Supporting Information

Room Temperature C-H Bond Alkynylation by Merging Cobalt and Photo-redox catalysis

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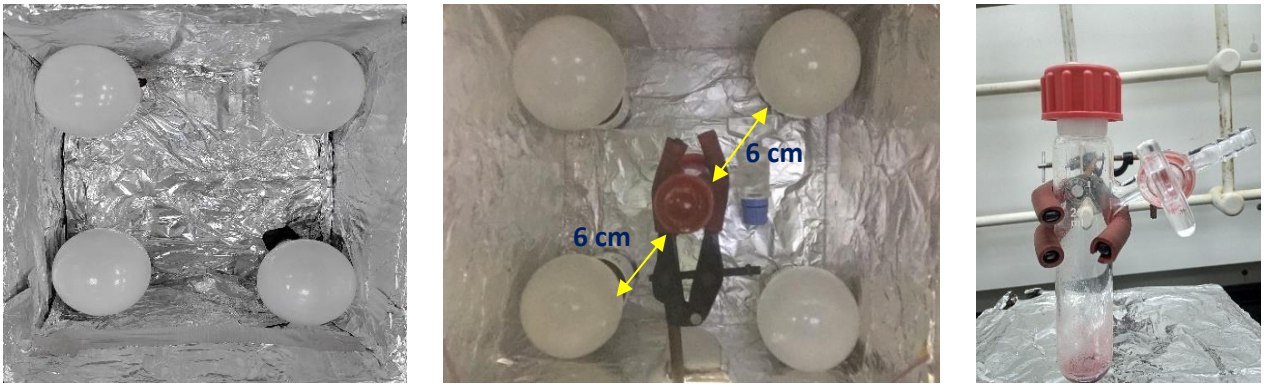
1. General: Unless otherwise mentioned, all catalytic reactions were carried out under air. Dicholormethane (DCM) was dried using calcium hydride (CaH_2) under the established protocol. Reagent grade 2,2,2-trifluoroethanol (TFE), 1,4-dioxane, HPLC grade ethyl acetate (EtOAc) were used as such from the commercial sources. ^1H and ^{13}C NMR were recorded on JEOL (400 MHz) and JEOL (500 MHz) using $CDCl_3$ and DMSO-d_6 as a solvent. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals used as references and the chemicals shifts converted to TMS scale ($CDCl_3$: δ_C = 77.0 ppm, δ_H = 7.26 ppm). All the reactions were monitored by analytical thin layer chromatography (TLC) using commercial aluminum sheets precoated with silica gel. Column chromatography was conducted on silica gel (Merck, 200-400 mesh). HRMS was recorded on a Quadrupole Time-of-Flight Mass Spectrometry mass spectrometer and ESI-MS was recorded on Agilent mass spectrometer. Unless otherwise mentioned, all other chemicals were received and used as such from the commercial sources.

All amides were prepared from the reaction of 8-aminoquinoline with carboxylic acid *via* the formation of acyl chloride according to reported literature.[1,2]

Figure 1. Pictorial representation of light setup, details of the LEDs, and reaction tube used for photocatalysis.

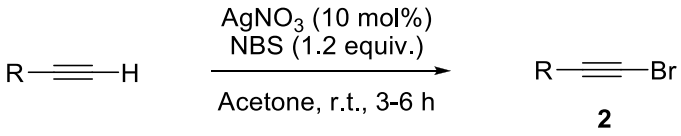


Dimension of the Light Setup: 20 cm * 20 cm
Distance of the reaction tube from the LEDs: 6 cm
Reaction Tube: Screw capped Schlenk tube made of borosilicate glass (13 cm * 2.3 cm)
Light Details: Energy saver LED lamps 7W B22
Brand: Phillips
Wattage: 7 W
Model: 9290024648
Photometric Code: 865/7107

[1] Aihara, Y.; Chatani, N. *J. Am. Chem. Soc.,* **2013**, *135*, 5308.

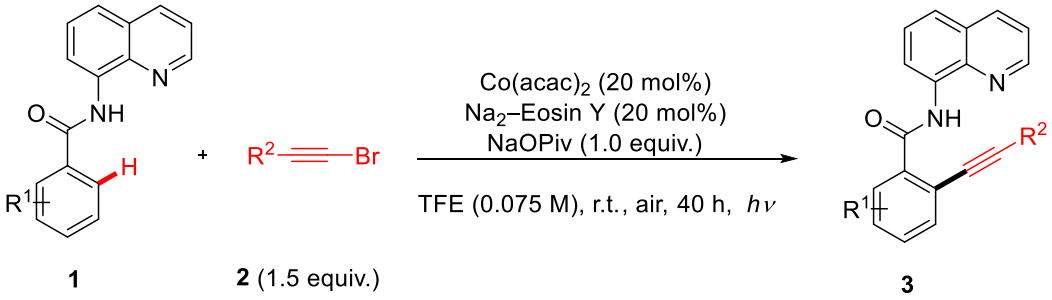
[2] a) Barsu, N.; Kalsi, D.; Sundararaju, B. *Chem. Eur. J.*, **2015**, *21*, 9364. b) Yong, G.; Pauls Henry**,** W. *Synlett*, **2000,** *6*, 829.

2. General procedure (A) for the the preparation of bromo alkyne



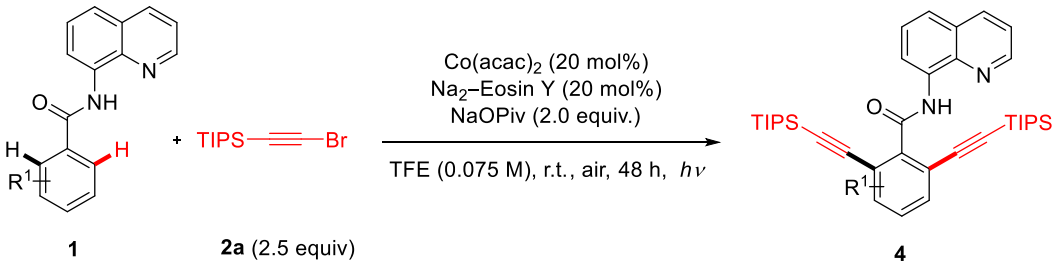
All the bromo alkynes are prepared according to the literature procedure.[3] Alkyne (4.45 mmol, 1.0 equiv) was dissolved in 30 mL of acetone. To this mixture *N*-bromosuccinimide (1.2 equiv.) and silver nitrate (10 mol%) was added. The resulting mixture was stirred under room temperature for 3-6 h, and it was then poured into crushed ice. After some time, the aqueous layer was extracted with pentane. The combined organic layers were dried, filtered, and concentrated. It was then purified by flash column chromatography using n-hexane to yield the product **2** as colorless oil.

3. General procedure (B) for the catalytic *mono*-C-H alkynylation of benzamide



An oven dried Schlenk tube (13 cm x 2.3 cm) was charged with magnetic stirr bar, benzamide **1** (0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol %), sodium pivalate (18.6 mg, 0.15 mmol, 1.0 equiv.), Na_2-Eosin Y (20.7 mg, 0.03 mmol, 20 mol%) and alkynyl bromide **2** (0.3 mmol, 1.5 equiv.) under air. Subsequently, 2,2,2-trifluroethanol (2.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and placed under white LED bulbs (4 * 7 watts) at r.t. for 40 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding *mono*-C-H alkynylated benzamide **3**. (Note: The exposure of LED bulbs produce the heat to the Schlenk tube (within the range of 40 – 50 °C)).

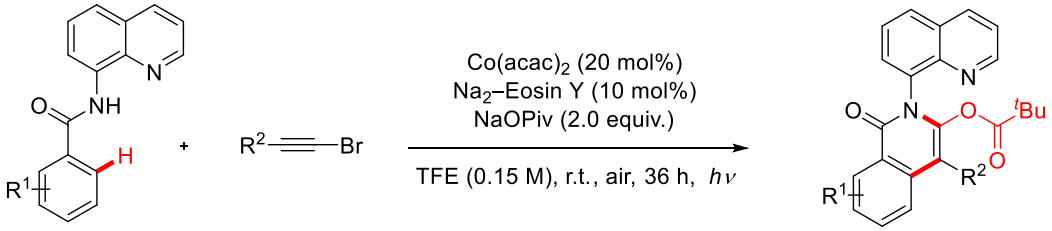
4. General procedure (C) for the catalytic *bis*-C-H alkynylation of benzamide



[3] Nicolai, S.; Piemontesi, C.l.; Waser, J.; *Angew. Chem. Int. Ed.*, **2011**, *50*, 4680.

An oven dried Schlenk tube (13 cm x 2.3 cm) charged with magnetic stirr bar, benzamide **1** (0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol %), sodium pivalate (37.2 mg, 0.3 mmol, 2.0 equiv.), Na_2-Eosin Y (20.7 mg, 0.03 mmol, 20 mol%) and (bromoethynyl)triisopropylsilane **2a** (0.375 mmol, 2.5 equiv.) under air. Subsequently, 2,2,2-trifluroethanol (2.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and placed under white LED bulbs (4 * 7 watts) at r.t. for 48 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding *bis*-C-H alkynylated benzamide **4**. (Note: The exposure of LED bulbs produce the heat to the Schlenk tube (within the range of 40 – 50 °C)).

5. General procedure (D) for the catalytic C-H and N-H bond annulation of substituted benzamides with bromo alkynes

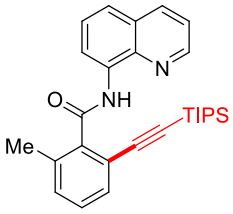


1 **2** (1.5 equiv) **5**

An oven dried Schlenk tube (13 cm x 2.3 cm) charged with magnetic stirr bar, benzamide **1** (0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol %), sodium pivalate (37.2 mg, 0.3 mmol, 2.0 equiv.), Na_2-Eosin Y (10.4 mg, 0.015 mmol, 10 mol%) and alkynyl bromide **2** (0.225 mmol, 1.5 equiv.) under air. Subsequently, 2,2,2-trifluroethanol (1.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and placed under white LED bulbs (4 * 7 watts) at r.t. for 36 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding annulated benzamide **5**. (Note: The exposure of LED bulbs produce the heat to the Schlenk tube (within the range of 40 – 50 °C)).

6. Analytical data of the products

2-Methyl-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3aa): Compound **3aa** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 89% yield (59.1 mg) as colourless liquid. The NMR data of **3aa** is in accordance with the literature.[4]

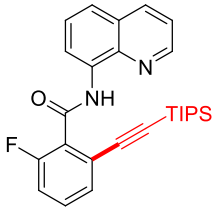


^{1}H NMR (400 MHz, Chloroform-d) δ 10.08 (s, 1H), 9.00 (dd, J = 7.4, 1.5 Hz, 1H), 8.73 (dd, J = 4.2, 1.5 Hz, 1H), 8.16 (dd, J = 8.2, 1.6 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.43 – 7.40 (m, 2H), 7.30 – 7.22 (m, 2H), 2.46 (s, 3H), 0.76 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 167.18, 148.08, 140.13, 138.51, 136.14, 135.65, 134.72, 130.46, 130.33, 28.86, 27.83, 27.28, 121.70, 121.44, 120.84, 116.82, 103.87, 94.93, 19.45, 18.23, 10.98.

[4] Landge, V. G.; Jaiswal, G.; Balaraman, E. *Org. Lett*. **2016**, *18*, 812.

2-Fluoro-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3ba): Compound **3ba** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 88% yield (58.9 mg) as colourless oil. The NMR data of **3ba** is in accordance with the literature.[5]

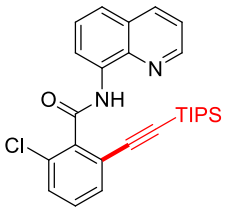


^{1}H NMR (400 MHz, Chloroform-d) δ 10.19 (s, 1H), 8.97 (dd, J = 4.2, 1.6 Hz, 1H), 8.75 (dd, J = 4.2, 1.6 Hz, 1H), 8.16 (dd, J = 8.2, 1.5 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.39 – 7.34 (m, 2H), 7.17 – 7.13 (m, 1H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 162.07, 159.18 (d, $^1J_{C\text{-}F}$ = 250.4Hz), 148.15, 138.41, 136.20, 134.40, 130.73 (d, J = 9.0 Hz), 128.86 (d, J = 3.3 Hz), 128.29 (d, J = 18.6 Hz), 127.79, 127.29, 123.16 (d, J = 4.8 Hz), 116.98, 116.46, 116.24, 102.32, 102.28, 97.07, 18.24, 10.95.

^{19}F NMR (377 MHz, Chloroform-d) δ - 114.71.

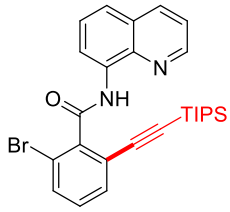
2-Chloro-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3ca): Compound **3ca** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 72% yield (50.0 mg) as colourless oil. The NMR data of **3ca** is in accordance with the literature.[5]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.09 (s, 1H), 8.98 (d, J = 7.2, 1.8 Hz, 1H), 8.74 (dd, J = 4.2, 1.4 Hz, 1H), 8.16 (dd, J = 8.3, 1.5 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.48 (m, 1H), 7.43 (dd, J = 8.3, 4.1 Hz, 2H), 7.32 (t, J = 7.9 Hz, 1H), 0.79 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.09, 148.12, 139.40, 138.42, 136.19, 134.41, 131.39, 131.13, 129.92, 129.68, 127.80, 127.27, 123.00, 121.98, 121.51, 117.07, 102.38, 96.92, 18.22, 10.94.

2-Bromo-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3da): Comp-ound **3da** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 72% yield (54.8 mg) as white solid. *Bis*-C-H alkynylated product was isolated in 5% yield.



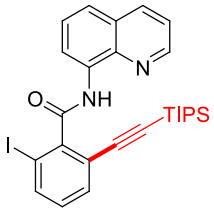
^{1}H NMR (400 MHz, Chloroform-d) δ 10.07 (s, 1H), 8.98 (dd, J = 7.1, 1.5 Hz, 1H), 8.74 (dd, J = 3.9, 1.3 Hz, 1H), 8.16 (dd, J = 8.3, 1.4 Hz, 1H), 7.61 – 7.56 (m, 3H), 7.52 (m, 1H), 7.42 (dd, J = 8.2, 4.2 Hz, 2H), 7.24 (m, 1H), 0.78 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.95, 148.12, 141.42, 138.42, 136.18, 134.39, 132.76, 131.64, 130.05, 127.79, 127.25, 123.02, 121.98, 121.50, 119.76, 117.08, 102.42, 96.95, 18.21, 10.93.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{32}BrN_2OSi$ is 507.1467, found 507.1460.

[5] Landge, V. G.; Shewale, C. H.; Jaiswal, G.; Sahoo, M. K.; Midya, S. P.; Balaraman, E. *Catal. Sci. Technol*. **2016**, *6*, 1946.

2-Iodo-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3ea): Compound **3ea** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 2:98) in 66% yield (54.9 mg) as colourless oil. *Bis*-C-H alkynylated product was isolated in 8% yield.

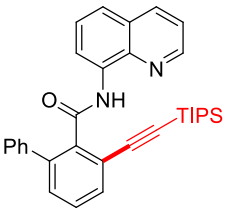


^{1}H NMR (400 MHz, Chloroform-d) δ 10.05 (s, 1H), 8.98 (dd, J = 7.2, 1.8 Hz, 1H), 8.75 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.6 Hz, 1H), 7.85 (d, J = 7.7 Hz, 1H), 7.61 – 7.53 (m, 3H), 7.43 (dd, J = 8.1, 4.2 Hz, 1H), 7.07 (t, J = 7.9 Hz, 1H), 0.78 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.61, 148.13, 145.42, 139.16, 138.48, 136.17, 134.45, 132.38, 130.10, 127.82, 127.26, 122.35, 121.96, 121.50, 117.12, 102.68, 96.85, 92.62, 18.21, 10.96.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{32}IN_2OSi$ is 555.1329, found 555.1321.

***N*-(Quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)biphenyl-2-carboxamide (3fa):** Compound **3fa** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 82% yield (62.1 mg) as white solid.

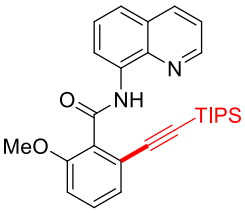


^{1}H NMR (400 MHz, Chloroform-d) δ 10.00 (s, 1H), 8.80 (dd, J = 6.2, 2.8 Hz, 1H), 8.69 (dd, J = 4.2, 1.4 Hz, 1H), 8.11 (dd, J = 8.2, 1.6 Hz, 1H), 7.60 (dd, J = 7.4, 1.6 Hz, 1H), 7.54 (m, 2H), 7.48 (m, 2H), 7.45 – 7.37 (m, 3H), 7.28 (m, 2H), 7.22 (m, 1H), 0.82 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.57, 147.95, 140.13, 139.64, 139.59, 138.42, 136.03, 134.57, 131.86, 130.24, 129.04, 128.61, 128.26, 127.71, 127.59, 127.21, 121.72, 121.50, 121.34, 116.78, 103.71, 95.56, 18.43, 11.04.

HRMS: $[M+H]^+$ calculated for $C_{33}H_{37}N_2OSi$ is 505.2675, found 505.2672.

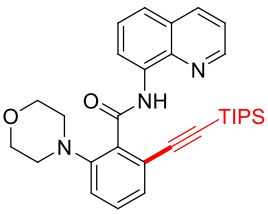
2-Methoxy-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3ga): Compound **3ga** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 6:94) in 58% yield (39.9 mg) as colourless oil. The NMR data of **3ga** is in accordance with the literature.[4]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.10 (s, 1H), 9.01 (dd, J = 7.5, 1.3 Hz, 1H), 8.73 (dd, J = 4.1, 1.5 Hz, 1H), 8.15 (dd, J = 8.2, 1.6 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.41 (dd, J = 8.4, 4.2 Hz, 1H), 7.33 (m, 1H), 7.17 (d, J = 8.1 Hz, 1H), 6.97 (d, J = 8.5 Hz, 1H), 3.86 (s, 3H), 0.80 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.86, 156.42, 147.97, 138.51, 136.12, 134.90, 130.10, 129.92, 127.81, 127.38, 125.04, 122.45, 121.50, 121.35, 116.93, 111.60, 103.36, 95.41, 56.02, 18.27, 11.02.

2-Morpholino-*N*-(quinolin-8-yl)-6-((triisopropylsilyl)ethynyl)benzamide (3ha): Compound **3ha** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 69% yield (53.2 mg) as colourless oil.



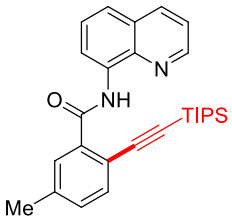
^{1}H NMR (400 MHz, Chloroform-d) δ 10.37 (s, 1H), 8.97 (m, 1H), 8.75 (dd, J = 4.2, 1.6 Hz, 1H), 8.17 (dd, J = 8.3, 1.3 Hz, 1H), 7.60 – 7.52 (m, 2H), 7.44 (dd, J = 8.2, 4.2 Hz,

1H), 7.36-7.30 (m, 2H), 7.09 (dd, *J* = 7.4, 1.6 Hz, 1H), 3.63 (m, 4H), 3.10 (m, 4H), 0.95 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.25, 149.81, 148.03, 138.44, 136.24, 135.42, 134.89, 129.95, 128.11, 127.99, 127.41, 123.23, 121.50 (overlapped), 119.46, 116.81, 103.98, 95.29, 66.88, 52.81, 18.44, 11.16.

HRMS: $[M+H]^+$ calculated for $C_{31}H_{40}N_3O_2Si$ is 514.2890, found 514.2895.

5-Methyl-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3ia): Compound **3ia** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 65% yield (43.1 mg) as colourless oil. *Bis*-C-H alkynylated product was isolated in 5% yield.

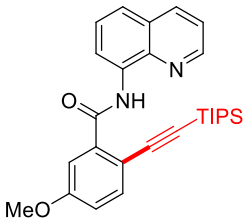


^{1}H NMR (400 MHz, Chloroform-d) δ 10.49 (s, 1H), 8.92 (d, *J* = 7.1 Hz, 1H), 8.75 (dd, *J* = 4.0, 1.2 Hz, 1H), 8.15 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.61 – 7.50 (m, 4H), 7.42 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.24 (dd, *J* = 7.9, 0.8 Hz, 1H), 2.41 (s, 3H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.56, 148.17, 139.02, 139.01, 138.83, 136.13, 134.64, 133.79, 130.89, 129.20, 127.84, 127.29, 121.74, 121.39, 117.70, 117.07, 103.97, 96.04, 21.37, 18.26, 11.00.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{31}N_2OSSi_2$ is 443.2519, found 443.2516.

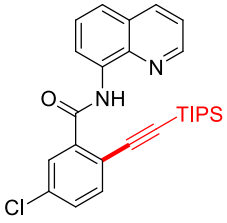
5-Methoxy-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3ja): Compound **3ja** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 5:95) in 53% yield (36.5 mg) as colourless oil. *Bis*-C-H alkynylated product was isolated in 3% yield. The NMR data of **3ja** is in accordance with the literature.[5]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.54 (s, 1H), 8.90 (dd, *J* = 7.4, 1.2 Hz, 1H), 8.76 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.16 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.60 – 7.52 (m, 3H), 7.42 (dd, *J* = 8.1, 4.2 Hz, 1H), 7.33 (d, *J* = 2.7 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.7 Hz, 1H), 3.87 (s, 3H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.16, 159.70, 148.26, 140.61, 138.92, 136.14, 135.41, 134.58, 127.88, 127.28, 121.89, 121.43, 117.18, 117.11, 113.08, 112.91, 103.85, 95.19, 55.57, 18.29, 11.05.

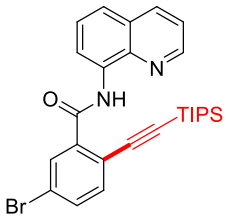
5-Chloro-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3ka): Compound **3ka** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 73% yield (50.7 mg) as colourless oil. *Bis*-C-H alkynylated product was isolated in 6% yield. The NMR data of **3ka** is in accordance with the literature.[5]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.49 (s, 1H), 8.89 (dd, *J* = 7.0, 1.6 Hz, 1H), 8.76 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.2, 1.6 Hz, 1H), 7.78 (d, *J* = 2.1 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.45 – 7.39 (m, 2H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.91, 148.30, 140.55, 138.79, 136.21, 136.05, 134.78, 134.34, 130.28, 128.83, 127.86, 127.28, 122.11, 121.52, 119.14, 117.21, 102.72, 98.40, 18.26, 10.91.

5-Bromo-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3la): Compound **3la** was prepared according to the general procedure **B** and purified by flash column chromatography (EtOAc: hexane = 3:97) in 51% yield (38.8 mg) as colourless oil. *Bis*-C-H alkynylated product was isolated in 8% yield. The NMR data of **3la** is in accordance with the literature.[5]

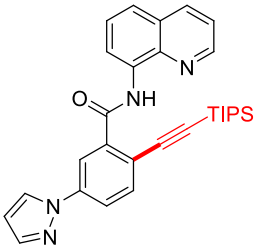


^{1}H NMR (400 MHz, Chloroform-d) δ 10.48 (s, 1H), 8.88 (dd, J = 7.0, 1.8 Hz, 1H), 8.76 (dd, J = 4.2, 1.7 Hz, 1H), 8.17 (dd, J = 8.2, 1.6 Hz, 1H), 7.93 (dd, J = 2.1 Hz, 1H), 7.61 – 7.54 (m, 3H), 7.48 – 7.42 (m, 2H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.79, 148.30, 140.65, 138.77, 136.21, 135.13, 134.33, 133.19, 131.69, 127.85, 127.28, 122.83, 122.11, 121.52, 119.57, 117.20, 102.78, 98.62, 18.25, 10.97.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{32}BrN_2OSi_2$ is 507.1467, found 507.1461.

5-(1*H*-Pyrazol-1-yl)-*N*-(quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3ma): Compound **3ma** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 53% yield (39.3 mg) as colourless oil.

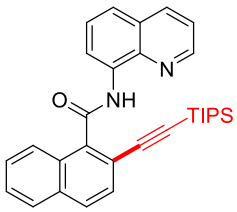


^{1}H NMR (400 MHz, Chloroform-d) δ 10.59 (s, 1H), 8.91 (dd, J = 7.2, 1.5 Hz, 1H), 8.77 (dd, J = 4.2, 1.4 Hz, 1H), 8.17 (dd, J = 8.3, 1.5 Hz, 1H), 8.06 (d, J = 2.3 Hz, 1H), 8.02 (d, J = 2.5 Hz, 1H), 7.92 (dd, J = 8.5, 2.4 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.62 – 7.55 (m, 2H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 6.51 (m, 1H), 0.83 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.47, 148.34, 141.75, 140.34, 139.82, 138.86, 136.20, 135.33, 134.42, 127.89, 127.29, 126.82, 122.10, 121.51, 120.64, 118.34, 117.28, 108.39, 103.14, 97.99, 29.68, 18.29, 11.04.

HRMS: $[M+H]^+$ calculated for $C_{30}H_{35}N_4OSi$ is 495.2580, found 495.2583.

***N*-(Quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)-1-naphthamide (3na):** Compound **3na** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 4:96) in 61 % yield (43.8 mg) as colourless oil.

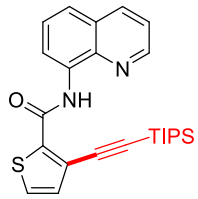


^{1}H NMR (400 MHz, Chloroform-d) δ 10.33 (s, 1H), 9.13 (d, J = 7.6 Hz, 1H), 8.69 (dd, J = 4.1, 1.5 Hz, 1H), 8.18 – 8.12 (m, 2H), 7.88 – 7.85 (m, 2H), 7.65 – 7.58 (m, 3H), 7.58 – 7.52 (m, 2H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 0.81 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.63, 148.10, 138.57, 138.49, 136.13, 134.81, 132.87, 129.92, 129.26, 128.76, 128.00, 127.84, 127.54, 127.31, 127.04, 125.59, 121.86, 121.47, 118.44, 116.92, 104.17, 96.64, 18.26, 11.01.

HRMS: $[M+H]^+$ calculated for $C_{31}H_{35}N_2OSi$ is 479.2519, found 479.2518.

***N*-(Quinolin-8-yl)-3-((triisopropylsilyl)ethynyl)thiophene-2-carboxamide (30a):** Compound **30a** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 4:96) in 57% yield (37.2 mg) as colourless oil.

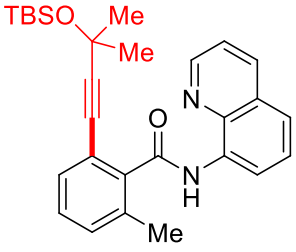


^{1}H NMR (400 MHz, Chloroform-d) δ 10.85 (s, 1H), 8.80 (dd, J = 4.2, 1.6 Hz, 1H), 8.71 (dd, J = 6.7, 2.3 Hz, 1H), 8.16 (dd, J = 8.2, 1.6 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.44 (dd, J = 8.7, 3.7 Hz, 2H), 7.20 (d, J = 5.1 Hz, 1H), 0.97 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 159.95, 148.44, 142.25, 139.42, 136.18, 134.22, 132.72, 129.00, 127.98, 127.10, 122.40, 121.67, 121.44, 118.75, 99.87, 99.29, 18.42, 11.09.

HRMS: $[M+H]^+$ calculated for $C_{25}H_{31}N_2OSSi_2$ is 435.1926, found 435.1920.

2-(3-(*Tert*-butyldimethylsilyloxy)-3-methylbut-1-ynyl)-6-methyl-N-(quinolin-8-yl)benzamide (3ab): Compound **3ab** was prepared according to the general procedure **B** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 5:95) in 62% yield (42.6 mg) as colourless oil.

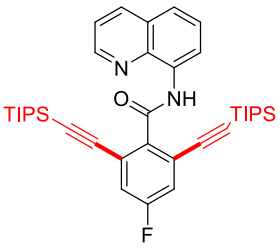


^{1}H NMR (500 MHz, Chloroform-d) δ 10.07 (s, 1H), 9.00 (dd, J = 7.6, 1.3 Hz, 1H), 8.76 (dd, J = 4.1, 1.6 Hz, 1H), 8.18 (dd, J = 8.3, 1.6 Hz, 1H), 7.60 (t, J = 7.8Hz, 1H), 7.55 (dd, J = 8.2, 1.3 Hz, 1H), 7.44 (dd, J = 8.2, 4.1 Hz, 1H), 7.35 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.24 (d, J = 7.7 Hz, 1H),2.47 (s, 3H), 1.05 (s, 6H), 0.76 (s, 9H), 0.05 (s, 6H).

^{13}C NMR (126 MHz, Chloroform-d) δ 167.15, 148.16, 139.83, 138.47, 136.28, 135.89, 134.64, 130.38, 129.47, 129.02, 127.92, 127.41, 121.79, 121.58, 120.55, 116.63, 98.57, 80.13, 66.43, 32.34, 25.61, 19.54, 17.80, -3.14.

ESI-MS: $[M+H]^+$ calculated for $C_{28}H_{35}N_2O2Si$ is 459.2468, found 459.2468.

4-Fluoro-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4pa): Compound **4pa** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 2:98) in 58% yield (54.5 mg) as white solid.



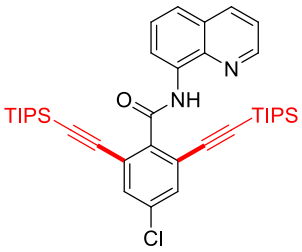
^{1}H NMR (400 MHz, Chloroform-d) δ 10.04 (s, 1H), 8.95 (dd, J = 7.2, 1.7 Hz, 1H), 8.73 (dd, J = 4.2, 1.4 Hz, 1H), 8.15 (dd, J = 8.2, 1.5 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.21 (d, J = 8.9 Hz, 2H), 0.85 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d$_3$) δ 164.81, 161.71 (d, $^1J_{C-F}$ = 249.6Hz), 147.99, 140.14 (d, $^4J_{C-F}$ = 3.5 Hz), 138.46, 136.09, 134.75, 127.71, 127.20, 123.46 (d, $^3J_{C-F}$ = 10.7 Hz), 121.46 (d, $^2J_{C-F}$ = 22.3 Hz), 119.47, 119.23, 117.05, 101.93 (d, $^4J_{C-F}$ = 3.2 Hz), 97.38, 18.29, 11.01.

^{19}F NMR (377 MHz, Chloroform-d) δ - 111.69.

HRMS: $[M+H]^+$ calculated for $C_{38}H_{52}FN_2OSi_2$ is 627.3602, found 627.3601.

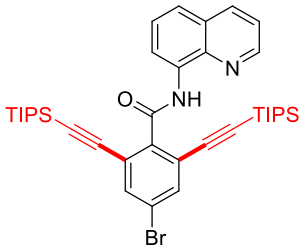
4-Chloro-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4qa): Compound **4qa** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 46% yield (44.4 mg) as colourless oil. The NMR data of **4qa** is in accordance with the literature.[5]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.04 (s, 1H), 8.93 (dd, J = 7.0, 2.0 Hz, 1H), 8.73 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.2, 1.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.48 (s, 2H), 7.42 (dd, J = 8.1, 4.2 Hz, 1H), 0.85 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.68, 148.01, 141.84, 138.44, 136.09, 134.67, 134.48, 132.05, 127.70, 127.19, 122.98, 121.63, 121.34, 117.06, 101.72, 97.61, 18.30, 11.00.

4-Bromo-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4ra): Compound **4ra** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 44% yield (45.4 mg) as colourless oil.

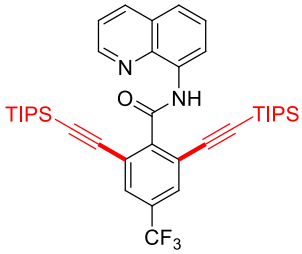


^{1}H NMR (400 MHz, Chloroform-d) δ 10.04 (s, 1H), 8.93 (dd, J = 7.0, 1.9 Hz, 1H), 8.73 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 (dd, J = 8.3, 1.6 Hz, 1H), 7.64 – 7.51 (m, 4H), 7.42 (dd, J = 8.4, 4.2 Hz, 1H), 0.85 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.70, 148.01, 142.24, 138.43, 136.09, 134.85, 134.65, 127.69, 127.19, 123.09, 122.23, 121.64, 121.38, 117.06, 101.58, 97.74, 18.30, 11.00.

HRMS: $[M+H]^+$ calculated for $C_{38}H_{52}BrN_2OSi_2$ is 687.2802, found 687.2807.

***N*-(Quinolin-8-yl)-4-(trifluoromethyl)-2,6 bis((triisopropylsilyl)ethynyl)benzamide (4sa):** Compound **4sa** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 56% yield (56.8 mg) as colourless oil. The NMR data of **4sa** is in accordance with the literature.[5]

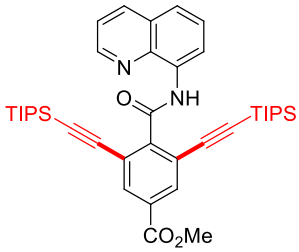


^{1}H NMR (400 MHz, Chloroform-d) δ 10.07 (s, 1H), 8.94 (m, 1H), 8.72 (m, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.73 (s, 2H), 7.55 (m, 2H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 0.86 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 164.38, 148.07, 146.07, 138.41, 136.13, 134.51, 132.41, 131.60, 131.26, 130.06, 128.78, 128.74, 128.27, 127.70, 127.16, 124.40, 122.47, 121.83, 121.66, 121.44, 117.19, 101.53, 98.27, 29.69, 18.30, 11.00.

^{19}F NMR (377 MHz, Chloroform-d) δ = - 63.09.

***N*-(Quinolin-8-yl)-4-(trifluoromethyl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4ta):** Compound **4ta** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 52% yield (52.0 mg) as colourless oil.

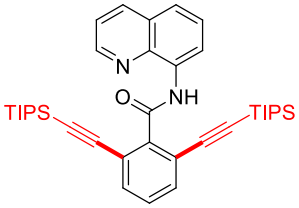


^{1}H NMR (400 MHz, Chloroform-d) δ 10.06 (s, 1H), 8.95 (dd, J = 7.0, 2.0 Hz, 1H), 8.72 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.3, 1.6 Hz, 1H), 8.14 (s, 2H), 7.58 – 7.51 (m, 2H), 7.42 (dd, J = 8.1, 4.2 Hz, 1H), 3.97 (s, 3H), 0.85 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.36, 164.82, 148.02, 146.66, 138.43, 136.10, 134.59, 133.14, 130.75, 127.69, 127.17, 121.97, 121.72, 121.39, 117.17, 102.04, 97.21, 52.58, 18.31, 11.01.

HRMS: $[M+H]^+$ calculated for $C_{40}H_{55}N_2O_3Si_2$ is 667.3751, found 667.3753.

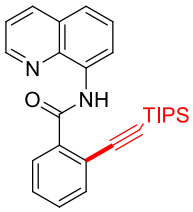
***N*-(Quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4ua):** Compound **4ua** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 10:90) afforded **4ua** in 46 % yield (42.0 mg) white solid. Along with the *bis*-C-H alkynylated product **4ua**, *mono*-C-H alkynylated product **3ua** was isolated in 12% yield. The NMR data of **4ua** is in accordance with the literature.[5]



^{1}H NMR (400 MHz, Chloroform-d) δ 10.05 (s, 1H), 8.98 (dd, J = 7.4, 1.2 Hz, 1H), 8.72 (dd, J = 4.1, 1.5 Hz, 1H), 8.15 (dd, J = 8.2, 1.4 Hz, 1H), 7.57 – 7.50 (m, 4H), 8.98 (dd, J = 7.4, 1.2 Hz, 1H), 7.32 (m, 1H), 0.86 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.56, 147.92, 143.52, 138.48, 136.05, 134.85, 132.35, 128.69, 127.68, 127.20, 121.43, 121.38, 121.29, 117.05, 103.01, 95.84, 18.32, 11.04.

***N*-(Quinolin-8-yl)-2-((triisopropylsilyl)ethynyl)benzamide (3ua):**

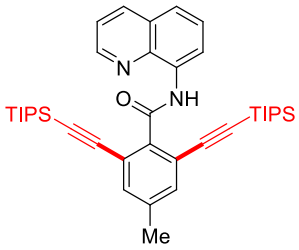


^{1}H NMR (400 MHz, Chloroform-d) δ 10.49 (s, 1H), 8.92 (dd, J = 7.5, 1.3 Hz, 1H), 8.76 (dd, J = 4.2, 1.7 Hz, 1H), 7.82 – 7.78 (m, 1H), 7.64-7.61 (m, 1H), 7.59 – 7.53 (m, 2H), 7.47 – 7.41 (m, 3H), 0.82 (s, 21H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.41, 148.22, 139.21, 138.87, 136.17, 134.64, 133.88, 130.09, 128.66, 127.88, 127.77, 127.33, 121.82, 121.43, 120.71, 117.10, 103.83, 97.12, 18.21, 11.02.

HRMS: $[M+H]^+$ calculated for $C_{27}H_{33}N_2OSi$ is 429.2362, found 429.2362.

4-Methyl-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4va): Compound **4va** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 52% yield (48.6 mg) as colourless oil. The NMR data of **4va** is in accordance with the literature.[4]

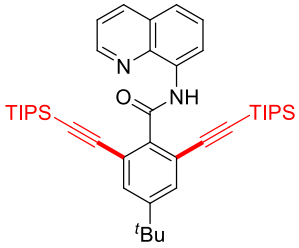


^{1}H NMR (400 MHz, Chloroform-d) δ 10.03 (s, 1H), 8.97 (dd, J = 7.4, 1.4 Hz, 1H), 8.71 (dd, J = 4.1, 1.5 Hz, 1H), 8.14 (dd, J = 8.3, 1.5 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.40 (dd, J = 8.3, 4.2 Hz, 1H), 7.33 (s, 2H), 2.35 (s, 3H), 0.86 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.70, 147.88, 140.99, 138.76, 138.48, 136.01, 134.93, 132.97, 127.67, 127.21, 121.31, 121.25, 121.23, 116.95, 103.25, 95.24, 20.83, 18.33, 11.05.

HRMS: $[M+H]^+$ calculated for $C_{39}H_{55}N_2OSi_2$ is 623.3853, found 623.3851.

4-*Tert*-butyl-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4wa): Compound **4wa** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 55% yield (54.9 mg) as colourless oil.

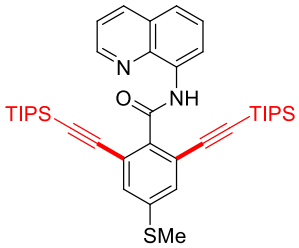


^{1}H NMR (400 MHz, Chloroform-d) δ 10.03 (s, 1H), 8.97 (dd, J = 7.4, 1.3 Hz, 1H), 8.71 (dd, J = 4.2, 1.6 Hz, 1H), 8.14 (dd, J = 8.3, 1.6 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.40 (dd, J = 8.2, 4.1 Hz, 1H), 1.35 (s, 9H), 0.86 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.81, 151.94, 147.87, 141.18, 138.47, 136.02, 134.93, 129.54, 127.66, 127.19, 121.32, 121.25, 120.97, 117.01, 103.60, 94.91, 34.68, 31.00, 18.35, 11.08.

HRMS: $[M+H]^+$ calculated for $C_{42}H_{61}N_2OSi_2$ is 665.4322, found 665.4323.

4-(Methylthio)-*N*-(quinolin-8-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4xa): Compound **4xa** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 47% yield (46.2 mg) as colourless oil.

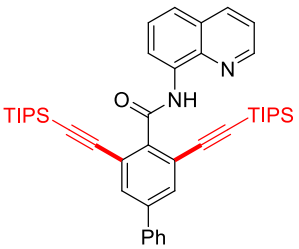


^{1}H NMR (400 MHz, Chloroform-d) δ 10.03 (s, 1H), 8.95 (dd, J = 7.3, 1.6 Hz, 1H), 8.72 (dd, J = 4.2, 1.7 Hz, 1H), 8.14 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.40 (dd, J = 8.1, 4.2 Hz, 1H), 7.34 (s, 2H), 2.52 (s, 3H), 0.85 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 166.22, 147.92, 140.20, 140.16, 138.46, 136.03, 134.84, 129.49, 127.67, 127.19, 121.87, 121.41, 121.29, 116.97, 102.68, 96.27, 18.32, 15.49, 11.04.

HRMS: $[M+H]^+$ calculated for $C_{39}H_{55}N_2OSSi_2$ is 655.3574, found 655.3572.

***N*-(Quinolin-8-yl)-3,5-bis((triisopropylsilyl)ethynyl)biphenyl-4-carboxamide (4ya):** Compound **4ya** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 55% yield (56.5 mg) as white solid.

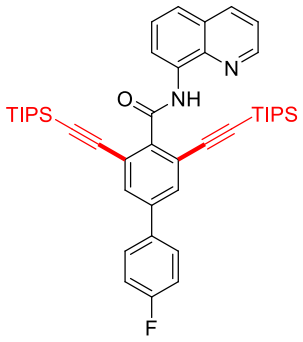


^{1}H NMR (400 MHz, Chloroform-d) δ 10.12 (s, 1H), 9.00 (dd, J = 7.35 Hz, 1H), 8.74 (d, J = 4.1 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.72 (m, 2H), 7.63 – 7.54 (m, 4H), 7.48 (t, J = 7.7 Hz, 2H), 7.43 – 7.39 (m, 2H), 0.88 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.49, 147.95, 142.16, 142.08, 139.09, 138.50, 136.06, 134.88, 131.06, 128.92, 128.17, 127.71, 127.22, 127.19, 121.89, 121.46, 121.31, 117.06, 103.09, 95.92, 18.35, 11.07.

