Supporting Information

Metal- and solvent-free domino reaction of 2-isocyanophenol esters to benzoxazines: long-range 1,5-acyl migration on 1,4-diazabutatriene

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1. General Considerations

- All final reactions were run in a flame-dried 50 mL Schenk tube filled with a 10 mm magnetic stirrer bar. Solvents and liquid reagents were added by Argon-flushed syringes or cannulas.

- All reagents and chemicals were purchased from chemical suppliers (Merck, Sigma-Aldrich, Fluka, Exir, and Alpha-Aesar) and used without further purification.

- **Solvents** employed for column chromatography and work-up were purchased in analytically pure grade and used without further purification. Solvents used for air and moisture-sensitive reactions were freshly distilled before use.

- **TLC** (Thin Layer Chromatography) was performed on silica gel pre-coated aluminum plates (Merck, 60 F-254) and was visualized by UV lamp (λ=254 nm).

- **Flash Column Chromatography** was performed using a normal phase silica column packed with silica gel 60 (230-240 mesh).

- **Microwave-assisted reactions** were performed with a CEM Discover Focused Microwave System apparatus (CEM GmbH).

- **NMR** (Nuclear Magnetic Resonance) spectra were recorded using Bruker Avance 250 spectrometer (250 MHz and 63 MHz for ^{1}H and ^{13}C, respectively) and Bruker Avance 300 spectrometer (300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively) and Bruker Avance 400 spectrometer (400 MHz and 101 MHz for ^{1}H and ^{13}C, respectively) and on a Bruker DRX 500 (500 MHz and 126 MHz for ^{1}H and 13C, respectively). Spectrometer in $CDCl_3$. Chemical shifts (δ) are given in ppm, relative to the signals for $CDCl_3$ (1H NMR: δ= 7.27 ppm, 13C NMR: δ= 77.00 ppm) or DMSO-d_6 (1H NMR: δ= 2.5 ppm, 13C NMR: δ= 39.52 ppm). Coupling constants (J) are reported in Hertz. Multiplicities for ^{1}H NMR are stated as follows: singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), and broad (br).

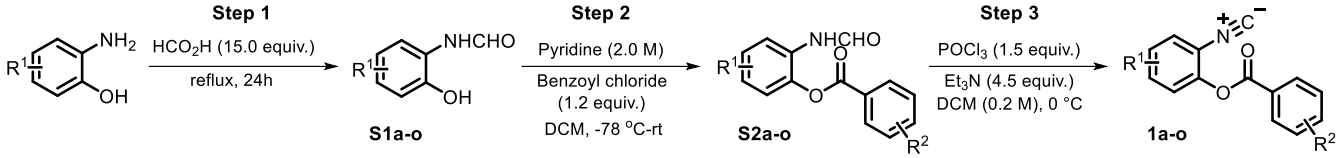
- **HRMS** (High-Resolution Mass Spectra) (ESI-TOF) was recorded using a Waters LCT Premier™ XE mass Spectrometer.

- **X-ray crystal data** were collected on Bruker APEX-II Quazar area detector. Ethanol was employed at room temperature for crystallizing 3b, while ethyl acetate was utilized for 2a.

- **Melting points** were measured in open capillary tubes on an Electrothermal 9100 digital melting point apparatus.

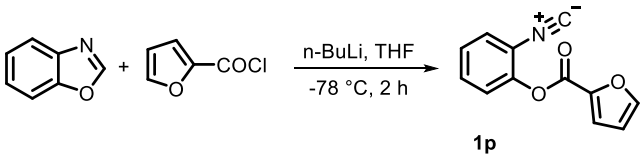
2. Experimental Procedures

2.1. General procedures for the synthesis of isocyanides 1a-o.



- **Step 1:** A solution of the substituted 2-aminophenol (1.0 equiv.) in HCO_2H (15 equiv.) was heated in an oil bath for 18-24 hours. The reaction mixture was added 5% HCl and was extracted with AcOEt. The organic layer was washed with brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was used for the next step without further purification.[S1]
- **Step 2:** To a solution of the substituted N-(2-hydroxyphenyl)formamide (1.0 equiv.) in pyridine (2 M) and DCM (0.2 M) was cooled in a dry ice bath, then benzoyl chloride (1.2 equiv.) was added dropwise over 10 min with stirring. Subsequently, the reaction mixture was then allowed to reach room temperature for 14 hours. After total consumption of the starting material was confirmed by TLC, the reaction mixture was extracted with dichloromethane (10 mL) and washed with a solution of diluted HCl (10 mL). The organic phase was then washed with water, dried on Na_2SO_4, filtrated, and evaporated under pressure. The residue was used for the next step without further purification.[S2]
- **Step 3:** A solution of the substituted 2-formamidophenyl benzoate (1.0 equiv.) and Et_3N (4.5 equiv.) in DCM (0.2 M) was cooled at 0 °C, then $POCl_3$ (1.5 equiv.) was added dropwise. After the reaction was completed, a saturated Na_2CO_3 aqueous solution was added at 0 °C, and the mixture was extracted with EA (3×50 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluting with *n*-hexane and ethyl acetate (15:1) to afford the desired products **1a-o**.[S3]

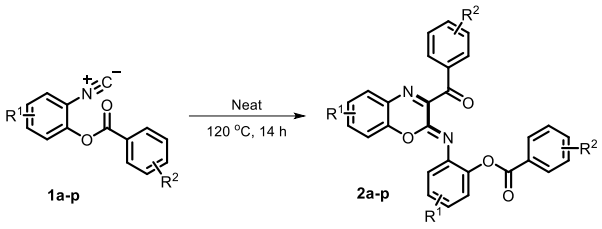
2.2. General procedures for the synthesis of isocyanide 1p.



A 50 mL round-bottom flask equipped with a magnetic stir bar and charged with benzoxazole (0.90 g, 7.56 mmol) and THF (18 mL) is allowed to cool to -78 °C for five min prior to the addition of *n*-BuLi (1.6 M solution in hexanes, 4.96 mL, 7.94 mmol). The reaction mixture was allowed to stir at the same temperature for 1.5 h. The furan-2-carbonyl chloride (7.94 mmol) was added dropwise to the solution. The solution was allowed to warm to room temperature and stirred for two hours. The reaction mixture was poured onto a mixture of ether (100 mL) and saturated aqueous $NaHCO_3$ (50 mL). The organic layer was washed with water (2 x 50 mL), dried, and concentrated in *vacuo*. The resulting residue was purified by silica gel flash column chromatography (n-hexane /ethyl acetate 15:1), and the organics were concentrated in vacuo to provide the title compound **1p**. [S4]

2. 2. Typical procedure for the formation of Benzoxazine.

2.2.1. General Procedure:

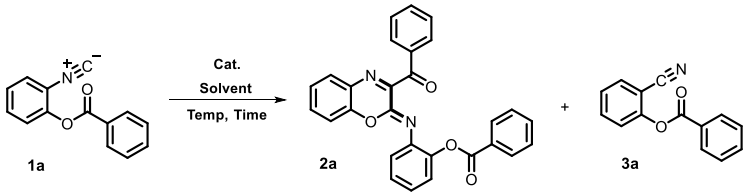


The Schlenk tube containing isocyanide **1a-p** (100 mg, 0.4 mmol) was placed in an oil bath and stirred at 120 °C for 14 h, in the absence of catalyst and solvent. After the completion of the reaction, the residue was chromatographed on silica gel using *n*-hexane and ethyl acetate (15:1) as an eluent to afford the products **2a-p**.

2.2.3. Representative Procedure for Synthesis of 1a in gram-scale reaction:

The Schlenk tube containing isocyanide **1a** (1 g, 0.4 mmol) was placed in an oil bath and stirred at 120 °C for 14 h, in the absence of catalyst and solvent. After the completion of the reaction, the residue was chromatographed on silica gel using *n*-hexane and ethyl acetate (12:1) as an eluent to afford the product **2a** in 68% yield (680 mg).

2.2.4. Table S1. Optimization of the reaction conditions:



Entry	Cat. (10 mol %)	Solvent	Temp (°C)	Time (h)	Yield[b] (%) (2a/3a)
1	-	Neat	**120**	**14**	**83,0**
2	-	DMF	130	12	-
3	-	DMSO	130	14	-
4	-	Dioxane	90	12	-
5	-	DMA	130	14	-
6	-	Toluene	100	16	-
7	-	Chlorobenzene	120	14	-
8	-	Xylene	120	14	-
9	-	Ethylene glycol	120	14	-
10	-	DCM	80	14	-
11	CuI	Toluene	100	12	-
12	$AlCl_3$	Toluene	100	12	-
13	CuI	Xylene	120	12	-
14	$AlCl_3$	DMF	130	12	-
15	CuI	DMF	130	12	-
16	$Pd(PPh_3)_4$	DMF	130	12	-
17	$Pd(OAc)_2$	DMF	130	12	-
18	$Sc(OTf)_3$	Xylene	120	12	-
19	$Ag(OTf)_3$	Toluene	110	12	-
20	$Pd(PPh_3)_4$	Toluene	110	12	-
21	$Pd(OAc)_2$	Toluene	110	12	-

[a] reaction condition: was performed with **1a** (0.2 mmol), catalyst (10 mol %) in solvent (1 mL) for 14 h. [b] Isolated yields are shown.

3. Follow-up Reactions

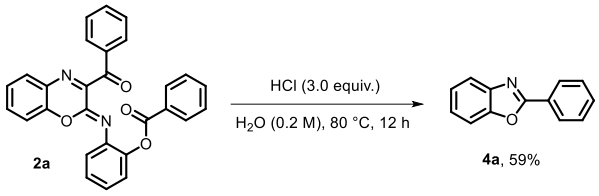


Figure S1. Compound 2a hydrolysis

Concentrated HCl (1.8 mmol, 3 equiv) was added to a solution of (Z)-2-((3-benzoyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl benzoate **2a** (0.60 mmol) in water (3 ml) and the reaction mixture was stirred in an oil bath at 80 °C for 6 h. then the reaction mixture was extracted with acetone (3×10 mL). The combined organic phases were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel, eluting with *n*-hexane and ethyl acetate (20:1) to afford the product **4a** in 59% yield (69 mg).

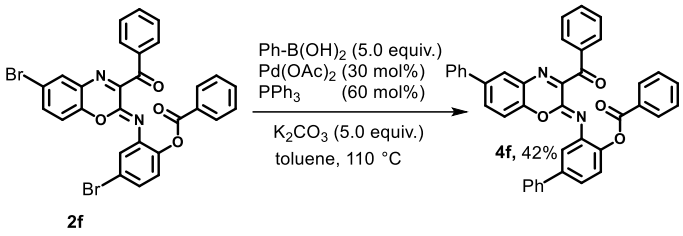


Figure S2. Cross-coupling reaction of compound 2f.

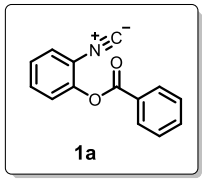
Compound **2f** (25 mg, 0.04 mmol) was added to a mixture of phenylboronic acid (25 mg, 0.2 mmol, 5.0 equiv.), $Pd(OAc)_2$ (2.8 mg, 0.012 mmol, 30 mol%), PPh_3 (6.5 mg, 0.024 mmol, 60 mol%), and K_2CO_3 (29 mg, 0.2 mmol, 5.0 equiv.) in toluene (1.0 mL). The mixture was then stirred at 110 °C. After completion of the reaction as indicated by TLC, the solvent was evaporated, and the residue was purified by column chromatography on silica gel to provide the product **4f** in 42% yield (10.4 mg).

4. Computational details

All the DFT calculations have been carried out with the Gaussian 16 package of program[S5], and visualization of computed structures was generated using CYLView.[S6] Full geometry optimization and Gibbs free energy correction were performed with the B3LYP-D3BJ/6-31+G(d,p) level in the gas phase (T=298 K, P=1 bar).[S7] The correctness of the optimized transition states (TS) and stable structures have been verified by intrinsic reaction coordinate (IRC) and the analytical frequency calculations respectively. In this study, the Non-Covalent Interaction (NCI) analysis[S8] was conducted using Multiwfn software,[S9] and the results were visualized using VMD.[S10]

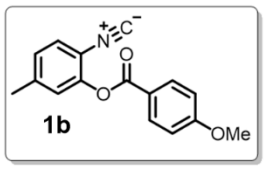
5. Compounds Characterization Data

2-isocyanophenyl benzoate (1a)



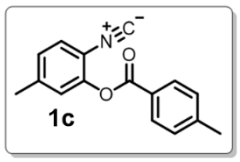
Colourless solid (870 mg, Yield 87%), mp 90-93°C; R_f = 0.20 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.27 (dd, *J* = 8.5, 1.4 Hz, 2H), 7.70 (tt, *J* = 7.5, 1.3 Hz, 1H), 7.55 (t, *J* = 7.5, 2H), 7.52 – 7.44 (m, 2H), 7.43 – 7.36 (m, 1H), 7.32 (td, *J* = 7.9, 1.6 Hz, 1H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_c = 169.2, 163.9, 146.6, 134.2, 130.5, 130.4, 128.8, 128.4, 127.7, 126.6, 123.6 ppm; **HRMS-ESI** (m/z): calculated for $C_{14}H_9NO_2$ $[M+H]^+$ 224.0705 found 224.0705.

2-isocyano-5-methylphenyl 4-methoxybenzoate (1b)



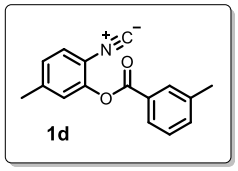
Pink solid (650 mg, Yield 65%), mp 92-95 °C, R_f = 0.21 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.14 (d, *J* = 9.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.13 (br s, 1H), 7.03 (dd, *J* = 8.1, 1 Hz, 1H), 6.95 (d, *J* = 9.1 Hz, 2H), 3.85 (s, 3H), 2.36 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_c = 168.2, 164.3, 163.7, 146.5, 141.2, 132.6(2C), 127.2, 127.1, 124.1, 120.7, 114.1(2C), 55.6, 21.5 ppm; **HRMS-ESI** (m/z): calculated for $C_{16}H_{13}NO_3$ $[M+H]^+$ 268.0967 found 268.0962.

2-isocyano-5-methylphenyl 4-methylbenzoate (1c)



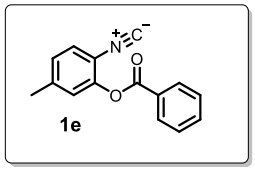
Colourless solid (750 mg, Yield 75%), mp 78-81°C, R_f = 0.25 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) (mixture of rotamers) δ_H = 8.15 (d, *J* = 8.3 Hz, 1H), 8.06 (d, *J* = 8.3 Hz, 2H), 7.39 – 7.31 (m, 3H), 7.22 – 7.08 (m, 1H), 2.51 – 2.41 (m, 6H, Me) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_c = 168.3, 164.1, 162.6, 146.4, 145.6, 145.1, 141.3, 130.7, 130.1, 129.6, 129.5, 127.2, 127.1, 126.2, 125.7, 124.1, 21.9, 21.5 ppm; **HRMS-ESI** (m/z): calculated for $C_{16}H_{13}NO_2$ $[M+H]^+$ 252.1018 found 252.1014.

2-isocyano-5-methylphenyl 3-methylbenzoate (1d)



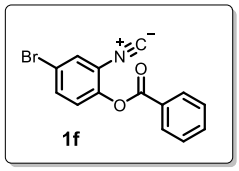
Colourless solid (485 mg, Yield 85%), mp 81-84°C, R_f = 0.19 (*n*-hexane /ethyl acetate 20:1); **^{1}H-NMR** (400 MHz,) δ_H = 8.00 – 7.96 (m, 2H) (7.98 (dd, *J* = 5.9, 1.7 Hz, 2H)), 7.41 (d, *J* = 7.7 Hz, 1H), 7.35(t, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 1.7 Hz, 1H), 7.03 (dd, *J* = 8.2, 1.7 Hz, 1H), 2.38 (s, 3H), 2.34 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_C = 168.2, 164.2, 146.4, 141.3, 138.6, 135.ٔ, 135.0, 130.9, 128.8, 128.7, 127.8, 127.6, 127.2, 124.0, 21.5, 21.3 ppm; **HRMS-ESI** (m/z): calculated for $C_{16}H_{13}NO_2$ $[M+H]^+$ 252.1018 found 252.1010.

2-isocyano-5-methylphenyl benzoate (1e)



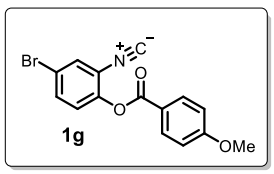
Colourless solid (710 mg, Yield 70 %), mp 108-111 °C, R_f = 0.22 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.25 (dd, *J* = 8.5, 1.3 Hz, 2H), 7.73 – 7.62 (m, 1H), 7.62 – 7.48 (m, 2H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.20 (br s, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 2.42 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 168.5, 164.0, 146.3, 141.3, 134.2, 130.4, 128.7, 127.2, 124.1, 124.0, 117.7, 21.4 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{13}NO_2$ $[M+H]^+$ 238.0862 found 238.0863.

4-bromo-2-isocyanophenyl benzoate (1f)



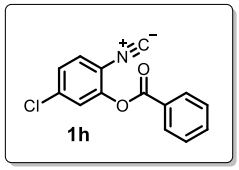
Colourless solid (420 mg, Yield 52%), mp 90-93 °C, R_f = 0.25 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.14 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.56 – 7.52 (m, 1H), 7.52 – 7.38 (m, 3H), 7.21 (d, *J* = 8.7 Hz, 1H) ppm; **^{13}C-NMR** (76 MHz, $CDCl_3$) δ_c = 171.0, 163.6, 162.3, 145.8, 134.6, 134.4, 133.5, 130.6, 130.5, 130.4, 128.9, 128.8, 128.1, 125.0, 118.9 ppm; **HRMS-ESI** (m/z): calculated for $C_{14}H_8BrNO_2$ $[M+H]^+$ 301.9810 found 301.9804.

4-bromo-2-isocyanophenyl 4-methoxybenzoate (1g)



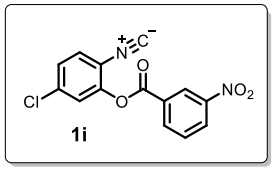
Colourless solid (370 mg, Yield 46%), mp 125-128 °C, R_f = 0.17 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.11 (d, *J* = 8. 6 Hz, 2H), 7.62 – 7.40 (m, 2H), 7.20 (br s, 1H), 6.93 (d, *J* = 8.6 Hz, 2H), 3.83 (s, 3H) ppm; **^{13}C-NMR** (76 MHz, $CDCl_3$) δ_c = 170.8, 164.6, 163.2, 146.0, 133.5, 132.8, 130.3, 125.1, 120.3, 118.6, 114.2, 55.6 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{10}BrNO_3$ $[M+H]^+$ 331.9916 found 331.9911.

5-chloro-2-isocyanophenyl benzoate (1h)



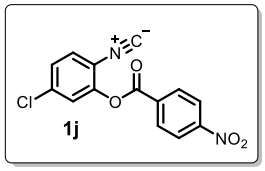
Colourless solid (375 mg, Yield 73%), mp 81-83ºC, R_f = 0.2 (n-hexane /ethyl acetate 12:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.26 (d, *J* = 7.1 Hz, 2H), 7.72 (t, *J* = 7.7 Hz, 1H), 7.58 (t, *J* = 7.7 Hz, 2H), 7.54 – 7.46 (m, 2H), 7.39 (d, *J* = 8.8 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 170.8, 163.7, 162.4, 145.3, 134.6, 134.5, 131.7, 130.6, 130.5, 128.9, 128.8, 128.0, 127.5, 124.7 ppm; **HRMS-ESI** (m/z): calculated for $C_{14}H_8ClNO_2$ $[M+H]^+$ 258.0316 found 258.0317.

5-chloro-2-isocyanophenyl 3-nitrobenzoate (1i)



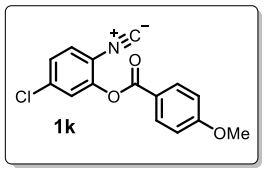
Colourless solid (280 mg, Yield 56%), mp 114-117ºC, R_f = 0.21 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 9.10 (s, 1H), 8.59 (d, *J* = 8.0 Hz, 2H), 7.82 (t, *J* = 8.0 Hz, 1H), 7.59 – 7.50 (m, 2H), 7.40 (d, *J* = 8.7 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 171.4,163.0, 161.7, 148.5, 144.7, 136.0, 132.5, 130.8, 130.3, 129.8, 128.8, 127.7, 125.5, 124.4 ppm; **HRMS-ESI** (m/z): calculated for $C_{14}H_7ClN_2O_4$ $[M+H]^+$ 303.0166 found 303.0161.

5-chloro-2-isocyanophenyl 4-nitrobenzoate (1j)



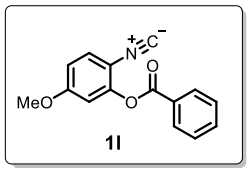
Colourless solid (254 mg, Yield 50%), 112-115ºC, R_f = 0.18 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) δ_H = 8.42 (d, *J* = 9.0 Hz, 4H), 7.55 – 7.46 (m, 2H), 7.39 (d, *J* = 8.9 Hz, 1H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 171.3, 163.7, 161.4, 151.0, 144.3, 133.0, 132.0, 131.1(2C), 130.2, 127.2, 123.8, 123.4(2C) ppm; **HRMS-ESI** (m/z): calculated for $C_{14}H_7ClN_2O_4$ $[M+H]^+$ 303.0166 found 303.0159.

5-chloro-2-isocyanophenyl 4-methoxybenzoate (1k)



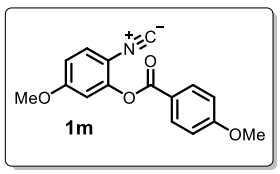
Colourless solid (322 mg, Yield 64%), 127-130ºC, R_f = 0.22 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ_H = 8.20 (d, *J* = 9.0 Hz, 2H), 7.49 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.03 (d, *J* = 9.0 Hz, 2H), 3.93 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_c = 170.6, 164.5, 163.3, 145.4, 132.8, 131.5, 130.5, 127.5, 124.8, 120.2, 114.2, 55.6 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{10}ClNO_3$ $[M+H]^+$ 288.0421 found 288.0414.

2-isocyano-5-methoxyphenyl benzoate (1l)



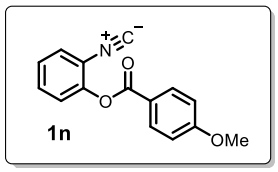
Colourless solid (370 mg, Yield 74%), mp 93-96ºC, R_f = 0.20 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (250 MHz, DMSO) (mixture of two rotamers, 72/28) major rotamer: δ_H = 8.15 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 2H), 7.55 – 7.40 (m, 2H), 7.34 (br s, 1H), 7.15 (dd, *J* = 8.7, 2.7 Hz ,1H), 3.80 (s, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ_c = 168.9, 164.3, 157.8, 139.9, 135.0, 133.3, 130.4, 129.6, 129.0, 128.4, 125.0, 120.3, 117.6, 112.7, 56.5 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{11}NO_3$ $[M+H]^+$ 254.0811 found 254.0818.

2-isocyano-5-methoxyphenyl 4-methoxybenzoate (1m)



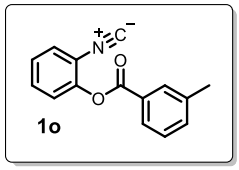
Colourless solid (350 mg, Yield 43%), 135-138ºC, R_f = 0.21 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (250 MHz, $CDCl_3$) δ_H = 8.19 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 5.6 Hz, 1H),7.12 – 6.88 (m, 4H), 3.90 (s, 3H), 3.83 (s, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$) δ_c = 168.7, 164.3, 164.0, 157.2, 140.2, 132.6, 124.3, 120.8, 116.3, 114.0, 112.2, 55.9, 55.5 ppm; **HRMS-ESI** (m/z): calculated for $C_{16}H_{13}NO_4$ $[M+H]^+$ 284.0917 found 284.0918.

2-isocyanophenyl 4-methoxybenzoate (1n)



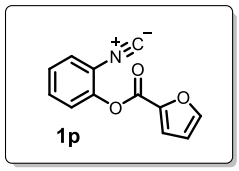
Colourless solid (770 mg, Yield 77%), mp 104-107ºC, R_f = 0.20 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 8.21 (d, *J* = 8.9 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.31 – 7.24 (m, 1H), 7.01 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 169.3, 164.0, 163.0, 146.4, 132.2 (2C), 129.6, 127.0, 125.7, 123.2, 120.4, 113.7 (2C), 55.0 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{11}NO_3$ $[M+H]^+$ 254.0811 found 254.0818.

2-isocyanophenyl 3-methylbenzoate (1o)



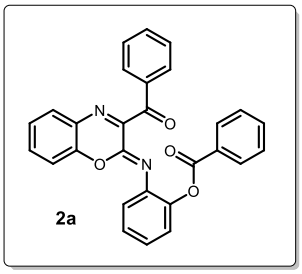
Colourless solid (412 mg, Yield 82%), mp 67-70°C; R_f = 0.21 (n-hexane /ethyl acetate 20:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) δ_H = 8.11 – 8.05 (m, 2H), 7.50 (td, *J* = 7.7, 2.0 Hz, 3H), 7.44 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.38 (m, 1H), 7.33 (td, *J* = 7.7, 1.5 Hz, 1H), 2.48 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) δ_c = 169.1, 164.1, 146.7, 138.7, 135.0, 131.0, 130.4, 128.7, 128.3, 127.7 (2C), 126.5, 123.6, 21.3 ppm; **HRMS-ESI** (m/z): calculated for $C_{15}H_{11}NO_2$ $[M+H]^+$ 238.0862 found 238.0857.

2-isocyanophenyl furan-2-carboxylate (1p)



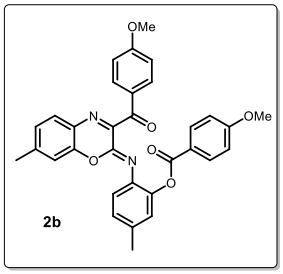
Colourless solid (550 mg, Yield 55%), mp 95-98°C, R_f = 0.20 (n-hexane /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H = 7.75 (dd, *J* = 2.4, 0.9 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.45 – 7.39 (m, 1H), 7.39 – 7.33 (m, 1H), 6.66 (dd, *J* = 3.6, 1.8 Hz, 1H). **^{13}C-NMR** (75 MHz, $CDCl_3$) δ_c = 169.4, 165.6, 155.4, 148.0, 145.8, 142.9, 130.4, 127.7, 126.8, 123.5, 120.8, 112.5 ppm; **HRMS-ESI** (m/z): calculated for $C_{12}H_7NO_3$ $[M+H]^+$ 214.0498 found 214.0491.

(*Z*)-2-((3-benzoyl-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl benzoate (2a)



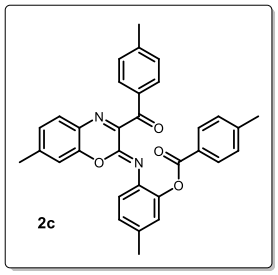
Yellow solid (83 mg, Yield 83%), mp 147-150°C, R_f = 0.18 (n-hexanes /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) (mixture of two rotamers, 67/33): δ_H= 8.37 (d, *J* = 7.7 Hz, 1H, minor rotamer), 8.25 (d, *J* = 8.8 Hz, 2H, major rotamer), 8.10 (br s, 2H, minor rotamer), 7.91 (d, *J* = 8.5 Hz, 2H, major rotamer), 7.75 (t, *J* = 9.0 Hz, 2H, mixture of two rotamers), 7.70 – 7.64 (m, 1H, minor rotamer), 7.63 – 7.47 (m, 3H, mixture of two rotamers), 7.44 – 7.27 (m, 5H, mixture of two rotamers), 7.29 – 7.15 (m, 4H, mixture of two rotamers) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) major rotamer: δ_c= 190.6, 165.3, 164.5, 156.6, 145.7, 143.8, 141.3, 136.3, 134.5, 134.0,131.4, 130.8, 130.3, 130.1, 129.2, 128.8, 128.6, 128.3, 127.1, 126.7, 126.2, 125.1, 123.2, 122.9, 122.3, 116.0 ppm; **HRMS-ESI** (m/z): calc. for $C_{28}H_{18}N_2O_4$ $[M+H]^+$ 447.1339, found 447.1335.

(*Z*)-2-((3-(4-methoxybenzoyl)-7-methyl-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)-5-methylphenyl 4-methoxybenzoate (2b)



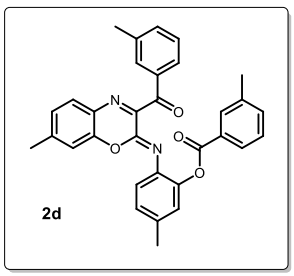
Yellow solid (67 mg, Yield 67%), mp 150-153°C, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 7.84 (d, *J* = 8.8 Hz, 2H), 7.71 (d, *J* = 8.9 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.07 (dd, *J* = 6.4, 2.0 Hz, 1H), 7.04 (dd, *J* = 7.4, 1.8 Hz, 1H), 7.00 (br s, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.65 (d, *J* = 8.9 Hz, 2H), 3.89 (s, 3H, OMe), 3.81 (s, 3H, OMe), 2.43 (s, 3H, Me), 2.39 (s, 3H,Me) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 189.6, 164.4, 164.1, 163.4, 156.0, 145.6, 144.2, 142.3, 141.3, 136.9, 133.8, 132.0, 128.9, 128.8, 127.3, 126.6, 125.9, 123.7, 123.4, 121.7, 116.3, 113.7, 113.4, 55.4, 55.3, 21.6, 21.1 ppm; **HRMS-ESI** (m/z): calc. for $C_{32}H_{26}N_2O_6$ $[M+H]^+$ 535.1863, found 535.1863.

(*Z*)-5-methyl-2-((7-methyl-3-(4-methylbenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 4-methylbenzoate (2c)



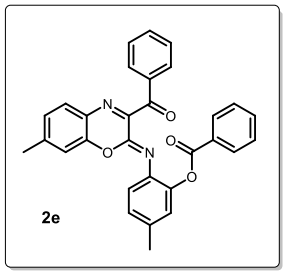
Yellow solid (57 mg, Yield 57%), mp 148-151°C, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.46 (dd, *J* = 8.0, 1.1 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 7.09 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.03 – 7.01 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H), 2.43 (s, 3H), 2.39 (s, 3H), 2.32 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 190.6, 164.7, 155.9, 145.6, 144.9, 144.0, 143.7, 142.4, 136.9, 133.7, 131.8, 130.0, 129.7, 129.1, 128.9, 128.8, 126.7, 126.6, 125.9, 123.7, 123.4, 116.3, 21.8, 21.7, 21.6, 21.1 ppm; **HRMS-ESI** (m/z): calc. for $C_{32}H_{26}N_2O_4$ $[M+H]^+$ 503.1965, found 503.1966.

(Z)-5-methyl-2-((7-methyl-3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2d)



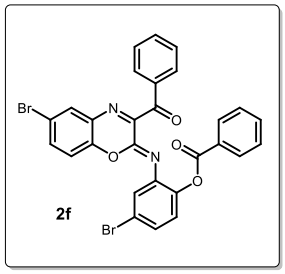
Yellow solid (63 mg, Yield 63%), mp 124-127°C, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 7.75 (d, *J* = 7.8 Hz, 1H), 7.72 (br s, 1H), 7.61 (br s, 1H), 7.55 – 7.48 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 8.7 Hz, 1H), 7.24 – 7.20 (m, 1H), 7.12 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.10 – 7.04 (m, 4H), 2.46 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 2.28 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 191.1, 164.9, 155.9, 145.6, 144.1, 142.5, 141.2, 138.2, 137.9, 137.0, 134.9, 134.2, 133.9, 133.6, 130.4, 129.8, 128.9, 128.3, 128.1, 127.2, 127.1, 126.8, 126.0, 123.9, 123.4, 116.3, 21.6, 21.2 ppm; **HRMS-ESI** (m/z): calc. for $C_{32}H_{26}N_2O_4$ $[M+H]^+$ 503.1965, found 503.1969.

(*Z*)-2-((3-benzoyl-7-methyl-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)-5-methylphenyl benzoate (2e)



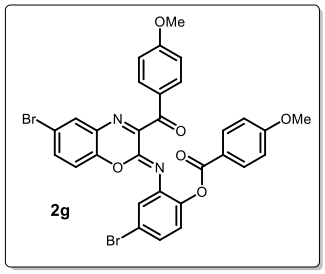
Yellow solid (78 mg, Yield 78%), mp 162-165ºC, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 7.91 (d, *J* = 7.0 Hz, 2H), 7.72 (d, *J* = 7.0 Hz, 2H), 7.56 – 7.50 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.19 (t, *J* = 7.8 Hz, 2H), 7.11 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.09 – 7.01 (m, 3H), 2.44 (s, 3H), 2.39 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 190.9, 164.6, 155.7, 145.6, 144.2, 142.5, 141.2, 137.1, 134.1, 134.0, 133.6, 133.1, 132.4, 130.0, 129.5, 129.3, 128.9, 128.4, 128.3, 126.8, 126.0, 123.8, 123.4, 116.3, 21.6, 21.2 ppm; **HRMS-ESI** (m/z): calc. for $C_{30}H_{22}N_2O_4$ $[M+H]^+$ 475.1652, found 475.1653.

(*Z*)-2-((3-benzoyl-6-bromo-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)-4-bromophenyl benzoate (2f)



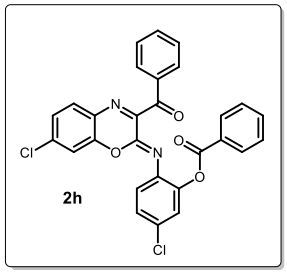
Yellow solid (62 mg, Yield 62%), mp 158-161ºC, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 7.91 (d, *J* = 6.9 Hz, 2H), 7.77 (d, *J* = 2.4 Hz, 1H), 7.72 (d, *J* = 6.8 Hz, 2H), 7.65 (d, *J* = 2.4 Hz, 1H), 7.63 – 7.54 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.24 (t, *J* = 7.8 Hz, 2H), 7.14 (d, *J* = 5.6 Hz, 1H), 7.11 (d, *J* = 5.4 Hz, 1H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 189.8, 164.2, 157.1, 144.5, 142.9, 141.3, 137.4, 134.4, 134.3, 133.7, 133.6, 132.0, 131.7, 130.0, 129.6, 129.5, 128.7, 128.6, 128.4, 126.6, 124.4, 118.8, 117.6, 117.5 ppm; **HRMS-ESI** (m/z): calc. for $C_{28}H_{16}Br_2N_2O_4$ $[M+H]^+$ 602.9549, found 602.9545.

(*Z*)-4-bromo-2-((6-bromo-3-(4-methoxybenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2g)



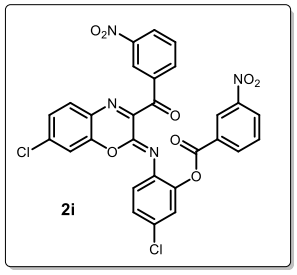
Yellow solid (56 mg, Yield 56%), mp 159-162ºC, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (250 MHz, $CDCl_3$): δ_H= 7.81 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.56 (dd, *J* = 8.7, 2.4 Hz, 2H), 7.34 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.08 (dd, *J* = 5.2, 3.5 Hz, 2H), 7.05 – 6.95 (m, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.69 (d, *J* = 8.4 Hz, 2H), 3.87 (s, 2H), 3.81 (s, 3H) ppm; **^{13}C-NMR** (63 MHz, $CDCl_3$): δ_c= 187.0, 165.2, 164.2, 163.8, 157.3, 152.1, 150.1, 146.0, 144.6, 135.7, 134.1, 132.8, 132.5, 132.1, 131.1, 129.5, 126.8, 126.5, 124.9, 124.5, 123.8, 121.0, 120.6, 119.2, 118.4, 117.6, 114.3, 114.0, 113.6, 55.7, 55.5 ppm; **HRMS-ESI** (m/z): calc. for $C_{30}H_{20}Br_2N_2O_6$ $[M+H]^+$ 662.9760, found 662.9768.

(*Z*)-2-((3-benzoyl-7-chloro-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)-5-chlorophenyl benzoate (2h)



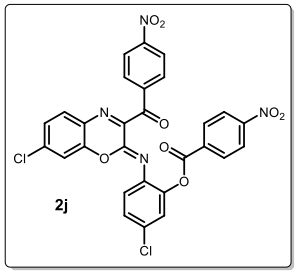
Yellow solid (55 mg, Yield 55%), mp 175-178ºC, R_f = 0.2 (n-hexane /ethyl acetate 8:1); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H= 7.90 (d, *J* = 7.2 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.61 (d, *J* = 2.5 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 2.5 Hz, 1H), 7.44 (dd, *J* = 5.1, 2.5 Hz, 1H), 7.42 – 7.31 (m, 3H), 7.27 – 7.14 (m, 5H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c= 189.9, 164.3, 157.2, 144.0, 142.4, 141.3, 137.1, 134.4, 133.6, 133.6, 131.4, 131.3, 131.3, 130.5, 130.0, 129.5, 129.0, 128.7, 128.6, 128.4, 126.6, 124.0, 123.7, 117.2 ppm; **HRMS-ESI** (m/z): calc. for $C_{28}H_{16}Cl_2N_2O_4$ $[M+H]^+$ 515.0559, found 515.0554.

(*Z*)-5-chloro-2-((7-chloro-3-(3-nitrobenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 3-nitrobenzoate (2i)



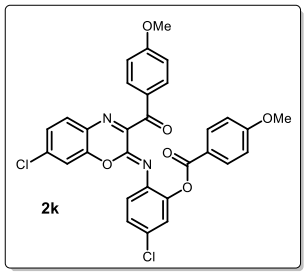
Yellow solid (37 mg, Yield 37%), mp 187-190ºC, R_f = 0.2 (n-hexane /ethyl acetate 10:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 8.66 (s, 1H), 8.48 – 8.40 (m, 2H), 8.30 (t, *J* = 7.5 Hz, 2H), 8.05 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 2.4 Hz, 1H), 7.65 (d, *J* = 7.8 Hz, 2H), 7.59 – 7.49 (m, 2H), 7.34 – 7.29 (m, 2H), 7.18 (d, *J* = 8.7 Hz, 1H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 187.3, 162.2, 155.6, 148.1, 148.0, 143.9, 143.5, 140.9, 136.0, 135.6, 135.0, 134.8, 132.2, 131.9, 131.2, 131.0, 130.5, 130.0, 129.8, 129.3, 128.4, 128.0, 127.7, 124.8, 124.2, 124.0, 123.6, 117.4 ppm; **HRMS-ESI** (m/z): calc. for $C_{28}H_{14}Cl_2N_4O_8$ $[M+H]^+$ 605.0261, found 605.0262.

(*Z*)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2j)



Yellow solid (43 mg, Yield 43%), mp 182-185ºC, R_f = 0.2 (n-hexane /ethyl acetate 10:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) (mixture of two rotamers, 67/33) major rotamer: δ_H= 8.42 (d, *J* = 8.8 Hz, 4H), 8.24 (d, *J* = 8.8 Hz, 4H), 7.87 (d, *J* = 2.5 Hz, 2H), 7.69 (dd, *J* = 8.9, 2.5 Hz, 2H), 7.42 (d, *J* = 8.9 Hz, 2H), ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 186.8, 161.1, 153.9, 151.1, 150.0, 149.6, 146.2, 145.7, 138.5, 134.0, 131.7, 131.2, 130.6, 130.5, 129.8, 128.6, 128.6, 126.7, 126.5, 126.5, 124.3, 124.2, 124.0, 121.8, 120.6, 119.2, 118.2, 111.7 ppm; **HRMS-ESI** (m/z): calc. for $C_{28}H_{14}Cl_2N_4O_8$ $[M+H]^+$ 605.0261, found 605.0259.

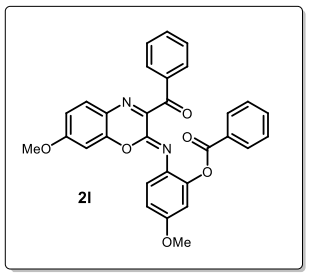
(*Z*)-5-chloro-2-((7-chloro-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2k)



Yellow solid (46 mg, Yield 46%), mp 167-170ºC, R_f = 0.2 (n-hexanes /ethyl acetate 15:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 7.85 (d, *J* = 8.9 Hz, 2H), 7.73 (d, *J* = 8.9 Hz, 2H), 7.62 (d, *J* = 2.5 Hz, 1H), 7.50 (d, *J* = 2.5 Hz, 1H), 7.43 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.24 (dd, *J* = 8.7, 2.5 Hz, 1H), 7.18 (t, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.72 (d, *J* = 8.9 Hz, 2H), 3.92 (s, 3H), 3.85 (s, 3H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 187.0, 165.1, 164.5, 164.2, 152.2, 150.1, 145.9, 145.5, 140.3, 132.9, 132.7, 132.2, 131.2, 130.8, 129.5, 126.9, 126.4, 125.1, 124.2, 118.0, 114.7, 114.3, 114.1, 113.9, 55.7, 55.6 ppm; **HRMS-ESI** (m/z): calc. for $C_{30}H_{20}Cl_2N_2O_6$ $[M+H]^+$ 575.0770, found 575.0776.

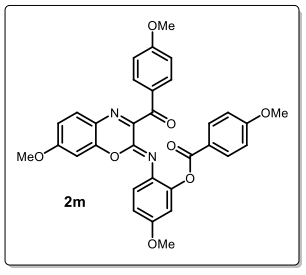
.

(*Z*)-2-((3-benzoyl-7-methoxy-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)-5-methoxyphenyl benzoate (2l)



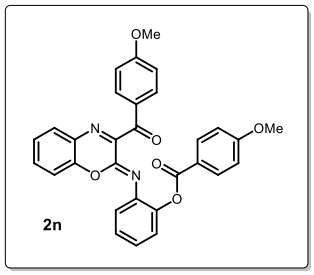
Yellow solid (52 mg, Yield 52%), mp 155-158ºC, R_f = 0.22 (n-hexanes /ethyl acetate 15:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): Since this product appears as the mixture of rotamers, the ^{1}H-NMR spectrum is not very characteristic (for more detail show Figure S83). [S11] **^{13}C-NMR** (76 MHz, $CDCl_3$): δ_c= 190.7, 165.3, 164.9, 157.8, 156.7, 134.2, 133.2, 132.1, 130.9, 130.3, 130.0, 129.6, 129.0, 128.9, 128.6, 128.3, 126.9, 122.7, 118.7, 116.6, 111.0, 107.4, 55.9, 55.8 ppm; **HRMS-ESI** (m/z): calc. for $C_{30}H_{22}N_2O_6$ $[M+H]^+$ 507.1550, found 507.15558.

(*Z*)-5-methoxy-2-((7-methoxy-3-(4-methoxybenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoateze (2m)



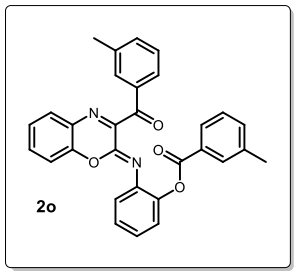
Yellow solid (65 mg, Yield 65%), mp 152-155ºC, R_f = 0.21 (n-hexanes /ethyl acetate 10:1); **^{1}H-NMR** (250 MHz, $CDCl_3$) (mixture of two rotamers, 81/19) major rotamer: δ_H= 7.82 (d, *J* = 8.2 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.27 (br s, 1H), 7.15 – 7.07 (m, 2H), 7.05 – 6.90 (m, 3H), 6.75 (d, *J* = 7.9 Hz, 2H), 6.62 (d, *J* = 8.4 Hz, 2H), 3.98 – 3.79 (m, 12H, 4OMe) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 187.7, 165.0, 164.1, 163.9, 157.3, 156.6, 151.5, 151.0, 141.2, 132.8(2C), 132.7, 132.1(2C), 127.1, 124.0, 121.3, 117.5, 116.6, 114.3, 114.0, 113.9, 113.8, 111.6, 56.0, 55.7, 55.4, 55.3 ppm; **HRMS-ESI** (m/z): calc. for $C_{32}H_{26}N_2O_8$ $[M+H]^+$ 567.1761, found 567.1761.

(*Z*)-2-((3-(4-methoxybenzoyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2n)



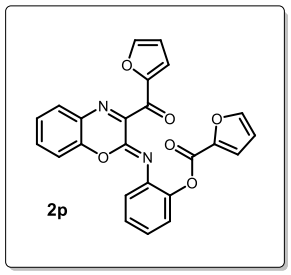
Yellow solid (81 mg, Yield 81%), mp 157-160ºC R_f = 0.2 (n-hexanes /ethyl acetate 15:1); **^{1}H-NMR** (300 MHz, $CDCl_3$) (mixture of two rotamers, 58/42): δ_H= 8.26 (d, *J* = 8.0 Hz, 1H, minor rotamer), 8.12 (d, *J* = 8.9 Hz, 1H, major rotamer), 7.95 – 7.91 (m, 1H, minor rotamer), 7.75 (d, *J* = 8.8 Hz, 2H, major rotamer), 7.70 – 7.65 (m, 2H, mixture of two rotamers), 7.51 (dd, *J* = 7.8, 1.7 Hz, 1H, minor rotamer), 7.43 (dd, *J* = 7.6, 1.9 Hz, 1H, minor rotamer), 7.37 – 7.30 (m, 1H, minor rotamer), 7.20 – 7.05 (m, 4H, mixture of two rotamers), 6.94 (d, *J* = 9.0 Hz, 1H, minor rotamer), 6.81 (d, *J* = 8.9 Hz, 1H, minor rotamer), 6.70 (d, *J* = 9.0 Hz, 2H, major rotamer), 6.58 (d, *J* = 8.9 Hz, 2H, major rotamer), 3.84 (s, 3H, OMe, minor rotamer), 3.79 (s, 3H, OMe, major rotamer), 3.76 (s, 3H, OMe, minor rotamer), 3.72 (s, 3H, OMe, major rotamer) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$) mixture of two rotamers: δ_c= 191.3, 164.8, 164.3, 163.5, 145.7, 144.0, 141.5, 136.5, 132.5, 132.1, 131.3, 130.9, 129.3, 128.9, 127.1, 126.5, 126.0, 125.1, 124.8, 123.7, 123.0, 121.6, 116.0, 114.2, 114.0, 113.8, 113.5, 55.4, 55.3 ppm. **HRMS-ESI** (m/z): calc. for $C_{30}H_{22}N_2O_6$ $[M+H]^+$ 507.1550, found 507.1557.

(Z)-2-((3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2o)



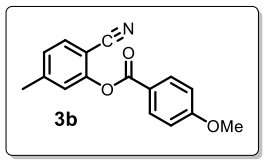
Yellow solid (66 mg, Yield 66%), mp 107-110°C, R_f = 0.2 (n-hexanes /ethyl acetate 15:1); **^{1}H-NMR** (400 MHz, $CDCl_3$) Since this product appears as the mixture of two rotamers, the ^{1}H-NMR spectrum is not very characteristic (for more detail show Figure S92, a mixture of two rotamers, 75/25): δ_H= 8.15 – 8.06 (m, 1H), 7.92 – 7.82 (m, 1H), 7.28 – 7.71 (m, 1H), 7.71 – 7.61 (m, 2H), 7.57 – 7.50 (m, 2H), 7.47 – 7.42 (m, 2H), 7.38 – 7.30 (m, 2H), 7.38 – 7.21 (m, 4H), 7.11 – 7.05 (m, 1H), 7.52 – 7.23 (m, 6H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$) major rotamer: δ_c= 189.4, 167.3, 163.9, 151.2, 150.7, 147.0, 138.9, 135.7, 134.8, 134.1, 133.1, 130.5 (2C), 130.2 (2C), 129.7, 128.8 (2C), 128.2, 127.6 (2C), 126.1, 122.4, 120.6, 119.8, 116.9, 21.4, 21.0 ppm; **HRMS-ESI** (m/z): calc. for $C_{30}H_{22}N_2O_4$ $[M+H]^+$ 475.1652, found 475.1658.

(*Z*)-2-((3-(furan-2-carbonyl)-2*H*-benzo[*b*][1,4]oxazin-2-ylidene)amino)phenyl furan-2-carboxylate (2p)



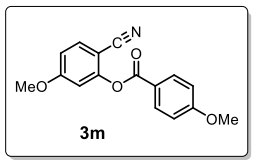
Yellow solid (47 mg, Yield 47%), mp 144-147°C, R_f = 0.15 (n-hexanes /ethyl acetate 10:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): Since this product appears as the mixture of rotamers, the ^{1}H-NMR spectrum is not very characteristic (for more detail show Figure S95). **^{13}C-NMR** (101 MHz, $CDCl_3$) mixture of two rotamers: δ_c= 175.9, 157.3, 155.4, 150.6, 150.2, 149.0, 147.7, 147.2, 145.2, 143.1, 133.6, 130.4, 128.8, 127.4, 127.3, 126.7, 126.2, 125.2, 124.1, 123.4, 122.7, 122.4, 121.1, 120.6, 119.9, 116.9, 116.7, 113.0, 112.2, 112.1 ppm; . **HRMS-ESI** (m/z): calc. for $C_{24}H_{14}N_2O_6$ $[M+H]^+$ 427.0924, found 427.0925.

2-cyano-5-methylphenyl 4-methoxybenzoate (3b)



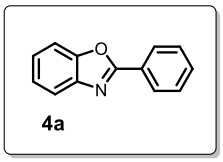
white solid (25 mg, Yield 25%), mp 184-187°C, R_f = 0.22 (n-hexanes /ethyl acetate 8:1); **^{1}H-NMR** (300 MHz, $CDCl_3$): δ_H= 8.20 (d, *J* = 9.0 Hz, 2H), 7.59 (d, *J* = 7.9 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.20 – 7.10 (m, 1H), 7.01 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H), 2.46 (s, 3H) ppm; **^{13}C-NMR** (75 MHz, $CDCl_3$): δ_c= 164.4, 163.7, 152.7, 145.5, 132.7, 127.0, 126.9, 123.9, 123.9, 120.6, 115.6, 114.1, 113.9, 103.9, 55.5, 21.9 ppm; **HRMS-ESI** (m/z): calc. for $C_{16}H_{13}NO_3$ $[M+H]^+$ 268.0967, found 268.0968.

2-cyano-5-methoxyphenyl 4-methoxybenzoate (3m)



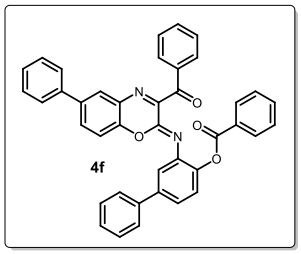
White solid (33 mg, Yield 33%), mp 148-151°C, R_f = 0.25 (n-hexanes /ethyl acetate 10:1); **^{1}H-NMR** (250 MHz, DMSO): δ_H= 8.09 (d, *J* = 9.2 Hz, 2H), 7.61 – 7.42 (m, 2H), 7.42 – 7.28 (m, 1H), 7.13 (d, *J* = 9.2 Hz, 2H), 3.86 (s, 3H, OMe), 3.81 (s, 3H, OMe) ppm; **^{13}C-NMR** (63 MHz, DMSO): δ_c= 164.6, 157.4, 146.1, 132.7 (2C), 125.3, 121.6, 120.3, 117.7, 115.6, 115.0, 107.2, 56.5, 56.2 ppm**;** **HRMS-ESI** (m/z): calc. for $C_{16}H_{13}NO_4$ $[M+H]^+$ 284.0917, found 284.0918.

2-phenylbenzo[d]oxazole (4a)



White solid (59 mg, Yield 59%), mp 101-103°C, R_f = 0.18 (n-hexanes /ethyl acetate 20:1); **^{1}H-NMR** (400 MHz, $CDCl_3$): δ_H= 8.34 – 8.27 (m, 2H), 7.86 – 7.78 (m, 1H), 7.67 – 7.60 (m, 1H), 7.60 – 7.52 (m, 3H), 7.42 – 7.36 (m, 2H) ppm; **^{13}C-NMR** (101 MHz, $CDCl_3$): δ_c= 163.1, 150.8, 142.2, 131.5, 128.9, 127.7, 127.2, 125.1, 124.6, 120.1, 110.6 ppm**;** **HRMS-ESI** (m/z): calc. for $C_{13}H_9NO$ $[M+H]^+$ 196.0756, found 196.0753.

(Z)-3-((3-benzoyl-6-phenyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-[1,1'-biphenyl]-4-yl benzoate (4f)



Yellow solid (12 mg, Yield 42%), R_f = 0.2 (n-hexane /ethyl acetate 12:1); **^{1}H-NMR** (500 MHz, $CDCl_3$): δ_H= 7.97 (d, *J* = 6.9 Hz, 2H), 7.85 (d, *J* = 2.2 Hz, 1H), 7.81 (d, *J* = 6.9 Hz, 2H), 7.73 (d, *J* = 2.2 Hz, 1H), 7.68 – 7.62 (m, 2H), 7.60 – 7.57 (m, 2H), 7.57 – 7.53 (m, 1H), 7.51 – 7.42 (m, 6H), 7.42 – 7.35 (m, 4H), 7.34 – 7.30 (m, 1H), 7.28 – 7.21 (m, 4H) ppm; **^{13}C-NMR** (126 MHz, $CDCl_3$): δ_c= 190.5, 164.5, 156.8, 145.0, 142.8, 141.6, 140.4, 139.5, 139.1, 138.6, 136.6, 134.1, 133.3, 131.0, 130.4, 130.3, 130.1, 129.6, 129.3, 129.0, 128.9, 128.5, 128.4, 127.9, 127.6, 127.5, 127.2, 126.9, 125.2, 123.2, 122.4, 116.3 ppm; **HRMS-ESI** (m/z): calc. for $C_{40}H_{26}N_2O_4$ $[M+H]^+$ 599.1965, found 599.1963.

6. References

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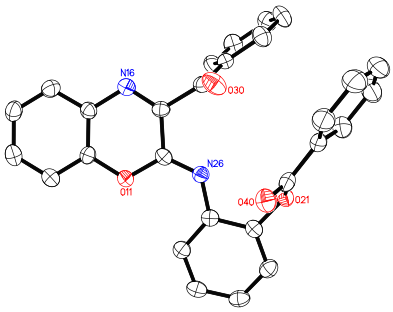
7. X-Ray Crystallographic Analysis

Table S2. Crystal data and structure refinement for sba188.

Identification code	sba188		
Empirical formula	$C_{28}H_{18}N_2O_4$		
Formula weight	446.44		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	triclinic		
Space group	$P\bar{1}$		
Z	2		
Unit cell dimensions	a = 10.0719(6) Å	α =	92.2576(15) deg.
	b = 10.5354(7) Å	β =	111.1719(14) deg.
	c = 10.8948(7) Å	γ =	93.0417(15) deg.
Volume	1074.38(12) $Å^3$		
Density (calculated)	1.38 g/cm^3		
Absorption coefficient	0.09 mm^{-1}		
Crystal shape	brick		
Crystal size	0.146 x 0.128 x 0.111 mm^3		
Crystal colour	yellow		
Theta range for data collection	1.9 to 27.6 deg.		
Index ranges	-12 ≤h ≤12, -13 ≤k ≤12, -13 ≤l ≤14		
Reflections collected	14852		
Independent reflections	4431 (R(int) = 0.0446)		
Observed reflections	2904 (I > 2σ(I))		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.96 and 0.93		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	4431 / 0 / 307		
Goodness-of-fit on F^2	1.01		
Final R indices (I>2sigma(I))	R1 = 0.052, wR2 = 0.103		
Largest diff. peak and hole	0.17 and -0.26 $eÅ^{-3}$		



1a: yellow crystal (brick), dimensions 0.146 x 0.128 x 0.111 mm^3, crystal system triclinic, space group $P\bar{1}$, Z=2, a=10.0719(6) Å, b=10.5354(7) Å, c=10.8948(7) Å, alpha=92.2576(15) deg, beta=111.1719(14) deg, gamma=93.0417(15) deg, V=1074.38(12) $Å^3$, rho=1.380 g/cm^3, T=200(2) K, $Theta_{max}$= 27.595 deg, radiation MoKα, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 2.98and a completeness of 88.8% to a resolution of 0.77 Å, 14852 reflections measured, 4431 unique (R(int)=0.0446), 2904 observed (I > 2□(I)), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.09mm^{-1}, T_{min}=0.93, T_{max}=0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 307 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.01 for observed reflections, final residual values R1(F)=0.052, wR(F^2)=0.103 for observed reflections, residual electron density -0.26 to 0.17 $eÅ^{-3}$. **CCDC 2337430** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

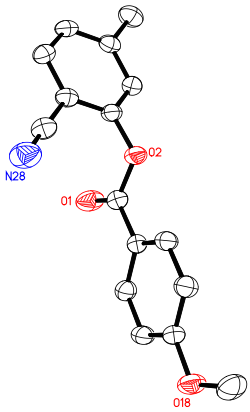
Lit. 2: (SHELXT - Integrated space-group and crystal structure determination)
Sheldrick G. M., Acta Cryst. A71 (2015) 3-8.

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

Table S3. Crystal data and structure refinement for sba200.

Identification code	sba200		
Empirical formula	$C_{16}H_{13}NO_3$		
Formula weight	267.27		
Temperature	200(2) K		
Wavelength	0.71073 Å		
Crystal system	triclinic		
Space group	P $\bar{1}$		
Z	2		
Unit cell dimensions	a = 6.7066(7) Å	α =	100.298(2) deg.
	b = 8.7863(9) Å	β =	96.3058(19) deg.
	c = 12.6844(13) Å	γ =	111.3892(18) deg.
Volume	672.14(12) Å^3		
Density (calculated)	1.32 g/cm^3		
Absorption coefficient	0.09 mm^{-1}		
Crystal shape	brick		
Crystal size	0.122 x 0.062 x 0.062 mm^3		
Crystal colour	colourless		
Theta range for data collection	1.7 to 29.3 deg.		
Index ranges	-9≤h ≤9, -12≤k ≤12, -17≤l ≤17		
Reflections collected	12848		
Independent reflections	3342 (R(int) = 0.0383)		
Observed reflections	2185 (I > 2□(I))		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.96 and 0.92		
Refinement method	Full-matrix least-squares on F^2		
Data/restraints/parameters	3342 / 0 / 183		
Goodness-of-fit on F^2	1.04		
Final R indices (I>2sigma(I))	R1 = 0.049, wR2 = 0.113		
Largest diff. peak and hole	0.20 and -0.20 eÅ^{-3}		



3b: colourless crystal (brick), dimensions 0.122 x 0.062 x 0.062 mm^3, crystal system triclinic, space group P $\bar{1}$, Z=2, a=6.7066(7) Å, b=8.7863(9) Å, c=12.6844(13) Å, alpha=100.298(2) deg, beta=96.3058(19) deg, gamma=111.3892(18) deg, V=672.14(12) Å^3, rho=1.321 g/cm^3, T=200(2) K, Theta$_{max}$= 29.291 deg, radiation MoK□, lambda=0.71073 Å, 0.5 deg omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.51and a completeness of 91.3% to a resolution of 0.73 Å, 12848 reflections measured, 3342 unique (R(int)=0.0383), 2185 observed (I > 2□(I)), intensities were corrected for Lorentz and polarization effects, an empirical scaling and absorption correction was applied using SADABS[1] based on the Laue symmetry of the reciprocal space, mu=0.09mm^{-1}, T$_{min}$=0.92, T$_{max}$=0.96, structure solved with SHELXT-2018/2 (Sheldrick 2015)[2] and refined against F^2 with a Full-matrix least-squares algorithm using the SHELXL-2018/3 (Sheldrick, 2018) software[3], 183 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.04 for observed reflections, final residual values R1(F)=0.049, wR(F^2)=0.113 for observed reflections, residual electron density -0.20 to 0.20 eÅ^{-3}. **CCDC 2337863** contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Lit. 1: (SADABS-2016/2 - Bruker AXS area detector scaling and absorption correction)
Krause, L., Herbst-Irmer, R., Sheldrick G.M. & Stalke D., J. Appl. Cryst. 48 (2015) 3-10.

Lit. 2: (SHELXT - Integrated space-group and crystal structure determination)
Sheldrick G. M., Acta Cryst. A71 (2015) 3-8.

Lit. 3: (program SHELXL-2018/3 (Sheldrick, 2018) for structure refinement)
Sheldrick G. M., Acta Cryst. (2015). C71, 3-8

Lit. APEX, APEX2, SMART, SAINT, SAINT-Plus:
Bruker (2007). "Program name(s)". Bruker AXS Inc., Madison, Wisconsin, USA.

