

**C-C Bond Formation Catalyzed Heterogeneously by
Nickel-on-Graphite (Ni/C_g)**

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Supporting Information

Standard Ni/C_g catalyzed cross-couplings of boronic acids with aryl halides using conventional heating. To a flame dried, argon purged 25 mL round bottom flask were added Ni/C_g (96.0 mg, 0.08 mmol) and PPh₃ (63.0 mg, 0.24 mmol) under argon at rt. THF (2 mL) was then added followed by *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol). The solution was allowed to stir at rt for 15 min. The aryl halide (1.00 mmol), boronic acid (2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL) were then added to the reaction mixture. The flask was loaded into a preheated oil bath and warmed to reflux. The reaction was allowed to stir until TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/ EtOAc).

4-Methoxybiphenyl (Table 1, entry A). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C (98.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.24 mmol), THF (2 mL), *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol), 4-chloroanisole (0.127 mL, 1.00 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir overnight at which point TLC indicated incomplete conversion of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/ EtOAc). After purification 74 mg of the title compound was isolated (40%). R_f = 0.75 (3:1 hex/ EtOAc). Spectral data of the product matched that of previously reported spectra.¹

3,4',4-Trimethoxybiphenyl (Table 1, entry B; using Ni/C). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C (98.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.24 mmol), THF (2 mL), *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol), 4-chloroanisole (0.127 mL, 1.00 mmol), 3,4-dimethoxyphenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120

mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir for 14 h at which point TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 221 mg of the title compound was isolated (90%). R_f = 0.33 (3:1 hex/EtOAc). Spectra matched entry B, Ni/C_g.

3,4',4-Trimethoxybiphenyl (Table 1, entry B; using Ni/C_g). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (96.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.24 mmol), THF (2 mL), *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol), 4-chloroanisole (0.127 mL, 1.00 mmol), 3,4-dimethoxyphenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir for 10 h at which point TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 223 mg of the title compound was isolated (92%). R_f = 0.33 (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.35 (t, *J* = 7.9, 1H), 7.15 (m, 2H), 7.11 (m, 2H), 6.94 (d, *J* = 8.3, 1H), 6.87 (m, 1H), 3.95 (s, 3H), 3.93 (s, 1H), 3.87 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 160.1, 149.2, 148.8, 142.8, 134.2, 129.9, 119.6, 113.0, 112.1, 111.5, 110.6, 56.1, 55.5; HREIMS *m/z* calcd for C₁₅H₁₆O₃ 244.1099; found 244.1097.

2-Methoxybiphenyl (Table 1, entry C; using Ni/C). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C (98.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.240 mmol), THF (2 mL), *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol), 2-chloroanisole (0.127 mL, 1.00 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir overnight at which point TLC indicated no consumption of the starting material.¹

2-Methoxybiphenyl (Table 1, entry C; using Ni/C_g + conventional heating). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (96.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.24 mmol), THF (2 mL), *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol), 2-chloroanisole (0.127 mL, 1.00 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir for 12 h at which point TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 164 mg of the title compound was isolated (89%). R_f = 0.75 (3:1 hex/EtOAc). Spectral data of the product matched that of previously reported spectra.¹

Representative Procedure for the Microwave-Assisted Nickel-on-Graphite Catalyzed Suzuki Coupling. Ni/C_g catalyzed cross-coupling of a boronic acid with an aryl halide; 2-methoxybiphenyl (Table 1, entry C). To a flame dried, argon purged Emrys Optimizer 2-5 mL pyrex reaction vessel were added Ni/C_g (96.0 mg, 0.08 mmol) and PPh₃ (63.0 mg, 0.24 mmol) under argon at rt. THF (2 mL) was then added followed by *n*-BuLi (63 µL, 2.55 M in hexanes, 0.16 mmol). The solution was allowed to stir at rt for 15 min. 2-Chloroanisole (0.127 mL, 1.00 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL) were then added to the reaction mixture. The reaction vessel was placed in the Emrys Optimizer using the following specifications: Temperature: 200 °C, Time: 2700 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 161 mg of the title compound was isolated (87%). R_f = 0.75 (3:1 hex/EtOAc).

2,3',4'-Trimethoxybiphenyl (Table 1, entry D). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (1 mL), *n*-BuLi (32 μL, 2.55 M in hexanes, 0.08 mmol), 2-chloroanisole (0.64 mL, 0.50 mmol), 3,4-dimethoxyphenylboronic acid (182 mg, 1.50 mmol), KF (87.0 mg, 1.50 mmol), LiOH (60.0 mg, 2.50 mmol), and dioxane (1.5 mL). Microwave conditions: Temperature: 200 °C, Time: 2700 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification 81 mg of the title compound was isolated (87%). R_f = 0.33 (3:1 hex/EtOAc). Spectral data on the product matched that of previously reported spectra.¹

4-Methylbiphenyl (Table 1, entry E). Using the standard conventional procedure outlined above, the following amounts of reagents were used: Ni/C_g (96.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.240 mmol), THF (2 mL), *n*-BuLi (63 μL, 2.55 M in hexanes, 0.16 mmol), 4-bromotoluene (171 mg, 1.00 mmol), phenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir for 9 h at which point TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 146 mg of the title compound was isolated (87%). R_f = 0.79 (3:1 hex/EtOAc). Spectral data of the product matched that of previously reported spectra.¹

3,4-Dimethoxy-4'-methylbiphenyl (Table 1, entry F). Using the standard conventional procedure outlined above, the following amounts of reagents were used: Ni/C_g (96.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.240 mmol), THF (2 mL), *n*-BuLi (63 μL, 2.55 M in hexanes, 0.16 mmol),), 4-bromotoluene (171 mg, 1.00 mmol), 3,4-dimethoxyphenylboronic acid (244 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL). The reaction was allowed to stir for 7 h at which point TLC indicated complete disappearance of the starting material. After cooling to rt, the reaction mixture

was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc). After purification 196 mg of the title compound was isolated (86%). R_f = 0.35 (3:1 hex/EtOAc). ¹H NMR (CDCl₃, 400 MHz) δ 7.49 (m, 2H), 7.25 (m, 2H), 7.20 (m, 1H), 7.13 (m, 2H), 6.90 (m, 1H), 3.97 (s, 3H), 3.92 (s, 3H), 2.40 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.3, 148.8, 138.4, 136.7, 134.4, 129.6, 126.9, 119.3, 111.6, 110.4, 56.1, 21.2; HREIMS *m/z* calcd for C₁₅H₁₆O₂ 228.1150; found 228.1156.

Standard Ni/C_g catalyzed cross-couplings of boronic acids with aryl tosylates. To an Emrys Optimizer 2-5 mL pyrex reaction vessel was added Ni/C_g (96.0 mg, 0.08 mmol) and PPh₃ (63.0 mg, 0.240 mmol) under argon at rt. THF (2 mL) was added followed by *n*-BuLi (63 μL, 2.55 M in hexanes, 0.16 mmol). The solution was allowed to stir at rt for 15 min. The aryl tosylate (1.00 mmol), boronic acid (2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol) and dioxane (2 mL) were then added to the reaction mixture. The reaction vessel was placed in the Emrys Optimizer using the following specifications: Temperature: 180 °C, Time: 2700 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After cooling to rt, the reaction mixture was filtered and extracted with Et₂O (3 x 10 mL) and H₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc).

1-Phenylnaphthalene (Table 2, entry 1). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (2 mL), *n*-BuLi (32 μL, 2.55 M in hexanes, 0.08 mmol), 2-tosyloxynaphthalene (149 mg, 0.50 mmol), phenylboronic acid (122 mg, 1.00 mmol), KF (87.0 mg, 1.50 mmol), LiOH (60.0 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 200 °C, Time: 7200 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. GC-MS analysis indicated 100% conversion.¹

3,4-Dimethoxy-4'-phenylbiphenyl (Table 2, entry 2). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (2 mL), *n*-BuLi (32 μL, 2.55 M in hexanes, 0.08 mmol), biphenyl-4-yl 4-methylbenzenesulfonate (162 mg, 0.50 mmol), 3,4-dimethoxyphenylboronic acid (182 mg, 1.00 mmol), KF (87.0 mg, 1.50 mmol), LiOH (60.0 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 180 °C, Time: 16200 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification 118 mg of the title compound was isolated (81%). R_f = 0.29 (3:1 hex/EtOAc). Spectral data on the product matched that of previously reported spectra.

3,4-Dimethoxy-4'-phenylbiphenyl (Table 2, entry 3). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (2 mL), *n*-BuLi (32 μL, 2.55 M in hexanes, 0.08 mmol), biphenyl-4-yl 4-methylbenzenesulfonate (162 mg, 0.50 mmol), 3,4-dimethoxyphenylboronic acid (182 mg, 1.00 mmol), KF (87.0 mg, 1.50 mmol), LiOH (60.0 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 200 °C, Time: 5400 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification on silica gel (3:1 hex:EtOAc), 120 mg of the title compound was isolated (83%). R_f = 0.29 (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.65 (m, 6H), 7.47 (m, 2H), 7.20 (m, 1H), 7.16 (m, 1H), 6.99 (s, 1H), 6.96 (s, 1H), 3.98 (s, 3H), 3.94 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 149.3, 148.8, 140.1, 139.9, 129.0, 127.6, 127.5, 127.4, 127.2, 119.5, 111.6, 110.4, 56.1; HREIMS *m/z* calcd for C₂₀H₁₈O₂ 290.1307; found 290.1301.

3,4-Dimethoxy-4'-phenylbiphenyl (using S-Phos). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (S-Phos, 15.7 mg, 0.04 mmol), THF (2 mL), *n*-BuLi (32 μL, 2.55 M in hexanes, 0.08 mmol), biphenyl-4-yl 4-methylbenzenesulfonate (162 mg, 0.50 mmol), 3,4-dimethoxyphenylboronic acid (182 mg, 1.00 mmol), KF (87.0 mg, 1.50 mmol), LiOH (60.0 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 200 °C, Time: 5400 sec., Fixed Hold Time: On, Sample

Absorption: Normal, Pre-stirring: 45 sec. After purification 126 mg of the title compound was isolated (87%). $R_f = 0.29$ (3:1 hex/EtOAc). Spectral data on the product matched that of previously reported spectra (listed above).