HRMS: $[M+H]^+$ calculated for $C_{44}H_{57}N_2OSi_2$ is 685.4009, found 685.4007.

4'-Fluoro-*N*-(quinolin-8-yl)-3,5-bis((triisopropylsilyl)ethynyl)biphenyl-4-carboxamide (4za): Compound **4za** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 55% yield (61.2 mg) as white solid.



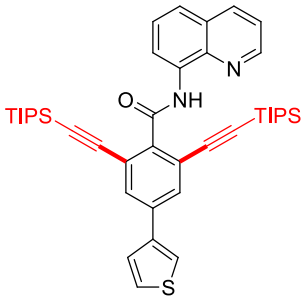
^{1}H NMR (400 MHz, Chloroform-d) δ 10.10 (s, 1H), 8.99 (dd, J = 7.3, 1.3 Hz, 1H), 8.73 (dd, J = 4.2, 1.7 Hz, 1H), 8.16 (dd, J = 8.2, 1.6 Hz, 1H), 7.66 (s, 2H), 7.60 – 7.51 (m, 4H), 7.42 (dd, J = 8.4, 4.2 Hz, 1H), 7.16 (t, J = 8.6 Hz, 2H), 0.87 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.40, 162.94 (d, $^1J_{C\text{-}F}$ = 248.0 Hz), 147.95, 142.19, 141.06, 136.08, 135.23, 135.20, 134.83, 130.84, 128.91, 128.83, 127.71, 127.22, 121.50, 121.32, 121.41 (d, J = 18.0 Hz), 117.08, 115.98, 115.77, 18.34, 11.06.

^{19}F NMR (377 MHz, Chloroform-d) δ = -113.99.

HRMS: $[M+H]^+$ calculated for $C_{44}H_{56}FN_2OSi_2$ is 703.3915, found 703.3913.

***N*-(Quinolin-8-yl)-4-(thiophen-3-yl)-2,6-bis((triisopropylsilyl)ethynyl)benzamide (4z'a):** Compound **4z'a** was prepared according to the general procedure **C** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 3:97) in 52% yield (53.9 mg) as colourless liquid.

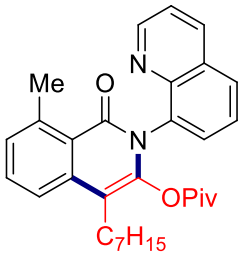


^{1}H NMR (400 MHz, Chloroform-d) δ 10.09(s, 1H), 8.98 (dd, J = 7.4, 1.4 Hz, 1H), 8.73 (dd, J = 4.2, 1.4 Hz, 1H), 8.15 (dd, J = 8.2, 1.5 Hz, 1H), 7.71 (s, 2H), 7.58 – 7.51 (m, 3H), 7.44 – 7.40 (m, 3H), 0.87 (s, 42H).

^{13}C NMR (100 MHz, Chloroform-d) δ 165.42, 147.94, 141.98, 140.10, 138.48, 136.59, 136.06, 134.85, 130.21, 127.69, 127.21, 126.70, 126.19, 121.94, 121.85, 121.45, 121.31, 117.04, 103.00, 95.99, 18.35, 11.06.

HRMS: $[M+H]^+$ calculated for $C_{42}H_{55}N_2OSSi_2$ is 691.3574, found 691.3574.

4-Heptyl-8-methyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5ac): Compound **5ac** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 15:85) in 67% yield (48.7 mg) as white solid.

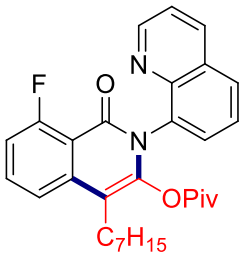


^{1}H NMR (500 MHz, Chloroform-d) δ 8.89 (dd, J = 3.8, 1.1 Hz, 1H), 8.20 (dd, J = 8.1, 1.0 Hz, 1H), 7.92 (d, J = 8.3 Hz, 1H), 7.71 (d, J = 6.7 Hz, 1H), 7.64-7.55 (m, 3H), 7.42 (dd, J = 8.2, 4.1 Hz, 1H), 7.24 (d, J = 7.1 Hz, 1H), 2.88 (s, 3H), 2.71 – 2.65 (m, 1H), 2.51 – 2.41 (m, 1H), 1.68 – 1.29 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H), 0.61 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.27, 163.14, 151.12, 144.77, 143.15, 140.51, 138.64, 135.91, 134.41, 131.73, 130.91, 129.35, 129.11, 129.04, 126.05, 123.92, 121.66, 121.77, 105.38, 38.54, 31.86, 29.91, 29.15, 28.93, 26.01, 25.76, 24.31, 22.59, 14.06.

ESI-MS: $[M+H]^+$ calculated for $C_{31}H_{37}N_2O3$ is 485.2804, found 485.2790.

8-Fluoro-4-heptyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5bc): Compound **5bc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 17:83) in 73% yield (53.5 mg) as crystalline solid.



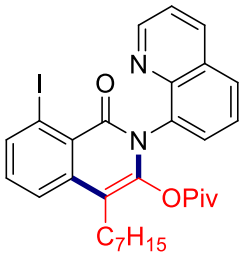
^{1}H NMR (500 MHz, Chloroform-d) δ 8.87 (dd, J = 4.1, 1.4 Hz, 1H), 8.20 (dd, J = 8.1, 1.2 Hz, 1H), 7.93 (dd, J = 8.2, 1.2 Hz, 1H), 7.70 (dd, J = 7.3, 1.1 HZ, 1H), 7.67 – 7.60 (m, 2H), 7.51 (d, J = 8.2 Hz, 1H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.10 (dd, J = 10.9, 8.1 Hz, 1H), 2.69 – 2.65 (m, 1H), 2.49 – 2.43 (m, 1H), 1.65 – 1.26 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H), 0.62 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.20, 163.4 (d, $^1J_{C\text{-}F}$ = 264.9 Hz), 159.90 (d, $^4J_{C\text{-}F}$ = 4.1 Hz), 151.08, 144.63, 141.70, 139.78, 135.89, 133.62, 133.36 (d, $^3J_{C\text{-}F}$ = 10.2 Hz), 130.90, 129.28, 129.03, 125.90, 121.67, 118.91 (d, $^4J_{C\text{-}F}$ = 3.78 Hz), 114.66 (d, $^4J_{C\text{-}F}$ = 4.3 Hz), 112.97 (d, $^2J_{C\text{-}F}$ = 21.7 Hz), 105.04, 38.58, 31.81, 29.82, 29.11, 28.89, 25.98, 25.78, 22.55, 14.02.

^{19}F NMR (376 MHz, Chloroform-d) δ – 111.55 .

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}FN_2O_3$ is 489.2553, found 489.2588.

4-Heptyl-8-iodo-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5ec): Compound **5ec** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 15:85) in 64% yield (57.3 mg) as brown solid.

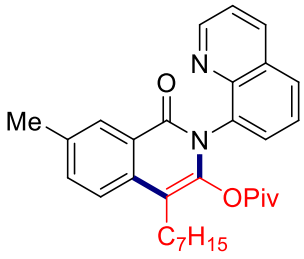


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, J = 4.1, 1.5 Hz, 1H), 8.20 – 8.17 (m, 2H), 7.92 (dd, J = 8.3, 1.2 Hz, 1H), 7.75 (d, J = 7.9 Hz, 1H), 7.64 – 7.58 (m, 1H), 7.42 (dd, J = 8.3, 4.2 Hz, 1H), 7.28 (t, J = 7.4 Hz, 1H), 2.67 – 2.65 (m, 1H), 2.49 – 2.42 (m, 1H), 1.64 – 1.26 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H), 0.61 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.19, 160.18, 151.09, 144.53, 141.06, 139.50, 135.87, 133.96, 132.67, 130.87, 129.22, 129.09, 126.05, 123.86, 123.77, 121.71, 105.47, 95.33, 38.59, 31.84, 29.82, 29.13, 28.89, 25.98, 25.61, 22.57, 14.05.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}IN_2O_3$ is 597.1614, found 597.1623.

4-Heptyl-7-methyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5hc): Compound **5hc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 15:85) in 64% yield (57.3 mg) as white solid.

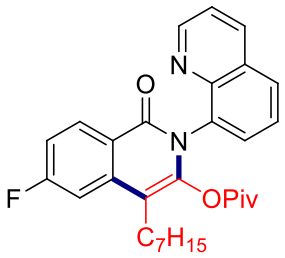


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, J = 4.1, 1.5 Hz, 1H), 8.28 (s, 1H), 8.19 (dd, J = 8.3, 1.4 Hz, 1H), 7.92 (dd, J = 8.2, 1.1 Hz, 1H), 7.70 (dd, J = 7.1, 1.1 Hz, 1H), 7.66 – 7.60 (m, 2H), 7.55 (dd, J = 8.3, 1.8 Hz, 1H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 2.72 – 2.64 (m, 1H), 2.51 – 2.46 (m, 4H), 1.68 – 1.26 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H), 0.61 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.51, 162.38, 151.09, 141.74, 139.97, 135.86, 134.65, 134.25, 134.14, 130.79, 129.17, 129.06, 128.60, 125.98, 125.33, 123.12, 121.68, 105.68, 97.76, 38.56, 31.85, 29.90, 29.17 (overlapped), 26.06, 25.46, 22.59, 21.22, 14.06.

ESI-MS: $[M+H]^+$ calculated for $C_{31}H_{37}N_2O_3$ is 485.28044, found 485.2819.

6-Fluoro-4-heptyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5pc): Compound **5pc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 15:85) in 70% yield (51.3 mg) as white solid.



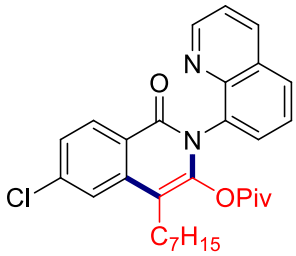
^{1}H NMR (500 MHz, Chloroform-d) δ 8.87 (dd, J = 4.1, 1.5 Hz, 1H), 8.49 (dd, J = 8.9, 6.1 Hz, 1H), 8.21 (dd, J = 8.2, 1.3 Hz, 1H), 7.94 (dd, J = 8.1, 1.0 Hz, 1H), 7.70 (dd, J = 7.3, 1.0 Hz, 1H), 7.63 (t, J = 7.8 Hz, 1H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.36 (dd, J = 10.5, 2.3 Hz, 1H), 7.18 (td, J = 8.5, 2.4 Hz, 1H), 2.66 – 2.60 (m, 1H), 2.47 – 2.41 (m, 1H), 1.62 – 1.25 (m, 10H), 0.88 (t, J = 6.8 Hz, 3H), 0.62 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.24, 166.86 (d, $^1J_{C\text{-}F}$ = 252.0 Hz), 161.66, 151.17, 144.56, 141.88, 139.67 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 135.92, 133.76, 132.12 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 130.72, 129.37, 129.05, 125.95, 121.94, 121.73, 114.36 (d, $^2J_{C\text{-}F}$ = 23.4 Hz), 108.65 (d, $^2J_{C\text{-}F}$ = 23.0 Hz), 105.48, 38.59, 31.81, 29.81, 29.11, 28.90, 25.99, 25.54, 22.56, 14.03.

^{19}F NMR (376 MHz, Chloroform-d) δ = – 108.04.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}FN_2O_3$ is 489.2553, found 489.2565.

6-Chloro-4-heptyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5qc): Compound **5qc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 20:80) in 66% yield (50.0 mg) as white solid.

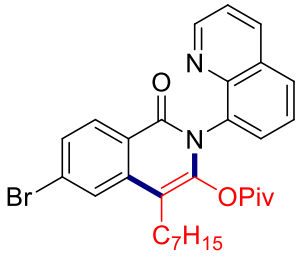


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, J = 4.1, 1.6 Hz, 1H), 8.41 (d, J = 8.5 Hz, 1H), 8.20 (dd, J = 8.3, 1.3 Hz, 1H), 7.93 (dd, J = 8.1, 1.1 Hz, 1H), 7.71 – 7.67 (m, 2H), 7.62 (t, J = 7.8 Hz, 1H), 7.42 (dd, J = 8.6, 1.3 Hz, 2H), 2.69 – 2.62 (m, 1H), 2.48-2.43 (m, 1H), 1.67 – 1.26 (m, 10H), 0.90 – 0.87 (m, 3H), 0.62 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.26, 161.85, 151.18, 166.47, 141.8, 139.46, 138.52, 135.91, 133.66, 130.73, 129.44, 129.06, 126.42, 125.99, 123.71, 122.75, 121.78, 115.63, 105.3, 38.61, 31.82, 29.80, 29.10, 28.97, 25.99, 25.35, 22.59, 14.00.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}ClN_2O_3$ is 505.2258, found 505.2259.

6-Bromo-4-heptyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5rc): Compound **5rc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 20:80) in 65% yield (53.4 mg) as white solid.

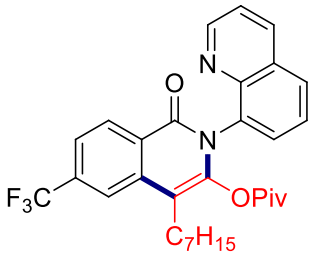


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, J = 4.0, 1.4 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.20 (dd, J = 8.3, 1.3 Hz, 1H), 7.94 (dd, J = 8.1, 1.1 Hz, 1H), 7.88(d, J = 1.6 Hz, 1H), 7.70 (dd, J = 7.2, 1.1 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.58 (dd, J = 8.6, 1.7 Hz, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 2.68 – 2.62 (m, 1H), 2.48 – 2.42 (m, 1H), 1.66 – 1.28 (m, 10H), 0.89 (t, J = 6.8 Hz, 3H), 0.62 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.26, 161.92, 151.2, 144.51, 141.83, 138.69, 135.92, 133.72, 130.75, 130.68, 129.42, 129.19, 129.06, 128.21, 125.98, 125.87, 124.10, 121.78, 105.08, 38.62, 31.82, 29.78, 29.10, 28.98, 26.01, 25.31, 22.59, 14.00.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}BrN_2O_3$ is 549.1753, found 549.1756.

4-Heptyl-1-oxo-2-(quinolin-8-yl)-6-(trifluoromethyl)-1,2-dihydroisoquinolin-3-yl pivalate (5sc): Compound **5sc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 75% yield (60.6 mg) as white solid.



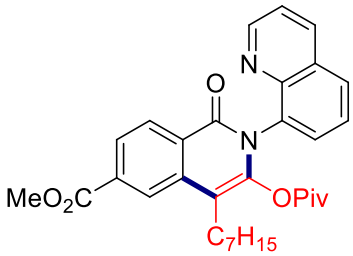
^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, J = 4.0, 1.4 Hz, 1H), 8.60 (d, J = 8.3 Hz, 1H), 8.22 (dd, J = 8.3, 1.1 Hz, 1H), 7.99 (s, 1H), 7.96 (dd, J = 8.0, 1.1 Hz 1H), 7.71 – 7.67 (m, 2H), 7.64 (t, J = 7.8 Hz, 1H), 7.44 (dd, J = 8.3, 4.2 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.49 – 2.55 (m, 1H), 1.67 – 1.28 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H), 0.63 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.24, 161.63, 151.23, 144.42, 142.09, 137.28, 135.95, 134.31 (q, $^3J_{C-F}$ = 32.3 Hz), 133.60, 133.36, 129.82 (q, $^2J_{C-F}$ = 60.3 Hz), 29.28, 127.63, 125.98, 123.89 (q, $^1J_{C-F}$ = 273.4 Hz), 121.91, 121.84, 120.44, 120.42, 105.74, 38.64, 31.76, 29.68, 29.02 (overlapped), 26.00, 25.25, 22.56, 14.01.

^{19}F NMR (376 MHz, Chloroform-d) δ – 65.39.

ESI-MS: $[M+H]^+$ calculated for $C_{31}H_{34}F_2N_2O_3$ is 539.2522, found 539.2542.

Methyl 4-heptyl-1-oxo-3-(pivaloyloxy)-2-(quinolin-8-yl)-1,2-dihydroisoquinoline-6-carboxylate (5tc): Compound **5tc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 60% yield (47.6 mg) as white solid.

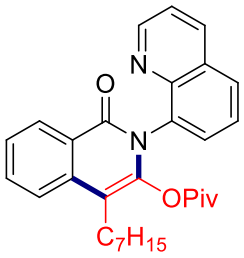


^{1}H NMR (500 MHz, Chloroform-d) δ 8.87 (dd, J = 4.0, 1.3 Hz, 1H), 8.53 (d, J = 8.3 Hz, 1H), 8.45 (s, 1H), 8.21 (dd, J = 8.5, 1.0 Hz, 1H), 8.07 (dd, J = 8.3, 1.1 Hz, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.71 (d, J = 6.6 Hz, 1H), 7.63 (t, J = 7.7 Hz, 1H), 7.43 (dd, J = 8.3, 4.2 Hz, 1H), 4.01 (s, 3H), 2.77 – 2.73 (m, 1H), 2.56 – 2.53 (m, 1H), 1.69 – 1.28 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H), 0.63 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.32, 166.70, 161.88, 151.21, 144.51, 141.44, 136.97, 135.95, 133.75, 133.61, 130.68, 129.44, 129.35, 129.08, 128.27, 126.00, 125.94, 125.16, 121.79, 106.09, 52.50, 38.61, 31.80, 29.75, 29.17, 29.09, 26.02, 25.31, 22.58, 14.05.

ESI-MS: $[M+H]^+$ calculated for $C_{32}H_{37}N_2O_5$ is 529.2702, found 529.2706.

4-Heptyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5uc): Compound **5uc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 20:80) in 75% yield (52.9 mg) as white solid.

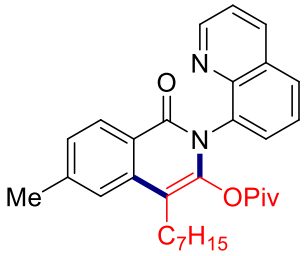


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (d, J = 3.6 Hz, 1H), 8.49 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.4 Hz, 1H), 7.93 (d, J = 8.1 Hz, 1H), 7.78 – 7.69 (m, 3H), 7.62 (t, J = 7.8 Hz, 1H), 7.48 (t, J = 7.3 Hz, 1H), 7.41 (dd, J = 8.3, 4.1 Hz, 1H), 2.71 (bs, 1H), 2.51 (bs, 1H), 1.69 – 1.26 (m, 10H), 0.88 (t, J = 6.7 Hz, 3H), 0.63 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.53, 162.54, 151.24, 144.81, 140.84, 137.17, 136.00, 134.20, 132.82, 130.92, 129.36, 129.18, 129.11, 126.09, 126.02, 125.54, 123.26, 121.79, 105.89, 38.70, 31.97, 30.02, 29.27, 26.16, 25.55, 22.71, 14.18.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{35}N_2O_3$ is 471.2648, found 471.2644.

4-Heptyl-6-methyl-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5vc): Compound **5vc** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 20:80) in 72% yield (52.3 mg) as white solid.

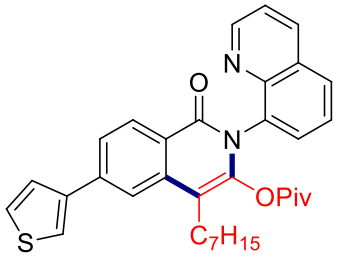


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, *J* = 4.0, 1.5 Hz, 1H), 8.37 (d, *J* = 8.1 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.92 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.71 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.52 (s, 1H), 7.41 (dd, J = 8.3, 4.2 Hz, 1H), 7.30 (d, J = 7.7 Hz, 1H), 2.70 – 2.66 (m, 1H), 2.54 (s, 3H), 2.51-2.15 (m, 1H), 1.70 – 1.26 (m, 10H), 0.88 (t, *J* = 6.8 Hz, 4H), 0.62 (s, 9H).

13C NMR (126 MHz, Chloroform-d) *δ* 175.39, 162.35, 151.08, 144.72, 143.20, 140.75, 137.13, 135.86, 134.12, 130.84, 129.16, 129.02, 128.95, 127.44, 125.96, 123.14, 122.98, 121.62, 105.56, 38.55, 31.84, 29.86, 29.13, 29.07, 26.03, 25.34, 22.59, 22.23, 14.06.

ESI-MS: $[M+H]^+$ calculated for $C_{31}H_{37}N_2O_3$ is 485.2804, found 485.2803.

4-Heptyl-1-oxo-2-(quinolin-8-yl)-6-(thiophen-3-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5z'c): Compound **5z'c** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 67% yield (55.5 mg) as white solid.

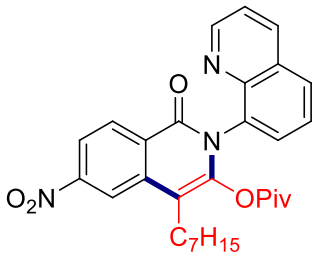


^{1}H NMR (500 MHz, Chloroform-d) δ 8.87 (dd, *J* = 4.1, 1.5 Hz, 1H), 8.50 (d, *J* = 8.2 Hz, 1H), 8.20 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.98 – 7.89 (m, 2H), 7.76 – 7.66 (m, 2H), 7.65 – 7.60 (m, 2H), 7.51 (dd, *J* = 5.1, 0.8 Hz, 1H), 7.46 (dd, *J* = 5.0, 2.9 Hz, 1H), 7.41 (dd, *J* = 8.2, 4.1 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.57 – 2.50 (m, 1H), 1.72 – 1.22 (m, 10H), 0.88 (t, *J* = 7.0 Hz, 5H), 0.63 (s, 9H).

13C NMR (126 MHz, Chloroform-d) *δ* 162.20, 151.14, 144.68, 141.84, 141.15, 139.90, 137.54, 135.89, 134.03, 130.82, 129.67, 129.26, 129.06, 126.69, 126.46, 125.99, 124.52, 124.13, 122.07, 121.69, 120.54, 105.77, 38.59, 31.84, 29.84, 29.12, 29.08, 26.04, 25.35, 22.61, 14.06.

HRMS: $[M+H]^+$ calculated for $C_{34}H_{37}N_2O_3S$ is 553.2525, found 553.2522.

4-Heptyl-6-nitro-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5z''c): Compound **5z''c** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 55% yield (42.5 mg) as white solid.

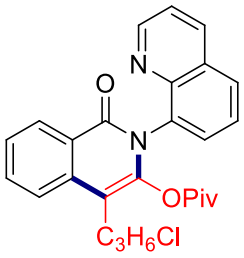


^{1}H NMR (500 MHz, Chloroform-d) *δ* 8.86 (dd, *J* = 4.1, 1.3 Hz, 1H), 8.61 (d, *J* = 8.8 Hz, 1H), 8.59 (d, *J* = 1.9 Hz, 1H), 8.24 – 8.21 (m, 2H), 7.97 (d, *J* = 7.3 Hz, 1H), 7.72 – 7.70 (m, 1H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 2.74 (bs, 1H), 2.54 (bs, 1H), 1.68 – 1.26 (m, 10H), 0.88 (t, *J* = 6.7 Hz, 3H), 0.64 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) *δ* 175.30, 161.36, 151.41, 150.77, 149.57, 144.34, 142.80, 138.12, 136.25, 133.38, 131.14, 129.86, 129.23, 126.17, 122.09, 119.69, 118.92, 115.89, 106.33, 38.81, 31.89, 29.83, 29.22, 29.19, 26.11, 25.51, 22.69, 14.16.

ESI-MS: $[M+H]^+$ calculated for $C_{30}H_{34}N_3O_5$ is 516.2498, found 516.2508.

4-(3-Chloropropyl)-1-oxo-2-(quinolin-8-yl)-1,2-dihydroisoquinolin-3-yl pivalate (5ud): Compound **5ud** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 67% yield (45.1 mg) as white solid.

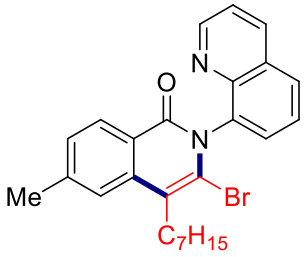


^{1}H NMR (500 MHz, Chloroform-d) δ 8.86 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.50 (d, *J* = 8.0 Hz, 1H), 8.20 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.76 – 7.70 (m, 3H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.42 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.67 (t, *J* = 5.9 Hz, 2H), 2.89 (bs, 1H), 2.79 – 2.65 (m, 1H), 2.21 – 2.06 (m, 3H), 0.62 (s, 9H).

^{13}C NMR (126 MHz, Chloroform-d) δ 175.47, 162.38, 151.15, 144.58, 141.28, 136.61, 135.91, 133.86, 132.94, 130.75, 129.33, 129.13, 129.08, 126.13, 125.98, 125.44, 122.84, 121.75, 104.04, 44.86, 38.62, 31.71, 26.03, 22.63.

ESI-MS: $[M+H]^+$ calculated for $C_{26}H_{26}ClN_2O_3$ is 449.1632, found 449.1629.

3-Bromo-4-heptyl-6-methyl-2-(quinolin-8-yl)isoquinolin-1(2H)-one (7): Compound **7** was prepared according to the general procedure **D** and the reaction mixture was purified by flash column chromatography (EtOAc: hexane = 30:70) in 53% yield (36.8 mg) as white solid.



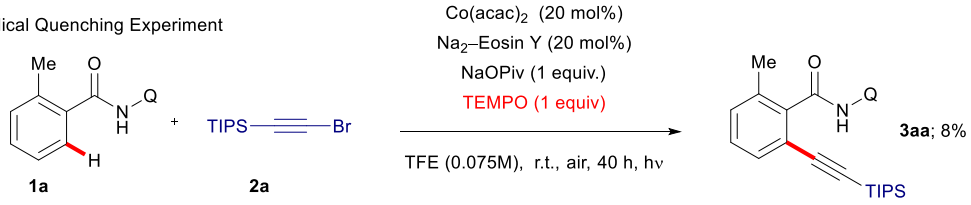
^{1}H NMR (500 MHz, Chloroform-d) *δ* 8.89 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.45 (d, *J* = 8.1 Hz, 1H), 8.22 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.92 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.81 (dd, *J* = 7.3 Hz, 1H), 7.65 (t, *J* = 7.8 Hz, 1H), 7.51 (s, 1H), 7.43 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 2.68 – 2.72 (m, 2H),2.55 (s, 3H), 1.70 – 1.66 (m, 2H), 1.45 – 1.27 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (126 MHz, Chloroform-d) *δ* 162.19, 151.06, 143.90, 142.62 (overlapped), 138.89, 137.44, 136.14, 130.78, 129.36, 128.99, 128.80 (overlapped), 128.00, 126.14, 124.38, 122.74, 121.65, 115.39, 31.78, 29.46, 29.36, 29.07 (overlapped), 22.58, 22.14, 14.03.

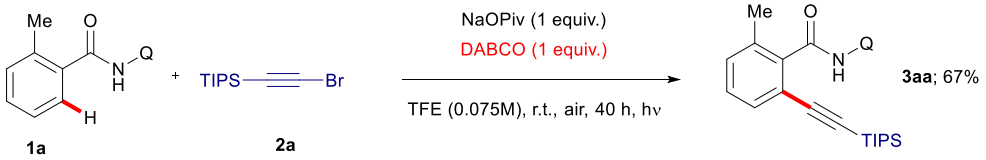
HRMS: $[M+H]^+$ calculated for $C_{26}H_{28}BrN_2O$ is 463.1385, found 463.1388.

7. Mechanistic Investigation

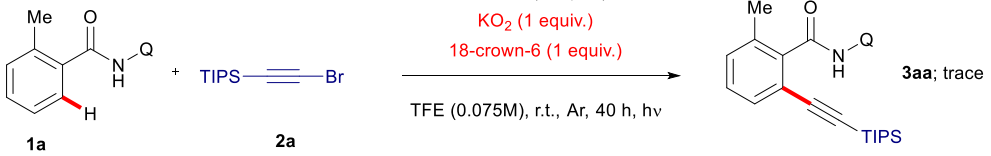
(a) Radical Quenching Experiment



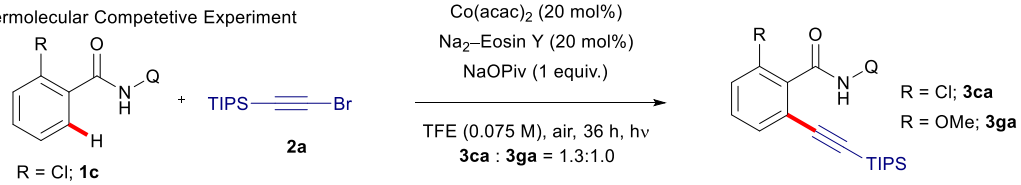
(b) DABCO Experiment



(c) Superoxide as Oxidant

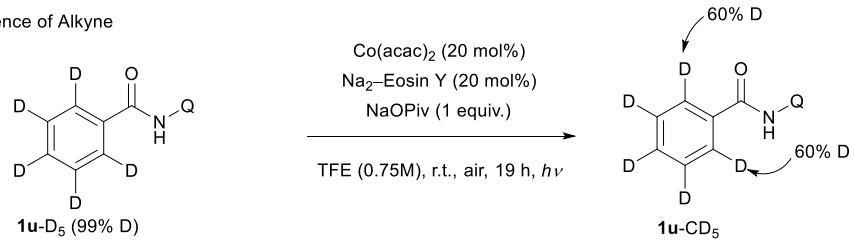


(d) Intermolecular Competetive Experiment

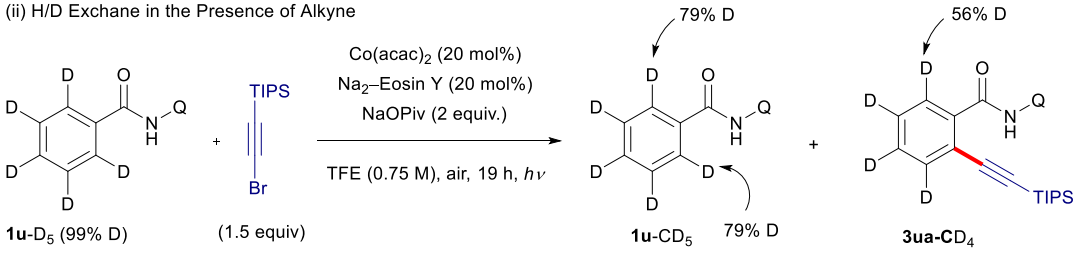


(e) Deuterium Labelling Experiments

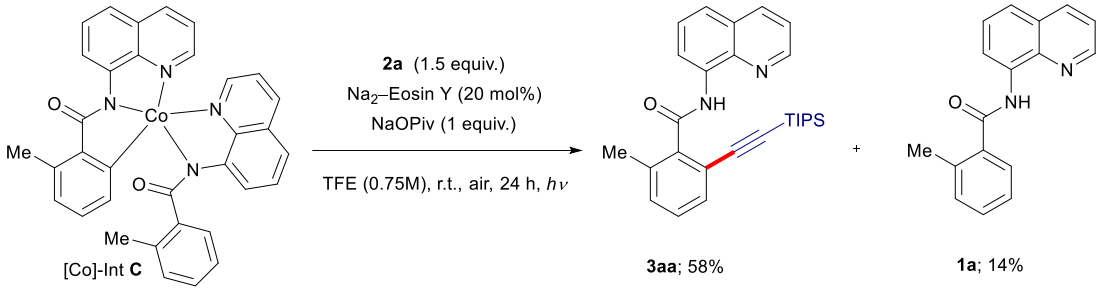
(i) In the Absence of Alkyne



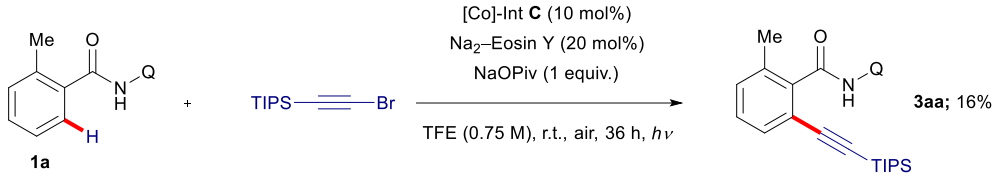
(ii) H/D Exchane in the Presence of Alkyne



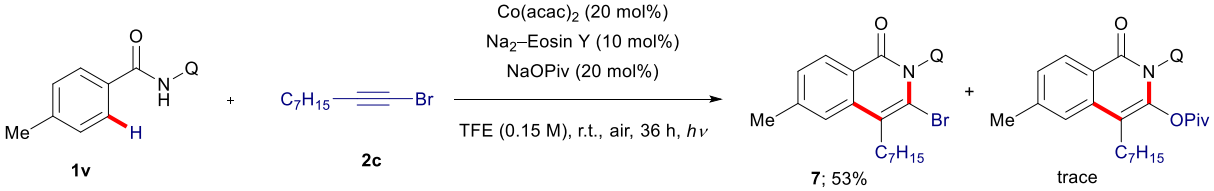
f) Stoichiometric Experiment



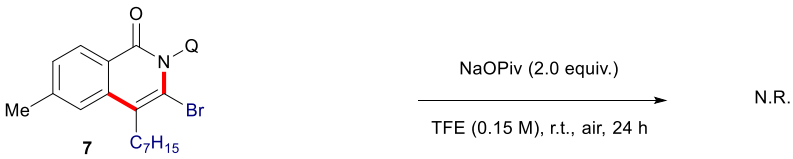
g) Catalytic Reaction with Cobalt Intermediate Complex as Catalyst



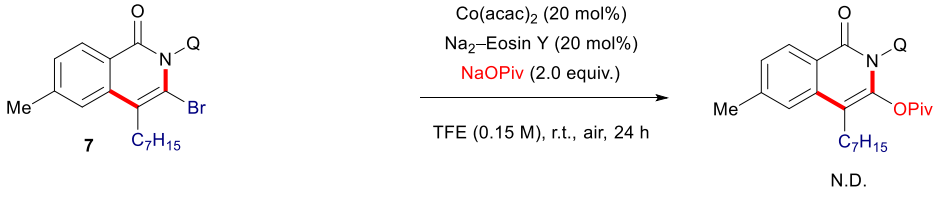
h) Control Experiments: (i) Annulation with **2c** with 20 mol% NaOPiv



(ii) Reaction of bromo annulated product **7** with stiochiometric amount of NaOPiv

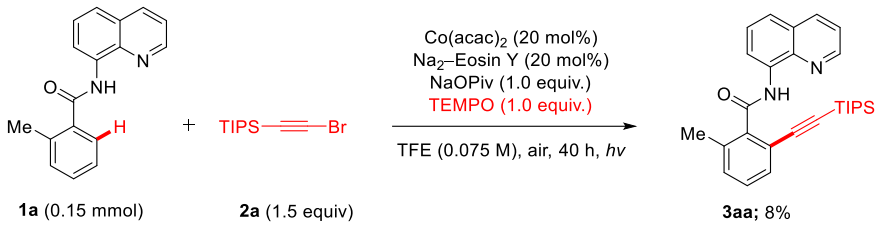


(iii) Reaction of bromo annulated product **7** under standard conditions



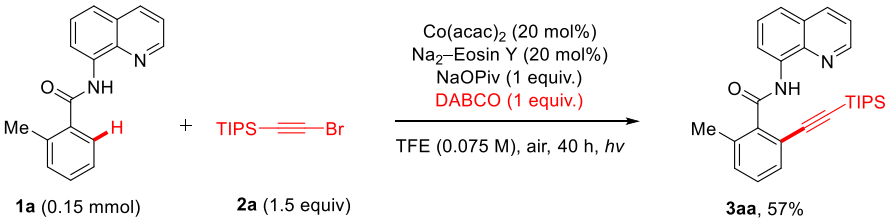
7. (a) Radical Quenching Experiment

An oven dried schlenk tube was charged with magnetic stirr bar, benzamide (39.3 mg, 0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol%), sodium pivalate (18.6 mg, 0.15 mmol, 1.0 equiv.), Na_2-Eosin Y (20.7 mg, 0.03 mmol, 20 mol%), (bromoethynyl)triisopropylsilane (58.8 mg, 0.225 mmol, 1.5 equiv.) and TEMPO (2,2,6,6-Tetramethyl-piperidin-1-yl)oxyl (23.4 mg, 0.15 mmol, 1.0 equiv.). Subsequently, 2,2,2-trifluroethanol (2.0 mL) was introduced as solvent under air. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 40 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding alkynylated benzamide **3aa** in 8% yield. This suggests the involvement of single electron in the reaction pathway.



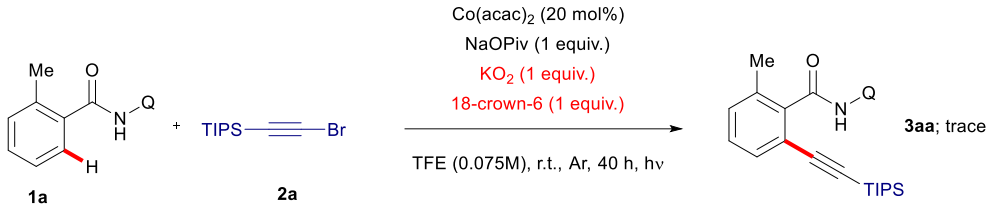
7. (b) DABCO Experiment

An oven dried schlenk tube was charged with magnetic stirr bar, benzamide (39.3 mg, 0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol%), sodium pivalate (18.6 mg, 0.15 mmol, 1.0 equiv.), Na_2-Eosin Y (20.7 mg, 0.03 mmol, 20 mol%), (bromoethynyl)triisopropylsilane (58.8 mg, 0.225 mmol, 1.5 equiv.) and DABCO (1,4-Diazabicyclo[2.2.2]octane) (16.8 mg, 0.15 mmol, 1.0 equiv.). Subsequently, 2,2,2-trifluroethanol (2.0 mL) was introduced as solvent under air. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 40 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding alkynylated benzamide **3aa** in 57% yield. This eliminates the possibility of singlet oxygen presence in the reaction.



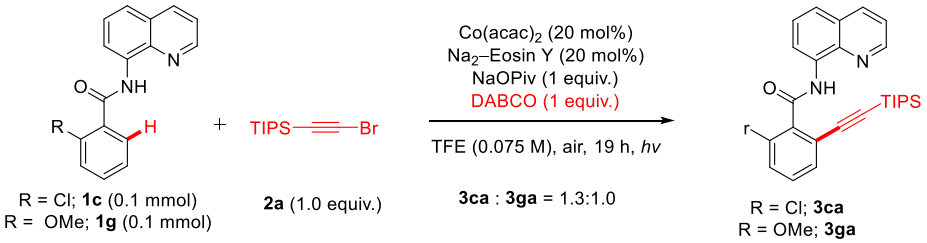
7. (c) Superoxide as an oxidant

An oven dried schlenk tube was charged with magnetic stirr bar, benzamide (39.3 mg, 0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol%), sodium pivalate (18.6 mg, 0.15 mmol, 1.0 equiv.), (bromoethynyl)triisopropylsilane (58.8 mg, 0.225 mmol, 1.5 equiv.), KO2 (11.0 mg, 0.15 mmol, 1.0 equiv.), and 18-crown-6 (39.6 mg, 0.15 mmol, 1.0 equiv.). Subsequently, degassed and dried 2,2,2-trifluroethanol (2.0 mL) using 4 Å M.S. was introduced as solvent under argon. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 40 hours. Thin Layer Chromatography analysis indicates the trace amount formation of *ortho* C-H alkynylated product. This possibly eliminates the involvement of superoxide generated *in-situ* in the oxidation of low valent Co(I) and Co(II).



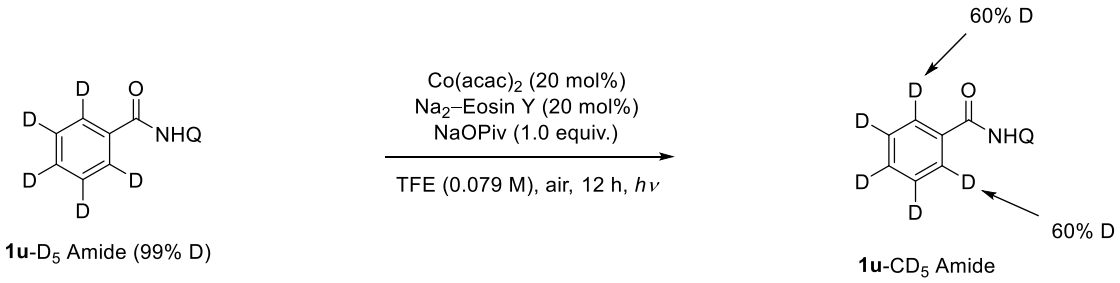
7. (d) Intermolecular Competitive Experiment

An oven dried schlenk tube was charged with magnetic stirr bar, 2-methoxy-*N*-(quinolin-8-yl)benzamide **1g** (27.8 mg, 0.1 mmol, 1.0 equiv.), 2-chloro-*N*-(quinolin-8-yl)benzamide (28.2 mg, 0.1 mmol, 1.0 equiv.) **1c** $Co(acac)_2$ (5.1 mg, 0.02 mmol, 20 mol%), sodium pivalate (12.4 mg, 0.1 mmol, 1.0 equiv.), Na_2-Eosin Y (13.8 mg, 0.02 mmol, 20 mol%) and (bromoethynyl)triisopropylsilane (26.1 mg, 0.1 mmol, 1.0 equiv.) Subsequently, 2,2,2-trifluroethanol (2.7 mL) was introduced as solvent under air. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 19 hours. Ratio of corresponding C-H alkynylated products (**3ca**:**3ga** = 1.3: 1.0) was obtained from the crude ^{1}H NMR analysis. The formation of alkynylated products with amide having electron-withdrawing substituents (**3ca**) in higher amount as compared with amide having electron donating substituents (**3ga**) suggests the C-H bond cleavage occurs *via* concerted metalation and deprotonation (CMD) pathway.



