Supporting Information

Non-Precious Metals Catalyze Formal [4+2] Cycloaddition Reactions of 1,2-Diazines and Siloxy Alkynes Under Ambient Conditions

Chintan S. Sumaria, Yunus E. Türkmen, and Viresh H. Rawal*

Department of Chemistry, The University of Chicago, 5735 South Ellis Avenue Chicago, Illinois, 60637, United States
vrawal@uchicago.edu

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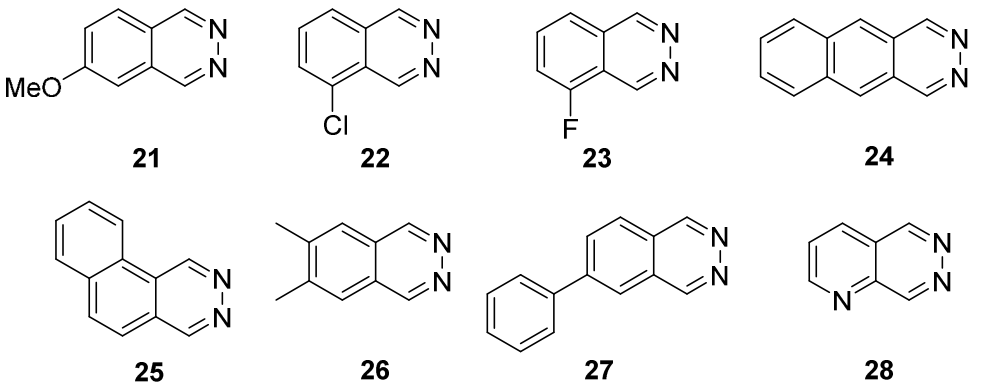
Experimental Section.

General: Reactions were run in flame-dried glassware under an atmosphere of argon, with septa dried over P_2O_5. Methylene chloride was purified by passage over activated alumina, through an Innovative Technologies Solvent Drying system. Thin-layer chromatography (TLC) was performed using Whatman silica gel 60 Å F254 plates (250 μm) with F-254 fluorescent indicator and visualized by UV fluorescence quenching, ceric ammonium molybdate or potassium permanganate staining. SiliCycle SiliaFlash P60 silica gel (particle size 40–63 μm) was used for flash chromatography. NMR spectra were measured on Bruker DRX and DMX spectrometers at 500 MHz for ^{1}H spectra and 125 MHz for ^{13}C spectra and calibrated from either TMS (δ = 0 for ^{1}H) or residual $CHCl_3$ (δ = 7.26 for ^{1}H and δ = 77.0 for ^{13}C). ^{19}F NMR spectra were measured on a Bruker DRX spectrometer at 470 MHz using external calibration with fluorobenzene (δ = -113.15). Mass spectral analysis was measured on Agilent technologies 6224 TOF LC/MS. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer and are reported in frequency of absorption (cm^{-1}) using NaBr salt plates using a thin film.

Materials: Distilled reagents were sealed under an inert atmosphere and stored in a freezer. All other reagents were stored in a desiccator.

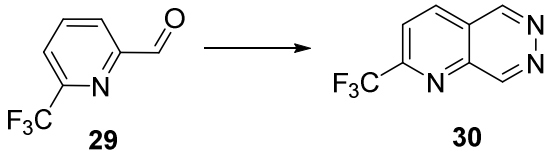
Preparation of 1,2-Diazines



21 **22** **23** **24**

25 **26** **27** **28**

The previously known 1,2-diazines **21**[1], **22**[1], **23**[1], **24**[2], **25**[1], **26**[2], **27**[1], **28**[1] were prepared according to reported procedures.



29 **30**

Compound **30** was prepared by modifying a procedure reported by Wegner and co-workers[1]. *n*-BuLi (2.00 ml, 3.20 mmol, 1.6 M in hexane, 1.07 equiv) was added dropwise under nitrogen to a stirred solution of *bis*(2-methoxyethyl)amine (0.49 mL, 3.30 mmol, 1.10 equiv) in a mixture of anhydrous hexanes (10 ml) and THF (2.5 ml) at –25 °C. After the addition, the mixture was stirred at –25 °C for 30 min to form the lithium amide. A solution of 6-(trifluoromethyl)pyridine-2-carboxaldehyde **29** (525.3 mg, 3.00 mmol, 1.00 equiv) in THF (2 mL) was added dropwise over a period of 30 min at –25 °C. The reaction mixture was stirred at -20 °C for 45 min and additional *n*-BuLi (2.80 ml, 4.50 mmol, 1.6 M in hexane, 1.50 equiv) was added at -20 °C. The reaction mixture was then stirred for another 2 h at the same temperature. After cooling to –78 °C, THF (3 ml) and DMF (0.70 ml, 9.0 mmol, 3.00 equiv) were added, and the resulting mixture was stirred for 10 min. It was then allowed to warm to 0 °C and stirred for 1.5 h. The reaction was quenched with a solution of NH_4Cl (0.48 g, 9.0 mmol, 3.00 equiv) and $N_2H_4 \bullet H_2O$ (0.70 ml, 11.5 mmol, 80% in H_2O, 3.80 equiv) in H_2O (3 ml). The reaction was allowed to warm to room temperature and stirred overnight. It was then diluted with ethyl acetate (10 ml) and the two phases were partitioned. The aqueous phase was extracted with ethyl acetate (3 × 15 ml), and the combined organic layers were dried over $MgSO_4$, filtered and thoroughly concentrated *in vacuo* to remove DMF. Purification by two successive flash column chromatographies over SiO_2 (first with 1:2 acetone:hexanes and second with ethyl acetate as eluent) afforded product **30** (401 mg, 67% yield) as a pale yellow solid.

30: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.95 (s, 1H), 9.74 (s, 1H), 8.59 (d, *J* = 8.5 Hz, 1H), 8.21 (d, *J* = 8.5 Hz, 1H)

[1] Kessler, S. N., Wegner, H. A. *Org. Lett.* **2012**, *14*, 3268.
[2] Türkmen, Y. E.; Montavon, T. J.; Kozmin, S. A.; Rawal, V. H. *J. Am. Chem. Soc.* **2012**, *134,* 9062.

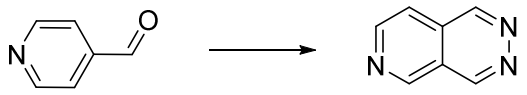
^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 153.9, 152.8, 150.4, 140.8, 137.0, 123.46, 123.44, 122.4, 121.6, 119.4

^{19}F NMR (470 MHz, $CDCl_3$) δ -68.1

HRMS (ESI) calcd for $C_8H_5F_3N_3^+$ $(M+H)^+$: 200.0430, Found: 200.0428

R_f 0.30-0.40 (ethyl acetate)

Melting Point 147-148 °C



31 **32**

Compound **32** was prepared by modifying a procedure reported by Wegner and co-workers[1]. *n*-BuLi (4.00 ml, 6.40 mmol, 1.6 M in hexane, 1.07 equiv) was added dropwise under nitrogen to a stirred solution of *bis*(2-methoxyethyl)amine (0.98 mL, 6.60 mmol, 1.10 equiv) in a mixture of anhydrous hexanes (10 ml) and THF (6 ml) at –25 °C. After the addition, the mixture was stirred at –25 °C for 30 min to form the lithium amide. A solution of 4-pyridinecarboxaldehyde **31** (643 mg, 6.00 mmol, 1.00 equiv) in THF (5 mL) was added dropwise over a period of 1 hour at –25 °C. The reaction mixture was stirred for 45 min and additional *n*-BuLi (5.60 ml, 9.00 mmol, 1.6 M in hexane, 1.50 equiv) was added at –25 °C. The reaction mixture was then stirred for another 2 h at the same temperature. After cooling to –78 °C, THF (5 ml) and DMF (1.40 ml, 18.0 mmol, 3.00 equiv) were added, and the resulting mixture was stirred for 10 min. It was then allowed to warm to 0 °C and stirred for 1.5 h. The reaction was quenched with a solution of NH_4Cl (0.96 g, 18.0 mmol, 3.00 equiv) and N_2H_4•H_2O (0.70 ml, 11.5 mmol, 80% in H_2O, 1.90 equiv) in H_2O (5 ml). The reaction was allowed to warm to room temperature and stirred overnight. It was then diluted with ethyl acetate (15 ml) and the two phases were partitioned. The aqueous phase was extracted with ethyl acetate (3 × 20 ml), and the combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash column chromatography over SiO_2 (3:1-20:1 EtOAc:hexanes) afforded product **32** (208 mg, 26% yield) as a pale yellow solid.

32: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.70 (s, 1H), 9.68 (s, 1H), 9.51 (s, 1H), 9.10 (d, J = 5.8 Hz, 1H), 7.82 (d, J = 5.8 Hz, 1H)

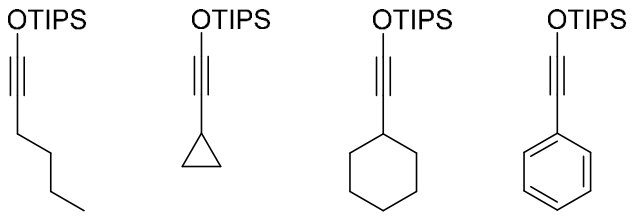
^{13}C NMR (125 MHz, $CDCl_3$) δ 151.3, 150.43, 150.42, 149.6, 128.7, 120.5, 117.9

HRMS (ESI) calcd for $C_7H_6N_3^+$ $(M+H)^+$: 132.0556, Found: 132.0556

R_f 0.25-0.35 (10% methanol in ethyl acetate)

Melting Point 168 °C

Preparation of Siloxy Alkynes



Siloxy alkynes **2**[3], **33**[4], **34**[4] and **35**[5] were prepared according to reported procedures.

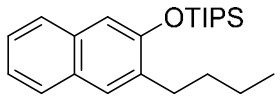
General procedure 1 for the cycloaddition reaction of 1,2-diazines and siloxy alkynes catalyzed by $Cu(MeCN)_4PF_6$

Tetrakis(acetonitrile)copper(I) hexafluorophosphate, $Cu(MeCN)_4PF_6$ (typically 0.1 equiv) and 1,2-diazine (1.0 equiv) were added to a a flame-dried test-tube or a round-bottomed flask equipped with a stir bar. The test-tube/round-bottom flask is then subjected to vacuum, flushed with argon, sealed with a septum, and connected to an argon balloon to maintain positive argon pressure throughout the remainder of the experiment. A stock solution of 2,2′-bipyridine (0.075-0.15 equiv) in CH_2Cl_2 was then used to add 2,2′-bipyridine via a syringe, followed by the addition of remaining CH_2Cl_2. This mixture was allowed to stir for 15 minutes before the addition of recently distilled siloxy alkyne (1.5-2.0 equiv) using a syringe, and the reaction monitored by thin-layer chromatography (TLC). After consumption of 1,2-diazine, the reaction was quenched by passing the reaction mixture through a plug of silica (washing with CH_2Cl_2), and was concentrated under reduced pressure. The excess unreacted siloxy alkyne was removed by Kugelrohr distillation, and the purified product was obtained by flash column chromatography.

General procedure 2 for the cycloaddition reaction of 1,2-diazines and siloxy alkynes catalyzed by $Ni(CO)_2(PPh_3)_2$

Bis(triphenylphosphine)nickel dicarbonyl, $Ni(CO)_2(PPh_3)_2$ (typically 0.1 equiv) and 1,2-diazine were added to a flame-dried test-tube equipped with a stir bar. This test-tube was then subjected to vacuum, flushed with argon, sealed with a septum, and connected to an argon balloon to maintain positive argon pressure throughout the remainder of the experiment. CH_2Cl_2 was added by a syringe and the mixture was allowed to stir for 15 minutes before the addition of freshly distilled siloxy alkyne (1.5-2.0 equiv) using another syringe. After complete consumption of 1,2-diazine (as monitored by TLC), the reaction was quenched by passing the reaction mixture through a plug of silica (washing with hexanes), and was concentrated under reduced pressure. The excess unreacted siloxy alkyne was removed by Kugelrohr distillation, and the purified product was obtained by flash column chromatography.

[3] Shubinets, V., Schramm, M. P., Kozmin, S. A. *Org. Synth*. **2010**, *87*, 253.
[4] Montavon, T. J., Li, J., Cabrera-Pardo, J. R., Mrksich, M., Kozmin, S. A. *Nat. Chem*. **2012**, *4*, 45.
[5] Sun, J., Keller, V. A., Meyer, S. T., Kozmin, S. A. *Adv. Synth. Catal.* **2010**, *352*, 839.



3

(3-butyl-naphth-2-yloxy)triisopropylsilane 3

General procedure 1 was employed for the cycloaddition of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (5.86 mg, 0.0375 mmol, 0.075 equiv) in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 4 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded compound **3** (143 mg, 80%) as a colorless oil.

General procedure 2 was employed for the cycloaddition of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 24 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded compound **3** (143 mg, 80%) as a colorless oil.

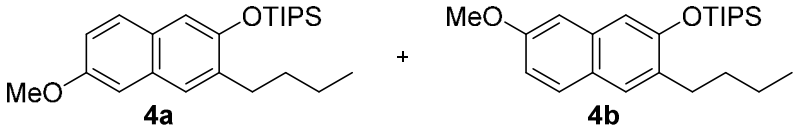
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.56 (s, 1H), 7.34 (dt, *J* = 8.1, 1.2, Hz, 1H), 7.28 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.09 (s, 1H), 2.77 (t, *J* = 7.8 Hz, 2H), 1.68-1.63 (m, 2H), 1.44-1.37 (m, 5H), 1.15 (d, *J* = 7.5 Hz, 18H), 0.95 (t, *J* = 7.3 Hz ,3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 135.0, 133.2, 129.0, 128.2, 127.0, 126.0, 125.1, 123.4, 112.4, 32.2, 31.2, 22.8, 18.1, 14.1, 13.1

HRMS (ESI) calcd for $C_{23}H_{37}OSi^+$ $(M+H)^+$: 357.2608, Found: 357.2605

IR (film): 2945, 2867, 1499, 1466, 1258, 1180, 929, 882, 862, 744, 685 cm^{-1}

R_f 0.57 (hexanes)



4a + **4b**

(3-butyl-6-methoxy-naphth-2-yloxy)triisopropylsilane 4a and (3-butyl-7-methoxy-naphth-2-yloxy)triisopropylsilane 4b:

General procedure 1 was employed for the cycloaddition of 6-methoxy phthalazine **21** (80.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (11.7 mg, 0.075 mmol, 0.15 equiv) in 3.0 mL of CH_2Cl_2. The reaction was quenched after a period of 8 h. Flash column chromatography (after Kuglerohr distillation) with 2% EtOAc in hexanes as the eluent afforded 155 mg (80%) of a product mixture consisting of regioisomers **4a** and **4b** (**4a**:**4b** = 50:50) as a pale yellow oil.

General procedure 2 was employed for the coupling of 6-methoxy phthalazine **21** (80.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 3.0 mL of CH_2Cl_2. The reaction was quenched after a period of 24 h. Flash chromatography (after Kuglerohr distillation) with 2% EtOAc in hexanes as the eluent afforded 144 mg (75%) of a product mixture consisting of regioisomers **4a** and **4b** (**4a**:**4b** = 62:38) as a pale yellow oil.

4a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 9 Hz, 1H), 7.47 (s, 1H), 7.06-6.99 (m, 2H), 6.97-6.92 (m, 1H), 3.88 (s, 3H), 2.76 (t, *J* = 8.0 Hz, 2H), 1.70-1.60 (m, 2H), 1.46-1.34 (m, 5H), 1.14 (d, *J* = 7.5 Hz, 18H), 0.95 (t, *J* = 7.5 Hz, 3H)

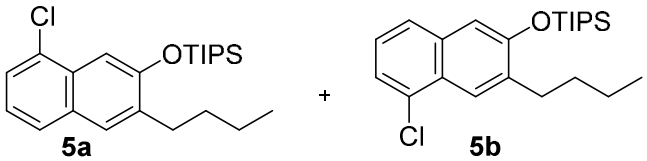
4b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.5 Hz, 1H), 7.48 (s, 1H), 7.06-6.99 (m, 2H), 6.97-6.92 (m, 1H), 3.90 (s, 3H), 2.73 (t, *J* = 8.0 Hz, 2H), 1.70-1.60 (m, 2H), 1.46-1.34 (m, 5H), 1.16 (t, *J* = 7.5 Hz, 18H), 0.94 (t, *J* = 7.0 Hz, 3H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 157.4, 156.1, 153.6, 151.3, 135.3, 134.3, 132.3, 129.8, 128.5, 128.4, 128.0, 127.5, 127.1, 124.5, 117.7, 115.9, 112.5, 111.8, 105.4, 104.4, 55.2 (2C), 32.32, 32.25, 31.18, 30.96, 22.8 (2C), 18.14, 18.13 14.1 (2C), 13.14, 13.10

HRMS (ESI) calcd for $C_{24}H_{39}O_2Si^+$ $(M+H)^+$: 387.2714, Found: 387.2715

IR (film): 2946, 2867, 1504, 1464, 1390, 1251, 883 cm^{-1}

R_f 0.20 (2% EtOAc in hexanes)



5a **5b**

(3-butyl-8-chloro-naphth-2-yloxy)triisopropylsilane 5a and (3-butyl-5-chloro-naphth-2-yloxy)triisopropylsilane 5b:

General procedure 1 was employed for the cycloaddition of 5-chloro phthalazine **22** (82.3 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a

catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 1.5 mL of CH_2Cl_2. The reaction was quenched after a period of 5 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 155 mg (79%) of a product mixture consisting of regioisomers **5a** and **5b** (**5a**:**5b** = 55:45) as a colorless oil.

General procedure 2 was employed for the coupling of 5-chloro phthalazine **22** (82.3 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 1.5 mL of CH_2Cl_2. The reaction was quenched after a period of 24 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 145 mg (74%) of a product mixture consisting of regioisomers **5a** and **5b** (**5a**:**5b** = 74:26) as a colorless oil.

5a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.5 Hz, 1H), 7.57 (s, 1H), 7.55 (s, 1H), 7.44 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 2.78 (t, *J* = 8.0 Hz, 2H), 1.71-1.62 (m, 2H), 1.48-1.36 (m, 5H), 1.17 (d, *J* = 7.5 Hz, 18H), 0.95 (t, *J* = 7.5 Hz, 3H)

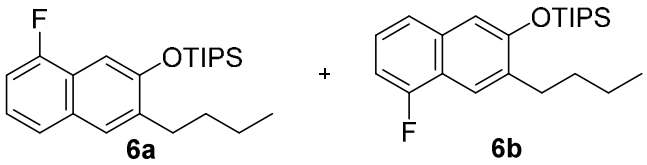
5b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.55-7.52 (m, 1H), 7.364 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.24 (t, *J* = 8.0 Hz, 1H), 7.10 (s, 1H), 2.82 (t, *J* = 8.0 Hz, 2H), 1.71-1.62 (m, 2H), 1.48-1.36 (m, 5H), 1.15 (d, *J* = 8.5 Hz, 18H), 0.96 (t, *J* = 7.3 Hz, 3H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 154.1, 153.7, 136.4, 135.9, 134.5, 131.2, 130.7, 130.0, 129.9, 128.6, 126.1, 125.29, 125.26, 125.1, 124.9, 123.7, 123.2, 123.1, 112.7, 109.3, 32.3, 32.1, 31.4, 31.0, 22.84, 22.77, 18.13, 18.10, 14.06, 14.05, 13.1, 13.0

HRMS (ESI) calcd for $C_{23}H_{36}ClOSi^{+}$ $(M+H)^{+}$: 391.2218, Found: 391.2225

IR (film): 2946, 2867, 1493, 1460, 1263, 1127, 882, 833, 681 cm^{-1}

R_f 0.74 (hexanes)



6a **6b**

(3-butyl-8-fluoro-naphth-2-yloxy)triisopropylsilane 6a and (3-butyl-5-fluoro-naphth-2-yloxy)triisopropylsilane 6b:

General procedure 1 was employed for the cycloaddition of 5-fluoro phthalazine **23** (74.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 3.5 mL of CH_2Cl_2. The reaction was

quenched after a period of 3.5 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 141.5 mg (76%) of a product mixture consisting of regioisomers **6a** and **6b** (**6a**:**6b** = 50:50) as a colorless oil.

General procedure 2 was employed for the coupling of 5-chloro phthalazine **23** (74.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 3.5 mL of CH_2Cl_2. The reaction was quenched after a period of 48 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 131 mg (70%) of a product mixture consisting of regioisomers **6a** and **6b** (**6a**:**6b** = 67:33) as a colorless oil.

6a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.33 (s, 1H), 7.21-7.15 (m, 1H), 7.01 (ddd, *J* = 10.9, 7.7, 0.9 Hz, 1H), 2.82-2.75 (m , 2H), 1.71-1.62 (m, 2H), 1.48-1.36 (m, 5H), 1.16 (d, *J* = 7.5 Hz, 18H) , 0.95 (t, *J* = 7.4 Hz, 3H)

6b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.39 (d, *J* = 8.3 Hz, 1H), 7.27-7.22 (m, 1H), 7.10 (d, *J* = 1.8 Hz, 1H), 6.94 (ddd, *J* = 11.1, 7.7, 0.9, 1H), 2.82-2.75 (m, 2H), 1.71-1.62 (m, 2H), 1.48-1.36 (m, 5H), 1.15 (d, *J* = 7.5 Hz, 18H), 0.95 (t, *J* = 7.4 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 159.7, 158.8, 157.7, 156.8, 153.9, 153.4, 136.1, 135.6, 135.5, 135.1, 130.7, 130.6, 128.1, 128.0, 125.1, 125.0, 123.4, 123.2, 122.9, 122.8, 122.7, 122.6, 121.8, 120.9, 120.8, 119.1, 119.0, 112.2, 108.7, 108.5, 107.1, 106.9, 105.1, 32.2, 32.1, 31.3, 31.2, 22.8, 18.1, 14.1, 13.1, 13.0

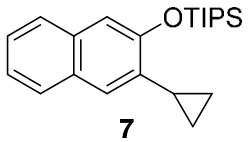
6a: ^{19}F NMR (470 MHz, $CDCl_3$) δ -125.0

6b: ^{19}F NMR (470 MHz, $CDCl_3$) δ -124.1

HRMS (ESI) calcd for: $C_{23}H_{36}FOSi^+$ $(M+H)^+$: 375.2514, Found: 375.2495

IR (film): 2946, 2868, 1607, 1497, 1457, 1262, 1211, 1150, 908, 883, 866, 685 cm^{-1}

R_f 0.56 (hexanes)



7

(3-cyclopropyl-naphth-2-yloxy)triisopropylsilane 7

General procedure 1 was employed for the cycloaddition of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclopropyl-1-(triisopropylsiloxy)ethyne **33** (238 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1

equiv) and 2,2′-bipyridine (5.86 mg, 0.0375 mmol, 0.075 equiv) in 1.3 mL of CH_2Cl_2. The reaction was quenched after a period of 2.5 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 124 mg (73%) of compound **7** as a colorless oil.

General procedure 2 was employed for the coupling of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclopropyl-1-(triisopropylsiloxy)ethyne **33** (238 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 1.3 mL of CH_2Cl_2. The reaction was quenched after a period of 48 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 150 mg (88%) of compound **7** as a colorless oil.

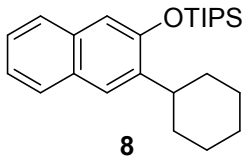
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.37-7.23 (m, 3H), 7.11 (s, 1H), 2.33-2.25 (m, 1H), 1.41 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 18H), 1.02-0.94 (m, 2H), 0.79-0.71 (m, 2H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 135.9, 132.9, 129.1, 127.0, 126.0, 125.1, 123.6, 123.4, 112.4, 18.1, 13.1, 10.9, 8.0

HRMS (ESI) calcd for $C_{22}H_{33}OSi^+$ $(M+H)^+$: 341.2295, Found: 341.2295

IR (film): 2944, 2866, 1498, 1472, 1179, 930, 883, 744, 684 cm^{-1}

R_f 0.44 (hexanes)



8

(3-cyclohexyl-naphth-2-yloxy)triisopropylsilane 8

General procedure 1 was employed for the cycloaddition of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclohexyl-1-(triisopropylsiloxy)ethyne **34** (281 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (5.86 mg, 0.0375 mmol, 0.075 equiv) in 1.3 mL of CH_2Cl_2. The reaction was quenched after a period of 4 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 145 mg (76%) of compound **8** as a colorless oil, which solidifies upon standing in the refrigerator to form a white solid.

General procedure 2 was employed for the coupling of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclohexyl-1-(triisopropylsiloxy)ethyne **34** (281 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 1.3 mL of CH_2Cl_2. The reaction was quenched after a period of 24 h. Flash column chromatography (after

Kuglerohr distillation) with hexanes as the eluent afforded 158 mg (82%) of compound **8** as a colorless oil, which solidifies upon standing in the refrigerator to form a white solid.

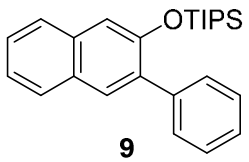
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.59 (s, 1H), 7.34 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.27 (dt, *J* = 7.5, 1.2 Hz, 1H), 7.09 (s, 1H), 3.10 (br t, 1H), 1.98 (br d, 2H), 1.87 (m, 2H), 1.79 (br d, *J* = 13.0 Hz, 1H), 1.49-1.37 (m, 7H), 1.34-1.25 (m, 1H), 1.16 (d, *J* = 7.5 Hz, 18H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 139.7, 132.8, 129.2, 127.2, 125.9, 125.2, 125.1, 123.3, 112.3, 37.5, 33.5, 27.2, 26.5, 18.2, 13.1

HRMS (ESI) calcd for $C_{25}H_{39}OSi^+$ $(M+H)^+$: 383.2765, Found: 383.2771

IR (film): cm^{-1}: 2925, 2866, 2361, 1653, 1497, 1465, 1448, 1252, 1179

R_f 0.62 (hexanes)



9

(3-phenyl-naphth-2-yloxy)triisopropylsilane 9

General procedure 1 was employed for the cycloaddition of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (206 mg, 0.75 mmol, 1.5 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (1.86 mg, 0.005 mmol, 0.01 equiv) and 2,2′-bipyridine (0.78 mg, 0.005 mmol, 0.01 equiv) in 1.0 mL of CH_2Cl_2. Note that instead of using a stock solution to add 2,2′-bipyridine, stock solutions were prepared to add both $Cu(MeCN)_4PF_6$ and 2,2′-bipyridine. The reaction was quenched after a period of 7 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 166 mg (88%) of compound **9** as a colorless oil.

General procedure 2 was employed for the coupling of phthalazine **1** (65.1 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (206 mg, 0.75 mmol, 1.5 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (16.0 mg, 0.025 mmol, 0.05 equiv) as catalyst in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 7 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 178 mg (94%) of compound **9** as a colorless oil.

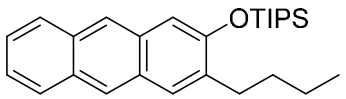
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.75 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.43-7.39 (m, 3H), 7.33 (dt, *J* = 7.7, 1.1 Hz, 2H), 7.24 (s, 1H), 1.20 (sept, *J* = 7.5 Hz, 3H), 0.99 (d, *J* = 7.5 Hz, 18H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.7, 139.1, 134.9, 133.9, 129.91, 129.86, 129.1, 127.7, 127.6, 126.9, 126.1, 126.0, 123.8, 113.8, 17.9, 12.9

HRMS (ESI) calcd for $C_{25}H_{33}OSi^+$ $(M+H)^+$: 377.2295, Found: 377.2296

IR (film): cm^{-1}: 2944, 2866, 1462, 1437, 1201, 1179, 857, 685

R_f 0.24 (hexanes)



10

(3-butylanthrac-2-yloxy)triisopropylsilane 10

General procedure 1 was employed for the cycloaddition of benzo[*g*]phthalazine **24** (90.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0. 10 equiv) in 2.0 mL of CH_2Cl_2. The reaction was quenched after a period of 3.5 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 151 mg (74%) of compound **10** as a colorless oil.

General procedure 2 was employed for the coupling of benzo[*g*]phthalazine **24** (90.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 2.0 mL of CH_2Cl_2. The reaction was quenched after a period of 24 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 130 mg (64%) of compound **10** as a colorless oil.

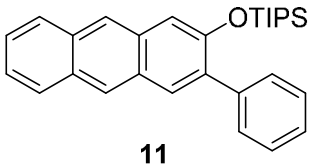
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.17 (s, 1H), 7.90 (t, *J* = 8.5 Hz, 2H), 7.71 (s, 1H), 7.41-7.31 (m, 2H), 7.22 (s, 1H), 2.81 (t, *J* = 7.8 Hz, 2H), 1.74-1.68 (m, 2H), 1.49-1.40 (m, 5H), 1.17 (d, *J* = 7.5 Hz, 18H), 0.97 (t, *J* = 7.3 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 136.2, 132.0, 131.5, 130.4, 128.5, 128.1, 127.8, 127.5, 125.0, 124.9, 124.1, 123.3, 110.7, 32.1, 31.4, 22.8, 18.2, 14.1, 13.1

HRMS (ESI) calcd for $C_{27}H_{39}OSi^+$ $(M+H)^+$: 407.2765, Found: 407.2764

IR (film): 2945, 2866, 1634, 1459, 1279, 1214, 1148, 882, 739, 685 cm^{-1}

R_f 0.42 (hexanes)



11

(3-phenylanthrac-2-yloxy)triisopropylsilane 11

General procedure 1 was employed for the cycloaddition of benzo[*g*]phthalazine **24** (90.1 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (206 mg, 0.75 mmol, 1.5 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (1.86 mg, 0.005 mmol, 0.01 equiv) and 2,2′-bipyridine (0.78 mg, 0.005 mmol, 0.01 equiv) in 2.0 mL of CH_2Cl_2. Note that instead of using a stock solution to add 2,2′-bipyridine, stock solutions were prepared to add both $Cu(MeCN)_4PF_6$ and 2,2′-bipyridine. The reaction was quenched after a period of 4 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 162 mg (76%) of compound **11** as pale yellow oil.

General procedure 2 was employed for the coupling of benzo[*g*]phthalazine **24** (90.1 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (206 mg, 0.75 mmol, 1.5 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (16.0 mg, 0.025 mmol, 0.05 equiv) as catalyst in 2.0 mL of CH_2Cl_2. The reaction was quenched after a period of 6 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 178 mg (83%) of compound **11** as pale yellow oil.

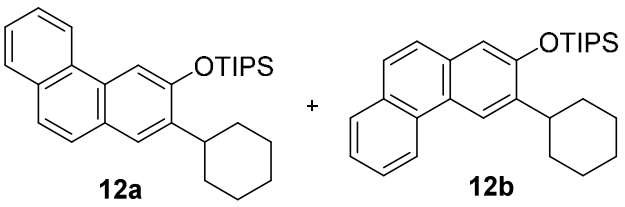
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (s, 1H), 8.23 (s, 1H), 7.96-7.89 (m, 3H), 7.61 (dt, *J* = 7.5, 1.5 Hz, 2H), 7.45-7.31 (m, 6H), 1.24 (sept, *J* = 7.5 Hz, 3H), 1,00 (d, *J* = 7.5 Hz, 18 H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 151.6, 139.0, 136.1, 132.3, 132.0, 130.61, 130.60, 129.9, 128.4, 128.2, 127.7, 127.6, 127.0, 126.1, 125.4, 124.4, 123.5, 112.2, 17.9, 12.9

HRMS (ESI) calcd for $C_{29}H_{35}OSi^+$ $(M+H)^+$: 427.2452, Found: 427.2434

IR (film): cm^{-1}: 2944, 2866, 1457, 1436, 1211, 1175, 899, 884, 698

R_f 0.26 (hexanes)



12a **12b**

(2-cyclohexylphenanthr-3-yloxy)triisopropylsilane 12a and (3-cyclohexylphenanthr-2-yloxy)triisopropylsilane 12b:

General procedure 1 was employed for the cycloaddition of benzo[*f*]phthalazine **25** (90.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclohexyl-1-(triisopropylsiloxy)ethyne **34** (281 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 10.0 mL of CH_2Cl_2. The reaction was quenched after a period of 14 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 152 mg (70%) of a product mixture consisting of regioisomers **12a** and **12b** (**12a**:**12b** = 64:36) as a colorless oil.

General procedure 2 was employed for the coupling of benzo[*f*]phthalazine **25** (90.1 mg, 0.5 mmol, 1.0 equiv) and 2-cyclohexyl-1-(triisopropylsiloxy)ethyne **34** (281 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 10.0 mL of CH_2Cl_2. The reaction was quenched after a period of 120 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 124 mg (57%) of a product mixture consisting of regioisomers **12a** and **12b** (**12a**:**12b** = 44:56) as a colorless oil.

12a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.47 (s, 1H), 7.86-7.80 (m, 1H), 7.67-7.47 (m, 4H), 7.18 (d, *J* = 1.4 Hz, 1H), 3.25-3.12 (m, 1H), 2.07-1.98 (m, 2H), 1.95-1.86 (m, 2H), 1.85-1.77 (m, 1H), 1.62-1.28 (m, 8H), 1.17 (d, 18H, *J* = 7.5 Hz)

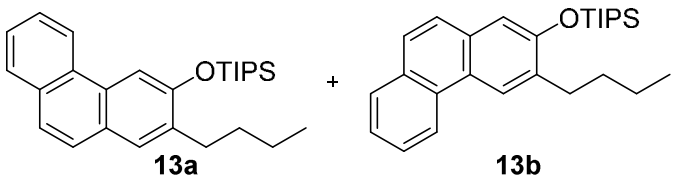
12b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.1, 1H), 7.99 (s, 1H), 7.86-7.80 (m, 1H), 7.67-7.47 (m, 5H), 3.25-3.12 (m, 1H), 2.07-1.98 (m, 2H), 1.95-1.86 (m, 2H), 1.85-1.77 (m, 1H), 1.62-1.28 (m, 8H), 1.20 (d, *J* = 7.5 Hz, 18H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 152.8, 139.0, 138.9, 132.0, 131.3, 131.1, 130.4, 129.6, 129.3, 128.52, 128.51, 126.9, 126.7, 126.34, 126.29, 126.26, 126.02, 125.98, 125.96, 125.3, 124.6, 124.2, 122.2, 122.1, 120.5, 114.5, 109.5, 37.7, 37.4, 33.7, 33.4, 27.3, 27.2, 26.51, 26.48, 18.23, 18.18, 13.2 (2C)

HRMS (ESI) calcd for $C_{29}H_{41}OSi^+$ $(M+H)^+$: 433.2921, Found: 433.2921

IR (film): 2866, 2851, 2361, 2339, 1498, 1461, 1265, 1222, 999, 879, 743, 684, 668 cm^{-1}

R_f 0.34 (hexanes)



(2-butylphenanthr-3-yloxy)triisopropylsilane 13a and (3-butylphenanthr-2-yloxy)triisopropylsilane 13b:

General procedure 1 was employed for the cycloaddition of benzo[*f*]phthalazine **25** (90.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 10.0 mL of CH_2Cl_2. The reaction was quenched after a period of 14 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 145 mg (71%) of a product mixture consisting of regioisomers **13a** and **13b** (**13a**:**13b** = 73:27) as a colorless oil.

General procedure 2 was employed for the coupling of benzo[*f*]phthalazine **25** (90.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 10.0 mL of CH_2Cl_2. The reaction was quenched after a period of 120 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 159 mg (78%) of a product mixture consisting of regioisomers **13a** and **13b** (**13a**:**13b** = 40:60) as a colorless oil.

