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Design and Synthesis of a New Class of Twin-Chain Amphiphiles for Self-Assembled Monolayer-based Electrochemical Biosensor Applications

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Abstract

A new class of twin-chain hydroxyalkylthiols (mercaptoalkanols) featuring a nearly constant cross-section and the potential for modification of one or both termini are available with complete regioselectivity through Pd-mediated couplings of benzene diiododitriflate, including an example of a previously unreported coupling to generate an ortho-substituted arene bis acetic acid. Self-assembled monolayers (SAMs) prepared from the new amphiphiles demonstrate improved stability in an electrochemical sensor system compared with monolayers prepared from analogous single chain thiols.

Keywords

amphiphile; multivalent; self-assembled monolayer; thiol; cross-coupling; sensor

Introduction

The use of functionalized amphiphiles is central to a wide array of applications and disciplines.^[1–3] One of the most important classes of amphiphiles is based upon long-chain thiols. The strength of the gold-sulfur interaction, combined with the selectivity of gold for thiols and related functional groups, provides the basis for creation of a robust self-assembled monolayers (SAMs) which can tolerate a diverse array of functionality (commonly, –OH, –N₃, or –CH₃) at the terminus, or “tail” of the amphiphile.^[4] When incorporated in SAM-based electrochemical biosensors, these functionalized amphiphiles serve to passivate and provide stability to the sensing element and/or to tether the sensing element to the surface. The stability of the SAM, and therefore of the sensor, increases with the chain length of the thiol component.^[5] However, in electrochemical biosensor applications, the use of very long chain thiol backbones would result in the formation of highly resistive monolayers consequently impeding electrochemical read-outs. To address this, we now report the synthesis of a new class of arene-crosslinked twin-chain dithiol amphiphiles. The new amphiphiles, which feature a nearly constant cross-section and functionalized termini, form stable SAM-based sensors more capable of withstanding multiple electrochemical perturbations compared to single-chain amphiphiles of similar length.

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The vast majority of amphiphiles utilized for surface passivation or substrate attachment in gold-thiolate biosensors are single-chain mercaptoalkanols (hydroxyalkylthiols),^[6] the limitations of which have been discussed elsewhere.^[7] A number of multidentate thiol-based amphiphiles have also been reported (Figure 1). Amphiphiles based upon multidentate thiols have several advantages over their single-chain counterparts; they absorb more rapidly onto the gold surface and they generate more stable SAMs.^[8, 9] These properties are directly relevant to the performance, stability, and reusability of biosensors. However, existing multidentate thiols either possess unfunctionalized termini, limiting the ability to create functional monolayers; or else feature a significant mismatch between the multivalent “head” and the termini.^[10,11,12] As part of a collaboration targeting creation of SAM-based sensors on nanomaterial surfaces, we became interested in multivalent amphiphiles incorporating functionalized termini and maintaining a nearly constant cross-section down the long axis. Herein, we report the synthesis of a new class of twin-chain thiols, which, upon incorporation in electrochemical biosensors, result in SAMs possessing improved stability compared those prepared from an analogous single-chain thiol

Results and Discussion

Our initial investigations focused on amphiphiles **1** and **2**, which were chosen for comparability to 13- and 11-carbon single-chain thiol amphiphiles, respectively. The key steps in the construction of the molecular frameworks were anticipated to be sequential cross-coupling reactions of diiododitriflate **3** (Scheme 1). Synthesis of the C₁₃ twin-chain amphiphile **1** was based upon research from our lab demonstrating the ability to prepare 1,2,4,5-tetralkynylarenes from **3** with complete regiochemical control through two-fold Sonogashira reactions.^[13] The synthesis of the shorter C₁₁ amphiphile **2** would require a new approach in which the two chains comprising the terminus would be introduced via two-fold cross-coupling of bistriflate with a silyl ketene acetal.

The synthesis of **1** commenced with the two-fold Sonogashira cross-coupling of **3** with the benzyl ether of 4-pentyn-1-ol (Scheme 2). Subsequent coupling of the resulting dialkynylditriflate **4** with the benzoyl ester of 4-pentyn-1-ol generated tetraalkyne **5**. We had originally planned to employ Pd-catalyzed reaction with H₂ to achieve saturation of all four alkynes and hydrogenolytic deprotection of both benzyl ethers. However, reaction at room temperature and atmospheric pressure delivered a mixture of partially saturated products.^[14] Reaction at 40 °C and 2 atm pressure furnished a modest yield (40%, not shown) of diol **6**, accompanied by byproducts which were saturated but retained one (30%) or both (10%) of the benzyl ethers. Although the overall yield could be improved by resubjecting the isolated byproducts to the reaction conditions, we found that complete saturation and deprotection of **5** could be easily achieved in high yield by tandem application of Raney nickel (Raney Ni) and Pd/ H₂. The alcohols of **6** were activated as methanesulfonates, which were displaced with KSAC to provide the bithioester in 74% yield over two steps. Reduction with DIBAL-H removed both the benzoate and thioacetate protecting groups to provide the C₁₃ twin-chain amphiphile (**1**).

The synthesis of the C₁₁ amphiphile **2**, illustrated in Scheme 3, also began with a two-fold Sonogashira coupling of **3**. The product, dialkynylditriflate **7**, was subjected to a Pd-mediated coupling with silyl ketene acetal **8** to provide bisester **9** in moderate yield. Although the coupling of silyl ketene acetals with iodoarenes or aryl triflates has been described, ours is the first example of application to *ortho* bisfunctionalization.^[15] The ketene acetal couplings proved considerably more challenging than the Sonogashira reactions described earlier. Attaining even moderate yields of the two-fold coupling product (**9**) required the use of dry lithium acetate and relatively pure silyl ketene acetal; the latter was frequently contaminated with the *C*-silylated isomer, ethyl 2-trimethylsilylacetate.^[16,17]

However, even after reaction optimization, the monocarboxyethyl/monotriflate derived from a single cross-coupling was often observed as a major byproduct.^[18]

The monotriflate byproduct readily undergoes Sonagashira coupling with simple alkynes (not shown), suggesting a potentially general pathway for introduction of differentially functionalized termini onto future generations of twin-chain amphiphiles. In marked contrast to what we had observed for the tetraalkynylarenes, the bisalkynes are easily saturated using Pd/C and hydrogen to furnish a nearly quantitative yield of the diol **10**, reflecting concomitant desilylation under the protic reaction conditions.^[19] Conversion of **10** to the corresponding diol/dithiol **2** was achieved in good yield as for the C₁₃ substrate above. No oxidative degradation of the thiols was observed during the reaction, workup, or purification process. The twin-chain amphiphiles **1** and **2** are easily handled oils and are stable indefinitely when stored cold in the absence of light and oxygen.

Electrochemical DNA sensor

The synthesized amphiphiles were applied to the fabrication of a folding based electrochemical DNA (E-DNA) sensor. An electrochemically-cleaned gold disc electrode was immersed for 10 minutes in a 2 mM ethanolic solution of either **1**, **2**, or 11-hydroxyundecanethiol. The resulting SAMs were further modified (drop casting, 3 h) with a stem-loop DNA sensing element thiolated at the 5'-terminus and modified with methylene blue (MB) at the 3'-terminus.^[20] The fabricated sensors were then rinsed with DI water and placed in an electrochemical cell where the stability of the sensors was assessed by monitoring the MB current using alternating current voltammetry, (ACV) scanning every 12 hours over a period of 72 hours (Fig. 2). Whereas the sensor prepared with the single chain amphiphile exhibited significant loss of response after 24–36 h, the sensors fabricated with **1** and **2** retained nearly 100% of the original response after 72 h, highlighting the stability of the SAMs derived from the twin-chain amphiphiles.

As a final test of stability, the sensors recovered from the ACV monitoring after 72 h (see above) were challenged/hybridized with 1.0 μM complete complementary target DNA to which all the sensors responded. Upon sensor regeneration with deionized water, the MB signal was also regenerated as would be expected for this class of sensors (Fig. 3).^[20]

Conclusions

A new class of twin-chain amphiphiles has been prepared using routes which should be easily adaptable to a range of backbones and functional groups. The hydroxyl groups of the new amphiphiles, while applied here as part of a wettable passivating layer, provide the foundation for synthesis of functionalized nanomaterials allowing control of nearest neighbour interactions at the surface of the monolayer.

In initial tests, sensors fabricated using the new amphiphiles showed improved stability compared to those prepared from a single chain thiol. Although the terminal hydroxyl groups of the amphiphiles Electrochemical characterization of SAMs derived from **1** and **2**, along with details of the performance of E-DNA sensors fabricated from these amphiphiles, will be reported separately.

Experimental Section

General Information

All reactions were carried out in flame dried glassware under an atmosphere of dry nitrogen with magnetic stirring. Solvents were used as purchased with the exception of THF and CH₂Cl₂, which were distilled from Na/Ph₂CO and CaH₂, respectively. Thin layer

chromatography (TLC) was performed on 0.25 mm hard-layer silica G plates; developed plates were visualized with UV lamp and/or by staining: 1% aq. KMnO_4 (for unsaturated compounds); I_2 (general); or vanillin or phosphomolybdic acid (general, after charring). NMR spectra were obtained in CDCl_3 . ^1H NMR spectra are reported as δ in ppm, (multiplicity, integration, coupling constant(s) in Hz). ^{13}C NMR spectra are reported as δ in ppm. Both ^1H and ^{13}C spectra are referenced to residual CDCl_3 . Infrared spectra were recorded as neat ATR films with selected absorbances reported in wavenumbers (cm^{-1}). HRMS analysis was obtained with the ionization source as listed for each compound. Melting points are uncorrected.

Abbreviations: RBF = round bottom flask; EtOAc = ethyl acetate; Hex = hexane; DMAP = *N,N'*-dimethylaminopyridine.

1,2-Diiodo-4,5-dimethoxybenzene:^[13,21]—To a flame-dried 100 mL RBF equipped with a short air condenser was added H_5IO_6 (0.41 equiv, 25.6 mmol, 5.84 g) and methanol (36 mL). The mixture was stirred at r.t., then I_2 (0.8 equiv, 50.2 mmol, 12.76 g) was added. The reaction was stirred vigorously for 10 min, after which 1,2-dimethoxybenzene (1 equiv, 63 mmol, 8.7 g, 8.0 mL) was added in one portion via syringe. The reaction was heated to 70 °C in an oil bath for 5 h, resulting in the formation of a white solid which made stirring difficult; however, the reaction proceeded even without efficient stirring. The hot solution was poured into dilute aqueous $\text{Na}_2\text{S}_2\text{O}_5$ (~100 mL) and the mixture was cooled to r.t. The solid collected by filtration through a glass frit was washed quickly with two 30 mL portions of cold MeOH and dried *in vacuo* to afford the diiodoarene (21.07 g, 54 mmol, 86%) as a white solid that was deemed pure by NMR and used without further purification. $R_f = 0.49$, 20% EtOAc/Hex. Mp = 134.5–136.0 °C. ^1H NMR (600 MHz): δ 7.25 (s, 2H), 3.85 (s, 6H). ^{13}C NMR (150 MHz): δ 149.6, 121.7, 96.1, 56.2.

1,2-Dihydroxy-4,5-diiodobenzene:^[13,22]—A flame-dried 250 mL RBF was charged with 1,2-diiodo-4,5-dimethoxybenzene (1 equiv, 10 mmol, 3.90 g) and then evacuated/backfilled with nitrogen (3 \times) before addition of CH_2Cl_2 (70 mL). The solution was cooled to 0 °C and BBr_3 (2.5 equiv, 25 mmol, 25 mL of a 1.0 M solution in CH_2Cl_2) was added via syringe pump over 20 min. The reaction was stirred at 0 °C for 4 h then quenched with H_2O (50 mL). The separated aqueous layer was extracted with Et_2O (2 \times 75 mL). The combined organic layers were dried with MgSO_4 , filtered through a pad of silica, and concentrated *in vacuo* to afford the dihydroxy diiodobenzene (3.61 g, 9.99 mmol, quantitative) as an off-white solid that was deemed pure by NMR and used without further purification. $R_f = 0.50$, 50% EtOAc/Hex. Mp = 116.0–116.5 °C. ^1H NMR (400 MHz, acetone- d_6): δ 8.48 (bs, 2H), 7.38 (s, 2H). ^{13}C NMR (150 MHz, acetone- d_6): δ 146.5, 125.6, 93.7.

4,5-Diiodo-1,2-phenylene bistrifluoromethanesulfonate (3):^[13]—To a flame-dried 100 mL RBF was added 1,2-dihydroxy-4,5-diiodobenzene (1 equiv, 7.85 mmol, 2.84 g), CH_2Cl_2 (55 mL), and pyridine (5 equiv, 39 mmol, 3.10 g, 3.16 mL). The solution was cooled to 0 °C and Tf_2O (2.2 equiv, 17.3 mmol, 4.88 g, 2.91 mL) was added dropwise via syringe over 10 min. The reaction was stirred for 6 h while warming to ambient temperature, then cooled to 0 °C and quenched with H_2O (30 mL). The separated aqueous layer was extracted with CH_2Cl_2 (2 \times 30 mL). The combined organic layers were dried with MgSO_4 and filtered through a tall pad of silica. The pad was washed carefully with CH_2Cl_2 to avoid the elution of impurities, and the filtrate was concentrated *in vacuo* to afford **3** (4.90 g, 7.82 mmol, quantitative) as an off-white solid that was deemed pure by NMR and used without further purification. (Note: For reaction runs in which small amounts of impurities were observed after filtration, the product could be obtained in pure form following column chromatography utilizing 10% EtOAc/Hex as the mobile phase.) $R_f = 0.60$, 10% EtOAc/

Hex. Mp = 46.5–47.7 °C. ^1H NMR (400 MHz): δ 7.91 (s, 2H). ^{13}C NMR (100 MHz): δ 139.6, 133.4, 118.5 (q, $J_{\text{C},\text{F}} = 321.0$ Hz), 108.0. FTIR: 1429, 1335, 1215, 1125, 1105, 868, 788, 745, 689 cm^{-1} . HRMS-ESI: calc. for $\text{C}_8\text{H}_2\text{F}_6\text{I}_2\text{NaO}_6\text{S}_2$ ($\text{M}+\text{Na}$) $^+$: 648.7184; found: 648.7164.

5-Benzyloxypentyne:^[23]—To a flame dried 250 mL RBF was added NaH (2 equiv, 47.6 mmol, 1.9 g of a 60% dispersion in mineral oil). The solid was washed with hexanes (15 mL). THF (95 mL) was added and the suspension was cooled to 0 °C. Pentynol (1 equiv, 23.8 mmol, 2.0 g) was added dropwise in THF (5 mL). BnBr (0.92 equiv, 21.9 mmol, 2.60 mL) was added dropwise. The reaction was allowed to come to r.t. over 16 h and then quenched with sat. aq. NH_4Cl (25 mL). The mixture was diluted with H_2O (20 mL) and extracted with EtOAc (2 \times 40 mL). The brine-washed (40 mL) organic layer was dried with Na_2SO_4 and concentrated *in vacuo*. Purification via flash chromatography (4% EtOAc/Hex) afforded the benzyl ether (3.60 g, 20.7 mmol, 94%) as a colorless liquid: $R_f = 0.41$, 5% EtOAc/Hex. ^1H NMR (300 MHz): δ 7.29–7.44 (5H), 4.55 (s, 2H), 3.61 (t, 2H, $J = 6.2$ Hz), 2.36 (td, 2H, $J = 7.1, 2.6$ Hz), 1.97 (t, 1H, $J = 2.6$ Hz), 1.81–1.93 (m, 2H). ^{13}C NMR (75 MHz): δ 138.5, 128.4, 127.63, 127.58, 84.0, 73.0, 68.7, 68.5, 28.7, 15.3. CAS: 57618-47-0.

4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene

bistrifluoromethanesulfonate (4):^[13]—A flame dried 20 mL vial fitted with a screw-cap septa was charged with $\text{PdCl}_2(\text{PPh}_3)_2$ (0.06 equiv, 0.12 mmol, 84 mg), CuI (0.12 equiv, 0.24 mmol, 45.6 mg), and 4-pentynol (1 equiv, 2 mmol, 1.25 g). The vessel was evacuated/backfilled with nitrogen (3 \times), after which were sequentially added THF (4 mL), Et_3N (3 equiv, 6 mmol, 0.85 mL), and 5-benzyloxypentyne (2.3 equiv, 4.6 mmol, 802 mg) in 1 mL THF. The reaction was stirred for 3 h at r.t., filtered through a pad of silica, which was washed with Et_2O , concentrated *in vacuo*, and purified via flash chromatography (step gradient Hex to 10% EtOAc/Hex) to afford **4** (1.14 g, 1.59 mmol, 79%). $R_f = 0.27$, 10% EtOAc/Hex. ^1H NMR (600 MHz): δ 7.42 (s, 2H), 7.27–7.39 (10H), 4.56 (s, 4H), 3.65 (t, 4H, $J = 6.0$ Hz), 2.62 (t, 4H, $J = 7.1$ Hz), 1.92–1.98 (m, 4H). ^{13}C NMR (150 MHz): δ 138.8, 138.3, 128.4, 128.2, 127.59, 127.56, 126.3, 121.7, 119.6, 117.5, 115.3, 98.1, 77.4, 73.0, 68.5, 28.6, 16.5. FTIR: 2859, 2230, 1489, 1433, 1210, 1178, 1135, 1080, 732 cm^{-1} . HRMS-ESI: calc. for $\text{C}_{32}\text{H}_{28}\text{F}_6\text{O}_8\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 741.1027; found: 741.1039.

5-Benzoyloxypentyne:^[24]—To a flame dried 100 mL RBF was added pentynol (1 equiv, 24 mmol, 2.0 g) and CH_2Cl_2 (80 mL). The reaction was cooled to 0 °C and BzCl (1.2 equiv, 28 mmol, 3.3 mL) was added dropwise, followed by DMAP (0.1 equiv, 2.4 mmol, 300 mg), and Et_3N (7 mL). The reaction was allowed to come to r.t. over 12 h, and then quenched with 2 N HCl (10 mL). The EtOAc extract (2 \times 40 mL) was washed with brine (40 mL) and dried with Na_2SO_4 . The residue obtained upon concentration *in vacuo* was purified via flash chromatography (2.5% EtOAc/Hex) to afford the protected alkynol (4.02 g, 21.4 mmol, 89%) as a colorless oil. $R_f = 0.57$, 10% EtOAc/Hex. ^1H NMR (600 MHz): δ 8.03–8.07 (2H), 7.53–7.60 (1H), 7.42–7.48 (2H), 4.44 (t, 2H, $J = 6.1$ Hz), 2.40 (td, 2H, $J = 7.3, 2.7$ Hz), 1.98–2.05 (overlapping signals, 3H). ^{13}C NMR (150 MHz): δ 166.5, 132.9, 130.3, 129.6, 128.3, 83.0, 69.1, 63.4, 27.7, 15.4. CAS: 5390-04-5.

4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene-bis(pent-4-yne-1-ol-5-yl,

benzoate ester) (5)—A flame dried 20 mL vial fitted with a screw-cap septa was charged with $\text{PdCl}_2(\text{PPh}_3)_2$ (0.12 equiv, 0.18 mmol, 127 mg), CuI (0.30 equiv, 0.45 mmol, 89.4 mg), and Bu_4NI (3 equiv, 4.5 mmol, 1.65 g). The vessel was evacuated/backfilled with nitrogen 3 \times and the solution was allowed to stir for 5 min at r.t, followed by the addition of bistriflate **4** in a 5:1 mixture of DMF/ Et_3N (7 mL). The mixture was stirred for 5 min at r.t., and 5-benzoyloxypentyne (4.1 equiv, 6.1 mmol, 980 mg) was then added in 1.5 mL of 5:1 DMF/

Et₃N. The reaction was heated to 70 °C (oil bath) for 5.5 h and then cooled to r.t. The crude reaction mixture was filtered through a pad of silica, which was washed with Et₂O. The filtrate was concentrated *in vacuo*, and the residue purified via flash chromatography (15% EtOAc/Hex) to afford **5** (930 mg, 1.17 mmol, 79%) as a colorless oil. *R_f* = 0.39, 20% EtOAc/Hex. ¹H NMR (600 MHz): δ 8.04–8.10 (4H), 7.54–7.60 (2H), 7.42–7.47 (4H), 7.39–7.41 (2H), 7.33–7.38 (8H), 7.27–7.31 (2H), 4.55 (s, 4H), 4.53 (t, 4H, *J* = 6.3 Hz), 3.66 (t, 4H, *J* = 6.2 Hz), 2.70 (t, 4H, *J* = 7.0 Hz), 2.60 (t, 4H, *J* = 7.0 Hz), 2.11 (quint, 4H, 6.6 Hz), 1.94 (quint., 4H, *J* = 6.6 Hz). ¹³C NMR (150 MHz): δ 166.5, 138.5, 135.3, 133.0, 130.2, 129.6, 128.38, 128.36, 127.60, 127.56, 125.3, 124.9, 95.0, 93.9, 79.6, 79.1, 73.0, 68.7, 63.7, 28.9, 28.0, 16.7, 16.6. FTIR: 3675, 2988, 2972, 2901, 2229, 1716, 1451, 1394, 1269, 1107, 1068, 1027, 900 cm⁻¹. HRMS-ESI: calc. for C₅₄H₅₀O₆Na (M+Na)⁺: 817.3505; found: 817.3503. Note: This procedure differs from a previous report in the use of 12 mol% PdCl₂(PPh₃)₂ rather than 6 mol%.^[13]

1,2-Bis(5-benzoyloxy)pentyl-4,5-bis(5-hydroxypentyl)benzene (6)—Raney Ni (120 mg, 50% in water) was added to an 8 mL vial. The solid was collected on a stir bar and washed with MeOH (3 × 5 mL). The vial was then fitted with a screw-cap septa and charged with a solution of **5** (1 equiv, 0.25 mmol, 199 mg) in 4 mL of 3:1 MeOH/EtOAc. The vial was placed under an atm of H₂ (balloon) and the reaction was stirred for 16 h. The reaction mixture was filtered through a silica plug and the filtrate was concentrated under vacuum. The residue was taken up in 3 mL THF and added to an 8 mL vial which had been charged with 20 mg of 10 wt% Pd/C. The reaction was placed under an atm of H₂ for 16 h and then filtered through a silica plug. The filtrate was concentrated *in vacuo*, and purified via flash chromatography (55% EtOAc/Hex) to afford **6** (129 mg, 0.21 mmol, 82%) as a colorless oil. *R_f* = 0.30, 60% EtOAc/Hex. ¹H NMR (600 MHz): δ 8.04–8.10 (4H), 7.54–7.61 (2H), 7.42–7.50 (4H), 6.94 (s, 2H), 4.36 (t, 4H, *J* = 6.7 Hz), 3.67 (t, 4H, *J* = 6.6 Hz), 2.53–2.68 (8H), 1.80–1.91 (6H), 1.53–1.72 (16H), 1.44–1.51 (4H). ¹³C NMR (150 MHz): δ 166.7, 137.6, 137.3, 132.8, 130.4, 129.9, 129.5, 128.3, 65.0, 62.7, 32.5, 32.21, 32.15, 31.2, 30.9, 28.6, 26.1, 25.8. FTIR: 3776, 2988, 2972, 2901, 1717, 1334, 1271, 1067, 1057, 1028 cm⁻¹. HRMS-ESI: calc. for C₄₀H₅₄O₆Na (M+Na)⁺: 653.3818; found: 653.3823.

1,2-Bis(5-benzoyloxy)pentyl-4,5-bis(5-methansulfonyl)pentyl benzene—To a flamed-dried 20 mL vial fitted with a screw-cap septa was added **6** (1 equiv, 0.34 mmol, 215 mg), CH₂Cl₂ (4 mL), and Et₃N (4 equiv, 1.36 mmol, 0.19 mL). DMAP (0.1 equiv, 0.034 mmol, 4.2 mg) was added followed by the dropwise addition of MsCl (3 equiv, 1.02 mmol, 0.08 mL). The reaction was stirred for 3 h and quenched with sat. aq. NaHCO₃ (10 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were washed with H₂O (20 mL), dried with Na₂SO₄, concentrated *in vacuo*, and purified via flash chromatography (45% EtOAc/Hex) to afford the bismethanesulfonate (294 mg, 0.37 mmol, 91%) as a colorless oil. *R_f* = 0.27, 40% EtOAc/Hex. ¹H NMR (600 MHz): δ 8.01–8.11 (4H), 7.54–7.62 (2H), 7.46 (t, 4H, *J* = 7.6), 6.92 (s, 2H), 4.35 (t, 4H, *J* = 6.6 Hz), 4.26 (t, 4H, *J* = 6.6 Hz), 3.02 (s, 6H), 2.60 (bt, 4H, *J* = 8.0 Hz), 2.57 (bt, 4H, *J* = 8.0), 1.77–1.88 (8H), 1.48–1.70 (16H). ¹³C NMR (150 MHz): δ 166.7, 137.6, 137.3, 132.9, 130.5, 129.9, 129.5, 128.3, 70.1, 65.0, 37.4, 32.2, 32.1, 31.1, 30.8, 29.1, 28.7, 26.2, 25.6. FTIR: 2937, 1714, 1352, 1272, 1173, 1114, 1070, 944, 908 cm⁻¹. HRMS-ESI: calc. for C₄₂H₅₈O₁₀S₂Na (M+Na)⁺: 809.3369; found: 809.3367.

1,2-Bis(5-benzoyloxy)pentyl-4,5-bis(5-(acetylthiyl)pentyl) benzene—To a flame dried 8 mL vial fitted with screw-cap septa was added the bis methanesulfonate (1 equiv, 0.282 mmol, 222 mg) and DMF (2.5 mL), followed by KSAc (3 equiv, 0.85 mmol, 97 mg). The reaction was stirred for 14 h and then diluted with Et₂O (20 mL) and H₂O (10 mL). The layers were separated and the organic layer was washed with sat. aq. NaHCO₃ (3 × 10 mL),

dried with Na₂SO₄, concentrated *in vacuo*, and purified via flash chromatography (10% EtOAc/Hex) to afford the bis thioacetate (170 mg, 0.228 mmol, 81%) as a colorless oil. $R_f = 0.32$, 15% EtOAc/Hex. ¹H NMR (600 MHz): δ 8.07 (d, 4H, $J = 7.3$ Hz), 7.58 (t, 2H, $J = 7.4$ Hz), 7.46 (t, 4H, $J = 7.8$ Hz), 6.92 (s, 2H), 4.36 (t, 4H, $J = 6.7$ Hz), 2.90 (t, 4H, $J = 7.3$ Hz), 2.60 (bt, 4H, $J = 7.9$ Hz), 2.55 (bt, 4H, $J = 7.9$ Hz), 2.35 (s, 6H), 1.80–1.89 (8H), 1.54–1.70 (8H), 1.44–1.51(4H). ¹³C NMR (150 MHz): δ 195.9, 166.7, 137.5, 137.3, 132.8, 130.5, 129.9, 129.5, 128.3, 65.0, 32.3, 32.2, 31.1, 30.9, 30.7, 29.5, 29.1, 28.7, 26.3. FTIR: 3684, 3675, 2988, 2972, 2901, 1717, 1688, 1406, 1394, 1383, 1230, 1057, 1028 cm⁻¹. HRMS-ESI: calc. for C₄₄H₅₈O₆S₂Na (M+Na)⁺: 769.3573; found: 769.3568.

