

SUPPORTING INFORMATION

Cobalt-Promoted Dimerization of Aminoquinoline Benzamides

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General considerations

Reactions were performed using standard glassware or were run in 2-dram vials with PTFE/Liner screw caps and 60 mL vials using screw caps. Column chromatography was performed on 60Å silica gel (Dynamic Adsorbents Inc.). ^1H , ^{13}C , ^{19}F -NMR and 2D-NMR spectra were recorded on JEOL EC-500 spectrometer using residual solvent peak as a reference. HRMS analysis was performed by electrospray ionization (ESI) using Agilent Technologies 6530 Accurate Mass QToF/MS spectrometer at the Mass Spectrometry Facility of the Department of Chemistry and Biochemistry of University of Texas-Austin. IR-spectra were obtained using a Perkin Elmer Spectrum 100 FT-IR spectrometer. Analytical thin layer chromatography was performed on silica gel IB-F (Baker-flex) by J. T. Baker. All procedures were performed under ambient air unless otherwise noted. Reagents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted. Room temperature is 23 °C.

Substrate synthesis

Amides were synthesized according to literature procedures from 8-aminoquinoline and corresponding acyl chloride (Procedure A)¹ or carboxylic acid (Procedure B)².

Procedure A:

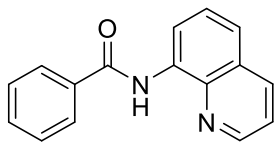
Synthesis of N-(quinolin-8-yl)benzamide is representative.

To a solution of 8-aminoquinoline (3.00 g, 21 mmol) and *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol) in anhydrous CH_2Cl_2 (30 mL) under nitrogen Et_3N (3.3 mL, 24 mmol, 1.2 equiv) was added and resulting solution was cooled to 0 °C. Benzoyl chloride (2.3 mL, 20 mmol) was added dropwise and reaction mixture was stirred at room temperature overnight. The mixture was quenched with water (30 mL) and extracted with CH_2Cl_2 (3 x 20 mL). Combined organic phase was dried over MgSO_4 and filtered. Concentration in vacuum followed by recrystallization from toluene afforded 4.6 g (94%) of *N*-(quinolin-8-yl)benzamide as a white solid.

¹ Grigorjeva, L.; Daugulis, O. *Org. Lett.*, **2014**, *16*, 4684.

² Ano, Y.; Tobisu, M.; Chatani, N. *Org. Lett.*, **2012**, *14*, 354.

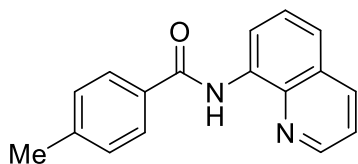
***N*-(Quinolin-8-yl)benzamide**



This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.76 (s, 1H), 8.95 (dd, J = 7.6, 1.3 Hz, 1H), 8.85 (dd, J = 4.2, 1.6 Hz, 1H), 8.19 (dd, J = 8.3, 1.6 Hz, 1H), 8.14-8.04 (m, 2H), 7.68 – 7.52 (m, 5H) and 7.48 (dd, J = 8.2, 4.2 Hz, 1H).

4-Methyl-*N*-(quinolin-8-yl)benzamide

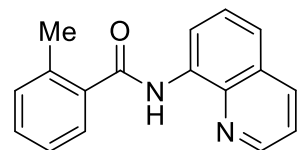


8-Aminoquinoline (6.00 g, 42 mmol), *N,N*-dimethyl-4-aminopyridine (160 mg, 1.3 mmol), Et₃N (6.6 mL, 48 mmol, 1.2 equiv), 4-toluoyl chloride (5.3 mL, 40 mmol), CH₂Cl₂ (60 mL). Recrystallization from toluene afforded 9.0 g (86%) of amide 4-methyl-*N*-(quinolin-8-

yl)benzamide as a white solid. This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.73 (s, 1H), 8.94 (dd, J = 7.6, 1.3 Hz, 1H), 8.85 (dd, J = 4.2, 1.7 Hz, 1H), 8.18 (dd, J = 8.3, 1.7 Hz, 1H), 8.02 – 7.96 (m, 2H), 7.59 (t, J = 7.9 Hz, 1H), 7.53 (dd, J = 8.3, 1.3 Hz, 1H), 7.47 (dd, J = 8.2, 4.2 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 2.45 (s, 3H).

2-Methyl-*N*-(quinolin-8-yl)benzamide

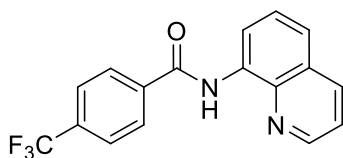


8-Aminoquinoline (3.00 g, 21 mmol), *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), Et₃N (3.3 mL, 24 mmol, 1.2 equiv), 2-toluoyl chloride (2.6 mL, 20 mmol), CH₂Cl₂ (30 mL). Recrystallization from hexanes/EtOAc 1:1 afforded 3.91 g (75%) of 2-methyl-*N*-(quinolin-8-

yl)benzamide as a white solid. This compound is known.³

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.22 (s, 1H), 8.95 (d, J = 7.3 Hz, 1H), 8.78 (dd, J = 4.2, 1.7 Hz, 1H), 8.19 (dd, J = 8.3, 1.6 Hz, 1H), 7.69 (d, J = 7.7 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.46 (dd, J = 8.3, 4.2 Hz, 1H), 7.41 (td, J = 7.5, 1.4 Hz, 1H), 7.33 (t, J = 8.0 Hz, 2H) and 2.61 (s, 3H).

4-Trifluoromethyl-*N*-(quinolin-8-yl)benzamide 4



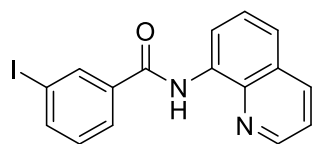
8-Aminoquinoline (3.00 g, 21 mmol), *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), Et₃N (3.3 mL, 24 mmol, 1.2 equiv), 4-trifluoromethylbenzoyl chloride (3.0 mL, 20 mmol), CH₂Cl₂ (30 mL).

Recrystallization from hexanes/EtOAc 4:1 afforded 5.50 g (88%) of 4-trifluoromethyl-*N*-(quinolin-8-yl)benzamide as a white solid. This compound is known.¹

³ Grigorjeva, L.; Daugulis, O. *Org. Lett.*, **2014**, *16*, 4688.

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.80 (s, 1H), 8.92 (dd, *J* = 7.2, 1.7 Hz, 1H), 8.86 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.25 – 8.16 (m, 3H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.65 – 7.56 (m, 2H) and 7.51 (dd, *J* = 8.3, 4.2 Hz, 1H).

3-Iodo-*N*-(quinolin-8-yl)benzamide **5**

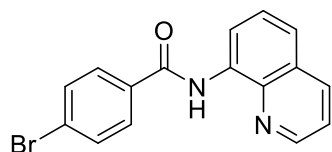


8-Aminoquinoline (1.50 g, 10.5 mmol), *N,N*-dimethyl-4-aminopyridine (40 mg, 0.33 mmol), Et₃N (1.65 mL, 12 mmol, 1.2 equiv), 3-iodobenzoyl chloride (2.67 g, 10 mmol), CH₂Cl₂ (15 mL). Recrystallization from hexanes/EtOAc 2:1 afforded 3.46 g (93%) of 3-iodo-*N*-(quinolin-8-yl)benzamide as a white solid.

This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.67 (s, 1H), 8.90 (dd, *J* = 7.4, 1.6 Hz, 1H), 8.86 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.41 (t, *J* = 1.7 Hz, 1H), 8.20 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.02 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.49 (dd, *J* = 8.2, 4.2 Hz, 1H) and 7.29 (t, *J* = 7.8 Hz, 1H).

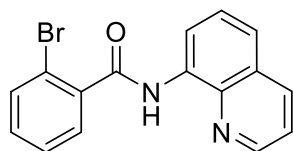
4-Bromo-*N*-(quinolin-8-yl)benzamide



8-Aminoquinoline (3.00 g, 21 mmol), *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), Et₃N (3.3 mL, 24 mmol, 1.2 equiv), 4-bromobenzoyl chloride (4.39 g, 20 mmol), CH₂Cl₂ (30 mL). Recrystallization from toluene afforded 5.84 g (89%) of 4-bromo-*N*-(quinolin-8-yl)benzamide as a white solid. This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.71 (s, 1H), 8.90 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.85 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.19 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.71 – 7.65 (m, 2H), 7.62 – 7.53 (m, 2H) and 7.48 (dd, *J* = 8.3, 4.2 Hz, 1H).

2-Bromo-*N*-(quinolin-8-yl)benzamide



8-Aminoquinoline (3.00 g, 21 mmol), *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), Et₃N (3.3 mL, 24 mmol, 1.2 equiv), 2-bromobenzoyl chloride (2.6 mL, 20 mmol), CH₂Cl₂ (50 mL). Recrystallization from hexanes/EtOAc 2:1 afforded 5.11 g (78%) of 2-bromo-*N*-(quinolin-8-yl)benzamide as a white solid. *R*_f = 0.78 (hexanes/EtOAc 3:1), mp 161 – 163 °C (hexanes/EtOAc 2:1).

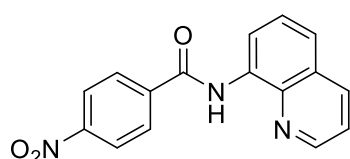
¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.30 (s, 1H), 8.95 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.78 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.7 Hz, 1H), 7.71 (dd, *J* = 7.6, 1.7 Hz, 1H), 7.69 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.47 – 7.42 (m, 2H), 7.37 – 7.32 (m, 1H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 165.9, 148.3, 138.5, 138.3, 136.3, 134.3, 133.6, 131.5, 129.5, 127.9, 127.6, 127.4, 122.1, 121.7, 119.7, 116.8.

HRMS (ESI) calcd. for C₁₆H₁₂BrN₂O [M+H]⁺: 327.0128; found: 327.0131.

FT-IR (neat, cm⁻¹) ν 1671, 1522, 1483, 1423, 1324.

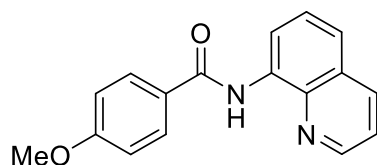
4-Nitro-*N*-(quinolin-8-yl)benzamide



8-Aminoquinoline (3.00 g, 21 mmol), *N,N*-dimethyl-4-aminopyridine (80 mg, 0.65 mmol), Et₃N (3.3 mL, 24 mmol, 1.2 equiv), 4-nitrobenzoyl chloride (3.71 g, 20 mmol), CH₂Cl₂ (30 mL). Recrystallization from hexanes/EtOAc 4:1 afforded 5.67 g (97%) of 4-nitro-*N*-(quinolin-8-yl)benzamide as a yellow solid. This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.83 (s, 1H), 8.91 (dd, *J* = 6.4, 2.5 Hz, 1H), 8.87 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.45 – 8.36 (m, 2H), 8.26-8.22 (m, 3H), 7.64-7.60 (m, 2H) and 7.52 (dd, *J* = 8.3, 4.2 Hz, 1H).

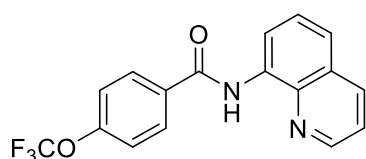
4-Methoxy-*N*-(quinolin-8-yl)benzamide 3



8-Aminoquinoline (1.44 g, 10 mmol), *N,N*-dimethyl-4-aminopyridine (40 mg, 0.33 mmol), Et₃N (1.7 mL, 12 mmol, 1.2 equiv), 4-methoxybenzoyl chloride (1.71 g, 10 mmol), CH₂Cl₂ (40 mL). Recrystallization from hexanes/EtOAc 4:1 afforded 2.31 g (83%) of 4-methoxy-*N*-(quinolin-8-yl)benzamide as a white solid. This compound is known.³

¹H-NMR (400 MHz, CDCl₃, ppm) δ 10.68 (s, 1H), 8.93 (dd, *J* = 7.6, 1.3 Hz, 1H), 8.84 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.09 – 8.04 (m, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.52 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 4.2 Hz, 1H), 7.07 – 7.01 (m, 2H), 3.89 (s, 3H).

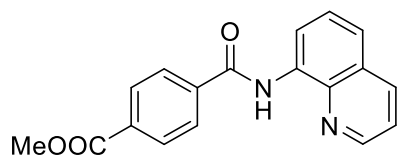
4-Trifluoromethoxy-*N*-(quinolin-8-yl)benzamide



8-Aminoquinoline (721 mg, 5 mmol), *N,N*-dimethyl-4-aminopyridine (20 mg, 0.16 mmol), Et₃N (0.8 mL, 6 mmol, 1.2 equiv), 4-trifluoromethoxybenzoyl chloride (0.8 mL, 5 mmol), CH₂Cl₂ (15 mL). Recrystallization from hexanes/Et₂O 3:1 afforded 1.34 g (81%) of 4-trifluoromethoxy-*N*-(quinolin-8-yl)benzamide as a white solid. This compound is known.³

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.71 (s, 1H), 8.90 (dd, *J* = 7.4, 1.4 Hz, 1H), 8.83 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.17 (dd, *J* = 8.3, 1.6 Hz, 1H), 8.14 – 8.08 (m, 2H), 7.61 – 7.52 (m, 2H), 7.46 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H).

Methyl 4-(quinolin-8-ylcarbamoyl)benzoate

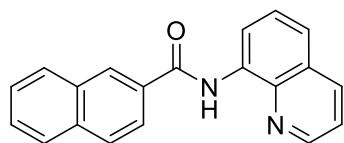


8-Aminoquinoline (721 mg, 5 mmol), *N,N*-dimethyl-4-aminopyridine (20 mg, 0.16 mmol), Et₃N (0.8 mL, 6 mmol, 1.2 equiv), acid chloride (993 mg, 5 mmol), CH₂Cl₂ (15 mL).

Recrystallization from hexanes/EtOAc 4:1 afforded 1.21 g (79%) of methyl 4-(quinolin-8-ylcarbamoyl)benzoate as a white solid. This compound is known.³

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.78 (s, 1H), 8.92 (dd, *J* = 7.4, 1.5 Hz, 1H), 8.85 (dd, *J* = 4.2, 1.6 Hz, 1H), 8.25 – 8.15 (m, 3H), 8.15 – 8.11 (m, 2H), 7.63 – 7.54 (m, 2H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 3.97 (s, *J* = 4.3 Hz, 3H).

N-(8-Quinoliny)-2-naphthamide

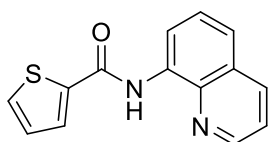


8-Aminoquinoline (1.514 g, 10.5 mmol), *N,N*-dimethyl-4-aminopyridine (40 mg, 0.33 mmol), Et₃N (1.7 mL, 12 mmol, 1.2 equiv), naphthoyl chloride (1.906 mg, 10 mmol), CH₂Cl₂ (40 mL).

Recrystallization from hexanes/EtOAc 4:1 afforded 2.60 g (87%) of *N*-(8-quinoliny)-2-naphthamide as a white solid. This compound is known.³

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.88 (s, 1H), 9.00 (d, *J* = 7.6 Hz, 1H), 8.91 – 8.83 (m, 1H), 8.59 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 8.03 (d, *J* = 7.4 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.63 – 7.53 (m, 4H), 7.49 – 7.44 (m, 1H).

N-(Quinolin-8-yl)thiophene-2-carboxamide



8-Aminoquinoline (1.50 g, 10.5 mmol), *N,N*-dimethyl-4-aminopyridine (40 mg, 0.33 mmol), Et₃N (1.65 mL, 12 mmol, 1.2 equiv), 2-thiophenecarbonyl chloride (1.1 mL, 10 mmol), CH₂Cl₂ (30 mL). Recrystallization from

hexanes/EtOAc 4:1 afforded 2.33 g (92%) of *N*-(quinolin-8-yl)thiophene-2-carboxamide as a white solid. This compound is known.¹

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.61 (s, 1H), 8.90 – 8.80 (m, 2H), 8.18 (dd, *J* = 8.3, 1.6 Hz, 1H), 7.84 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.62 – 7.56 (m, 2H), 7.54 (dd, *J* = 8.3, 1.4 Hz, 1H), 7.48 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.19 (dd, *J* = 5.0, 3.7 Hz, 1H).

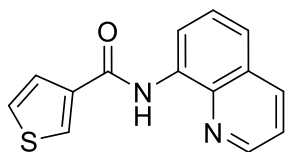
Procedure B:

Synthesis of N-(Quinolin-8-yl)thiophene-3-carboxamide.

To a solution of 3-thiophenecarboxylic acid (1.92 g, 15 mmol) and DMF (5 drops) in DCM (30 mL) under N₂ atmosphere, oxalyl chloride (1.4 mL, 16.5 mmol, 1.1 equiv) was added dropwise at 0 °C. The mixture was stirred for 1.5 h at room temperature, and then the solvent was evaporated in vacuum. Resulting acid chloride was used immediately without further purification.

A solution of acid chloride in CH₂Cl₂ (10 mL) at 0 °C temperature was added dropwise to the solution of 8-aminoquinoline (2.16 g, 19.5 mmol, 1.3 equiv) and Et₃N (2.8 mL, 19.5 mmol, 1.3 equiv) in CH₂Cl₂ (30 mL), then the solution was warmed to room temperature. After stirring overnight, the reaction mixture was quenched with H₂O (30 mL) and the organic layer was separated. The aqueous layer was extracted with CH₂Cl₂ (2 x 30 mL). The combined organic phase was dried over MgSO₄, filtered and evaporated. Recrystallization from hexanes/EtOAc 4:1 afforded 3.26 g (85%) of *N*-(quinolin-8-yl)thiophene-3-carboxamide as a white solid.

N-(Quinolin-8-yl)thiophene-3-carboxamide



This compound is known.⁴

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.50 (s, 1H), 8.84 (dd, J = 7.5, 1.4 Hz, 1H), 8.79 (dd, J = 4.2, 1.7 Hz, 1H), 8.15 – 8.11 (m, 2H), 7.65 (dd, J = 5.0, 1.3 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.49 (dd, J = 8.3, 1.4 Hz, 1H), 7.43 (dd, J = 8.2, 4.2 Hz, 1H), 7.39 (dd, J = 5.1, 3.0 Hz, 1H).

1. Optimization of cobalt-promoted homo-dimerization

1.1. Base

General procedure for base optimization experiments.

2-Dram vial with a screw cap (PTFE/Liner) was charged with 4-methyl-*N*-(quinolin-8-yl)benzamide (26.2 mg, 0.1 mmol), Mn(OAc)₂ (17 mg, 0.1 mmol, 1 equiv), Co(acac)₂ (13 mg, 0.05 mmol, 50 mol%), base (0.1 mmol, 1 equiv), and EtOH (1 mL). Resulting solution was purged with O₂ gas for 2 min, heated at 100 °C temperature for 16 h, monitored by TLC after 2, 6, 16 h. After each opening, the reaction mixture was purged with O₂ for 1 minute. Reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (5 mL), and washed with 1M potassium sodium tartrate

⁴ Katayev, D.; Pfister, K. F.; Wendling, T.; Gooßen, L. J. *Chem. Eur. J.*, **2014**, 20, 9902.

aqueous solution (3 x 5 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. 1,1,2-Trichloroethane (9.3 μ L, 0.2 mmol) was added and reaction mixture was analyzed by ¹H-NMR spectroscopy.

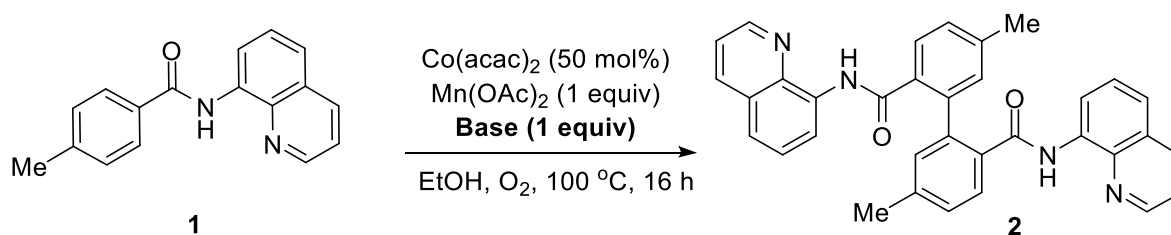


Table S1. Base Screening

Entry	Base	Substrate 1 : Product 2 ratio (Yield, %) ^a
1	NaOPiv	1 : 2 (53)
2	K ₂ CO ₃	1 : 6 (84)
3	Na₂CO₃	0 : 1 (97)
4	CsOPiv	1 : 5 (41)
5 ^b	Na ₂ CO ₃	1 : 20 (84)

^a NMR yield using 1,1,2-trichloroethane as internal standard. ^b 0.5 equiv base.

1.2. Solvent

General procedure for solvent optimization experiments.

2-Dram vial with a screw cap (PTFE/Liner) was charged with 4-methyl-*N*-(quinolin-8-yl)benzamide (26.2 mg, 0.1 mmol), Mn(OAc)₂ (17 mg, 0.1 mmol, 1 equiv), Co(acac)₂ (13 mg, 0.05 mmol, 50 mol%), Na₂CO₃ (11 mg, 0.1 mmol, 1 equiv), and solvent (1 mL). Resulting solution was purged with O₂ gas for 2 min, heated at 100 °C temperature for 16 h, monitored by TLC after 2, 6, 16 h. After each opening, the reaction mixture was purged with O₂ for 1 minute. Reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (5 mL), and washed with 1M potassium sodium tartrate aqueous solution (3 x 5 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. 1,1,2-Trichloroethane (9.3 μ L, 0.2 mmol) was added and reaction mixture was analyzed by ¹H-NMR spectroscopy.

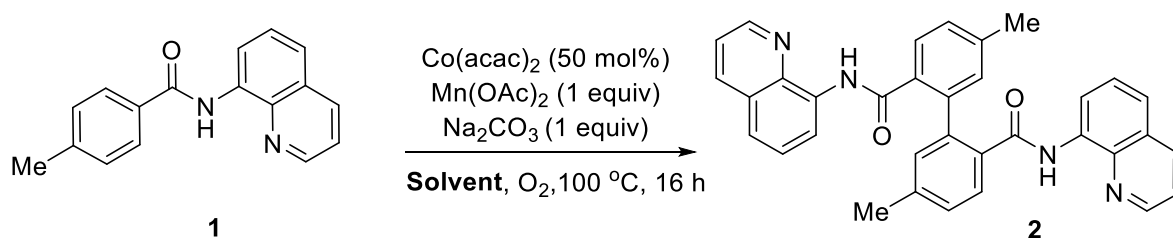


Table S2. Solvent Screening

Entry	Solvent	Substrate 1 : Product 2 ratio (Yield, %) ^a
1	CF ₃ CH ₂ OH	0 : 1 (12)
2	EtOH	0 : 1 (97)
3	Toluene	10 : 1 (9)
4	DCE	3 : 1 (27)

^a NMR yield using 1,1,2-trichloroethane as internal standard.

1.3. Oxidant

General procedure for oxidant optimization experiments.

2-Dram vial with a screw cap (PTFE/Liner) was charged with 4-methyl-*N*-(quinolin-8-yl)benzamide (26.2 mg, 0.1 mmol), oxidant (0.1 mmol, 1 equiv), Co(acac)₂ (13 mg, 0.05 mmol, 50 mol%), Na₂CO₃ (11 mg, 0.1 mmol, 1 equiv), and EtOH (1 mL). Resulting mixture was heated at 100 °C for 16 h. Then cooled to room temperature, diluted with CH₂Cl₂ (5 mL), and washed with 1M potassium sodium tartrate aqueous solution (3 x 5 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. 1,1,2-Trichloroethane (9.3 μL, 0.2 mmol) was added and reaction mixture was analyzed by ¹H-NMR spectroscopy.

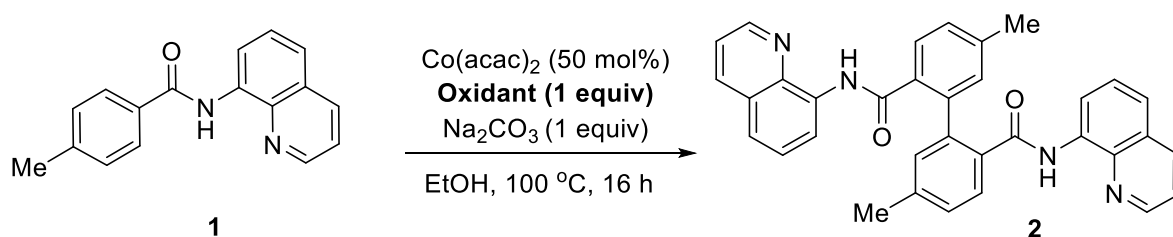


Table S3. Oxidant Screening

Entry	Oxidant	Substrate 1 : Product 2 ratio (Yield, %) ^a
1	Mn(OAc) ₃ ·2H ₂ O	1 : 3 (40)
2	AgOAc	2 : 1 (18)
3	AgNO ₃	2 : 1 (26)
4	K ₂ S ₂ O ₈	3.5 : 1 (29)
5	Mn(OAc) ₂ /air	1 : 3 (70)
6	Mn(OAc)₂/O₂	0 : 1 (97)
7 ^b	-	3 : 1 (25)
8 ^c	Mn(OAc) ₂ /O ₂	1 : 0
9 ^d	Mn(OAc) ₂ /O ₂	1 : 1 (49)
10 ^e	Mn(OAc) ₂	1 : 0

^a NMR yield using 1,1,2-trichloroethane as internal standard. ^b Reaction was performed under air. ^c Reaction was performed without Co(acac)₂. ^d 10 mol% of Co(acac)₂ was used. ^e Deoxygenated EtOH was used under inert atmosphere.

1.4. Temperature

General procedure for temperature optimization experiments.

2-Dram vial with a screw cap (PTFE/Liner) was charged with 4-methyl-*N*-(quinolin-8-yl)benzamide (26.2 mg, 0.1 mmol), Mn(OAc)₂ (17 mg, 0.1 mmol, 1 equiv), Co(acac)₂ (13 mg, 0.05 mmol, 50 mol%), Na₂CO₃ (11 mg, 0.1 mmol, 1 equiv), and EtOH (1 mL). Resulting solution was purged with O₂ gas for 2 min, heated at given temperature for 16 h, monitored by TLC after 2, 6, 16 h. After each opening, the reaction mixture was purged with O₂ for 1 minute. Reaction mixture was cooled to room temperature, diluted with CH₂Cl₂ (5 mL), and washed with 1M potassium sodium tartrate aqueous solution (3 x 5 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. 1,1,2-Trichloroethane (9.3 μL, 0.2 mmol) was added and reaction mixture was analyzed by ¹H-NMR spectroscopy.

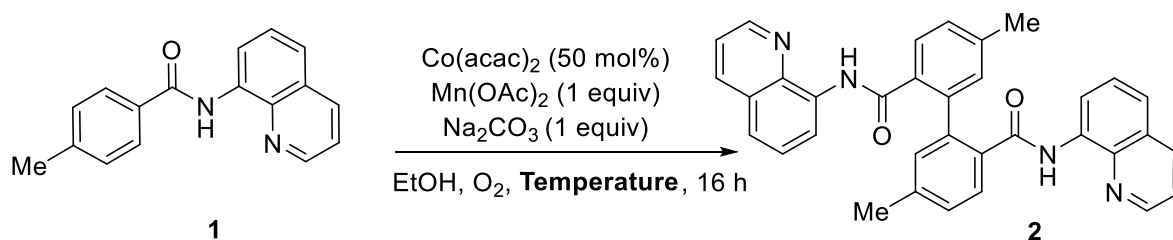


Table S4. Temperature Screening

Entry	Temperature, °C	Substrate 1 : Product 2 ratio (Yield, %) ^a
1	100	0 : 1 (97)
2	80	1 : 2 (35)
3	60	10 : 1 (8)

^a NMR yield using 1,1,2-trichloroethane as internal standard.

2. Cobalt-promoted homo-dimerization and characterization of products

General procedure for cobalt-promoted homo-dimerization.

A 60 mL vial with septum screw cap was equipped with a magnetic stir bar and was charged with amide (1.0 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL). Resulting solution was purged with O₂ gas for 2 min, heated at 100 °C temperature for indicated time, monitored by TLC after 6 h, 16 h, and 20 h. After each opening, the reaction mixture was purged with O₂ for 1 minute. Reaction mixture was cooled to room temperature and product was isolated using method **A** or **B**.

Method A.

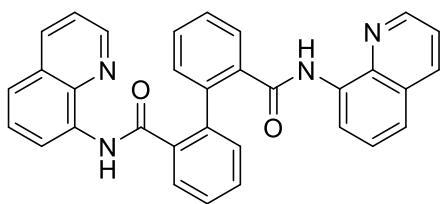
Reaction mixture was diluted with CH₂Cl₂ (30 mL) and washed with 1M potassium sodium tartrate aqueous solution (3 x 20 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. Product was purified using column chromatography on silica gel using appropriate eluent. After purification product was dried under reduced pressure.

Note: *The products are rather insoluble and may crystallize on the column complicating purification.*

Method B.

To the reaction mixture Na₂S·xH₂O (500 mg), CH₂Cl₂ (50 mL) and dist. H₂O (50 mL) were added. Resulting biphasic solution was stirred 10 min at room temperature and filtered through a pad of celite. Organic layer was separated and aqueous layer was extracted with CH₂Cl₂ (2 x 50 mL). Combined organic phase was dried over MgSO₄, filtered and solvent was evaporated. Product was purified using column chromatography on silica gel using appropriate eluent. After purification product was dried under reduced pressure.

***N*²,*N*^{2'}-Di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 1)**



N-(Quinolin-8-yl)benzamide (248 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 17 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 1:1 to CH₂Cl₂, then CH₂Cl₂/MeOH 95:5) 206

mg (83%) of a white solid was obtained. *R*_f = 0.34 (hexanes/EtOAc 2:1), mp 211 – 213 °C (Et₂O).

