Supporting Information

Modular Synthesis of *N*-Vinyl Benzotriazoles

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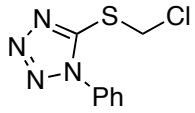
GENERAL EXPERIMENTAL CONSIDERATIONS

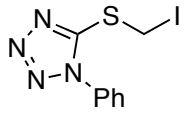
THF was distilled over $LiAlH_4$ and then over sodium, and MeCN was distilled over CaH_2. All other solvents and reagents were obtained from commercial sources and used without further purification. For reactions performed under a nitrogen atmosphere, glassware was dried with heat gun under vacuum. LHMDS (1.0 M in THF), KHMDS (0.5 M in toluene), NaHMDS (1.0 M in THF), and H_2O_2 (50% aqueous solution) were obtained from commercial sources. Thin layer chromatography was performed on aluminum foil-backed silica gel plates (200 μm). Column chromatographic purifications were performed on 200–300 mesh silica gel. ^{1}H NMR spectra were recorded at 500 MHz and are referenced to residual solvent. ^{13}C NMR spectra were recorded at 125 MHz and are referenced to the carbon resonance of the deuterated solvent. ^{19}F NMR spectra were recorded at 282 MHz with $CFCl_3$ as internal standard. Chemical shifts (δ) are reported in parts per million and coupling constants (J) are in hertz (Hz). HRMS data were gathered using a TOF analyzer, and the ionization modes are specified under each compound heading.

5-[(Chloromethyl)thio]-1-phenyl-1*H*-tetrazole (1)



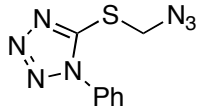
Potassium carbonate (19.4 g, 141 mmol, 5.00 molar equiv) was added to a solution of 1-phenyl-1*H*-tetrazole-5-thiol (5.00 g, 28.1 mmol, 1.00 molar equiv) and bromochloromethane (4.36 g, 33.7 mmol, 1.20 molar equiv) in acetone (75.0 mL), and the reaction mixture was heated at reflux for 3 h, at which time TLC (SiO_2, 20% EtOAc in hexanes) showed complete consumption of the starting material. The solvent was concentrated under reduced pressure and water was added to the reaction mixture. The aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and the solvent evaporated under reduced pressure. The crude product was purified by column chromatography (SiO_2, eluted with 10% EtOAc in hexanes, with a stepwise increase to 20% EtOAc in hexanes) to yield 4.36 g (70%) of **1** as a white solid. R_f (20% EtOAc in hexanes) = 0.44. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.54 (m, 5H, Ar-H), 5.37 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.5, 133.0, 130.6, 130.0, 123.9, 45.7. HRMS (ESI) calcd for $C_8H_8ClN_4S$ $[M+H]^+$ 227.0153, found 227.0172.

5-[(Iodomethyl)thio]-1-phenyl-1*H*-tetrazole (2)



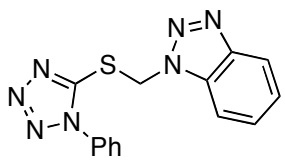
A solution of 5-[(chloromethyl)thio]-1-phenyl-1*H*-tetrazole (**1**, 0.950 g, 4.19 mmol, 1.00 molar equiv) and sodium iodide (2.51 g, 16.8 mmol, 4.00 molar equiv) in acetone (100 mL) was heated at reflux for 4 h, at which time TLC (SiO_2, 30% EtOAc in hexanes) showed complete consumption of **1**. The solvent was concentrated under reduced pressure, and water was added to the reaction mixture. The aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and 1.08 g (82%, yellow solid) of crude product **2** was isolated, that was used in the next step without further purification. R_f (30% EtOAc in hexanes) = 0.46. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60-7.53 (m, 5H, Ar-H), 4.81 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.9, 133.3, 130.7, 130.1, 124.0, –6.81. HRMS (ESI) calcd for $C_8H_8IN_4S$ $[M+H]^+$ 318.9509, found 318.9512.

5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole (3)



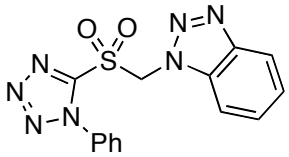
A solution of 5-[(iodomethyl)thio]-1-phenyl-1*H*-tetrazole (**2**, 2.60 g, 8.17 mmol, 1.00 molar equiv) and sodium azide (1.06 g, 16.3 mmol, 2.00 molar equiv) in DMF (80.0 mL) was allowed to stir at 50 ˚C for 4 h, at which time TLC (SiO_2, 20% EtOAc in hexanes) showed complete consumption of **2**. The reaction mixture was cooled to rt, poured into water, and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and the solvent was evaporated under reduced pressure to yield 1.70 g (89%) of **3** as a brown solid. No purification was required and crude azide **3** was used in the subsequent step. R_f (30% EtOAc in hexanes) = 0.36. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.62-7.56 (m, 5H, Ar-H), 5.14 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 133.2, 130.5, 130.0, 123.8, 53.9. HRMS (ESI) calcd for $C_8H_8N_7S$ $[M+H]^+$ 234.0556, found 234.0564.

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (4)



To a mixture of 5-[(azidomethyl)thio]-1-phenyl-1*H*-tetrazole (**3**, 0.870 g, 3.73 mmol, 1.00 molar equiv), 2-(trimethylsilyl)phenyltrifluoromethanesulfonate (1.67 g, 5.60 mmol, 1.50 molar equiv), 18-Cr-6 (2.96 g, 11.2 mmol, 3.00 molar equiv) and KF (0.867 g, 14.9 mmol, 4.00 molar equiv) under N_2, dry CH_3CN (70.0 mL) was added. The reaction mixture was allowed to stir at rt for 1 h, until TLC (SiO_2, 40% EtOAc in hexanes) showed complete consumption of **3**, water was added, and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine, dried over anhydrous Na_2SO_4, and the solvent evaporated under reduced pressure. Purification by column chromatography (SiO_2, 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes) yielded 0.979 g (85%) of **4** as a white solid. R_f (40% EtOAc in hexanes) = 0.54. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.06 (d, 1H, Ar-H, *J* = 8.3 Hz), 7.93 (d, 1H, Ar-H, *J* = 8.3 Hz), 7.56 (t, 1H, Ar-H, *J* = 7.3 Hz), 7.53-7.51 (m, 3H, Ar-H), 7.42-7.39 (m, 3H, Ar-H), 6.65 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.2, 146.3, 133.1, 132.7, 130.8, 130.1, 128.7, 124.8, 124.0, 120.3, 110.8, 49.3. HRMS (ESI) calcd for $C_{14}H_{12}N_7S$ $[M+H]^+$ 310.0869, found 310.0880.

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl]methyl}-1*H*-benzo[*d*][1,2,3]triazole (5)



In our initial work, sulfide **4** was oxidized to sulfone **5** using H_5IO_6/CrO_3. Subsequently we found that oxidation of **4** to **5** using $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O/H_2O_2$ gave a superior yield, and the crude product did not require any additional purification. Both oxidation procedures are described below. Screening of olefination conditions (Table 1 in the manuscript) and synthesis of vinyl benzotriazoles (Table 2 in the manuscript) were performed with **5**, obtained via H_5IO_6/CrO_3 oxidation.

Oxidation of 4 with H_5IO_6/CrO_3

H_5IO_6 (2.86 g, 12.5 mmol, 4.00 molar equiv) was dissolved in dry CH_3CN (26.0 mL) by vigorous stirring at rt for 30 min. CrO_3 (0.016 g, 0.159 mmol, 0.050 molar equiv) was added and the reaction mixture was stirred for an additional 5 min to give an orange colored solution. After 5 min, H_5IO_6/CrO_3 mixture was added to a solution of 1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (**4**, 0.970 g, 3.14 mmol, 1.00 molar equiv) in CH_3CN (52.0 mL) under a N_2 balloon. The reaction mixture was stirred at rt for 10 h at which time TLC (SiO_2, 30% acetone in hexanes) showed a complete consumption of **4**. The reaction mixture was cooled on

ice and sat aq $NaHCO_3$ was added, followed by solid sodium bisulfite addition. The aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, 10% acetone in hexanes) to yield 0.730 g (68%) of **5** as a yellow solid. R_f (40% acetone in hexanes) = 0.47. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, 1H, Ar-H, *J* = 8.3 Hz), 7.66 (d, 1H, Ar-H, *J* = 8.3 Hz), 7.58 (t, 1H, Ar-H, *J* = 7.6 Hz), 7.53 (t, 1H, Ar-H, *J* = 7.4 Hz), 7.45 (t, 3H, Ar-H, *J* = 7.8 Hz), 7.37 (d, 2H, Ar-H, *J* = 7.8 Hz), 6.46 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 146.2, 133.2, 132.4, 131.9, 129.7, 129.6, 125.4, 125.4, 120.8, 109.7, 67.6. HRMS (ESI) calcd for $C_{14}H_{12}N_7O_2S$ $[M+H]^+$ 342.0768, found 342.0764.

Oxidation of 4 with $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O/H_2O_2$

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole **4** (0.400 g, 1.29 mmol, 1.00 molar equiv) was dissolved in CH_3CN (40.0 mL). Separately, H_2O_2 (50% H_2O_2 in water, d = 1.2 g/mL, 9.20 mL, 5.52 g of H_2O_2, 162 mmol, 126 molar equiv) was slowly added to $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O$ (1.60 g, 1.29 mmol, 1.00 molar equiv), and the resulting solution was added to the solution of **4** in CH_3CN. The reaction mixture was stirred at rt for 20 h at which time TLC (SiO_2, 30% acetone in hexanes) showed a complete consumption of **4**. Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo to yield 386 mg (88%) of **5** as a yellow solid. Sulfone **5** was of sufficient purity based on its ^{1}H NMR and was used in the synthesis of (*E*/*Z*)-**6** without further purification.

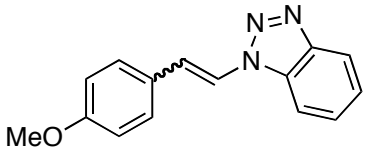
Condensations of Sulfone 5 with Carbonyl Compounds.

Method A. General Procedure. A stirring solution of aldehyde or a ketone (1.20-1.50 molar equiv) and benzotriazole-derived sulfone **5** (1.00 molar equiv) in THF (17.0 mL/mmol of sulfone **5**) was cooled to 0 ˚C and under N_2, LHMDS (1.0 M solution in THF, 2.40 molar equiv) was added to the reaction mixture. The reaction mixture was stirred at 0 ˚C and monitored by TLC for disappearance of sulfone **5**. Upon complete consumption of **5**, saturated aq NH_4Cl was added and the mixture was poured into EtOAc. Organic layer was separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the combined *E*/*Z* product mixture was isolated by column chromatography using silica gel (mesh 200–300). The product *E*/*Z* ratio was determined by ^{1}H NMR, prior to purification by column chromatography. For each substrate, the quantities of reactants and solvent, reaction

time, product yield, eluting solvent for chromatography, R_f value, and spectroscopic data are provided under the individual compound headings.

Method B. General Procedure. A stirred solution of the aldehyde (1.5 molar equiv) and benzotriazole-derived sulfone **5** (1.00 molar equiv) in THF (17.0 mL/mmol of sulfone **5**) was brought to reflux under N_2. DBU (2.00 molar equiv) was added and the reflux was continued while the reaction progress was monitored by TLC for disappearance of compound **5**. Upon complete consumption of **5**, water was added and the mixture was poured into EtOAc. Organic layer was separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the combined *E*/*Z* product mixture was isolated by column chromatography using silica gel (mesh 200–300). The product *E*/*Z* ratio was determined by ^{1}H NMR, prior to purification by column chromatography. The only exception was the reaction with 2-ethylbutanal, where the *E*/*Z* ratio of product **15** was determined after purification. This was due to the presence of an impurity that had proton resonances overlapping with those of product **15**. For each substrate, reaction time, *E*/*Z* ratio, eluting solvent for chromatography, and the yield, are provided under the individual compound headings.

(*E*/*Z*)-1-(4-Methoxystyryl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-6)

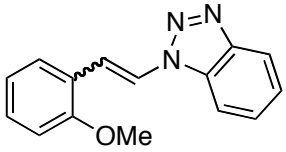


Method A. 4-Methoxybenzaldehyde: 61.3 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv); LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 4 h. Column chromatography: eluting solvent 10% EtOAc in hexanes. Yield: 57.1 mg (76%) of *E*/*Z*-**6** (*E*/*Z* 79/21) as a white solid. R_f (30% EtOAc in hexanes) = 0.38. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.09-8.07 (m, 1H, *Z*-isomer), 7.83 (d, 1H, *J* = 14.6 Hz, *E*-isomer) 7.76 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.58 (t, 1H, *J* = 7.8 Hz, *E*-isomer), 7.50 (d, 2H, *J* = 8.8 Hz, *E*-isomer), 7.45-7.42 (m, 2H, *E*-isomer), 7.35-7.33 (m, 2H, *Z*-isomer), 7.17 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 7.11-7.09 (m, 1H, *Z*-isomer), 6.96 (d, 2H, *J* = 8.3 Hz, *E*-isomer), 6.91 (d, 2H, *J* = 8.8 Hz, *Z*-isomer), 6.72 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 6.67 (d, 2H, *J* = 8.8 Hz, *Z*-isomer), 3.86 (s, 3H, OCH_3, *E*-isomer), 3.73 (s, 3H, OCH_3, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.1, 159.9, 146.4, 145.8, 132.2, 131.6, 130.5, 128.2, 128.1, 128.0,

127.8, 127.0, 125.7, 124.7, 124.3, 121.3, 120.4, 120.1, 120.0, 119.3, 114.6, 114.1, 111.1, 110.2, 55.5, 55.3. HRMS (ESI) calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$ 252.1131, found 252.1136.

Method B. Reaction time: 2h. *E*/*Z*-**6** 26/74. Column chromatography: eluting solvent 10% EtOAc in hexanes, 47% yield.

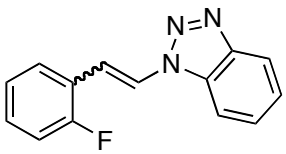
(*E*/*Z*)-1-(2-Methoxystyryl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-7)



Method A. 2-Methoxybenzaldehyde: 58.3 mg (0.428 mmol, 1.46 molar equiv); sulfone **5**: 100 mg (0.293 mmol, 1.00 molar equiv); LHMDS: 703 μL (0.703 mmol, 2.4 molar equiv); THF: 5.0 mL. Reaction time: 30 min. Column chromatography: eluting solvent 20% EtOAc in hexanes. Yield: 63.5 mg (86%) of *E*/*Z*-**7** (*E*/*Z* 93/7) as a yellow solid. R_f (30% EtOAc in hexanes) = 0.42. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.17 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 8.12 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.03 (d, 1H, *J* = 8.3 Hz, *Z*-isomer), 7.80 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.66 (d, 1H, *J* = 15.1 Hz, *E*-isomer), 7.58 (td, 1H, *J* = 6.8; 1.0 Hz, *E*-isomer), 7.53 (dd, 1H, *J* = 7.8; 1.4 Hz, *E*-isomer), 7.44 (t, 1H, *J* = 7.3 Hz, *E*-isomer), 7.39 (d, 1H, *J* = 9.2 Hz, *Z*-isomer), 7.33 (td, 1H, *J* = 8.3; 1.5 Hz, *E*-isomer), 7.30-7.22 (m, 2H, *Z*-isomer, overlapping with $CDCl_3$), 7.18 (td, 1H, *J* = 8.3; 1.0 Hz, *Z*-isomer), 7.03 (td, 1H, *J* = 7.3; 1.0 Hz, *E*-isomer), 6.98 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 6.94 (d, 1H, *J* = 8.3 Hz, *Z*-isomer), 6.91 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 6.81 (d, 1H, *J* = 7.8 Hz, *Z*-isomer), 6.76 (d, 1H, *J* = 7.8 Hz, *Z*-isomer), 6.64 (t, 1H, *J* = 7.3 Hz, *Z*-isomer), 3.97 (s, 3H, OCH_3 *E*-isomer), 3.67 (s, 3H, OCH_3, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$, due to a small amount of the *Z*-isomer, some C resonances of this minor isomer may not have been detected): δ 157.5, 146.5, 131.7, 130.2, 129.6, 128.4, 128.2, 127.5, 124.7, 124.1, 123.3, 123.1, 122.3, 121.8, 121.1, 120.6, 120.5, 119.9, 117.6, 111.2, 111.1, 110.8, 110.5, 55.7, 55.4. HRMS (ESI) calcd for $C_{15}H_{14}N_3O$ $[M+H]^+$ 252.1131, found 252.1149.

Method B. Reaction time: 5h. *E*/*Z*-**7** 15/85. Column chromatography: eluting solvent 20% EtOAc in hexanes, 57% yield.

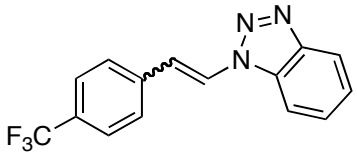
(*E*/*Z*)-1-(2-Fluorostyryl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-8)



Method A. 2-Fluorobenzaldehyde: 54.5 mg (0.439 mmol, 1.50 molar equiv); sulfone **5**: 100 mg (0.293 mmol, 1.00 molar equiv); LHMDS: 703 μL (0.703 mmol, 2.4 molar equiv); THF: 5.0 mL. Reaction time: 30 min. Column chromatography: eluting solvent 20% EtOAc in hexanes, increase to 40% EtOAc in hexanes after elution of first component. Yield: 58.1 mg (83%) of *E*/*Z*-**8** (*E*/*Z* 41/59) as a white solid. R_f (30% EtOAc in hexanes) = 0.58. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.12 (d, 1H, *J* = 15.1 Hz, *E*-isomer), 8.08-8.04 (m, 1H, *Z*-isomer), 7.79 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.61 (td, 1H, *J* = 7.8; 1.0 Hz, *E*-isomer), 7.59-7.54 (m, 2H, *E*-isomer), 7.46 (t, 1H, *J* = 8.3 Hz, *E*-isomer), 7.43 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 7.35-7.30 (m, 2H *Z*-isomer, 1H *E*-isomer), 7.23-7.10 (m, 2H *E*-isomer, 1H *Z*-isomer), 7.08-7.05 (m, 1H *Z*-isomer), 7.02 (t, 1H, *J* = 9.0 Hz, *Z*-isomer), 6.87-6.82 (m, 3H *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.8 (d, $^1J_{CF}$ = 250.4 Hz), 160.3 (d, $^1J_{CF}$ = 249.9 Hz), 146.5, 145.8, 132.0, 131.7, 130.6 (d, J_{CF} = 8.2 Hz), 129.9 (d, J_{CF} = 2.3 Hz), 129.8 (d, J_{CF} = 8.7 Hz), three resonances at 128.64, 128.61, and 128.60 account for 2 C-atoms, 128.0, 124.9, 124.8 (d, J_{CF} = 3.2 Hz), 124.4, three resonances at 124.31, 124.24, and 124.21 account for 2 C-atoms, 123.1 (d, J_{CF} = 1.4 Hz), 122.5 (d, J_{CF} = 12.4 Hz), 121.7 (d, J_{CF} = 13.7 Hz), 120.6, 120.2, 119.1 (d, J_{CF} = 3.7 Hz), 116.3 (d, J_{CF} = 22.0 Hz), 115.8 (d, J_{CF} = 21.5 Hz), 114.5 (d, J_{CF} = 1.4 Hz), 110.6, 110.3. ^{19}F NMR (282 MHz, $CDCl_3$): δ –114.32 (s, *Z*-isomer), –115.37 (s, *E*-isomer). HRMS (ESI) calcd for $C_{14}H_{11}FN_3$ $[M+H]^+$ 240.0932, found 240.0935.

Method B. Reaction time: 5h, *E*/*Z*-**8** 11/89. Column chromatography: eluting solvent 20% EtOAc in hexanes, with stepwise increase to 30% EtOAc in hexanes, 57% yield.

(*E*/*Z*), (*E*)-, and (*Z*)-1-[(4-Trifluoromethyl)styryl]-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-9, *E*-9, *Z*-9)

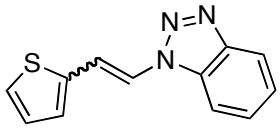


Method A. 4-(Trifluoromethyl)benzaldehyde: 78.0 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 120 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 20% EtOAc in hexanes (isomers separate under these conditions, but were collected together). Yield: 54.0 mg (62%) of *E*/*Z*-**9** (*E*/*Z* 29/71) as a yellow solid. R_f (20% EtOAc in hexanes) = 0.28 and 0.41. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.10-8.06 (m, 1H, *Z* isomer), 8.02 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 7.78 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.68-7.64 (m, 4H, *E* isomer), 7.61 (t, 1H, *J* = 8.3 Hz, *E*-isomer), 7.51

(d, 1H, *J* = 15.1 Hz, *E*-isomer), 7.46 (t, 1H, *J* = 8.3 Hz, *E*-isomer), 7.43 (d, 2H, *J* = 8.3 Hz, *Z*-isomer), 7.38-7.35 (m, 3H, *Z* isomer), 7.17 (d, 2H, *J* = 8.3 Hz, *Z*-isomer), 7.08-7.04 (m, 1H, *Z*-isomer), 6.77 (d, 1H, *J* = 9.3 Hz, *Z*-isomer). ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.10 (s, *E*-isomer), –63.39 (s, *Z*-isomer). HRMS (ESI) calcd for $C_{15}H_{11}F_3N_3$ $[M+H]^+$ 290.0900, found 290.0913.

E/*Z*-**9** mixture was separated by column chromatography (SiO_2, 30% EtOAc in hexanes) to yield *E*-**9** as the early eluting and *Z*-**9** as the late eluting isomer. *E*-**9**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.15 (d, 1H, *J* = 8.3 Hz), 8.03 (d, 1H, *J* = 14.6 Hz), 7.78 (d, 1H, *J* = 8.3 Hz), 7.69-7.65 (m, 4H), 7.62 (t, 1H, *J* = 7.8 Hz), 7.53 (d, 1H, *J* = 14.6 Hz), 7.47 (t, 1H, *J* = 7.8 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.7, 138.3, 131.7, 130.4 (q, $^2J_{CF}$ = 32.5 Hz), 128.8, 126.9, 126.2 (q, $^3J_{CF}$ = 3.7 Hz), 125.1, 124.2 (q, $^1J_{CF}$ = 271.9 Hz), 123.8, 120.9, 119.2, 110.1. *Z*-**9**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11-8.07 (m, 1H), 7.44 (d, 2H, *J* = 7.8 Hz), 7.39-7.35 (m, 3H), 7.17 (d, 2H, *J* = 8.3 Hz), 7.09-7.04 (m, 1H), 6.78 (d, 1H, *J* = 9.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.9, 137.1, 132.0, 130.5 (q, $^2J_{CF}$ = 32.5 Hz), 129.3, 128.3, 125.6 (q, $^3J_{CF}$ = 3.7 Hz), 125.5, 124.7, 124.0 (q, $^1J_{CF}$ = 271.9 Hz), 122.9, 120.4, 110.6.

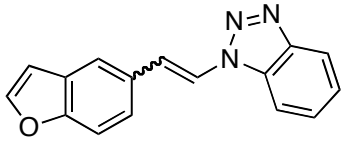
(*E*) and (*Z*)-1-[2-(Thiophen-2-yl)vinyl]-1*H*-benzo[*d*][1,2,3]triazole (*E*-10 and *Z*-10)



Method A. 2-Thiophenecarboxaldehyde: 43.9 mg (0.391 mmol, 1.34 molar equiv); sulfone **5**: 100 mg (0.293 mmol, 1.00 molar equiv); LHMDS: 703 μL (0.703 mmol, 2.4 molar equiv); THF: 5.0 mL. Reaction time: 30 min. Column chromatography: eluting solvent 20% EtOAc in hexanes, *E*- and *Z*-isomer collected separately (*E*-**10** first eluting, *Z*-**10** second eluting). Yield: *Z*-**10**: 36.0 mg (54%, brown solid); *E*-**10**: 24.0 mg (36%, brown solid). *Z*-**10**: R_f (30% EtOAc in hexanes) = 0.50; *E*-**10**: R_f (30% EtOAc in hexanes) = 0.60. *Z*-**10**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.14 (d, 1H, *J* = 7.8 Hz), 7.47 (t, 1H, *J* = 8.3 Hz), 7.41 (td, 1H, *J* = 8.3; 1.0 Hz), 7.36 (d, 1H, *J* = 8.3 Hz), 7.18 (d, 1H, *J* = 4.9 Hz), 7.06-7.02 (m, 3H), 6.90 (dd, 1H, *J* = 5.4; 3.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): 146.0, 135.2, 132.7, 131.1, 128.7, 128.1, 127.0, 124.5, 124.0, 120.2, 117.8, 110.4. *E*-**10**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.11 (d, 1H, *J* = 8.3 Hz), 7.81 (d, 1H, *J* = 14.2 Hz), 7.74 (d, 1H, *J* = 8.3 Hz), 7.64 (d, 1H, *J* = 14.2 Hz), 7.59 (t, 1H, *J* = 7.3 Hz), 7.44 (t, 1H, *J* = 7.3 Hz), 7.29 (d, 1H, *J* = 4.8 Hz), 7.20 (d, 1H, *J* = 2.9 Hz), 7.07 (dd, 1H, *J* = 4.9; 3.9 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 138.5, 131.6, 128.5, 128.1, 127.8, 125.5, 124.9, 120.8, 120.6, 115.1, 110.1. HRMS (ESI) calcd for $C_{12}H_{10}N_3S$ $[M+H]^+$ 228.0590, found 228.0588.

Method B. Reaction time: 5 h, *E*/*Z*-**10** 25/75. Column chromatography: eluting solvent 20% EtOAc in hexanes, 47% yield.

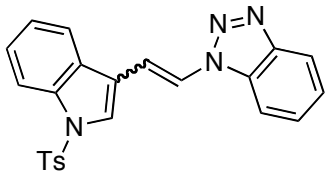
(*E*/*Z*)-1-[2-(Benzofuran-5-yl)vinyl]-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-11)



Method A. Benzofuran-5-carbaldehyde: 65.7 g, (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 60 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 15% EtOAc in hexanes. Yield: 51.0 mg (65%) of *E*/*Z*-**11** (*E*/*Z* 64/36) as a white solid. R_f (20% EtOAc in hexanes) = 0.38. ^{1}H NMR (500 MHz, $CDCl_3$, assignments based on COSY): δ 8.09 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.04 (d, 1H, *J* = 7.8 Hz, *Z*-isomer), 7.89 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 7.76-7.73 (m, 2H, *E*-isomer), 7.63 (d, 1H, *J* = 2.0 Hz, *E*-isomer), 7.55 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 7.55-7.47 (m, 3H *E*-isomer and 1H *Z*-isomer), 7.41 (t, 1H, *J* = 7.8 Hz, *E*-isomer), 7.29-7.21 (m, 5H *Z*-isomer, overlapping with $CHCl_3$ in $CDCl_3$), 6.98 (d, 1H, *J* = 8.3 Hz, *Z*-isomer), 6.88-6.84 (m, 2H, *Z*-isomer), 6.78 (d, 1H, *J* = 2.0 Hz, *E*-isomer), 6.55 (d, 1H, *J* = 2.0 Hz, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 155.2, 154.9, 146.5, 146.1, 145.9, 132.2, 131.7, 129.5, 128.4, 128.2, 127.9, 127.8, 125.4, 124.8, 124.3, 123.1, 122.2, 122.0, 121.1, 120.6, 120.5, 120.1, 119.8, 112.2, 111.7, 111.1, 110.2, 106.9, 106.8. HRMS (ESI) calcd for $C_{16}H_{12}N_3O$ $[M+H]^+$ 262.0975, found 262.0980.

Method B. Reaction time: 14h, *E*/*Z*-**11** 20/80. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 15% EtOAc in hexanes, 60% yield.

(*E*/*Z*), (*E*)-, and (*Z*)-1-[2-(1-Tosyl-1*H*-indol-3-yl)vinyl]-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-12, *E*-12, *Z*-12)

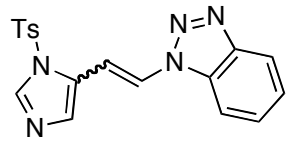


Method A. 1-Tosyl-1*H*-indole-3-carbaldehyde: 135 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 180 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes (isomers separate under these

conditions, but were collected together). Yield: 89.0 mg (72%) of *E*/*Z*-**12** (*E*/*Z* 71/29) as a pale pinkish colored solid. R_f (40% EtOAc in hexanes) = 0.41 and 0.57. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.12 (d, 2H, *J* = 8.3 Hz, 1H *E*-isomer and 1H *Z*-isomer), 8.05 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.00 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 7.94 (d, 1H, *J* = 8.3 Hz, *Z*-isomer), 7.82-7.76 (m, 5H, *E*-isomer), 7.62-7.57 (m, both *E* and *Z* isomers), 7.55 (d, 1H, *J* = 14.7 Hz, *E*-isomer), 7.49 (s, 1H, *Z*-isomer), 7.46-7.23 (m, both *E* and *Z* isomers), 7.20-7.16 (m, 3H, *Z*-isomer), 6.81 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 2.34 (s, 3H, CH_3, *E*-isomer), 2.32 (s, 3H, CH_3, *Z*-isomer). HRMS (ESI) calcd for $C_{23}H_{19}N_4O_2S$ $[M+H]^+$ 415.1223, found 415.1224.

E/*Z*-**12** mixture was separated by column chromatography (SiO_2, 30% EtOAc in hexanes) to yield *E*-**12** as the early eluting and *Z*-**12** as the late eluting isomer. *E*-**12**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 8.3 Hz), 8.06 (d, 1H, *J* = 8.3 Hz), 8.01 (d, 1H, *J* = 14.6 Hz), 7.83-7.81 (m, 4H), 7.77 (d, 1H, *J* = 8.3 Hz), 7.60 (t, 1H, *J* = 7.8 Hz), 7.56 (d, 1H, *J* = 14.6 Hz), 7.46 (t, 1H, *J* = 7.8 Hz), 7.41 (t, 1H, *J* = 8.0 Hz), 7.36 (t, 1H, *J* = 7.3 Hz), 7.25 (d, 2H, *J* = 7.8 Hz), 2.35 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 145.5, 135.7, 135.0, 131.6, 130.2, 128.6, 128.5, 127.1, 125.6, 124.9, 124.8, 124.0, 122.2, 120.6, 120.3, 117.6, 114.1, 112.5, 110.1, 21.7. *Z*-**12**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 8.3 Hz), 7.95 (d, 1H, *J* = 8.3 Hz), 7.62 (d, 2H, *J* = 8.3 Hz), 7.47 (s, 1H), 7.40-7.28 (m, 6H), 7.21-7.18 (m, 3H), 6.83 (d, 1H, *J* = 8.8 Hz), 2.34 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.7, 145.3, 135.0, 134.5, 132.1, 130.1, 129.8, 128.1, 127.1, 126.7, 125.3, 124.6, 123.8, 121.1, 120.5, 119.2, 116.5, 114.9, 113.8, 110.5, 21.8.

(*E*/*Z*), (*E*)-, and (*Z*)-1-[2-(1-Tosyl-1*H*-imidazol-4-yl)vinyl]-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-13, *E*-13, *Z*-13)

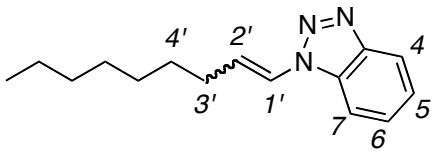


Method A. 1-Tosyl-1*H*-imidazole-5-carbaldehyde: 90.0 mg (0.360 mmol, 1.20 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 120 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes). Yield: 78.0 mg (71%) of *E*/*Z*-**13** (*E*/*Z* 29/71) as a pale pinkish colored solid. R_f (40% EtOAc in hexanes) = 0.37. HRMS (ESI) calcd for $C_{18}H_{16}N_5O_2S$ $[M+H]^+$ 366.1019, found 366.1005.

E/*Z*-**13** mixture was separated by column chromatography (20% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes) to yield *E*-**13** as the early eluting and *Z*-**13** as the late eluting isomer. *E*-**13**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.16 (d, 1H, *J* = 14.2 Hz), 8.10 (d, 1H, *J*

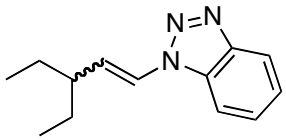
= 8.3 Hz), 8.04 (s, 1H), 7.87 (d, 2H, *J* = 8.3 Hz), 7.70 (d, 1H, *J* = 8.3 Hz), 7.56 (t, 1H, *J* = 7.8 Hz), 7.44-7.38 (m, 3H), 7.33 (s, 1H), 7.33 (d, 1H, *J* = 13.7 Hz), 2.46 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.8, 146.4, 140.0, 137.4, 134.9, 131.9, 130.8, 128.6, 127.7, 124.9, 122.7, 120.6, 115.5, 110.9, 109.9, 22.0. *Z*-**13**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.13 (d, 1H, *J* = 7.3 Hz), 7.94-7.92 (m, 2H), 7.75 (d, 2H, *J* = 8.8 Hz), 7.60 (s, 1H), 7.52 (t, 1H, *J* = 8.3 Hz), 7.45-7.32 (m, 3H), 7.15 (d, 1H, *J* = 9.8 Hz), 6.66 (d, 1H, *J* = 9.8 Hz), 2.43 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.7, 145.6, 137.6, 136.3, 134.8, 132.4, 130.7, 128.3, 127.7, 124.8, 120.5, 119.6, 118.4, 118.1, 110.4, 22.0.

(*E*/*Z*)-1-(Non-1-enyl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-14)



Method A. *n*-Octanal: 56.3 mg (0.439 mmol, 1.50 molar equiv); sulfone **5**: 100 mg (0.293 mmol, 1.00 molar equiv); LHMDS: 703 μL (0.703 mmol, 2.4 molar equiv); THF: 5.0 mL. Reaction time: 30 min. Column chromatography: eluting solvent 20% EtOAc in hexanes. Yield: 48.0 mg (67%) of *E*/*Z*-**14** (*E*/*Z* 4/96) as a yellow solid. R_f (30% EtOAc in hexanes) = 0.81. Due to the presence of just 4% of *E*-**14**, only the resonance at δ 6.54 ppm could be unequivocally assigned to *E*-**14**. Some proton assignments are based upon the NOESY spectrum of the product mixture. ^1H NMR (500 MHz, $CDCl_3$): δ 8.09 (d, 1H, Ar-H_4, *J* = 8.8 Hz, *Z*-isomer), 7.53-7.48 (m, 2H, Ar-H_6, Ar-H_7, *Z*-isomer), 7.40 (ddd, 1H, Ar-H_5, *J* = 8.0; 6.6; 1.5 Hz, *Z*-isomer), 7.01 (td, 1H, $H_{1'}$, *J* = 8.8; 1.7 Hz, *Z*-isomer), 6.54 (dt, 1H, $H_{1'}$, *J* = 14.6; 7.3 Hz, *E*-isomer), 5.87 (q, 1H, $H_{2'}$, J_{app} = 7.3 Hz, *Z*-isomer), 2.42 (dq, 2H, CH_2, $H_{3'}$, *J* = 8.8; 1.7 Hz, *Z*-isomer), 1.49 (quint, 2H, CH_2, $H_{4'}$, *J* = 7.3 Hz, Z-isomer), 1.31-1.23 (m, 8H, *Z*-isomer), 0.85 (t, 3H, *J* = 7.0 Hz, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$, due to a small amount of the *E*-isomer, some C resonances of this minor isomer may not have been detected): δ 145.4, 133.1, 131.6, 130.2, 128.0, 127.9, 124.4, 124.3, 124.0, 123.0, 120.4, 120.1, 110.2, 109.9, 31.96, 31.90, 30.4, 29.39, 29.32, 29.31, 29.2, 27.9, 22.82, 22.76, 14.2. HRMS (ESI) calcd for $C_{15}H_{22}N_3$ $[M+H]^+$ 244.1808, found 244.1808.

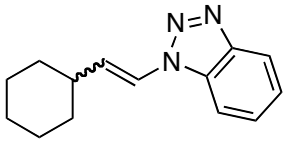
(*E*/*Z*)-1-(3-Ethylpent-1-enyl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-15)



Method A. 2-Ethylbutanal: 44.0 mg (0.439 mmol, 1.50 molar equiv); sulfone **5**: 100 mg (0.293 mmol, 1.00 molar equiv); LHMDS: 703 μL (0.703 mmol, 2.4 molar equiv); THF: 5.0 mL. Reaction time: 30 min. Column chromatography: eluting solvent 20% EtOAc in hexanes. Yield: 46.0 mg (73%) of *E*/*Z*-**15** (*E*/*Z* 22/78) as a yellow oily product. R_f (30% EtOAc in hexanes) = 0.62. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.08 (d, *J* = 8.3 Hz, 1H *Z*-isomer and 1H *E*-isomer), 7.66 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.55-7.49 (m, 2H *Z*-isomer and 1H *E*-isomer), 7.41-7.38 (m, 1H *Z*-isomer and 1H *E*-isomer), 7.28 (d, 1H, *J* = 14.2 Hz, *E*-isomer), 7.03 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.26 (dd, 1H, *J* = 14.2; 9.3 Hz, *E*-isomer), 5.62 (dd, 1H, *J* = 10.3; 8.8 Hz, *Z*-isomer), 2.78-2.70 (m, 1H, *Z*-isomer), 2.13-2.03 (m, 1H, *E*-isomer), 1.65-1.32 (m, 2 CH_2 *E*-isomer and 2 CH_2 *Z*-isomer), 0.97 (t, 2 CH_3, *J* = 7.5 Hz, *E*-isomer), 0.86 (t, 2 CH_3, *J* = 7.3 Hz, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.3, 145.4, 135.3, 133.2, 131.6, 128.0, 127.8, 127.7, 124.4, 124.2, 123.0, 120.6, 120.3, 120.1, 110.3, 109.7, 44.7, 40.4, 27.8, 27.6, 12.0, 11.7. HRMS (ESI) calcd for $C_{13}H_{18}N_3$ $[M+H]^+$ 216.1495, found 216.1493.

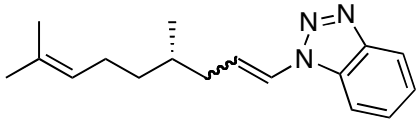
Method B. Reaction time: 16 h, *E*/*Z*-**15** 3/97. Column chromatography: eluting solvent 10% EtOAc in hexanes, 50% yield.

(*E*/*Z*)-1-(2-Cyclohexylvinyl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-16)



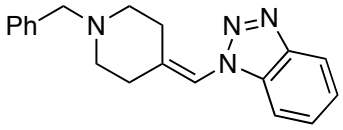
Method A. Cyclohexanecarbaldehyde: 51.0 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 120 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 20% EtOAc in hexanes. Yield: 36.0 mg (53%) of *E*/*Z*-**16** (*E*/*Z* 20/80) as a white solid. R_f (20% EtOAc in hexanes) = 0.50. ^{1}H NMR (500 MHz, $CDCl_3$, assignments based on COSY): δ 8.07 (d, 1H, *J* = 8.3 Hz, *Z*-isomer), 8.06 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.63 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.52-7.49 (m, 1H *E*-isomer and 2H *Z*-isomer), 7.41-7.39 (m, 1H *E*-isomer and 1H *Z*-isomer), 7.27 (dd, 1H, *J* = 14.6; 1.8 Hz, *E*-isomer), 6.86 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.47 (dd, 1H, *J* = 14.6; 7.3 Hz, *E*-isomer), 5.67 (dd, 1H, *J* = 9.6; 8.8 Hz, *Z*-isomer), 2.80-2.71 (m, 1H, *Z*-isomer), 2.32-2.23 (m, 1H, *E*-isomer), 1.93-1.78 (m, both *E* and *Z* isomers), 1.74-1.60 (m, both *E* and *Z* isomers), 1.41-1.12 (m, both *E* and *Z* isomers). ^{13}C NMR (125 MHz, $CDCl_3$): δ 146.4, 145.4, 135.5, 133.2, 131.7, 129.4, 128.0, 127.9, 124.4, 124.3, 121.6, 120.4, 120.1, 118.4, 110.3, 109.7, 39.1, 36.5, 33.0, 32.9, 26.1, 26.0, 25.6. HRMS (ESI) calcd for $C_{14}H_{18}N_3$ $[M+H]^+$ 228.1495, found 228.1495.

(*S*,*E*/*Z*)-1-(4,8-Dimethylnona-1,7-dienyl)-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-17)



Method A. (*S*)-(–)-Citronellal: 69.4 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 60 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 15% EtOAc in hexanes. Yield: 65.0 mg (80%) of *E*/*Z*-**17** (*E*/*Z* 16/84) as a yellow oily product. R_f (20% EtOAc in hexanes) = 0.61. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, 1H, *J* = 8.8 Hz, *Z*-isomer) 7.64 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 7.53-7.47 (m, both *E* and *Z* isomers), 7.39 (ddd, 1H, *J* = 8.1; 6.8; 1.0 Hz, *Z*-isomer), 7.29 (d, 1H, *J* = 14.6 Hz, *E*-isomer), 7.04 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.49 (dt, 1H, *J* = 14.6; 7.2 Hz, *E*-isomer), 5.87 (app q, 1H, *J* ~ 7.2 Hz, *Z*-isomer), 5.12-5.02 (m, both *E* and *Z* isomers), 2.40-1.80 (m, both *E* and *Z* isomers), 1.64-0.74 (m, both *E* and *Z* isomers). ^{13}C NMR (125 MHz, $CDCl_3$, due to smaller amount of the *E*-isomer, some C resonances of this minor isomer may not have been detected): δ 145.4, 133.1, 131.5, 128.9, 128.1, 127.9, 124.7, 124.6, 124.5, 124.3, 123.8, 122.4, 121.1, 120.4, 120.2, 110.2, 109.9, 37.7, 36.79, 36.75, 34.8, 32.9, 25.90, 25.86, 25.74, 25.65, 19.6, 17.9, 17.8. HRMS (ESI) calcd for $C_{17}H_{24}N_3$ $[M+H]^+$ 270.1965, found 270.1980.

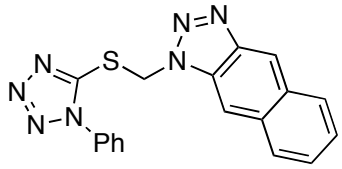
1-[(1-Benzylpiperidin-4-ylidene)methyl]-1*H*-benzo[*d*][1,2,3]triazole (18)



Method A. *N*-Benzylpiperidone: 85.0 mg (0.450 mmol, 1.50 molar equiv); sulfone **5**: 102 mg (0.300 mmol, 1.00 molar equiv). LHMDS: 720 μL (0.720 mmol, 2.4 molar equiv); THF: 5.1 mL. Reaction time: 180 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes. Yield: 70.0 mg (77%) of **18** as a brown solid. R_f (20% EtOAc in hexanes) = 0.34. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.07 (d, 1H, *J* = 8.5 Hz), 7.50 (ddd, 1H, *J* = 7.9; 6.8; 0.9 Hz), 7.45 (d, 1H, *J* = 8.2 Hz), 7.38 (td, 1H, *J* = 7.9; 6.9; 1.2 Hz), 7.35-7.25 (m, 5H), 6.89 (s, 1H), 3.58 (s, 2H), 2.66-2.43 (m, 8H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.5, 140.8, 137.5, 133.5, 129.5, 128.6, 127.9, 127.6, 124.3, 120.2, 115.2, 110.0, 62.7, 54.4, 53.8, 32.8, 28.6. HRMS (ESI) calcd for $C_{19}H_{21}N_4$ $[M+H]^+$ 305.1761, found 305.1773.

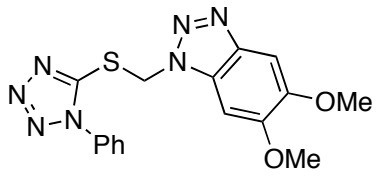
Cycloaddition Reactions of Azide 3 with Substituted Benzynes: General Procedure. To a mixture of 5-[(azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**, 3-(trimethylsilyl)aryl trifluoromethanesulfonate (1.50–2.50 molar equiv, see individual compound headings), 18-Cr-6 (4.00 molar equiv) and KF (4.00 molar equiv) under N_2, dry CH_3CN was added. The reaction mixture was allowed to stir at room temperature until TLC (SiO_2, 40% EtOAc in hexanes) showed complete consumption of **3**, water was added, and the aqueous layer was extracted with ethyl acetate (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the products were isolated by column chromatography using silica gel (mesh 200–300). For details, please see individual compound headings.

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-naphtho[2,3-*d*][1,2,3]triazole (19)



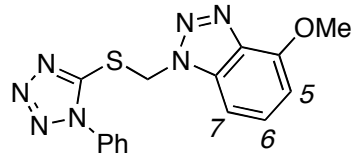
5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 300 mg (1.28 mmol, 1.00 molar equiv); 3-(trimethylsilyl)-2-naphthyl trifluoromethanesulfonate: 1.12 g (3.22 mmol, 2.50 molar equiv); 18-Cr-6: 1.37 g (5.12 mmol, 4.00 molar equiv); KF: 300 mg (5.12 mmol, 4.00 molar equiv); CH_3CN: 60.0 mL. Reaction time: 7 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 351 mg (76%) of **19** as a white solid. R_f (40% EtOAc in hexanes) = 0.33. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (s, 1H, Ar-H), 8.28 (s, 1H, Ar-H), 8.05 (d, 1H, Ar-H, J = 8.8 Hz), 8.02 (d, 1H, Ar-H, J = 8.3 Hz), 7.55 (t, 1H, Ar-H, J = 6.8 Hz), 7.49-7.46 (m, 4H, Ar-H), 7.38-7.37 (m, 2H, Ar-H), 6.78 (s, 2H, CH_2). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 145.5, 133.6, 133.2, 131.0, 130.8, 130.7, 130.1, 129.5, 128.5, 127.4, 125.4, 124.0, 118.7, 106.7, 49.9. HRMS (ESI) calcd for $C_{18}H_{14}N_7S$ $[M+H]^+$ 360.1026, found 360.1025.

