 123.67, 75,5, 69.1, 46.8, 44.6, 41.9, 37.3, 35.9, 28.7, 28.5, 25.1, 23.9 ;IR (neat) 2953, 2926, 1721, 1526, 1346, 1269, 1115, 1101, 1015, 718 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{31}H_{32}N_2O_8$: *m/z* 583.2051 ([M + Na]$^+$), found: *m/z* 583.2058 ([M + Na]$^+$).

The product **B** was recrystallized from hexane/CH_2Cl_2. The single crystal was mounted on a MicroMesh^{TM} (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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.

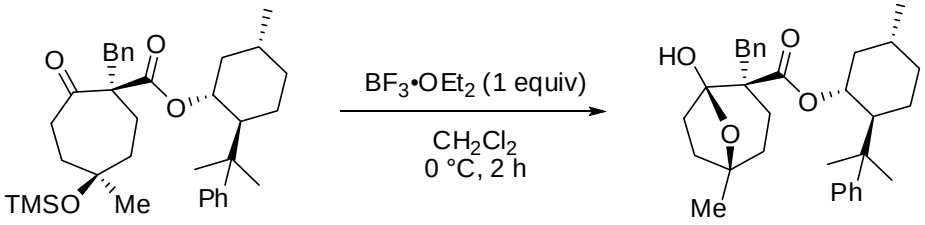
empirical formula	$C_{31}H_{32}O_8N_2$
formula weight	560.60
crystal system	orthorhombic
space group	P212121 (#19)
a, Å	13.3018(3)
b, Å	14.3633(3)

c, Å	29.3280(6)
V , Å^3	5603.32(20)
Z	8
D_{calc}, g/cm^3	1.329
T, °C	–150
μ (CuKα), cm^{-1}	7.994
no. of reflns meased	57031
no. of reflns obsd	10202
no. of reflns variable	740
R (All reflections)	0.0925
R_w (All reflections)	0.1771
Goodness of Fit	1.089

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 695532). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.



(1*R*,2*S*,5*R*)-8-Phenylmenthyl
(1*R*,2*R*,5*R*)- 2-benzyl-1-hydroxy-5-methyl-8-oxabicyclo[3.2.1]octane-2-carboxylate (12).



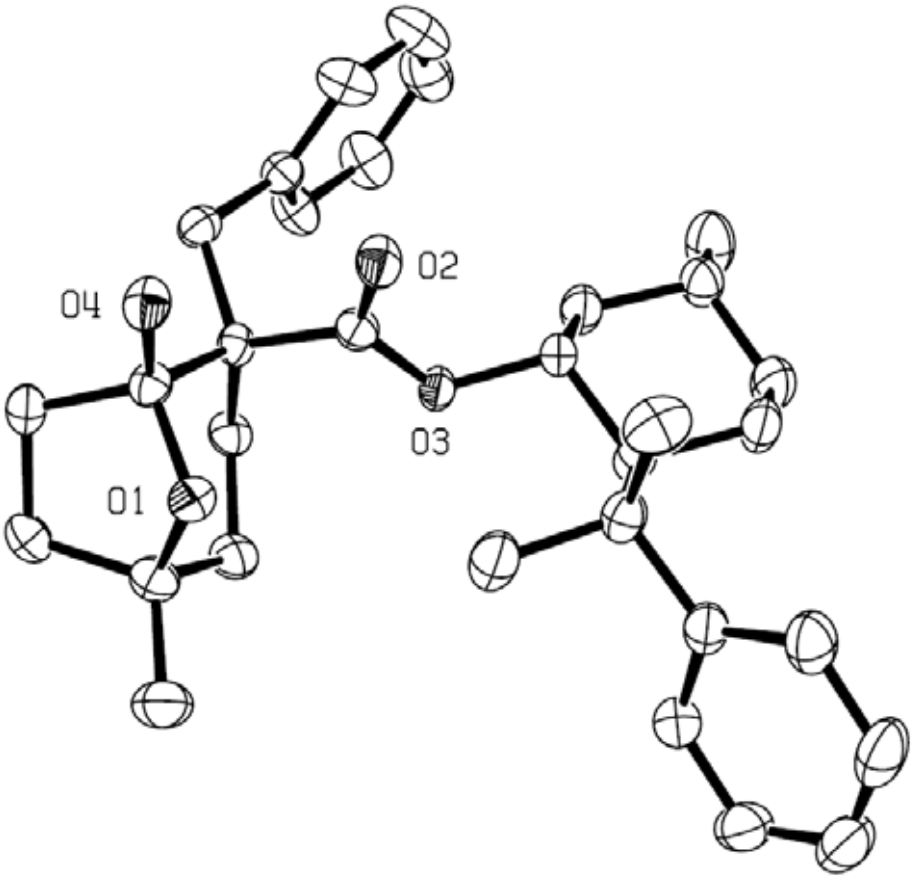
11c **12**

To a stirred solution of (1*R*,2*S*,5*R*)-8-phenylmenthyl (1*R*,5*S*)-1-benzyl-5-methyl-2-oxo-5-(trimethylsilyloxy)cycloheptanecarboxylate (34.2 mg, 0.061 mmol) and in dichloromethane (1.0 mL) was added $BF_3{\cdot}OEt_2$ (7.7 μL, 0.061 mmol) at 0 °C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 2 h. 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 to give the bicyclic compound.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04-7.40 (10H, m, Ar**H**), 5.79 (1H, s, O**H**), 5.04 (1H, app dt, *J* = 10.8, 4.4 Hz, OC**H**), 3.06 (1H, d, *J* = 14.0 Hz, PhC**H**H), 2.61 (1H, d, *J* = 14.0 Hz, PhCH**H**), 2.11-2.22 (2H, m, Cy), 1.74-1.99 (4H, m, Cy), 1.51-1.66 (3H, m, Cy), 1.12-1.50 (4H, m, Cy), 1.41 (3H, s, C**H**$_3$), 1.32 (3H, s, C**H**$_3$), 1.25 (3H, s, C**H**$_3$), 0.94 (1H, m, Cy), 0.60-0.78 (2H, m, Cy), 0.72 (3H, d, *J* = 6.8 Hz, CHC**H**$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.3, 150.7, 136.1, 130.7, 128.2, 128.1, 126.8, 125.5, 107.0, 82.4, 77.4, 54.7, 50.2, 41.4, 41.0, 40.4, 34.8, 34.1, 33.2, 31.2, 30.1, 27.6, 27.3, 26.2, 24.0, 21.5; IR (neat) 3420, 2959, 2926, 1678, 1454, 1225, 1182, 1099, 1055, 912 cm^{-1}; HRMS (ESI) exact mass calcd. for $C_{32}H_{42}O_4Si$: *m/z* 513.2975 ([M + Na]$^+$), found: *m/z* 513.2971 ([M + Na]$^+$); $[\alpha]_D^{29}$ = –8.1 (*c* = 1.0, $CHCl_3$).
The product **12** was recrystallized from methanol. The single crystal was mounted on a MicroMesh™ (MiTeGen). Data of X-ray diffraction were collected by a Rigaku RAXIS-RAPID Imaging Plate two-dimensional area detector using graphite-monochromated CuKa (l = 1.54187 Å) to a maximam 2θ value of 136.5°. The crystal structure was solved by the direct methods and refined by the full-matrix least squares using the program SHELXL-97.[4] 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	$C_{32}H_{42}O_4$
formula weight	490.68
crystal system	monoclinic
space group	C2 (#5)
a, Å	21.8528(4)
b, Å	6.46778(12)

c, Å	19.9076(4)
β, °	98.2792(11)
V , Å^3	2784.40(9)
Z	4
D_{calc}, g/cm^3	1.170
T, °C	–150
μ (CuKα), cm^{-1}	5.930
no. of reflns meased	14614
no. of reflns obsd	4977
no. of reflns variable	326
R (All reflections)	0.0496
R_w (All reflections)	0.1072
Goodness of Fit	1.064

The crystal structure has been deposited at the Cambridge Crystallographic Data Centre (CCDC 705655). The data can be obtained free of charge via the Internet at www.ccdc.cam.ac.uk/conts/retrieving.html.



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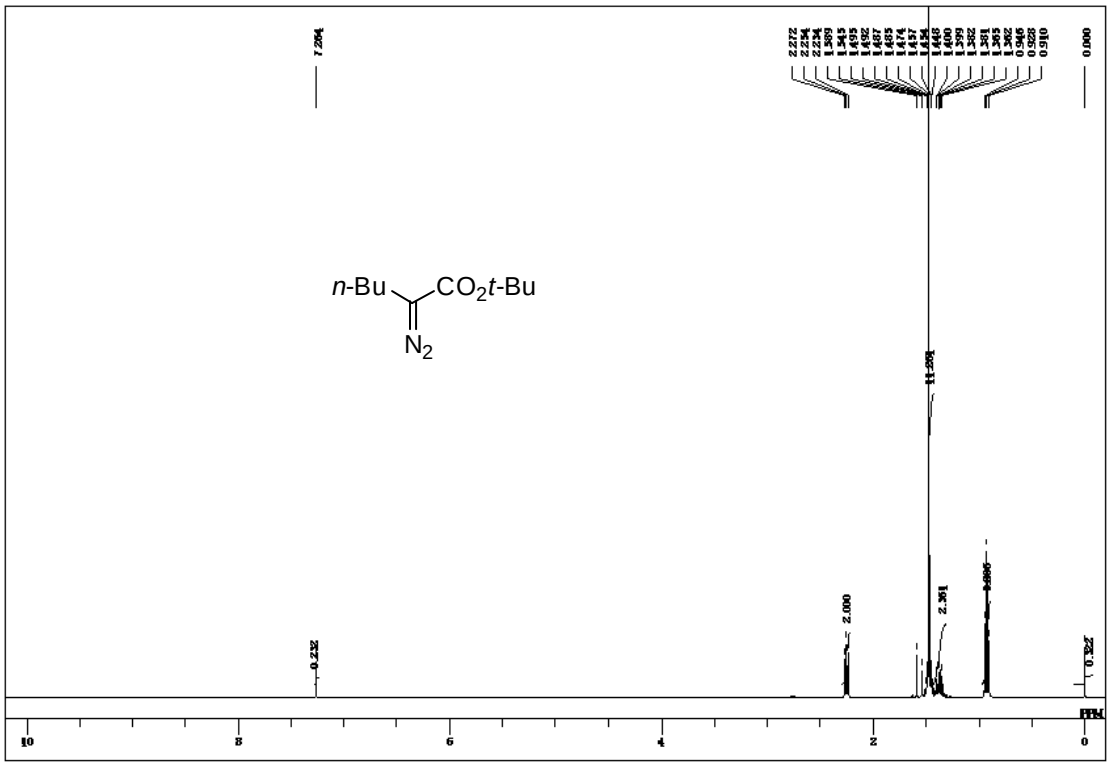
·Complete list of authors in ref 1b.

Kirk R. Gustafson, John H. Cardellina II, James B. McMahon, Robert J. Gulakowski, Junichi Ishitoya, Zoltan Szallasi, Nancy E. Lewin, Peter M. Blumberg, Owen S. Weislow, John A. Beutler, Robert W. Buckheit, Jr., Gordon M. Cragg, Paul A. Cox, John P. Bader, Michael R. Boyd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1.400
1.399
1.382
1.361
1.353
1.362
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0.928
0.910
0.000
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0.227
PPM
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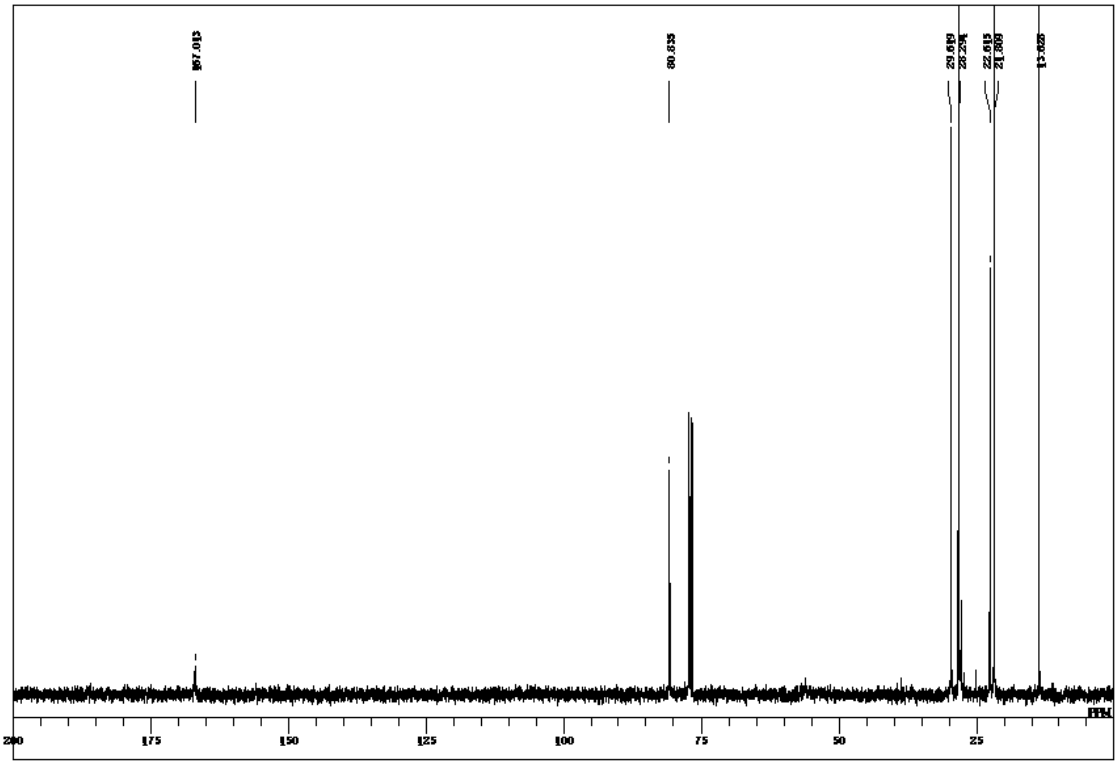
8
6
4
2
0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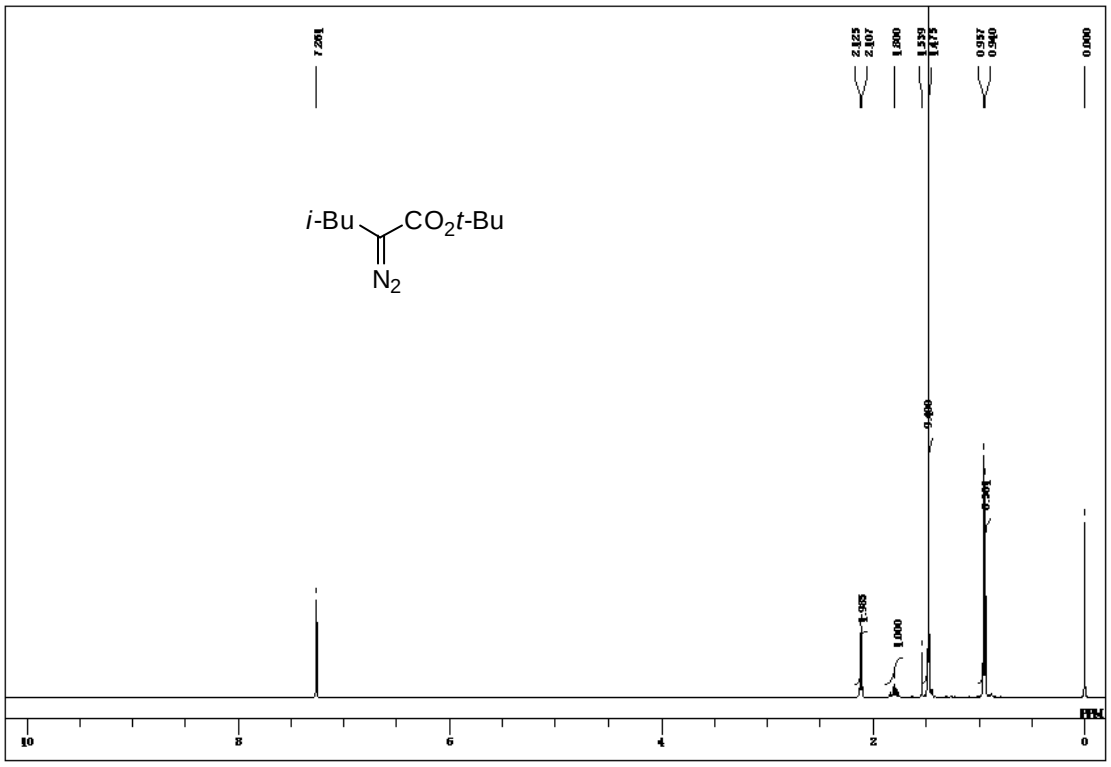
75
50
25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10
8
6
4
2
0
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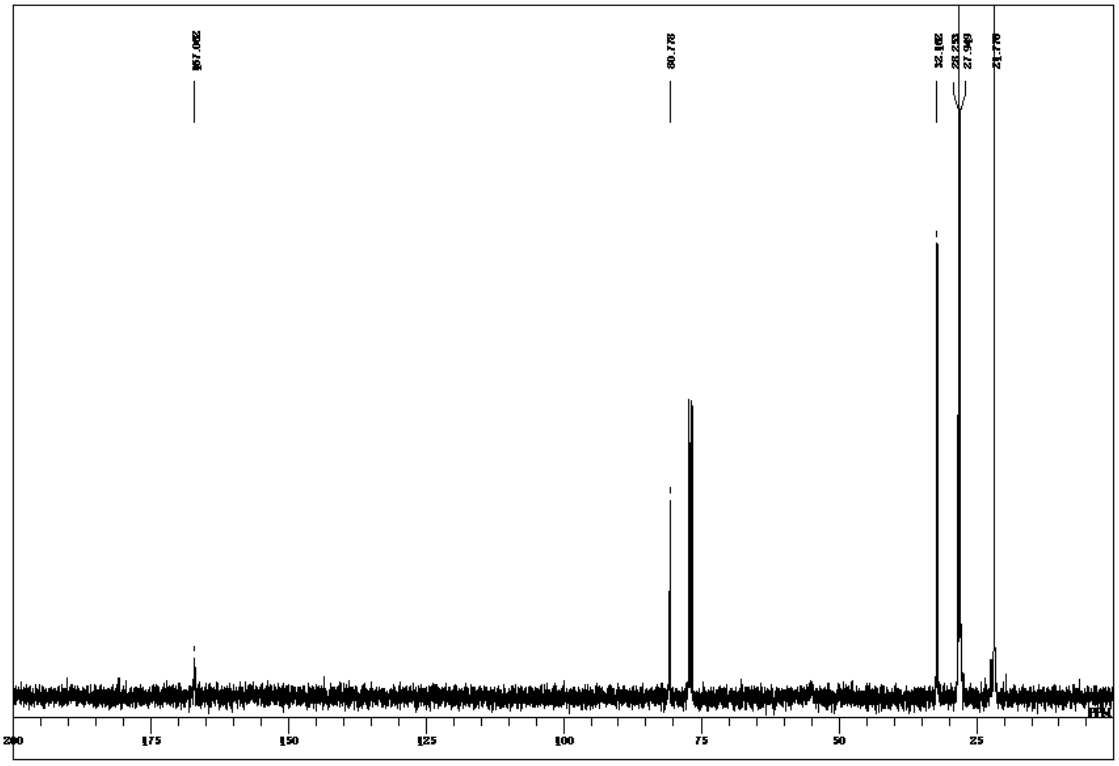
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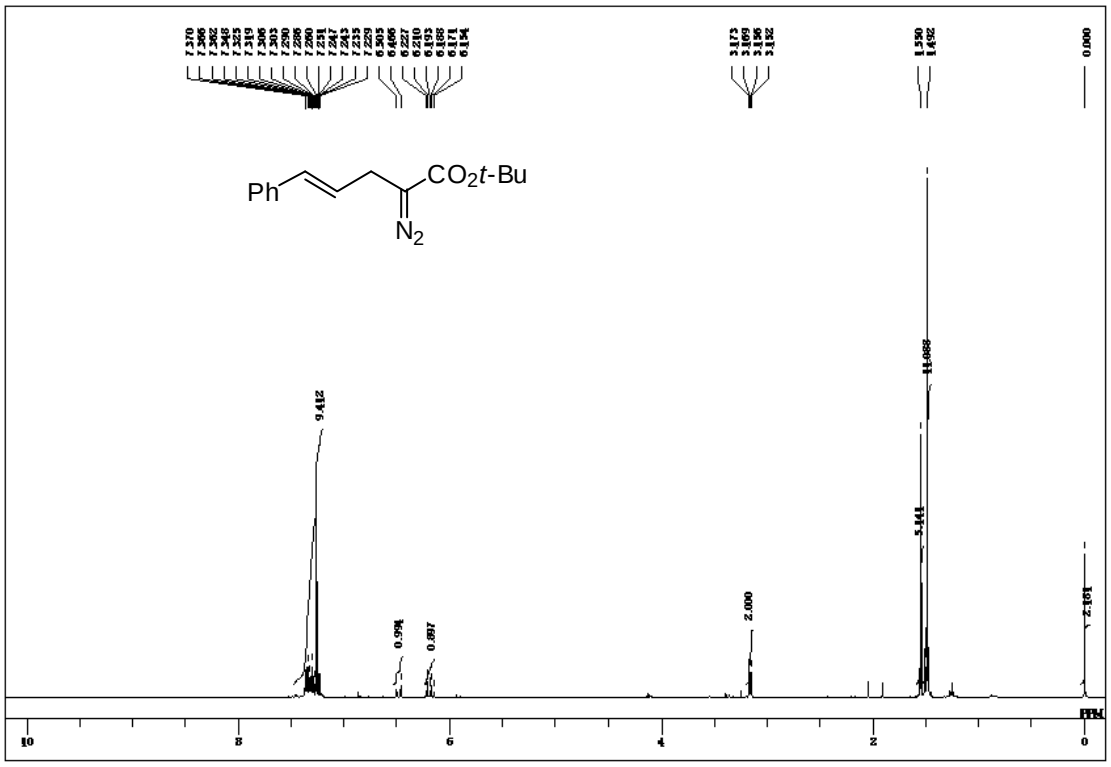
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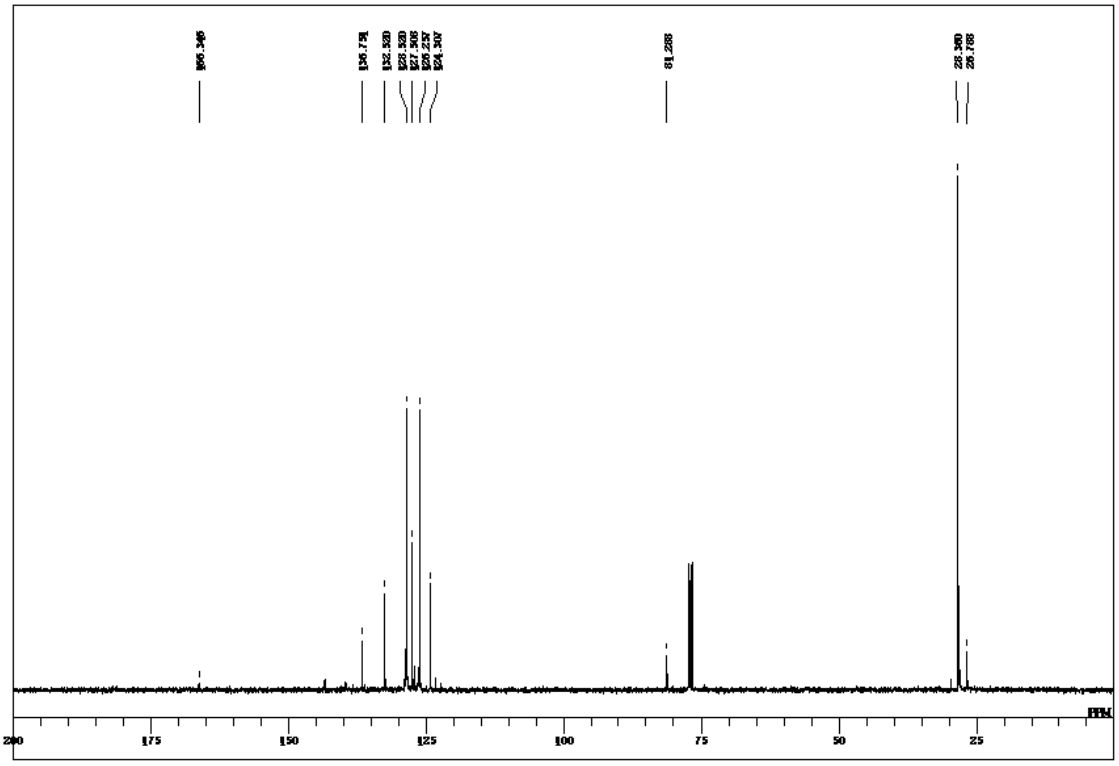
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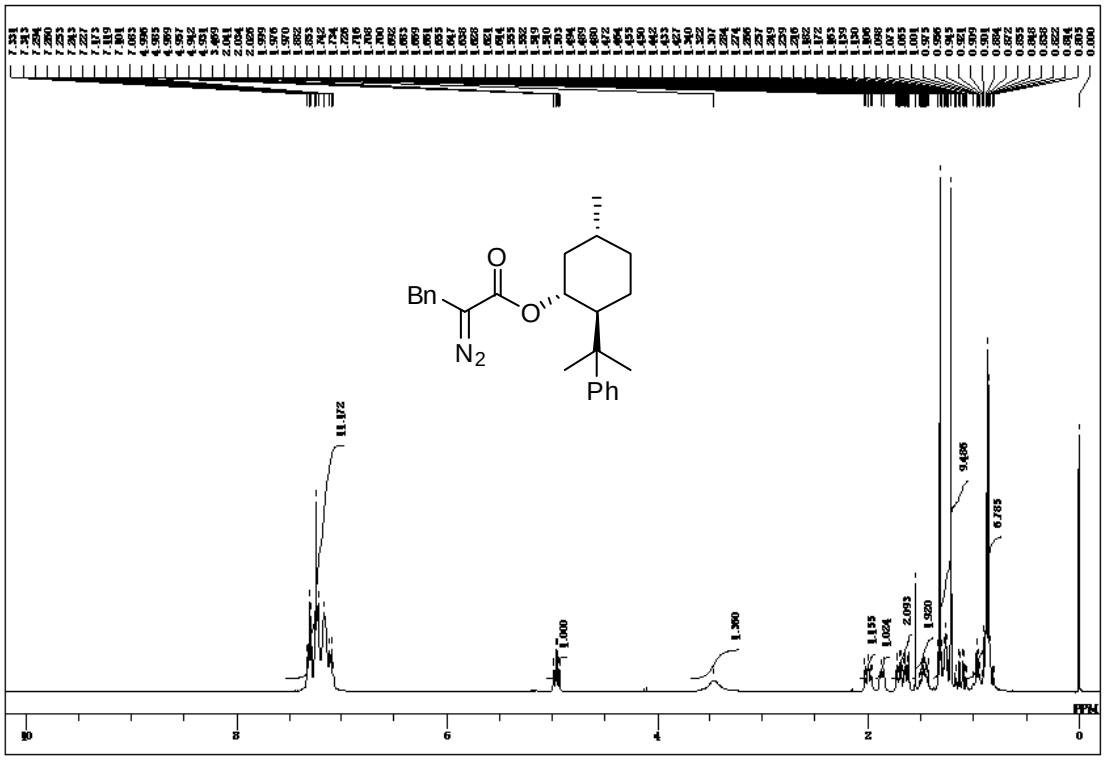
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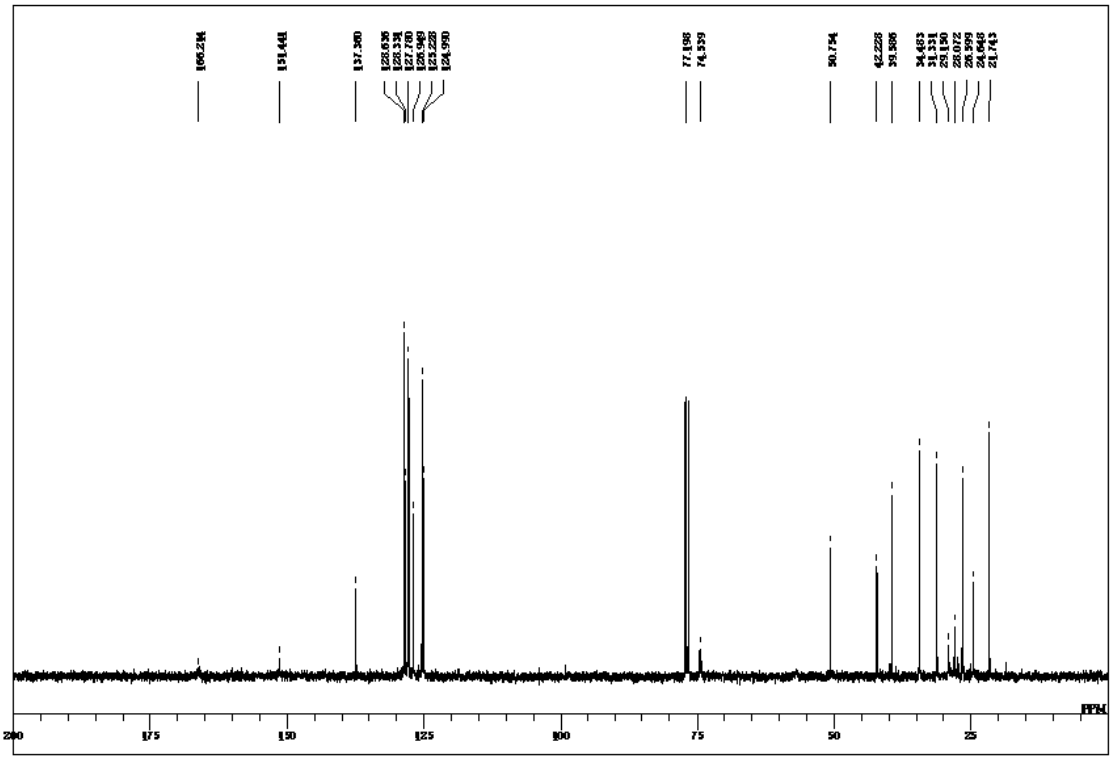
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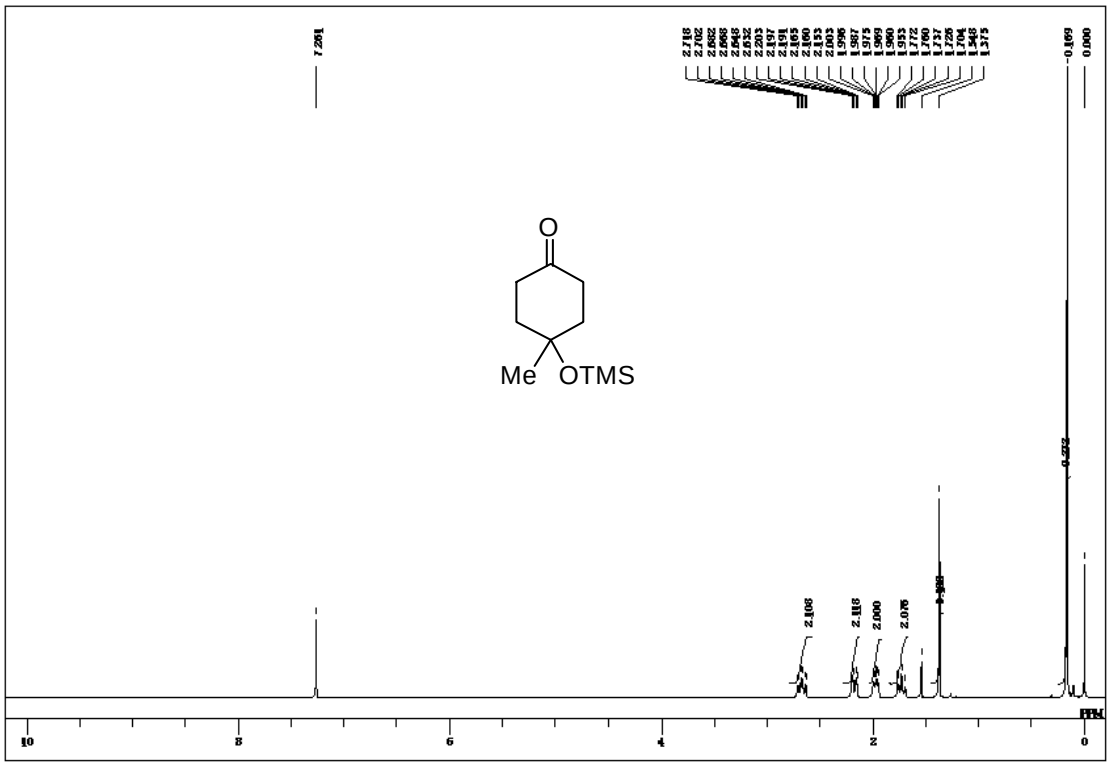
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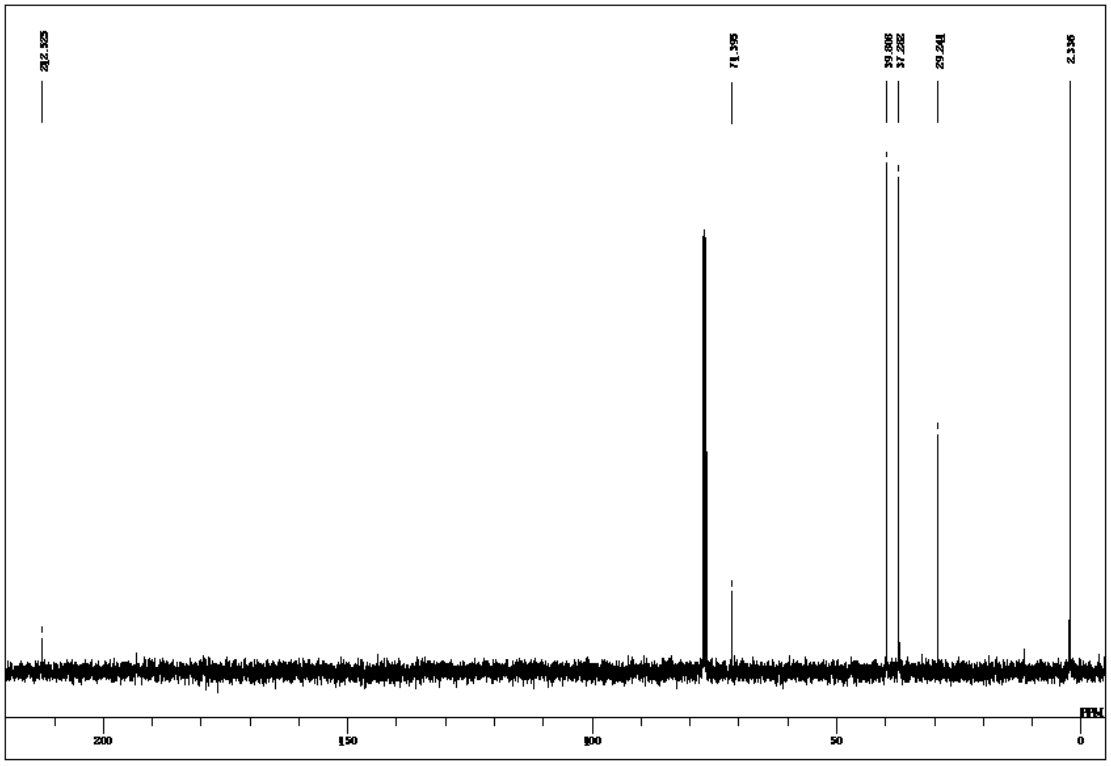