8. Z-matrices

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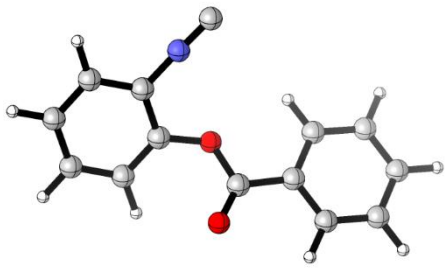

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Thermal Correction to Free Energy = 0.150366 Hartree

Imaginary Freq= 0

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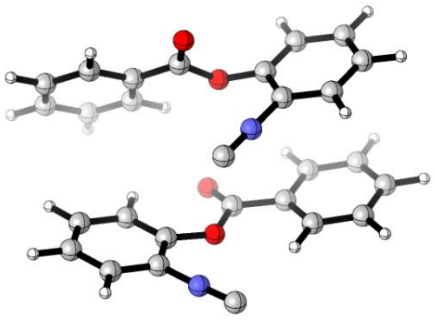

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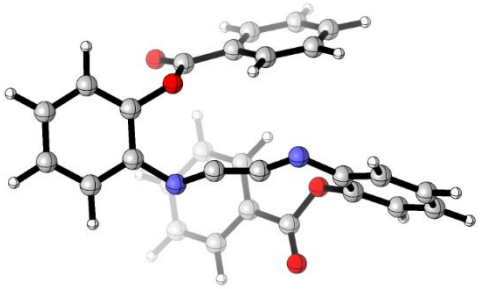

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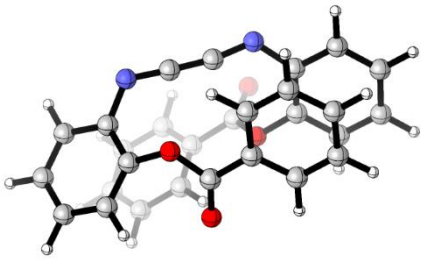

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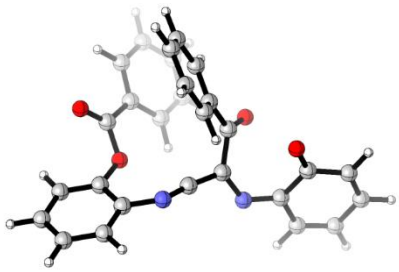

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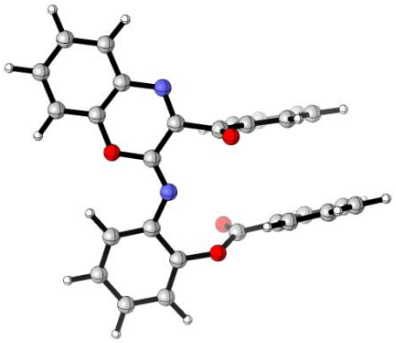
H	0.06233800	4.93141300	-2.39914100
O	3.51624600	-0.19027500	1.59954100
C	1.28238200	0.59202600	0.51063800
O	1.94240200	1.41653300	-0.10563300
C	0.35065500	0.98721900	1.60171300
C	-0.22363000	2.26577000	1.55528900
C	0.04762800	0.12576300	2.66519200
C	-1.12354600	2.66252700	2.54059300
H	0.03441100	2.92425200	0.73414600
C	-0.84080800	0.53252800	3.66035800
H	0.53022900	-0.84327800	2.72815700
C	-1.43625400	1.79507400	3.59244300
H	-1.58482800	3.64380200	2.48806300
H	-1.06586300	-0.13249700	4.48826800
H	-2.13914900	2.10446300	4.36013900
N	2.26110700	-1.39985100	-0.73747000
N	-0.72756700	-2.34348200	0.47623300

Electronic Energy = -1488.354907 Hartree

Thermal Correction to Free Energy = 0.328090 Hartree

Imaginary Freq= 0

Pr$_z$



C	-5.27144000	-0.04864200	0.23844900
C	-3.96122800	-0.41757100	-0.04592000
C	-3.60399300	-1.75559600	-0.27753500
C	-4.60153300	-2.73898200	-0.21445600
C	-5.91704900	-2.38550700	0.07057200
C	-6.24938300	-1.04234300	0.29557000
H	-5.50742700	0.99577300	0.41081700
H	-4.31132400	-3.76818800	-0.39687000
H	-6.68587400	-3.14937600	0.11726500
H	-7.27537300	-0.76669900	0.51689700
C	-1.41191600	-1.16785400	-0.62722400
C	-1.69205900	0.24443300	-0.36092800
C	-0.77671000	2.44848100	-0.10759700
C	0.47693600	3.10051700	-0.11345600
C	-1.91819600	3.24178800	0.13469100

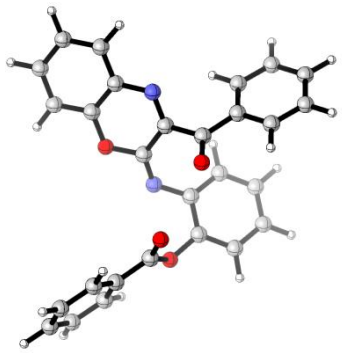
C	0.60078800	4.46387400	0.10509400
C	-1.79755700	4.61331700	0.35289800
H	-2.89368200	2.77883700	0.14340400
C	-0.54394400	5.22894400	0.33948300
H	1.58935300	4.90927600	0.08857200
H	-2.69046400	5.20355000	0.53393300
H	-0.45462900	6.29674900	0.51131900
O	1.61831100	2.37546000	-0.42349600
C	2.10475500	1.50382100	0.51701400
O	1.70814800	1.47228100	1.66109300
C	3.19480400	0.66721400	-0.04246600
C	4.10604900	0.08593800	0.84821000
C	3.32258500	0.45154200	-1.42145600
C	5.15875700	-0.68399900	0.35965400
H	3.97458600	0.24814400	1.91215000
C	4.36499700	-0.33874700	-1.90295300
H	2.59684200	0.88317100	-2.09972200
C	5.28981000	-0.89633400	-1.01563100
H	5.87073600	-1.12608200	1.04965100
H	4.45423800	-0.51974600	-2.96943400
H	6.10706100	-1.50276100	-1.39514000
O	-3.00421800	0.57215200	-0.09228200
C	0.00321700	-1.54177400	-1.05061700
O	0.28547700	-1.46660300	-2.23608300
C	0.93064900	-2.04955900	-0.01500200
C	2.08537600	-2.73807100	-0.41787500
C	0.67539100	-1.85235100	1.34888100
C	2.96148900	-3.24128000	0.53651600
H	2.27227500	-2.86495500	-1.47809000
C	1.56729200	-2.33872900	2.30291900
H	-0.20093400	-1.29781300	1.66548300
C	2.70352500	-3.04176200	1.89761700
H	3.85230700	-3.77660100	0.22480300
H	1.37849400	-2.16467500	3.35716100
H	3.39493200	-3.42697200	2.64131300
N	-2.28755300	-2.11318800	-0.57130500
N	-0.73263700	1.08424800	-0.35927800

Electronic Energy = -1488.424466 Hartree

Thermal Correction to Free Energy = 0.333645 Hartree

Imaginary Freq= 0

Pr_E



C	-0.11266800	4.55623700	-0.82186500
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C	1.69826800	3.17339500	0.04805600

C	2.48213200	4.32113200	0.24105800	C	-5.92371300	0.48507000	1.60403900
C	1.97982600	5.57143000	-0.10224300	H	-4.00005600	0.01287400	2.47901800
C	0.68220900	5.68487000	-0.62529100	C	-6.22732700	-0.23917800	-0.68802900
H	-1.11536500	4.62248700	-1.22922300	H	-4.54740400	-1.26308500	-1.57743900
H	3.47001200	4.19825800	0.67235200	C	-6.72013400	0.39106000	0.45811400
H	2.58464900	6.45975400	0.04496300	H	-6.30547400	0.97564800	2.49404900
H	0.28805200	6.66246900	-0.88391500	H	-6.84418100	-0.30860800	-1.57867500
C	1.43079600	0.88581100	0.23685200	H	-7.72233400	0.80943400	0.45821200
C	0.16070300	0.93496500	-0.53704400	O	-0.35752300	2.20225100	-0.71972400
C	-0.15526200	-1.32909000	-1.11133700	C	1.83483700	-0.36947700	0.99218400
C	-1.13367900	-2.30827400	-0.85360300	O	1.03222600	-0.80215500	1.80159000
C	1.11251900	-1.76532400	-1.52943400	C	3.18312000	-0.96414200	0.79309700
C	-0.83573200	-3.66195400	-0.91846000	C	3.50491700	-2.10827900	1.53898100
C	1.41637500	-3.12361300	-1.60586900	C	4.10523100	-0.46020400	-0.13563400
H	1.85111100	-1.02698500	-1.81975300	C	4.73101600	-2.74100700	1.35660900
C	0.44827300	-4.07621400	-1.28554600	H	2.77313500	-2.48835600	2.24330000
H	-1.61806100	-4.37801000	-0.69123300	C	5.33318600	-1.09582400	-0.31686700
H	2.40910200	-3.43163200	-1.91786500	H	3.86806600	0.42824300	-0.70816000
H	0.68006700	-5.13494000	-1.33678800	C	5.64733000	-2.23654400	0.42685400
O	-2.45071700	-1.92916800	-0.63119500	H	4.97369200	-3.62831100	1.93309100
C	-2.76282000	-1.23355400	0.51073000	H	6.04441300	-0.70116100	-1.03582000
O	-2.00002400	-1.11485100	1.44057700	H	6.60326300	-2.73133900	0.28311800
C	-4.14324200	-0.68625200	0.45657800	N	2.15973400	1.92938300	0.46153800
C	-4.63768300	-0.05069500	1.60403300	N	-0.53058700	0.00971800	-1.06711400
C	-4.94086500	-0.77816800	-0.69233600				

Electronic Energy = -1488.409252 Hartree

Thermal Correction to Free Energy = 0.331456 Hartree

Imaginary Freq= 0

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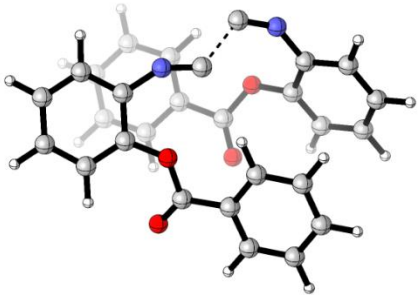


C	3.20448700	-1.07749300	1.31811300
C	2.23660200	-1.68988300	0.52599400
C	2.57713300	-2.24096600	-0.72531500
C	3.90428800	-2.17000900	-1.16511300
C	4.86713600	-1.53273100	-0.38519700
C	4.51777700	-0.99160500	0.85420900
H	2.92246000	-0.65518100	2.27230400
H	4.15635500	-2.61820400	-2.11989300
H	5.89063400	-1.46973800	-0.74071100
H	5.26576500	-0.49967800	1.46702500
C	0.51434400	-2.71152100	-1.96745800
C	-0.27294800	-1.11106600	-1.82670800
C	-2.47310900	-0.01013100	-1.51042300
C	-2.17903300	1.26471600	-0.97737000
C	-3.80148000	-0.38972200	-1.72093300
C	-3.21348700	2.14841700	-0.67353900
C	-4.83452100	0.48977300	-1.40884600
H	-3.99700200	-1.37819700	-2.12033500
C	-4.53531800	1.75119500	-0.88956000
H	-2.98462300	3.12020100	-0.26199600
H	-5.86548300	0.19305600	-1.56945700
H	-5.33648500	2.44252700	-0.64796600
O	-0.83832900	1.54081700	-0.86840800
C	-0.29560700	2.41599500	0.04887000
O	-0.95922900	3.04036800	0.84668900
C	1.17663600	2.47184500	-0.09147300
C	1.87684900	3.34603600	0.75063500
C	1.87365200	1.65905000	-0.99763200
C	3.26656500	3.40954400	0.68419900
H	1.31977000	3.95447800	1.45419200
C	3.26334600	1.72309800	-1.05552200
H	1.33365800	0.96272600	-1.62666500
C	3.96082000	2.59688500	-0.21768700
H	3.80876700	4.08550800	1.33804400
H	3.80148100	1.07472800	-1.73845200
H	5.04514200	2.63914800	-0.26163400
O	0.92240300	-1.87732100	0.92951500
C	0.19427700	-0.86063100	1.48899900
O	0.67876500	0.18802900	1.85580400
C	-1.24744500	-1.19838000	1.55640200
C	-2.12349800	-0.20571400	2.01966900
C	-1.74983200	-2.43472900	1.12459200

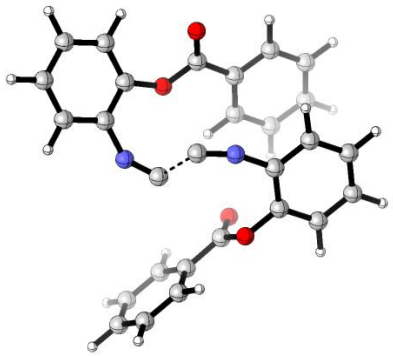
C	-3.49446300	-0.44825000	2.04850900
H	-1.71815100	0.75114400	2.32898200
C	-3.12215600	-2.67319400	1.16360400
H	-1.07039500	-3.18937700	0.74835100
C	-3.99443000	-1.68145700	1.62217400
H	-4.17178200	0.32794100	2.38885300
H	-3.51174700	-3.62835500	0.82587100
H	-5.06425700	-1.86673700	1.63819500
N	1.61704500	-2.89265300	-1.48861700
N	-1.45025800	-0.88957000	-1.80319300

Electronic Energy = -1488.328381 Hartree

Thermal Correction to Free Energy = 0.327668 Hartree

Imaginary Freq= -409.60

TS1$_{Trans}$



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C	2.94364700	-1.82203500	0.15758300
C	1.95547900	-2.77326000	-0.16101200
C	2.33992500	-4.05860900	-0.55684100
C	3.69125300	-4.37867500	-0.67007400
C	4.66490900	-3.42729100	-0.35457400
H	5.04004000	-1.40709100	0.31881600
H	1.56615700	-4.78542800	-0.77812800
H	3.98285800	-5.37208900	-0.99511000
H	5.71803300	-3.67684300	-0.43252300
C	-0.14777900	-1.58155200	-0.44614300
C	0.36091300	-0.37145000	-1.56724300
C	-0.70497200	1.91243000	-1.43047700
C	-2.02999400	1.82649800	-0.97249400
C	-0.12602800	3.17068700	-1.63708900
C	-2.76249500	2.97844700	-0.71770200
C	-0.85649400	4.32411200	-1.36995400
H	0.90051400	3.21633900	-1.98068900
C	-2.17364900	4.22942500	-0.91215200
H	-3.78231700	2.88198900	-0.36164900
H	-0.39716800	5.29583200	-1.51552300
H	-2.74530300	5.12827500	-0.70505800
O	-2.62083300	0.57949600	-0.84313600
C	-2.62500700	0.00004200	0.40748800
O	-2.15916000	0.55398500	1.37894400
C	-3.28374500	-1.32514200	0.39974000
C	-3.35386100	-2.02430800	1.61214400
C	-3.81958100	-1.88619100	-0.76756900
C	-3.95586100	-3.27931200	1.65663400
H	-2.92500300	-1.57481400	2.50067300

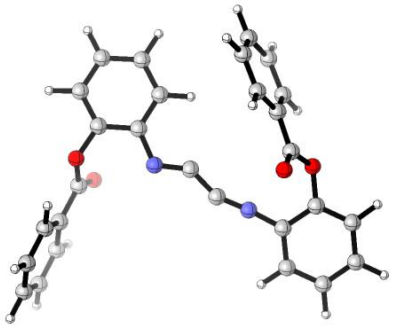
C	-4.42276300	-3.14159500	-0.71736500
H	-3.75095400	-1.34443200	-1.70287000
C	-4.49100200	-3.83914200	0.49231400
H	-4.00510400	-3.82251200	2.59505700
H	-4.83512500	-3.57838000	-1.62148400
H	-4.95834500	-4.81872300	0.52704900
O	2.48097600	-0.61334600	0.65636000
C	3.00976600	0.58670100	0.26009700
O	3.98257900	0.69119000	-0.45536600
C	2.23280000	1.72250400	0.81740700
C	2.75849400	3.01360100	0.65571500
C	0.99348300	1.54488200	1.44853300
C	2.05402800	4.11554100	1.13348300
H	3.71397300	3.13011900	0.15586300
C	0.28388800	2.65320400	1.90890400
H	0.57111200	0.55397500	1.55419900
C	0.81493200	3.93563000	1.75817200
H	2.46519900	5.11335800	1.01405800
H	-0.69133700	2.50415300	2.35751700
H	0.25877100	4.79706100	2.11582100
N	0.60988400	-2.44128400	-0.03533800
N	0.03812000	0.77540000	-1.66878400

Electronic Energy = -1488.326944 Hartree

Thermal Correction to Free Energy = 0.326357 Hartree

Imaginary Freq= -440.23

TS_{Rot}



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C	4.21527200	-1.92916200	-0.20977500
C	2.93824700	-2.53309300	-0.30185500
C	2.85647300	-3.93342100	-0.40981800
C	4.01878000	-4.69898700	-0.44102900
C	5.27175100	-4.08515300	-0.33861800
H	6.33057800	-2.19956300	-0.13528500
H	1.87590500	-4.39120400	-0.47809800
H	3.94789500	-5.77766900	-0.53409300
H	6.17481900	-4.68644700	-0.35065600
C	0.83507300	-1.09598500	-0.16994000
C	0.05612100	-0.01005600	-0.23174000
C	-1.51172500	1.67347500	-0.13564000
C	-0.61026900	2.72466300	-0.38024300
C	-2.88117900	1.97980000	-0.04164400
C	-1.06459700	4.03096200	-0.51714300
C	-3.34454500	3.28216400	-0.18596900
C	-2.43317200	4.31318300	-0.42078000
H	-0.35364900	4.83189300	-0.69461000

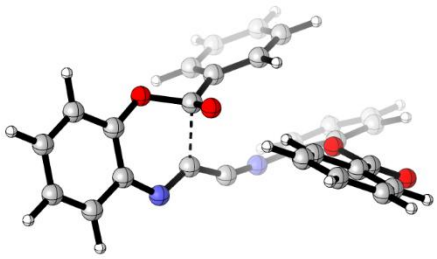
H	-4.40987000	3.47128800	-0.11291400
H	-2.79058800	5.33247100	-0.52810400
N	1.84933100	-1.73128800	-0.30430200
N	-1.13200800	0.33753100	0.07246500
H	0.44648400	2.48906400	-0.44070600
O	-3.79473800	0.98208400	0.26332200
C	-3.99099600	-0.01641800	-0.65962800
O	-3.58761500	0.04926600	-1.79883200
C	-4.77971100	-1.13855000	-0.09167300
C	-5.18279400	-2.16156600	-0.96129500
C	-5.11126100	-1.20373500	1.26874400
C	-5.91820400	-3.23987500	-0.47432800
H	-4.90955700	-2.09309000	-2.00852100
C	-5.84565100	-2.28641300	1.75201900
H	-4.78696300	-0.41380800	1.93518700
C	-6.25060000	-3.30331800	0.88280100
H	-6.23135200	-4.03029700	-1.14934200
H	-6.09940200	-2.33848600	2.80621400
H	-6.82259900	-4.14484200	1.26229600
O	4.30358700	-0.54920500	-0.20086900
C	3.71436300	0.12903100	0.84999700
O	3.46067800	-0.40674100	1.90439400
C	3.44183700	1.54562700	0.51491600
C	2.94031700	2.37222000	1.53119200
C	3.61822000	2.05287000	-0.77999100
C	2.62727200	3.70076900	1.25553400
H	2.79421400	1.95415600	2.52087000
C	3.30160800	3.38380300	-1.05099500
H	3.98817500	1.40312000	-1.56358300
C	2.80991300	4.20806900	-0.03494900
H	2.23261900	4.33749400	2.04066000
H	3.43198500	3.77535500	-2.05478100
H	2.56258500	5.24339000	-0.24992500

Electronic Energy = -1488.333713 Hartree

Thermal Correction to Free Energy = 0.324999 Hartree

Imaginary Freq= -175.25

$TS_{Acylshift}$



C	5.26620100	-0.48089700	0.75772500
C	3.99509600	-0.52680900	0.18246200
C	3.77911600	0.02469100	-1.10575100
C	4.85383400	0.63964900	-1.77755400
C	6.10887100	0.70692500	-1.19126200
C	6.31260600	0.13548500	0.07563000
H	5.40598500	-0.91895200	1.73990900
H	4.66142600	1.05001000	-2.76346100
H	6.93017900	1.18886200	-1.71082900

H	7.29513400	0.17869500	0.53571400
C	1.54959500	-0.51401700	-1.13112500
C	0.26952900	-0.76452600	-1.58214300
C	-2.13736000	-1.48583700	-1.22103300
C	-2.95973200	-0.54147700	-0.57216200
C	-2.63672000	-2.75302200	-1.55079800
C	-4.27540500	-0.86814200	-0.25965000
C	-3.95387400	-3.07053500	-1.23578800
H	-1.97957200	-3.46674100	-2.03350400
C	-4.76788500	-2.13148200	-0.59559500
H	-4.90297200	-0.13816600	0.23245800
H	-4.34315900	-4.05131900	-1.48689900
H	-5.79527500	-2.38023700	-0.35134200
O	-2.33413000	0.62959500	-0.21675900
C	-2.96002600	1.85958700	-0.31991500
O	-4.09851500	1.98525000	-0.71217200
C	-2.05398600	2.94972900	0.10067200
C	-2.55336500	4.26194300	0.06413800
C	-0.73666600	2.70840700	0.51959600
C	-1.73798700	5.32349900	0.44595100
H	-3.57353600	4.42720200	-0.26458100
C	0.07387400	3.77674000	0.90062500
H	-0.32786700	1.70773900	0.55784400
C	-0.42384300	5.08165300	0.86485400
H	-2.12321700	6.33798900	0.41823400
H	1.08977300	3.57305200	1.22215600
H	0.20965800	5.91229500	1.16197000
O	3.00560000	-1.18255400	0.83636200
C	1.68389000	-0.55621000	0.82751900
O	1.60249700	0.63297300	1.16142800
C	0.66843600	-1.58910800	1.23107000
C	-0.48559200	-1.15116300	1.88787000
C	0.80153900	-2.94264500	0.89543500
C	-1.50452000	-2.05384700	2.19683200
H	-0.57312100	-0.10128600	2.14172700
C	-0.21592200	-3.84384500	1.20699100
H	1.69789900	-3.27858800	0.38571800
C	-1.37577100	-3.40030100	1.85180300
H	-2.40141900	-1.70301300	2.69791900
H	-0.10691400	-4.89207200	0.94444200
H	-2.17286400	-4.10065200	2.08177100
N	2.57054300	-0.07971400	-1.77632900
N	-0.84159200	-1.15365800	-1.48917300

Electronic Energy = -1488.333561 Hartree

Thermal Correction to Free Energy = 0.329100 Hartree

Imaginary Freq= -367.06

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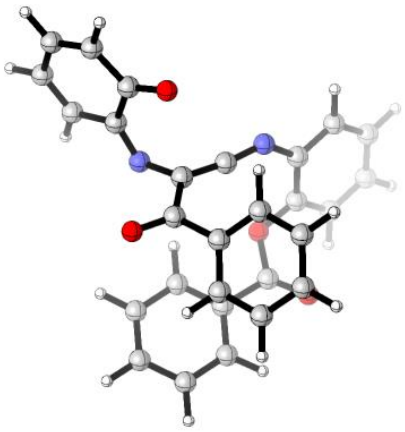

C	-5.57645600	0.47643100	0.78628200
C	-4.11070000	0.44825600	0.70972000
C	-3.50642400	0.03661800	-0.64116100
C	-4.42383700	-0.16881000	-1.76304600
C	-5.76116400	-0.06907000	-1.60271200
C	-6.34179200	0.24944100	-0.30627700
H	-6.00065400	0.72452400	1.75343400
H	-3.96987100	-0.42704400	-2.71377500
H	-6.42837300	-0.23939300	-2.44167900
H	-7.42425500	0.30482000	-0.22913000
C	-1.27508500	-0.08934500	0.16755400
C	-0.63184400	1.06222700	0.32648300
C	0.88046100	2.88702900	-0.01487900
C	1.83656700	2.29827900	-0.86213700
C	1.00692000	4.24165800	0.31813500
C	2.89232500	3.04976100	-1.36945600
C	2.05789300	4.99809400	-0.19265200
H	0.26412100	4.67515500	0.97881000
C	3.00008900	4.40014800	-1.03492600
H	3.62227200	2.57360700	-2.01195000
H	2.14557000	6.04749100	0.06816800
H	3.82484900	4.98282200	-1.43219700
O	1.64281500	0.97478500	-1.20996500
C	2.65201700	0.05519400	-0.98634800
O	3.71980800	0.35998500	-0.50633600
C	2.24314600	-1.30731500	-1.39304800
C	3.17742600	-2.33996400	-1.22140700
C	0.96296600	-1.59139200	-1.88874300
C	2.82856600	-3.64978000	-1.53594100
H	4.15791900	-2.09739800	-0.82742700
C	0.61441400	-2.90762600	-2.18714800
H	0.23655800	-0.79902400	-2.01129400
C	1.54344300	-3.93555100	-2.01190800
H	3.54976800	-4.44970500	-1.40014900
H	-0.38981500	-3.12826000	-2.53149100
H	1.26514800	-4.96045800	-2.23806800
O	-3.40858900	0.74163000	1.67083300
C	-0.86074200	-1.35526500	0.80221900
O	-1.42959700	-2.40457100	0.50832800
C	0.28669700	-1.32857400	1.75795000
C	1.22582700	-2.36637700	1.68106000
C	0.44291300	-0.31835000	2.71705100
C	2.33393100	-2.36946300	2.52451200

H	1.08347000	-3.14770600	0.94328500
C	1.54625500	-0.33466000	3.57206300
H	-0.30621800	0.45965500	2.81445000
C	2.49858800	-1.35131600	3.46904500
H	3.07186700	-3.16168600	2.44298400
H	1.65984000	0.44522100	4.31871100
H	3.36371000	-1.35341400	4.12522500
N	-2.26102400	-0.19949100	-0.86406300
N	-0.19266300	2.17870300	0.54513500

Electronic Energy = -1488.343889 Hartree

Thermal Correction to Free Energy = 0.328683 Hartree

Imaginary Freq= -70.72

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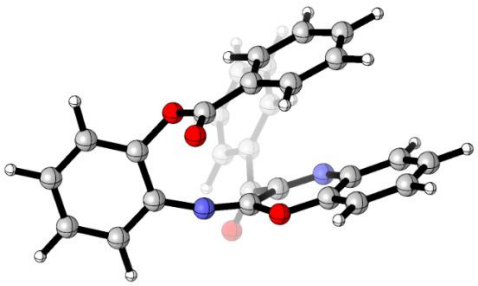

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C	2.41262900	0.50333600	-1.35486600
C	3.68958200	1.06900500	-1.21783400
C	4.81870300	0.26055800	-1.26093700
C	4.68133800	-1.12331500	-1.45350800
H	3.29323800	-2.77309200	-1.72509600
H	3.75837000	2.14317600	-1.08295300
H	5.80558900	0.69812100	-1.15410100
H	5.56435400	-1.75333100	-1.49382800
C	0.12661600	0.76037200	-1.42736700
C	-0.08974600	-0.70994000	-1.40584100
C	-2.26057000	-1.83163500	-0.64327300
C	-2.34392600	-1.91765200	0.76541800
C	-3.33839600	-2.32358800	-1.39912600
C	-3.44474000	-2.46887400	1.39735800
C	-4.44602400	-2.87819900	-0.75903900
H	-3.28917400	-2.25544600	-2.47977100
C	-4.51048300	-2.95634300	0.63442000
H	-3.45571400	-2.50959500	2.48146100
H	-5.26835600	-3.25175500	-1.36141500
H	-5.37500400	-3.39073400	1.12437200
O	-1.31352000	-1.33759800	1.51117400
C	-0.09344400	-1.96620100	1.49555100
O	0.05800100	-3.11826600	1.15847500
C	1.00320300	-1.04438300	1.89427300
C	2.32129300	-1.51045200	1.78721500
C	0.75806700	0.27184500	2.30940200
C	3.38644400	-0.66427400	2.08365900
H	2.48698800	-2.52818300	1.45300600
C	1.82825000	1.11208500	2.61518200
H	-0.26229500	0.62809500	2.38074900

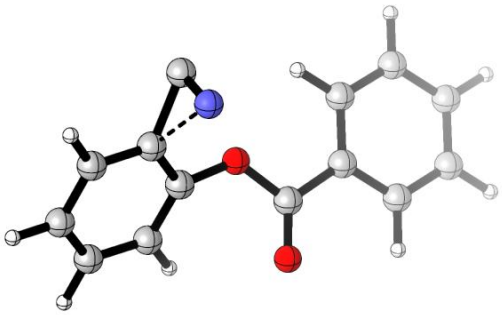
C	3.14115200	0.64818900	2.49747800
H	4.40550200	-1.02110600	1.97857200
H	1.63857000	2.13102600	2.93861200
H	3.97207600	1.30980600	2.72282700
O	1.06574300	-1.47193800	-1.62083700
C	-1.11043100	1.61990500	-1.58607400
O	-1.84909100	1.36686600	-2.52844800
C	-1.38887400	2.71862100	-0.62557800
C	-2.57009700	3.45907000	-0.80453600
C	-0.54671100	3.01033300	0.45892000
C	-2.90260600	4.47398600	0.08681700
H	-3.21179800	3.21529100	-1.64401500
C	-0.88379900	4.02887600	1.34981700
H	0.36919000	2.45330700	0.59625500
C	-2.05966700	4.76031900	1.16728100
H	-3.81757800	5.04076900	-0.05413200
H	-0.22789000	4.25324500	2.18553900
H	-2.32064800	5.55136100	1.86396300
N	1.28683600	1.31890500	-1.34618500
N	-1.16361300	-1.27747200	-1.19951500

Electronic Energy = -1488.397647 Hartree

Thermal Correction to Free Energy = 0.332582 Hartree

Imaginary Freq= -151.98

TS_{Iso}



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C	-2.40072100	0.92282800	0.06447200
C	-3.79265700	0.79447200	0.13378000
C	-4.38473500	-0.42932300	-0.16280200
C	-3.58651400	-1.52410500	-0.51164600
H	-1.57542000	-2.25422700	-0.82350100
H	-4.38744900	1.65691300	0.40991300
H	-5.46374000	-0.53071400	-0.11657600
H	-4.04645700	-2.48002000	-0.74003500
C	-1.71055200	2.39216600	0.06344600
O	-0.24770700	0.04136000	-0.35356500
C	0.66484400	-0.82103300	0.21414700
O	0.34874400	-1.84254000	0.78080500
C	2.04915100	-0.32435200	0.03249800
C	3.09679400	-1.13089600	0.50110700
C	2.32799900	0.90976500	-0.57388500
C	4.41599200	-0.70813400	0.35883000
H	2.85769700	-2.07825700	0.97147300
C	3.65098400	1.32731100	-0.71226600

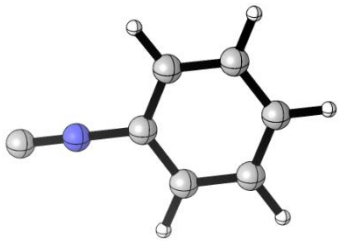
H	1.51402900	1.53192700	-0.92523000
C	4.69412400	0.52088100	-0.24831100
H	5.22628800	-1.33305100	0.72066900
H	3.86770100	2.28286700	-1.17905300
H	5.72298000	0.85035000	-0.35778400
N	-1.69713900	2.10621000	1.23039400

Electronic Energy = -744.109053 Hartree

Thermal Correction to Free Energy = 0.148442 Hartree

Imaginary Freq= -385.79

Phenyl isocyanide



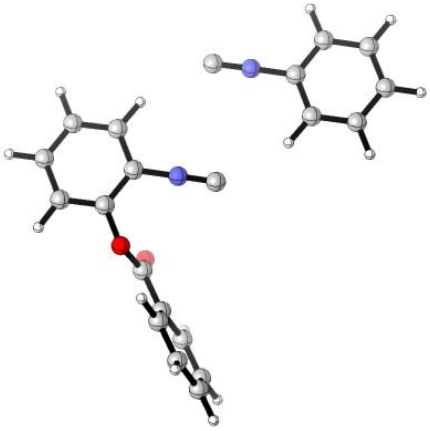
C	-1.44944300	1.21006200	0.00004800
C	-0.05545600	1.21840200	-0.00008100
C	0.63534100	0.00008600	0.00001000
C	-0.05532200	-1.21830000	0.00002400
C	-1.44931100	-1.21017300	-0.00004100
C	-2.14876400	-0.00010000	0.00002100
H	-1.98927300	2.15154700	0.00007600
H	0.50367500	-2.14718300	0.00002200
H	-1.98904500	-2.15170700	-0.00010800
H	-3.23400700	-0.00017000	0.00008200
C	3.19930000	-0.00012500	0.00002800
N	2.02103400	0.00014300	-0.00000100
H	0.50334300	2.14740000	-0.00010600

Electronic Energy = -324.504998 Hartree

Thermal Correction to Free Energy = 0.068291 Hartree

Imaginary Freq= 0

Com-M



C	-6.79705600	-1.49352400	0.08514800
C	-6.14958900	-0.25932900	0.10261100
C	-4.75371400	-0.22054000	-0.00505000
C	-4.00112200	-1.39493400	-0.12958400
C	-4.66636600	-2.62024300	-0.14495400
C	-6.05898900	-2.67436700	-0.03837000
H	-7.87850700	-1.53169900	0.16840200
H	-2.92121200	-1.33246900	-0.21024400
H	-4.09060800	-3.53529300	-0.24038000
H	-6.56800100	-3.63298200	-0.05107200
C	-3.53654600	2.03506400	0.02554500
C	-0.63020000	-0.27656500	-0.31058400
C	0.55767200	1.98358600	-0.18228900

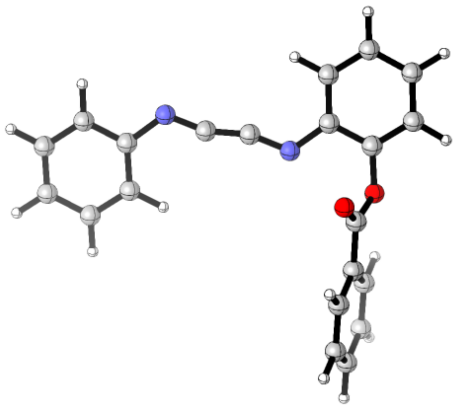
C	-0.17276000	3.16864700	-0.03941200
C	1.95724300	2.02606400	-0.26240300
C	0.50471900	4.38538900	0.01750900
C	2.62796200	3.24030000	-0.20634100
C	1.89916800	4.42348500	-0.06691200
H	-0.06098700	5.30451500	0.12738800
H	3.71038300	3.24305500	-0.27003100
H	2.42289900	5.37279400	-0.02169800
N	-4.10450900	1.00542500	0.01201700
N	-0.08771400	0.76524800	-0.25068900
H	-1.25447100	3.11331400	0.02050500
O	2.67197700	0.85640200	-0.47112700
C	2.82367100	0.00433400	0.60422900
O	2.44786400	0.29038000	1.71756000
C	3.49680500	-1.25690300	0.21360500
C	3.76453800	-2.19212200	1.22362100
C	3.85481400	-1.53402000	-1.11358700
C	4.38995600	-3.39583000	0.90796600
H	3.47391000	-1.95872200	2.24190500
C	4.48000000	-2.74105800	-1.42383600
H	3.63888400	-0.80953800	-1.88938100
C	4.74843200	-3.67118200	-0.41560000
H	4.59659400	-4.11932600	1.69023100
H	4.75539900	-2.95721400	-2.45123400
H	5.23482200	-4.61049600	-0.66103700
H	-6.70409600	0.66756300	0.19799500

Electronic Energy = -1068.685577 Hartree

Thermal Correction to Free Energy = 0.234774 Hartree

Imaginary Freq= 0

INT_{Trans}-M



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C	-4.09560800	-1.07092400	-0.21151700
C	-5.08263200	-2.04783300	-0.28238000
C	-6.43125500	-1.70350100	-0.11881600
H	-7.83213400	-0.10397100	0.24534700
H	-3.04764300	-1.32672600	-0.33488000
H	-4.80524600	-3.08171100	-0.46436500
H	-7.19707600	-2.47092700	-0.17485200
C	-2.28850400	1.13094400	-0.03264900
C	-1.02555900	1.32159300	-0.11943800
C	1.14358000	2.15767000	-0.19467100
C	0.81428400	3.52029800	-0.08798300

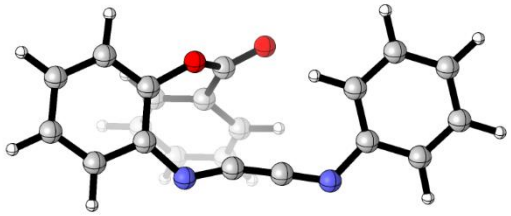
C	2.50318400	1.79976700	-0.25171500
C	1.81134500	4.48830900	-0.05207500
C	3.50465100	2.76212000	-0.21344600
C	3.15862900	4.11072100	-0.11688400
H	1.54342300	5.53713100	0.02556700
H	4.54009700	2.44309500	-0.25667300
H	3.93831200	4.86504500	-0.08820600
N	-3.52342600	1.32344100	0.11398400
N	0.20732300	1.11802900	-0.26724100
H	-0.23464800	3.79686500	-0.04242100
O	2.86252500	0.47201100	-0.41483400
C	2.62038900	-0.39097300	0.62990900
O	2.30511000	-0.01191100	1.73457400
C	2.82777200	-1.80478400	0.23080900
C	2.72804800	-2.78627800	1.22704800
C	3.10254100	-2.17454900	-1.09329600
C	2.90735300	-4.12879900	0.90158700
H	2.50935100	-2.47751700	2.24331500
C	3.27985700	-3.52007500	-1.41420100
H	3.16992600	-1.41063800	-1.85831400
C	3.18372500	-4.49699200	-0.41915100
H	2.83129000	-4.88756200	1.67411400
H	3.49071700	-3.80673100	-2.43973000
H	3.32270600	-5.54380300	-0.67239800
H	-6.05456600	1.65072700	0.37351400

Electronic Energy = -1068.685073 Hartree

Thermal Correction to Free Energy = 0.241267 Hartree

Imaginary Freq= 0

INT_{Cis}-M



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C	-2.13236400	-1.23699700	-0.88307800
C	-3.35433900	-1.58998500	-1.48900900
C	-4.41989600	-2.09174700	-0.75143700
C	-4.29113800	-2.24598800	0.63288800
H	-2.97957600	-1.96714100	2.33676300
H	-3.42013700	-1.46828600	-2.56478700
H	-5.34311000	-2.36660300	-1.25065800
H	-5.11046000	-2.64588200	1.22154200
C	0.07626800	-0.63029500	-1.49485700
C	1.32171700	-0.38645500	-1.61761100
C	3.52452400	-0.31155100	-0.78016300
C	3.25612200	-0.78087500	0.51806400
C	4.83845600	0.02241300	-1.14899800
C	4.29750600	-0.90467900	1.43151800
C	5.87549400	-0.10679400	-0.22819000

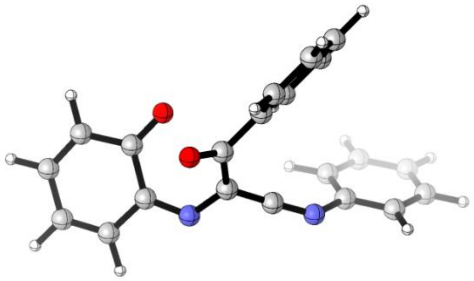
H	5.01587200	0.37806700	-2.15847200
C	5.60713800	-0.57058900	1.06366400
H	4.08661000	-1.25634400	2.43654200
H	6.88981400	0.15244600	-0.51504300
H	6.41417500	-0.67020000	1.78318900
O	-0.90085200	-1.03619000	1.23645000
C	-0.37194900	0.23197900	1.33873200
O	0.68851900	0.33807600	1.90857500
C	-1.09748900	1.39270100	0.74742600
C	-0.30475100	2.37287800	0.13129700
C	-2.48537100	1.57066700	0.82895300
C	-0.89777500	3.49964000	-0.43170600
H	0.76982800	2.23313100	0.09433900
C	-3.07166900	2.71301000	0.28343200
H	-3.10791500	0.83635300	1.32394900
C	-2.28326100	3.67082800	-0.35768600
H	-0.28062700	4.24403900	-0.92444500
H	-4.14569000	2.85078200	0.35726600
H	-2.74606100	4.55103200	-0.79331800
N	-1.14694400	-0.78842400	-1.76539600
N	2.54489400	-0.15515300	-1.77570500
H	2.24039800	-1.02097400	0.80811500

Electronic Energy = -1068.675300 Hartree

Thermal Correction to Free Energy = 0.242136 Hartree

Imaginary Freq= 0

INTγ-M



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C	-3.11369100	-0.09954000	-0.78868700
C	-2.85947700	-1.04803200	0.35962300
C	-3.89871700	-1.99863100	0.70671500
C	-5.11600000	-1.96614400	0.10668800
C	-5.39222500	-1.00688200	-0.93979000
H	-4.64330700	0.58172400	-2.16969000
H	-3.66484300	-2.70357700	1.49769600
H	-5.89581300	-2.65927600	0.40507800
H	-6.38130300	-1.00209300	-1.39022600
C	-0.70527800	-0.25369600	0.91134000
C	0.54244000	-0.69824900	1.17333800
C	2.71500700	-1.49666400	0.58694200
C	2.45849900	-1.93980000	-0.71816900
C	4.01357300	-1.50626200	1.10223000
C	3.51642900	-2.37997600	-1.50984200
C	5.06733100	-1.94201100	0.29839300
H	4.17923200	-1.16552000	2.11830700
C	4.82187900	-2.37869200	-1.00585800

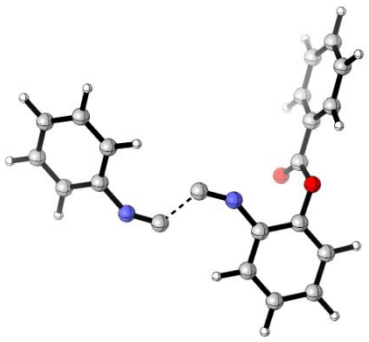
H	3.32257300	-2.72589000	-2.52033500
H	6.07851500	-1.94394800	0.69240700
H	5.64274500	-2.72244900	-1.62715700
O	-2.21368500	0.61200400	-1.25253500
C	-0.89266200	1.24742200	0.83395000
O	-1.87742400	1.75507800	1.34621000
C	0.21280100	2.05974100	0.25166400
C	0.41793400	3.35808800	0.74001700
C	1.03331000	1.56609100	-0.77168200
C	1.45176900	4.14114700	0.23108100
H	-0.23781300	3.73031100	1.51990600
C	2.06091300	2.35454300	-1.28752500
H	0.84131000	0.58394300	-1.18774600
C	2.27661600	3.63913300	-0.78130800
H	1.61629300	5.14097100	0.62091600
H	2.68682500	1.97005100	-2.08679200
H	3.08094000	4.25078500	-1.17909800
N	-1.72070100	-1.17522700	0.99048500
N	1.67704900	-1.03131900	1.42567200
H	1.44022000	-1.94420900	-1.09436500

Electronic Energy = -1068.679911 Hartree

Thermal Correction to Free Energy = 0.242071 Hartree

Imaginary Freq= 0

TS1-M



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C	4.04667300	-1.02006800	0.74287700
C	4.90742500	-2.10918200	0.86401500
C	6.12766100	-2.12613300	0.17956400
H	7.43657400	-1.05779200	-1.16233400
H	3.09200400	-0.98915800	1.25751500
H	4.62593000	-2.94681800	1.49478900
H	6.79404900	-2.97721400	0.27984700
C	2.46606800	1.58954200	0.00896700
C	1.08058400	0.68151600	0.68892800
C	-0.88460600	2.14556700	0.38989600
C	-0.36720800	3.44394100	0.31281300
C	-2.25498200	1.93322000	0.18681600
C	-1.21794300	4.51258900	0.03700100
C	-3.10396800	2.99665000	-0.09145000
C	-2.58404000	4.29099700	-0.16260700
H	-0.81511300	5.51869300	-0.01884000
H	-4.15842200	2.79859000	-0.24879100

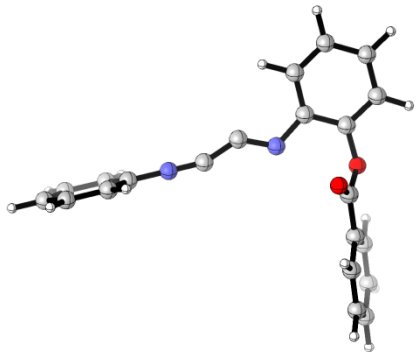
H	-3.24645300	5.12395500	-0.37480700
N	3.56710900	1.15626100	-0.20658500
N	-0.06416500	1.06154200	0.68191400
H	0.69680800	3.58921200	0.46497800
O	-2.78707800	0.65977700	0.32445800
C	-2.47740400	-0.27032600	-0.64271000
O	-1.88201800	0.01350900	-1.65684200
C	-2.97805600	-1.62011600	-0.28509100
C	-2.79686700	-2.65111700	-1.21795300
C	-3.60635100	-1.88455200	0.94021200
C	-3.24507700	-3.93775300	-0.92836600
H	-2.30398800	-2.42447800	-2.15689500
C	-4.05233900	-3.17464900	1.22538700
H	-3.73695800	-1.08412700	1.65830300
C	-3.87337500	-4.20069300	0.29321000
H	-3.10458600	-4.73496700	-1.65149600
H	-4.53724600	-3.38011600	2.17455200
H	-4.22175100	-5.20418800	0.51867000
H	5.90001800	0.90099800	-1.37913500

Electronic Energy = -1068.652636 Hartree

Thermal Correction to Free Energy = 0.236223 Hartree

Imaginary Freq= -465.90

TS_{Rot}-M



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C	4.48818600	0.15425800	-0.07552800
C	5.07941500	0.40003600	1.17956800
C	6.42365900	0.75678900	1.24346300
C	7.19298700	0.86336500	0.08058900
H	7.18742900	0.69371100	-2.07044600
H	4.47796200	0.31098100	2.07726700
H	6.87340800	0.94864900	2.21280200
H	8.24069100	1.13824400	0.14103500
C	2.02268800	-0.50061800	-0.19205000
C	0.92188800	-1.28264800	-0.12331200
C	-1.22728000	-2.14978500	-0.18115200
C	-0.86133600	-3.50251000	-0.06906500
C	-2.59751600	-1.82964500	-0.19388200
C	-1.83067400	-4.49538500	0.01573200
C	-3.57301000	-2.81557400	-0.10424000
C	-3.18894500	-4.15327900	-0.00293300
H	-1.53361200	-5.53642200	0.09499100

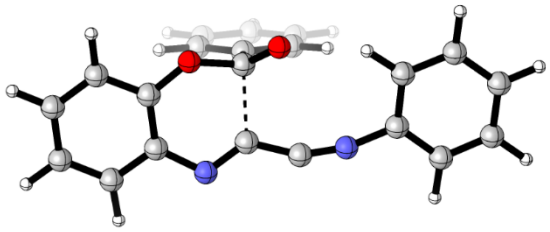
H	-4.61717700	-2.52312700	-0.11310600
H	-3.94749000	-4.92674200	0.06357900
N	3.17551400	-0.19161800	-0.14945500
N	-0.32430700	-1.08387000	-0.31212800
H	0.19646100	-3.74520900	-0.06064200
O	-3.00124800	-0.51482100	-0.36393600
C	-2.71666400	0.38192300	0.63858300
O	-2.33987600	0.04362300	1.73760100
C	-2.96705200	1.78017500	0.20852100
C	-2.84415400	2.79250600	1.17055400
C	-3.30291300	2.10587400	-1.11295200
C	-3.06120600	4.12160200	0.81424100
H	-2.57778800	2.51771800	2.18520600
C	-3.51771900	3.43808500	-1.46514700
H	-3.38709800	1.31826800	-1.85181400
C	-3.39843300	4.44575100	-0.50387400
H	-2.96689900	4.90422700	1.56055000
H	-3.77537200	3.69053900	-2.48901200
H	-3.56630400	5.48212600	-0.78144800
H	4.78674500	0.07812800	-2.21177400

Electronic Energy = -1068.663300 Hartree

Thermal Correction to Free Energy = 0.239361 Hartree

Imaginary Freq= -89.42

$TS_{Acylshift}$-M



C	-4.09432800	-0.66575600	1.31365400
C	-2.82551800	-0.76962100	0.72723000
C	-2.71327400	-1.24608500	-0.60519100
C	-3.88242000	-1.56254000	-1.32502100
C	-5.13612000	-1.41246200	-0.75264500
C	-5.23451300	-0.97352200	0.57837600
H	-4.15519100	-0.32673500	2.34220700
H	-3.75899000	-1.93220300	-2.33777200
H	-6.03018300	-1.64853500	-1.31956200
H	-6.21017400	-0.87100300	1.04380100
C	-0.43959000	-1.06457000	-0.62707000
C	0.89044300	-1.25688300	-0.93084900
C	3.34365000	-0.91843400	-0.37466800
C	3.54268800	-0.48624100	0.94873400
C	4.41822500	-1.10735700	-1.25699200
C	4.84599400	-0.24504000	1.37713100
C	5.71058000	-0.85111400	-0.80776700
H	4.22689900	-1.44559600	-2.26933600
C	5.92640800	-0.42234400	0.50664600
H	5.01611900	0.08540500	2.39675900
H	6.54995400	-0.98946900	-1.48131600

H	6.93705800	-0.22805500	0.85153000
O	-1.76266900	-0.48102300	1.50929200
C	-0.46485700	0.00319500	1.00918700
O	0.49319600	-0.28740700	1.73465400
C	-0.55979600	1.37418500	0.36825900
C	0.65449900	2.00143500	0.04623300
C	-1.76081700	2.03322400	0.07721000
C	0.66785300	3.24604900	-0.57905100
H	1.58340600	1.51031700	0.31089900
C	-1.74532100	3.28500900	-0.54336900
H	-2.71153100	1.59098500	0.34345600
C	-0.53503500	3.89172900	-0.88223400
H	1.61602500	3.71761400	-0.82020600
H	-2.68455200	3.78694200	-0.75592300
H	-0.52749000	4.86374800	-1.36610700
N	-1.49217700	-1.51110100	-1.20658400
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H	2.67592100	-0.35508900	1.58961400

Electronic Energy = -1068.653984 Hartree

Thermal Correction to Free Energy = 0.244205 Hartree

Imaginary Freq= -285.11

9. ^{1}H-NMR and ^{13}C-NMR of unknown compounds

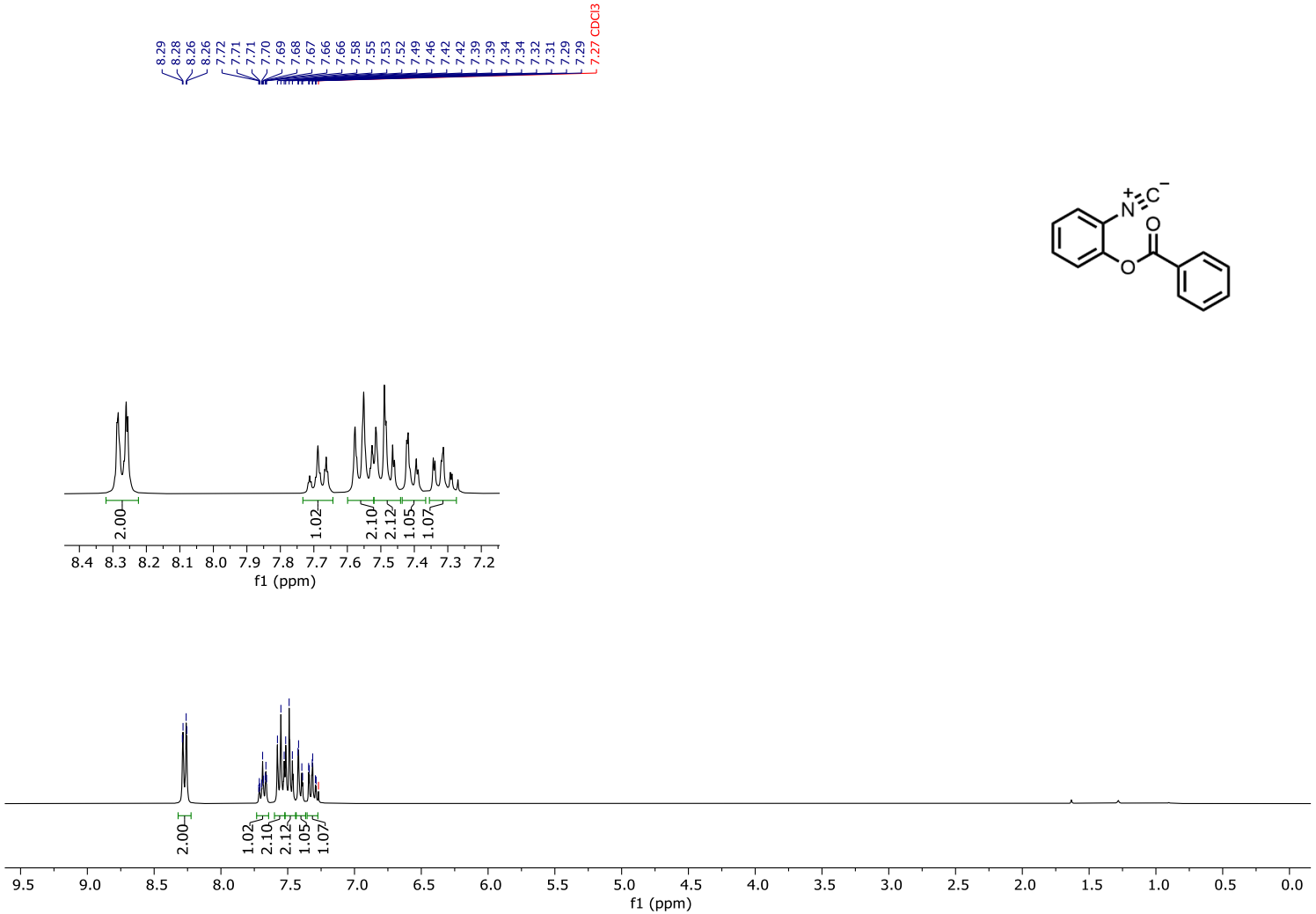

Figure S3. ^{1}H NMR (300 MHz, $CDCl_3$) 2-isocyanophenyl benzoate (1a).

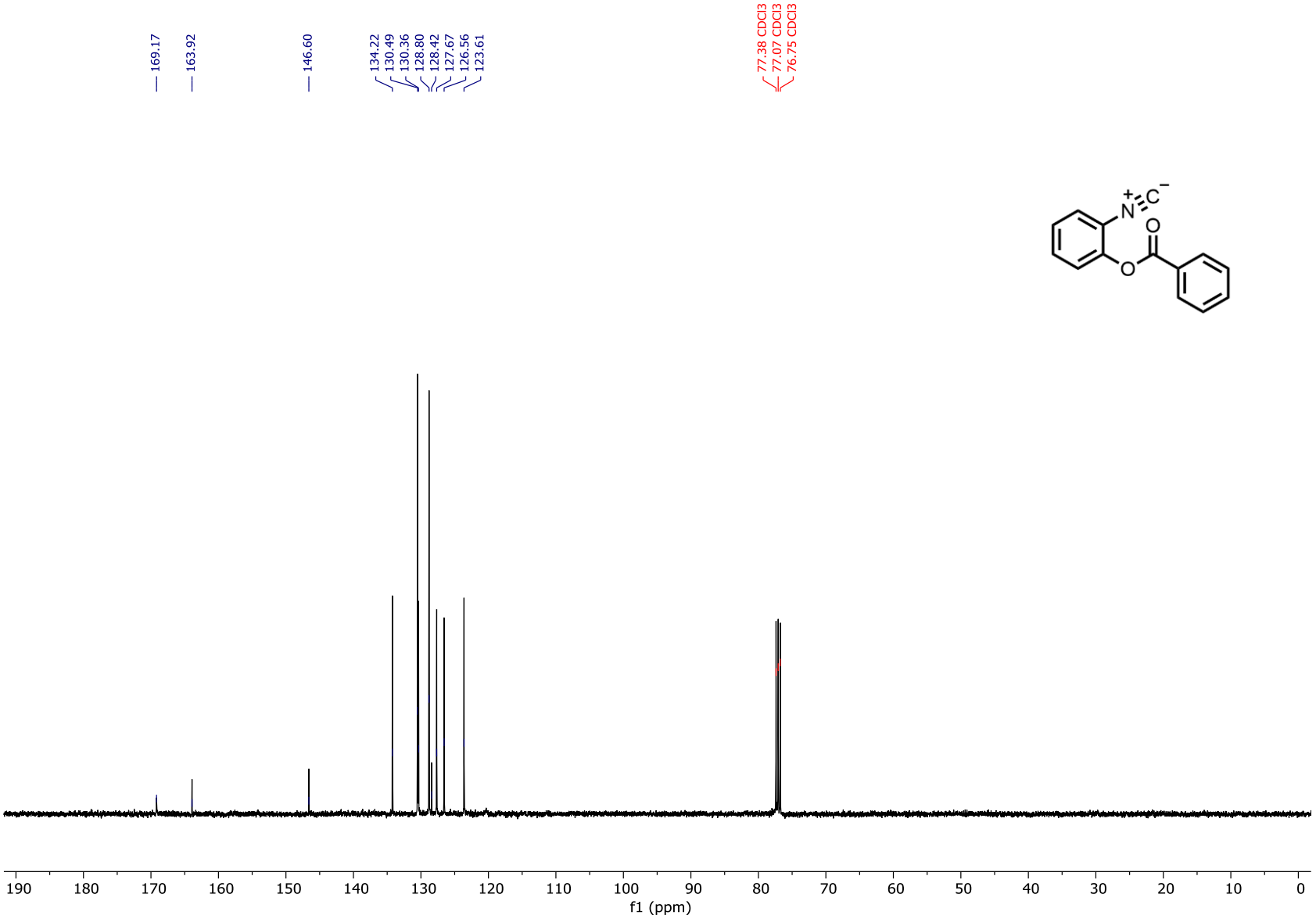

Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$) 2-isocyanophenyl benzoate (1a).

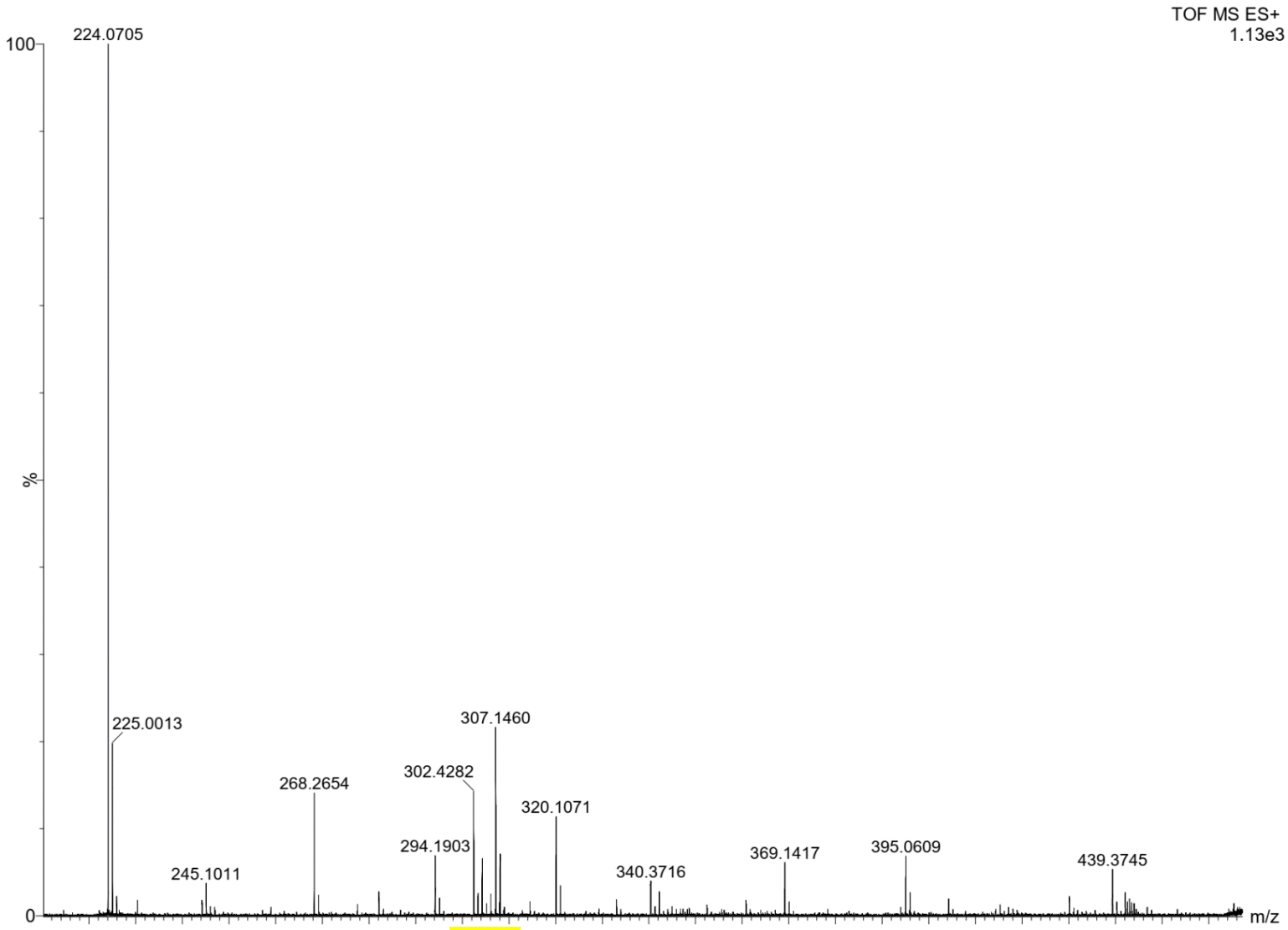

Figure S5. HRMS-ESI 2-isocyanophenyl benzoate (1a).

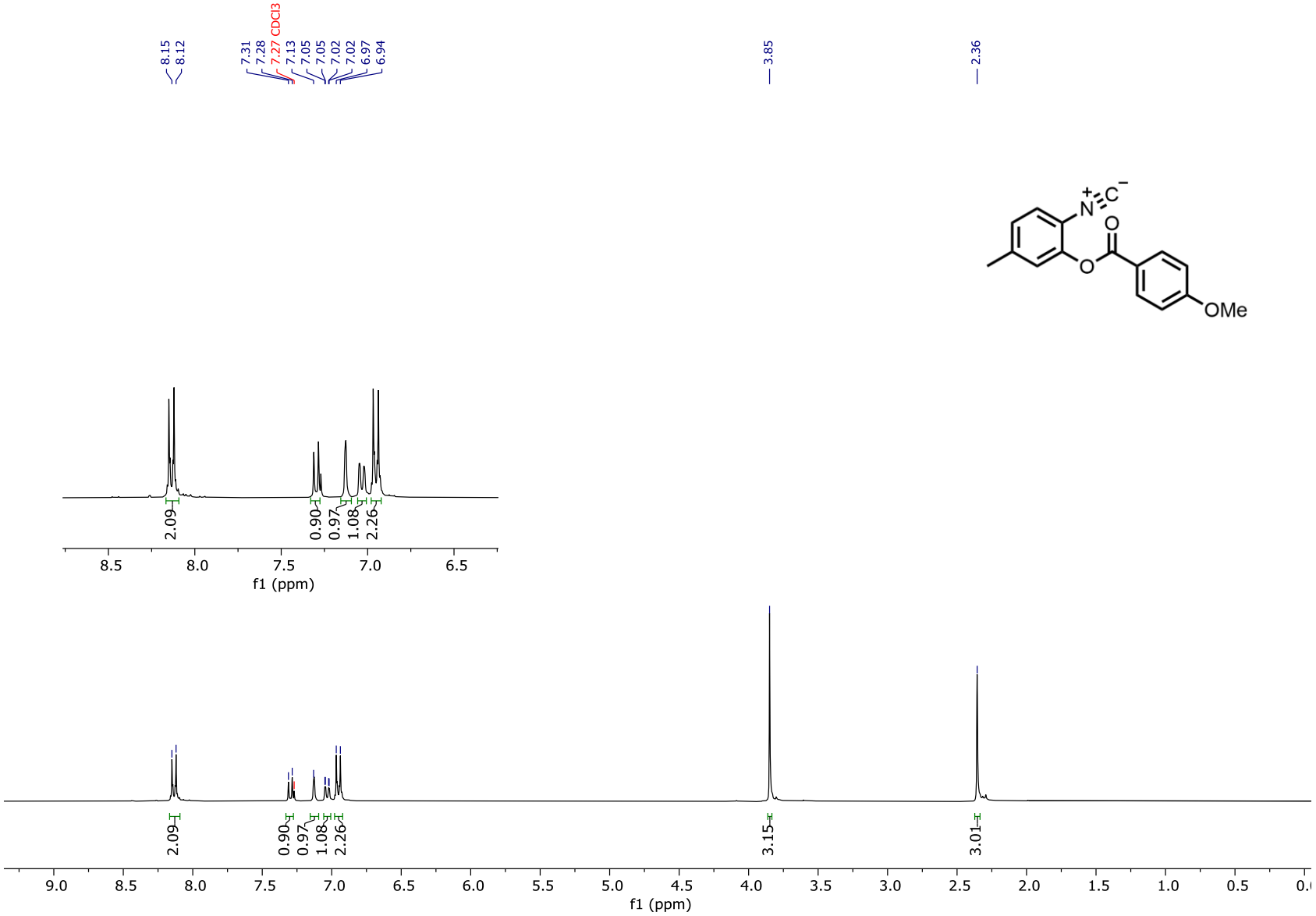

Figure S6. ^{1}H NMR (300 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 4-methoxybenzoate (1b).

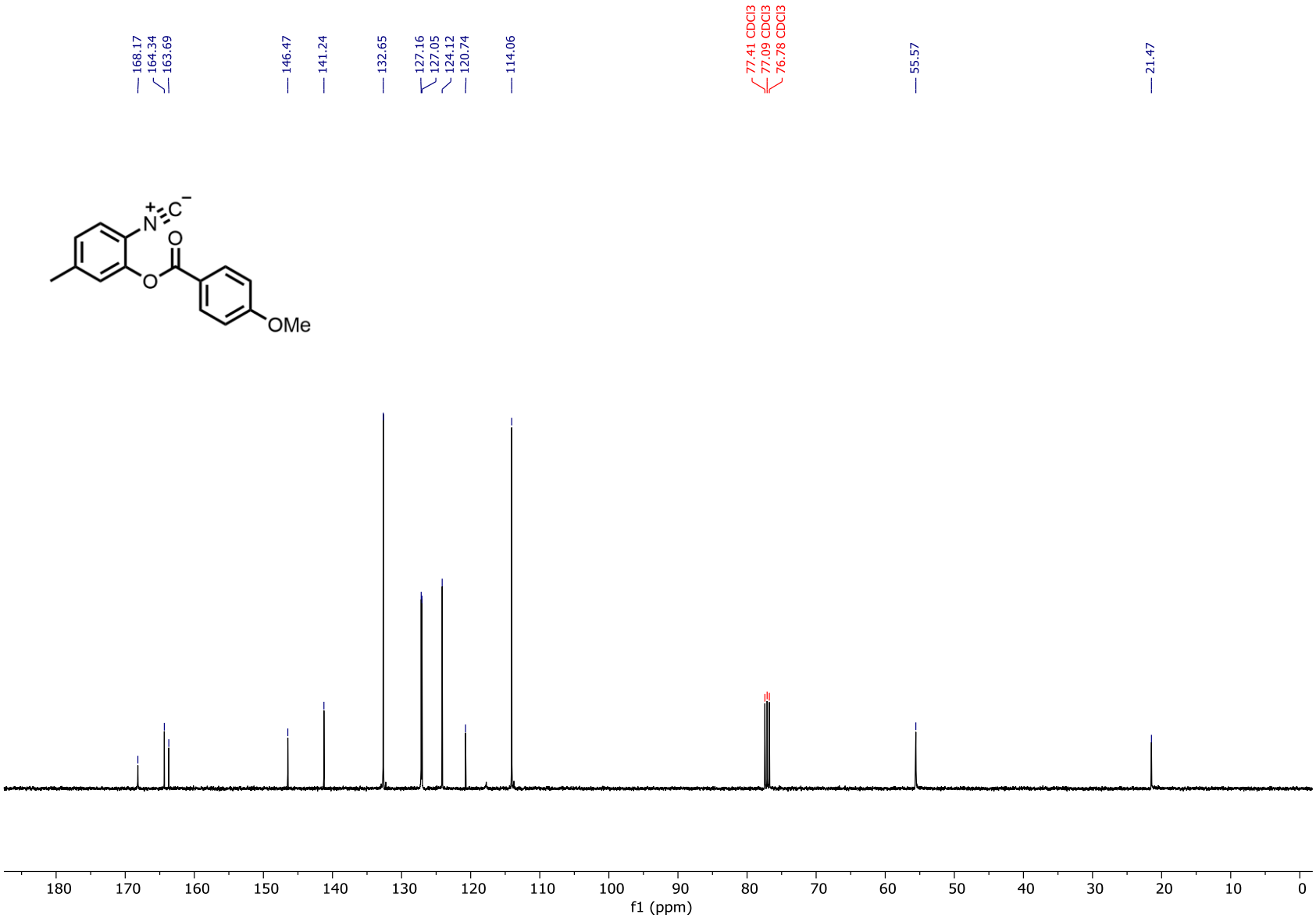

Figure S7. ^{13}C NMR (101 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 4-methoxybenzoate (1b).