5,6-Dimethoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (20)



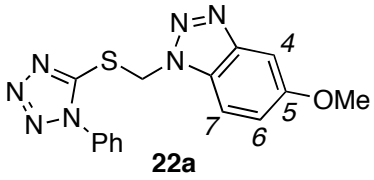
5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 116 mg (0.500 mmol, 1.00 molar equiv); 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: 269 mg (0.750 mmol, 1.5 molar equiv); 18-Cr-6: 528 mg (2.00 mmol, 4.00 molar equiv); KF: 116 mg (2.00 mmol, 4.00 molar equiv); CH_3CN: 24.0 mL. Reaction time: 4 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 157 mg (85%) of **20** as a white solid. R_f (30% EtOAc in hexanes) = 0.15. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52-7.51 (m, 3H, Ar-H), 7.42-7.39 (m, 3H, Ar-H), 7.32 (s, 1H, Ar-H), 6.59 (s, 2H, CH_2), 4.01 (s, 3H, OCH_3), 3.95 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 152.4, 149.2, 140.8, 133.1, 130.8, 130.1, 128.1, 124.0, 99.0, 91.5, 56.8, 56.5, 49.5. HRMS (ESI) calcd for $C_{16}H_{16}N_7O_2S$ $[M+H]^+$ 370.1081, found 370.1060.

4-Methoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio)methyl]}-1*H*-benzo[*d*][1,2,3]triazole (21)



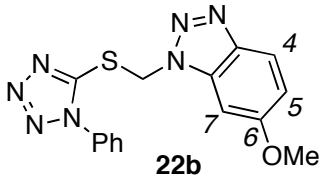
5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 70.0 mg (0.300 mmol, 1.00 molar equiv); 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: 197 mg (0.600 mmol, 2.00 molar equiv); 18-Cr-6: 317 mg (1.20 mmol, 4.00 molar equiv); KF: 70.0 mg (1.20 mmol, 4.00 molar equiv); CH_3CN: 14.0 mL. Reaction time: 2 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 69.0 mg (68%) of **21** as a yellow oily product. R_f (30% EtOAc in hexanes) = 0.24. Structure assignment was based upon the NOESY spectrum, which showed a correlation between the CH_2 and Ar-H_7, but no correlation was observed between the CH_2 and the OCH_3. Proton assignments are based on the NOESY spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.51-7.50 (m, 3H, Ar-H), 7.45-7.39 (m, 4H, Ar-H), 6.72 (d, 1H, Ar-H_5, J = 7.8 Hz), 6.60 (s, 2H, CH_2), 4.09 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 151.8, 138.0, 134.5, 133.0, 130.6, 130.0, 129.9, 123.9, 104.3, 102.5, 56.5, 49.4. HRMS (ESI) calcd for $C_{15}H_{14}N_7OS$ $[M+H]^+$ 340.0975, found 340.0979.

5- and 6-Methoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (22a and 22b)



22a

and

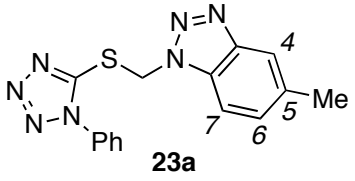


22b

5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 70.0 mg (0.300 mmol, 1.00 molar equiv); 4-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: 197 mg (0.600 mmol, 2.00 molar equiv); 18-Cr-6: 317 mg (1.20 mmol, 4.00 molar equiv); KF: 70.0 mg (1.20 mmol, 4.00 molar equiv); CH_3CN: 14.0 mL. Reaction time: 2 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 86.0 mg (85%) of **22a** and **22b** (40:60, respectively) as a white solid. R_f (30% EtOAc in hexanes) = 0.18. HRMS (ESI) calcd for $C_{15}H_{14}N_7OS$ $[M+H]^+$ 340.0975, found 340.0973.

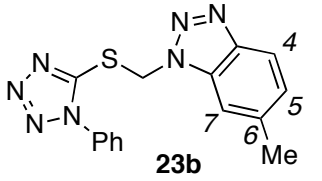
For the purpose of structure determination, small amounts of pure **22a** and **22b** were obtained by partial separation of a mixture by column chromatography (20% EtOAc in hexanes, with very slow increase to 30% EtOAc in hexanes), **22b** eluted first, followed by the mixture, and then **22a**. Structure assignment was based upon the NOESY spectrum of **22a**, which showed a correlation between the CH_2 and Ar-H_7 doublet at δ 7.81 ppm. Proton assignments in **22a** are based on the NOESY spectrum. Proton assignments in **22b** are based upon comparisons to the chemical shifts and splitting pattern of the protons in **22a**. ^{1}H NMR (500 MHz, $CDCl_3$): **22a**: δ 7.81 (d, 1H, Ar-H_7, J = 8.8 Hz), 7.53-7.51 (m, 3H, Ar-H), 7.42-7.41 (m, 2H, Ar-H), 7.35 (d, 1H, Ar-H_4, J = 2.0 Hz), 7.20 (dd, 1H, Ar-H_6, J = 8.8; 2.0 Hz), 6.60 (s, 2H, CH_2), 3.88 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.9, 152.3, 147.5, 133.2, 130.8, 130.2, 128.2, 124.0, 121.3, 111.5, 99.2, 56.0, 49.5. **22b**: δ 7.87 (d, 1H, Ar-H_4, J = 9.3 Hz), 7.52-7.51 (m, 3H, Ar-H), 7.41-7.39 (m, 2H, Ar-H), 7.33 (d, 1H, Ar-H_7, J = 2.0 Hz), 7.00 (dd, 1H, Ar-H_5, J = 9.3; 2.0 Hz), 6.60 (s, 2H, CH_2), 3.92 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 161.0, 152.5, 141.6, 134.0, 133.2, 130.8, 130.2, 124.0, 120.9, 117.5, 91.2, 56.2, 49.4.

5- and 6-Methyl-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (23a and 23b)



23a

and

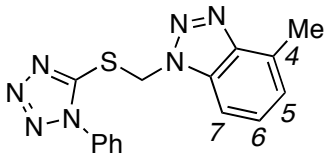


23b

5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 70.0 mg (0.300 mmol, 1.00 molar equiv); 4-methyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: 187 mg (0.600 mmol, 2.00 molar

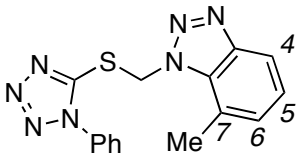
equiv); 18-Cr-6: 317 mg (1.20 mmol, 4.00 molar equiv); KF: 70.0 mg (1.20 mmol, 4.00 molar equiv); CH_3CN: 14.0 mL. Reaction time: 4 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 77.8 mg (80%) of **23a** and **23b** (45:55, respectively) as a brown solid. R_f (20% EtOAc in hexanes) = 0.09. Structures were assigned based upon the NOESY spectrum of the product mixture. A correlation was observed between the CH_2 at δ 6.58 ppm and the Ar-H singlet at δ 7.60 ppm for the major isomer, indicating it to be **23b**. For the minor isomer, a correlation was observed between the CH_2 at δ 6.61 ppm and the Ar-H doublet at δ 7.78 ppm, consistent with **23a**. Proton assignments are based on the NOESY and COSY spectra. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.90 (d, 1H, *J* = 8.8 Hz, **23b**), 7.79 (s, 1H, Ar-H, **23a**), 7.78 (d, 1H, *J* = 9.3 Hz, **23a**), 7.60 (s, 1H, **23b**), 7.52-7.50 (m, **23a** and **23b**), 7.41-7.38 (m, **23a** and **23b**), 7.35 (s, 1H, Ar-H, **23a**), 7.22 (d, 1H, *J* = 8.3 Hz, **23b**), 6.61 (s, 2H, CH_2, **23a**), 6.58 (s, 2H, CH_2, **23b**), 2.53 (s, 3H, CH_3, **23b**), 2.50 (s, 3H, CH_3, **23a**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.24, 152.16, 147.0, 145.0, 139.6, 135.0, 133.2, 133.1, 131.2, 130.79, 130.76, 130.4, 130.12, 130.10, 127.1, 124.0, 123.98, 121.4, 119.8, 119.2, 110.2, 109.8, 49.4, 49.3, 22.3, 21.6. HRMS (ESI) calcd for $C_{15}H_{14}N_7S$ $[M+H]^+$ 324.1026, found 324.1029.

4- and 7-Methyl-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (24a and 24b)



24a

and

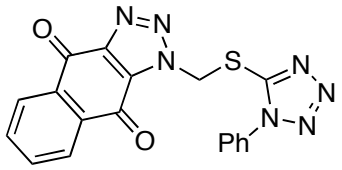


24b

5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 70.0 mg (0.300 mmol, 1.00 molar equiv); 2-methyl-6-(trimethylsilyl)phenyl trifluoromethanesulfonate: 187 mg (0.600 mmol, 2.00 molar equiv); 18-Cr-6: 317 mg (1.20 mmol, 4.00 molar equiv); KF: 70.0 mg (1.20 mmol, 4.00 molar equiv); CH_3CN: 14.0 mL. Reaction time: 2 h. Column chromatography: eluting solvent 20% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 86.0 mg (89%) of **24a** and **24b** (49:51, respectively) as a brown solid. R_f (20% EtOAc in hexanes) = 0.10. Structures were assigned based upon the NOESY spectrum of the product mixture. A correlation was observed between the CH_2 at δ 6.61 ppm and the Ar-H doublet at δ 7.67 ppm, indicating it to be **24a**. A correlation observed between the CH_2 at δ 6.67 ppm and the Me singlet at δ 2.80 ppm is consistent with **24b**. Assignments of some of the proton resonances are

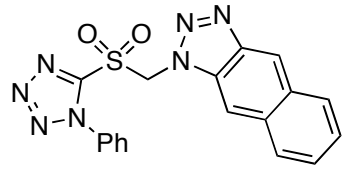
based on the NOESY spectrum. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.88 (d, 1H, *J* = 7.8 Hz, **24b**), 7.67 (d, 1H, *J* = 8.3 Hz, **24a**) 7.51-7.48 (m, **24a** and **24b**), 7.45-7.37 (m, **24a** and **24b**), 7.30-7.22 (m, **24a** and **24b** overlapping with $CDCl_3$), 7.15 (d, 1H, *J* = 7.8 Hz, **24a**), 6.67 (s, 2H, CH_2, **24b**), 6.61 (s, 2H, CH_2, **24a**), 2.80 (s, 3H, CH_3, **24b**), 2.77 (s, 3H, CH_3, **24a**). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 151.0, 146.7, 146.1, 133.1, 133.0, 132.5, 131.9, 131.1, 130.62, 130.60, 130.01, 129.97, 129.95, 128.5, 125.1, 124.6, 123.94, 123.88, 120.9, 118.3, 107.8, 50.8, 49.4, 18.3, 16.7. HRMS (ESI) calcd for $C_{15}H_{14}N_7S$ $[M+H]^+$ 324.1026, found 324.1032.

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-naphtho[2,3-*d*][1,2,3]triazole-4,9-dione (25)



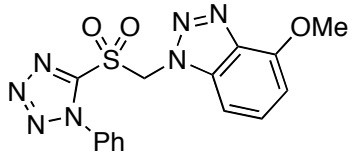
H_5IO_6 (126 mg, 0.553 mmol, 3.98 molar equiv) was dissolved in dry CH_3CN (2.50 mL) by vigorous stirring at rt for 30 min. A catalytic amount of CrO_3 (ca 1.0 mg) was added and the reaction mixture was stirred for an additional 5 min to give an orange colored solution. After 5 min, H_5IO_6/CrO_3 mixture was added to a solution of 1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-naphtho[2,3-*d*][1,2,3]triazole (**19**, 50.0 mg, 0.139 mmol, 1.00 molar equiv) in CH_3CN (5.0 mL) under a N_2 balloon. The reaction mixture was stirred at rt for 3 h at which time TLC (SiO_2, 40% EtOAc in hexanes) showed a complete consumption of **19**. The reaction mixture was cooled on ice and sat aq $NaHCO_3$ was added, followed by solid sodium bisulfite addition. The aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, 10% EtOAc in hexanes with a stepwise increase to 40% EtOAc in hexanes) to yield 36.0 mg (67%) of **25** as a yellow solid. R_f (40% acetone in hexanes) = 0.35. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 (d, 1H, Ar-H, *J* = 7.5 Hz), 8.24 (d, 1H, Ar-H, *J* = 7.8 Hz), 7.89 (t, 1H, Ar-H, *J* = 7.5 Hz), 7.84 (t, 1H, Ar-H, *J* = 7.5 Hz), 7.52-7.47 (m, 5H, Ar-H), 6.58 (s, 2H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 176.5, 175.7, 150.6, 145.6, 135.8, 134.7, 133.7, 133.6, 133.2, 132.7, 130.9, 130.2, 128.3, 127.7, 124.3, 50.7. HRMS (ESI) calcd for $C_{18}H_{11}N_7NaO_2S$ $[M+Na]^+$ 412.0587, found 412.0562.

1-{[(1-Phenyl-1*H*-tetrazol-5-yl)sulfonyl]methyl}-1*H*-naphtho[2,3-*d*][1,2,3]triazole (26)



1-{[(1-Phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-naphtho[2,3-*d*][1,2,3]triazole **19** (300 mg, 0.831 mmol, 1.00 molar equiv) was dissolved in CH_3CN (30.0 mL). Separately, H_2O_2 (50% H_2O_2 in water, d = 1.2 g/mL, 5.89 mL, 3.53 g of H_2O_2, 104 mmol, 125 molar equiv) was slowly added to $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O$ (1.023 g, 0.831 mmol, 1.00 molar equiv), and the resulting solution was added to the solution of **19** in CH_3CN. The reaction mixture was stirred at rt for 24 h at which time TLC (SiO_2, 40% EtOAc in hexanes) showed a complete consumption of **19**. Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, 20% EtOAc in hexanes with a stepwise increase to 40% EtOAc in hexanes) to yield 225 mg (69%) of **26** as a white solid. R_f (30% EtOAc in hexanes) = 0.49. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1H, Ar-H), 8.09-8.08 (m, 2H, Ar-H), 7.99 (d, 1H, Ar-H, *J* = 8.3 Hz), 7.58 (t, 1H, Ar-H, *J* = 7.5 Hz), 7.52 (t, 1H, Ar-H, *J* = 7.0 Hz), 7.48 (t, 1H, Ar-H, *J* = 7.0 Hz), 7.43-7.36 (m, 4H, Ar-H), 6.59 (s, 2H, CH_2). ^{13}C NMR (125 MHz, DMSO-d_6): 151.9, 144.1, 132.9, 132.4, 131.5, 131.1, 130.5, 129.3, 129.1, 128.0, 127.5, 126.2, 125.3, 118.1, 106.7, 67.5. HRMS (ESI) calcd for $C_{18}H_{14}N_7O_2S$ $[M+H]^+$ 392.0924, found 392.0912.

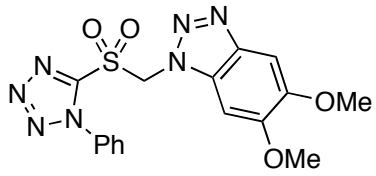
4-Methoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)sulfonyl]methyl}-1*H*-benzo[*d*][1,2,3]triazole (27)



4-Methoxy1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole **21** (15.0 mg, 0.044 mmol, 1.00 molar equiv) was dissolved in CH_3CN (1.5 mL). Separately, H_2O_2 (50% H_2O_2 in water, d = 1.2 g/mL, 312 μL, 187 mg of H_2O_2, 5.50 mmol, 125 molar equiv) was slowly added to $Mo_7O_{24}(NH_4)_6{\cdot}4H_2O$ (55.0 mg, 0.044 mmol, 1.00 molar equiv), and the resulting solution was added to the solution of **21** in CH_3CN. The reaction mixture was stirred at rt for 24 h at which time TLC (SiO_2, 40% EtOAc in hexanes) showed a complete consumption of **21**. Water was added to the reaction mixture and the aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by

column chromatography (SiO_2, 10% EtOAc in hexanes with a stepwise increase to 40% EtOAc in hexanes) to yield 8.4 mg (51%) of **27** as a white solid. R_f (30% EtOAc in hexanes) = 0.26. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.52 (t, 1H, Ar-H, J = 7.8 Hz), 7.49-7.45 (m, 3H, Ar-H), 7.40-7.38 (m, 2H, Ar-H), 7.16 (d, 1H, Ar-H, J = 8.3 Hz), 6.75 (d, 1H, Ar-H, J = 7.8 Hz), 6.41 (s, 2H, CH_2), 4.11 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.3, 152.1, 138.0, 135.2, 132.5, 131.9, 131.0, 129.7, 125.5, 105.2, 101.5, 67.7, 56.8. HRMS (ESI) calcd for $C_{15}H_{14}N_7O_3S$ $[M+H]^+$ 372.0873, found 372.0895.

5,6-Dimethoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)sulfonyl]methyl}-1*H*-benzo[*d*][1,2,3]triazole (28)



Due to poor solubility of purified 5,6-dimethoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*-benzo[*d*][1,2,3]triazole (**20**) in $CHCl_3$, crude sulfide **20,** obtained in a cycloaddition reaction of **3** and dimethoxy substituted benzyne, was subjected to oxidation to sulfone **28**.

Step 1: 5-[(Azidomethyl)thio]-1-phenyl-1*H*-tetrazole **3**: 116 mg (0.500 mmol, 1.00 molar equiv); 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate: 269 mg (0.750 mmol, 1.5 molar equiv); 18-Cr-6: 528 mg (2.00 mmol, 4.00 molar equiv); KF: 116 mg (2.00 mmol, 4.00 molar equiv); CH_3CN: 24.0 mL. Reaction time: 4 h. Upon complete consumption of **3**, water was added, and the aqueous layer was extracted with ethyl acetate (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product **20** was subjected to oxidation.

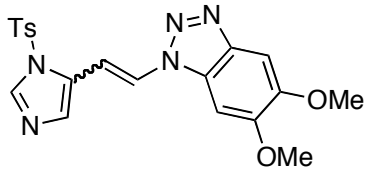
Step 2: To a stirred solution of crude 5,6-dimethoxy-1-{[(1-phenyl-1*H*-tetrazol-5-yl)thio]methyl}-1*H*benzo[*d*][1,2,3] triazole **20** in $CHCl_3$ (20.0 mL) at –10 ˚C (ice/NaCl cooling bath), a solution of *m*-CPBA (690 mg, 4.00 mmol, 8.00 molar equiv) in $CHCl_3$ (40.0 mL) was added dropwise. After complete addition, the mixture was allowed to warm to rt. The reaction mixture was stirred at rt for 30 h at which time TLC (SiO_2, 40% EtOAc in hexanes) showed complete consumption of starting material **20**. The reaction was quenched with aqueous solution of $NaHCO_3$ and sodium bisulfite. The aqueous layer was extracted with EtOAc (3 x), the combined organic layer was washed with water and brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the crude product was purified by column chromatography (SiO_2, 20% EtOAc in hexanes with a stepwise increase to 50% EtOAc in hexanes) to yield 115 mg

(57% over two steps) of **28** as a white solid. R_f (40% EtOAc in hexanes) = 0.41. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.53 (t, 1H, Ar-H, J = 7.3 Hz), 7.47 (t, 2H, Ar-H, J = 8.3 Hz), 7.38-7.36 (m, 3H, Ar-H), 7.01 (s, 1H, Ar-H), 6.38 (s, 2H, CH_2), 3.99 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.0, 152.3, 149.5, 140.6, 132.5, 131.9, 129.8, 128.6, 125.5, 99.5, 90.3, 67.8, 56.8, 56.6. HRMS (ESI) calcd for $C_{16}H_{16}N_7O_4S$ $[M+H]^+$ 402.0979, found 402.0973.

Condensations of Sulfone 28 with Carbonyl Compounds

Method A. General Procedure. A stirring solution of aldehyde (1.20 molar equiv) and benzotriazole-derived sulfone **28** (1.00 molar equiv) in THF (40.0 mL/mmol of sulfone **28**) was cooled to 0 ˚C and under N_2, LHMDS (1.0 M solution in THF, 2.40 molar equiv) was added to the reaction mixture. The reaction mixture was stirred at 0 ˚C and monitored by TLC for disappearance of sulfone **28**. Upon complete consumption of **28**, saturated aq NH_4Cl was added and the mixture was poured into EtOAc. Organic layer was separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the combined *E*/*Z* product mixture was isolated by column chromatography using silica gel (mesh 200–300). The product *E*/*Z* ratio was determined by ^{1}H NMR, prior to purification by column chromatography. For each substrate, the quantities of reactants and solvent, reaction time, product yield, eluting solvent for chromatography, R_f value, and spectroscopic data are provided under the individual compound headings.

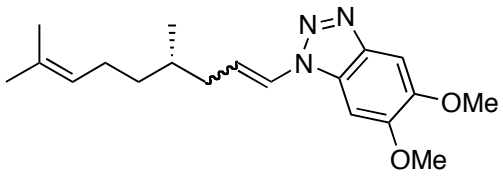
(*E* / *Z*), (*E*)-, and (*Z*)-5,6-Dimethoxy-1-[2-(1-tosyl-1*H*-imidazol-5-yl)vinyl]-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-29, *E*-29, *Z*-29)



1-Tosyl-1*H*-imidazole-5-carbaldehyde: 45.0 mg (0.180 mmol, 1.20 molar equiv); sulfone **28**: 60.0 mg (0.150 mmol, 1.00 molar equiv); LHMDS: 360 µL (0.360 mmol, 2.40 molar equiv); THF: 6.0 mL. Reaction time: 25 min. Column chromatography: eluting solvent 10% EtOAc in hexanes, with a stepwise increase to 40% EtOAc in hexanes (isomers separate under these conditions, but were collected together). Yield: 51.0 mg of *E/Z*-**29** (80%, *E/Z* 60/40, white solid). R_f (40% EtOAc in hexanes): *E*-**29** = 0.21; *Z*-**29** = 0.13. HRMS (ESI) calcd for $C_{20}H_{20}N_5O_4S$ $[M+H]^+$ 426.1231, found 426.1217.

E/*Z*-**29** mixture was separated by column chromatography (60% EtOAc in hexanes, with a stepwise increase to 100% EtOAc) to yield *E*-**29** as the early eluting and *Z*-**29** as the late eluting isomer. *E*-**29**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (s, 1H), 8.02 (d, 1H, *J* = 14.2 Hz), 7.87 (d, 2H, *J* = 7.8 Hz), 7.39 (d, 2H, *J* = 8.8 Hz), 7.38 (s, 1H), 7.32 (s, 1H), 7.31 (d, 1H, *J* = 13.2 Hz), 6.98 (s, 1H), 4.00 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3) 2.46 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.4, 149.2, 146.8, 140.6, 140.0, 137.4, 134.8, 130.8, 127.6, 127.3, 122.4, 115.4, 110.5, 99.4, 90.3, 56.7, 56.5, 22.0. *Z*-**29**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (s, 1H), 7.70 (d, 2H, *J* = 8.3 Hz), 7.43 (s, 2H), 7.31 (d, 2H, *J* = 7.8 Hz), 7.10 (d, 1H, *J* = 9.3 Hz), 6.62 (d, 1H, *J* = 9.8 Hz), 6.53 (s, 1H), 3.97 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 2.44 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.1, 149.2, 146.8, 140.0, 137.6, 136.2, 134.6, 130.7, 127.6, 127.5, 120.3, 118.3, 118.2, 99.3, 90.8, 56.5, 56.4, 22.0.

(*S*,*E*/*Z*)-1-(4,8-Dimethylnona-1,7-dienyl)-5,6-dimethoxy-1*H*-benzo[*d*][1,2,3]triazole (*E*/*Z*-30)

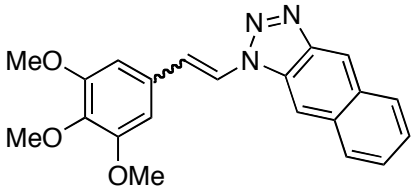


(*S*)-(–)-Citronellal: 28.0 mg (0.182 mmol, 1.21 molar equiv); sulfone **28**: 60.0 mg (0.150 mmol, 1.00 molar equiv); LHMDS: 360 µL (0.360 mmol, 2.40 molar equiv); THF: 6.0 mL. Reaction time: 25 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 10% EtOAc in hexanes. Yield: 34.0 mg (69%) of *E/Z*-**30** (*E/Z* 41/59) as a yellow oily product. R_f (40% EtOAc in hexanes) = 0.65. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (s, 1H, *Z*-isomer), 7.38 (s, 1H, *E*-isomer), 7.18 (d, 1H, *J* = 14.2 Hz, *E*-isomer), 6.97 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.92 (s, 1H, *Z*-isomer), 6.78 (s, 1H, *E*-isomer), 6.45 (dt, 1H, *J* = 14.2; 7.8 Hz, *E*-isomer), 5.85 (app q, 1H, *J* ~ 7.3 Hz, *Z*-isomer), 5.11 (t, 1H, *J* = 7.3 Hz, *E*-isomer), 5.04 (t, 1H, *J* = 7.3 Hz, *Z*-isomer), 4.00 (s, 3H, OCH_3, *E*-isomer), 3.98 (s, one OCH_3 *E*-isomer and two OCH_3 *Z*-isomer), 2.46-1.87 (m, both *E* and *Z*-isomers), 1.69 (s, CH_3, *E*-isomer), 1.65 (s, CH_3, *Z*-isomer), 1.61 (s, CH_3, *Z*-isomer), 1.55 (s, CH_3, *E*-isomer), 1.00 (d, CH_3, *J* = 6.4 Hz, *E*-isomer), 0.95 (d, CH_3, *J* = 6.8 Hz, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.0, 151.9, 148.94, 148.93, 140.7, 139.8, 131.7, 131.6, 129.0, 128.4, 126.9, 124.7, 124.6, 123.6, 122.2, 121.3, 99.3, 99.2, 90.5, 90.2, 56.54, 56.52, 56.48, 56.45, 37.7, 36.83, 36.78, 34.8, 33.0, 32.9, 25.92, 25.89, 25.80, 25.7, 19.6, 17.9, 17.8. HRMS (ESI) calcd for $C_{19}H_{28}N_3O_2$ $[M+H]^+$ 330.2176, found 330.2169.

Condensations of Sulfone 26 with Carbonyl Compounds

Method A, General Procedure. A stirring solution of aldehyde (1.50-2.20 molar equiv) and benzotriazole-derived sulfone **26** (1.00 molar equiv) in THF or DMF (see individual compound headings) was cooled to 0 ˚C and under N_2, LHMDS (1.0 M solution in THF, 2.40 molar equiv) was added to the reaction mixture. The reaction mixture was stirred at 0 ˚C and monitored by TLC for disappearance of sulfone **26**. Upon complete consumption of **26**, saturated aq NH_4Cl was added and the mixture was poured into EtOAc. Organic layer was separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water and brine and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the combined *E*/*Z* product mixture was isolated by column chromatography using silica gel (mesh 200–300). The product *E*/*Z* ratio was determined by ^{1}H NMR, prior to purification by column chromatography. For each substrate, the quantities of reactants and solvent, reaction time, product yield, eluting solvent for chromatography, R_f value, and spectroscopic data are provided under the individual compound headings. Due to poor solubility of sulfone **26** in THF at 0 ˚C, crude sulfone **26** was used (~70% purity) when THF was used as solvent.

(*E*/*Z*)-1-(3,4,5-Trimethoxystyryl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*E*/*Z*-31)



Method A. *In THF as solvent:*

3,4,5-Trimethoxybenzaldehyde: 45.0 mg (0.229 mmol, 2.14 molar equiv); sulfone **26**: 60.0 mg (crude **26**, ~70% purity, ~0.107 mmol, 1.00 molar equiv); LHMDS: 360 µL (0.360 mmol, 3.36 molar equiv); THF: 6.0 mL. Reaction time: 20 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 31.0 mg (80%) of *E/Z*-**31** (*E/Z* 65/35) as a yellow solid. R_f (30% EtOAc in hexanes) = 0.30. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H, *E*-isomer), 8.65 (s, 1H, *Z*-isomer), 8.24 (s, 1H, *E*-isomer), 8.10 (d, 1H, *J* = 8.3 Hz, *E*-isomer), 8.08-8.05 (m, both *E* and *Z* isomers), 7.76 (d, 1H, *J* = 7.8 Hz, *Z*-isomer), 7.58 (t, 1H, *J* = 7.6 Hz, *E*-isomer), 7.53 (t, 1H, *J* = 7.3 Hz, *E*-isomer), 7.47-7.42 (m, both *E* and *Z* isomers), 7.38 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.82 (s, 2H, *E*-isomer), 6.74 (d, 1H, *J* = 9.3 Hz, *Z*-isomer), 6.28 (s, 2H, *Z*-isomer), 3.97 (s, 2 OCH_3, *E*-isomer), 3.91 (s, 1 OCH_3, *E*-isomer), 3.74 (s, 1 OCH_3, *Z*-isomer), 3.44 (s, 2 OCH_3, *Z*-isomer). ^{13}C NMR (125 MHz, $CDCl_3$): δ 153.9, 153.1, 145.8, 144.9, 138.71, 138.66, 133.6, 133.2, 131.1, 130.8, 130.5, 130.4, 129.9, 129.7,

129.5, 128.9, 128.3, 127.4, 127.1, 125.4, 125.2, 122.4, 121.0, 119.8, 118.9, 118.2, 107.4, 106.6, 106.5, 103.9, 61.2, 61.1, 56.5, 56.0. HRMS (ESI) calcd for $C_{21}H_{20}N_3O_3$ $[M+H]^+$ 362.1499, found 362.1490.

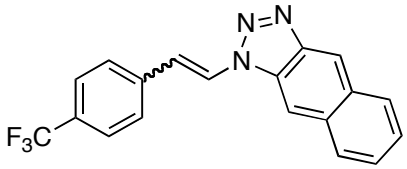
Method A. *In DMF as solvent:*

3,4,5- Trimethoxybenzaldehyde: 7.5 mg (0.038 mmol, 1.50 molar equiv); sulfone **26**: 10.0 mg (pure **26**, 0.025 mmol, 1.00 molar equiv); LHMDS: 60 µL (0.060 mmol, 2.40 molar equiv); DMF: 1.0 mL. Reaction time: 40 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes. Yield: 8.4 mg (93%) of *E/Z*-**31** (*E/Z* 37/63) as a yellow solid.

Method B. To a stirring solution of 3,4,5-trimethoxybenzaldehyde (11.2 mg, 0.057 mmol, 1.50 molar equiv) and pure sulfone **26** (14.8 mg, 0.038 mmol, 1.00 molar equiv) in refluxing THF (1.5 mL) under N_2, was added DBU (11 µL, 0.076 mmol, 2.0 molar equiv). Heating was continued at reflux for 4 h, at which time TLC showed complete consumption of sulfone **26**. The mixture was cooled, water was added, and the mixture was poured into EtOAc. The organic layer was separated and the aqueous layer was extracted with EtOAc (3 x). The combined organic layer was washed with water, brine, and dried over anhydrous Na_2SO_4. The solvent was evaporated under reduced pressure and the *E*/*Z* ratio of the product was determined by ^{1}H NMR prior to purification. The combined *E*/*Z* product mixture was purified by column chromatography (silica gel, eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 30% EtOAc in hexanes) to yield 7.1 mg (52%) of *E/Z*-**31** (*E/Z* 25/75) as a yellow solid.

Note: pure sulfone **26** was used in Method B because it dissolves in refluxing THF.

(*E*/*Z*), (*E*)-, and (*Z*)-1-(4-(Trifluoromethyl)styryl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*E*/*Z*-32, *E*-32, *Z*-32)



Method A. *In DMF as solvent:*

4-(Trifluoromethyl)benzaldehyde: 20.0 mg (0.115 mmol, 1.51 molar equiv); sulfone **26**: 30.0 mg (pure **27**, 0.076 mmol, 1.00 molar equiv); LHMDS: 180 µL (0.180 mmol, 2.40 molar equiv); DMF: 3.0 mL. Reaction time: 40 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 20% EtOAc in hexanes (isomers separate under these conditions, but were collected together). Yield: 16.0 mg (62%) of *E/Z*-**32** (*E/Z* 41/59) as a yellow

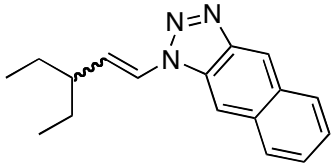
solid. R_f (30% EtOAc in hexanes): *E*-**32** = 0.75 and *Z*-**32** = 0.65. ^{19}F NMR (282 MHz, $CDCl_3$): δ –63.02 (s, *E*-isomer), –63.29 (s, *Z*-isomer). HRMS (ESI) calcd for $C_{19}H_{13}F_3N_3$ $[M+H]^+$ 340.1056, found 340.1050.

E/*Z*-**32** mixture was separated by column chromatography (SiO_2, 20% EtOAc in hexanes) to yield *E*-**32** as the early eluting and *Z*-**32** as the late eluting isomer. *E*-**32**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.70 (s, 1H), 8.22 (s, 1H), 8.19 (d, 1H, *J* = 14.6 Hz), 8.11 (d, 1H, *J* = 8.3 Hz), 8.05 (d, 1H, *J* = 8.3 Hz) 7.72-7.68 (m, 4H), 7.60 (ddd, 1H, *J* = 8.1; 6.3; 1.0 Hz), 7.54-7.51 (m, 1H, partially buried under d at 7.53 ppm), 7.53 (d, 1H, *J* = 14.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.8, 138.6, 133.7, 131.2, 130.1 (q, $^2J_{CF}$ = 33.0 Hz), 129.8, 129.7, 128.3, 127.7, 126.8, 126.2 (q, $^3J_{CF}$ = 3.8 Hz), 125.6, 124.4, 124.3 (q, $^1J_{CF}$ = 271.9 Hz), 119.2, 117.6, 106.4. *Z*-**32**: ^1H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.07 (d, 1H, *J* = 7.8 Hz), 7.74 (d, 1H, *J* = 7.8 Hz), 7.52-7.45 (m, 5H), 7.41 (s, 1H), 7.27 (d, overlapping with $CHCl_3$ in $CDCl_3$, 2H, *J* = 8.3 Hz), 6.78 (d, 1H, *J* = 9.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.1, 137.6, 133.4, 131.0, 130.5 (q, $^2J_{CF}$ = 32.5 Hz), 130.2, 129.6, 129.5, 128.2, 127.4, 125.6, (q, $^3J_{CF}$ = 3.8 Hz), 125.4, 124.0 (q, $^1J_{CF}$ = 271.9 Hz), 123.7, 123.2, 118.8, 106.9.

Method A. *In THF as solvent:*

4-(Trifluoromethyl)benzaldehyde: 6.6 mg (0.038 mmol, 2.17 molar equiv); sulfone **26**: 10.0 mg (crude **26**, ~70% purity, ~0.0175 mmol, 1.00 molar equiv); LHMDS: 60 µL (0.060 mmol, 3.43 molar equiv); THF: 1.0 mL. Reaction time: 20 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 20% EtOAc in hexanes. Yield: 3.4 mg (56%) of *E*/*Z*-**32** (*E*/*Z* 44/56) as a yellow solid.

(*E*/*Z*)-1-(3-Ethylpent-1-enyl)-1*H*-naphtho[2,3-*d*][1,2,3]triazole (*E*/*Z*-33)



Method A. *In DMF as solvent:*

2-Ethylbutanal: 11.0 mg (0.110 mmol, 1.45 molar equiv); sulfone **26**: 30.0 mg (pure **26**, 0.076 mmol, 1.00 molar equiv); LHMDS: 180 µL (0.180 mmol, 2.40 molar equiv); DMF: 3.0 mL. Reaction time: 40 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 10% EtOAc in hexanes. Yield: 15.0 mg (74%) of *E*/*Z*-**33** (*E*/*Z* 33/67) as a yellow oily product. R_f (30% EtOAc in hexanes) = 0.74. ^1H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H, *Z*-isomer), 8.08 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 8.02-7.96 (m, both *E* and *Z* isomers), 7.56-

7.42 (m, both *E* and *Z* isomers), 7.15 (d, 1H, *J* = 8.8 Hz, *Z*-isomer), 6.31 (dd, 1H, *J* = 14.2; 9.5 Hz, *E*-isomer), 5.63 (dd, 1H, *J* = 10.8; 8.8 Hz, *Z*-isomer), 2.89-2.81 (m, 1H, *Z*-isomer), 2.17-2.12 (m, 1H, *E*-isomer), 1.70-1.23 (m, both *E* and *Z* isomers), 1.01 (t, 3H, *J* = 7.8 Hz, *E*-isomer), 0.89 (t, 3H, *J* = 7.8 Hz, *Z*-isomer). HRMS (ESI) calcd for $C_{17}H_{20}N_3$ $[M+H]^+$ 266.1652, found 266.1664. *E*/*Z*-**33** mixture was separated by column chromatography (SiO_2, 5% EtOAc in hexanes) to yield *Z*-**33** as the early eluting and *E*-**33** as the late eluting isomer. *Z*-**33**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (s, 1H), 8.08 (d, 1H, *J* = 8.3 Hz), 7.99 (d, 1H, *J* = 8.8 Hz), 7.96 (s, 1H), 7.53 (t, 1H, *J* = 7.3 Hz), 7.50 (t, 1H, *J* = 7.3 Hz), 7.15 (t, 1H, *J* = 8.3 Hz), 5.64 (dd, 1H, *J* = 10.8; 8.8 Hz), 2.88-2.81 (m, 1H), 1.68-1.52 (m, 2H), 1.45-1.36 (m, 2H), 0.89 (t, 6H, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 144.7, 134.4, 133.3, 131.9, 130.9, 129.7, 128.2, 127.0, 125.0, 120.7, 118.2, 105.5, 40.5, 27.8, 11.8. *E*-**33**: ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.66 (s, 1H), 8.10 (s, 1H), 8.08 (d, 1H, *J* = 8.8 Hz), 8.02 (d, 1H, *J* = 8.3 Hz), 7.54 (t, 1H, *J* = 7.8 Hz), 7.48 (t, 1H, *J* = 7.8 Hz), 7.44 (d, 1H, *J* = 14.2 Hz), 6.31 (dd, 1H, *J* = 14.2; 9.5 Hz), 2.18-2.10 (m, 1H), 1.71-1.46 (m, 4H), 1.01 (t, 6H, *J* = 7.6 Hz). ^{13}C NMR (125 MHz, $CDCl_3$): δ 145.7, 133.5, 131.0, 130.2, 129.7, 128.3, 127.1, 126.2, 125.2, 123.5, 118.5, 106.4, 44.9, 28.1, 12.1.

Method A. *In THF as solvent:*

2-Ethylbutanal: 3.8 mg (0.038 mmol, 2.17 molar equiv); sulfone **26**: 10.0 mg (crude **26**, ~70% purity, ~0.0175 mmol, 1.00 molar equiv); LHMDS: 60 µL (0.060 mmol, 3.43 molar equiv); THF: 1.0 mL. Reaction time: 25 min. Column chromatography: eluting solvent 5% EtOAc in hexanes, with a stepwise increase to 10% EtOAc in hexanes. Yield: 2.5 mg (54%) of *E*/*Z*-**33** (*E*/*Z* 22/78) as a yellow oily product.

Attempted Isomerizations of *E*/*Z*-6 (*E*/*Z* 23/77)

I_2-Catalyzed.[1] A solution of *E*/*Z*-**6** (15.0 mg, 0.0595 mmol, 1 molar equiv) and I_2 (2.1 mg, 5.95 µmol, 0.1 molar equiv) in $CHCl_3$ (1.0 mL) was stirred at room temperature for 24 h. The reaction mixture was diluted with $CHCl_3$ and washed with aqueous sodium bisulfite, water, dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. Analysis of the crude product by ^{1}H NMR showed no change in the *E*/*Z* ratio.

Pd(II)-Catalyzed.[2] A solution of *E*/*Z*-**6** (15.0 mg, 0.0595 mmol, 1 molar equiv) in CH_2Cl_2 (0.120 mL) was added to $(CH_3CN)_2PdCl_2$ (1.5 mg, 5.95 µmol, 0.1 molar equiv) in a N_2 atmosphere. The mixture was allowed to stir at room temperature for 24 h. The mixture was filtered through Celite, the residue was washed with CH_2Cl_2, and the solvent was removed in vacuo. Analysis of the crude product by ^{1}H NMR showed no change in the *E*/*Z* ratio.

Under Basic Conditions. To a solution of *E*/*Z*-**6** (15.0 mg, 0.0595 mmol, 1 molar equiv) in dry THF (0.750 mL) under N_2 at room temperature, was added LHMDS (1.0 M in THF, 90.0 μL, 0.090 mmol, 1.5 molar equiv) dropwise. Upon complete addition, the reaction mixture was heated at reflux for 24 h and then aqueous NH_4Cl was added. The mixture was extracted with EtOAc, the organic layer was dried over anhydrous sodium sulfate, and the solvent was removed in vacuo. Analysis of the crude product by ^{1}H NMR showed no change in the *E*/*Z* ratio.

Under Photochemical Conditions. A solution of *E*/*Z*-**6** (50 mg, 0.198 mmol) in PhH (260 mL) was placed in a Hanovia photoreactor and flushed with N_2. This solution was irradiated with a 450 W medium-pressure Hg lamp for 3.5 h, using a quartz filter. The solvent was removed under reduced pressure, and analysis of the crude mixture by ^{1}H NMR showed decomposition.

References

(1) Gaukroger, K.; Hadfield, J. A.; Hepworth, L. A.; Lawrence, N. J.; McGown, A. T. *J. Org. Chem.* **2001**, *66*, 8135-8138, and references therein.

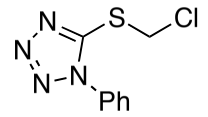
(2) Yu, J.; Gaunt, M. J.; Spencer, J. B. *J. Org. Chem.* **2002**, *67*, 4627-4629.

