Supporting Information

Iridium-Catalyzed Orthogonal and Regioselective Synthesis of Triazole Disulfides in Aqueous Media under Mild Conditions

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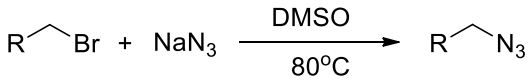
1 General Remarks

Unless otherwise noted, all commercially available reagents and solvents were used without further purification. Thin layer chromatography was performed using precoated silica gel plates and visualized with UV light at 254 nm. Flash column chromatography was performed with silica gel (40-60 μm). ^{1}H and ^{13}C nuclear magnetic resonance spectra (NMR) were obtained on a Bruker Avance II 400 MHz or Bruker Avance III 500 MHz recorded in ppm (δ) downfield of TMS (δ = 0) in $CDCl_3$ unless noted otherwise. Signal splitting patterns were described as singlet (s), doublet (d), triplet(t), quartet (q), quintet (quint), or multiplet (m), with coupling constants (*J*) in hertz (Hz). High resolution mass spectra (HRMS) were performed by an Agilent apparatus (TOF mass analyzer type) on an Electron Spray Injection (ESI) mass spectrometer and Waters MALDI micro MX (MALDI-TOF mass analyzer type) mass spectrometer. The particle sizes of polymeric nano particles were detected by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS90 (Malvern, UK). All the sizes were presented in terms of intensity diameter. Scanning electron microscopy (SEM) was performed on NOVA NanoSEM 450 (FEI). Melting points were determined by an XP-4 melting point apparatus.

2 General procedures for the preparation of substrates

All internal disulfanyl alkynes **1** were prepared according to the literature procedure.[S1]

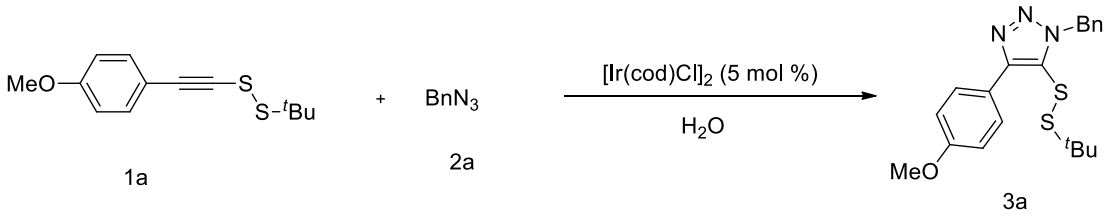
The azides **2m**-**2r** were prepared according to the literature procedure.[S2]



To a stirred solution of NaN_3 (71.5 mg, 1.1 mmol) in DMSO (2 mL) was added bromoalkane (1 mmol). The reaction mixture was stirred at 80℃ overnight. Then the reaction mixture was cooled to room temperature and diluted with water (5 mL). The mixture was extracted with ether (3×5 mL) and washed by brine, dried over Na_2SO_4 and concentrated under vacuum to give the products in quantitative yields. It was used directly without further purification.

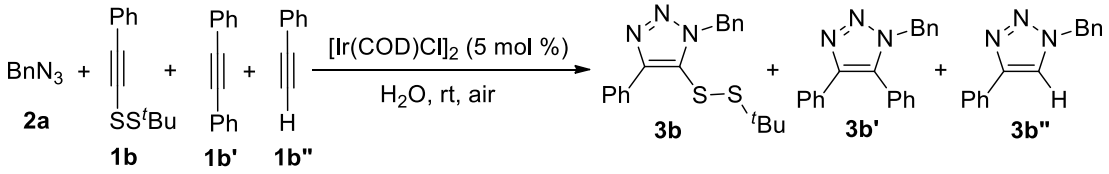
Products **3a, 3b** are known coumpounds.[S3]

3 Representative procedures for the synthesis of fully substituted triazole disulfides in water



To a vial containing 1-(*tert*-butyl)-2-((4-methoxyphenyl) ethynyl) disulfane **1a** (25.2 mg, 0.1 mmol, 1 equiv) in H_2O (1 mL) and $[Ir(cod)Cl]_2$ (3.4 mg, 5 mol %) was added BnN_3 (26.6 mg, 0.2 mmol, 2 equiv). The vial was ultrasonic for 5 min (120 W, 40 KHz). Then the mixture was stirred at rt for 12 h. DCM (2 ml) was added to the reaction mixture. Organic layer was separated and aqueous layer was extracted with DCM for three times. The extracts were dried over anhydrous sodium sulfate, and then solvent was evaporated under reduced pressure. The residue was purified with flash column chromatography (20% EtOAc in petroleum ether) to give the pure product **3a** (29.6 mg, 77%) as a yellow oil.

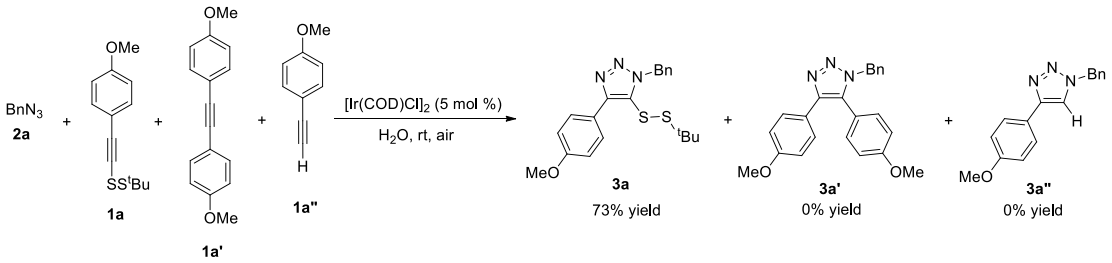
4 Procedures for the orthogonal experiment in water



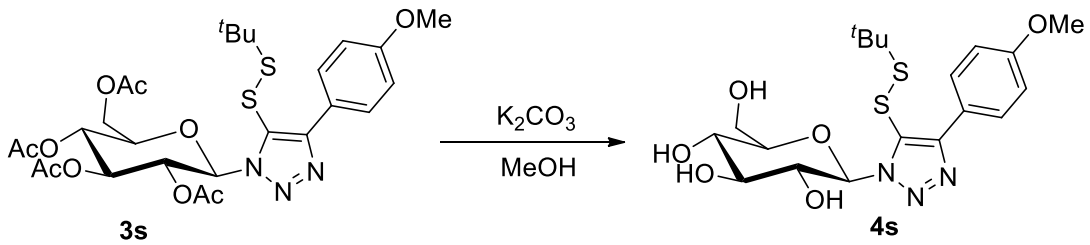
To a vial containing 1-(*tert*-butyl)-2-((4-phenyl) ethynyl) disulfane **1b** (22.2 mg, 0.1 mmol, 1 equiv), 1,2-diphenylethyne **1b'** (17.8 mg, 0.1 mmol, 1 equiv) and ethynylbenzene **1b"** (10.2 mg, 0.1 mmol, 1 equiv) in H_2O (1 mL), $[Ir(cod)Cl]_2$ (3.4 mg, 5 mol %) and BnN_3 (26.6 mg, 0.2 mmol, 2 equiv) was added. The vial was ultrasonic for 5 min. Then the mixture was stirred at rt for 24 h. DCM (2 ml) was added to the reaction mixture. Organic layer was separated and aqueous layer was extracted with DCM for three times. The extracts were dried over anhydrous sodium sulfate, and then solvent was evaporated under reduced pressure. The residue was purified with flash column chromatography (20% EtOAc in petroleum ether) to give the pure product **3b** (25.6 mg, 72%) as a yellow oil. No **3b'** and **3b"** were observed or

isolated.

Besides above example, 1-(*tert*-butyl)-2-((4-(*p*-methoxyphenyl) ethynyl) disulfane **1a** (25.2 mg, 0.1 mmol, 1 equiv), 1,2-bis(4-methoxyphenyl)ethyne **1a'** (23.8 mg, 0.1 mmol, 1 equiv) and 1-ethynyl-4-methoxybenzene **1a"** (13.2 mg, 0.1 mmol, 1 equiv) were used as the substrates in the same conditions. The similar results were acquired as follows:

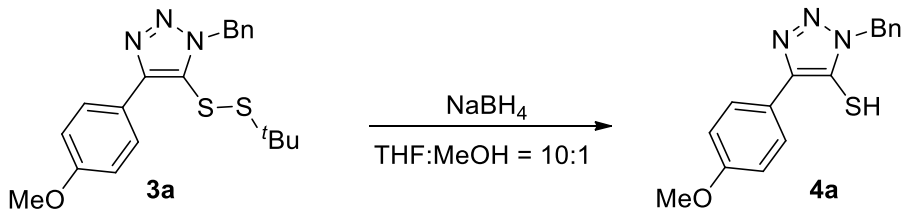


5 Procedures for the deprotection reaction



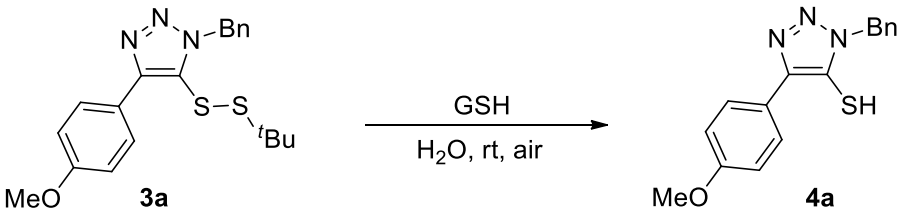
To a vial containing **3s** (31.3 mg, 0.05 mmol, 1 equiv) in MeOH (1 mL) was added K_2CO_3 (4.1mg, 0.03mmol, 0.6 equiv). Then the mixture was stirred at rt for 1h. Diluted with 5 mL petroleum ether, filtered through celite, and then the solvent was evaporated under reduced pressure. Purified with flash column chromatography (20% MeOH in DCM) to give the pure product **4s** (22.6 mg, 99%) as a yellow oil.[S4]

6 Procedures for the reduction reactions



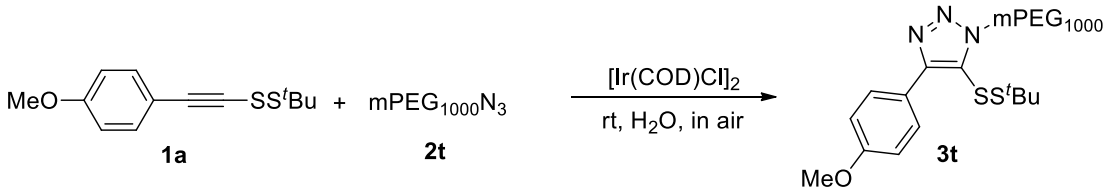
To the mixture of **3a** (38.5 mg, 0.1 mmol) and $NaBH_4$ (9.5 mg, 0.25 mmol) in THF

(400 μL), MeOH (40 μL) was added slowly. After reflux for 4 h, the mixture was cooled to room temperature. 1 M HCl (200 μL) was added to the reaction mixture. After stir for 30 min, then 6 M HCl (300 μL) was added to the reaction mixture. Organic layer was separated and aqueous layer was extracted with DCM for three times. The extracts were dried over anhydrous sodium sulfate, and then solvent was evaporated under reduced pressure. Purified with flash column chromatography (50% EtOAc in petroleum ether) to give the pure product **4a** (16.1 mg, 54%) as a yellow oil.[S5]



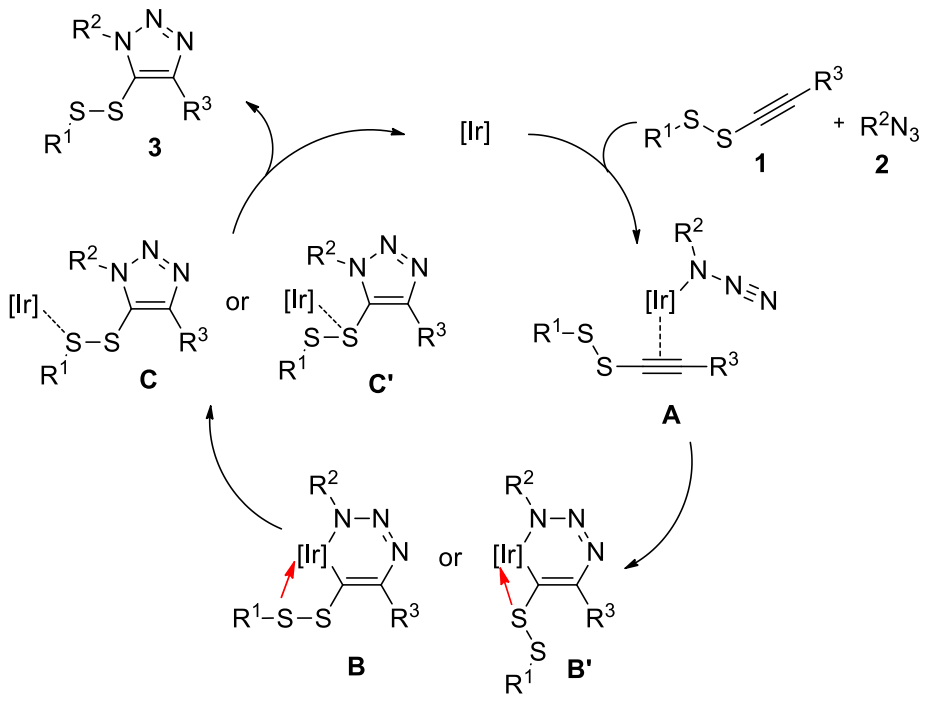
To the mixture of **3a** (38.5 mg, 0.1 mmol) in H_2O (1 mL) was added GSH (122 mg, 0.2 mmol, 2 equiv). After stirring for 4 h, DCM (2 mL) was added to the reaction mixture. Organic layer was separated and aqueous layer was extracted with DCM for three times. The extracts were dried over anhydrous sodium sulfate, and then solvent was evaporated under reduced pressure. Purified with flash column chromatography (50% EtOAc in petroleum ether) to give the pure product **4a** (15.1 mg, 51%) as a yellow oil.

7 Procedures for the synthesis of nano particle



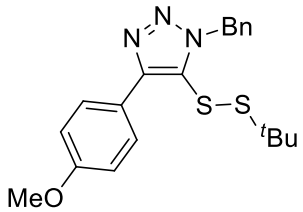
To a vial containing 1-(*tert*-butyl)-2-((4-methoxyphenyl) ethynyl) disulfane **1a** (25.2 mg, 0.1 mmol, 1 equiv) in H_2O (1 mL) and $[Ir(cod)Cl]_2$ (3.4 mg, 5 mol%) was added $mPEG_{1000}$-N_3 (20 mg, 0.2 mmol, 2 equiv). Then the mixture was stirred overnight. The product was precipitated using hexane and collected by centrifugation. Then the product was dried under vacuum for 24 h and **3t** was acquired (93.1 mg, 65% yield).

8 Proposed mechanism for the aqueous reaction



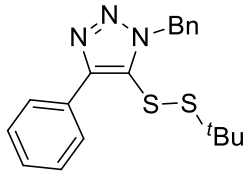
We proposed the mechanism based on the results we acquired. The cycloaddition is initiated by the combination of π-acidic Ir with internal disulfanyl alkyne (**1**) and azide (**2**) to give intermediate **A**. The azide coordinates with Ir by the internal nitrogen atom in intermediate A.[S6] Oxidative cyclization yields metallacycle **B** or **B'**, in which the sulfur strongly coordinates to the Ir in the form of three-membered (**B'**) or four-membered ring (**B**), stabilizing the system and providing the high 1,5-regioselectivity. We considered that the transition state of four-membered ring (**B**) could be more stable and favorable than three-membered ring (**B'**) due to lower ring strain.[S7-S8] None of the other groups on the internal alkyne can coordinate to the iridium. Then reductive elimination of intermediate **B** or **B'** generates intermediate **C** or **C'**. Desired fully substituted triazole disulfide **3** could be acquired from **C** or **C'** with excellent 1,5-regioselectivity.

9 Characterization data of products



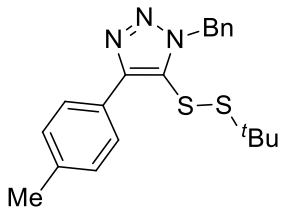
1-benzyl-5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3a)
29.6 mg, 77% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.41-7.30(m, 5H), 7.01 (d, *J* = 8.0 Hz, 2H), 5.77 (s, 2H), 3.88 (s, 3H), 1.12 (s, 9H).

Compound **3a** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]

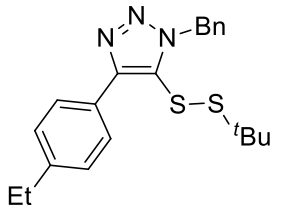


1-benzyl-5-(*tert*-butyldisulfanyl)-4-phenyl-1*H*-1,2,3-triazole (3b)
26.3 mg, 74% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.05-8.00 (m, 2H), 7.52-7.46 (m, 2H), 7.44-7.41 (m, 1H), 7.40-7.34 (m, 5H), 5.79 (s, 2H), 1.10 (s, 9H).

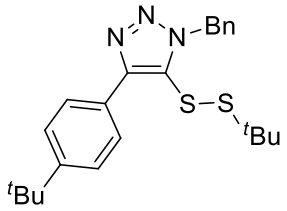
Compound **3b** is known compound, and the proton spectrum is fully consistent with literature reported.[S3]



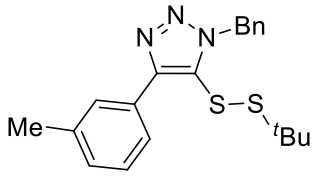
1-benzyl-5-(*tert*-butyldisulfanyl)-4-(*p*-tolyl)-1*H*-1,2,3-triazole (3c)
30.3 mg, 82% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.41-7.32 (m, 5H), 7.29 (d, *J* = 8.0 Hz, 2H), 5.78 (s, 2H), 2.43 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 138.5, 134.9, 129.2, 128.8, 128.3, 128.1, 127.7, 127.6, 127.1, 52.6, 49.4, 29.7, 21.4. HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3S_2$ $(M+Na)^+$ 392.1226, found 392.1227.



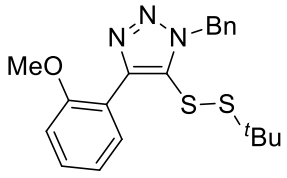
1-benzyl-5-(*tert*-butyldisulfanyl)-4-(4-ethylphenyl)-1*H*-1,2,3-triazole (3d)
27.2 mg, 71% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.41-7.35 (m, 5H), 7.31 (d, *J* = 8.2 Hz, 2H), 5.78 (s, 2H), 2.73 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 144.8, 134.9, 128.8, 128.3, 128.1, 128.0, 127.8, 127.8, 127.1, 52.6, 49.4, 29.7, 28.7, 15.4. HRMS (ESI) m/z calcd for $C_{21}H_{25}N_3S_2$ $(M+Na)^+$ 406.1382, found 406.1389.



1-benzyl-4-(4-(*tert*-butyl)phenyl)-5-(*tert*-butyldisulfanyl)-1*H*-1,2,3-triazole (3e)
25.5 mg, 62% yield, brown solid, mp = 53-57°C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.40-7.29 (m, 5H), 5.76 (s, 2H), 1.35 (s, 9H), 1.09 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 149.3, 134.9, 128.8, 128.3, 128.0, 127.5, 127.2, 125.4, 52.6, 49.4, 34.7, 31.3, 29.7. HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3S_2$ $(M+H)^+$ 412.1876, found 412.1877.

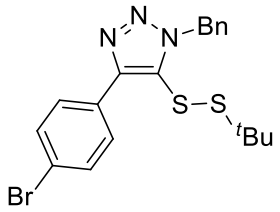


1-benzyl-5-(*tert*-butyldisulfanyl)-4-(*m*-tolyl)-1*H*-1,2,3-triazole (3f)
27.3 mg, 74% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.89 (s, 1H), 7.84 (d, *J* = 7.7 Hz, 1H), 7.39-7.34 (m, 6H), 7.23 (d, *J* = 7.6 Hz, 1H), 5.78 (s, 2H), 2.44 (s, 3H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 138.2, 134.8, 130.3, 129.4, 128.8, 128.5, 128.4, 128.3, 128.1, 127.5, 125.0, 52.6, 49.4, 29.6, 21.5. HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3S_2$ $(M+Na)^+$ 392.1226, found 392.1226.

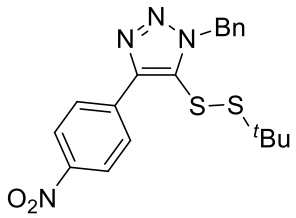


1-benzyl-5-(*tert*-butyldisulfanyl)-4-(2-methoxyphenyl)-1*H*-1,2,3-triazole (3g)
25.4 mg, 66% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.53-7.48 (m, 1H), 7.47-7.41 (m, 1H), 7.41-7.32 (m, 5H), 7.09-6.99 (m, 2H), 5.77 (s, 2H), 3.81 (s, 3H), 1.01 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 147.1, 135.0, 131.4, 130.4,

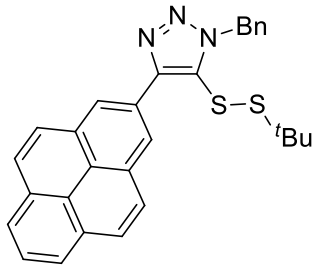
130.0, 128.7, 128.2, 128.1, 120.7, 119.8, 111.0, 55.4, 52.6, 48.8, 29.4. HRMS (ESI) m/z calcd for $C_{20}H_{23}N_3OS_2$ $(M+Na)^+$ 408.1175, found 408.1176.



1-benzyl-4-(4-bromophenyl)-5-(*tert*-butyldisulfanyl)-1*H*-1,2,3-triazole (3h)
30.7 mg, 71% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.93 (d, *J* = 7.4 Hz, 2H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.41-7.32 (m, 5H), 5.77 (s, 2H), 1.11 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 148.1, 134.6, 131.7, 129.4, 129.3, 128.8, 128.4, 128.1, 127.8, 122.9, 52.7, 49.6, 29.7. HRMS (ESI) m/z calcd for $C_{19}H_{20}BrN_3S_2$ $(M+Na)^+$ 456.0180, found 456.0185.

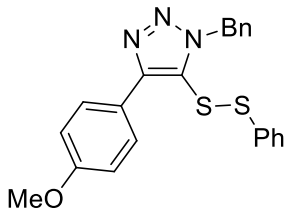


1-benzyl-5-(*tert*-butyldisulfanyl)-4-(4-nitrophenyl)-1*H*-1,2,3-triazole (3i)
30.4 mg, 76% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.35 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.8 Hz, 2H), 7.43-7.34 (m, 5H), 5.79 (s, 2H), 1.13 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.6, 146.6, 136.7, 134.3, 129.5, 128.9, 128.6, 128.2, 128.1, 123.9, 52.9, 49.8, 29.6. HRMS (ESI) m/z calcd for $C_{19}H_{20}N_4O_2S_2$ $(M+H)^+$ 401.1100, found 401.1105.



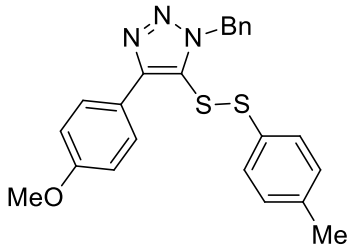
1-benzyl-5-(*tert*-butyldisulfanyl)-4-(pyren-2-yl)-1*H*-1,2,3-triazole (3j)
30.7 mg, 64% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.34 (d, *J* = 9.2 Hz, 1H), 8.30-8.21 (m, 3H), 8.18-8.03 (m, 5H), 7.55-7.38 (m, 5H), 5.90 (s, 2H), 0.80 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 134.9, 131.7, 131.3, 131.0, 130.2, 129.7, 129.0, 128.9, 128.3, 128.1, 128.1, 127.4, 126.1, 125.4, 125.3, 125.2, 125.1,

124.8, 124.7, 124.4, 53.0, 49.1, 29.7, 29.4. HRMS (ESI) m/z calcd for $C_{29}H_{25}N_3S_2$ $(M+Na)^+$ 502.1388, found 502.1388.



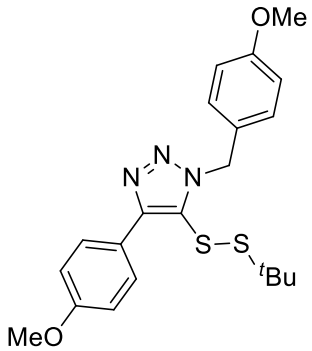
1-benzyl-4-(4-methoxyphenyl)-5-(phenyldisulfanyl)-1*H*-1,2,3-triazole (3k)

30.0 mg, 74% yield, white solid, mp = 88-92 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.24-7.18 (m, 5H), 7.16-7.09 (m, 3H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.88-6.83 (m, 2H), 5.57 (s, 2H), 3.80 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 150.8, 134.6, 133.7, 129.4, 128.7, 128.4, 128.2, 128.1, 126.5, 126.4, 122.8, 121.3, 114.0, 55.3, 52.3. HRMS (ESI) m/z calcd for $C_{22}H_{19}N_3OS_2$ $(M+H)^+$ 406.1048, found 406.1049.



1-benzyl-4-(4-methoxyphenyl)-5-(*p*-tolyldisulfanyl)-1*H*-1,2,3-triazole (3l)

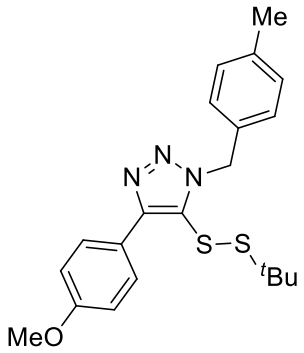
31.9 mg, 76% yield, white solid, mp = 70-74 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.05 (d, *J* = 8.8 Hz, 2H), 7.27-7.23 (m, 5H), 6.96 (dd, *J* = 10.3, 8.6 Hz, 4H), 6.81 (d, *J* = 8.2 Hz, 2H), 5.58 (s, 2H), 3.84 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 150.5, 136.7, 134.7, 130.2, 130.1, 128.7, 128.4, 128.1, 128.0, 126.8, 122.9, 122.0, 114.0, 55.3, 52.2, 20.9. HRMS (ESI) m/z calcd for $C_{23}H_{21}N_3OS_2$ $(M+H)^+$ 420.1204, found 420.1206.



5-(*tert*-butyldisulfanyl)-1-(4-methoxybenzyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triaz

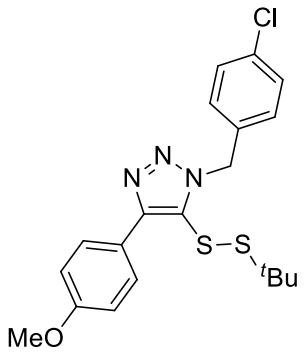
ole (3m)

34.0 mg, 82% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.7 Hz, 2H), 7.34 (d, *J* = 8.6 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 5.69 (s, 2H), 3.87 (s, 3H), 3.81 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 159.6, 149.2, 129.7, 129.2, 126.9, 126.4, 123.1, 114.1, 113.9, 55.3, 55.3, 52.1, 49.4, 29.7. HRMS (ESI) m/z calcd for $C_{21}H_{25}N_3O_2S_2$ $(M+Na)^+$ 438.1280, found 438.1283.



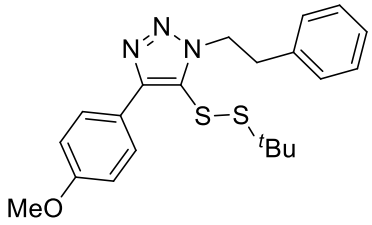
5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1-(4-methylbenzyl)-1*H*-1,2,3-triazol e (3n)

32.0 mg, 80% yield, brown solid, mp = 59-62 °C. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 5.72 (s, 2H), 3.88 (s, 3H), 2.36 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 149.2, 138.1, 131.9, 129.4, 129.2, 128.1, 126.5, 123.1, 113.9, 55.3, 52.4, 49.4, 29.7, 21.2. HRMS (ESI) m/z calcd for $C_{21}H_{25}N_3OS_2$ $(M+Na)^+$ 422.1331, found 422.1332.

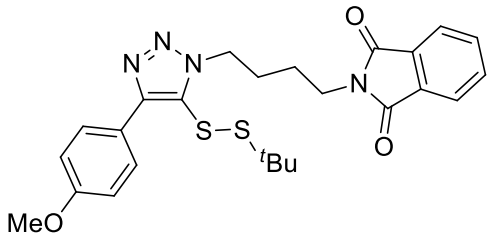


5-(*tert*-butyldisulfanyl)-1-(4-chlorobenzyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3o)

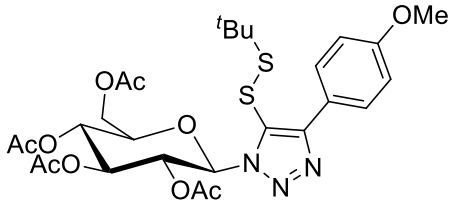
31.4 mg, 75% yield, brown oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.96 (d, *J* = 8.7 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 5.72 (s, 2H), 3.88 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 149.3, 134.3, 133.3, 129.5, 129.2, 129.0, 126.6, 122.9, 114.0, 55.3, 51.8, 49.5, 29.6. HRMS (ESI) m/z calcd for $C_{20}H_{22}ClN_3OS_2$ $(M+Na)^+$ 442.0785, found 442.0786.