7. (e) Deuterium Labelling Experiments

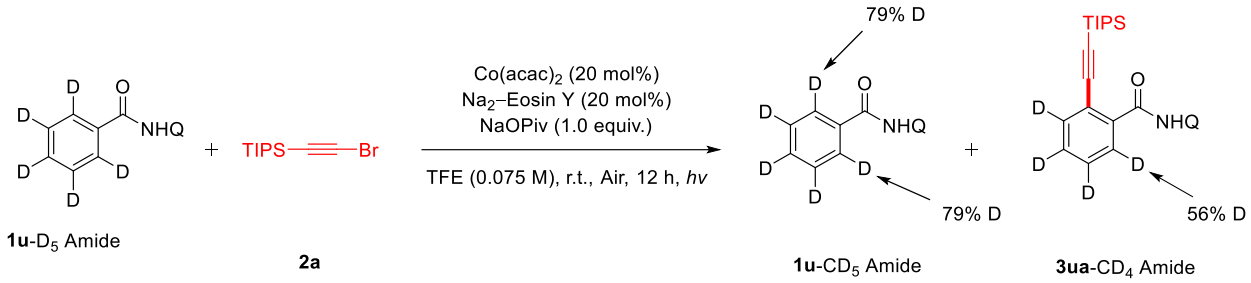
(i) In the Absence of Alkyne



An oven dried schlenk tube was charged with magnetic stirr bar, benzamide **1u**-D5 (20.0 mg, 0.079 mmol, 1.0 equiv.), $Co(acac)_2$ (4.0 mg, 0.0158 mmol, 20 mol%), sodium pivalate 9.7 mg, 0.079 mmol, 1.0 equiv.) and Na_2-Eosin Y (10.9 mg, 0.0158 mmol, 20 mol%). Subsequently, 2,2,2-trifluroethanol (1.0 mL) was introduced as solvent under air. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 12 hours.

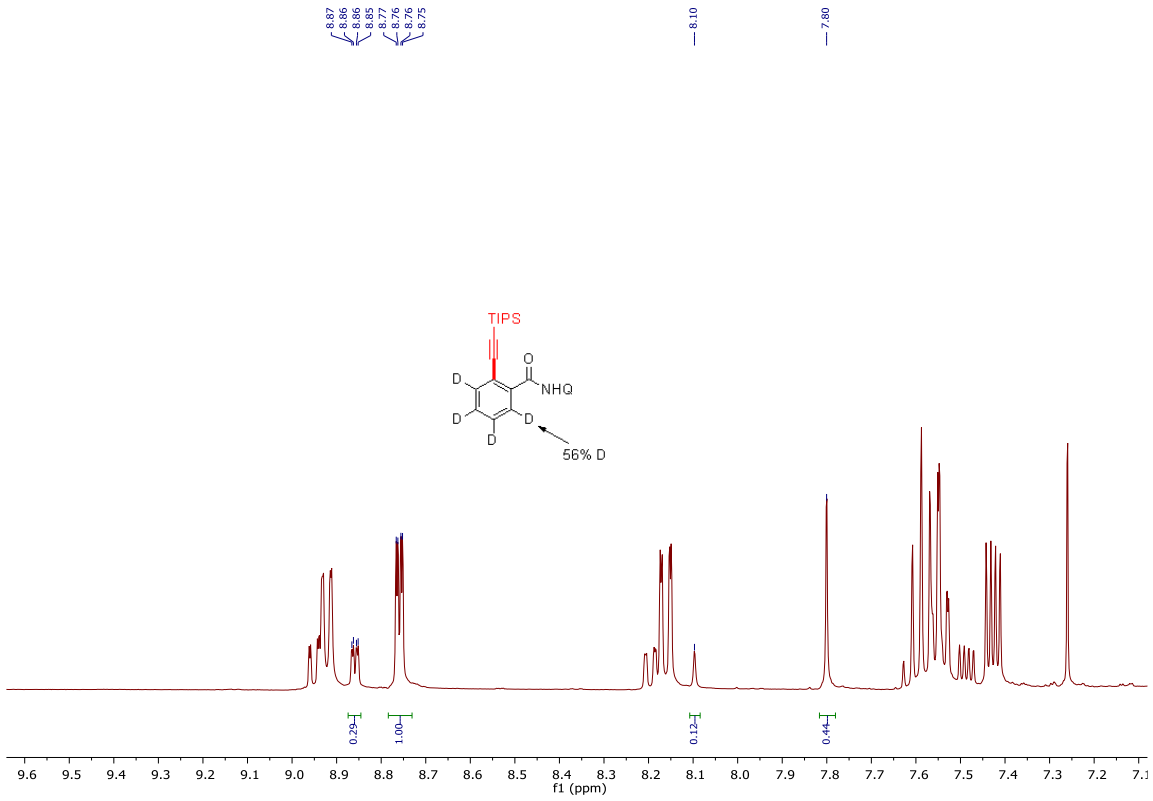
Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the **1u**-CD5. ^{1}H NMR analysis of the isolated compound revealed that 40% H incorporation occurs at the each *ortho*-position of the purified compound **1u**-CD5.

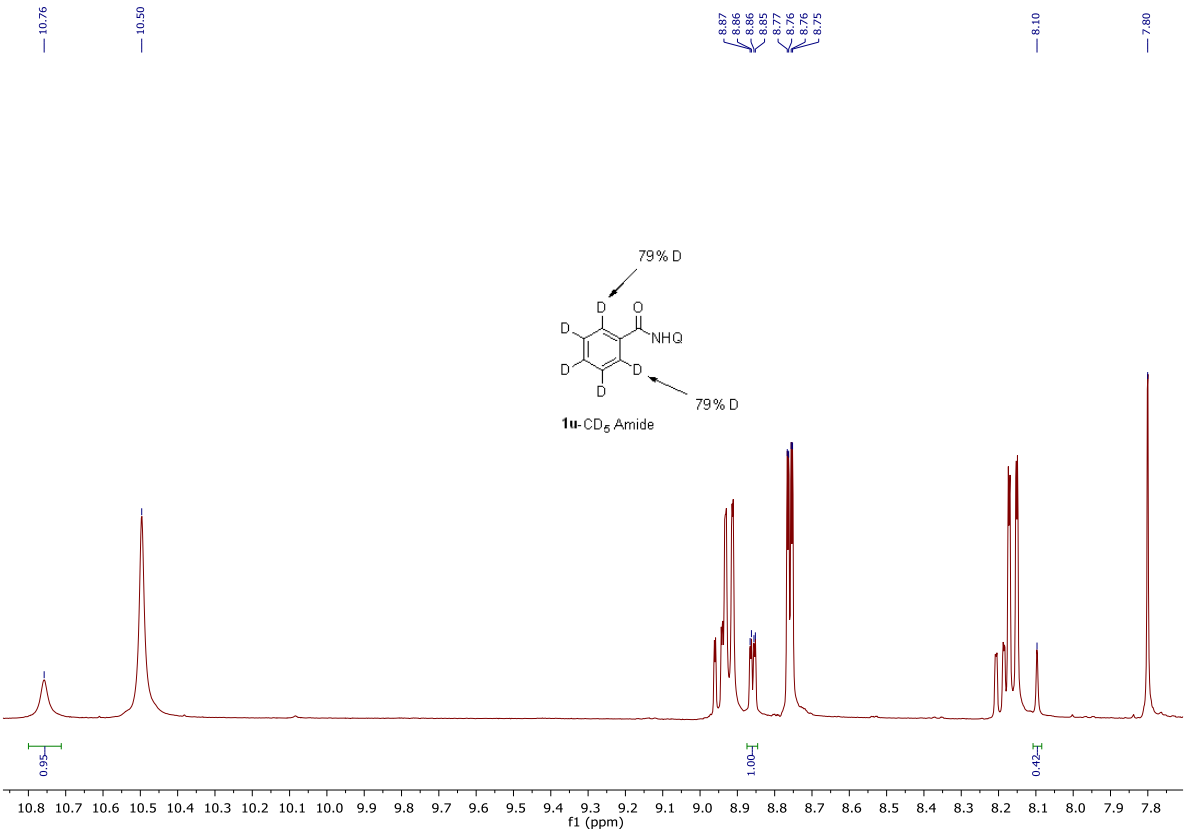
(ii) In the presence of alkyne



An oven dried schlenk tube was charged with magnetic stirr bar, benzamide **1u**-D5 (20.0 mg, 0.079 mmol, 1.0 equiv.), $Co(acac)_2$ (4.0 mg, 0.0158 mmol, 20 mol %), sodium pivalate (9.7 mg, 0.079 mmol, 1.0 equiv.), Na_2-Eosin Y (10.9 mg, 0.0158 mmol, 20 mol%) and (bromoethynyl)triisopropylsilane (58.5 mg, 0.3 mmol, 1.5 equiv.). Subsequently, 2,2,2-trifluroethanol (1 mL) was introduced as solvent under air. The Schlenk tube was closed and placed under visible light (7 W*4 LED bulbs) for 12 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding alkynylated benzamide **3ua**-CD4 and **1u**-CD5. ^{1}H NMR analysis of the isolated compounds revealed that 21% of H incorporation occurs at the each *ortho*-positions of the starting material **1u**-D_5 and 44% of H incorporation at the *ortho*-position of the product **3ua**-CD_4.

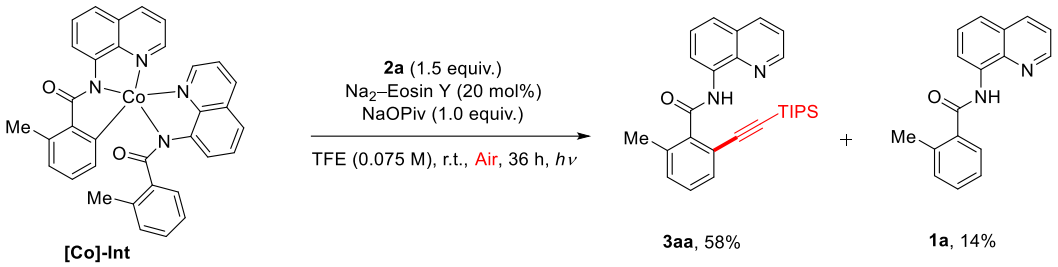
In both the deuterium scrambling experiments, substantial amount of hydrogen incorporation occurs at the *ortho*-position of the benzamide **1u**-D5 and mono C-H alkynylated benzamide **3ua**-CD4. This suggests the C-H metallation step is reversible in nature.


8.87
8.86
8.86
8.85
8.77
8.76
8.76
8.75
8.10
7.80
TIPS
O
NHQ
D
D
D
D
56% D
0.29
1.00
0.12
0.44
9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
f1 (ppm)


10.76
10.50
8.87
8.86
8.86
8.85
8.77
8.76
8.76
8.75
8.10
7.80
79% D
D
O
NHQ
D
D
D
D
D
79% D
1u-CD5 Amide
0.95
1.00
0.42
10.8 10.7 10.6 10.5 10.4 10.3 10.2 10.1 10.0 9.9 9.8 9.7 9.6 9.5 9.4 9.3 9.2 9.1 9.0 8.9 8.8 8.7 8.6 8.5 8.4 8.3 8.2 8.1 8.0 7.9 7.8
f1 (ppm)

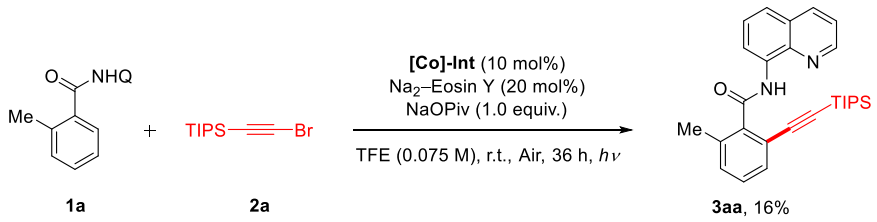
7. (f) Stoichiometric experiment with isolated cyclometallated intermeidate

An oven dried Schlenk tube was charged with a Teflon coated magnetic stir bar, Co-Int complex **C** (14.5 mg, 0.025 mmol, 1.0 equiv.), **2a** (9.8 mg, 0.0375 mmol, 1.5 equiv.), NaOPiv (3.1 mg, 0.025 mmol, 1.0 equiv.) and Na_2-Eosin Y (3.5 mg, 0.005 mmol, 20 mol%). Subsequently, 2,2,2-trifluoroethanol (0.35 mL) solvent was introduced under air. The closed Schlenk tube was kept under visible light (7 W*4 LED bulbs) for 36 hours. After completion of reaction, solvent was concentrated under reduced pressure followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded 58% of alkynylated product **3aa** and 14% of **1a**, which



7. (g) Catalytic reaction with cobalt intermediate complex as catalyst

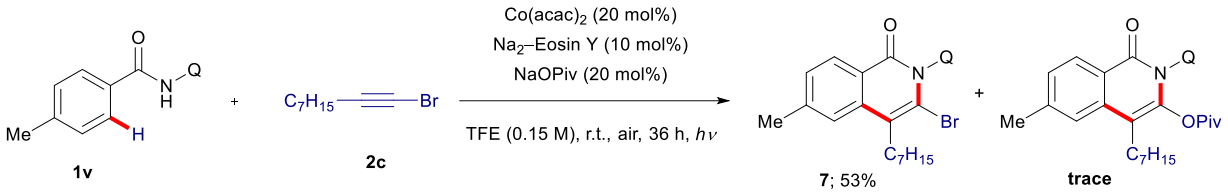
An oven dried Schlenk tube was charged with a Teflon coated magnetic stir bar, benzamide **1a** (26.2 mg, 0.10 mmol, 1.0 equiv.), [Co]-Int complex (5.8 mg, 0.01 mmol, 10 mol%), **2a** (39.2 mg, 0.15 mmol, 1.5 equiv.), NaOPiv (12.4 mg, 0.1 mmol, 1.0 equiv.) and Na_2-Eosin Y (13.8 mg, 0.02 mmol, 20 mol%). Subsequently, 2,2,2-trifluoroethanol (1.3 mL) solvent was introduced under air. The closed Schlenk tube was kept under visible light (7 W*4 LED bulbs) for 36 hours. After completion of reaction, solvent was concentrated under reduced pressure followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded 16% of alkynylated product **3aa**.



Additional stoichiometric and catalytic experiments with isolated cobaltacycle ascertain the involvement of octahedral cyclometallated species **C** in the catalytic cycle.

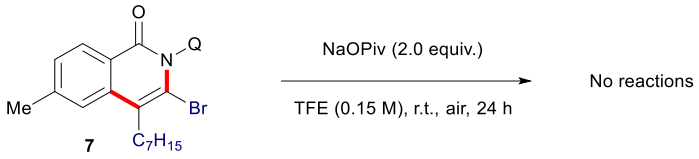
7. (h) Control Experiments (i): The annulation with 2c in presence of 20 mol% NaOPiv.

An oven dried Schlenk tube (13 cm x 2.3 cm) charged with magnetic stirr bar, benzamide **1v** (0.15 mmol, 1.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol %), sodium pivalate (3.7 mg, 0.03 mmol, 20 mol%), Na_2-Eosin Y (20.7 mg, 0.015 mmol, 10 mol%) and alkynyl bromide **2c** (0.225 mmol, 1.5 equiv.) under air. Subsequently, 2,2,2-trifluroethanol (1.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and placed under white LED bulbs (4 * 7 watts) at r.t. for 36 hours. Removal of solvent, followed by flash column chromatography (EtOAc/Hexane) on silica gel afforded the corresponding bromo-isoquinolone benzamide **7**.

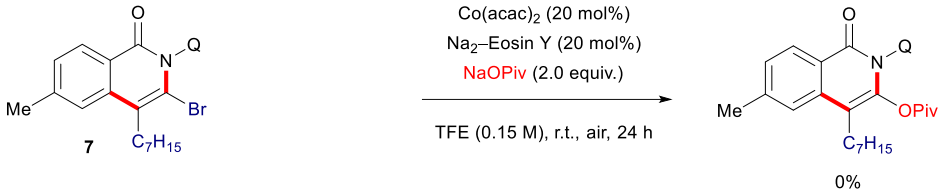


7. (h)(ii): ***Reaction of bromo-isoquinolone 7 in presence of stoichiometric sodium pivalate.***

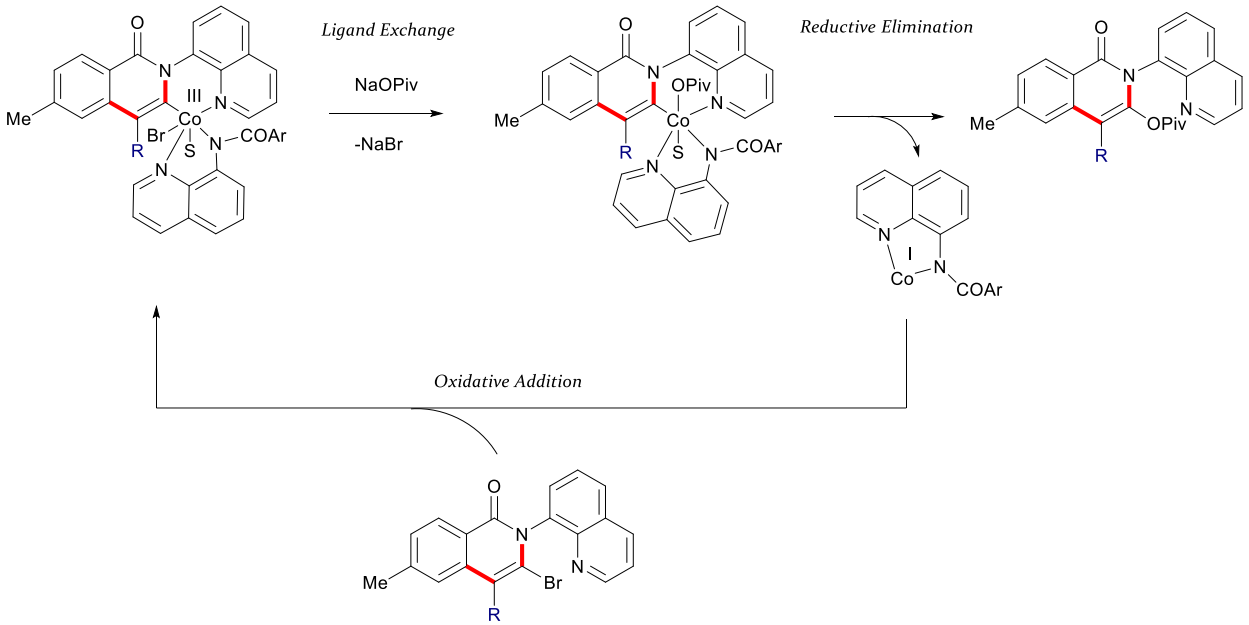
An oven dried Schlenk tube (13 cm x 2.3 cm) charged with magnetic stirr bar, bromo-isoquinolne **7** (0.15 mmol, 1.0 equiv.), sodium pivalate (0.37 mg, 0.3 mmol, 2.0 equiv.) in air. Subsequently, 2,2,2-trifluroethanol (1.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and stirred at r.t. for 36 hours. The crude ^{1}H NMR analysis indicated the bromide displacement did not occur with stoichiometric amount of NaOPiv suggesting that there is role cobalt in the bromide exchange with pivalate.



7. (h)(iii): The reaction of bromo-isoquinolone 7 under standard condition.



An oven dried Schlenk tube (13 cm x 2.3 cm) charged with magnetic stirr bar, bromo-isoquinolne **7** (0.15 mmol, 1.0 equiv.), sodium pivalate (37.2 mg, 0.3 mmol, 2.0 equiv.), $Co(acac)_2$ (7.7 mg, 0.03 mmol, 20 mol%), and Na_2-Eosin Y (21.0 mg, 0.03 mmol, 20 mol%) in air. Subsequently, 2,2,2-trifluroethanol (1.0 mL) was added in the Schlenk tube. The Schlenk tube was closed with screw cap and stirred at r.t. under exposure of light for 36 hours. The crude ^{1}H NMR analysis indicated the bromide displacement did not occur with stoichiometric amount of NaOPiv suggesting the involvement of low valent Co(I) in the displacement of bromide with pivalate. The probable reaction pathway shown below, might involve oxidative addition of liberated Co(I) after reductive elimination to the C-Br bond, followed by bromide exchange with pivalate and successive reductive elimination delivered the desired annulated product **5**.



Scheme 1. Plausible mechanism of bromide displacement by pivalate.

8. Crystallographic Summary

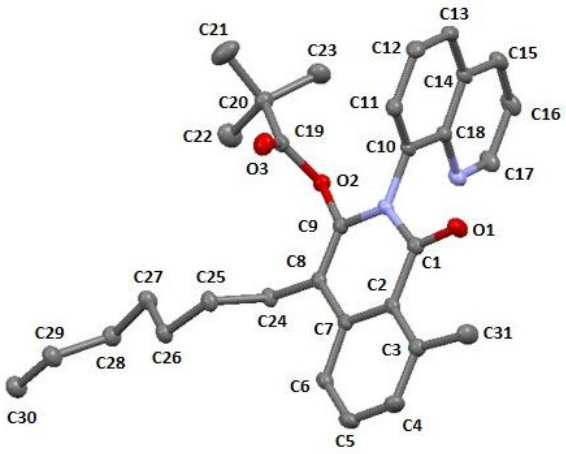
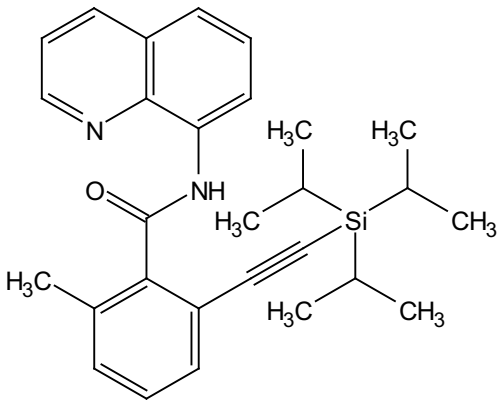


Figure S1: Structure of compound **5ac** in solid state. Hydrogen atoms are omitted for clarity.

X-ray Crystal Structure Analysis : $C_{31}H_{36}N_2O_3$, MW = 484.62 g.mol^{-1} , colourless, crystal size = 0.1 × 0.0.2 × 0.2 mm^3, triclinic, space group P-1, a = 8.2757 (6) Å, b = 12.3903(9) Å, c = 13.7007(10) Å , T = 273 K , Z = 2, D_{calc} = 1.218 g.cm^{-3} , λ = 0.71073 Å (Mo-Kα), CCD Bruker SMART APEX diffractometer, 2.581 < θ < 25.05, 27036 measured reflections, structures were solved by direct methods and refined (SHELXL-97) by full matrix least squares based on F^2. Atomic displacement ellipsoids are drawn at a 50% probability level. Slow evaporation method was used to grow both the crystals in DCM solvent. (CCDC No. of **5ac** is 2110289)

*


N
NH
O
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H_3C
H_3C
Si
CH_3
H_3C
H_3C
CH_3

3aa

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9.01
9.01
8.99
8.99
8.74
8.73
8.73
8.72
8.17
8.17
8.15
8.14
7.60
7.56
7.52
7.43
7.41
7.40
7.30
7.28
7.26
7.24
7.22
2.46
0.76
1.00
1.00
1.00
1.08
2.27
2.18
2.43
3.24
21.07
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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4.5
4.0
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2.0
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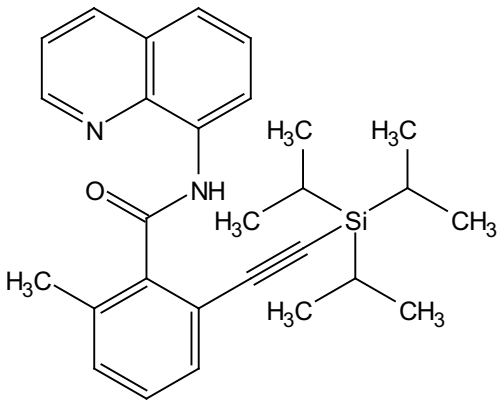
0.0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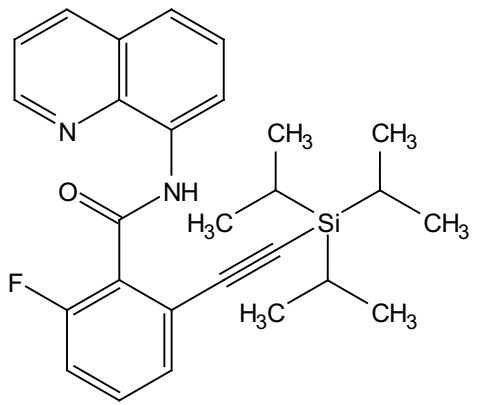
O
NH
H3C
H3C
H3C
Si
CH3
H3C
H3C
CH3

3aa

167.18
148.08
140.13
138.51
136.14
135.65
134.72
130.46
130.33
128.86
127.83
127.28
121.70
121.44
120.84
116.82
103.87
94.93
19.45
18.23
10.98
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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O
F
Si
CH3
CH3
H3C
CH3
H3C
CH3

3ba

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8.96
8.96
8.75
8.75
8.74
8.74
8.17
8.17
8.15
8.15
7.60
7.56
7.53
7.44
7.43
7.42
7.41
7.39
7.38
7.34
7.17
7.16
7.15
7.13
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1.03
1.09
1.12
2.39
1.17
2.25
1.11
21.26
11.5
11.0
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8.0
7.5
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6.0
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5.0
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2.0
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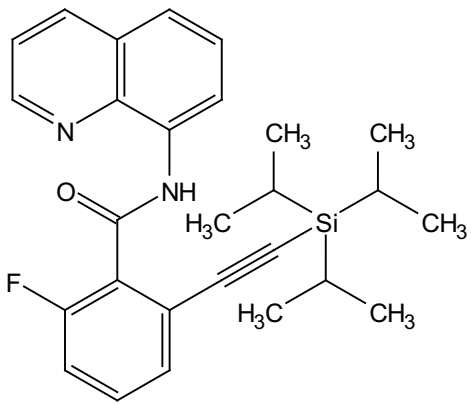
0.5
0.0
-0.5
f1 (ppm)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O
F
Si
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CH3
CH3
H3C
H3C

3ba

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138.41
136.20
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130.68
128.88
128.85
128.38
128.20
127.79
127.29
123.18
123.13
121.99
121.51
116.98
116.46
116.24
102.32
102.28
97.07
18.24
10.95
200
190
180
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50
40
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10
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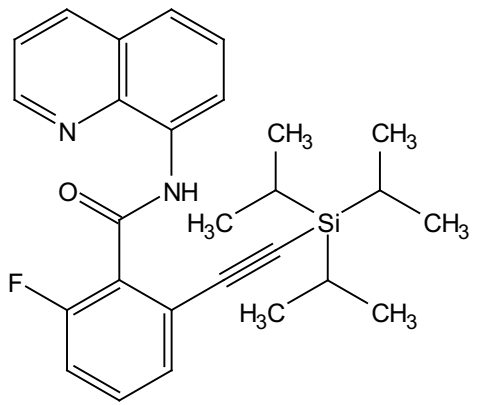
f1 (ppm)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Si
CH3
H3C
CH3

3ba

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-50
-70
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-170
-190
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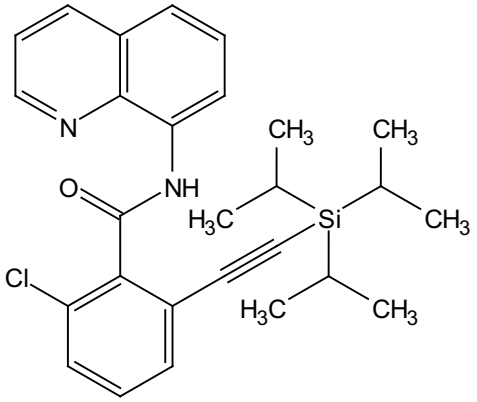
-290
-310
-330
-35
f1 (ppm)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Si
CH3
H3C
CH3

3ca

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8.15
7.60
7.58
7.56
7.54
7.49
7.47
7.47
7.44
7.43
7.42
7.41
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1.01
1.02
1.06
2.15
1.01
2.08
1.11
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11.0
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5.5
5.0
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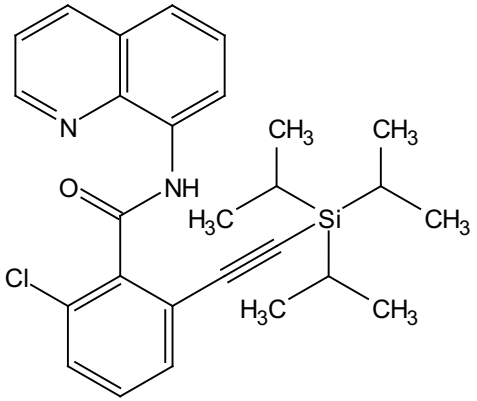
0.0
-0
f1 (ppm)


N
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Cl
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CH3
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Si
CH3
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CH3

3ca

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138.42
136.19
134.41
131.39
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129.92
129.68
127.80
127.27
123.00
121.98
121.51
117.07
102.38
96.92
18.22
10.94
200
190
180
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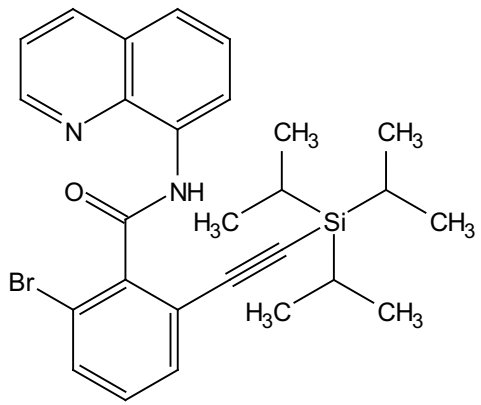
10
0
f1 (ppm)


N
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O
Br
Si
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CH3
H3C
H3C
CH3

3da

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8.75
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7.58
7.56
7.56
7.53
7.51
7.44
7.43
7.42
7.41
7.26
7.24
7.22
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1.00
0.99
1.10
3.00
1.27
1.33
1.13
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11.0
10.5
10.0
9.5
9.0
8.5
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5.0
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3.0
2.5
2.0
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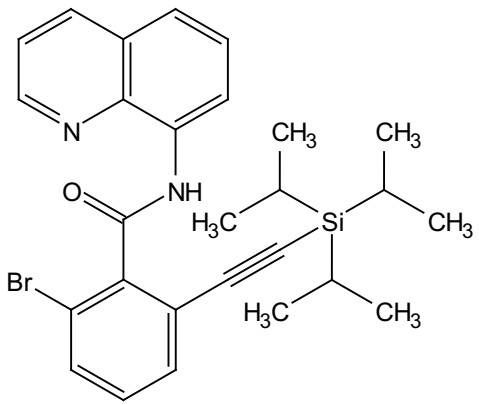
0.5
0.0
-0.5
f1 (ppm)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Br
Si
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CH3
CH3
H3C
H3C
CH3

3da

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136.18
134.39
132.76
131.64
130.05
127.79
127.25
123.02
121.98
121.50
119.76
117.08
102.42
96.95
18.21
10.93
00
190
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140
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80
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60
50
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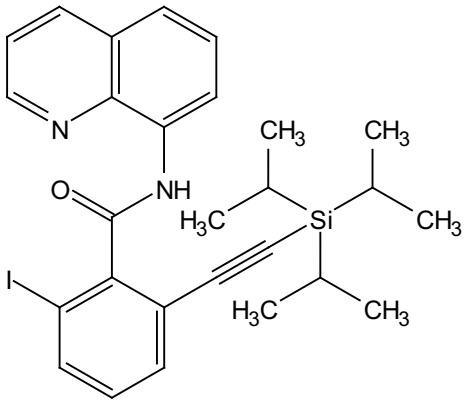
20
10
f1 (ppm)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Si
CH3
I
H3C
CH3

3ea

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7.45
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7.07
7.05
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1.10
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3.0
2.5
2.0
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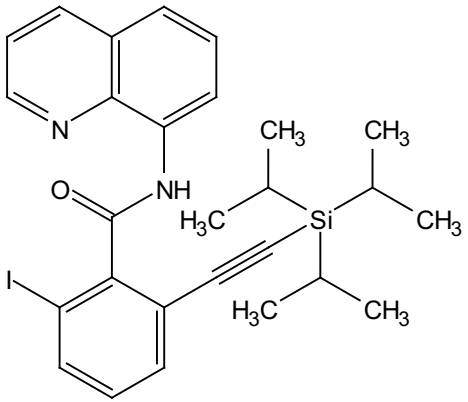
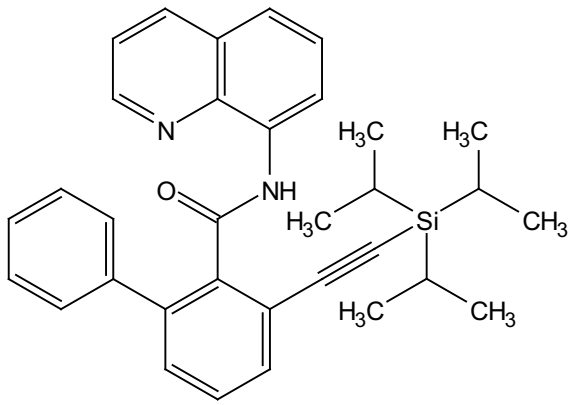
1.0
0.5
0.0
f1 (ppm)


N
NH
O
CH3
CH3
H3C
Si
CH3
I
H3C
CH3

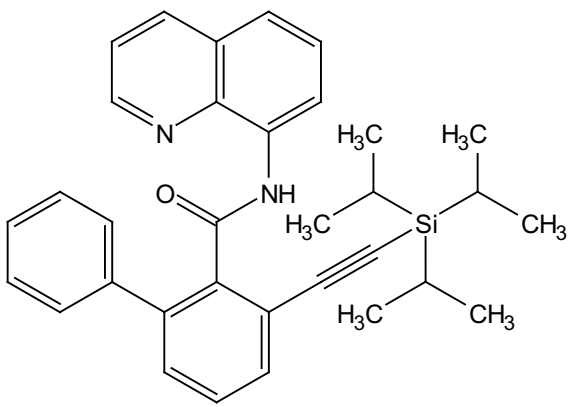
3ea

166.61
148.13
145.42
139.16
138.48
136.17
134.45
132.38
130.10
127.82
127.26
122.35
121.96
121.50
117.12
102.68
96.85
92.62
18.21
10.96
f1 (ppm)


N
O
NH
H3C
H3C
Si
CH3
H3C
CH3

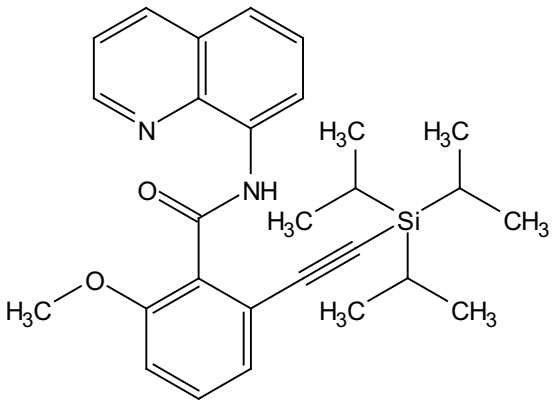
3fa

10.00
8.81
8.80
8.80
8.79
8.70
8.69
8.69
8.68
8.12
8.12
8.10
8.10
7.61
7.60
7.59
7.58
7.55
7.54
7.52
7.49
7.48
7.47
7.45
7.42
7.39
7.37
7.30
7.28
7.26
7.23
7.22
7.20
0.82
1.00
1.04
1.00
1.05
1.03
2.06
2.21
3.29
2.28
1.14
21.30
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


N
O
NH
H3C
H3C
H3C
Si
CH3
H3C
CH3

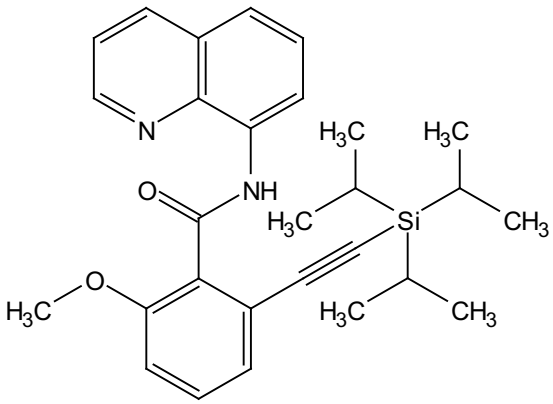
3fa

166.57
147.95
140.13
139.64
139.59
138.42
136.03
134.57
131.86
130.24
129.04
128.61
128.26
127.71
127.59
127.21
121.72
121.50
121.34
116.78
103.71
95.56
18.43
11.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
H3C
H3C
H3C
Si
CH3
O
H3C
H3C
CH3

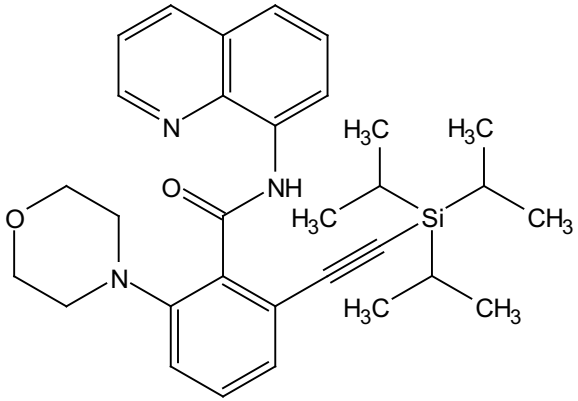
3ga

10.10
9.02
9.01
9.00
9.00
8.74
8.73
8.73
8.72
8.16
8.16
8.14
8.14
7.59
7.55
7.53
7.50
7.43
7.42
7.41
7.39
7.35
7.33
7.31
7.18
7.16
6.98
6.96
3.86
0.80
1.00
1.04
1.05
1.14
2.45
1.13
1.20
1.07
1.16
3.09
21.33
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


N
O
NH
H3C
H3C
H3C
Si
CH3
O
H3C
H3C
CH3

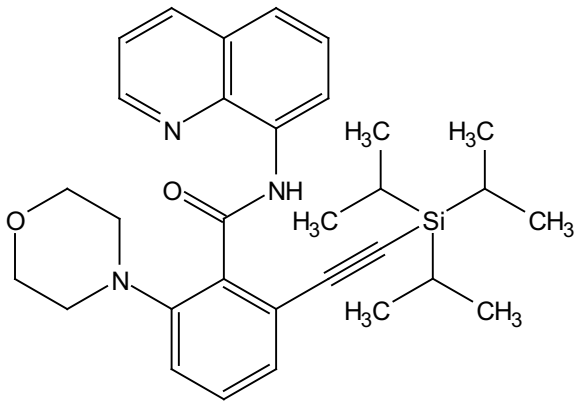
3ga

164.86
156.42
147.97
138.51
136.12
134.90
130.10
129.92
127.81
127.38
125.04
122.45
121.50
121.35
116.93
111.60
103.36
95.41
56.02
18.27
11.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
H3C
H3C
Si
CH3
O
N
H3C
CH3

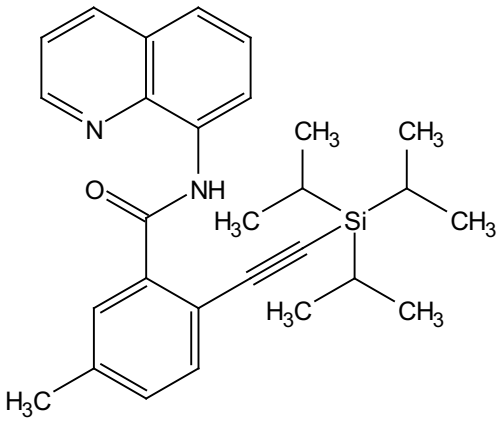
3ha

10.37
8.98
8.97
8.96
8.76
8.76
8.75
8.75
8.18
8.18
8.16
8.16
7.60
7.56
7.52
7.45
7.44
7.43
7.42
7.36
7.32
7.30
7.10
7.09
7.08
3.64
3.63
3.62
3.11
3.10
3.09
0.95
1.00
1.02
1.04
1.16
2.37
1.07
2.24
1.11
4.24
4.22
21.17
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
O
NH
O
N
H3C
H3C
Si
CH3
H3C
CH3

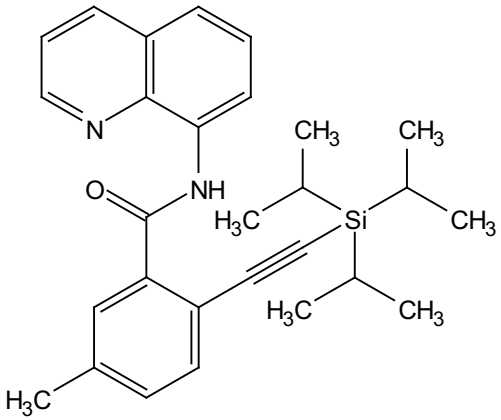
3ha

166.25
149.81
148.03
138.44
136.24
135.42
134.89
129.95
128.11
127.99
127.41
123.23
121.50
119.46
116.81
103.98
95.29
66.88
52.81
18.44
11.16
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
CH3
CH3
H3C
Si
CH3
H3C
CH3
H3C