GS-1231-01-51-PureTS

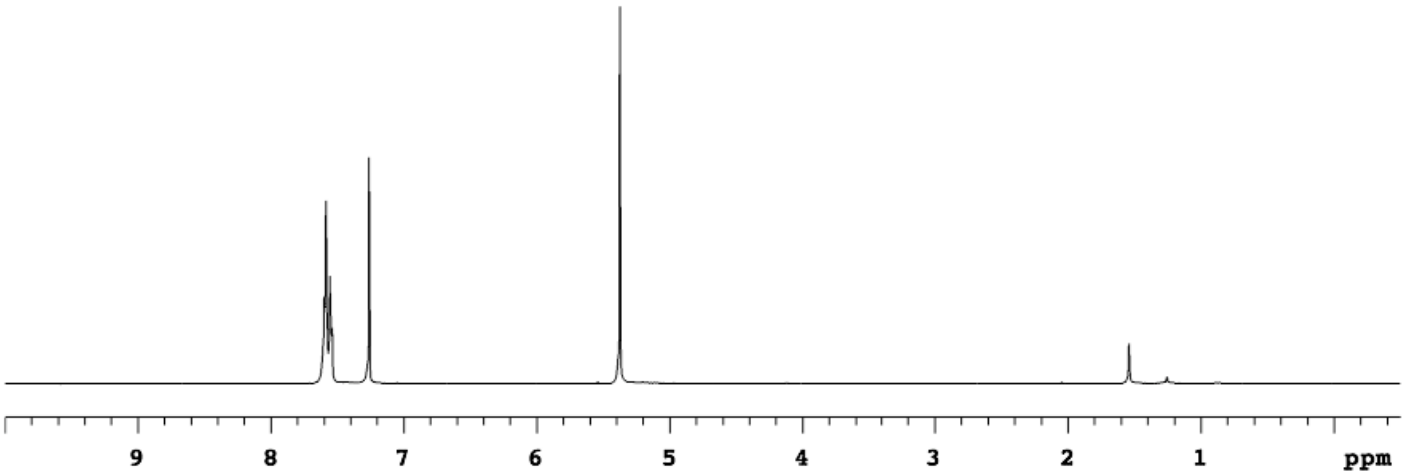
Pulse Sequence: s2pul

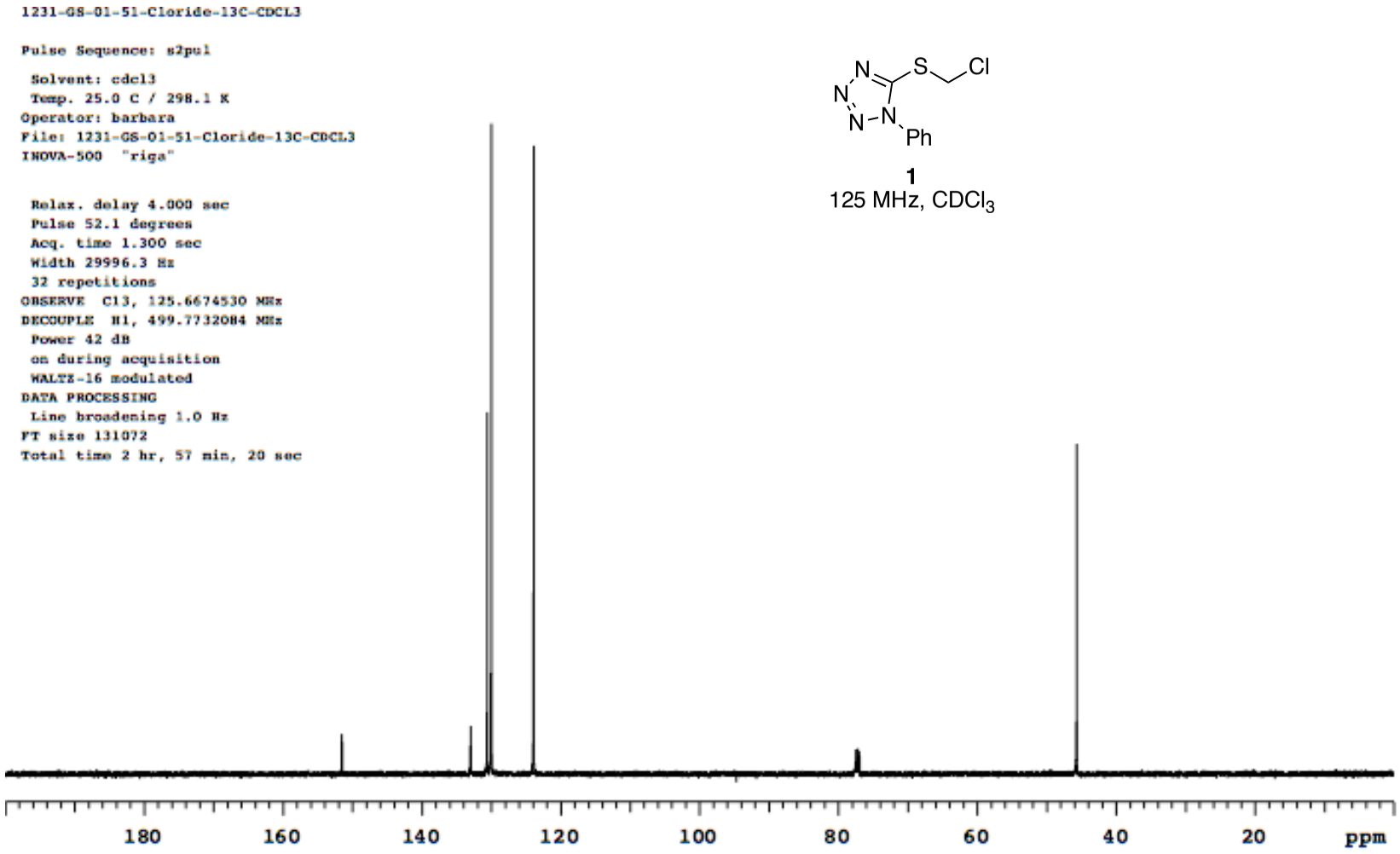
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-51-PureTS
INOVA-500 "capella500"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707226 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



1
500 MHz, $CDCl_3$





1

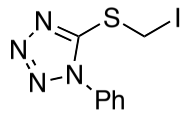
125 MHz, $CDCl_3$

GS-1231-01-72-PTSulfide-I

Pulse Sequence: s2pul

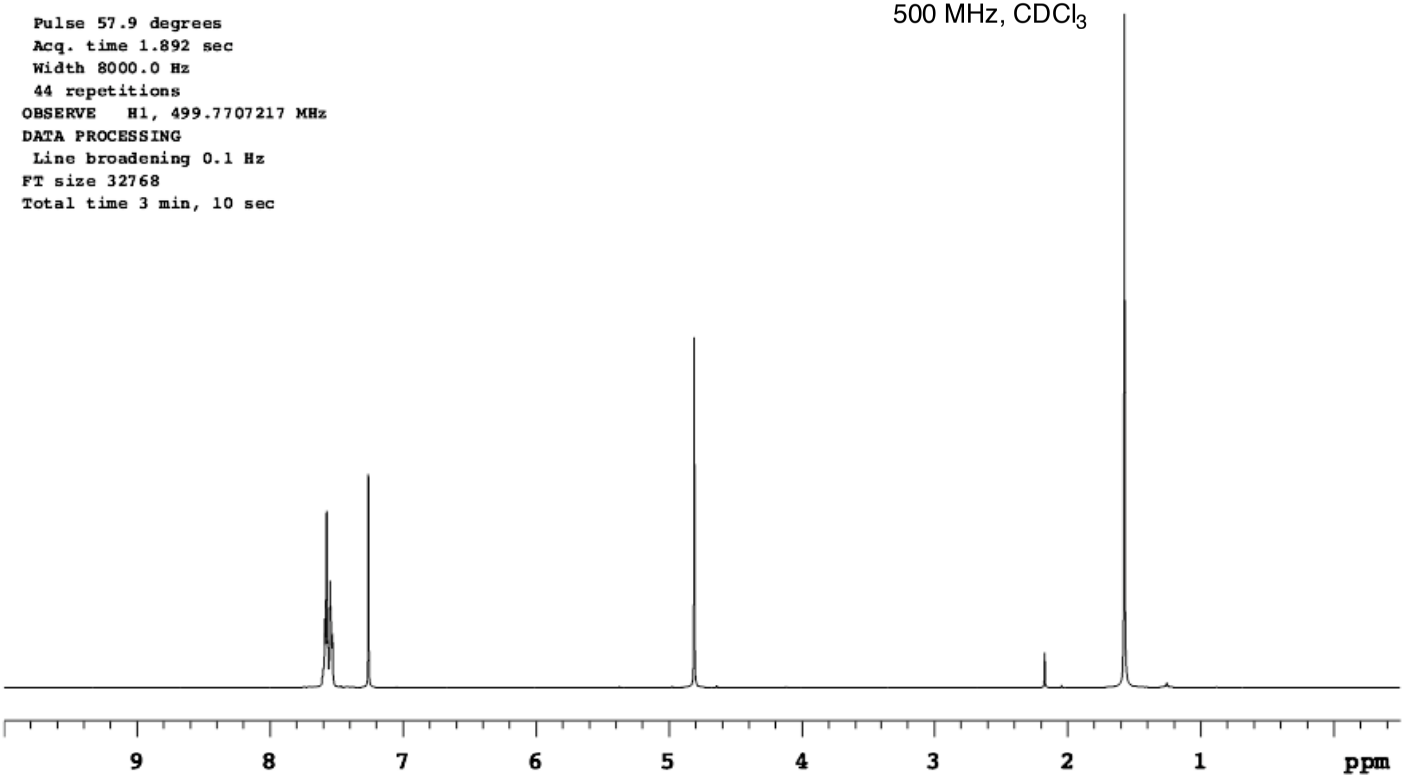
Solvent: CDCl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-72-PTSulfide-I
INOVA-500 "riga"

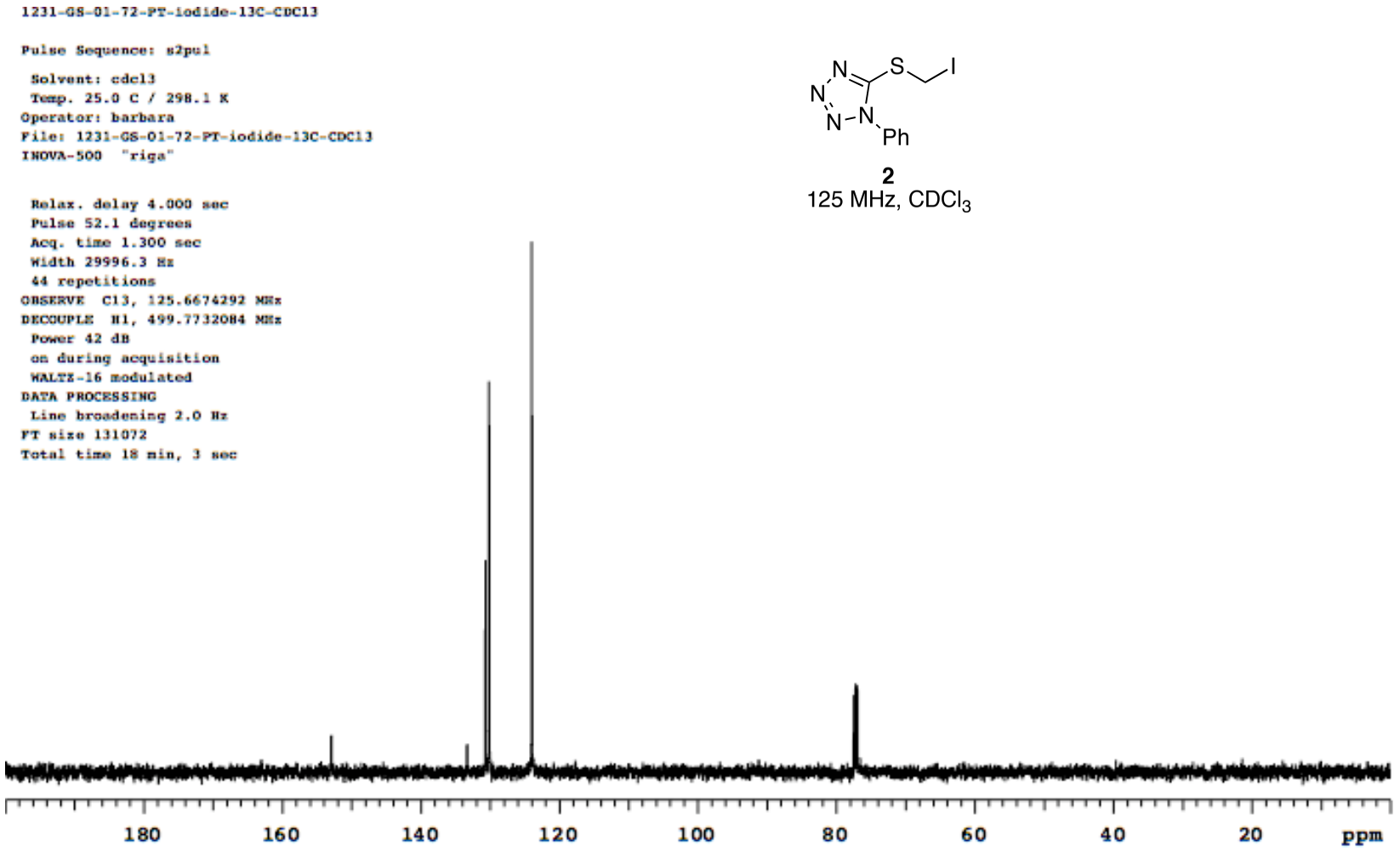
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
44 repetitions
OBSERVE H1, 499.7707217 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



2

500 MHz, $CDCl_3$





2

125 MHz, $CDCl_3$

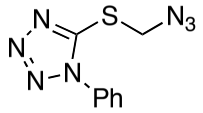
GS-1231-01-90-Azide

Archive directory: /export/home/mkl/vnmrsys/data
Sample directory: auto_13Dec2004

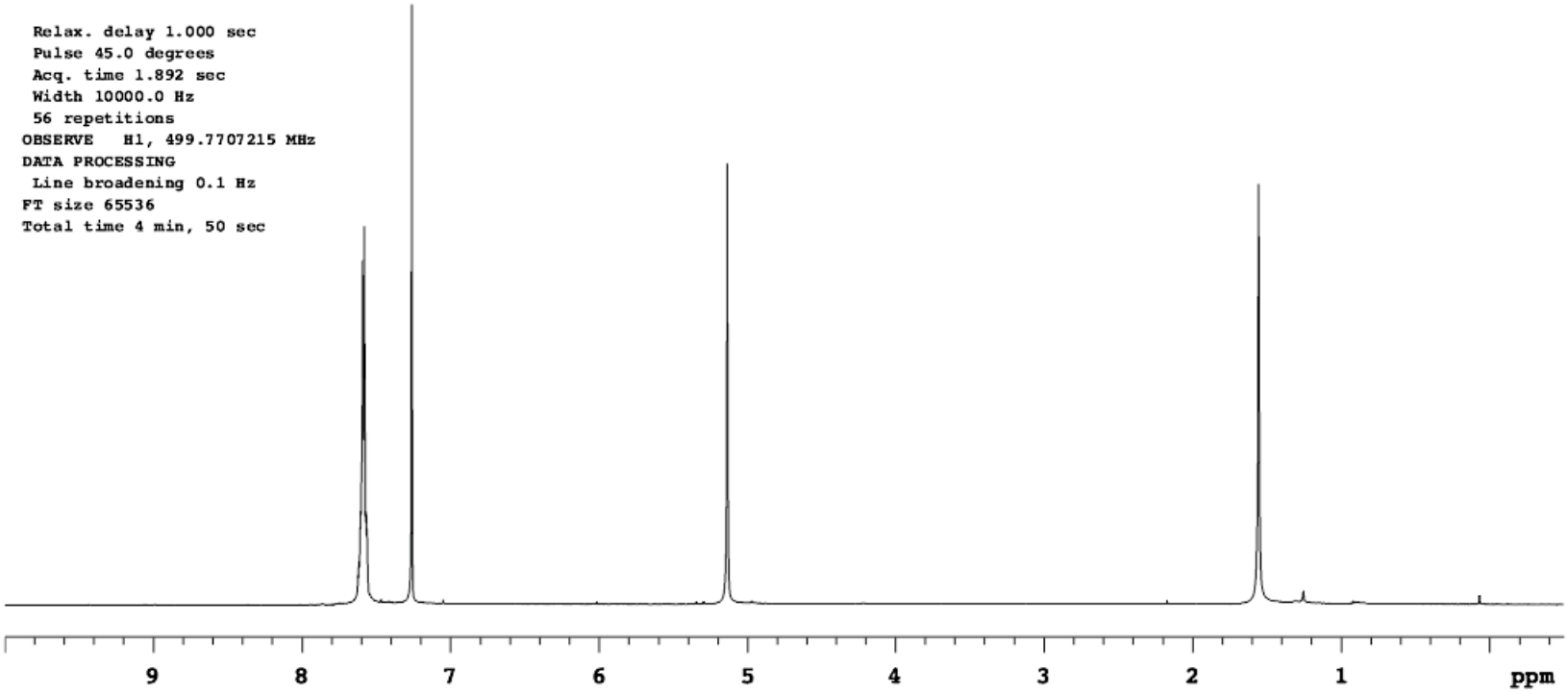
Pulse Sequence: s2pul

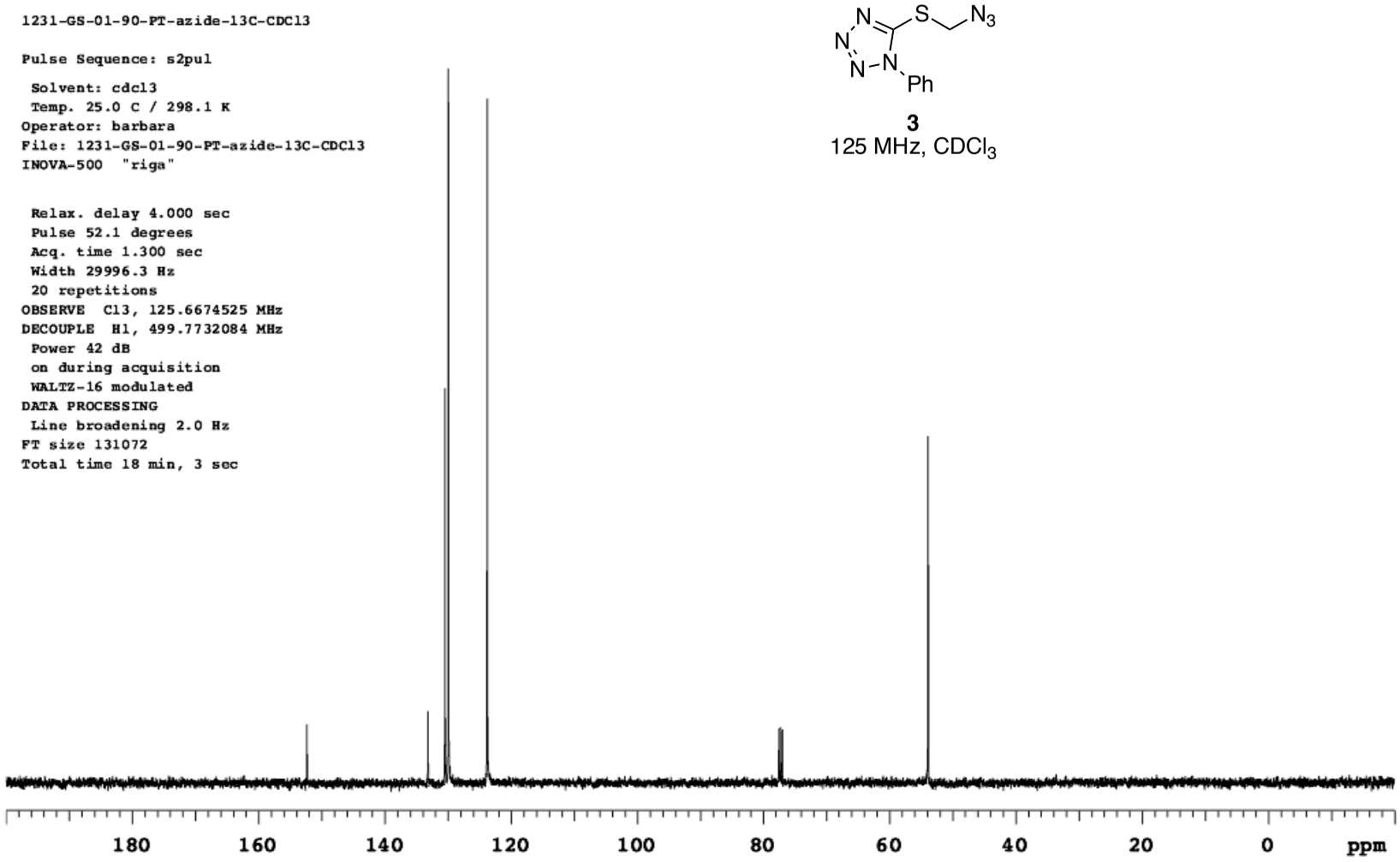
Solvent: cdcl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-90-Azide
INOVA-500 "riga"

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.892 sec
Width 10000.0 Hz
56 repetitions
OBSERVE H1, 499.7707215 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 4 min, 50 sec



3
500 MHz, $CDCl_3$



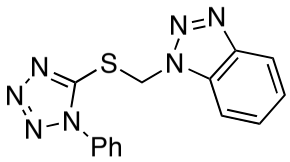

1231-GS-01-90-PT-azide-13C-CDCl3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: 1231-GS-01-90-PT-azide-13C-CDCl3
INOVA-500 "riga"
Relax. delay 4.000 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
20 repetitions
OBSERVE C13, 125.6674525 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 18 min, 3 sec
N
N
N
N
S
N3
Ph
3
125 MHz, CDCl3
180
160
140
120
100
80
60
40
20
0
ppm

GS-1231-01-54-PureCompound

Pulse Sequence: s2pul

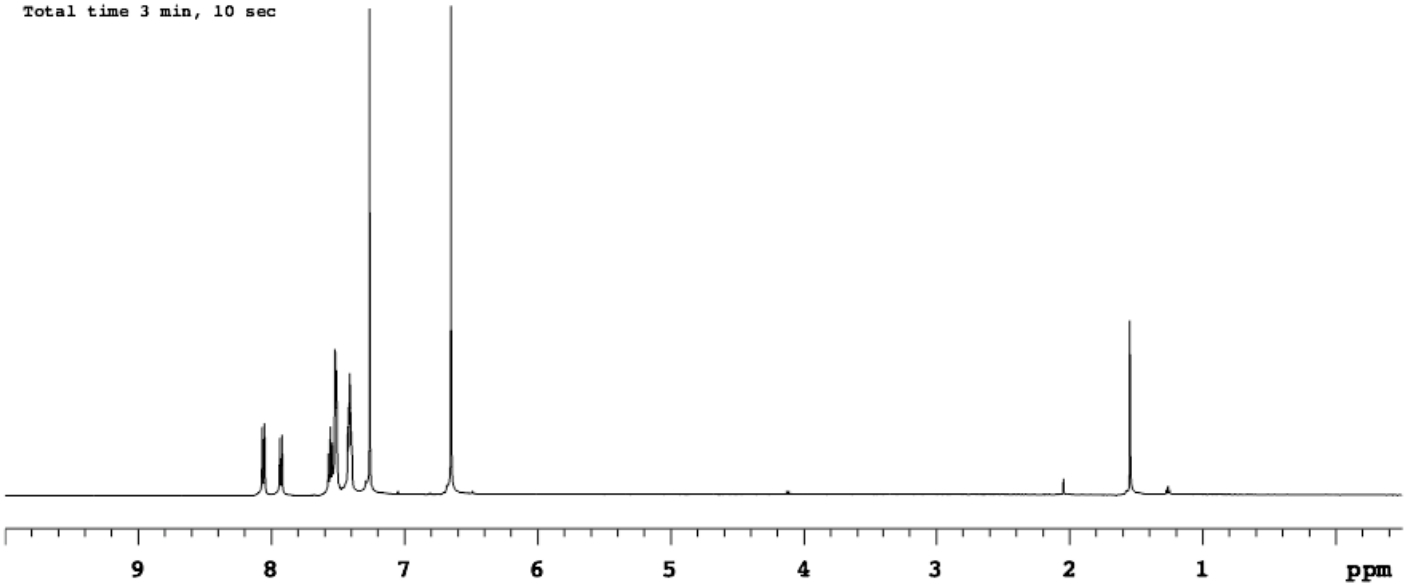
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-54-PureCompound
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
68 repetitions
OBSERVE H1, 499.7707217 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec

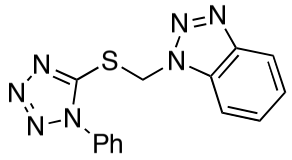


4

500 MHz, $CDCl_3$

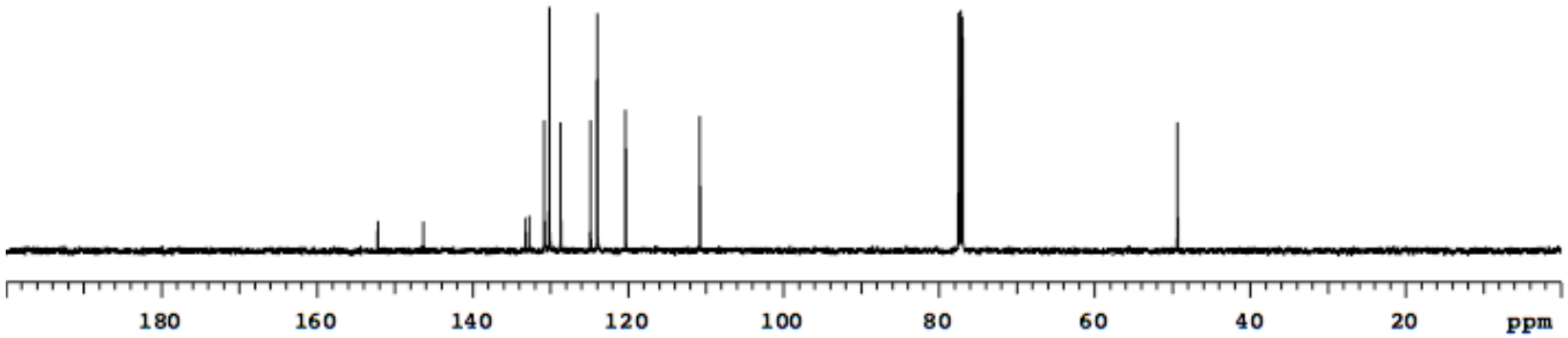


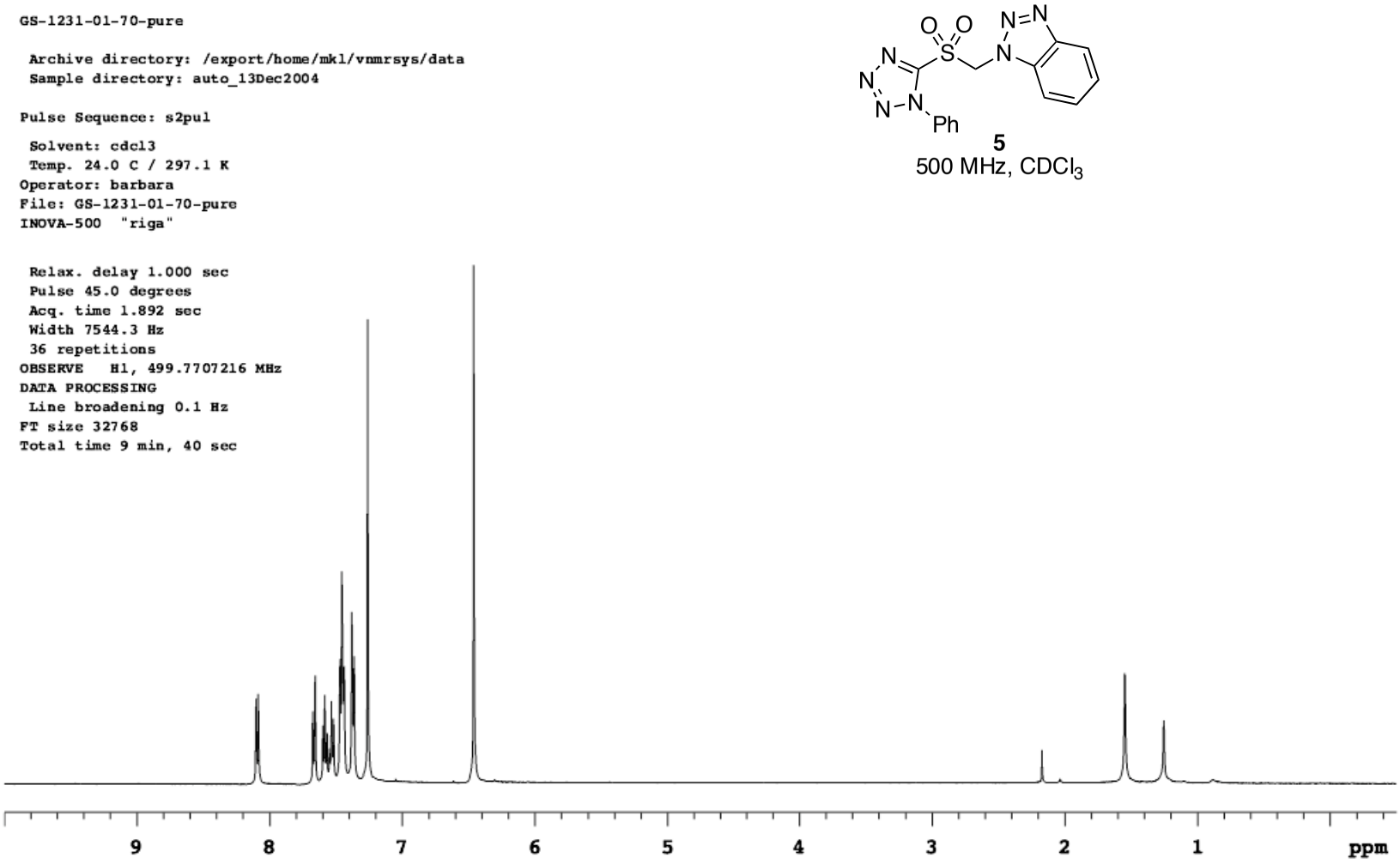
```
PT-Triazole-C13

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: PT-Triazole-C13
INOVA-500  "riga"

 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 576 repetitions
OBSERVE  C13, 125.6674232 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 3 min, 44 sec
```



4

125 MHz, $CDCl_3$

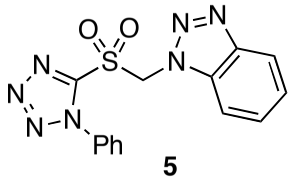




5

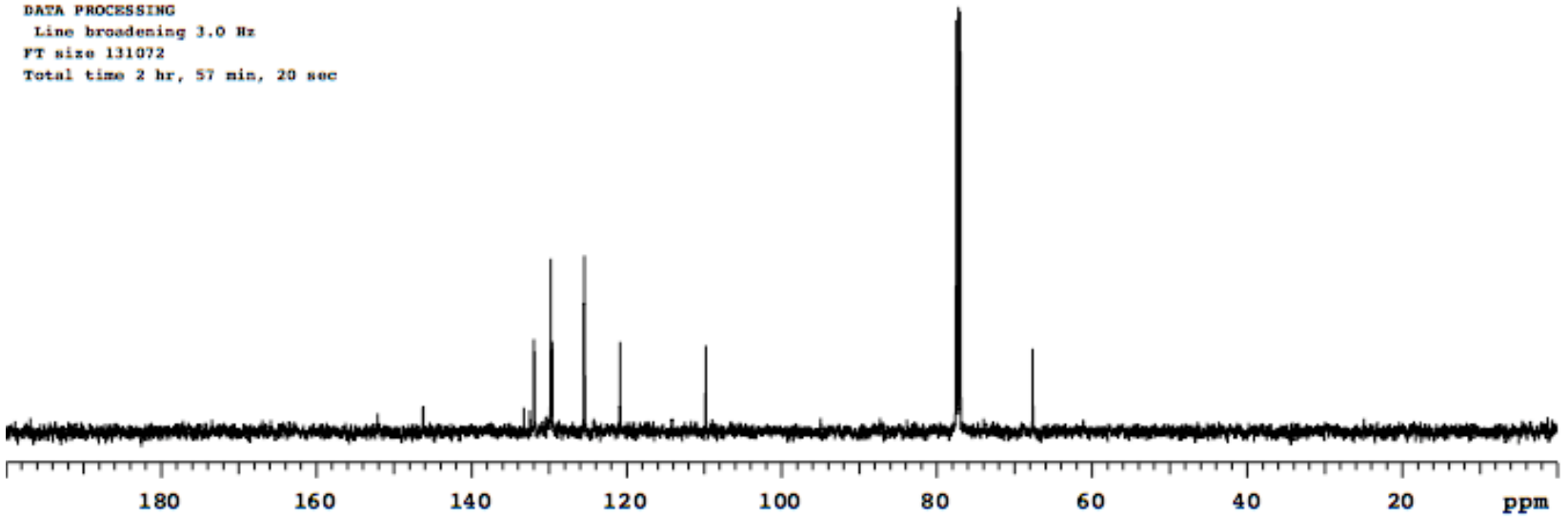
500 MHz, $CDCl_3$

```
GS-1231-01-57-PTBT-Sulfone-13C-CDCL3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-57-PTBT-Sulfone-13C-CDCL3
INOVA-500  "riga"


 Relax. delay 4.000 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 380 repetitions
OBSERVE  C13, 125.6674186 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 3.0 Hz
FT size 131072
Total time 2 hr, 57 min, 20 sec
```



5

125 MHz, $CDCl_3$

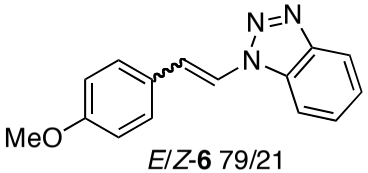


JS-01-75-pure

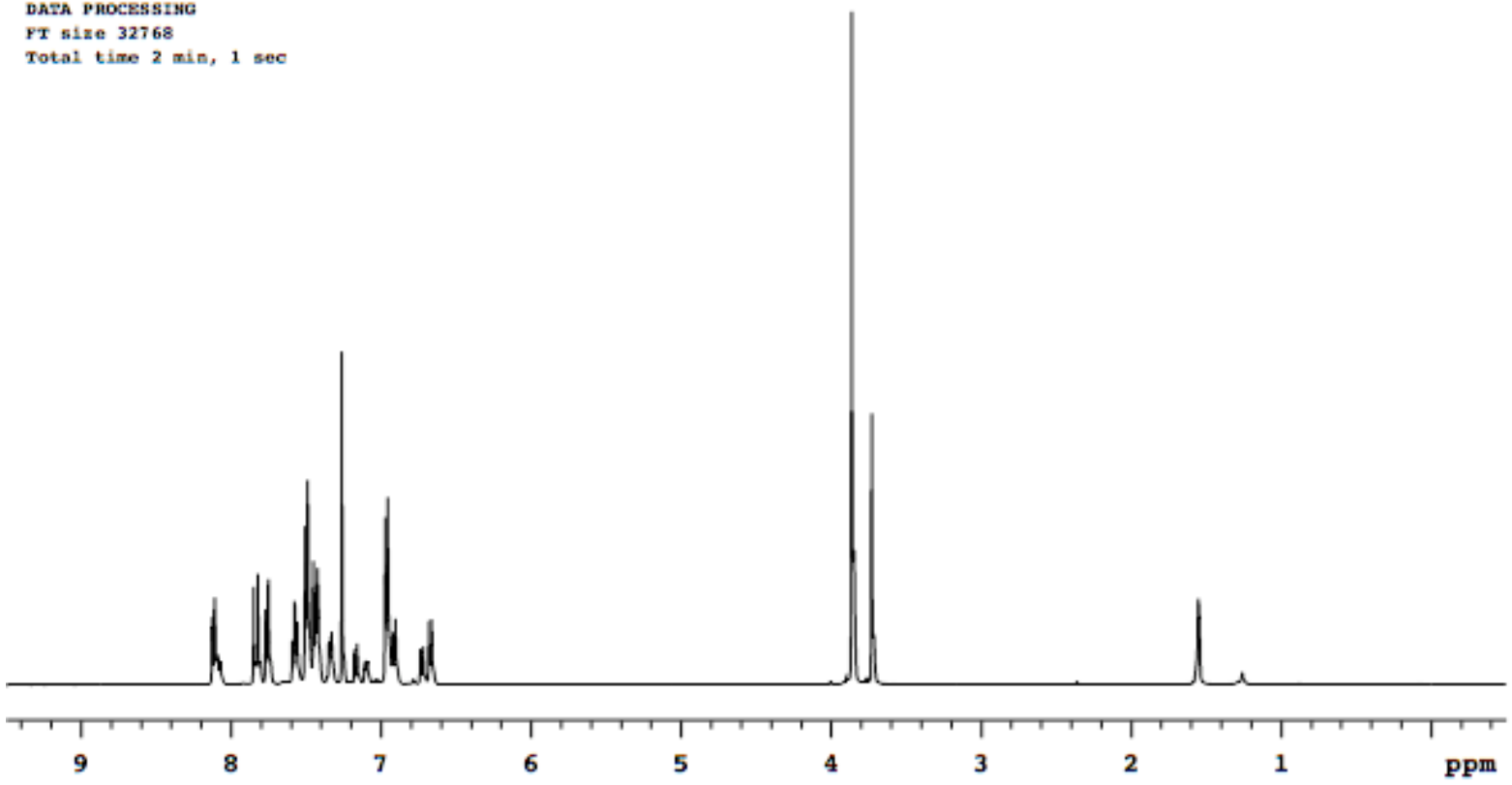
Pulse Sequence: s2pul

Solvent: CDCl3
Ambient temperature
Operator: barbara
File: 1231-JS-01-75-pure
INOVA-500 "riga"

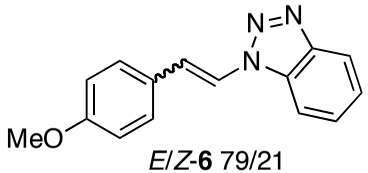
Pulse 38.6 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.7707202 MHz
DATA PROCESSING
FT size 32768
Total time 2 min, 1 sec



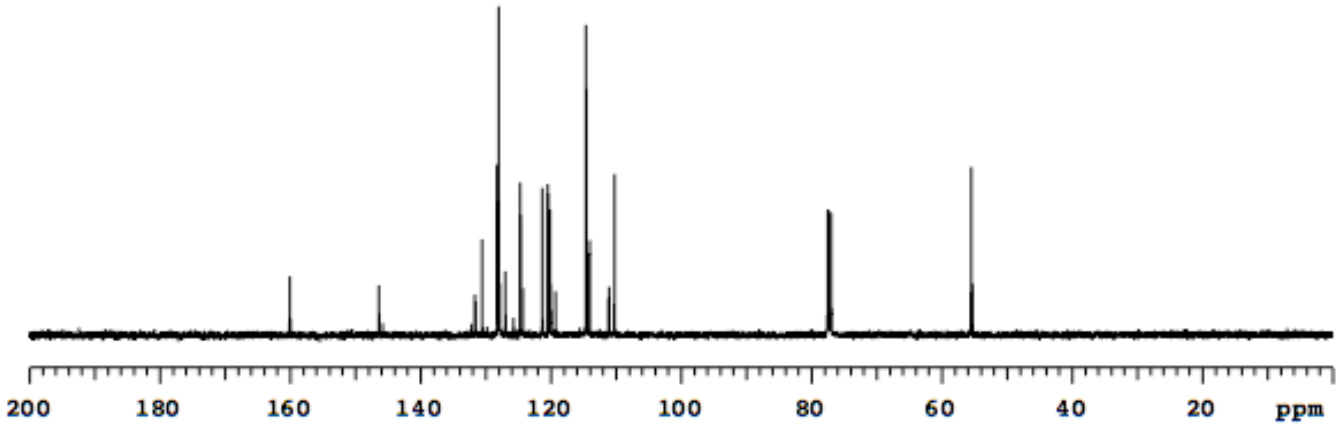
E/*Z*-**6** 79/21
500 MHz, $CDCl_3$



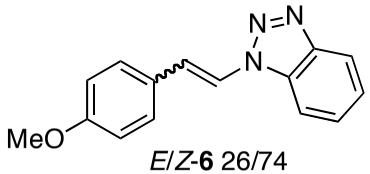
```
GS-1231-04-pMethoxy-C13-CDCl3

Pulse Sequence: s2pul
 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-04-pMethoxy-C13-CDCl3
INOVA-500  "riga"

 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 556 repetitions
OBSERVE  C13, 125.6674315 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.5 Hz
FT size 131072
Total time 1 hr, 35 min, 29 sec
```



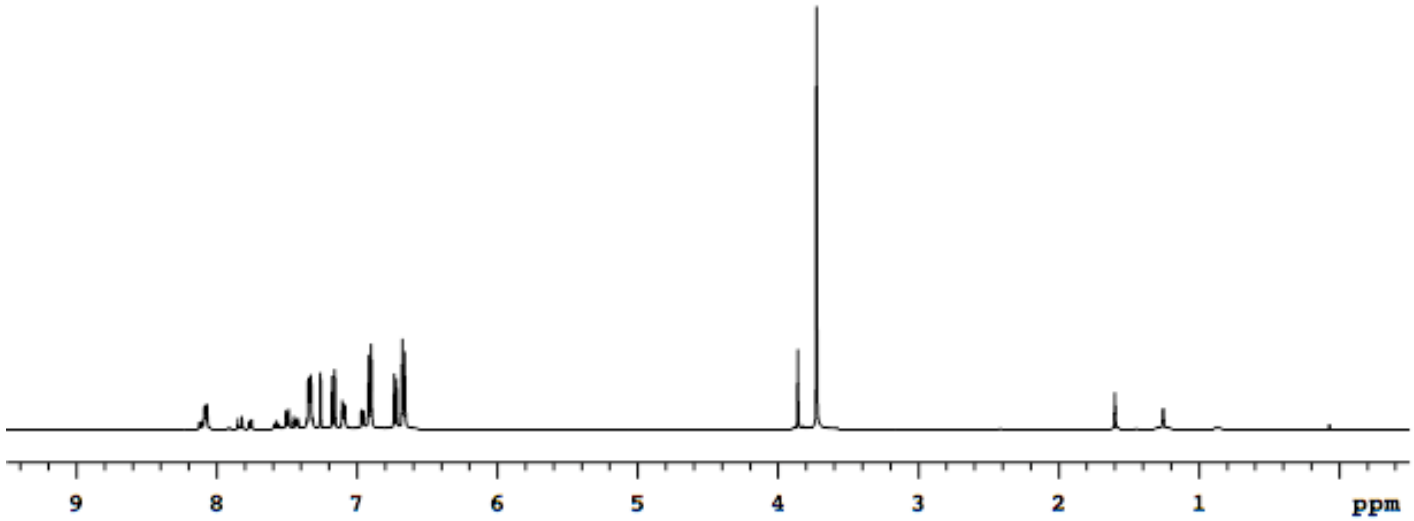
E/*Z*-**6** 79/21
125 MHz, $CDCl_3$

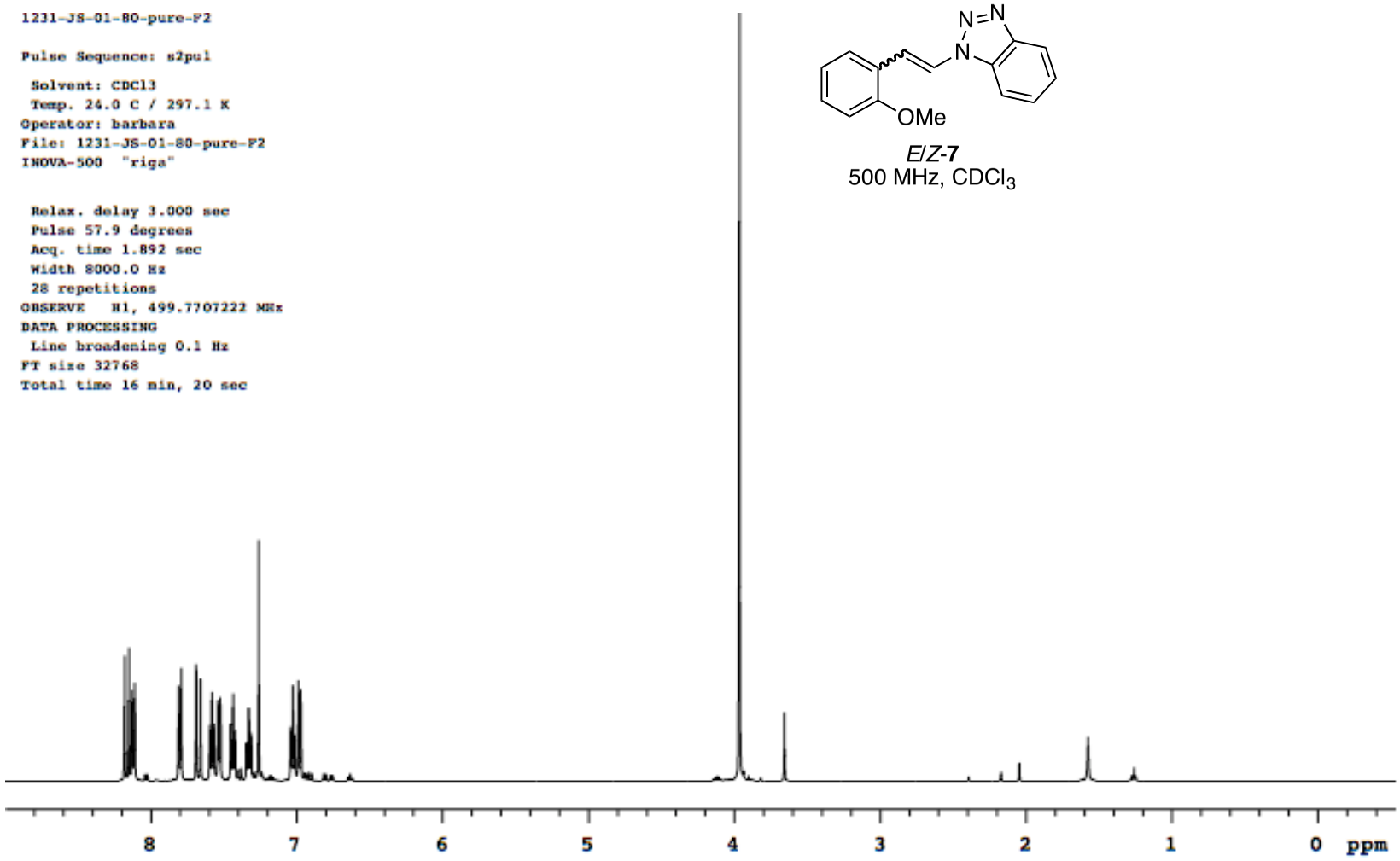


```
GS-1231-04-cond-pMethoxy-THF-DBUReflux-pure

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-04-cond-pMethoxy-THF-DBUReflux-pure
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 64 repetitions
OBSERVE   H1, 499.7707222 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```



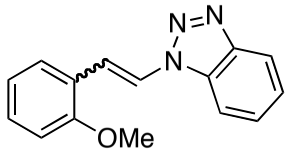
E/*Z*-**6** 26/74
500 MHz, $CDCl_3$



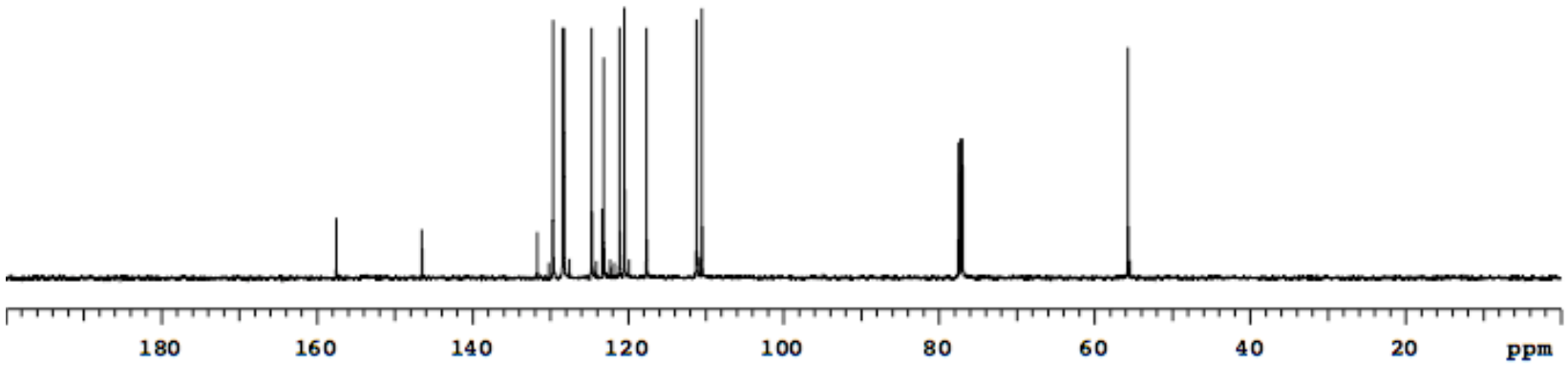


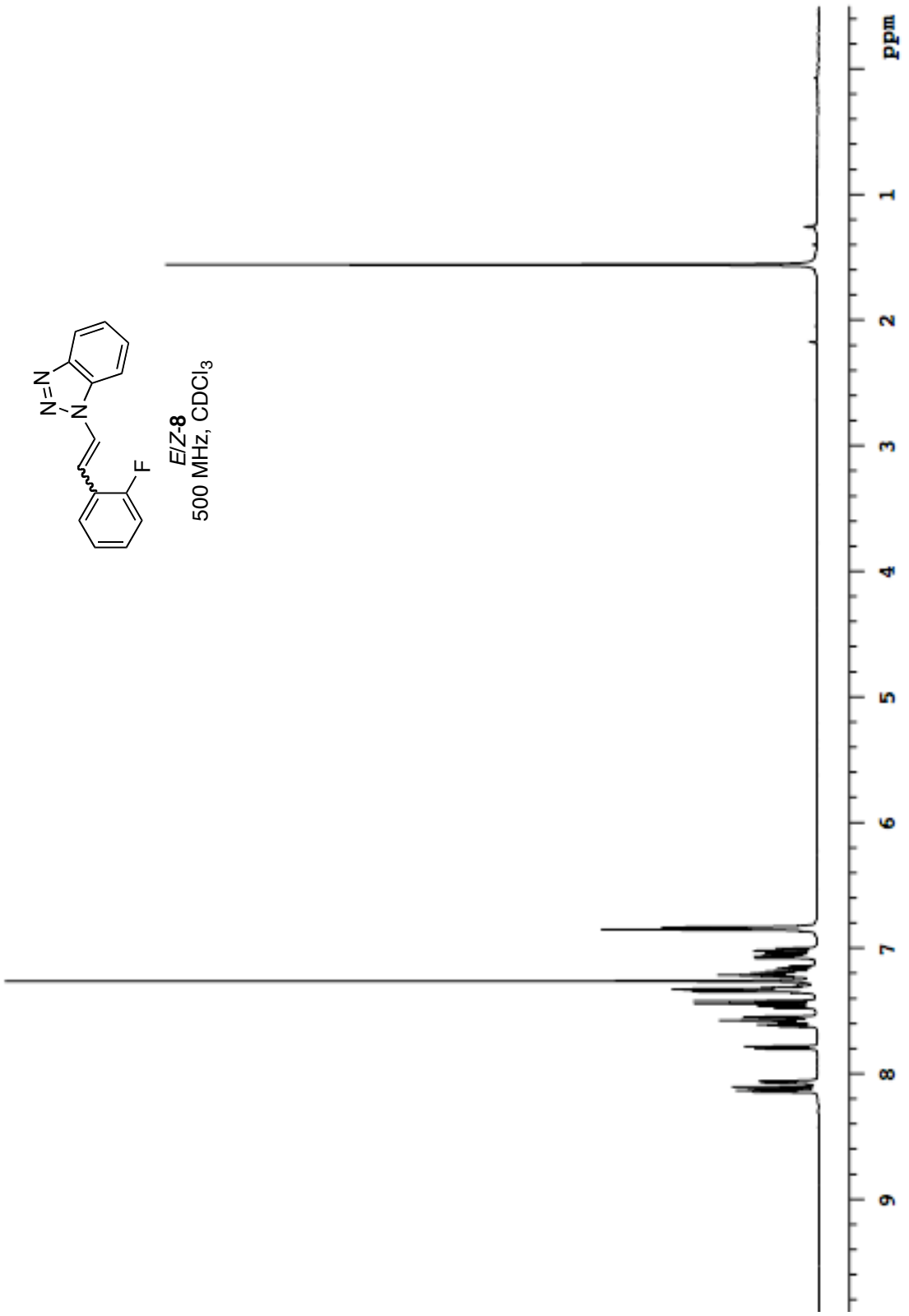
E/*Z*-**7**
500 MHz, $CDCl_3$