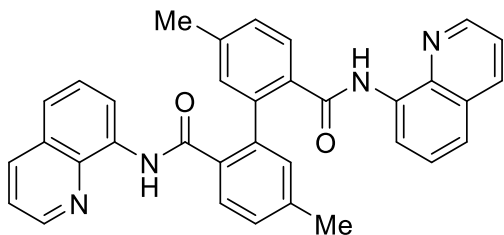
¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.36 (s, 2H), 8.68 (dd, *J* = 7.4, 1.5 Hz, 2H), 8.45 (dd, *J* = 4.2, 1.7 Hz, 2H), 7.93 (dd, *J* = 8.2, 1.7 Hz, 2H), 7.85 (dt, *J* = 7.3, 0.8 Hz, 2H), 7.46 – 7.43 (m, 4H), 7.42 – 7.38 (m, 2H), 7.29 – 7.22 (m, 6H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 167.4, 147.6, 139.7, 138.2, 136.3, 135.7, 134.6, 130.8, 130.4, 127.9, 127.8, 127.4, 126.9, 121.3, 121.2, 116.5.

HRMS (ESI) calcd. for C₃₂H₂₂N₄O₂Na [M+Na]⁺: 517.1635; found: 517.1632.

FT-IR (neat, cm⁻¹) ν 1678, 1653, 1521, 1483, 1423, 1323.

***5,5'*-Dimethyl-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 2)**



4-Methyl-*N*-(quinolin-8-yl)benzamide (262 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 16 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 2:1 to CH₂Cl₂, then CH₂Cl₂/MeOH 95:5) 198 mg (76%) of a white solid

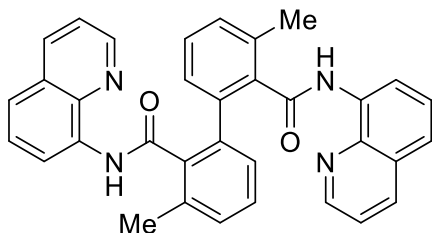
was obtained. *R*_f = 0.43 (hexanes/EtOAc 2:1), mp 227 – 229 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.28 (s, 2H), 8.66 (d, *J* = 7.0 Hz, 2H), 8.44 (dd, *J* = 4.0, 1.3 Hz, 2H), 7.88 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 2H), 7.29 – 7.11 (m, 10H), 2.39 (s, 6H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 167.4, 147.5, 140.6, 140.0, 138.1, 135.5, 134.5, 133.5, 131.5, 128.4, 127.8, 127.2, 126.8, 121.1, 120.9, 116.2, 21.4.

HRMS (ESI) calcd. for C₃₄H₂₆N₄O₂Na [M+Na]⁺: 545.1948; found: 545.1944.

FT-IR (neat, cm⁻¹) ν 1671, 1519, 1483, 1423, 1324.

3,3'-Dimethyl-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 3)

2-Methyl-*N*-(quinolin-8-yl)benzamide (262 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 24 h, 100 °C. After column chromatography (gradient hexanes/EtOAc 2:1 to 1:1, then CH₂Cl₂ and CH₂Cl₂/MeOH 95:5) 97 mg (37%) of a white solid was

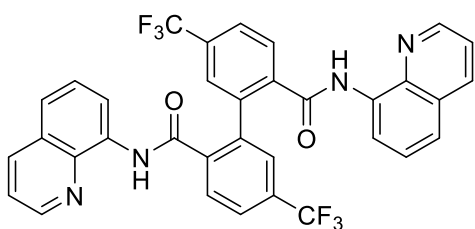
obtained. *R*_f = 0.41 (hexanes/EtOAc 2:1), mp 218 – 220 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.99 (s, 2H), 8.66 (dd, *J* = 7.5, 0.9 Hz, 2H), 8.42 (dd, *J* = 4.2, 1.5 Hz, 2H), 8.03 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.54 (t, *J* = 7.9 Hz, 2H), 7.48 (dd, *J* = 8.2, 0.9 Hz, 2H), 7.28 (d, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.6 Hz, 2H), 2.49 (s, 6H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 168.6, 147.5, 139.2, 137.7, 137.3, 136.2, 134.9, 134.4, 129.2, 128.5, 128.0, 127.5, 127.1, 122.4, 121.1, 119.2, 19.7.

HRMS (ESI) calcd. for C₃₄H₂₆N₄O₂Na [M+Na]⁺: 545.1948; found: 545.1945.

FT-IR (neat, cm⁻¹) ν 1670, 1525, 1484, 1424, 1324.

5,5'-Bis(trifluoromethyl)-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 4)

4-Trifluoromethyl-*N*-(quinolin-8-yl)benzamide (316 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 16 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 2:1 to CH₂Cl₂,

then CH₂Cl₂/MeOH 95:5) 251 mg (80%) of a white solid was obtained. *R*_f = 0.62 (hexanes/EtOAc 2:1), mp 235 – 237 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.28 (s, 2H), 8.53 (dd, *J* = 6.2, 2.7 Hz, 2H), 8.47 (dd, *J* = 4.2, 1.6 Hz, 2H), 7.93 – 7.89 (m, 4H), 7.79 (s, 2H), 7.75 (dd, *J* = 8.0, 1.0 Hz, 2H), 7.28 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.15 – 7.10 (m, 4H).

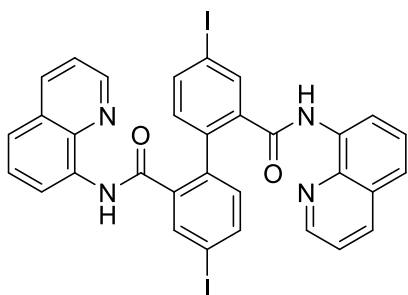
¹³C-NMR (125 MHz, CDCl₃, ppm) δ 165.50, 147.8, 139.5, 139.4, 137.8, 135.7, 133.8, 132.7 (q, *J*_{C-F} = 33.2 Hz), 128.2, 127.7, 127.2, 126.7, 125.4, 123.5 (q, *J*_{C-F} = 274.1 Hz), 121.7, 121.4, 116.5.

¹⁹F-NMR (470 MHz, CDCl₃, ppm) δ -62.58.

HRMS (ESI) calcd. for C₃₄H₂₀F₆N₄O₂Na [M+Na]⁺: 653.1383; found: 653.1380.

FT-IR (neat, cm^{-1}) ν 1671, 1526, 1484, 1323, 1125.

4,4'-Diiodo- $N^2,N^{2'}$ -di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 5)



3-Iodo- N -(quinolin-8-yl)benzamide (374 mg, 1 mmol), $\text{Co}(\text{acac})_2$ (129 mg, 0.5 mmol, 50 mol%), Na_2CO_3 (106 mg, 1 mmol, 1 equiv), $\text{Mn}(\text{OAc})_2$ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 20 h, 100 °C. After column chromatography (gradient hexanes/ CH_2Cl_2 2:1 to CH_2Cl_2 , then $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95:5) 222 mg (60%, method A) of a white solid was obtained. R_f = 0.64

(hexanes/EtOAc 2:1), mp 281 – 283 °C (Et_2O). If isolation according to method B was performed, 264 mg (71%) of product was obtained.

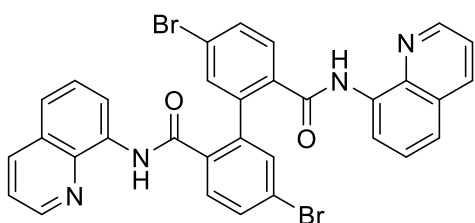
^1H -NMR (500 MHz, CDCl_3 , ppm) δ 10.29 (s, 2H), 8.63 (dd, J = 6.9, 1.9 Hz, 2H), 8.48 (dd, J = 4.2, 1.6 Hz, 2H), 8.17 (d, J = 1.7 Hz, 2H), 7.97 (dd, J = 8.2, 1.5 Hz, 2H), 7.76 (dd, J = 8.1, 1.8 Hz, 2H), 7.32 – 7.27 (m, 6H), 7.15 (d, J = 8.1 Hz, 2H).

^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 165.3, 147.9, 139.5, 138.2, 138.1, 138.0, 136.8, 135.8, 134.1, 132.3, 127.4, 126.9, 121.8, 121.4, 116.8, 93.7.

HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{20}\text{I}_2\text{N}_4\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 768.9568; found: 768.9558.

FT-IR (neat, cm^{-1}) ν 1671, 1654, 1522, 1484, 1423, 1323, 1261.

5,5'-Dibromo- $N^2,N^{2'}$ -di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 6)



4-Bromo- N -(quinolin-8-yl)benzamide (327 mg, 1 mmol), $\text{Co}(\text{acac})_2$ (129 mg, 0.5 mmol, 50 mol%), Na_2CO_3 (106 mg, 1 mmol, 1 equiv), $\text{Mn}(\text{OAc})_2$ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 20 h, 100 °C. After column chromatography (gradient hexanes/ CH_2Cl_2 1:1 to CH_2Cl_2 ,

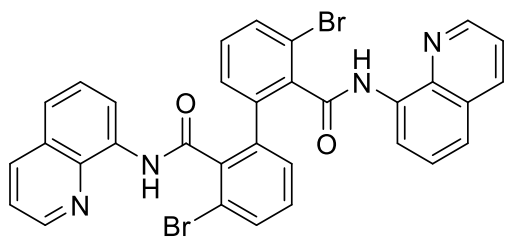
then $\text{CH}_2\text{Cl}_2/\text{MeOH}$ 95:5) 232 mg (71%) of a white solid was obtained. R_f = 0.54 (hexanes/EtOAc 2:1), mp 245 – 247 °C (Et_2O).

^1H -NMR (500 MHz, CDCl_3 , ppm) δ 10.22 (s, 2H), 8.57 (dd, J = 5.7, 3.2 Hz, 2H), 8.48 (dd, J = 4.1, 1.5 Hz, 2H), 7.90 (dd, J = 8.2, 1.5 Hz, 2H), 7.71 – 7.64 (m, 4H), 7.60 (dd, J = 8.2, 1.8 Hz, 2H), 7.27 (dd, J = 8.2, 4.2 Hz, 2H), 7.18 – 7.13 (m, 4H).

^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 165.9, 147.7, 140.4, 137.9, 135.7, 135.1, 134.1, 133.6, 131.4, 129.2, 127.2, 126.8, 125.0, 121.5, 121.3, 116.4.

HRMS (ESI) calcd. for $\text{C}_{32}\text{H}_{20}\text{Br}_2\text{N}_4\text{O}_2\text{Na}$ $[\text{M}+\text{Na}]^+$: 672.9845; found: 672.9833.

FT-IR (neat, cm^{-1}) ν 1670, 1522, 1484, 1423, 1325.

3,3'-Dibromo-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 7)

2-Bromo-*N*-(quinolin-8-yl)benzamide (327 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 24 h, 100 °C. After column chromatography (gradient hexanes/EtOAc 3:1 to 1:1, then EtOAc/MeOH 95:5) 175 mg (54%) of a white solid was

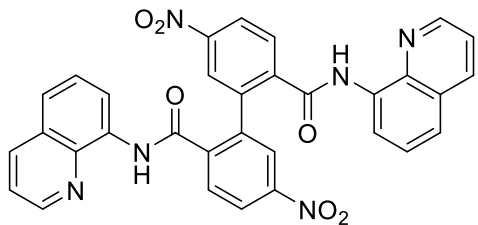
obtained. *R*_f = 0.48 (hexanes/EtOAc 3:1), mp 261 – 263 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 11.97 (s, 2H), 8.61 – 8.45 (m, 4H), 8.03 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.61 – 7.53 (m, 4H), 7.42 (t, *J* = 7.9 Hz, 2H), 7.29 (d, *J* = 7.6 Hz, 2H), 7.23 (dd, *J* = 8.2, 4.3 Hz, 2H), 6.99 (t, *J* = 7.9 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.1, 148.1, 140.1, 138.9, 138.1, 136.6, 133.4, 131.9, 129.8, 129.3, 128.3, 126.9, 123.9, 122.4, 121.2, 119.5.

HRMS (ESI) calcd. for C₃₂H₂₁Br₂N₄O₂ [M+H]⁺: 651.0026; found: 651.0028.

FT-IR (neat, cm⁻¹) ν 1678, 1528, 1423, 1323, 1276.

5,5'-Dinitro-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 8)

4-Nitro-*N*-(quinolin-8-yl)benzamide (293 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), reaction was performed under air, 24 h, 100 °C. After column chromatography (gradient

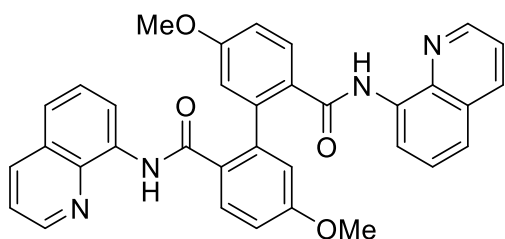
hexanes/EtOAc 2:1 to 1:1, then CH₂Cl₂ and CH₂Cl₂/MeOH 95:5) 242 mg (83%) of a yellow solid was obtained. *R*_f = 0.28 (hexanes/EtOAc 2:1), mp 155 – 157 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.39 (s, 2H), 8.54 – 8.44 (m, 4H), 8.44 – 8.30 (m, 4H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.30 (dd, *J* = 8.0, 4.1 Hz, 2H), 7.19 – 7.10 (m, 4H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 164.6, 148.7, 147.9, 141.5, 139.8, 137.8, 135.8, 133.5, 128.8, 127.2, 126.7, 125.6, 123.8, 122.1, 121.5, 116.7.

HRMS (ESI) calcd. for C₃₂H₂₀N₆O₆Na [M+Na]⁺: 607.1337; found: 607.1332.

FT-IR (neat, cm⁻¹) ν 1674, 1520, 1483, 1423, 1323, 1260.

5,5'-Dimethoxy-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 9)

4-Methoxy-*N*-(quinolin-8-yl)benzamide (278 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 20 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 3:2 to CH₂Cl₂, then CH₂Cl₂/MeOH 95:5) 253 mg (91%) of a white solid

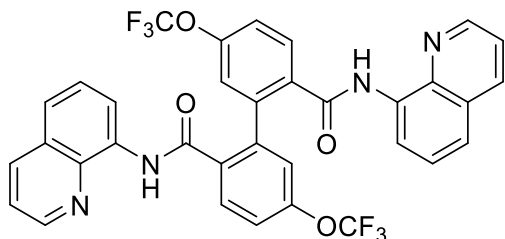
was obtained. *R*_f = 0.19 (hexanes/EtOAc 2:1), mp 181 – 183 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.25 (s, 2H), 8.69 (d, *J* = 7.4 Hz, 2H), 8.46 (dd, *J* = 4.0, 1.4 Hz, 2H), 7.93 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.84 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.20 (m, 6H), 6.98 – 6.90 (m, 4H), 3.80 (s, 6H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.8, 160.9, 147.5, 141.6, 138.2, 135.6, 134.8, 130.0, 128.8, 127.4, 127.0, 121.2, 121.0, 116.3, 115.7, 113.5, 55.4.

HRMS (ESI) calcd. for C₃₄H₂₆N₄O₄Na [M+Na]⁺: 577.1846; found: 577.1842.

FT-IR (neat, cm⁻¹) ν 1676, 1521, 1482, 1423, 1324, 1262.

5,5'-Bis(trifluoromethoxy)-*N*²,*N*^{2'}-di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (Table 2, Entry 10)

4-Trifluoromethoxy-*N*-(quinolin-8-yl)benzamide (332 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 16 h, 100 °C. After column chromatography (gradient hexanes/EtOAc 3:1 to

1:1, then hexanes/EtOAc/MeOH 45:50:5) 151 mg (46%) of a white solid was obtained. *R*_f = 0.57 (hexanes/EtOAc 3:1), mp 231 – 233 °C (Et₂O).

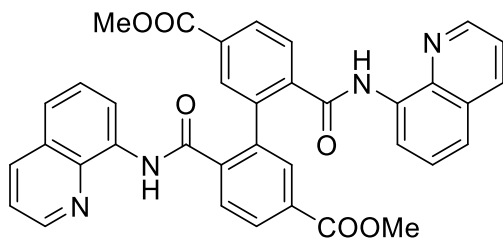
¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.30 (s, 2H), 8.65 – 8.57 (m, 2H), 8.49 (d, *J* = 2.9 Hz, 2H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.87 (d, *J* = 8.4 Hz, 2H), 7.33 (s, 2H), 7.32 – 7.27 (m, 4H), 7.25 – 7.19 (m, *J* = 3.8 Hz, 4H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 165.6, 150.3, 147.8, 140.6, 138.1, 135.8, 134.9, 134.1, 129.7, 127.4, 126.9, 122.8, 121.7, 121.3, 120.2 (q, *J*_{C-F} = 258.9 Hz), 120.1, 116.6.

¹⁹F-NMR (470 MHz, CDCl₃, ppm) δ -57.54.

HRMS (ESI) calcd. for C₃₄H₂₁F₆N₄O₄ [M+H]⁺: 663.1462; found: 663.1469.

FT-IR (neat, cm⁻¹) ν 1668, 1523, 1483, 1325, 1258.

Dimethyl 6,6'-bis(quinolin-8-ylcarbamoyl)biphenyl-3,3'-dicarboxylate (Table 2, Entry 11)

Methyl 4-(quinolin-8-ylcarbamoyl)benzoate (306 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and MeOH (5 mL), 20 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 3:2 to CH₂Cl₂,

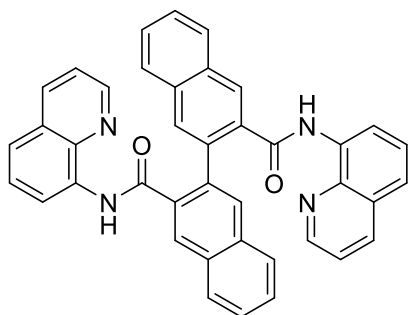
then CH₂Cl₂/MeOH 95:5) 221 mg (73%) of a white solid was obtained. R_f = 0.16 (hexanes/EtOAc 3:1), mp 248 – 250 °C (Et₂O).

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.36 (s, 2H), 8.57 (dd, *J* = 4.9, 4.0 Hz, 2H), 8.45 (dd, *J* = 4.1, 1.5 Hz, 2H), 8.19 – 8.12 (m, 4H), 7.92 – 7.87 (m, 4H), 7.26 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.17 – 7.12 (m, 4H), 3.92 (s, 6H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 166.0, 147.7, 139.9, 139.5, 137.9, 135.7, 134.0, 131.9, 131.8, 129.4, 127.8, 127.2, 126.8, 121.6, 121.3, 116.5, 52.4.

HRMS (ESI) calcd. for C₃₆H₂₇N₄O₆ [M+H]⁺: 611.1925; found: 611.1939.

FT-IR (neat, cm⁻¹) ν 1674, 1522, 1485, 1424, 1324, 1279.

N³,N^{3'}-Di(quinolin-8-yl)-2,2'-binaphthyl-3,3'-dicarboxamide (Table 2, Entry 12)

N-(8-Quinoliny)-2-naphthamide (298 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 16 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 1:1 to CH₂Cl₂, then CH₂Cl₂/MeOH 90:10) 219 mg (73%) of a white solid was obtained. R_f = 0.45 (hexanes/EtOAc 2:1), mp 267 – 269 °C (Et₂O).

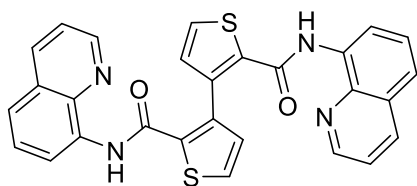
¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.36 (s, 2H), 8.60 (d, *J* = 7.3 Hz, 2H), 8.33 (s, 2H), 8.20 (d, *J* = 2.9 Hz, 2H), 8.13 (s, 2H), 7.96 (t, *J* = 8.6 Hz, 4H), 7.81 (d, *J* = 8.0 Hz, 2H), 7.63 – 7.53 (m, 4H), 7.18 (dd, *J* = 8.0, 4.1 Hz, 2H), 7.13 – 6.99 (m, 4H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 161.1, 147.4, 137.8, 137.2, 135.4, 134.7, 134.4, 134.3, 132.2, 130.6, 128.6, 128.1, 128.0, 127.7, 127.0, 126.8, 126.7, 121.0, 116.3.

HRMS (ESI) calcd. for C₄₀H₂₆N₄O₂Na [M+Na]⁺: 617.1948; found: 617.1941.

FT-IR (neat, cm⁻¹) ν 1671, 1525, 1484, 1423, 1324.

***N*²,*N*^{2'}-Di(quinolin-8-yl)-3,3'-bithiophene-2,2'-dicarboxamide (Table 2, Entry 13)**



N-(Quinolin-8-yl)thiophene-2-carboxamide (254 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 16 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 2:1 to CH₂Cl₂, then CH₂Cl₂/MeOH

95:5) 179 mg (71%) of a white solid was obtained. *R*_f = 0.43 (hexanes/EtOAc 2:1), mp 200 – 202 °C (Et₂O).

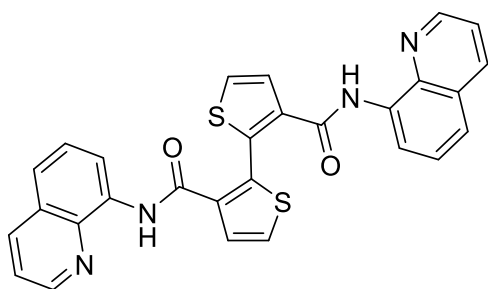
¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.34 (s, 2H), 8.77 (dd, *J* = 7.6, 1.3 Hz, 2H), 8.68 (dd, *J* = 4.2, 1.6 Hz, 2H), 8.01 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.65 (d, *J* = 5.0 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H), 7.40 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.33 (dd, *J* = 8.2, 4.2 Hz, 2H), 7.16 (d, *J* = 5.0 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 159.7, 148.2, 139.7, 138.5, 133.9, 134.3, 134.2, 131.3, 130.9, 127.7, 127.1, 121.7, 121.5, 116.6.

HRMS (ESI) calcd. for C₂₈H₁₈N₂O₂S₂Na [M+Na]⁺: 529.0763; found: 529.0762.

FT-IR (neat, cm⁻¹) ν 1520, 1483, 1423, 1323, 1263.

***N*³,*N*^{3'}-Di(quinolin-8-yl)-2,2'-bithiophene-3,3'-dicarboxamide (Table 2, Entry 14)**



N-(Quinolin-8-yl)thiophene-3-carboxamide (254 mg, 1 mmol), Co(acac)₂ (129 mg, 0.5 mmol, 50 mol%), Na₂CO₃ (106 mg, 1 mmol, 1 equiv), Mn(OAc)₂ (173 mg, 1 mmol, 1 equiv), and EtOH (5 mL), 20 h, 100 °C. After column chromatography (gradient hexanes/CH₂Cl₂ 1:1 to CH₂Cl₂, then CH₂Cl₂/MeOH 95:5) 189 mg (75%) of a white solid

was obtained. *R*_f = 0.36 (hexanes/EtOAc 2:1), mp 217 – 219 °C (Et₂O)

¹H-NMR (500 MHz, CDCl₃, ppm) δ 10.41 (s, 2H), 8.78 (dd, *J* = 7.5, 1.4 Hz, 2H), 8.56 (dd, *J* = 4.2, 1.7 Hz, 2H), 8.01 (dd, *J* = 8.3, 1.6 Hz, 2H), 7.85 (d, *J* = 5.4 Hz, 2H), 7.51 (d, *J* = 5.4 Hz, 2H), 7.41 (t, *J* = 7.9 Hz, 2H), 7.36 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.31 (dd, *J* = 8.3, 4.2 Hz, 2H).

¹³C-NMR (125 MHz, CDCl₃, ppm) δ 160.7, 147.9, 138.8, 138.5, 135.9, 134.5, 133.1, 129.7, 127.7, 127.6, 127.1, 121.5, 121.4, 116.5.

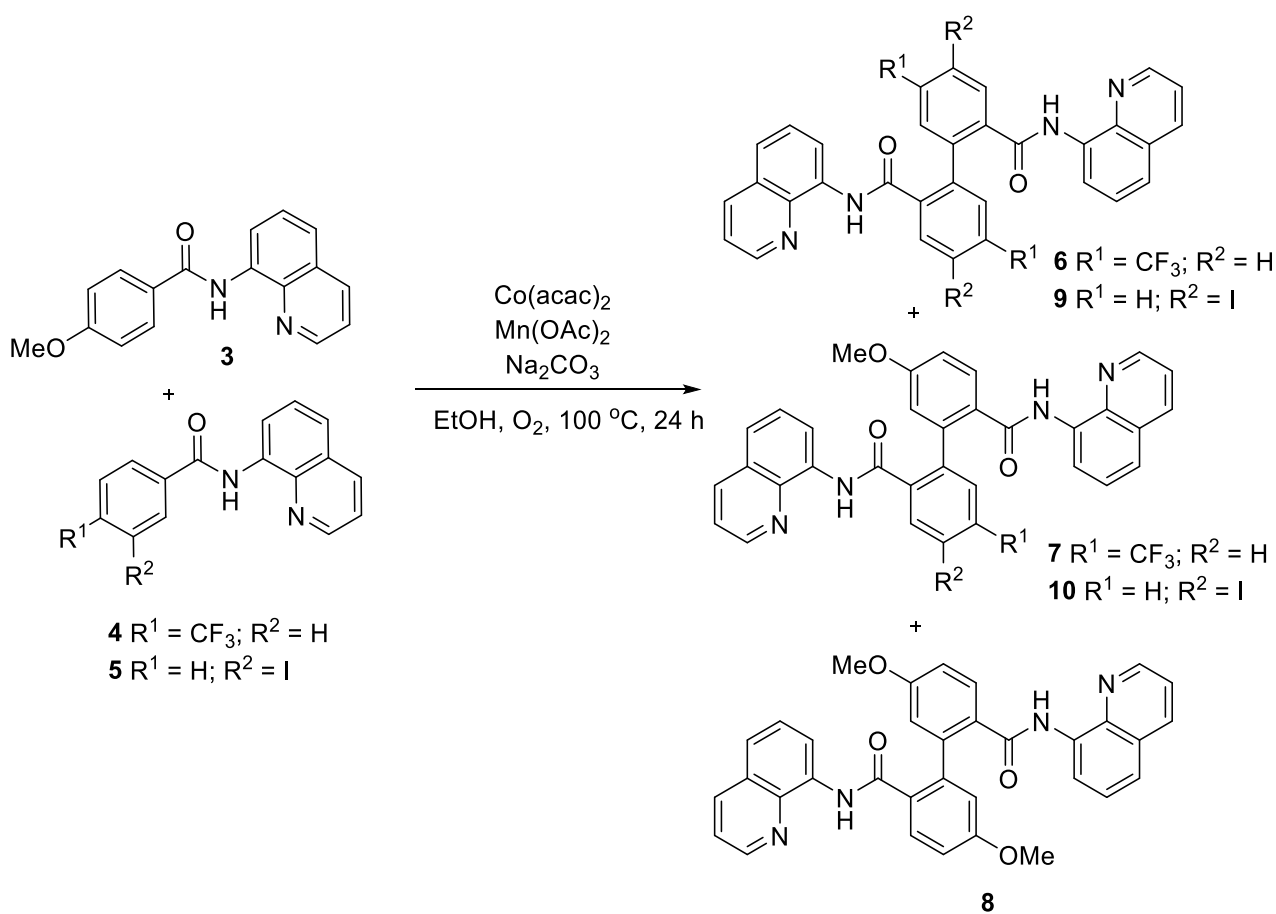
HRMS calcd. for C₂₈H₁₈N₄O₂S₂Na [M+Na]⁺: 529.0769; found: 529.0764.

FT-IR (neat, cm⁻¹) ν 1647, 1521, 1483, 1425, 1323, 1261.

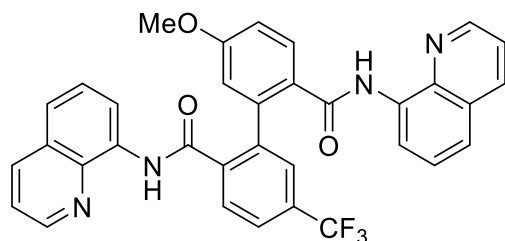
3. Cobalt-promoted hetero-dimerization and characterization of products

General procedure for cobalt-promoted hetero-dimerization.

A 60 mL vial (septum screw cap) equipped with a magnetic stir bar was charged with 4-methoxy-*N*-(quinolin-8-yl)benzamide (139 mg, 0.5 mmol), amide (0.5 mmol), Co(acac)₂ (193 mg, 0.75 mmol), Na₂CO₃ (106 mg, 1 mmol), Mn(OAc)₂ (173 mg, 1 mmol), and EtOH (5 mL). Resulting solution was purged with O₂ gas for 2 min, heated at 100 °C temperature for 24 h, monitored by TLC after 16 h, 20 h. After each opening, the reaction mixture was purged with O₂ for 1 minute. Reaction mixture was cooled to room temperature and isolated using method **A** or **B** described above.



5-Methoxy-*N*,*N'*-di(quinolin-8-yl)-5'-(trifluoromethyl)biphenyl-2,2'-dicarboxamide **7**



4-Methoxy-*N*-(quinolin-8-yl)benzamide (139 mg, 0.5 mmol), 4-trifluoromethoxy-*N*-(quinolin-8-yl)benzamide (158 mg, 0.5 mmol), Co(acac)₂ (193 mg, 0.75 mmol), Na₂CO₃ (106 mg, 1 mmol), Mn(OAc)₂ (173 mg, 1 mmol),

and EtOH (5 mL), 24 h, 100 °C. Product ratio was determined by ^1H -NMR spectra of crude reaction mixture (**6** : **7** : **8** = 0.1 : 1 : 0.6). After column chromatography (gradient hexanes/EtOAc 4:1 to 1:1, then EtOAc) 153 mg (52%, method **A**) of a colorless oil that slowly solidifies was obtained. R_f = 0.25 (hexanes/EtOAc 3:1). If isolation according to method **B** was performed, 147 mg (50%) of product was isolated.

^1H -NMR (500 MHz, CDCl_3 , ppm) δ 10.41 (s, 1H), 10.21 (s, 1H), 8.64 (dd, J = 7.4, 1.5 Hz, 1H), 8.60 (dd, J = 5.7, 3.3 Hz, 1H), 8.53 (dd, J = 4.2, 1.7 Hz, 1H), 8.41 (dd, J = 4.2, 1.7 Hz, 1H), 7.96 (dd, J = 8.3, 1.7 Hz, 1H), 7.92 (d, J = 7.9 Hz, 1H), 7.88 (dd, J = 8.3, 1.6 Hz, 1H), 7.81 (d, J = 8.6 Hz, 1H), 7.75 – 7.69 (m, 2H), 7.31 (dd, J = 8.2, 4.2 Hz, 1H), 7.23 – 7.17 (m, 5H), 6.99 (d, J = 2.6 Hz, 1H), 6.94 (dd, J = 8.6, 2.6 Hz, 1H), 3.85 (s, 3H).