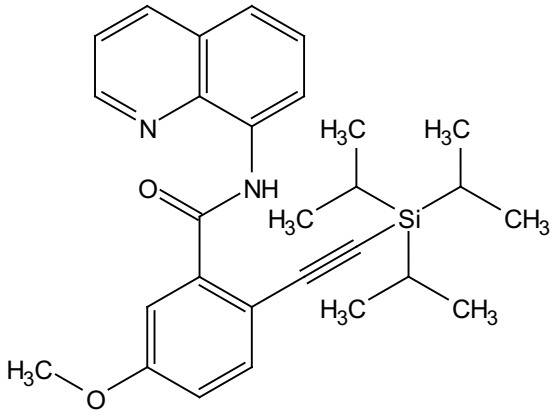
3ia

10.49
8.93
8.91
8.76
8.76
8.75
8.75
8.16
8.16
8.14
8.14
7.61
7.58
7.56
7.52
7.50
7.43
7.42
7.41
7.40
7.25
7.25
7.23
7.23
2.41
0.81
1.00
1.08
1.05
1.10
4.45
1.16
1.15
3.17
21.25
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


N
O
NH
CH3
CH3
H3C
Si
CH3
H3C
CH3
H3C

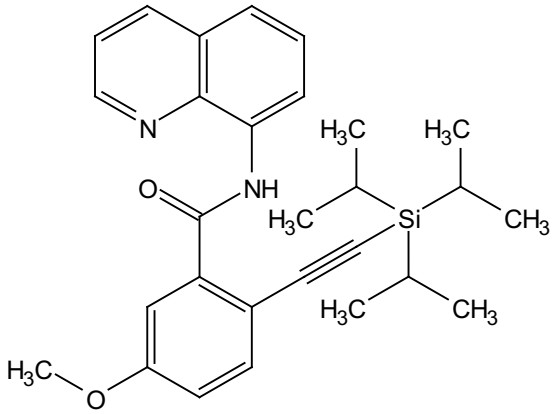
3ia

166.56
148.17
139.02
139.01
138.83
136.13
134.64
133.79
130.89
129.20
127.84
127.29
121.74
121.39
117.70
117.07
103.97
96.04
21.37
18.26
11.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NH
O
H3C
H3C
Si
H3C
CH3
H3C
CH3
H3C
O

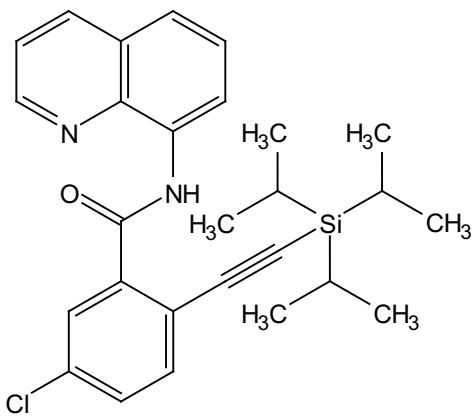
3ja

10.54
8.91
8.91
8.90
8.89
8.77
8.77
8.76
8.76
8.17
8.16
8.15
8.14
7.60
7.56
7.55
7.52
7.44
7.43
7.42
7.41
7.33
7.32
6.99
6.98
6.97
6.96
3.87
0.81
1.00
1.00
1.05
1.09
3.26
1.09
0.90
1.10
3.12
21.08
f1 (ppm)


N
NH
O
H3C
H3C
H3C
Si
CH3
H3C
CH3
H3C
O

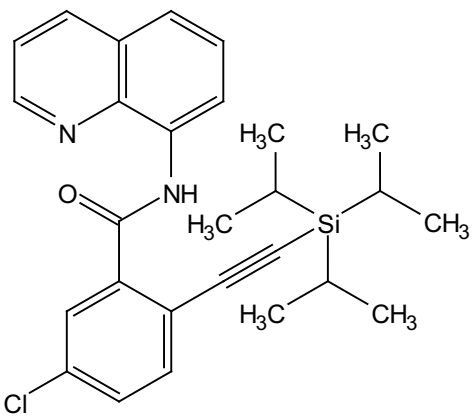
3ja

166.16
159.70
148.26
140.61
138.92
136.14
135.41
134.58
127.88
127.28
121.89
121.43
117.18
117.11
113.08
112.91
103.85
95.19
55.57
18.29
11.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NH
O
Si
H3C
CH3
Cl

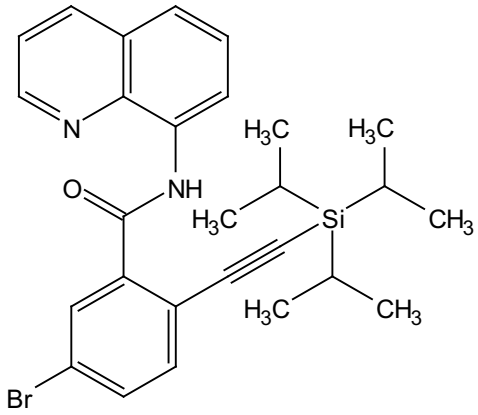
3ka

10.49
8.90
8.89
8.88
8.88
8.77
8.77
8.76
8.76
8.18
8.17
8.16
8.15
7.78
7.78
7.61
7.59
7.54
7.45
7.41
7.40
7.39
0.81
1.00
1.01
1.07
1.11
0.80
3.24
2.18
f1 (ppm)


N
NH
O
Si
Cl
H3C
CH3

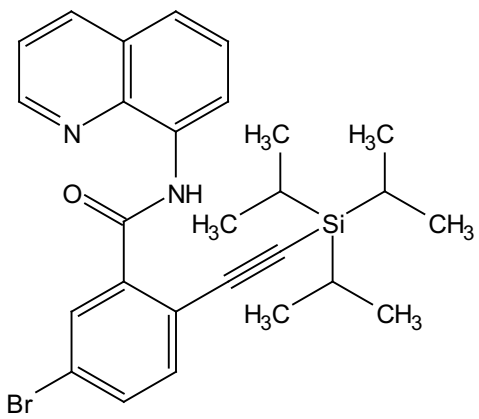
3ka

164.91
148.30
140.55
138.79
136.21
135.05
134.78
134.34
130.28
128.83
127.86
127.28
122.11
121.52
119.14
117.21
102.72
98.40
18.26
10.98
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
Br

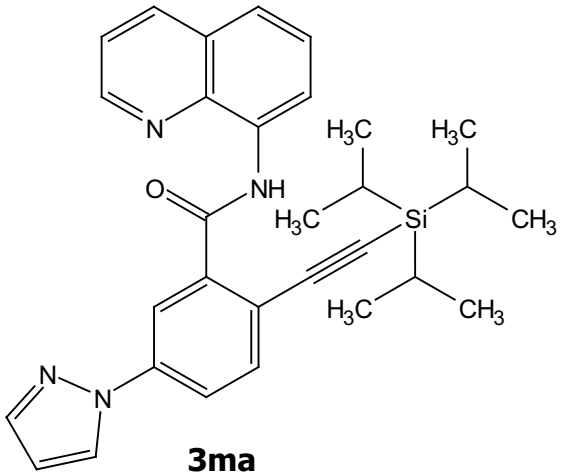
3la

10.48
8.90
8.89
8.88
8.87
8.77
8.77
8.76
8.76
8.18
8.17
8.16
8.15
7.93
7.93
7.61
7.58
7.58
7.56
7.54
7.48
7.46
7.43
7.42
0.81
1.00
0.98
1.04
1.10
0.83
3.30
2.30
21.27
f1 (ppm)


N
O
NH
H3C
H3C
Si
H3C
CH3
H3C
CH3
Br

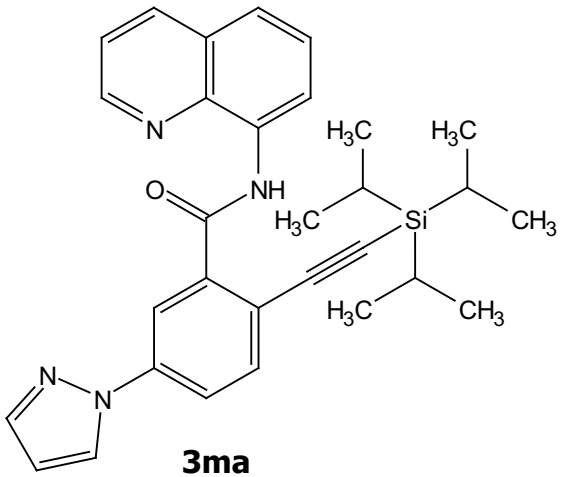
3la

164.79
148.30
140.65
138.77
136.21
135.13
134.33
133.19
131.69
127.85
127.28
122.83
122.11
121.52
119.57
117.20
102.78
98.62
18.25
10.97
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
H3C
H3C
H3C
Si
CH3
H3C
CH3
N
N

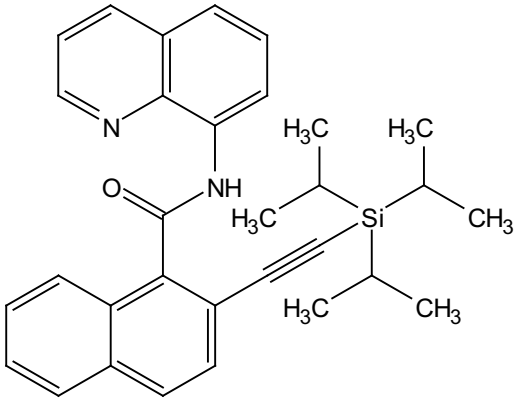
3ma

10.59
8.92
8.92
8.91
8.90
8.78
8.78
8.77
8.77
8.19
8.18
8.16
8.16
8.06
8.05
8.02
8.02
7.94
7.93
7.91
7.91
7.76
7.72
7.70
7.62
7.58
7.55
7.46
7.44
7.43
7.42
6.51
6.51
6.50
0.83
1.00
1.03
1.05
1.09
0.97
1.08
1.10
2.12
2.38
1.21
1.05
21.07
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


N
O
NH
H3C
H3C
H3C
Si
CH3
H3C
CH3
N
N

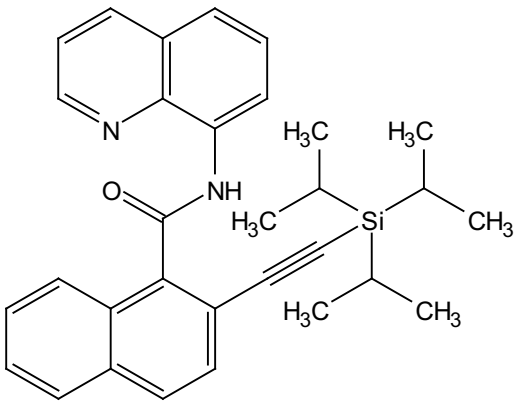
3ma

165.47
148.34
141.75
140.34
139.82
138.86
136.20
135.33
134.42
127.89
127.29
126.82
122.10
121.51
120.64
118.34
117.28
108.39
103.14
97.99
29.68
18.29
11.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NH
O
H3C
H3C
Si
CH3
H3C
CH3

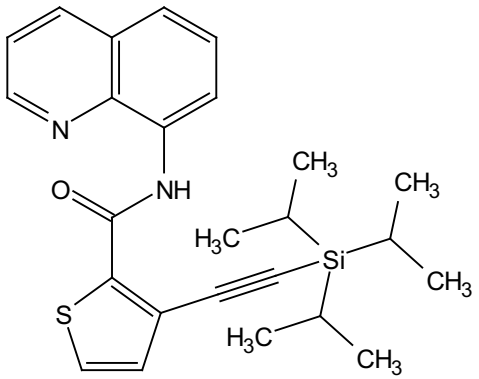
3na

10.33
9.14
9.12
8.70
8.69
8.69
8.68
8.18
8.16
8.14
8.12
7.88
7.87
7.86
7.85
7.65
7.63
7.61
7.58
7.56
7.53
7.52
7.42
7.41
7.40
7.39
0.81
1.00
1.04
1.02
2.18
2.25
2.93
2.48
1.13
21.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


N
O
NH
H3C
H3C
Si
CH3
H3C
CH3

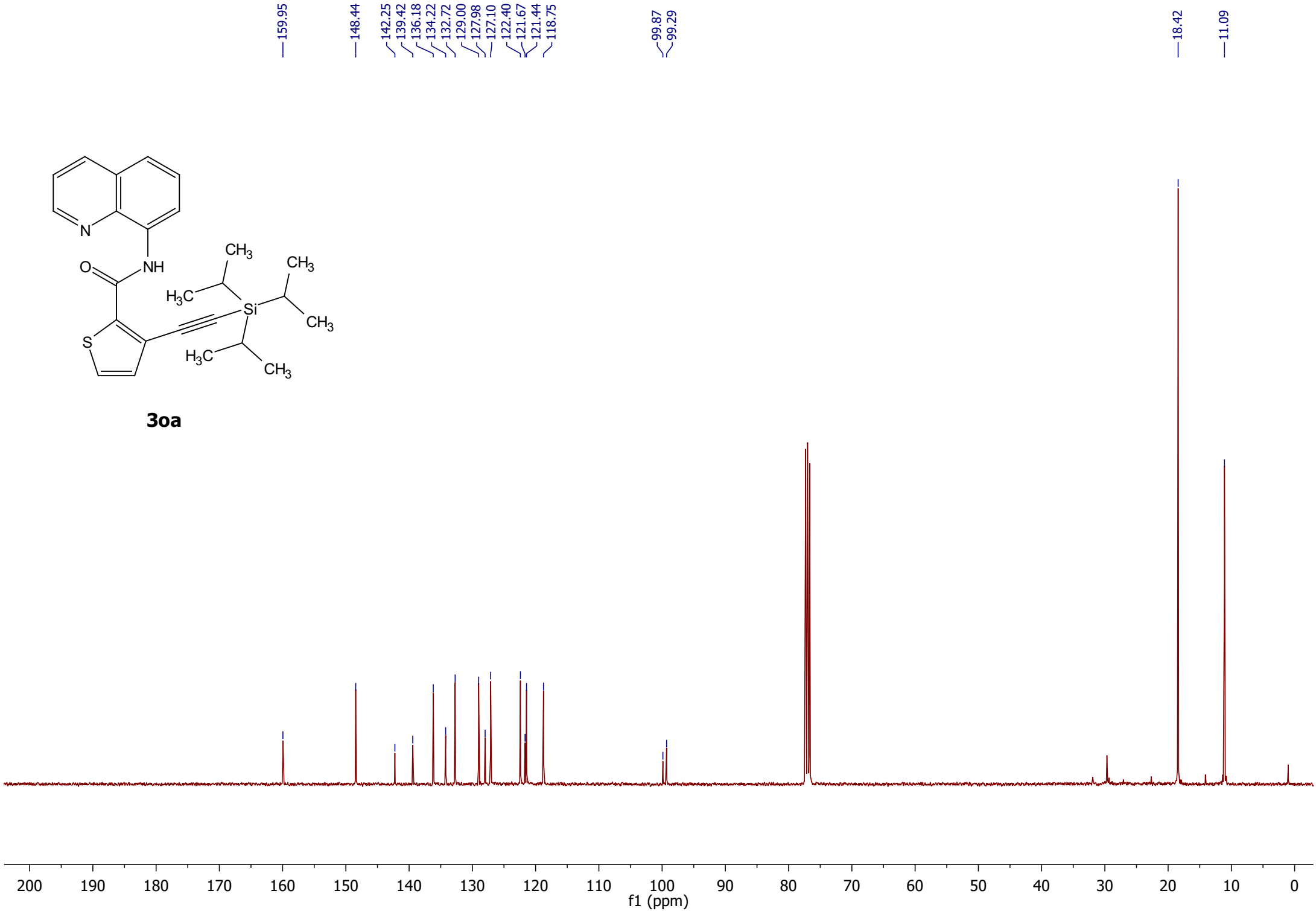
3na

166.63
148.10
138.57
138.49
136.13
134.81
132.87
129.92
129.26
128.76
128.00
127.84
127.54
127.31
127.04
125.59
121.86
121.47
118.44
116.92
104.17
96.64
18.26
11.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

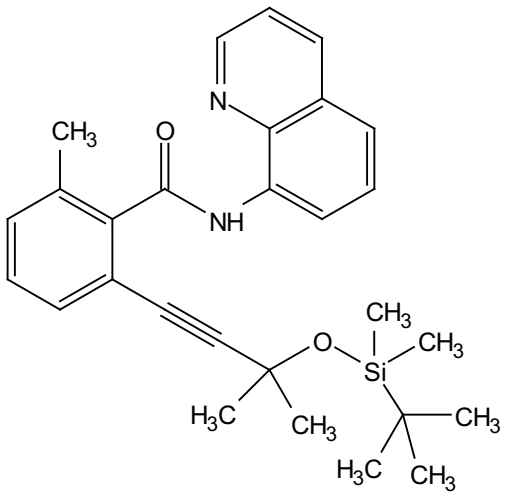

N
O
NH
CH3
H3C
Si
CH3
CH3
S
H3C
CH3

3oa

10.85
8.81
8.81
8.80
8.80
8.72
8.72
8.71
8.70
8.18
8.17
8.16
8.15
7.60
7.58
7.55
7.46
7.45
7.43
7.42
7.20
7.19
0.97
1.00
1.04
0.90
1.05
2.18
2.02
0.92
20.96
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

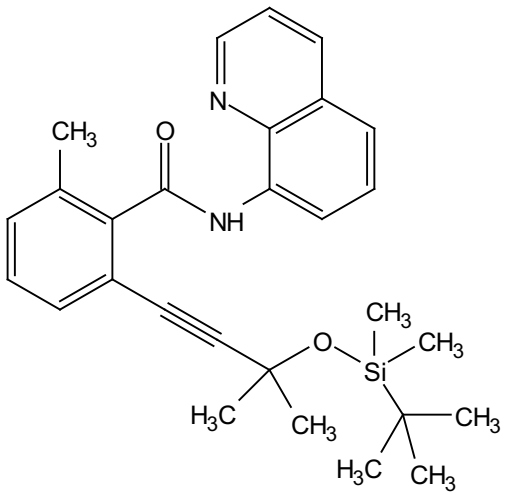

159.95
148.44
142.25
139.42
136.18
134.22
132.72
129.00
127.98
127.10
122.40
121.67
121.44
118.75
99.87
99.29
18.42
11.09
N
O
NH
S
Si
CH3
H3C
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3oa


CH3
O
N
NH
CH3
O
Si
CH3
CH3
H3C
CH3
CH3
H3C
CH3

3ab

10.07
9.01
9.01
8.99
8.99
8.76
8.76
8.76
8.75
8.19
8.18
8.17
8.17
7.62
7.60
7.59
7.56
7.56
7.54
7.54
7.45
7.45
7.44
7.43
7.35
7.34
7.31
7.29
7.28
7.24
7.23
2.47
1.05
0.76
0.05
1.00
0.98
0.99
1.02
1.05
1.08
1.06
0.99
1.12
1.12
3.34
6.41
9.25
6.03
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

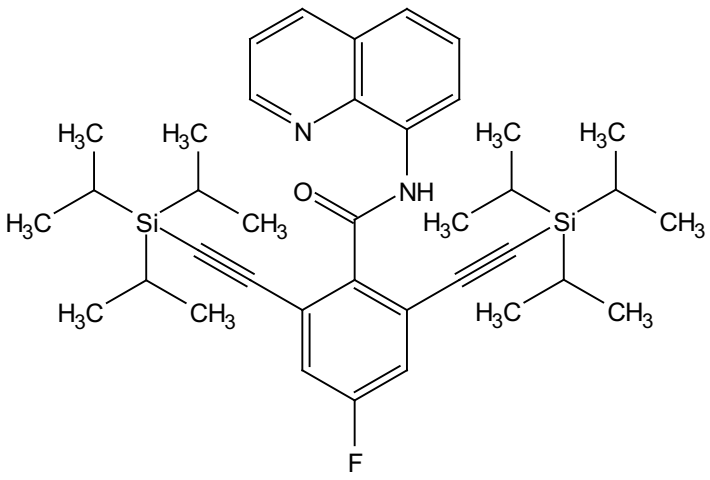


3ab

167.15
148.16
139.83
138.47
136.28
135.89
134.64
130.38
129.47
129.02
127.92
127.41
121.79
121.58
120.55
116.63
98.57
80.13
66.43
32.34
25.61
19.54
17.80
-3.14

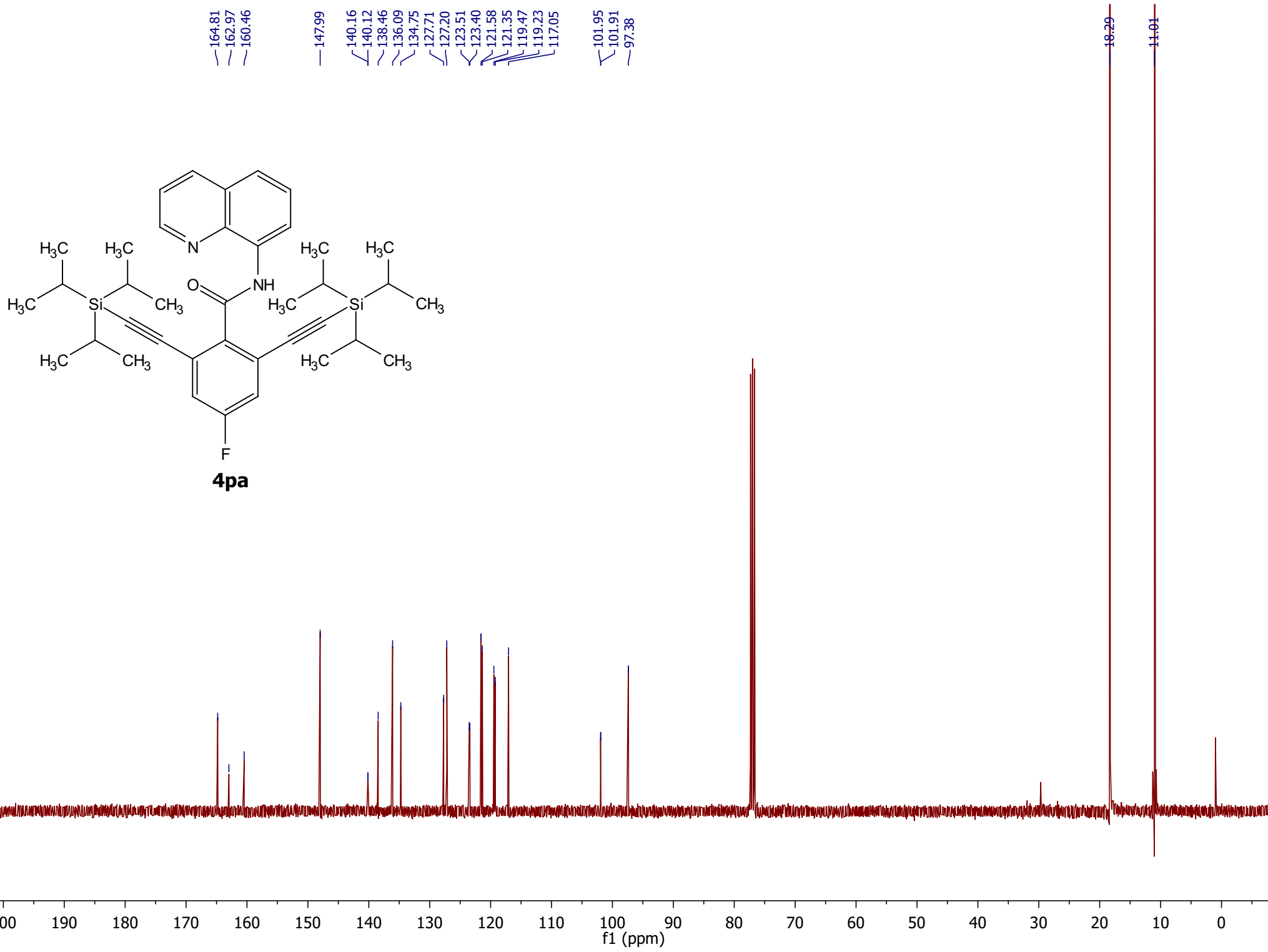
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

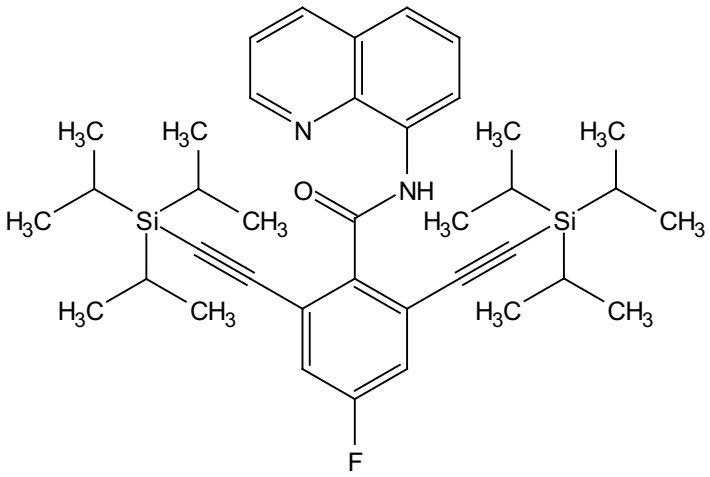

H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3
F

4pa

10.04
8.96
8.95
8.94
8.94
8.74
8.73
8.73
8.72
8.17
8.16
8.14
8.14
7.57
7.53
7.53
7.50
7.43
7.42
7.41
7.40
7.22
7.19
0.85
1.04
1.08
1.03
1.09
2.25
1.12
1.97
42.22
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

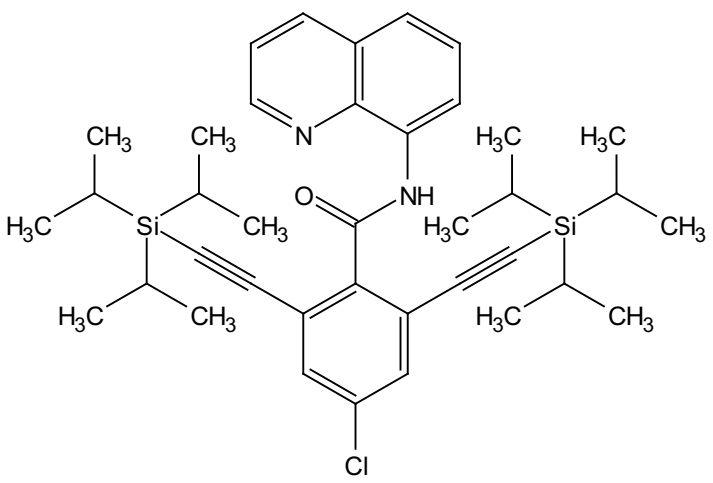

164.81
162.97
160.46
147.99
140.16
140.12
138.46
136.09
134.75
127.71
127.20
123.51
123.40
121.58
121.35
119.47
119.23
117.05
101.95
101.91
97.38
18.29
11.01
H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
F
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4pa


H3C
H3C
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
F

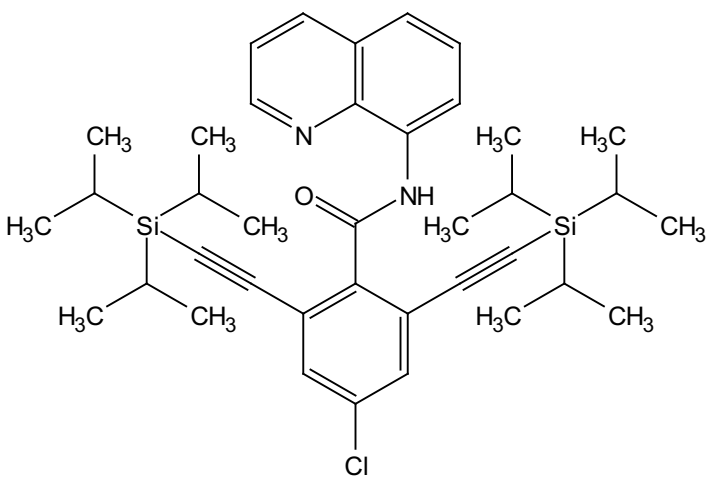
4pa

-111.69
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
f1 (ppm)


CH3
CH3
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
Cl

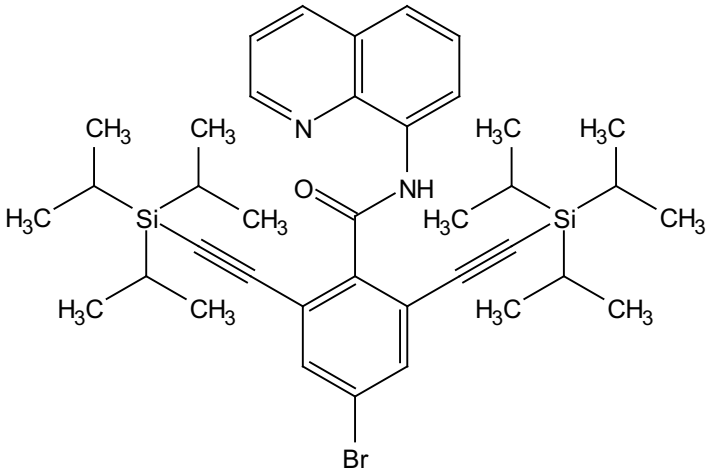
4qa

10.04
8.95
8.94
8.93
8.92
8.73
8.73
8.72
8.72
8.17
8.16
8.14
8.14
7.57
7.53
7.51
7.48
7.43
7.42
7.41
7.40
0.85
1.00
1.03
1.02
1.04
3.90
1.10
42.39
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


CH3
CH3
H3C
Si
CH3
N
O
NH
H3C
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3
Cl

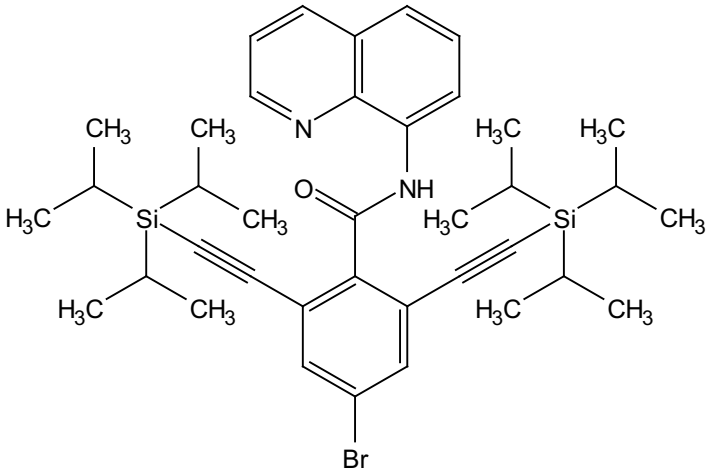
4qa

164.68
148.01
141.84
138.44
136.09
134.67
134.48
132.05
127.70
127.19
122.98
121.63
121.37
117.06
101.72
97.61
18.30
11.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
CH3
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
Br

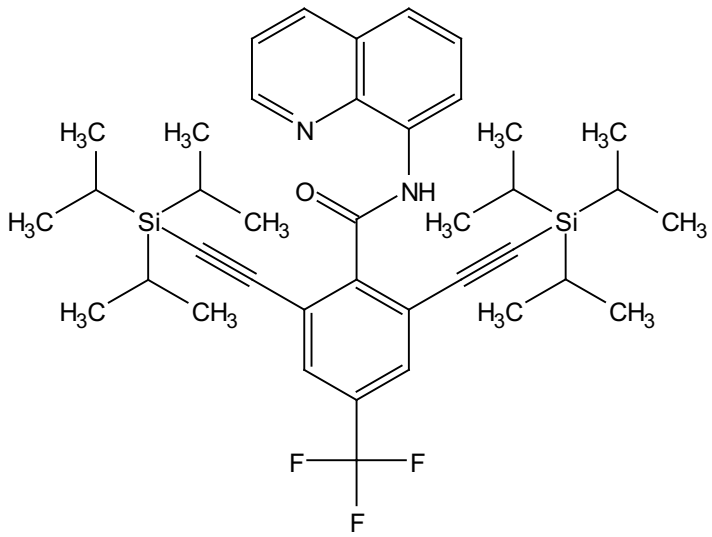
4ra

10.04
8.94
8.94
8.92
8.92
8.73
8.73
8.72
8.72
8.16
8.16
8.14
8.14
7.64
7.55
7.53
7.51
7.43
7.42
7.41
7.40
0.85
1.00
0.99
1.03
1.03
4.24
42.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


CH3
CH3
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
Br

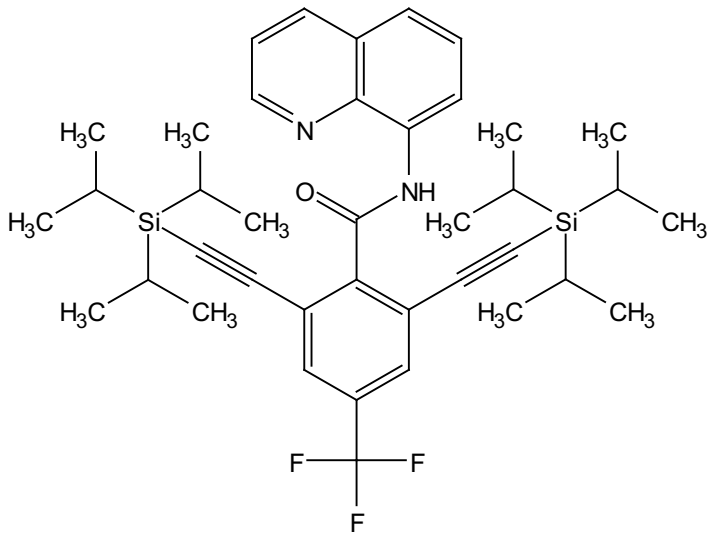
4ra

164.70
148.01
142.24
138.43
136.09
134.85
134.65
127.69
127.19
123.09
122.23
121.64
121.38
117.06
101.58
97.74
18.30
11.00
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
F
F
F

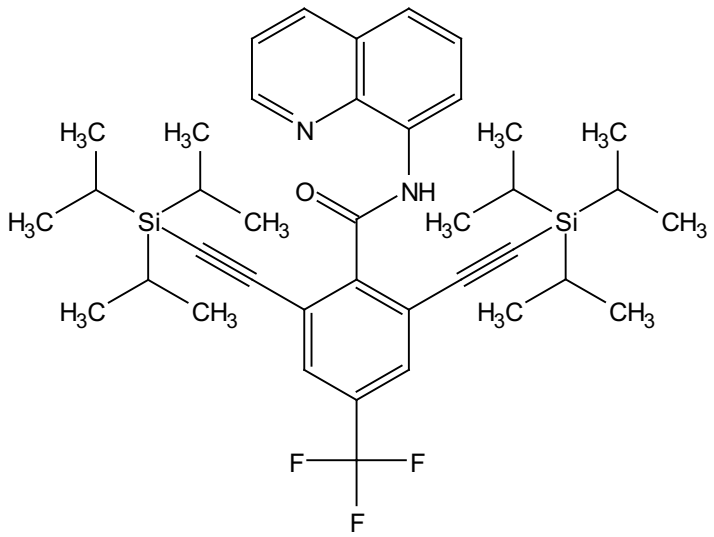
4sa

10.07
8.95
8.94
8.93
8.73
8.72
8.17
8.15
7.73
7.56
7.55
7.44
7.43
7.42
7.41
0.86
1.00
1.01
1.01
1.02
1.92
2.30
1.12
42.32
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
F
F
F

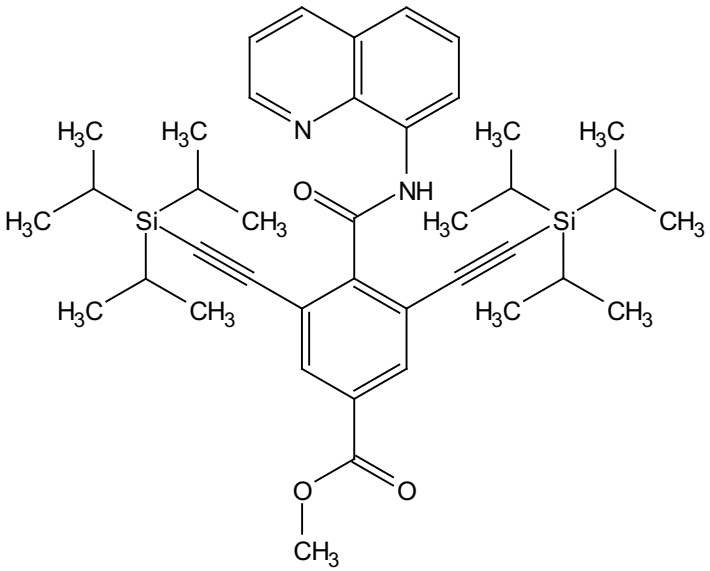
4sa

164.38
148.07
146.07
138.41
136.13
134.51
132.41
131.60
131.26
130.06
128.78
128.74
128.27
127.70
127.16
124.40
122.47
121.83
121.66
121.44
117.19
101.53
98.27
29.69
18.30
11.00
1.1
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
F
F
F

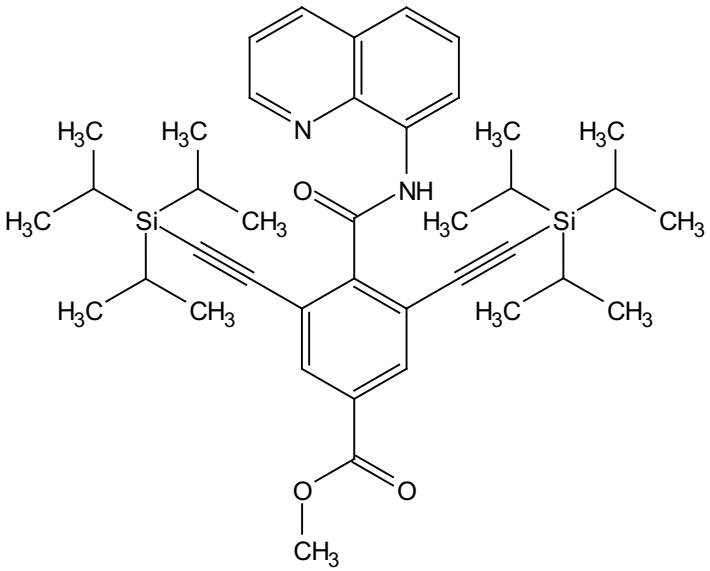
4sa

-63.09
55
50
45
40
35
30
25
20
15
10
5
0
-5
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
f1 (ppm)


H3C
H3C
H3C
H3C
Si
CH3
Si
CH3
H3C
CH3
H3C
CH3
N
O
NH
O
O
CH3

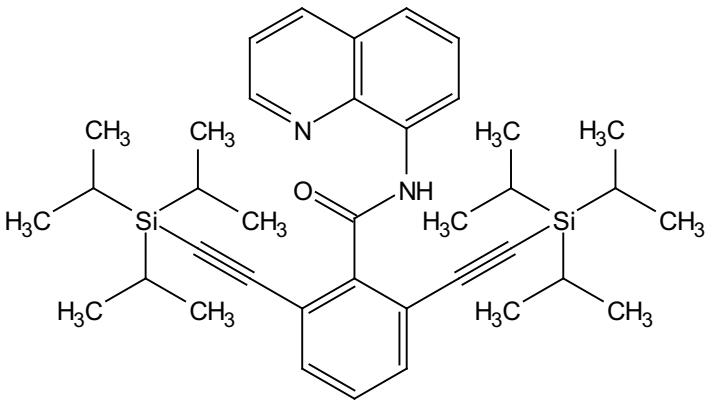
4ta

10.06
8.96
8.95
8.94
8.94
8.73
8.73
8.72
8.72
8.17
8.16
8.15
8.14
8.14
7.58
7.56
7.54
7.53
7.51
7.43
7.42
7.41
7.40
3.97
0.85
1.00
1.05
1.04
1.17
1.82
2.32
1.14
3.10
42.31
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3
O
O
O
CH3

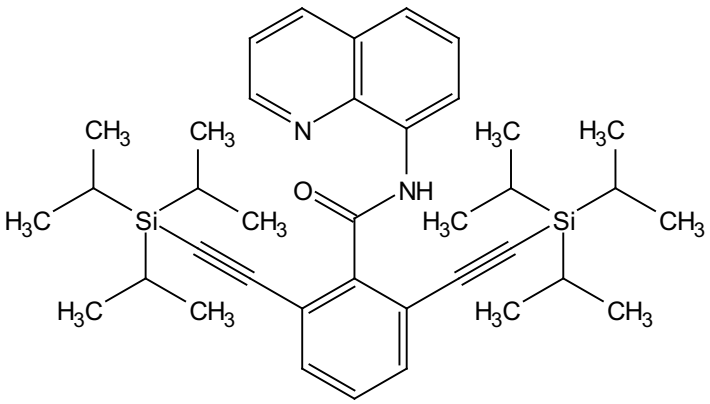
4ta

165.36
164.82
148.02
146.66
138.43
136.10
134.59
133.14
130.75
127.69
127.17
121.97
121.72
121.39
117.17
102.04
97.21
52.58
18.31
11.01
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
CH3
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3

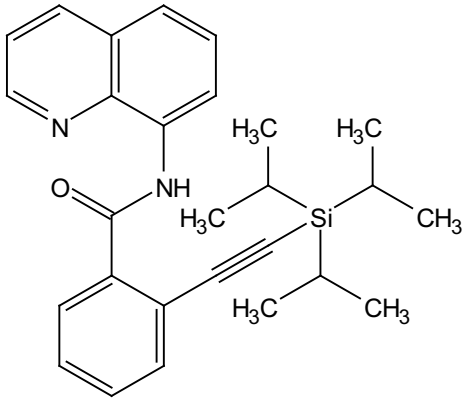
4ua

10.05
8.99
8.98
8.97
8.96
8.73
8.72
8.72
8.71
8.16
8.15
8.14
8.13
7.57
7.53
7.50
7.42
7.41
7.40
7.39
7.34
7.32
7.30
0.86
1.00
1.00
0.96
1.04
4.01
1.03
1.09
42.40
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