13a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.0 Hz, 1H), 8.41 (s, 1H), 7.80-7.77 (m, 1H), 7.62-7.43 (m, 4H), 7.19 (s, 1H), 2.88 (t, *J* = 7.9 Hz, 2H), 1.77-1.66 (m, 2H), 1.51-1.35 (m, 5H), 1.154 (d, *J* = 7.5 Hz, 18H), 0.97 (t, *J* = 7.5 Hz, 3H)

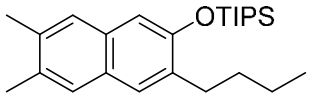
13b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.44 (d, J = 8.0 Hz, 1H), 8.00 (s,1H), 7.82-7.78 (m, 1H), 7.62-7.43 (m, 5H), 2.814 (t, *J* = 7.9 Hz, 2H), 1.77-1.66 (m, 2H), 1.51-1.35 (m, 5H), 1.186 (d, *J* = 7.5 Hz, 18H), 0.96 (t, *J* = 7.5 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 153.4, 134.22, 134.20, 132.0, 131.7, 131.1, 130.3, 129.69, 129.68, 129.3, 128.55, 128.49, 126.8, 126.5, 126.32, 126.29, 126.05, 126.0, 125.3, 124.58, 124.57, 124.3, 123.9, 122.2, 122.1, 114.6, 109.5, 32.6, 32.3, 31.6, 30.9, 22.9, 22.8, 18.19, 18.15, 14.13, 14.11, 13.18, 13.14

HRMS (ESI) calcd for $C_{27}H_{39}OSi^+$ $(M+H)^+$: 407.2765, Found: 407.2753

IR (film): 2945, 2866, 1499, 1460, 1274, 1224, 1152, 999, 882, 866, 742, 646 cm^{-1}

R_f 0.41 (hexanes)



14

(3-butyl-6,7-dimethylnaphth-2-yloxy)triisopropylsilane 14

General procedure 1 was employed for the cycloaddition of 6,7-dimethylphthalazine **26** (79.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0. 10 equiv) in 6.0 mL of CH_2Cl_2. The reaction was quenched after a period of 12 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 143 mg (74%) of compound **14** as a colorless oil.

General procedure 2 was employed for the coupling of 6,7dimethylphthalazine **26** (79.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 6.0 mL of CH_2Cl_2. The reaction was quenched after a period of 48 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 146 mg (76%) of compound **14** as a colorless oil.

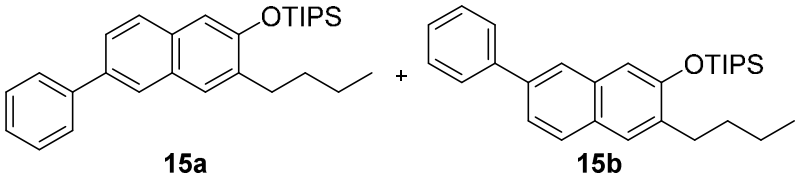
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 2H), 7.39 (s, 1H), 7.00 (s, 1H), 2.74 (t, *J* = 7.8 Hz, 2H), 2.37 (s, 3H), 2.36 (s, 3H), 1.67-1.61 (m, 2H), 1.44-1.34 (m, 5H), 1.14 (d, *J* = 7.5 Hz, 18H), 0.94 (t, *J* = 7.5 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 134.6, 133.9, 132.7, 132.0, 127.9, 127.2, 126.5, 125.7, 111.6, 32.3, 31.1, 22.7, 20.1, 20.0, 18.1, 14.1, 13.1

HRMS (ESI) calcd for $C_{25}H_{41}OSi^+$ $(M+H)^+$: 385.2921, Found: 385.2918

IR (film): 2944, 2867, 1498, 1466, 1372, 1253, 1208, 1146, 905, 882 cm^{-1}

R_f 0.56 (hexanes)



15a **15b**

(3-butyl-6-phenyl-naphth-2-yloxy)triisopropylsilane 15a and (3-butyl-7-phenyl-naphth-2-yloxy)triisopropylsilane 15b:

General procedure 1 was employed for the cycloaddition of 6-phenyl phthalazine **27** (103.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 8.0 mL of CH_2Cl_2. The reaction was quenched after a period of 7 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 156 mg (72%) of a product mixture consisting of regioisomers **15a** and **15b** (**15a**:**15b** = 60:40) as a colorless oil.

General procedure 2 was employed for the coupling of 6-phenyl phthalazine **27** (103.1 mg, 0.5 mmol, 1.0 equiv) and 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) using bis(triphenylphosphine)nickel(0) dicarbonyl (32.0 mg, 0.05 mmol, 0.1 equiv) as catalyst in 8.0 mL of CH_2Cl_2. The reaction was quenched after a period of 96 h. Flash column chromatography (after Kuglerohr distillation) with hexanes as the eluent afforded 46 mg (21%) of a product mixture consisting of regioisomers **15a** and **15b** (**15a**:**15b** = 50:50) as a colorless oil.

15a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.79-7.53 (m, 5H), 7.49-7.42 (m, 2H), 7.38-7.31 (m, 1H), 7.12 (s, 1H), 2.84-2.76 (m, 2H), 1.73-1.63 (m, 2H), 1.50-1.38 (m, 5H), 1.16 (d, J = 7.5 Hz, 18H), 0.96 (t, J = 7.4 Hz, 3H)

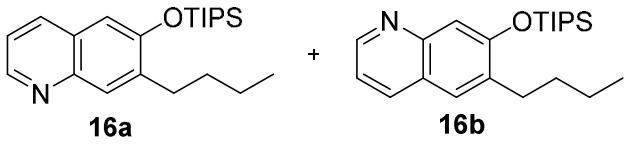
15b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.79-7.53 (m, 5H), 7.49-7.42 (m, 2H), 7.38-7.31 (m, 1H), 7.16 (m, 1H), 2.84-2.76 (m, 2H), 1.73-1.63 (m, 2H), 1.50-1.38 (m, 5H), 1.16 (d, J = 7.5 Hz, 18H), 0.96 (t, J = 7.4 Hz, 3H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 153.4, 153.2, 141.56, 141.52, 137.9, 136.3, 135.5, 135.2, 133.5, 132.4, 129.3, 128.74, 128.71, 128.6, 128.3, 128.0, 127.5, 127.4, 127.2, 127.1, 126.9, 126.6, 125.0, 124.9, 124.1, 123.2, 112.7, 112.2, 32.23, 32.22 31.2 (2C), 22.8 (2C), 18.2 (2C), 14.1 (2C), 13.1 (2C)

HRMS (ESI) calcd for $C_{29}H_{41}OSi^+$ $(M+H)^+$: 433.2921, Found: 433.2910

IR (film): 2946, 2867, 1466, 1253, 1217, 884, 696 cm^{-1}

R_f 0.34 (hexanes)



16a **16b**

(7-butyl-6-quinolyloxy)-triisopropylsilane 16a and (6-butyl-7-quinolyloxy)-triisopropylsilane 16b

Tetrakis(acetonitrile)copper(I) hexafluorophosphate, $Cu(MeCN)_4PF_6$ (18.6 mg, 0.05 mmol, 0.1 equiv) and pyrido[2,3-*d*]pyridazine **28** (65.6 mg, 0.5 mmol, 1.0 equiv) were added to a a flame-dried test-tube equipped with a stir bar. This test-tube was subjected to vacuum, flushed with argon, sealed with a septum, and connected to an argon balloon to maintain positive argon pressure throughout the remainder of the experiment. A stock solution (0.4 mL) of 2,2′-bipyridine in anhydrous 1,2-dichloroethane was then used to add 2,2′-bipyridine (11.7 mg, 0.075 mmol, 0.15 equiv) via a syringe, followed by the addition of another 0.6 mL of anhydrous 1,2-dichloroethane. The test-tube was transferred to an oil bath at about 85 °C for 1,2-dichloroethane to undergo reflux over the sides of the test-tube. The reaction mixture was then allowed to stir for 15 minutes before the addition of freshly distilled 1-(triisopropylsiloxy)-1-hexyne **2** (254 mg, 1.0 mmol, 2.0 equiv) with a syringe. After 48 h,

heating was discontinued to cool the reaction mixture to room temperature. The catalyst was separated by passing it through a plug of silica (washing with CH_2Cl_2), thus quenching the reaction. The mixture was consequently concentrated and the excess unreacted siloxy alkyne removed by Kugelrohr distillation. By using a 10% ethyl acetate in hexanes solvent mixture as an eluent, flash column chromatography (after Kuglerohr distillation) afforded 74 mg (41%) of a product mixture consisting of **16a** and **16b** (**16a**:**16b** = 55:45).

16a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 4.3, 1.7 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (s, 1H), 7.28-7.24 (m, 1H), 7.032 (s, 1H), 2.82 (t, *J* = 7.8 Hz, 2H), 1.73-1.63 (m, 2H), 1.52-1.35 (m, 5H), 1.16 (d, *J* = 7.5 Hz, 18H), 0.95 (t, *J* = 7.4 Hz, 3H)

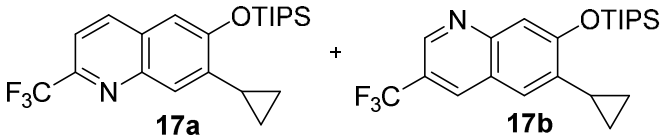
16b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.52 (s, 1H), 7.39 (s, 1H), 7.21 (dd, *J* = 4.3, 3.9, 1H), 2.80 (t, *J* = 7.8 Hz, 2H), 1.73-1.63 (m, 2H), 1.52-1.35 (m, 5H), 1.16 (d, *J* = 7.5 Hz, 18H), 0.96 (t, *J* = 7.4 Hz, 3H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 156.2, 153.3, 149.2, 147.6, 144.2, 139.2, 136.1, 135.2, 134.2, 129.3, 127.8, 127.4, 123.7, 120.3, 118.8, 117.7, 113.4, 111.5, 32.0, 31.8, 31.1, 31.0, 22.7, 22.6, 18.04, 18.03 13.97, 13.95 13.03, 12.99

HRMS (ESI) calcd for $C_{22}H_{36}NOSi^+$ $(M+H)^+$: 358.2561, Found: 358.2570

IR (film): 2945, 2866, 1498, 1462, 1271, 1223, 908, 882, 865, 742, 683, 645 cm^{-1}

R_f 0.40-0.45 (1:3 ethyl acetate:hexanes)



7-cyclopropyl-2-(trifluoromethyl)-6-(triisopropylsiloxy)quinoline 17a and 6-cyclopropyl-2-(trifluoromethyl)-7-(triisopropylsiloxy)quinoline 17b

General procedure 1 was employed for the cycloaddition of 2-(trifluoromethyl)-pyrido[2,3-*d*]pyridazine **30** (99.6 mg, 0.5 mmol, 1.0 equiv) and 2-cyclopropyl-1-(triisopropylsiloxy)ethyne **33** (238 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 6 h. Flash column chromatography (after Kuglerohr distillation) with 2% EtOAc in hexanes solvent mixture as the eluent afforded 132 mg (64%) of a product mixture consisting of regioisomers **17a** and **17b** (**17a**:**17b** = 55:45) as pale yellow oil.

Catalysis by $AgNTf_2$: Silver bis(trifluoromethanesulfonyl)imide, $AgNTf_2$ (9.3 mg, 0.025 mmol, 0.05 equiv) and 2-(trifluoromethyl)-pyrido[2,3-*d*]pyridazine **30** (99.6 mg, 0.5 mmol, 1.0 equiv) were added to a flame-dried test-tube equipped with a stir bar. The test-tube is then subjected to vacuum, flushed with N_2, sealed with a septum, and positive N_2 pressure throughout the remainder of the experiment. 2,2′-bipyridine (3.90 mg, 0.025 mmol, 0.05 equiv) in CH_2Cl_2 (0.2 mL) was added via a syringe, followed by the addition of 0.8 mL of CH_2Cl_2. This mixture was allowed to stir for 15 minutes before the addition of 2-cyclopropyl-1-(triisopropylsiloxy)ethyne **33** (238 mg, 1.0 mmol, 2.0 equiv) using a syringe, and the reaction monitored by thin-layer chromatography (TLC). After 2 hours, the reaction was quenched by passing the reaction mixture through a plug of silica (washing with CH_2Cl_2), and was concentrated under reduced pressure. Flash column chromatography (after Kuglerohr distillation to remove unreacted siloxy alkyne) with 2% ethyl acetate in hexanes as the eluent afforded 145 mg (71%) of a product mixture consisting of regioisomers **17a** and **17b** (**17a**:**17b** = 67:33) as pale yellow oil.

17a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.14-8.08 (m, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 8.5Hz, 1H), 7.11 (s, 1H), 2.40-2.30 (m, 1H), 1.42 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 18H), 1.14-1.04 (m, 2H), 0.88-0.83 (m, 2H)

17b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.14-8.08 (m, 1H), 7.53 (d, *J* = 8.5 Hz, 1H), 7.45 (s, 1H), 7.30 (s, 1H), 2.40-2.30 (m, 1H), 1.48 (septet, *J* = 7.5 Hz, 3H), 1.16 (d, *J* = 7.5 Hz, 18H), 1.14-1.04 (m, 2H), 0.81-0.76 (m, 2H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 158.0, 155.7, 147.5, 147.1, 146.9, 145.6, 143.4, 142.5, 139.8, 136.5, 135.6, 128.31, 128.30, 125.2, 124.5, 122.9, 122.7, 122.6, 120.77, 120.76, 115.89, 115.87, 114.44, 114.42, 113.95, 113.94, 111.2, 18.01, 17.97, 13.06, 13.02, 11.0, 10.8, 9.2, 8.4

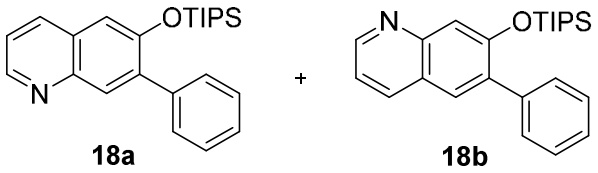
17a: ^{19}**F NMR** (470 MHz, $CDCl_3$) δ -67.3

17b: ^{19}**F NMR** (470 MHz, $CDCl_3$) δ -67.3

HRMS (ESI) calcd for $C_{22}H_{31}F_3NOSi^+$ $(M+H)^+$: 410.2122, Found: 410.2118

IR (film): 2947, 2869, 1473, 1334, 1229, 1183, 1090, 883 cm^{-1}

$\mathbf{R_f}$ 0.5-0.6 (5% ethyl acetate in hexanes)



18a **18b**

(7-phenyl-6-quinolyloxy)-triisopropylsilane 18a and (6-phenyl-7-quinolyloxy)-triisopropylsilane 18b

General procedure 1 was employed for the cycloaddition of pyrido[2,3-*d*]pyridazine **28** (65.6 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (275 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 6 h. Flash column chromatography (after Kuglerohr distillation) with 5-20% EtOAc in hexanes solvent mixture as the eluent afforded 140 mg (74%) of a product mixture consisting of regioisomers **18a** and **18b** (**18a**:**18b** = 73:27) as pale brown oil.

18a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.06 (s, 1H), 8.00 (d, *J* = 8.5 Hz, 1H), 7.63-7.33 (m, 5H), 7.30 (q, *J* = 4.2 Hz, 1H), 7.19 (s, 1H), 1.20 (septet, *J* = 7.5 Hz, 3H), 0.99 (d, *J* = 7.5 Hz, 18H)

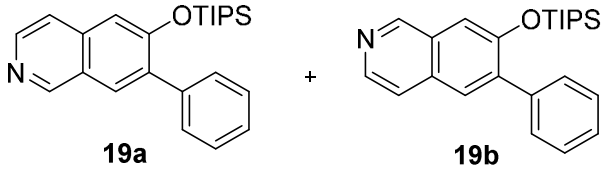
18b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.82 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.09-8.04 (m, 1H), 7.70 (s, 1H), 7.63-7.33 (m, 6H), 7.24 (q, *J* = 4.2 Hz, 1H), 1.28 (septet, *J* = 7.5 Hz, 3H) 1.00 (d, *J* = 7.0 Hz, 18H)

^{13}**C NMR** (125 MHz, $CDCl_3$) δ 154.9, 152.0, 150.3, 149.0, 148.4, 144.3, 138.4, 138.3, 135.8, 135.5, 134.1, 131.1, 129.8, 129.76, 129.74, 129.1, 128.5, 127.78, 127.76, 127.3, 127.2, 123.6, 121.0, 119.2, 115.1, 113.1, 17.78, 17.75, 12.81, 12.80

HRMS (ESI) calcd for $C_{24}H_{32}NOSi^+$ $(M+H)^+$: 378.2248, Found: 378.2248

IR (film): 2945, 2867, 1479, 1458, 1436, 1329, 1229, 932, 882, 868, 767, 698 cm^{-1}

R_f 0.51-0.60 (1:3 ethyl acetate:hexanes)



19a **19b**

(7-phenyl-6-isoquinolyloxy)-triisopropylsilane 19a and (6-phenyl-7-isoquinolyloxy)-triisopropylsilane 19b

General procedure 1 was employed for the cycloaddition of pyrido[3,4-*d*]pyridazine **32** (65.6 mg, 0.5 mmol, 1.0 equiv) and 2-phenyl-1-(triisopropylsiloxy)ethyne **35** (275 mg, 1.0 mmol, 2.0 equiv) using a catalyst combination of tetrakis(acetonitrile)copper(I) hexafluorophosphate (18.6 mg, 0.05 mmol, 0.1 equiv) and 2,2′-bipyridine (7.8 mg, 0.05 mmol, 0.10 equiv) in 1.0 mL of CH_2Cl_2. The reaction was quenched after a period of 6 h. Flash chromatography (after Kuglerohr distillation) with 5-20% ethyl acetate in hexanes solvent mixture as the eluent afforded 127 mg (67%) of a product mixture consisting of regioisomers **19a** and **19b** (**19a**:**19b** = 54:46) as pale yellow oil.

19a: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 9.13 (s, 1H), 8.43 (d, *J* = 6.0 Hz, 1H), 7.87 (s, 1H), 7.57-7.53 (m, 2H), 7.50 (d, *J* = 6.0 Hz), 7.45-7.41 (m, 2H), 7.39-7.35 (m, 1H), 7.17 (s, 1H), 1.32-1.20 (m, 3H), 0.99 (d, *J* = 7.5 Hz, 18H)

19b: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 9.11 (s, 1H), 8.41 (d, *J* = 5.0 Hz, 1H), 7.74 (s, 1H), 7.58 (d, *J* = 5.5 Hz, 1H), 7.57-7.53 (m, 2H), 7.45-7.41 (m, 2H), 7.40-7.35 (m, 1H), 7.32 (s, 1H), 7.31-7.19 (m, 3H), 0.99 (d, *J* = 7.5 Hz, 18H)

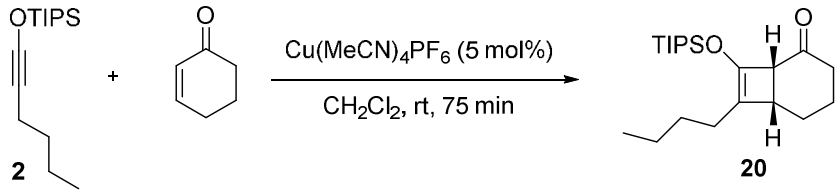
^{13}**C NMR** (125 MHz, $CDCl_3$) δ 155.5, 152.7, 151.8, 150.6, 143.0, 141.4, 139.7, 138.11, 138.09, 136.7, 136.5, 131.2, 129.7, 129.6, 128.4, 127.83, 127.82, 127.5, 127.3, 112.9, 112.0, 17.74, 17.72, 12.8 (2C)

HRMS (ESI) calcd for $C_{24}H_{32}NOSi^+$ $(M+H)^+$: 378.2248, Found: 378.2245

IR (film): 2943, 2866, 1625, 1487, 1459, 1413, 1263, 1216, 1206, 883, 854, 697, 687, 644 cm^{-1}

R_f 0.20-0.30 (1:3 ethyl acetate:hexanes)

Copper-Catalyzed Formal [2+2] Cycloaddition Reaction of Siloxy Alkynes and Cyclohexenone



An oven-dried test-tube fitted with a septum was charged with 1-(triisopropylsiloxy)-1-hexyne **2** (153.0 mg, 0.6 mmol, 1.2 equiv) and 3.0 mL of anhydrous CH_2Cl_2 in an inert atmosphere. Neat cyclohexenone (48 μL, 0.5 mmol, 1.0 equiv) was added followed by the addition of $Cu(MeCN)_4PF_6$ (9.3 mg, 0.025 mmol, 0.05 equiv) dissolved in 1.0 mL of CH_2Cl_2 (using a stock solution). The resulting clear light yellow solution is stirred at room temperature under nitrogen for 75 minutes. The mixture was then passed through a plug of silica and washed with CH_2Cl_2 in order to remove the catalyst. The mixture was purified by flash column chromatography (after Kuglerohr distillation),

using 2-5% ethyl acetate in hexanes solvent mixture as eluent to afford the 130 mg (74%) of the product **20** as colorless oil. Spectral data is consistent with that reported earlier.[6]

20: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.38 (s, 1H), 2.81 (s, 1H), 2.56-2.50 (m, 1H), 2.14-2.09 (m, 2H), 1.92-1.86 (m, 3H), 1.68-1.61 (m, 1H), 1.59-1.54 (m, 1H), 1.43-1.31 (m, 4H), 1.15-1.10 (m, 3H), 1.08 (d, J = 7.0 Hz, 18H), 0.91 (t, J = 7.0 Hz, 3H)

^{13}C NMR (125 MHz, $CDCl_3$) 211.5, 138.3, 122.1, 58.0, 40.1, 34.8, 29.6, 25.1, 24.8, 23.3, 18.1, 17.9, 14.2, 13.0

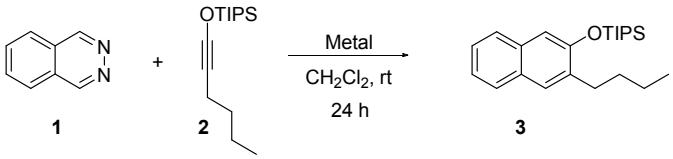
HRMS (ESI) calcd for $C_{21}H_{39}O_2Si^+$ $(M+H)^+$: 351.2714, Found: 351.2708

IR (film): 2943, 2868, 1699, 1465, 1283, 1255, 1001, 884, 687, 668 cm^{-1}

R_f ~ 0.4 (15:85 ethyl acetate:hexanes)

Evaluation of Other Metal Catalysts

Apart from the Ag(I), Cu(I) and Ni(0) complexes discussed, various other metal salts were evaluated for their ability to catalyze the formal [4+2] cycloaddition reaction. For every equivalent of phthalazine, 1.5 equivalents of 1-siloxyhexyne along with a 10 mol % loading of the metal salt were employed. The following yields were determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard. Though the hydrate of $Mn(OAc)_3$ catalyzed the reaction, the reaction was slower and lower yielding than the isoelectronic Cu(I) and Ni(0) complexes, and was hence not pursued further.

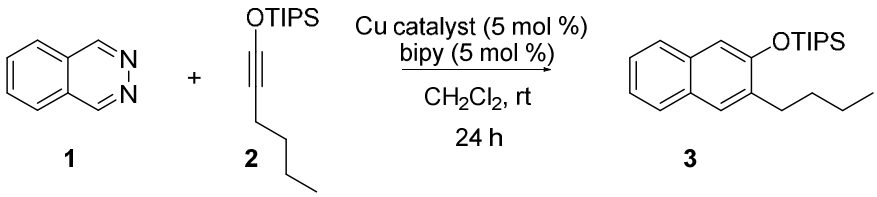


Metal Salt	**Yield (%)**
$Sc(OTf)_3$	3
$MnBr_2$	0
$Mn(OAc)_3{\cdot}2H_2O$	62
$FeCl_2$	0
$FeCl_3$	0
$Co(BF_4)_2.6H_2O$	0
$NiCl_2$	0
$ZnBr_2$	0
$CdCl_2.2H_2O$	0
$CrCl_2$	4
$CrCl_3$	0
LiBr	0

[6] Sweis, R. F.; Schramm, M. P.; Kozmin, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7442.

$CeCl_3$	0
$Yb(OTf)_3$	0
$La(OTf)_3$	0
$ZrCl_4.(THF)_2$	0
$In(OTf)_3$	0
$Bi(OTf)_3$	0

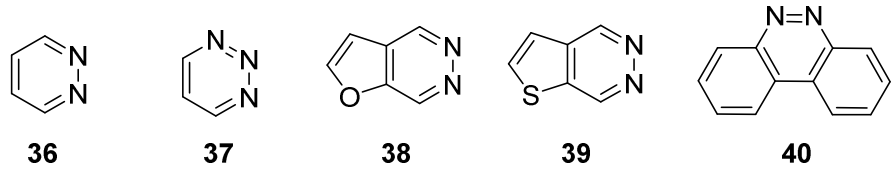
Evaluation of Cu(II) salts and changing the nucleophilicity of the anion:



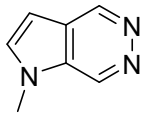
Catalyst (mol %)	**Yield**
CuOTf (5)	34%
Cu(1,10-phenanthroline)(PPh_3)Br (5)	NR
CuI (5)	NR
CuBr.$(CH_3)_2S$ (5)	NR
CuCl (5)	5%
$Cu(OTf)_2$ (5)	16%
Cu(hexafluoroacetylacetonate)$_2$ (5)	4%
$Cu(MeCN)_4OTf$ (5)	38%
$Cu(MeCN)_4PF_6$ (5)	49%

Evaluation of Other Azadienes

The following azadienes (**36**-**40**) reported in literature were evaluated with Cu(I) and Ni(0) based methodology developed in this publication. However, no conversion to the corresponding addition product was observed.

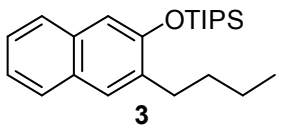


Potential diazine precursor to *N*-methyl indole **41** could be prepared by employing a modification of the methodology developed by Wagner and co-workers.[1] However, this highly polar diazine was only sparingly soluble in CH_2Cl_2. This limited its use with the methodology described in this publication. (Also, note that the reaction of **41** and siloxy alkyne **2** in CH_2Cl_2 with DMSO as the co-solvent failed to afford any transformation with Cu(I).)



41

1H and 13C NMR spectra



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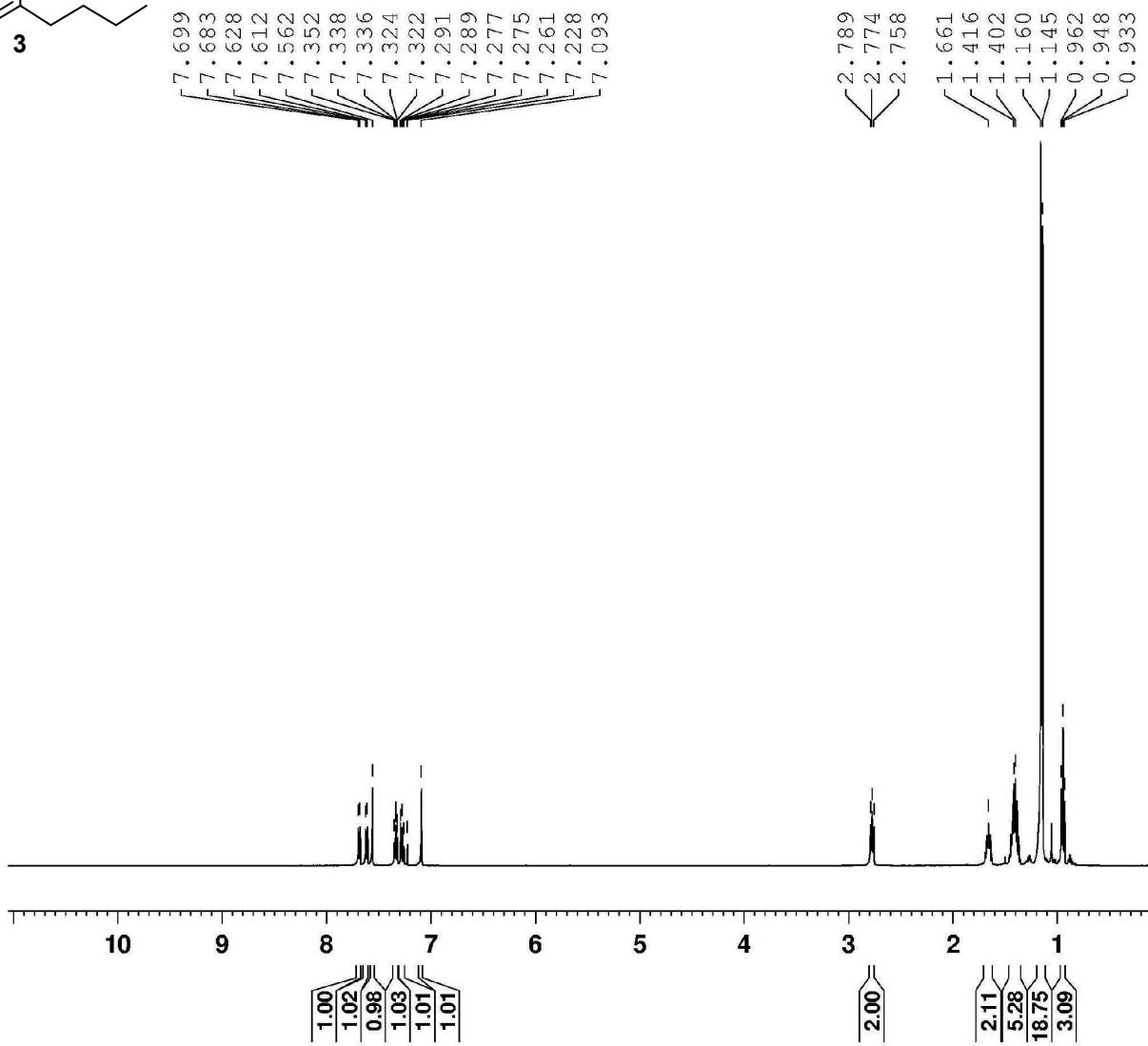


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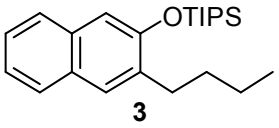
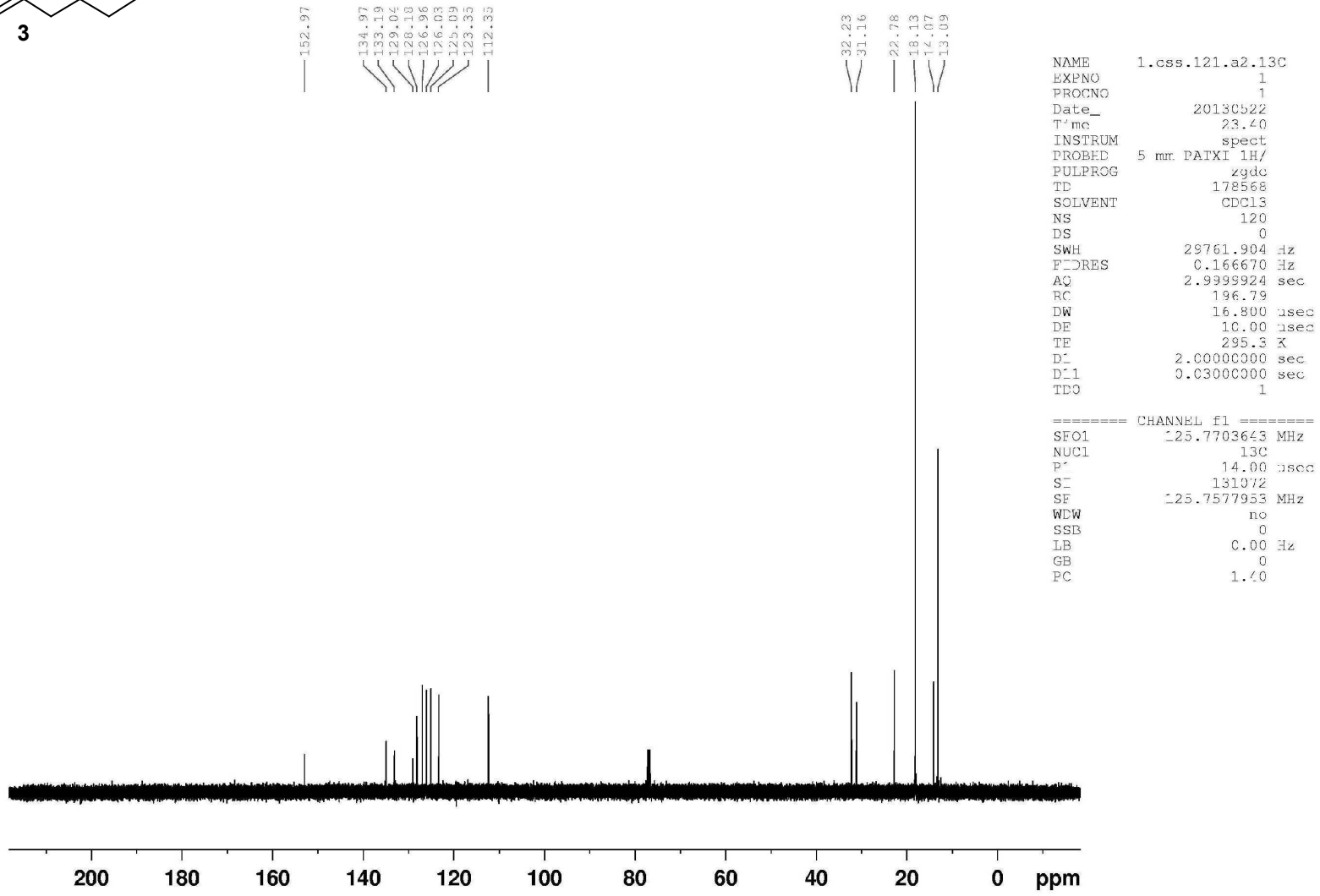
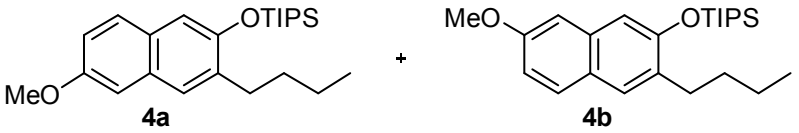


