

Enantioselective Palladium-Catalyzed [3+2] Cycloadditions of Trimethylenemethane with Nitroalkenes

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Supporting Information

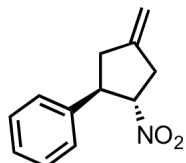
A. General Methods. All TMM reactions were carried out under an argon atmosphere. Solvents were dried by passing through an Alumina column. All compounds were purchased from commercial sources and used directly unless listed. *m*-chloroperoxybenzoic acid was purified by the known method.¹ Diaza(1,3)bicyclo[5.4.0]undene (DBU) and 3-buten-2-one were purified by distillation prior to use. Solutions of potassium *tert*-butoxide were prepared by combining equimolar amounts of distilled *tert*-butanol and potassium hydride (from a 30-35% mineral oil dispersion thrice rinsed with hexanes and dried under vacuum) in THF; after stirring 30 minutes the suspension was allowed to settle and the supernatant was used directly. The following compounds were prepared according to known literature procedures: Pd(dba)₂,² 3-acetoxy-2-trimethylsilylmethyl-1-propene **1**,³ **L1**,⁴ and **L2-L5**.⁵ Nitroalkenes that were not commercially available were prepared following the general procedure of Worrall.⁶

Flash chromatography was performed with 0.040-0.063 μm Silica Gel. ¹H and ¹³C NMR spectroscopy was performed on a Mercury NMR at 400 (¹H) or 100 (¹³C) MHz and Unity NMR at 500 (¹H) or 125 (¹³C) MHz. Chemical shifts are reported in ppm relative to tetramethylsilane or residual protiated solvent. All ¹³C NMR spectra were proton decoupled. Infrared spectroscopic data was recorded on sodium chloride plates as thin films on a Perkin-Elmer Paragon 500 FT-IR spectrometer. Chiral HPLC analysis was performed on a Thermo Separation Products Spectra Series P-100 and on an Agilent Technologies 1200 Series using Chiralcel® columns. Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using 5 cm glass cells with a Na 589 nm filter.

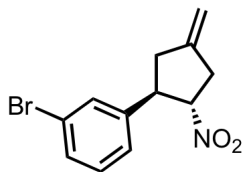
B. Synthesis of Nitrocyclopentanes

General procedure A for the asymmetric TMM cycloadditions with nitroalkenes.

To an argon-purged vial of substrate (0.075 mmol), ligand **L5** (0.0075 mmol) and Pd(dba)₂ (0.0038 mmol) was added toluene (0.5 ml) and the solution stirred for 2 minutes before 2-((trimethylsilyl)methyl)allyl acetate (25 μL, 0.12 mmol) was added. After stirring for 4 or 24 hours (at 50 or 23 °C, respectively), the solution was concentrated and purified by flash chromatography.

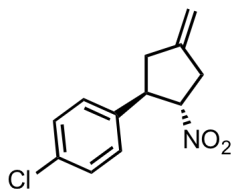


((1R,2S)-4-methylene-2-nitrocyclopentyl)benzene (6): The reaction was performed with 11.3 mg (0.076 mmol) of trans-β-nitrostyrene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (14.4 mg, 93% yield) that solidified on standing. ¹H NMR (500 MHz, CDCl₃): δ 7.35-7.22 (m, 5H), 5.07 (quintet, *J* = 2.5 Hz, 1H), 5.06 (quintet, *J* = 2.5 Hz, 1H), 4.95 (q, *J* = 7.9 Hz, 1H), 3.82 (q, *J* = 3.82 Hz, 1H), 3.11-3.06 (m, 2H), 3.02-2.96 (m, 1H), 2.67-2.60 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 144.8, 139.9, 129.2, 127.9, 127.3, 109.2, 91.5, 50.7, 39.1, 38.5. IR (thin film): 3031, 2919, 1662, 1549, 1495, 1432, 1369 cm⁻¹. [α]₂₆^D = +123.9 (c 0.49, CHCl₃). Chiral HPLC: Chiralcel IA, 0.8 mL/min, 1% *i*-PrOH in heptane, λ = 220 nm, *t*_{R, major} = 9.5 min, *t*_{R, minor} = 10.9 min. HRMS: calcd for (M+Na⁺) C₁₂H₁₃NO₂Na 226.0844; found 226.0852. MP 58-59 °C.

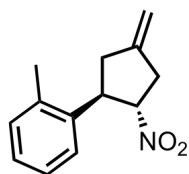


1-bromo-3-((1R,2S)-4-methylene-2-nitrocyclopentyl)benzene (7): The reaction was performed with 17.1 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to

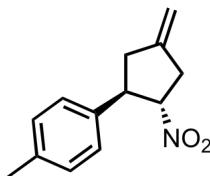
give the product as a clear, colorless oil (13.3 mg, 63% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.43-7.38 (m, 2H), 7.21 (t, $J = 7.6$ Hz, 1H), 7.16 (dt, $J = 1.6, 7.6$ Hz, 1H), 5.08 (apparent septet, $J = 2.2$ Hz, 2H), 4.93 (q, $J = 8$ Hz, 1H), 3.79 (q, $J = 8.4$ Hz, 1H), 3.12-3.07 (m, 2H), 3.04-2.95 (m, 1H), 2.65-2.55 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.1, 142.3, 131.2, 130.8, 130.4, 126.2, 123.3, 109.7, 91.2, 50.2, 39.1, 38.5. IR (thin film): 3078, 2918, 1662, 1595, 1549, 1477, 1429, 1368, 1074 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 67.9$ (c 1.27, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 240$ nm, $t_{\text{R, major}} = 8.5$ min, $t_{\text{R, minor}} = 9.4$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{12}\text{H}_{13}\text{BrNO}_2$ 282.0129; found 282.0124.



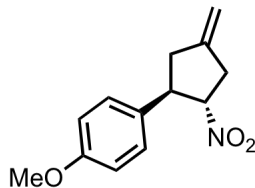
1-chloro-4-((1R,2S)-4-methylene-2-nitrocyclopentyl)benzene (8): The reaction was performed with 13.8 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (11.7 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.33-7.28 (m, 2H), 7.20-7.14 (m, 2H), 5.07 (apparent septet, $J = 2.2$ Hz, 2H), 4.90 (q, $J = 8.0$ Hz, 1H), 3.79 (q, $J = 9.2$ Hz, 1H), 3.12-3.05 (m, 2H), 2.98 (dd, $J = 9.2$ Hz, 17.6, 1H), 2.64-2.53 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.3, 138.4, 133.8, 129.5, 128.7, 109.6, 91.4, 50.1, 39.1, 38.5. IR (thin film): 2923, 1636, 1594, 1550, 1494, 1369, 1341, 1092, 1014 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 66.4$ (c 1.12, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 240$ nm, $t_{\text{R, major}} = 7.0$ min, $t_{\text{R, minor}} = 8.0$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{12}\text{H}_{13}\text{ClNO}_2$ 238.0635; found 238.0630.



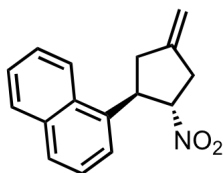
1-methyl-2-((1*R*,2*S*)-4-methylene-2-nitrocyclopentyl)benzene (9): The reaction was performed with 13.6 μ l (0.075 mmol) of nitroalkene according to general procedure A in toluene at 23 °C and purified by flash chromatography (2% ethyl acetate in hexanes) to give the product as a clear, colorless oil (14.7 mg, 91% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.22-7.13 (m, 4H), 5.08 (apparent sextet, $J = 2.4$ Hz, 2H), 4.98 (q, $J = 7.2$ Hz, 1H), 4.13-4.06 (m, 1H), 3.10-2.97 (m, 3H), 2.59-2.48 (m, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.6, 138.6, 136.7, 131.1, 127.6, 127.0, 125.5, 109.1, 91.0, 46.4, 38.9, 38.1, 20.0. IR (thin film): 3076, 3022, 2957, 1661, 1549, 1493, 1462, 1435, 1367, 1173, 1053 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 61.1$ (c 1.46, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 240$ nm, $t_{\text{R, major}} = 6.8$ min, $t_{\text{R, minor}} = 8.2$ min. HRMS: calcd for ($\text{M}+\text{H}^+$) $\text{C}_{13}\text{H}_{16}\text{NO}_2$ 218.1181; found 218.1176.



1-methyl-4-((1*R*,2*S*)-4-methylene-2-nitrocyclopentyl)benzene (10): The reaction was performed with 12.2 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (2% ethyl acetate in hexanes) to give the product as a clear, colorless oil (13.3 mg, 82% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.16-7.10 (m, 4H), 5.08-5.03 (m, 2H), 4.92 (q, $J = 8.0$, 1H), 3.78 (q, $J = 9.2$ Hz, 1H), 3.10-3.05 (m, 2H), 2.97 (dd, 8.4, 16.8 Hz, 1H), 2.65-2.56 (m, 1H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.9, 137.7, 136.9, 129.9, 127.2, 109.2, 91.7, 50.5, 39.2, 38.6, 21.4. IR (thin film): 3024, 2922, 1661, 1550, 1517, 1432, 1368, 1319, 1258, 1167, 1112 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 106.2$ (c 1.25, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 1% *i*-PrOH in heptane, $\lambda = 220$ nm, $t_{\text{R, major}} = 8.6$ min, $t_{\text{R, minor}} = 10.5$ min. HRMS: calcd for ($\text{M}+\text{H}^+$) $\text{C}_{13}\text{H}_{16}\text{NO}_2$ 218.1181; found 218.1176.

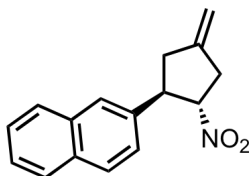


1-methoxy-4-((1R,2S)-4-methylene-2-nitrocyclopentyl)benzene (11): The reaction was performed with 13.4 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 23 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (12.6 mg, 72% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.18-7.13 (m, 2H), 6.89-6.84 (m, 2H), 5.08-5.03 (m, 2H), 4.90 (q, *J* = 8.0 Hz, 1H), 3.79 (s, 3H), 3.78-3.72 (m, 1H), 3.10-3.04 (m, 2H), 2.96 (dd, *J* = 8.4 Hz, 16.8 Hz, 1H), 2.64-2.54 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 159.3, 144.8, 131.8, 128.4, 114.6, 109.2, 91.9, 55.6, 50.2, 39.2, 38.5. IR (thin film): 3077, 2958, 2838, 1661, 1613, 1549, 1515, 1464, 1441, 1369, 1305, 1250, 1181, 1111, 1034 cm⁻¹. [α]₂₄^D = 113.1 (c 1.20, CHCl₃). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, λ = 220 nm, *t*_{R, major} = 12.2 min, *t*_{R, minor} = 13.8 min. HRMS: calcd for (M+H⁺) C₁₃H₁₆NO₃ 234.1130; found 234.1124.



1-((1R,2S)-4-methylene-2-nitrocyclopentyl)naphthalene (12): The reaction was performed with 14.9 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 23 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (12.7 mg, 67% yield). ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, *J* = 7.6 Hz, 1H), 7.89 (d, *J* = 6.8 Hz, 1H), 7.79 (dd, *J* = 2.0, 5.2 Hz, 1H), 7.62-7.59 (m, 1H), 7.55-7.52 (m, 1H), 7.46-7.42 (m, 2H), 5.19-5.13 (m, 3H), 4.73-4.68 (m, 1H), 3.23-3.15 (m, 2H), 3.40-2.97 (m, 1H), 2.82-2.76 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 146.1, 136.2, 134.3, 131.6, 129.5, 128.6, 127.1, 126.3, 125.8, 123.3, 123.2, 109.2, 90.9, 46.1, 38.2, 37.4. IR (thin film): 3050, 2923, 2853, 1660, 1598, 1546,

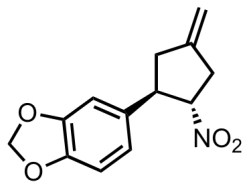
1433, 1399, 1367, 1320 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 2.1$ (c 1.27, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 254$ nm, $t_{\text{R, major}} = 10.9$ min, $t_{\text{R, minor}} = 12.6$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{16}\text{H}_{16}\text{NO}_2$ 254.1181; found 254.1174.



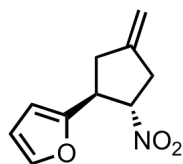
2-((1R,2S)-4-methylene-2-nitrocyclopentyl)naphthalene (13):

Small Scale: The reaction was performed with 14.9 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (15.5 mg, 82% yield).

Large Scale: A mixture of nitroalkene (300 mg, 1.5 mmol), $\text{Pd}(\text{dba})_2$ (21.6 mg, 0.038 mmol) and ligand **L5** (48.4 mg, 0.076 mmol) was purged with argon for 15 minutes. Toluene (10 ml) was added and the solution was stirred for 2 minutes before 2-((trimethylsilyl)methyl)allyl acetate (0.45 mL, 2.4 mmol) was added. The solution was immersed in a 50 °C oil bath and stirred for 16 hours. It was then cooled, concentrated, and purified by flash chromatography (4% ethyl acetate in hexanes) to give a white solid (297 mg, 78% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.85-7.76 (m, 3H), 7.67 (s, 1H), 7.51-7.44 (m, 2H), 7.25 (s, 1H), 5.13-5.01 (m, 3H), 3.99 (q, $J = 9.2$ Hz, 1H), 3.16-3.00 (m, 3H), 2.79-2.69 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.8, 137.2, 133.7, 133.1, 129.2, 128.1, 128.0, 126.8, 126.4, 126.3, 125.1, 109.4, 91.5, 50.9, 39.2, 38.6. IR (thin film): 3055, 2959, 2920, 1601, 1548, 1509, 1431, 1369, 1315 cm^{-1} . $[\alpha]_{25}^{\text{D}} = 107.1$ (c 1.46, CHCl_3). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 10% *i*-PrOH in heptane, $\lambda = 220$ nm, $t_{\text{R, major}} = 6.2$ min, $t_{\text{R, minor}} = 7.3$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{16}\text{H}_{16}\text{NO}_2$ 254.1181; found 254.1176. MP 69-70° C.

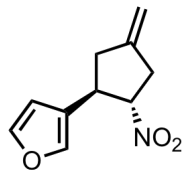


5-((1R,2S)-4-methylene-2-nitrocyclopentyl)benzo[d][1,3]dioxole (14): The reaction was performed with 14.5 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (15.0 mg, 80% yield). ¹H NMR (400 MHz, CDCl₃): δ 6.77-6.66 (m, 3H), 5.95 (s, 2H), 5.08-5.03 (m, 2H), 4.88 (q, *J* = 8.0 Hz, 1H), 3.73 (q, *J* = 8.8 Hz, 1H), 3.06 (d, *J* = 8.4 Hz, 2H), 2.95 (dd, *J* = 8.4 Hz, 16.8 Hz, 1H), 2.62-2.52 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.4, 147.3, 144.6, 133.6, 120.8, 109.3, 108.9, 107.4, 101.5, 91.8, 50.7, 39.2, 38.5. IR (thin film): 3078, 2908, 2780, 1661, 1610, 1549, 1504, 1445, 1368, 1248, 1037 cm⁻¹. [α]₂₄^D = 108.1 (c 1.50, CHCl₃). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, λ = 220 nm, *t*_{R, major} = 16.6 min, *t*_{R, minor} = 18.4 min. HRMS: calcd for (M+H⁺) C₁₃H₁₄NO₄ 248.0923; found 248.0917.

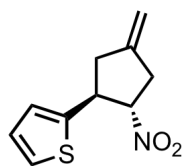


2-((1S,2S)-4-methylene-2-nitrocyclopentyl)furan (15): The reaction was performed with 10.4 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 23 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (9.5 mg, 66% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.35 (dd, *J* = 0.8, 1.9 Hz, 1H), 6.30 (dd, *J* = 1.9, 3.4 Hz, 1H), 6.14 (dt, *J* = 0.8, 3.4 Hz, 1H), 5.07-4.99 (m, 3H), 3.97-3.90 (m, 1H), 3.07-3.02 (m, 2H), 3.00-2.91 (m, 1H), 2.74-2.64 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 153.0, 144.3, 142.6, 110.7, 109.5, 106.8, 89.2, 44.0, 38.4, 36.4. IR (thin film): 3081, 2920, 2851, 1663, 1551, 1433, 1368, 1260, 1149, 1074, 1012 cm⁻¹. [α]₂₃^D = 69.8 (c 1.10, CHCl₃). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, λ = 240 nm, *t*_{R, major} = 8.5 min, *t*_{R, minor} = 9.7 min. HRMS:

calcd for (M+Na⁺) C₁₀H₁₁NO₃Na 216.0637; found 216.0640.

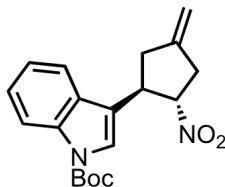


3-((1R,2S)-4-methylene-2-nitrocyclopentyl)furan (16): The reaction was performed with 10.4 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (3% ethyl acetate in hexanes) to give the product as a clear, colorless oil (8.3 mg, 58% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.39 (m, 1H), 7.32-7.31 (m, 1H), 6.30-6.29 (m, 1H), 5.05 (doublet of quintets, *J* = 1.8, 9.2 Hz, 2H), 4.82 (q, *J* = 6.0 Hz, 1H), 3.74 (q, *J* = 6.4 Hz, 1H), 3.07-3.03 (m, 2H), 2.97-2.91 (m, 1H), 2.55-2.48 (m, 1H). ¹³C NMR (125 MHz, CDCl₃): δ 144.5, 144.1, 139.5, 124.3, 109.4, 109.2, 91.1, 41.7, 38.3, 38.1. IR (thin film): 3146, 3079, 2920, 2851, 1549, 1432, 1369, 1159, 1026 cm⁻¹. [α]₂₄^D = 80.1 (c 1.27, CHCl₃). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, λ = 220 nm, *t*_{R, major} = 8.8 min, *t*_{R, minor} = 9.6 min. HRMS: calcd for (M+H⁺) C₁₀H₁₂NO₃ 194.0817; found 194.0813.



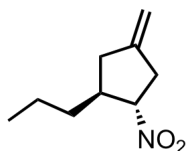
2-((1S,2S)-4-methylene-2-nitrocyclopentyl)thiophene (17): The reaction was performed with 11.6 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 23 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (11.7 mg, 75% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.21 (dd, *J* = 1.2, 5.2 Hz, 1H), 6.95 (dd, *J* = 3.4, 5.2 Hz, 1H), 6.92-6.90 (m, 1H), 5.07 (doublet of quintets, *J* = 2.16, 11.2 Hz, 2H), 4.92 (q, *J* = 7.6 Hz, 1H), 4.17-4.10 (m, 1H), 2.72-2.63 (m, 3H) 3.17-3.01 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 143.9, 143.1, 127.5, 125.2, 124.8, 109.7, 92.1, 45.9, 40.4, 38.5. IR (thin film): 3078, 2921, 1663, 1549, 1432, 1367, 1244 cm⁻¹. [α]₂₄^D = 88.4 (c 0.62, CHCl₃). Chiral HPLC:

Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, $\lambda = 220$ nm, $t_{R, \text{major}} = 8.2$ min, $t_{R, \text{minor}} = 10.5$ min. HRMS: calcd for $(M+H^+)$ $C_{10}H_{12}NO_2S$ 210.0588; found 210.0582.



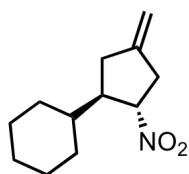
***tert*-butyl-2-((1*S*,2*S*)-4-methylene-2-nitrocyclopentyl)-1*H*-indole-1-carboxylate (18):**

The reaction was performed with 21.6 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (23.3 mg, 91% yield). 1H NMR (400 MHz, $CDCl_3$): δ 8.12 (bs, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.47 (bs, 1H), 7.37-7.32 (m, 1H), 7.29-7.25 (m, 1H), 5.14 - 5.07 (m, 3H), 4.08 (q, $J = 8.0$ Hz, 1H), 3.19-2.99 (m, 3H), 2.78-2.70 (m, 1H), 1.67 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.9, 145.2, 136.0, 129.3, 125.2, 123.1, 122.8, 119.8, 119.2, 115.9, 109.5, 90.2, 84.4, 42.4, 37.8, 37.6, 28.5. IR (thin film): 2979, 2931, 1733, 1550, 1453, 1372, 1309, 1256, 1156, 1089, 1019 cm^{-1} . $[\alpha]_{24}^D = 35.3$ (c 2.24, $CHCl_3$). Chiral HPLC: Chiralpak IA, 1.0 mL/min, 2% ethyl acetate in hexane, $\lambda = 254$ nm, $t_{R, \text{major}} = 12.4$ min, $t_{R, \text{minor}} = 15.3$ min. HRMS: calcd for $(M+Na^+)$ $C_{19}H_{23}N_2O_4Na$ 365.1478; found 365.1473.