1-(4'-Benzoylbiphenyl-3-yl)ethanone (Table 2, entry 4). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (96.0 mg, 0.08 mmol), PPh₃ (63.0 mg, 0.24 mmol), THF (2 mL), *n*-BuLi (63 μ L, 2.55 M in hexanes, 0.16 mmol), 4-benzoylphenyl 4-methylbenzenesulfonate (352 mg, 1.00 mmol), 3-acetylphenylboronic acid (328 mg, 2.00 mmol), KF (174 mg, 3.00 mmol), LiOH (120 mg, 5.00 mmol), and dioxane (2 mL). Microwave conditions: Temperature: 180 °C, Time: 16200 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification 240 mg of the title compound was isolated (80%). $R_f = 0.23$ (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 8.25 (s, 1H), 8.01 (m, 1H), 7.93 (m, 2H), 7.85 (m, 3H), 7.75 (m, 2H), 7.61 (m, 2H), 7.52 (m, 2H), 2.69 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 198.1, 196.4, 144.3, 140.7, 137.9, 137.7, 136.9, 132.7, 132.0, 131.0, 130.2, 129.5, 128.5, 128.3, 127.2, 27.0; HREIMS m/z calcd for C₂₁H₁₆O₂ 300.1150; found 300.1139.

1-(4'-Methoxybiphenyl-2-yl)ethanone (Table 2, entry 5). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (2 mL), *n*-BuLi (32 μ L, 2.55 M in hexanes, 0.08 mmol), 2-acetylphenyl-4-methylbenzenesulfonate (145 mg, 0.50 mmol), 4-methoxyphenylboronic acid (152 mg, 1.00 mmol), KF (87 mg, 1.50 mmol), LiOH (60 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 200 °C, Time: 5400 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification 90 mg of the title compound was isolated (80%). $R_f = 0.40$ (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.51 (m, 2H), 7.386 (m, 2H), 7.26 (m, 2H), 6.98 (m, 2H), 3.86 (s, 3H), 2.02 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 205.6, 159.7, 141.1, 140.3, 133.2, 130.9, 130.3, 130.2, 128.0, 127.2, 114.3, 55.5, 30.6; HREIMS m/z calcd for C₁₅H₁₄O₂ 226.0994; found 226.0998.

1-(3'-(Trifluoromethyl)biphenyl-2-yl)ethanone (Table 2, entry 6). Using the standard procedure outlined above, the following amounts of reagents were used: Ni/C_g (48.0 mg, 0.04 mmol), PPh₃ (31.5 mg, 0.120 mmol), THF (2 mL), *n*-BuLi (32 μ L, 2.55 M in hexanes, 0.08 mmol), 2-acetylphenyl-4-methylbenzenesulfonate (145 mg, 0.50 mmol), 3-(trifluoromethyl)phenylboronic acid (190 mg, 1.00 mmol), KF (87 mg, 1.50 mmol), LiOH (60 mg, 2.50 mmol), and dioxane (1 mL). Microwave conditions: Temperature: 200 °C, Time: 5400 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. After purification 120 mg of the title compound was isolated (91%). R_f = 0.33 (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (m, 3H), 7.55 (m, 2H), 7.49 (m, 2H), 7.38 (m, 1H), 2.18 (s, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 203.7, 141.8, 139.3, 132.4, 131.3, 130.7, 129.2, 128.5, 128.3, 125.6, 124.7, 30.5; HREIMS *m/z* calcd for C₁₅H₁₁F₃O 264.0762; found 264.0771.

Negishi Carboalumination of a terminal alkyne using catalytic Cp₂ZrCl₂ / catalytic IBAO / excess Me₃Al followed by Ni/C_g catalyzed cross-coupling with an aryl tosylate; (*E*)-4-(2-methyloct-1-enyl)biphenyl (Scheme 3). To a flame dried argon purged 25 mL round bottomed (rb) flask was added bis(cyclopentadienyl)zirconium dichloride (14.6 mg, 0.05 mmol, 5.0 mol %), followed by the dropwise addition at 0 °C of Me₃Al (2.0 M solution in toluene, 0.75 mL, 1.50 mmol, 1.5 equiv). While stirring at 0 °C, IBAO (0.28 mL, 0.100 mmol, 10 mol %) was then added. Lastly, octyne (0.150 mL, 1.00 mmol) was introduced and the homogeneous pale yellow solution stirred at rt for 2 h until TLC analysis (5% CH₂Cl₂/pet ether) indicated that the carboalumination was complete.

In a separate flame dried argon purged 10 mL microwave vial was combined triphenylphosphine (32 mg, 0.12 mmol) and Ni/C_g (48 mg, 0.03 mmol, 0.03 equiv) in the glove box. THF (0.5 mL) was then added via syringe followed by the dropwise addition of *n*-BuLi (20.5 μ L, 0.06 mmol) to form the active Ni(0)/C_g complex. After stirring at rt for 5 min, the vinylalane generated above was transferred to the vial via cannula. Lastly, 4-tosyloxybiphenyl (162.2 mg, 0.5 mmol) was added and the reaction vessel was placed in the Emrys Optimizer and exposed to microwave irradiation according to the following specifications: Temperature: 200 °C, Time: 3600 sec., Fixed Hold Time: On, Sample Absorption:

Normal, Pre-stirring: 45 sec. The reaction mixture was then extracted with water (3 x 10 mL) and Et₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc) yielding 116 mg of compound **10** as a colorless oil (83%). The other regioisomer was not detected by GC. R_f = 0.70 (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.50 (m, 2H), 7.46 (m, 2H), 7.35 (m, 4H), 7.20 (s, 1H), 6.17 (m, 1H), 1.92 (m, 2H), 1.70 (s, 3H), 1.30 (m, 5H), 1.23 (m, 3H), 0.91 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 137.3, 136.0, 134.2, 131.1, 129.8, 128.6, 127.5, 127.4, 123.6, 115.3, 33.2, 31.9, 29.5, 29.1, 22.8, 15.8, 14.3; HREIMS *m/z* calcd for C₂₁H₂₆ 278.2034; found 278.2036.

Standard Ni/C_g catalyzed cross-couplings of vinylzirconocenes with aryl halides. To a flame dried, argon purged 25 mL round bottom (rb) flask were added bis(cyclopentadienyl)zirconium chloride hydride (135 mg, 0.50 mmol) in the glove box, followed by THF (1.0 mL) via syringe. Octyne (0.075 mL, 0.50 mmol) was then added and the reaction was allowed to stir at rt until GC analysis indicated complete disappearance of the starting material. In a separate flame dried argon purged 10 mL microwave vial was combined triphenylphosphine (21 mg, 0.08 mmol) and Ni/C_g (48 mg, 0.04 mmol) in the glove box. THF (0.5 mL) was then added via syringe followed by the dropwise addition of *n*-BuLi (30.75 μL, 0.08 mmol) to form the active Ni(0)/C_g complex. After stirring at rt for 5 min, the vinylzirconocene generated above was transferred to the vial via cannula. Lastly, the aryl halide (0.50 mmol) was added and the reaction vessel was placed in the Emrys Optimizer and exposed to microwave irradiation according to the following specifications: Temperature: 200 °C, Time: 900 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec.

(*E*)-1-(Oct-1-enyl)-3-(trifluoromethyl)benzene (Table 3, entry 1). Using the standard procedure outlined above, the following amounts of reagents were used: zirconocene (135 mg, 0.50 mmol), octyne (0.075 mL, 0.5 mmol), Ni/C_g (48 mg, 0.04 mmol, 0.1 equiv), *n*-BuLi (30.75 μL, 0.08 mmol, 0.2 equiv), and 1-iodo-3-(trifluoromethyl)benzene (0.072 mL, 0.50 mmol). The hydrozirconation was allowed to proceed for 45 min and the reaction vessel was then placed in the Emrys Optimizer using the following

specifications: Temperature: 200 °C, Time: 600 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. The reaction mixture was then extracted with water (3 x 10 mL) and Et₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (hexanes) affording 110 mg of the title compound as a colorless oil (85%). R_f = 0.60 (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.60 (s, 1H), 7.51 (m, 1H), 7.41 (m, 1H), 7.29 (m, 1H), 6.40 (m, 1H), 6.25 (m, 1H), 2.21 (q, *J*=6.0 Hz, 2H), 1.43 (m, 2H), 1.30 (m, 6H), 0.91 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 141.1, 138.8, 133.5, 129.2, 129.0, 128.6, 123.9, 122.7, 33.2, 31.9, 31.8, 29.3, 29.1, 22.9, 14.3; HREIMS *m/z* calcd for C₁₅H₁₉F₃ 256.1439; found 256.1442.

(*E*)-1-Fluoro-4-(oct-1-enyl)benzene (Table 3, entry 2). Using the standard procedure outlined above, the following amounts of reagents were used: zirconocene (135 mg, 0.50 mmol), octyne (0.075 mL, 0.5 mmol), Ni/C_g (48 mg, 0.040 mmol, 0.1 equiv), PPh₃ (21 mg, 0.08 mmol, 0.2 equiv), *n*-BuLi (30.75 μL, 0.08 mmol, 0.2 equiv), and 1-bromo-4-fluorobenzene (0.044 mL, 0.40 mmol). The hydrozirconation was allowed to proceed for 45 min and the reaction was then subjected to microwave irradiation according to the following specifications: Temperature: 200 °C, Time: 900 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. The reaction mixture was then extracted with water (3 x 10 mL) and Et₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (3:1 hex/EtOAc), isolating 171 mg of the title compound as a colorless oil (83%). R_f = 0.67 (3:1 hex/EtOAc); ¹H NMR (CDCl₃, 400 MHz) δ 7.35 (m, 2H), 6.95 (m, 2H), 6.38 (m, 1H), 6.17 (m, 1H), 2.18 (q, *J* = 6.1 Hz, 2H), 1.23 (m, 8H), 0.91 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 163.2, 134.2, 131.1, 128.6, 127.5, 127.4, 115.5, 115.3, 33.2, 31.9, 29.5, 29.1, 22.8, 14.3; HREIMS *m/z* calcd for C₁₄H₁₉F 206.1471; found 206.1475.