3

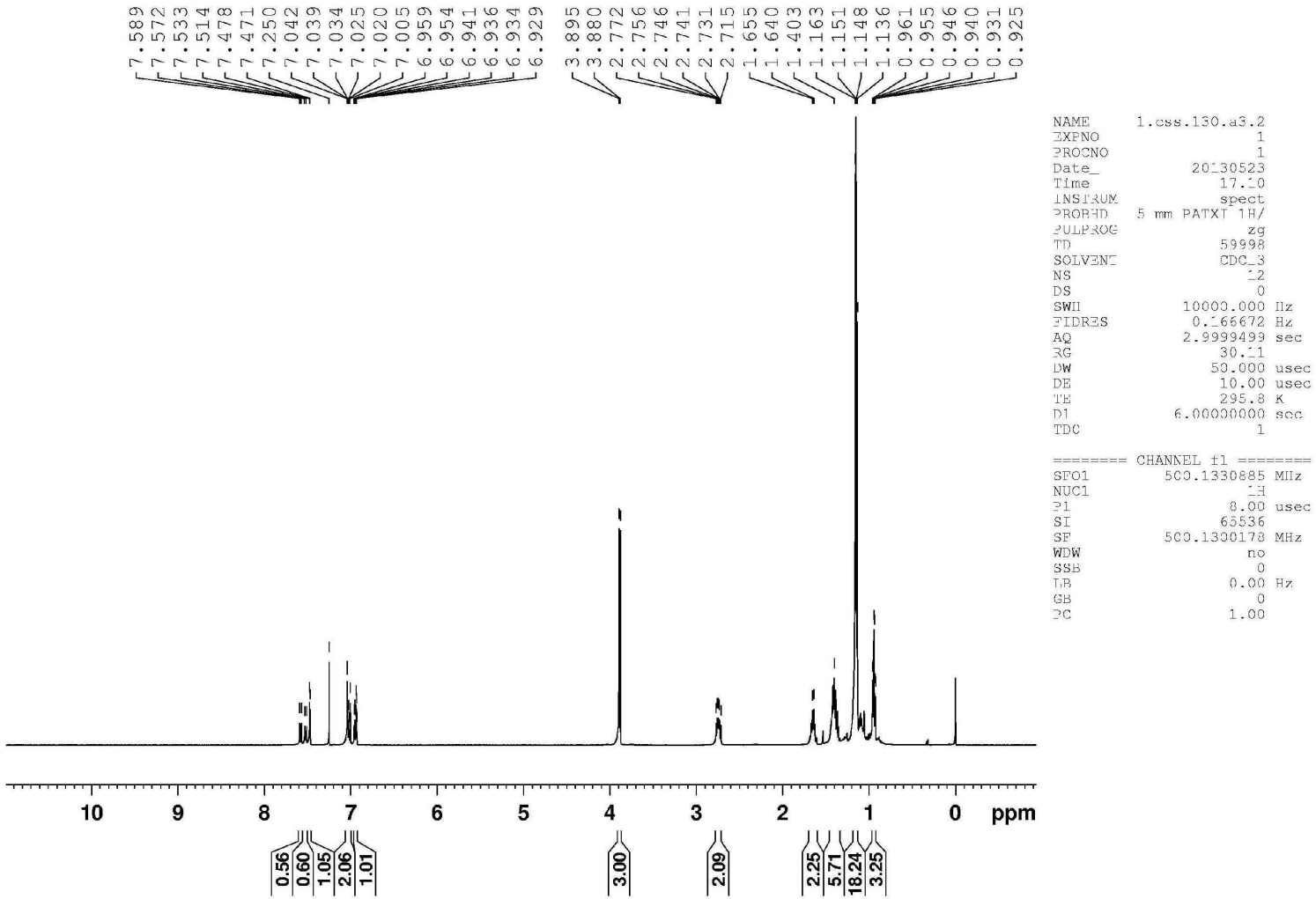


NAME	1.css.121.a2.13C
EXPNO	1
PROCNO	1
Date_	20130522
Time	23.40
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	120
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	295.3 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
========	CHANNEL f1 ========
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577953 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

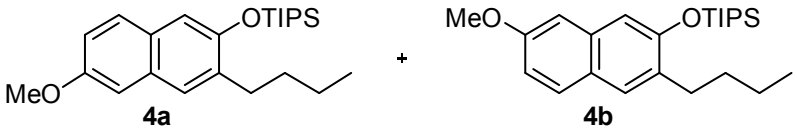


4a + **4b**

(General procedure 1)

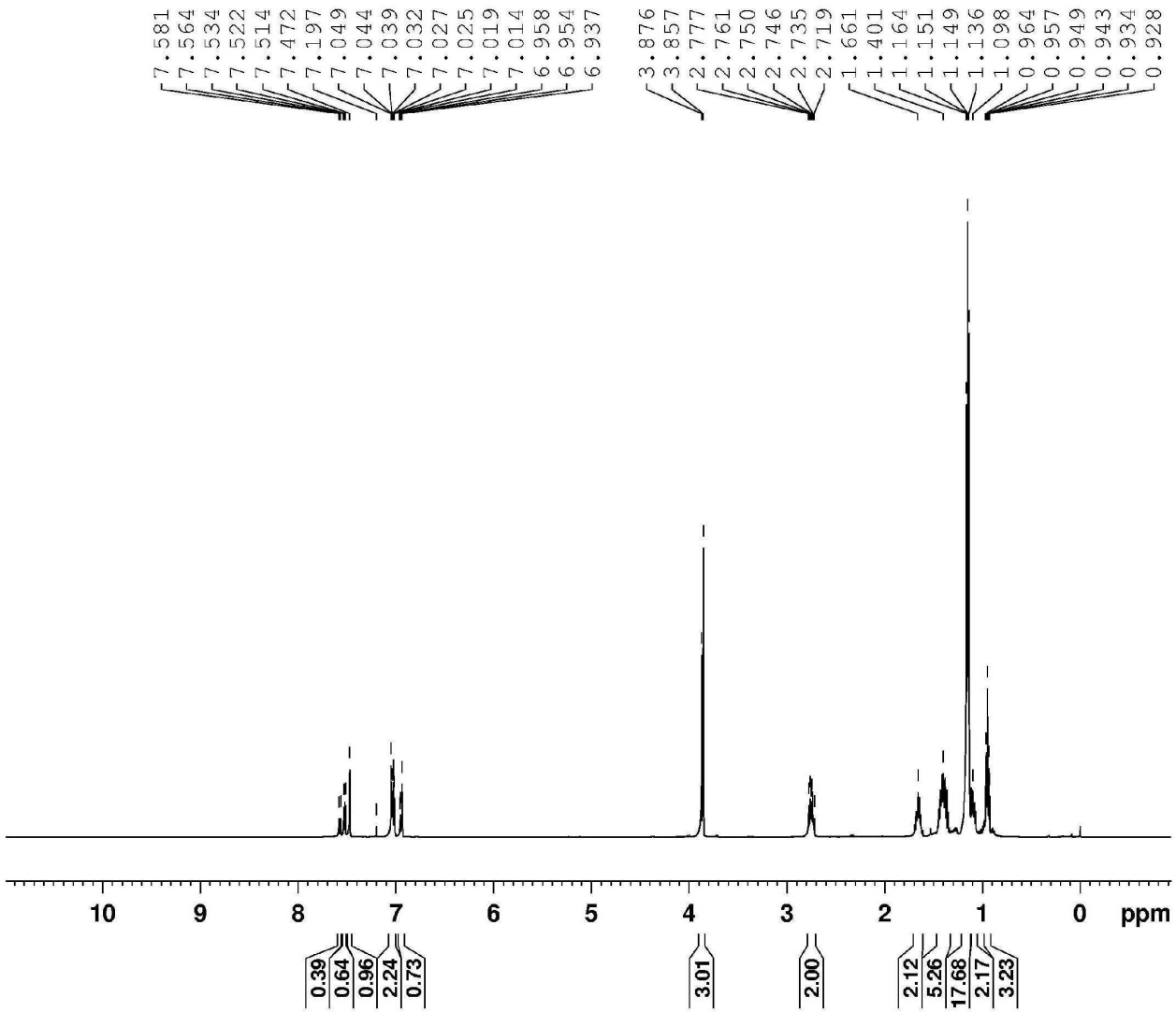



```
NAME          1.css.130.a3.2
EXPNO                      1
PROCNO                     1
Date_               20130523
Time                   17.10
INSTRUM                spect
PROBHD   5 mm PATXT 1H/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                        12
DS                         0
SWH               10000.000 Hz
FIDRES                0.166672 Hz
AQ                    2.9999499 sec
RG                        30.11
DW                    50.000 usec
DE                    10.00 usec
TE                    295.8 K
D1                    6.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1             500.1330885 MHz
NUC1                       1H
P1                    8.00 usec
SI                     65536
SF               500.1300178 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                    1.00
```

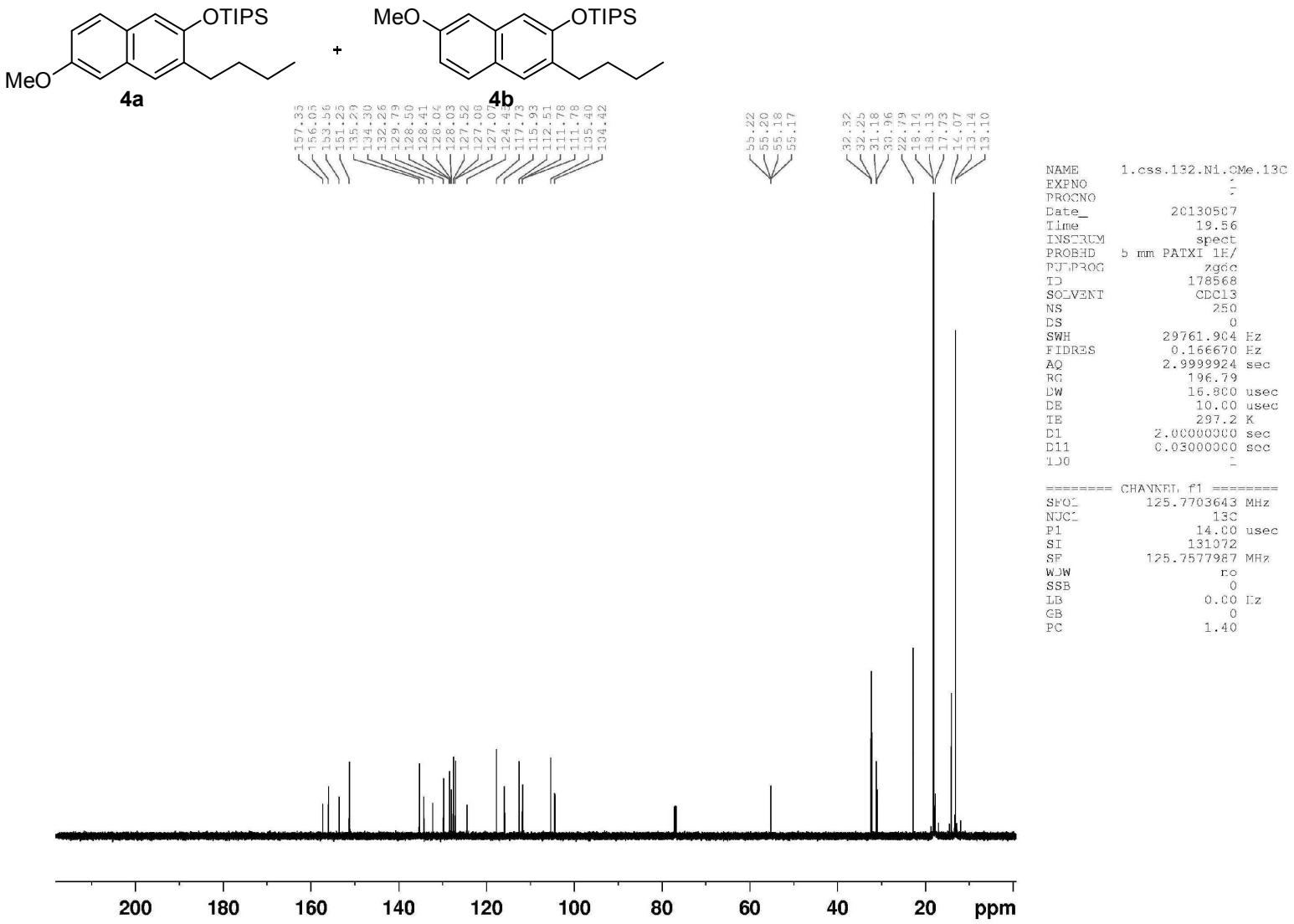


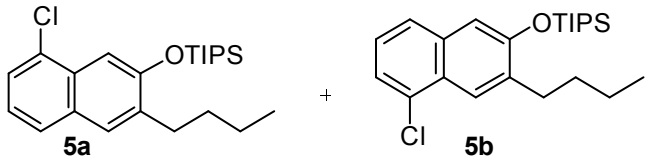
4a **4b**

(General procedure 2)

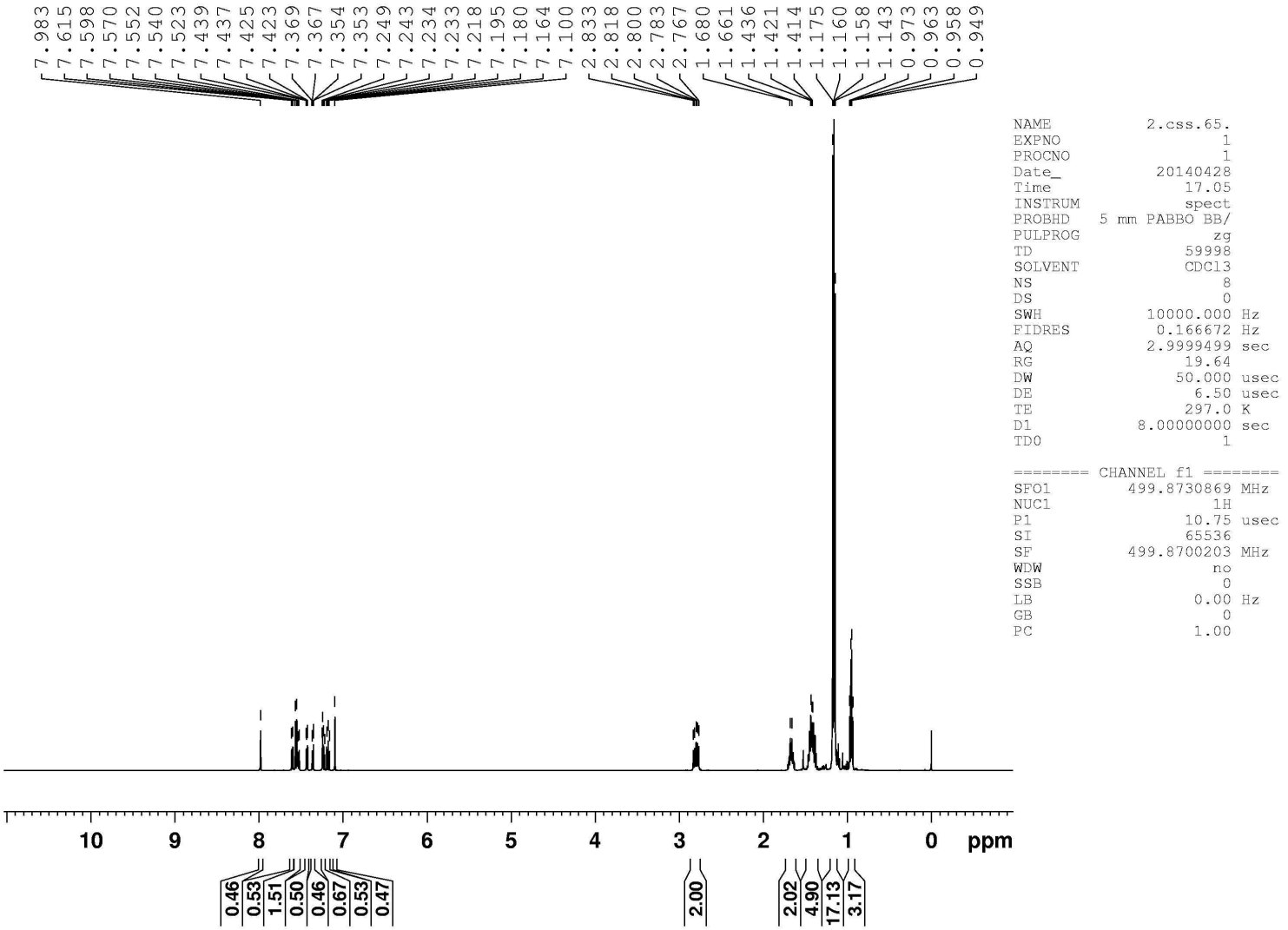



```
NAME        1.ess.132.Ni.OMe
EXPNO                      1
PROCNO                     1
Date_               20130507
Time                   19.26
INSTRUM                spect
PROBHD   5 mm PATXI 1H/
PULPROG                   zg
TD                     59998
SOLVENT                CDCl3
NS                        12
DS                         0
SWH                10000.000 Hz
FIDRES             0.166672 Hz
AQ                 2.9999499 sec
RG                      6.92
DW                    50.000 usec
DE                    10.00 usec
TE                    295.8 K
D1                 5.00000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1              500.1330885 MHz
NUC1                      1H
P1                     8.00 usec
SI                     65536
SF                500.1300438 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.00
```

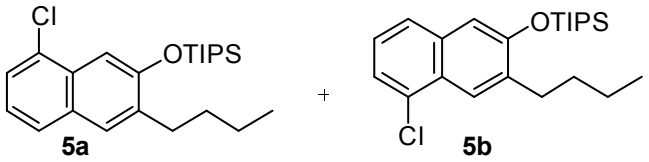

OTIPS
MeO
4a
+
MeO
OTIPS
4b
157.33
156.03
153.56
151.25
135.29
134.30
132.26
129.79
128.50
128.41
128.04
128.03
127.52
127.08
127.07
124.48
117.73
115.93
112.51
111.78
111.78
105.40
104.42
55.22
55.20
55.18
55.17
32.32
32.25
31.18
30.96
22.79
18.14
18.13
17.73
14.07
13.14
13.10
NAME 1.ess.132.Ni.OMe.13C
EXPNO 1
PROCNO 1
Date_ 20130507
Time 19.56
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 250
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 297.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577987 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm



(General procedure 1)

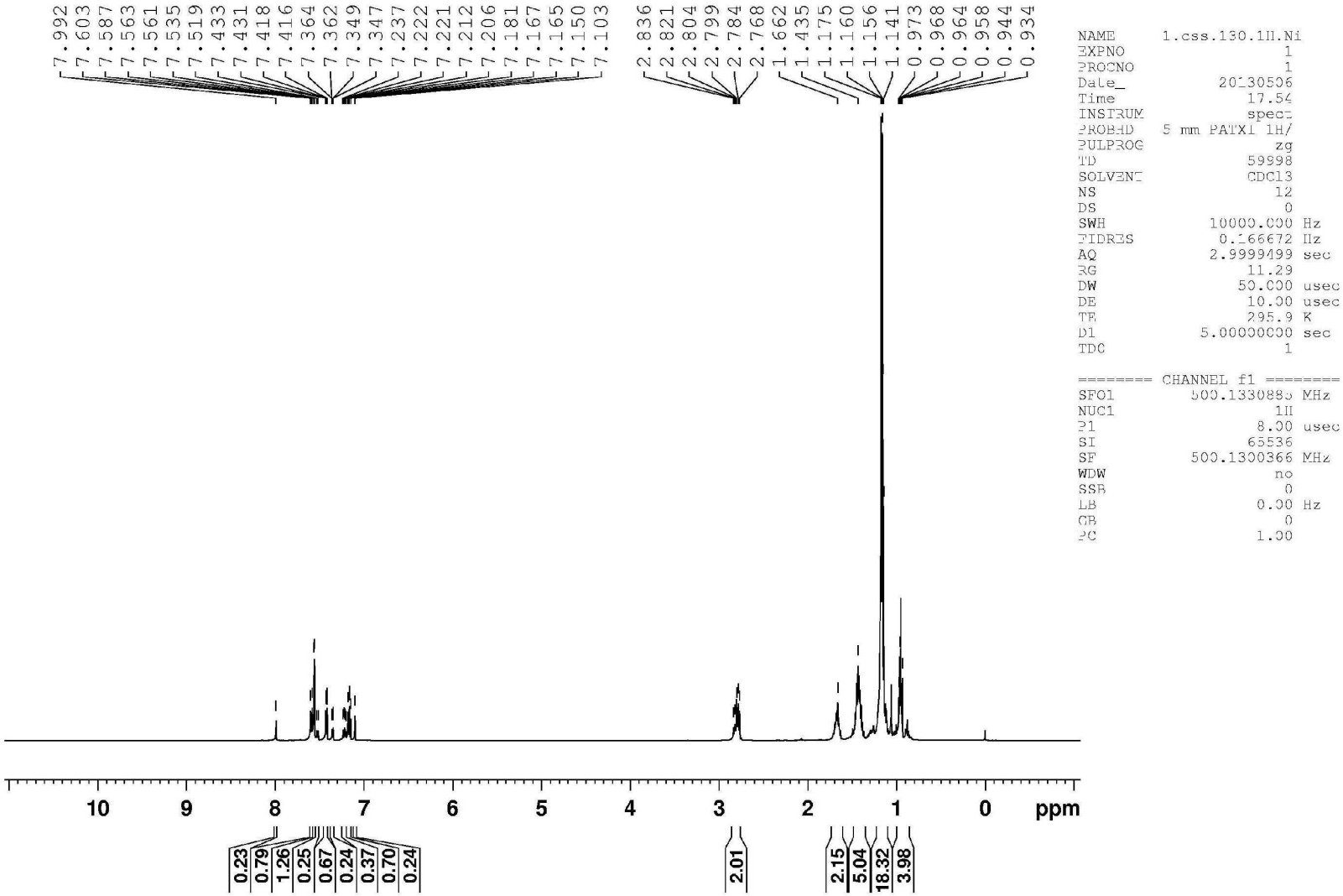


NAME	2.css.65.
EXPNO	1
PROCNO	1
Date_	20140428
Time	17.05
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	19.64
DW	50.000 usec
DE	6.50 usec
TE	297.0 K
D1	8.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	499.8730869 MHz
NUC1	1H
P1	10.75 usec
SI	65536
SF	499.8700203 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

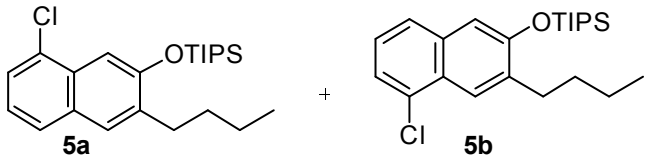


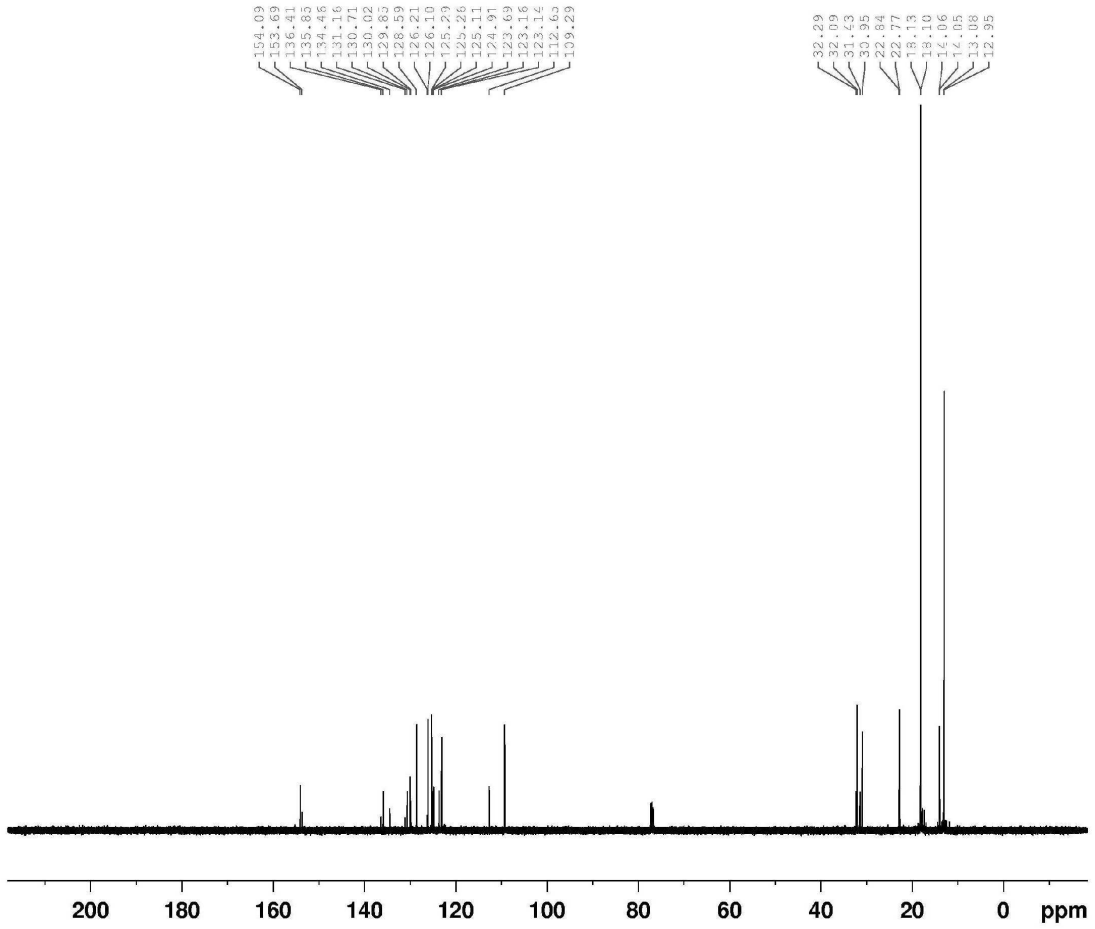
5a + **5b**

(General procedure 2)

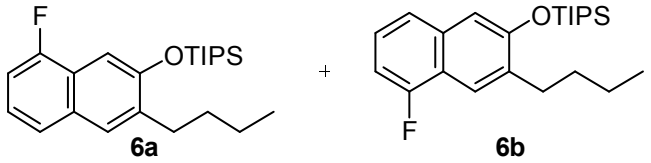


NAME	1.css.130.1H.Ni
EXPNO	1
PROCNO	1
Date_	20130506
Time	17.54
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	12
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	11.29
DW	50.000 usec
DE	10.00 usec
TE	295.9 K
D1	5.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300366 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



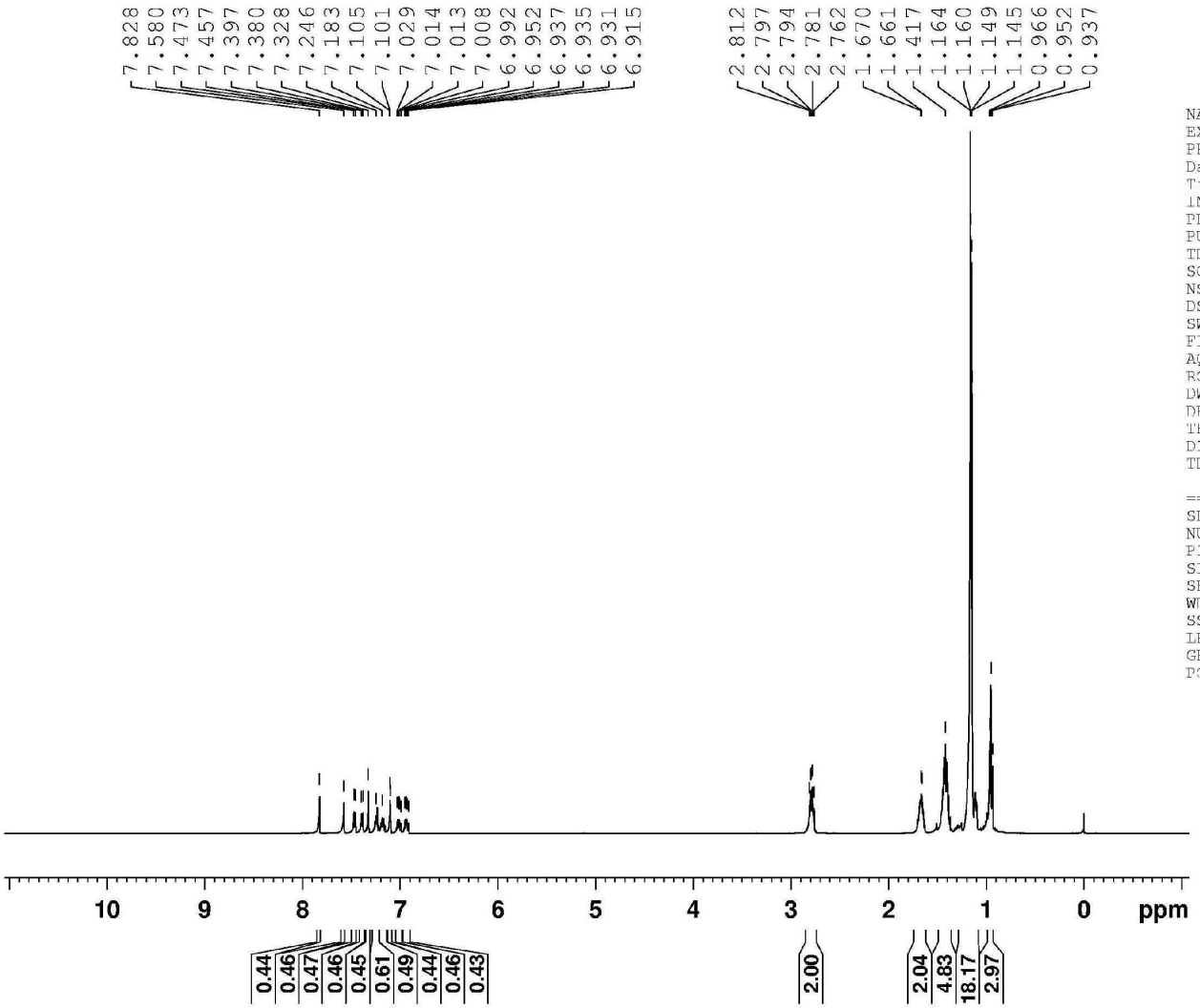



```
NAME        1.oss.130.Ni.13C
EXPNO                      1
PROCNO                     1
Date_           20130506
Time                 18.26
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zgdc
TD                    178568
SOLVENT                CDCl3
NS                       250
DS                         0
SWH                29761.904 Hz
FIDRES             0.166670 Hz
AQ                 2.9999924 sec
RG                    196.79
DW                   16.800 usec
DE                   10.00 usec
TE                   296.7 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1          125.7703643 MHz
NUC1                    13C
P1                   14.00 usec
SI                    131072
SF             125.7577858 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
```

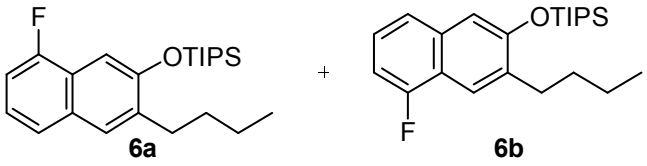


6a **6b**

(General Procedure 1)

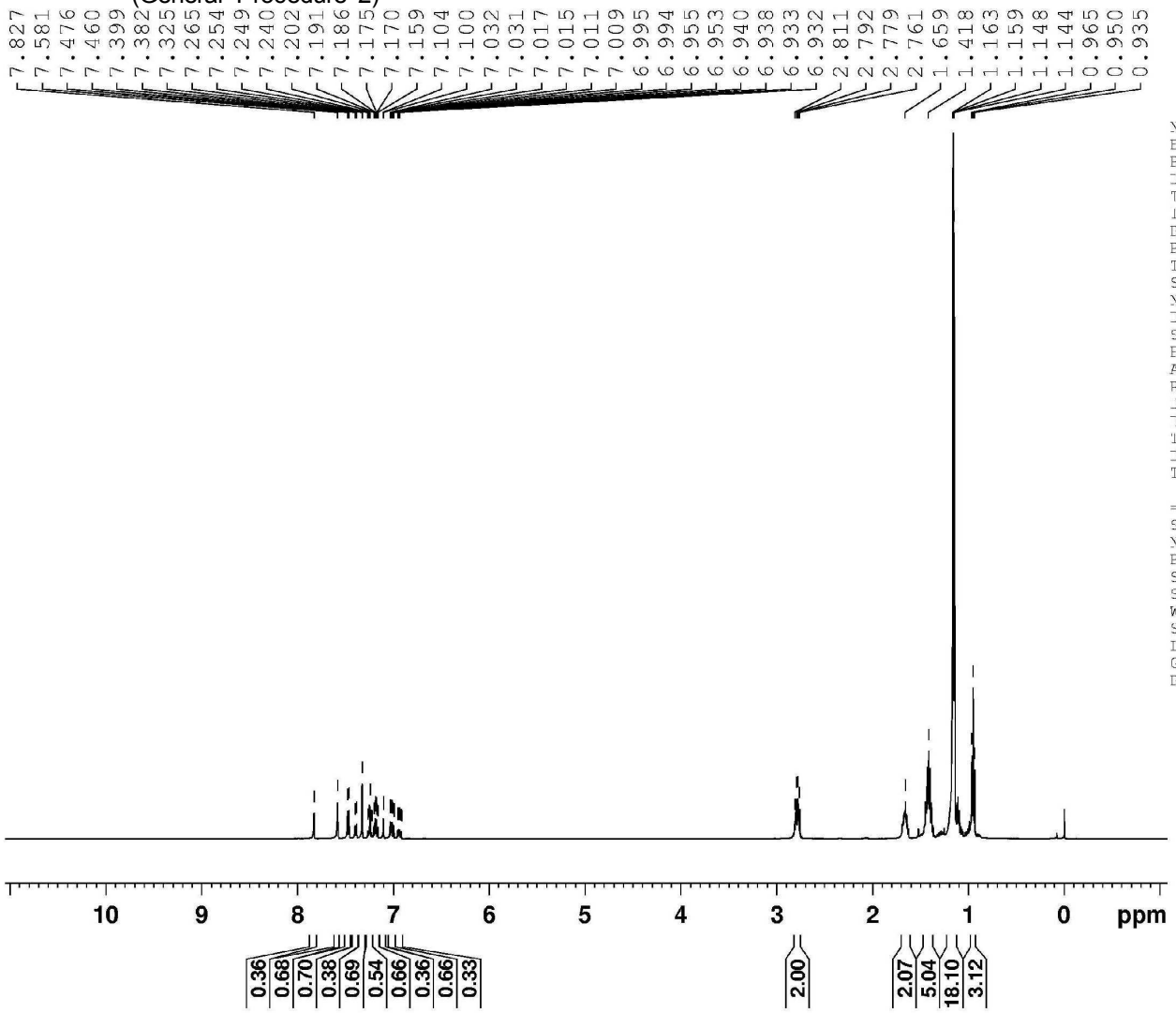



```
NAME          1.ess.146.a2
EXPNO                    1
PROCNO                   1
Date_             20130613
Time                 14.58
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                      12
DS                       0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ             2.9999498 sec
RG                   15.84
DW                  50.000 usec
DE                  10.00 usec
TE                  297.6 K
D1             6.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                   1H
P1                   8.00 usec
SI                  65536
SF          500.1300256 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

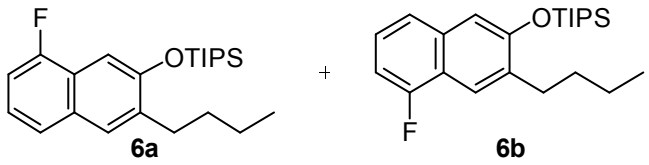


6a + **6b**

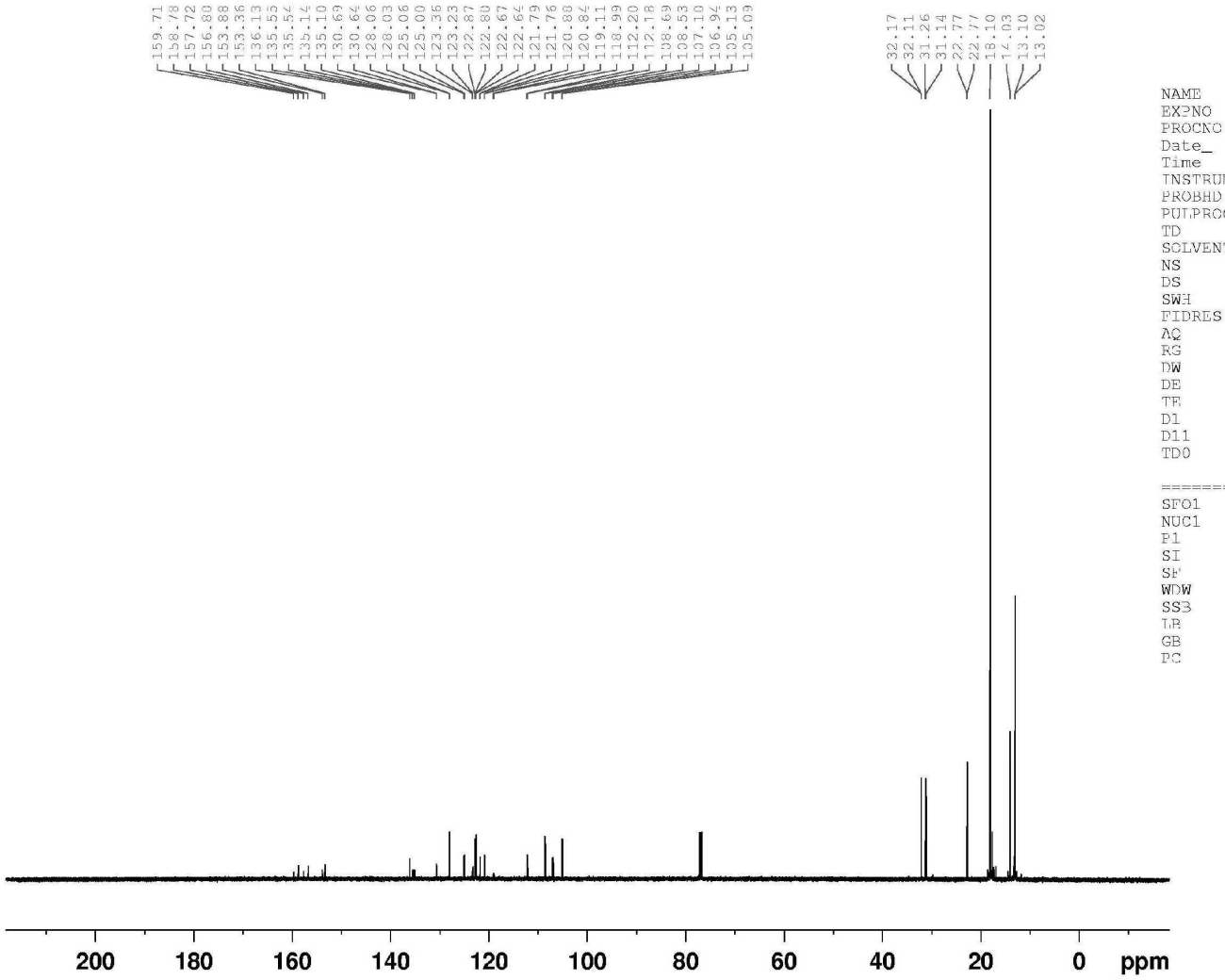
(General Procedure 2)



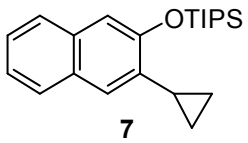