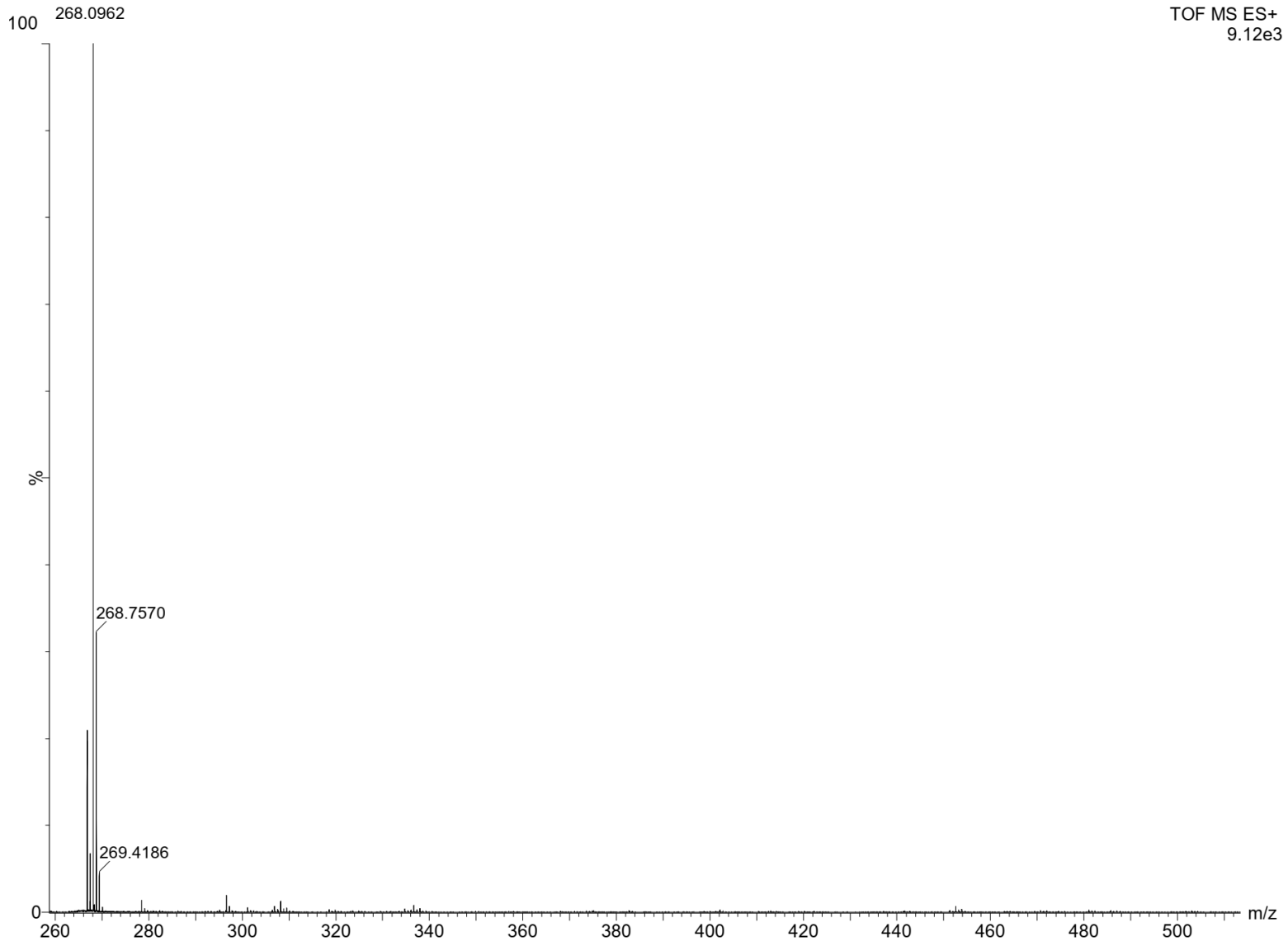

Figure S8. HRMS-ESI 2-isocyano-5-methylphenyl 4-methoxybenzoate (1b).

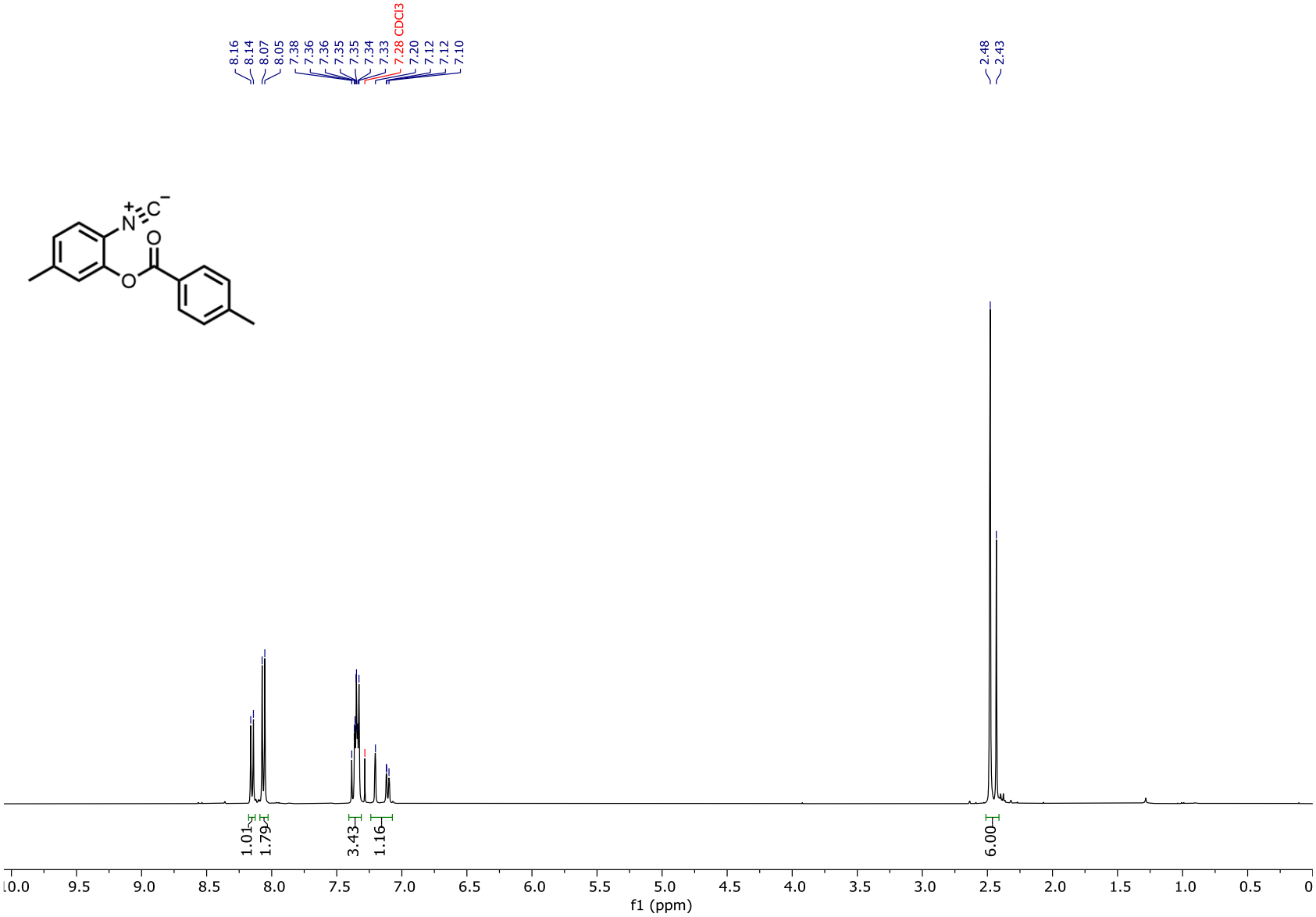

Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 4-methylbenzoate (1c).

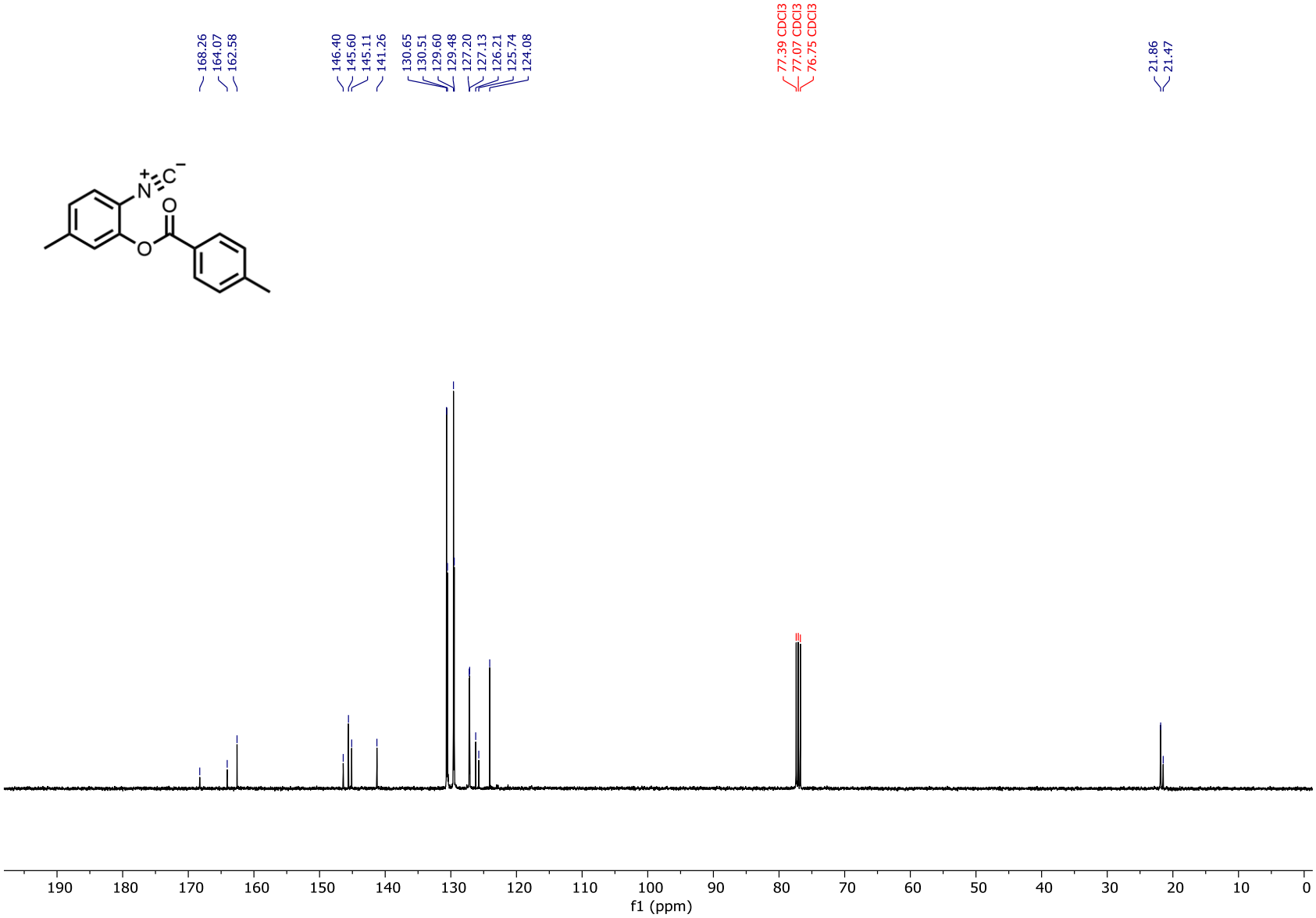

Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 4-methylbenzoate (1c).

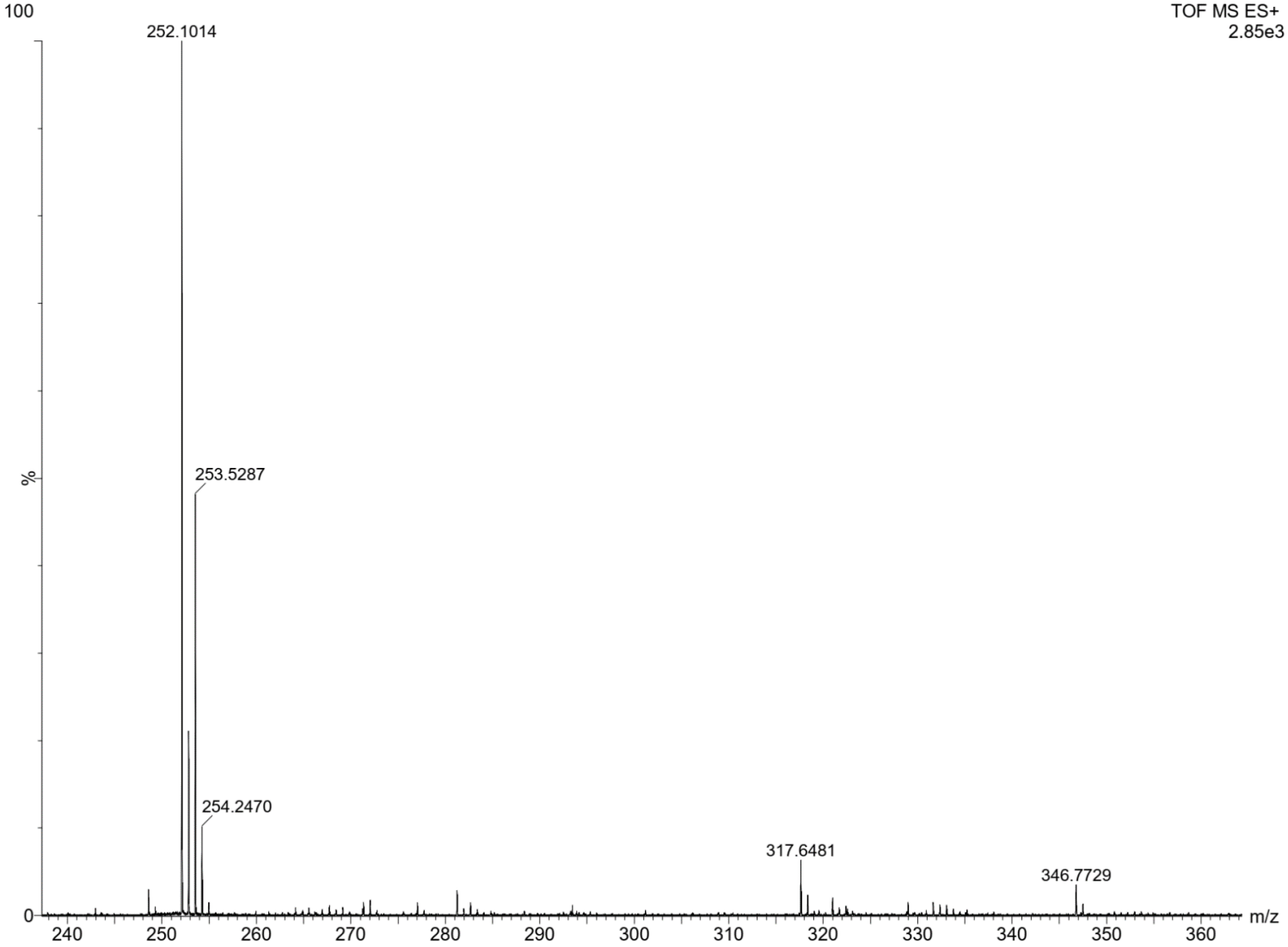

Figure S11. HRMS-ESI 2-isocyano-5-methylphenyl 4-methylbenzoate (1c).

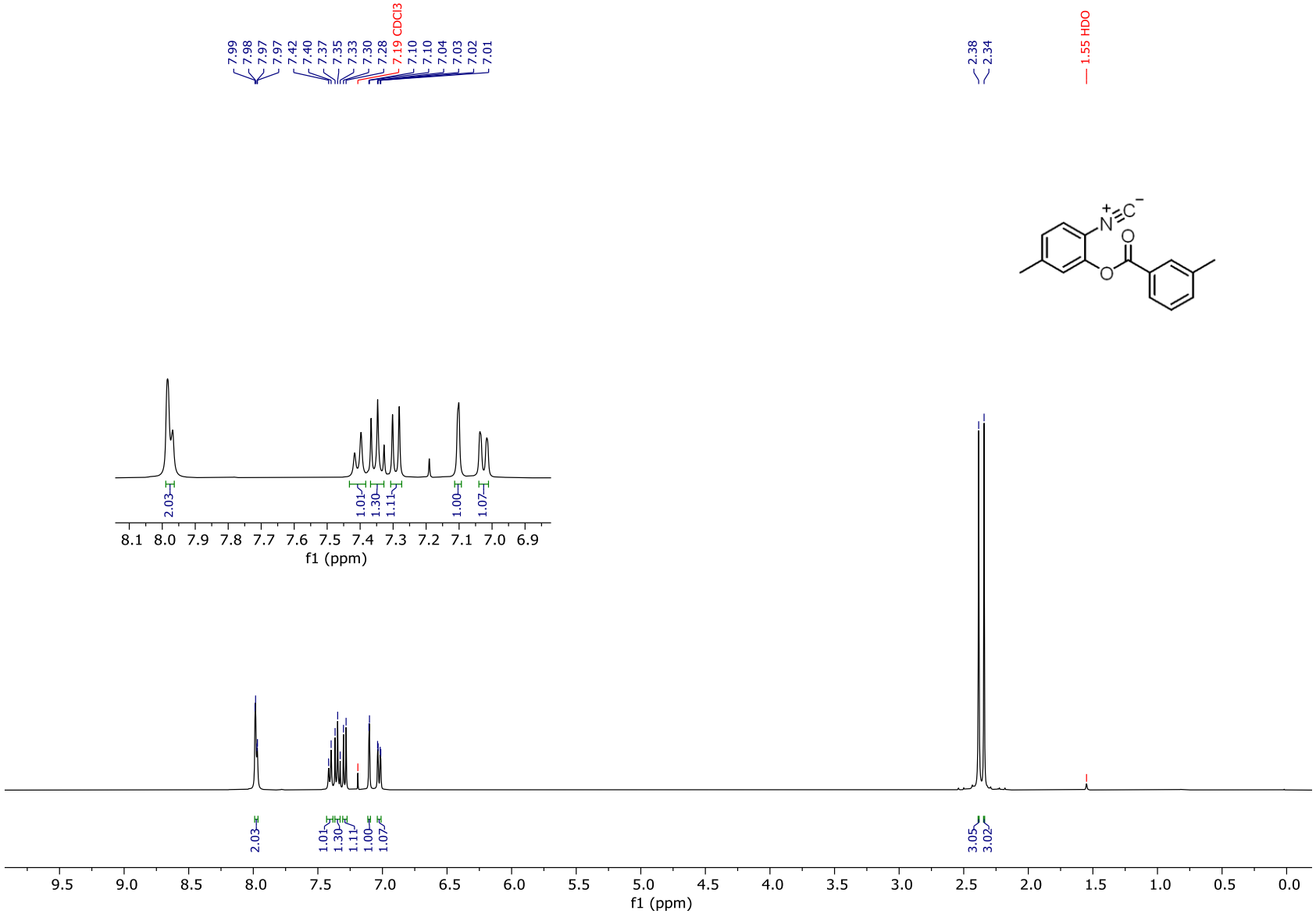

Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 3-methylbenzoate (1d).

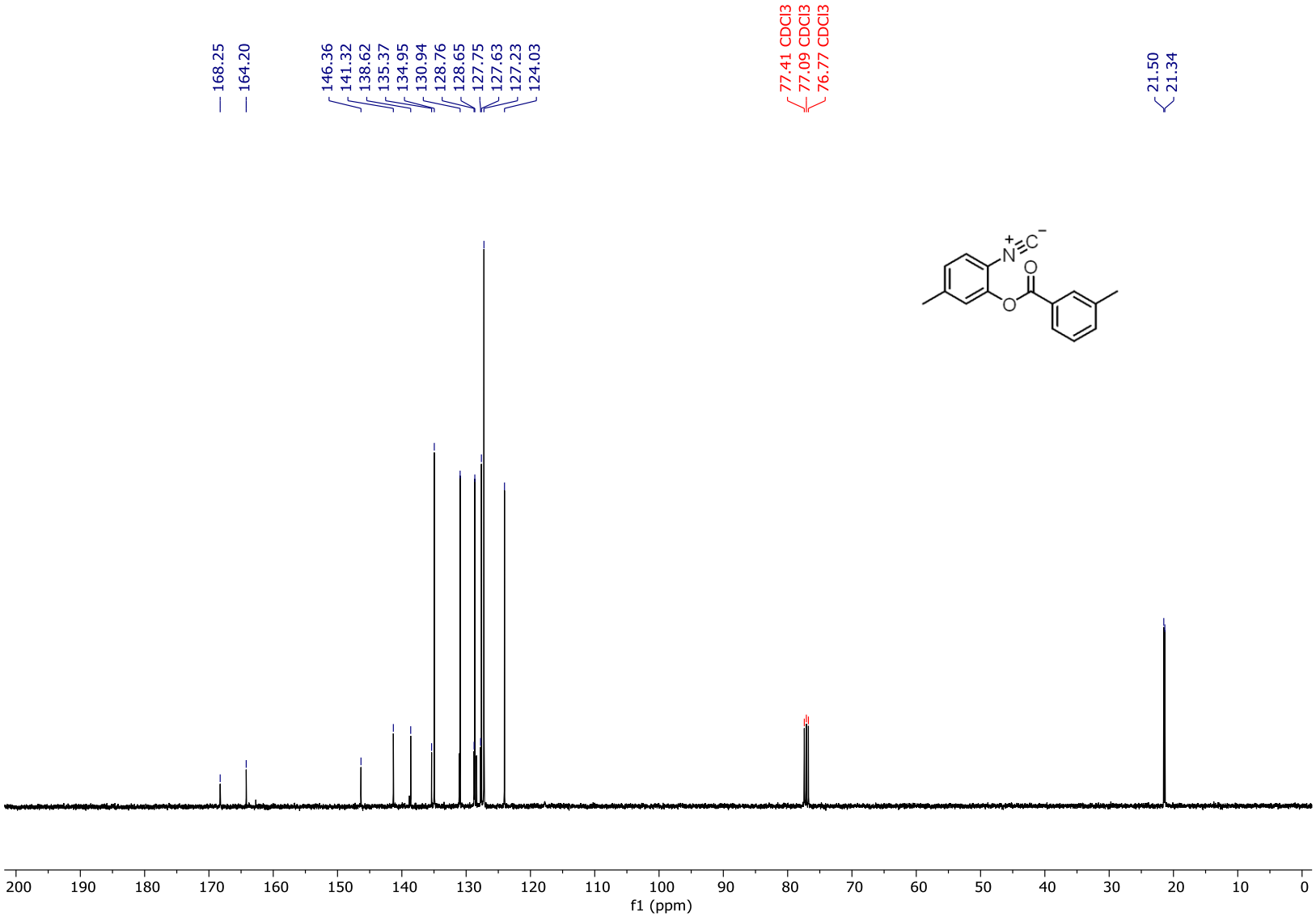

Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl 3-methylbenzoate (1d).

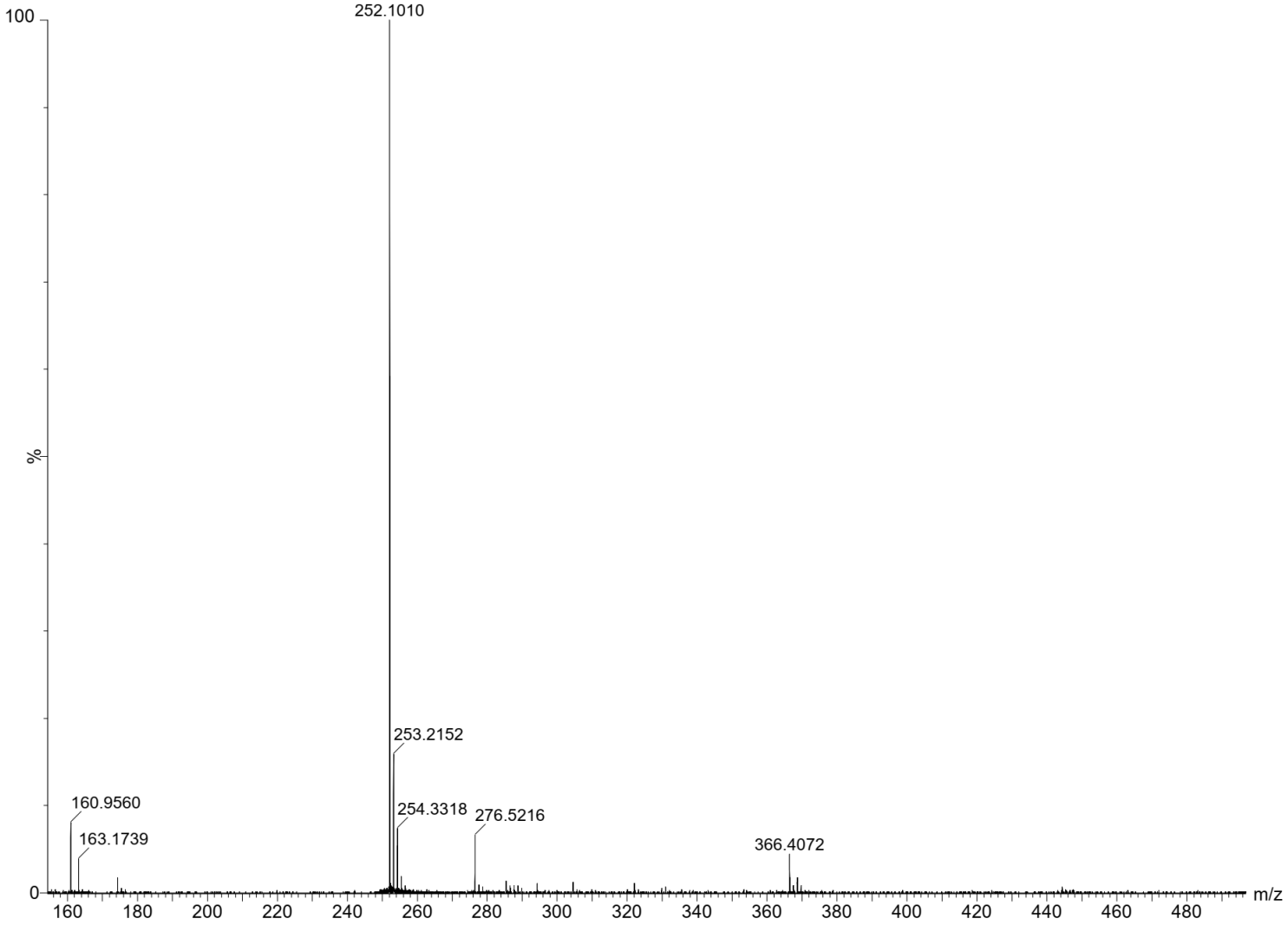

Figure S14. HRMS-ESI 2-isocyano-5-methylphenyl 4-methylbenzoate (1d).

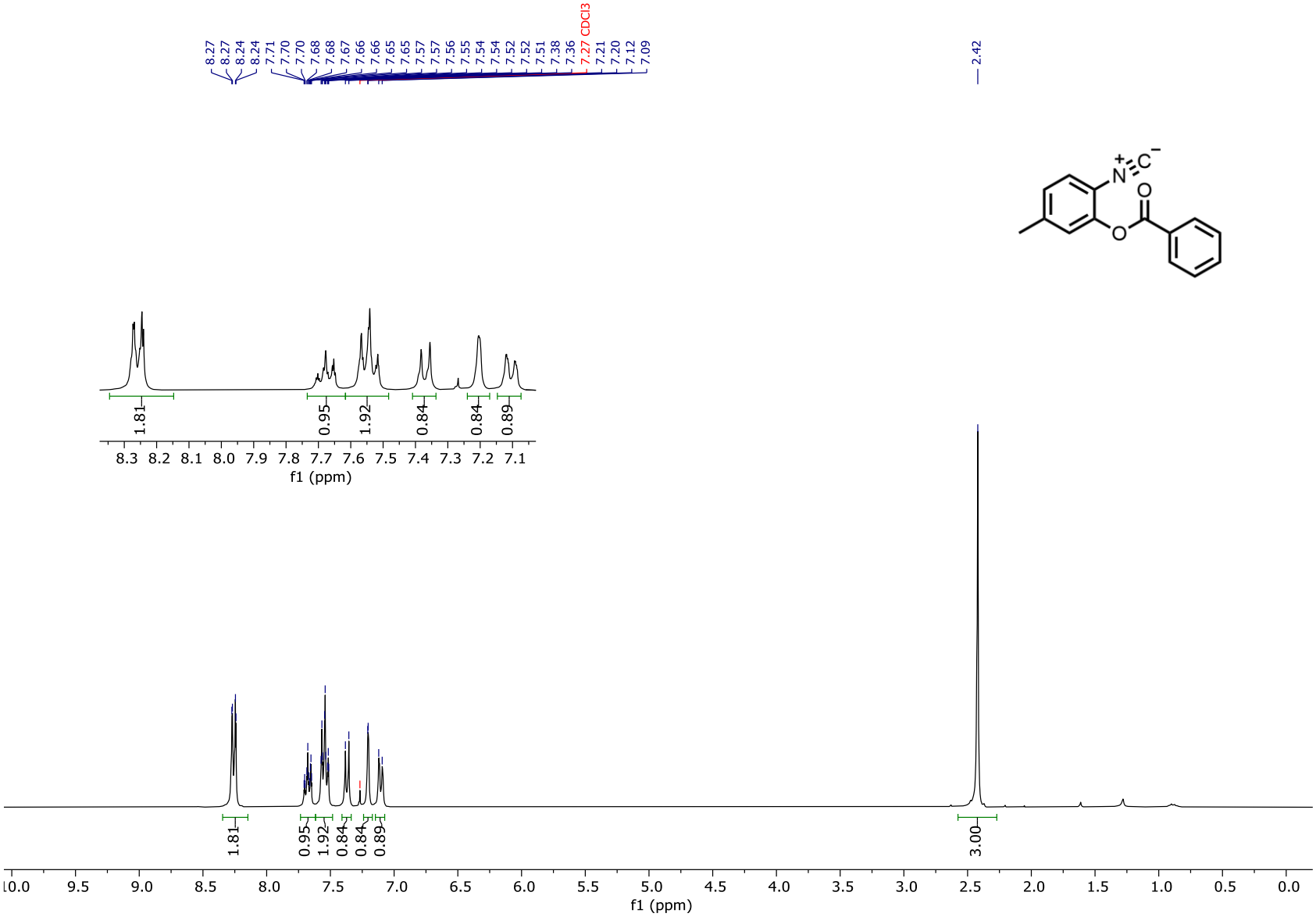

Figure S15. ^{1}H NMR (300 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl benzoate (1e).

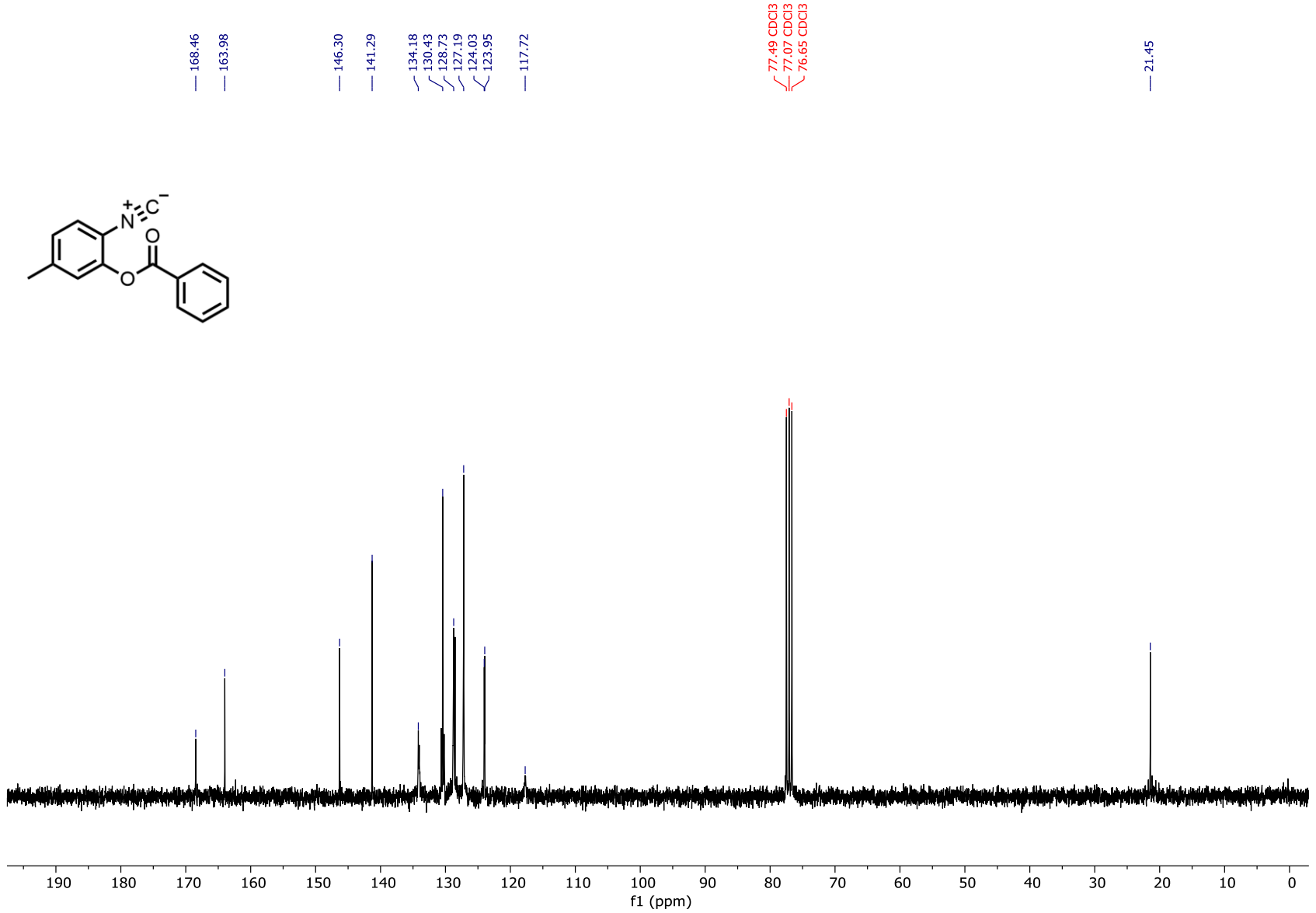

Figure S16. ^{13}C NMR (75 MHz, $CDCl_3$) 2-isocyano-5-methylphenyl benzoate (1e)..

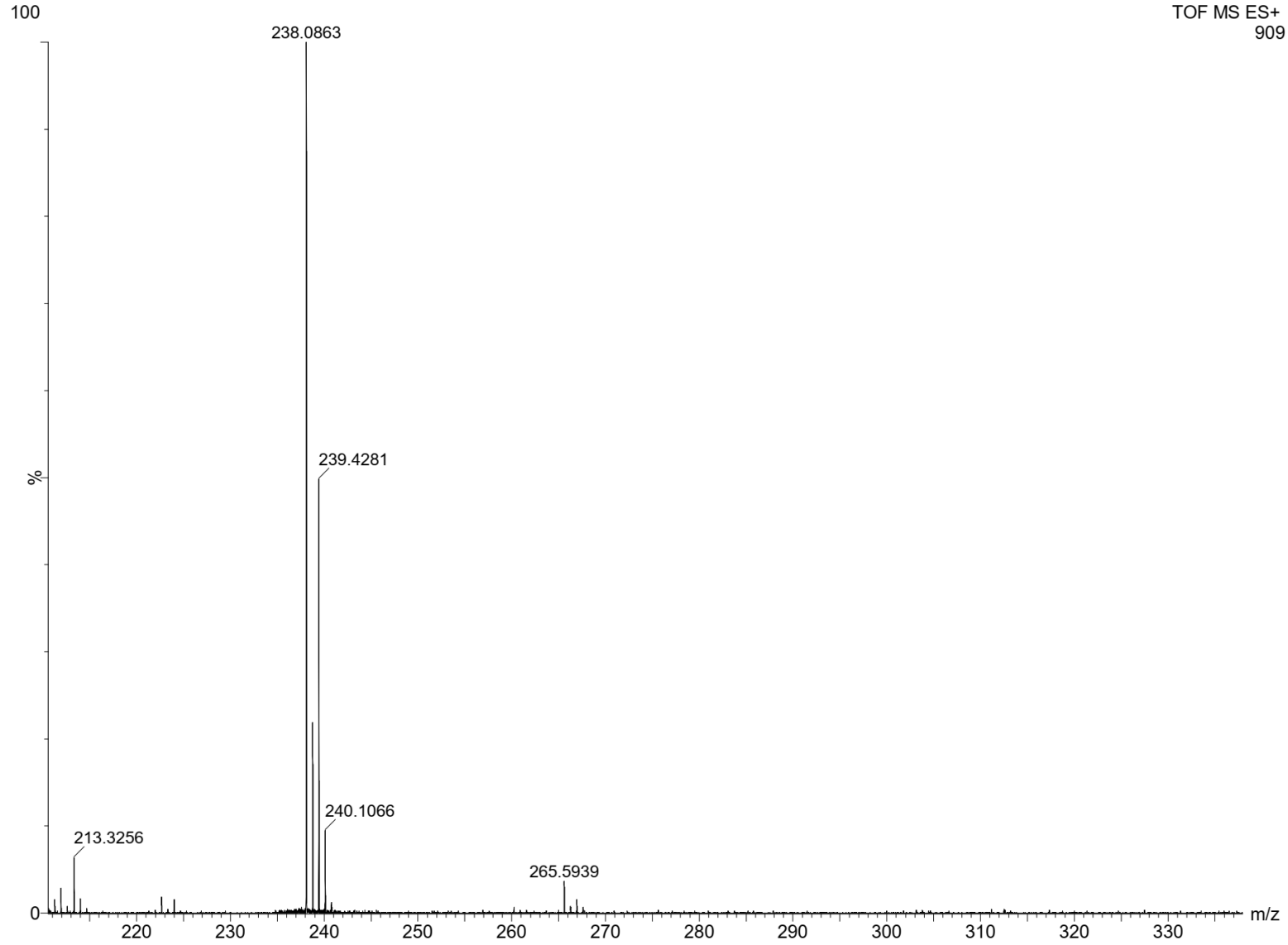

Figure S17. HRMS-ESI 2-isocyano-5-methylphenyl benzoate (1e).

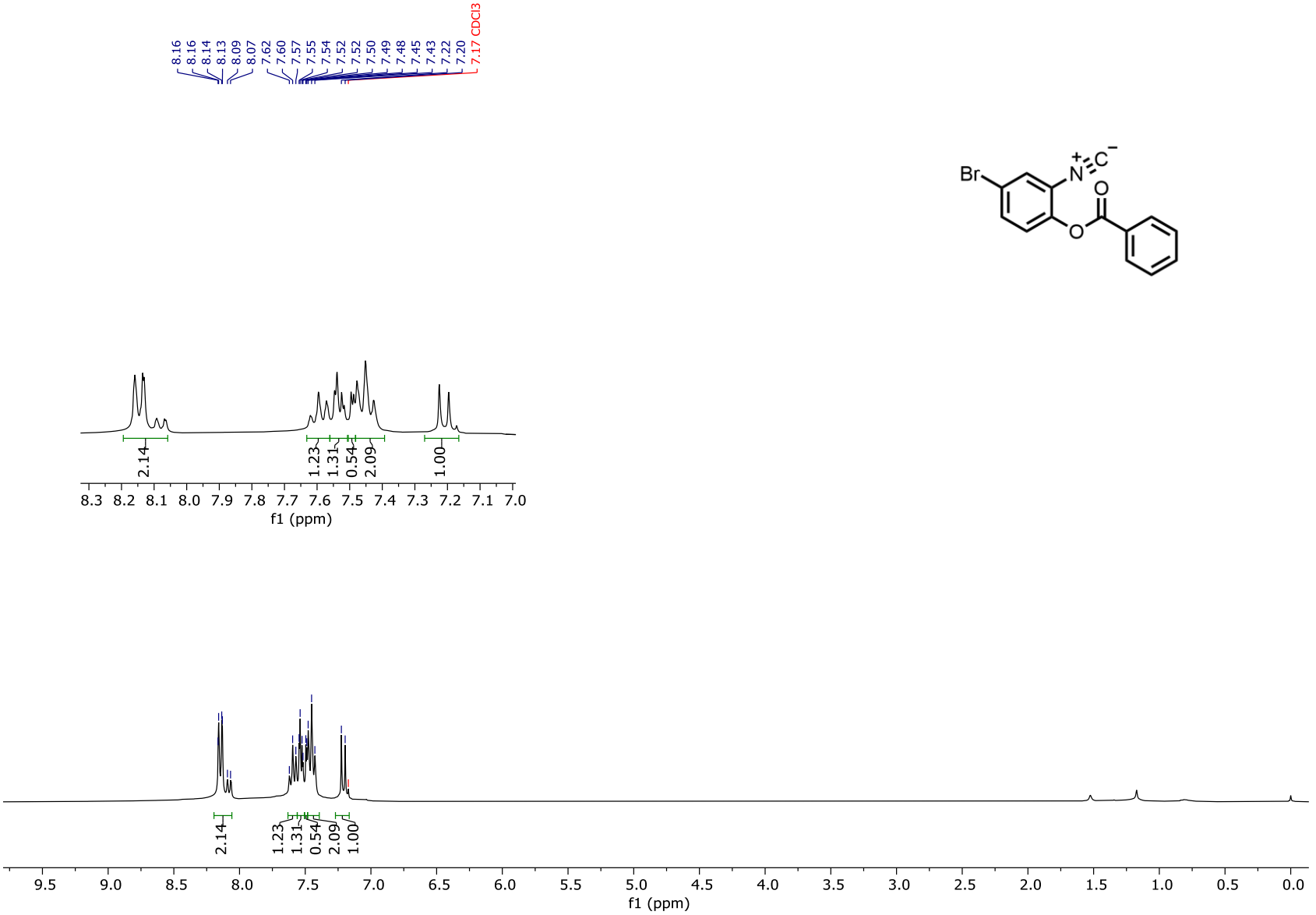

Figure S18. ^{1}H NMR (300 MHz, $CDCl_3$) 4-bromo-2-isocyanophenyl benzoate (1f).

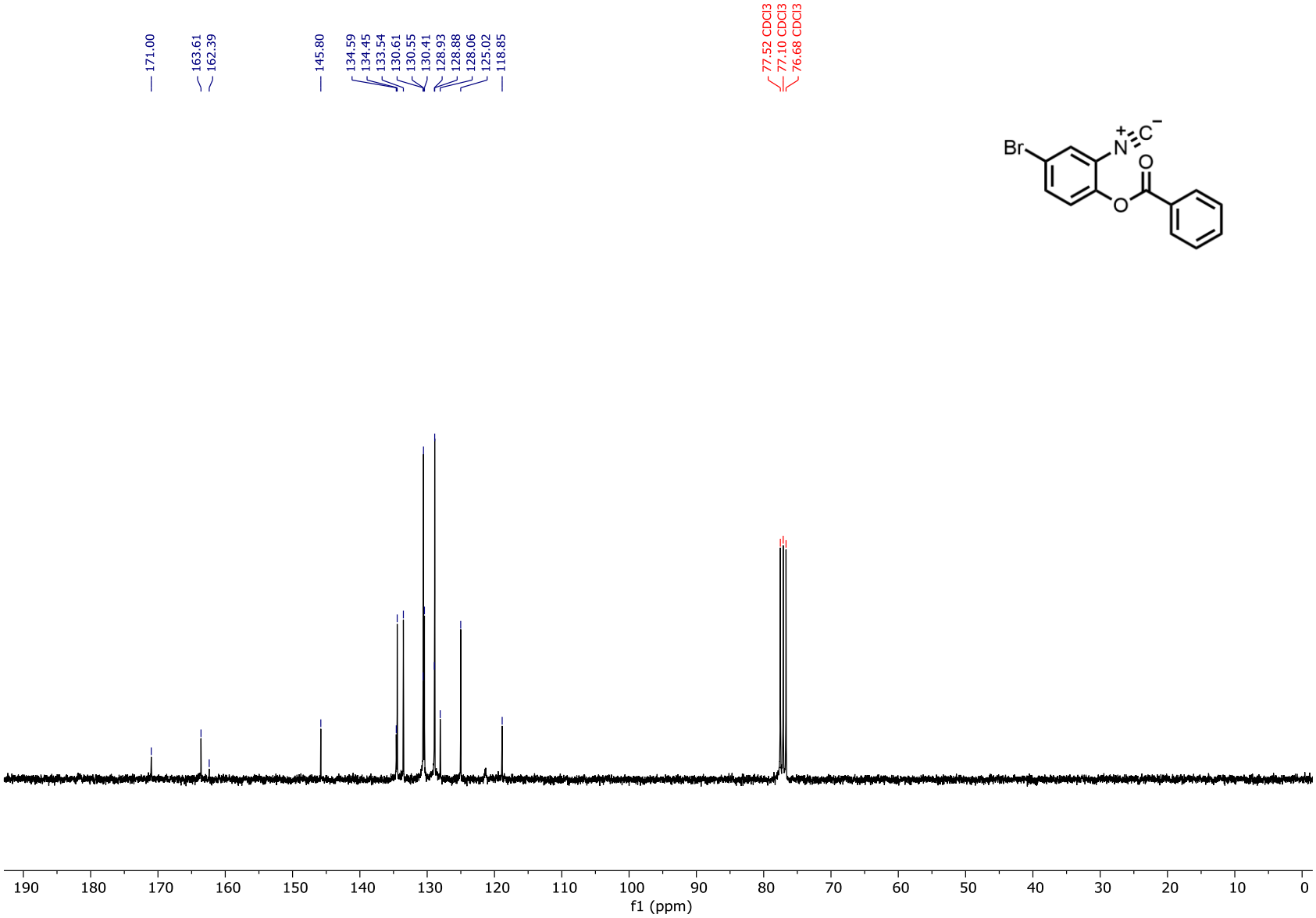

Figure S19. ^{13}C NMR (75 MHz, $CDCl_3$) 4-bromo-2-isocyanophenyl benzoate (1f).

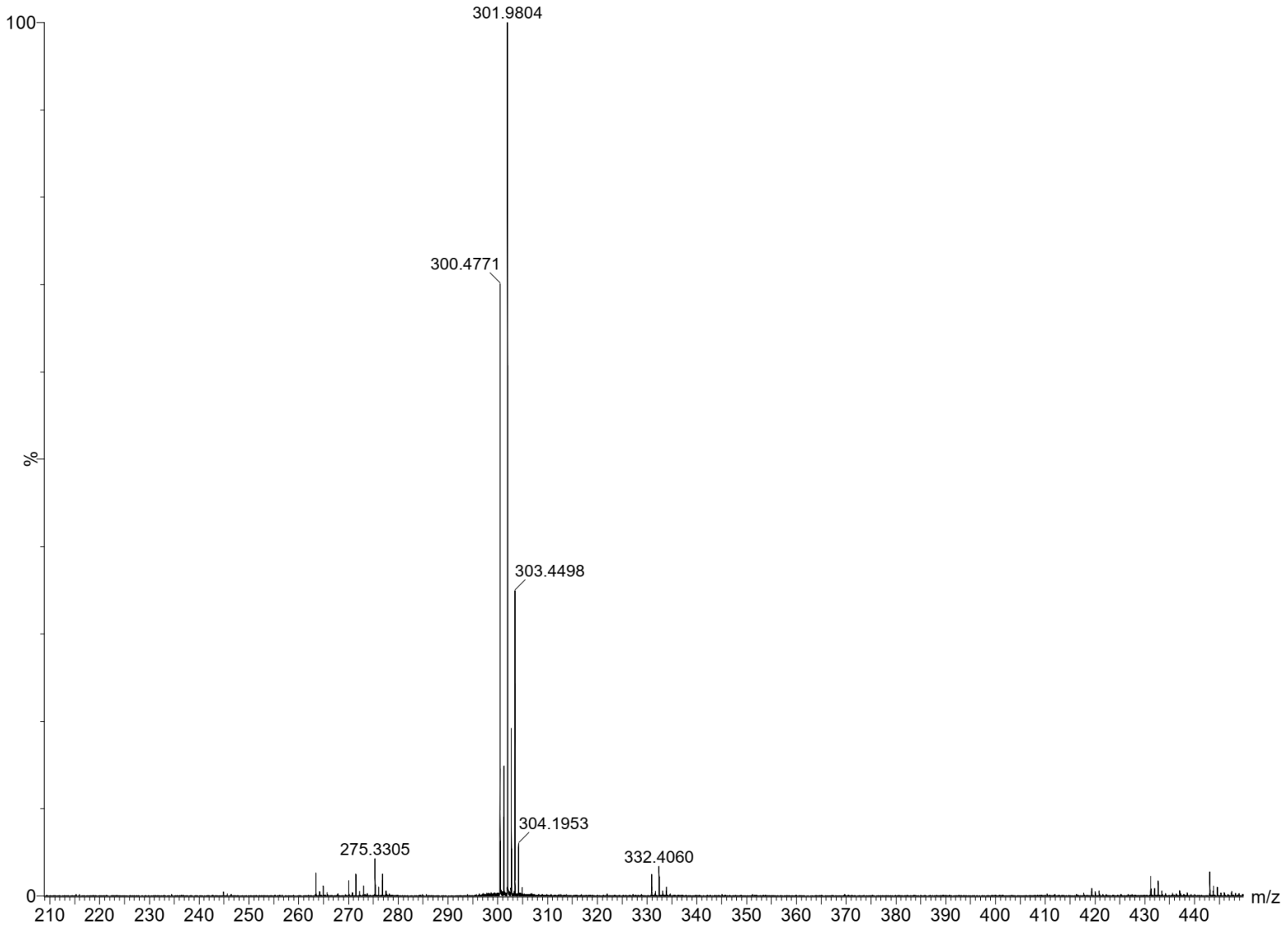

Figure S20. HRMS-ESI 4-bromo-2-isocyanophenyl benzoate (1f).

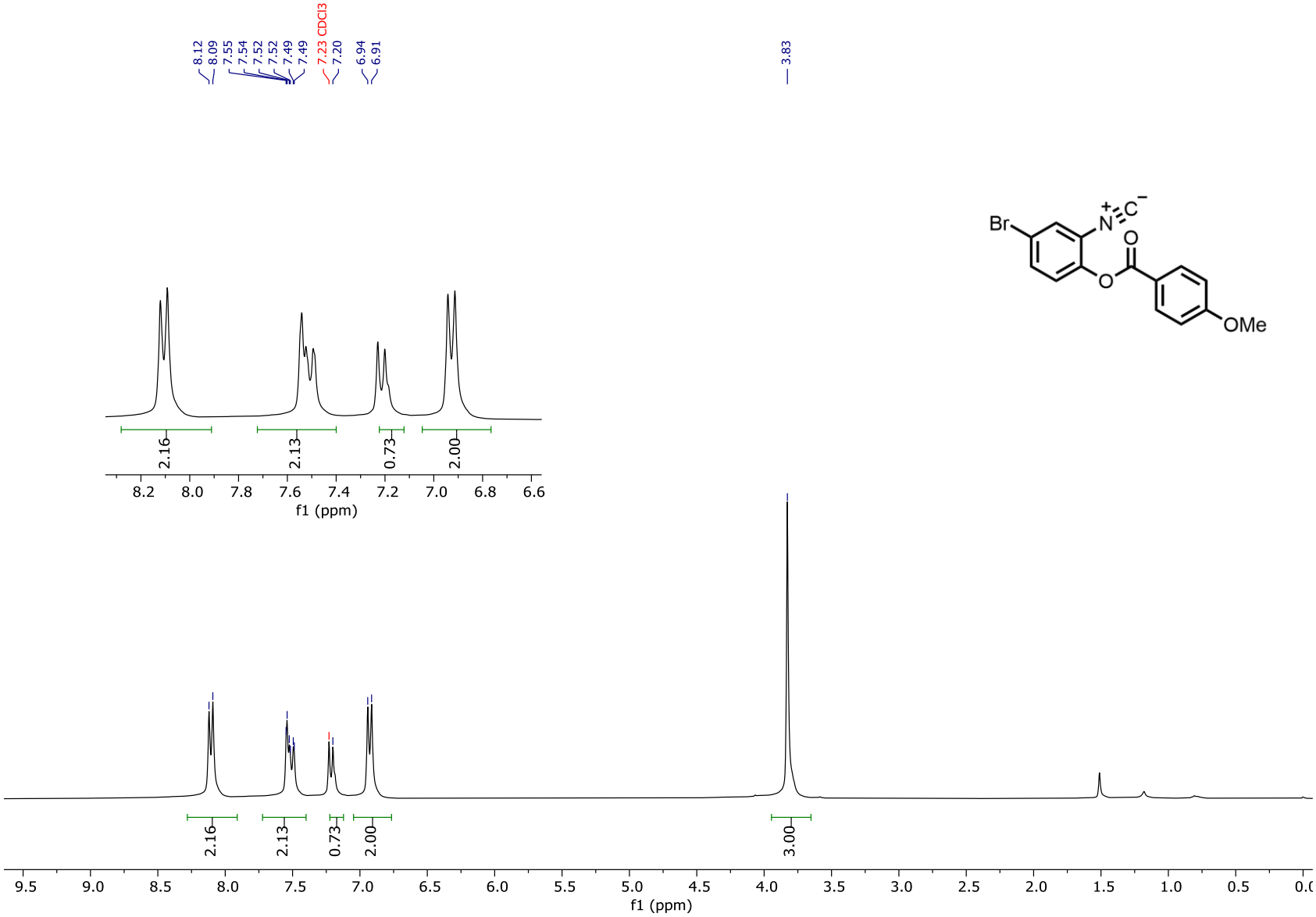

Figure S21. ^{1}H NMR (300 MHz, $CDCl_3$) 4-bromo-2-isocyanophenyl 4-methoxybenzoate (1g).

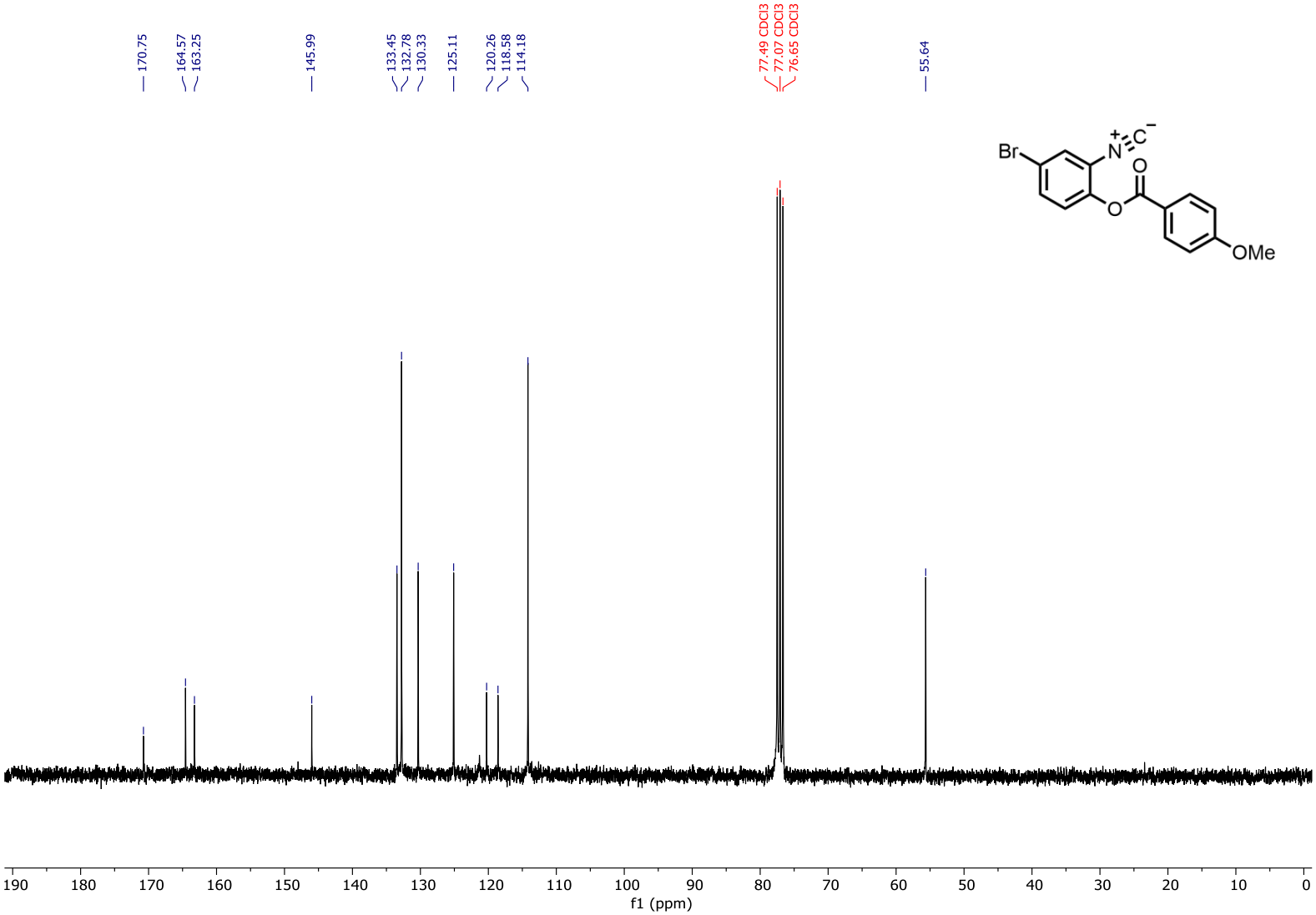

Figure S22. ^{13}C NMR (75 MHz, $CDCl_3$) 4-bromo-2-isocyanophenyl 4-methoxybenzoate (1g).

Figure S23. HRMS-ESI 4-bromo-2-isocyanophenyl 4-methoxybenzoate (1g).

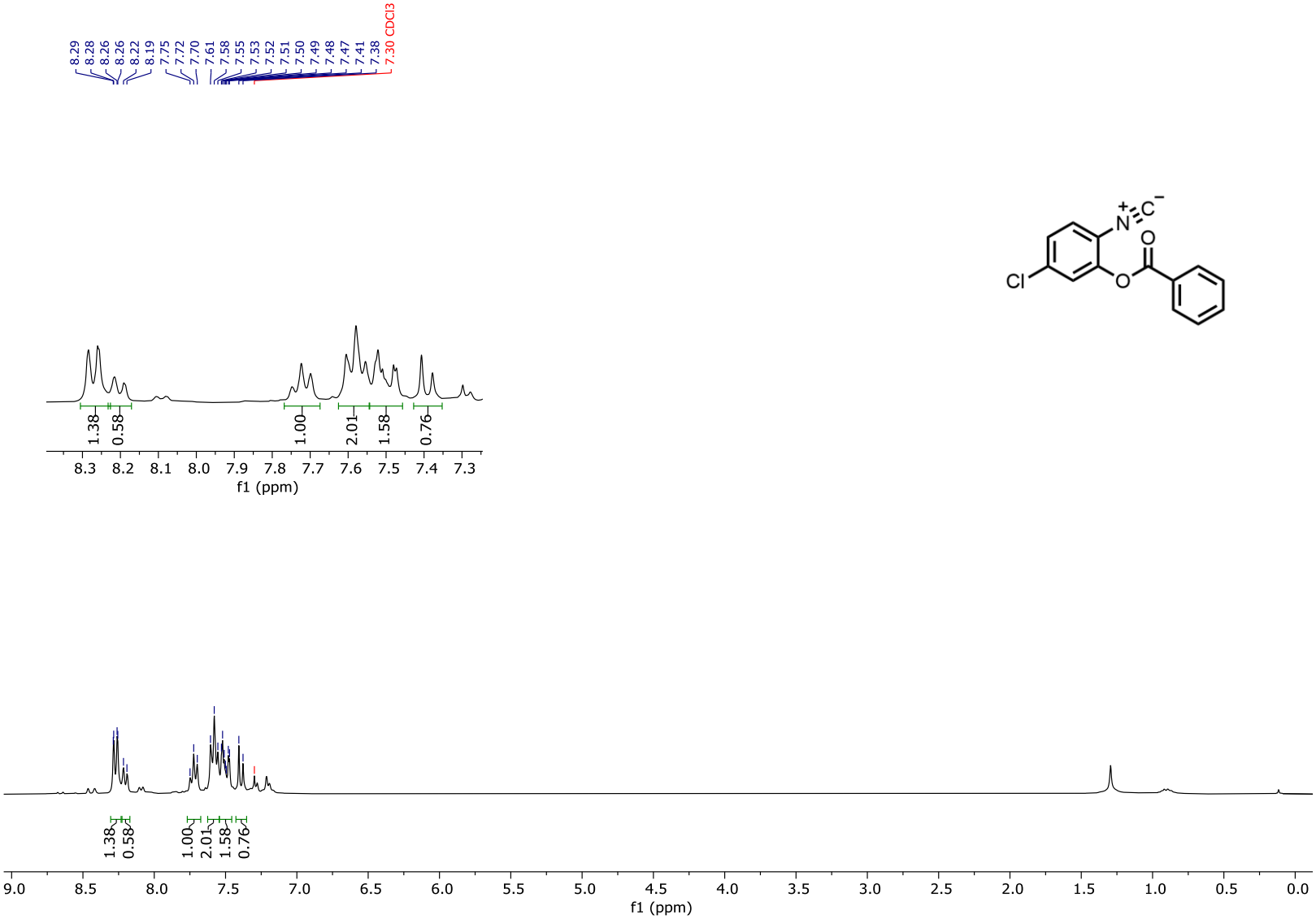

Figure S24. ^{1}H NMR (300 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl benzoate (1h).