1,2-Bis(5-hydroxypentyl)-4,5-bis(5-thiylpentyl)benzene (1)—A flame dried 8 mL vial fitted with a screw-top cap was charged with the bithioacetate (1 equiv, 0.193 mmol, 144 mg) and THF (2.5 mL). *i*-Bu₂AlH (DIBAL-H) (12 equiv, 2.3 mmol, 1.55 mL of a nominally 1.5 M solution in toluene) was added dropwise. The reaction was stirred at r.t. for 2.5 h, cooled to 0 °C, and quenched by the careful addition of 2N HCl (4 mL). The solution was diluted with H₂O (10 mL) and extracted with Et₂O (3 × 10 mL). The organic layers were washed with brine (10 mL) and dried with Na₂SO₄. The residue obtained upon concentrated *in vacuo* was purified via flash chromatography (50% EtOAc/Hex) to afford **1** (74 mg, 0.163 mmol, 84%) of a colorless oil. $R_f = 0.19$, 45% EtOAc/Hex. ¹H NMR (600 MHz): δ 6.92 (s, 2H), 3.68 (t, 4H, 6.6 Hz), 2.53–2.61 (12H), 1.56–1.72 (18H), 1.45–1.53 (8H), 1.37 (t, 2H, $J = 7.9$ Hz). ¹³C NMR (150 MHz): δ 137.6, 137.4, 129.9, 62.9, 33.9, 32.6, 32.3, 32.2, 31.2, 30.8, 28.5, 25.9, 24.6. FTIR: 3353, 2930, 2857, 2358, 2338, 1775, 1460, 1143 cm⁻¹. HRMS-ESI: calc. for C₂₆H₄₆O₂S₂Na (M+Na)⁺: 477.2837; found: 477.2821.

6-(tert-Butyldimethylsilyloxy)hexyne:^[25]—A flame dried 100 mL RBF was charged with hexynol (1 equiv, 25.5 mmol, 2.50 g), CH₂Cl₂ (60 mL), TBSCl (1.1 equiv, 28.1 mmol, 4.23 g), and imidazole (2.2 equiv, 56.1 mmol, 3.82 g). The reaction was stirred for 1.5 h, and then quenched with 40 mL sat. aq. NaHCO₃. The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were dried with Na₂SO₄, concentrated *in vacuo*, and filtered through a pad of silica to afford the silyl-protected alkyne (4.93 g, 23.2 mmol, 91%) as a colorless oil. $R_f = 0.70$, 5% EtOAc/Hex. ¹H NMR (400 MHz): δ 3.65 (t, 2 H, $J = 6.0$ Hz), 2.24 (td, 2 H, $J = 6.8, 2.7$ Hz), 1.96 (t, 1 H, $J = 2.5$ Hz), 1.56–1.70 (2 H), 0.92 (s, 9 H), 0.07 (s, 6 H). ¹³C NMR (100 MHz): δ 84.5, 68.2, 62.6, 31.8, 25.9, 25.0, 18.3, 18.2, -5.3. CAS: 73448-13-2.

4,5-Bis[6-(tert-butyldimethylsilyloxy)hex-1-ynyl]-1,2-phenylene bis(trifluoromethanesulfonate) (7)—A flame dried 20 mL vial fitted with a screw-cap septa was charged with PdCl₂(PPh₃)₂ (0.06 equiv, 0.18 mmol, 126 mg), CuI (0.12 equiv, 0.36 mmol, 68 mg), and **3** (1 equiv, 3 mmol, 1.88 g). The vessel was evacuated/backfilled with nitrogen 3 ×, after which were sequentially added THF (5 mL), Et₃N (3 equiv, 9 mmol, 1.29 mL), and 6-(tert-Butyldimethylsilyloxy)hexyne (2.3 equiv, 6.9 mmol, 1.46 g; as a solution in 2.5 mL THF). The reaction was stirred for 3 h at r.t. and then filtered through a pad of silica, which was washed with Et₂O. The filtrate was concentrated *in vacuo* and the residue was purified via flash chromatography (step gradient, 0 to 2% EtOAc/Hex) to afford **7** (2.29 g, 2.29 mmol, 96%) as a colorless oil. $R_f = 0.27$, 2.5 % EtOAc/Hex. ¹H NMR (400 MHz): δ 7.44 (s, 2 H), 3.66–3.72 (4 H), 2.49–2.61 (4 H), 1.66–1.77 (8 H), 0.92 (s, 18 H), 0.08 (s, 12 H). ¹³C NMR (150 MHz): δ 138.8, 128.3, 126.3, 118.5 (q, $J_{C,F} = 320.9$ Hz), 98.6, 77.3, 62.5, 31.9, 25.9, 24.9, 19.4, 18.3, -5.3. FTIR: 2945, 2930, 2858, 2230, 1489, 1436, 11247, 1211, 1179, 1137, 1087, 834, 807, 774 cm⁻¹. HRMS (ESI): calcd. for C₃₂H₄₈F₆O₈S₂Na [M + Na]⁺ 817.2131; found 817.2120.

((1-Ethoxyvinyl)oxy)trimethylsilane (8):^[26]—To a flame-dried 250 mL RBF was added *i*Pr₂NH (1.2 equiv, 34.1 mmol, 4.8 mL) and THF (33 mL). The solution was cooled to 0 °C, and BuLi (1.1 equiv, 31.2 mmol, 19.5 mL of a nominally 1.6 M solution in Hexane) was added dropwise. The mixture was stirred for 15 min and then cooled to –78 °C. A mixture of EtOAc (1 equiv, 28.4 mmol, 2.8 mL) and TMSCl (1.2 equiv, 34.3 mmol, 4.4 mL) in THF (15 mL) was added over 5 min and the cooling bath was removed. The reaction was allowed to warm to r.t. and stirred for 4 h, after which solvent was removed *in vacuo*. The residue is taken up in 50 mL of Hex and filtered through a pad of Celite, which was washed with two 15 mL portions of Hex. Concentration *in vacuo* followed by distillation (70–80 °C, 40–50 torr) provided **8** as a colorless liquid (see NMR for approx. composition). CAS: 18295-66-4.

4,5-Bis[6-((tert-butylidimethylsilyl)oxy)hex-1-ynyl]-1,2-phenylene

bis(trifluoromethanesulfonate) (9)—A flame-dried 8 mL vial fitted with a screw-top septa cap was charged with Pd(PPh₃)₄ (0.15 equiv, 0.075 mmol, 87 mg) and anhydrous LiOAc (4 equiv, 2 mmol, 133 mg). The vessel was evacuated and backfilled with dry N₂ three times, followed by the addition of **7** (1 equiv, 0.5 mmol, 398 mg) and **8** (4 equiv (based on mass, ca. 75% purity by ¹H NMR), 2 mmol, 321 mg) in 3.5 mL THF. The sealed reaction vessel was placed in a 70 °C oil bath for 5 h and then cooled to r.t. before dilution with 10 mL H₂O and 10 mL EtOAc. The separated aqueous layer was extracted with EtOAc (2 × 10 mL) and the combined organic layers were washed with brine (1 × 20 mL) and dried with Na₂SO₄. The residue obtained upon concentrated *in vacuo* was purified *via* flash chromatography (8% EtOAc/Hex) to afford **9** (134 mg, 0.20 mmol, 40%) as a colorless oil. R_f = 0.30, 10% EtOAc/Hex. ¹H NMR (400 MHz): δ 7.28 (s, 2H), 4.14 (q, 4H, *J* = 7.1 Hz), 3.68 (t, 4H, *J* = 5.8 Hz), 3.64 (s, 4H), 2.49 (t, 4H, *J* = 6.5 Hz), 1.64–1.78 (8H), 1.25 (t, 6H, *J* = 7.1 Hz), 0.92 (s, 18H), 0.07 (s, 12H). ¹³C NMR (150 MHz): δ 170.8, 134.1, 132.5, 125.5, 94.0, 79.3, 62.7, 61.0, 38.7, 31.9, 26.0, 25.2, 19.4, 18.4, 14.1, –5.3. FTIR: 2987, 2856, 1735, 1250, 1211, 1102, 1030, 833, 773 cm⁻¹. HRMS-ESI: calc. for C₃₈H₆₂O₆Si₂Na (M+Na)⁺: 693.3983; found: 693.3961.

Diethyl 2,2'-(4,5-bis(6-hydroxyhexyl)-1,2-phenylene)diacetate (10)—A flame-dried 20 mL vial fitted with a screw-cap septa was charged with 10% (w/w) Pd/C (10 mg), followed by the addition of a solution of **9** (1 equiv, 0.155 mmol, 103 mg) in 8 mL 1:1 MeOH:EtOAc. The reaction was placed under an atmosphere of H₂ (balloon) and stirred for 18 h. The solution obtained after filtration through a pad of Celite was concentrated *in vacuo* to provide **10** (66 mg, 0.149 mmol, 97%) as a colorless oil. R_f = 0.41, 75% EtOAc/Hex. ¹H NMR (600 MHz): δ 7.03 (s, 2H), 4.15 (q, 4H, *J* = 7.1 Hz), 3.63–3.70 (overlapping s/t, 8H), 2.54–2.62 (m, 4H), 1.55–1.64 (10H), 1.39–1.45 (8H), 1.27 (t, 6H, *J* = 7.1 Hz). ¹³C NMR (150 MHz): δ 171.7, 139.6, 131.5, 130.4, 62.9, 60.8, 38.6, 32.7, 32.2, 31.0, 29.4, 25.6, 14.2. FTIR: 3346, 2930, 2856, 1729, 1367, 1256, 1155, 1027 cm⁻¹. HRMS-ESI: calc. for C₂₆H₄₂O₆Na (M+Na)⁺: 473.2879; found: 473.2888.

Diethyl 2,2'-(4,5-bis(6-((methylsulfonyl)oxy)hexyl)-1,2-phenylene)diacetate—

To a flame-dried 8 mL vial fitted with a screw-cap septa were sequentially added **10** (1 equiv, 0.124 mmol, 55 mg), CH₂Cl₂ (1.5 mL), Et₃N (4 equiv, 0.5 mmol, 0.075 mL), and DMAP (0.1 equiv, 0.013 mmol, 1.6 mg), and MsCl (3 equiv, 0.372 mmol, 0.031 mL, dropwise). The reaction was stirred for 3 h, then quenched with sat. aq. NaHCO₃ (10 mL). The layers are separated and the aqueous layer was extracted with CH₂Cl₂ (3 × 10 mL). The combined organic layers were dried with Na₂SO₄ and the residue obtained upon concentration *in vacuo*, was purified *via* flash chromatography (55% EtOAc/Hex) to afford the bis methanesulfonate (64 mg, 0.105 mmol, 85%) as a colorless oil. R_f = 0.86, 75% EtOAc/Hex. ¹H NMR (400 MHz): δ 7.03 (s, 2H), 4.25 (t, 4H, *J* = 6.5 Hz), 4.15 (q, 4H, *J* =

7.1 Hz), 3.66 (s, 4H), 2.60 (s, 6H), 2.54–2.62 (m, 4H), 1.79 (4H), 1.55–1.65 (4H), 1.39–1.45 (8H), 1.27 (t, 6H, $J = 7.1$ Hz). ^{13}C NMR (150 MHz): δ 171.6, 139.3, 131.5, 130.5, 70.1, 60.8, 38.6, 37.4, 32.1, 30.9, 29.1, 25.4, 14.2. FTIR: 2935, 2860, 1729, 1349, 1332, 1170, 1028, 948, 914, 729 cm^{-1} . HRMS-ESI: calc. for $\text{C}_{28}\text{H}_{46}\text{O}_{10}\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 629.2430; found: 629.2459.

Diethyl 2,2'-(4,5-bis(6-(acetylthio)hexyl)-1,2-phenylene) diacetate—To a flame-dried 8 mL vial fitted with a screw-cap septa was added diethyl 2,2'-(4,5-bis(6-(methylsulfonyl)oxy)hexyl)-1,2-phenylene)diacetate (1 equiv, 0.101 mmol, 61 mg) in 1.5 mL DMF, followed by KSAc (5 equiv, 0.505 mmol, 58 mg). The reaction was stirred for 14 h and then quenched with sat. aq. NaHCO_3 (5 mL). After the mixture was diluted with 20 mL Et_2O , the separated organic layer was washed with sat. aq. NaHCO_3 (2×5 mL) and dried with Na_2SO_4 . The residue obtained upon concentration *in vacuo*, was purified *via* flash chromatography (15% EtOAc/Hex) to afford the bis thioacetate (46 mg, 0.081 mmol, 80%) as a colorless oil. $R_f = 0.22$, 10% EtOAc/Hex. ^1H NMR (400 MHz): δ 7.02 (s, 2H), 4.15 (q, 4H, $J = 7.1$ Hz), 3.66 (s, 4H), 2.89 (t, 4H, 7.3 Hz), 2.52–2.60 (m, 4H), 2.35 (s, 6H), 1.52–1.64 (8H), 1.38–1.46 (8H), 1.27 (t, 6H, $J = 7.1$ Hz). ^{13}C NMR (150 MHz): δ 196.0, 171.6, 139.5, 131.5, 130.4, 60.8, 38.6, 32.2, 31.0, 30.6, 29.5, 29.2, 29.1, 28.7, 14.2. FTIR: 2927, 2855, 1732, 1688, 1254, 1133, 1029, 950 cm^{-1} . HRMS-ESI: calc. for $\text{C}_{30}\text{H}_{46}\text{O}_6\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 589.2634; found: 589.2651.

2,2'-(4,5-Bis(6-thiylhexyl)-1,2-phenylene)diethanol (2)—A flame-dried 8 mL vial fitted with a screw-cap septa was charged with the bis thioacetate (1 equiv, 0.078 mmol, 44 mg) and 1 mL THF, after which was dropwise added DIBAL-H (12 equiv, 0.93 mmol; 0.65 mL of a nominally 1.5 M solution in toluene). The reaction was stirred for 3 h and then quenched by slow dropwise addition of 2 N HCl (2 mL) at 0 °C. The mixture was diluted with 10 mL H_2O and extracted with Et_2O (3×10 mL). The combined organic layers were washed with brine (10 mL) and dried with Na_2SO_4 . The residue obtained upon concentration *in vacuo* was and purified *via* flash chromatography (70% EtOAc/Hex) to afford **2** (22 mg, 0.055 mmol, 71%) as a colorless oil. $R_f = 0.22$, 50% EtOAc/Hex. ^1H NMR (600 MHz): δ 6.98 (s, 2H), 3.85 (t, 4H, $J = 6.5$ Hz), 2.90 (t, 4H, $J = 6.7$ Hz), 2.52–2.60 (m, 8H), 2.12 (s, 2H), 1.65 (quint., 4H, $J = 7.2$ Hz), 1.58 (quint., 4H, $J = 7.5$ Hz), 1.38–1.49 (8H), 1.36 (t, 2H, $J = 7.5$ Hz). ^{13}C NMR (150 MHz): δ 138.8, 134.3, 130.8, 63.6, 35.3, 33.9, 32.2, 31.2, 29.2, 28.2, 24.6. FTIR: 3332, 2925, 2853, 1503, 1460, 1040 cm^{-1} . HRMS-ESI: calc. for $\text{C}_{22}\text{H}_{38}\text{O}_2\text{S}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$: 421.2211; found: 421.2212.

E-DNA sensor fabrication—Prior to SAM formation, gold disk electrodes (2-mm diameter, CHI, Instruments, Austin, TX) were electrochemically cleaned by cycling between -0.4 and 1.6 V vs. Ag/AgCl in 0.5 M sulfuric acid until the gold oxide formation region of the voltammograms displayed three distinct peaks and successive scans showed minimal to no change. The E-DNA sensors were fabricated in two steps: (1) The electrochemically-cleaned gold disc electrodes were immersed in 2 mM ethanolic solution of either **1**, **2** or 11-hydroxyundecaneundecanol for 10 minutes. The electrodes were then rinsed with deionized water and dried with N_2 . (2) A stem-loop DNA sensing element thiolated at the 5'-end and modified with methylene blue (MB) at the 3'-end (see representation of sensor construct below) was then dropcasted on the pre-formed SAMs for 3 hours.^[19] Electrochemical measurements were performed at room temperature (22 ± 1 °C) using a CHI 1040A Electrochemical Workstation (CH Instruments, Austin, TX). The modified electrodes were analyzed using alternating current voltammetry (ACV) at a frequency of 10 Hz and an amplitude of 25 mV. All voltammograms were recorded in a physiological buffer solution (Phys2) consisting of 20 mM Tris, 140 mM NaCl, 5 mM KCl, 1 mM MgCl_2 , and 1 mM CaCl_2 ; the solution was adjusted to pH 7.4 with hydrochloric acid. For sensor stability

monitoring, ACV scans were collected every 12 hours for a total of 72 hours. The sensors were then interrogated/hybridized with 1.0 μM complete complementary target DNA (see sequence below) until no change in the MB current was observed. The sensors were then regenerated by continuous rinsing with deionized water for 30 seconds. The sensors were subsequently transferred to a fresh Phys2 buffer solution for electrochemical monitoring of the regenerated current.

K-ras probe sequence: 5' HS-(CH₂)₁₁-CCGTTACGCCACCAGCTCCAACGG-C7-MB-3'

K-ras target sequence: 5'-TTGGAGCTGGTGGCGTA-3'

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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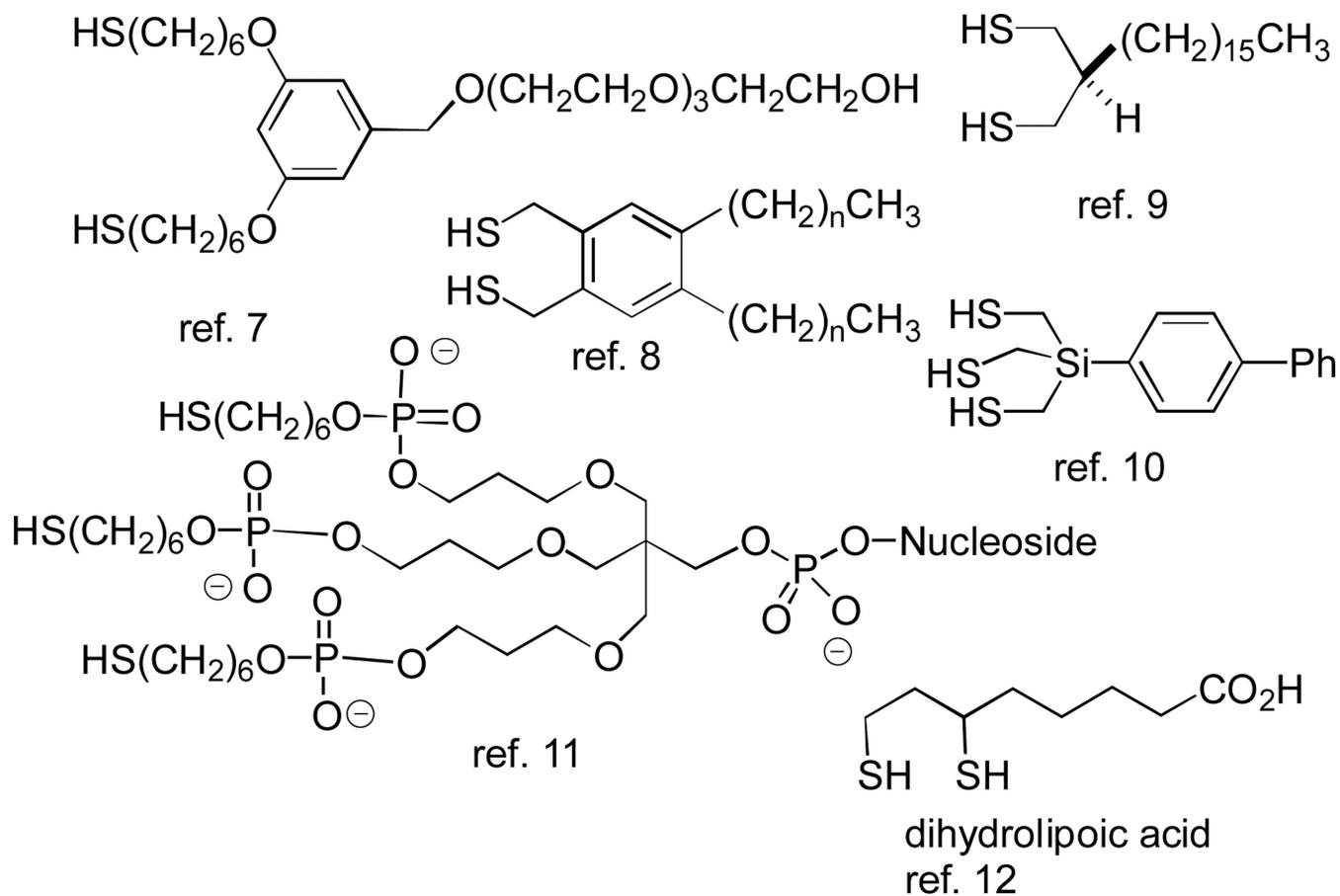


Figure 1.
Examples of multidentate thiol amphiphiles.

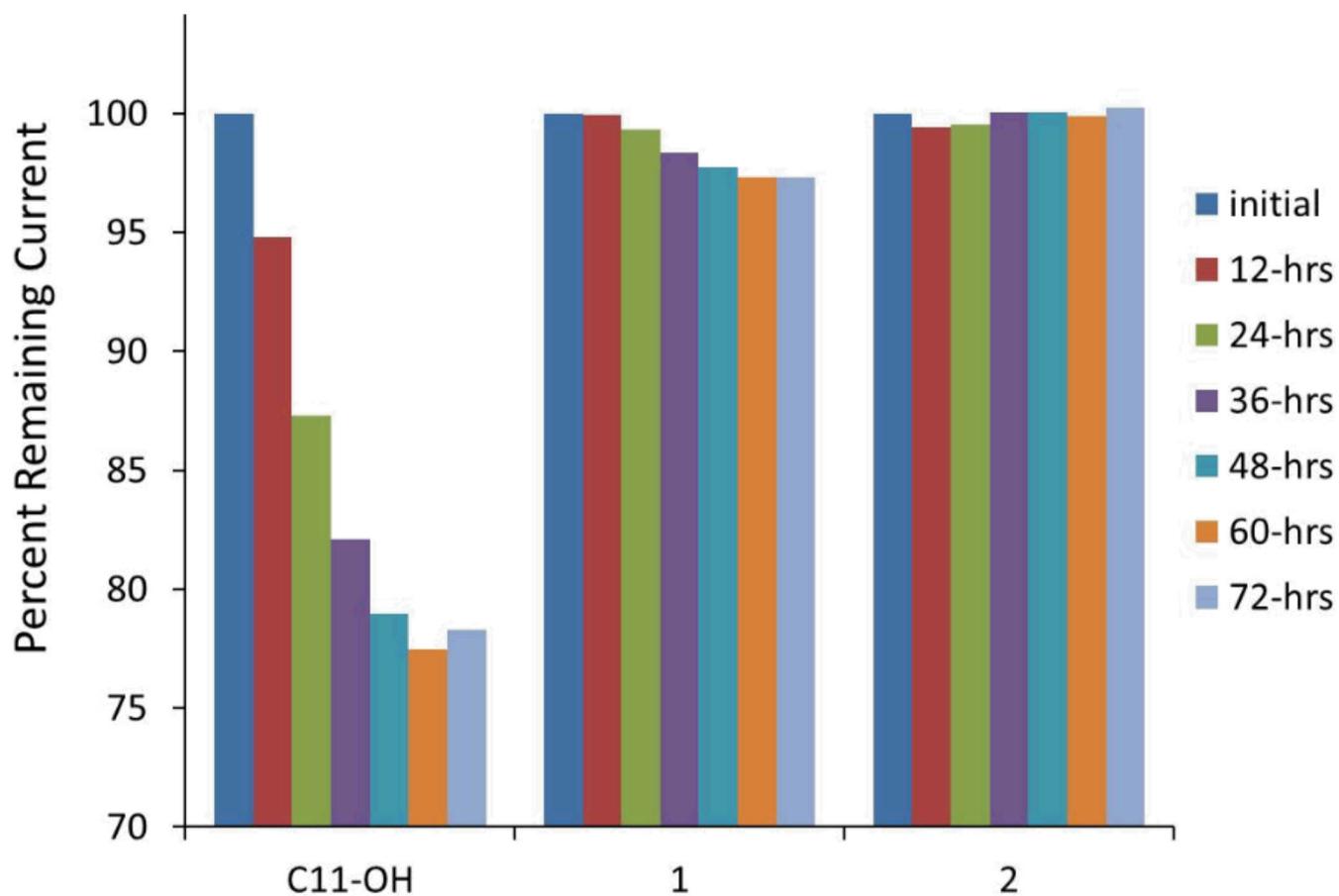


Figure 2.
Comparison of stability of E-DNA sensors formed from 11-hydroxyundecanethiol, **1**, and **2**.