```
NAME            1.css.147
EXPNO                   1
PROCNO                  1
Date_          20130618
Time                10.49
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                  59998
SOLVENT             CDCl3
NS                     12
DS                      0
SWH          10000.000 Hz
FIDRES         0.166672 Hz
AQ           2.9999499 sec
RG                  15.84
DW                50.000 usec
DE                10.00 usec
TE                294.5 K
D1            6.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1        500.1330885 MHz
NUC1                   1H
P1                  8.00 usec
SI                 65536
SF          500.1300235 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



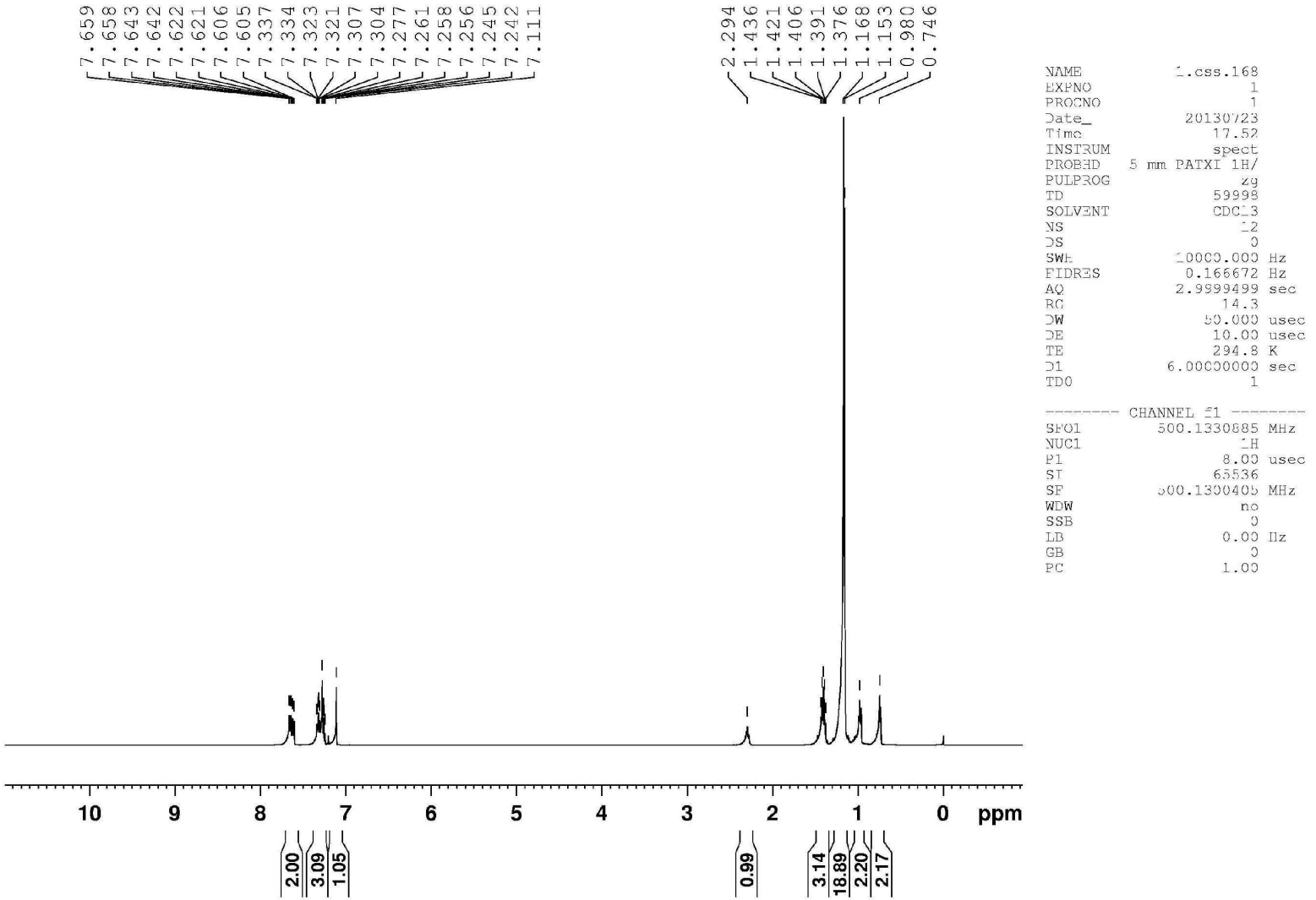
6a + **6b**



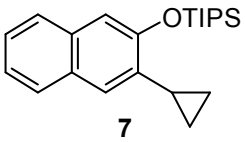

```
NAME          1.css.147.13C.2
EXPNO                       1
PROCNO                      1
Date_              20130623
Time                    2.34
INSTRUM                 spect
PROBHD     5 mm PATX1 1H/
PULPROG                 zgdc
TD                    178568
SOLVENT                CDCl3
NS                       3072
DS                          0
SWH               29761.904 Hz
FIDRES             0.166670 Hz
AQ                 2.9999924 sec
RG                     196.79
DW                     16.800 usec
DE                     10.00 usec
TE                     295.9 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                         1

======== CHANNEL f1 ========
SFO1            125.7703643 MHz
NUC1                    13C
P1                    14.00 usec
SI                    131072
SF              125.7577917 MHz
WDW                       no
SSB                        0
LB                      0.00 Hz
GB                         0
PC                      1.40
```



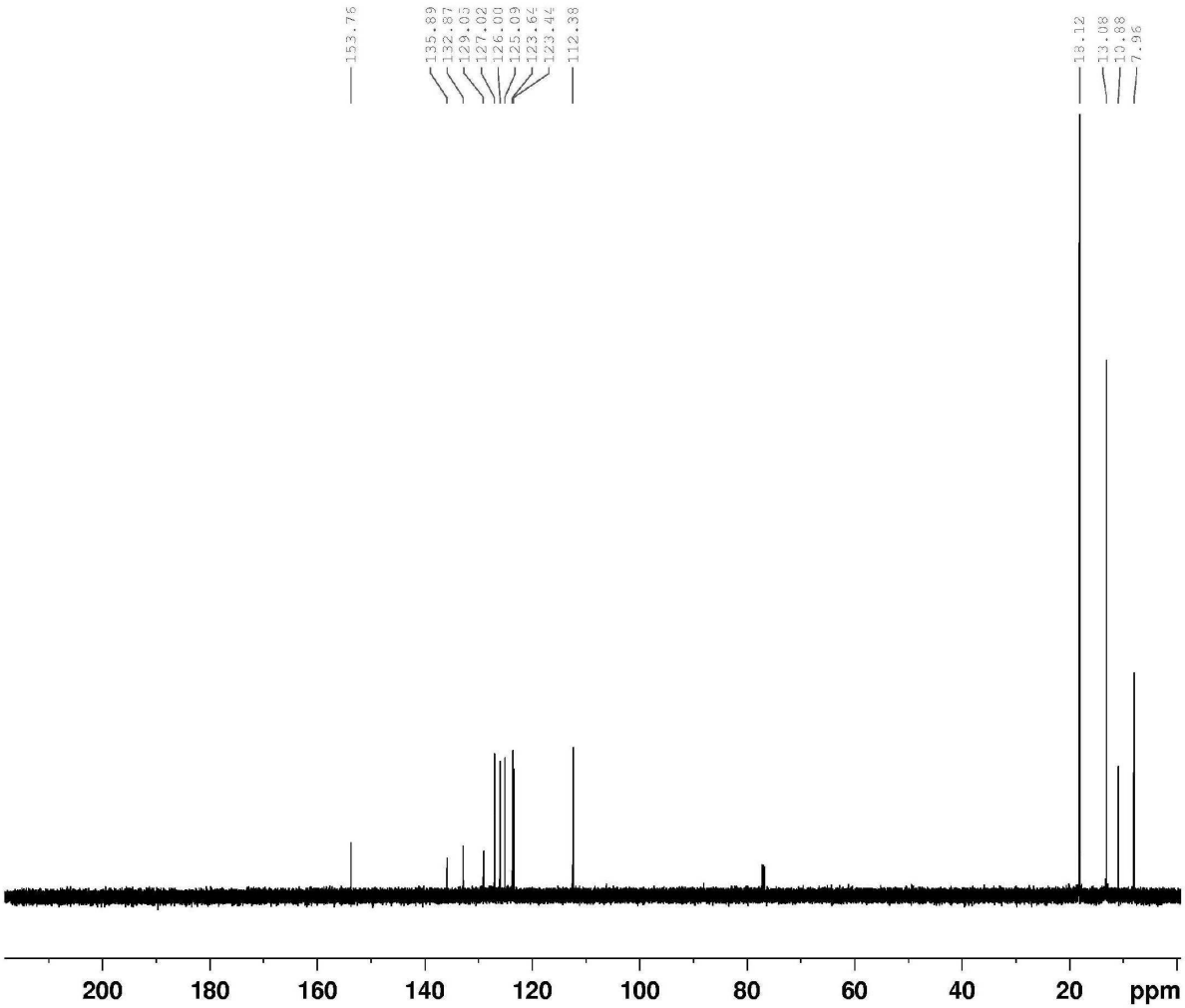
7



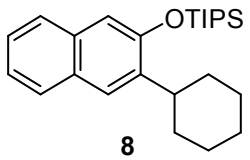
NAME	1.css.168
EXPNO	1
PROCNO	1
Date_	20130723
Time	17.52
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	12
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	14.3
DW	50.000 usec
DE	10.00 usec
TE	294.8 K
D1	6.00000000 sec
TD0	1
-------- CHANNEL f1 --------	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
ST	65536
SF	500.1300405 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



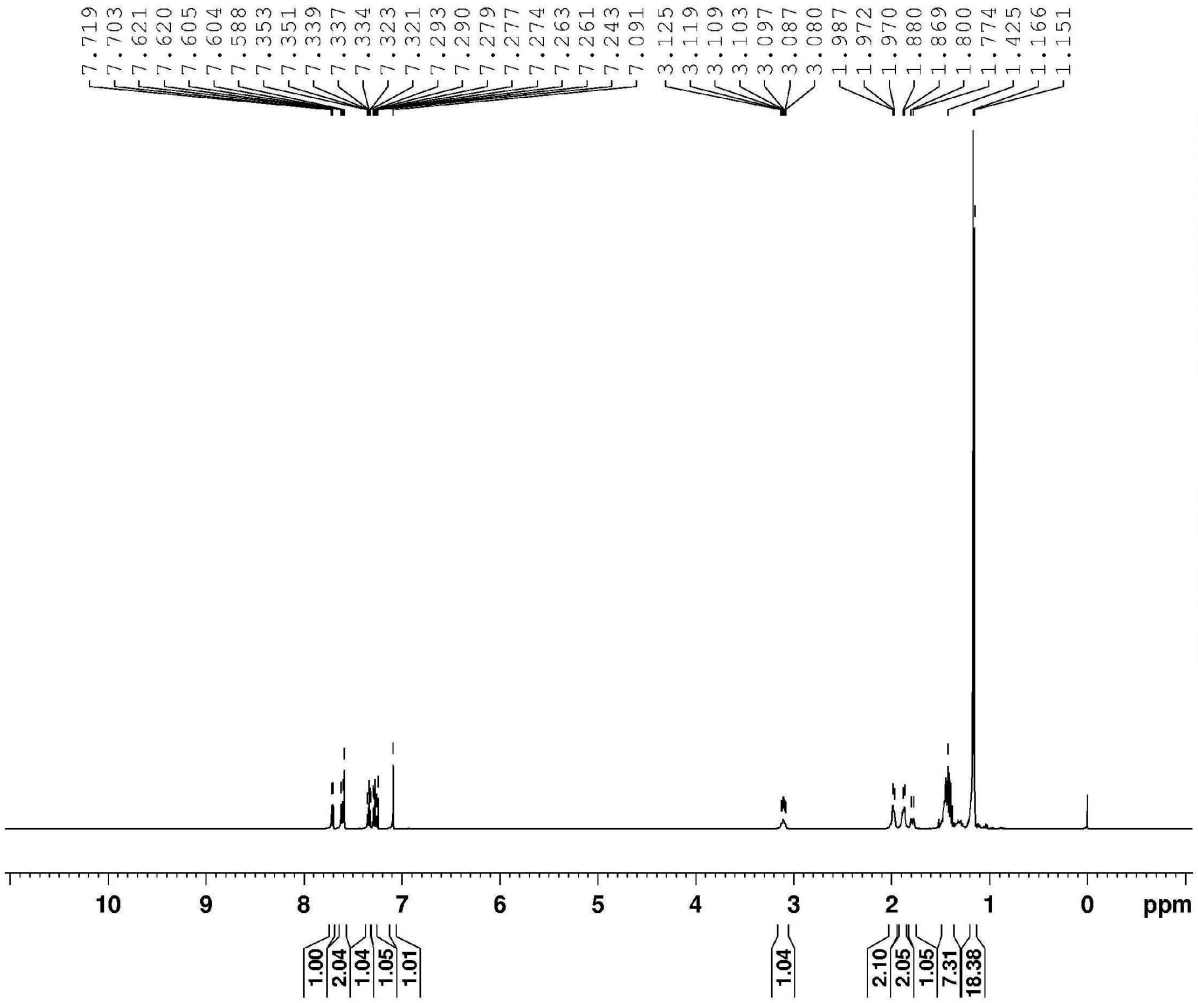
7



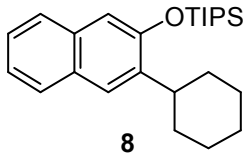
NAME	1.ess.168.13C
EXPNO	1
PROCNO	1
Date_	20130723
Time	18.17
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	180
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	295.6 K
D1	2.00000000 sec
D11	0.03000000 sec
TDC	1
======== CHANNEL f1 ========	
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577973 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40



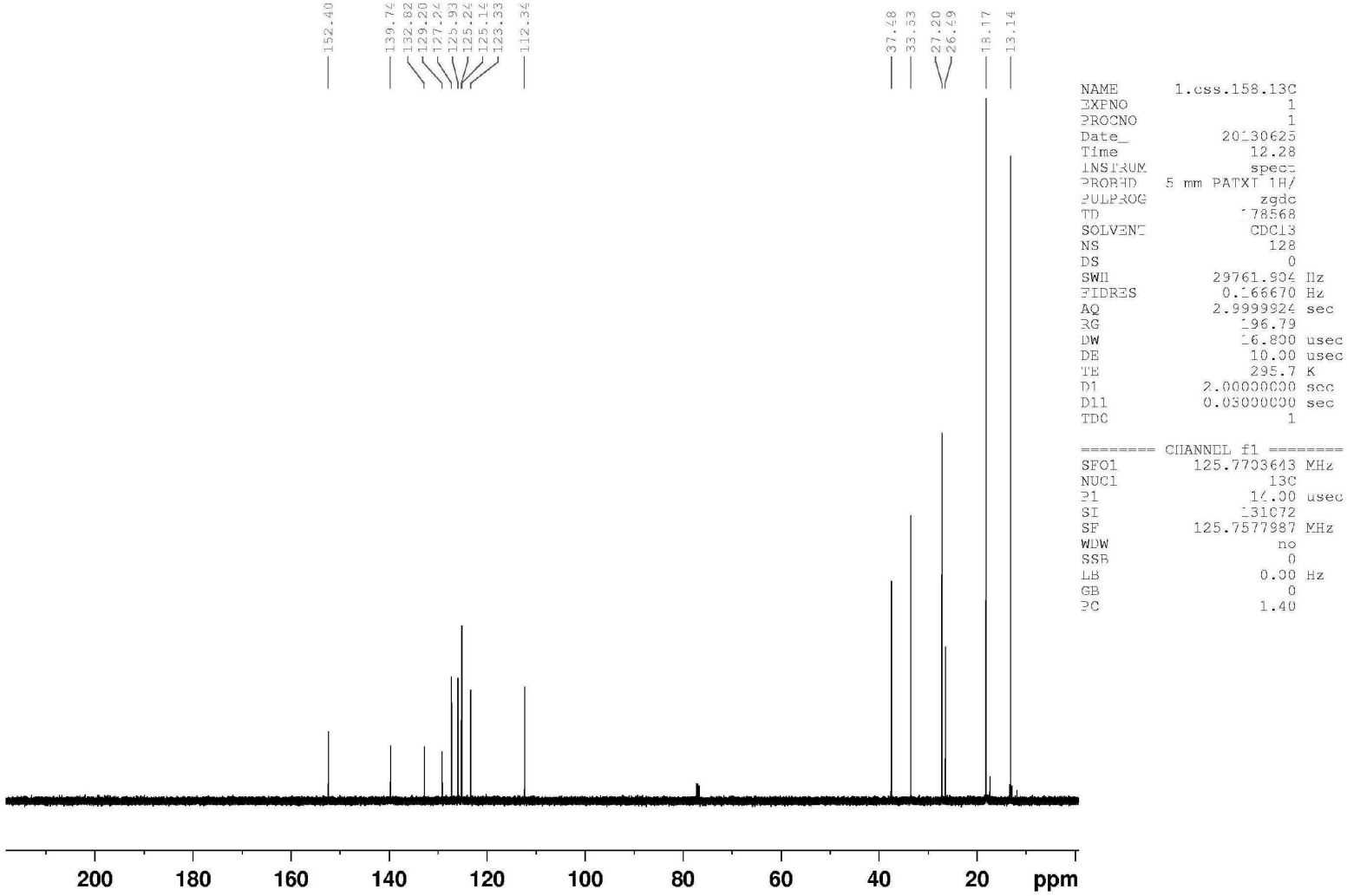
8



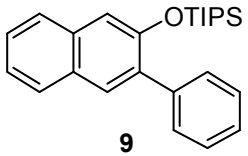

```
NAME            1.css.157
EXPNO                   1
PROCNO                  1
Date_            20130624
Time                14.23
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDCl3
NS                     12
DS                      0
SWH             10000.000 Hz
FIDRES              0.166672 Hz
AQ              2.9999499 sec
RG                   30.11
DW                 50.000 usec
DE                 10.00 usec
TE                 294.9 K
D1              6.00000000 sec
TD0                     1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                   8.00 usec
SI                  65536
SF           500.1300217 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```



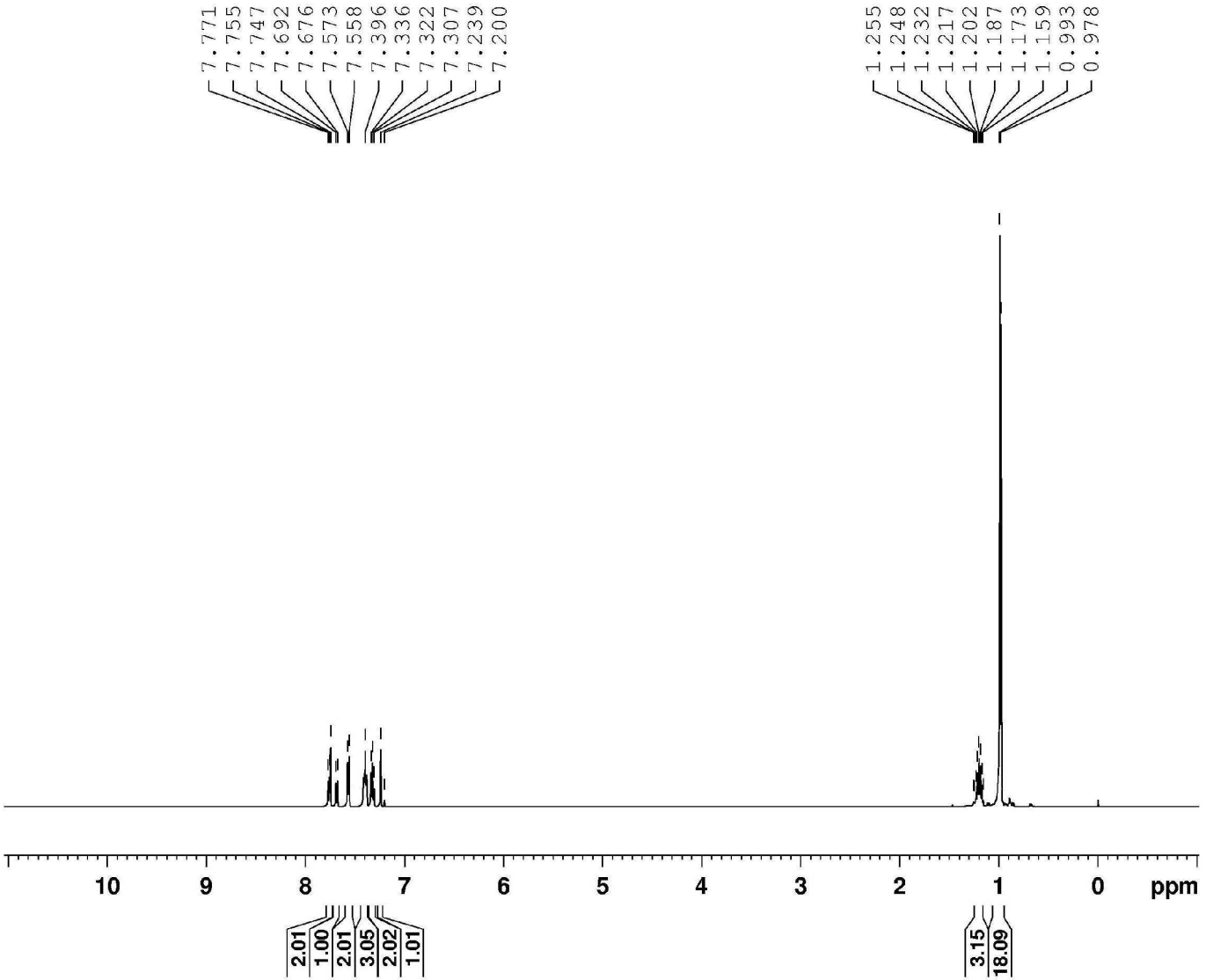
8



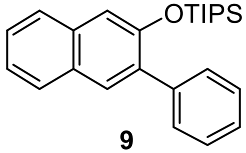

```
NAME          1.ess.158.13C
EXPNO                     1
PROCNO                    1
Date_              20130625
Time                  12.28
INSTRUM                spect
PROBHD   5 mm PATXT 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                       128
DS                         0
SWH                29761.904 Hz
FIDRES             0.166670 Hz
AQ                 2.9999924 sec
RG                    196.79
DW                    16.800 usec
DE                    10.00 usec
TE                    295.7 K
D1                 2.00000000 sec
D11                0.03000000 sec
TD0                        1

======== CHANNEL f1 ========
SFO1           125.7703643 MHz
NUC1                    13C
P1                    14.00 usec
SI                    131072
SF             125.7577987 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
```



9




```
Current Data Parameters
NAME          1.css.214.2
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20131127
Time               18.23
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG              zg
TD                59998
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10000.000 Hz
FIDRES            0.166672 Hz
AQ             2.9999499 sec
RG                 22.6
DW                50.000 usec
DE                 7.50 usec
TE                294.7 K
D1           10.00000000 sec
TD0                   1

-------- CHANNEL f1 --------
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         499.8740056 MHz

F2 - Processing parameters
SI                32768
SF           499.8700507 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```


OTIPS

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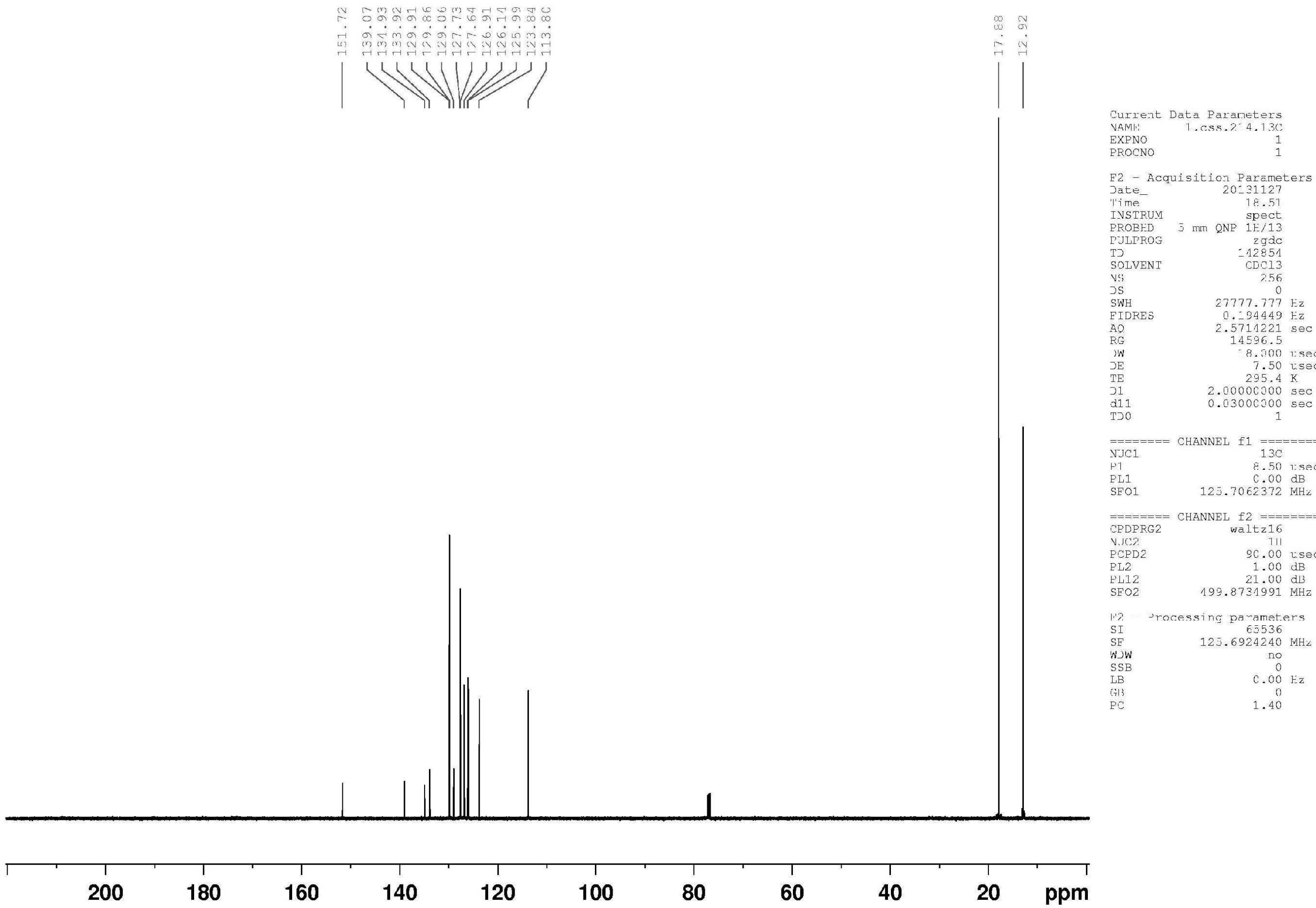
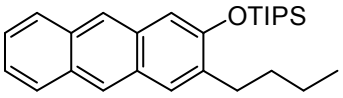
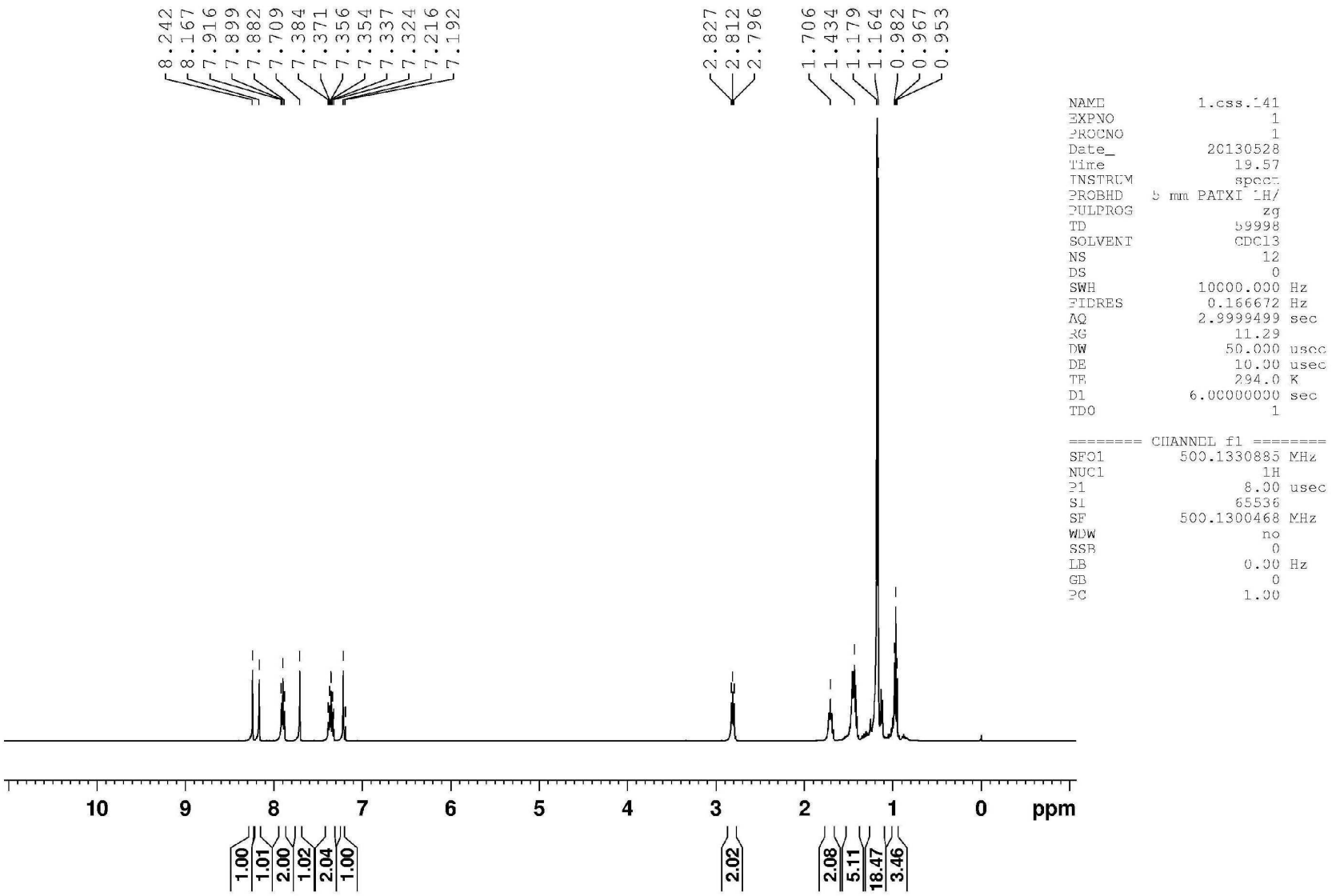
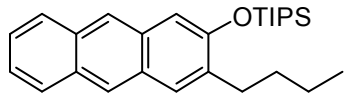

151.72
139.07
134.93
133.92
129.91
129.86
129.06
127.73
127.64
126.91
126.14
125.99
123.84
113.80
17.88
12.92
Current Data Parameters
NAME 1.css.214.13C
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20131127
Time 18.51
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 142854
SOLVENT CDCl3
NS 256
DS 0
SWH 27777.777 Hz
FIDRES 0.194449 Hz
AQ 2.5714221 sec
RG 14596.5
DW 18.000 usec
DE 7.50 usec
TE 295.4 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 0.00 dB
SFO1 125.7062372 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 1.00 dB
PL12 21.00 dB
SFO2 499.8734991 MHz
F2 - Processing parameters
SI 65536
SF 125.6924240 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm



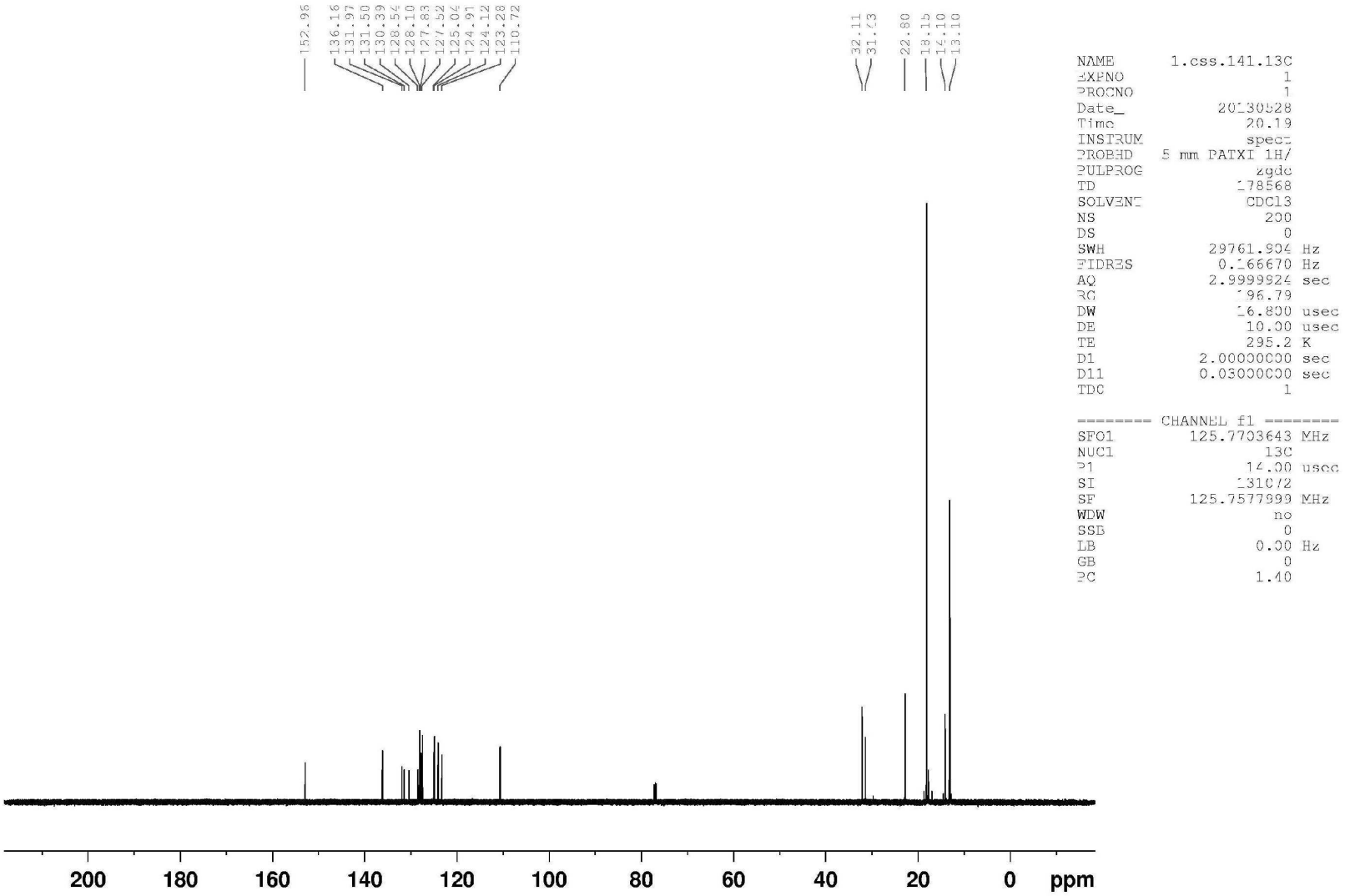
10

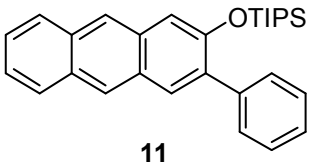


NAME	1.css.141
EXPNO	1
PROCNO	1
Date_	20130528
Time	19.57
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	12
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	11.29
DW	50.000 usec
DE	10.00 usec
TE	294.0 K
D1	6.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300468 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00