CH3
CH3
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3

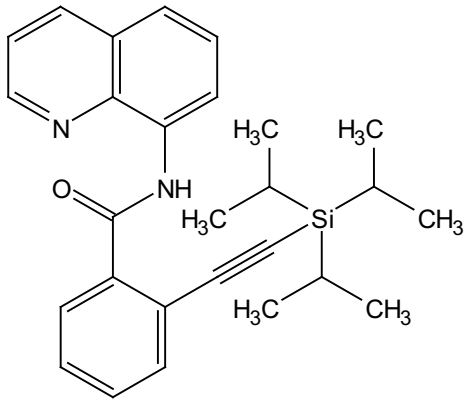
4ua

165.56
147.92
143.52
138.48
136.05
134.85
132.35
128.69
127.68
127.20
121.43
121.38
121.29
117.05
103.01
95.84
18.32
11.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NH
O
H3C
H3C
Si
CH3
H3C
CH3

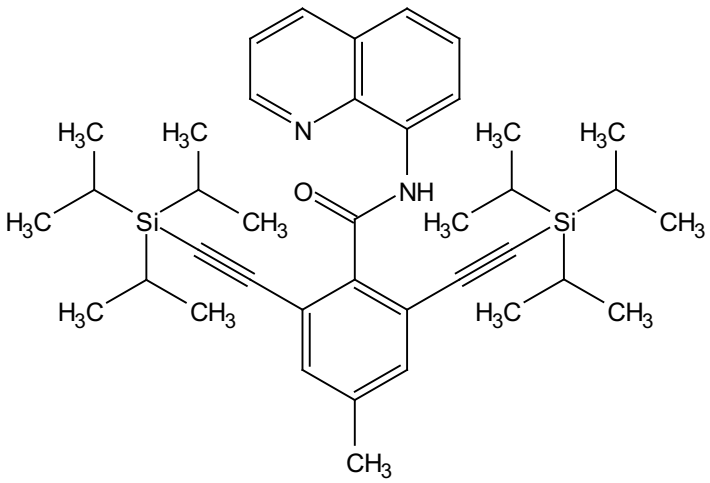
3ua

10.49
8.93
8.93
8.92
8.91
8.77
8.76
8.76
8.75
8.17
8.17
8.15
8.15
7.82
7.80
7.79
7.78
7.64
7.63
7.61
7.59
7.55
7.53
7.47
7.44
7.41
0.82
1.00
0.97
1.00
1.01
0.95
1.11
2.00
3.15
20.96
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
NH
O
H3C
H3C
H3C
Si
CH3
H3C
CH3

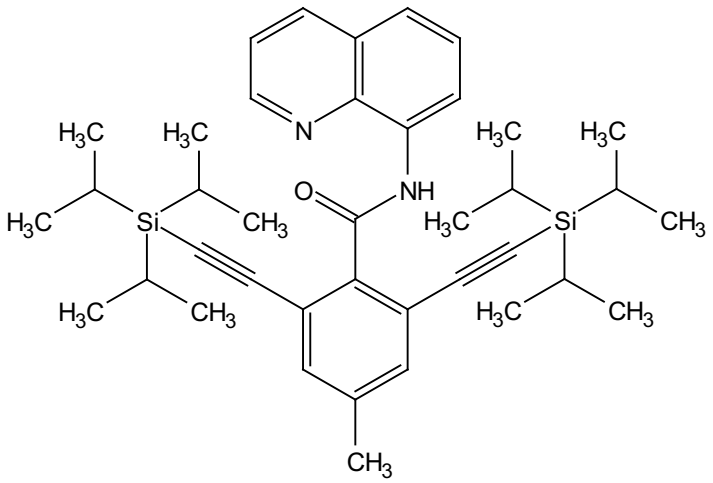
3ua

166.41
148.22
139.21
138.87
136.17
134.64
133.88
130.09
128.66
127.88
127.77
127.33
121.82
121.43
120.71
117.10
103.83
97.12
18.28
11.02
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H3C
H3C
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
CH3

4va

10.03
8.98
8.97
8.96
8.96
8.72
8.71
8.71
8.70
8.15
8.15
8.13
8.13
7.57
7.55
7.51
7.49
7.41
7.40
7.39
7.38
7.33
2.35
0.86
1.00
1.01
1.00
1.03
2.22
1.08
1.95
3.16
42.06
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)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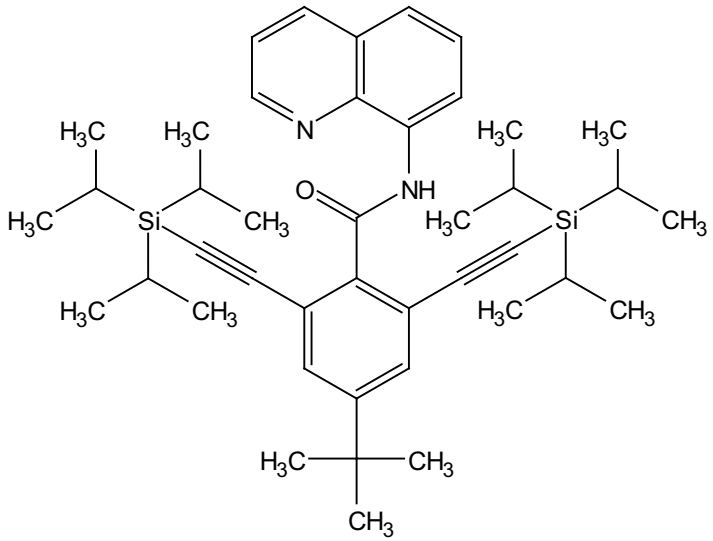
H3C
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
CH3

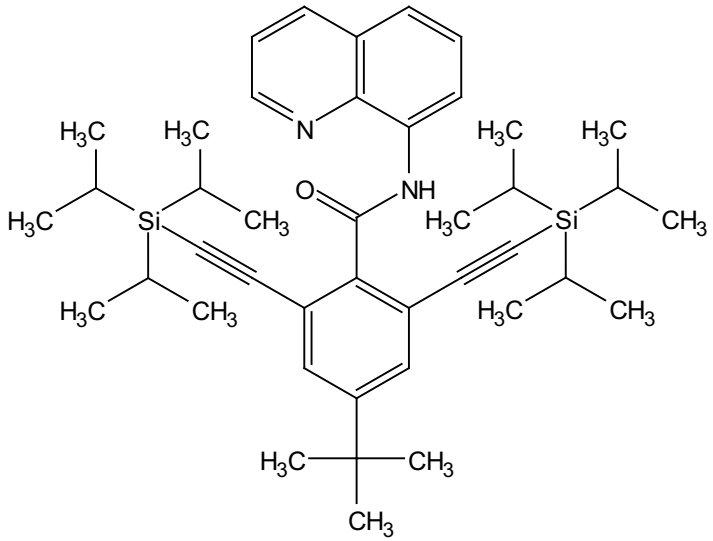
4va

165.70
147.88
140.99
138.76
138.48
136.01
134.93
132.97
127.67
127.21
121.31
121.25
121.23
116.95
103.25
95.24
20.83
18.33
11.05
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H3C
H3C
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
H3C
CH3
CH3

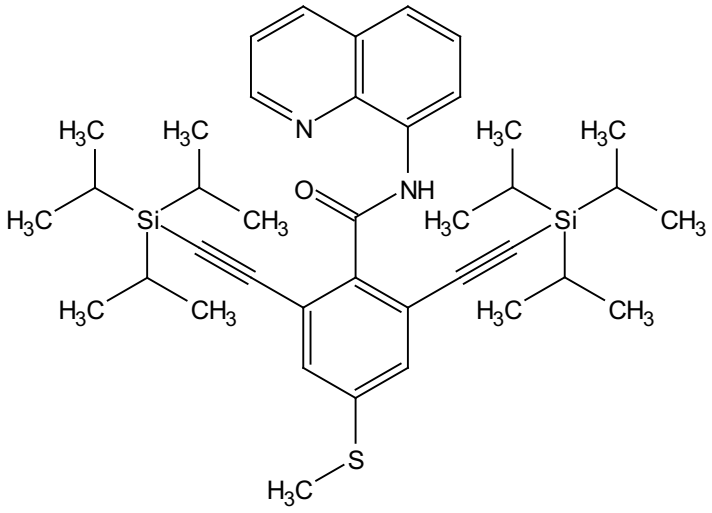
4wa

10.03
8.99
8.98
8.97
8.96
8.72
8.71
8.71
8.70
8.15
8.15
8.13
8.13
7.57
7.53
7.50
7.49
7.41
7.40
7.39
7.38
1.35
0.86
1.00
1.01
1.03
1.14
4.31
1.21
9.05
41.94
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0
f1 (ppm)


H3C
H3C
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
H3C
CH3
CH3

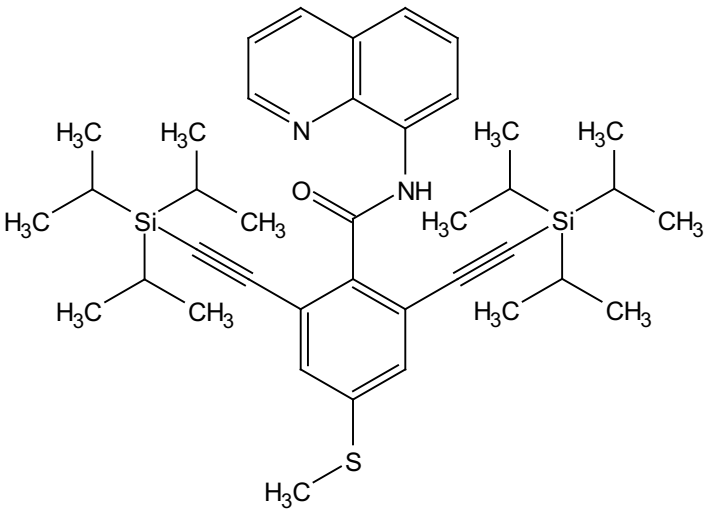
4wa

165.81
151.94
147.87
141.18
138.47
136.02
134.93
129.54
127.66
127.19
121.32
121.25
120.97
117.01
103.60
94.91
34.68
31.00
18.35
11.08
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
S
H3C

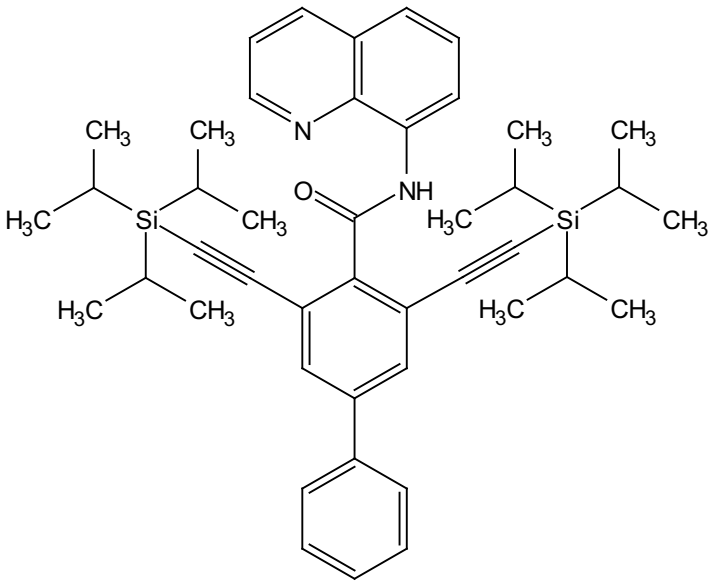
4xa

10.03
8.96
8.96
8.94
8.94
8.72
8.72
8.71
8.71
8.15
8.15
8.13
8.13
7.56
7.54
7.52
7.49
7.42
7.41
7.40
7.39
7.34
2.52
0.85
1.00
1.04
1.05
1.07
2.26
1.12
1.92
3.22
41.93
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.
f1 (ppm)


N
O
NH
Si
Si
S
H_3C
CH_3

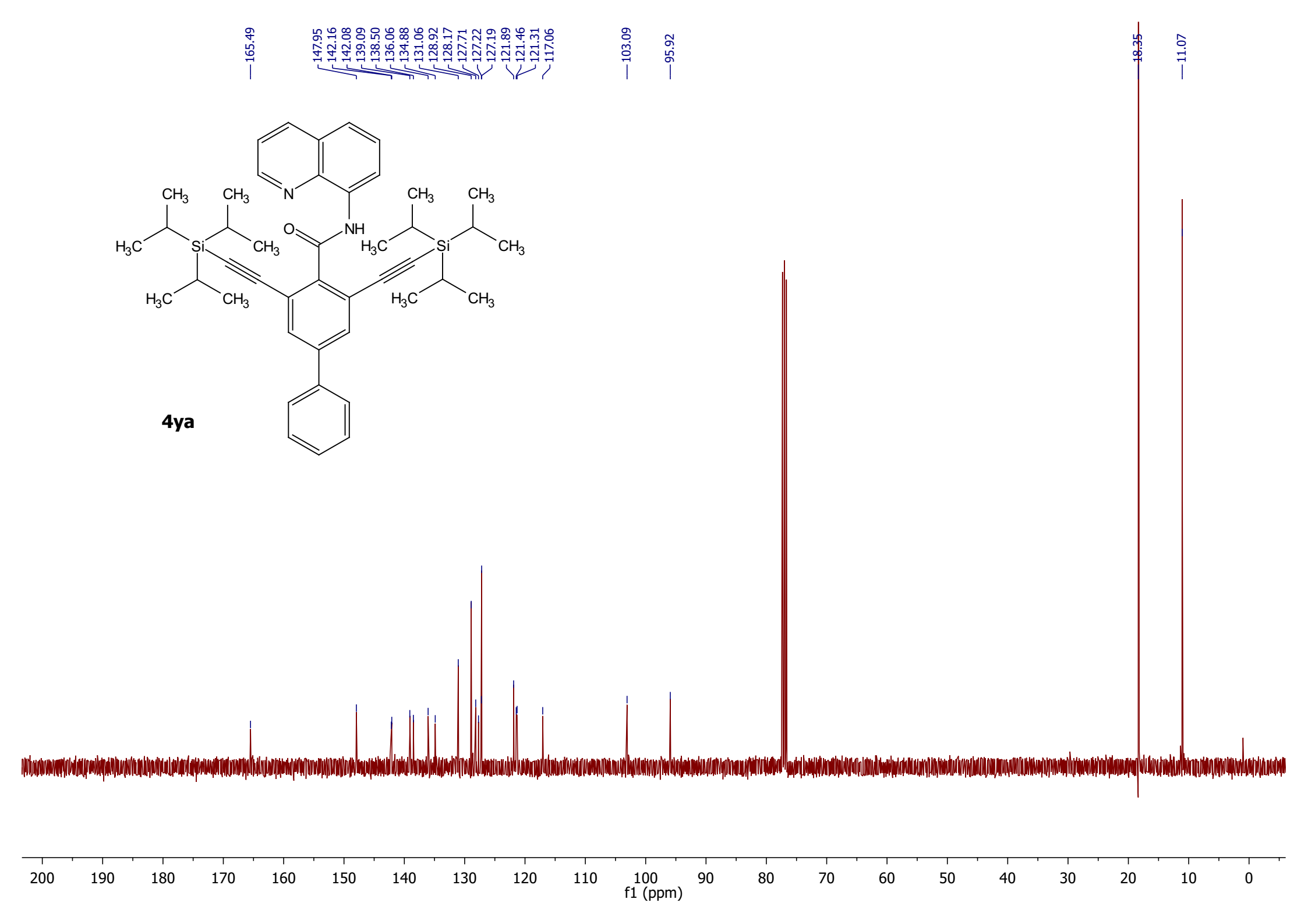
4xa

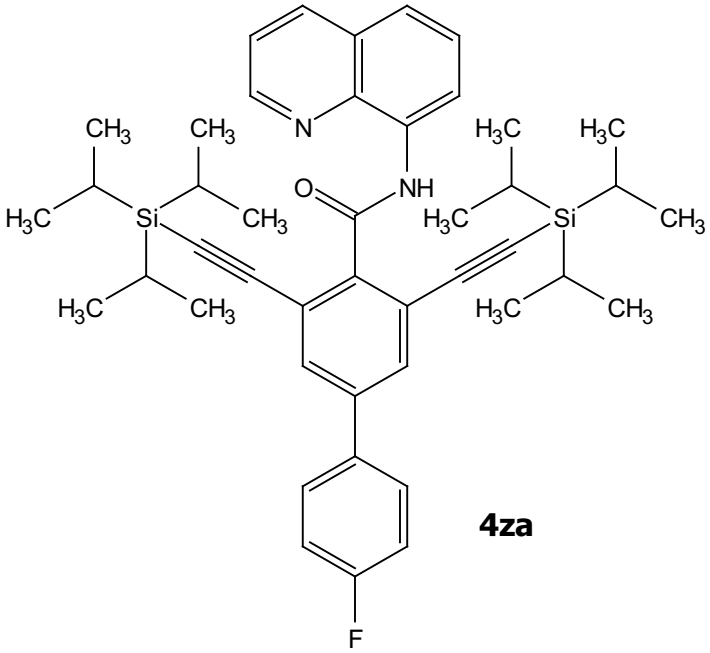
165.23
147.92
140.20
140.16
138.46
136.03
134.84
129.49
127.67
127.19
121.87
121.41
121.29
116.97
102.68
96.27
18.32
15.49
11.04
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
NH
Si
Si
CH3
H3C

4ya

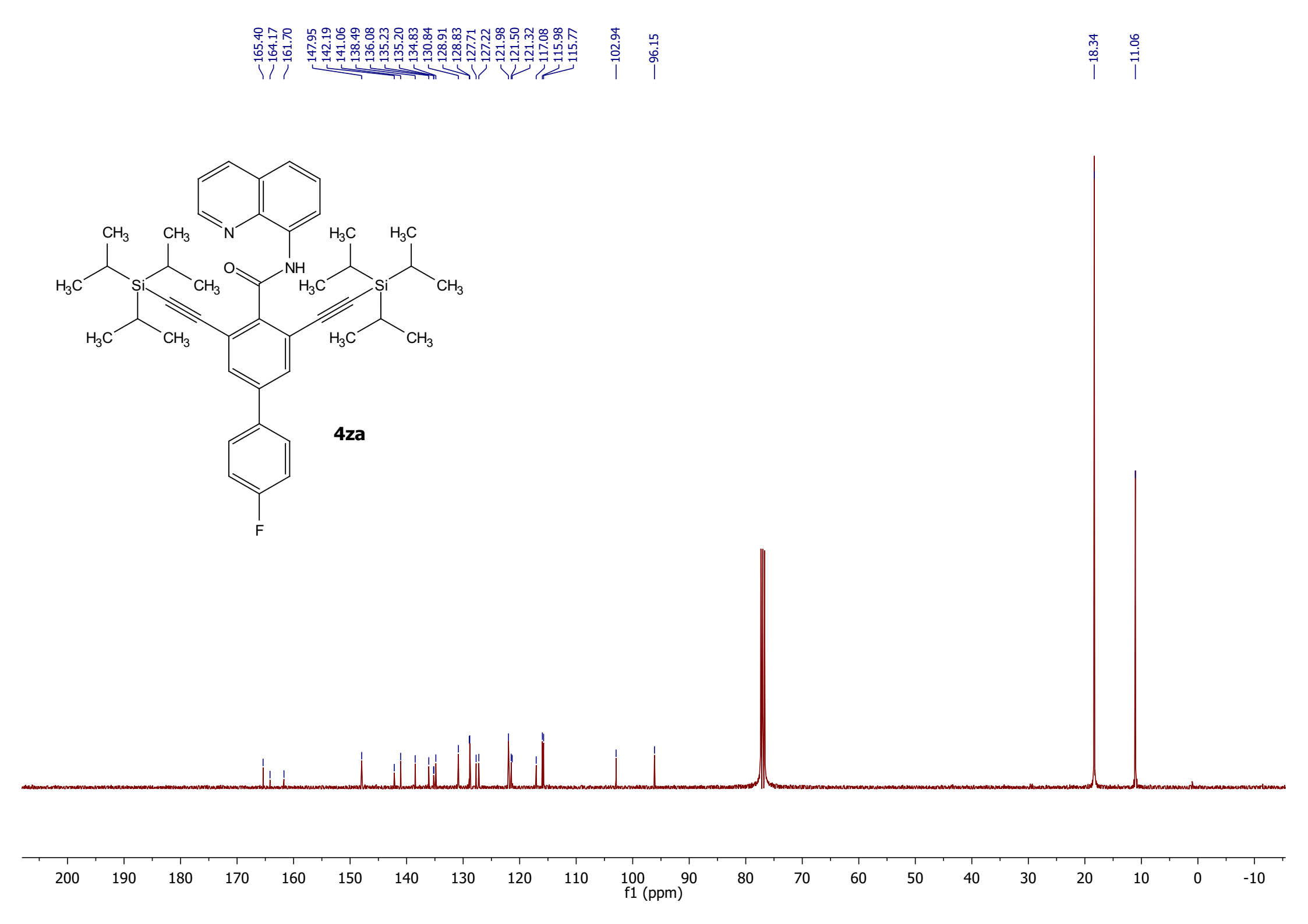
10.12
9.01
8.99
8.74
8.73
8.17
8.15
7.72
7.72
7.63
7.61
7.57
7.54
7.50
7.48
7.46
7.43
7.41
7.39
0.88
1.00
1.01
0.98
1.14
1.99
4.16
2.13
2.25
42.47
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

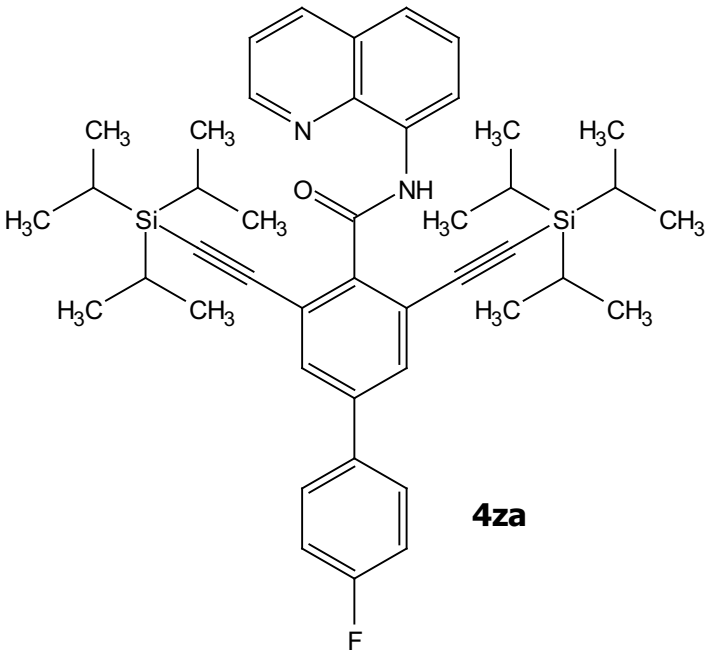

165.49
147.95
142.16
142.08
139.09
138.50
136.06
134.88
131.06
128.92
128.17
127.71
127.22
127.19
121.89
121.46
121.31
117.06
103.09
95.92
18.35
11.07
CH3
CH3
N
O
NH
H3C
Si
CH3
H3C
CH3
CH3
CH3
H3C
Si
CH3
H3C
CH3
4ya
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
CH3
N
H3C
H3C
O
NH
H3C
Si
CH3
H3C
Si
CH3
H3C
CH3
H3C
CH3
F

4za

9.00
9.00
8.98
8.98
8.74
8.74
8.73
8.72
8.17
8.17
8.15
8.15
7.66
7.60
7.57
7.56
7.55
7.51
7.43
7.42
7.41
7.40
7.18
7.16
7.14
0.87
1.00
1.00
1.01
1.08
1.95
4.42
1.11
2.04
42.28
f1 (ppm)


165.40
164.17
161.70
147.95
142.19
141.06
138.49
136.08
135.23
135.20
134.83
130.84
128.91
128.83
127.71
127.22
121.98
121.50
121.32
117.08
115.98
115.77
102.94
96.15
18.34
11.06
CH3
CH3
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3
F
4za
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

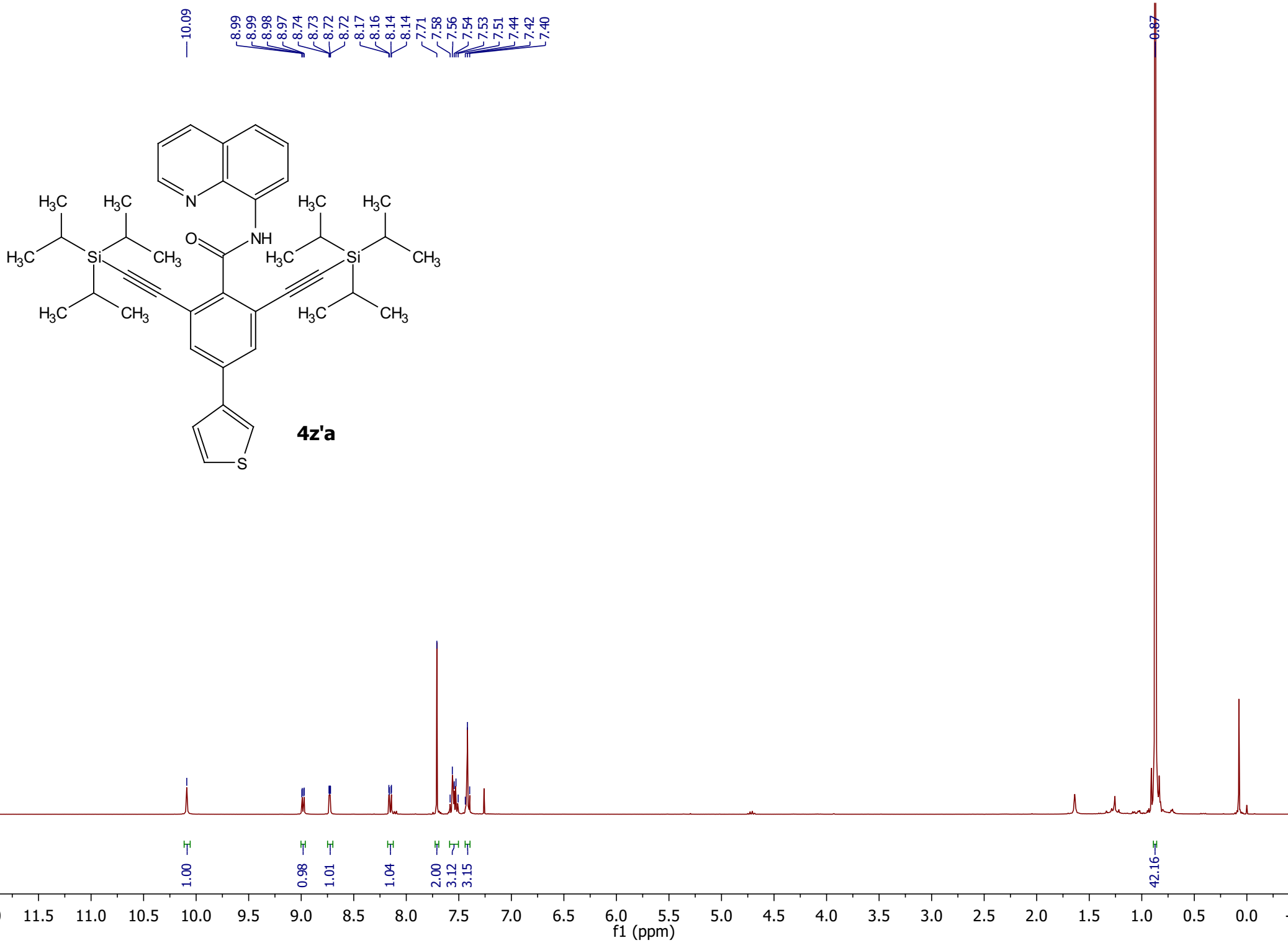


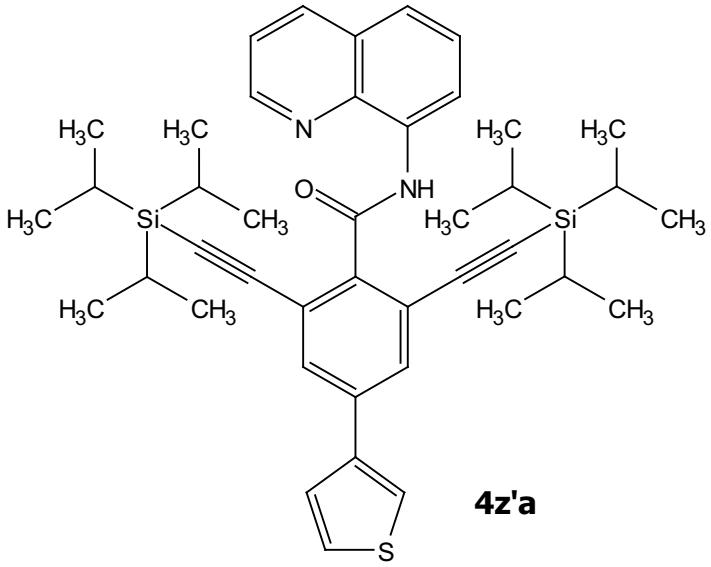
4za

-113.99

-85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -15

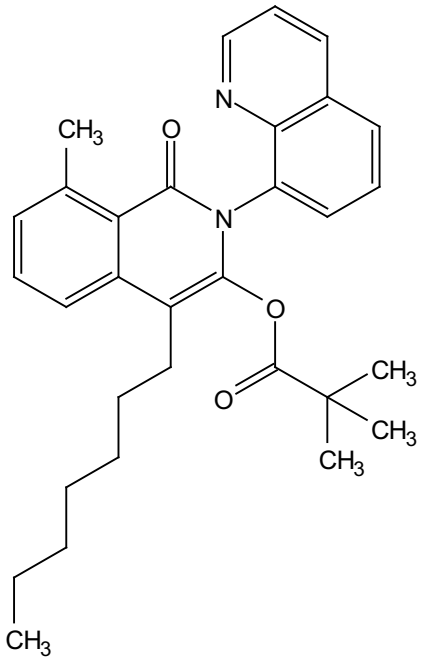
f1 (ppm)


10.09
8.99
8.99
8.98
8.97
8.74
8.73
8.72
8.72
8.17
8.16
8.14
8.14
7.71
7.58
7.56
7.54
7.53
7.51
7.44
7.42
7.40
0.87
4z'a
1.00
0.98
1.01
1.04
2.00
3.12
3.15
42.16
f1 (ppm)


H3C
H3C
Si
CH3
H3C
CH3
N
O
NH
H3C
H3C
Si
CH3
H3C
CH3
H3C
CH3
S

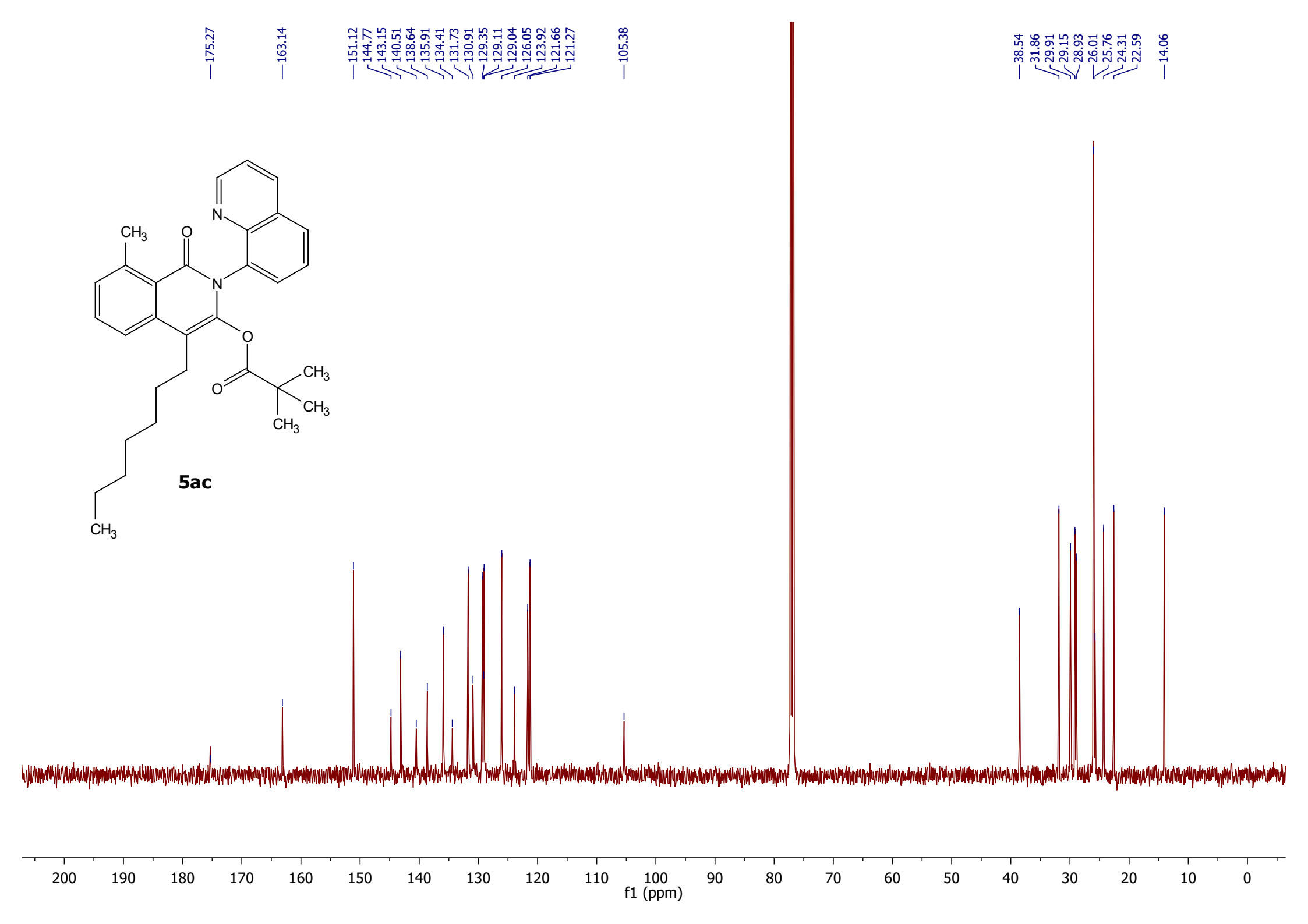
4z'a

165.42
147.94
141.98
140.10
138.48
136.59
136.06
134.85
130.21
127.69
127.21
126.70
126.19
121.94
121.85
121.45
121.31
117.04
103.00
95.99
18.35
11.06
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


CH3
O
N
N
O
O
CH3
CH3
CH3
CH3

5ac

8.89
8.89
8.88
8.88
8.21
8.20
8.19
8.19
7.93
7.91
7.71
7.70
7.64
7.62
7.55
7.43
7.42
7.42
7.41
7.25
7.23
2.88
2.71
2.65
2.51
2.41
1.68
1.54
1.29
0.89
0.88
0.87
0.61
1.01
1.05
1.05
0.96
3.46
1.09
1.02
3.07
1.14
1.12
10.51
3.17
9.10
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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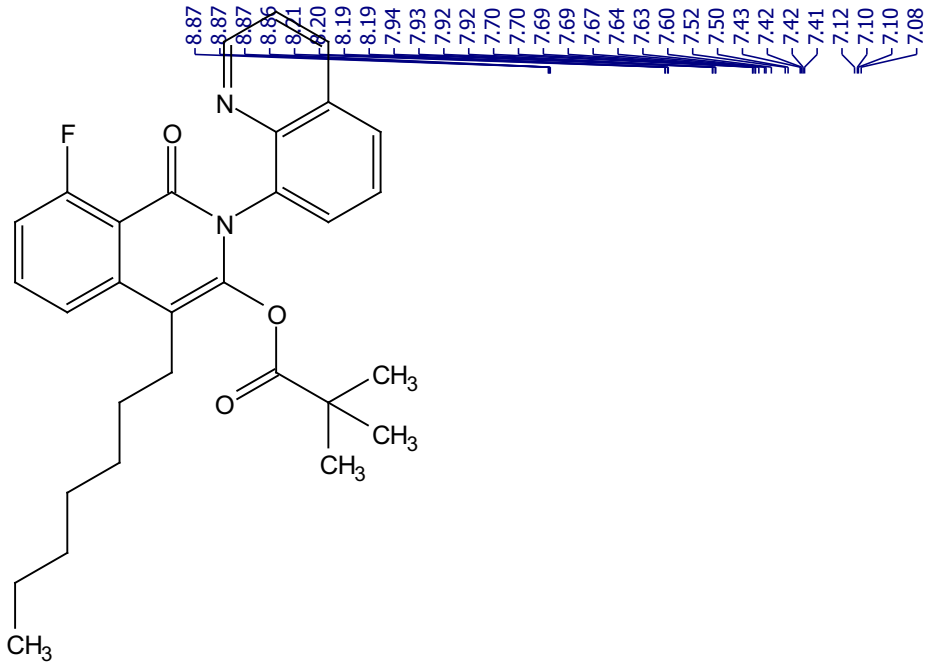
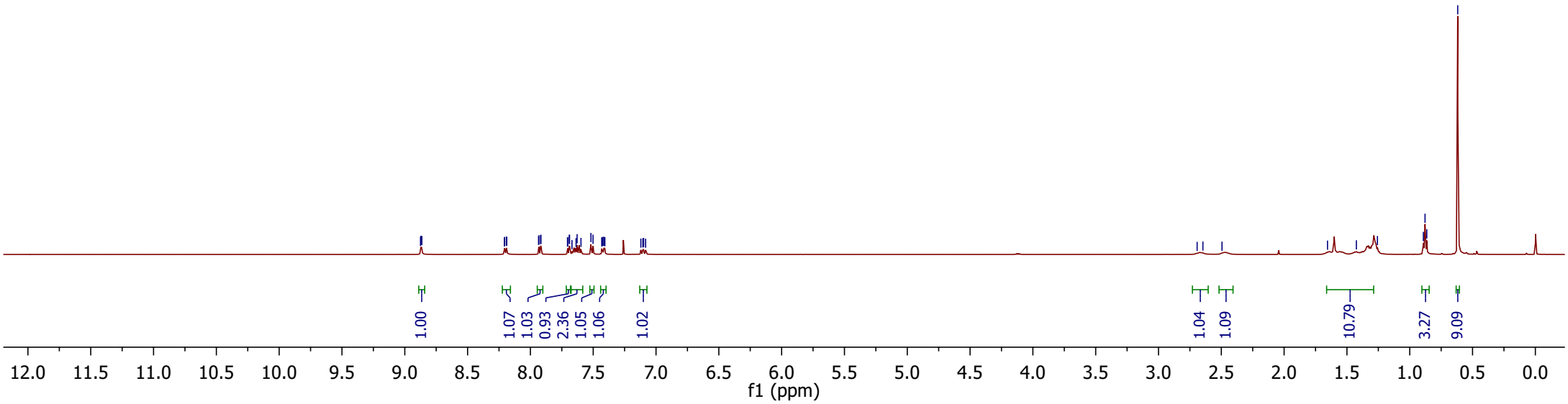
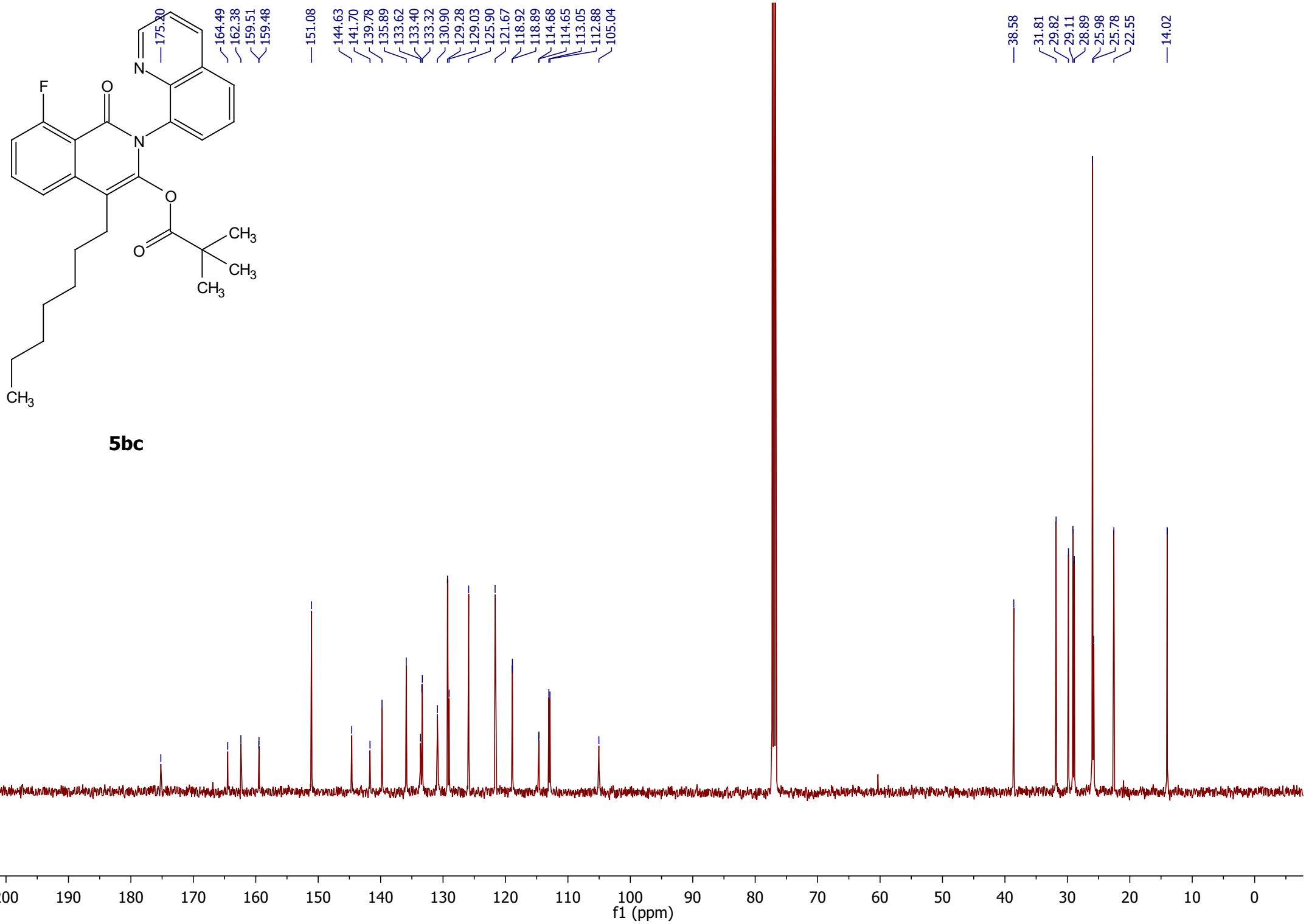
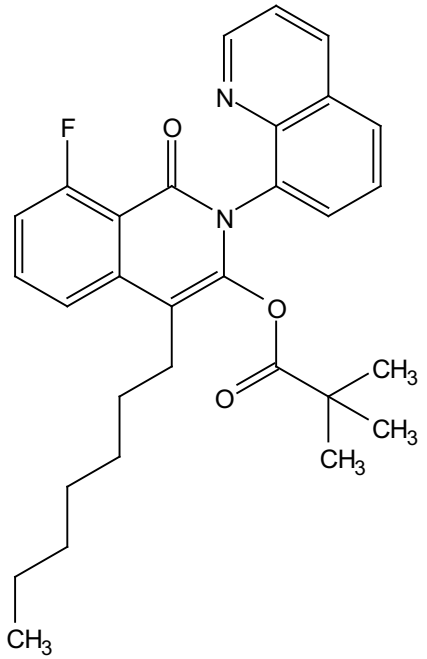
135.91
134.41
131.73
130.91
129.35
129.11
129.04
126.05
123.92
121.66
121.27
105.38
38.54
31.86
29.91
29.15
28.93
26.01
25.76
24.31
22.59
14.06
CH3
O
N
N
O
O
CH3
CH3
CH3
CH3
5ac
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
N
N
O
O
CH3
CH3
CH3
CH3

