Supporting Information:

Nickel-Catalyzed Direct Alkynylation of C(sp^2)-H Bonds of Amides: An "Inverse Sonogashira Strategy" to *ortho*-alkynylbenzoic acids

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Contents

1. General Information

All catalytic experiments were carried out using standard Schlenk techniques. All solvents were reagent grade or better. Deuterated solvents were used as received. Toluene was refluxed over sodium/benzophenone ketyl and distilled under argon atmosphere and stored over sodium. Metal complexes and other chemicals used in catalysis reactions were used without additional purification. Thin layer chromatography (TLC) was performed using silica gel precoated glass plates, which were visualized with visualized with UV light at 254 nm or under iodine. Column chromatography was performed with SiO_2 (Silicycle Siliaflash F60 (230-400 mesh). ^{1}H NMR (400 or 500 MHz), $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra were recorded on the NMR spectrometer. Deuterated chloroform was used as the solvent, and chemical shift values (δ) are reported in parts per million relative to the residual signals of this solvent [δ 7.26 for ^{1}H (chloroform-d), δ 77.2 for 13C$\{^{1}H\}$ (chloroform-d). Abbreviations used in the NMR follow-up experiments: br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. GC analysis was carried out using a HP-5 column (30 m, 0.25 mm, 0.25μ). Mass spectra were obtained on a GCMS-QP 5000 instruments with ionization voltages of 70 eV. High resolution mass spectra (HRMS) were obtained on a High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electron impact (EI) ionization technique (magnetic sector−electric sector double focusing mass analyzer).

2. Experimental Section

2.1 Synthesis of the Starting Materials

All amides bearing 8-aminoquinoline moiety were prepared by the reaction of the corresponding acid chlorides with 8-aminoquinoline.[S1,S2] (Bromoethynyl)triisopropylsilane (**2**, CAS 111409-79-1) was prepared by previously reported $AgNO_3$-catalyzed bromination of (triisopropylsilyl)acetylene with *N*-bromosuccinimide.[S3]

2.2 General Procedure for the Ni(II)-Catalyzed C-H Alkynylation

To an oven-dried 10 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide **1a** (0.1 mmol), (bromoethynyl)triisopropylsilane **2** (0.2 mmol), $Ni(OTf)_2$ (5 mol%), benzoic acid (10 mol%), Na_2CO_3 (0.2 mmol) and toluene (1 mL) were added under a gentle stream of argon. The mixture was stirred for 24 hrs at 110 °C (reflux temperature of toluene) followed by cooling to room temperature. The mixture was filtered through a celite pad and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether/EtOAc) to afford the desired alkynylated products.

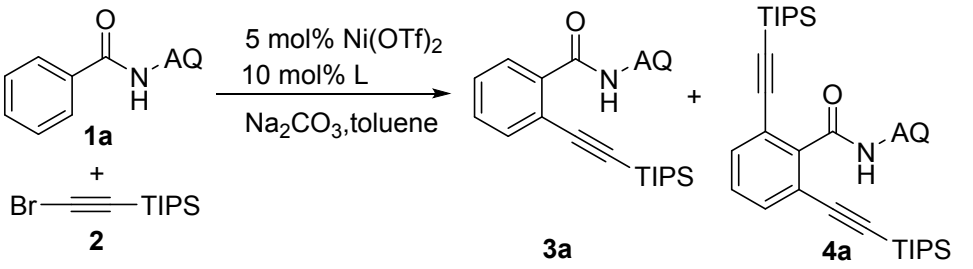
2.3 Gram-scale reaction of the Ni(II)-Catalyzed *ortho*-C-H Alkynylation

To an oven-dried 20 mL screw-capped vial, *2-chloro-N-(quinolin-8-yl)benzamide* **1d** (987 mg, 3.5 mol), (bromoethynyl)triisopropylsilane **2** (1820 mg, 7 mol), $Ni(OTf)_2$ (62 mg, 5 mol%), benzoic acid (42 mg, 10 mol%), Na_2CO_3 (735 mg, 7 mol) and toluene (10 mL) were

added under a gentle stream of argon. The mixture was stirred for 24 hrs at 110 °C (reflux temperature of toluene) followed by cooling to room temperature. The mixture was filtered through a celite pad and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether/EtOAc = 10/1) the yield of desired mono alkynylated product **3d** (1.377 g; 85%).

3. Optimization of Reaction Conditions

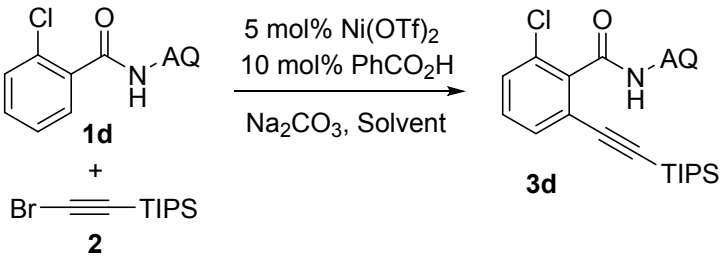
3.1 Effect of Ligand[a]



Entry	Ligand (L)	Yield(%)[b] 3a	4a	Recovery of **1a** (%)[b]
1	PPh_3	21%	trace	69%
2	PCy_3	17%	21%	51%
3	Xantphos	4%	15%	79%
4	Dppb	trace	7%	88%
5	AdCOOH	21%	33%	40%

[a] Reaction conditions: **1a** (0.1 mmol), $Ni(OTf)_2$ (5 mol%), ligand (10 mol%), **2** (0.2 mmol), Na_2CO_3 (2 equiv), and toluene (1 mL) at 110 ^oC for 24 hrs under argon. [b] Isolated yields.

3.2 Effect of Solvent[a]



Entry	Solvent	Temp. (^{o}C)	Yield(%)[b] **3d**
1	Toluene	110	92%
2	DCE	85	41%
3	DMF	100	23%
4	DMSO	100	7%
5	1,4-Dioxane	100	13%

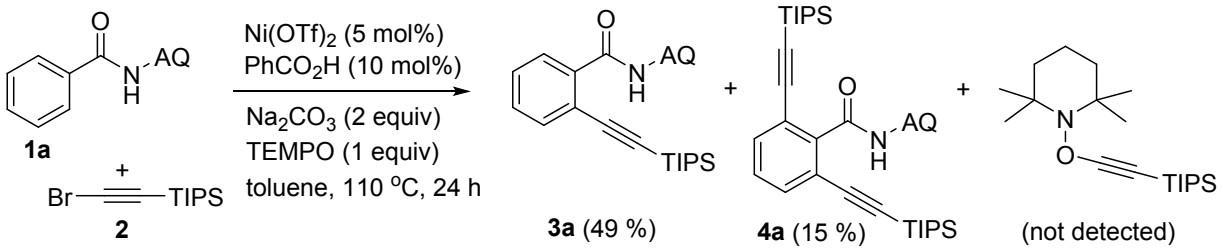
[a] Reaction conditions: **1d** (0.1 mmol), $Ni(OTf)_2$ (5 mol%), $PhCO_2H$ (10 mol%), **2** (0.2 mmol), Na_2CO_3 (2 equiv), and solvent (1 mL) at specified temperature for 24 hrs under argon. [b] Isolated yields.

4. Mechanistic Investigation

4.1 Radical Trapping Experiment

To an oven-dried 5 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide **1a** (0.3 mmol), (triisopropylsilyl)ethynyl bromide (0.9 mmol), TEMPO (0.3 mmol), $Ni(OTf)_2$ (5 mol %), $PhCO_2H$ (10 mol%), Na_2CO_3 (0.6 mmol) and toluene (1 mL) were added under Ar. The mixture was stirred for 24 hrs at 110 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was

concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (eluent: pet ether/EtOAc) to afford the alkynylated products **3a** and **4a** with isolated yield of 49% and 15% respectively along with 18% recovery of amide **1a**.



4.2 Product Distribution Studies: Product Distribution by Ni(0)

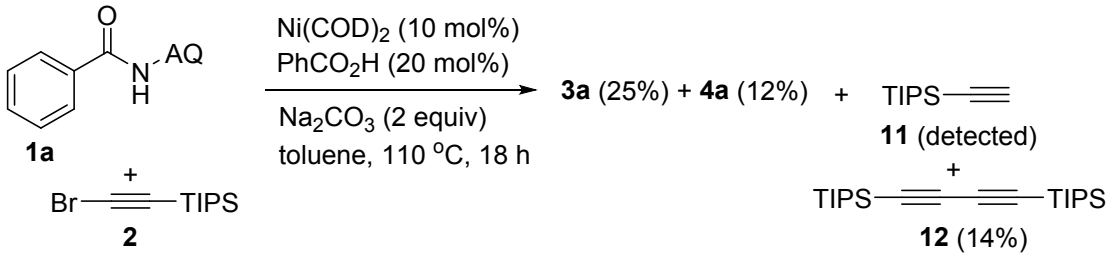
(a) To an oven-dried 5 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide **1a** (0.3 mmol), (triisopropylsilyl)ethynyl bromide (0.9 mmol), $Ni(cod)_2$ (10 mol%), $PhCO_2H$ (20 mol%), Na_2CO_3 (0.6 mmol) and toluene (1 mL) were added under argon atm. The mixture was stirred for 18 hrs at 110 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated. The yields of (triisopropylsilyl)acetylene (**11**) and 1,4-bis(triisopropylsilyl)buta-1,3-diyne (**12**) were determined by GC. And the self-coupled product (**12**) was isolated (~10%; and the GC yield is 14%).

GC programming:

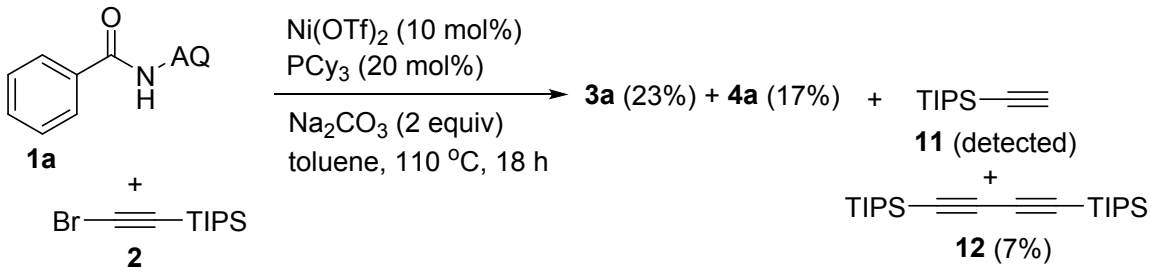
GC Column – HP-5 (30m x 0.25mm x 0.25mm); Injector temperature – 280 °C; Detector temperature – 280 °C; Column flow – 1.0 mL/min; Carrier gas – Nitrogen gas; Split Ratio – 10:1

(80 °C hold for 5 min, heated up to 280 °C with ramping rate 10 °C/min)

(Triisopropylsilyl)acetylene (**11**) R_t: 5.201 min, and 1,4 bis(triisopropylsilyl)buta-1,3-diyne (**12**) R_t: 11.099 min).

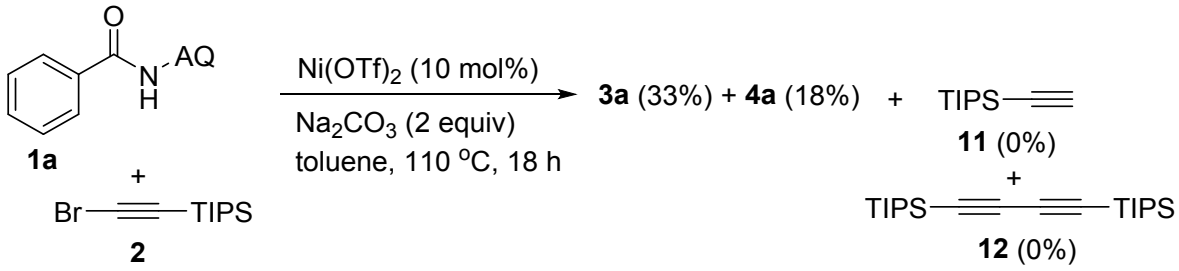


(b) To an oven-dried 5 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide **1a** (0.3 mmol), (triisopropylsilyl)ethynyl bromide (0.9 mmol), $Ni(OTf)_2$ (10 mol%), PCy_3 (20 mol%), Na_2CO_3 (0.6 mmol) and toluene (1 mL) were added under Ar. The mixture was stirred for 18 hrs at 110 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated. The yields of (triisopropylsilyl)acetylene (**11**) and 1,4-bis(triisopropylsilyl)buta-1,3-diyne (**12**) were determined by GC.

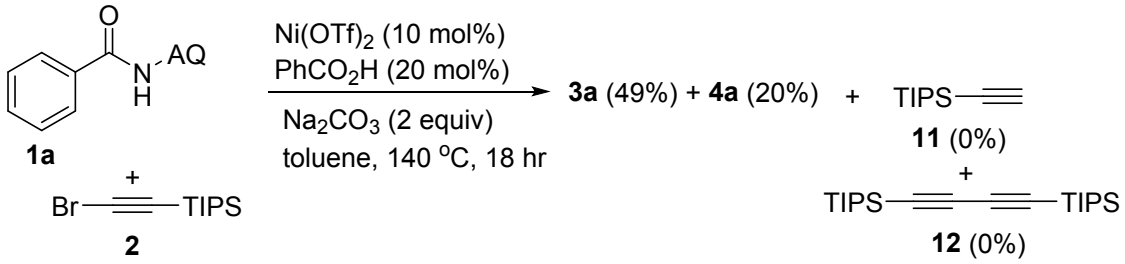


Product Distribution by Ni(II)

(a) To an oven-dried 5 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide (0.3 mmol), (triisopropylsilyl)ethynyl bromide (0.9 mmol), $Ni(OTf)_2$ (10 mol%), Na_2CO_3 (0.6 mmol) and toluene (1 mL) were added under argon atm. The mixture was stirred for 18 hrs at 110 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated. The products were analyzed by GC and GC-MS and no formation of either **11** or **12** were observed.

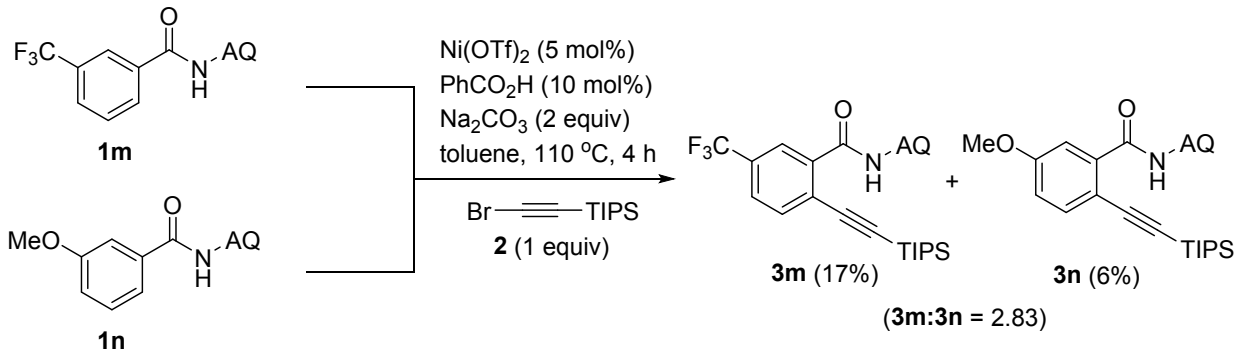


(b) To an oven-dried 5 mL screw-capped vial, *N*-(quinolin-8-yl)benzamide (0.3 mmol), (triisopropylsilyl)ethynyl bromide (0.9 mmol), $Ni(OTf)_2$ (10 mol%), $PhCO_2H$ (20 mol%), Na_2CO_3 (0.6 mmol) and toluene (1mL) were added under Ar. The mixture was stirred for 18 hr at 140 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated. The products were analyzed by GC and GC-MS and no formation of either **11** or **12** were observed.

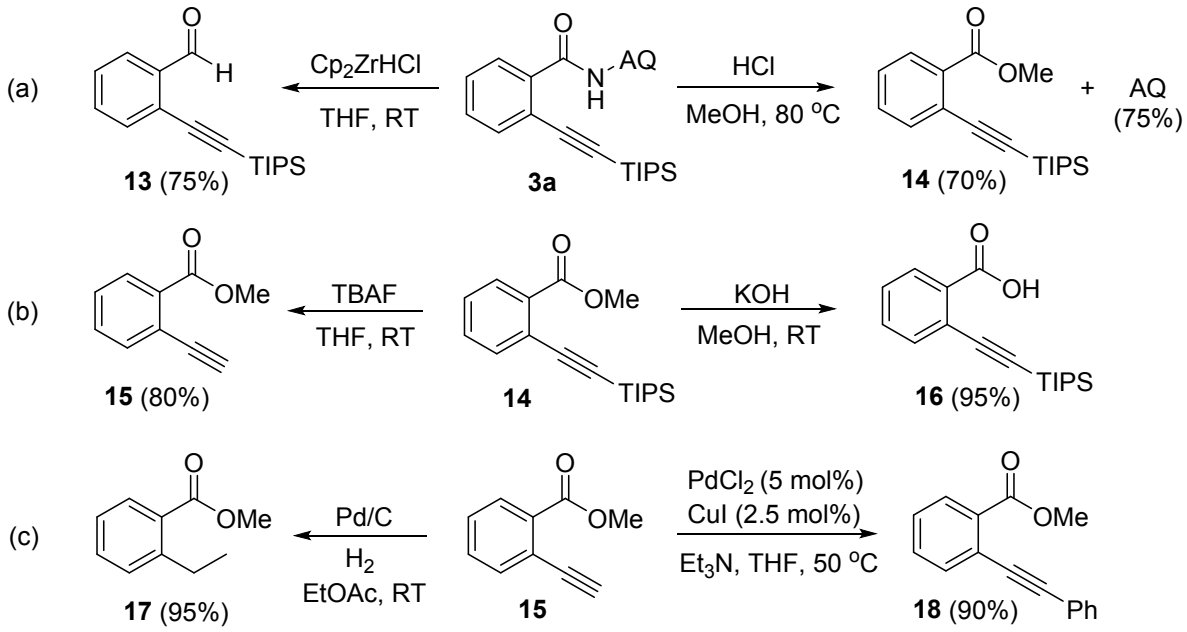


4.3 Competitive Experiment

To an oven-dried 5 mL screw-capped vial, benzamides **1m** (0.1 mmol) and **1n** (0.1 mmol), (triisopropylsilyl)ethynyl bromide **2** (0.11 mmol), $Ni(OTf)_2$ (5 mol%), $PhCO_2H$ (10 mol%), Na_2CO_3 (0.2 mmol) and toluene (1 mL) were added under argon. The mixture was stirred for 4 hrs at 110 °C followed by cooling to room temperature. The solution was filtered through a celite pad and washed with 10-20 mL of dichloromethane. The filtrate was concentrated *in vacuo*. The products (**3m** and **3n**) and unreacted amides were isolated. Isolated yield of **3m** = 17%; **3n** = 6% Recovered yield of **1m** and **1n** are 76% and 91% respectively.



5. Synthetic Application



5.1 Synthesis of 13

Under argon atm **3a** (100 mg, 0.23 mmol), Cp_2ZrHCl (0.46 mmol), and THF (2 mL) were charged to a 25 mL Schlenk tube. The reaction mixture was stirred at room temperature for 6 hrs before carefully being quenched by saturated ammonium chloride at 0°C. After being extracted with CH_2Cl_2 (3 × 25 mL), the combined organic extract was washed with brine, dried over $MgSO_4$, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (eluent: pet ether/EtOAc) to afford **13**.

5.2 Synthesis of 14

To an oven-dried 5 mL screw-capped vial, alkynylated amide **3a** (100 mg, 0.23 mmol) and 1.25 M HCl in MeOH (3 mL) were added under a gentle stream of argon. The mixture was stirred for 24 hrs at 80 °C followed by cooling to room temperature. The mixture was concentrated *in vacuo* and EtOAc (15 mL) and saturated aq. $NaHCO_3$ (10 mL) were then added. The aqueous layer was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and concentrated in *in vacuo*. The residue was purified by column chromatography on silica gel to afford **14**.

5.3 Synthesis of 15

14 (50 mg, 0.15 mmol) was dissolved in THF (2.8 mL) and TBAF (1.0 M in THF, 0.45 mL) were then added at room temperature. The reaction progress was monitored by TLC. The mixture was concentrated *in vacuo*. The residue was extracted with EtOAc (3 × 5 mL), and the combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, filtered and evaporated *in vacuo*. The obtained crude product was purified by column chromatography to afford the desired terminal alkyne **15**.

5.4 Synthesis of 16

In a 25 mL of schlenk tube, **14** (50 mg, 0.15 mmol), KOH (0.3 mmol), and MeOH (1 mL) were added. The reaction mixture was stirred at room temperature for 1 h. Then the reaction was quenched by addition of ice-cold water. The aqueous portion was acidified to *p*H = 2 with 6 N hydrochloric acid and extracted with diethyl ether. The combined organic layers were dried with

Na_2SO_4 and concentrated *in vacuo*. The desired carboxylic acid (**16**) was obtained after drying under vacuum and characterized by ^1H NMR.

5.5 Synthesis of 17

To an oven-dried 100 mL Fischer-porter tube, **15** (50 mg, 0.31 mmol), Pd/C (5 mol%) and EtOAc (1 mL) were added and pressurized with H_2 gas (2 atm). The mixture was stirred for 6 hrs at room temperature. The mixture was filter through celite and concentrated *in vacuo* to afford the desired **17**.

5.6 Synthesis of 18

Under argon atm **15** (100 mg, 0.3 mmol), iodobenzene (0.4 mmol), $PdCl_2$ (5 mol%), CuI (2.5mol%), Et_3N (0.9 mmol), and THF (2 mL) were charged to a 25 mL Schlenk tube. The reaction mixture was stirred at 50 °C for 6 hrs. The mixture was filter through celite and concentrated *in vacuo*. The obtained crude product was purified by column chromatography to afford **18**.

6. Characterization Data

*N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3a**)*

11.2 mg, 45% isolated yield. R_f = 0.21 (hexane/EtOAc = 20/1). Colorless oil. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.80-0.85 (m, 21H), 7.42-7.47 (m, 3H), 7.54-7.64 (m, 3H), 7.80 (m, 1H), 8.16-8.18 (dd, *J* = 8.2 Hz, 1H), 8.76 (dd, *J* = 4.2, 1H), 8.93-8.95 (dd, *J* = 6.1 Hz, 1H), 10.51 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.0, 18.3, 97.1, 103.9, 117.1, 120.7, 121.4, 121.8, 127.3, 127.9,

128.7, 130.1, 133.9, 134.7, 136.2, 138.9, 139.2, 148.2, 166.4; HRMS (EI): *m/z* Calcd for $C_{27}H_{33}N_2OSi$ $[M+H]^+$: 429.2362; Found: 429.2357.

*N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4a**)*

6.2 mg, 25% isolated yield. R_f = 0.30 (hexane/EtOAc = 30/1). White solid. ^1H NMR ($CDCl_3$, 500 MHz) δ 0.84-0.87 (m, 42H),7.31-7.35 (t, *J* = 7.6 Hz, 1H), 7.40-7.43 (dd, *J* = 8.2 Hz, 1H), 7.51-7.58 (m, 4H), 8.14-8.16 (dd, *J* = 8.2 Hz, 1H), 8.72 (dd, *J* = 4.2, 1H), 8.98-9.00 (dd, *J* = 7.3 Hz, 1H), 10.06 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.0, 18.3, 95.8, 103.0, 117.0, 121.3, 121.4, 121.4, 127.2, 127.7, 128.7, 132.3, 134.9, 136.0, 138.5, 143.5, 147.9, 165.5; HRMS (EI): *m/z* Calcd for $C_{38}H_{53}N_2OSi_2$ $[M+H]^+$: 609.3696; Found: 609.3691.

*2-methoxy-N-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (**3b**)*

21.0 mg, 75% isolated yield. R_f = 0.24 (hexane/EtOAc = 10/1). Yellow solid. ^1H NMR ($CDCl_3$, 500 MHz) δ 1.12 (m, 21H), 4.17 (s, 3H), 7.04-7.06 (d, *J* = 7.9 Hz, 1H), 7.14-7.15 (d, *J* = 7.3 Hz, 1H), 7.42-7.59 (m, 3H), 8.12-8.14 (d, *J* = 7.9 Hz, 1H), 8.39-8.40 (d, *J* = 7.6 Hz, 1H), 8.84 (s, 1H), 9.07-9.08 (d, *J* = 6.1 Hz, 1H), 12.36 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 18.9, 55.9, 61.7, 83.4, 111.4, 117.1, 121.1, 121.3, 121.3, 122.2, 127.4, 127.9, 132.2, 133.0, 135.6, 136.0, 139.1, 148.1, 157.6, 163.4; HRMS (EI): *m/z* Calcd for $C_{28}H_{35}N_2O_2Si$: 459.2468; Found: 459.2462.

*2-fluoro-N-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (**3c**)*

23.0 mg, 86% isolated yield. R_f = 0.32 (hexane/EtOAc = 10/1). Yellow solid ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (s, 21H), 7.14-7.17 (m, 1H),7.37-7.39 (m, 2H), 7.43-7.45 (q, *J* = 4.2 Hz, 1H), 7.55-7.61 (m, 2H), 8.16-8.18 (d, *J* = 8.2 Hz, 1H), 8.75-8.76 (d, *J* = 4.2 Hz, 1H), 8.97-8.99 (d, *J* = 7.3 Hz, 1H), 10.20 (brs, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 10.9, 18.2, 97.1, 102.3, 116.3, 116.4, 117.0, 121.5, 121.9, 122.0, 123.1, 123.2, 127.3, 127.8, 128.2, 128.4, 128.9, 128.9, 130.7, 130.8, 134.4, 136.2, 138.4, 148.2, 148.9, 158.2, 160.2, 162.1; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}N_2OFSi$ $[M+H]^+$: 447.2268; Found: 447.2262.

*2-chloro-N-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (**3d**)*

26.0 mg, 92% isolated yield. R_f = 0.32 (hexane/EtOAc = 10/1). Yellow solid ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80 (s, 21H), 7.28-7.33 (m, 1H),7.40-7.48 (m, 3H), 7.53-7.60 (m, 2H), 8.14-8.16 (d, *J* = 8.3 Hz, 1H), 8.73-8.74 (q, *J* = 4.1 Hz, 1H), 8.99-9.01 (dd, *J* = 7.0 Hz, 1H), 10.11 (brs, 1H); ^{13}C NMR ($CDCl_3$, 400 MHz) δ 10.9, 18.2, 96.8, 102.4, 116.9, 121.5, 121.9, 122.9, 127.1, 127.7, 129.6, 129.9, 131.1, 131.3, 134.3, 136.1, 138.3, 139.3, 148.1, 164.0; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}ClN_2OSi$: 463.1972; Found: 463.1967.

*4-fluoro-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3e**)*

4.0 mg, 15% isolated yield. R_f = 0.21 (hexane/EtOAc = 20/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.80-0.86 (m, 21H), 7.13-7.17 (dt, *J* = 8.3 Hz, 1H), 7.29-7.32 (dd, *J* = 9.0 Hz, 1H), 7.42-7.45 (dd, *J* = 8.3 Hz, 1H), 7.54-7.61 (m, 2H), 7.80-7.84 (dd, *J* = 8.8 Hz, 1H), 8.16-8.18 (dd,

J = 8.3 Hz, 1H), 8.77-8.78 (dd, *J* = 4.1, 1H), 8.99-8.91 (dd, *J* = 7.5 Hz, 1H), 10.50 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 10.9, 18.3, 98.8, 102.6, 116.1, 116.3, 117.1, 120.2, 120.4, 121.5, 121.9, 122.8, 122.9, 127.3, 127.9, 131.0, 131.1, 134.5, 135.5, 135.5, 136.2, 138.8, 148.3, 161.9, 164.4, 165.4; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}N_2OFSi$ $[M+H]^+$: 447.2268; Found: 447.2262.

*4-fluoro-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4e**)*

20.0 mg, 75% isolated yield. R_f = 0.35 (hexane/EtOAc = 30/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (s, 42H), 7.20-7.22 (d, *J* = 8.5 Hz, 2H), 7.40-7.43 (dd, *J* = 8.3 Hz, 1H), 7.51-7.58 (m, 2H), 8.14-8.16 (dd, *J* = 8.2 Hz, 1H), 8.73-8.74 (dd, *J* = 4.4 Hz, 1H), 8.95-8.98 (dd, *J* = 7.3 Hz, 1H), 10.06 (brs, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) 10.9, 18.3, 97.4, 101.9, 117.0, 119.2, 119.4, 121.3, 121.6, 123.9, 123.5, 127.1, 127.7, 134.7, 136.1, 138.4, 140.1, 147.9, 160.4, 162.9, 164.8; HRMS (EI): *m/z* Calcd for $C_{38}H_{52}FN_2OSi_2$: 627.3602; Found: 627.3597.

*4-chloro-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3f**)*

2.0 mg, 6% isolated yield. R_f = 0.30 (hexane/EtOAc = 20/1). Yellow solid ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83 (s, 21H), 7.41-7.46 (m, 2H),7.55-7.61 (m, 3H), 7.75-7.76 (d, *J* = 8.5 Hz, 1H), 8.17-8.19 (dd, *J* = 8.2 Hz, 1H), 8.76-8.78 (dd, *J* = 4.2 Hz, 1H), 8.88-8.90 (dd, *J* = 7.6 Hz, 1H), 10.51 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.3, 98.9, 102.4, 117.1, 121.5, 122.0, 122.3, 127.3, 127.9, 128.9, 130.2, 133.4, 134.4, 136.1, 136.2, 137.5, 138.8, 148.3, 165.3; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}ClN_2OSi$: 463.1972; Found: 463.1967.

*4-chloro-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4f**)*

23.1 mg, 82% isolated yield. R_f = 0.30 (hexane/EtOAc = 30/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (s, 42H), 7.40-7.42 (d, *J* = 4.2 Hz, 1H),7.48 (s, 2H), 7.51-7.57 (m, 2H), 8.14-8.15 (d, *J* = 8.2 Hz, 1H), 8.72-8.73 (dd, *J* = 4.2 Hz, 1H), 8.95-8.97 (dd, *J* = 7.6 Hz, 1H), 10.07 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 10.9, 18.2, 97.5, 101.7, 116.9, 121.3, 121.6, 122.9, 127.1, 127.6, 131.9, 134.4, 134.6, 136.0, 138.3, 141.8, 147.9, 164.6; HRMS (EI): *m/z* Calcd for $C_{38}H_{51}ClN_2OSi_2$: 642.3228; Found: 642.3806 (we did not good HRMS data for this compound).

*N-(quinolin-8-yl)-4-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzamide (**3g**)*

12.6 mg, 40% isolated yield. R_f = 0.30 (hexane/EtOAc = 10/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84 (s, 21H), 7.44-7.48 (dd, *J* = 8.2 Hz, 1H), 7.56-7.62 (m, 2H), 7.68-7.70 (dd, *J* = 8.2 Hz, 1H), 7.86 (s, 1H), 7.90-7.91 (d, *J* = 7.9 Hz, 1H), 8.17-8.19 (dd, *J* = 8.2 Hz, 1H), 8.76-8.77 (dd, *J* = 4.2 Hz, 1H), 8.92-8.94 (d, *J* = 7.3 Hz, 1H), 10.51 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.2, 99.3, 117.2, 121.6, 122.2, 125.2, 125.2, 127.3, 127.9, 129.2, 130.5, 134.3, 136.2, 138.2, 138.7, 142.3, 148.3, 165.1; HRMS (EI): *m/z* Calcd for $C_{28}H_{32}F_3N_2OSi$: 497.2236; Found: 497.2231.

*N-(quinolin-8-yl)-4-(trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4g**)*

14.0 mg, 44% isolated yield. R_f = 0.30 (hexane/EtOAc = 20/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.88 (s, 42H), 7.41-7.44 (m, 1H), 7.53-7.57 (m, 2H), 7.75 (s, 2H) 8.15-8.17 (d, *J* = 8.2 Hz, 1H), 8.72-8.74 (m, 1H) 8.97 (d, *J* = 7.2 Hz, 1H), 10.11 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125

MHz) δ 10.9, 18.3, 98.3, 101.5, 117.1, 121.4, 121.8, 121.5, 127.1, 127.7, 128.7, 128.7, 134.5, 136.1, 138.4, 146.1, 148.6, 164.3; HRMS (EI): *m/z* Calcd for $C_{39}H_{52}F_3N_2OSi_2$: 677.3570; Found: 677.3565.

*4-methyl-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3h**)*

8.4 mg, 32% isolated yield. R_f = 0.30 (hexane/EtOAc = 10/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.85-0.87 (s, 21H), 2.43 (s, 3H), 7.27-7.29 (d, *J* = 7.3 Hz, 1H), 7.43-7.46 (m, 2H), 7.54-7.62 (m, 2H), 7.73-7.75 (d, *J* = 7.9 Hz, 1H), 8.17-8.19 (dd, *J* = 8.2 Hz, 1H), 8.77-8.79 (dd, *J* = 4.2 Hz, 1H), 8.92-8.94 (d, *J* = 7.3 Hz, 1H), 10.51 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 18.3, 21.1, 96.7, 104.1, 117.1, 120.6, 121.4, 121.7, 127.3, 127.9, 128.9, 129.6, 134.3, 134.8, 136.1, 138.9, 140.4, 148.2, 166.4; HRMS (EI): *m/z* Calcd for $C_{28}H_{35}N_2OSi$: 443.2519; Found: 443.2513.

*4-methyl-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4h**)*

7.0 mg, 26% isolated yield. R_f = 0.30 (hexane/EtOAc = 20/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (s, 42H), 2.36 (s, 3H), 7.34 (s, 1H), 7.40-7.42 (dd, *J* = 8.2 Hz, 1H), 7.50-7.57 (m, 2H), 8.14-8.16 (dd, *J* = 8.2 Hz, 1H), 8.72-8.73 (dd, *J* = 4.2 Hz, 1H), 8.96-8.98 (dd, *J* = 7 Hz, 1H), 10.03 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 11.1, 18.4, 20.7, 95.3, 103.3, 116.9, 121.3, 121.3, 127.3, 127.7, 133.0, 134.9, 136.0, 138.5, 138.8, 141.0, 147.9, 165.8; HRMS (EI): *m/z* Calcd for $C_{39}H_{55}N_2OSi_2$: 623.3853; Found: 623.3847.

*4-methoxy-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3i**)*

7.8 mg, 28% isolated yield. R_f = 0.20 (hexane/EtOAc = 10/1). Pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.84-0.85 (m, 21H), 3.88 (s, 1H), 6.97-7.00 (dd, *J* = 8.5 Hz, 1H), 7.10-7.11 (d, *J* = 2.7 Hz, 1H), 7.42-7.44 (dd, *J* = 8.2 Hz, 1H), 7.52-7.54 (dd, *J* = 6.7 Hz, 1H), 7.57-7.60 (td, *J* = 7.6 Hz, 1H), 7.79-7.81(d, *J* = 8.5 Hz, 1H), 8.15-8.17 (dd, *J* = 8.2 Hz, 1H), 8.76-8.78 (dd, *J* = 4.2 Hz, 1H), 8.88-8.90 (dd, *J* = 7.6 Hz, 1H), 10.53 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.0, 18.3, 55.5, 97.3 103.9, 114.9, 117.1, 118.5, 121.4, 121.6, 122.1, 127.3, 127.9, 130.8, 131.7, 134.8, 136.1, 138.9, 148.2, 160.7, 166.0; HRMS (EI): *m/z* Calcd for $C_{28}H_{35}N_2O_2Si$: 459.2468; Found: 459.2462.

*4-methoxy-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4i**)*

7.0 mg, 25% isolated yield. R_f = 0.30 (hexane/EtOAc = 15/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (m, 42H), 3.86 (s, 1H), 7.03 (s, 1H), 7.40-7.42 (q, *J* = 4.2 Hz, 1H), 7.50-7.57 (m, 2H), 8.14-8.16 (dd, *J* = 7.9 Hz, 1H), 8.72-8.73 (dd, *J* = 4.2 Hz, 1H), 8.96-8.98 (dd, *J* = 7.6 Hz, 1H), 10.03 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.0, 18.3, 55.6, 95.5, 103.0, 116.9, 117.9, 121.2, 127.2, 127.7, 134.9, 136.0, 136.8, 138.4, 147.8, 159.1, 165.5. HRMS (EI): *m/z* Calcd for $C_{39}H_{55}N_2O_2Si_2$: 639.3802; Found: 639.3802.

*4-(dimethylamino)-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4j**)*

67% isolated yield. Yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.87 (m, 42H), 3.01 (s, 6H), 6.81 (s, 2H), 7.39-7.41 (dd, *J* = 4.2 Hz, 1H), 7.48-7.54 (m, 2H), 8.13-8.15 (dd, *J* = 8.2 Hz, 1H),

8.71-8.72 (dd, *J* = 3.9, 1H), 8.97-8.99 (d, *J* = 7.6 Hz, 1H), 10.02 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 18.4, 40.3, 94.0, 104.2, 110.7, 115.8, 116.8, 120.9, 121.1, 122.0, 127.3, 127.7, 131.9, 132.3, 135.3, 138.6, 147.8, 150.0, 166.1.

*N-(quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)isonicotinamide (**3k**)*

42% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.86 (m, 21H),7.45-7.48 (q, *J* = 4.1 Hz, 1H), 7.59-7.61 (m, 2H), 7.68-7.69 (d, *J* = 5.1 Hz, 1H), 8.18-8.20 (d, *J* = 7.5 Hz, 1H), 8.68-8.69 (d, *J* = 4.8, 1H), 8.78-8.79 (d, *J* = 3.4 Hz, 1H), 8.88-8.90 (m, 2H), 10.58 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.2, 100.5, 116.8, 117.4, 121.6, 121.9, 122.5, 127.2, 127.9, 134.0, 136.3, 138.7, 145.2, 148.4, 149.1, 154.4, 164.0; HRMS Calcd for $C_{26}H_{32}N_3OSi$ $[M+H]^+$: 430.2314; Found: 430.2315.

*(Z)-2-methyl-N-(quinolin-8-yl)-5-(triisopropylsilyl)pent-2-en-4-ynamide (**3l**)*

56% isolated yield. White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.72-0.78 (m, 21H), 5.94 (s, 1H), 7.41-7.43 (q, *J* = 4.2 Hz, 1H), 7.51-7.54 (m, 2H), 8.13-8.15 (d, *J* = 8.2 Hz, 1H), 8.78-8.82 (dd, *J* = 7.0 Hz, 2H), 10.42 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.1, 20.2, 98.7, 101.9, 111.1, 117.1, 121.3, 121.8, 127.2, 127.8, 134.2, 136.1, 138.8, 145.7, 148.2, 166.3; HRMS Calcd for $C_{24}H_{33}N_2OSi$ $[M+H]^+$: 393.2362; Found: 393.2362.

*5-fluoro-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3m**)*

16.0 mg, 60% isolated yield. R_f = 0.25 (hexane/EtOAc = 10/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (s, 21H), 7.14-7.16 (dt, *J* = 8.2 Hz, 1H), 7.44-7.46 (dd, *J* = 8.2 Hz, 1H), 7.51-7.53 (m, 2H), 7.56-7.64 (m, 1H), 8.17-8.19 (dd, *J* = 8.5 Hz, 1H), 8.77-8.79 (dd, *J* = 5.8 Hz, 1H), 8.89-8.91 (dd, *J* = 8.5 Hz, 1H), 10.54 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.0, 18.2, 96.9, 102.8, 115.9, 116.1, 116.9, 117.3, 117.5, 117.7, 121.5, 122.1, 127.3, 127.9, 134.4, 135.9, 136.0, 136.2, 138.9, 141.2, 141.3, 148.3, 161.3, 163.3, 164.9; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}FN_2OSi$: 447.2268; Found: 447.2262.