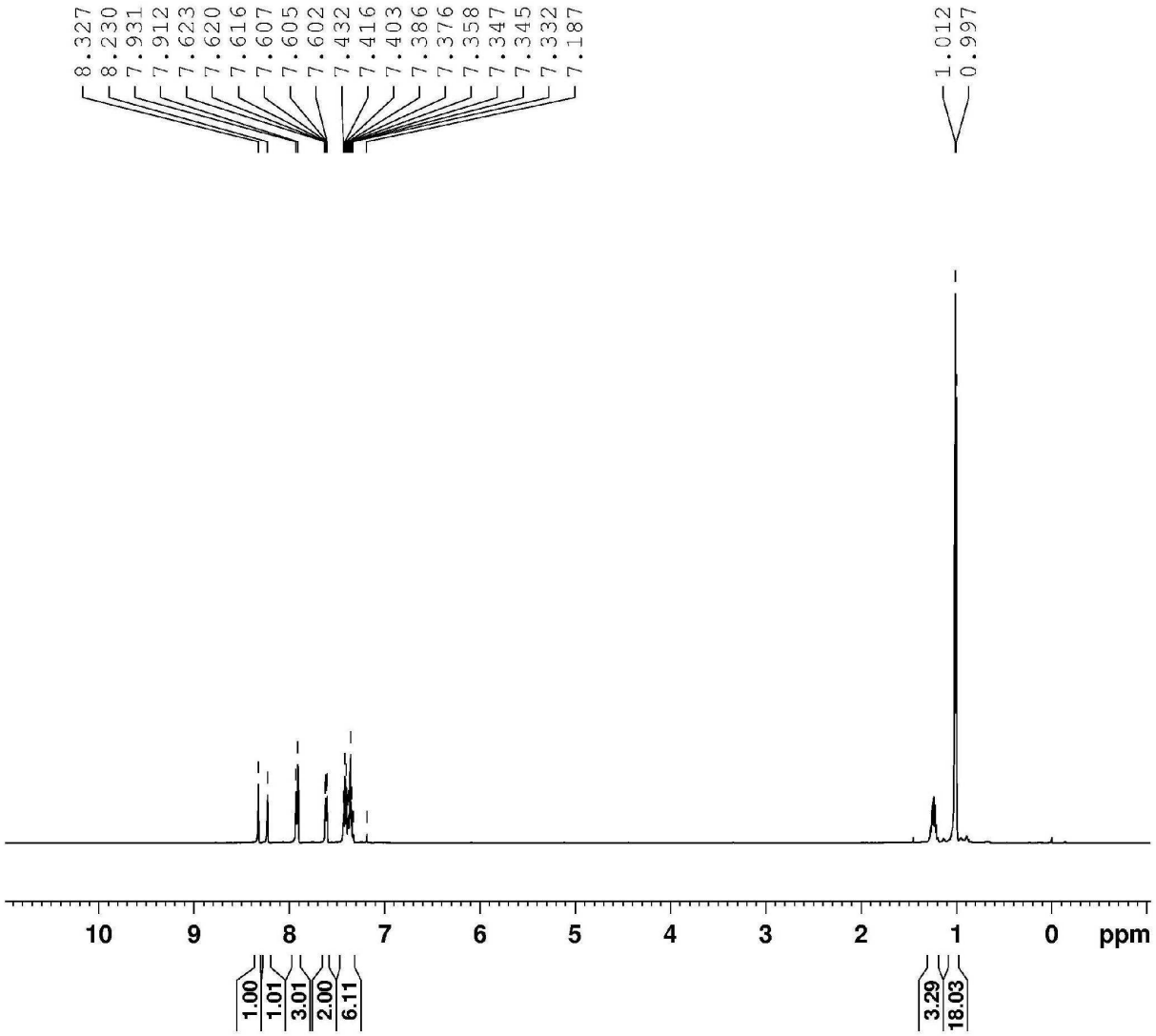

OTIPS

10

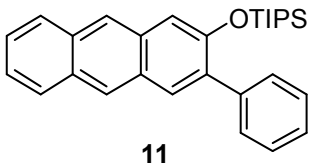

152.96
136.16
131.97
131.50
130.39
128.54
128.10
127.83
127.52
125.04
124.91
124.12
123.28
110.72
32.11
31.23
22.80
18.15
14.10
13.10
NAME 1.css.141.13C
EXPNO 1
PROCNO 1
Date_ 20130528
Time 20.19
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zgdc
TD 178568
SOLVENT CDCl3
NS 200
DS 0
SWH 29761.904 Hz
FIDRES 0.166670 Hz
AQ 2.9999924 sec
RG 196.79
DW 16.800 usec
DE 10.00 usec
TE 295.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 125.7703643 MHz
NUC1 13C
P1 14.00 usec
SI 131072
SF 125.7577999 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
0
ppm



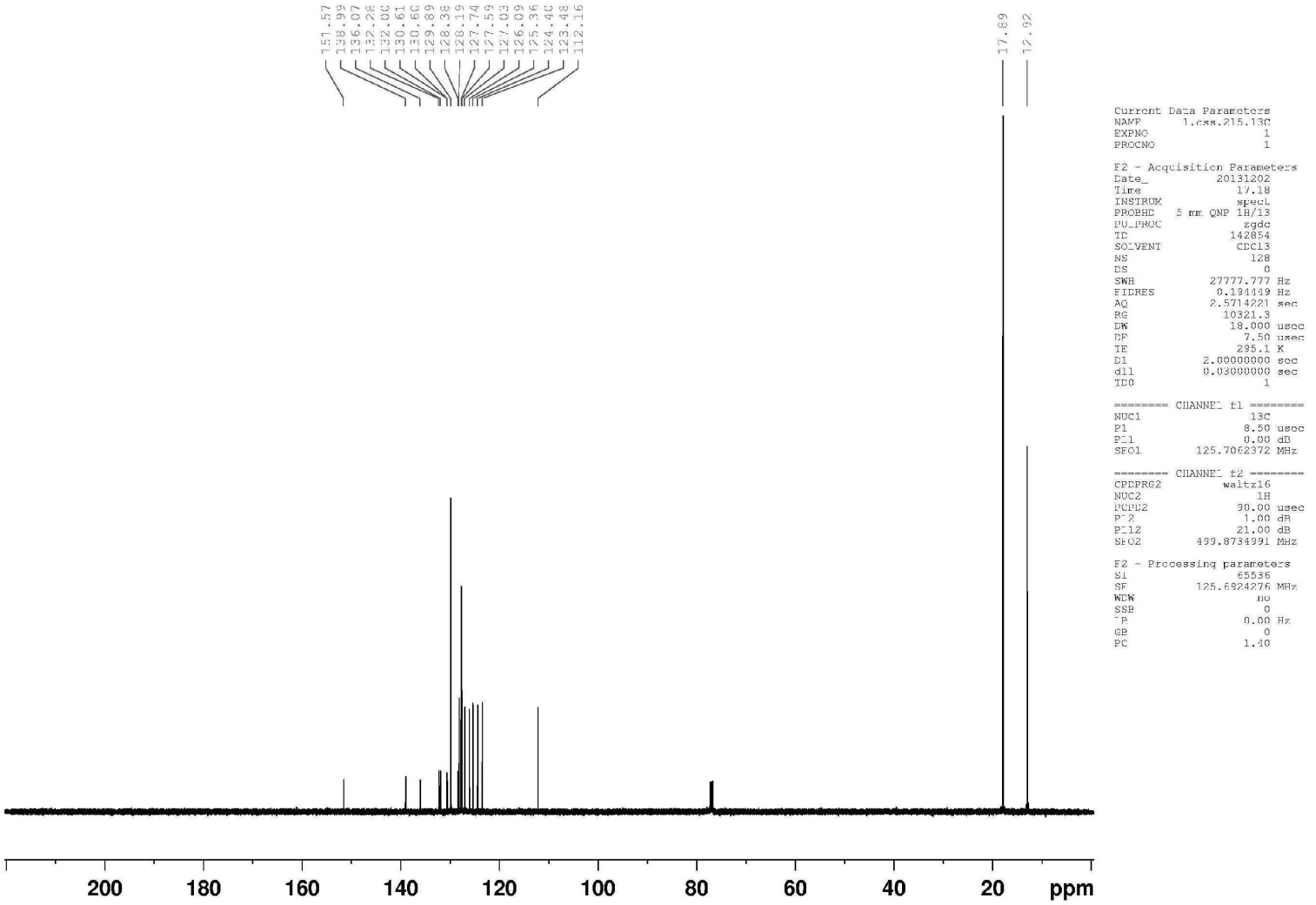
11



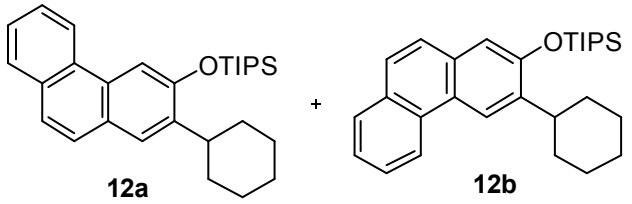

```
Current Data Parameters
NAME          1.ess.215.3
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20131202
Time              16.58
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg
TD                59998
SOLVENT           CDCl3
NS                    4
DS                    0
SWH           10000.000 Hz
FIDRES        0.166672 Hz
AQ            2.9999499 sec
RG                 20.2
DW               50.000 usec
DE                7.50 usec
TE               294.6 K
D1            8.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.00 usec
PL1                0.00 dB
SFO1         499.8740056 MHz

F2 - Processing parameters
SI                32768
SF          499.8700566 MHz
WDW                  no
SSB                   0
LB                0.00 Hz
GB                    0
PC                1.00
```



11

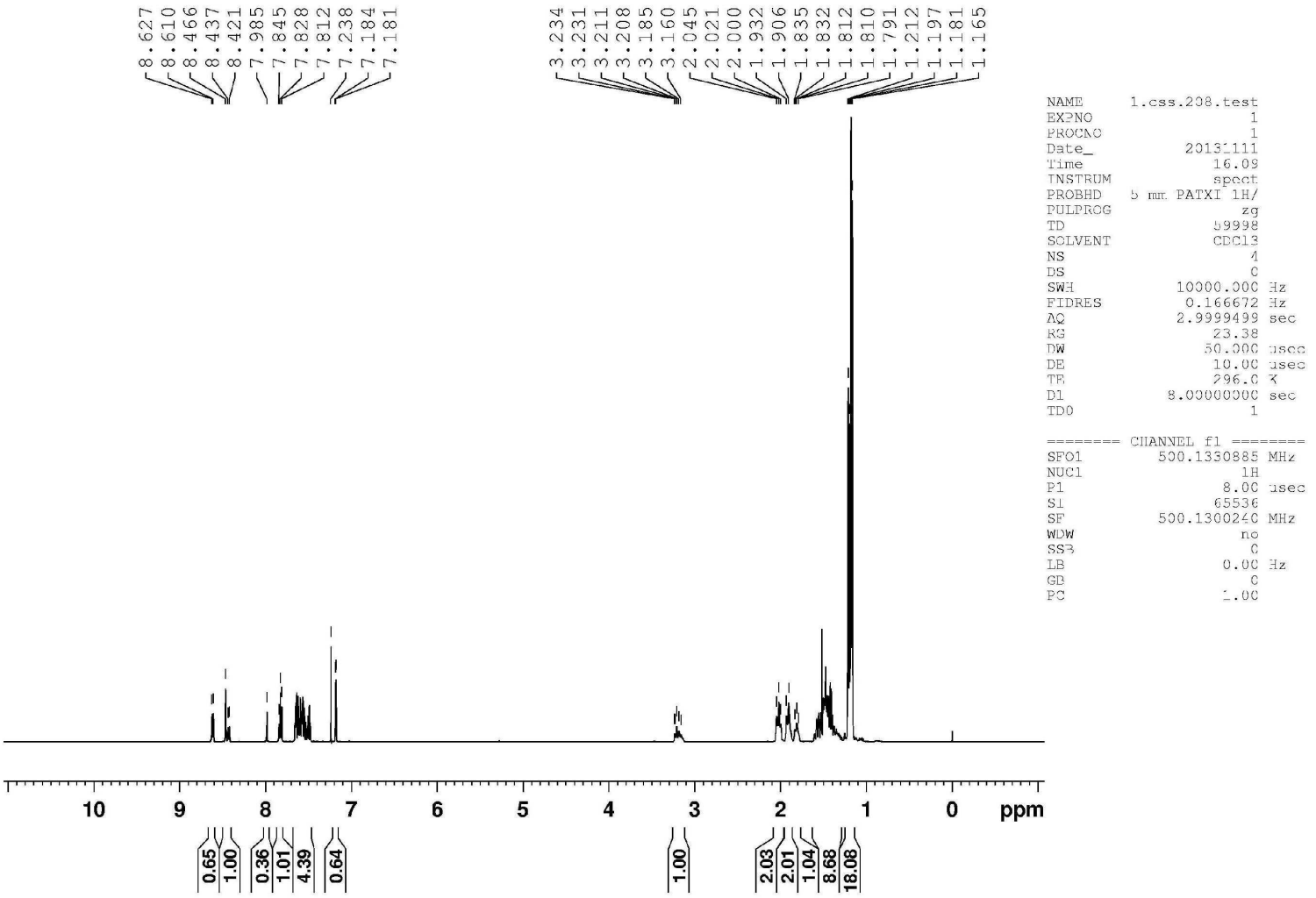



```
Current Data Parameters
NAME       1.ess.215.13C
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20131202
Time              17.18
INSTRUM           spect
PROBHD   5 mm QNP 1H/13
PULPROG           zgdc
TD              142854
SOLVENT           CDCl3
NS                 128
DS                   0
SWH          27777.777 Hz
FIDRES        0.194449 Hz
AQ            2.5714221 sec
RG              10321.3
DW               18.000 usec
DE                7.50 usec
TE               295.1 K
D1            2.00000000 sec
d11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               13C
P1                8.50 usec
PL1               0.00 dB
SFO1       125.7062372 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                1H
PCPD2           90.00 usec
PL2              1.00 dB
PL12            21.00 dB
SFO2       499.8734991 MHz

F2 - Processing parameters
SI                65536
SF         125.6924276 MHz
WDW                  no
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.40
```

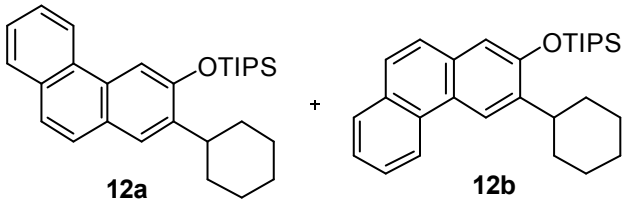


12a **12b**

(General Procedure 1)

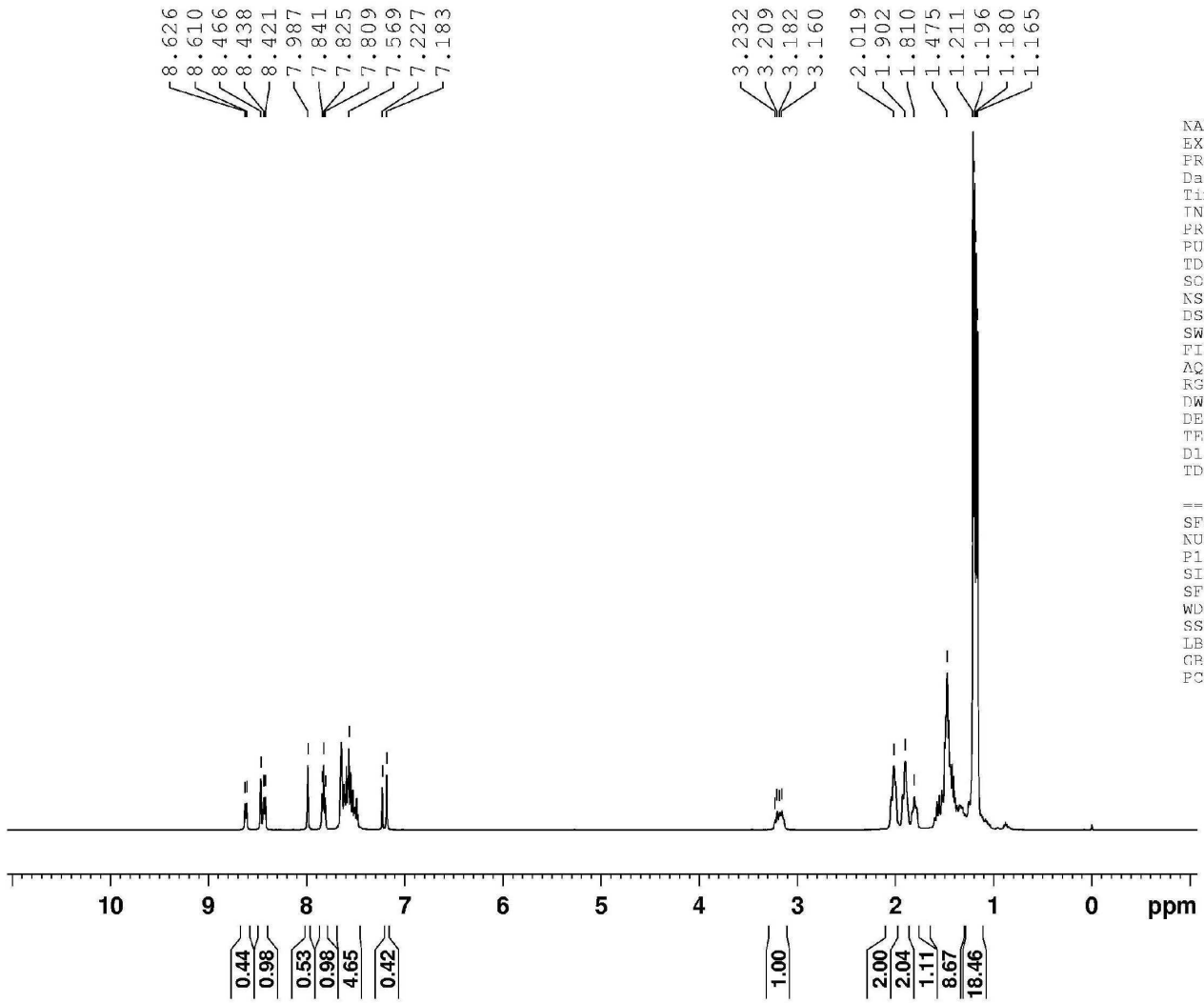



```
NAME        1.css.208.test
EXPNO                    1
PROCNO                   1
Date_           20131111
Time                16.09
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH             10000.000 Hz
FIDRES          0.166672 Hz
AQ              2.9999499 sec
RG                   23.38
DW                  50.000 usec
DE                  10.00 usec
TE                  296.0 K
D1           8.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                   8.00 usec
SI                  65536
SF           500.1300240 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.00
```

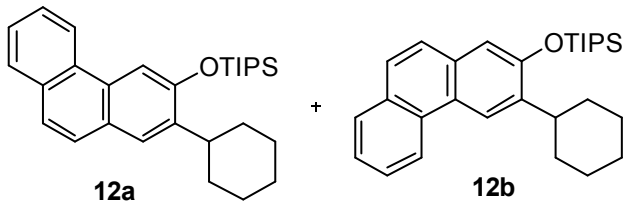


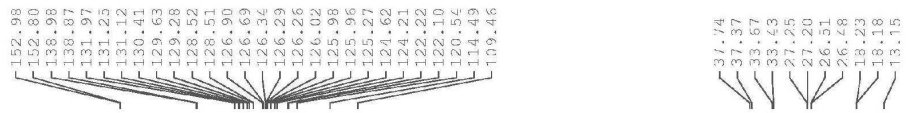
12a + **12b**

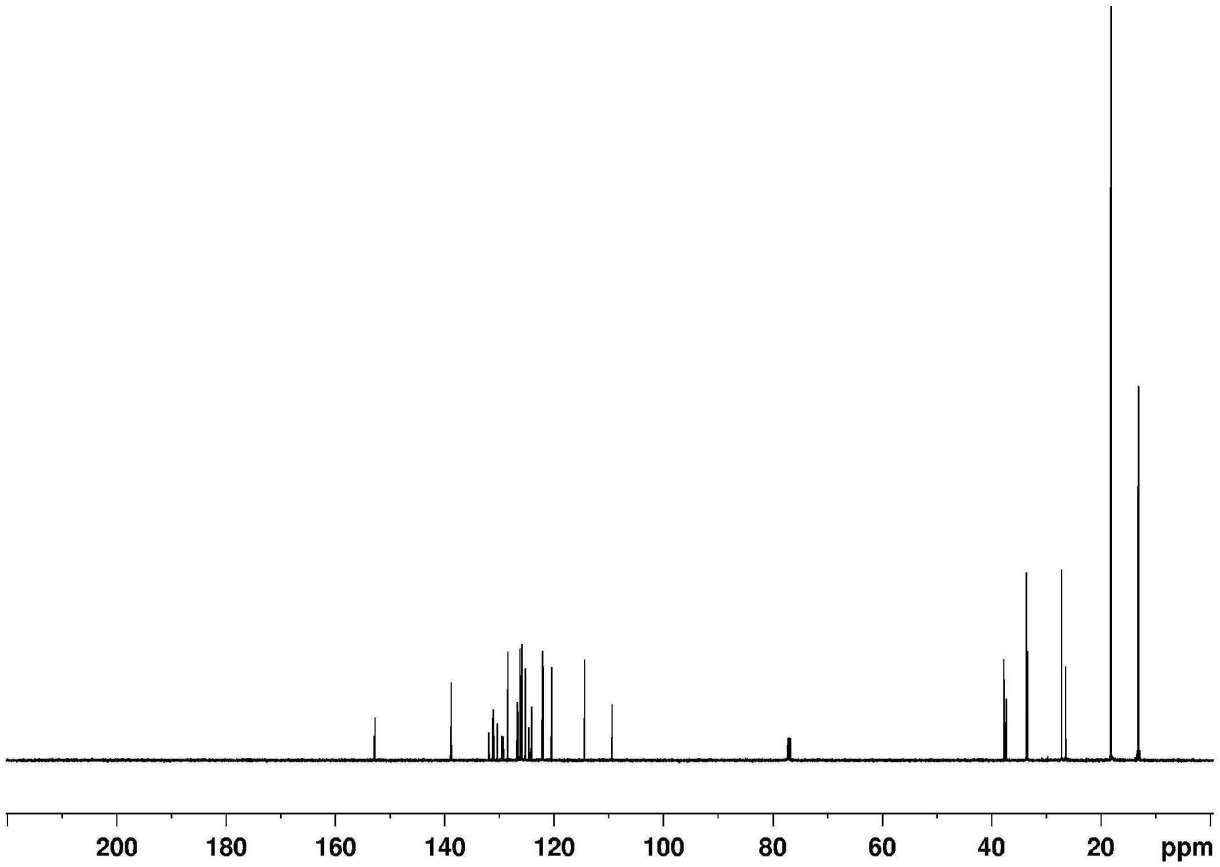
(General Procedure 2)



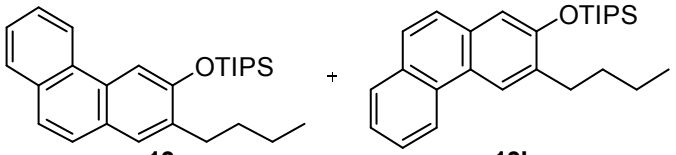
NAME	1.css.209
EXPNO	1
PROCNO	1
Date_	20131115
Time	15.53
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	4
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	15.84
DW	50.000 usec
DE	10.00 usec
TE	295.7 K
D1	8.00000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300296 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00





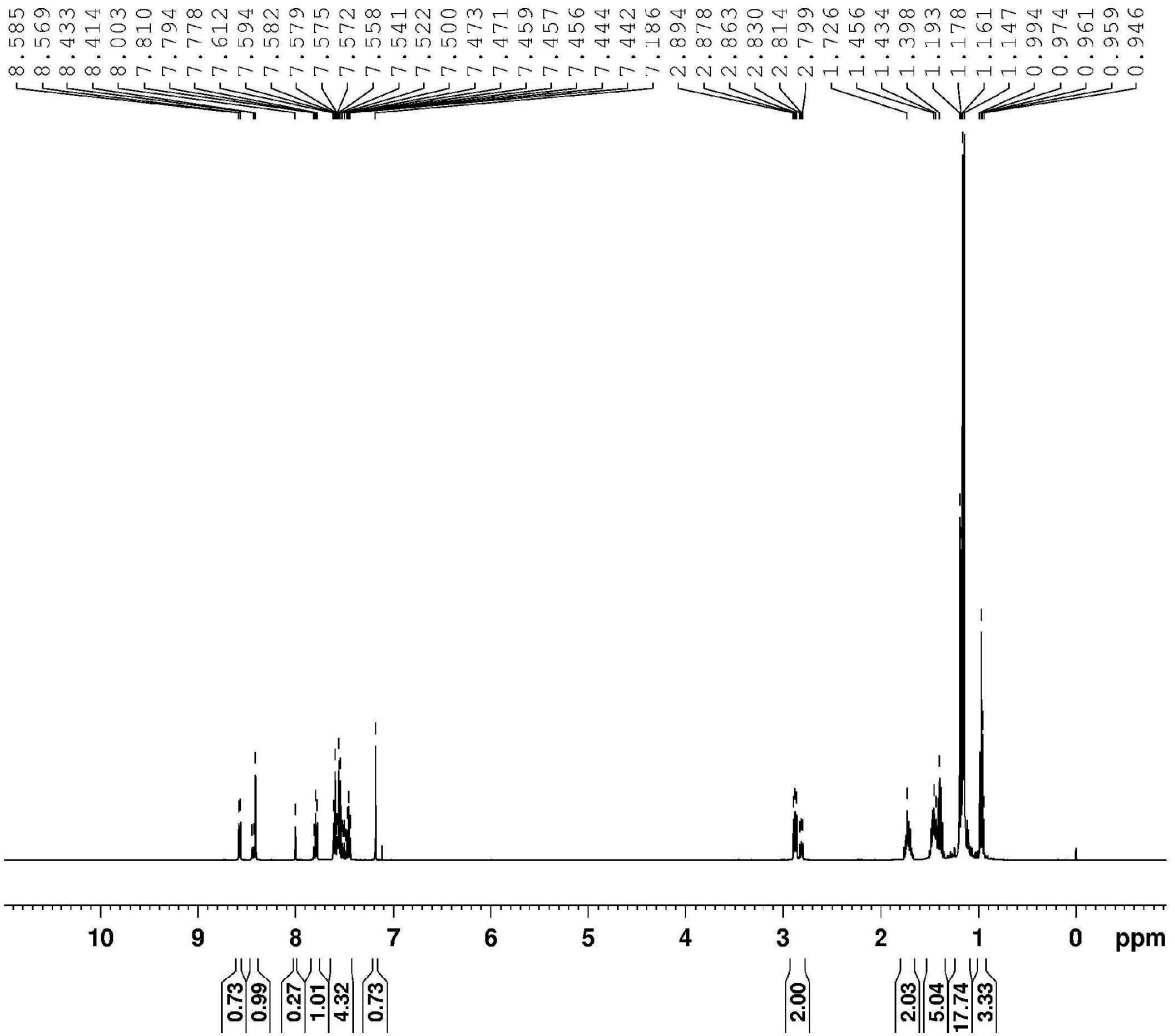



```
NAME          1.css.208.13C
EXPNO                     1
PROCNO                    1
Date_              2013'111
Time                   8.17
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG                zgdc
TD                   142854
SOLVENT               CDCl3
NS                      256
DS                        0
SWH              27777.777 Hz
FIDRES           0.194449 Hz
AQ               2.5714221 sec
RG                  9195.2
DW                  18.000 usec
DE                   7.50 usec
TE                  295.3 K
D1               2.00000000 sec
d11              0.03000000 sec
TD0                       1

-------- CHANNEL f1 --------
NUC1                    13C
P1                     8.50 usec
PL1                    0.00 dB
SFO1          125.7062372 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                     1H
PCPD2                 90.00 usec
PL2                    1.00 dB
PL12                  21.00 dB
SFO2          499.8734991 MHz
SI                    65536
SF            125.6924334 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.40
```

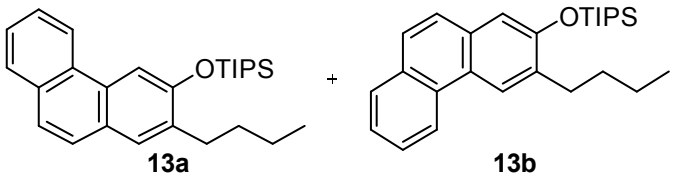


13a **13b**

(General Procedure 1)

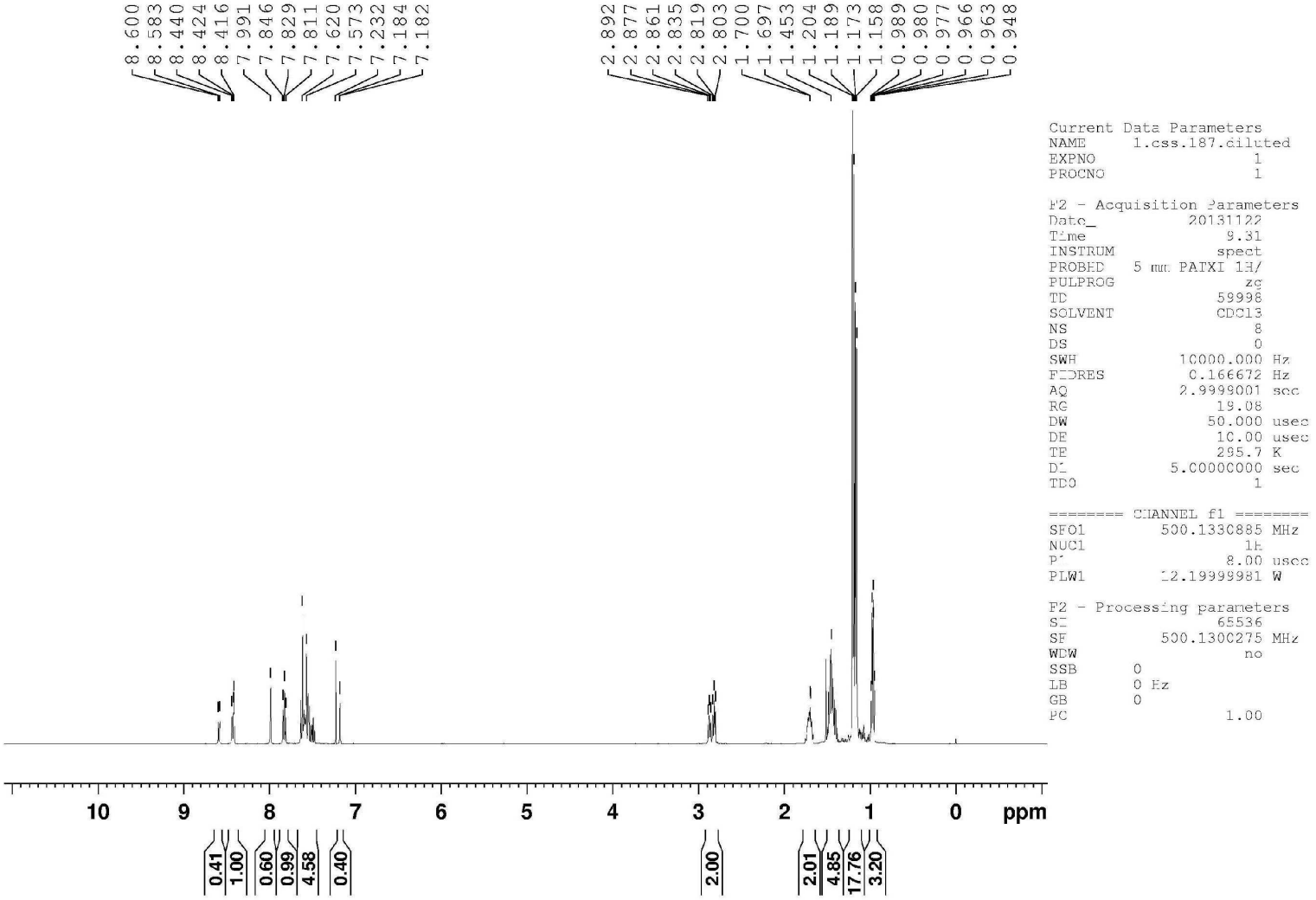


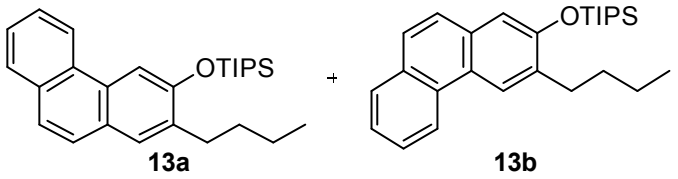

```
NAME        1.css.186.test
EXPNO                    1
PROCNO                   1
Date_           20130919
Time                15.37
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG                 zg
TD                   59998
SOLVENT              CDCl3
NS                       4
DS                       0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999499 sec
RG                    6.92
DW                50.000 usec
DE                10.00 usec
TE                296.2 K
D1            8.00000000 sec
TD0                      1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                 8.00 usec
SI                 65536
SF           500.1300837 MHz
WDW                   no
SSB                    0
LB                0.00 Hz
GB                     0
PC                1.00
```