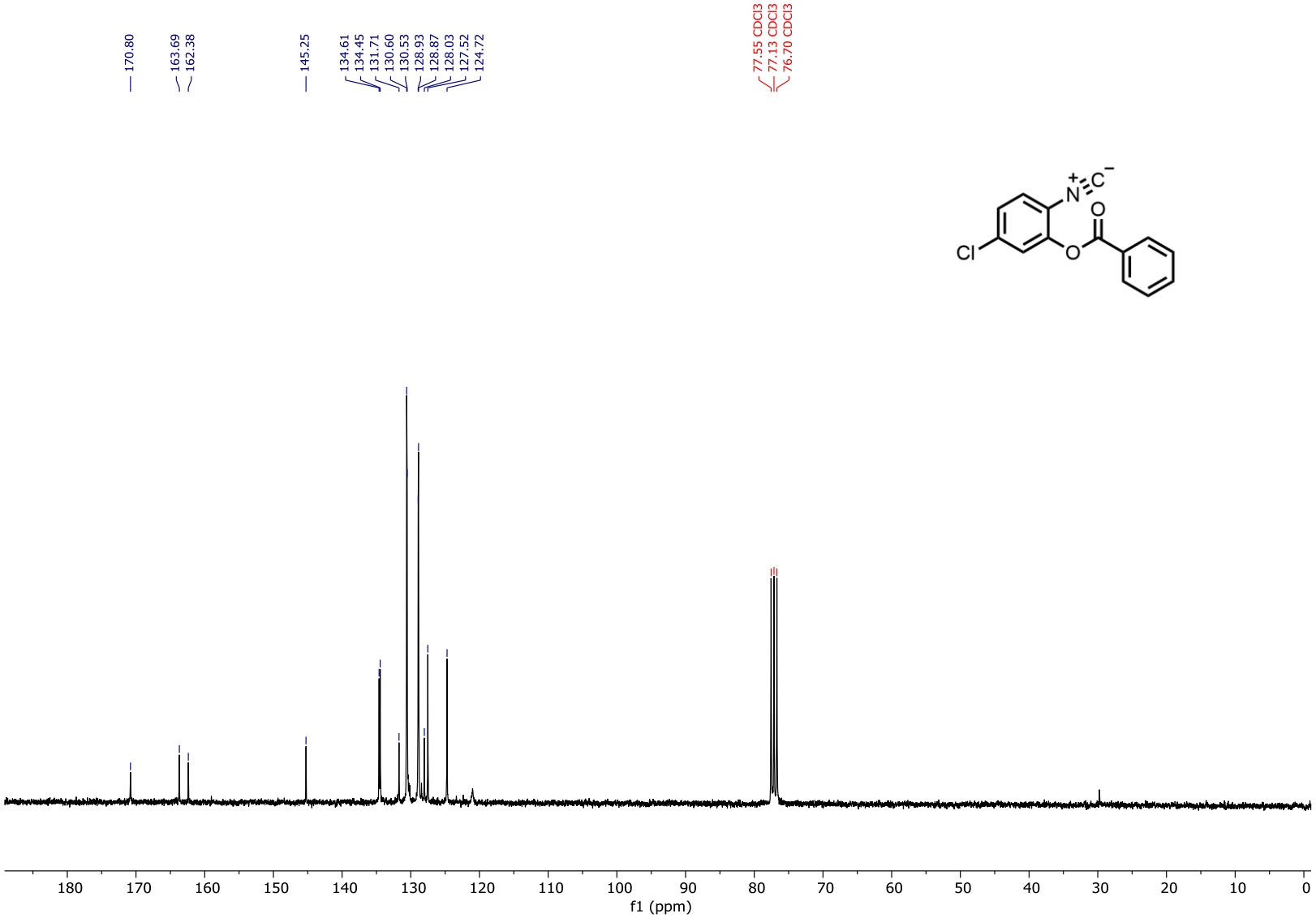

Figure S25. ^{13}C NMR (75 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl benzoate (1h).

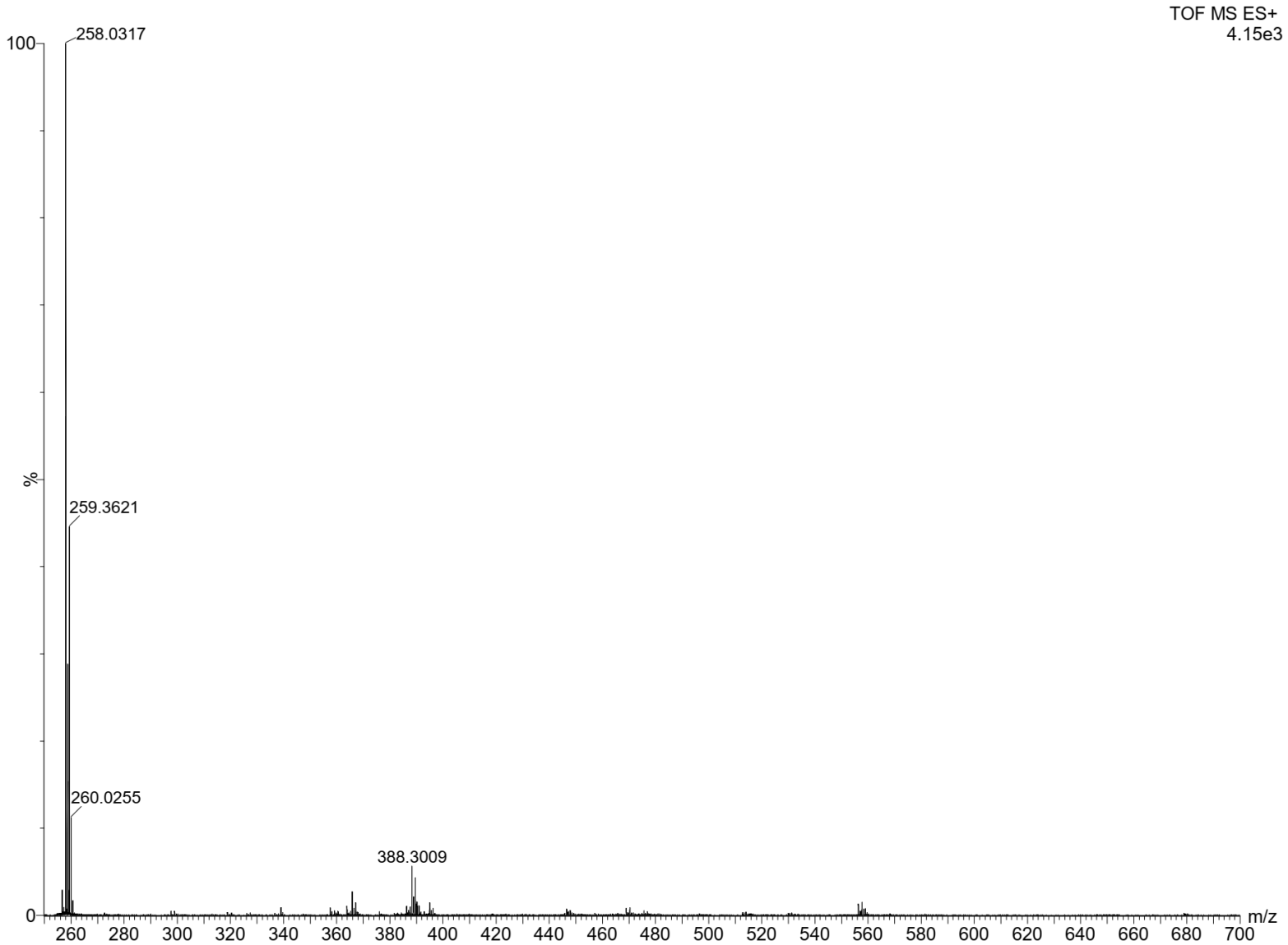

Figure S26. HRMS-ESI 5-chloro-2-isocyanophenyl benzoate (1h).

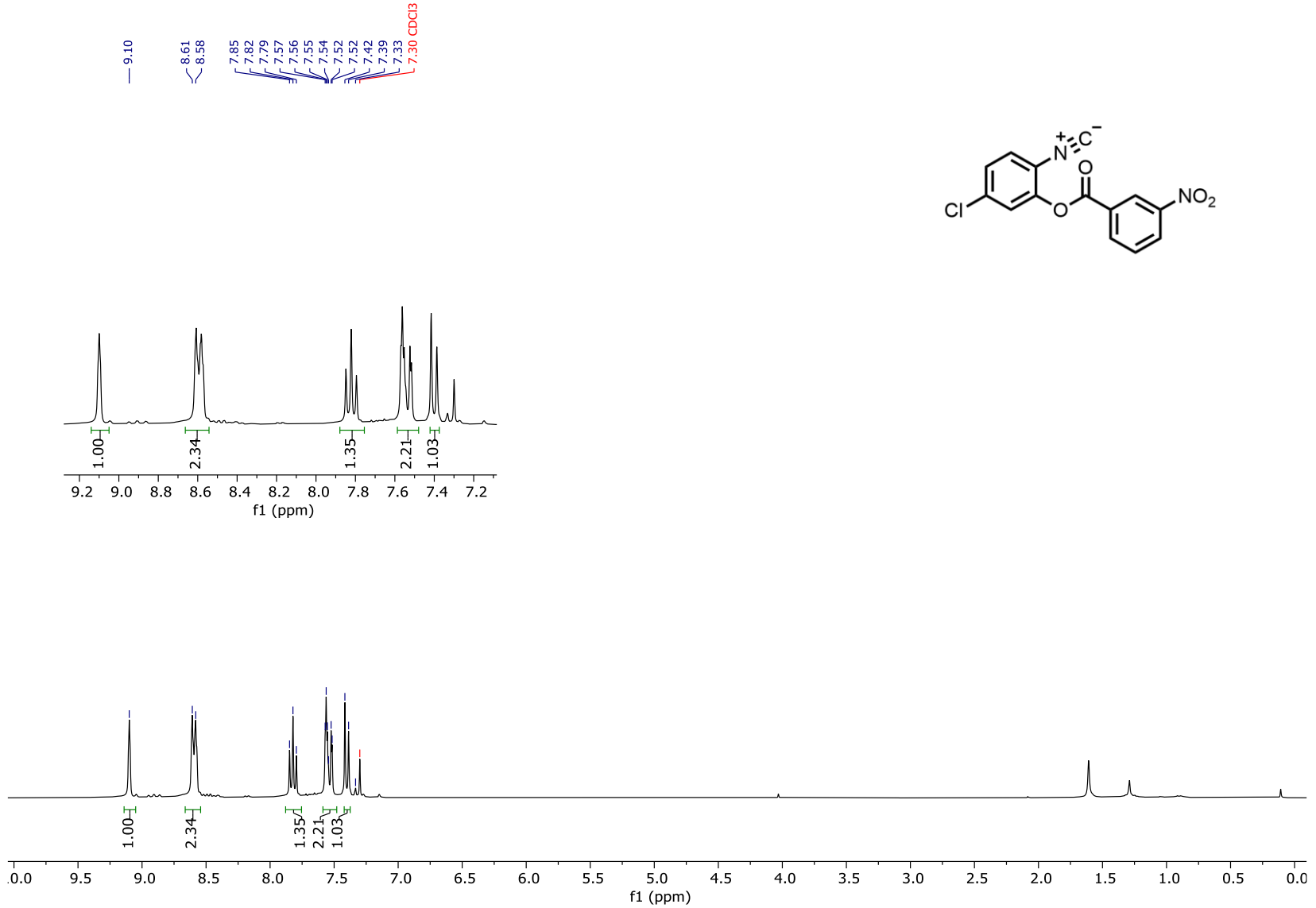

Figure S27. ^{1}H NMR (300 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 3-nitrobenzoate (1i).

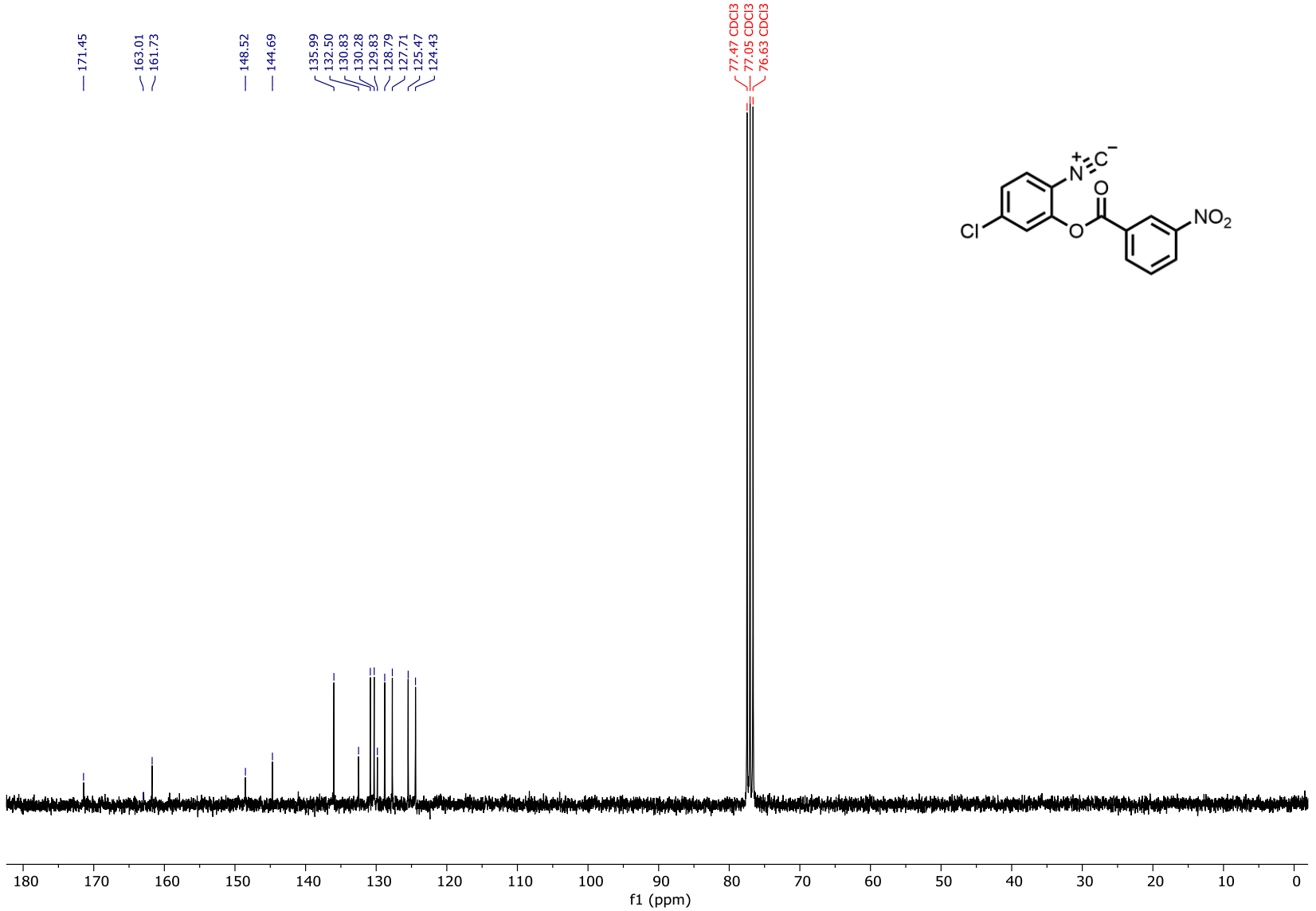

Figure S28. ^{13}C NMR (75 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 3-nitrobenzoate (1i).

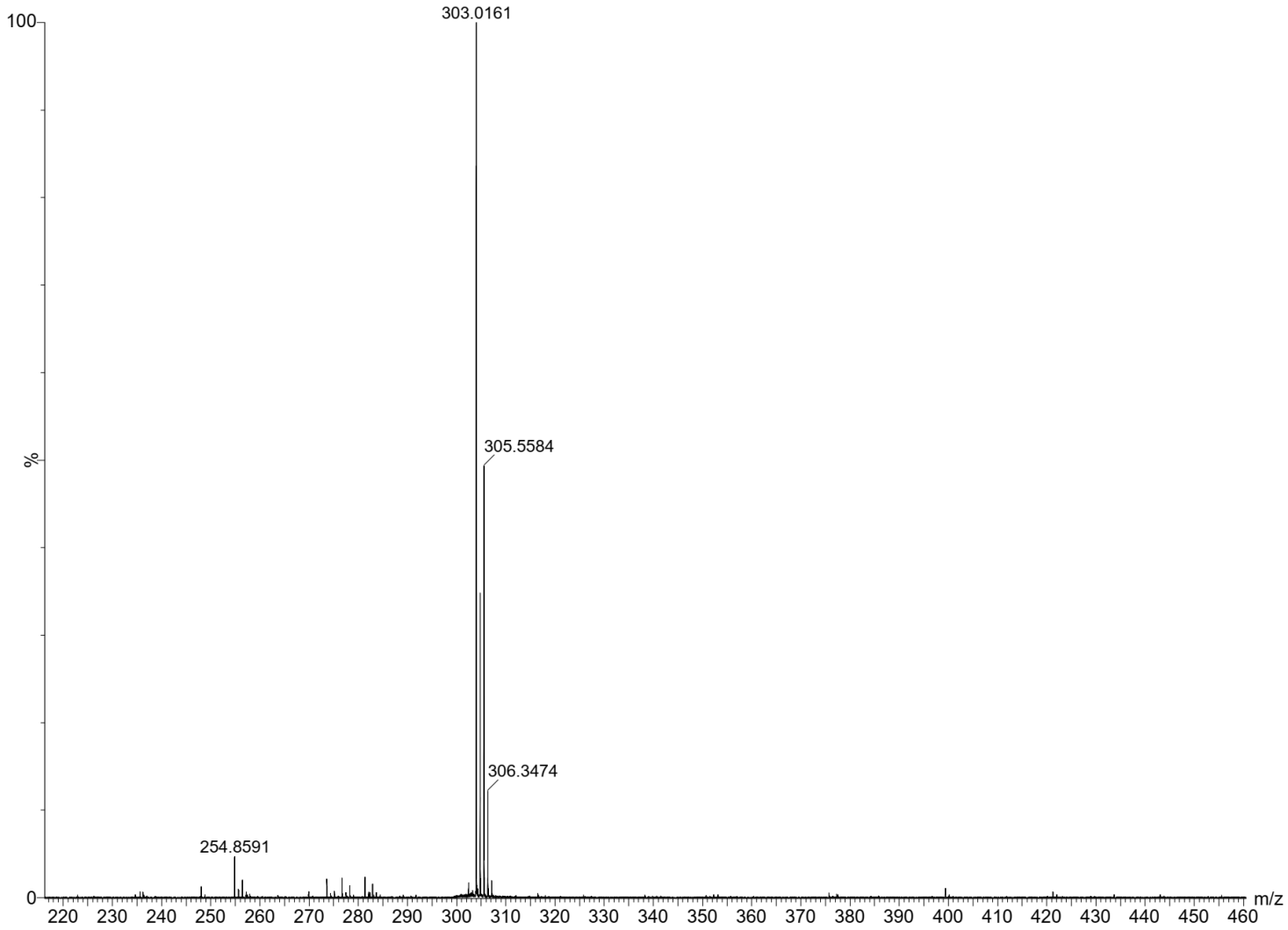

Figure S29. HRMS-ESI 5-chloro-2-isocyanophenyl 3-nitrobenzoate (1i).

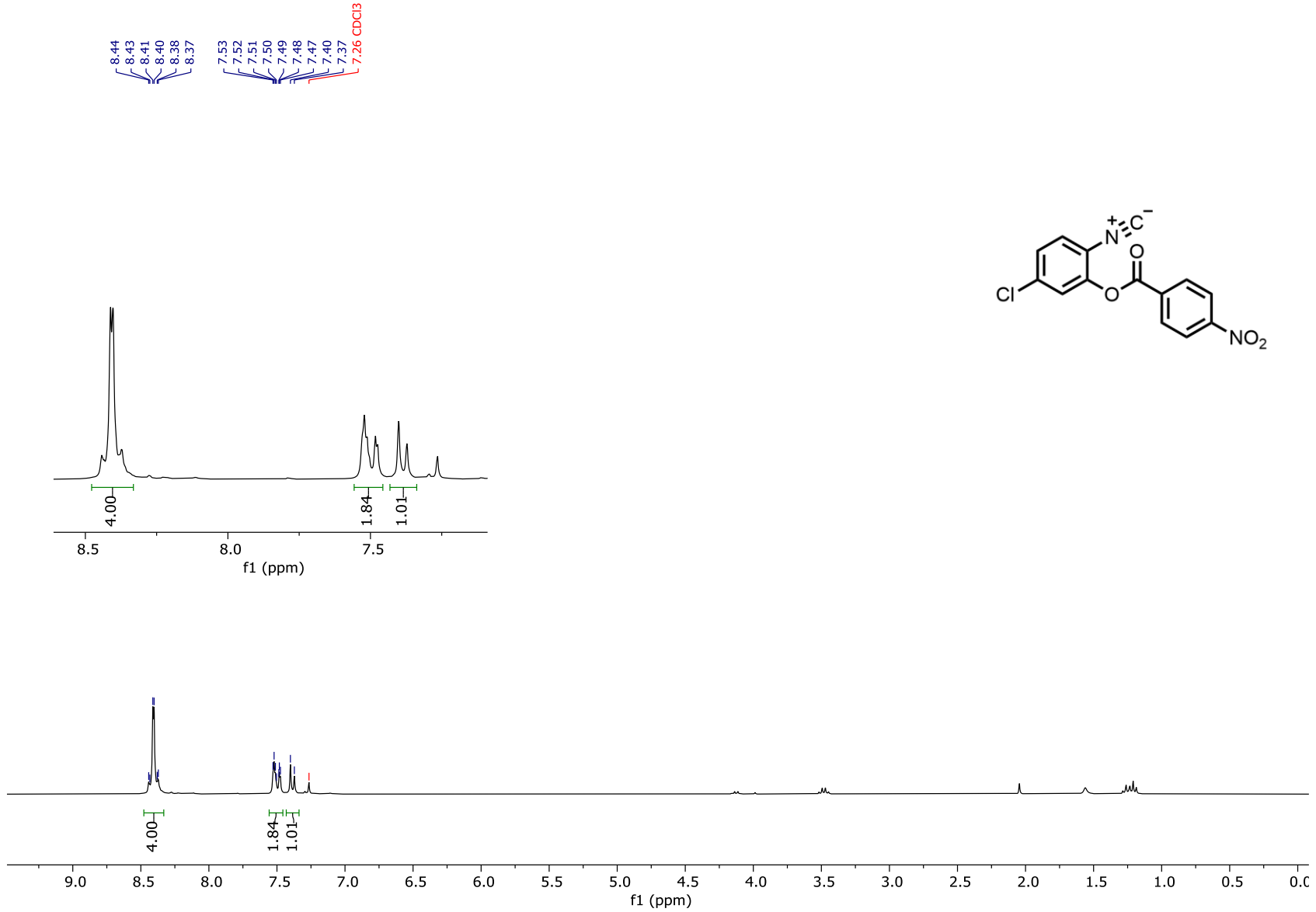

Figure S30. ^{1}H NMR (300 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 4-nitrobenzoate (1j).

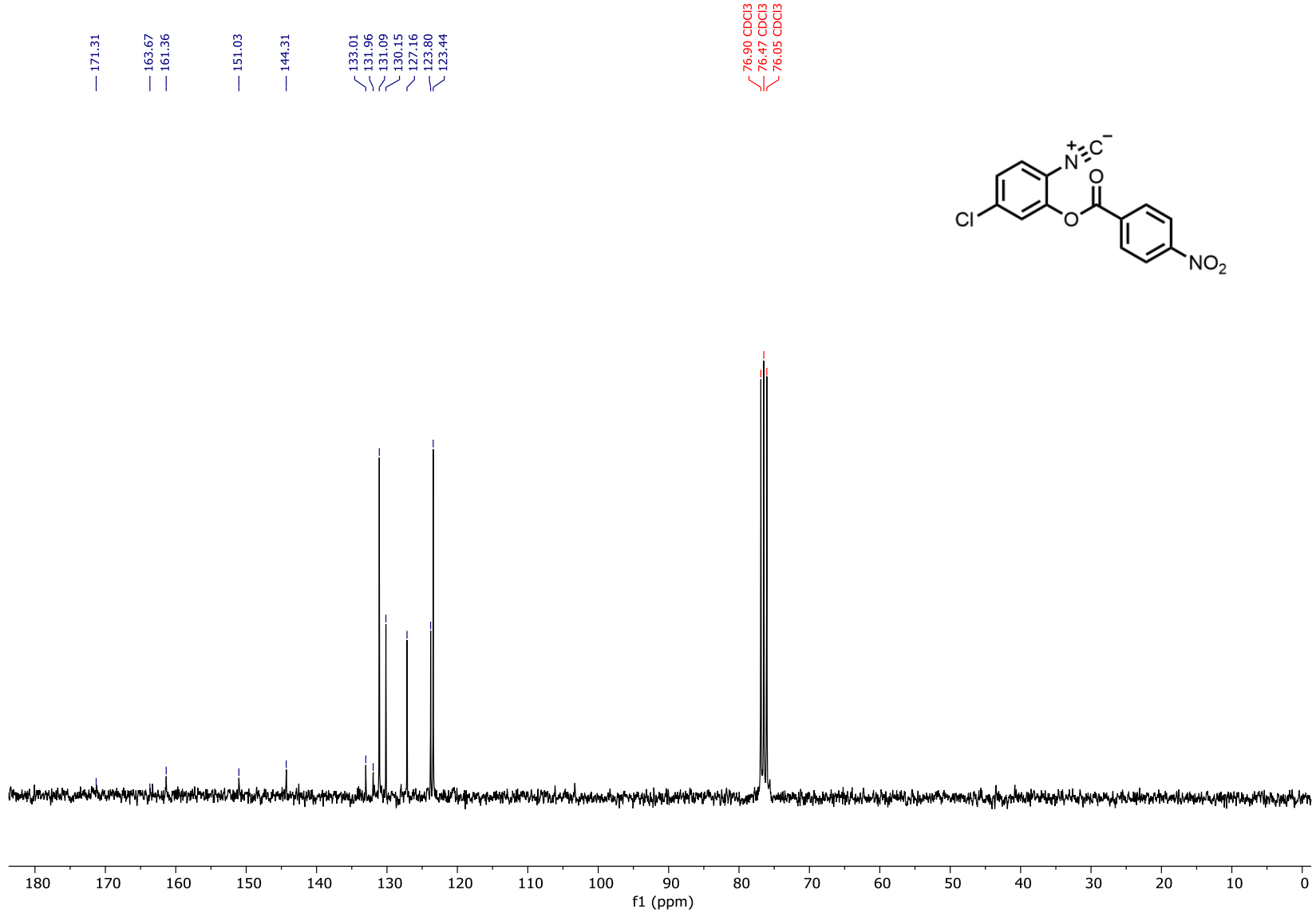

Figure S31. ^{13}C NMR (75 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 4-nitrobenzoate (1j).

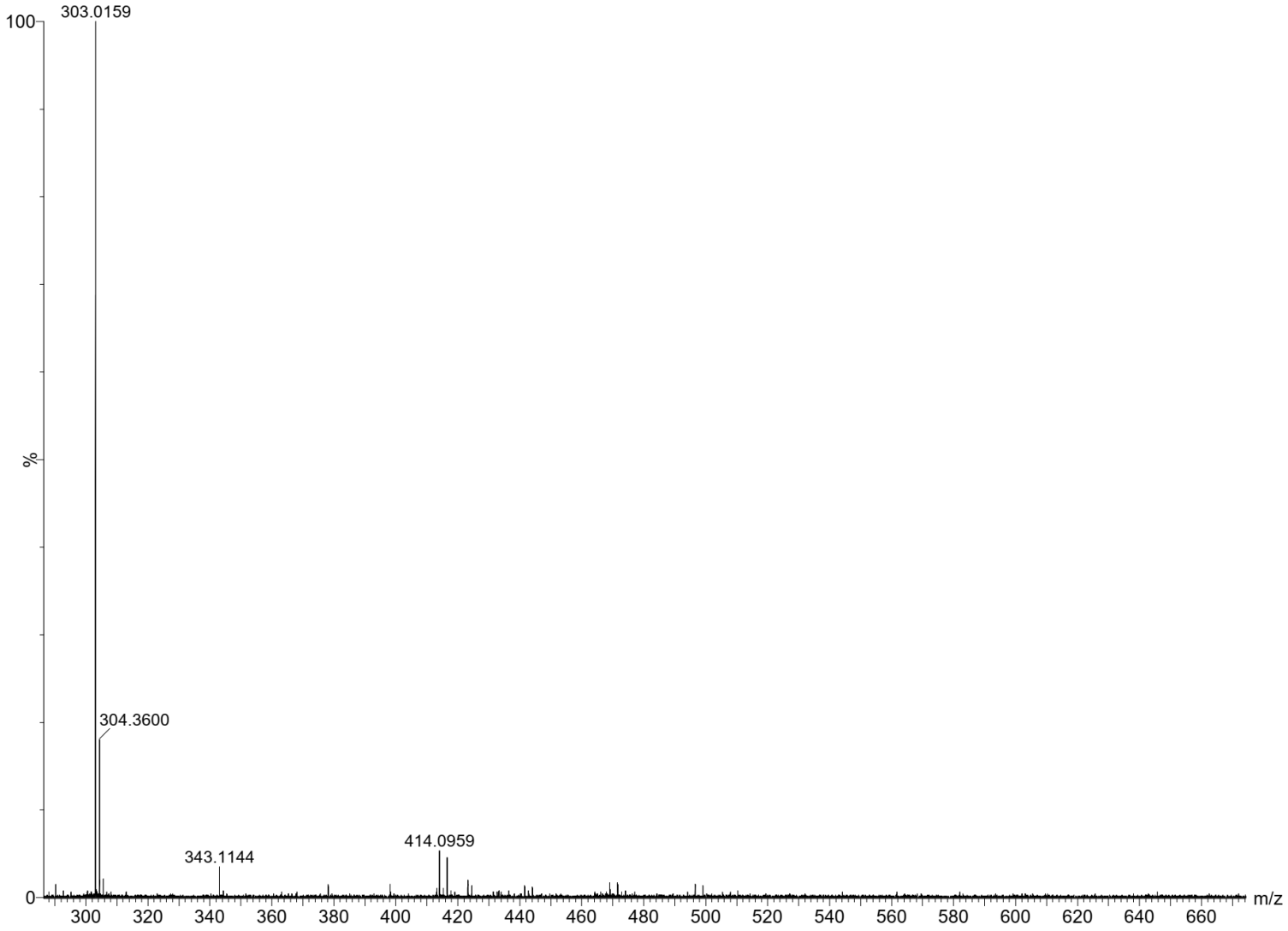

Figure S32. HRMS-ESI 5-chloro-2-isocyanophenyl 4-nitrobenzoate (1j).

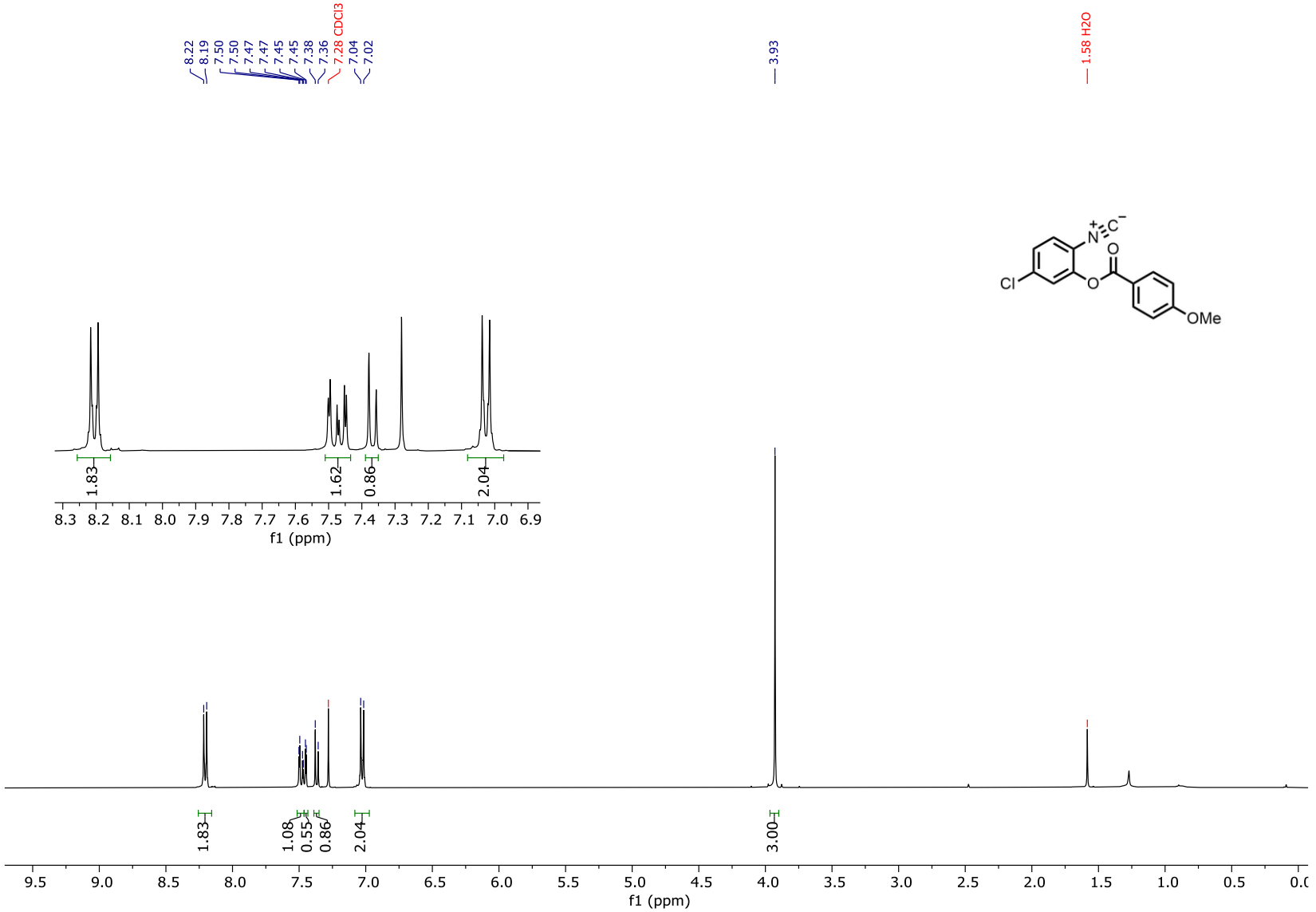

Figure S33. ^{1}H NMR (400 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 4-methoxybenzoate (1k).

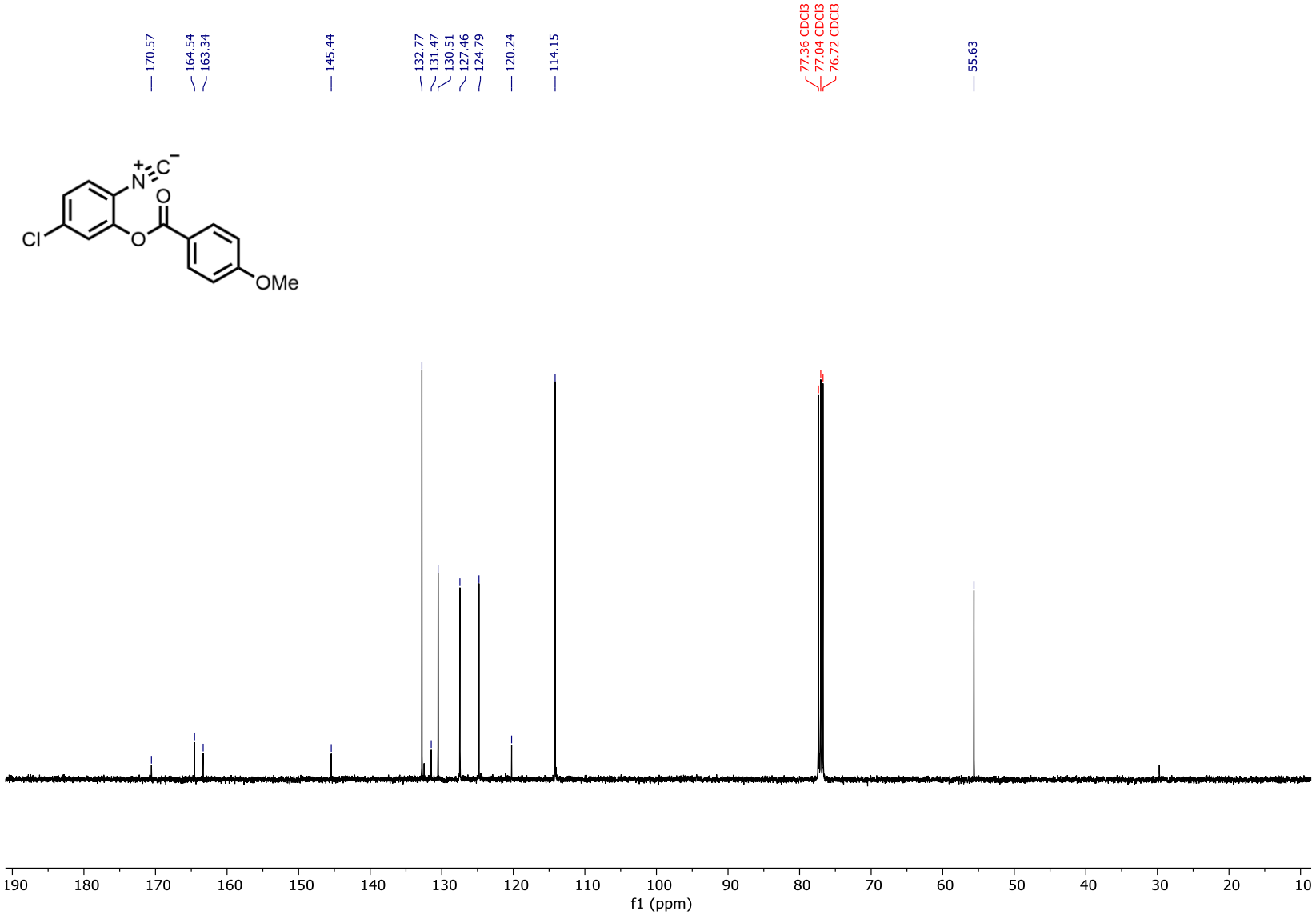

Figure S34. ^{13}C NMR (100 MHz, $CDCl_3$) 5-chloro-2-isocyanophenyl 4-methoxybenzoate (1k).

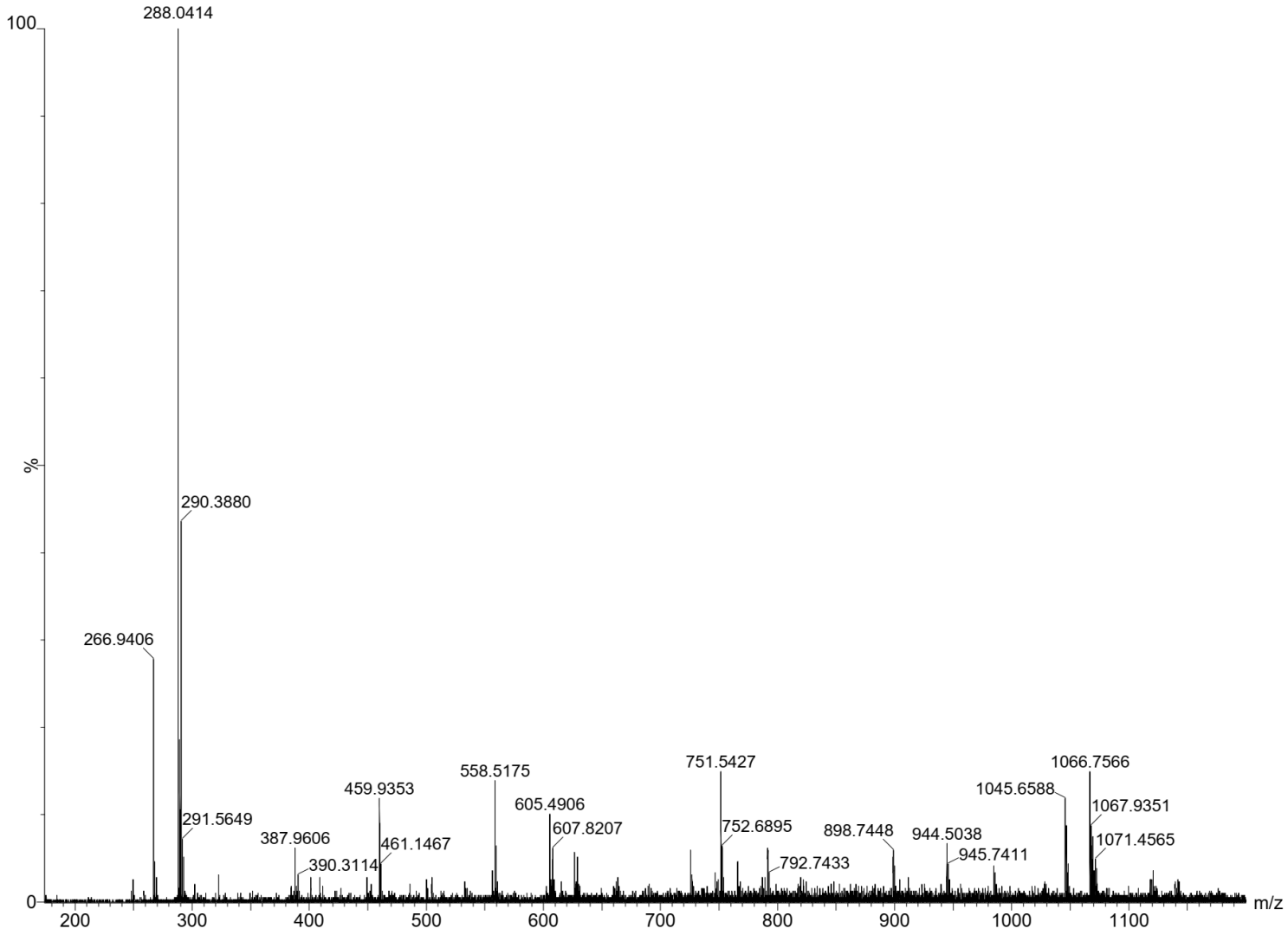

Figure S35. HRMS-ESI 5-chloro-2-isocyanophenyl 4-methoxybenzoate (1k).

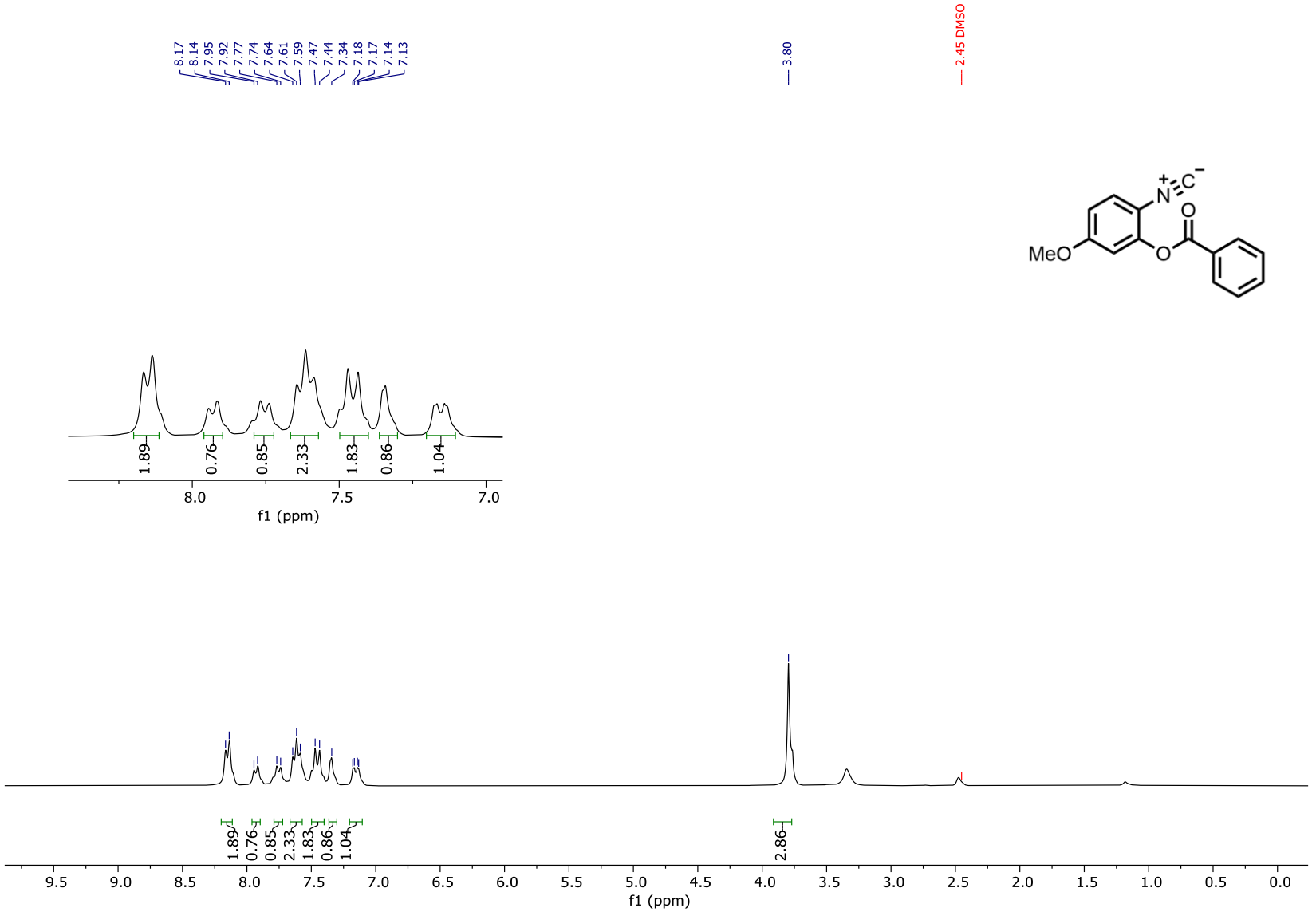

Figure S36. ^{1}H NMR (250 MHz, DMSO) 2-isocyano-5-methoxyphenyl benzoate (1l).

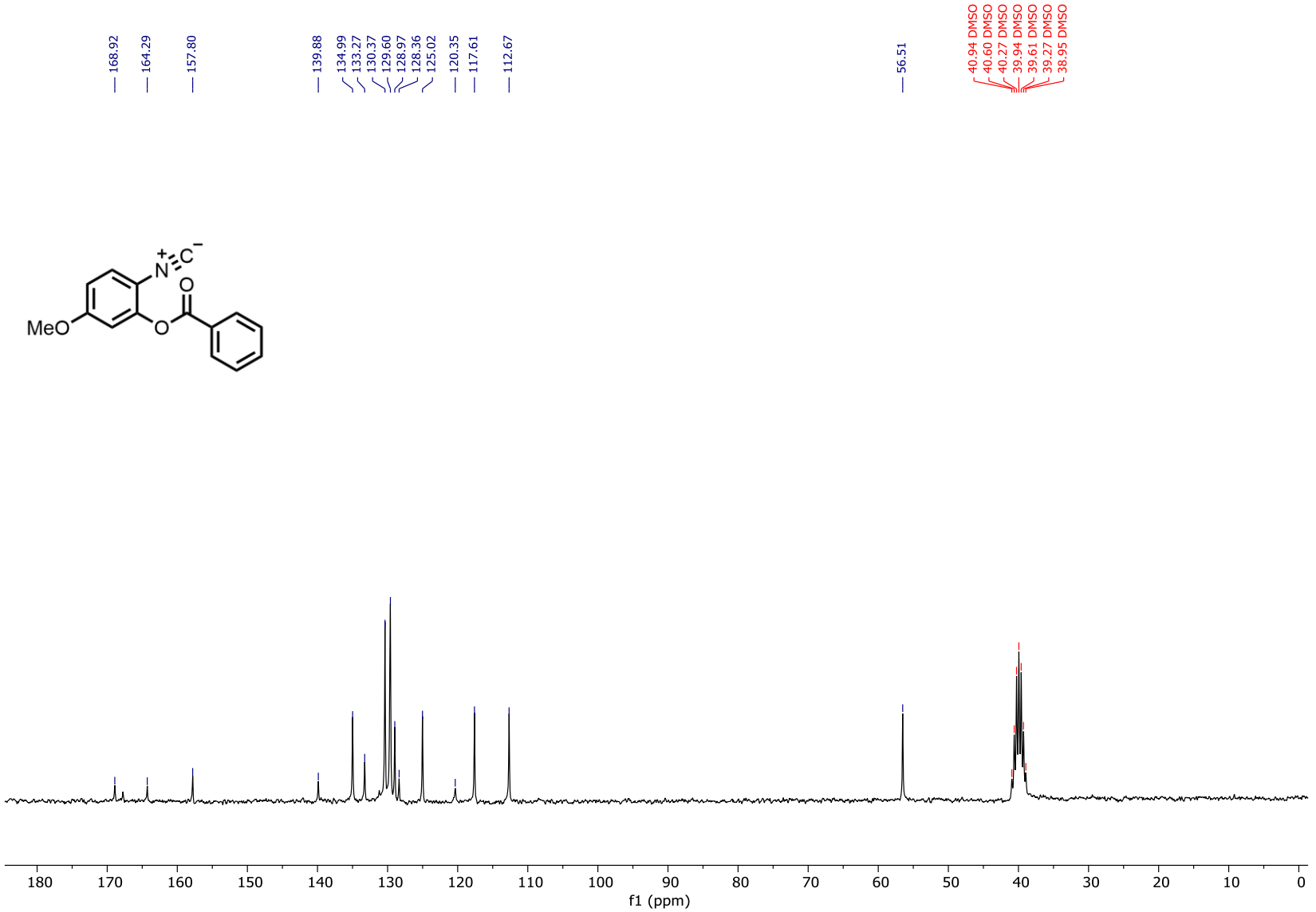

Figure S37. ^{13}C NMR (63 MHz, DMSO) 2-isocyano-5-methoxyphenyl benzoate (1l).

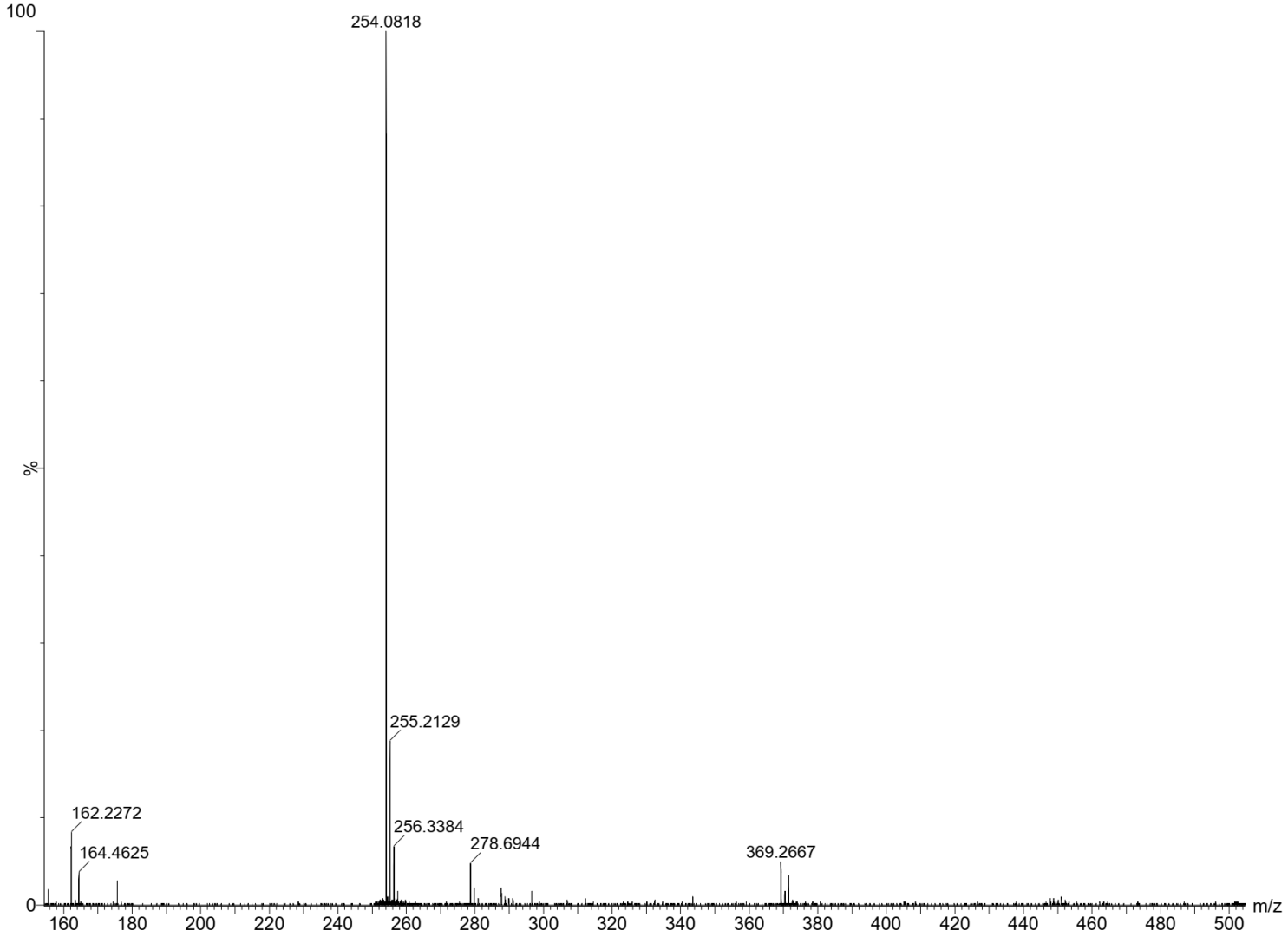

Figure S38. HRMS-ESI 2-isocyano-5-methoxyphenyl benzoate (1l).

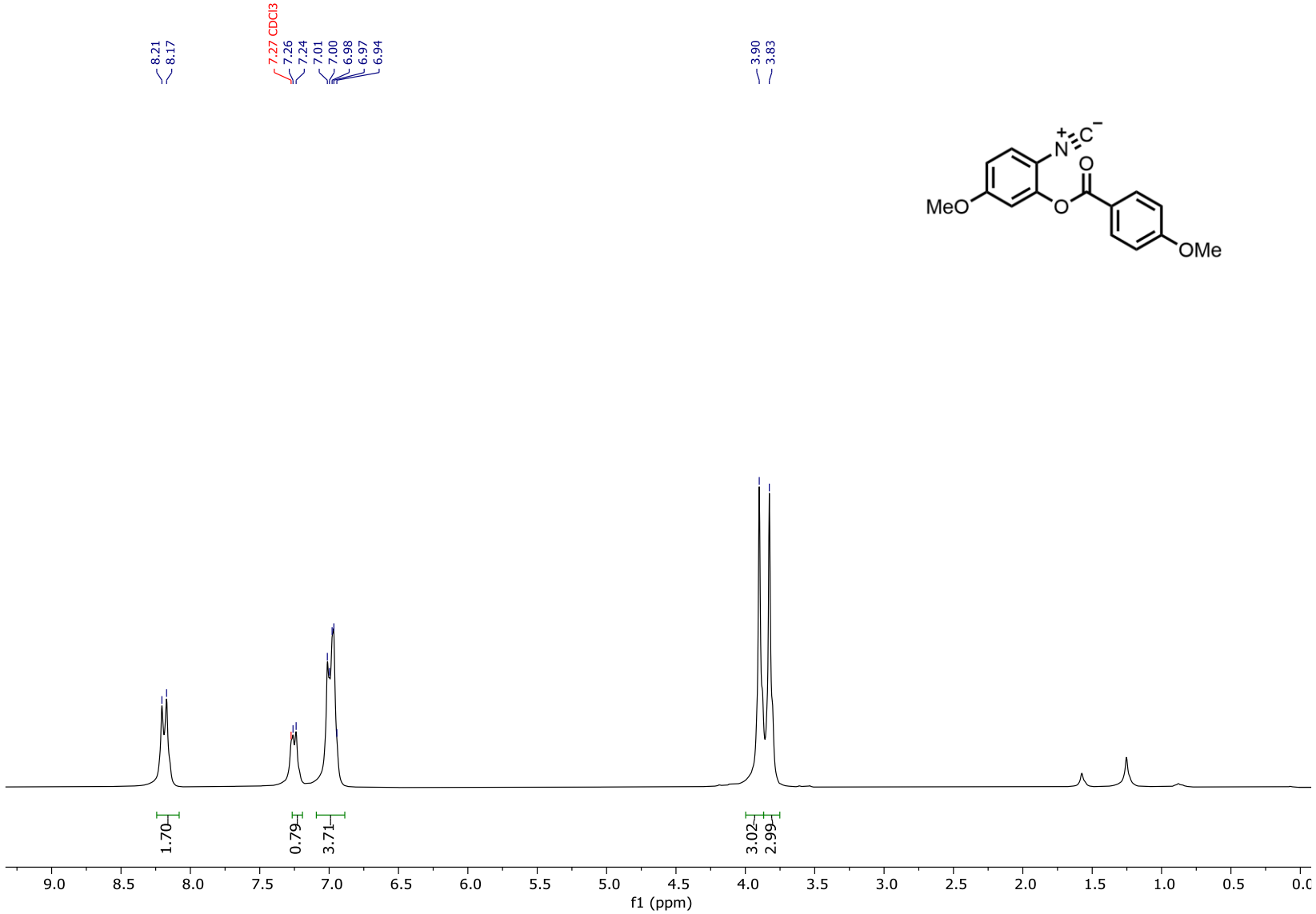

Figure S39. ^{1}H NMR (250 MHz, $CDCl_3$) 2-isocyano-5-methoxyphenyl 4-methoxybenzoate (1m).

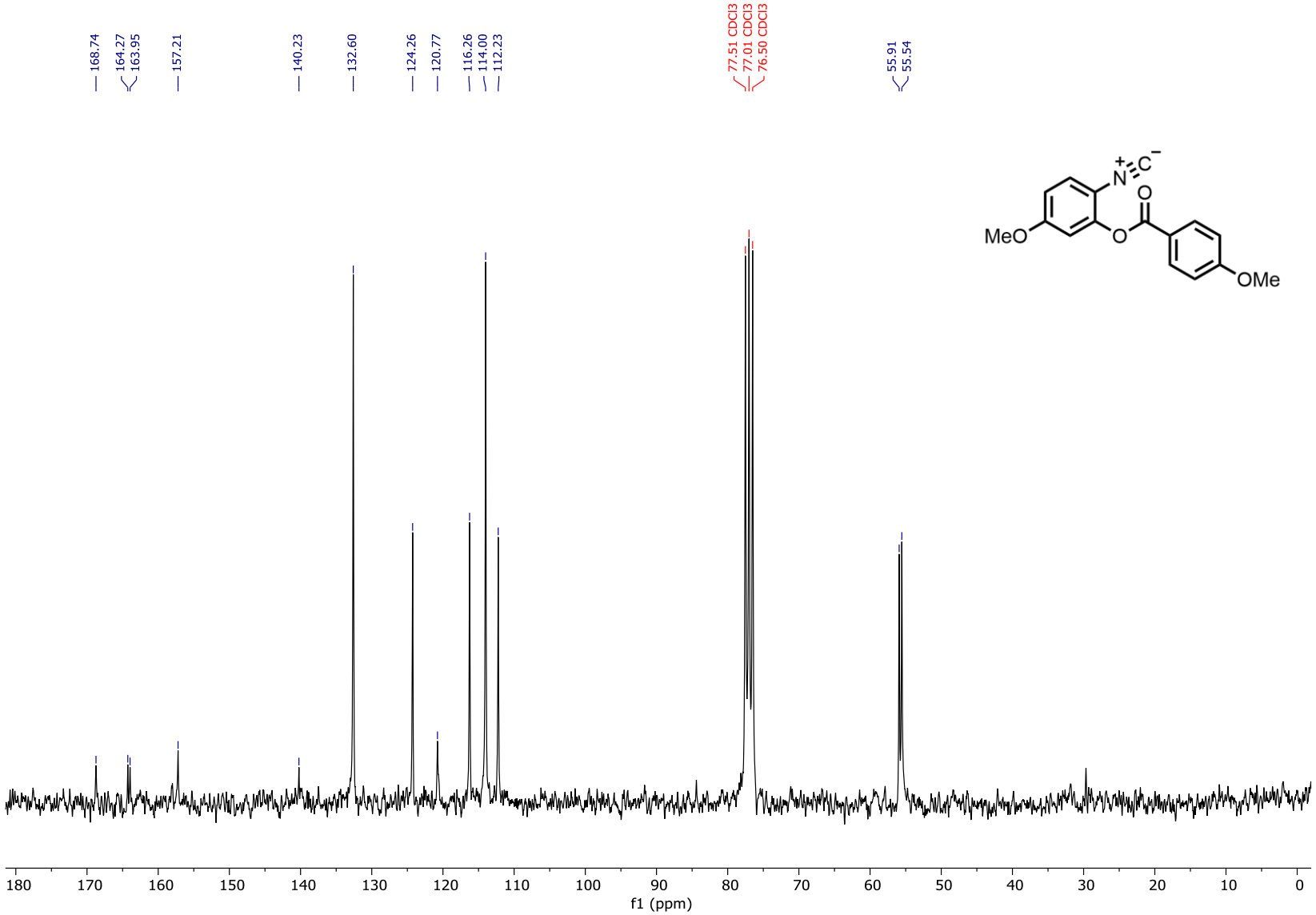

Figure S40. ^{13}C NMR (63 MHz, $CDCl_3$) 2-isocyano-5-methoxyphenyl 4-methoxybenzoate (1m).

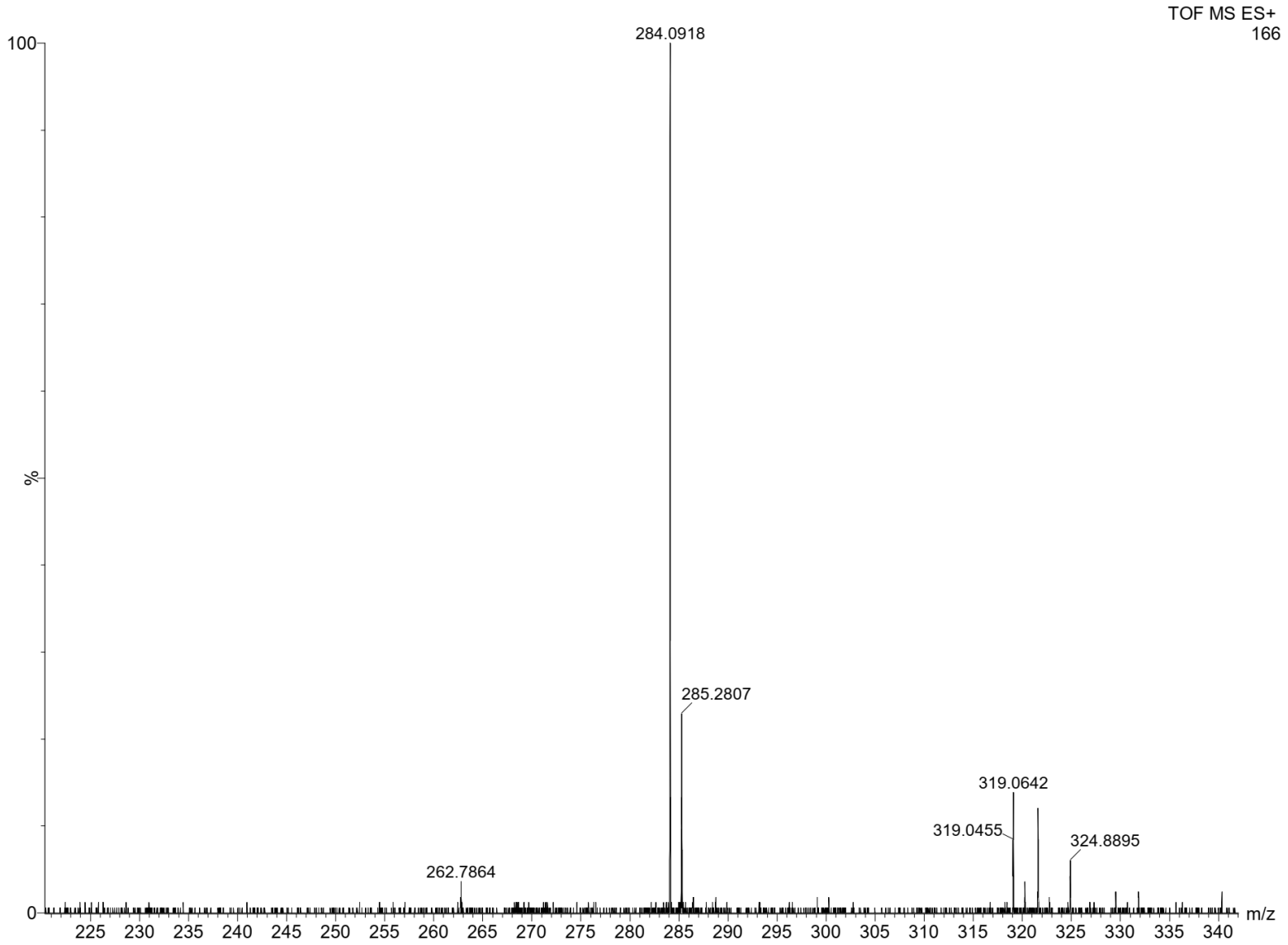

Figure S41. HRMS-ESI 2-isocyano-5-methoxyphenyl 4-methoxybenzoate (1m).