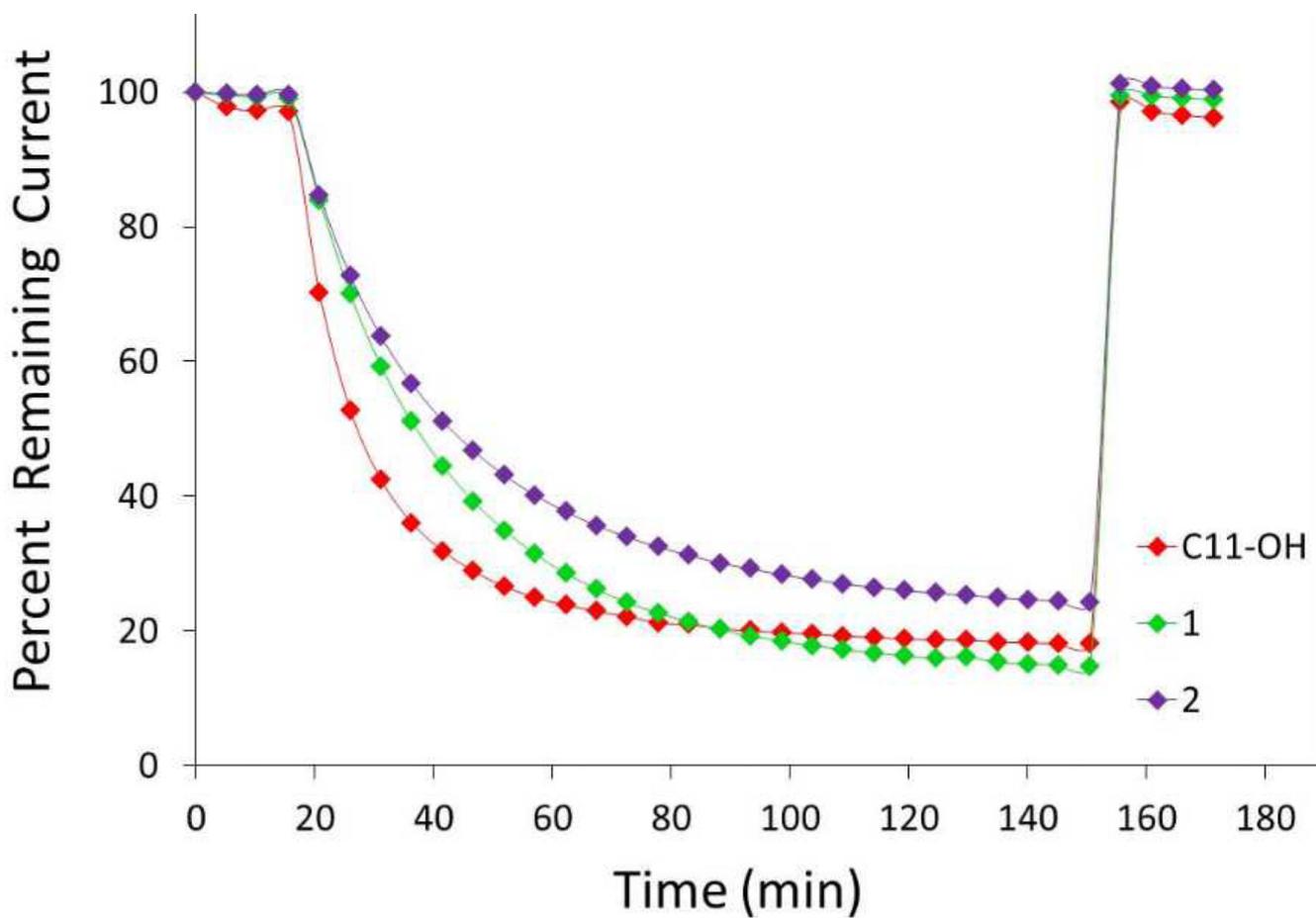
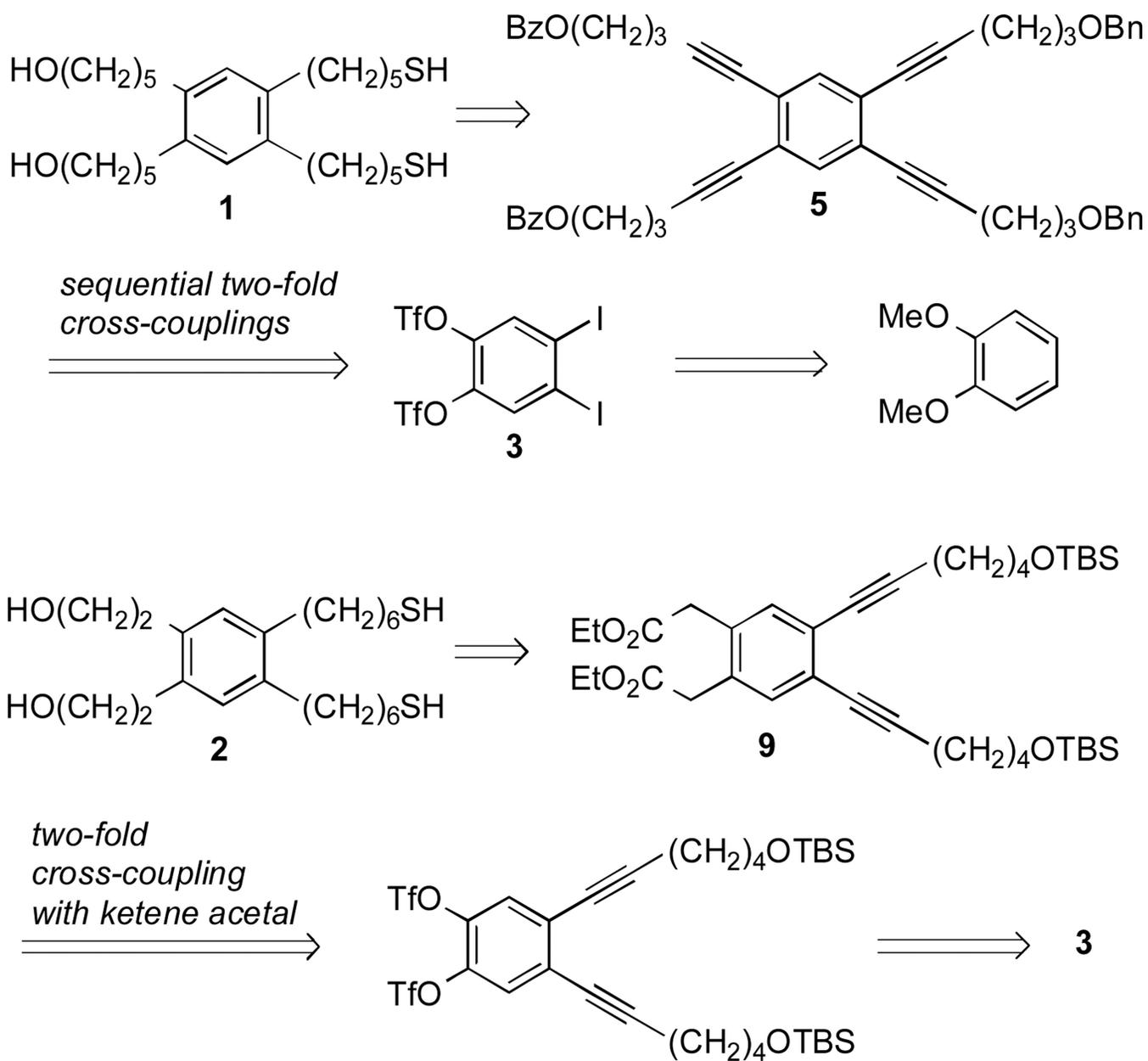
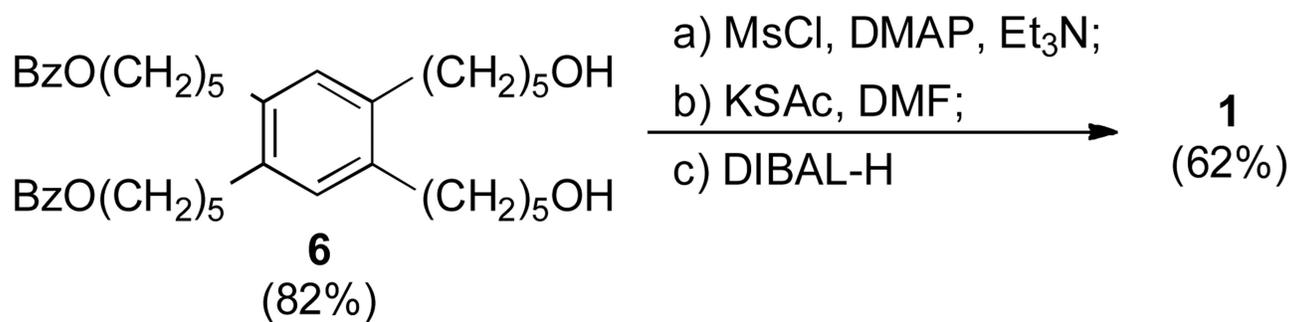
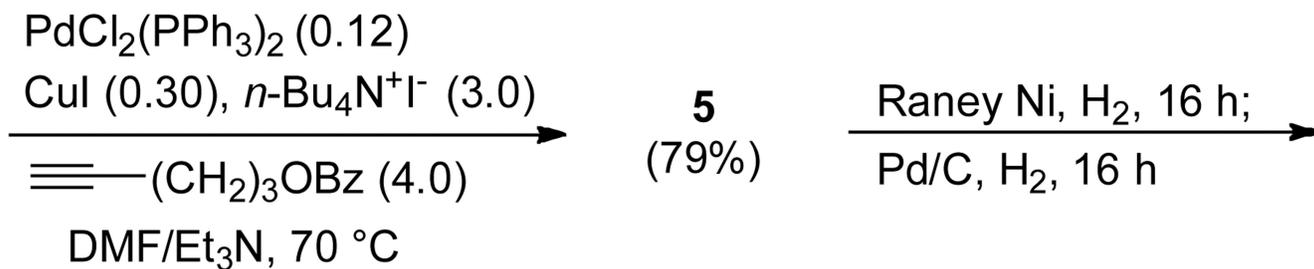
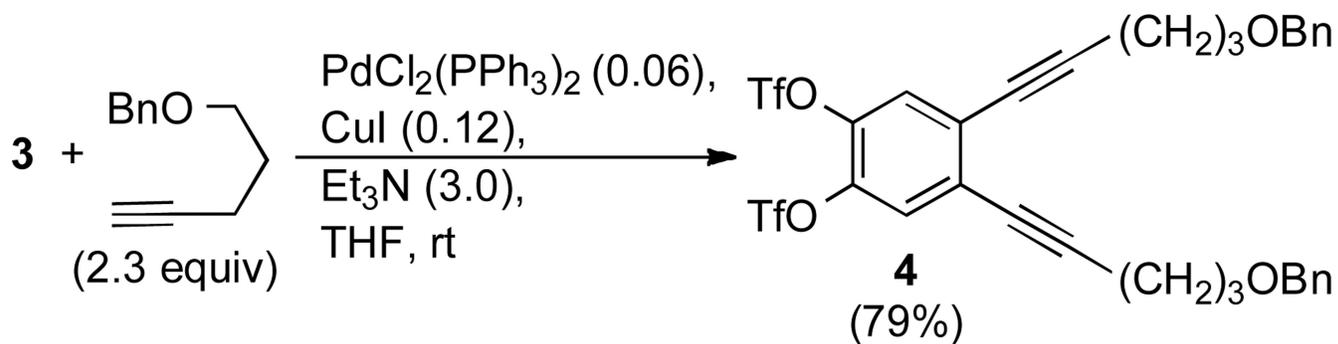


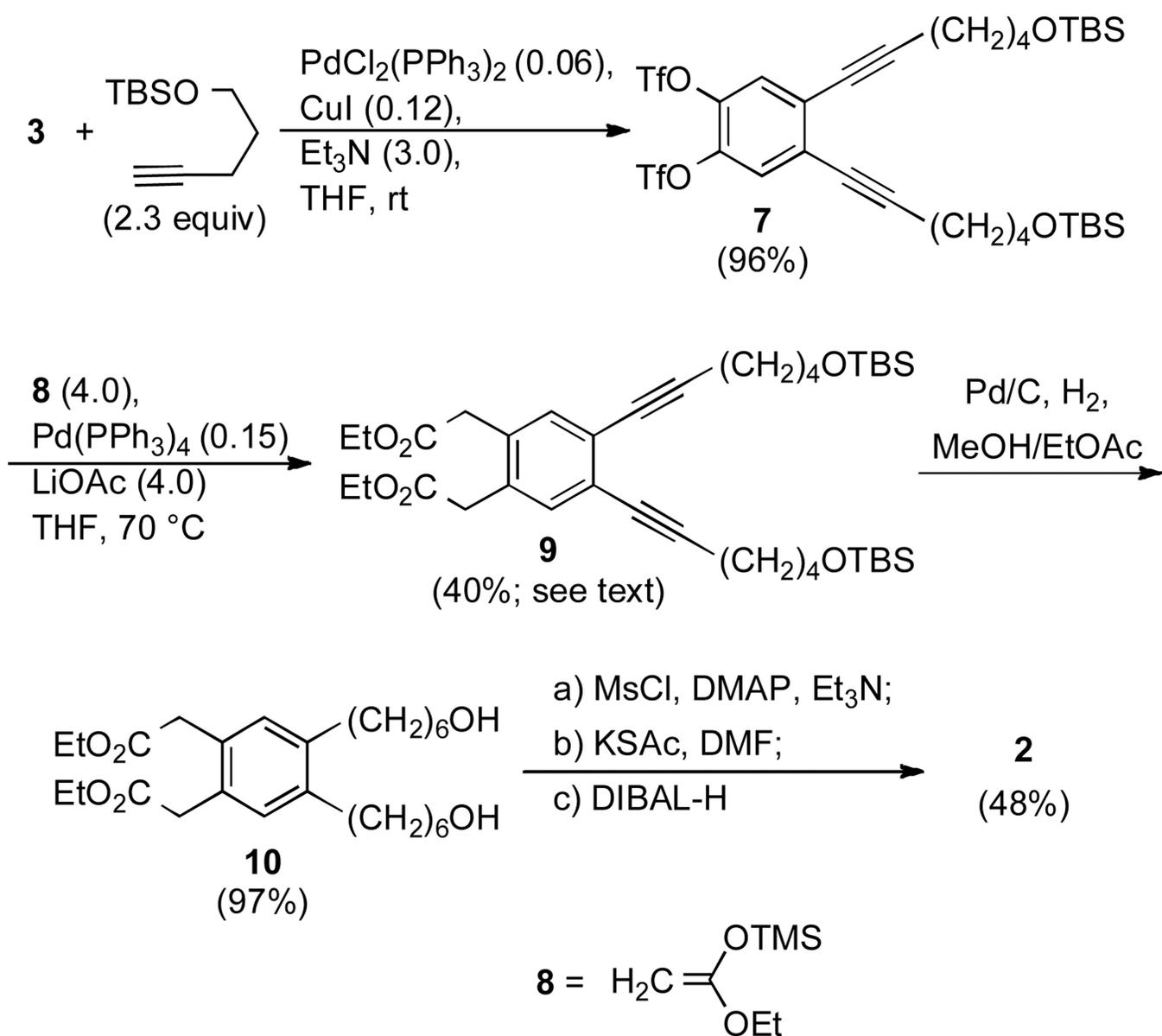
Figure 3. Hybridization curves obtained from sensors passivated with 11-hydroxyundecanethiol (red), 1 (purple) and 2 (green) in the presence of 1.0 μM target DNA in Phys2 buffer after the 72-hr stability run. *K-ras* probe sequence: 5' HS-(CH₂)₁₁-CCGTTACGCCACCAGCTCCAAACGG-C7-MB-3'. *K-ras* target sequence: 5'-TTGGAGCTGGTGGCGTA-3'



Scheme 1.
Retrosynthetic analysis for the 13- and 11-carbon amphiphiles.



Scheme 2.
Synthesis of amphiphile **1**.



Scheme 3.
Synthesis of amphiphile **2**.

SUPPORTING INFORMATION

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Title: Design and Synthesis of a Class of Twin-Chain Amphiphiles for Self-Assembled Monolayer-Based Electrochemical Biosensor Applications

Author(s): Thomas J. Fisher, Socrates Jose P. Cañete, Rebecca Y. Lai, Patrick H. Dussault*

^1H and ^{13}C NMR Spectra

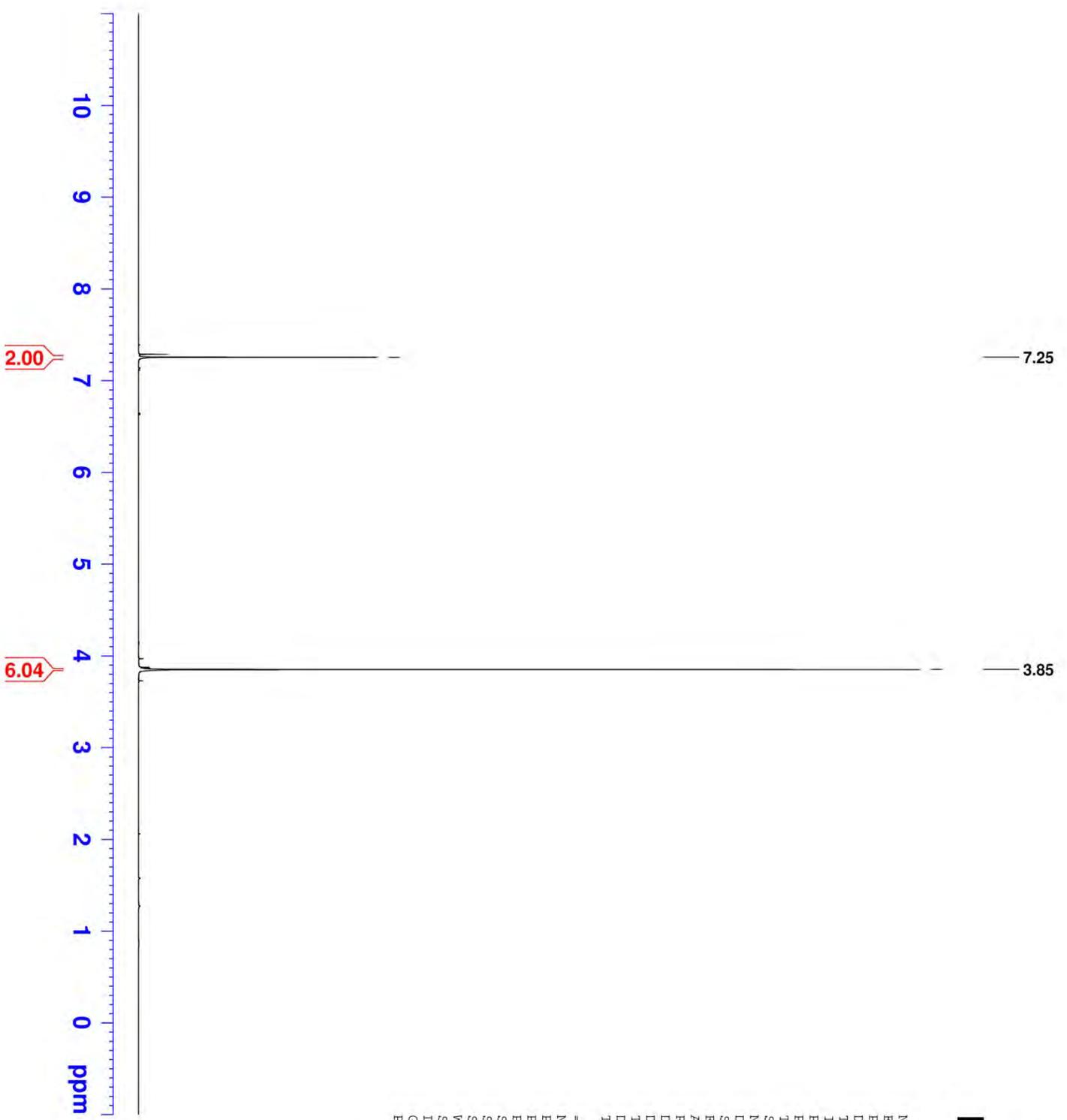
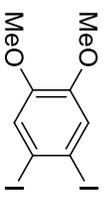
1,2-diiodo-4,5-dimethoxybenzene (^1H)	2
1,2-diiodo-4,5-dimethoxybenzene (^{13}C)	3
1,2-dihydroxy-4,5-diiodobenzene (^1H)	4
1,2-dihydroxy-4,5-diiodobenzene (^{13}C)	5
4,5-diiodo-1,2-phenylene bis(trifluoromethanesulfonate) (3) (^1H)	6
4,5-diiodo-1,2-phenylene bis(trifluoromethanesulfonate) (3) (^{13}C)	7
5-benzyloxypentyne (^1H)	8
5-benzyloxypentyne (^{13}C)	9
4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene bistrifluoromethanesulfonate (4) (^1H)	10
4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene bistrifluoromethanesulfonate (4) (^{13}C)	11
5-benzoyloxypentyne (^1H)	12
5-benzoyloxypentyne (^{13}C)	13
4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene-bis(pent-4-yne-1-ol-5-yl, benzoate ester) (5) (^1H)	14
4,5-Bis(5-benzyloxypent-1-yn-1-yl)-1,2-phenylene-bis(pent-4-yne-1-ol-5-yl, benzoate ester) (5) (^{13}C)	15
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-hydroxypentyl)benzene (6) (^1H)	16
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-hydroxypentyl)benzene (6) (^{13}C)	17
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-methansulfonylpentyl)benzene (^1H)	18
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-methansulfonylpentyl)benzene (^{13}C)	19
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-(acetylthiyl)pentyl)benzene (^1H)	20
1,2-bis(5-benzoyloxypentyl)-4,5-bis(5-(acetylthiyl)pentyl)benzene (^{13}C)	21
1,2-bis(5-hydroxypentyl)-4,5-bis(5-thiylpentyl)benzene (1) (^1H)	22
1,2-bis(5-hydroxypentyl)-4,5-bis(5-thiylpentyl)benzene (1) (^{13}C)	23
6-(<i>tert</i> -Butyldimethylsilyloxy)hexyne (^1H)	24
6-(<i>tert</i> -Butyldimethylsilyloxy)hexyne (^{13}C)	25
4,5-Bis[6-(<i>tert</i> -butyldimethylsilyloxy)hex-1-ynyl]-1,2-phenylene bis(trifluoromethanesulfonate) (7) (^1H) ..	26
4,5-Bis[6-(<i>tert</i> -butyldimethylsilyloxy)hex-1-ynyl]-1,2-phenylene bis(trifluoromethanesulfonate) (7) (^{13}C) ..	27
((1-ethoxyvinyl)oxy)trimethylsilane (8) (^1H)	28
((1-ethoxyvinyl)oxy)trimethylsilane (8) (^{13}C)	29
4,5-Bis[6-((<i>tert</i> -butyldimethylsilyloxy)oxy)hex-1-ynyl]-1,2-phenylene bis(trifluoromethanesulfonate) (9) (^1H) ..	30
4,5-Bis[6-((<i>tert</i> -butyldimethylsilyloxy)oxy)hex-1-ynyl]-1,2-phenylene bis(trifluoromethanesulfonate) (9) (^{13}C) ..	31
diethyl 2,2'-(4,5-bis(6-hydroxyhexyl)-1,2-phenylene)diacetate (10) (^1H)	32
diethyl 2,2'-(4,5-bis(6-hydroxyhexyl)-1,2-phenylene)diacetate (10) (^{13}C)	33
diethyl 2,2'-(4,5-bis(6-((methylsulfonyl)oxy)hexyl)-1,2-phenylene)diacetate (^1H)	34
diethyl 2,2'-(4,5-bis(6-((methylsulfonyl)oxy)hexyl)-1,2-phenylene)diacetate (^{13}C)	35
diethyl 2,2'-(4,5-bis(6-(acetylthio)hexyl)-1,2-phenylene)diacetate (^1H)	36
diethyl 2,2'-(4,5-bis(6-(acetylthio)hexyl)-1,2-phenylene)diacetate (^{13}C)	37
2,2'-(4,5-bis(6-mercaptohexyl)-1,2-phenylene)diethanol (2) (^1H)	38
2,2'-(4,5-bis(6-mercaptohexyl)-1,2-phenylene)diethanol (2) (^{13}C)	39



NAME TF1sh0773_Product_022411

EXPNO 1
 PROCNO 1
 Date_ 20110224
 Time_ 14.02
 INSTRUM spect
 PROBHD BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 12376.237 Hz
 FIDRES 0.188846 Hz
 AQ 2.6477449 sec
 RG 181
 DW 40.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 14.50 usec
 PL1 0.20 dB
 PL1W 35.98249435 W
 SFO1 600.1827064 MHz
 SI 32768
 SF 600.1789953 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

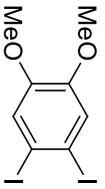
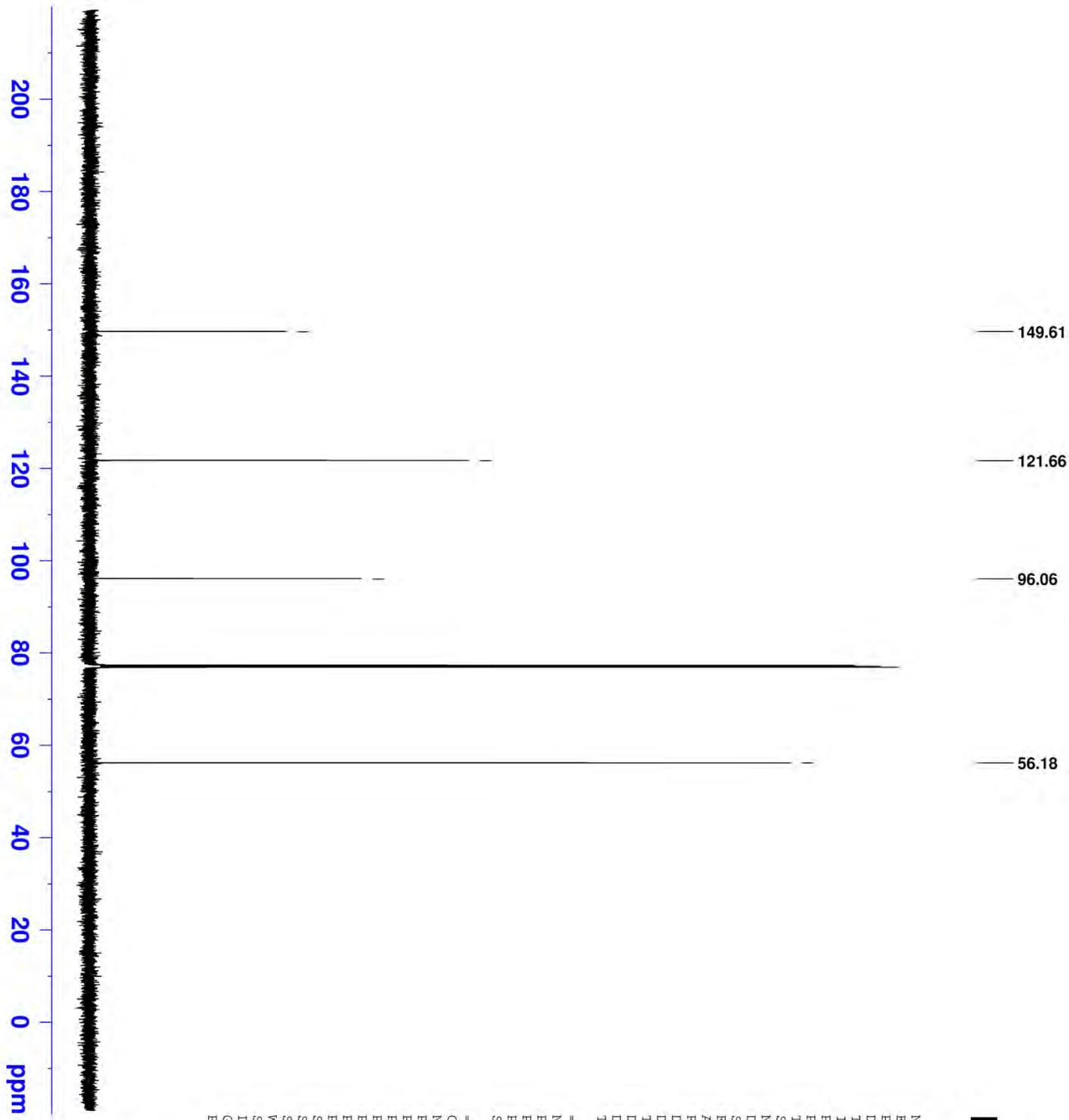




NAME TF1sh0773_Product_022411
 EXPNO 2
 PROCNO 1
 Date_ 20110224
 Time_ 14.06
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 129
 DS 4
 SMH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 9195.2
 DW 13.900 usec
 DE 6.50 usec
 TE 298.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL F1 =====
 NUC1 13C
 P1 9.70 usec
 PL1 1.00 dB
 PL1W 59.85786819 W
 SFO1 150.9302211 MHz

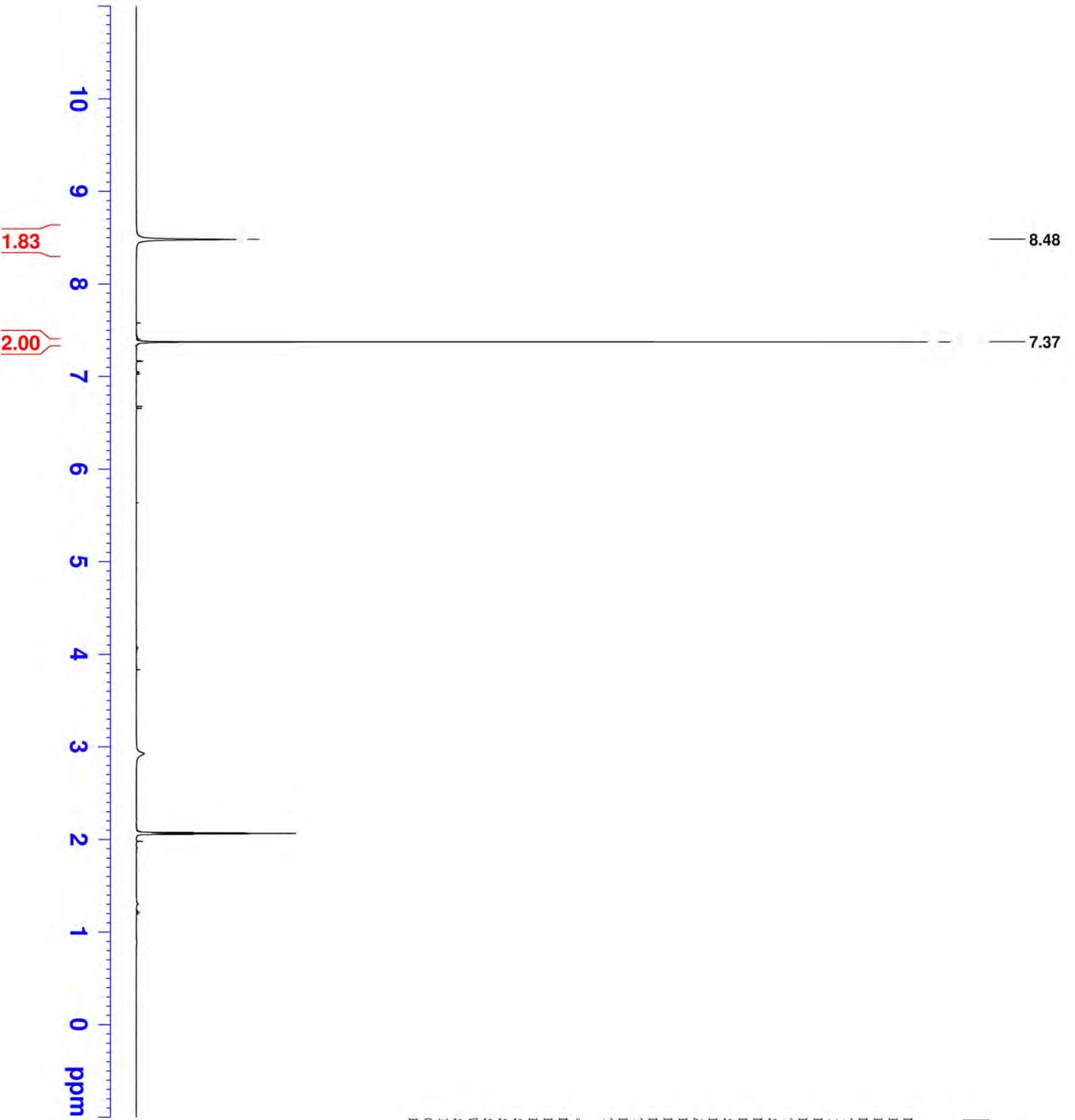
==== CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 60.00 usec
 PL2 0.20 dB
 PL12 12.54 dB
 PL13 12.54 dB
 PL2W 35.98249435 W
 PL12W 2.09938097 W
 PL13W 2.09938097 W
 SFO2 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





```

NAME TF1sh0774_Product_022411
EXPNO 1
PROCNO 1
Date_ 20110224
Time_ 23.24
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT Acetone
NS 16
DS 2
SMH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 574.7
DE 60.400 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1
===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 -2.30 dB
SFO1 400.1324710 MHz
SI 65536
SF 400.1300000 MHz
MWDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
```