5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1-phenethyl-1*H*-1,2,3-triazole (3q)
33.5 mg, 84% yield, brown solid, mp = 80-83 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.95 (d, *J* = 8.6 Hz, 2H), 7.36-7.25 (m, 5H), 7.03 (d, *J* = 8.6 Hz, 2H), 4.81-4.68 (m, 2H), 3.89 (s, 3H), 3.44-3.32 (m, 2H), 1.11 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 148.9, 137.3, 129.3, 129.0, 128.8, 127.0, 126.9, 123.2, 114.0, 55.3, 50.0, 49.4, 36.3, 29.7. HRMS (ESI) m/z calcd for $C_{21}H_{25}N_3OS_2$ $(M+Na)^+$ 422.1331, found 422.1330.

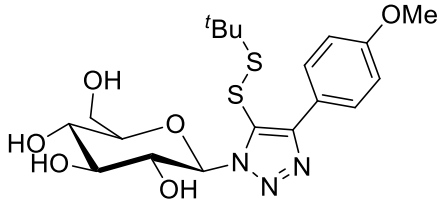


2-(4-(5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)butyl)isoindoline-1,3-dione (3r)
41.2 mg, 83% yield, brown oil. 1H NMR (400 MHz, CDCl3) δ 7.93 (d, *J* = 8.6 Hz, 2H), 7.86-7.81 (m, 2H), 7.74-7.69 (m 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.56 (t, *J* = 7.2 Hz, 2H), 3.86 (s, 3H), 3.78 (t, *J* = 6.9 Hz, 2H), 2.17-2.06 (m, 2H), 1.90-1.78 (m, 2H), 1.07 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.3, 159.8, 149.0, 134.0, 132.1, 129.3, 126.6, 123.3, 123.1, 113.9, 55.3, 49.4, 48.2, 37.2, 29.6, 27.0, 25.7. HRMS (ESI) m/z calcd for $C_{25}H_{28}N_4O_3S_2$ $(M+Na)^+$ 519.1495, found 519.1498.



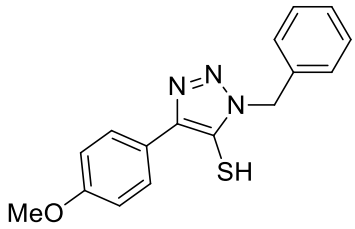
(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(acetoxymethyl)-6-(5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3s)
39.4 mg, 63% yield, colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.97 (d, *J* = 8.9 Hz, 2H), 7.00 (d, *J* = 8.9 Hz, 2H), 6.17 (t, *J* = 9.4 Hz, 1H), 6.05 (d, *J* = 9.5 Hz, 1H), 5.47 (t, *J* = 9.4 Hz, 1H), 5.36 (t, *J* = 9.7 Hz, 1H), 4.33-4.27 (m, 1H), 4.20 (dd, *J* = 12.5, 2.2 Hz, 1H), 4.03 (ddd, *J* = 10.0, 4.3, 2.3 Hz, 1H), 3.87 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.85 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

170.6, 170.4, 169.2, 168.3, 160.2, 149.2, 129.4, 128.3, 122.3, 114.0, 83.1, 74.9, 73.8, 69.5, 67.7, 61.5, 55.3, 49.6, 29.7, 20.7, 20.6, 20.6, 20.4. HRMS (ESI) m/z calcd for $C_{27}H_{35}N_3O_{10}S_2$ $(M+Na)^+$ 648.1661, found 648.1660.



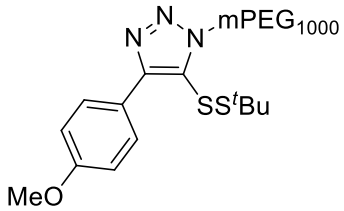
(2*R*,3*R*,4*S*,5*S*,6*R*)-2-(5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazol-1-yl)-6-(hydroxymethyl)tetrahydro-2*H*-pyran-3,4,5-triol (4s)

22.6 mg, 99% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.76 (d, *J* = 8.8 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.82 (d, *J* = 9.0 Hz, 1H), 5.72 (brs, 2H), 5.48 (brs, 1H), 4.69 (t, *J* = 9.0 Hz, 1H), 4.36-4.17 (m, 1H), 4.14 (d, *J* = 7.2 Hz, 1H), 4.05-3.91 (m, 2H), 3.83 (s, 3H), 3.68 (d, *J* = 9.4 Hz, 1H), 2.89 (brs, 1H), 1.03 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 148.2, 129.3, 122.0, 113.9, 85.5, 78.9, 72.0, 68.7, 65.6, 61.0, 60.4, 55.3, 49.4, 29.6. HRMS (ESI) m/z calcd for $C_{19}H_{27}N_3O_6S_2$ $(M+Na)^+$ 480.1239, found 480.1189.



1-benzyl-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole-5-thiol (4a)

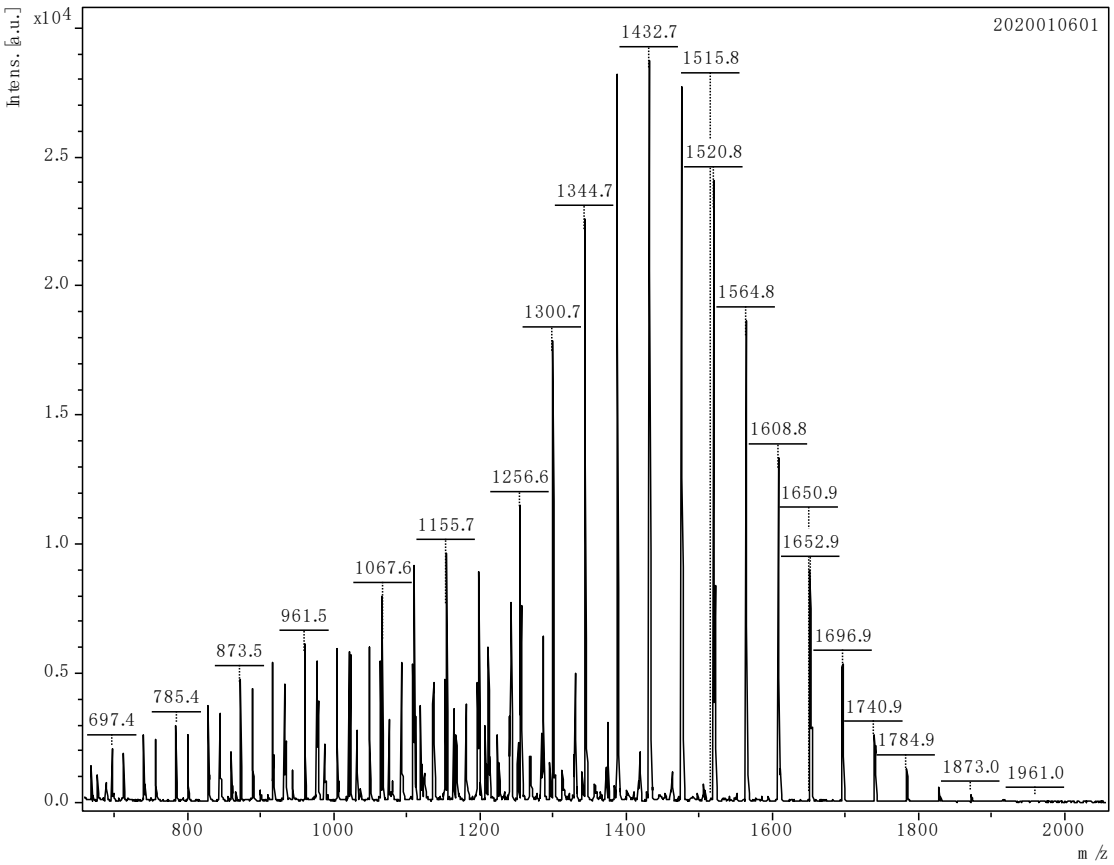
16.1 mg, 54% yield, yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.72 (d, *J* = 8.8 Hz, 2H), 7.36-7.30 (m, 3H), 7.21 (dd, *J* = 6.6, 2.8 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 5.32 (s, 2H), 3.87 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 160.3, 150.5, 134.4, 128.9, 128.6, 128.3, 128.0, 123.2, 121.8, 114.1, 55.4, 52.3. HRMS (ESI) m/z calcd for $C_{16}H_{15}N_3OS$ $(M+H)^+$ 298.1014, found 298.1013.



1-polyethyleneglycol-5-(*tert*-butyldisulfanyl)-4-(4-methoxyphenyl)-1*H*-1,2,3-triazole (3t)

93.1 mg, 65% yield, brown solid. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 7.97 (d, *J* =

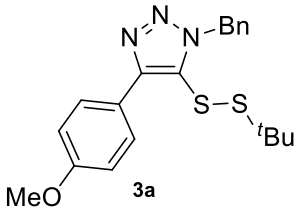
8.4 Hz, 2H), 7.02 (d, *J* = 8.5 Hz, 2H), 4.73 (t, *J* = 6.1 Hz, 2H), 4.08 (t, *J* = 6.1 Hz, 2H), 3.89 (s, 3H), 3.66 (s, 108H), 3.40 (s, 3H), 1.12 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.8, 148.8, 129.2, 127.3, 123.1, 113.9, 71.9, 70.7, 70.6, 70.6, 70.5, 69.0, 59.0, 55.3, 49.3, 48.2, 29.7. MALDI-TOF m/z found 1432.7.



10 References

(S1) Gui, Y.; Qiu, L.; Li, Y.; Li, H.; Dong, S. *J. Am. Chem. Soc.* **2016**, *138*, 4890.
(S2) (a) Xu, J.; Song, Q. *Org. Chem. Front*. **2017**, *4*, 938. (b) Liu, E.-C.; Topczewski, J. J. *J. Am. Chem. Soc*. **2019**, *141*, 5135.
(S3) Wang, W.; Lin, Y.; Ma, Y.; Tung, C. -H.; Xu, Z. *Org. Lett.* **2018**, *21*, 2956.
(S4) Perrin, C. L.; Fabian M. A.; Brunckova, J.; Ohta, B. K. *J. Am. Chem. Soc.* **1999**, 6911.
(S5) Ookawa, A.; Yokoyama, S.; Soai, K. *Synth. Commun.* **1986**, *16*, 819.
(S6) Albertin, G.; Antoniutti, S.; Baldan, D.; Castro, J.; Garc á-Font án, S. *Inorg. Chem.* **2008**, *47*, 742.
(S7) For the three-membered-ring iridium-sulfur interaction, see: (a) S. Ding, G. Jia and J. Sun, *Angew. Chem. Int. Ed*. **2014**, *53*, 1877. (b) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, 28, 5536.
(S8) For the four-membered-ring iridium-sulfur interaction, see: S. Basu, R. Acharyya, F. Basuli, S.-M. Peng, G.-H. Lee, G. Mostafa, S. Bhattacharya, *Inorg. Chim. Acta*, **2010**, *363*, 2848.

11 NMR Spectra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N
N
Bn
S
S
tBu
MeO

3a

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7.96
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7.03
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3.88
1.12
2.00
4.84
2.01
2.00
3.06
9.24
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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8.0
7.5
7.0
6.5
6.0
5.5
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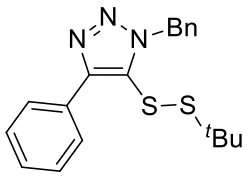
N
N
N
Bn
S
S
tBu

3b

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8.02
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7.43
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5.79
1.10
2.00
2.07
0.92
5.09
2.11
9.53
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
6.0
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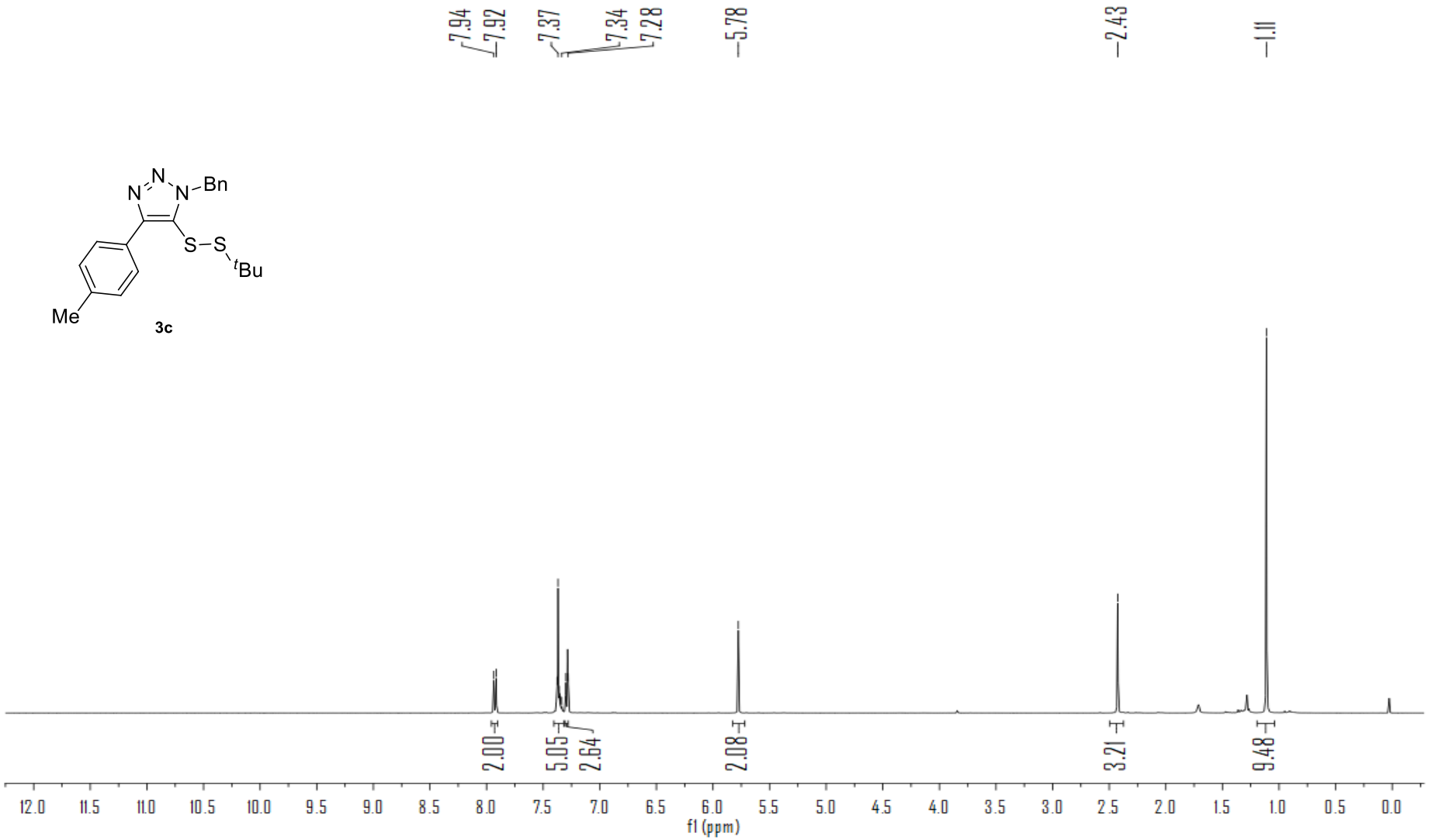
f1 (ppm)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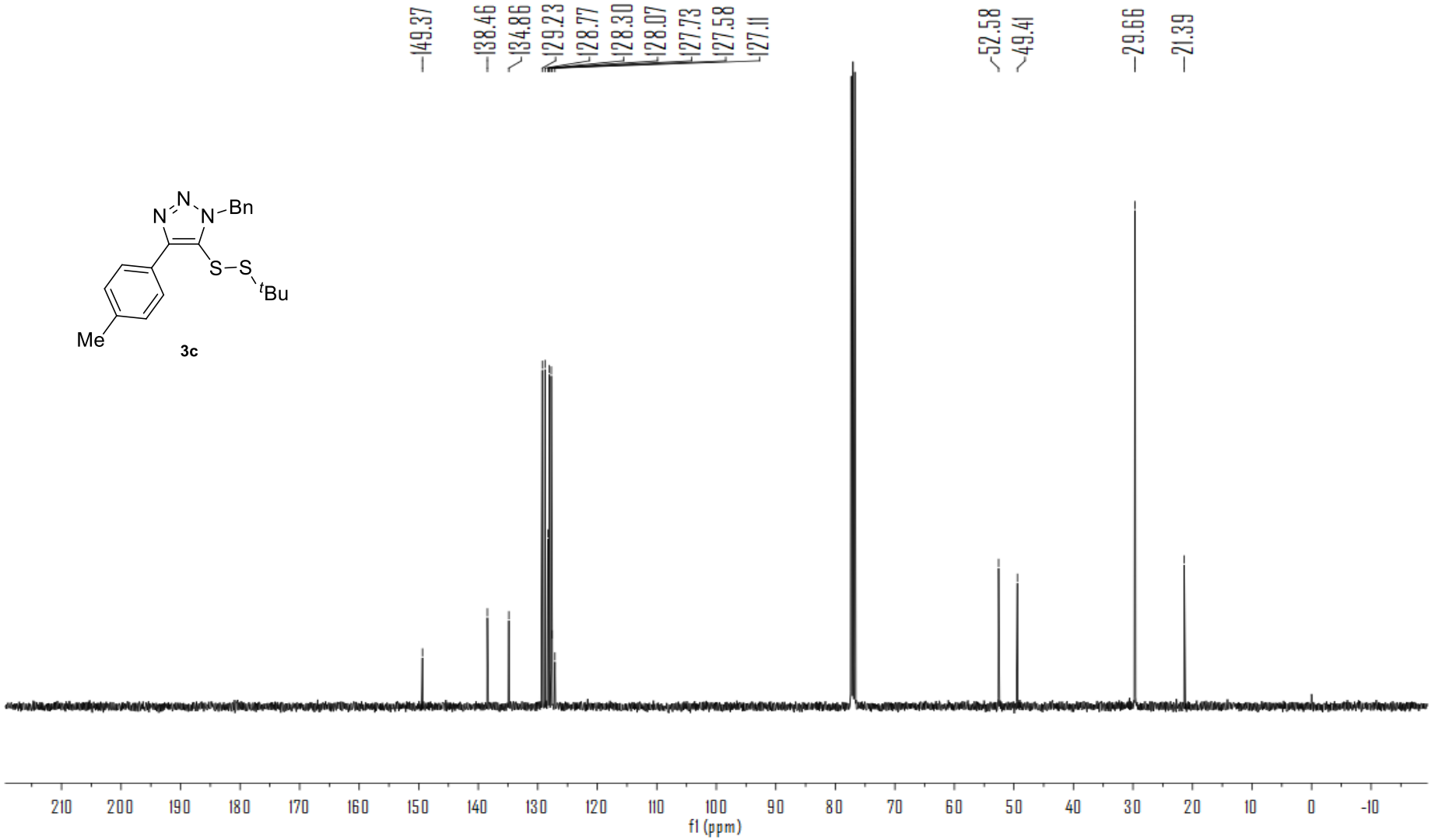
f1 (ppm)

3c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N
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Bn
S
S
tBu
Me
3c
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200
190
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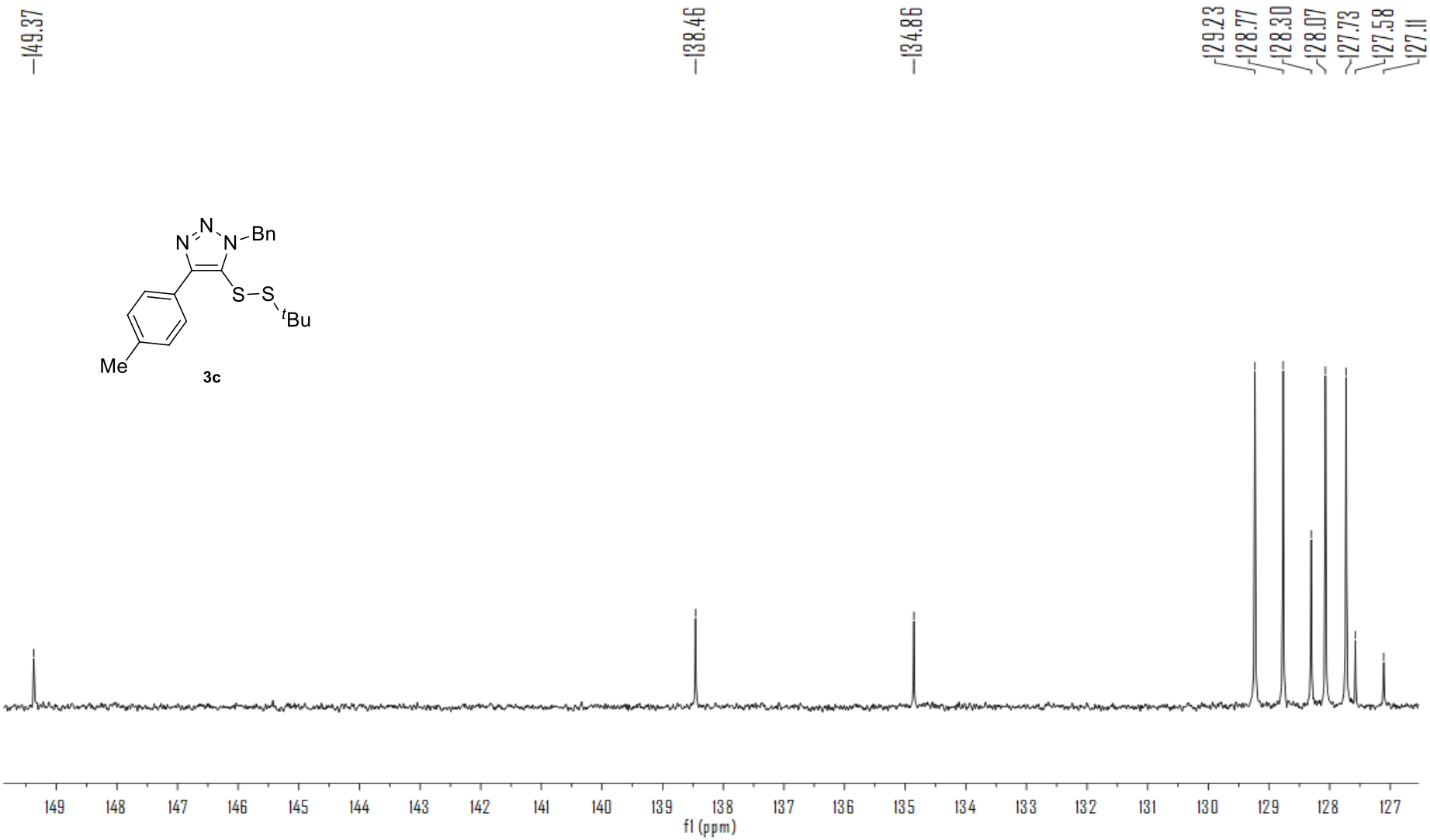
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S
S
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Me
3c
149
148
147
146
145
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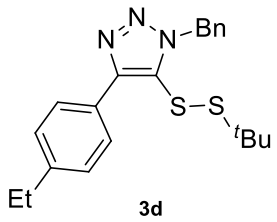
128
127
f1 (ppm)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N
N
Bn
S
S
tBu
Et

3d

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7.94
7.37
7.35
7.30
5.78
2.75
2.73
2.72
2.70
1.31
1.29
1.27
1.11
1.95
4.83
2.03
2.00
2.08
3.62
9.06
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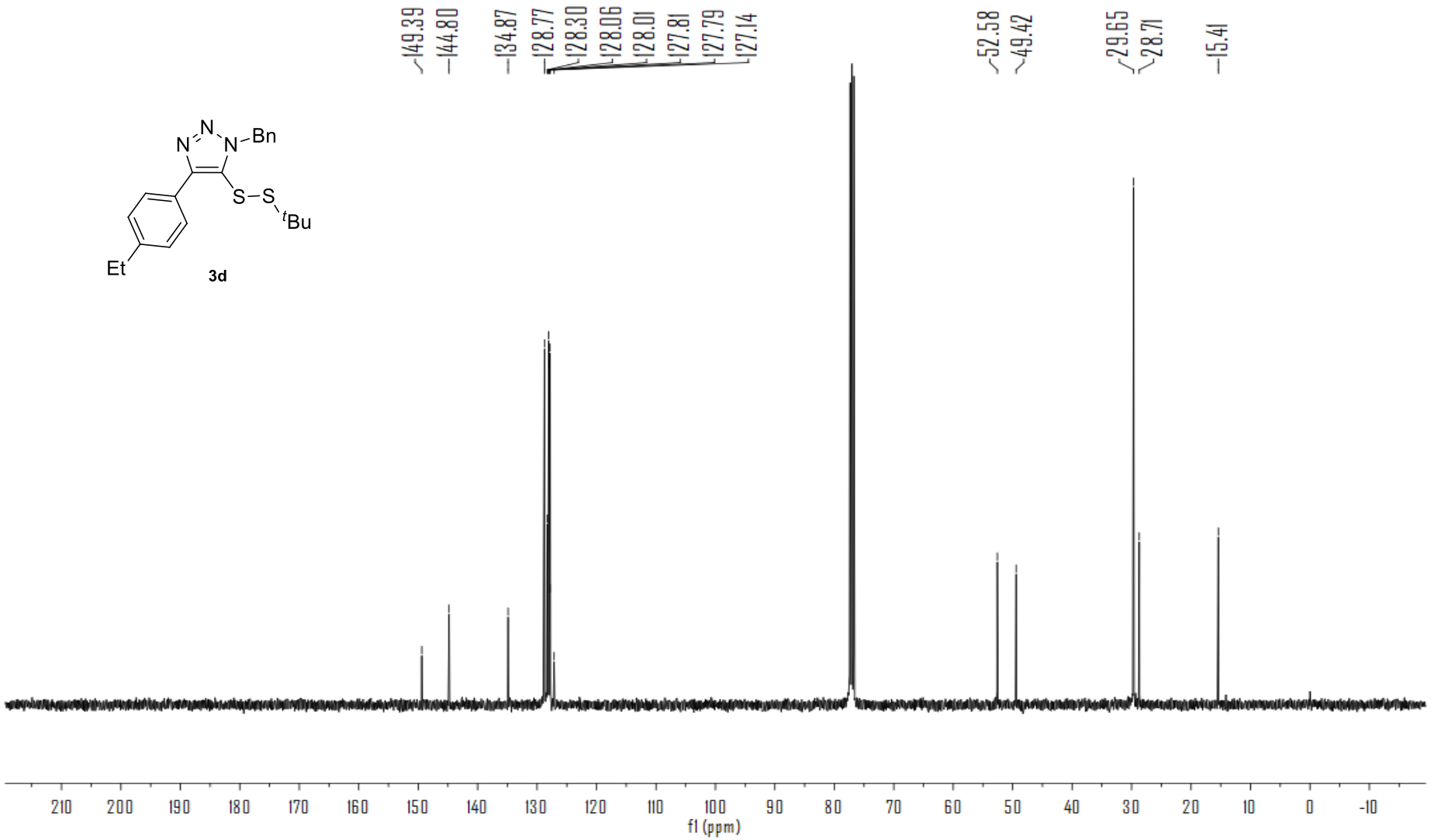
f1 (ppm)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15.41
N
N
N
Bn
S
S
tBu
Et
3d
210
200
190
180
170
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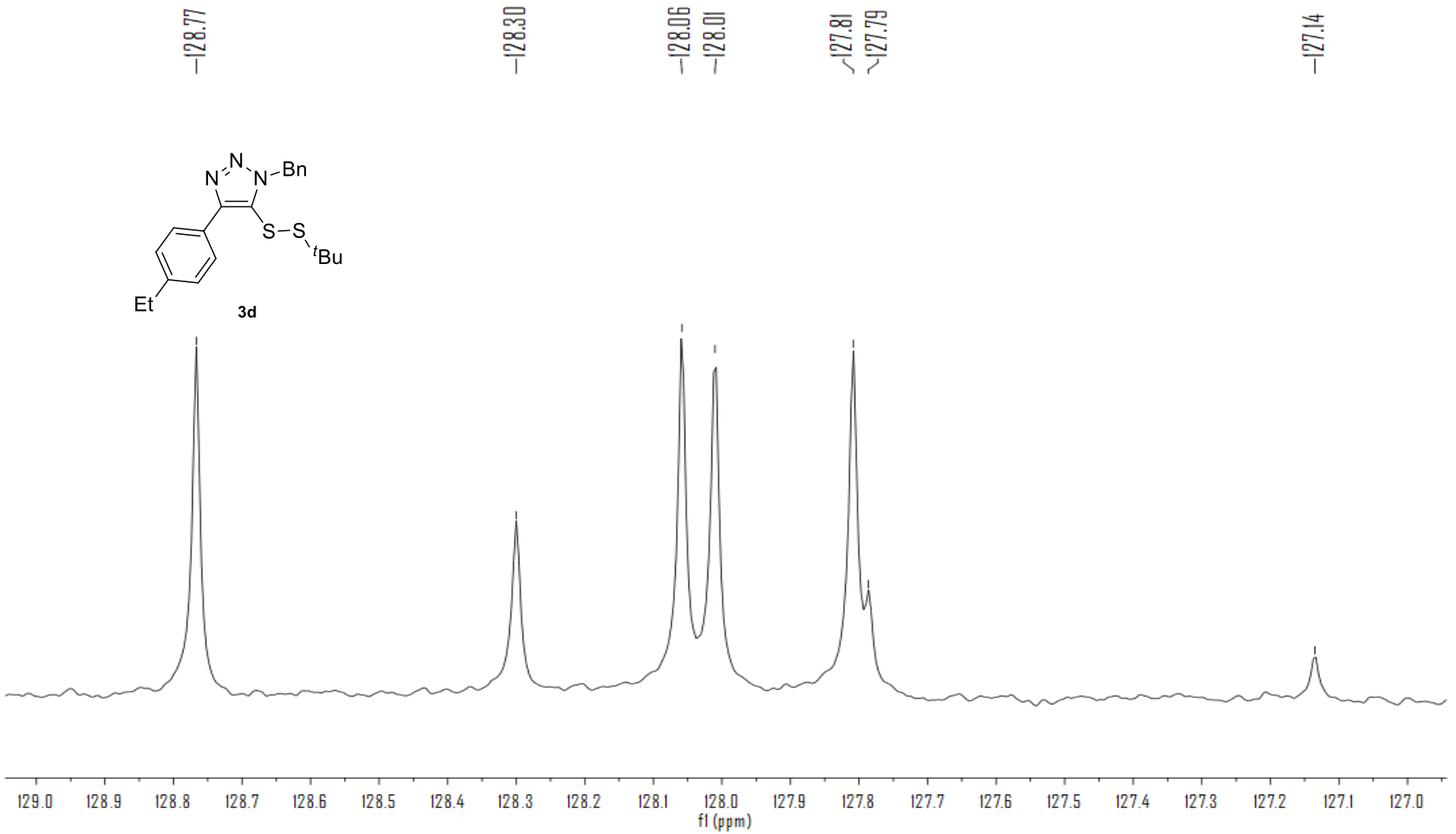
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Et
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128.4
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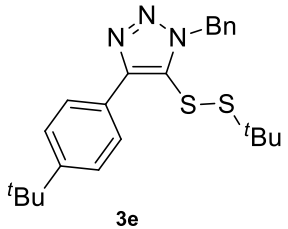
f1 (ppm)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N
Bn
S
S
tBu
tBu