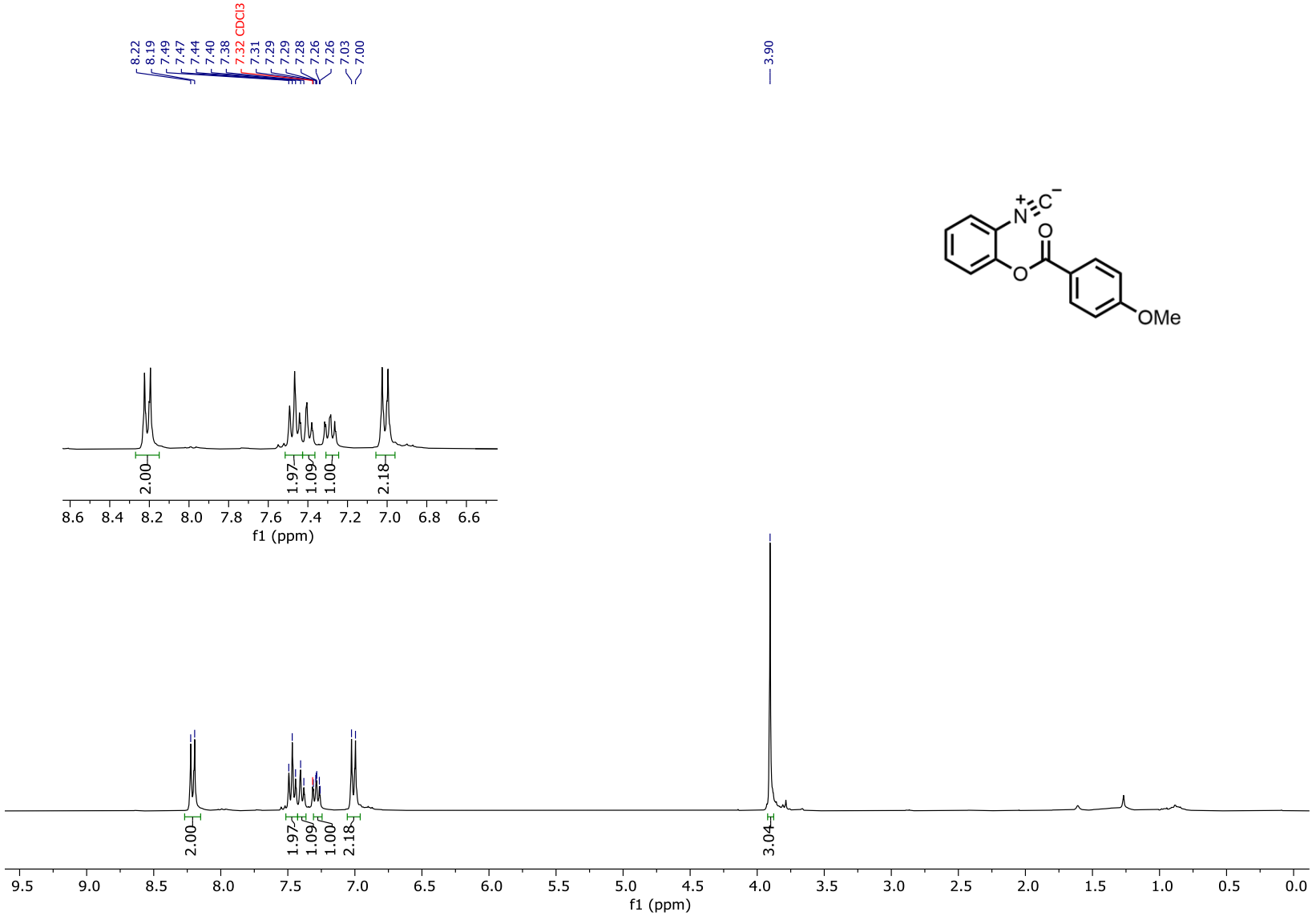

Figure S42. ^{1}H NMR (300 MHz, $CDCl_3$) 2-isocyanophenyl 4-methoxybenzoate (1n).

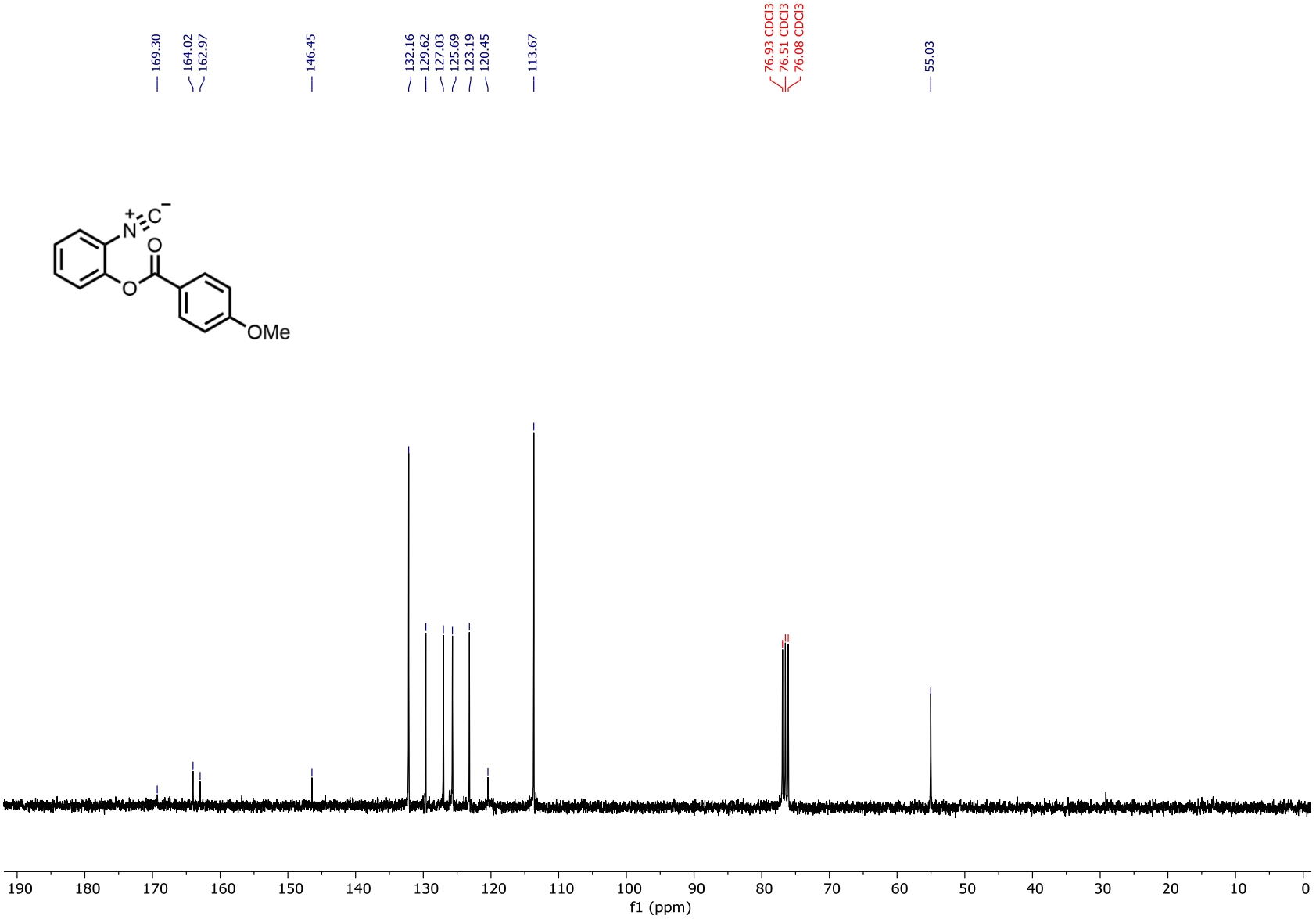

Figure S43. ^{13}C NMR (75 MHz, $CDCl_3$) 2-isocyanophenyl 4-methoxybenzoate (1n).

Figure S44. HRMS-ESI 2-isocyanophenyl 4-methoxybenzoate (1n).

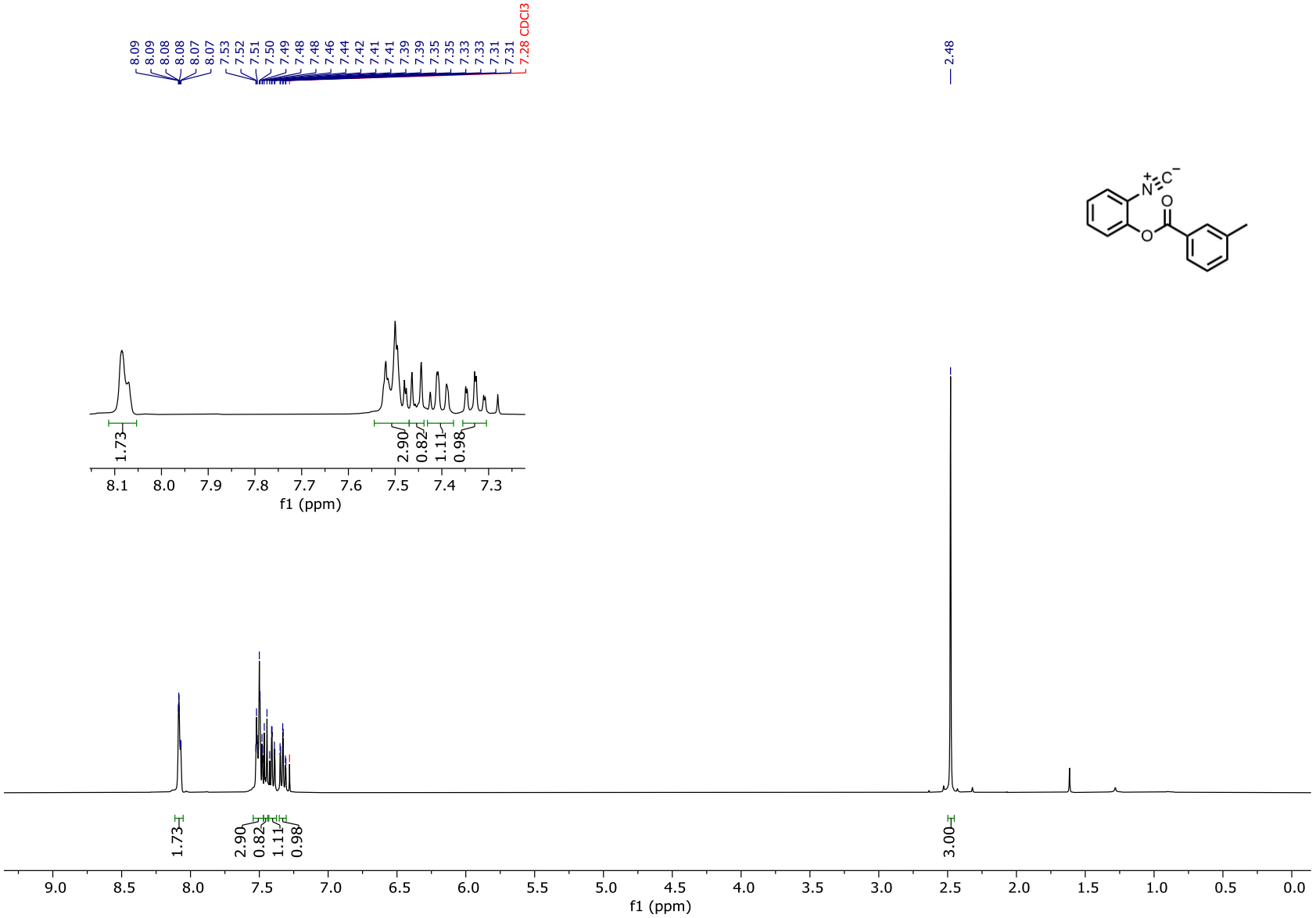

Figure S45. ^{1}H NMR (400 MHz, $CDCl_3$) 2-isocyanophenyl 3-methylbenzoate (1o).

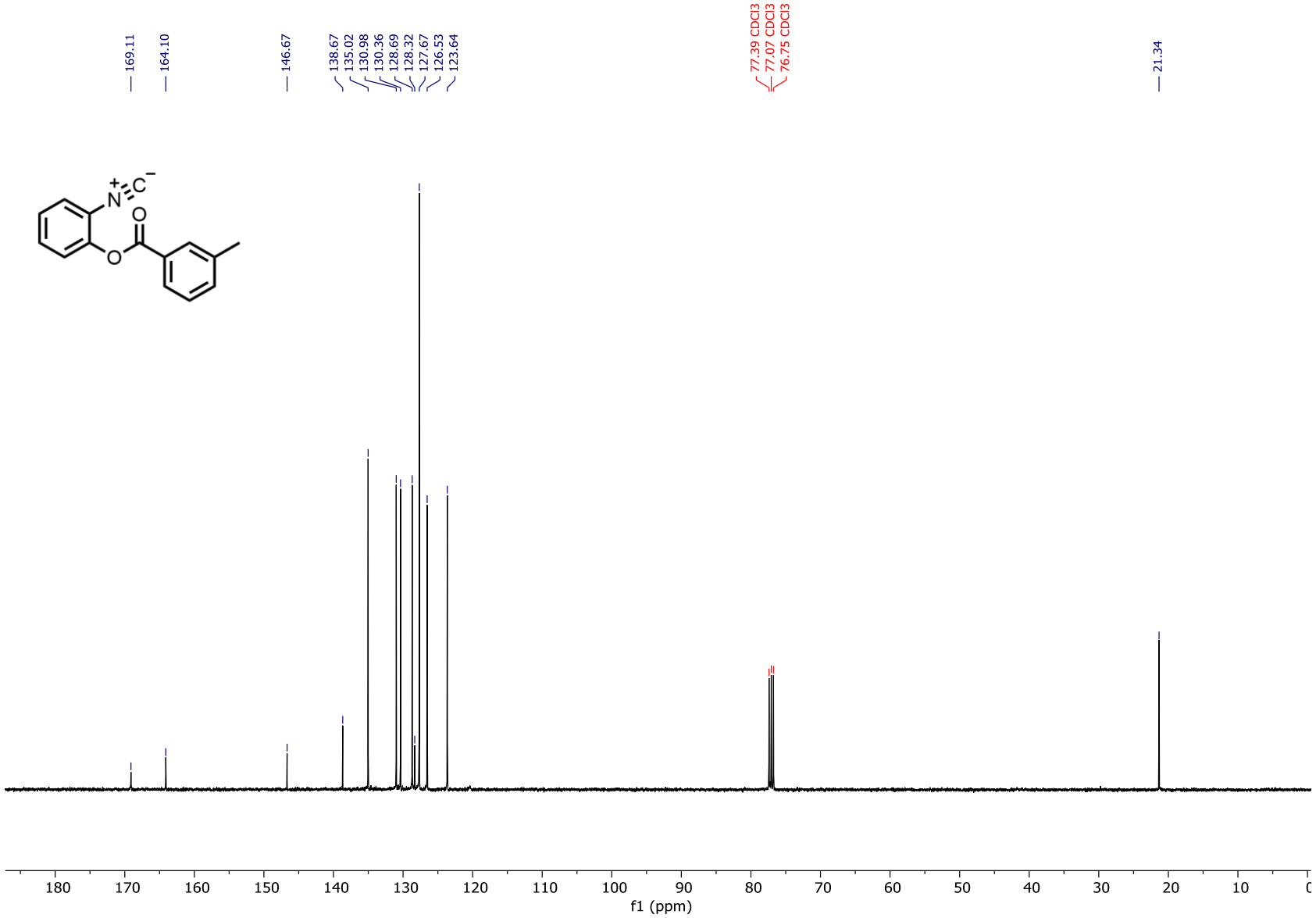

Figure S46. ^{13}C NMR (101 MHz, $CDCl_3$) 2-isocyanophenyl 3-methylbenzoate (1o).

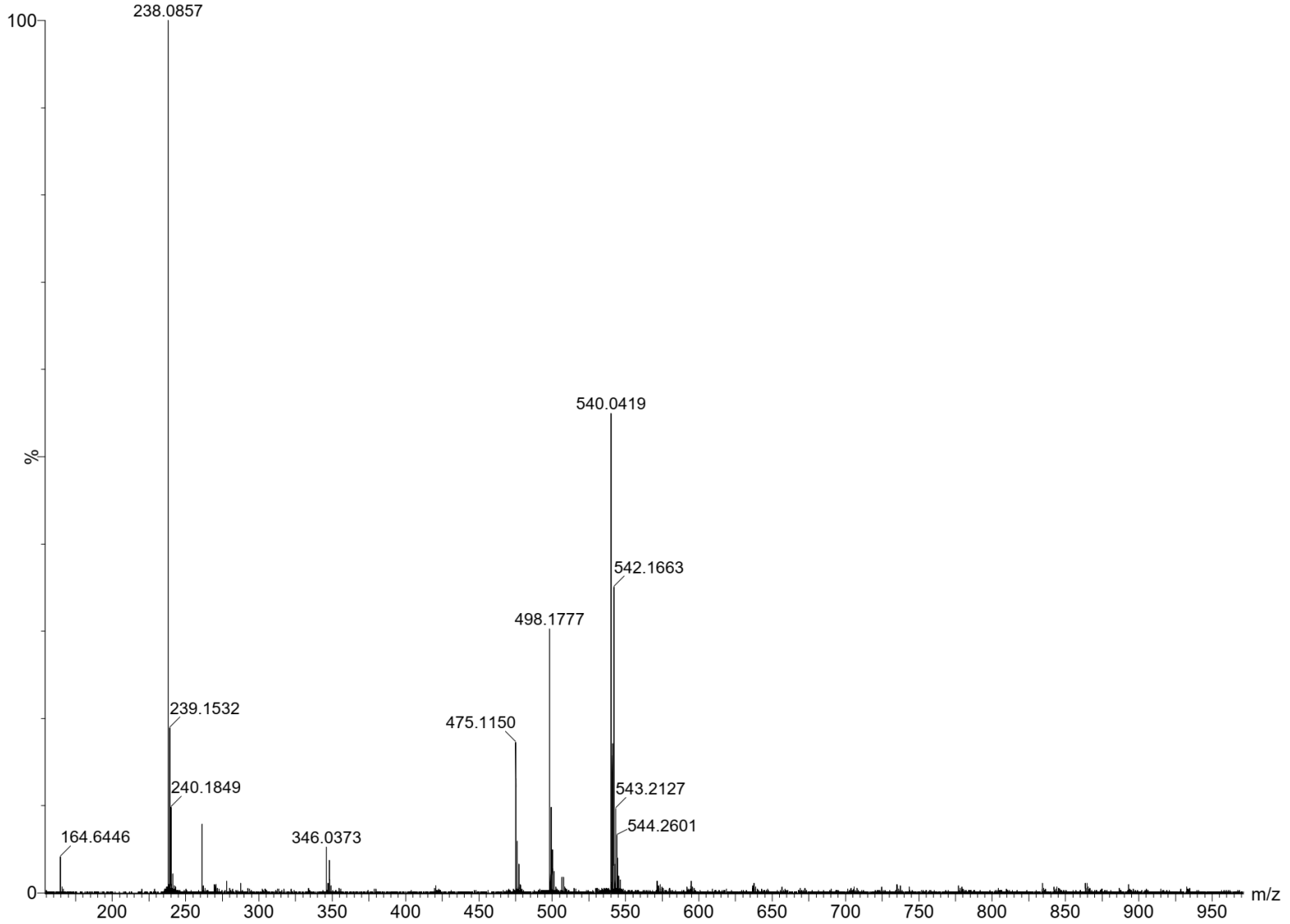

Figure S47. HRMS-ESI 2-isocyanophenyl 3-methylbenzoate (1o).

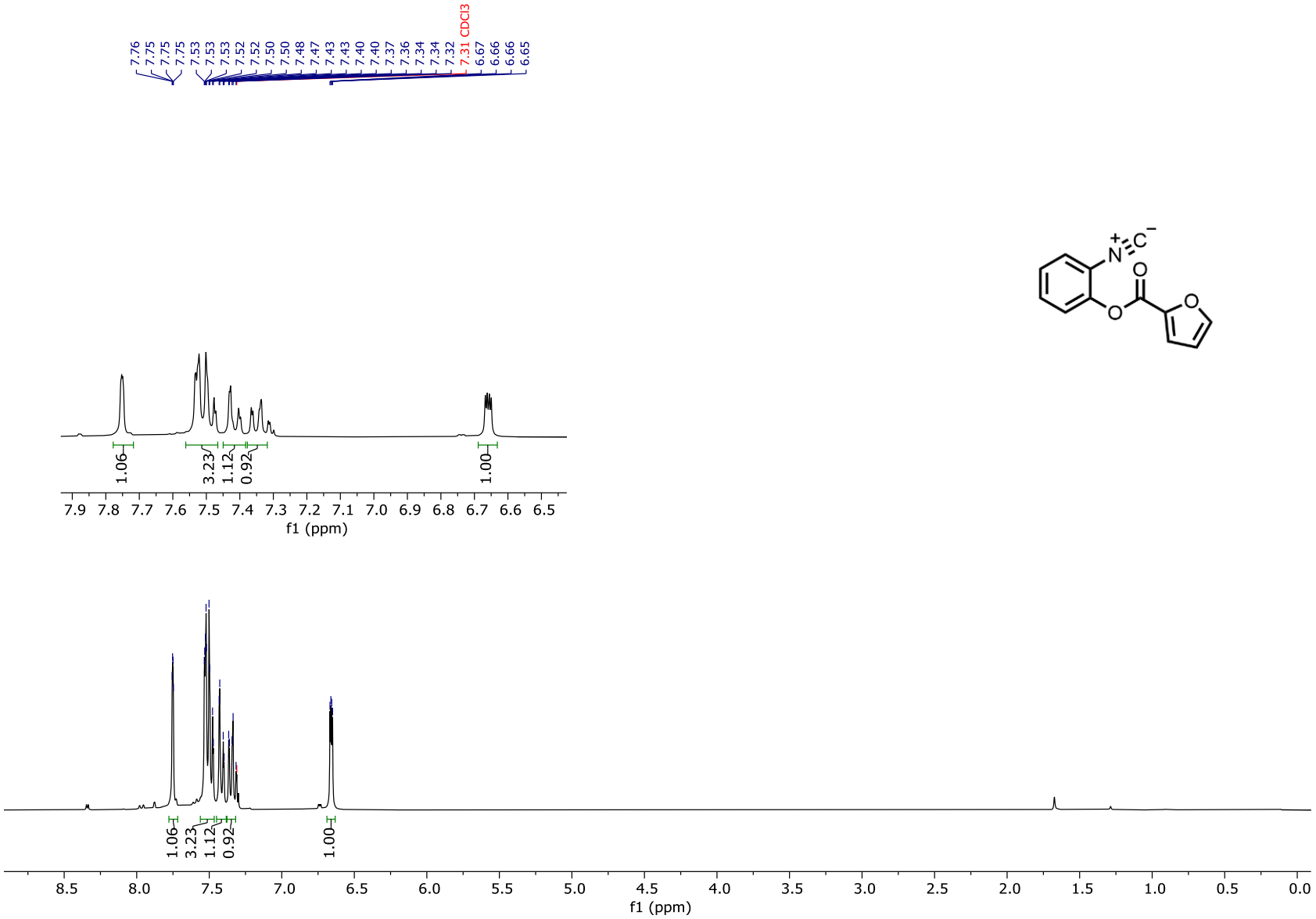

Figure S48. ^{1}H NMR (300 MHz, $CDCl_3$) 2-isocyanophenyl furan-2-carboxylate (1p).

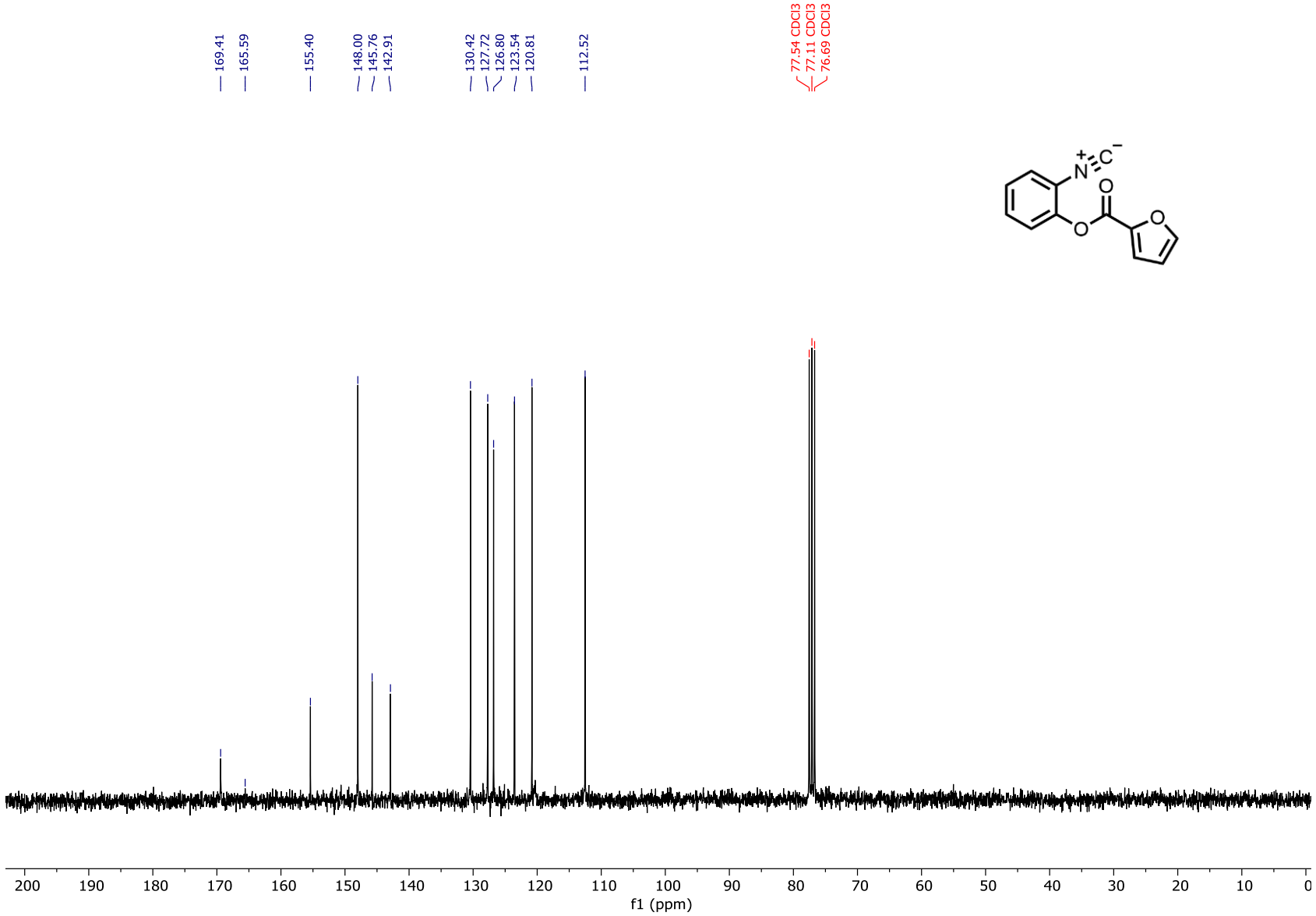

Figure S49. ^{13}C NMR (76 MHz, $CDCl_3$) 2-isocyanophenyl furan-2-carboxylate (1p).

Figure S50. HRMS-ESI 2-isocyanophenyl furan-2-carboxylate (1p).

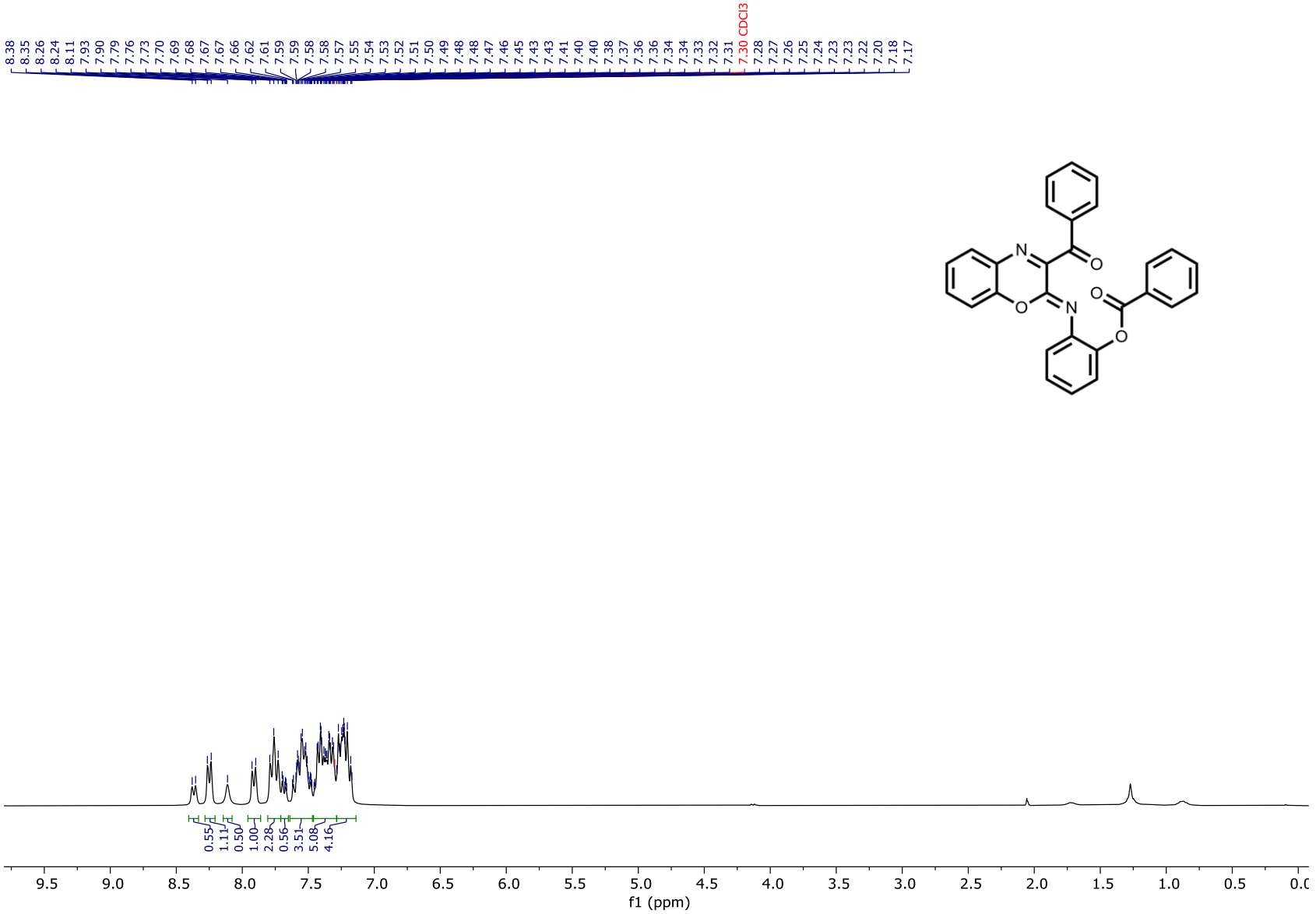

Figure S51. ^{1}H NMR (300 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl benzoate (2a).

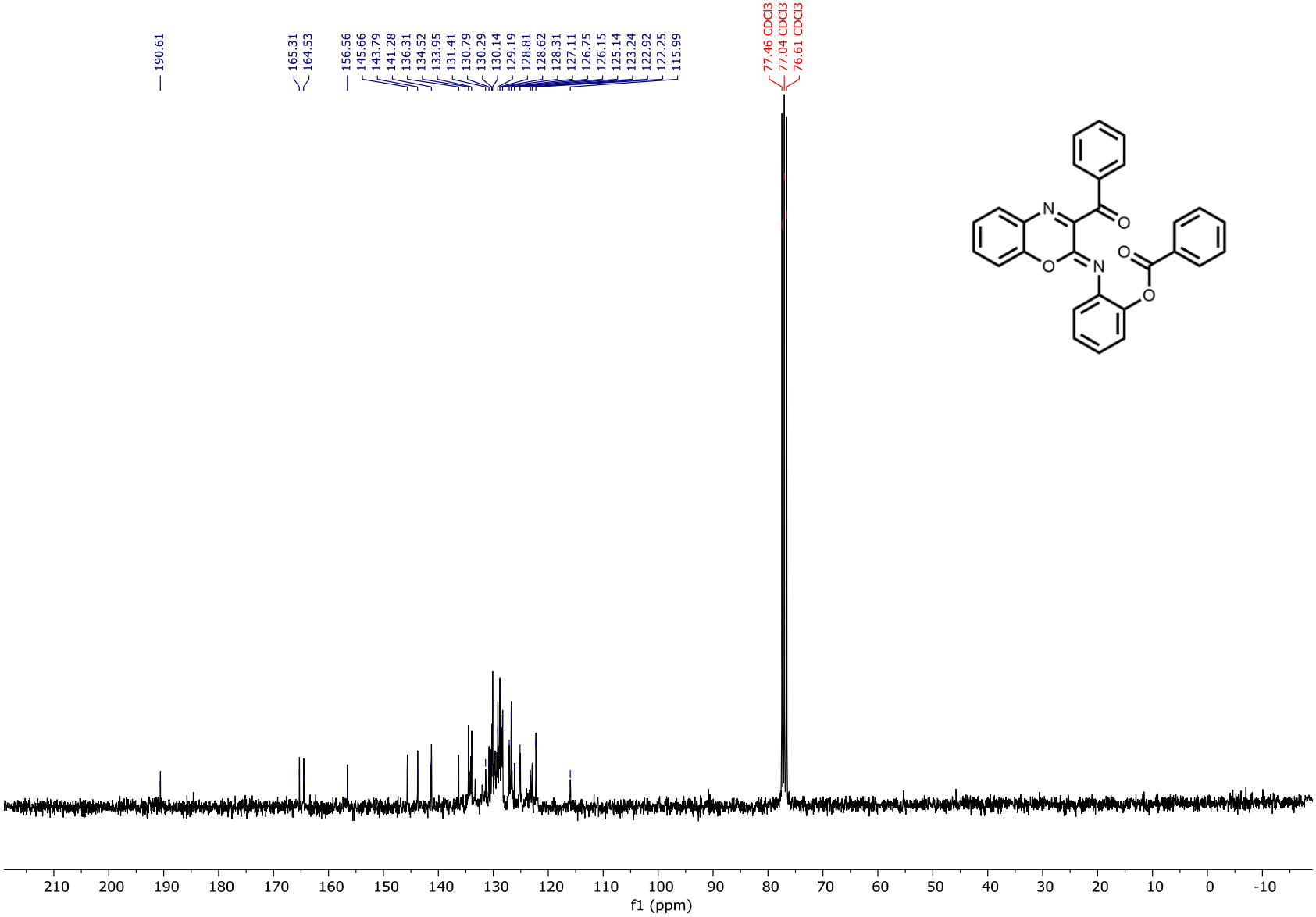

Figure S52. ^{13}C NMR (75 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl benzoate (2a).

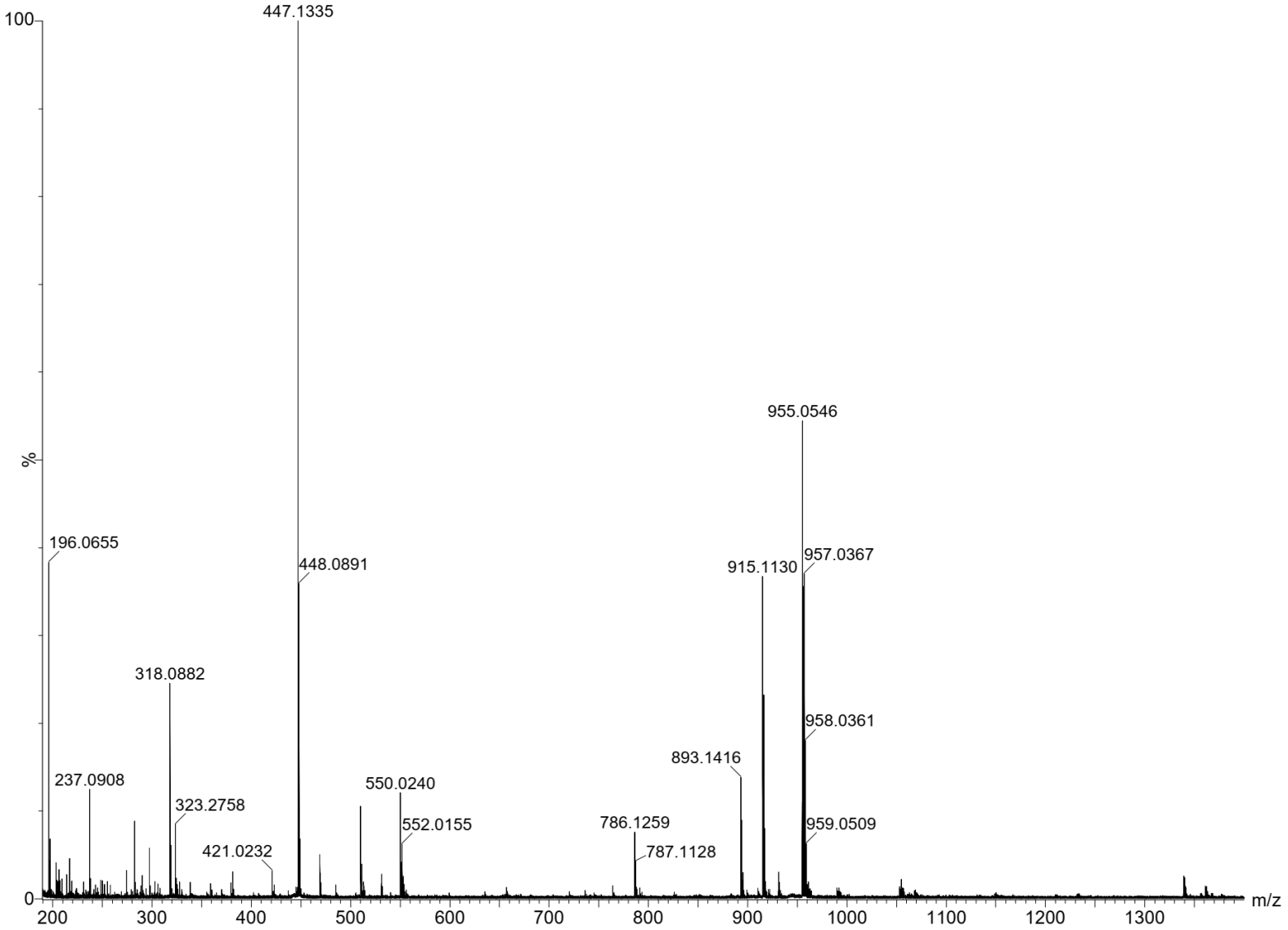

Figure S53. HRMS-ESI (Z)-2-((3-benzoyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl benzoate (2a).

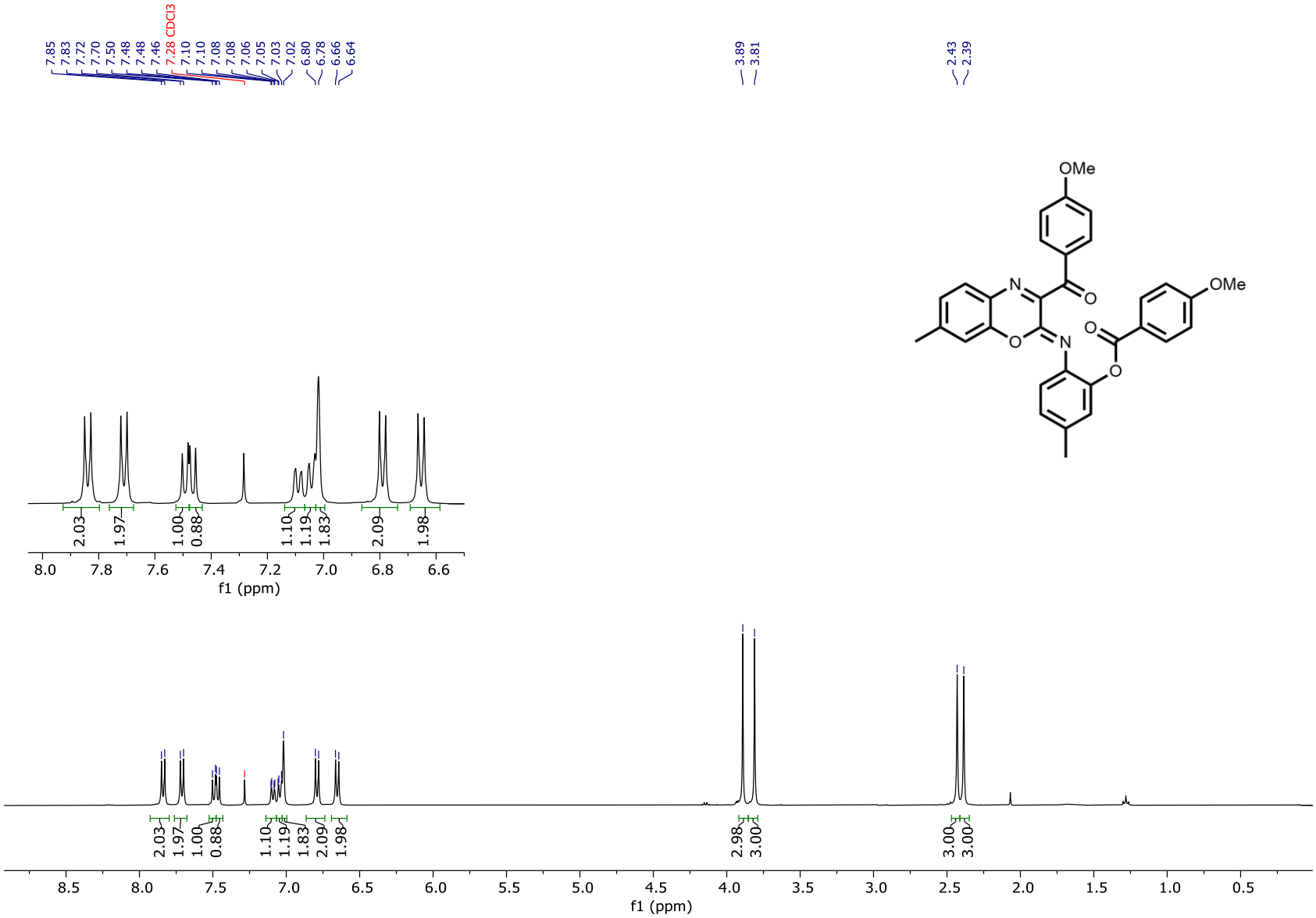

Figure S54. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-(4-methoxybenzoyl)-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl 4-methoxybenzoate (2b).

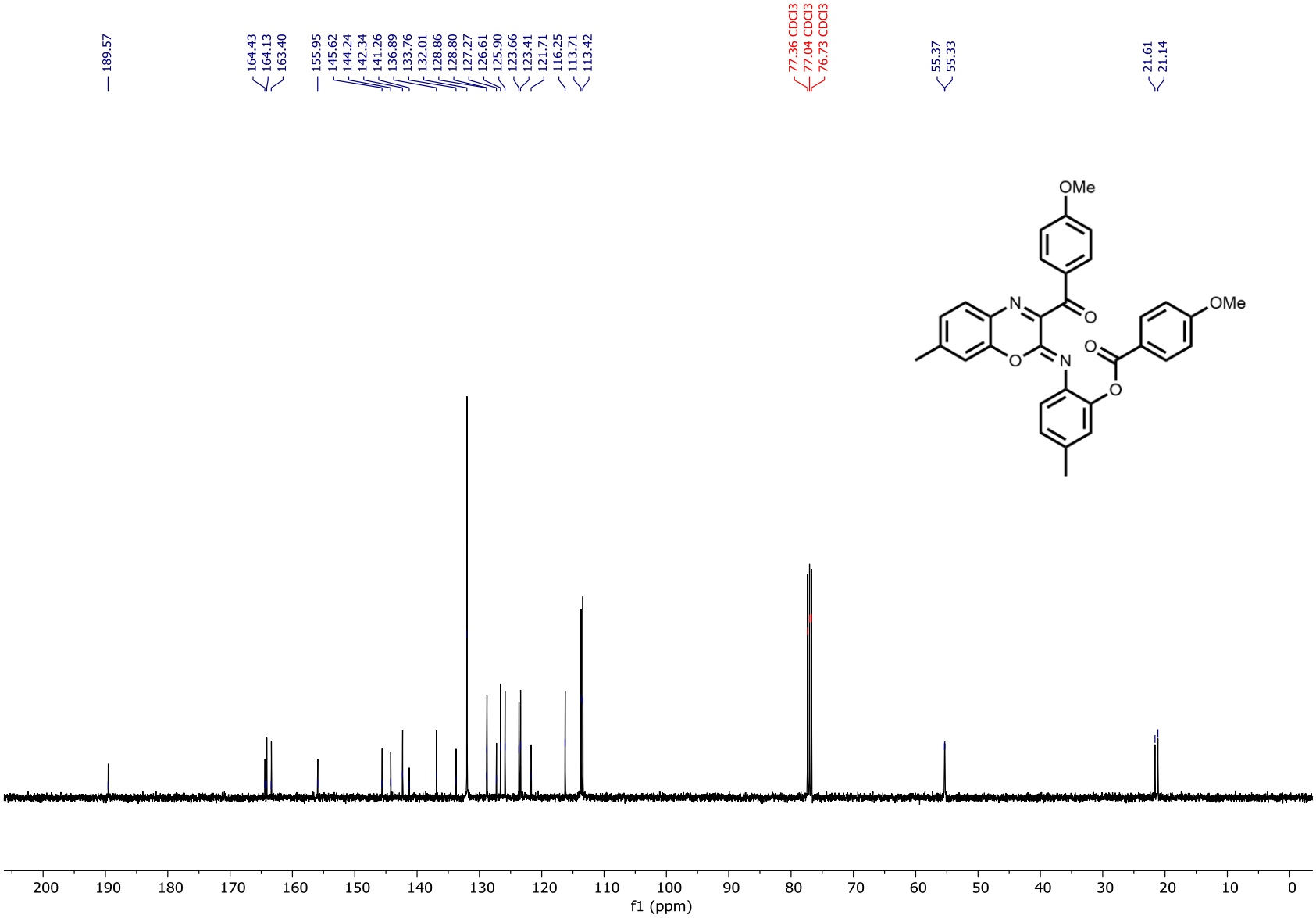

Figure S55. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-(4-methoxybenzoyl)-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl 4-methoxybenzoate (2b).

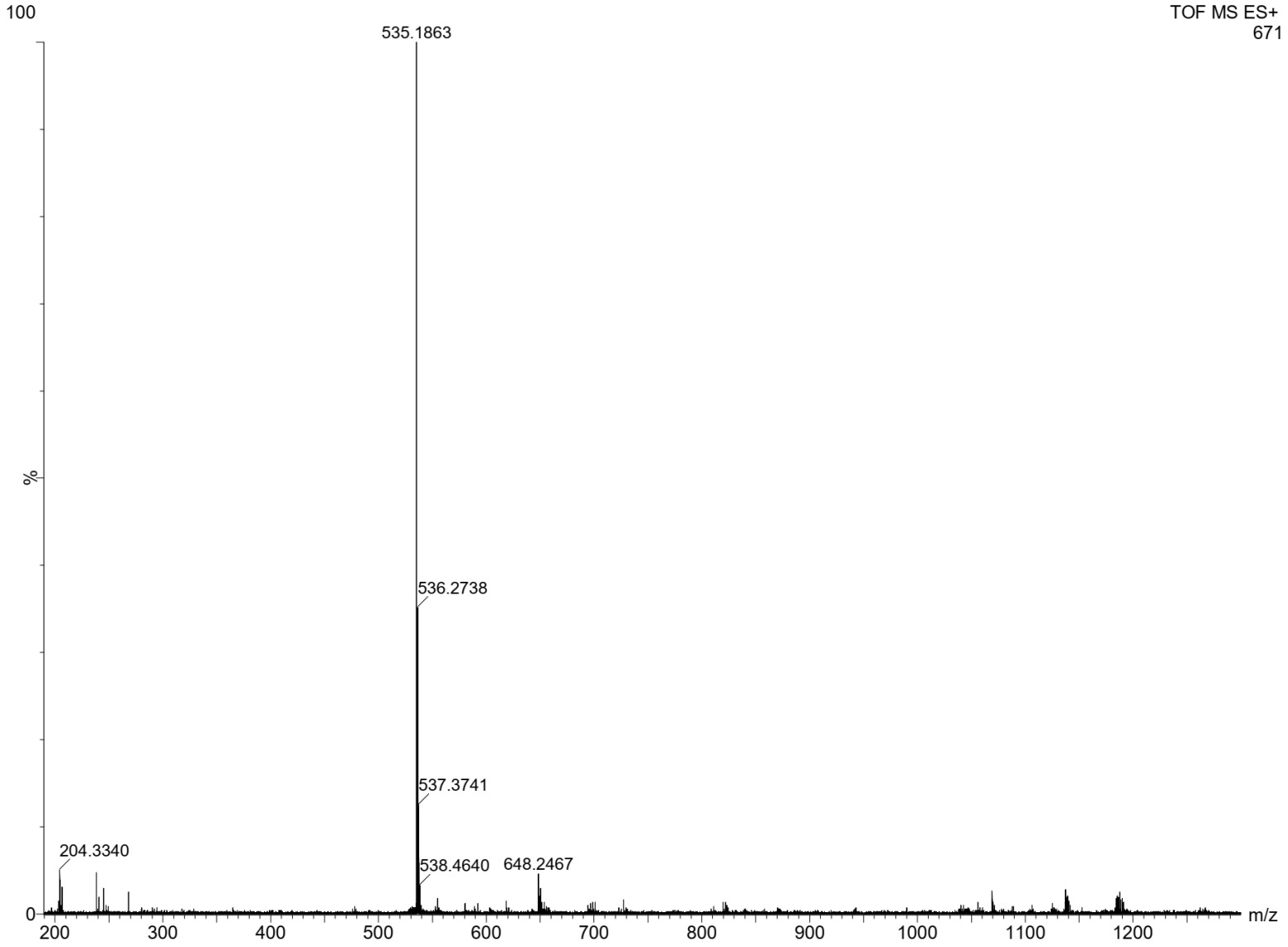

Figure S56. HRMS-ESI (Z)-2-((3-(4-methoxybenzoyl)-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl 4-methoxybenzoate (2b).

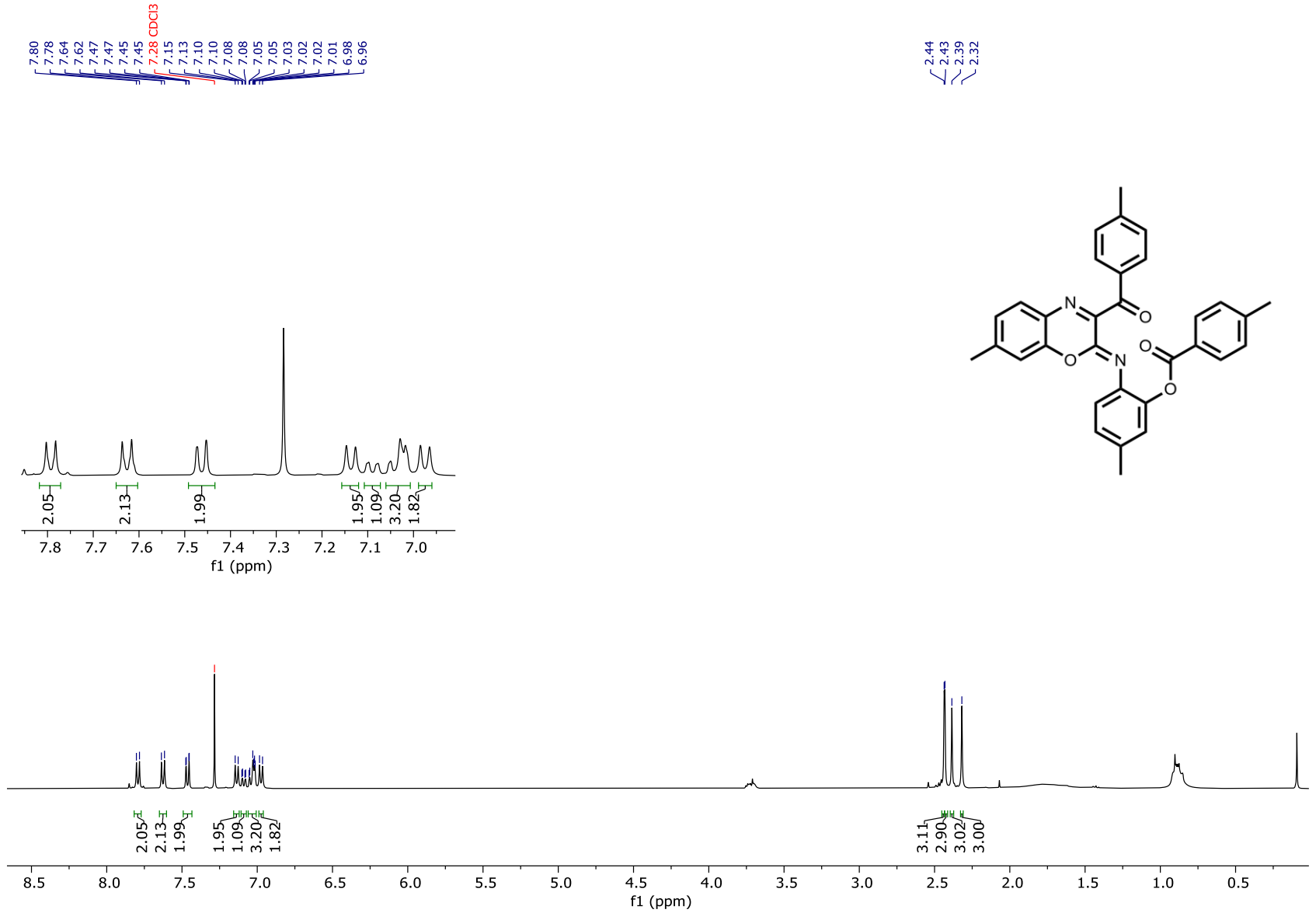

Figure S57. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-5-methyl-2-((7-methyl-3-(4-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methylbenzoate (2c).

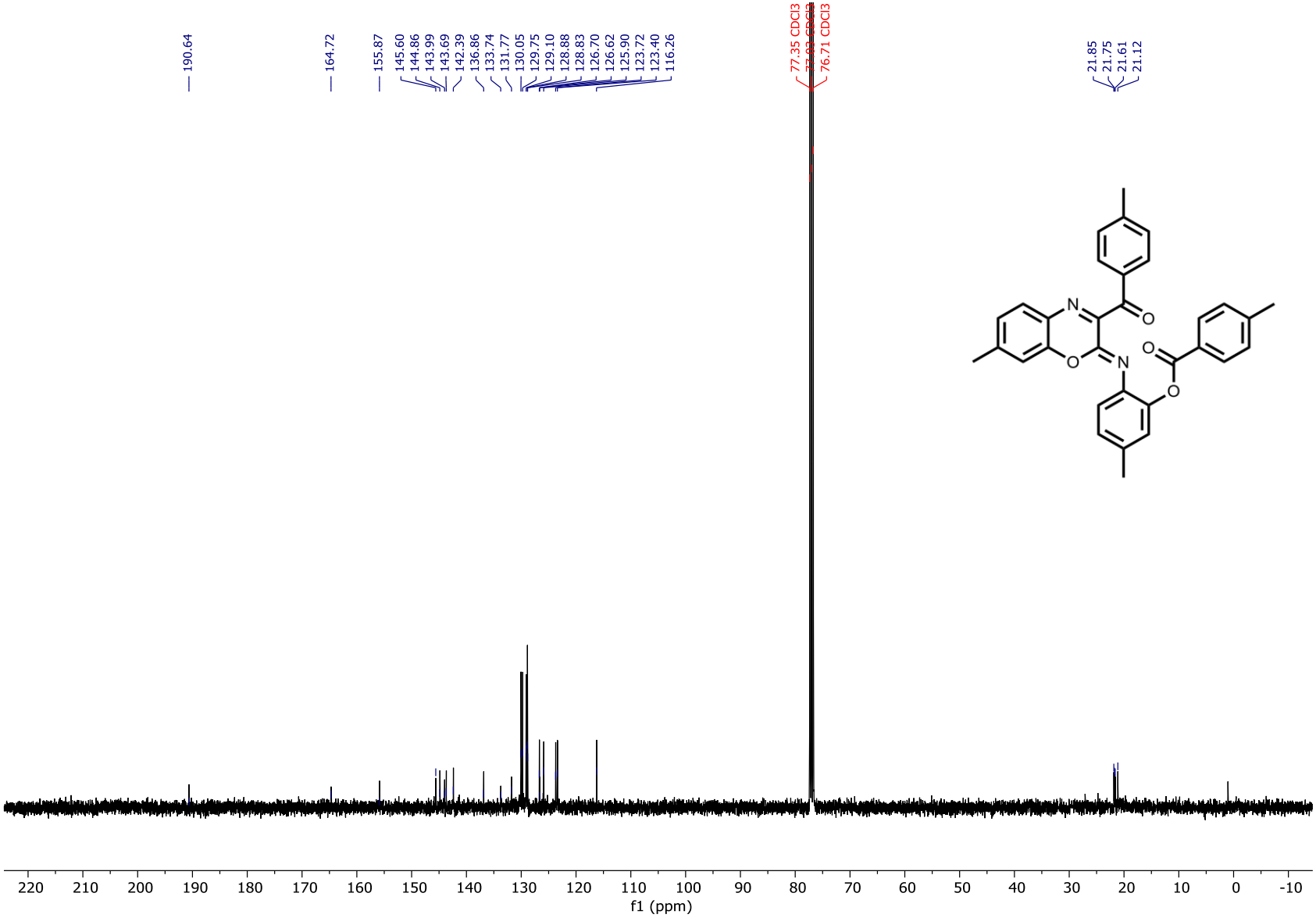

Figure S58. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-methyl-2-((7-methyl-3-(4-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methylbenzoate (2c).

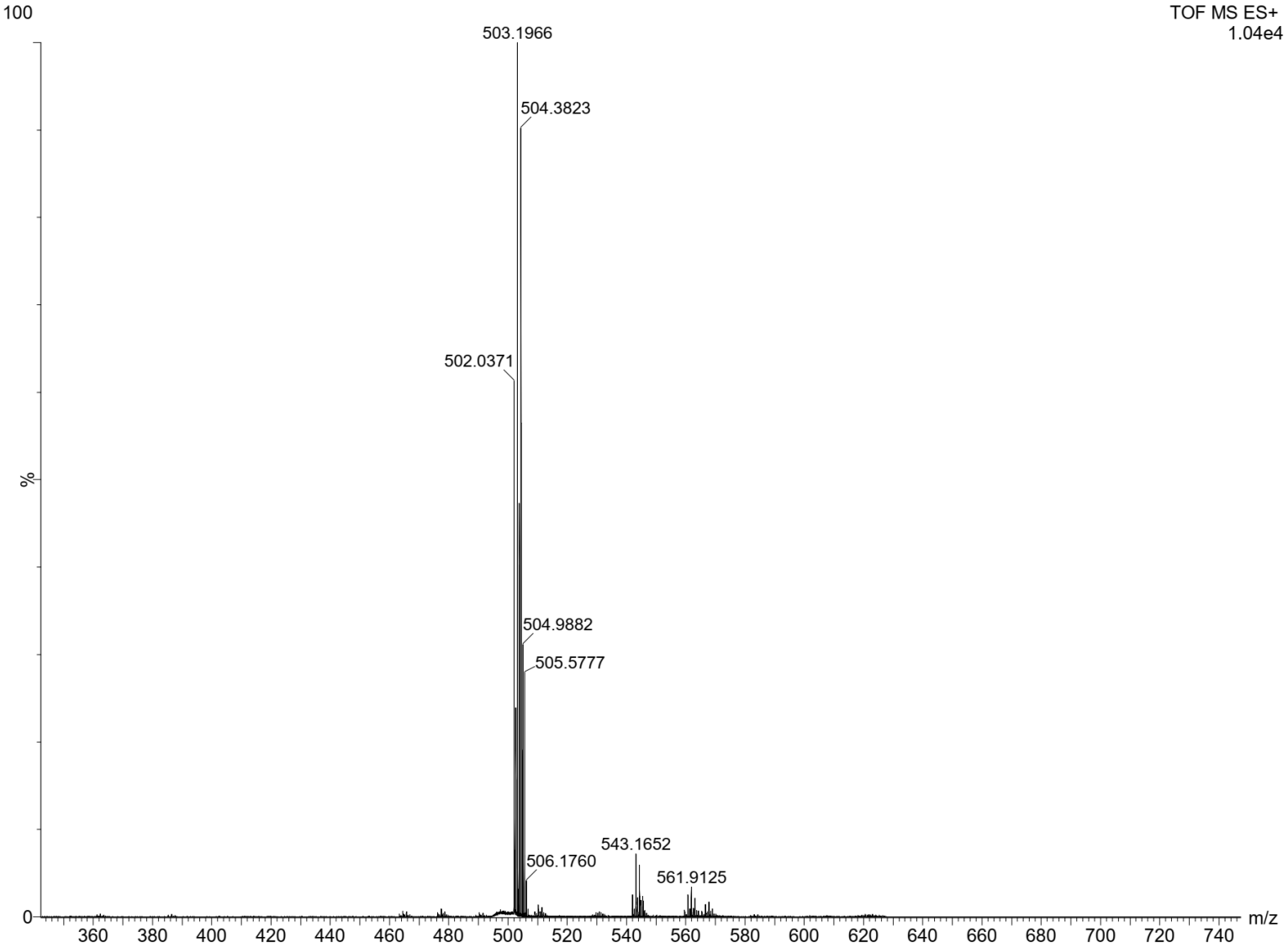

Figure S59. HRMS-ESI (Z)-5-methyl-2-((7-methyl-3-(4-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methylbenzoate (2c).

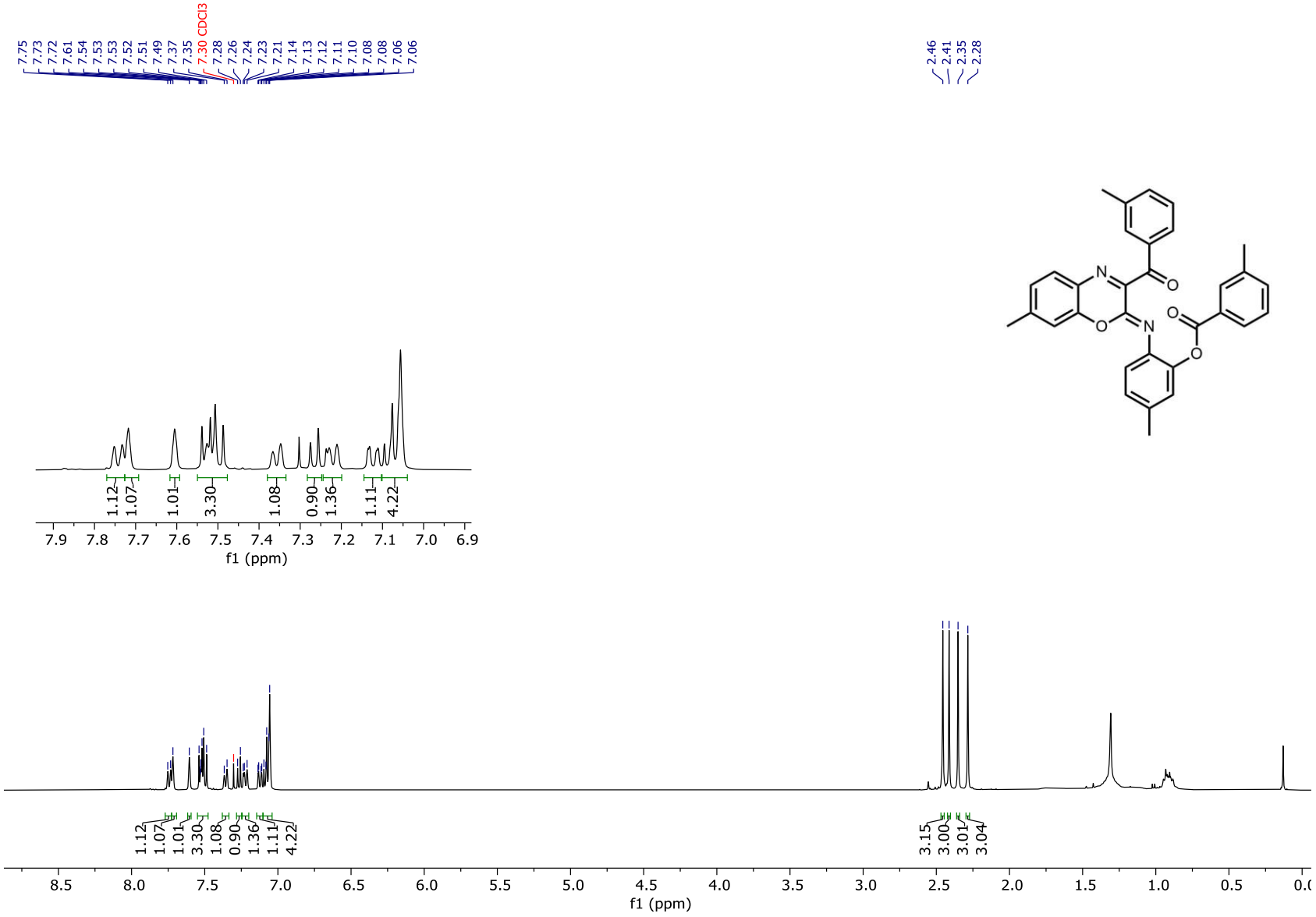

Figure S60. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-5-methyl-2-((7-methyl-3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2d).