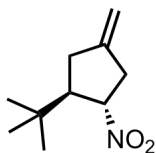


(1*S*,2*S*)-4-methylene-1-nitro-2-propylcyclopentane (19): The reaction was performed with 8.6 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (2% ethyl acetate in hexanes) to give the product as a clear, colorless oil (11.2 mg, 88% yield). 1H NMR (400 MHz, $CDCl_3$): δ

4.94 (apparent quintet, $J = 2.3$ Hz, 2H), 4.57 (q, $J = 7.6$ Hz, 1H), 3.02-2.83 (m, 2H), 2.77-2.68 (m, 1H), 2.63-2.53 (m, 1H), 2.09-2.01 (m, 1H), 1.55-1.46 (m, 1H), 1.43-1.23 (m, 3H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.5, 108.8, 90.7, 45.6, 38.3, 37.4, 35.8, 20.9, 14.3. IR (thin film): 2960, 2931, 2874, 1664, 1450, 1433, 1371 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 59.4$ (c 0.38, CHCl_3). Chiral HPLC: Chiralcel OB, 0.8 mL/min, 1% *i*-PrOH in heptane, $\lambda = 220$ nm, $t_{\text{R, minor}} = 6.7$ min, $t_{\text{R, major}} = 7.2$ min. HRMS: calcd for $(\text{M}+\text{Na}^+)$ $\text{C}_9\text{H}_{15}\text{NO}_2\text{Na}$ 192.1000; found 192.0989.

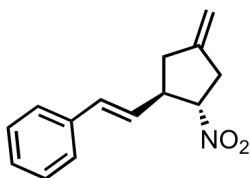


((1R,2S)-4-methylene-2-nitrocyclopentyl)cyclohexane (20): The reaction was performed with 11.6 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 °C and purified by flash chromatography (1% ethyl acetate in hexanes) to give the product as a clear, colorless oil (15.3 mg, 97% yield). ^1H NMR (400 MHz, CDCl_3): δ 4.93 (apparent septet, $J = 2.4$ Hz, 2H), 4.76 (q, $J = 7.6$ Hz, 1H), 2.94-2.87 (m, 2H), 2.65 (dd, $J = 9.2$ Hz, 15.6 Hz, 1H), 2.57-2.47 (m, 1H), 2.22-2.13 (m, 1H), 1.78-1.62 (m, 5H), 1.40-1.29 (m, 1H), 1.28-1.06 (m, 3H), 1.05-0.91 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3): δ 145.8, 108.4, 88.6, 51.0, 40.9, 39.6, 35.1, 31.0, 30.2, 26.5, 26.5, 26.4. IR (thin film): 3078, 2927, 2853, 1663, 1549, 1448, 1368, 1310, 1260 cm^{-1} . $[\alpha]_{23}^{\text{D}} = 47.6$ (c 1.55, CHCl_3). Chiral HPLC: Chiralpak IA, 1.0 mL/min, 1% THF in heptane, $\lambda = 220$ nm, $t_{\text{R, major}} = 11.3$ min, $t_{\text{R, minor}} = 14.3$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{12}\text{H}_{20}\text{NO}_2$ 210.1494; found 210.1489.



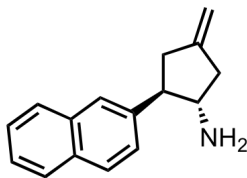
(1R,2S)-1-tert-butyl-4-methylene-2-nitrocyclopentane (21): The reaction was

performed with 11 μl (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 $^{\circ}\text{C}$ and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (13.3 mg, 97% yield). ^1H NMR (400 MHz, CDCl_3): δ 4.95-4.89 (m, 2H), 4.85-4.78 (m, 1H), 2.91-2.86 (m, 2H), 2.68-2.56 (m, 2H), 2.33-2.20 (m, 1H), 0.91 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.2, 108.2, 87.5, 55.3, 40.9, 33.9, 33.0, 27.4. IR (thin film): 2963, 1665, 1552, 1473, 1431, 1399, 1369 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 41.9$ (c 1.00, CHCl_3). Chiral HPLC: Chiralpak IC, 1.0 mL/min, 1% THF in heptane, $\lambda = 220$ nm, $t_{\text{R, major}} = 8.0$ min, $t_{\text{R, minor}} = 8.5$ min). HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{10}\text{H}_{18}\text{NO}_2$ 184.1337; found 184.1333.

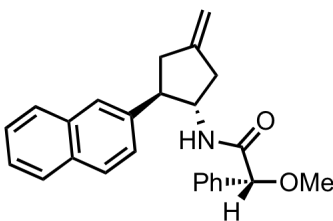


((E)-2-((1R,2S)-4-methylene-2-nitrocyclopentyl)vinyl)benzene (22): The reaction was performed with 13.1 mg (0.075 mmol) of nitroalkene according to general procedure A in toluene at 50 $^{\circ}\text{C}$ and purified by flash chromatography (4% ethyl acetate in hexanes) to give the product as a clear, colorless oil (11.8 mg, 53% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.37-7.38 (m, 4H), 7.27-7.21 (m, 1H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.10 (dd, $J = 8.4$ Hz, 15.6, 1H), 5.03 (apparent septet, $J = 2.3$ Hz, 2H), 4.77 (q, $J = 8.0$ Hz, 1H), 3.43-3.34 (m, 1H), 3.11-2.96 (m, 2H), 2.88-2.78 (m, 1H), 2.45-2.35 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 144.4, 136.7, 133.0, 128.9, 128.2, 127.9, 126.7, 109.4, 90.3, 49.1, 38.1, 37.9. IR (thin film): 3027, 2913, 1662, 1549, 1493, 1432, 1369, 1320, 1256 cm^{-1} . $[\alpha]_{24}^{\text{D}} = 135.2$ (c 0.45, CHCl_3). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 10% *i*-PrOH in heptane, $\lambda = 220$ nm, $t_{\text{R, major}} = 5.8$ min, $t_{\text{R, minor}} = 6.7$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{14}\text{H}_{16}\text{NO}_2$ 230.1181; found 230.1175.

C. Synthesis of Cyclopentane Derivatives

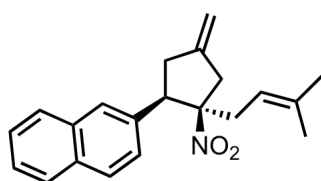


(1S,2R)-4-methylene-2-(naphthalen-2-yl)cyclopentanamine (23): A suspension of nitrocyclopentane (8.0 mg, 0.032 mmol) in concentrated HCl (63 μ L, 0.76 mmol) and methanol (0.32 ml) was placed in an ambient water bath. Zinc dust (84.8 mg, 1.30 mmol) was carefully added with vigorous stirring over 1 minute, and the mixture was stirred for 10 minutes. The reaction was then quenched with sat. NaHCO₃ (6 ml) and extracted with ethyl acetate (3 x 4 ml). The combined extracts were dried over MgSO₄, concentrated and purified by flash chromatography (DCM to 5% methanol in DCM) to afford the product as a pale yellow oil (6.3 mg, 88% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.84-7.78 (m, 3H), 7.70 (m, 1H), 7.49-7.42 (m, 2H), 7.40 (dd, *J* = 1.7, 8.4 Hz, 1H), 4.97-4.93 (m, 2H), 3.47-3.39 (m, 1H), 2.94-2.82 (m, 3H), 2.70-2.60 (m, 1H), 2.32-2.23 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 148.1, 139.9, 133.9, 132.9, 128.7, 128.0, 127.9, 126.6, 126.5, 125.9, 125.8, 107.2, 60.0, 55.6, 42.2, 40.4. IR (thin film): 3361, 3280, 3054, 2926, 1716, 1600, 1508, 1429 cm⁻¹. [α]₂₄^D = 56.4 (c 0.91, CHCl₃). Chiral HPLC (the title compound was converted into its acetamide according to standard procedures (acetyl chloride, pyridine) for analysis: Chiralpak AD, 1.0 mL/min, 10% *i*-PrOH in heptane, λ = 254 nm, *t*_{R, minor} = 11.4 min, *t*_{R, major} = 15.0 min. HRMS: calcd for (M+H⁺) C₁₆H₁₈N 224.1439; found 224.1425.



(R)-2-methoxy-N-((1S,2R)-4-methylene-2-(naphthalen-2-yl)cyclopentyl)-phenylacetamide (24): To a solution of aminocyclopentane (2.0 mg, 0.0090 mmol) in DCM (200 μ L) was added (*R*)-*O*-methylmandelic acid (1.7 mg, 0.010 mmol) followed by *N,N'*-dicyclohexylcarbodiimide (2.3 mg, 0.011 mmol). The mixture was stirred under

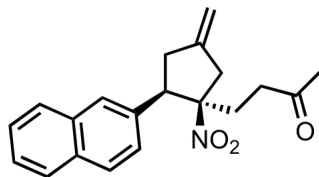
nitrogen for 1 hour, filtered, washed with DCM and concentrated. Purified by flash chromatography (20% ethyl acetate in hexanes) to yield the product as a white powder (2.5 mg, 75% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.80-7.78 (m, 1H), 7.75-7.71 (m, 2H), 7.64 (m, 1H), 7.46-7.44 (m, 2H), 7.38 (dd, $J = 1.9, 8.5$ Hz, 1H), 7.08 (dt, $J = 1.8, 1.8, 7.5$ Hz, 1H), 6.92-6.86 (m, 4H), 6.81 (d, $J = 9.0$ Hz, 1H), 5.02-5.00 (m, 2H), 4.62-4.55 (m, 1H), 4.51 (s, 1H), 3.28-3.22 (m, 1H), 3.26 (s, 3H), 3.07-3.01 (m, 1H), 2.94-2.88 (m, 1H), 2.66-2.59 (m, 1H), 2.40-2.34 (m, 1H).



2-((1R,2R)-2-(3-methylbut-2-enyl)-4-methylene-2-nitrocyclopentyl)naphthalene

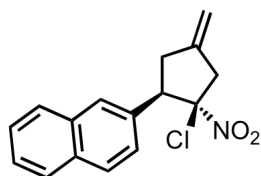
(25): To a solution of nitrocyclopentane (8.0 mg, 0.032 mmol), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (1.3 mg, 0.0016 mmol), 1,3-bis(diphenylphosphino)propane (2.0 mg, 0.0048 mmol) and Cs_2CO_3 (10.4 mg, 0.032 mmol) in DMSO (0.5 ml) was added *tert*-butyl 2-methylbut-3-en-2-yl carbonate (11 μL , 0.051 mmol) under Ar. The mixture was warmed to 50 $^\circ\text{C}$ and stirred for 5 hours. It was then cooled, quenched with water (2 ml) and extracted with diethyl ether (4 x 2 ml). The combined organics were washed with brine, dried over MgSO_4 and concentrated. Purified by flash chromatography (1% ethyl acetate in hexanes) to yield the product as a clear, colorless oil that solidified on standing (7.0 mg, 68% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.84-7.77 (m, 3H), 7.62-7.61 (m, 1H), 7.48-7.45 (m, 2H), 7.26 (dd, $J = 1.9, 8.4$ Hz, 1H), 5.14-5.10 (m, 2H), 5.07-5.02 (m, 1H), 3.59 (dd, $J = 8.0, 9.6$ Hz, 1H), 3.43 (bd, $J = 18.0$ Hz, 1H), 3.21-3.13 (m, 1H), 3.03 (dd, $J = 6.8, 15.2$ Hz, 1H), 2.92-2.84 (m, 1H), 2.76 (dq, $J = 2.2, 18.0$ Hz, 1H), 2.57 (dd, $J = 7.6, 14.8$ Hz, 1H), 1.72 (s, 3H), 3.64 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 146.4, 137.5, 135.0, 133.6, 133.3, 128.5, 128.3, 127.9, 127.6, 126.5, 126.4, 126.1, 117.4, 108.5, 100.6, 55.2, 41.2, 37.6, 35.9, 26.4, 18.6. IR (thin film): 3057, 2926, 1662, 1601, 1537, 1434, 1354 cm^{-1} . $[\alpha]_{24}^{\text{D}} = -47.8$ (c 0.61, CHCl_3). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1.0% *i*-PrOH in heptane,

$\lambda = 254 \text{ nm}$, $t_{R, \text{major}} = 8.8 \text{ min}$, $t_{R, \text{minor}} = 11.2 \text{ min}$. HRMS: calcd for $(M+H^+)$ $C_{21}H_{24}NO_2$ 322.1807; found 322.1796. MP 90-92 °C.



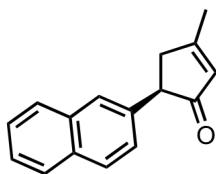
4-((1R,2R)-4-methylene-2-(naphthalen-2-yl)-1-nitrocyclopentyl)butan-2-one (26):

To a solution of nitrocyclopentane (40.0 mg, 0.16 mmol) in acetonitrile (2.5 ml) was added DBU (24 μL , 0.16 mmol) and 3-buten-2-one (13.4 μL , 0.16 mmol). The pale yellow solution was stirred at room temperature for 30 minutes, concentrated and purified by flash chromatography (15% ethyl acetate in hexanes) to yield a white solid (43.6 mg, 84% yield). ^1H NMR (400 MHz, CDCl_3): δ 7.82-7.77 (m, 3H), 7.62 (bd, $J = 1.6 \text{ Hz}$, 1H), 7.50-7.44 (m, 2H), 7.25 (dd, $J = 2.0, 8.4 \text{ Hz}$, 1H), 5.15-5.13 (m, 1H), 5.11-5.08 (m, 1H), 3.55 (dd, $J = 7.6, 11.2 \text{ Hz}$, 1H), 3.42 (bd, $J = 18.0 \text{ Hz}$, 1H), 3.25-3.16 (m, 1H), 2.90-2.82 (m, 1H), 2.72-2.66 (m, 1H), 2.65-2.59 (m, 1H) 2.54-2.35 (m, 2H), 2.17-2.09 (m, 1H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 206.9, 145.7, 134.0, 133.5, 133.4, 128.6, 128.3, 127.9, 127.6, 126.6, 126.5, 125.8, 108.6, 100.2, 56.8, 41.9, 39.2, 37.4, 31.2, 30.4. IR (thin film): 3058, 2918, 2849, 1716, 1535, 1435, 1355 cm^{-1} . $[\alpha]_{24}^D = -68.2$ (c 1.11, CHCl_3). Chiral HPLC: Chiralcel OD, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 254 \text{ nm}$, $t_{R, \text{minor}} = 16.9 \text{ min}$, $t_{R, \text{major}} = 17.9 \text{ min}$. HRMS: calcd for $(M+H^+)$ $C_{20}H_{22}NO_3$ 324.1599; found 324.1585. MP 119-121 °C.



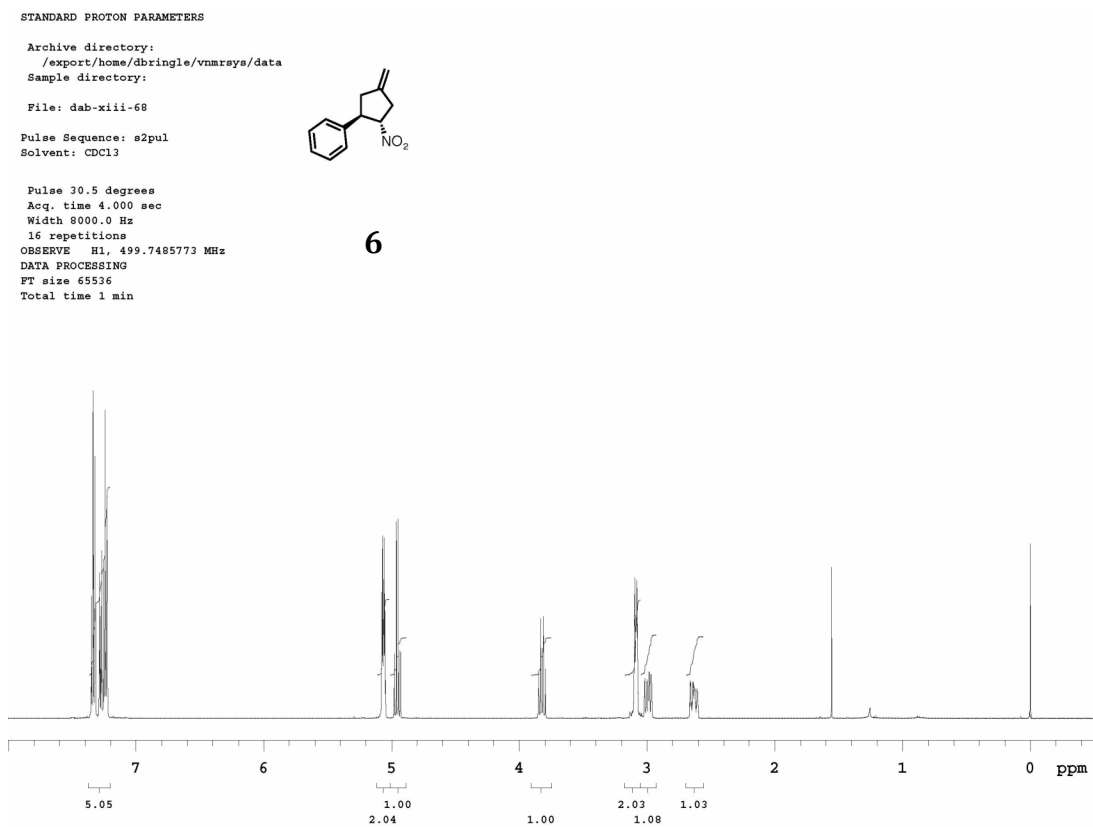
2-((1R,2R)-2-chloro-4-methylene-2-nitrocyclopentyl)naphthalene (27): To a solution of nitrocyclopentane (8.0 mg, 0.032 mmol) in DCM (0.5 ml) at 0 °C was added DBU (5.7 μL , 0.038 mmol) and TMSCl (8.1 μL , 0.064 mmol) and the reaction was stirred

for 30 minutes. *m*-Chloroperoxybenzoic acid (7.7 mg, 0.045 mmol) in DCM (0.1 ml) was added dropwise over 1 minute, the solution was stirred at 0 °C for 60 minutes, then quenched with sat. Na₂SO₃ (2 ml). The layers were separated, and the organics were washed with 1 M HCl (2 ml), sat. NaHCO₃ (2 ml), water (2 ml) and dried over MgSO₄. The solution was concentrated and purified by flash chromatography (3% ethyl acetate in hexanes) to yield the product as a white solid (5.9 mg, 64% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.75-7.71 (m, 3H), 7.63 (d, *J* = 1.5 Hz, 1H), 7.43-7.38 (m, 2H), 7.29 (dd, *J* = 1.9, 8.6 Hz, 1H), 5.15 (quintet, *J* = 2.2 Hz, 1H), 5.11 (quintet, *J* = 2.2 Hz, 1H), 4.00 (t, *J* = 8.7 Hz, 1H), 3.85-3.78 (m, 1H), 3.25-3.16 (m, 2H), 3.08-2.99 (m, 1H). ¹³C NMR (100 MHz, CDCl₃): δ 143.4, 133.6, 133.5, 132.5, 128.8, 128.5, 127.9, 127.9, 126.8, 126.7, 125.8, 110.1, 110.0, 58.9, 48.2, 37.2. IR (thin film): 3058, 2927, 1665, 1556, 1433, 1348, 1274 cm⁻¹. [α]₂₄^D = -34.8 (c 0.60, CHCl₃). Chiral HPLC: Chiralpak AD, 1.0 mL/min, 1% *i*-PrOH in heptane, λ = 254 nm, t_{R, major} = 9.0 min, t_{R, minor} = 11.5 min. HRMS: calcd for (M⁺) C₁₆H₁₄ClNO₂ 287.0713; found 287.0699. MP 104-105 °C.



(*R*)-3-methyl-5-(naphthalen-2-yl)cyclopent-2-enone (28): To a solution of nitrocyclopentane (14.9 mg, 0.06 mmol) in THF (0.6 ml) at 0 °C was added KO*t*-Bu (66 μl, 1 M in THF, 0.066 mmol) and the yellow solution was stirred for 15 minutes at 0 °C. It was then cooled to approximately -20 °C and dimethyldioxirane (0.7 ml, approx. 1 M in acetone, 0.07 mmol) was added. The mixture was stirred for 5 minutes and then added to a well-stirred solution of 0.25 M, pH 7.0 phosphate buffer (5 ml) and extracted with DCM (3 x 3 ml). The combined organics were dried over MgSO₄, concentrated and purified by flash chromatography (20% ethyl acetate in hexanes) to yield the product as a pale yellow solid (11.3 mg, 86% yield). ¹H NMR (400 MHz, CDCl₃): δ 7.81-7.76 (m, 3H), 7.63 (bs, 1H), 7.48-7.41 (m, 2H), 7.21 (dd, *J* = 1.8, 8.5 Hz, 1H), 6.09-6.06 (m, 1H),

3.79 (dd, $J = 2.8, 7.2$ Hz, 1H), 3.18 (ddq, $J = 0.8, 0.8, 0.8, 7.2, 18.8$ Hz, 1H), 2.80-2.74 (m, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3): δ 209.4, 178.4, 137.5, 133.8, 132.8, 130.2, 129.0, 128.0, 127.9, 127.0, 126.5, 126.0, 125.7, 53.1, 43.1, 19.8. IR (thin film): 2923, 2852, 1696, 1622 cm^{-1} . $[\alpha]_{24}^D = -107.6$ (c 1.34, CHCl_3). Chiral HPLC: Chiralpak AD-H, 0.8 mL/min, 10% *i*-PrOH in heptane, $\lambda = 254$ nm, $t_{R, \text{major}} = 14.8$ min, $t_{R, \text{minor}} = 17.1$ min. HRMS: calcd for $(\text{M}+\text{H}^+)$ $\text{C}_{16}\text{H}_{15}\text{O}$ 223.1123; found 223.1113. MP 71-72 $^\circ\text{C}$.