5bc

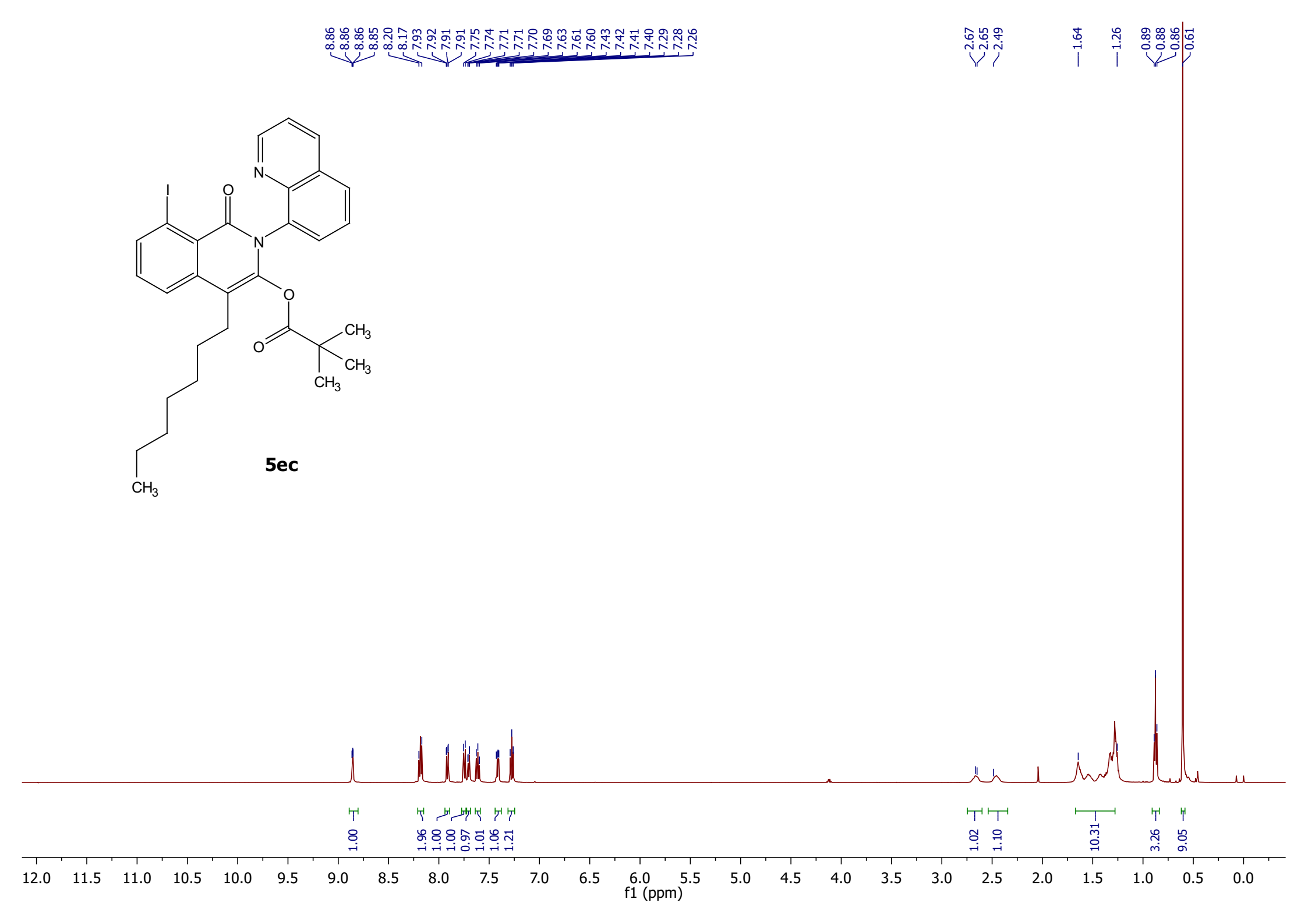

8.87
8.87
8.87
8.86
8.21
8.20
8.19
8.19
7.94
7.93
7.92
7.92
7.70
7.70
7.69
7.69
7.67
7.64
7.63
7.60
7.52
7.50
7.43
7.42
7.42
7.41
7.12
7.10
7.10
7.08
2.69
2.65
2.49
1.65
1.42
1.26
0.89
0.88
0.86
0.62
1.00
1.07
1.03
0.93
2.36
1.05
1.06
1.02
1.04
1.09
10.79
3.27
9.09
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.20
164.49
162.38
159.51
159.48
151.08
144.63
141.70
139.78
135.89
133.62
133.40
133.32
130.90
129.28
129.03
125.90
121.67
118.92
118.89
114.68
114.65
113.05
112.88
105.04
38.58
31.81
29.82
29.11
28.89
25.98
25.78
22.55
14.02
F
O
N
N
O
O
CH3
CH3
CH3
CH3
5bc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


F
O
N
N
O
O
CH3
CH3
CH3
CH3

5bc

-111.55
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
-270
-290
-310
-330
-35
f1 (ppm)


8.86
8.86
8.86
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8.20
8.17
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7.92
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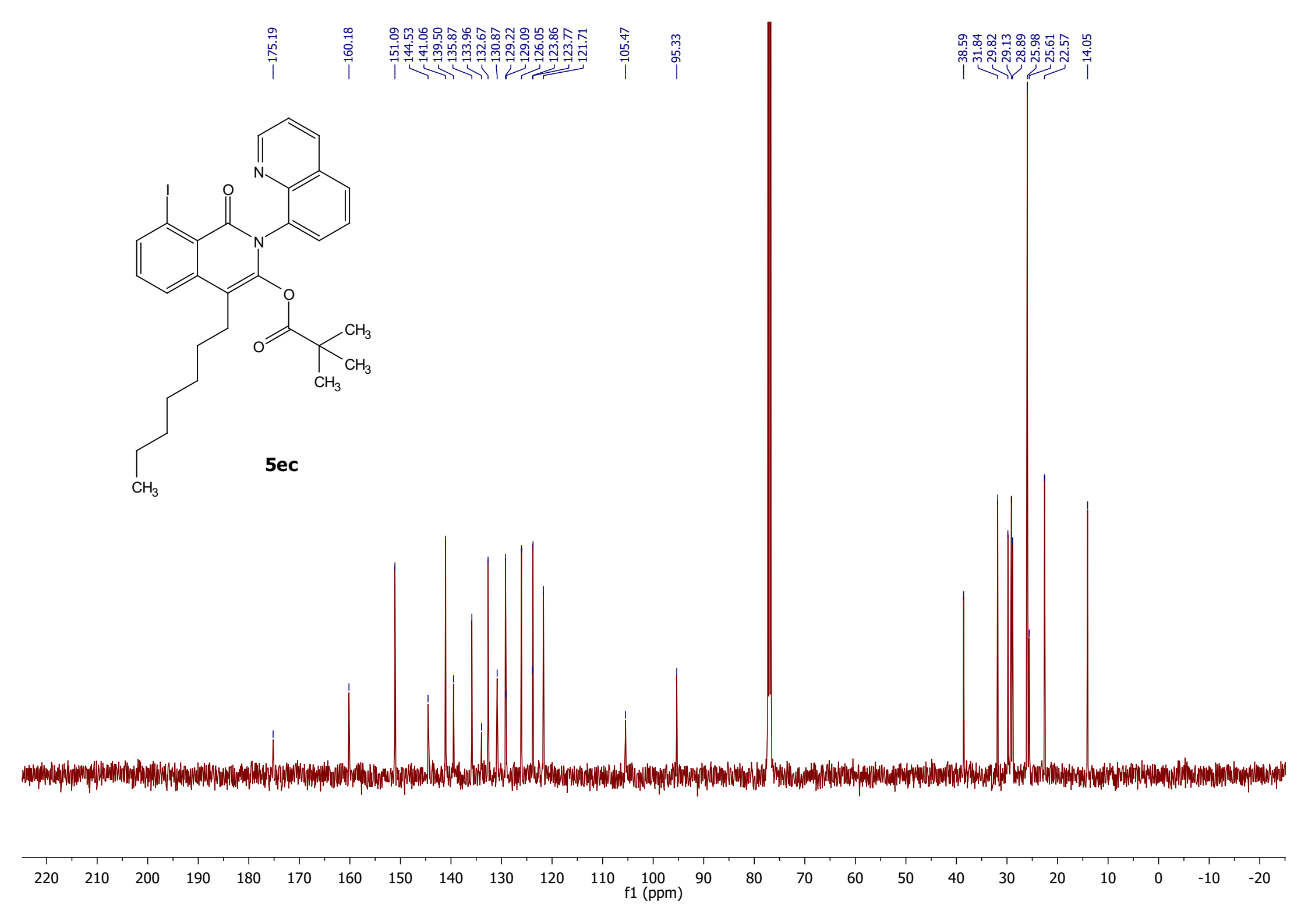
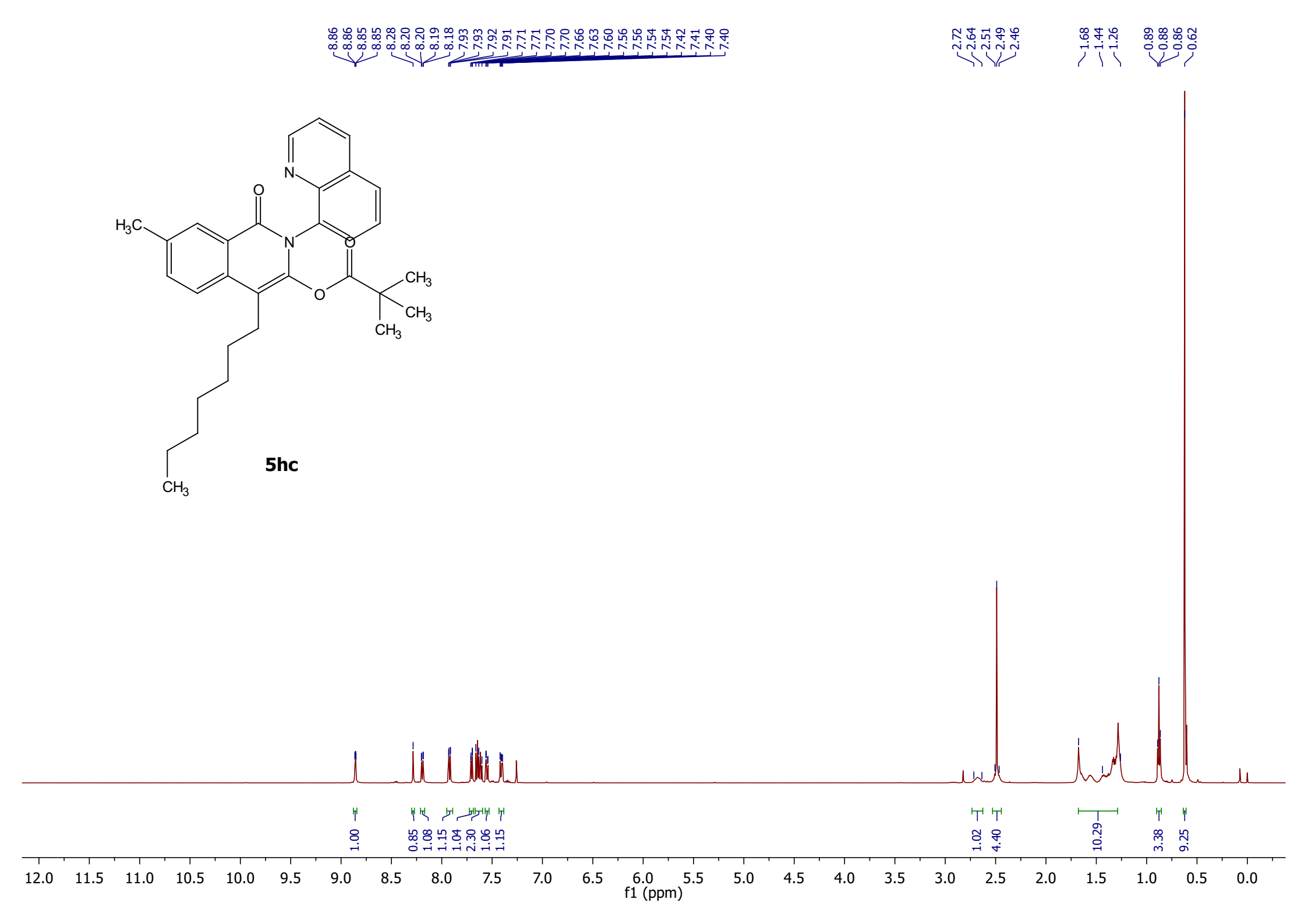
7.91
7.75
7.74
7.71
7.71
7.70
7.69
7.63
7.61
7.60
7.43
7.42
7.41
7.40
7.29
7.28
7.26
2.67
2.65
2.49
1.64
1.26
0.89
0.88
0.86
0.61
I
O
N
N
O
O
CH3
CH3
CH3
CH3
5ec
1.00
1.96
1.00
1.00
0.97
1.01
1.06
1.21
1.02
1.10
10.31
3.26
9.05
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


175.19
160.18
151.09
144.53
141.06
139.50
135.87
133.96
132.67
130.87
129.22
129.09
126.05
123.86
123.77
121.71
105.47
95.33
38.59
31.84
29.82
29.13
28.89
25.98
25.61
22.57
14.05
I
O
N
N
O
O
CH3
CH3
CH3
CH3
5ec
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
f1 (ppm)


8.86
8.86
8.85
8.85
8.28
8.20
8.20
8.19
8.18
7.93
7.93
7.92
7.91
7.71
7.71
7.70
7.70
7.66
7.63
7.60
7.56
7.56
7.54
7.54
7.42
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7.40
7.40
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2.49
2.46
1.68
1.44
1.26
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0.88
0.86
0.62
N
O
O
N
O
H3C
CH3
CH3
CH3
CH3
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1.15
1.04
2.30
1.06
1.15
1.02
4.40
10.29
3.38
9.25
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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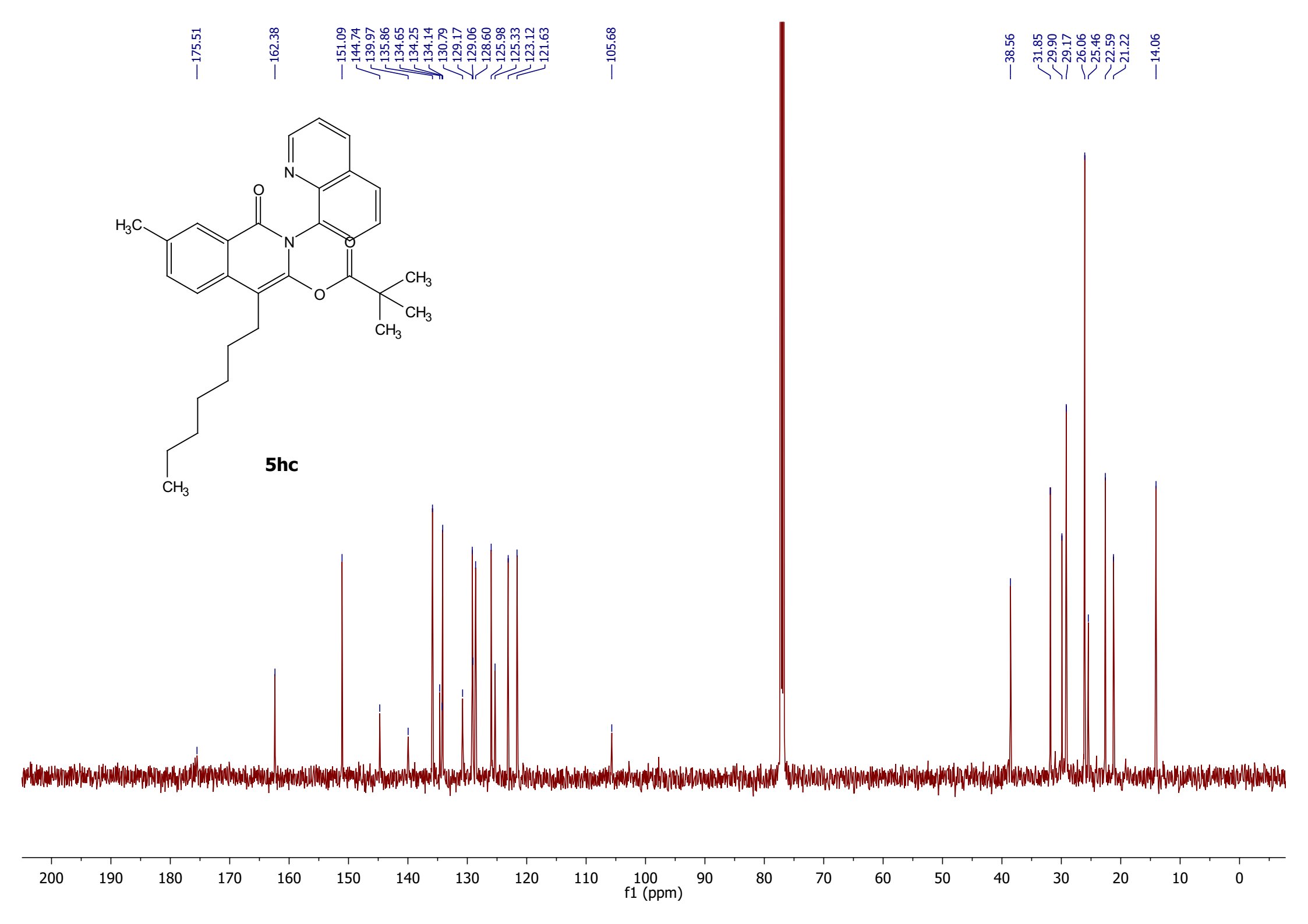
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125.33
123.12
121.63
105.68
38.56
31.85
29.90
29.17
26.06
25.46
22.59
21.22
14.06
N
O
H3C
N
O
O
CH3
CH3
CH3
CH3
5hc
200
190
180
170
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150
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130
120
110
100
90
80
70
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50
40
30
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10
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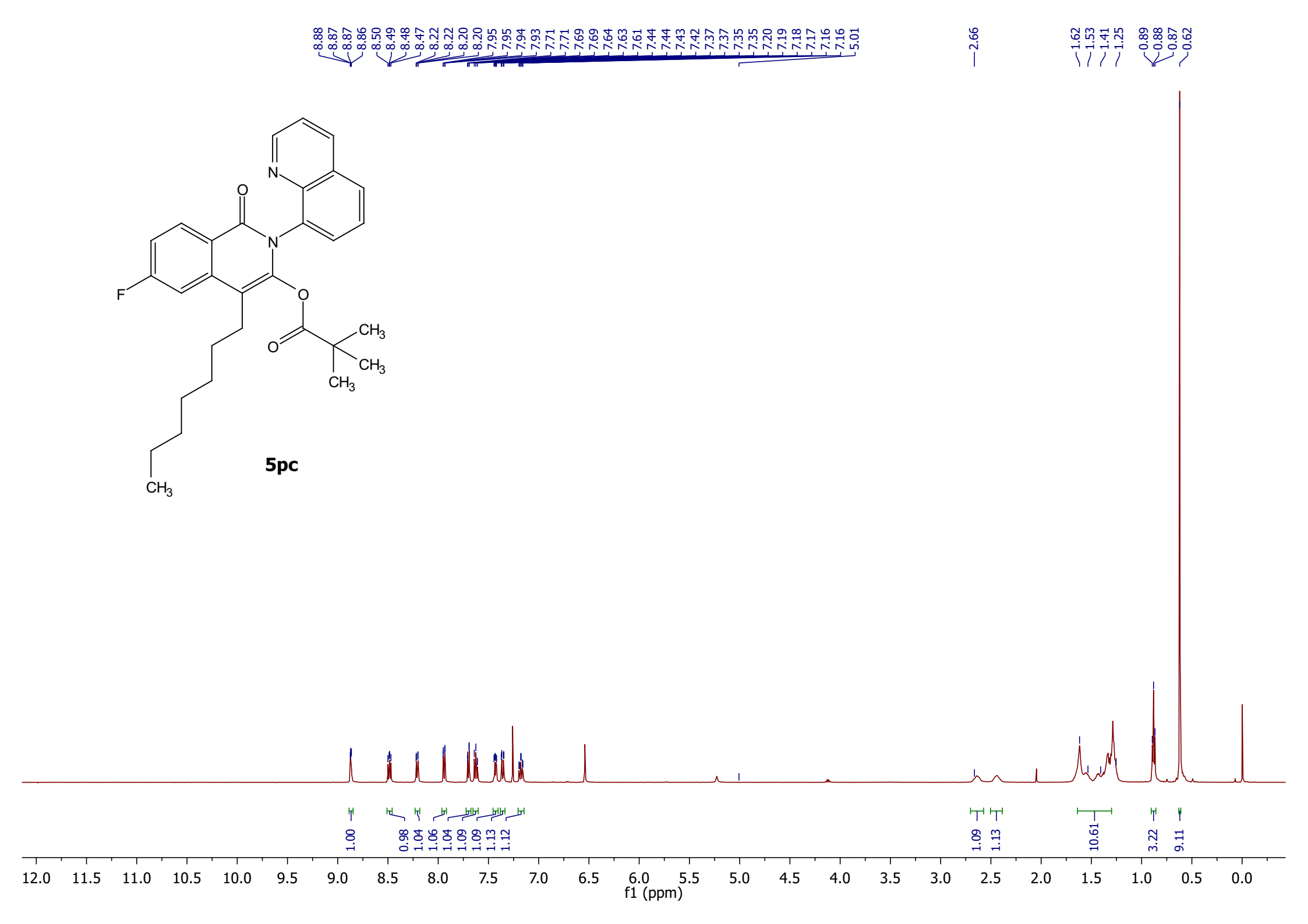
f1 (ppm)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7.95
7.94
7.93
7.71
7.71
7.69
7.69
7.64
7.63
7.61
7.44
7.44
7.43
7.42
7.37
7.37
7.35
7.35
7.20
7.19
7.18
7.17
7.16
7.16
5.01
2.66
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1.53
1.41
1.25
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0.88
0.87
0.62
N
O
N
F
O
O
CH3
CH3
CH3
CH3
5pc
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0.98
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1.06
1.04
1.09
1.09
1.13
1.12
1.09
1.13
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3.22
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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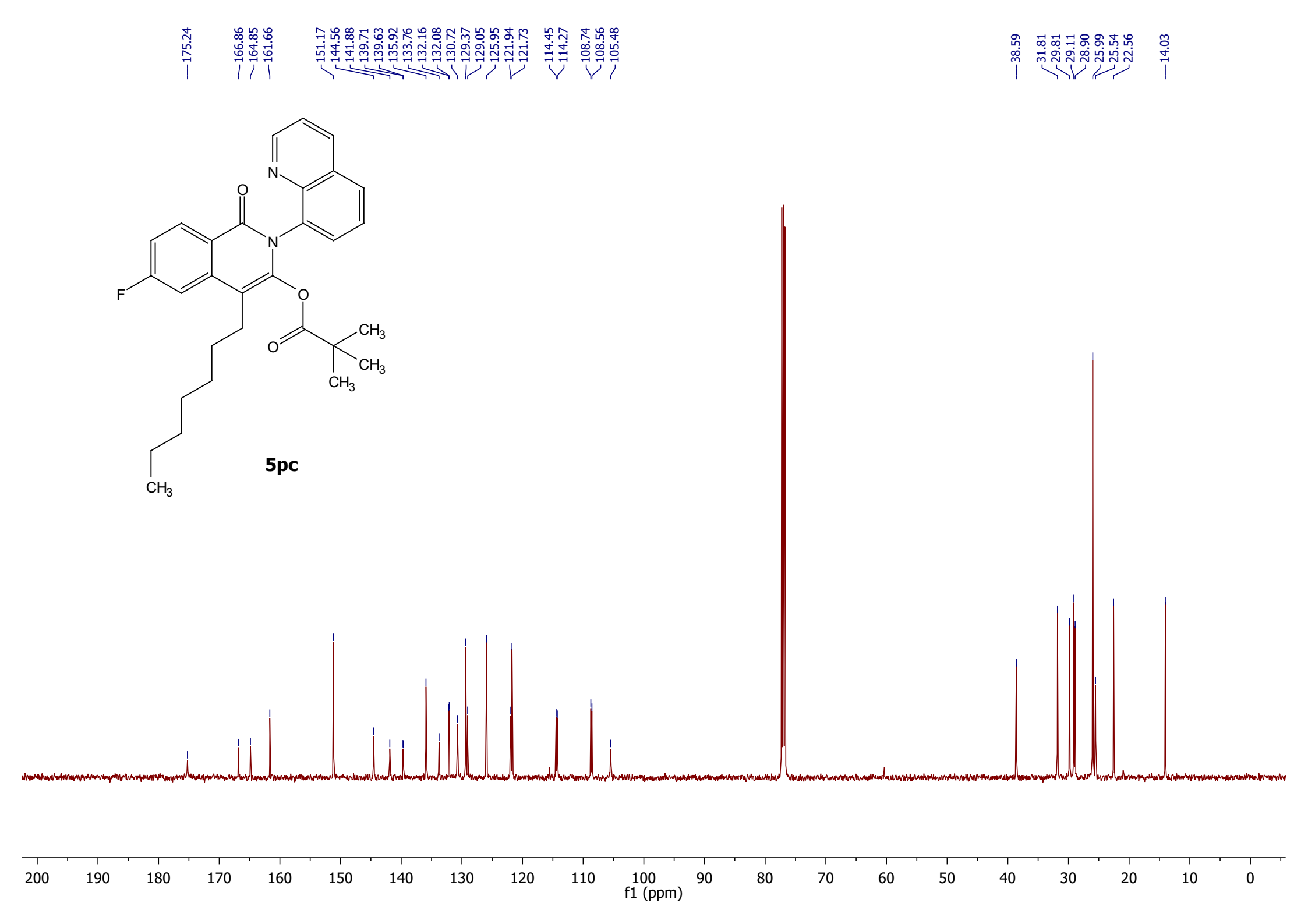
0.0
f1 (ppm)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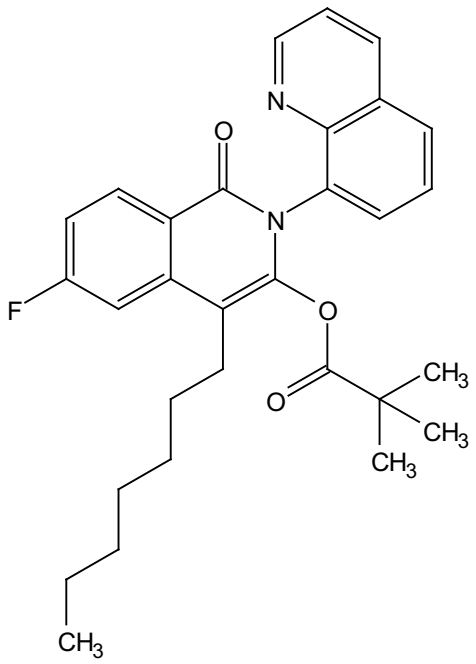
135.92
133.76
132.16
132.08
130.72
129.37
129.05
125.95
121.94
121.73
114.45
114.27
108.74
108.56
105.48
38.59
31.81
29.81
29.11
28.90
25.99
25.54
22.56
14.03
N
O
N
F
O
O
CH3
CH3
CH3
CH3
5pc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
O
N
F
O
O
CH3
CH3
CH3
CH3