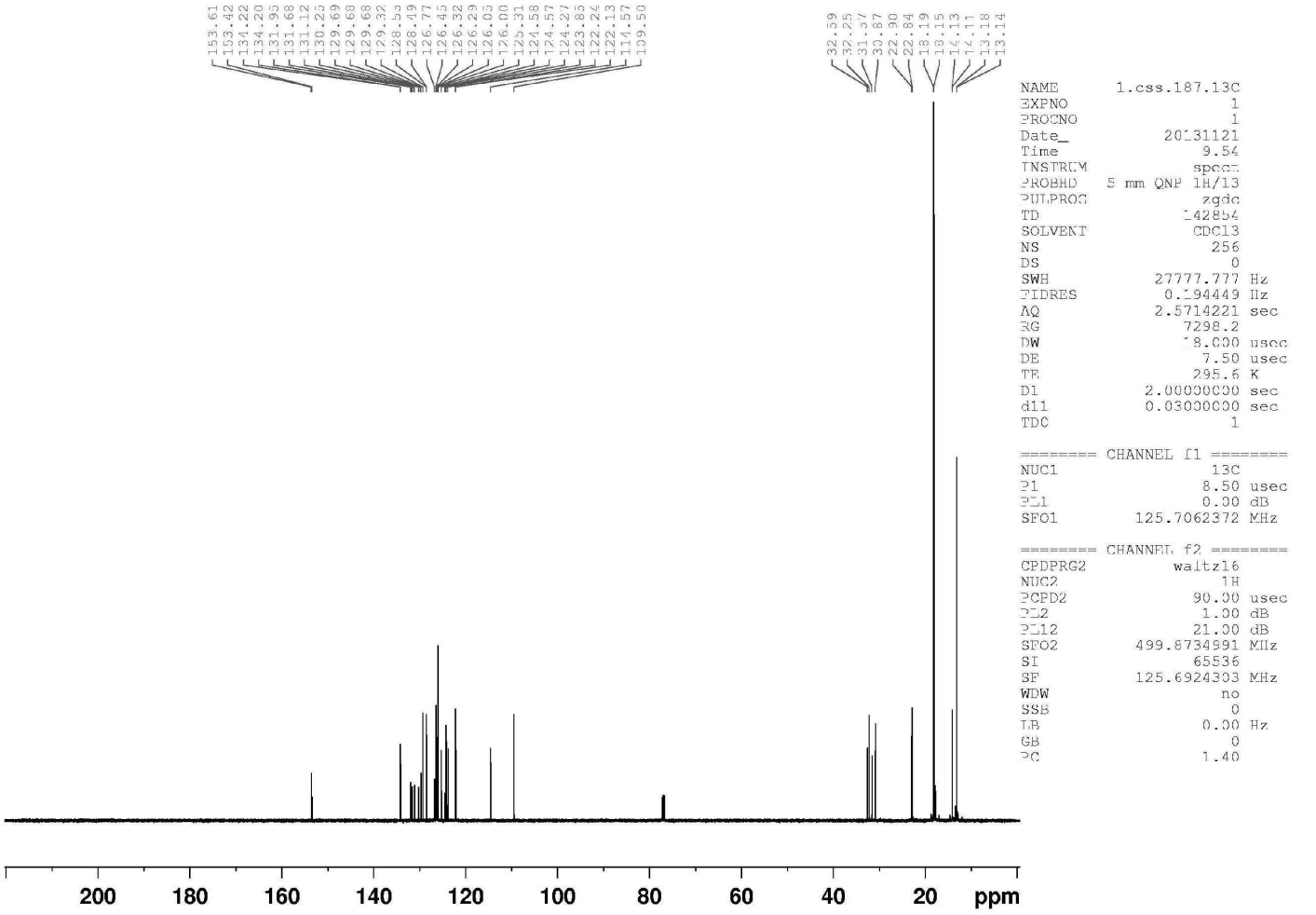
13a **13b**

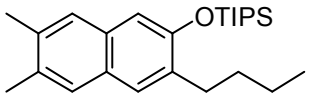
(General Procedure 2)



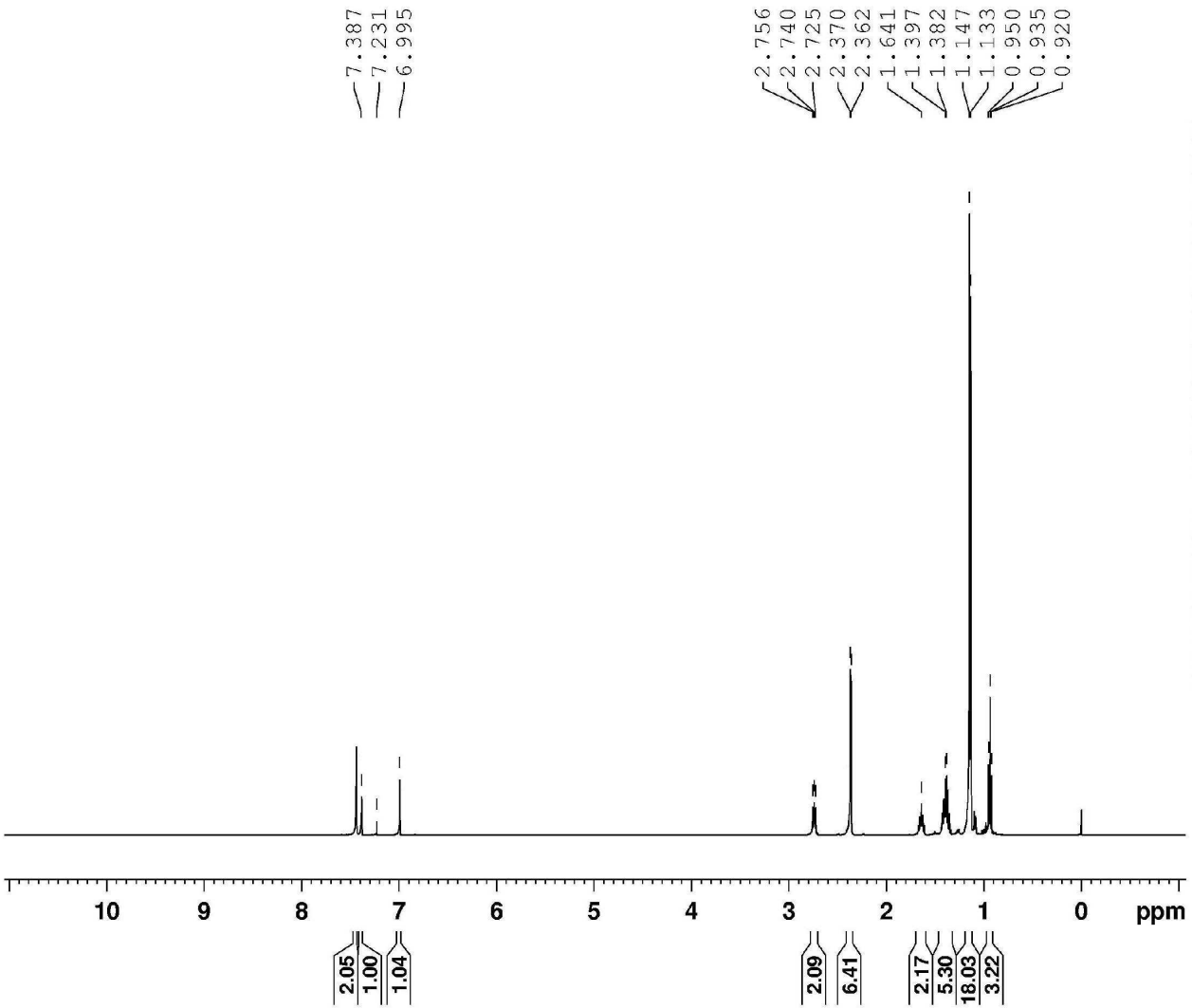

OTIPS
OTIPS

13a **13b**

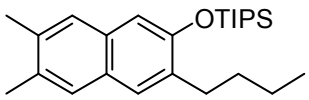

153.61
153.42
134.22
134.20
131.95
131.68
131.12
130.25
129.69
129.68
129.68
129.32
128.53
128.49
126.77
126.45
126.32
126.29
126.05
126.00
125.31
121.58
124.57
124.27
123.85
122.24
122.13
114.57
109.50
32.59
32.25
31.37
30.87
22.90
22.84
18.19
18.15
14.13
14.11
13.18
13.14
NAME 1.css.187.13C
EXPNO 1
PROCNO 1
Date_ 20131121
Time 9.54
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgdc
TD 142854
SOLVENT CDCl3
NS 256
DS 0
SWH 27777.777 Hz
FIDRES 0.194449 Hz
AQ 2.5714221 sec
RG 7298.2
DW 18.000 usec
DE 7.50 usec
TE 295.6 K
D1 2.00000000 sec
d11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 8.50 usec
PL1 0.00 dB
SFO1 125.7062372 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 1.00 dB
PL12 21.00 dB
SFO2 499.8734991 MHz
SI 65536
SF 125.6924303 MHz
WDW no
SSB 0
LB 0.00 Hz
GB 0
PC 1.40
200
180
160
140
120
100
80
60
40
20
ppm



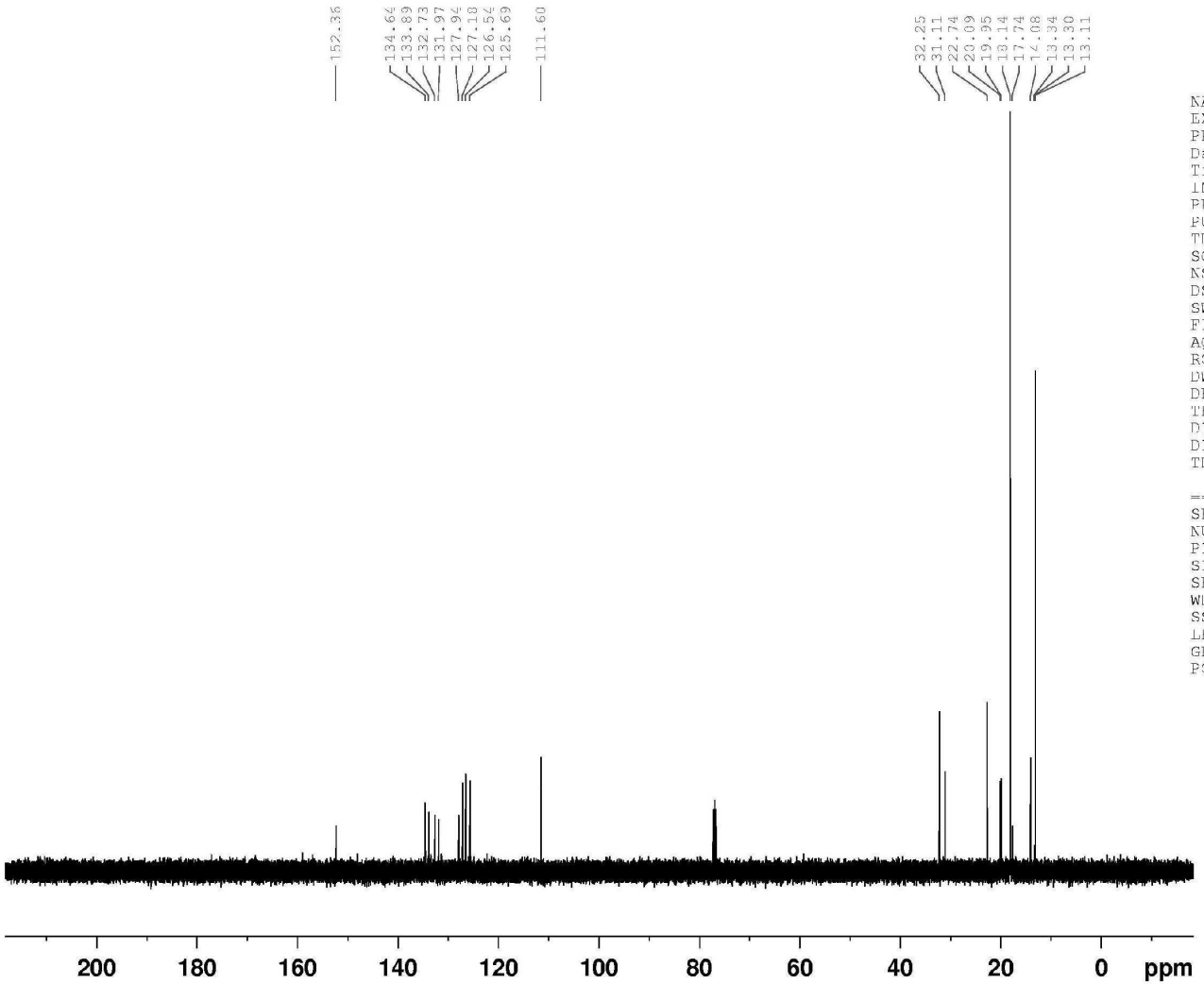
14



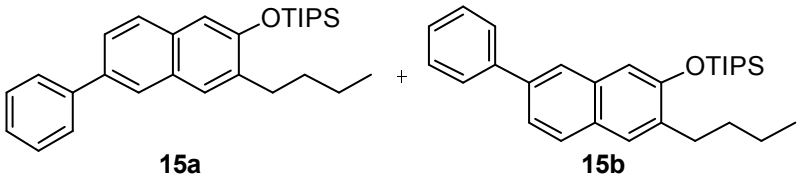
NAME	1.css.137
EXPNO	1
PROCNO	1
Date_	20130524
Time	18.42
INSTRUM	spect
PROBHD	5 mm PATX1 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	12
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	19.08
DW	50.000 usec
DE	10.00 usec
TE	295.2 K
D1	6.00000000 sec
TDC	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300274 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



14

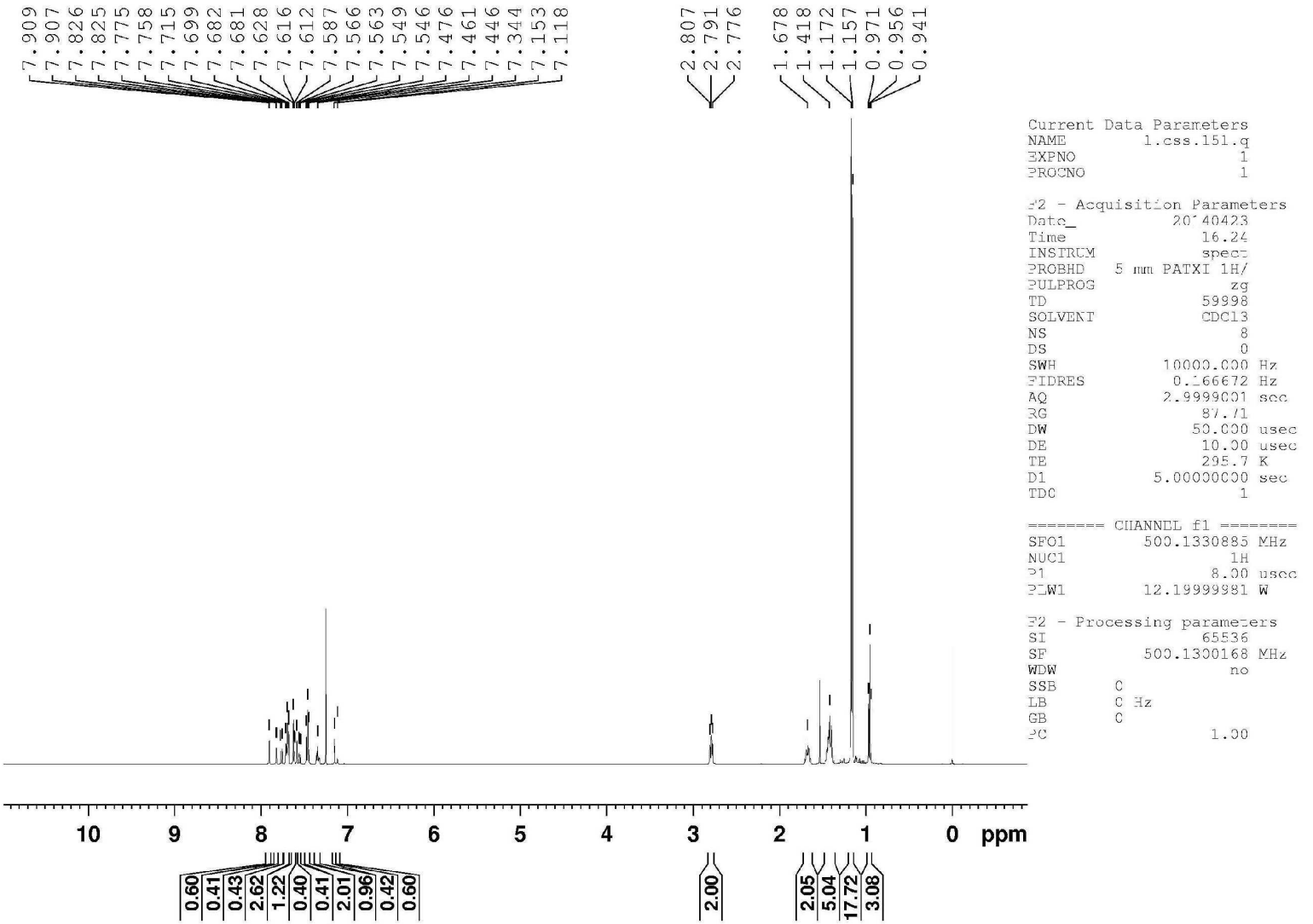


NAME	1.css.137.13C
EXPNO	1
PROCNO	1
Date_	20130524
Time	18.59
INSTRUM	spect
PROBHD	5 mm PATXT 1H/
PULPROG	zgdc
TD	178568
SOLVENT	CDCl3
NS	150
DS	0
SWH	29761.904 Hz
FIDRES	0.166670 Hz
AQ	2.9999924 sec
RG	196.79
DW	16.800 usec
DE	10.00 usec
TE	296.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
SFO1	125.7703643 MHz
NUC1	13C
P1	14.00 usec
SI	131072
SF	125.7577942 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40

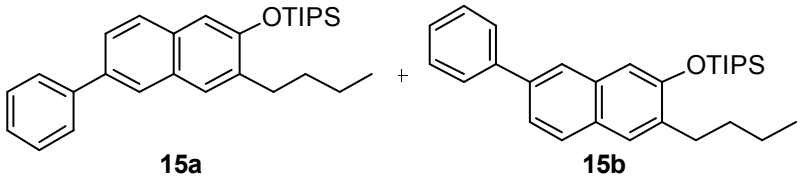


15a **15b**

(General Procedure 1)

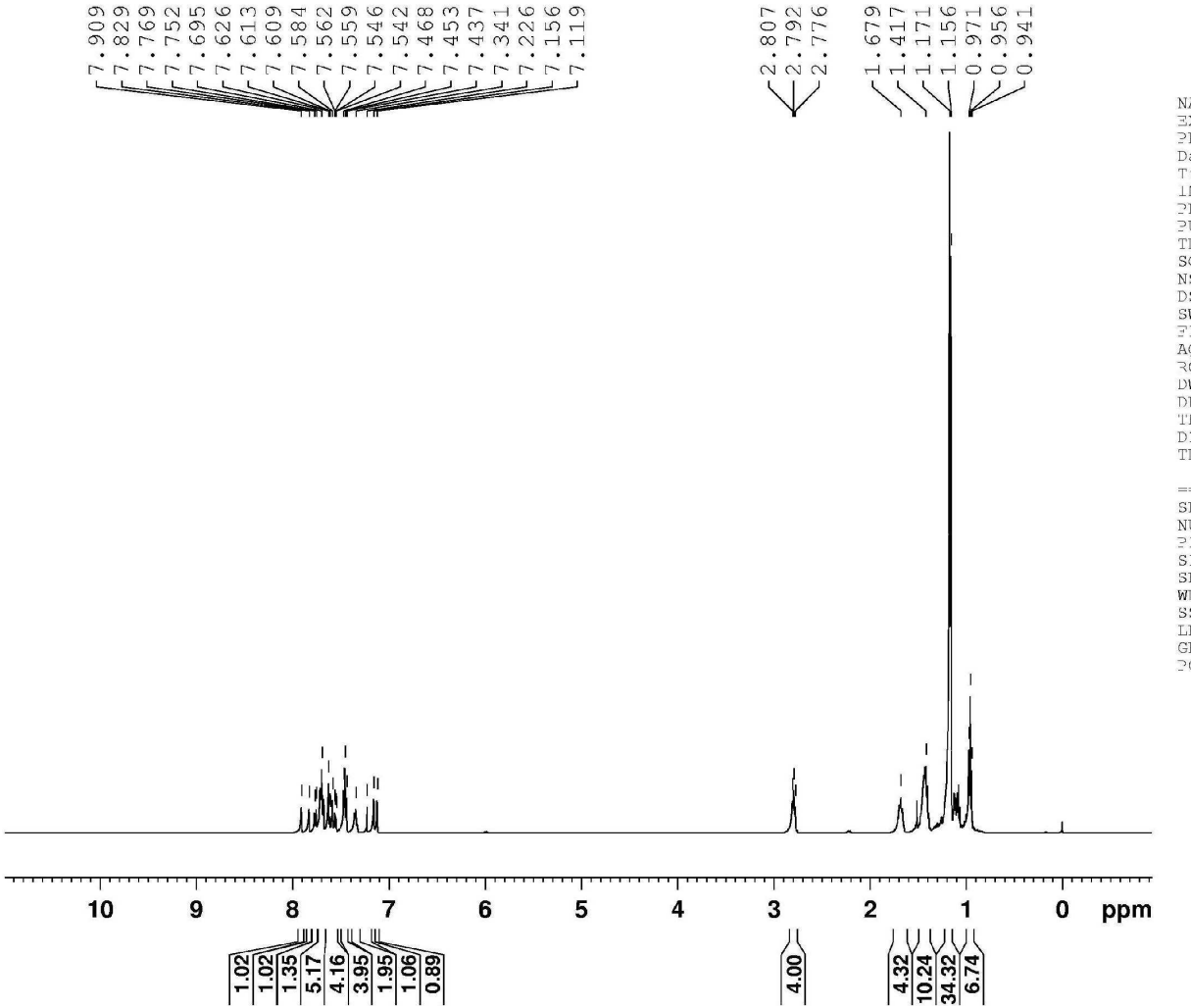



```
Current Data Parameters
NAME         1.css.151.q
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140423
Time               16.24
INSTRUM             spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES             0.166672 Hz
AQ             2.9999001 sec
RG                  87.71
DW                 50.000 usec
DE                 10.00 usec
TE                 295.7 K
D1             5.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                  8.00 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                 65536
SF           500.1300168 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.00
```

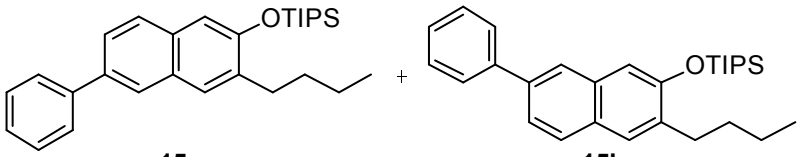


15a **15b**

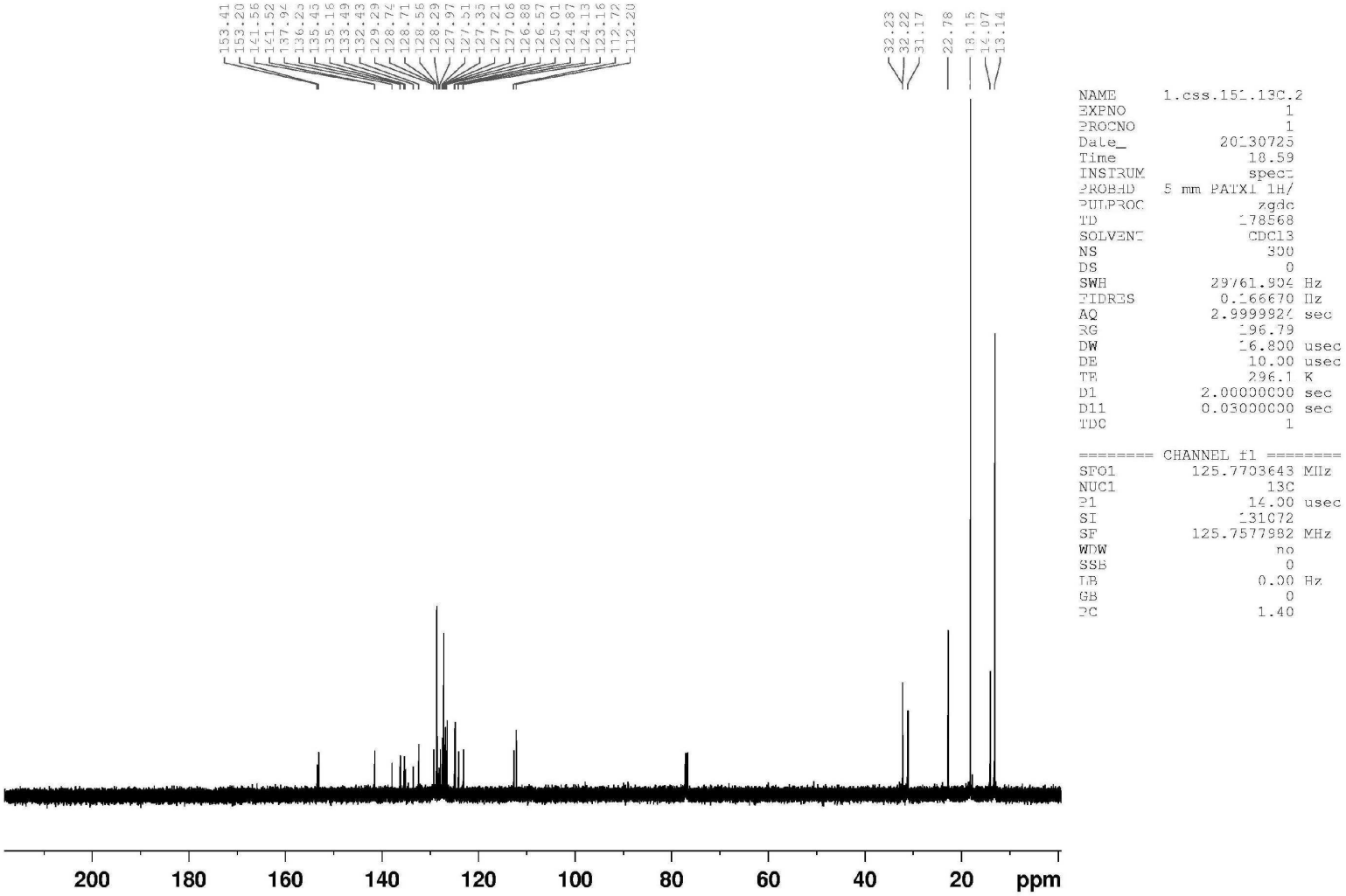
(General Procedure 2)



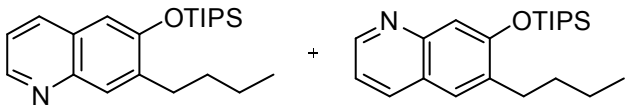

```
NAME            1.ess.152.1
EXPNO                     1
PROCNO                    1
Date_            20130717
Time                 18.48
INSTRUM              spect
PROBHD   5 mm PATXI 1H/
PULPROG                zg
TD                  59998
SOLVENT             CDC_3
NS                        8
DS                        0
SWH              10000.000 Hz
FIDRES           0.166672 Hz
AQ               2.9999499 sec
RG                   20.66
DW                  50.000 usec
DE                  10.00 usec
TE                  294.9 K
D1               5.00000000 sec
TDC                       1

======== CHANNEL f1 ========
SFO1          500.1330885 MHz
NUC1                     1H
P1                    8.00 usec
SI                   65536
SF            500.1300306 MHz
WDW                      no
SSB                       0
LB                     0.00 Hz
GB                        0
PC                     1.00
```



15a + **15b**




```
NAME        1.css.151.13C.2
EXPNO                     1
PROCNO                    1
Date_              20130725
Time                  18.59
INSTRUM               spect
PROBHD   5 mm PATX1 1H/
PULPROG                zgdc
TD                   178568
SOLVENT               CDCl3
NS                      300
DS                        0
SWH                29761.904 Hz
FIDRES             0.166670 Hz
AQ                 2.9999924 sec
RG                    196.79
DW                   16.800 usec
DE                   10.00 usec
TE                    296.1 K
D1                 2.00000000 sec
D11                0.03000000 sec
TDC                       1

======== CHANNEL f1 ========
SFO1            125.7703643 MHz
NUC1                    13C
P1                   14.00 usec
SI                    131072
SF              125.7577982 MHz
WDW                       no
SSB                        0
LB                    0.00 Hz
GB                         0
PC                      1.40
```



16a

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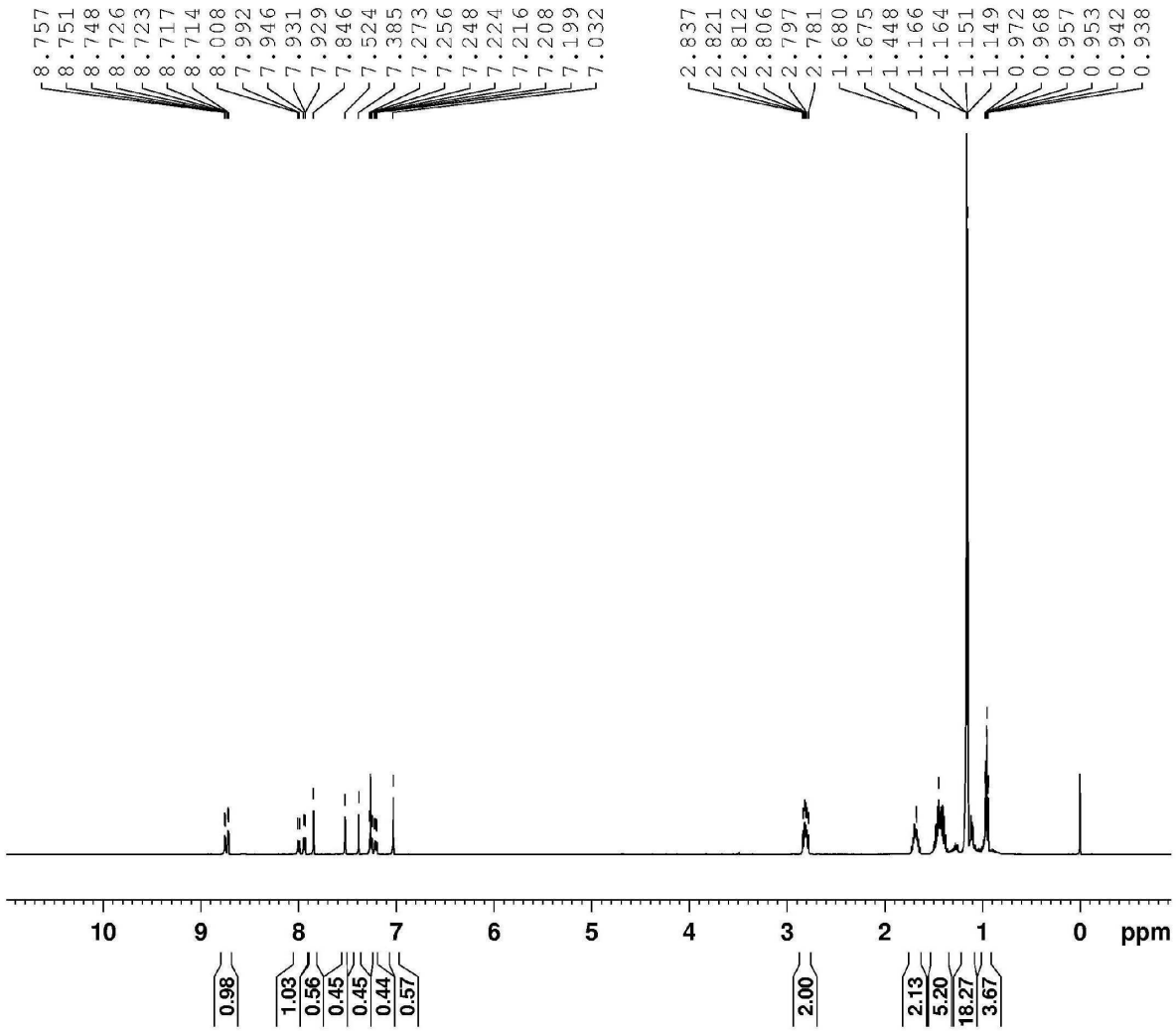
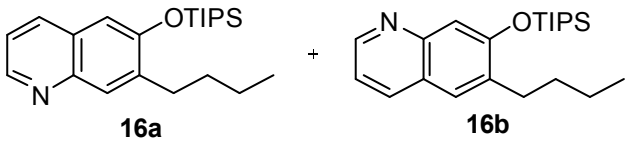
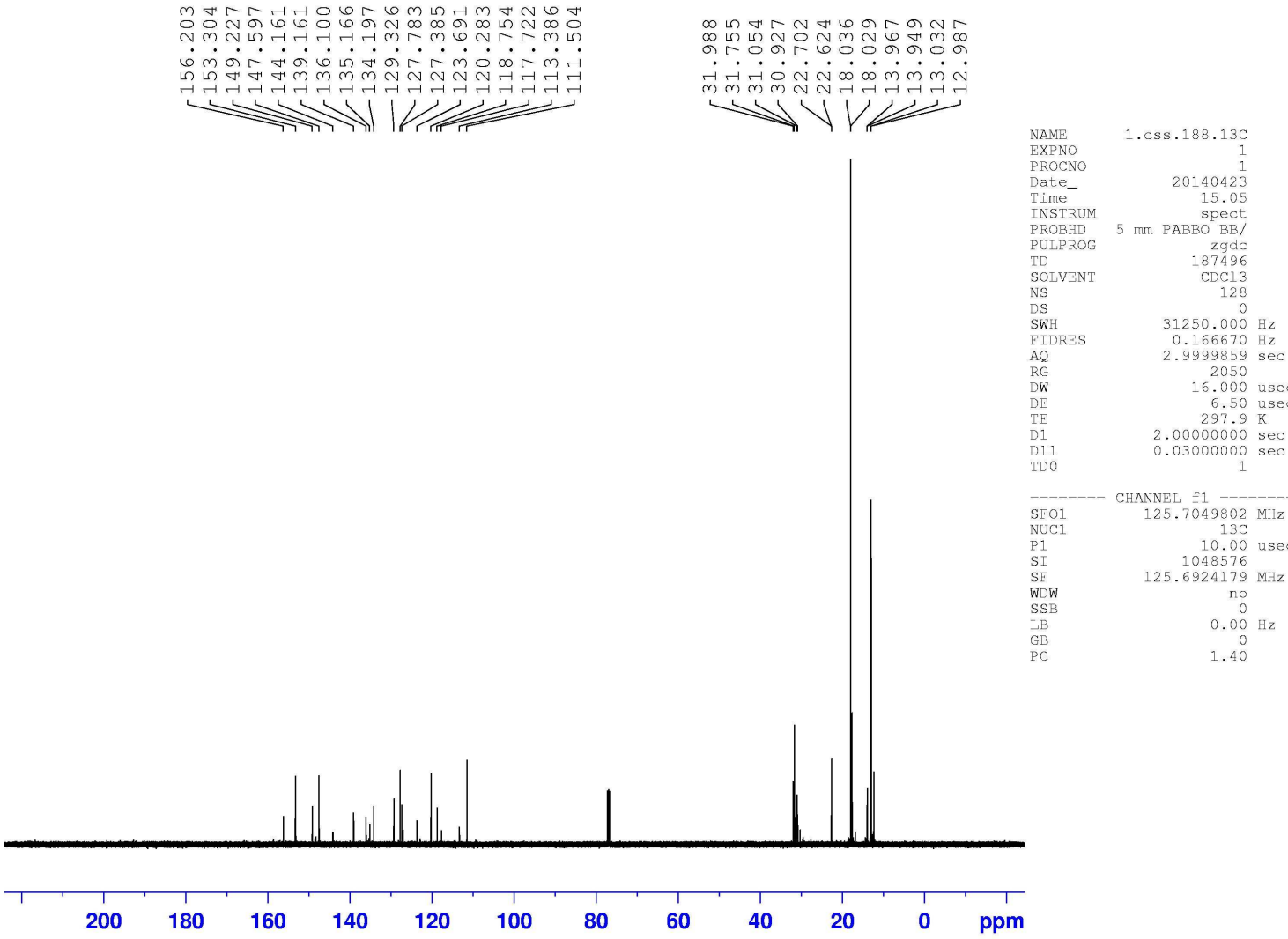
16b