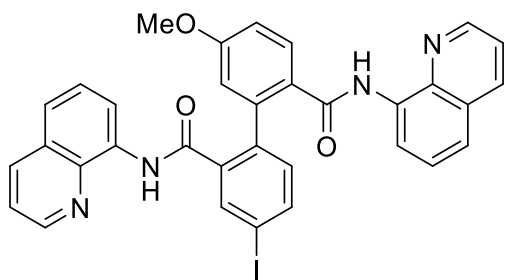
^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 166.3, 166.2, 161.2, 147.7, 147.6, 140.8, 140.6, 139.7, 138.1, 138.0, 135.8, 135.6, 134.4, 134.3, 132.0 (q, $J_{\text{C-F}}$ = 32.5 Hz), 129.7, 128.4, 128.3, 127.4, 127.3, 127.1 (q, $J_{\text{C-F}}$ = 3.8 Hz), 127.0, 126.8, 124.7 (q, $J_{\text{C-F}}$ = 3.8 Hz), 123.6 (q, $J_{\text{C-F}}$ = 272.8 Hz), 121.6, 121.3, 121.2, 121.1, 116.6, 116.4, 116.3, 113.9, 55.5.

^{19}F -NMR (470 MHz, CDCl_3 , ppm) δ -62.51.

HRMS (ESI) calcd. for $\text{C}_{34}\text{H}_{24}\text{F}_3\text{N}_4\text{O}_3$ $[\text{M}+\text{H}]^+$: 593.1795; found: 593.1795.

FT-IR (neat, cm^{-1}) ν 1669, 1522, 1482, 1424, 1327, 1264.

4-Iodo-5'-methoxy- $N^2,N^{2'}$ -di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide **10**



4-Methoxy- N -(quinolin-8-yl)benzamide (139 mg, 0.5 mmol), 3-iodo- N -(quinolin-8-yl)benzamide (187 mg, 0.5 mmol), $\text{Co}(\text{acac})_2$ (193 mg, 0.75 mmol), Na_2CO_3 (106 mg, 1 mmol), $\text{Mn}(\text{OAc})_2$ (173 mg, 1 mmol), and EtOH (5 mL), 24 h, 100 °C. Product ratio was determined by ^1H -NMR spectra of crude reaction mixture (**9** : **10** : **8** = 0.2 : 1 :

0.5). After column chromatography (gradient hexanes/EtOAc 4:1 to 1:1, then EtOAc) 151 mg (46%) of a colorless oil (that solidifies) was obtained. R_f = 0.28 (hexanes/EtOAc 3:1).

^1H -NMR (500 MHz, CDCl_3 , ppm) δ 10.36 (s, 1H), 10.23 (s, 1H), 8.68 (dd, J = 7.3, 1.5 Hz, 1H), 8.65 (dd, J = 7.4, 1.2 Hz, 1H), 8.54 (dd, J = 4.2, 1.6 Hz, 1H), 8.41 (dd, J = 4.2, 1.6 Hz, 1H), 8.18 (d, J = 1.7 Hz, 1H), 7.99 (dd, J = 8.2, 1.5 Hz, 1H), 7.91 (dd, J = 8.2, 1.5 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.77 (dd, J = 8.1, 1.8 Hz, 1H), 7.35 – 7.20 (m, 6H), 7.16 (d, J = 8.1 Hz, 1H), 6.96 – 6.87 (m, 2H), 3.79 (s, 3H).

^{13}C -NMR (125 MHz, CDCl_3 , ppm) δ 166.5, 165.8, 161.0, 147.8, 147.7, 140.8, 139.2, 139.1, 138.3, 138.25, 138.2, 136.8, 135.9, 135.6, 134.6, 134.4, 132.0, 130.0, 128.4, 127.5, 127.3, 127.1, 126.9, 121.6, 121.3, 121.25, 121.2, 116.6, 116.4, 116.1, 113.8, 93.4, 55.5.

HRMS (ESI) calcd. for $\text{C}_{33}\text{H}_{24}\text{IN}_4\text{O}_3$ $[\text{M}+\text{H}]^+$: 651.0888; found: 651.0887.

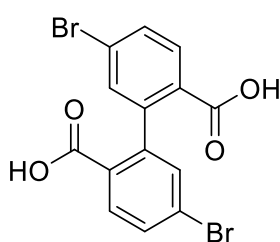
FT-IR (neat, cm^{-1}) ν 1670, 1521, 1482, 1423, 1324, 1262.

Removal of directing group

Synthesis of 5,5'-dibromobiphenyl-2,2'-dicarboxylic acid.

3,3'-Dibromo- $N^2,N^{2'}$ -di(quinolin-8-yl)biphenyl-2,2'-dicarboxamide (150 mg, 0.23 mmol) and KOH (774 mg, 13.8 mmol) were dissolved in MeOH (5 mL). Resulting solution was heated at 120 °C temperature for 36 h. Mixture was cooled to room temperature, diluted with EtOAc (30 mL), 1M HCl aqueous solution (30 mL) was added. Organic phase was separated, dried over MgSO_4 , filtered, and evaporated. After recrystallization from hexanes: EtOAc (6:1) 65 mg (71%) of a white solid was obtained.

5,5'-Dibromobiphenyl-2,2'-dicarboxylic acid 12

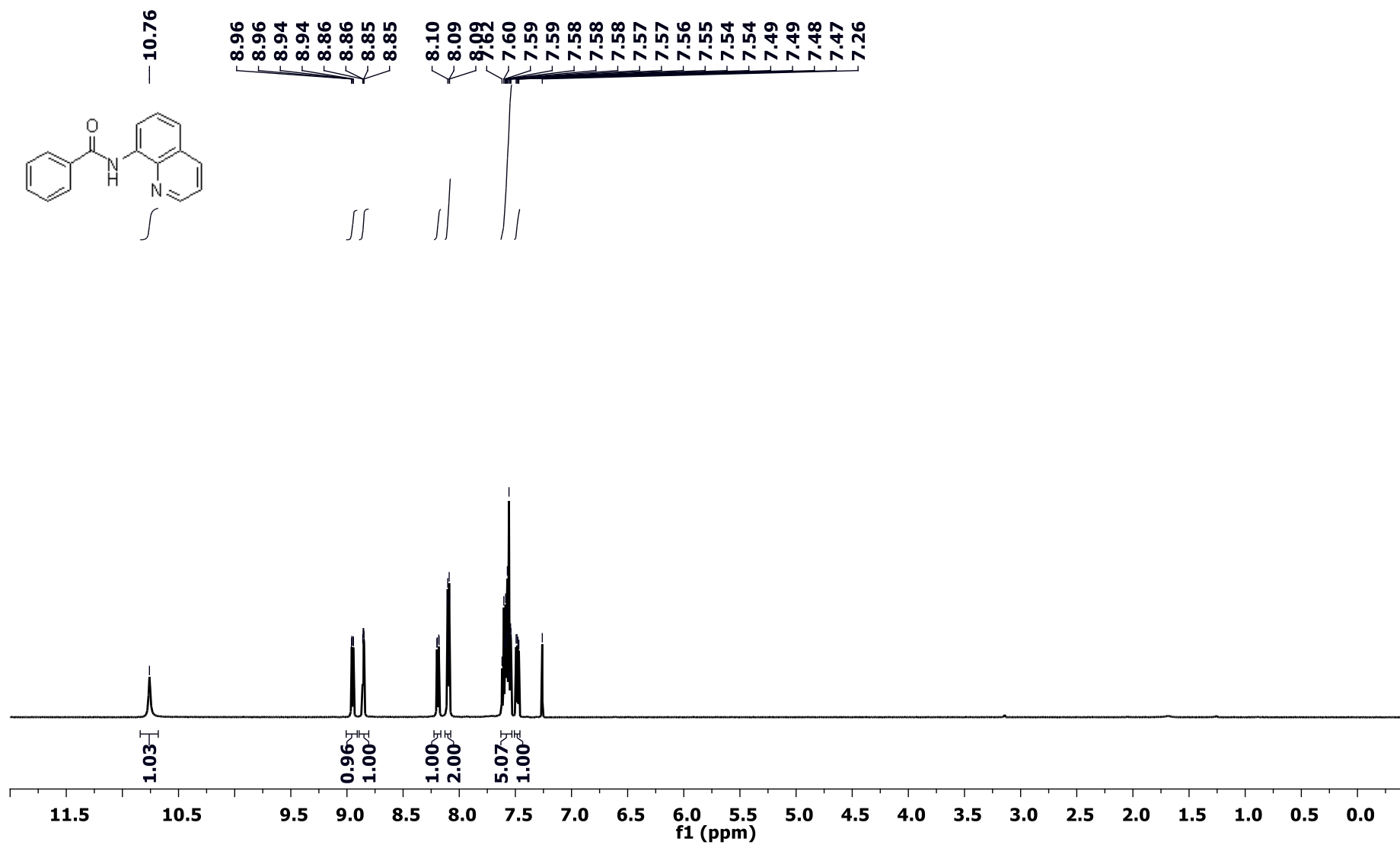


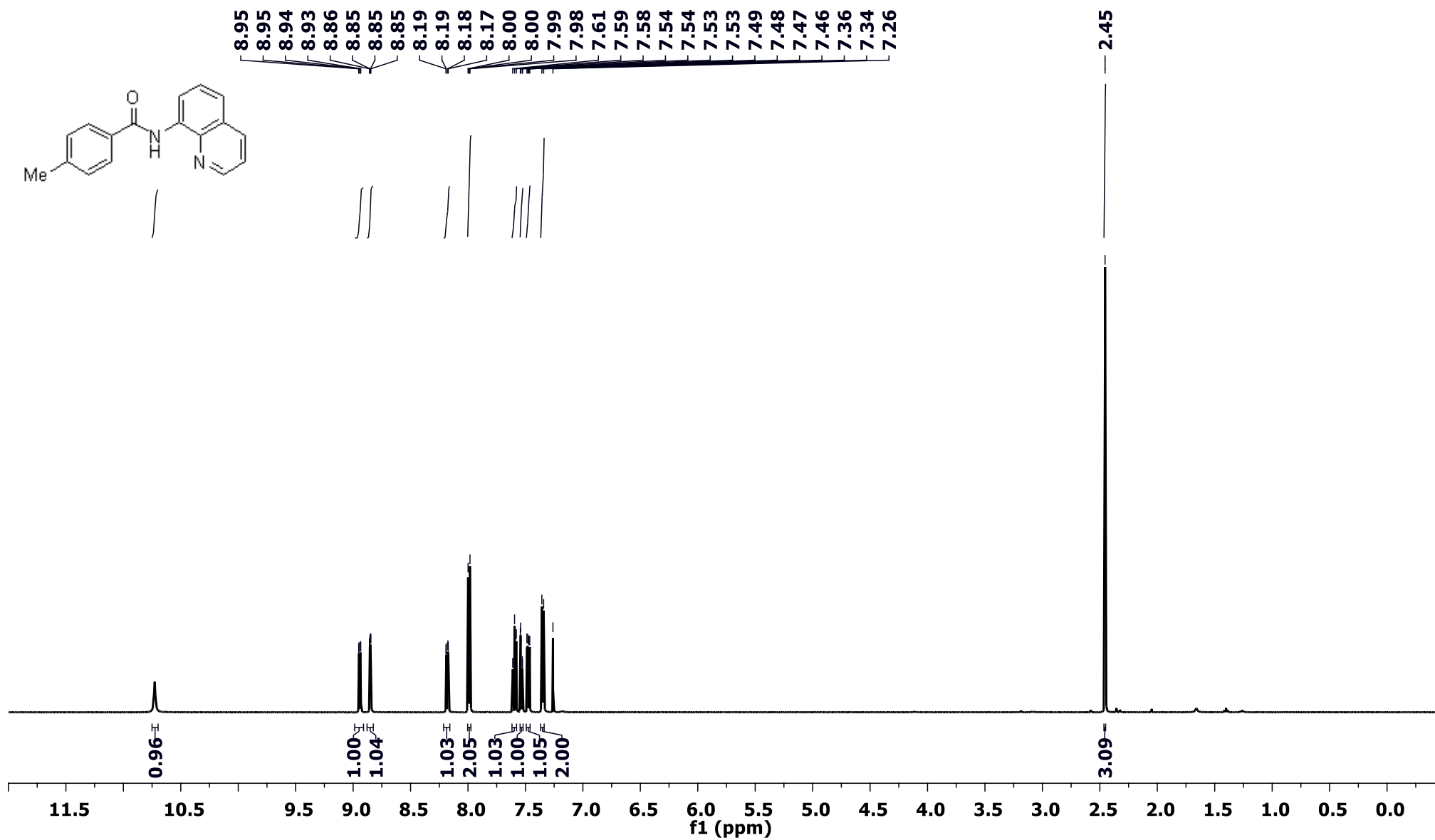
This compound is known.⁵

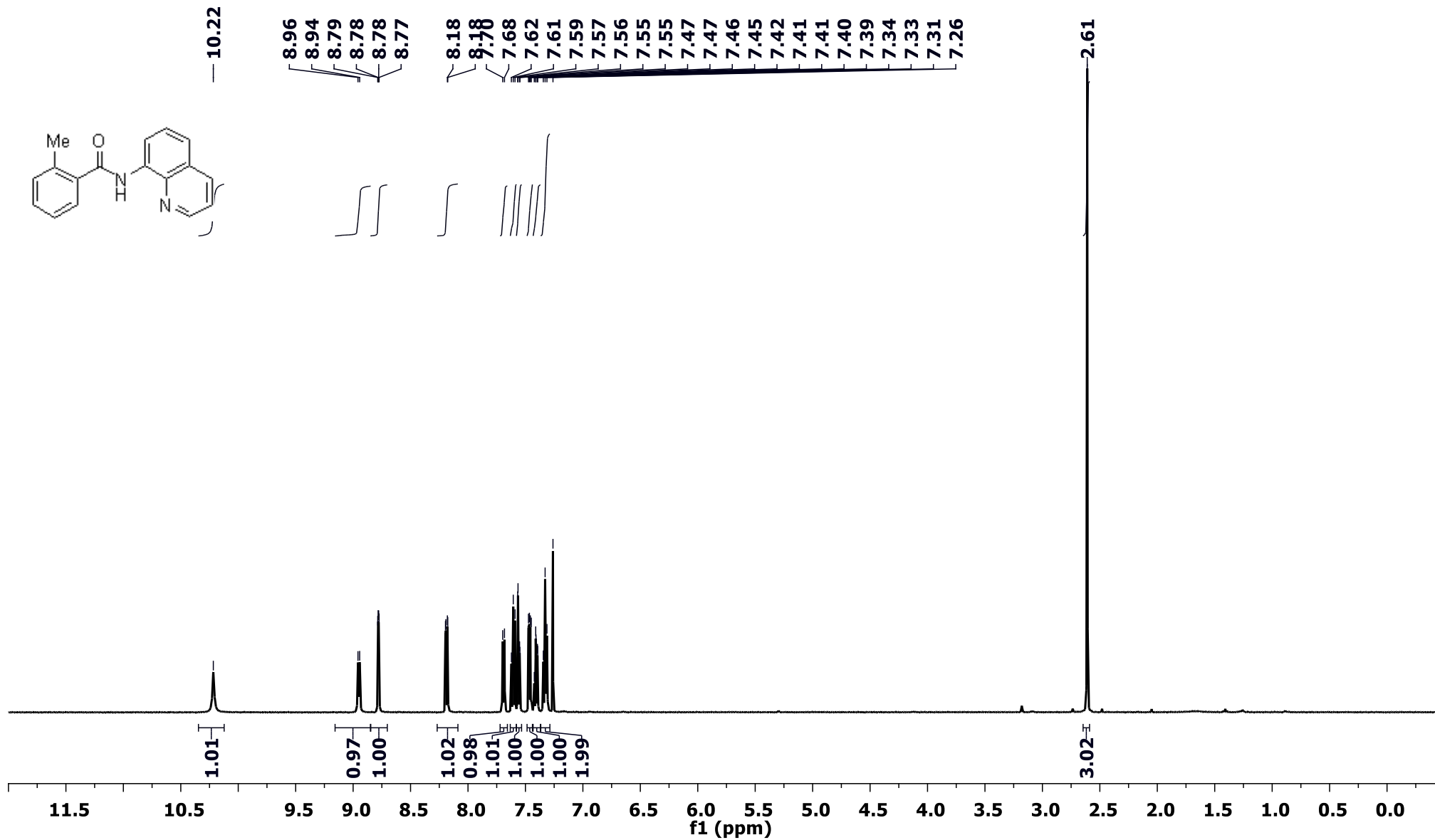
^1H -NMR (500 MHz, $\text{DMSO}-d_6$, ppm) δ 12.77 (brs, 2H), 7.84 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.43 (s, 2H).

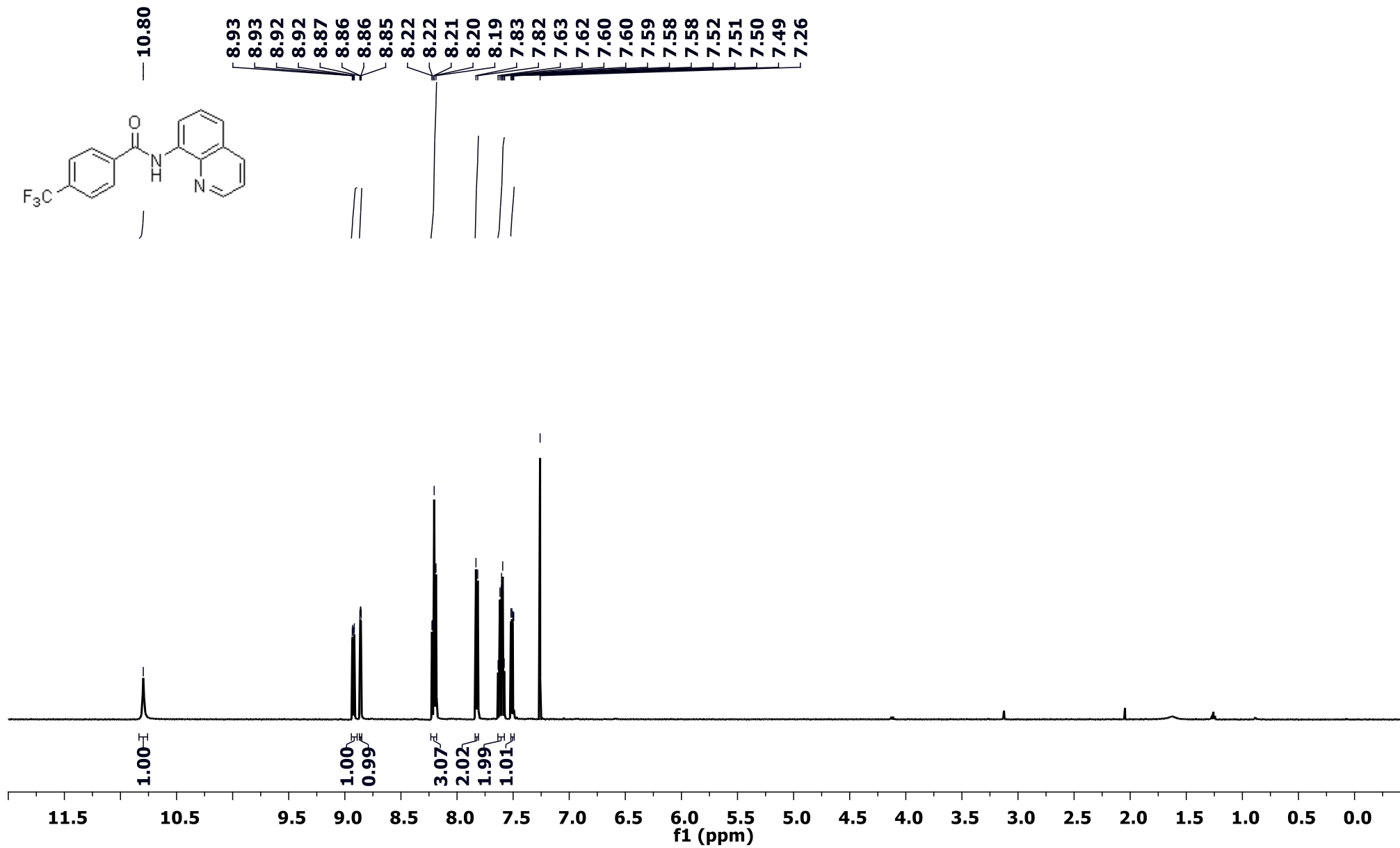
⁵ Zhang, D.-L.; Zhou, L.-Y.; Quan, J.-M.; Zhang, W.; Gu, L.-Q.; Huang, Z.-S.; An, L.-K. *Org. Lett.*, **2013**, *15*, 1162.