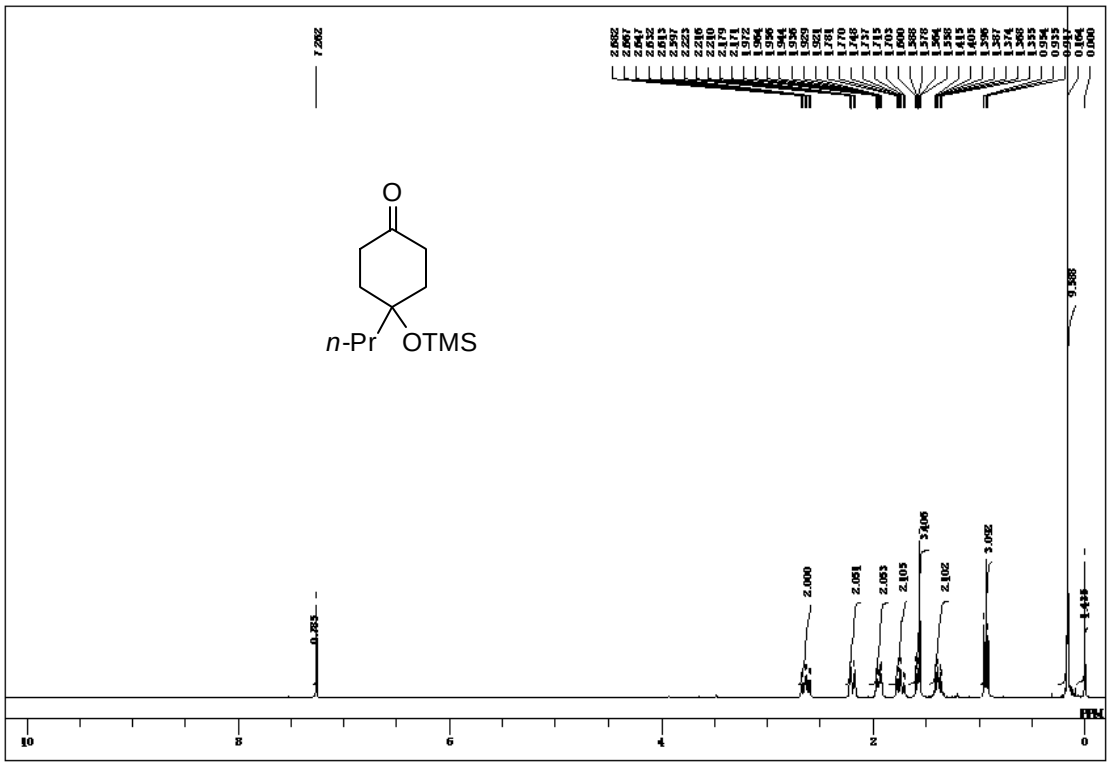
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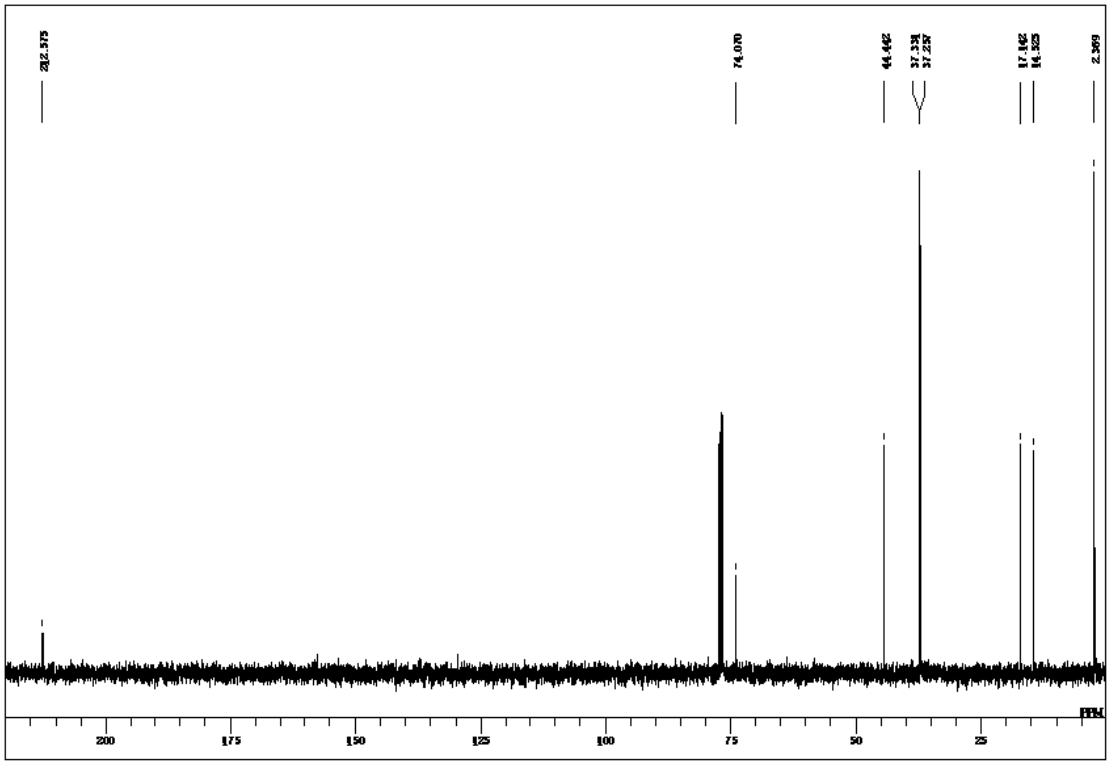
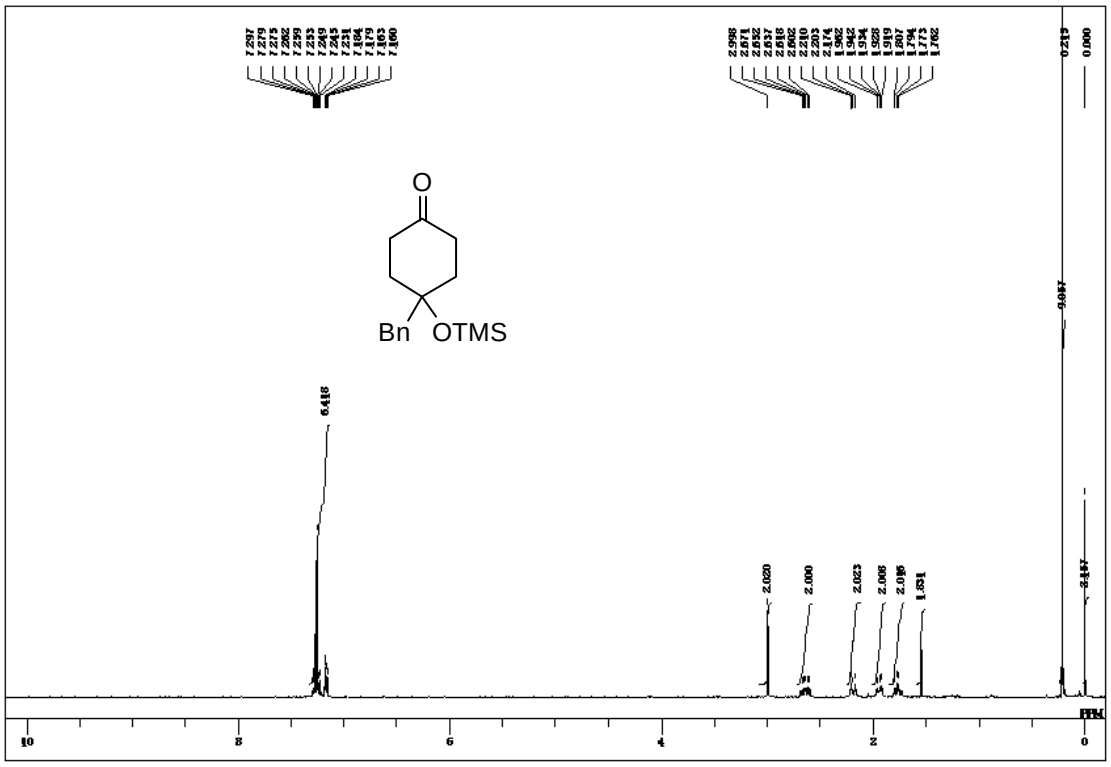
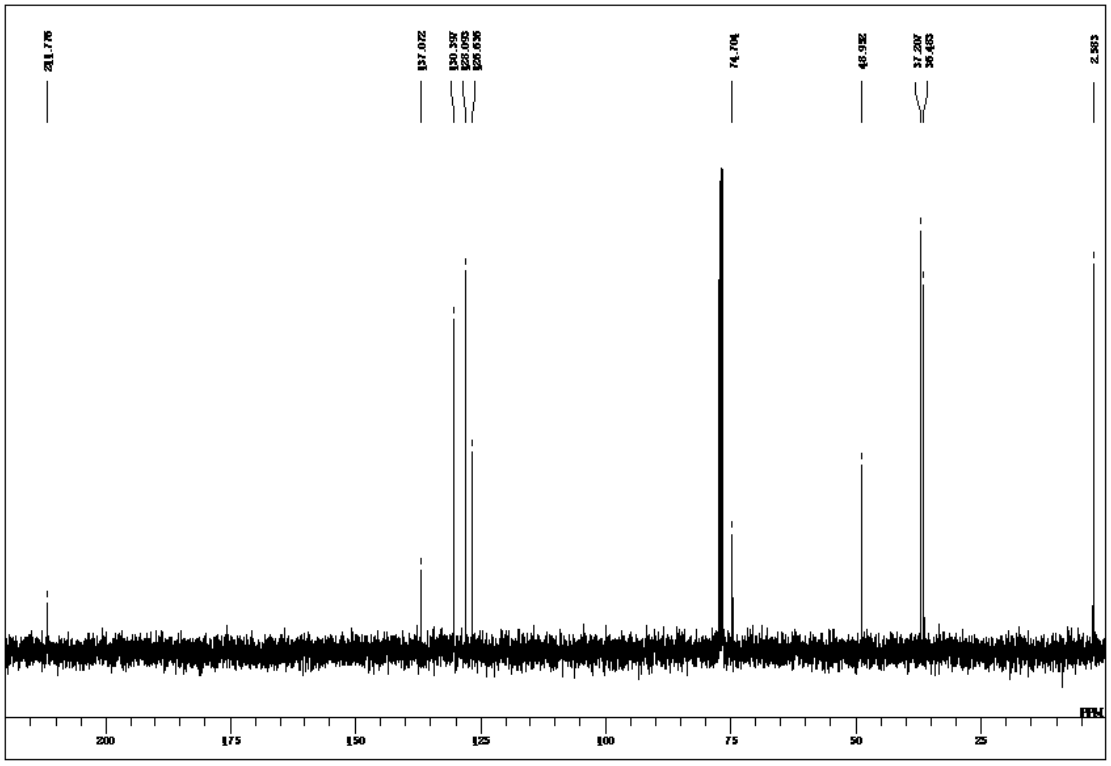
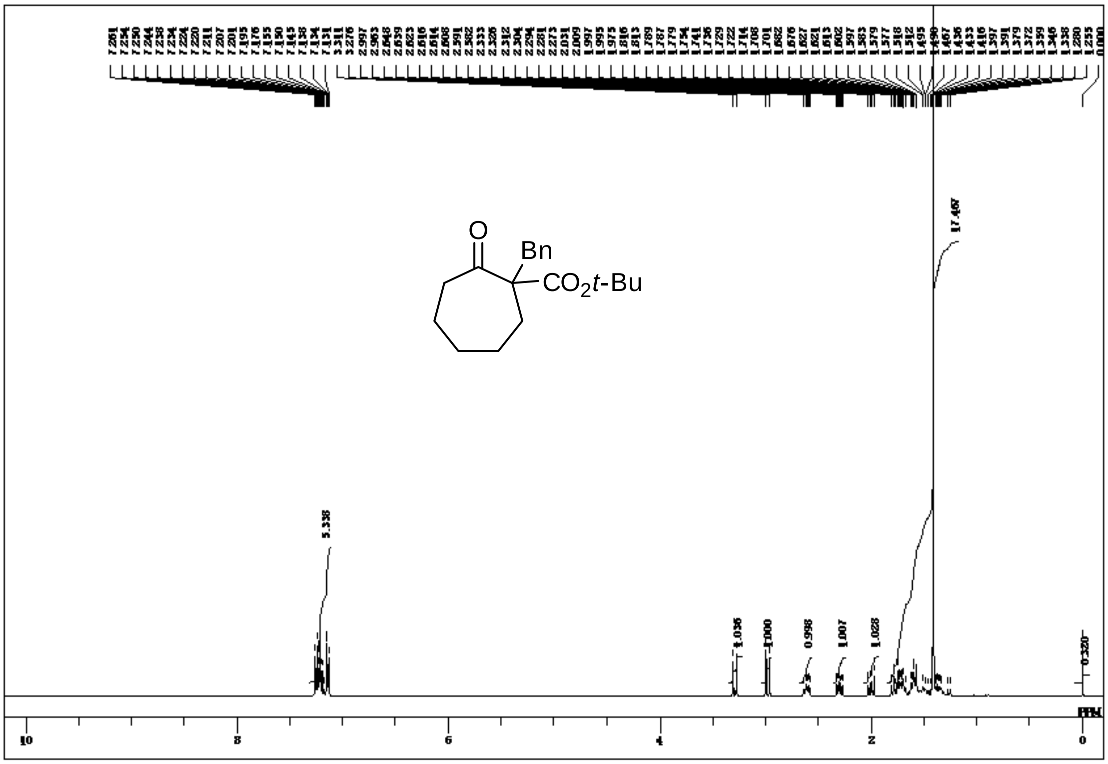
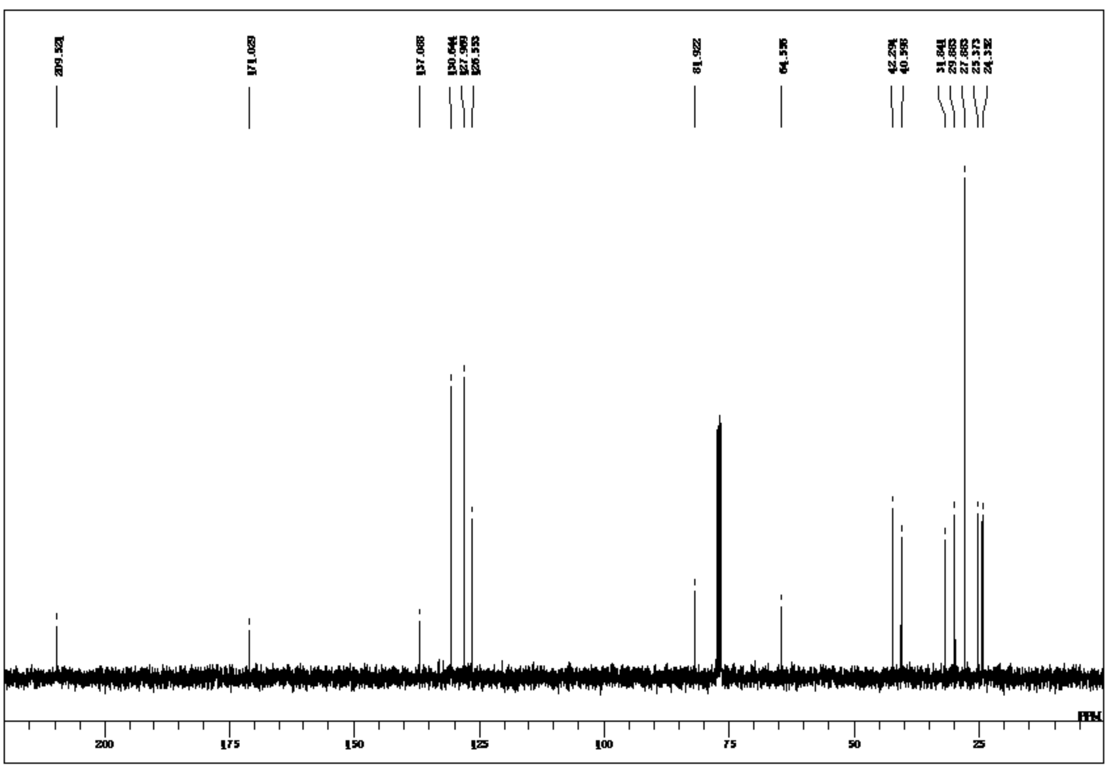
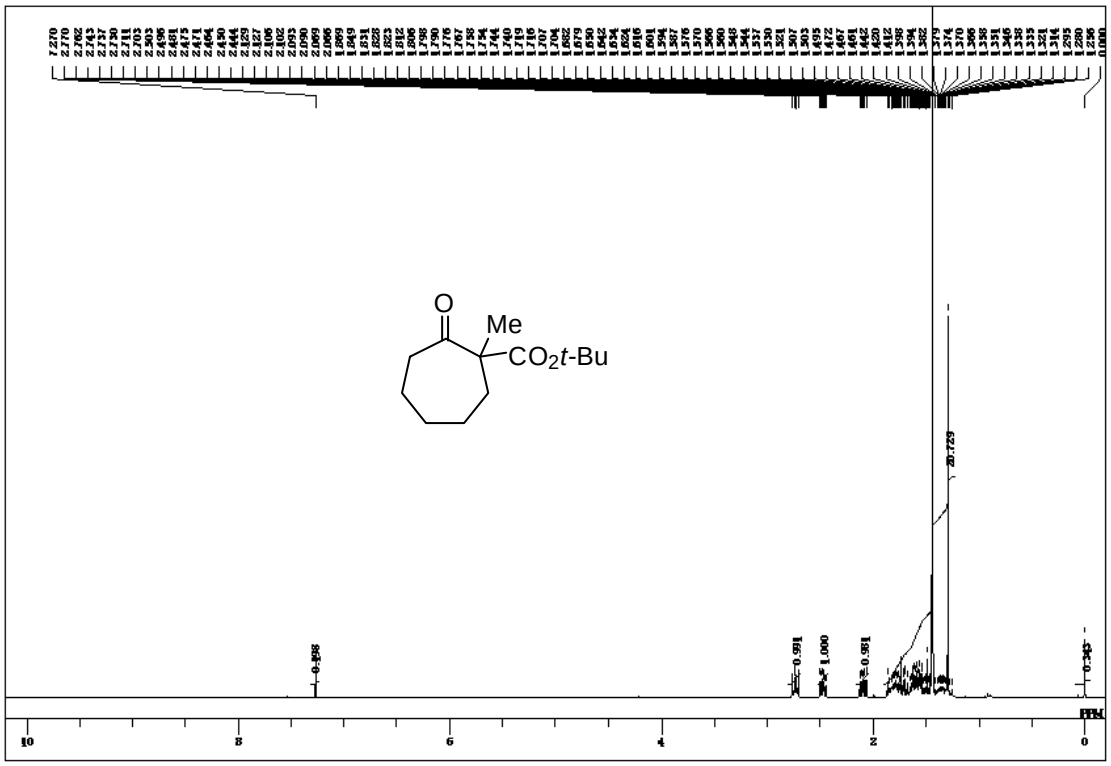



O
Bn OTMS





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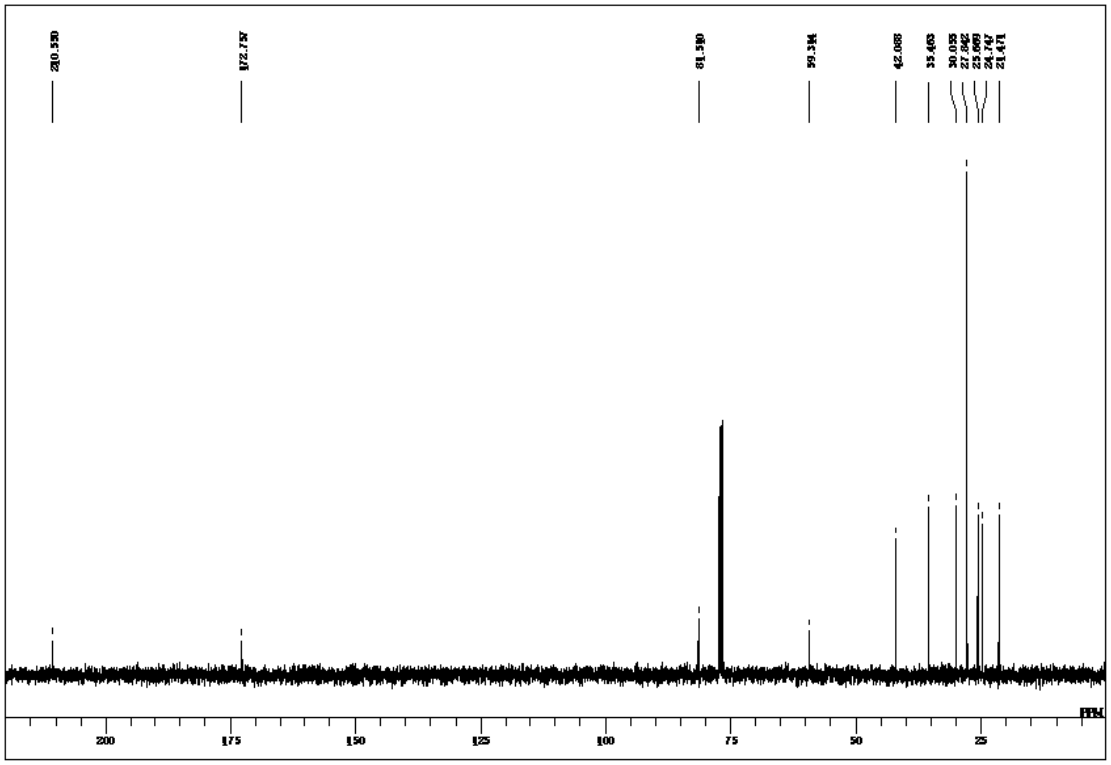
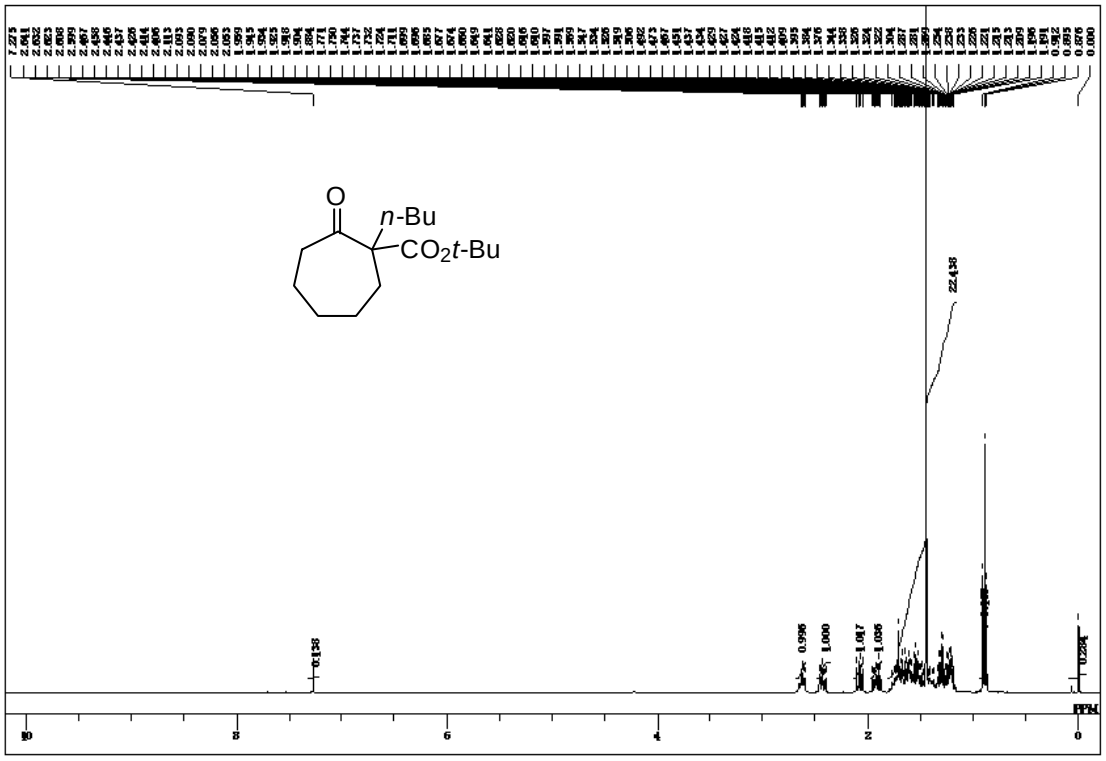
Me
CO2t-Bu

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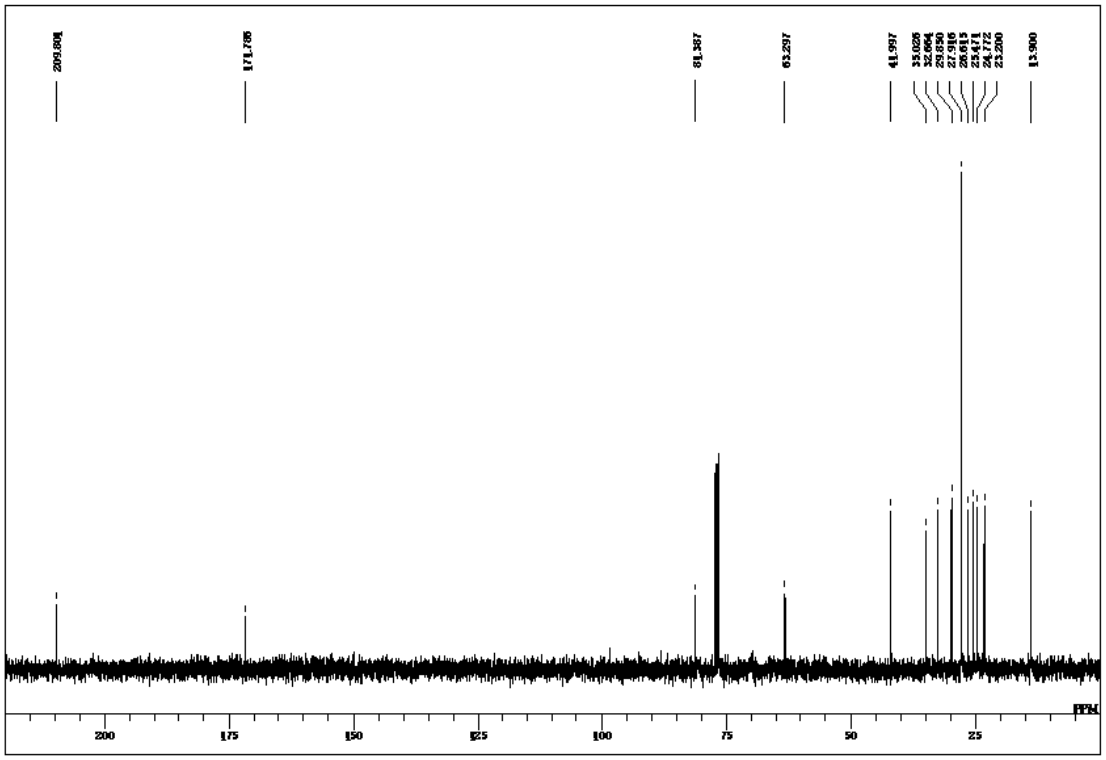
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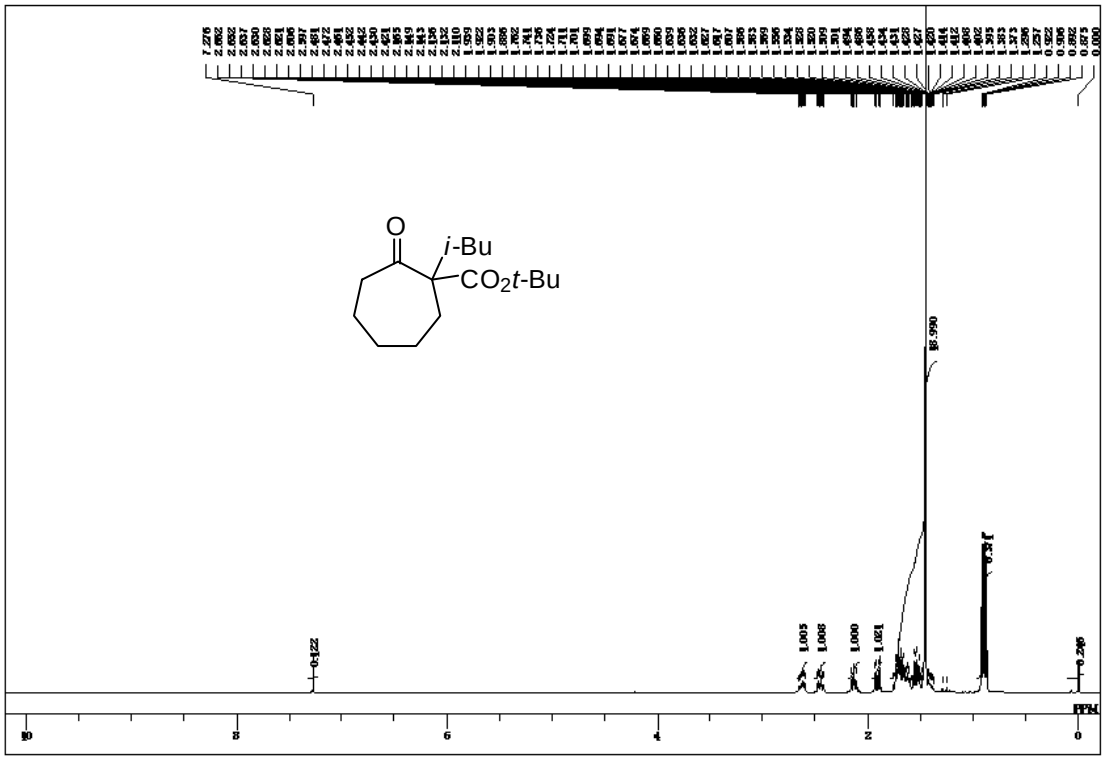
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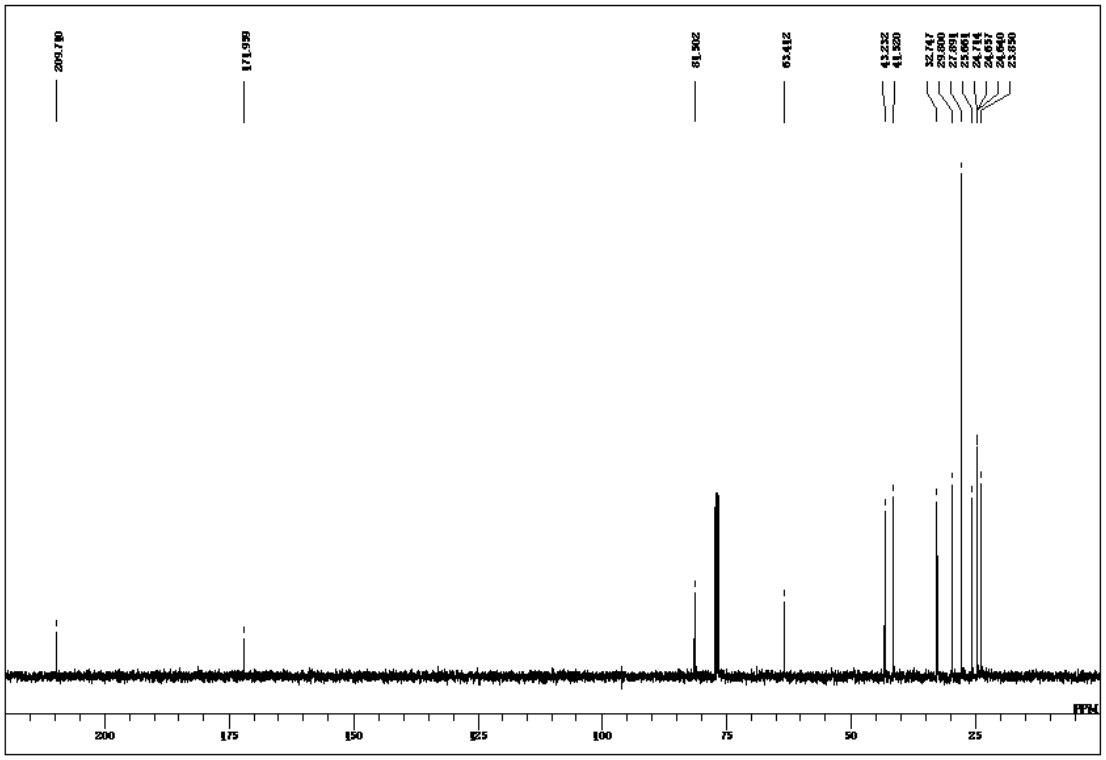
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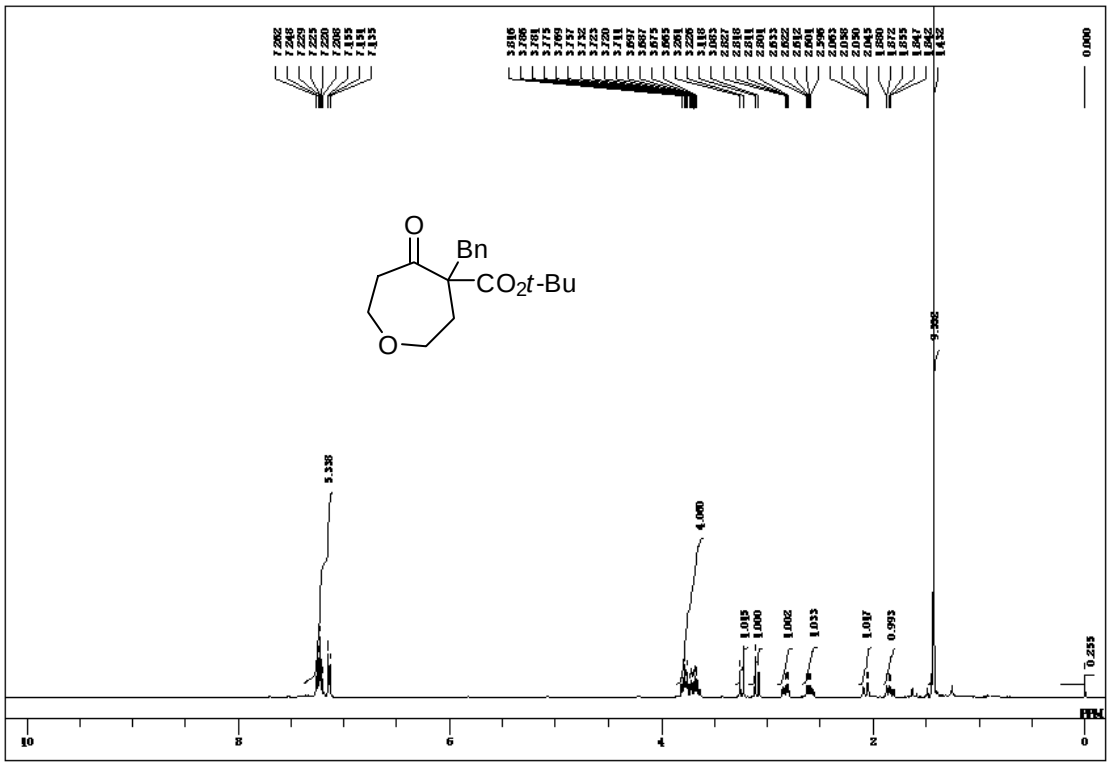
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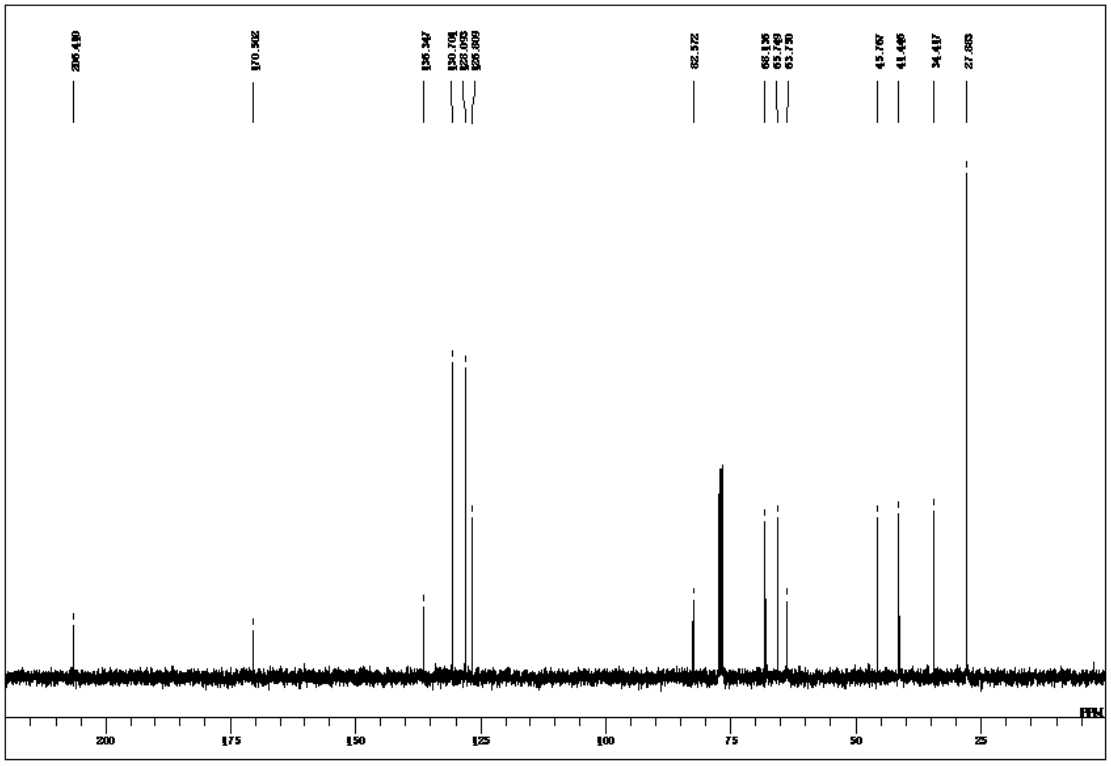
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50
25
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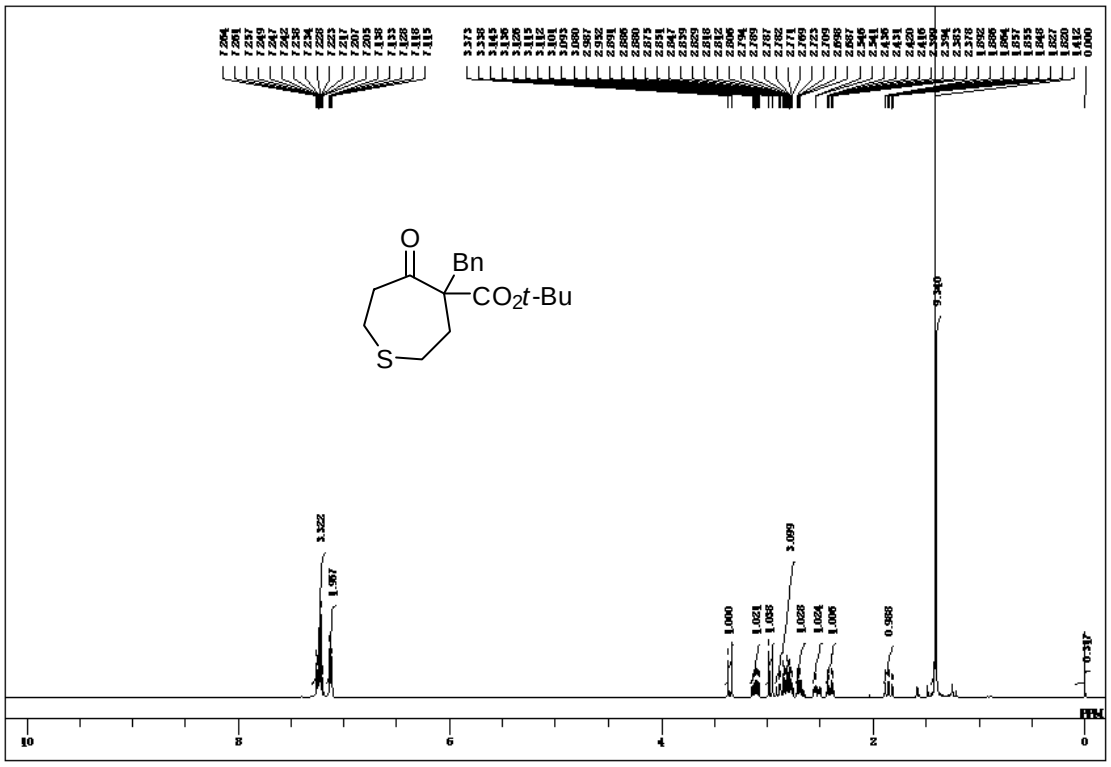
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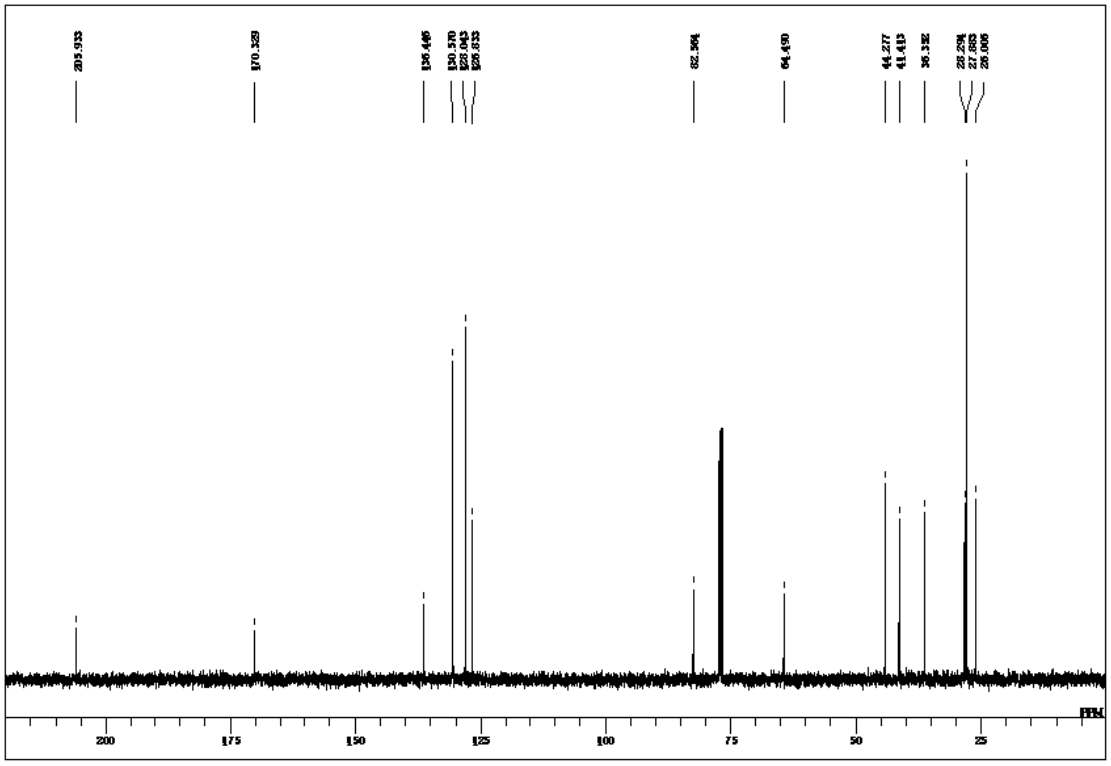