*3-fluoro-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4m**)*

3.0 mg, 11% isolated yield. R_f = 0.30 (hexane/EtOAc = 20/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.85-0.86 (s, 42H), 7.08-7.12 (t, *J* = 8.5 Hz, 1H), 7.41-7.44 (dd, *J* = 4.2 Hz, 1H), 7.47-7.50 (dd, *J* = 8.5 Hz, 1H), 7.53-7.56 (m, 2H), 8.15-8.17 (d, *J* = 8.5 Hz, 1H), 8.73-8.74 (dd *J* = 4.2 Hz, 1H), 8.96-8.98 (d, *J* = 7 Hz, 1H), 10.09 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.3, 95.4, 95.8, 102.1, 102.2, 110.8, 116.1, 116.3, 117.1, 117.4, 117.4, 121.4, 121.7, 127.1, 127.7, 133.8, 133.9, 134.6, 136.1, 138.4, 145.3, 148.0, 161.4, 163.5, 164.2; HRMS (EI): *m/z* Calcd for $C_{38}H_{52}FN_2OSi_2$: 627.3602; Found: 627.3597.

*5-chloro-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3n**)*

13.8 mg, 49% isolated yield. R_f = 0.30 (hexane/EtOAc = 10/1). Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (s, 21H), 7.40-7.45 (m, 2H), 7.55-7.61 (m, 3H), 7.78-7.79 (d, *J* = 2.1 Hz, 1H),

8.16-8.18 (dd, *J* = 8.2 Hz, 1H), 8.77-8.78 (d, *J* = 3.9 Hz, 1H), 8.89-8.91 (dd, *J* = 7.3 Hz, 1H), 10.50 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) 10.9, 18.2, 984, 102.7, 117.2, 119.1, 121.5, 122.1, 127.3, 127.8, 128.8, 130.3, 134.3, 134.8, 135.0, 136.2, 134.3, 134.7, 135.0, 136.2, 138.8, 140.5, 148.3, 164.9; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}ClN_2OSi$: 463.1972; Found: 463.1967.

*5-bromo-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3o**)*

24.1 mg, 74% isolated yield. R_f = 0.28 (hexane/EtOAc = 15/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.82 (s, 21H), 7.44-7.46 (dd, *J* = 3.9 Hz,1H), 7.48-7.49 (d, *J* = 8.5 Hz, 1H), 7.56-7.61 (m, 3H), 7.94-7.95 (d, *J* = 2.1 Hz, 1H), 8.17-8.19 (dd, *J* = 8.5 Hz, 1H), 8.77-8.78 (dd, *J* = 4.2 Hz, 1H), 8.89-8.90 (dd, *J* = 7.2 Hz, 1H), 10.94 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.3, 102.6, 117.2, 119.6, 121.5, 122.1, 122.8, 127.3, 127.9, 131.7, 122.2, 134.4, 135.1, 127.9, 131.7, 133.2, 134.4, 135.1, 136.2, 138.8, 140.7, 148.3, 164.8; HRMS (EI): *m/z* Calcd for $C_{27}H_{32}BrN_2OSi$: 507.1467; Found: 507.1462.

*N-(quinolin-8-yl)-5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)benzamide (**3p**)*

18.3 mg, 58% isolated yield. R_f = 0.35 (hexane/EtOAc = 10/1). White solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.83 (s, 21H), 7.43-7.46 (dd, *J* = 4.2 Hz, 1H), 7.56-7.62 (m, 2H), 7.68-7.70 (d, *J* = 8.2 Hz, 1H), 7.73-7.75 (d, *J* = 8.2 Hz, 1H), 8.09 (s, 1H), 8.17-8.19 (dd, *J* = 8.2 Hz, 1H), 8.76-8.78 (dd, *J* = 3.9 Hz, 1H), 8.91-8.93 (dd, *J* = 7.3 Hz, 1H), 10.55 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.9, 18.2, 100.6, 102.4, 117.2, 121.5, 122.2, 124.2, 125.9, 126.6, 126.6, 127.3, 127.9,

134.3, 136.2, 138.7, 139.7, 148.3, 164.9; HRMS (EI): *m/z* Calcd for $C_{28}H_{32}F_3N_2OSi$: 497.2236; Found: 497.2231.

*5-methoxy-N-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (**3q**)*

5.8 mg, 21% isolated yield. R_f = 0.25 (hexane/EtOAc = 10/1). Pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.76-0.83 (m, 21H), 3.88 (s,1H), 6.97-7.00 (dd, *J* = 8.5 Hz, 1H),7.33-7.34 (s, 1H), 7.42-7.45 (m, 1H), 7.54-7.59 (m, 3H), 8.15-8.18 (dd, *J* = 8.2 Hz, 1H), 8.77-8.78 (s, 1H), 8.90-8.92 (dd, *J* = 7.9 Hz, 1H), 10.56 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 10.0, 18.2, 55.6, 95.2, 103.9, 112.9, 113.1, 117.1, 117.2, 121.4, 121.9, 127.9, 127.9, 134.6, 135.4, 136.1, 138.9, 140.6, 148.3, 159.7, 166.1; HRMS (EI): *m/z* Calcd for $C_{28}H_{35}N_2O_2Si$: 459.2468; Found: 459.2462.

*3-methoxy-N-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (**4q**)*

4.72 mg, 17% isolated yield. R_f = 0.35 (hexane/EtOAc = 15/1). Yellow solid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 0.86 (m, 42H), 3.92 (s,1H), 6.86-7.6.88 (d, *J* = 8.8 Hz, 1H),7.39-7.42 (dd, *J* = 4.2 Hz, 1H),7.47-7.57 (m, 3H), 8.13-8.15 (d, *J* = 8.2 Hz, 1H), 8.71-8.72 (d, *J* = 4.2 Hz, 1H), 8.96-8.98 (d, *J* = 7.3 Hz, 1H), 10.56 (brs, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.1, 18.4, 18.3, 56.3, 93.4, 98.8, 10.4, 103.1, 112.2, 113.3, 116.9, 121.3, 121.3, 127.2, 127.6, 133.8, 134.9, 135.9, 138.5, 145.3, 147.9, 160.5, 165.2; HRMS (EI): *m/z* Calcd for $C_{39}H_{55}N_2O_2Si_2$: 639.3802; Found: 639.3802.

*1,4-bis(triisopropylsilyl)buta-1,3-diyne (**12**)*[S4]

White Solid. ^{1}H NMR ($CDCl_3$, 200 MHz) δ 1.11 (s, 42H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 18.5, 81.5, 90.2.

*2-((triisopropylsilyl)ethynyl)benzaldehyde (**13**)*

50.1 mg, 75% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.14-1.18 (s, 21H), 7.42-7.45 (t, *J* = 7.6 Hz, 1H), 7.53-7.56 (t, *J* = 7.3 Hz, 1H), 7.60-7.61 (d, *J* = 7.6 Hz, 1H), 7.92-7.93 (d, *J* = 7.9 Hz, 1H), 10 62 (s, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.2, 18.6, 99.1, 101.9, 126.8, 127.1, 128.6, 133.6, 133.8, 136.1, 191.7; HRMS Calcd for $C_{18}H_{27}O$ Si$[M+H]^+$: 287.1831; Found: 287.1831.

*methyl 2-((triisopropylsilyl)ethynyl)benzoate (**14**)*

50.8 mg, 70% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.92 (s, 3H), 7.35-7.38 (t, *J* = 7.6 Hz, 1H), 7.42-7.45 (t, *J* = 7.6 Hz, 1H), 7.59-7.61 (d, *J* = 7.9 Hz, 1H), 7.88-7.90 (d, *J* = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 18.6, 52.1, 96.2, 105.0, 123.3, 127.9, 130.1, 132.5, 134.8, 167.1; HRMS Calcd for $C_{16}H_{29}O_2$ Si$[M+H]^+$: 317.1936; Found: 317.1937.

*methyl 2-ethynylbenzoate (**15**)*

20.2 mg, 80% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.41 (s, 1H), 3.93 (s,1H), 7.39-7.43 (t, *J* = 7.5 Hz, 1H), 7.46-7.50 (t, *J* = 7.5 Hz, 1H), 7.62-7.64 (d, *J* = 7.5 Hz, 1H),

7.93-7.96 (d, J = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.1, 81.9, 82.2, 122.5, 128.4, 130.2, 131.6, 132.4, 134.9, 166.4; HRMS Calcd for $C_{10}H_9O_2[M+H]^+$: 161.060; Found: 161.0603.

*2-((triisopropylsilyl)ethynyl)benzoic acid (**16**)*

41.2 mg, 95% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.17 (s, 21H), 7.40-7.43 (t, J = 6.7 Hz, 1H), 7.50-7.53 (t, J = 7.3 Hz, 1H), 7.64-7.66 (d, J = 7.3 Hz, 1H), 8.06-8.08 (d, J = 7.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 11.3, 18.6, 98.3, 104.6, 124.1, 128.0, 130.9, 131.2, 132.2, 134.9, 170.7.

*methyl 2-ethylbenzoate (**17**)*

48.2 mg, 95% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.25-1.28 (t, J = 7.6 Hz, 3H), 2.98-3.02 (q, J = 7.6 Hz, 2H), 3.91 (s, 3H), 7.24-7.30 (m, 2H), 7.43-7.44 (t, J = 6.4 Hz, 1H), 7.86-7.88 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 15.8, 27.5, 51.8, 125.6, 129.3, 130.1, 130.4, 131.9, 145.9, 168.1.

*methyl 2-(phenylethynyl)benzoate (**18**)*

67.7 mg, 90% isolated yield. Yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.97 (s, 3H), 7.36-7.40 (m, 4H), 7.48-7.51 (t, J = 7.6 Hz, 1H), 7.60-7.61 (d, J = 6.4 Hz, 2H), 7.65-7.67 (d, J = 7.6 Hz, 1H), 7.98-8.00 (d, J = 7.9 Hz, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 52.0, 88.1, 94.2, 123.2, 123.5, 127.7, 128.2, 128.4, 130.3, 131.6, 131.7, 133.8, 166.6; HRMS Calcd for $C_{16}H_{13}O_2$ $[M+H]^+$: 237.0915; Found: 237.0916.

7. References

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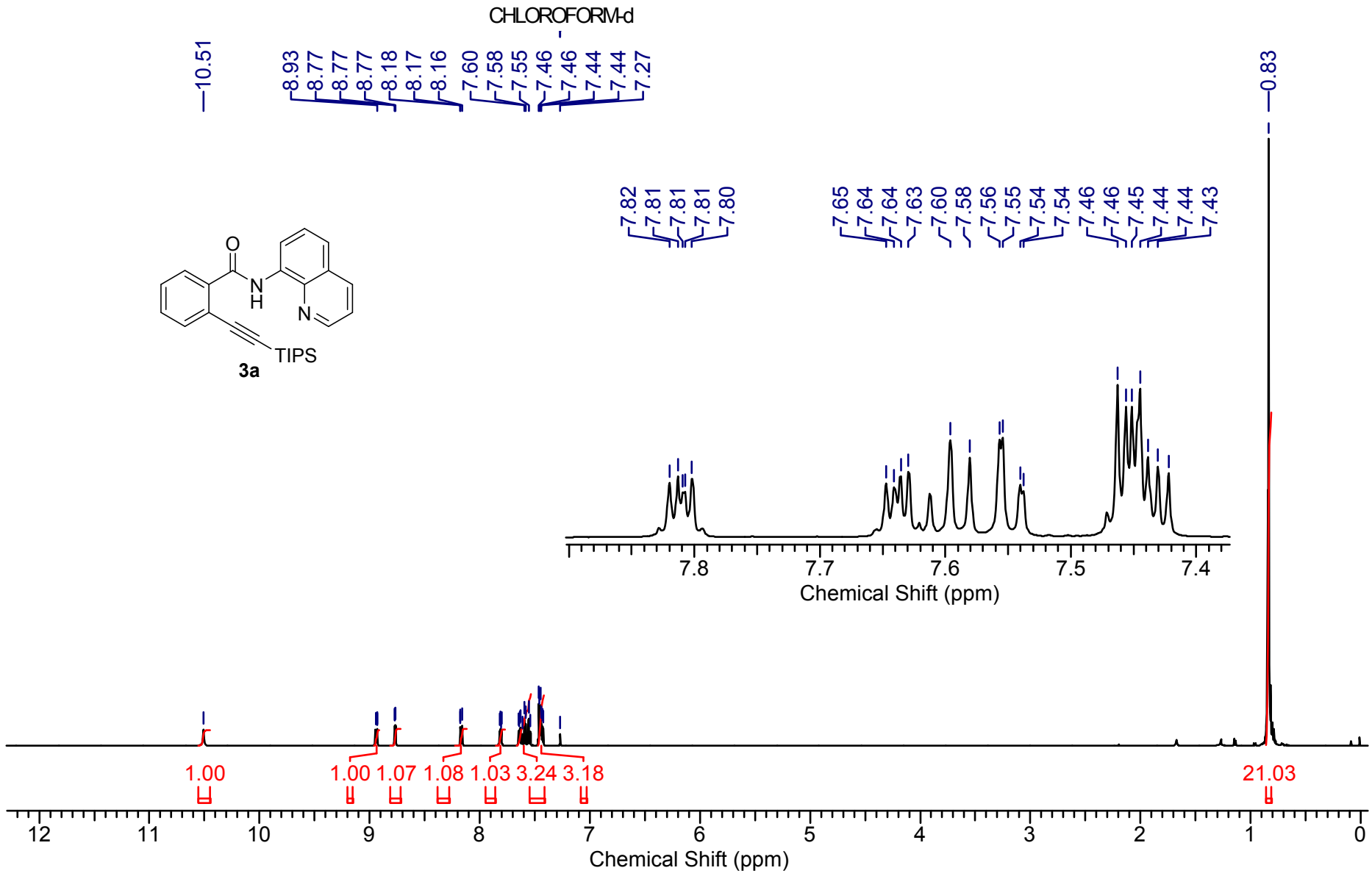
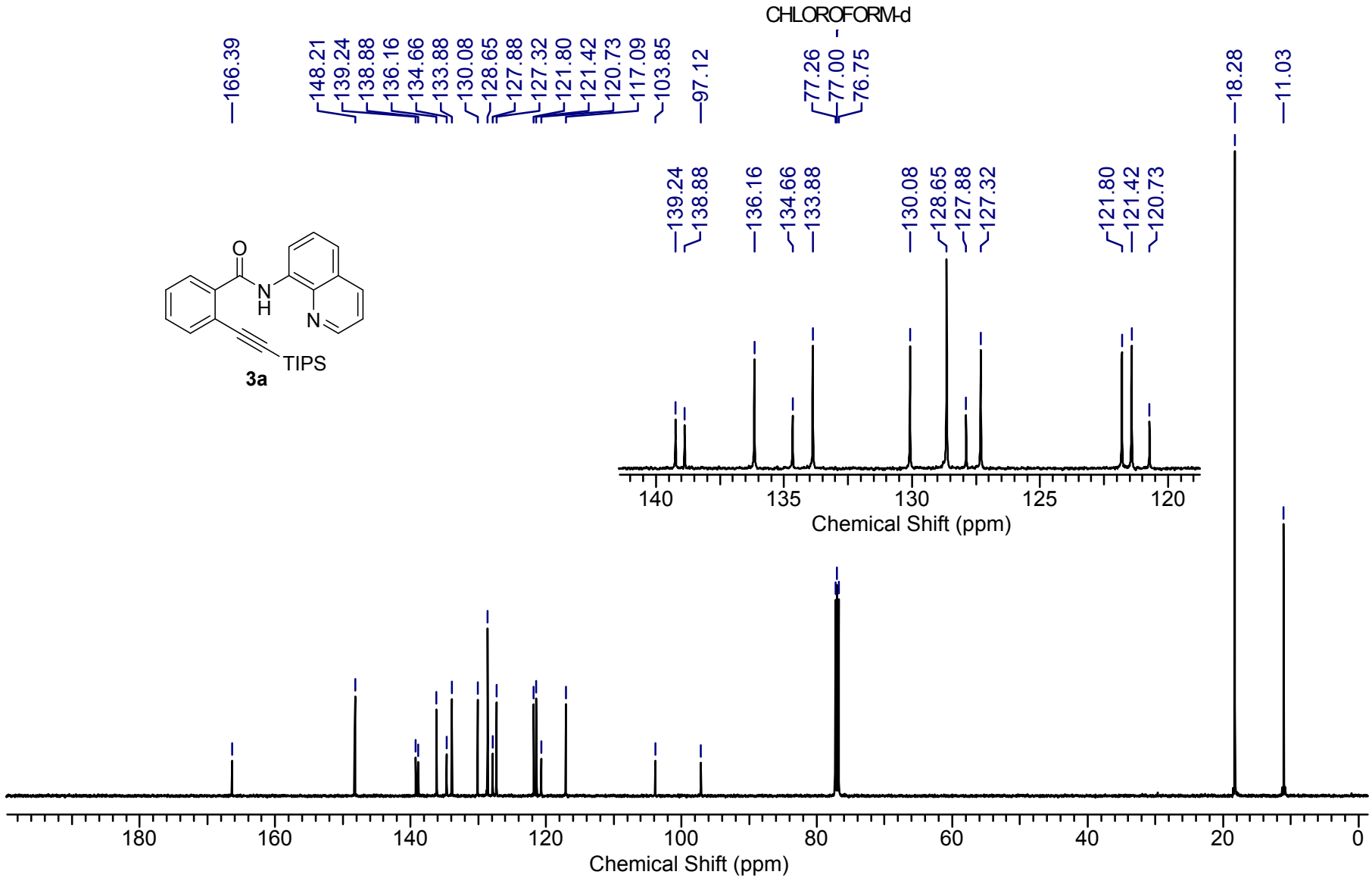
S2. (a) Y. Aihara, N. Chatani, *J. Am. Chem. Soc*. **2013**, *135*, 5308. (b) L. Grigorjeva, O. Daugulis, *Org. Lett*. 2014, **16,** 4684.

S3. M. X.-W. Jiang, M. Rawat, W. D. Wulff, *J. Am. Chem. Soc*. 2004, **126**, 5970.

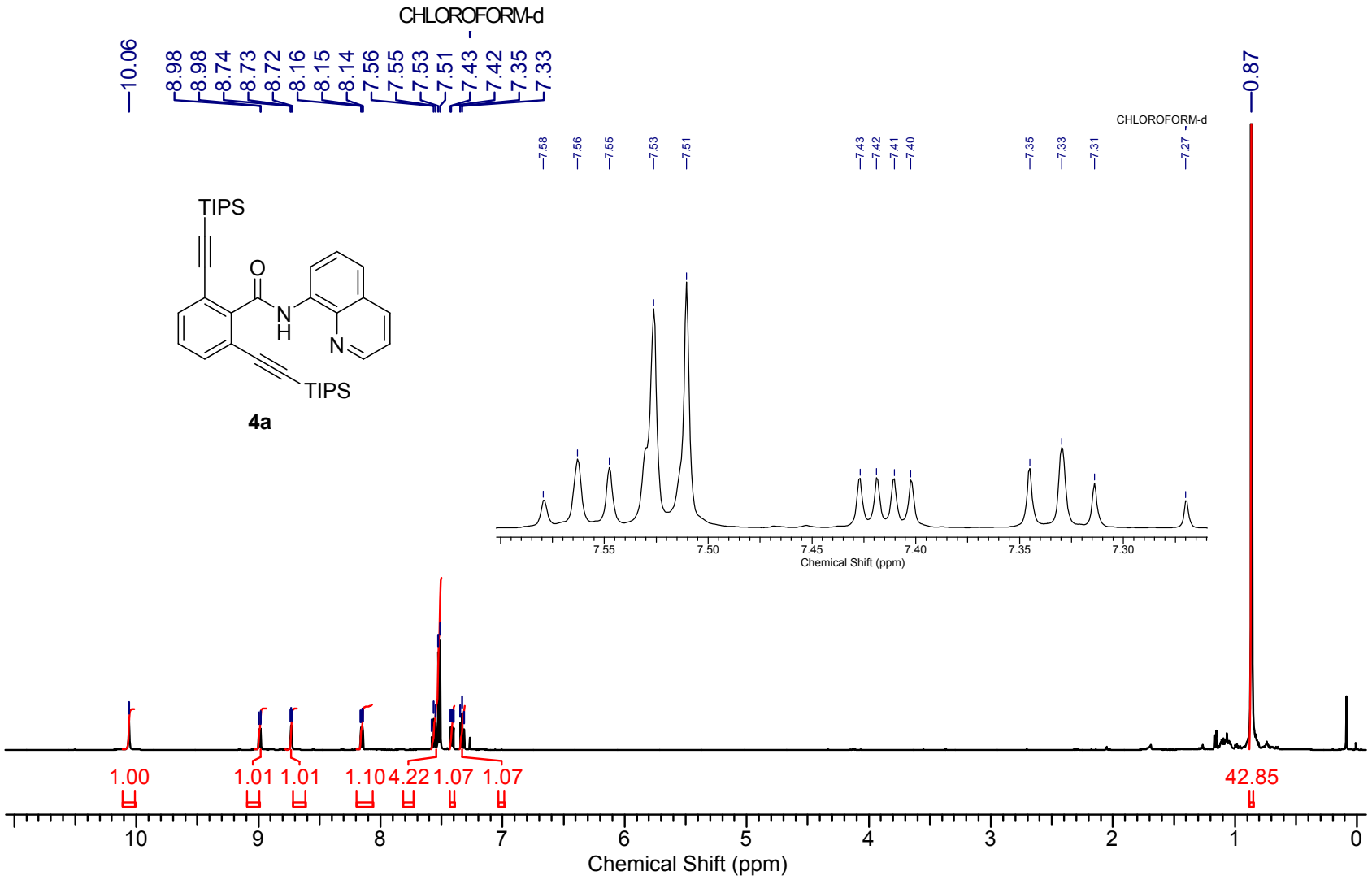
S4. T. Oishi, K. Yamaguchi, N. Mizuno, ACS Catal. 2011, **1**, 1351.


CHLOROFORM-d
10.51
8.93
8.77
8.77
8.77
8.18
8.17
8.16
7.60
7.58
7.55
7.46
7.46
7.44
7.44
7.27
0.83
7.82
7.81
7.81
7.81
7.80
7.65
7.64
7.64
7.63
7.60
7.58
7.56
7.55
7.54
7.54
7.46
7.46
7.45
7.44
7.44
7.43
O
N
H
N
TIPS
3a
7.8
7.7
7.6
7.5
7.4
Chemical Shift (ppm)
1.00
1.00
1.07
1.08
1.03
3.24
3.18
21.03
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

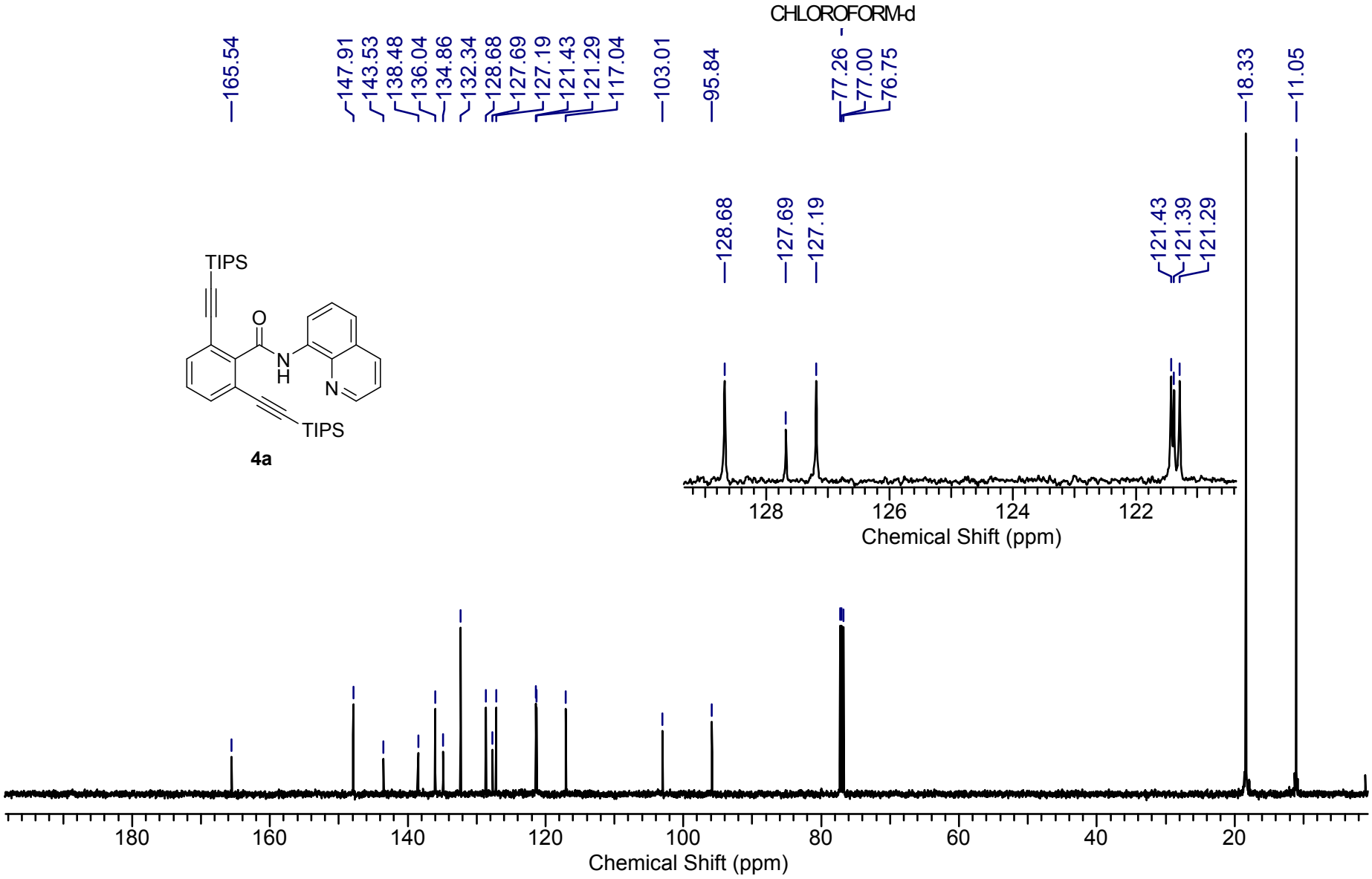
^{1}H NMR of **3a**


CHLOROFORM-d
166.39
148.21
139.24
138.88
136.16
134.66
133.88
130.08
128.65
127.88
127.32
121.80
121.42
120.73
117.09
103.85
97.12
77.26
77.00
76.75
18.28
11.03
O
N
H
N
TIPS
3a
Chemical Shift (ppm)
Chemical Shift (ppm)

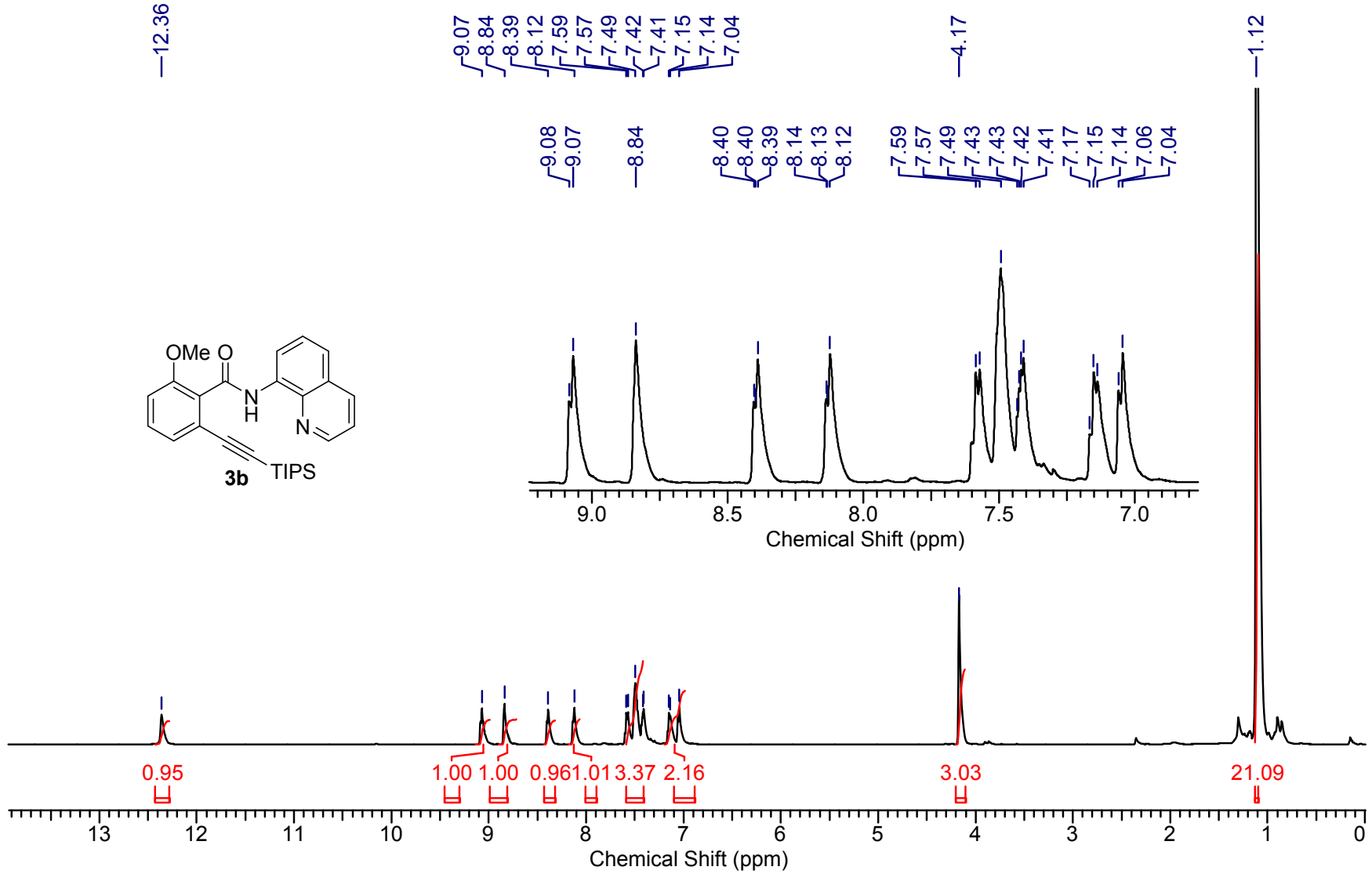
^{13}C NMR of **3a**


CHLOROFORM-d
10.06
8.98
8.98
8.74
8.73
8.72
8.16
8.15
8.14
7.56
7.55
7.53
7.51
7.43
7.42
7.35
7.33
0.87
TIPS
O
N
H
N
TIPS
4a
7.58
7.56
7.55
7.53
7.51
7.43
7.42
7.41
7.40
7.35
7.33
7.31
7.27
CHLOROFORM-d
7.55
7.50
7.45
7.40
7.35
7.30
Chemical Shift (ppm)
1.00
1.01
1.01
1.10
4.22
1.07
1.07
42.85
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

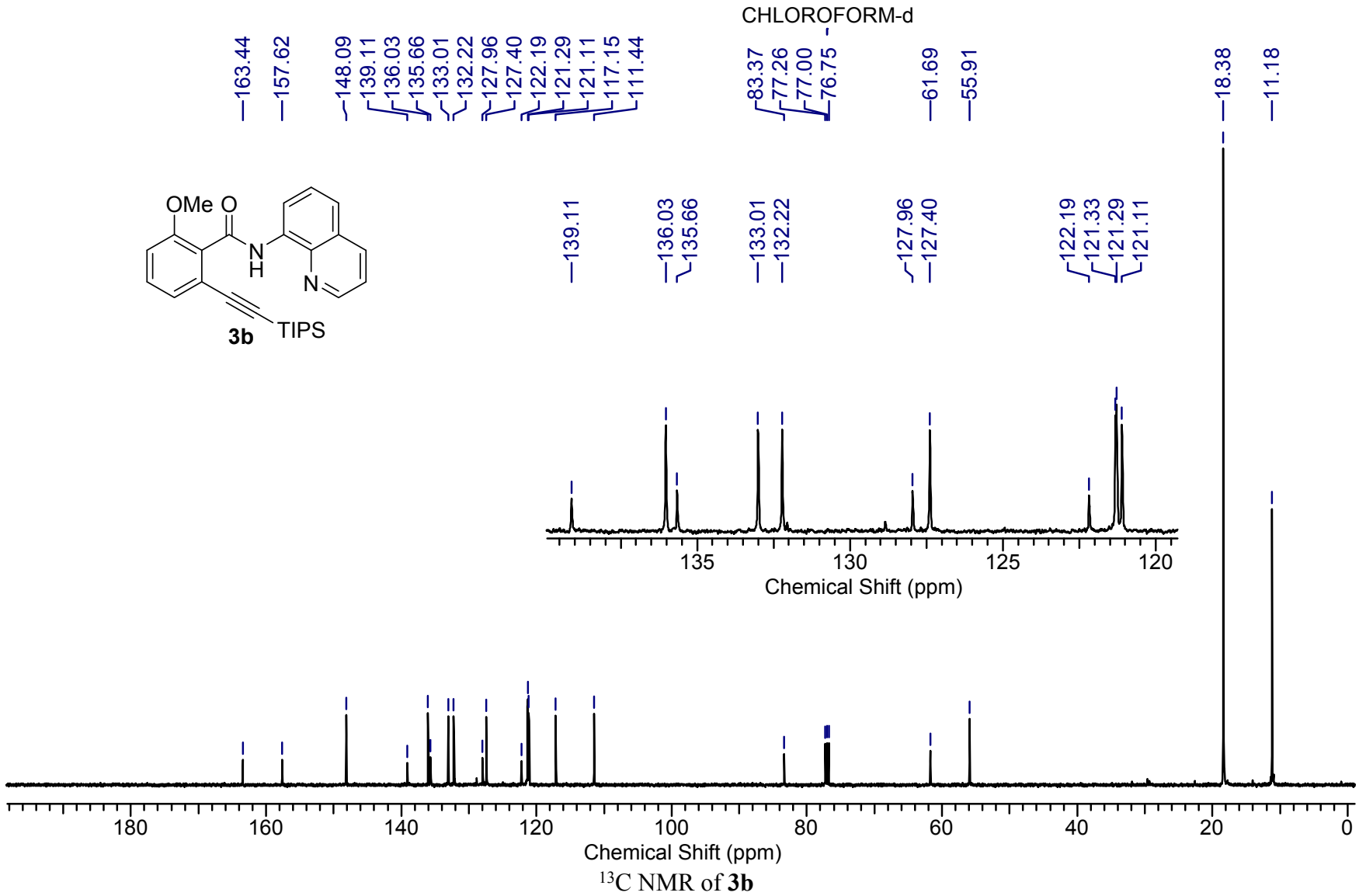
^{1}H NMR of **4a**


CHLOROFORM-d
165.54
147.91
143.53
138.48
136.04
134.86
132.34
128.68
127.69
127.19
121.43
121.29
117.04
103.01
95.84
77.26
77.00
76.75
18.33
11.05
TIPS
O
N
H
N
TIPS
4a
Chemical Shift (ppm)
Chemical Shift (ppm)

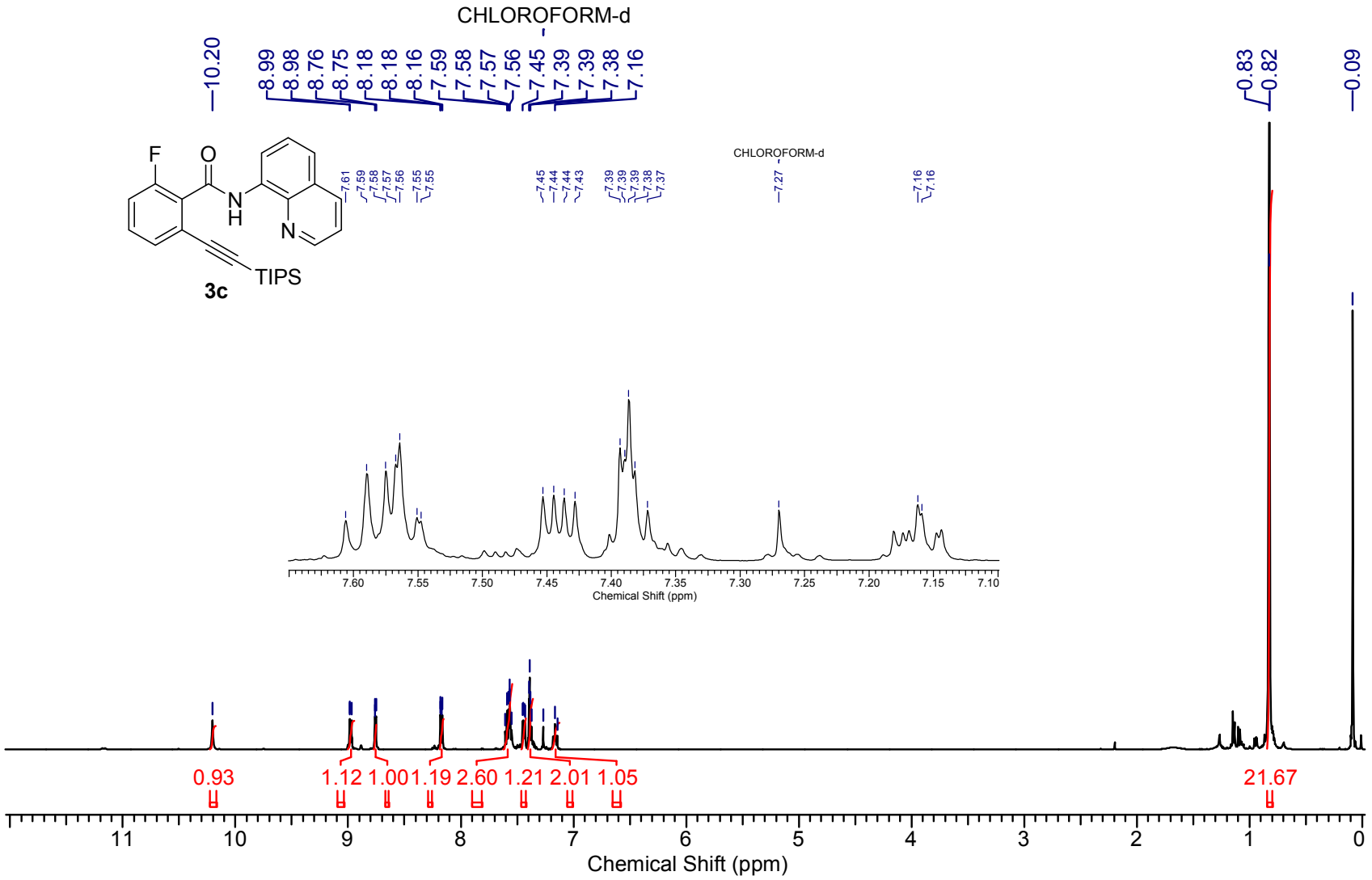
^{13}C NMR of **4a**


12.36
9.07
8.84
8.39
8.12
7.59
7.57
7.49
7.42
7.41
7.15
7.14
7.04
4.17
1.12
9.08
9.07
8.84
8.40
8.40
8.39
8.14
8.13
8.12
7.59
7.57
7.49
7.43
7.43
7.42
7.41
7.17
7.15
7.14
7.06
7.04
OMe
O
N
H
N
TIPS
3b
9.0
8.5
8.0
7.5
7.0
Chemical Shift (ppm)
0.95
1.00
1.00
0.96
1.01
3.37
2.16
3.03
21.09
13
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

