Palladium-Catalyzed Direct C3-Selective Arylation of N-Unsubstituted Indoles with Aryl Chlorides and Triflates

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Supporting Information

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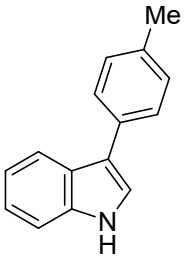
1. General method and materials

General. All reactions were performed under argon atmosphere. Reactions were monitored by TLC on Merck silica gel 60 F_{254} plates or Wako Pure Chemical Industry NH_2 silica gel 60 F_{254} plates and visualized by UV lump at 254 nm. Column chromatography was performed on Fuji Silysia Chromatorex NH-DM1020. Preparative TLC was performed on Merck silica gel 60 F_{254} 0.5 mm plates Wako Pure Chemical Industry NH_2 silica gel 60 F_{254} 0.5 mm plates. NMR spectra were measured on a JEOL AL-400 NMR spectrometer (400 MHz for ^{1}H spectra and 100 MHz for ^{13}C spectra), a JEOL ECA500 NMR spectrometer (500 MHz for ^{1}H spectra, 125 MHz for ^{13}C spectra, and 470 MHz for ^{19}F spectra) and a JEOL JNM-ECX500 NMR spectrometer (500 MHz for ^{1}H spectra and 125 MHz for ^{13}C spectra). For ^{1}H NMR, tetramethylsilane (TMS) ($\delta = 0$) in $CDCl_3$ served as an internal standard. For ^{13}C NMR, $CDCl_3$ ($\delta = 77.0$) served as an internal standard. For ^{19}F NMR spectroscopic analysis, $CFCl_3$ ($\delta = 0$) served as an external standard. Infrared spectra were measured on a SHIMADZU IR Prestige-21 spectrometer (ATR). High-resolution mass spectra (HRMS) were measured on a Bruker MicrOTOF time-of-flight mass spectrometer (ESI) and a JEOL JMS-T100TD time-of-flight mass spectrometer (DART). Preparative HPLC was performed on Japan Analytical Industry LC-9201 using JALGEL-1H, 2H columns (solvent: $CHCl_3$, flow rate: 3.5 mL/min, detection: 254 nm).

Materials. Ligands **1a**·HBF_4 and **1b** were prepared according to the reported procedure.[1] 7-(4-Methoxyphenyl)indole was prepared according to the reported procedure.[2] 4-Methylphenyl trifluoromethanesulfonate,[3] 4-methoxyphenyl trifluoromethanesulfonate,[4] 4-fluorophenyl trifluoromethanesulfonate,[5] benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate,[6] 5,6,7,8-tetrahydronaphthalen-1-yl trifluoromethanesulfonate,[6] and 2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate[7] were prepared from corresponding phenols using trifluoromethanesulfonyl anhydride and pyridine in dichloromethane.[8] 5-Chloro-1-methyl-1*H*-indole was prepared from 5-chloro-1*H*-indole according to the reported procedure.[9] Chlorpromazine **28** and (±)-chlorphenylamine **30** were prepared from corresponding commercially available HCl salt by extraction with dichloromethane and washing with saturated aqueous $NaHCO_3$. Other reagents and anhydrous solvents were purchased from commercial suppliers and used without further purification.

2. Experimental procedure and analytical data of the products

C3-selective arylation of N-nonsubstituted indole



3-(*p*-tolyl)-1*H*-indole (4)[10] (Table 1, entry 10)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Wako NH_2 silica gel, hexane/ethyl acetate = 5/1, twice) to give 3-(*p*-tolyl)-1*H*-indole **4** (83.6 mg, 81% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.92 (d, 2H, *J* = 7.8 Hz), 7.55 (d, 2H, *J* = 7.8 Hz), 7.33 (d, 1H, *J* = 7.8 Hz), 7.29-7.10 (m, 5H), 2.39 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 136.6, 135.6, 132.5, 129.4, 127.4, 125.7, 122.3, 121.5, 120.2, 119.8, 118.1, 111.4, 21.1

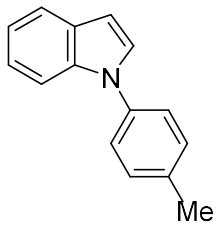
1-mmol scale reaction:

Toluene (1.0 mL) was added to $Pd(OAc)_2$ (2.4 mg, 0.02 mmol), **1a**·HBF_4 (21.8 mg, 0.04 mmol), *t*-BuOLi (240 mg, 3.0 mmol), and indole **2** (117 mg, 1.0 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (236 μL, 2.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (10 mL) at rt and extracted with diethyl ether (40 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Wako NH_2 silica gel, hexane/ethyl acetate = 5/1, twice) to give 3-(*p*-tolyl)-1*H*-indole **4** (168 mg, 81% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

Reaction using 4-bromotoluene: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-bromotoluene (123 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 5/1) to give 3-(*p*-tolyl)-1*H*-indole **4** (65.1 mg, 63% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

Reaction using 4-methylphenyl trifluoromethanesulfonate: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-methylphenyl trifluoromethanesulfonate[3] (240 mg, 1.0 mmol). The reaction

mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and preparative HPLC to give 3-(*p*-tolyl)-1*H*-indole **4** (77.2 mg, 75% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

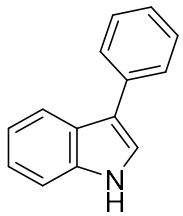


1-(*p*-tolyl)-1*H*-indole (5)[11] (Table 1, entry 5)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), Cy-JohnPhos (7.1 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.4 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 100/1, twice) to give 1-(*p*-tolyl)-1*H*-indole **5** (88.7 mg, 86% yield) as a pale-yellow oil. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.66 (d, 1H, *J* = 8.0 Hz), 7.51 (d, 1H, *J* = 8.0 Hz), 7.34 (d, 2H, *J* = 8.0 Hz), 7.29-7.22 (m, 3H), 7.22-7.10 (m, 2H), 6.64 (d, 1H, *J* = 3.0 Hz) , 2.38 (s, 3H)

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 137.3, 136.3, 136.0, 130.1, 129.2, 128.0, 124.3, 122.2, 121.1, 120.2, 110.5, 103.2, 20.9



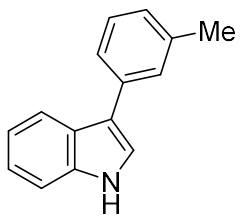
3-phenyl-1*H*-indole (7)[12]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added chlorobenzene (101 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 5/1) to give 3-phenyl-1*H*-indole **7** (74.1 mg, 77% yield) as a white solid. Spectral data matches that reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.94 (d, 2H, *J* = 7.5 Hz), 7.65 (d, 2H, *J* = 8.0 Hz), 7.54-7.37 (m, 2H), 7.36-7.25 (m, 2H),

7.25-7.07 (m, 3H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 136.6, 135.5, 128.7, 127.4, 125.9, 125.6, 122.3, 121.8, 120.3, 119.7, 118.1, 111.4

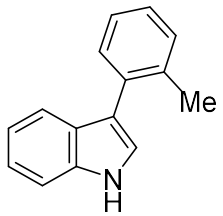


3-(*m*-tolyl)-1*H*-indole (8)[13]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.8 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 3-chlorotoluene (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) to give 3-(*m*-tolyl)-1*H*-indole **8** (80.8 mg, 78% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ =7.94 (d, 1H, *J* = 7.3 Hz), 7.90 (br s, 1H), 7.49-7.42 (m, 2H), 7.37-7.27 (m, 2H), 7.25-7.13 (m, 3H), 7.10 (d, 1H, *J* = 7.8 Hz), 2.40 (s, 3H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 138.3, 136.5, 135.4, 128.7, 128.1, 126.7, 125.7, 124.5, 122.3, 121.8, 120.2, 119.8, 118.2, 111.4, 21.5

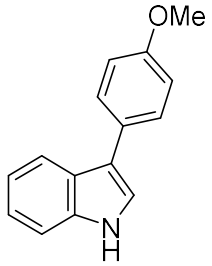


3-(*o*-tolyl)-1*H*-indole (9)[13a, 14]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 2-chlorotoluene (116 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 5/1) to give 3-(*o*-tolyl)-1*H*-indole **9** (84.8 mg, 82% yield) as a pale-yellow oil. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (br s, 1H), 7.52 (d, 1H, *J* = 7.8 Hz), 7.48-7.38 (m, 1H), 7.35 (d, 1H, *J* = 7.8 Hz), 7.33-7.29 (m, 1H), 7.29-7.18 (m, 3H), 7.12 (t, 1H, *J* = 7.8 Hz), 7.08 (d, 1H, *J* = 2.4 Hz), 2.30 (s, 3 H)

$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ = 136.8, 135.8, 134.4, 130.8, 130.3, 127.1, 126.7, 125.6, 122.8, 122.1, 120.0, 119.9, 117.3, 111.2, 20.7



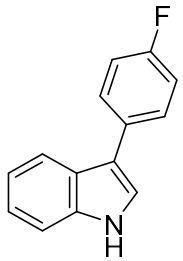
3-(4-methoxyphenyl)-1*H*-indole (10)[15]

Reaction using 4-chloroanisole: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chloroanisole (121 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/dichloromethane = 1/1) to give 3-(4-methoxyphenyl)-1*H*-indole **10** (81.4 mg, 73% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (br s, 1H), 7.90 (d, 1H, *J* = 7.8 Hz), 7.57 (d, 2H, *J* = 8.3 Hz), 7.34 (d, 1H, *J* = 8.3 Hz), 7.26-7.13 (m, 3H), 6.99 (d, 2H, *J* = 8.3 Hz), 3.83 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 158.0, 136.5, 128.6, 128.1, 125.8, 122.2, 121.2, 120.1, 119.7, 117.8, 114.2, 111.3, 55.3

Reaction using 4-methoxyphenyl trifluoromethanesulfonate: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.8 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-methoxyphenyl trifluoromethanesulfonate[4] (256 mg, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/dichloromethane = 1/1) to give 3-(4-methoxyphenyl)-1*H*-indole **10** (87.1 mg, 78% yield) as a pale-yellow solid. Spectral data matches that reported in the literature.



3-(4-fluorophenyl)-1*H*-indole (11)[16]

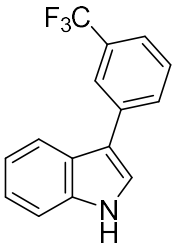
Reaction using 1-chloro-4-fluorobenzene: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.5 mg, 0.50 mmol) in a sealed tube under argon. To

this solution was added 1-chloro-4-fluorobenzene (106 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1, three times) to give 3-(4-fluorophenyl)-1*H*-indole **11** (37.1 mg, 35% yield) as a white solid. Spectral data matches that reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.15 (br s, 1H), 7.87 (d, 1H, *J* = 7.9 Hz), 7.69-7.54 (m, 2H), 7.41 (d, 1H, *J* = 8.5 Hz), 7.32-7.17 (m, 3H), 7.13 (t, 2H, *J* = 8.8 Hz)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 161.5 (d, $^1J_{CF}$ = 224.5 Hz), 136.5, 131.5 (d, $^4J_{CF}$ = 2.5 Hz), 128.9 (d, $^3J_{CF}$ = 8.0 Hz), 125.7, 122.5, 121.6, 120.4, 119.5, 117.4, 115.6 (d, $^2J_{CF}$ = 21.5 Hz), 111.4

Reaction using 4-fluorophenyl trifluoromethanesulfonate[5]: Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.5 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-fluorophenyl trifluoromethanesulfonate[5] (244 mg, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and preparative HPLC to give 3-(4-fluorophenyl)-1*H*-indole **11** (60.7 mg, 51% yield) as a white solid. Spectral data matches that reported in the literature.

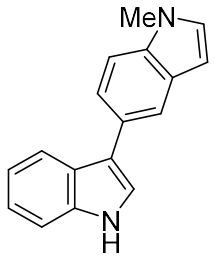


3-(3-(trifluoromethyl)phenyl)-1*H*-indole (12)[17]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.9 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 3-chlorobenzotrifluoride (81 μL, 0.60 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 3/1) and preparative HPLC to give 3-(3-(trifluoromethyl)phenyl)-1*H*-indole **12** (64.2 mg, 49% yield) as a white solid. Spectral data matches that reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.19 (br s, 1H), 7.92-7.88 (m, 2H), 7.84-4.80 (m, 1H), 7.54-7.50 (m, 2H), 7.41 (d , 1H, *J* = 8.0 Hz), 7.35 (d, 1H, *J* = 2.9 Hz), 7.27 (t, 1H, *J* = 7.7 Hz), 7.22 (t, 1H, *J* = 7.8 Hz)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 136.6, 136.4, 131.1 (q, $^2J_{CF}$ = 32.5 Hz), 130.5, 129.2, 125.4, 124.4 (q, $^1J_{CF}$ = 270.0 Hz), 123.9 (q, $^3J_{CF}$ = 3.8 Hz), 122.8, 122.5 (q, $^3J_{CF}$ = 3.8 Hz), 122.3, 120.7, 119.4, 117.0, 111.6



1'-methyl-1*H*,1'*H*-3,5'-biindole (14)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (11.0 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (70.6 mg, 0.60 mmol) in a sealed tube under argon. To this solution was added 5-chloro-1-methyl-1*H*-indole[9] (87.0 mg, 0.50 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1, then 1/1) and preparative HPLC to give 1'-methyl-1*H*,1'*H*-3,5'-biindole **14** (107.1 mg, 87% yield) as a pale-brown solid.

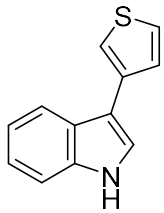
Mp 163-164 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (d, 2H, *J* = 7.4 Hz), 7.90 (s, 1H), 7.53 (dd, 1H, *J* = 1.1, 8.5 Hz), 7.39-7.33 (m, 2H), 7.25 (d, 1H, *J* = 2.3 Hz), 7.22 (d, 1H, *J* = 7.9 Hz), 7.20-7.13 (m, 1H), 7.04 (d, 1H, *J* = 2.8 Hz), 6.52 (d, 1H, *J* = 2.8 Hz), 3.77 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 136.6, 135.6, 129.2, 129.0, 126.6, 126.2, 122.2, 122.1, 121.2, 119.9, 119.6, 119.4, 111.3, 109.4, 100.9, 32.8

IR (ATR) 3416, 1485, 1452, 1412, 1333, 1236, 1092, 889, 804, 752 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{17}H_{15}N_2$ ([M+H]$^+$) 247.1230; found: 247.1240

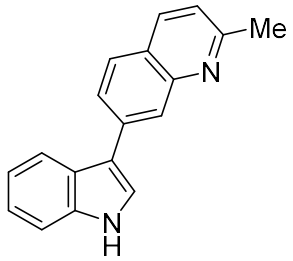


3-(thiophen-3-yl)-1*H*-indole (15)[18]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **1a**·HBF_4 (21.8 mg, 0.04 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (35.1 mg, 0.6 mmol) in a sealed tube under argon. To this solution was added 3-chlorothiophene (30.0 mg, 0.5 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 3/1) and preparative HPLC to give 3-(thiophen-3-yl)-1*H*-indole **15** (17.4 mg, 35% yield) as a white solid. Spectral data matches that reported in the literature.

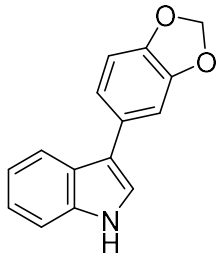
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (br s, 1H), 7.92 (d, 1H, *J* = 7.9 Hz), 7.47-7.43 (m, 1H), 7.43-7.38 (m, 3H), 7.36 (d, 1H, *J* = 2.8 Hz), 7.28-7.23 (m, 1H), 7.23-7.17 (m, 1H)

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ =136.4, 135.8, 127.2, 125.8, 125.5, 122.5, 121.7, 120.3, 119.8, 118.6, 113.5, 111.3
IR (ATR) 2883, 1207, 1103, 821, 738 cm^{-1}



7-(1*H*-indol-3-yl)-2-methylquinoline (16)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **1a**·HBF_4 (21.8 mg, 0.04 mmol), *t*-BuOLi (120 mg, 1.5 mmol), indole **2** (88.0 mg, 0.75 mmol), and 7-chloro-2-methylquinoline (89.2 mg, 0.5 mmol) in a sealed tube under argon. The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 48 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 1/1, twice) and preparative HPLC to give 7-(1*H*-indol-3-yl)-2-methylquinoline **16** (38.2 mg, 30% yield) as a yellow solid.
Mp 172-175 ºC
^1H NMR (500 MHz, $CDCl_3$) δ = 8.70 (br s, 1H), 8.36 (s, 1H), 8.13 (d, 1H, *J* = 8.0 Hz), 8.05 (d, 1H, *J* = 8.6 Hz), 7.89-7.78 (m, 2H), 7.54 (d, 1H, *J* = 2.3 Hz), 7.45 (d, 1H, *J* = 8.0 Hz), 7.30-7.18 (m, 3H), 2.77 (s, 3H)
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ = 159.2, 148.4, 137.1, 136.8, 136.1, 127.7, 126.0, 125.3, 125.1, 124.9, 122.9, 122.7, 121.4, 121.1, 120.5, 117.6, 111.4, 25.4
IR (ATR) 1614, 1537, 1452, 1263, 1146, 866, 731 cm^{-1}
HRMS (ESI) *m/z* calcd. for $C_{18}H_{15}N_2$ ($[M+H]^+$) 259.1230; found: 259.1241

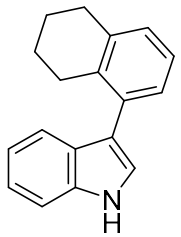


3-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-indole (17)[19]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.5 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added benzo[*d*][1,3]dioxol-5-yl trifluoromethanesulfonate[6] (270 mg, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1, twice) and preparative HPLC to give 3-(benzo[*d*][1,3]dioxol-5-yl)-1*H*-indole **17** (60.5 mg, 51% yield) as a white solid. Spectral data matches that reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.14 (br s, 1H), 7.88 (d, 1H, *J* = 8.0 Hz), 7.39 (d, 1H, *J* = 8.0 Hz), 7.29-7.21 (m, 2H), 7.18 (t, 1H, *J* = 7.5 Hz), 7.15-7.08 (m, 2H), 6.90 (d, 1H, *J* = 7.5 Hz), 5.98 (s, 2H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 147.9, 145.9, 136.5, 129.5, 125.7, 122.4, 121.4, 120.7, 120.2, 119.6, 118.1, 111.4, 108.7, 108.2, 100.9



3-(5,6,7,8-tetrahydronaphthalen-1-yl)-1*H*-indole (18)

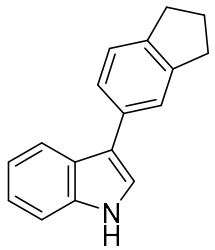
Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.5 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 5,6,7,8-tetrahydronaphthalen-1-yl trifluoromethanesulfonate[6] (280 mg, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and preparative HPLC to give 3-(5,6,7,8-tetrahydronaphthalen-1-yl)-1*H*-indole **18** (118.0 mg, 95% yield) as a colorless oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.91 (br s, 1H), 7.49 (d, 1H, *J* = 8.0 Hz), 7.32 (d, 1H, *J* = 8.0 Hz), 7.24-7.19 (m, 2H), 7.19-7.14 (m, 1H), 7.13-7.07 (m, 2H), 7.02 (d, 1H, *J* = 2.3 Hz), 2.86 (t, 2H, *J* = 6.3 Hz), 2.65 (t, 2H, *J* = 6.3 Hz), 1.82-1.74 (m, 2H), 1.70-1.62 (m, 2H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 137.5, 136.4, 135.7, 134.4, 128.3, 128.0, 127.2, 125.1, 122.8, 122.0, 120.1, 119.7, 117.2, 111.2, 30.0, 28.0, 23.4, 23.0

IR (ATR) 3418, 2959, 1609, 1545, 1454, 1256, 1086, 806, 739 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{18}H_{18}N$ ($[M+H]^+$) 248.1434; found: 248.1439



3-(2,3-dihydro-1*H*-inden-5-yl)-1*H*-indole (19)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and indole **2** (58.5 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 2,3-dihydro-1*H*-inden-5-yl trifluoromethanesulfonate[7] (266 mg, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by

preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and preparative HPLC to give 3-(2,3-dihydro-1*H*-inden-5-yl)-1*H*-indole **19** (72.7 mg, 62% yield) as a white solid.

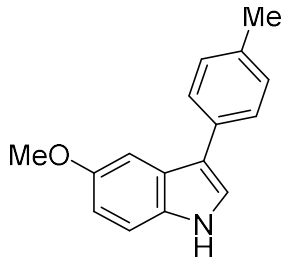
Mp 130-131 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.93 (d, 1H, *J* = 8.0 Hz), 7.86 (br s, 1H), 7.50 (s, 1H), 7.43 (d, 1H, *J* = 8.0 Hz), 7.34-7.22 (m, 2H), 7.22-7.09 (m, 3H), 3.02-2.85 (m, 4H), 2.09 (quint, 2H, *J* = 7.3 Hz)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 144.8, 142.0, 136.5, 133.3, 125.7, 125.5, 124.6, 123.5, 122.2, 121.6, 120.0, 119.8, 118.4, 111.3, 32.9, 32.6, 25.5

IR (ATR) 2832, 1582, 1454, 1329, 1238, 1090, 1009, 812, 739 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{17}H_{16}N$ ([M+H]$^+$) 234.1277; found: 234.1282

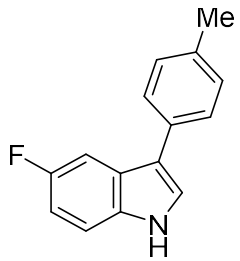


5-methoxy-3-(*p*-tolyl)-1*H*-indole (20)[20]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 5-methoxyindole (73.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 20/1) to give 5-methoxy-3-(*p*-tolyl)-1*H*-indole **20** (98.0 mg, 83% yield) as a white solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.99 (br s, 1H), 7.52 (d, 2H, *J* = 7.9 Hz), 7.36 (d, 1H, *J* = 1.7 Hz), 7.25 (d, 2H, *J* = 7.9 Hz), 7.23-7.15 (m, 2H), 6.89 (dd, 1H, *J* = 8.8 Hz, 2.0 Hz), 3.83 (s, 3H), 2.39 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 154.5, 135.5, 132.7, 131.7, 129.5, 127.2, 126.1, 122.4, 117.9, 112.5, 112.1, 101.5, 55.9, 21.1



5-fluoro-3-(*p*-tolyl)-1*H*-indole (21)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 5-fluoroindole (67.3 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene

3 (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 40/1) to give 5-fluoro-3-(*p*-tolyl)-1*H*-indole **21** (60.1 mg, 53% yield) as a pale-yellow solid.

Mp 85-86 ºC

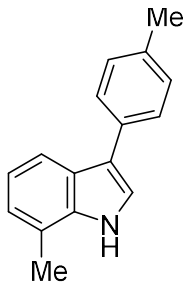
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.11 (br s, 1H), 7.56 (dd, 1H, *J* = 10.0 Hz, 2.2 Hz), 7.50 (d, 2H, *J* = 7.8 Hz), 7.33-7.24 (m, 4H), 6.98 (td, 1H, *J* = 9.0 Hz, 2.4 Hz), 2.39 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 158.3 (d, $^1J_{CF}$ = 235.3 Hz), 135.8, 133.1, 132.0, 129.5, 127.1, 126.1 (d, $^3J_{CF}$ = 9.6 Hz), 123.2, 118.4 (d, $^4J_{CF}$ = 4.8 Hz), 111.9 (d, $^3J_{CF}$ = 9.6 Hz), 110.7 (d, $^2J_{CF}$ = 26.3 Hz), 104.8 (d, $^2J_{CF}$ = 24.0 Hz), 21.1

^{19}F NMR (470 MHz, $CDCl_3$) δ = -123.8 (m)

IR (ATR) 1580, 1543, 1476, 1169, 1113, 922, 851, 810, 791 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{15}H_{11}FN$ ([M-H]$^-$) 224.0870; found: 224.0872

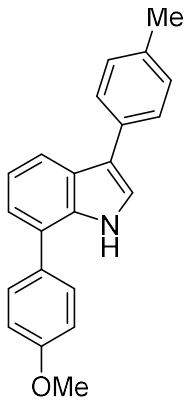


7-methyl-3-(*p*-tolyl)-1*H*-indole (22)[21]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 7-methylindole (65.5 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 40/1 to 5/1) to give 7-methyl-3-(*p*-tolyl)-1*H*-indole **22** (88.0 mg, 80% yield) as a white solid. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 (br s, 1H), 7.78 (d, 1H, *J* = 8.3 Hz), 7.56 (d, 2H, *J* = 8.3 Hz), 7.40-7.20 (m, 3H), 7.16-7.07 (m, 1H), 7.07-6.97 (m, 1H), 2.46 (s, 3H), 2.39 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 136.1, 135.5, 132.7, 129.4, 127.4, 125.3, 122.8, 121.2, 120.44, 120.37, 118.6, 117.6, 21.1, 16.5



7-(4-methoxyphenyl)-3-(*p*-tolyl)-1*H*-indole (23)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 7-(4-methoxyphenyl)indole[2] (73.6 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 10/1 to 5/1) to give 7-(4-methoxyphenyl)-3-(*p*-tolyl)-1*H*-indole **23** (78.7 mg, 50% yield) as a white solid.