(E)-1-(Oct-1-enyl)-3-(trifluoromethyl)benzene (Table 3, entry 3). Using the standard procedure outlined above, the following amounts of reagents were used: zirconocene (135 mg, 0.50 mmol), octyne (0.075 mL, 0.5 mmol), Ni/C_g (48 mg, 0.04 mmol, 0.1 equiv), *n*-BuLi (30.75 μ L, 0.08 mmol, 0.2 equiv), and 1-chloro-3-(trifluoromethyl)benzene (0.068 mL, 0.50 mmol). The hydrozirconation was allowed to proceed for 45 min and the reaction vessel was then placed in the Emrys Optimizer using the following specifications: Temperature: 200 °C, Time: 600 sec., Fixed Hold Time: On, Sample Absorption: Normal, Pre-stirring: 45 sec. The reaction mixture was then extracted with water (3 x 10 mL) and Et₂O (3 x 10 mL). The combined organics were washed with brine and dried over anhydrous MgSO₄. The solvent was removed *in vacuo* and the crude product was purified by silica gel chromatography (hexanes), affording 115 mg of the title compound as a colorless oil (90%). R_f = 0.60 (hexanes). ¹H NMR (CDCl₃, 400 MHz) δ 7.58 (m, 1H), 7.51 (m, 1H), 7.41 (m, 2H), 6.40 (m, 1H), 6.35 (m, 1H), 2.21 (m, 2H), 1.47 (m, 2H), 1.30 (m, 8H), 0.89 (m, 3H); ¹³C NMR (CDCl₃, 100 MHz) δ 138.8, 133.5, 129.2, 129.0, 128.6, 122.7, 33.2, 31.9, 31.8, 29.3, 29.1, 22.8, 14.3; HREIMS *m/z* calcd for C₁₅H₁₉F₃ 256.1439; found 256.1442.

¹. Riggleman, S.; Deshong, P.; *J. Org. Chem.* **2003**, 68, 8106.

TOPSPIN20.13C-CDCl3-000

Pulse sequence: zgpg30

Solvent: cdcl3

Acquisition temperature

INSTRUMENT: spect

Relax. delay: 4.000 sec

Pulse width: 12.000 sec

Acq. time: 9.140 sec

Width: 33441.7 Hz

Frequency: 125.761 MHz

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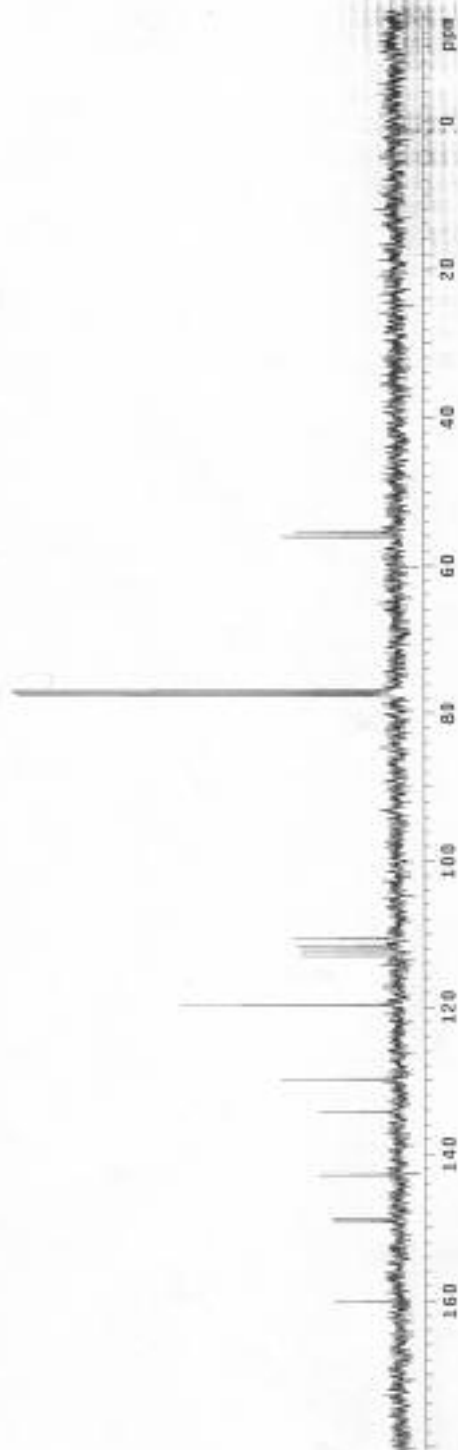
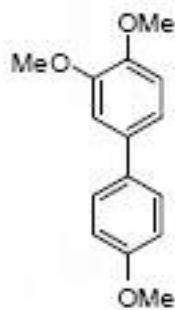
Observed: 125.761 MHz

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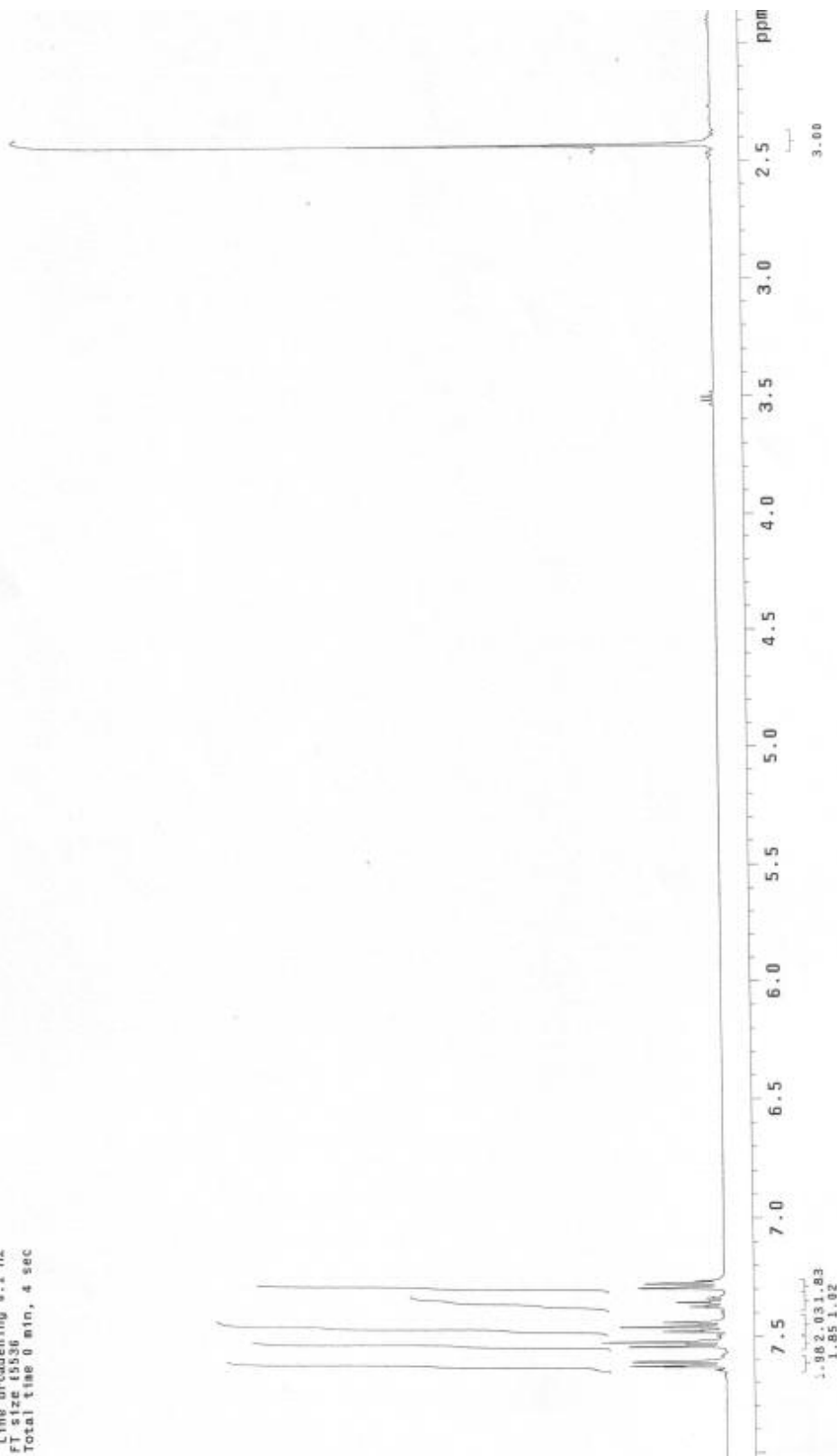


STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: cdc13
Ambient temperature
INOVA-400 "hmr400"

Relax. delay 1.000 sec
Pulse 67.5 degrees
Acq. time 3.734 sec
Width 5431.4 Hz

Single scan 399.9486712 MHz
OBSERVED
DATA PROCESSING
Line broadening 0.1 Hz
F1 size 1556
Total time 0 min, 4 sec