3e

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2.01
5.01
2.01
9.10
9.10
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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3.0
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2.0
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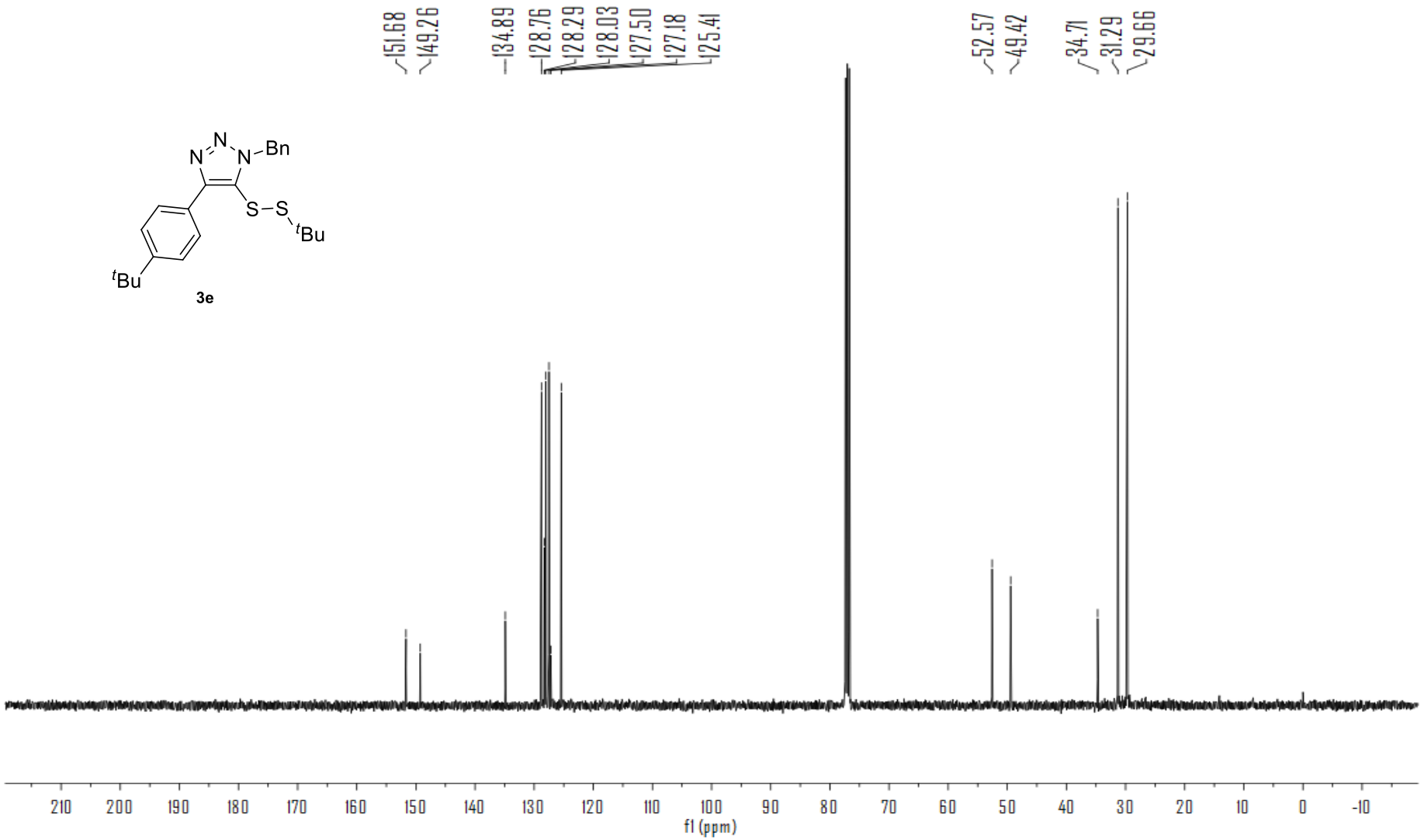
1.0
0.5
0.0
f1 (ppm)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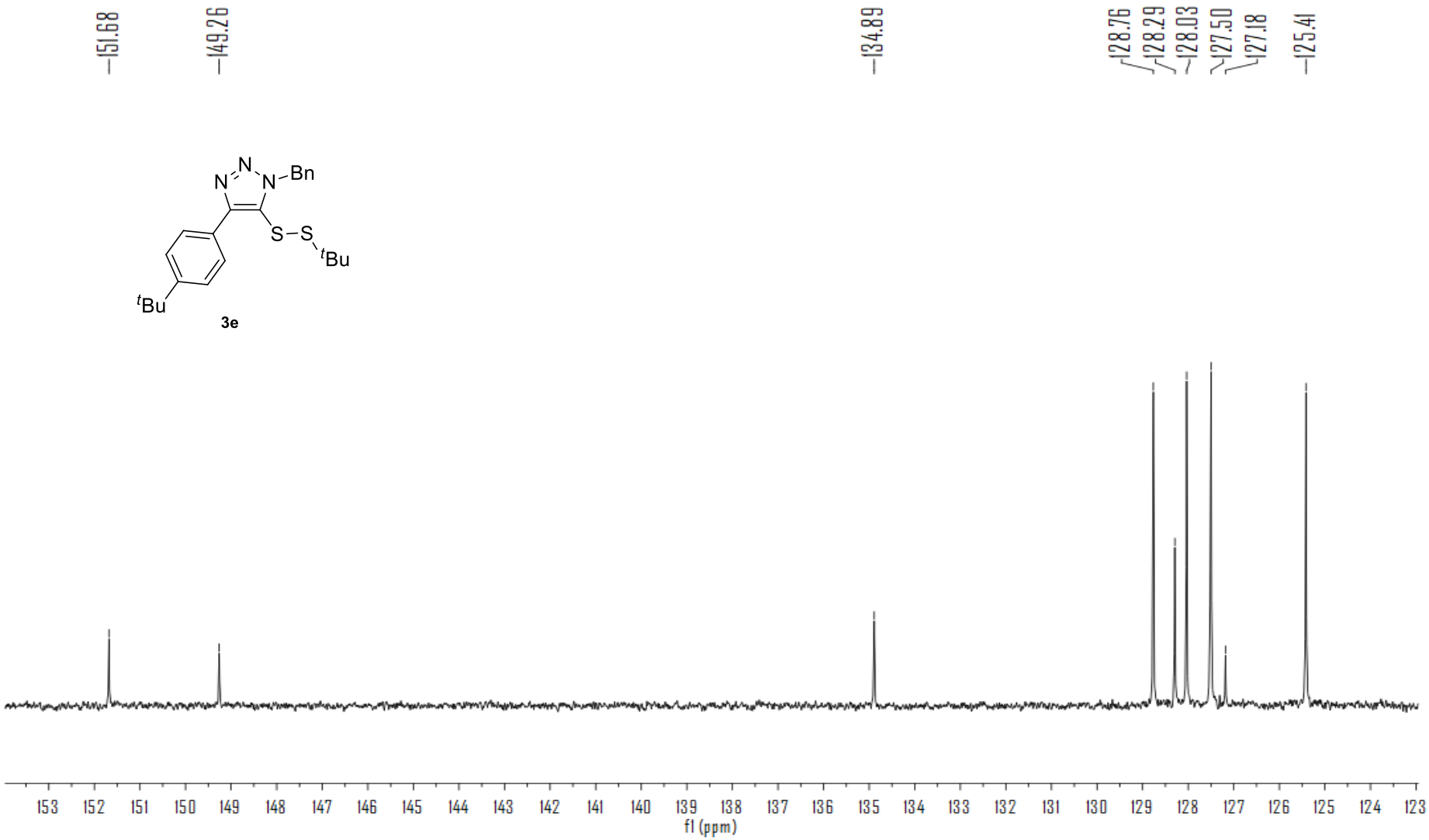
134.89
128.76
128.29
128.03
127.50
127.18
125.41
52.57
49.42
34.71
31.29
29.66
N
N
Bn
S
S
tBu
tBu
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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128.03
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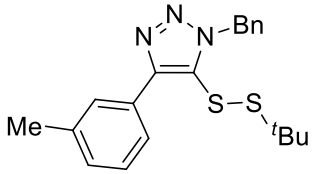
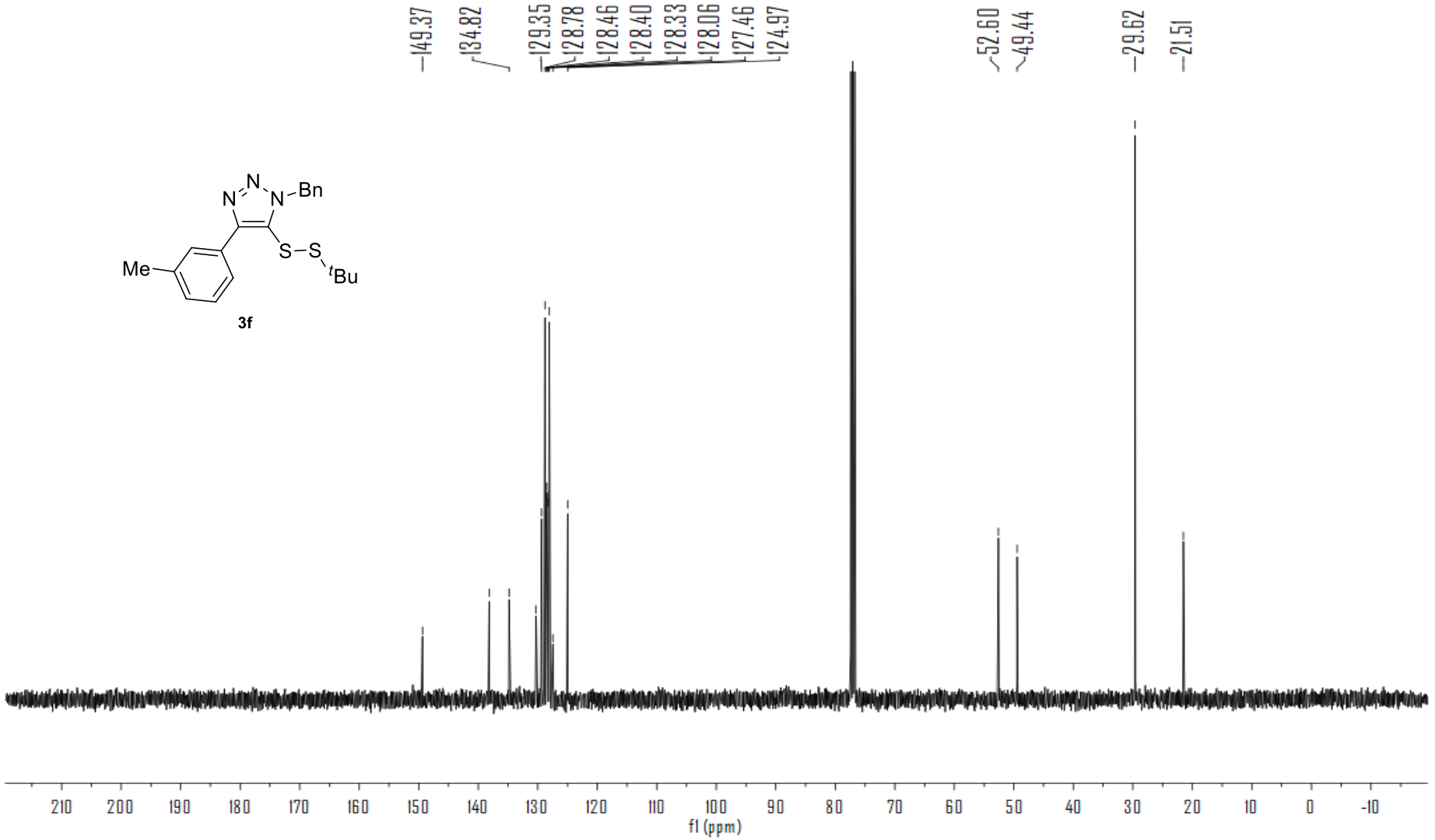
127.18
125.41
N
N
N
Bn
S
S
tBu
tBu
3e
153 152 151 150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123
f1 (ppm)


N
N
N
Bn
S
S
tBu
Me

3f

7.89
7.84
7.83
7.37
7.35
7.22
5.78
2.44
1.11
0.92
0.98
6.02
1.05
2.00
3.13
9.26
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.82
129.35
128.78
128.46
128.40
128.33
128.06
127.46
124.97
52.60
49.44
29.62
21.51
N
N
N
Bn
S
S
tBu
Me
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
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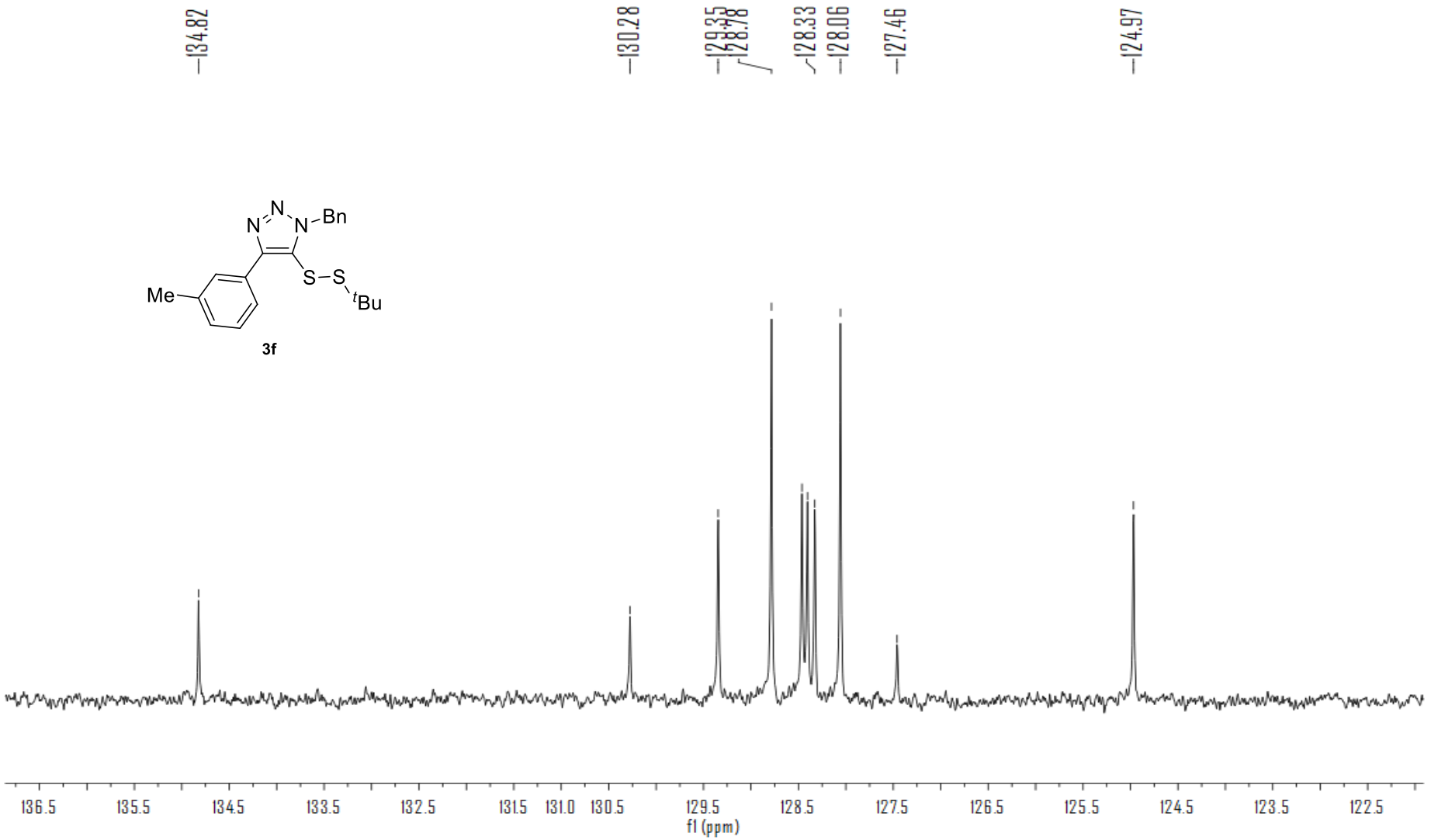
0
-10
f1 (ppm)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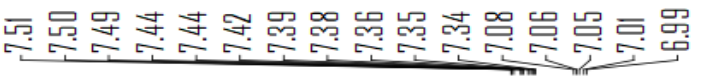
130.28
129.35
128.78
128.33
128.06
127.46
124.97
N
N
N
Bn
S
S
tBu
Me
3f
136.5
135.5
134.5
133.5
132.5
131.5
131.0
130.5
129.5
128.5
127.5
126.5
125.5
124.5
123.5
122.5
f1 (ppm)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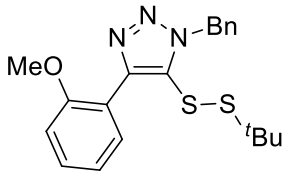
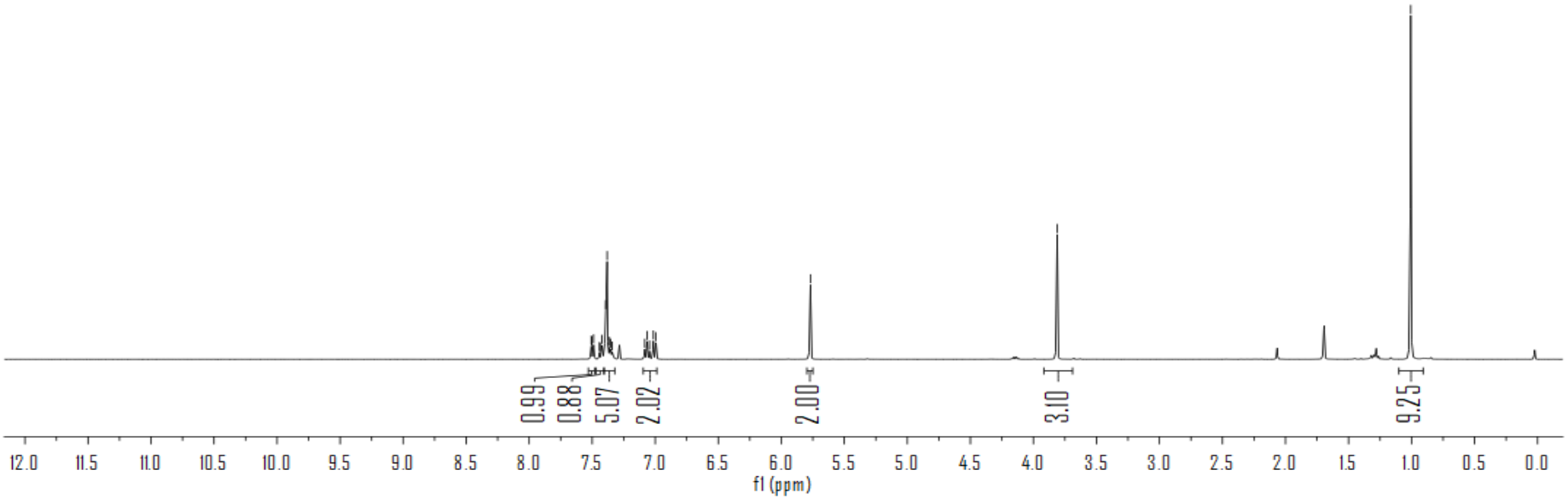
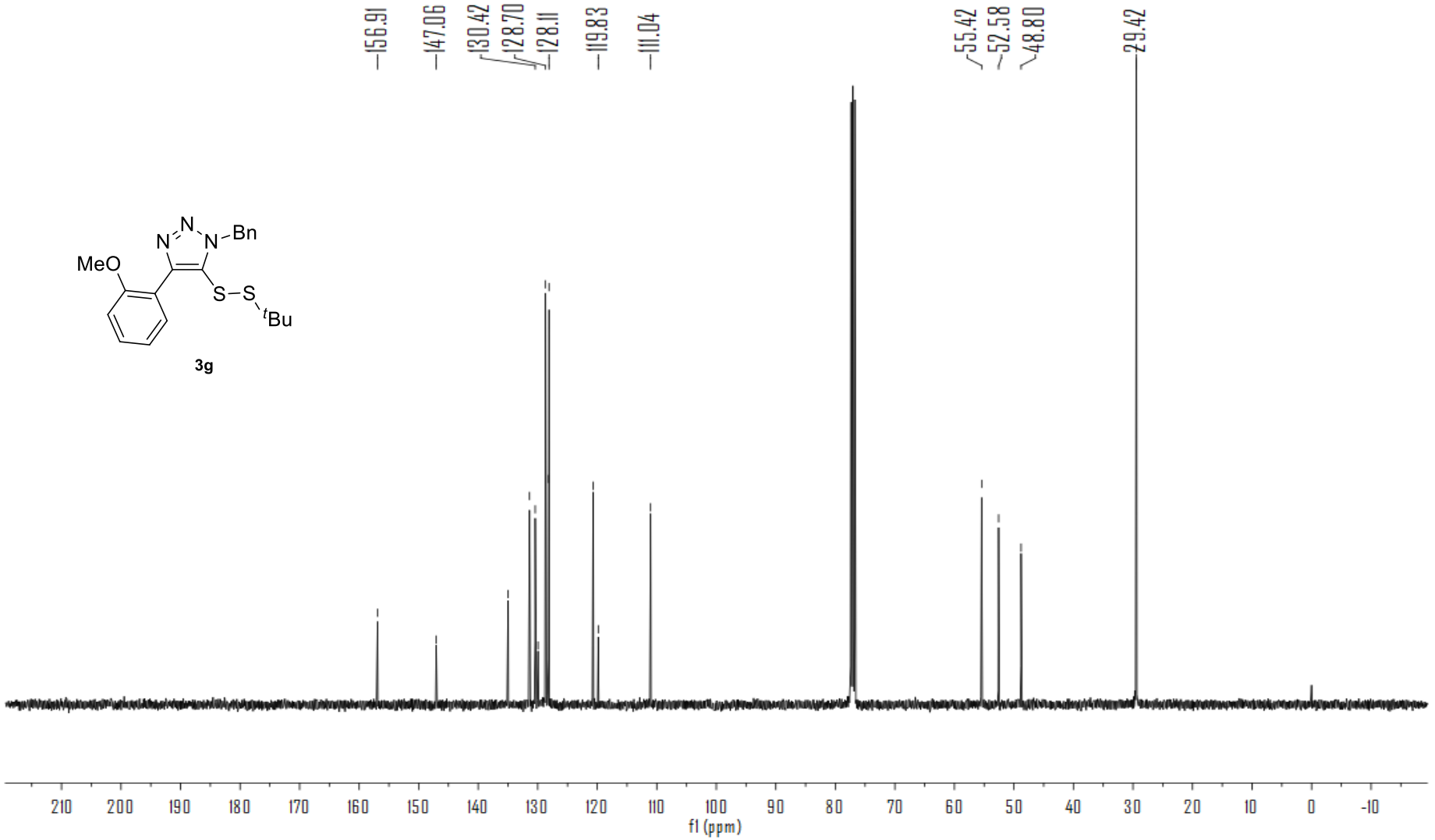
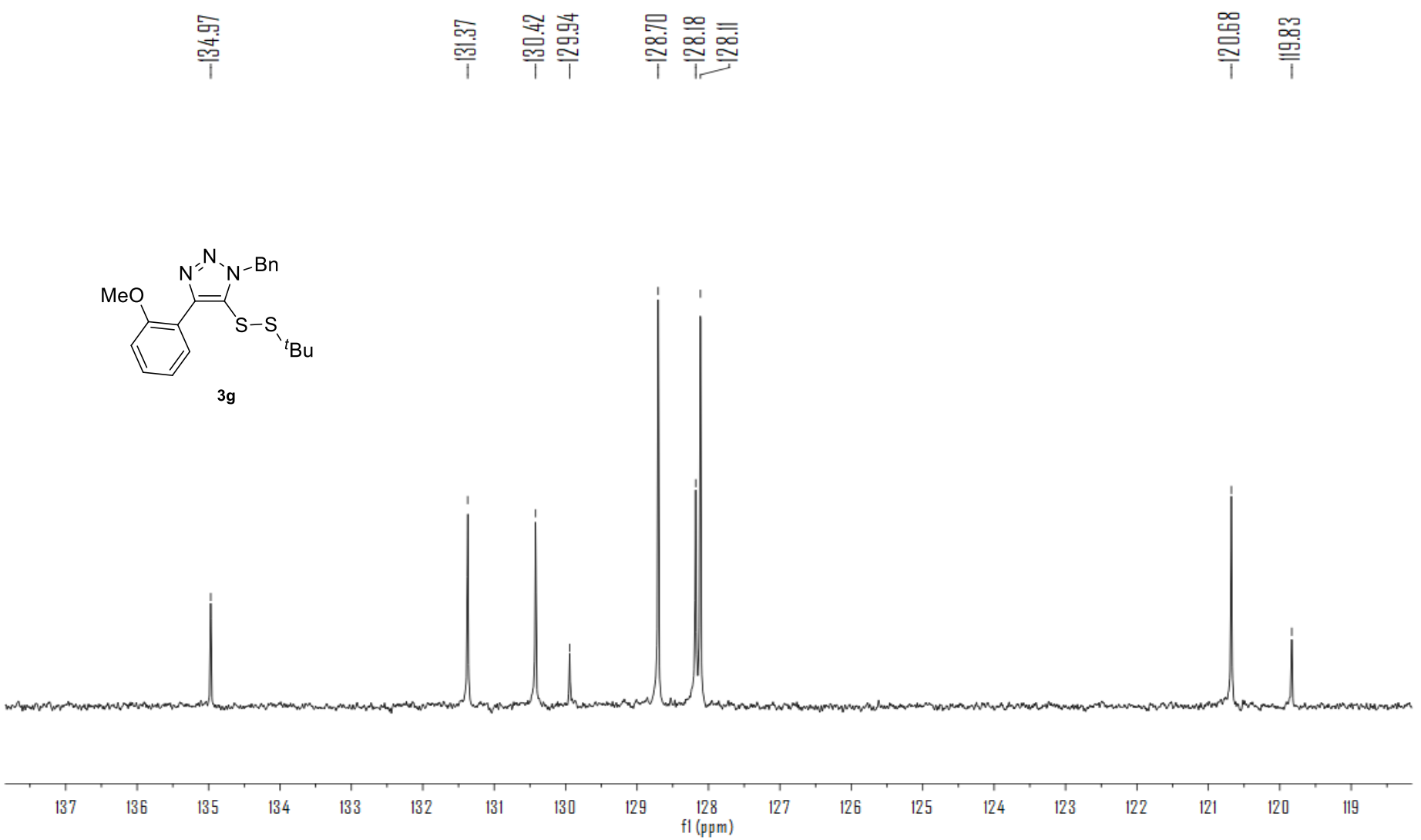
7.50
7.49
7.44
7.44
7.42
7.39
7.38
7.36
7.35
7.34
7.08
7.06
7.05
7.01
6.99
5.77
3.81
1.01


MeO
N
N
Bn
S
S
tBu

3g


0.99
0.88
5.07
2.02
2.00
3.10
9.25
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


