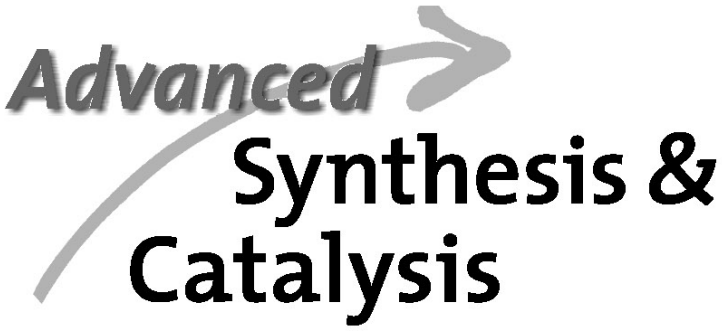


Supporting Information

Intermolecular Gold(I)-Catalyzed Alkyne Carboalkoxylation Reactions for the Multicomponent Assembly of β-Alkoxy Ketones

Danielle M. Schultz,* Nicholas R. Babij, and John P. Wolfe*

Department of Chemistry, University of Michigan, 930 N. University Avenue, Ann Arbor, Michigan 48109-1055

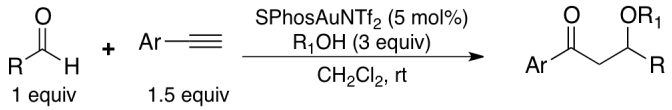
Supporting Information

Experimental procedures and characterization data for new compounds in Tables 1–2 and Equations 1–5.

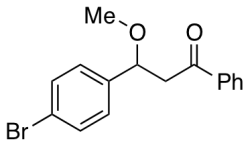
Table of Contents

General: All reactions were carried out at room temperature in sealed tubes under a nitrogen atmosphere. All (NHC)AuNTf$_2$ and (phosphine)AuNTf$_2$ catalysts were prepared according to procedures reported by Gagosz.[1] All aldehydes, alcohols and alkynes used in Tables 1-2 and Equation 1 were purchased from commercial sources (Sigma-Aldrich Chemical Co. or Acros Chemical Co.) and used without further purification. Compounds **29** and **31** in Equations 3–4 were purchased from Sigma-Aldrich Chemical Co. and used without further purification. Dichloromethane was purified using a GlassContour solvent purification system. Structural and stereochemical assignments were made on the basis of 2-D COSY, HSQC, and NOESY experiments. Ratios of diastereomers were determined by ^{1}H NMR analysis. Yields refer to isolated yields of compounds estimated to be ≥95% pure as determined by ^{1}H NMR analysis unless otherwise noted.

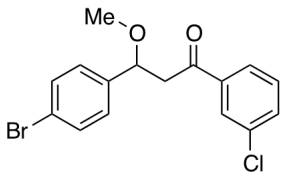
Synthesis and Characterization of β-Alkoxy Ketone Products



General procedure: Au(I)-catalyzed synthesis of β-alkoxy ketones. An oven-dried test tube was equipped with a magnetic stir bar and cooled under a stream of N_2 before being charged with $SPhosAuNTf_2$ (5 mol%). The tube was then charged with a 0.1 M CH_2Cl_2 solution of aldehyde (1 equiv), alkyne (1.5 equiv) and alcohol (3 equiv) before being sealed with a septum. The resulting mixture was stirred at room temperature and monitored by TLC analysis. After the starting material was consumed, the mixture was concentrated *in vacuo* and purified by flash chromatography on silica gel using hexanes/ethyl acetate as the eluent.

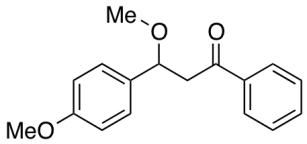


3-(4-Bromophenyl)-3-methoxy-1-phenylpropan-1-one (10). The reaction of 2-chlorobenzaldehyde (65 mg, 0.35 mmol) with phenylacetylene (59 μl, 0.53 mmol) and methanol (43 μl, 1.05 mmol) was conducted according to the general procedure. This procedure afforded 65 mg (59%) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.5 Hz, 2 H), 7.55 (t, *J* = 7.0 Hz, 1 H), 7.49 (d, *J* = 8.0 Hz, 2 H), 7.44 (t, *J* = 7.5 Hz, 2 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 4.84 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.56 (dd, *J* = 8.0, 16.5 Hz, 1 H), 3.22 (s, 3 H), 3.06 (dd, *J* = 4.5, 16.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.3, 140.5, 136.9, 133.2, 131.7, 128.6, 128.4, 128.2, 121.7, 78.9, 56.9, 46.9; IR (film) 3052, 1688, 1265, 1098 cm^{-1}. MS (ESI) 341.0159 (341.0148 calcd for $C_{16}H_{15}BrO_2$, M + Na^+).

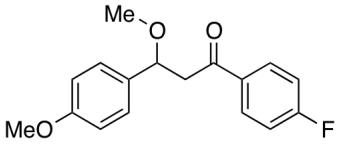


3-(4-Bromophenyl)-1-(3-chlorophenyl)-3-methoxypropan-1-one (15). The reaction of 4-bromobenzaldehyde (30 mg, 0.16 mmol) with 3-chloro-1-ethynylbenzene (30 μl, 0.24 mmol) and methanol (20 μl, 0.48 mmol) was conducted according to the general procedure using 5 mol% of $JohnPhosAuNTf_2$ in place of $SPhosAuNTf_2$. This procedure afforded 40 mg (69%) of the title compound as an off white solid: mp = 68–70 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1 H), 7.79 (d, *J* = 8.0 Hz, 1 H), 7.51 (d, *J* = 8.0 Hz, 1 H), 7.49 (d, *J* = 9.0 Hz, 2 H), 7.39 (t, *J* = 8.0 Hz, 1 H), 7.28 (d, *J* = 8.0 Hz, 2 H), 4.82 (dd, *J* = 4.5, 8.0 Hz, 1 H), 3.52 (dd, *J* = 8.5, 16.5 Hz, 1 H), 3.21 (s, 3 H), 3.01 (dd, *J* = 4.5, 16.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.0, 140.2, 138.5, 134.9,

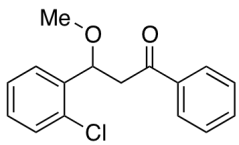
133.1, 131.7, 129.9, 128.4, 128.3, 126.3, 121.8, 78.8, 56.9, 47.0; IR (film) 3052, 1690, 1421, 1265, 1098 cm^{-1}. MS (ESI) 374.9754 (374.9758 calcd for $C_{16}H_{14}BrClO_2$, M + Na^+).



3-Methoxy-3-(4-methoxyphenyl)-1-phenylpropan-1-one (16). The reaction of *p*-anisaldehyde (40 mg, 0.29 mmol) with phenylacetylene (49 μl, 0.44 mmol) and methanol (35 μl, 0.87 mmol) was conducted according to the general procedure. This procedure afforded 54 mg (69%) of the title compound as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.5 Hz, 2 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 7.44 (t, *J* = 8.0 Hz, 2 H), 7.33 (d, *J* = 7.0 Hz, 2 H), 6.91 (d, *J* = 6.5 Hz, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.8, 159.3, 137.2, 133.4, 133.0, 128.5, 128.2, 127.9, 113.9, 79.1, 56.6, 55.2, 47.1; IR (film) 3053, 1684, 1511, 1264, 1172 cm^{-1}. MS (ESI) 293.1154 (293.1148 calcd for $C_{17}H_{18}O_3$, M + Na^+).

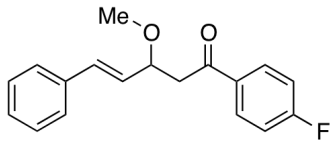


1-(4-Fluorophenyl)-3-methoxy-3-(4-methoxyphenyl)propan-1-one (17). The reaction of *p*-anisaldehyde (40 mg, 0.29 mmol) with 1-ethynyl-4-fluorobenzene (50 μl, 0.44 mmol) and methanol (59 μl, 1.47 mmol) was conducted according to the general procedure. This procedure afforded 68 mg (81%) of the title compound as an orange oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.93 (m, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 7.10–7.06 (m, 2 H), 6.88 (d, *J* = 8.4 Hz, 2 H), 4.78 (dd, *J* = 4.8, 8.4 Hz, 1 H), 3.79 (s, 3 H), 3.53 (dd, *J* = 8.4, 16.4 Hz, 1 H), 3.18 (s, 3 H), 3.01 (dd, *J* = 4.8, 16.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.2, 165.6 (d, *J* = 254.6 Hz), 159.2, 133.6 (d, *J* = 3.1 Hz), 133.1, 130.8 (d, *J* = 9.3 Hz), 127.8, 115.5 (d, *J* = 21.8 Hz), 113.9, 79.1, 56.5, 55.2, 46.9; IR (film) 3053, 1684, 1598, 1511, 1264, 1156 cm^{-1}. MS (ESI) 311.1059 (311.1054 calcd for $C_{17}H_{17}FO_3$, M + Na^+).

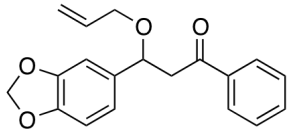


3-(2-Chlorophenyl)-3-methoxy-1-phenylpropan-1-one (18). The reaction of 2-chlorobenzaldehyde (40 mg, 0.28 mmol) with phenylacetylene (44 μl, 0.43 mmol) and methanol

(34 μl, 0.84 mmol) was conducted according to the general procedure using 5 mol% of JohnPhosAuNTf$_2$ in place of SPhosAuNTf$_2$. This procedure afforded 54 mg (69%) of the title compound as a pale yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.0 Hz, 2 H), 7.58–7.54 (m, 2 H), 7.45 (t, *J* = 8.0 Hz, 2 H), 7.37 (d, *J* = 8.0 Hz, 1 H), 7.33 (t, *J* = 7.5 Hz, 1 H), 7.24 (t, *J* = 7. 5 Hz, 1 H), 5.34 (dd, *J* = 3.0, 9.5 Hz, 1 H), 3.39 (dd, *J* = 9.5, 16.5 Hz, 1 H), 3.28 (s, 3 H), 3.15 (dd, *J* = 3.0, 16.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.1, 138.9, 136.9, 133.1, 132.6, 129.6, 128.7, 128.5, 128.2, 127.3, 127.2, 76.1, 57.4, 45.5; IR (film) 3053, 1684, 1264, 1107 cm^{-1}. MS (ESI) 297.0655 (297.0653 calcd for $C_{16}H_{15}ClO_2$, M + Na$^+$).

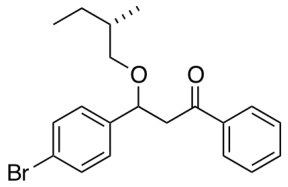


(*E*)-1-(4-Fluorophenyl)-3-methoxy-5-phenylpent-4-en-1-one (19). The reaction of *trans*-cinnamaldehyde (40 mg, 0.30 mmol) with 1-ethynyl-4-fluorobenzene (52 μl, 0.45 mmol) and methanol (36 μl, 0.90 mmol) was conducted according to the general procedure. This procedure afforded 48 mg (56%) of the title compound as an orange oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 7.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 6.66 (d, *J* = 16.0 Hz, 1 H), 6.15 (dd, *J* = 7.5, 16.0 Hz, 1 H), 4.44 (ddd, *J* = 4.5, 8.0, 8.0 Hz, 1 H), 3.43 (dd, *J* = 8.0, 16.5 Hz, 1 H), 3.33 (s, 3 H), 3.01 (dd, *J* = 4.5, 16.0 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.1, 165.7 (d, *J* = 254.2 Hz), 136.2, 133.6 (d, *J* = 2.9 Hz), 132.6, 130.9 (d, *J* = 8.8 Hz), 128.6, 128.5, 127.9, 126.5, 115.6 (d, *J* = 21.6 Hz), 78.3, 56.6, 44.7; IR (film) 3053, 2985, 1686, 1598, 1506, 1265, 1156 cm^{-1}. MS (ESI) 307.1111 (307.1105 calcd for $C_{18}H_{17}FO_2$, M + Na$^+$).

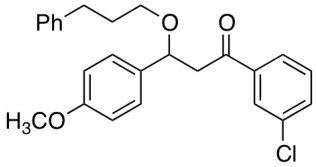


3-(Allyloxy)-3-(benzo[*d*][1,3]dioxol-5-yl)-1-phenylpropan-1-one (20). The reaction of piperonal (39 mg, 0.26 mmol) with phenylacetylene (43 μl, 0.39 mmol) and allyl alcohol (53 μl, 0.78 mmol) was conducted according to the general procedure. This procedure afforded 52 mg (64%) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.0 Hz, 2 H), 7.53 (t, *J* = 7.5 Hz, 1 H), 7.43 (t, *J* = 7.5 Hz, 2 H), 6.92 (s, 1 H), 6.85 (d, *J* = 8.0 Hz, 1 H), 6.77 (d, *J* = 8.0 Hz, 1 H), 5.94 (d, *J* = 4.0 Hz, 2 H), 5.87–5.79 (m, 1 H), 5.19–5.09 (m, 2 H), 4.95 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.92–3.88 (m, 1 H), 3.80 (dd, *J* = 6.0, 12.5 Hz, 1 H), 3.58 (dd, *J* = 8.0, 16.5 Hz, 1 H), 3.09 (dd, *J* = 5.0, 16.5 Hz, 1 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.6, 147.9,

147.2, 137.2, 135.6, 134.6, 133.1, 128.5, 128.2, 120.3, 116.9, 108.1, 106.9, 101.0, 77.1, 69.5, 47.2; IR (film) 3053, 1686, 1487, 1264, 1040 cm^{-1}. MS (ESI) 333.1110 (333.1097 calcd for $C_{19}H_{18}O_4$, M + Na^+).

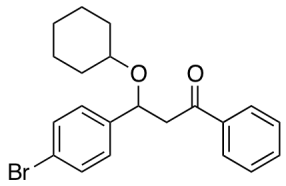


(2*S*)-3-(4-Bromophenyl)-3-(2-methylbutoxy)-1-phenylpropan-1-one (21). The reaction of 4-bromobenzaldehyde (40 mg, 0.22 mmol) with phenylacetylene (36 μl, 0.32 mmol) and (*S*)-2-methylbutan-1-ol (71 μl, 0.66 mmol) was conducted according to the general procedure. This procedure afforded 57 mg (69%) of the title compound as a 1:1 mixture of diastereomers that were inseparable by flash chromatography. Data are for the mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.2 Hz, 2 H), 7.53 (t, *J* = 5.6 Hz, 1 H), 7.48–7.41 (m, 4 H), 7.27 (d, *J* = 8.4 Hz, 2 H), 4.87 (dd, *J* = 5.2, 8.8 Hz, 1 H), 3.55 (dd, *J* = 8.4, 16.0 Hz, 1 H), 3.15–3.11 (m, 1 H), 3.08–3.03 (m, 1 H), 2.99 (ddd, *J* = 2.4, 4.8, 16.4 Hz, 1 H), 1.54–1.48 (m, 1 H), 1.36–1.26 (m, 1 H), 1.05–0.95 (m, 1 H), 0.78-0.76 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 141.3, 137.3, 133.1, 131.6, 128.5, 128.4, 128.3, 128.2, 121.4, 77.8, 77.7, 74.5, 74.4, 47.2, 35.0, 34.9, 26.1, 26.0, 16.6, 16.4, 11.3, 11.2; IR (film) 3053, 1684, 1511, 1264, 1010 cm^{-1}. MS (ESI) 397.0775 (397.0774 calcd for $C_{20}H_{23}BrO_2$, M + Na^+).

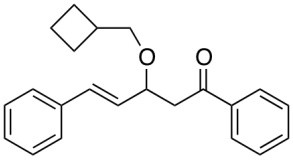


1-(3-Chlorophenyl)-3-(4-methoxyphenyl)-3-(3-phenylpropoxy)propan-1-one (22). The reaction of *p*-anisaldehyde (35 mg, 0.26 mmol) with 3-chloro-1-ethynylbenzene (48 μl, 0.39 mmol) and 3-phenyl-1-propanol (106 mg, 0.78 mmol) was conducted according to the general procedure. This procedure afforded 56 mg (53%) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (s, 1 H), 7.84 (d, *J* = 8.0 Hz, 1 H), 7.50 (d, *J* = 7.5 Hz, 1 H), 7.38 (t, *J* = 7.5 Hz, 1 H), 7.31 (d, *J* = 8.5 Hz, 2 H), 7.23 (t, *J* = 7.0 Hz, 2 H), 7.14 (t, *J* = 7.5 Hz, 1 H), 7.08 (d, *J* = 8.5 Hz, 2 H), 6.90 (d, *J* = 8.5 Hz, 2 H), 4.87 (dd, *J* = 4.5, 8.5 Hz, 1 H), 3.80 (s, 3 H), 3.57 (dd, *J* = 8.5, 16.0 Hz, 1 H), 3.55–3.31 (m, 1 H), 3.29–3.24 (m, 1 H), 3.00 (dd, *J* = 4.5, 16.0 Hz, 1 H), 2.61–2.49 (m, 2 H), 1.80–1.74 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 159.3, 142.1, 139.0, 134.8, 133.7, 132.9, 129.8, 128.5, 128.4, 128.2, 127.8, 126.4, 125.7, 113.9, 77.8, 67.9,

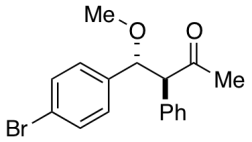
55.3, 47.4, 32.3, 31.4; IR (film) 3052, 1689, 1511, 1263, 1098 cm^{-1}. MS (ESI) 431.1383 (431.1384 calcd for $C_{25}H_{25}ClO_3$, M + Na^+).