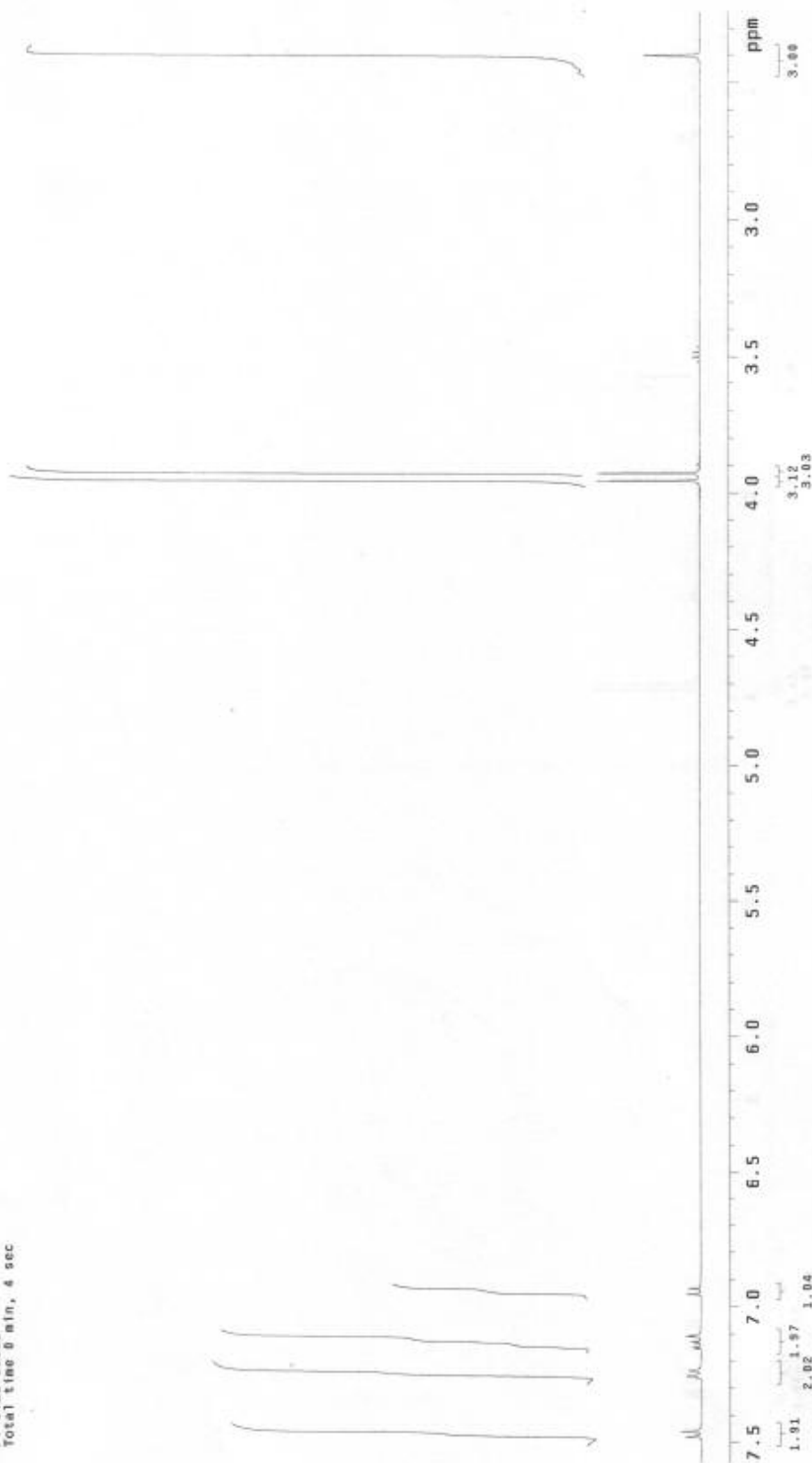


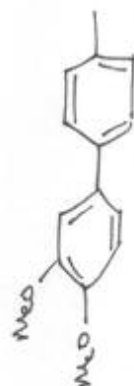
STANDARD 1H OBSERVE

Pulse Sequence: s2pu1
Solvent: cdcl3
Ambient temperature
INOVA-400 "har400"



Relax. delay 1.000 sec
Pulse 47.5 degrees
Acq. time 3.744 sec
Width 5631.4 Hz
OBSERVE scan 399.9486712 MHz
ONLINE PROCESSING
Offline processing 0.1 Hz
FT size 65536
Total time 8 min, 4 sec





bp05992d.13c.cdcl3.qnp

Pulse Sequence: zgpg30

Solvent: cdcl3

Ambient temperature

INOVA-400 "nmr400"

Relax. delay 4.000 sec

Pulse 99.20 degrees

Acq. time 0.140 sec

Width 33641.7 Hz

55 repetitions

OBSERVE C13, 100.6271566 MHz

DECOUPLE H1, 399.9435797 MHz

Power 42 dB

on during acquisition

off during delay

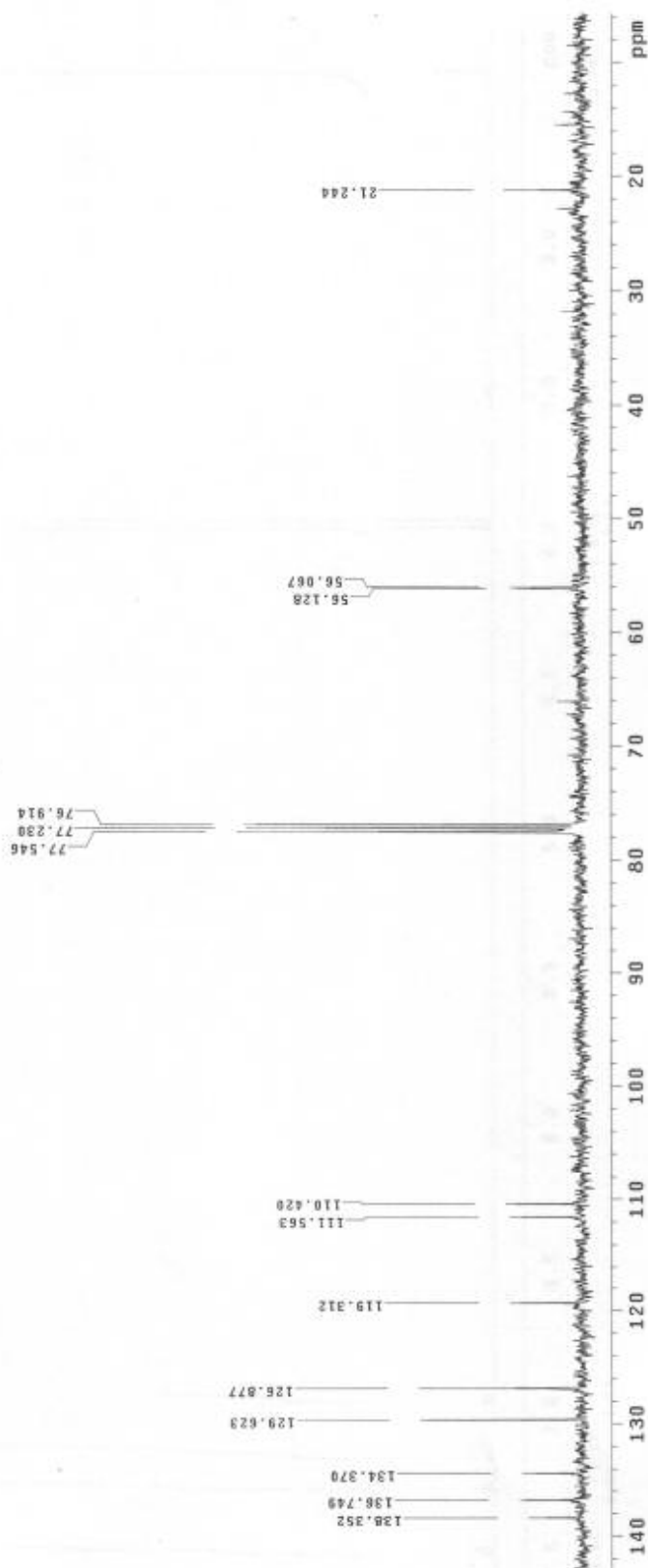
VALT2-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 860 hr, 53 min, 51 sec

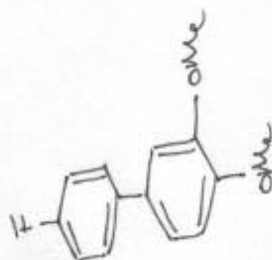


STANDARD IN OBSERVE

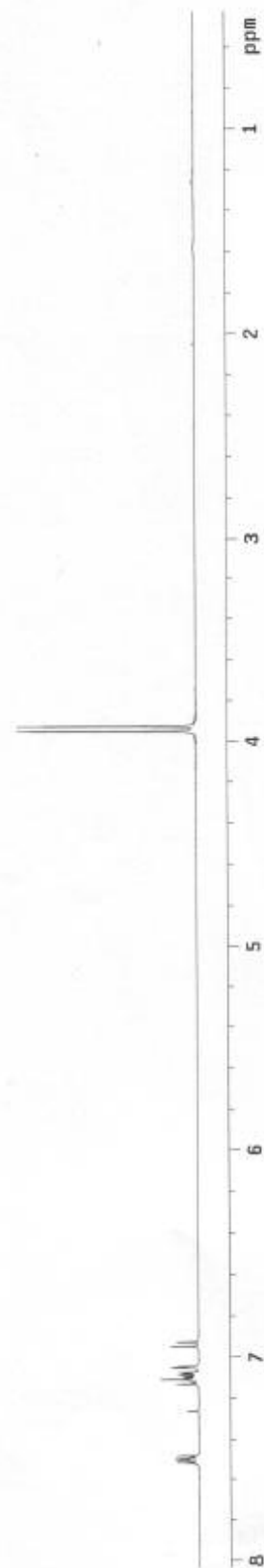
Pulse Sequence: zgpg30
Solvent: cdcl3
Ambient temperature
INNOVA-400 400 MHz

Relax. delay 1.000 sec
Pulse 67.5 degrees
Acq. time 3.744 sec
Width 503.4 Hz

Single scan
OBSERVE M1 399.9486712 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 0 min, 4 sec



3



tbp050922d-13c.cdcl3.qnp

Pulse Sequence: s2pul

Solvent: cdcl3

Acq. time 0.540 sec

Width 33641.7 Hz

176 repetitions

OBSERVE C13, 100.5671566 MHz

DECOUPLE H1, 399.8435797 MHz

Power 42 dB

on during acquisition

off during delay

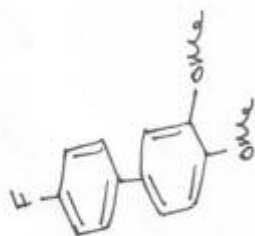
WALTZ-16 modulated

DATA PROCESSING

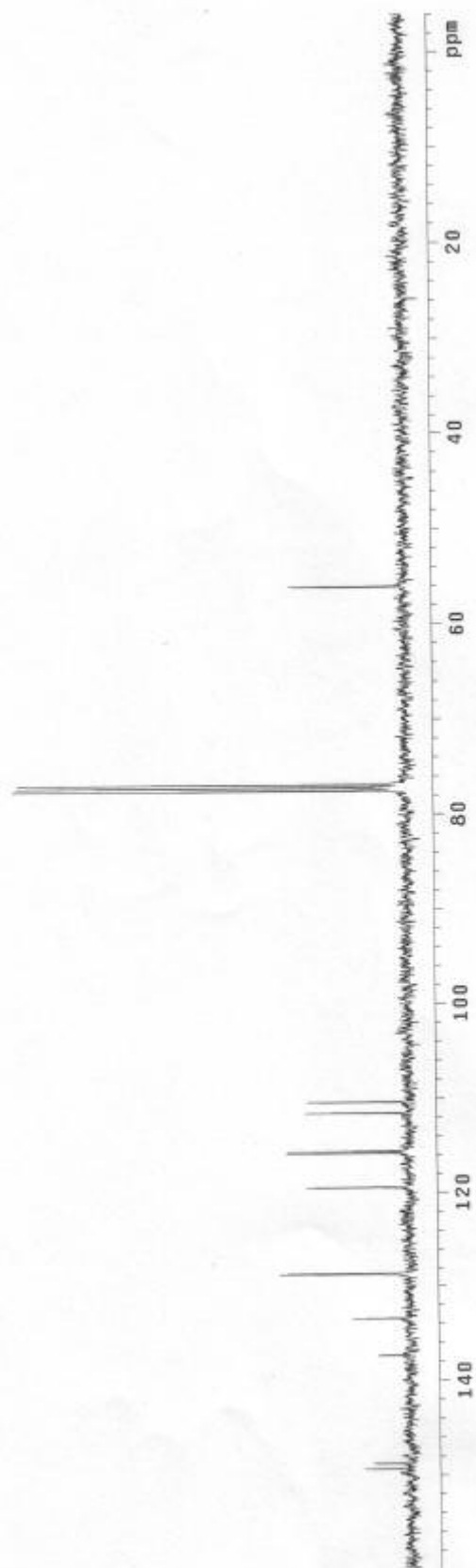
Line broadening 3.0 Hz

FT size 65536

Total time 360 hr, 53 min, 56 sec



3

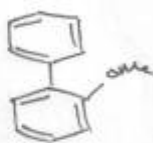


STANDARD 1H OBSERVE

Pulse Sequence: s2pul
Solvent: cdcl3
Ambient temperature
INOVA-400 "mr400"