156.91
147.06
130.42
128.70
128.11
119.83
111.04
55.42
52.58
48.80
29.42
MeO
N
N
N
Bn
S
S
tBu
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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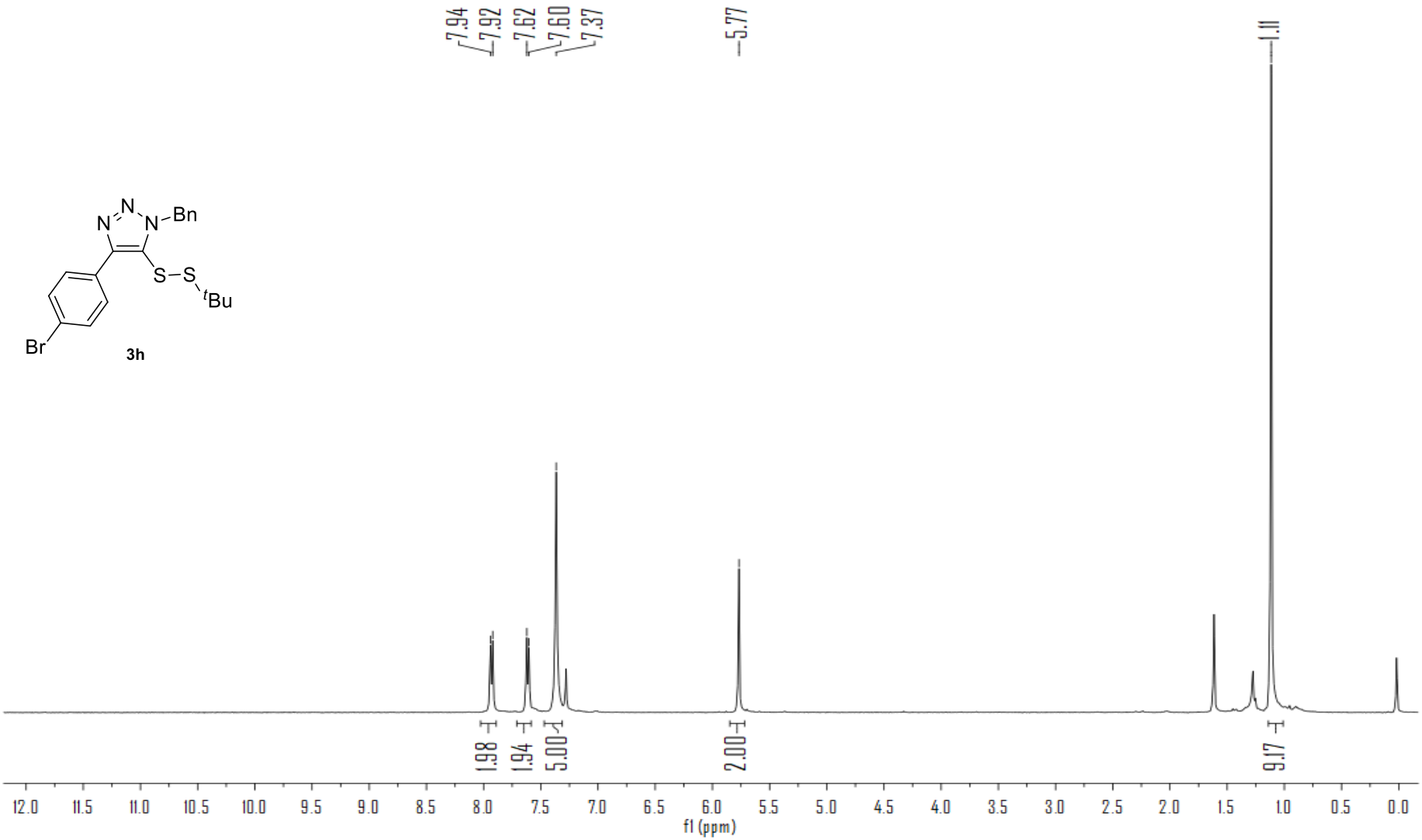
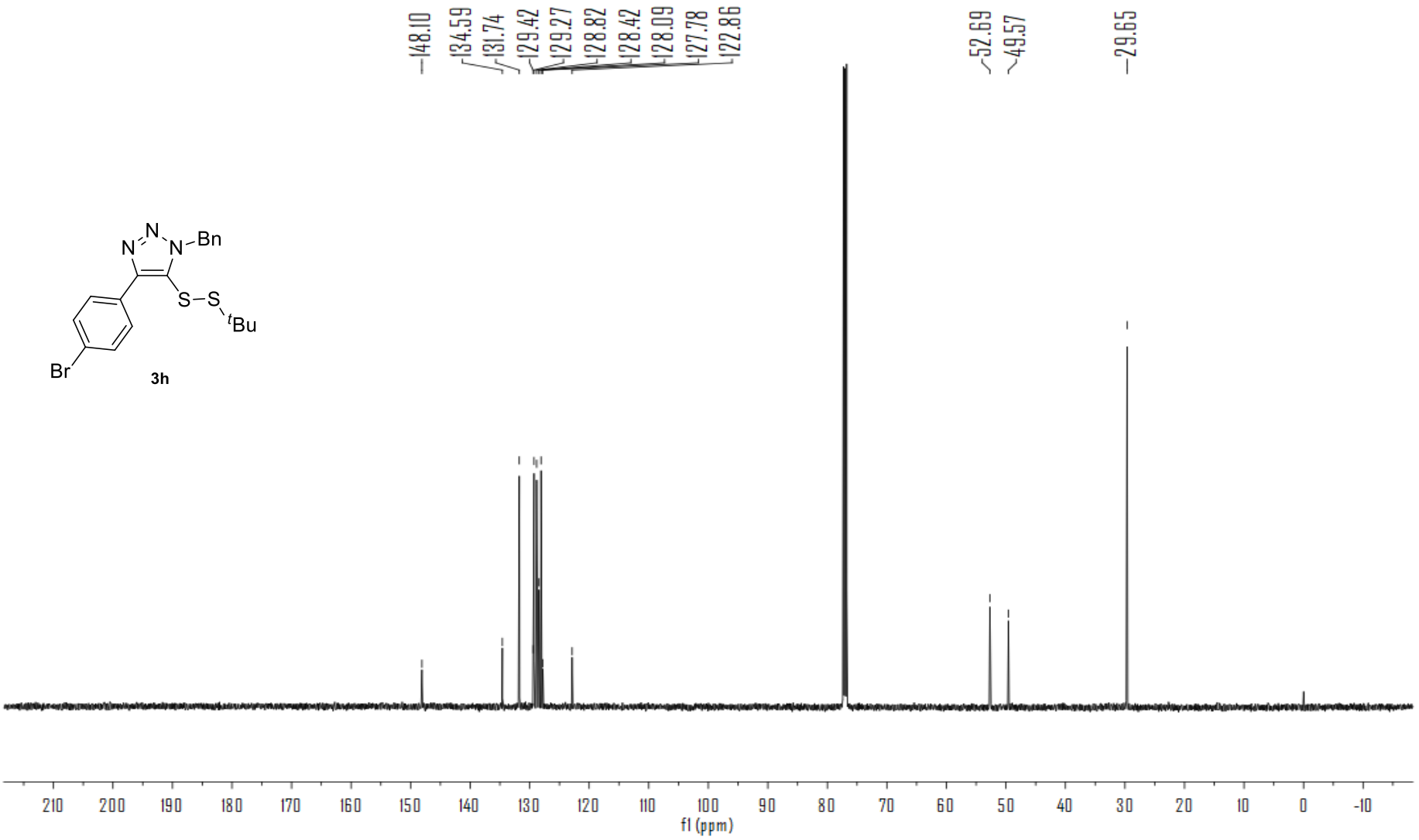
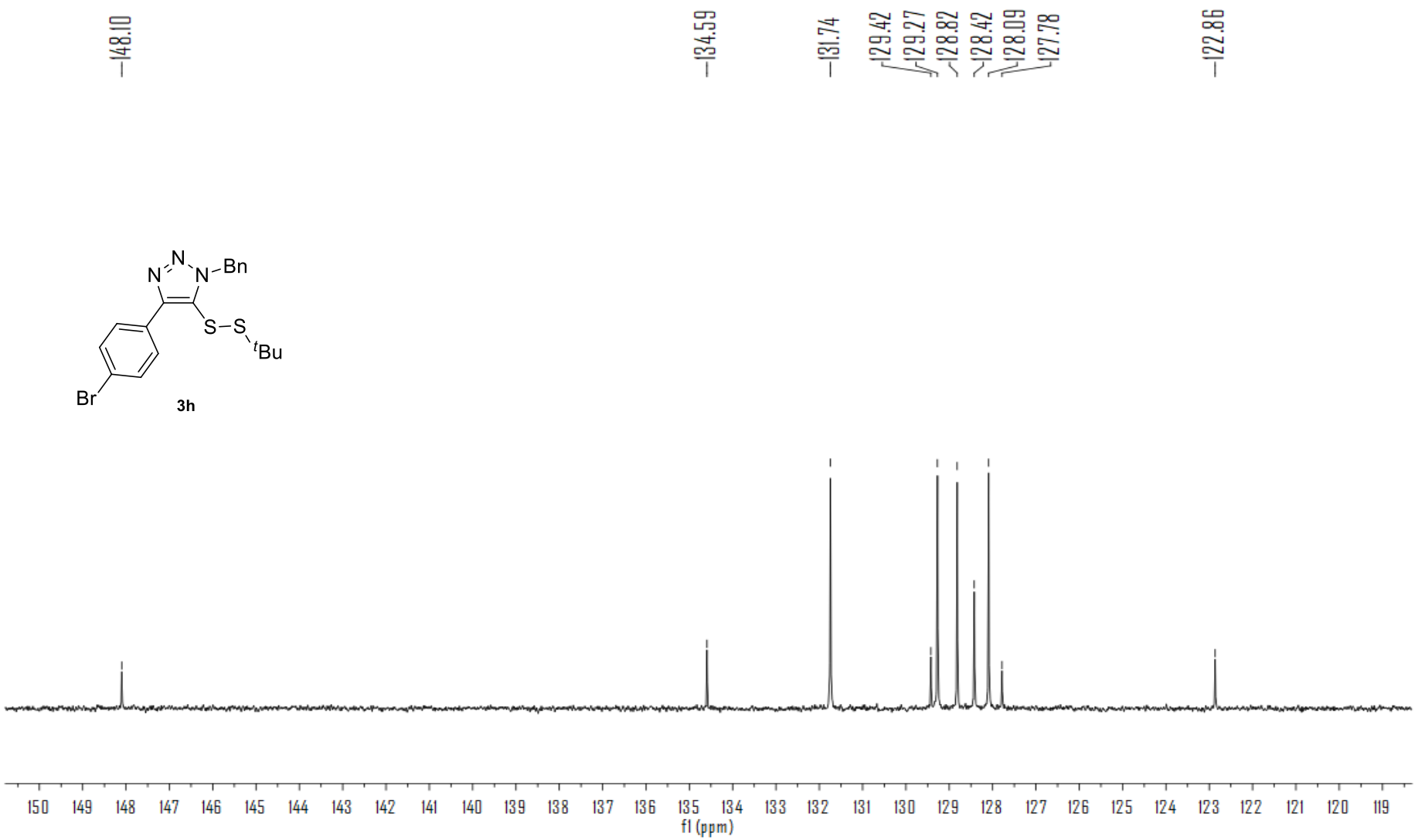
131.37
130.42
129.94
128.70
128.18
128.11
120.68
119.83
N
N
N
Bn
MeO
S
S
tBu
3g
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
f1 (ppm)


7.94
7.92
7.62
7.60
7.37
5.77
1.11
Bn
S–S
tBu
Br
3h
1.98
1.94
5.00
2.00
9.17
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


148.10
134.59
131.74
129.42
129.27
128.82
128.42
128.09
127.78
122.86
52.69
49.57
29.65
N
N
N
Bn
S
S
tBu
Br
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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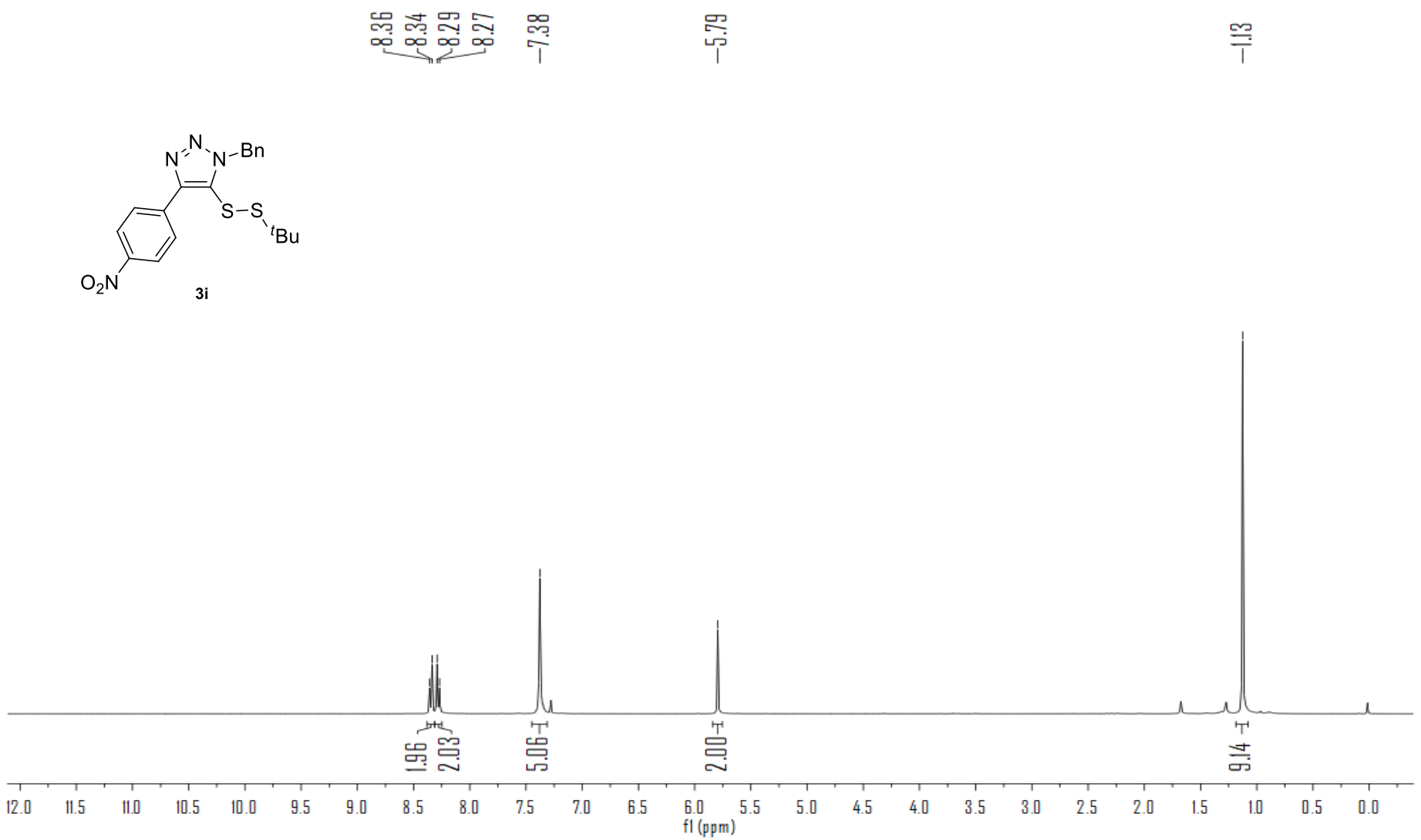
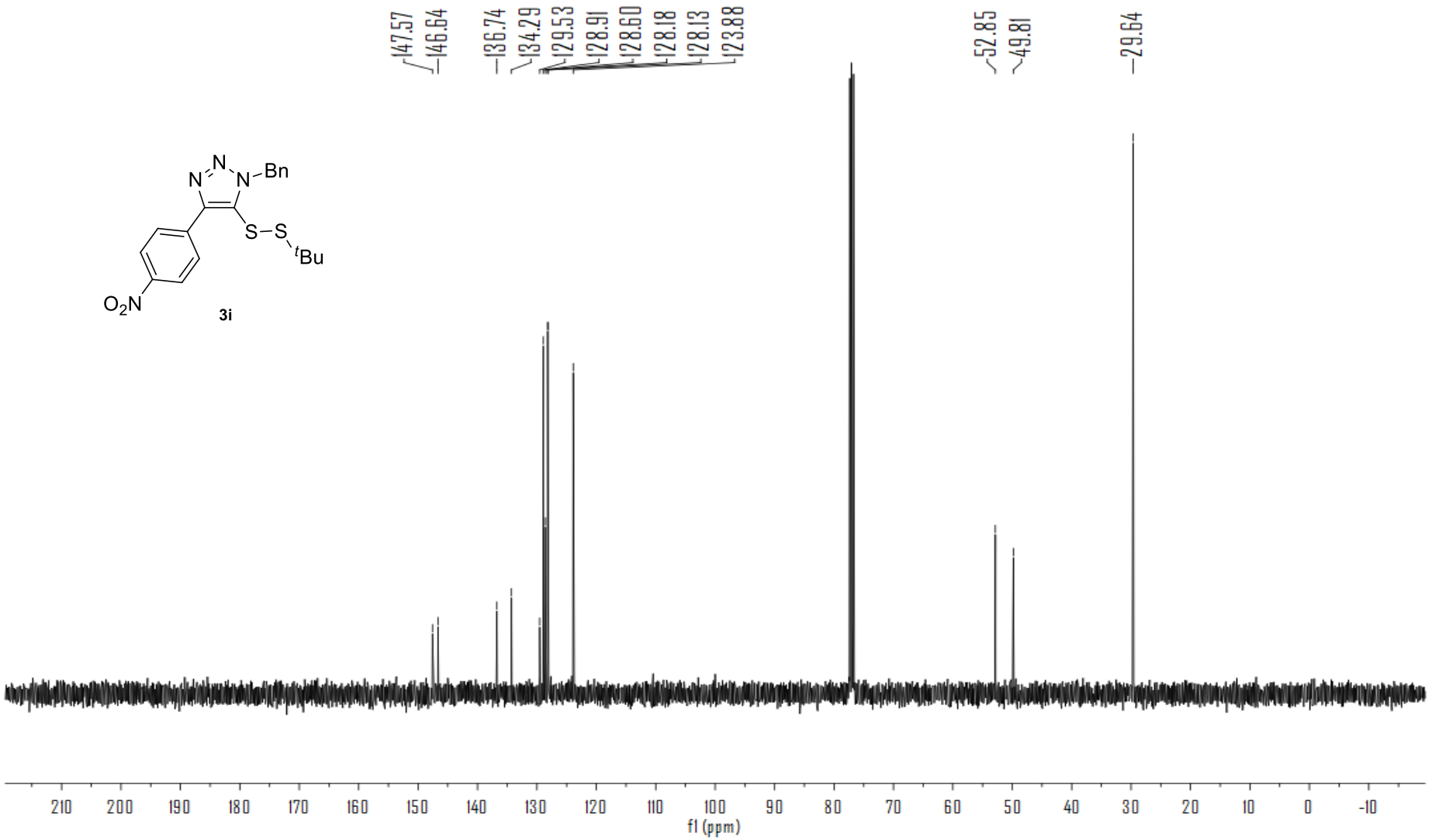
134.59
131.74
129.42
129.27
128.82
128.42
128.09
127.78
122.86
N
N
N
Bn
S
S
tBu
Br
3h
150 149 148 147 146 145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)