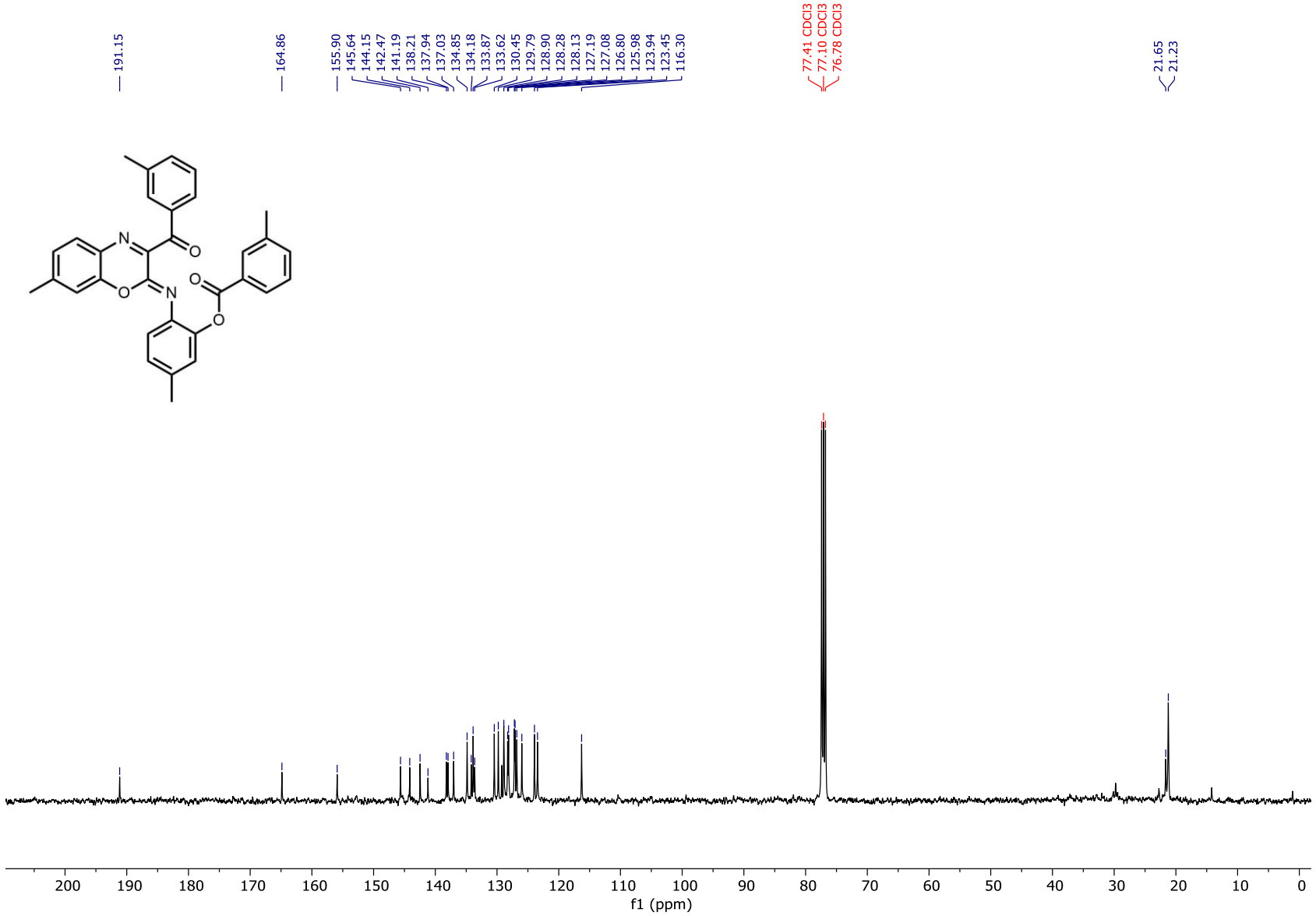

Figure S61. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-methyl-2-((7-methyl-3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2d).

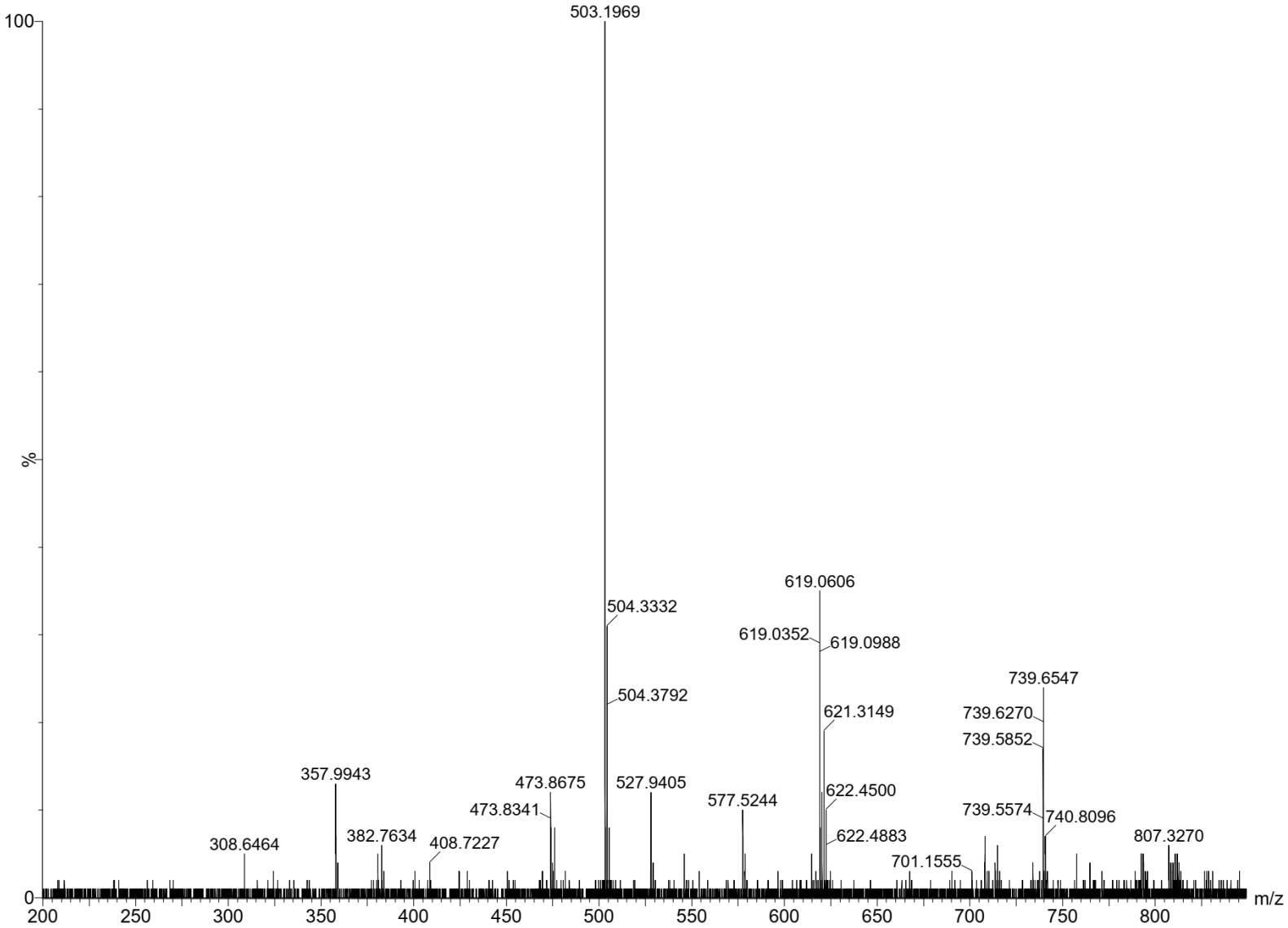

Figure S62. HRMS-ESI (Z)-5-methyl-2-((7-methyl-3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2d).

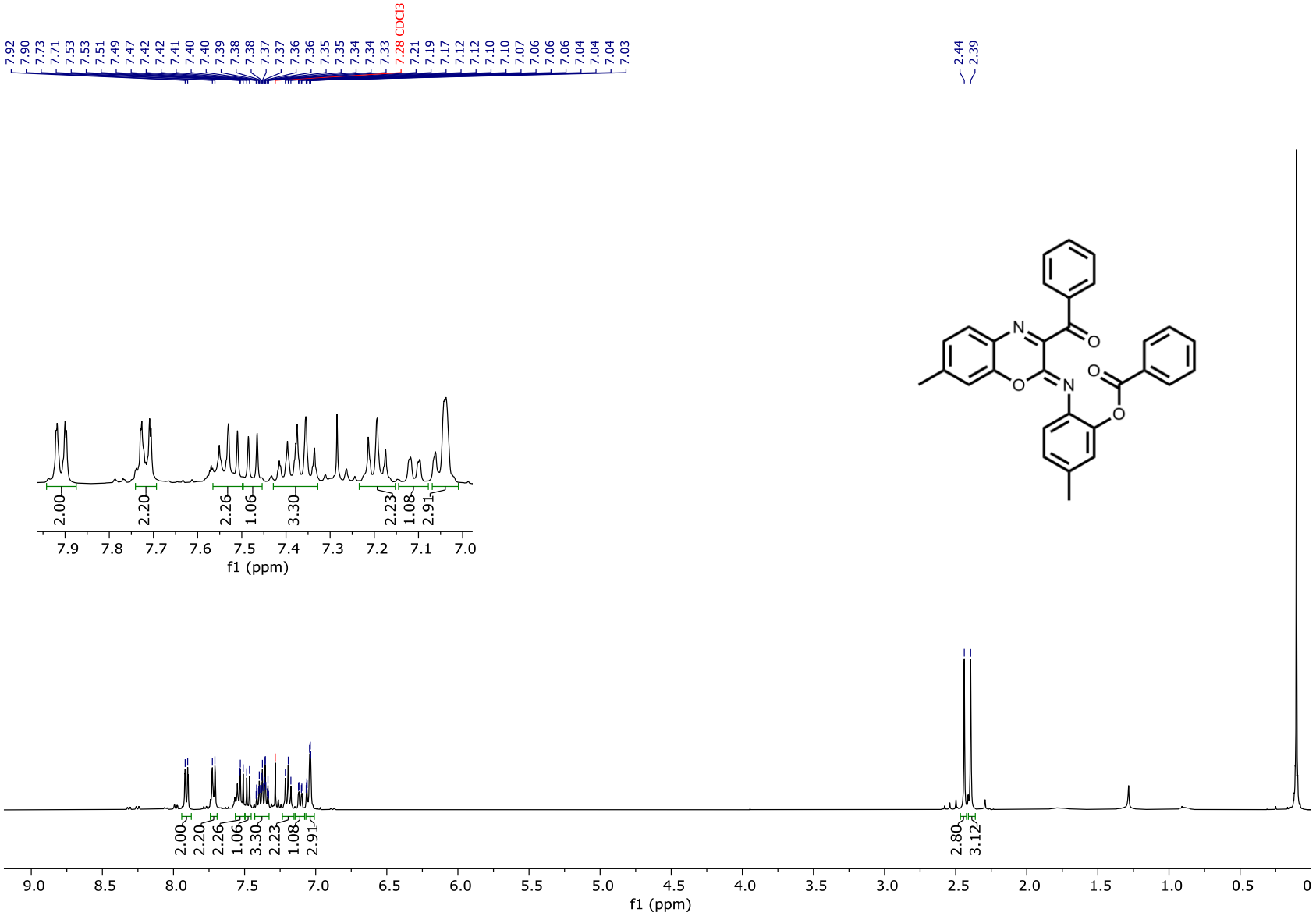

Figure S63. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl benzoate (2e).

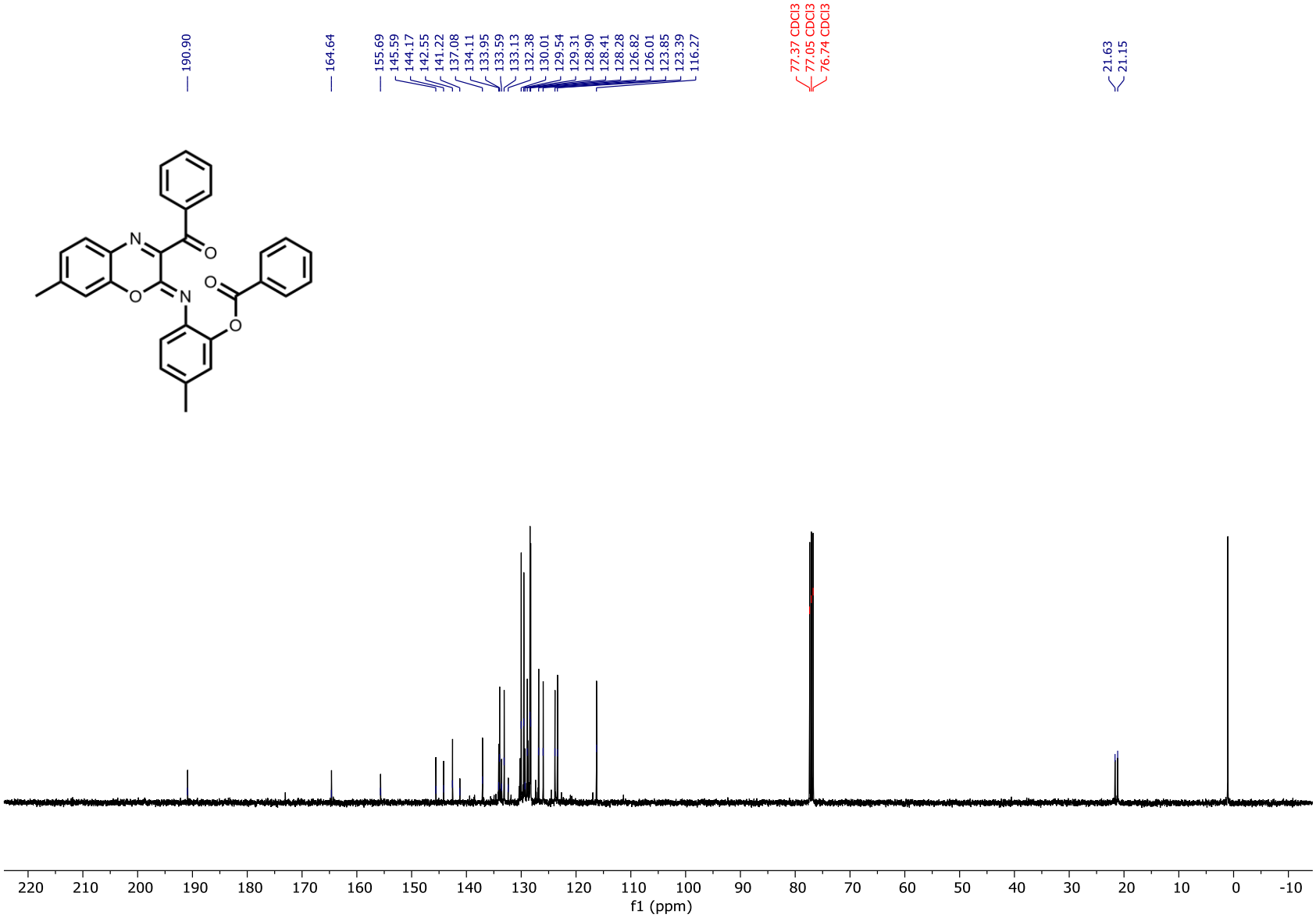

Figure S64. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl benzoate (2e).

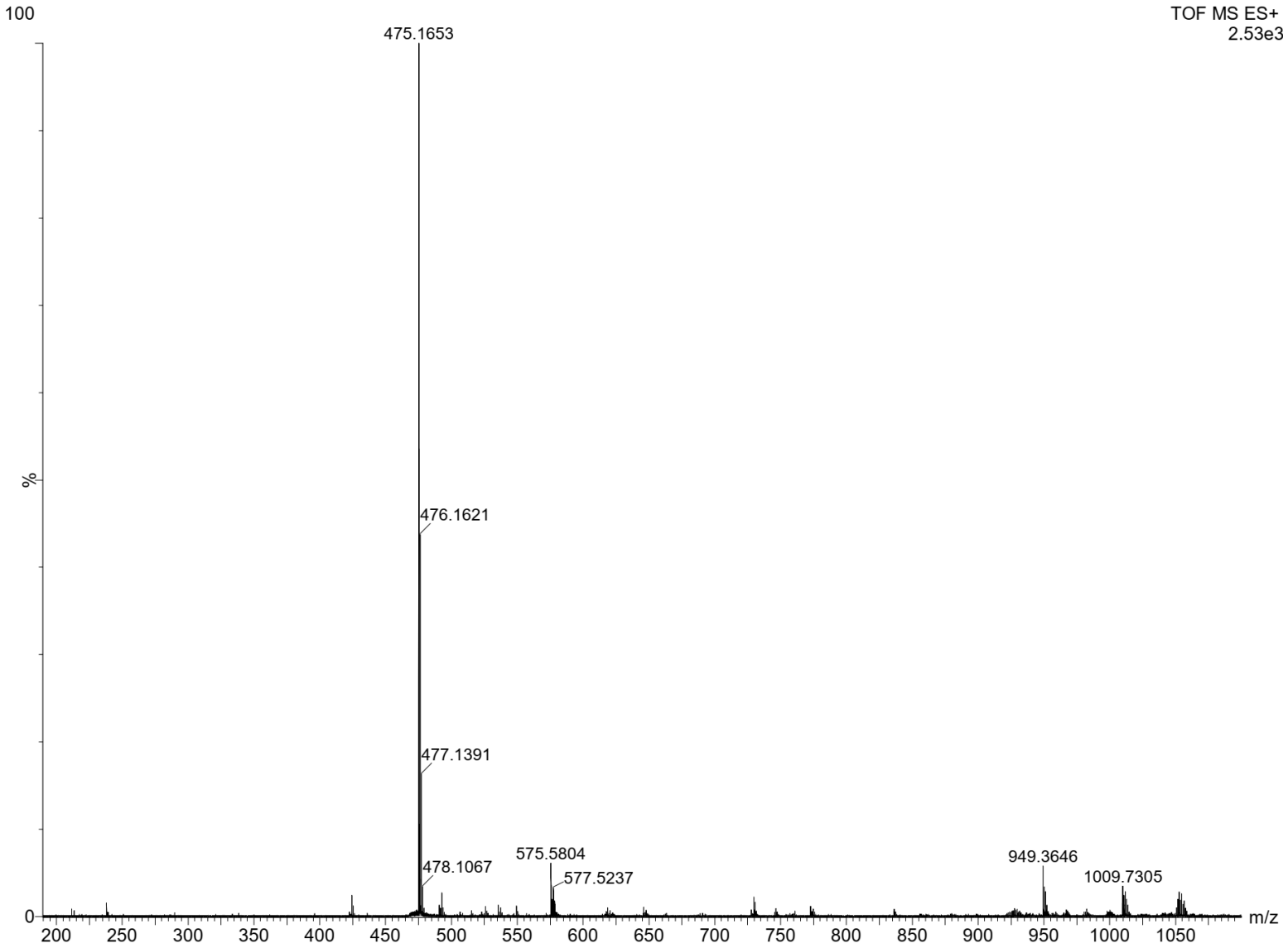

Figure S65. HRMS-ESI (Z)-2-((3-benzoyl-7-methyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methylphenyl benzoate (2e).

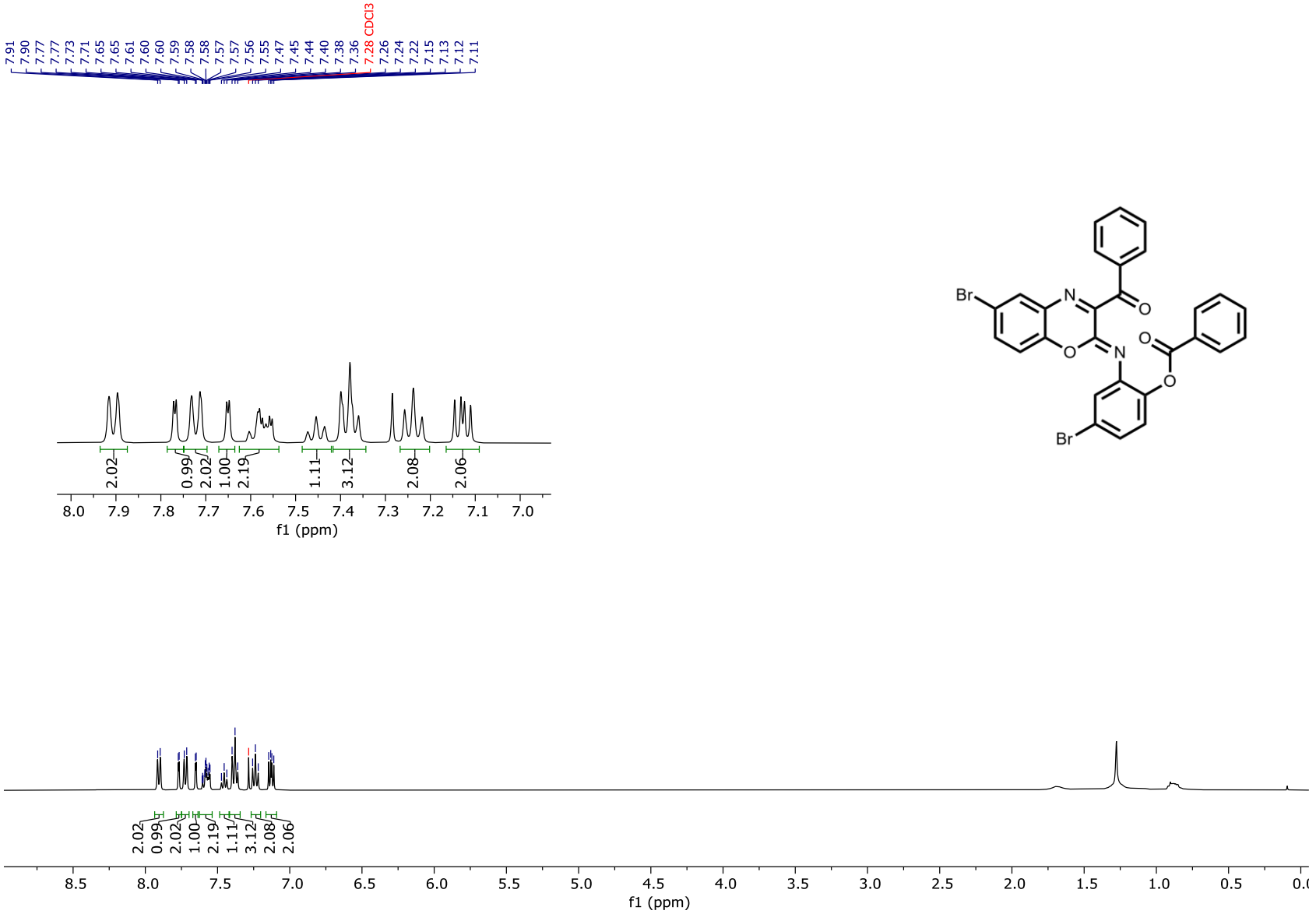

Figure S66. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-6-bromo-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-4-bromophenyl benzoate (2f).

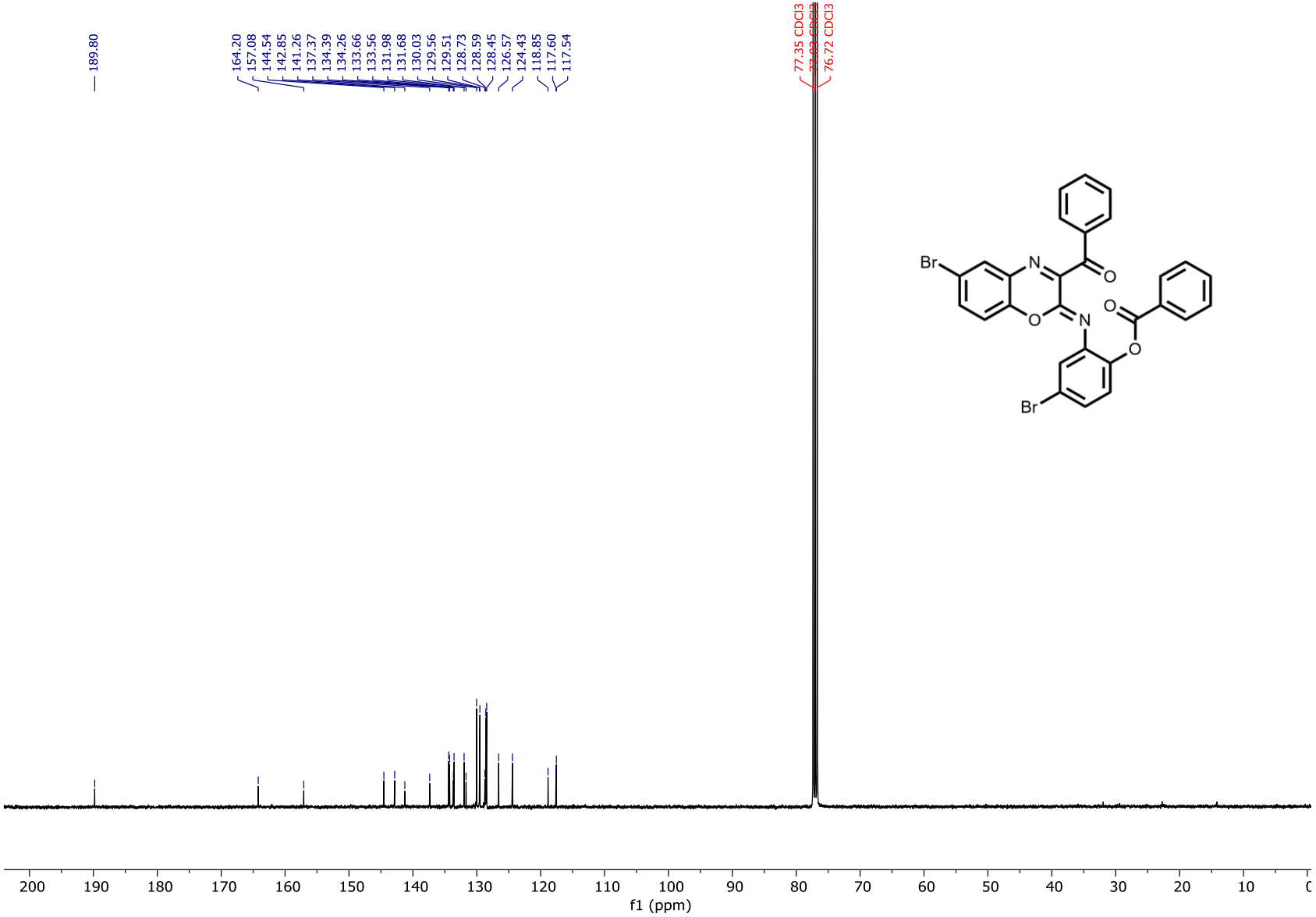

Figure S67. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-6-bromo-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-4-bromophenyl benzoate (2f).

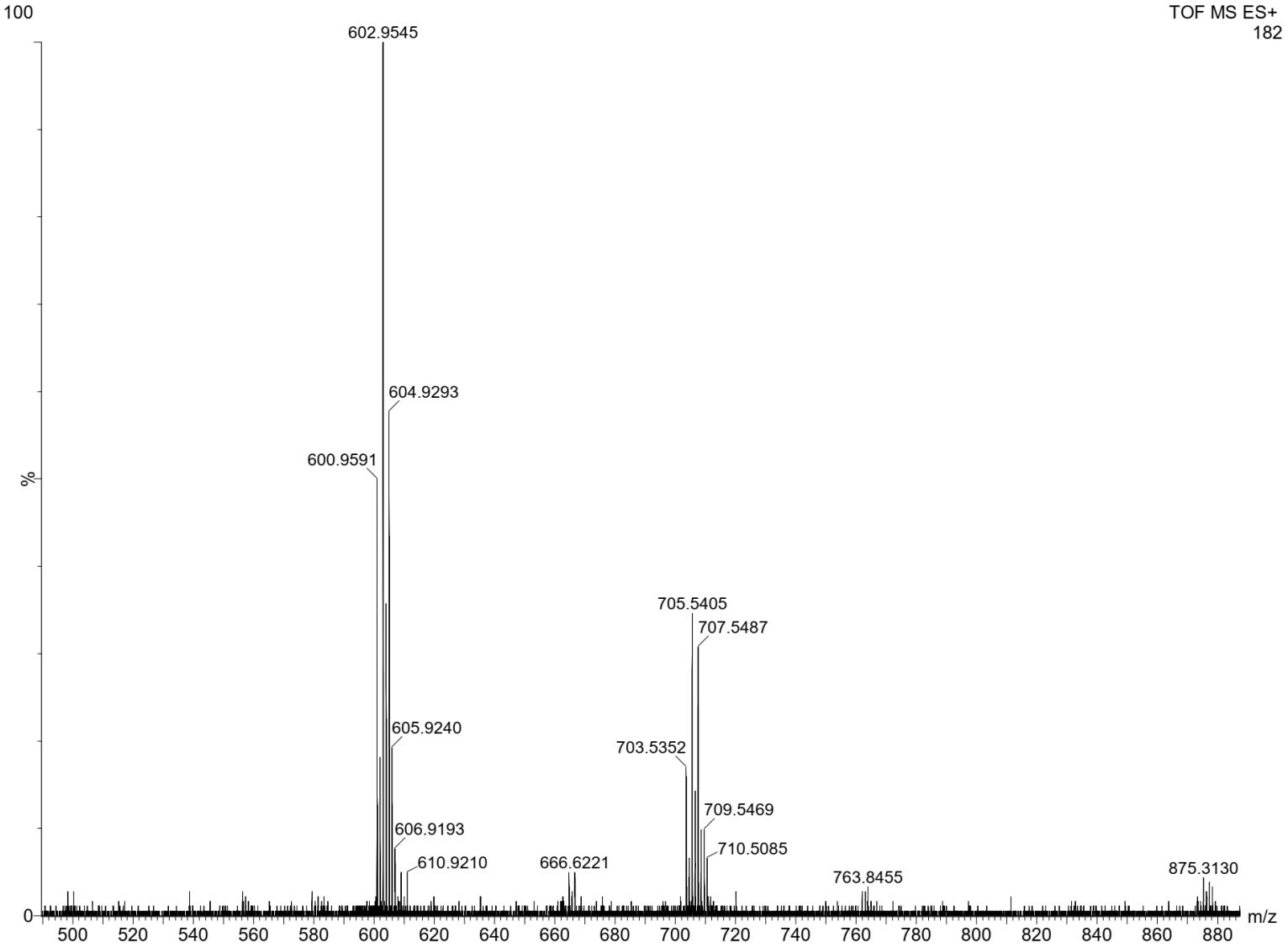

Figure S68. HRMS-ESI (Z)-2-((3-benzoyl-6-bromo-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-4-bromophenyl benzoate (2f).

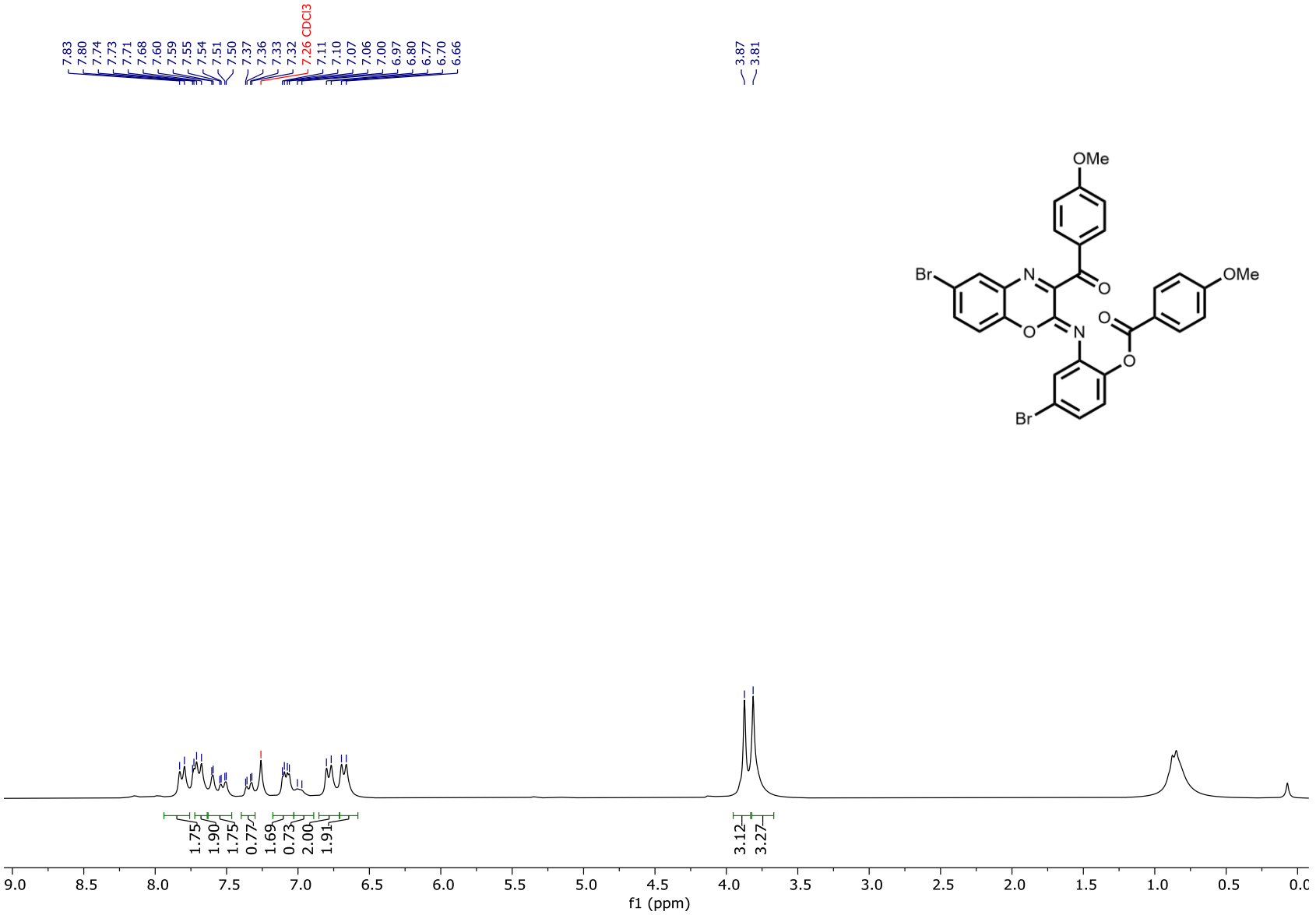

Figure S69. ^{1}H NMR (250 MHz, $CDCl_3$) (Z)-4-bromo-2-((6-bromo-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2g).

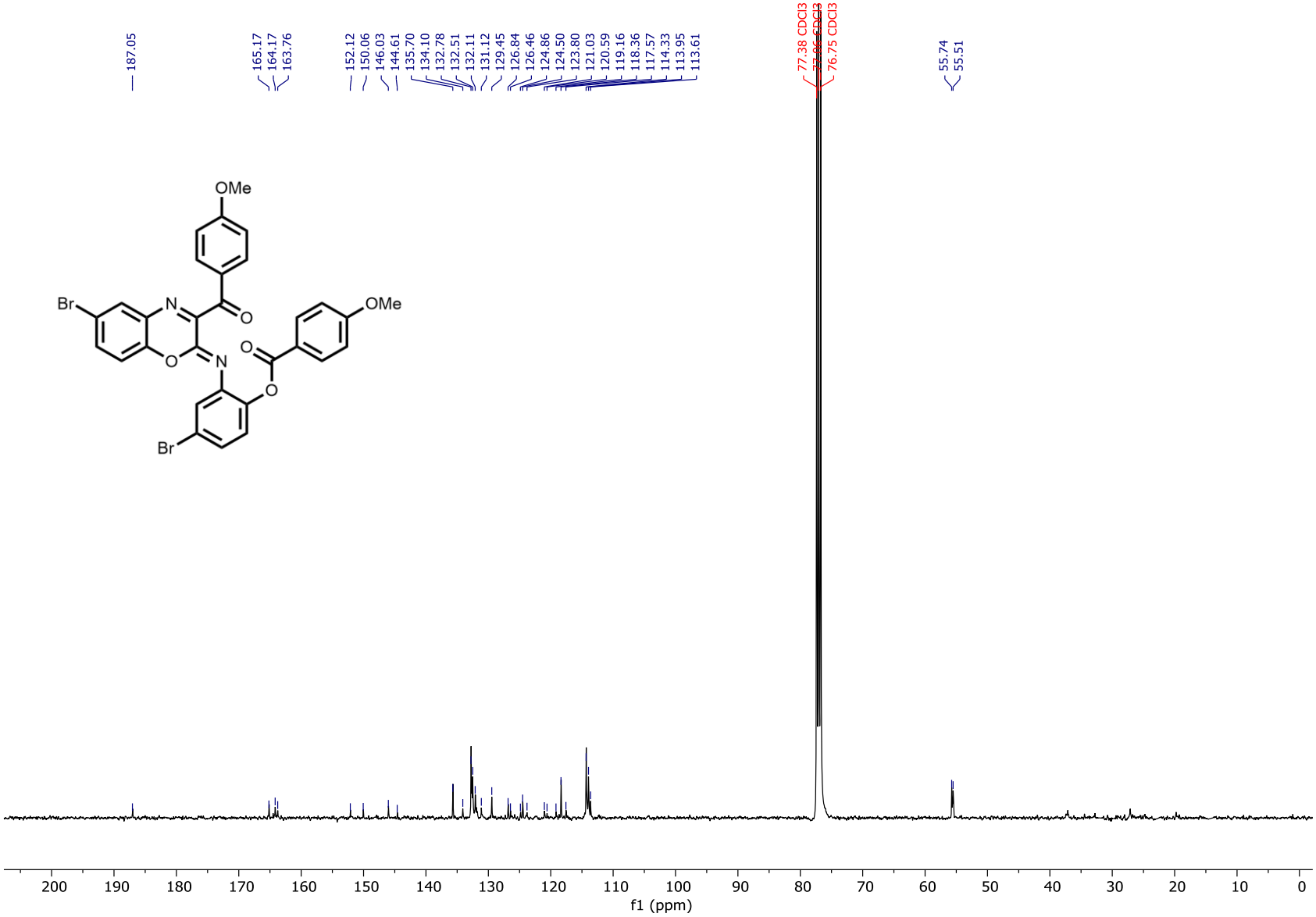

Figure S70. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-4-bromo-2-((6-bromo-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2g).

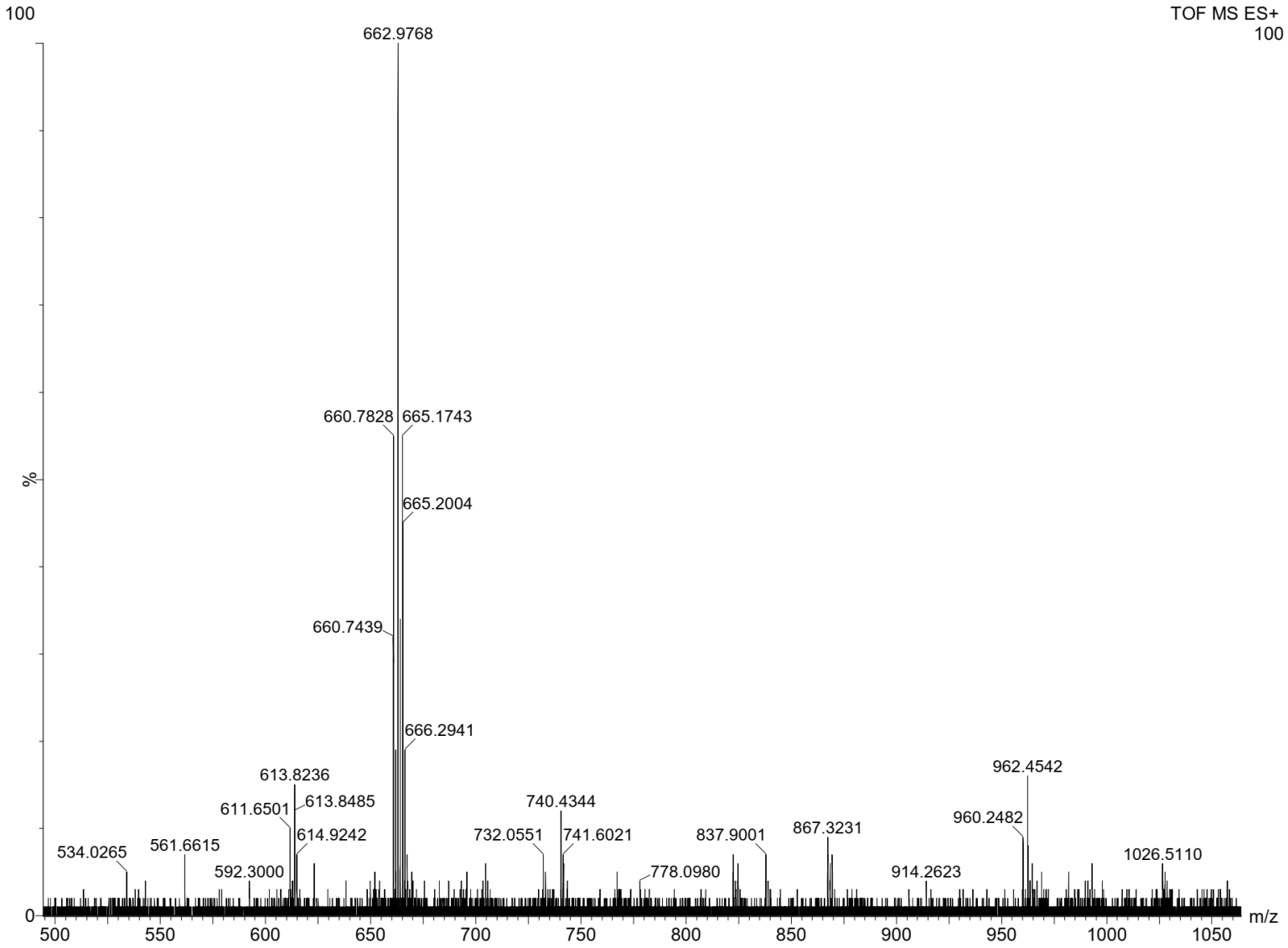

Figure S71. HRMS-ESI (Z)-4-bromo-2-((6-bromo-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2g).

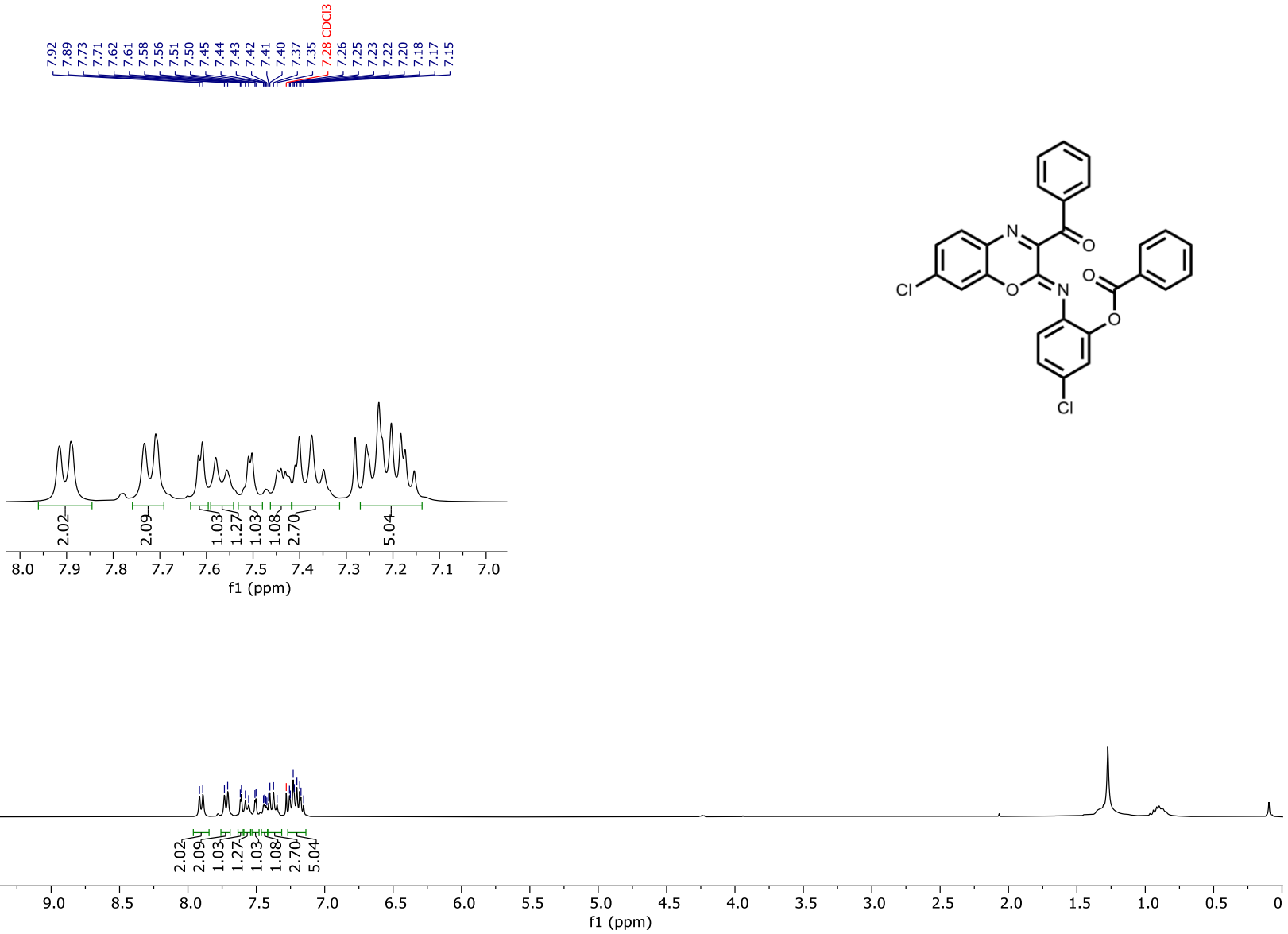

Figure S72. ^{1}H NMR (300 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-chloro-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-chlorophenyl benzoate (2h).

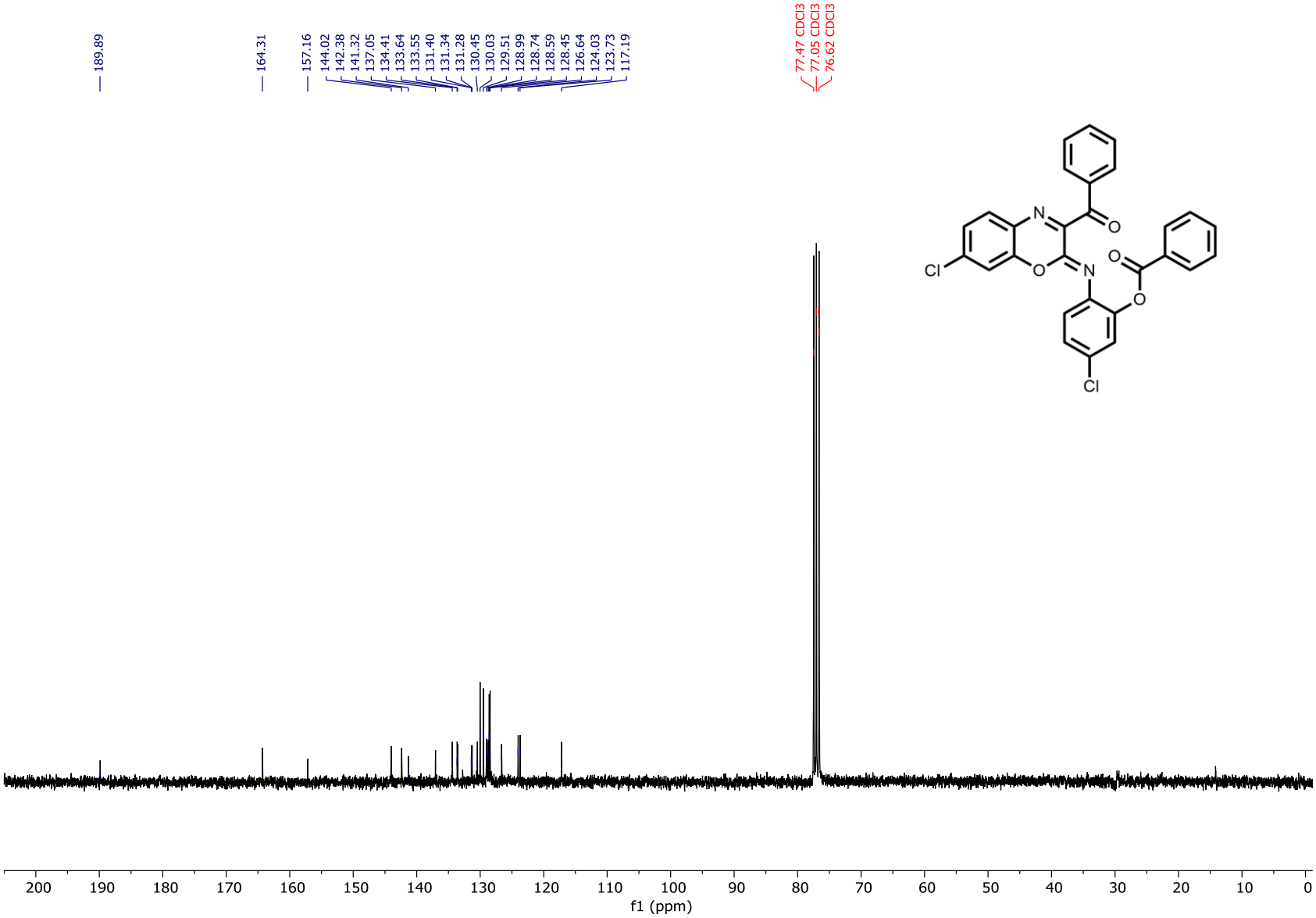

Figure S73. ^{13}C NMR (75 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-chloro-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-chlorophenyl benzoate (2h).

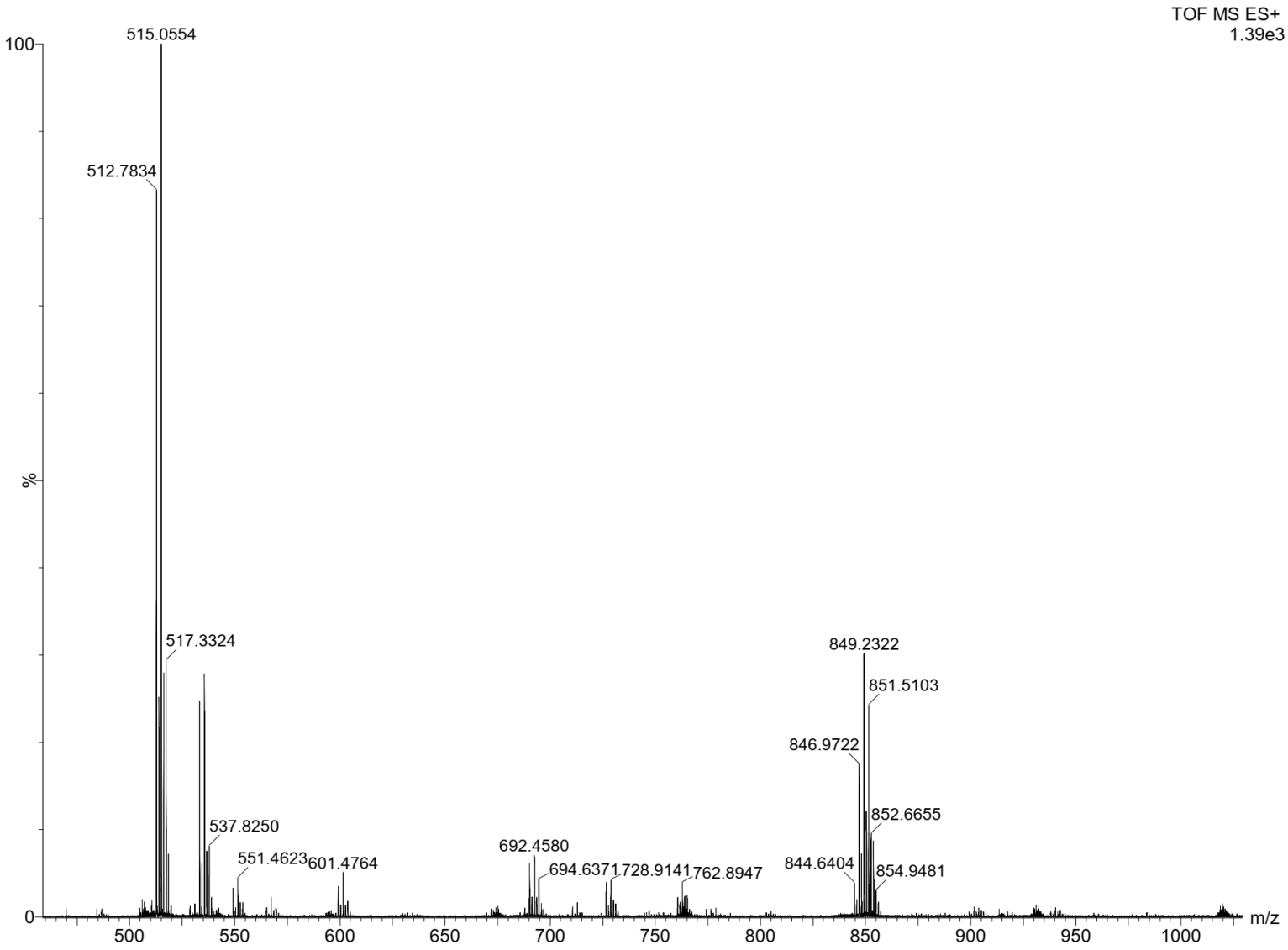

Figure S74. HRMS-ESI (Z)-2-((3-benzoyl-7-chloro-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-chlorophenyl benzoate (2h).

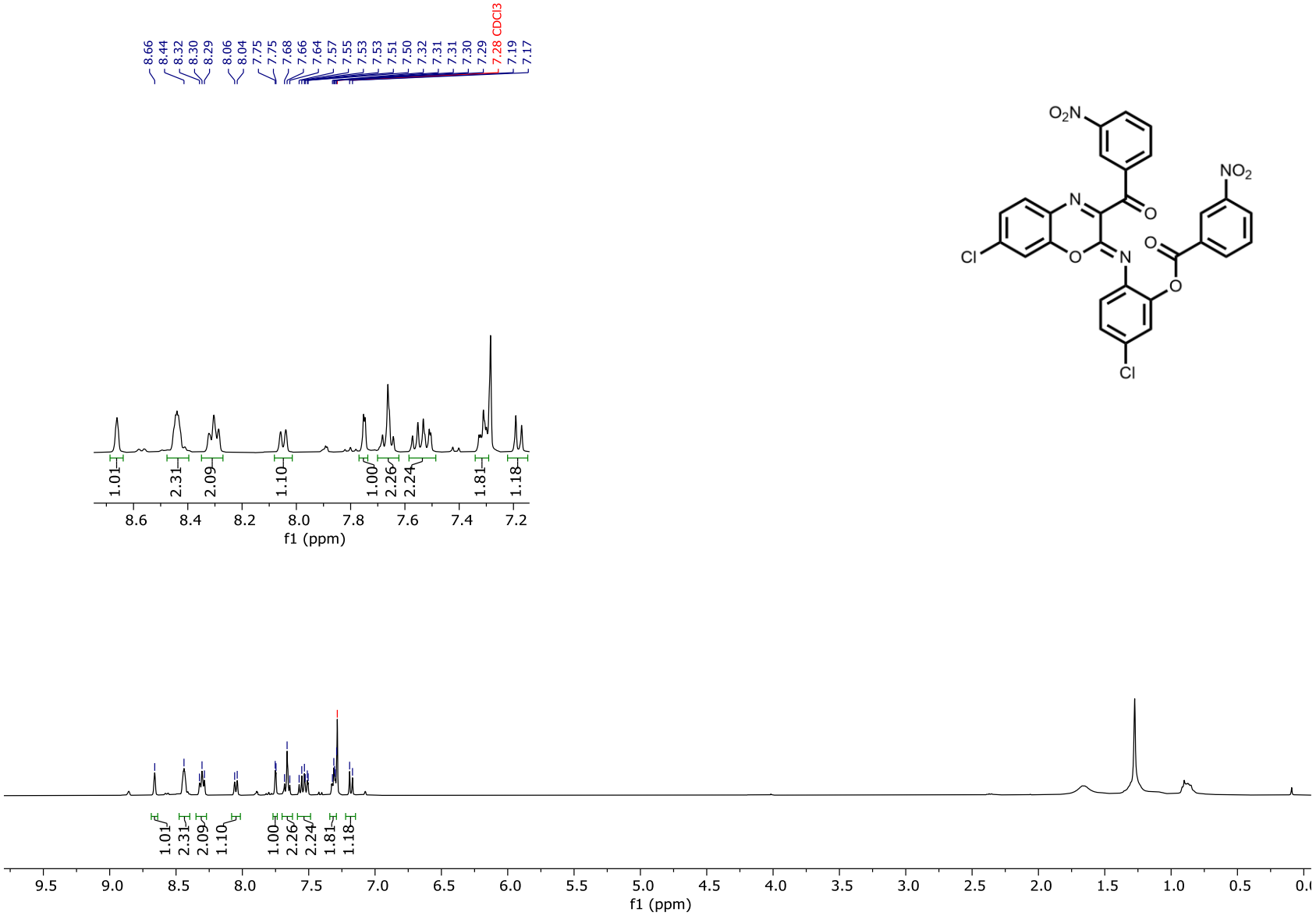

Figure S75. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(3-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-nitrobenzoate (2i).

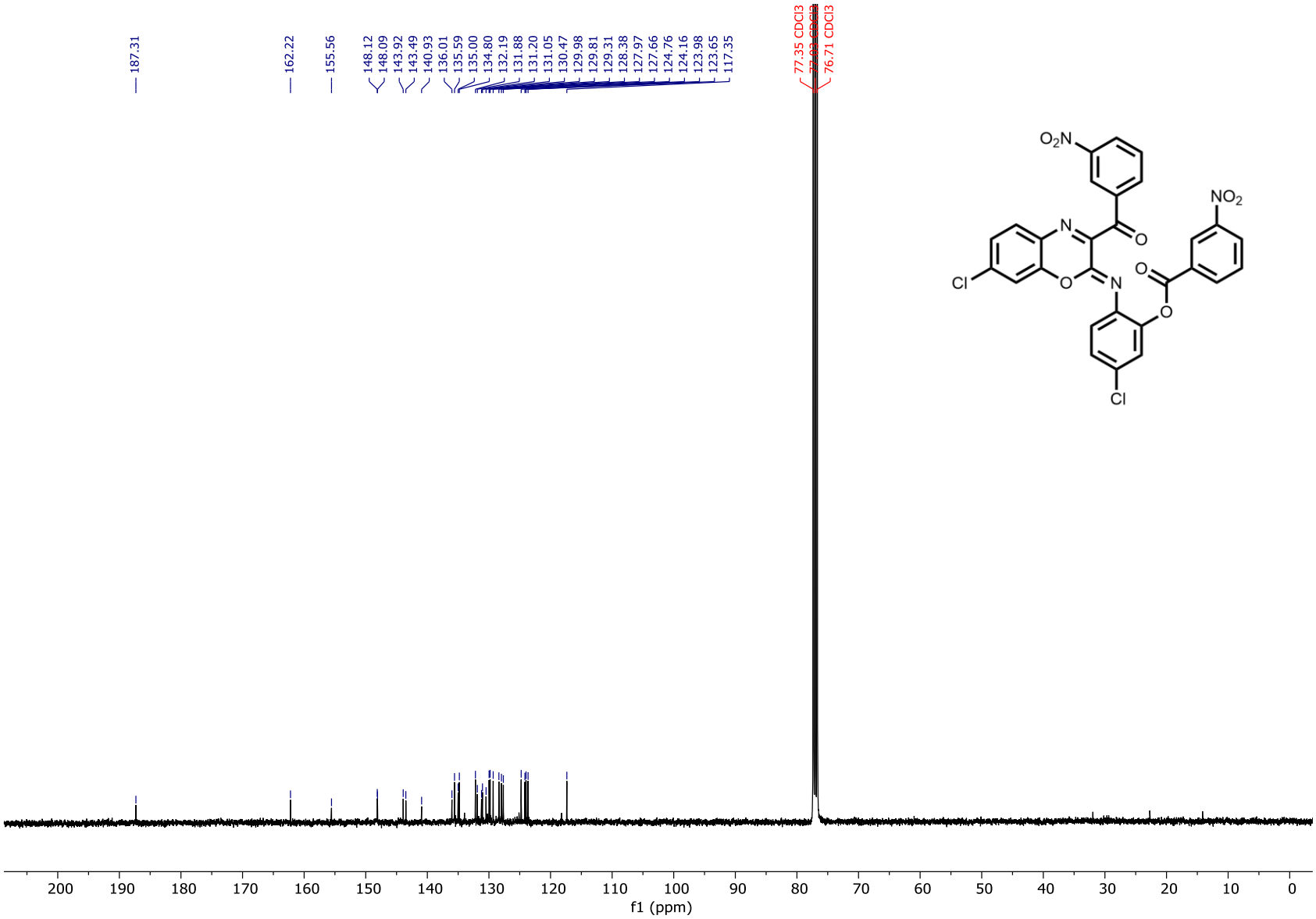

Figure S76. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(3-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-nitrobenzoate (2i).

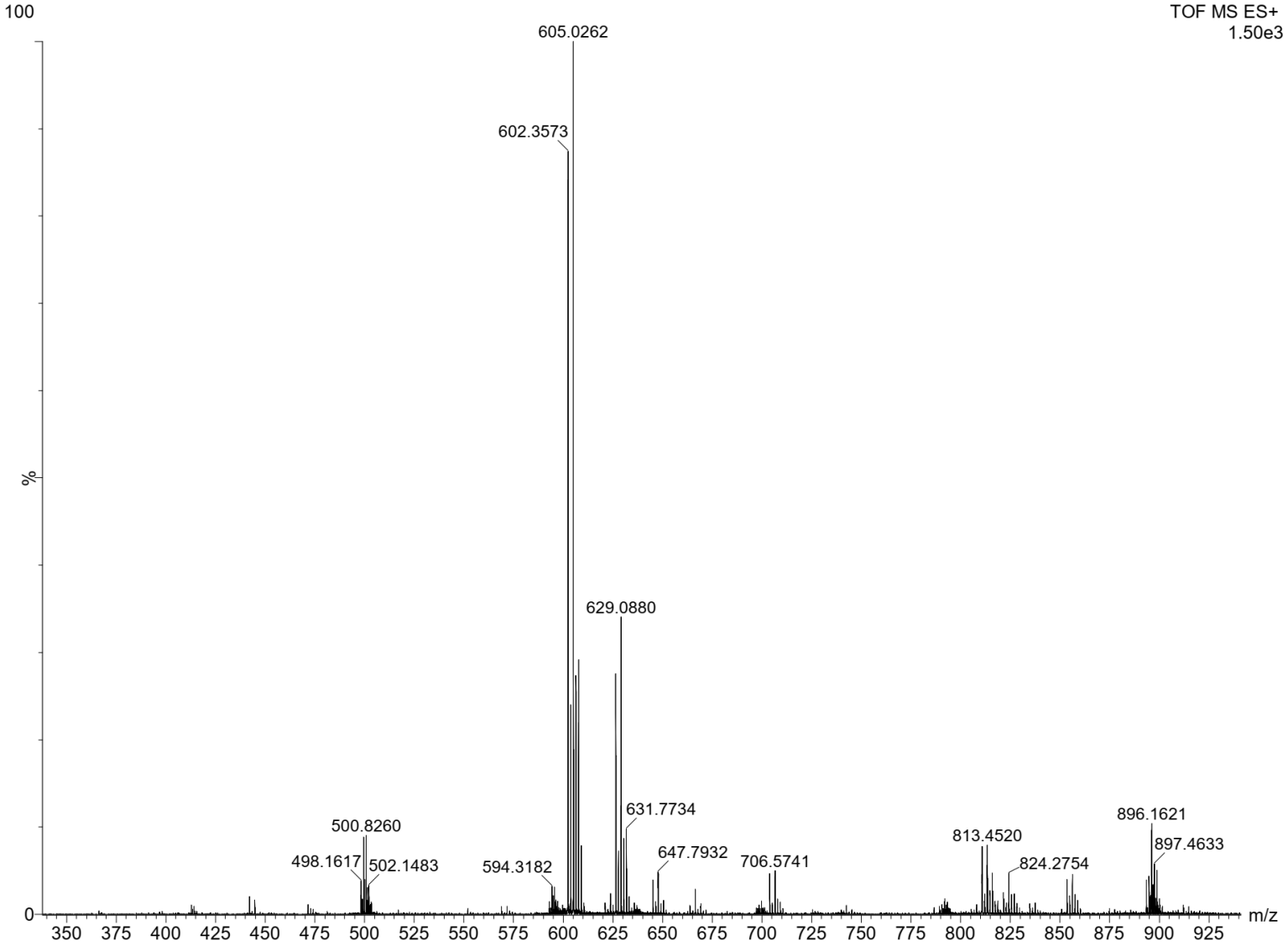

Figure S77. HRMS-ESI (Z)-5-chloro-2-((7-chloro-3-(3-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-nitrobenzoate (2i).