Relax. delay 1.000 sec
Pulse 67.5 degrees
Acq. time 3.744 sec
Width 5031.4 Hz

SINGLE scan
OBSERVE M1 399.9486712 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 65536
Total time 0 min, 4 sec



tbp050922d.13c.cd13.qnp

Pulse Sequence: s2pul1

Solvent: cdcl3

Ambient temperature

INOVA-400 "nmr400"

Relax. delay 4.000 sec

Pulse 99.2 degrees

Acq. time 0.640 sec

Width 33641.7 Hz

52 repetitions

OBSERVE C13, 100.5671566 MHz

DECOUPLE H1, 399.5495737 MHz

Power 42 dB

on during acquisition

off during delay

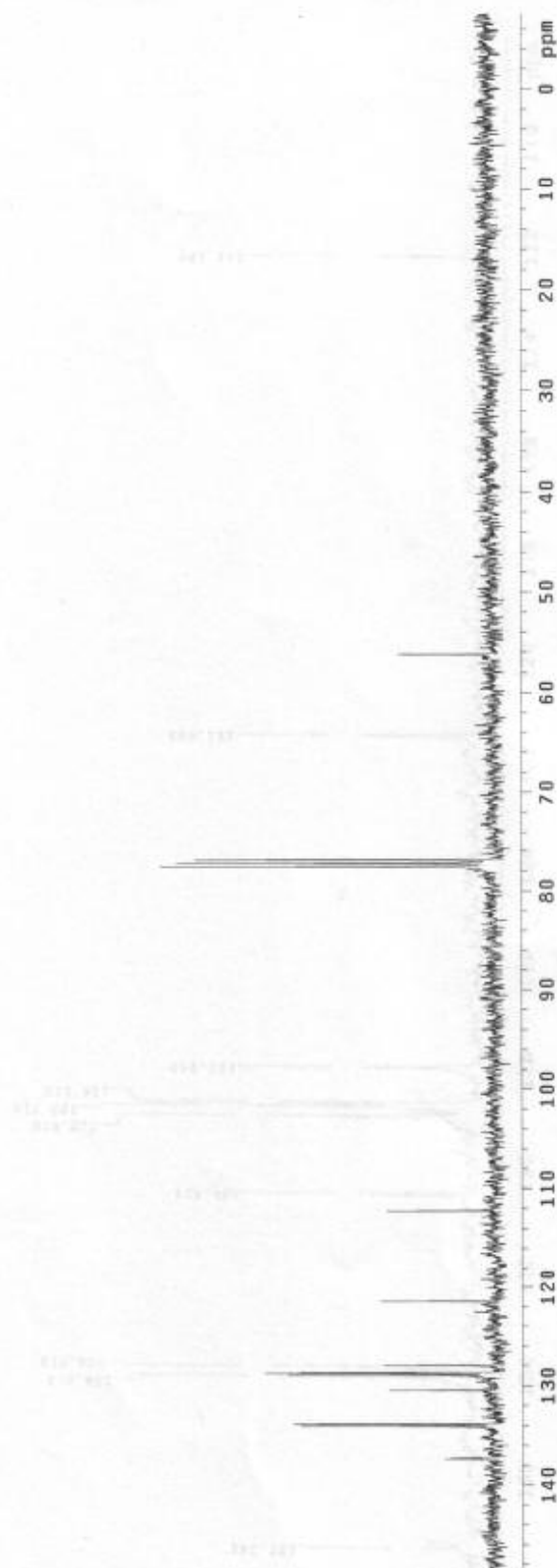
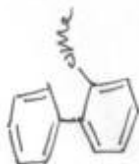
WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 860 hr, 53 min, 56 sec

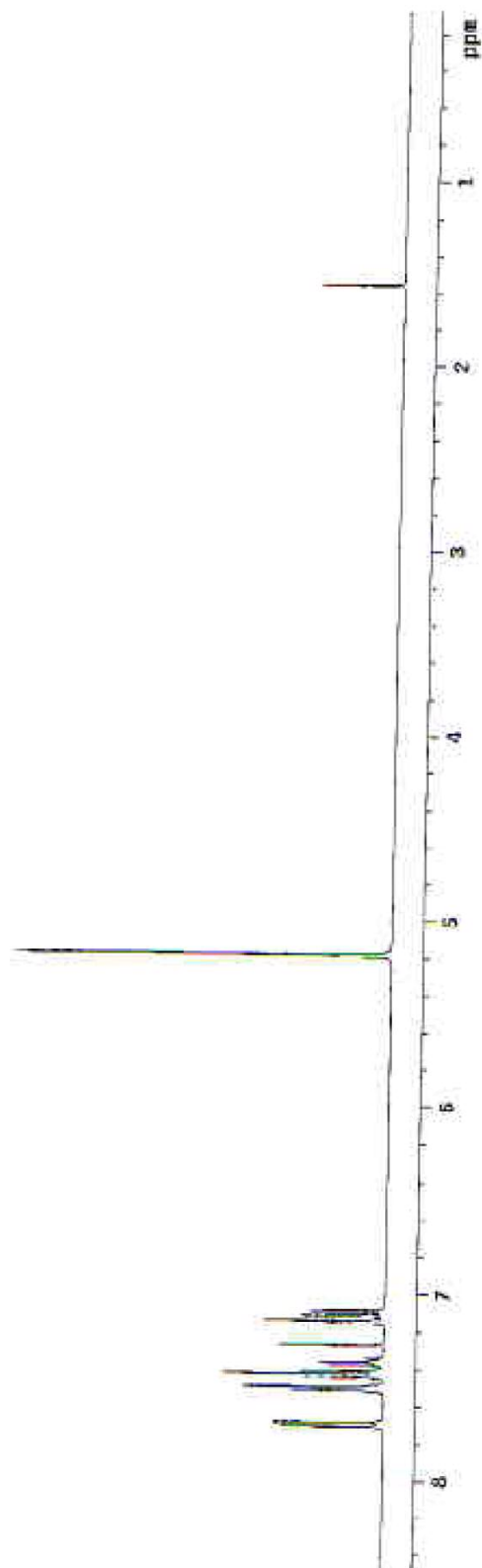
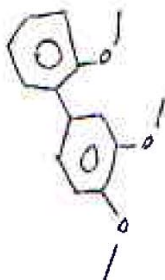


STANDARD 1H OBSERVE

Pulse Sequence: zgpg30
 Solvent: cdcl3
 Ambient temperature
 File: 105V
 INOVA-400 "nmr400"

Relax. delay 1.000 sec
 Pulse 97.5 degrees
 Acq. time 3.744 sec
 Width 5931.3 Hz
 32 repetitions

OBSERVE H3 399.9488882 MHz
 DATA PROCESSING
 Line broadening 0.1 Hz
 FI size 35536
 Total time 2 min, 32 sec





Pulse Sequence: 120w1

Solvent: CHCl_3

Ambient temperature

INOVA-400™ 400R400™

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Relax. delay 1.000 sec
Pulse 67.5 degrees