8.36
8.34
8.29
8.27
7.38
5.79
1.13
N
N
N
Bn
S
S
tBu
O2N
3i
1.96
2.03
5.06
2.00
9.14
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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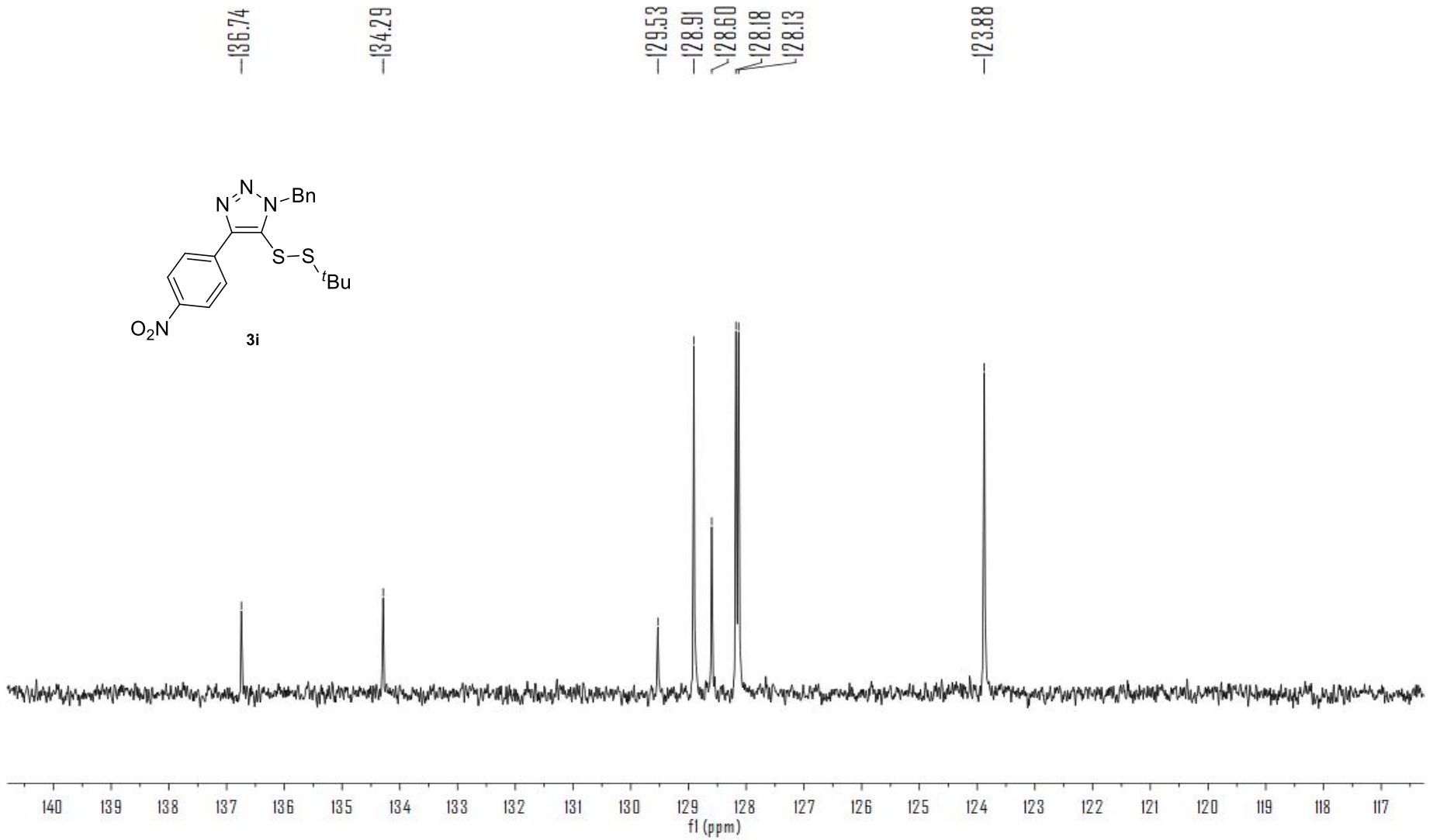
146.64
136.74
134.29
129.53
128.91
128.60
128.18
128.13
123.88
52.85
49.81
29.64
N
N
N
Bn
S
S
tBu
O2N
3i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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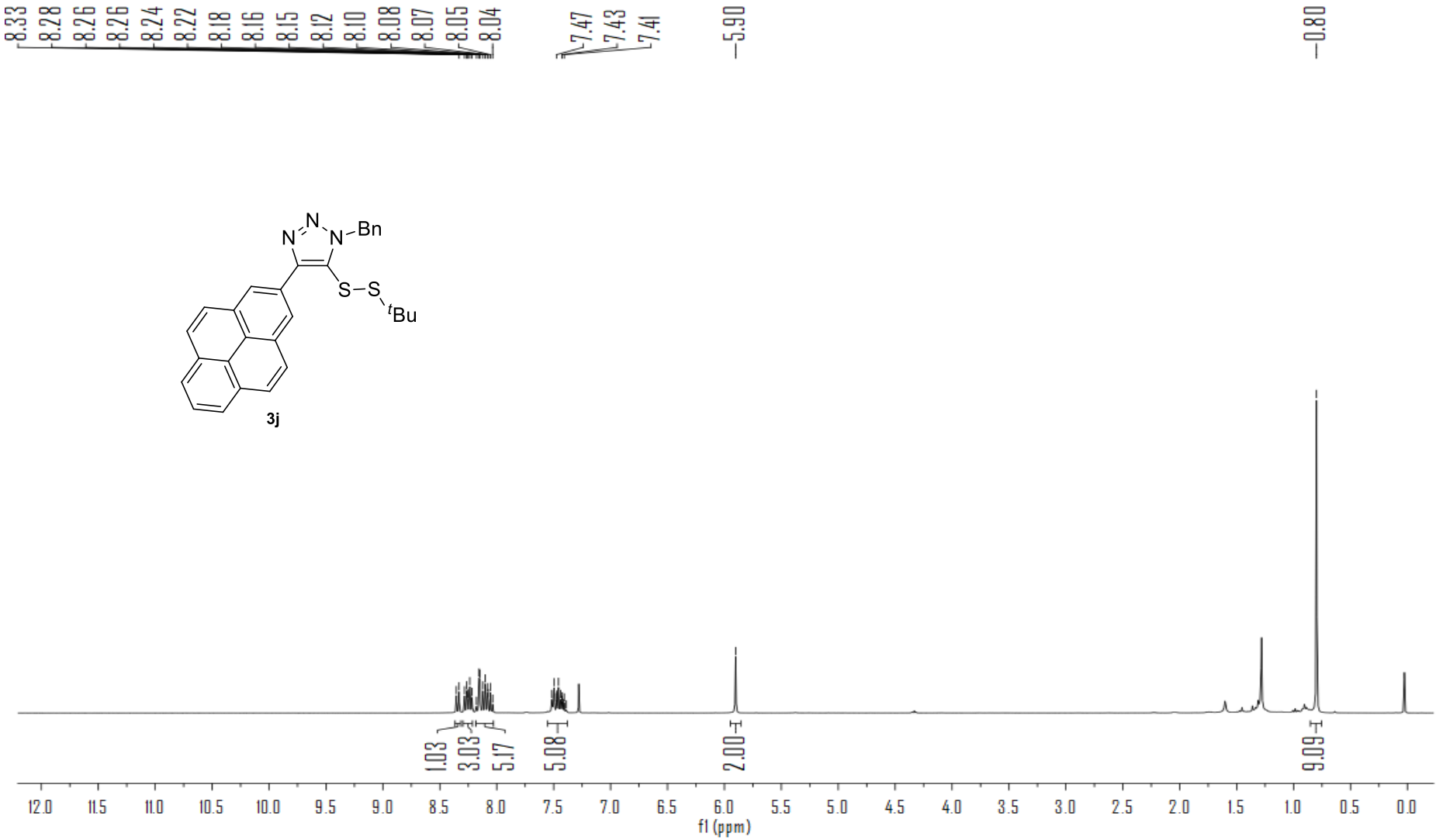
134.29
129.53
128.91
128.60
128.18
128.13
123.88
N
N
N
Bn
S
S
tBu
O2N
3i
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
118
117
f1 (ppm)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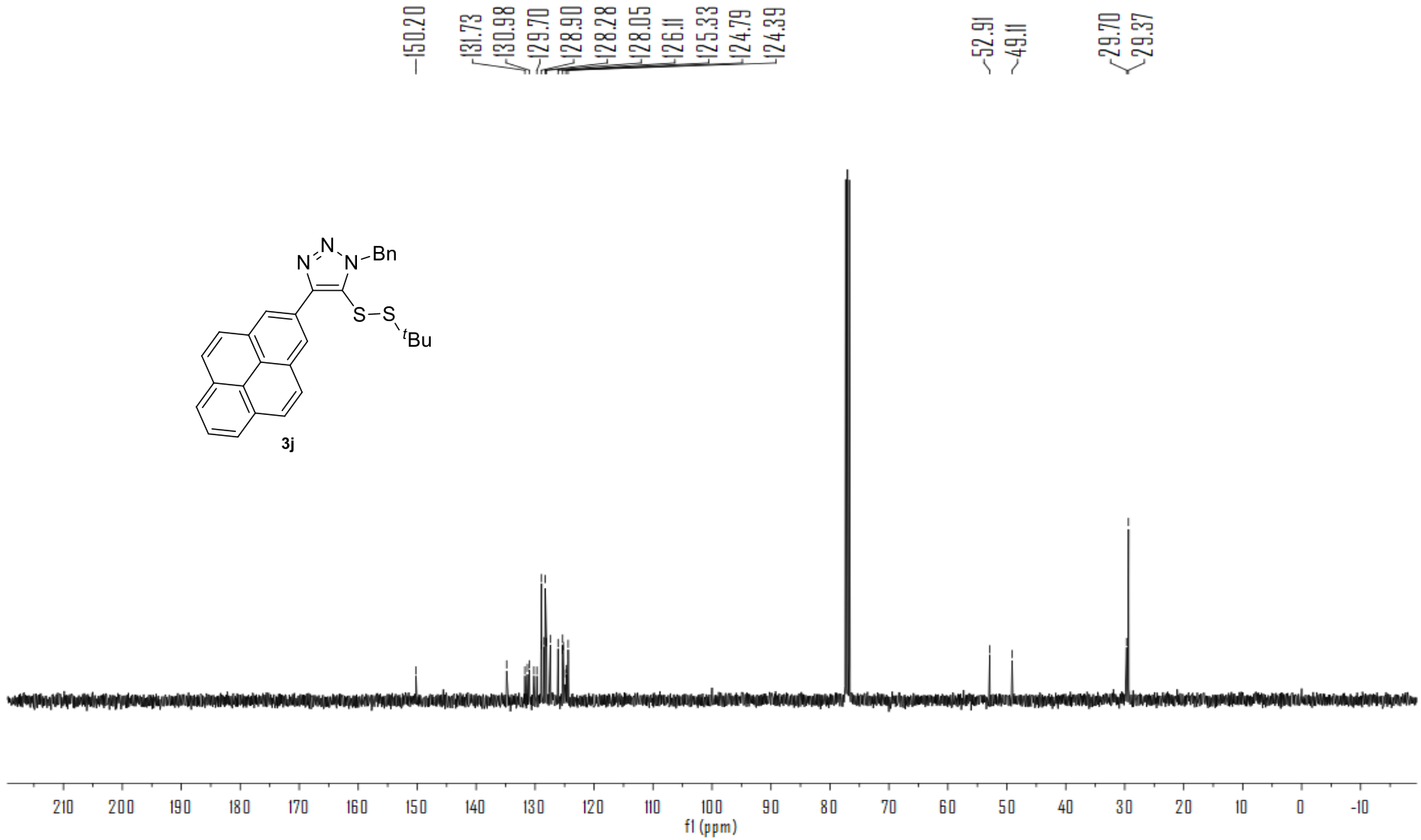
8.26
8.26
8.24
8.22
8.18
8.16
8.15
8.12
8.10
8.08
8.07
8.05
8.04
7.47
7.43
7.41
5.90
0.80
N
N
N
Bn
S
S
tBu
3j
1.03
3.03
5.17
5.08
2.00
9.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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131.73
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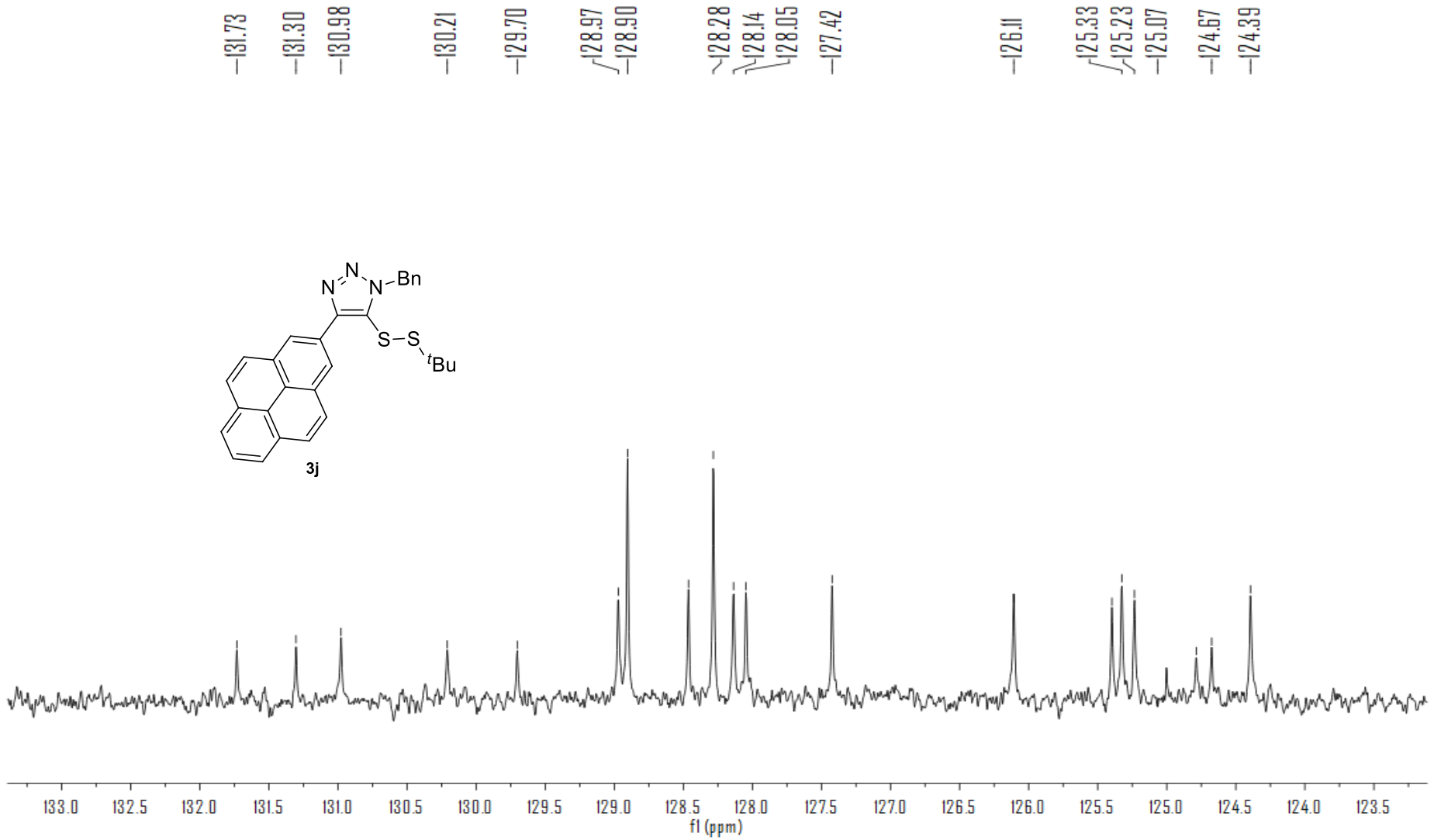
129.70
128.90
128.28
128.05
126.11
125.33
124.79
124.39
52.91
49.11
29.70
29.37
N
N
N
Bn
S
S
tBu
3j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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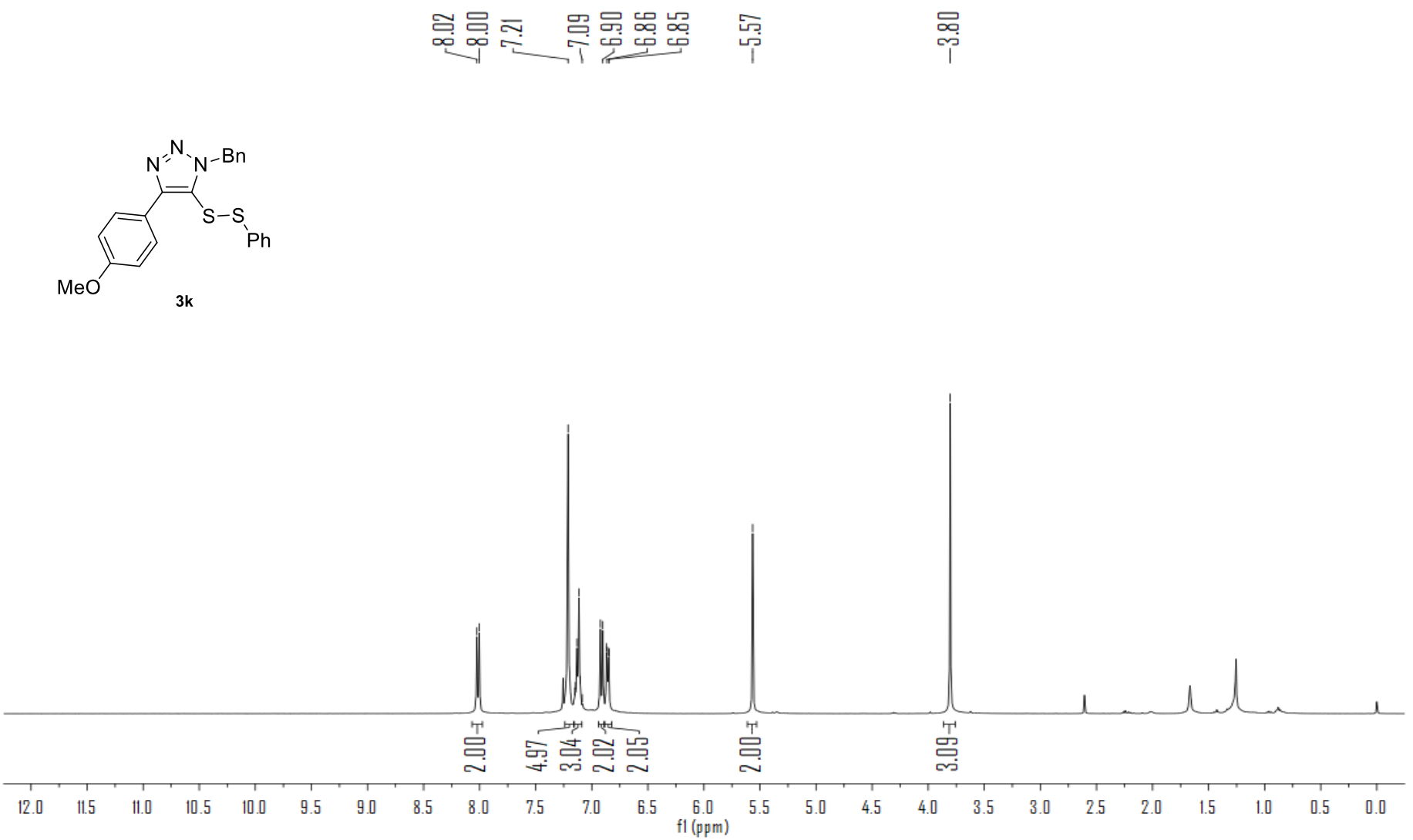
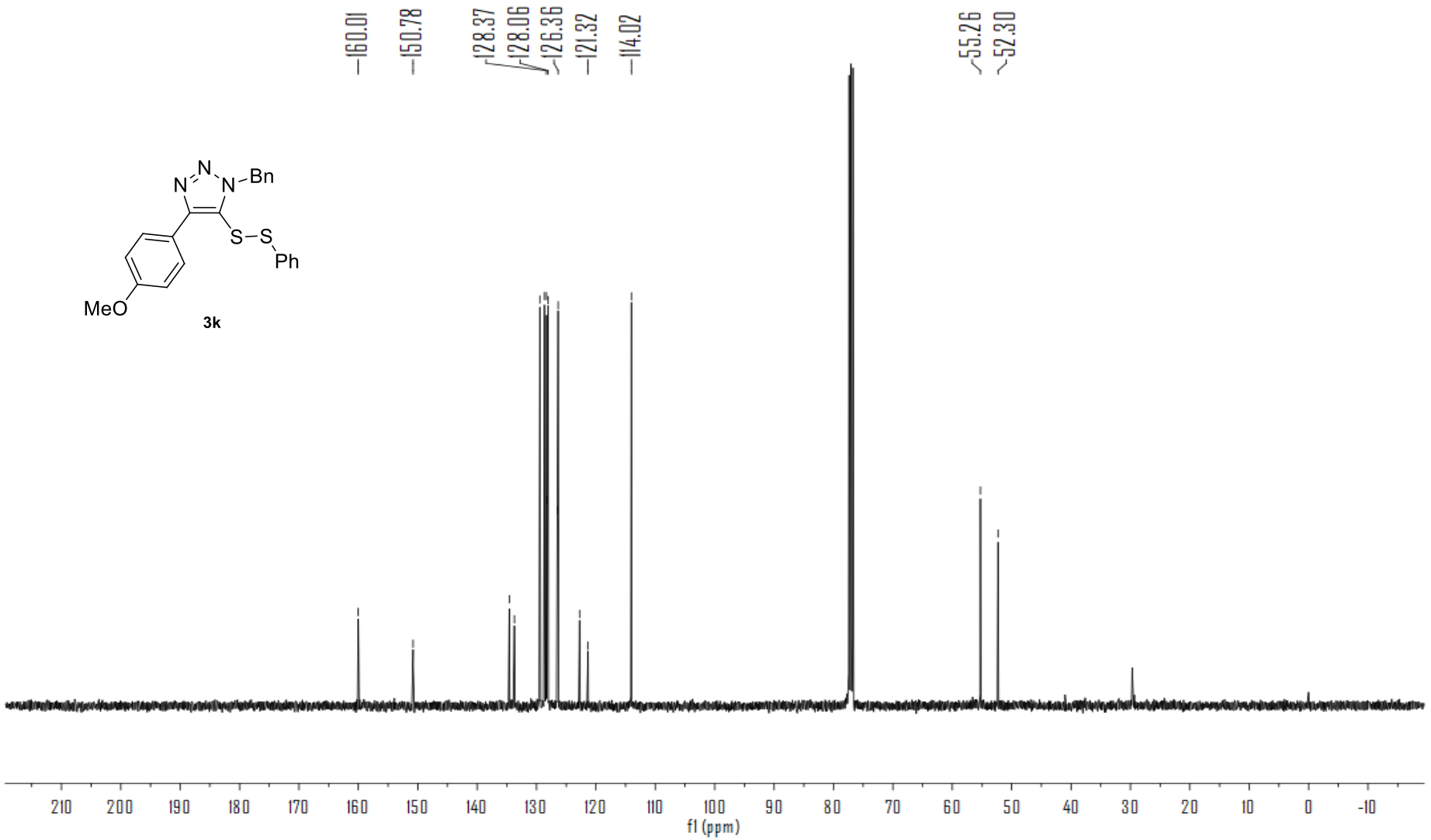
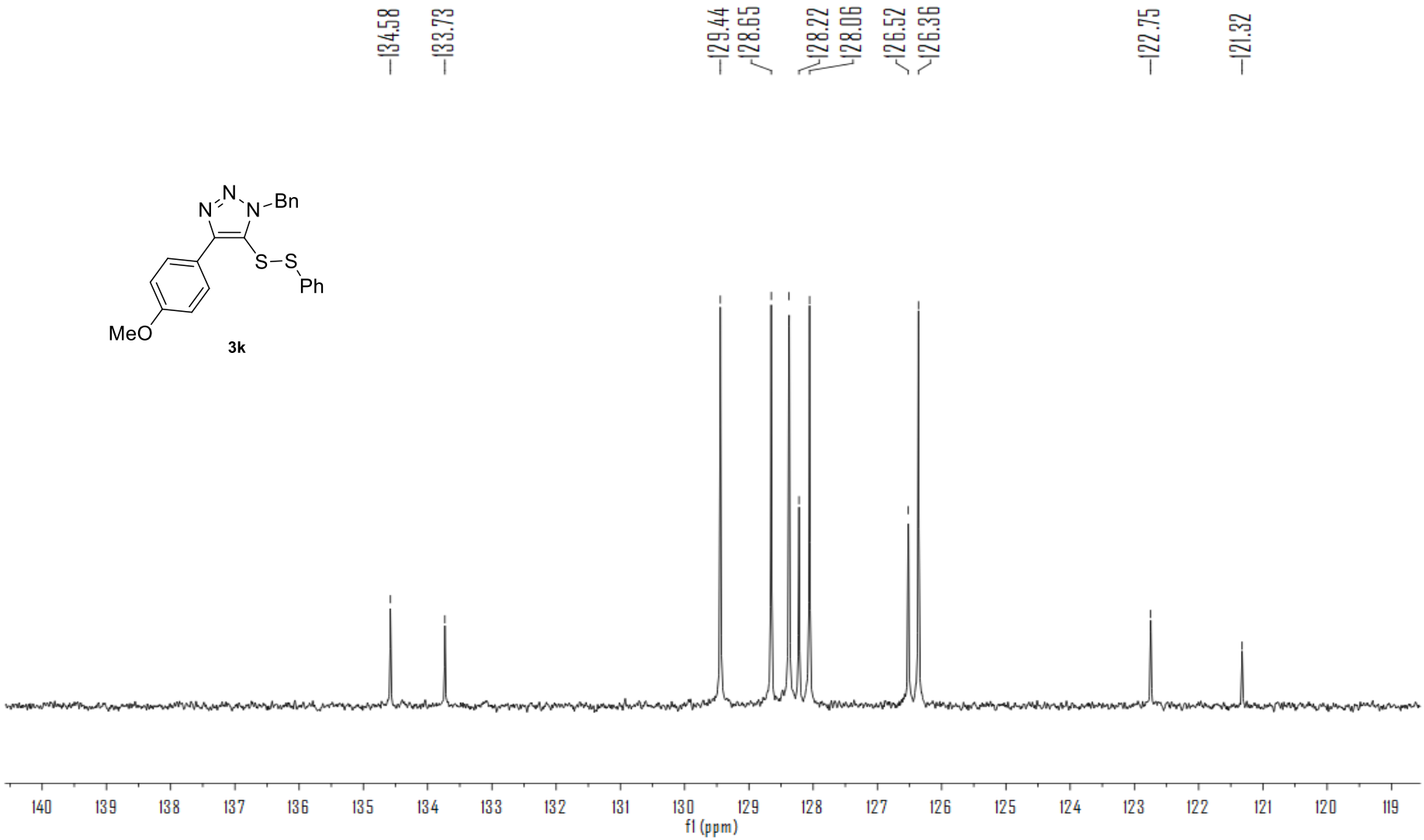
129.70
128.97
128.90
128.28
128.14
128.05
127.42
126.11
125.33
125.23
125.07
124.67
124.39
N
N
N
Bn
S
S
tBu
3j
133.0
132.5
132.0
131.5
131.0
130.5
130.0
129.5
129.0
128.5
128.0
127.5
127.0
126.5
126.0
125.5
125.0
124.5
124.0
123.5
f1 (ppm)


8.02
8.00
7.21
7.09
6.90
6.86
6.85
5.57
3.80
N
N
N
Bn
S
S
Ph
MeO
2.00
4.97
3.04
2.02
2.05
2.00
3.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

3k


160.01
150.78
128.37
128.06
126.36
121.32
114.02
55.26
52.30
N
N
N
Bn
S
S
Ph
MeO
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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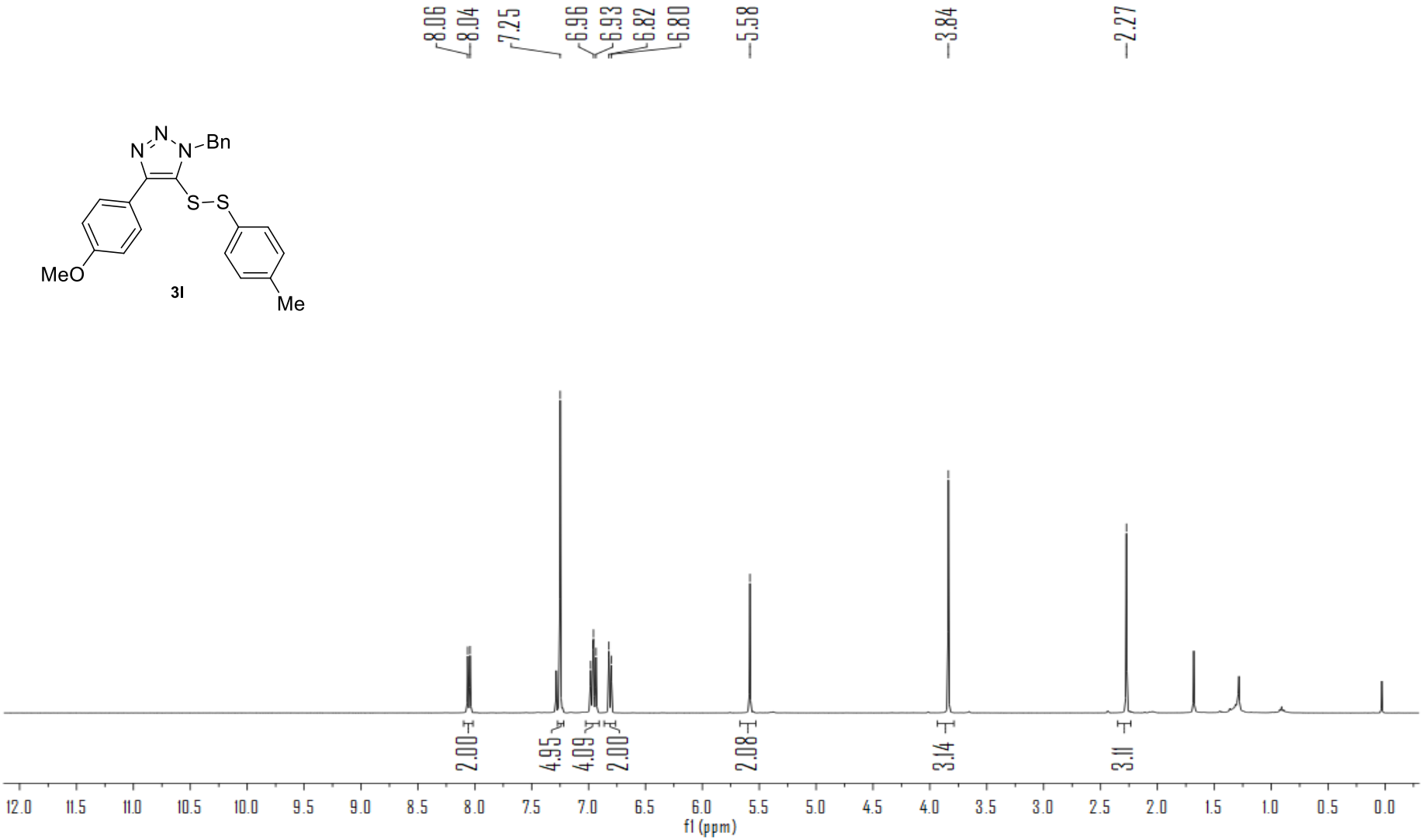
133.73
129.44
128.65
128.22
128.06
126.52
126.36
122.75
121.32
N
N
N
Bn
S
S
Ph
MeO
3k
140
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
120
119
f1 (ppm)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8.04
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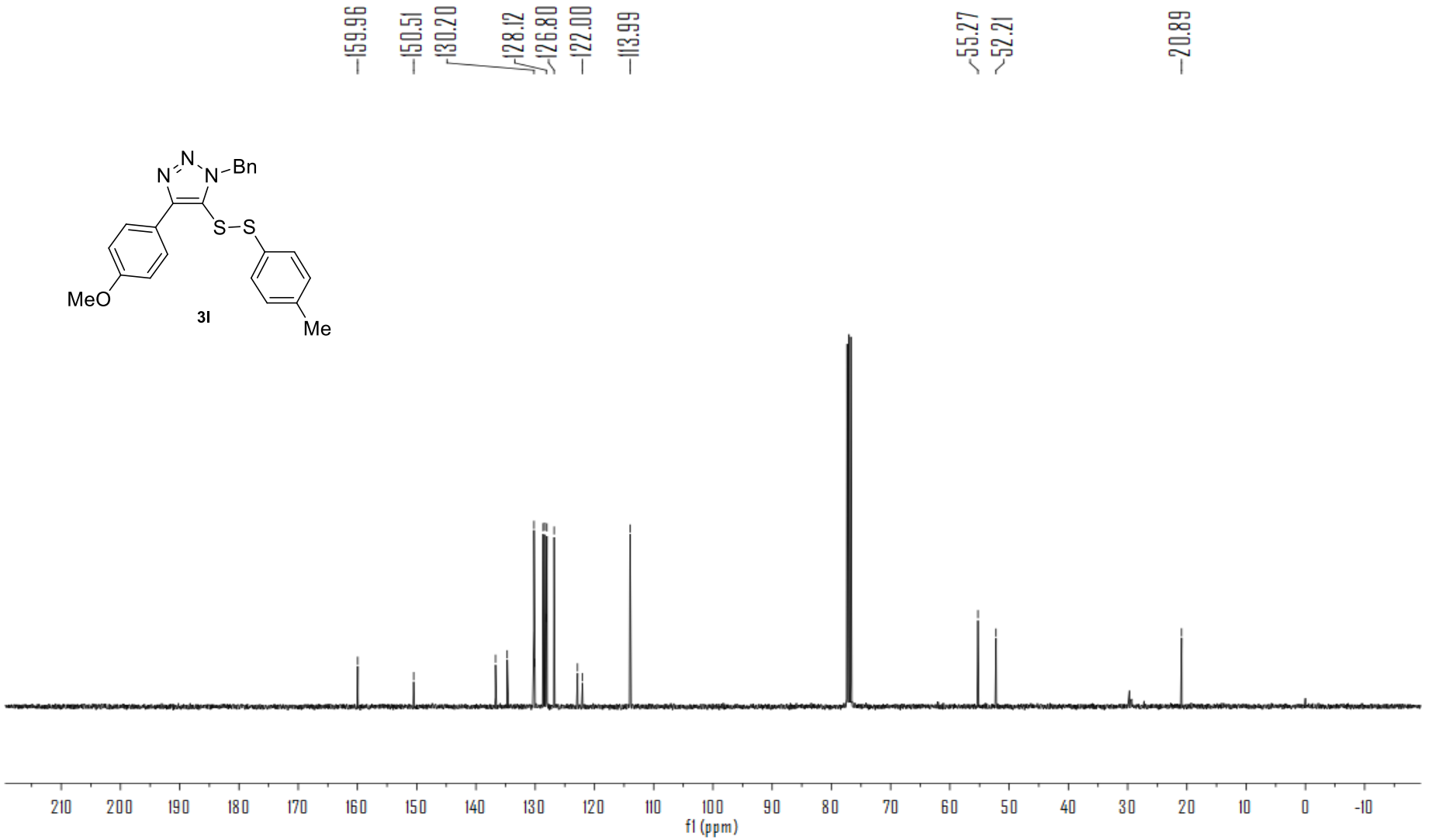
6.96
6.93
6.82
6.80
5.58
3.84
2.27
N
N
N
Bn
S
S
MeO
Me
3l
2.00
4.95
4.09
2.00
2.08
3.14
3.11
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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150.51
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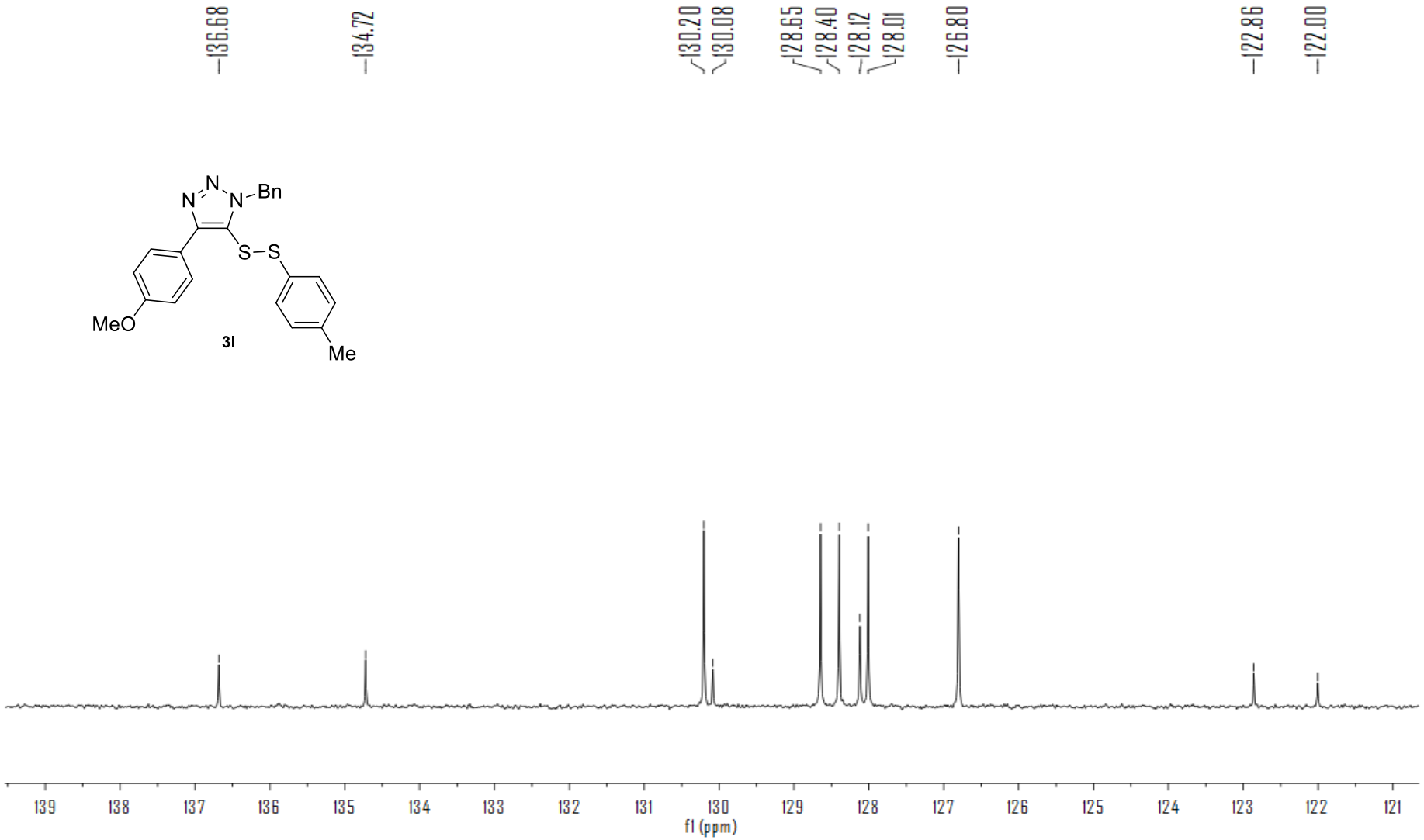
128.12
126.80
122.00
113.99
55.27
52.21
20.89
N
N
N
Bn
S
S
MeO
Me
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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134.72
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130.08
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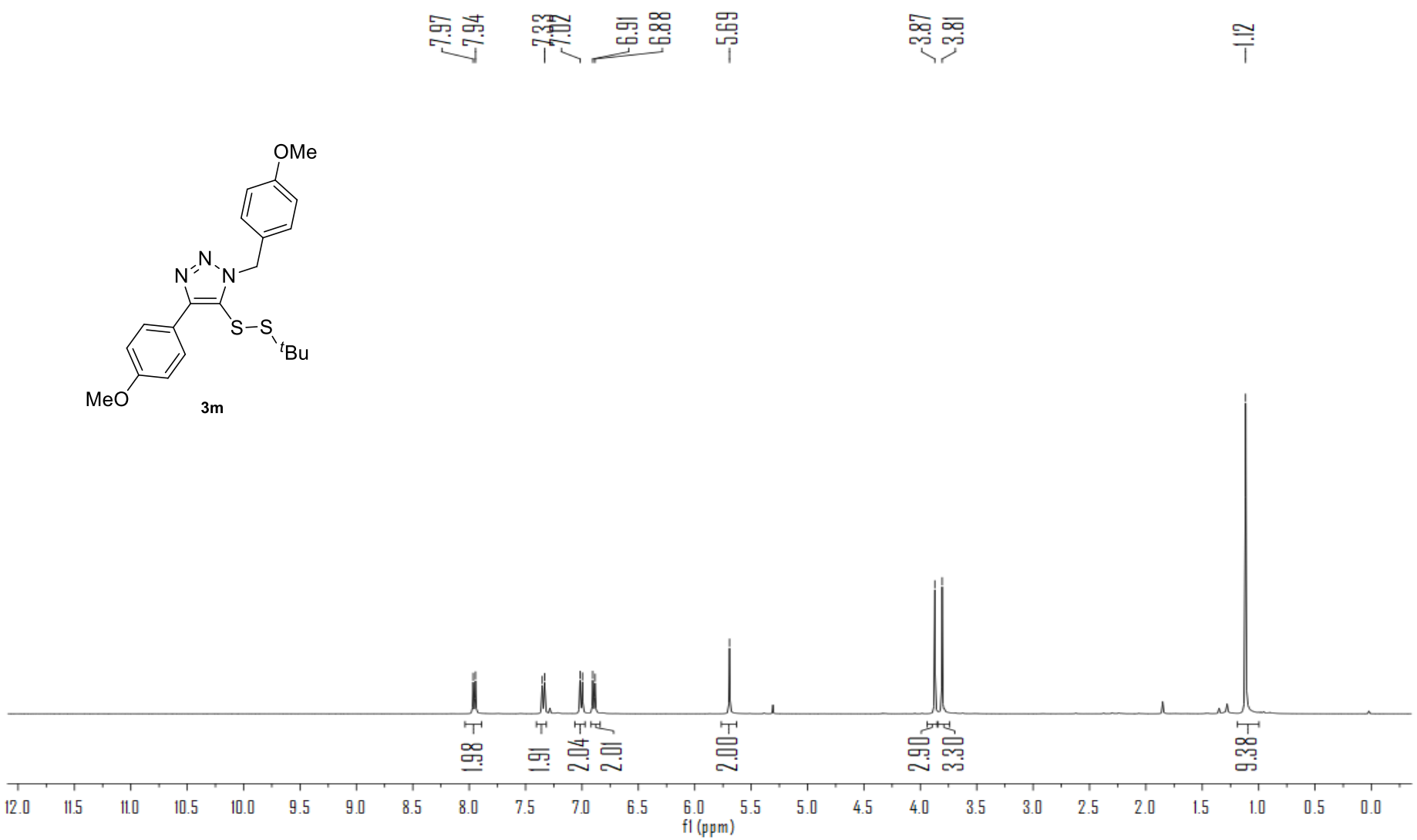
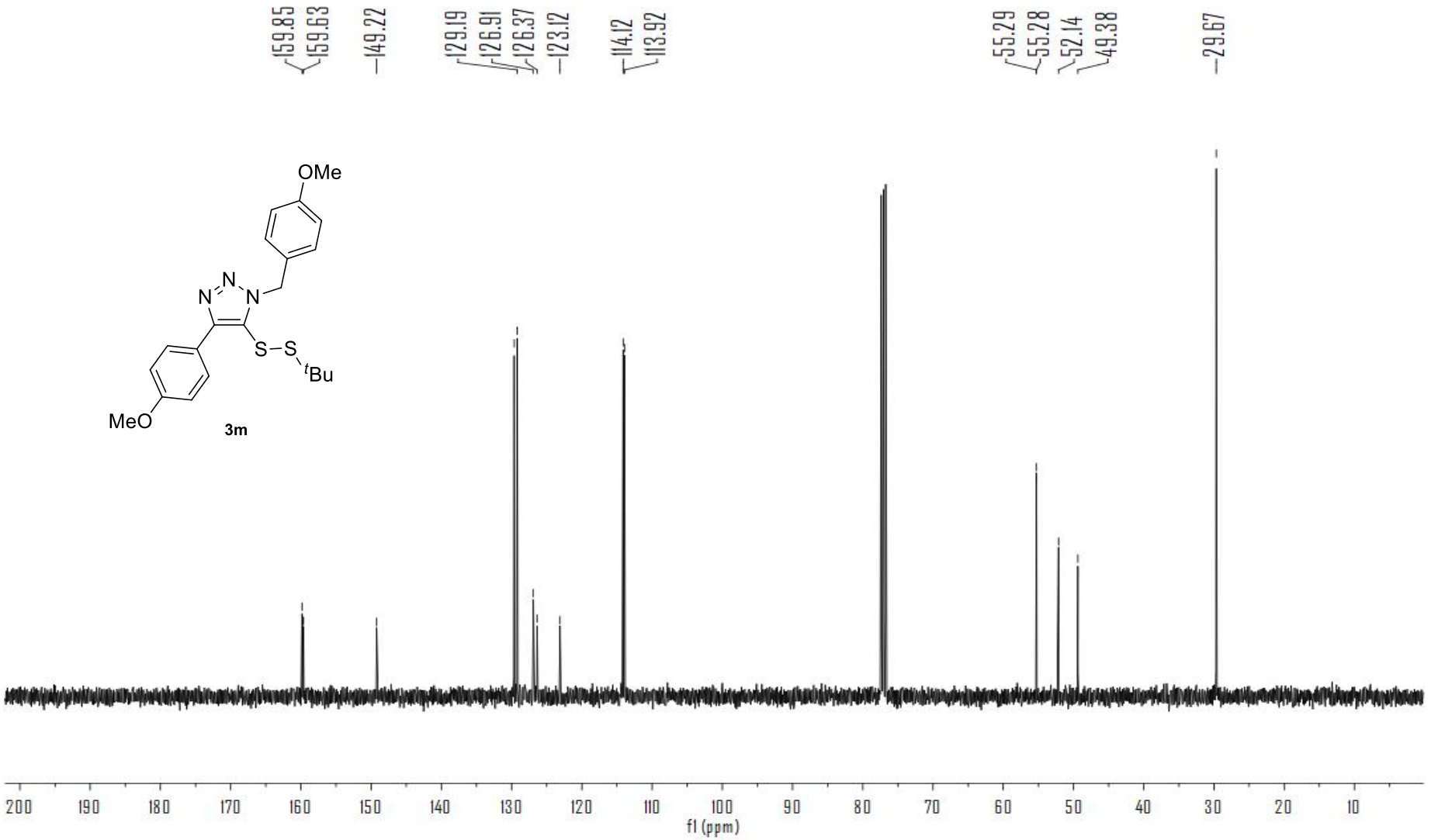
128.40
128.12
128.01
126.80
122.86
122.00
N
N
N
Bn
S
S
MeO
Me
3l
139
138
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)