3-(4-Bromophenyl)-3-(cyclohexyloxy)-1-phenylpropan-1-one (23). The reaction of 4-bromobenzaldehyde (40 mg, 0.22 mmol) with phenylacetylene (36 μl, 0.32 mmol) and cyclohexanol (64 mg, 0.64 mmol) was conducted according to the general procedure. This procedure afforded 48 mg (57%) of the title compound as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 2 H), 7.53 (t, *J* = 7.2 Hz, 1 H), 7.46–7.40 (m, 4 H), 7.30 (d, *J* = 8.8 Hz, 2 H), 5.09 (dd, *J* = 4.8, 8.4 Hz, 1 H), 3.53 (dd, *J* = 8.4, 15.9 Hz, 1 H), 3.19–3.13 (m, 1 H), 2.96 (dd, *J* = 4.4, 15.9 Hz, 1 H), 1.87–1.84 (m, 1 H), 1.63–1.55 (m, 3 H), 1.41–1.39 (m, 1 H), 1.24–1.07 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 142.3, 137.3, 133.1, 131.5, 128.5, 128.3, 128.2, 121.2, 75.6, 74.4, 47.7, 33.4, 31.1, 25.7, 24.0, 23.8; IR (film) 3052, 2933, 1685, 1448, 1265, 1010 cm^{-1}. MS (ESI) 409.0783 (409.0774 calcd for $C_{21}H_{23}BrO_2$, M + Na^+).



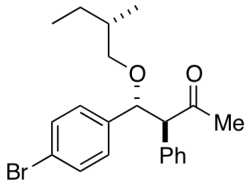
(*E*)-3-(Cyclobutylmethoxy)-1,5-diphenylpent-4-en-1-one (24). The reaction of *trans*-cinnamaldehyde (42 mg, 0.32 mmol) with phenylacetylene (49 μl, 0.45 mmol) and cyclobutanemethanol (86 μl, 0.91 mmol) was conducted according to the general procedure. This procedure afforded 43 mg (42%) of the title compound as a yellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.5 Hz, 2 H), 7.55 (t, *J* = 7.5 Hz, 1 H), 7.46 (t, *J* = 7.5 Hz, 2 H), 7.40 (d, *J* = 7.5 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 2 H), 7.24 (t, *J* = 7.0 Hz, 1 H), 6.65 (d, *J* = 16.0 Hz, 1 H), 6.19 (dd, *J* = 7.5, 16.0 Hz, 1 H), 4.54 (dd, *J* = 7.0, 13.0 Hz, 1 H), 3.55 (dd, *J* = 7.0, 9.5 Hz, 1 H), 3.47 (dd, *J* = 8.0, 16.0 Hz, 1 H), 3.35 (dd, *J* = 6.5, 9.5 Hz, 1 H), 3.04 (dd, *J* = 5.5, 16.0 Hz, 1 H), 2.53–2.50 (m, 1 H), 2.00–1.95 (m, 2 H), 1.89–1.79 (m, 2 H), 1.69–1.64 (m, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 198.1, 137.5, 136.5, 132.9, 131.8, 129.7, 128.6, 128.5, 128.3, 127.7, 126.5, 77.0, 73.7, 45.1, 35.1, 25.0, 24.9, 18.5; IR (film) 3052, 2979, 1684, 1597, 1448, 1264, 909 cm^{-1}. MS (ESI) 343.1682 (343.1669 calcd for $C_{22}H_{24}O_2$, M + Na^+).



(3*R,4*S**)-4-(4-Bromophenyl)-4-methoxy-3-phenylbutan-2-one (26).** The reaction of 4-bromobenzaldehyde (40 mg, 0.22 mmol) with 3-phenyl-1-propyne (40 μl, 0.32 mmol) and methanol (27 μl, 0.66 mmol) was conducted according to the general procedure. The crude product was formed as a 3:1 mixture of diastereomers as judged by ^{1}H NMR analysis. Purification by flash chromatography afforded 48 mg (65%) of the title compound as a white solid with >20:1 dr. In addition, a small amount of the minor diastereomer (10 mg, 14%) was also isolated.

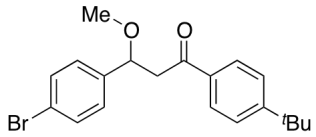
Major (3*R,4*S**) diastereomer:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 8.5 Hz, 2 H), 7.14–7.13 (m, 3 H), 6.99–6.98 (m, 2 H), 6.89 (d, *J* = 8.5 Hz, 2 H), 4.74 (d, *J* = 10.0 Hz, 1 H), 3.92 (d, *J* = 10.5 Hz, 1 H), 3.19 (s, 3 H), 2.21 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.7, 138.0, 133.9, 131.0, 129.0, 128.9, 128.6, 127.6, 121.4, 84.4, 65.8, 56.9, 30.9; IR (film) 3053, 1714, 1264, 1101 cm^{-1}. MS (ESI) 355.0310 (355.0304 calcd for $C_{17}H_{17}BrO_2$, M + Na^+).

Minor (3*R,4*R**)-diastereomer:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.5 Hz, 2 H), 7.35 (m, 5 H), 7.22 (d, *J* = 8.5 Hz, 2 H), 4.75 (d, *J* = 8.5 Hz, 1 H), 3.96 (d, *J* = 9.0 Hz, 1 H), 3.03 (s, 3 H), 1.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 206.3, 139.4, 135.5, 131.4, 129.4, 129.0, 128.7, 127.6, 121.8, 82.8, 66.6, 56.9, 30.5; IR (film) 3053, 1715, 1421, 1265, 895 cm^{-1}. MS (ESI) 355.0311 (355.0304 calcd for $C_{17}H_{17}BrO_2$, M + Na^+).

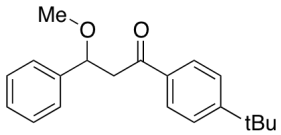


(2*S*,3*R,4*S**)-4-(4-Bromophenyl)-4-(2-methylbutoxy)-3-phenylbutan-2-one (27).** The reaction of 4-bromobenzaldehyde (40 mg, 0.22 mmol) with 3-phenyl-1-propyne (40 μl, 0.32 mmol) and (*S*)-2-methylbutan-1-ol (71 μl, 0.66 mmol) was conducted according to the general procedure. This procedure afforded 65 mg (76%) of the title compound as a 3:3:1:1 mixture of diastereomers that were inseparable by flash chromatography. Data are for the mixture. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.5 Hz, 0.7 H), 7.32–7.31 (m, 1.32 H), 7.24 (d, *J* = 8.5 Hz, 1.7 H), 7.20 (d, *J* =8.0 Hz, 0.7 H), 7.14–7.13 (m, 2 H), 7.03–7.01 (m, 1.4 H), 6.89 (d, *J* = 8.5 Hz, 1.4 H), 4.79 (d, *J* = 10.0 Hz, 1 H), 3.94 (d, *J* = 10.5 Hz, 1 H), 3.16–3.02 (m, 1.7 H), 2.88-2.80 (m, 0.3 H), 2.23 (s, 2 H), 1.89 (s, 1H), 1.57–1.54 (m, 0.7 H), 1.40-1.34 (m, 1 H), 1.16-1.06 (m, 1 H),

0.88–0.82 (m, 6.4 H), 0.67–0.64 (m, 1 H), 0.59-0.57 (m, 1 H). ^{13}C NMR (125 MHz) 206.1, 206.4, 140.1, 138.8, 134.1, 131.5, 131.3, 130.9, 129.5, 129.3, 129.2, 128.9, 128.8, 128.5, 128.3, 127.4, 127.3, 121.5, 121.3, 83.3, 83.2, 81.4, 81.3, 74.4, 74.3, 74.1, 74.0, 66.8, 66.7, 65.8, 35.0, 34.9, 34.8, 34.6, 31.2, 30.6, 26.1, 26.0, 25.8, 25.7, 16.6, 16.5, 16.4, 16.2, 11.2, 11.1, 10.9; IR (film) 3053, 2962, 1717, 1264, 1071, 1010 cm^{-1}. MS (ESI) 411.0939 (411.0930 calcd for $C_{21}H_{25}BrO_2$, M + Na^+).

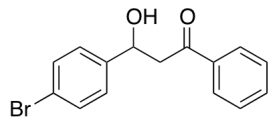


3-(4-Bromophenyl)-1-[4-(*tert*-butyl)phenyl]-3-methoxypropan-1-one (30). The reaction of 4-bromobenzaldehyde (37 mg, 0.2 mmol) with 4-(*tert*-butyl)phenylacetylene (54.1 μL, 0.3 mmol) and methanol (24 μL, 0.6 mmol) was conducted according to the general procedure. Flash chromatography yielded a mixture of the title compound and 4'-(*tert*-butyl)acetophenone. The ketone impurity was removed by placing the impure product under vacuum at 0.25 torr for 36 hrs. This procedure afforded 30.0 mg (40%) of the title compound as a clear colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 2 H), 7.50–7.45 (m, 4 H), 7.29 (d, *J* = 8.0 Hz, 2 H), 4.85 (dd, *J* = 5.0, 8.0 Hz, 1 H), 3.54 (dd, *J* = 8.0, 16.5 Hz, 1 H), 3.22 (s, 3 H), 3.05 (dd, *J* = 5.0, 16.5 Hz, 1 H), 1.33 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.9, 157.0, 140.6, 134.4, 131.7, 128.5, 128.1, 125.5, 121.6, 79.0, 56.9, 46.8, 35.1, 31.0; IR (film) 1680 cm^{-1}. MS (ESI) 397.0769 (397.0774 calcd for $C_{20}H_{23}BrO_2$, M + Na^+).



1-[4-(*tert*-Butyl)phenyl]-3-methoxy-3-phenylpropan-1-one (32). The reaction of benzaldehyde (20.4 μL, 0.2 mmol) with 4-(*tert*-butyl)phenylacetylene (54.1 μL, 0.3 mmol) and methanol (24 μL, 0.6 mmol) was conducted according to the general procedure. Flash chromatography yielded a mixture of the title compound and 4'-(*tert*-butyl)acetophenone. The ketone impurity was removed by placing the impure product under vacuum at 0.25 torr for 48 h. This procedure afforded 36.8 mg (62%) of the title compound as a clear colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.5 Hz, 2 H), 7.47 (d, *J* = 9.0 Hz, 2 H), 7.43–7.37 (m, 4 H), 7.33-7.29 (m, 1 H), 4.90 (dd, *J* = 4.5, 8.5 Hz, 1 H), 3.59 (dd, *J* = 8.5, 16.5 Hz, 1 H), 3.24 (s, 3 H), 3.08 (dd, *J* = 4.5, 16.5 Hz, 1 H), 1.34 (s, 9 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.0, 156.8, 141.5,

134.6, 128.5, 128.2, 127.8, 126.7, 125.5, 79.6, 56.9, 47.0, 35.1, 31.0; IR (film) 1684 cm^{-1}. MS (ESI) 319.1669 (319.1669 calcd for $C_{20}H_{24}O_2$, M + Na^+).



3-(4-Bromophenyl)-3-hydroxy-1-phenylpropan-1-one (34). A flame-dried flask was cooled under a stream of N_2 and charged with diisopropylamine (169 μL, 1.2 mmol) and THF (5 mL). The flask was cooled to 0 °C and *n*-BuLi (0.79 mL, 1.4 M in hexanes, 1.1 mmol) was added slowly. After stirring for 10 min at 0 °C, acetophenone (122 μL, 1.0 mmol) was added to the reaction flask and the mixture was stirred at 0 °C for 30 min. 4-Bromobenzaldehyde (278 mg, 1.5 mmol) was added to the reaction flask and the mixture was stirred for at 0 °C for 1 hr. The reaction was quenched slowly with saturated aqueous ammonium chloride (5 mL) at 0 °C and gradually warmed to rt. The mixture was transferred to a separatory funnel, extracted with ethyl acetate (5 mL), and the layers were separated. The organic layer was dried over anhydrous sodium sulfate, filtered, and concentrated *in vacuo*. The crude material was purified by flash chromatography on silica gel to afford 97 mg (32%) of the title compound as a white solid with spectroscopic properties identical to those previously reported.[2] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.5 Hz, 2 H), 7.61 (t, *J* = 7.5 Hz, 1 H), 7.52-7.47 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 2 H), 5.32 (dt, *J* = 3.0, 8.5 Hz, 1 H), 3.65 (d, *J* = 3 Hz, 1 H), 3.36-3.34 (m, 2 H).

Assignment of Stereochemistry of 26 and 27

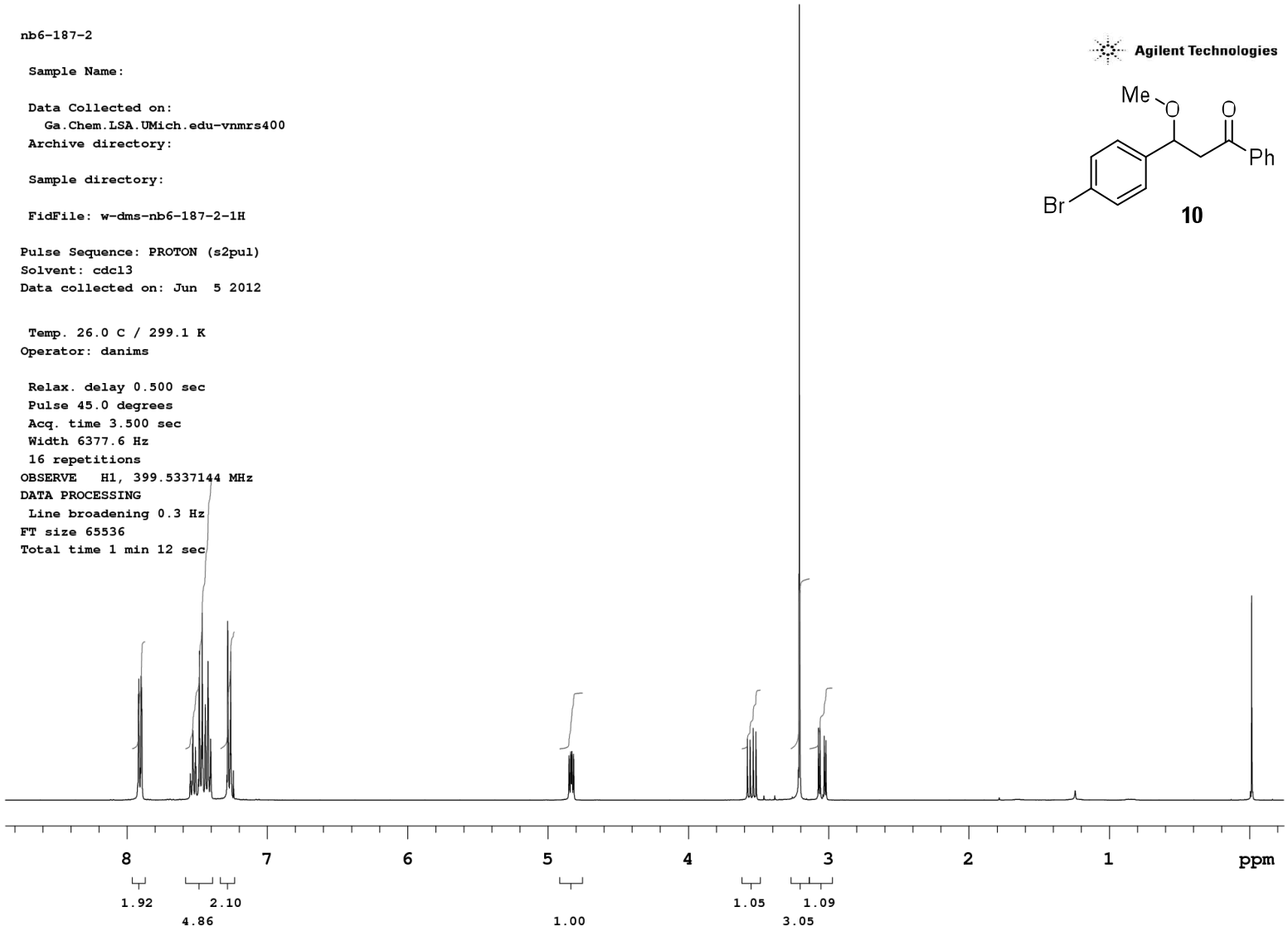
The relative stereochemistry assignments of *anti* for compounds **26** and **27** were assigned based on the ^{1}H NMR chemical shifts of structurally related *anti*-4-hydroxy-3,4-diphenyl-butan-2-one.[3]