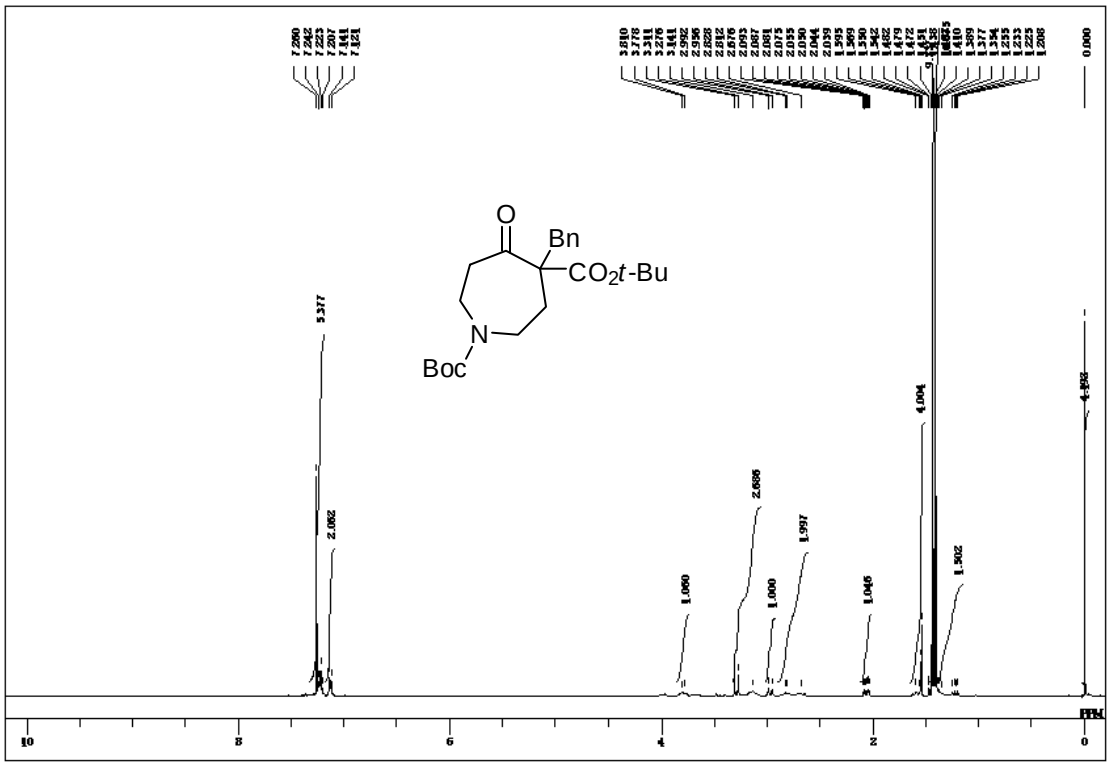
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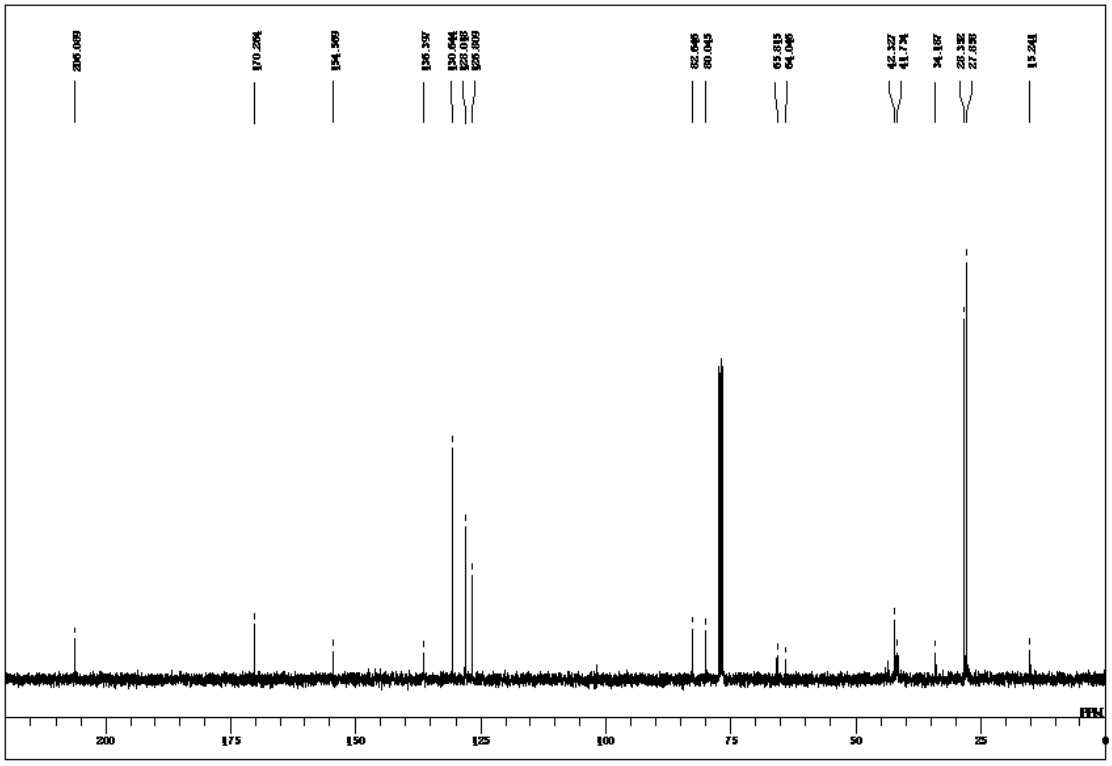
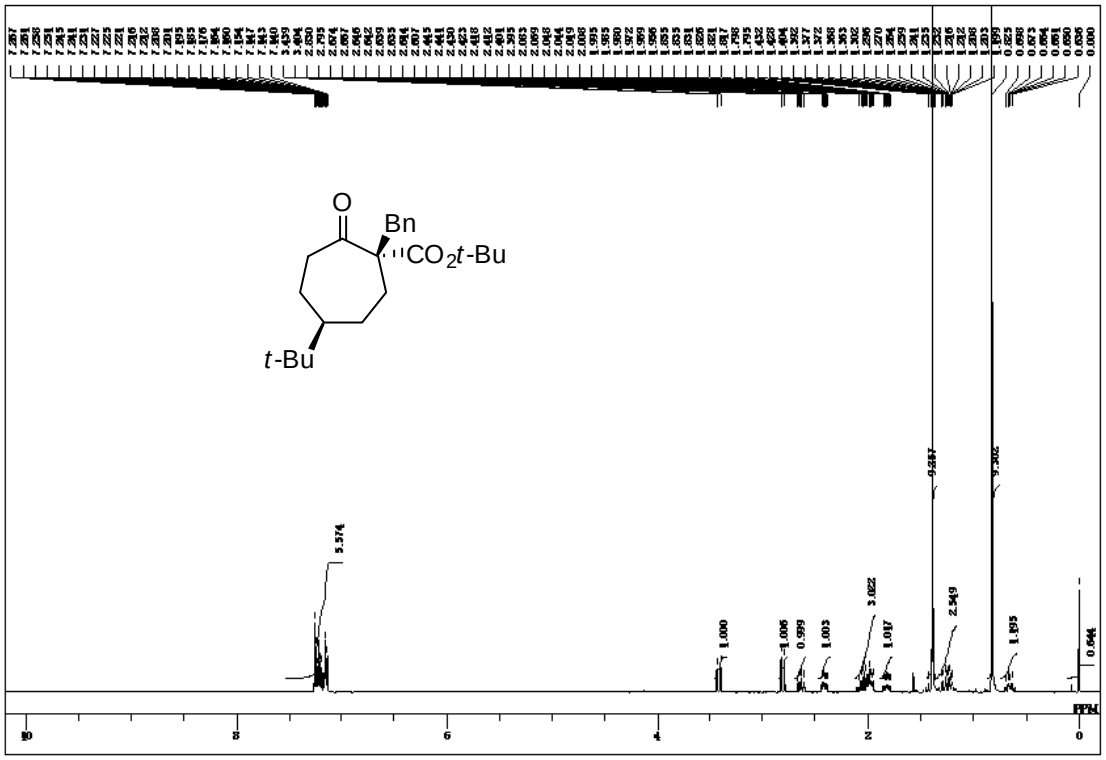
N
Boc

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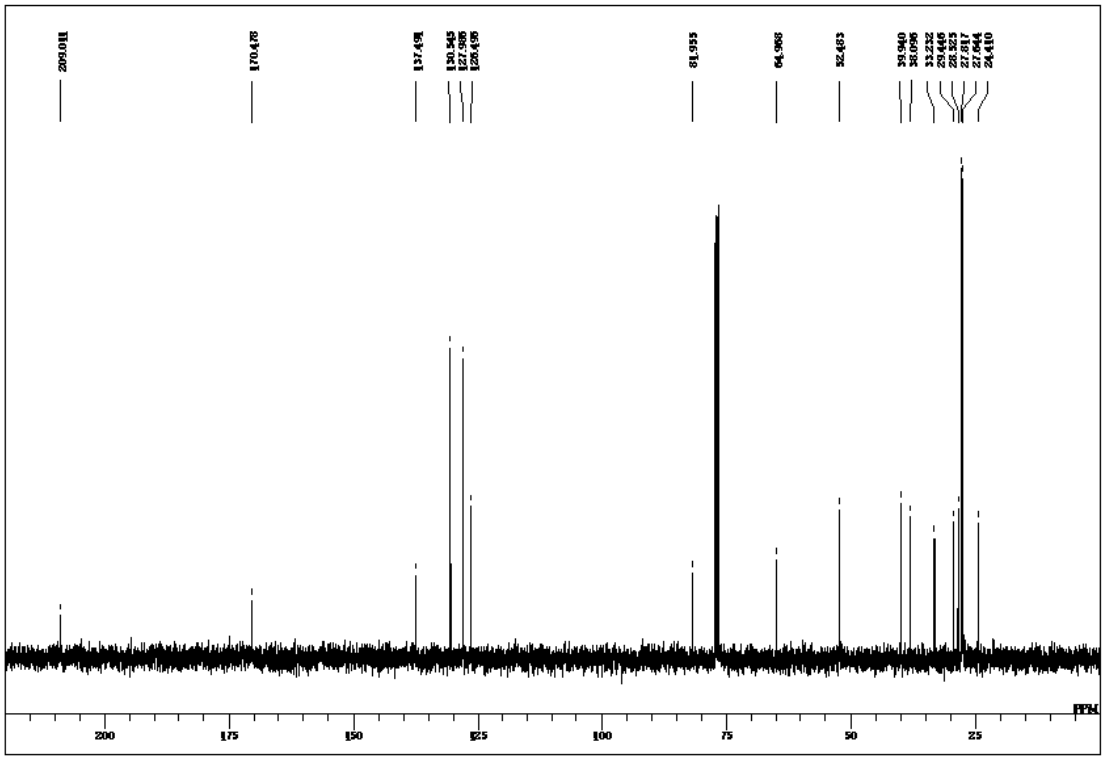
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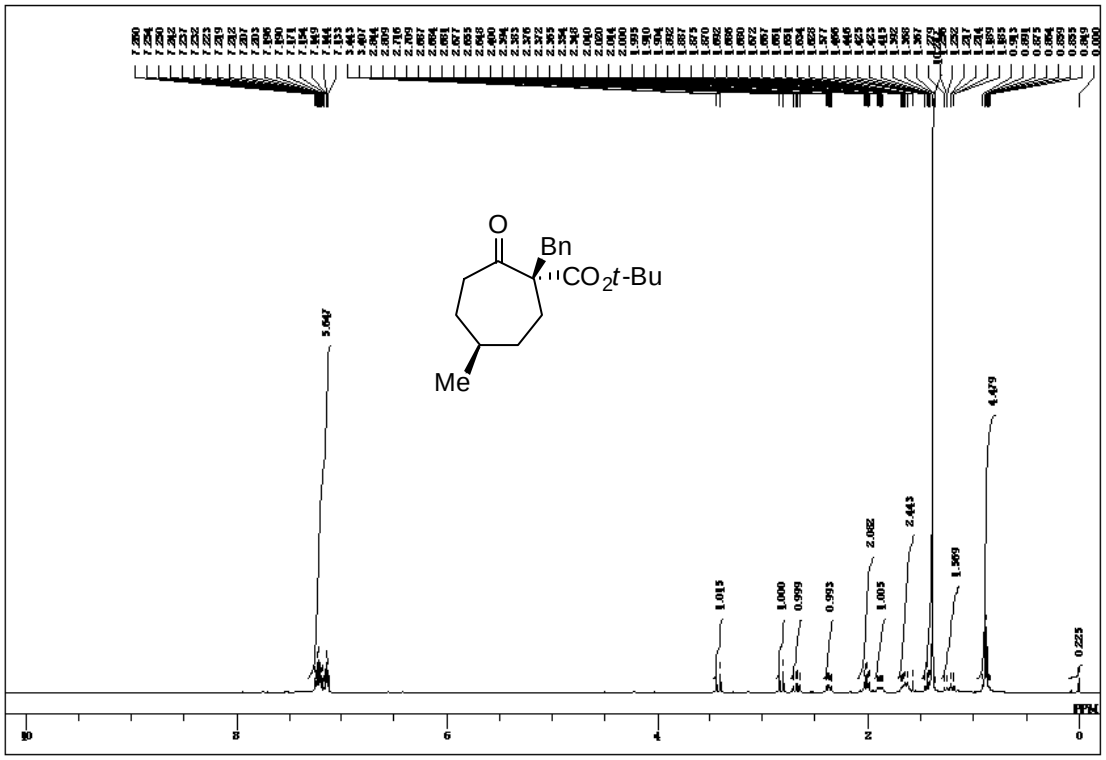
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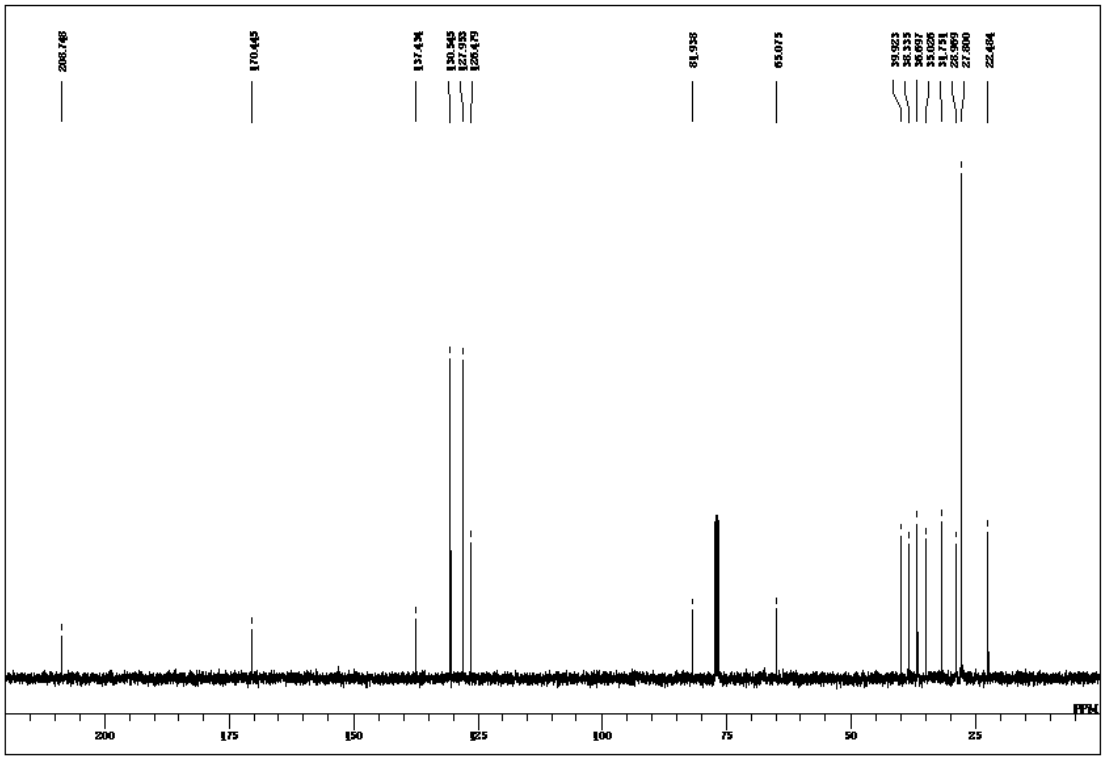
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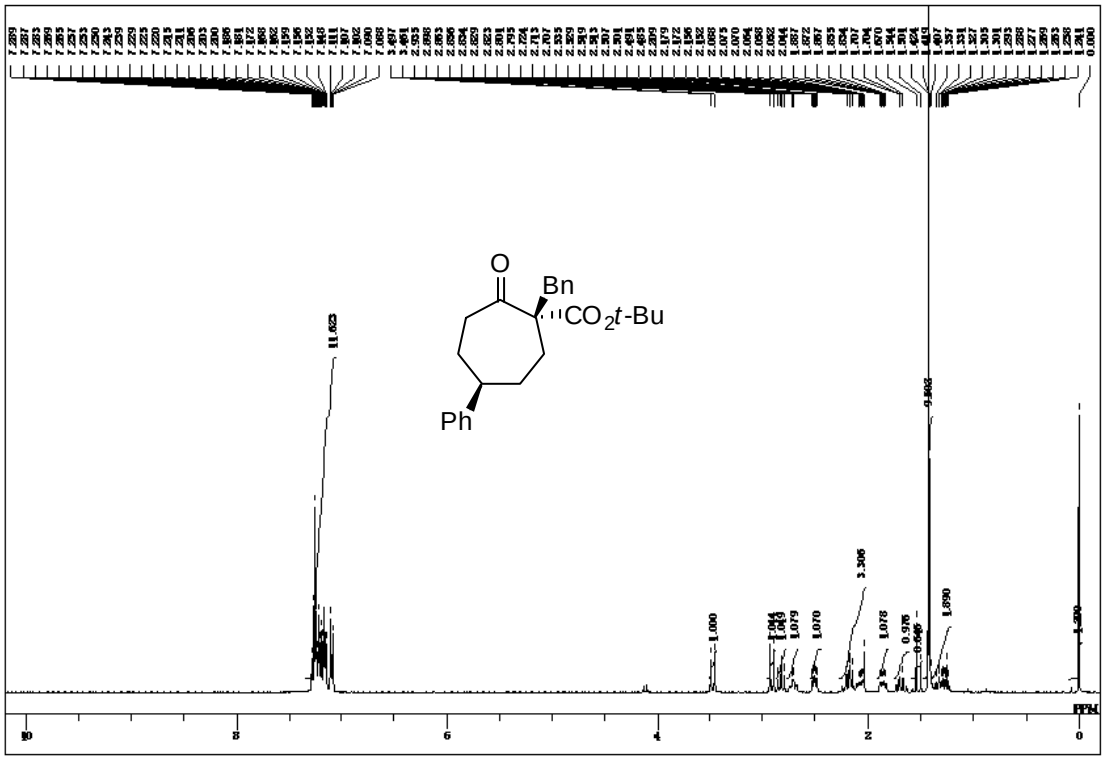
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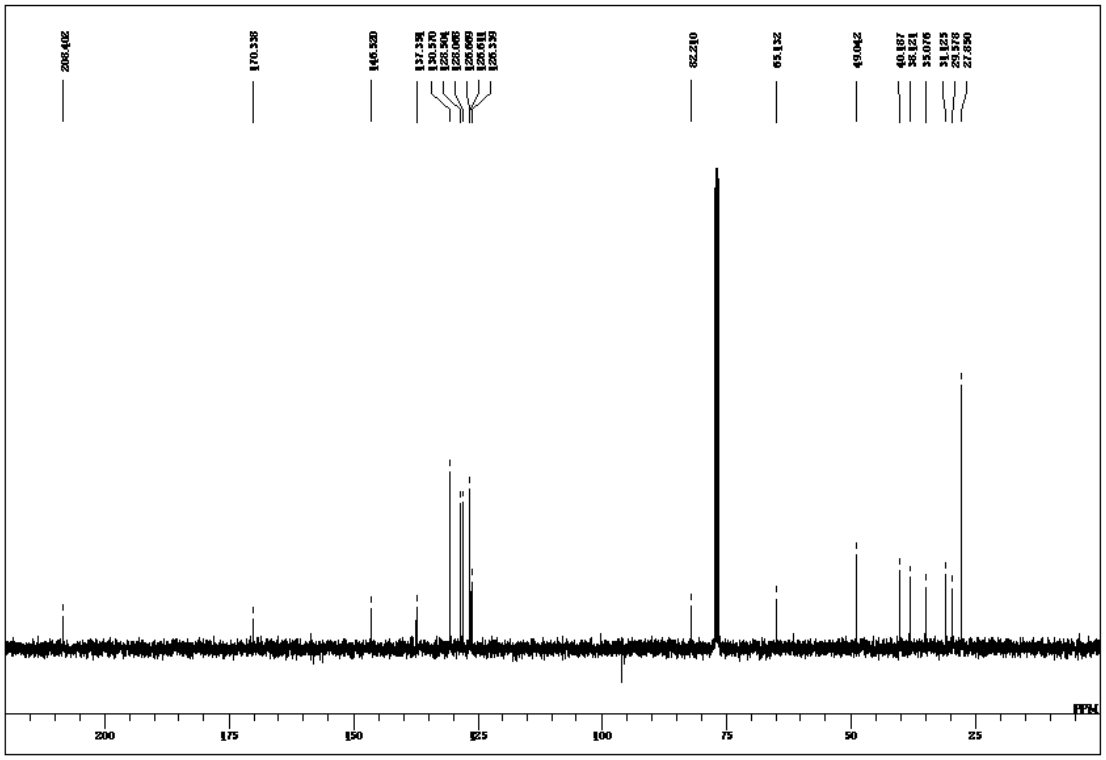
10
8
6
4
2
0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40.187
35.821
33.076
31.625
28.338
27.830
PPM
200
175
150
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100
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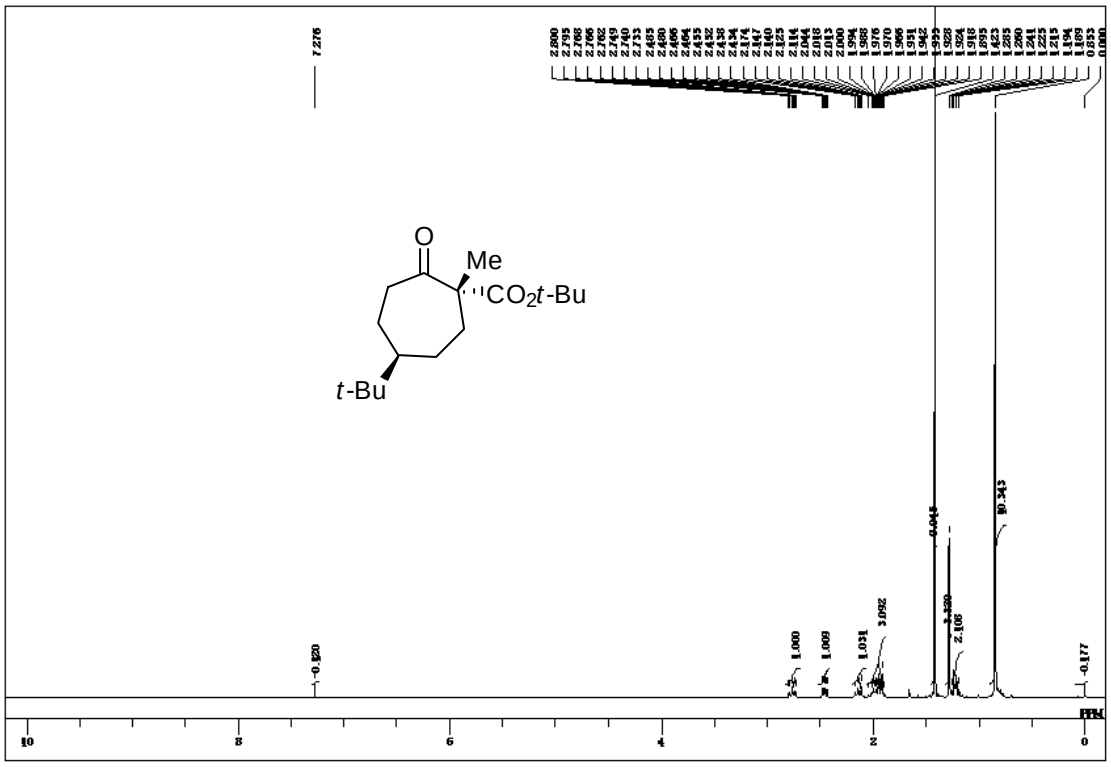
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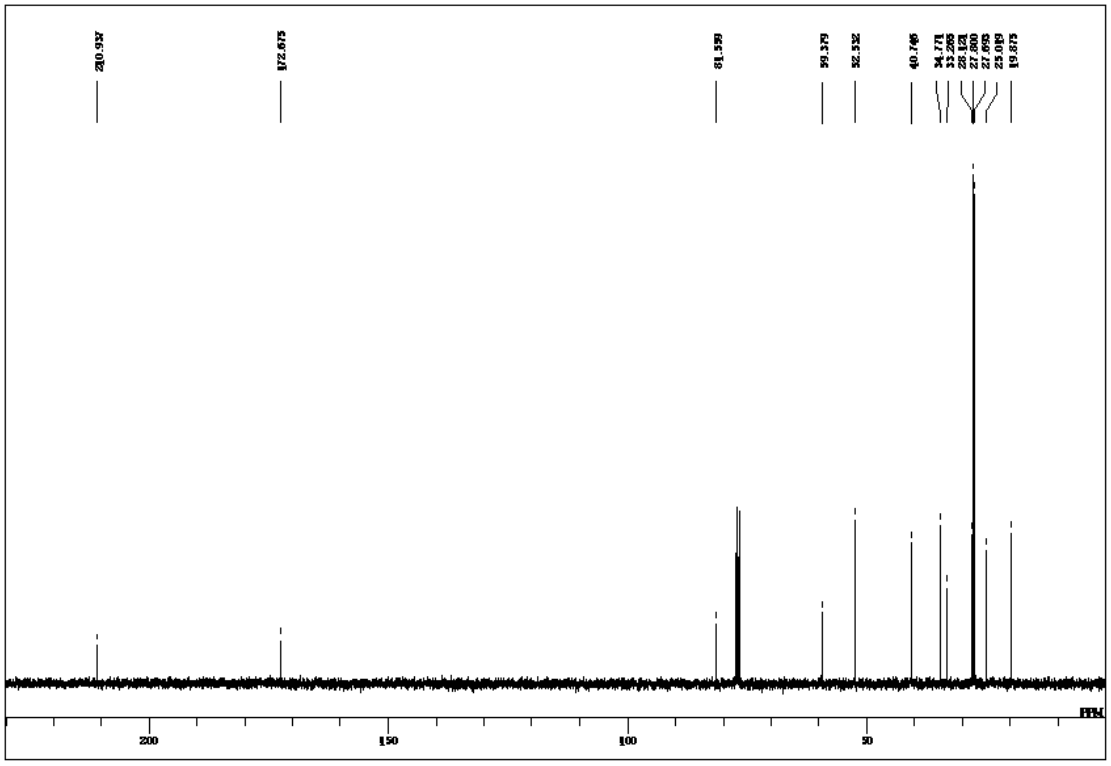
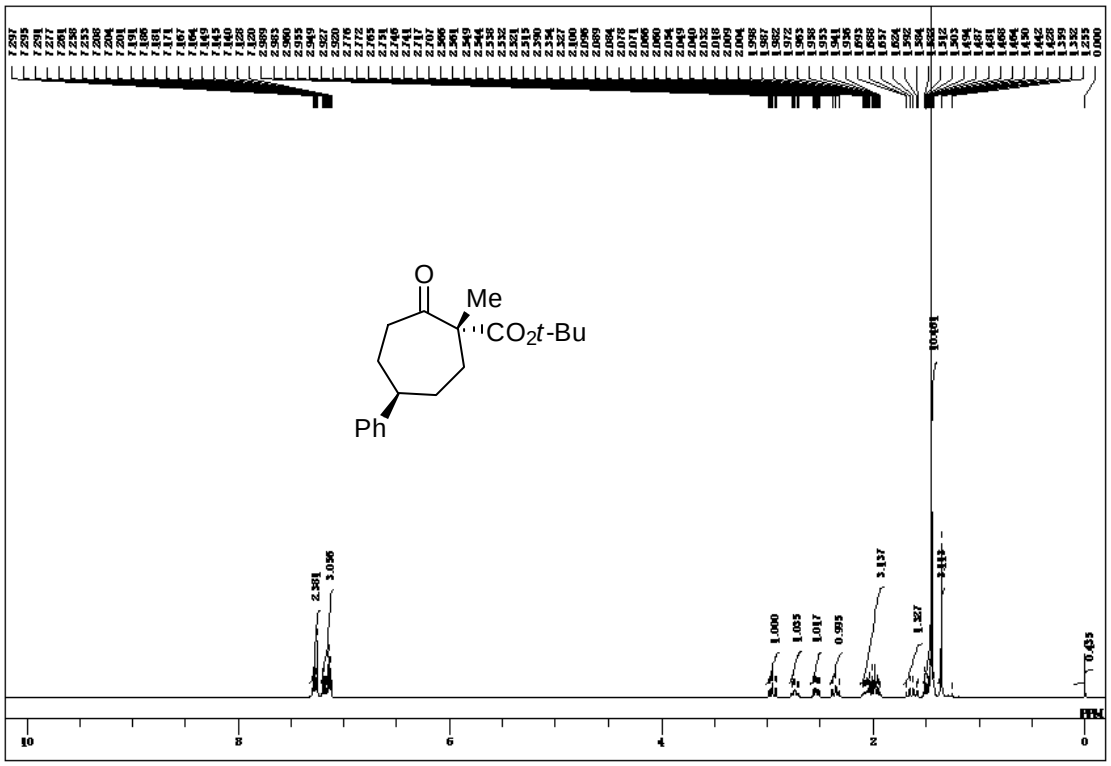
Me
CO2t-Bu
t-Bu