```
orthomethoxy-benzotriazole-c13-cdcl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: orthomethoxy-benzotriazole-c13-cdcl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 612 repetitions
OBSERVE  C13, 125.6674278 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 35 min, 29 sec
```

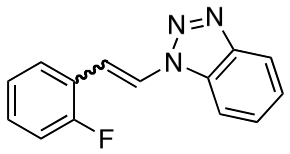


E/*Z*-**7**
125 MHz, $CDCl_3$

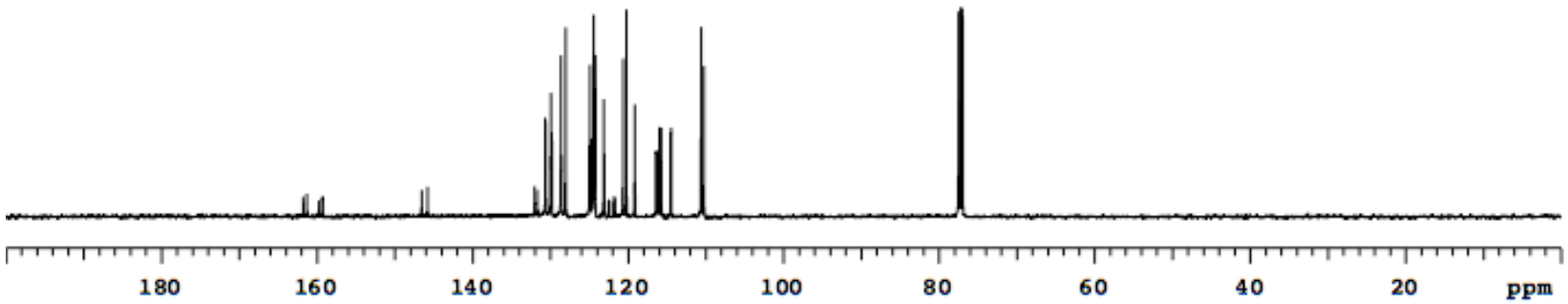



N=N
N
F
E/Z-8
500 MHz, CDCl3
ppm
1
2
3
4
5
6
7
8
9

```
orthoFluoro-benzotriazole-c13-cdcl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: orthoFluoro-benzotriazole-c13-cdcl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 1500 repetitions
OBSERVE  C13, 125.6674264 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 35 min, 29 sec
```



E/*Z*-**8**
125 MHz, $CDCl_3$

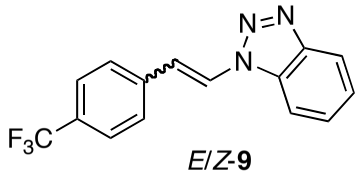


GS-1231-01-79-pure

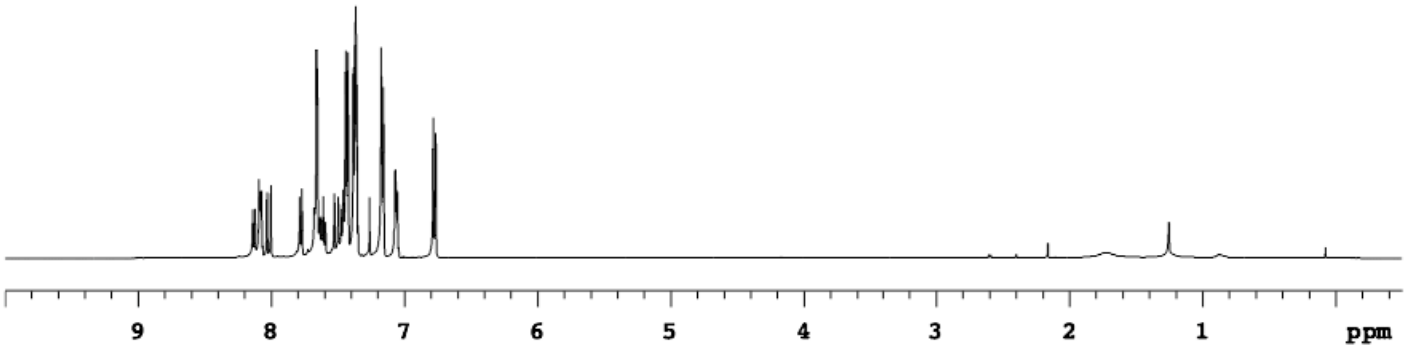
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-79-pure
INOVA-500 "riga"

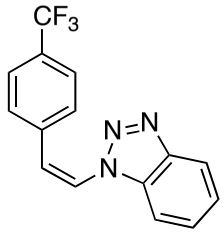
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



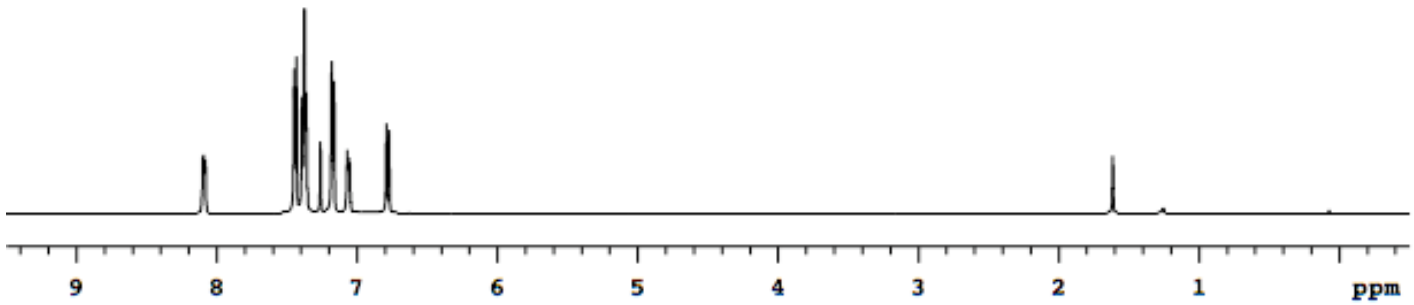
E/*Z*-**9**
500 MHz, $CDCl_3$

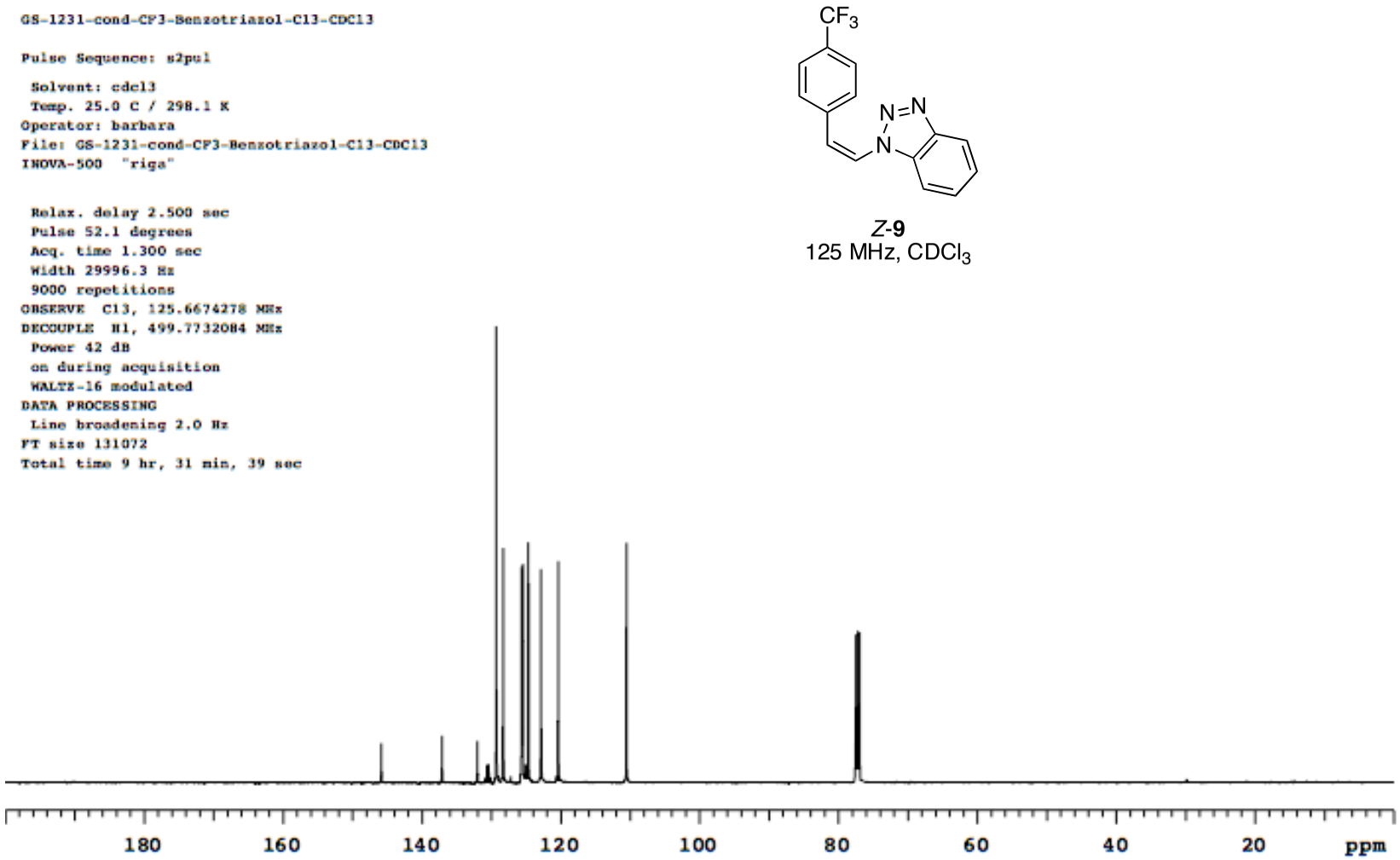


```
GS-1231-cond-CF3-pureBS

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-CF3-pureBS
INOVA-500  "riga"


 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 68 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec
```



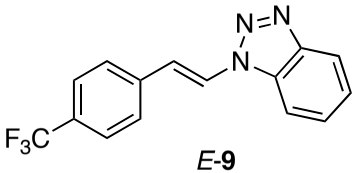
Z-**9**
500 MHz, $CDCl_3$



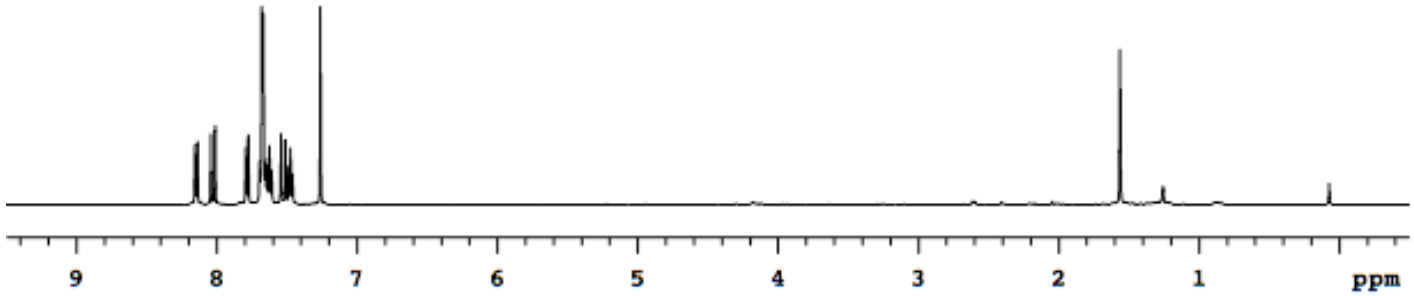


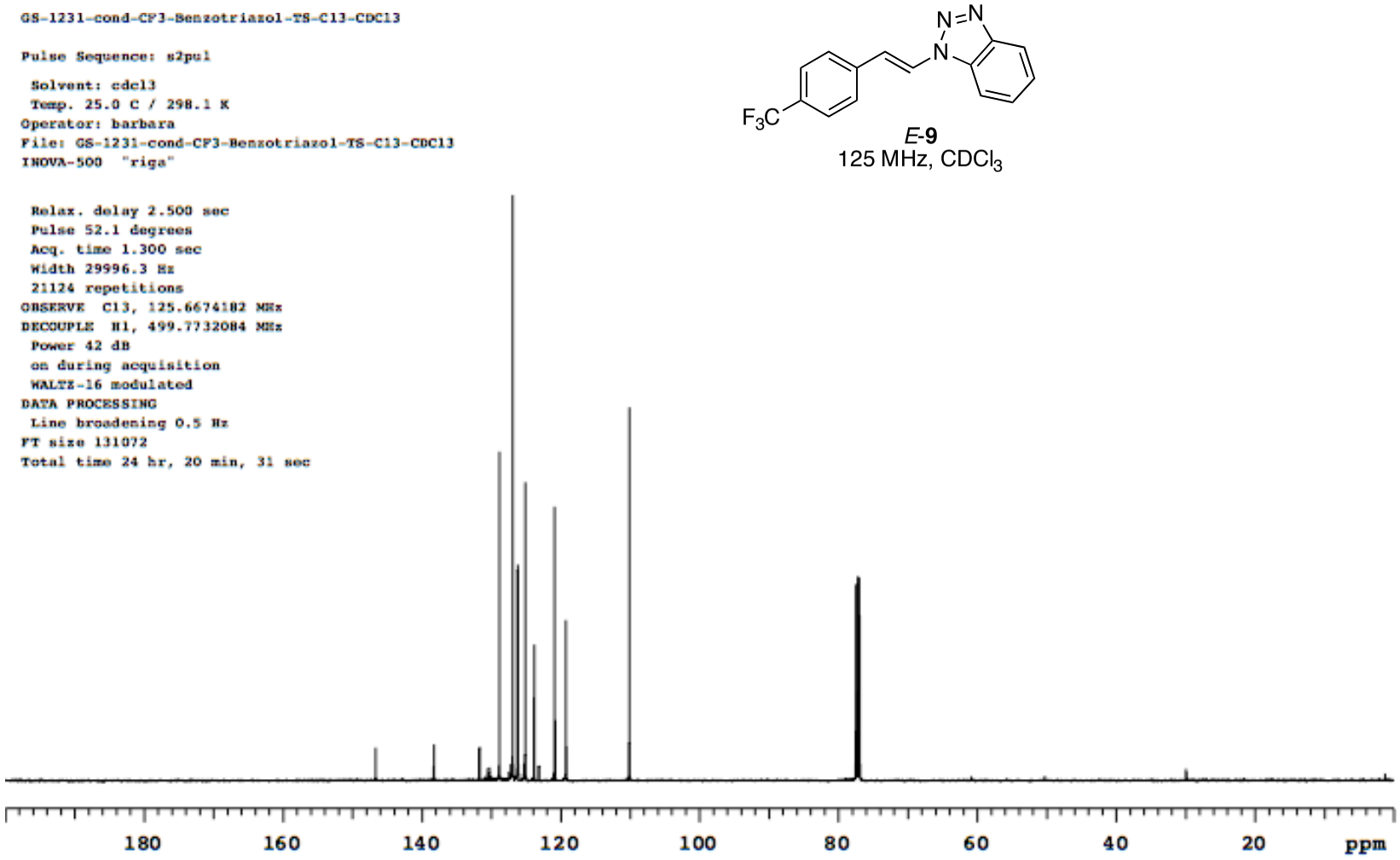
Z-**9**
125 MHz, $CDCl_3$

```
GS-1231-cond-CF3-pureTS

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-CF3-pureTS
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 40 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec
```



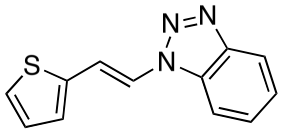
E-**9**
500 MHz, $CDCl_3$



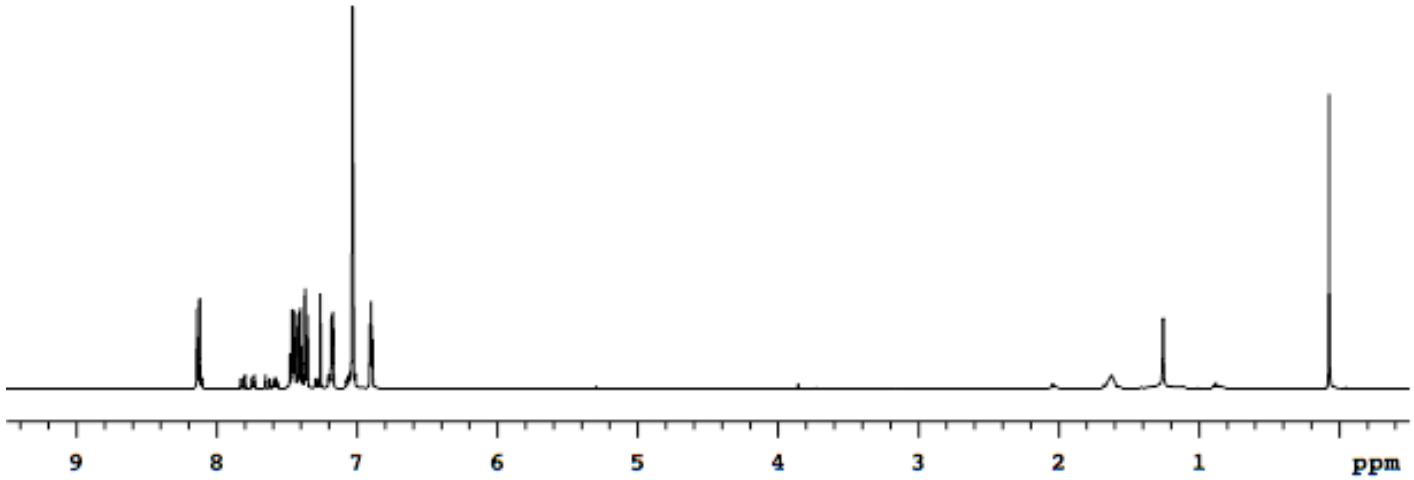


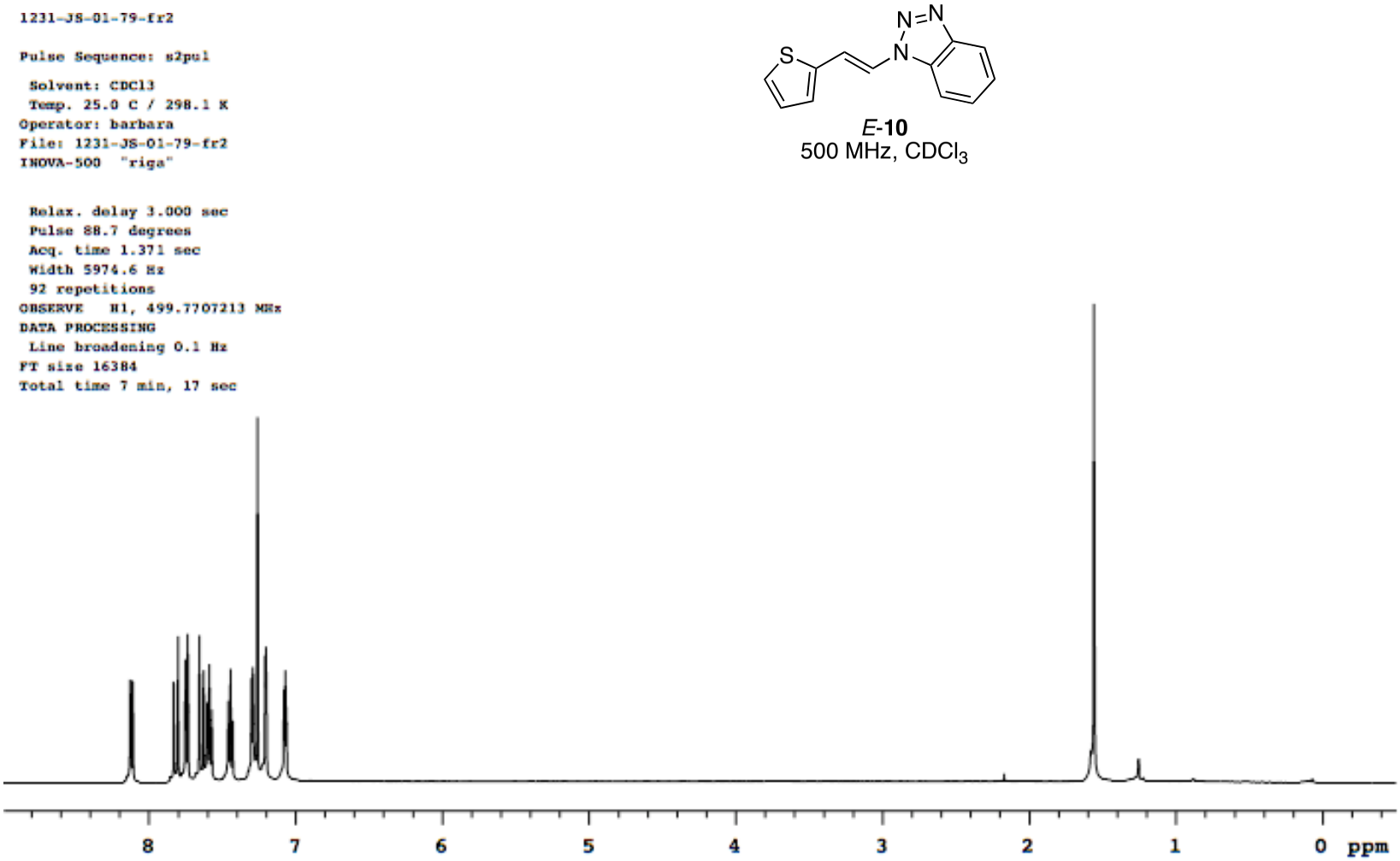
E-**9**
125 MHz, $CDCl_3$

```
GS-1231-04-cond-Thiophene-THF-DBUReflux-pure

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-04-cond-Thiophene-THF-DBUReflux-pure
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 36 repetitions
OBSERVE   H1, 499.7707222 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```

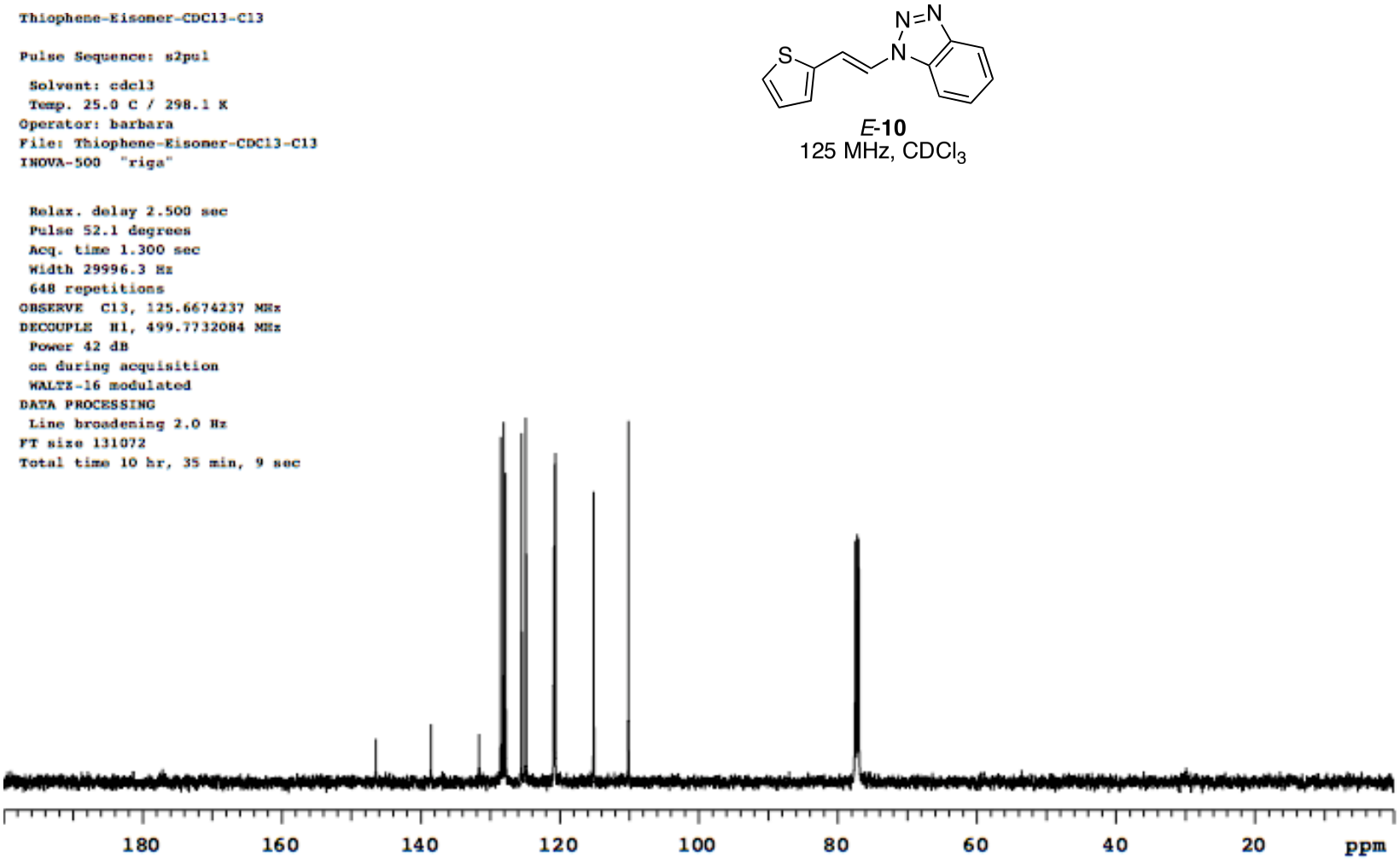


E/*Z*-**10** 25/75
500 MHz, $CDCl_3$

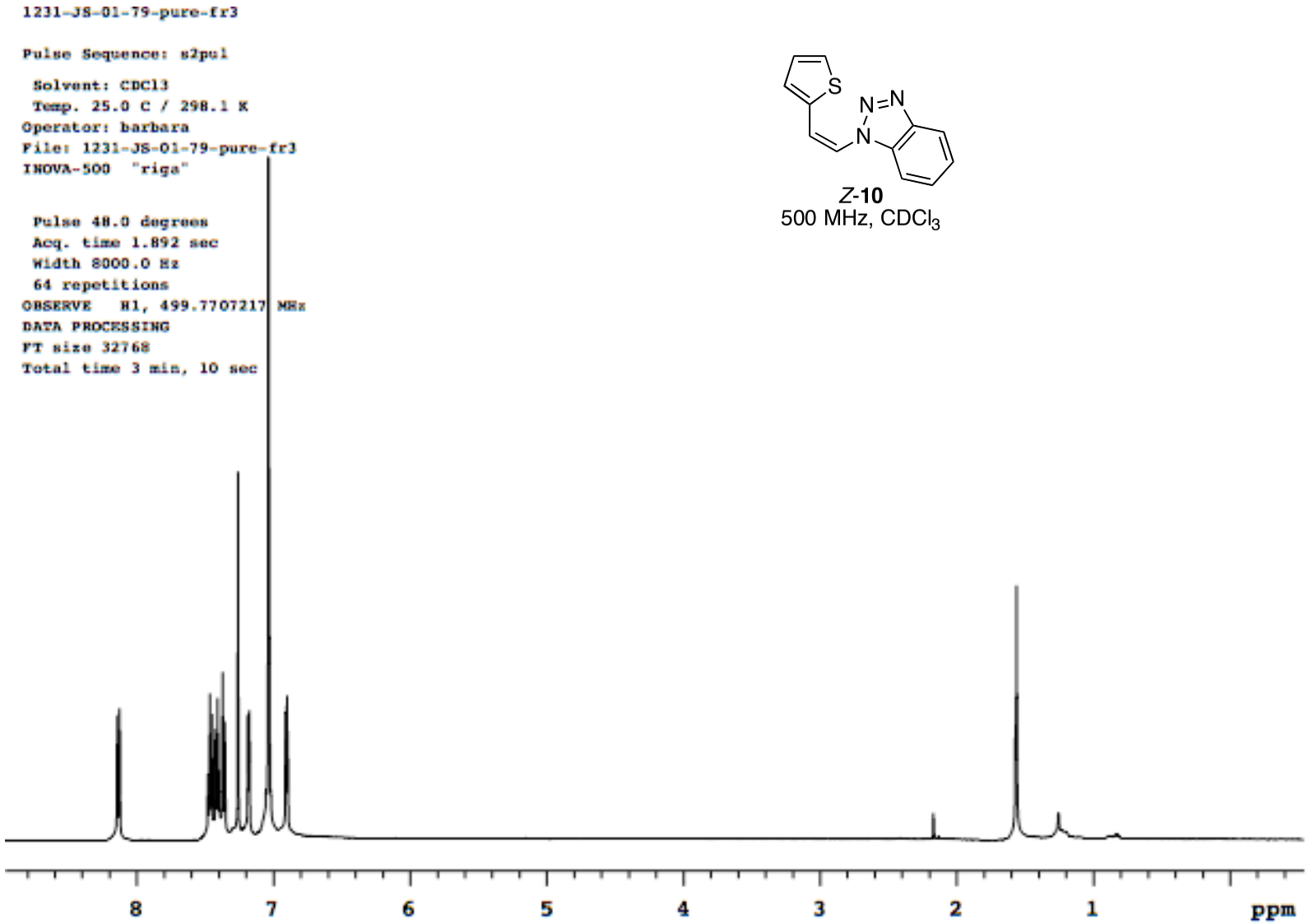




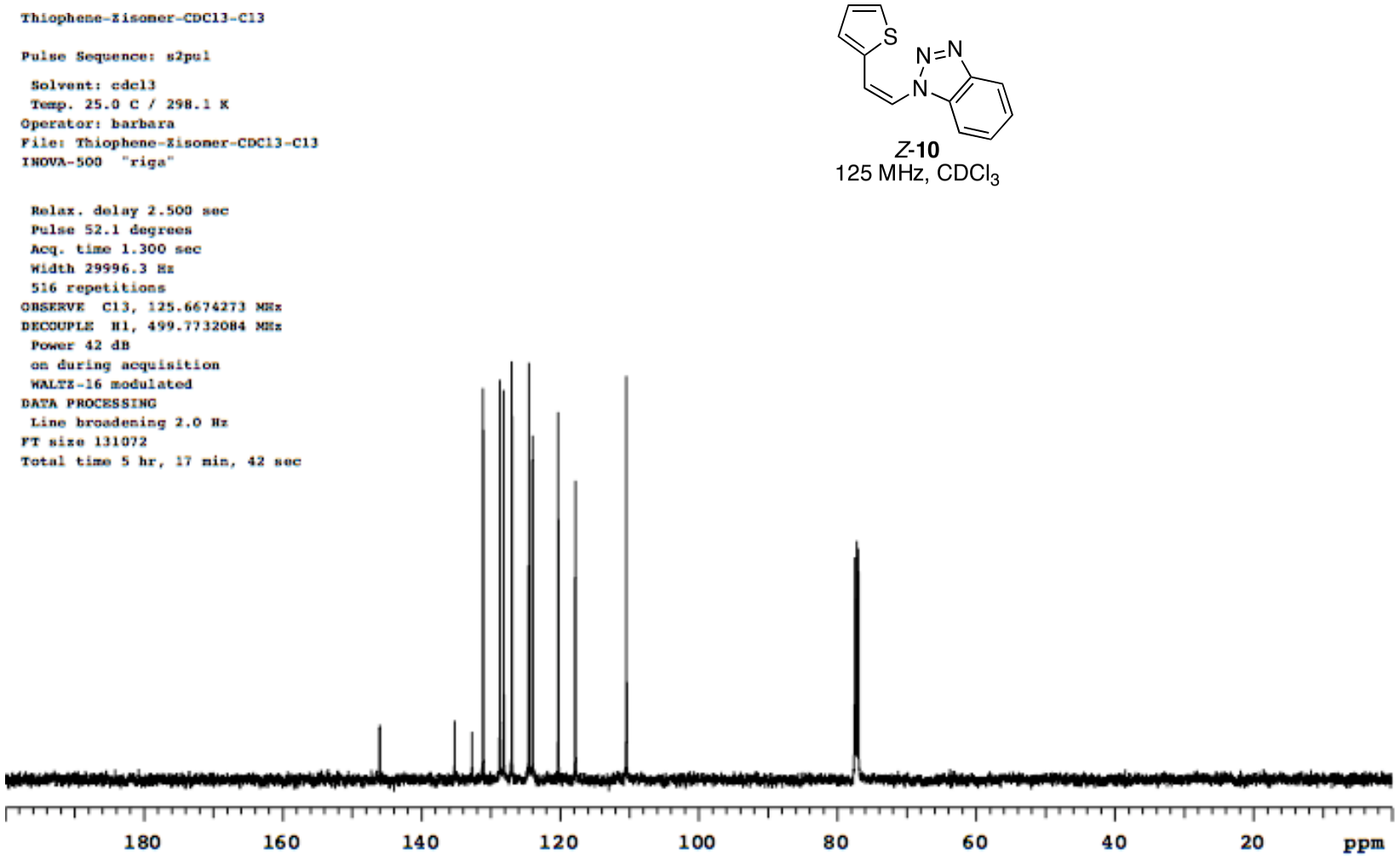
E-**10**
500 MHz, $CDCl_3$



E-**10**
125 MHz, $CDCl_3$

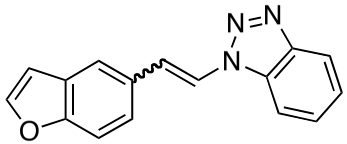


***Z*-10**
500 MHz, $CDCl_3$

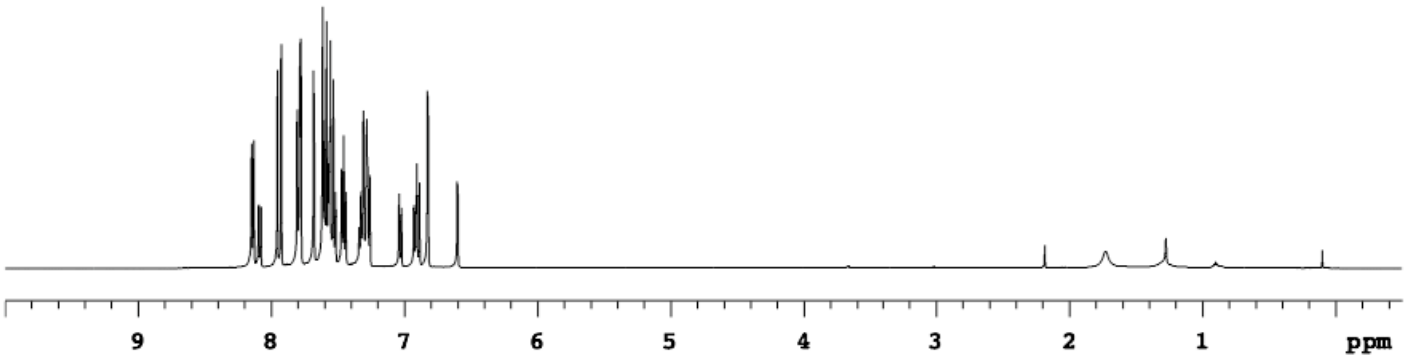


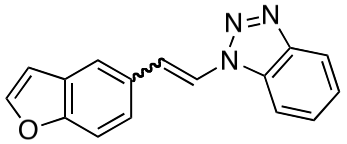
Z-**10**
125 MHz, $CDCl_3$

```
GS-1231-01-85-pure

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-85-pure
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 92 repetitions
OBSERVE   H1, 499.7707111 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```



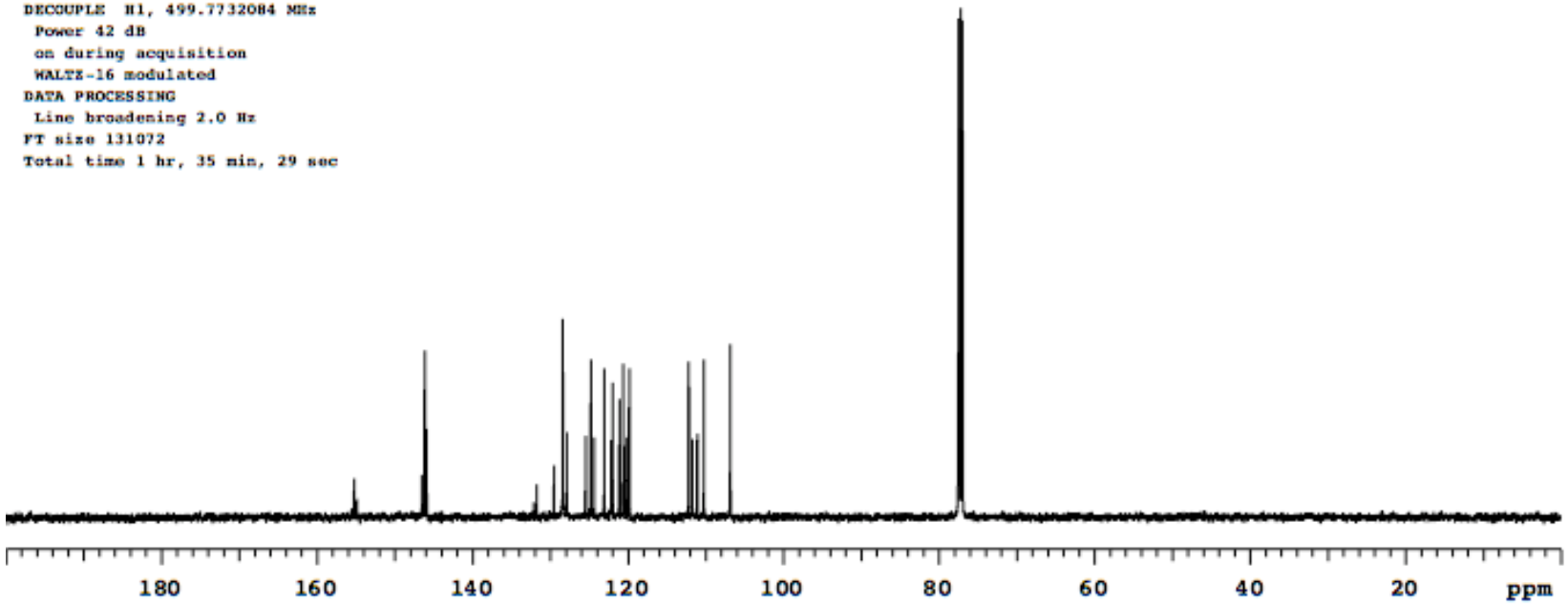
E/*Z*-**11**
500 MHz, $CDCl_3$





E/*Z*-**11**
125 MHz, $CDCl_3$

```
GS-1231-01-85-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-85-C13-CDCl3
INOVA-500  "riga"

 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 1304 repetitions
OBSERVE  C13, 125.6674232 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 35 min, 29 sec
```

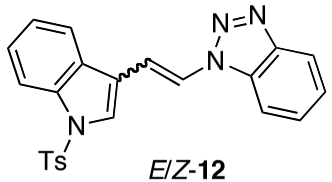


GS-1231-01-80-pureIndol

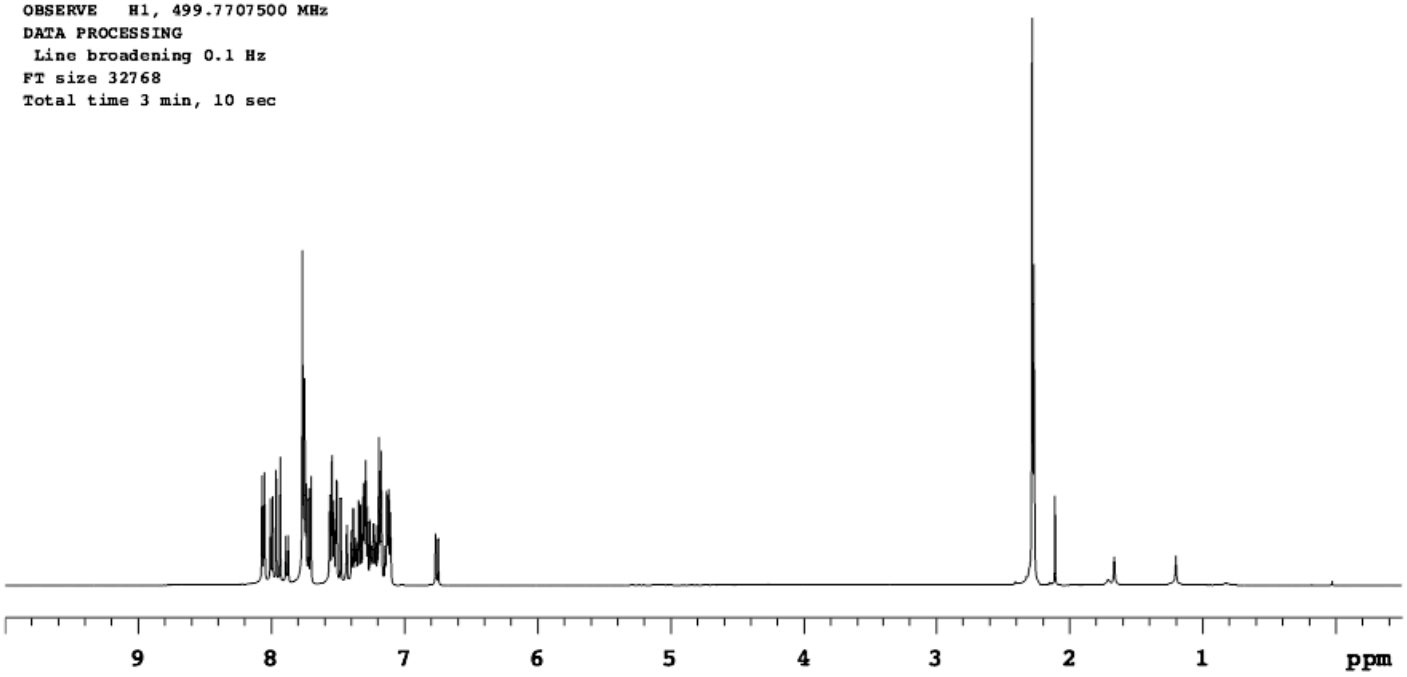
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-80-pureIndol
INOVA-500 "riga"

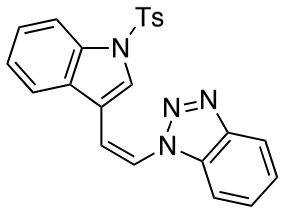
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707500 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



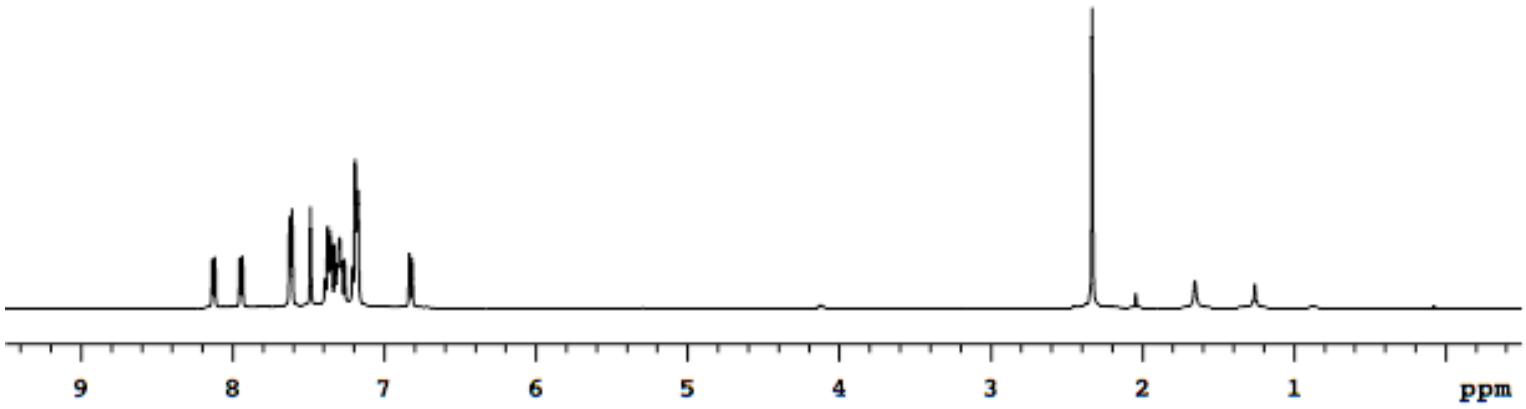
E/*Z*-**12**
500 MHz, $CDCl_3$



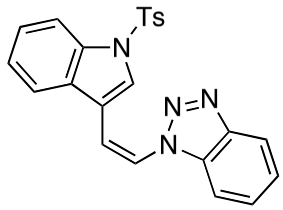
```
GS-1231-cond-Indol-pureBS-s2