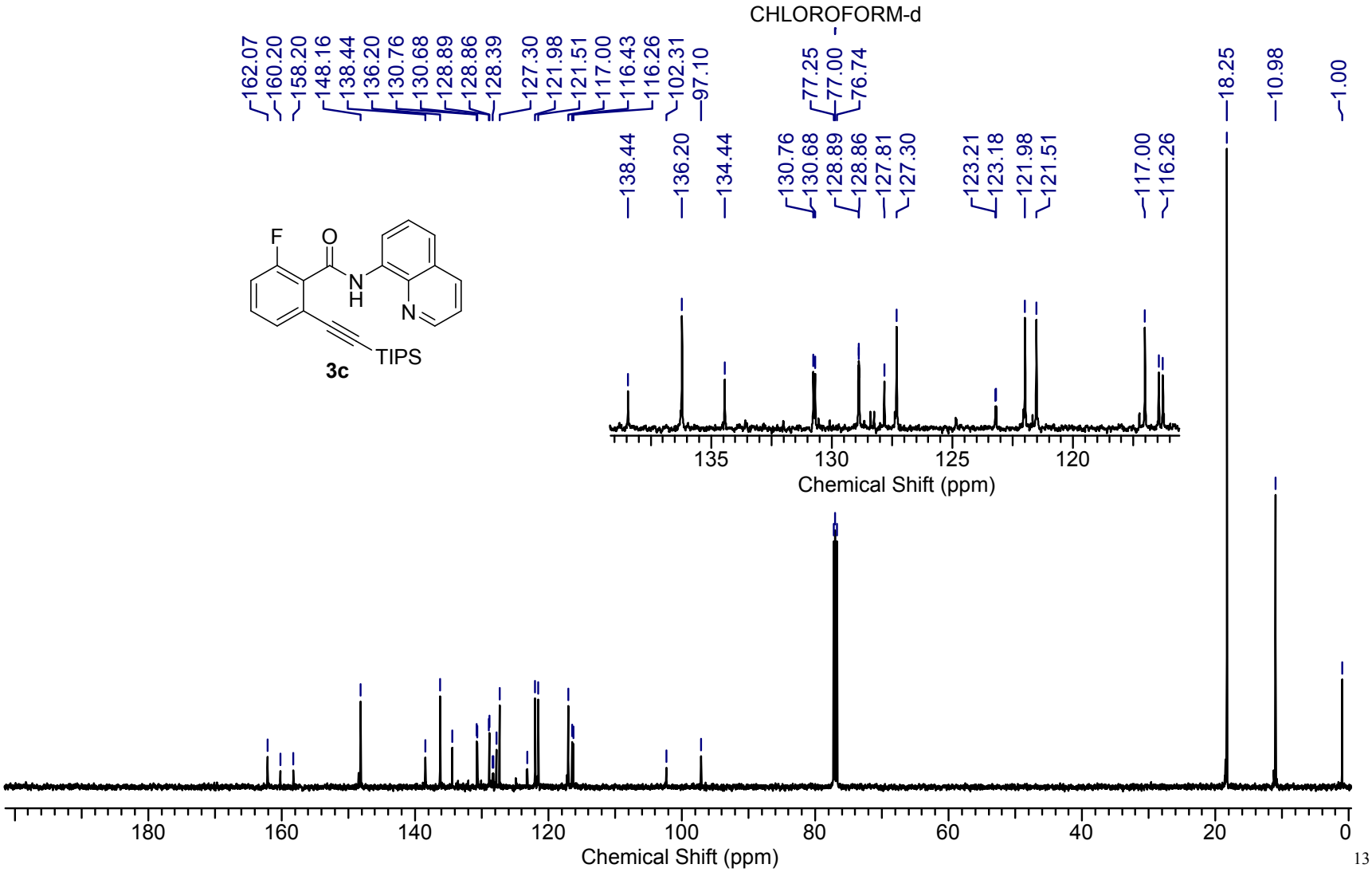
^{1}H NMR of **3b**


CHLOROFORM-d
163.44
157.62
148.09
139.11
136.03
135.66
133.01
132.22
127.96
127.40
122.19
121.29
121.11
117.15
111.44
83.37
77.26
77.00
76.75
61.69
55.91
18.38
11.18
OMe O
N
H
N
TIPS
3b
139.11
136.03
135.66
133.01
132.22
127.96
127.40
122.19
121.33
121.29
121.11
135
130
125
120
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

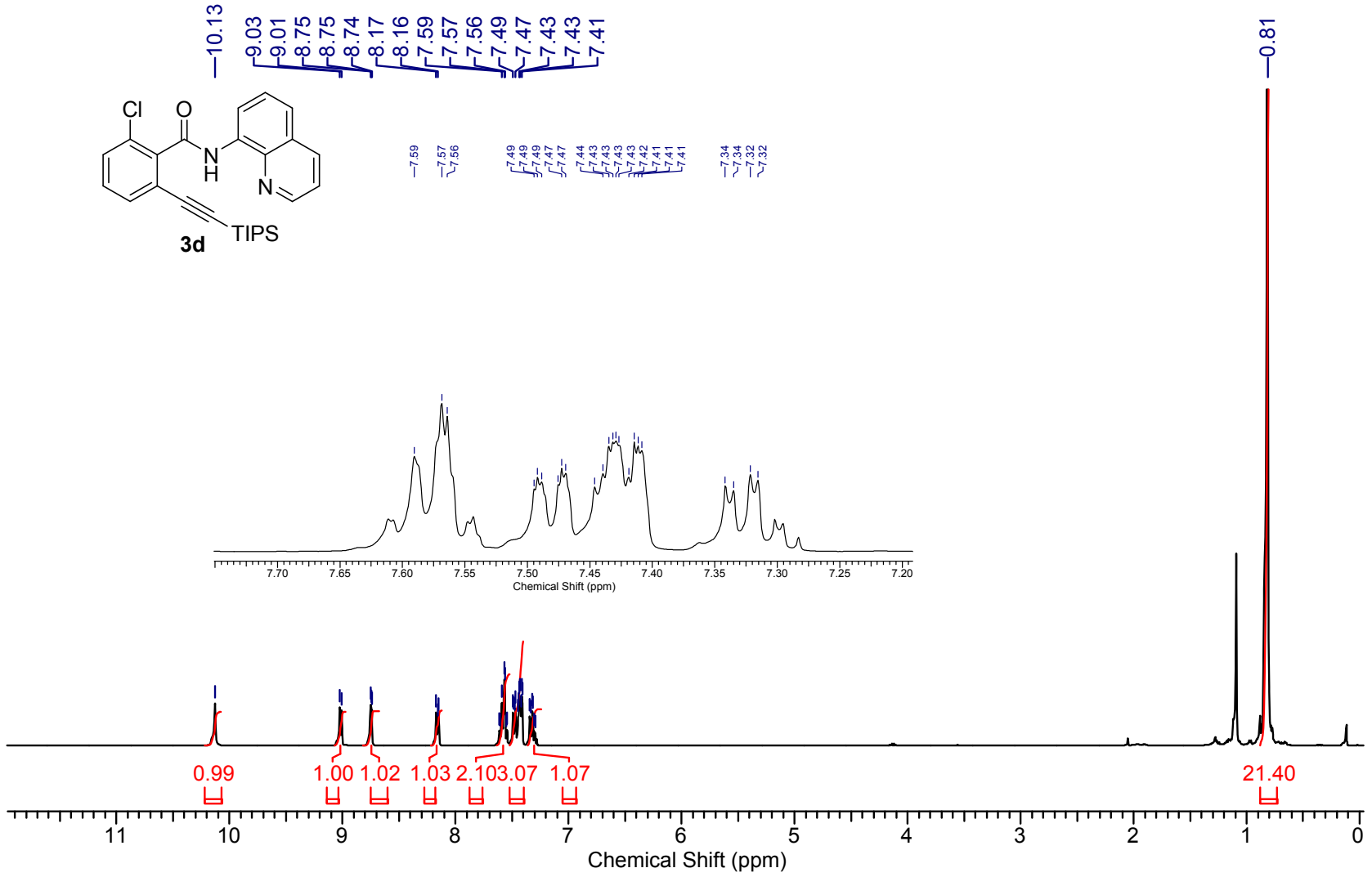
^{13}C NMR of **3b**


CHLOROFORM-d
10.20
8.99
8.98
8.76
8.75
8.18
8.18
8.16
7.59
7.58
7.57
7.56
7.45
7.39
7.39
7.38
7.16
0.83
0.82
0.09
F
O
N
H
N
TIPS
3c
CHLOROFORM-d
7.61
7.59
7.58
7.57
7.56
7.55
7.55
7.45
7.44
7.44
7.43
7.39
7.39
7.39
7.38
7.37
7.27
7.16
7.16
7.60
7.55
7.50
7.45
7.40
7.35
7.30
7.25
7.20
7.15
7.10
Chemical Shift (ppm)
0.93
1.12
1.00
1.19
2.60
1.21
2.01
1.05
21.67
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

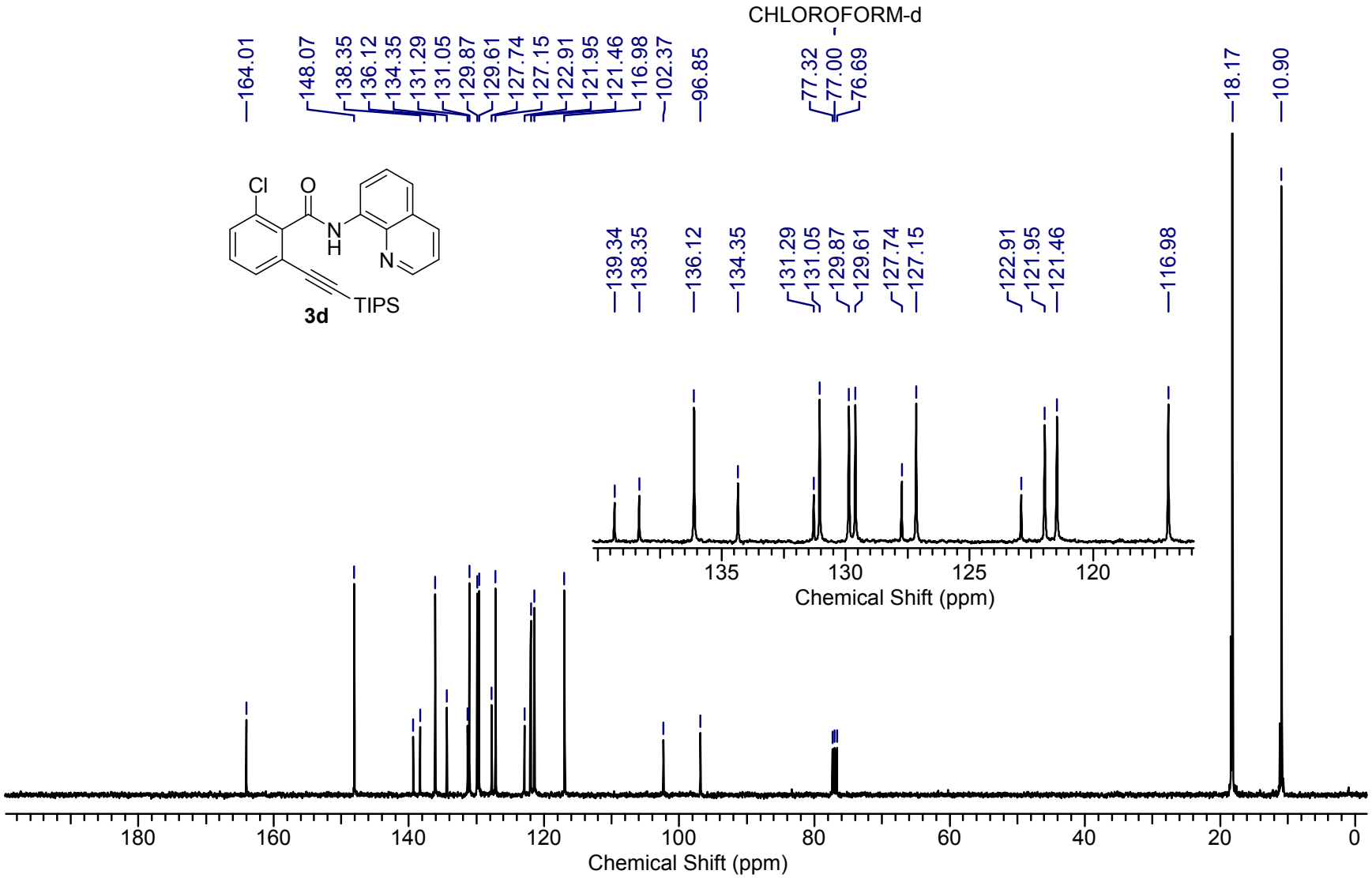
^{1}H NMR of **3c**


CHLOROFORM-d
162.07
160.20
158.20
148.16
138.44
136.20
130.76
130.68
128.89
128.86
128.39
127.30
121.98
121.51
117.00
116.43
116.26
102.31
97.10
77.25
77.00
76.74
18.25
10.98
1.00
138.44
136.20
134.44
130.76
130.68
128.89
128.86
127.81
127.30
123.21
123.18
121.98
121.51
117.00
116.26
F
O
N
H
N
TIPS
3c
135
130
125
120
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)
13

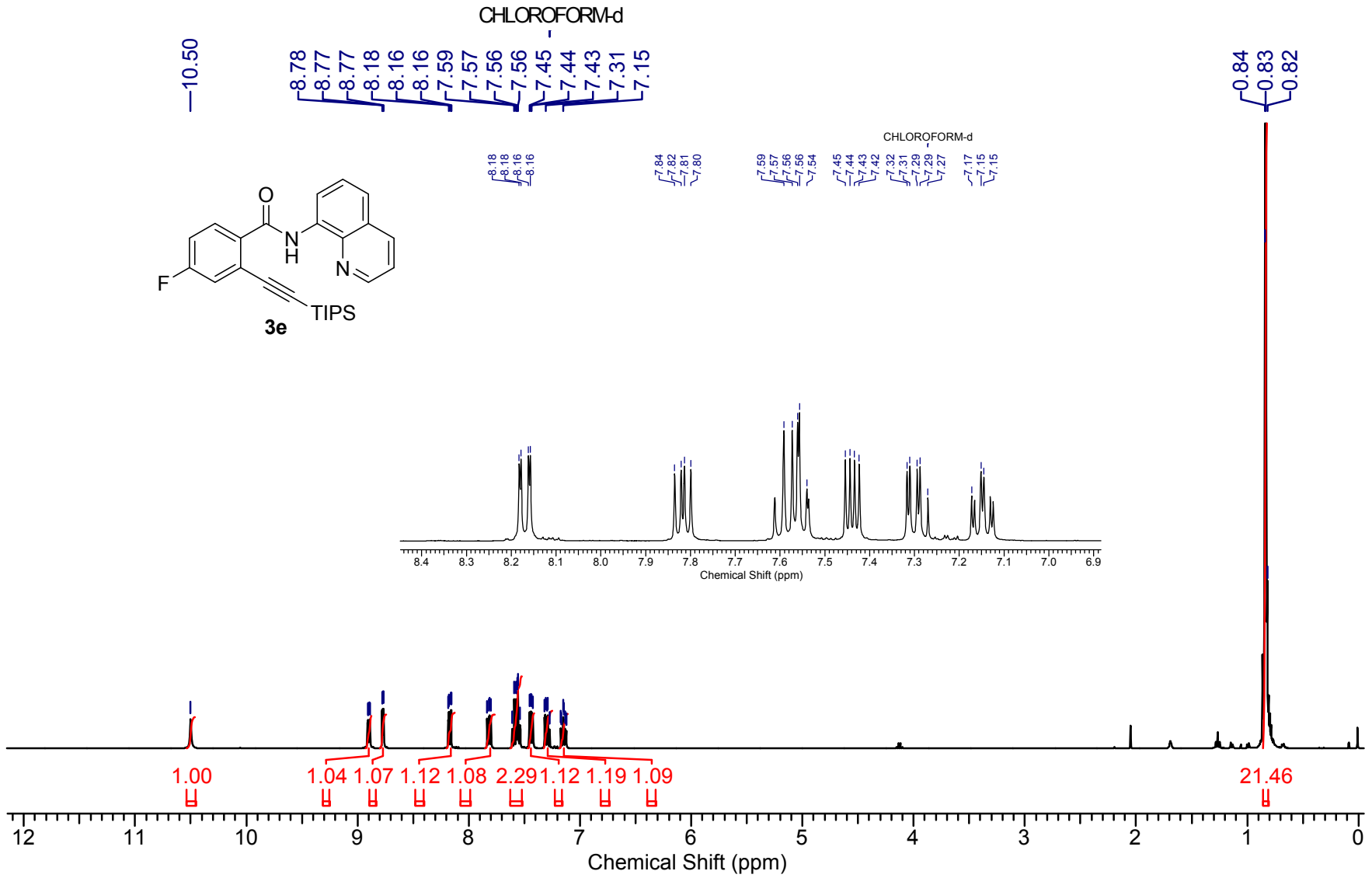
C NMR of **3c**


10.13
9.03
9.01
8.75
8.75
8.74
8.17
8.16
7.59
7.57
7.56
7.49
7.47
7.43
7.43
7.41
0.81
Cl
O
N
H
N
TIPS
3d
Chemical Shift (ppm)
0.99
1.00
1.02
1.03
2.10
3.07
1.07
21.40
Chemical Shift (ppm)

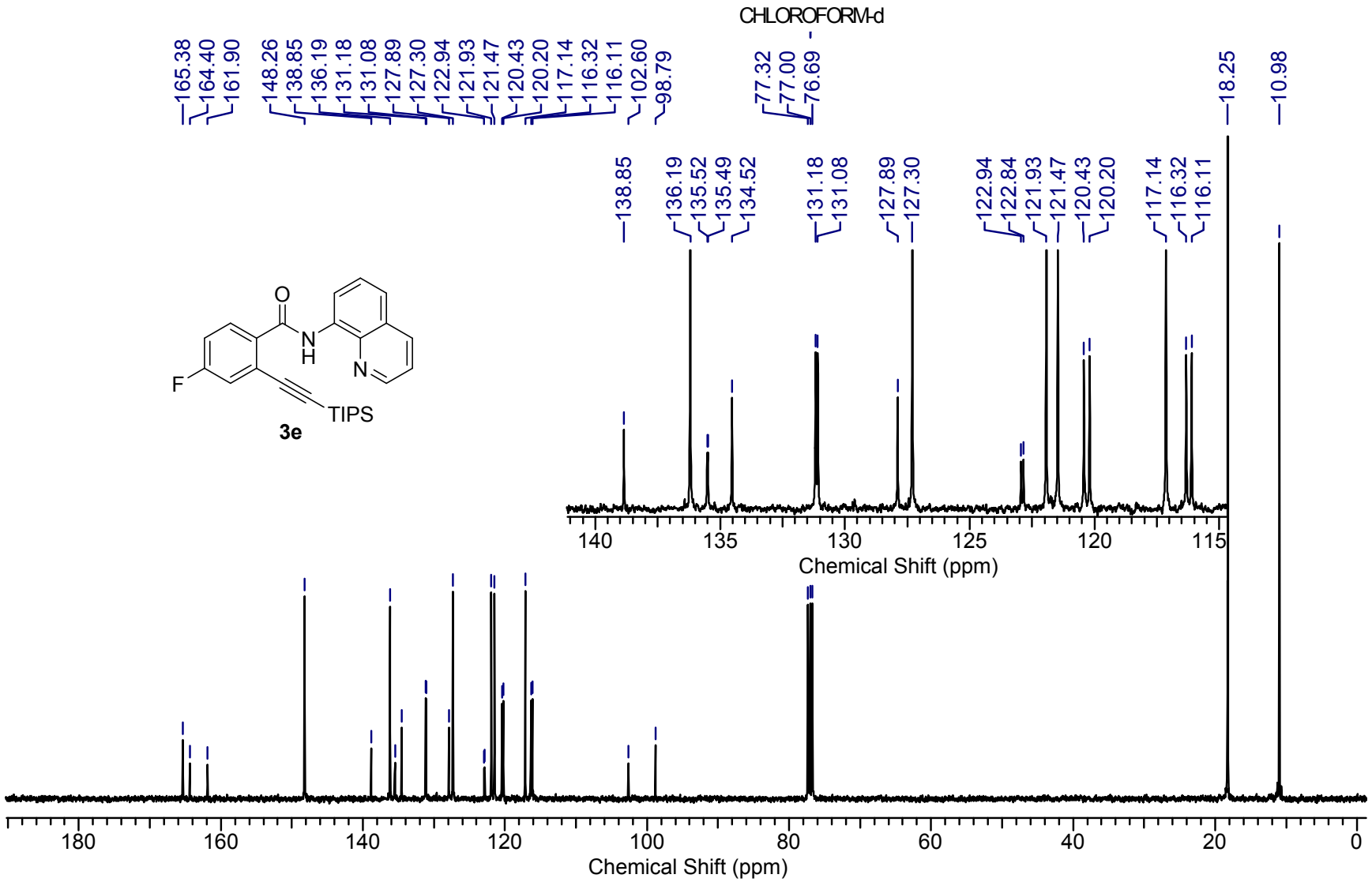
^{1}H NMR of **3d**


CHLOROFORM-d
164.01
148.07
138.35
136.12
134.35
131.29
131.05
129.87
129.61
127.74
127.15
122.91
121.95
121.46
116.98
102.37
96.85
77.32
77.00
76.69
18.17
10.90
Cl
O
N
H
N
TIPS
3d
139.34
138.35
136.12
134.35
131.29
131.05
129.87
129.61
127.74
127.15
122.91
121.95
121.46
116.98
135
130
125
120
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

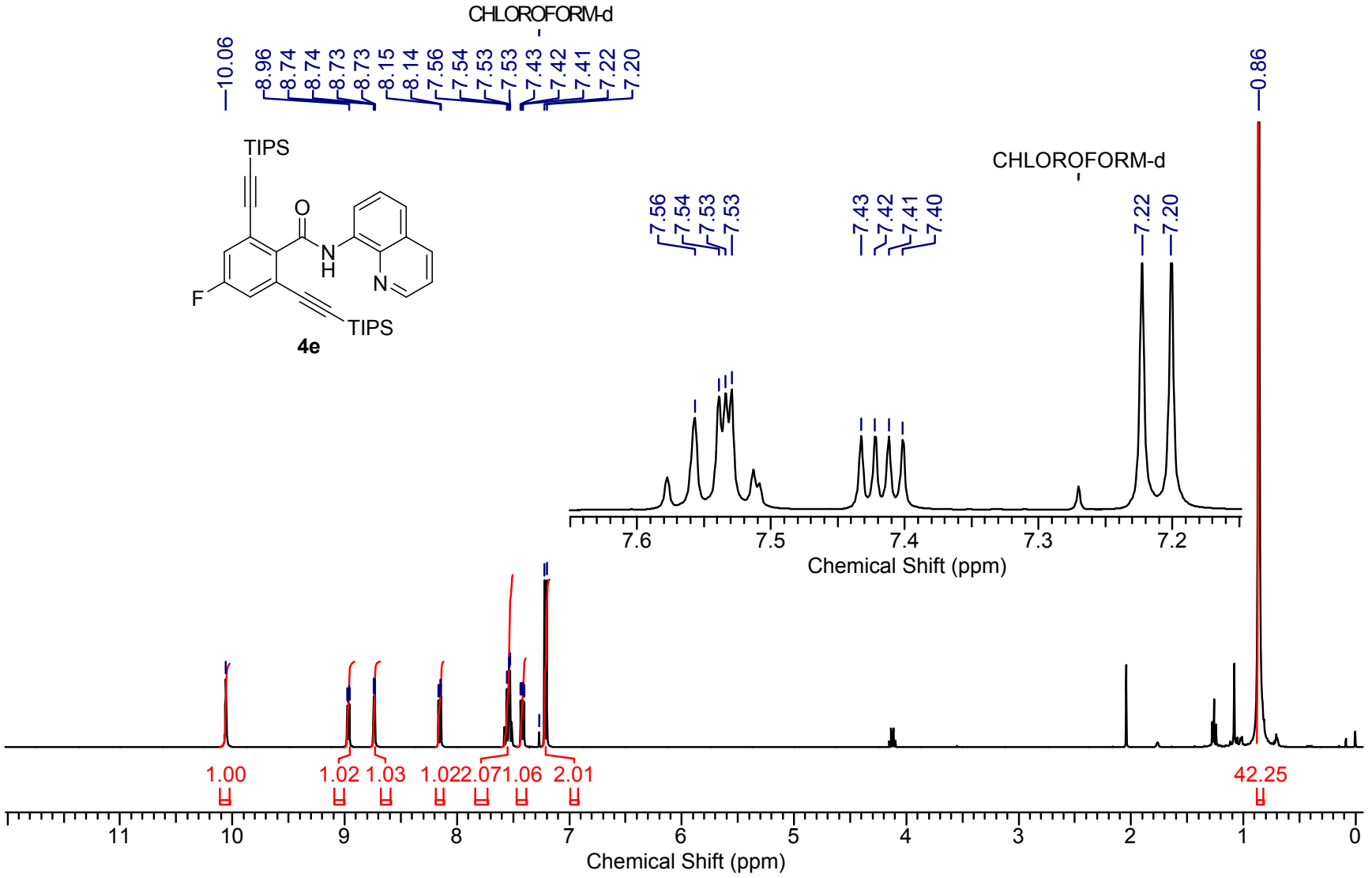
^{13}C NMR of **3d**


CHLOROFORM-d
10.50
8.78
8.77
8.77
8.18
8.16
8.16
7.59
7.57
7.56
7.56
7.45
7.44
7.43
7.31
7.15
0.84
0.83
0.82
O
N
H
N
F
TIPS
3e
Chemical Shift (ppm)
1.00
1.04
1.07
1.12
1.08
2.29
1.12
1.19
1.09
21.46
Chemical Shift (ppm)

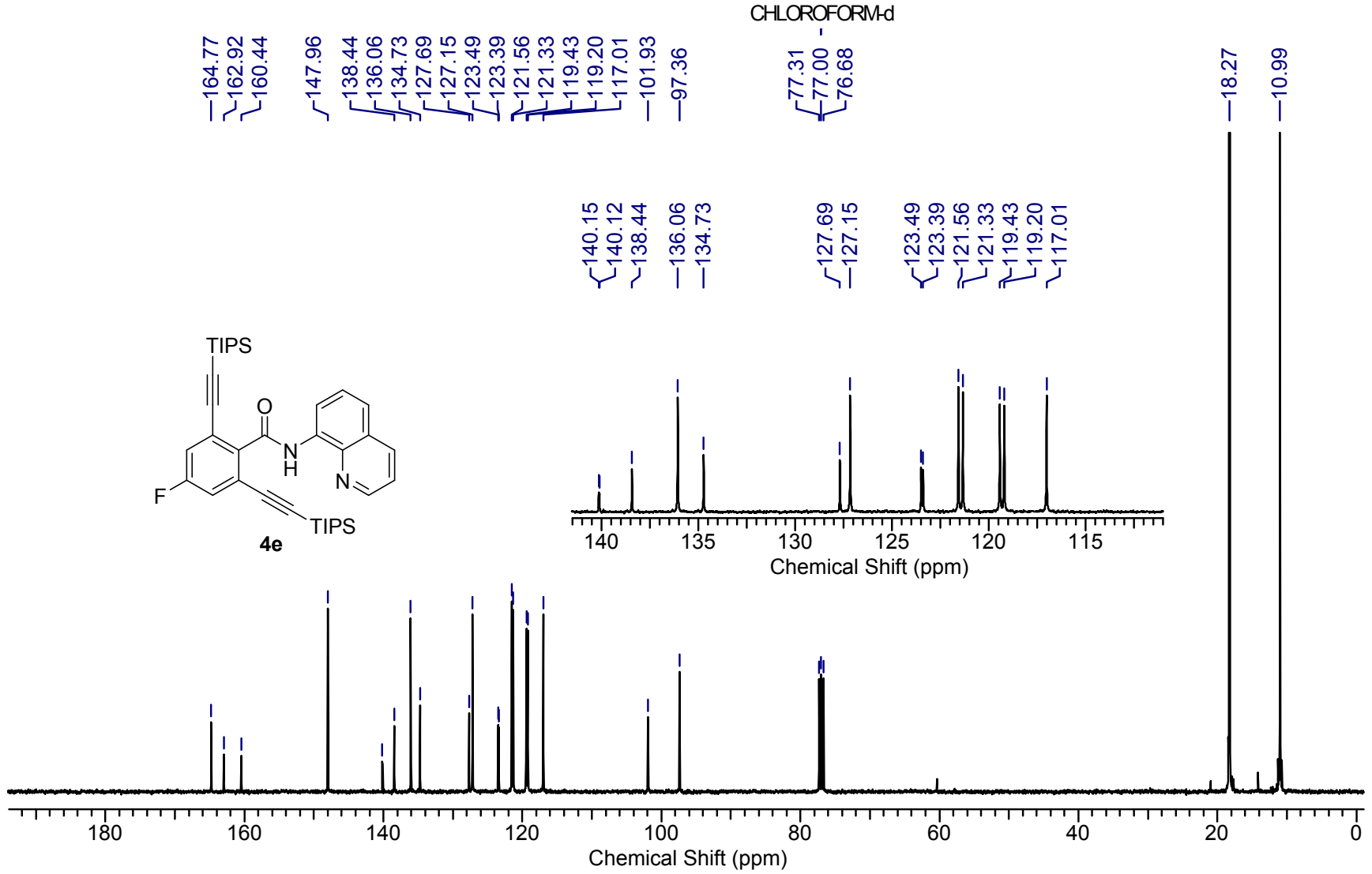
^{1}H NMR of **3e**


CHLOROFORM-d
165.38
164.40
161.90
148.26
138.85
136.19
131.18
131.08
127.89
127.30
122.94
121.93
121.47
120.43
120.20
117.14
116.32
116.11
102.60
98.79
77.32
77.00
76.69
18.25
10.98
O
N
H
N
F
TIPS
3e
Chemical Shift (ppm)
Chemical Shift (ppm)

^{13}C NMR of **3e**


CHLOROFORM-d
10.06
8.96
8.74
8.74
8.73
8.73
8.15
8.14
7.56
7.54
7.53
7.53
7.43
7.42
7.41
7.22
7.20
0.86
TIPS
O
N
H
N
F
TIPS
4e
CHLOROFORM-d
7.56
7.54
7.53
7.53
7.43
7.42
7.41
7.40
7.22
7.20
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)
1.00
1.02
1.03
1.02
2.07
1.06
2.01
42.25
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

^{1}H NMR of **4e**


CHLOROFORM-d
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162.92
160.44
147.96
138.44
136.06
134.73
127.69
127.15
123.49
123.39
121.56
121.33
119.43
119.20
117.01
101.93
97.36
77.31
77.00
76.68
18.27
10.99
TIPS
O
N
H
N
F
TIPS
4e
140.15
140.12
138.44
136.06
134.73
127.69
127.15
123.49
123.39
121.56
121.33
119.43
119.20
117.01
140
135
130
125
120
115
Chemical Shift (ppm)
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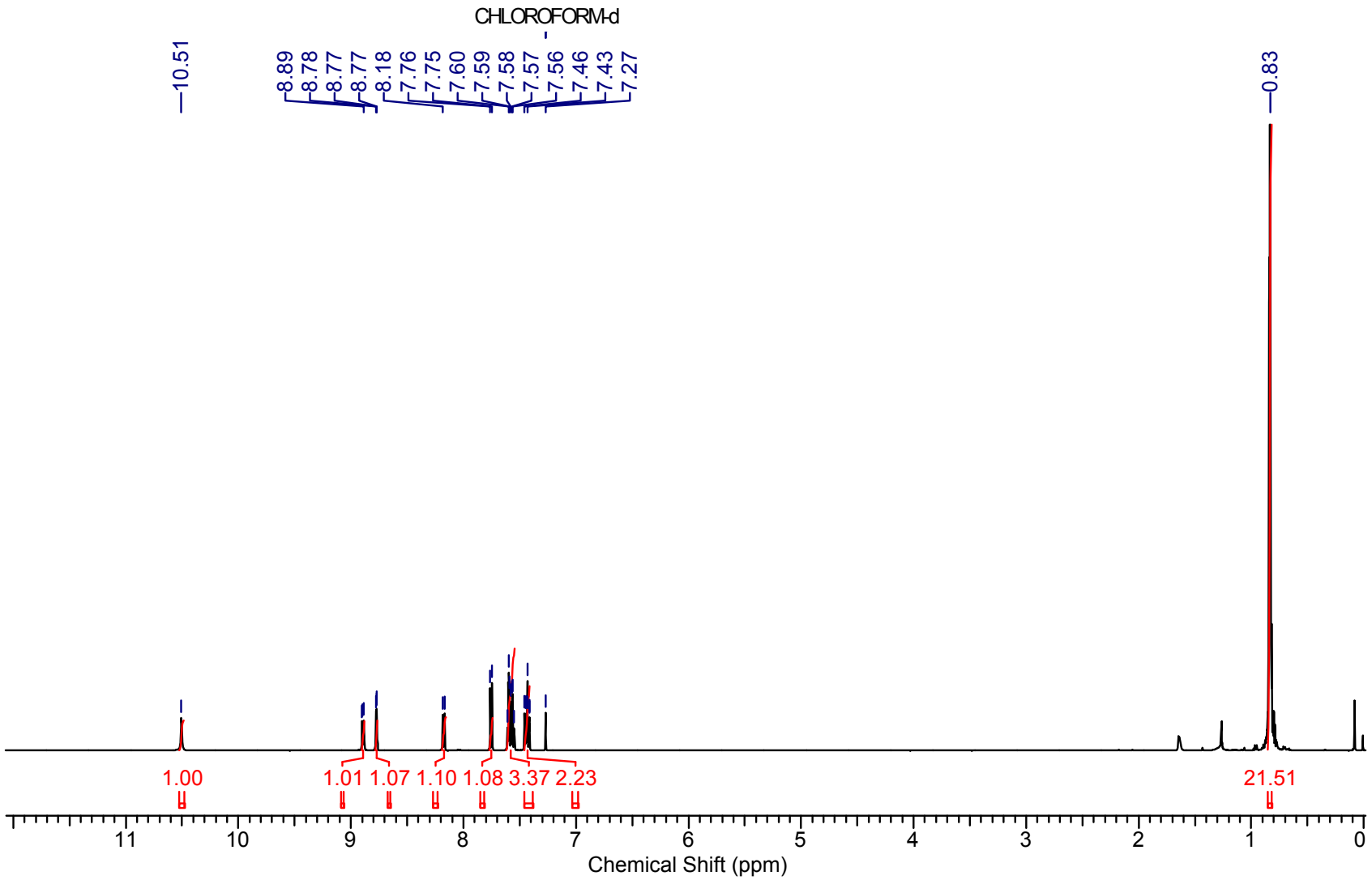
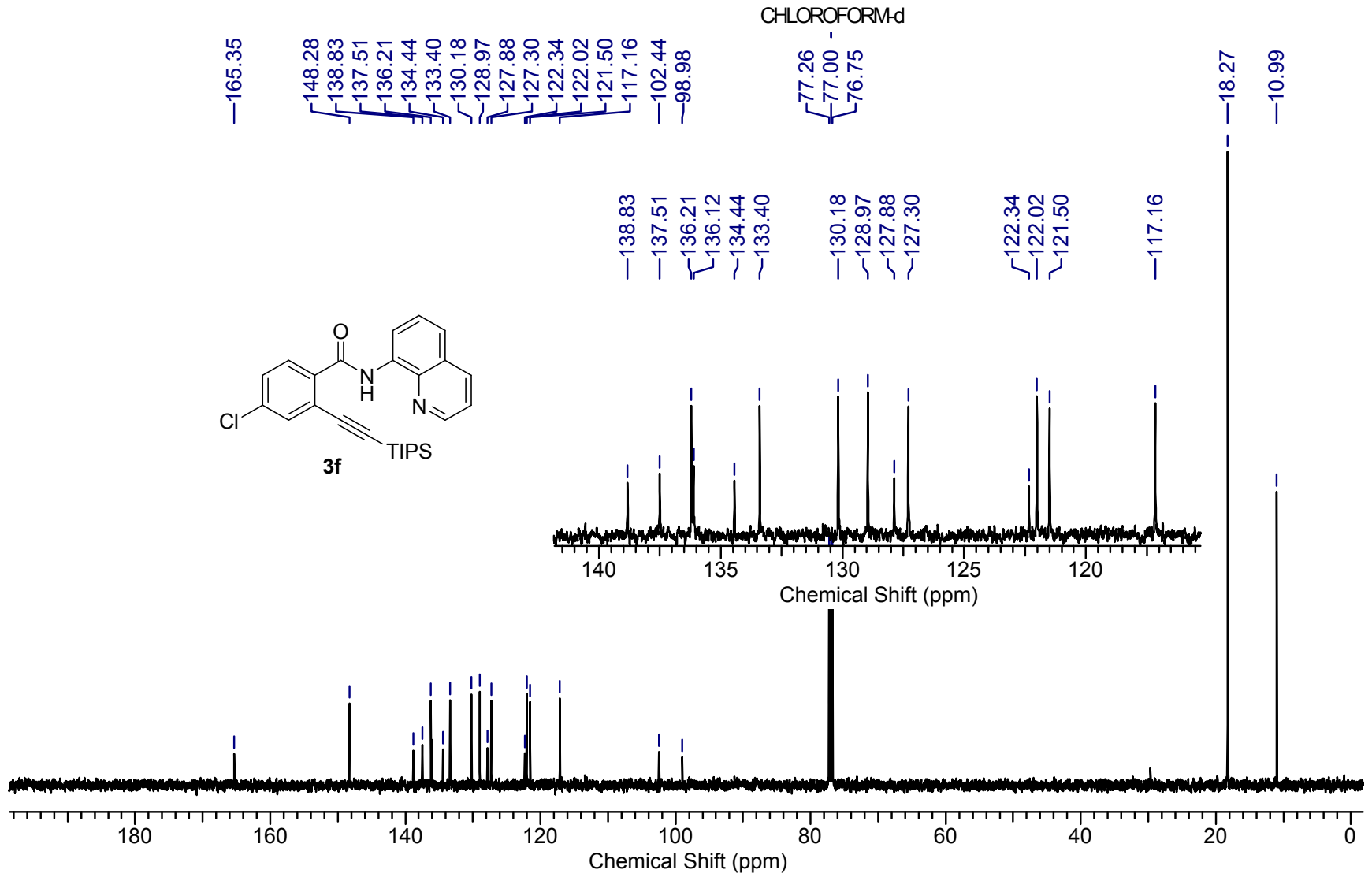
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

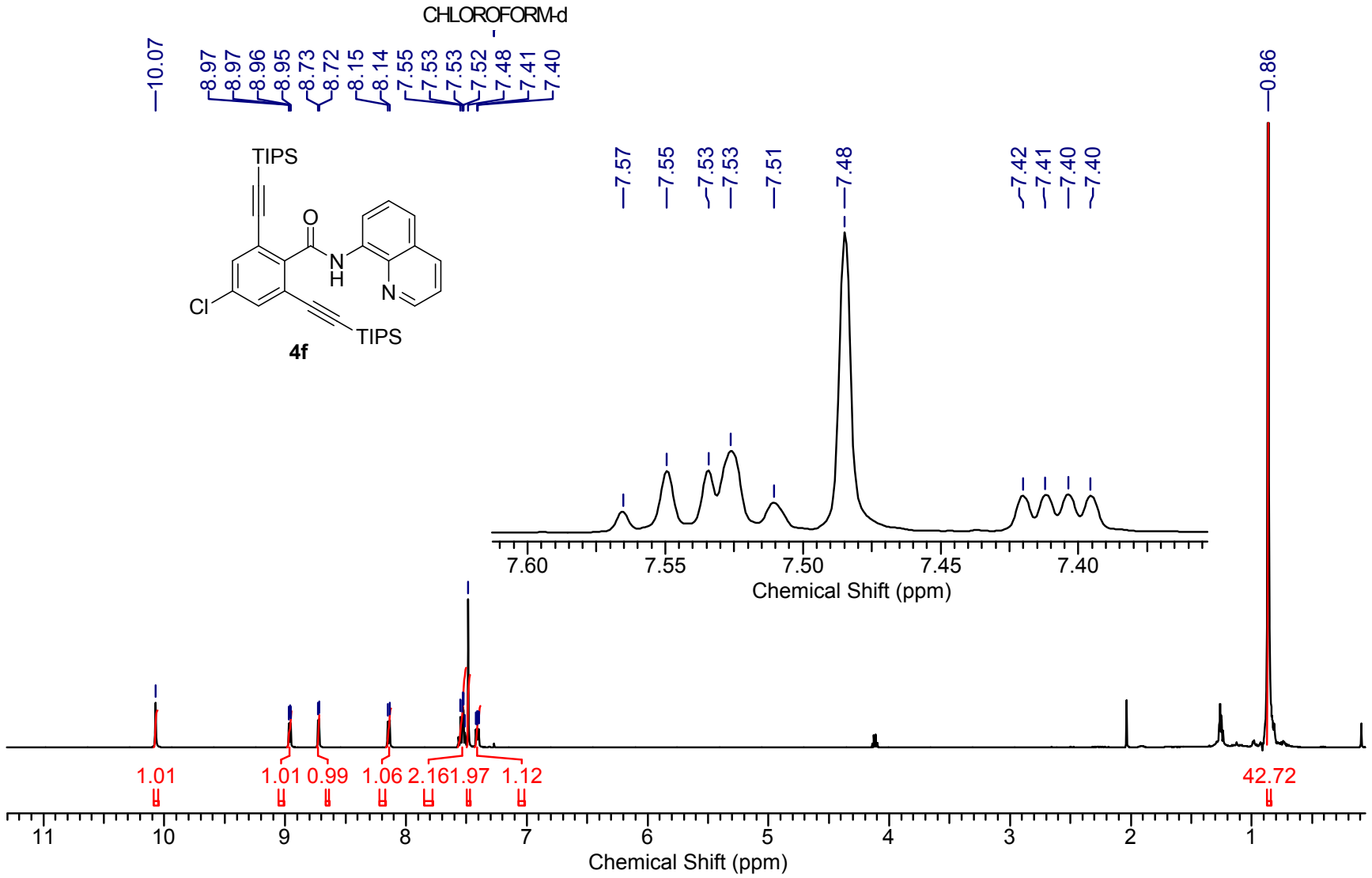
^{13}C NMR of **4e**


CHLOROFORM-d
10.51
8.89
8.78
8.77
8.77
8.18
7.76
7.75
7.60
7.59
7.58
7.57
7.56
7.46
7.43
7.27
0.83
1.00
1.01
1.07
1.10
1.08
3.37
2.23
21.51
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