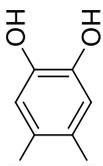
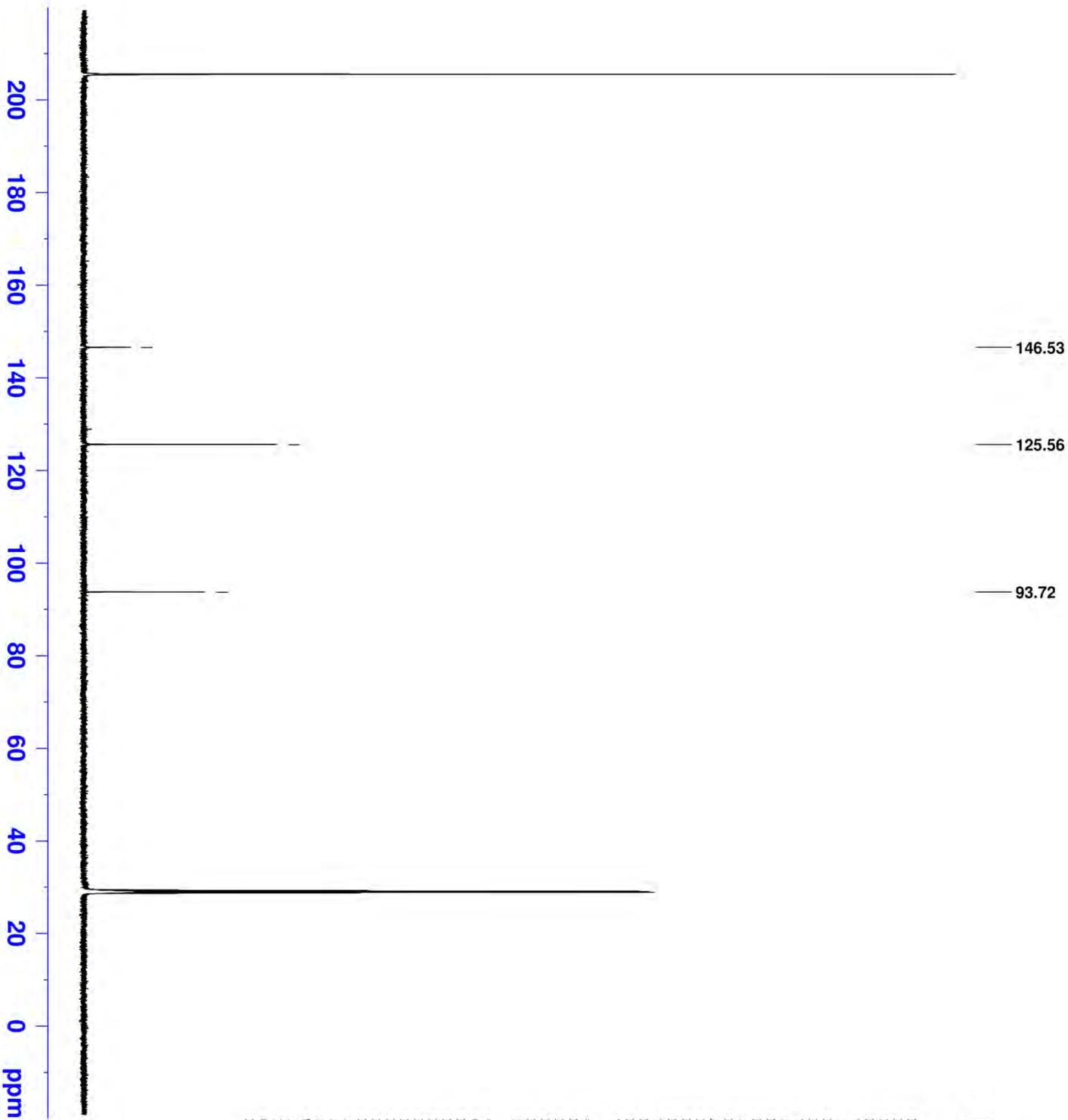




NAME TFish0774_2_product_030511
 EXPNO 1
 PROCNO 1
 Date_ 20110305
 Time_ 20.41
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT Acetone
 NS 152
 DS 4
 SWH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 7298.2
 DW 13.900 usec
 DE 6.50 usec
 TE 298.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 9.70 usec
 PL1 1.00 dB
 PL1W 59.85786819 W
 SFO1 150.9302211 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPBD2 60.00 usec
 PL2 0.20 dB
 PL12 12.54 dB
 PL13 12.54 dB
 PL1W 35.98249435 W
 PL12W 2.09938097 W
 PL13W 2.09938097 W
 SFO2 600.1814007 MHz
 ST 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

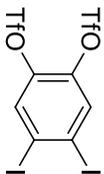




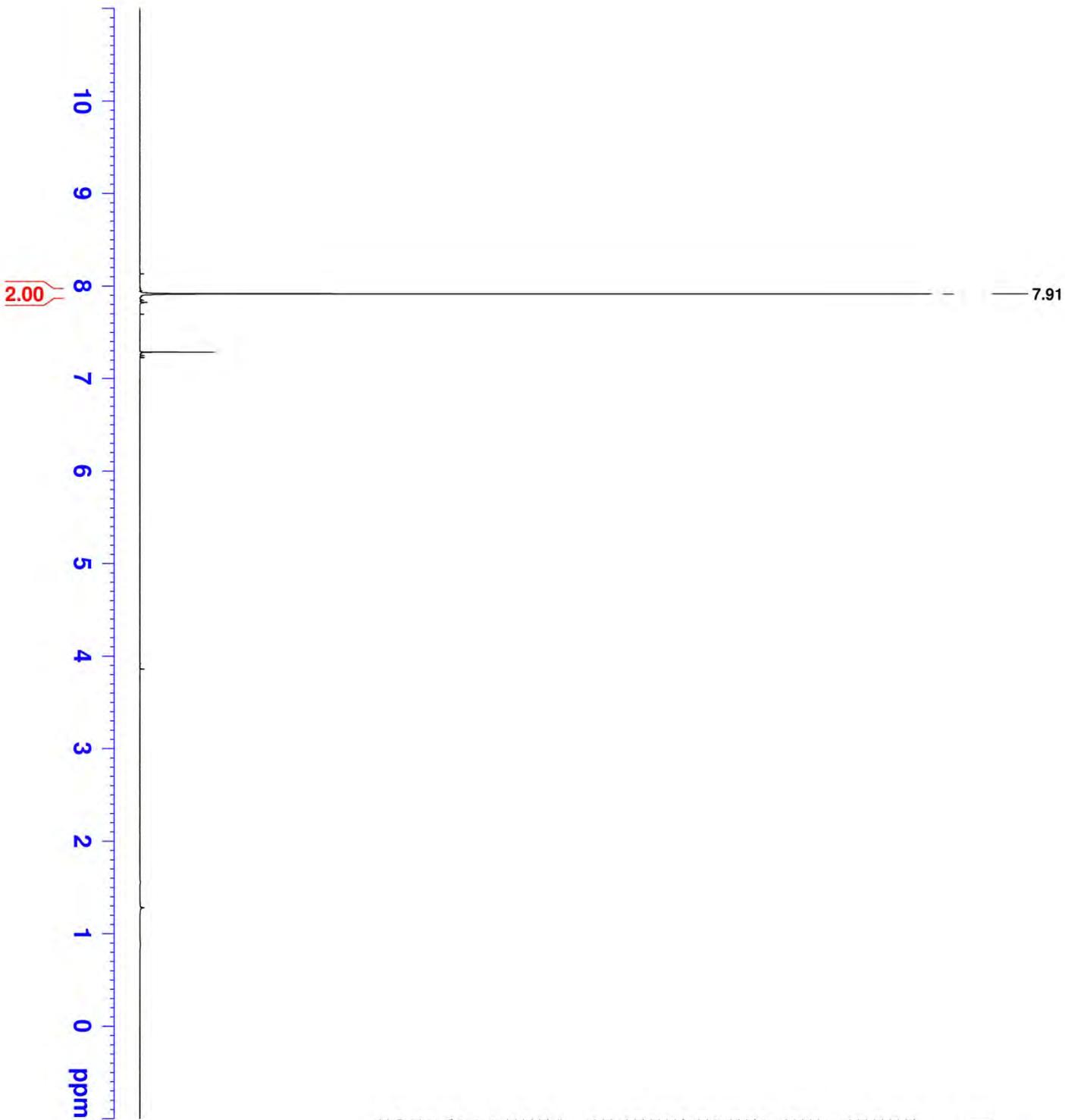
NAME TFish0776_crude_022511

EXPNO 1
 PROCNO 1
 Date_ 20110225
 Time 20.48
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 456.1
 DW 60.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

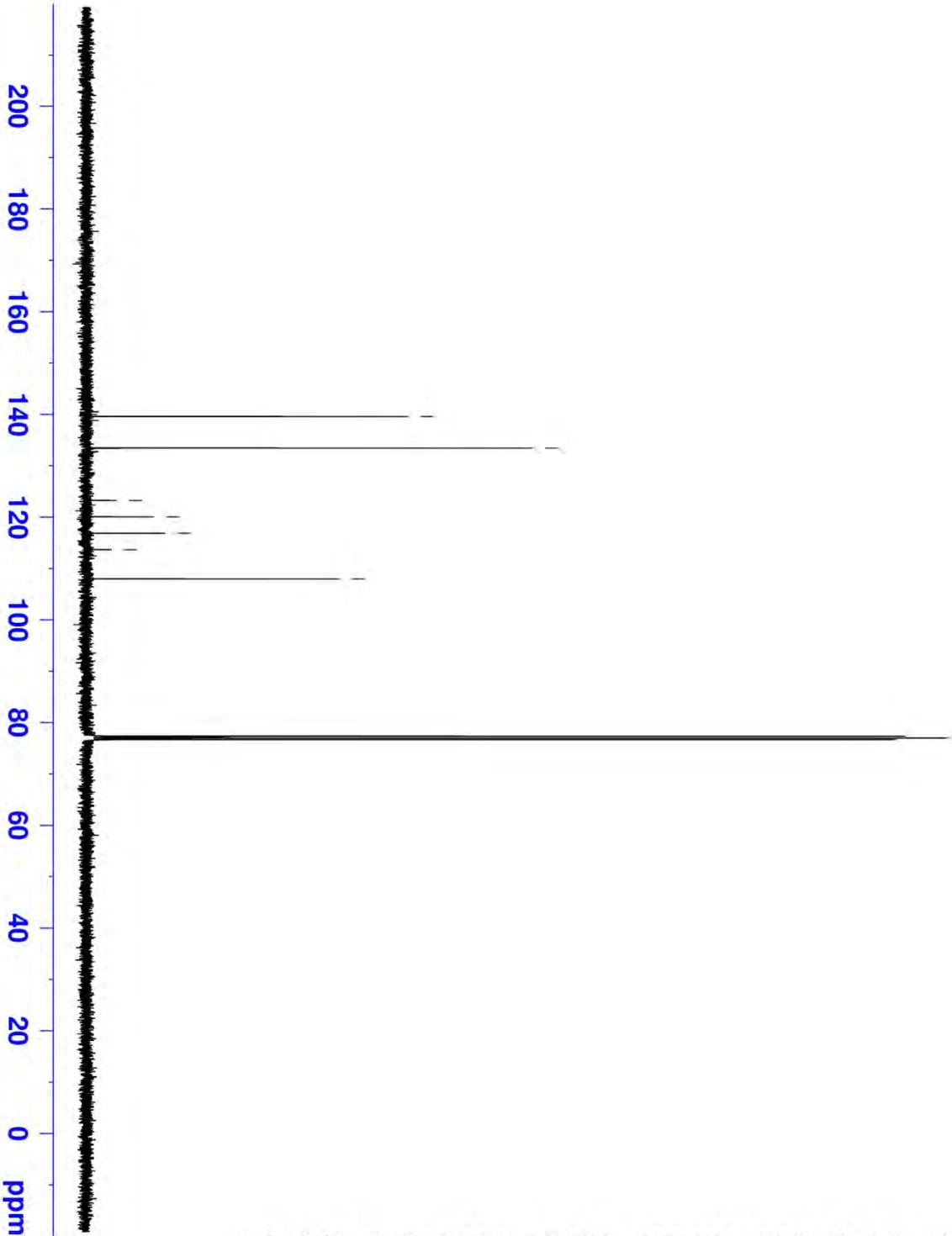
===== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -2.30 dB
 SF01 400.1324710 MHz
 SI 32768
 SE 400.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



3



139.61
 133.44
 123.25
 120.06
 116.87
 113.68
 107.97

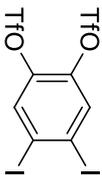


NAME TFish0776_crude_022511

EXPNO 1
 PROCNO 2
 Date_ 20110225
 Time 20.52
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 661
 DS 4
 SWH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 4597.6
 DW 20.850 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.50 dB
 SF01 100.6228298 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 70.00 usec
 PL2 -3.35 dB
 PL12 13.34 dB
 PL13 13.34 dB
 SF02 400.1316005 MHz
 SI 32768
 SE 100.6127690 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