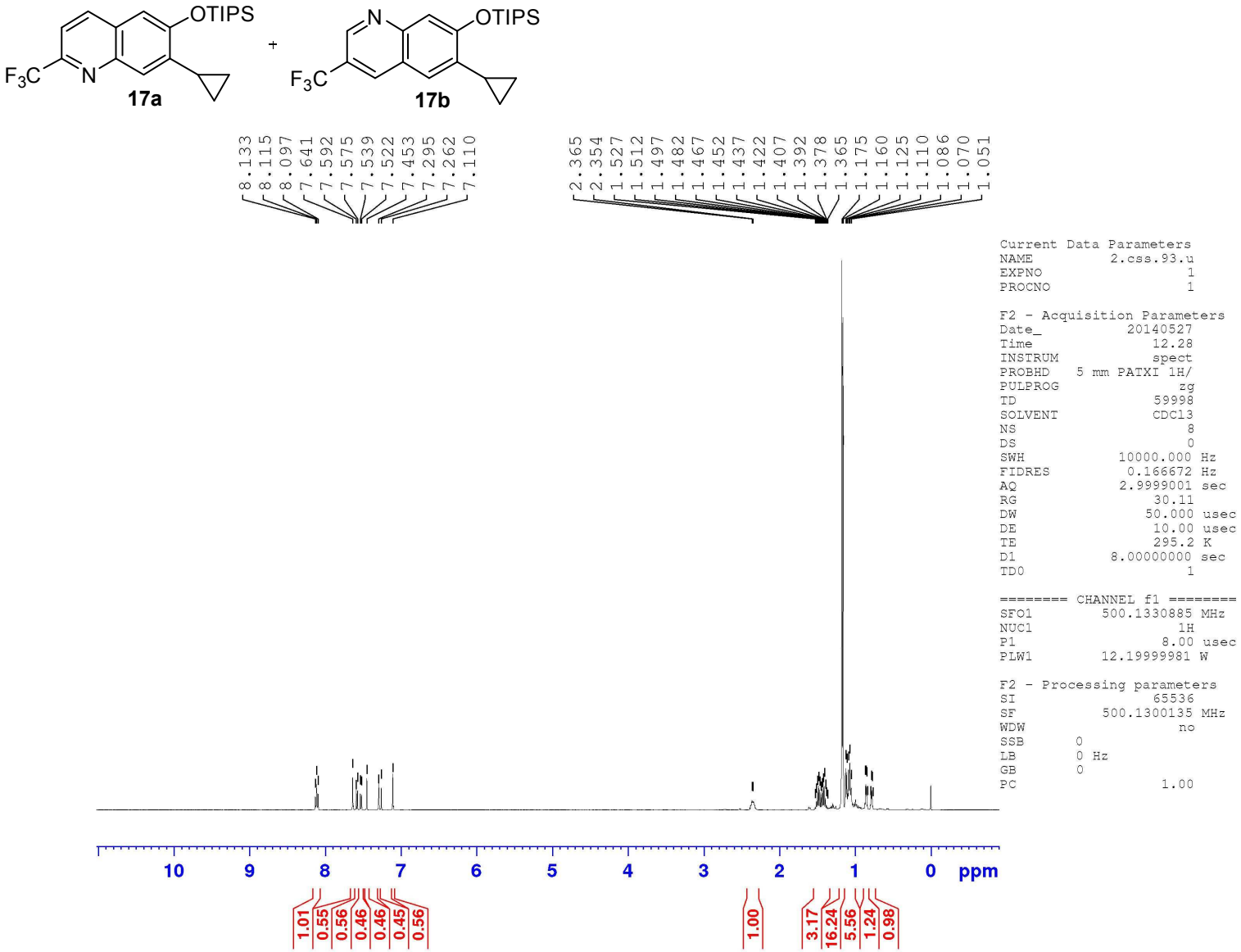


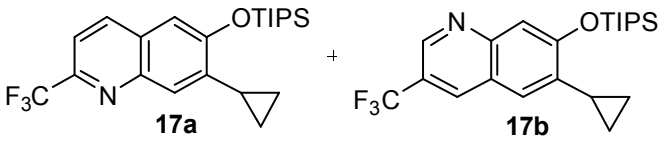

```
NAME        1.css.188.test
EXPNO               1
PROCNO              1
Date_         20130923
Time            17.24
INSTRUM         spect
PROBHD   5 mm PATXI 1H/
PULPROG             zg
TD              59998
SOLVENT         CDCl3
NS                  4
DS                  0
SWH         10000.000 Hz
FIDRES       0.166672 Hz
AQ           2.9999499 sec
RG              37.62
DW              50.000 usec
DE              10.00 usec
TE              296.1 K
D1           8.00000000 sec
TDC                 1

======== CHANNEL f1 ========
SFO1       500.1330885 MHz
NUC1               1H
P1                8.00 usec
ST               65536
SF         500.1300123 MHz
WDW                no
SSB                 0
LB                0.00 Hz
GB                  0
PC                1.00
```



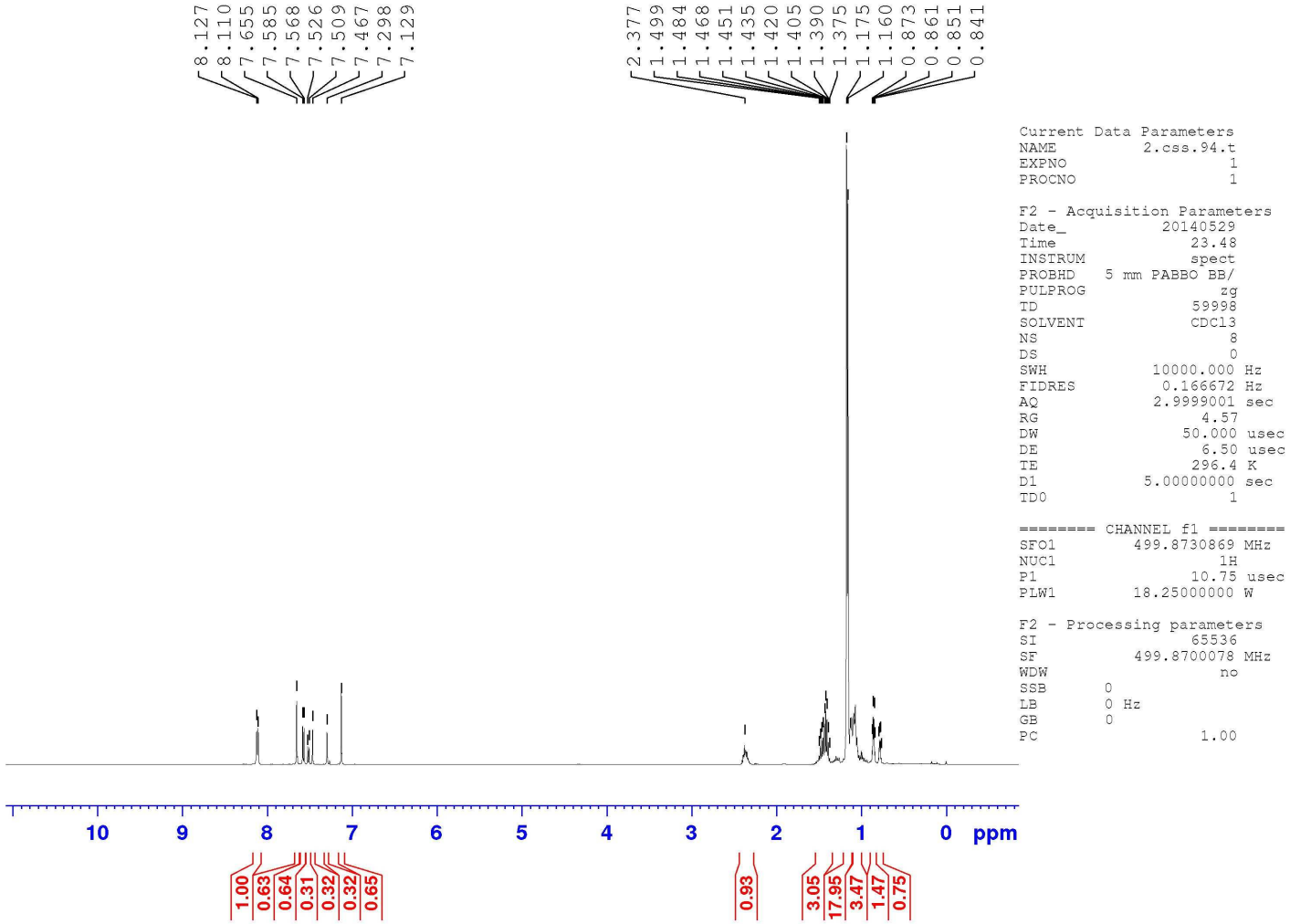



```
NAME          1.css.188.13C
EXPNO                     1
PROCNO                    1
Date_              20140423
Time                  15.05
INSTRUM               spect
PROBHD    5 mm PABBO BB/
PULPROG                zgdc
TD                   187496
SOLVENT               CDCl3
NS                      128
DS                        0
SWH              31250.000 Hz
FIDRES           0.166670 Hz
AQ               2.9999859 sec
RG                     2050
DW                 16.000 usec
DE                  6.50 usec
TE                  297.9 K
D1              2.00000000 sec
D11             0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
SFO1           125.7049802 MHz
NUC1                    13C
P1                   10.00 usec
SI                  1048576
SF             125.6924179 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                     1.40
```

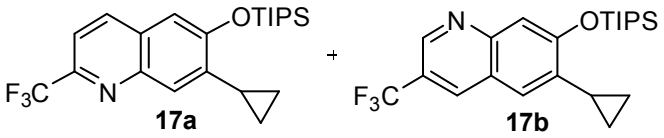

OTIPS
F3C
N
17a
+
N
OTIPS
F3C
17b
8.133
8.115
8.097
7.641
7.592
7.575
7.539
7.522
7.453
7.295
7.262
7.110
2.365
2.354
1.527
1.512
1.497
1.482
1.467
1.452
1.437
1.422
1.407
1.392
1.378
1.365
1.175
1.160
1.125
1.110
1.086
1.070
1.051
Current Data Parameters
NAME 2.css.93.u
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20140527
Time 12.28
INSTRUM spect
PROBHD 5 mm PATXI 1H/
PULPROG zg
TD 59998
SOLVENT CDCl3
NS 8
DS 0
SWH 10000.000 Hz
FIDRES 0.166672 Hz
AQ 2.9999001 sec
RG 30.11
DW 50.000 usec
DE 10.00 usec
TE 295.2 K
D1 8.00000000 sec
TD0 1
======== CHANNEL f1 ========
SFO1 500.1330885 MHz
NUC1 1H
P1 8.00 usec
PLW1 12.19999981 W
F2 - Processing parameters
SI 65536
SF 500.1300135 MHz
WDW no
SSB 0
LB 0 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
1.01
0.55
0.56
0.46
0.46
0.45
0.56
1.00
3.17
16.24
5.56
1.24
0.98

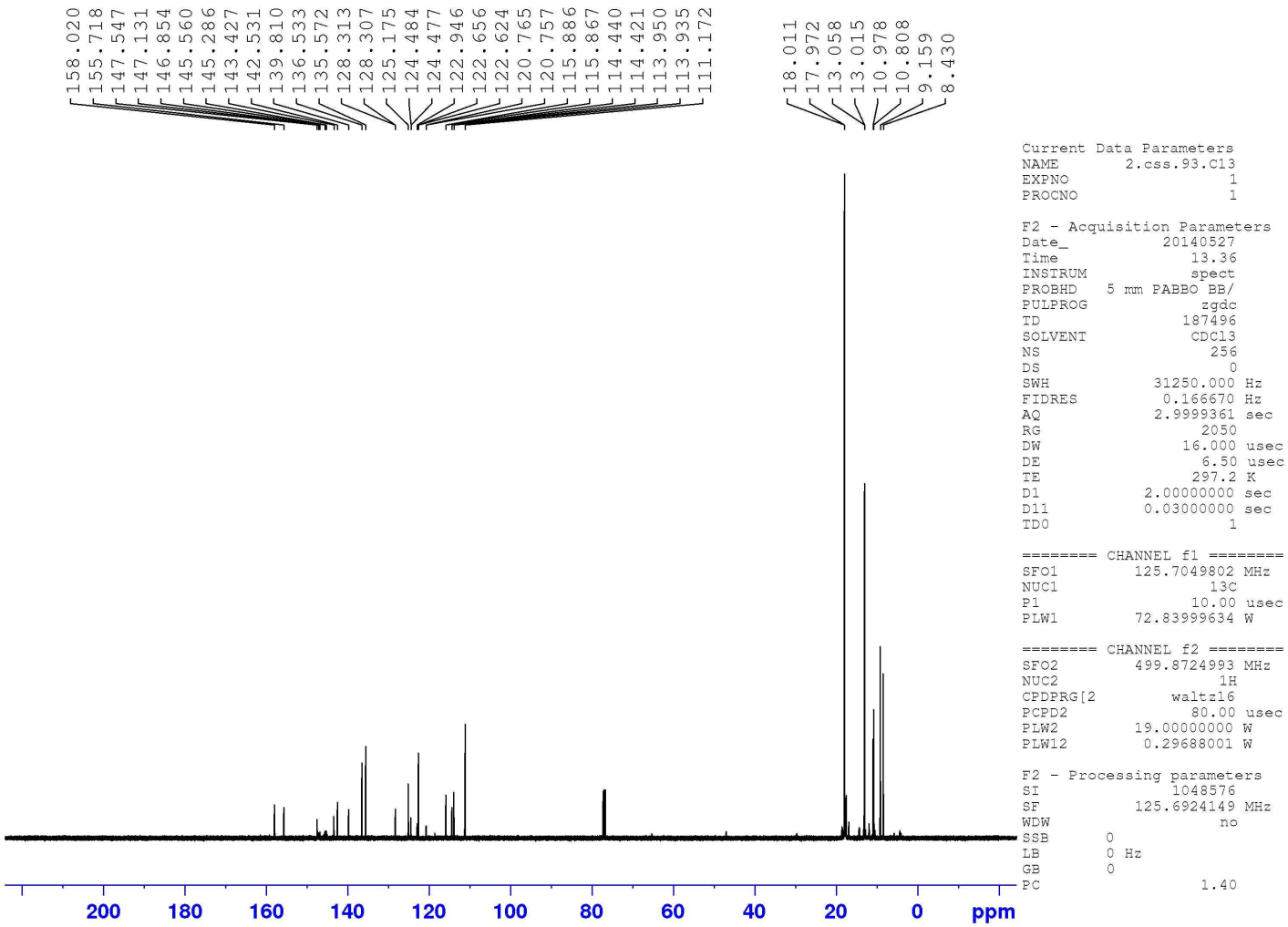


(Reaction Catalyzed with $AgNTf_2$)

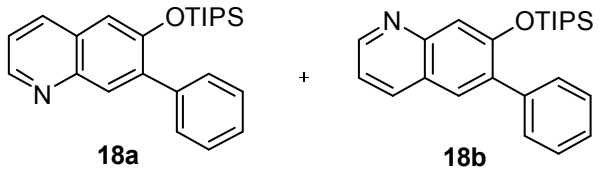



```
Current Data Parameters
NAME          2.css.94.t
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140529
Time               23.48
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH           10000.000 Hz
FIDRES         0.166672 Hz
AQ            2.9999001 sec
RG                  4.57
DW                50.000 usec
DE                 6.50 usec
TE                296.4 K
D1           5.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         499.8730869 MHz
NUC1                   1H
P1                10.75 usec
PLW1         18.25000000 W

F2 - Processing parameters
SI                 65536
SF           499.8700078 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```






```
Current Data Parameters
NAME        2.css.93.C13
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140527
Time               13.36
INSTRUM            spect
PROBHD   5 mm PABBO BB/
PULPROG             zgdc
TD                187496
SOLVENT             CDCl3
NS                    256
DS                      0
SWH             31250.000 Hz
FIDRES          0.166670 Hz
AQ              2.9999361 sec
RG                   2050
DW                16.000 usec
DE                 6.50 usec
TE                 297.2 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1          125.7049802 MHz
NUC1                  13C
P1                 10.00 usec
PLW1          72.83999634 W

======== CHANNEL f2 ========
SFO2          499.8724993 MHz
NUC2                  1H
CPDPRG[2         waltz16
PCPD2              80.00 usec
PLW2          19.00000000 W
PLW12          0.29688001 W

F2 - Processing parameters
SI                 1048576
SF            125.6924149 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                  1.40
```



18a

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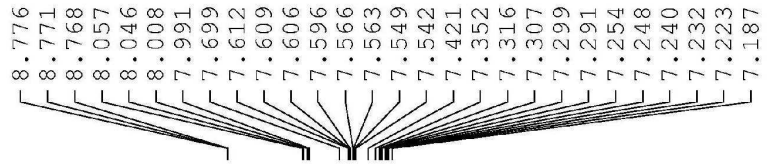
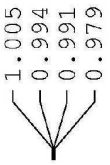
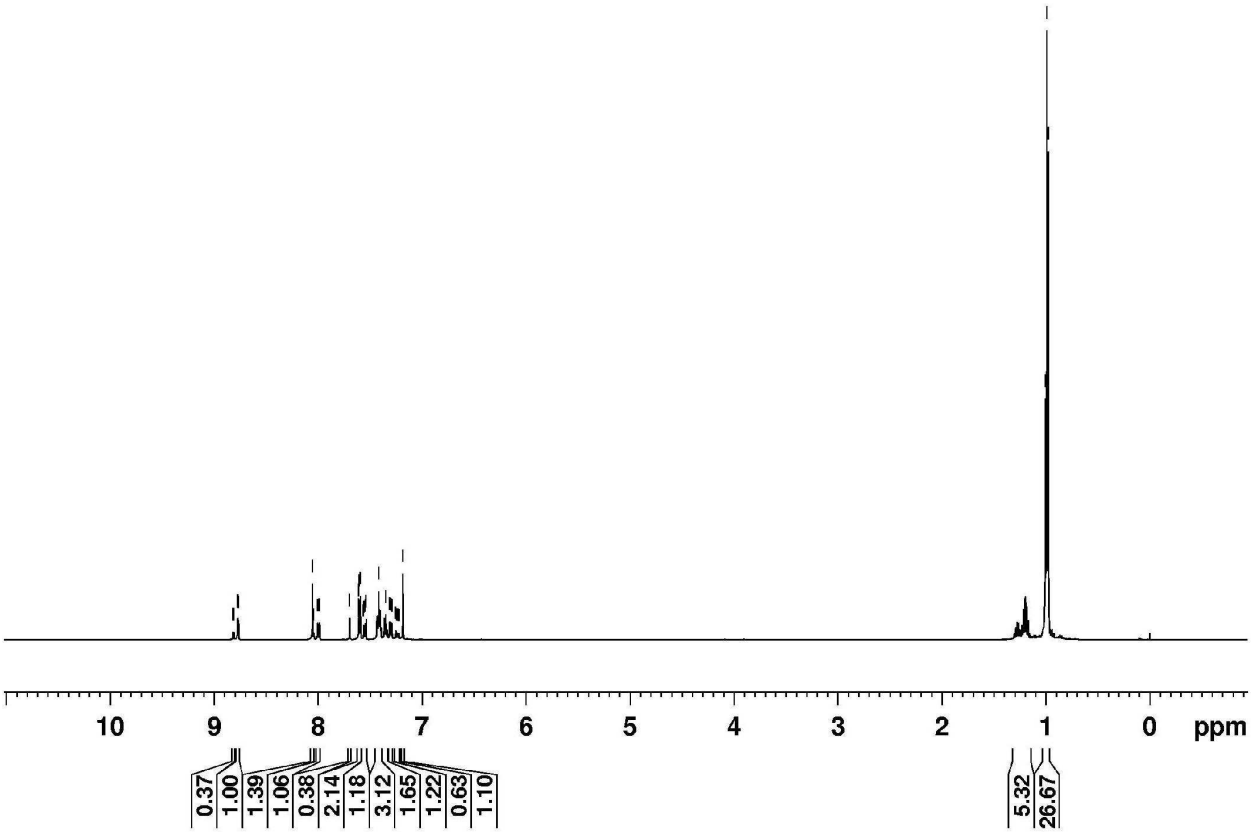
18b





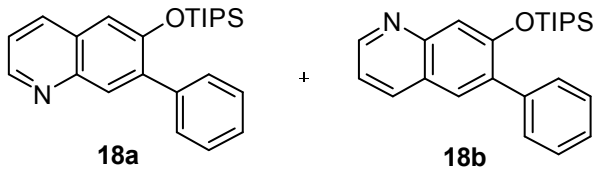



```
Current Data Parameters
NAME                  1.css.216
EXPNO                         1
PROCNO                        1

F2 - Acquisition Parameters
Date_              20131203
Time                  16.13
INSTRUM               spect
PROBHD    5 mm QNP 1H/13
PULPROG                   zg
TD                     59998
SOLVENT               CDCl3
NS                        4
DS                        0
SWH               10000.000 Hz
FIDRES                0.166672 Hz
AQ                2.9999499 sec
RG                       16
DW                   50.000 usec
DE                    7.50 usec
TE                   295.0 K
D1              8.00000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                     1H
P1                   10.00 usec
PL1                   0.00 dB
SFO1          499.8740056 MHz

F2 - Processing parameters
SI                    32768
SF             499.8700239 MHz
WDW                      no
SSB                       0
LB                    0.00 Hz
GB                        0
PC                     1.00
```



18a

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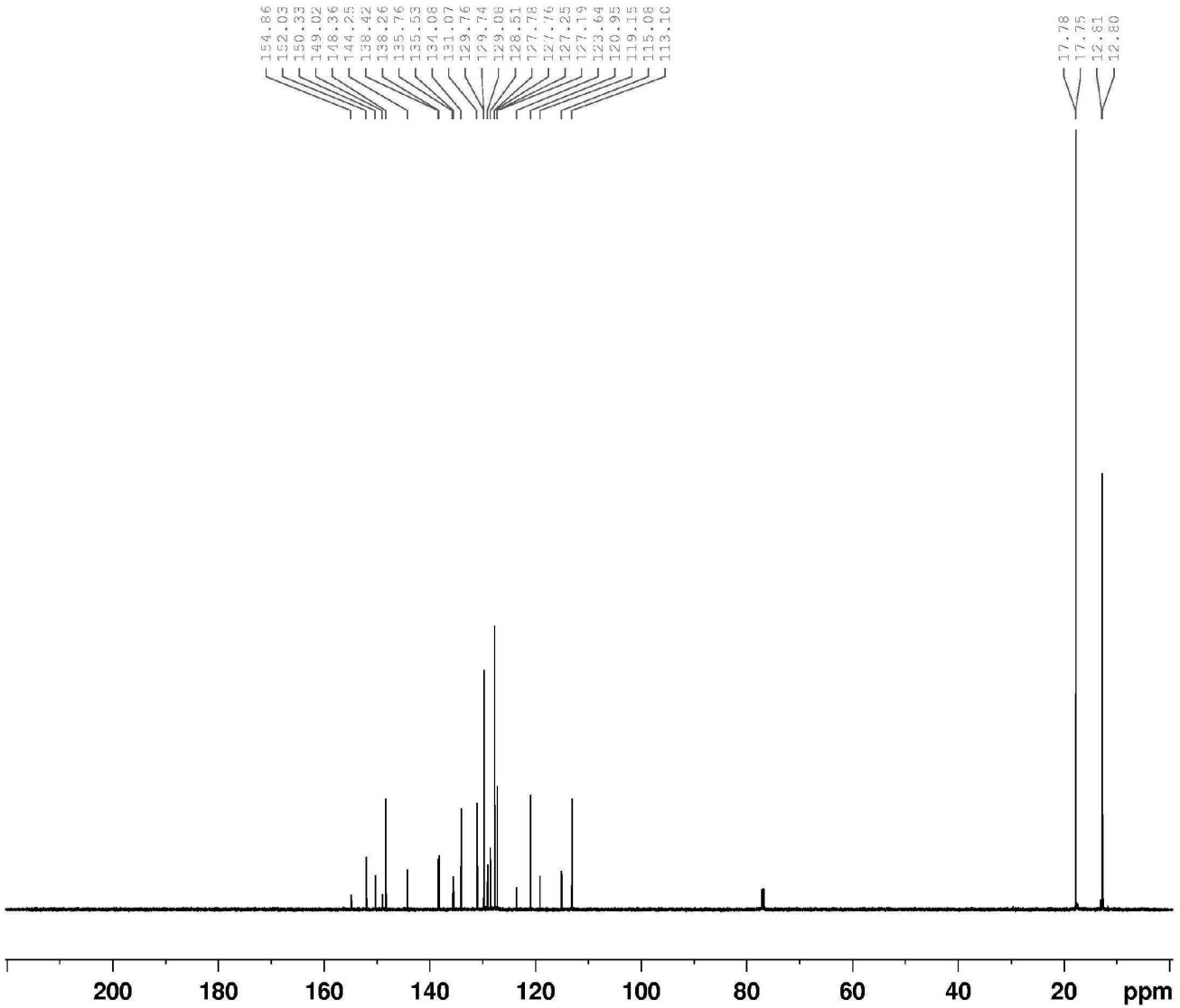
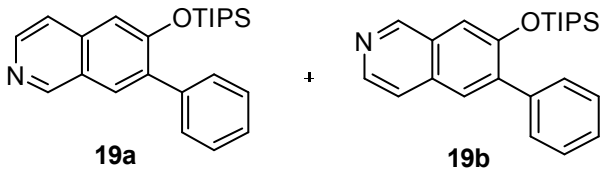
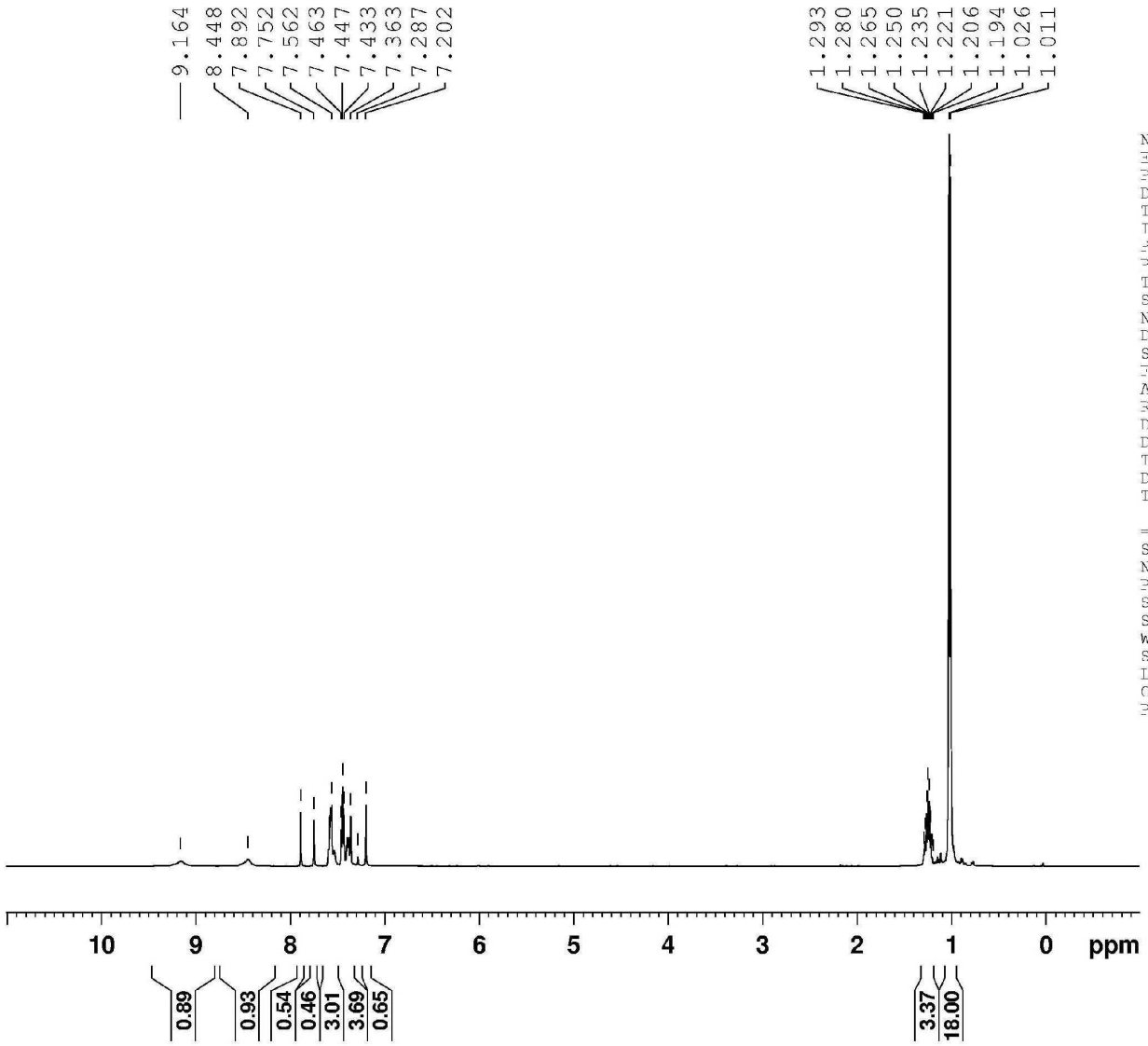
18b

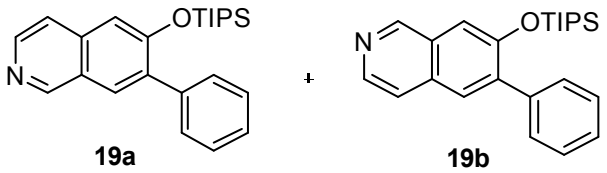



```
Current Data Parameters
NAME       1.ess.216.13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date             20131203
Time                16.38
INSTRUM              spect
PROBHD   5 mm QNP 1H/13
PULPROG              zgdc
TD                 142854
SOLVENT             CDCl3
NS                    200
DS                      0
SWH              27777.777 Hz
FIDRES           0.194449 Hz
AQ               2.5714221 sec
RG                   13004
DW                 18.000 usec
DE                  7.50 usec
TE                 295.6 K
D1           2.00000000 sec
d11          0.03000000 sec
TD0                     1

-------- CHANNEL f1 --------
NUC1                  13C
P1                   8.50 usec
PL1                  0.00 dB
SFO1         125.7062372 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                  1.00 dB
PL12                21.00 dB
SFO2         499.8734991 MHz

F2 - Processing parameters
SI                   65536
SF           125.6924292 MHz
WDW                    no
SSB                     0
LB                   0.00 Hz
GB                      0
PC                   1.40
```





NAME	1.css.232
EXPNO	1
PROCNO	1
Date_	20140123
Time	11.46
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	4
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	7.89
DW	50.000 usec
DE	10.00 usec
TE	295.4 K
D1	8.00000000 sec
TDC	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300000 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



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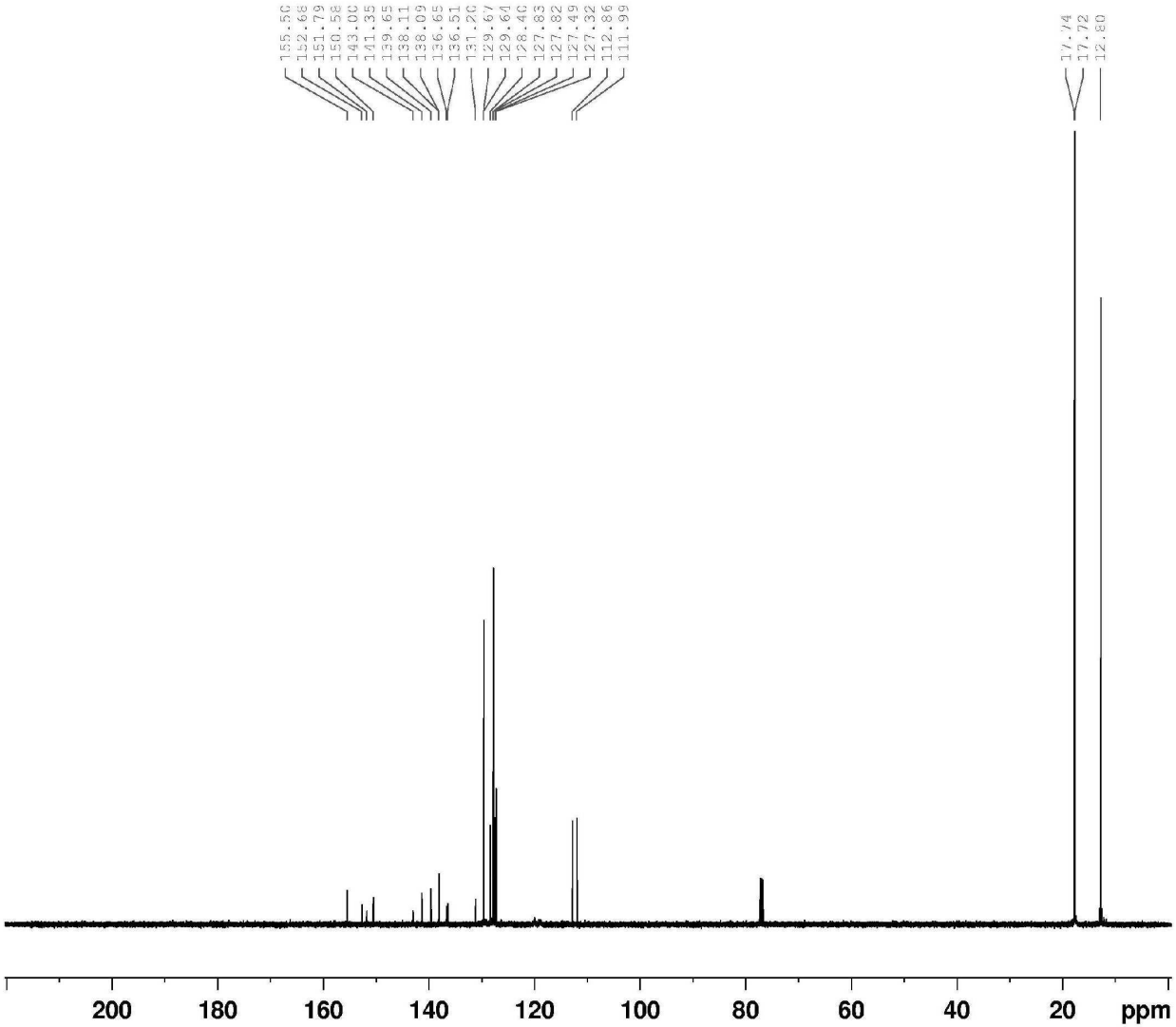
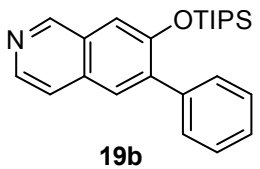
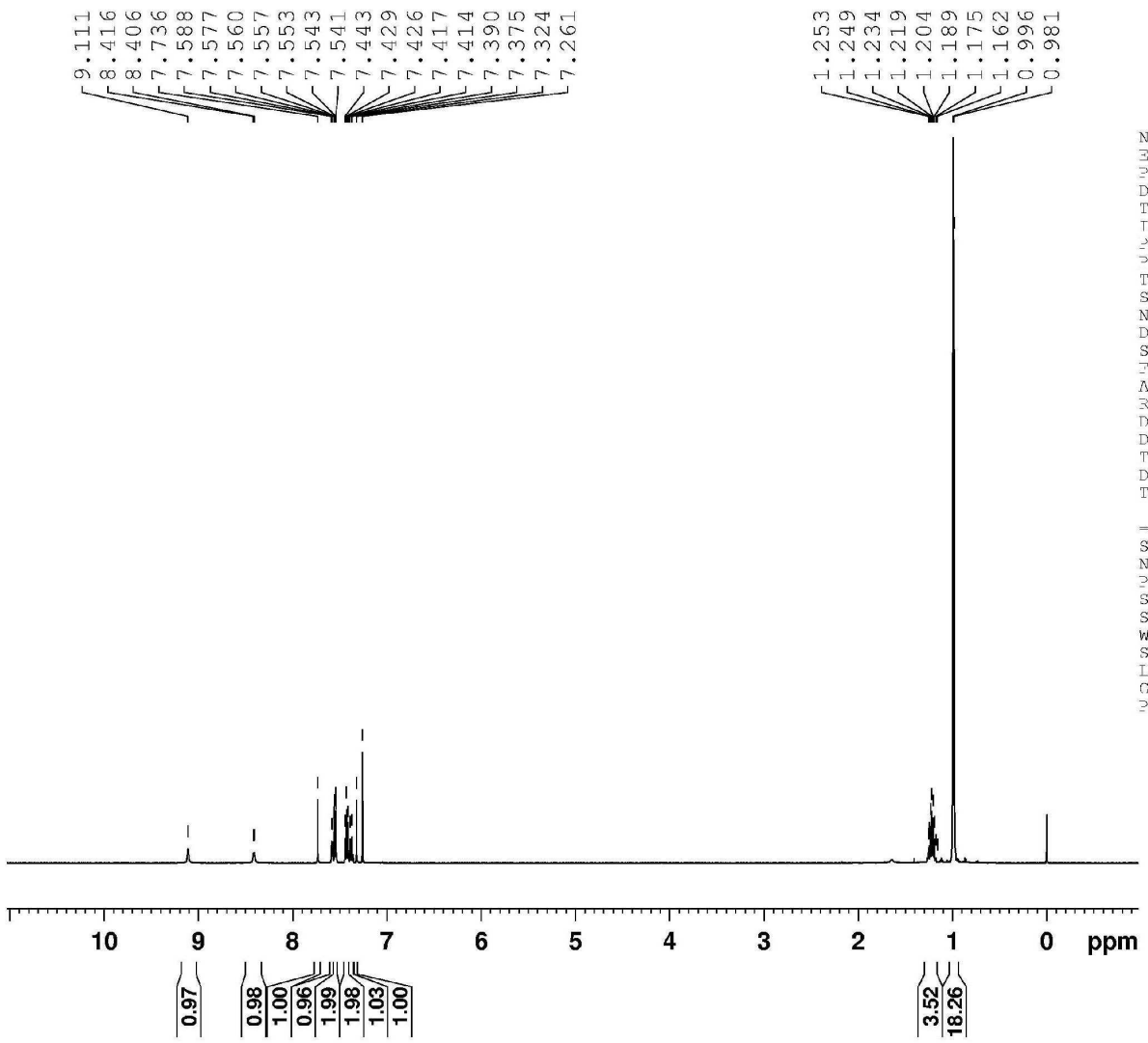
19b



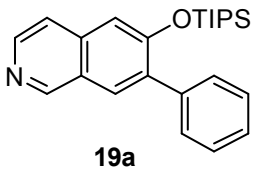