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-Indol-pureBS-s2
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 64 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec
```



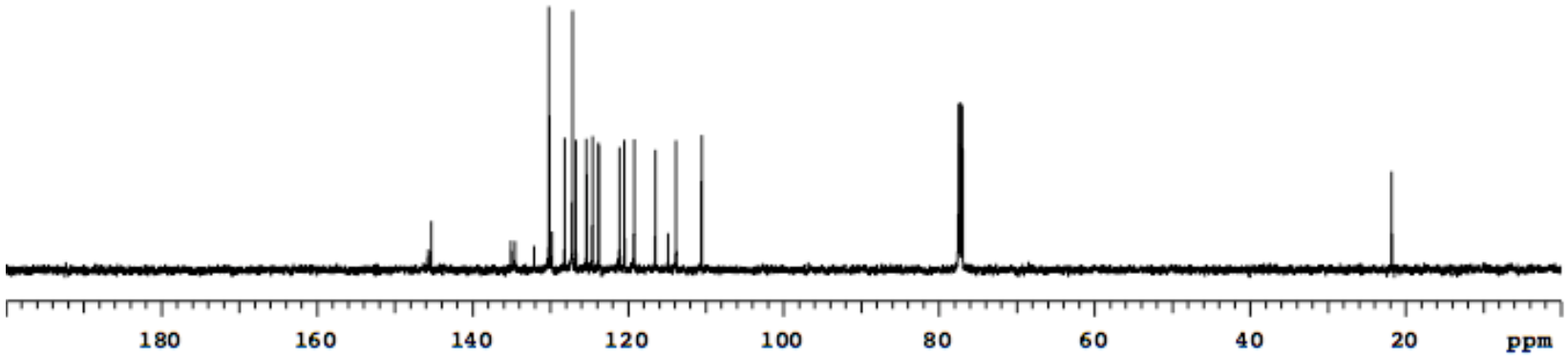
***Z*-12**
500 MHz, $CDCl_3$



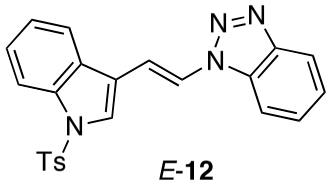
```
GS-1231-cond-Indol8S-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-Indol8S-C13-CDCl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 612 repetitions
OBSERVE  C13, 125.6674228 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 2 hr, 7 min, 14 sec
```



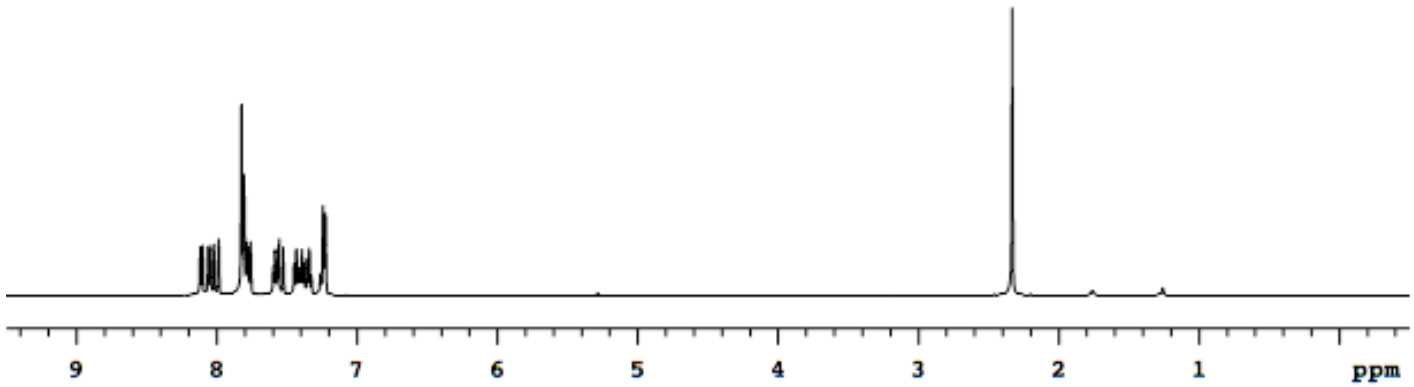
Z-**12**
125 MHz, $CDCl_3$



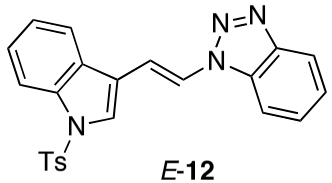
```
GS-1231-cond-Indol-pureTS-beforeC13

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-Indol-pureTS-beforeC13
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 28 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec
```



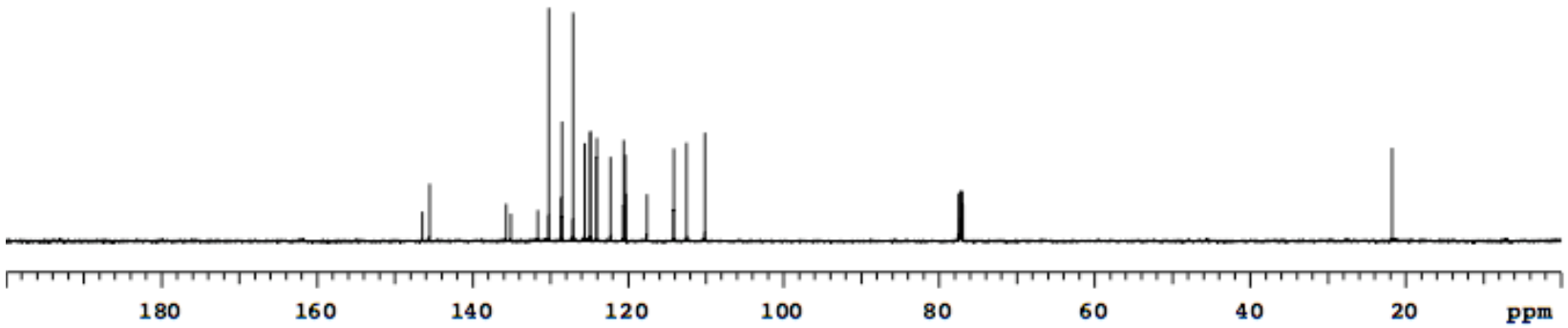
E-**12**
500 MHz, $CDCl_3$

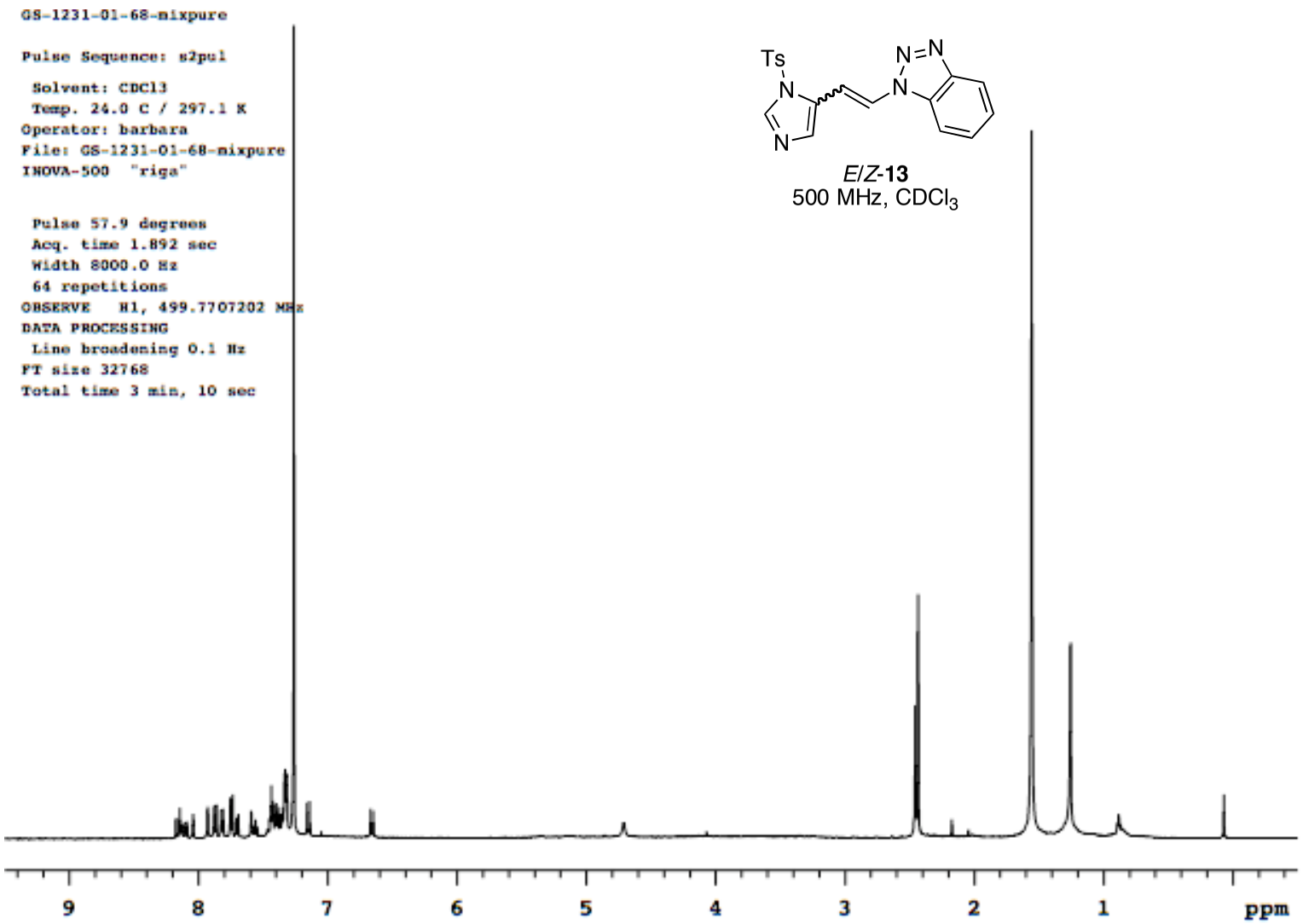


```
GS-1231-cond-IndolTS-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-IndolTS-C13-CDCl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 516 repetitions
OBSERVE  C13, 125.6674292 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 2 hr, 7 min, 14 sec
```

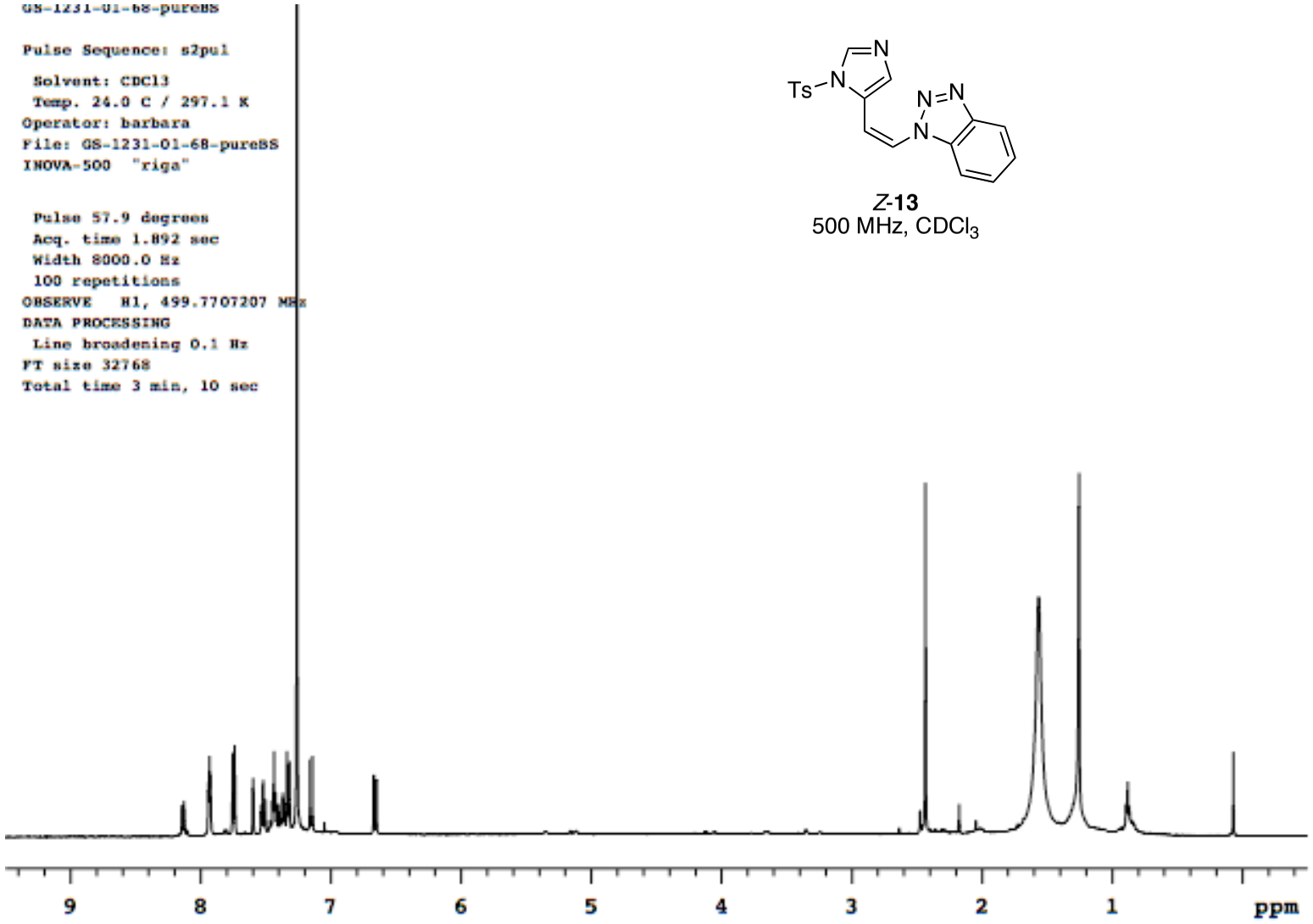


E-**12**
125 MHz, $CDCl_3$





E/*Z*-**13**
500 MHz, $CDCl_3$



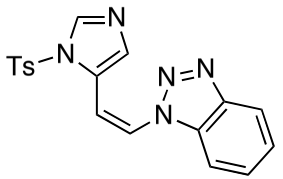
***Z*-13**
500 MHz, $CDCl_3$

GS-1231-cond-benzotriazole-imidizoleBS-c13-cdcl3

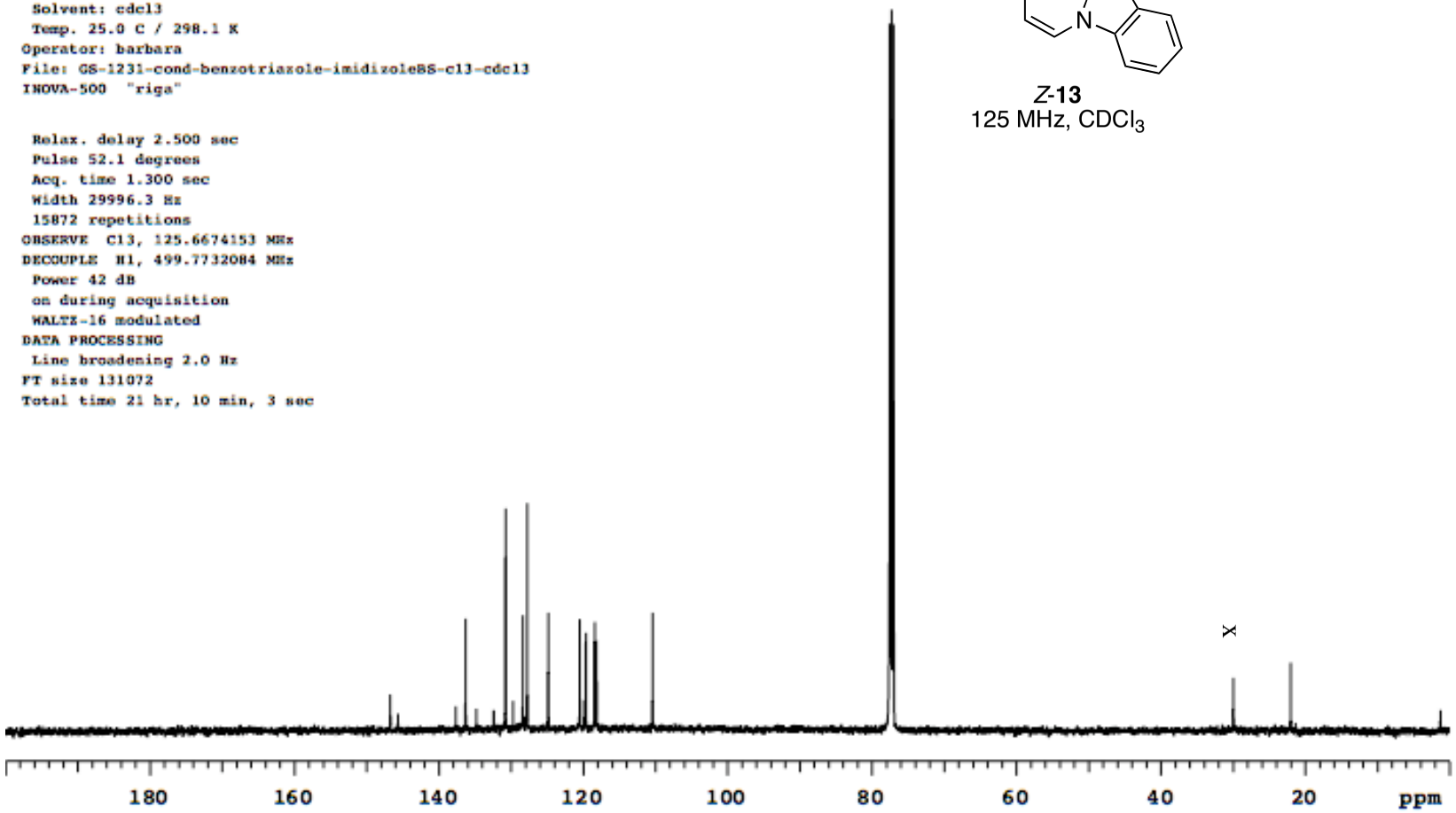
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-benzotriazole-imidizoleBS-c13-cdcl3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
15872 repetitions
OBSERVE C13, 125.6674153 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 21 hr, 10 min, 3 sec



***Z*-13**
125 MHz, $CDCl_3$

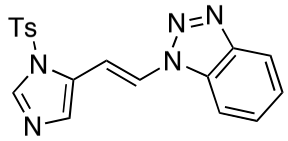


GS-1231-01-68-pure-TS

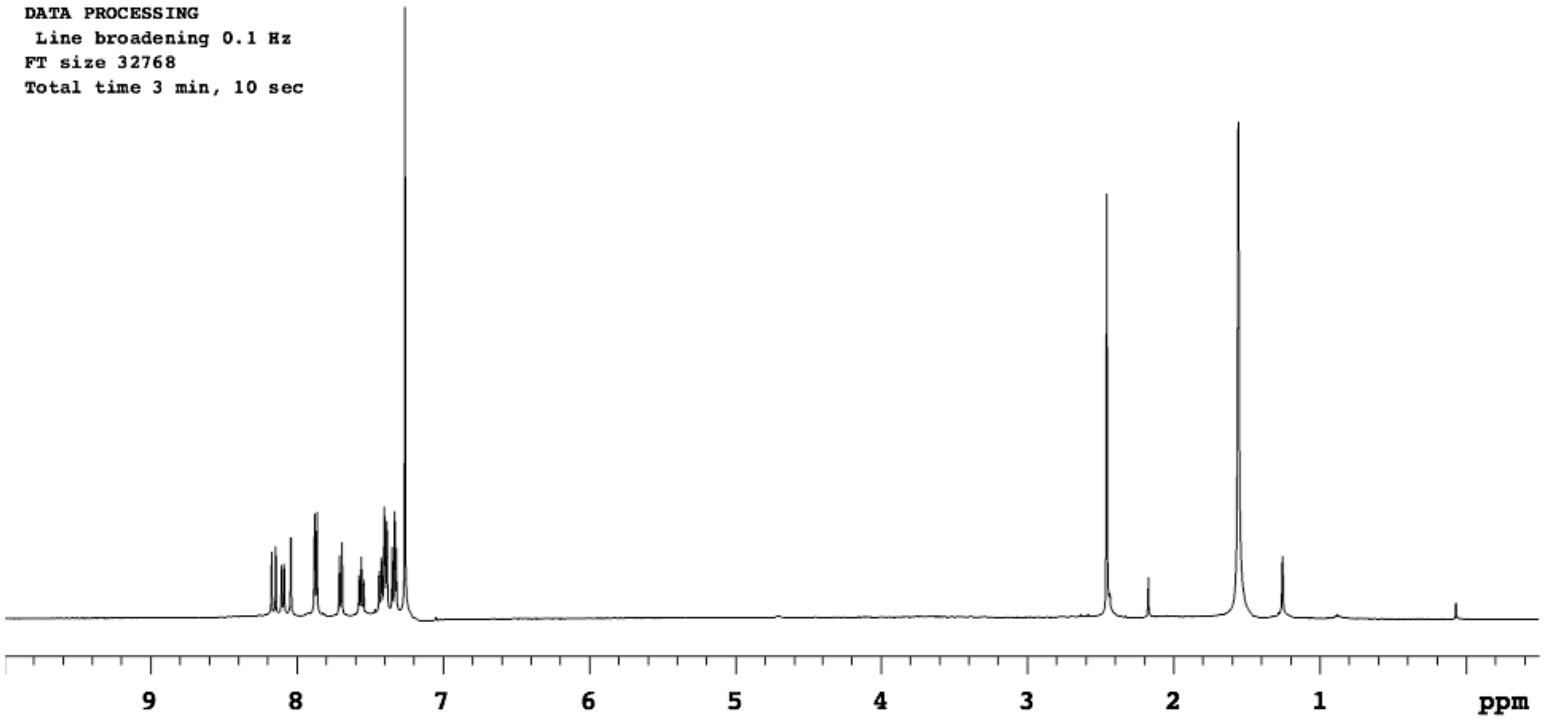
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-68-pure-TS
INOVA-500 "riga"

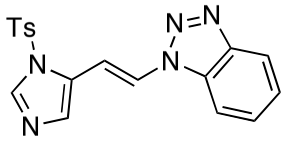
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
84 repetitions
OBSERVE H1, 499.7707207 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



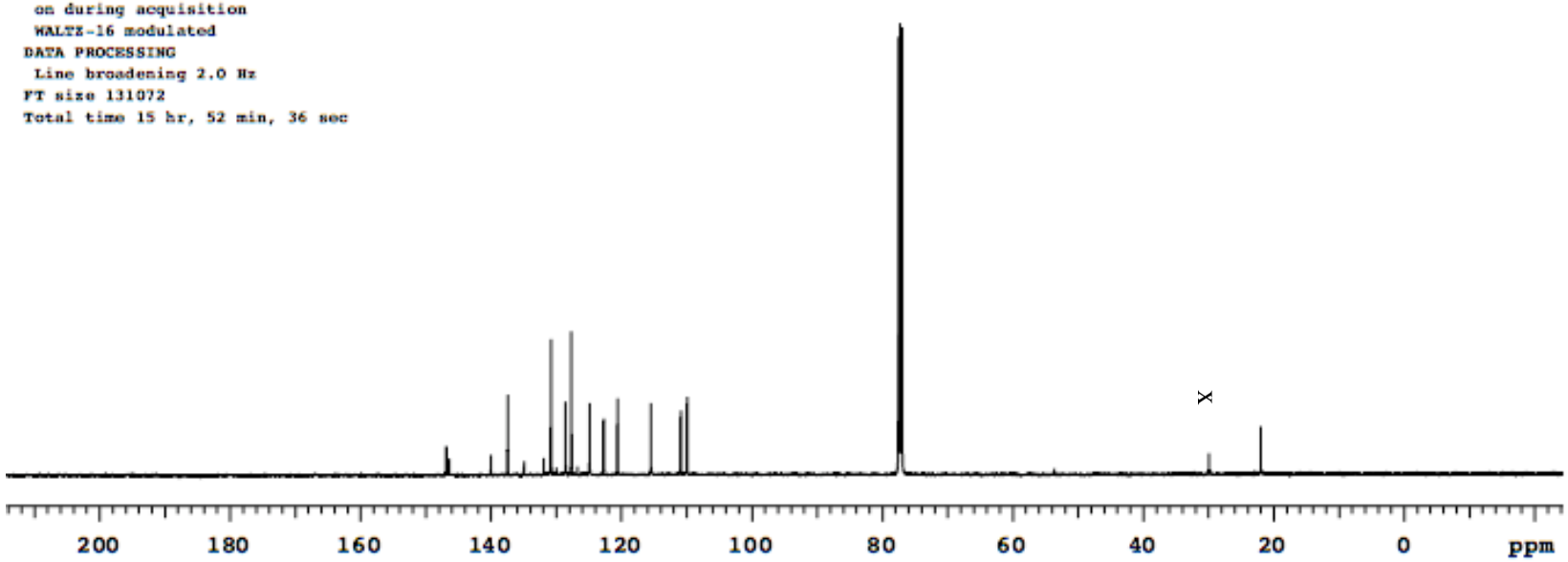
E-**13**
500 MHz, $CDCl_3$

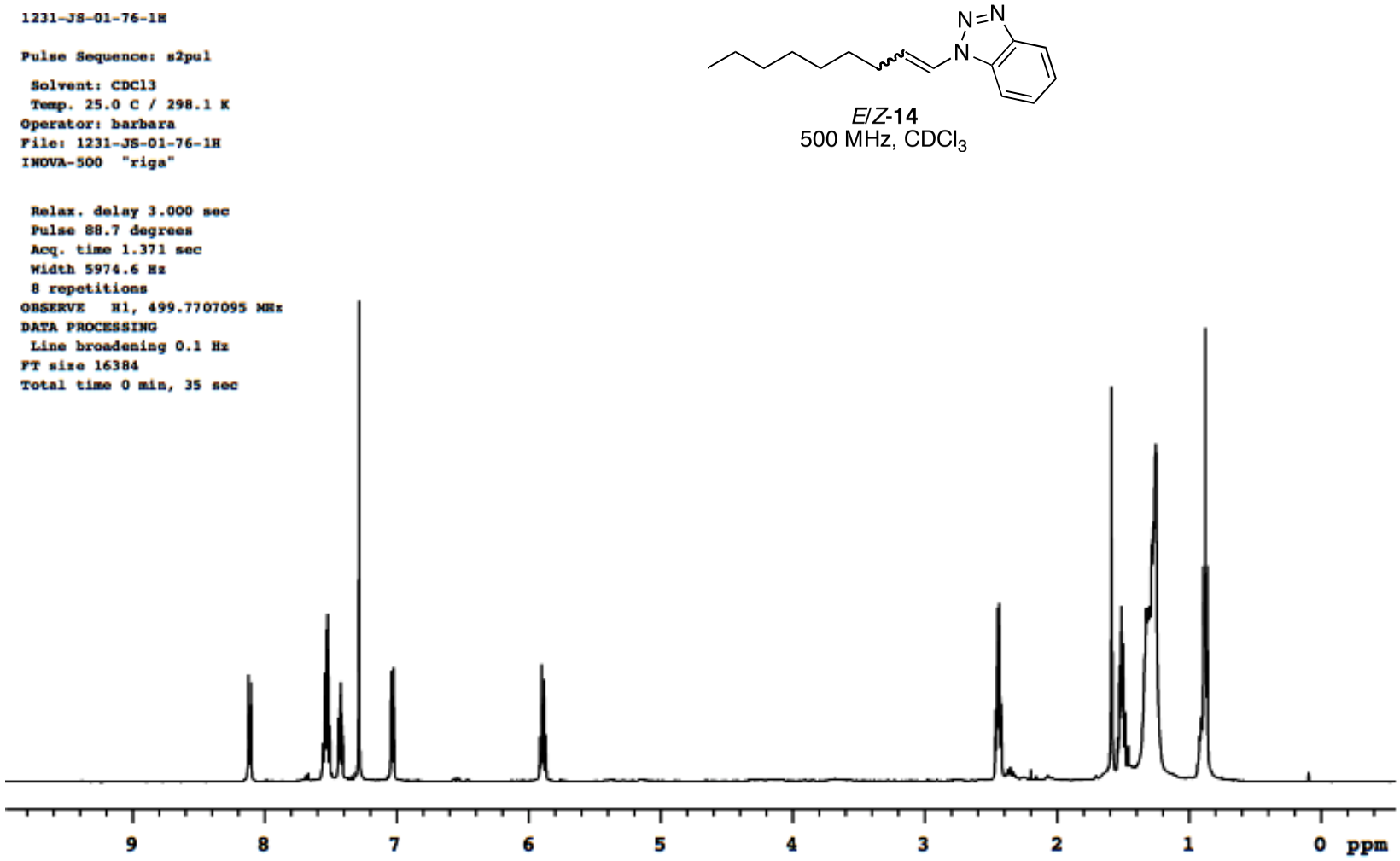


```
GS-1231-cond-BenzotriazoleImidizole-TS-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-BenzotriazoleImidizole-TS-C13-CDCl3
INOVA-500  "riga"

 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 15000 repetitions
OBSERVE  C13, 125.6674182 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 15 hr, 52 min, 36 sec
```



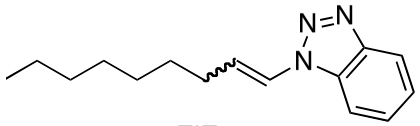
E-**13**
125 MHz, $CDCl_3$



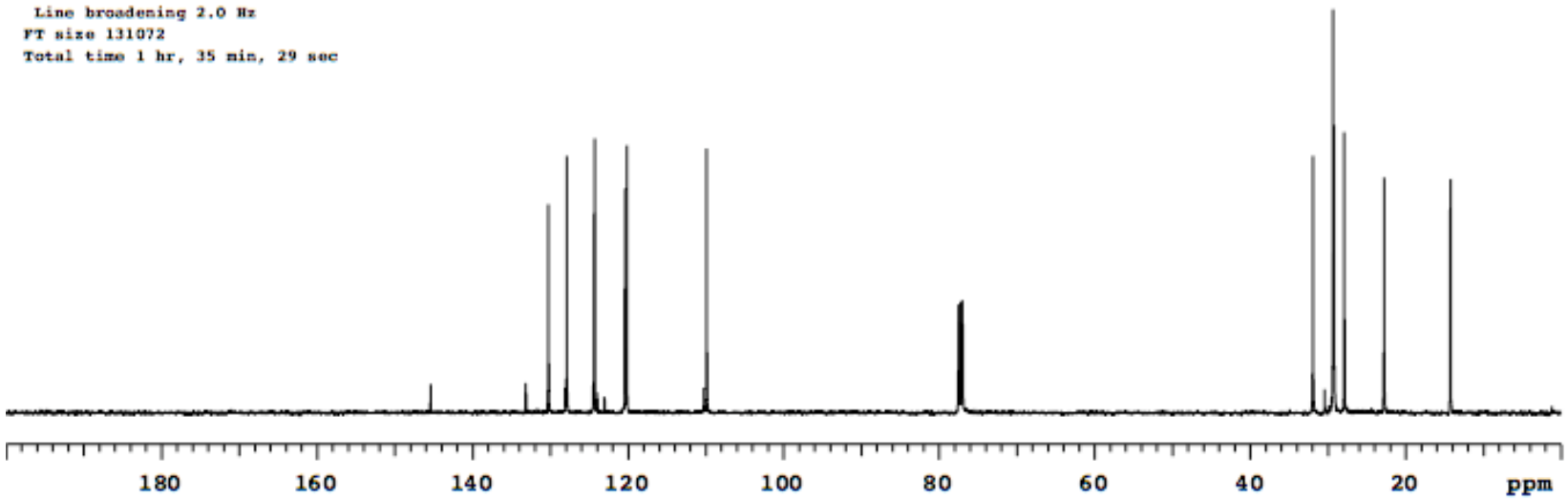


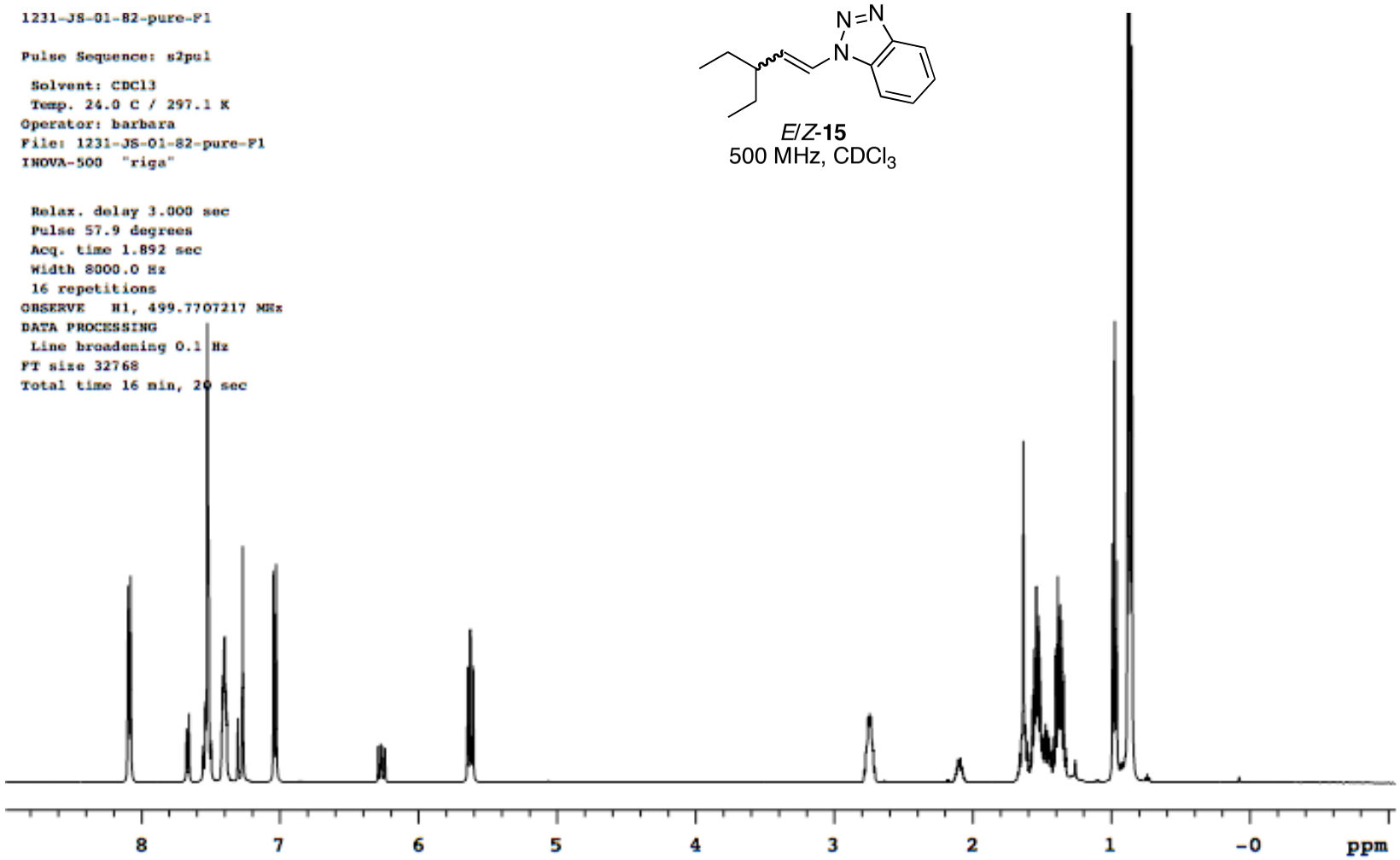
E/*Z*-**14**
500 MHz, $CDCl_3$

```
octanal-benzotriazole-c13-cdcl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: octanal-benzotriazole-c13-cdcl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 1472 repetitions
OBSERVE  C13, 125.6674232 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 35 min, 29 sec
```

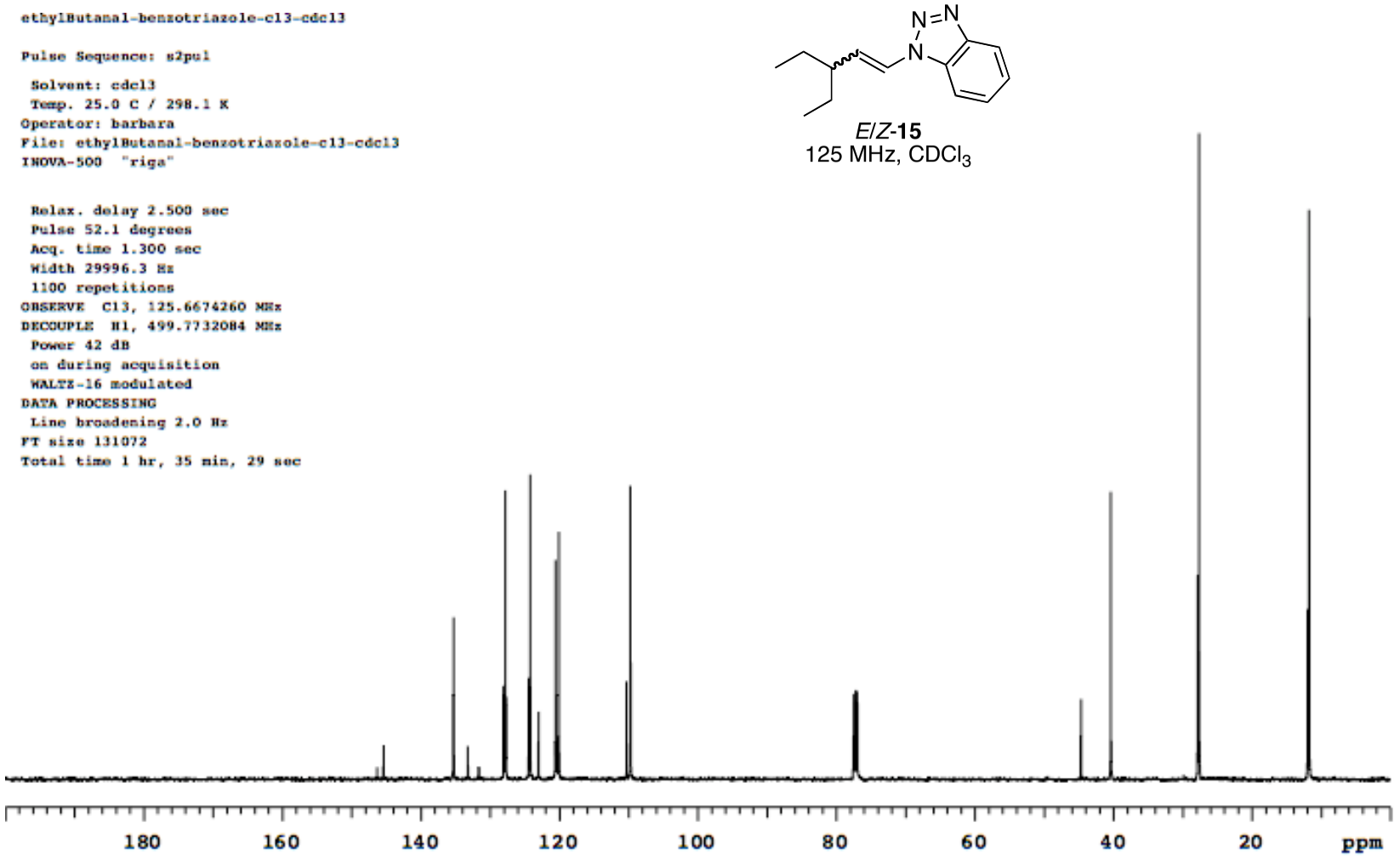


E/*Z*-**14**
125 MHz, $CDCl_3$



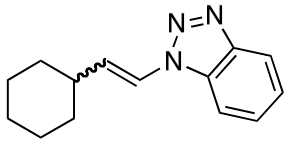


E/*Z*-**15**
500 MHz, $CDCl_3$

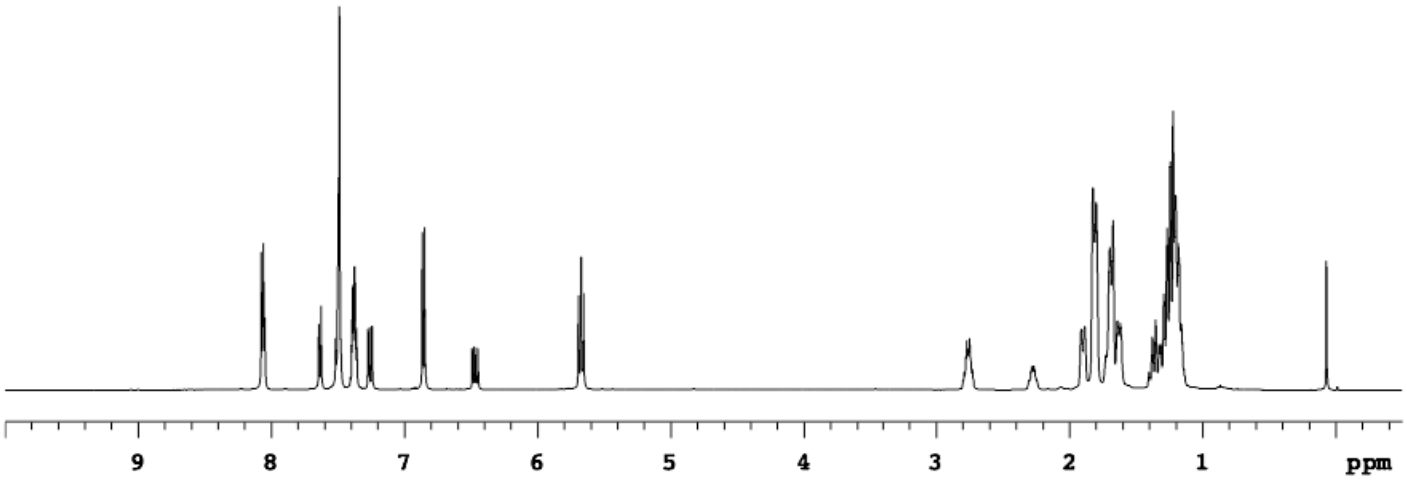


E/*Z*-**15**
125 MHz, $CDCl_3$

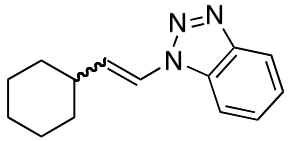
```
GS-1231-01-78-pure

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-78-pure
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 100 repetitions
OBSERVE   H1, 499.7707222 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```



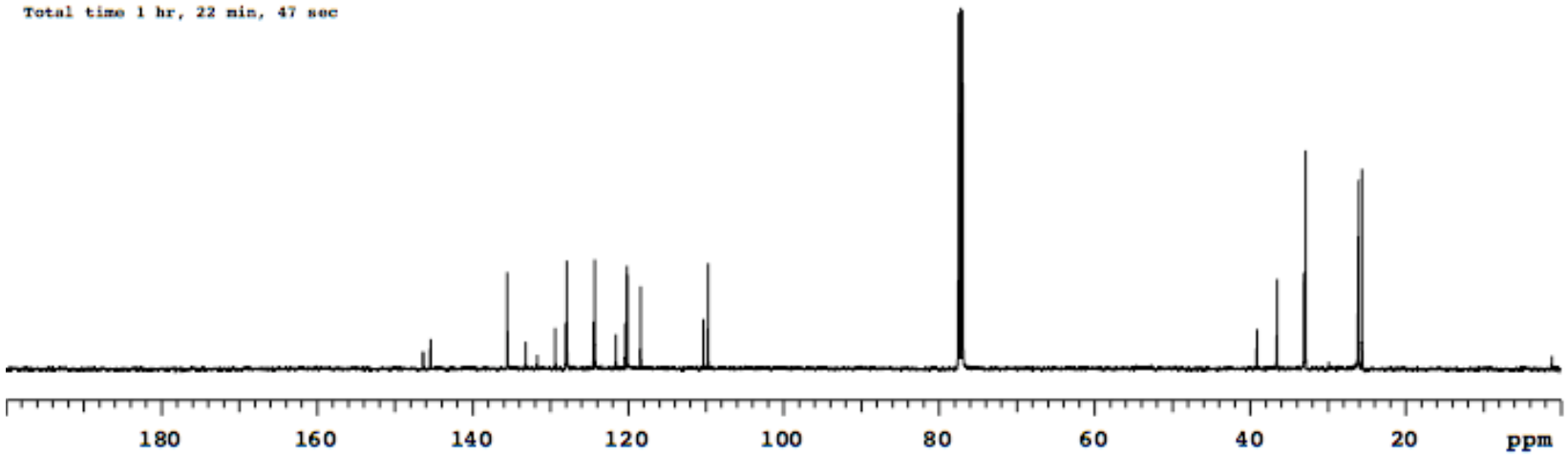
E/*Z*-**16**
500 MHz, $CDCl_3$



```
GS-1231-01-78-c13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-78-c13-CDCl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 1224 repetitions
OBSERVE  C13, 125.6674241 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 22 min, 47 sec
```