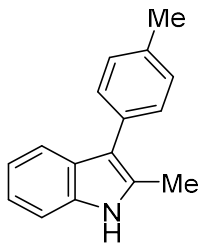
Mp 180-182 ºC

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.40 (br s, 1H), 7.89 (d, 1H, *J* = 7.3 Hz), 7.64-7.51 (m, 4H), 7.31 (d, 1H, *J* = 2.4 Hz), 7.30-7.20 (m, 4H), 7.04 (d, 2H, *J* = 8.3 Hz), 3.87 (s, 3H), 2.41 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 159.1, 135.6, 134.6, 132.6, 131.4, 129.5, 129.3, 127.5, 126.1, 125.6, 122.1, 121.7, 120.7, 118.72, 118.65, 114.6, 55.4, 21.2

IR (ATR) 3433, 1608, 1242, 1177, 1107, 1026, 829, 795, 752, 552 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{22}H_{20}NO$ ([M+H]$^+$) 314.1539; found: 314.1538

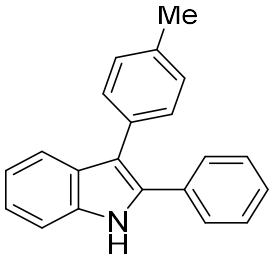


2-methyl-3-(*p*-tolyl)-1*H*-indole (24)[22]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 2-methylindole (65.3 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and column chromatography (NH silica, hexane/ethyl acetate = 20/1) to give 2-methyl-3-(*p*-tolyl)-1*H*-indole **24** (39.0 mg, 35% yield) as a pale-yellow oil. Spectral data matches that reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.86 (br s, 1H), 7.65 (d, 1H, *J* = 7.8 Hz), 7.41 (d, 2H, *J* = 8.3 Hz), 7.34-7.23 (m, 3H), 7.19-7.01 (m, 2H), 2.47 (s, 3H), 2.41 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 135.3, 135.2, 132.4, 131.2, 129.3, 129.2, 127.9, 121.4, 119.8, 118.8, 114.3, 110.3, 21.2, 12.4

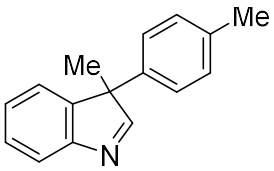


2-phenyl-3-(*p*-tolyl)-1*H*-indole (25)[23]

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (120 mg, 1.5 mmol), and 2-phenylindole (96.4 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, hexane/ethyl acetate = 5/1) and preparative HPLC to give 2-phenyl-3-(*p*-tolyl)-1*H*-indole 2**5** (50.6 mg, 36% yield) as a pale-green solid. Spectral data matches that reported in the literature.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.14 (br s, 1H), 7.67 (d, 1H, *J* = 8.0 Hz), 7.46-7.35 (m, 3H), 7.35-7.20 (m, 6H), 7.18 (d, 2H, *J* = 7.4 Hz), 7.13 (t, 1H, *J* = 7.8 Hz, 2.38 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 135.9, 135.8, 133.8, 132.8, 132.0, 130.0, 129.1, 128.9, 128.6, 128.1, 127.6, 122.6, 120.3, 119.8, 115.0, 110.9, 21.4



3-methyl-3-(*p*-tolyl)-3*H*-indole (27)

Toluene (0.5 mL) was added to $Pd(OAc)_2$ (4.5 mg, 0.02 mmol), **1a**·HBF_4 (21.8 mg, 0.04 mmol), *t*-BuOLi (140 mg, 1.75 mmol), and 3-methylindole (65.8 mg, 0.50 mmol) in a sealed tube under argon. To this solution was added 4-chlorotoluene **3** (118 μL, 1.0 mmol). The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated to give crude mixture. The crude mixture including **27** was dissolved in dichloromethane (13 mL) and methanol solution (3 mL) of $NaBH_3CN$ (314 mg, 5.0 mmol) was added. After 30 min of stirring at rt, silica gel (3.29 g) was added and stirred for 30 min. The resulting suspension was filtered, and solvent was removed in vaduo. To the residue was added water (5 mL) and extracted with dichloromethane (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated. The residue was purified by preparative TLC (Merck

SiO_2, hexane/ethyl acetate =20/1, twice) to give 58.5 mg (52% yield) of 3-methyl-3-(*p*-tolyl)-indoline (**S1**) as a pale yellow solid. Spectral data matches that reported in the literature.[24]

^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.42-7.20 (m, 3H), 7.17-7.06 (m, 3H), 6.96 (d, 1H, *J* = 7.5 Hz), 6.70-9.78 (m, 2H), 3.69 (d, 2H, *J* = 8.6 Hz), 3.54 (d, 1H, *J* = 9.2 Hz), 2.31 (s, 3H), 1.69 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 150.7, 144.7, 137.2, 135.7, 128.9, 127.6, 126.5, 124.0, 119.0, 109.9, 63.8, 49.4, 26.2, 20.9

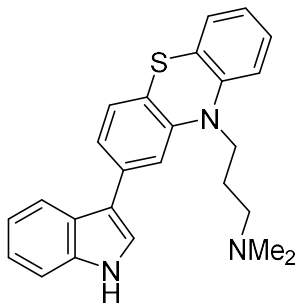
3-Methyl-3-(*p*-tolyl)-3*H*-indole (**27**) was unstable and garadually decomposed during purification. When **27** was purified by preparative TLC (Merck SiO_2, hexane/dichloromethane = 5/1) and isolated without reducing with $NaBH_3CN$, 34.7 mg (31% yield) of **27** was obtained as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.10 (s, 1H), 7.68 (d, 1H, *J* = 7.5 Hz), 7.43-7.32 (m, 1H), 7.25 (d, 2H, *J* = 4.6 Hz), 7.16-6.98 (m, 4H), 2.30 (s, 3H) , 1.71 (s, 3H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 178.4, 154.7, 145.0, 137.1, 134.9, 129.5, 127.9, 126.6, 126.0, 122.5, 121.4, 61.0, 20.9, 20.1

IR (ATR) 2920, 1600, 1508, 1454, 1377, 1161, 1018, 814, 745 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{16}H_{16}N$ ([M+H]$^+$) 222.1277; found: 222.1288



3-(2-(1*H*-indol-3-yl)-10*H*-phenothiazin-10-yl)-*N,N*-dimethylpropan-1-amine (29)

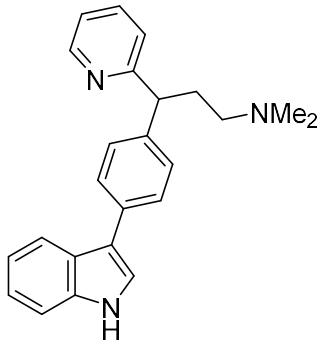
To a sealed tube containing $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.9 mg, 0.02 mmol), *t*-BuOLi (60.3 mg, 0.75 mmol), and indole **2** (29.2 mg, 0.25 mmol) under argon, toluene solution (0.5 mL) of chlorpromazine **28** (79.7 mg, 0.25 mmol) was added. The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 20 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, ethyl acetate/triethylamine = 9/1) to give 3-(2-(1*H*-indol-3-yl)-10*H*-phenothiazin-10-yl)-*N,N*-dimethylpropan-1-amine 2**9** (64.6 mg, 65% yield) as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.59 (br s, 1H), 7.87 (d, 1H, *J* = 8.0 Hz), 7.41 (d, 1H, *J* = 8.0 Hz), 7.29 (d, 1H, *J* = 2.3 Hz), 7.27-7.23 (m, 1H), 7.23-7.06 (m, 6H), 6.96-6.87 (m, 2H), 3.97 (t, 2H, *J* = 6.9 Hz), 2.47 (t, 2H, *J* = 7.2 Hz), 2.22 (s, 6H), 2.07-1.99 (m, 2H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 145.6, 145.3, 136.6, 134.9, 127.6, 127.5, 127.2, 125.6, 125.4, 122.5, 122.42, 122.37, 121.9, 121.8, 120.3, 119.6, 117.9, 115.6, 114.8, 111.5, 57.1, 45.4, 29.7, 25.1

IR (ATR) 1585, 1462, 1408, 1236, 845, 738 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{25}H_{26}N_3S$ ([M+H]$^+$) 400.1842; found: 400.1850



(±)-3-(4-(1*H*-indol-3-yl)phenyl)-*N,N*-dimethyl-3-(pyridin-2-yl)propan-1-amine (31)

To a sealed tube containing $Pd(OAc)_2$ (2.2 mg, 0.01 mmol), **1a**·HBF_4 (10.8 mg, 0.02 mmol), *t*-BuOLi (60.5 mg, 0.75 mmol), and indole **2** (29.3 mg, 0.25 mmol) under argon, toluene solution (0.5 mL) of (±)-chlorphenylamine **30** (68.7 mg, 0.25 mmol) was added. The reaction mixture was stirred at rt for 1 h, and then at 110 ºC for 48 h. The resulting suspension was quenched with brine (5 mL) at rt and extracted with diethyl ether (20 mL × 3). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated, and then the residue was purified by preparative TLC (Merck SiO_2, dichloromethane/methanol = 10/1) to (±)-3-(4-(1*H*-indol-3-yl)phenyl)-*N,N*-dimethyl-3-(pyridin-2-yl)propan-1-amine **31** (47.3 mg, 53% yield) as a brown oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.91 (br s, 1H), 8.58 (d, 1H, *J* = 4.0 Hz), 7.91 (d, 1H, *J* = 8.0 Hz), 7.61-7.53 (m, 3H), 7.41 (d, 1H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.6 Hz), 7.29 (d, 1H, *J* = 1.7 Hz), 7.24-7.18 (m, 2H), 7.18-7.13 (m, 1H), 7.10 (dd, 1H, *J* = 4.9, 6.6 Hz), 4.17 (t, 1H, *J* = 7.2 Hz), 2.59-2.47 (m, 1H), 2.47-2.34 (m, 3H), 2.31 (s, 6H)

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ = 163.3, 149.2, 140.6, 136.7, 136.6, 134.0, 128.3, 127.5, 125.7, 122.9, 122.2, 122.0, 121.4, 120.1, 119.8, 117.7, 111.5, 57.6, 50.9, 44.9, 32.1

IR (ATR) 1545, 1456, 1431, 1013, 960, 808, 738 cm^{-1}

HRMS (ESI) *m/z* calcd. for $C_{24}H_{26}N_3$ ($[M+H]^+$) 356.2121; found: 356.2131

3. References

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4. NMR spectra of the products

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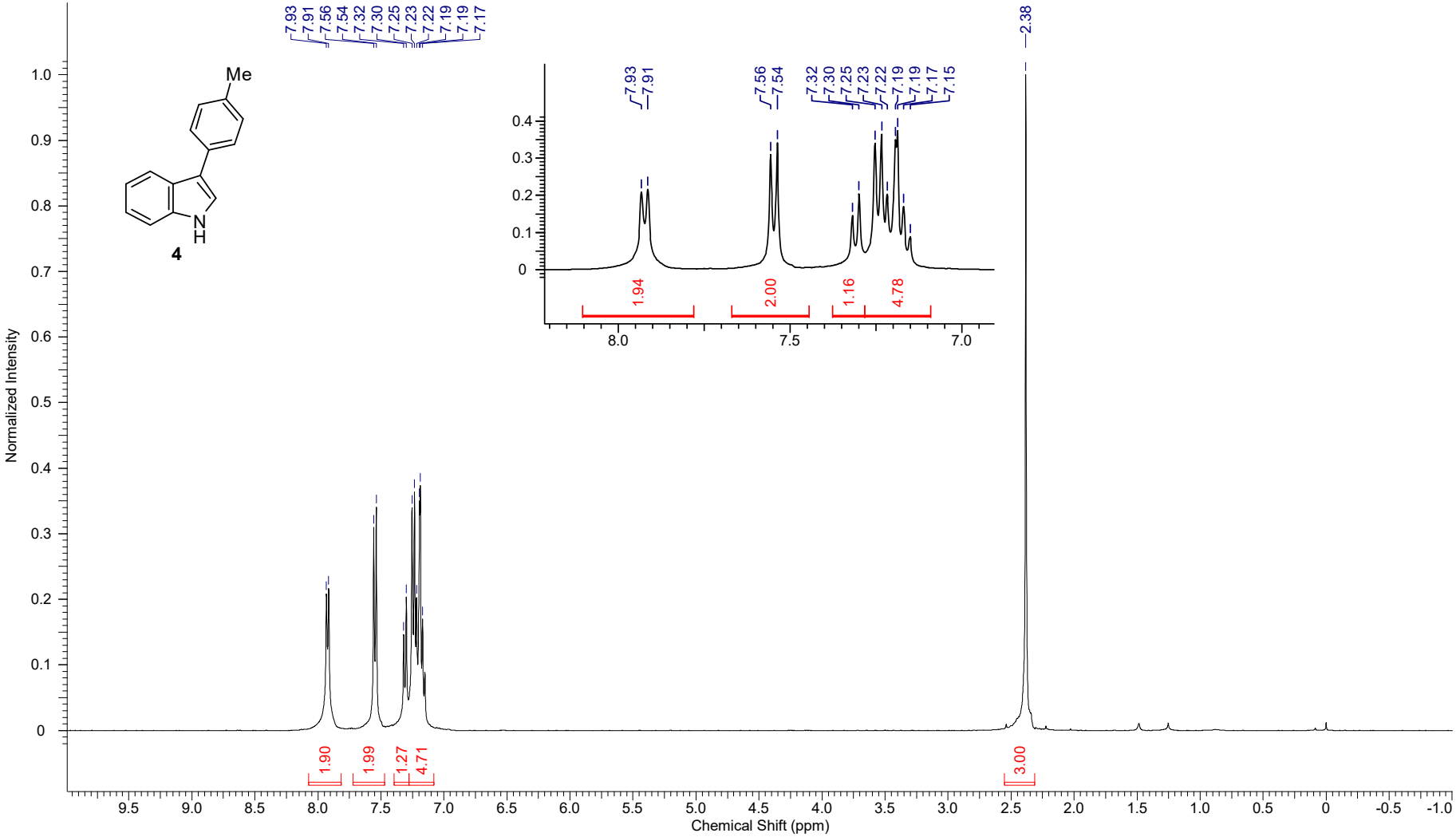

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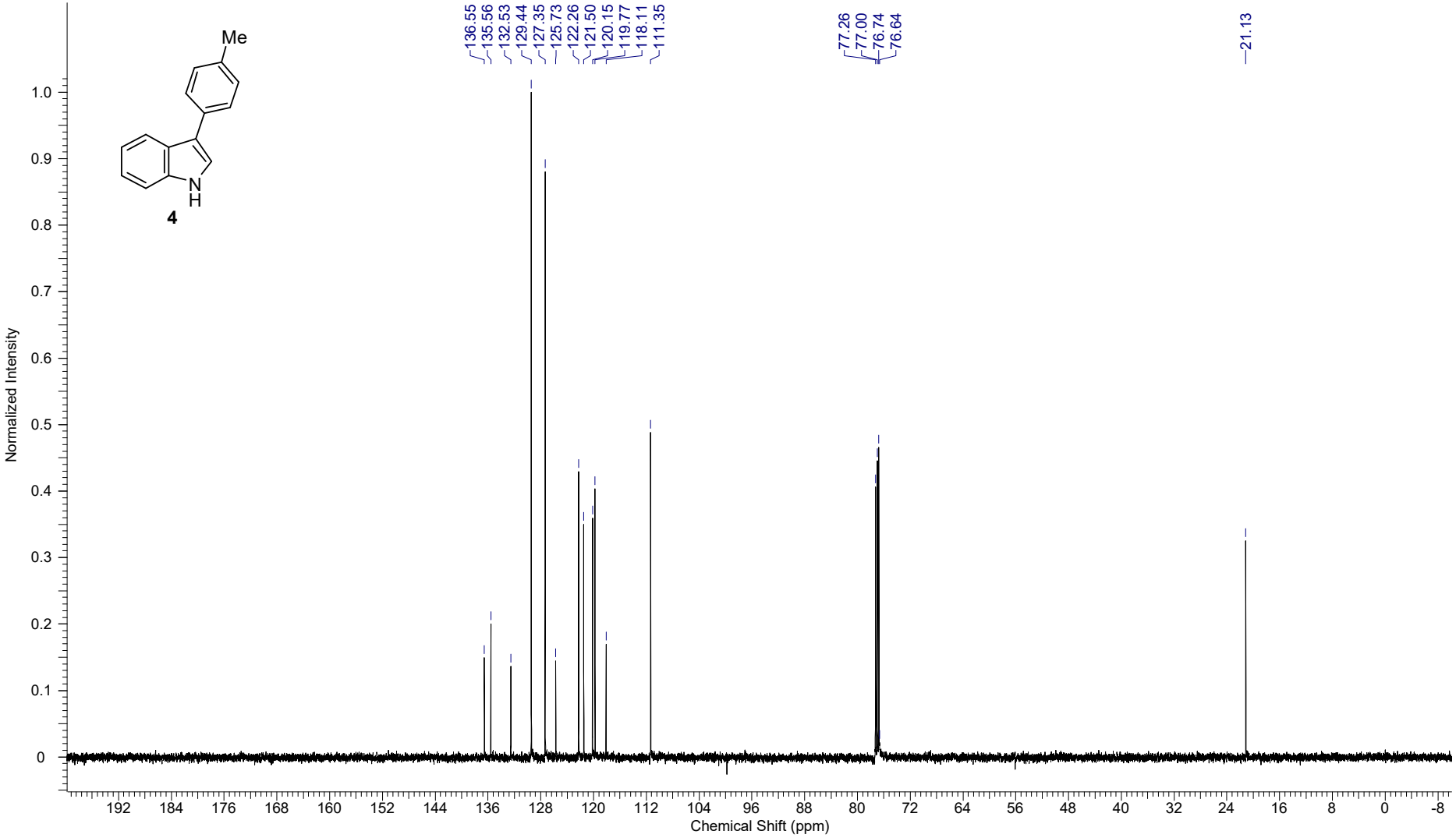

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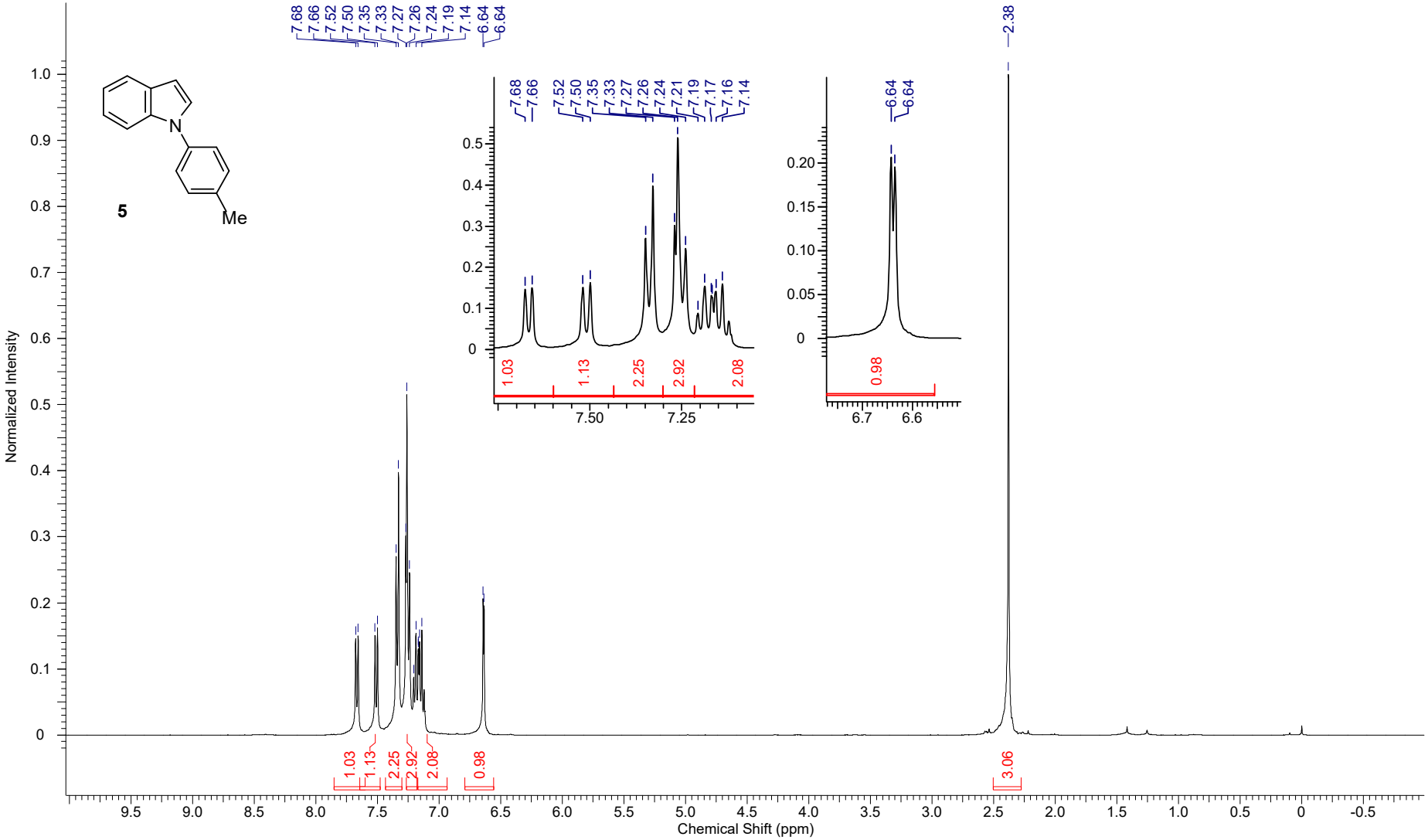

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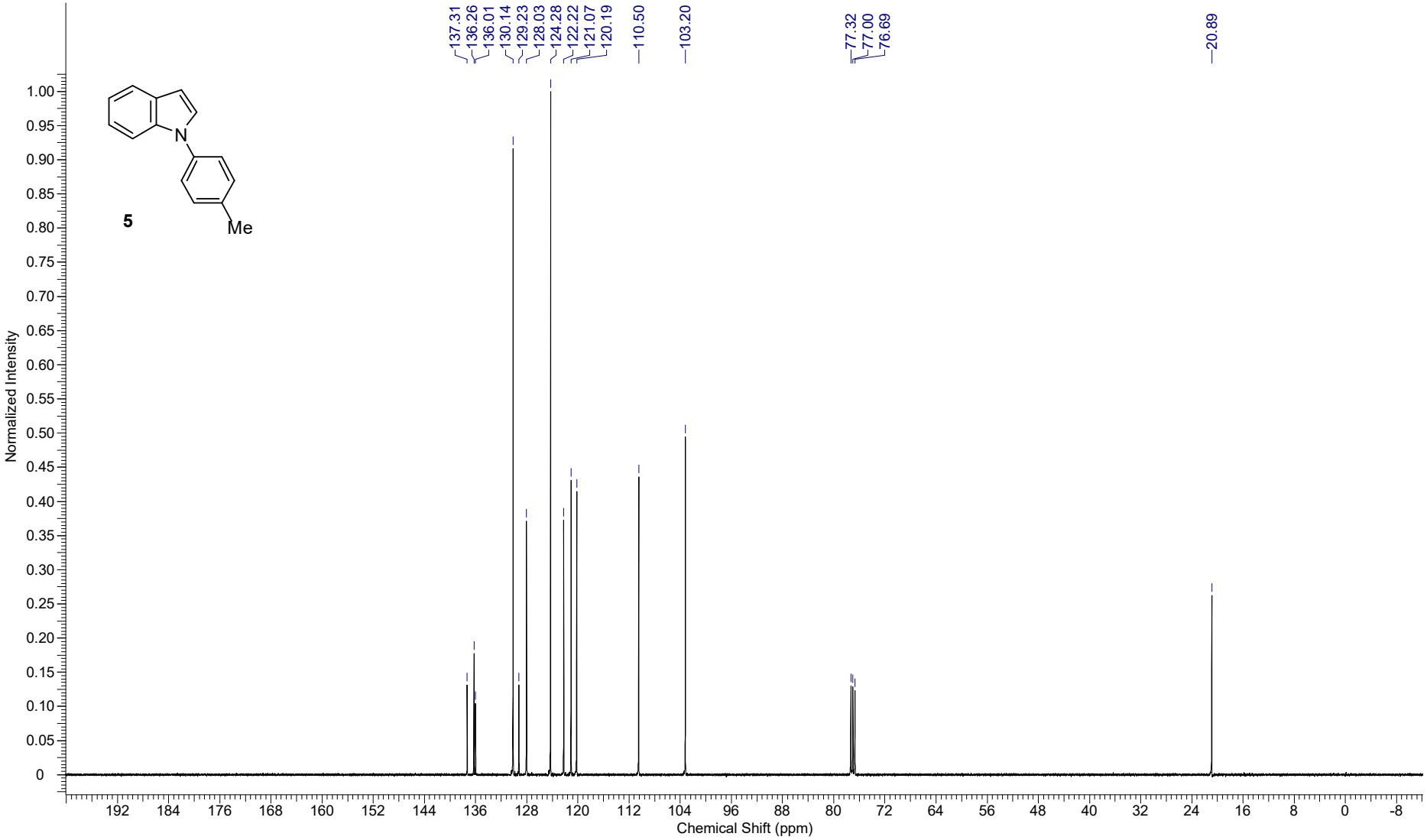

Acquisition Time (sec)	1.7459	*Comment*	YS 143 column 2			*Date*	07 Mar 2017 08:29:55
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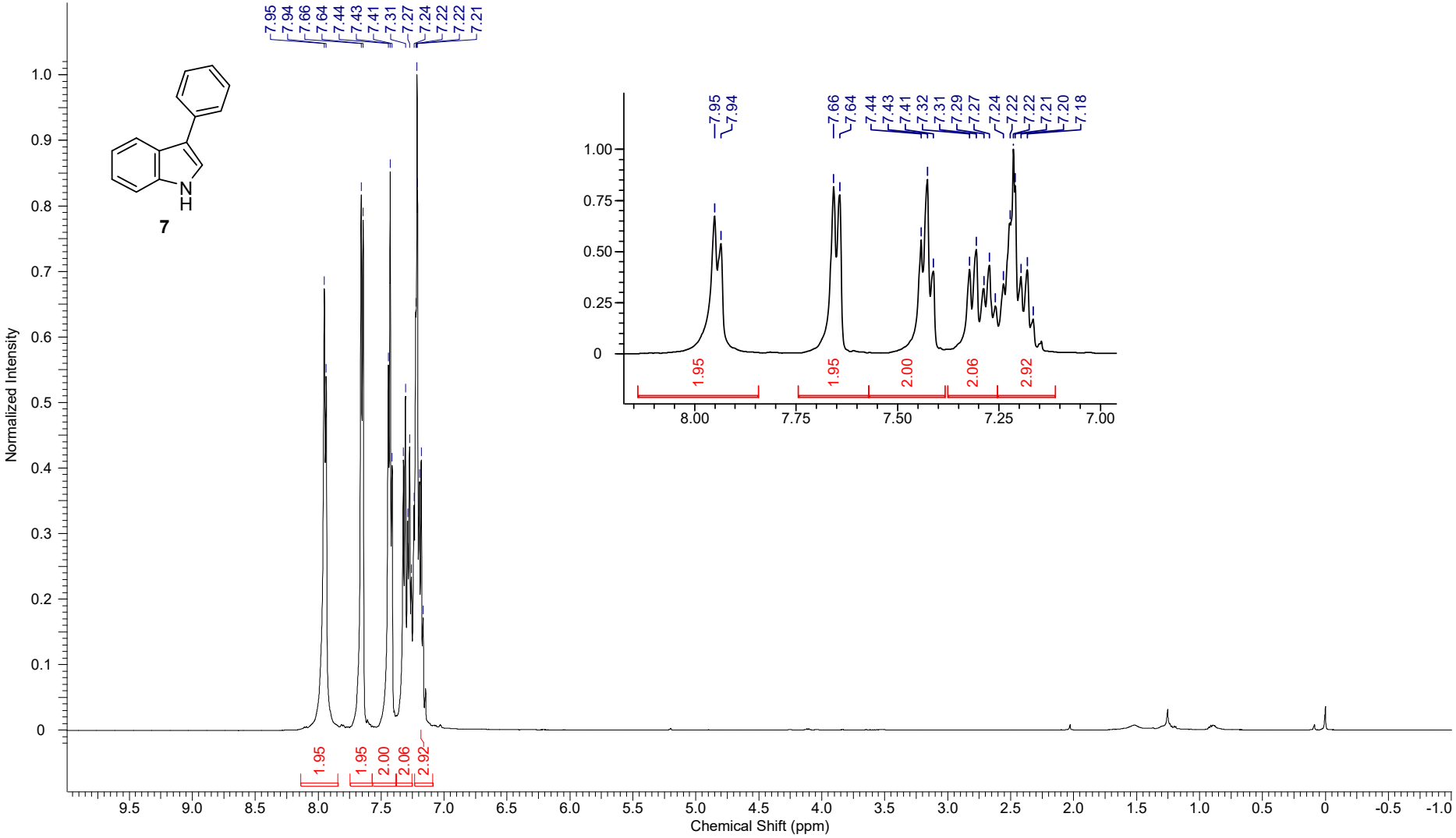

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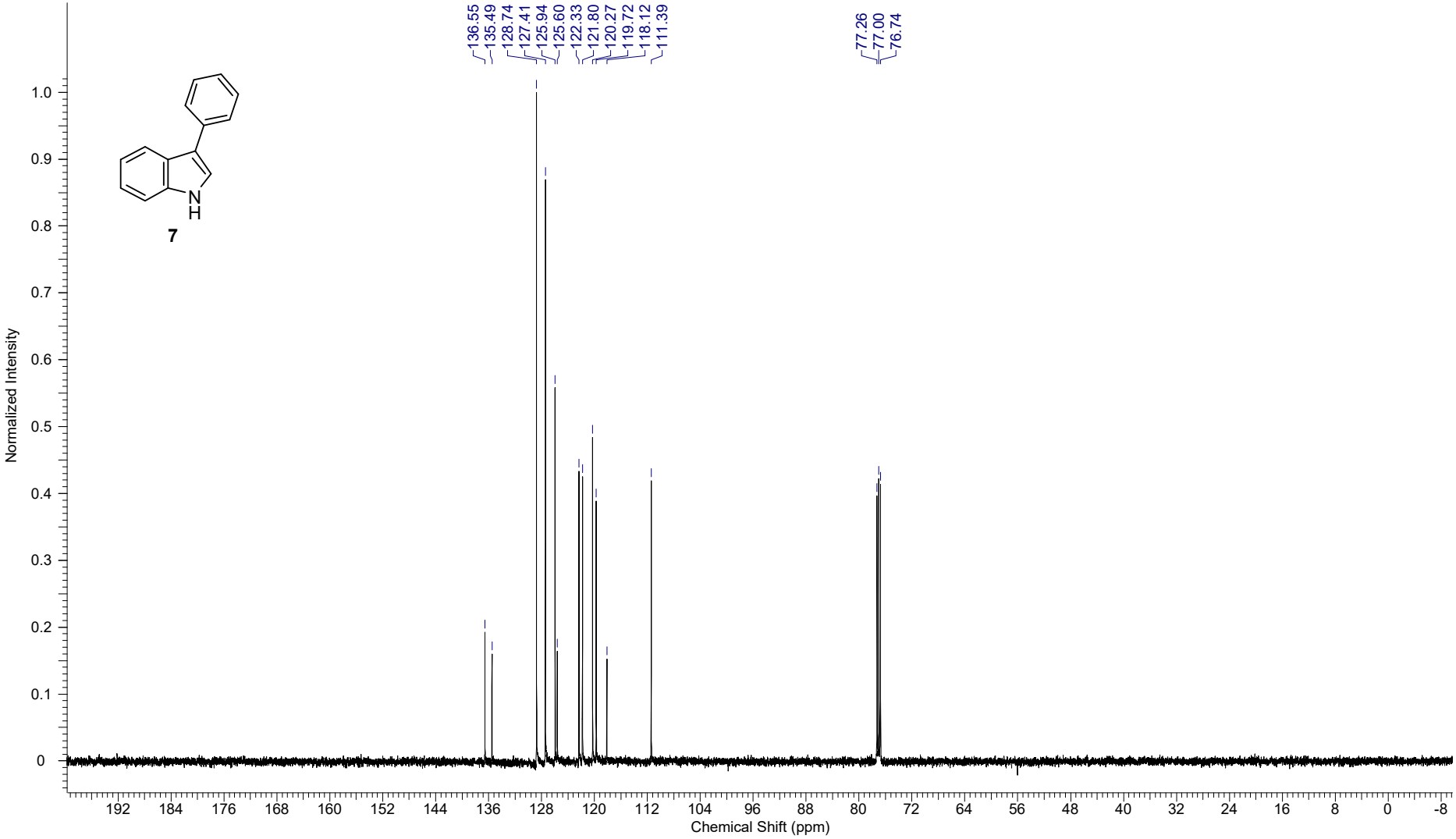
Temperature (degree C)	22.000						