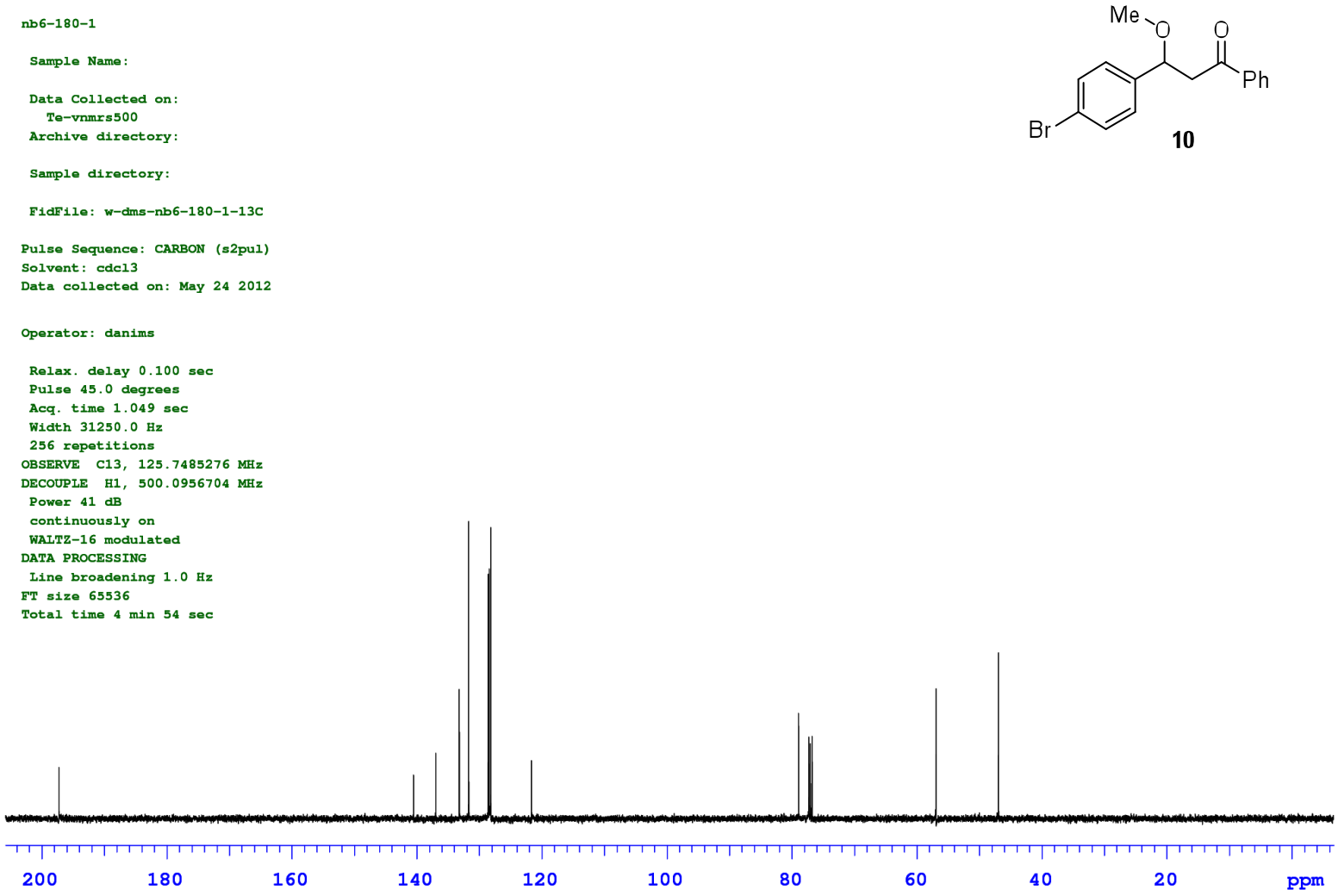
References

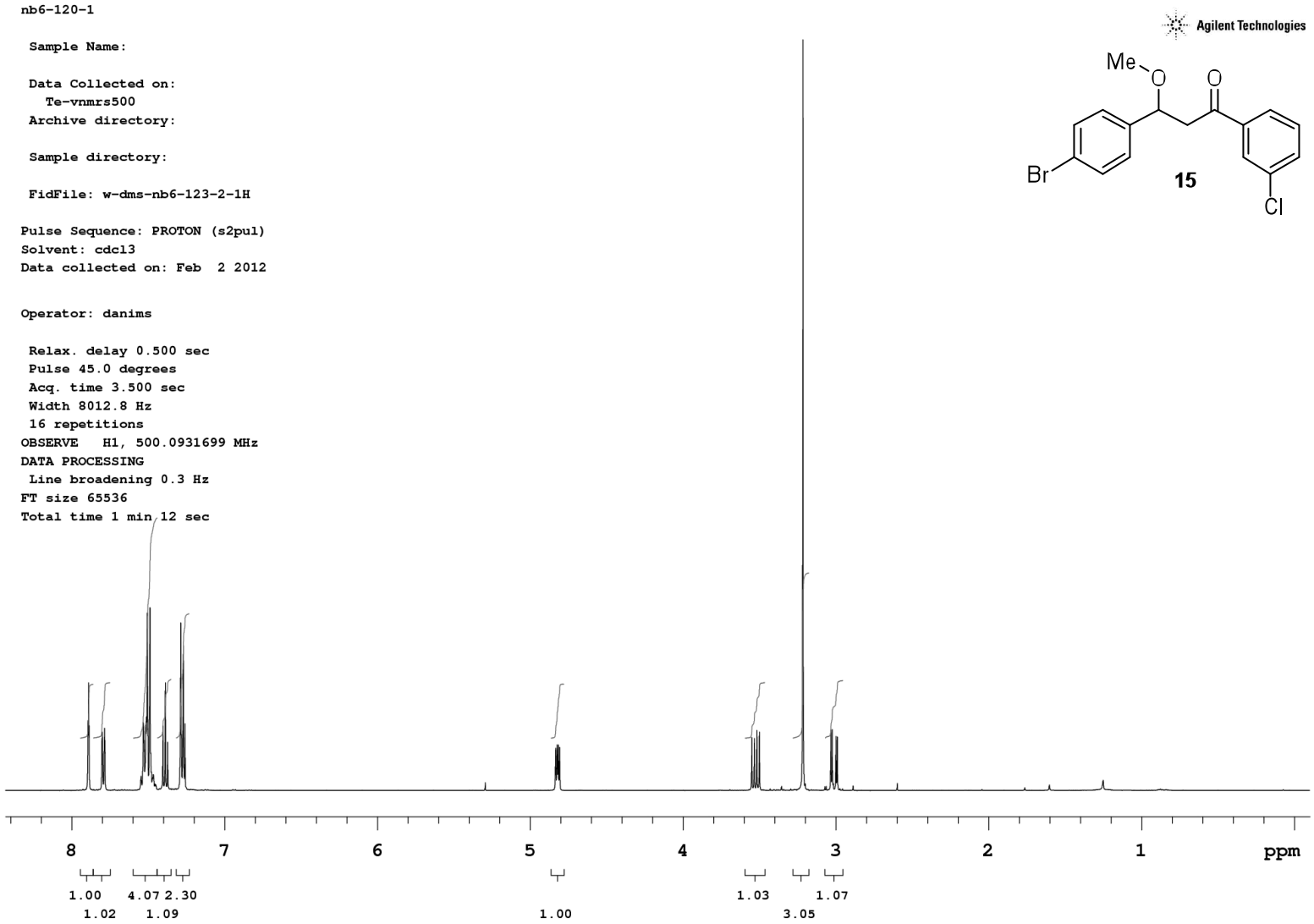
[1] a) N. Mezailles, L. Ricard, R. Gagosz, *Org. Lett.* **2005**, *7*, 4133. b) L. Ricard, F. Gagosz, *Organometallics* **2007**, *26*, 4704.

[2] C. H. Cheon, H. Yamamoto, *Tetrahedron* **2010**, *66*, 4257–4264.

[3] B. Schetter, B. Ziemer, G. Schnakenburg, R. Mahrwald, *J. Org. Chem.* **2008**, *73*, 813.


nb6-187-2
Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: w-dms-nb6-187-2-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jun 5 2012
Temp. 26.0 C / 299.1 K
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6377.6 Hz
16 repetitions
OBSERVE H1, 399.5337144 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
Me
O
O
Ph
Br
10
8
7
6
5
4
3
2
1
ppm
1.92
2.10
4.86
1.00
1.05
1.09
3.05


nb6-180-1
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-180-1-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2012
Operator: danims
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.049 sec
Width 31250.0 Hz
256 repetitions
OBSERVE C13, 125.7485276 MHz
DECOUPLE H1, 500.0956704 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 min 54 sec
Me
O
O
Ph
Br
10
200
180
160
140
120
100
80
60
40
20
ppm


nb6-120-1
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-123-2-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 2 2012
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min, 12 sec
Agilent Technologies
Me
O
O
Br
Cl
15
8
7
6
5
4
3
2
1
ppm
1.00
1.02
4.07
1.09
2.30
1.00
1.03
3.05
1.07

nb6-132-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

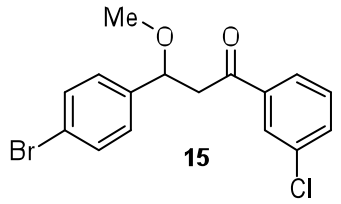
FidFile: w-dms-nb6-132-2-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 8 2012

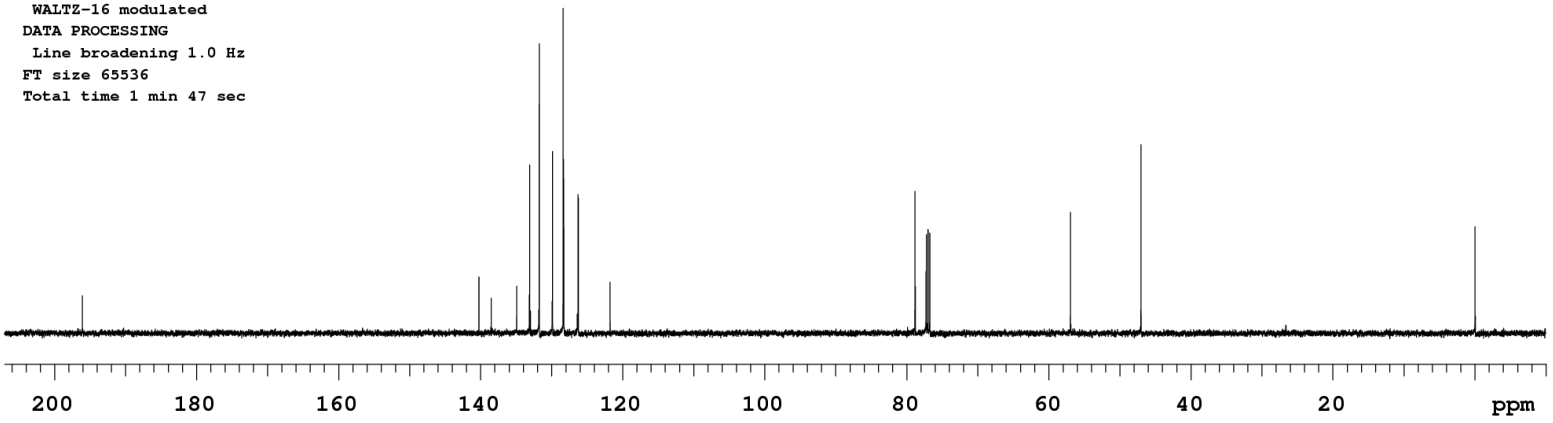
Operator: danims

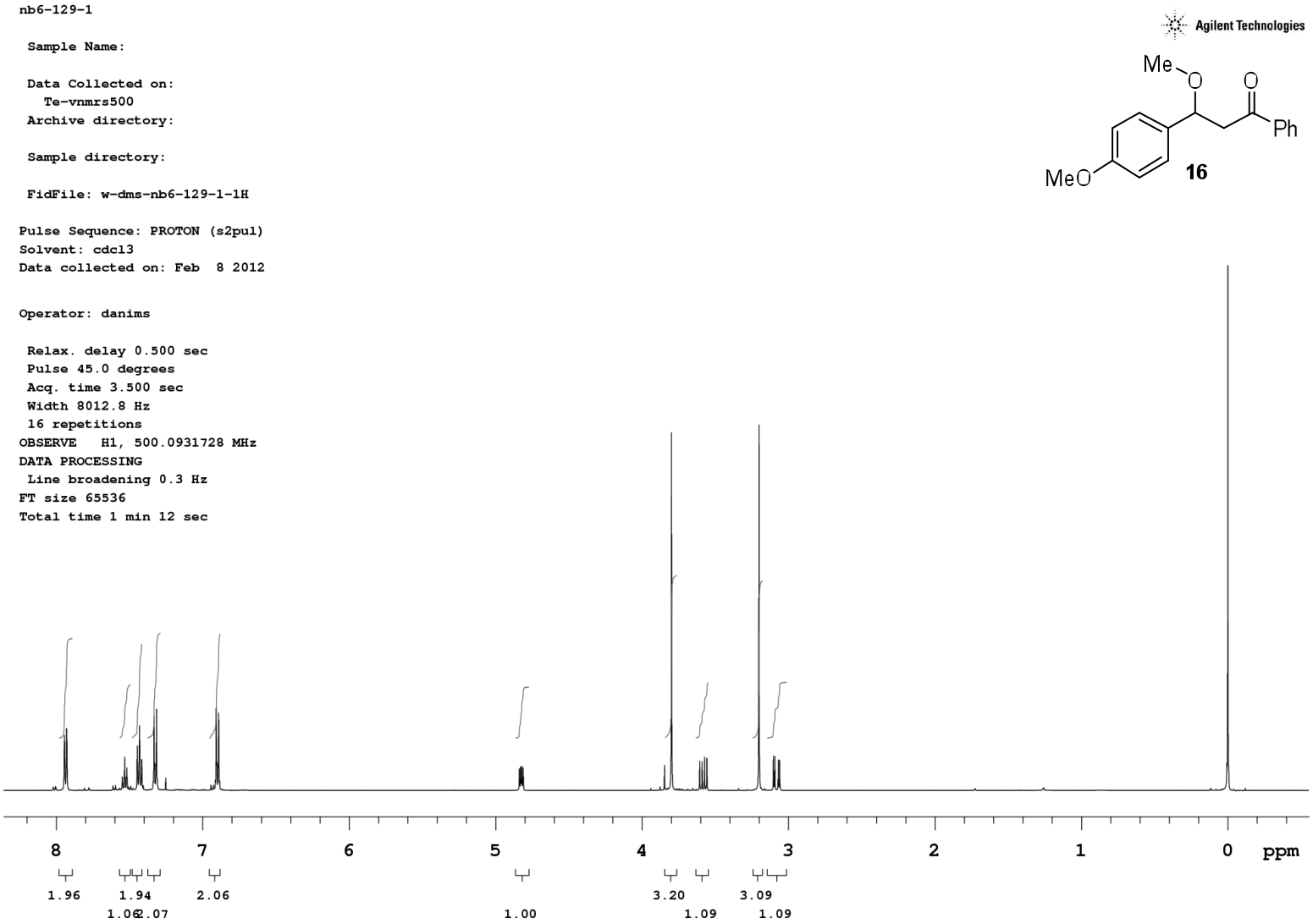
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
96 repetitions
OBSERVE C13, 125.7485320 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 min 47 sec

Agilent Technologies



15




nb6-129-1
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-129-1-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 8 2012
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931728 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
Me
O
O
Ph
MeO
16
8
7
6
5
4
3
2
1
0
ppm
1.96
1.94
1.06
2.07
2.06
1.00
3.20
1.09
3.09
1.09

nb6-129-1

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

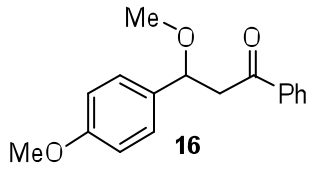
FidFile: w-dms-nb6-129-1-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 8 2012

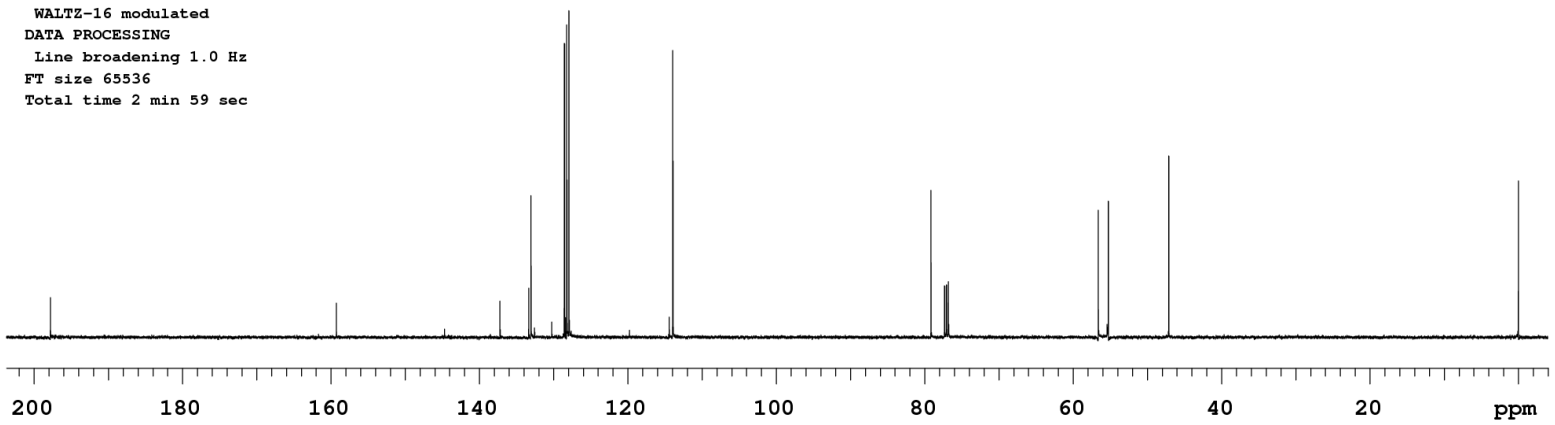
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
160 repetitions
OBSERVE C13, 125.7485276 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 min 59 sec