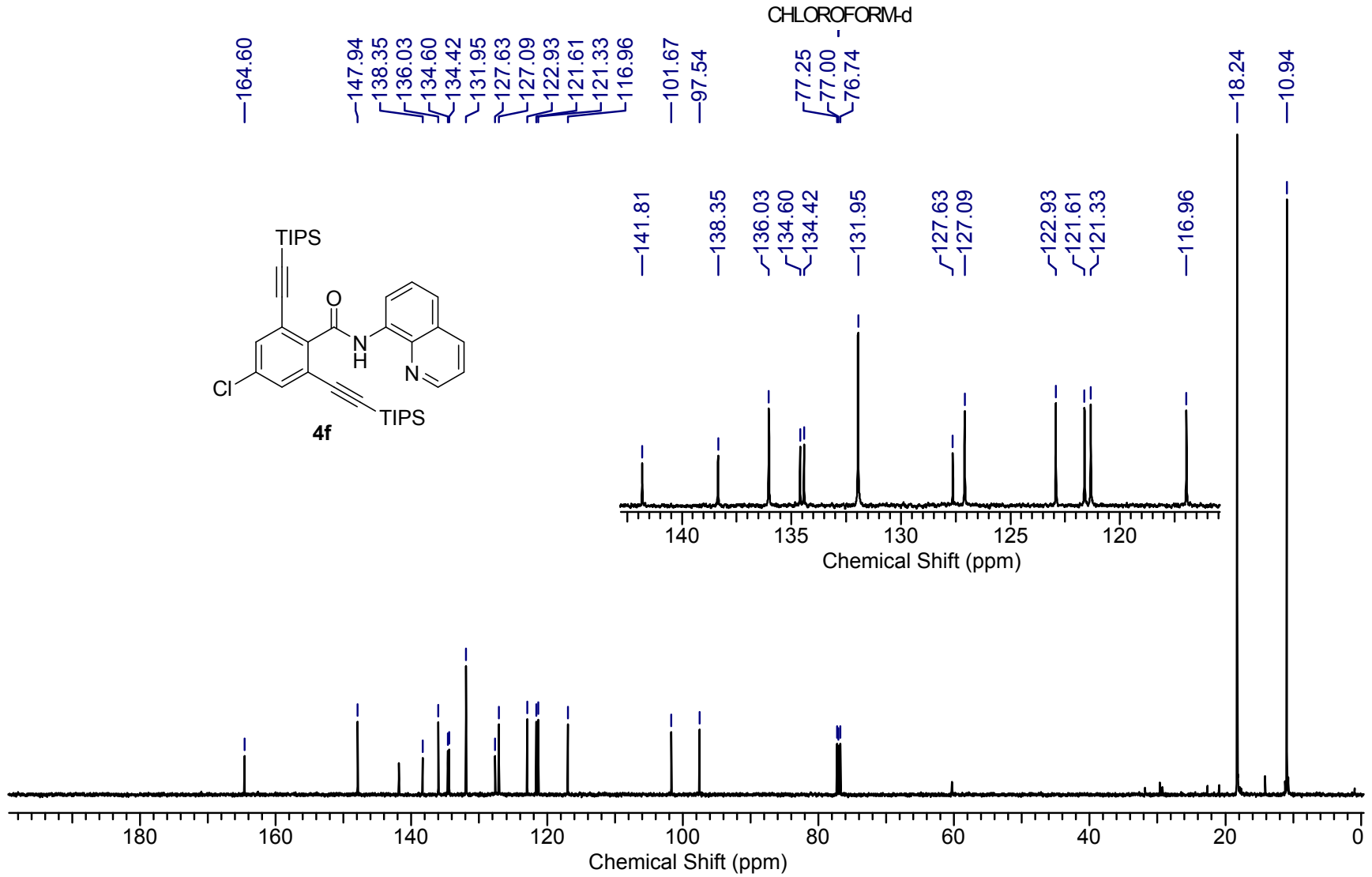
^{1}H NMR of **3f**


CHLOROFORM-d
165.35
148.28
138.83
137.51
136.21
134.44
133.40
130.18
128.97
127.88
127.30
122.34
122.02
121.50
117.16
102.44
98.98
77.26
77.00
76.75
18.27
10.99
O
N
H
N
Cl
TIPS
3f
Chemical Shift (ppm)
Chemical Shift (ppm)

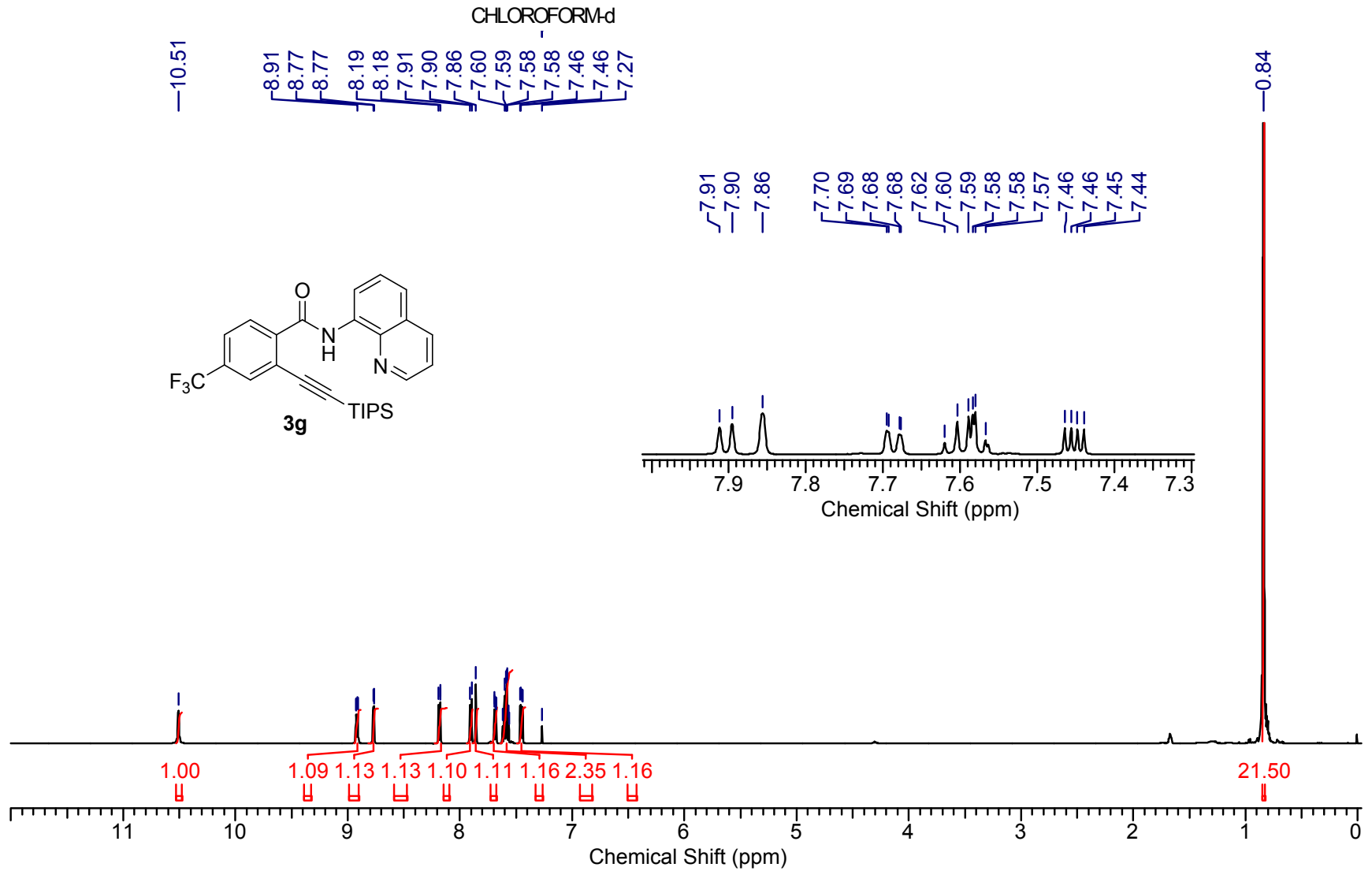
^{13}C NMR of **3f**


CHLOROFORM-d
10.07
8.97
8.97
8.96
8.95
8.73
8.72
8.15
8.14
7.55
7.53
7.53
7.52
7.48
7.41
7.40
0.86
TIPS
O
N
H
N
Cl
TIPS
4f
7.57
7.55
7.53
7.53
7.51
7.48
7.42
7.41
7.40
7.40
7.60
7.55
7.50
7.45
7.40
Chemical Shift (ppm)
1.01
1.01
0.99
1.06
2.16
1.97
1.12
42.72
11
10
9
8
7
6
5
4
3
2
1
Chemical Shift (ppm)

^{1}H NMR of **4f**


CHLOROFORM-d
164.60
147.94
138.35
136.03
134.60
134.42
131.95
127.63
127.09
122.93
121.61
121.33
116.96
101.67
97.54
77.25
77.00
76.74
18.24
10.94
TIPS
O
N
H
N
Cl
TIPS
4f
141.81
138.35
136.03
134.60
134.42
131.95
127.63
127.09
122.93
121.61
121.33
116.96
140
135
130
125
120
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

^{13}C NMR of **4f**


CHLOROFORM-d
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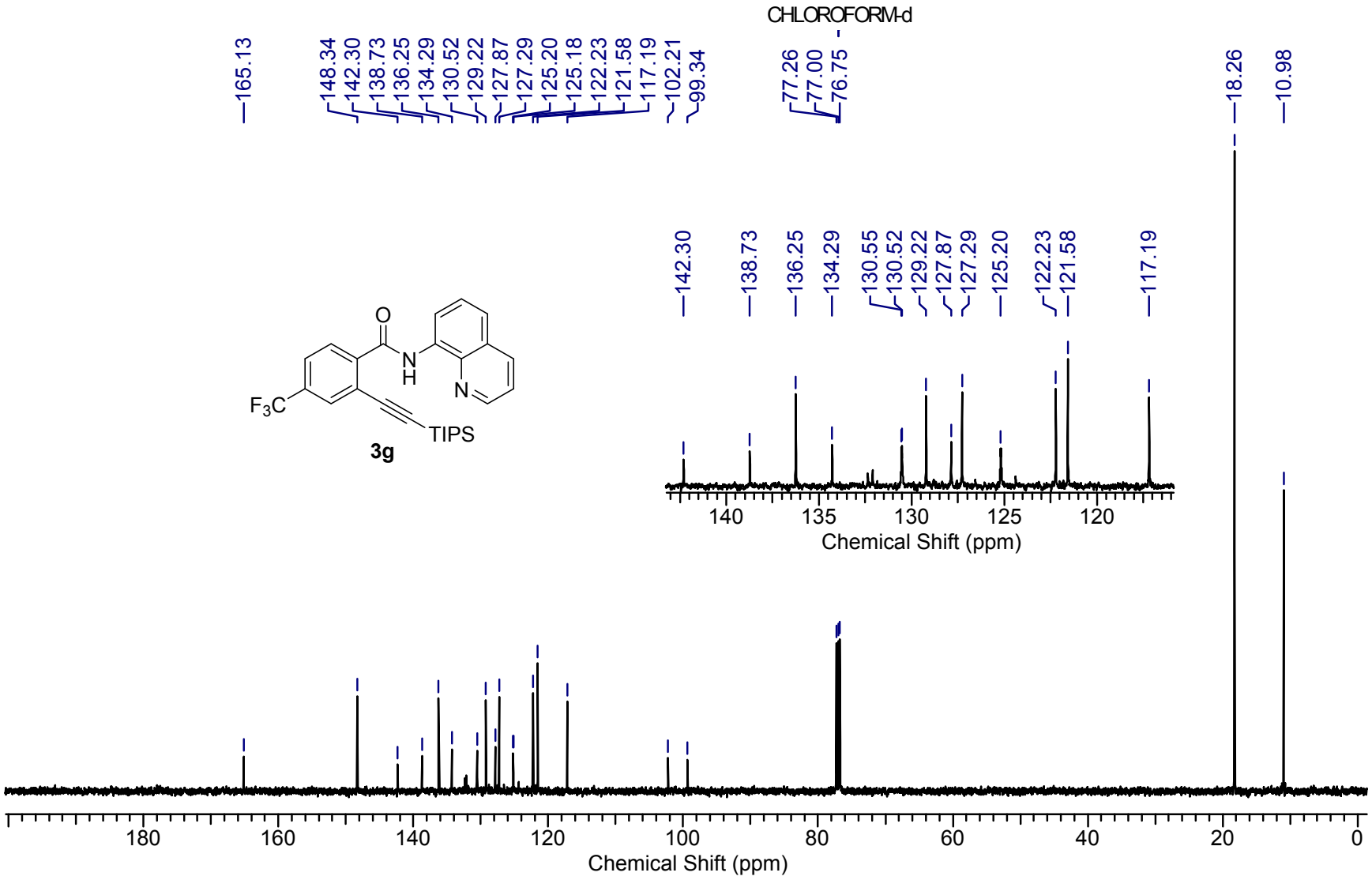
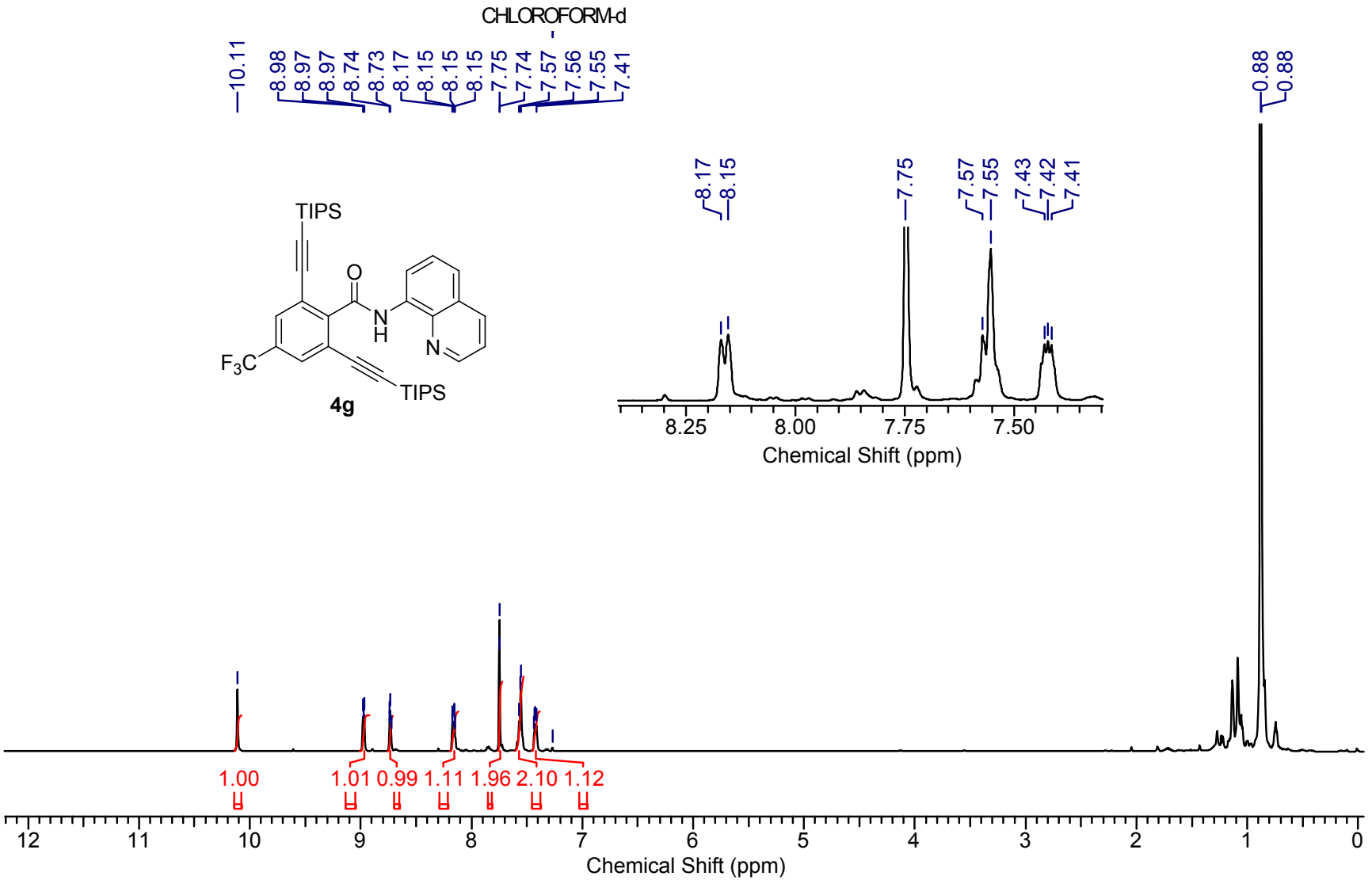
8.91
8.77
8.77
8.19
8.18
7.91
7.90
7.86
7.60
7.59
7.58
7.58
7.46
7.46
7.27
0.84
7.91
7.90
7.86
7.70
7.69
7.68
7.68
7.62
7.60
7.59
7.58
7.58
7.57
7.46
7.46
7.45
7.44
O
N
H
N
F3C
TIPS
3g
7.9
7.8
7.7
7.6
7.5
7.4
7.3
Chemical Shift (ppm)
1.00
1.09
1.13
1.13
1.10
1.11
1.16
2.35
1.16
21.50
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

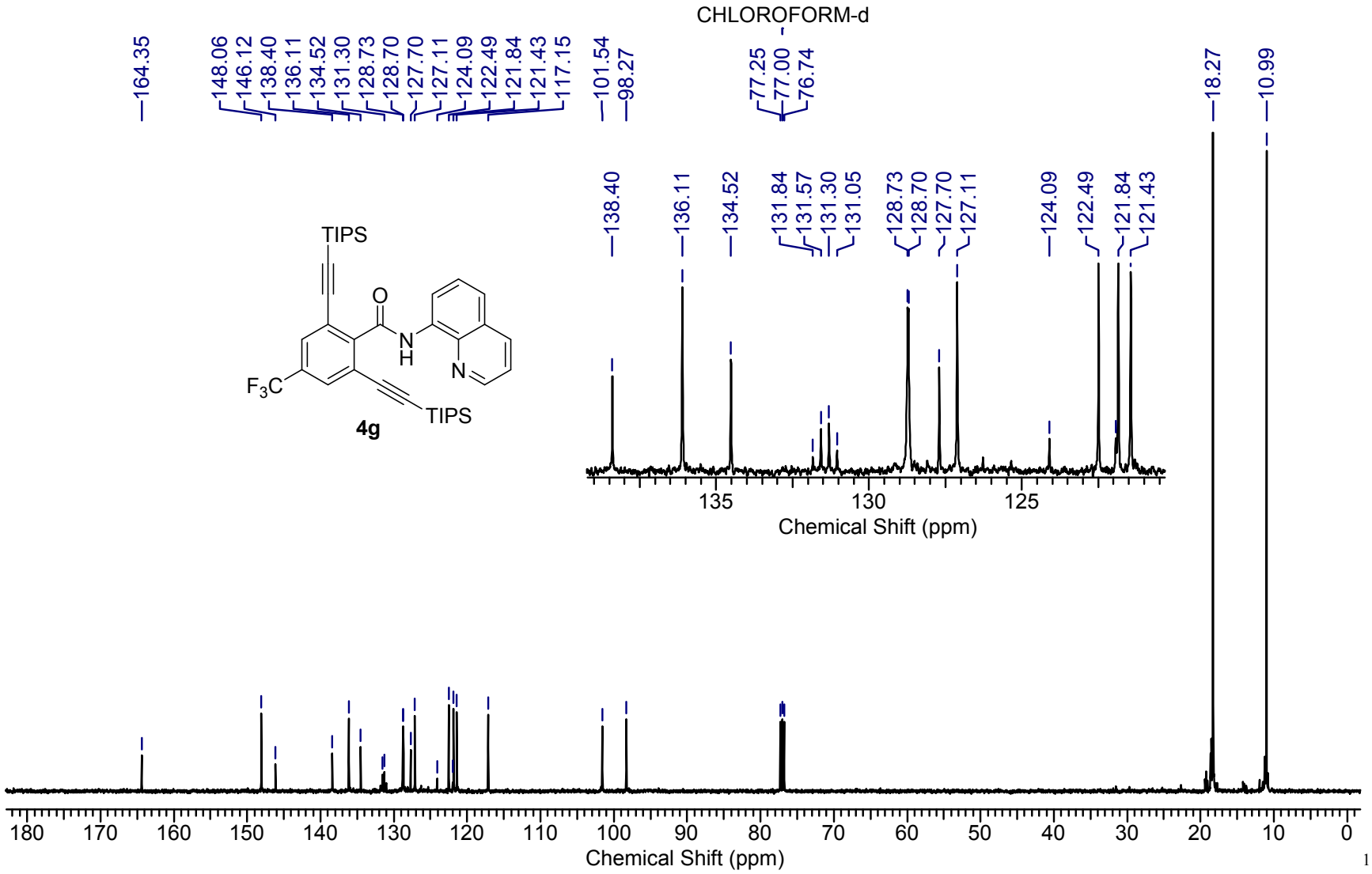
^{1}H NMR of **3g**


CHLOROFORM-d
165.13
148.34
142.30
138.73
136.25
134.29
130.52
129.22
127.87
127.29
125.20
125.18
122.23
121.58
117.19
102.21
99.34
77.26
77.00
76.75
18.26
10.98
O
N
H
N
F3C
TIPS
3g
Chemical Shift (ppm)
Chemical Shift (ppm)

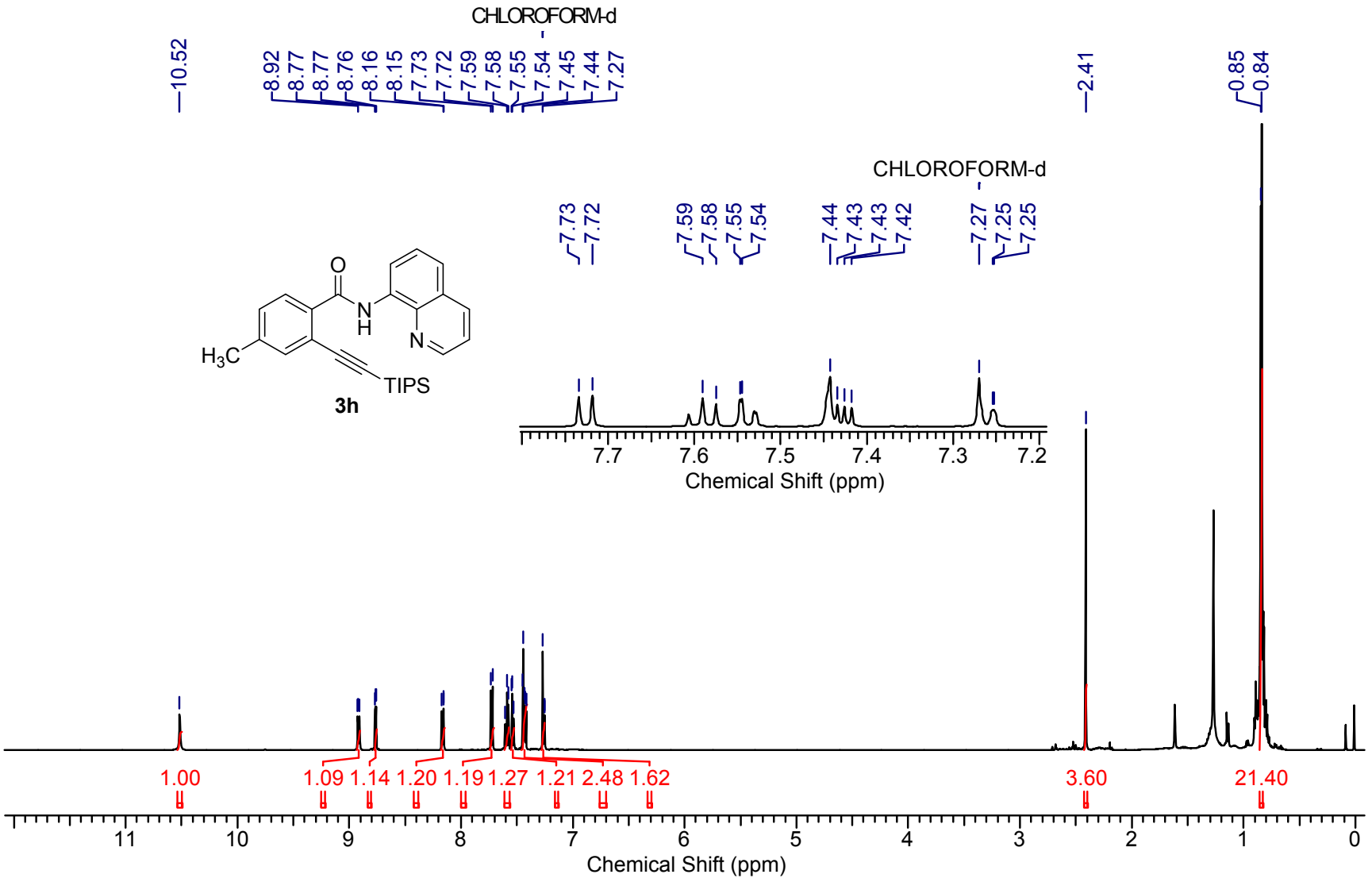
^{13}C NMR of **3g**


CHLOROFORM-d
10.11
8.98
8.97
8.97
8.74
8.73
8.17
8.15
8.15
8.15
7.75
7.74
7.57
7.56
7.55
7.41
0.88
0.88
TIPS
O
N
H
N
F3C
TIPS
4g
8.17
8.15
7.75
7.57
7.55
7.43
7.42
7.41
8.25
8.00
7.75
7.50
Chemical Shift (ppm)
1.00
1.01
0.99
1.11
1.96
2.10
1.12
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

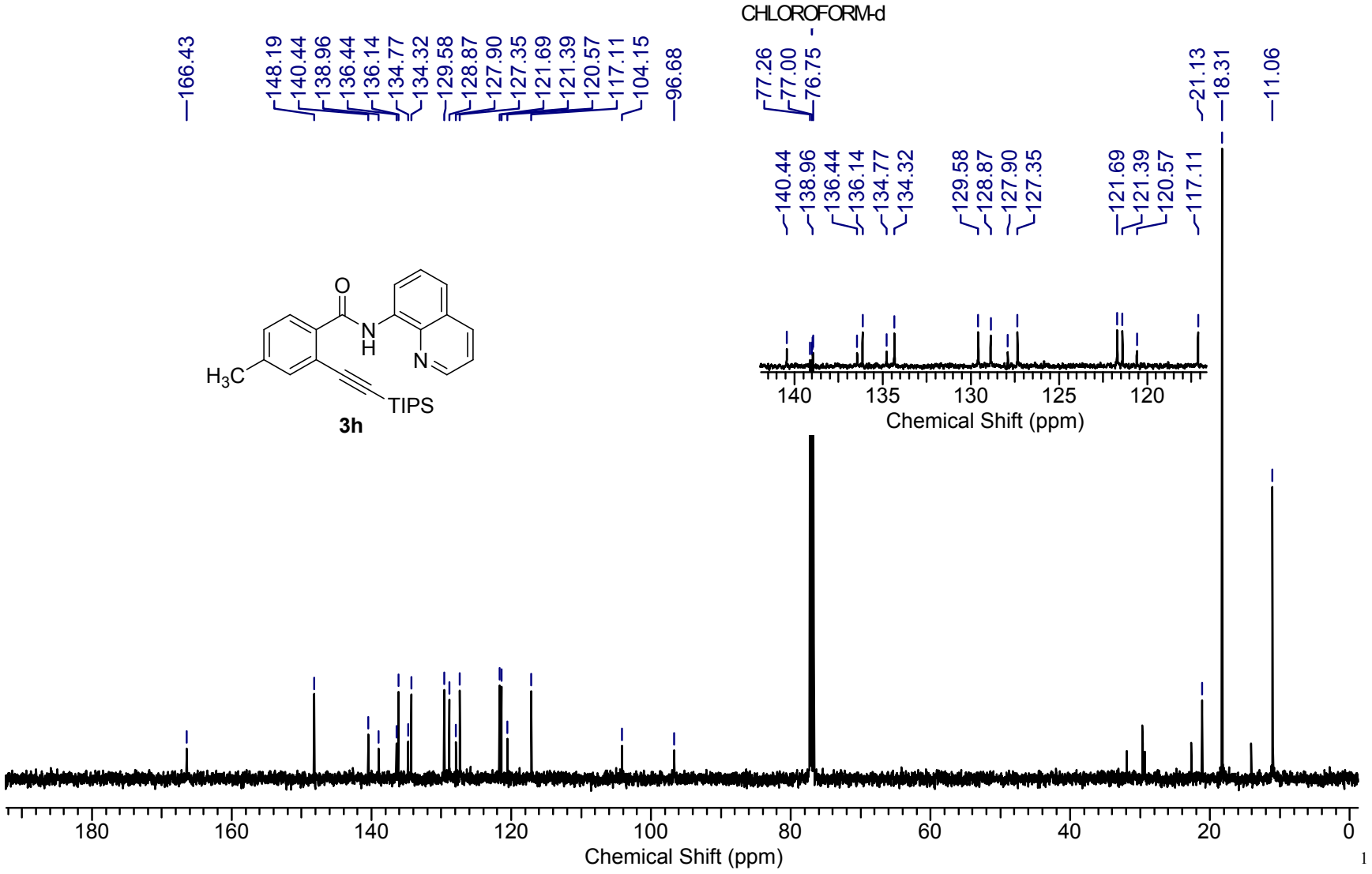
^{1}H NMR of **4g**


CHLOROFORM-d
164.35
148.06
146.12
138.40
136.11
134.52
131.30
128.73
128.70
127.70
127.11
124.09
122.49
121.84
121.43
117.15
101.54
98.27
77.25
77.00
76.74
18.27
10.99
TIPS
O
N
H
N
F3C
TIPS
4g
138.40
136.11
134.52
131.84
131.57
131.30
131.05
128.73
128.70
127.70
127.11
124.09
122.49
121.84
121.43
135
130
125
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
Chemical Shift (ppm)

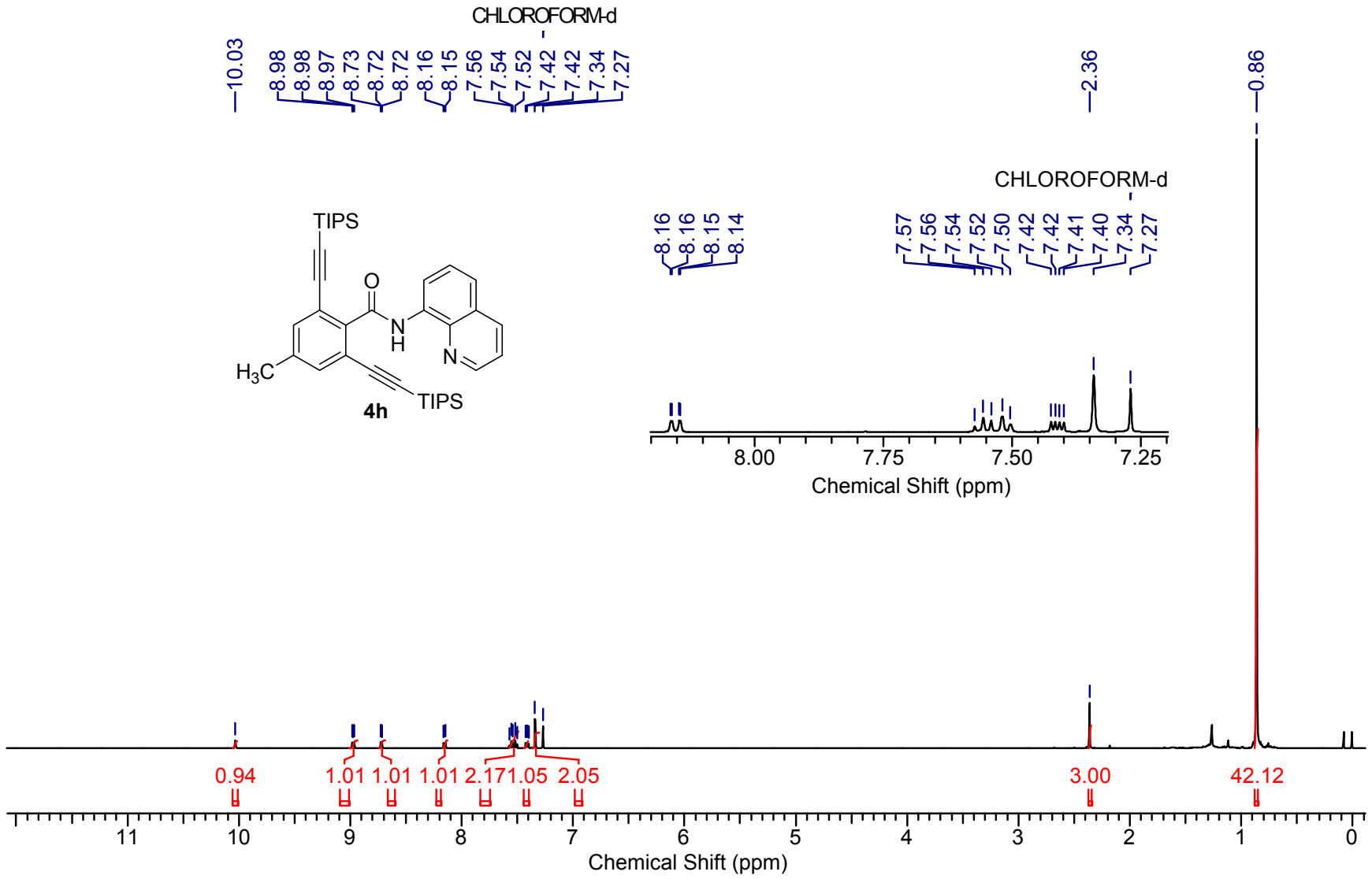
^{3}C NMR of**4g**


CHLOROFORM-d
10.52
8.92
8.77
8.77
8.76
8.16
8.15
7.73
7.72
7.59
7.58
7.55
7.54
7.45
7.44
7.27
2.41
0.85
0.84
CHLOROFORM-d
7.73
7.72
7.59
7.58
7.55
7.54
7.44
7.43
7.43
7.42
7.27
7.25
7.25
O
N
H
N
H3C
TIPS
3h
7.7
7.6
7.5
7.4
7.3
7.2
Chemical Shift (ppm)
1.00
1.09
1.14
1.20
1.19
1.27
1.21
2.48
1.62
3.60
21.40
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

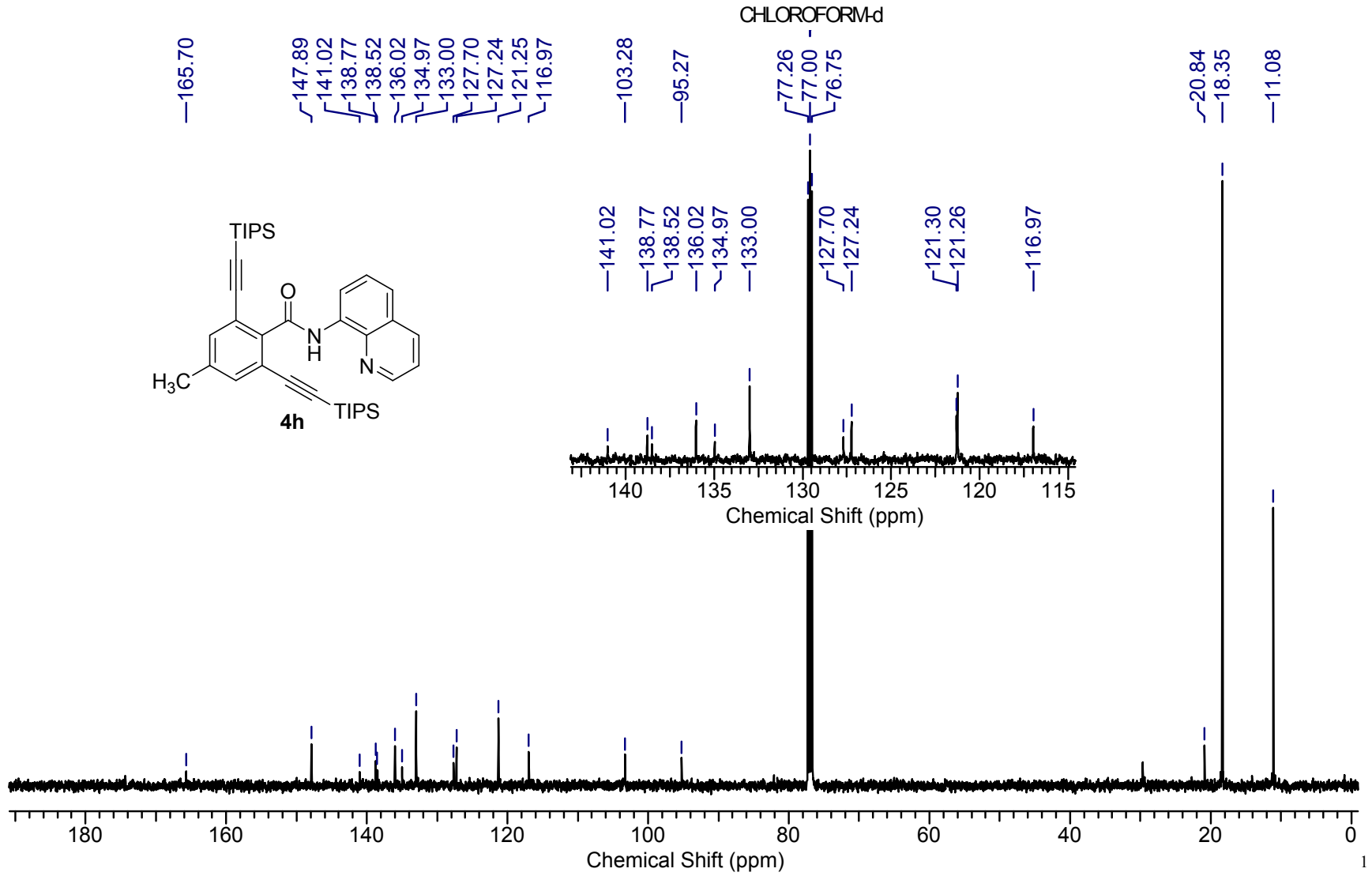
^{1}H NMR of **3h**


CHLOROFORM-d
166.43
148.19
140.44
138.96
136.44
136.14
134.77
134.32
129.58
128.87
127.90
127.35
121.69
121.39
120.57
117.11
104.15
96.68
77.26
77.00
76.75
21.13
18.31
11.06
O
N
H
N
H3C
TIPS
3h
Chemical Shift (ppm)
Chemical Shift (ppm)