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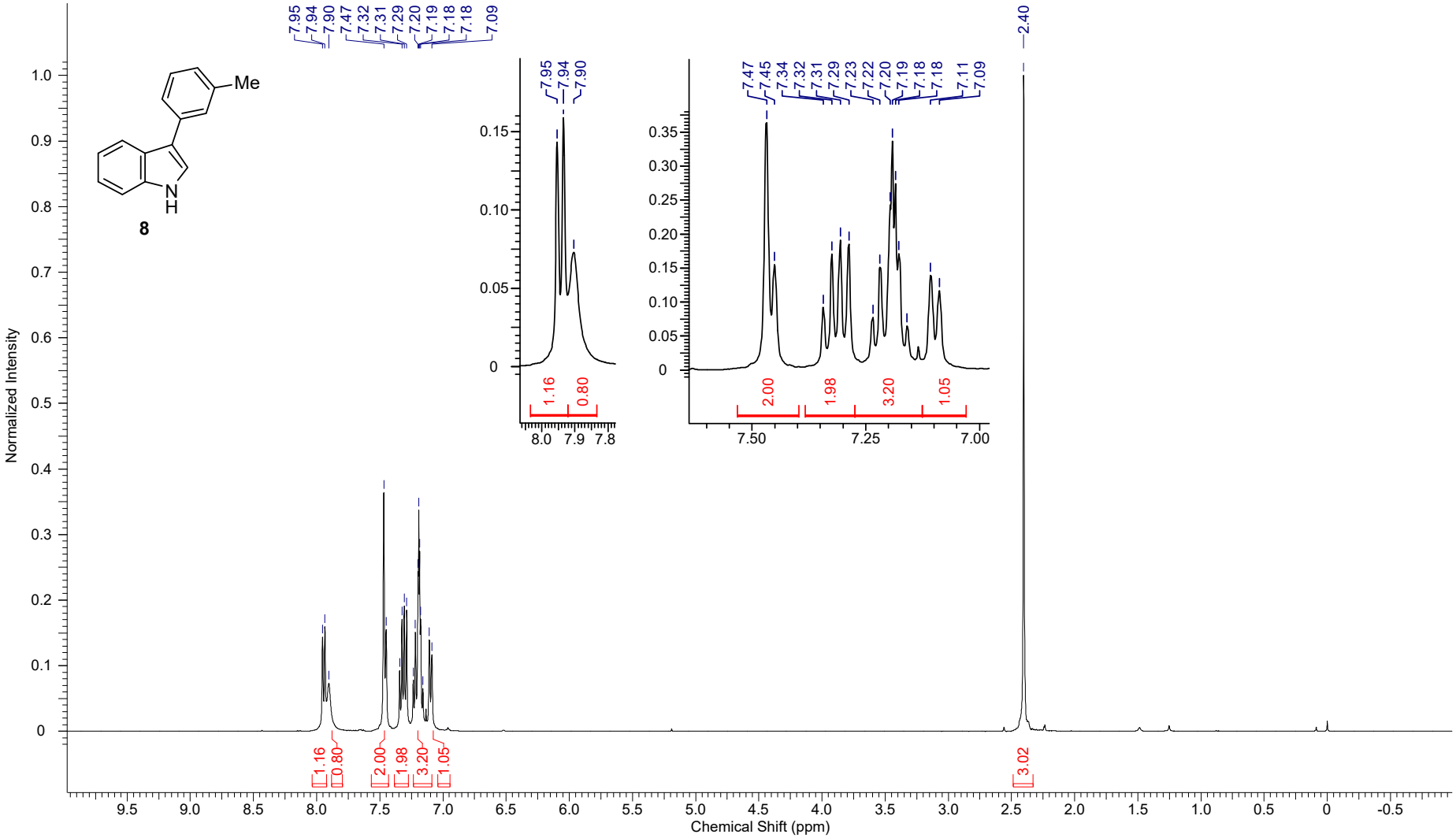

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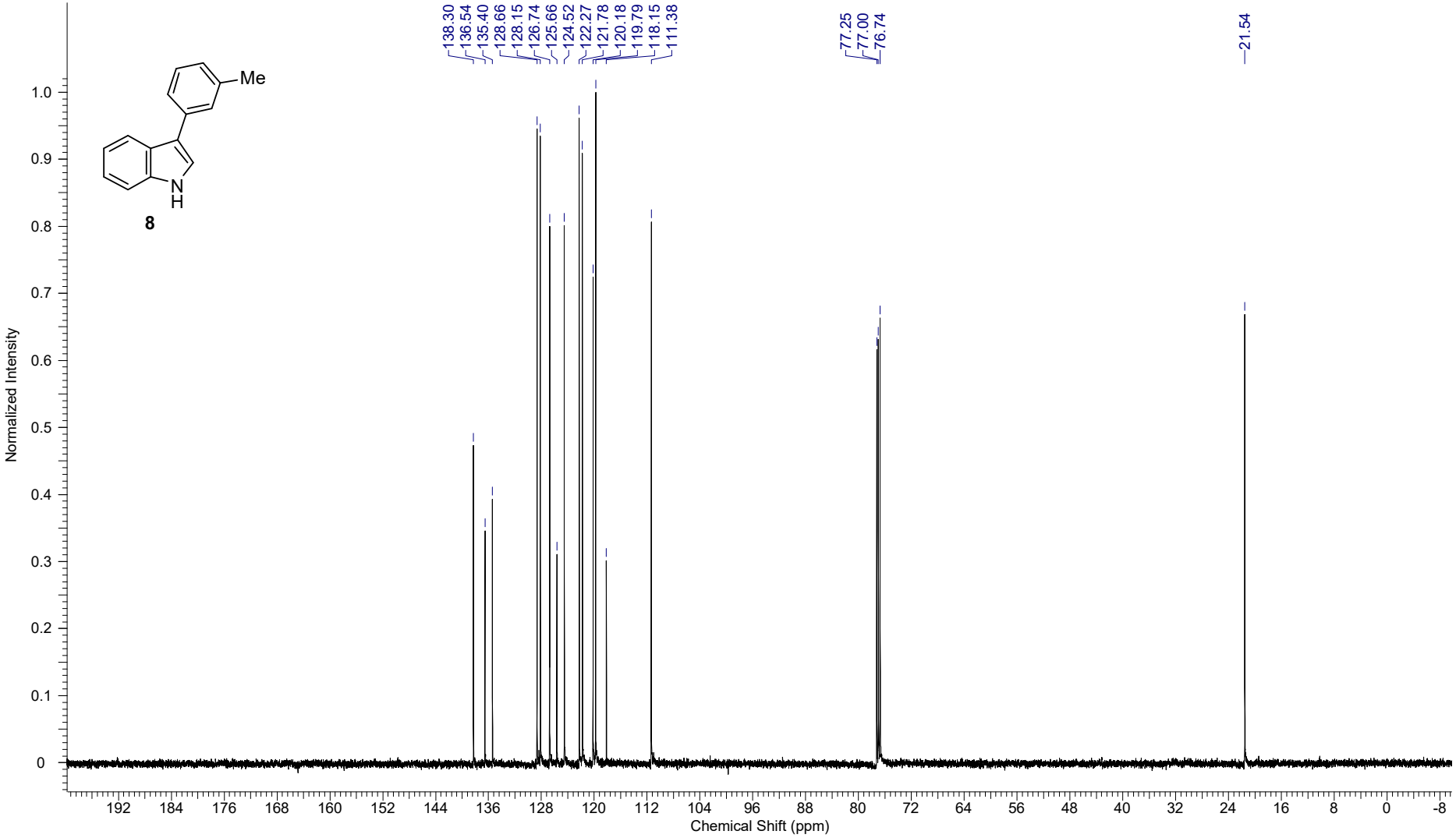

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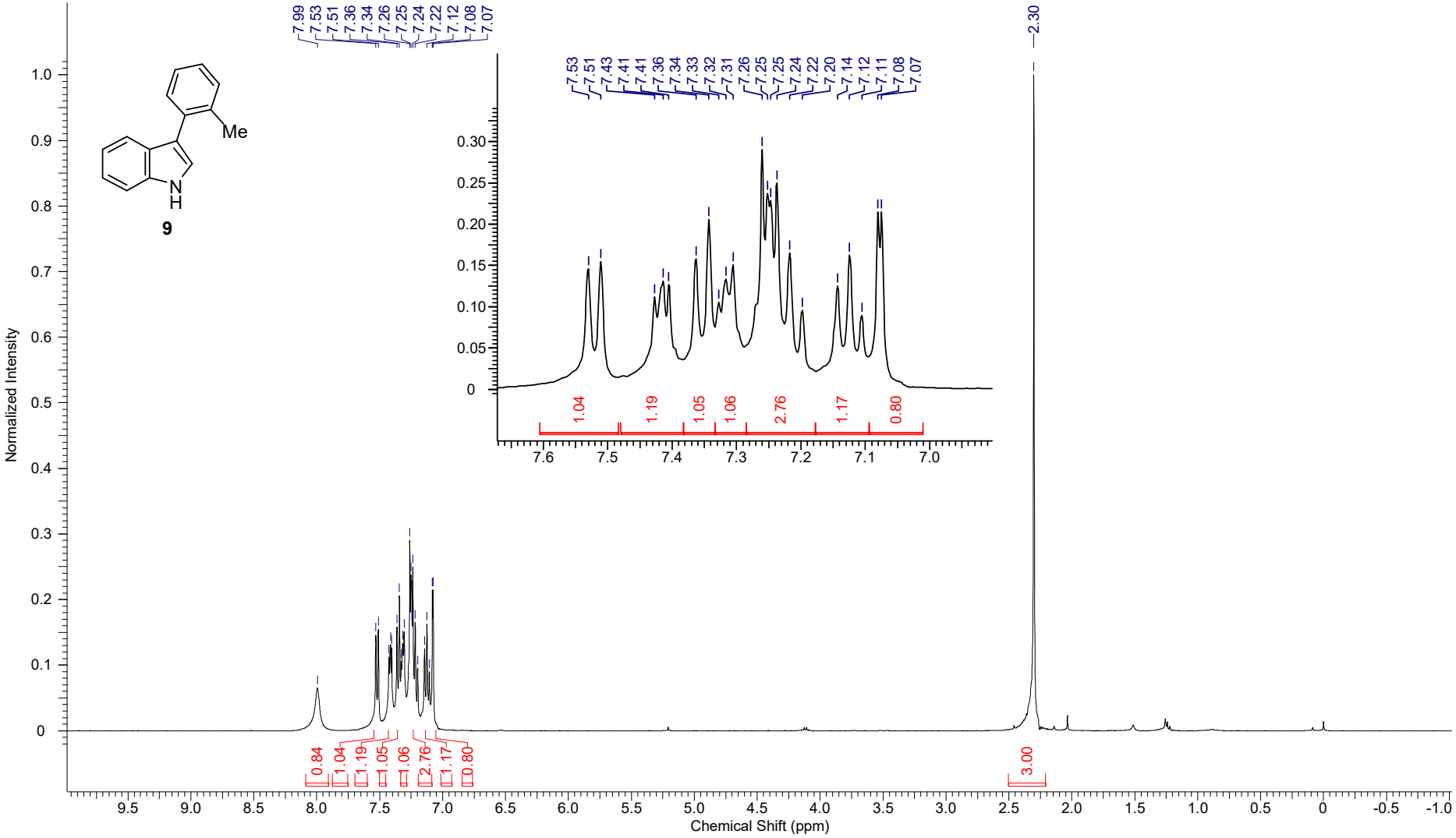

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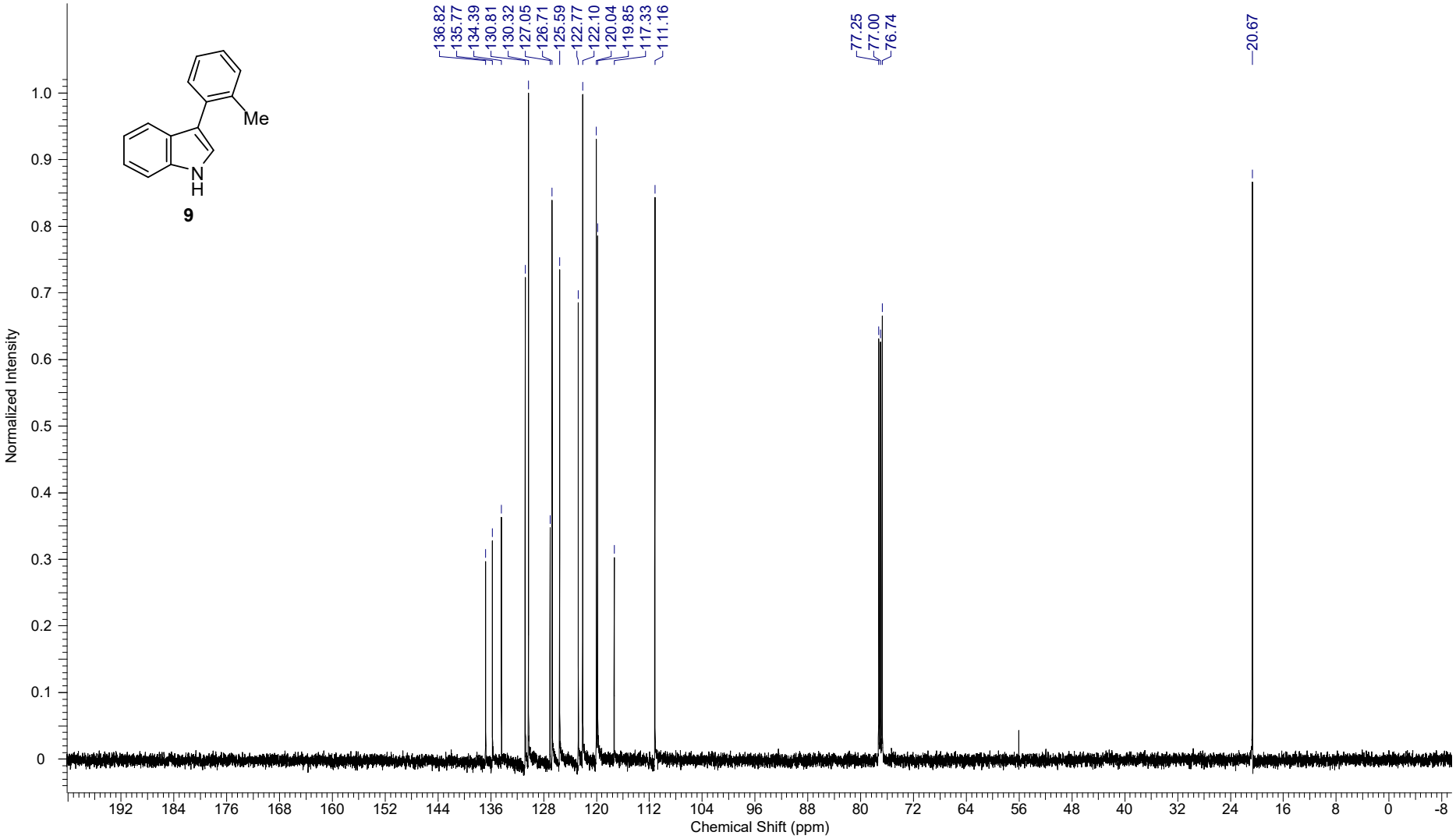
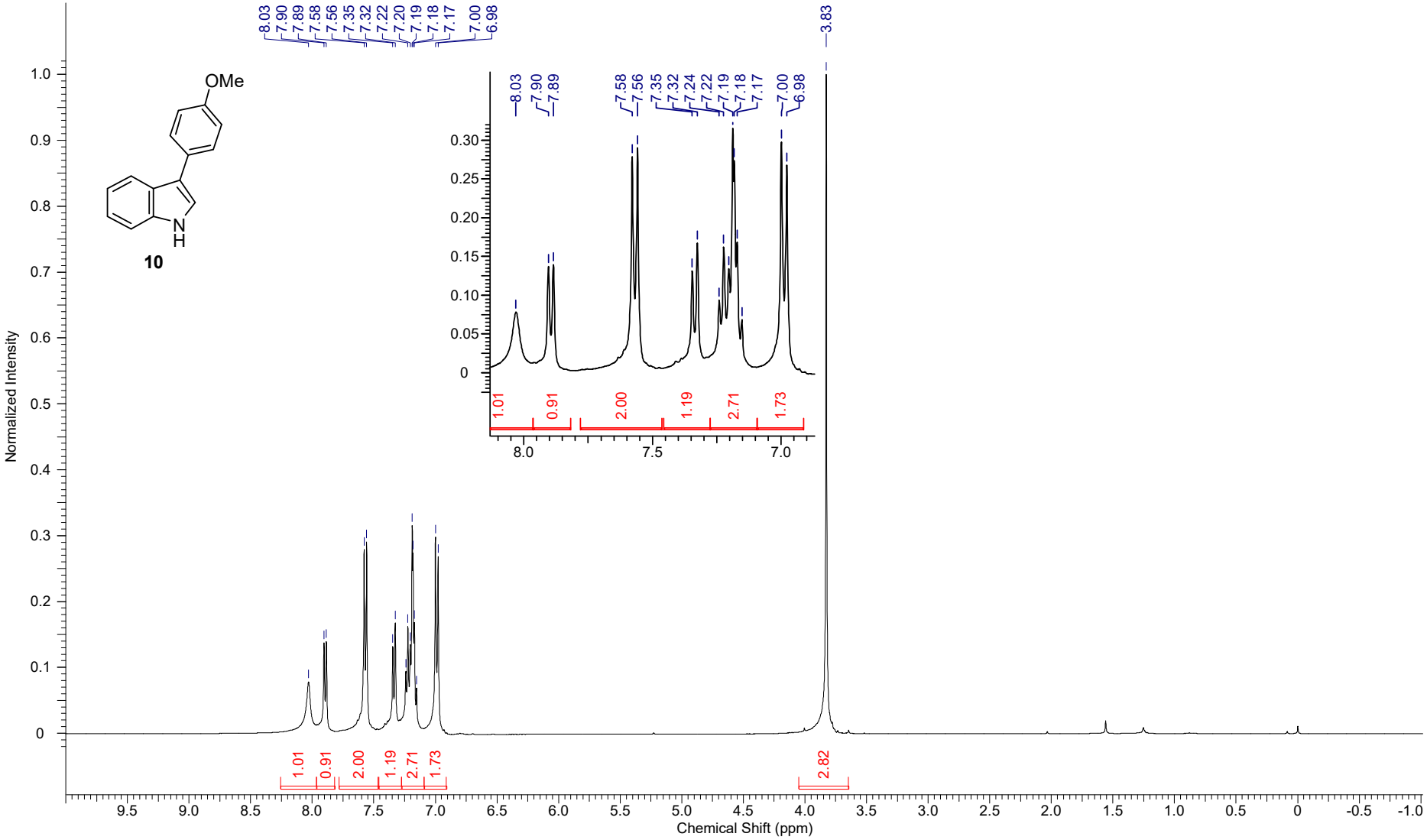
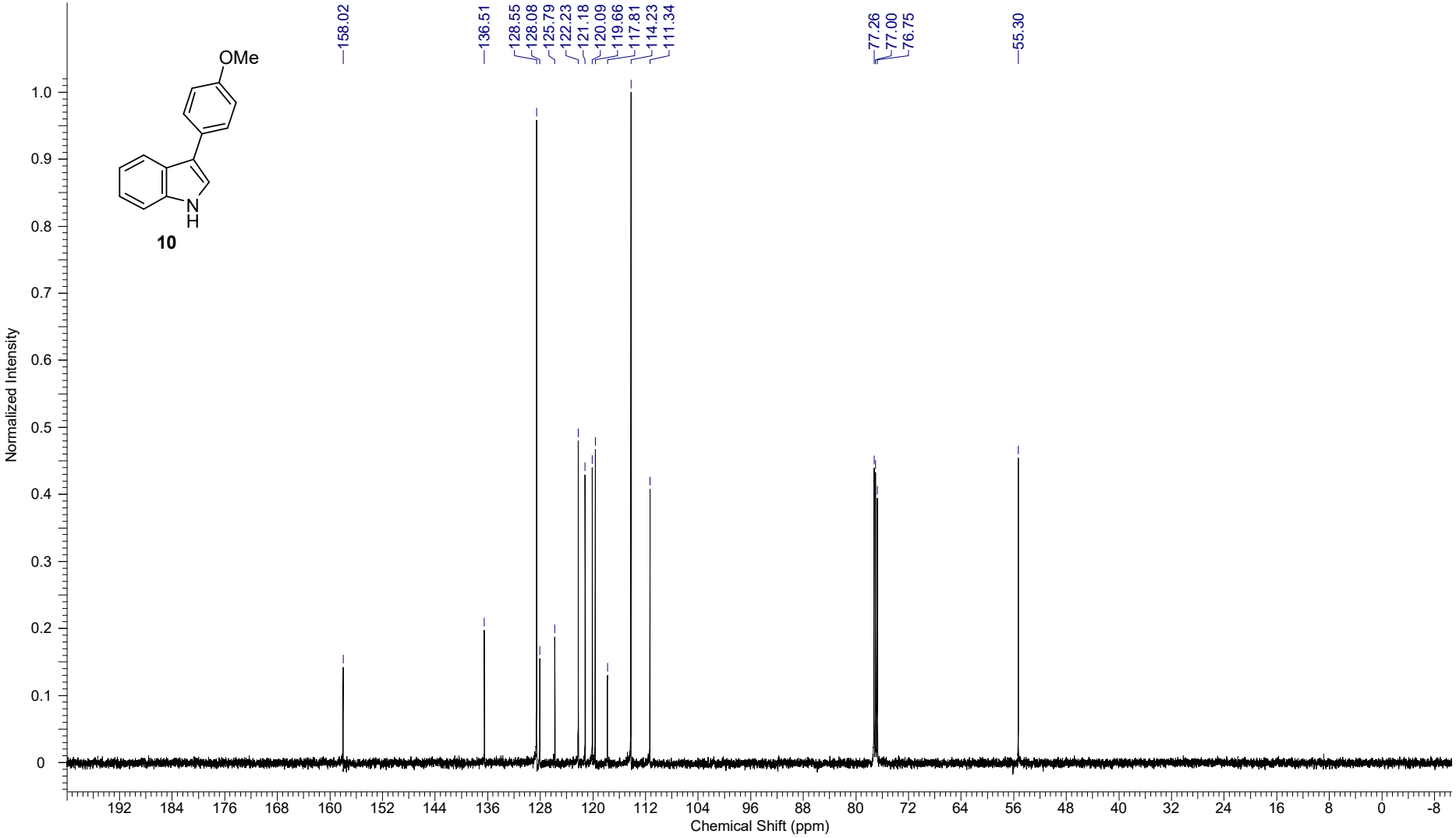
Solvent	CHLOROFORM-d	***Spectrum Offset (Hz)***	12418.4805	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50
Temperature (degree C)	22.000						



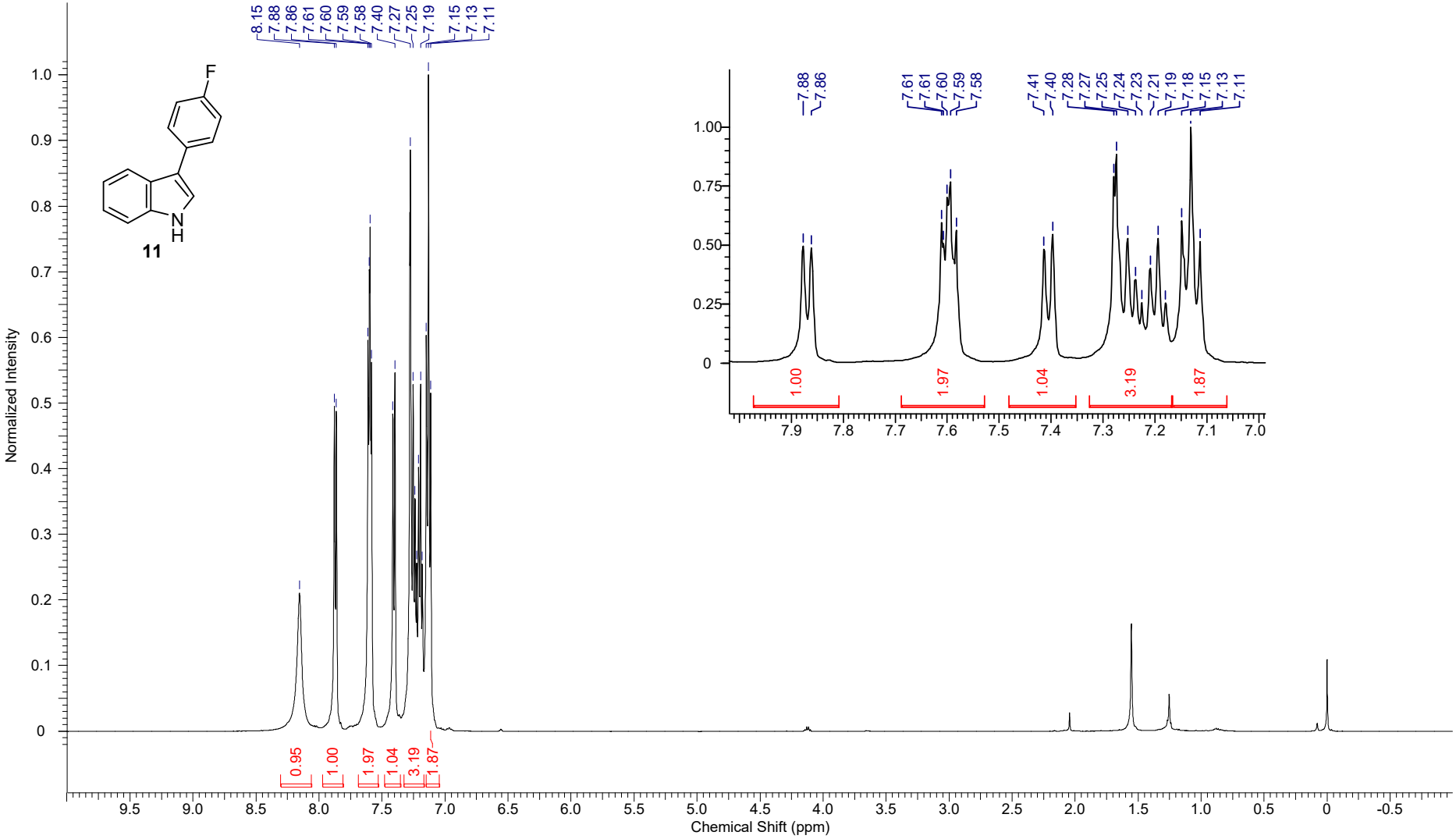
Acquisition Time (sec)	2.0500	*Comment*	YS 134 shita	*Date*	03 Feb 2017 10:46:00			*Date Stamp*	Fri Feb 03 10:45:59 2017
File Name	E:¥NMRspectra¥compound10¥compound10_1H.als			*Frequency (MHz)*	399.65	*Nucleus*	1H	*Number of Transients*	8
Original Points Count	16384	*Points Count*	16384	*Pulse Sequence*	NON	*Receiver Gain*	10.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	1960.3176	*Sweep Width (Hz)*	7992.01	*Temperature (degree C)*	21.300				



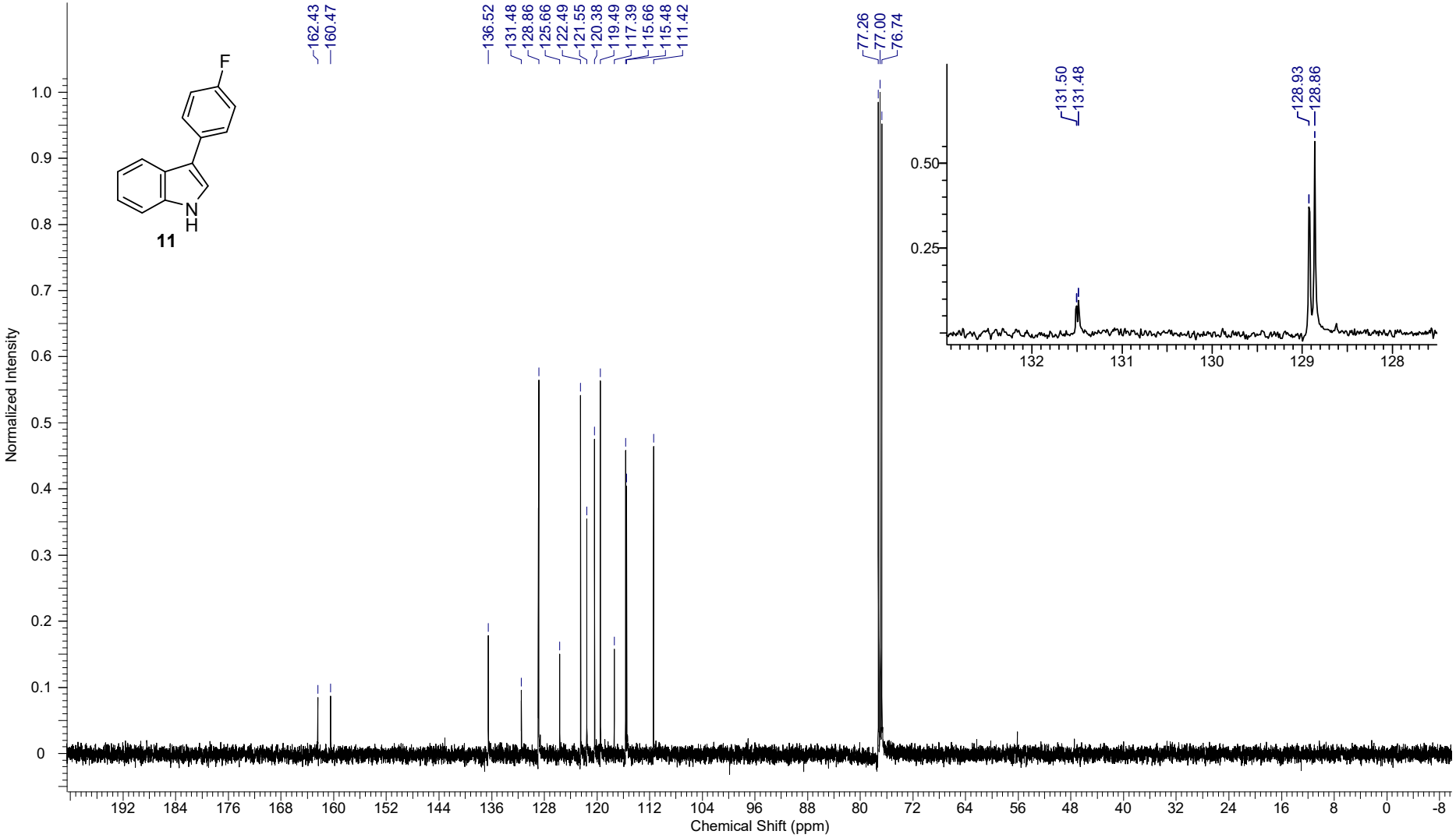
Acquisition Time (sec)	0.8389	***Comment***	single pulse decoupled gated NOE			***Date***	03 Feb 2017 09:58:51
Date Stamp	03 Feb 2017 09:32:17			***File Name***	E:¥NMRspectra¥compound10¥compound10_13C.jdf	***Frequency (MHz)***	124.50
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA 500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec	***Receiver Gain***	48.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12423.2500	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50	***Temperature (degree C)***	23.200