3



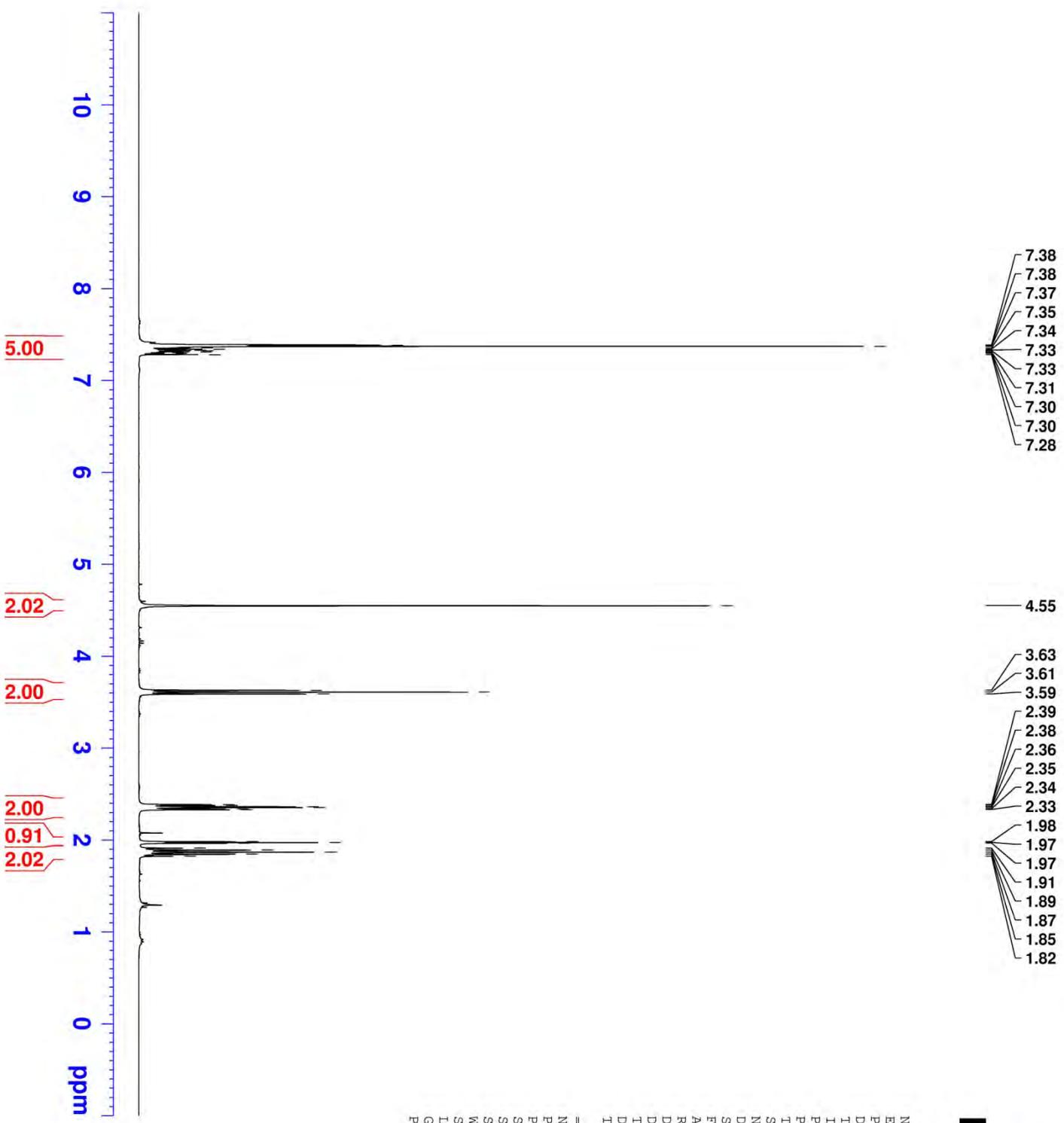
TF1sh0784_product_030511

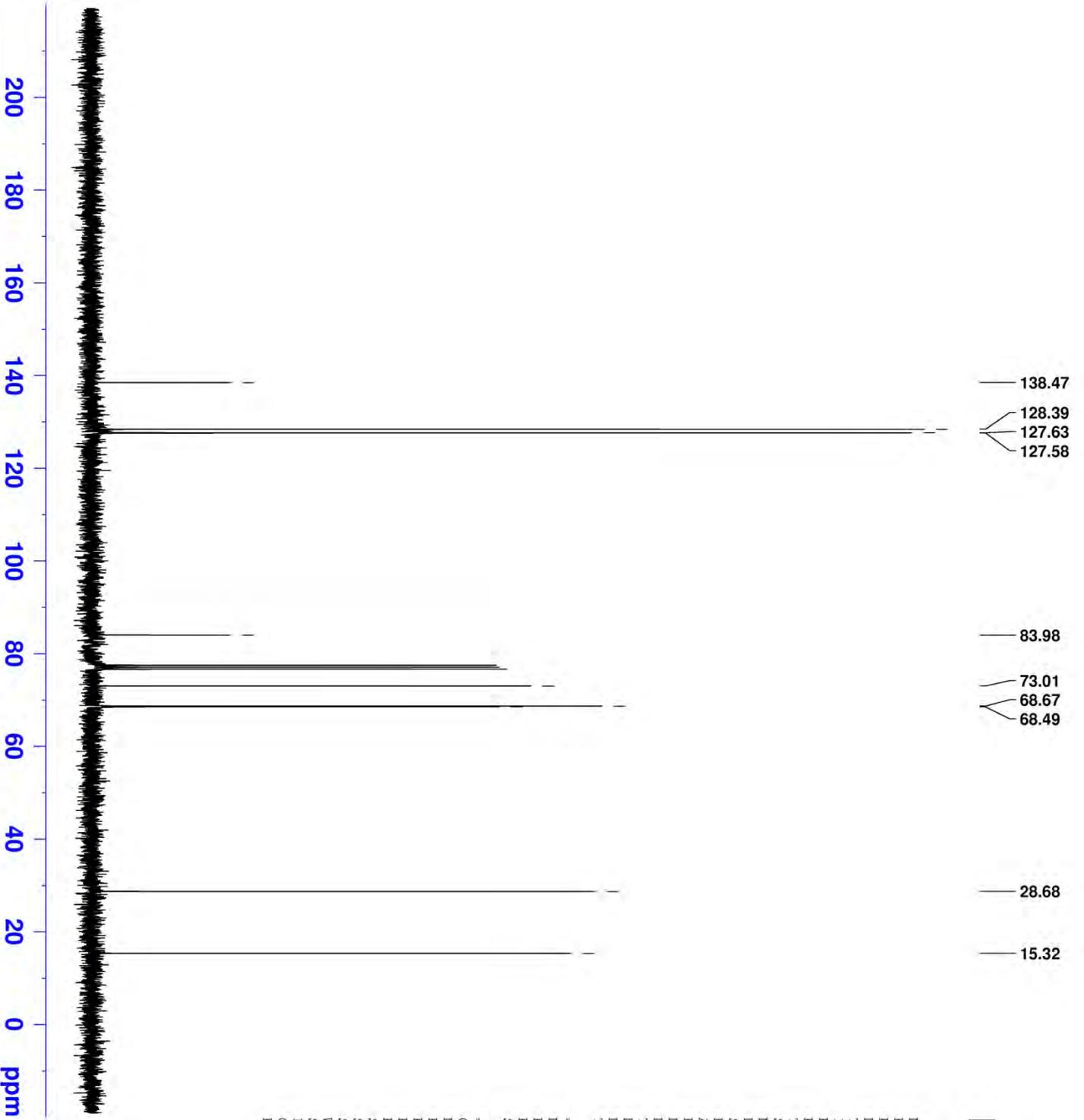
```

NAME      TF1sh0784_product_030511
EXPNO     1
PROCNO    1
Date_     20110305
Time_     13.01
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         2
SMH        5995.204 Hz
FIDRES    0.182959 Hz
AQ         2.7329011 sec
RG         128
DM         83.400 usec
DE         6.50 usec
TE         293.8 K
D1         1.00000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        15.00 usec
PL1       -4.40 dB
SFO1     300.1318534 MHz
SI        32768
SF        300.1300000 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
    
```





```

NAME TF1sh0784_Product_030511
EXPNO 2
PROCNO 1
Date_ 20110305
Time_ 13.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 152
DS 4
SMH 17985.611 Hz
FIDRES 0.548877 Hz
AQ 0.9110004 sec
RG 11585.2
DW 27.800 usec
DE 6.50 usec
TE 294.6 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 10.00 usec
PL1 5.00 dB
SFO1 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 70.00 usec
PL2 -4.40 dB
PL12 8.98 dB
PL13 8.98 dB
SFO2 300.1312005 MHz
SI 33768
SE 75.4677490 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

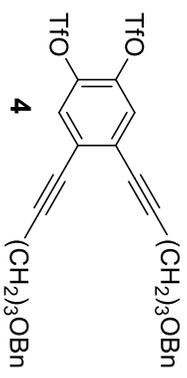
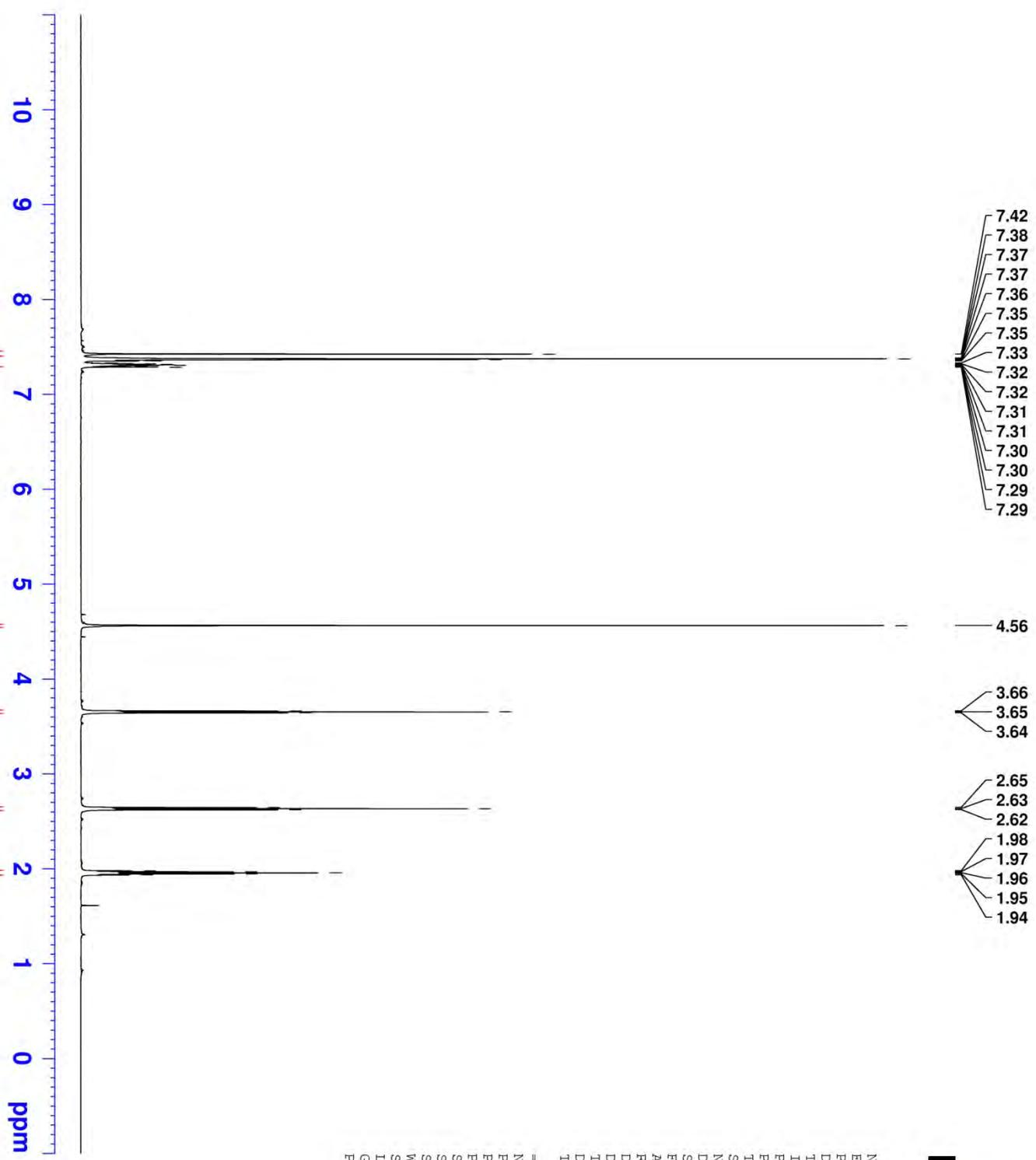
≡—(CH₂)₃OBN

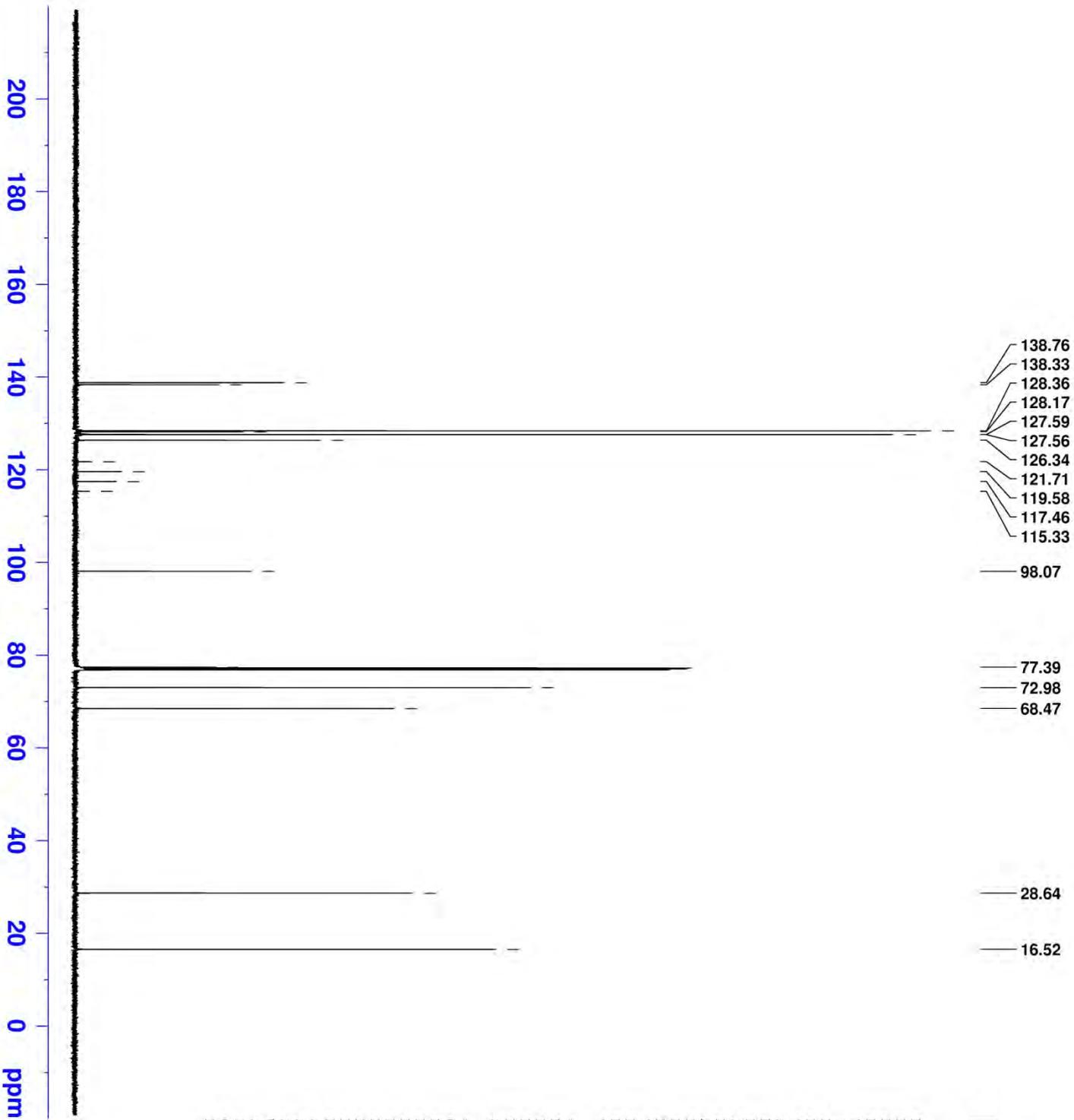


NAME TF1sh0786_Product_030511

EXPNO 1
 PROCNO 3
 Date_ 20110306
 Time 14.14
 INSTRUM Spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 12376.237 Hz
 FIDRES 0.188846 Hz
 AQ 2.6477449 sec
 RG 71.8
 DW 40.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 14.50 usec
 PL1 0.20 dB
 PL1W 35.98249435 W
 SFO1 600.1827064 MHz
 SI 32768
 SF 600.1789953 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





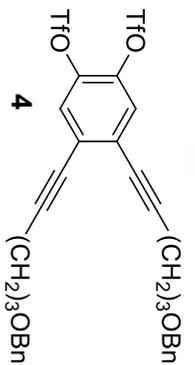
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128.17
127.59
127.56
126.34
121.71
119.58
117.46
115.33
98.07
77.39
72.98
68.47
28.64
16.52

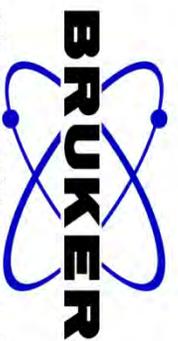
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NAME TF1sh0786_Product_030511
EXPNO 1
PROCNO 2
Date_ 20110306
Time_ 14.21
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 701
DS 4
SMH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 11585.2
DW 13.900 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.70 usec
PL1 1.00 dB
PL1W 59.85786819 W
SFO1 150.9302211 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL2 0.20 dB
PL12 12.54 dB
PL13 12.54 dB
PL2W 35.98249435 W
PL12W 2.09938097 W
PL13W 2.09938097 W
SFO2 600.1814007 MHz
SI 32768
SF 150.9151355 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```





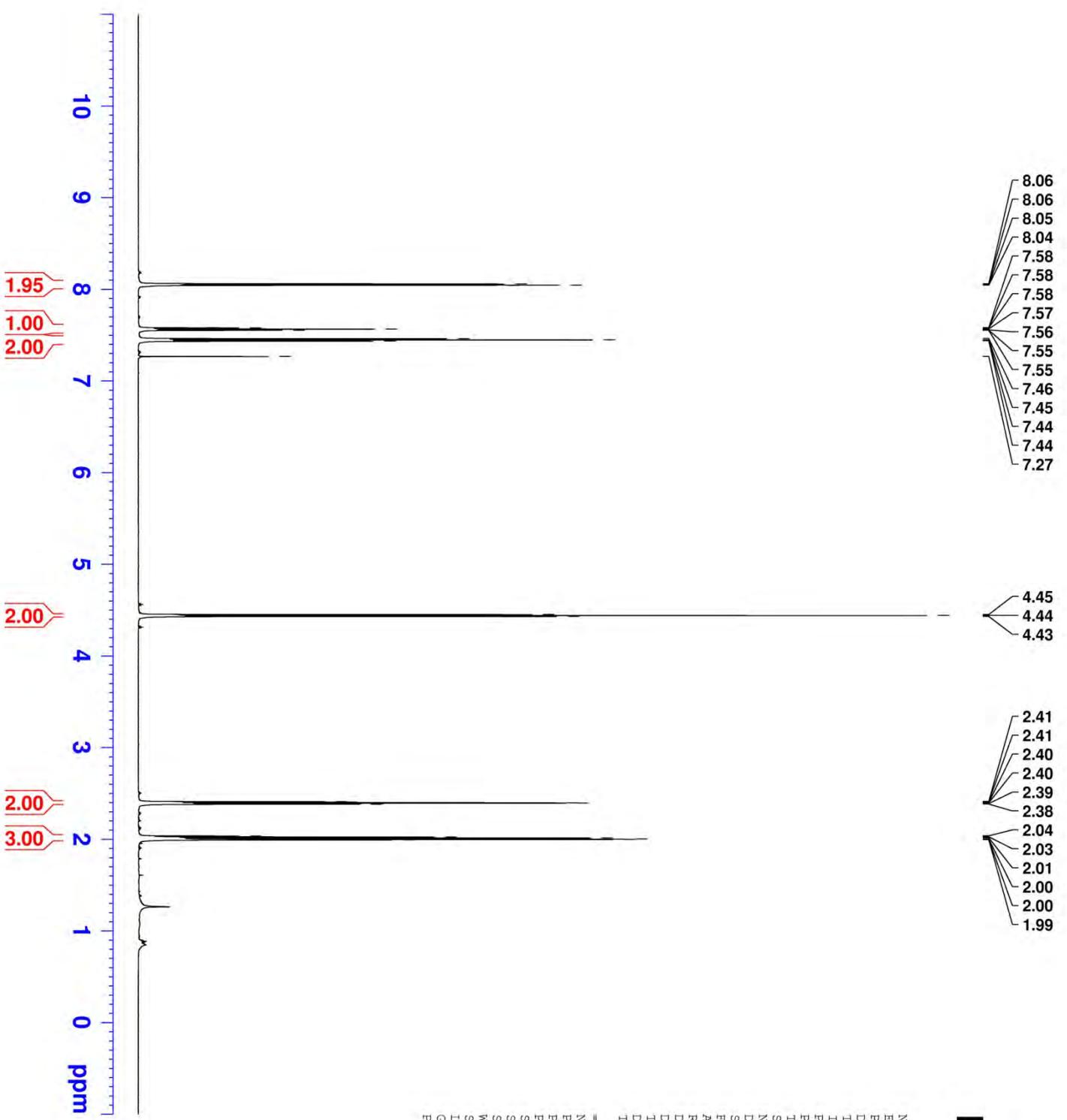
TFish0730_2_product_011911

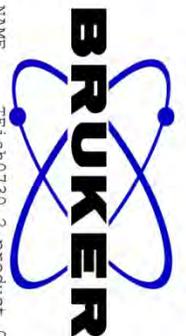
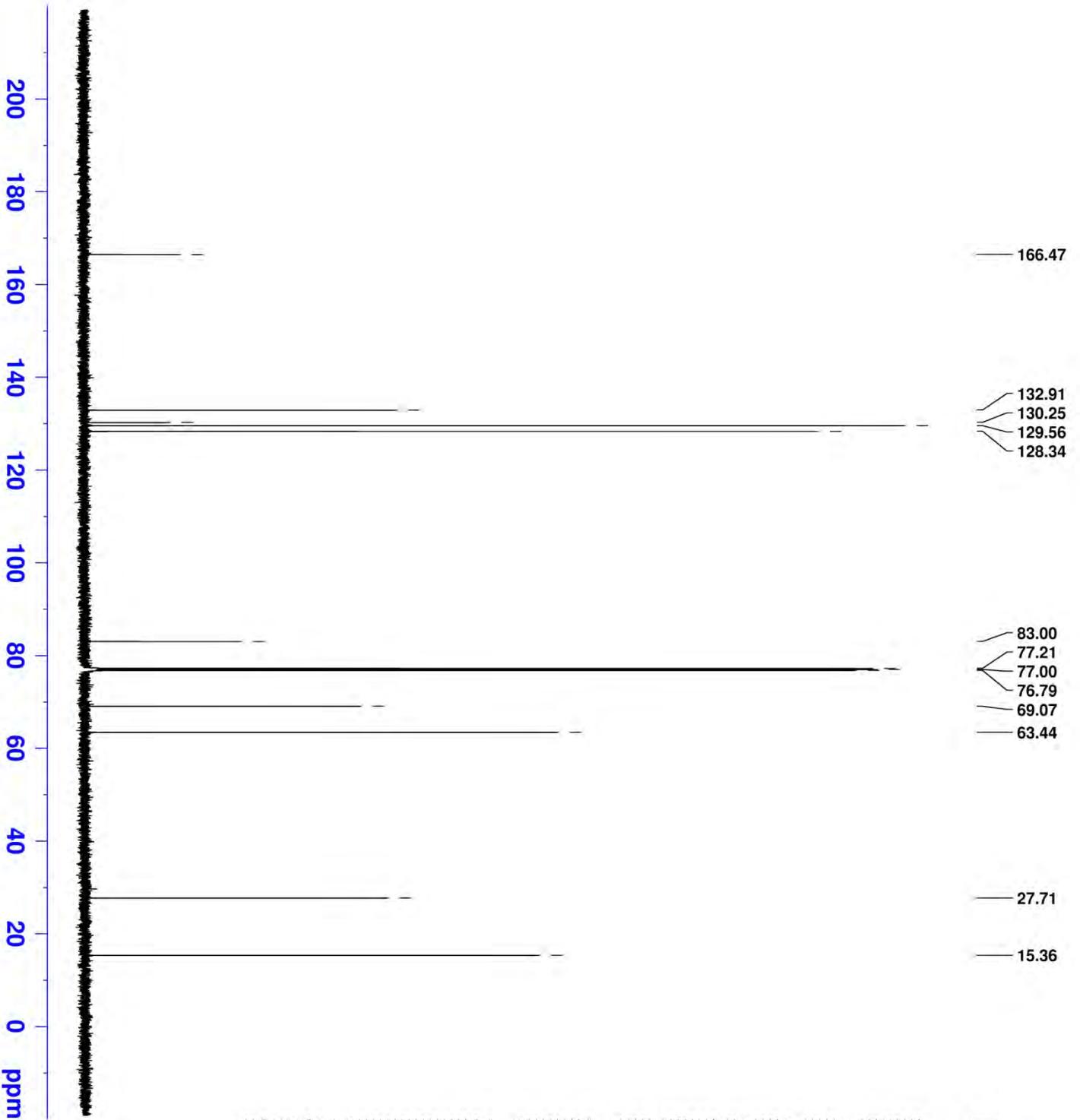
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NAME      TFish0730_2_product_011911
EXPNO     1
PROCNO    1
Date_     20110119
Time      19.28
INSTRUM   spect
PROBHD    5 mm BBO BB-1H
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SWH        12376.237 Hz
FIDRES     0.188846 Hz
AQ         2.6477449 sec
RG         128
DW         40.400 usec
DE         6.50 usec
TE         298.0 K
D1         1.00000000 sec
ID0        1
    
```

```

===== CHANNEL f1 =====
NUC1      1H
P1        14.50 usec
PL1       0.20 dB
PL1W      35.98249435 W
SFO1      600.1827064 MHz
SI         32768
SF         600.1790062 MHz
MDW       EM
SSB       0
LB        0.30 Hz
GB         0
PC         1.00
    
```





```

NAME      TF1sh0730_2_product_011911
EXPNO     2
PROCNO    1
Date_     20110119
Time      19.33
INSTRUM   spect
PROBHD    5 mm BBO BB-1H
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         256
DS         4
SWH        35971.223 Hz
FIDRES    0.548877 Hz
AQ         0.9110143 sec
RG         9195.2
DE         13.900 usec
TE         299.9 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1
    
```

```

===== CHANNEL f1 =====
NUC1      13C
P1        9.70 usec
PL1       1.00 dB
PL1W      59.85786819 W
SFO1      150.9302211 MHz

===== CHANNEL f2 =====
CPDPRG2   waitz16
NUC2      1H
PCPD2     60.00 usec
PI2       0.20 dB
PL12      12.54 dB
PL13      12.54 dB
PL1W      35.98249435 W
PI12W     2.09938097 W
PI13W     2.09938097 W
SFO2      600.1814007 MHz
SI         32768
SF         150.9151318 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

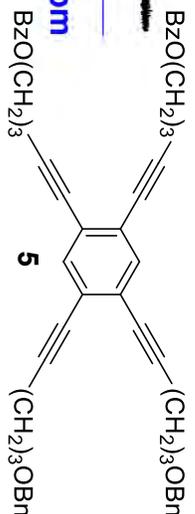
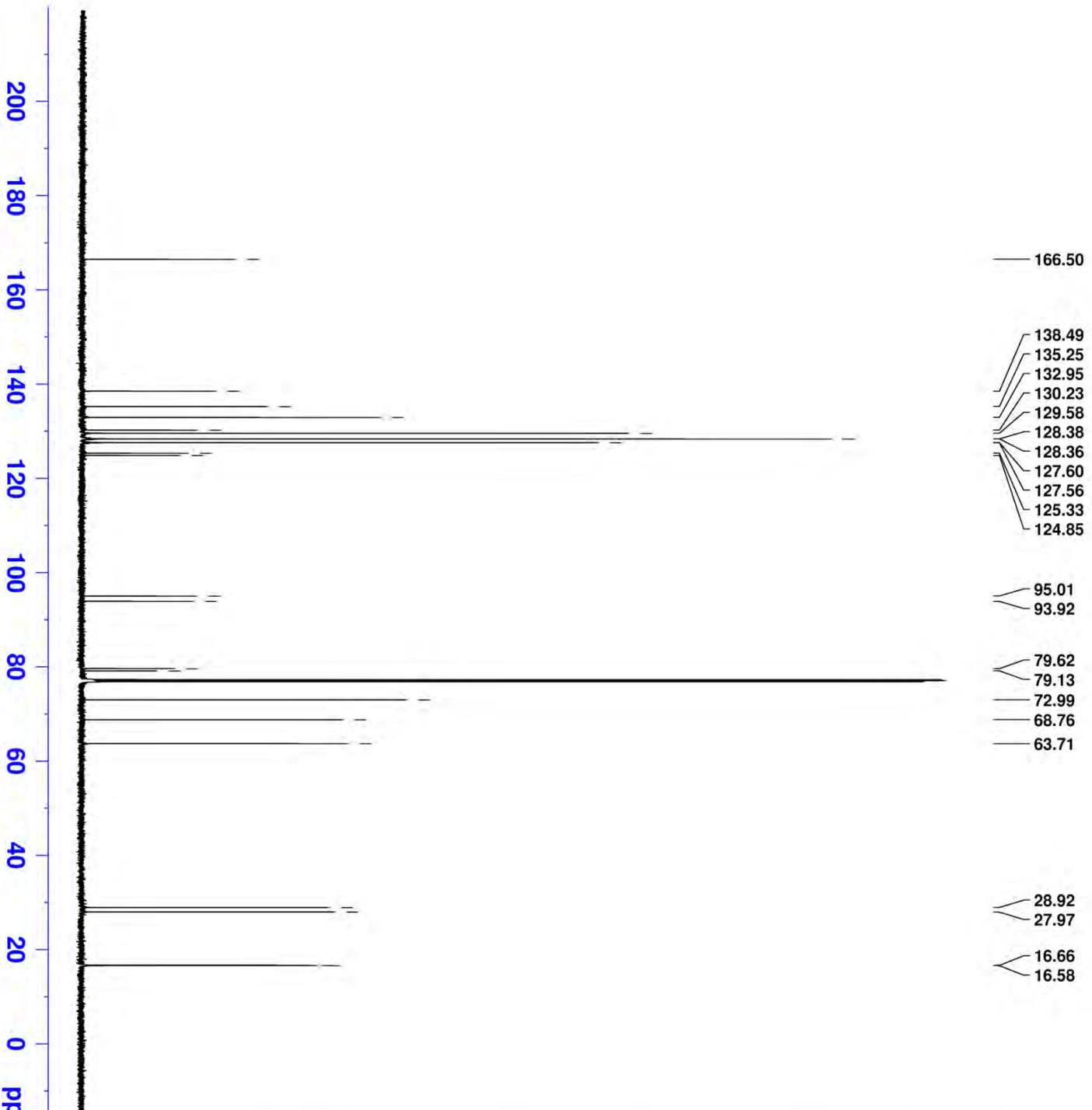




NAME TFish0787_product_030611
 EXPNO 2
 PROCNO 1
 Date_ 20110307
 Time_ 8.13
 INSTRUM spect
 PROBHD BB-IH
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SMH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 14596.5
 DW 13.900 usec
 DE 6.50 usec
 TE 298.2 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

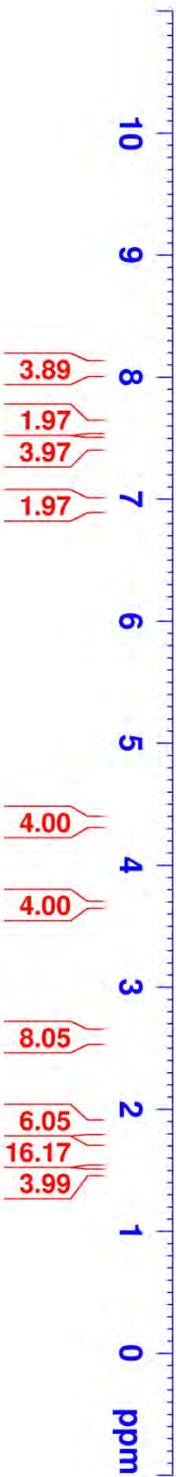
==== CHANNEL F1 =====
 NUC1 13C
 P1 9.70 usec
 PL1 1.00 dB
 SFO1 150.9302211 MHz

==== CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 60.00 usec
 PL2 0.20 dB
 PL12 12.54 dB
 PL13 12.54 dB
 PL1W 35.98249435 W
 PL12W 2.09938097 W
 PL13W 2.09938097 W
 SFO2 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



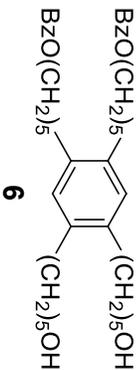
8.08
8.08
8.07
8.06
7.59
7.58
7.57
7.47
7.46
7.45
7.29
6.94

4.37
4.36
4.35
3.69
3.67
3.66
2.63
2.61
2.60
2.58
2.57
1.87
1.86
1.85
1.84
1.82
1.70
1.69
1.68
1.67
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1.61
1.59
1.58
1.56
1.55
1.54
1.50



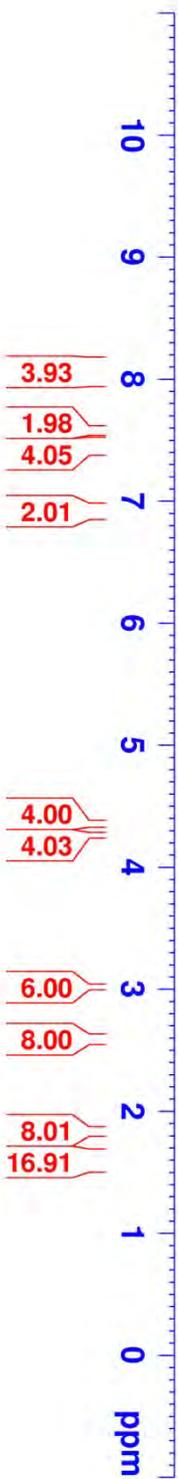
NAME TF1sh0788_Product_031011
 EXPNO 1
 PROCNO 1
 Date_ 20110310
 Time_ 20.21
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 12376.237 Hz
 FIDRES 0.188846 Hz
 AQ 2.6477449 sec
 RG 40.3
 DW 40.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.50 usec
 PL1 0.20 dB
 PL1W 35.98249435 W
 SFO1 600.1827064 MHz
 SI 65536
 SF 600.1789953 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



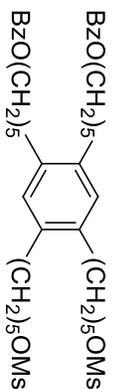
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8.06
8.06
7.59
7.58
7.57
7.47
7.46
7.45
7.29
6.92

4.36
4.35
4.34
4.27
4.26
4.25
3.02
2.62
2.60
2.59
2.58
2.57
2.56
1.87
1.86
1.85
1.83
1.82
1.81
1.80
1.69
1.68
1.66
1.65
1.64
1.63
1.62
1.61
1.59
1.57
1.56
1.55
1.53



NAME TF1sh0791_Product_031111
EXPNO 1
PROCNO 1
Date_ 20110311
Time_ 20.02
INSTRUM spect
PROBHD BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SMH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6477449 sec
RG 114
DW 40.400 usec
DE 6.50 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.50 usec
PL1 0.20 dB
PL1W 35.98249435 W
SFO1 600.1827064 MHz
SI 32768
SF 600.1789957 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



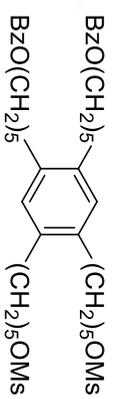
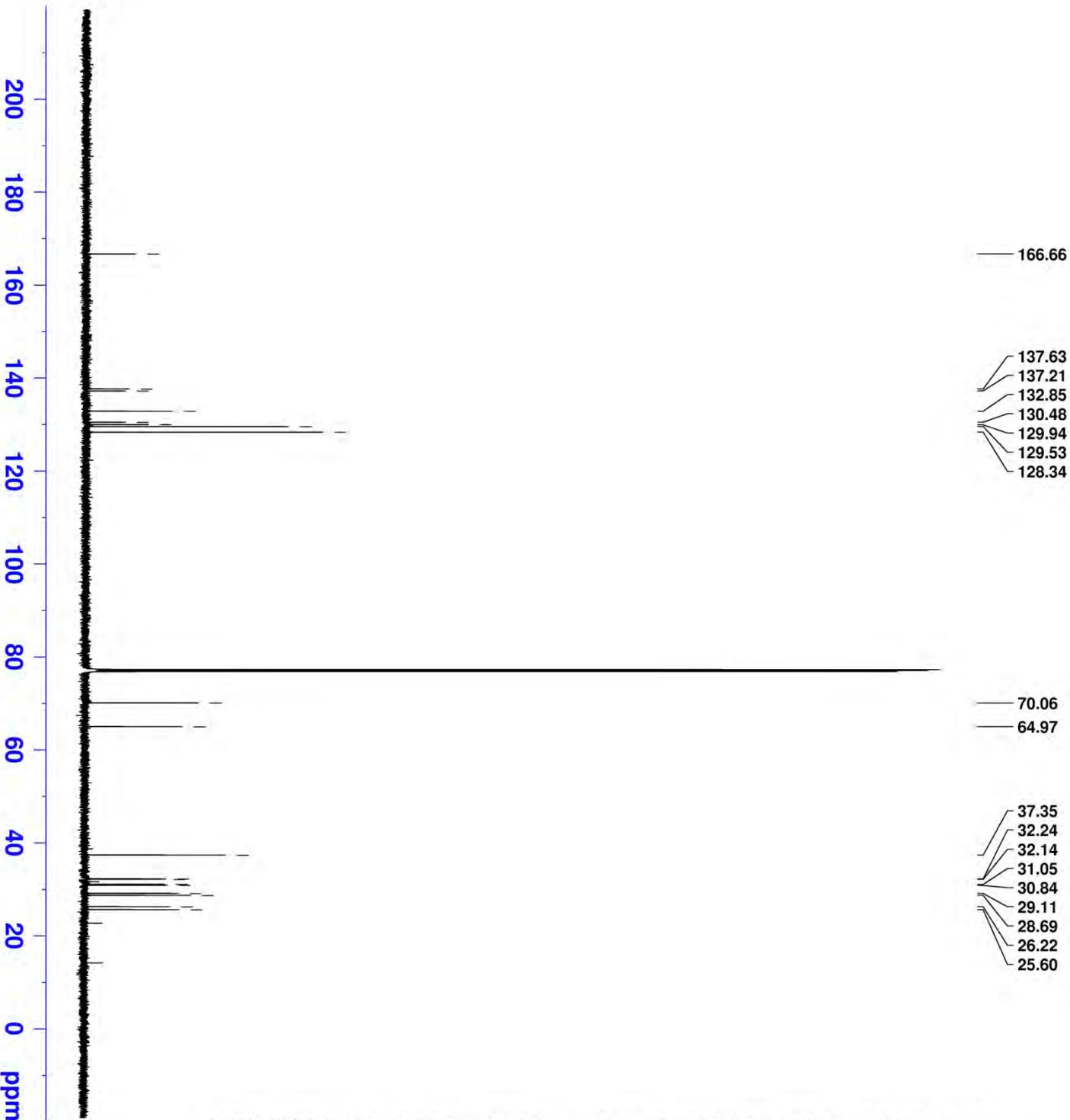


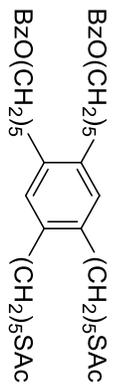
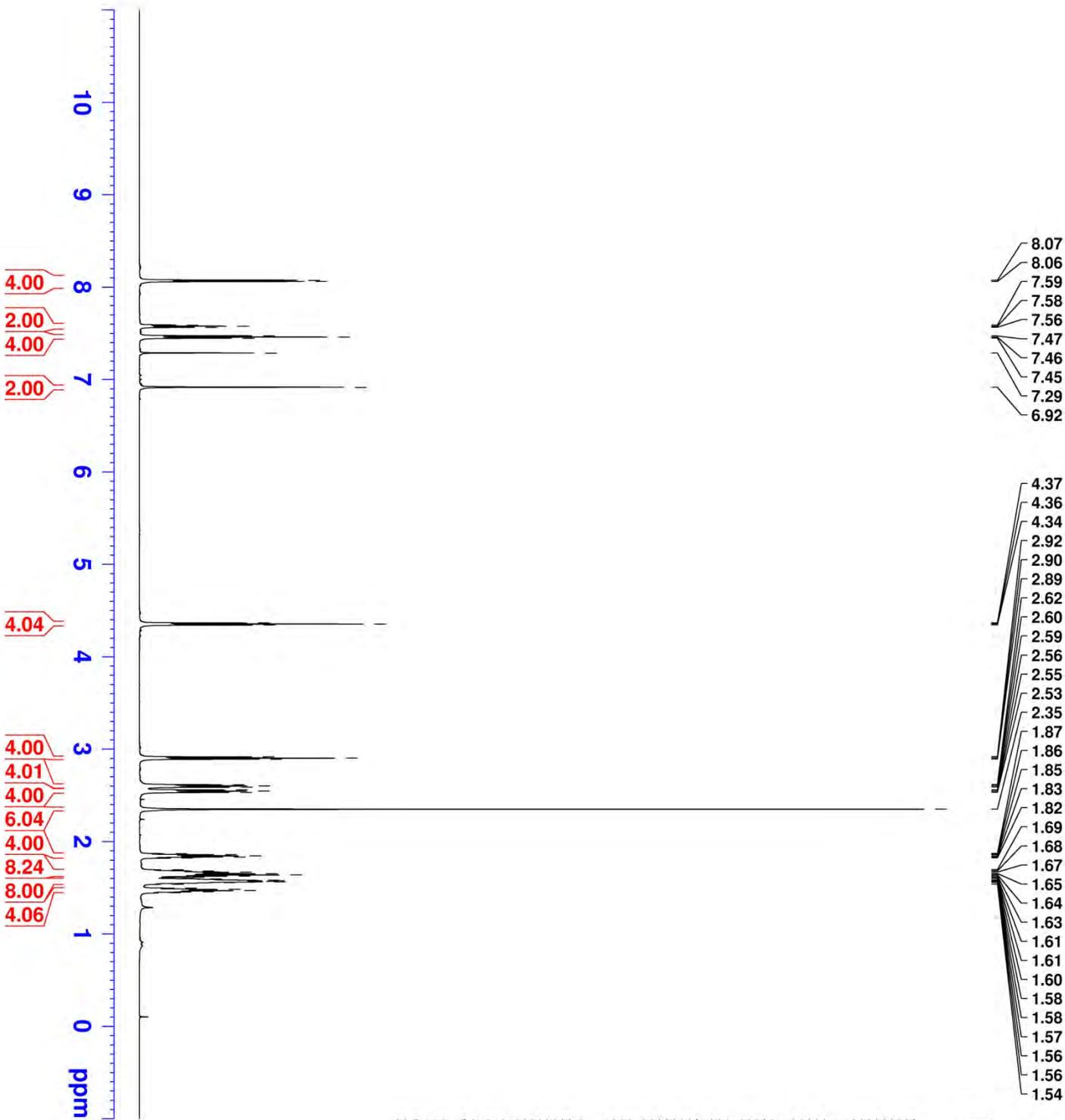
NAME TF1sh0791_Product_031111

EXPNO 2
 PROCNO 1
 Date_ 20110311
 Time_ 20.08
 INSTRUM spect
 PROBH 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 827
 DS 4
 SMH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 4597.6
 DW 13.900 usec
 DE 6.50 usec
 TE 298.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

==== CHANNEL F1 =====
 NUC1 13C
 P1 9.70 usec
 PL1 1.00 dB
 PL1W 59.85786819 W
 SFO1 150.9302211 MHz

==== CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 60.00 usec
 PL2 0.20 dB
 PL12 12.54 dB
 PL13 12.54 dB
 PL2W 35.98249435 W
 PL12W 2.09938097 W
 PL13W 2.09938097 W
 SFO2 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



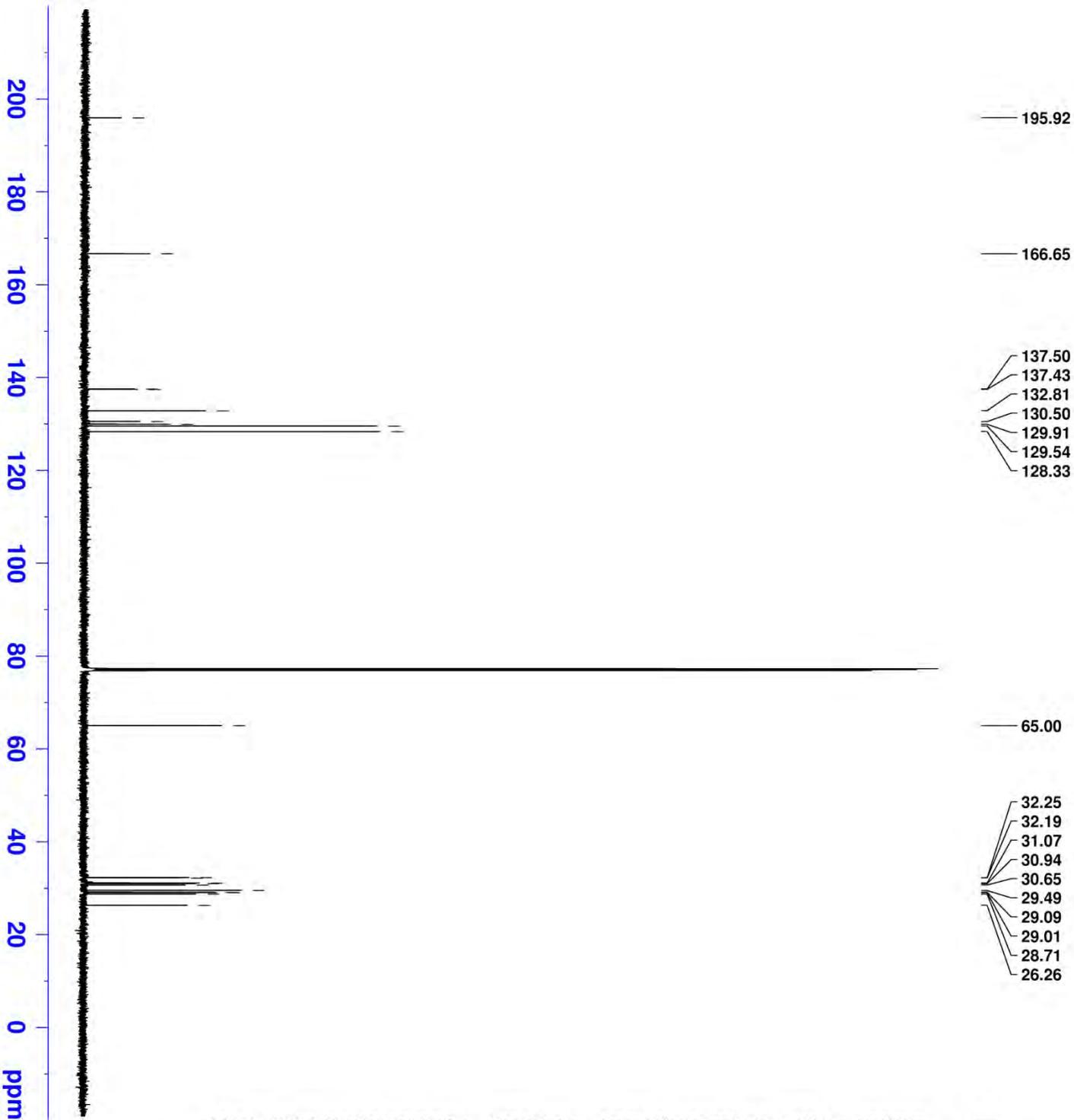