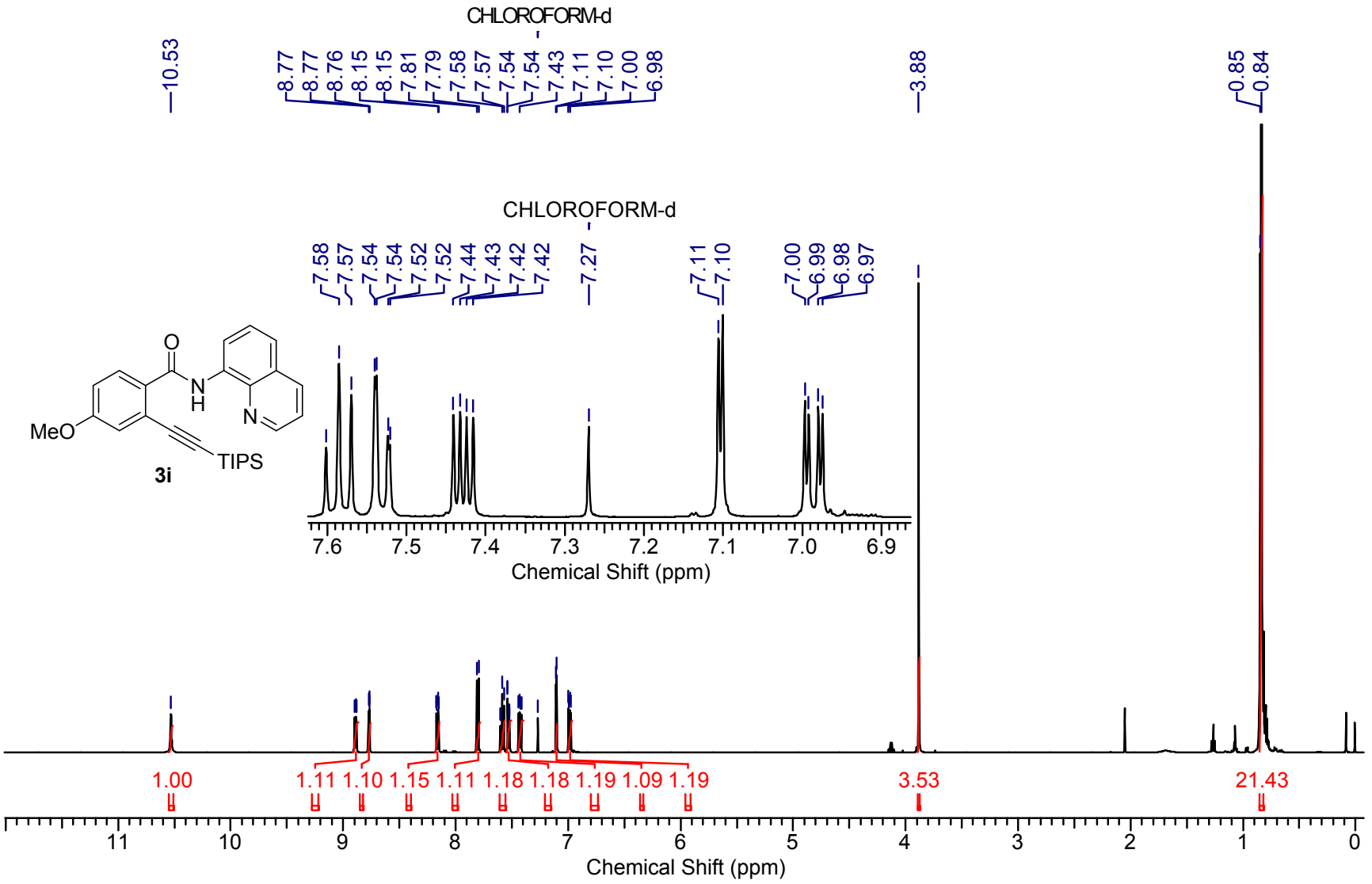
^{3}C NMR of **3h**


CHLOROFORM-d
10.03
8.98
8.98
8.97
8.73
8.72
8.72
8.16
8.15
7.56
7.54
7.52
7.42
7.42
7.34
7.27
2.36
0.86
TIPS
O
N
H
N
H3C
TIPS
4h
CHLOROFORM-d
8.16
8.16
8.15
8.14
7.57
7.56
7.54
7.52
7.50
7.42
7.42
7.41
7.40
7.34
7.27
8.00
7.75
7.50
7.25
Chemical Shift (ppm)
0.94
1.01
1.01
1.01
2.17
1.05
2.05
3.00
42.12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

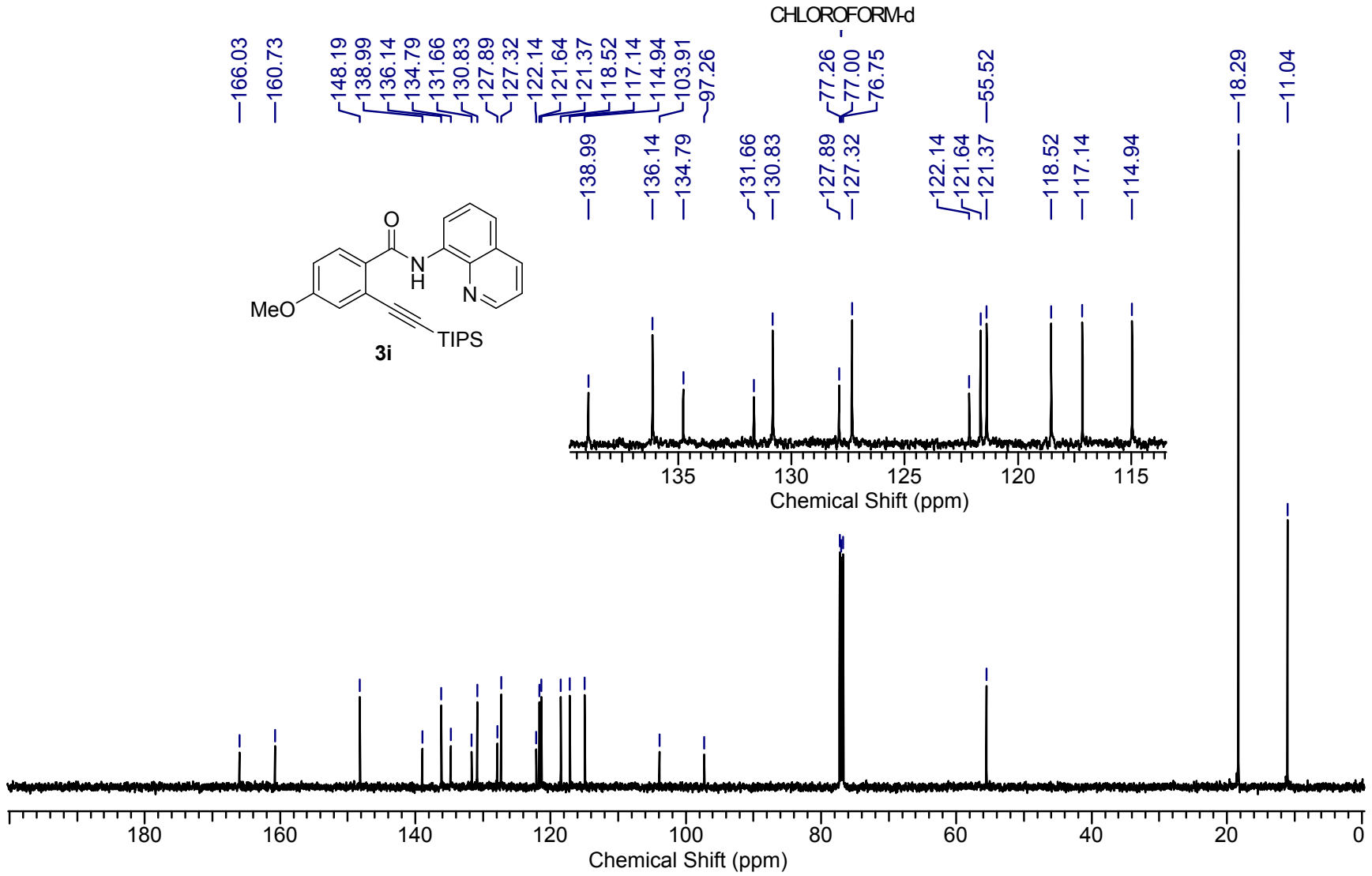
^{1}H NMR of **4h**


CHLOROFORM-d
165.70
147.89
141.02
138.77
138.52
136.02
134.97
133.00
127.70
127.24
121.25
116.97
103.28
95.27
77.26
77.00
76.75
20.84
18.35
11.08
TIPS
O
N
H
N
H3C
TIPS
4h
Chemical Shift (ppm)
Chemical Shift (ppm)

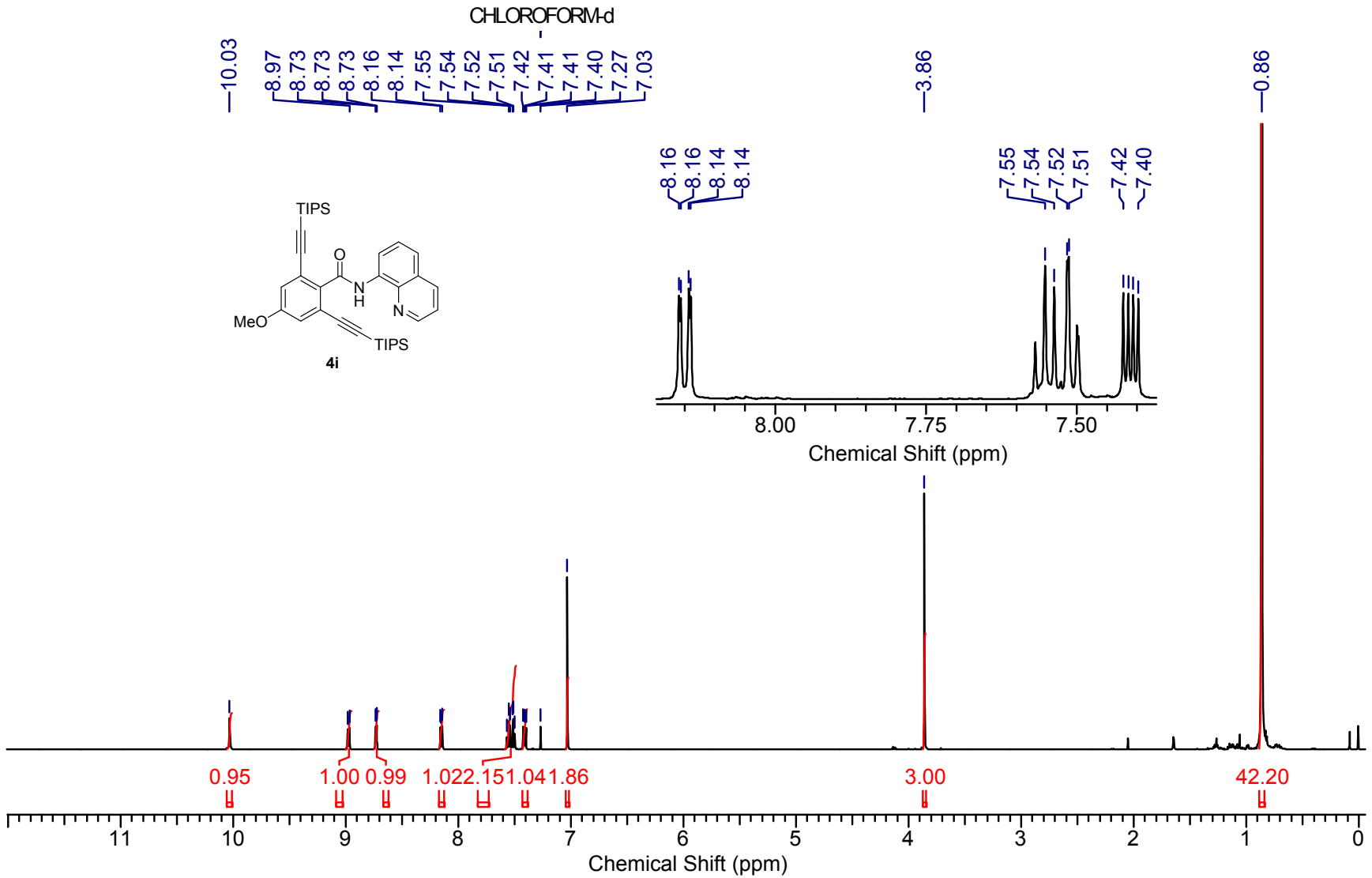
^{3}C NMR of **4h**


CHLOROFORM-d
10.53
8.77
8.77
8.76
8.15
8.15
7.81
7.79
7.58
7.57
7.54
7.54
7.43
7.11
7.10
7.00
6.98
3.88
0.85
0.84
CHLOROFORM-d
7.58
7.57
7.54
7.54
7.52
7.52
7.44
7.43
7.42
7.42
7.27
7.11
7.10
7.00
6.99
6.98
6.97
MeO
O
N
H
N
TIPS
3i
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
Chemical Shift (ppm)
1.00
1.11
1.10
1.15
1.11
1.18
1.18
1.19
1.09
1.19
3.53
21.43
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

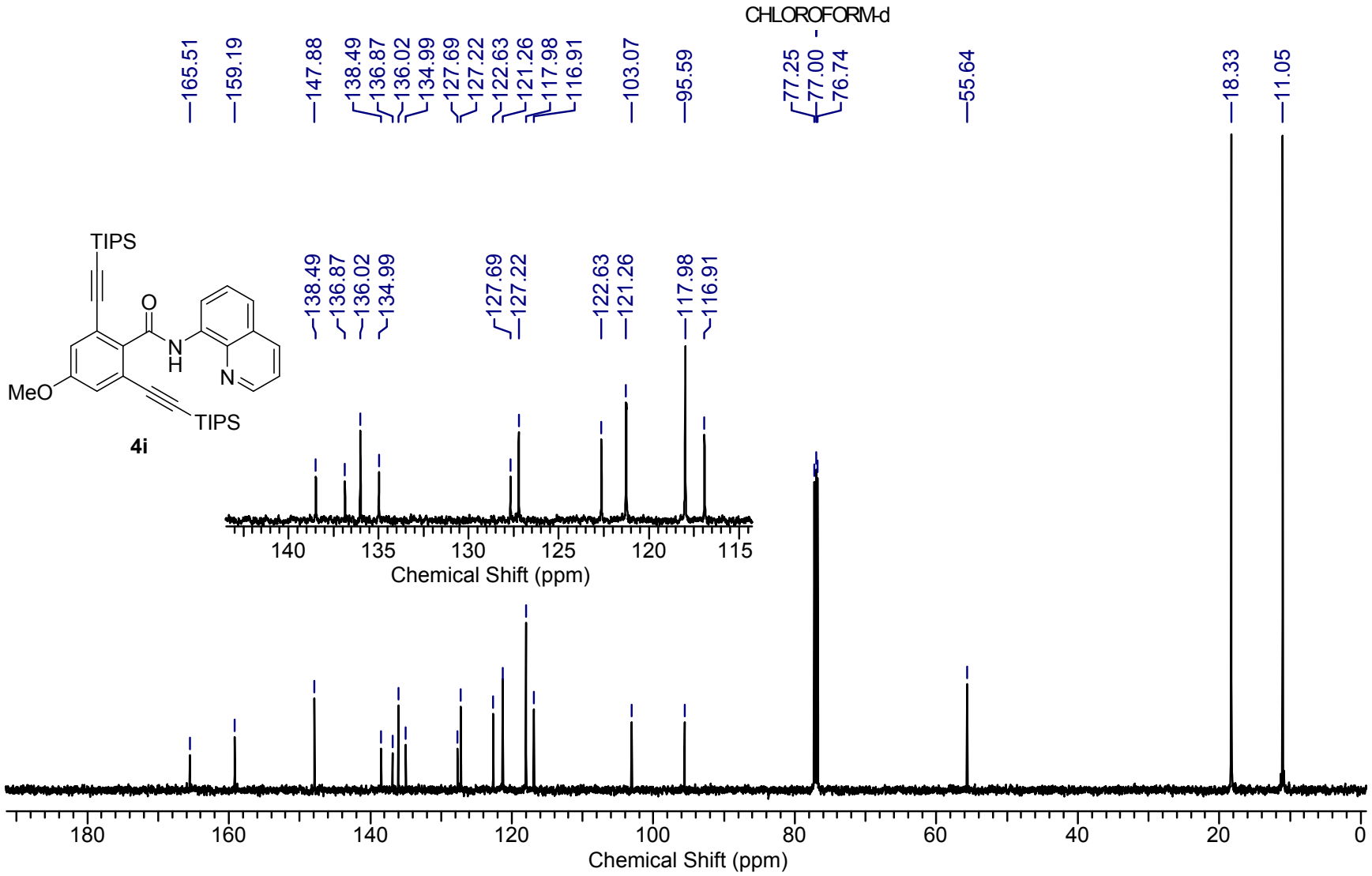
^{1}H NMR of **3i**


CHLOROFORM-d
166.03
160.73
148.19
138.99
136.14
134.79
131.66
130.83
127.89
127.32
122.14
121.64
121.37
118.52
117.14
114.94
103.91
97.26
77.26
77.00
76.75
55.52
18.29
11.04
O
N
H
N
MeO
TIPS
3i
Chemical Shift (ppm)
Chemical Shift (ppm)

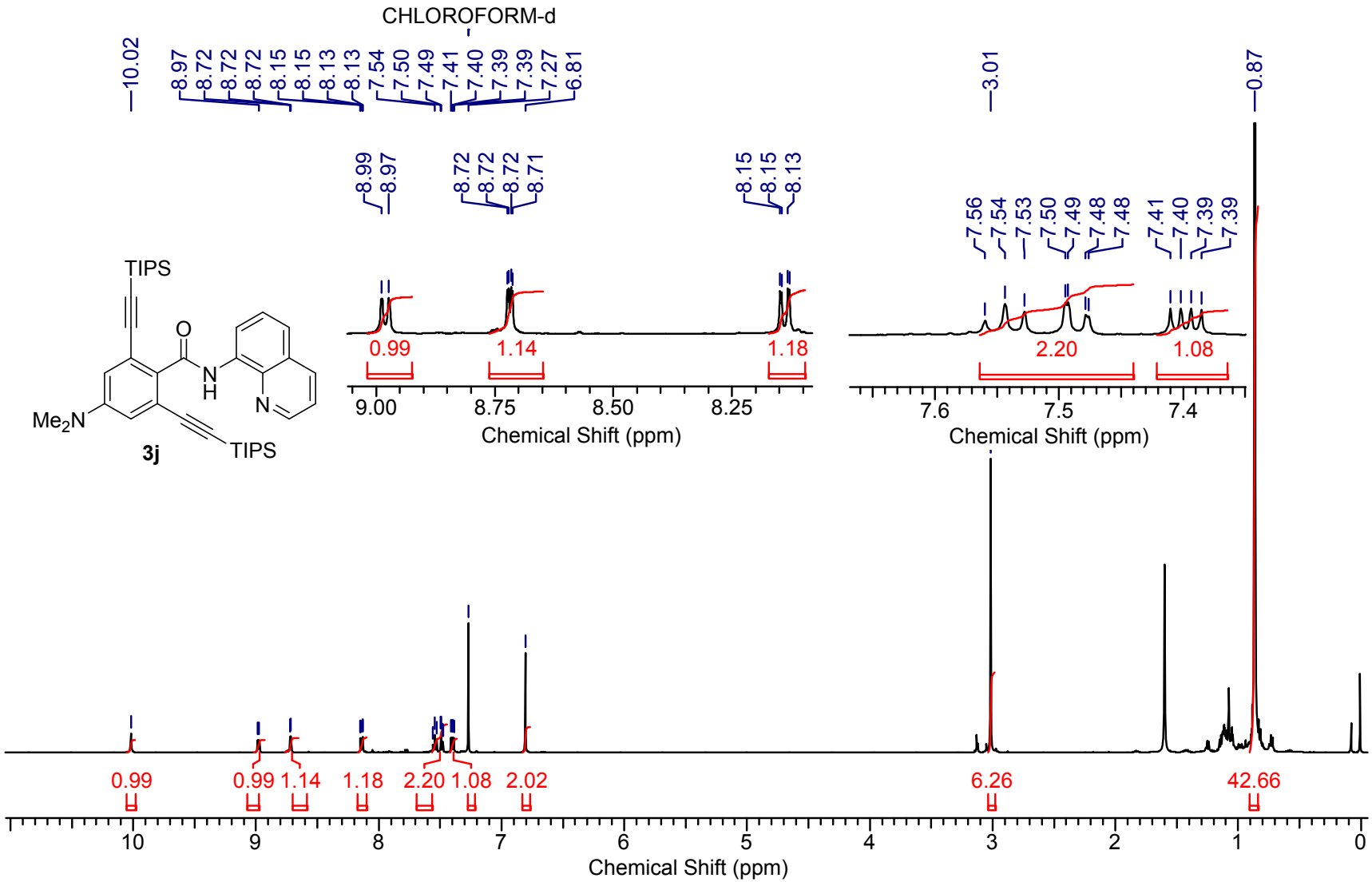
^{13}C NMR of **3i**


CHLOROFORM-d
10.03
8.97
8.73
8.73
8.73
8.16
8.14
7.55
7.54
7.52
7.51
7.42
7.41
7.41
7.40
7.27
7.03
3.86
0.86
TIPS
O
N
H
N
MeO
TIPS
4i
8.16
8.16
8.14
8.14
7.55
7.54
7.52
7.51
7.42
7.40
8.00
7.75
7.50
Chemical Shift (ppm)
0.95
1.00
0.99
1.02
2.15
1.04
1.86
3.00
42.20
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

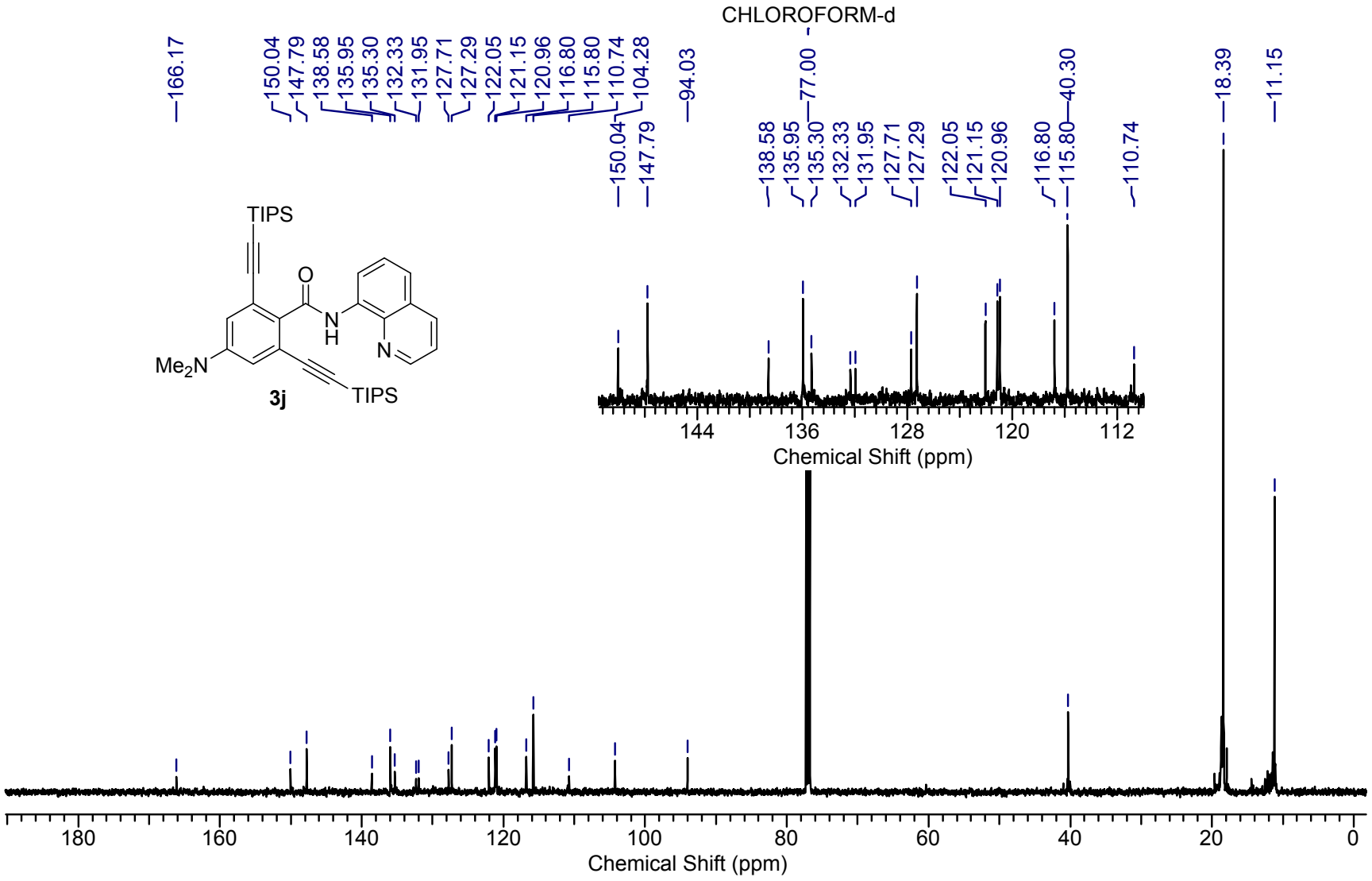
^{1}H NMR of **4i**


CHLOROFORM-d
165.51
159.19
147.88
138.49
136.87
136.02
134.99
127.69
127.22
122.63
121.26
117.98
116.91
103.07
95.59
77.25
77.00
76.74
55.64
18.33
11.05
TIPS
O
N
H
N
MeO
TIPS
4i
Chemical Shift (ppm)
Chemical Shift (ppm)

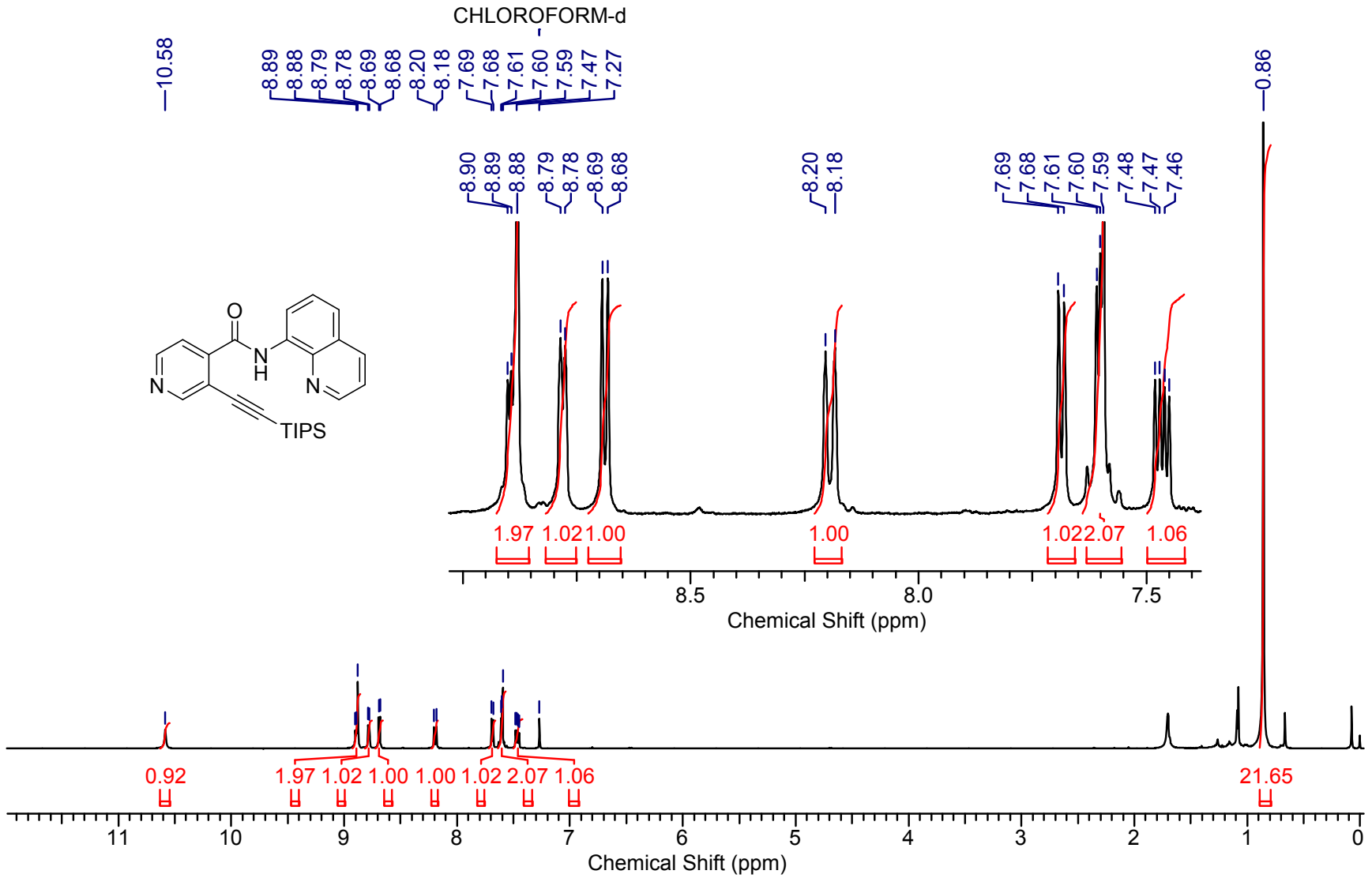
^{13}C NMR of **4i**


CHLOROFORM-d
10.02
8.97
8.72
8.72
8.72
8.15
8.15
8.13
8.13
7.54
7.50
7.49
7.41
7.40
7.39
7.39
7.27
6.81
3.01
0.87
TIPS
O
N
H
N
Me2N
TIPS
3j
0.99
1.14
1.18
2.20
1.08
Chemical Shift (ppm)
0.99
0.99
1.14
1.18
2.20
1.08
2.02
6.26
42.66
Chemical Shift (ppm)

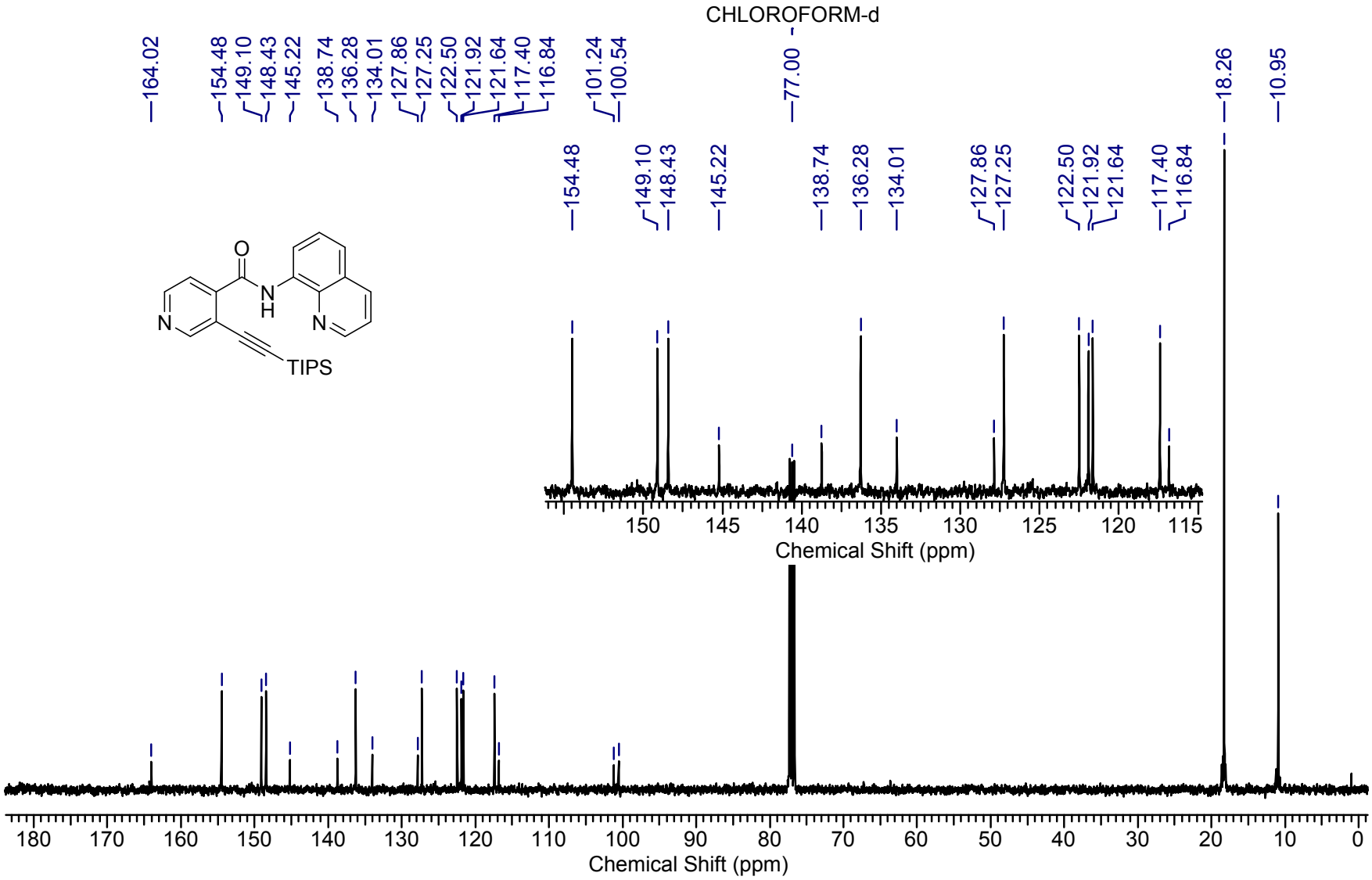
^{1}H NMR of **4j**


CHLOROFORM-d
166.17
150.04
147.79
138.58
135.95
135.30
132.33
131.95
127.71
127.29
122.05
121.15
120.96
116.80
115.80
110.74
104.28
94.03
77.00
40.30
18.39
11.15
TIPS
O
N
H
N
Me2N
TIPS
3j
Chemical Shift (ppm)
Chemical Shift (ppm)

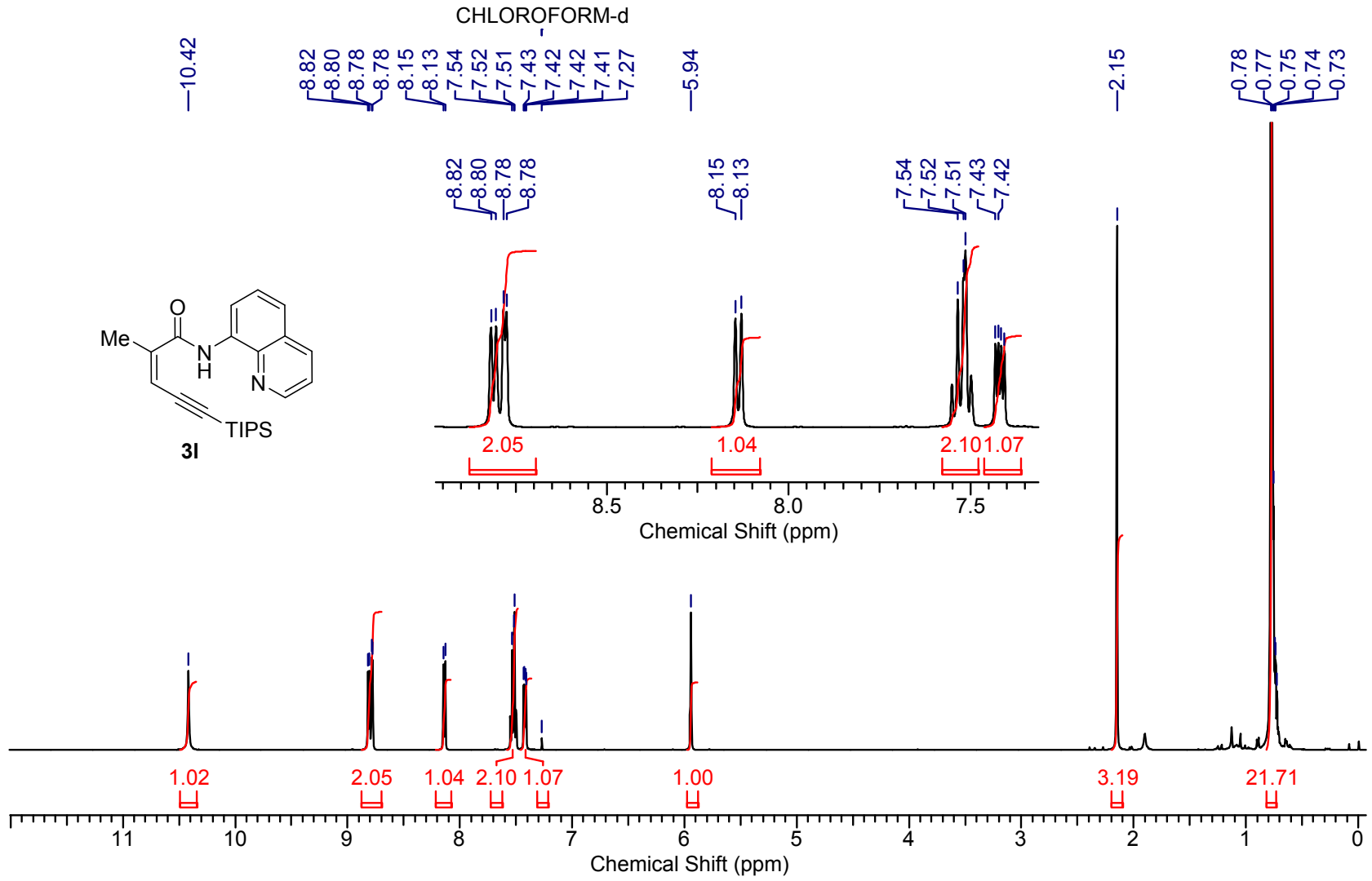
^{13}C NMR of **4j**


CHLOROFORM-d
10.58
8.89
8.88
8.79
8.78
8.69
8.68
8.20
8.18
7.69
7.68
7.61
7.60
7.59
7.47
7.27
0.86
8.90
8.89
8.88
8.79
8.78
8.69
8.68
8.20
8.18
7.69
7.68
7.61
7.60
7.59
7.48
7.47
7.46
O
N
H
N
N
TIPS
1.97 1.02 1.00
1.00
1.02 2.07 1.06
8.5
8.0
7.5
Chemical Shift (ppm)
0.92
1.97 1.02 1.00 1.00 1.02 2.07 1.06
21.65
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