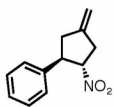


C13par

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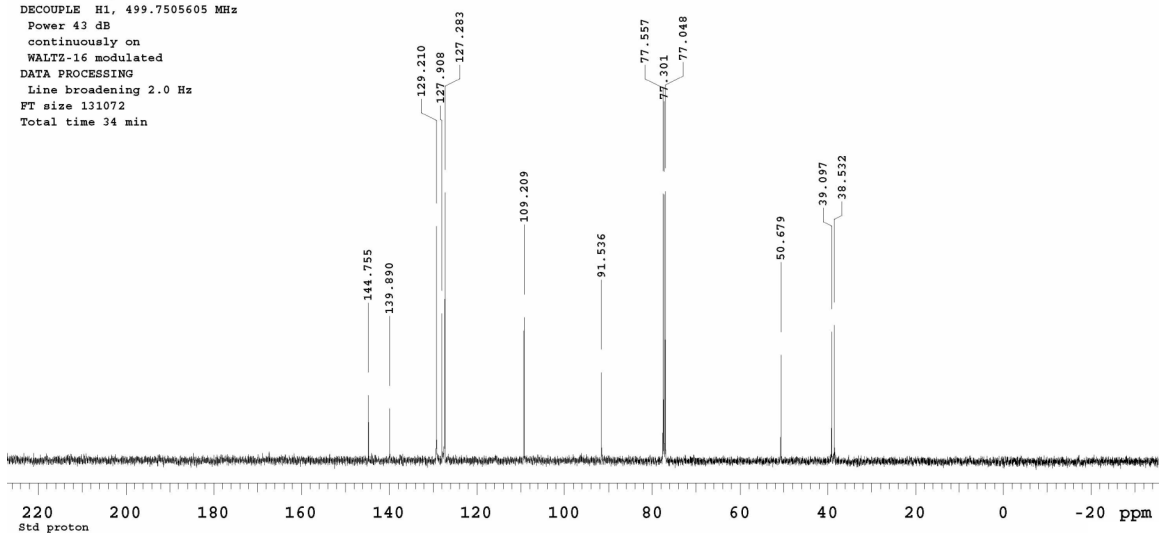
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Pulse Sequence: s2pul
Solvent: CDCl3
User: 1-15-87



6

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Acq. time 1.500 sec
Width 33003.3 Hz
80 repetitions
OBSERVE C13, 125.6618455 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min

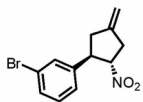


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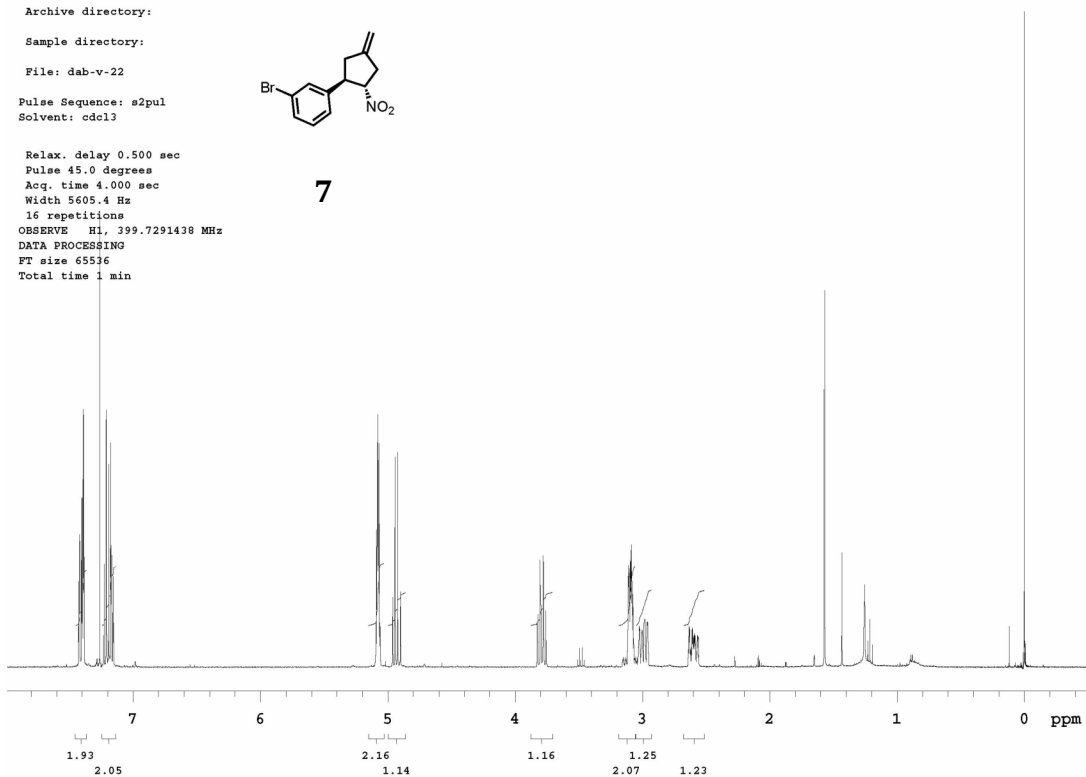
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Solvent: cdcl3



7

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16 repetitions
OBSERVE H1, 399.7291438 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



Std proton

Archive directory:

Sample directory:

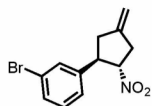
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Pulse Sequence: s2pul

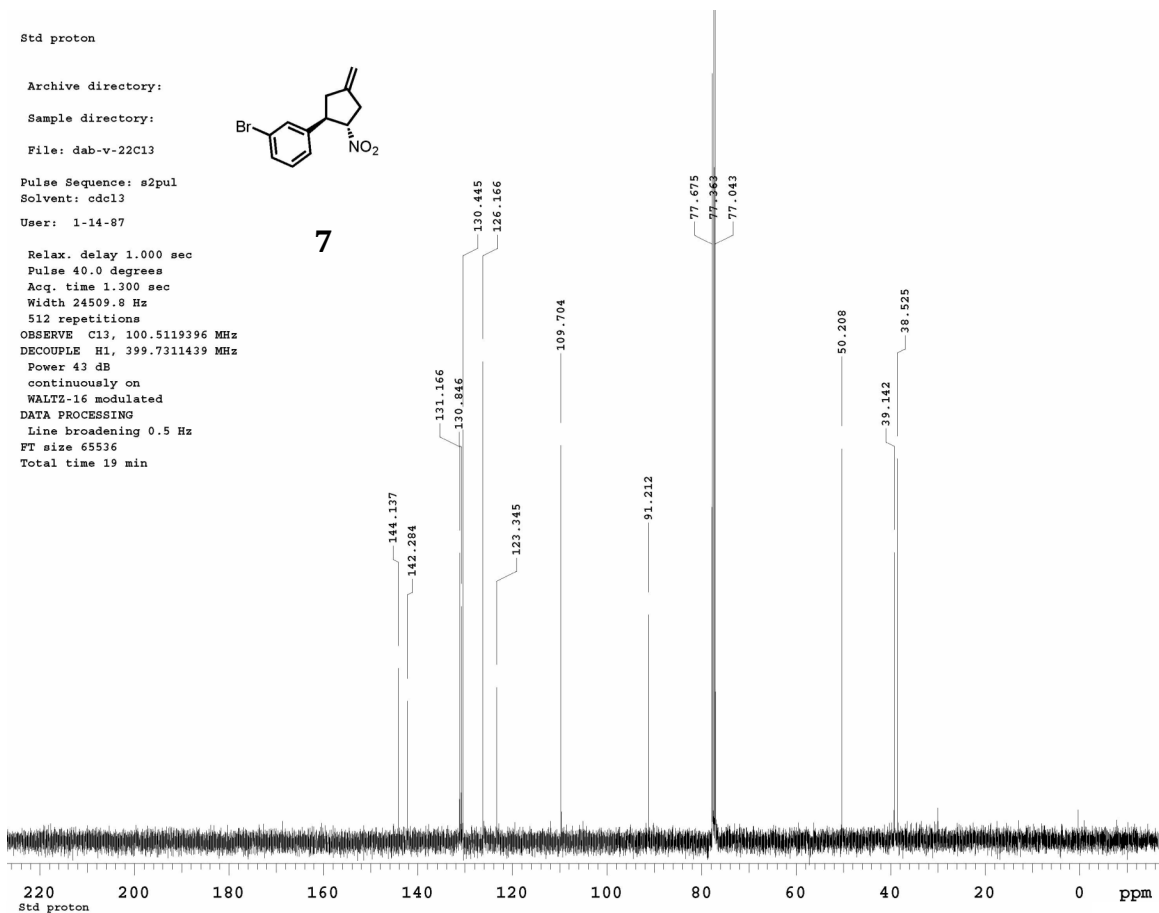
Solvent: cdcl3

User: 1-14-87

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DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



7



Archive directory:

Sample directory:

File: dab-xv-82

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 23.0 C / 296.1 K

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5605.4 Hz

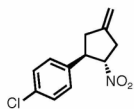
4 repetitions

OBSERVE H1, 399.7345515 MHz

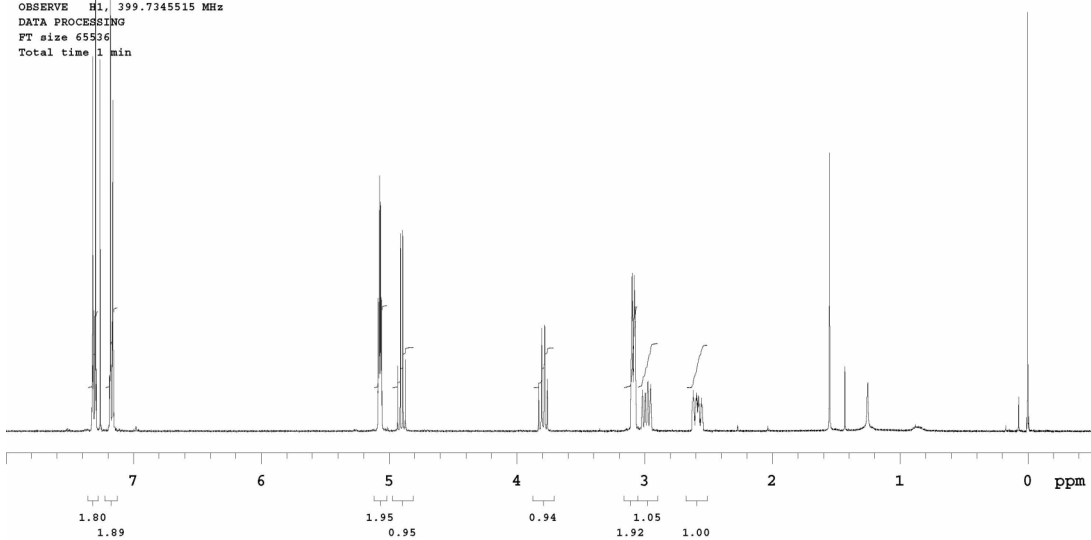
DATA PROCESSING

FT size 65536

Total time 1 min



8



Std proton

Archive directory:

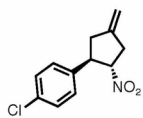
Sample directory:

File: dab-xv-82C13

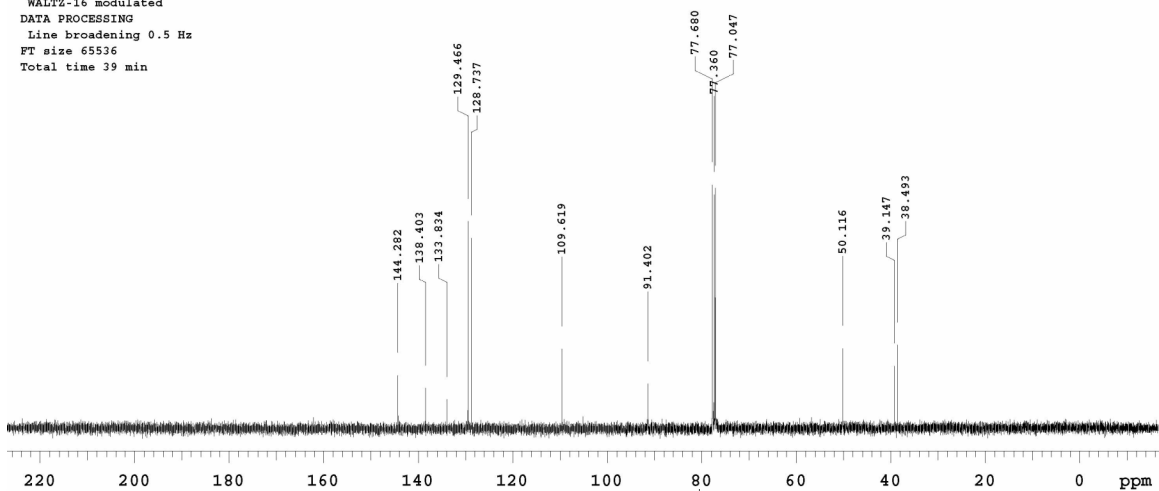
Pulse Sequence: s2pul
Solvent: cdcl3

Temp. 23.0 C / 296.1 K
User: 1-14-87

Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
176 repetitions
OBSERVE C13, 100.5132975 MHz
DECOUPLE H1, 399.7365548 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 39 min



8



Std proton

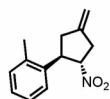
Archive directory:

Sample directory:

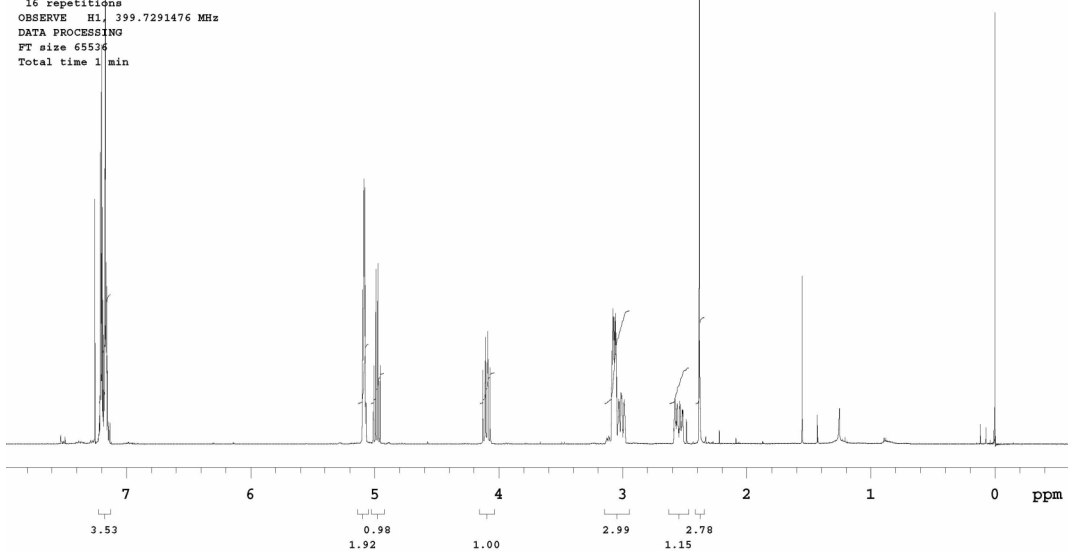
File: pss-i-15-1

Pulse Sequence: s2pul
Solvent: cdcl3

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291476 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



9



Std proton

Archive directory:

Sample directory:

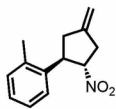
File: pss-i-15-1c13

Pulse Sequence: s2pul

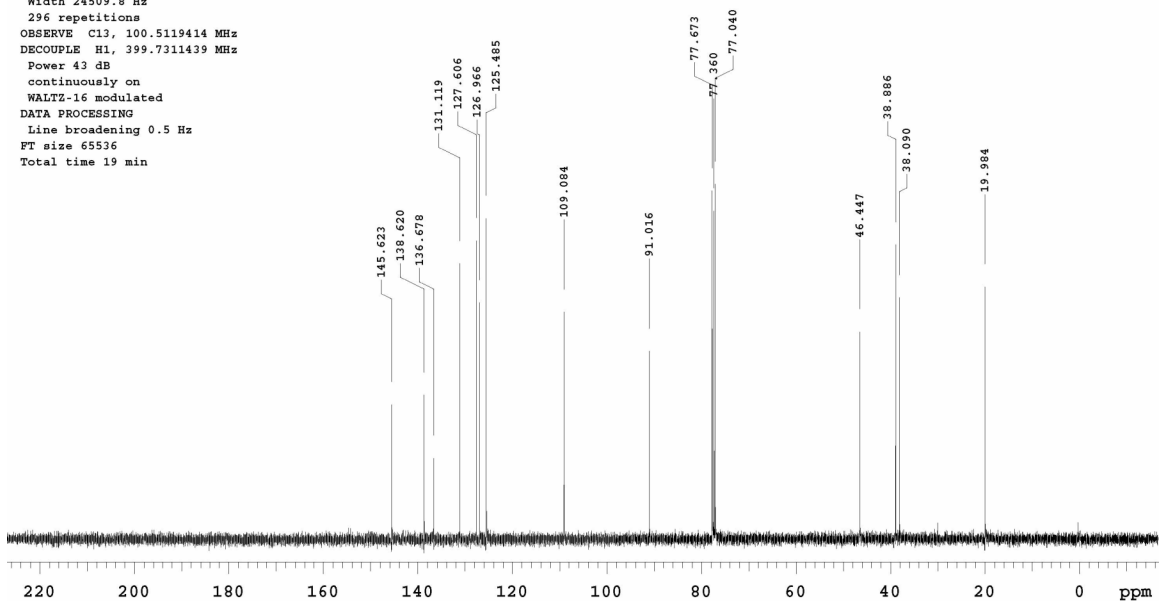
Solvent: cdcl3

User: 1-14-87

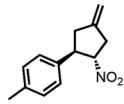
Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
296 repetitions
OBSERVE C13, 100.5119414 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



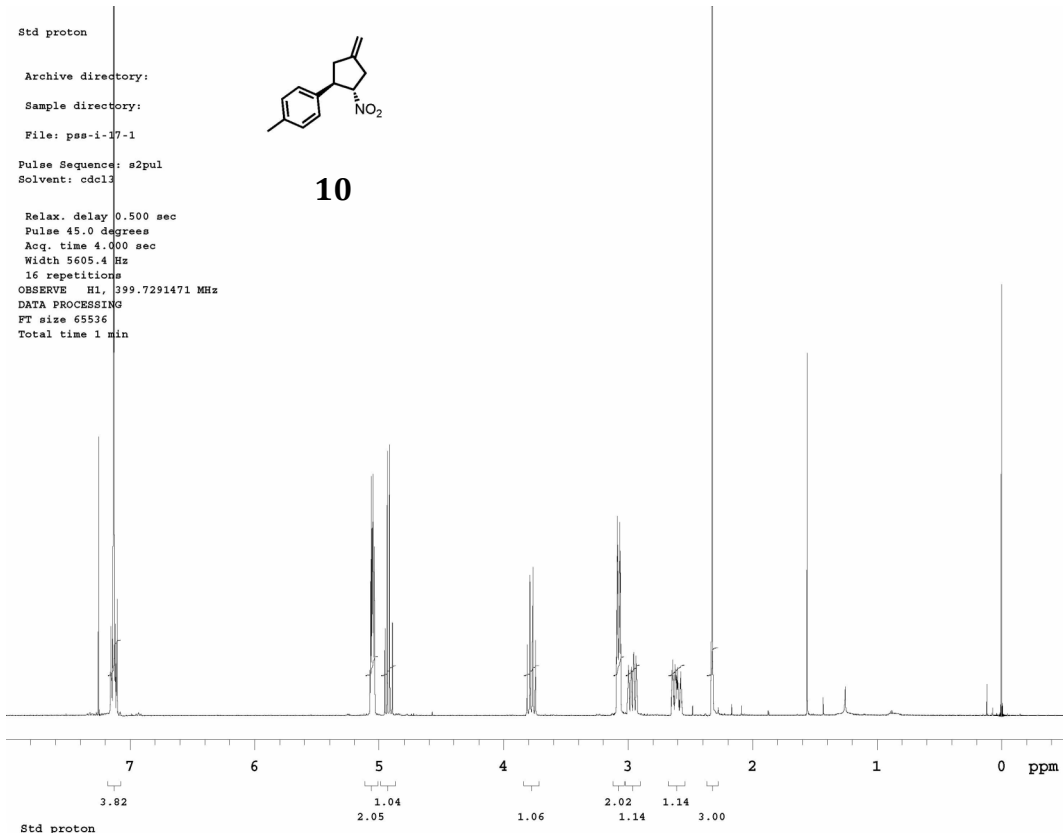
9



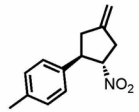
Std proton
 Archive directory:
 Sample directory:
 File: pss-i-17-1
 Pulse Sequence: s2pul
 Solvent: cdcl3
 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 5605.4 Hz
 16 repetitions
 OBSERVE H1, 399.7291471 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min