```

===== CHANNEL f1 =====
NUC1      1H
P1         14.50 usec
PL1        0.20 dB
PL1W       35.98249435 W
SFO1       600.1827064 MHz
SI         65536
SF         600.1789956 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00

NAME      TF1sh0793_product_031211
EXPNO     1
PROCNO    1
Date_     20110312
Time      13.04
INSTRUM   spect
PROBHD    5 mm BBO BB-1H
PULPROG   zg30
TD         65536
SOLVENT   CDCl3
NS         16
DS         2
SMH        12376.237 Hz
FIDRES     0.188846 Hz
AQ         2.6477449 sec
RG         90.5
DW         40.400 usec
DE         6.50 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1
    
```



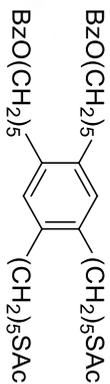


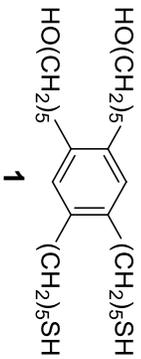
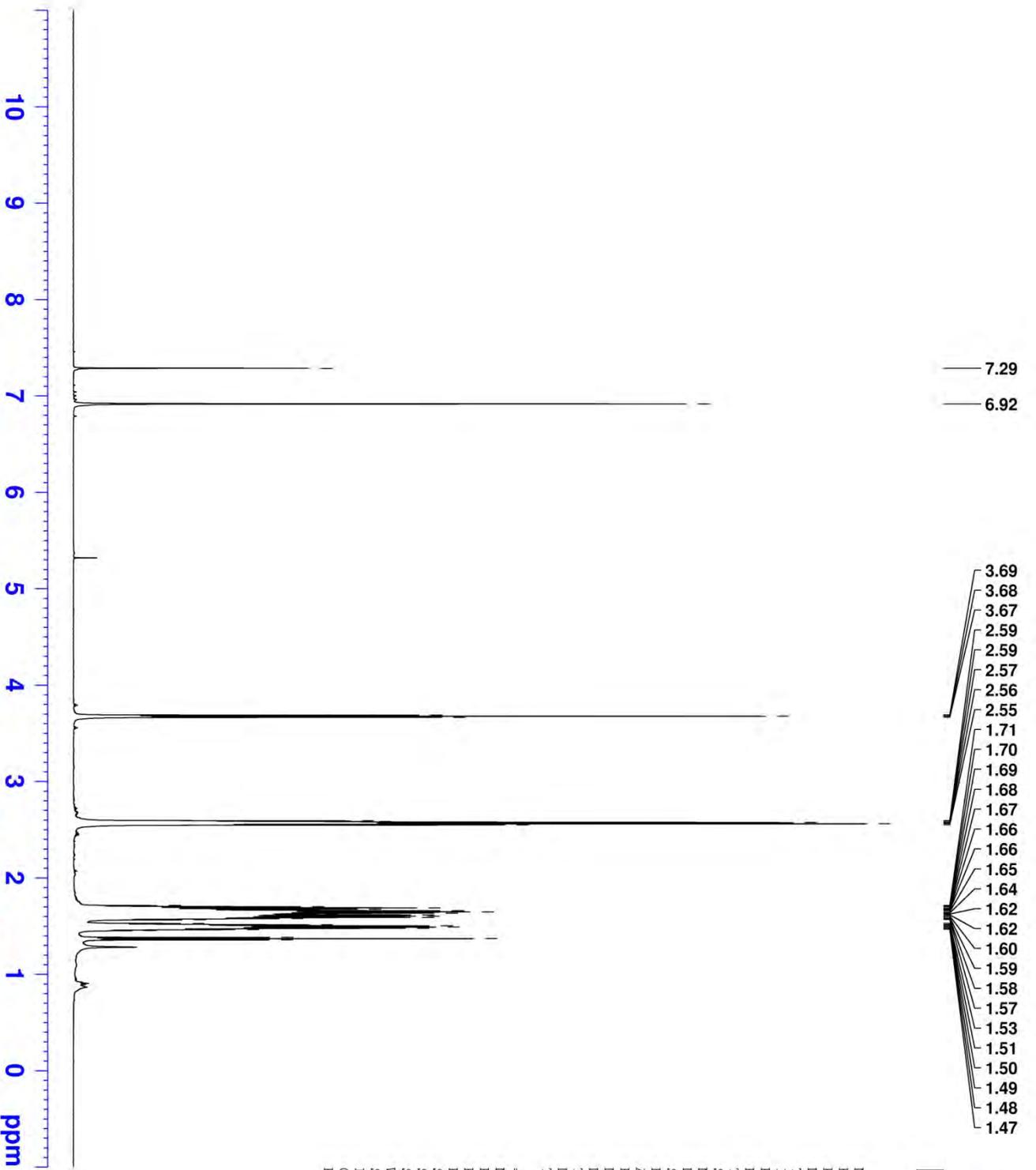
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NAME TF1sh0793_Product_031211
EXPNO 2
PROCNO 1
Date_ 20110312
Time_ 13.10
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SMH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 16384
DW 13.900 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.70 usec
PL1 1.00 dB
PL1W 59.85786819 W
SFO1 150.9302211 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL2 0.20 dB
PL12 12.54 dB
PL13 12.54 dB
PL2W 35.98249435 W
PL12W 2.09938097 W
PL13W 2.09938097 W
SFO2 600.1814007 MHz
SI 32768
SF 150.9151300 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

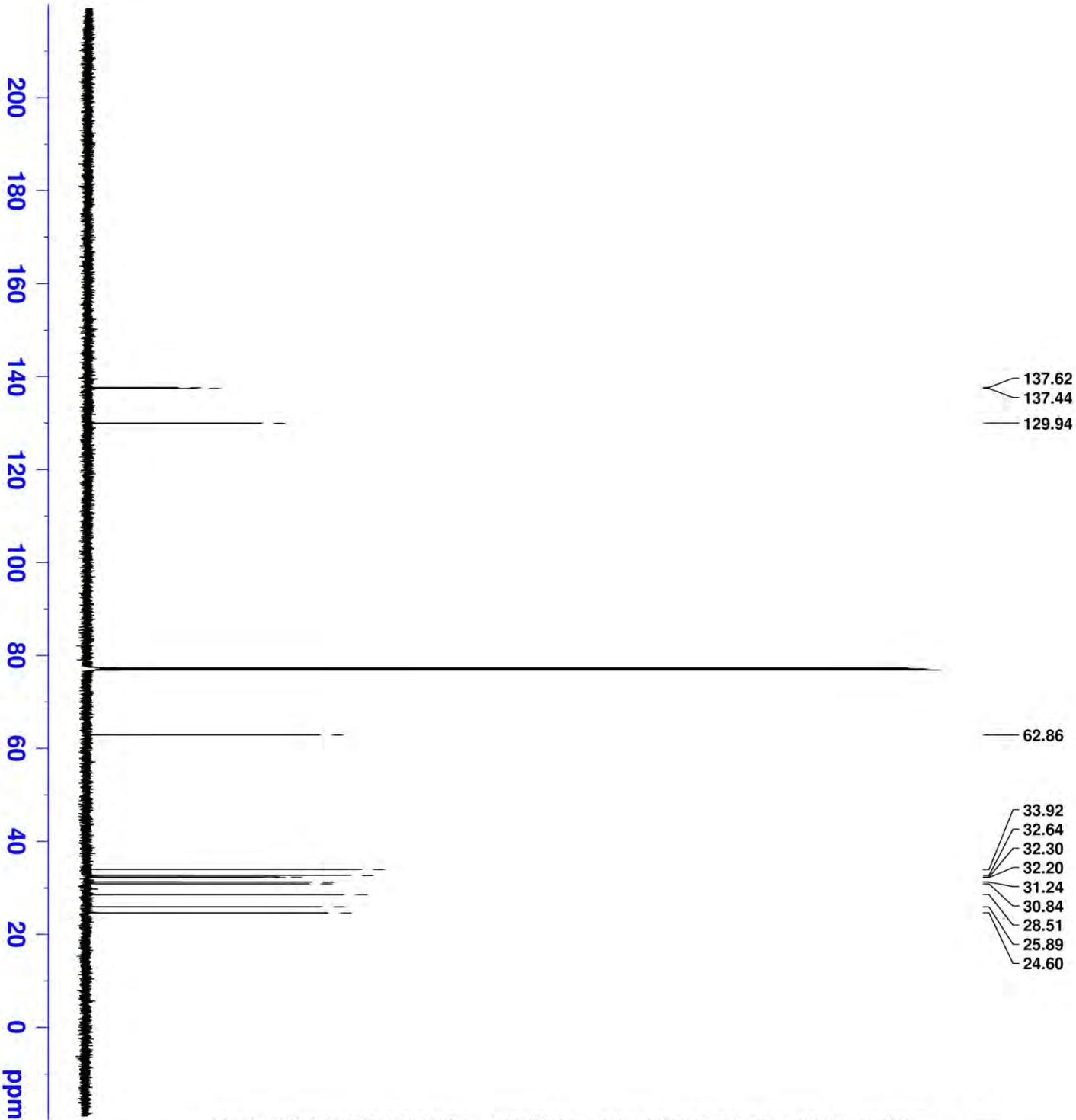




```

NAME TF1sh0794_Product_031211
EXPNO 1
PROCNO 1
Date_ 20110314
Time_ 10.30
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SMH 12376.237 Hz
FIDRES 0.188846 Hz
AQ 2.6477449 sec
RG 71.8
DE 40.400 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.50 usec
PL1 0.20 dB
PL1W 35.98249435 W
SFO1 600.1827064 MHz
SI 32768
SF 600.1789954 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
```

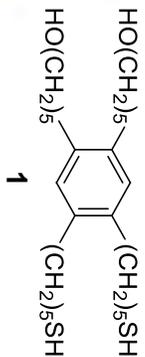


```

NAME TF1sh0794_Product_031211
EXPNO 2
PROCNO 1
Date_ 20110314
Time_ 10.35
INSTRUM spect
PROBHD 5 mm BBO BB-1H
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 470
DS 4
SMH 35971.223 Hz
FIDRES 0.548877 Hz
AQ 0.9110143 sec
RG 9195.2
DE 13.900 usec
TE 298.1 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 9.70 usec
PL1 1.00 dB
PL1W 59.85786819 W
SFO1 150.9302211 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 60.00 usec
PL2 0.20 dB
PL12 12.54 dB
PL13 12.54 dB
PL12W 35.98249435 W
PL13W 2.09938097 W
SFO2 600.1814007 MHz
SI 32768
SF 150.9151300 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
    
```

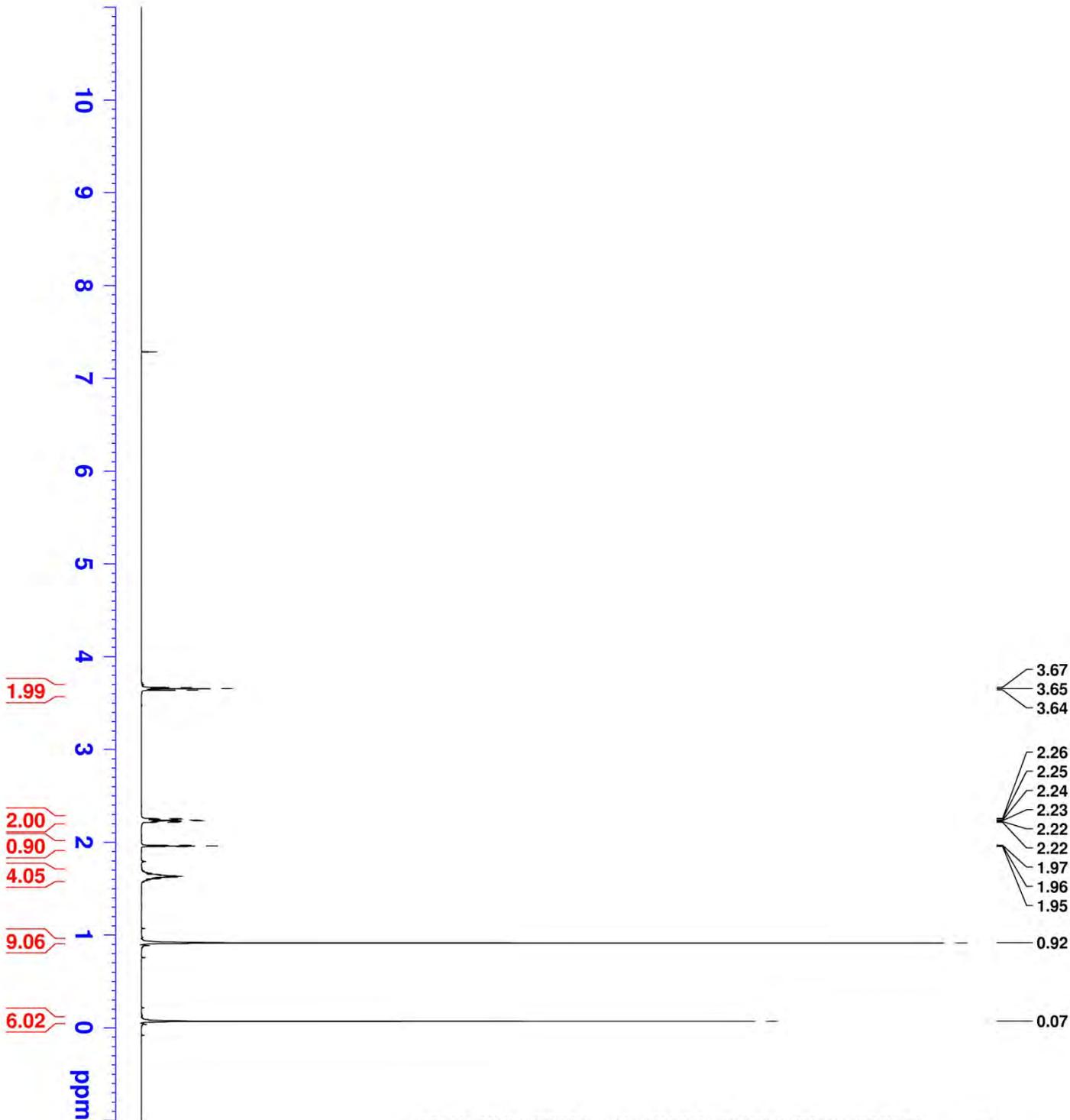




```

NAME IFish0835_product_061411
EXPNO 1
PROCNO 1
Date_ 20110614
Time 10.06
INSTRUM spect
PROBHD 5 mm QNP 1H/13
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SMH 8278.146 Hz
FIDRES 0.126314 Hz
AQ 3.9584243 sec
RG 57
DE 60.400 usec
TE 298.0 K
D1 1.00000000 sec
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 12.00 usec
PL1 2.30 dB
SFO1 400.1324710 MHz
SI 32768
SF 400.1239991 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
    