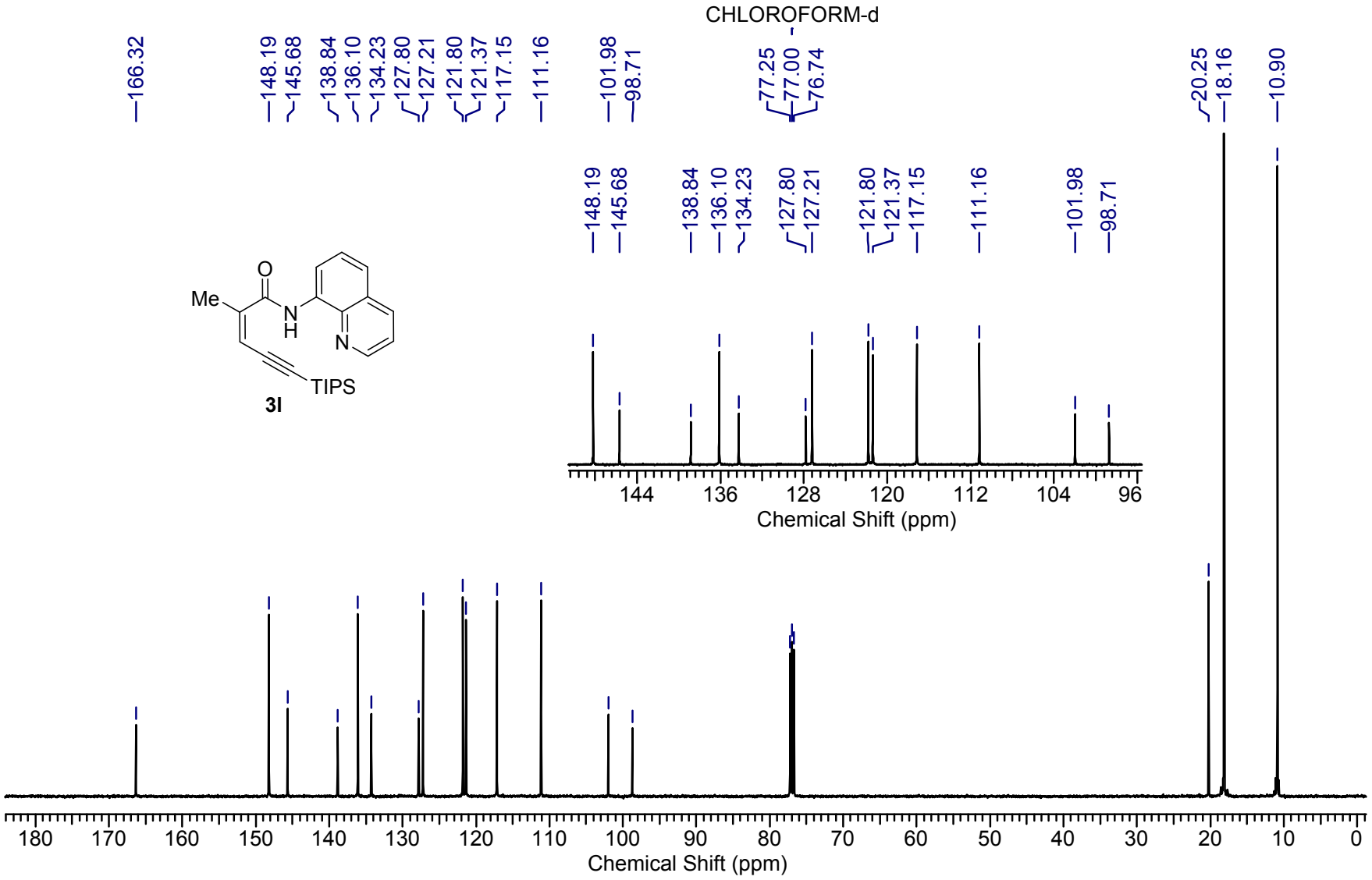
^{1}H NMR of **3k**


CHLOROFORM-d
164.02
154.48
149.10
148.43
145.22
138.74
136.28
134.01
127.86
127.25
122.50
121.92
121.64
117.40
116.84
101.24
100.54
77.00
18.26
10.95
O
N
H
N
N
TIPS
Chemical Shift (ppm)
Chemical Shift (ppm)

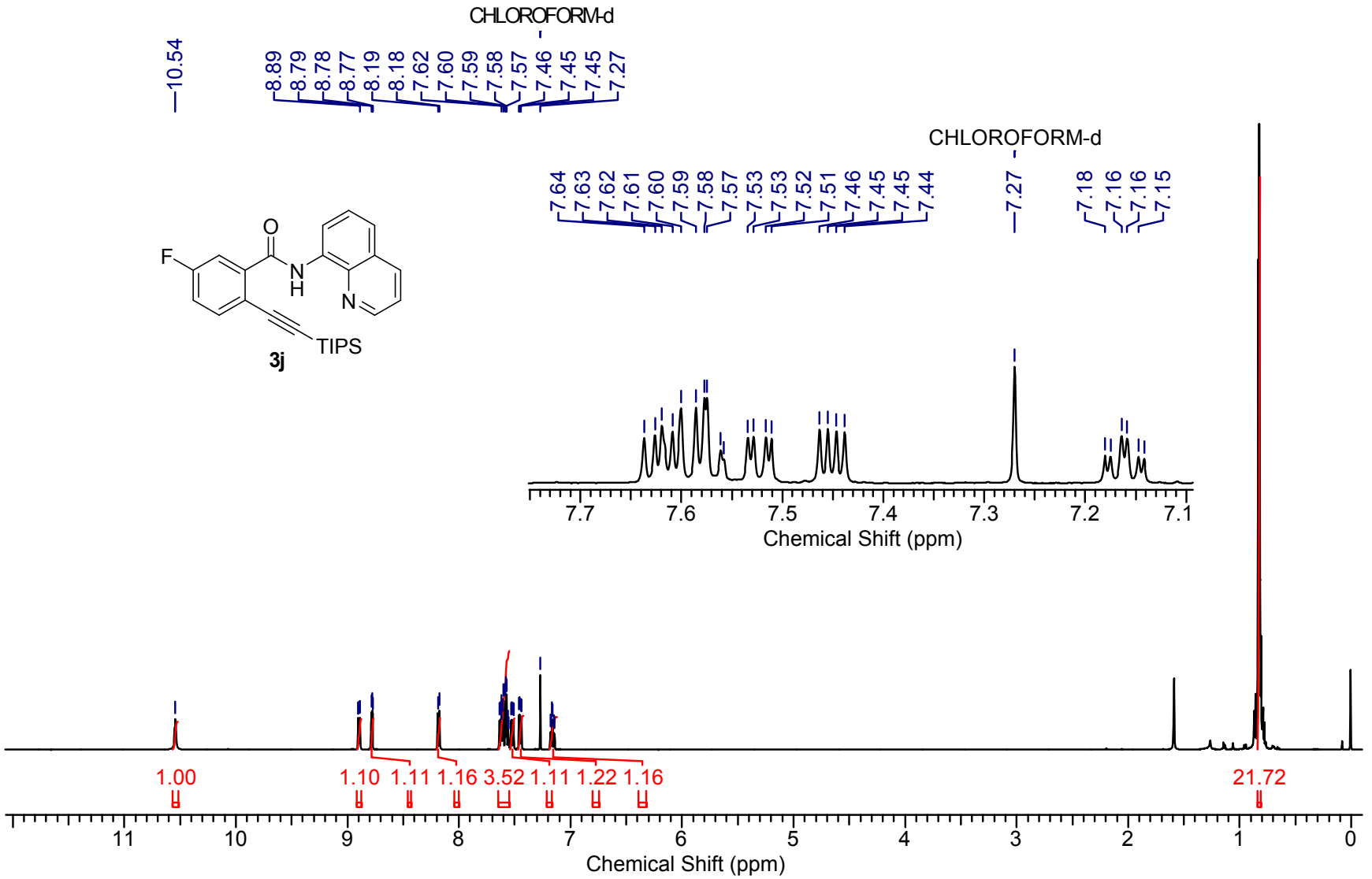
^{13}C NMR of **3k**


CHLOROFORM-d
10.42
8.82
8.80
8.78
8.78
8.15
8.13
7.54
7.52
7.51
7.43
7.42
7.42
7.41
7.27
5.94
2.15
0.78
0.77
0.75
0.74
0.73
Me
O
N
H
N
TIPS
3l
2.05
1.04
2.10
1.07
Chemical Shift (ppm)
1.02
2.05
1.04
2.10
1.07
1.00
3.19
21.71
Chemical Shift (ppm)

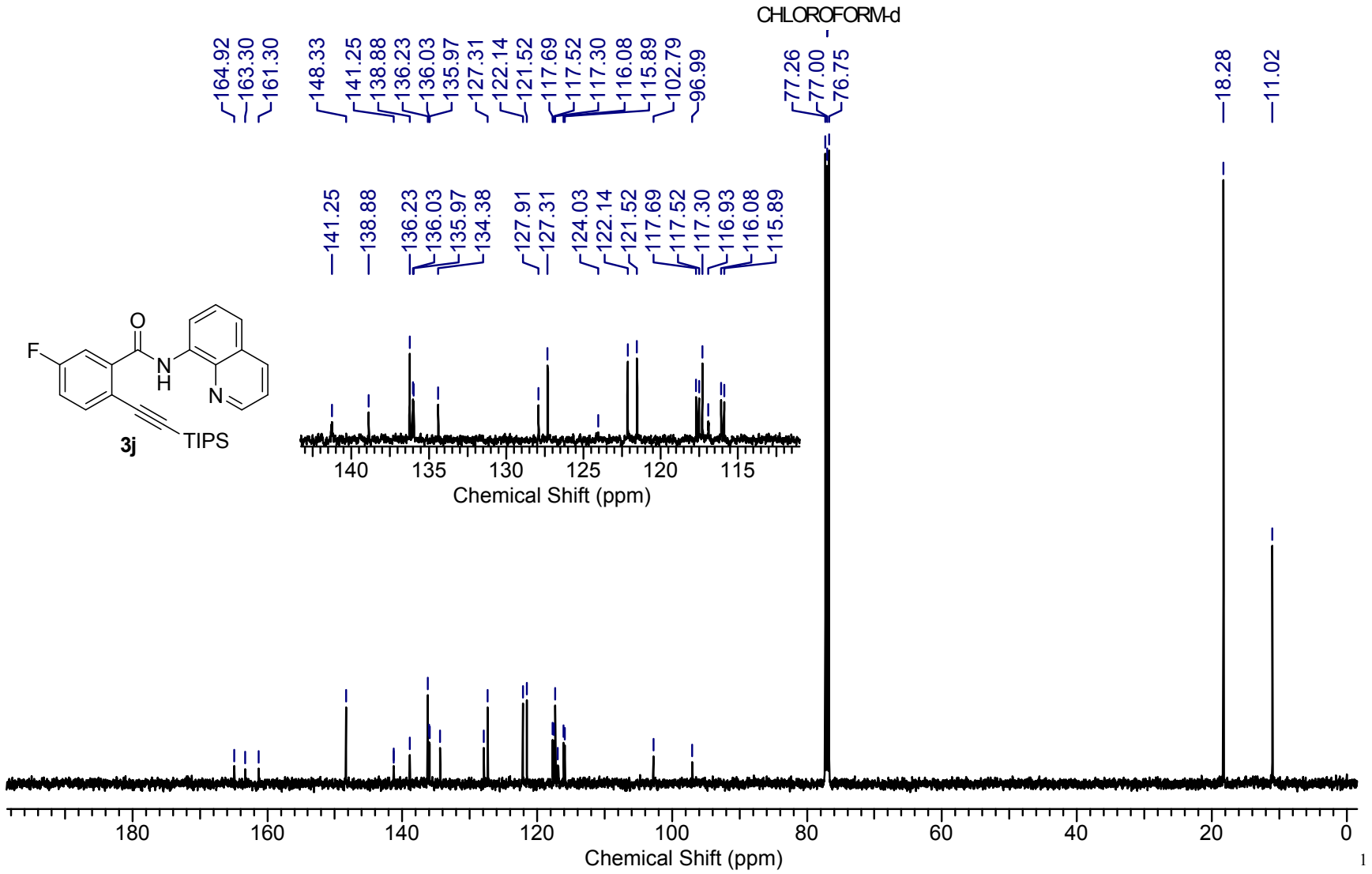
^{1}H NMR of **3l**


CHLOROFORM-d
166.32
148.19
145.68
138.84
136.10
134.23
127.80
127.21
121.80
121.37
117.15
111.16
101.98
98.71
77.25
77.00
76.74
20.25
18.16
10.90
Me
O
N
H
N
TIPS
3l
Chemical Shift (ppm)
Chemical Shift (ppm)

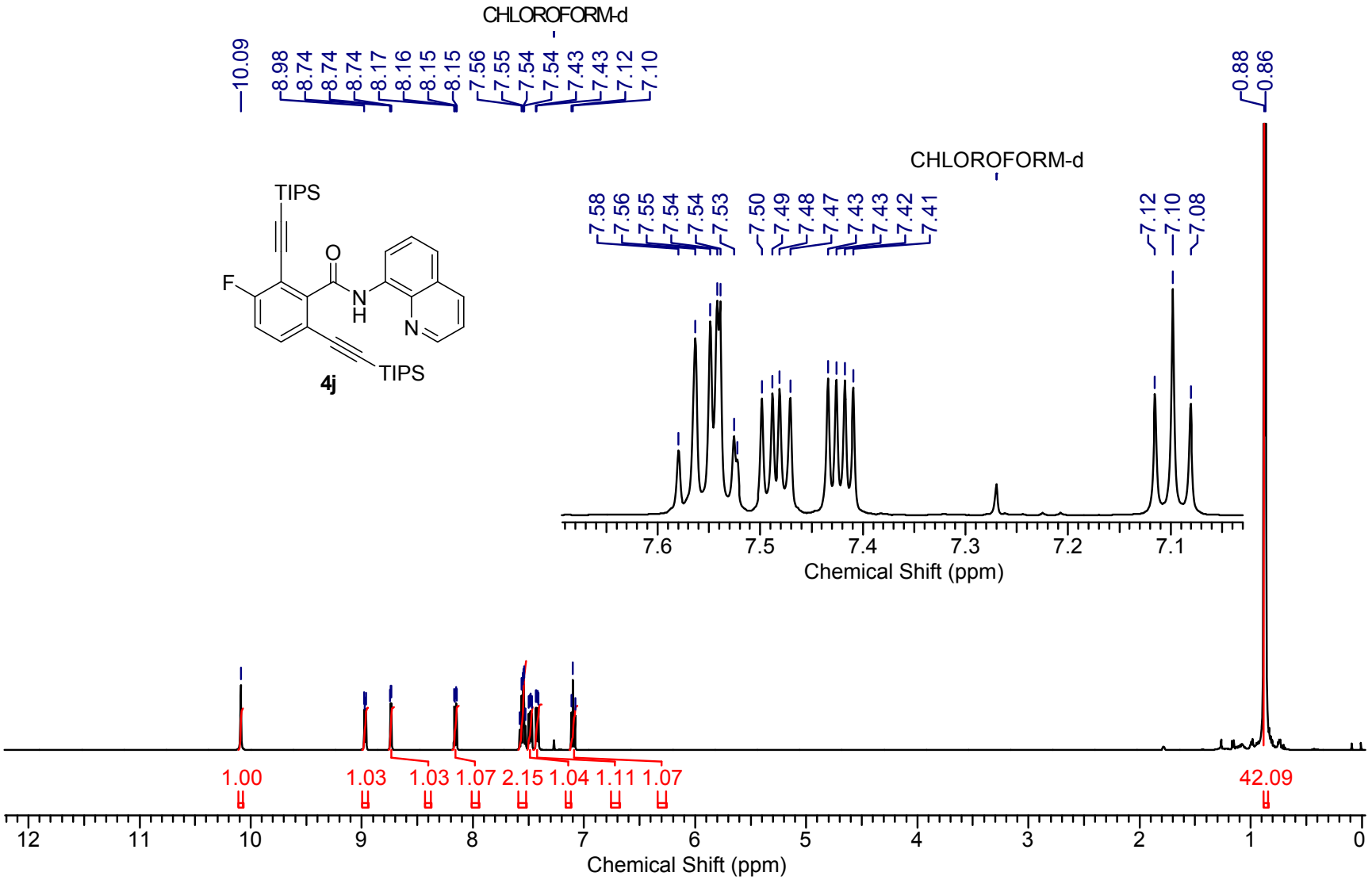
^{13}C NMR of **3l**


CHLOROFORM-d
10.54
8.89
8.79
8.78
8.77
8.19
8.18
7.62
7.60
7.59
7.58
7.57
7.46
7.45
7.45
7.27
CHLOROFORM-d
7.64
7.63
7.62
7.61
7.60
7.59
7.58
7.57
7.53
7.53
7.52
7.51
7.46
7.45
7.45
7.44
7.27
7.18
7.16
7.16
7.15
F
O
N
H
N
TIPS
3j
7.7
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
1.00
1.10
1.11
1.16
3.52
1.11
1.22
1.16
21.72
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

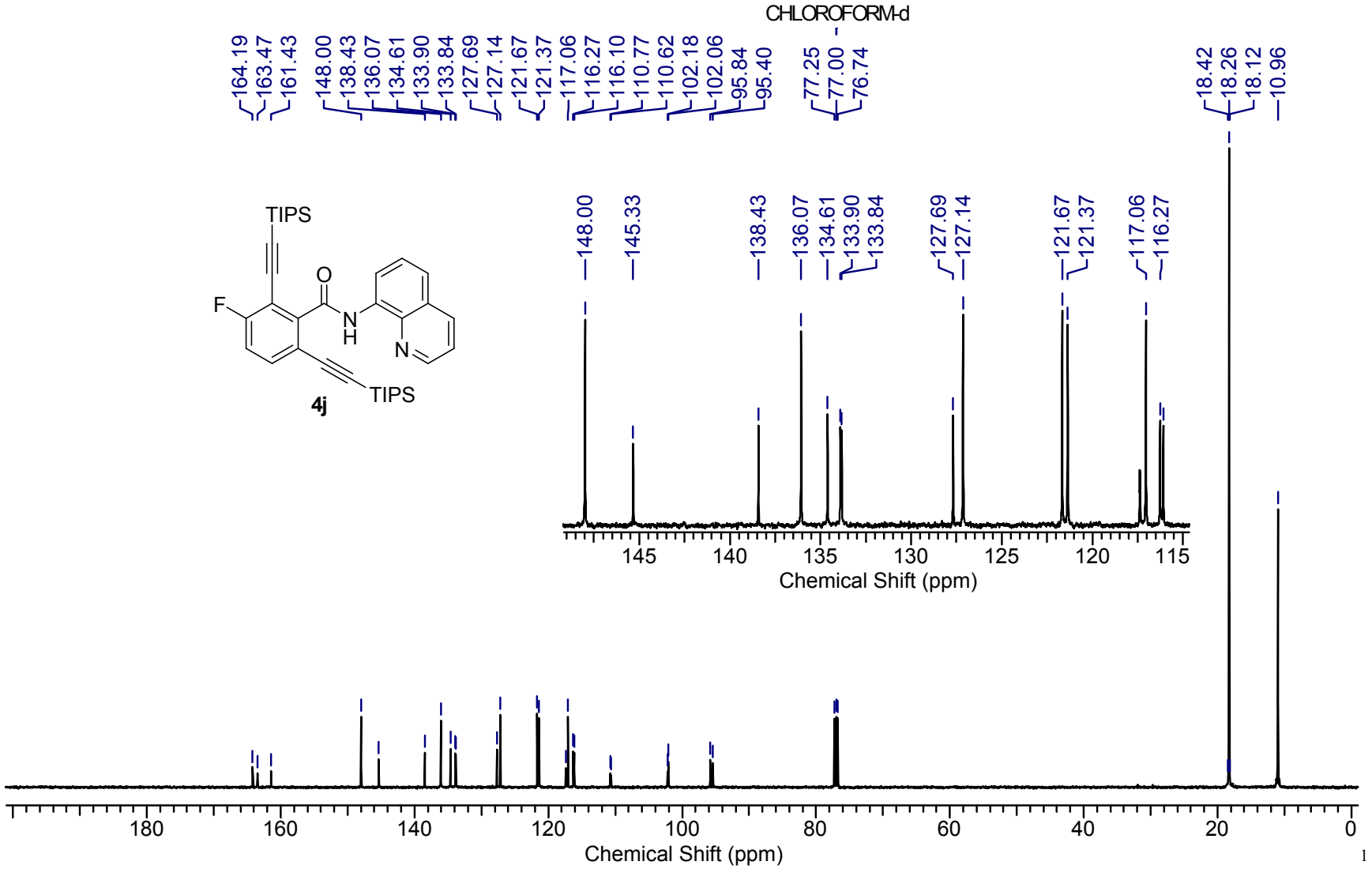
^{1}H NMR of **3m**


CHLOROFORM-d
164.92
163.30
161.30
148.33
141.25
138.88
136.23
136.03
135.97
127.31
122.14
121.52
117.69
117.52
117.30
116.08
115.89
102.79
96.99
77.26
77.00
76.75
18.28
11.02
141.25
138.88
136.23
136.03
135.97
134.38
127.91
127.31
124.03
122.14
121.52
117.69
117.52
117.30
116.93
116.08
115.89
O
F
N
H
N
TIPS
3j
140
135
130
125
120
115
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

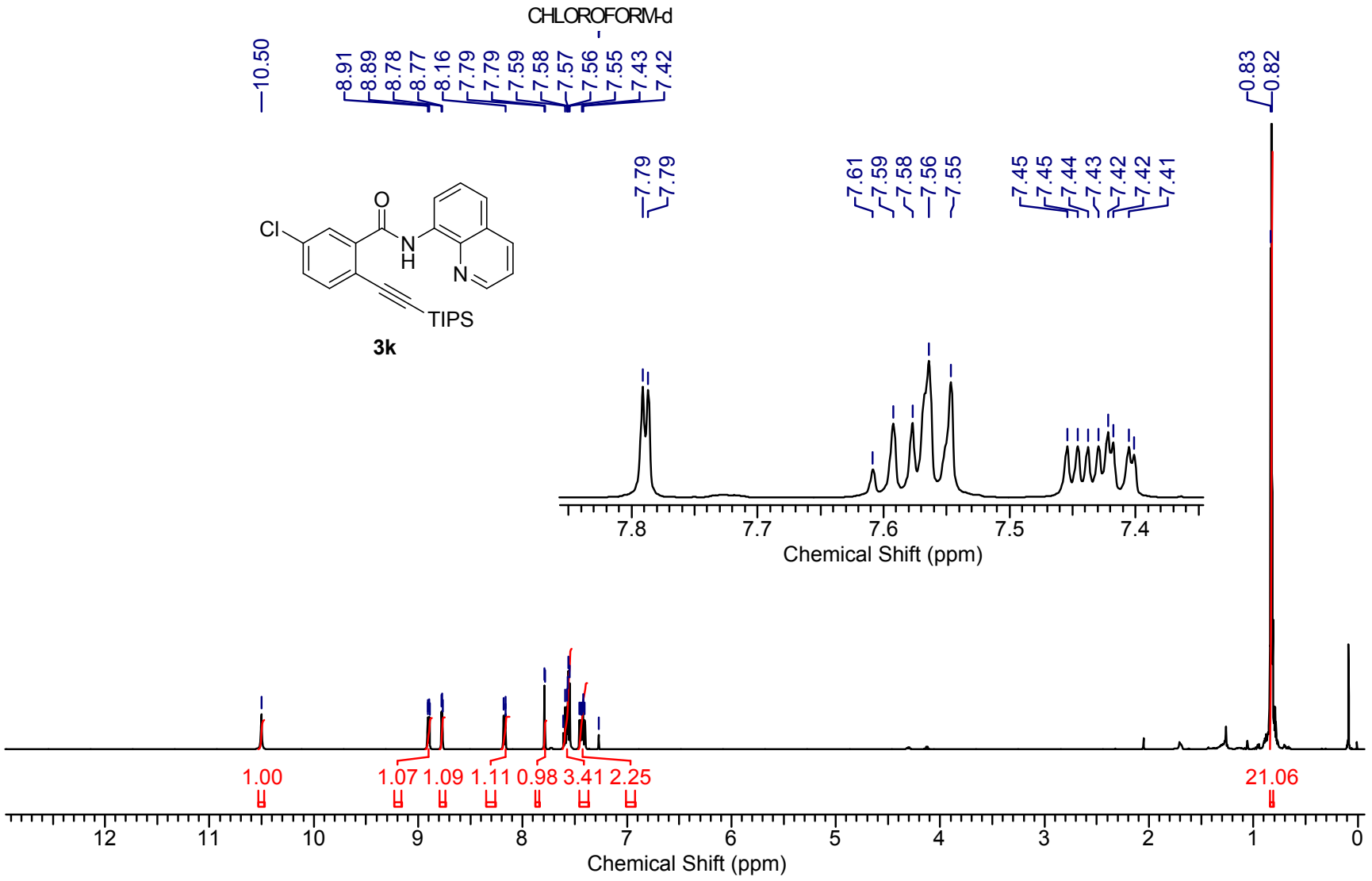
^{3}C NMR of **3m**


CHLOROFORM-d
10.09
8.98
8.74
8.74
8.74
8.17
8.16
8.15
8.15
7.56
7.55
7.54
7.54
7.43
7.43
7.12
7.10
0.88
0.86
TIPS
O
F
N
H
N
TIPS
4j
CHLOROFORM-d
7.58
7.56
7.55
7.54
7.54
7.53
7.50
7.49
7.48
7.47
7.43
7.43
7.42
7.41
7.12
7.10
7.08
7.6
7.5
7.4
7.3
7.2
7.1
Chemical Shift (ppm)
1.00
1.03
1.03
1.07
2.15
1.04
1.11
1.07
42.09
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

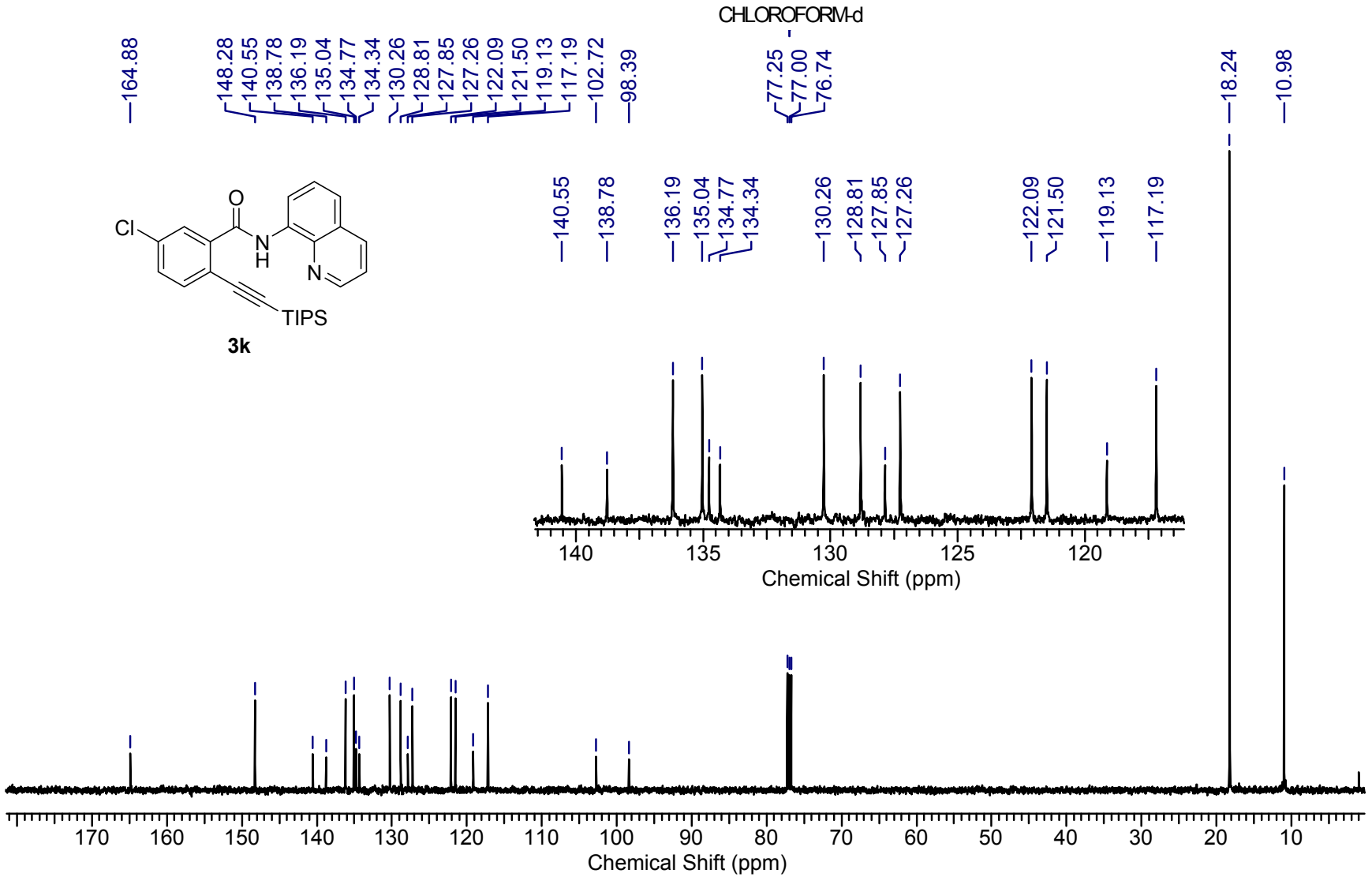
^{1}H NMR of **4m**


CHLOROFORM-d
164.19
163.47
161.43
148.00
138.43
136.07
134.61
133.90
133.84
127.69
127.14
121.67
121.37
117.06
116.27
116.10
110.77
110.62
102.18
102.06
95.84
95.40
77.25
77.00
76.74
18.42
18.26
18.12
10.96
TIPS
O
F
N
H
N
TIPS
4j
148.00
145.33
138.43
136.07
134.61
133.90
133.84
127.69
127.14
121.67
121.37
117.06
116.27
145
140
135
130
125
120
115
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

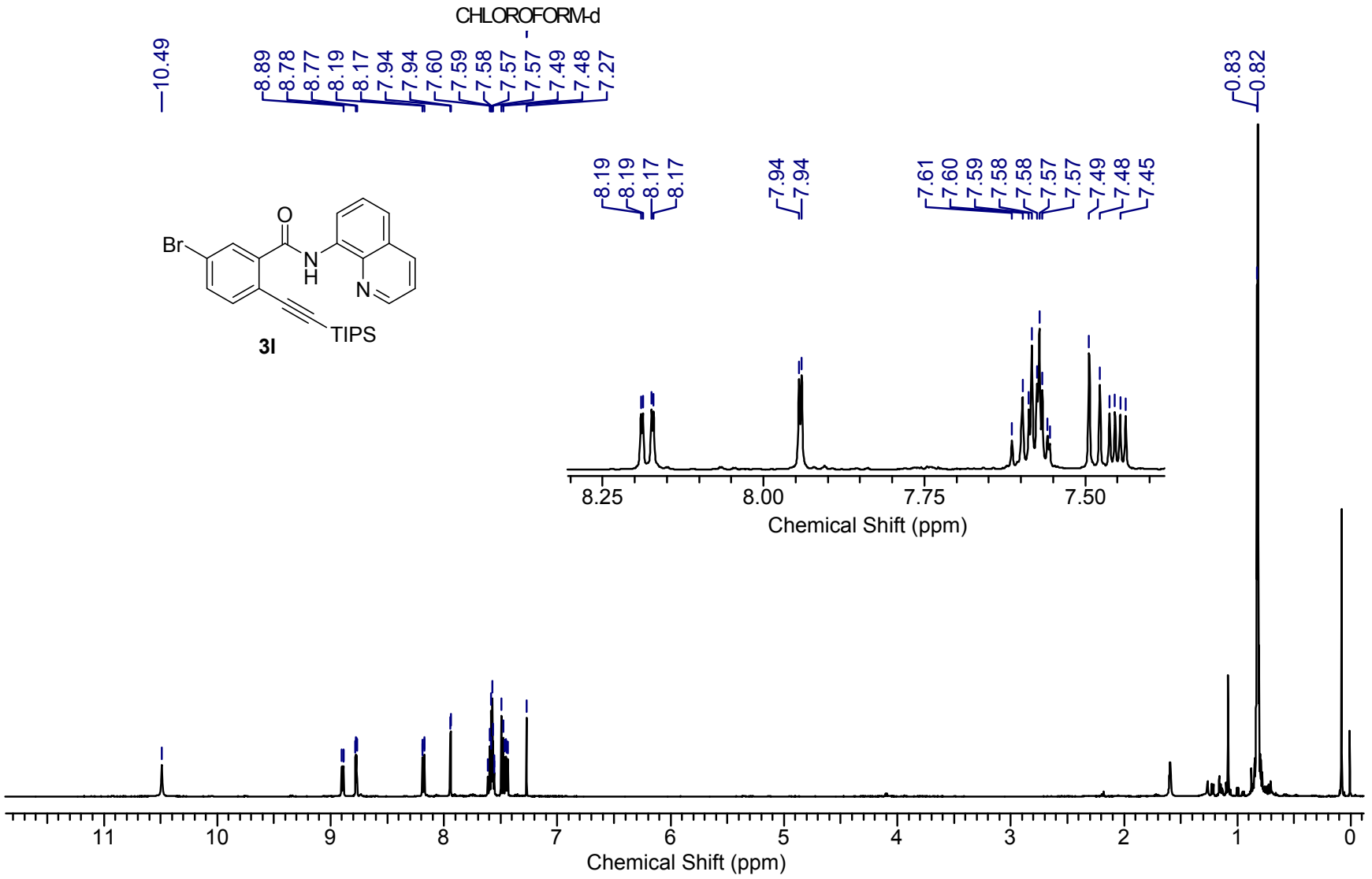
^{3}C NMR of **4m**


CHLOROFORM-d
10.50
8.91
8.89
8.78
8.77
8.16
7.79
7.79
7.59
7.58
7.57
7.56
7.55
7.43
7.42
0.83
0.82
Cl
O
N
H
N
TIPS
3k
7.79
7.79
7.61
7.59
7.58
7.56
7.55
7.45
7.45
7.44
7.43
7.42
7.42
7.41
7.8
7.7
7.6
7.5
7.4
Chemical Shift (ppm)
1.00
1.07
1.09
1.11
0.98
3.41
2.25
21.06
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

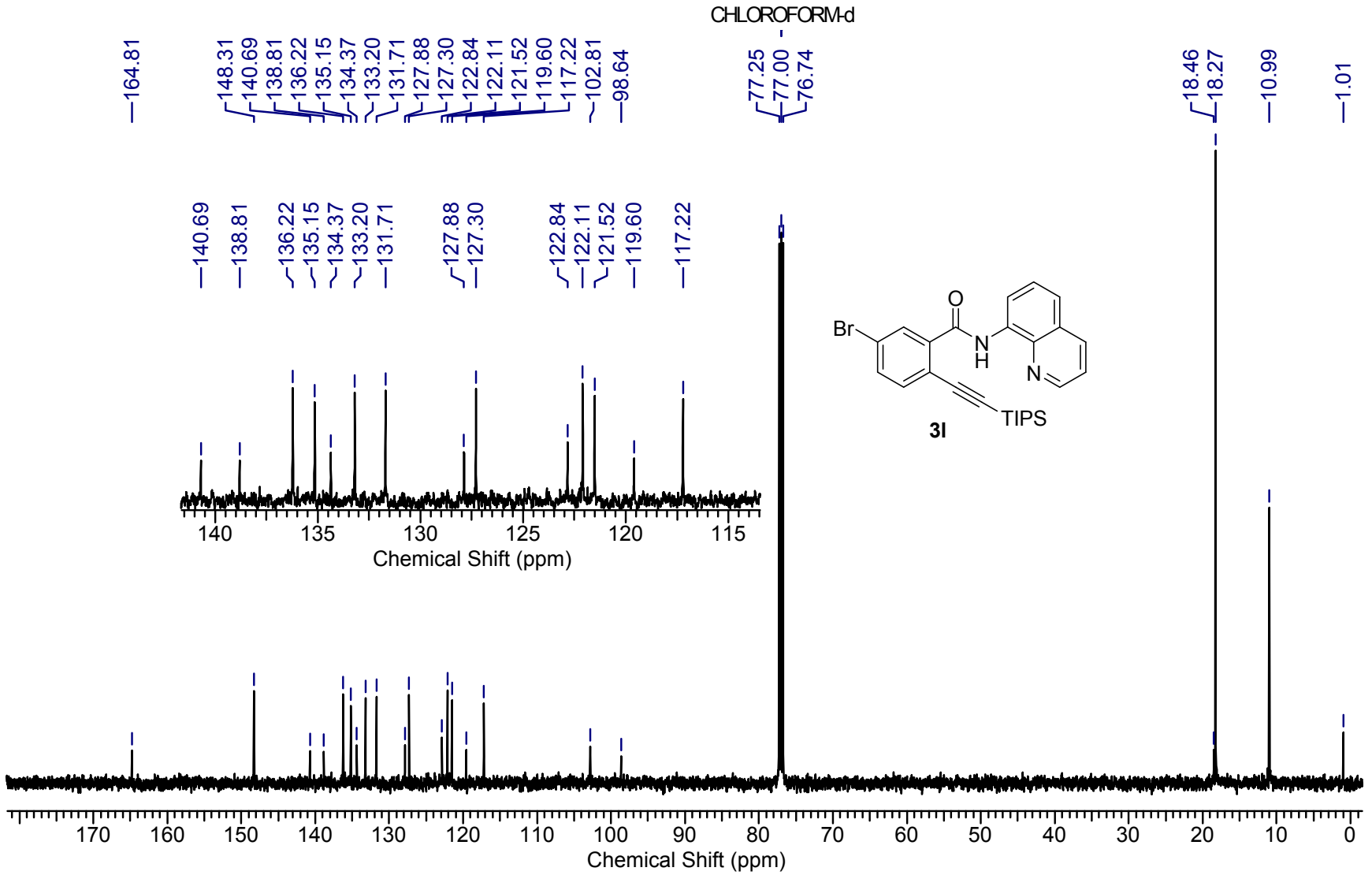
^{1}H NMR of **3n**


CHLOROFORM-d
164.88
148.28
140.55
138.78
136.19
135.04
134.77
134.34
130.26
128.81
127.85
127.26
122.09
121.50
119.13
117.19
102.72
98.39
77.25
77.00
76.74
18.24
10.98
Cl
O
N
H
N
TIPS
3k
Chemical Shift (ppm)
Chemical Shift (ppm)

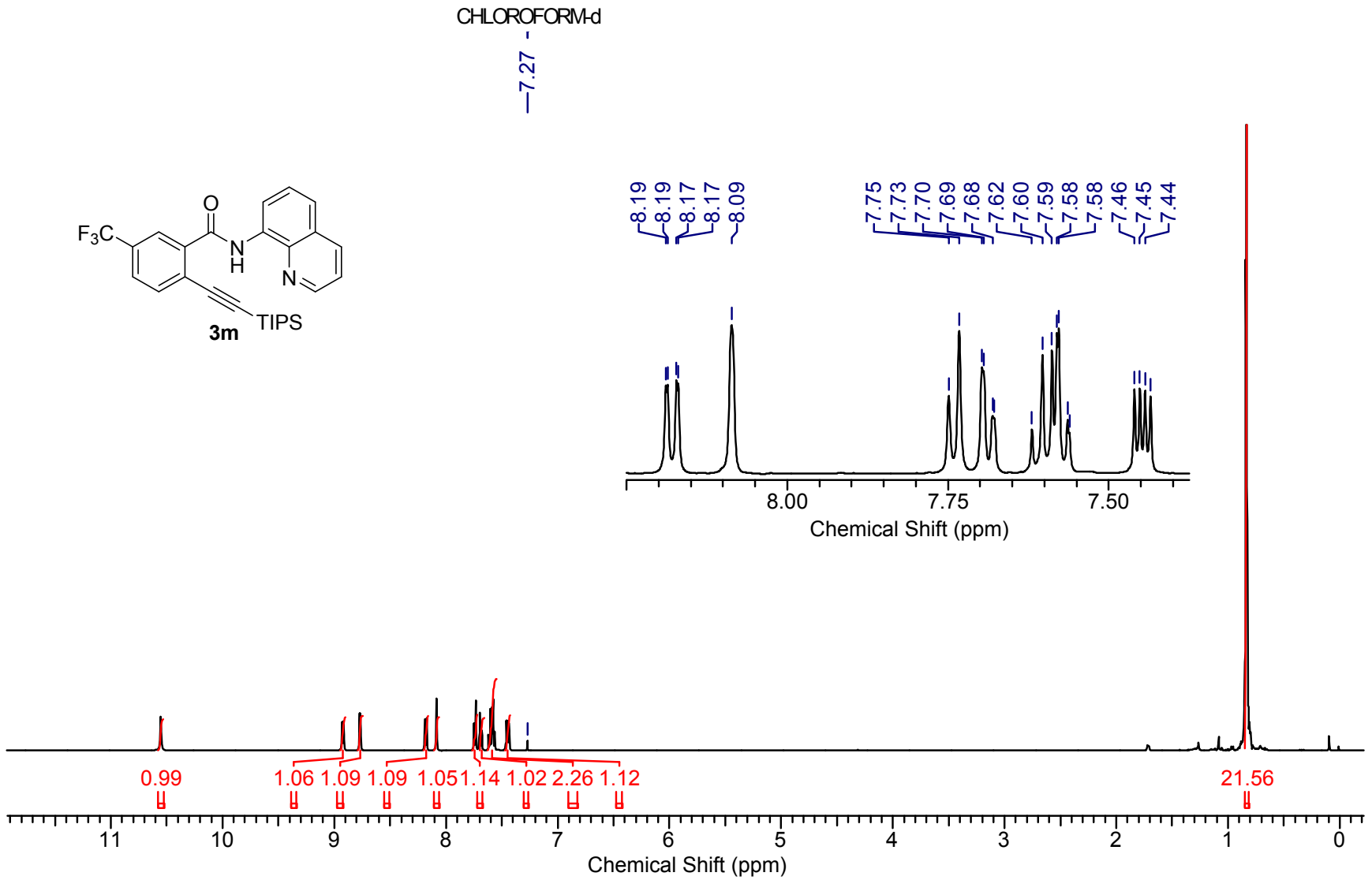
^{13}C NMR of **3n**


CHLOROFORM-d
10.49
8.89
8.78
8.77
8.19
8.17
7.94
7.94
7.60
7.59
7.58
7.57
7.57
7.49
7.48
7.27
0.83
0.82
8.19
8.19
8.17
8.17
7.94
7.94
7.61
7.60
7.59
7.58
7.58
7.57
7.57
7.49
7.48
7.45
Br
O
N
H
N
TIPS
3l
8.25
8.00
7.75
7.50
Chemical Shift (ppm)
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