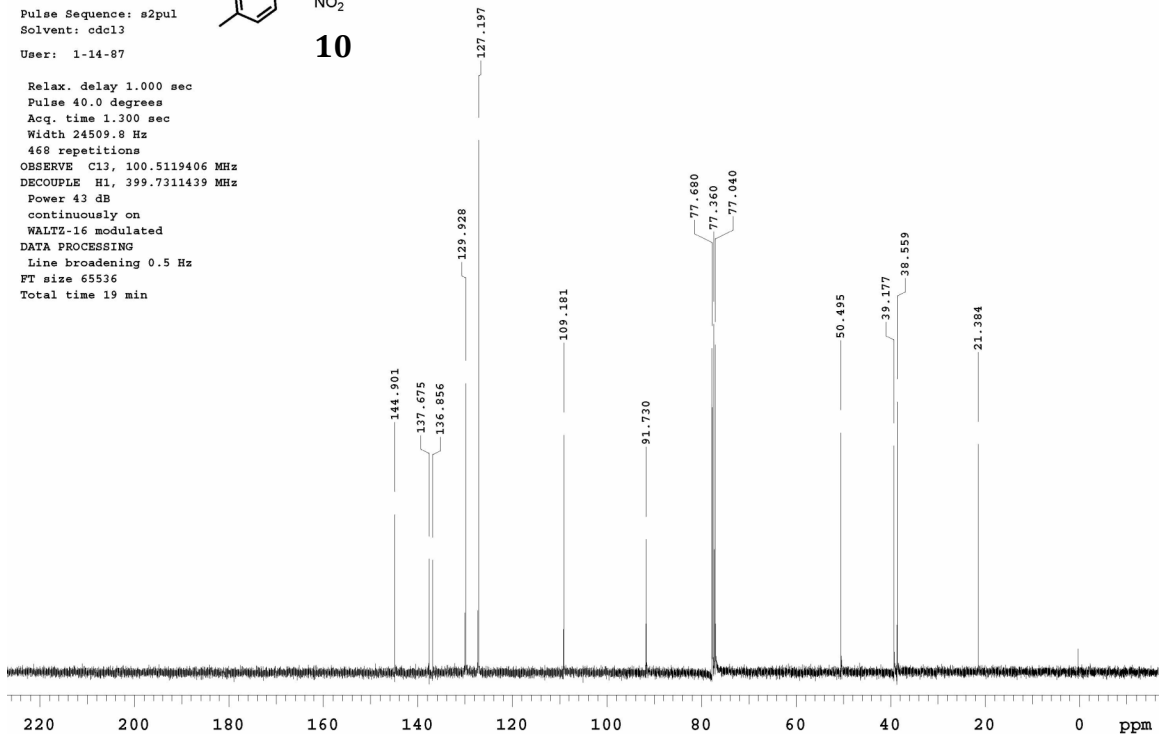
10



Archive directory:
 Sample directory:
 File: pss-i-17-1c13
 Pulse Sequence: s2pul
 Solvent: cdcl3
 User: 1-14-87
 Relax. delay 1.000 sec
 Pulse 40.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 468 repetitions
 OBSERVE C13, 100.5119406 MHz
 DECOUPLE H1, 399.7311439 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 19 min



10



Std proton

Archive directory:

Sample directory:

File: pss-i-54-1

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 20.0 C / 293.1 K

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5605.4 Hz

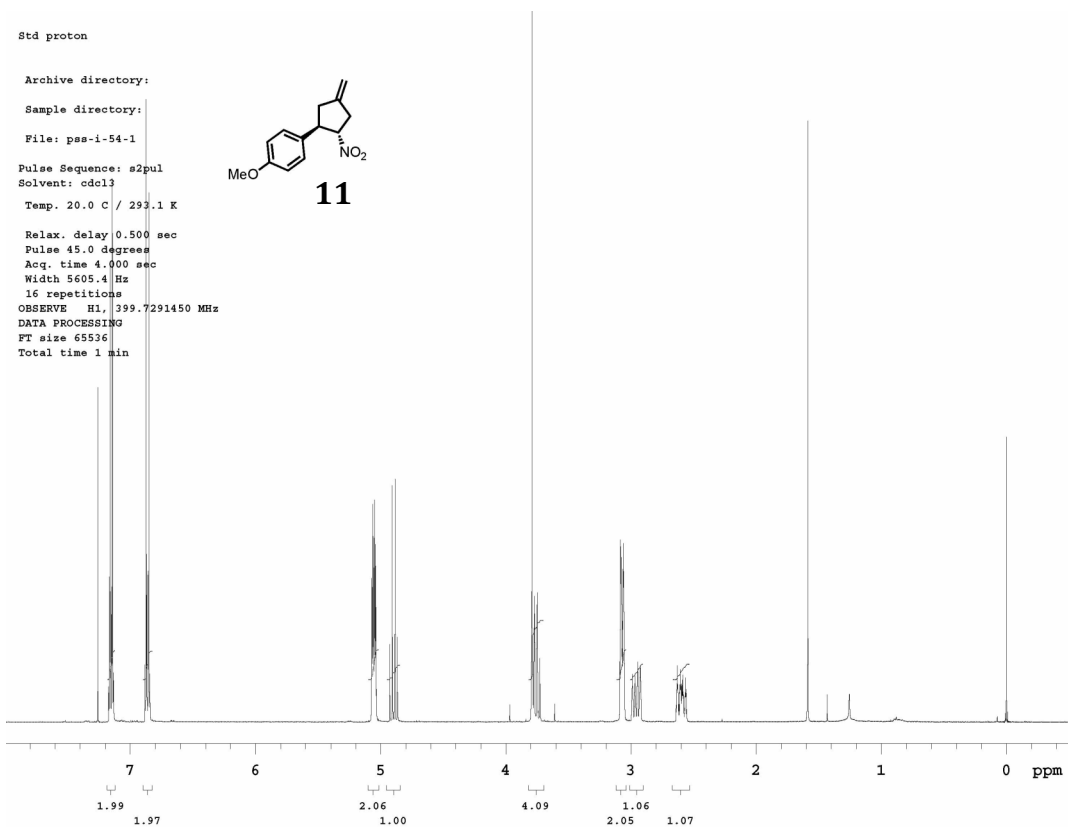
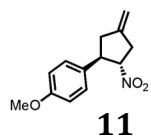
16 repetitions

OBSERVE H1, 399.7291450 MHz

DATA PROCESSING

FT size 65536

Total time 1 min



Std proton

Archive directory:

Sample directory:

File: pss-i-54-1c13

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 20.0 C / 293.1 K

User: 1-14-87

Relax. delay 1.000 sec

Pulse 40.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

404 repetitions

OBSERVE C13, 100.5119406 MHz

DECOUPLE H1, 399.7311439 MHz

Power 43 dB

continuously on

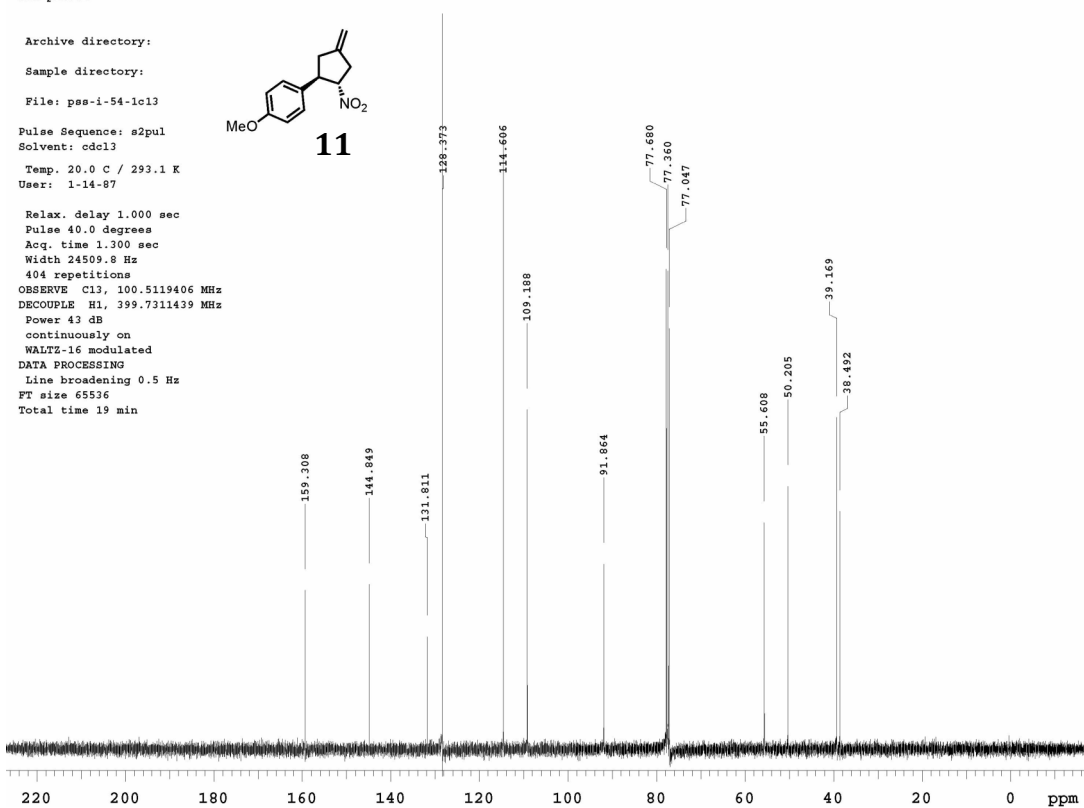
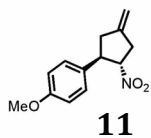
WALTZ-16 modulated

DATA PROCESSING

Line broadening 0.5 Hz

FT size 65536

Total time 19 min



Std proton

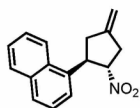
Archive directory:

Sample directory:

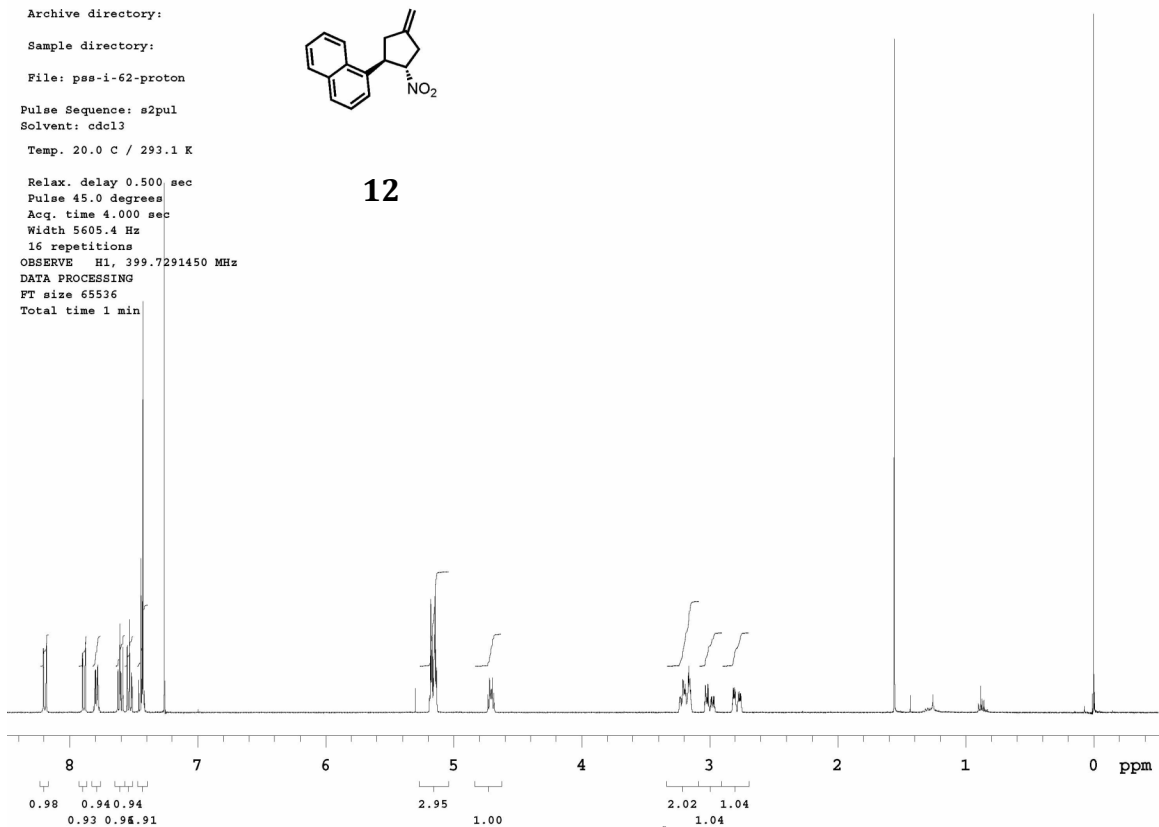
File: pss-i-62-proton

Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291450 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



12



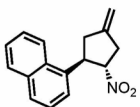
C13par

Archive directory:
/export/home/dbringle/vnmrsys/data
Sample directory:

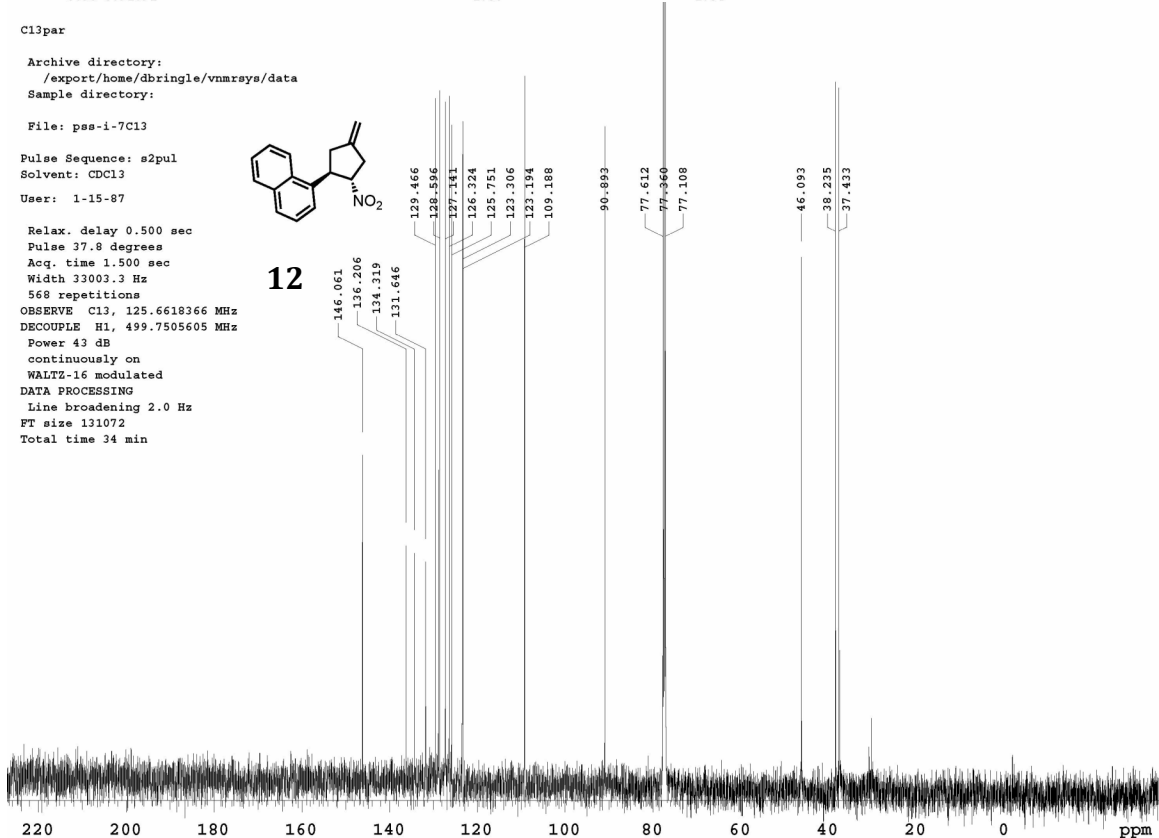
File: pss-i-7C13

Pulse Sequence: s2pul
Solvent: CDCl3
User: 1-15-87

Relax. delay 0.500 sec
Pulse 37.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
568 repetitions
OBSERVE C13, 125.6618366 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min

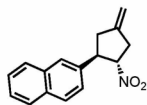


12



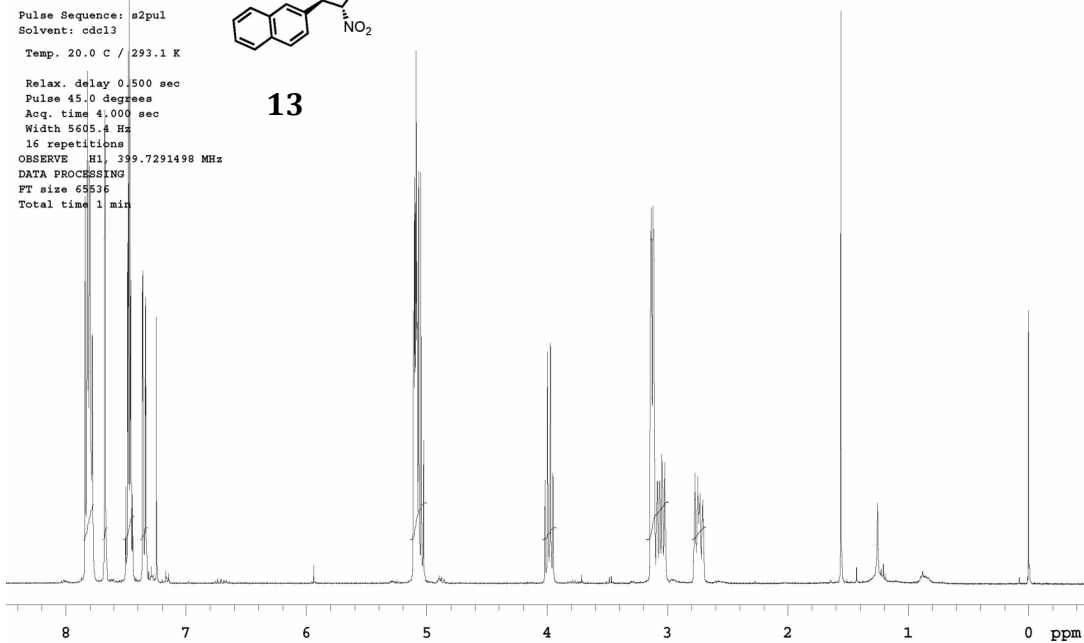
Std proton

Archive directory:
Sample directory:
File: pss-i-40-1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K



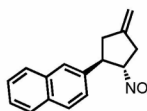
13

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291498 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