Pulse 67.5 degrees
Acq. time 3.744 sec

Width 5031.4 Hz

Single scan
needed HT
see page 21

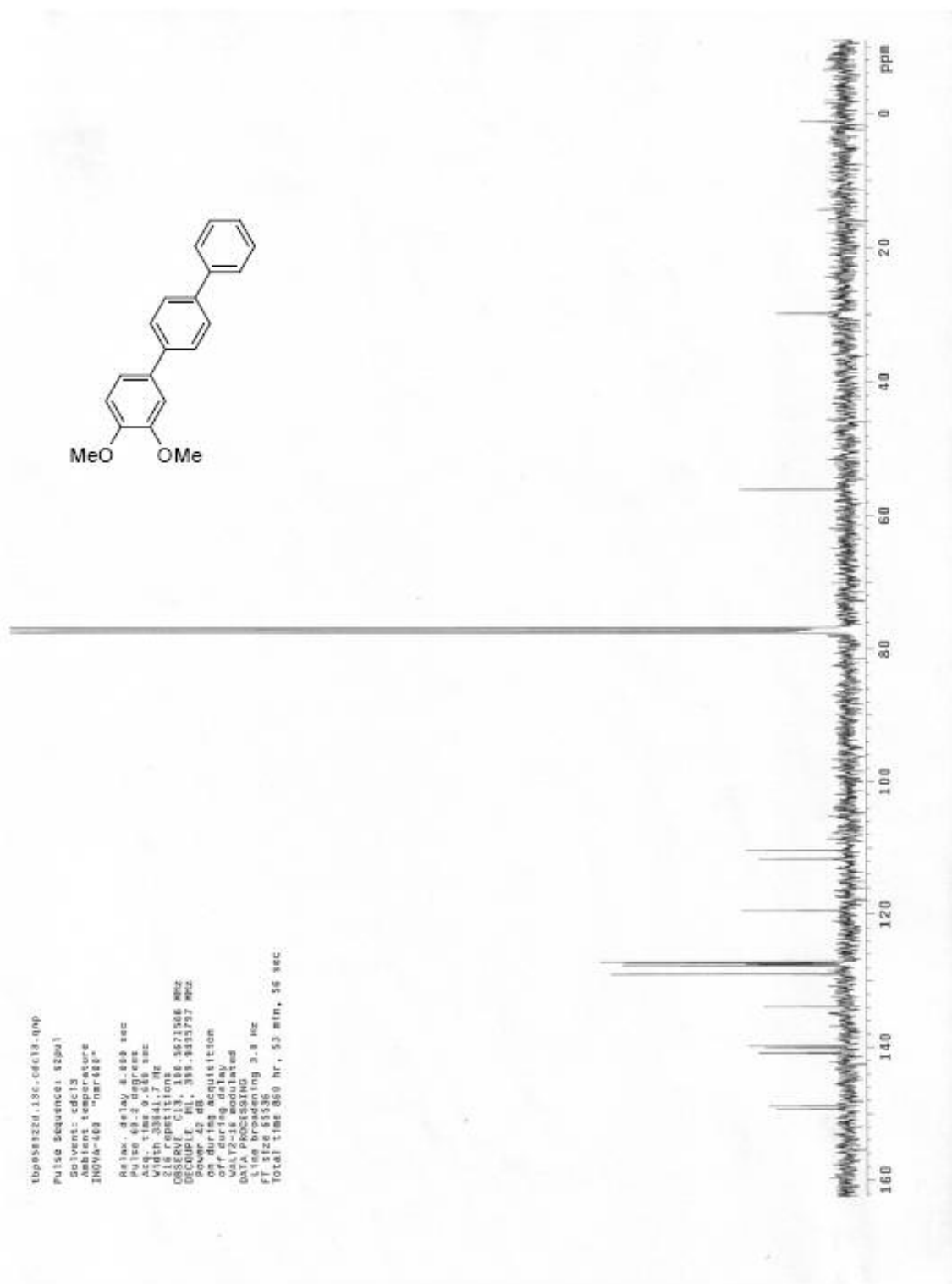
RESERVE HI, 959.948671
DATA PROCESSING

Line broadening 0.1 Hz

FT 0120 65536

Total time 0 min, 4 sec

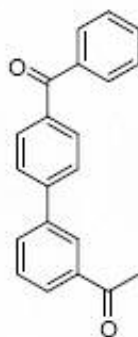




STANDARD 1H OBSERVE

Pulse Sequence: zgpg30
Solvent: cdcl3
Ambient temperature
F1: C556
INOVA-400 "hmr32g"

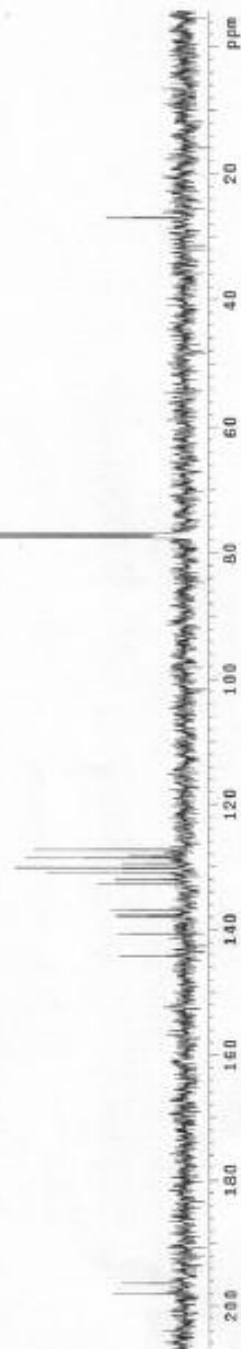
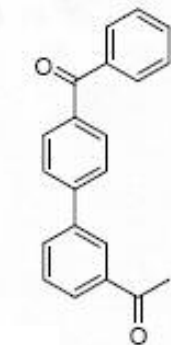
Relax. delay 1.800 sec
Acq. time 3.744 sec
Acq. time 3.744 sec
width 386.5 Hz
Single scan
OBSERVE H1, 399.540861 MHz
DATA PROCESSING 0.1 Hz
FT 1280000
Total time 0 min, 4 sec



6



t2p01022d.13c.cd13.exp
 Pulse Sequence: zgpg30
 Solvent: cdcl3
 Acquisition Temperature: 125.000000
 INOVA-100 1H/13C-400+
 Relax, delay 4.000 sec
 Pulse 52.2 degrees
 Acq. time 8.549 sec
 Relax, delay 1.000 sec
 30 repetitions
 OBSERVE C13, 100.6251565 MHz
 DECOUPLE H1, 200.1405797 MHz
 Power 42.000
 Acquisition
 off during delay
 VAL12-16 Modulated
 DATA PROCESSING
 F1 time processing 3.8 Hz
 F1 time 1.000000
 Total time 850 hr, 53 min, 56 sec

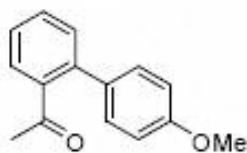


STANDARD IN OBSERVE

Pulse Sequence: zgpg30
 Solvent: cdcl3
 Acquisition temperature
 100MHz-400 MHz/400 MHz

Relax. delay 1.000 sec
 Pulse 67.5 degrees
 Acq. time 3.18 sec
 Width 5023.4 Hz
 SFO 100.626 MHz

OBSERVE F1: 393.9166712 MHz
 DATA PROCESSING
 F1 time processing 0.1 Hz
 F2 time processing 0.1 Hz
 Total time 4 min, 4 sec



tb0559226.13r.cdcl3.qmg

Pulse Sequence: zgpg30

Solvent: cdcl3

Acquisition Temperature

400 MHz

Relax. delay 4.000 sec

Pulse 69.2 deg/sec

Acq. time 2.400 sec

Width 33641.7 Hz

SI: FID

Observed 13C, 100.621556 MHz

Decouple 1H, 399.945757 MHz

Power 42 dB

on during acquisition

off during delay

off during delay

off during delay

off during delay

off during delay

off during delay

off during delay

off during delay

off during delay

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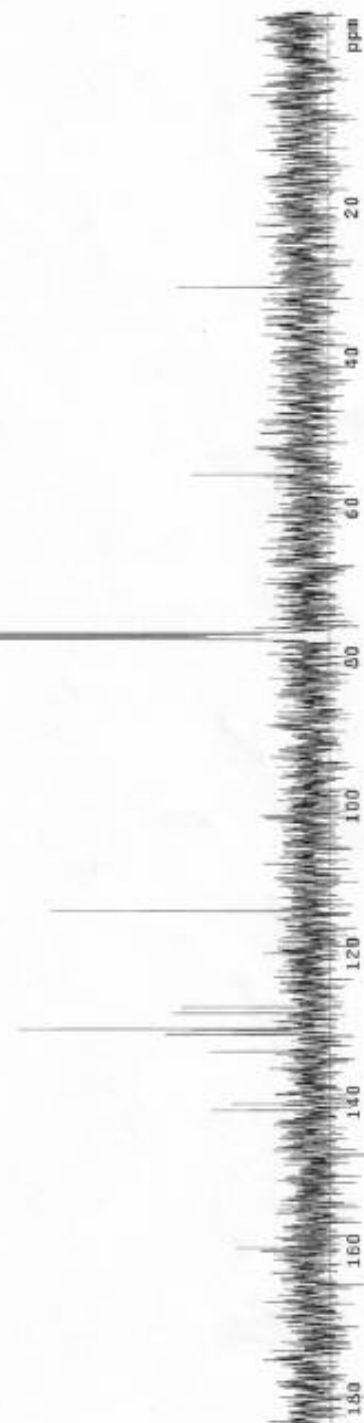
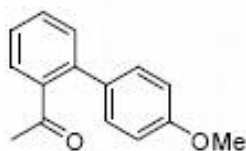
off during delay

off during delay

off during delay

off during delay

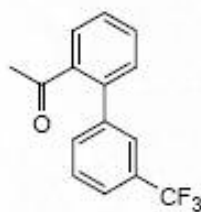
off during delay



STANDARD IN OBSERVE

Pulse Sequence: zgpg30
Solvent: cdcl3
Acquisition temperature: 25.00
INSTRUMENT: spect

Relax. delay: 1.000 sec
Pulse: zgpg30
Acq. time: 5.74 sec
Sweep rate: 1 Hz
Sweep range: 200 Hz
Sweep center: 300.135 MHz
OBSERVE: 1H, 300.135 MHz
DATA PROCESSING
Line broadening: 0.1 Hz
FT size: 65536
Total time: 6 min, 4 sec



43p030220.13c.cdc18.npp

Pulse Sequence: zgpg30

Solvent: cdc18

Acquisition Temperature

INSTRUMENT: spect

Relax. delay 4.000 sec

Pulse 88.2 degrees

Acq. time 1.00 sec

Width 32641.7 Hz

64 repetitions

OBSERVE C13, 101.567156 MHz

DECOUPLE H1, 399.943577 MHz

Power 32 dB

Channel 1 acquisition

OTF 0.000000

VAL2-16 modified

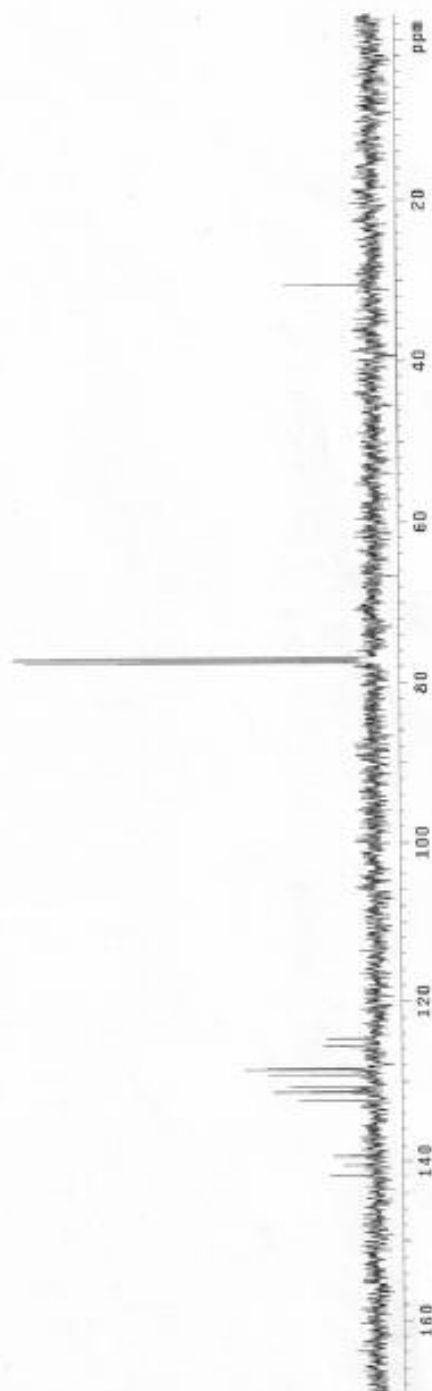
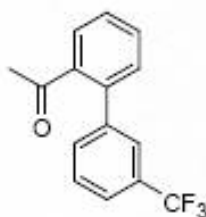
DATA PROCESSING