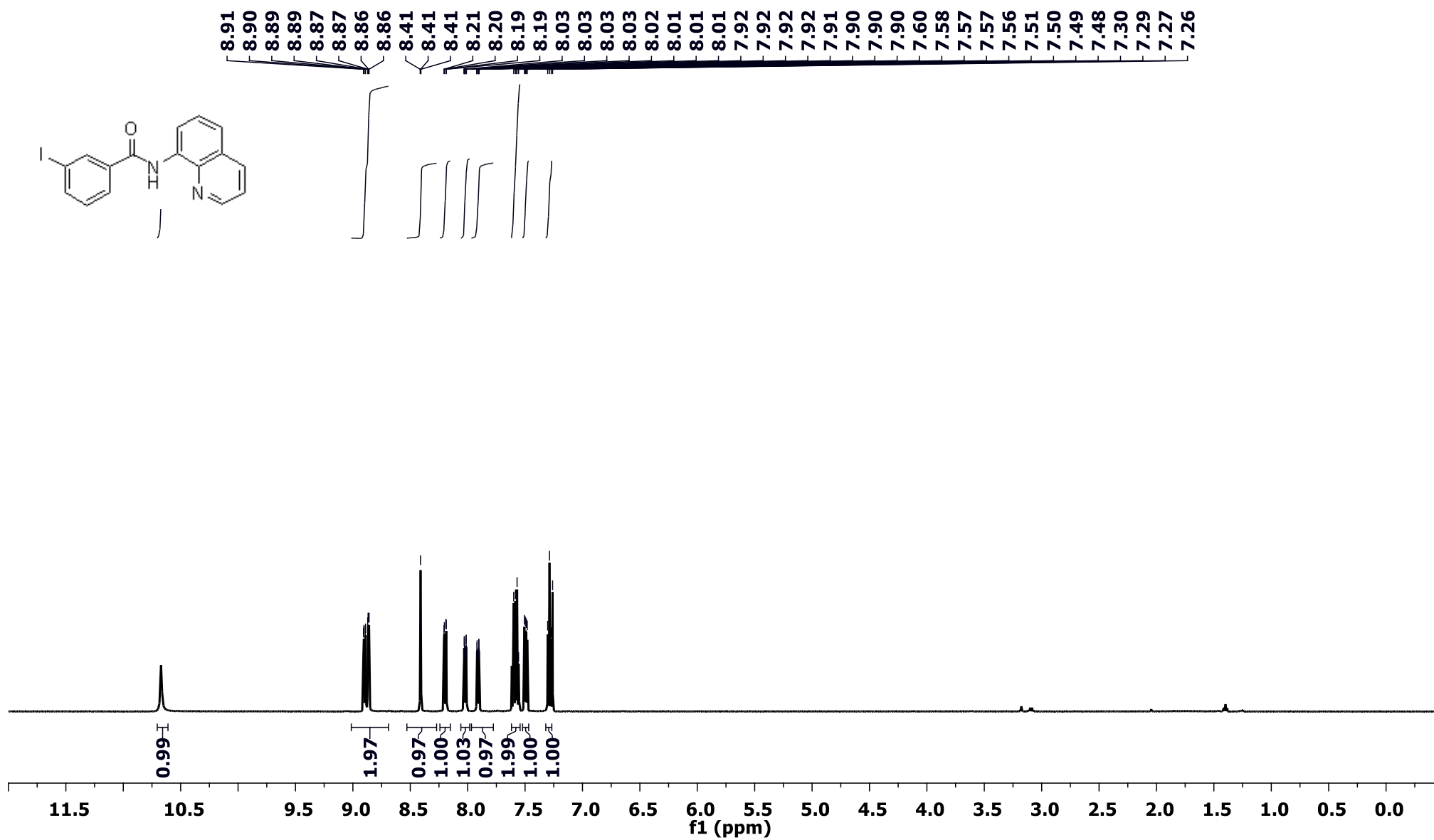
Spectra

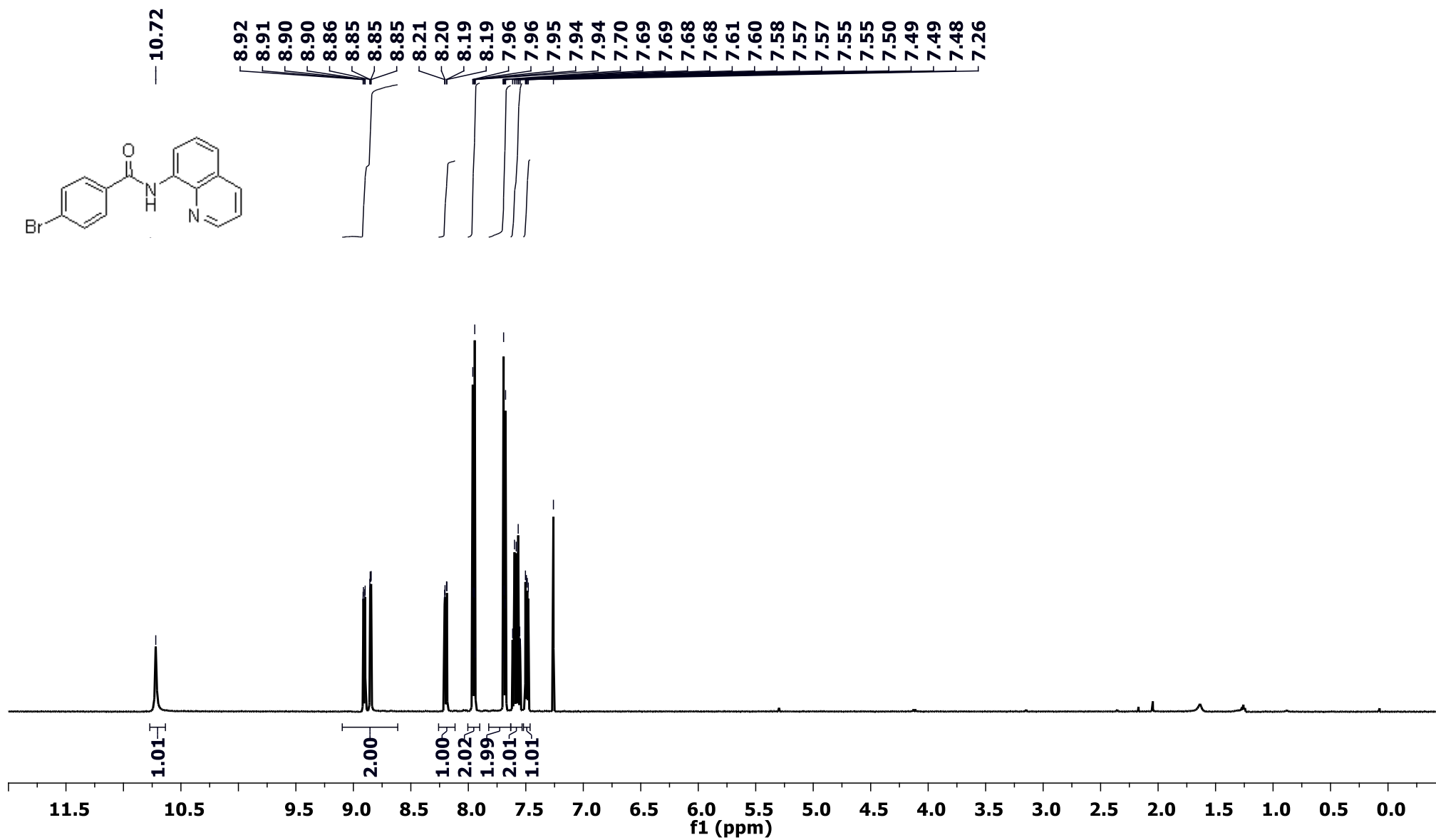


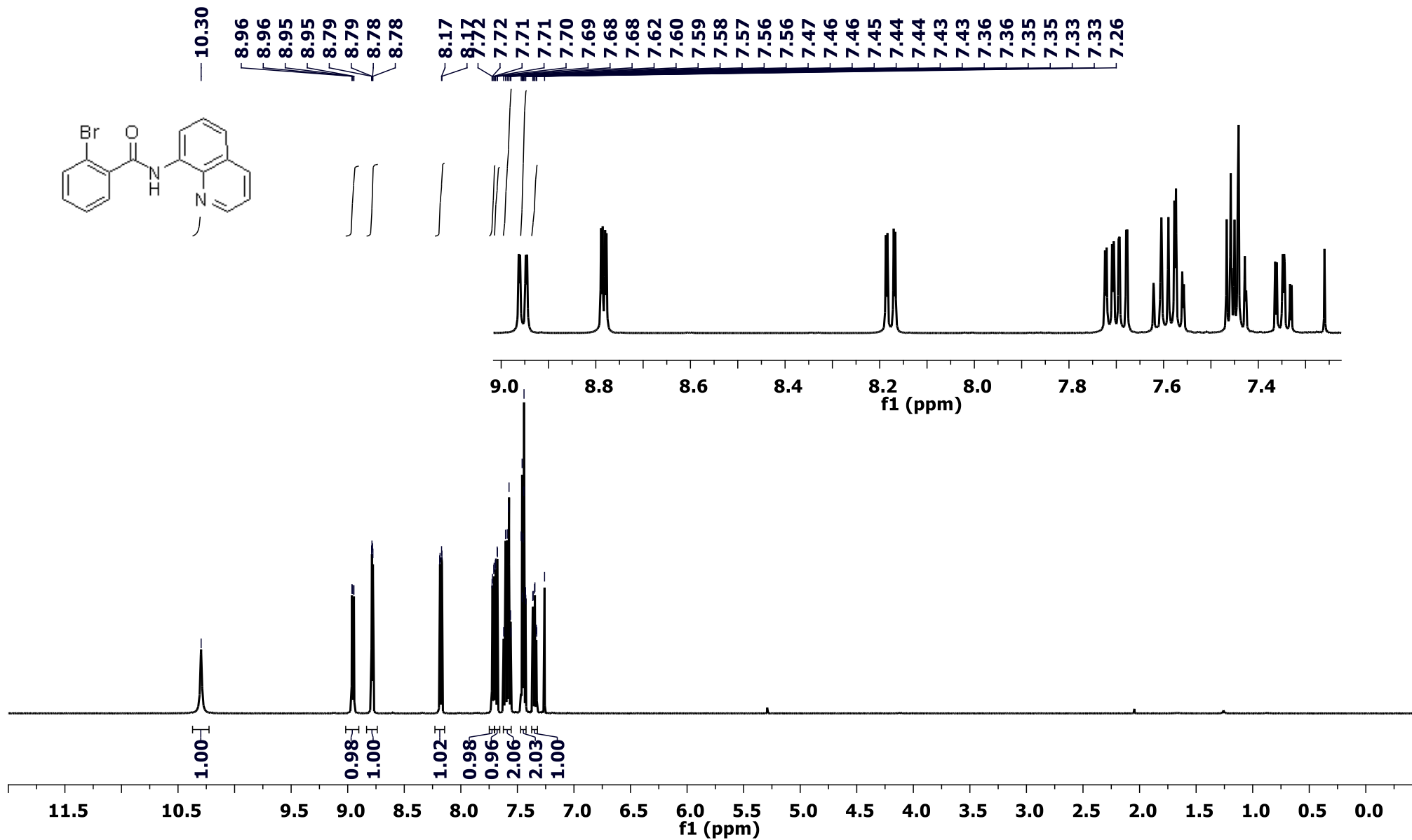


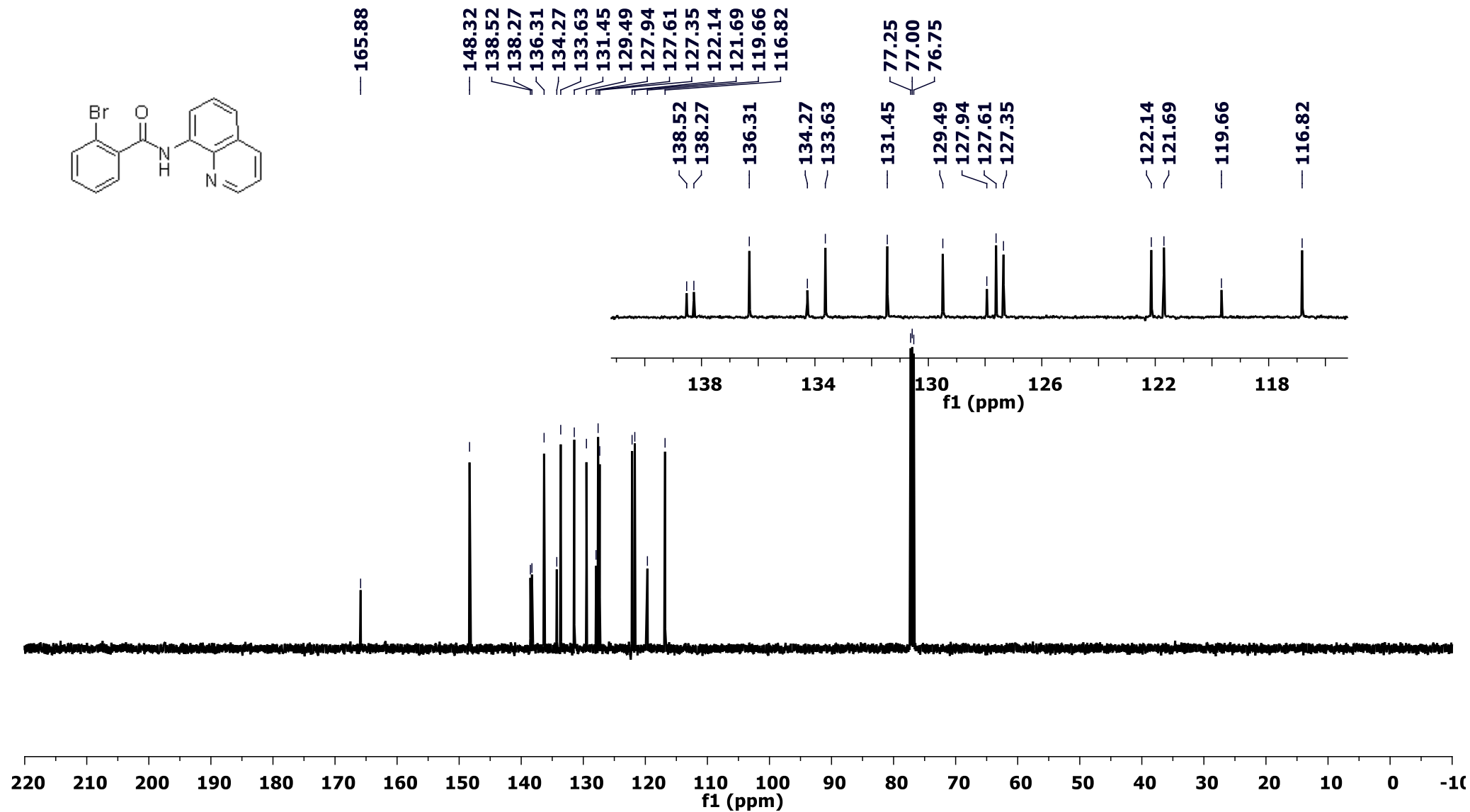
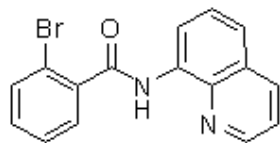