E/*Z*-**16**
125 MHz, $CDCl_3$

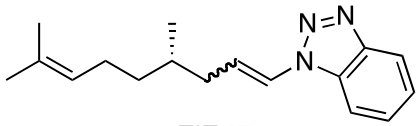


GS-1231-01-64-Cond4-Citrunellal-Pure

Pulse Sequence: s2pul

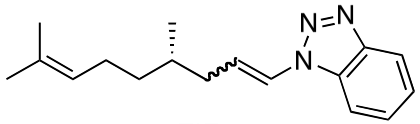
Solvent: CDCl3
Temp. 24.0 C / 297.1 K
Operator: barbara
File: GS-1231-01-64-Cond4-Citrunellal-Pure
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
48 repetitions
OBSERVE H1, 499.7707222 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec

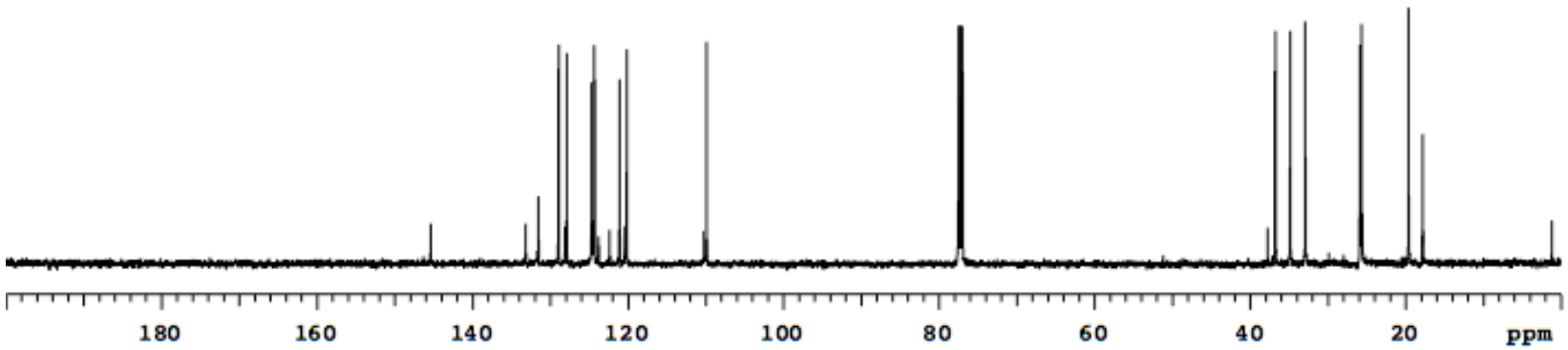


E/*Z*-**17**
500 MHz, $CDCl_3$

```
GS-1231-01-81-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-81-C13-CDCl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 1200 repetitions
OBSERVE  C13, 125.6674237 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 16 min, 26 sec
```



E/*Z*-**17**
125 MHz, $CDCl_3$

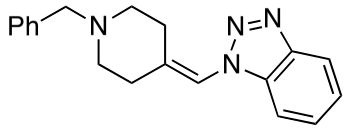


GS-1231-01-piperidonecondenstaion-7

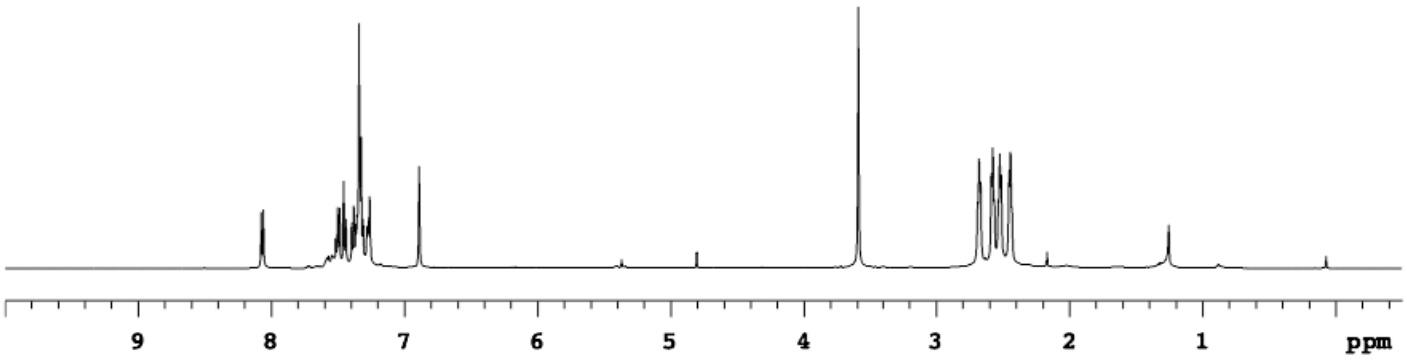
Pulse Sequence: s2pul

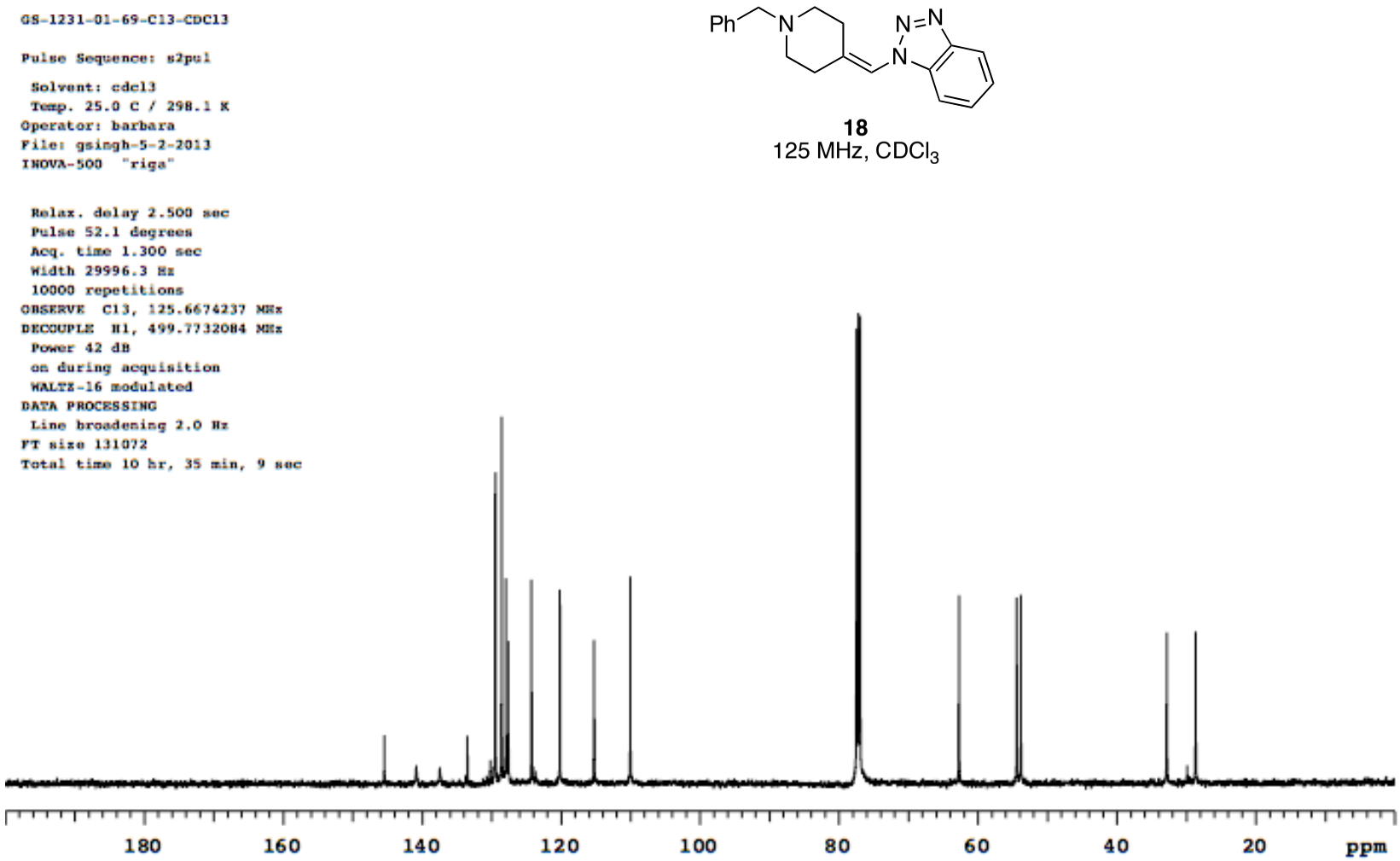
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-piperidonecondenstaion-7
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
36 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 6 min, 20 sec



18
500 MHz, $CDCl_3$





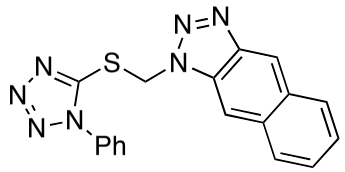
18
125 MHz, $CDCl_3$

GS-1231-03-179-PureNapthyl

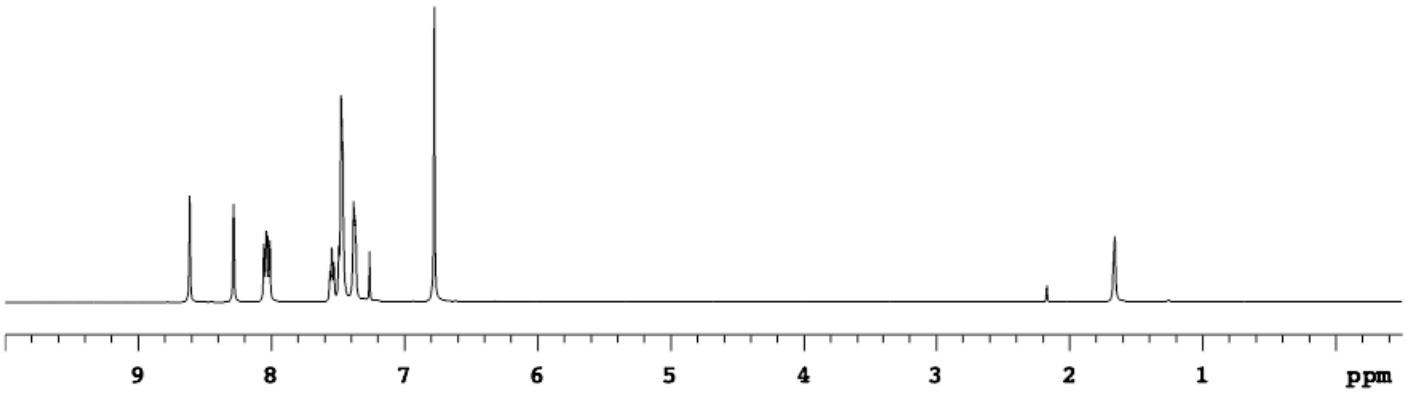
Pulse Sequence: s2pul

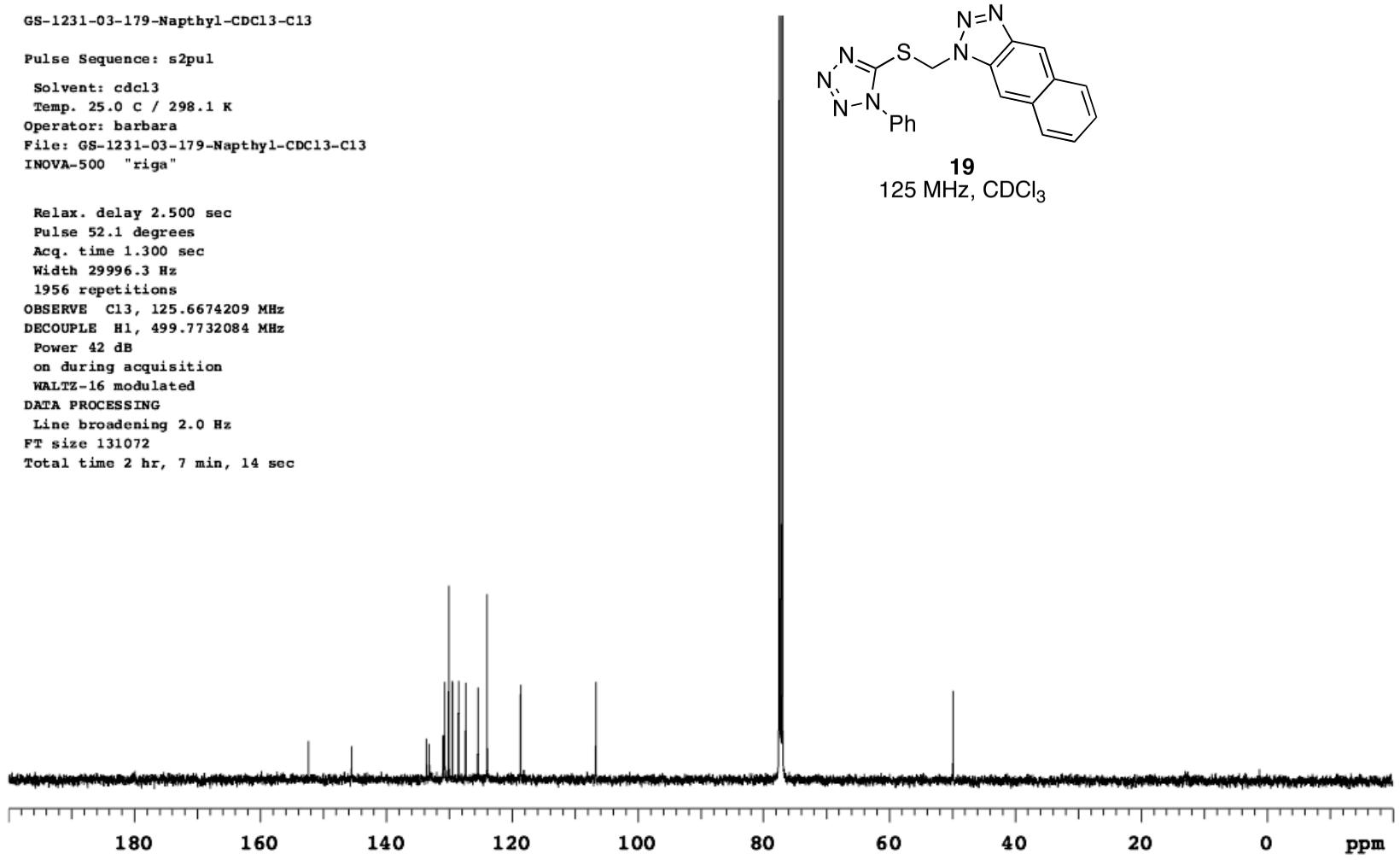
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-179-PureNapthyl
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
56 repetitions
OBSERVE H1, 499.7707197 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



19
500 MHz, $CDCl_3$





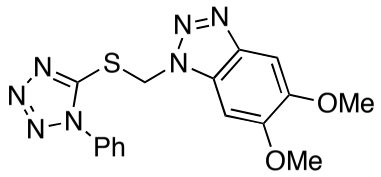
19
125 MHz, $CDCl_3$

GS-1231-02-147-pure

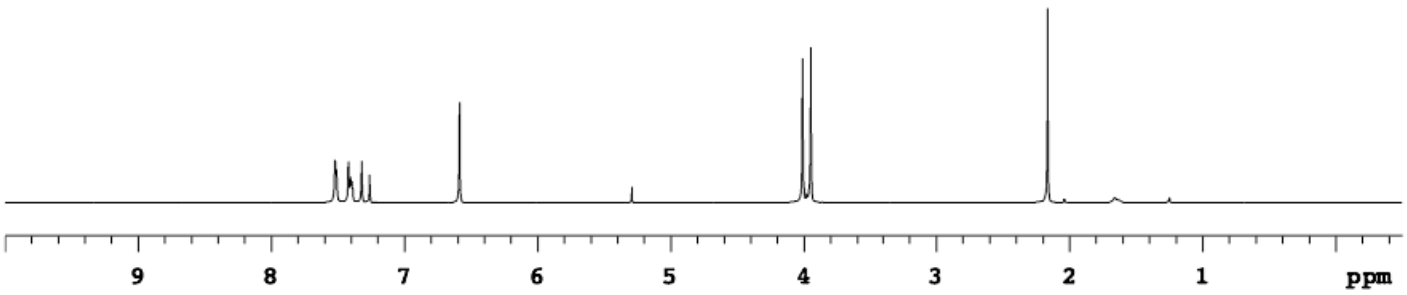
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-147-pure
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707202 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



20
500 MHz, $CDCl_3$

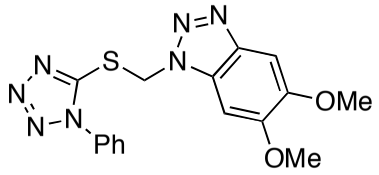


GS-1231-02-147-C13-CDCl3

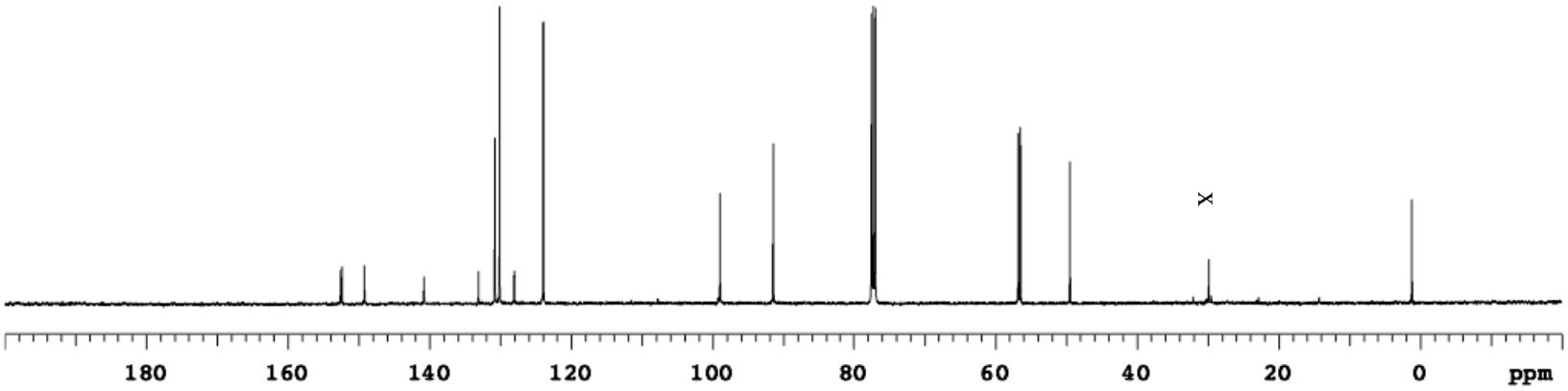
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-147-C13-CDCl3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
8804 repetitions
OBSERVE C13, 125.6674223 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 9 hr, 31 min, 39 sec



20
125 MHz, $CDCl_3$

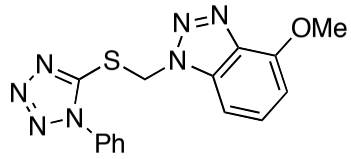


GS-1231-02-105-pure

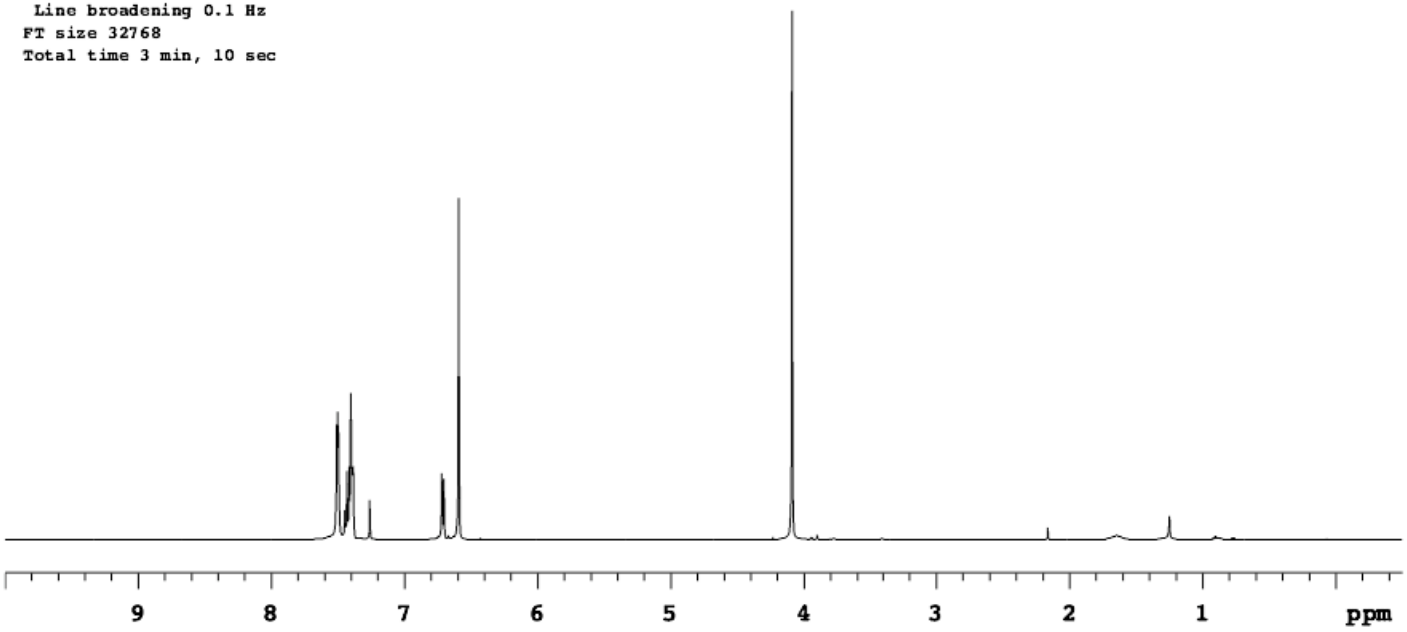
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-105-pure
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
76 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



21
500 MHz, $CDCl_3$

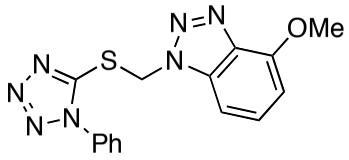


GS-1231-02-119-monomethoxysulfide-C13-CDCl3

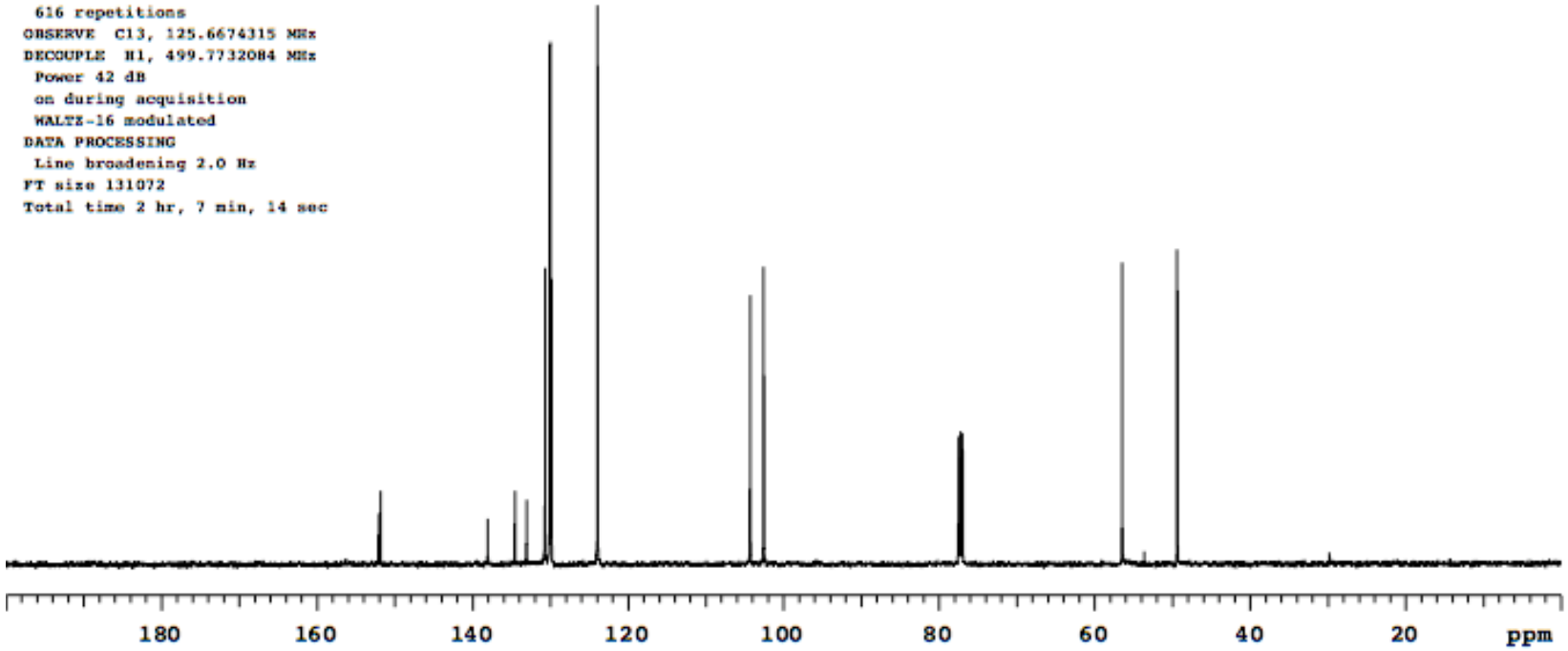
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-119-monomethoxysulfide-C13-CDCl3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
616 repetitions
OBSERVE C13, 125.6674315 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 2 hr, 7 min, 14 sec



21
125 MHz, $CDCl_3$

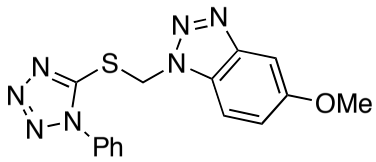


GS-1231-01-94-ClickMethoxy-LS

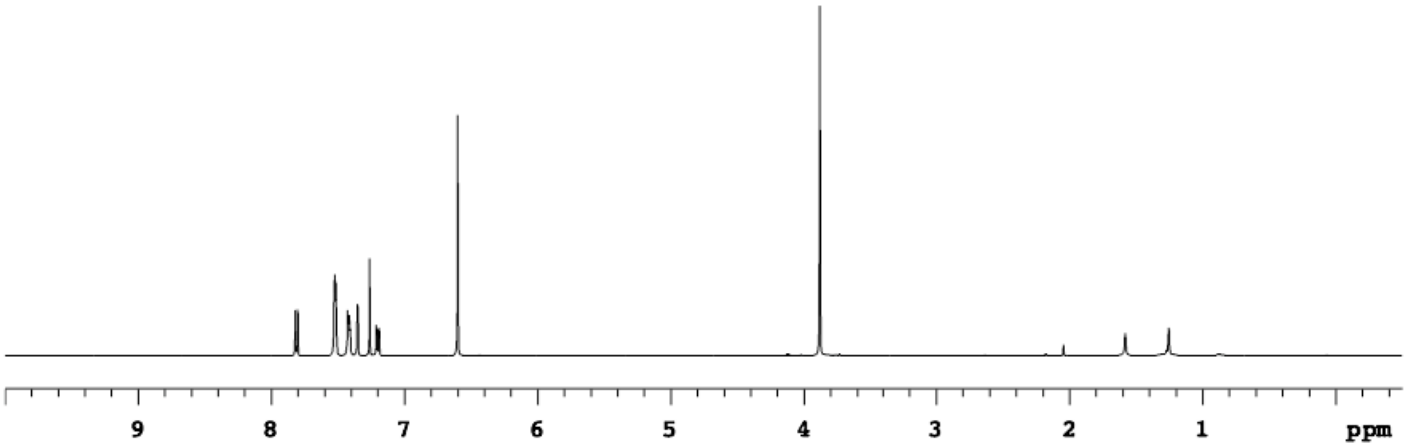
Pulse Sequence: s2pul

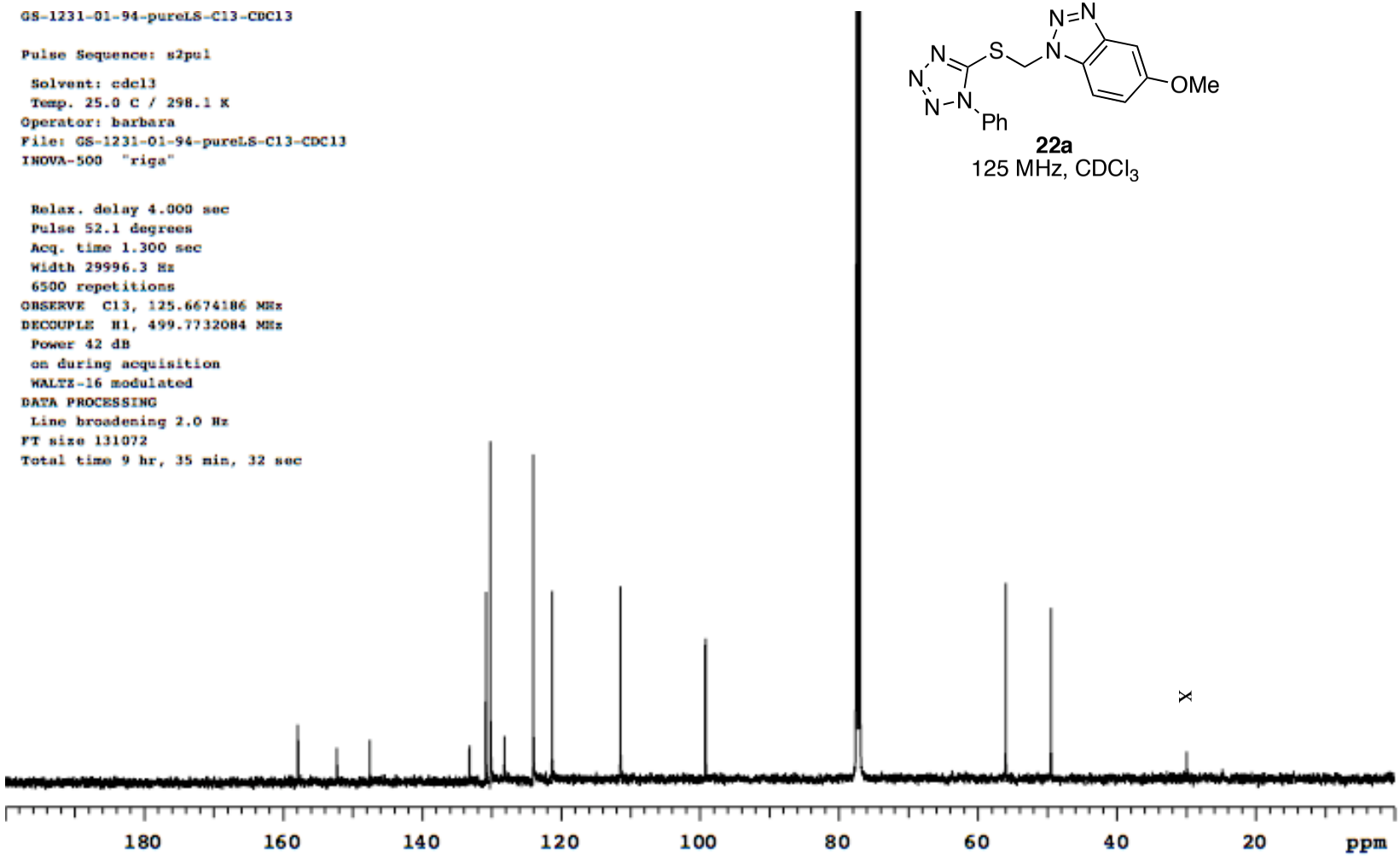
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-94-ClickMethoxy-LS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
48 repetitions
OBSERVE H1, 499.7707222 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



22a
500 MHz, $CDCl_3$



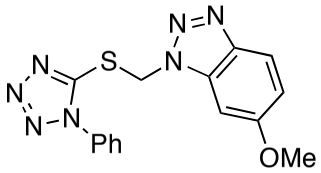

GS-1231-01-94-pureLS-C13-CDCl3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-94-pureLS-C13-CDCl3
INOVA-500 "riga"
Relax. delay 4.000 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
6500 repetitions
OBSERVE C13, 125.6674186 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 9 hr, 35 min, 32 sec
N
N
N
N
S
N
N
Ph
OMe
22a
125 MHz, CDCl3
X
180
160
140
120
100
80
60
40
20
ppm

GS-1231-01-94-clickMethoxy-TS

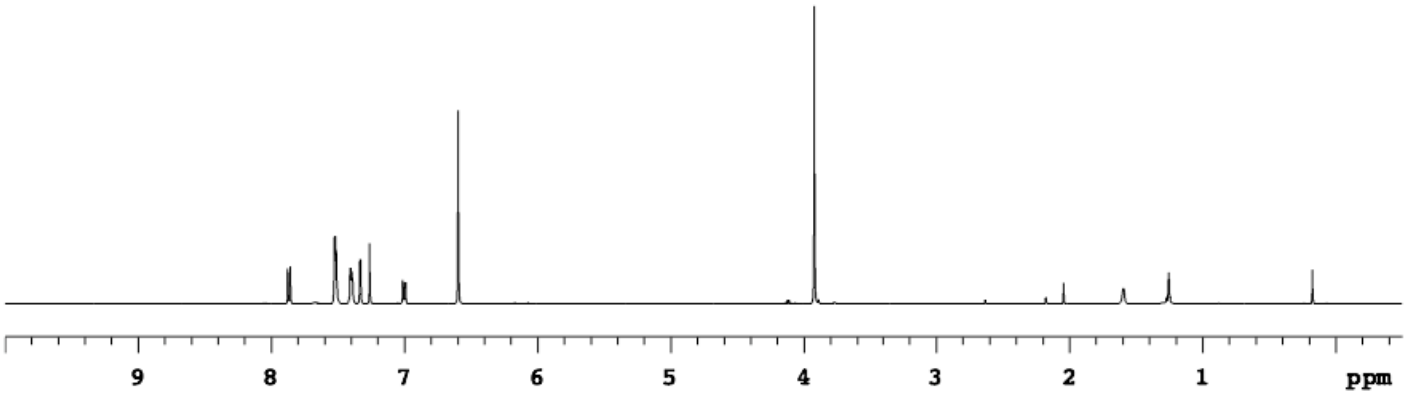
Pulse Sequence: s2pul

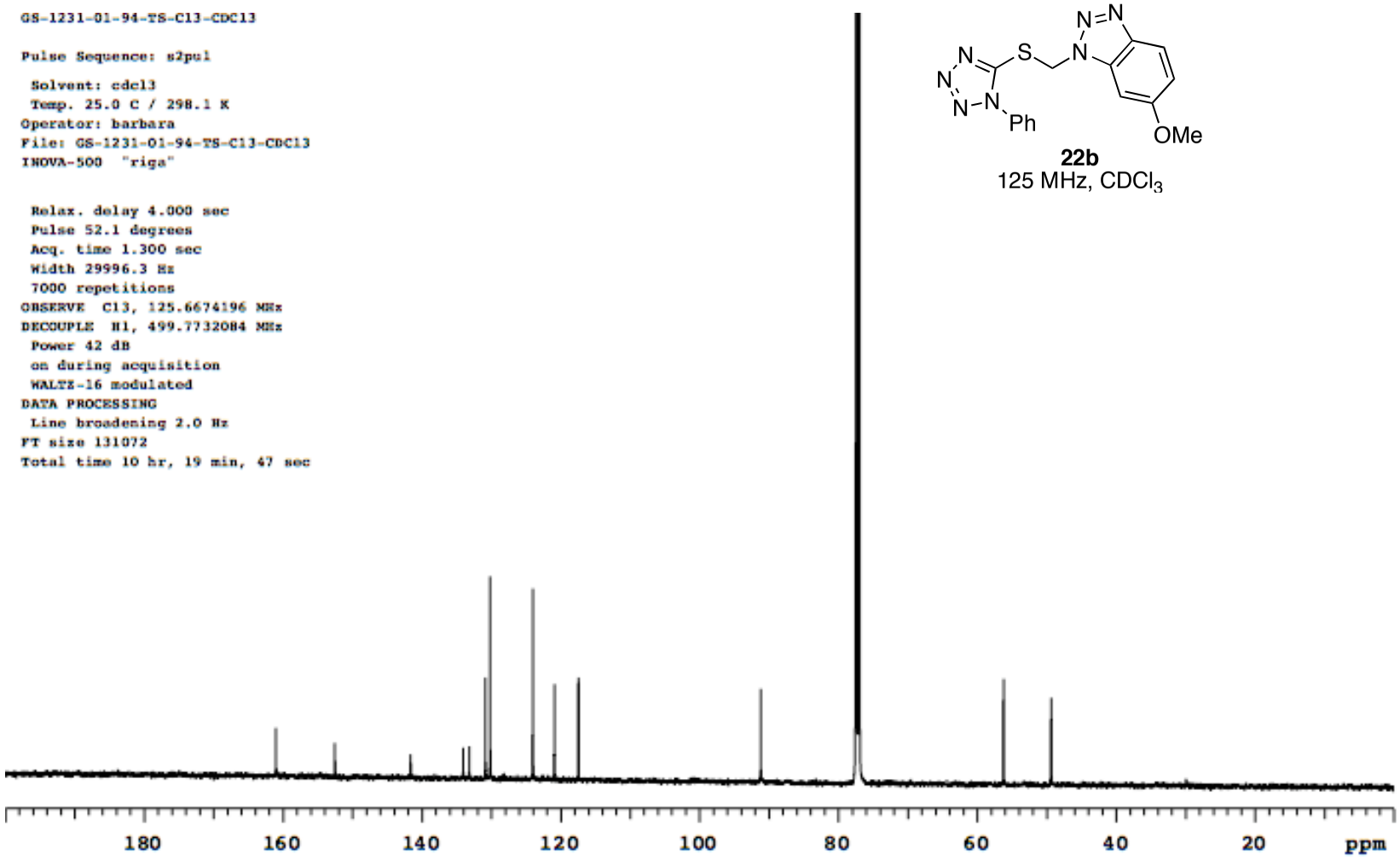
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-94-clickMethoxy-TS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707222 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec

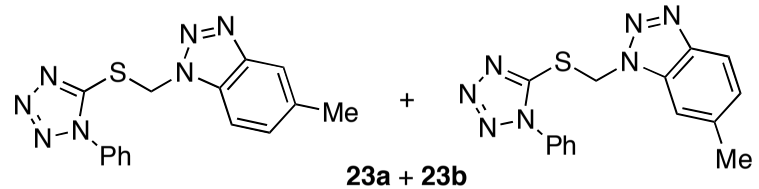


22b
500 MHz, $CDCl_3$

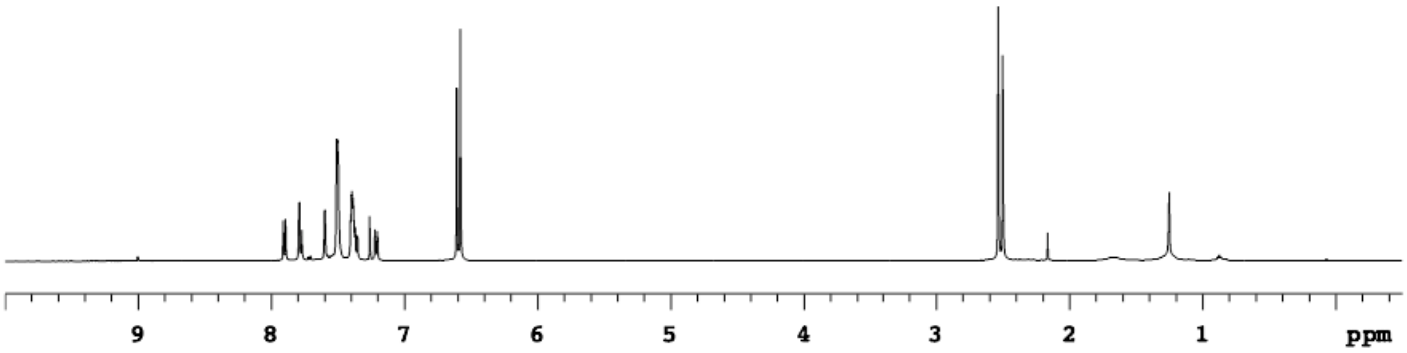


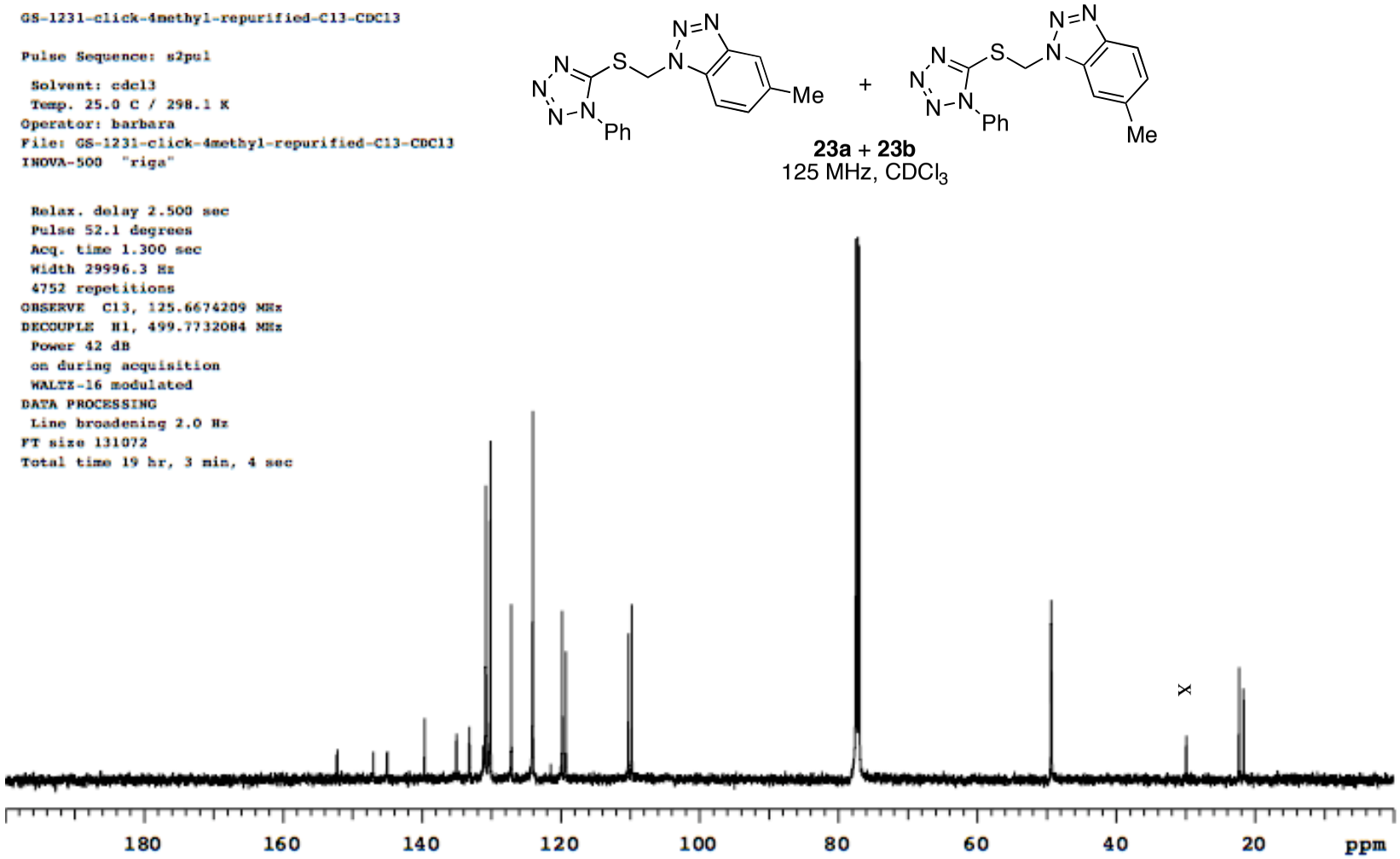

GS-1231-01-94-TS-C13-CDCl3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-01-94-TS-C13-CDCl3
INOVA-500 "riga"
Relax. delay 4.000 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
7000 repetitions
OBSERVE C13, 125.6674196 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 10 hr, 19 min, 47 sec
N=N
N
S
N
N
N
Ph
OMe
22b
125 MHz, CDCl3
180
160
140
120
100
80
60
40
20
ppm

```
GS-1231-02-117-pure

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-117-pure
INOVA-500  "riga"

 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 56 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```

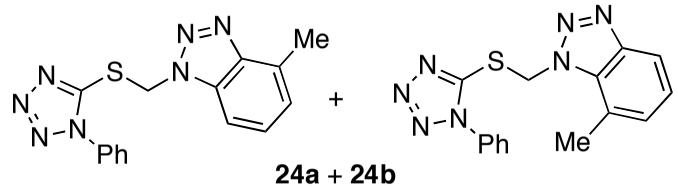


23a + **23b**
500 MHz, $CDCl_3$

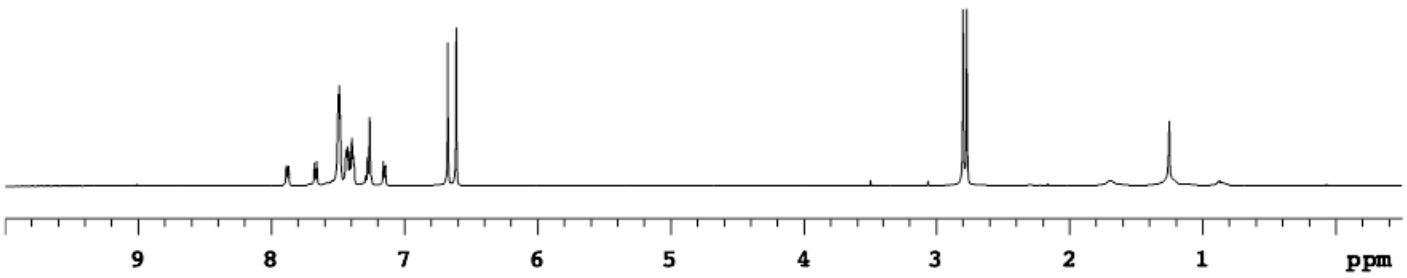


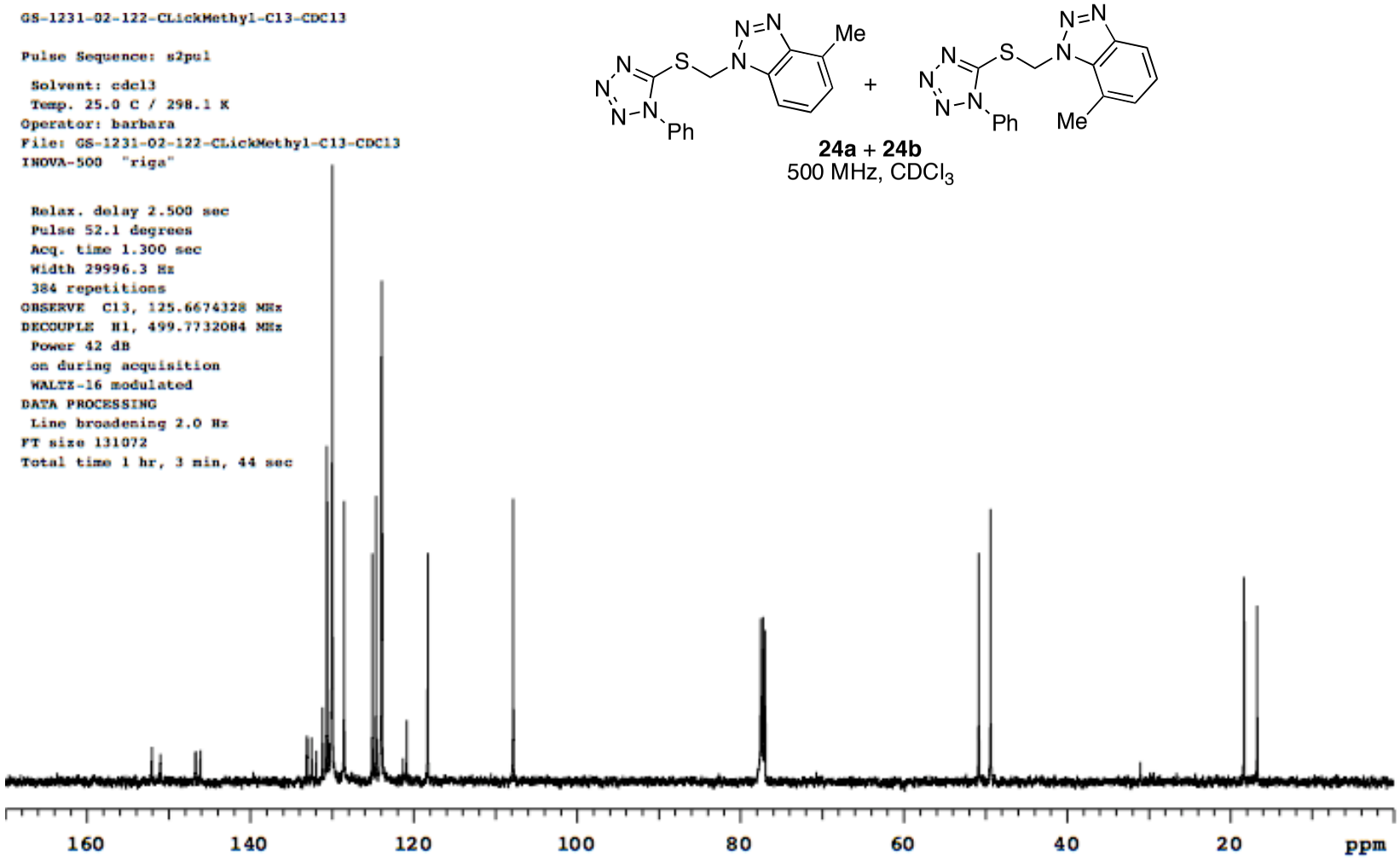

GS-1231-click-4methyl-repurified-C13-CDCl3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-click-4methyl-repurified-C13-CDCl3
INOVA-500 "riga"
Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
4752 repetitions
OBSERVE C13, 125.6674209 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 19 hr, 3 min, 4 sec
Me
Ph
+
Me
Ph
23a + 23b
125 MHz, CDCl3
X
180
160
140
120
100
80
60
40
20
ppm