5pc

-108.04
50
30
10
-10
-30
-50
-70
-90
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-170
-190
-210
-230
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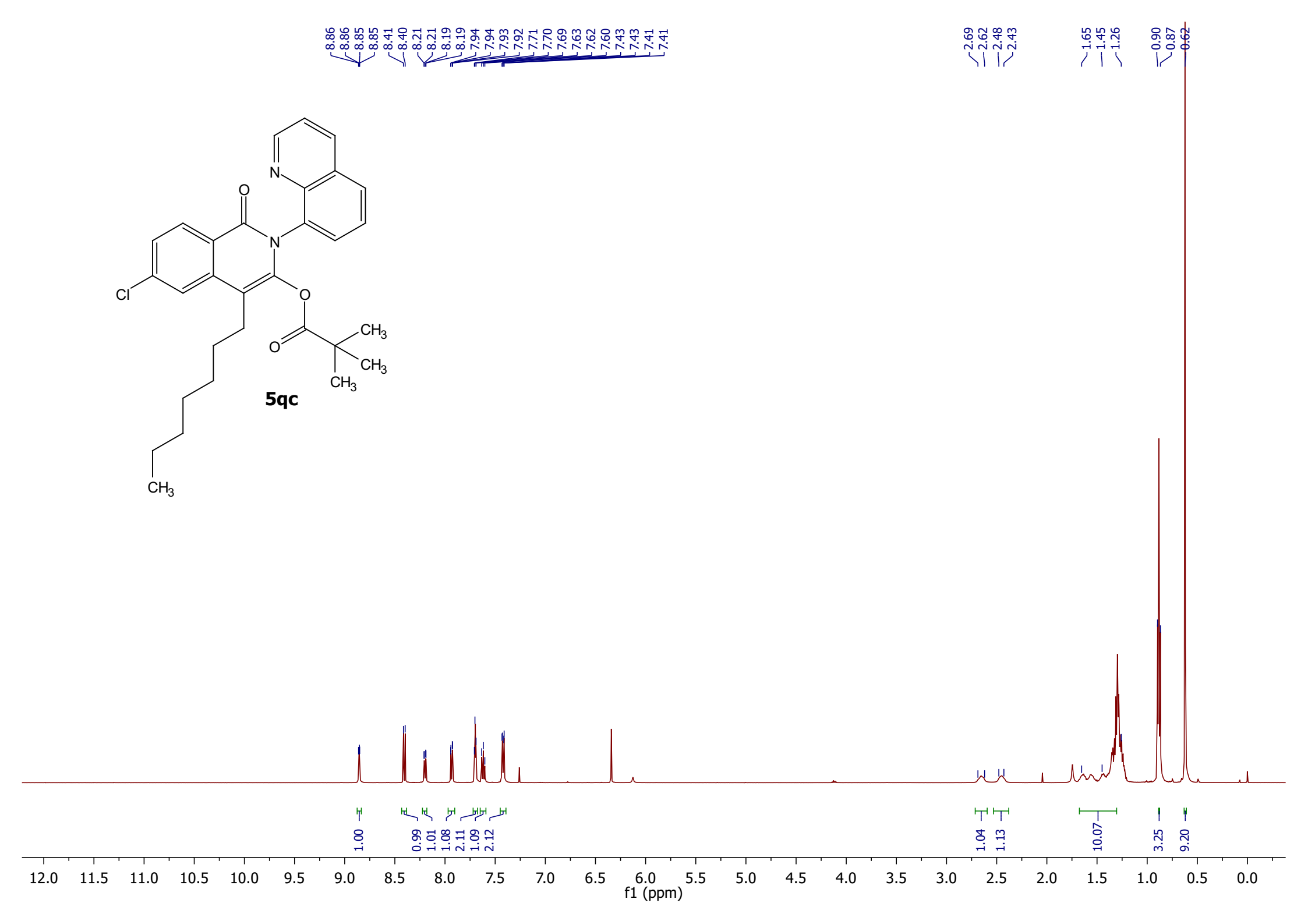
-270
-290
-310
-330
-35
f1 (ppm)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7.92
7.71
7.70
7.69
7.63
7.62
7.60
7.43
7.43
7.41
7.41
2.69
2.62
2.48
2.43
1.65
1.45
1.26
0.90
0.87
0.62
N
O
N
Cl
O
O
CH3
CH3
CH3
CH3
5qc
1.00
0.99
1.01
1.08
2.11
1.09
2.12
1.04
1.13
10.07
3.25
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11.0
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10.0
9.5
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8.0
7.5
7.0
6.5
6.0
5.5
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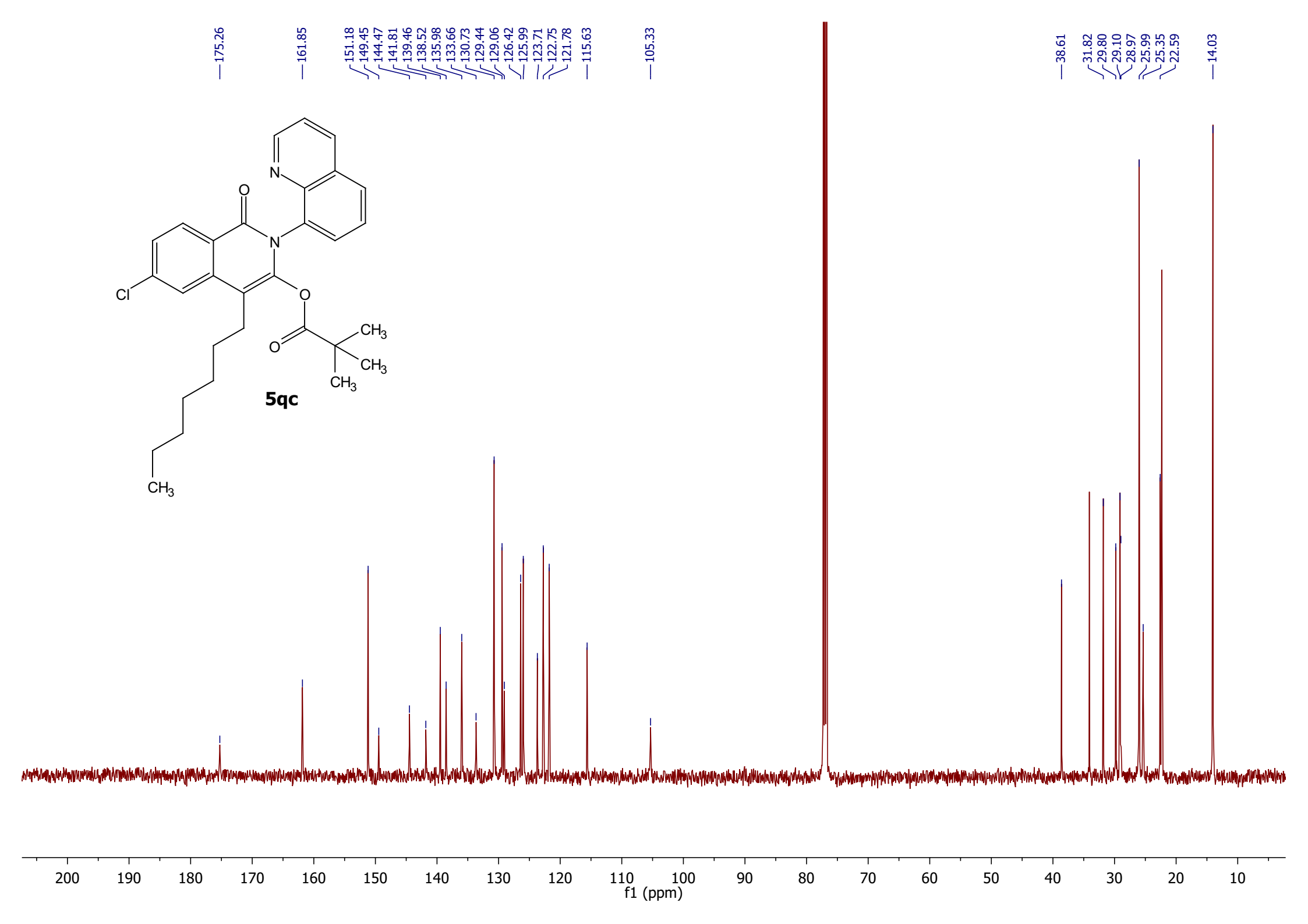
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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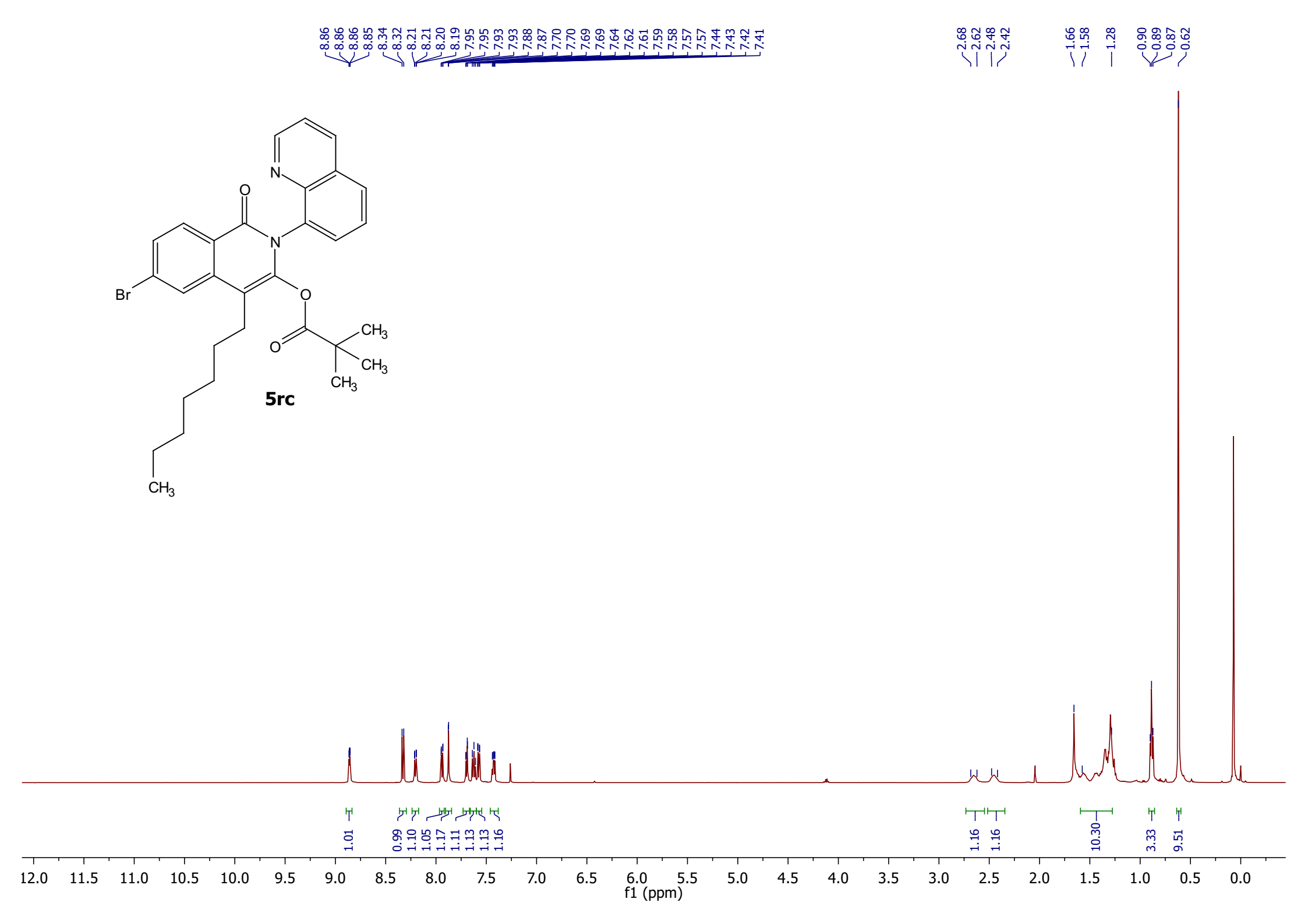
141.81
139.46
138.52
135.98
133.66
130.73
129.44
129.06
126.42
125.99
123.71
122.75
121.78
115.63
105.33
38.61
31.82
29.80
29.10
28.97
25.99
25.35
22.59
14.03
N
O
N
Cl
O
O
CH3
CH3
CH3
CH3
5qc
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)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7.88
7.87
7.70
7.70
7.69
7.69
7.64
7.62
7.61
7.59
7.58
7.57
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7.43
7.42
7.41
2.68
2.62
2.48
2.42
1.66
1.58
1.28
0.90
0.89
0.87
0.62
Br
O
N
N
O
O
CH3
CH3
CH3
CH3
5rc
1.01
0.99
1.10
1.05
1.17
1.11
1.13
1.13
1.16
1.16
1.16
10.30
3.33
9.51
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11.5
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10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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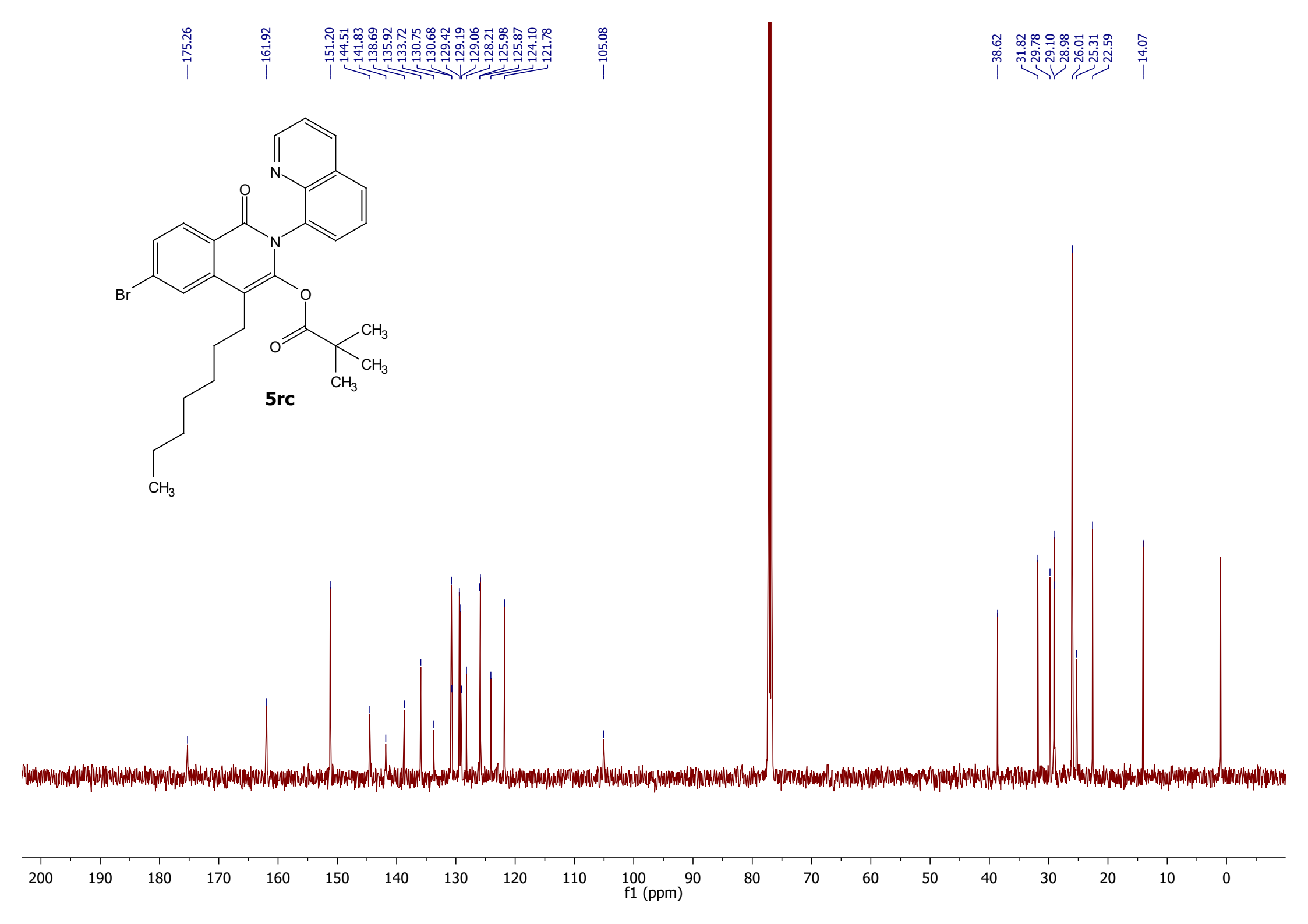
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.42
129.19
129.06
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125.98
125.87
124.10
121.78
105.08
38.62
31.82
29.78
29.10
28.98
26.01
25.31
22.59
14.07
N
O
N
Br
O
O
CH3
CH3
CH3
CH3
5rc
200
190
180
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150
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130
120
110
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80
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50
40
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20
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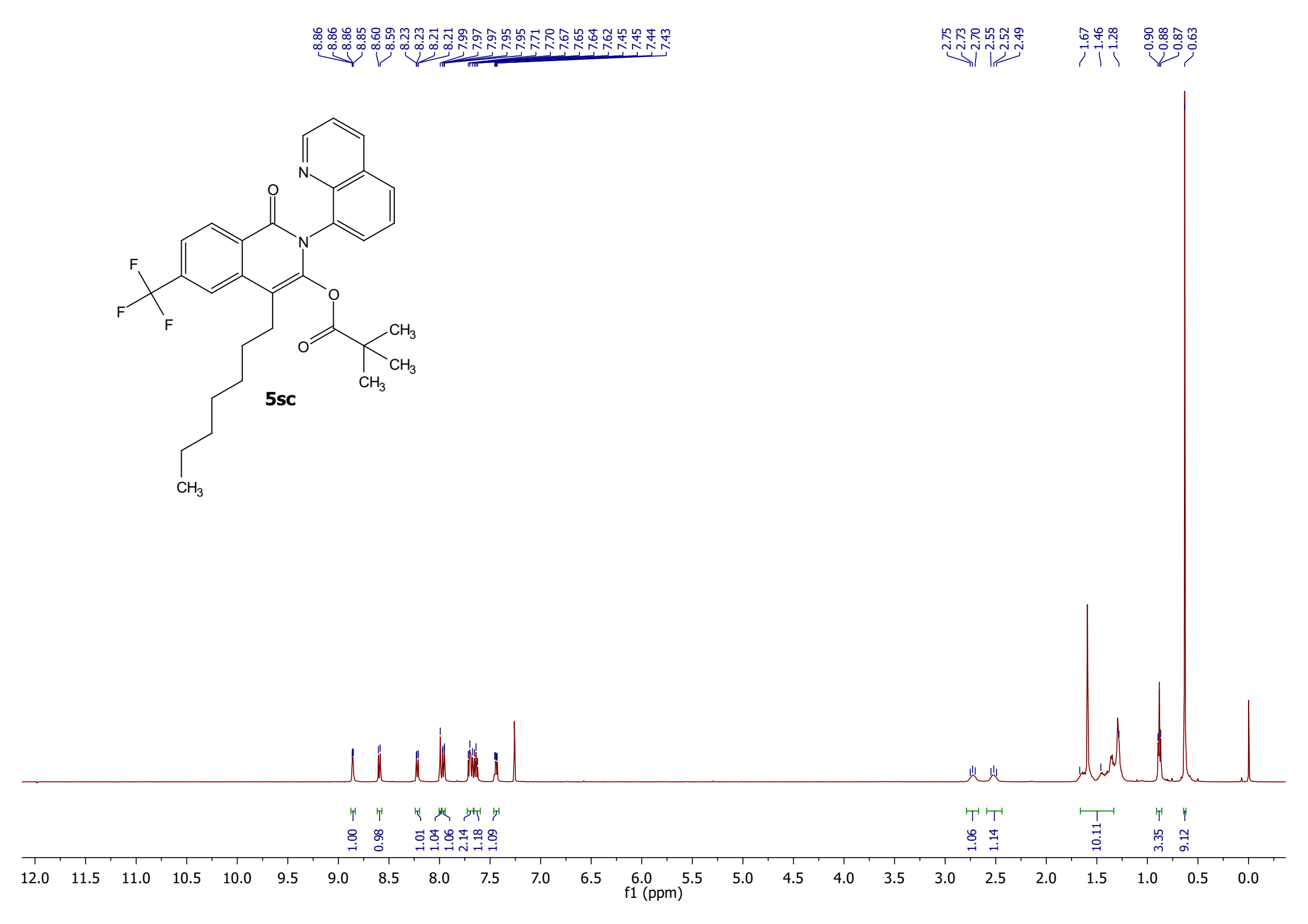
f1 (ppm)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7.95
7.95
7.71
7.70
7.67
7.65
7.64
7.62
7.45
7.45
7.44
7.43
2.75
2.73
2.70
2.55
2.52
2.49
1.67
1.46
1.28
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0.88
0.87
0.63
N
O
N
F
F
F
O
O
CH3
CH3
CH3
CH3
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0.98
1.01
1.04
1.06
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1.18
1.09
1.06
1.14
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
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2.0
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1.0
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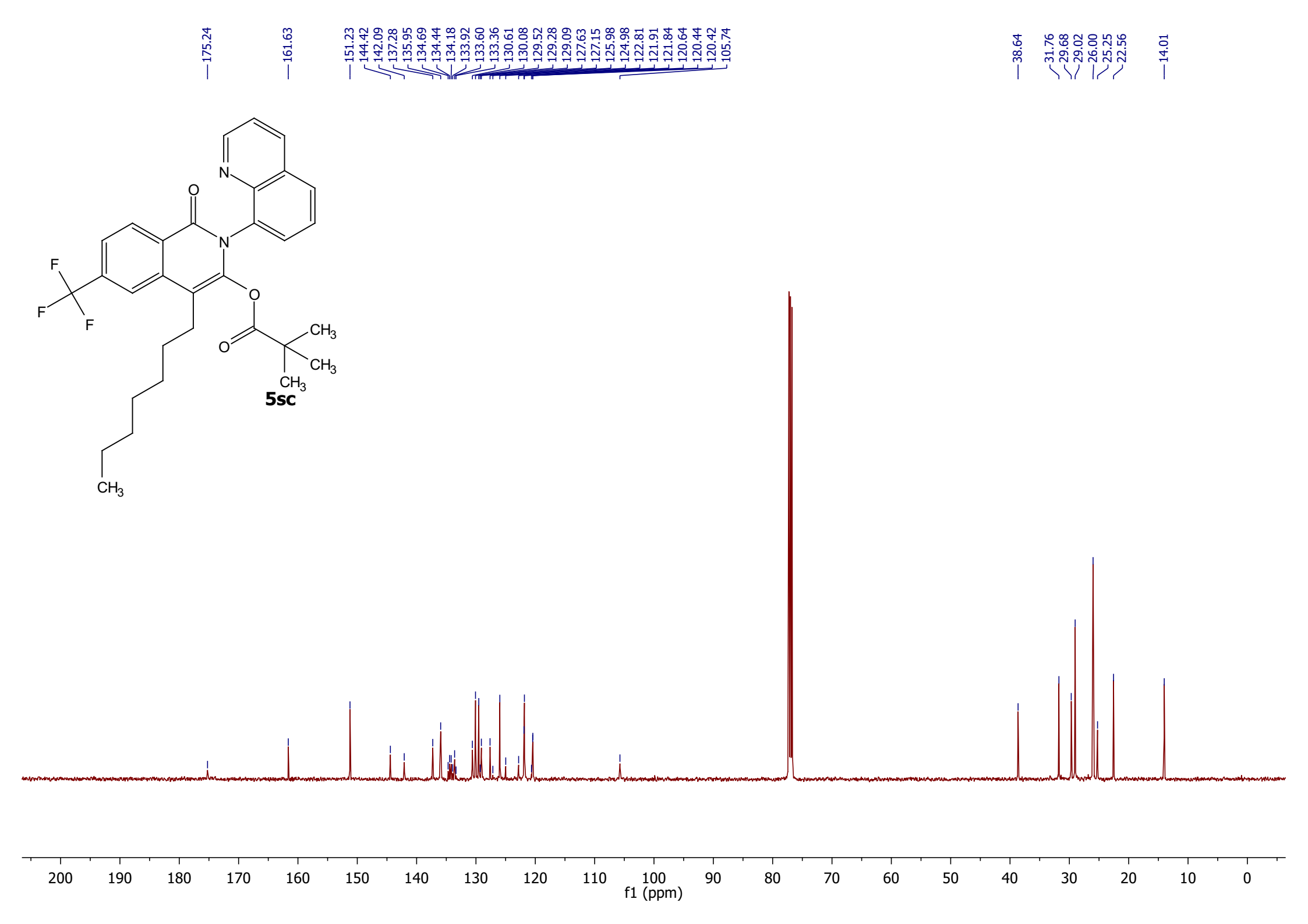
f1 (ppm)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133.92
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130.08
129.52
129.28
129.09
127.63
127.15
125.98
124.98
122.81
121.91
121.84
120.64
120.44
120.42
105.74
38.64
31.76
29.68
29.02
26.00
25.25
22.56
14.01
N
O
N
F
F
F
O
O
CH3
CH3
CH3
CH3
5sc
200
190
180
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130
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110
100
90
80
70
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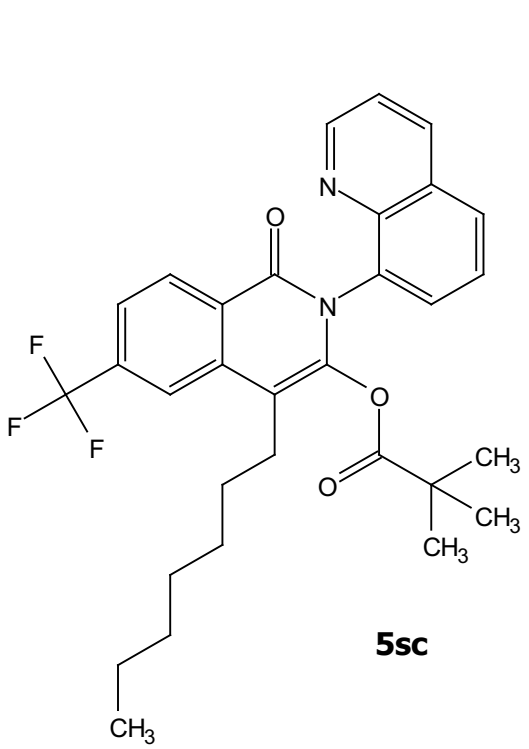
50
40
30
20
10
0
f1 (ppm)


O
N
F
F
F
O
O
CH3
CH3
CH3
CH3

5sc

-65.39
50
30
10
-10
-30
-50
-70
-90
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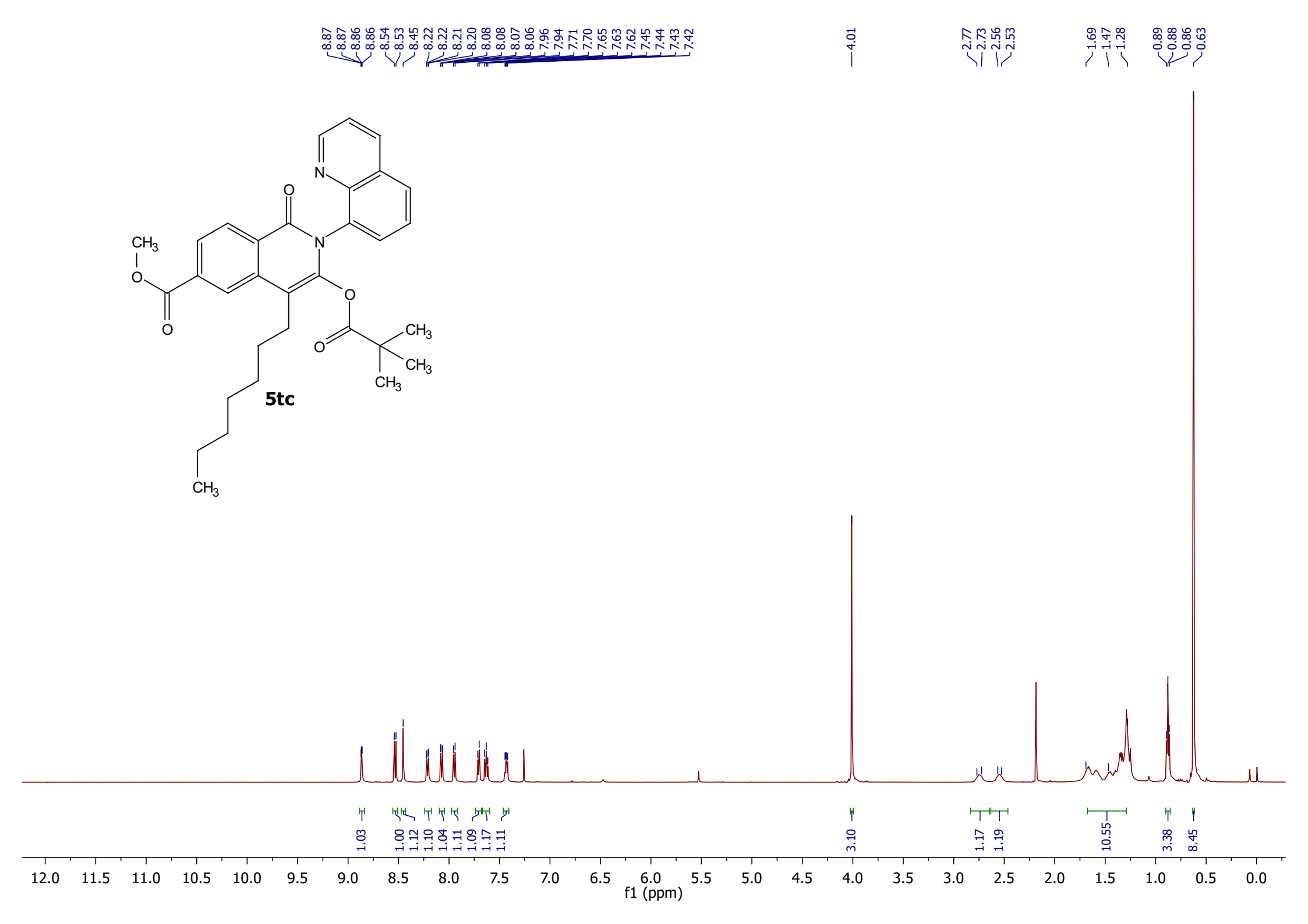
-150
-170
-190
-210
-230
-250
-270
-290
-310
-330
-35
f1 (ppm)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8.21
8.20
8.08
8.08
8.07
8.06
7.96
7.94
7.71
7.70
7.65
7.63
7.62
7.45
7.44
7.43
7.42
4.01
2.77
2.73
2.56
2.53
1.69
1.47
1.28
0.89
0.88
0.86
0.63
5tc
1.03
1.00
1.12
1.10
1.04
1.11
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1.11
3.10
1.17
1.19
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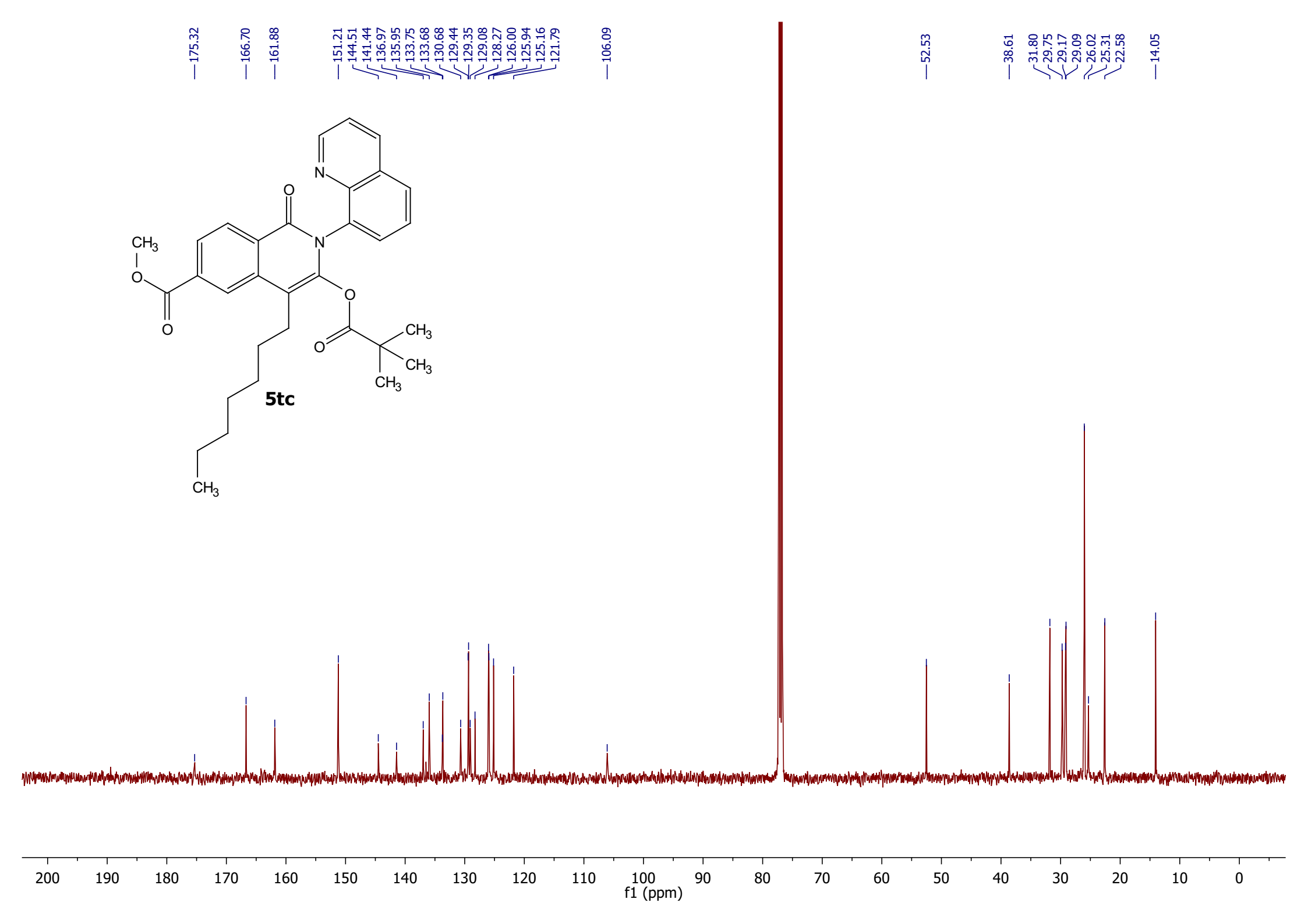
8.45
f1 (ppm)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130.68
129.44
129.35
129.08
128.27
126.00
125.94
125.16
121.79
106.09
52.53
38.61
31.80
29.75
29.17
29.09
26.02
25.31
22.58
14.05
N
O
N
O
O
O
O
CH3
CH3
CH3
CH3
CH3
5tc
200
190
180
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150
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130
120
110
100
90
80
70
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50
40
30
20
10
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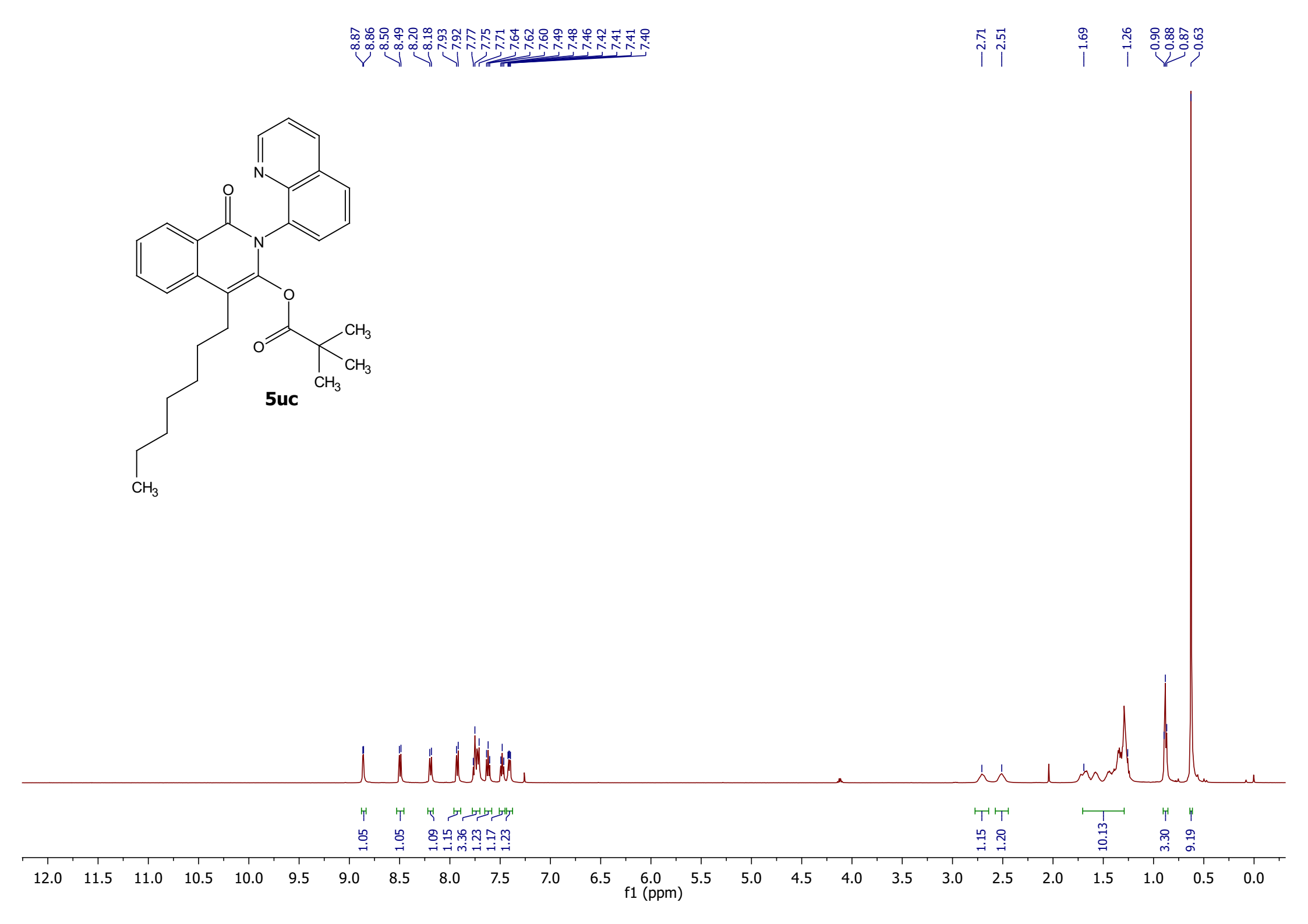
f1 (ppm)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7.60
7.49
7.48
7.46
7.42
7.41
7.41
7.40
2.71
2.51
1.69
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0.88
0.87
0.63
N
O
N
O
O
CH3
CH3
CH3
CH3
5uc
1.05
1.05
1.09
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1.23
1.17
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3.30
9.19
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11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
1.0
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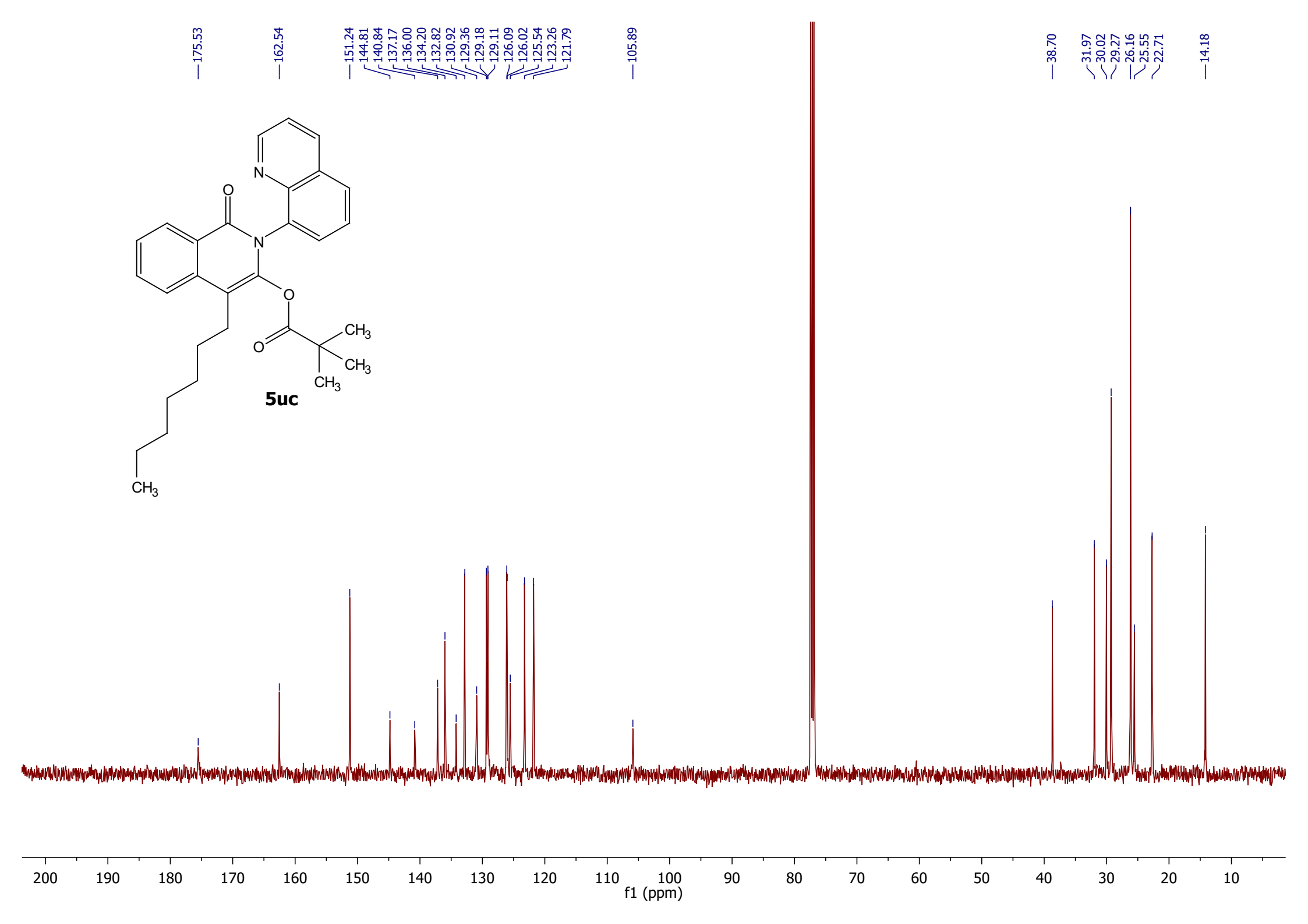
0.0
f1 (ppm)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134.20
132.82
130.92
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126.02
125.54
123.26
121.79
105.89
38.70
31.97
30.02
29.27
26.16
25.55
22.71
14.18
N
O
N
O
O
CH3
CH3
CH3
CH3
5uc
200
190
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140
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120
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100
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80
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60
50
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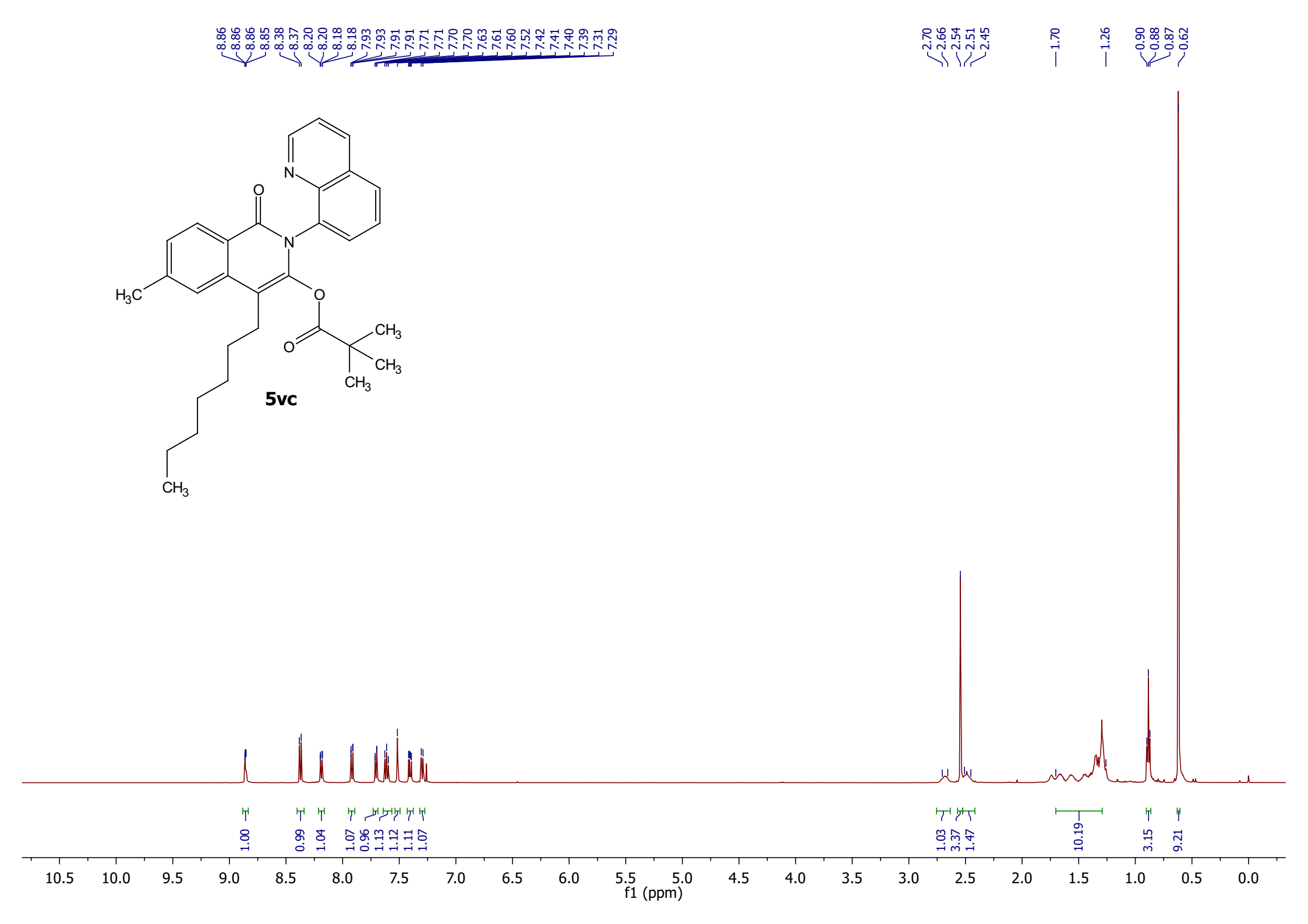
20
10
f1 (ppm)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7.71
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7.70
7.63
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7.60
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7.42
7.41
7.40
7.39
7.31
7.29
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2.54
2.51
2.45
1.70
1.26
0.90
0.88
0.87
0.62
N
O
N
O
O
CH3
CH3
CH3
H3C
CH3
5vc
1.00
0.99
1.04
1.07
0.96
1.13
1.12
1.11
1.07
1.03
3.37
1.47
10.19
3.15
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10.5
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7.5
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6.5
6.0
5.5
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2.5
2.0
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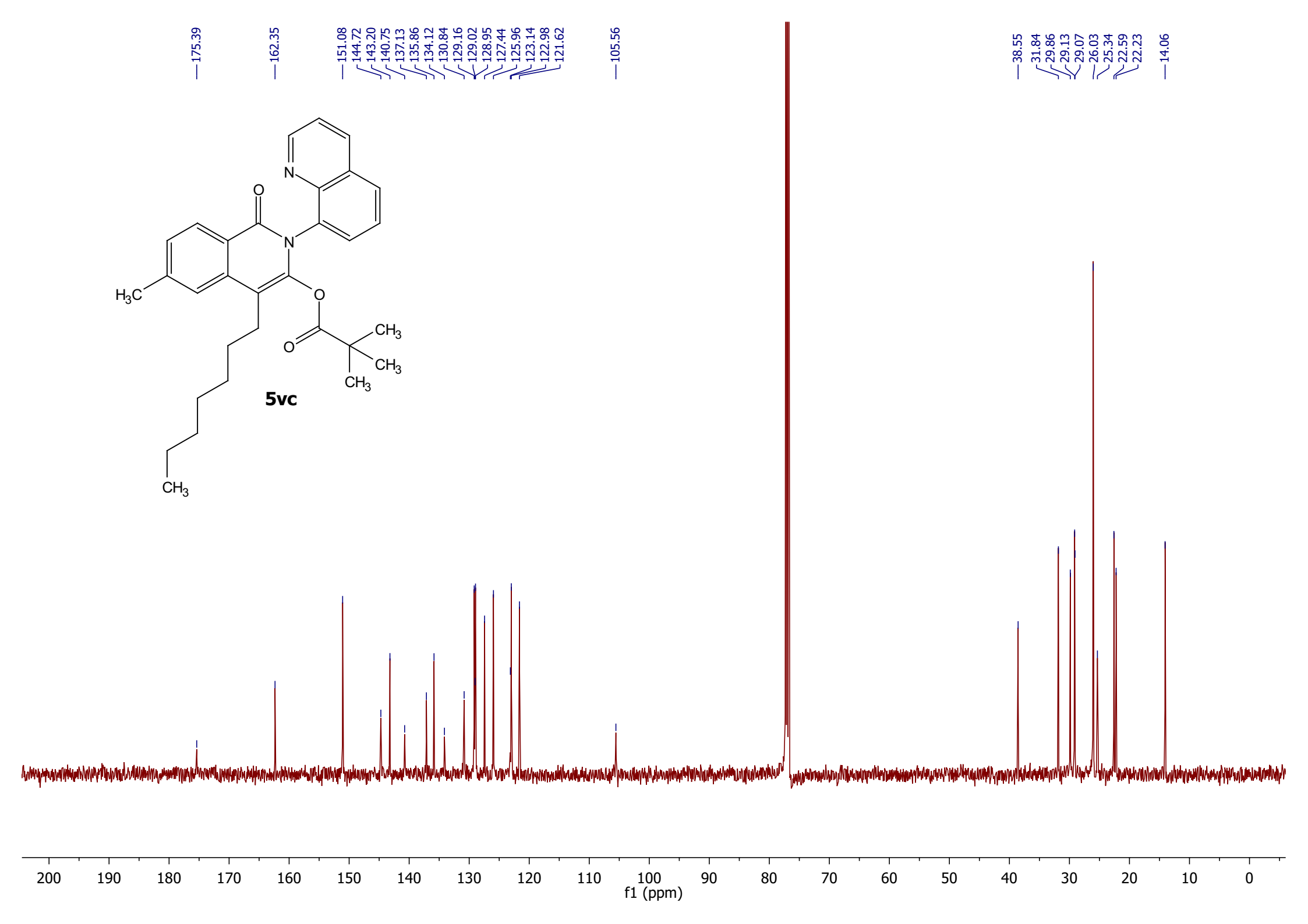
1.0
0.5
0.0
f1 (ppm)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135.86
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129.16
129.02
128.95
127.44
125.96
123.14
122.98
121.62
105.56
38.55
31.84
29.86
29.13
29.07
26.03
25.34
22.59
22.23
14.06
N
O
N
O
H3C
O
CH3
CH3
CH3
CH3
5vc
200
190
180
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160
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130
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110
100
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80
70
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50
40
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20
10
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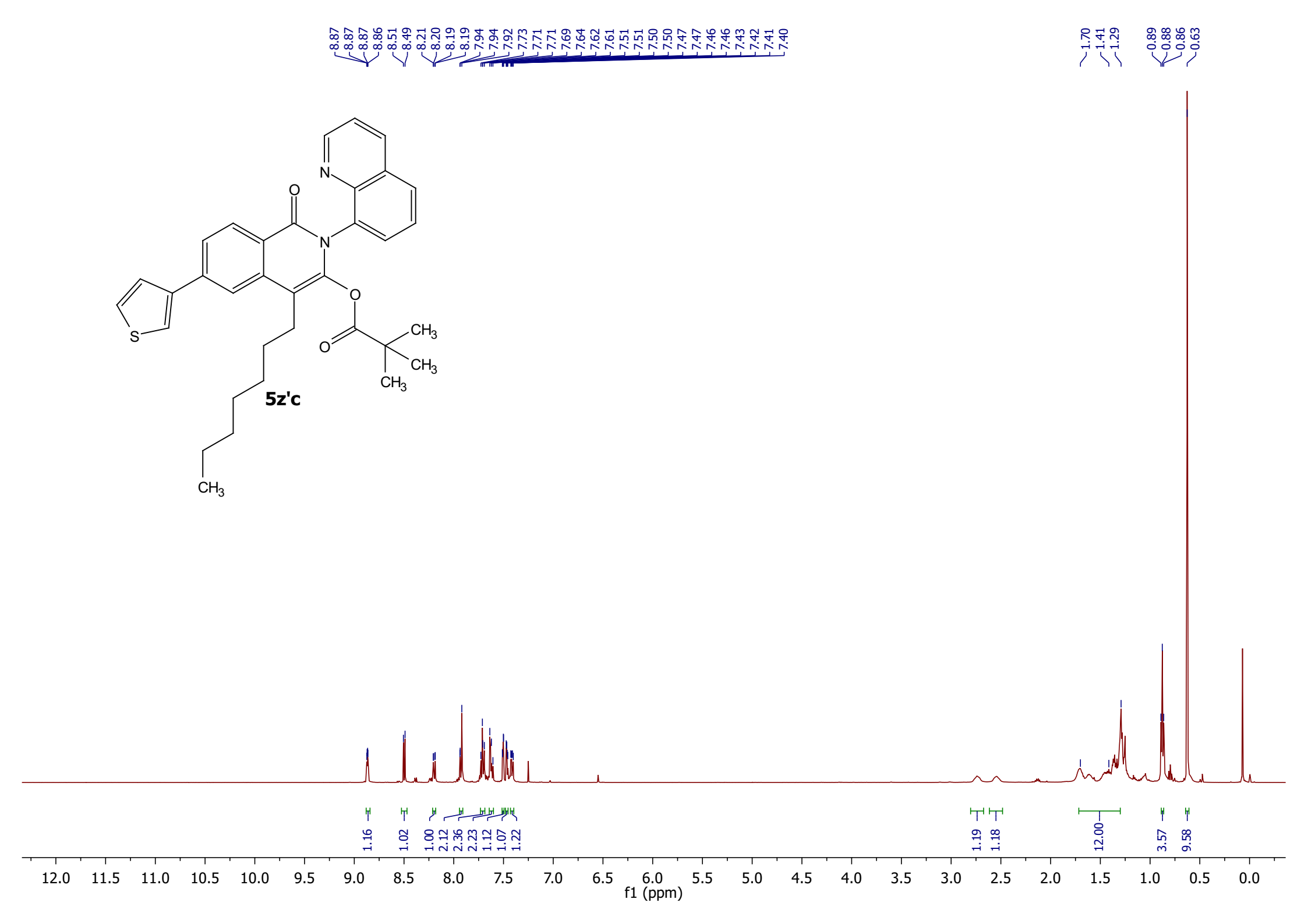
f1 (ppm)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7.94
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7.73
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7.71
7.69
7.64
7.62
7.61
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7.51
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7.50
7.47
7.47
7.46
7.46
7.43
7.42
7.41
7.40
1.70
1.41
1.29
0.89
0.88
0.86
0.63
N
O
N
O
S
O
CH3
CH3
CH3
CH3
5z'c
1.16
1.02
1.00
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2.36
2.23
1.12
1.07
1.22
1.19
1.18
12.00
3.57
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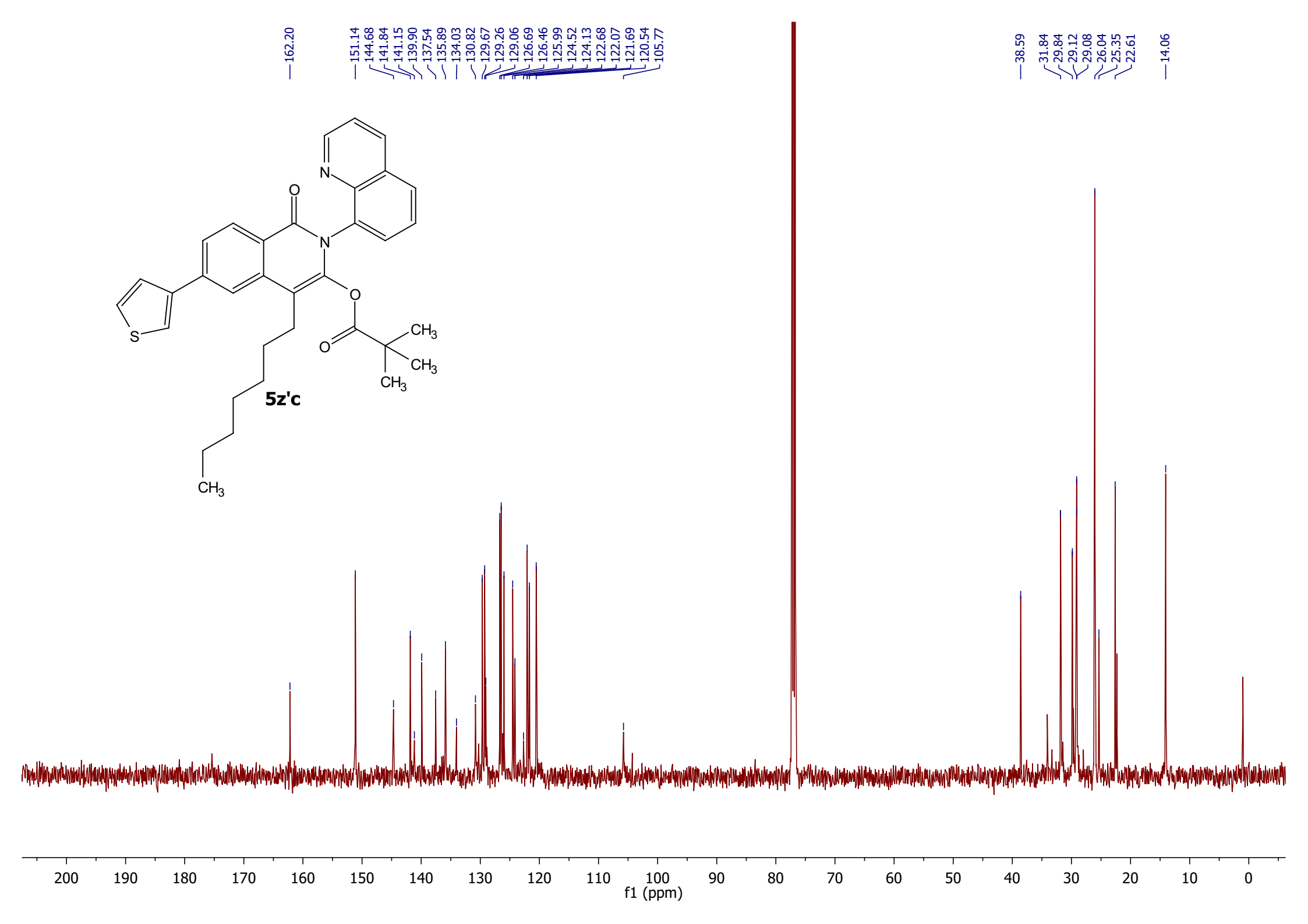
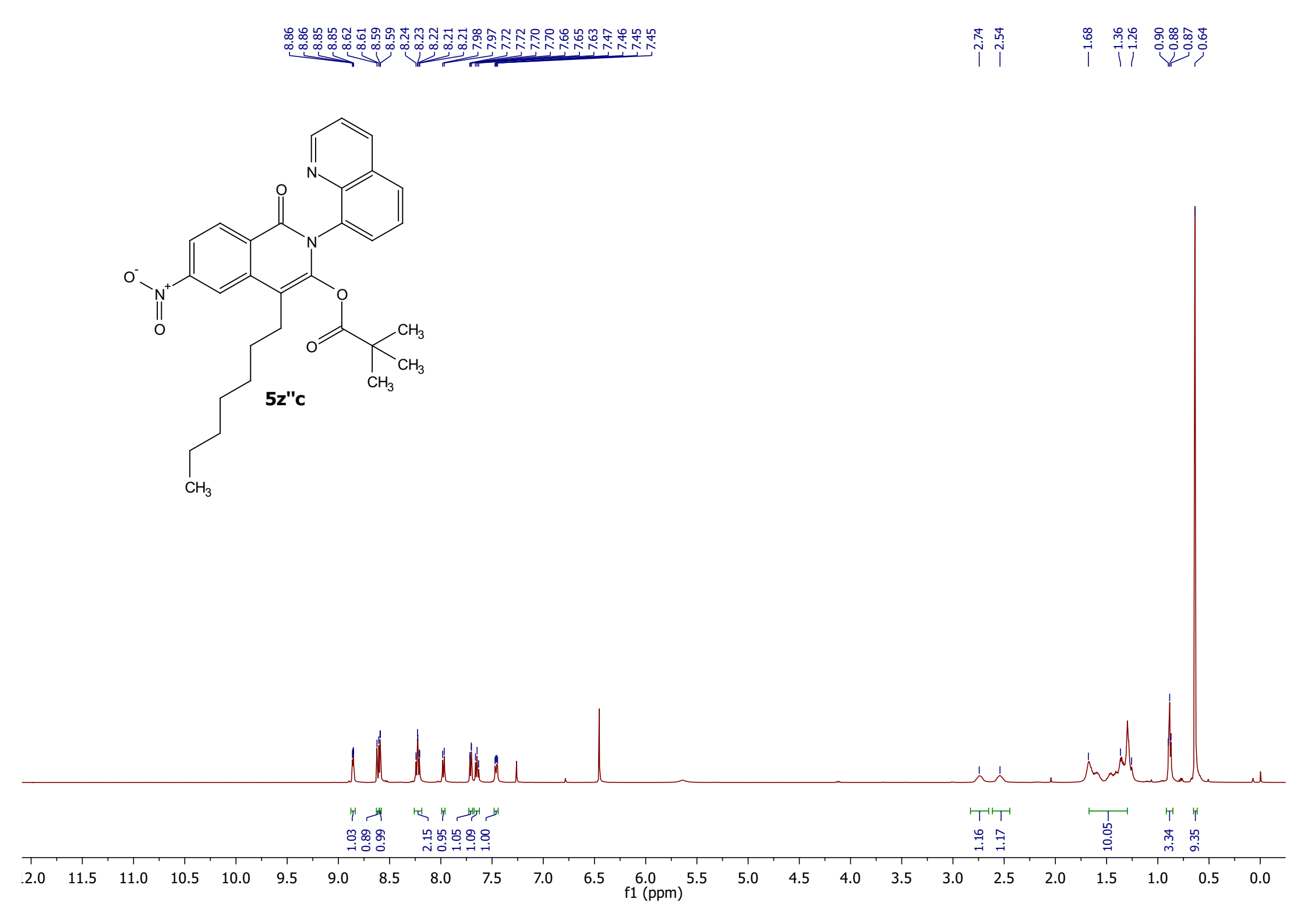
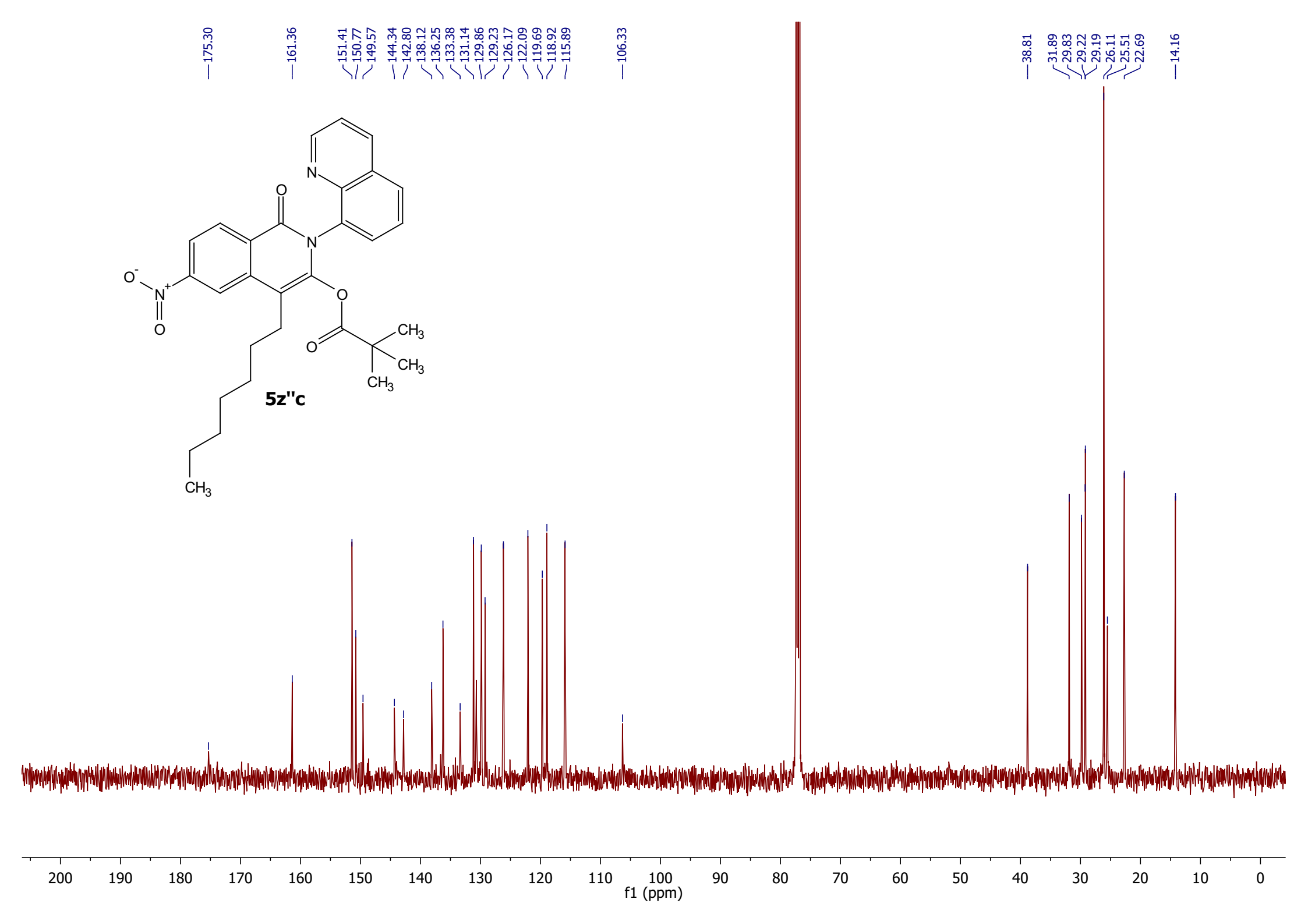
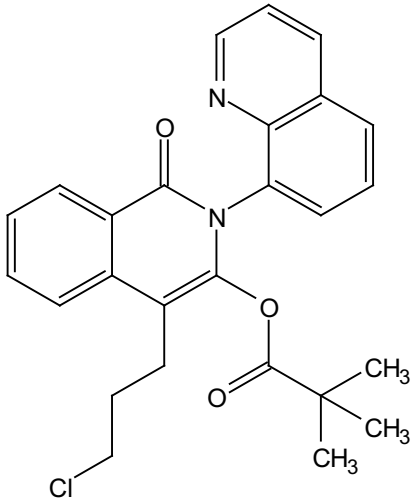
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