7.97
7.94
7.33
7.02
6.91
6.88
5.69
3.87
3.81
1.12
OMe
MeO
S
S
tBu
3m
1.98
1.91
2.04
2.01
2.00
2.90
3.30
9.38
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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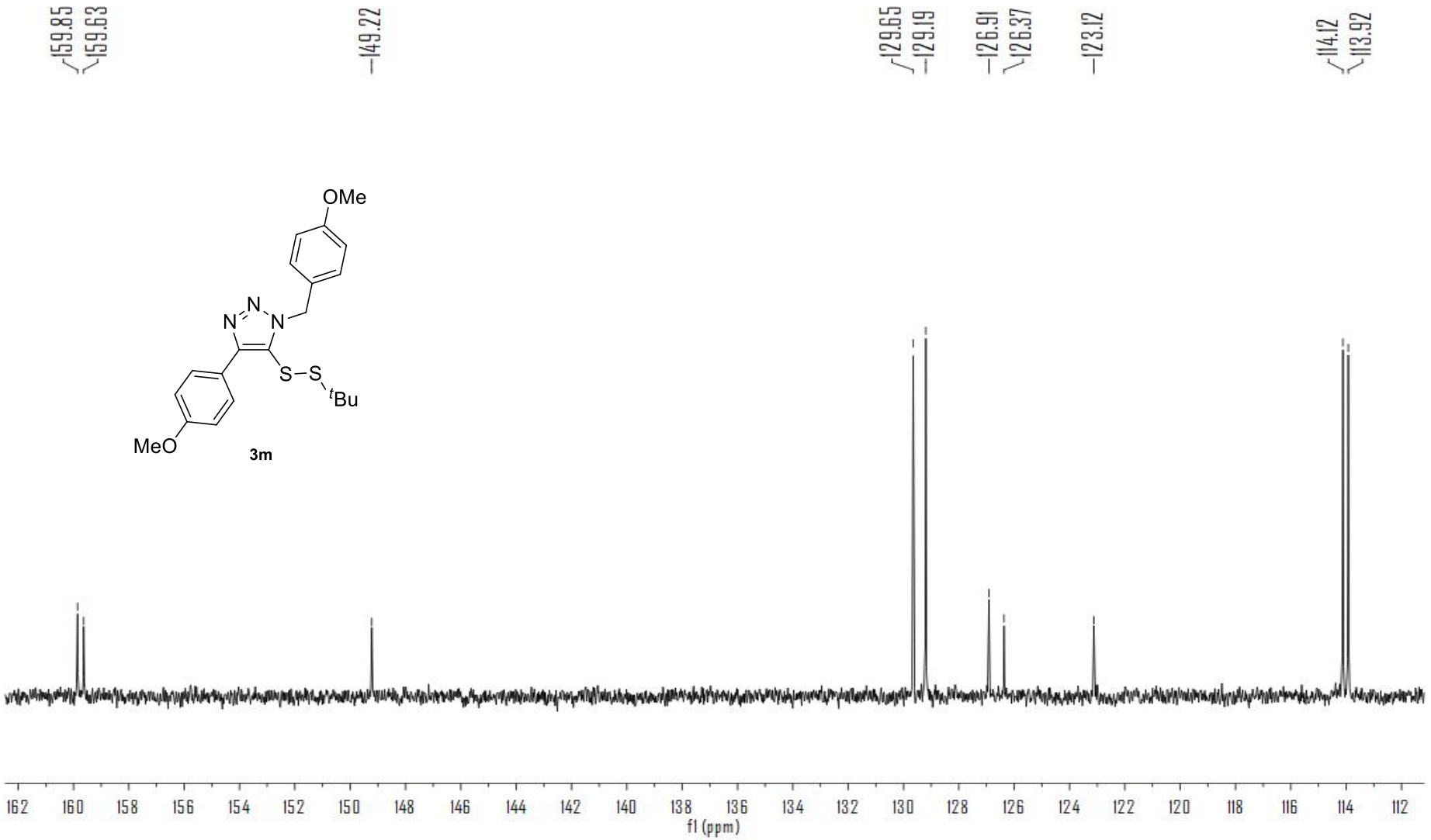
159.63
149.22
129.19
126.91
126.37
123.12
114.12
113.92
55.29
55.28
52.14
49.38
29.67
OMe
MeO
S–S
tBu
3m
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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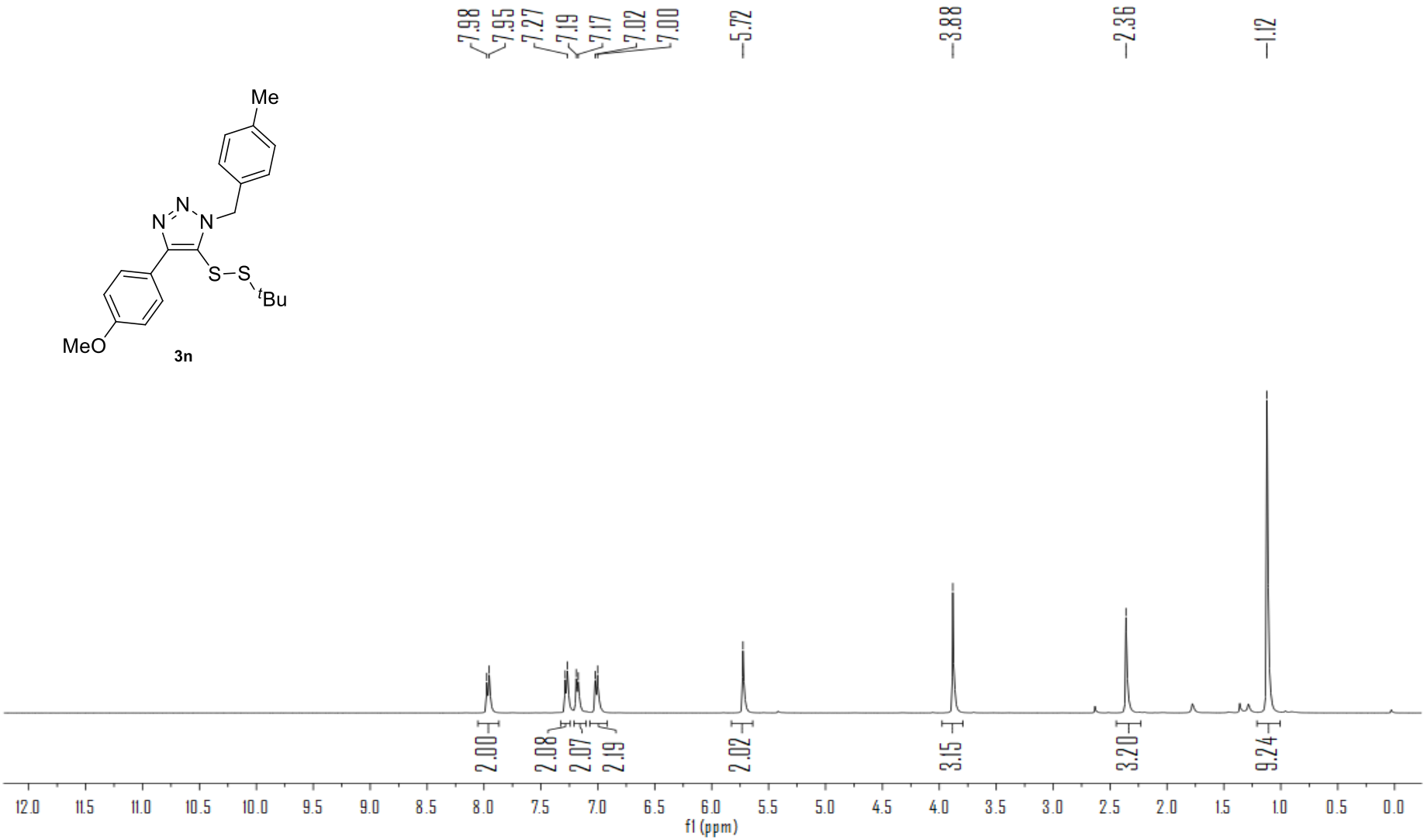
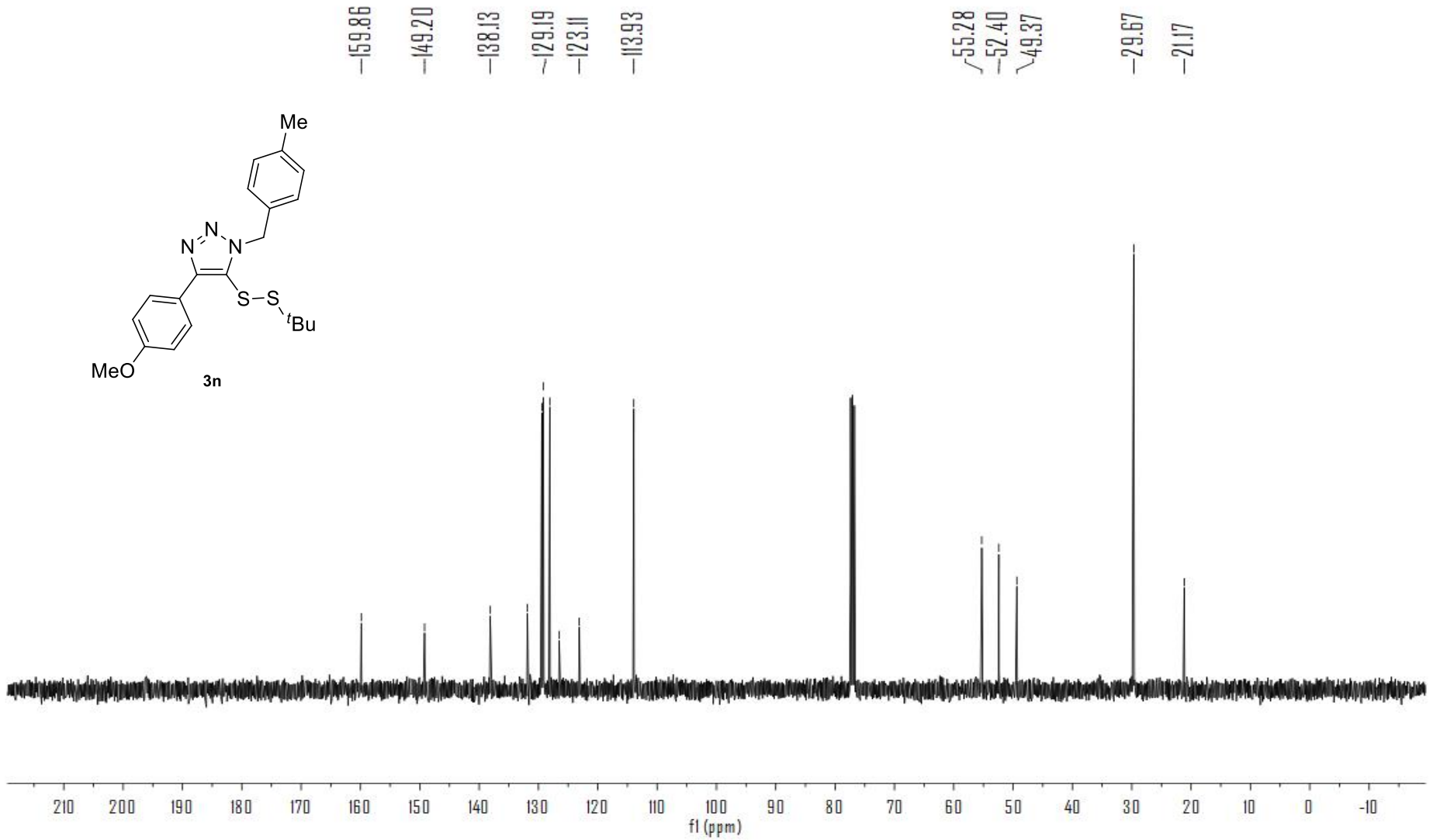
159.63
149.22
129.65
129.19
126.91
126.37
123.12
114.12
113.92
OMe
MeO
S–S
tBu
3m
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)


7.98
7.95
7.27
7.19
7.17
7.02
7.00
5.72
3.88
2.36
1.12
Me
N
N
N
S
S
tBu
MeO
3n
2.00
2.08
2.07
2.19
2.02
3.15
3.20
9.24
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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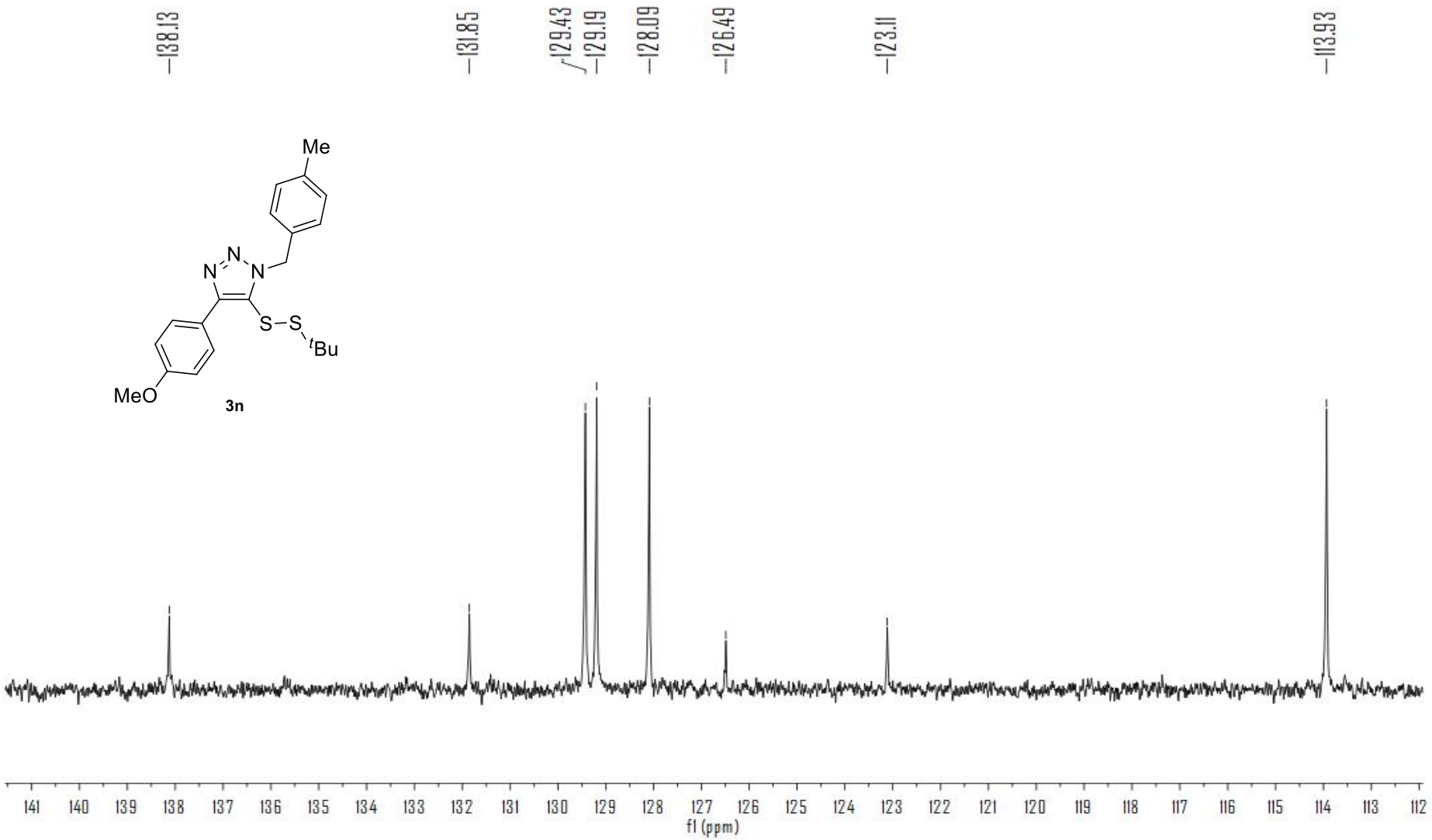
149.20
138.13
129.19
123.11
113.93
55.28
52.40
49.37
29.67
21.17
Me
MeO
S–S
tBu
3n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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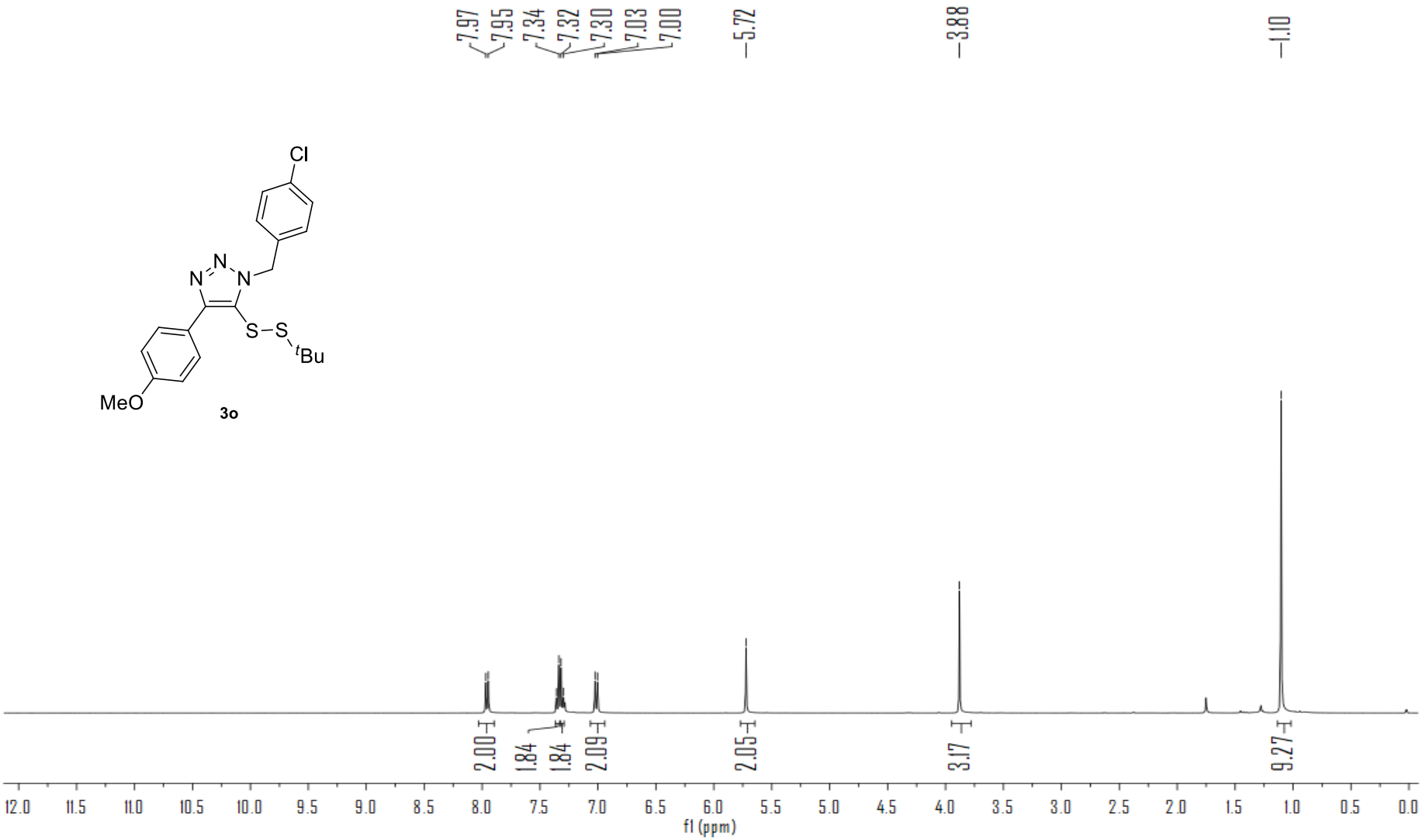
131.85
129.43
129.19
128.09
126.49
123.11
113.93
Me
MeO
S–S
tBu
3n
141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119 118 117 116 115 114 113 112
f1 (ppm)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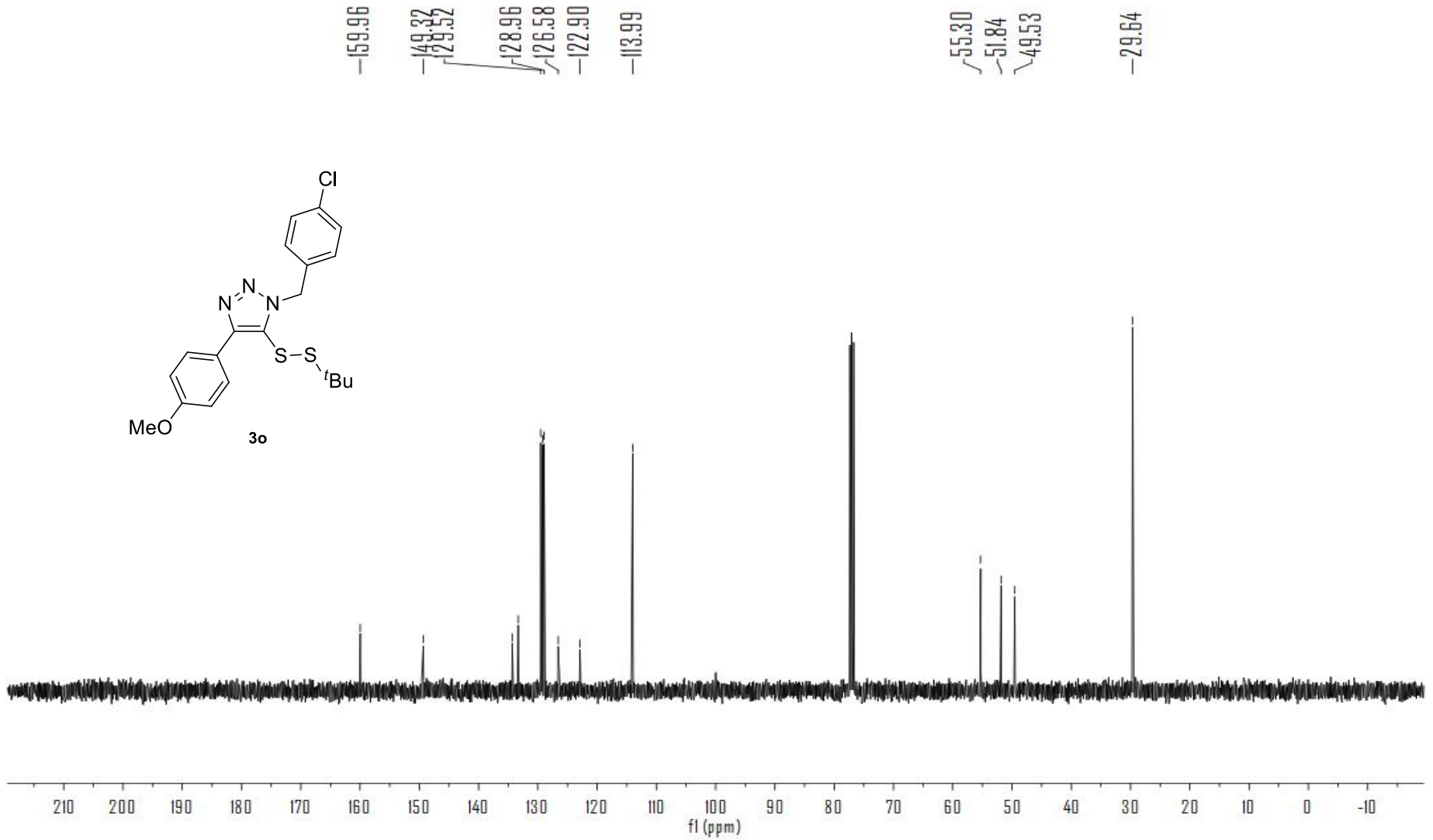
7.95
7.34
7.32
7.30
7.03
7.00
5.72
3.88
1.10
Cl
N
N
N
S
S
tBu
MeO
3o
2.00
1.84
1.84
2.09
2.05
3.17
9.27
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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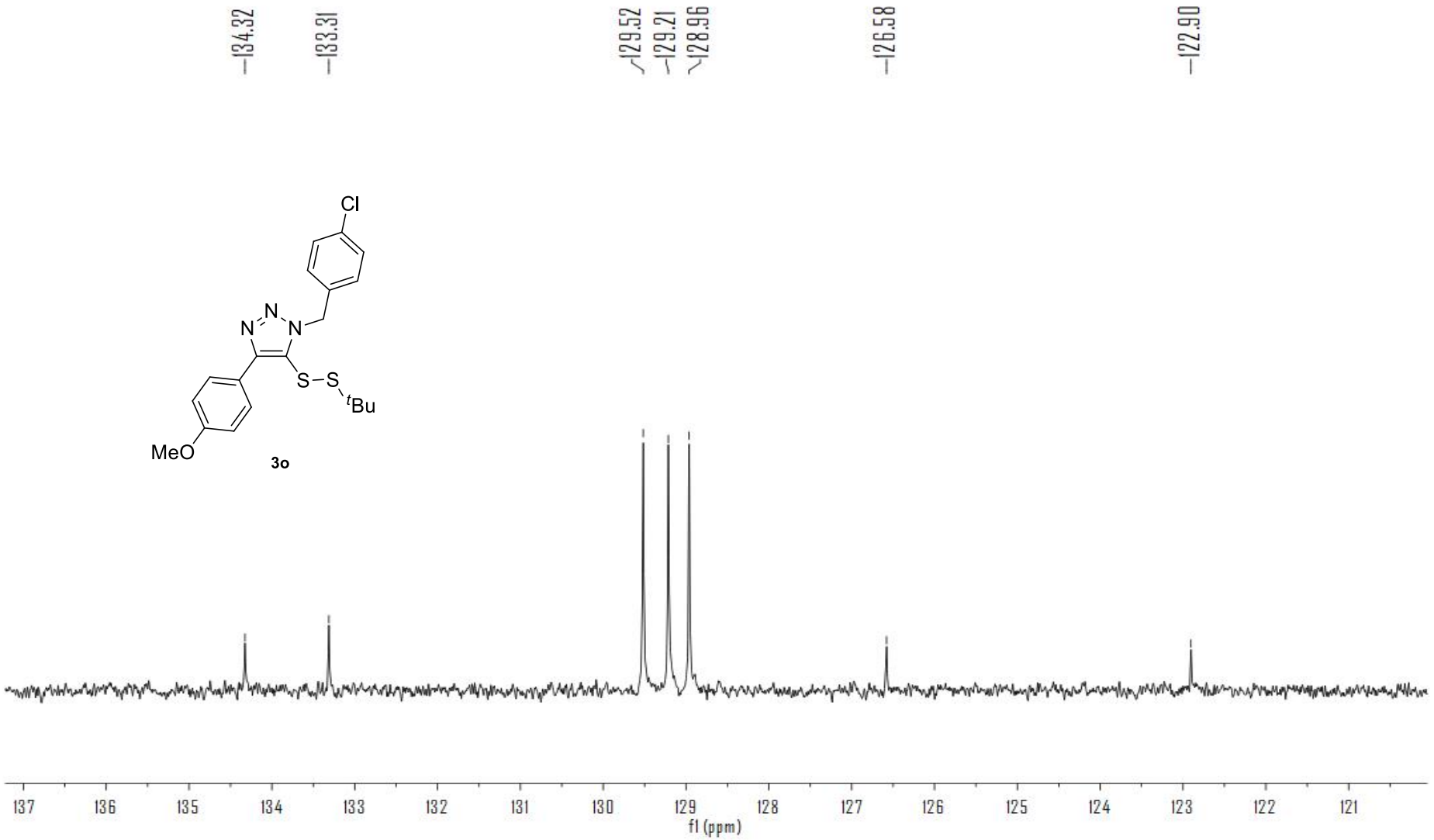
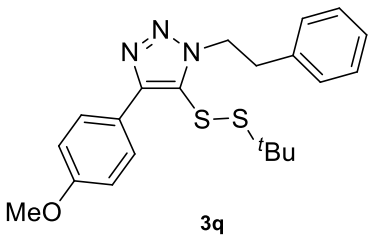
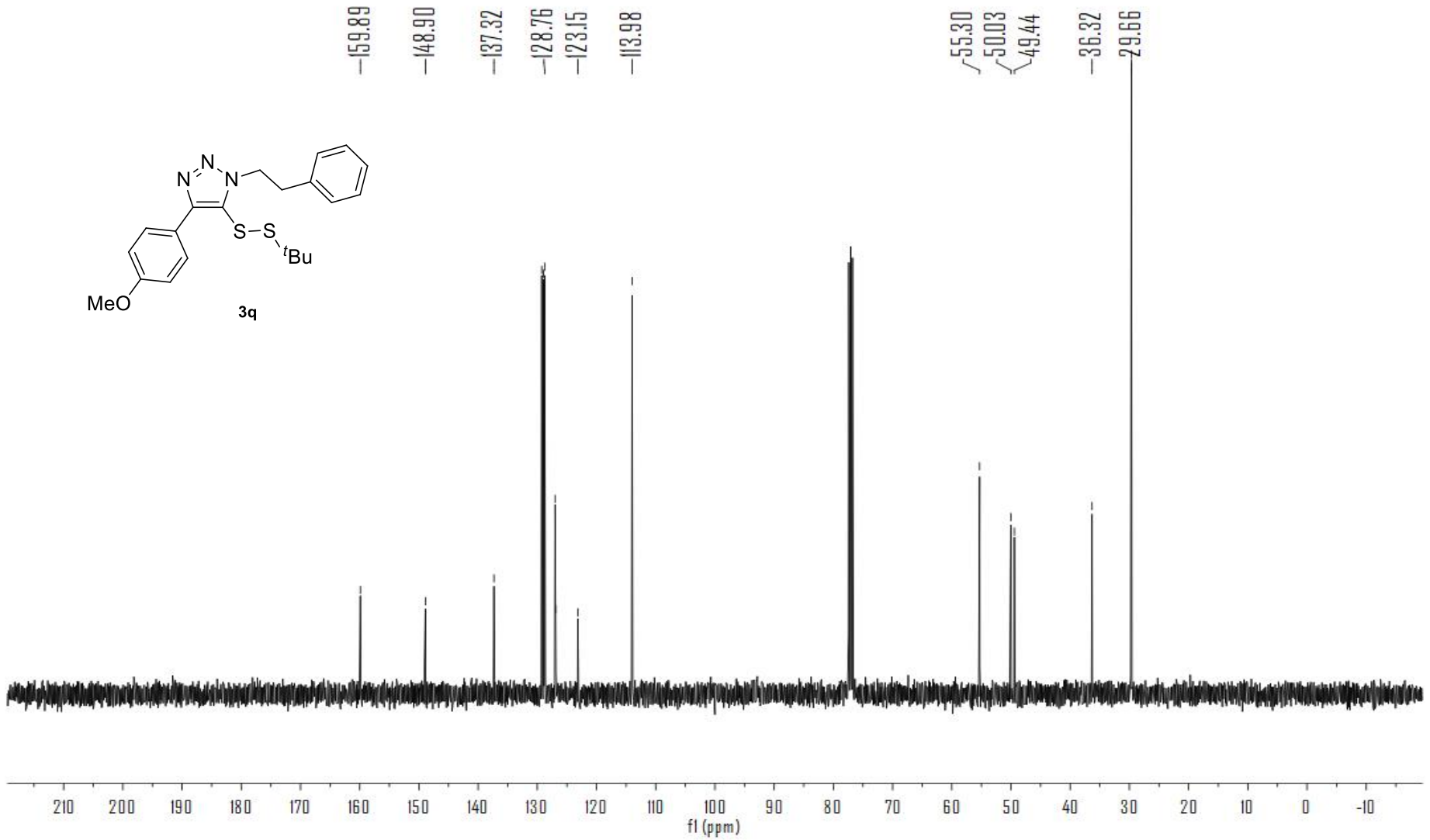
149.32
129.52
128.96
126.58
122.90
113.99
55.30
51.84
49.53
29.64
Cl
N
N
N
S
S
tBu
MeO
3o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