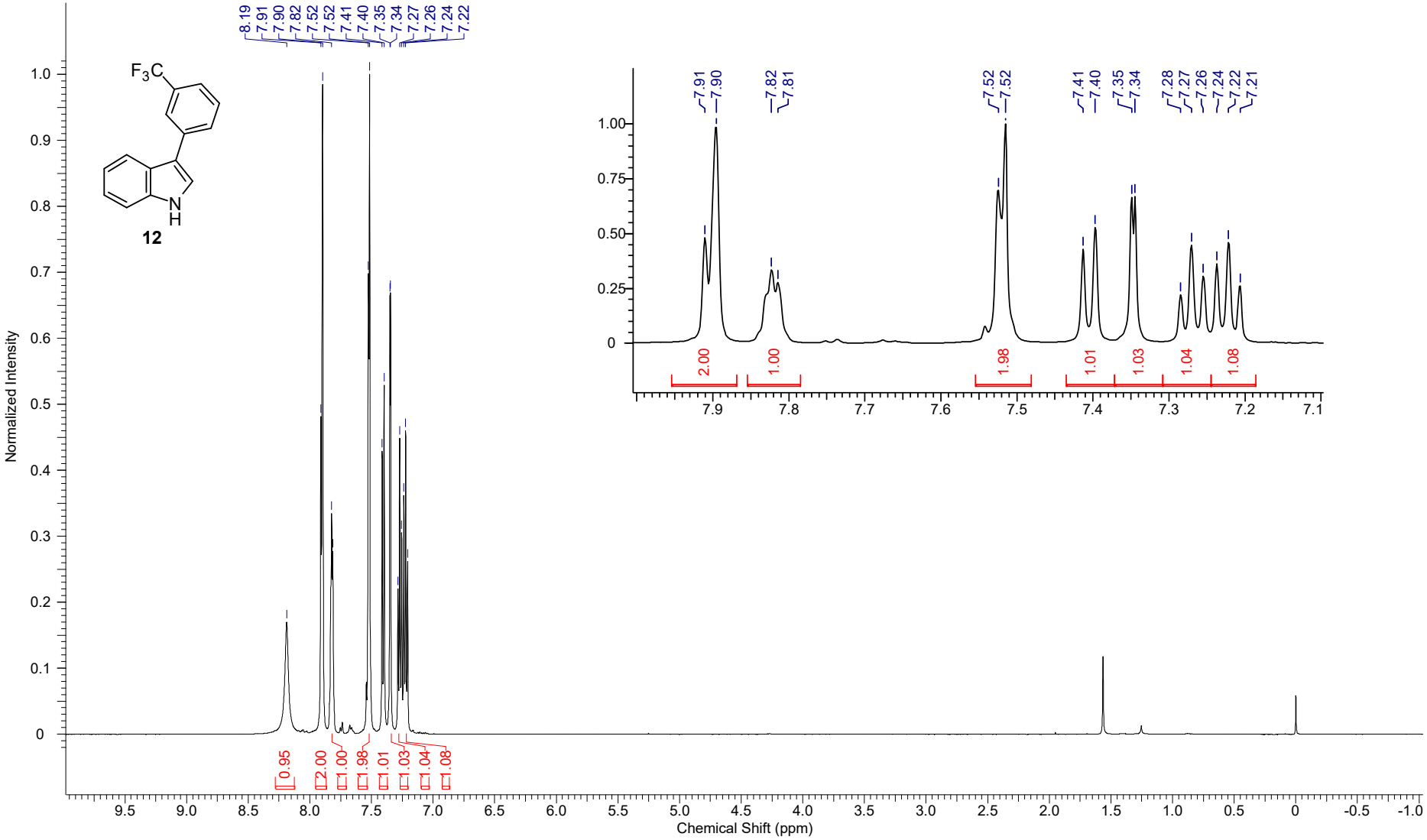
Acquisition Time (sec)	1.7642	*Comment*	YS 145 shita	*Date*	13 Mar 2017 08:16:19			*Date Stamp*	13 Mar 2017 07:49:03
File Name	E:¥NMRspectra¥compound11¥compound11_1H.jdf			*Frequency (MHz)*	495.13	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA 500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	40.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2461.5652	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9286.78	*Temperature (degree C)*	21.700						



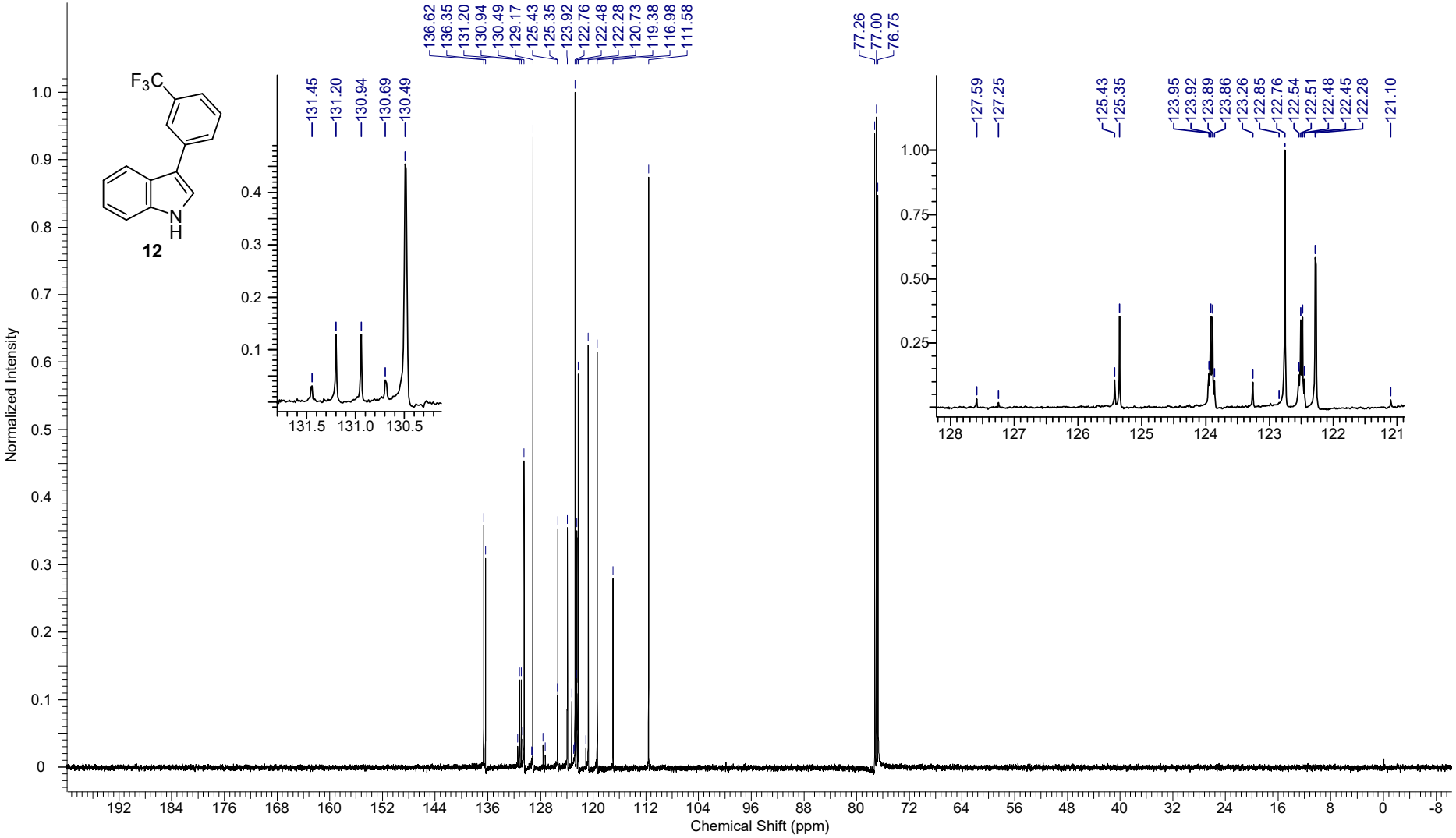
Acquisition Time (sec)	0.8389	***Comment***	YS 145 shita carbon			***Date***	13 Mar 2017 08:36:13
Date Stamp	13 Mar 2017 08:08:57			***File Name***	E:¥NMRspectra¥compound11¥compound11_13C.jdf	***Frequency (MHz)***	124.50
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA 500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec			***Receiver Gain***	52.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12431.5947	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50	***Temperature (degree C)***	21.900		



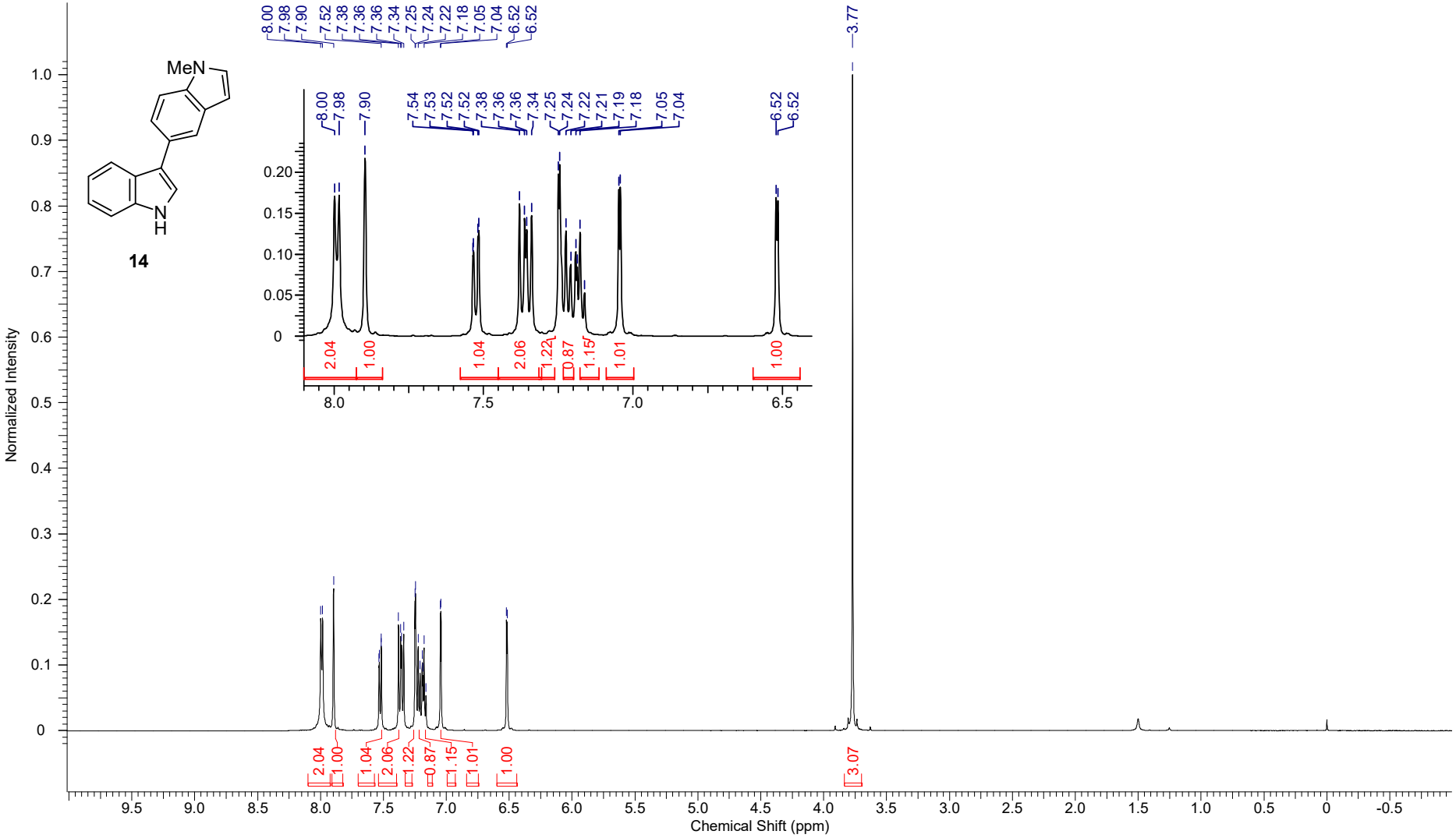
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	02 May 2017 16:52:58			*Date Stamp*	02 May 2017 16:52:11
File Name	E:¥NMRspectra¥compound12¥compound12_1H.jdf			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	proton.jxp
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2476.5542	*Sweep Width (Hz)*	9384.38	*Temperature (degree C)*	21.900



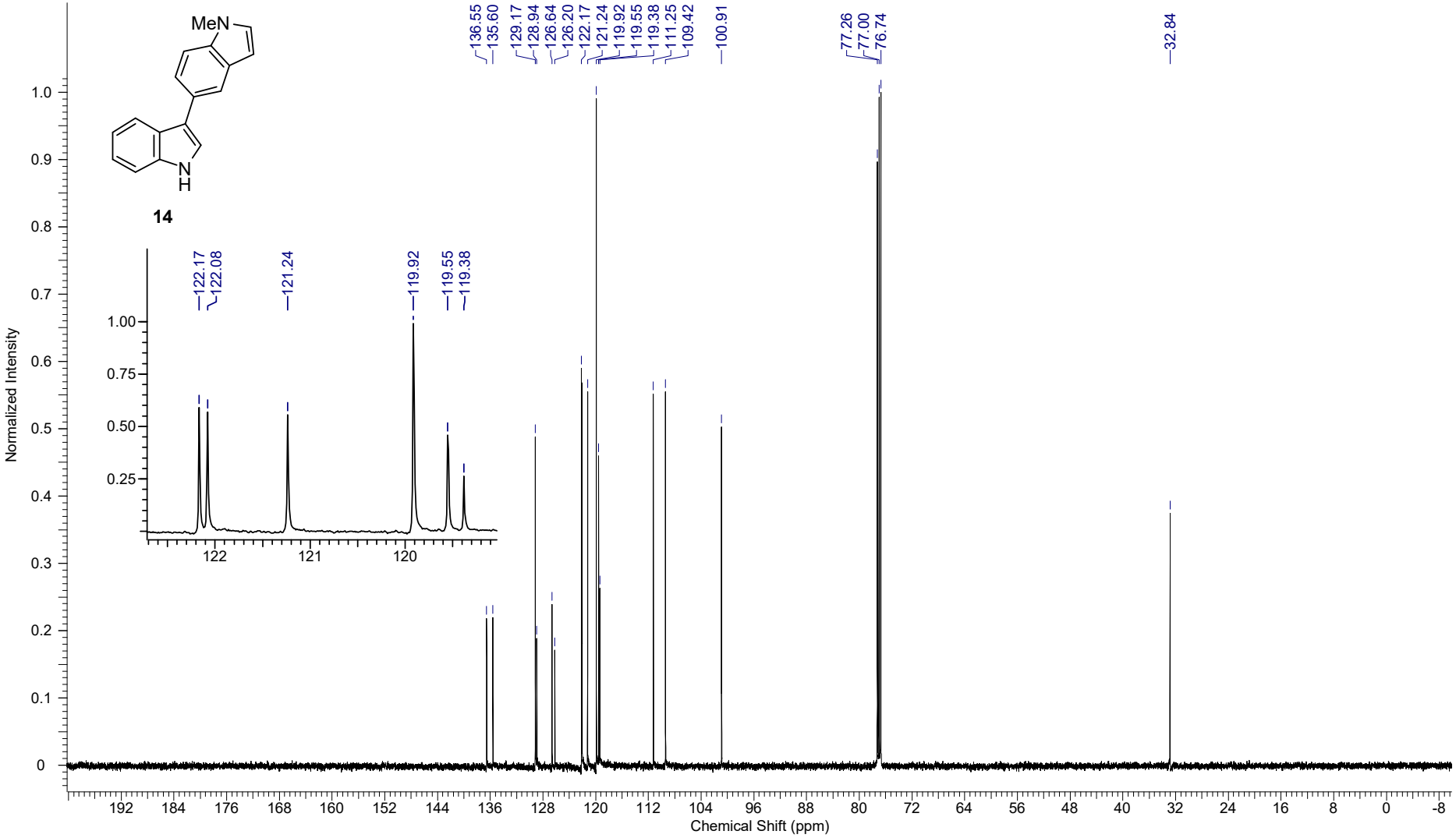
Acquisition Time (sec)	0.8336	*Comment*	single pulse decoupled gated NOE			*Date*	02 May 2017 17:29:59
Date Stamp	02 May 2017 16:53:08			*File Name*	E:¥NMRspectra¥compound12¥compound12_13C.jdf	*Frequency (MHz)*	125.77
Nucleus	13C	*Number of Transients*	1024	*Origin*	ECA	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	carbon.jxp	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12556.4355
Sweep Width (Hz)	39308.18	*Temperature (degree C)*	22.000						



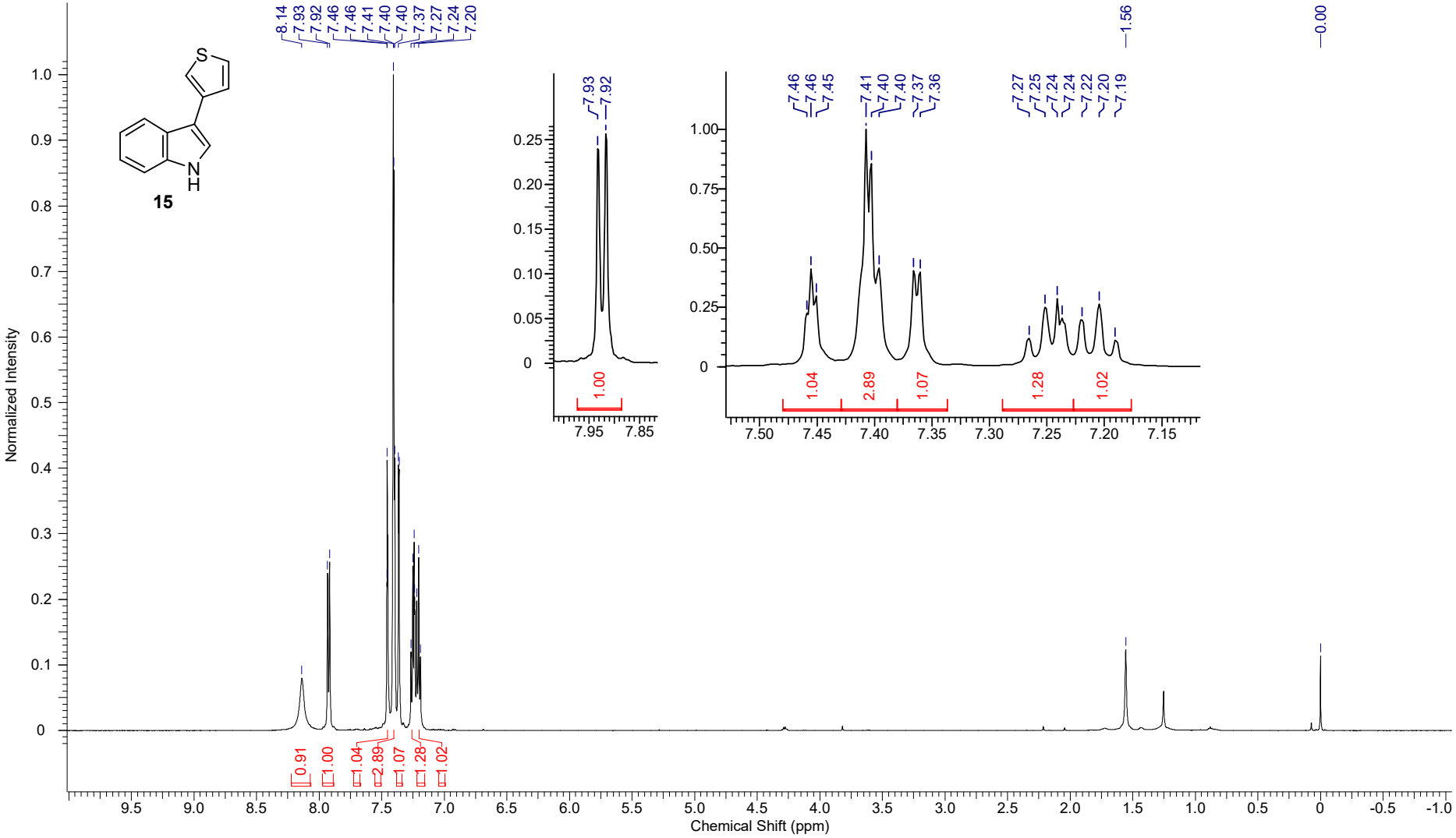
Acquisition Time (sec)	1.7642	*Comment*	single_pulse	*Date*	14 Apr 2017 07:26:55			*Date Stamp*	14 Apr 2017 07:00:13
File Name	E:¥NMRspectra¥compound14¥compound14_1H.jdf			*Frequency (MHz)*	495.13	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA 500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	34.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2442.2922	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9286.78	*Temperature (degree C)*	21.100						



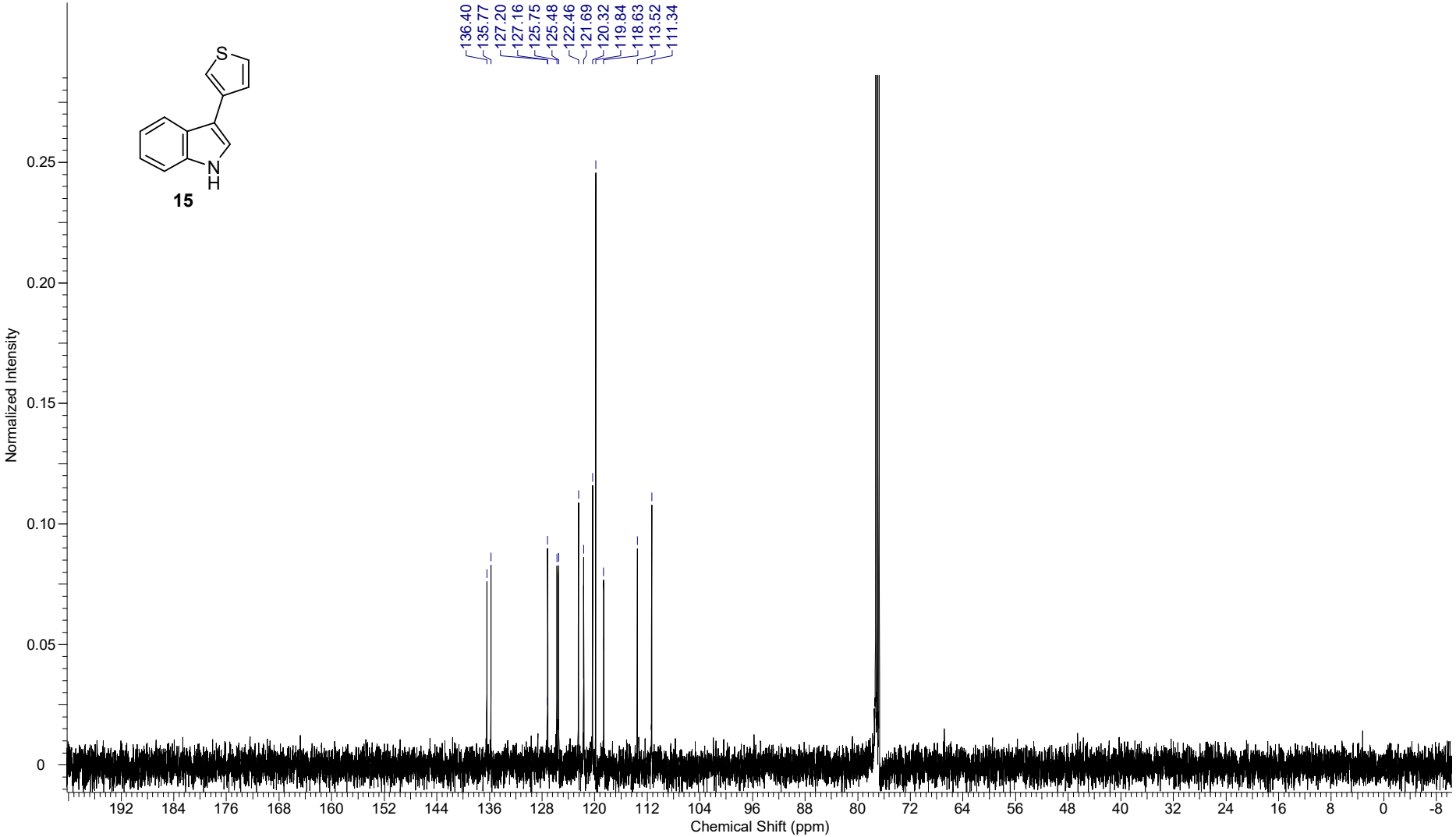
Acquisition Time (sec)	0.8389	*Comment*	single pulse decoupled gated NOE			*Date*	14 Apr 2017 08:50:08
Date Stamp	14 Apr 2017 08:23:26			*File Name*	E:¥NMRspectra¥compound14¥compound14_13C-1.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	2300	*Origin*	ECA 500	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	54.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	12424.4404	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50	*Temperature (degree C)*	22.000



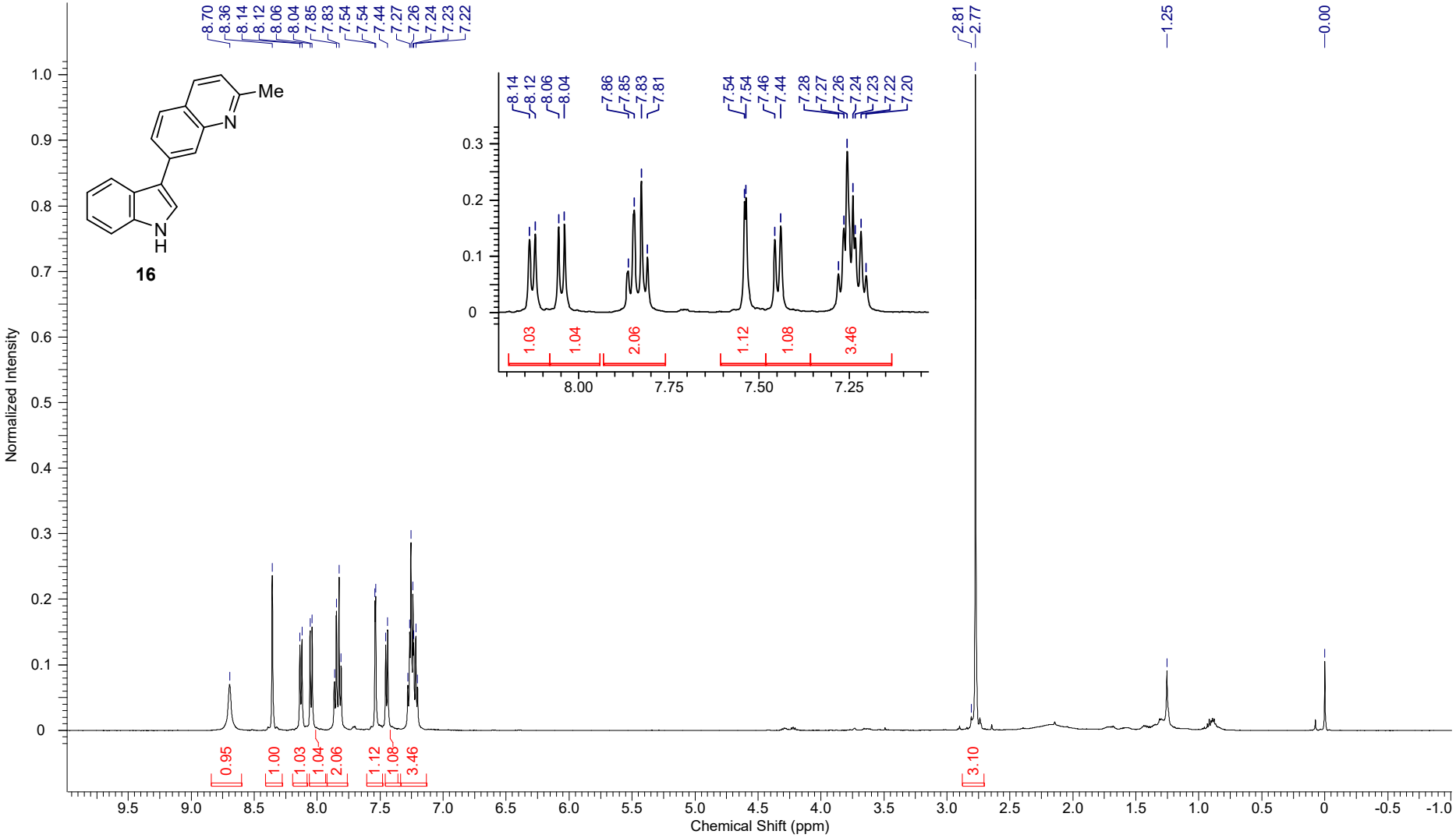
Acquisition Time (sec)	1.7642	*Comment*	single_pulse	*Date*	01 May 2017 08:40:44			*Date Stamp*	01 May 2017 08:11:26
File Name	E:¥NMRspectra¥compound15¥compound15_1H.jdf			*Frequency (MHz)*	495.13	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA 500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	50.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2468.9343	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9286.78	*Temperature (degree C)*	21.300						