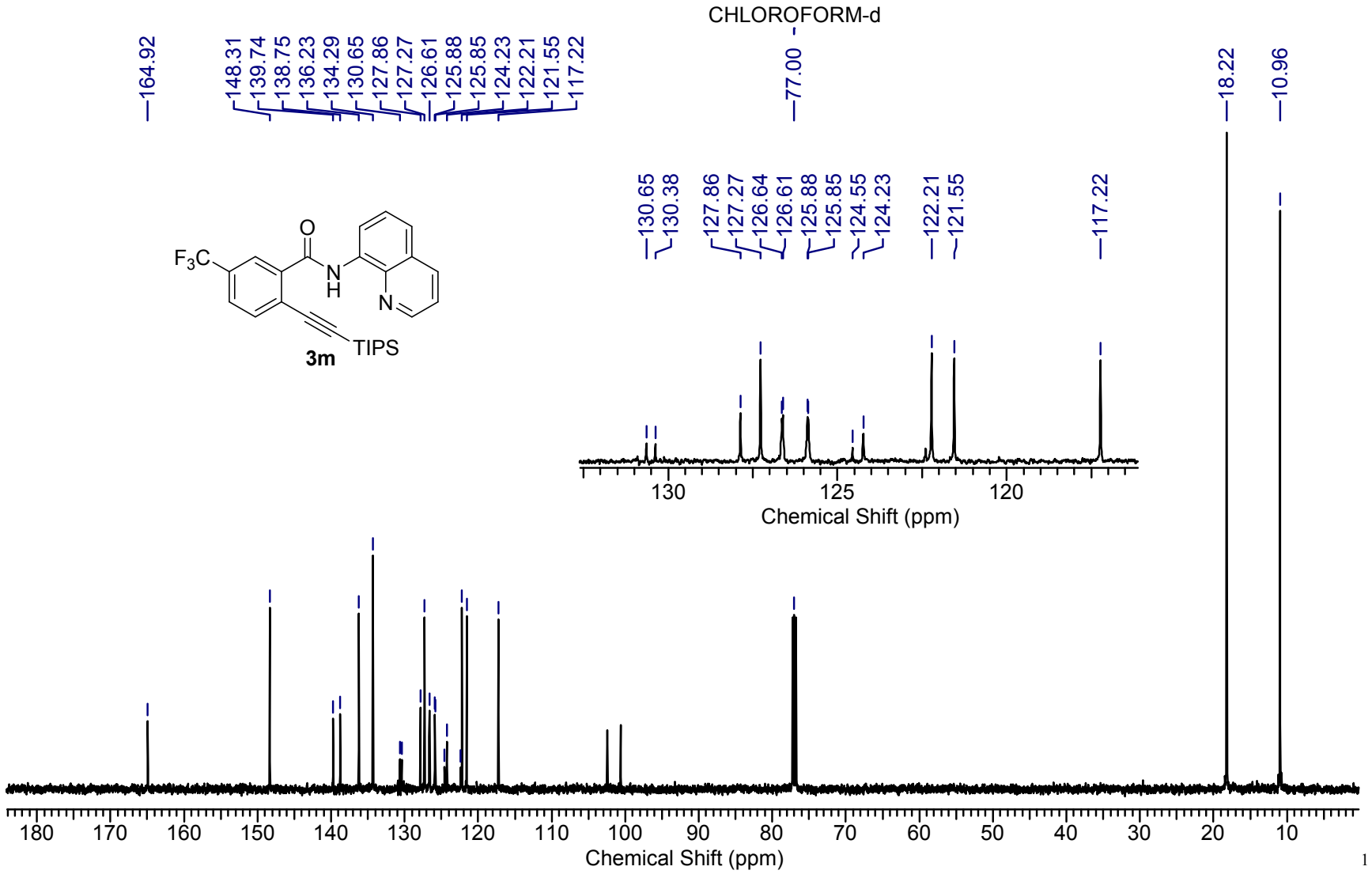
^{1}H NMR of **3o**


CHLOROFORM-d
164.81
148.31
140.69
138.81
136.22
135.15
134.37
133.20
131.71
127.88
127.30
122.84
122.11
121.52
119.60
117.22
102.81
98.64
77.25
77.00
76.74
18.46
18.27
10.99
1.01
Chemical Shift (ppm)
Br
O
N
H
N
TIPS
3l

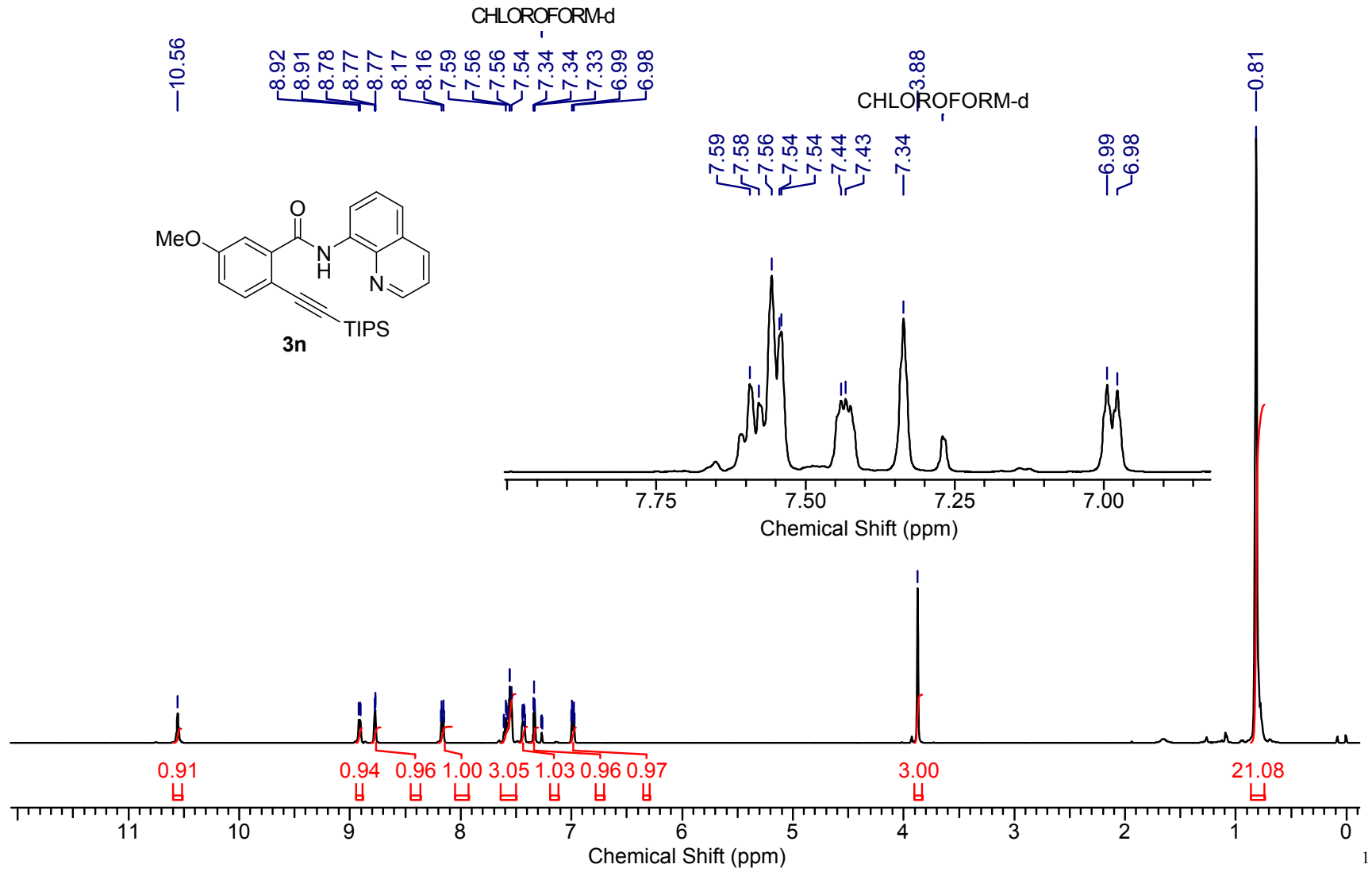
^{13}C NMR of **3o**


CHLOROFORM-d
7.27
F3C
O
N
H
N
TIPS
3m
8.19
8.19
8.17
8.17
8.09
7.75
7.73
7.70
7.69
7.68
7.62
7.60
7.59
7.58
7.58
7.46
7.45
7.44
8.00
7.75
7.50
Chemical Shift (ppm)
0.99
1.06
1.09
1.09
1.05
1.14
1.02
2.26
1.12
21.56
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

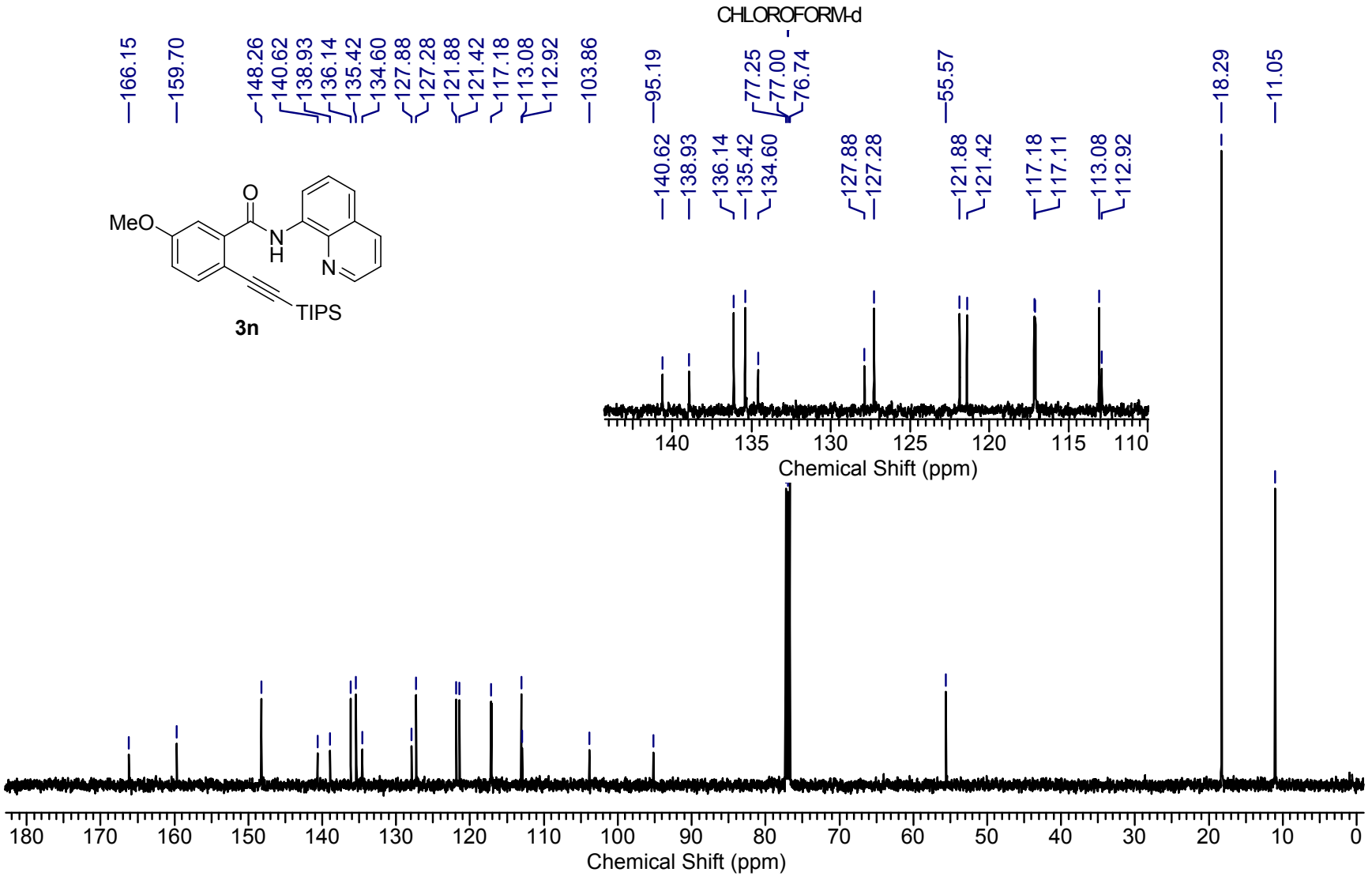
^{1}H NMR of **3p**


CHLOROFORM-d
164.92
148.31
139.74
138.75
136.23
134.29
130.65
127.86
127.27
126.61
125.88
125.85
124.23
122.21
121.55
117.22
77.00
18.22
10.96
130.65
130.38
127.86
127.27
126.64
126.61
125.88
125.85
124.55
124.23
122.21
121.55
117.22
F3C
O
N
H
N
TIPS
3m
130
125
120
Chemical Shift (ppm)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
Chemical Shift (ppm)

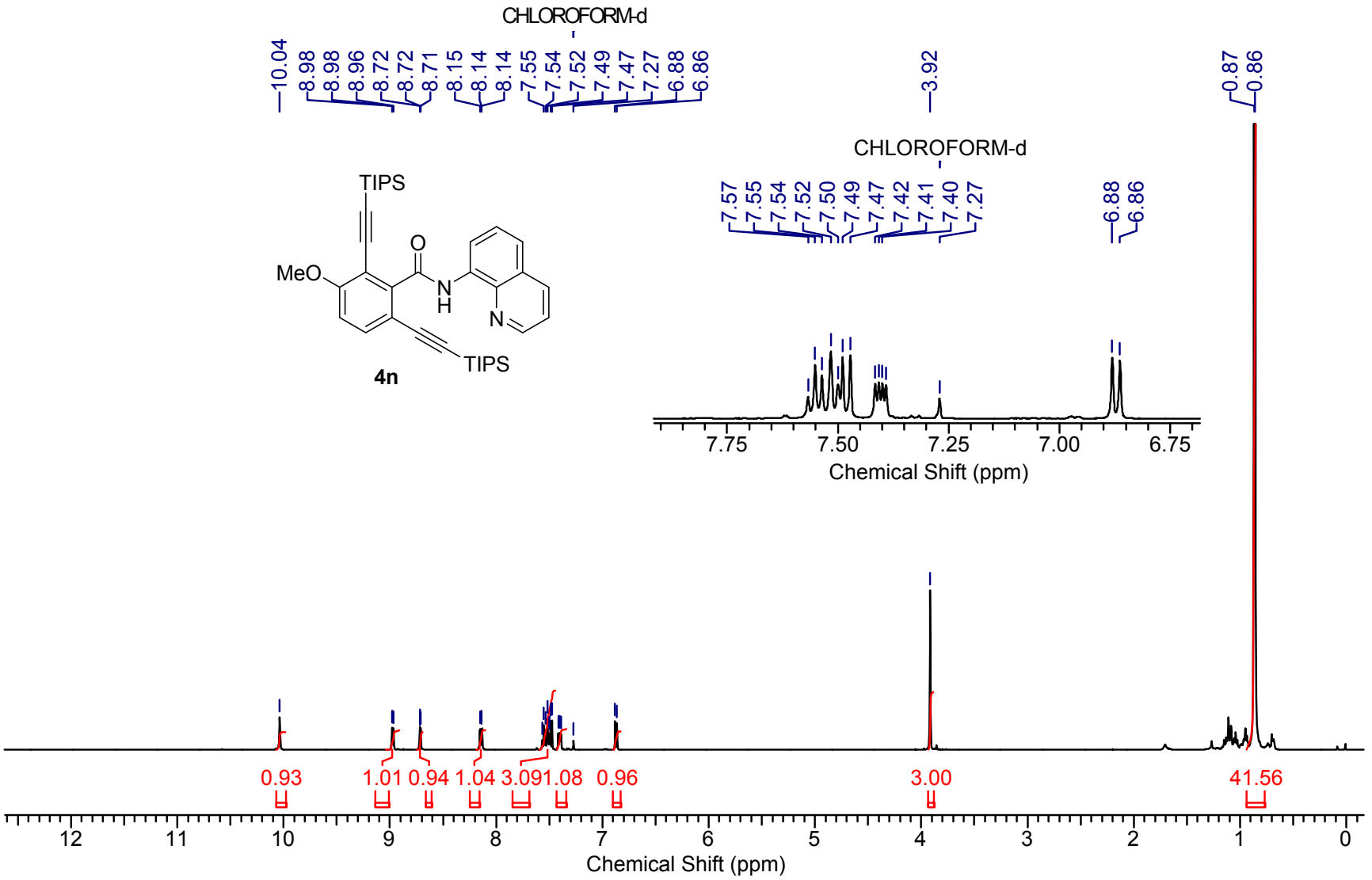
^{3}C NMR of **3p**


CHLOROFORM-d
10.56
8.92
8.91
8.78
8.77
8.77
8.17
8.16
7.59
7.56
7.56
7.54
7.34
7.34
7.33
6.99
6.98
3.88
CHLOROFORM-d
0.81
7.59
7.58
7.56
7.54
7.54
7.44
7.43
7.34
6.99
6.98
MeO
O
N
H
N
TIPS
3n
7.75
7.50
7.25
7.00
Chemical Shift (ppm)
0.91
0.94
0.96
1.00
3.05
1.03
0.96
0.97
3.00
21.08
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

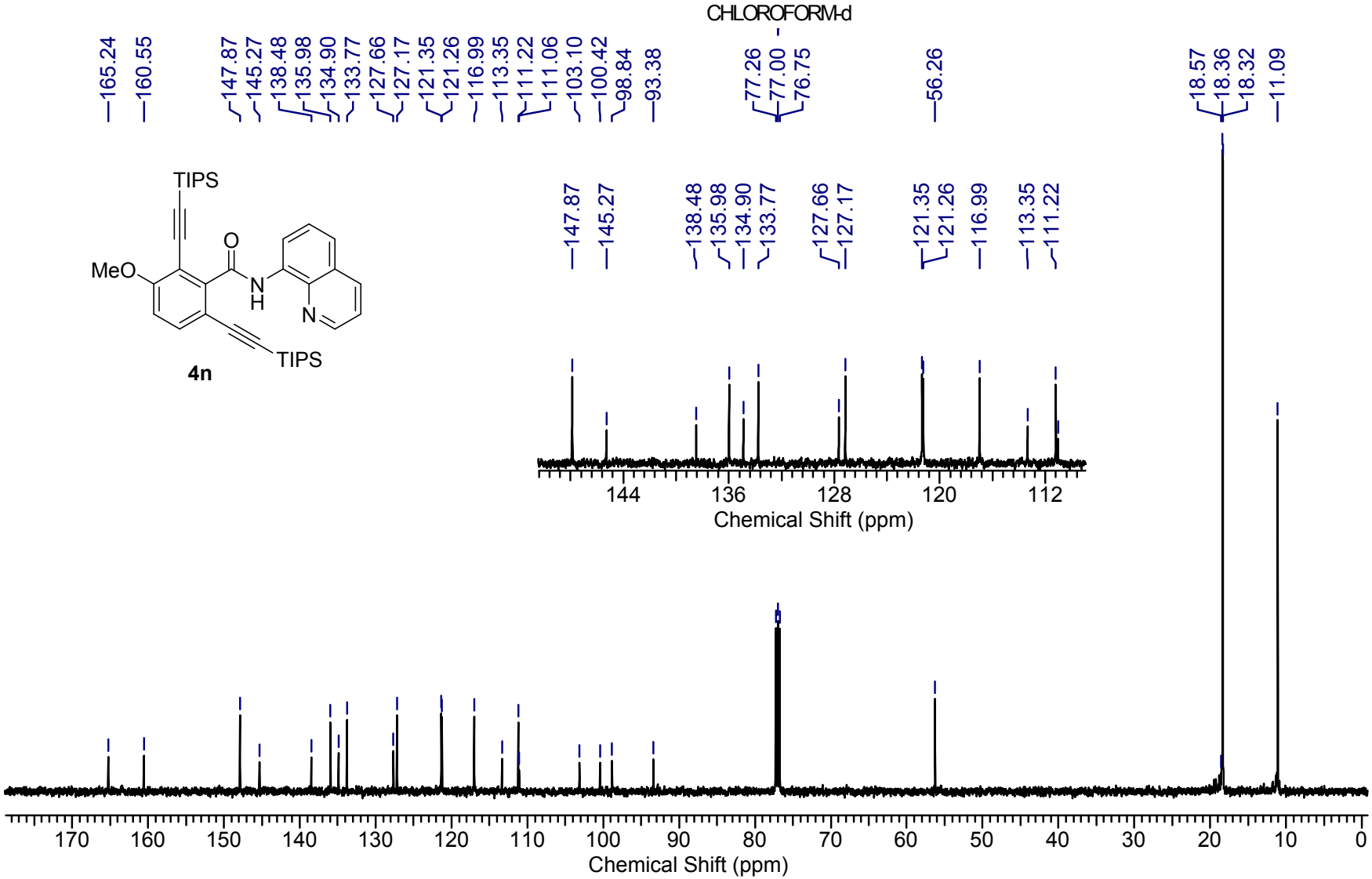
H NMR of **3q**


CHLOROFORM-d
166.15
159.70
148.26
140.62
138.93
136.14
135.42
134.60
127.88
127.28
121.88
121.42
117.18
113.08
112.92
103.86
95.19
77.25
77.00
76.74
55.57
18.29
11.05
MeO
O
N
H
N
TIPS
3n
Chemical Shift (ppm)
Chemical Shift (ppm)

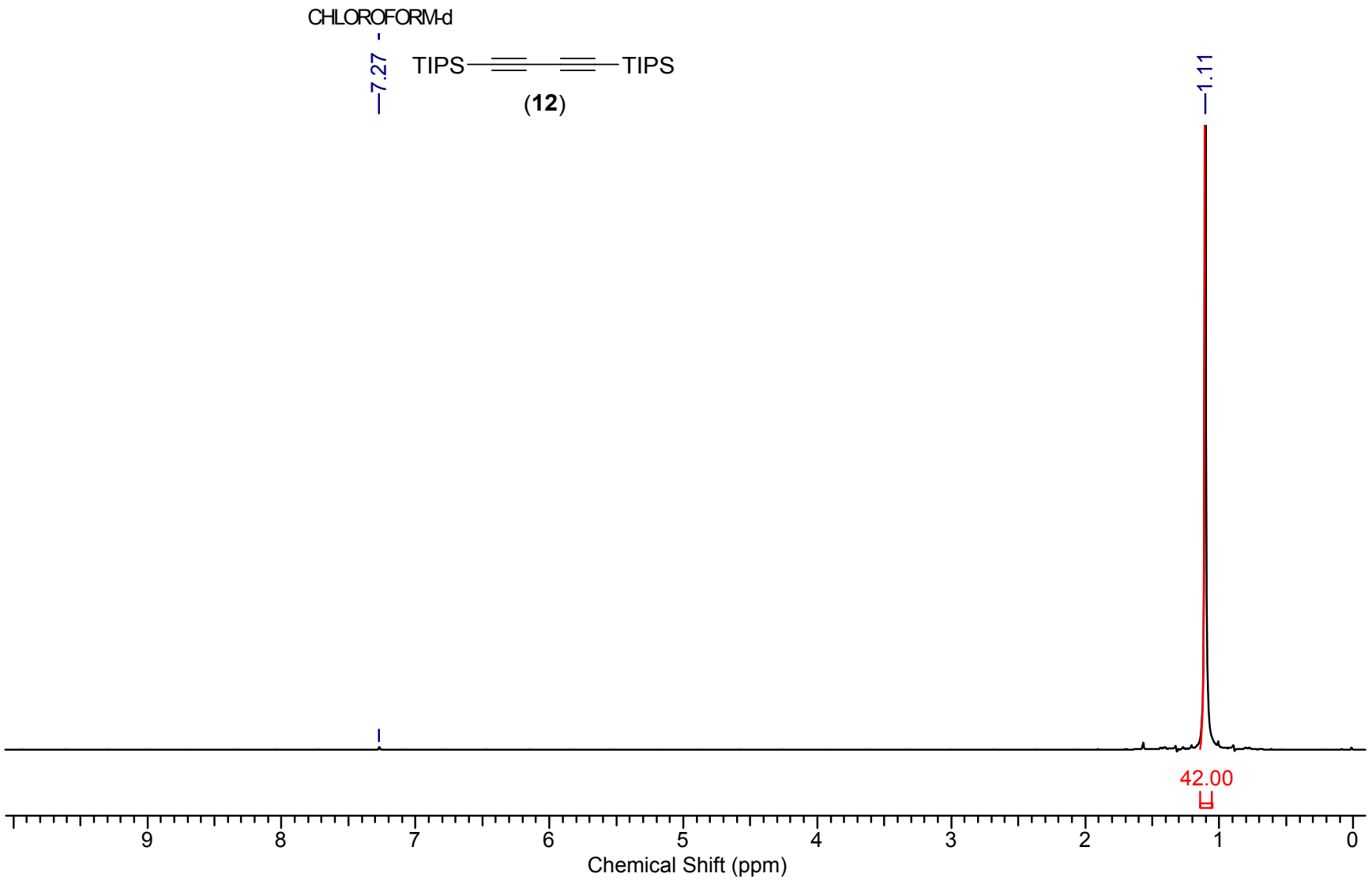
^{13}C NMR of **3q**


CHLOROFORM-d
10.04
8.98
8.98
8.96
8.72
8.72
8.71
8.15
8.14
8.14
7.55
7.54
7.52
7.49
7.47
7.27
6.88
6.86
3.92
0.87
0.86
TIPS
O
MeO
N
H
N
TIPS
4n
CHLOROFORM-d
7.57
7.55
7.54
7.52
7.50
7.49
7.47
7.42
7.41
7.40
7.27
6.88
6.86
7.75
7.50
7.25
7.00
6.75
Chemical Shift (ppm)
0.93
1.01
0.94
1.04
3.09
1.08
0.96
3.00
41.56
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

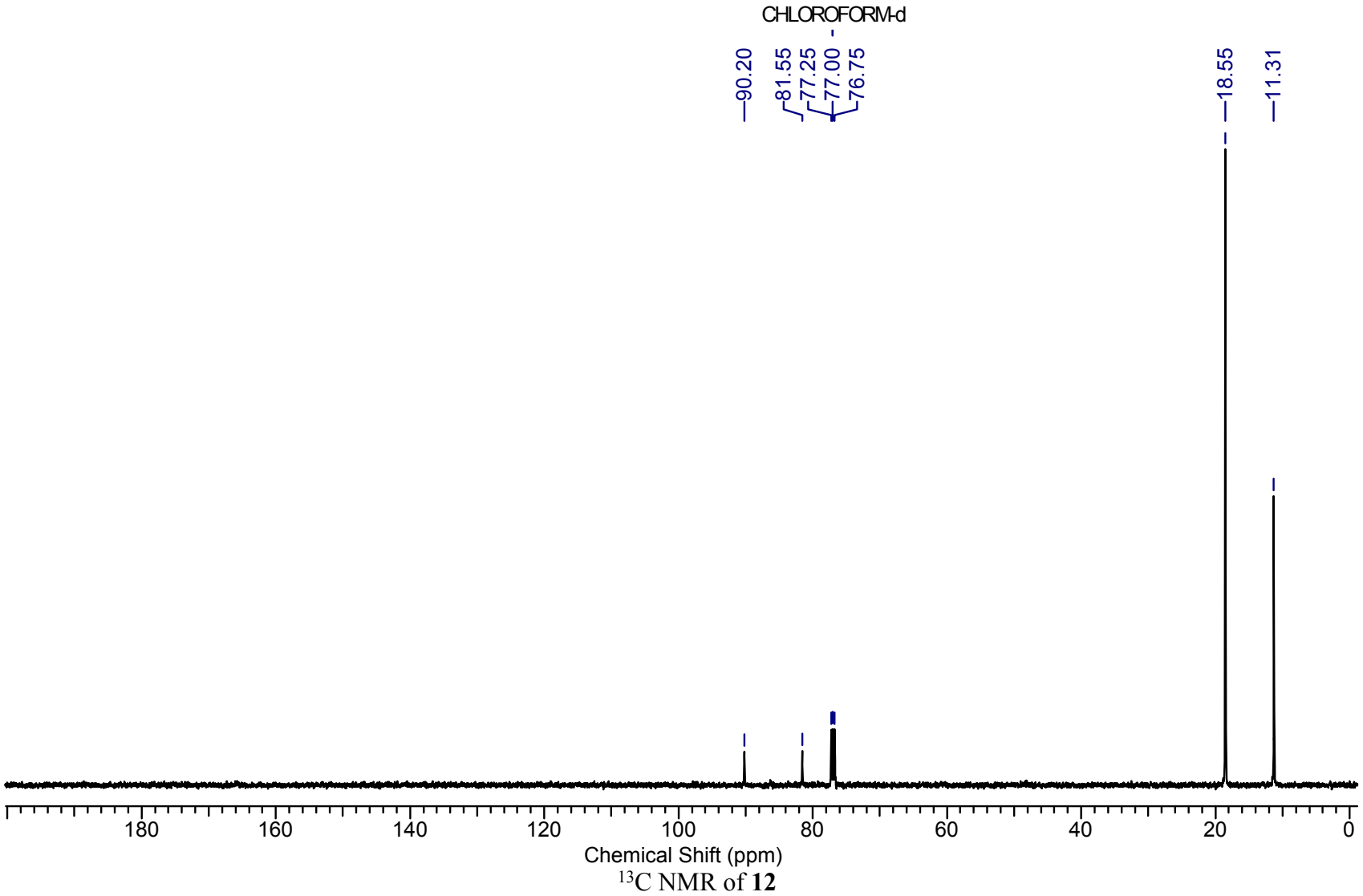
^{1}H NMR of **4q**


CHLOROFORM-d
165.24
160.55
147.87
145.27
138.48
135.98
134.90
133.77
127.66
127.17
121.35
121.26
116.99
113.35
111.22
111.06
103.10
100.42
98.84
93.38
77.26
77.00
76.75
56.26
18.57
18.36
18.32
11.09
TIPS
MeO
O
N
H
N
TIPS
4n
Chemical Shift (ppm)
Chemical Shift (ppm)

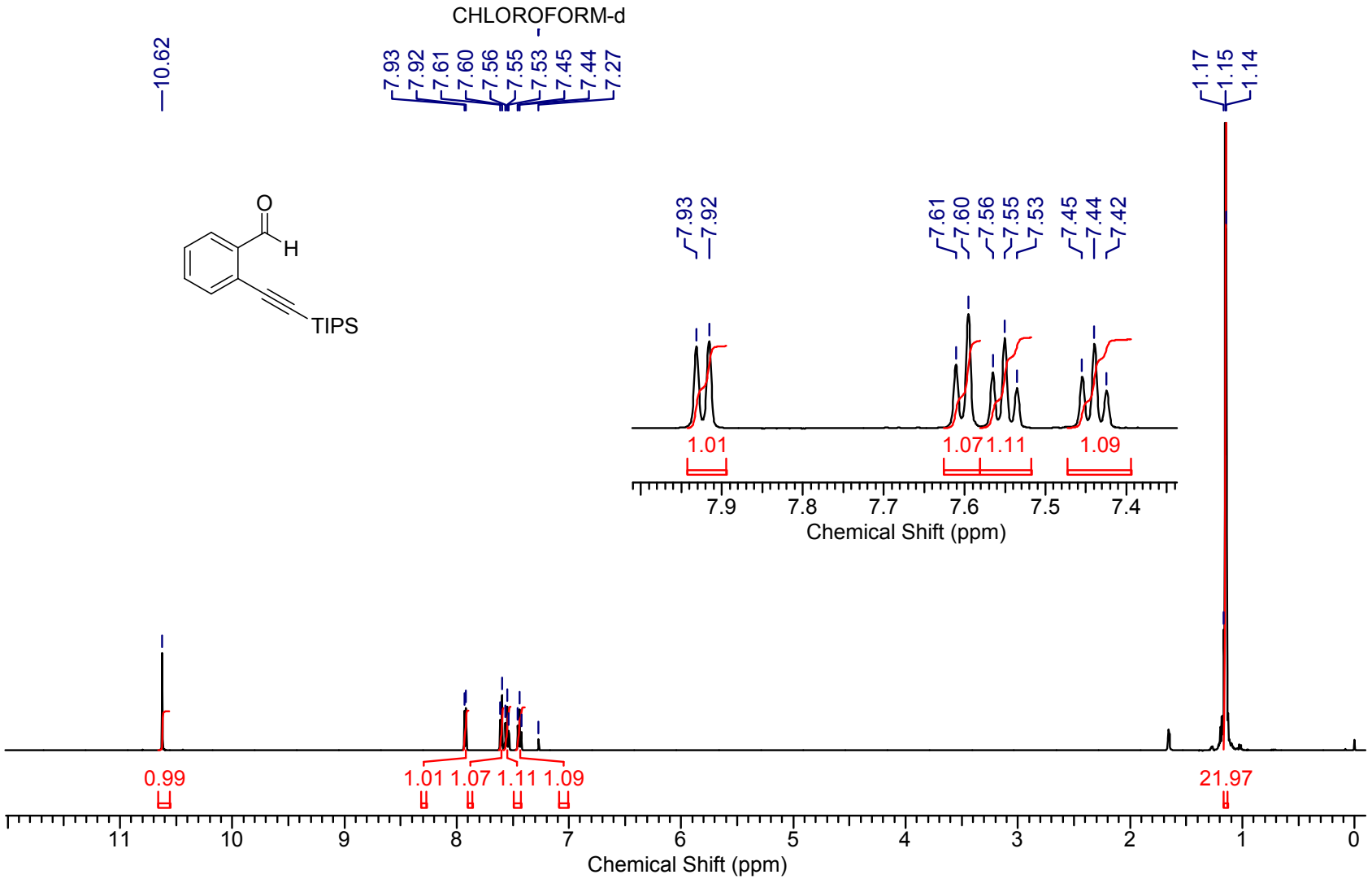
^{13}C NMR of **4q**


CHLOROFORM-d
7.27
TIPS
TIPS
(12)
1.11
42.00
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

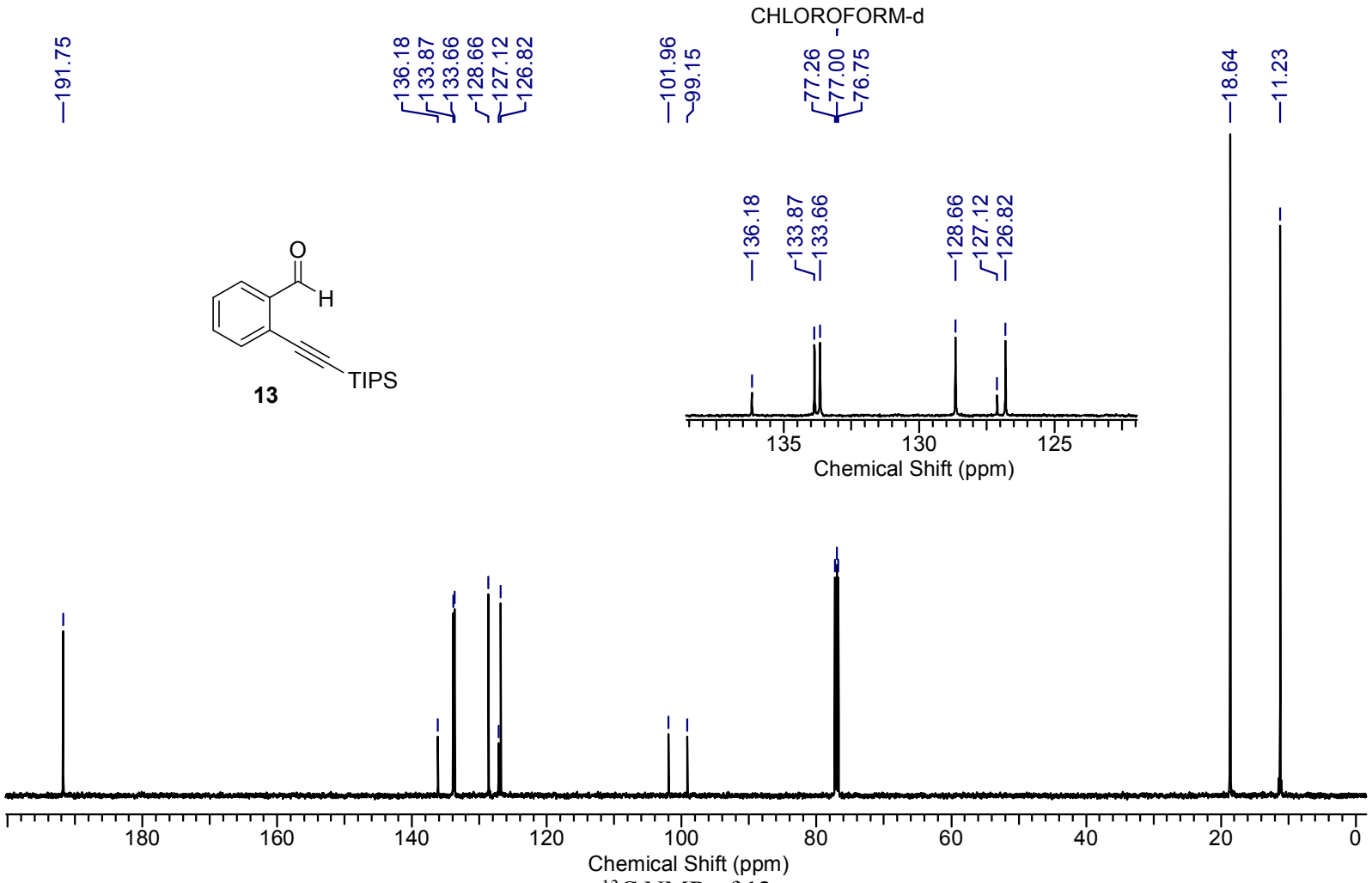
^{1}H NMR of **12**


CHLOROFORM-d
90.20
81.55
77.25
77.00
76.75
18.55
11.31
TIPS
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