134.32
133.31
129.52
129.21
128.96
126.58
122.90
Cl
N
N
N
S
S
tBu
MeO
3o
137
136
135
134
133
132
131
130
129
128
127
126
125
124
123
122
121
f1 (ppm)


MeO
S–S
tBu

3q

7.97
7.94
7.33
7.29
7.27
7.04
7.02
4.77
4.75
4.73
3.89
3.41
3.39
3.37
1.11
2.00
5.17
2.02
2.01
3.10
2.02
9.24
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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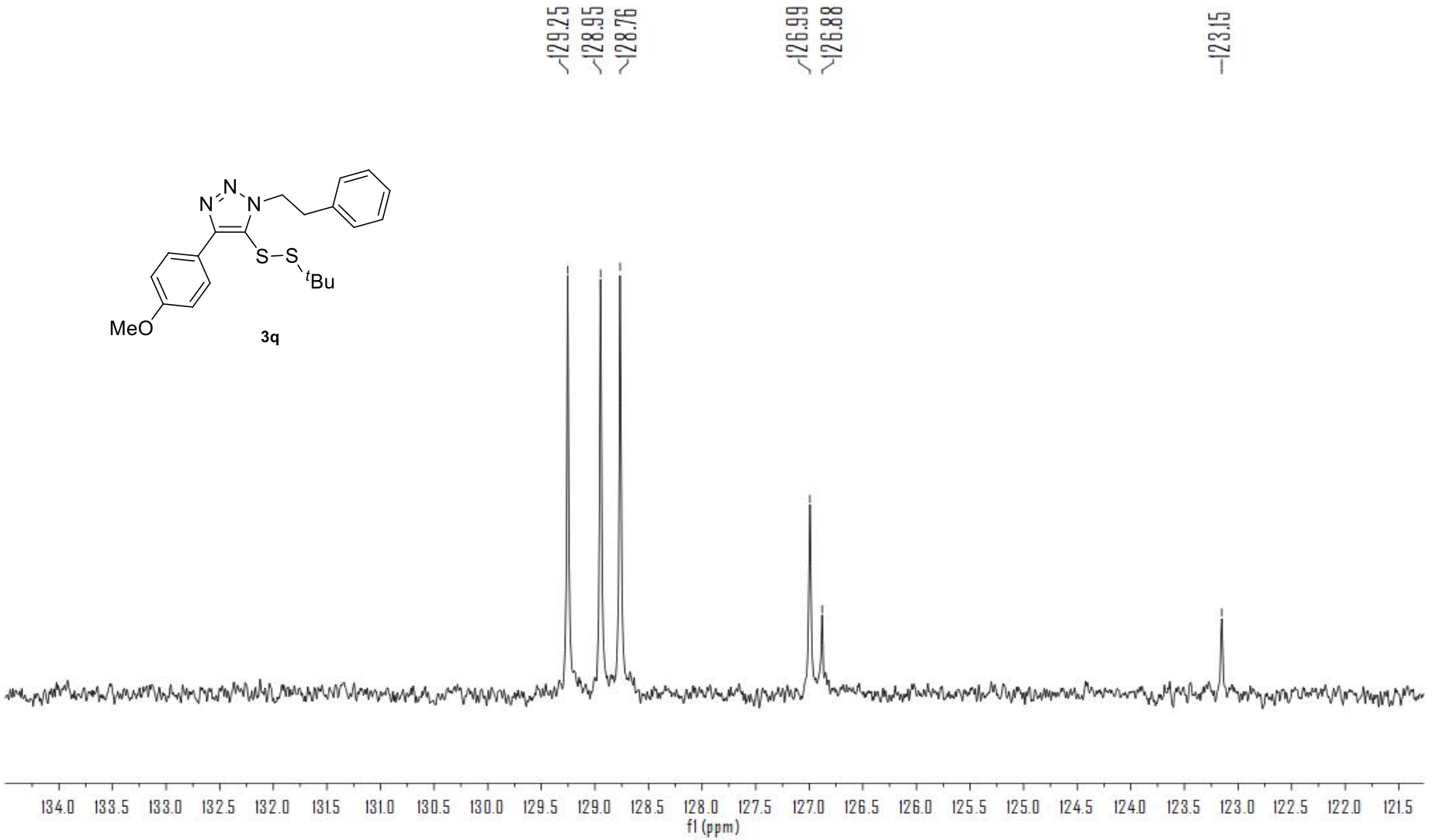
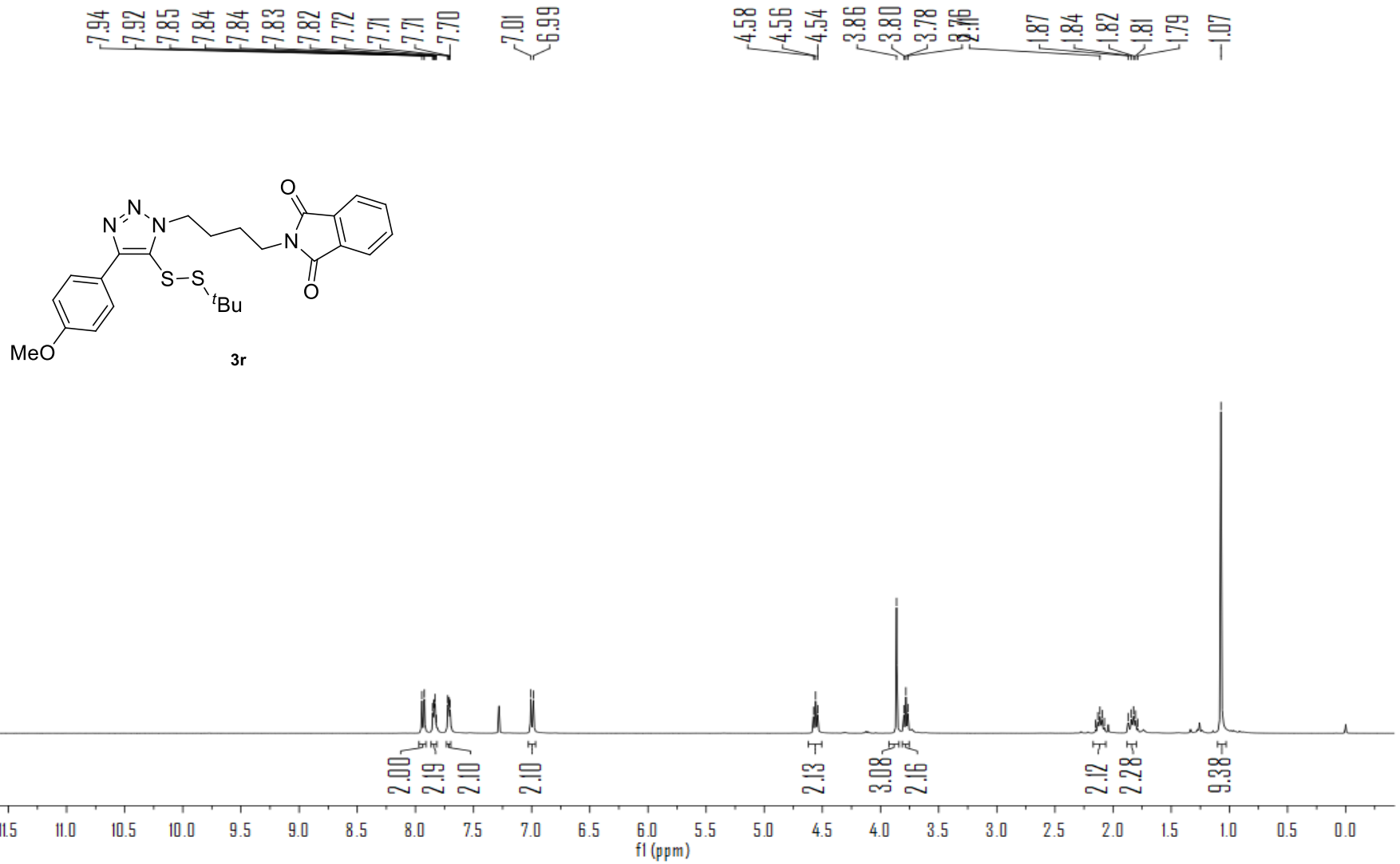
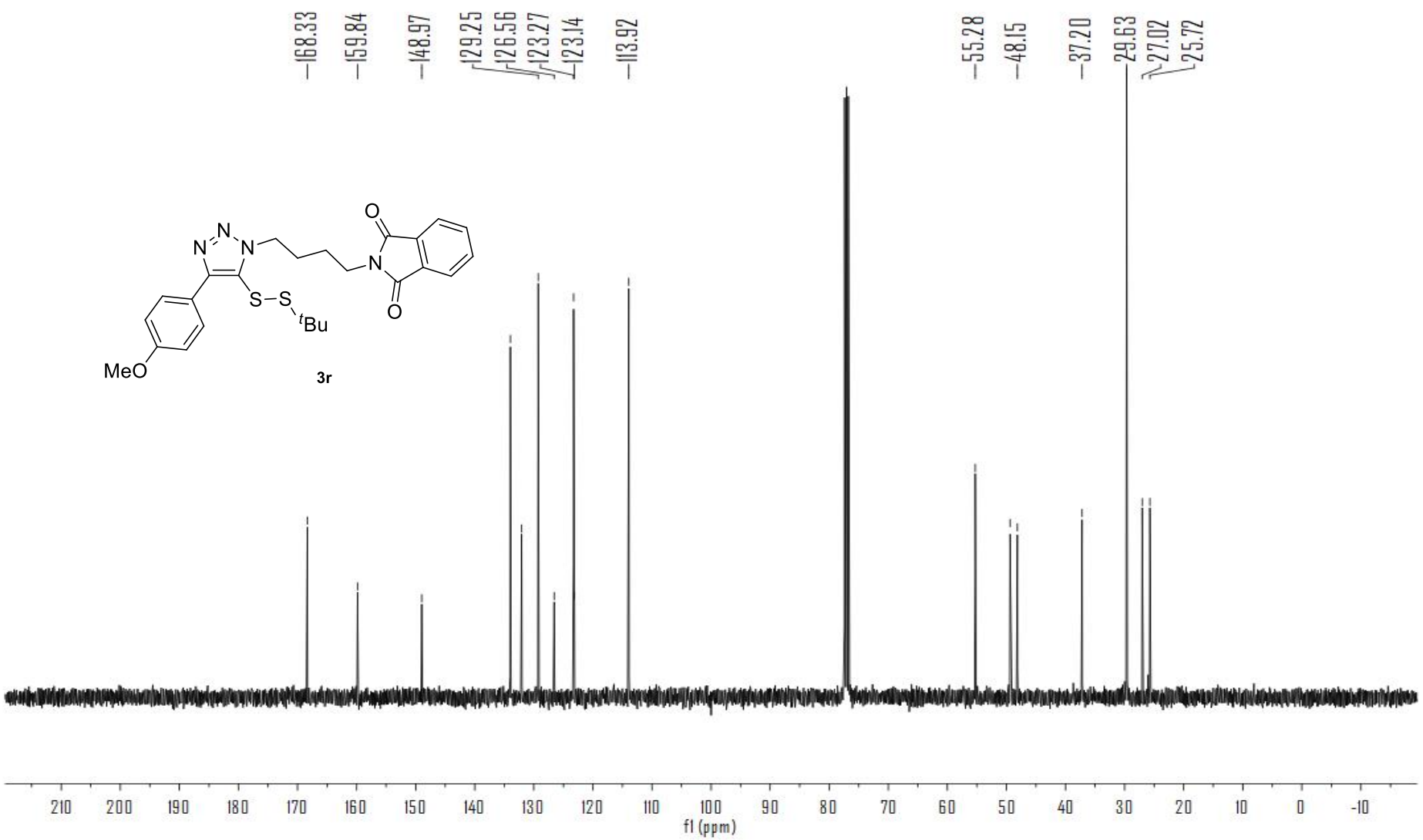
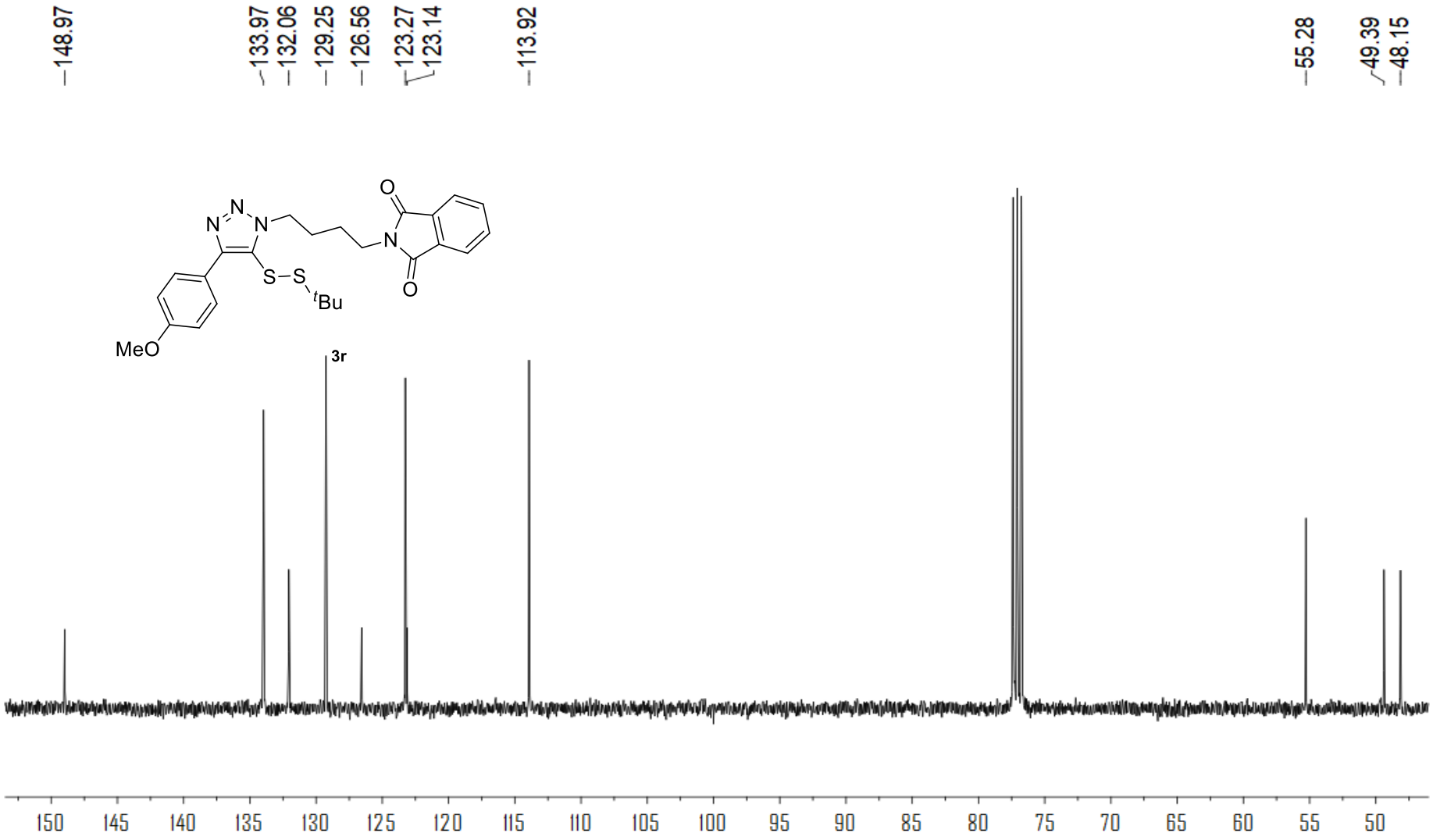
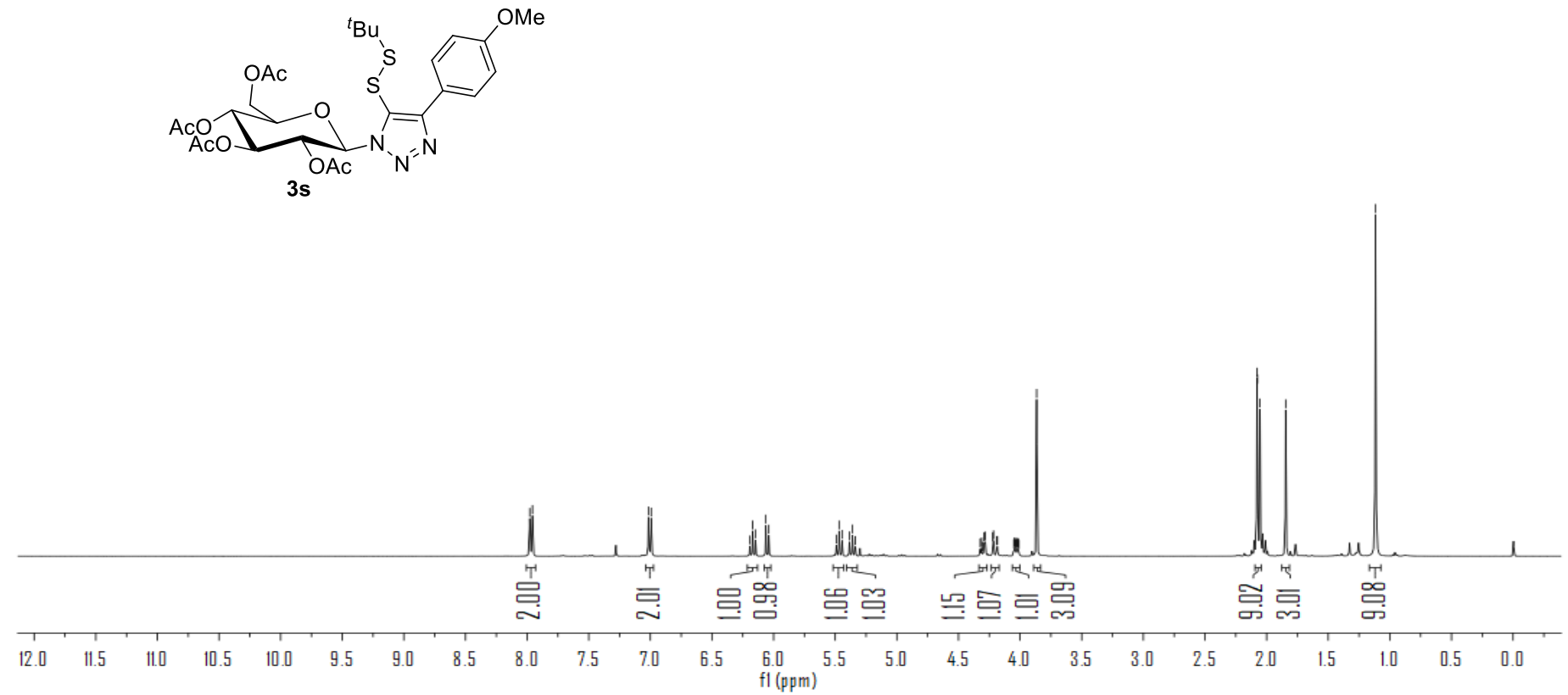
137.32
128.76
123.15
113.98
55.30
50.03
49.44
36.32
29.66
N
N
N
S
S
tBu
MeO
3q
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


129.25
128.95
128.76
126.99
126.88
123.15
N
N
N
S–S
tBu
MeO
3q
134.0 133.5 133.0 132.5 132.0 131.5 131.0 130.5 130.0 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5 125.0 124.5 124.0 123.5 123.0 122.5 122.0 121.5
f1 (ppm)