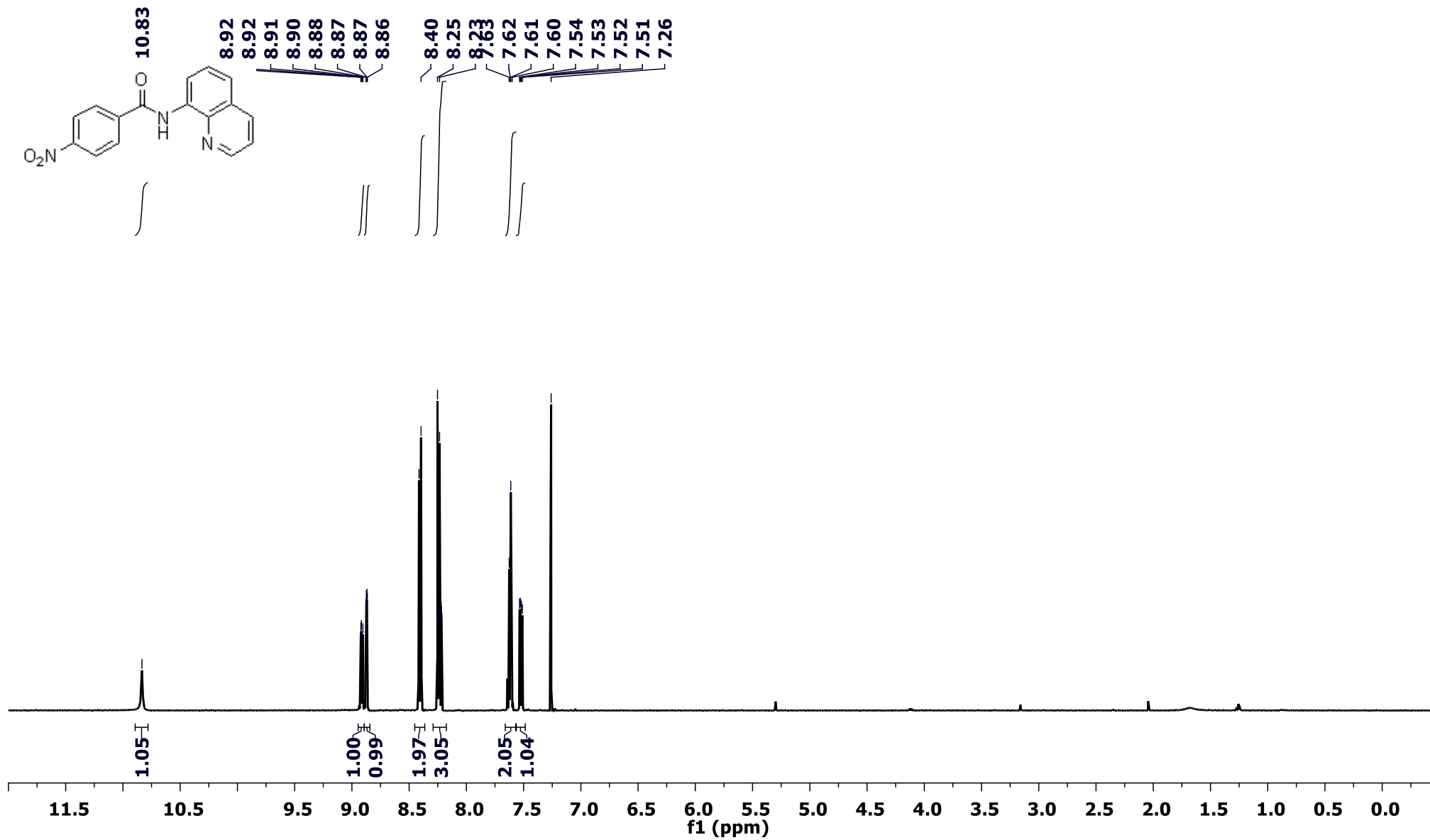


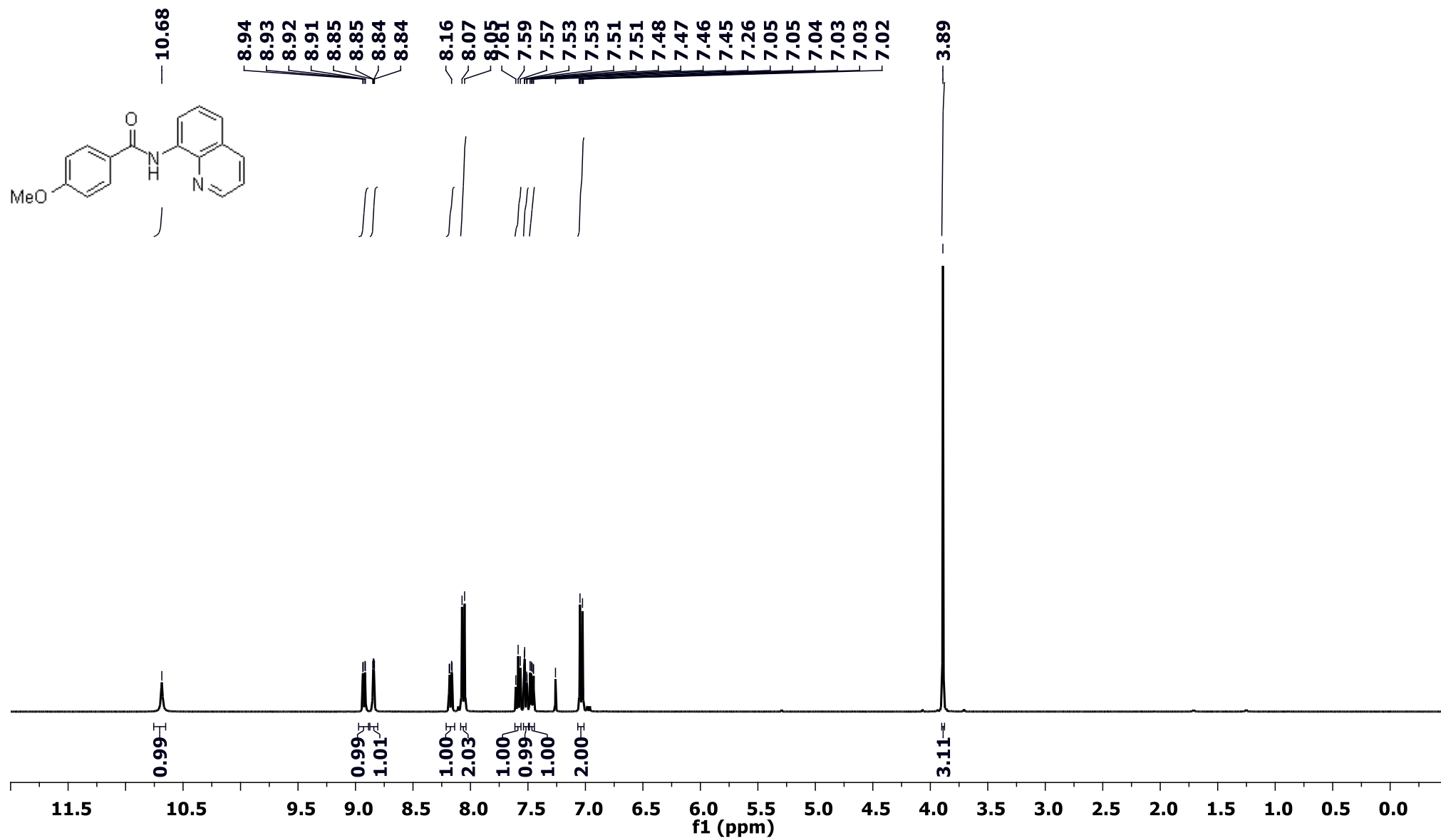


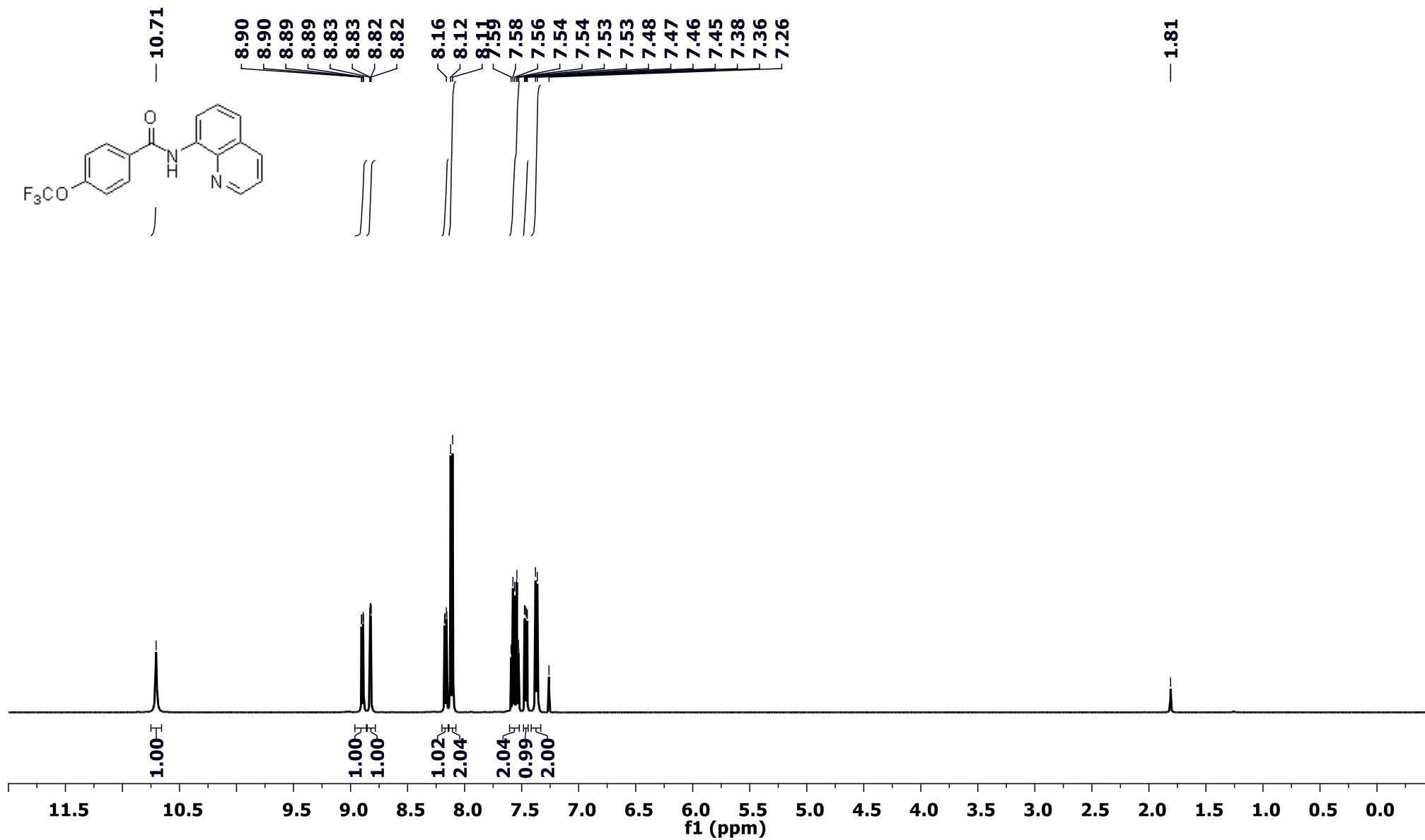


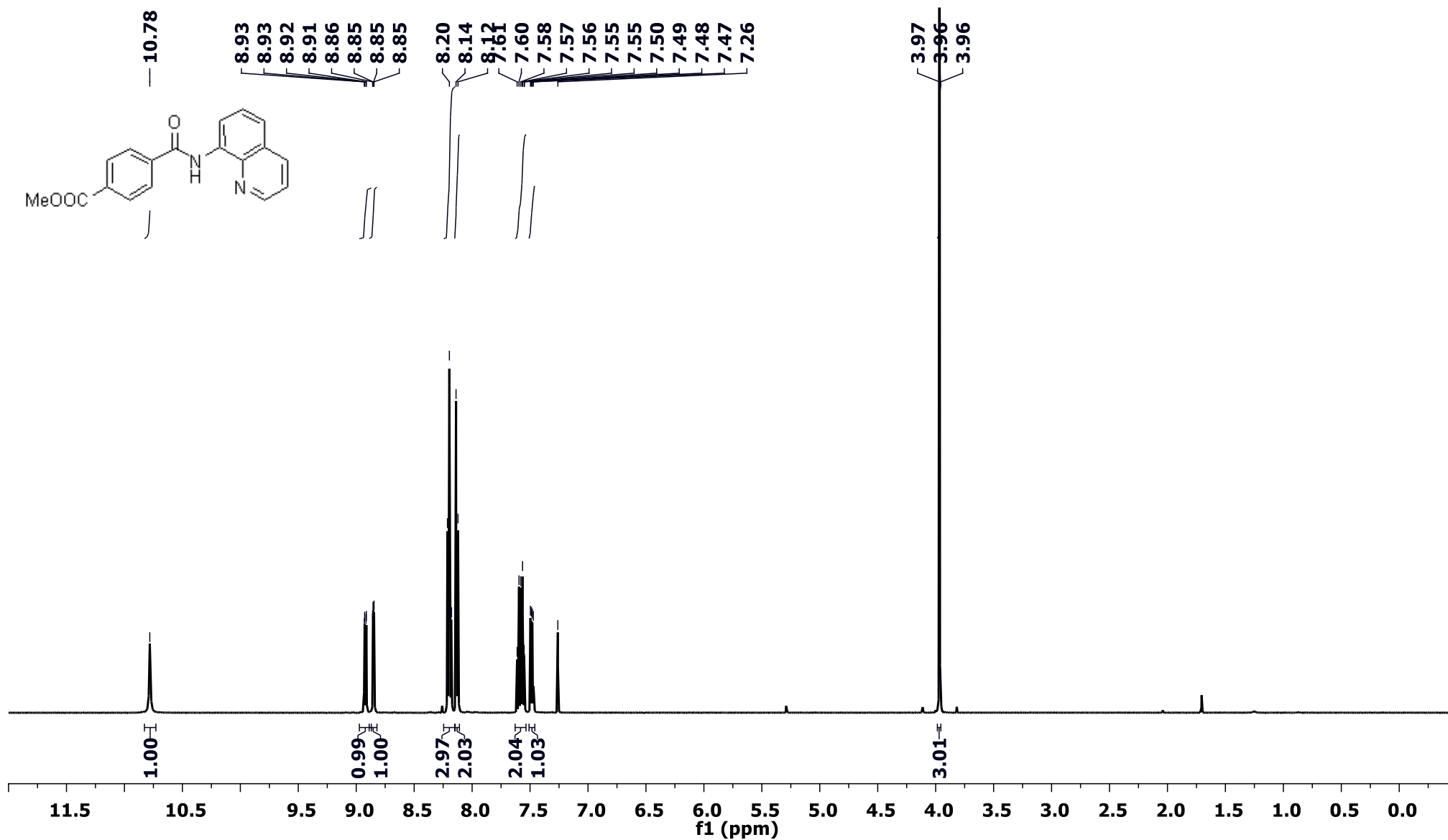


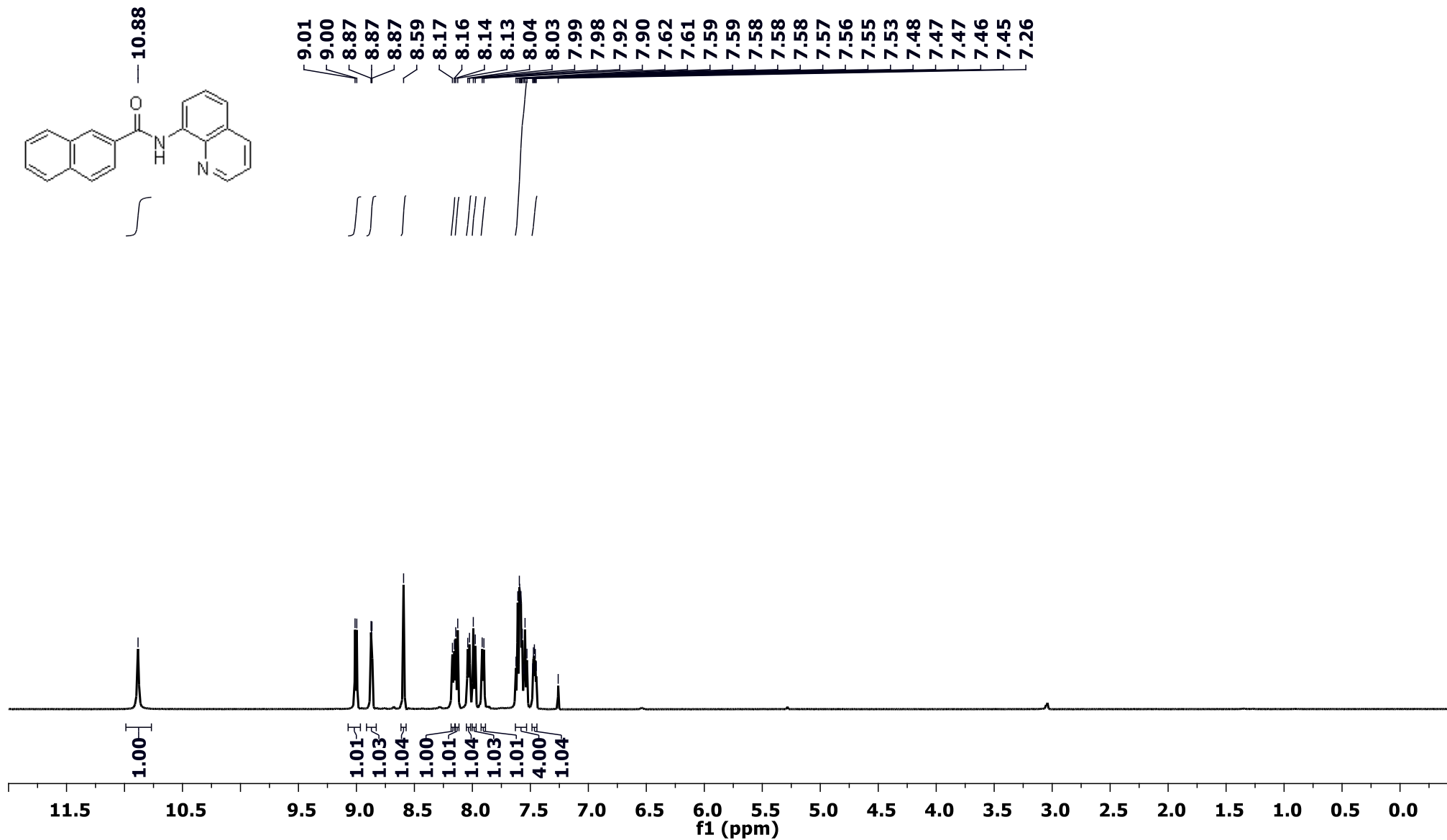


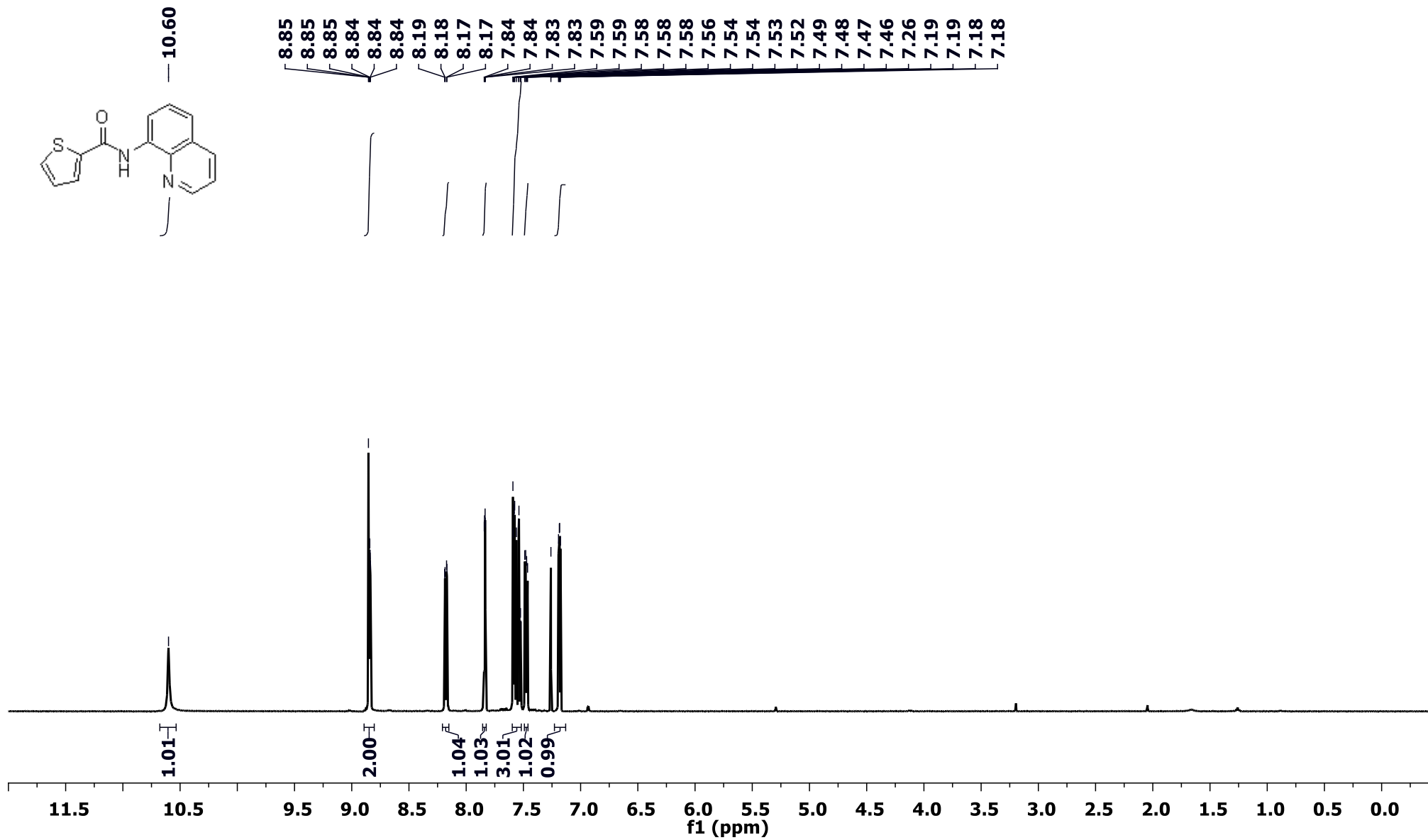


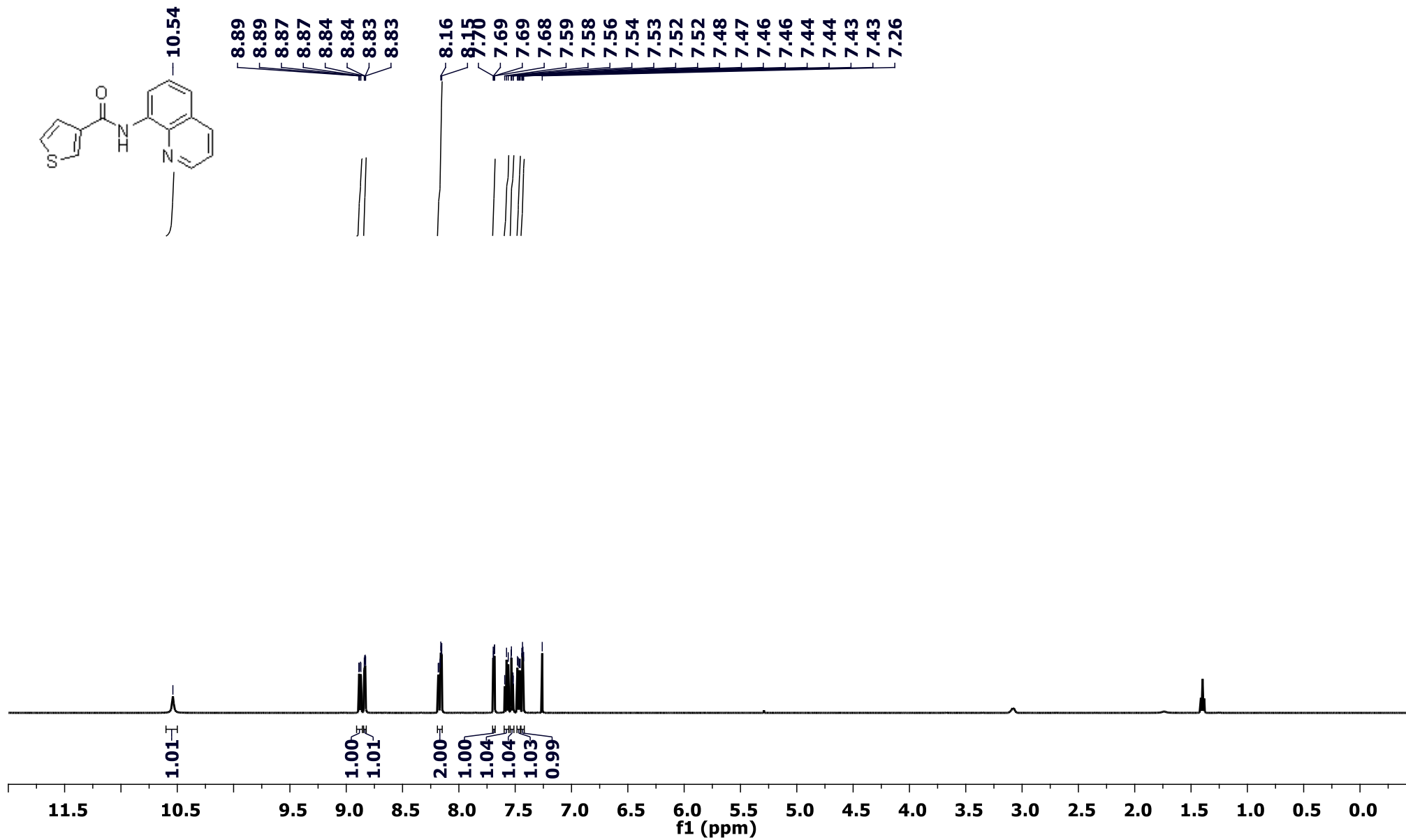












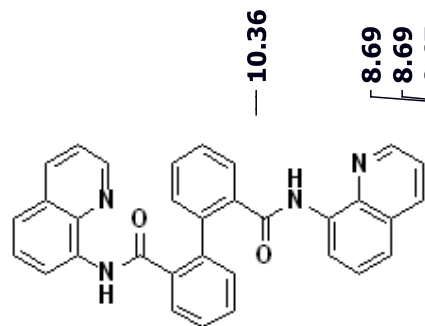
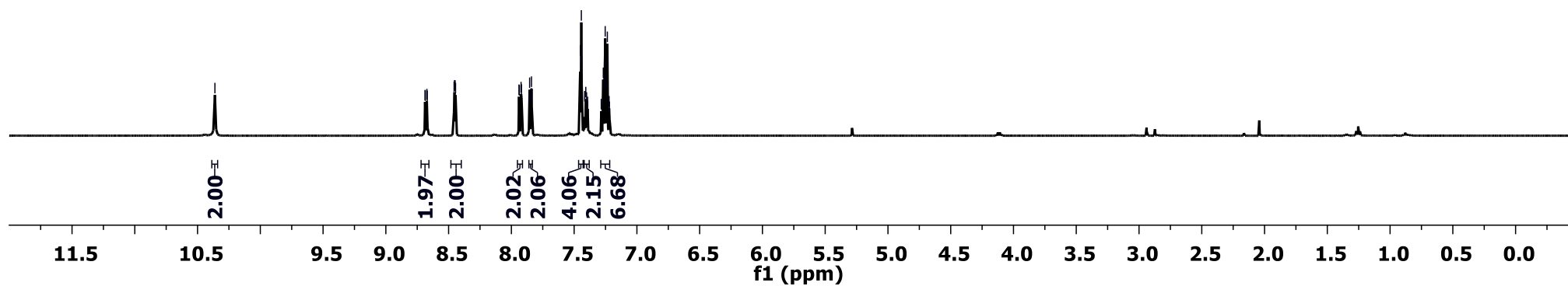
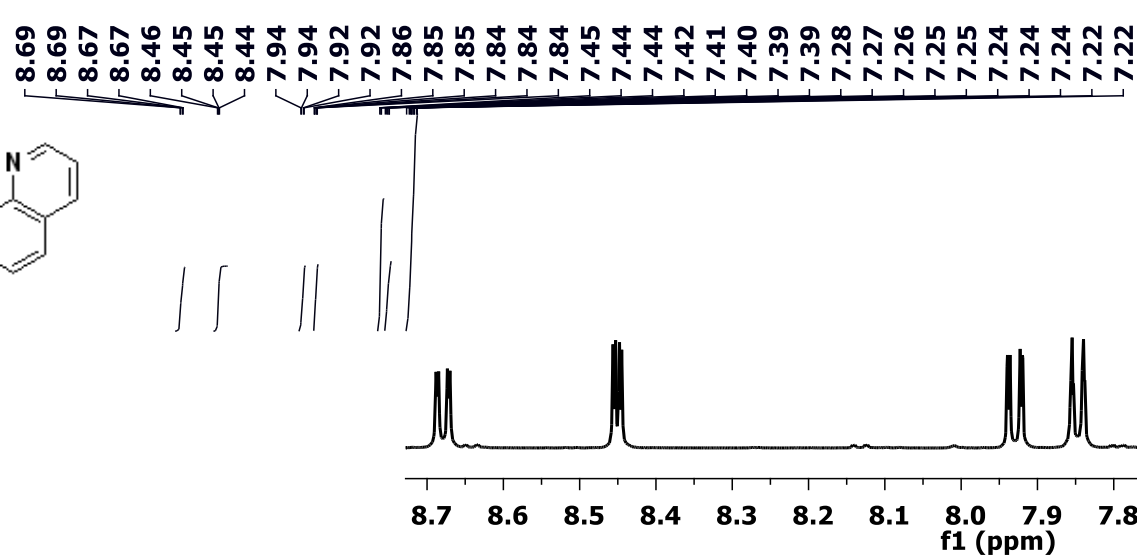


Table 2, Entry 1



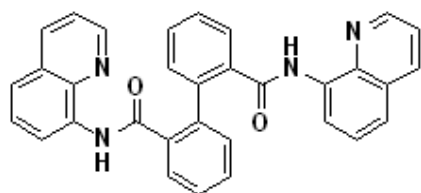
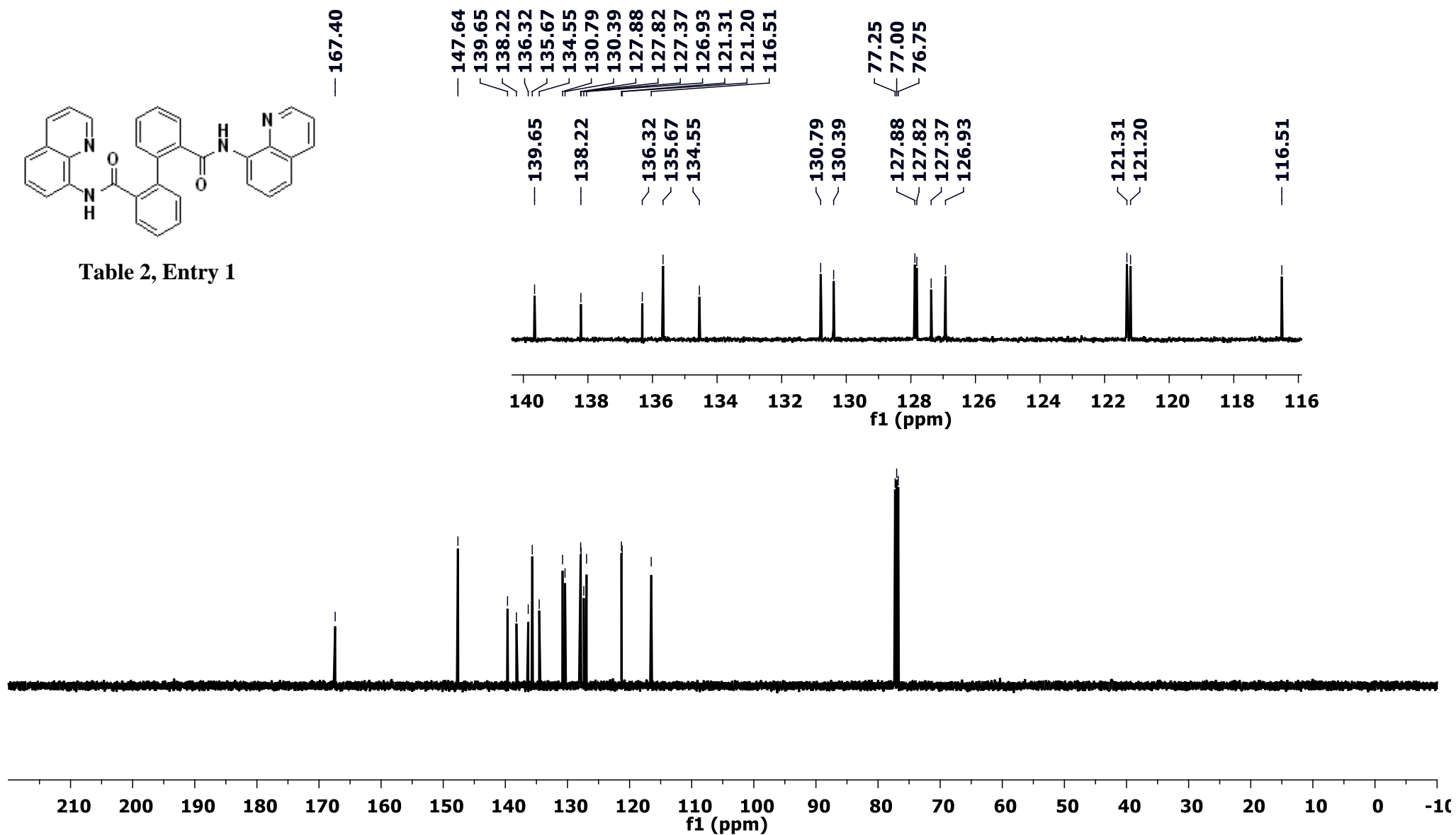
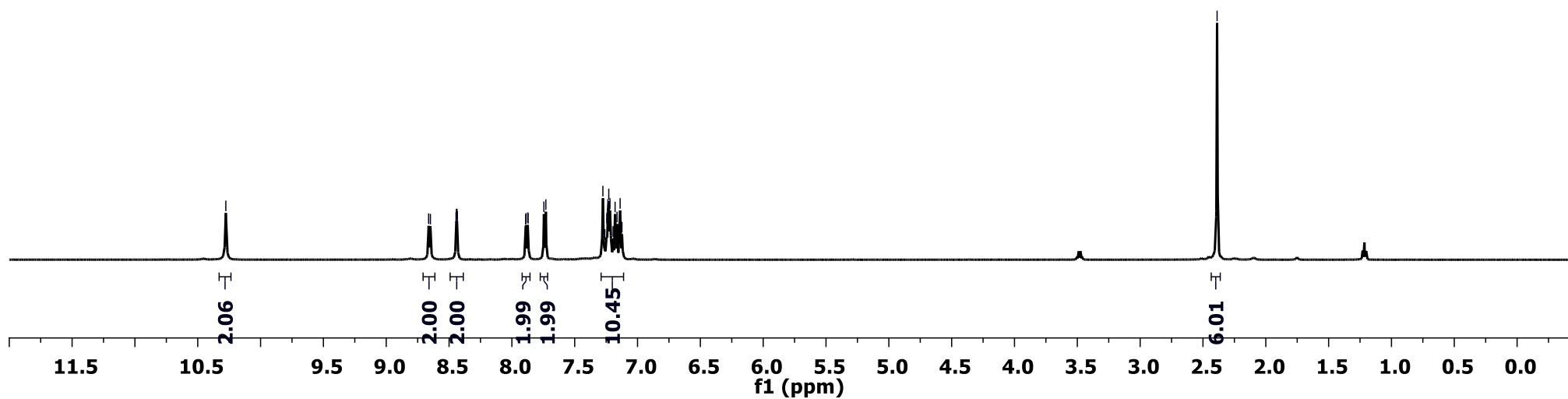
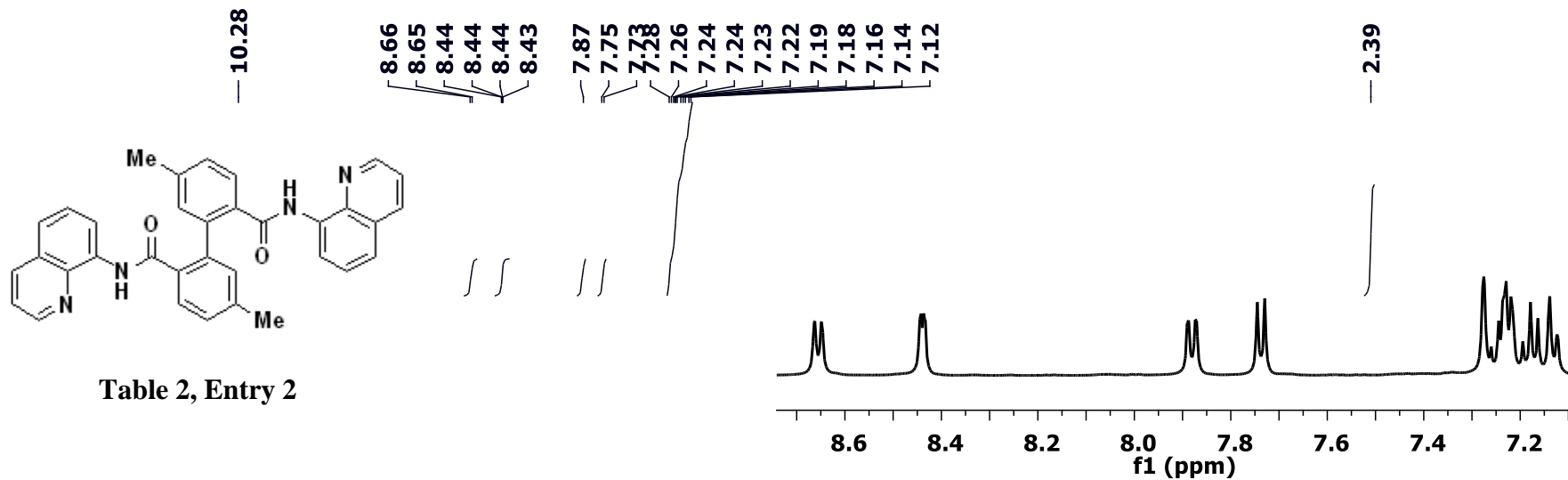


Table 2, Entry 1





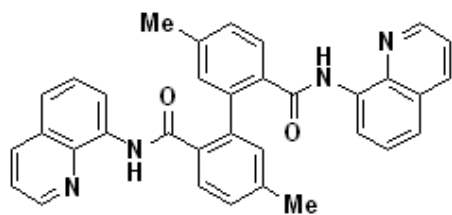
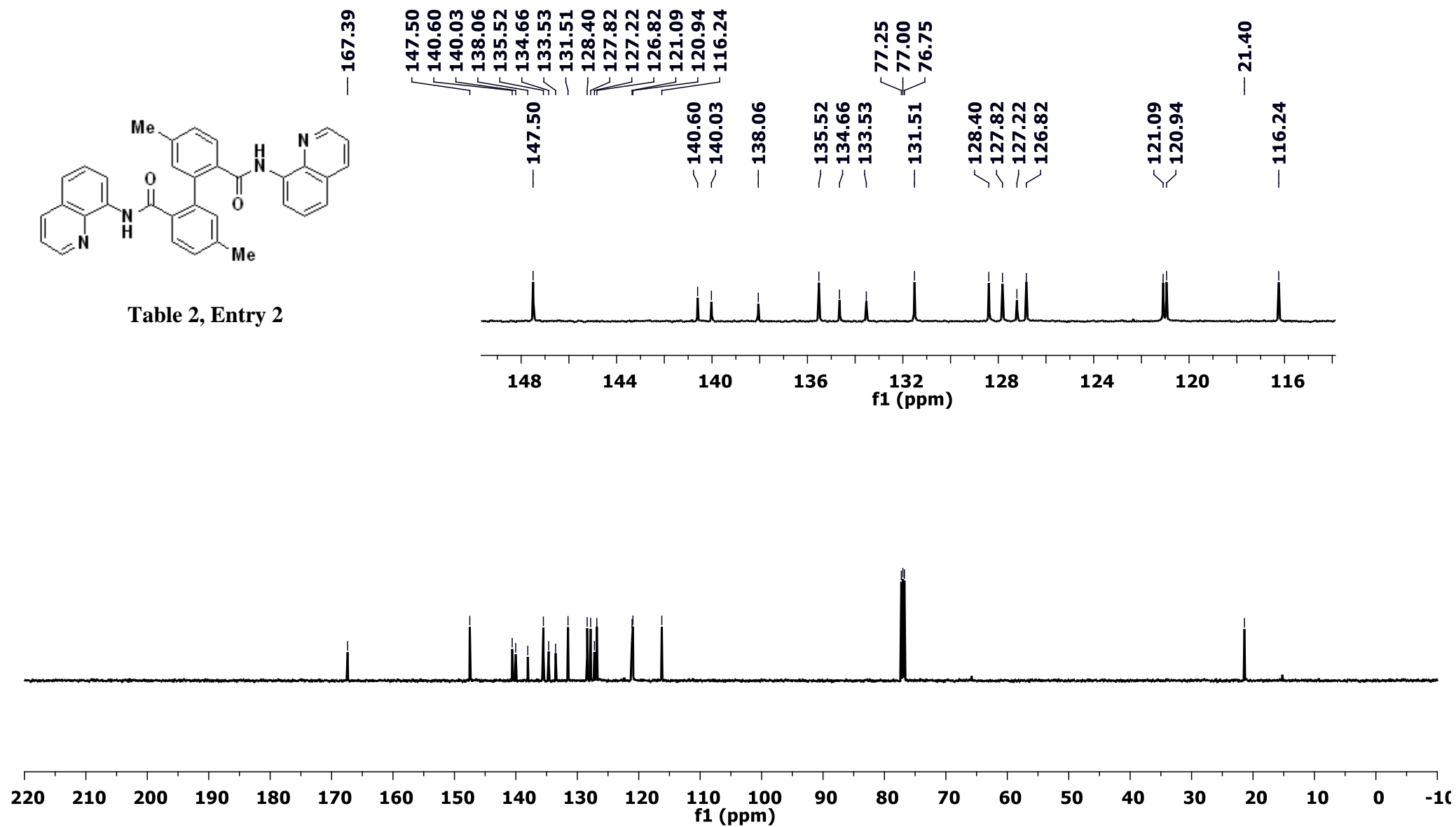
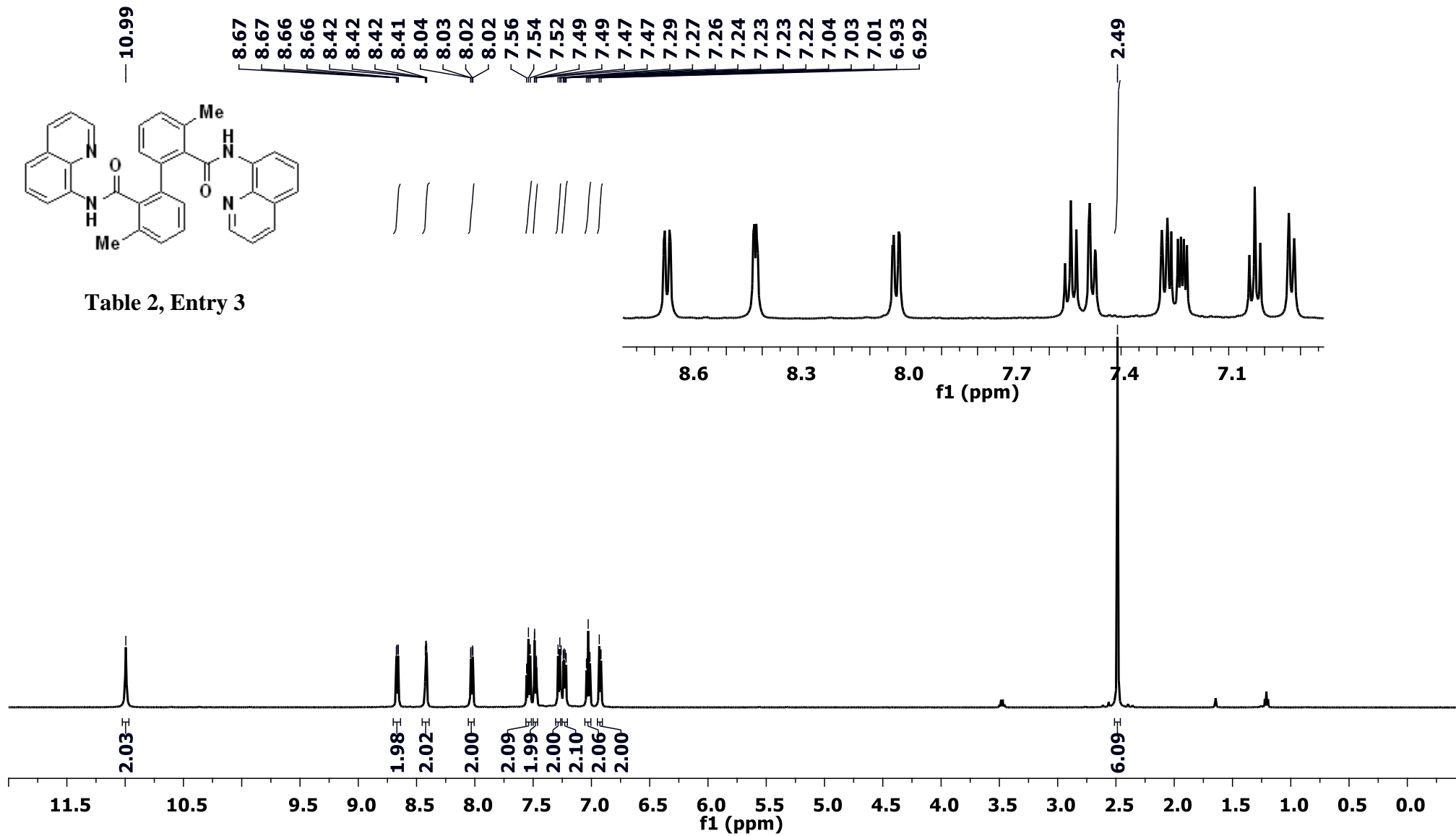


Table 2, Entry 2





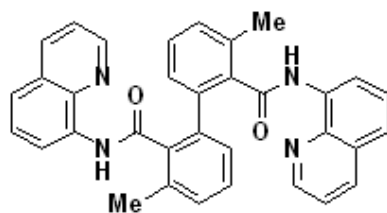
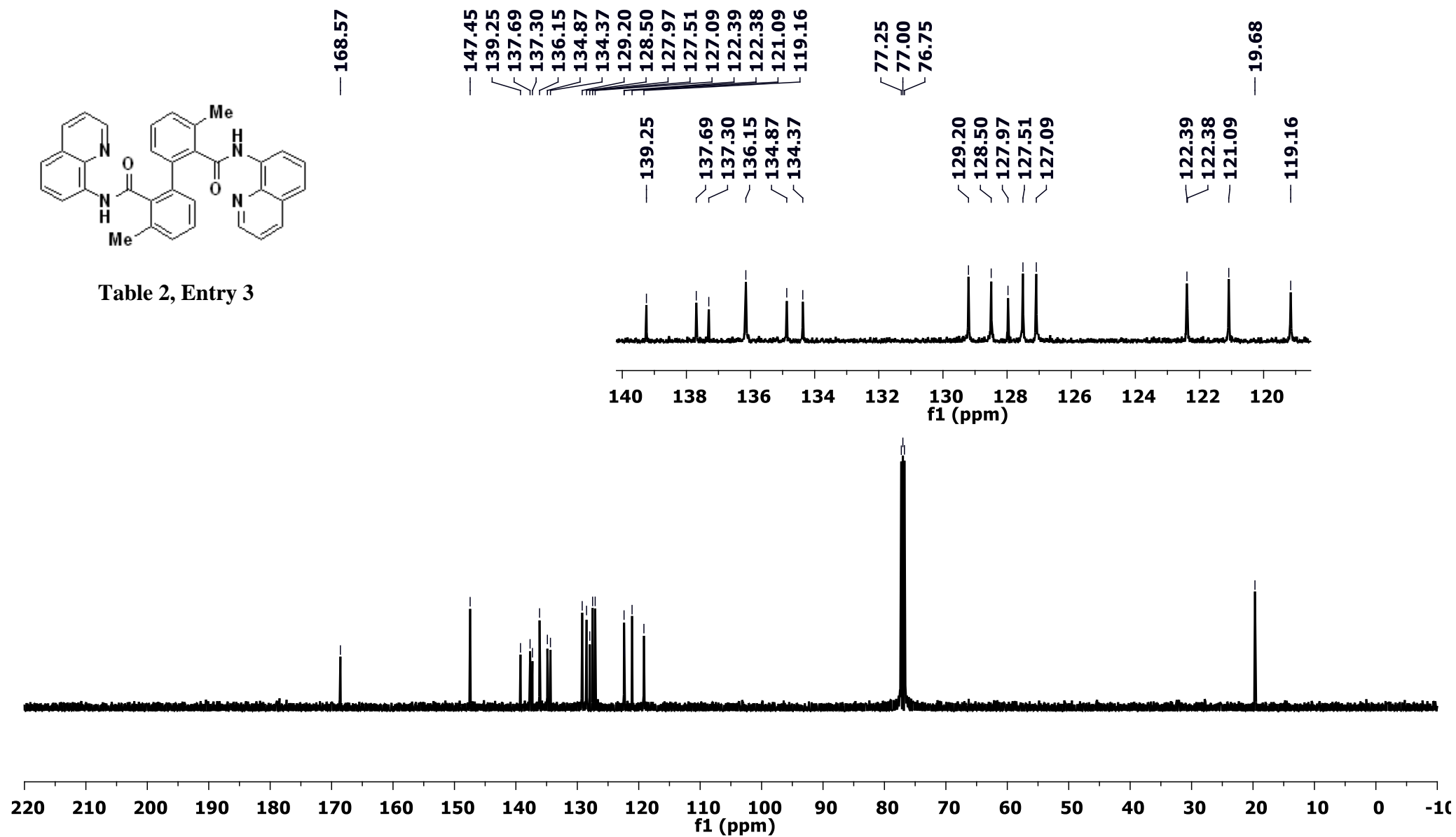


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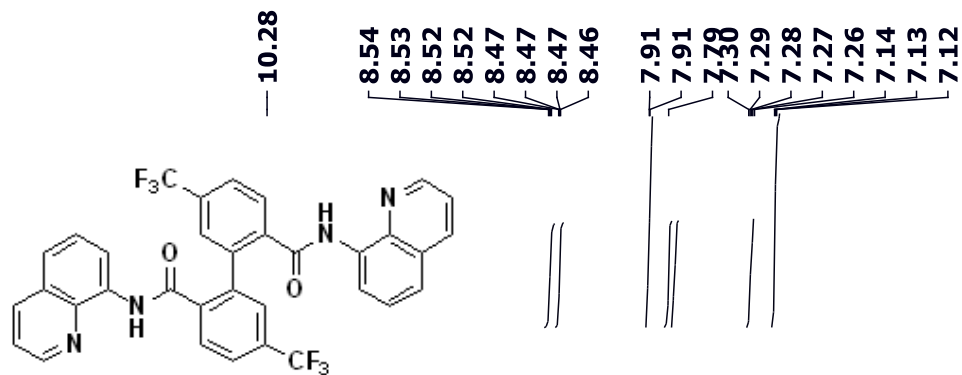
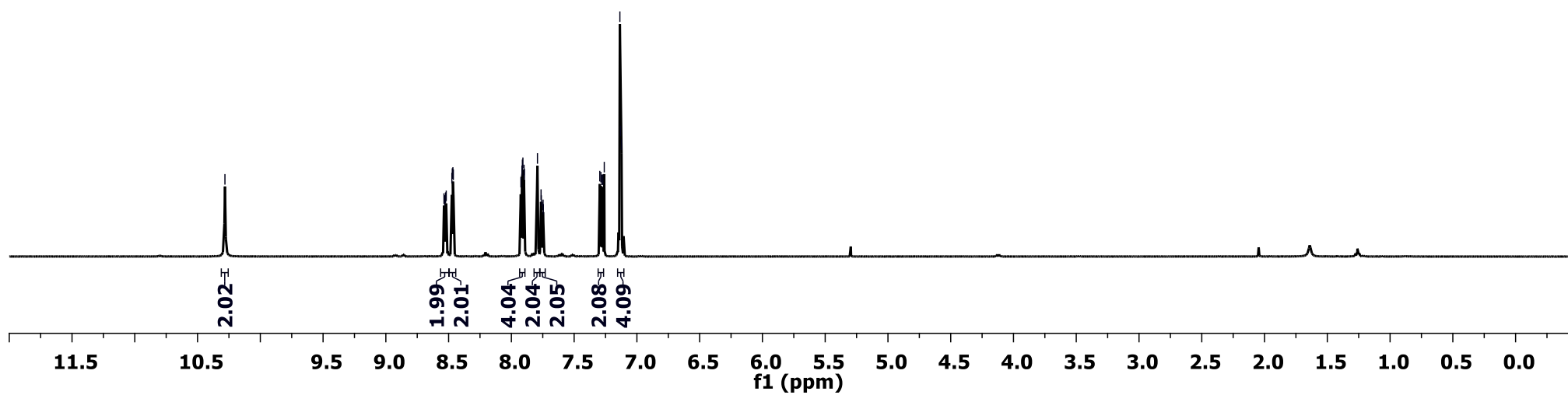
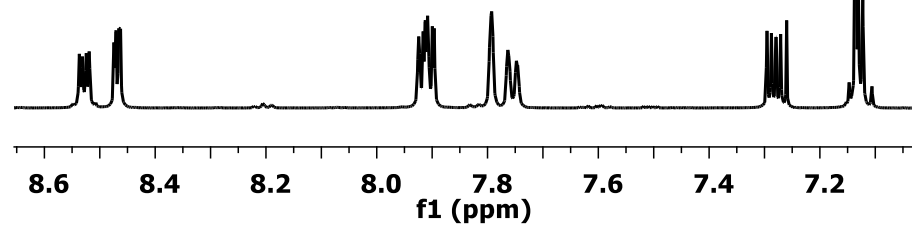