Agilent Technologies



16



nb6-130-2

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

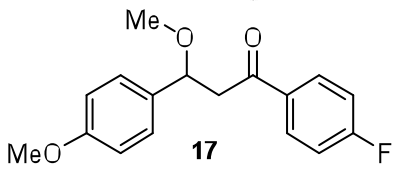
FidFile: w-dms-nb6-130-2-column

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 8 2012

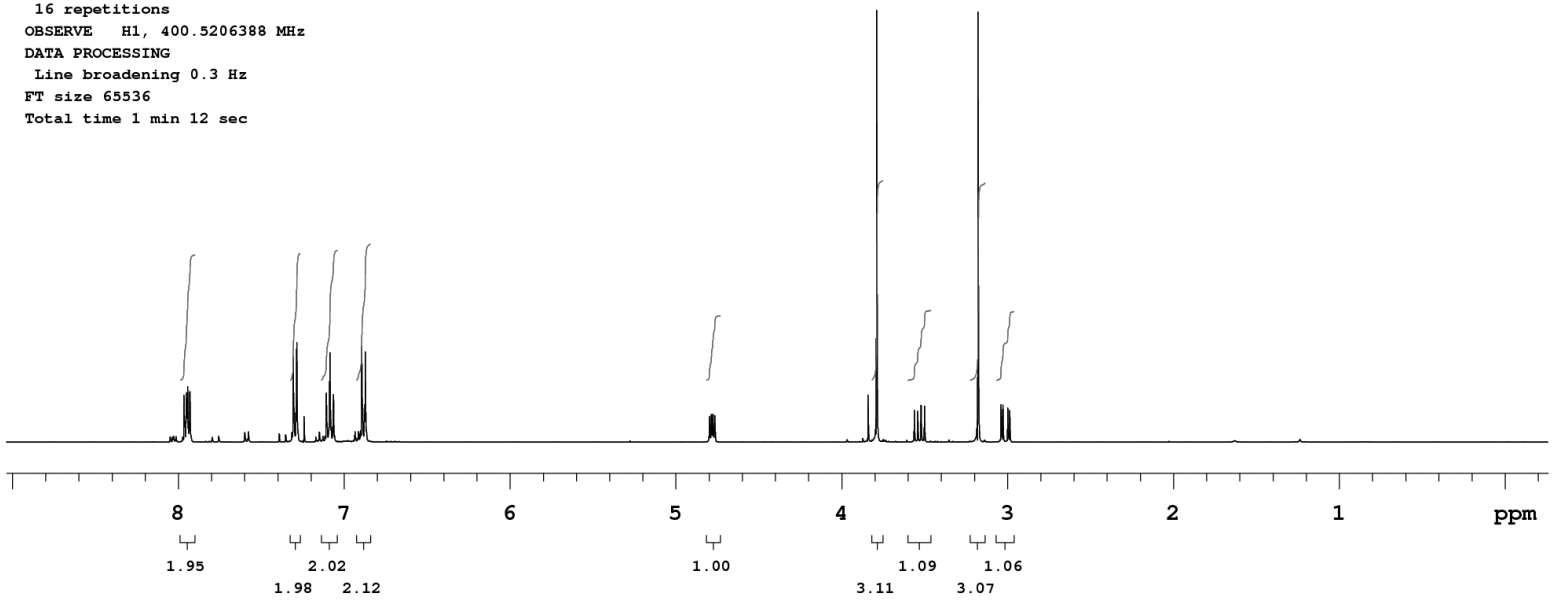
Operator: danims

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5206388 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec

Agilent Technologies



17



nb6-148-2

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

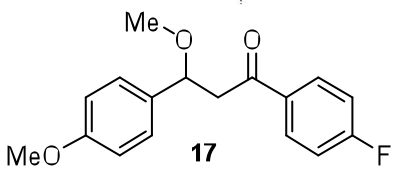
FidFile: w-dms-nb6-148-2-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2012

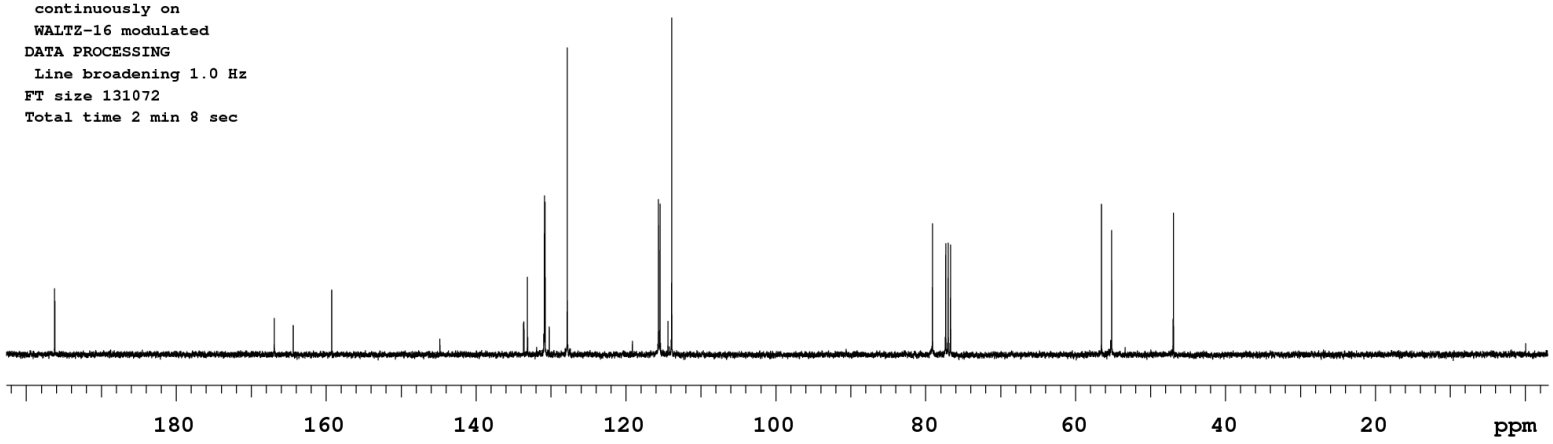
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
48 repetitions
OBSERVE C13, 100.4628374 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 2 min 8 sec

Agilent Technologies



17



nb6-134-1

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

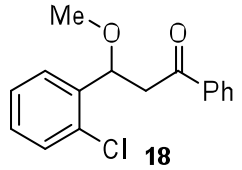
FidFile: w-dms-nb6-134-1-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Apr 13 2012

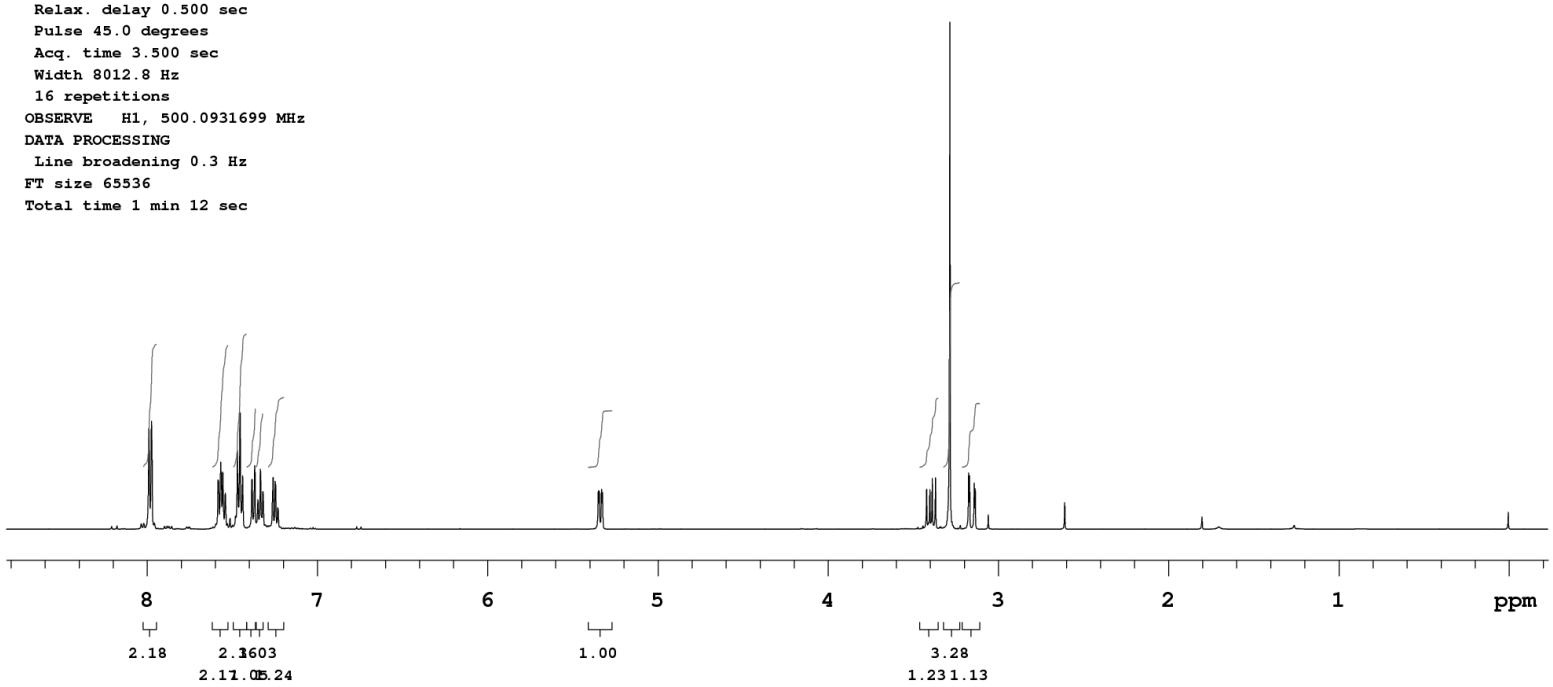
Operator: danims

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec

Agilent Technologies



18



nb6-134-1

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

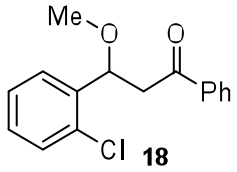
FidFile: w-dms-nb6-134-1-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Apr 13 2012

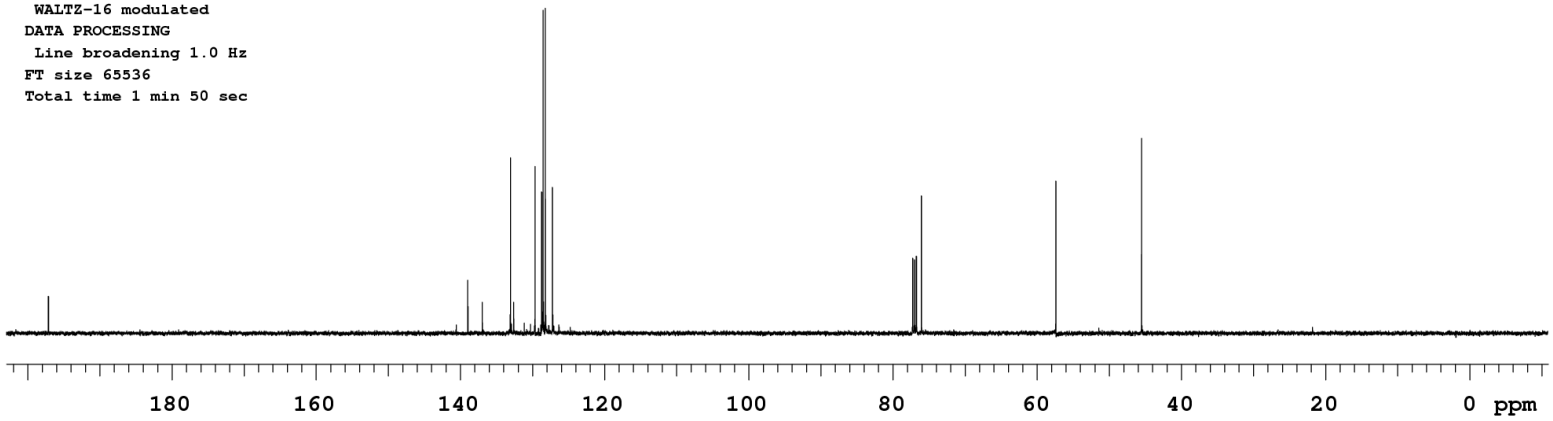
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.049 sec
Width 31250.0 Hz
96 repetitions
OBSERVE C13, 125.7485345 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 min 50 sec

Agilent Technologies



18



nb6-161-2

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

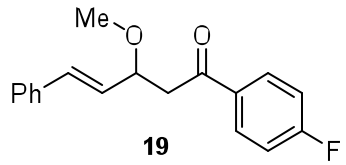
FidFile: w-dms-nb6-162-1-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 27 2012

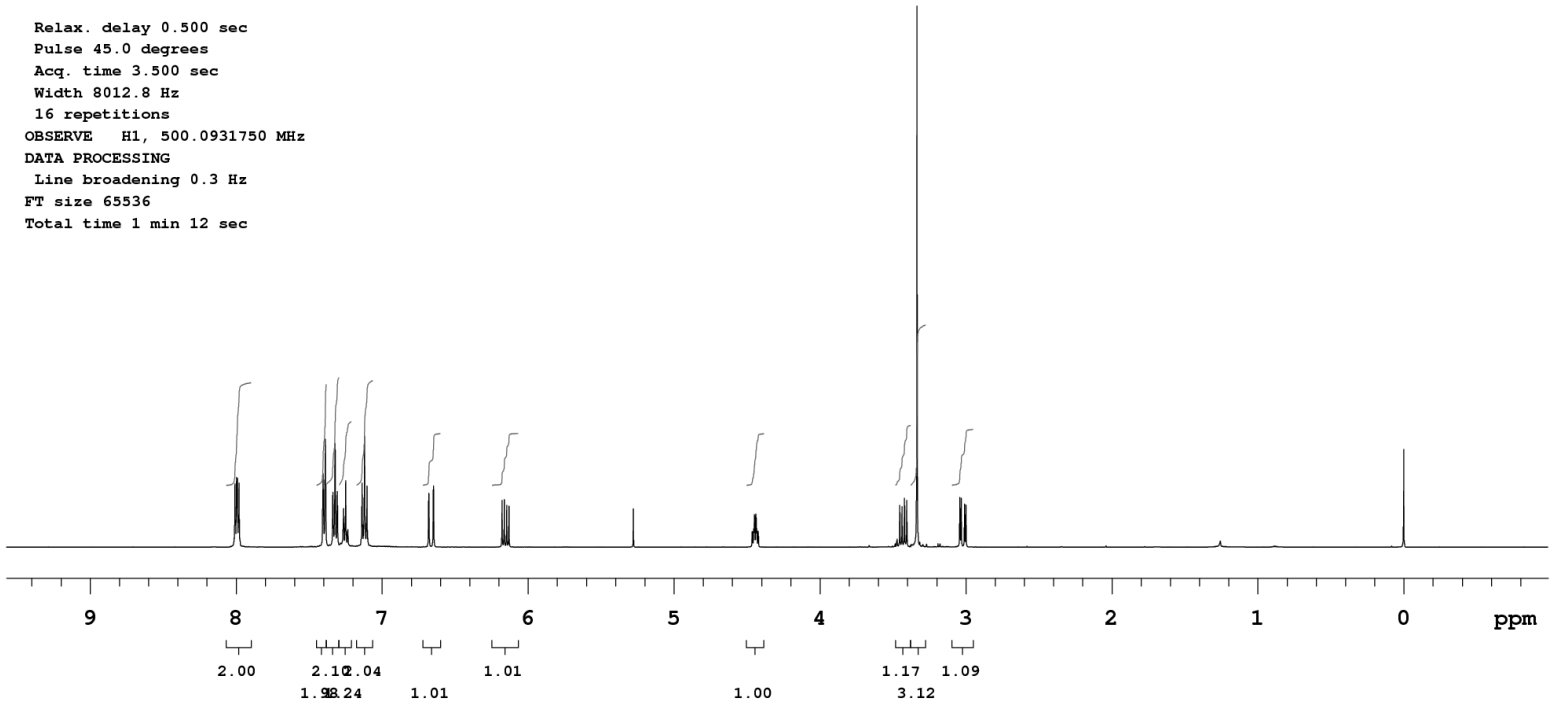
Operator: danims

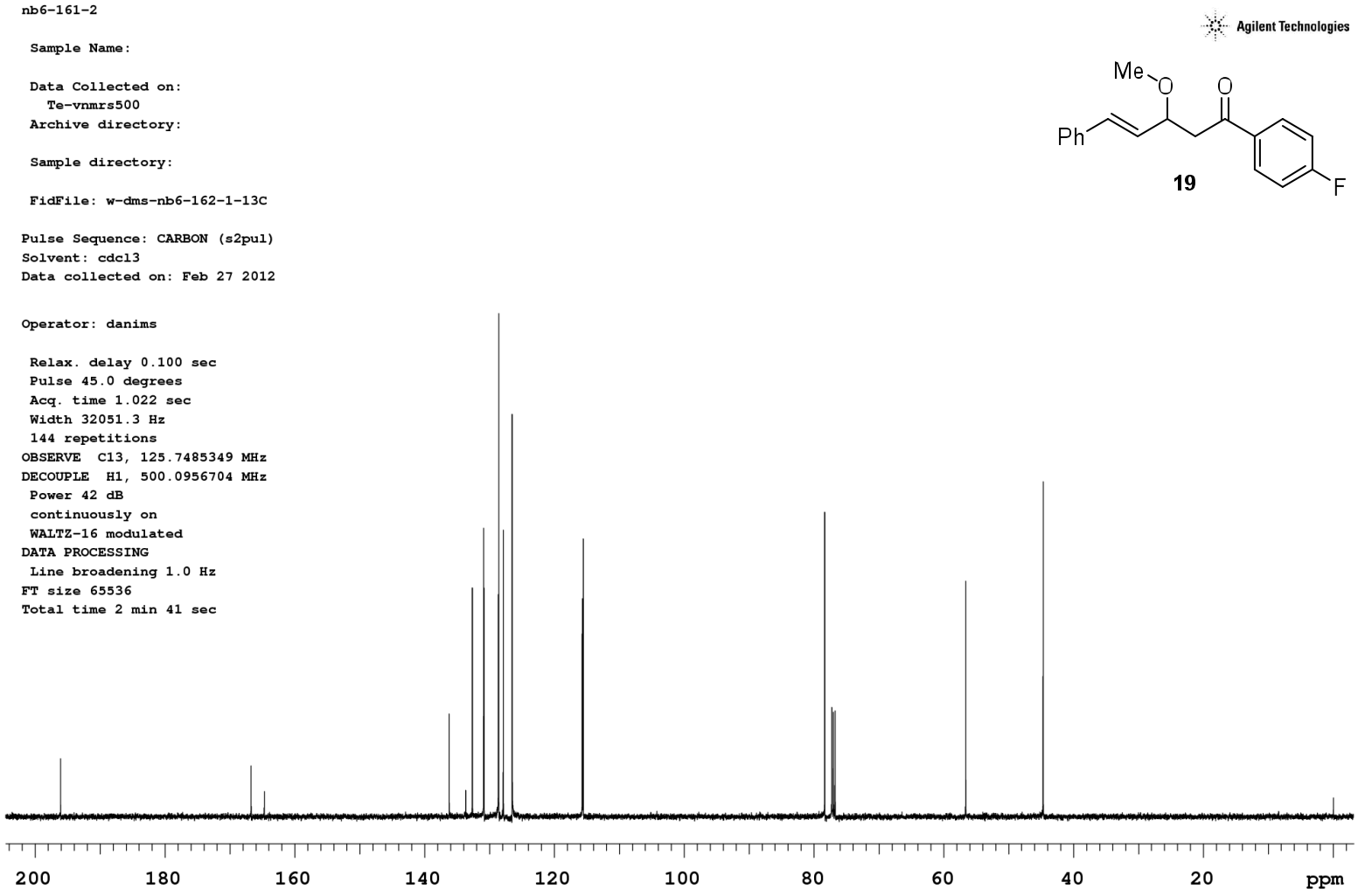
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931750 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec

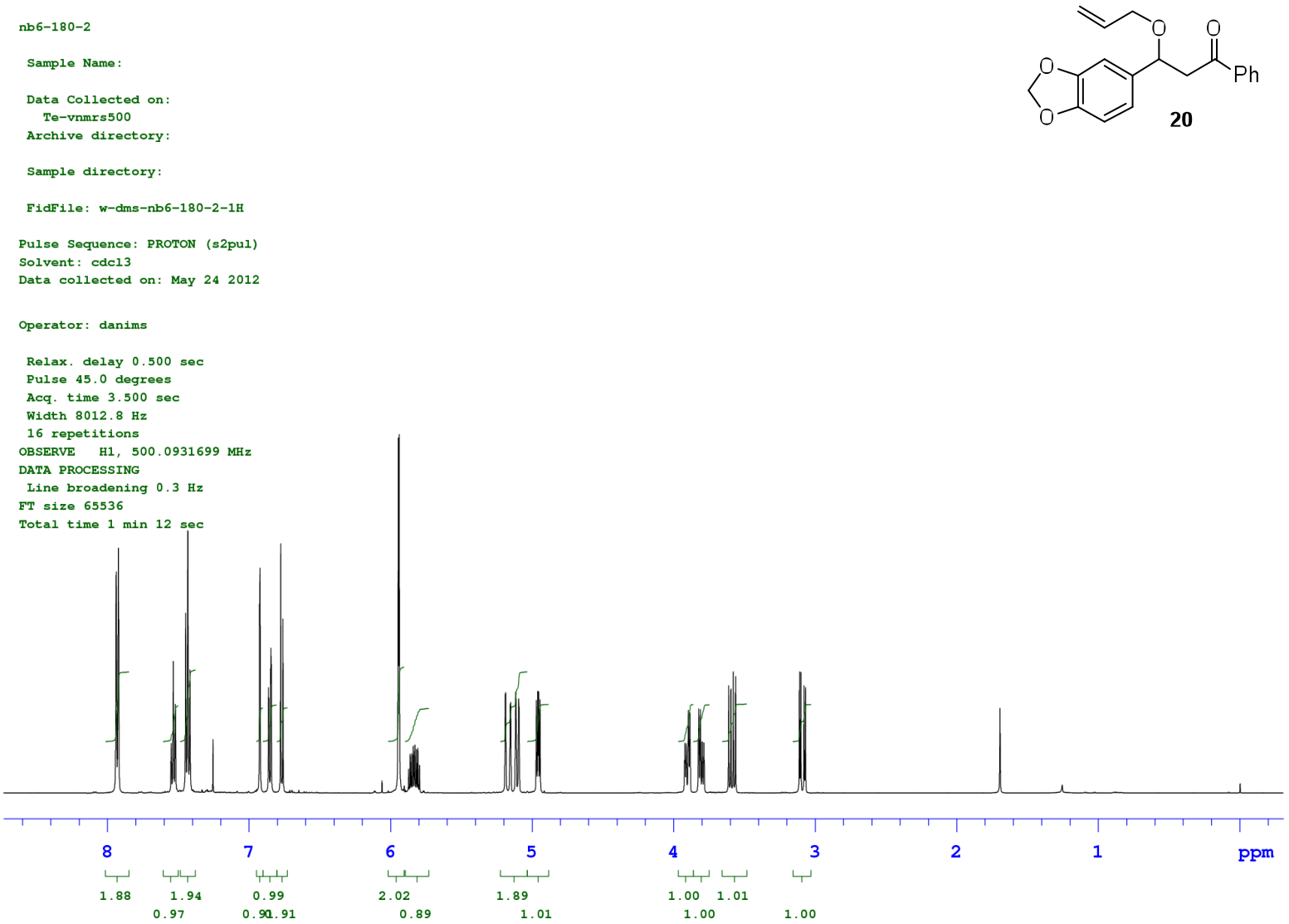
Agilent Technologies

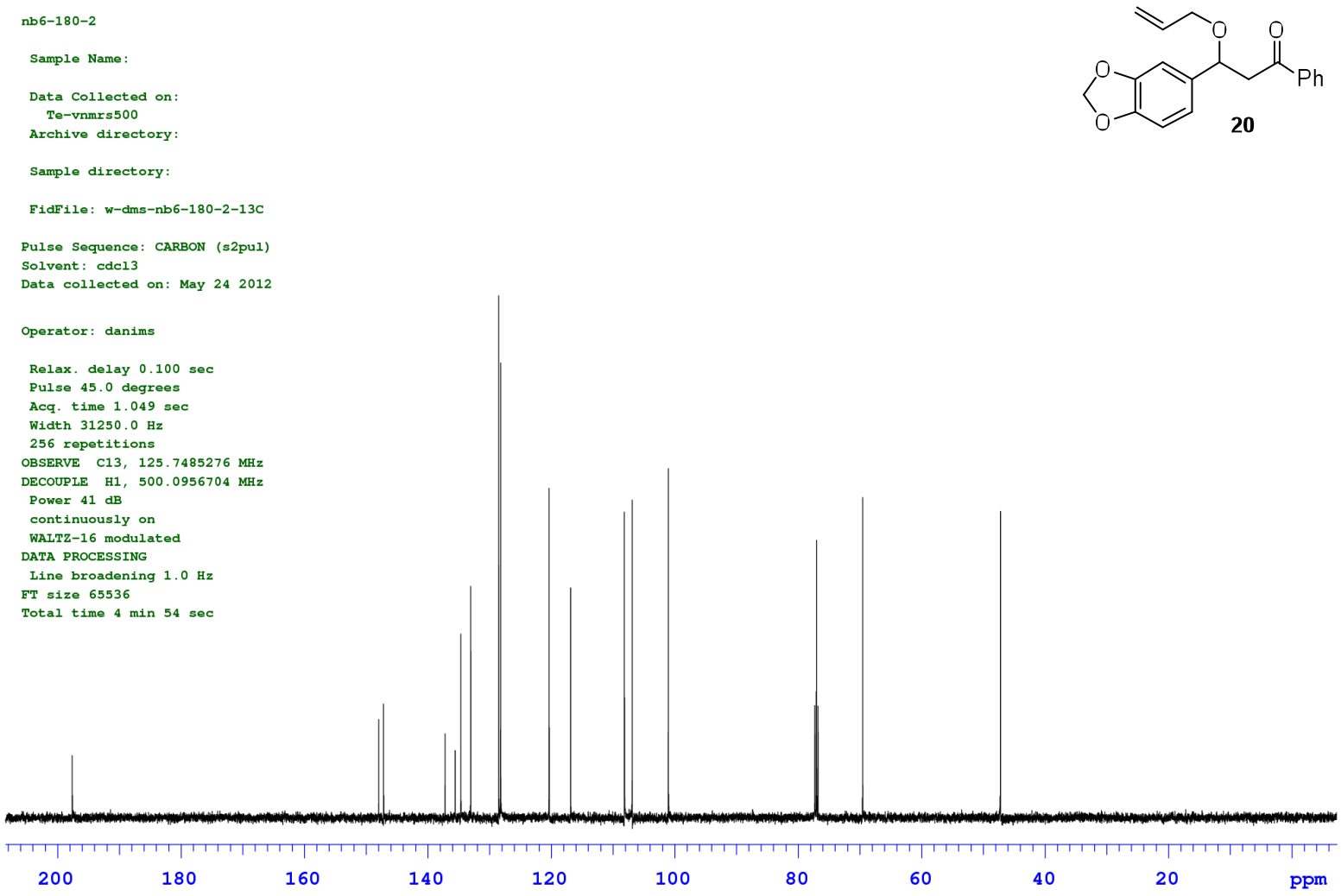


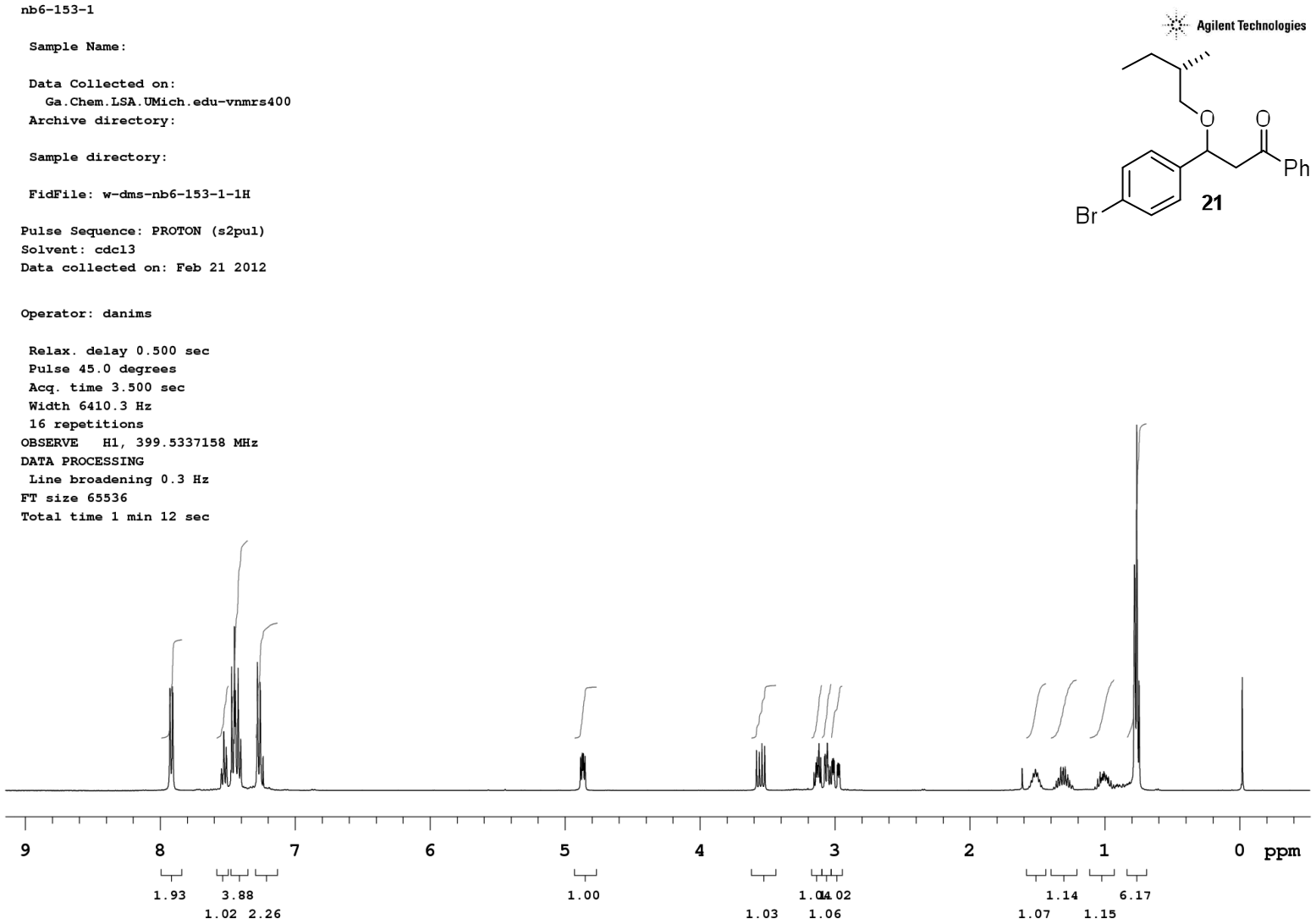
19




nb6-161-2
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-162-1-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 27 2012
Operator: danims
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
144 repetitions
OBSERVE C13, 125.7485349 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 2 min 41 sec
Agilent Technologies
Me
O
O
Ph
F
19
200
180
160
140
120
100
80
60
40
20
ppm


nb6-180-2
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-180-2-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2012
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
O
O
O
O
Ph
20
8
7
6
5
4
3
2
1
ppm
1.88
1.94
0.99
2.02
1.89
1.00
1.01
0.97
0.91
0.89
1.01
1.00
1.00


nb6-180-2
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-180-2-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 24 2012
Operator: danims
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.049 sec
Width 31250.0 Hz
256 repetitions
OBSERVE C13, 125.7485276 MHz
DECOUPLE H1, 500.0956704 MHz
Power 41 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 4 min 54 sec
O
O
O
O
Ph
20
200
180
160
140
120
100
80
60
40
20
ppm


nb6-153-1
Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: w-dms-nb6-153-1-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2012
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.5337158 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
O
O
Ph
Br
21
9
8
7
6
5
4
3
2
1
0
ppm
1.93
3.88
1.02
2.26
1.00
1.03
1.06
1.14
6.17
1.07
1.15

nb6-153-1

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

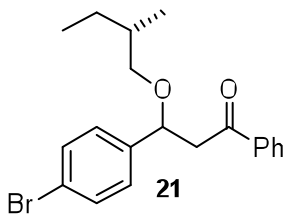
FidFile: w-dms-nb6-153-1-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2012

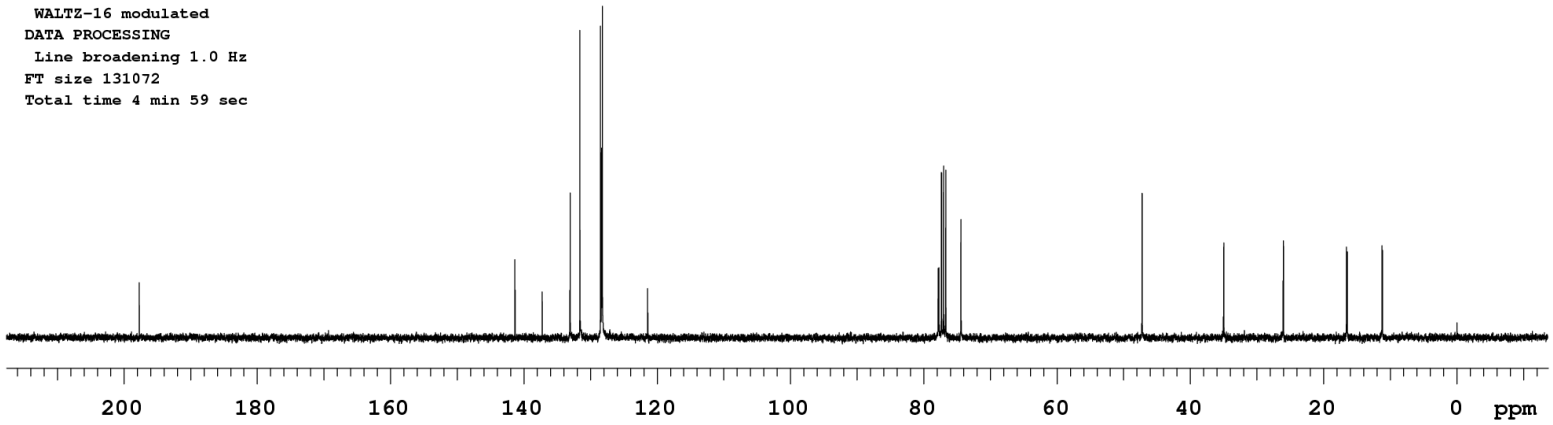
Operator: danims

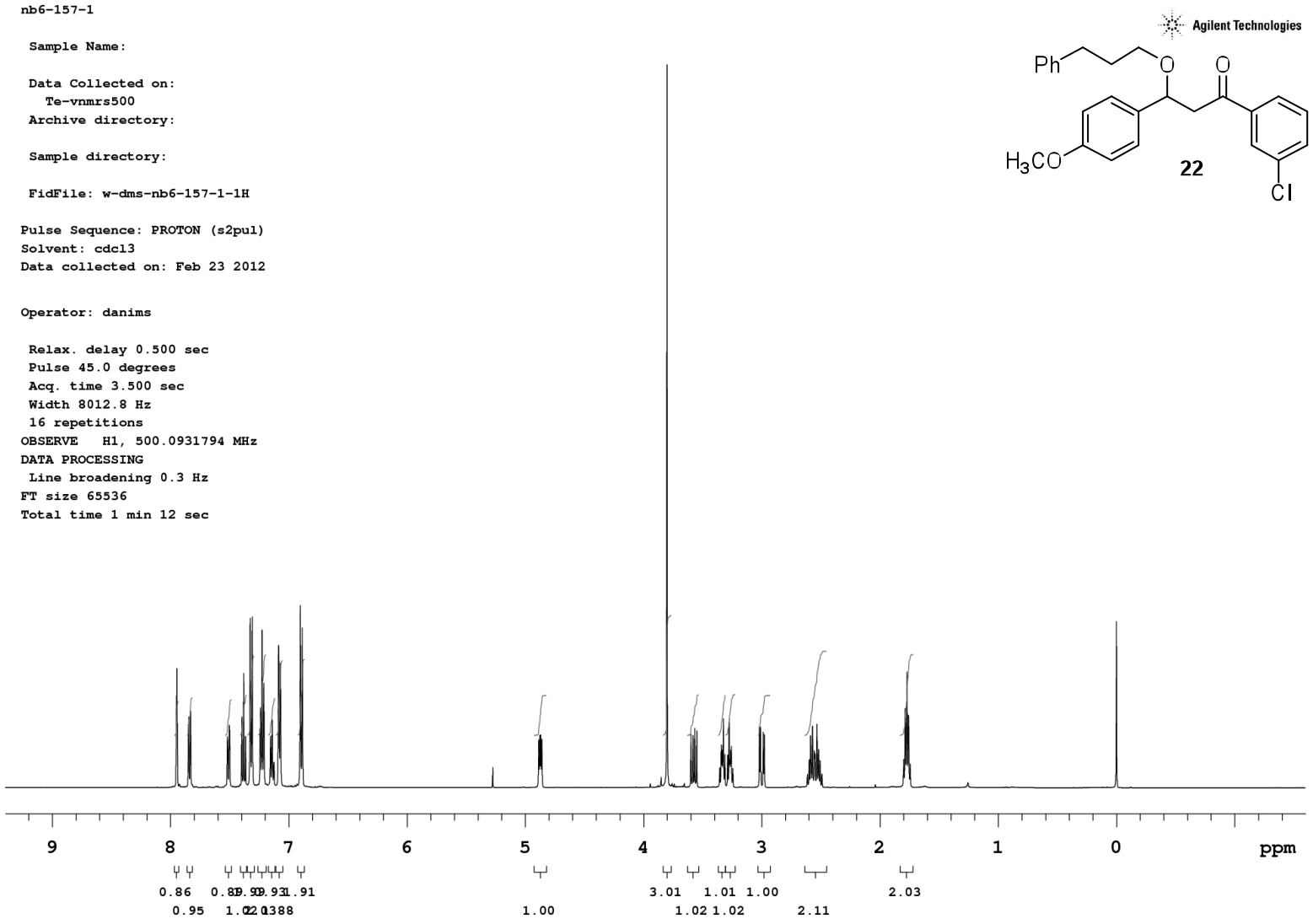
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
112 repetitions
OBSERVE C13, 100.4628343 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 min 59 sec