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Me
CO2t-Bu
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1.000
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1.017
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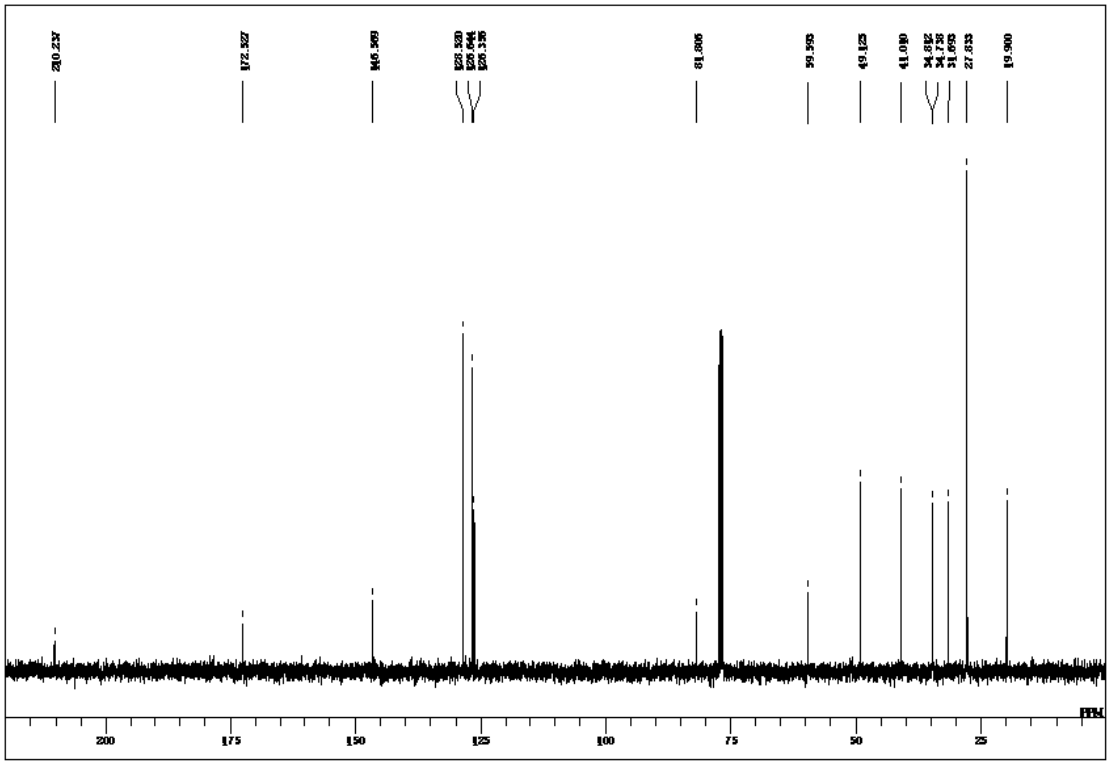
1.327
0.635
PPM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59.595
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41.080
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34.735
31.695
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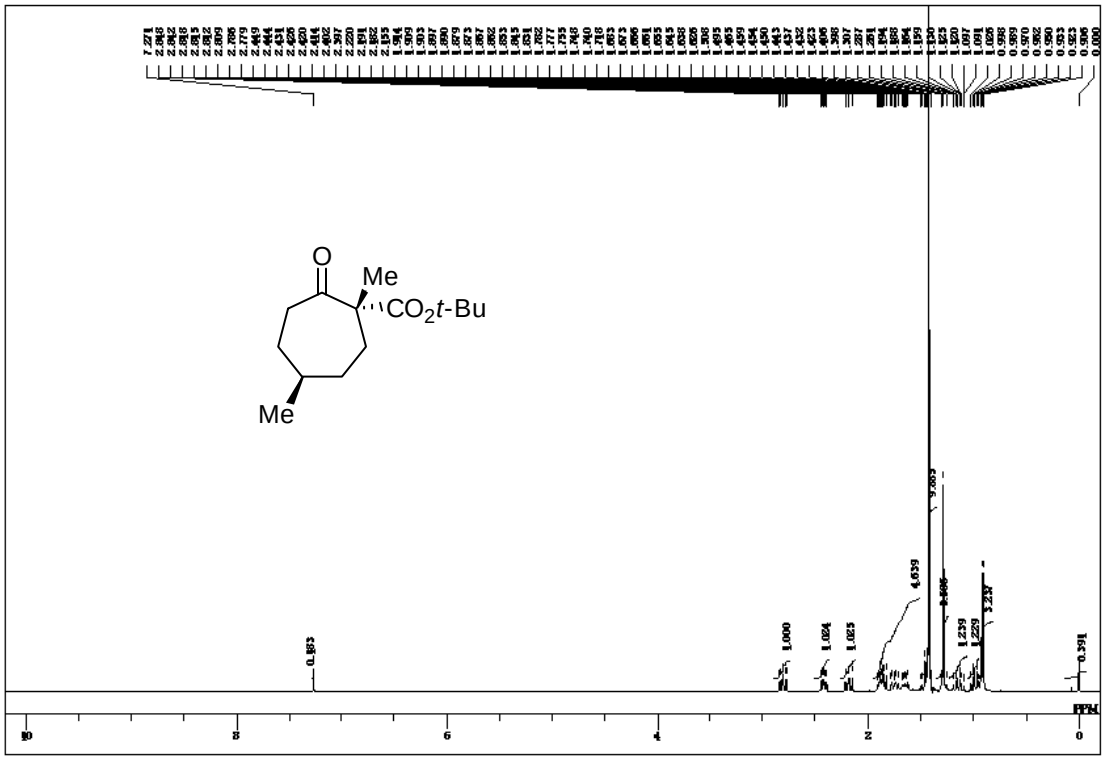
PPM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Me
CO2t-Bu
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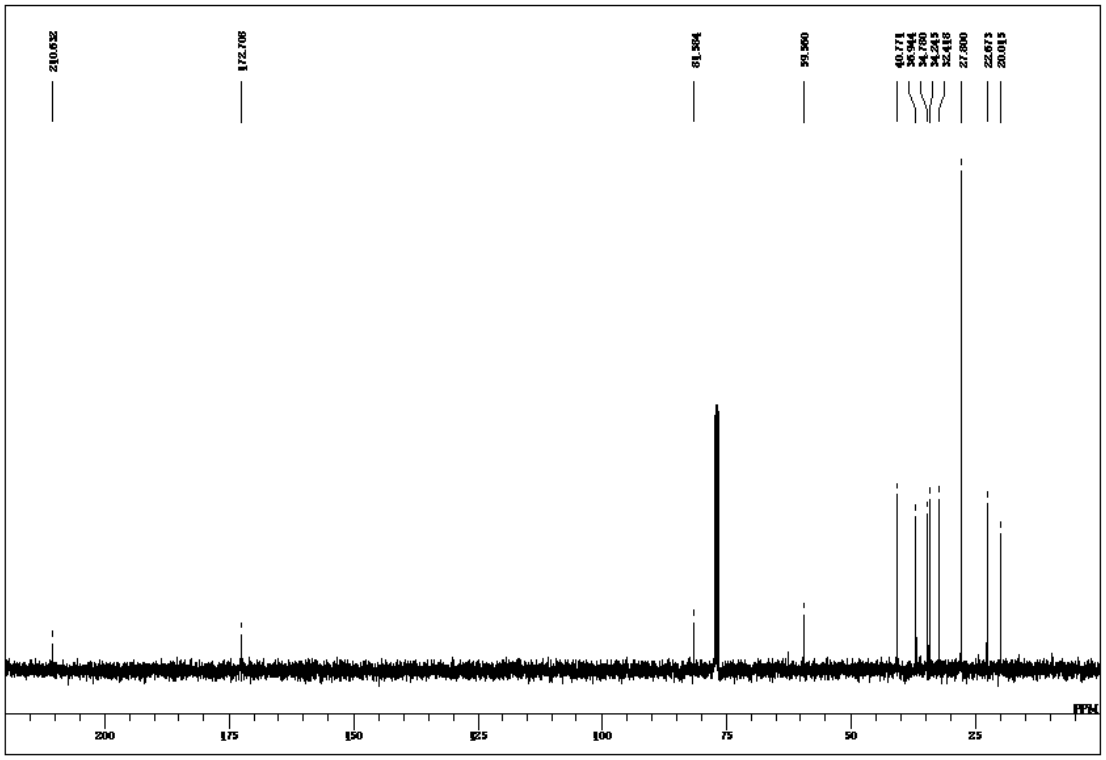
PPM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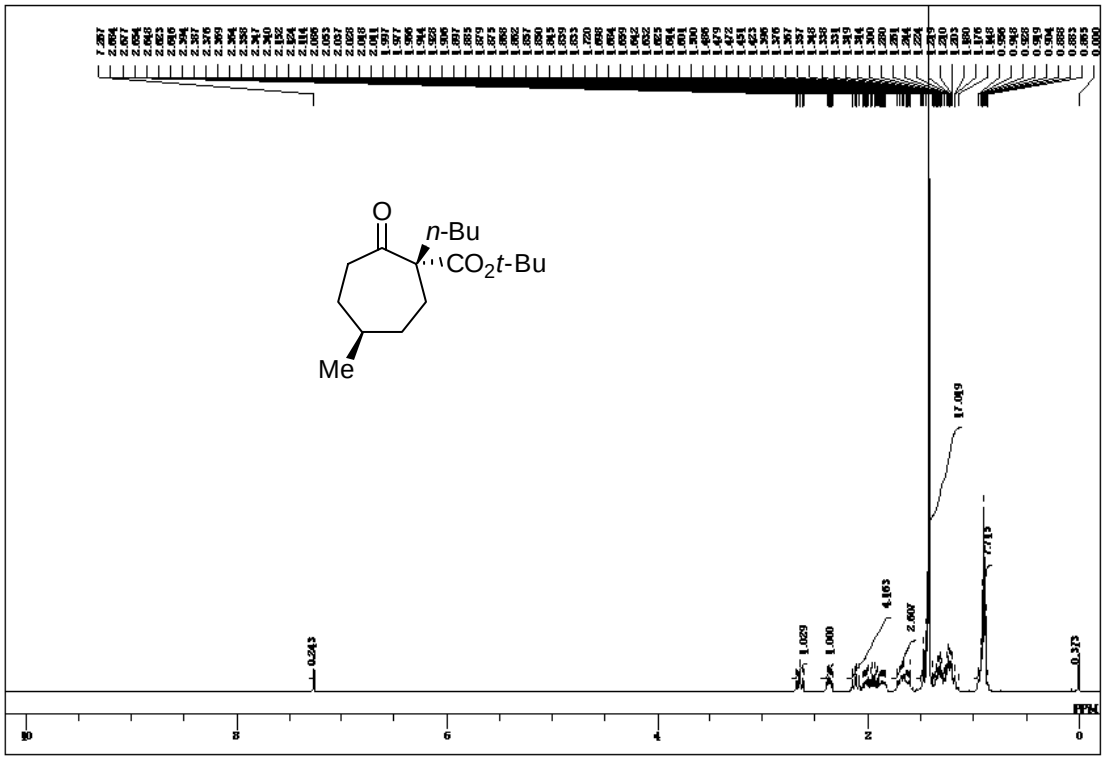
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n-Bu
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Me
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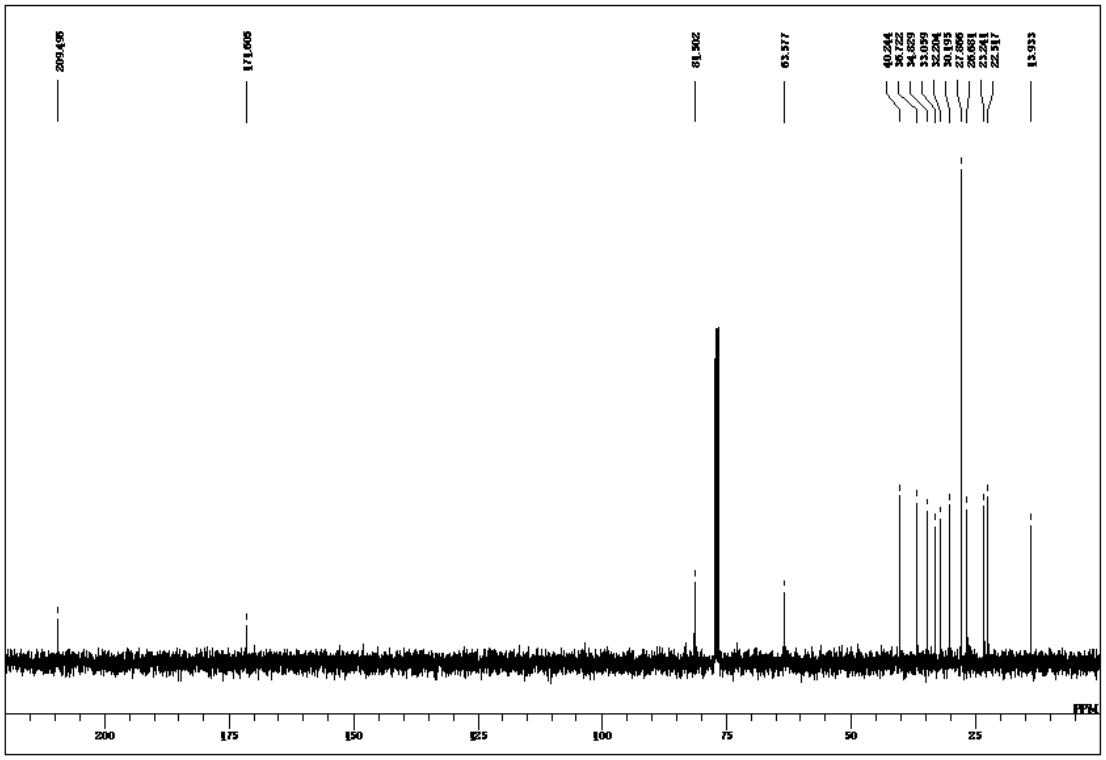
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33.059
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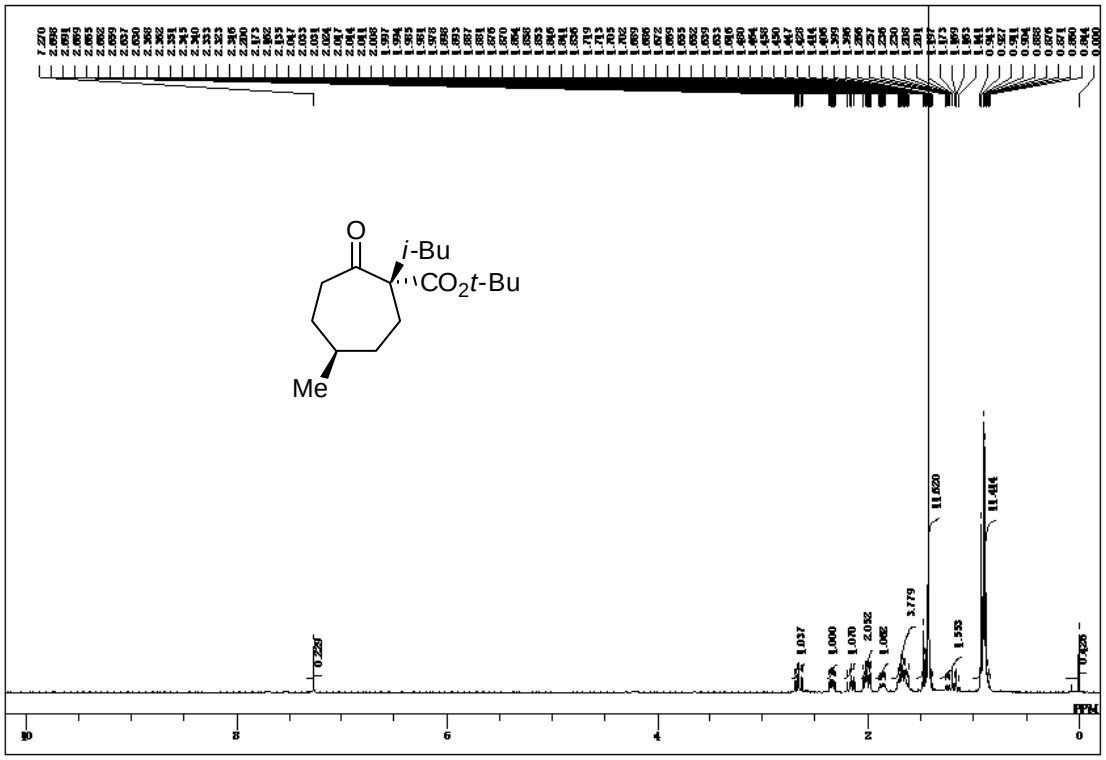
23.741
22.917
13.933
PPM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i-Bu
CO2t-Bu
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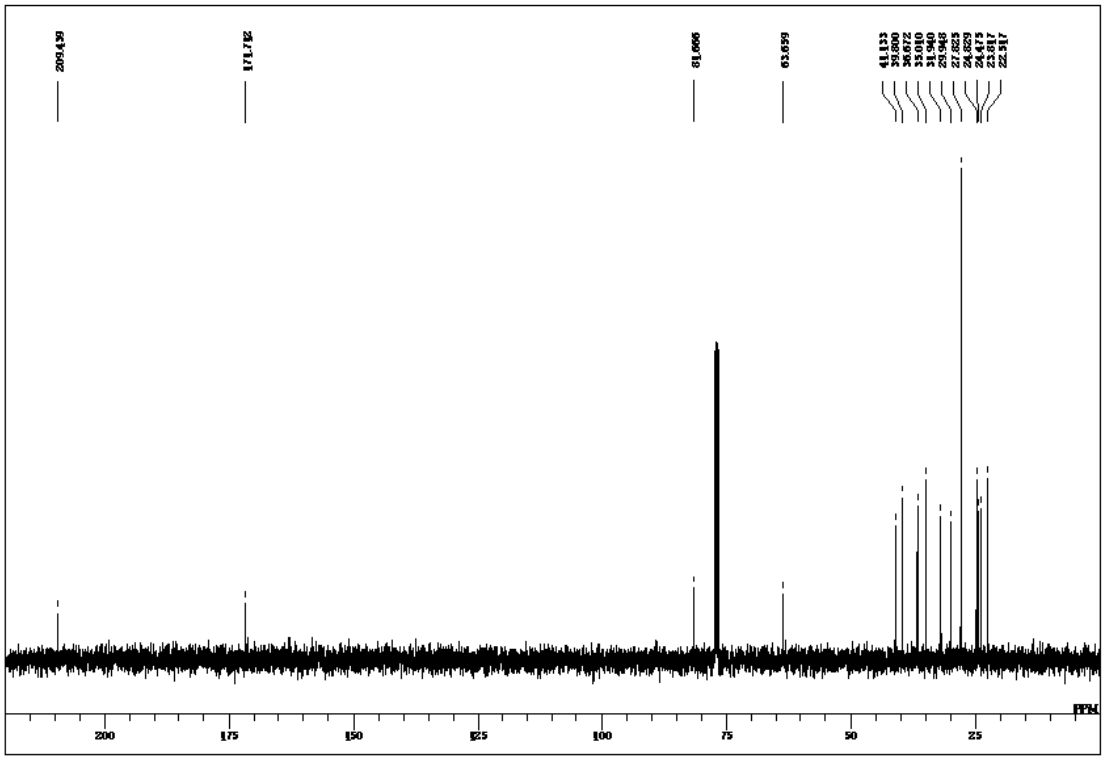
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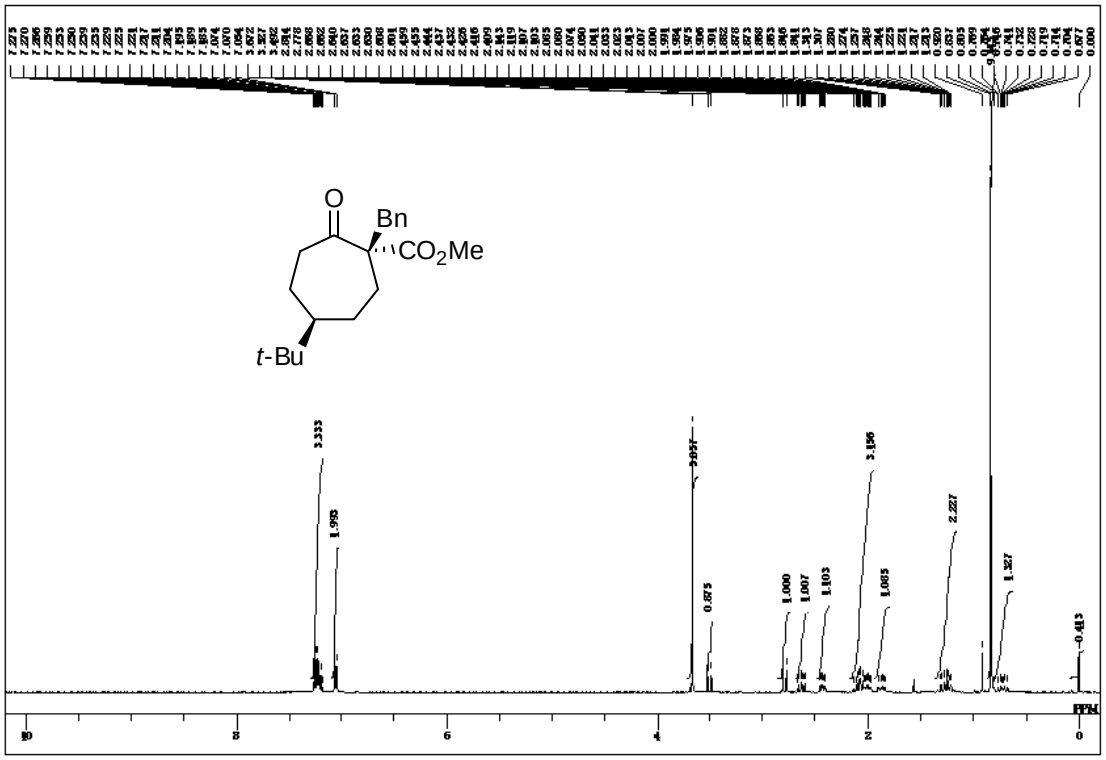
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Bn
CO2Me
t-Bu
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0.875
1.000
1.007
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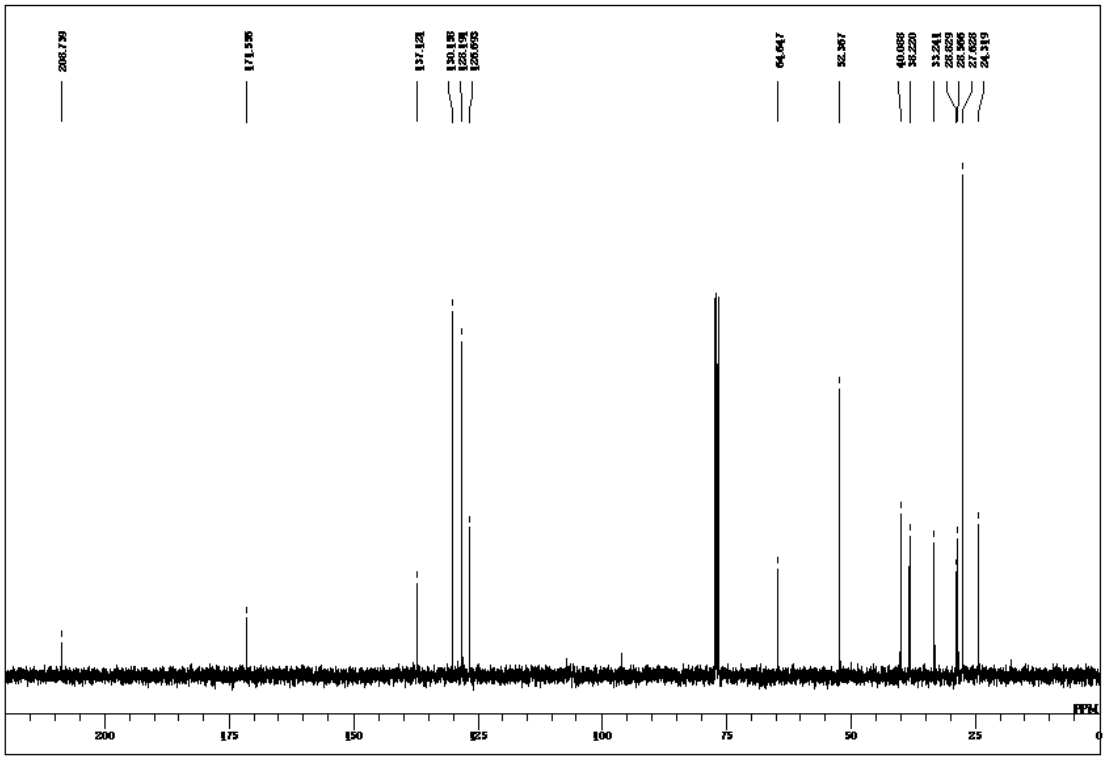
1.327
0.413
PPM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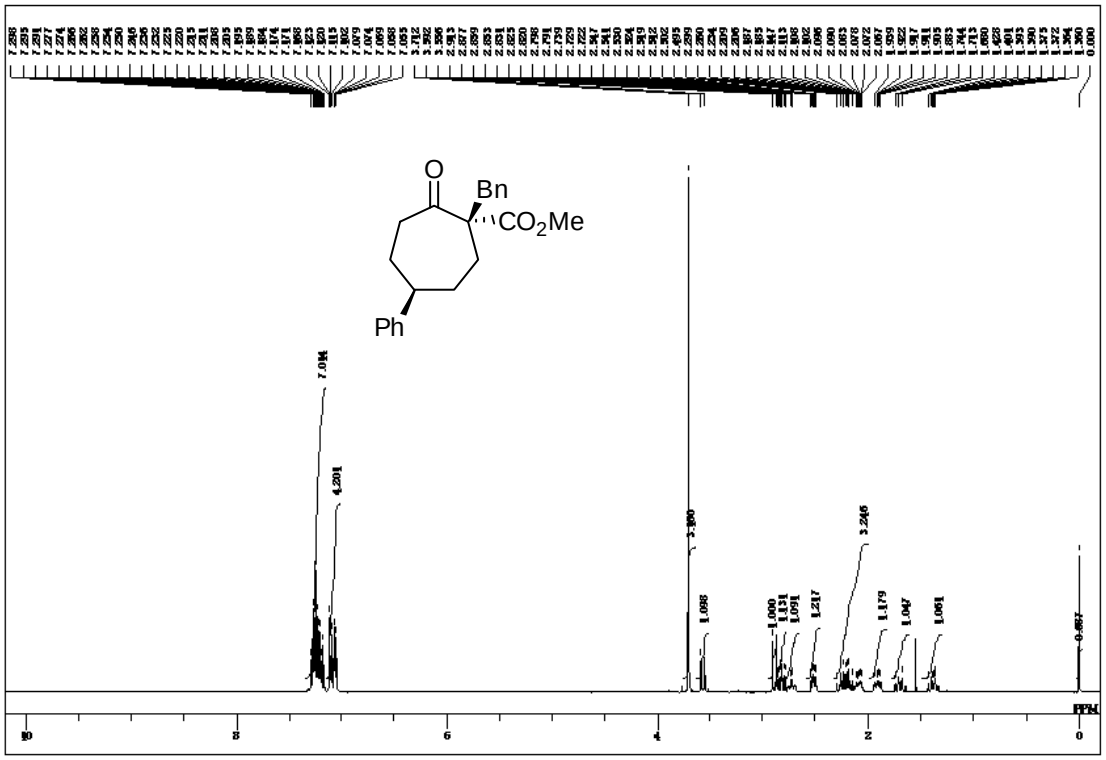
24.319
PPM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Bn
CO2Me
Ph
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1.091
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1.179
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1.061
0.887
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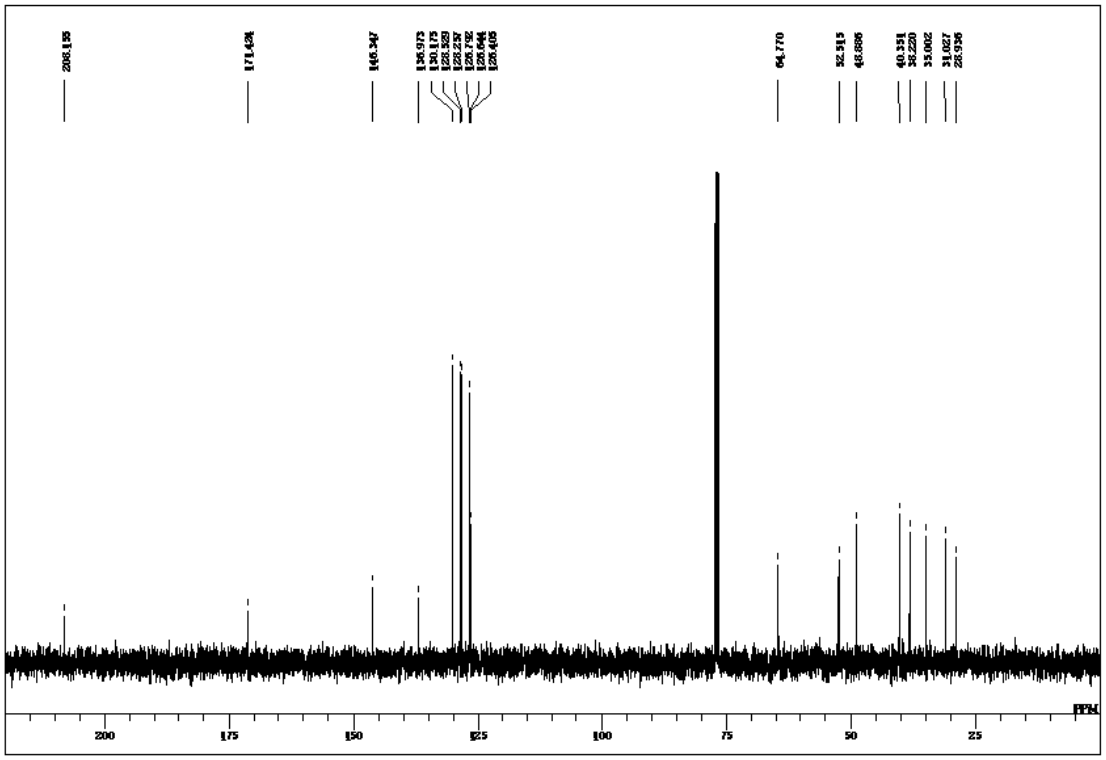
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35.220
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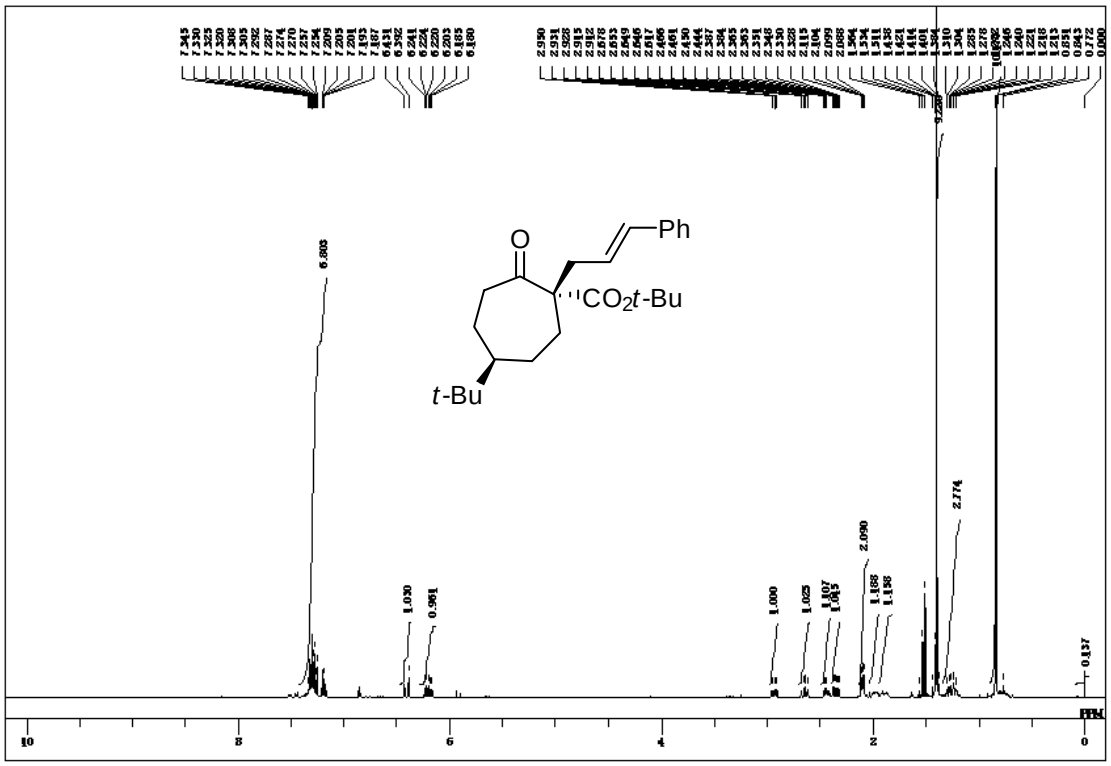
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Ph
CO2t-Bu
t-Bu
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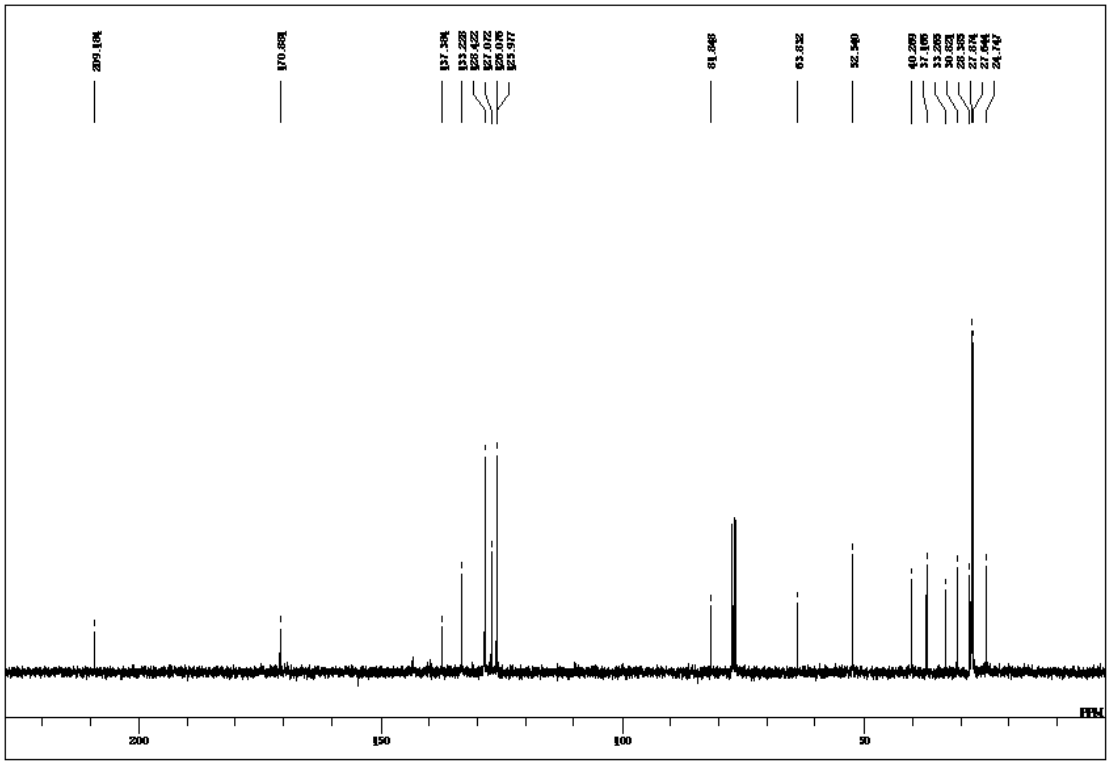
1.000
1.025
1.107
1.043
1.188
1.156
2.090
2.774
0.137
PPM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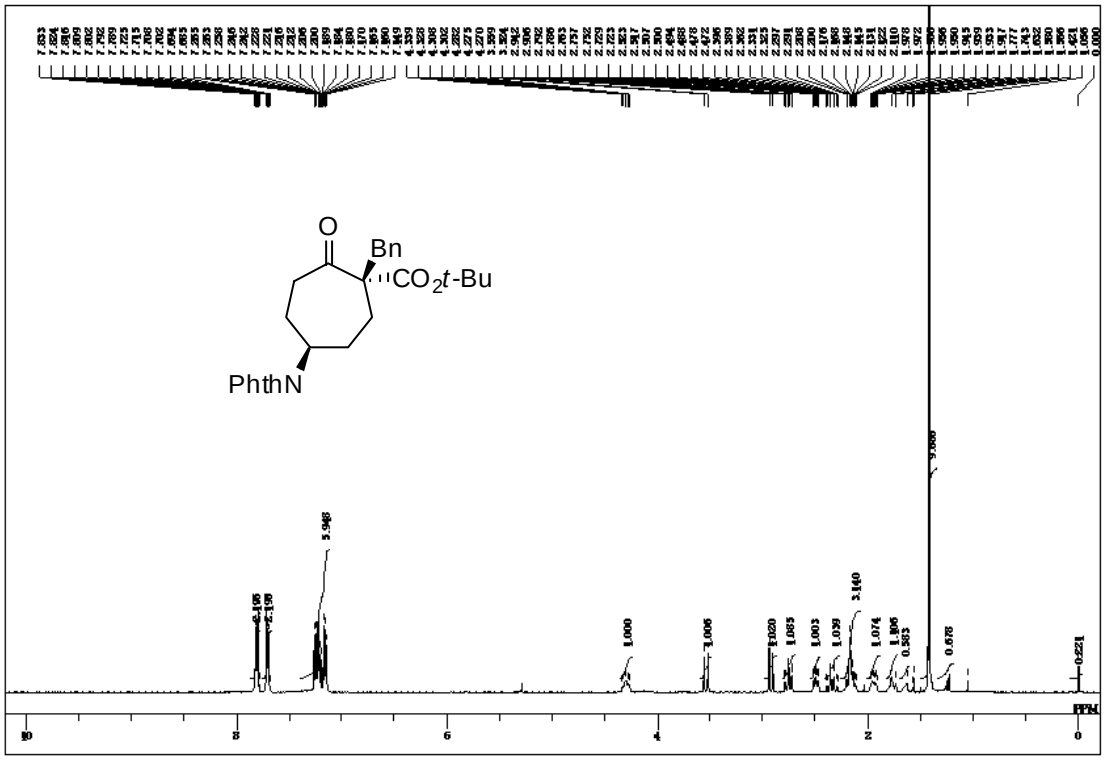
24.747
PPM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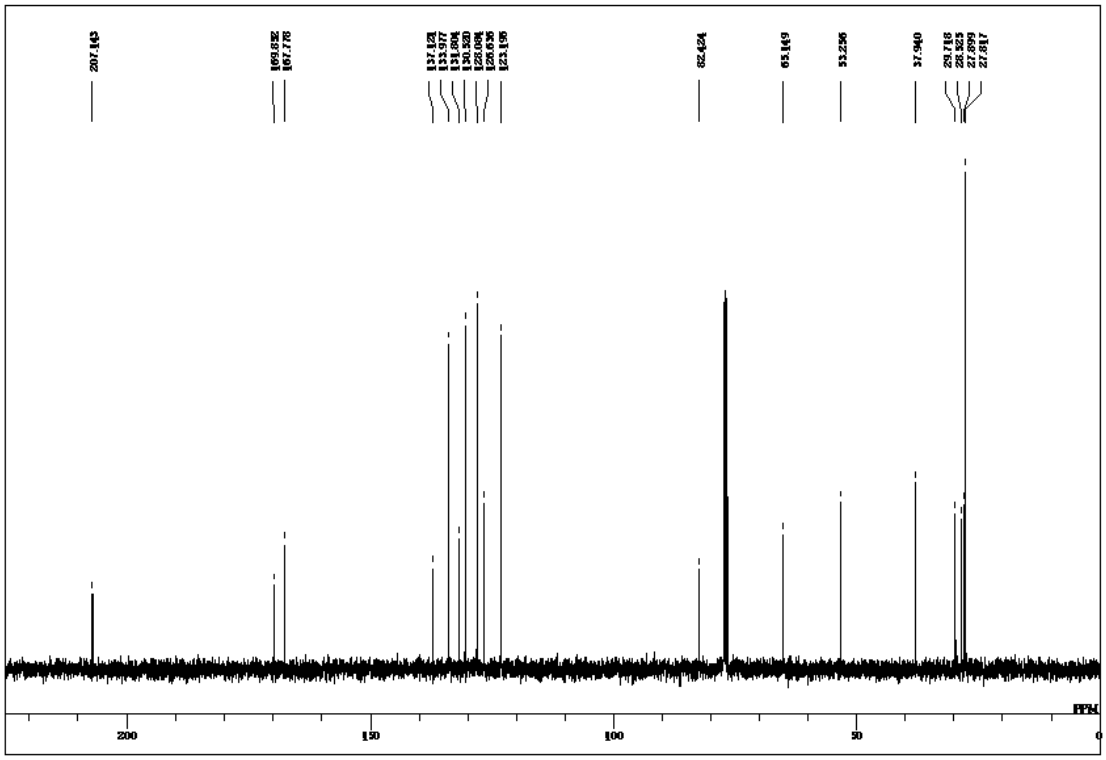
Bn
CO2t-Bu
PhthN
PPM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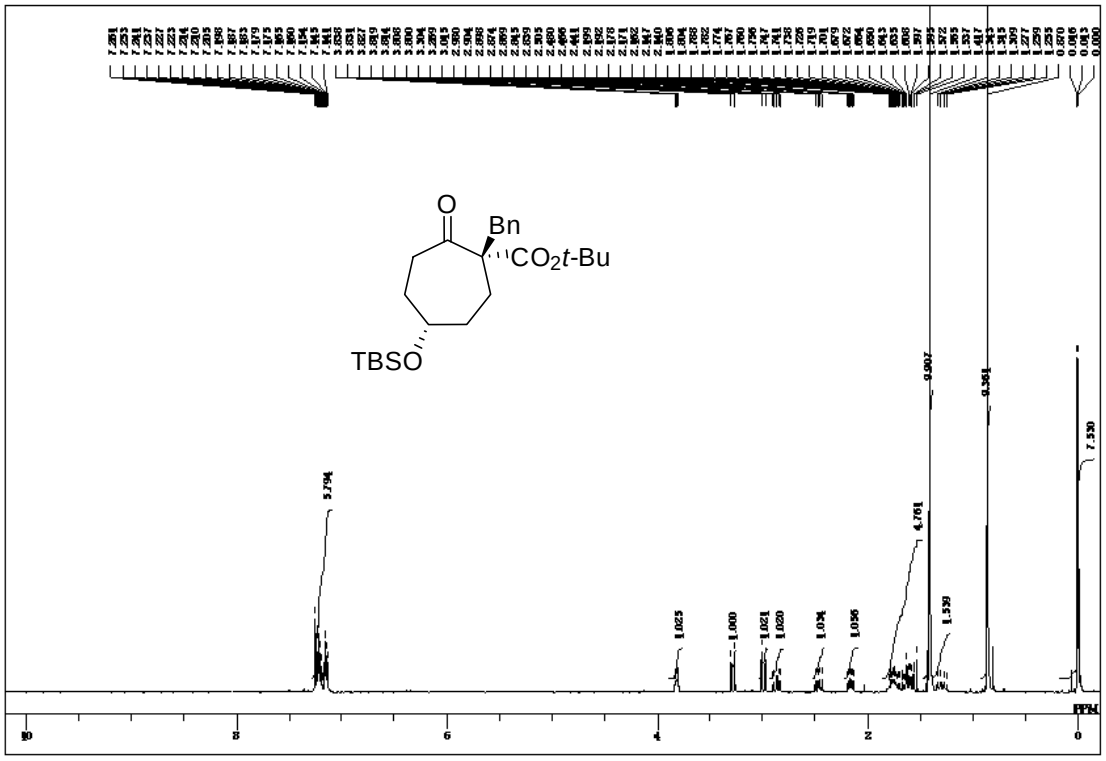
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Bn
CO2t-Bu
TBSO
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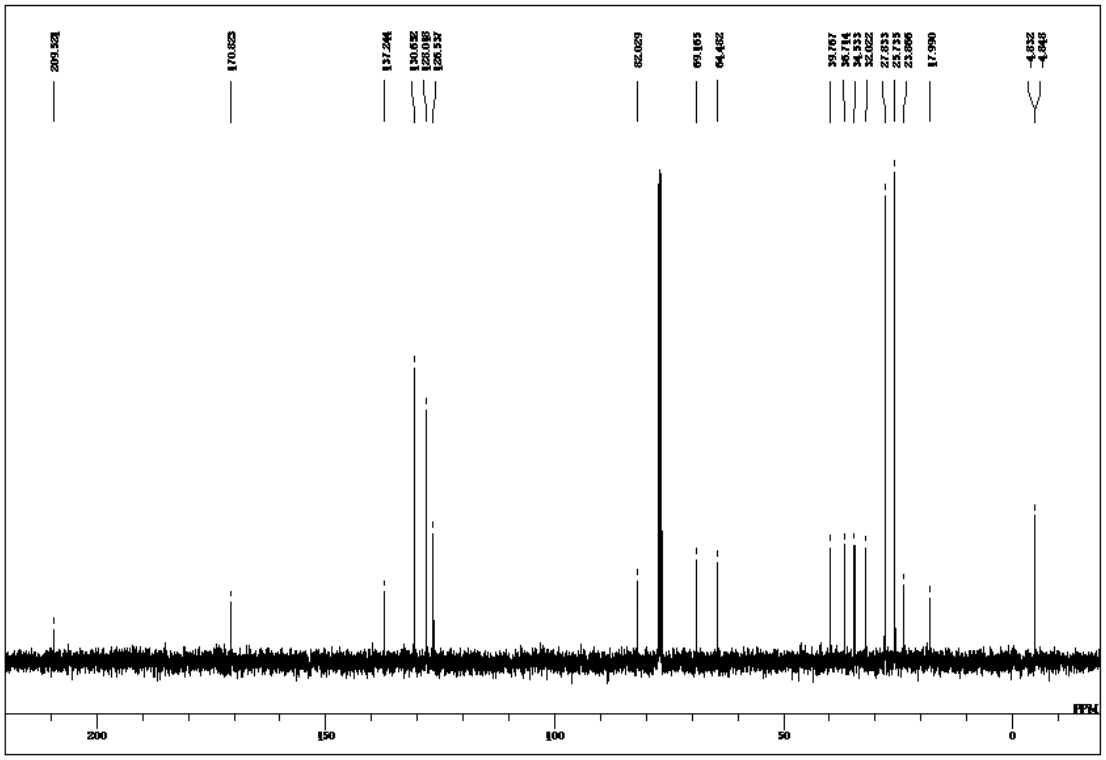
5.794
4.761
1.599
1.025
1.000
1.021
1.020
1.034
1.056
PPM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82.029
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64.402
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32.022
27.833
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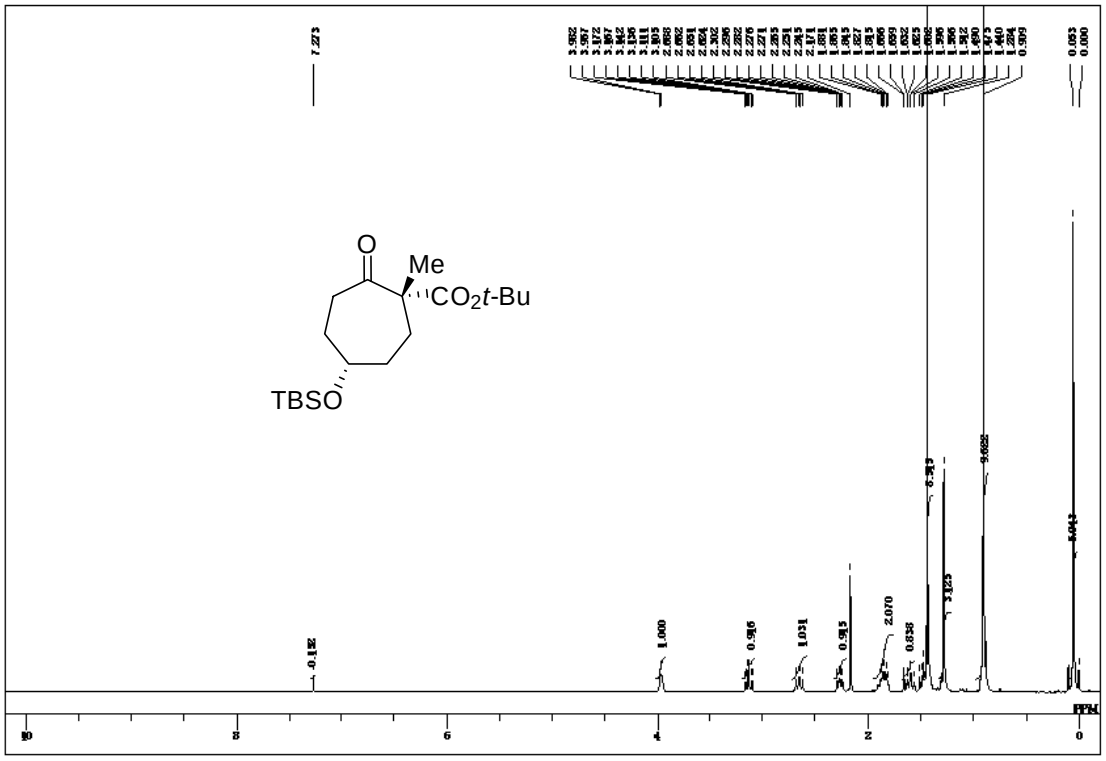
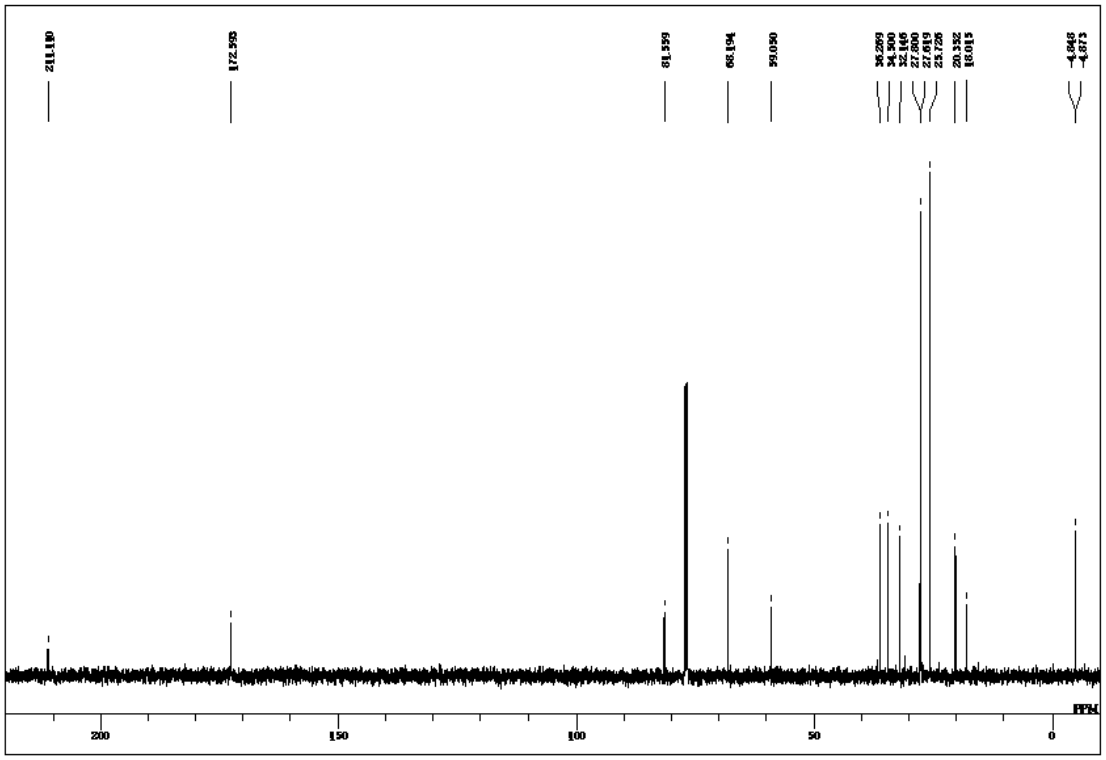
PPM