Table 2, Entry 4



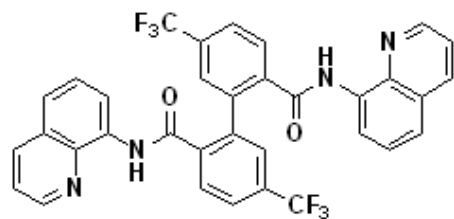
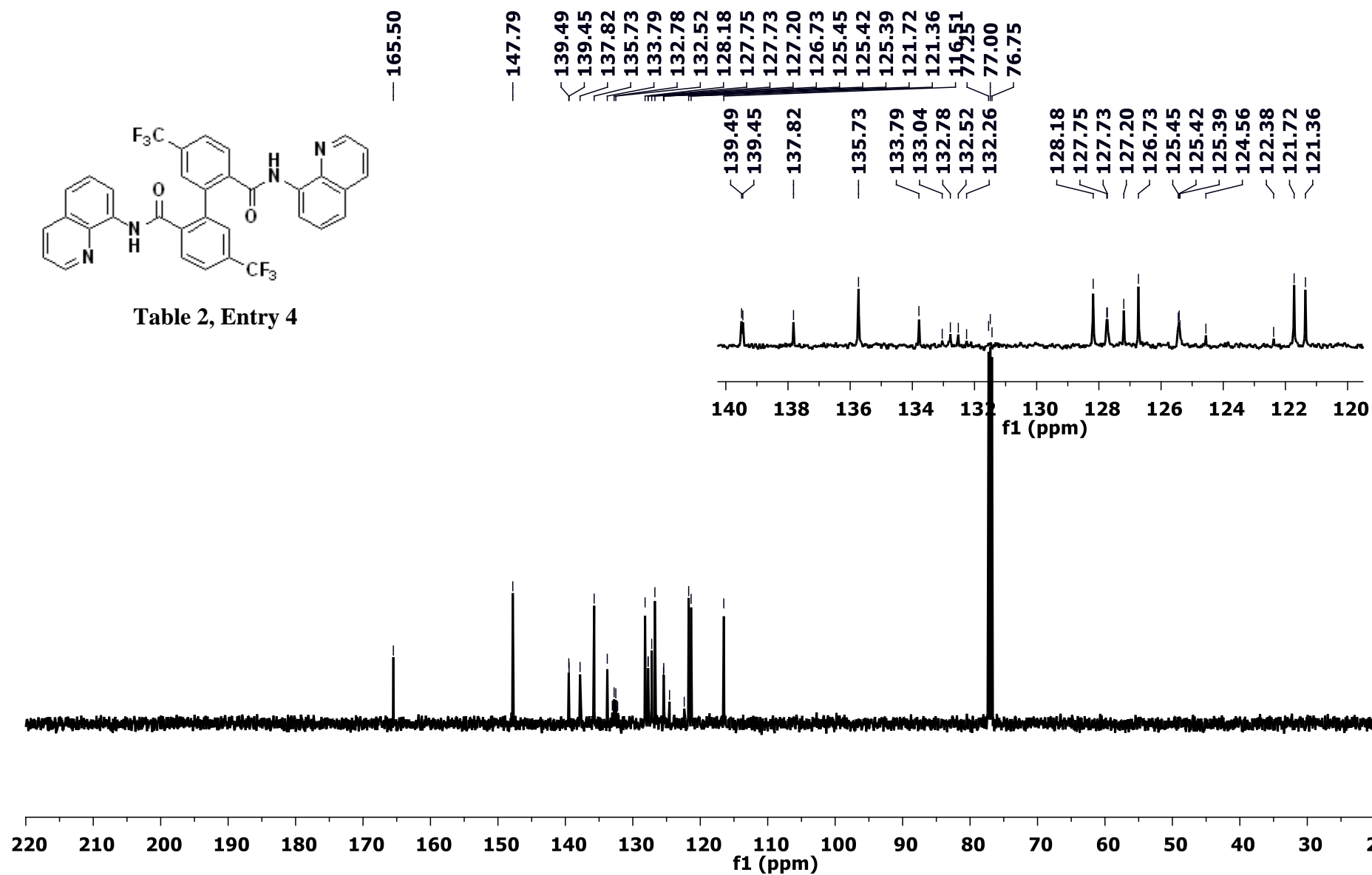


Table 2, Entry 4



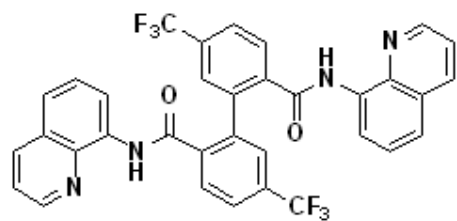
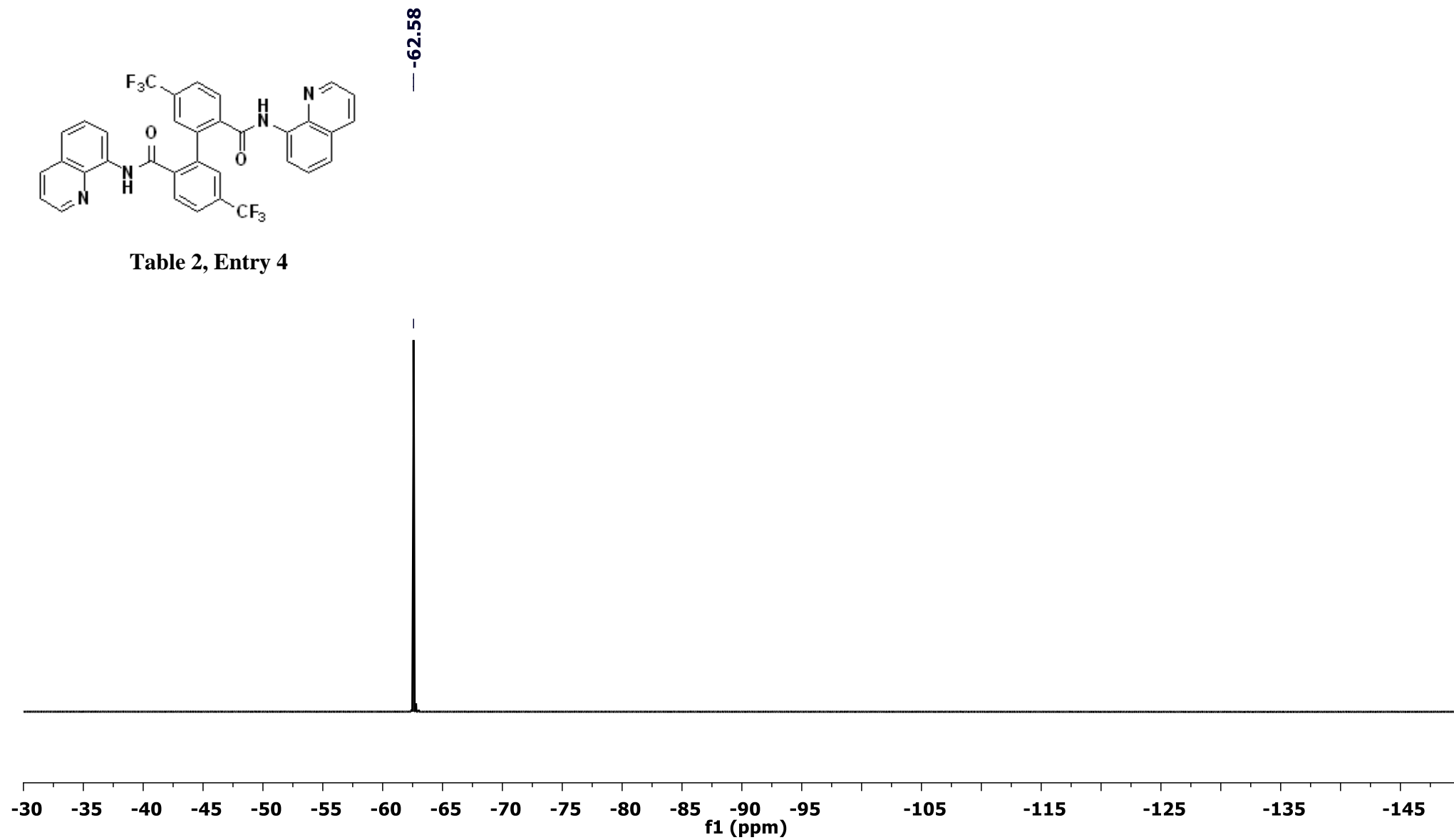
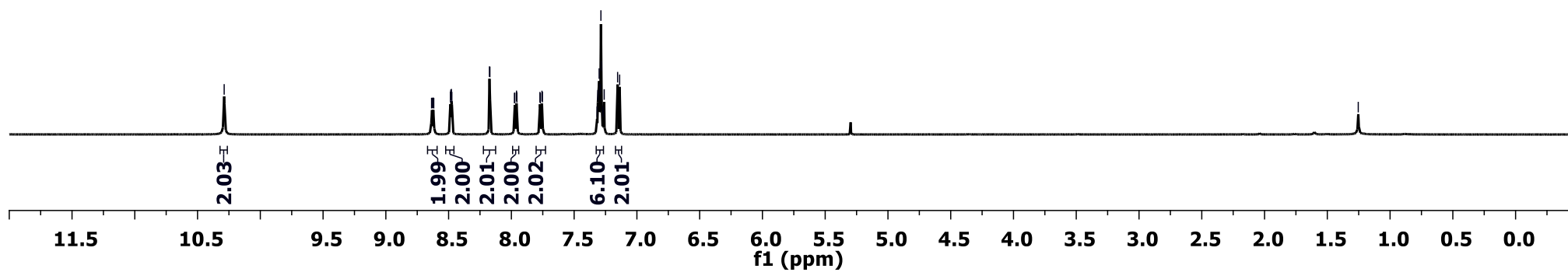
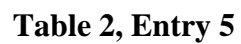


Table 2, Entry 4





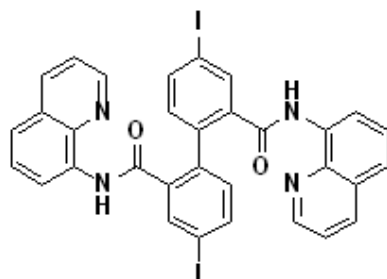


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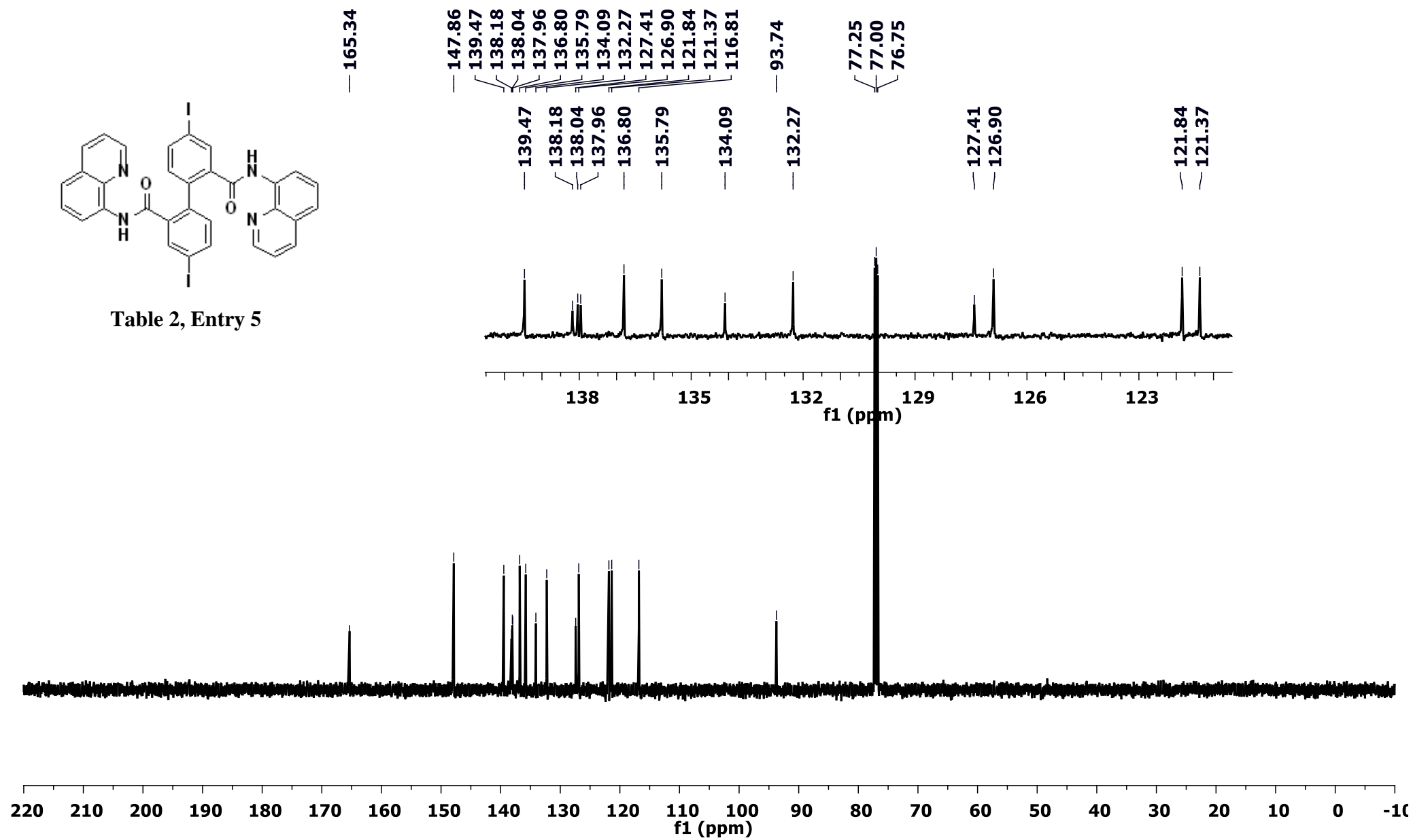




Table 2, Entry 6

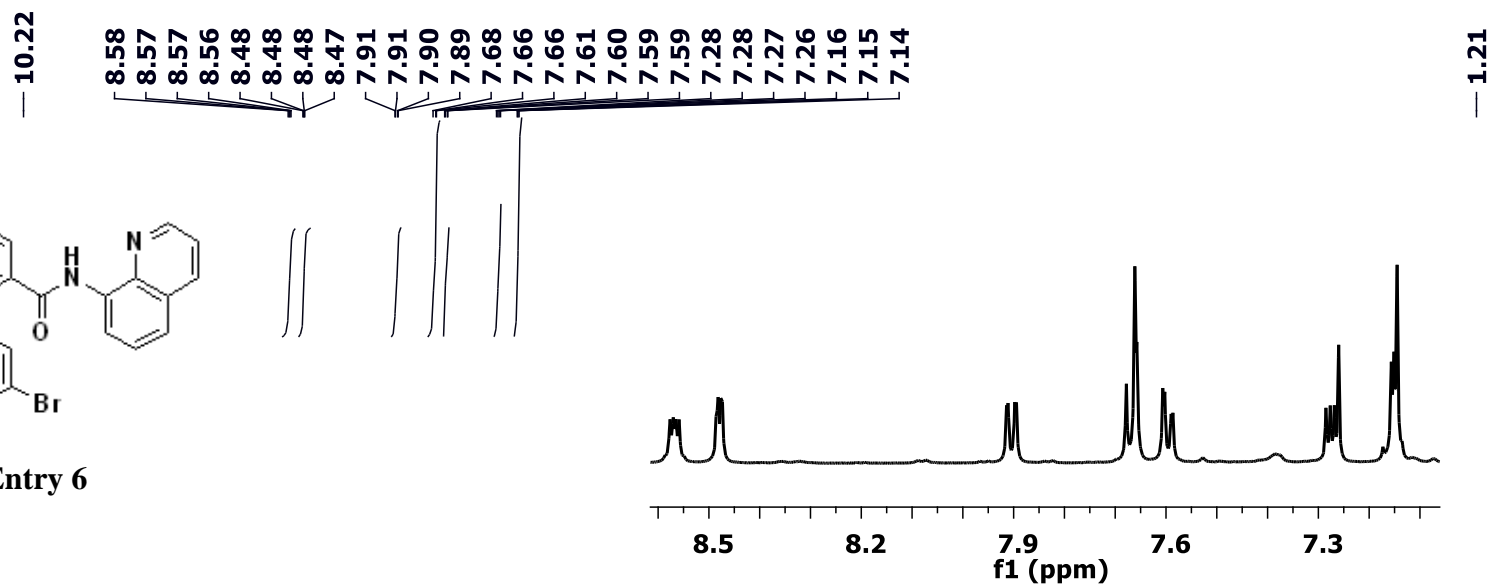
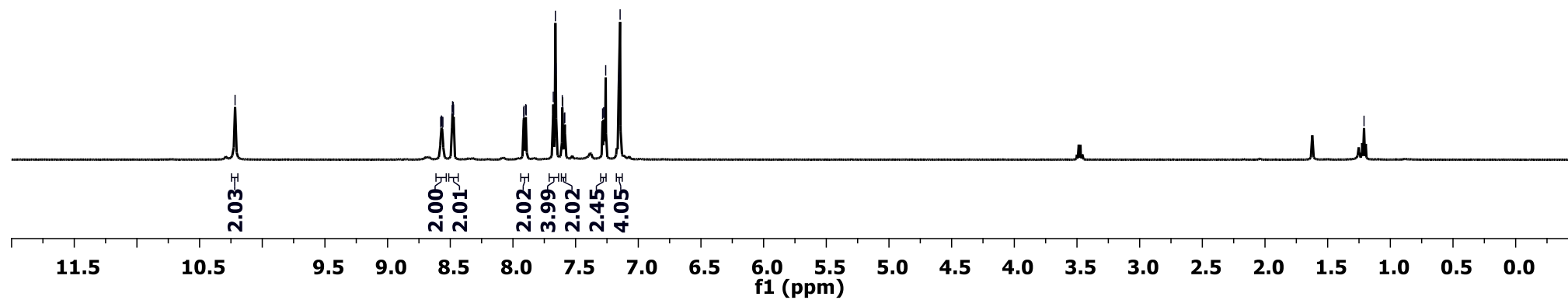
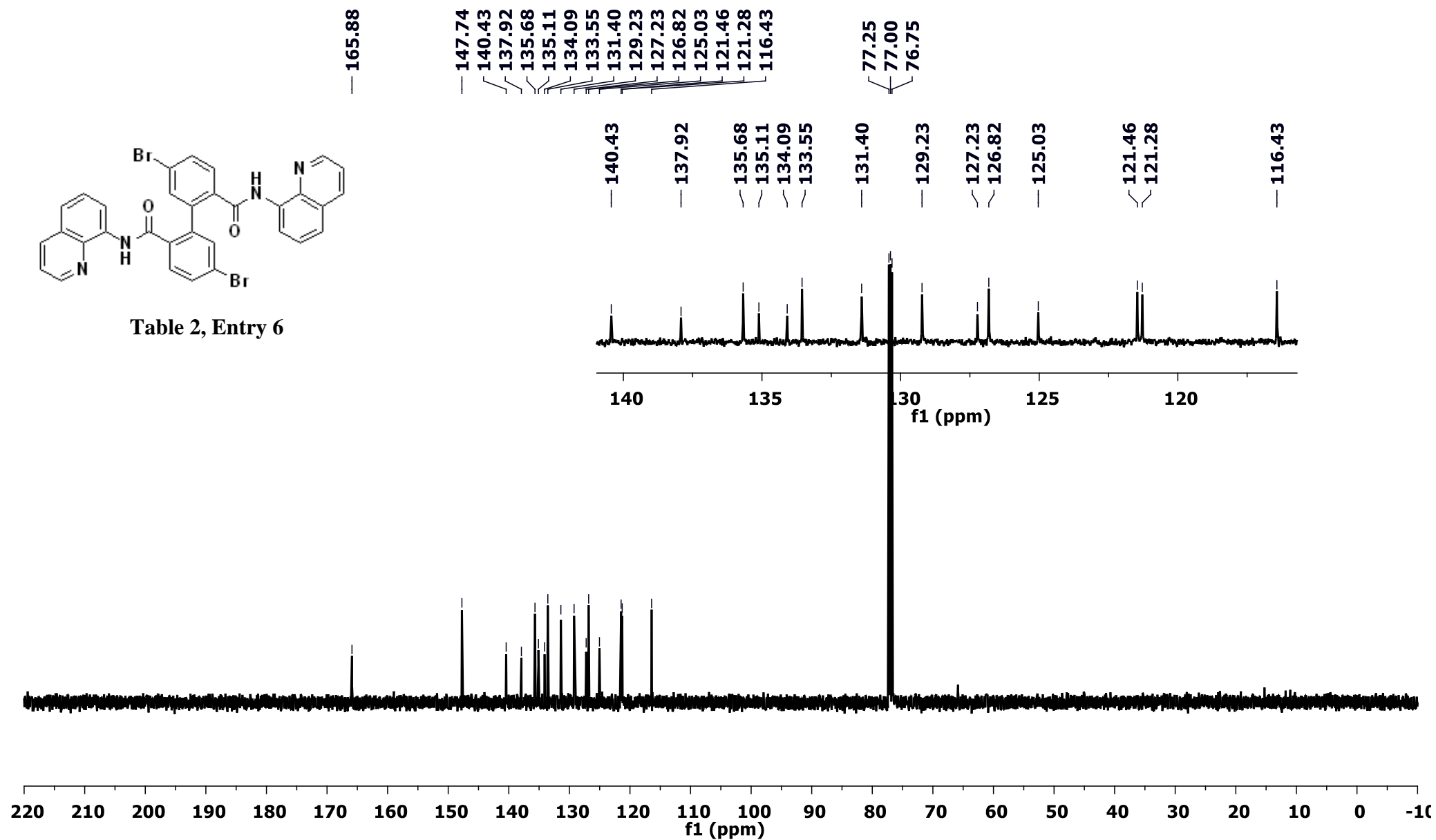




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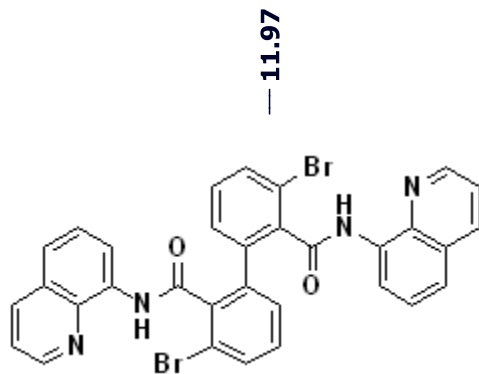
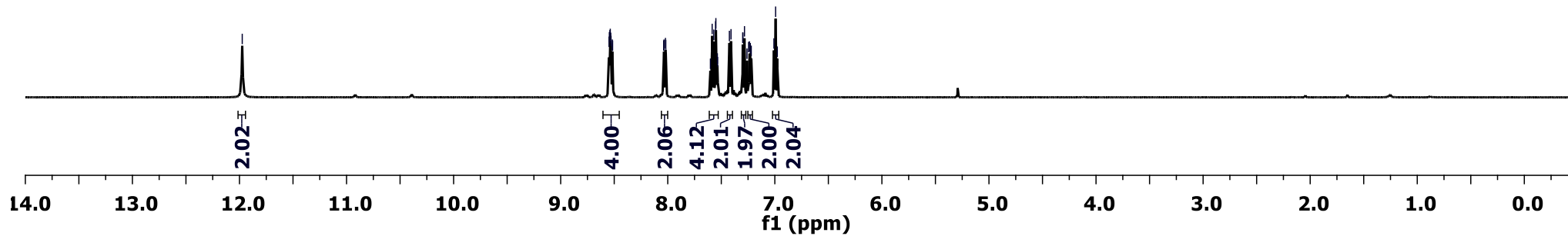
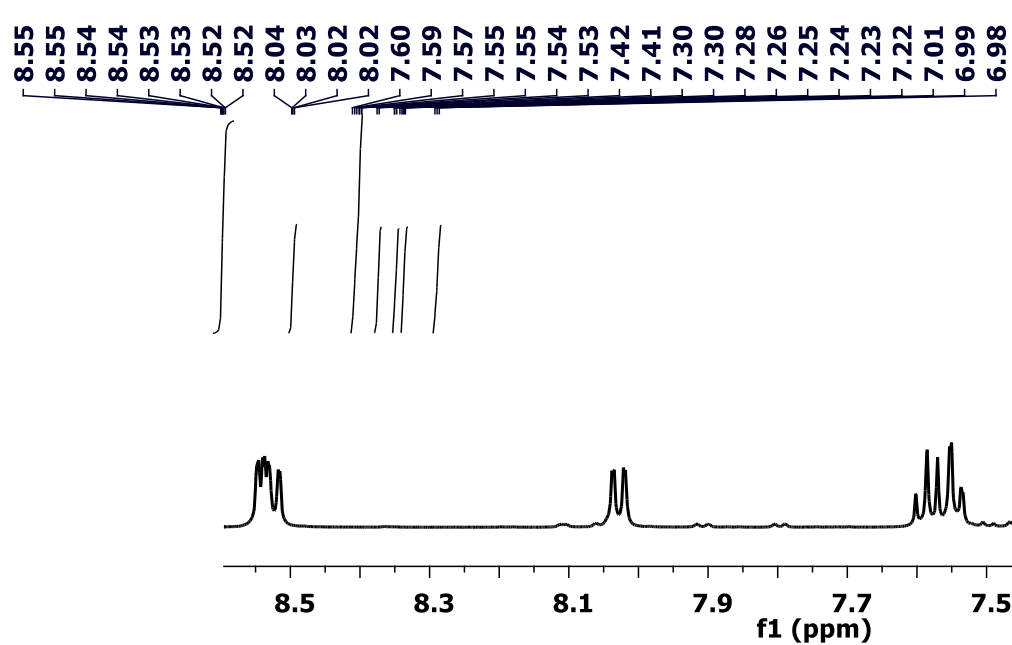


Table 2, Entry 7



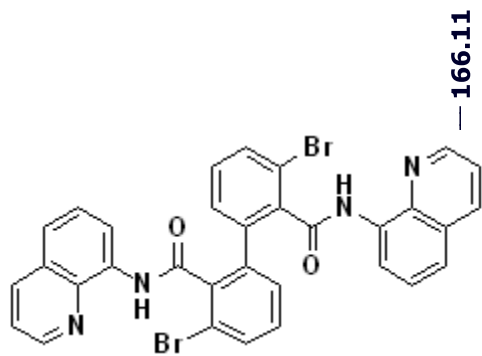
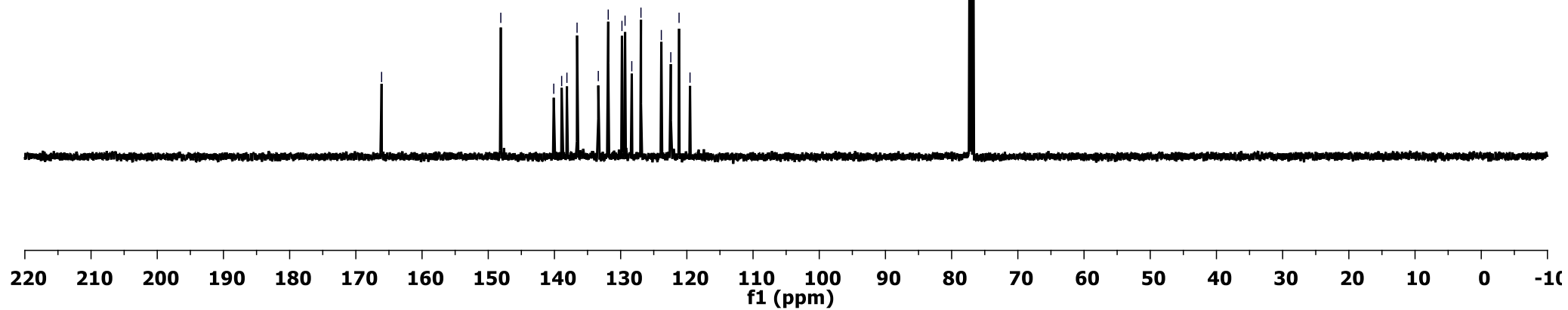
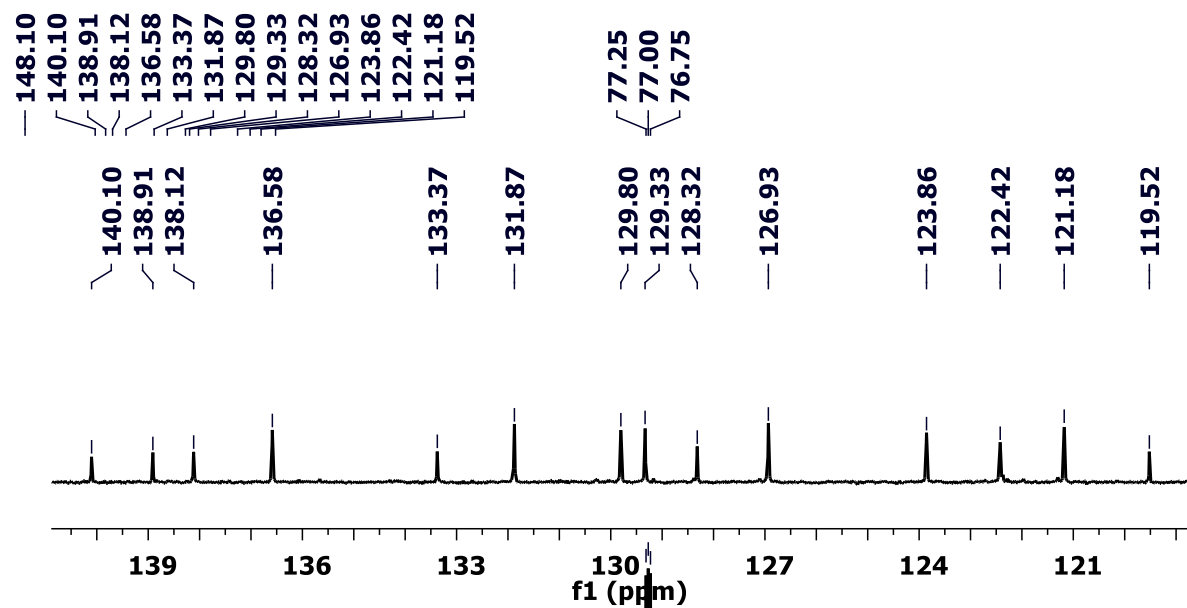