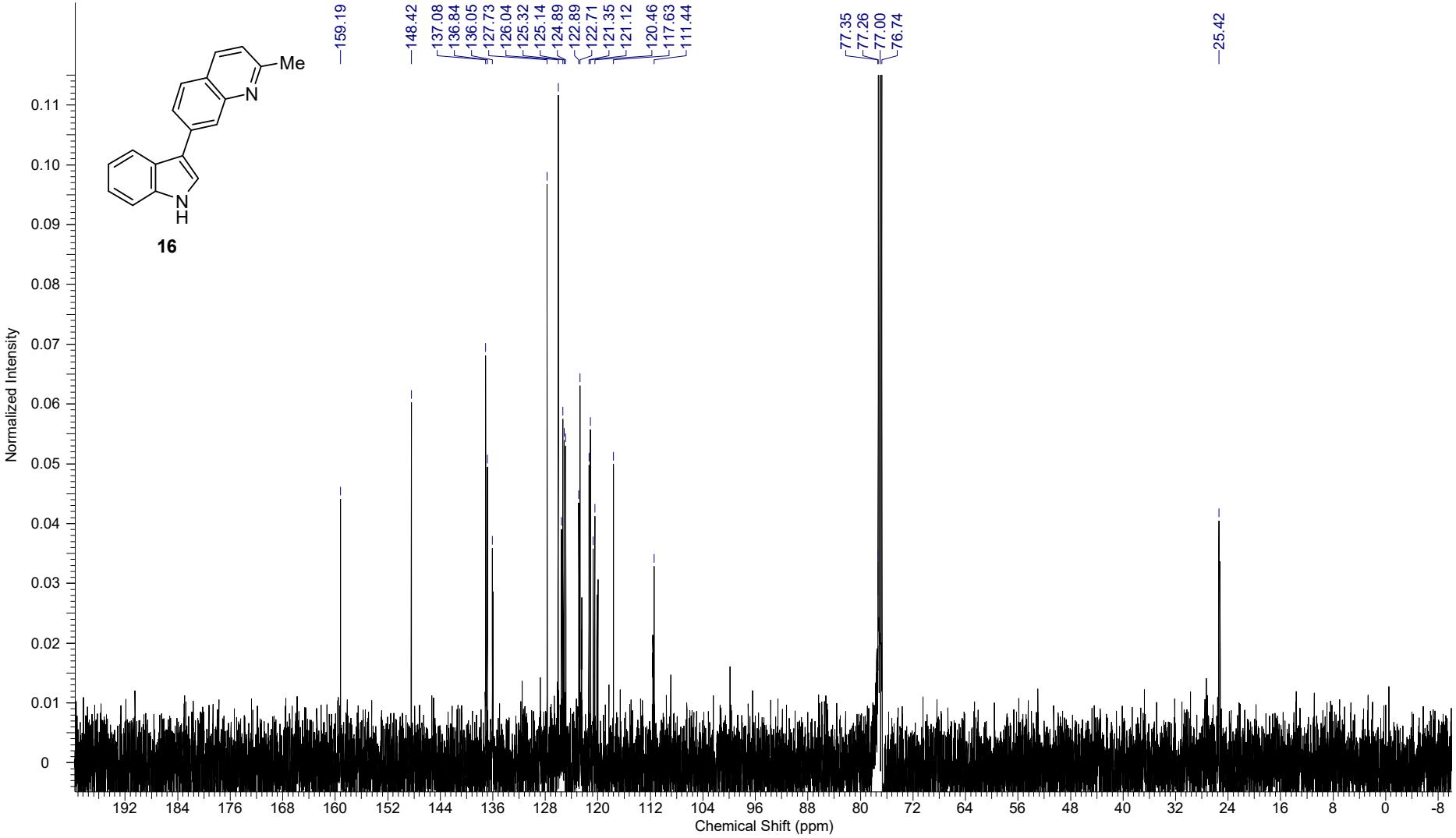
Acquisition Time (sec)	0.8389	*Comment*	single pulse decoupled gated NOE		*Date*	01 May 2017 09:17:02	
Date Stamp	01 May 2017 08:47:44			*File Name*	E:¥NMRspectra¥compound15¥compound15_13C.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	1000	*Origin*	ECA 500	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d		
Spectrum Offset (Hz)	12432.7861	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50	*Temperature (degree C)*	21.500		



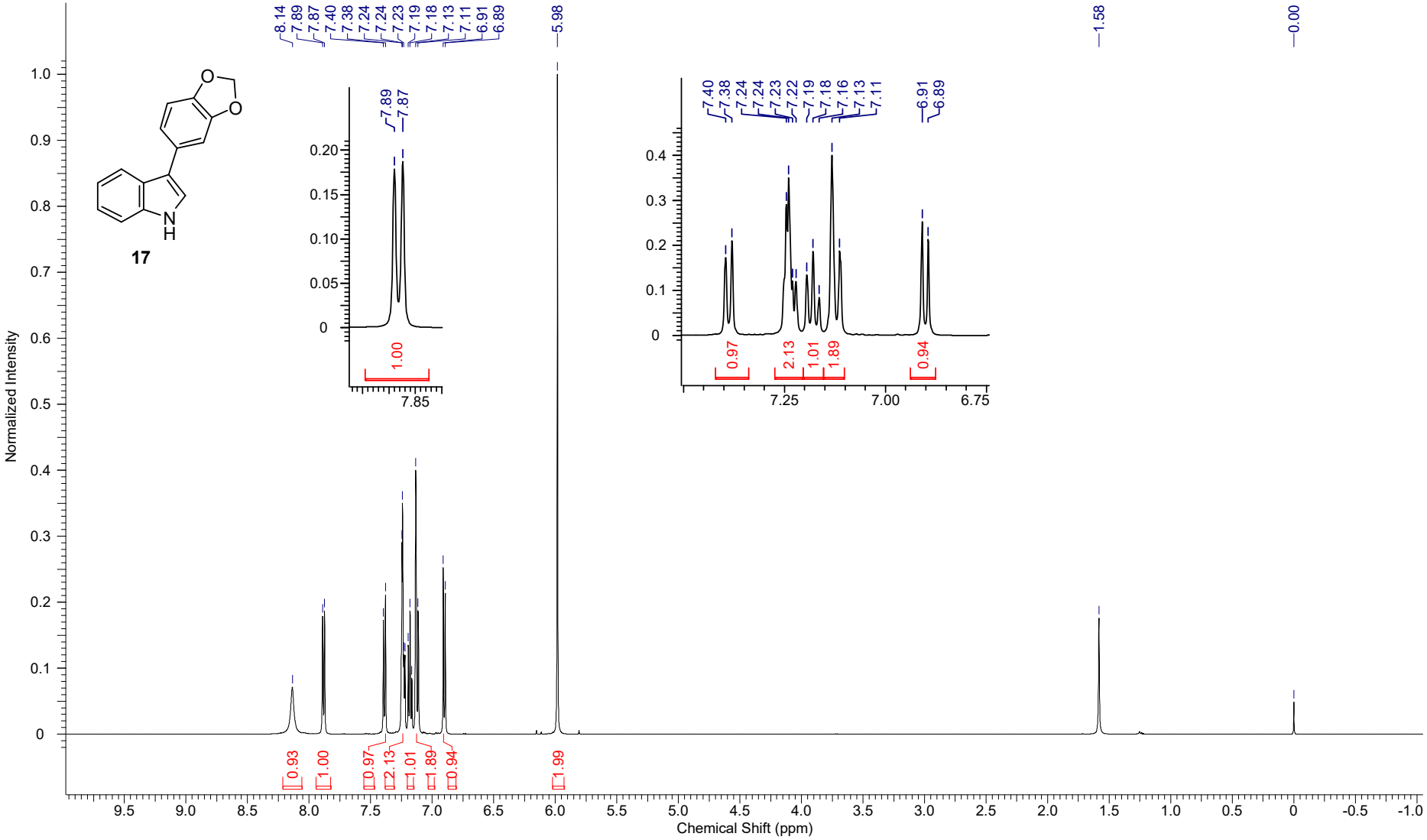
Acquisition Time (sec)	1.7642	*Comment*	single_pulse	*Date*	19 May 2017 13:01:59			*Date Stamp*	19 May 2017 12:32:59
File Name	E:¥NMRspectra¥compound16¥compound16_1H.jdf			*Frequency (MHz)*	495.13	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA 500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	54.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2475.6594	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9286.78	*Temperature (degree C)*	21.700						



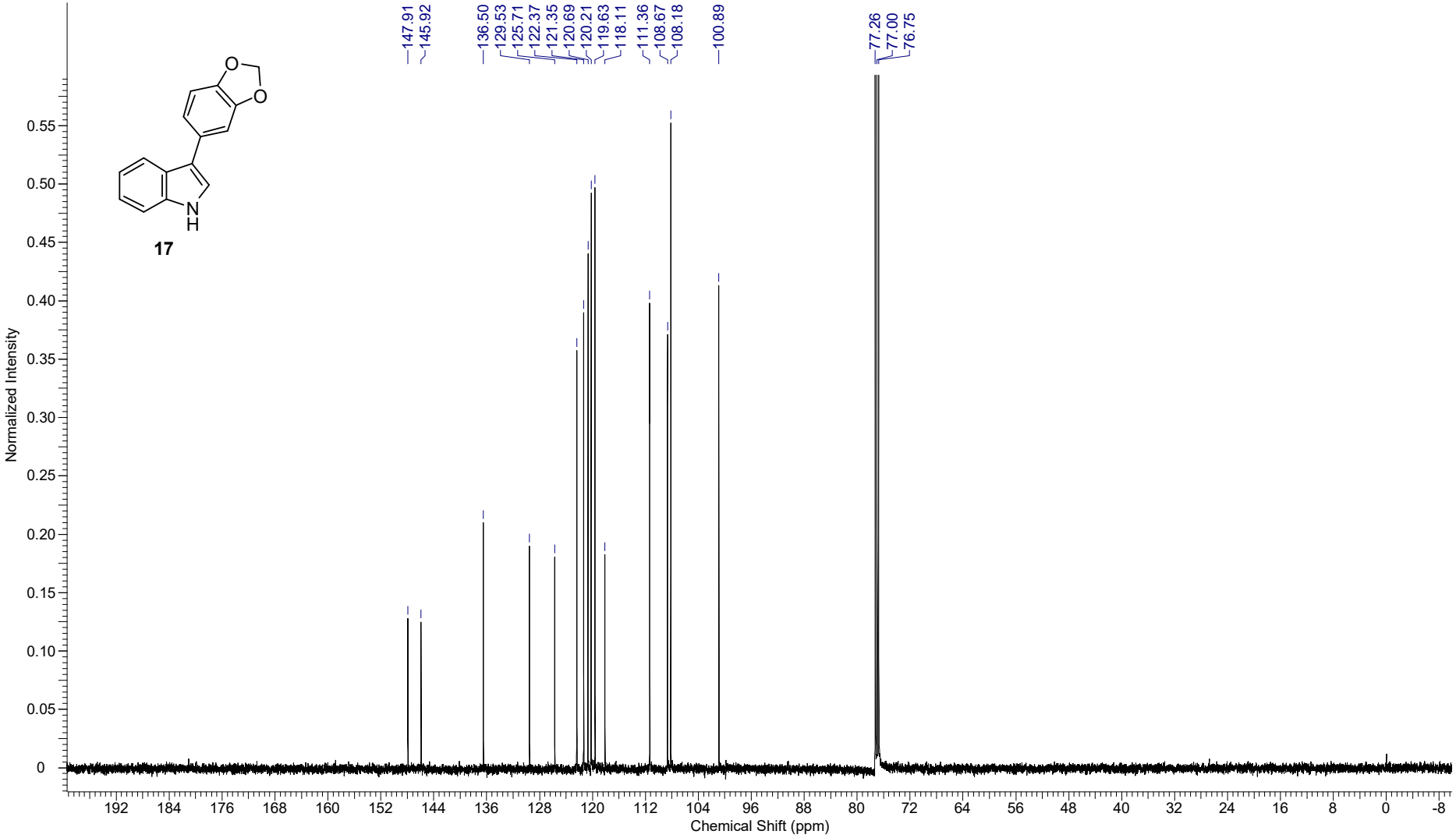
Acquisition Time (sec)	0.8389	*Comment*	single pulse decoupled gated NOE			*Date*	19 May 2017 13:38:19
Date Stamp	19 May 2017 13:09:18			*File Name*	E:¥NMRspectra¥compound16¥compound16_13C.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	1000	*Origin*	ECA 500	*Original Points Count*	32768
Owner	delta						
Points Count	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	12433.9775	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50	*Temperature (degree C)*	21.800



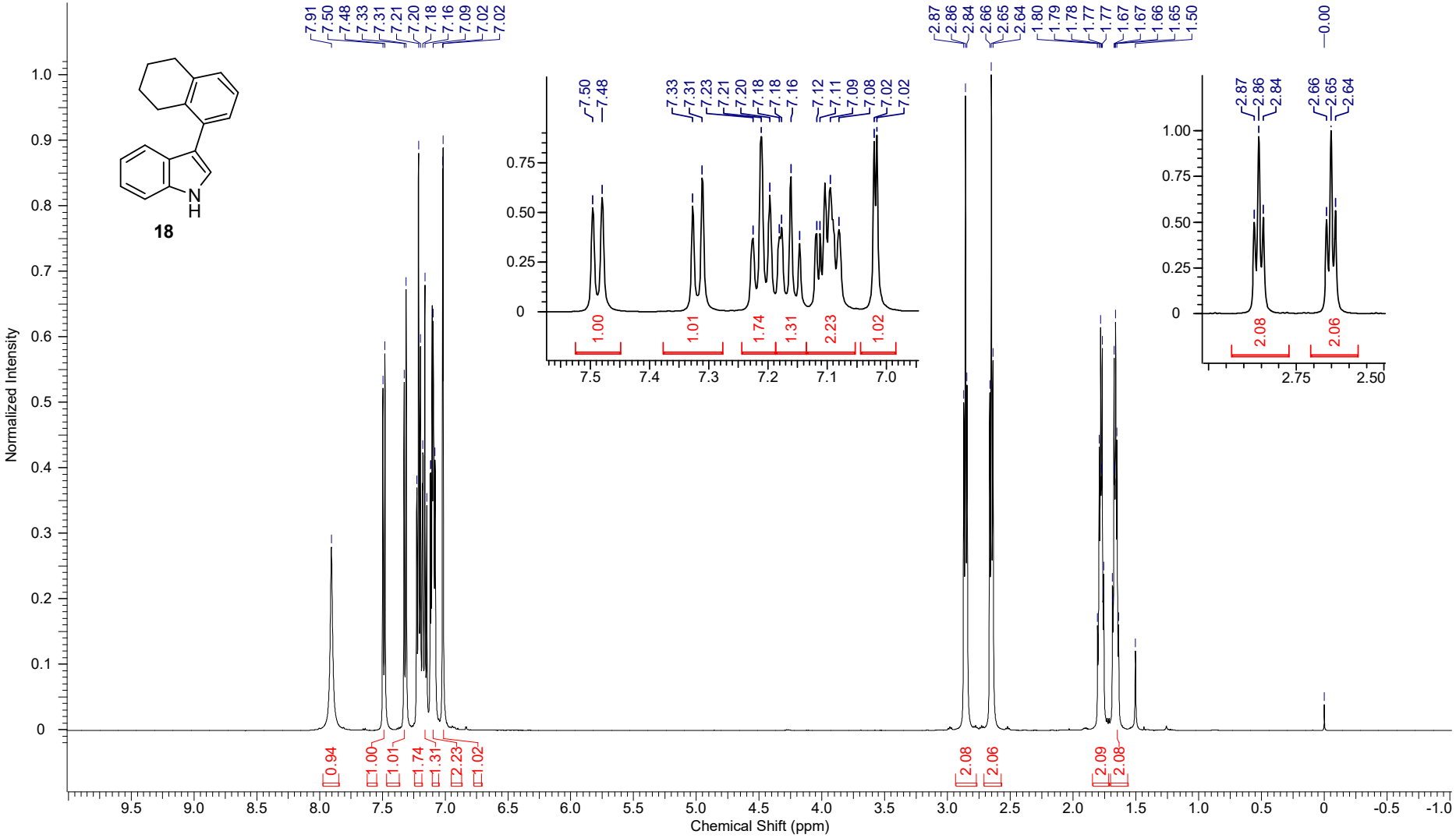
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	02 Jun 2017 07:40:04			*Date Stamp*	02 Jun 2017 07:39:17
File Name	E:¥NMRspectra¥compound17¥compound17_1H.jdf			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	proton.jxp
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2488.5833	*Sweep Width (Hz)*	9384.38	*Temperature (degree C)*	22.400



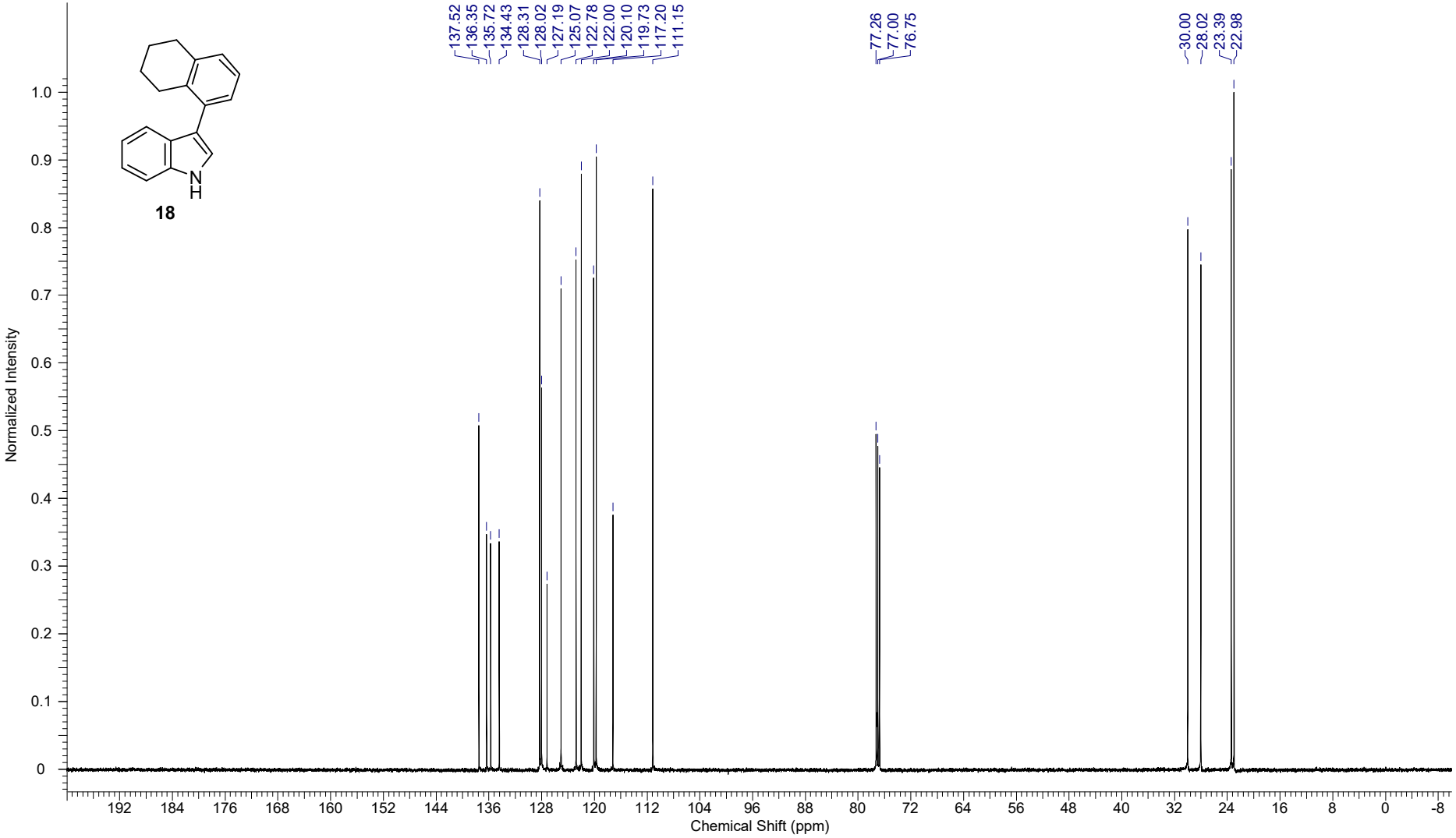
Acquisition Time (sec)	0.8336	*Comment*	single pulse decoupled gated NOE			*Date*	02 Jun 2017 08:17:05
Date Stamp	02 Jun 2017 07:40:14			*File Name*	E:¥NMRspectra¥compound17¥compound17_13C.jdf	*Frequency (MHz)*	125.77
Nucleus	13C	*Number of Transients*	1024	*Origin*	ECA	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	carbon.jxp	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12557.6338
Sweep Width (Hz)	39308.18	*Temperature (degree C)*	22.600						



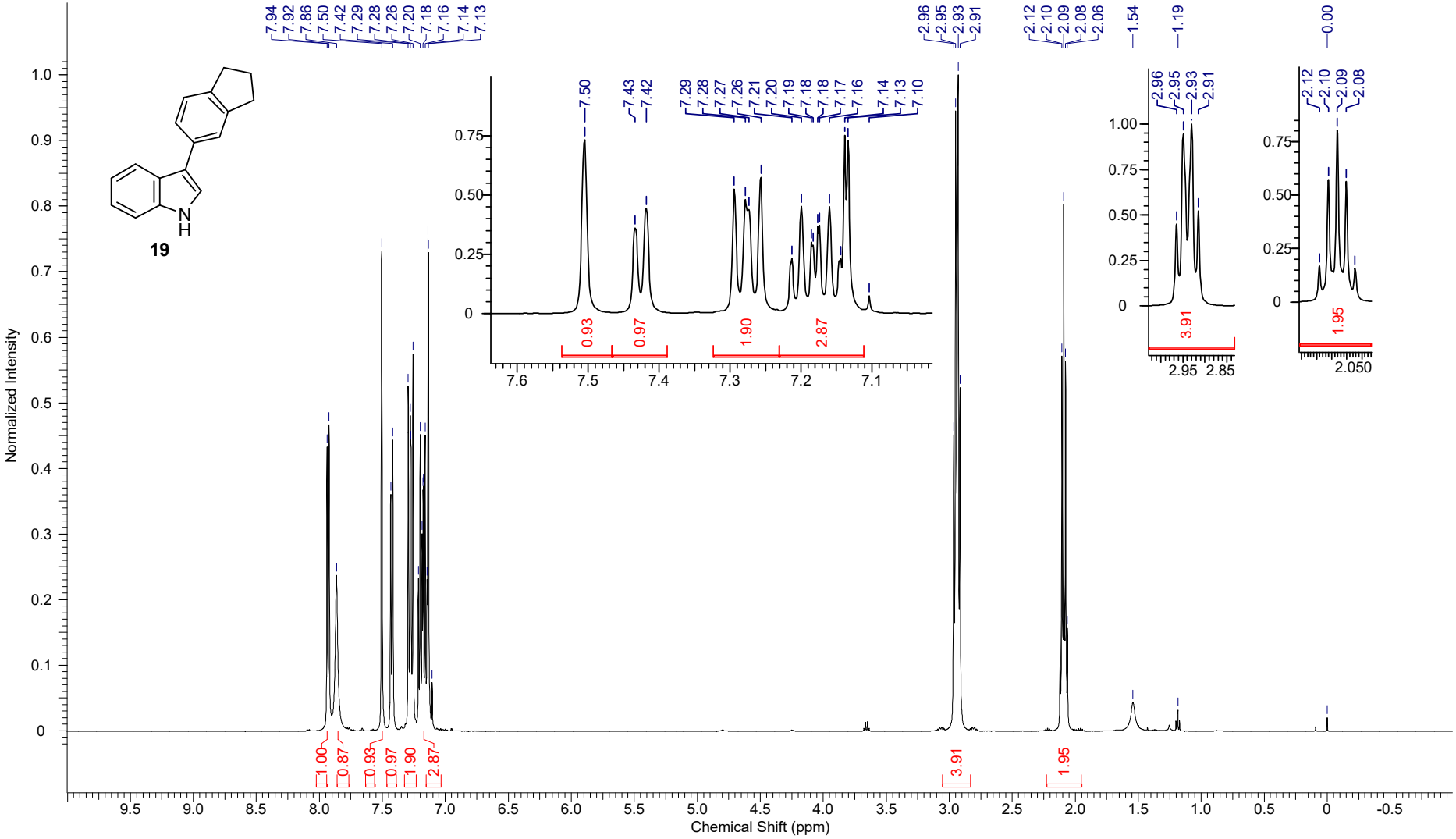
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	30 Jun 2017 12:10:09			*Date Stamp*	30 Jun 2017 12:04:29
File Name	E:¥NMRspectra¥compound18¥compound18_1H.1			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	30.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2429.5835	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9384.38	*Temperature (degree C)*	21.500						



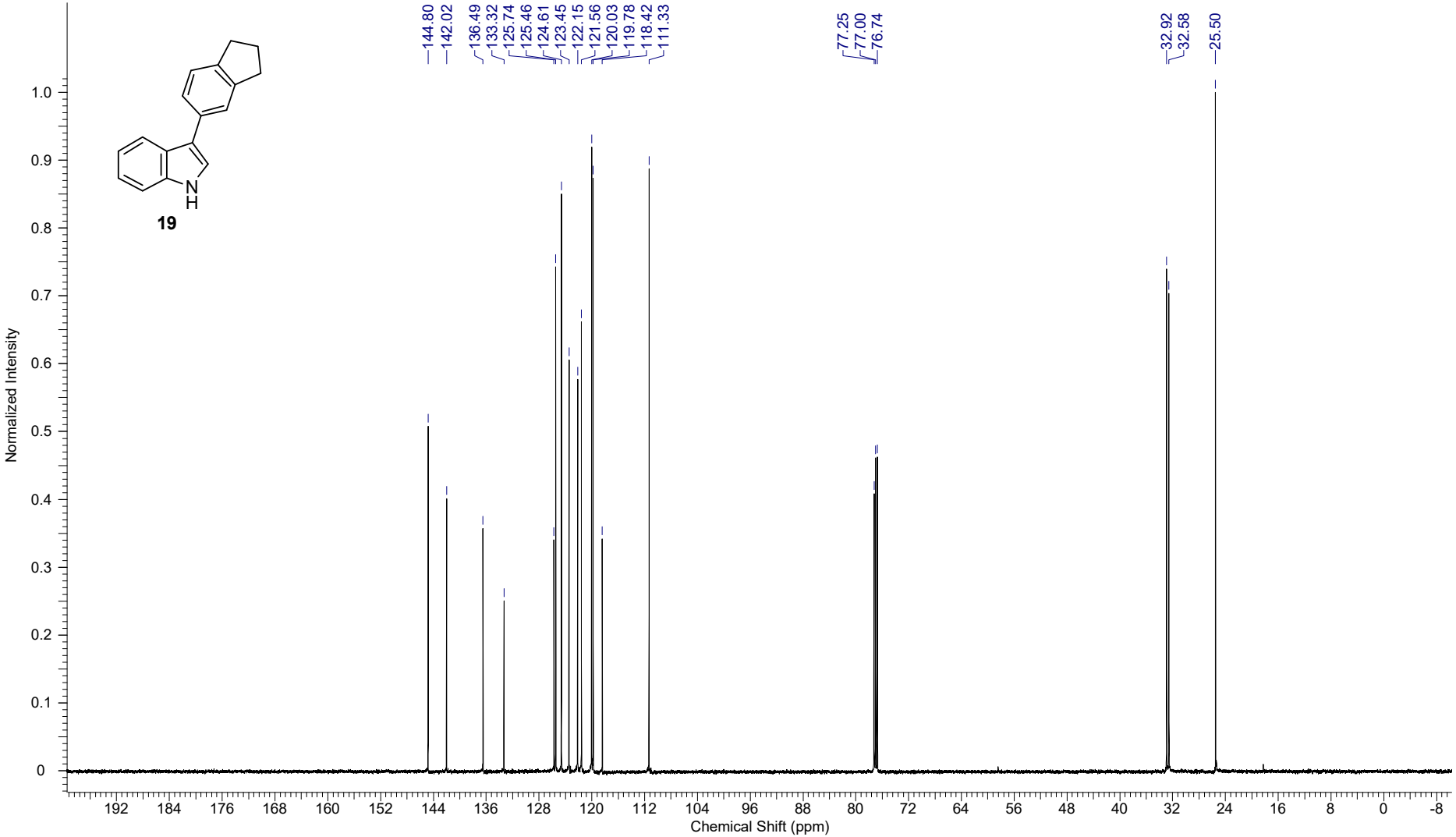
Acquisition Time (sec)	0.8336	***Comment***	single pulse decoupled gated NOE			***Date***	30 Jun 2017 12:46:42
Date Stamp	30 Jun 2017 12:41:02			***File Name***	E:¥NMRspectra¥compound18¥compound18_13C.1	***Frequency (MHz)***	125.77
Nucleus	13C	***Number of Transients***	1000	***Origin***	ECA500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec	***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12539.6396	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39308.18	***Temperature (degree C)***	22.100