```
GS-1231-02-116-pure

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-116-pure
INOVA-500  "riga"


 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 56 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```

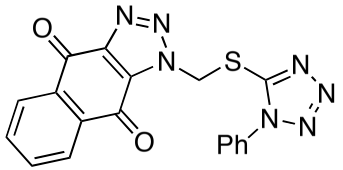


24a + **24b**
500 MHz, $CDCl_3$

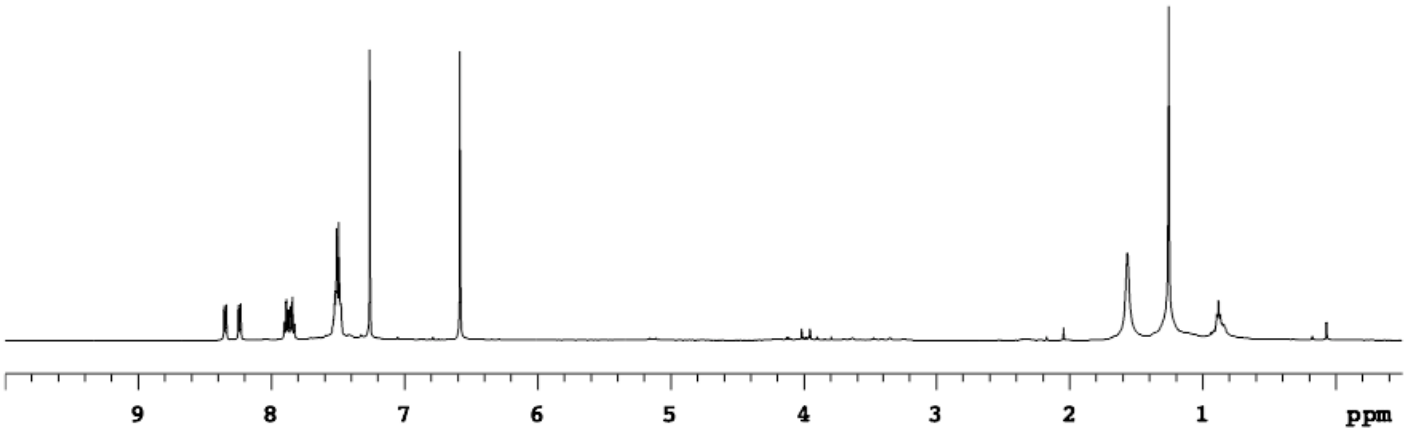


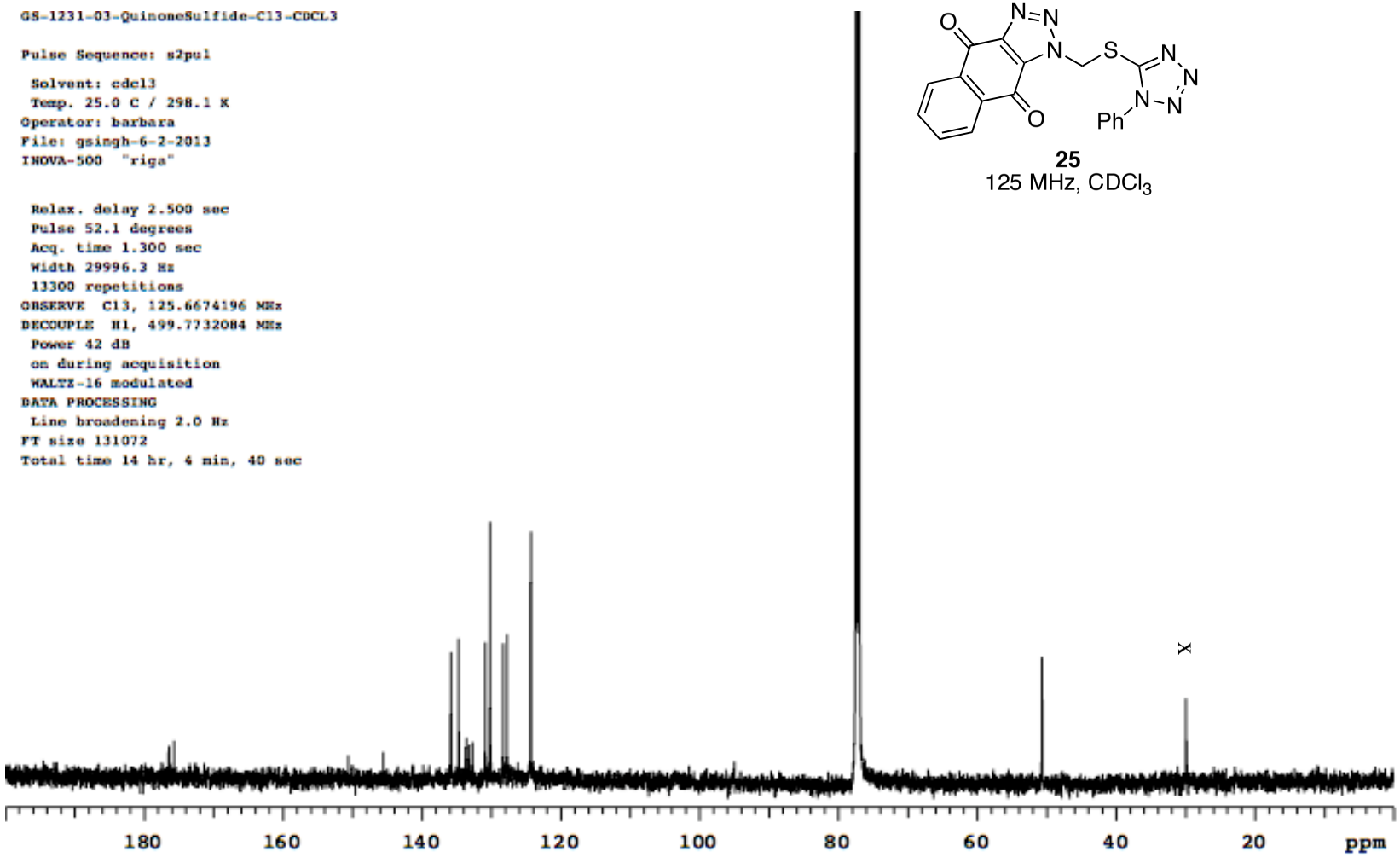

GS-1231-02-122-CLickMethyl-C13-CDCl3
Pulse Sequence: s2pul
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-122-CLickMethyl-C13-CDCl3
INOVA-500 "riga"
Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
384 repetitions
OBSERVE C13, 125.6674328 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 1 hr, 3 min, 44 sec
Me
Ph
+
Ph
Me
24a + 24b
500 MHz, CDCl3
160
140
120
100
80
60
40
20
ppm

```
GS-1231-02-146-pure-f2

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-146-pure-f2
INOVA-500  "riga"


 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 100 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```

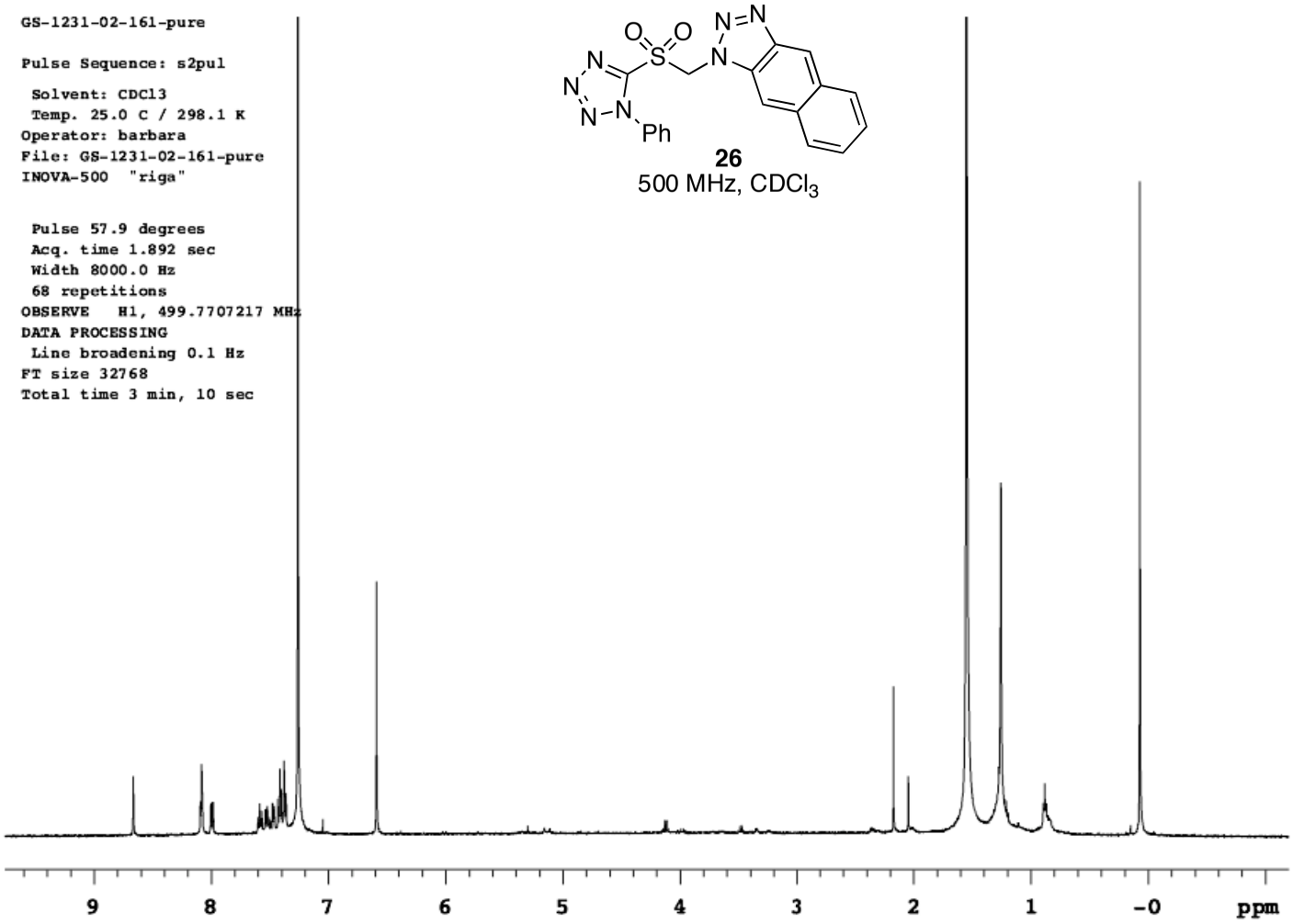


25
500 MHz, $CDCl_3$





25
125 MHz, $CDCl_3$



26

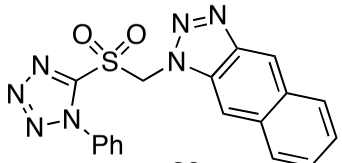
500 MHz, $CDCl_3$

GS-1231-03-PureNapthylSulfone-C13-DMSO-D6

Pulse Sequence: s2pul

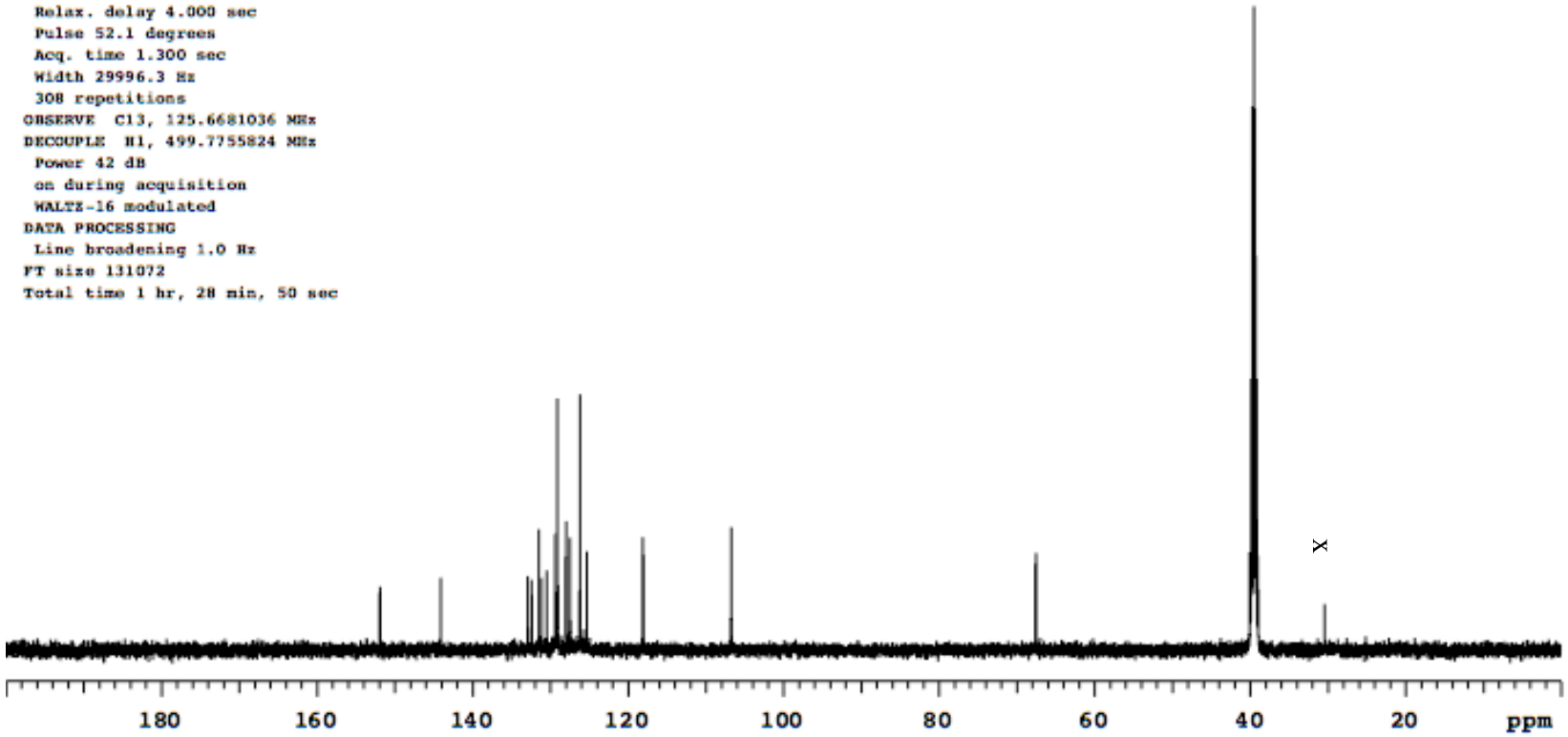
Solvent: dmso
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-PureNapthylSulfone-C13-DMSO-D6
INOVA-500 "riga"

Relax. delay 4.000 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
308 repetitions
OBSERVE C13, 125.6681036 MHz
DECOUPLE H1, 499.7755824 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 1 hr, 28 min, 50 sec

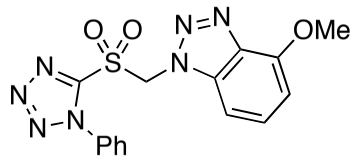


26

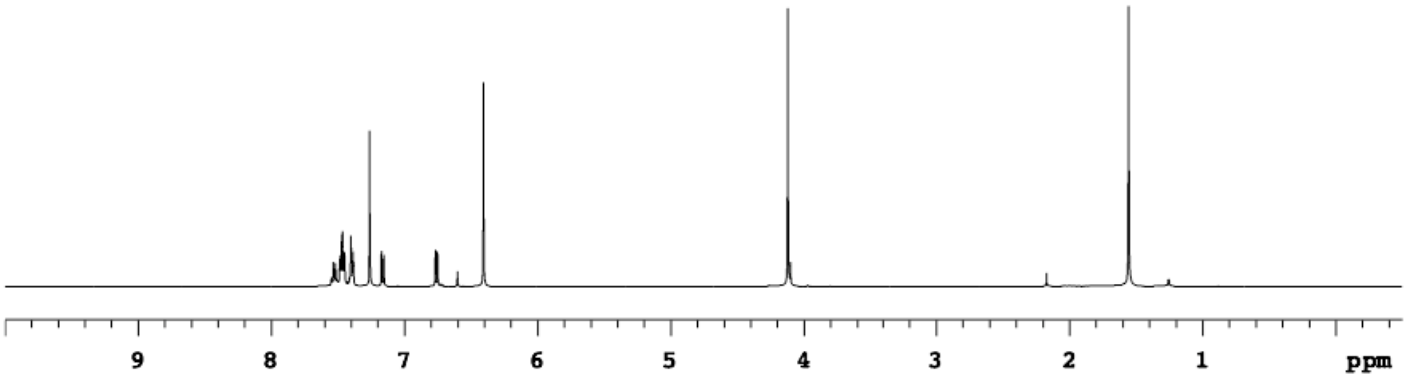
125 MHz, DMSO-d_6

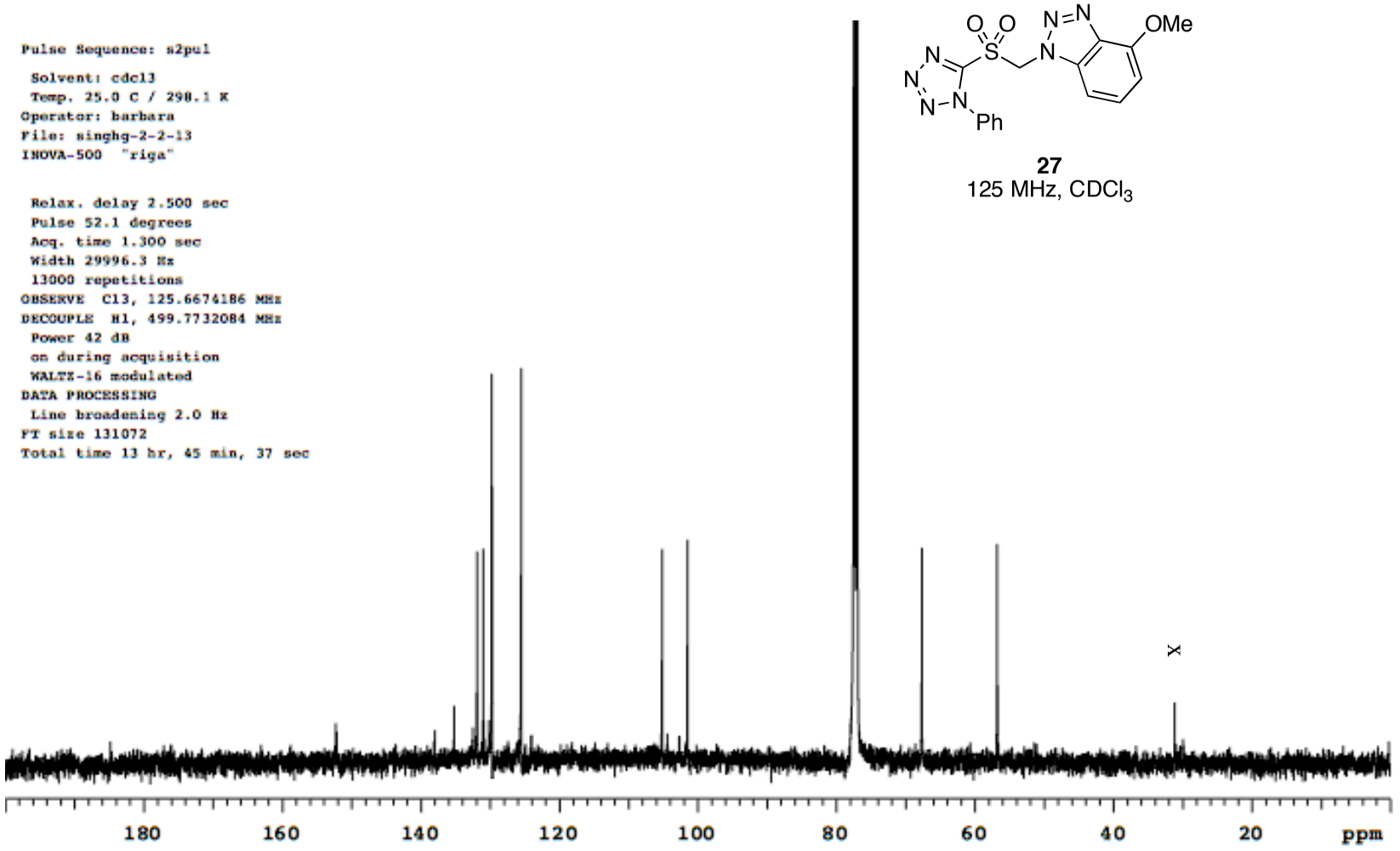


```
GS-1231-196-monomethoxySulfone

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-196-monomethoxySulfone
INOVA-500  "riga"


 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 100 repetitions
OBSERVE   H1, 499.7707207 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```



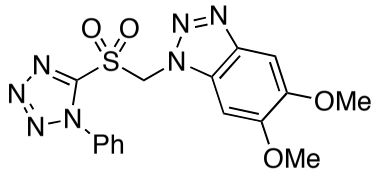
27
500 MHz, $CDCl_3$





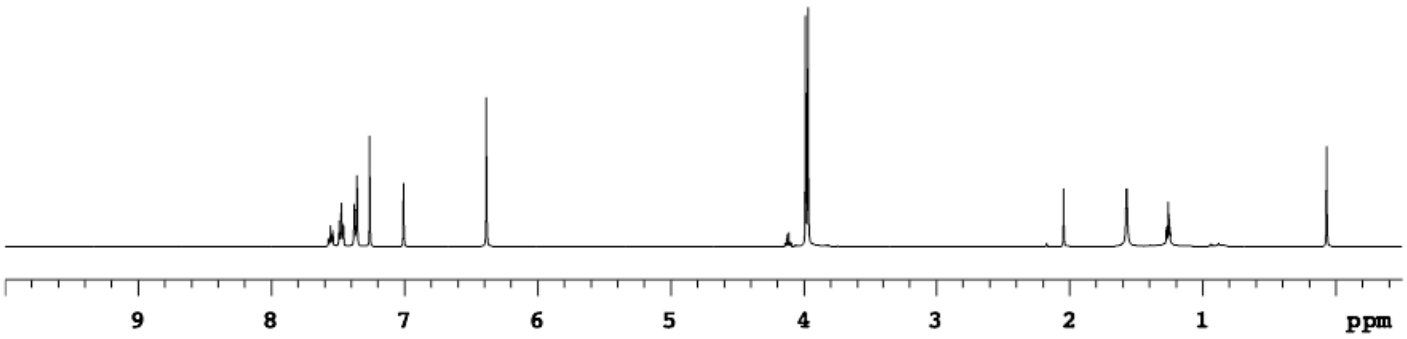
27
125 MHz, $CDCl_3$

```
GS-1231-02-169-pure

Pulse Sequence: s2pul

 Solvent: CDCl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-02-169-pure
INOVA-500  "riga"


 Pulse 57.9 degrees
 Acq. time 1.892 sec
 Width 8000.0 Hz
 92 repetitions
OBSERVE   H1, 499.7707212 MHz
DATA PROCESSING
 Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec
```



28

500 MHz, $CDCl_3$

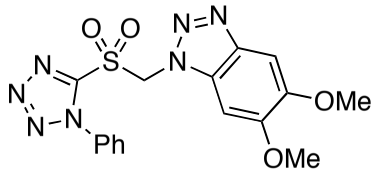


GS-1231-03-182-C13-CDCl3

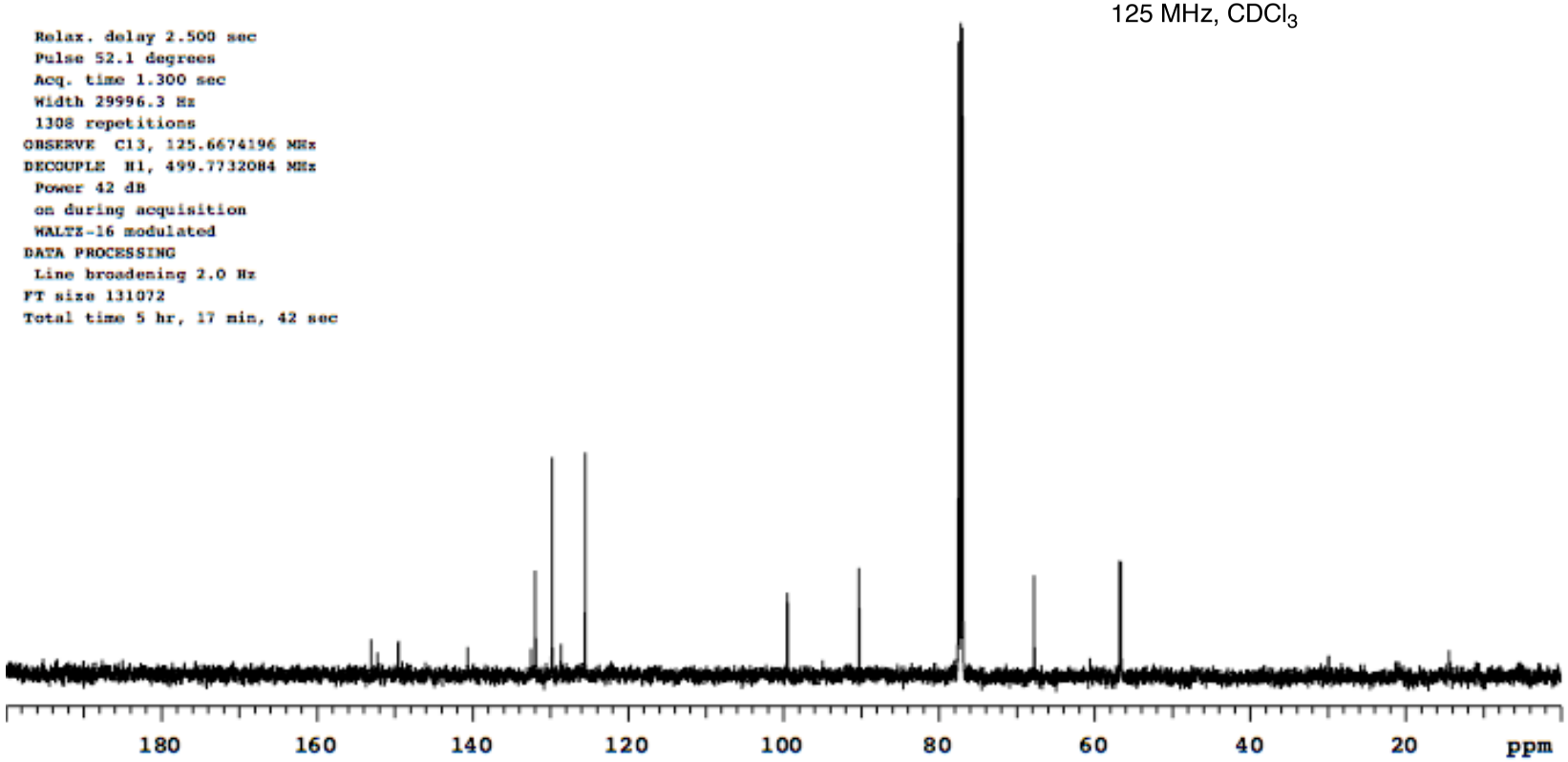
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-182-C13-CDCl3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
1308 repetitions
OBSERVE C13, 125.6674196 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 5 hr, 17 min, 42 sec



28
125 MHz, $CDCl_3$

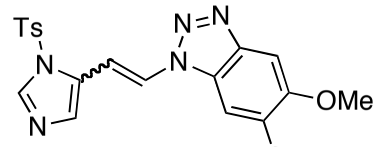


GS-1231-03-185-pureTS

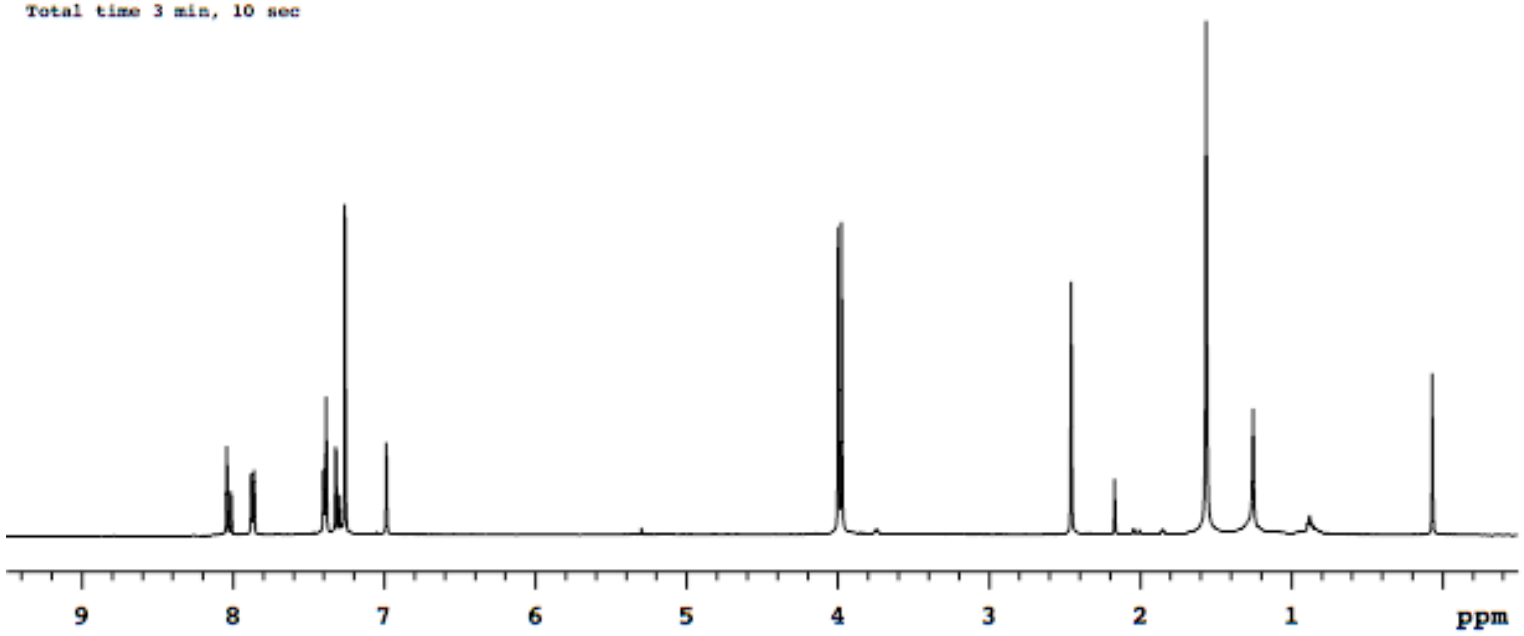
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-185-pureTS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
44 repetitions
OBSERVE H1, 499.7707236 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



E/*Z*-**29**
500 MHz, $CDCl_3$

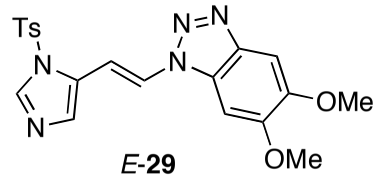


GS-1231-cond-DimethoxyImidizole-pureTS

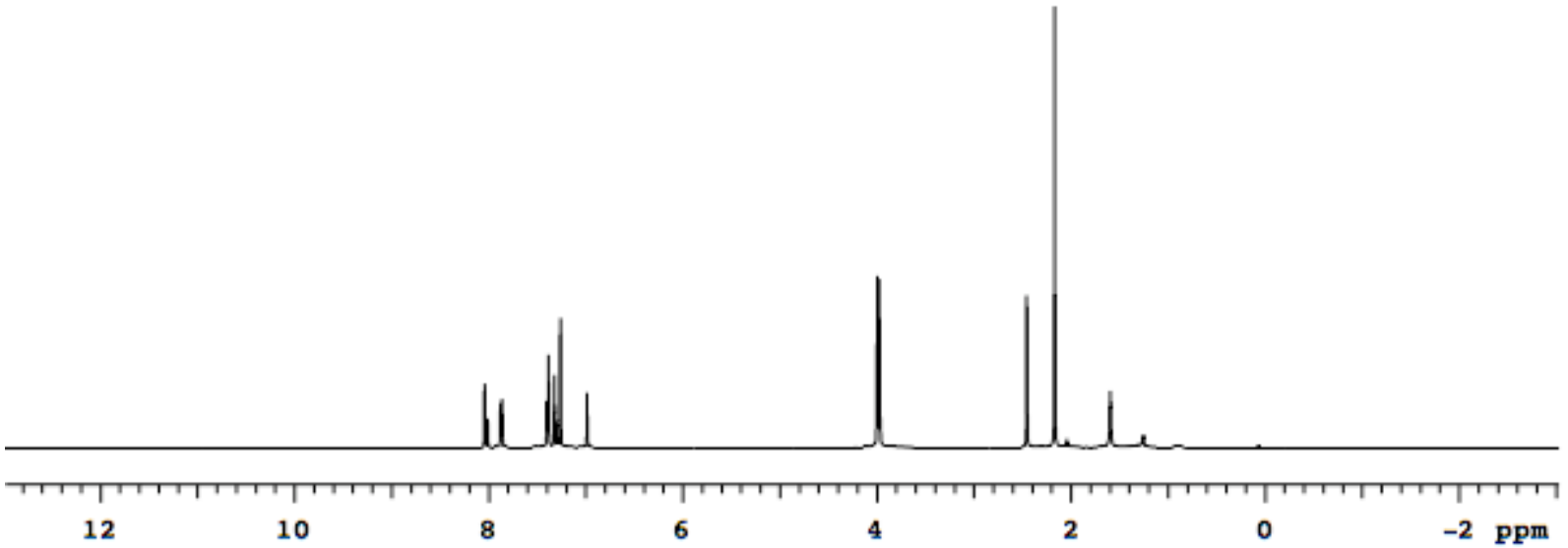
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-DimethoxyImidizole-pureTS
INOVA-500 "riga"

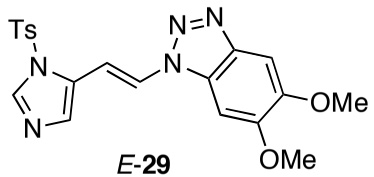
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec



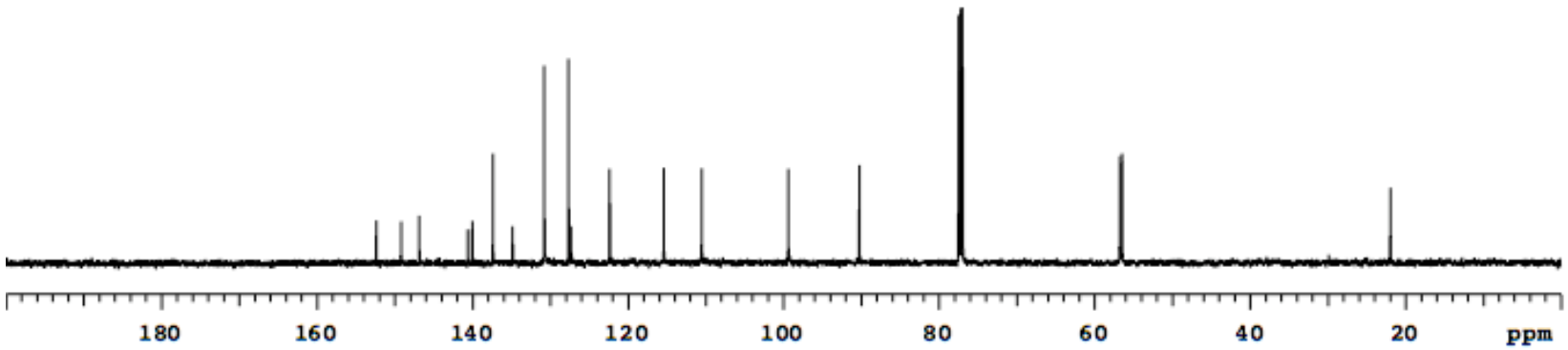
E-**29**
500 MHz, $CDCl_3$



```
GS-1231-cond-DiMethoxyImidizole-TS-C13-CDCl3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-DiMethoxyImidizole-TS-C13-CDCl3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 996 repetitions
OBSERVE  C13, 125.6674218 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 11 hr, 38 min, 38 sec
```



E-**29**
125 MHz, $CDCl_3$

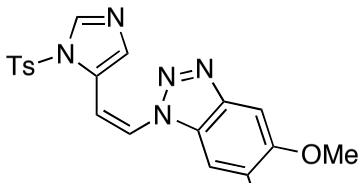


GS-1231-cond-DimethoxyImidizole-pureBS

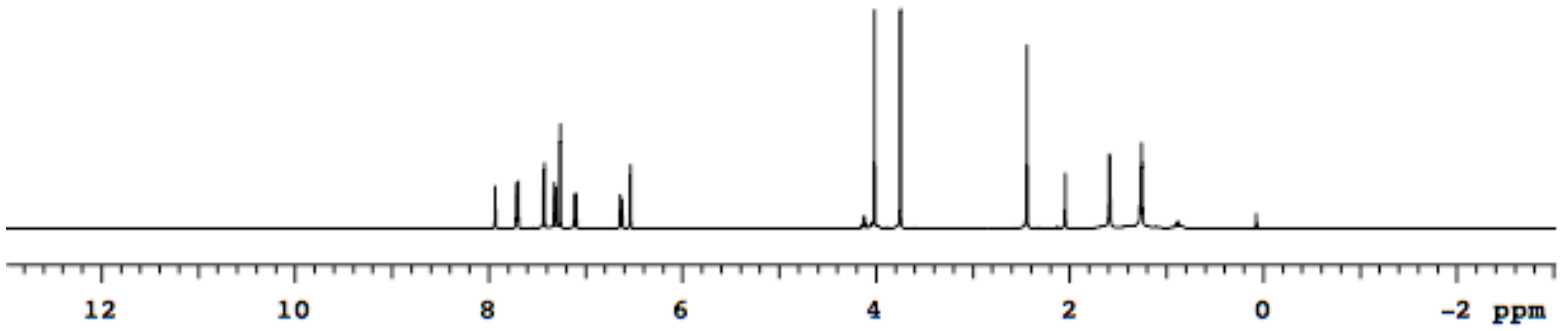
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-DimethoxyImidizole-pureBS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
48 repetitions
OBSERVE H1, 499.7707207 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec



Z-**29**
500 MHz, $CDCl_3$

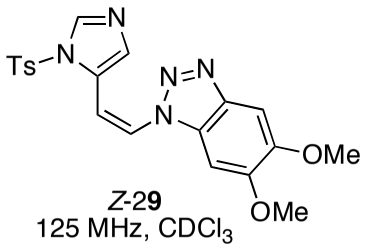


GS-1231-cond-DimethoxyImidizole-BS-C13-CDCl3

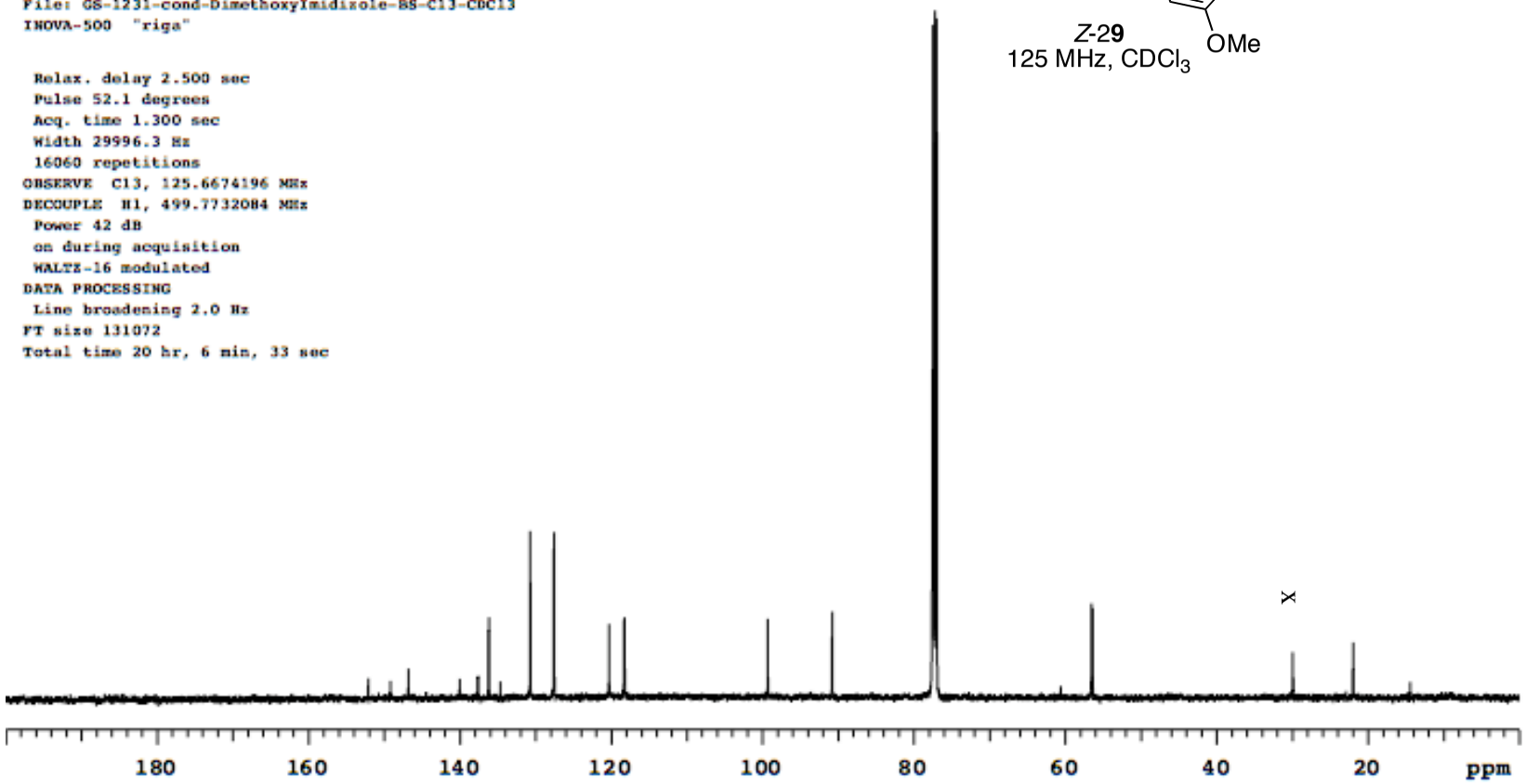
Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-DimethoxyImidizole-BS-C13-CDCl3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
16060 repetitions
OBSERVE C13, 125.6674196 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 20 hr, 6 min, 33 sec