Table 2, Entry 7



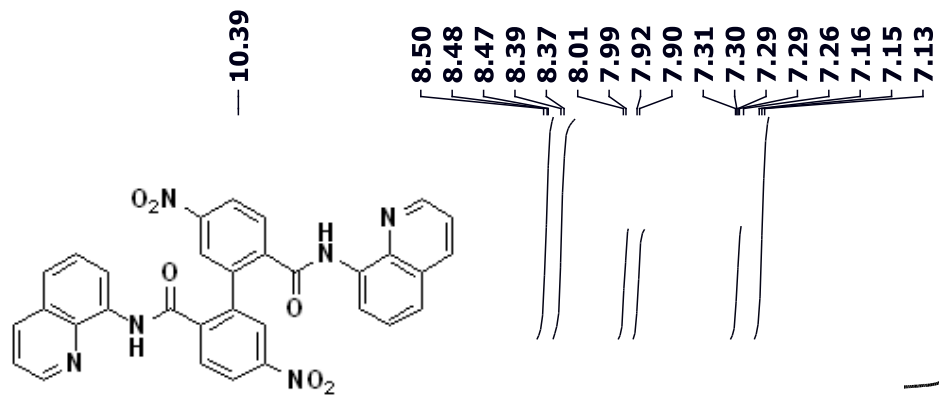
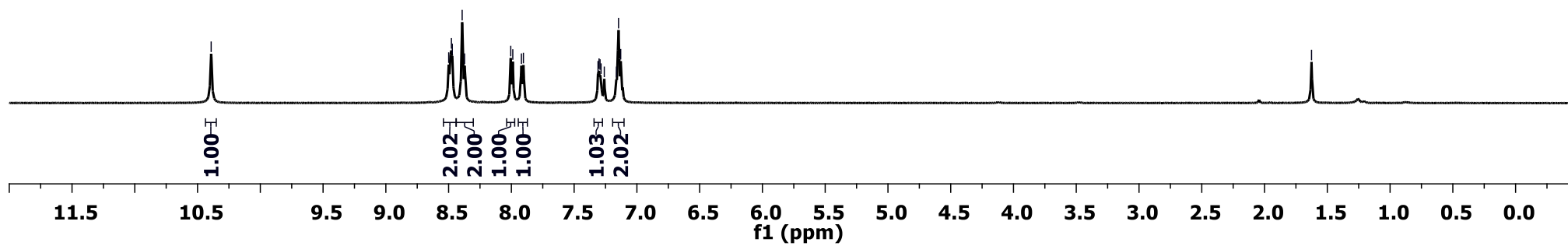
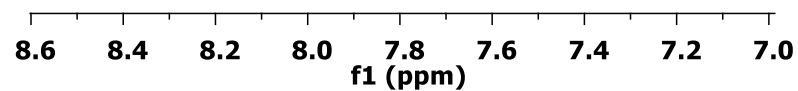


Table 2, Entry 8



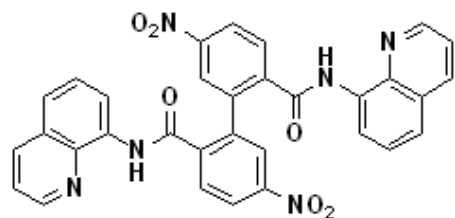
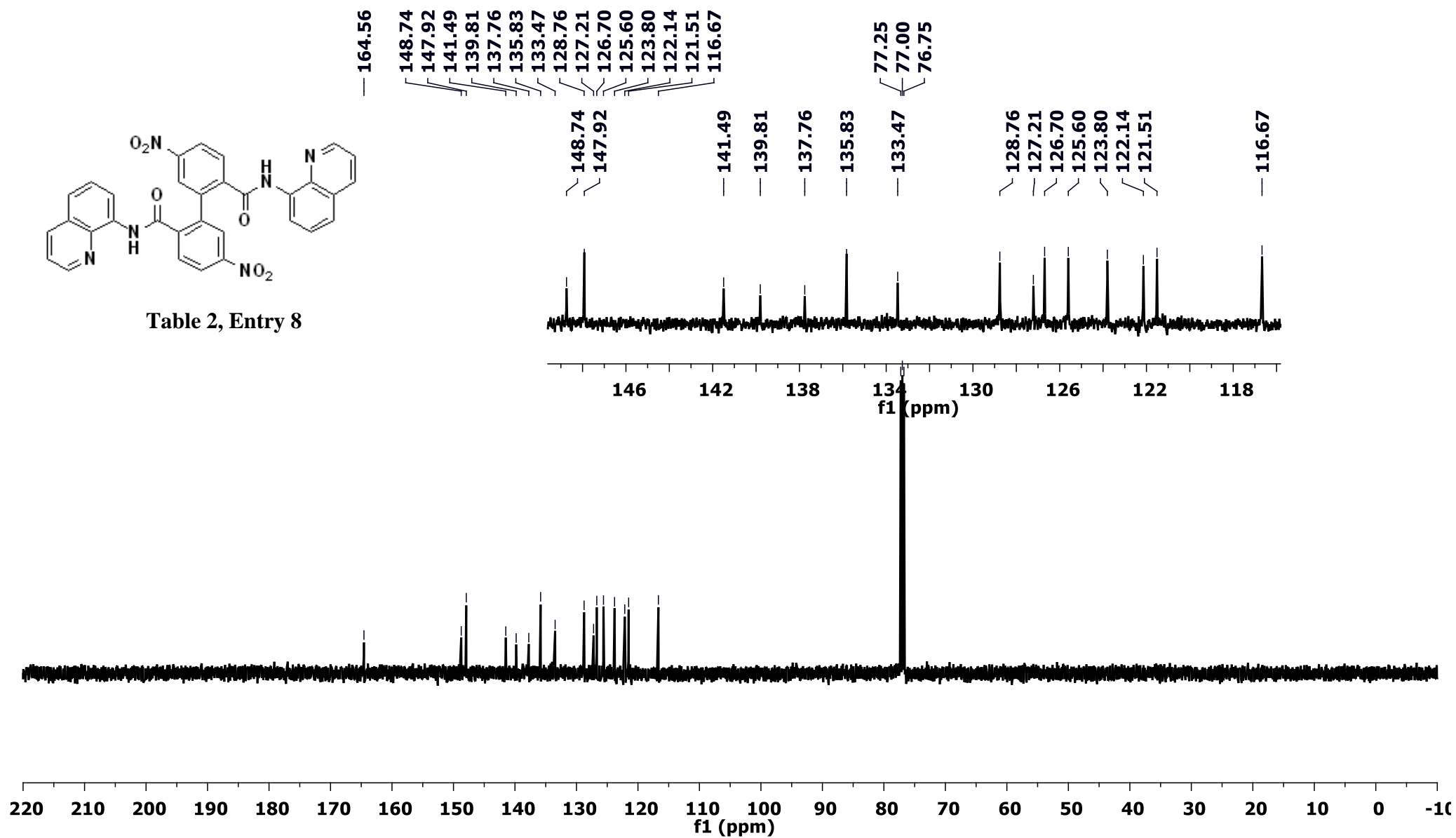


Table 2, Entry 8



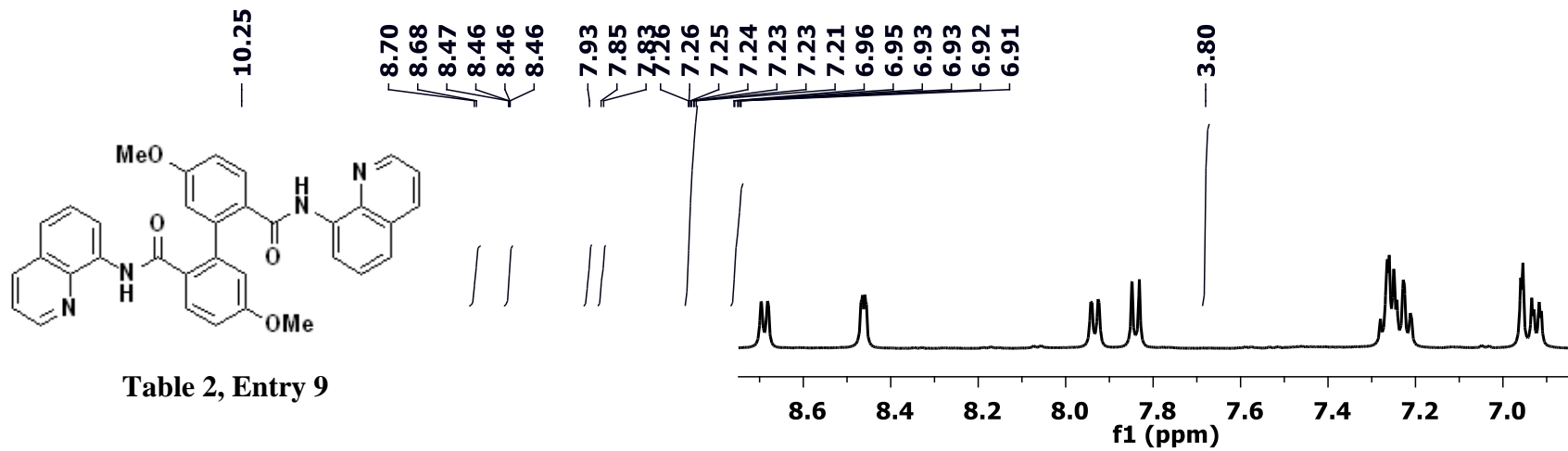
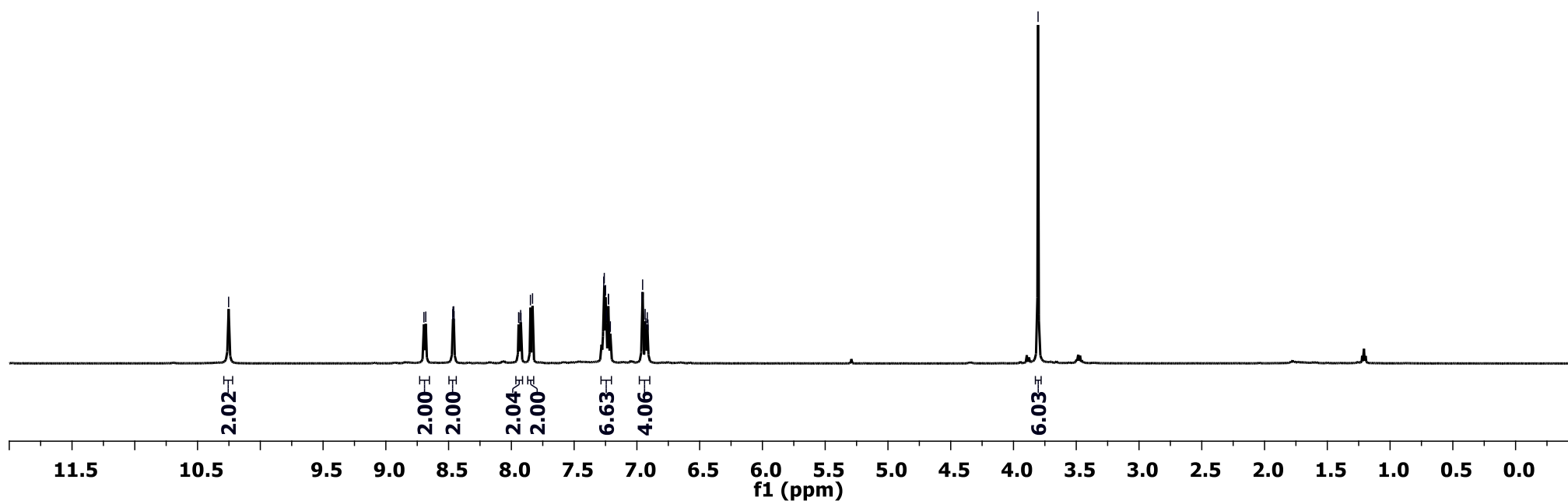


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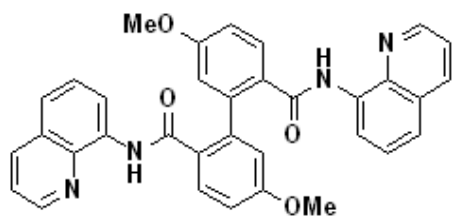
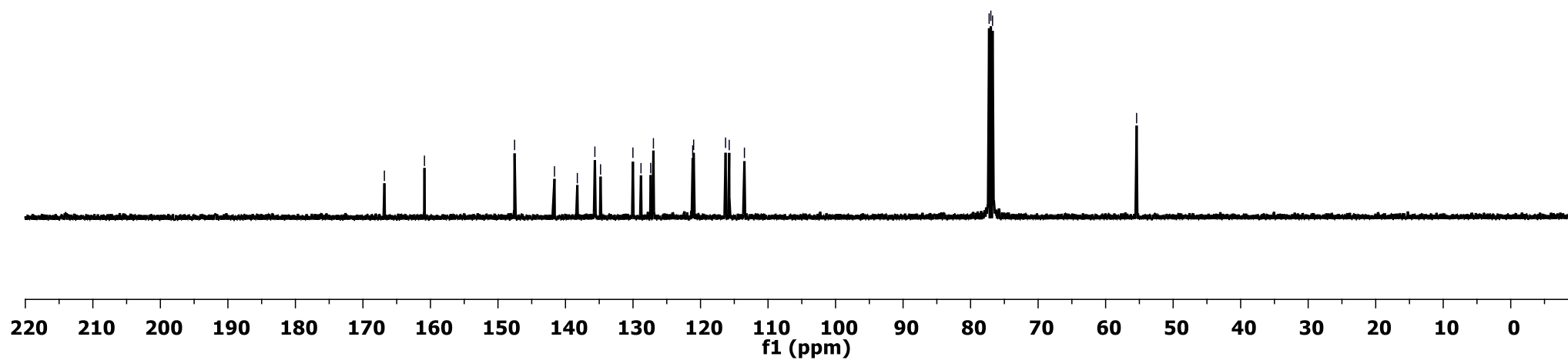
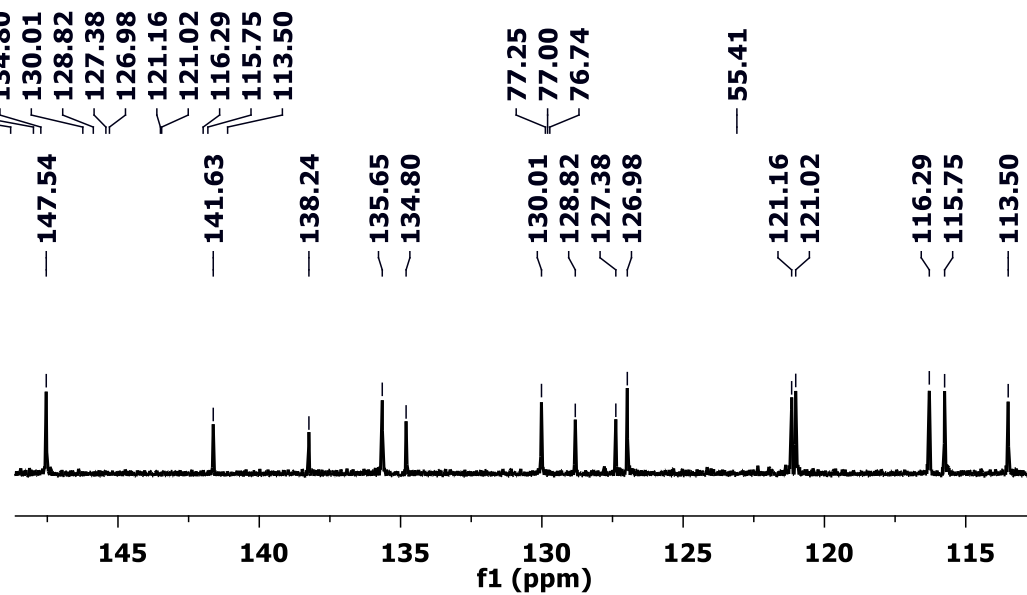


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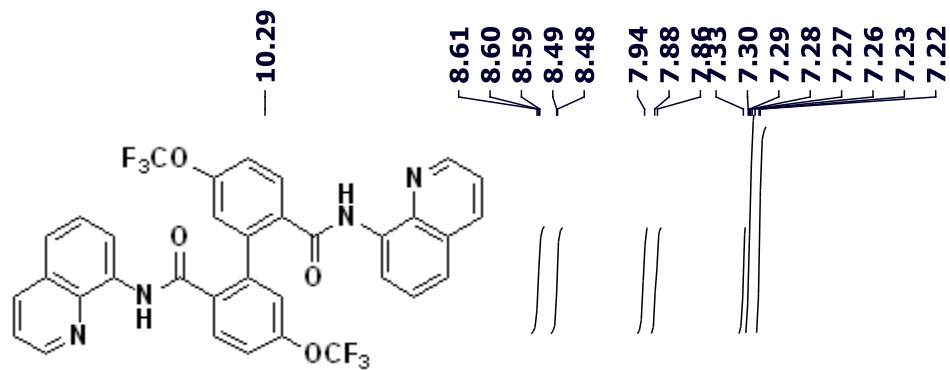
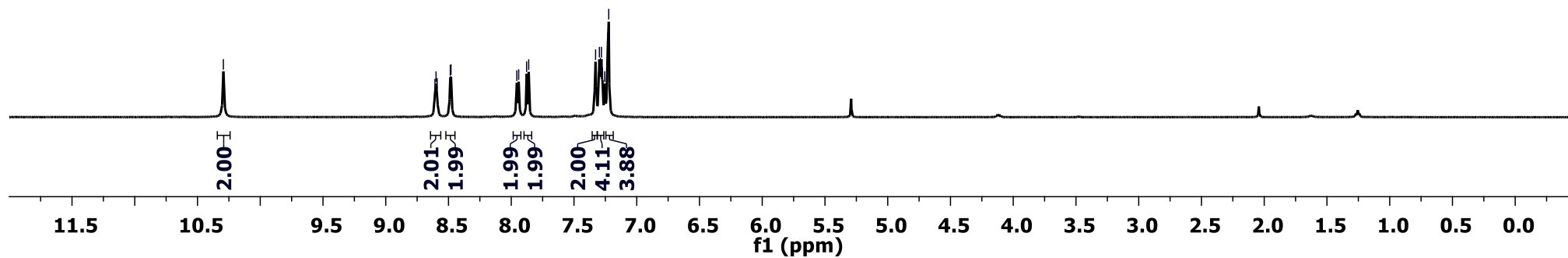
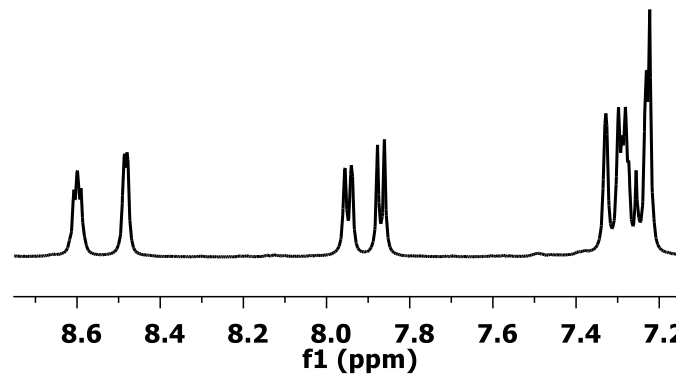


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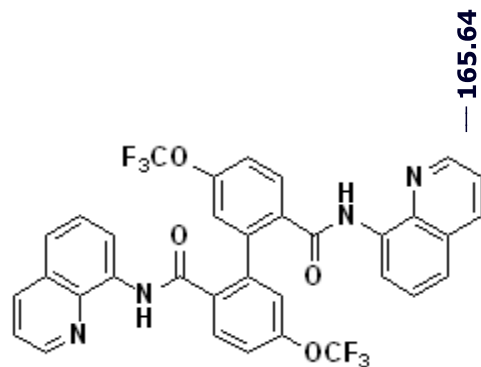
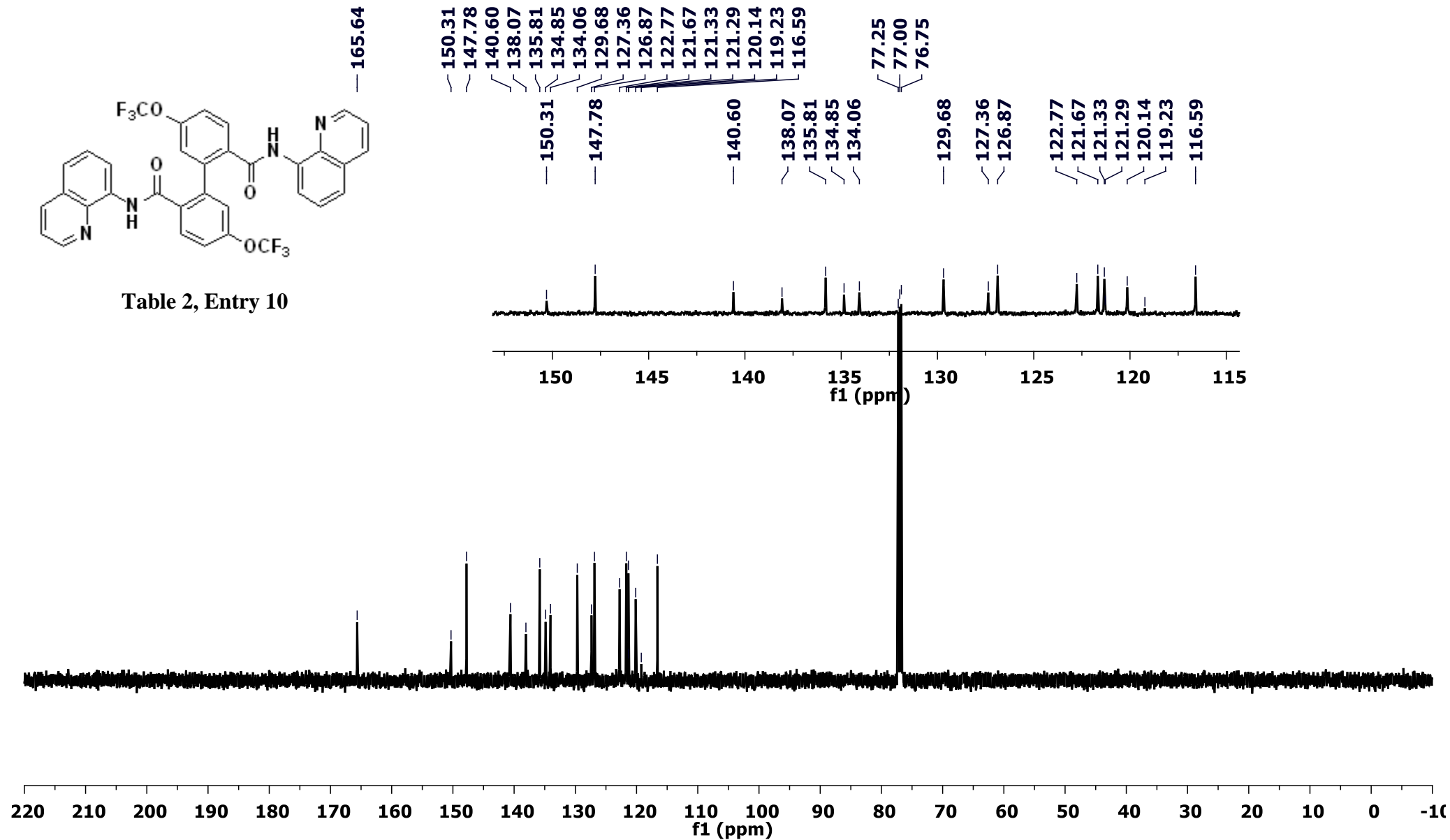


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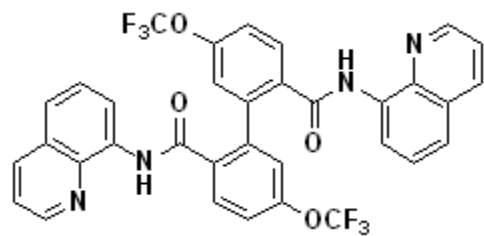
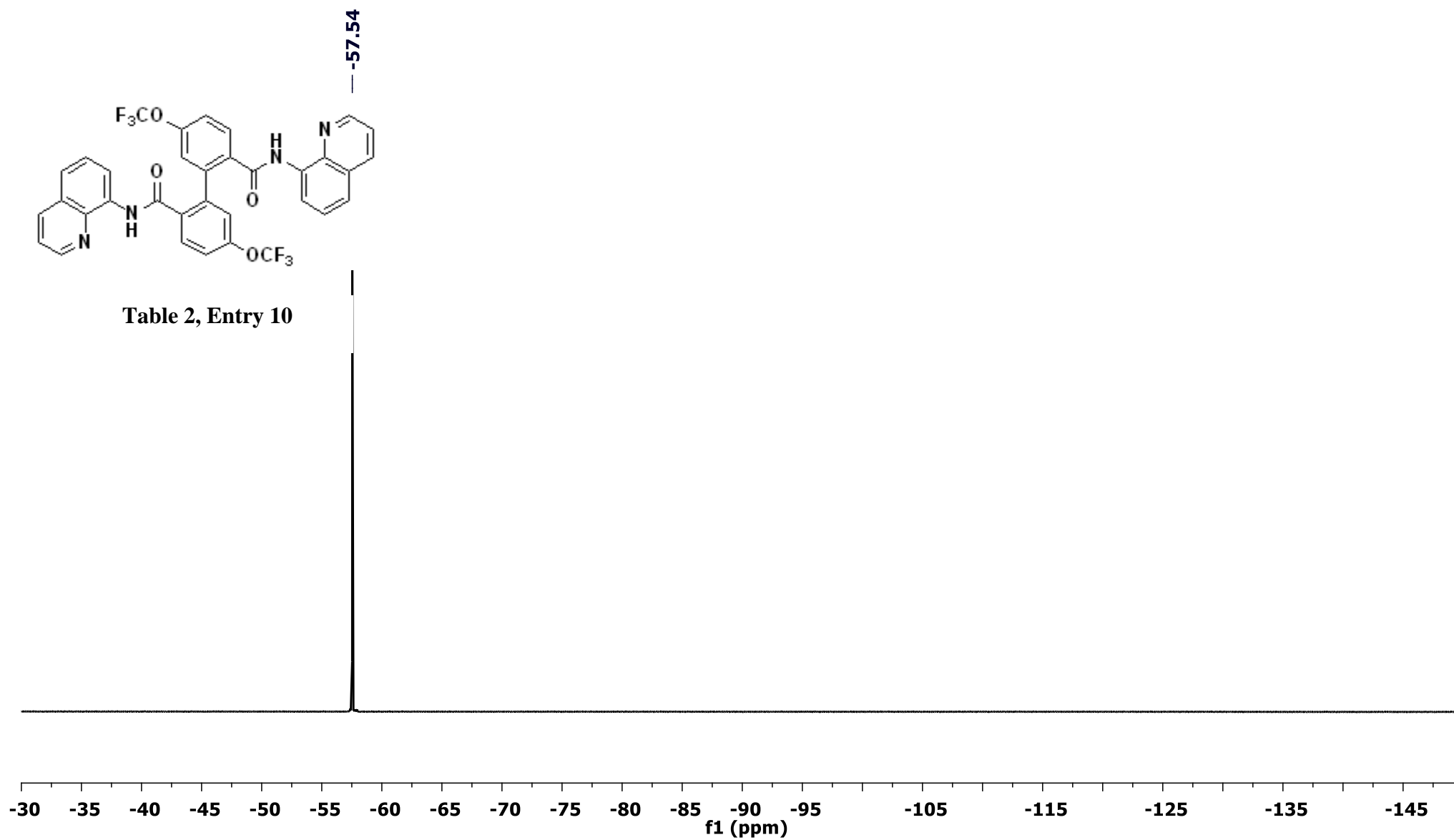
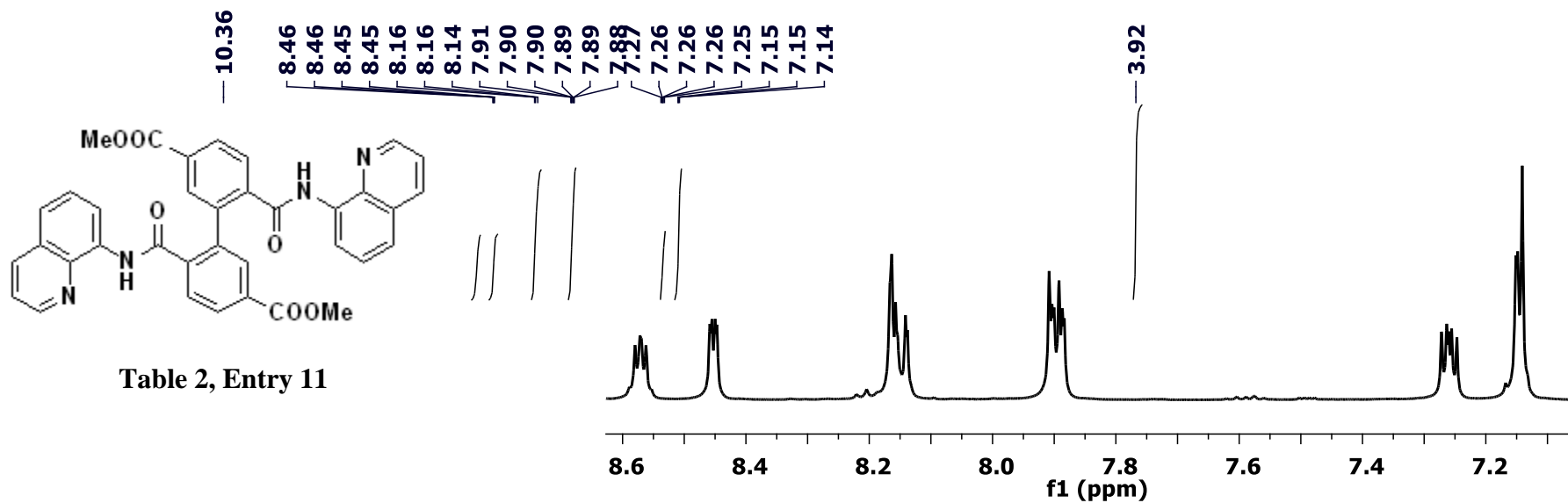