Agilent Technologies



21




nb6-157-1
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-157-1-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 23 2012
Operator: danims
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931794 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
Agilent Technologies
Ph
O
O
H3CO
22
Cl
9
8
7
6
5
4
3
2
1
0
ppm
0.86
0.95
1.00
3.01
1.02
1.01
1.02
1.00
2.11
2.03

nb6-157-1

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

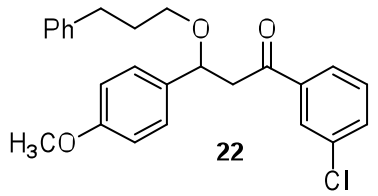
FidFile: w-dms-nb6-157-1-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 23 2012

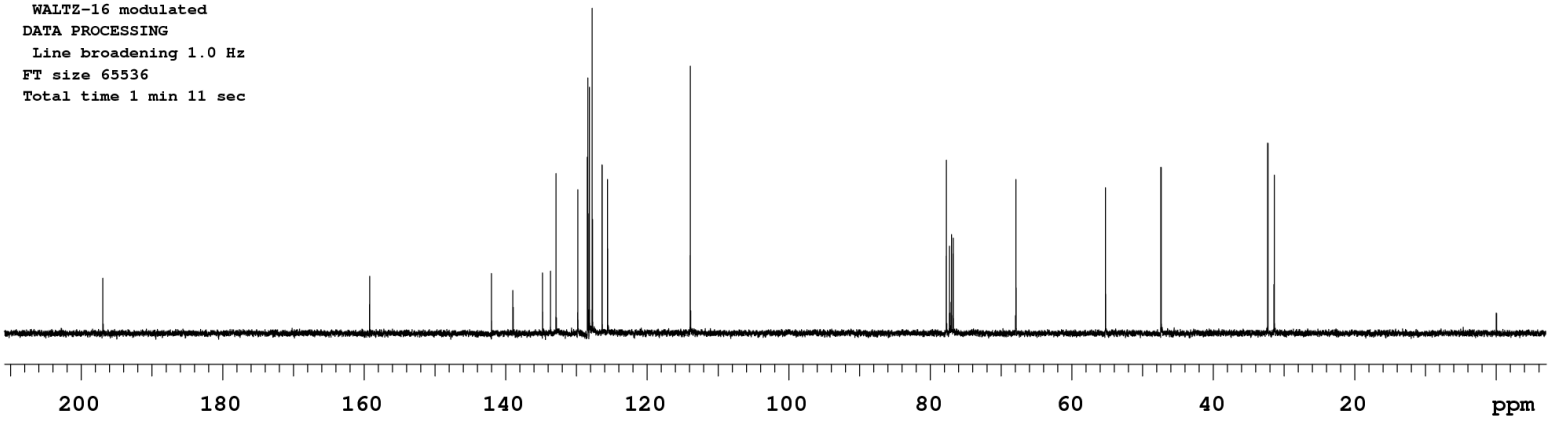
Operator: danims

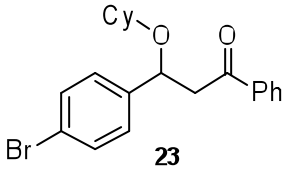
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.022 sec
Width 32051.3 Hz
64 repetitions
OBSERVE C13, 125.7485349 MHz
DECOUPLE H1, 500.0956704 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536
Total time 1 min 11 sec

Agilent Technologies



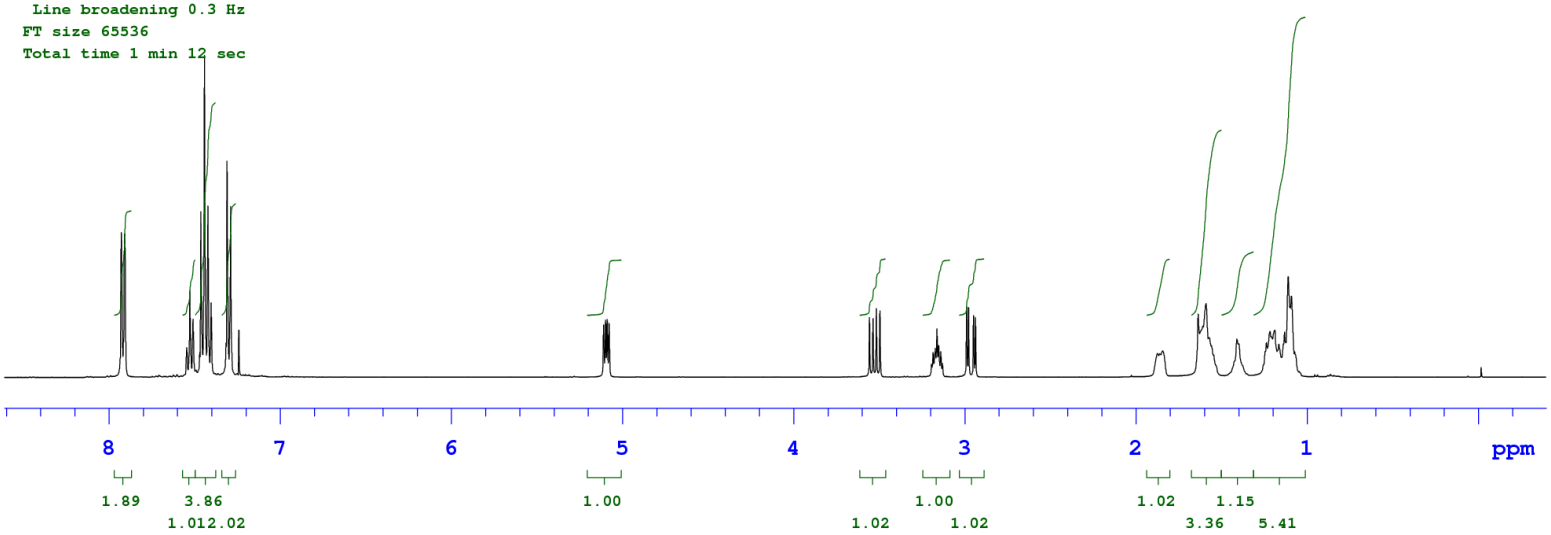
22





23

```
nb6-176-1

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: w-dms-nb6-176-1-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 22 2012

Operator: danims

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6377.6 Hz
 16 repetitions
OBSERVE   H1, 399.5337144 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```



nb6-176-1

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

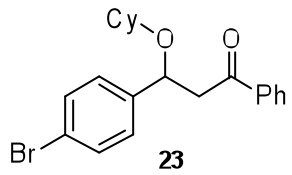
Sample directory:

FidFile: w-dms-nb6-176-1-13C

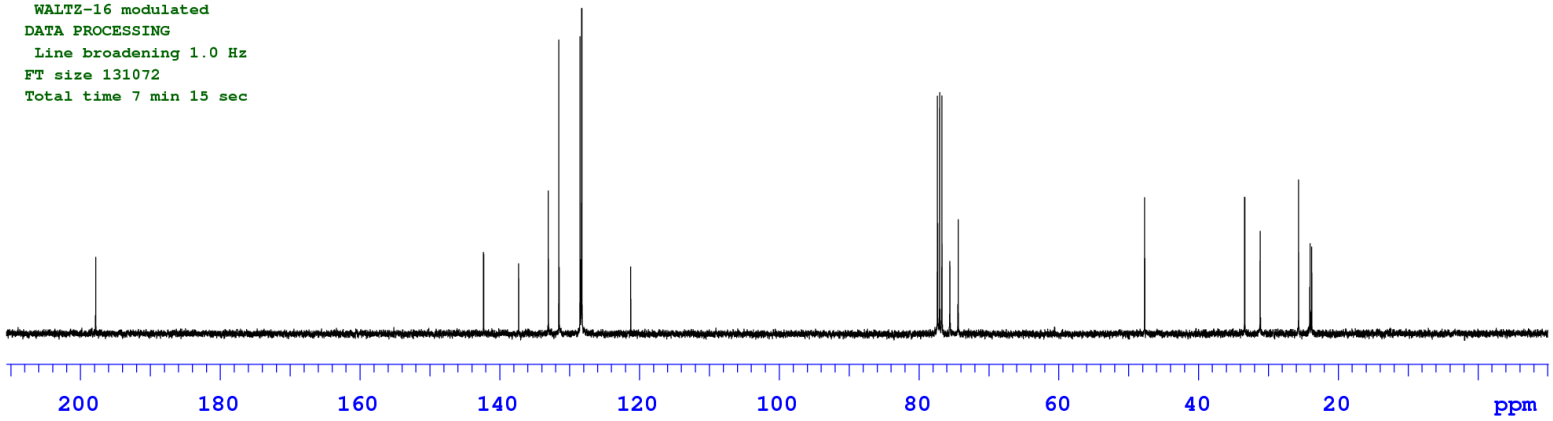
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 22 2012

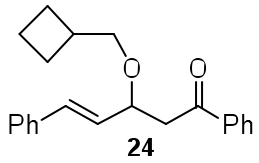
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.621 sec
Width 25000.0 Hz
160 repetitions
OBSERVE C13, 100.4628324 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 7 min 15 sec



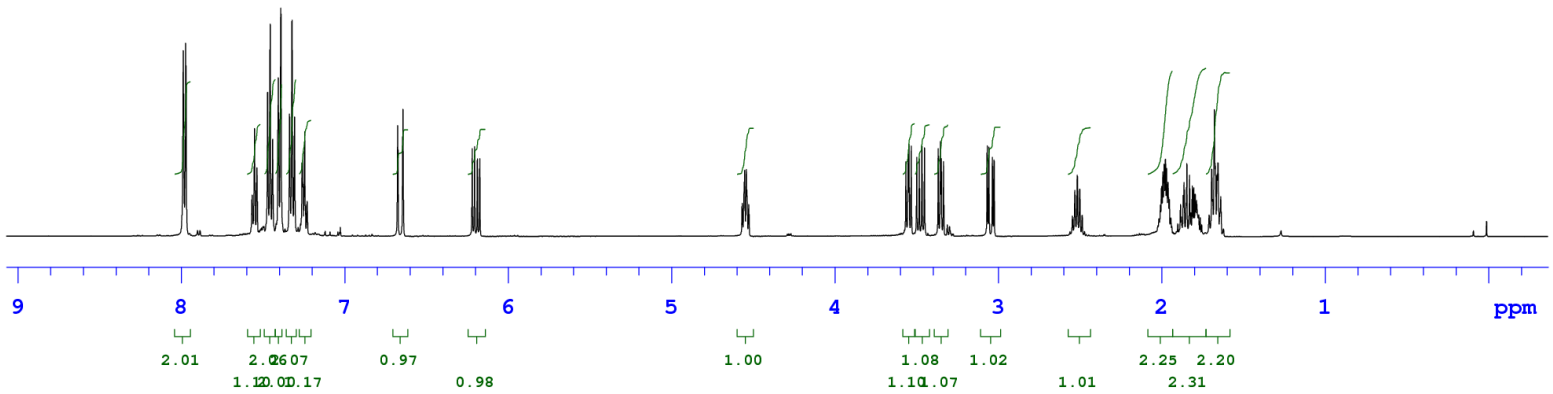
23

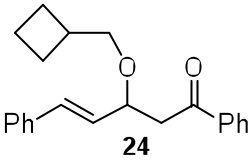




24

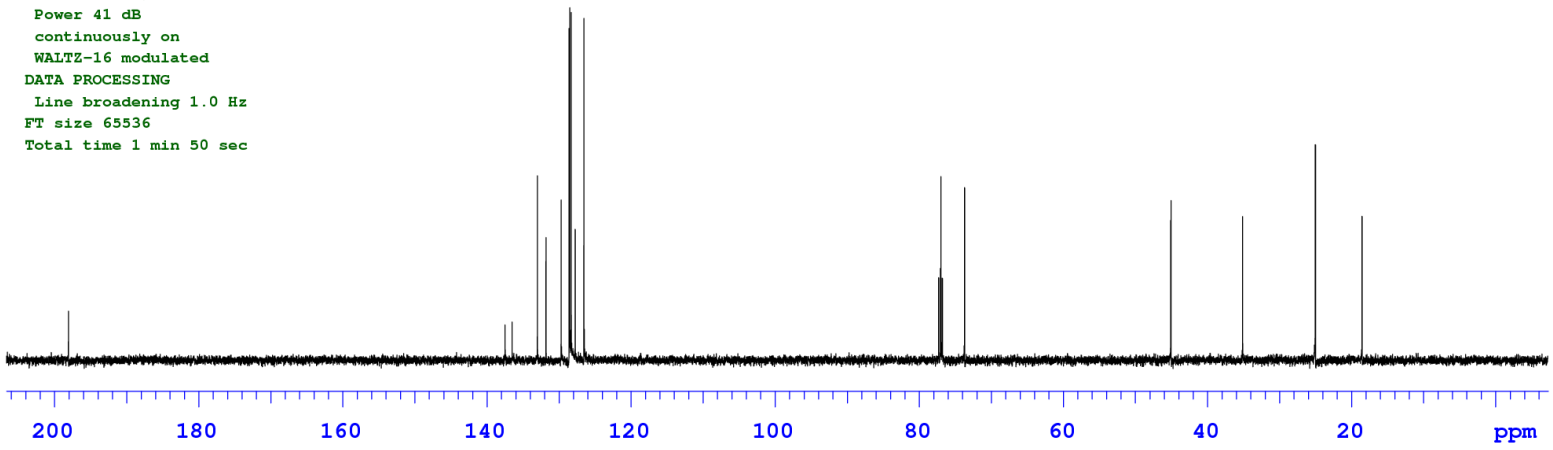
```
nb6-171-1

 Sample Name:

 Data Collected on:
   Te-vnmrs500
 Archive directory:

 Sample directory:

 FidFile: w-dms-nb6-171-1-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2012


 Temp. 25.0 C / 298.1 K
Operator: danims

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 8012.8 Hz
 16 repetitions
OBSERVE   H1, 500.0931699 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```





24

```
nb6-171-1

 Sample Name:

 Data Collected on:
   Te-vnmrs500
 Archive directory:

 Sample directory:

 FidFile: w-dms-nb6-171-1-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: May 14 2012

 Temp. 25.0 C / 298.1 K
Operator: danims

 Relax. delay 0.100 sec
 Pulse 45.0 degrees
 Acq. time 1.049 sec
 Width 31250.0 Hz
 96 repetitions
OBSERVE  C13, 125.7485276 MHz
DECOUPLE  H1, 500.0956704 MHz
 Power 41 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 65536
Total time 1 min 50 sec
```



nb6-144-1
major diastereomer

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

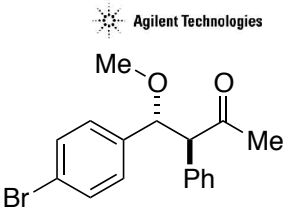
Sample directory:

FidFile: w-dms-nb6-144-1-1H

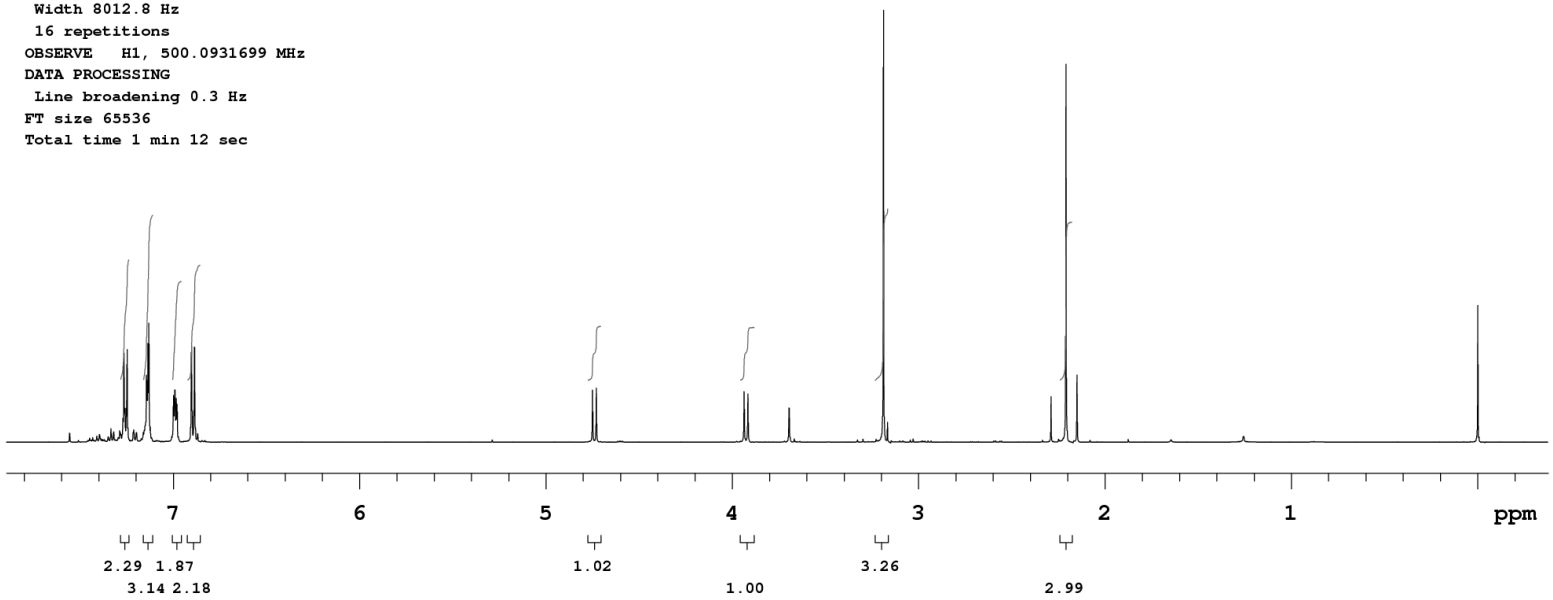
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2012

Operator: danims

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



26 (major diastereomer)



nb6-147-2-1

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

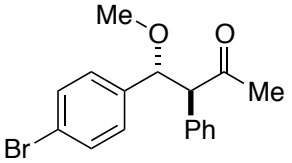
FidFile: w-dms-nb6-144-1-majord-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2012

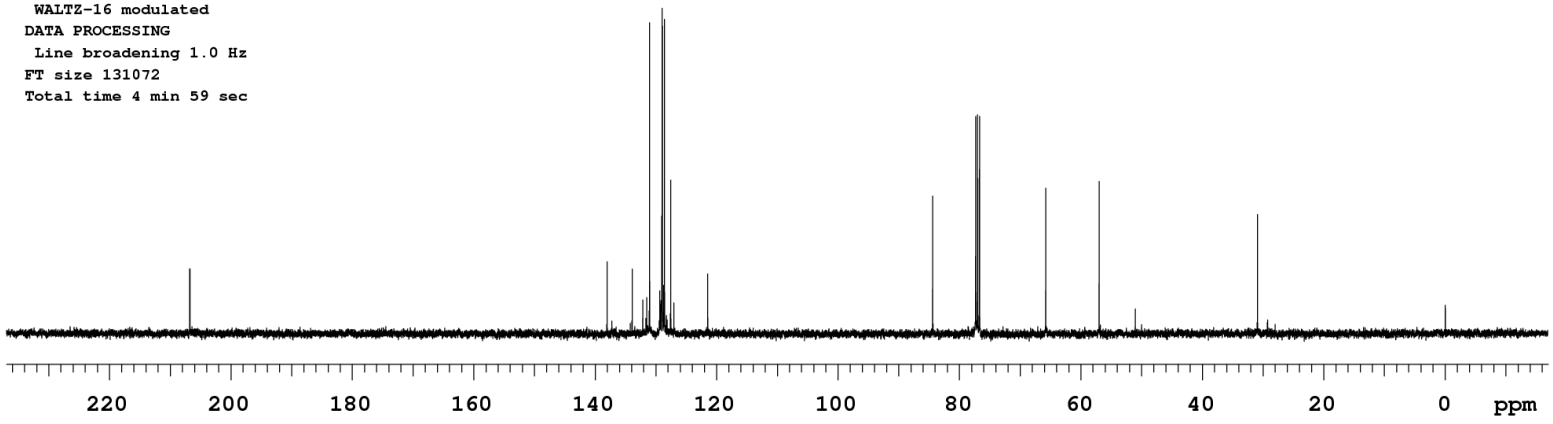
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
112 repetitions
OBSERVE C13, 100.4628343 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 min 59 sec

Agilent Technologies



26 (major diastereomer)



nb6-144-1
minor diastereomer

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

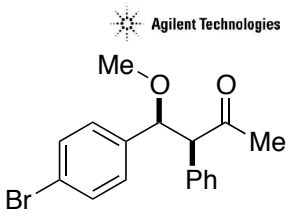
Sample directory:

FidFile: w-dms-nb6-144-1-minord-1H

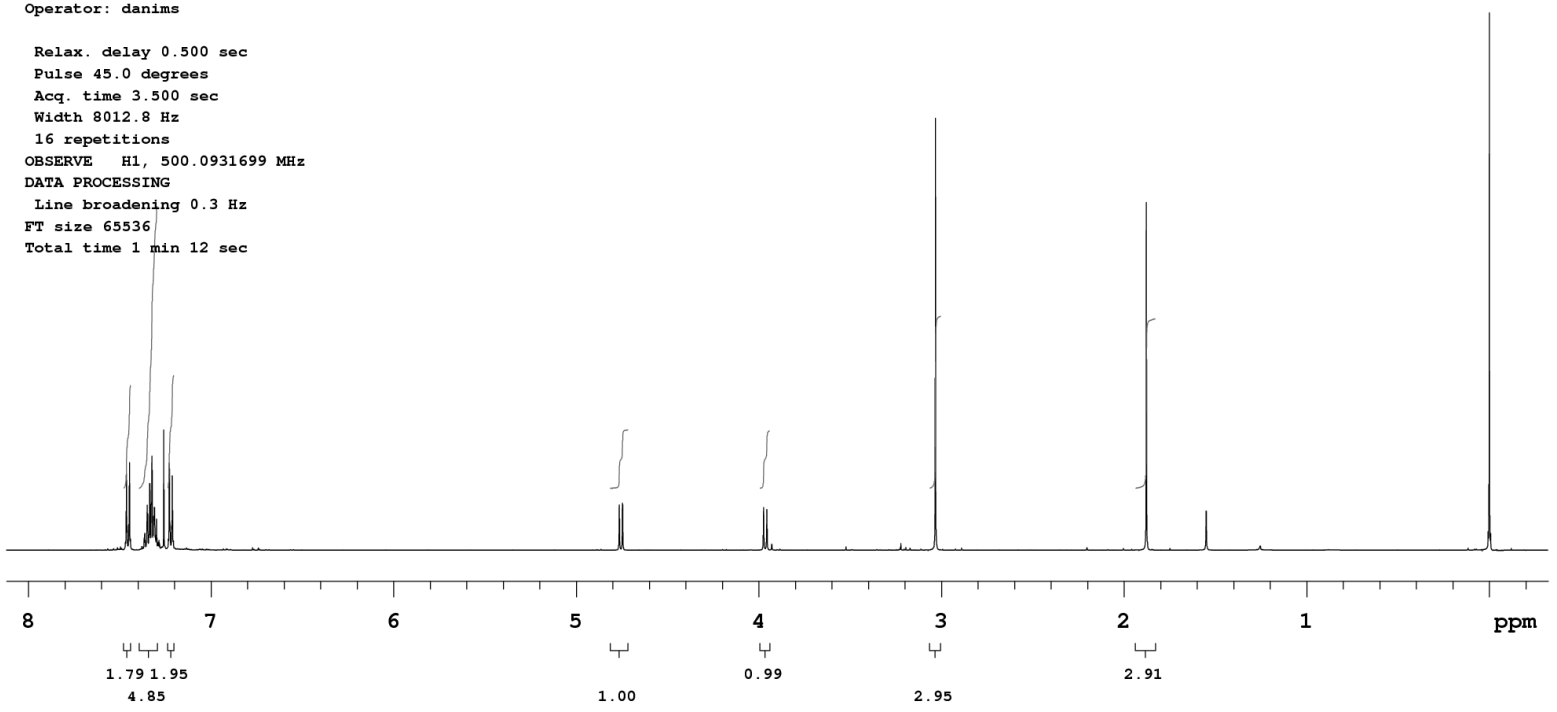
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 17 2012

Operator: danims

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec



26 (minor diastereomer)



nb6-148-1-minordiastereomer

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

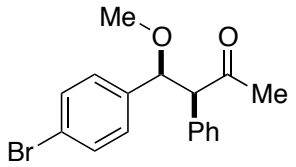
FidFile: w-dms-nb6-148-1-minord-13C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 21 2012

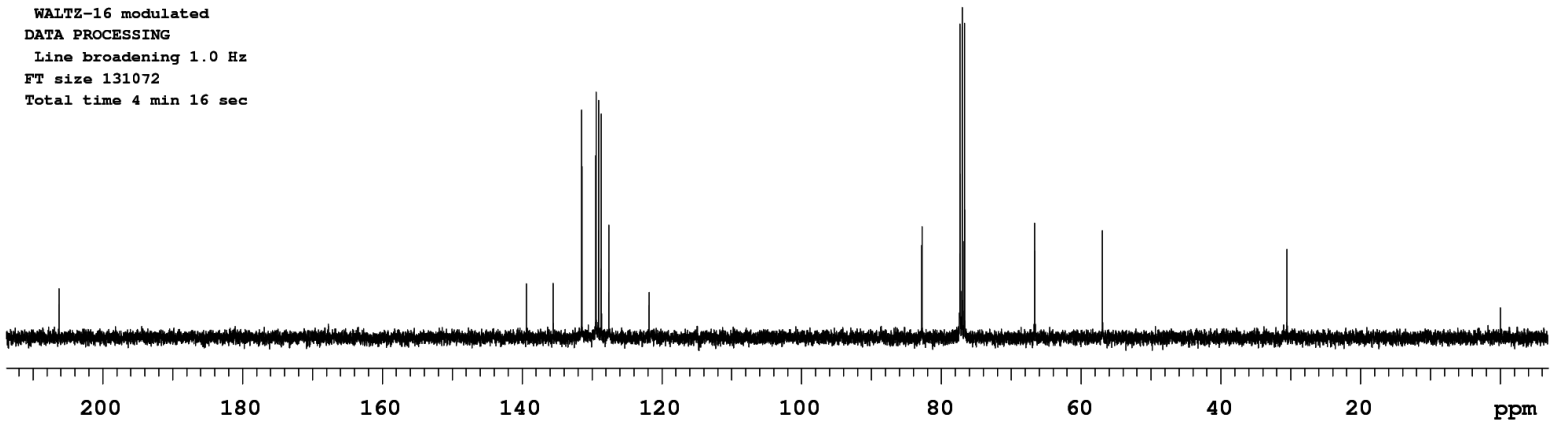
Operator: danims

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
96 repetitions
OBSERVE C13, 100.4628324 MHz
DECOUPLE H1, 399.5357121 MHz
Power 42 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 4 min 16 sec

Agilent Technologies



26 (minor diastereomer)



nb6-161-1

Sample Name:

Data Collected on:
Te-vnmrs500
Archive directory:

Sample directory:

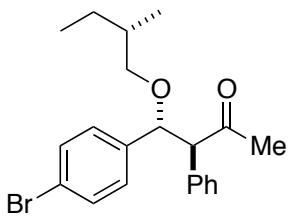
FidFile: w-dms-nb6-161-1-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Feb 27 2012

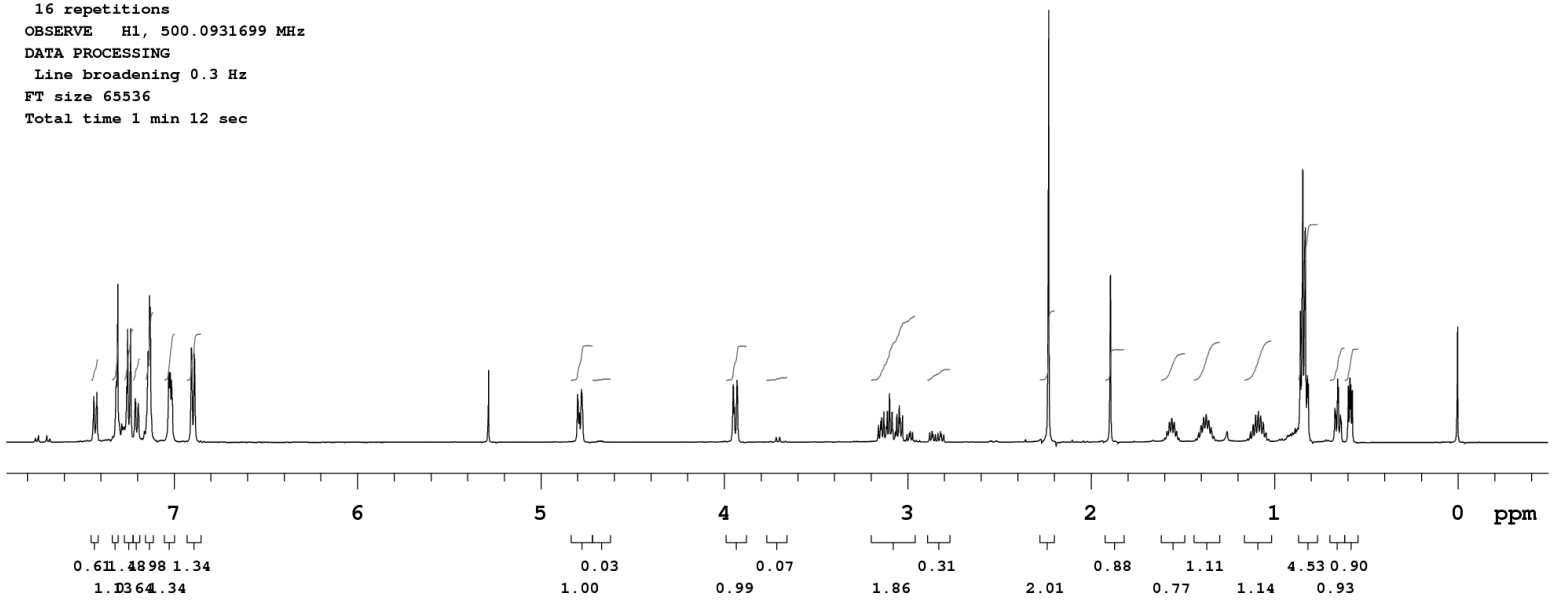
Operator: danims

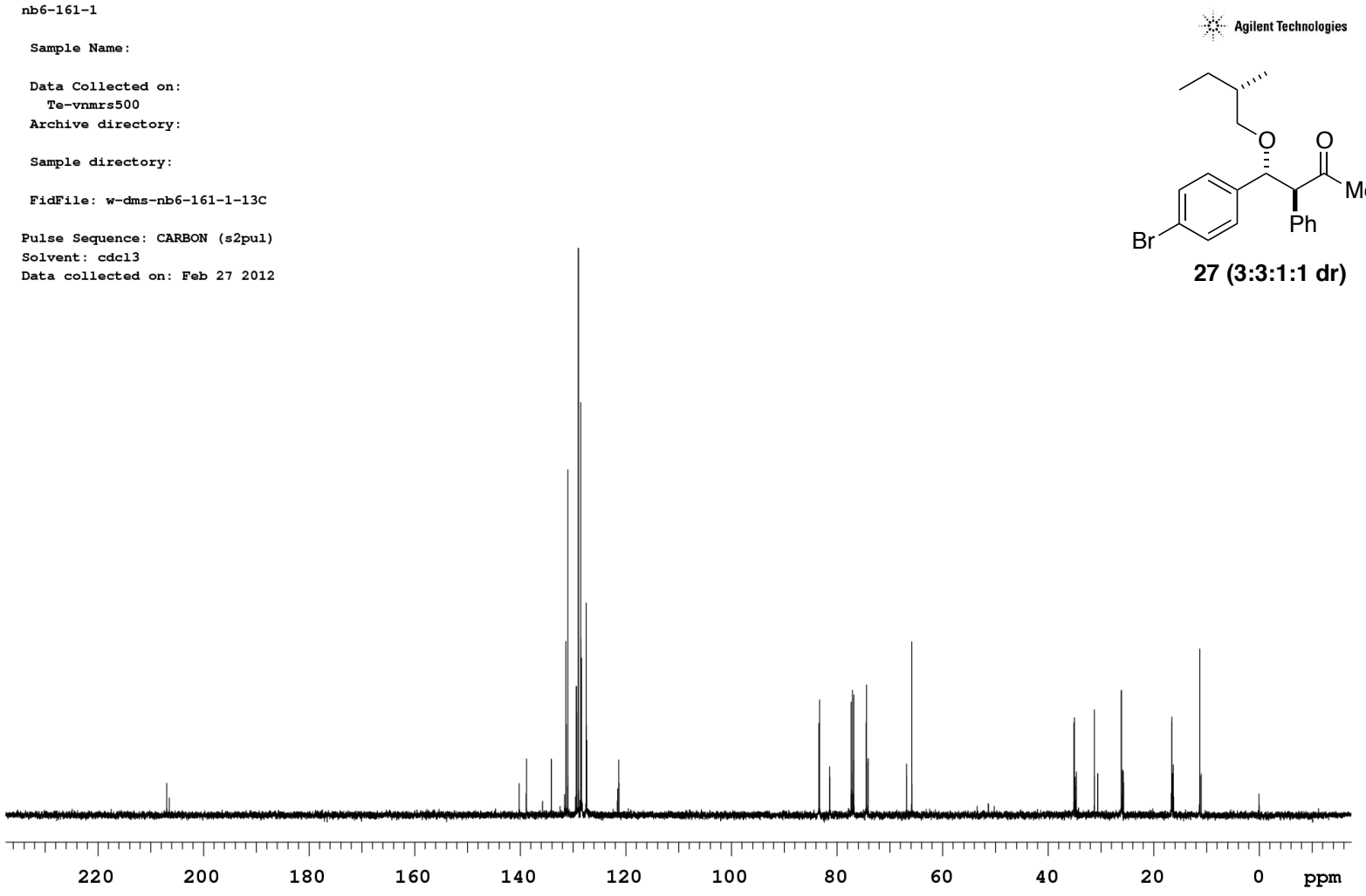
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 8012.8 Hz
16 repetitions
OBSERVE H1, 500.0931699 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec

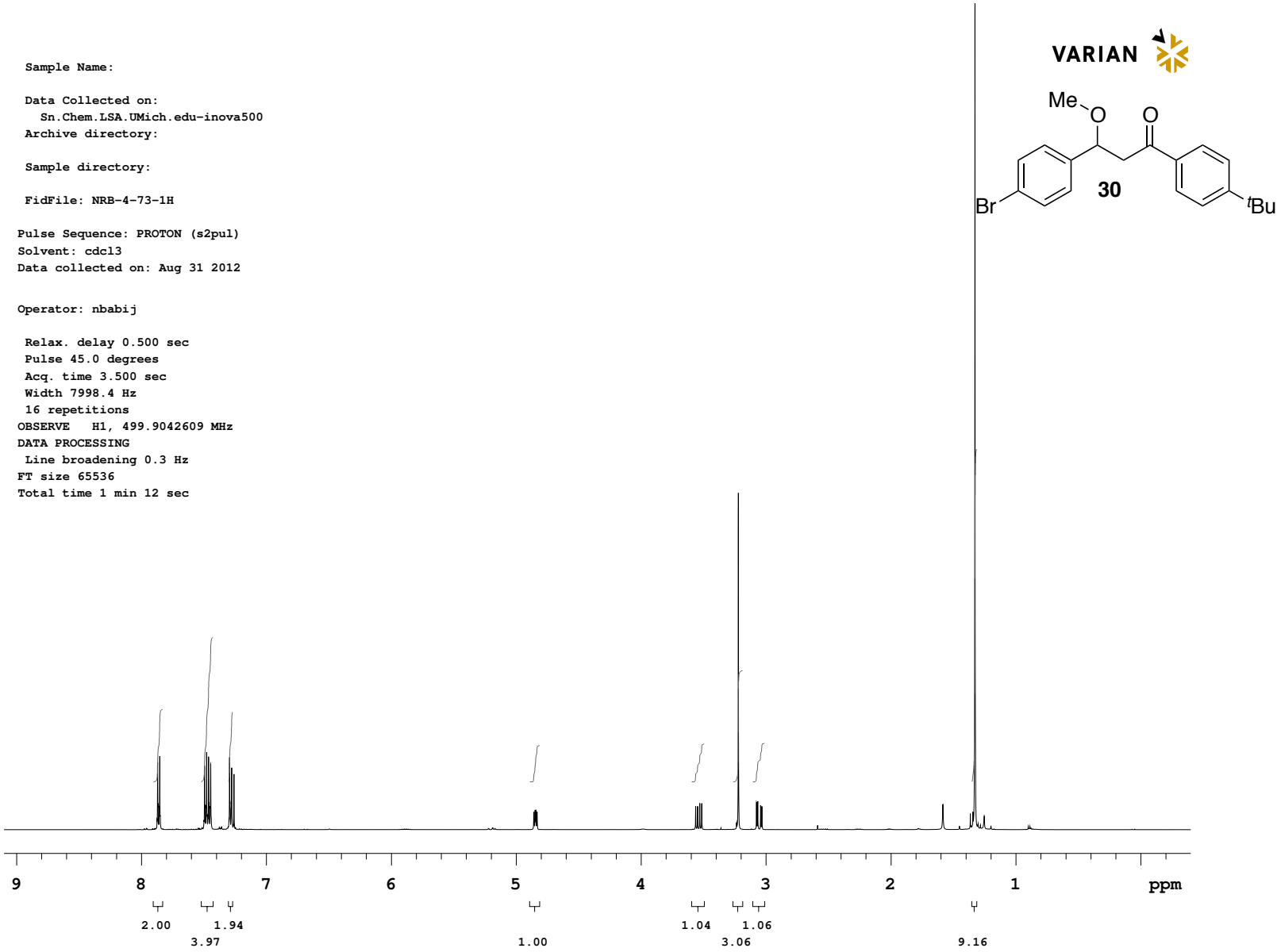
Agilent Technologies

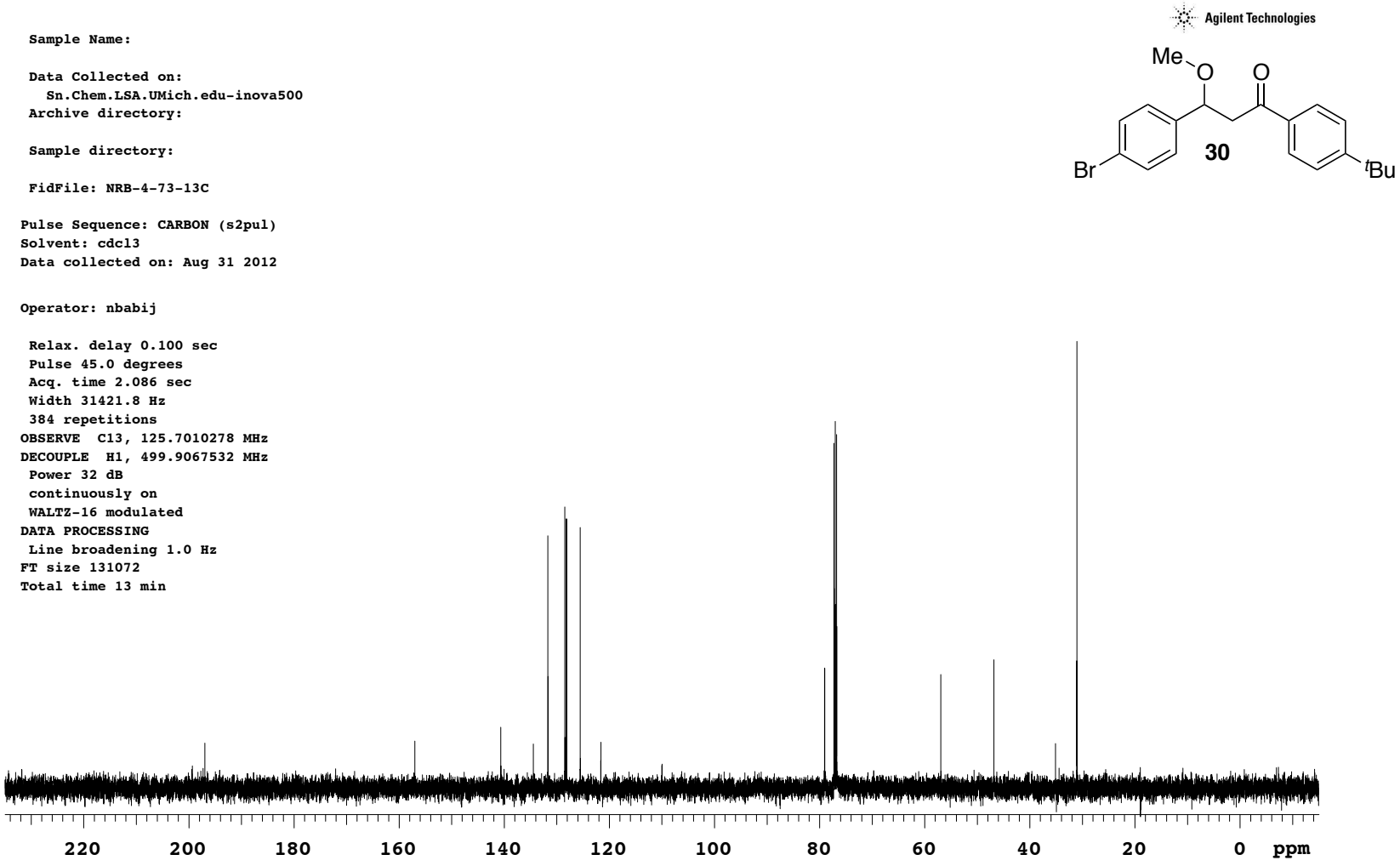


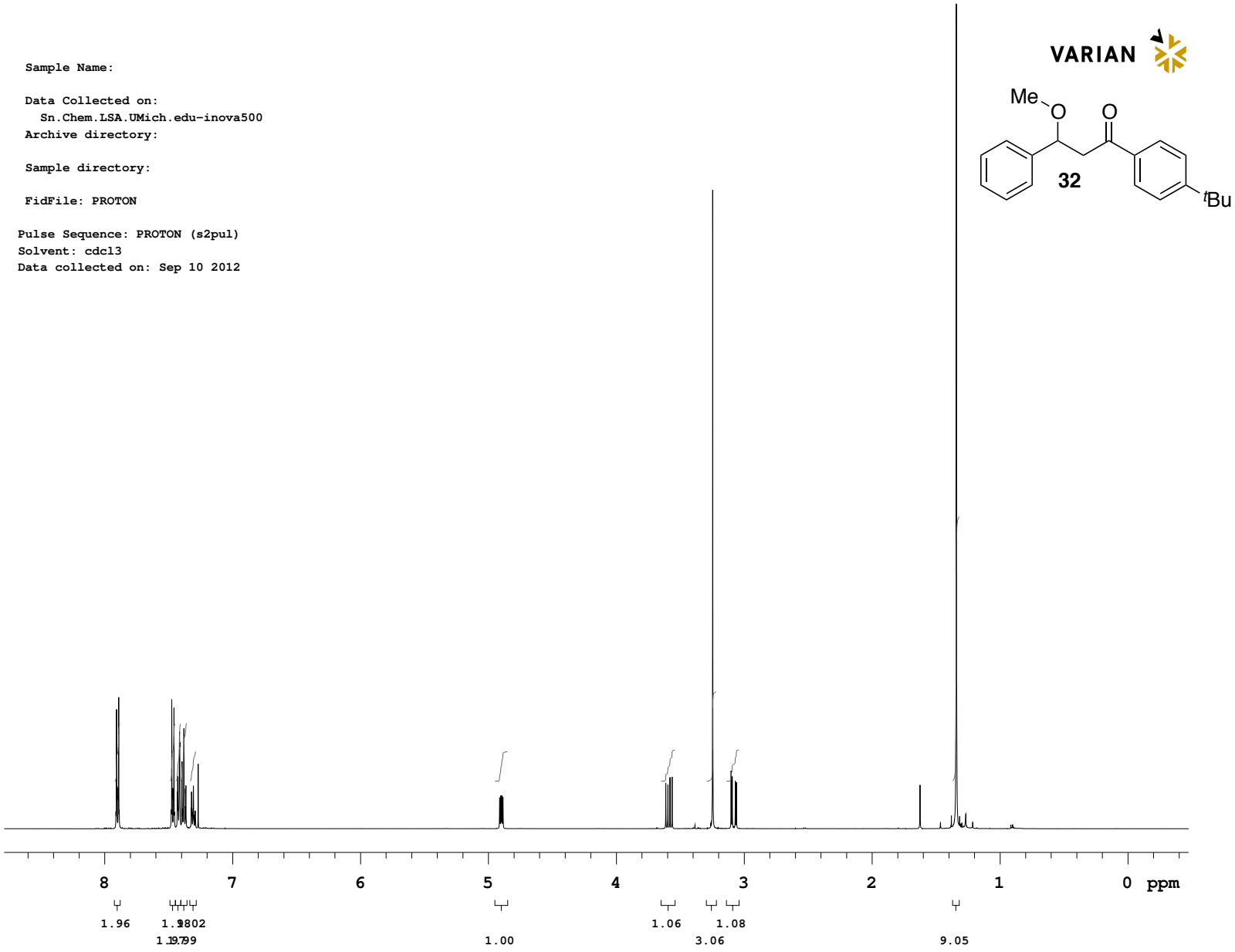
27 (3:3:1:1 dr)

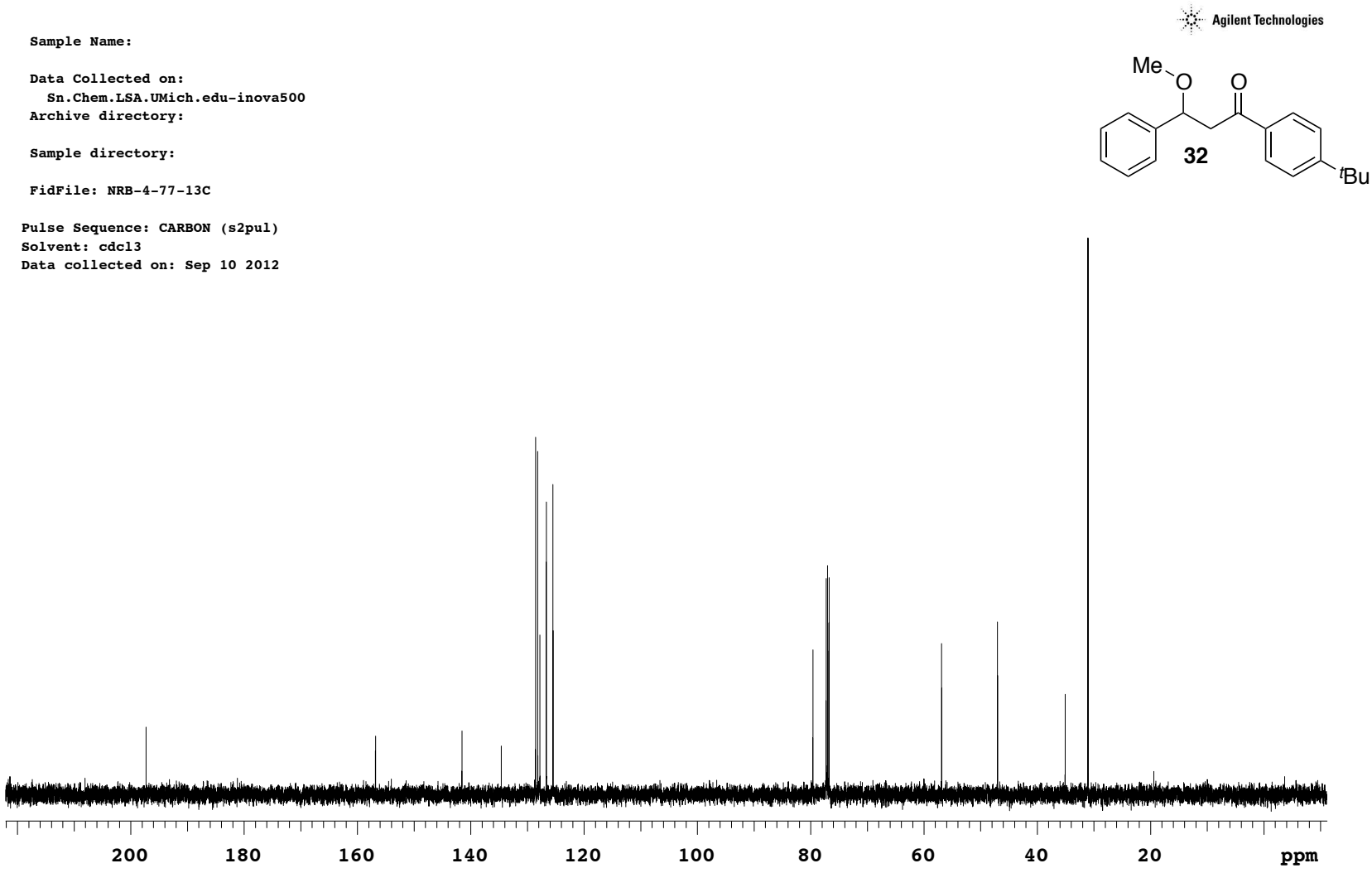



nb6-161-1
Sample Name:
Data Collected on:
Te-vnmrs500
Archive directory:
Sample directory:
FidFile: w-dms-nb6-161-1-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Feb 27 2012
Agilent Technologies
O
O
Me
Ph
Br
27 (3:3:1:1 dr)
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: NRB-4-73-1H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Aug 31 2012
Operator: nbabij
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 7998.4 Hz
16 repetitions
OBSERVE H1, 499.9042609 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
VARIAN
Me
O
O
Br
30
tBu
9
8
7
6
5
4
3
2
1
ppm
2.00
1.94
3.97
1.00
1.04
1.06
3.06
9.16


Agilent Technologies
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: NRB-4-73-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Aug 31 2012
Operator: nbabij
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.086 sec
Width 31421.8 Hz
384 repetitions
OBSERVE C13, 125.7010278 MHz
DECOUPLE H1, 499.9067532 MHz
Power 32 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 13 min
Me
O
O
Br
30
tBu
220
200
180
160
140
120
100
80
60
40
20
0
ppm


Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: PROTON
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 10 2012
VARIAN
Me
O
O
32
tBu
8
7
6
5
4
3
2
1
0 ppm
1.96
1.06
1.08
1.00
3.06
9.05


Agilent Technologies
Sample Name:
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:
Sample directory:
FidFile: NRB-4-77-13C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 10 2012
Me
O
O
32
tBu
200
180
160
140
120
100
80
60
40
20
ppm

Sample Name:

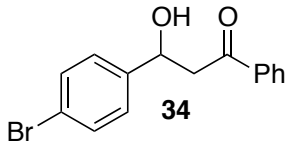
Data Collected on:
Sn.Chem.LSA.UMich.edu-inova500
Archive directory:

Sample directory:

FidFile: NRB-4-69-1H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 10 2012

VARIAN



34