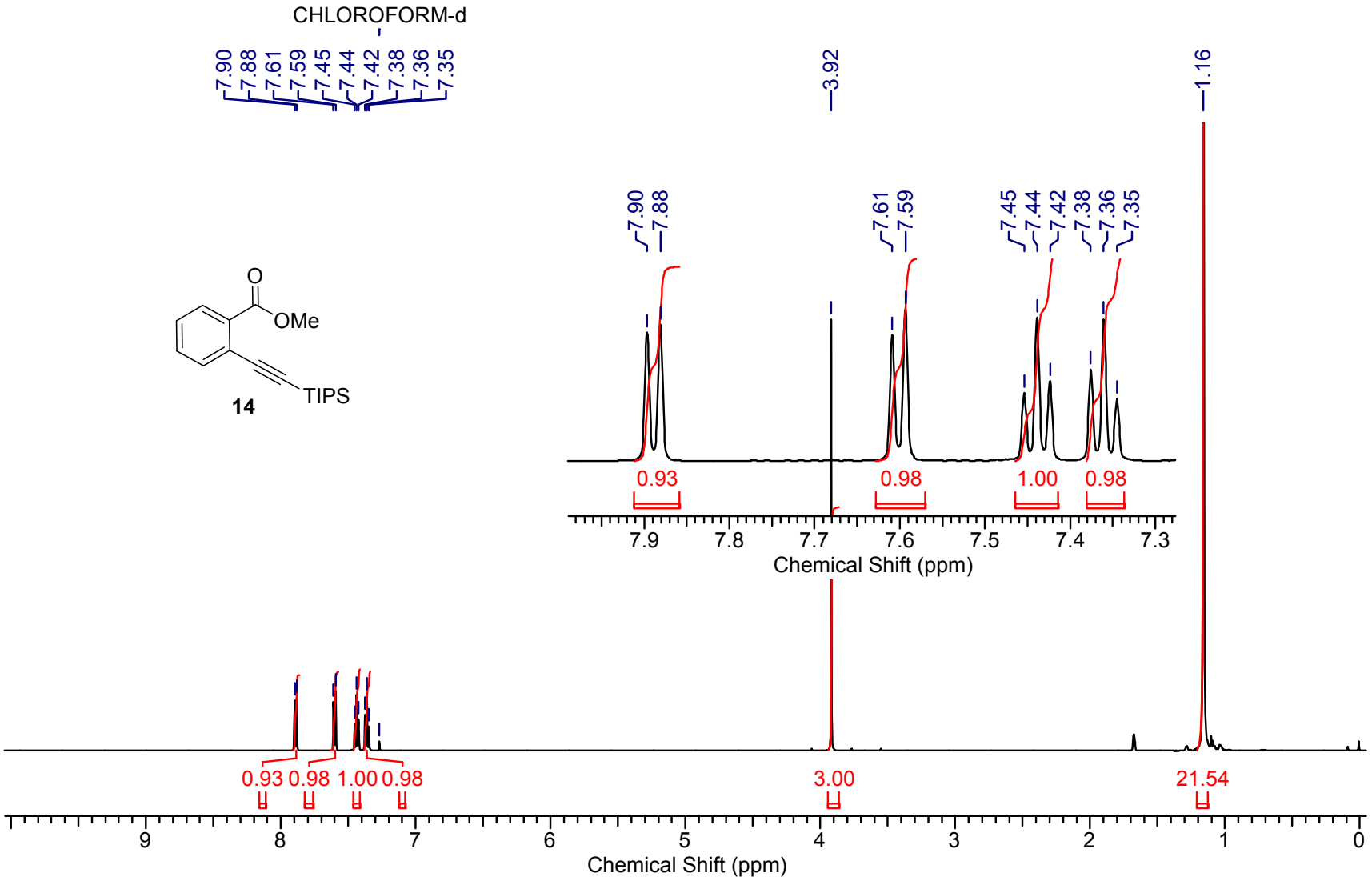
^{13}C NMR of **12**


CHLOROFORM-d
10.62
7.93
7.92
7.61
7.60
7.56
7.55
7.53
7.45
7.44
7.27
1.17
1.15
1.14
O
H
TIPS
1.01
1.07
1.11
1.09
Chemical Shift (ppm)
0.99
1.01
1.07
1.11
1.09
21.97
Chemical Shift (ppm)

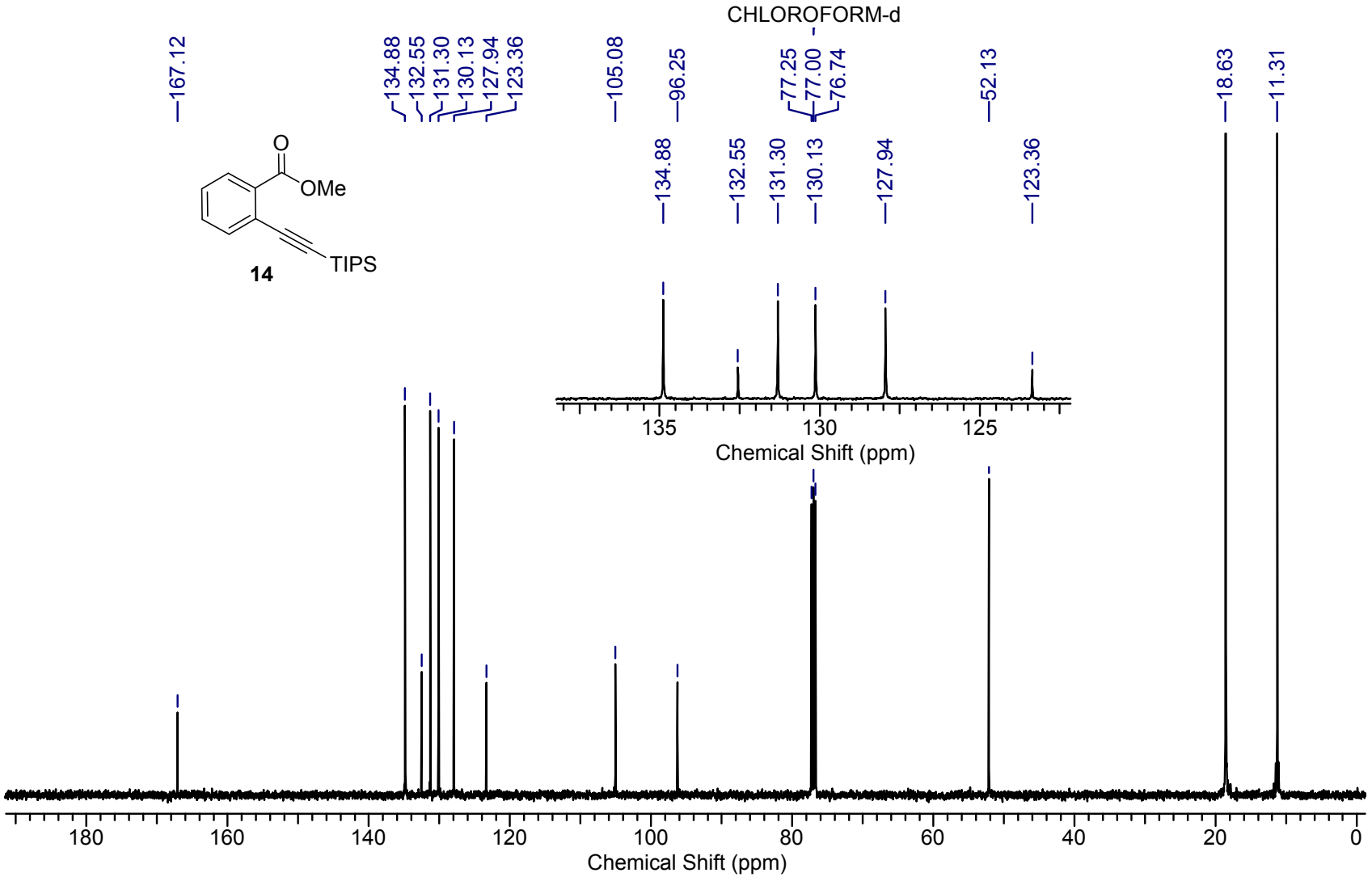
^{1}H NMR of **13**


CHLOROFORM-d
191.75
136.18
133.87
133.66
128.66
127.12
126.82
101.96
99.15
77.26
77.00
76.75
18.64
11.23
O
H
TIPS
13
Chemical Shift (ppm)
Chemical Shift (ppm)

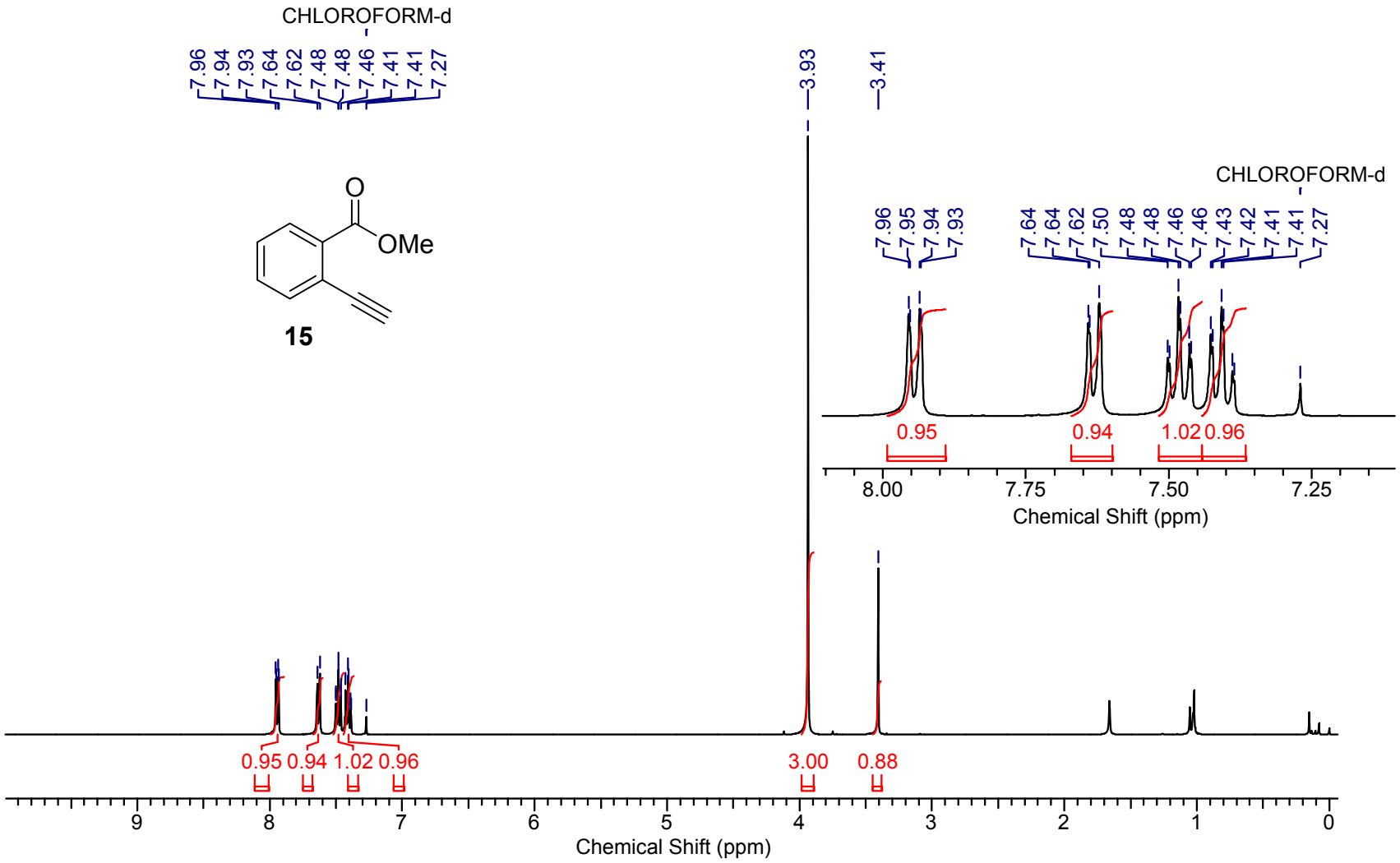
^{13}C NMR of **13**


CHLOROFORM-d
7.90
7.88
7.61
7.59
7.45
7.44
7.42
7.38
7.36
7.35
3.92
1.16
O
OMe
TIPS
14
0.93
0.98
1.00
0.98
Chemical Shift (ppm)
0.93 0.98 1.00 0.98
3.00
21.54
Chemical Shift (ppm)

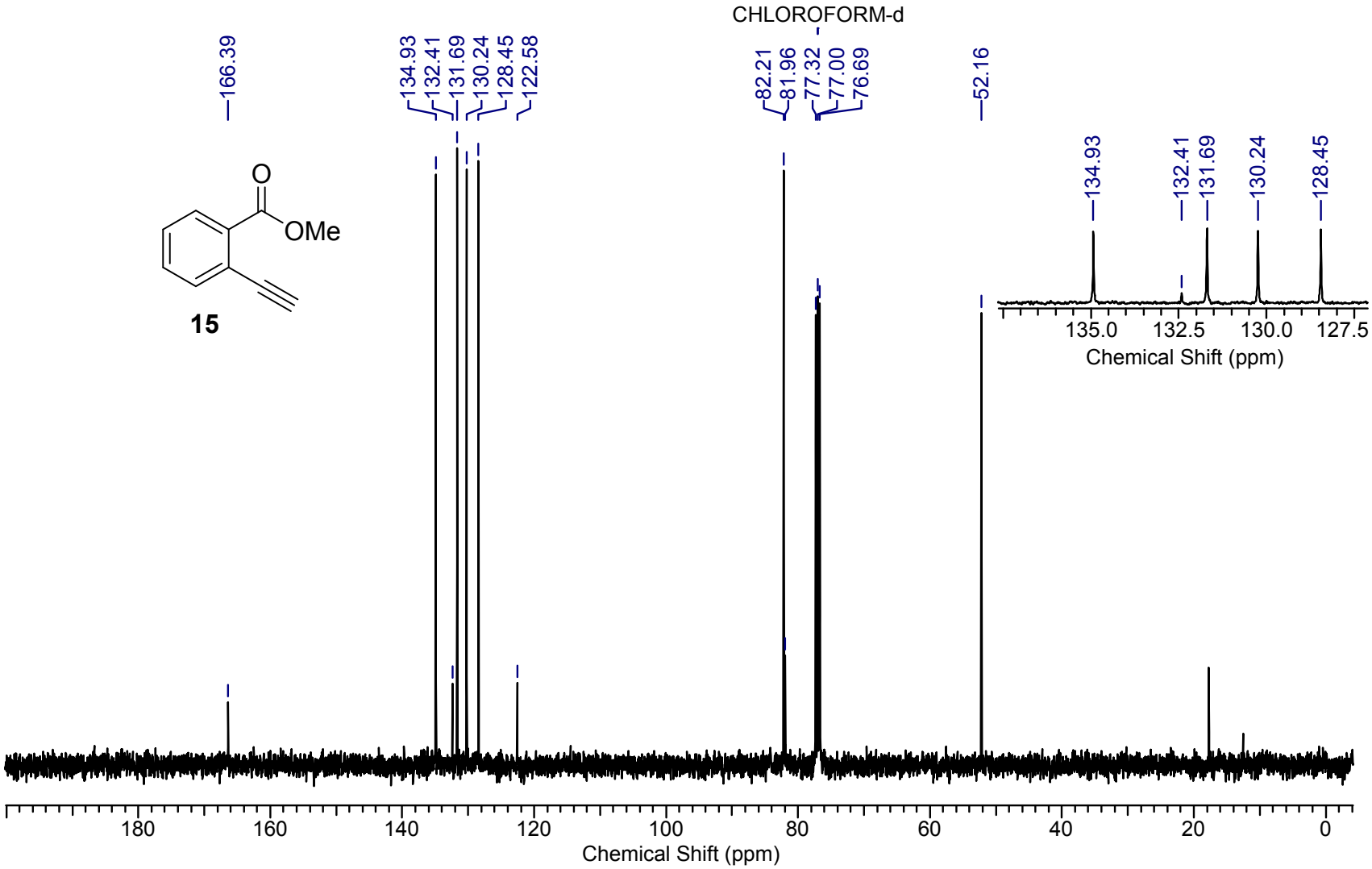
^{1}H NMR of **14**


CHLOROFORM-d
167.12
134.88
132.55
131.30
130.13
127.94
123.36
105.08
96.25
77.25
77.00
76.74
52.13
18.63
11.31
O
OMe
TIPS
14
Chemical Shift (ppm)
Chemical Shift (ppm)

^{13}C NMR of **14**

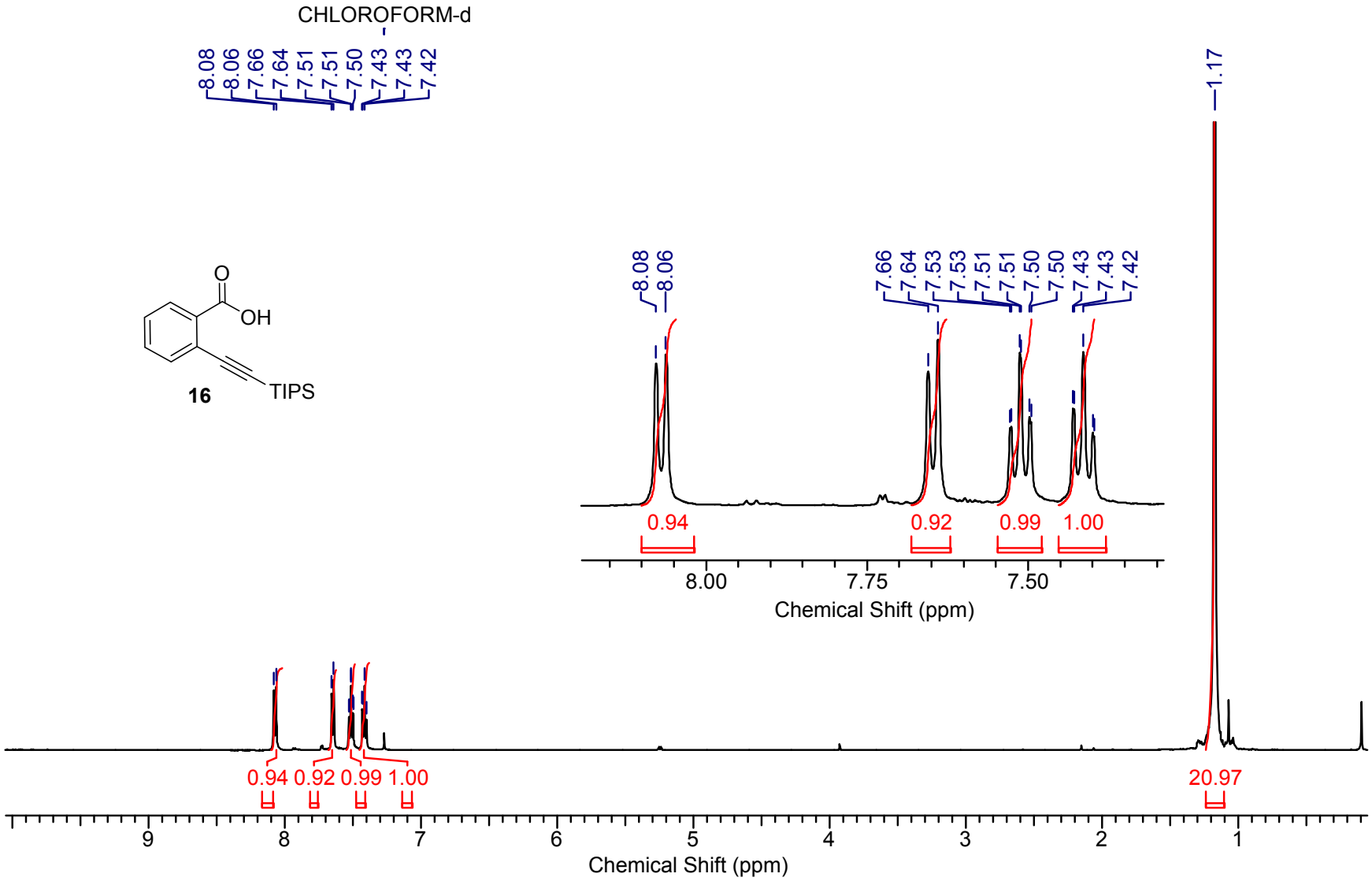

CHLOROFORM-d
7.96
7.94
7.93
7.64
7.62
7.48
7.48
7.46
7.41
7.41
7.27
3.93
3.41
O
OMe
15
CHLOROFORM-d
7.96
7.95
7.94
7.93
7.64
7.64
7.62
7.50
7.48
7.48
7.46
7.46
7.43
7.42
7.41
7.41
7.27
0.95
0.94
1.02
0.96
8.00
7.75
7.50
7.25
Chemical Shift (ppm)
0.95
0.94
1.02
0.96
3.00
0.88
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

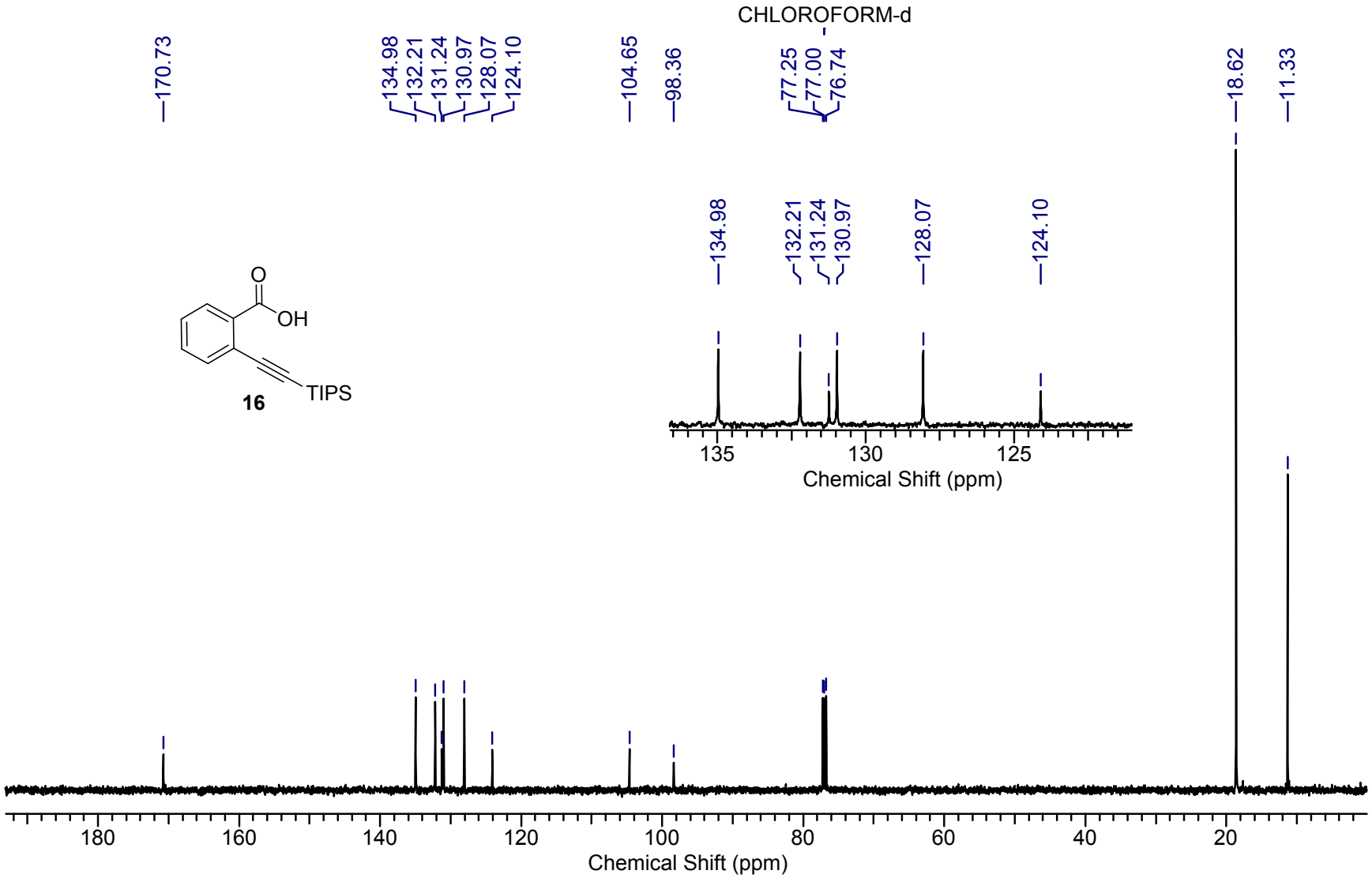
^{1}H NMR of **15**


CHLOROFORM-d
166.39
134.93
132.41
131.69
130.24
128.45
122.58
82.21
81.96
77.32
77.00
76.69
52.16
O
OMe
15
135.0
132.5
130.0
127.5
Chemical Shift (ppm)
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

^{13}C NMR of **15**

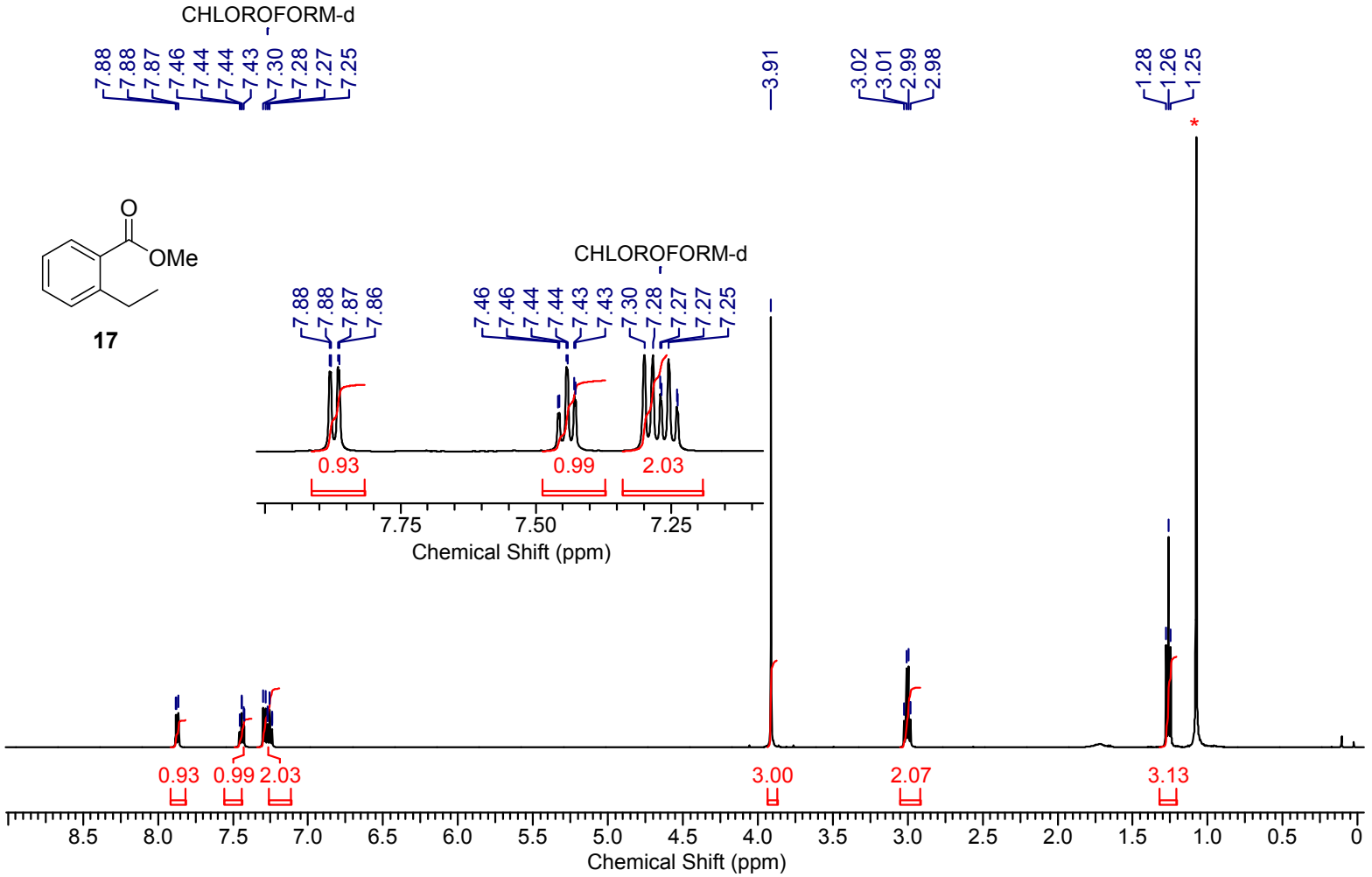
^{1}H NMR of **16**

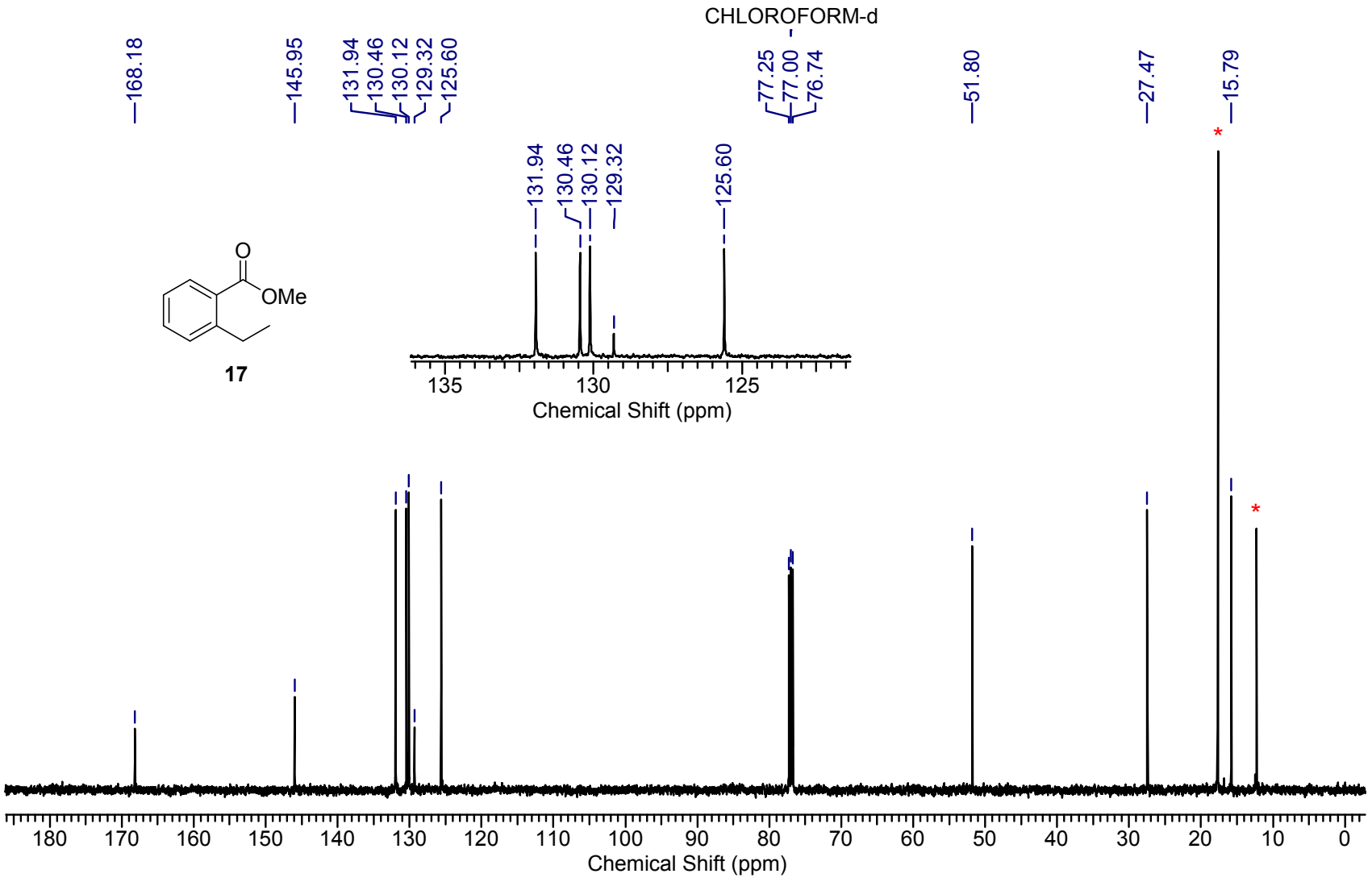

CHLOROFORM-d
8.08
8.06
7.66
7.64
7.51
7.51
7.50
7.43
7.43
7.42
1.17
O
OH
16
TIPS
0.94
0.92
0.99
1.00
20.97
Chemical Shift (ppm)


CHLOROFORM-d
170.73
134.98
132.21
131.24
130.97
128.07
124.10
104.65
98.36
77.25
77.00
76.74
18.62
11.33
O
OH
TIPS
16
Chemical Shift (ppm)
Chemical Shift (ppm)

^{13}C NMR of **16**

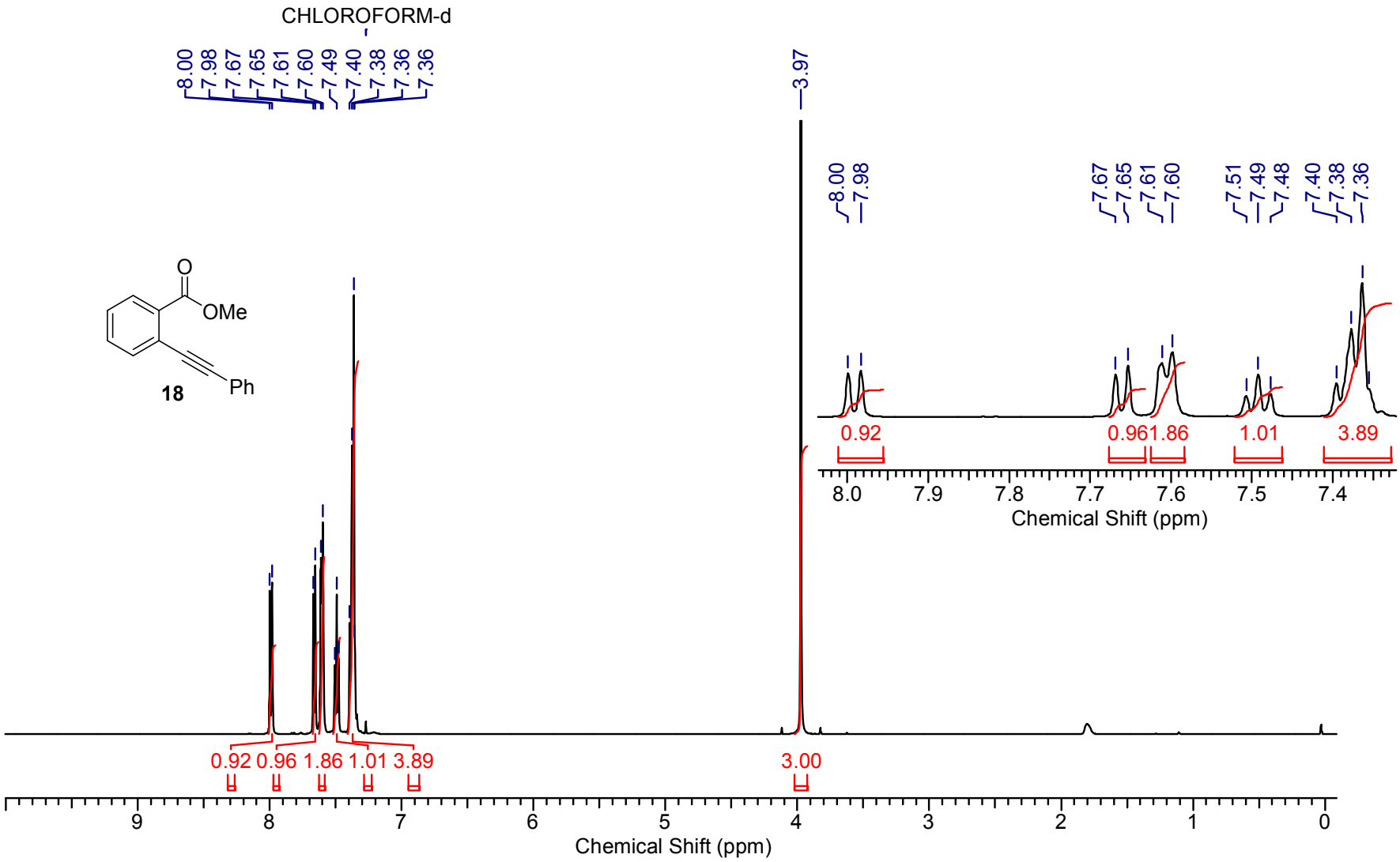
^{1}H NMR of **17** (* due to TIPS-F)

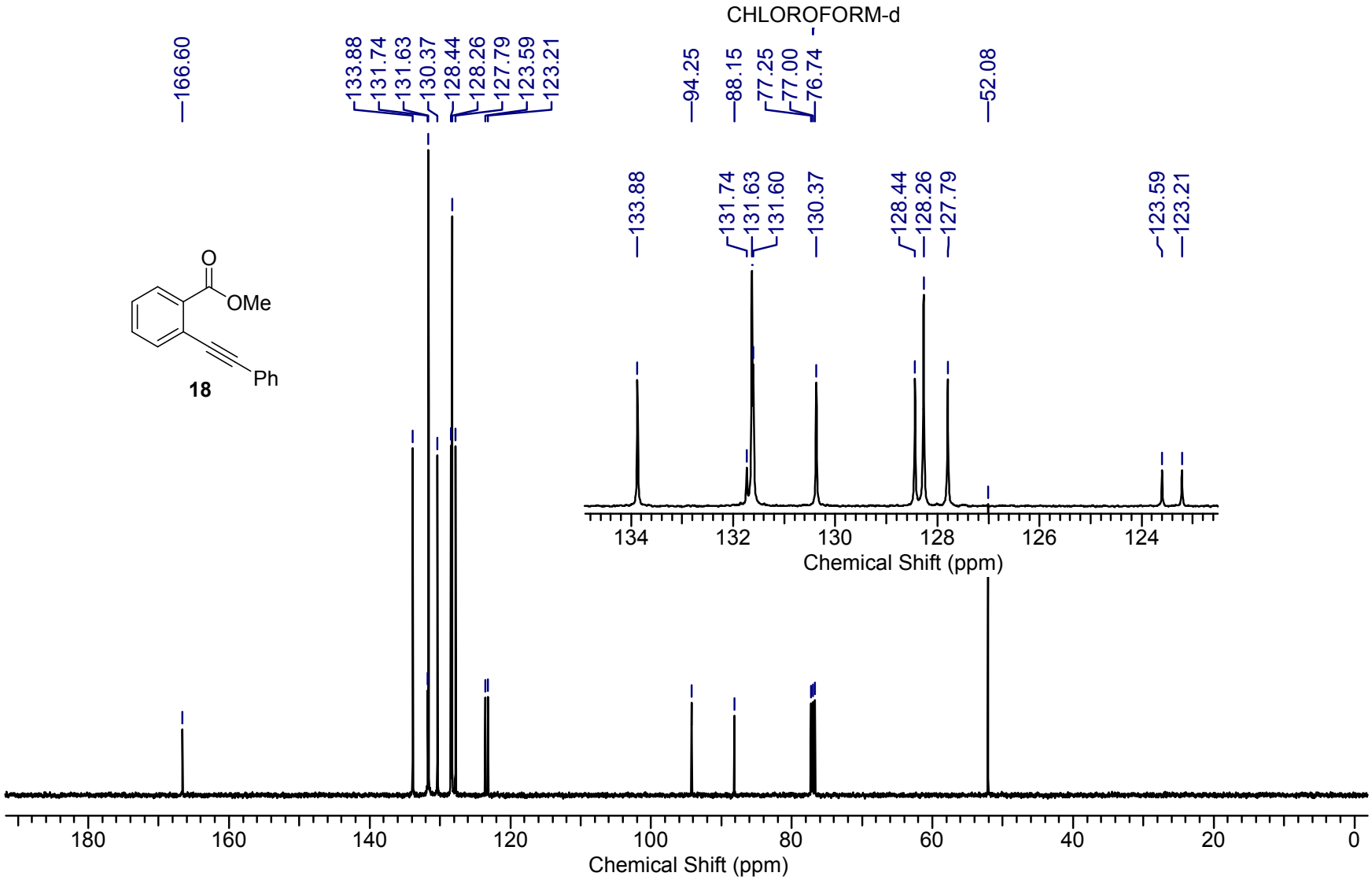




^{13}C NMR of **18** (*due to TIPS-F)

^{1}H NMR of **18**


CHLOROFORM-d
8.00
7.98
7.67
7.65
7.61
7.60
7.49
7.40
7.38
7.36
7.36
3.97
O
OMe
Ph
18
0.92 0.96 1.86 1.01 3.89
3.00
Chemical Shift (ppm)
0.92
0.96 1.86
1.01
3.89
Chemical Shift (ppm)


CHLOROFORM-d
166.60
133.88
131.74
131.63
130.37
128.44
128.26
127.79
123.59
123.21
94.25
88.15
77.25
77.00
76.74
52.08
O
OMe
Ph
18
Chemical Shift (ppm)
Chemical Shift (ppm)

^{13}C NMR of **18**