O
Me
CO2t-Bu
TBSO
PPM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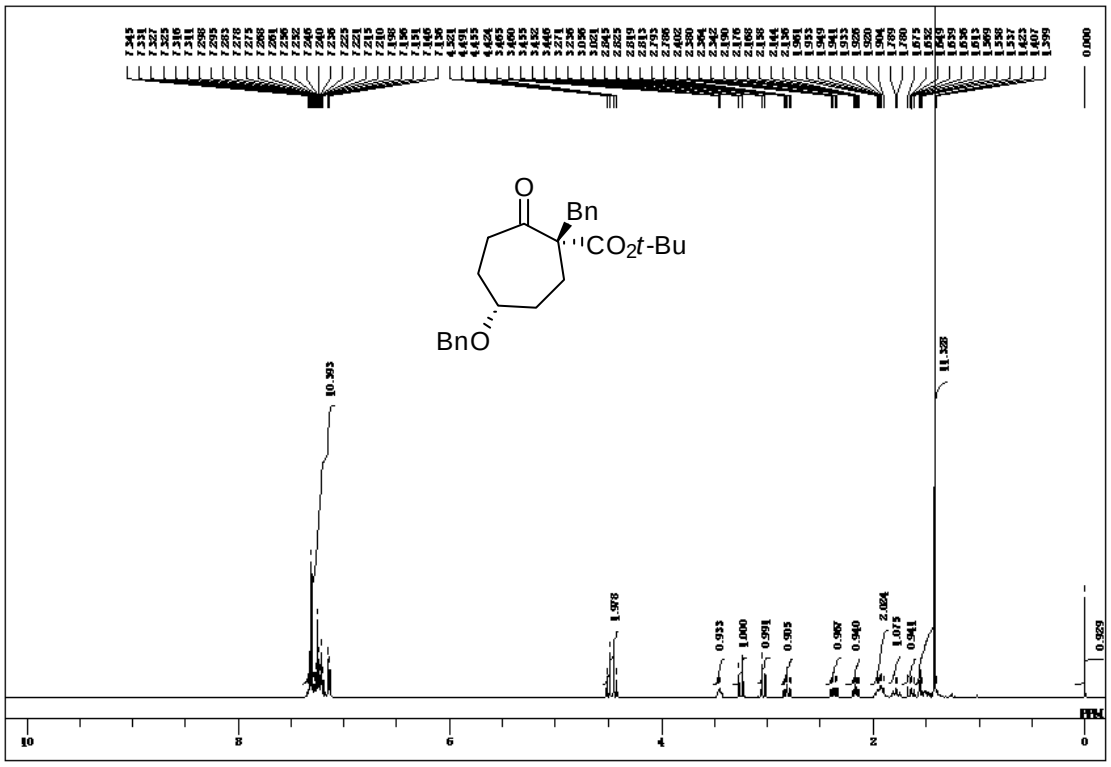
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Bn
CO2t-Bu
BnO
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0.935
0.967
0.940
2.024
1.075
0.941
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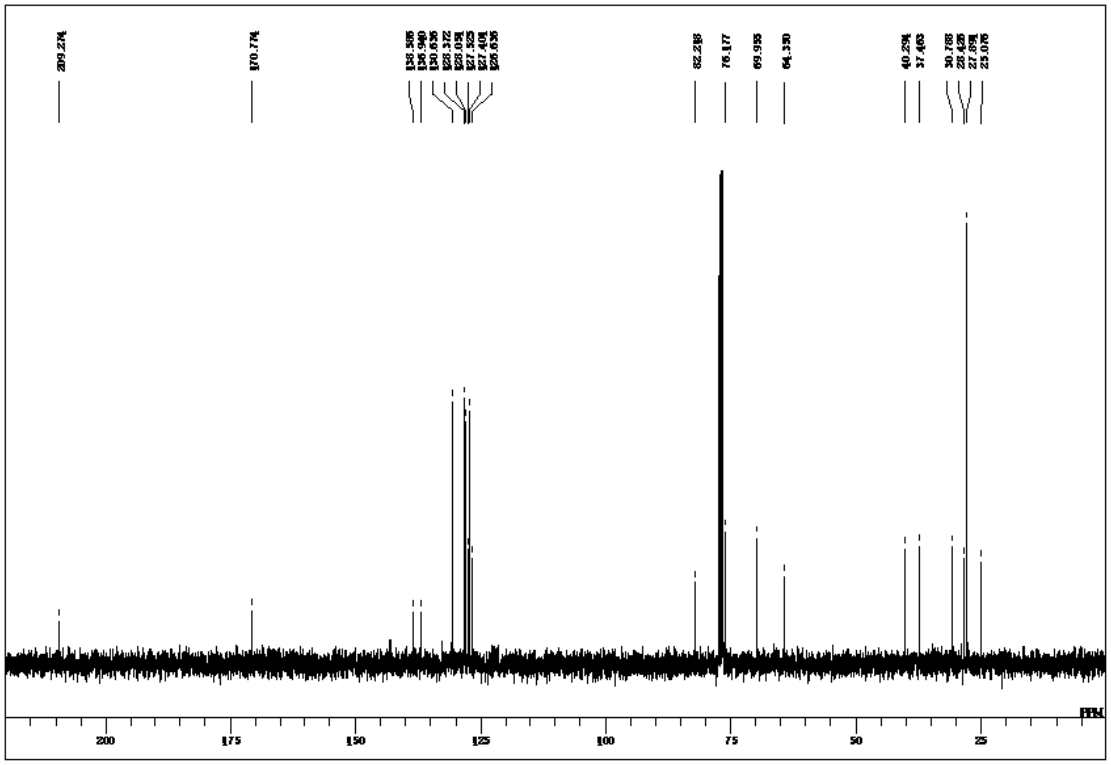
0.000
PPM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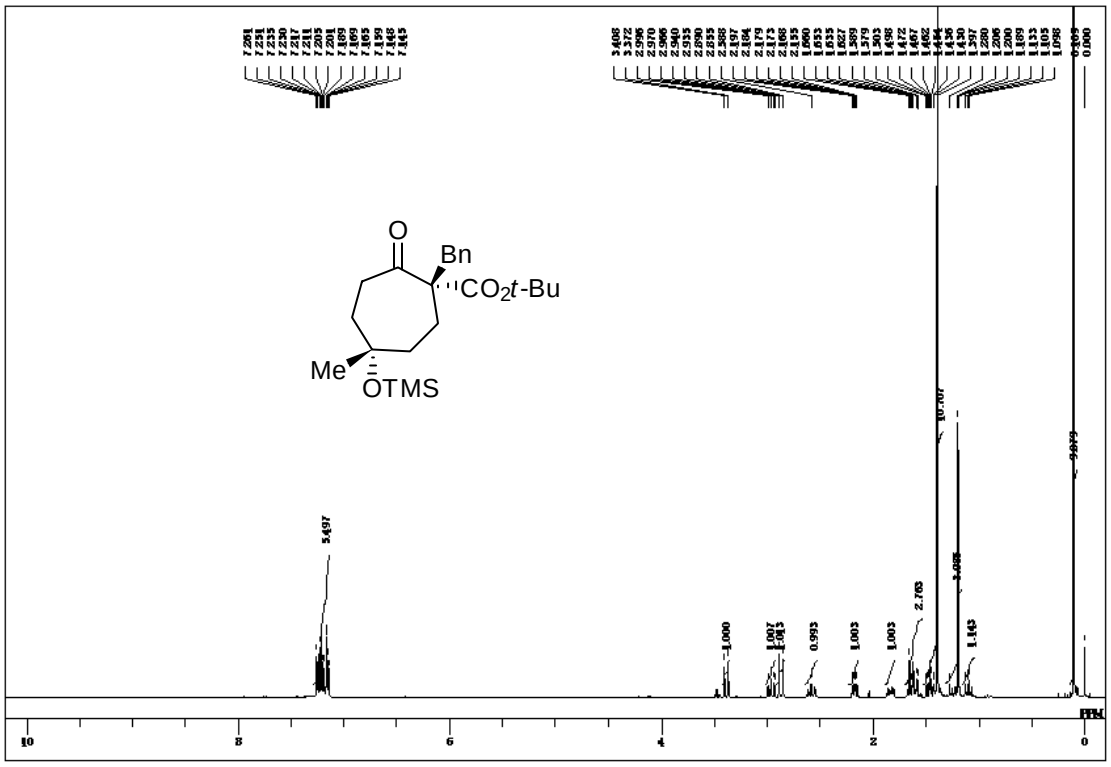
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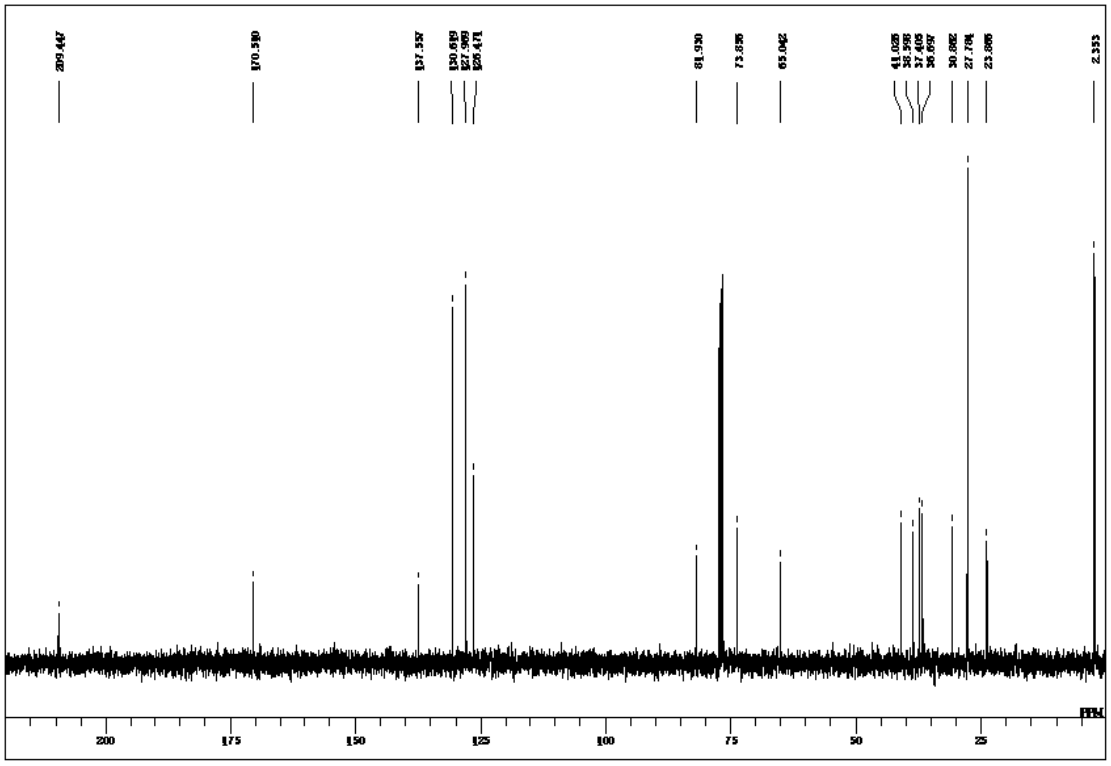
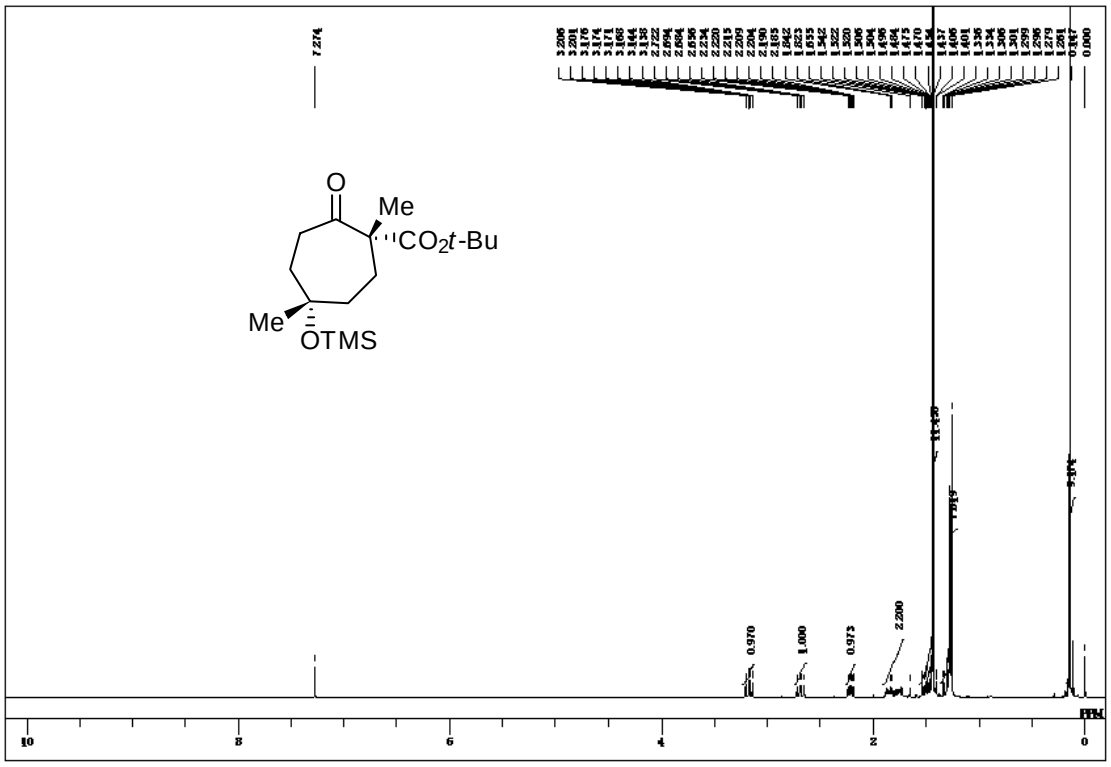
CO2t-Bu
Me
OTMS