Z-**29**
125 MHz, $CDCl_3$

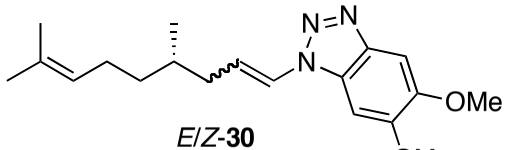


GS-1231-03-193-pure

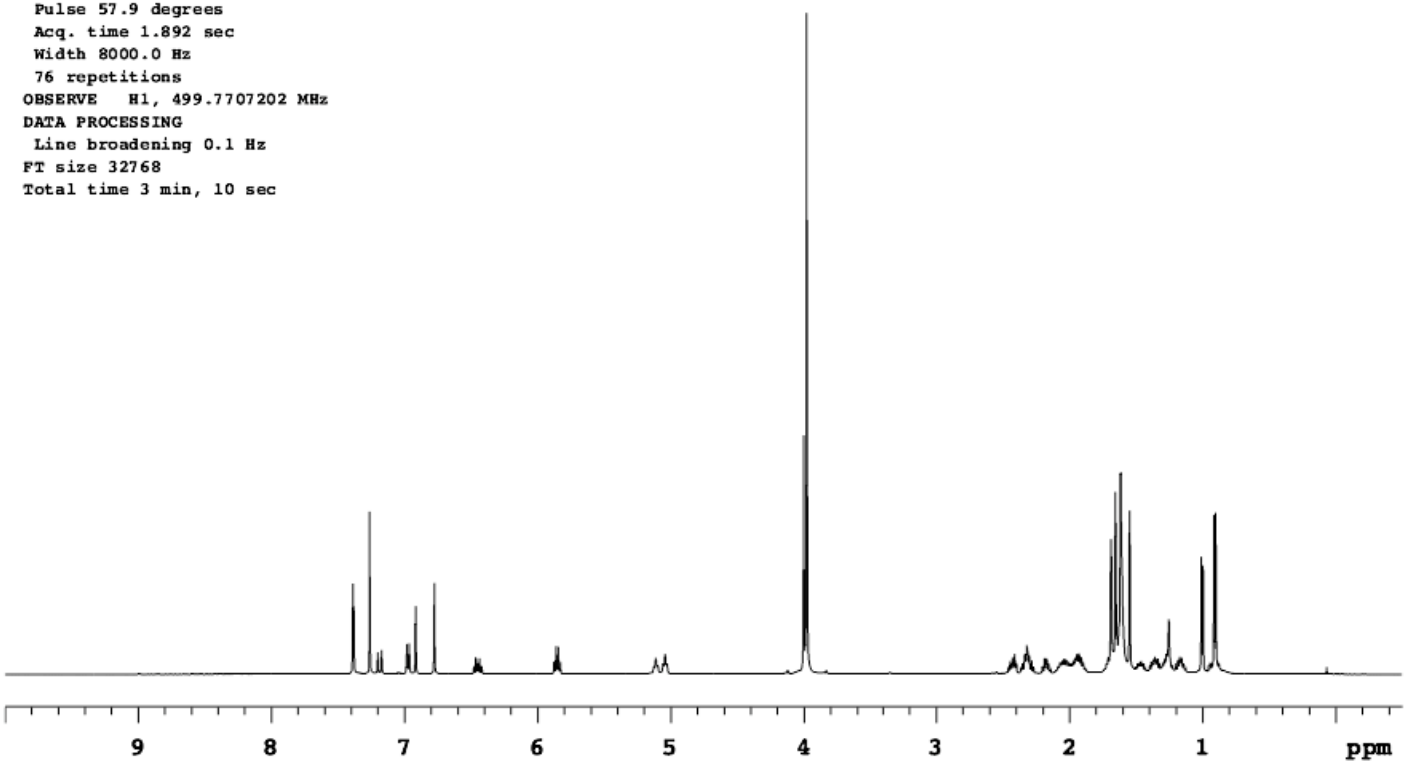
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-193-pure
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
76 repetitions
OBSERVE H1, 499.7707202 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



E/*Z*-**30**
500 MHz, $CDCl_3$

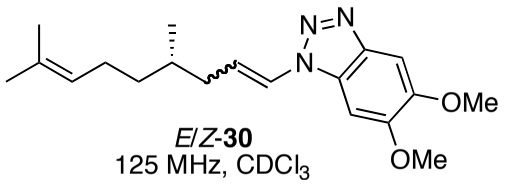


GS-1231-03-204-C13-CDCl3-dimethoxyCitronellal

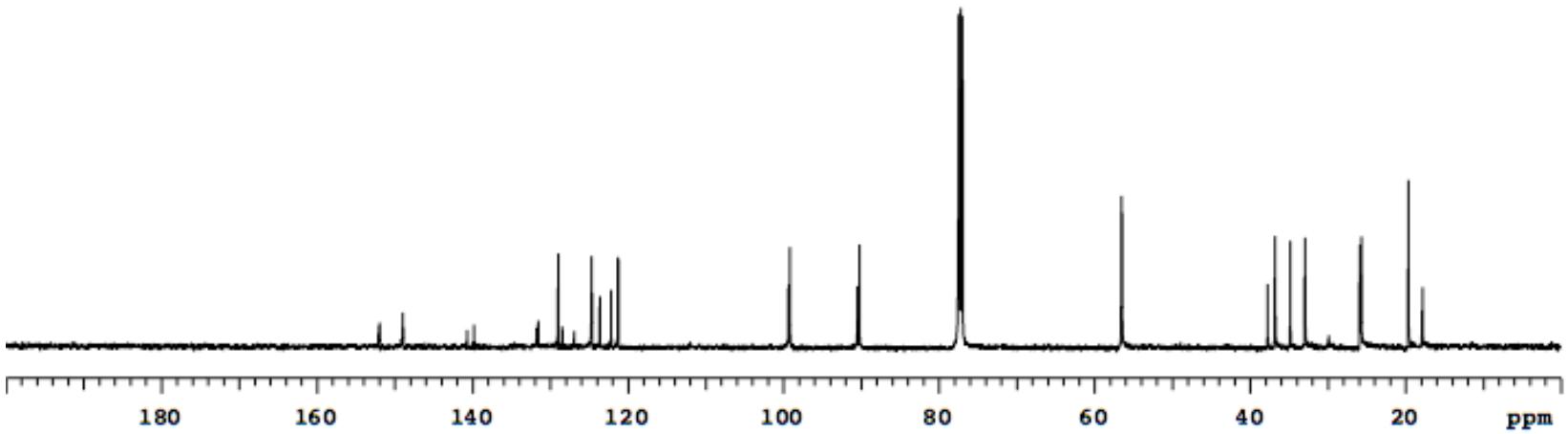
Pulse Sequence: s2pul

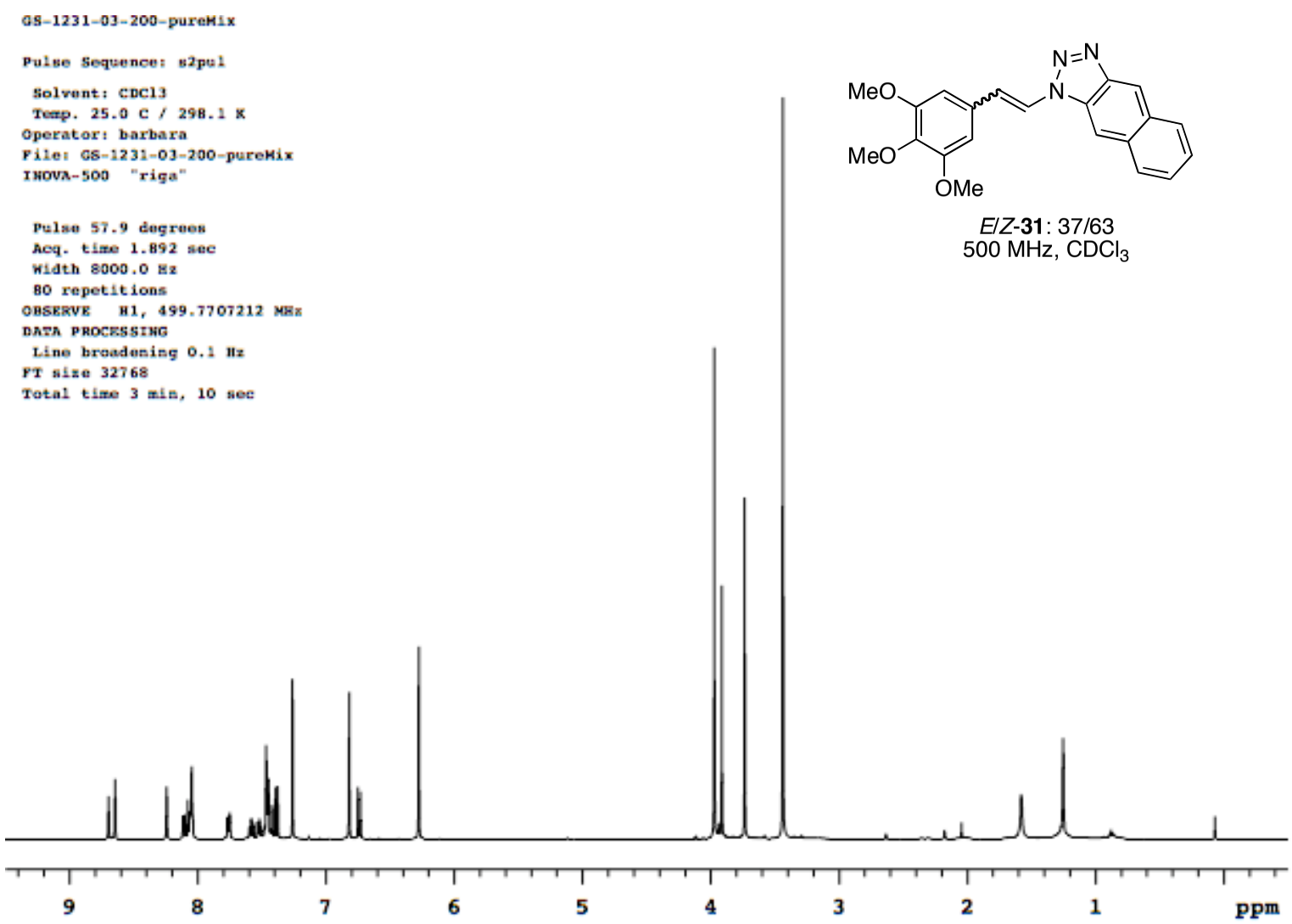
Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-204-C13-CDCl3-dimethoxyCitronellal
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
9000 repetitions
OBSERVE C13, 125.6674205 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 9 hr, 31 min, 39 sec

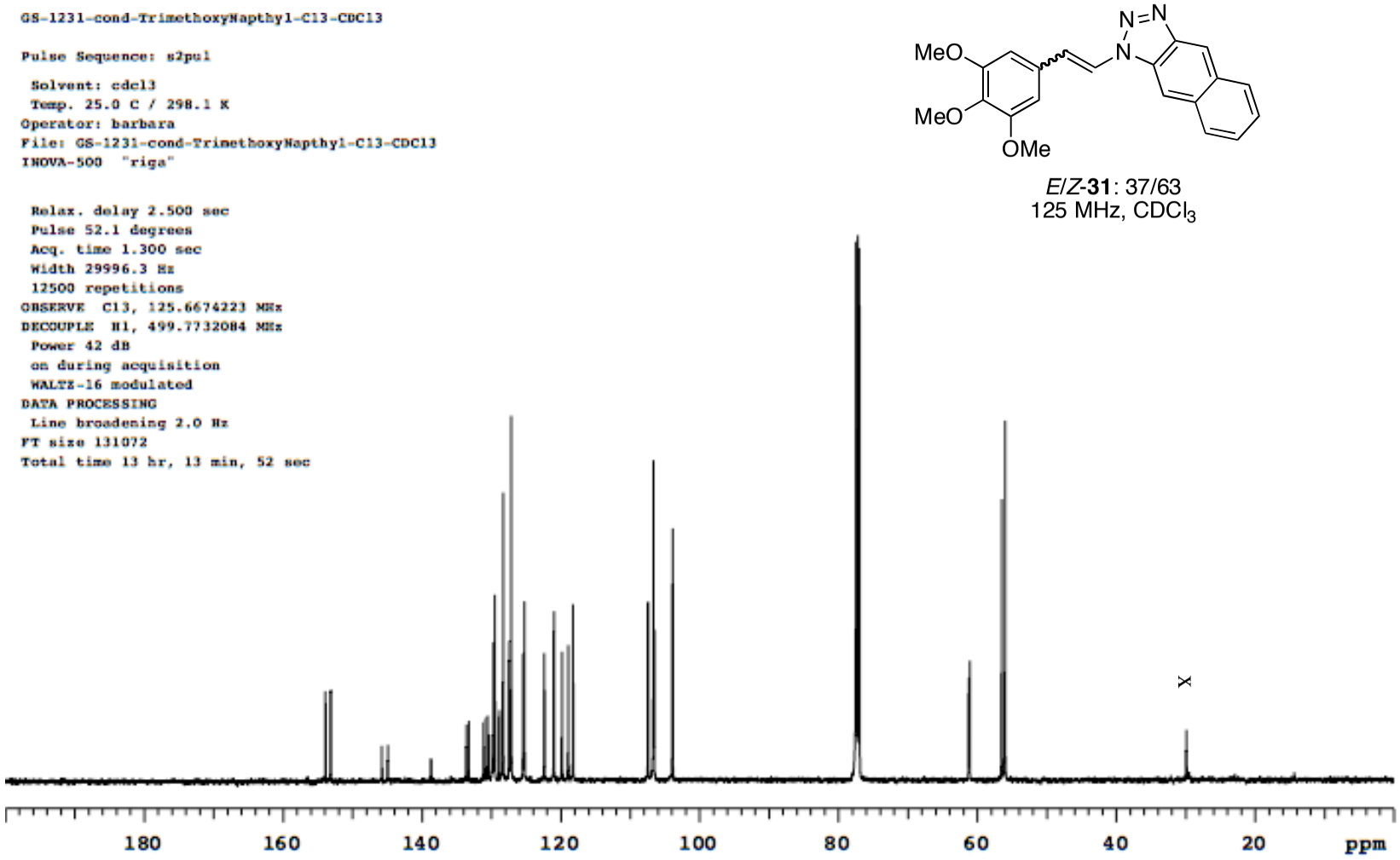


E/*Z*-**30**
125 MHz, $CDCl_3$





E/*Z*-**31**: 37/63
500 MHz, $CDCl_3$



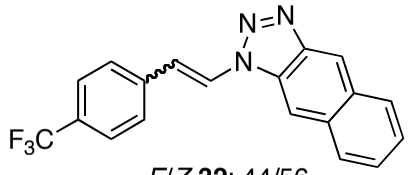
E/*Z*-**31**: 37/63
125 MHz, $CDCl_3$

GS-1231-03-188-pure

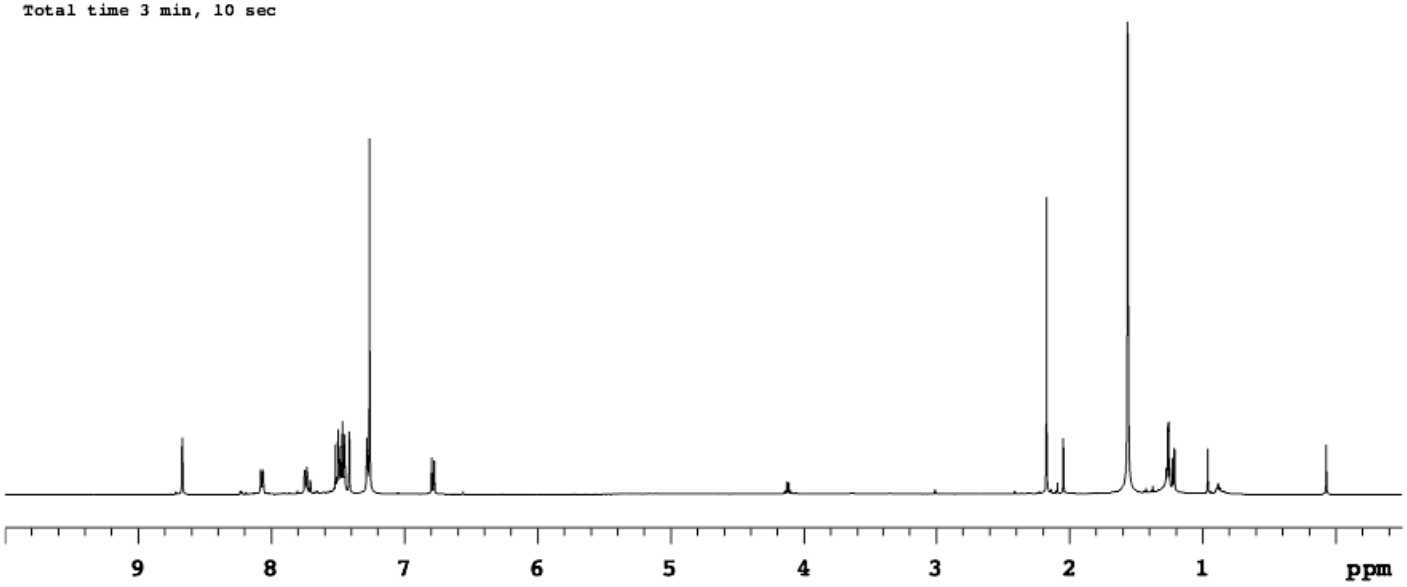
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-188-pure
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707207 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



E/*Z*-**32**: 44/56
500 MHz, $CDCl_3$

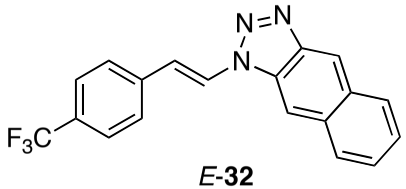


GS-1231-03-207-pureTs

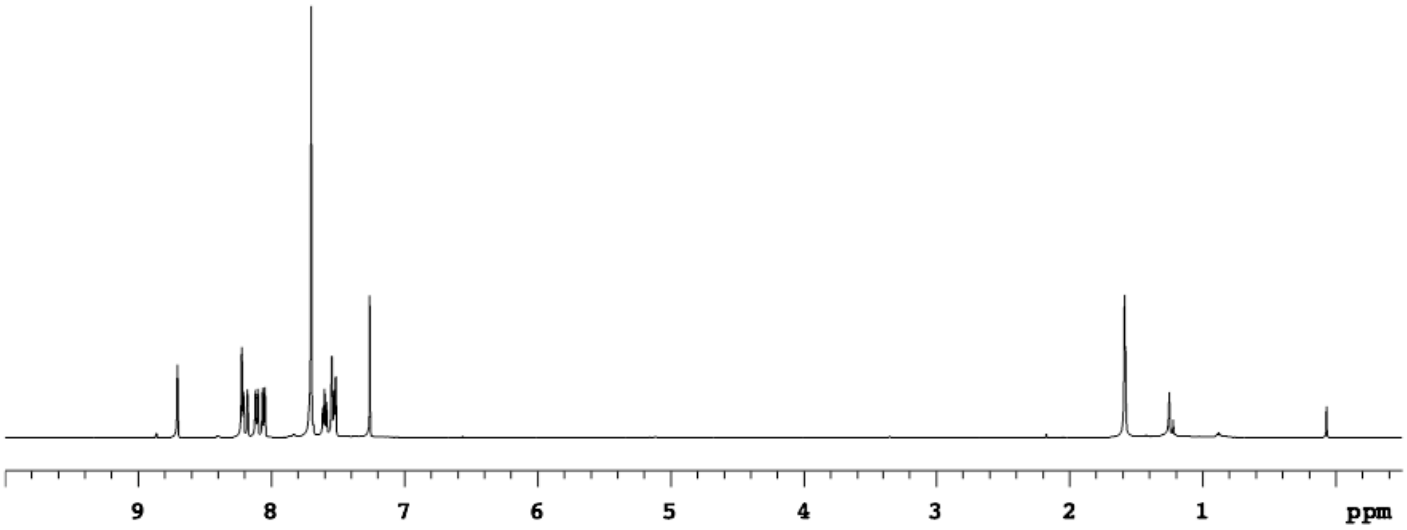
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-207-pureTs
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
100 repetitions
OBSERVE H1, 499.7707217 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



E-**32**
500 MHz, $CDCl_3$

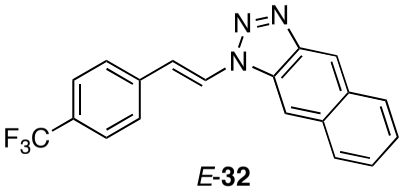


GS-1231-04-cond-CF3Napthyl-TS-C13-CDCL3

Pulse Sequence: s2pul

Solvent: cdcl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-04-cond-CF3Napthyl-TS-C13-CDCL3
INOVA-500 "riga"

Relax. delay 2.500 sec
Pulse 52.1 degrees
Acq. time 1.300 sec
Width 29996.3 Hz
40232 repetitions
OBSERVE C13, 125.6674205 MHz
DECOUPLE H1, 499.7732084 MHz
Power 42 dB
on during acquisition
WALTZ-16 modulated
DATA PROCESSING
Line broadening 2.0 Hz
FT size 131072
Total time 44 hr, 26 min, 50 sec



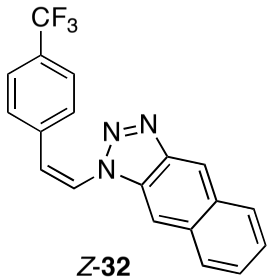
E-**32**
125 MHz, $CDCl_3$

GS-1231-03-207-pureBs

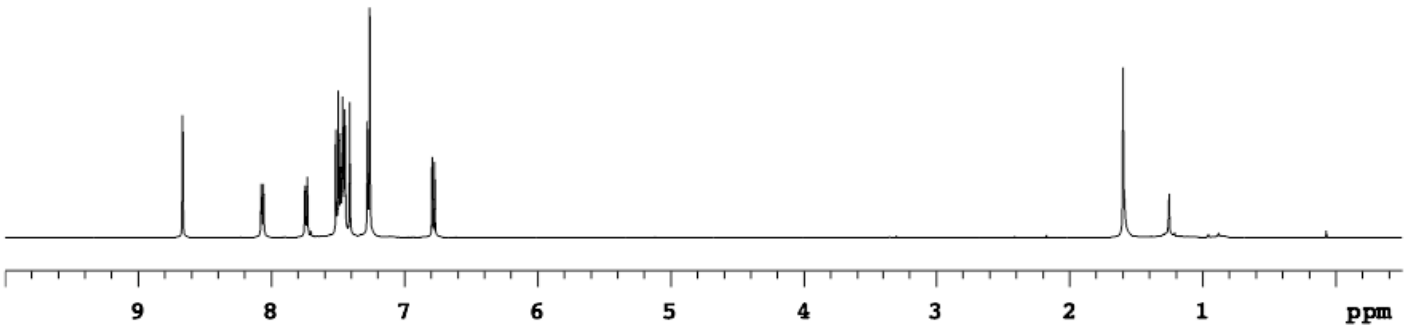
Pulse Sequence: s2pul

Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-03-207-pureBs
INOVA-500 "riga"

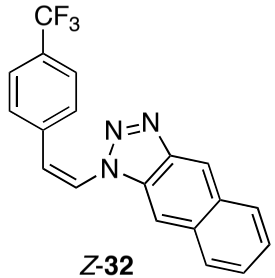
Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
52 repetitions
OBSERVE H1, 499.7707222 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768
Total time 3 min, 10 sec



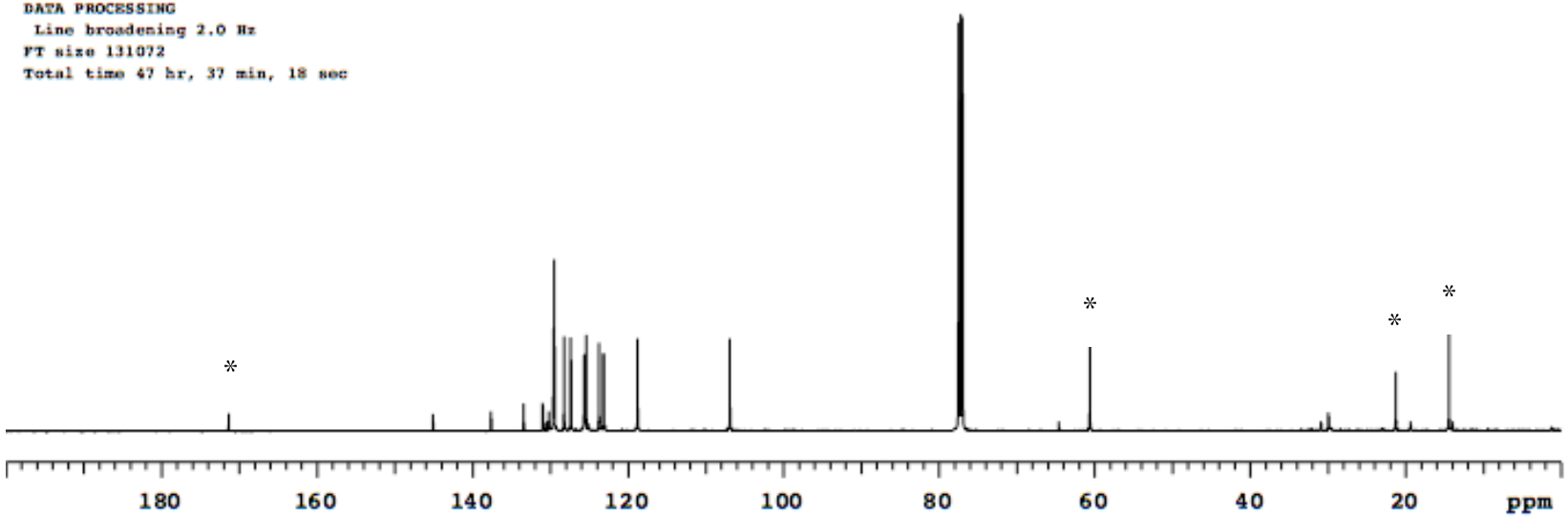
Z-**32**
500 MHz, $CDCl_3$

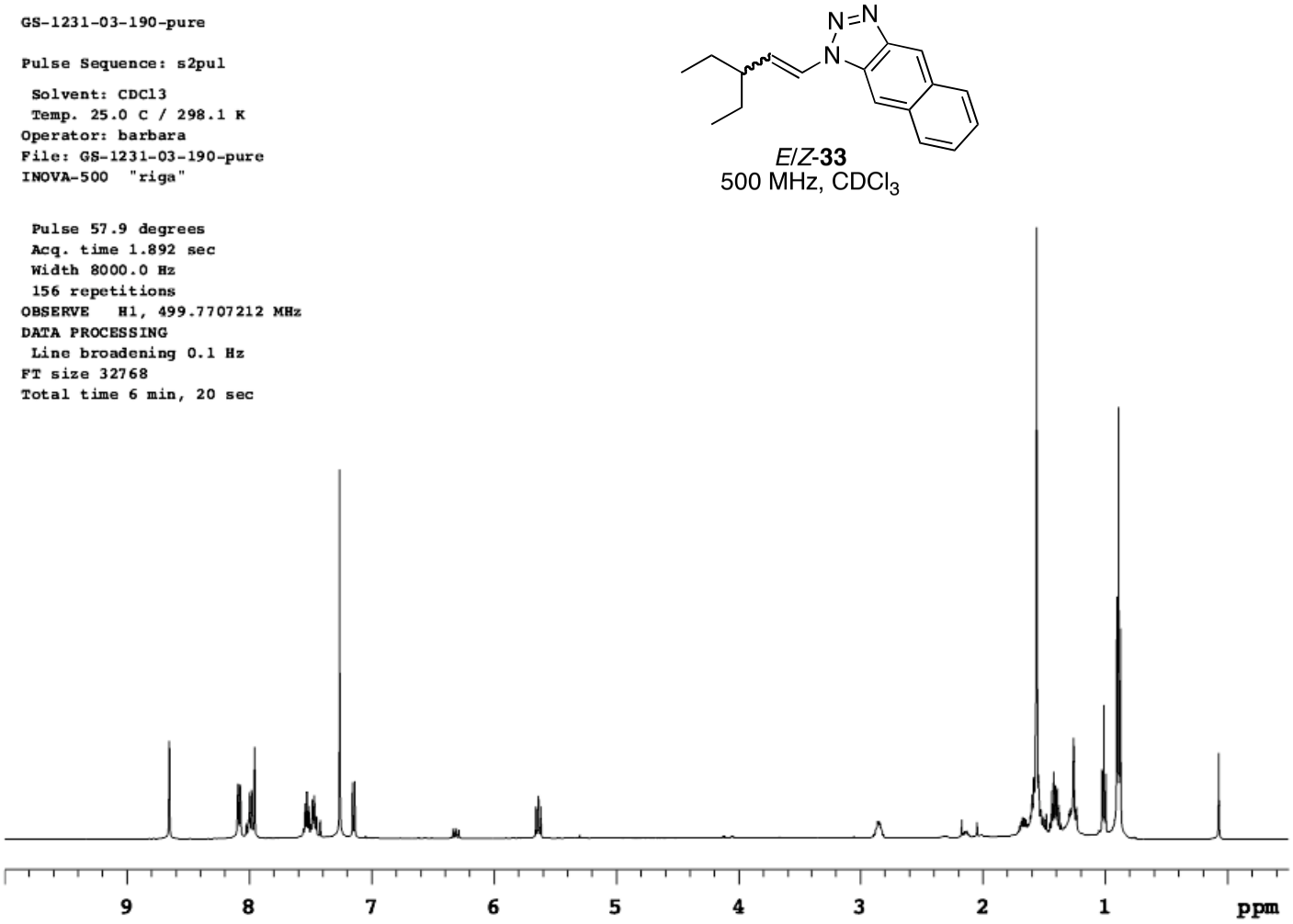


```
GS-1231-04-cond-CF3Napthyl-BS-C13-CDCL3

Pulse Sequence: s2pul

 Solvent: cdcl3
 Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-04-cond-CF3Napthyl-BS-C13-CDCL3
INOVA-500  "riga"


 Relax. delay 2.500 sec
 Pulse 52.1 degrees
 Acq. time 1.300 sec
 Width 29996.3 Hz
 45000 repetitions
OBSERVE  C13, 125.6674196 MHz
DECOUPLE  H1, 499.7732084 MHz
 Power 42 dB
 on during acquisition
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 2.0 Hz
FT size 131072
Total time 47 hr, 37 min, 18 sec
```



Z-**32**
125 MHz, $CDCl_3$
(* EtOAc)





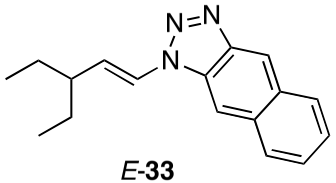
E/*Z*-**33**
500 MHz, $CDCl_3$

GS-1231-cond-NapthylButanal-pureBS

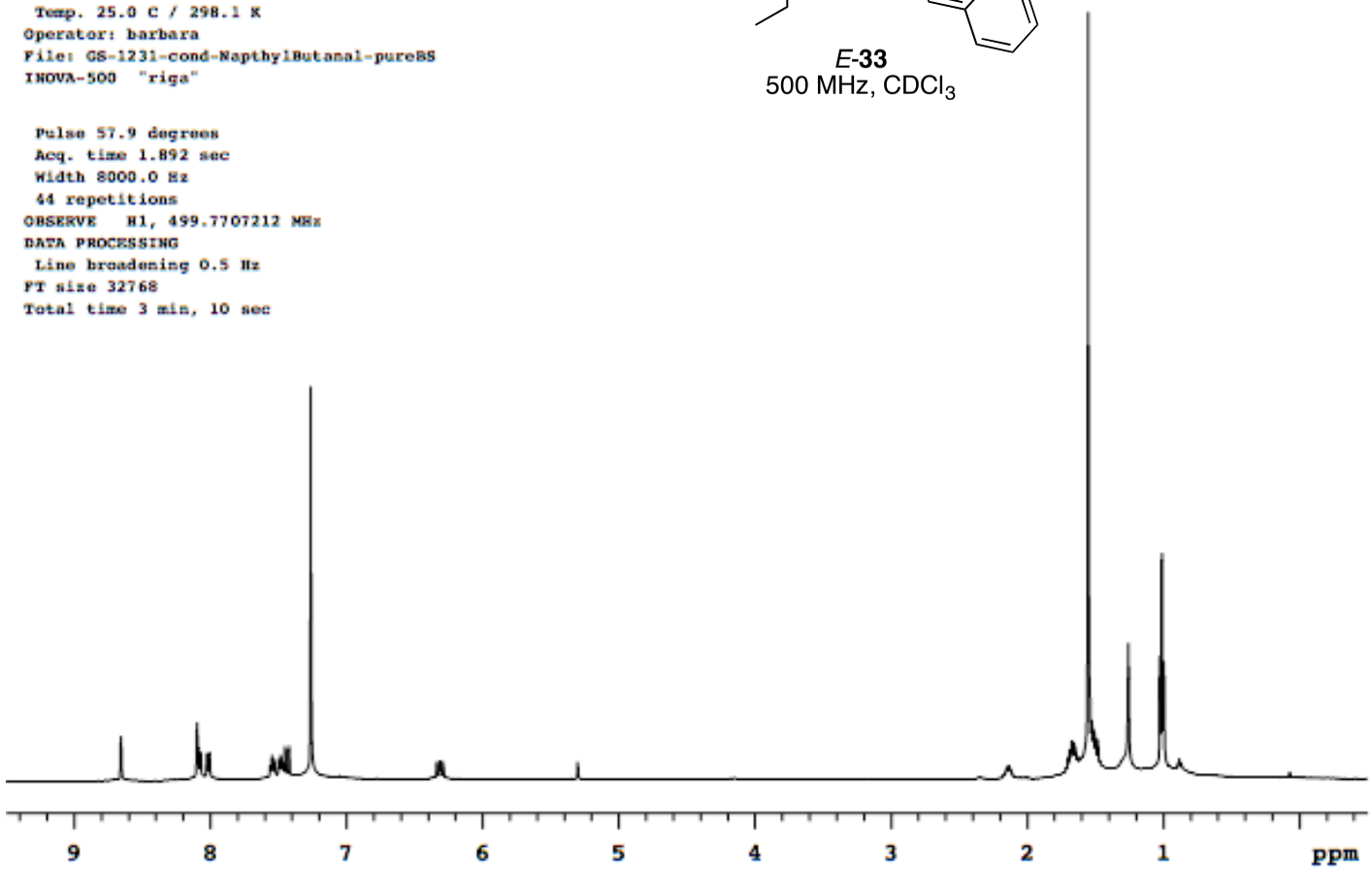
Pulse Sequence: s2pul

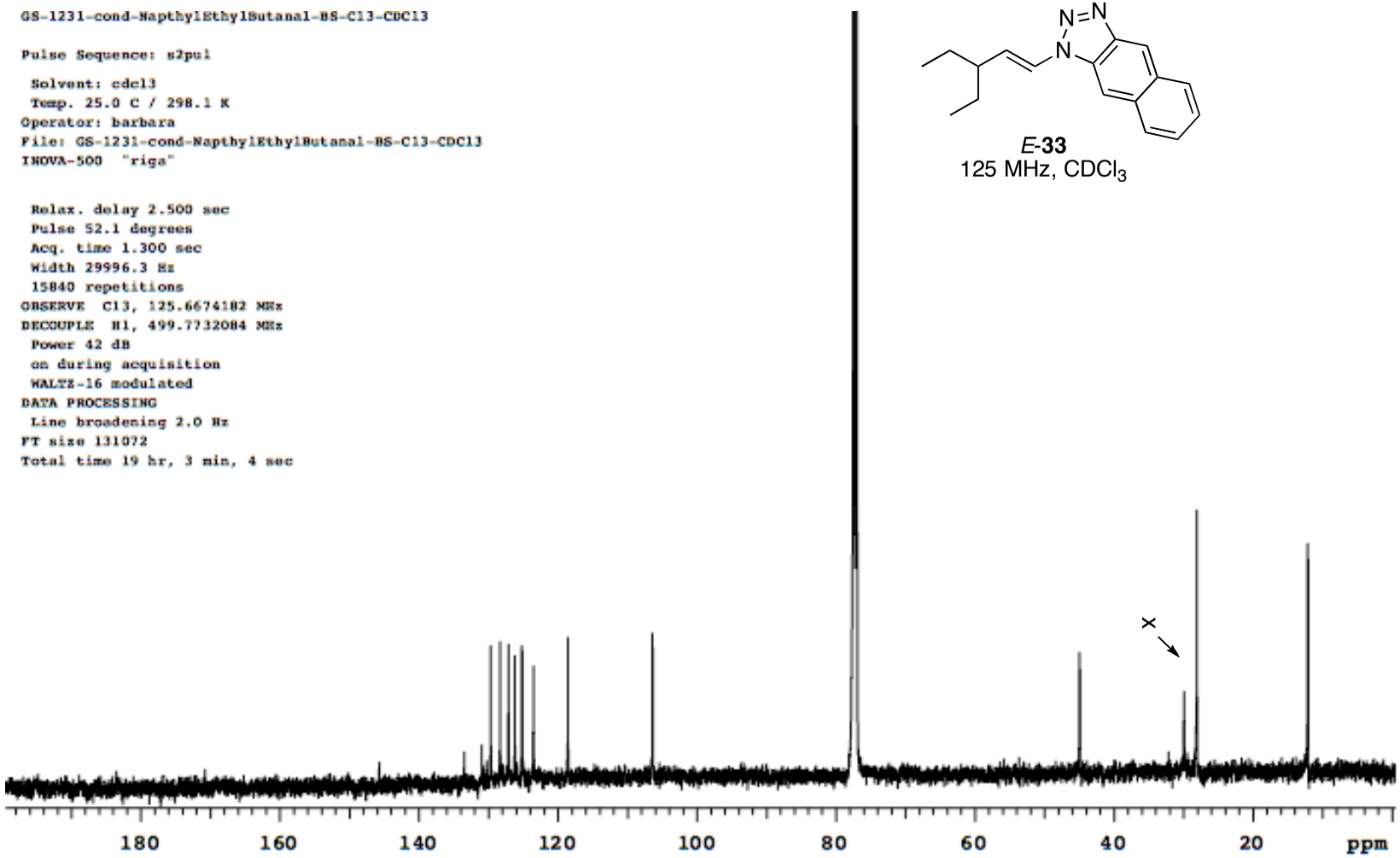
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-NapthylButanal-pureBS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
44 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec



E-**33**
500 MHz, $CDCl_3$





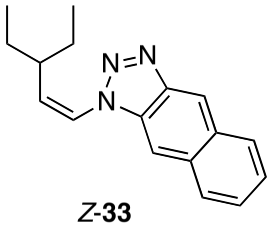
E-**33**
125 MHz, $CDCl_3$

GS-1231-cond-NapthylButanal-pureTS

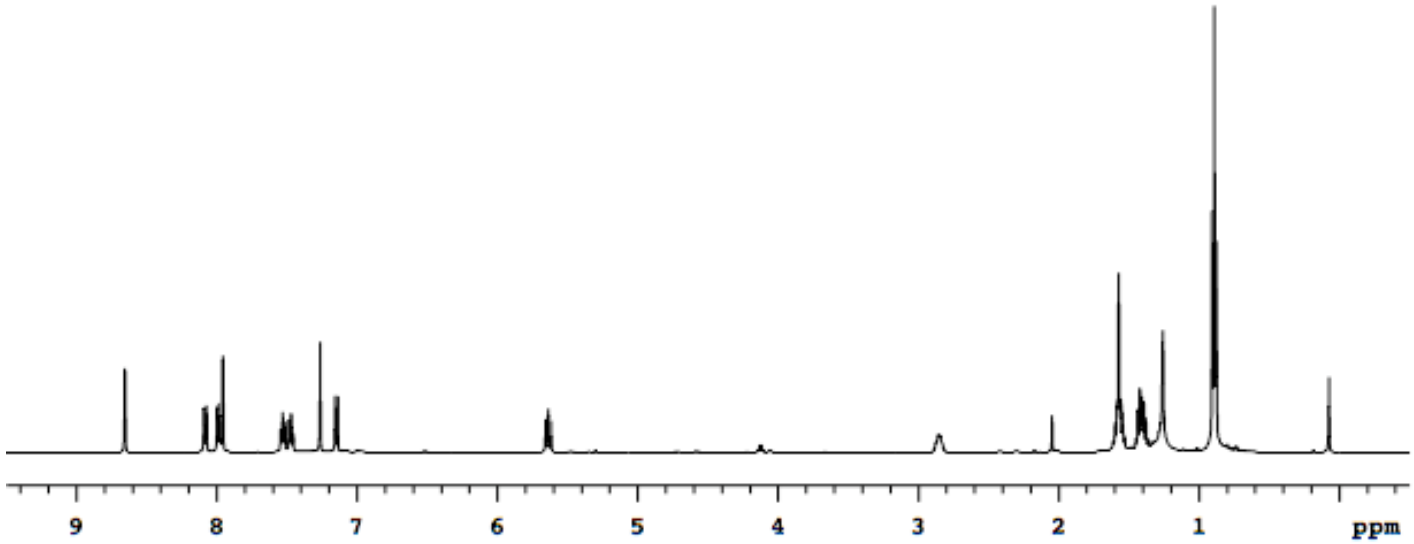
Pulse Sequence: s2pul

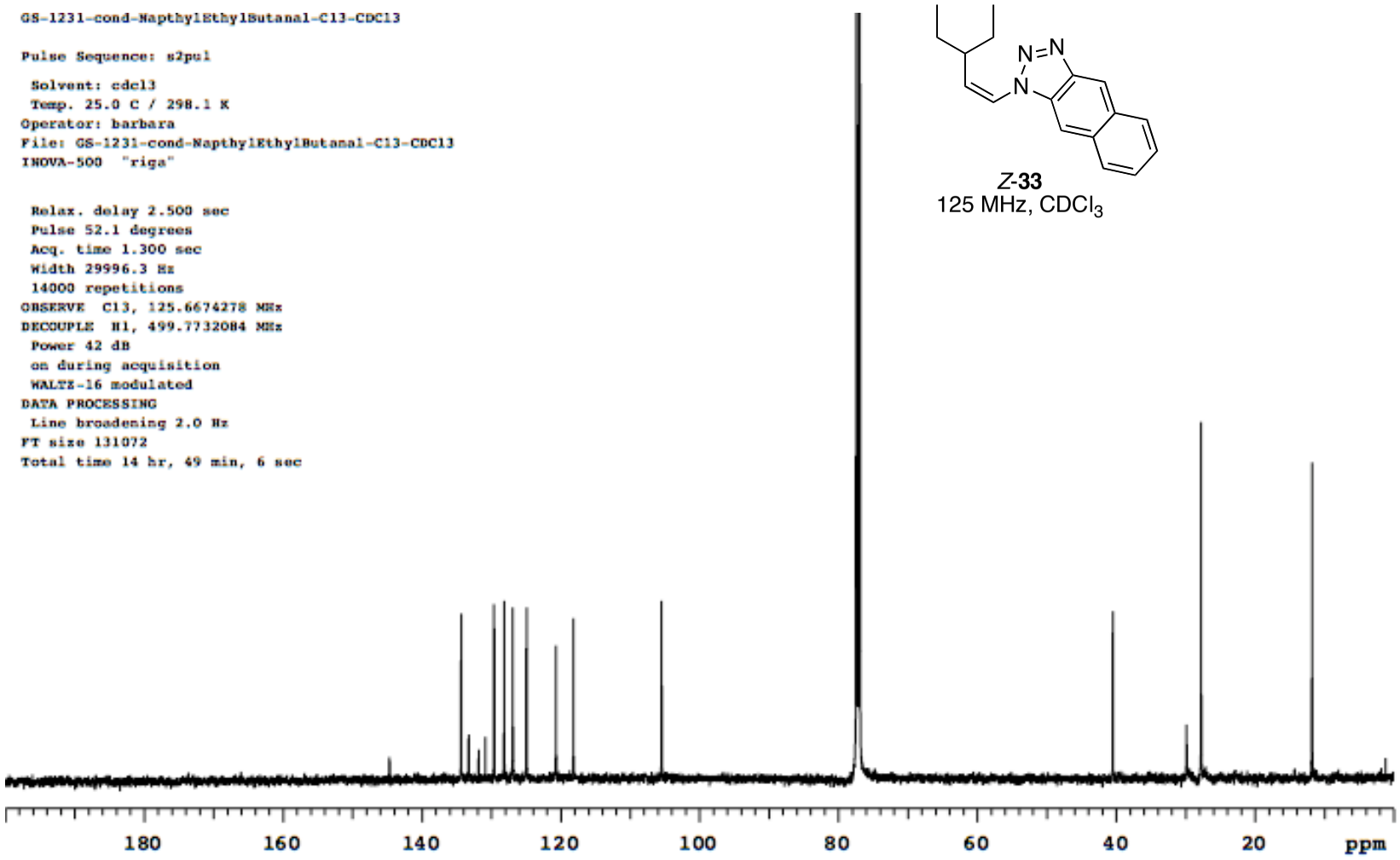
Solvent: CDCl3
Temp. 25.0 C / 298.1 K
Operator: barbara
File: GS-1231-cond-NapthylButanal-pureTS
INOVA-500 "riga"

Pulse 57.9 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
28 repetitions
OBSERVE H1, 499.7707212 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 32768
Total time 3 min, 10 sec



Z-**33**
500 MHz, $CDCl_3$





Z-**33**
125 MHz, $CDCl_3$