```

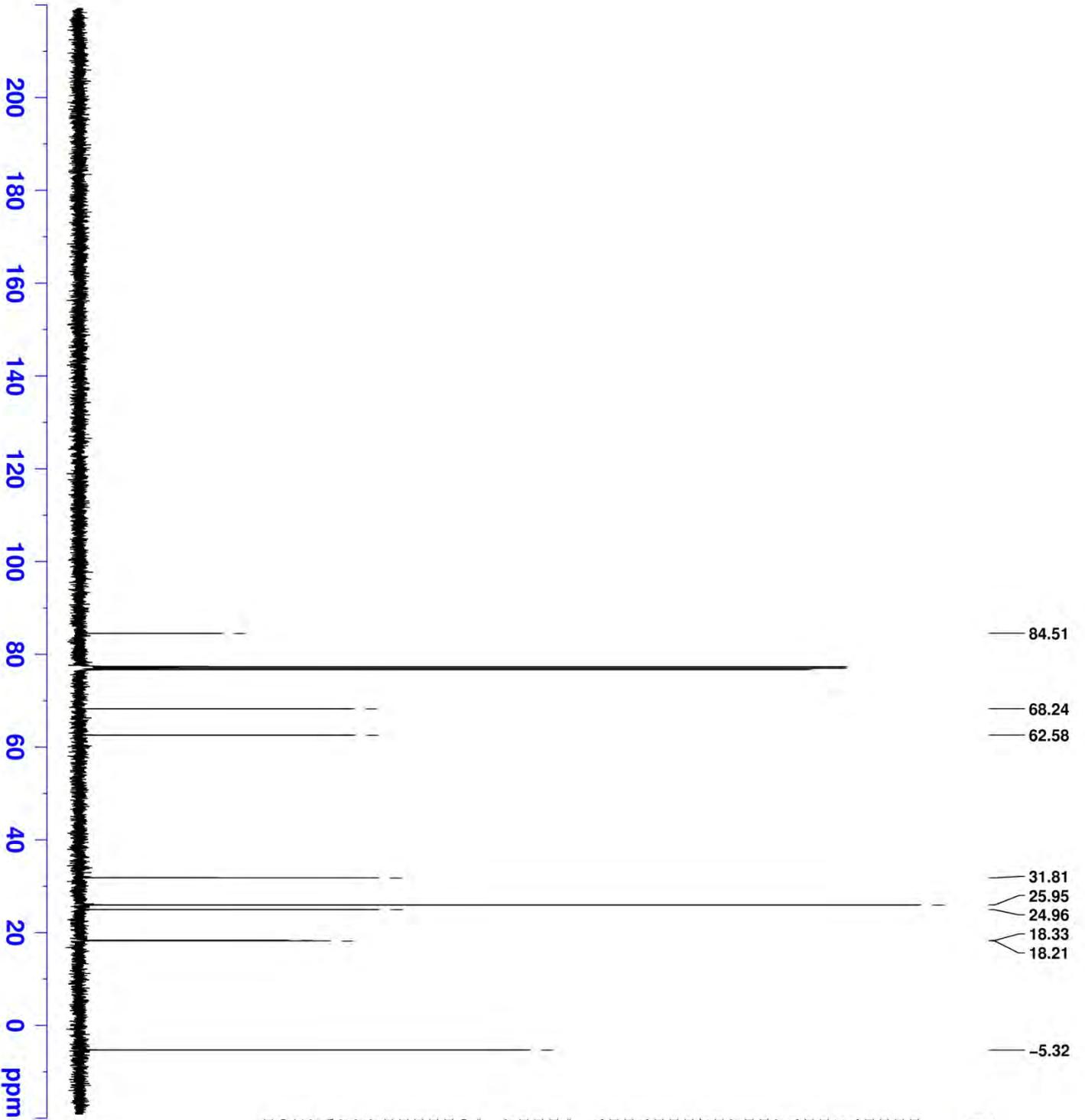


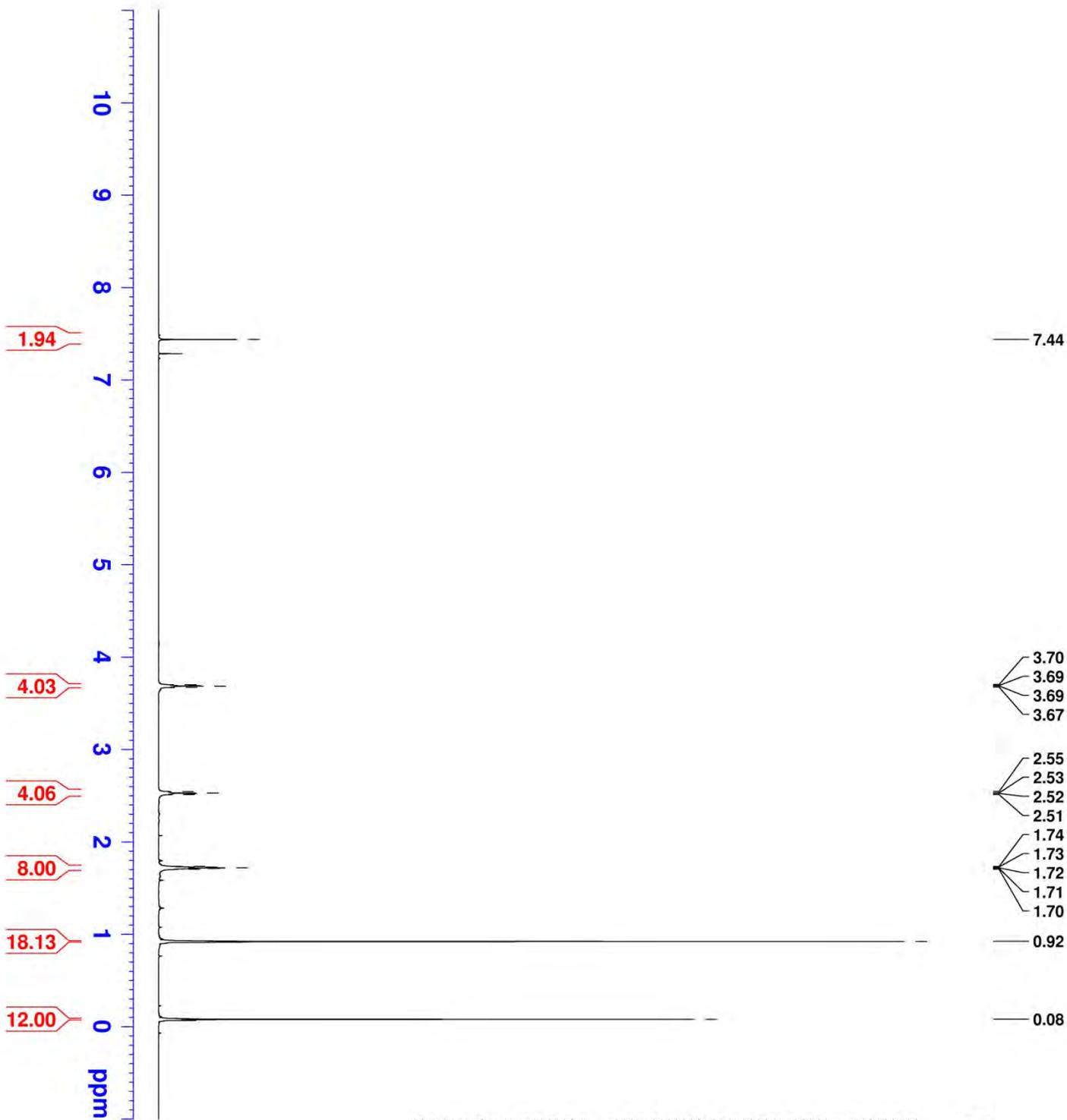


NAME IFish0835_product_061411
 EXPNO 2
 PROCNO 1
 Date_ 20110614
 Time 10.12
 INSTRUM spect
 PROBH 5 mm QNP 1H/13
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 347
 DS 4
 SMH 23980.814 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 2048
 DW 20.850 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL F1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 0.50 dB
 SFO1 100.6228298 MHz

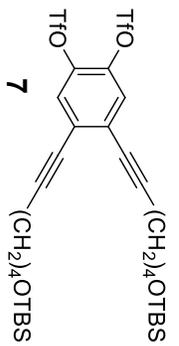
==== CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 70.00 usec
 PL2 -3.35 dB
 PLI2 13.34 dB
 PLI3 13.34 dB
 SFO2 400.1316005 MHz
 SI 32768
 SF 100.6127690 MHz
 SE EM
 WDW 0
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

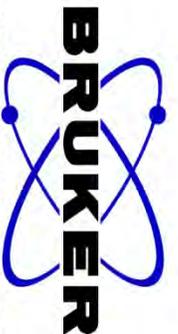




NAME TF1sh0836_product_061311
 EXPNO 1
 PROCNO 1
 Date_ 20110613
 Time_ 19.51
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 71.8
 DW 60.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

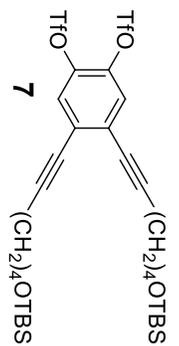
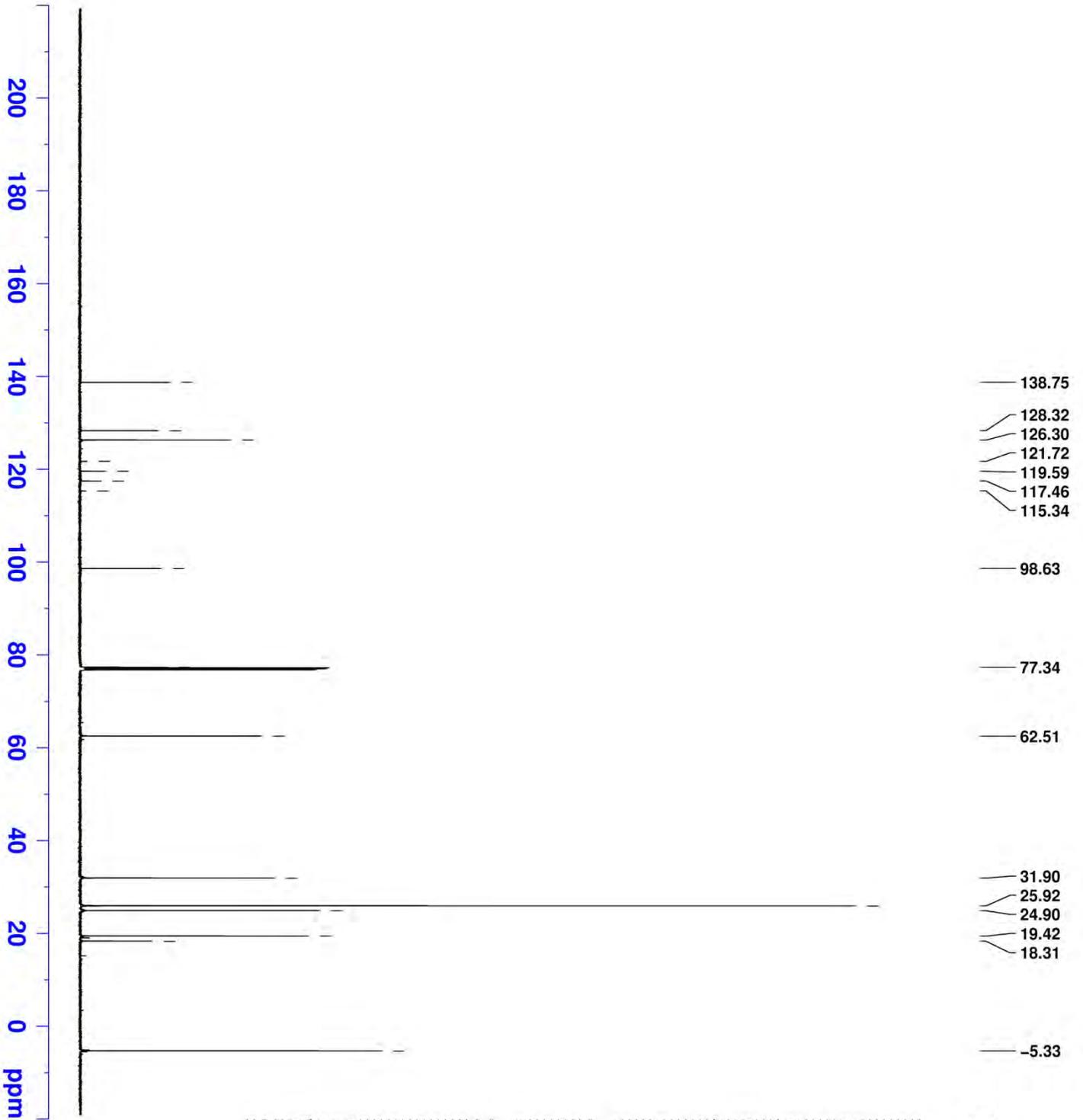
==== CHANNEL f1 =====
 NUC1 1H
 P1 12.00 usec
 PL1 -2.30 dB
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1299991 MHz
 MWDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME TFish0880_2_product_100511
 EXPNO 1
 PROCNO 2
 Date_ 20111005
 Time 13.22
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SMH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 11585.2
 DW 13.900 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

==== CHANNEL F1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -4.30 dB
 PL1W 202.82490540 W
 SFO1 150.9302211 MHz
 =====
 CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 0.00 dB
 PL12 16.66 dB
 PL13 16.66 dB
 PL2W 37.67829514 W
 PL12W 0.81300133 W
 PL13W 0.81300133 W
 SFO2 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

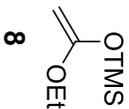
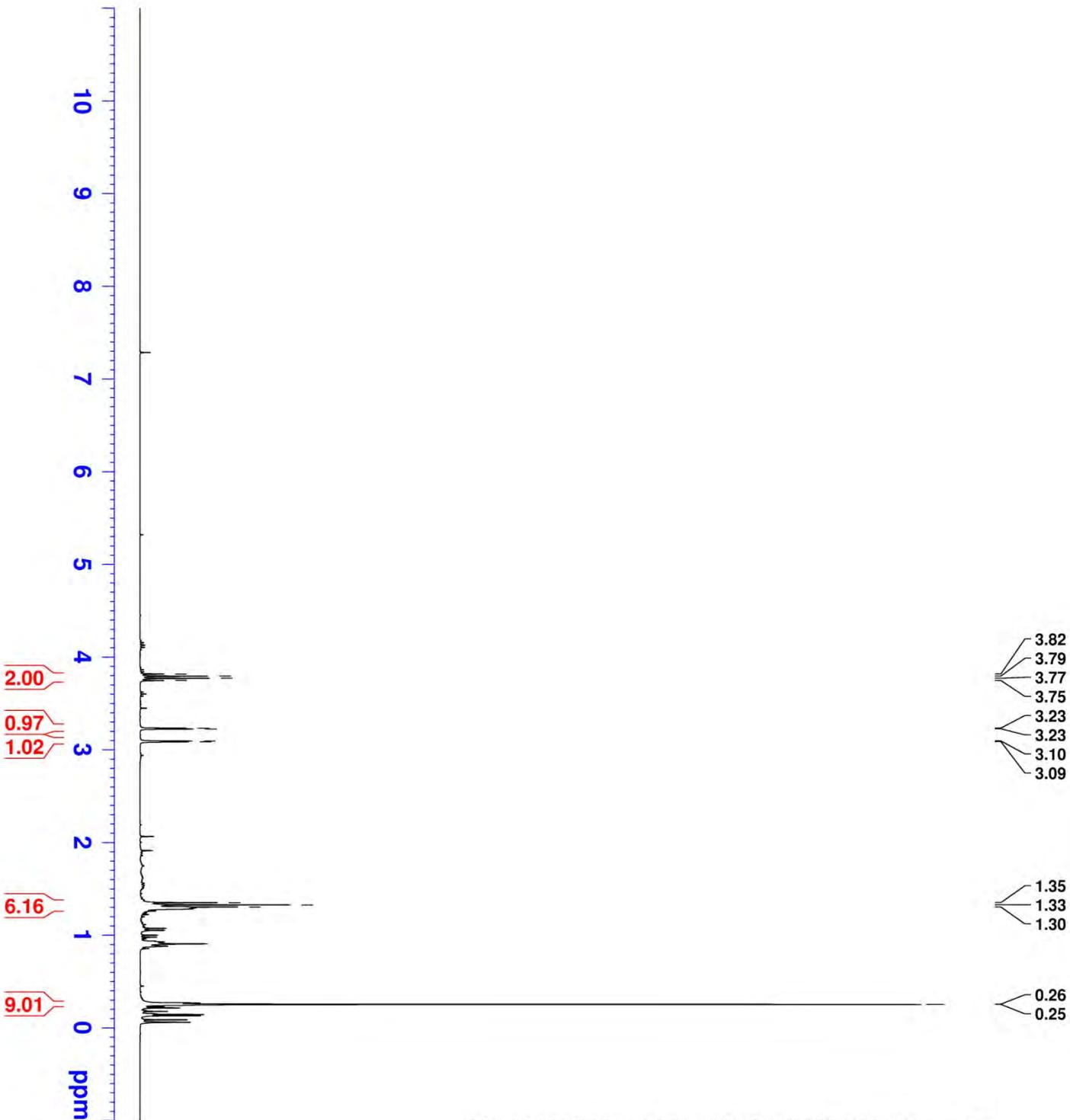


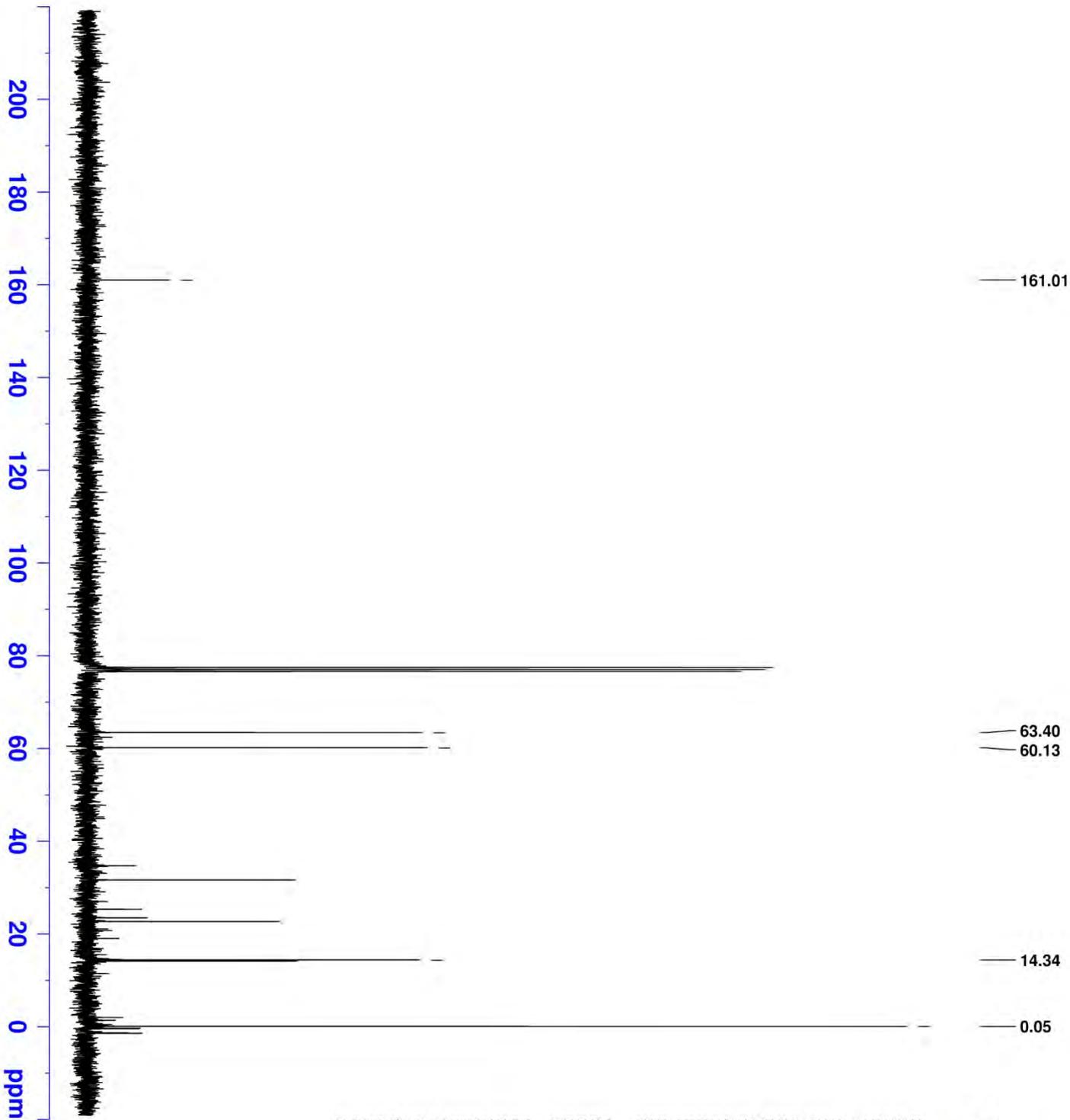


```

NAME      Tfish0921_7_dish11led_092012
EXPNO     1
PROCNO    1
Date_     20120920
Time      18.40
INSTRUM   spect
PROBHD    5 mm QNP 1H/13
PULPROG   zg30
TD         32768
SOLVENT   CDCl3
NS         16
DS         2
SMH        5995.204 Hz
FIDRES    0.162959 Hz
AQ         2.7329011 sec
RG         90.5
DE         83.400 usec
TE         298.0 K
D1         1.00000000 sec
TD0        1

===== CHANNEL f1 =====
NUC1       1H
P1         10.00 usec
PL1        2.20 dB
SFO1       300.1318534 MHz
SI         32768
SF         300.1299983 MHz
WDW        EM
SSB        0
LB         0.30 Hz
GB         0
PC         1.00
    
```



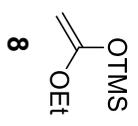


```

NAME: TF1sh0921_7_distill1ed_092012
EXPNO: 1
PROCNO: 2
Date_: 20120920
Time: 18.44
INSTRUM: spect
PROBHD: 5 mm QNP 1H/13
PULPROG: zgpg30
TD: 32768
SOLVENT: CDCl3
NS: 233
DS: 4
SWH: 17985.611 Hz
FIDRES: 0.548877 Hz
AQ: 0.9110004 sec
RG: 8192
DE: 27.800 usec
TE: 298.0 K
D1: 2.00000000 sec
D11: 0.03000000 sec
TDO: 1

===== CHANNEL f1 =====
NUC1: 13C
P1: 10.00 usec
PL1: 5.20 dB
SFO1: 75.4752953 MHz

===== CHANNEL f2 =====
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 70.00 usec
PL2: 2.20 dB
PL12: 19.10 dB
PL13: 19.10 dB
SFO2: 300.1312005 MHz
SI: 32768
SF: 75.4677490 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40
    