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Me
CO2t-Bu
Me
OTMS
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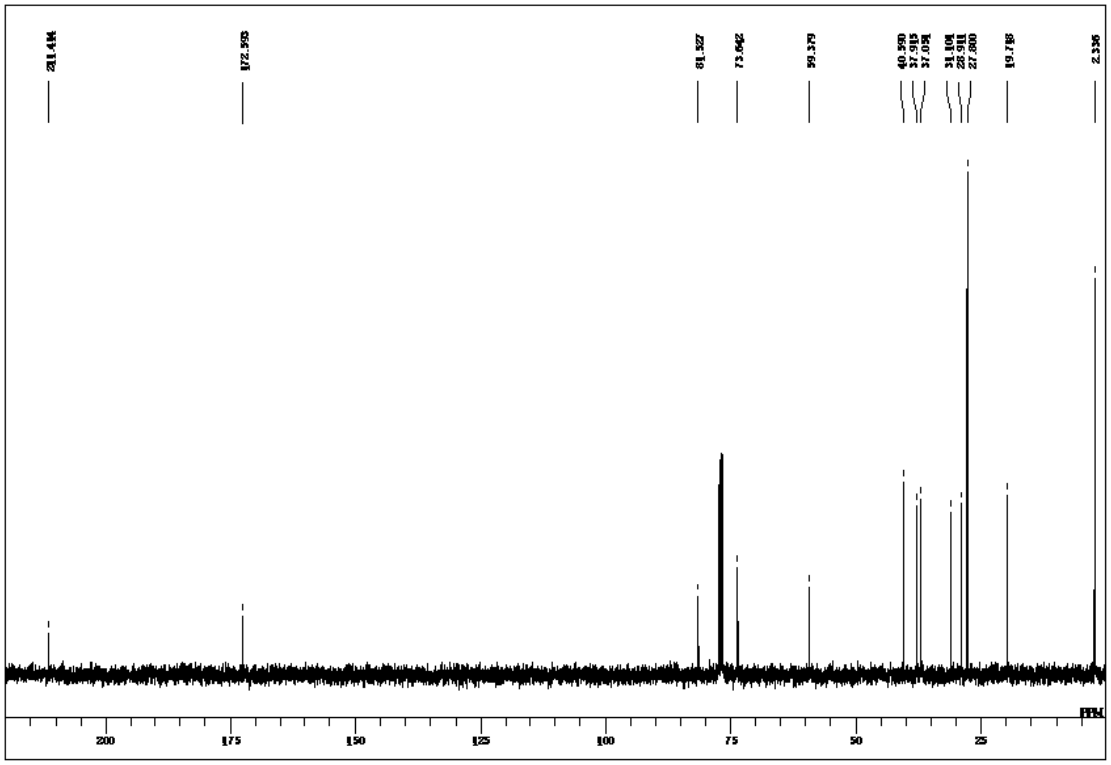
10
8
6
4
2
0
PPM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73.642
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25.911
27.880
19.785
2.136
200
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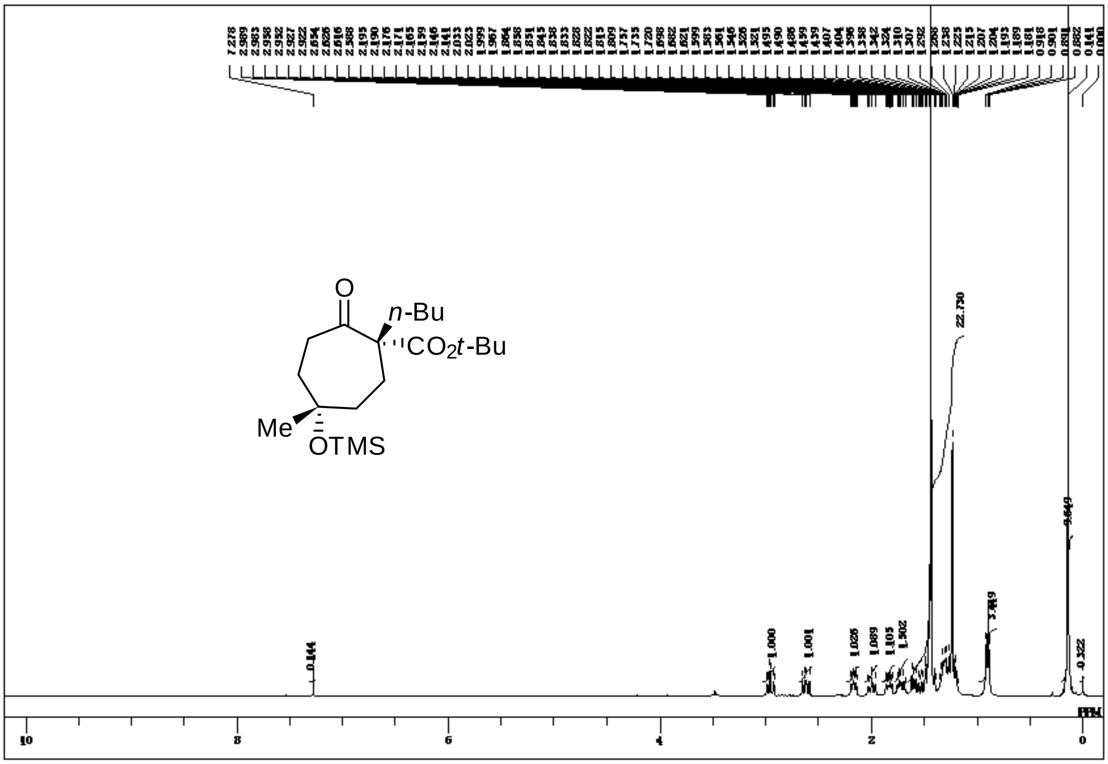
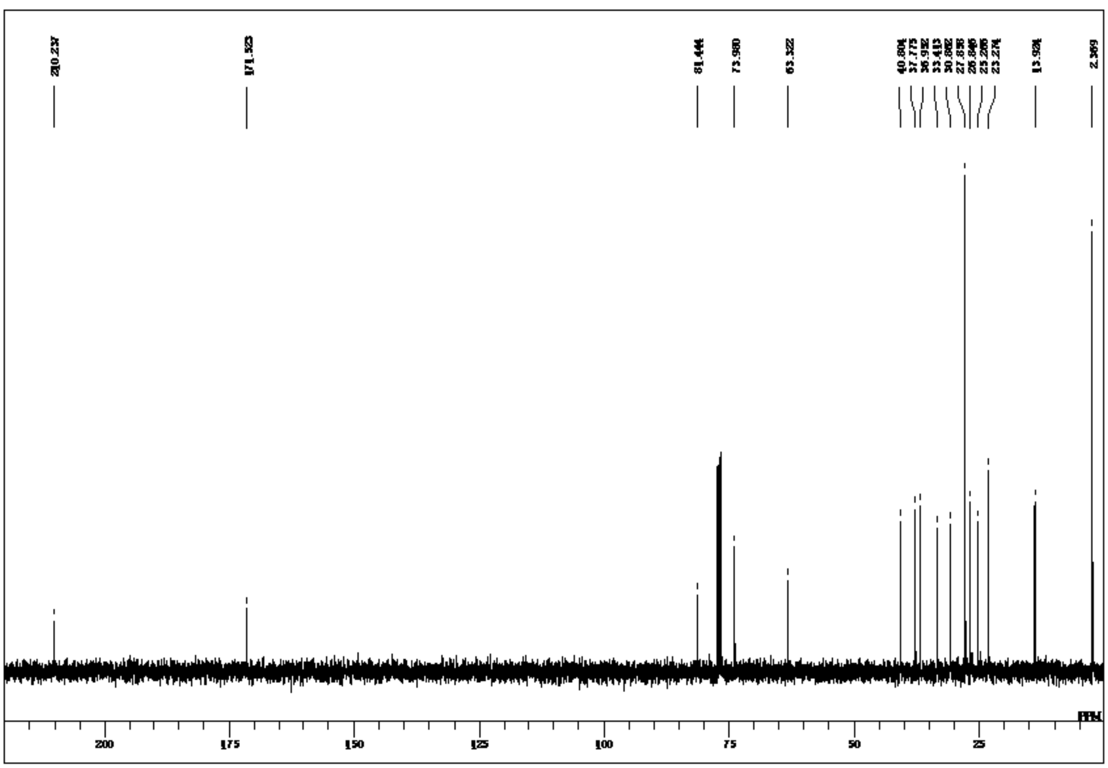
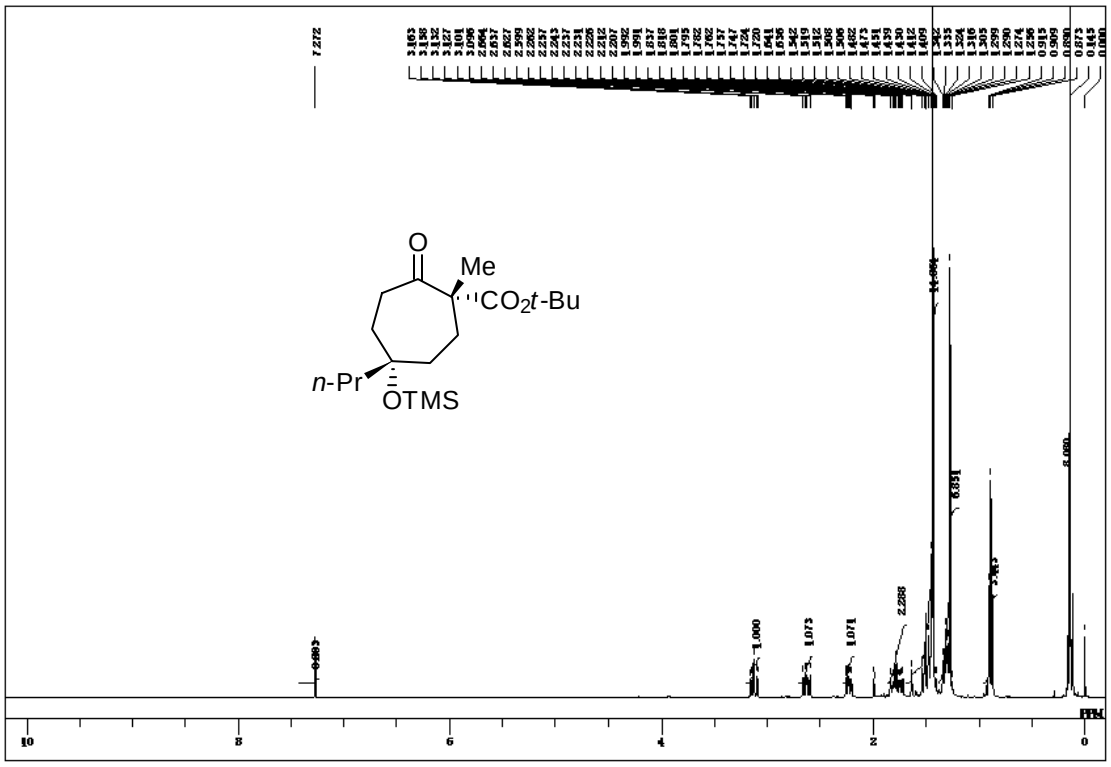
150
125
100
75
50
25
PPM



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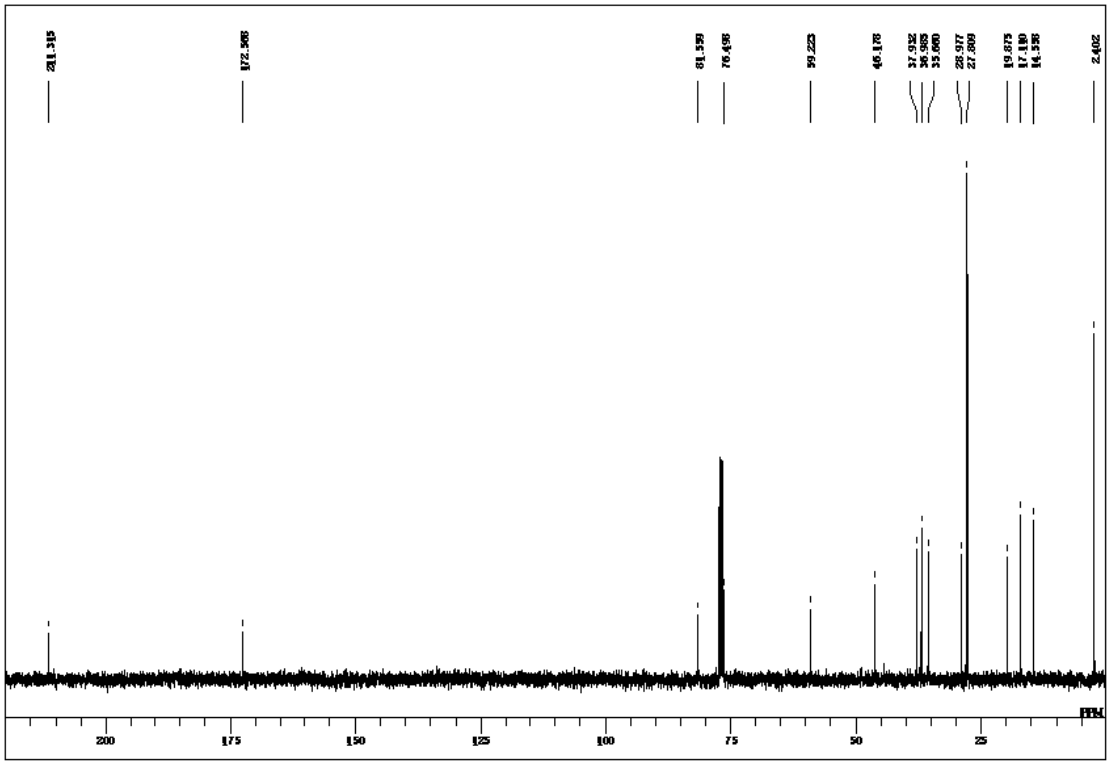
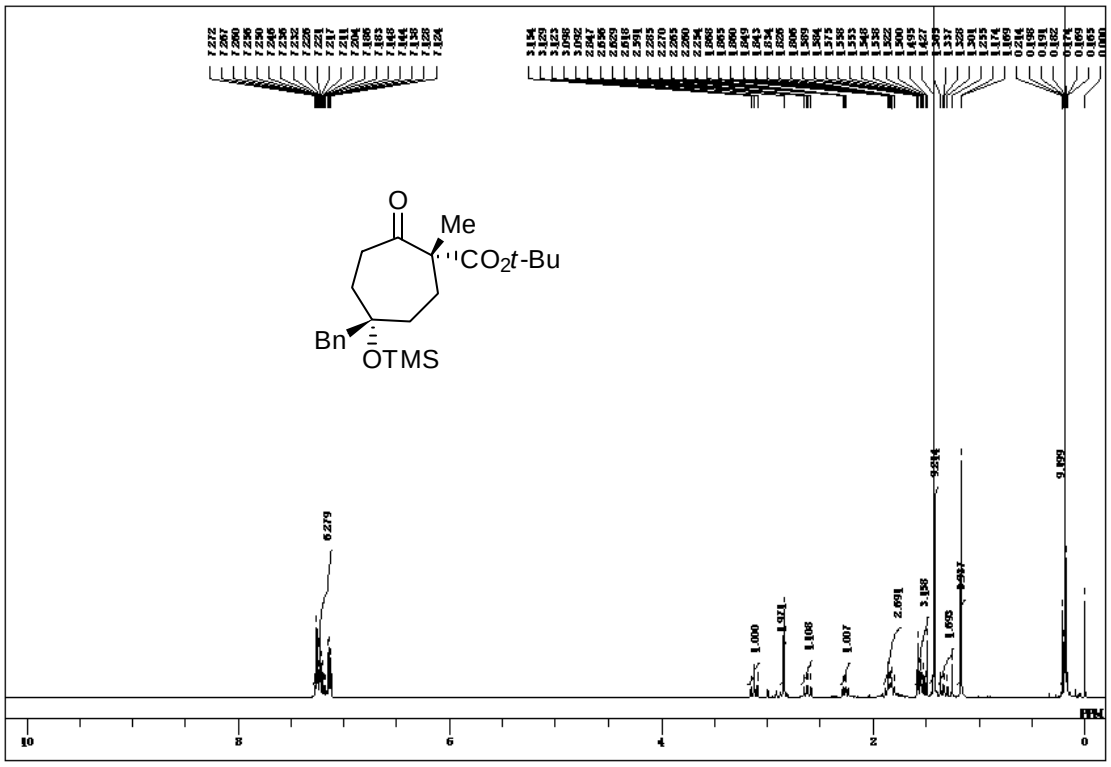
Me
CO2t-Bu
n-Pr
OTMS

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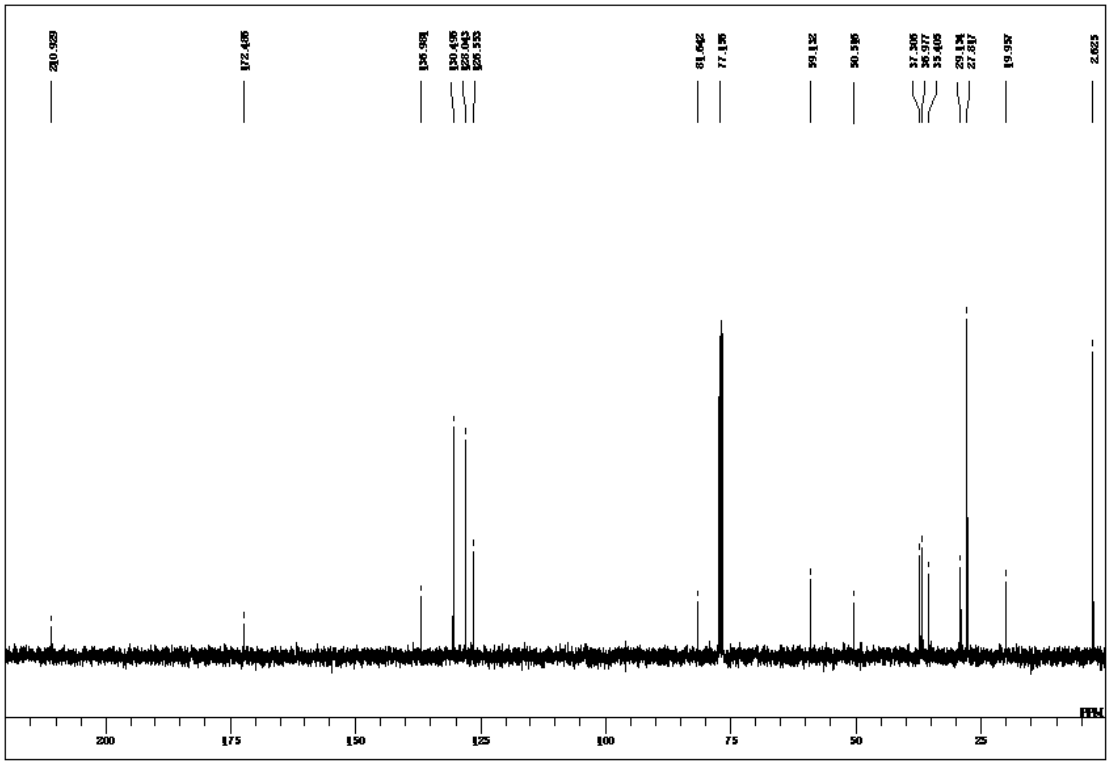
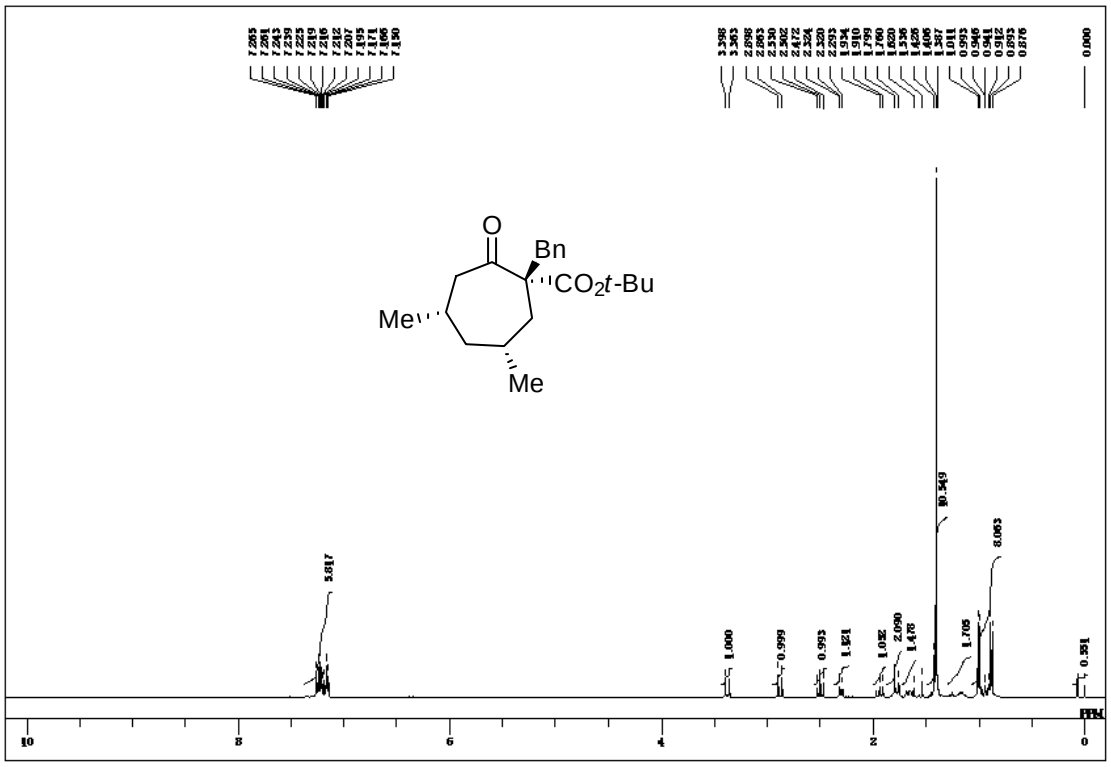
Me
CO2t-Bu
Bn
OTMS

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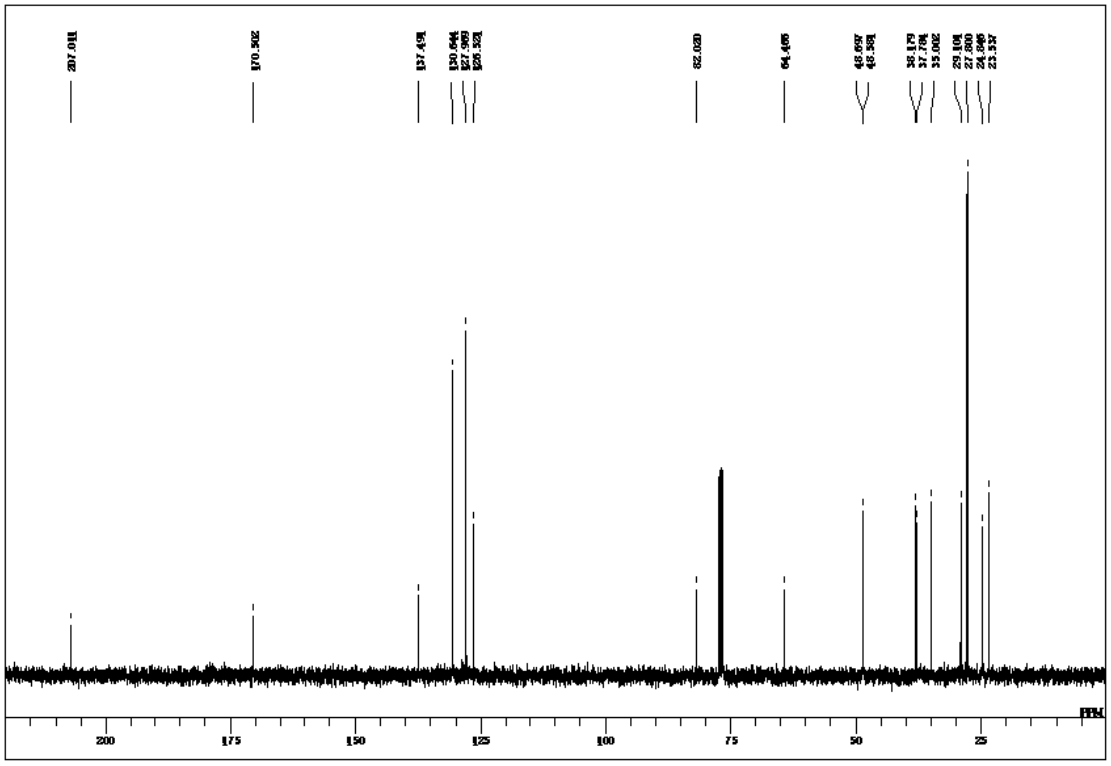
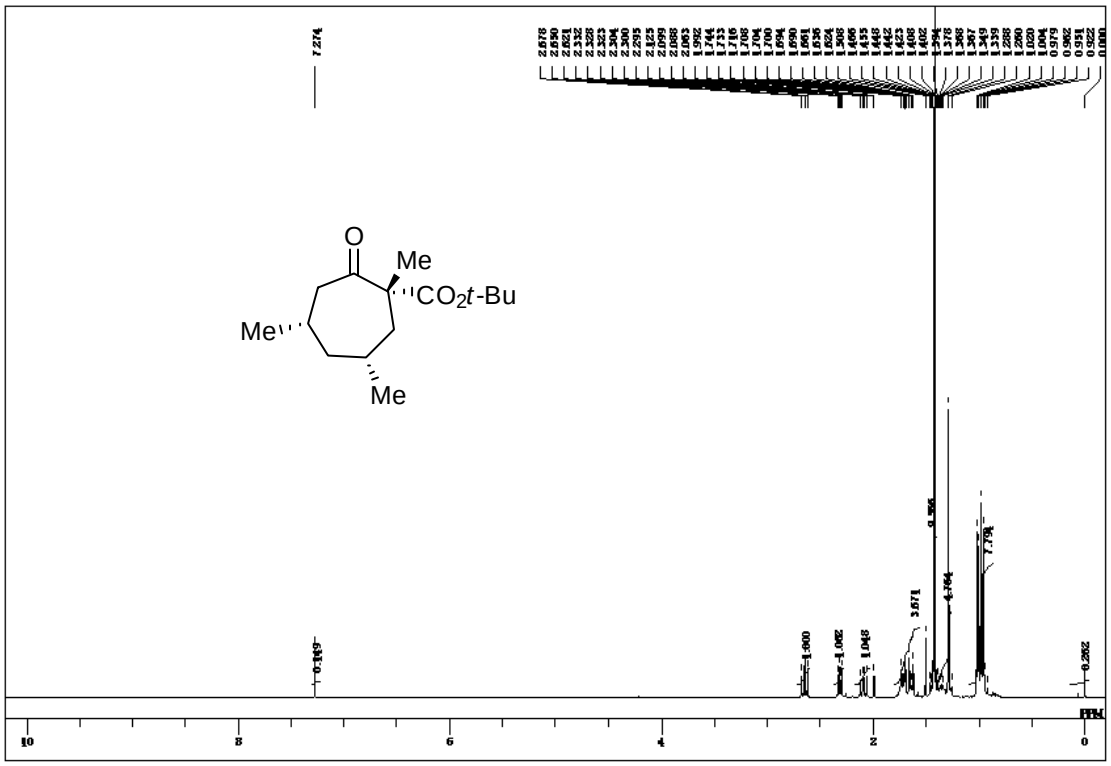
Bn
CO2t-Bu
Me
Me

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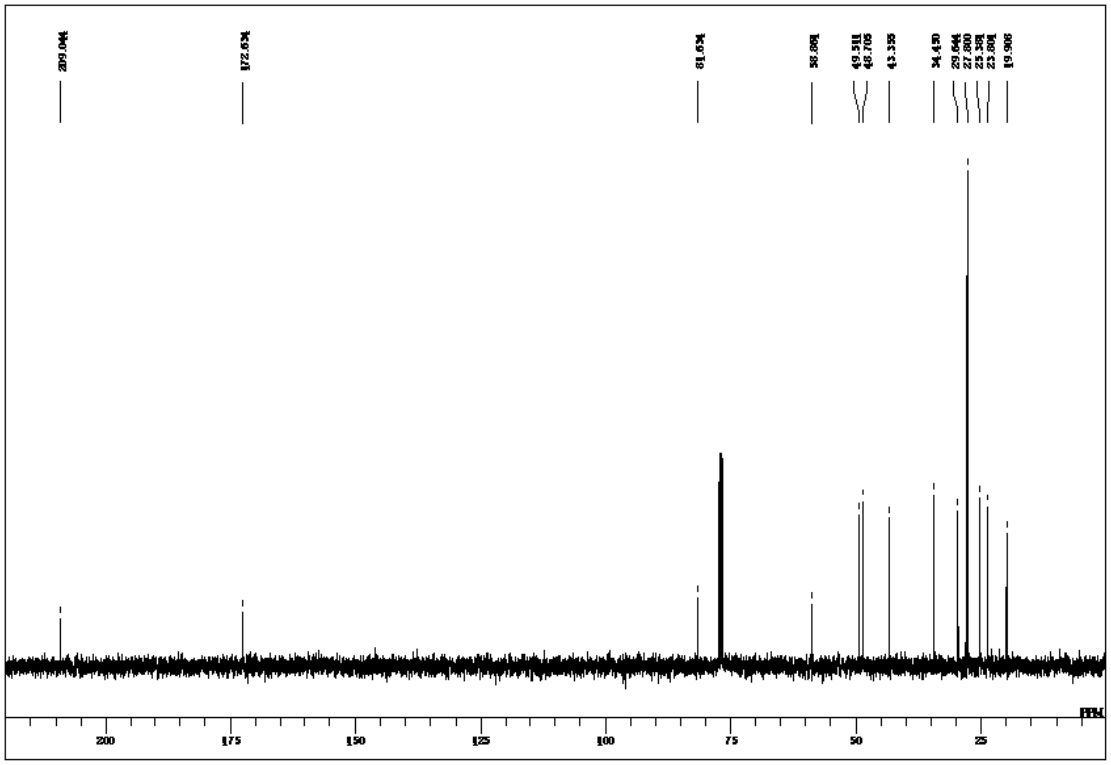
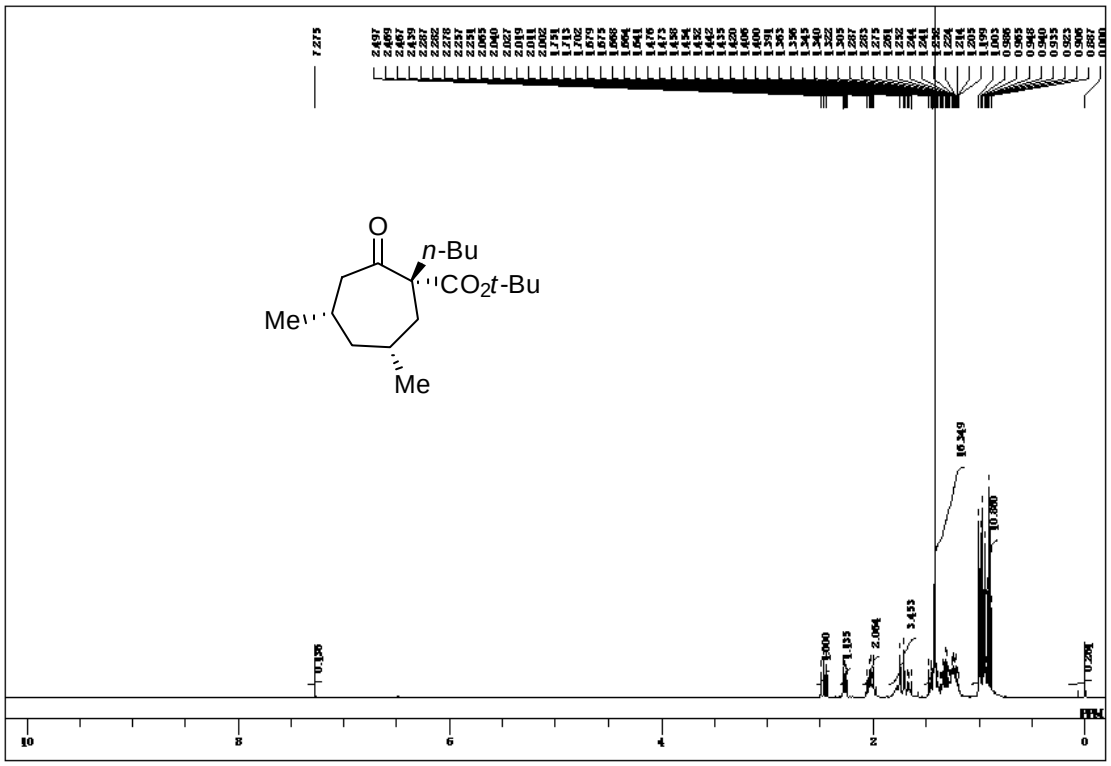
Me
CO2t-Bu
Me
Me

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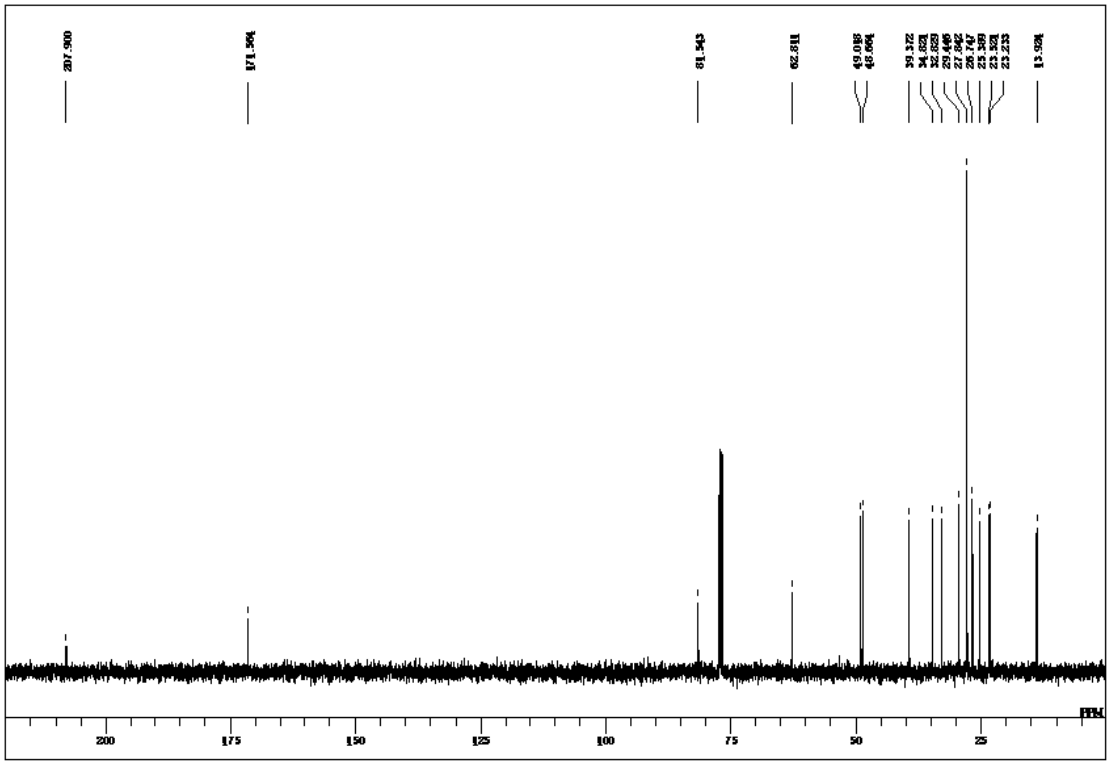
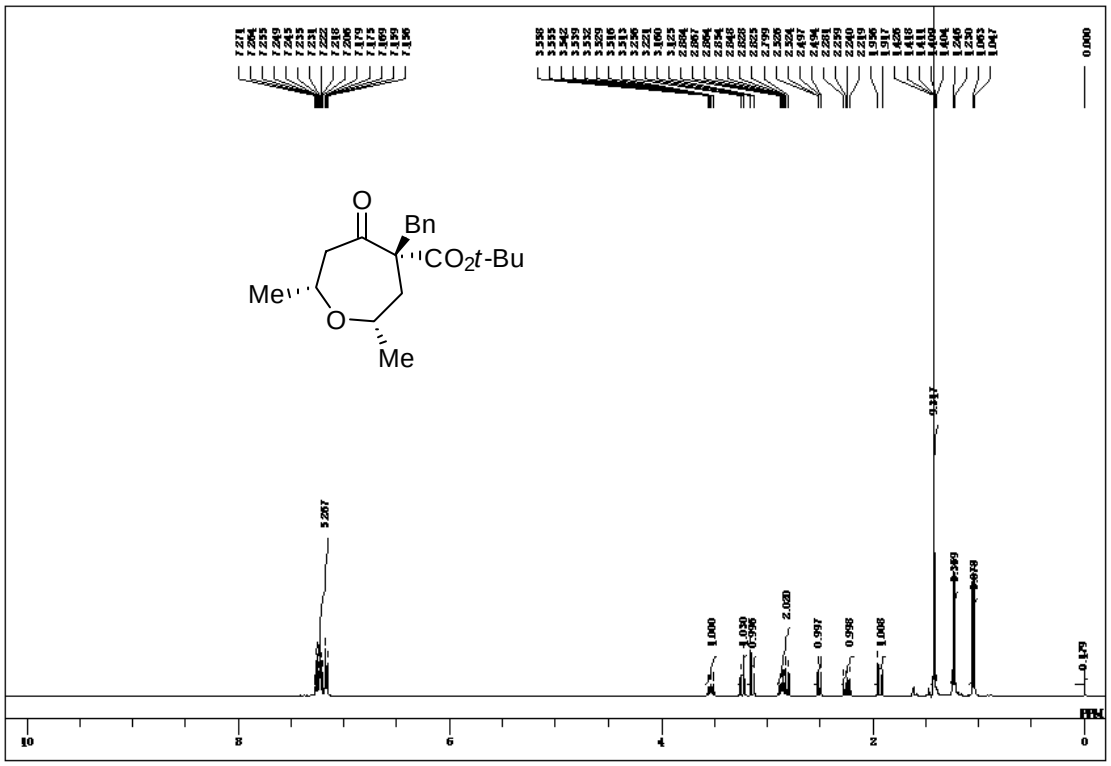
n-Bu
CO2t-Bu
Me
Me

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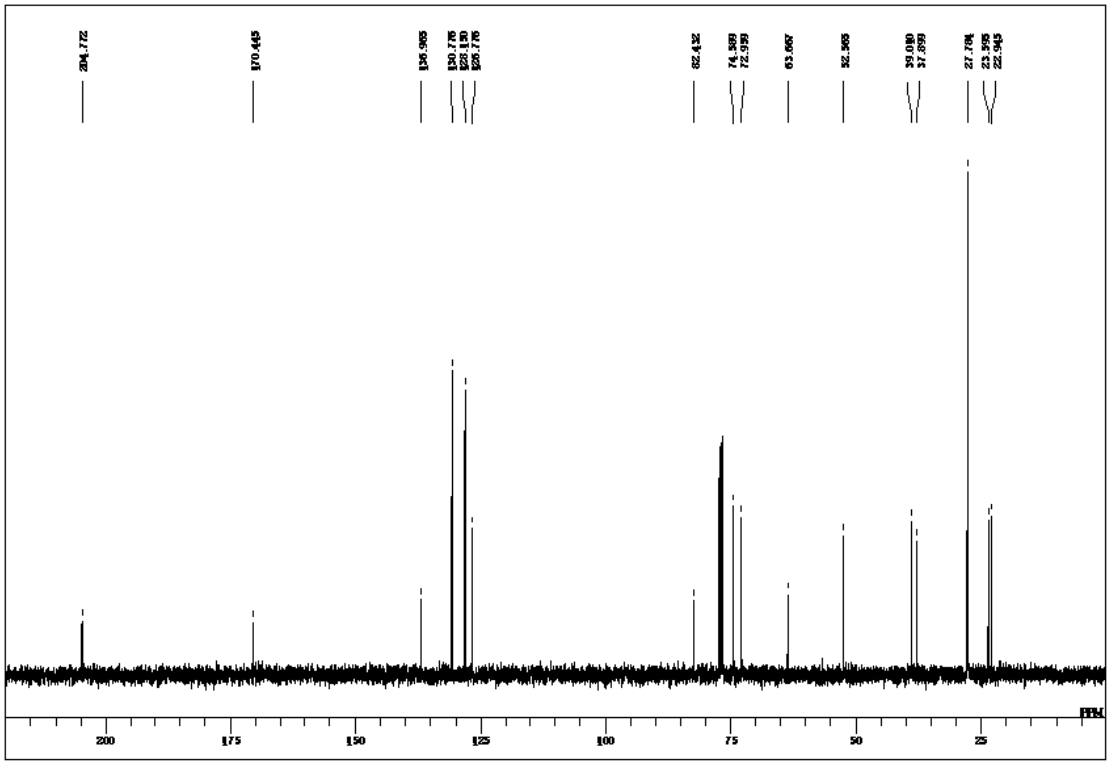
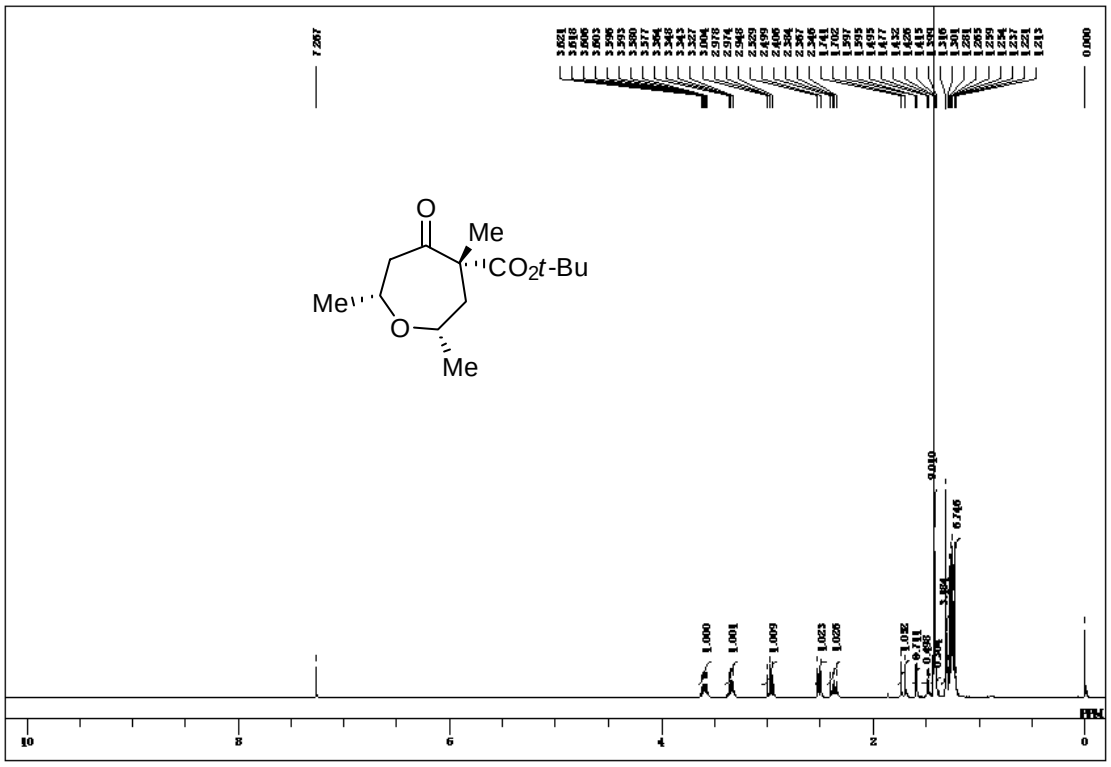
Bn
CO2t-Bu
Me
O
Me