162.20
151.14
144.68
141.84
141.15
139.90
137.54
135.89
134.03
130.82
129.67
129.26
129.06
126.69
126.46
125.99
124.52
124.13
122.68
122.07
121.69
120.54
105.77
38.59
31.84
29.84
29.12
29.08
26.04
25.35
22.61
14.06
N
O
N
O
S
O
CH3
CH3
CH3
CH3
5z'c
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

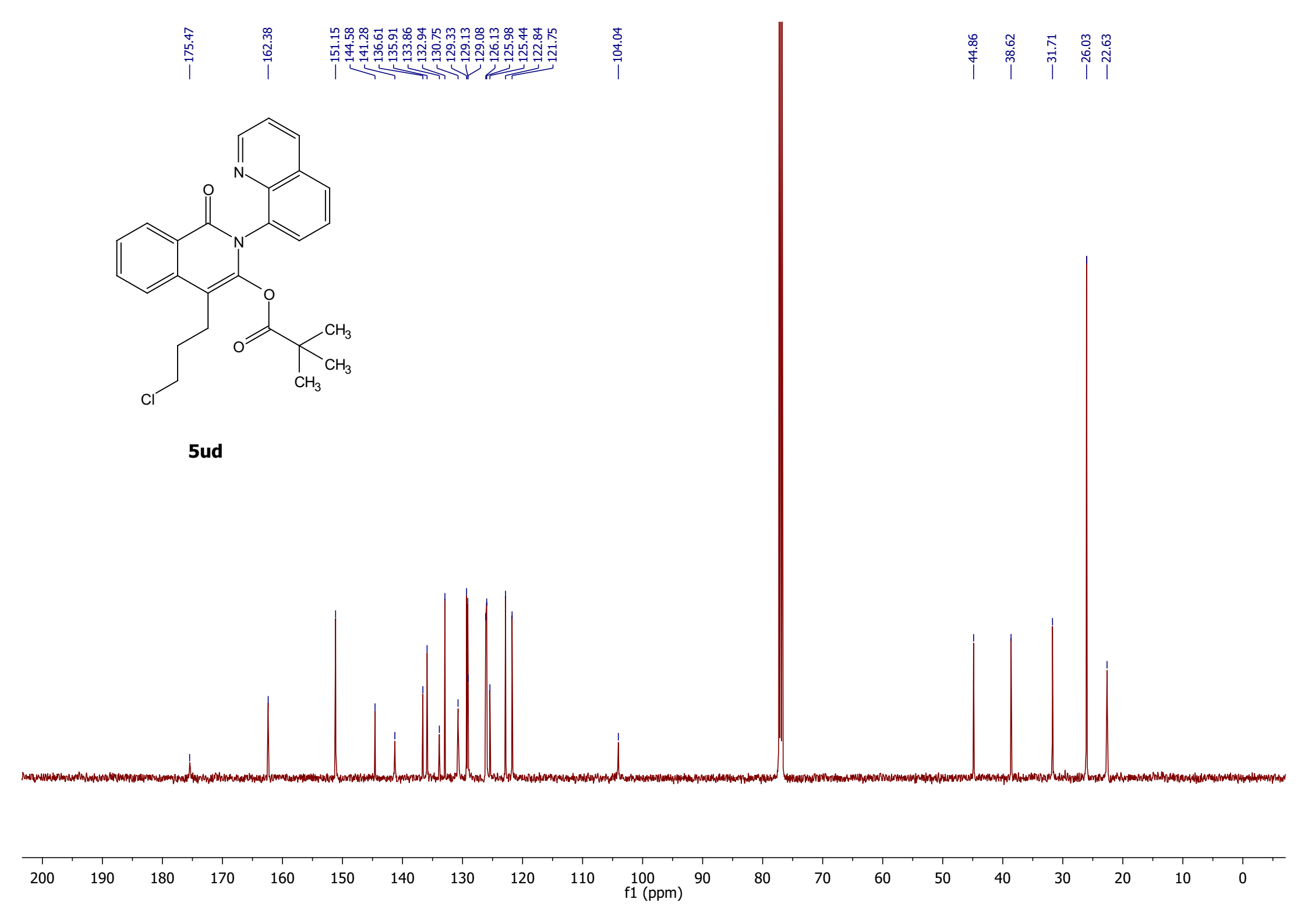

8.86
8.86
8.85
8.85
8.62
8.61
8.59
8.59
8.24
8.23
8.22
8.21
8.21
7.98
7.97
7.72
7.72
7.70
7.70
7.66
7.65
7.63
7.47
7.46
7.45
7.45
2.74
2.54
1.68
1.36
1.26
0.90
0.88
0.87
0.64
5z''c
1.03
0.89
0.99
2.15
0.95
1.05
1.09
1.00
1.16
1.17
10.05
3.34
9.35
f1 (ppm)

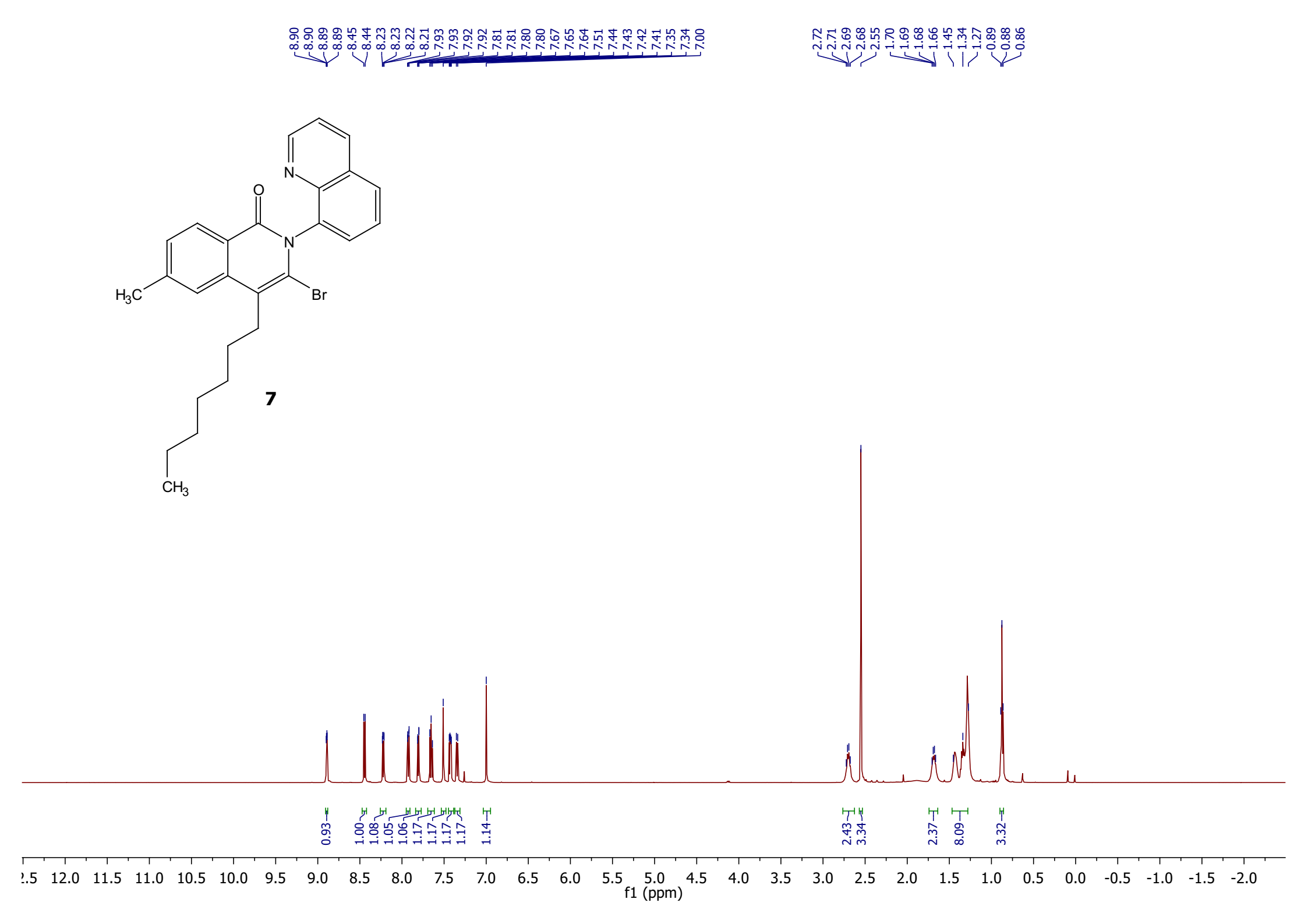

175.30
161.36
151.41
150.77
149.57
144.34
142.80
138.12
136.25
133.38
131.14
129.86
129.23
126.17
122.09
119.69
118.92
115.89
106.33
38.81
31.89
29.83
29.22
29.19
26.11
25.51
22.69
14.16
5z''c
f1 (ppm)

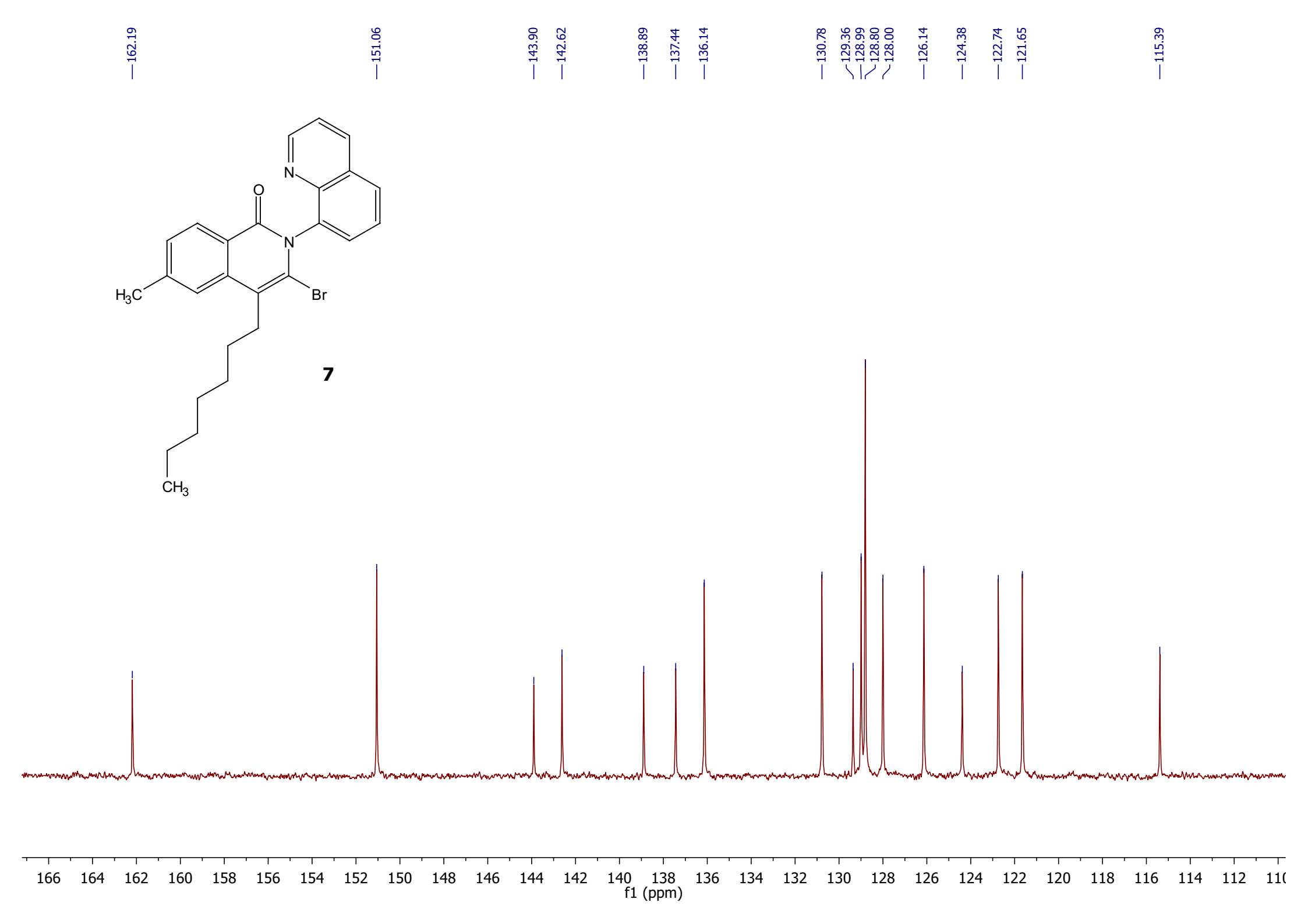

N
O
N
O
O
CH3
CH3
CH3
Cl

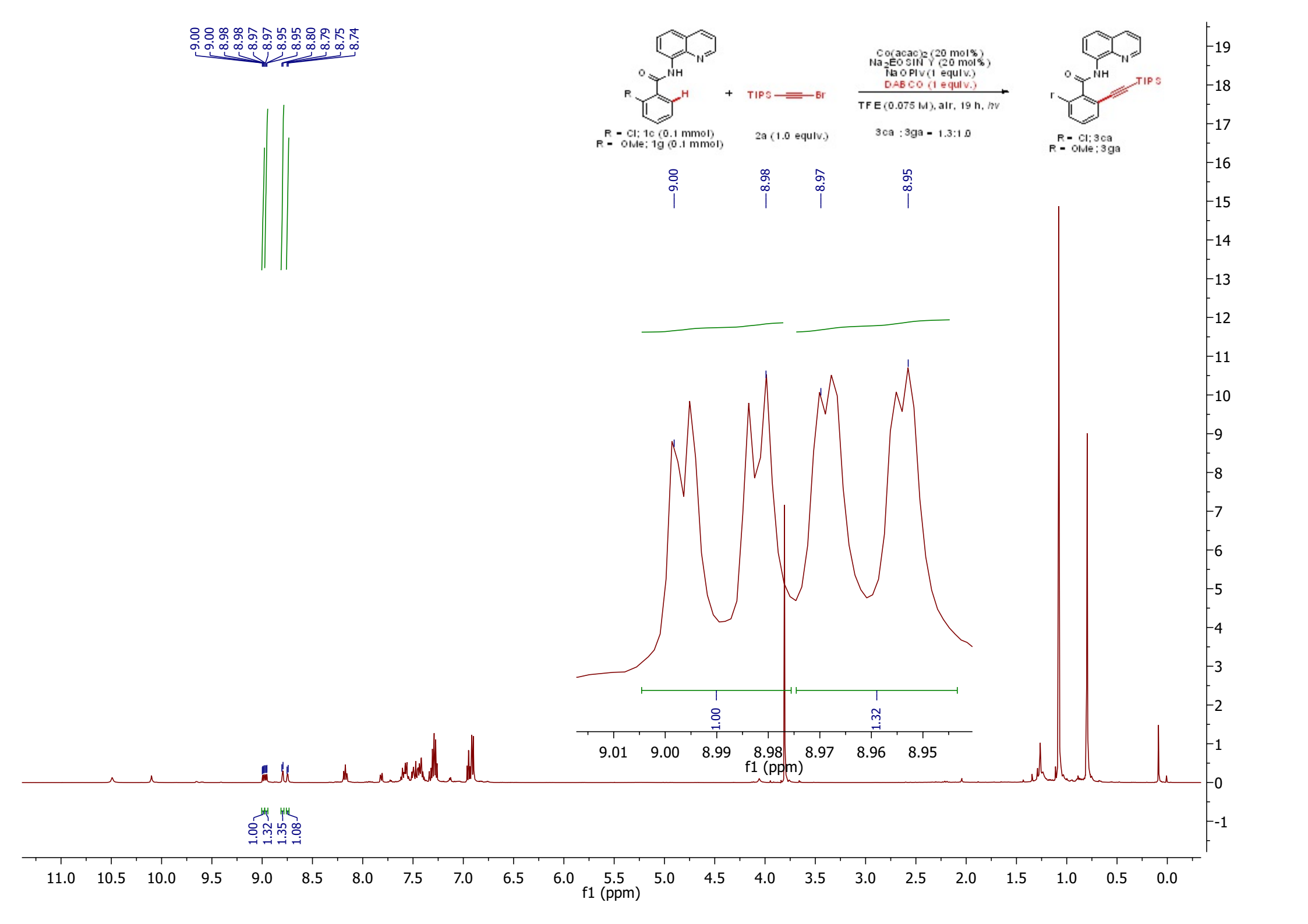
5ud

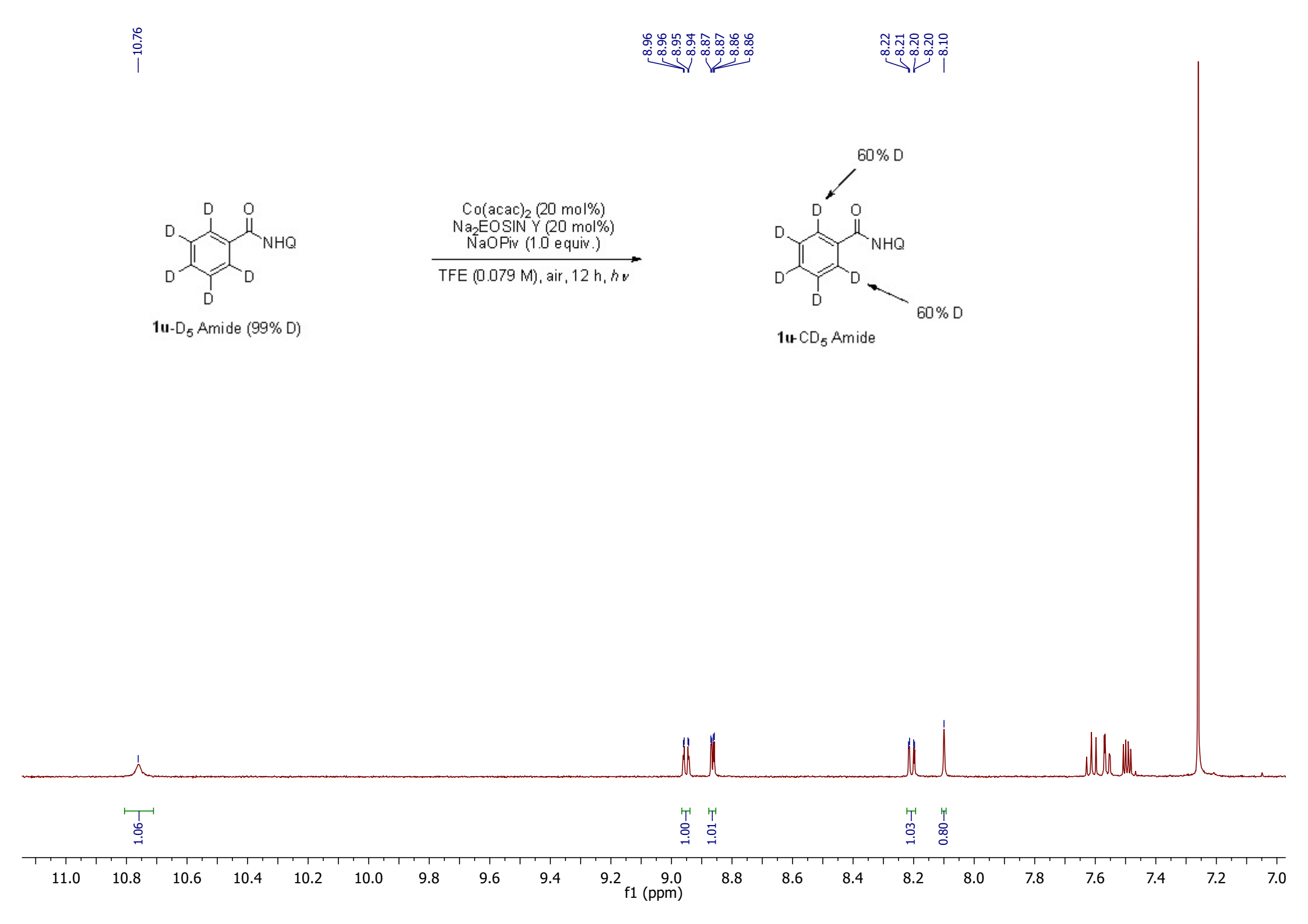
8.87
8.86
8.86
8.85
8.51
8.49
8.21
8.21
8.19
8.19
7.95
7.94
7.93
7.93
7.76
7.76
7.75
7.70
7.64
7.63
7.61
7.51
7.51
7.50
7.48
7.43
7.42
7.42
7.41
3.68
3.67
3.66
2.89
2.76
2.74
2.70
2.21
2.17
2.14
2.06
0.62
1.00
1.05
1.14
1.13
3.22
1.15
1.13
1.17
2.58
1.22
1.34
2.25
9.16
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

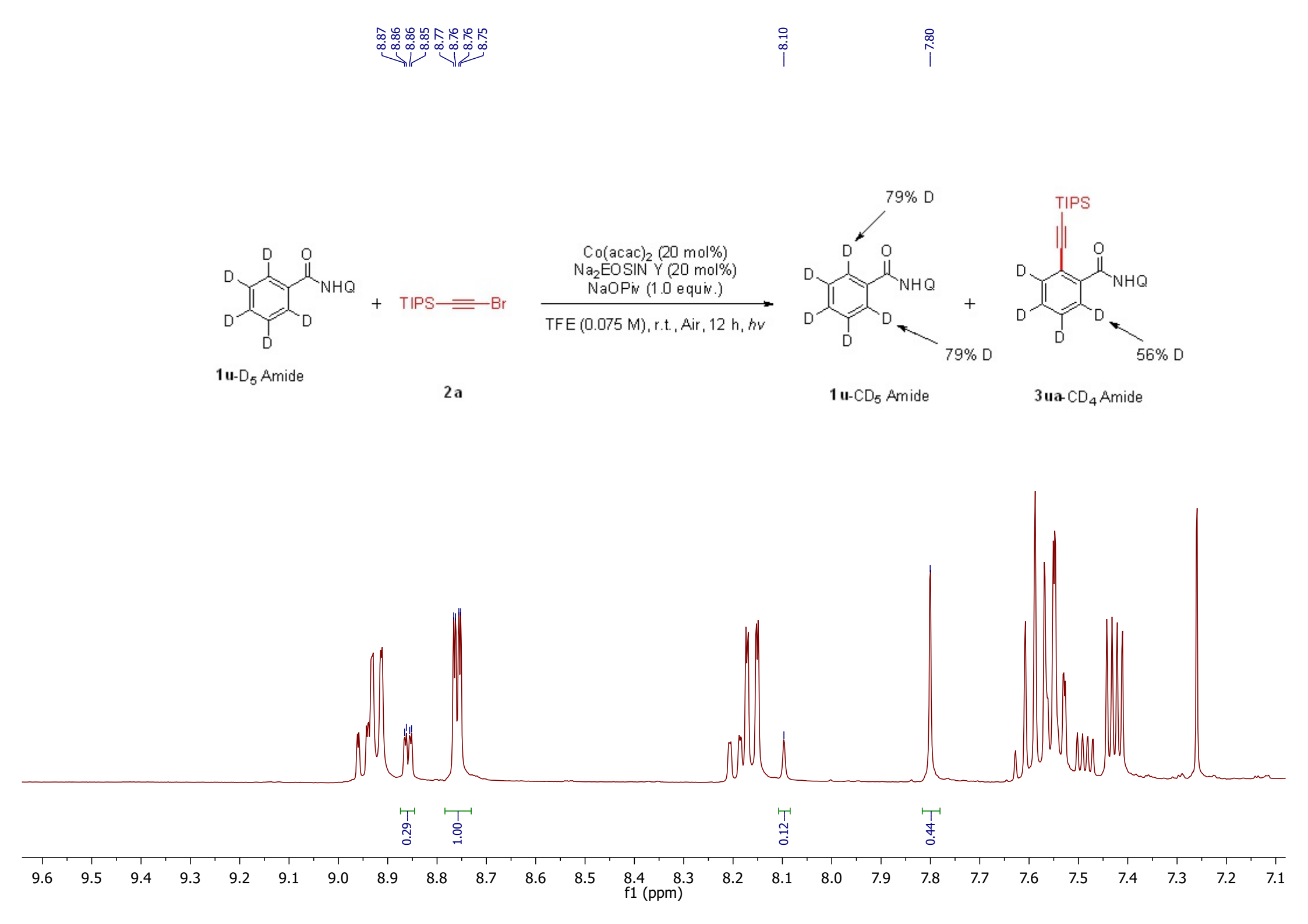

175.47
162.38
151.15
144.58
141.28
136.61
135.91
133.86
132.94
130.75
129.33
129.13
129.08
126.13
125.98
125.44
122.84
121.75
104.04
44.86
38.62
31.71
26.03
22.63
N
O
N
O
O
CH3
CH3
CH3
Cl
5ud
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.90
8.90
8.89
8.89
8.45
8.44
8.23
8.23
8.22
8.21
7.93
7.93
7.92
7.92
7.81
7.81
7.80
7.80
7.67
7.65
7.64
7.51
7.44
7.43
7.42
7.41
7.35
7.34
7.00
2.72
2.71
2.69
2.68
2.55
1.70
1.69
1.68
1.66
1.45
1.34
1.27
0.89
0.88
0.86
N
O
N
H3C
Br
CH3
7
0.93
1.00
1.08
1.05
1.06
1.17
1.17
1.17
1.17
1.14
2.43
3.34
2.37
8.09
3.32
f1 (ppm)


162.19
151.06
143.90
142.62
138.89
137.44
136.14
130.78
129.36
128.99
128.80
128.00
126.14
124.38
122.74
121.65
115.39
N
O
N
H3C
Br
CH3
7
166
164
162
160
158
156
154
152
150
148
146
144
142
140
138
136
134
132
130
128
126
124
122
120
118
116
114
112
f1 (ppm)


9.00
9.00
8.98
8.98
8.97
8.97
8.95
8.95
8.80
8.79
8.75
8.74
Co(acac)2 (20 mol%)
NaEOSIN Y (20 mol%)
NaOPiv (1 equiv.)
DABCO (1 equiv.)
TFE (0.075 M), air, 19 h, hv
R = Cl; 1c (0.1 mmol)
R = OMe; 1g (0.1 mmol)
2a (1.0 equiv.)
3ca : 3ga = 1.3:1.0
R = Cl; 3ca
R = OMe; 3ga
9.00
8.98
8.97
8.95
1.00
1.32
1.35
1.08
f1 (ppm)


10.76
8.96
8.96
8.95
8.94
8.87
8.87
8.86
8.86
8.22
8.21
8.20
8.20
8.10
D
O
D
NHQ
D
D
D
D
1u-D5 Amide (99% D)
Co(acac)2 (20 mol%)
Na2EOSIN Y (20 mol%)
NaOPiv (1.0 equiv.)
TFE (0.079 M), air, 12 h, hν
60% D
60% D
1u-CD5 Amide
1.06
1.00
1.01
1.03
0.80
11.0
10.8
10.6
10.4
10.2
10.0
9.8
9.6
9.4
9.2
9.0
8.8
8.6
8.4
8.2
8.0
7.8
7.6
7.4
7.2
7.0
f1 (ppm)


8.87
8.86
8.86
8.85
8.77
8.76
8.76
8.75
8.10
7.80
D
O
NHQ
D
D
D
D
+
TIPS
Br
Co(acac)2 (20 mol%)
Na2EOSIN Y (20 mol%)
NaOPiv (1.0 equiv.)
TFE (0.075 M), r.t., Air, 12 h, hv
79% D
79% D
+
TIPS
56% D
1u-D5 Amide
2a
1u-CD5 Amide
3ua-CD4 Amide
0.29
1.00
0.12
0.44
9.6
9.5
9.4
9.3
9.2
9.1
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
f1 (ppm)