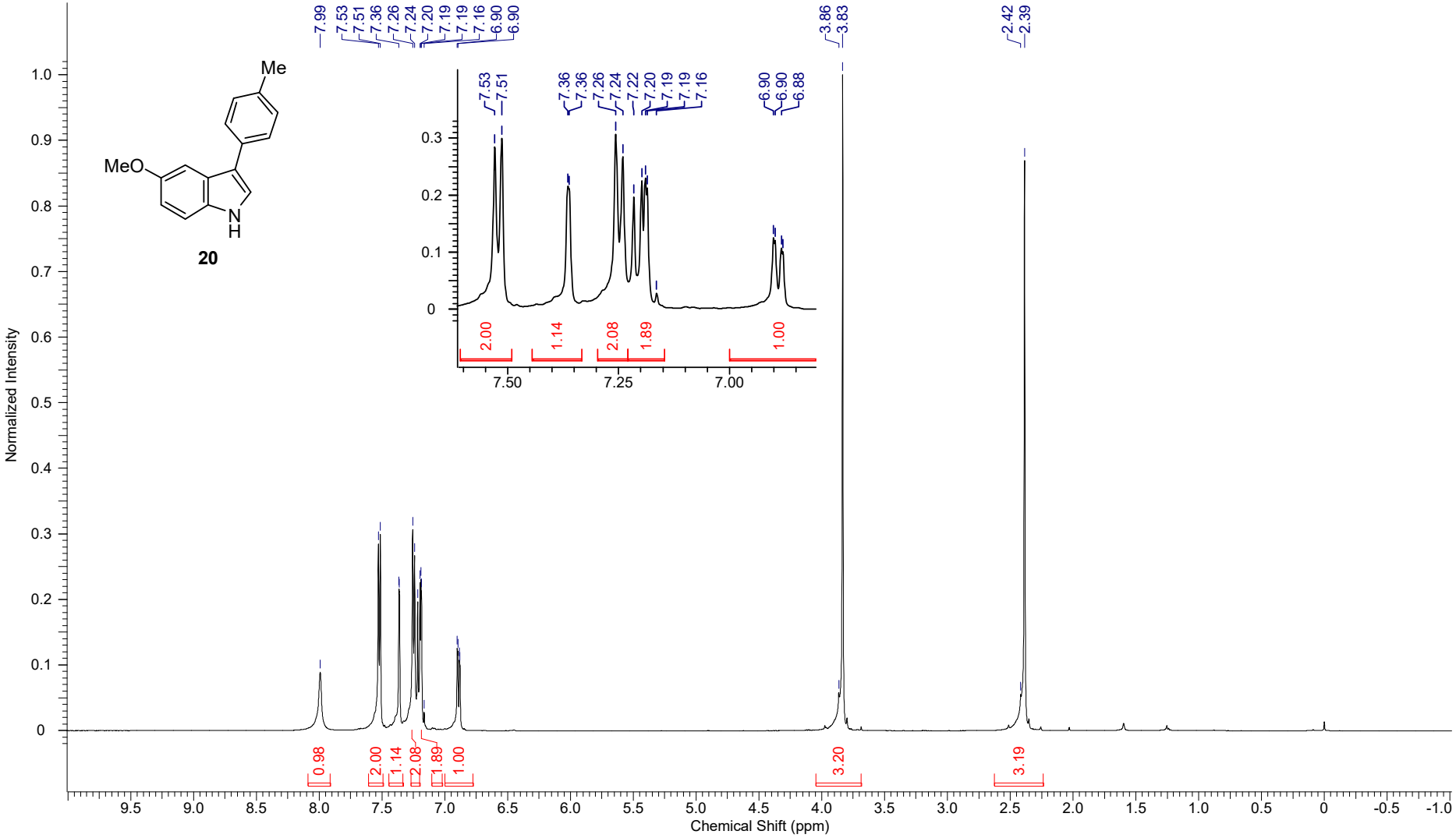
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	01 Jul 2017 13:02:10			*Date Stamp*	01 Jul 2017 12:56:29
File Name	E:¥NMRspectra¥compound19¥compound19_1H.1			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	32.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2425.5740	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9384.38	*Temperature (degree C)*	21.400						



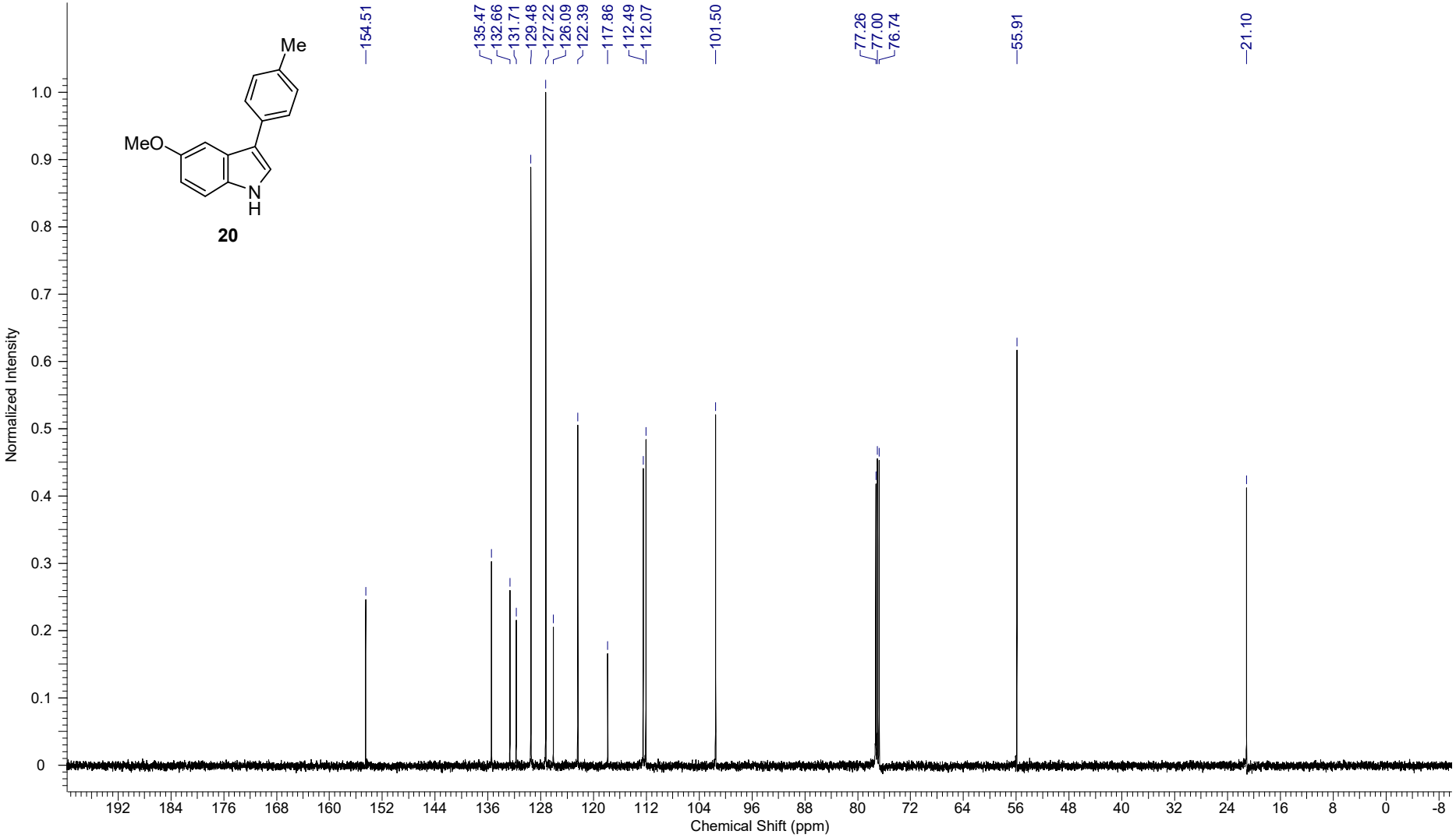
Acquisition Time (sec)	0.8336	*Comment*	single pulse decoupled gated NOE			*Date*	01 Jul 2017 13:38:41
Date Stamp	01 Jul 2017 13:33:01			*File Name*	E:¥NMRspectra¥compound19¥compound19_13C.1	*Frequency (MHz)*	125.77
Nucleus	13C	*Number of Transients*	1000	*Origin*	ECA500	*Original Points Count*	32768
Owner	delta	*Points Count*	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	60.00
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	12537.2402	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39308.18
Temperature (degree C)	22.000						



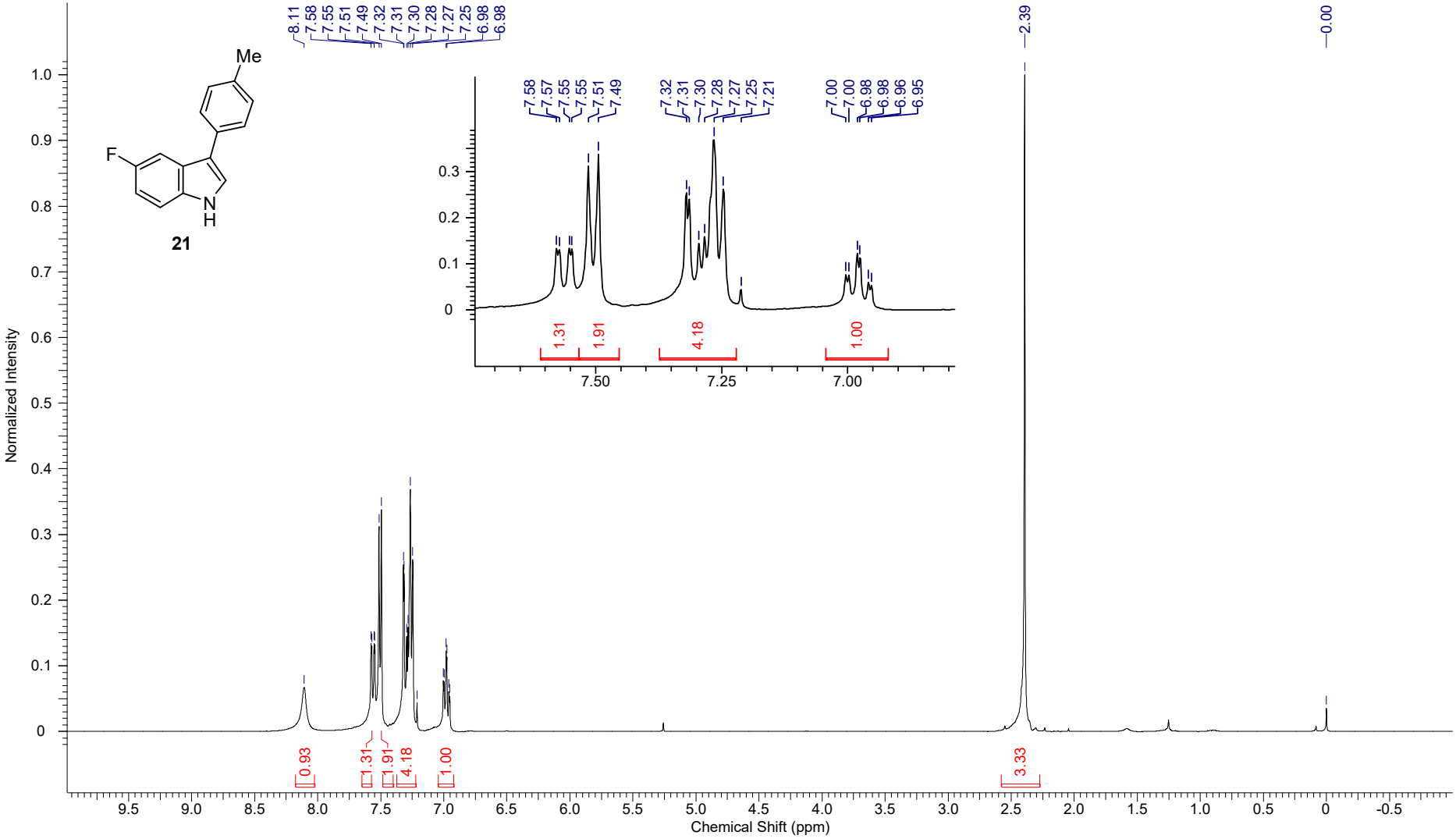
Acquisition Time (sec)	1.7642	*Comment*	YS 131 column-2		*Date*	29 Jan 2017 11:13:08	
Date Stamp	29 Jan 2017 10:46:26		*File Name*	E:¥NMRspectra¥compound20¥compound20_1H.jdf		*Frequency (MHz)*	495.13
Nucleus	1H	*Number of Transients*	8	*Origin*	ECA 500	*Original Points Count*	16384	*Owner*	delta
Points Count	16384	*Pulse Sequence*	single_pulse.ex2			*Receiver Gain*	28.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	2431.5220	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	9286.78	*Temperature (degree C)*	22.500		



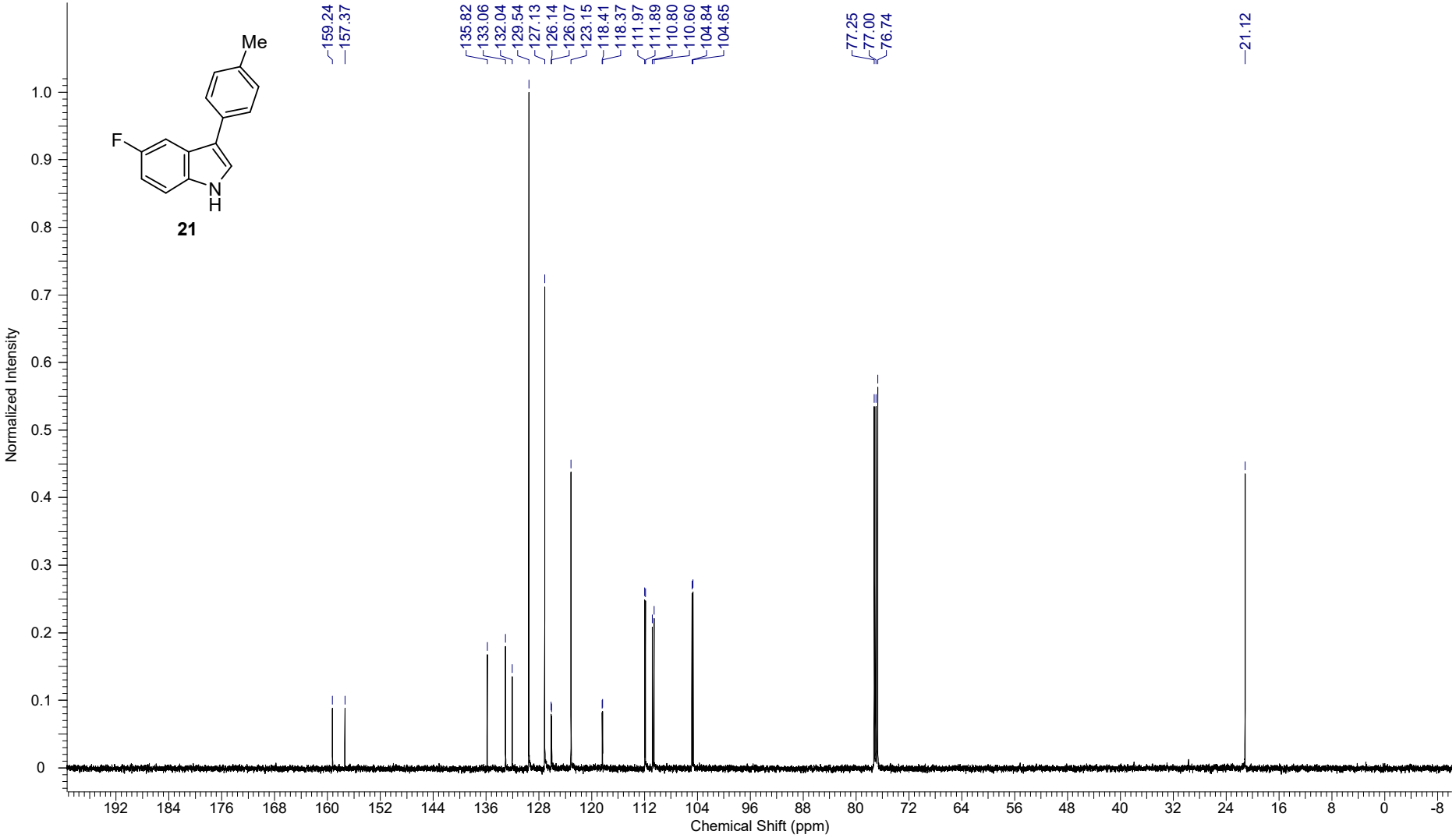
Acquisition Time (sec)	0.8389	*Comment*	YS 131 column-2 carbon			*Date*	29 Jan 2017 11:31:35
Date Stamp	29 Jan 2017 11:04:53			*File Name*	E:¥NMRspectra¥compound20¥compound20_13C.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	500	*Origin*	ECA 500	*Original Points Count*	32768
Owner	delta	*Points Count*	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	50.00
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	12419.6738	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50
Temperature (degree C)	22.800						



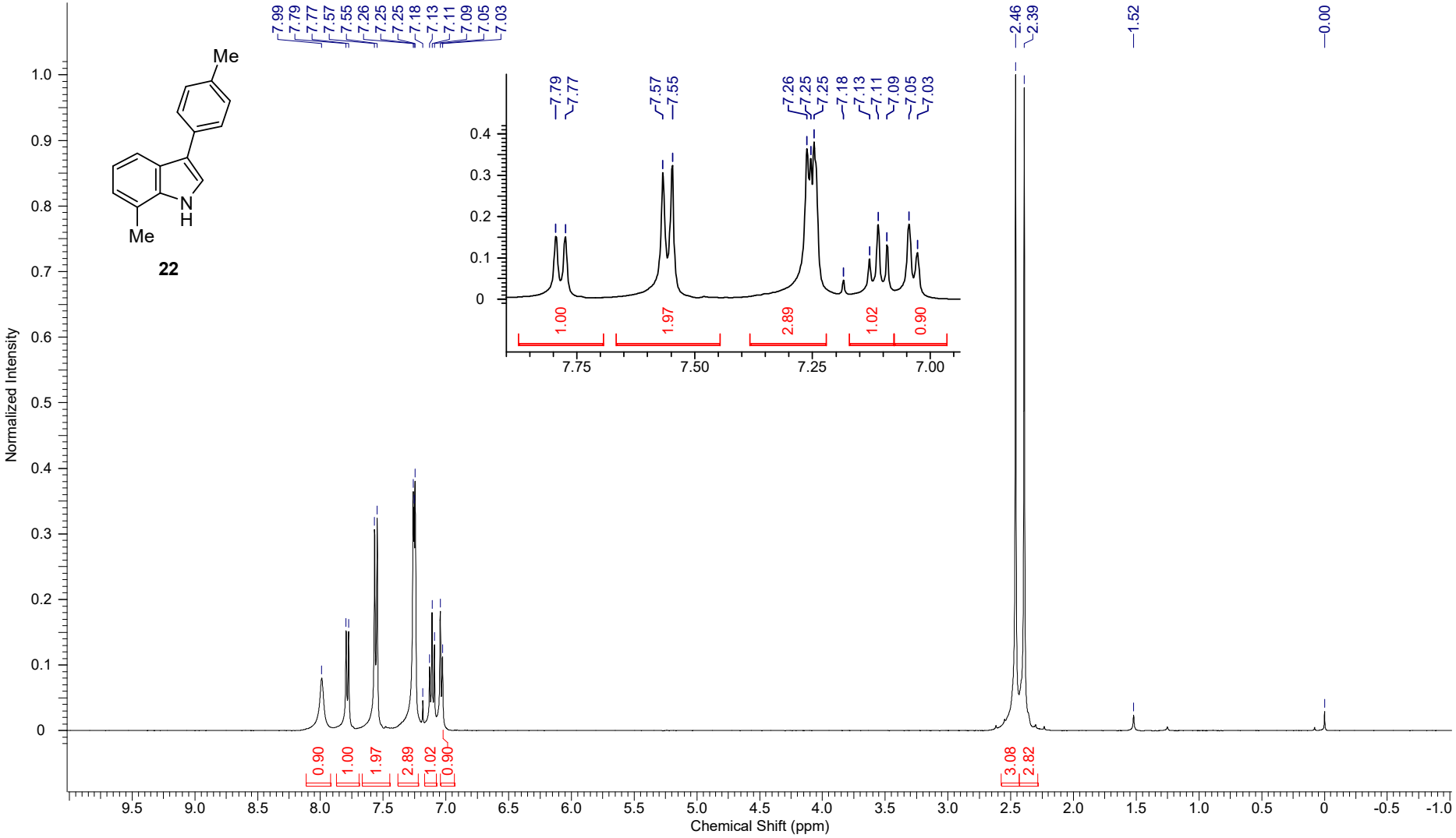
Acquisition Time (sec)	2.0500	*Comment*	YS 135-2 dried			*Date*	20 Feb 2017 09:49:24
Date Stamp	Mon Feb 20 09:49:23 2017			*File Name*	E:¥NMRspectra¥compound21¥compound21_1H.als	*Frequency (MHz)*	399.65
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	NON
Receiver Gain	11.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	1972.5132	*Sweep Width (Hz)*	7992.01
Temperature (degree C)	19.100								



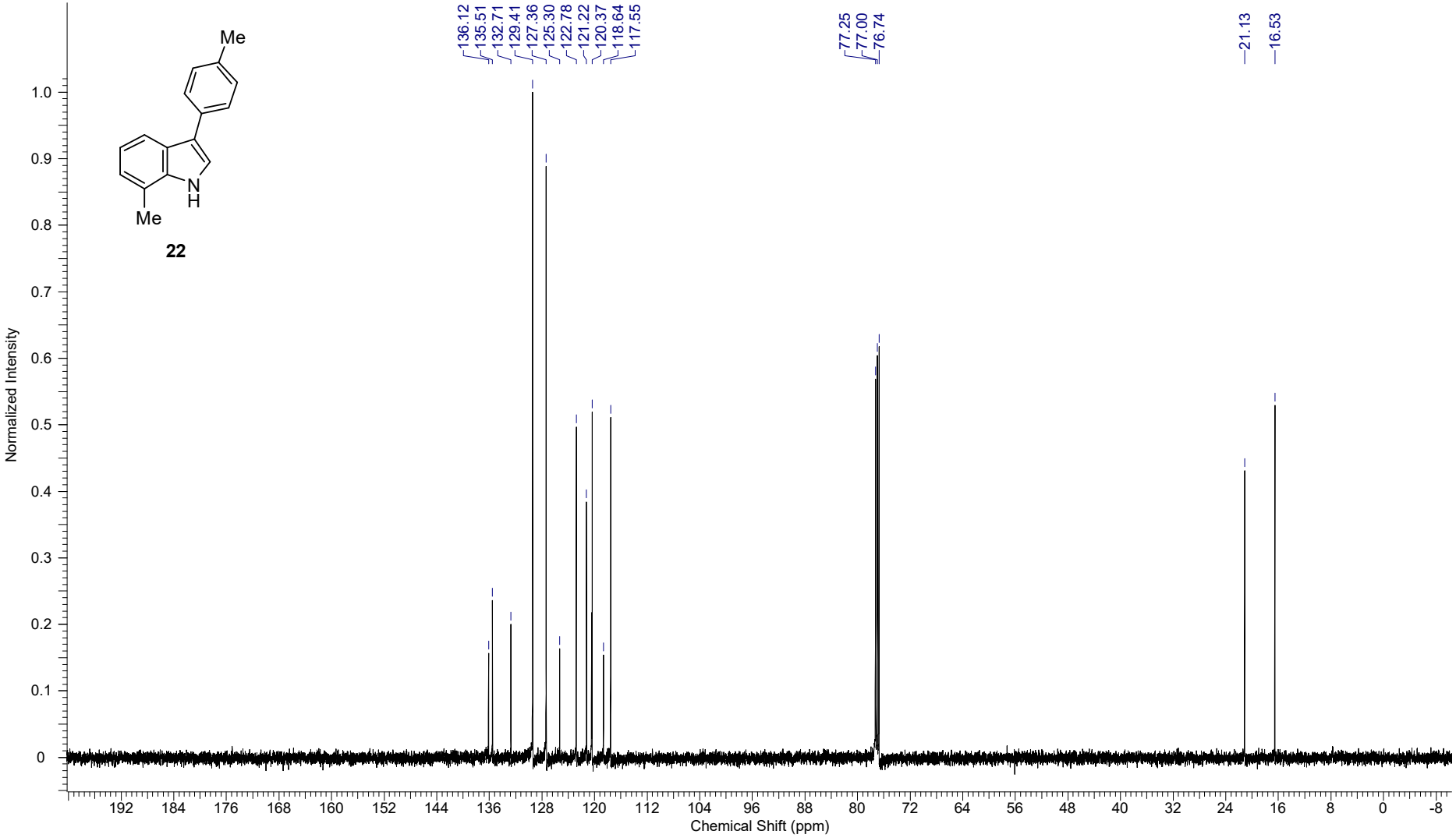
Acquisition Time (sec)	0.8336	*Comment*	YS 135-2	*Date*	20 Feb 2017 13:36:02			*Date Stamp*	20 Feb 2017 13:29:50
File Name	E:¥NMRspectra¥compound21¥compound21_13C.1			*Frequency (MHz)*	125.77	*Nucleus*	13C	*Number of Transients*	500
Origin	ECA500	*Original Points Count*	32768	*Owner*	delta	*Points Count*	32768	*Pulse Sequence*	single_pulse_dec
Receiver Gain	60.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12554.0352	*Spectrum Type*	STANDARD
Sweep Width (Hz)	39308.18	*Temperature (degree C)*	21.100						



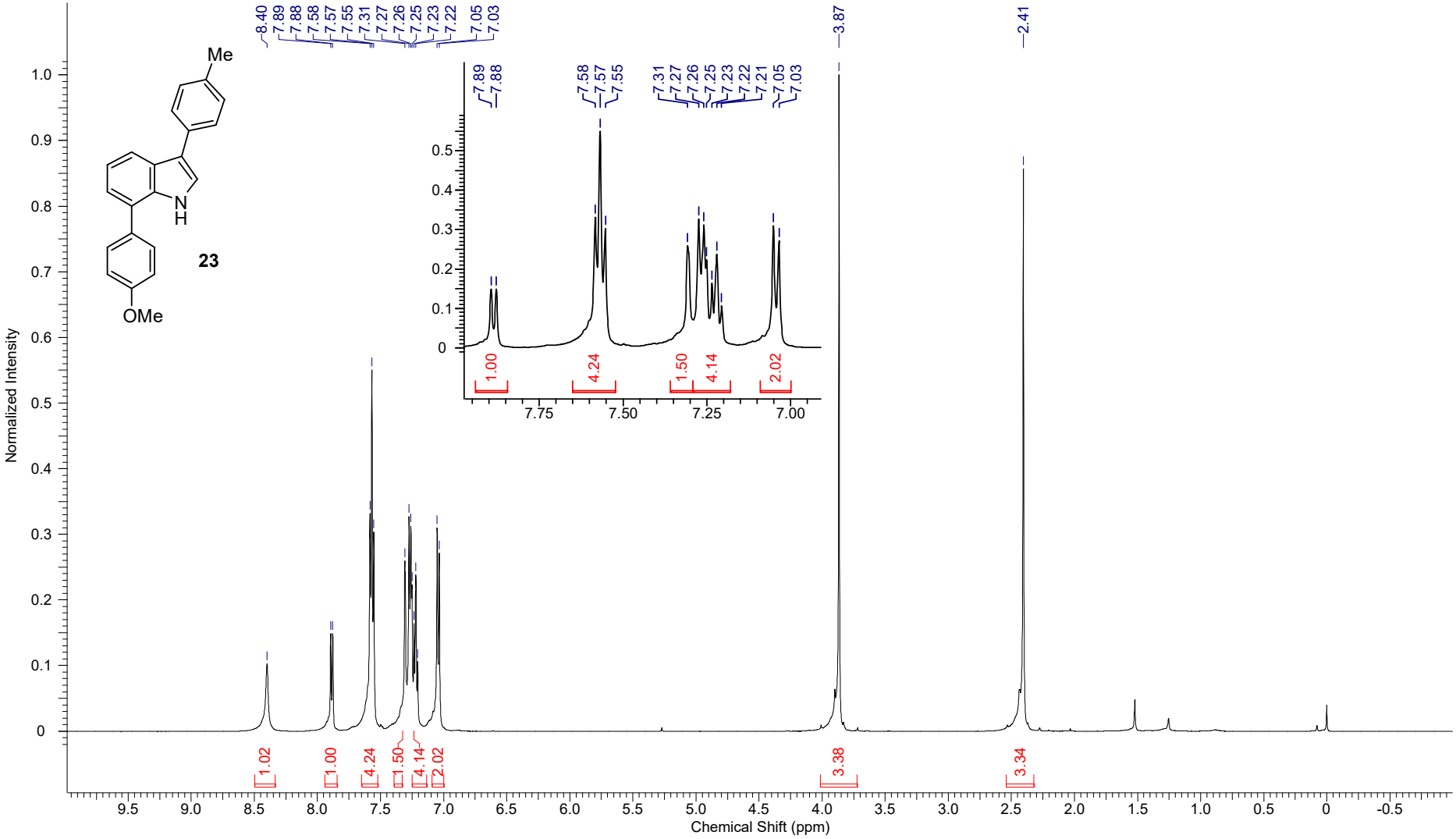
Acquisition Time (sec)	2.0500	*Comment*	YS 142 column-2			*Date*	02 Mar 2017 10:38:28
Date Stamp	Thu Mar 02 10:38:27 2017			*File Name*	E:¥NMRspectra¥compound22¥compound22_1H.als	*Frequency (MHz)*	399.65
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	NON
Receiver Gain	11.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	1961.2931	*Sweep Width (Hz)*	7992.01
Temperature (degree C)	15.900								