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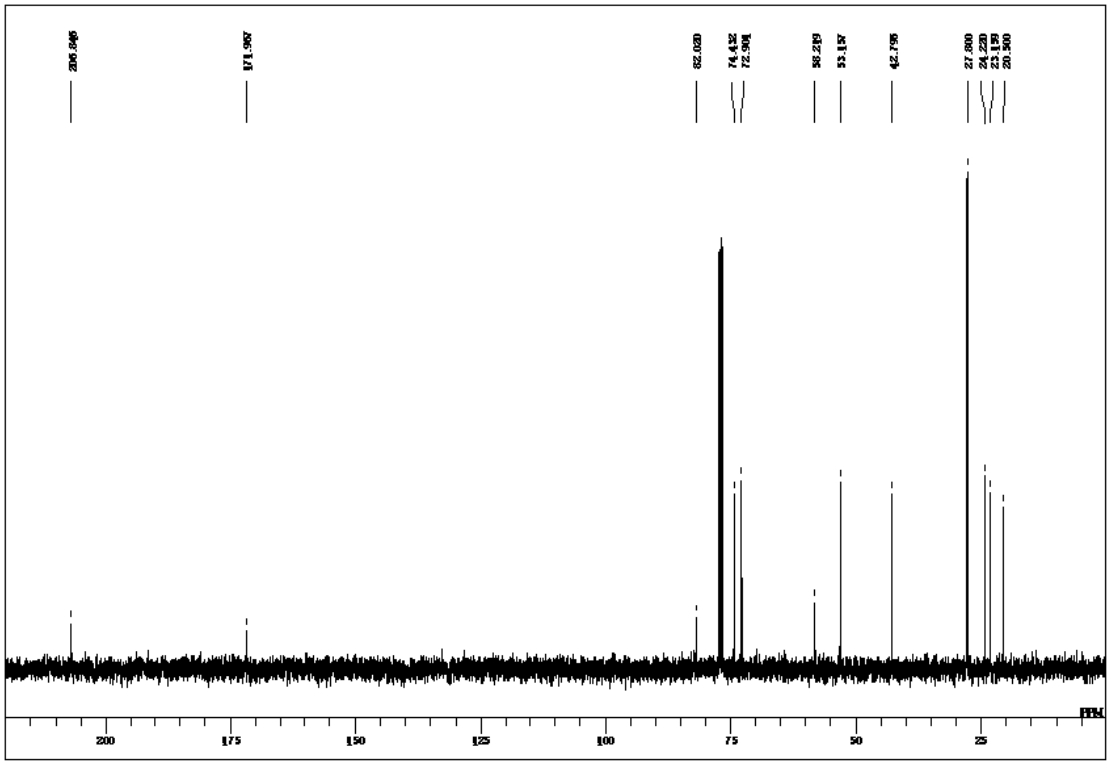
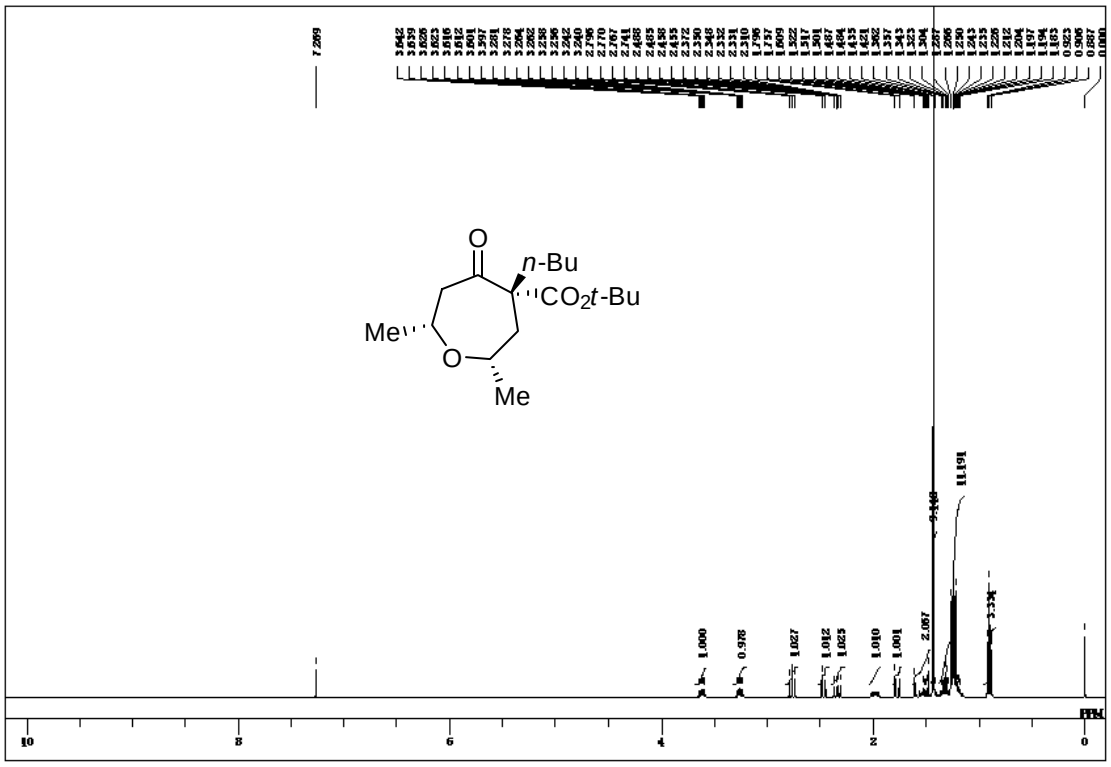
Me
CO2t-Bu
Me
O
Me

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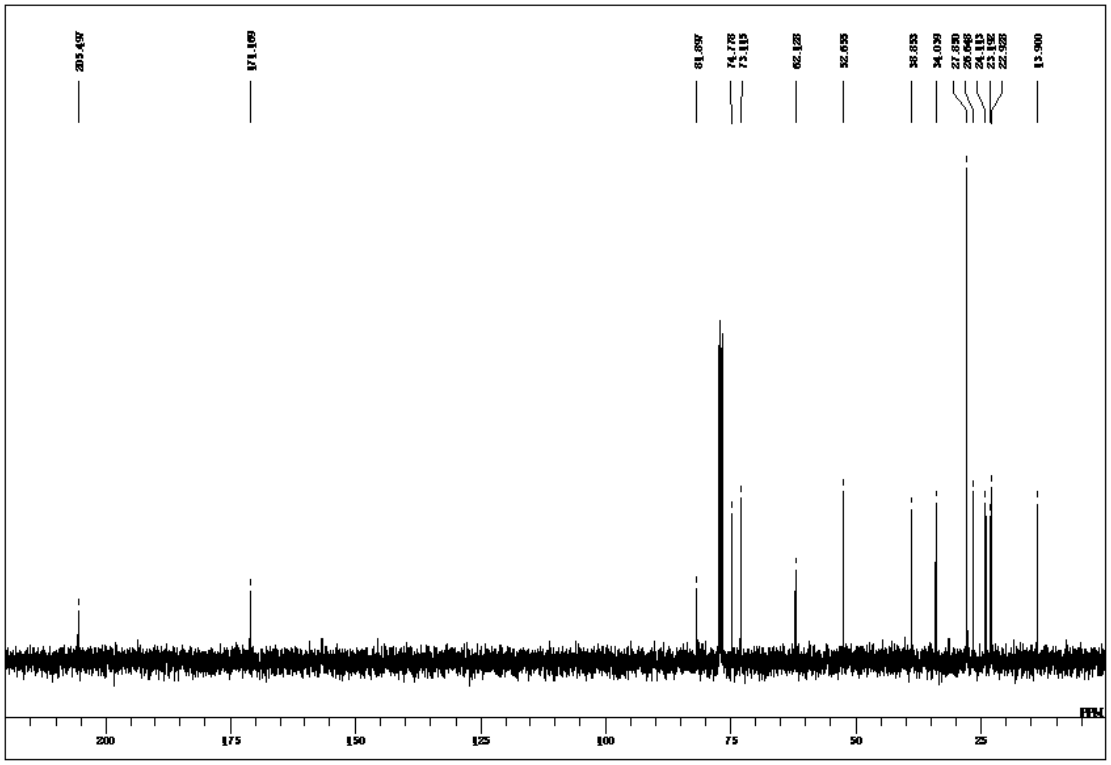
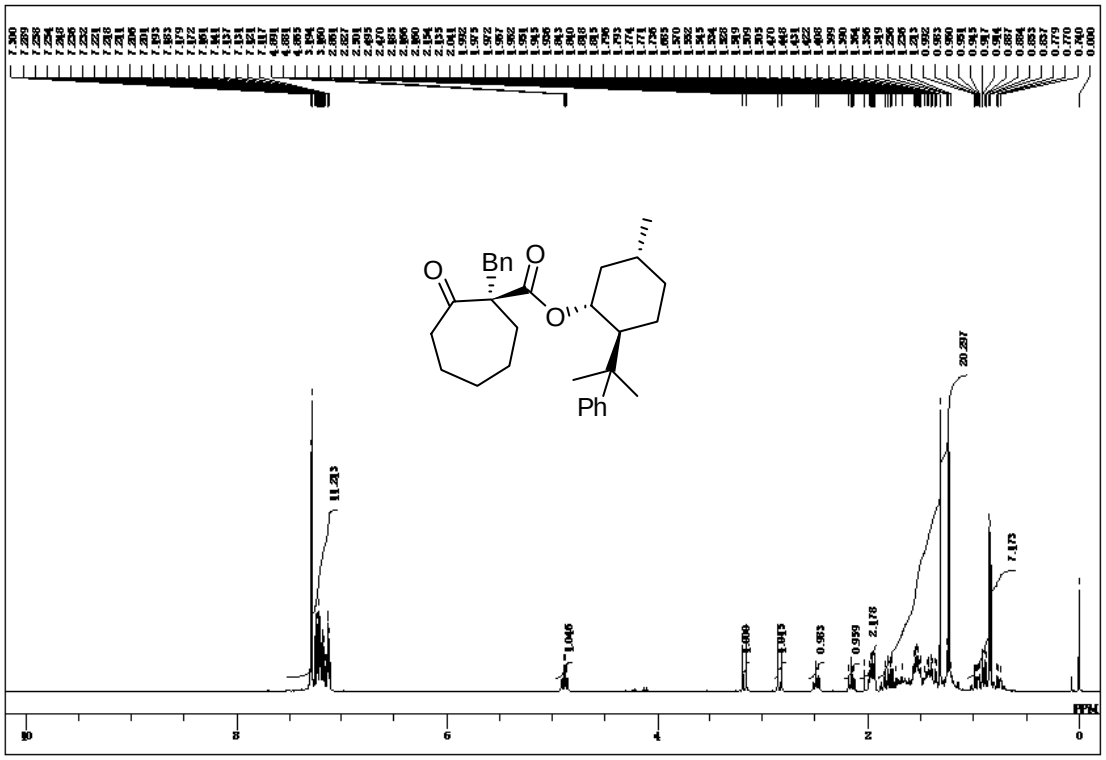
n-Bu
CO2t-Bu
Me
O
Me




Bn
O
O
O
Ph
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1.000
1.043
0.983
0.959
2.178
20.297
7.173
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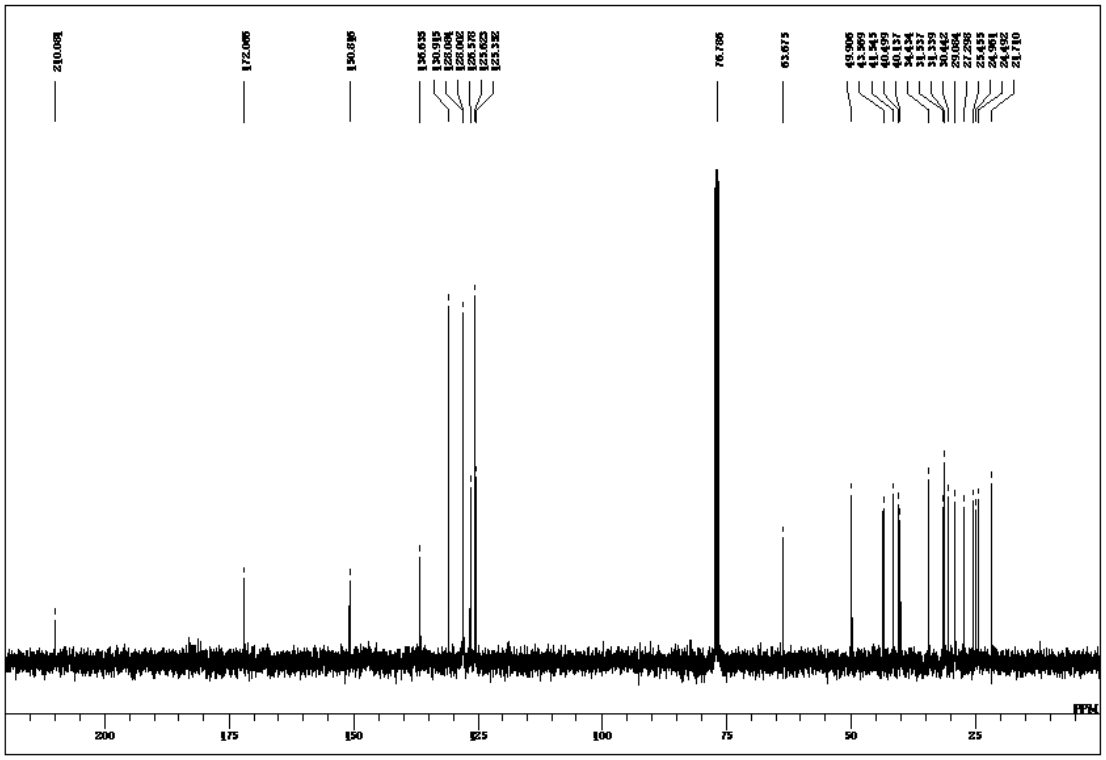
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172.006
150.595
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130.913
128.004
128.002
126.576
123.623
123.532
76.706
63.673
49.906
43.909
41.545
40.659
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31.537
31.339
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29.054
27.256
23.455
24.981
24.492
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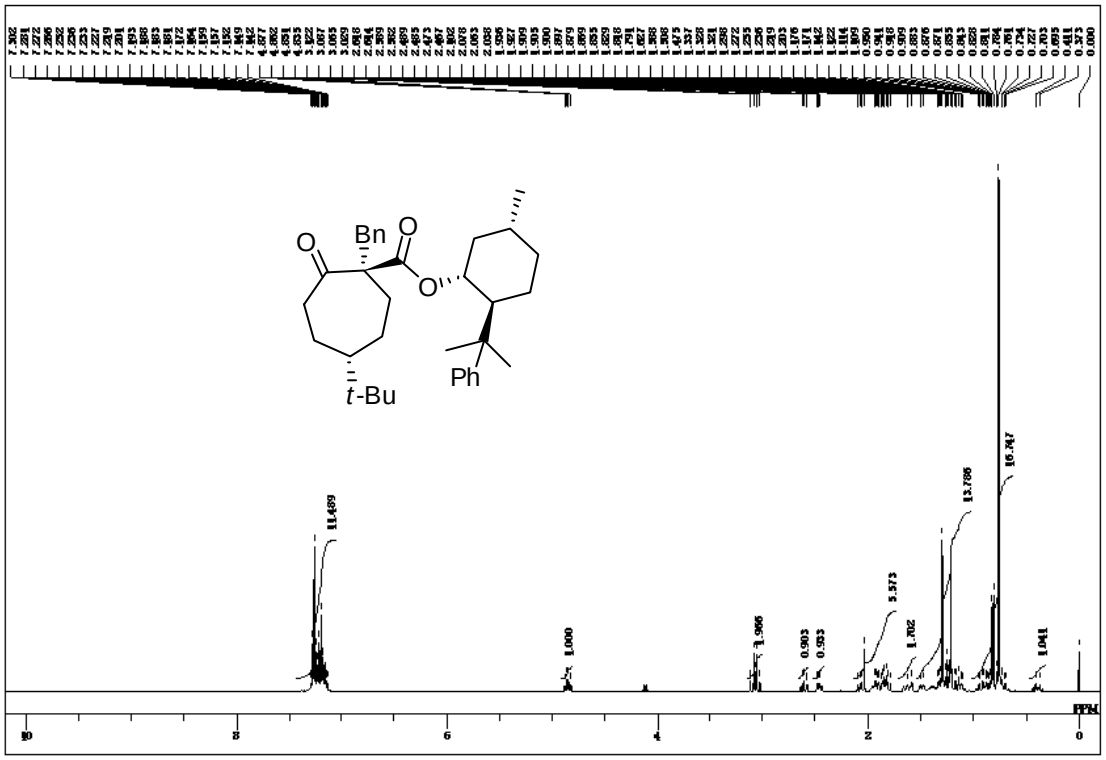
PPM


Bn
O
O
O
t-Bu
Ph
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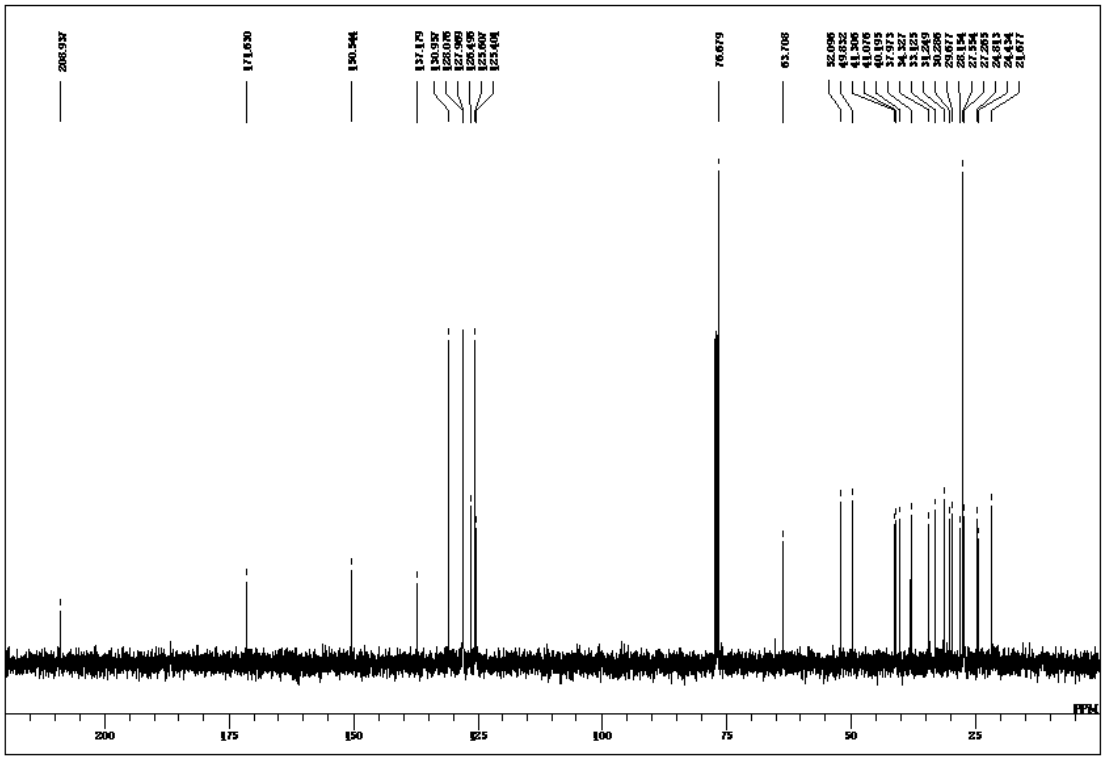
PPM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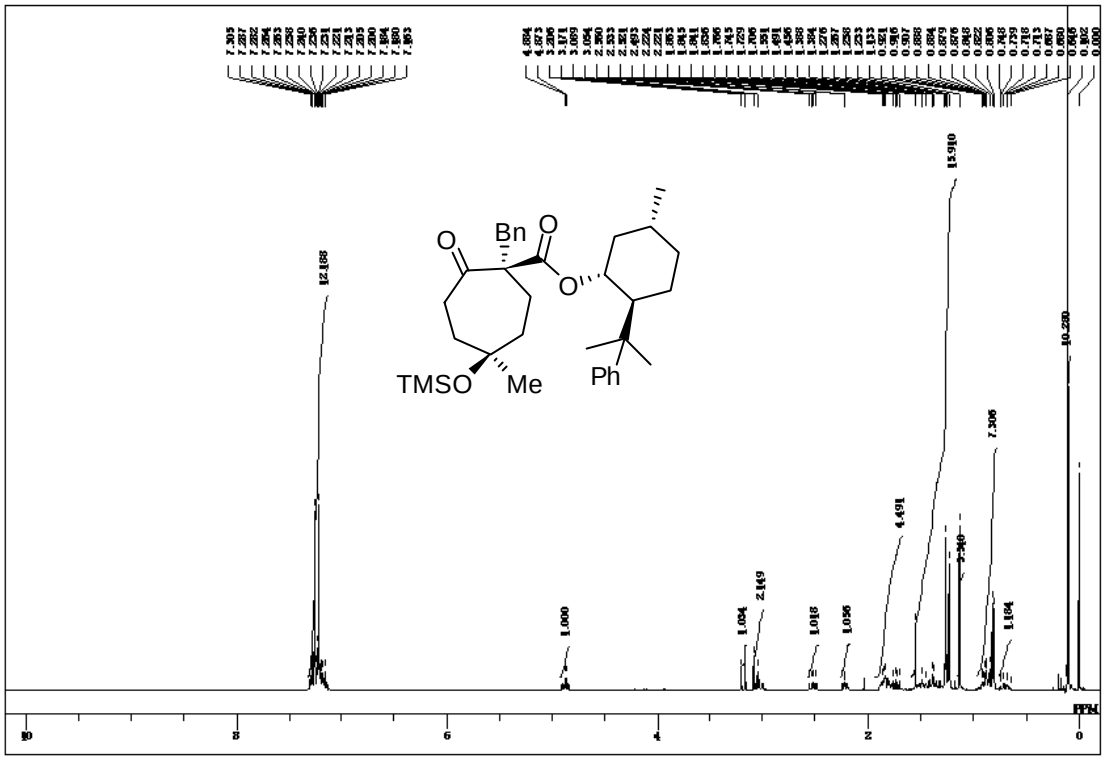
126.496
125.607
125.404
76.679
63.708
PPM


Bn
O
O
O
TMSO
Me
Ph
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1.034
1.018
1.036
1.184
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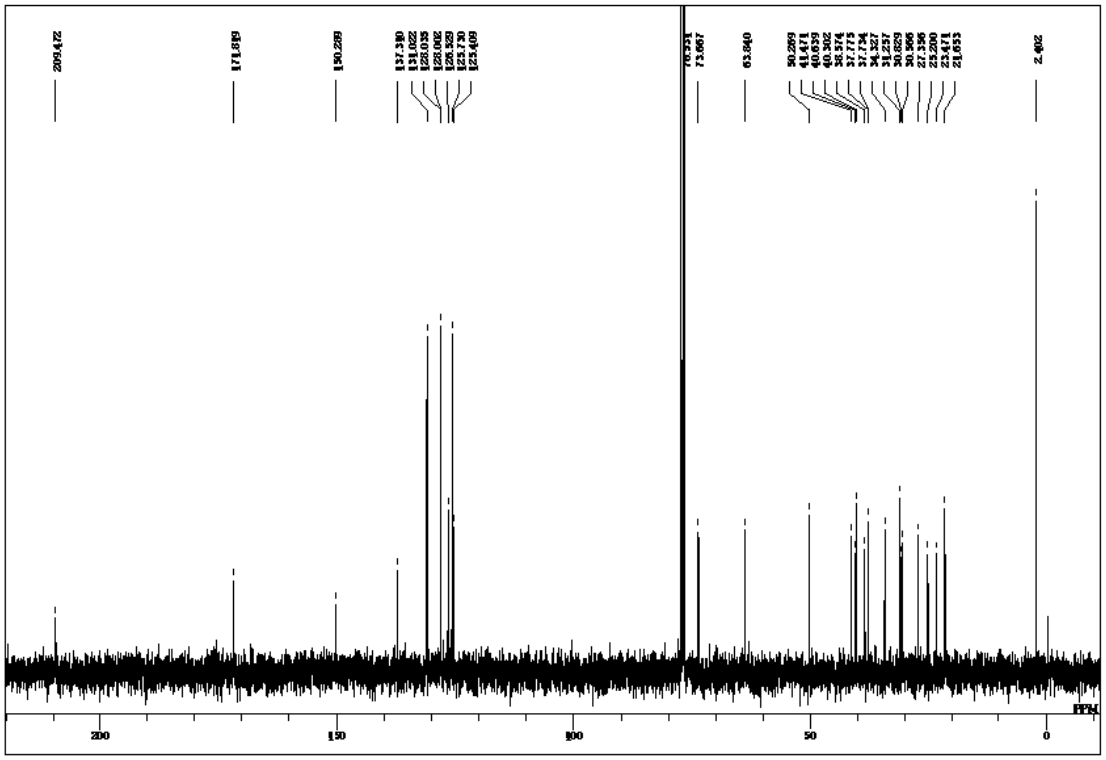
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128.035
128.008
126.923
123.730
123.409
76.251
73.667
63.040
50.299
41.471
40.653
40.302
38.574
37.775
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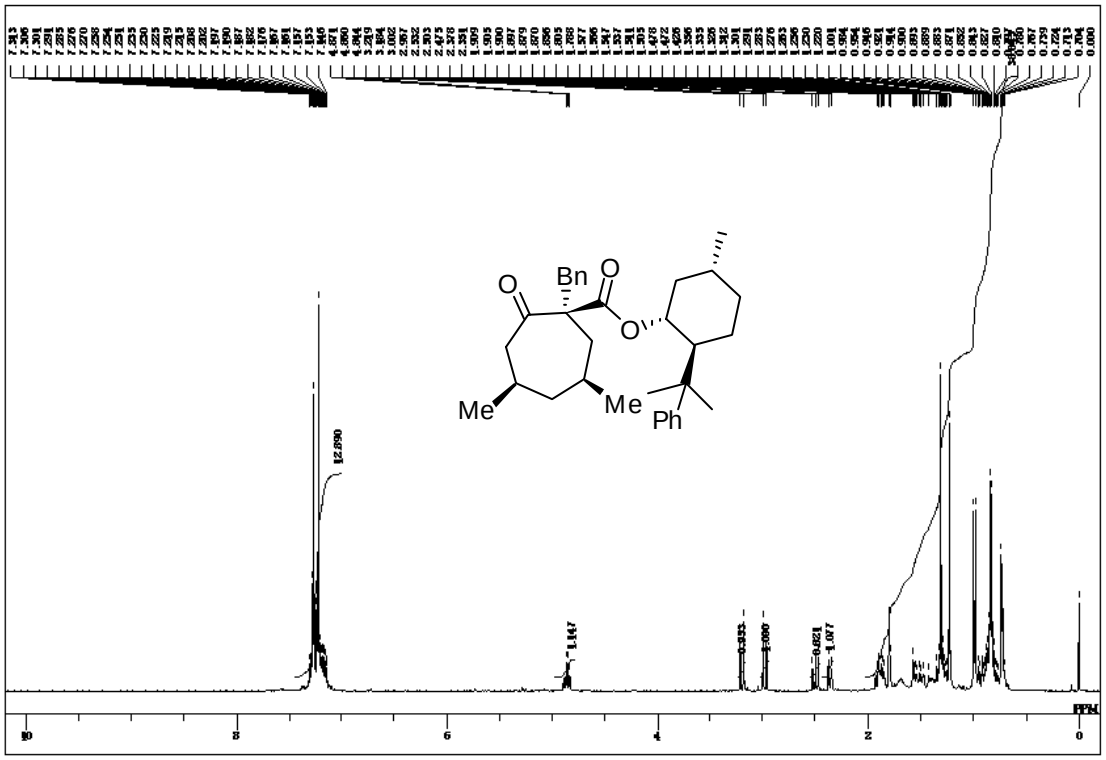
34.327
31.227
30.629
30.506
27.396
25.200
23.471
21.653
2.402
PPM


Bn
O
O
O
Me
Me
Ph
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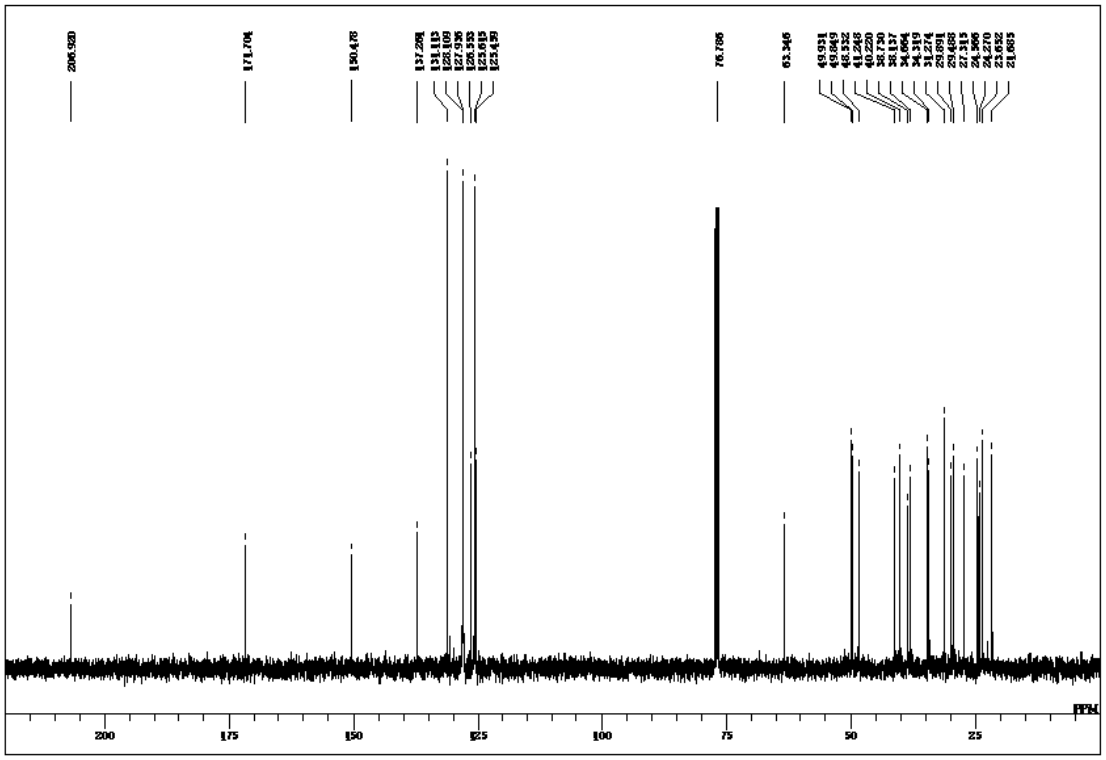
0.833
1.000
0.821
1.077
PPM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131.113
128.109
127.936
126.533
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123.439
76.706
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49.931
43.849
40.532
34.684
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29.498
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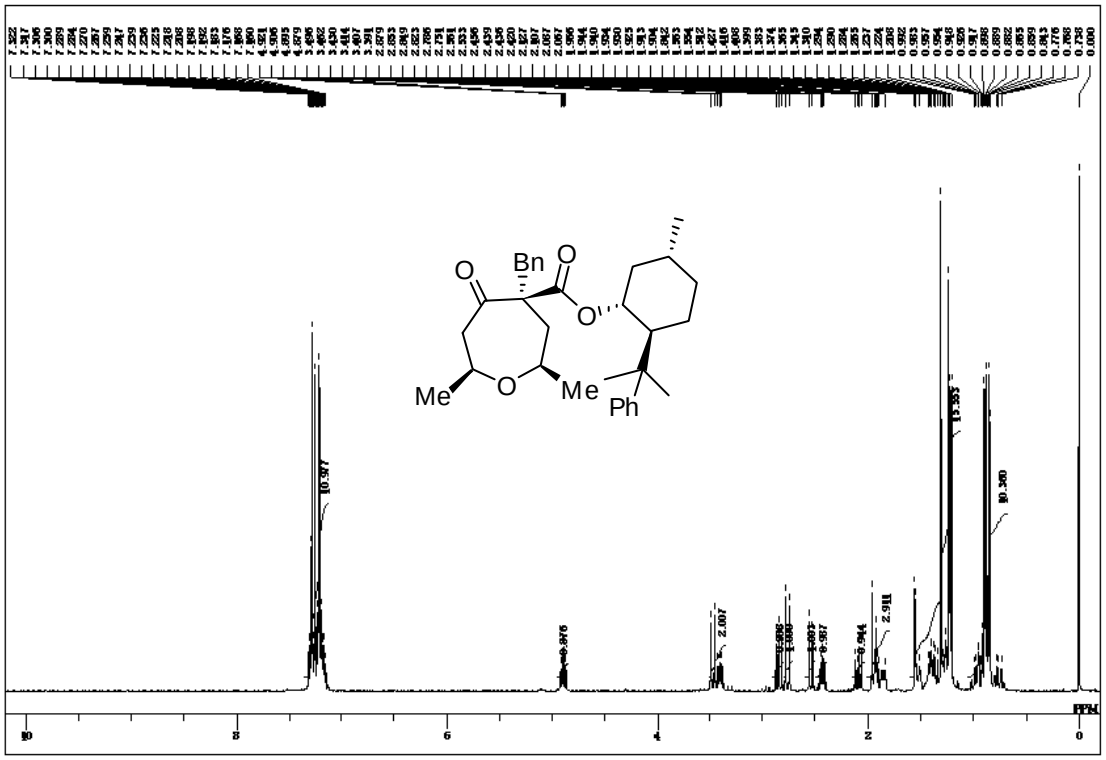
24.986
24.270
23.622
21.865
PPM