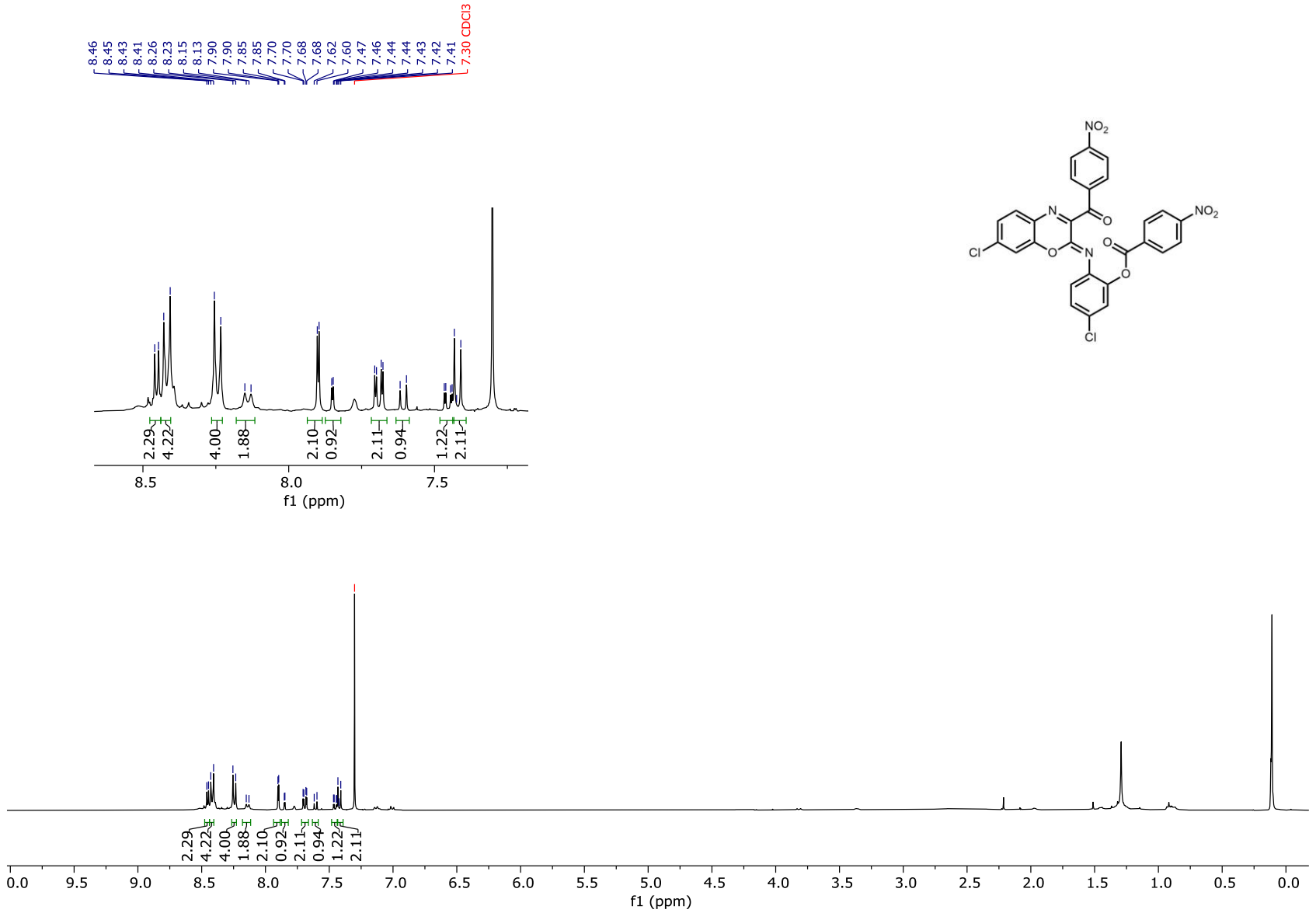

Figure S78. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2j).

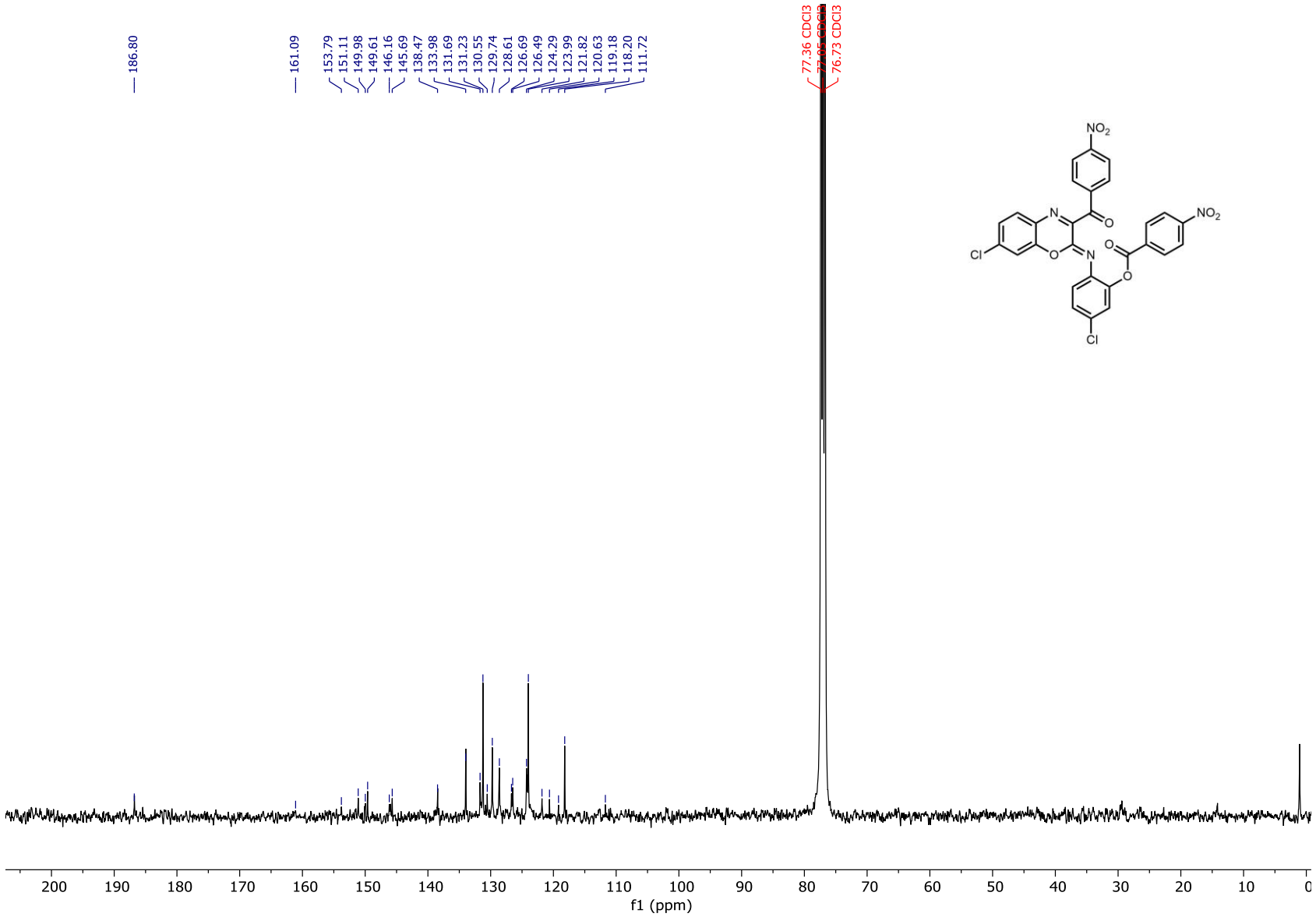

Figure S79. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2j).

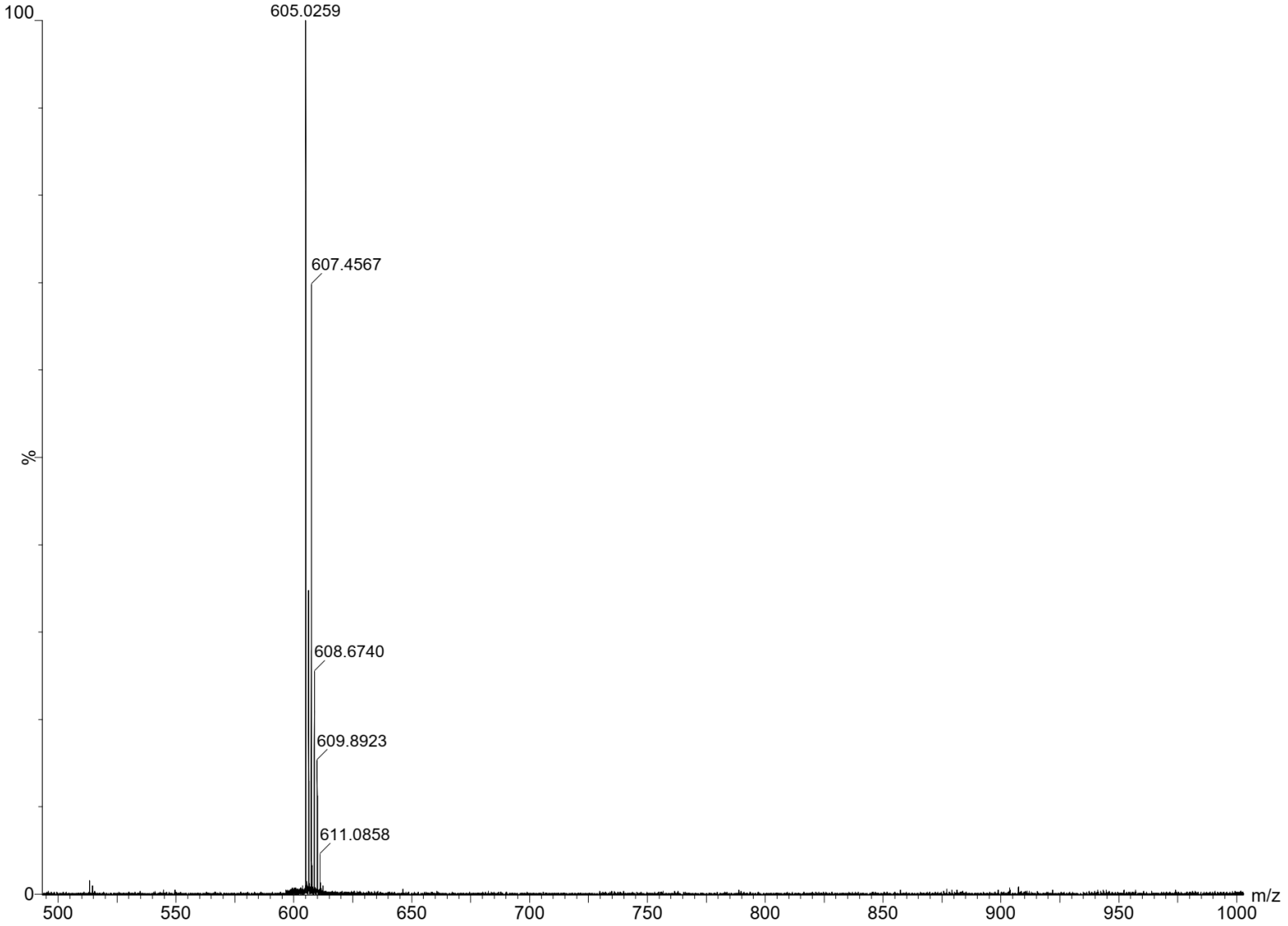

Figure S80. HRMS-ESI (Z)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2j).

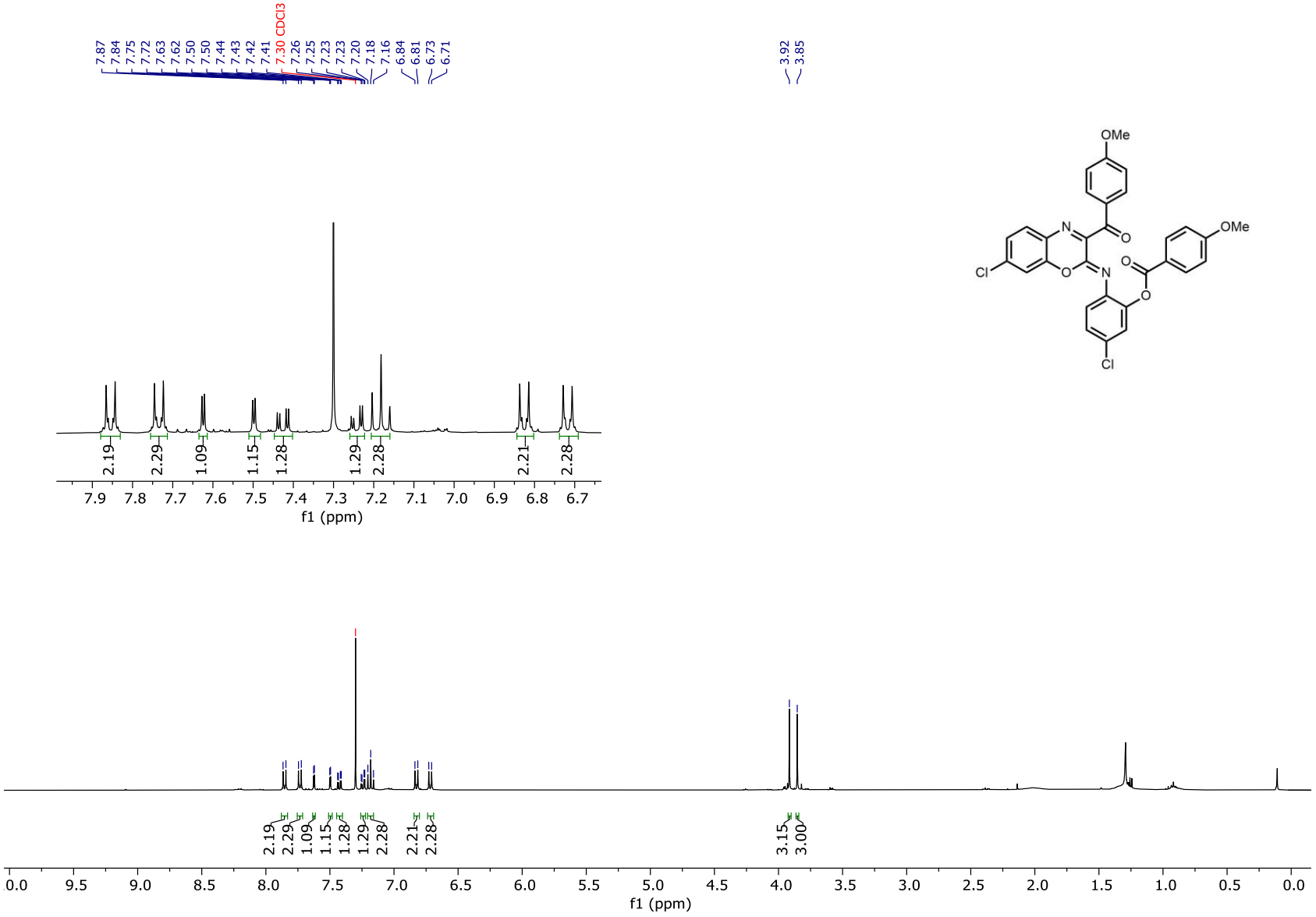

Figure S81. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2k).

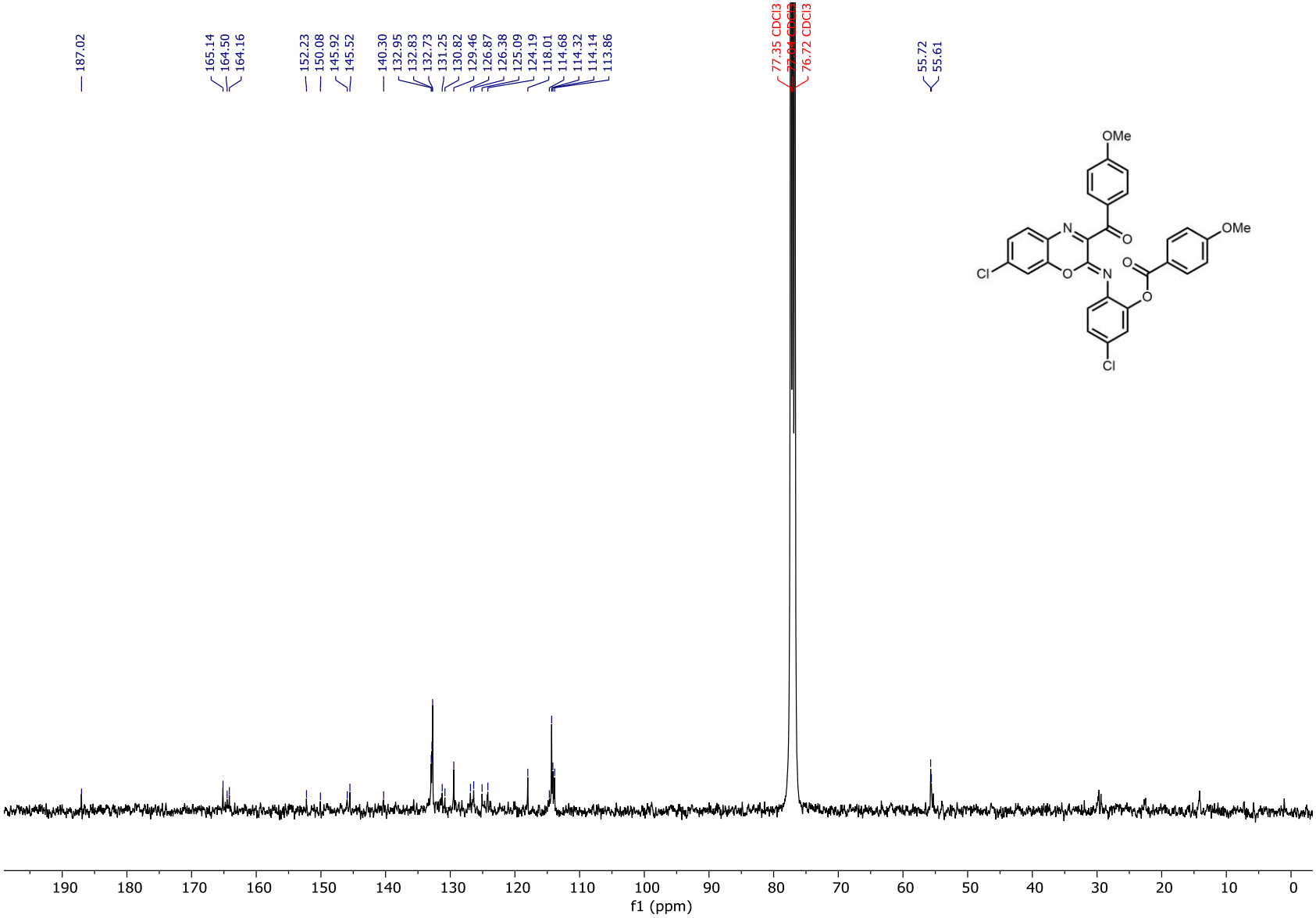

Figure S82. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2k).

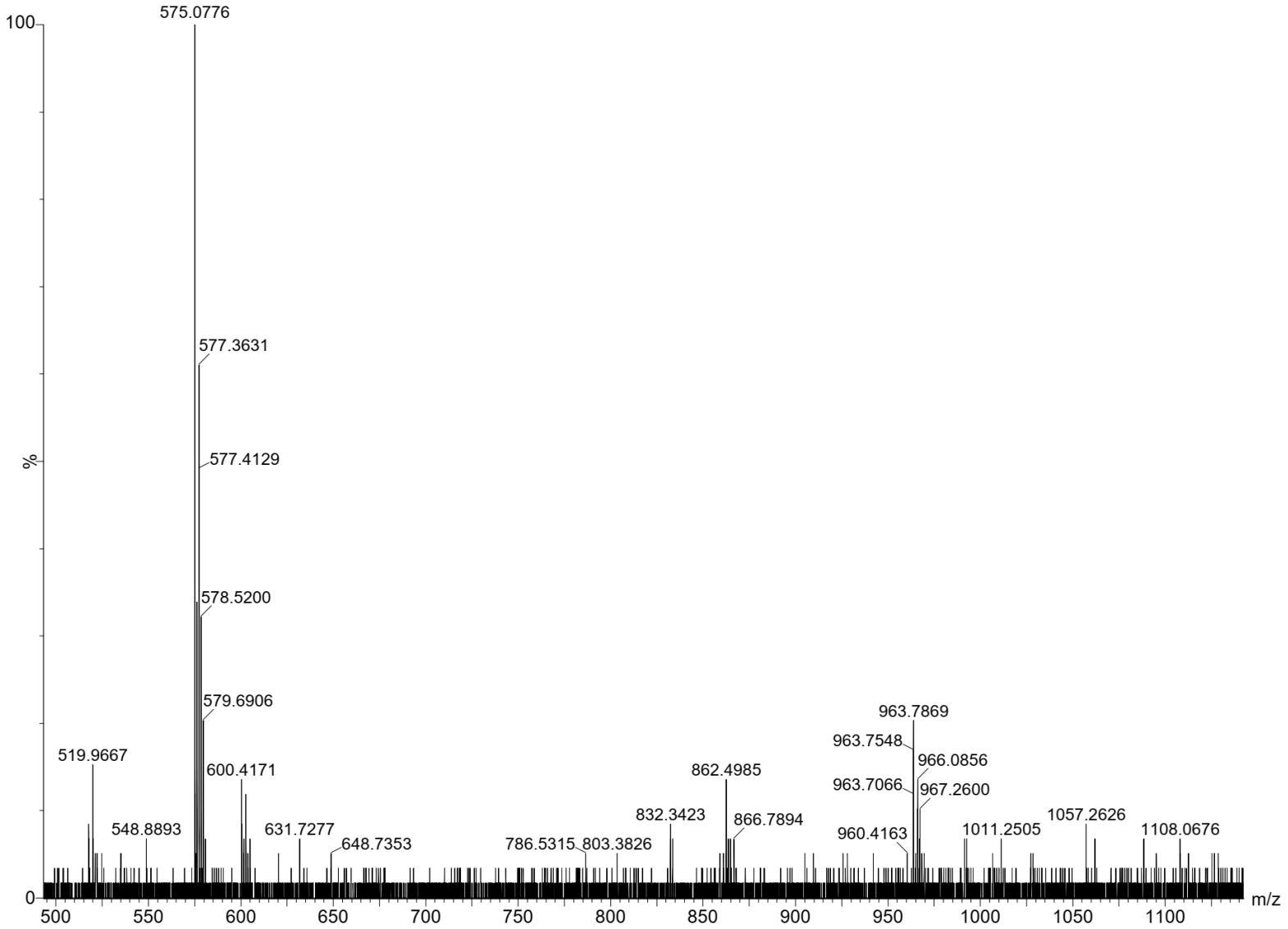

Figure S83. HRMS-ESI (Z)-5-chloro-2-((7-chloro-3-(4-nitrobenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-nitrobenzoate (2k).

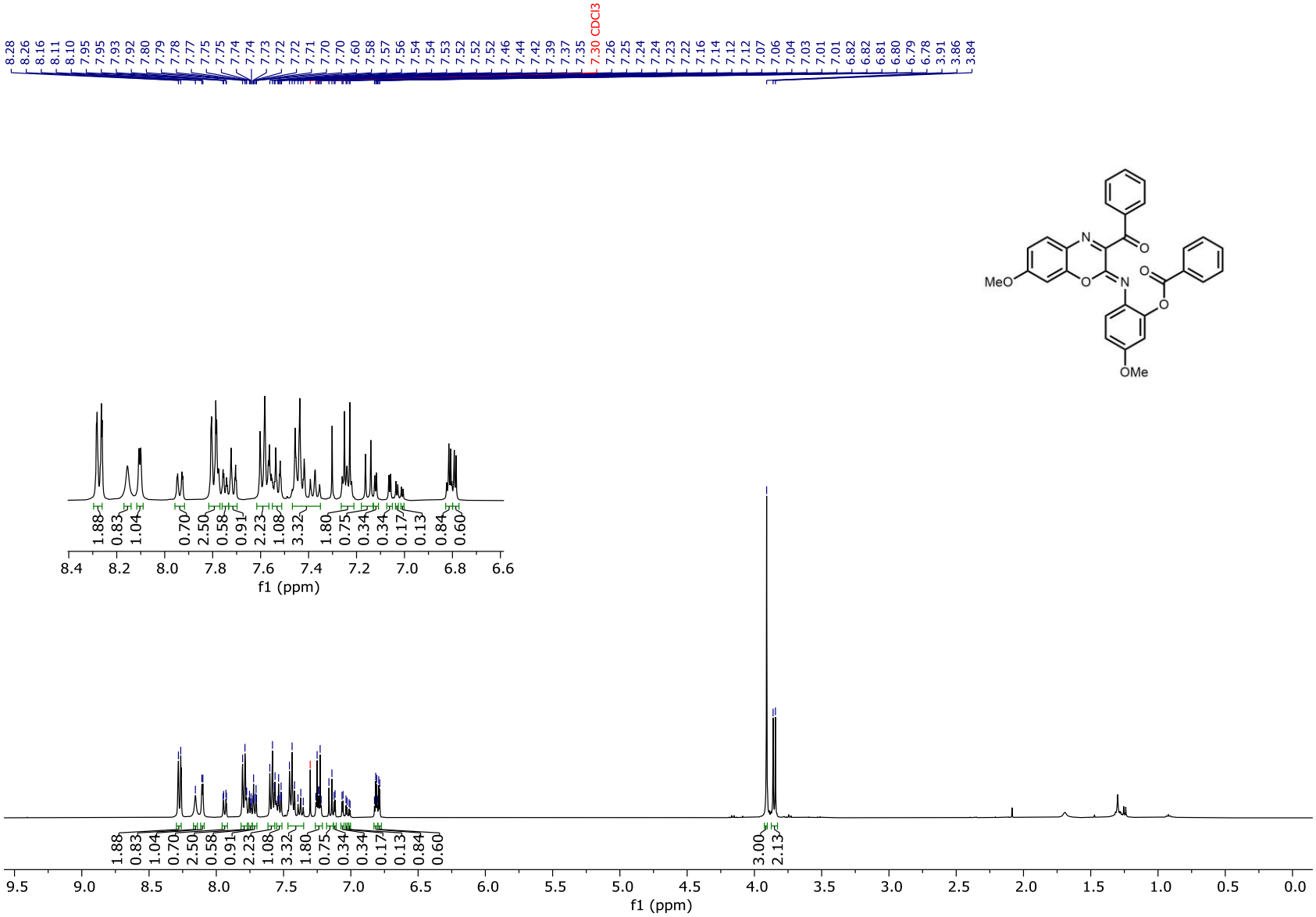

Figure S84. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-methoxy-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methoxyphenyl benzoate (2l).

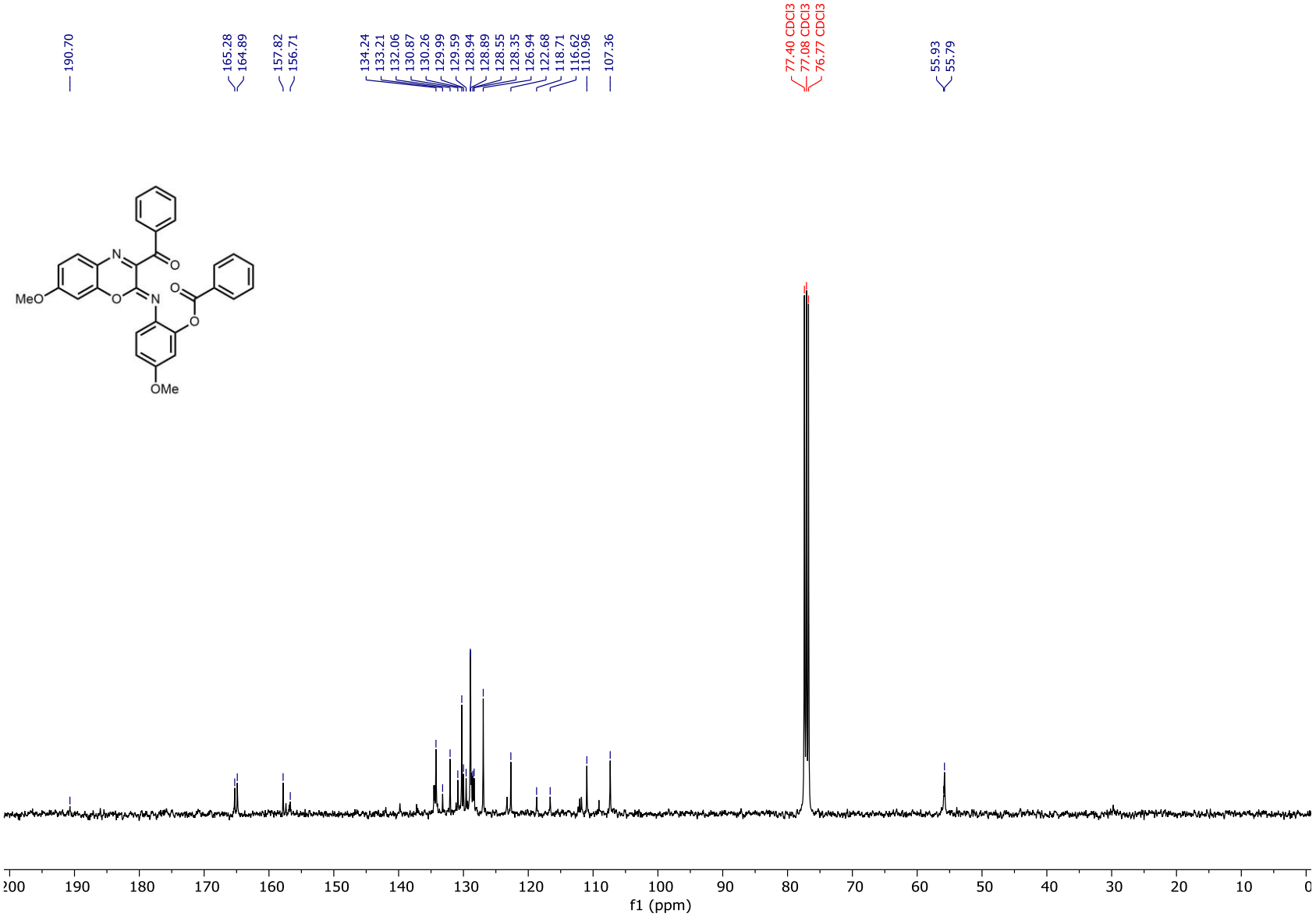

Figure S85. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-benzoyl-7-methoxy-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methoxyphenyl benzoate (2l).

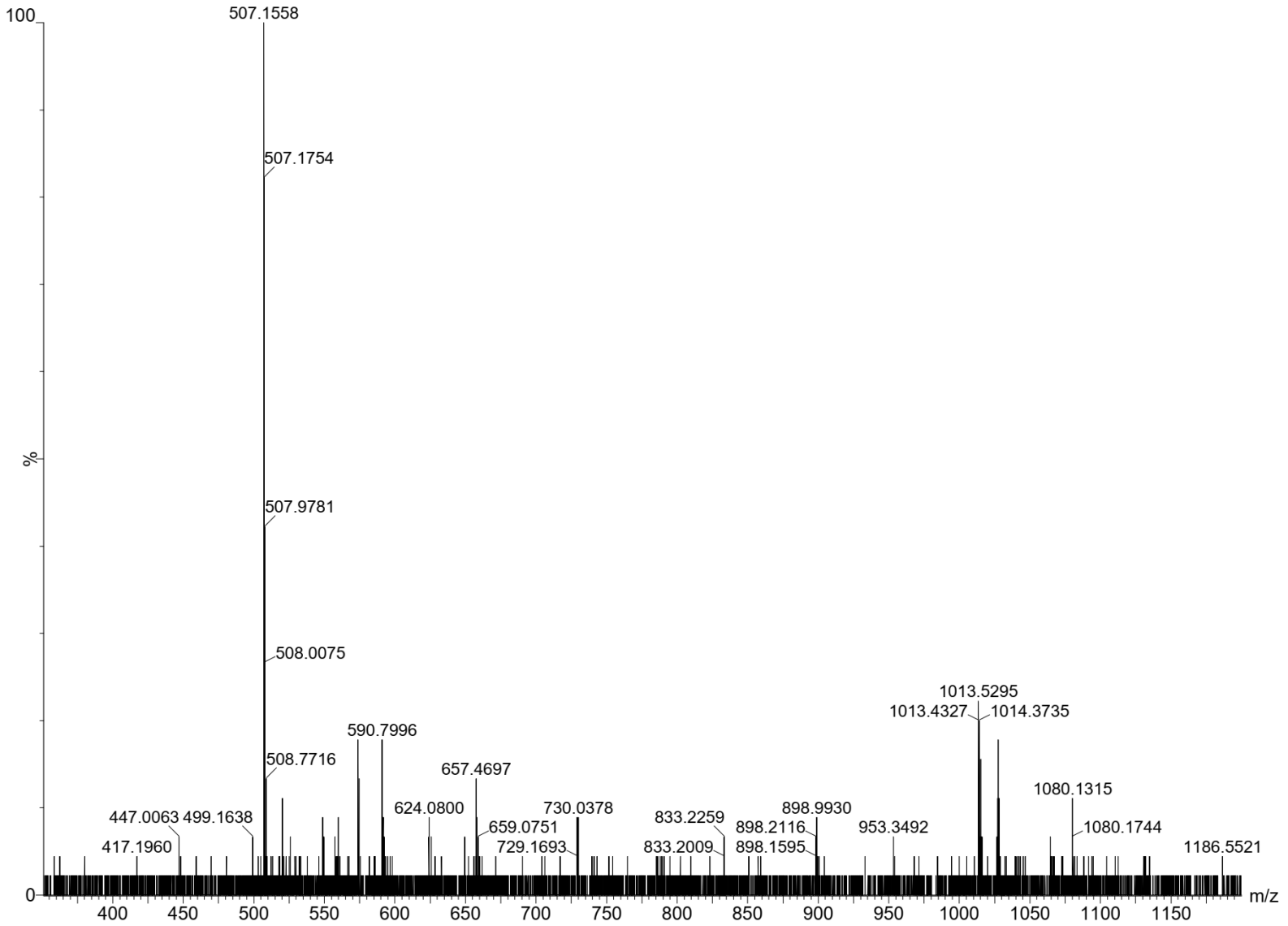

Figure S86. HRMS-ESI (Z)-2-((3-benzoyl-7-methoxy-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-5-methoxyphenyl benzoate (2l).

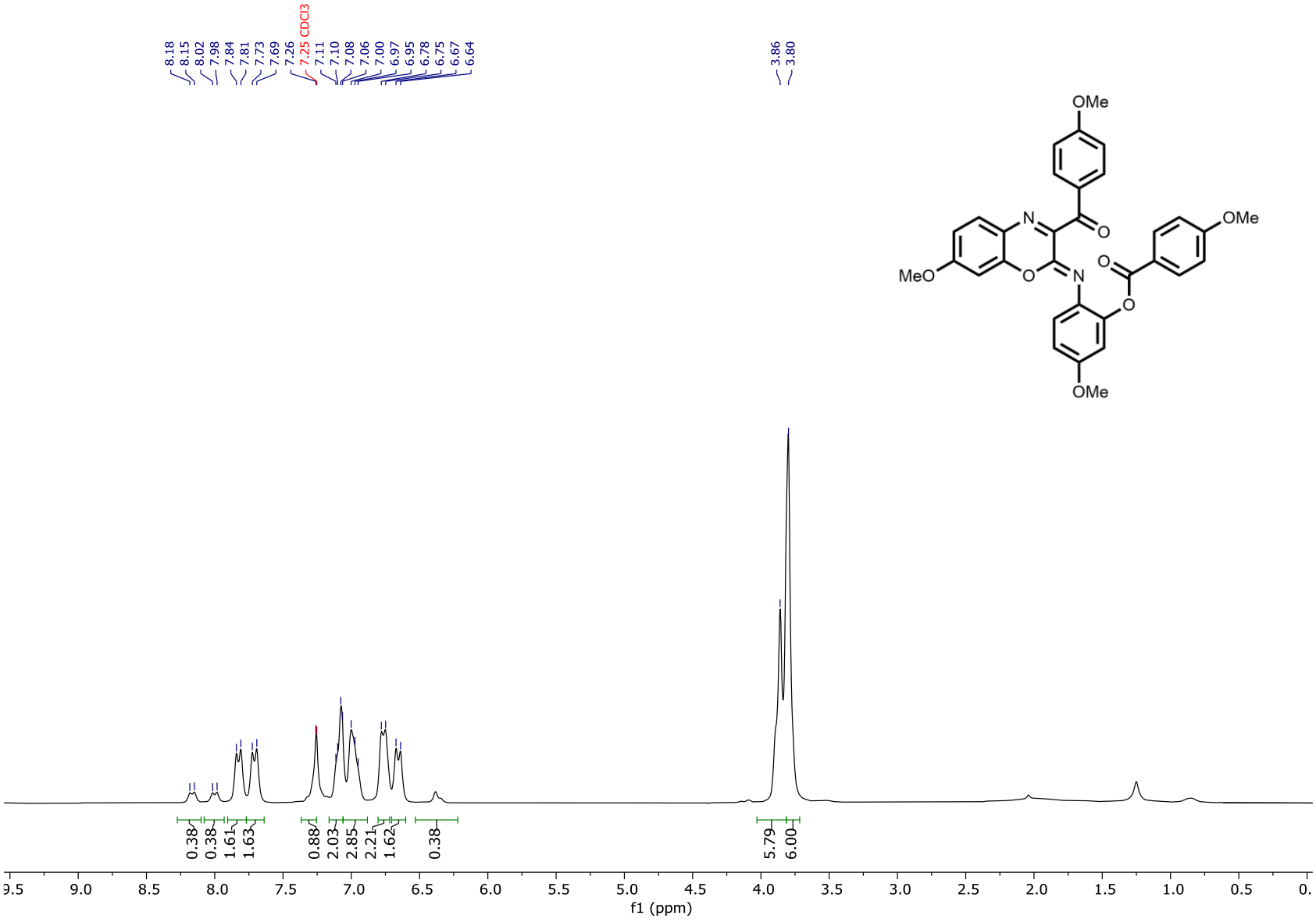

Figure S87. ^{1}H NMR (250 MHz, $CDCl_3$) (Z)-5-methoxy-2-((7-methoxy-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2m).

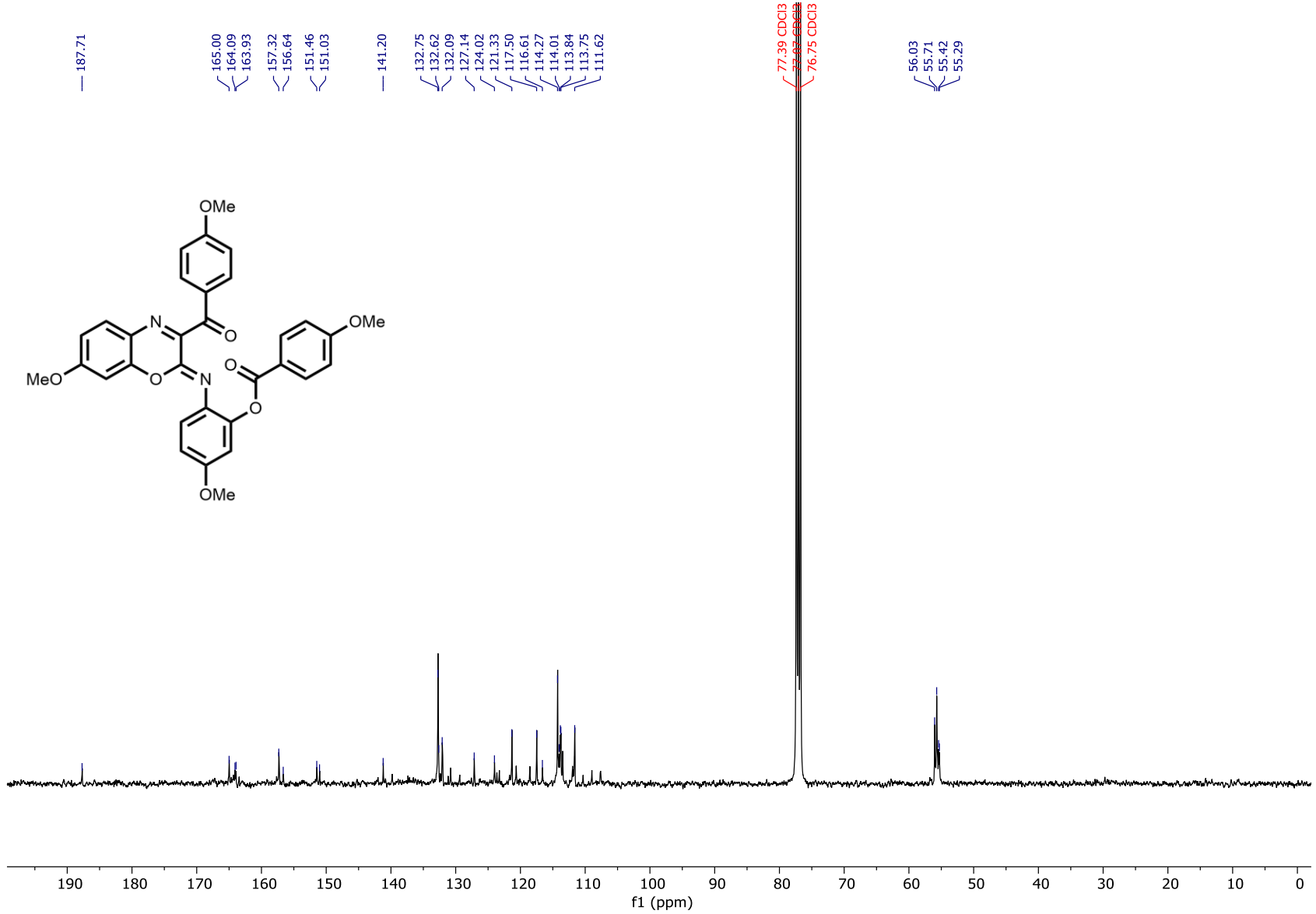

Figure S88. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-5-methoxy-2-((7-methoxy-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2m).

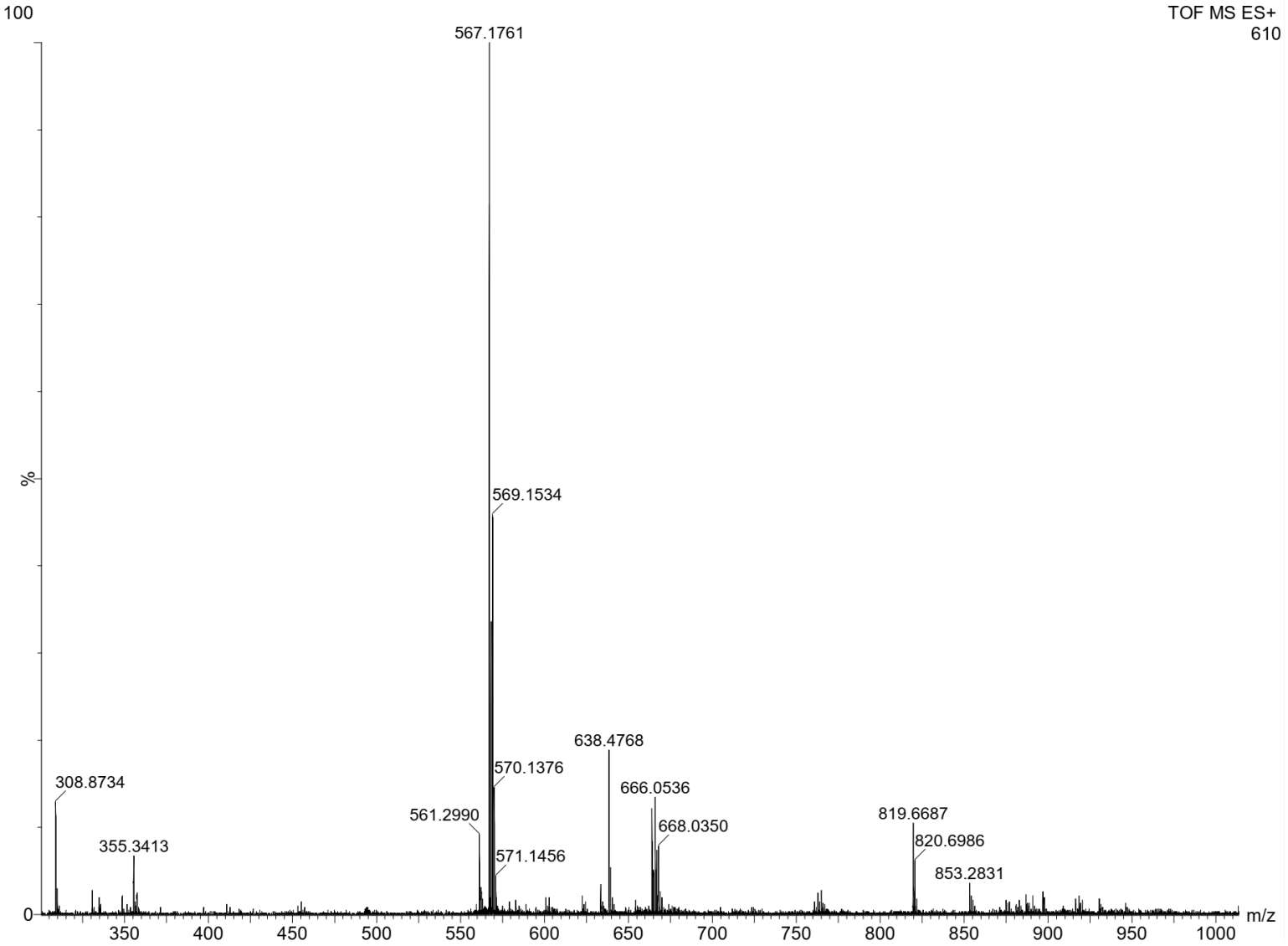

Figure S89. HRMS-ESI (Z)-5-methoxy-2-((7-methoxy-3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2m).

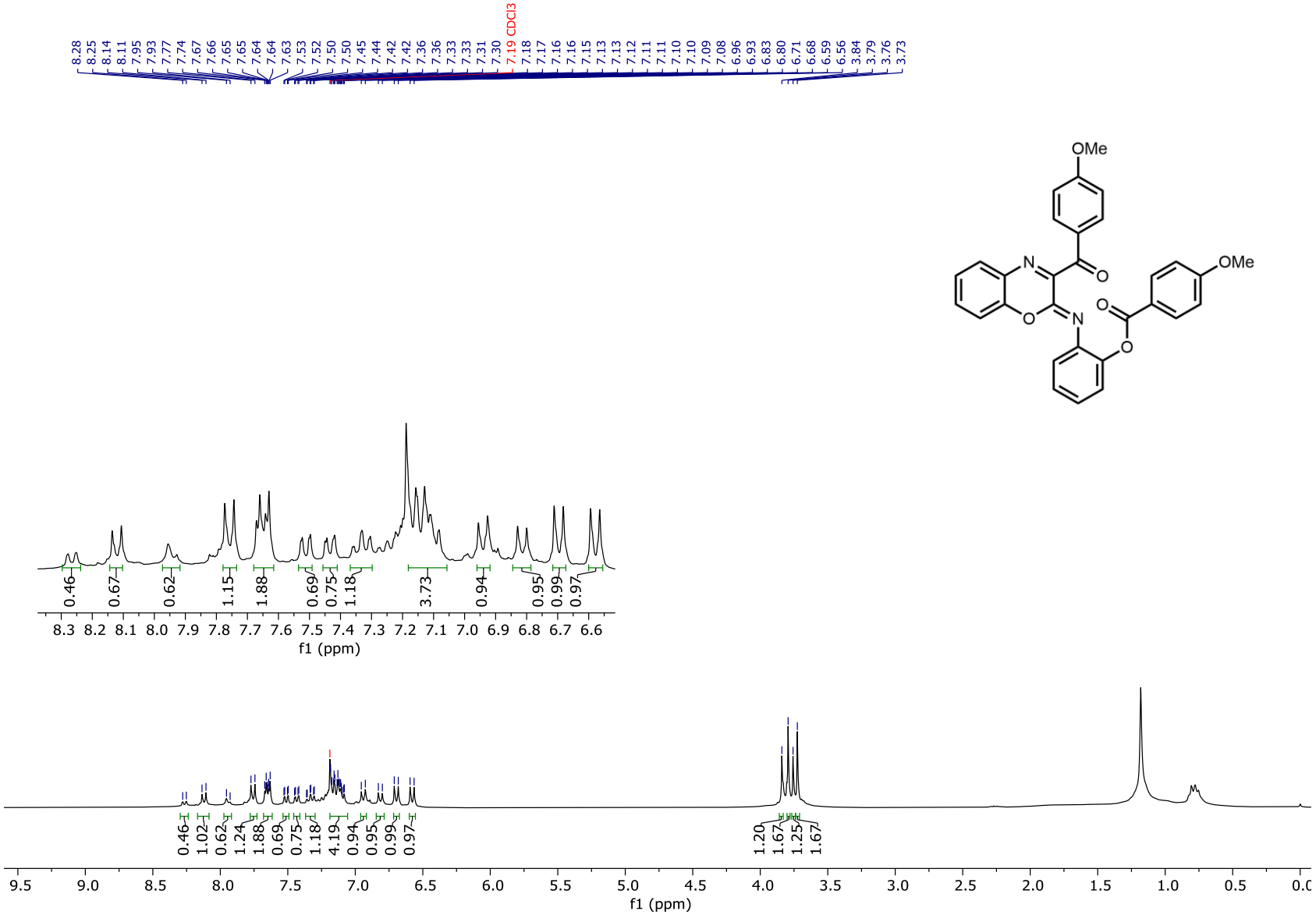

Figure S90. ^{1}H NMR (300 MHz, $CDCl_3$) (Z)-2-((3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2n).

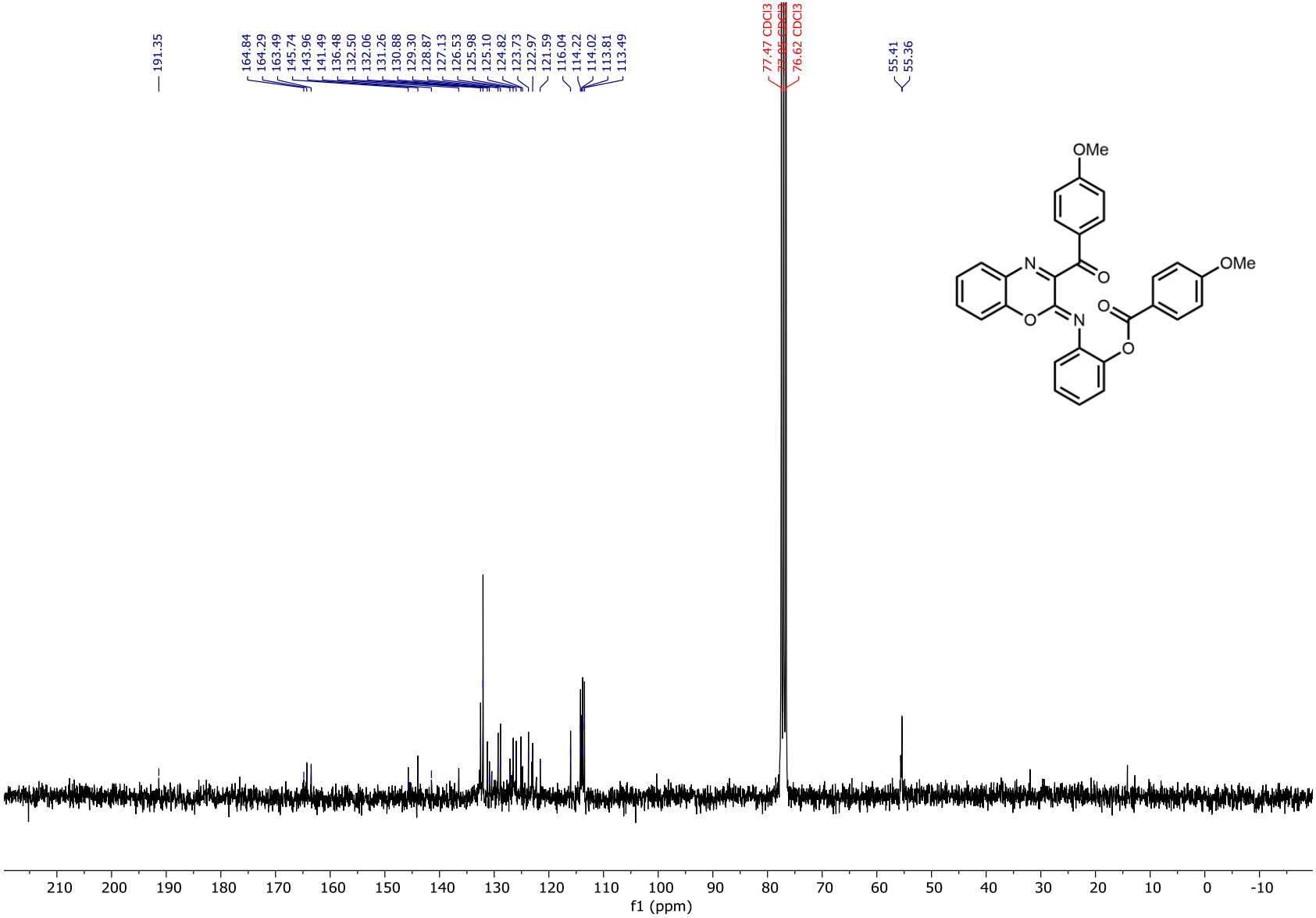

Figure S91. ^{13}C NMR (76 MHz, $CDCl_3$) (Z)-2-((3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2n).

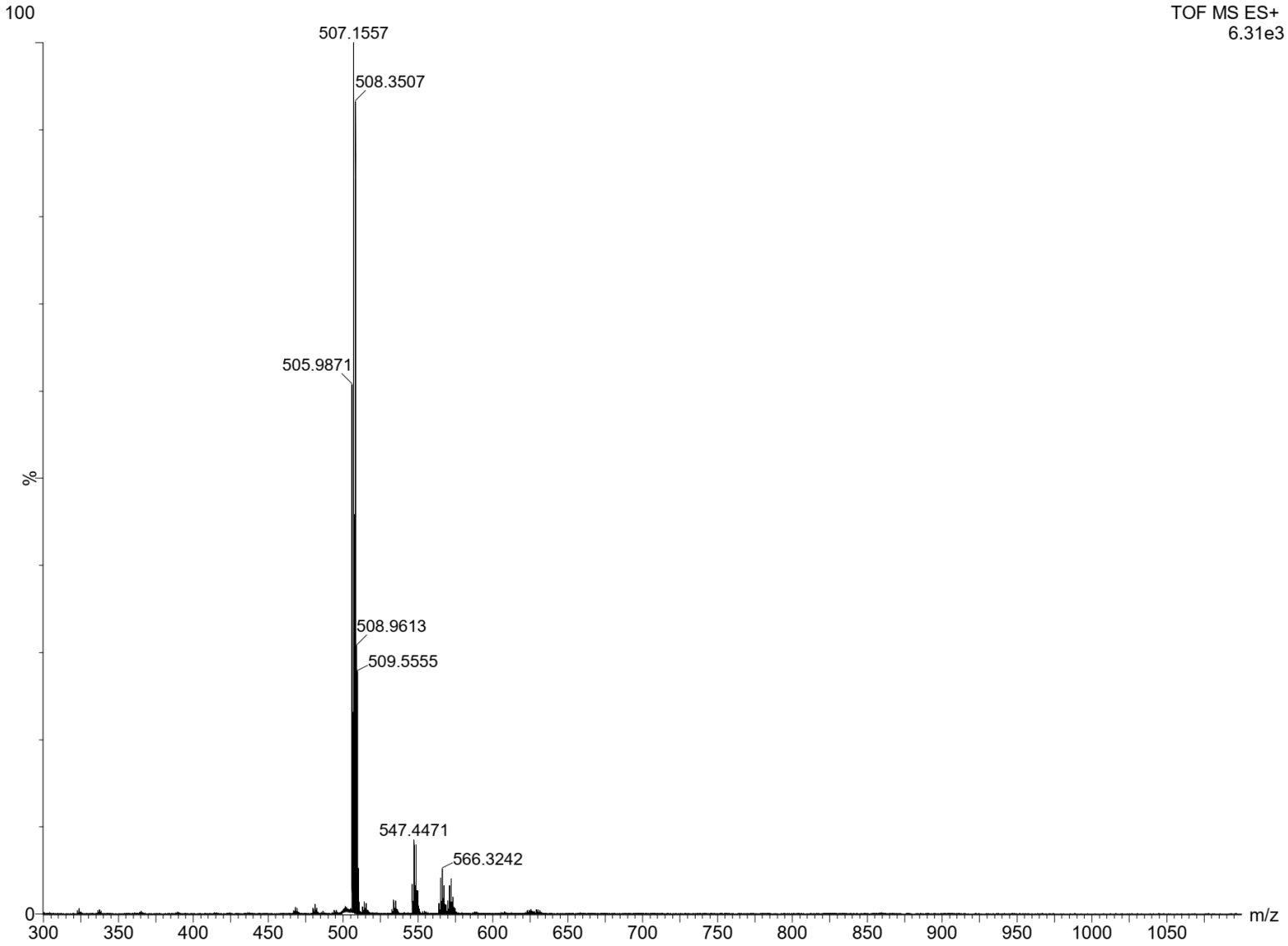

Figure S92. HRMS-ESI (Z)-2-((3-(4-methoxybenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 4-methoxybenzoate (2n).

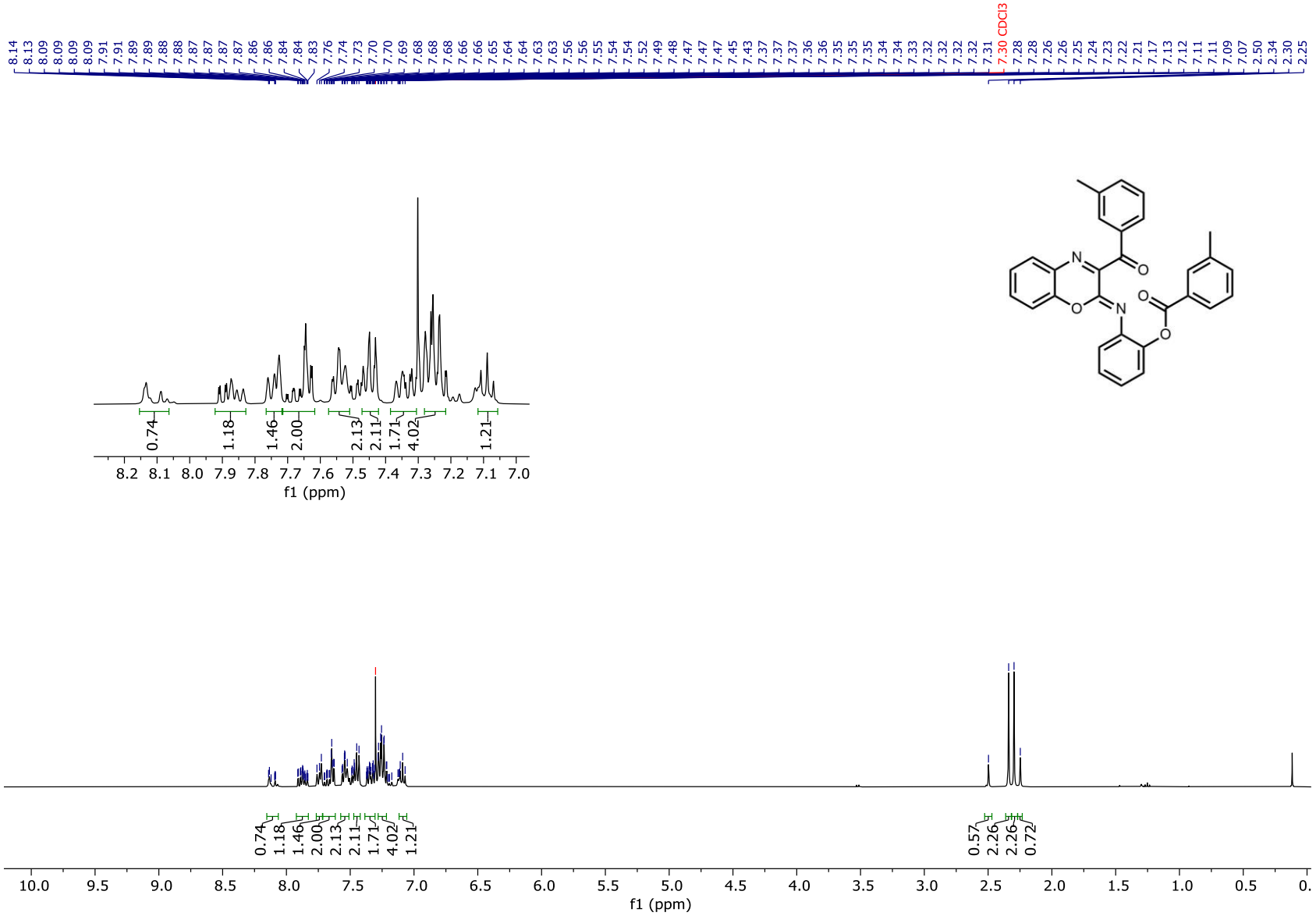

Figure S93. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2o).