Line broadening 3.0 Hz

FT 216350

Time 3.00 min, 50 sec

Total time 3.00 hr, 50 min, 50 sec



tb05692d.13c.cd13-4sp

Pulse Sequence: zgpg30

Solvent: cdcl3

Acquire temperature

File: 4375

PROBHD-133 1mm-130

Relax. delay: 4.000 sec

Pulse sequence: zgpg30

Acq: 130.643 sec

Width: 33601.7 Hz

58 repetitions

OBSERVE C13, 100.627166 MHz

DECOUPLE H1, 333.945197 MHz

Power: 2.000000 W

Off-resonance decoupling

off during delay

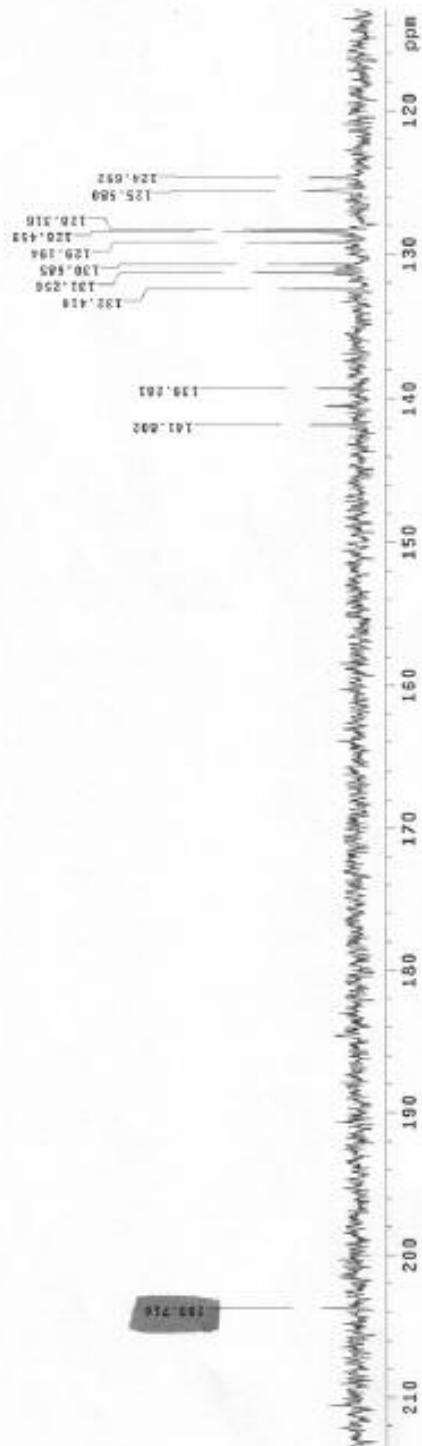
WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 56 hr, 53 min, 58 sec



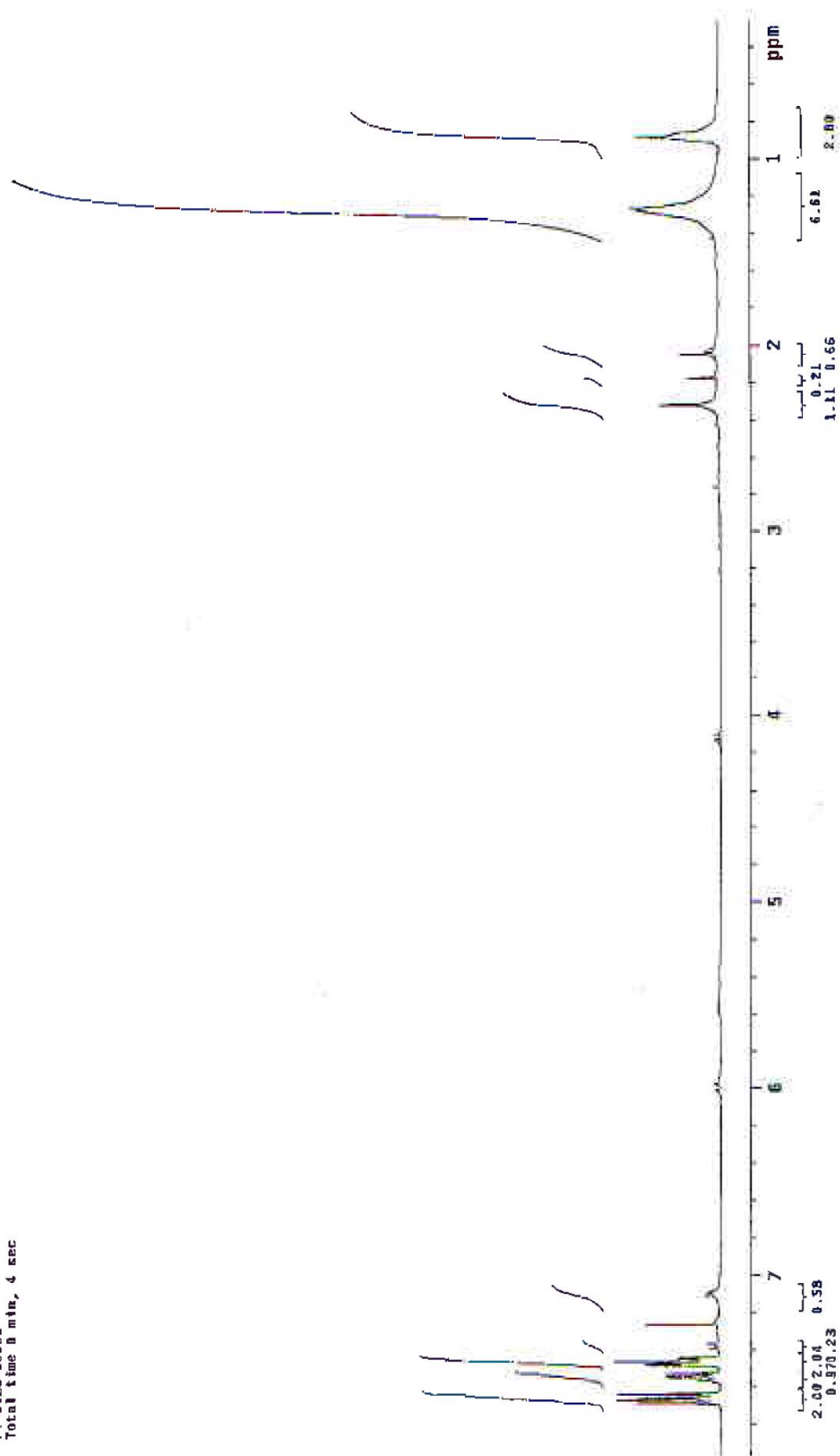
10

CCCCC/C=C/c1ccc(cc1)-c2ccccc2

```

Pulse Sequence: s2p01
Solvent: cdcl3
Ambient temperature
INOVA-400 "hmr430"
1H
Relax. delay 1.000 sec
p1 67.5 degrees
p2 67.5 degrees
Acq. time 3.744 sec
Width 5031.4 Hz
Single scan
RESERVE H1, 339.94565
DATA PROCESSING
Line broadening 0.1 Hz
FI size 85536
Total time 0 min, 4 sec