```

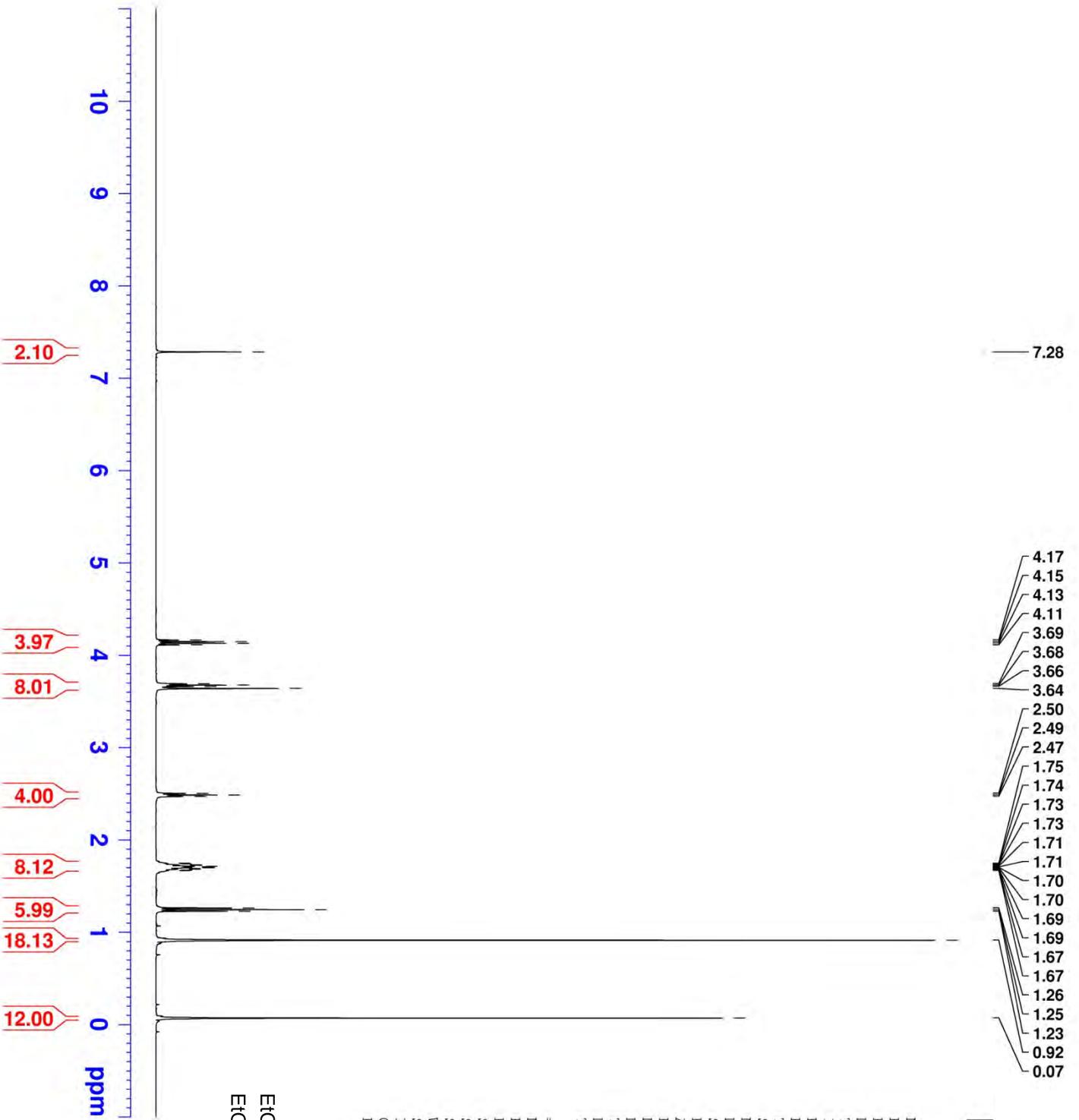
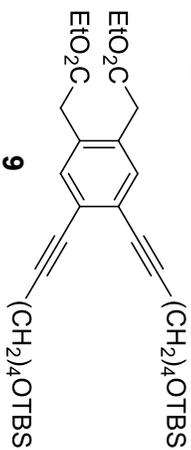




NAME TFish0926_5-15_012812

EXPNO 1
 PROCNO 1
 Date_ 20120128
 Time 19.23
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 35.9
 DW 60.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 -4.00 dB
 SF01 400.1324710 MHz
 SI 32768
 SF 400.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

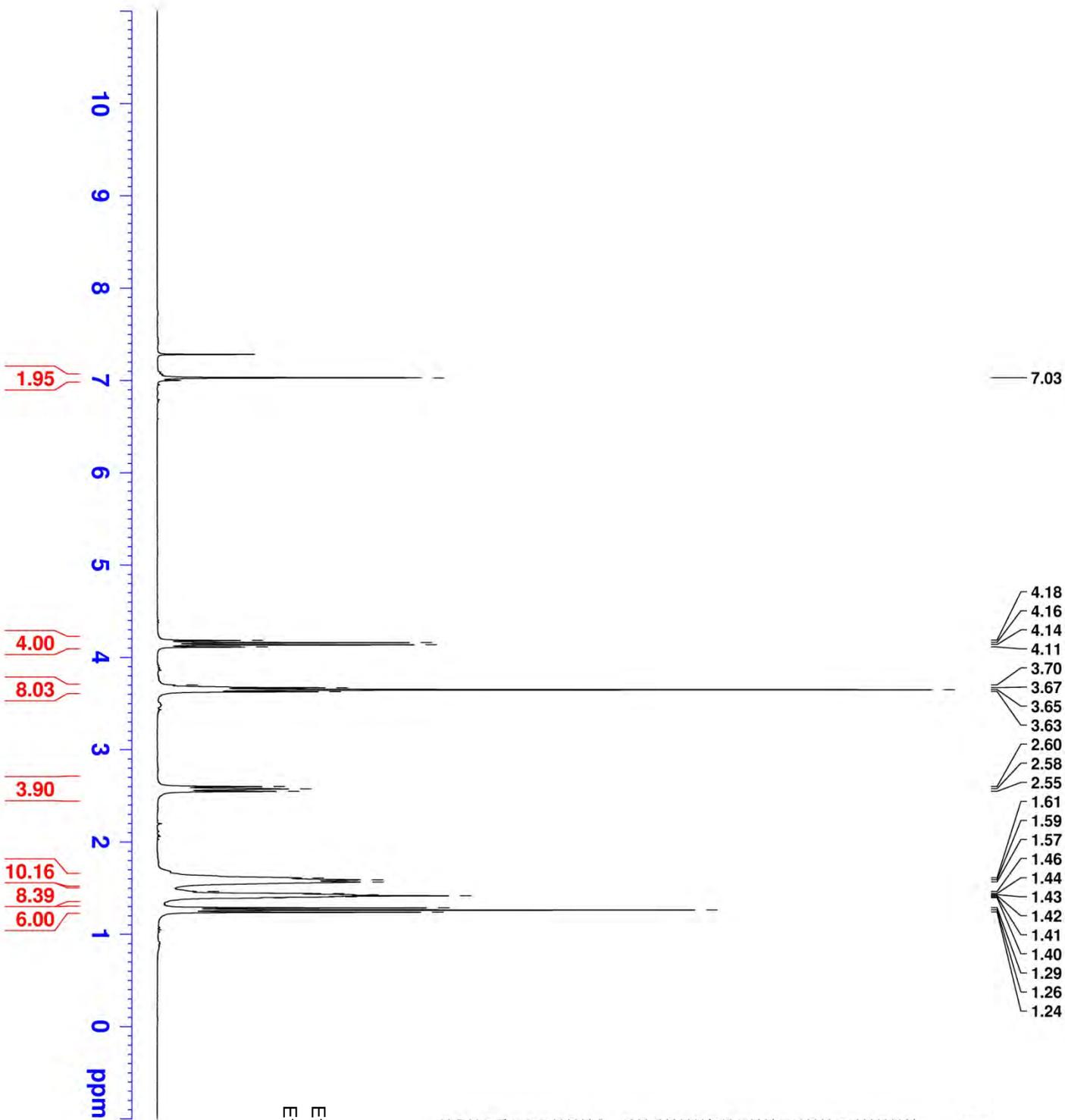
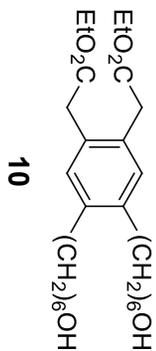




NAME TFish0928_3_product_072612

EXPNO 3
 PROCNO 1
 Date_ 20120726
 Time 18.42
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 32768
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 5995.204 Hz
 FIDRES 0.182959 Hz
 AQ 2.7329011 sec
 RG 161.3
 DW 83.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PL1 2.20 dB
 SFO1 300.1318534 MHz
 SI 32768
 SF 300.1300000 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





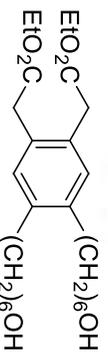
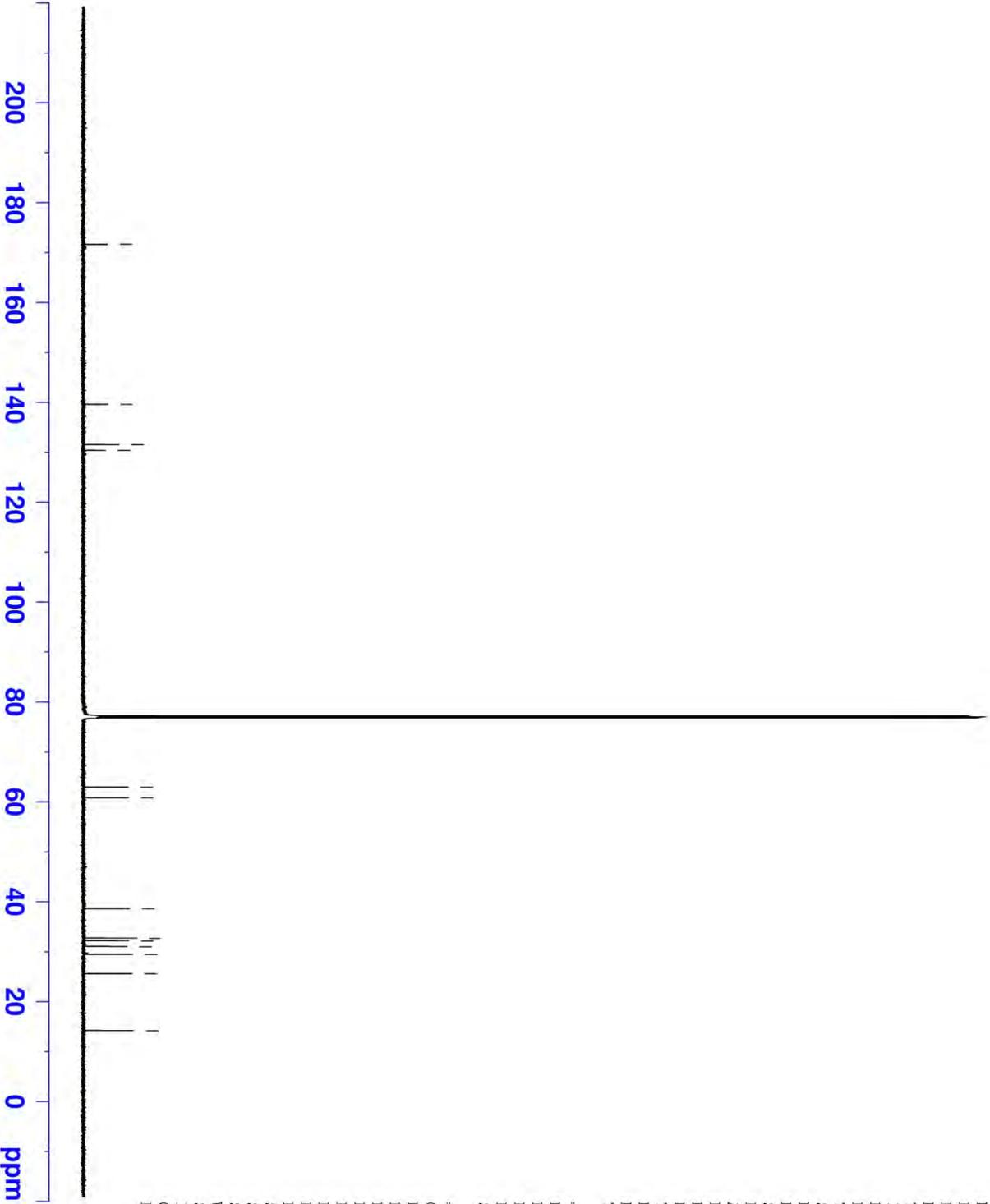
NAME TFish0929_Prod_050712

EXPNO 2
 PROCNO 1
 Date_ 20120507
 Time 10.49
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1833
 DS 4
 SWH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 9195.2
 DM 13.900 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -5.00 dB
 PL1W 238.29847717 W
 SF01 150.9302211 MHz

==== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.30 dB
 PL12 14.74 dB
 PL13 14.75 dB
 PL12W 63.98692703 W
 PL13W 1.26500225 W
 PL13W 1.26209271 W
 SF02 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

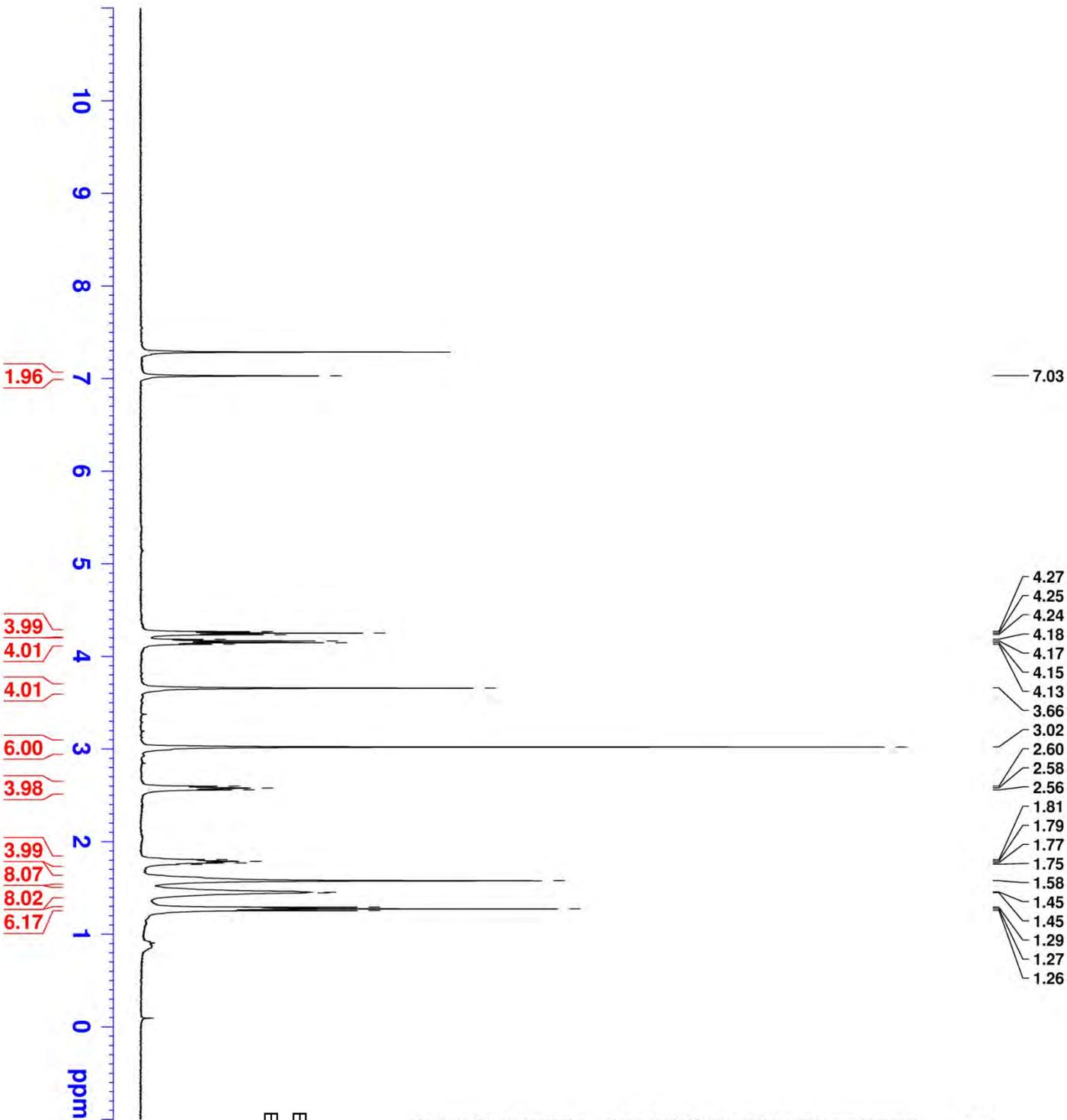
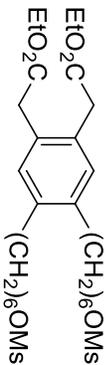
- 171.68
- 139.63
- 131.53
- 130.39
- 62.93
- 60.81
- 38.59
- 32.69
- 32.18
- 31.03
- 29.43
- 25.58
- 14.18





NAME TFish0930_product_050512
 EXPNO 1
 PROCNO 1
 Date_ 20120505
 Time 15.27
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 456.1
 DW 60.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

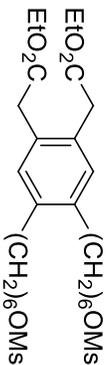
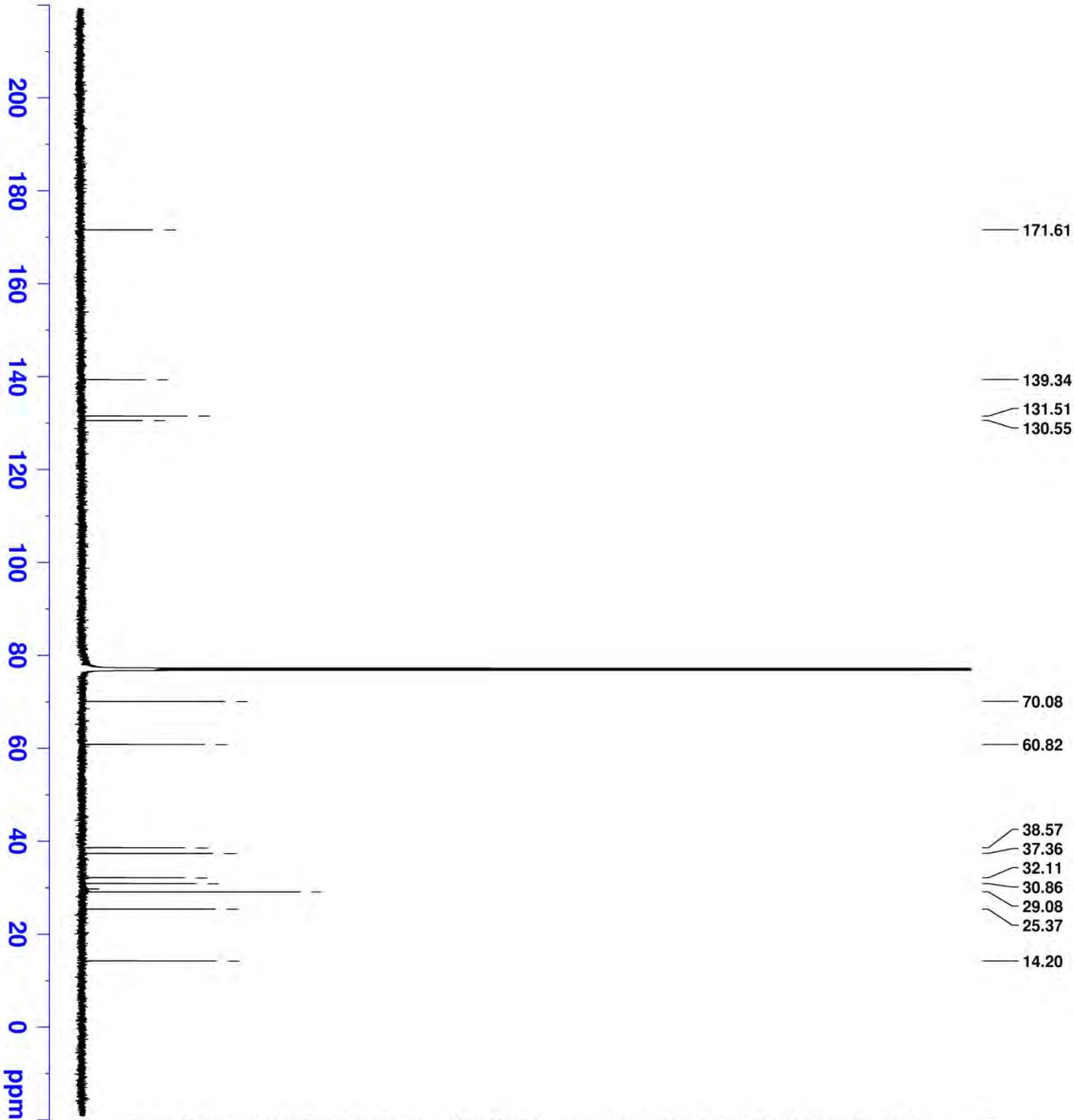
===== CHANNEL f1 =====
 NUC1 1H
 P1 10.00 usec
 PLI -4.00 dB
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1300000 MHz
 WDM EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME TFish0930_pure_050812
 EXPNO 2
 PROCNO 1
 Date_ 20120508
 Time 16.19
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 28628
 DS 4
 SWH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 9195.2
 DM 13.900 usec
 DE 1.000 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

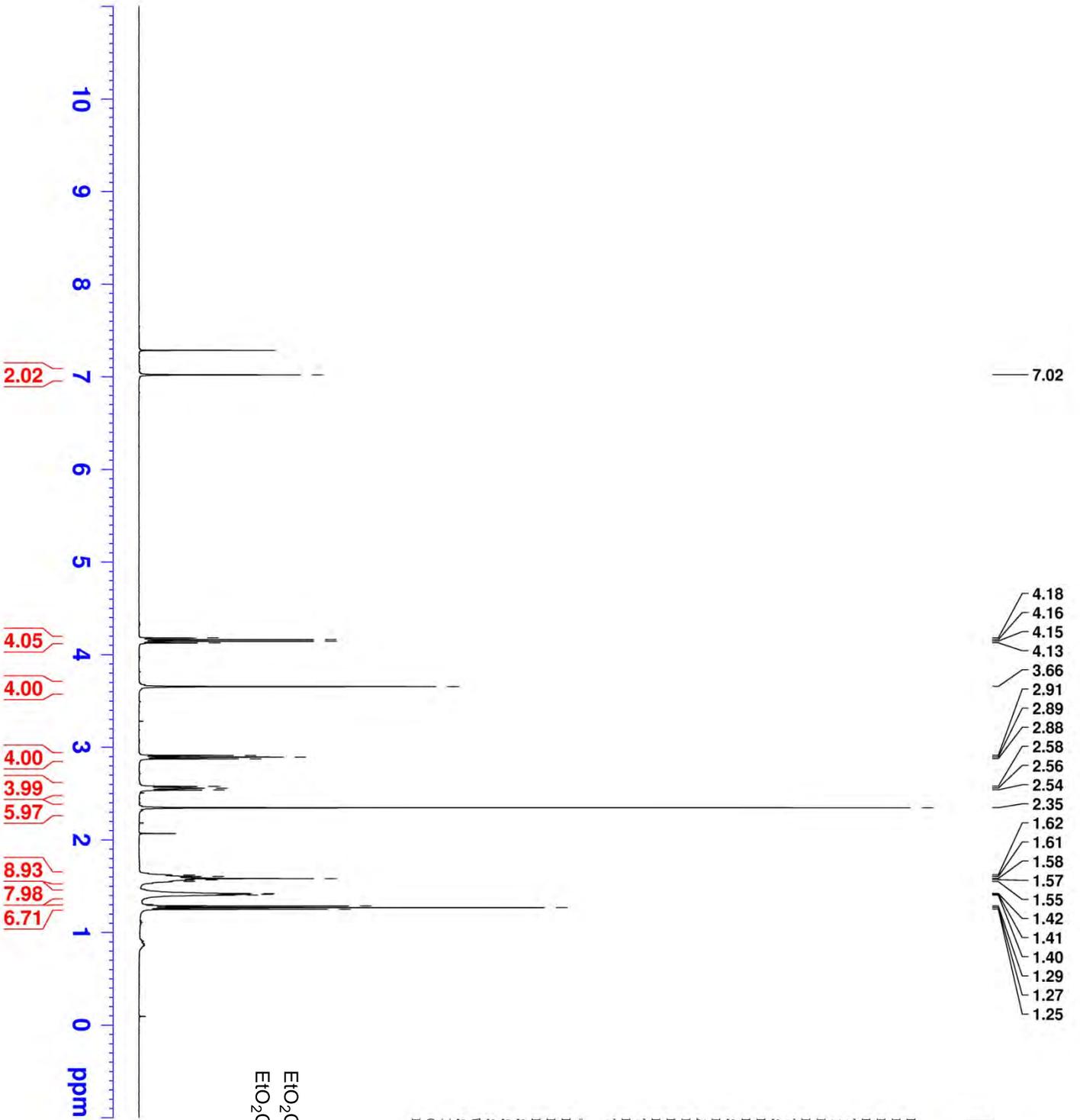
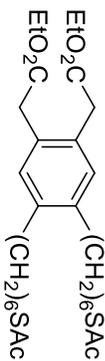
==== CHANNEL F1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -5.00 dB
 PL1W 238.29847717 W
 SF01 150.9302211 MHz
 ===== CHANNEL F2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.30 dB
 PL12 14.74 dB
 PL13 14.75 dB
 PL12W 63.98692703 W
 PL13W 1.26500225 W
 SF02 1.26209271 W
 SF01 600.1814007 MHz
 SI 32768
 SE 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

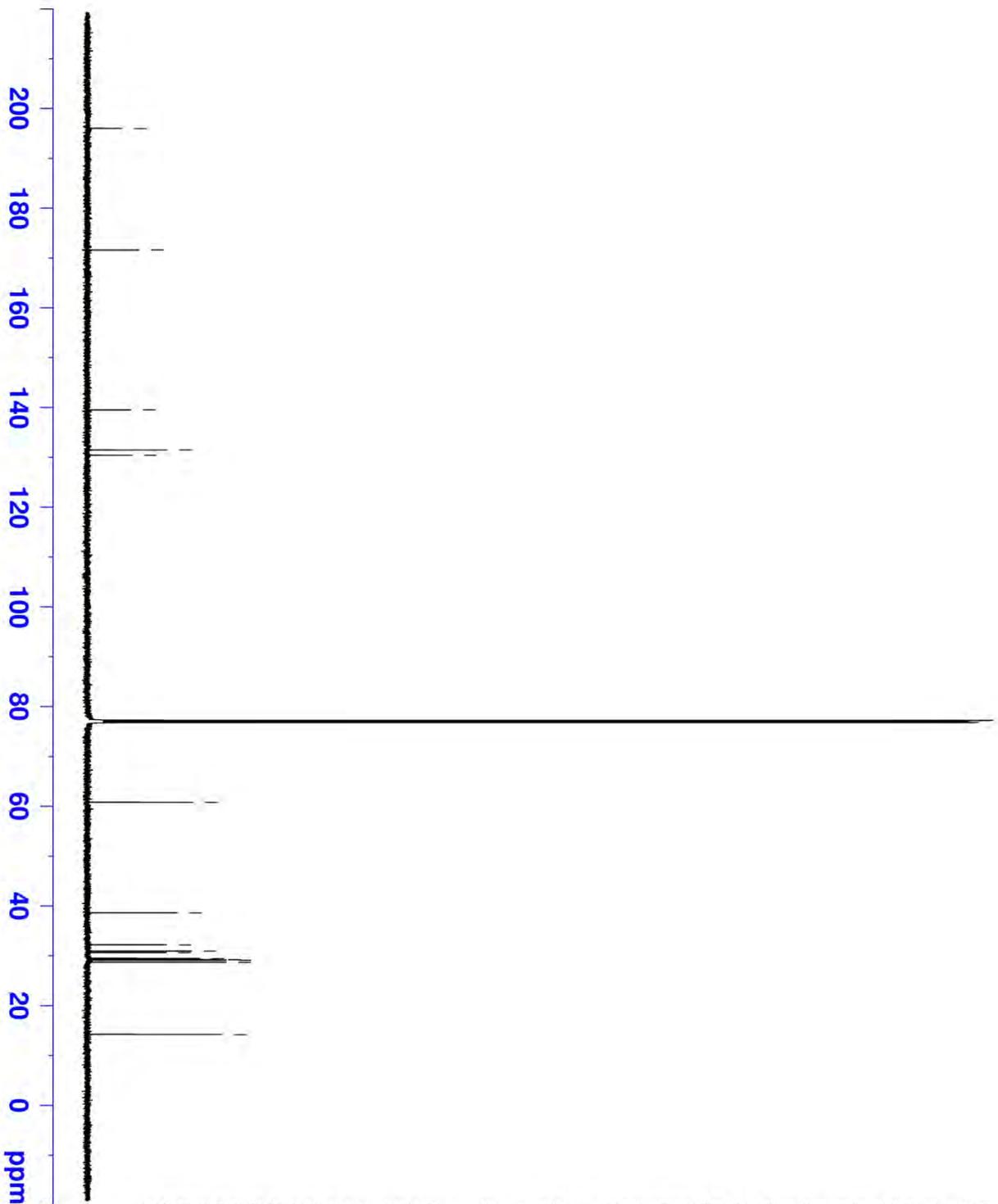
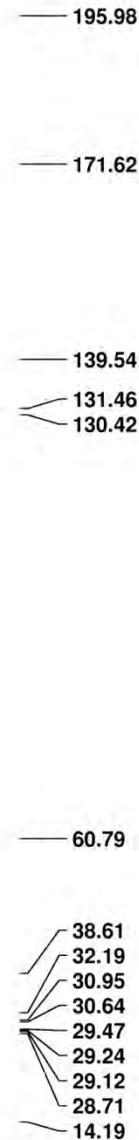




NAME TFish0931_product_020412
 EXPNO 1
 PROCNO 1
 Date_ 20120204
 Time 16.08
 INSTRUM spect
 PROBHD 5 mm QNP 1H/13
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SMH 8278.146 Hz
 FIDRES 0.126314 Hz
 AQ 3.9584243 sec
 RG 256
 DW 60.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

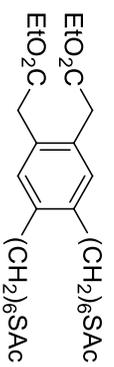
===== CHANNEL f1 =====
 NUCL1 1H
 P1 10.00 usec
 PL1 -4.00 dB
 SFO1 400.1324710 MHz
 SI 32768
 SF 400.1299989 MHz
 MWDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00





NAME TFish0931_Prod_050712
 EXPNO 2
 PROCNO 1
 Date_ 20120507
 Time 12.32
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 1024
 DS 4
 SWH 35971.223 Hz
 FIDRES 0.548877 Hz
 AQ 0.9110143 sec
 RG 3649.1
 DW 13.900 usec
 DE 6.50 usec
 TE 298.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 13C
 P1 10.00 usec
 PL1 -5.00 dB
 PL1W 238.29847717 W
 SFO1 150.9302211 MHz
 ===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 PCPD2 80.00 usec
 PL2 -2.30 dB
 PL12 14.74 dB
 PL13 14.75 dB
 PL12W 63.98692703 W
 PL12W 1.26500225 W
 PL13W 1.26209271 W
 SFO2 600.1814007 MHz
 SI 32768
 SF 150.9151300 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

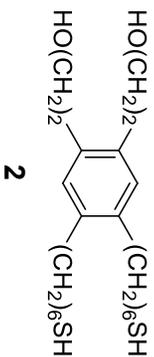




NAME TFfish0932_product_020612

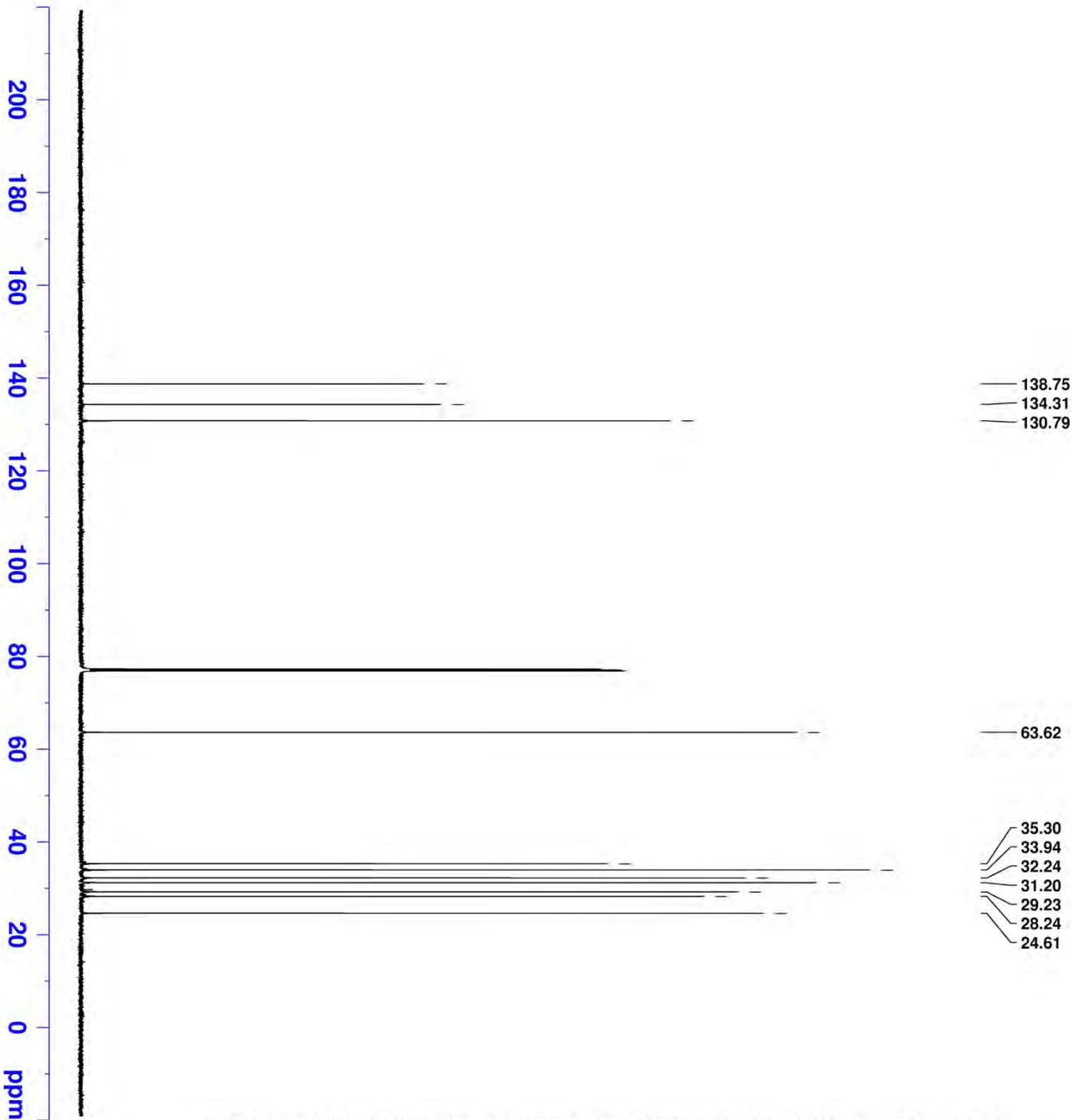
EXPNO 1
 PROCNO 3
 Date_ 20120207
 Time_ 10.32
 INSTRUM spect
 PROBHD 5 mm BBO BB-1H
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 12376.237 Hz
 FIDRES 0.188846 Hz
 AQ 2.6477449 sec
 RG 57
 DW 40.400 usec
 DE 6.50 usec
 TE 298.0 K
 D1 1.00000000 sec
 TD0 1

==== CHANNEL f1 =====
 NUC1 1H
 P1 11.25 usec
 PL1 -2.30 dB
 PL1W 63.98692703 W
 SF01 600.1827064 MHz
 SI 32768
 SE 600.1789961 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00



Integration values (red):
 1.99
 4.00
 4.00
 8.00
 1.97
 4.01
 4.01
 10.07

Peak list (ppm):
 3.86
 3.85
 3.84
 2.91
 2.90
 2.88
 2.58
 2.57
 2.56
 2.55
 2.53
 2.12
 1.67
 1.66
 1.65
 1.64
 1.63
 1.61
 1.60
 1.58
 1.57
 1.56
 1.48
 1.47
 1.47
 1.46
 1.45
 1.44
 1.42
 1.41



```

NAME      If1sh0932_product_020612
EXPNO     2
PROCNO    1
Date_     20120207
Time      10.35
INSTRUM   spect
PROBHD    5 mm BBO BB-1H
PULPROG   zgpg30
TD         65536
SOLVENT   CDCl3
NS         859
DS         4
SWH        35971.223 Hz
FIDRES     0.548877 Hz
AQ          0.9110143 sec
RG          5160.6
DW          13.900 usec
DE          6.50 usec
TE          298.0 K
D1          2.00000000 sec
D11         0.03000000 sec
TD0         1

===== CHANNEL f1 =====
NUC1       13C
P1         10.00 usec
PL1        -5.00 dB
PL1W       238.29847717 W
SFO1       150.9302211 MHz

===== CHANNEL f2 =====
CPDPRG2   waltz16
NUC2       1H
PCPD2     80.00 usec
PL2        -2.30 dB
PL12       14.74 dB
PL13       14.75 dB
PL1W       63.98692703 W
PL12W      1.26500225 W
PL13W      1.26209271 W
SFO2       600.1814007 MHz
SI         32768
SE         150.9151300 MHz
MDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
    
```