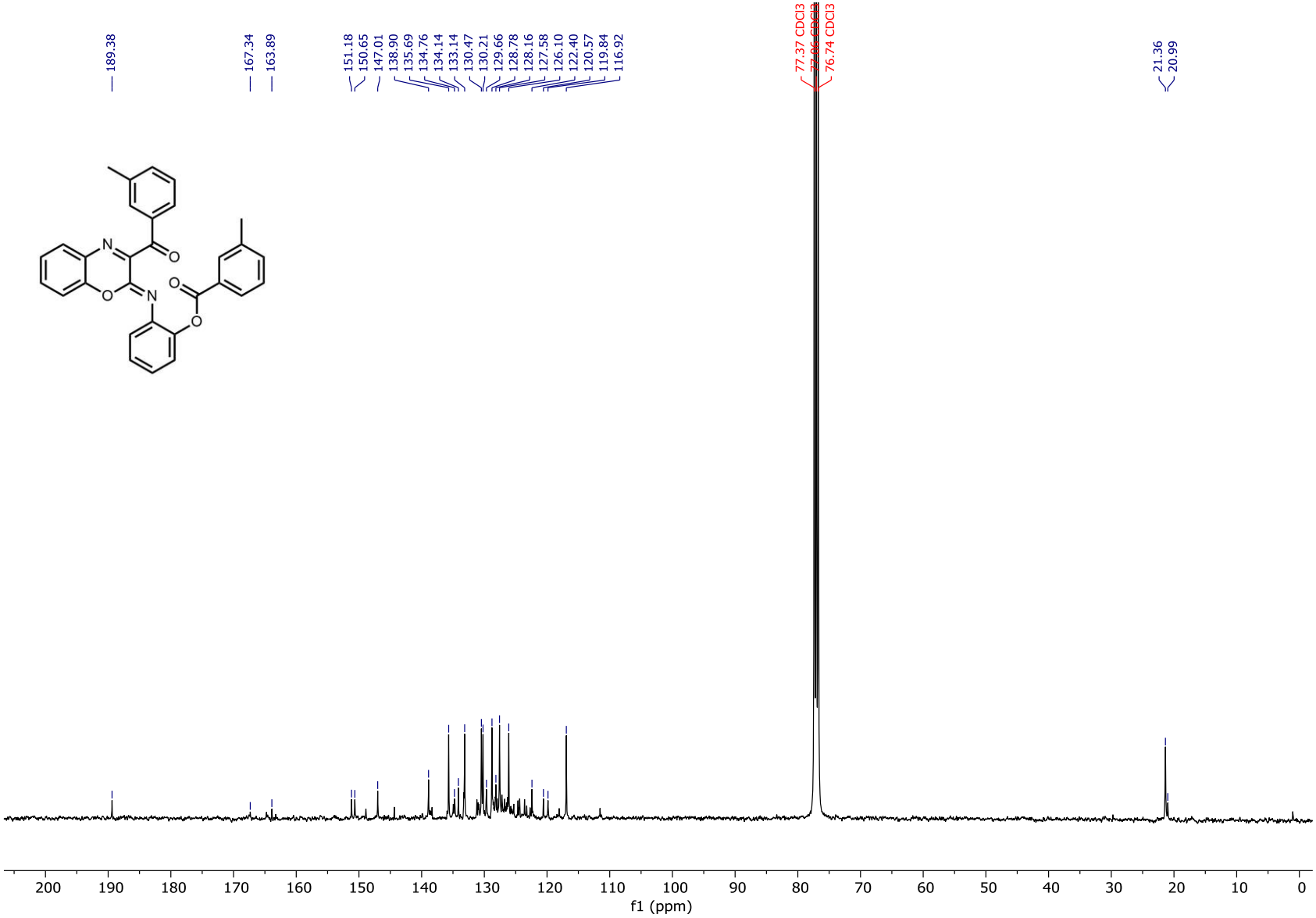

Figure S94. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2o).

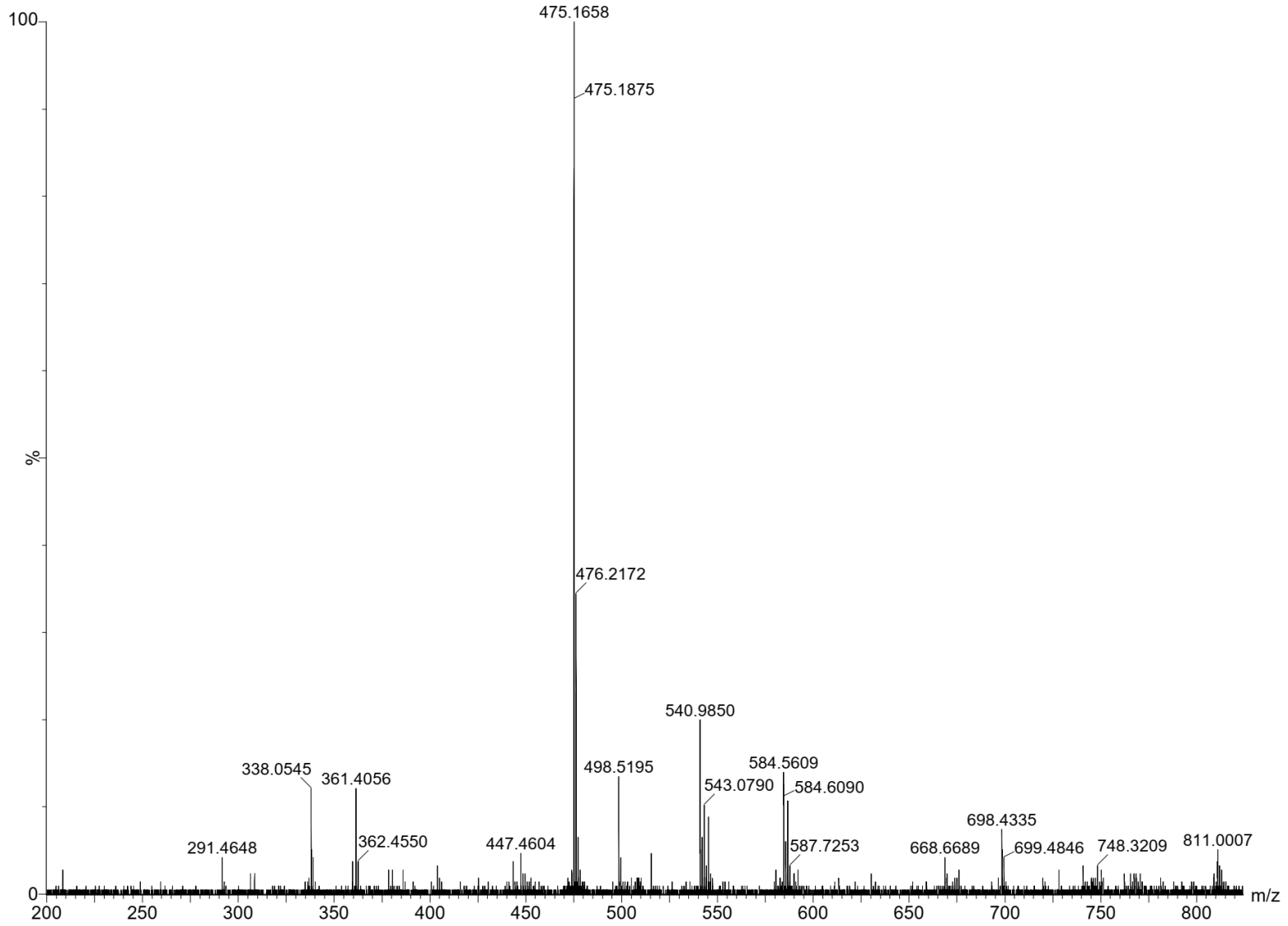

Figure S95. HRMS-ESI (Z)-2-((3-(3-methylbenzoyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl 3-methylbenzoate (2o).

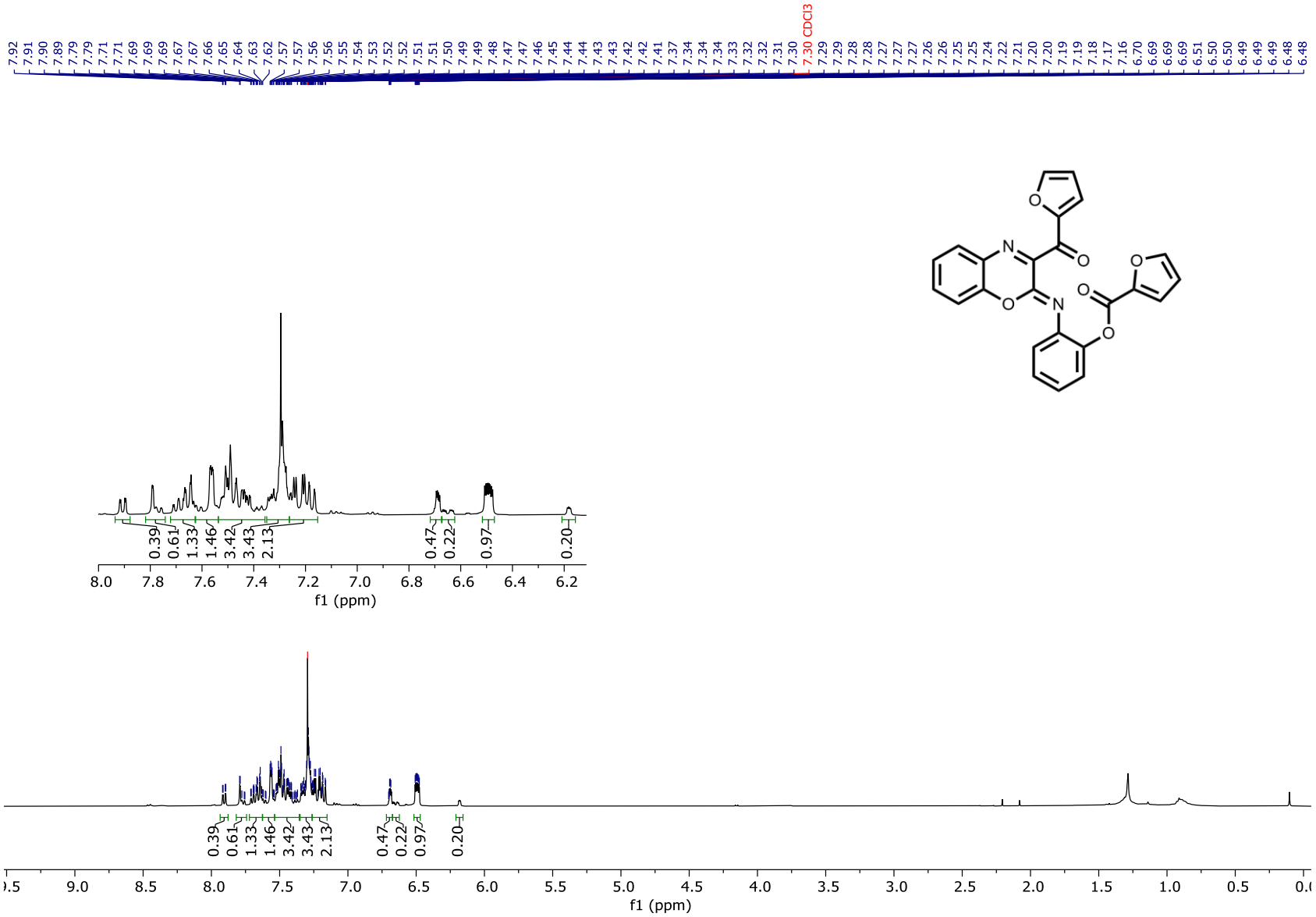

Figure S96. ^{1}H NMR (400 MHz, $CDCl_3$) (Z)-2-((3-(furan-2-carbonyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl furan-2-carboxylate (2p).

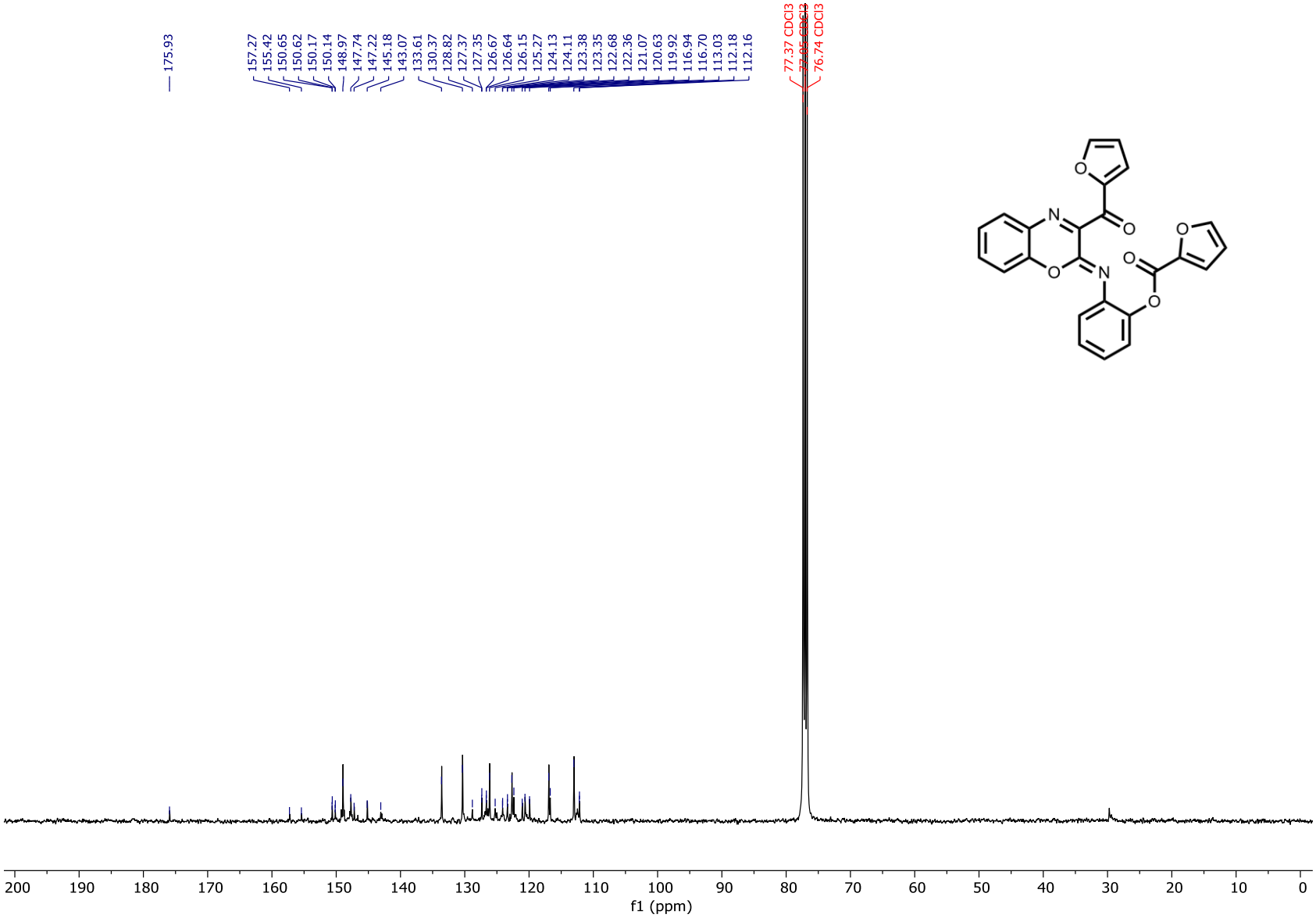

Figure S97. ^{13}C NMR (101 MHz, $CDCl_3$) (Z)-2-((3-(furan-2-carbonyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl furan-2-carboxylate (2p).

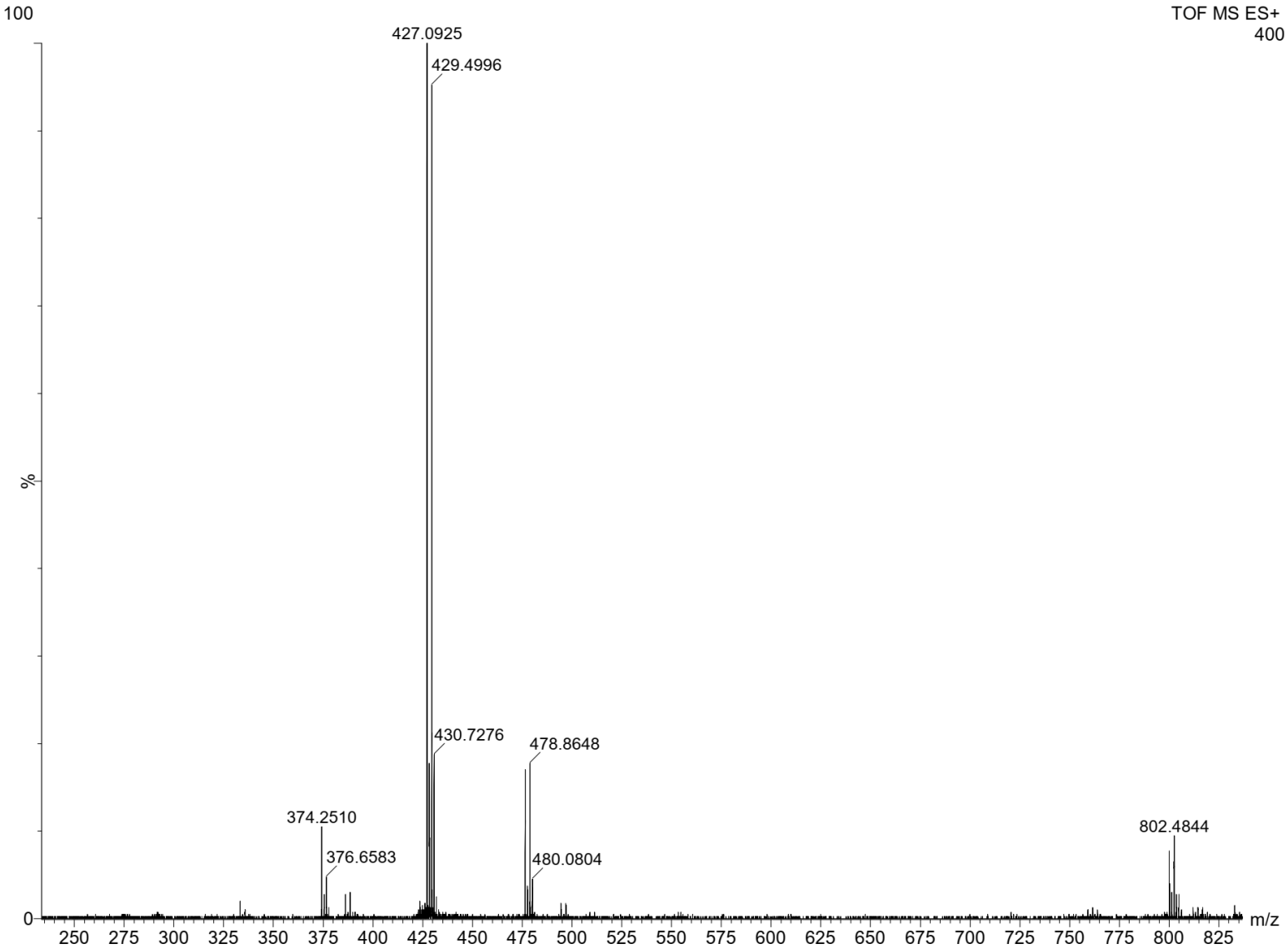

Figure S98. HRMS-ESI (Z)-2-((3-(furan-2-carbonyl)-2H-benzo[b][1,4]oxazin-2-ylidene)amino)phenyl furan-2-carboxylate (2p).

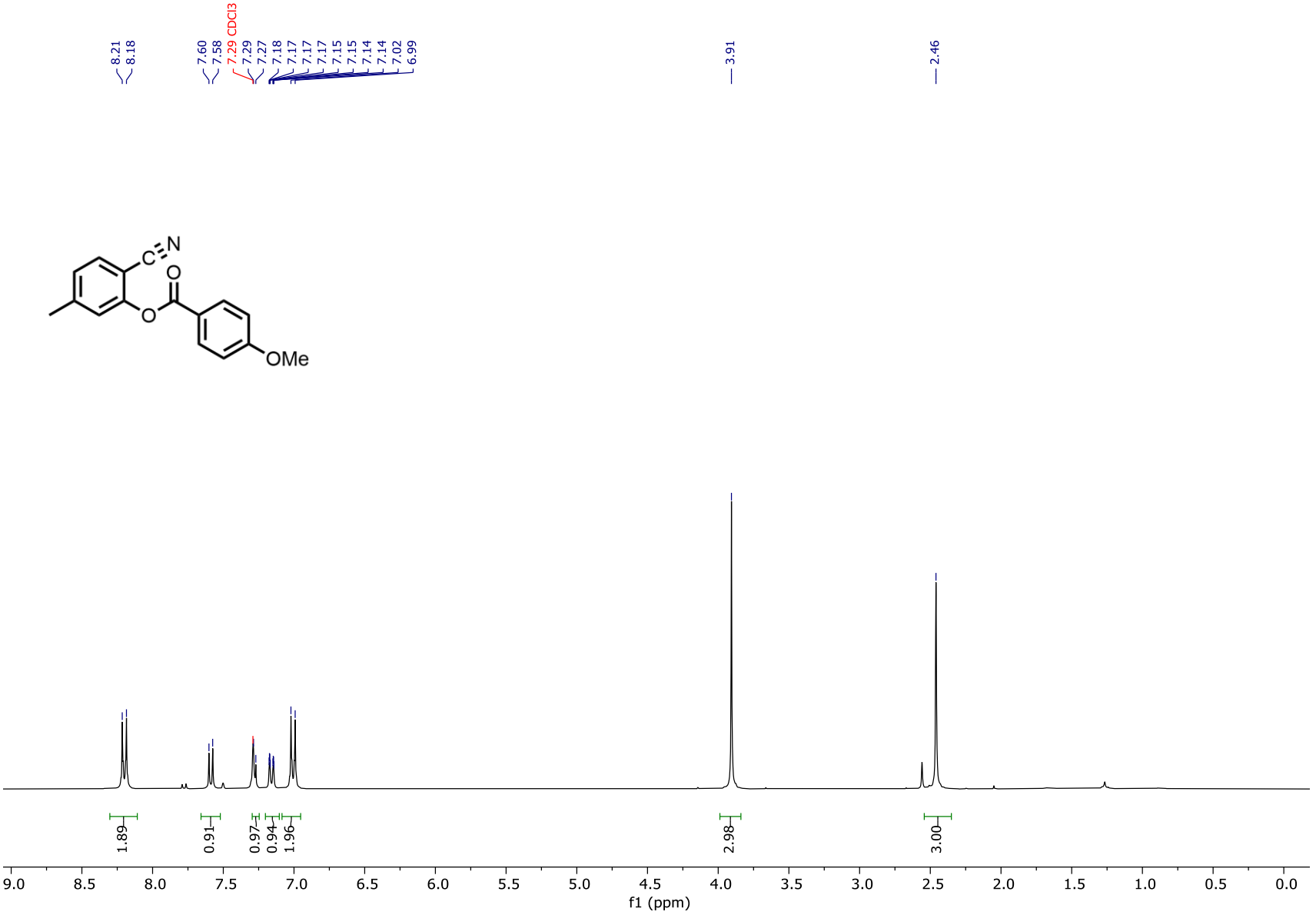

Figure S99. ^{1}H NMR (300 MHz, $CDCl_3$) 2-cyano-5-methylphenyl 4-methoxybenzoate (3b).

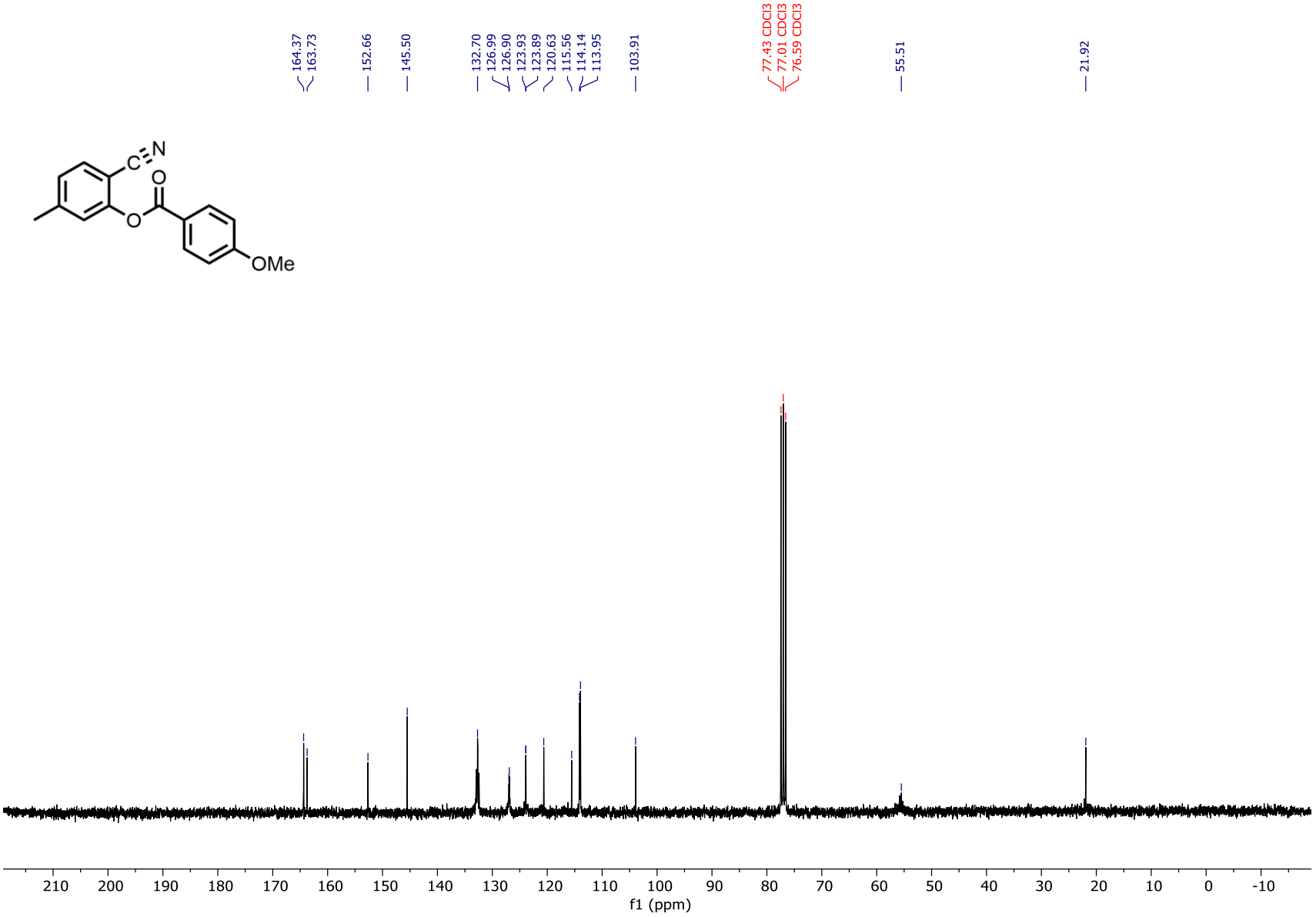

Figure S100. ^{13}C NMR (75 MHz, $CDCl_3$) 2-cyano-5-methylphenyl 4-methoxybenzoate (3b).

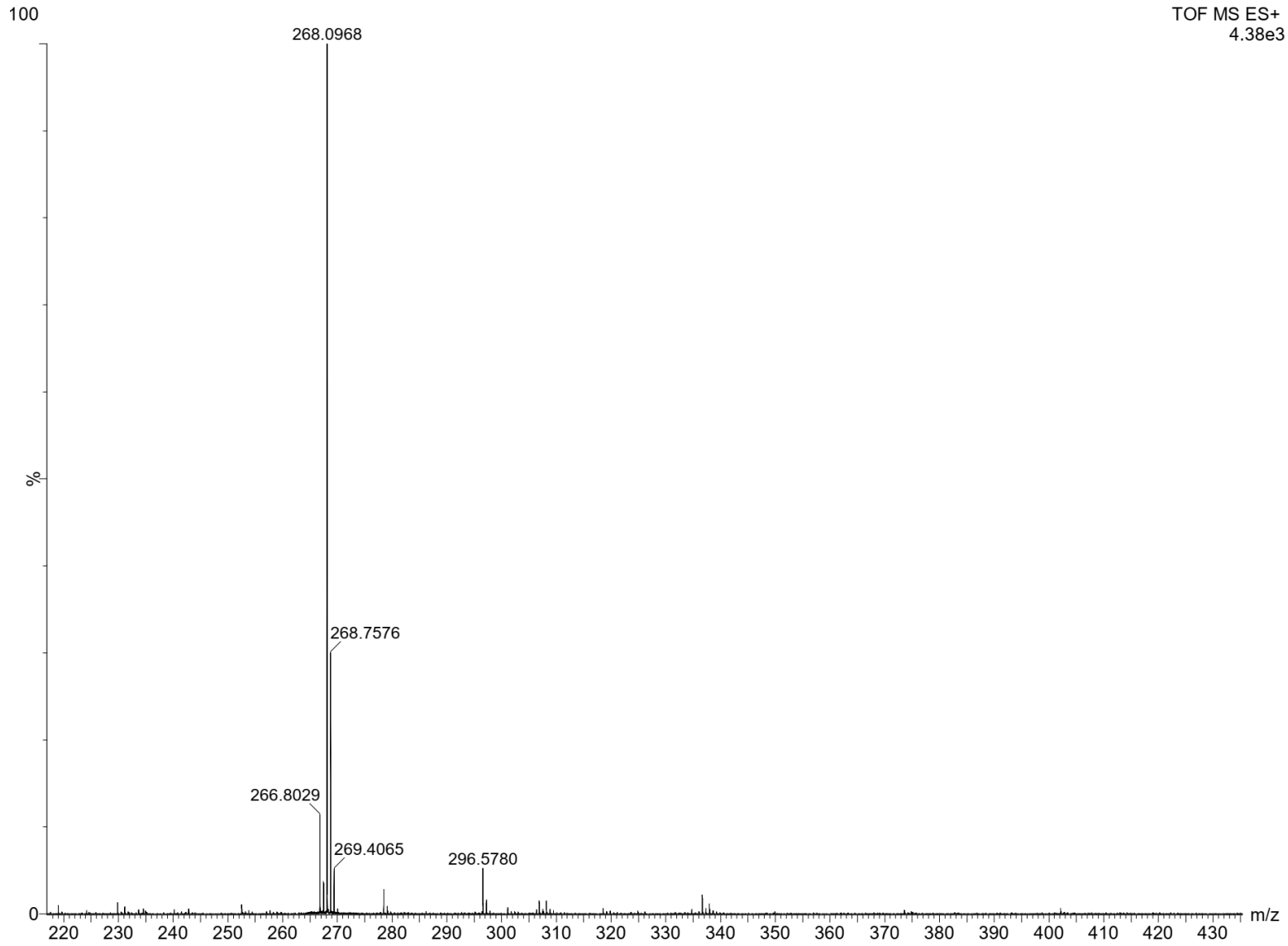

Figure S101. HRMS-ESI 2-cyano-5-methylphenyl 4-methoxybenzoate (3b).

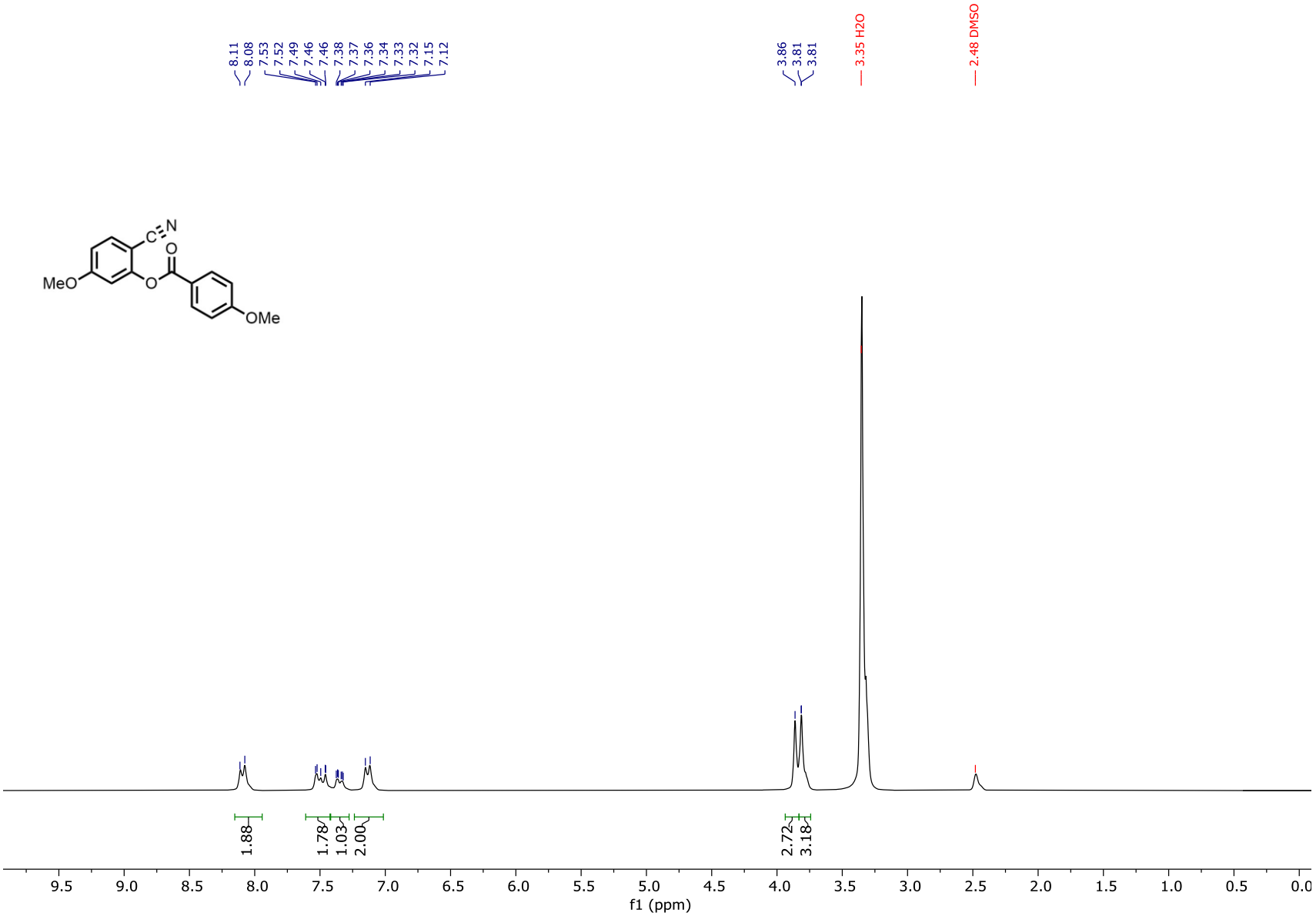

Figure S102. ^{1}H NMR (250 MHz, DMSO) 2-cyano-5-methoxyphenyl 4-methoxybenzoate (3m).

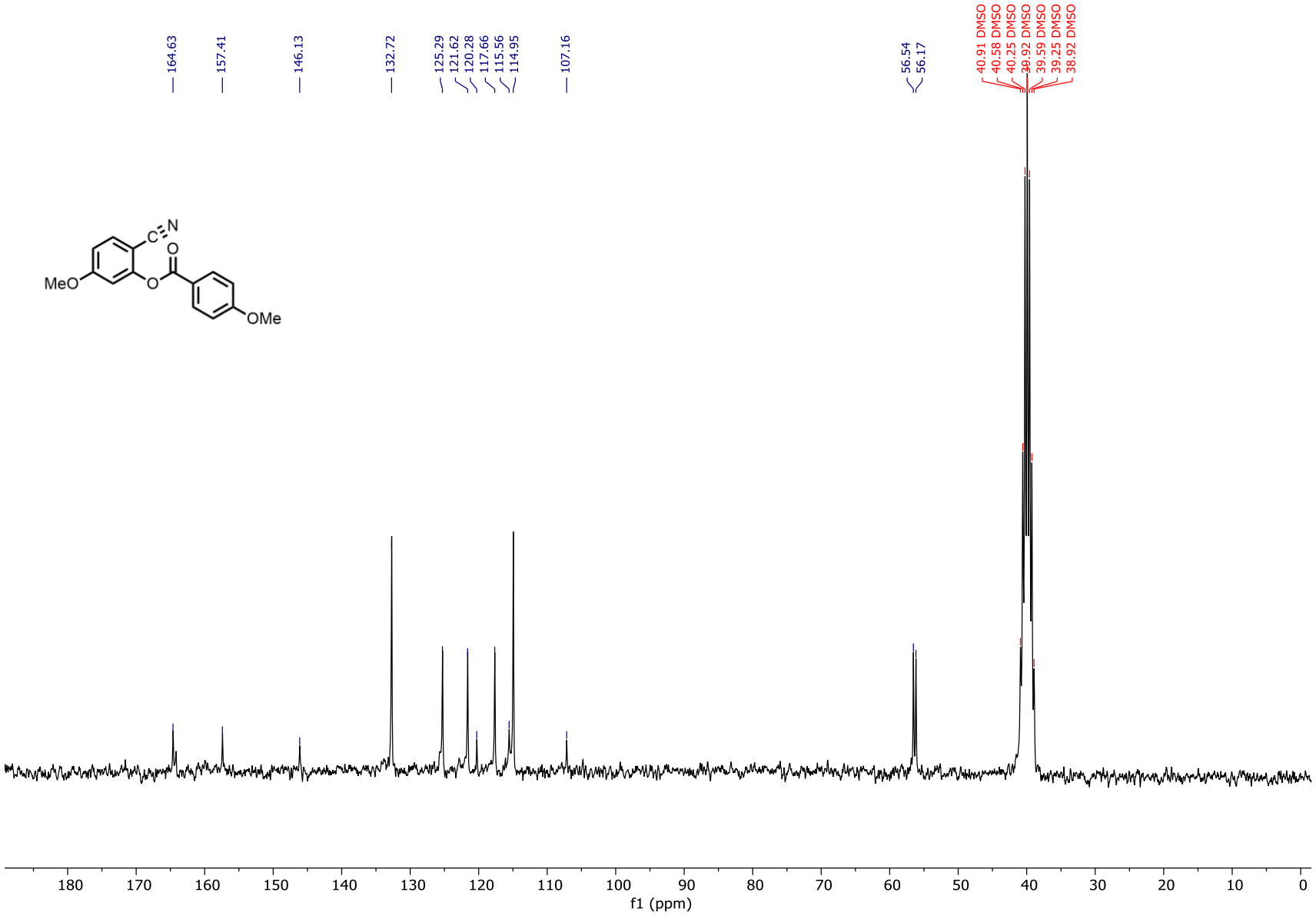

Figure S103. ^{13}**C NMR (63 MHz, DMSO)** 2-cyano-5-methoxyphenyl 4-methoxybenzoate (3m).

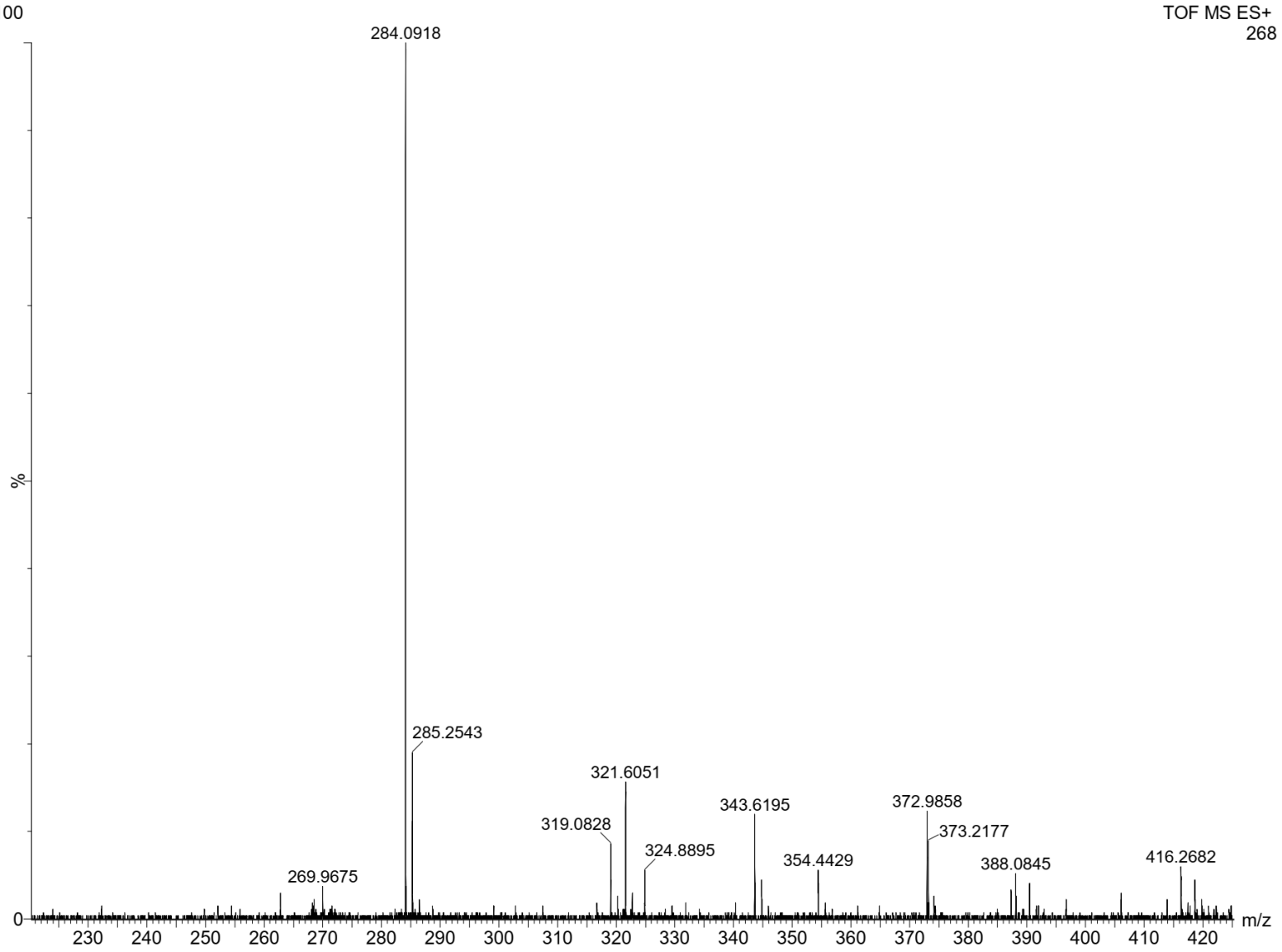

Figure S104. HRMS-ESI 2-cyano-5-methoxyphenyl 4-methoxybenzoate (3m).

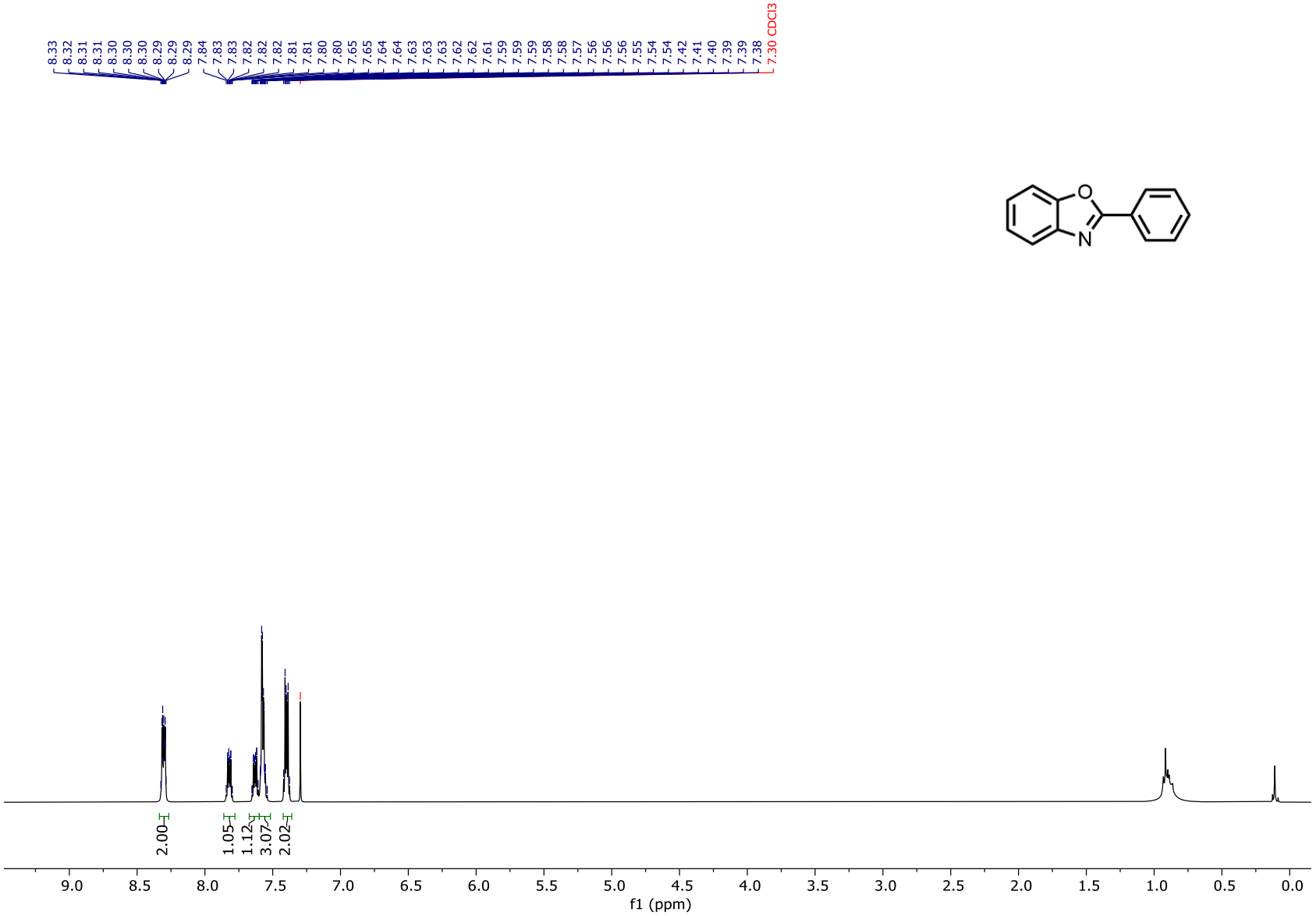

Figure S105. ^{1}H NMR (400 MHz, $CDCl_3$) 2-phenylbenzo[d]oxazole (4a).

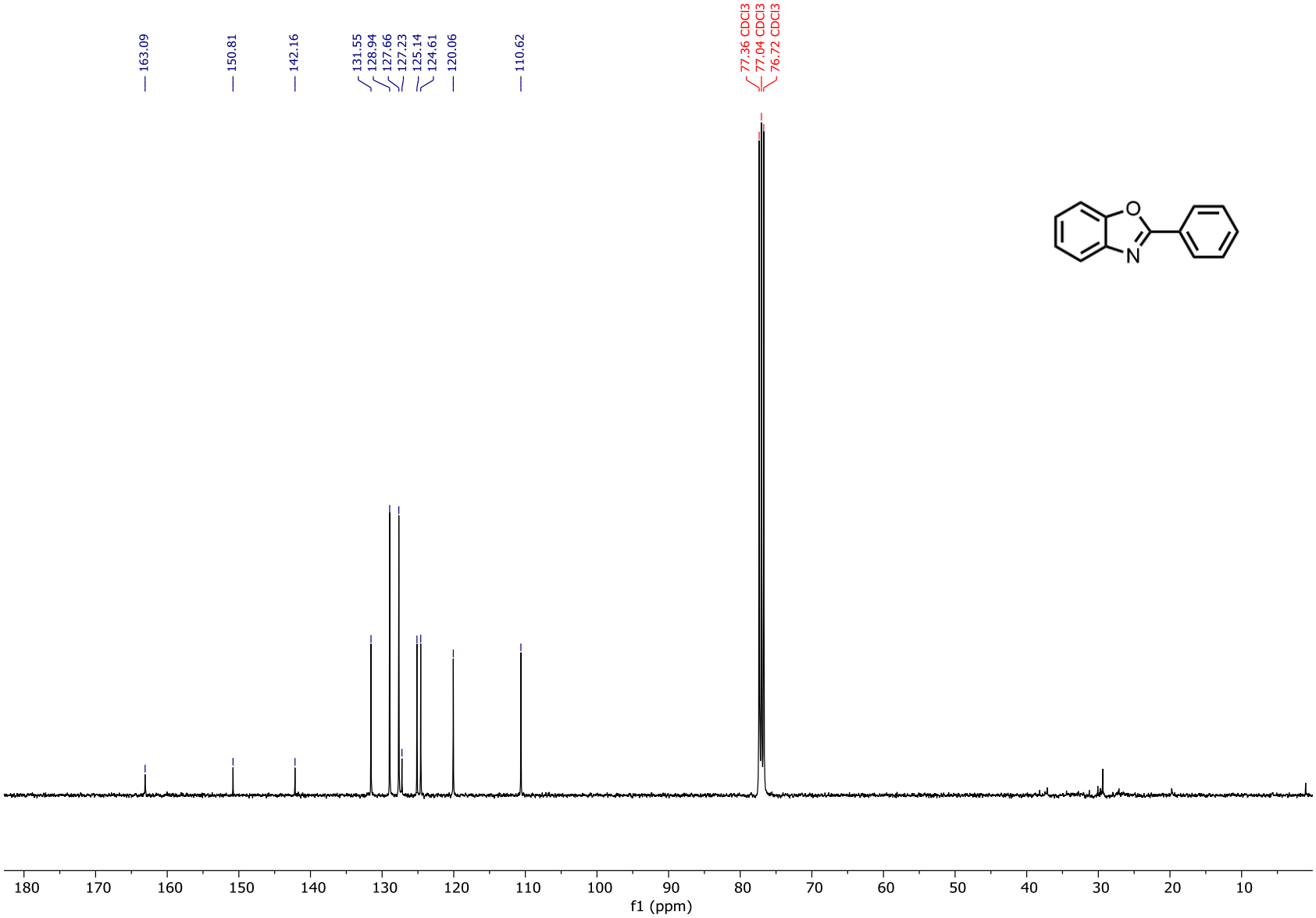

Figure S106. ^{13}C NMR (101 MHz, $CDCl_3$) 2-phenylbenzo[d]oxazole (4a).

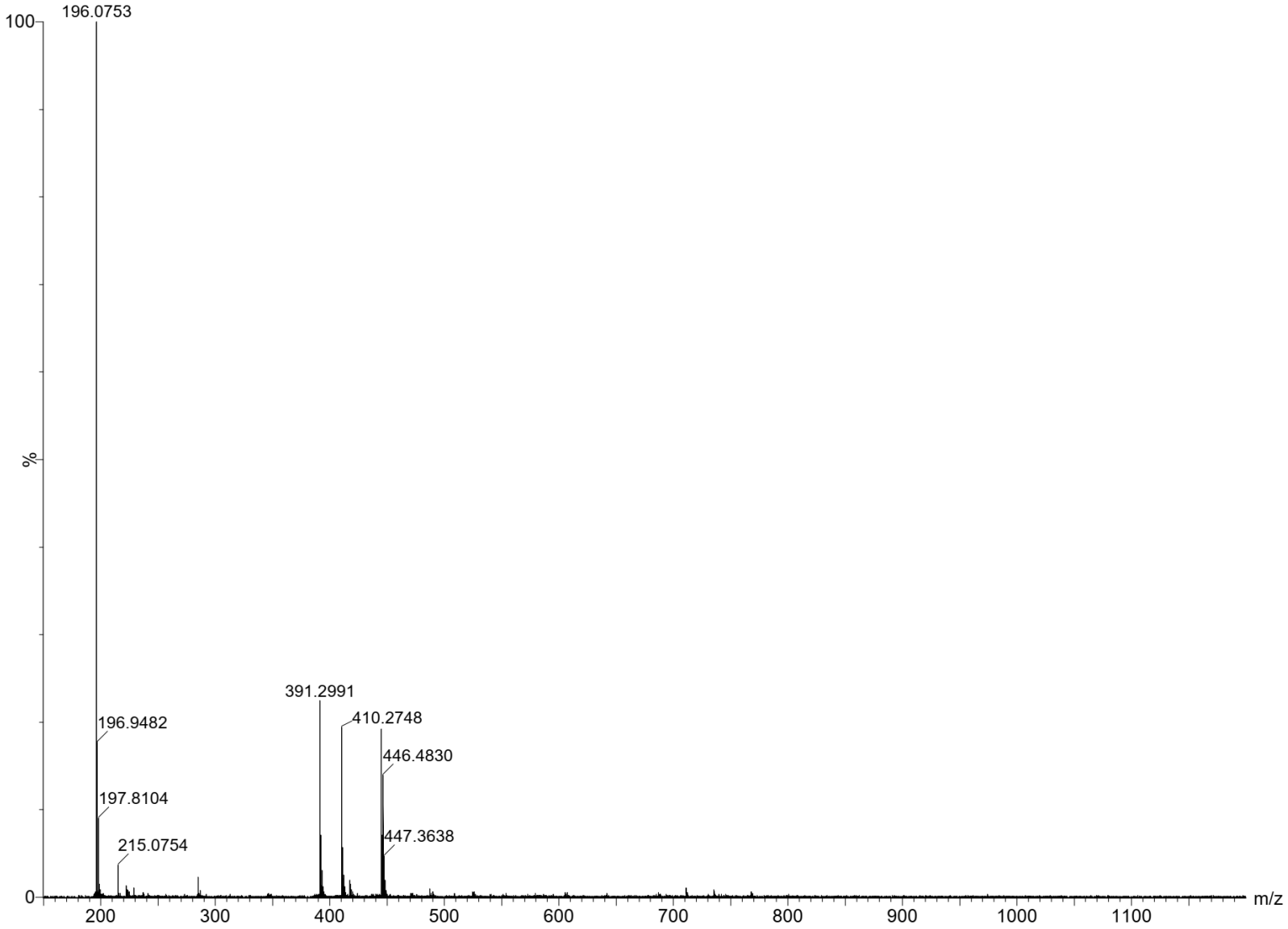

Figure S107. HRMS-ESI 2-phenylbenzo[d]oxazole (4a).

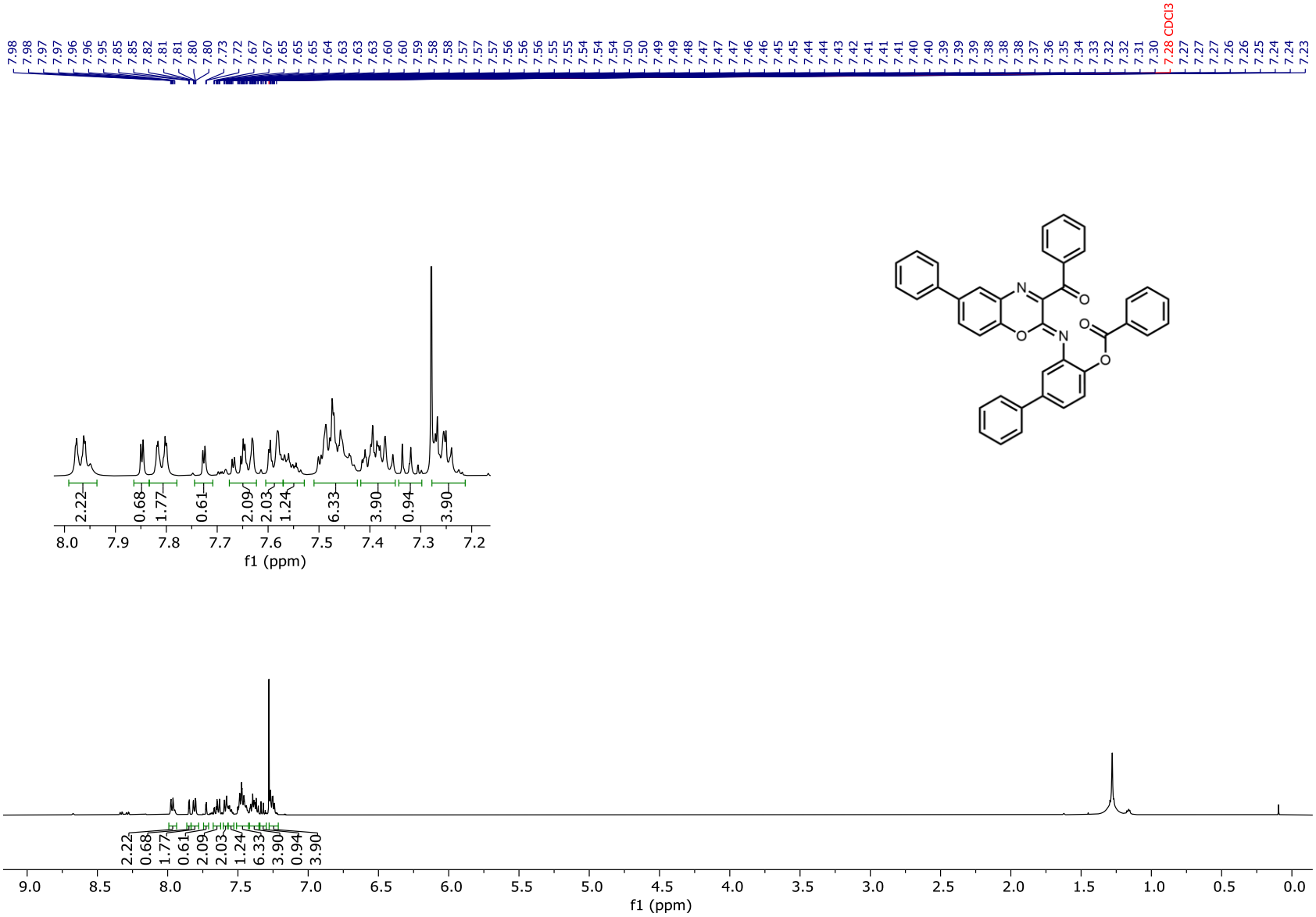

Figure S108. ^{1}H NMR (500 MHz, $CDCl_3$) (*Z*)-3-((3-benzoyl-6-phenyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-[1,1'-biphenyl]-4-yl benzoate (4f).

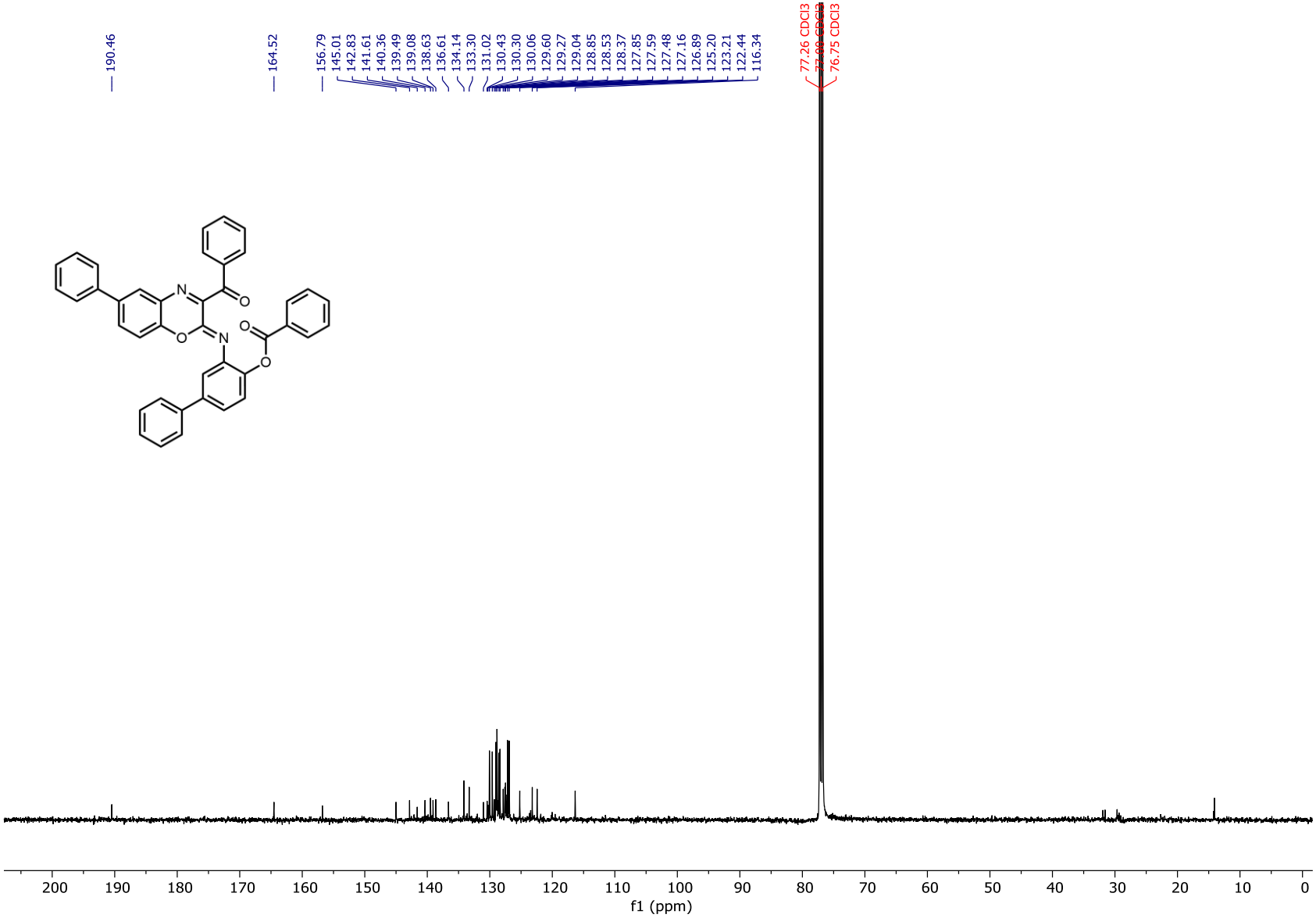

Figure S109. ^{1}H NMR (126 MHz, $CDCl_3$) (Z)-3-((3-benzoyl-6-phenyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-[1,1'-biphenyl]-4-yl benzoate (4f).

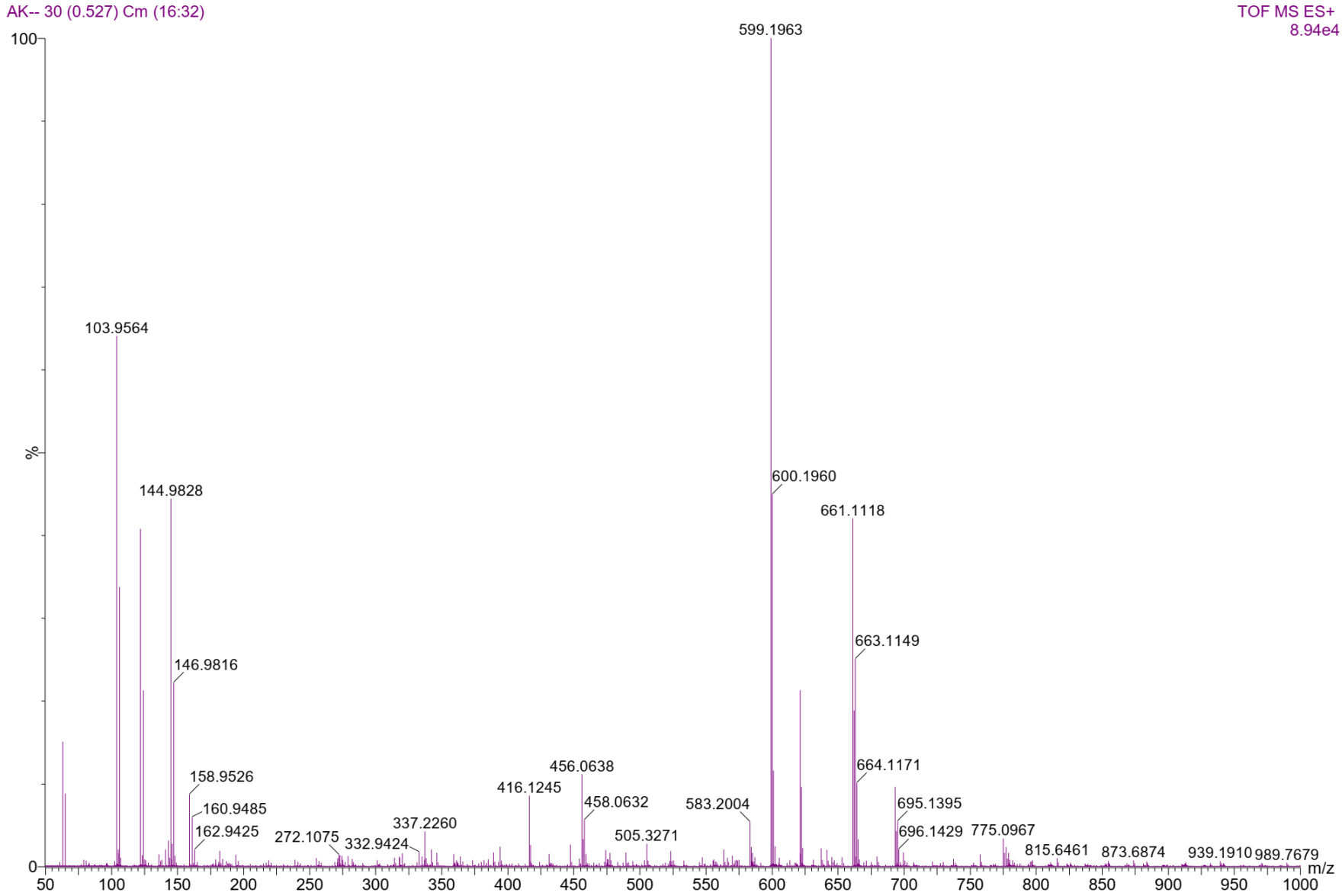

Figure S110. HRMS-ESI (Z)-3-((3-benzoyl-6-phenyl-2H-benzo[b][1,4]oxazin-2-ylidene)amino)-[1,1'-biphenyl]-4-yl benzoate (4f).