Bn
O
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O
O
Me
Me
Ph
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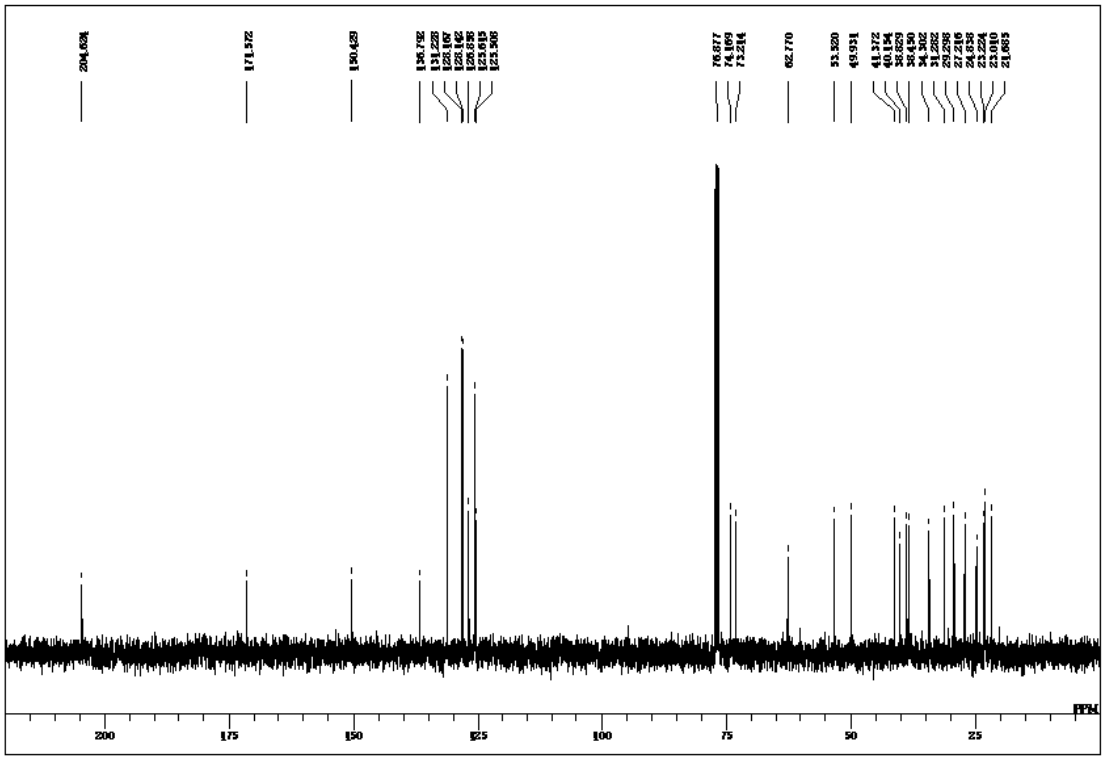
0.976
2.007
2.911
10.360
PPM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128.142
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125.500
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74.169
73.214
62.770
53.320
49.931
41.372
40.154
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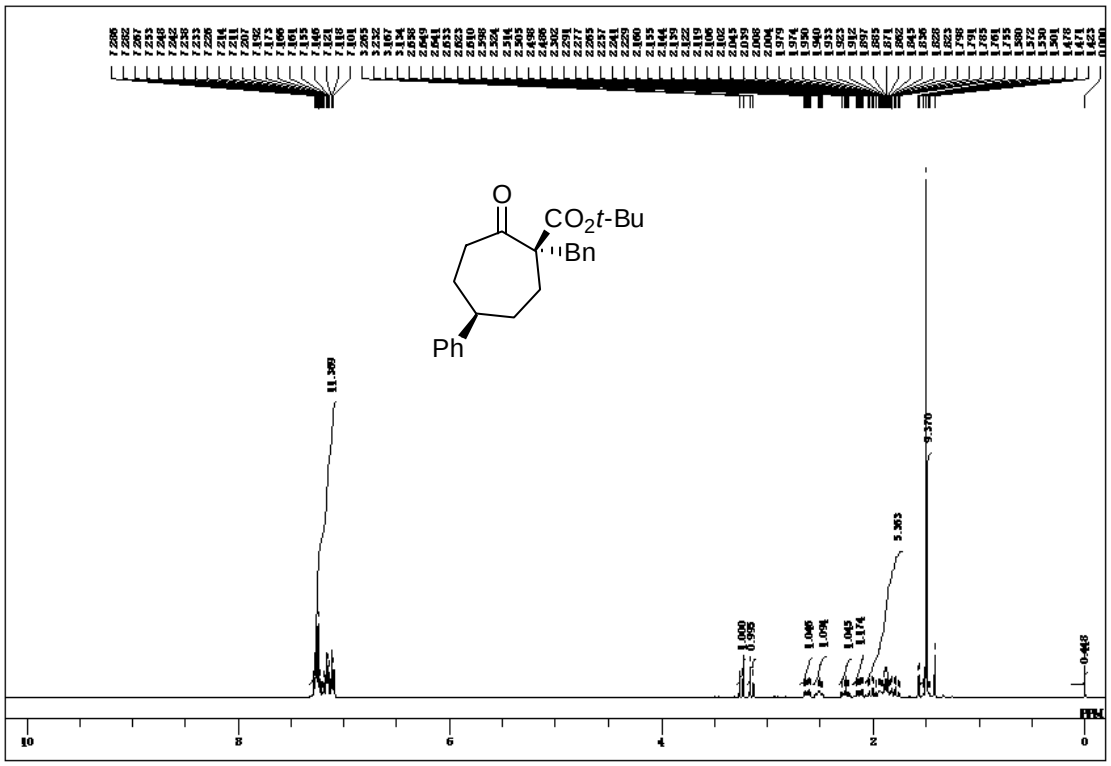
35.430
34.302
31.282
29.298
27.216
26.535
25.224
23.010
21.665
PPM


O
CO2t-Bu
Bn
Ph
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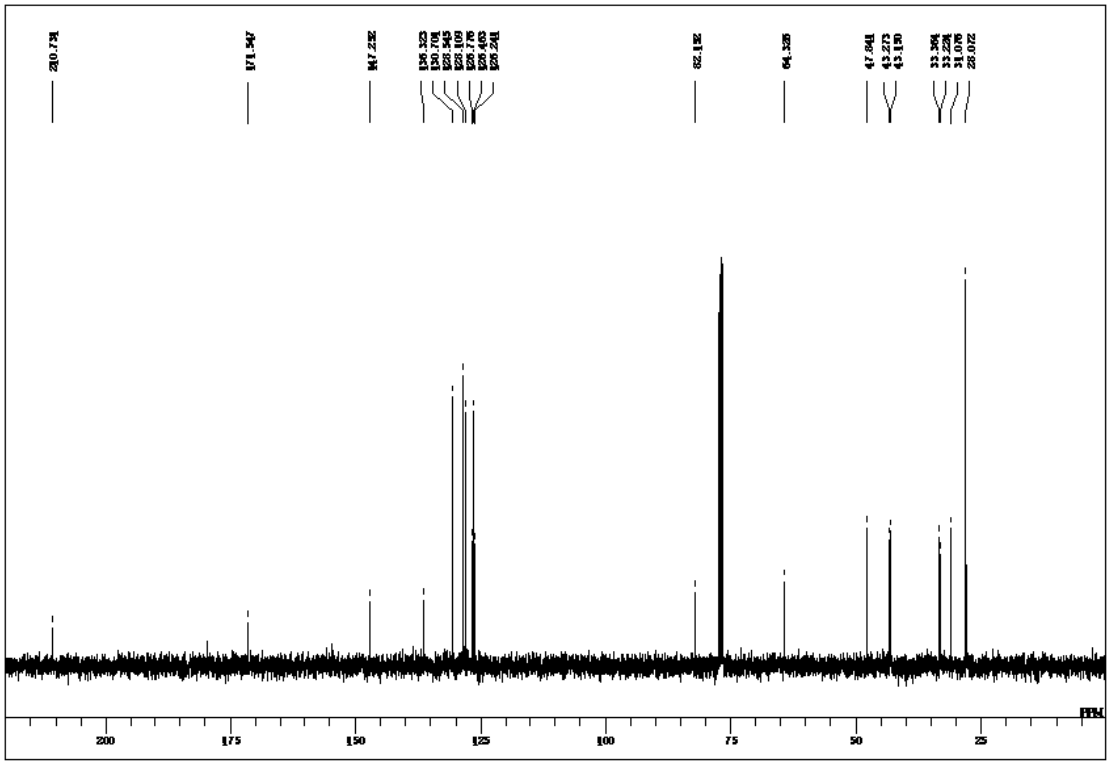
9.370
5.363
1.000
0.995
1.045
1.094
1.045
1.174
0.446
PPM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128.109
126.776
126.405
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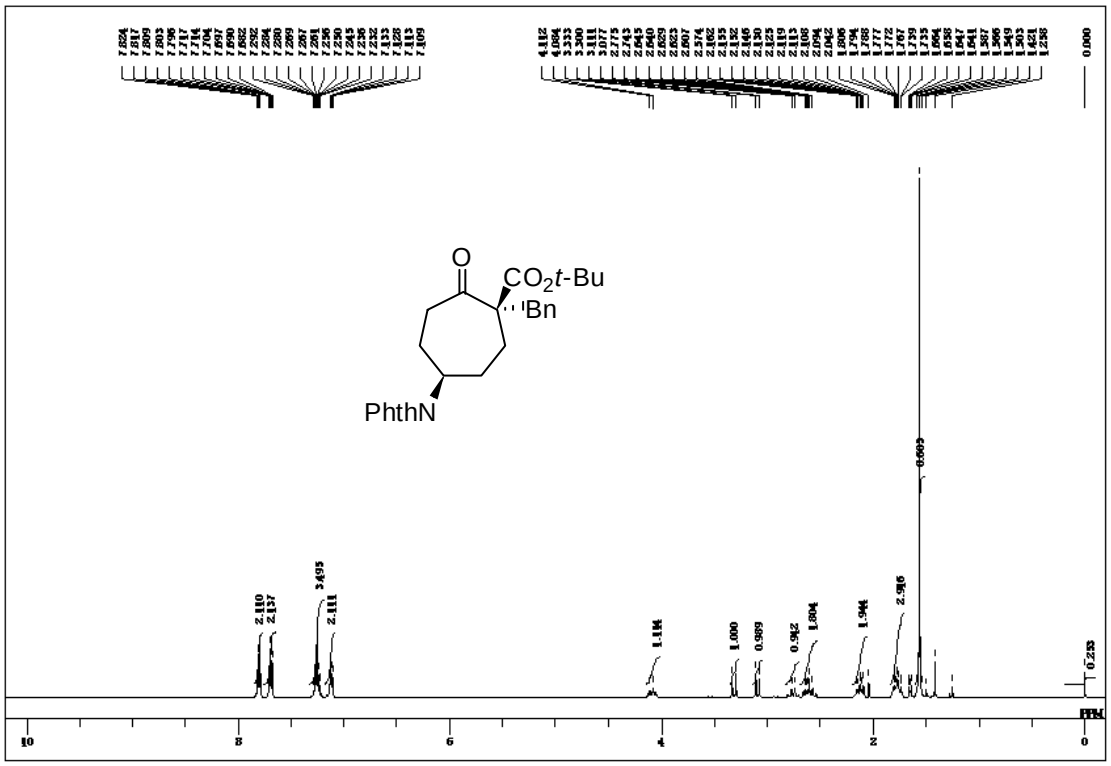
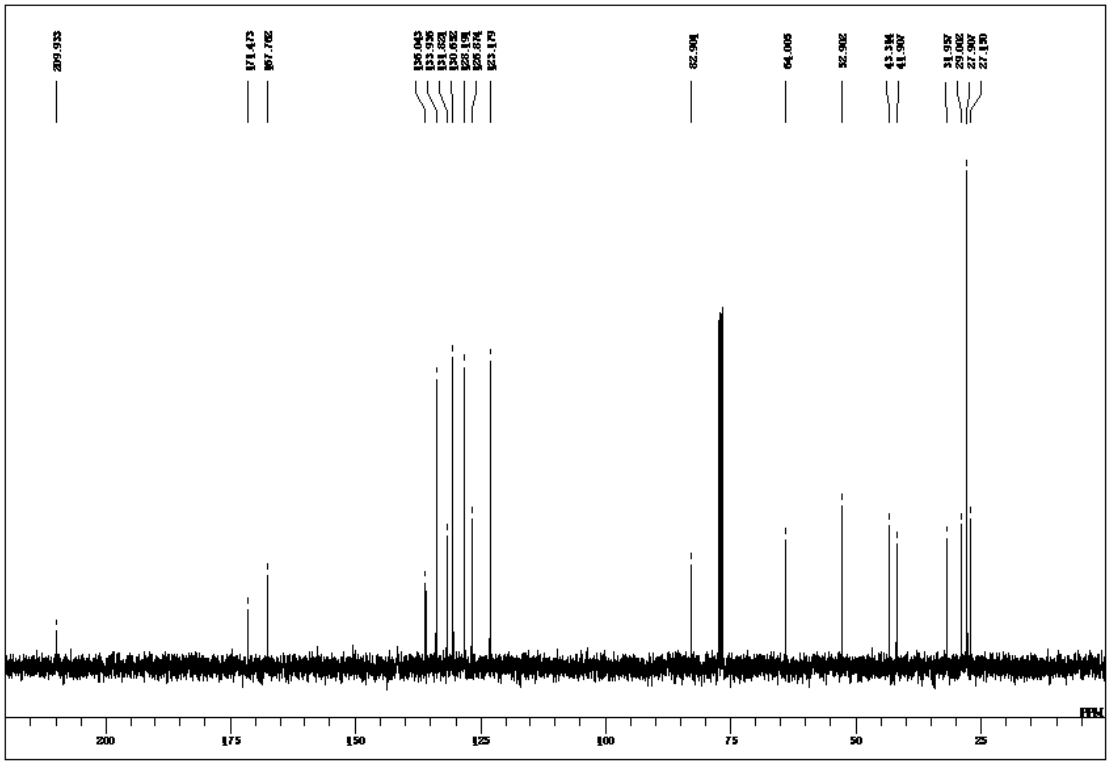
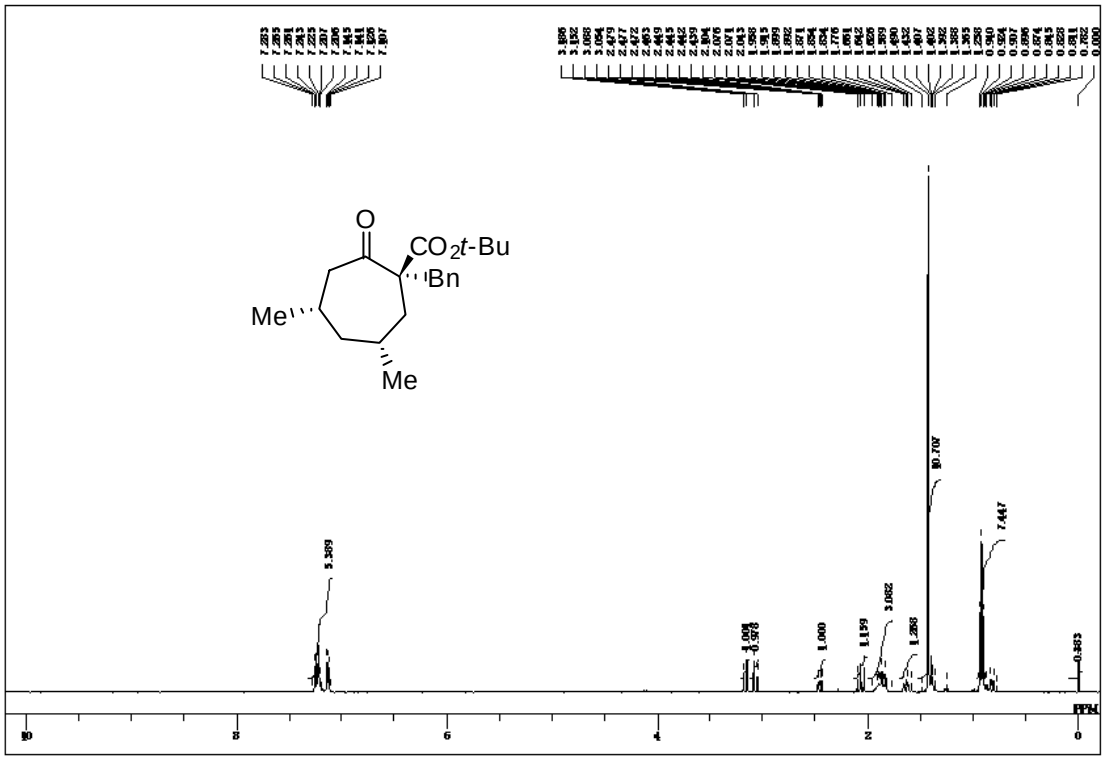
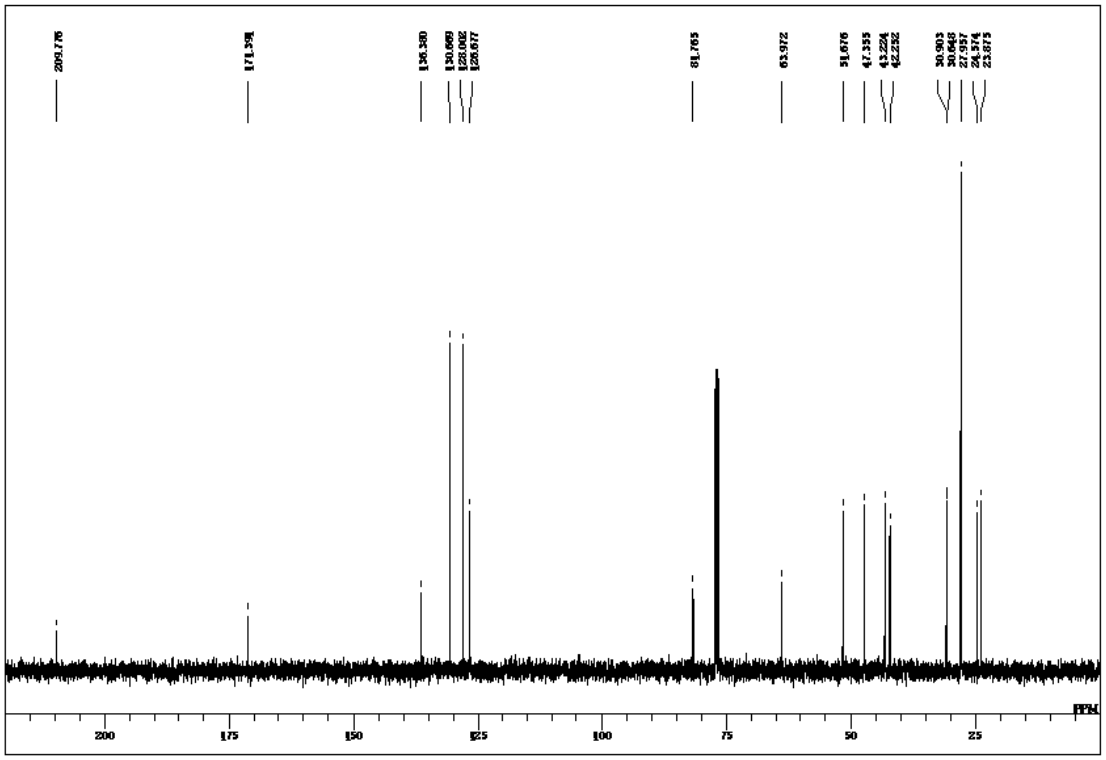
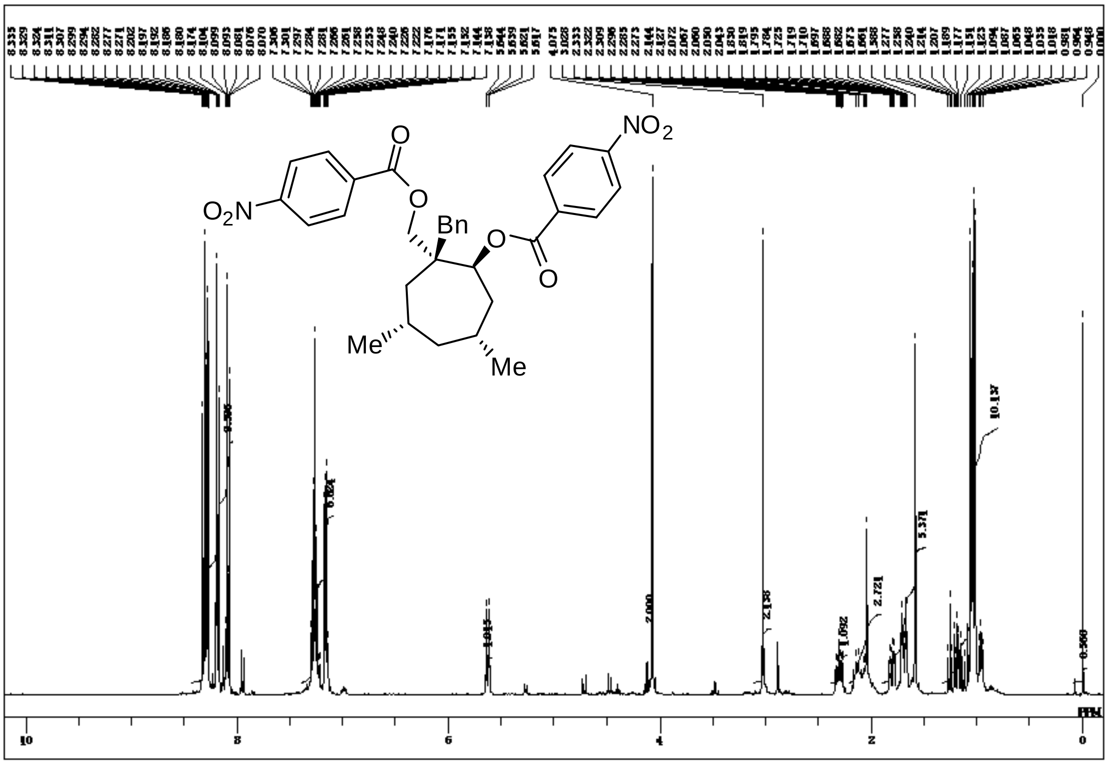
82.182
64.328
47.841
43.273
43.150
33.394
33.228
31.076
28.072
PPM

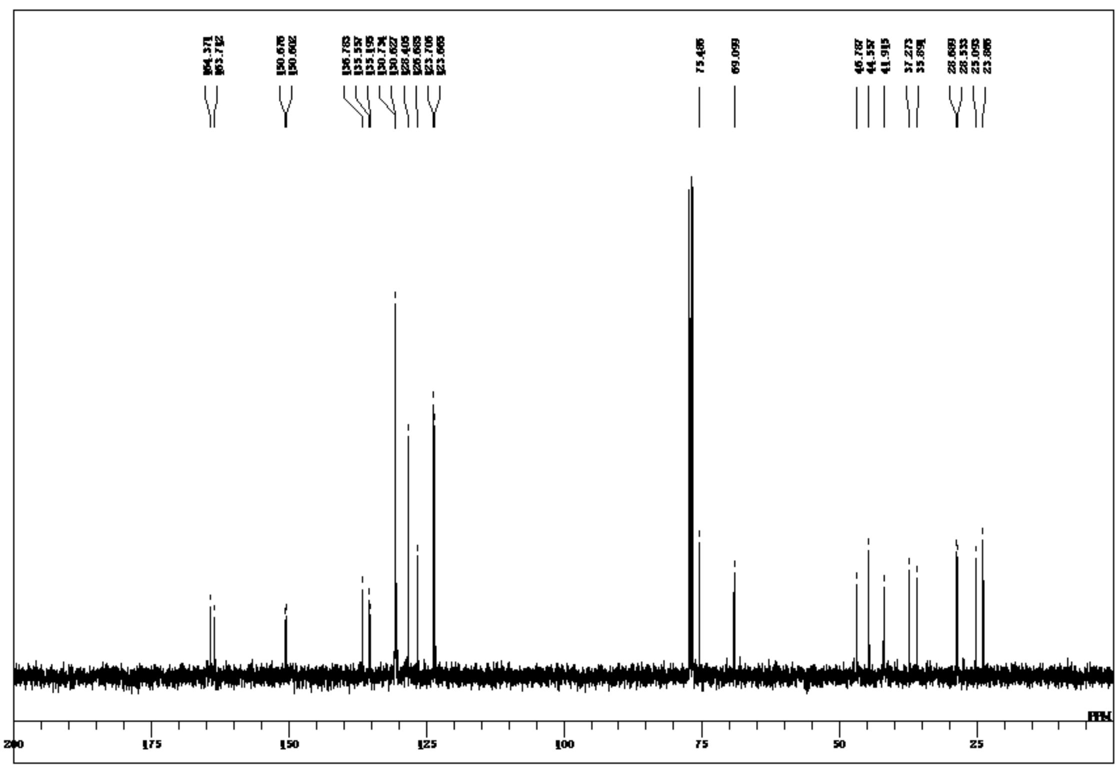

O
CO2t-Bu
Bn
PhthN

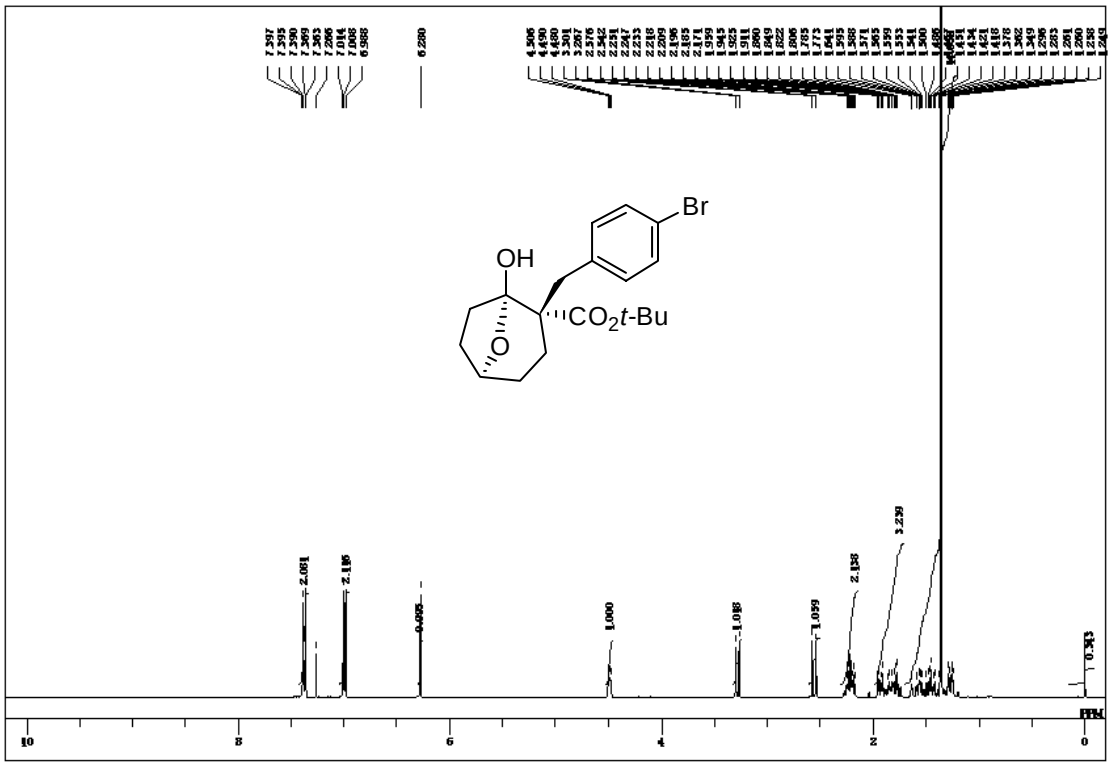


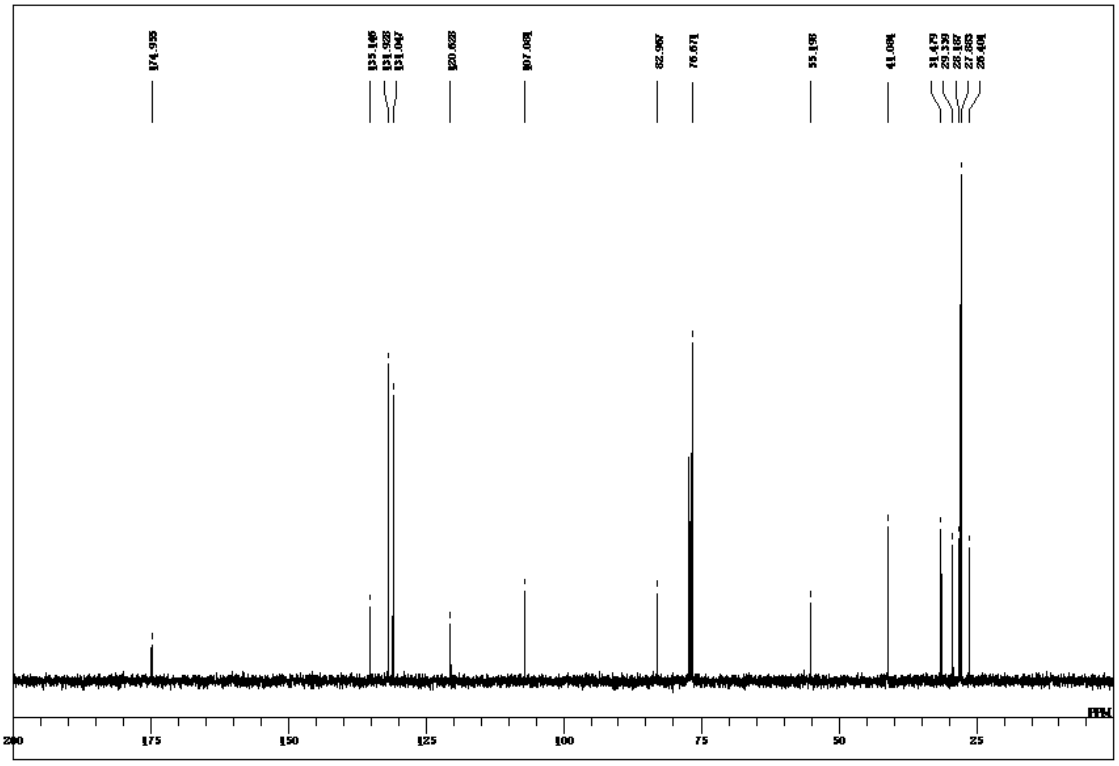

O
CO2t-Bu
Bn
Me
Me

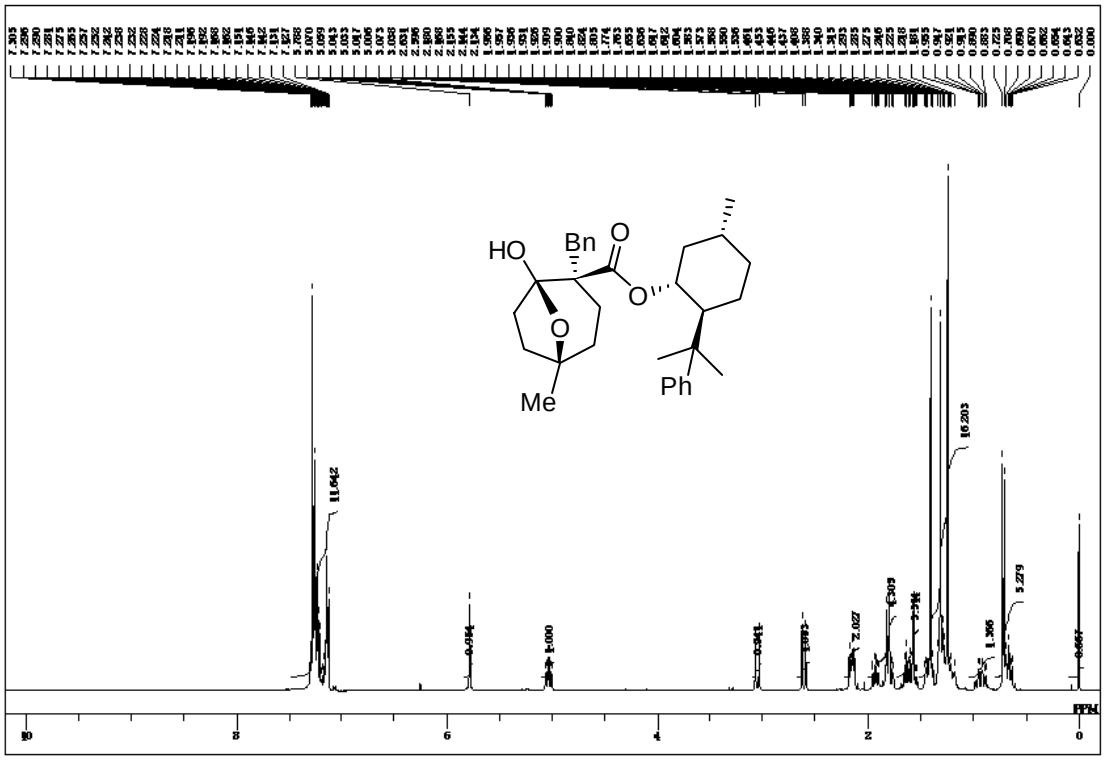



NO2
O
O2N
O
Bn
O
O
Me
Me




Br
OH
CO_2t-Bu
O
PPM


PPM


HO
Bn
O
O
O
Me
Ph
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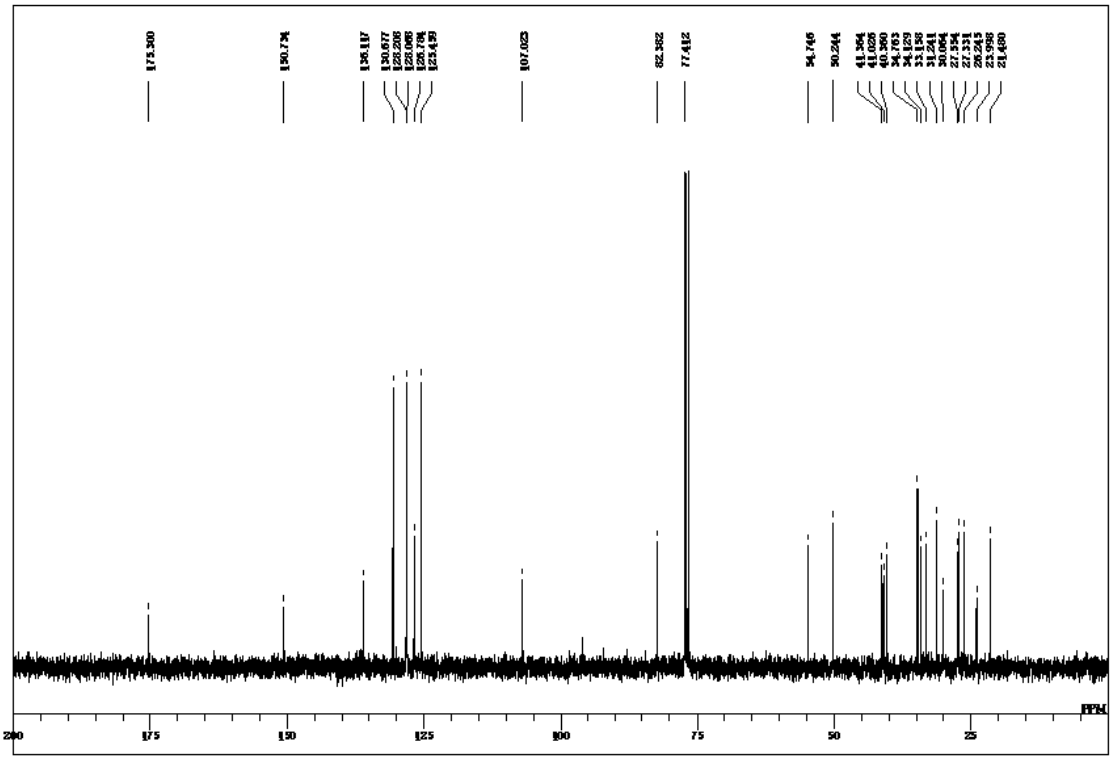
3.993
2.027
6.309
7.516
16.203
1.306
5.279
0.667
PPM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128.086
126.704
125.439
107.023
82.582
77.412
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50.244
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41.025
40.360
34.783
34.179
33.158
31.241
30.064
27.554
27.331
26.241
23.956
21.490
PPM