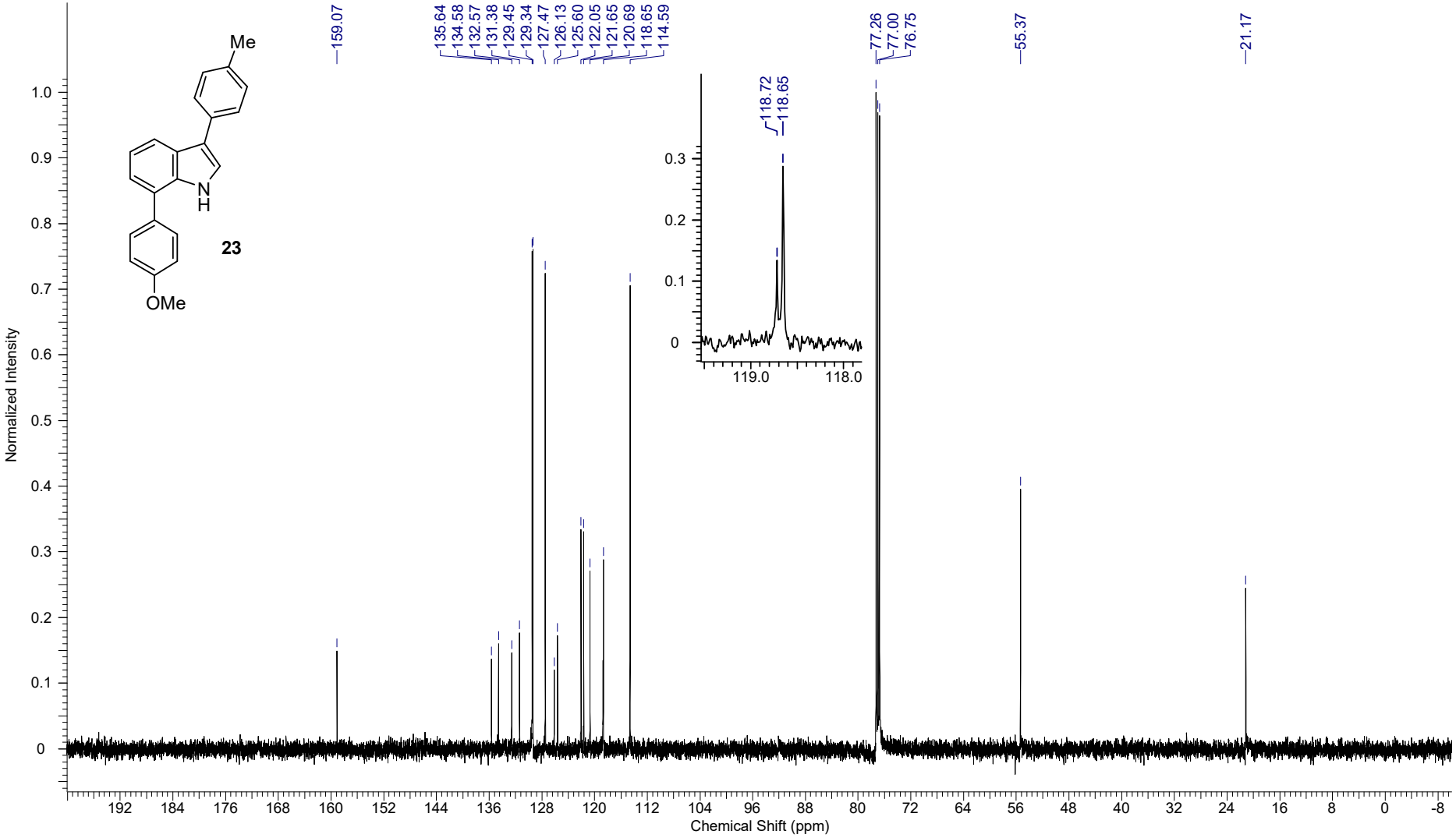
Acquisition Time (sec)	0.8389	*Comment*	YS 142-2 carbon			*Date*	06 Mar 2017 08:01:48
Date Stamp	06 Mar 2017 07:34:24			*File Name*	E:¥NMRspectra¥compound22¥compound22_13C.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	500	*Origin*	ECA 500	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	single_pulse_dec			*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	12424.4404	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50	*Temperature (degree C)*	22.000		



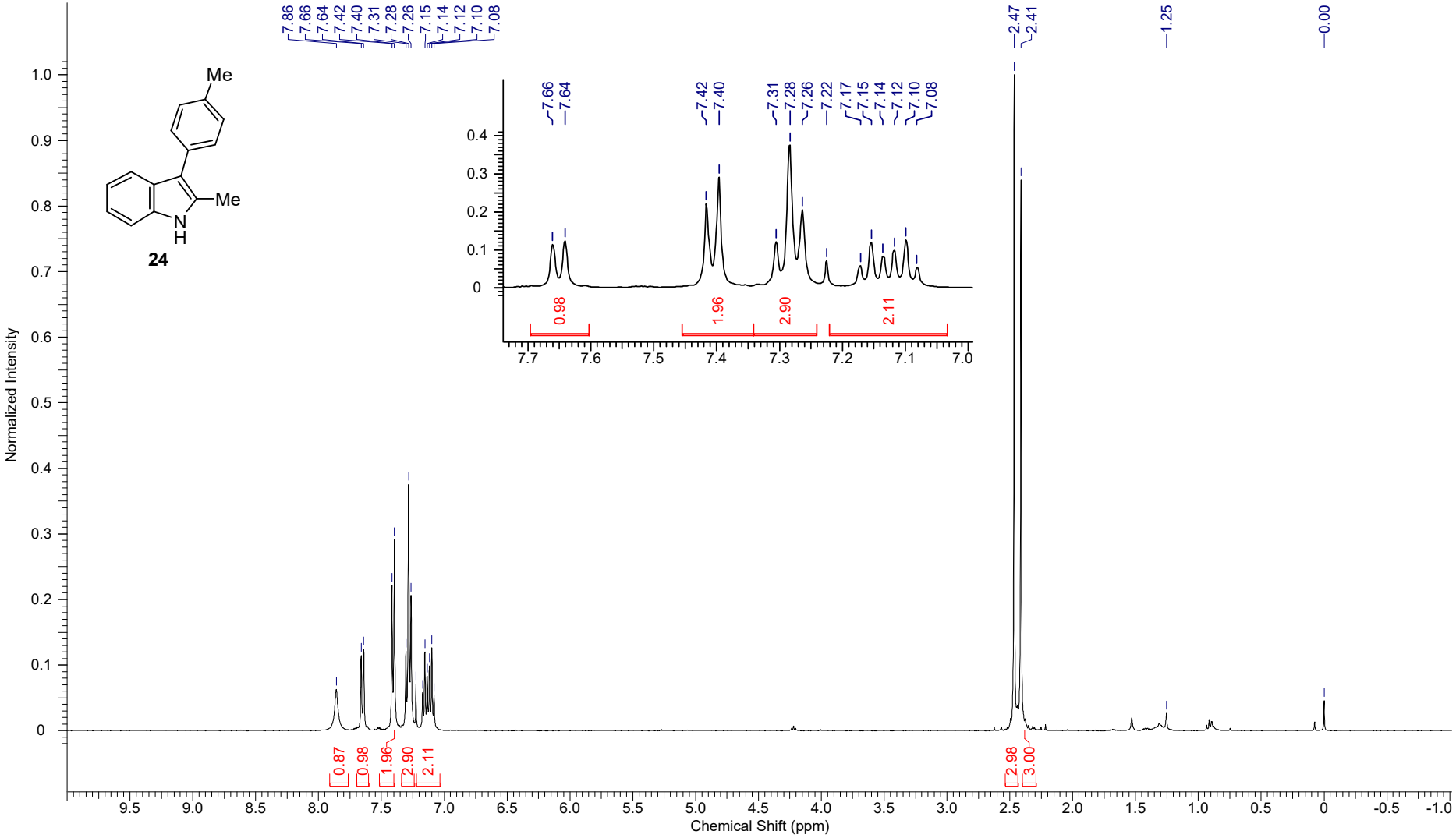
Acquisition Time (sec)	1.7642	*Comment*	single_pulse	*Date*	22 Jan 2017 14:03:01			*Date Stamp*	22 Jan 2017 13:37:48
File Name	E:¥NMRspectra¥compound23¥compound23_1H.jdf			*Frequency (MHz)*	495.13	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA 500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	34.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2460.9983	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9286.78	*Temperature (degree C)*	21.000						



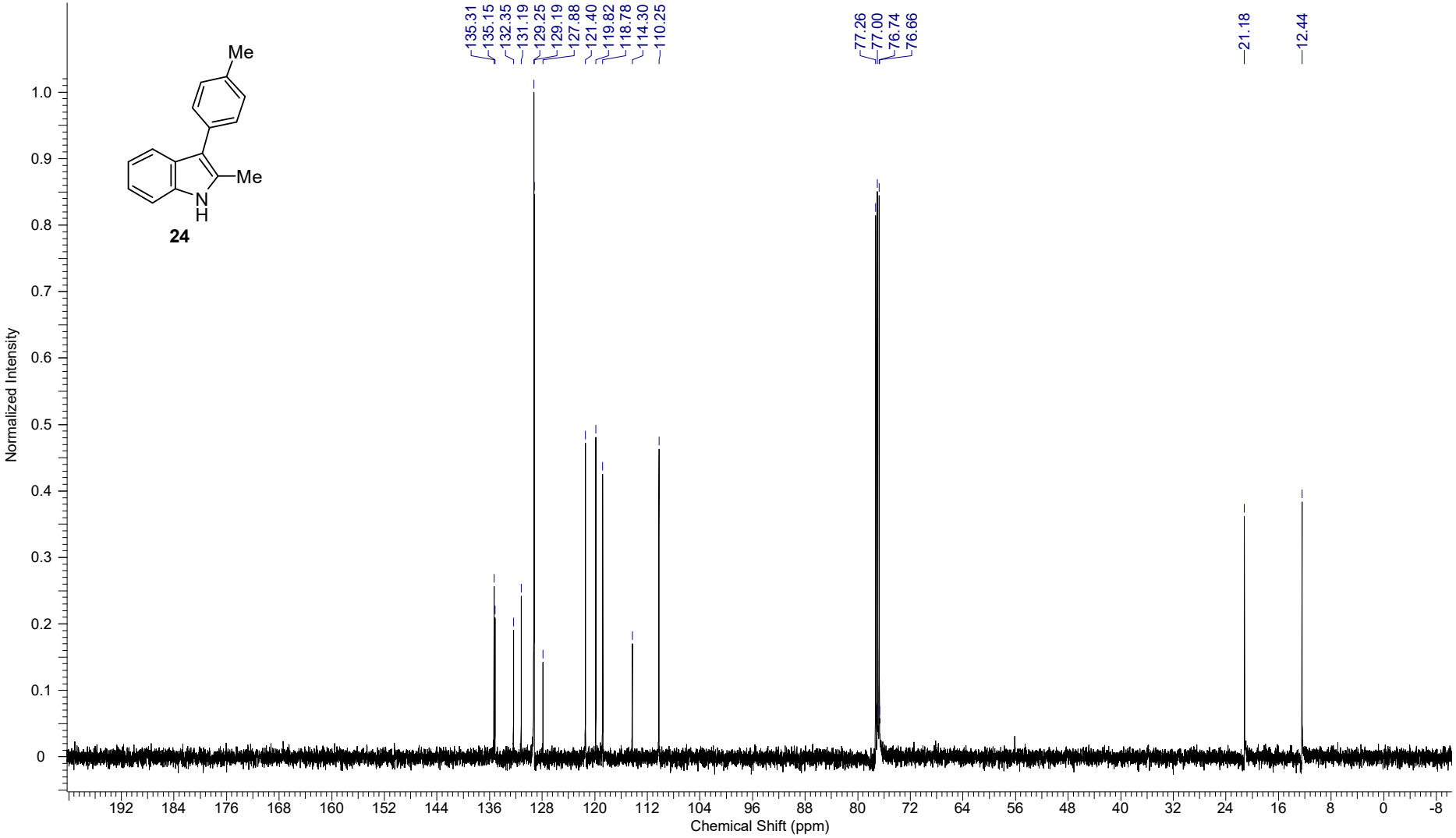
Acquisition Time (sec)	0.8389	***Comment***	single pulse decoupled gated NOE			***Date***	22 Jan 2017 14:22:43
Date Stamp	22 Jan 2017 13:57:30			***File Name***	E:¥NMRspectra¥compound23¥compound23_13C.jdf	***Frequency (MHz)***	124.50
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA 500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec	***Receiver Gain***	56.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12431.5947	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50	***Temperature (degree C)***	21.300



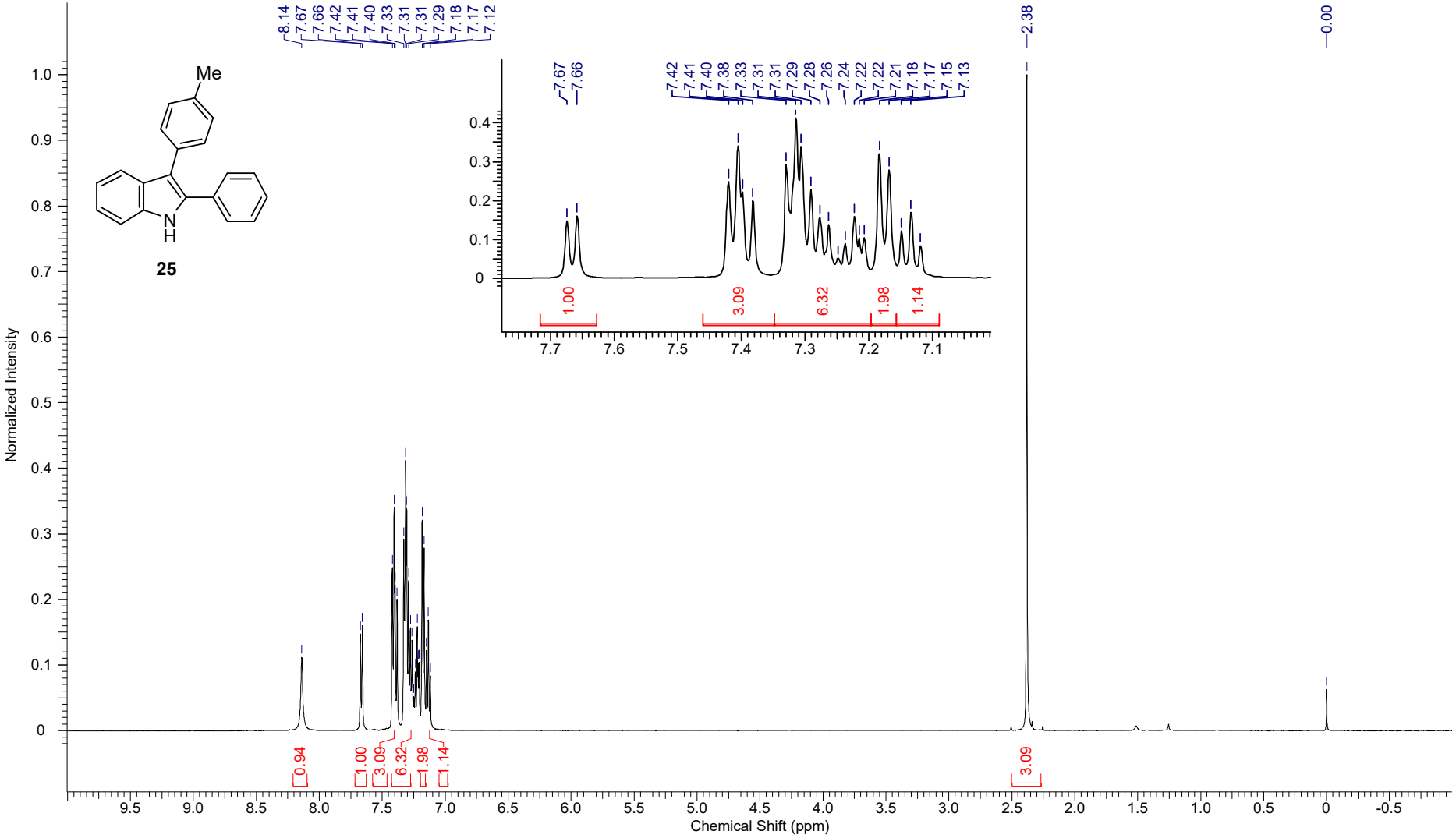
Acquisition Time (sec)	2.0500	*Comment*	YS 129 column third-2 dried			*Date*	26 Jan 2017 10:05:52
Date Stamp	Thu Jan 26 10:05:50 2017			*File Name*	E:¥NMRspectra¥compound24¥compound24_1H.als	*Frequency (MHz)*	399.65
Nucleus	1H	*Number of Transients*	8	*Original Points Count*	16384	*Points Count*	16384	*Pulse Sequence*	NON
Receiver Gain	13.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	1977.8792	*Sweep Width (Hz)*	7992.01
Temperature (degree C)	20.500								



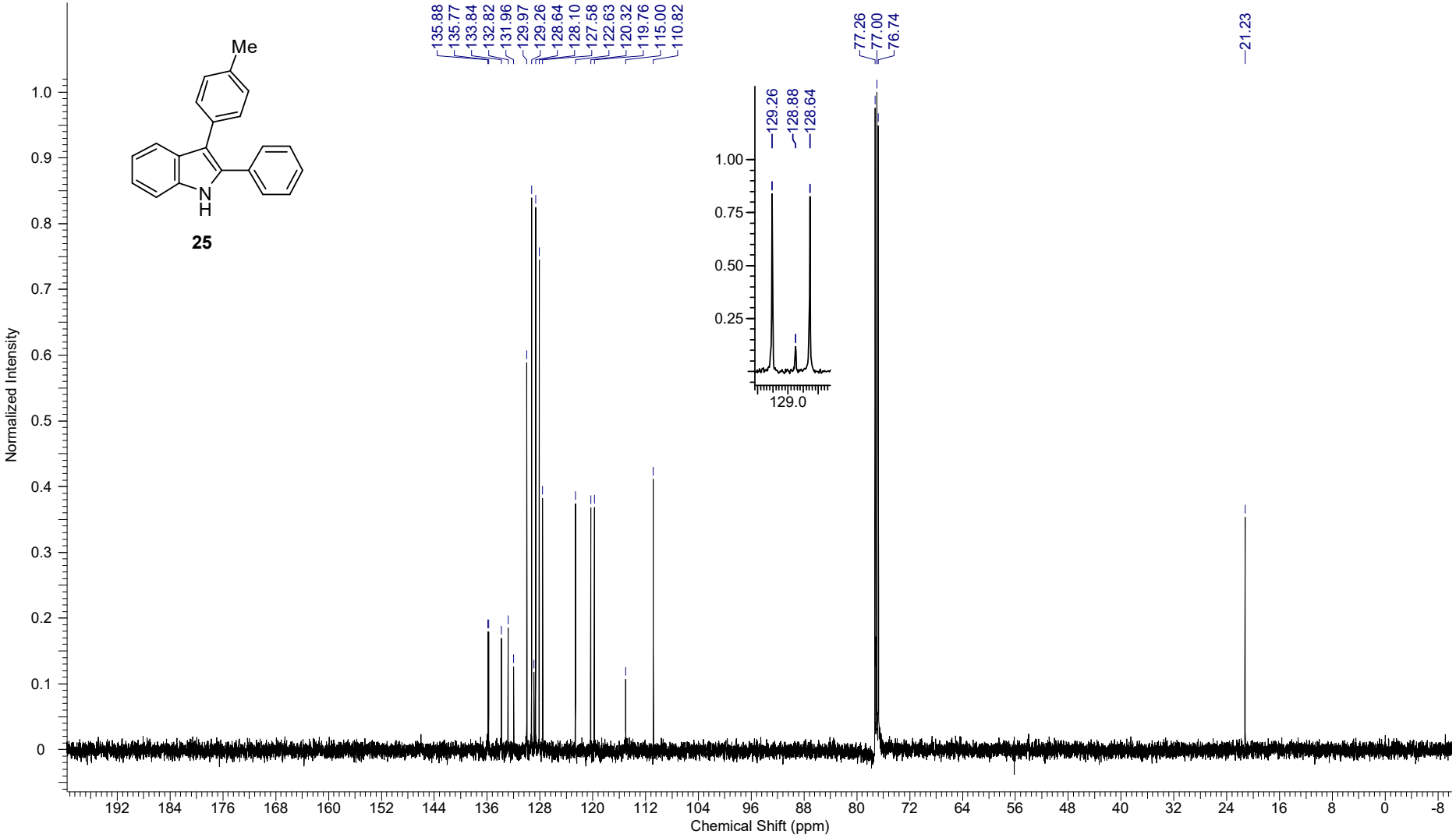
Acquisition Time (sec)	0.8389	***Comment***	YS 129 column third-2 carbon			***Date***	25 Jan 2017 15:08:53
Date Stamp	25 Jan 2017 14:42:07			***File Name***	E:¥NMRspectra¥compound24¥compound24_13C.jdf	***Frequency (MHz)***	124.50
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA 500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec			***Receiver Gain***	50.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12428.0186	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50	***Temperature (degree C)***	22.300		



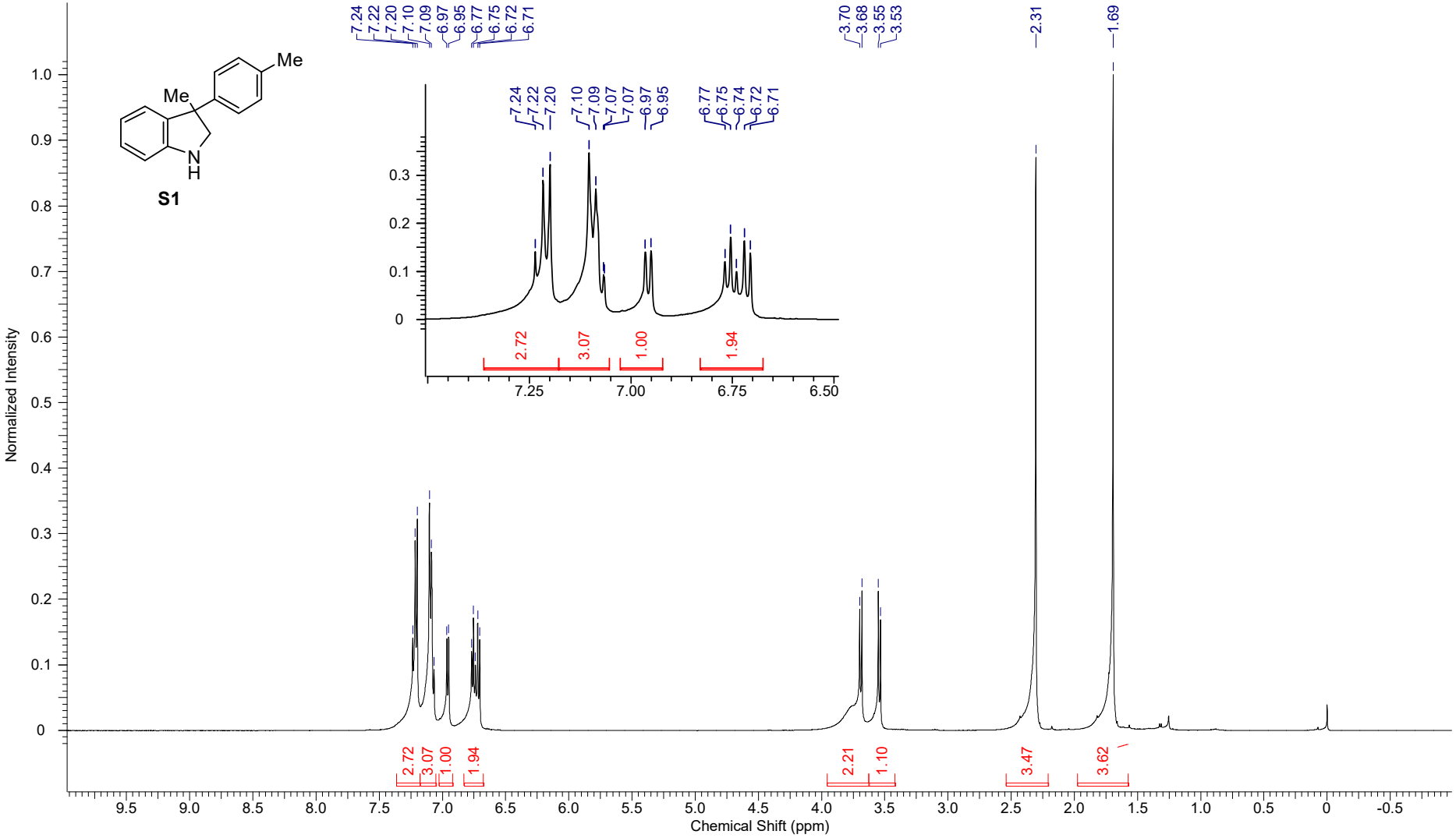
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	06 Jan 2017 08:04:53			*Date Stamp*	06 Jan 2017 07:56:48
File Name	E:¥NMRspectra¥compound25¥compound25_1H.1			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	40.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2481.1367	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9384.38	*Temperature (degree C)*	23.000						



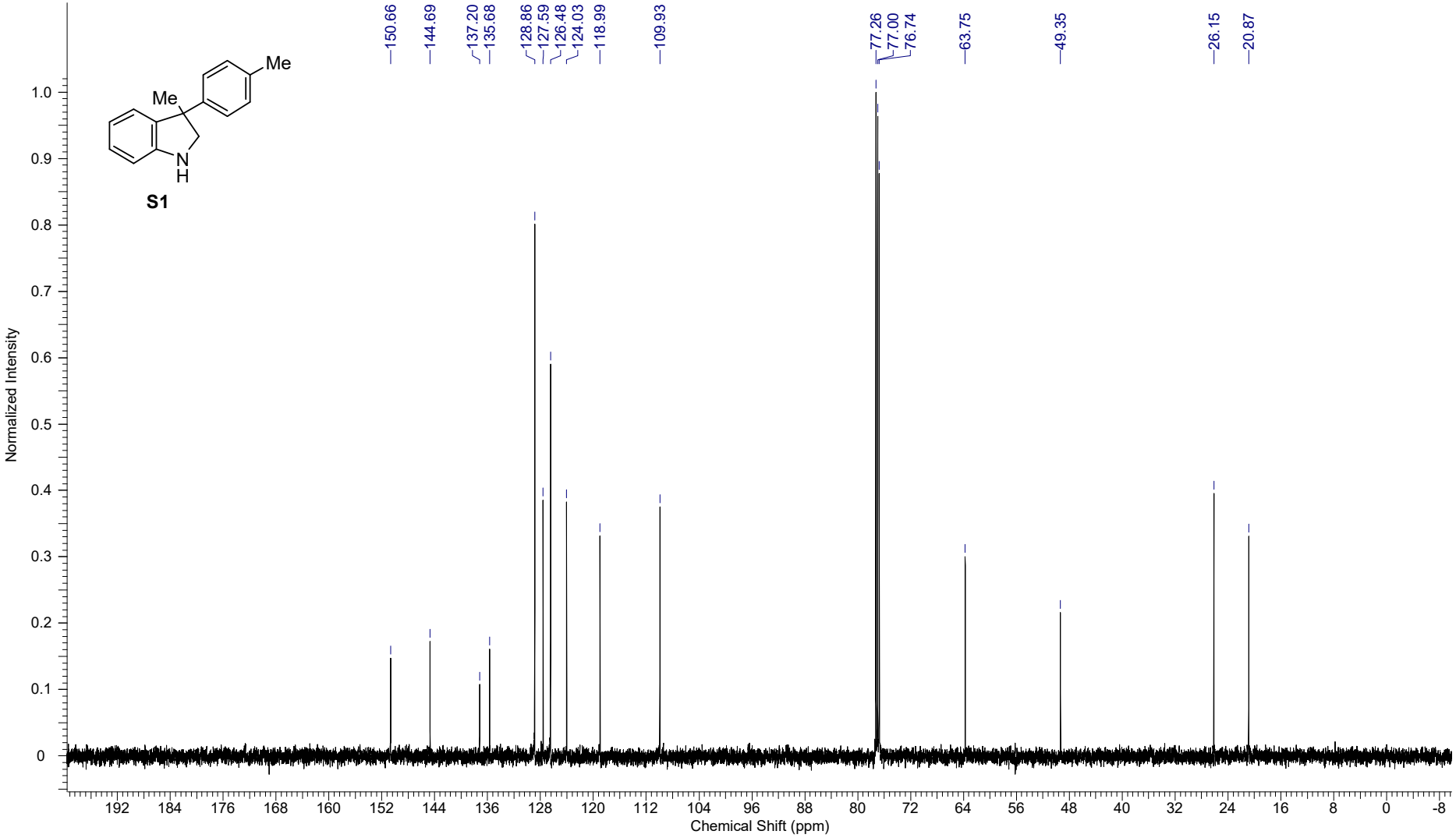
Acquisition Time (sec)	0.8389	***Comment***	single pulse decoupled gated NOE			***Date***	24 Dec 2016 02:02:16
Date Stamp	24 Dec 2016 01:36:18			***File Name***	E:¥NMRspectra¥compound25¥compound25_13C.jdf	***Frequency (MHz)***	124.50
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA 500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec	***Receiver Gain***	48.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12432.7861	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39062.50	***Temperature (degree C)***	25.600