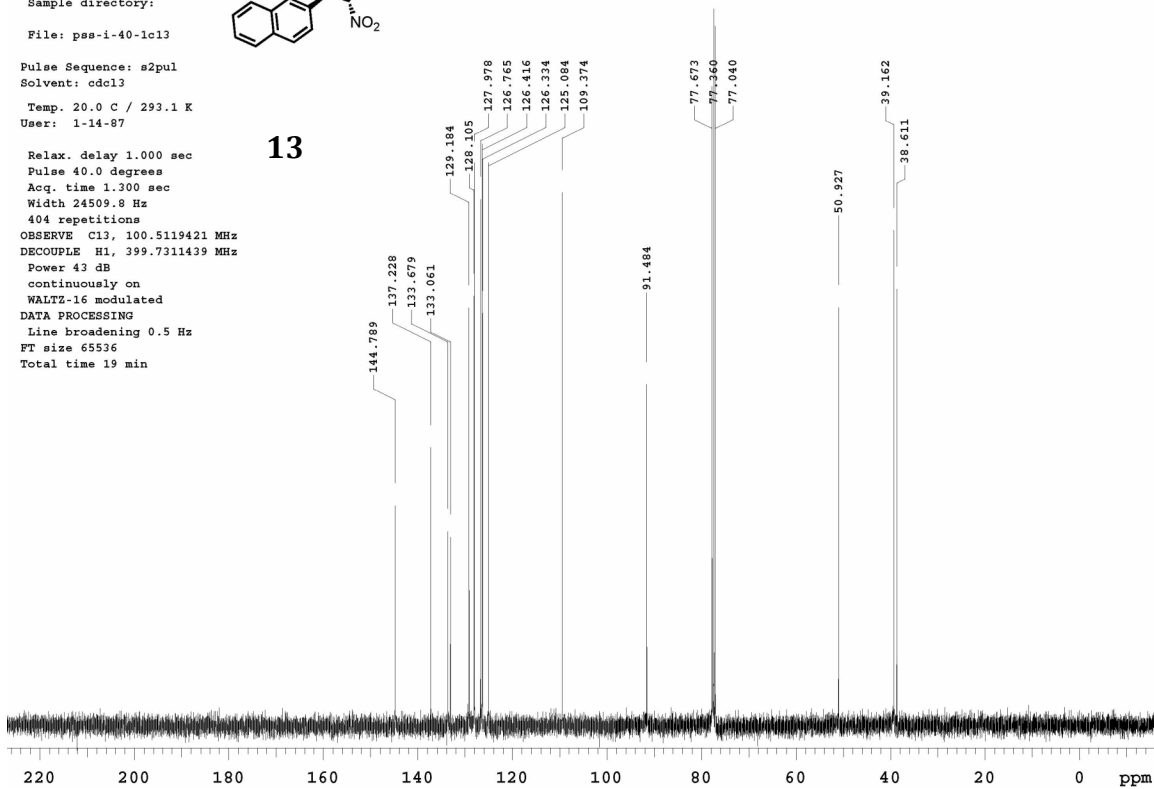
Std proton

Archive directory:
Sample directory:
File: pss-i-40-1c13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
User: 1-14-87



13

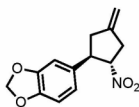
Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
404 repetitions
OBSERVE C13, 100.5119421 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



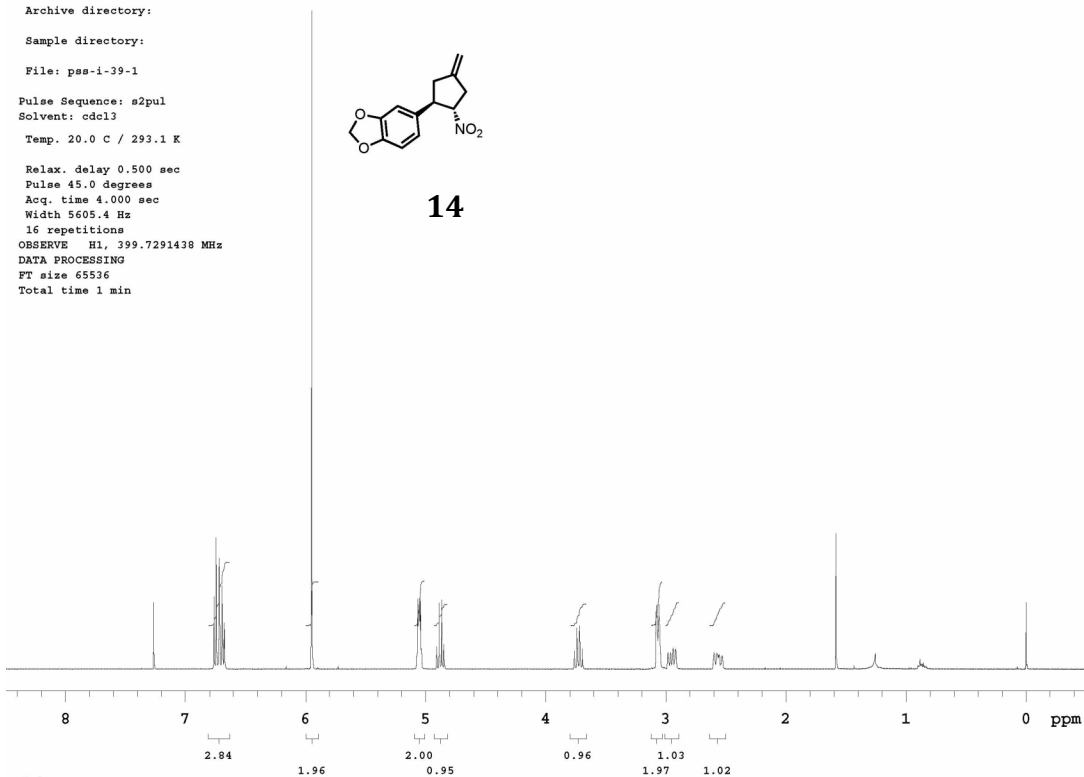
Std proton

Archive directory:
Sample directory:
File: pss-i-39-1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291438 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



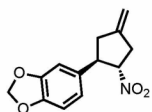
14



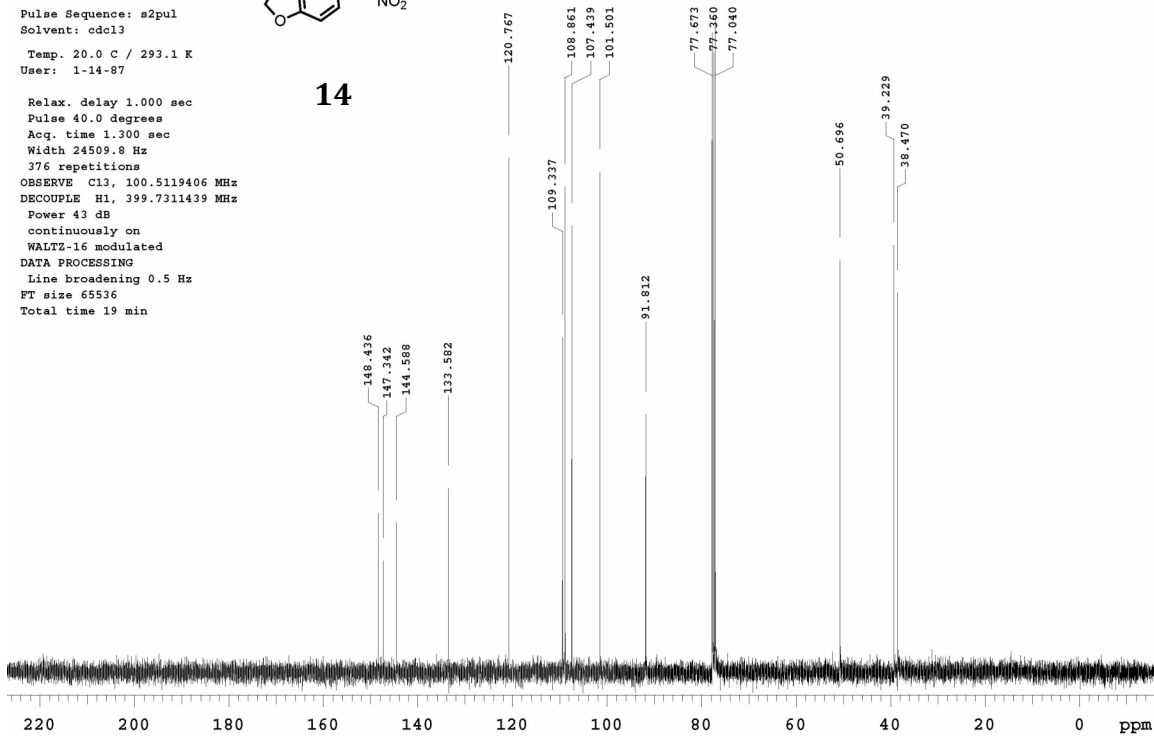
Std proton

Archive directory:
Sample directory:
File: pss-i-39-1c13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
User: 1-14-87

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
376 repetitions
OBSERVE C13, 100.5119406 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



14



Std proton

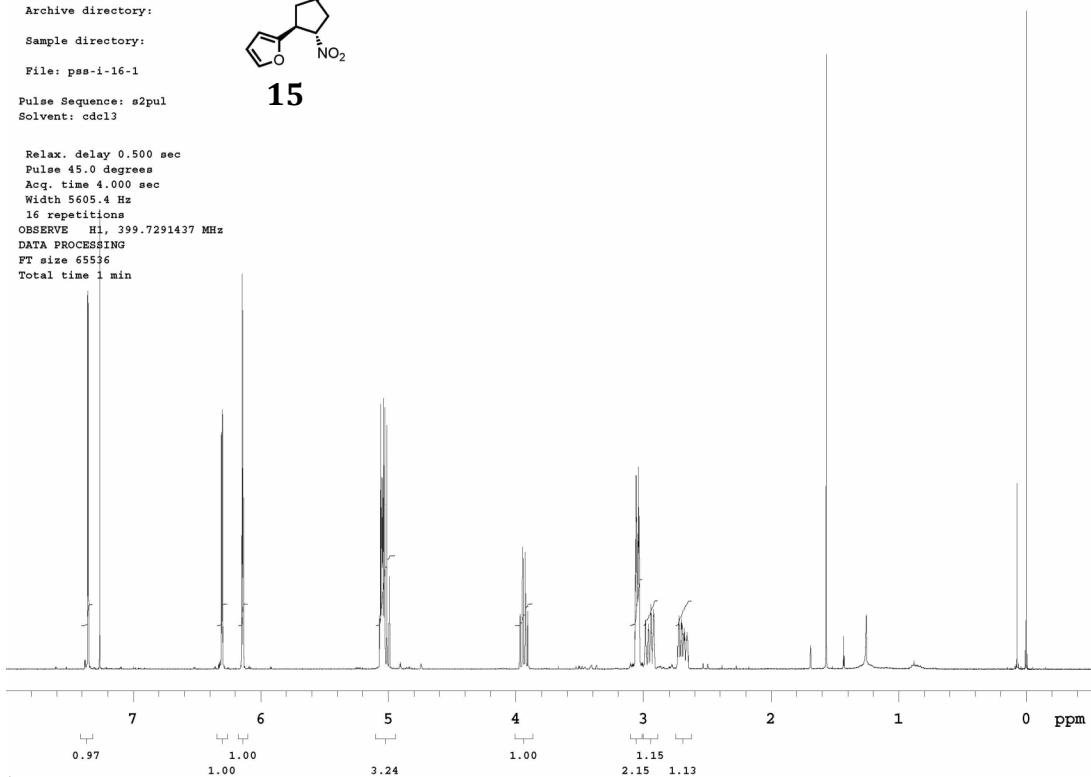
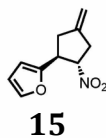
Archive directory:

Sample directory:

File: pss-i-16-1

Pulse Sequence: s2pul
Solvent: cdcl3

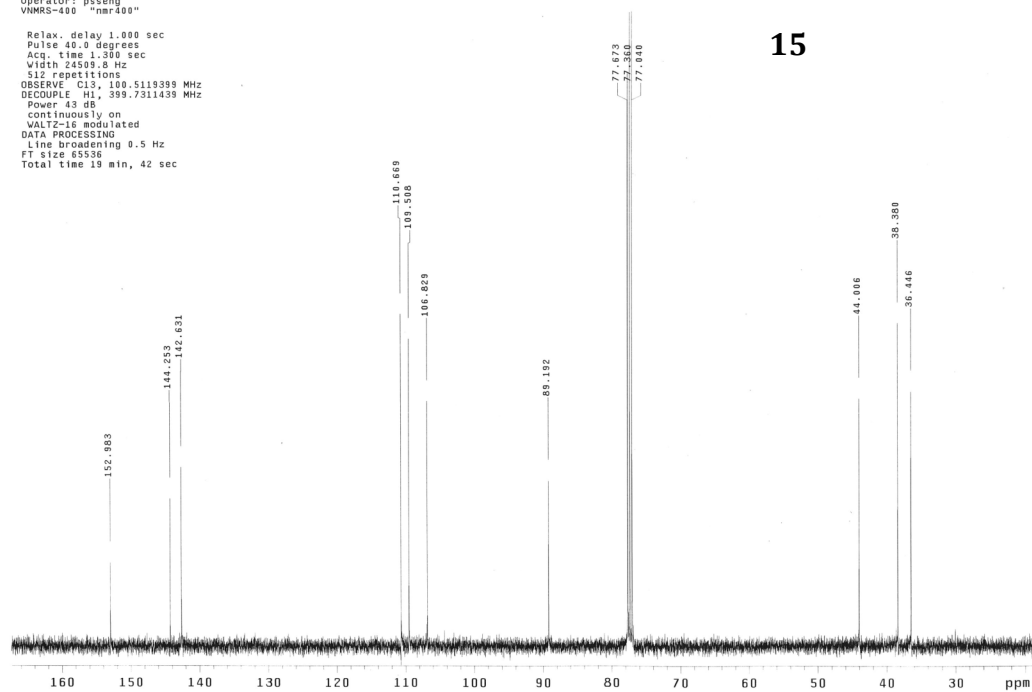
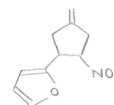
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291437 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



Std proton

File: Carbon PSS-i-16-1cd3
Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
Operator: psseng
VNMRS-400 "nmr400"

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5119399 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min, 42 sec

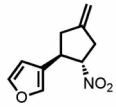


STANDARD 1H OBSERVE

Archive directory:
/export/home/dbringl/vnmrsys/data
Sample directory:

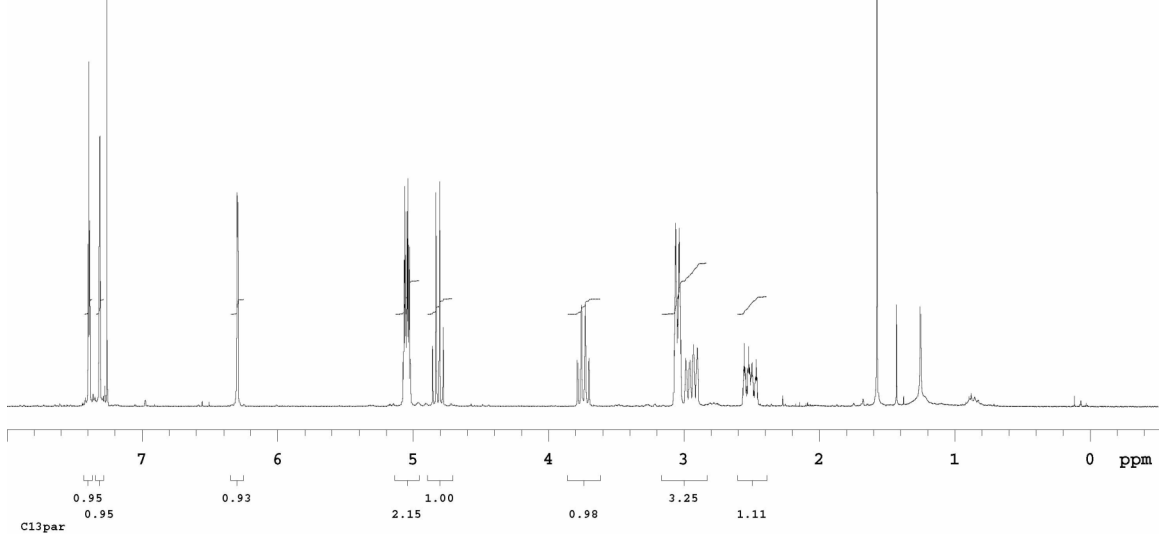
File: pss-i-10

Pulse Sequence: s2pul
Solvent: CDCl3



16

Pulse 44.3 degrees
Acq. time 3.744 sec
Width 4000.0 Hz
16 repetitions
OBSERVE H1, 299.945569 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 32768
Total time 1 min



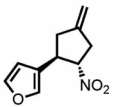
Archive directory:
/export/home/dbringl/vnmrsys/data
Sample directory:

File: pss-i-8Cl3

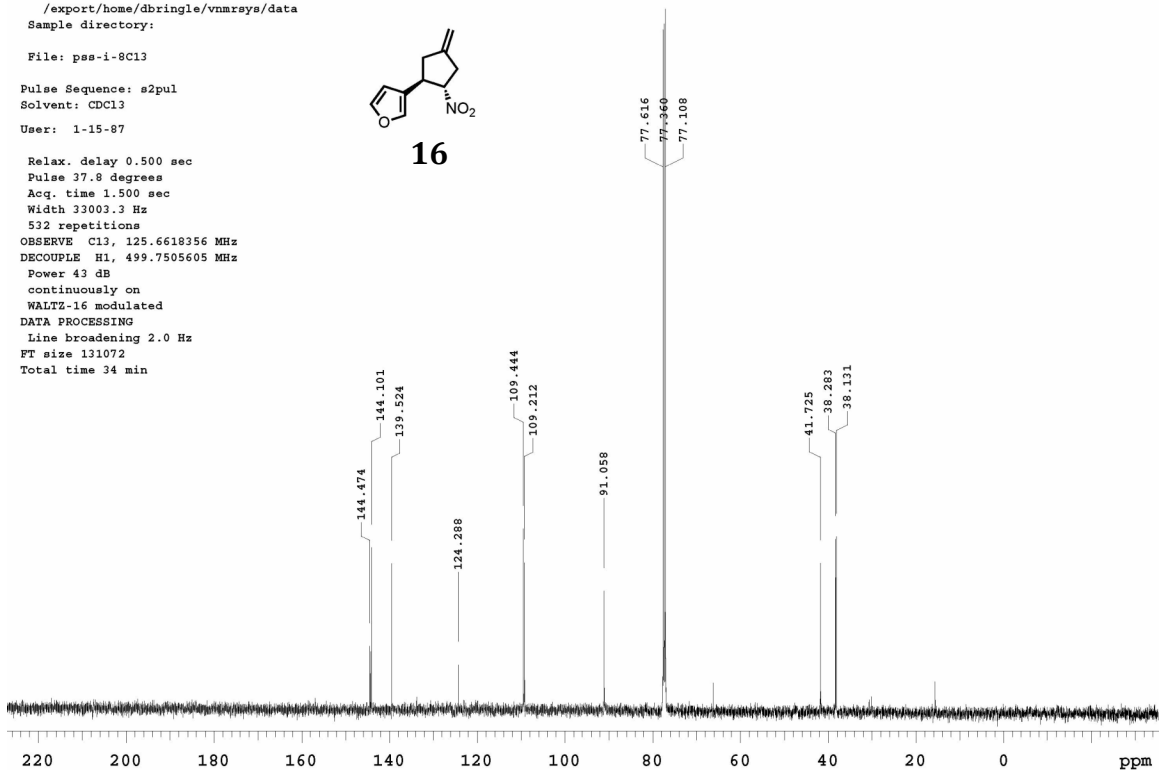
Pulse Sequence: s2pul
Solvent: CDCl3

User: 1-15-87

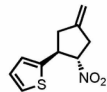
Relax. delay 0.500 sec
Pulse 37.8 degrees
Acq. time 1.500 sec
Width 33003.3 Hz
532 repetitions
OBSERVE C13, 125.6618356 MHz
DECOUPLE H1, 499.7505605 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 34 min



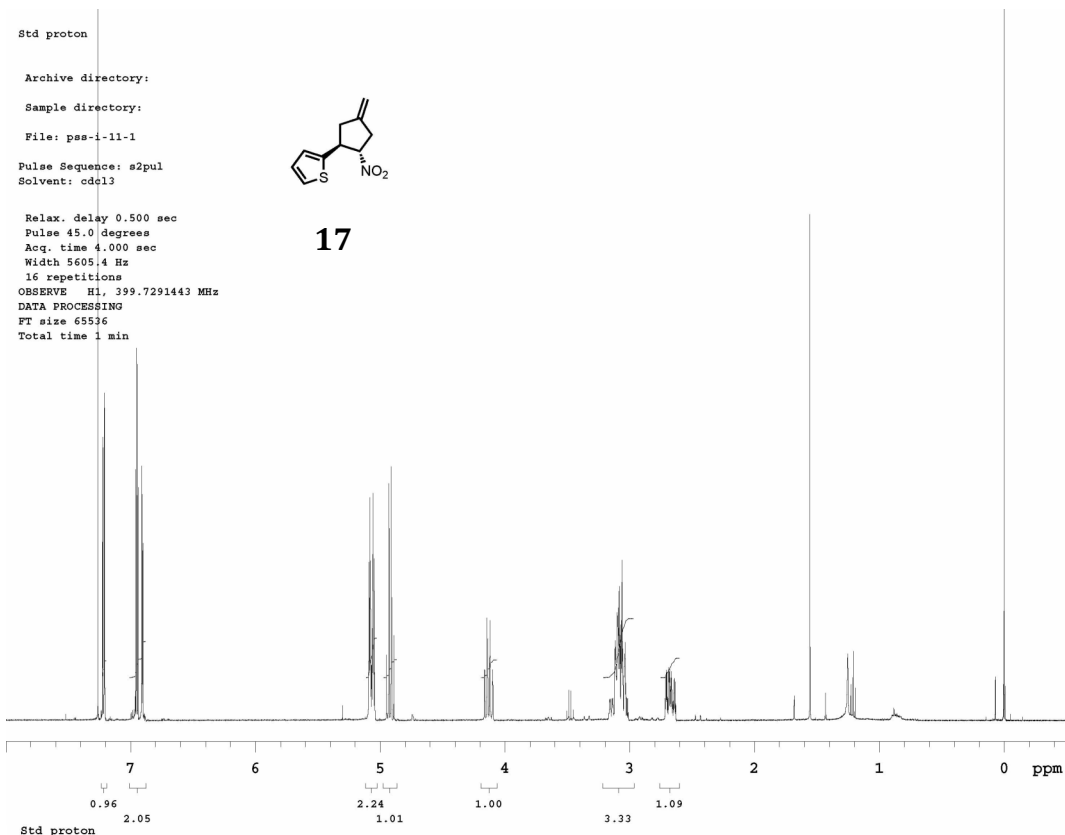
16



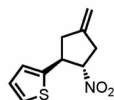
Std proton
 Archive directory:
 Sample directory:
 File: pss-i-11-1
 Pulse Sequence: s2pul
 Solvent: cdcl3
 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 5605.4 Hz
 16 repetitions
 OBSERVE H1, 399.7291443 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min