Table 2, Entry 10





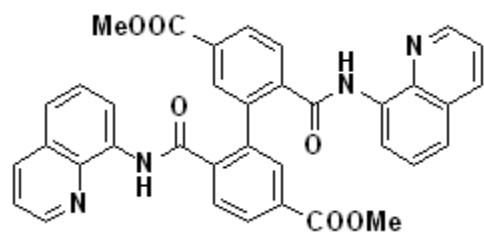
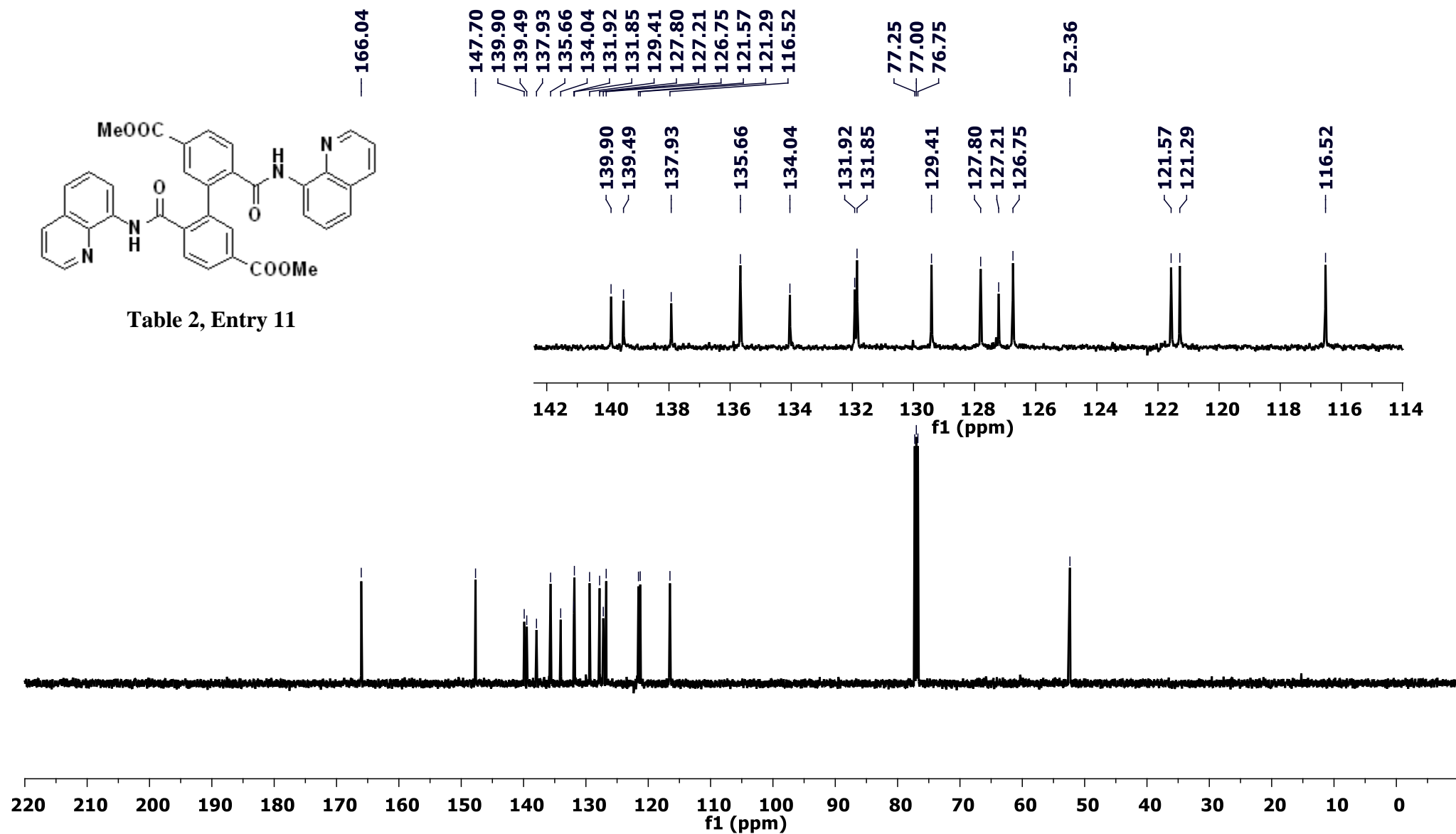


Table 2, Entry 11



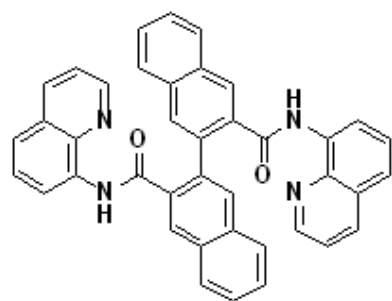
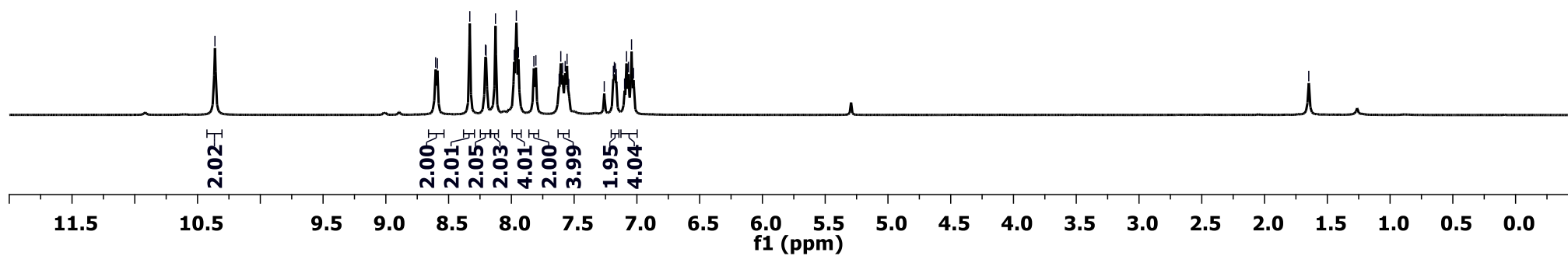
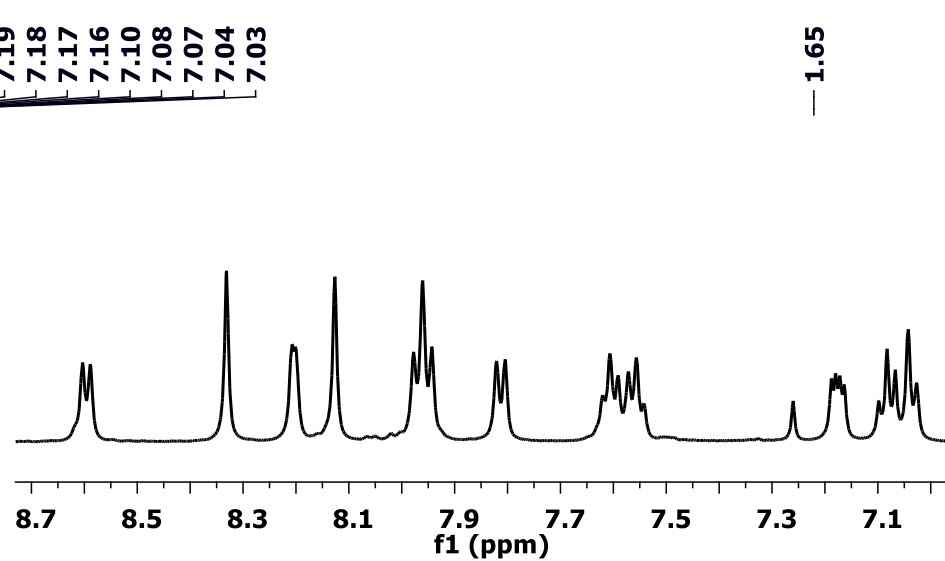


Table 2, Entry 12



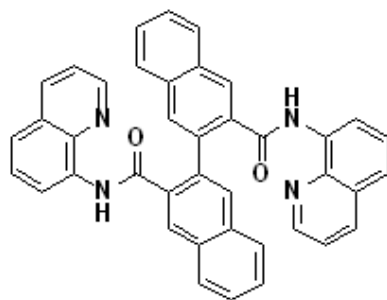
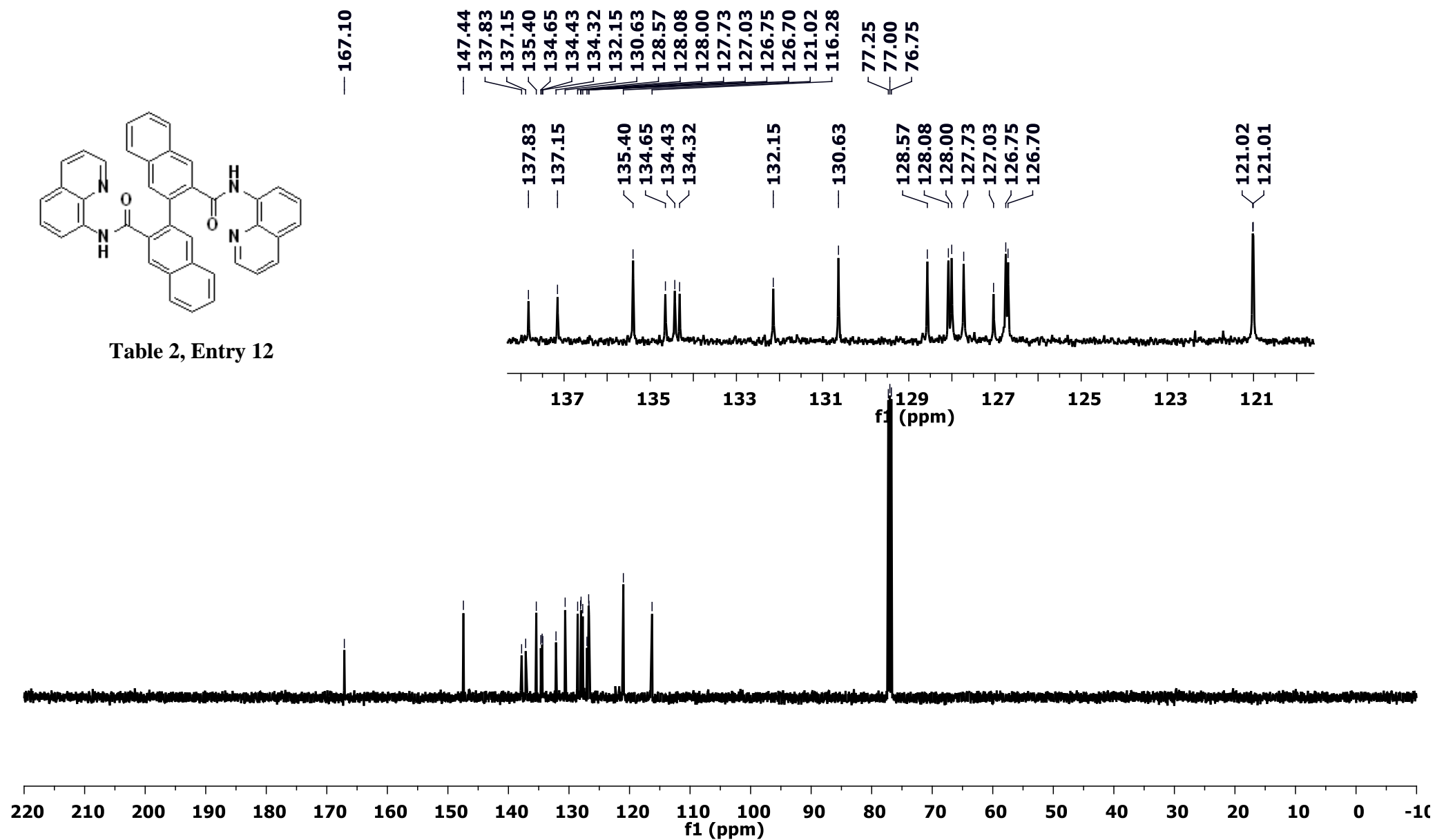


Table 2, Entry 12



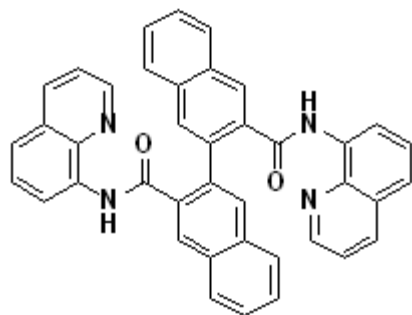
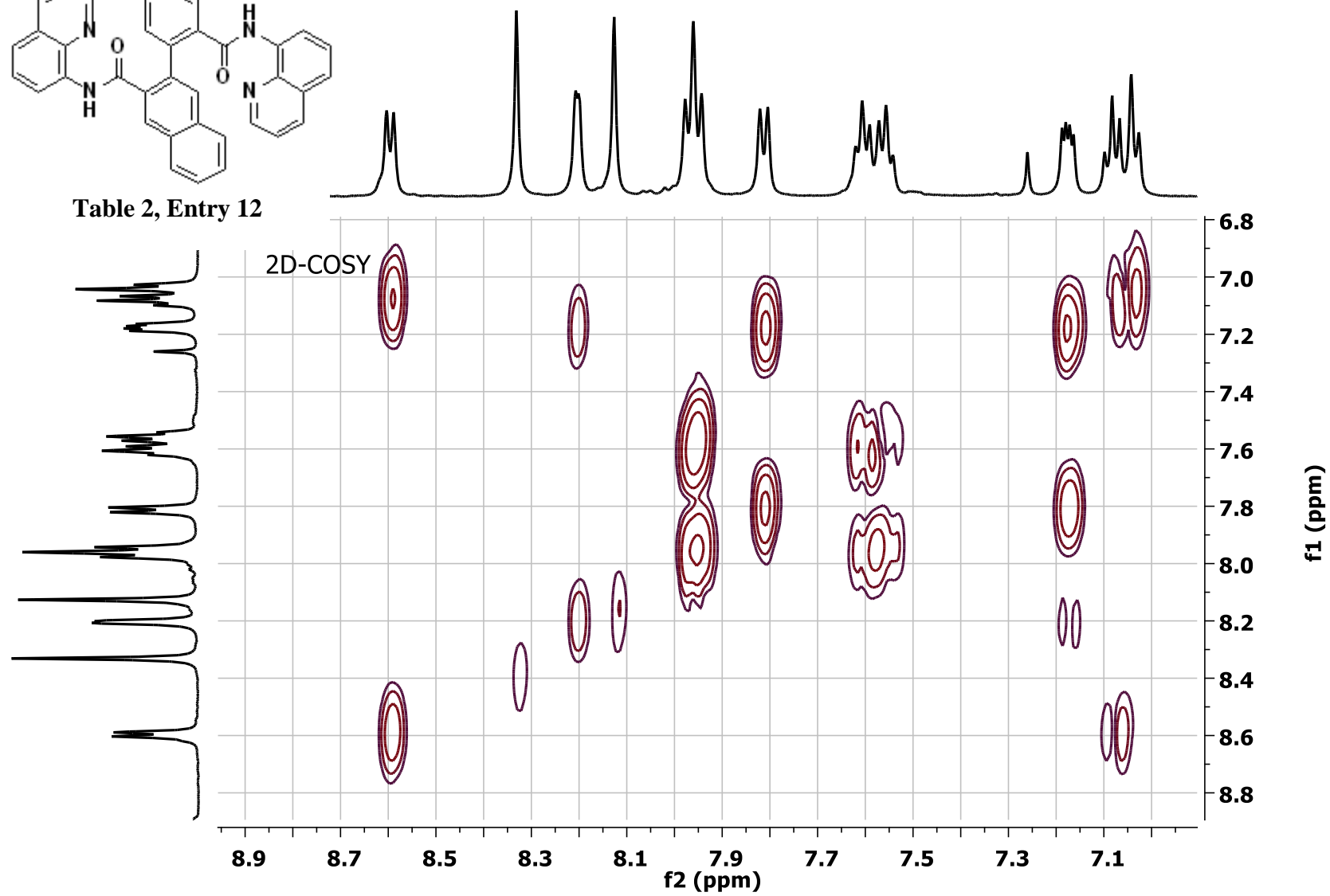


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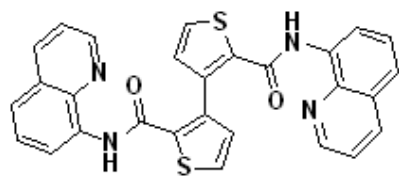
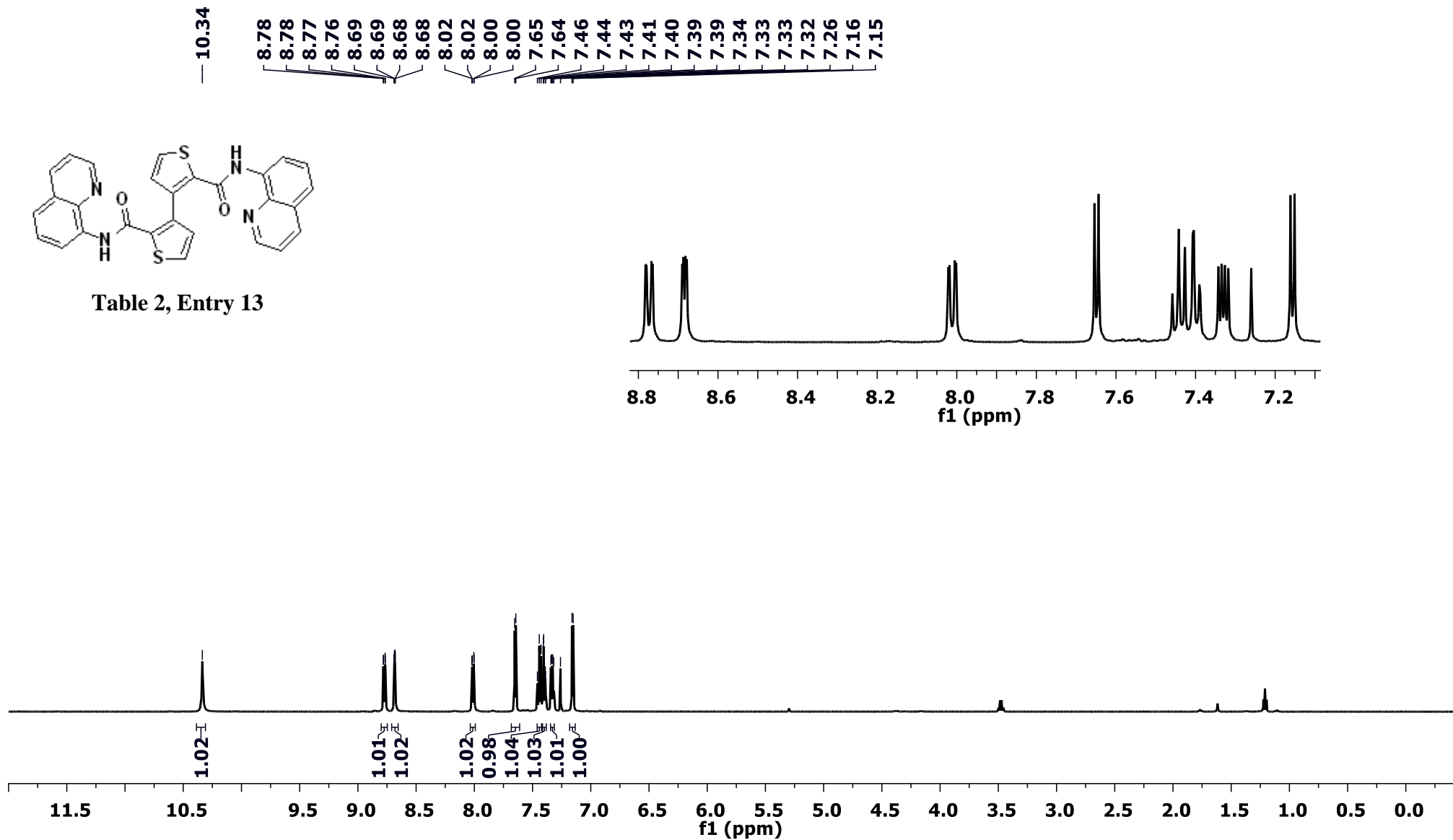


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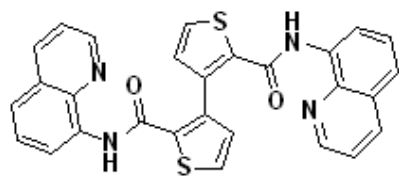
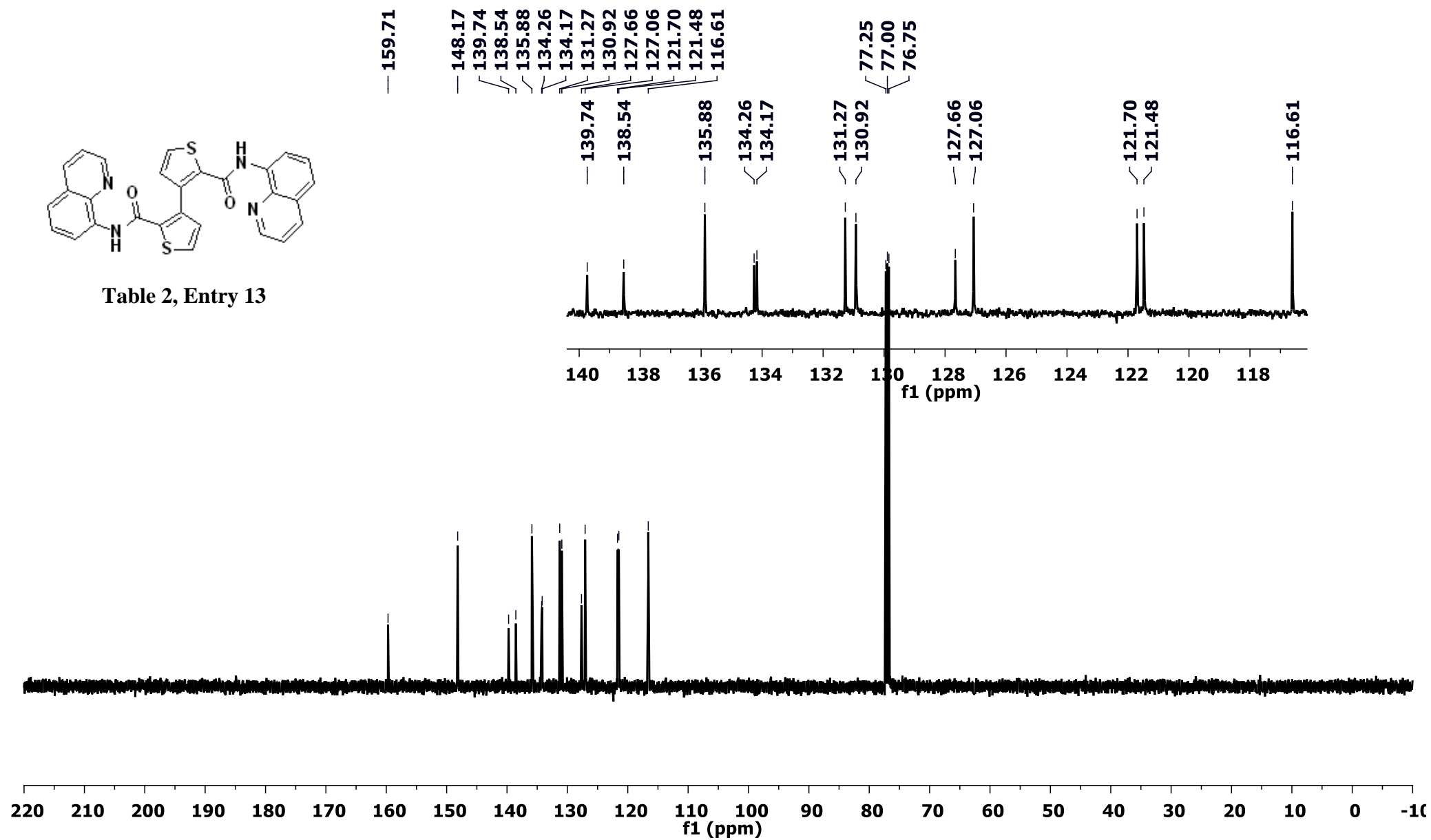


Table 2, Entry 13



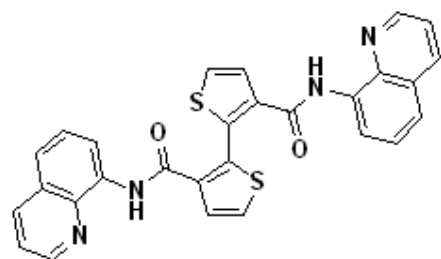
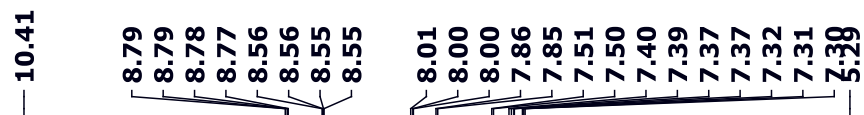
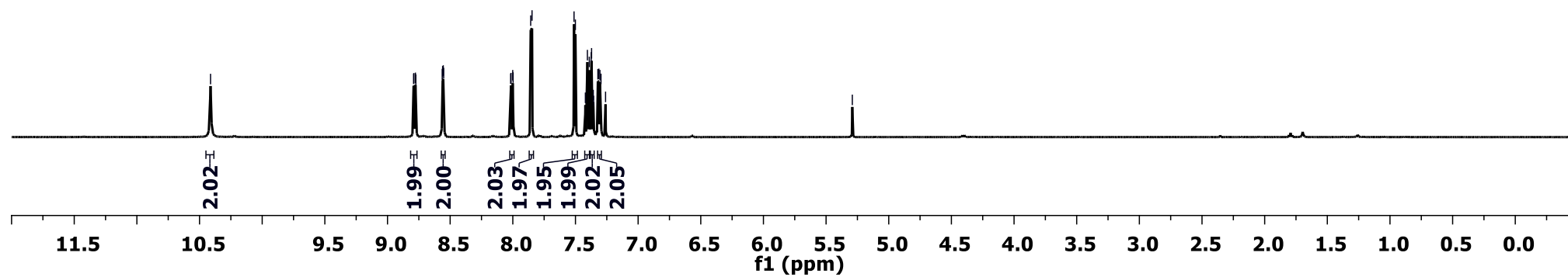


Table 2, Entry 14



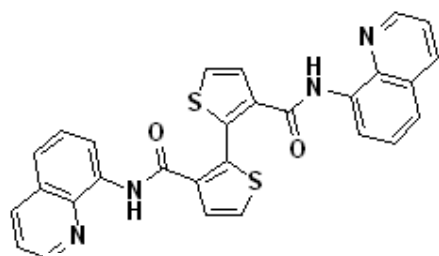
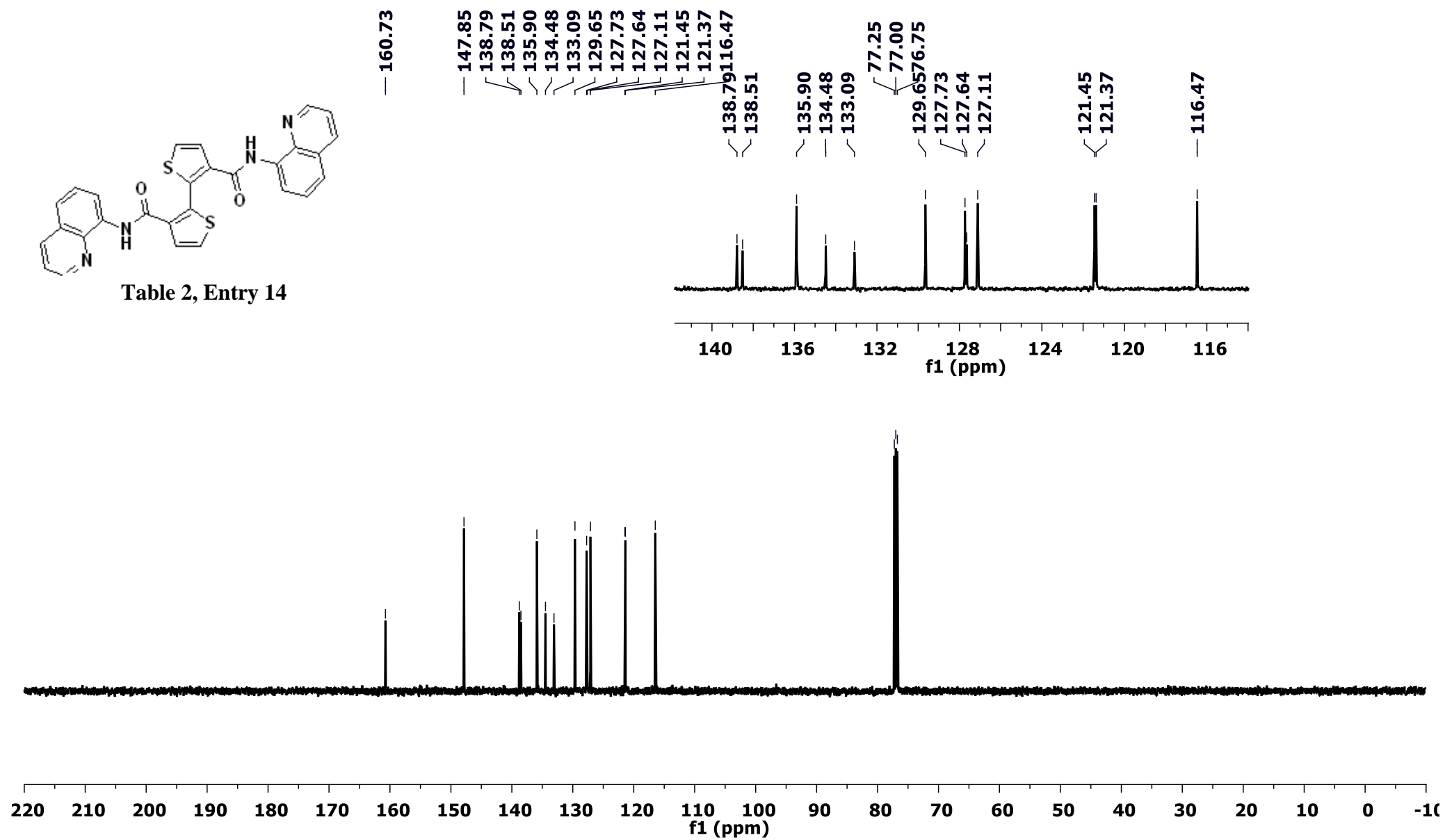


Table 2, Entry 14



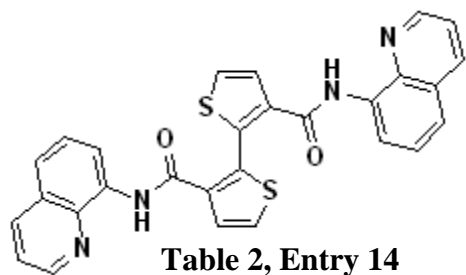


Table 2, Entry 14