```
Current Data Parameters
NAME       1.ess.225.13C
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140113
Time               15.22
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG            zgdc
TD                142854
SOLVENT            CDCl3
NS                   256
DS                     0
SWH            27777.777 Hz
FIDRES         0.194449 Hz
AQ             2.5714221 sec
RG               11585.2
DW                18.000 usec
DE                 7.50 usec
TE                295.4 K
D1             2.00000000 sec
d11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                  8.50 usec
PL1                 0.00 dB
SFO1         125.7062372 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2              90.00 usec
PL2                 1.00 dB
PL12               21.00 dB
SFO2         499.8734991 MHz

F2 - Processing parameters
SI                 65536
SF           125.6924284 MHz
WDW                   no
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
```



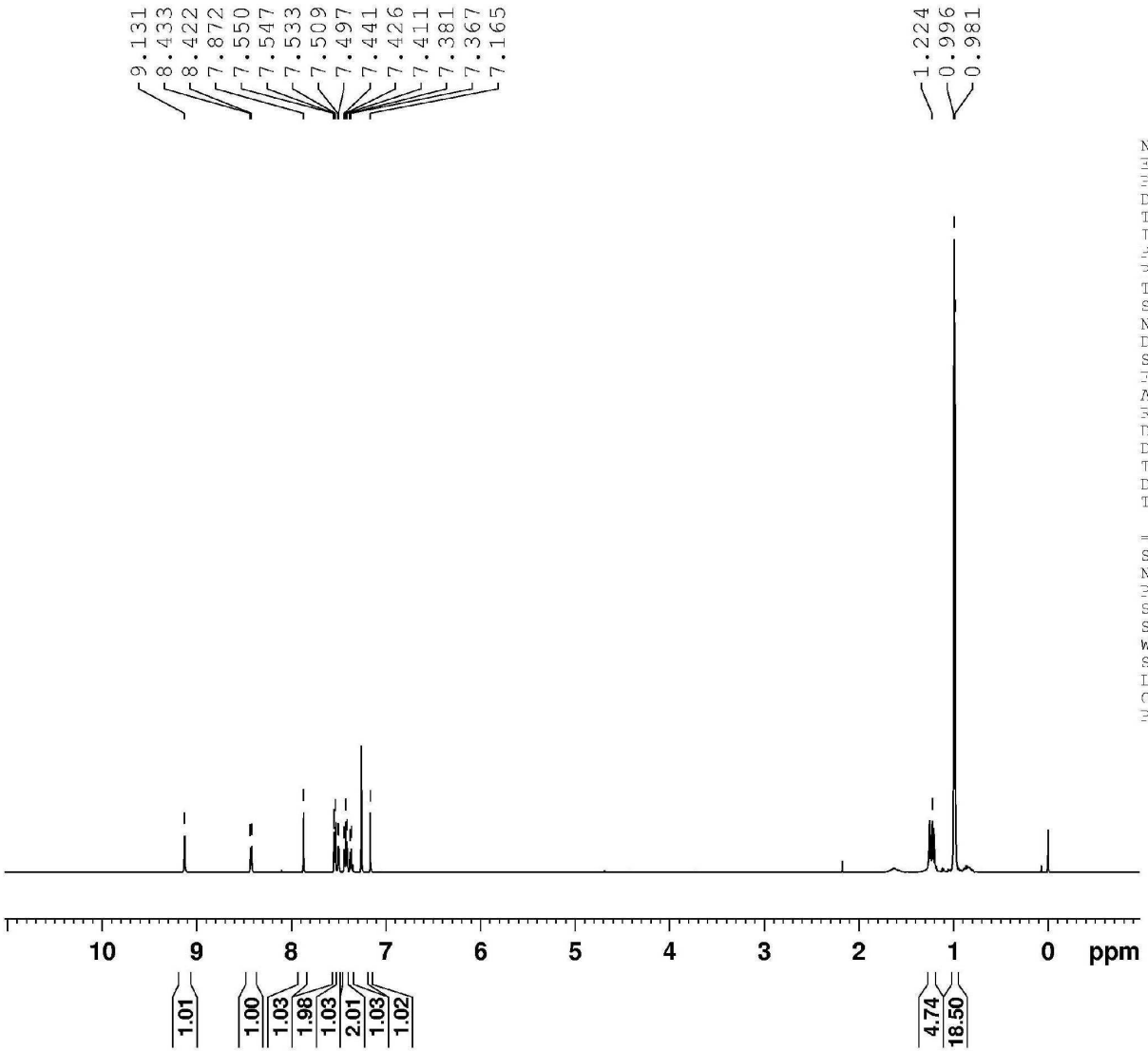
19b



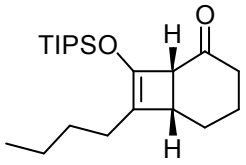
NAME	1.css.232.spota
EXPNO	1
PROCNO	1
Date_	20140123
Time	18.21
INSTRUM	spect
PROBHD	5 mm PATXI 1H/
PULPROG	zg
TD	59998
SOLVENT	CDCl3
NS	8
DS	0
SWH	10000.000 Hz
FIDRES	0.166672 Hz
AQ	2.9999499 sec
RG	110.37
DW	50.000 usec
DE	10.00 usec
TE	295.5 K
D1	5.00000000 sec
TDC	1
======== CHANNEL f1 ========	
SFO1	500.1330885 MHz
NUC1	1H
P1	8.00 usec
SI	65536
SF	500.1300133 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.00



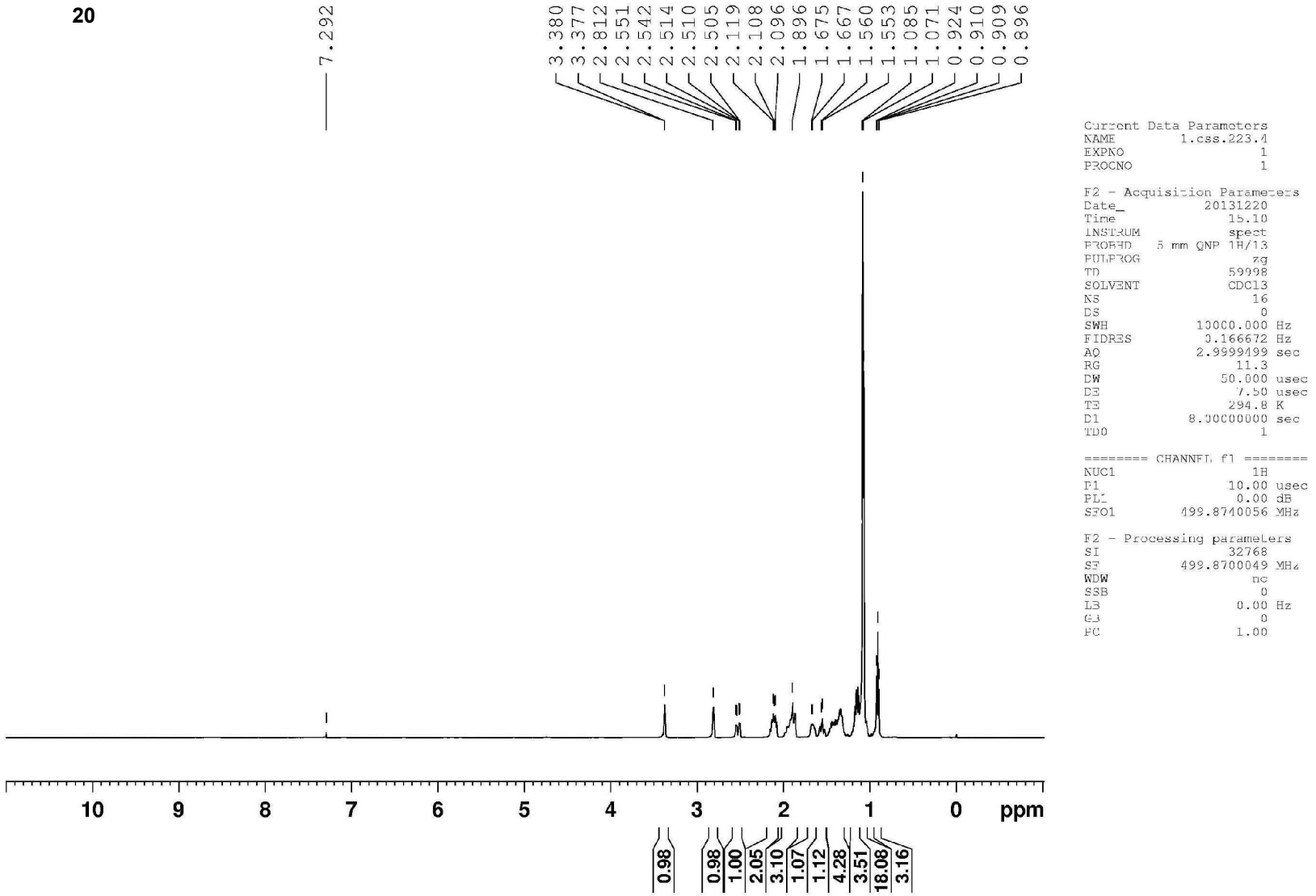
19a



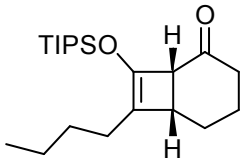

```
NAME          1.css.232.spectb.2
EXPNO                          1
PROCNO                         1
Date_                   20140124
Time                       13.17
INSTRUM                    spect
PROBHD    5 mm PATXI 1H/
PULPROG                       zg
TD                         59998
SOLVENT                    CDCl3
NS                             8
DS                             0
SWH                    10000.000 Hz
FIDRES                 0.166672 Hz
AQ                     2.9999499 sec
RG                         155.5
DW                        50.000 usec
DE                        10.00 usec
TE                        295.5 K
D1                     5.00000000 sec
TDC                            1

======== CHANNEL f1 ========
SFO1                500.1330885 MHz
NUC1                        1H
P1                        8.00 usec
SI                        65536
SF                  500.1300131 MHz
WDW                          no
SSB                           0
LB                         0.00 Hz
GB                            0
PC                         1.00
```



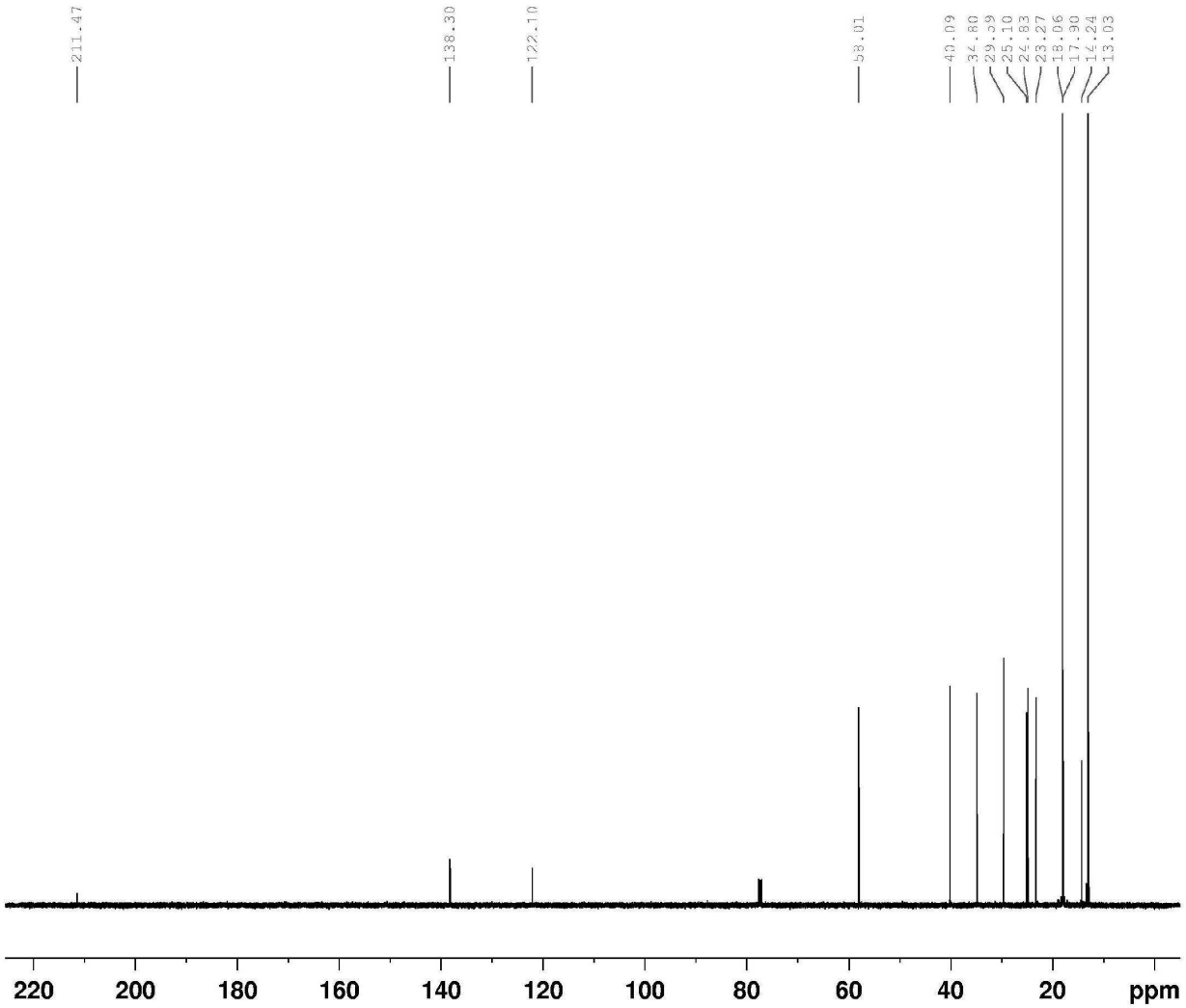
20



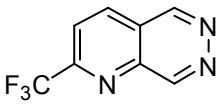

```
Current Data Parameters
NAME          1.css.223.4
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_          20131220
Time               15.10
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG                zg
TD                 59998
SOLVENT            CDCl3
NS                    16
DS                     0
SWH            10000.000 Hz
FIDRES             3.166672 Hz
AQ             2.9999499 sec
RG                  11.3
DW                 50.000 usec
DE                  7.50 usec
TE                294.8 K
D1             8.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.00 usec
PL1                 0.00 dB
SFO1         499.8740056 MHz

F2 - Processing parameters
SI                 32768
SF           499.8700049 MHz
WDW                   nc
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.00
```



20



NAME	1.css.223.13C.2
EXPNO	1
PROCNO	1
Date_	20131220
Time	9.02
INSTRUM	spect
PROBHD	5 mm QNP 1H/13
PULPROG	zgdc
TD	142854
SOLVENT	CDCl3
NS	128
DS	0
SWH	28985.508 Hz
FIDRES	0.202903 Hz
AQ	2.4642815 sec
RG	7298.2
DW	17.250 usec
DE	7.50 usec
TE	295.4 K
D1	2.00000000 sec
d11	0.03000000 sec
TDC	1
======== CHANNEL f1 ========	
NUC1	13C
P1	8.50 usec
PL1	0.00 dB
SFO1	125.7062372 MHz
-------- CHANNEL f2 --------	
CPDPRG2	waltz16
NUC2	1H
PCPD2	90.00 usec
PL2	1.00 dB
PL12	21.00 dB
SFO2	499.8734991 MHz
SI	65536
SF	125.6923718 MHz
WDW	no
SSB	0
LB	0.00 Hz
GB	0
PC	1.40



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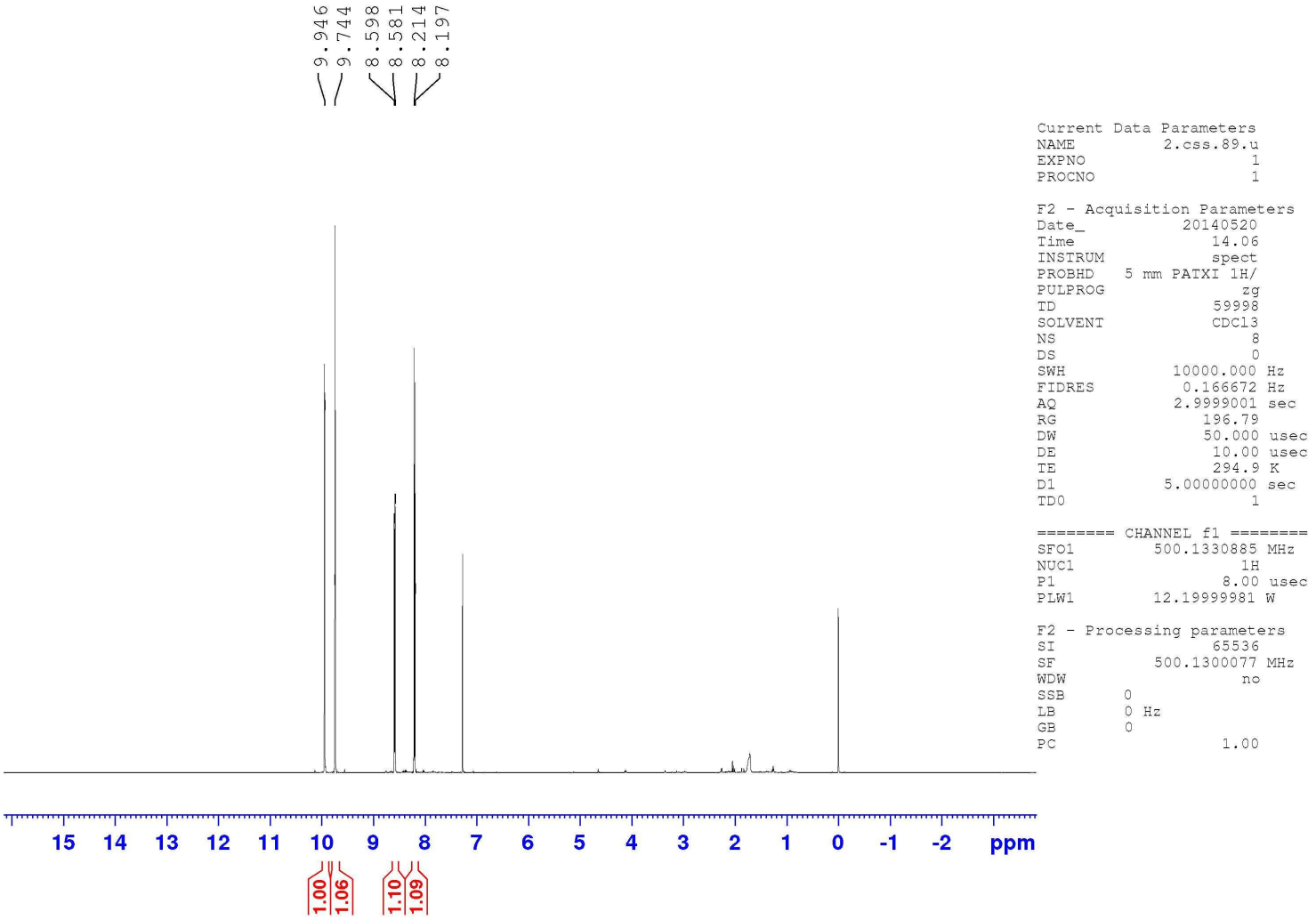
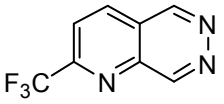
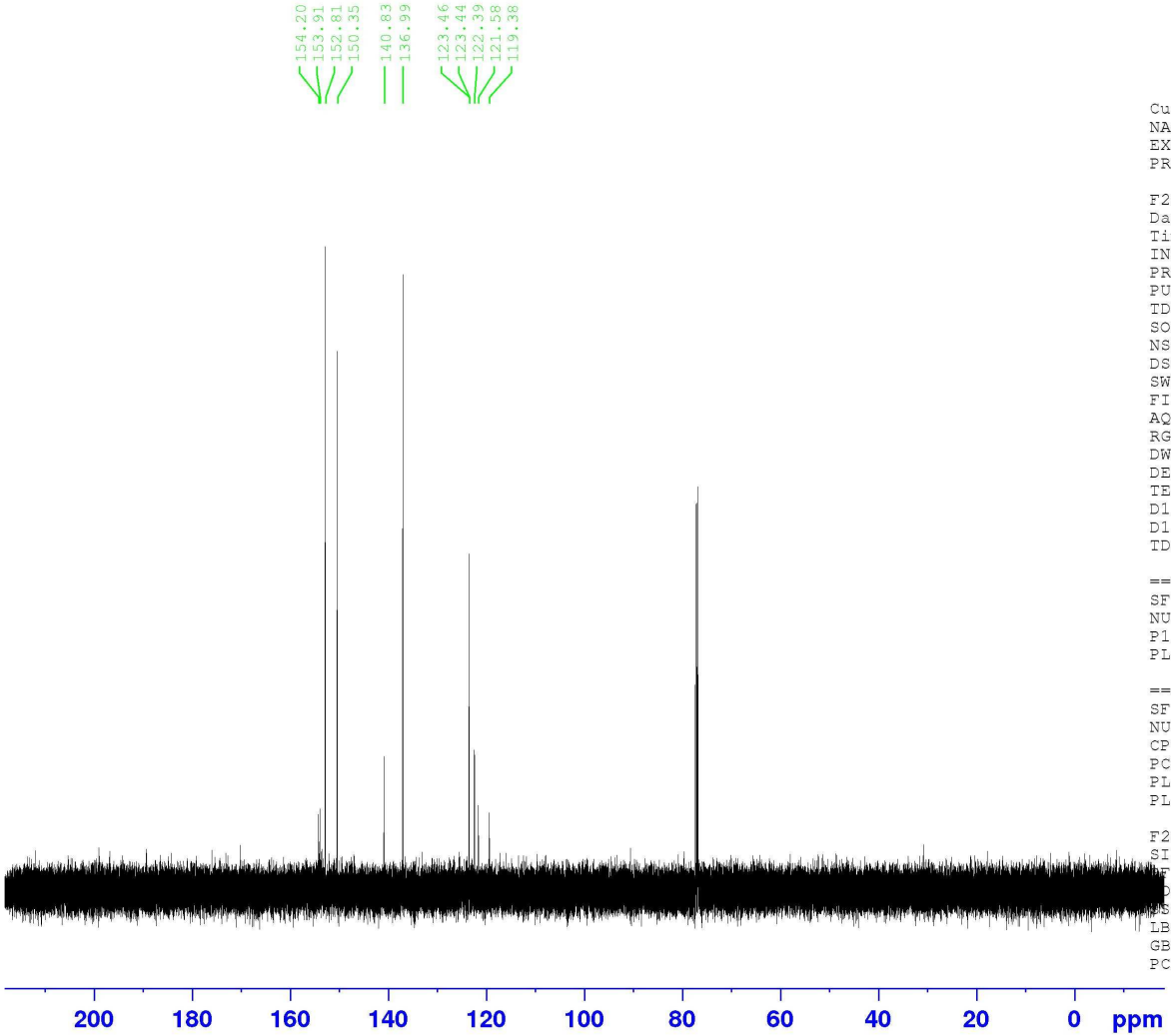


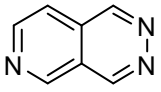

```
Current Data Parameters
NAME          2.css.89.u
EXPNO                  1
PROCNO                 1

F2 - Acquisition Parameters
Date_           20140520
Time               14.06
INSTRUM            spect
PROBHD   5 mm PATXI 1H/
PULPROG               zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES          0.166672 Hz
AQ             2.9999001 sec
RG                196.79
DW                50.000 usec
DE                10.00 usec
TE                294.9 K
D1             5.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                  8.00 usec
PLW1         12.19999981 W

F2 - Processing parameters
SI                 65536
SF           500.1300077 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```



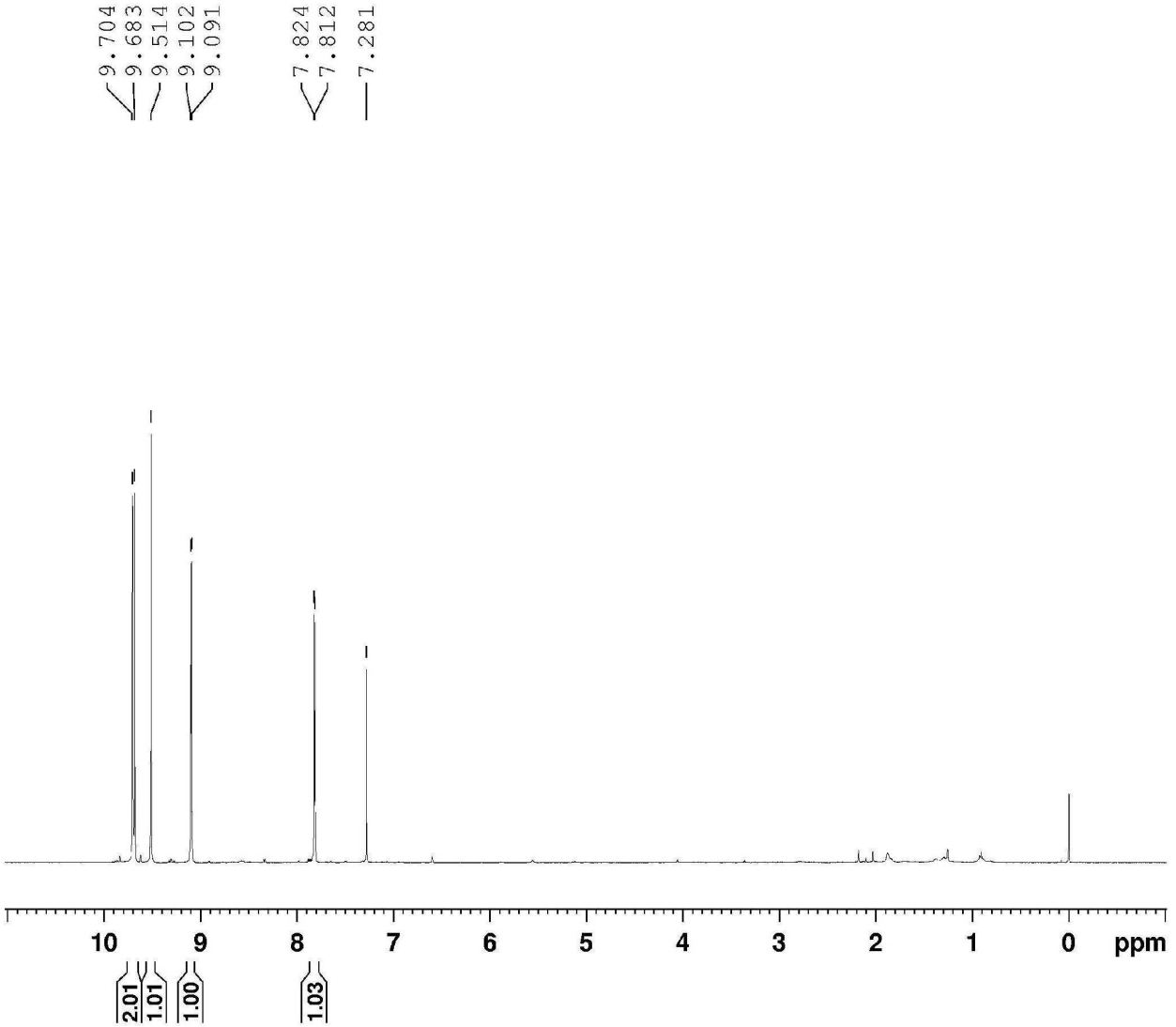
30



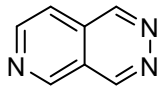

```
Current Data Parameters
NAME       2.css.89.C_13
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_           20140520
Time              16.13
INSTRUM           spect
PROBHD   5 mm PATXI 1H/
PULPROG           zgdc
TD              178568
SOLVENT           CDCl3
NS                  256
DS                    0
SWH           29761.904 Hz
FIDRES         0.166670 Hz
AQ             2.9999423 sec
RG                196.79
DW                16.800 usec
DE                10.00 usec
TE                295.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
SFO1        125.7703643 MHz
NUC1                13C
P1                14.00 usec
PLW1       170.00000000 W

======== CHANNEL f2 ========
SFO2        500.1320005 MHz
NUC2                1H
CPDPRG[2         waltz16
PCPD2             90.00 usec
PLW2         12.19999981 W
PLW12         0.20893000 W

F2 - Processing parameters
SI                131072
SF          125.7577968 MHz
WDW                 no
SSB       0
LB        0 Hz
GB        0
PC                1.40
```



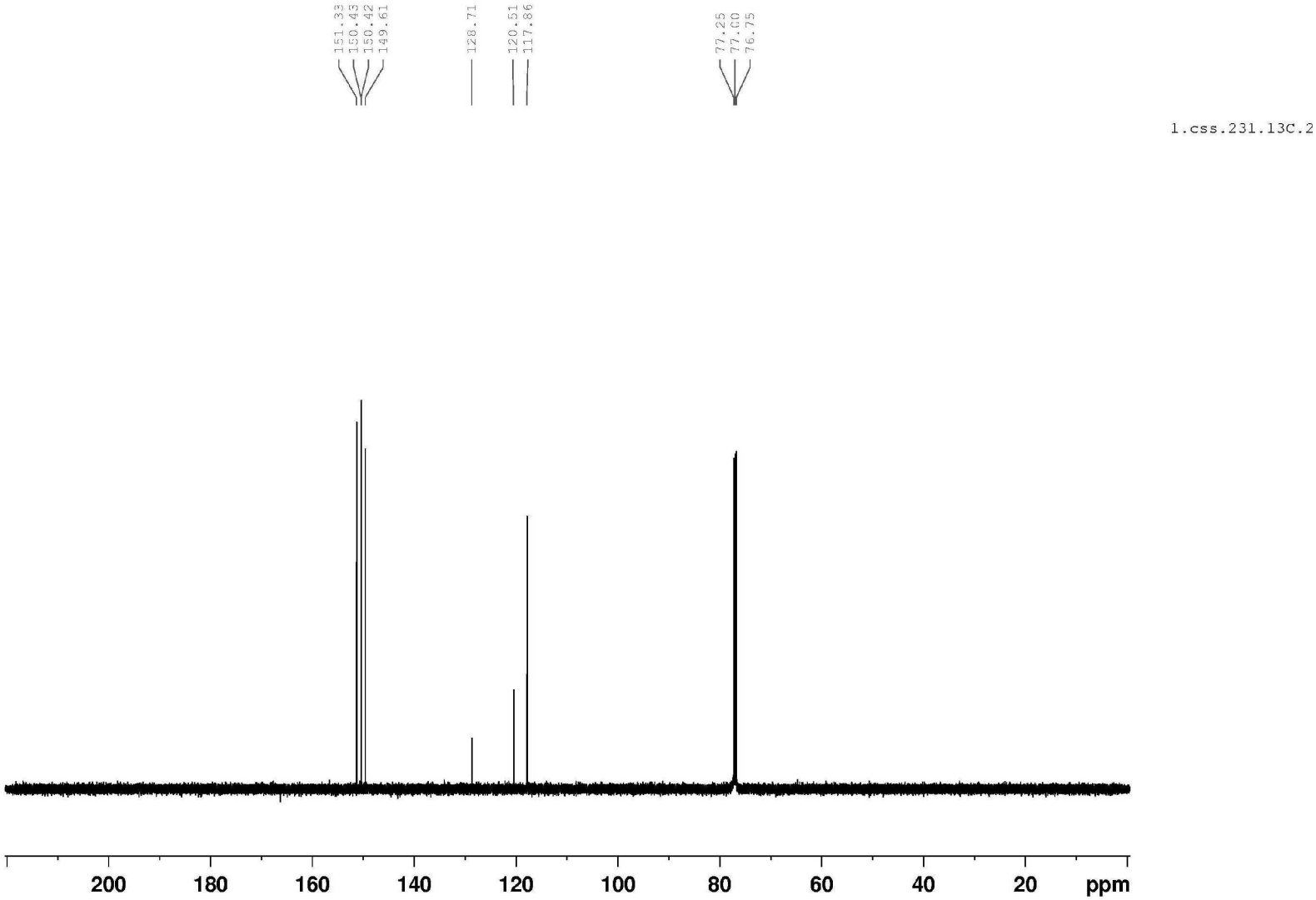
32




```
Current Data Parameters
NAME         1.css.231.1t
EXPNO                   1
PROCNO                  1

F2 - Acquisition Parameters
Date_           20140123
Time               14.52
INSTRUM            spect
PROBHD   5 mm PATX1 1H/
PULPROG                zg
TD                 59998
SOLVENT            CDCl3
NS                     8
DS                     0
SWH            10000.000 Hz
FIDRES         0.166672 Hz
AQ             2.9999001 sec
RG                175.42
DW                50.000 usec
DE                10.00 usec
TE                295.6 K
D1             8.00000000 sec
TD0                    1

======== CHANNEL f1 ========
SFO1         500.1330885 MHz
NUC1                   1H
P1                  8.00 usec
PLW1        12.19999981 W

F2 - Processing parameters
SI                 65536
SF          500.1300030 MHz
WDW                   no
SSB       0
LB        0 Hz
GB        0
PC                 1.00
```



32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150.43
150.42
149.61
128.71
120.51
117.86
77.25
77.00
76.75
1.css.231.13C.2
200
180
160
140
120
100
80
60
40
20
ppm