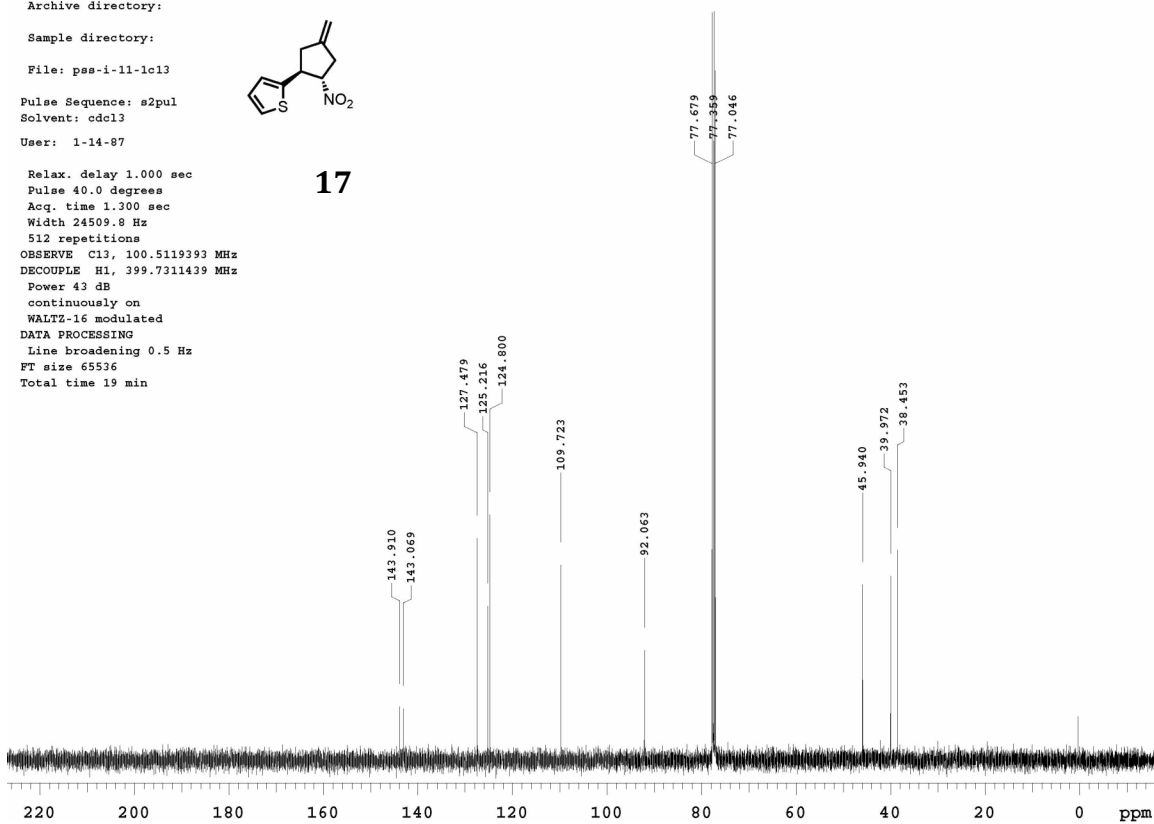
17



Archive directory:
 Sample directory:
 File: pss-i-11-1c13
 Pulse Sequence: s2pul
 Solvent: cdcl3
 User: 1-14-87
 Relax. delay 1.000 sec
 Pulse 40.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 512 repetitions
 OBSERVE C13, 100.5119393 MHz
 DECOUPLE H1, 399.7311439 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 19 min



17



Std proton

Archive directory:

Sample directory:

File: dab-xv-84

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 23.0 C / 296.1 K

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5605.4 Hz

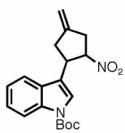
4 repetitions

OBSERVE H1, 399.7345544 MHz

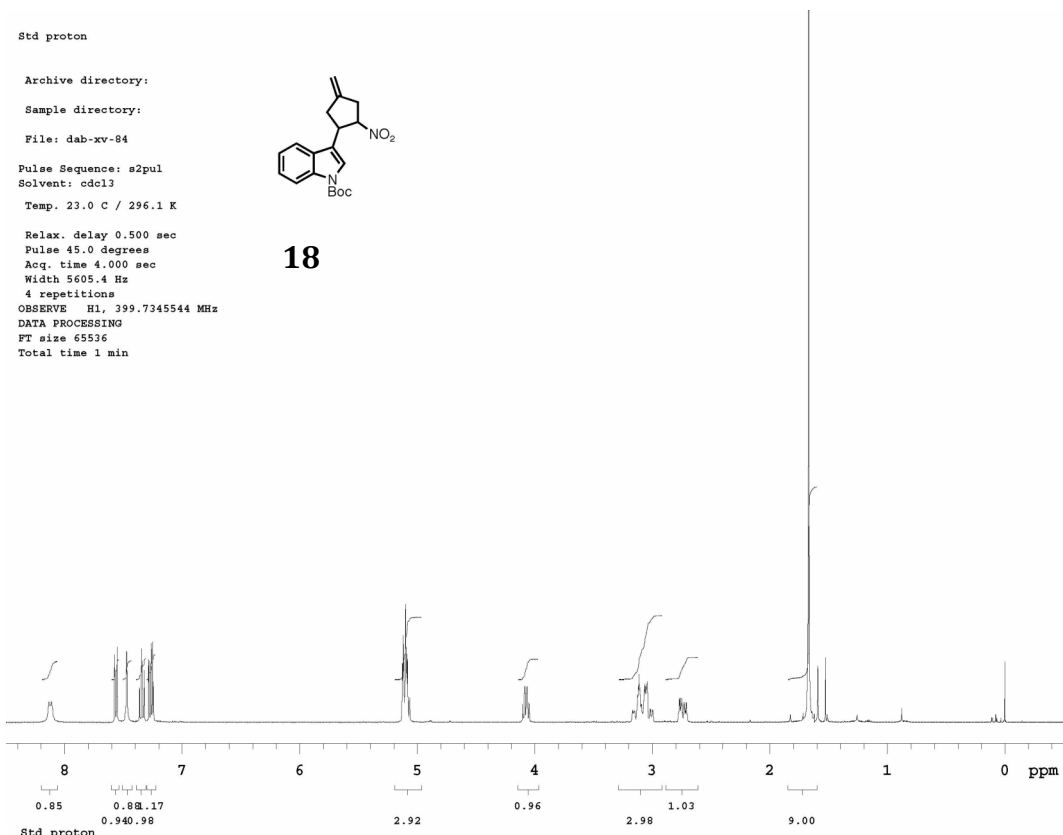
DATA PROCESSING

FT size 65536

Total time 1 min



18



Archive directory:

Sample directory:

File: dab-xv-84Cl3

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 23.0 C / 296.1 K

User: 1-14-87

Relax. delay 2.500 sec

Pulse 39.5 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

524 repetitions

OBSERVE C13, 100.5133005 MHz

DECOUPLE H1, 399.7365548 MHz

Power 43 dB

continuously on

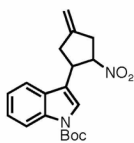
WALTZ-16 modulated

DATA PROCESSING

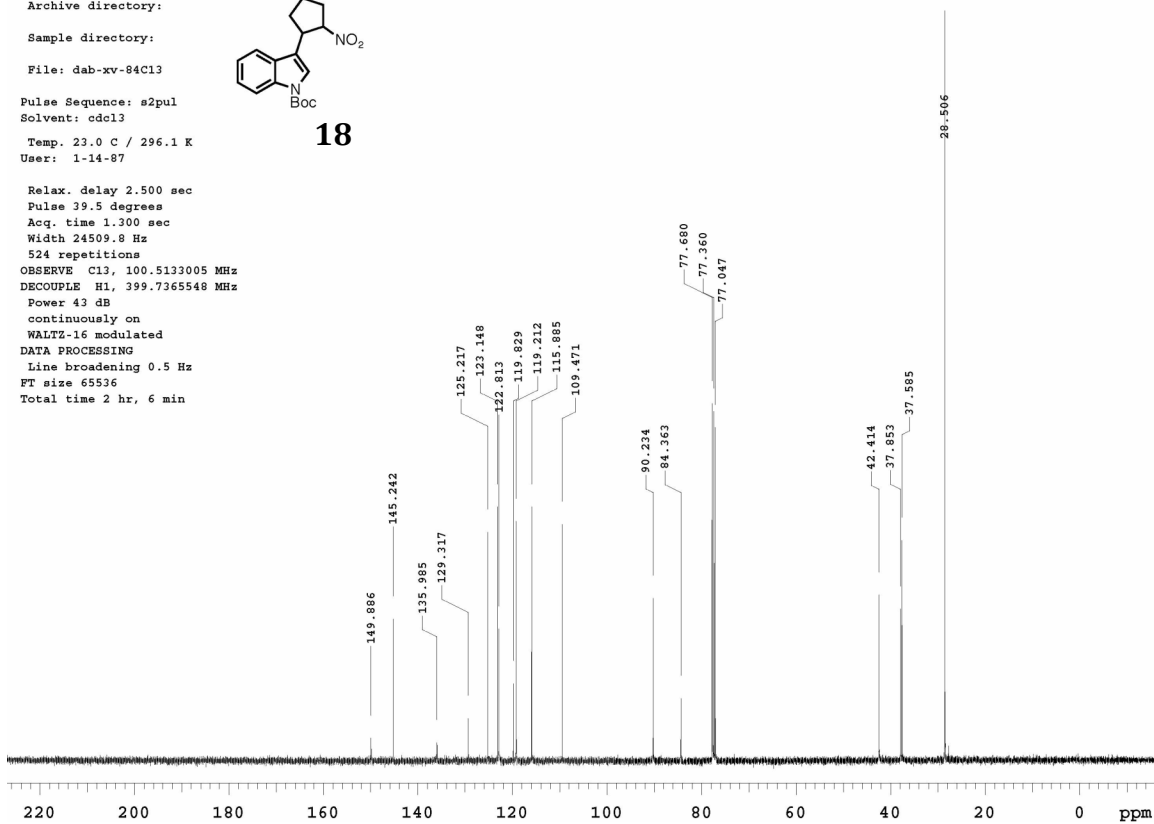
Line broadening 0.5 Hz

FT size 65536

Total time 2 hr, 6 min

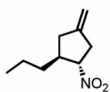


18

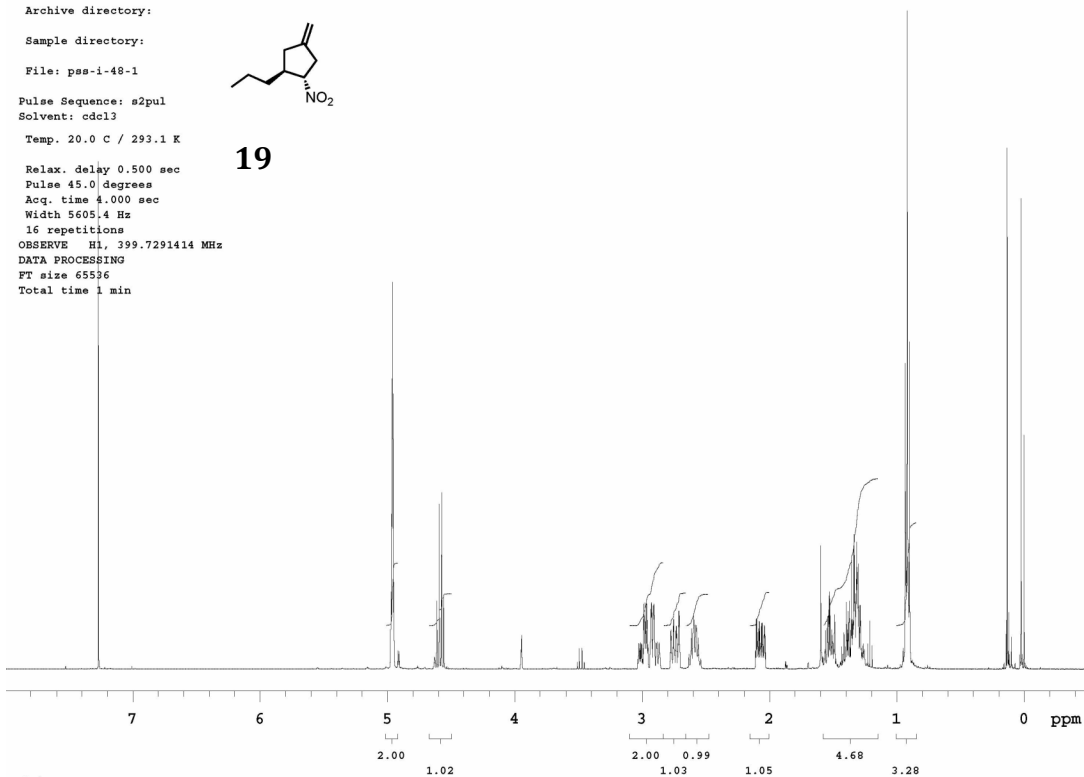


Std proton

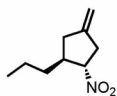
Archive directory:
Sample directory:
File: pss-i-48-1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291414 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



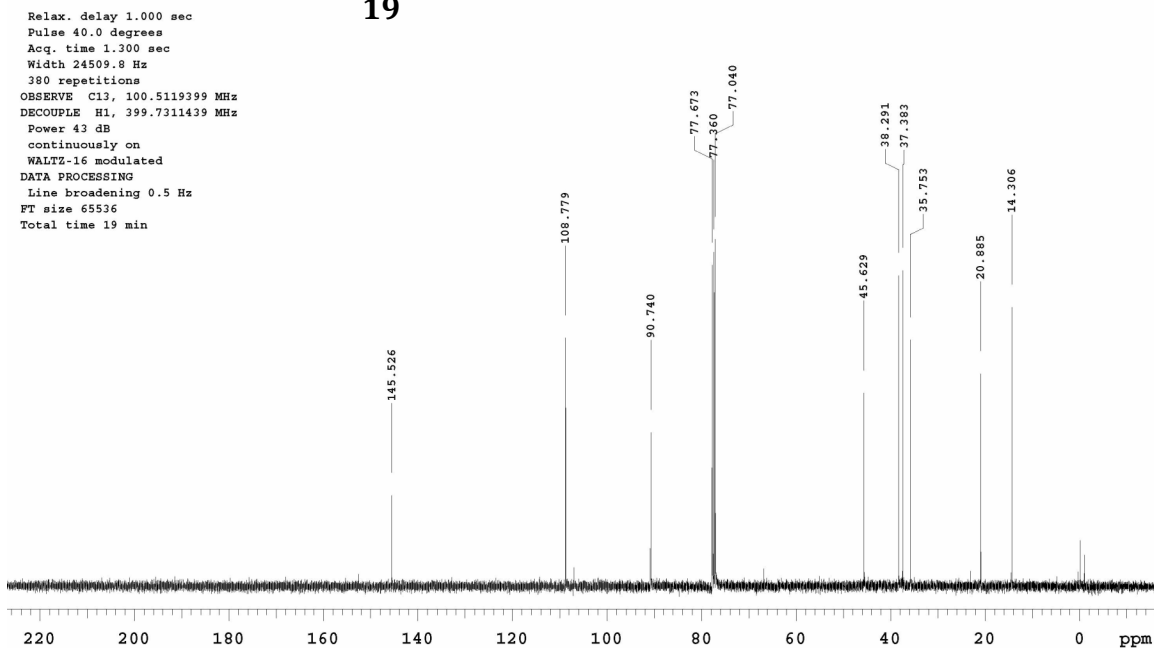
19



Archive directory:
Sample directory:
File: pss-i-48-1c13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
User: 1-14-87

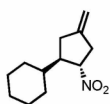


19



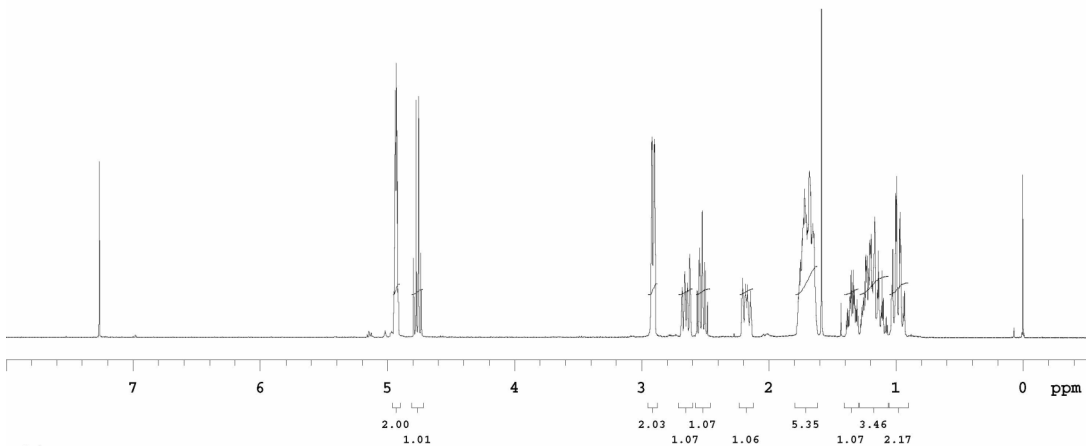
Std proton

Archive directory:
Sample directory:
File: pss-i-46-1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K



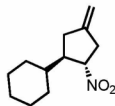
20

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291421 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



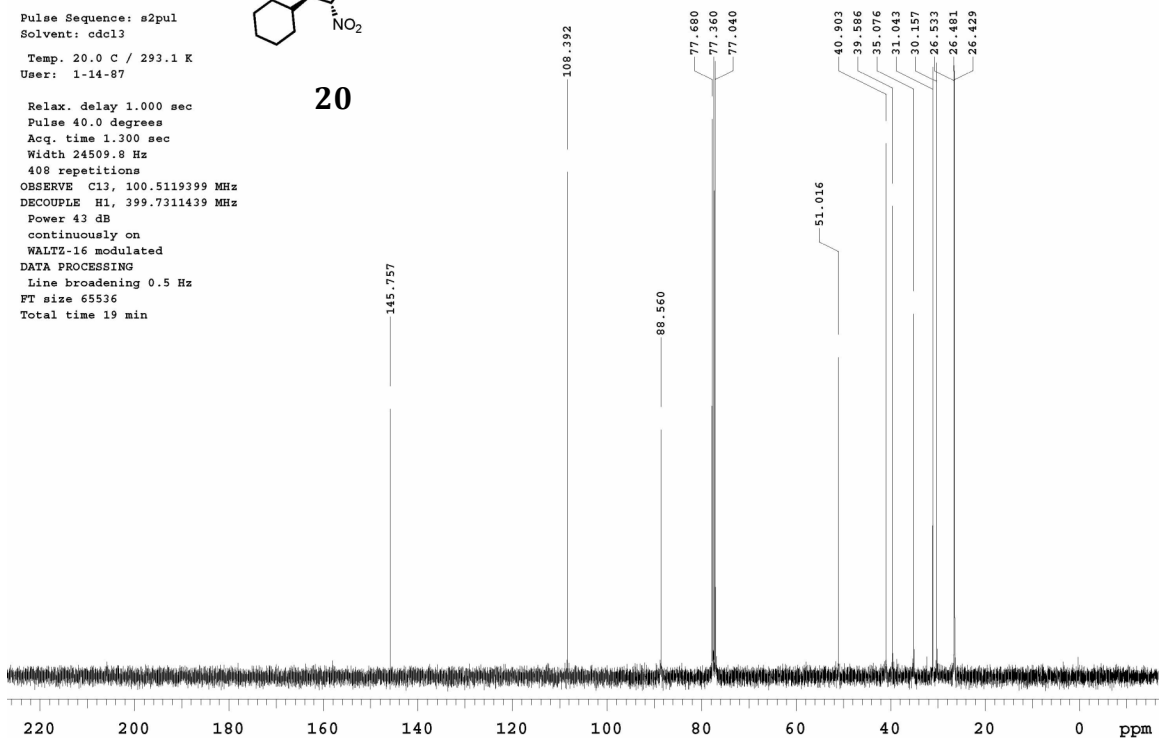
Std proton

Archive directory:
Sample directory:
File: pss-i-46-1c13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
User: 1-14-87