7.94
7.92
7.85
7.84
7.84
7.83
7.82
7.72
7.71
7.71
7.70
7.01
6.99
4.58
4.56
4.54
3.86
3.80
3.78
1.87
1.84
1.82
1.81
1.79
1.07
MeO
3r
2.00
2.19
2.10
2.10
2.13
3.08
2.16
2.12
2.28
9.38
f1 (ppm)


168.33
159.84
148.97
129.25
126.56
123.27
123.14
113.92
55.28
48.15
37.20
29.63
27.02
25.72
MeO
S
S
tBu
O
O
N
N
N
3r
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


148.97
133.97
132.06
129.25
126.56
123.27
123.14
113.92
55.28
49.39
48.15
MeO
3r
150
145
140
135
130
125
120
115
110
105
100
95
90
85
80
75
70
65
60
55
50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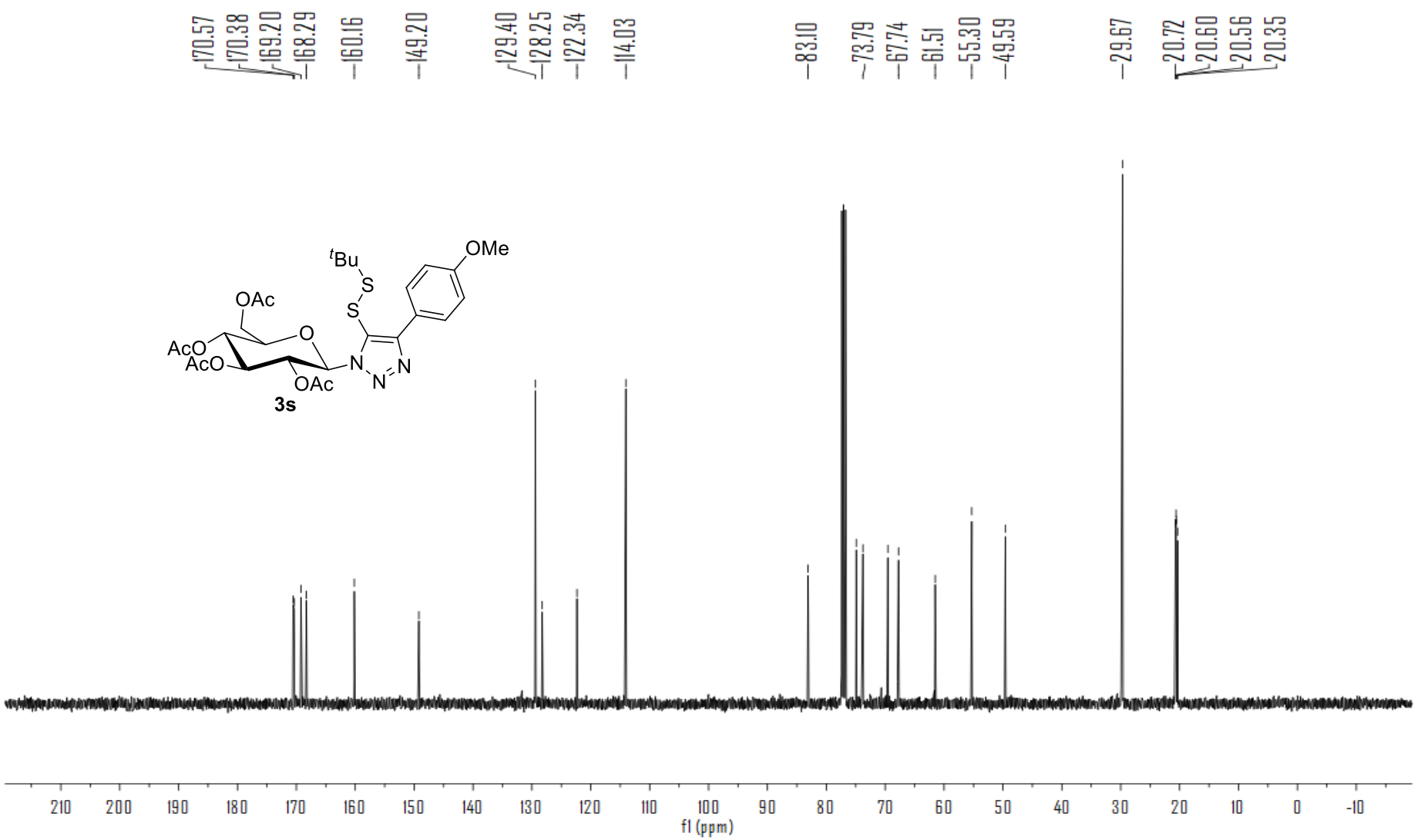
7.96
7.02
6.99
6.15
6.04
5.47
5.39
5.34
4.30
4.22
4.18
4.04
4.02
3.87
2.08
2.07
2.05
1.85
1.12
OMe
tBu
S
S
OAc
AcO
AcO
O
N
N
N
OAc
3s
2.00
2.01
1.00
0.98
1.06
1.03
1.15
1.07
1.01
3.09
9.02
3.01
9.08
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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170.38
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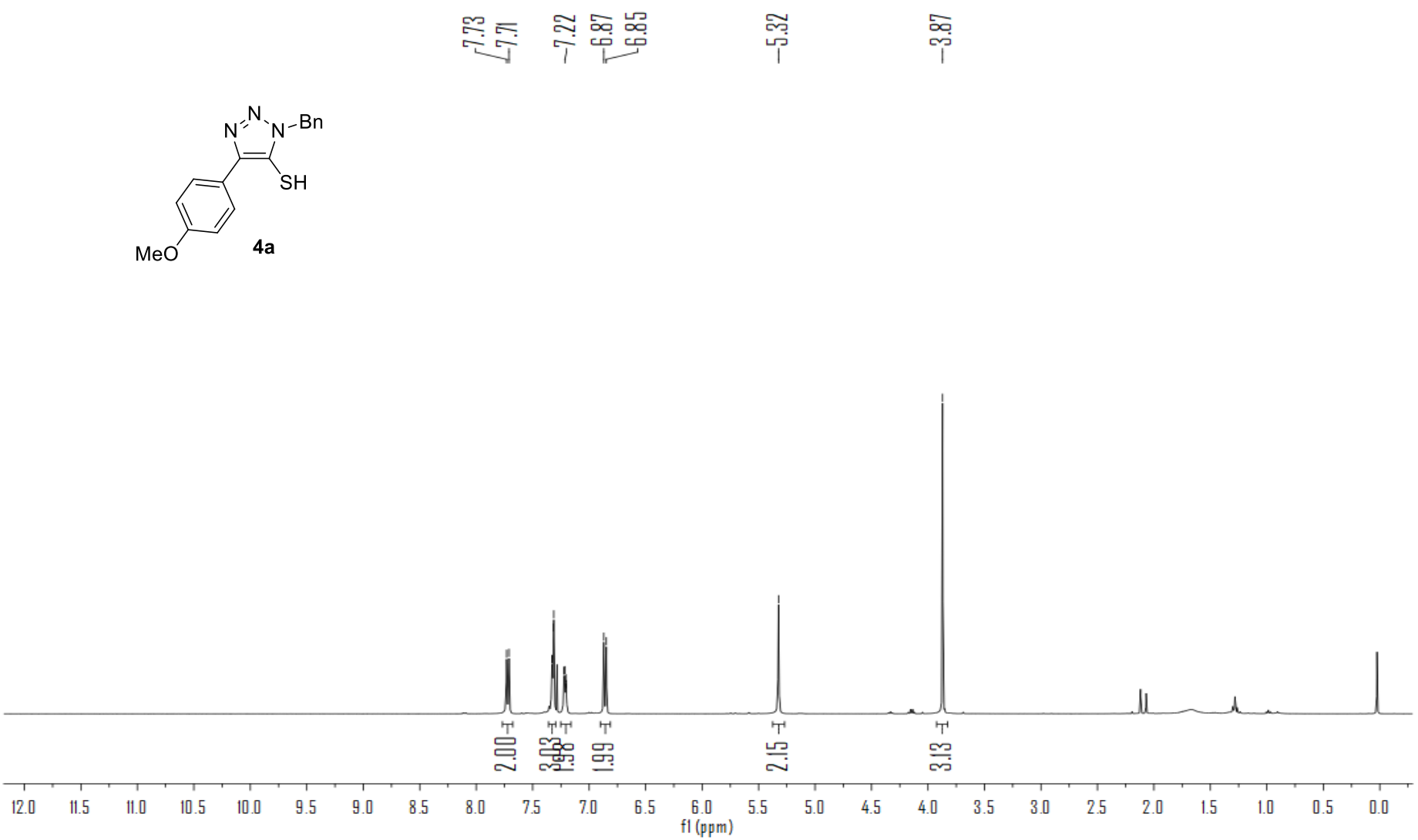
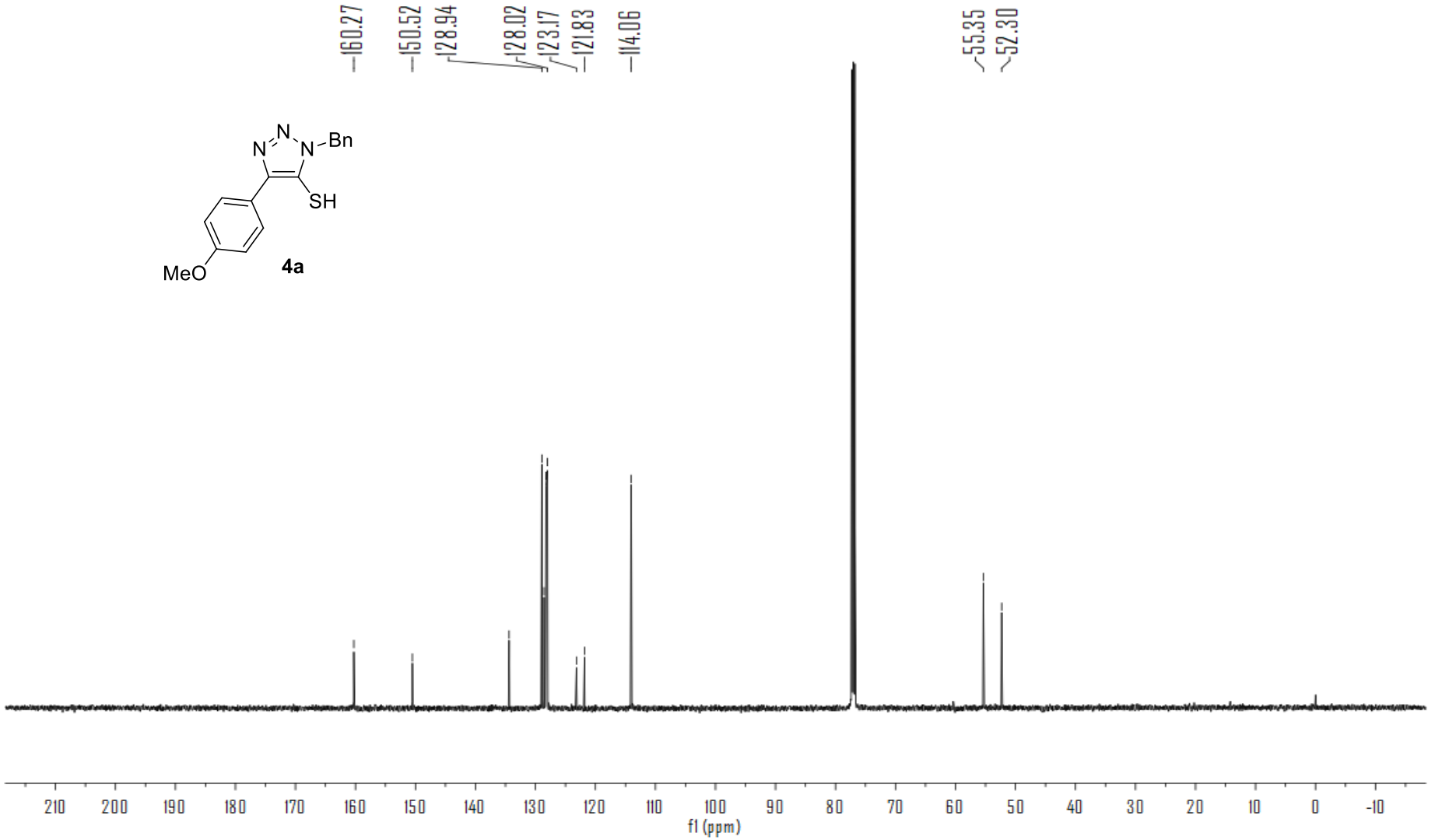
168.29
160.16
149.20
129.40
128.25
122.34
114.03
83.10
73.79
67.74
61.51
55.30
49.59
29.67
20.72
20.60
20.56
20.35
OMe
tBu
S
S
OAc
AcO
AcO
O
N
N
N
OAc
3s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.73
7.71
7.22
6.87
6.85
5.32
3.87
N
N
N
Bn
SH
MeO
4a
2.00
3.03
1.98
1.99
2.15
3.13
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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150.52
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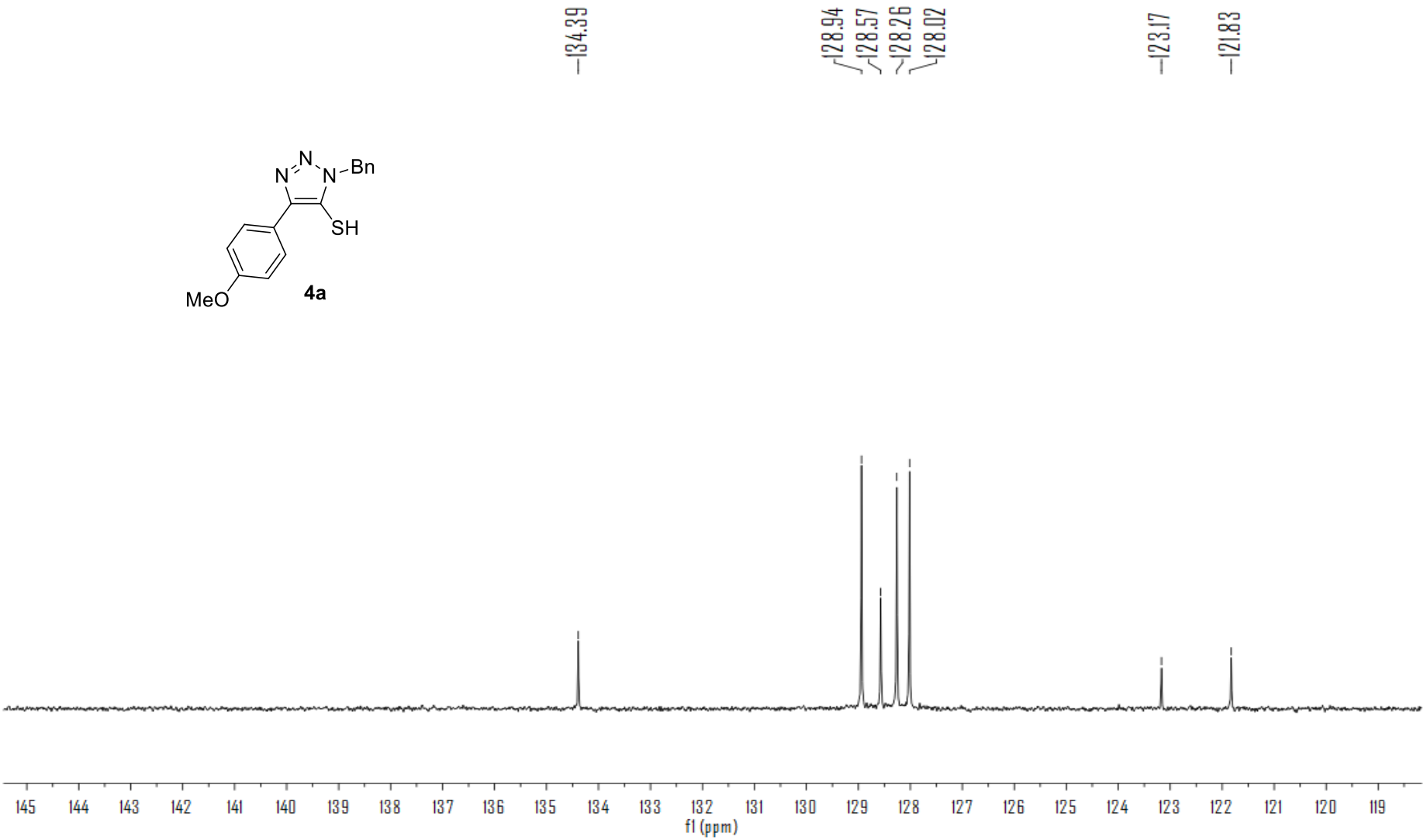
128.02
123.17
121.83
114.06
55.35
52.30
N
N
N
Bn
SH
MeO
4a
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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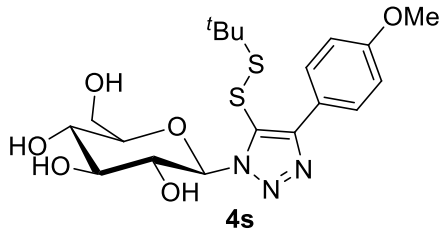
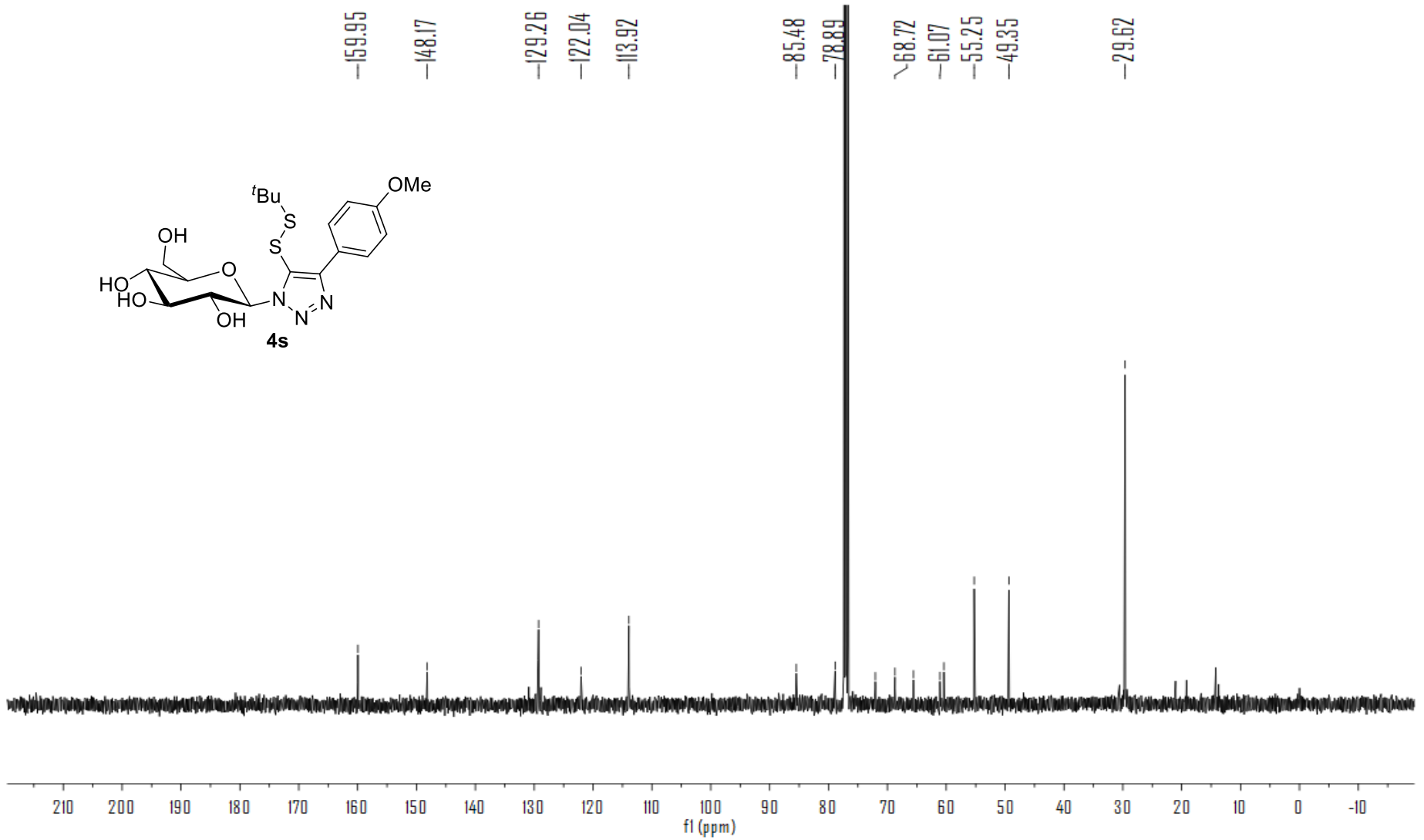
128.57
128.26
128.02
123.17
121.83
N
N
N
Bn
SH
MeO
4a
145 144 143 142 141 140 139 138 137 136 135 134 133 132 131 130 129 128 127 126 125 124 123 122 121 120 119
f1 (ppm)


tBu
S
S
OMe
OH
O
HO
HO
OH
N
N
N

4s

7.77
7.75
6.92
6.90
5.83
5.81
4.69
4.15
4.00
3.98
3.94
3.83
3.69
3.67
1.03
2.00
2.04
1.17
1.96
1.00
1.05
1.37
1.19
2.20
3.33
1.19
1.30
9.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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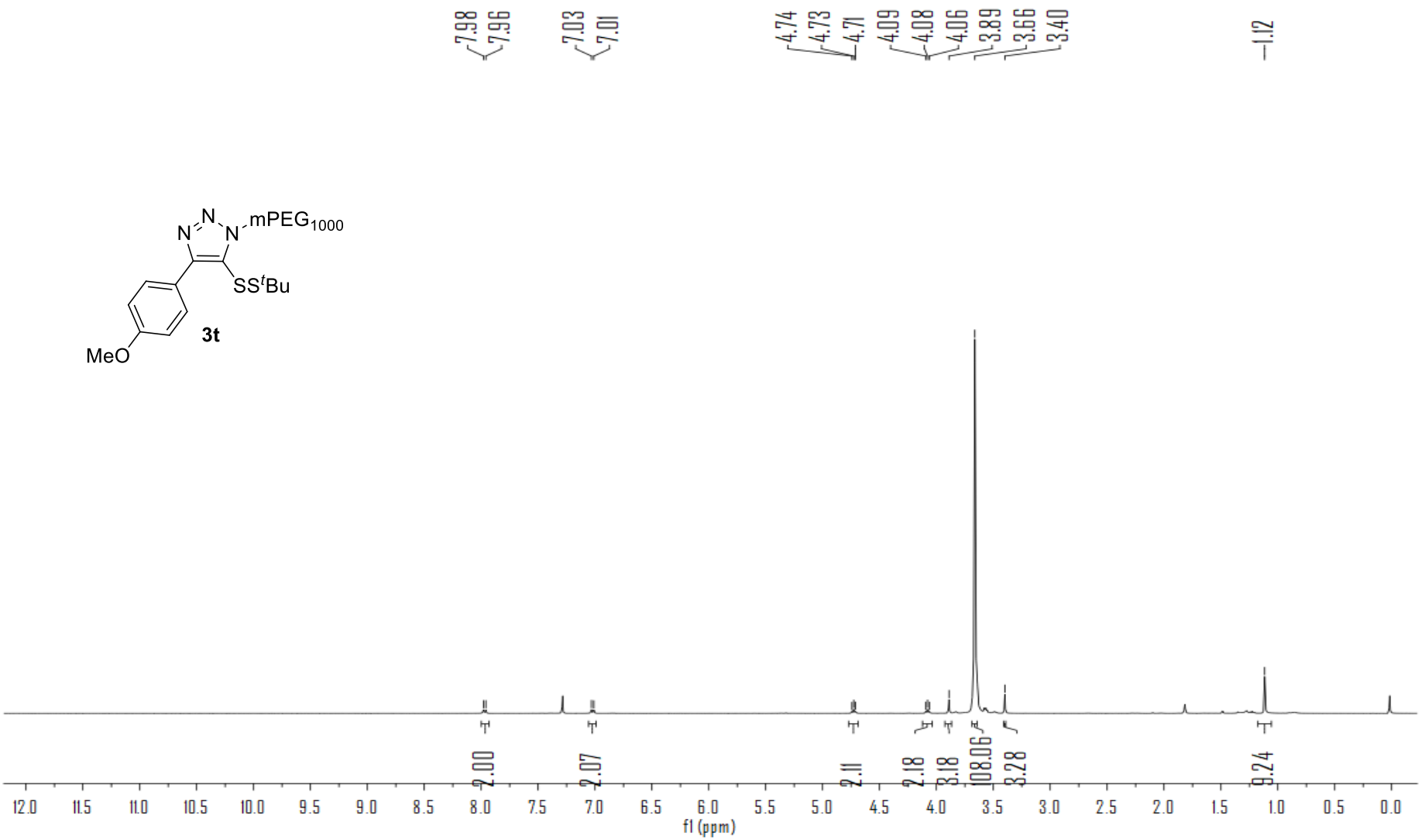
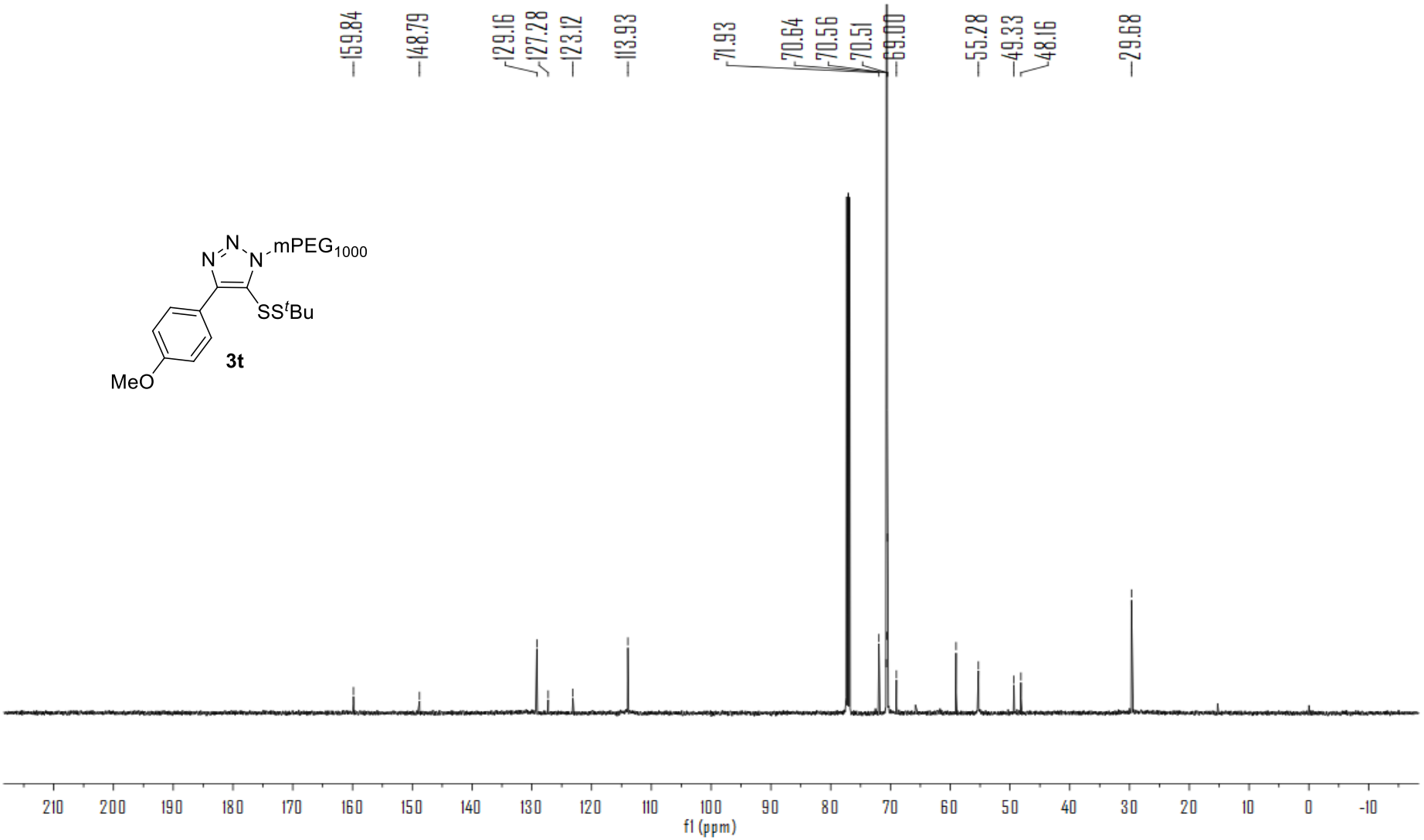
122.04
113.92
85.48
78.89
68.72
61.07
55.25
49.35
29.62
OMe
tBu
S
S
OH
O
HO
HO
OH
N
N
N
4s
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.98
7.96
7.03
7.01
4.74
4.73
4.71
4.09
4.08
4.06
3.89
3.66
3.40
1.12
mPEG1000
SStBu
MeO
3t
2.00
2.07
2.11
2.18
3.18
108.06
3.28
9.24
f1 (ppm)


159.84
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127.28
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113.93
71.93
70.64
70.56
70.51
69.00
55.28
49.33
48.16
29.68
mPEG1000
SStBu
MeO
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)