```



10



tkp0509224.13c.cdcl3.qnp

pulse sequence: zgpg30

Solvent: cdcl3

Acquisition temperature

INDRA-400 1H/400

Relax: delay 3.000 sec

Pulse program: zgpg30

Acq. time 3.500 sec

Width 33621.7 Hz

224 repetitions

OBSERVE C13, 100.625000 MHz

DECOUPLE H1, 399.345797 MHz

Power 42 dB

on during acquisition

off during delay

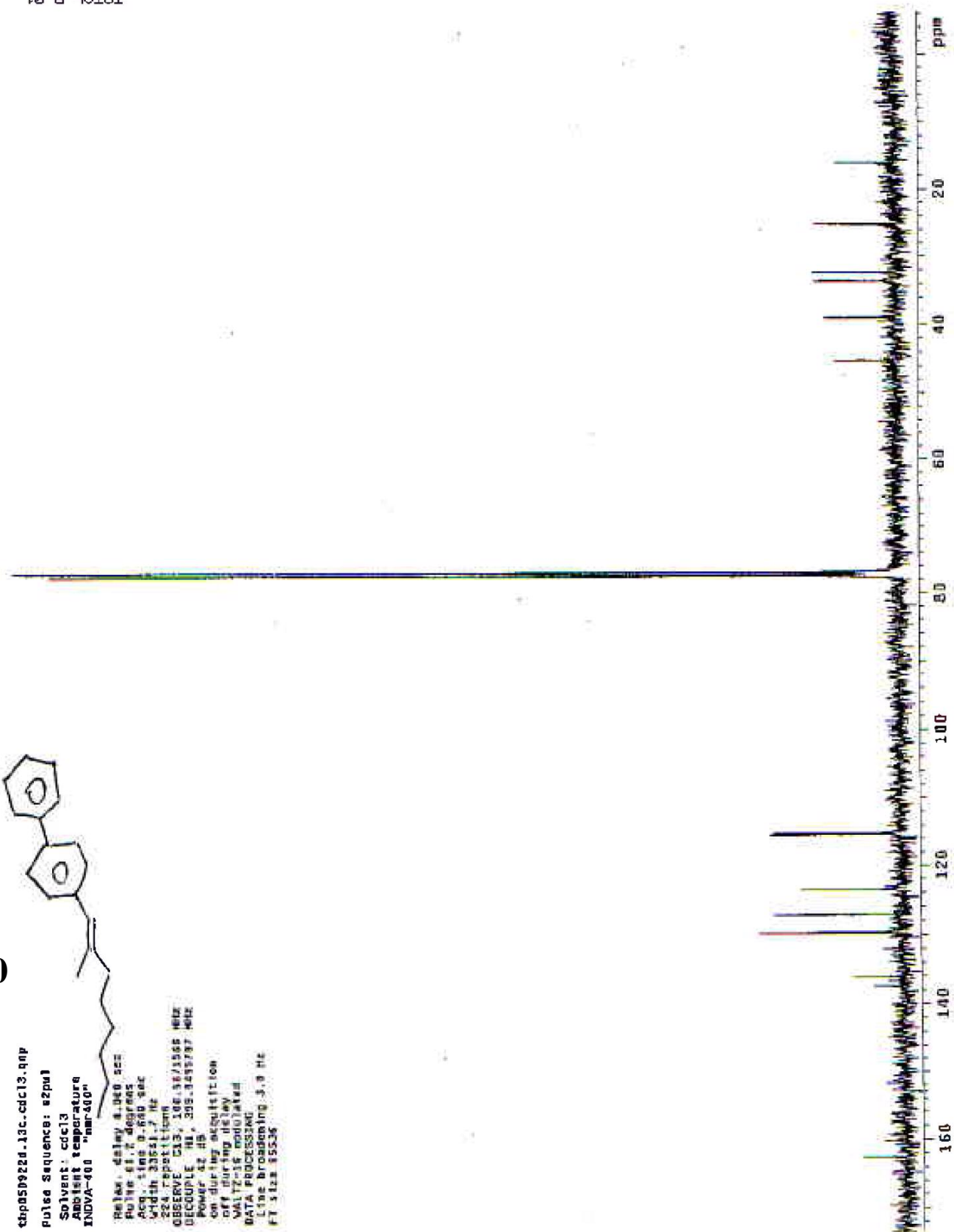
WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 5536

TOTAL P.01



STANDARD 1H OBSERVE

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

INOVA-400 ¹Hmr400-

Relax. delay 1.000 sec

Pulse 67.5 degrees

Acq. time 3.744 sec

Width 5031.4 Hz

Single scan

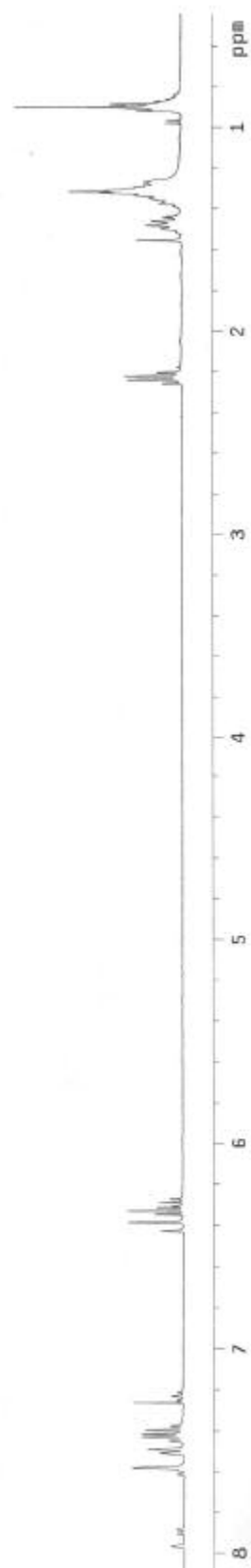
OBSERVE H1, 399.5486712 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 65536

Total time 0 min, 4 sec



tbp050922d-13c.cdc13.qnp

Pulse Sequence: zgpg30

Solvent: cdcl3

Ambient temperature

INDVA-400 "nmr400"

Relax. delay 4.000 sec

Pulse 65.2 degrees

Acq. time 9.458 sec

Acq. date 17-07-2005

256 repetitions

OBSERVE C13, 100.621588 MHz

DECOUPLE H1, 399.945797 MHz

Power 42 dB

on during acquisition

off during delay

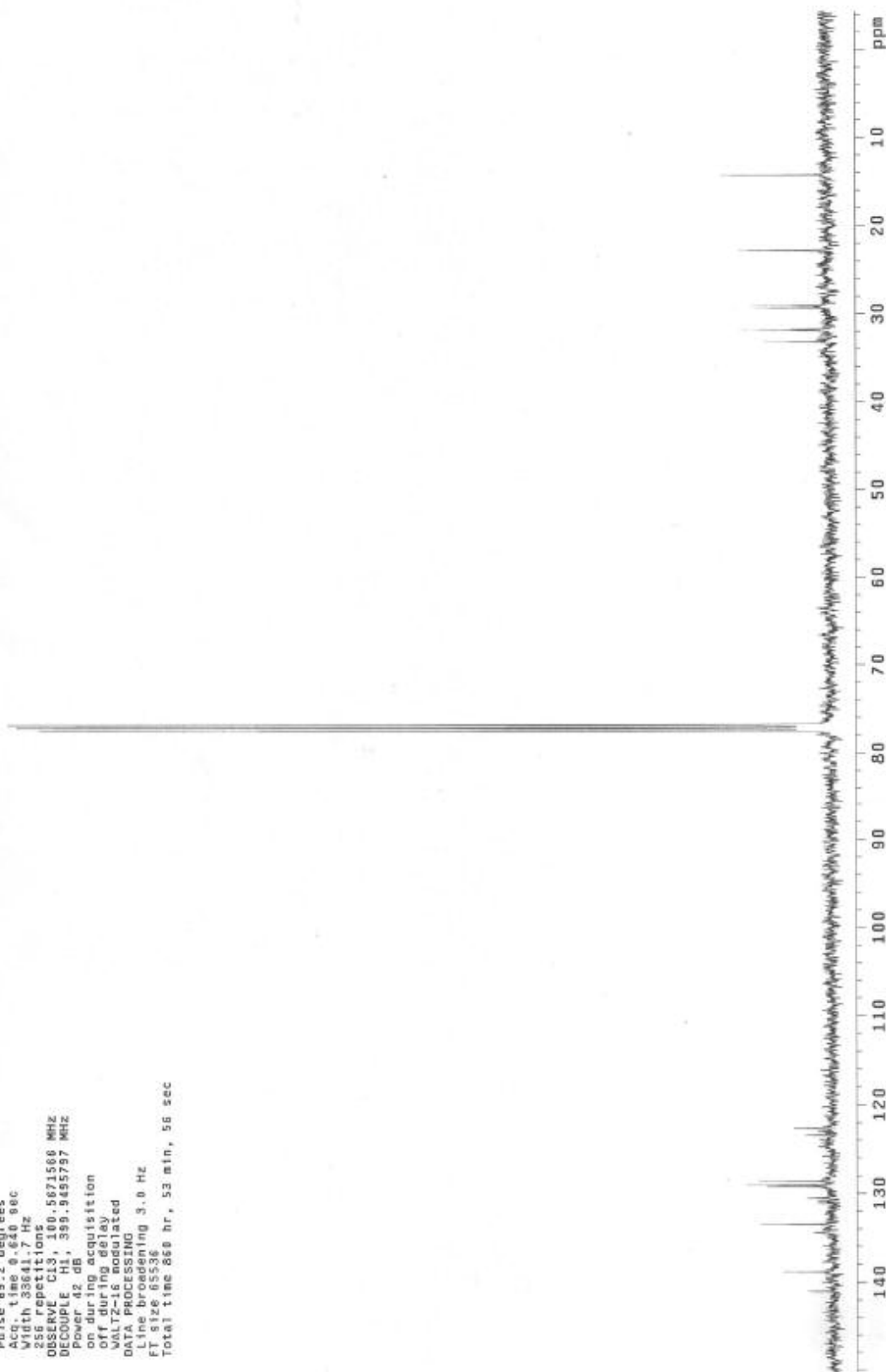
WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 860 hr, 53 min, 56 sec





STANDARD 1H OBSERVE

Pulse Sequence: zgpg30

Solvent: cdcl3

Ambient temperature

INDVA=400 "nmr400"

Relax. delay 1.000 sec

Pulse 67.5 degrees

Acq. time 3.744 sec

Width 5931.4 Hz

Single scan

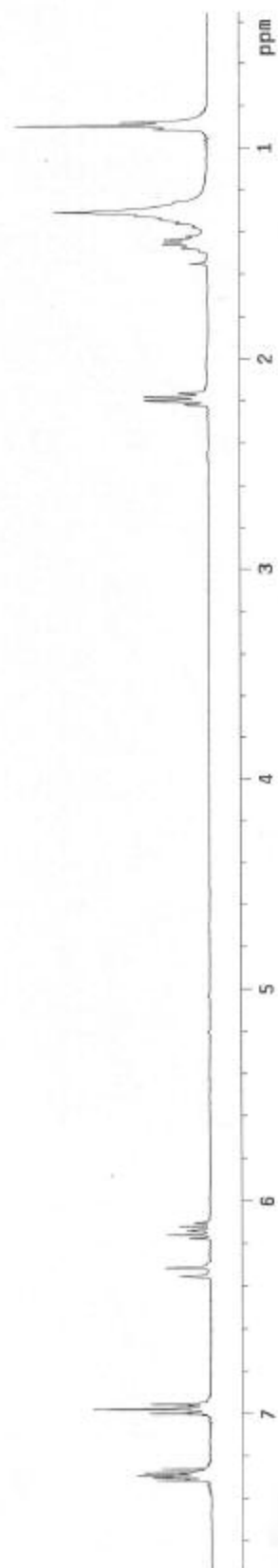
OBSERVE M1, 399.9486712 MHz

DATA PROCESSING

Line broadening 0.1 Hz

FT size 65536

Total time 0 min, 4 sec



tbp050822d.13c.cdcl3.qnp

Pulse Sequence: s2pul

Solvent: cdcl3

Ambient temperature

INOVA-400 "nmr400"

Relax. delay 4.000 sec

Pulse 65.2 degrees

Acq. time 0.549 sec

Waltz 32041.7 Hz

72 repetitions

OBSERVE CH1, 100.627156 MHz

DECOUPLE CH1, 399.3495797 MHz

Power 42 dB

on during acquisition

off during delay

WALTZ-16 modulated

DATA PROCESSING

Line broadening 3.0 Hz

FT size 65536

Total time 860 hr, 53 min, 56 sec