20

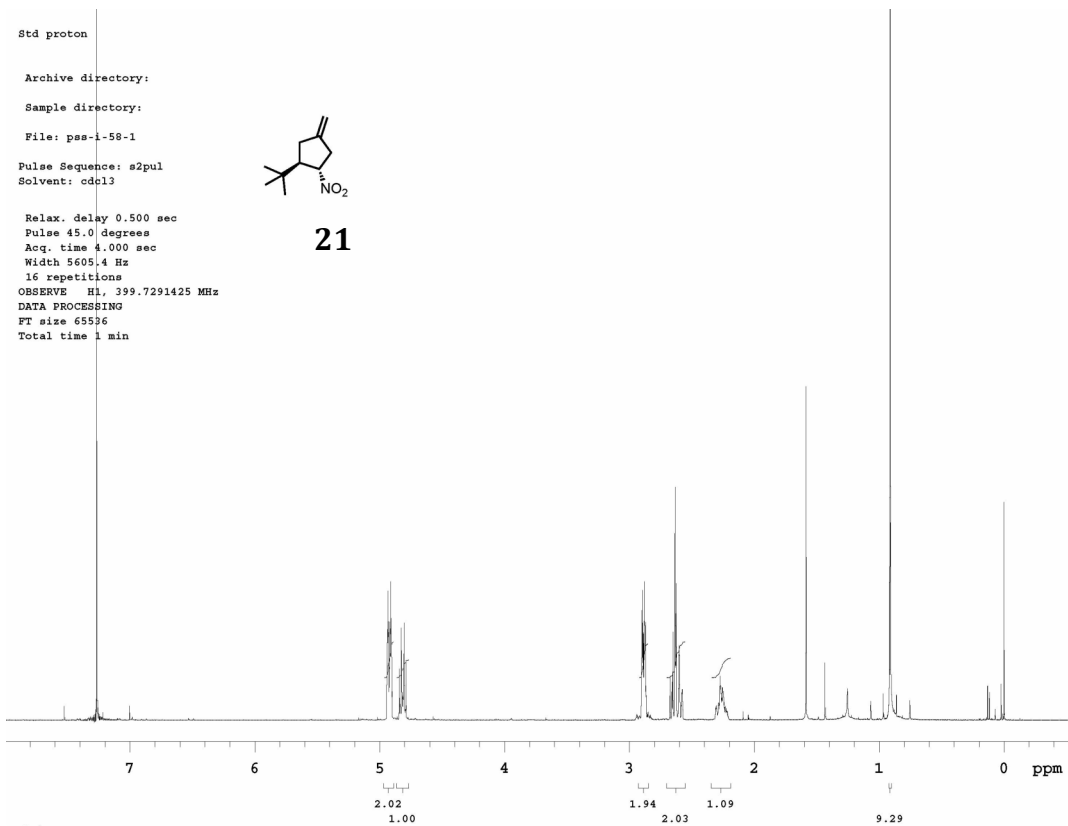
Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
408 repetitions
OBSERVE C13, 100.5119399 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



Std proton
 Archive directory:
 Sample directory:
 File: pss-i-58-1
 Pulse Sequence: s2pul
 Solvent: cdcl3
 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 4.000 sec
 Width 5605.4 Hz
 16 repetitions
 OBSERVE H1, 399.7291425 MHz
 DATA PROCESSING
 FT size 65536
 Total time 1 min



21

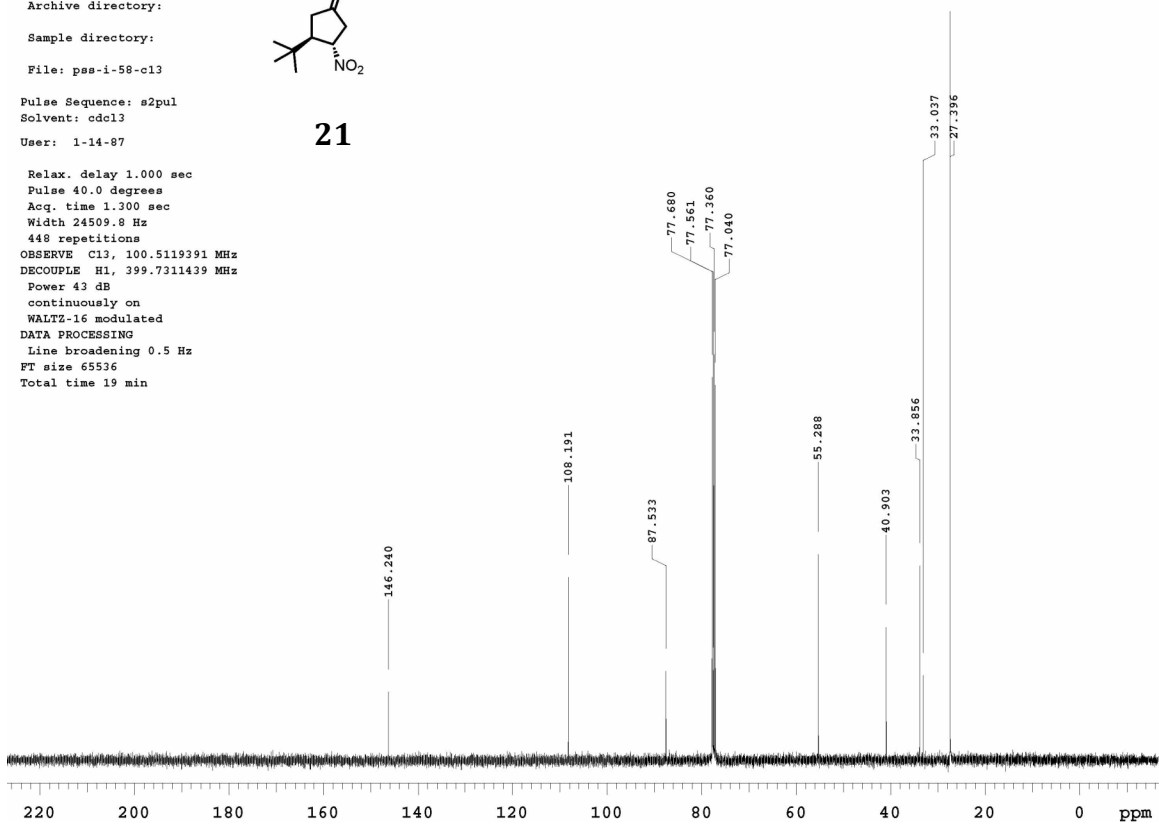


Std proton

Archive directory:
 Sample directory:
 File: pss-i-58-cl3
 Pulse Sequence: s2pul
 Solvent: cdcl3
 User: 1-14-87
 Relax. delay 1.000 sec
 Pulse 40.0 degrees
 Acq. time 1.300 sec
 Width 24509.8 Hz
 448 repetitions
 OBSERVE C13, 100.5119391 MHz
 DECOUPLE H1, 399.7311439 MHz
 Power 43 dB
 continuously on
 WALTZ-16 modulated
 DATA PROCESSING
 Line broadening 0.5 Hz
 FT size 65536
 Total time 19 min

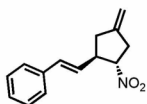


21



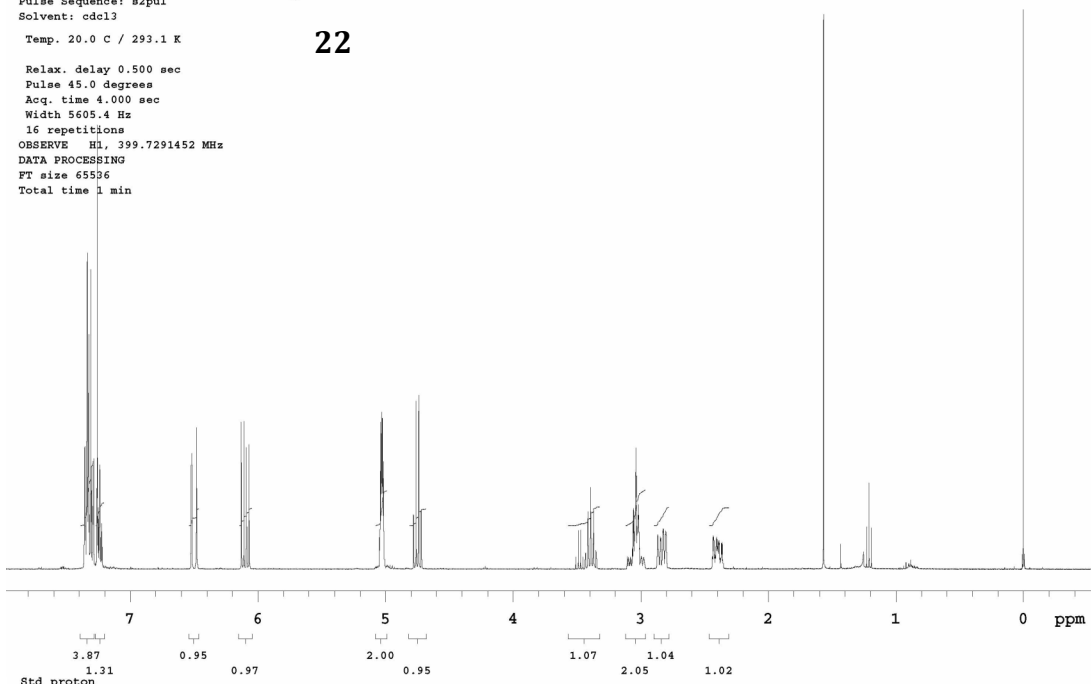
Std proton

Archive directory:
Sample directory:
File: pss-i-32-1
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K

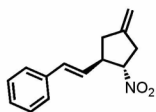


22

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291452 MHz
DATA PROCESSING
FT size 65536
Total time 1 min

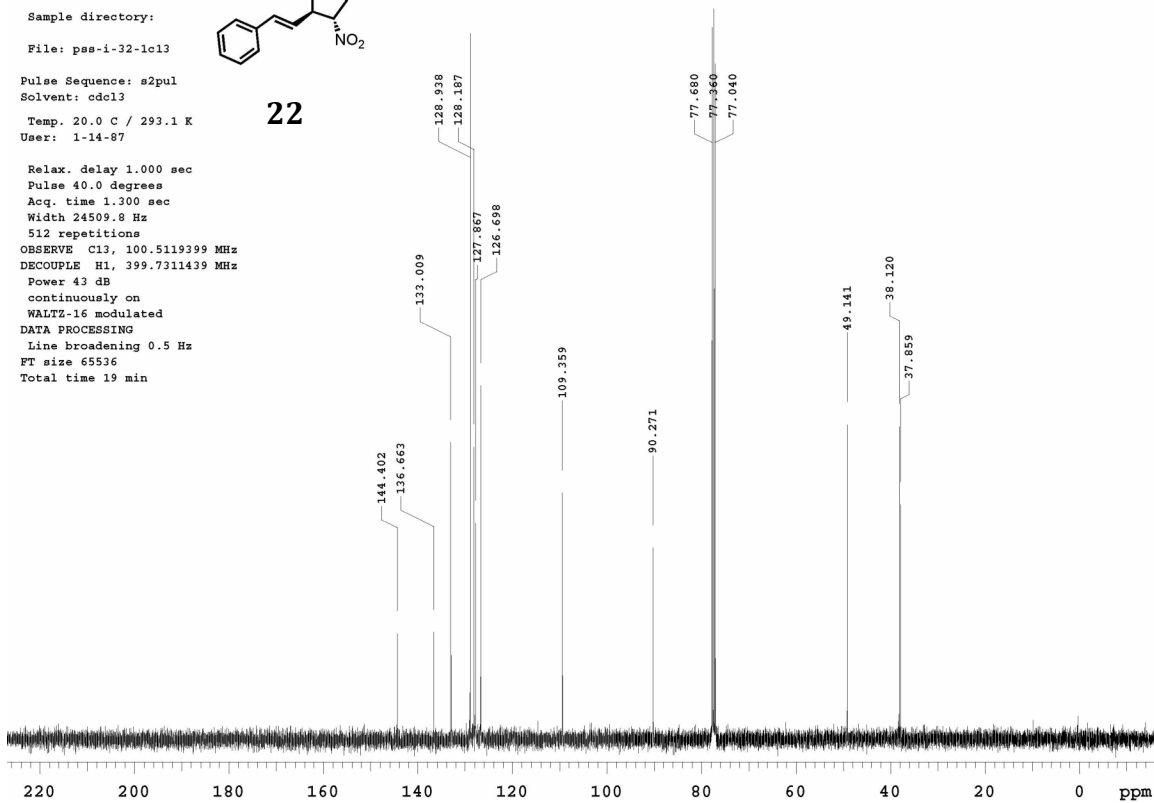


Archive directory:
Sample directory:
File: pss-i-32-1c13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 20.0 C / 293.1 K
User: 1-14-87



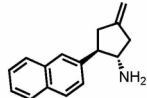
22

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
512 repetitions
OBSERVE C13, 100.5119399 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min

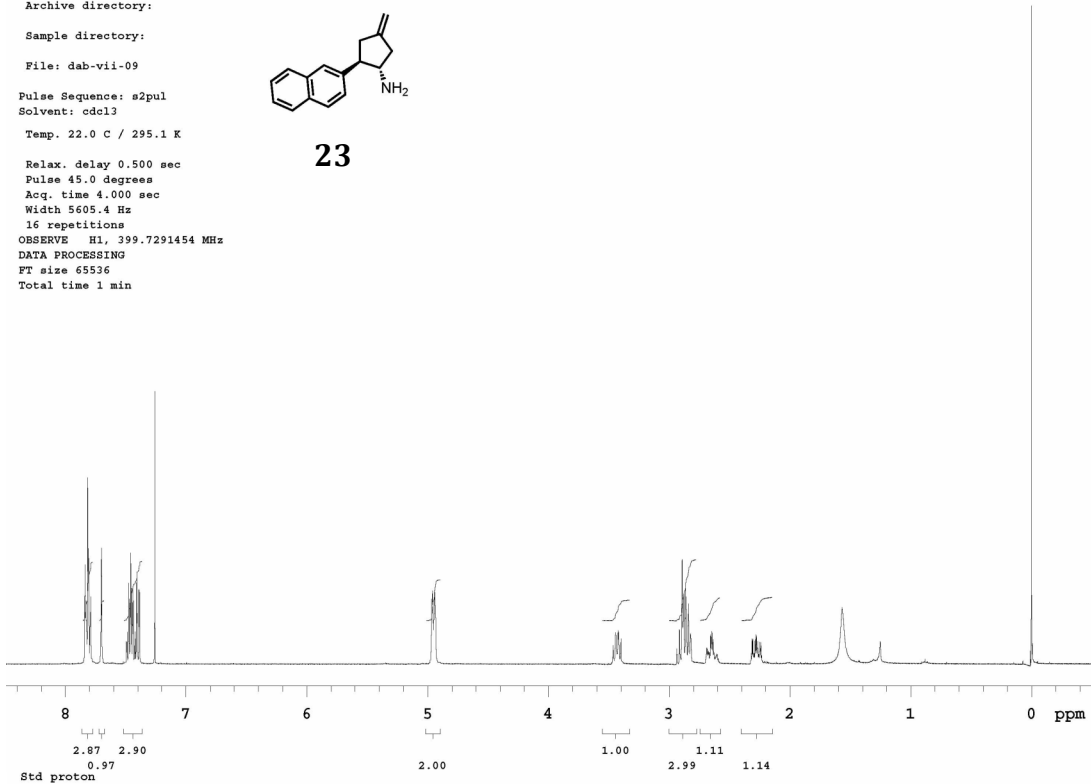


Std proton

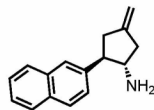
Archive directory:
Sample directory:
File: dab-vii-09
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291454 MHz
DATA PROCESSING
FT size 65536
Total time 1 min



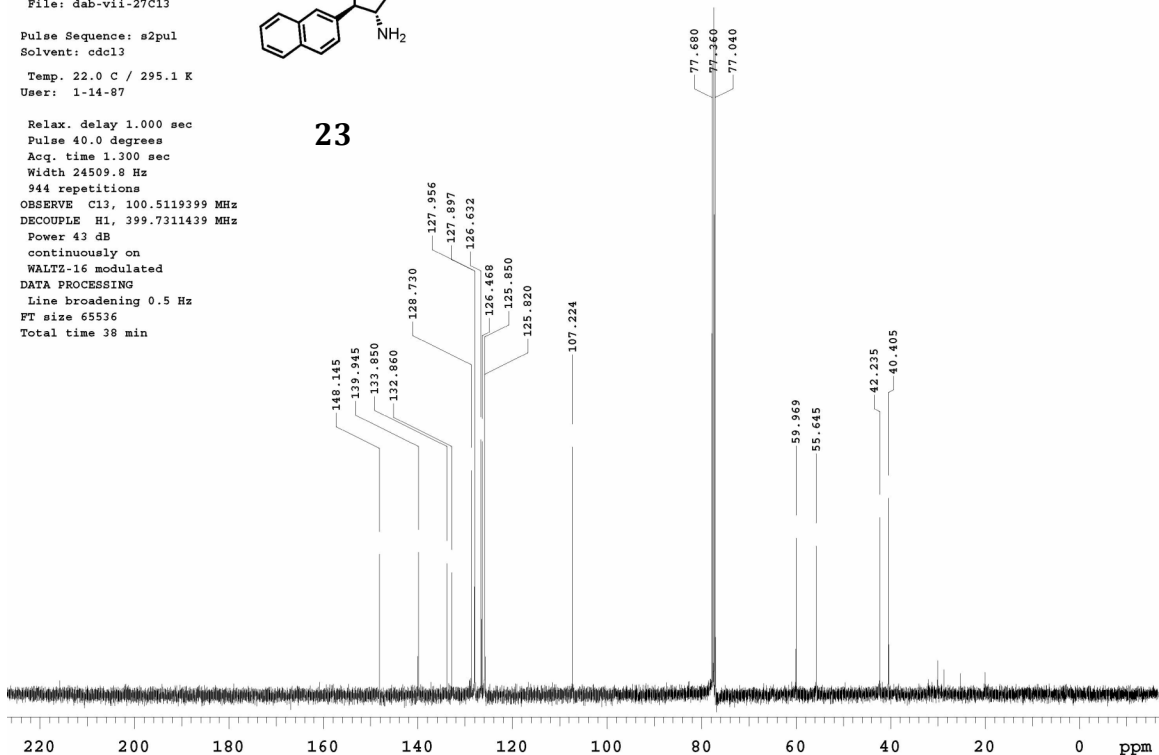
23



Archive directory:
Sample directory:
File: dab-vii-27C13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
User: 1-14-87
Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
944 repetitions
OBSERVE C13, 100.5119399 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 38 min



23



Std proton

Archive directory:

Sample directory:

File: dab-vii-16

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 22.0 C / 295.1 K

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5605.4 Hz

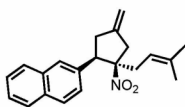
16 repetitions

OBSERVE H1, 399.7291446 MHz

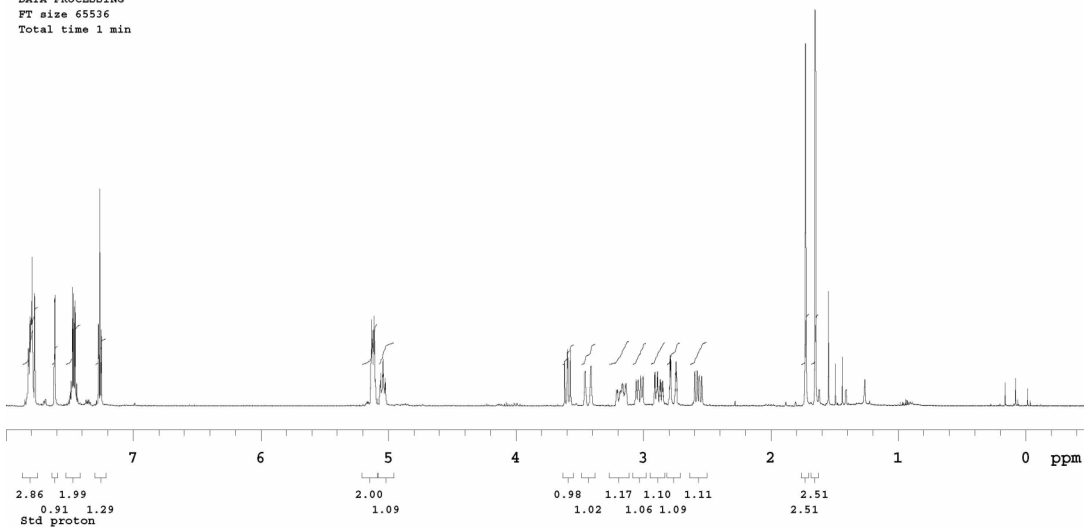
DATA PROCESSING

FT size 65536

Total time 1 min



25



Archive directory:

Sample directory:

File: dab-vii-16C13

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 22.0 C / 295.1 K

User: 1-14-87

Relax. delay 1.000 sec

Pulse 40.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

512 repetitions

OBSERVE C13, 100.5119391 MHz

DECOUPLE H1, 399.7311439 MHz

Power 43 dB

continuously on

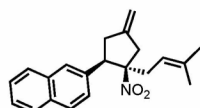
WALTZ-16 modulated

DATA PROCESSING

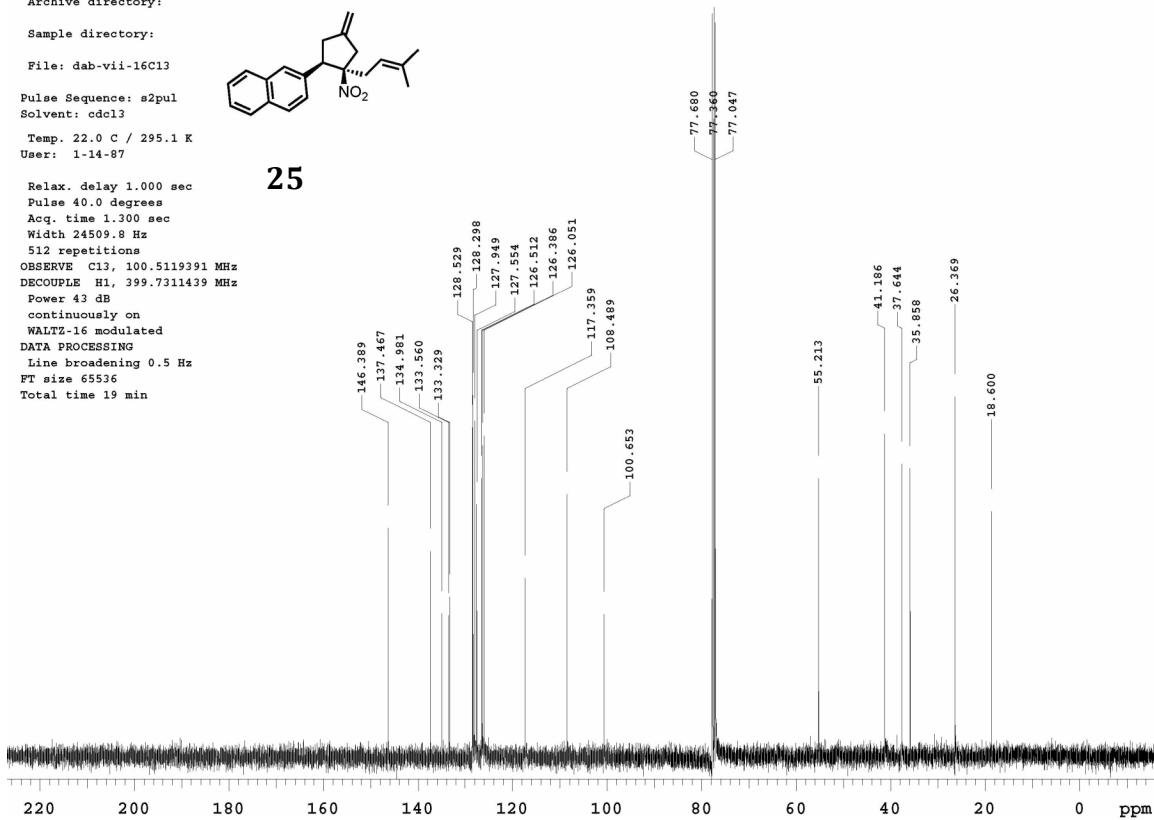
Line broadening 0.5 Hz

FT size 65536

Total time 19 min



25



Std proton

Archive directory:

Sample directory:

File: dab-vii-01Proton

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 22.0 C / 295.1 K

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 4.000 sec

Width 5605.4 Hz

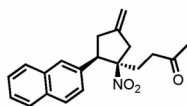
16 repetitions

OBSERVE H1, 399.7291444 MHz

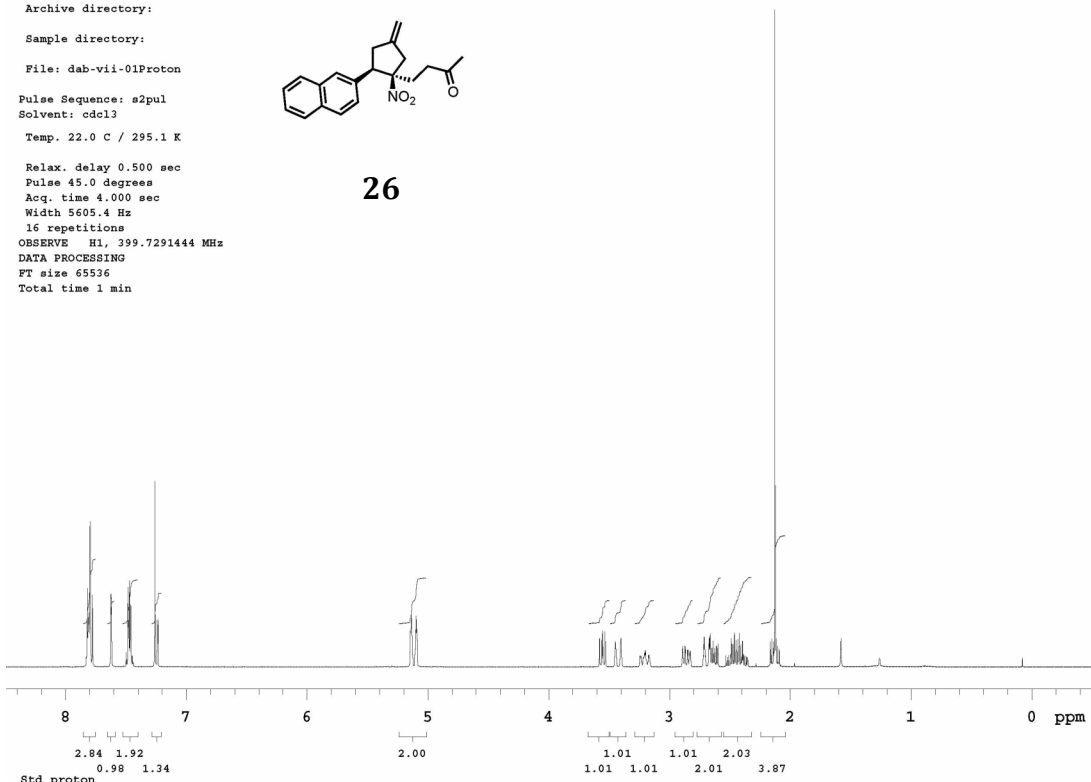
DATA PROCESSING

FT size 65536

Total time 1 min



26



Std proton

Archive directory:

Sample directory:

File: dab-vii-01C13

Pulse Sequence: s2pul

Solvent: cdcl3

Temp. 22.0 C / 295.1 K

User: 1-14-87

Relax. delay 1.000 sec

Pulse 40.0 degrees

Acq. time 1.300 sec

Width 24509.8 Hz

664 repetitions

OBSERVE C13, 100.5119406 MHz

DECOUPLE H1, 399.7311439 MHz

Power 43 dB

continuously on

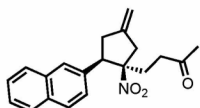
WALTZ-16 modulated

DATA PROCESSING

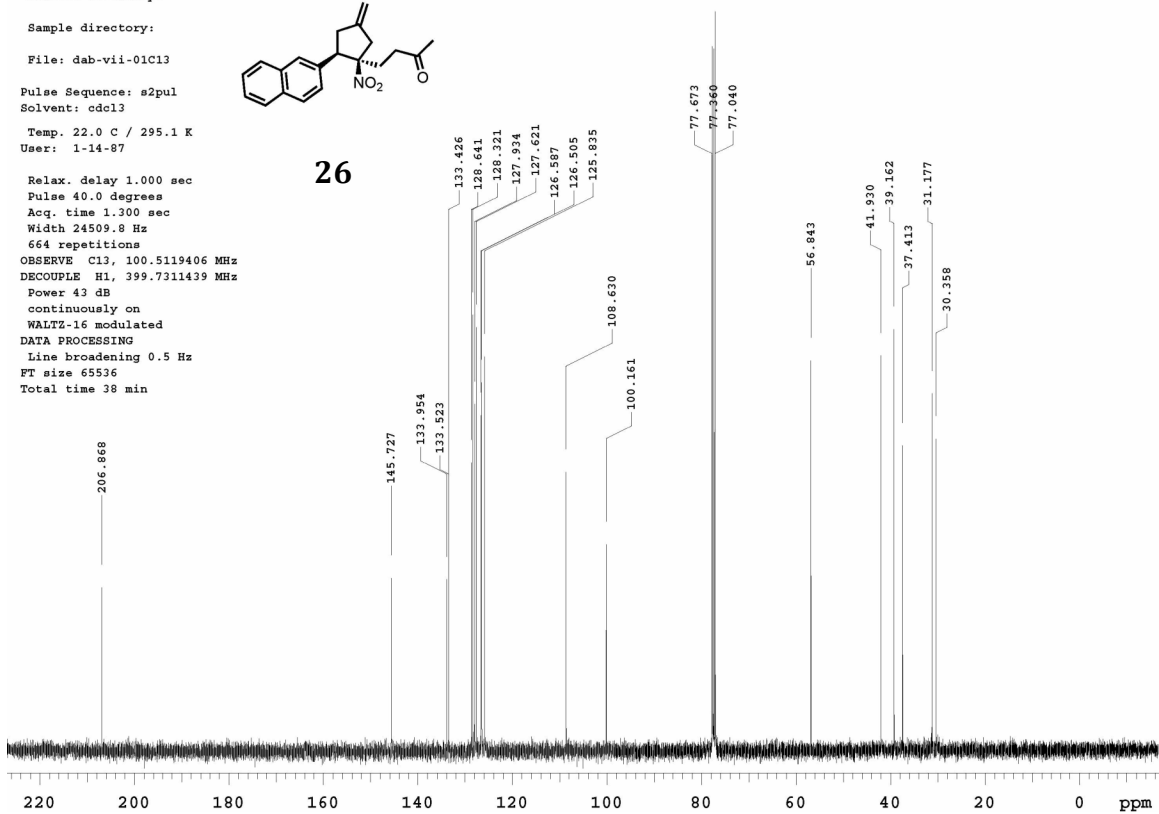
Line broadening 0.5 Hz

FT size 65536

Total time 38 min

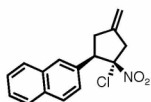


26



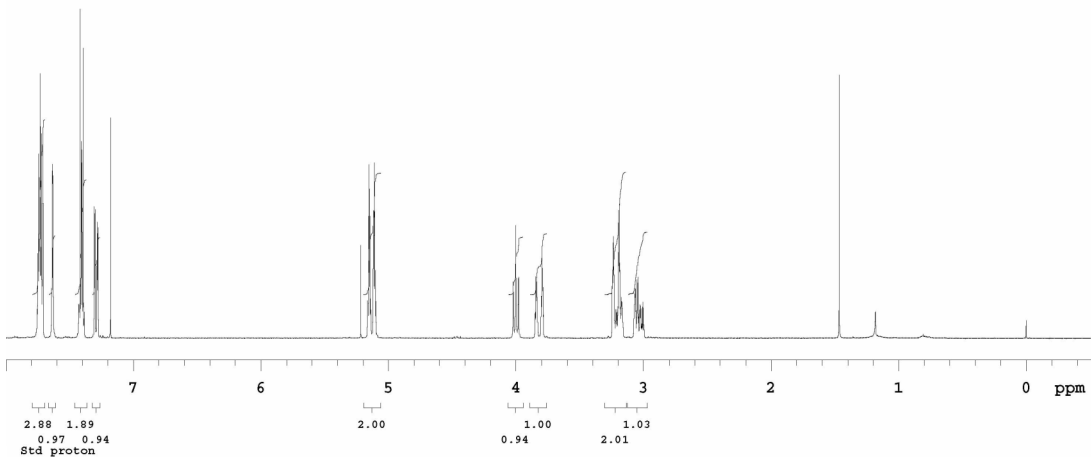
Std proton

Archive directory:
Sample directory:
File: dab-vii-25
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K

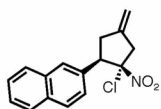


27

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
16 repetitions
OBSERVE H1, 399.7291775 MHz
DATA PROCESSING
FT size 65536
Total time 1 min

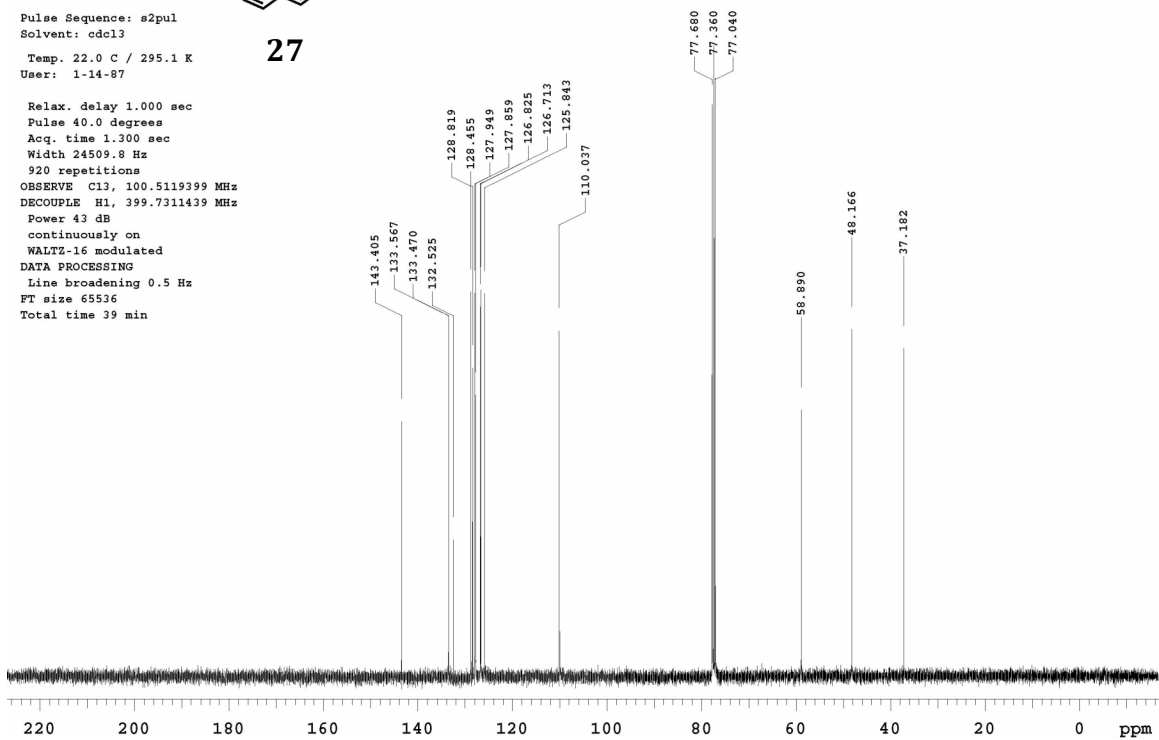


Archive directory:
Sample directory:
File: dab-vii-25C13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 22.0 C / 295.1 K
User: 1-14-87



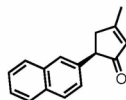
27

Relax. delay 1.000 sec
Pulse 40.0 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
920 repetitions
OBSERVE C13, 100.5119399 MHz
DECOUPLE H1, 399.7311439 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 39 min



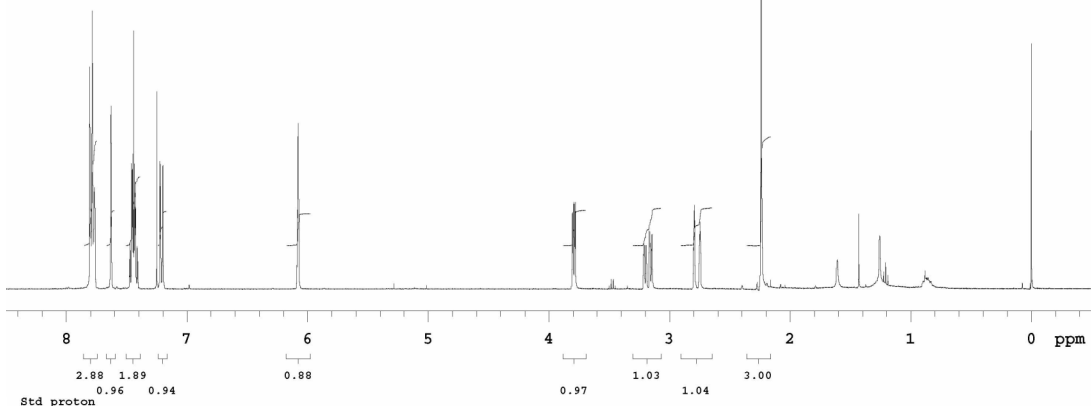
Std proton

Archive directory:
Sample directory:
File: dab-xv-71
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 23.0 C / 296.1 K

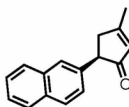


28

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 4.000 sec
Width 5605.4 Hz
8 repetitions
OBSERVE H1, 399.7345551 MHz
DATA PROCESSING
FT size 65536
Total time 1 min

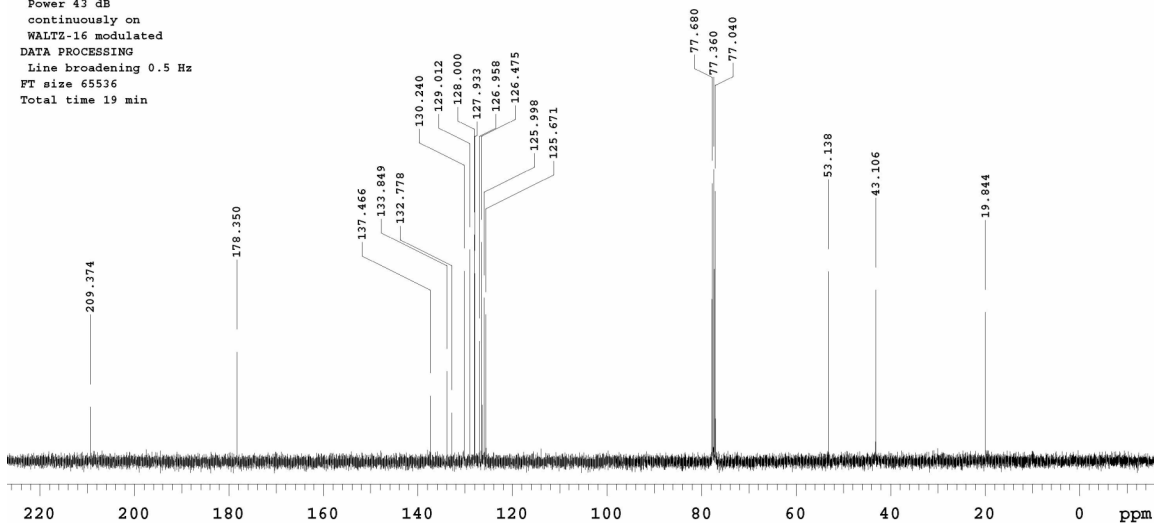


Archive directory:
Sample directory:
File: dab-xv-71C13
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 23.0 C / 296.1 K
User: 1-14-87



28

Relax. delay 1.000 sec
Pulse 39.5 degrees
Acq. time 1.300 sec
Width 24509.8 Hz
180 repetitions
OBSERVE C13, 100.5133005 MHz
DECOUPLE H1, 399.7365548 MHz
Power 43 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 19 min



¹ Perrin, D. D.; Armarego, W. L. F. *Purification of Laboratory Chemicals*, 5th Ed.; Pergamon Press: Oxford, 1988.

² Komiya, S. *Synthesis of Organometallic Compounds. A Practical Guide*; John Wiley & Sons: New York, 1997.

³ Trost, B. M.; Chan, D. M. T. *J. Am. Chem. Soc.* **1979**, *101*, 6429.

⁴ Rimkus, A.; Sewald, N. *Org. Lett.* **2003**, *5*, 79.

⁵ Trost, B. M.; Silverman, S. M.; Stambuli, J. P. *J. Am. Chem. Soc.* **2007**, *129*, 12398.

⁶ Worrall, D. E. *Org. Synth.* **1929**, *9*, 66.