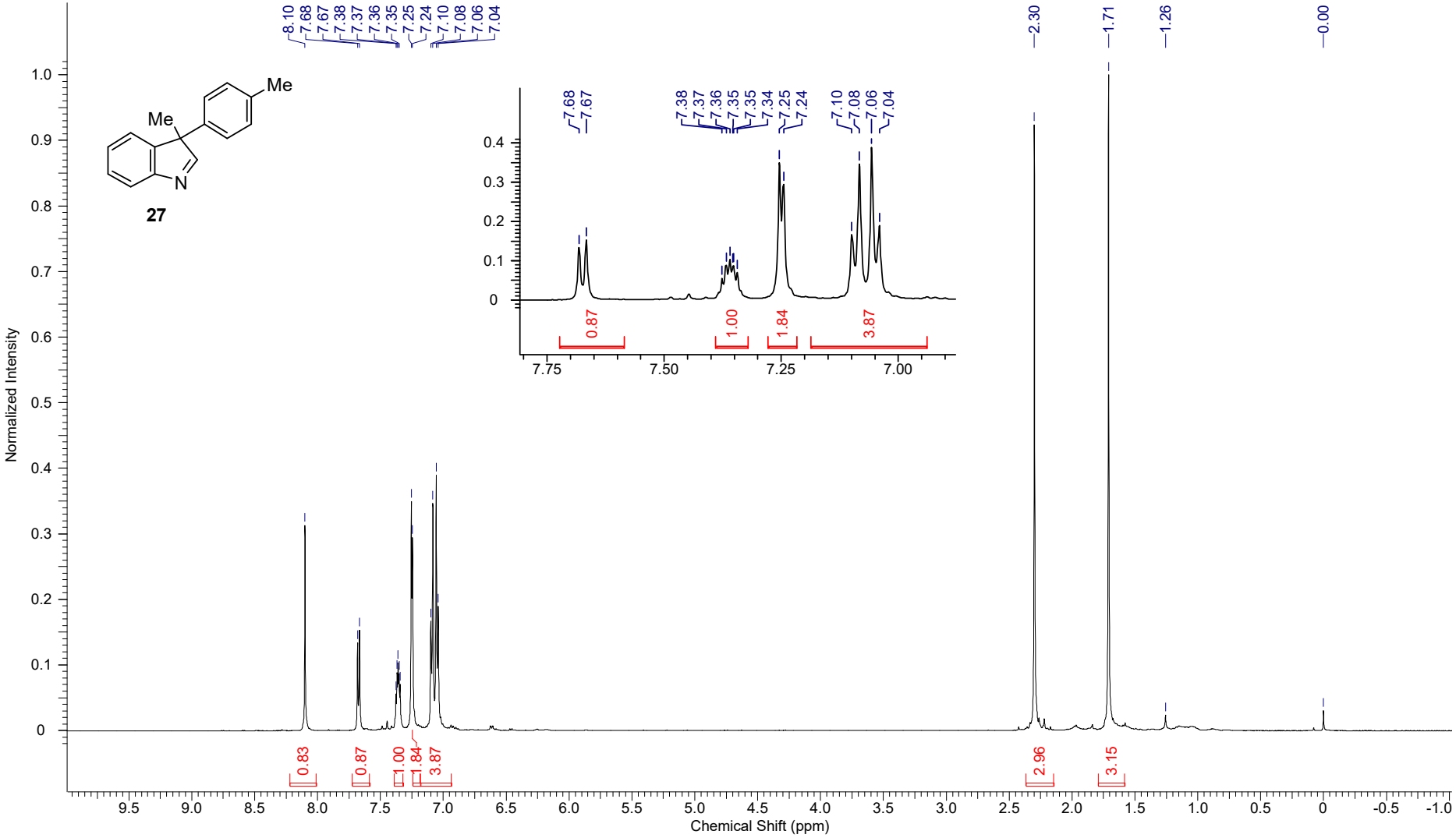
Acquisition Time (sec)	1.7459	*Comment*	YS 148 PTLC-5			*Date*	16 Mar 2017 13:13:58
Date Stamp	16 Mar 2017 13:07:38			*File Name*	E:¥NMRspectra¥compoundS1¥compoundS1_1H.1	*Frequency (MHz)*	500.16
Nucleus	1H	*Number of Transients*	8	*Origin*	ECA500	*Original Points Count*	16384
Owner	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2	*Receiver Gain*	42.00
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	2492.0200	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	9384.38



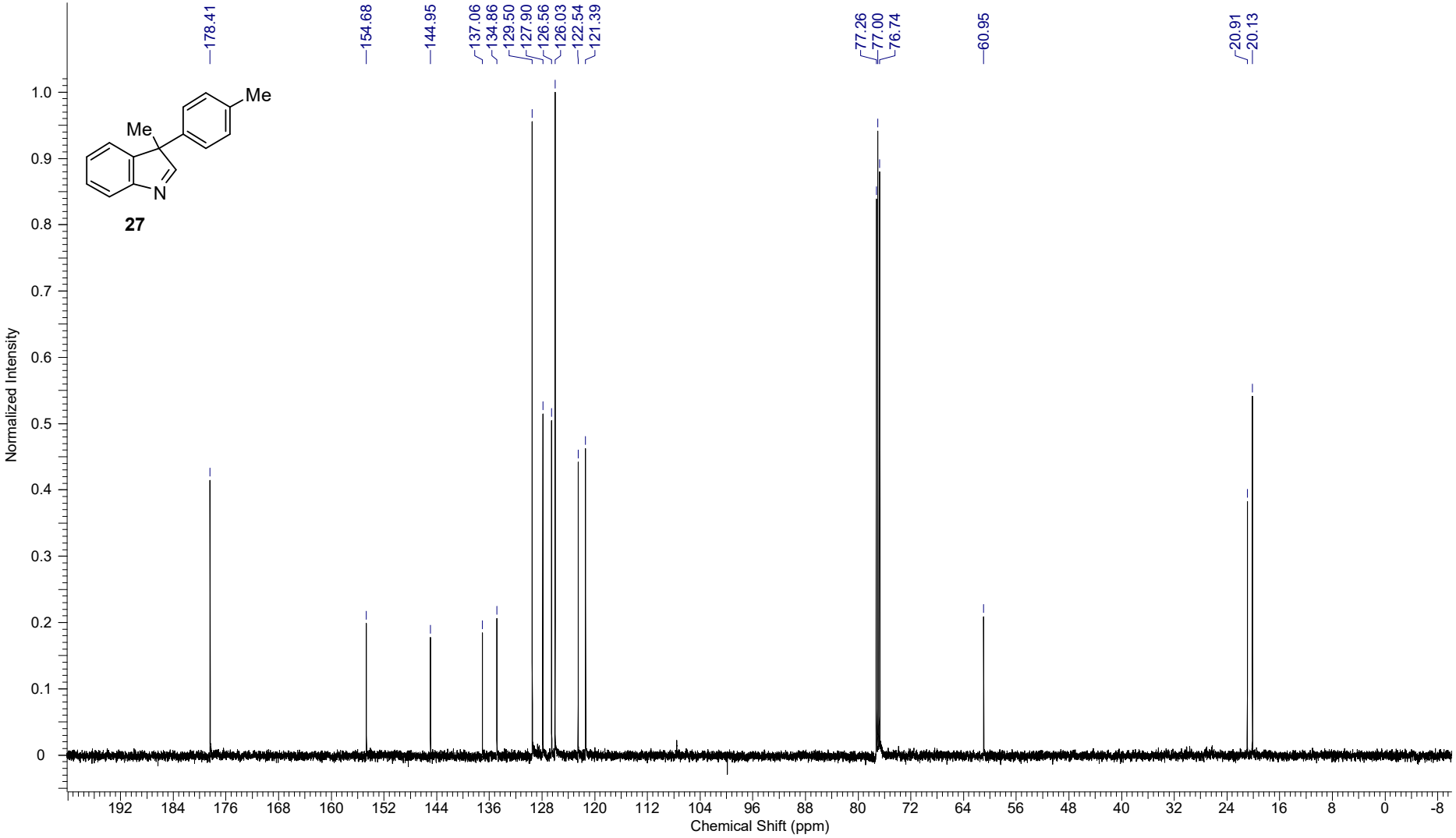
Acquisition Time (sec)	0.8389	*Comment*	YS 148 PTLC-5 carbon			*Date*	18 Mar 2017 13:19:23
Date Stamp	18 Mar 2017 12:52:13			*File Name*	E:¥NMRspectra¥compoundS1¥compoundS1-13C.jdf	*Frequency (MHz)*	124.50
Nucleus	13C	*Number of Transients*	500	*Origin*	ECA 500	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	single_pulse_dec			*Receiver Gain*	50.00	*Solvent*	CHLOROFORM-d
Spectrum Offset (Hz)	12432.7861	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39062.50	*Temperature (degree C)*	22.000		



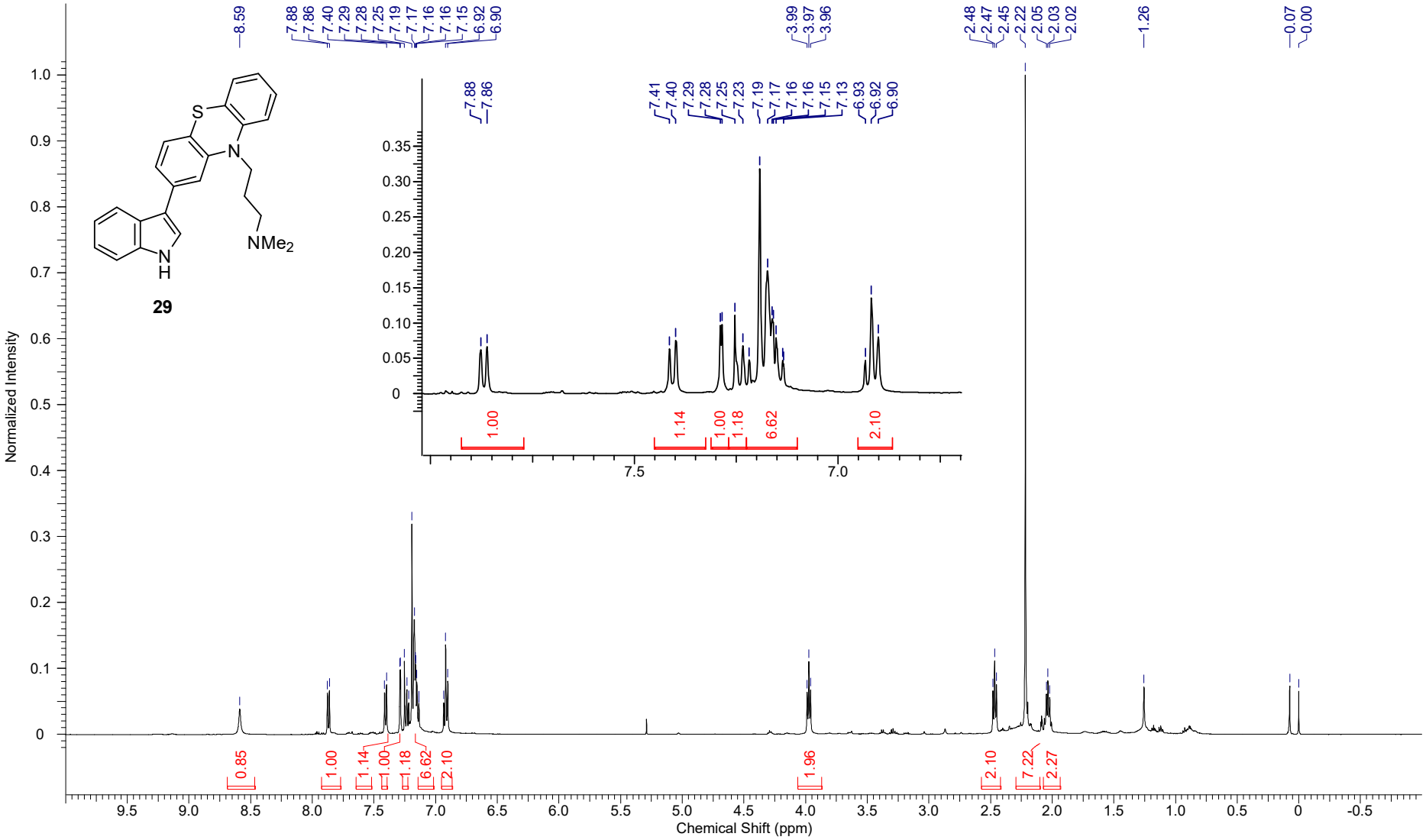
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	06 Jan 2017 07:49:19			*Date Stamp*	06 Jan 2017 07:41:15
File Name	E:¥NMRspectra¥compound27¥compound27_1H.1			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	40.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2496.0298	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9384.38	*Temperature (degree C)*	23.300						



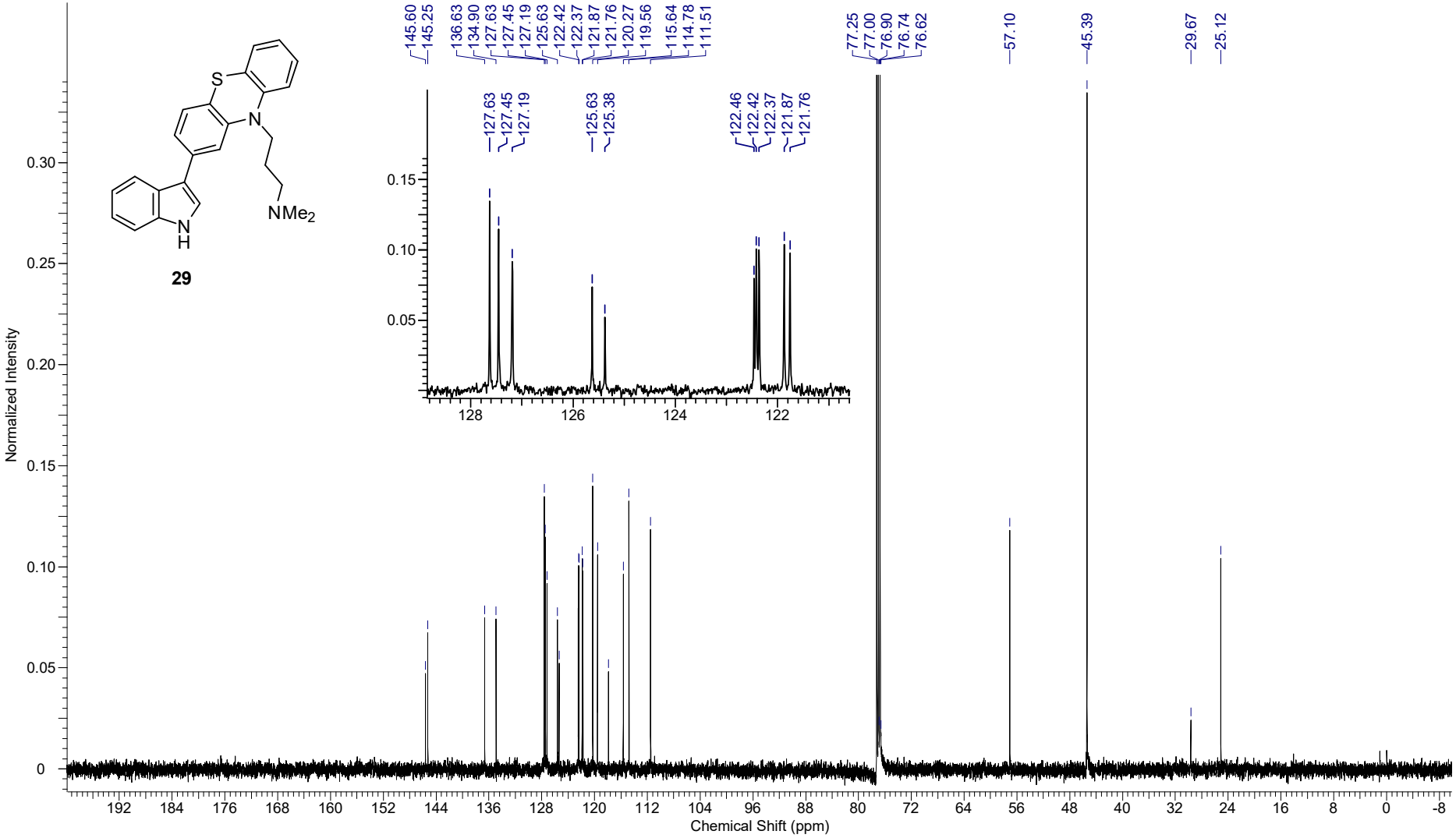
Acquisition Time (sec)	0.8336	***Comment***	single pulse decoupled gated NOE			***Date***	06 Jan 2017 09:04:44
Date Stamp	06 Jan 2017 08:56:40			***File Name***	E:¥NMRspectra¥compound27¥compound27_13C.1	***Frequency (MHz)***	125.77
Nucleus	13C	***Number of Transients***	500	***Origin***	ECA500	***Original Points Count***	32768	***Owner***	delta
Points Count	32768	***Pulse Sequence***	single_pulse_dec			***Receiver Gain***	60.00	***Solvent***	CHLOROFORM-d
Spectrum Offset (Hz)	12557.6338	***Spectrum Type***	STANDARD	***Sweep Width (Hz)***	39308.18	***Temperature (degree C)***	23.400		



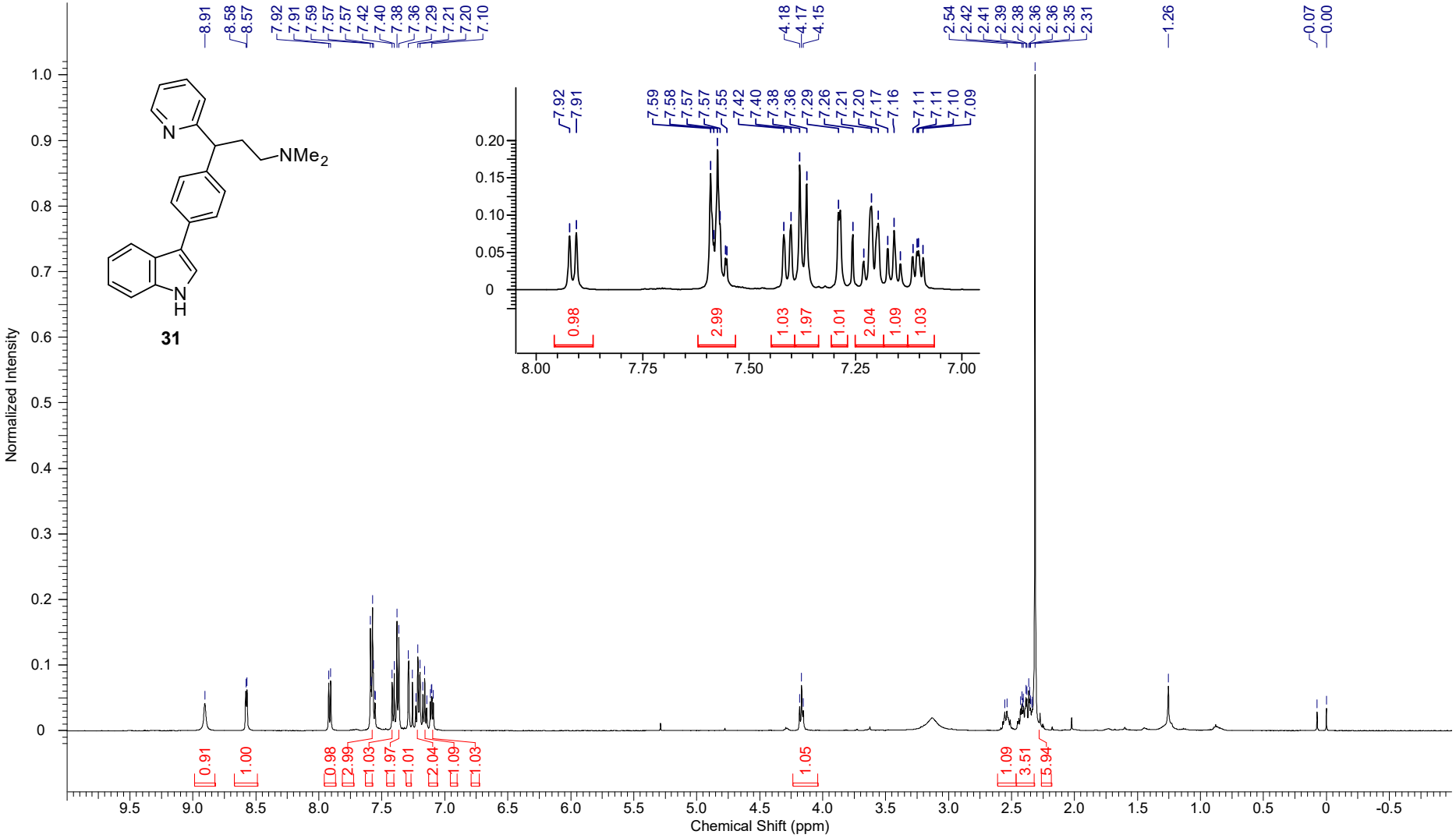
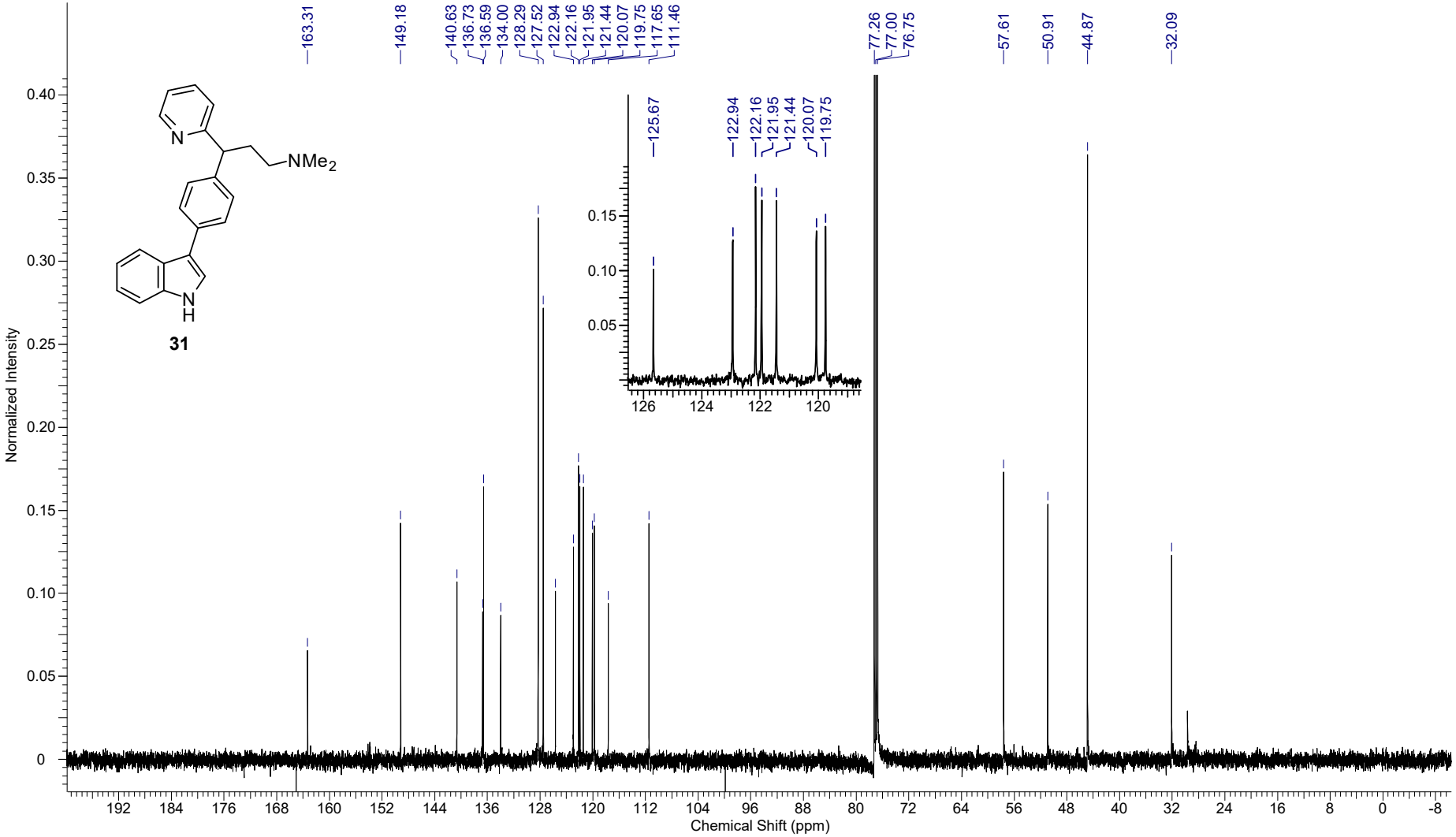
Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	28 Jun 2017 15:58:10			*Date Stamp*	28 Jun 2017 15:57:22
File Name	E:¥NMRspectra¥compound29¥compound29_1H.jdf			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	proton.jxp
Solvent	CHLOROFORM-d			*Spectrum Offset (Hz)*	2500.0396	*Sweep Width (Hz)*	9384.38	*Temperature (degree C)*	22.100



Acquisition Time (sec)	0.8336	*Comment*	single pulse decoupled gated NOE			*Date*	28 Jun 2017 16:35:11
Date Stamp	28 Jun 2017 15:58:20			*File Name*	E:¥NMRspectra¥compound29¥compound29_13C.jdf	*Frequency (MHz)*	125.77
Nucleus	13C	*Number of Transients*	1024	*Origin*	ECA	*Original Points Count*	32768	*Owner*	delta
Points Count	32768	*Pulse Sequence*	carbon.jxp	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	12560.0332
Sweep Width (Hz)	39308.18	*Temperature (degree C)*	22.200						



Acquisition Time (sec)	1.7459	*Comment*	single_pulse	*Date*	12 Jul 2017 16:45:24			*Date Stamp*	12 Jul 2017 16:39:54
File Name	E:¥NMRspectra¥compound31¥compound31_1H.1			*Frequency (MHz)*	500.16	*Nucleus*	1H	*Number of Transients*	8
Origin	ECA500	*Original Points Count*	16384	*Owner*	delta	*Points Count*	16384	*Pulse Sequence*	single_pulse.ex2
Receiver Gain	42.00	*Solvent*	CHLOROFORM-d			*Spectrum Offset (Hz)*	2501.7581	*Spectrum Type*	STANDARD
Sweep Width (Hz)	9384.38	*Temperature (degree C)*	21.700						



Acquisition Time (sec)	0.8336	*Comment*	single pulse decoupled gated NOE			*Date*	12 Jul 2017 17:22:01
Date Stamp	12 Jul 2017 17:16:30			*File Name*	E:¥NMRspectra¥compound31¥compound31_13C.1	*Frequency (MHz)*	125.77
Nucleus	13C	*Number of Transients*	1000	*Origin*	ECA500	*Original Points Count*	32768
Owner	delta	*Points Count*	32768	*Pulse Sequence*	single_pulse_dec	*Receiver Gain*	60.00
Solvent	CHLOROFORM-d	*Spectrum Offset (Hz)*	12560.0332	*Spectrum Type*	STANDARD	*Sweep Width (Hz)*	39308.18
Temperature (degree C)	22.300