Supporting Information

Environmentally benign access to isoindolinones: synthesis, separation and resource recycling

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I. General Information

Unless otherwise noted, all reactions were carried out in glassware and all commercially available compounds including organic solvents were used as purchased without further purification. ^{1}H NMR was recorded on 400 MHz or 600 MHz nuclear magnetic resonance spectra. Chemical shifts (δ) are given in parts per million (ppm) and are referenced to residual solvent peaks (^{1}H NMR: $CHC1_3$ 7.26 ppm, DMSO 2.50 ppm). Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, td = triplet of doublet, q = quartet, m = multiplet), coupling constant (Hz), integration. HRMS (ESI) spectra were recorded on a Waters Q-Tof premierTM mass spectrometer. Reactions were monitored by TLC on glass-backed plates coated with a 0.2 mm thickness of silica gel 60 F254. Flash column chromatography was performed with silica gel 300−400 mesh.

II. General Experimental Process

Preparation of 3a-3h.

To a stirred solution of **1** (1.5 mmol, 1 equiv), **5** (20 mol%), H_2O (160 μL) in ethyl acetate (EA, 3.8 mL) was added methyl vinyl ketone (MVK) (**2a**, 1.8 mmol, 1.2 equiv). The resulting reaction mixture was stirred at rt for several hours until the reaction is complete as indicated by TLC. The reaction mixture was filtered, and the precipitation was washed with EA to afford **3**.

Preparation of 4a-4h and 4i.

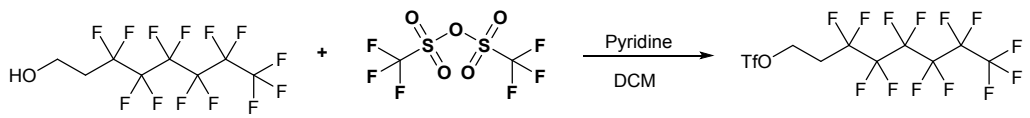
To a stirred solution of **1** (1.5 mmol, 1 equiv), **5** (20 mol%), *t*-BuOH (1.1 mL) ($V_{t\text{-BuOH}}$: $V_{anisole}$ = 1 : 2.5) in anisole (2.7 mL) (For more inactive substrate **1a-1c**, 3.8 mL *i*-PrOH was directly used as solvents) was added **2b** or **2b'** (5.25 mmol, 3.5 equiv). The resulting reaction mixture was stirred at rt for several hours until the reaction is complete as indicated by TLC. The reaction mixture was filtered, and the precipitation was washed with EA to afford **4**.

III. Preparation and recovery of fluorous-catalyst (5).

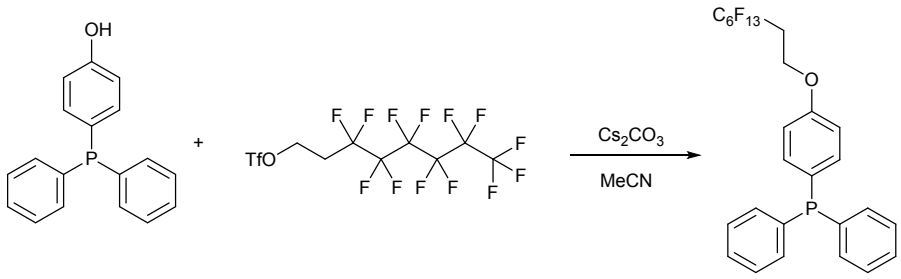
Preparation of (4-Hydroxyphenyl)-diphenylphosphine.

The (4-Hydroxyphenyl)-diphenylphosphine was prepared according to the known references.[1]

Preparation of 2-(perfluorohexyl)ethyl triflate.[2]



This reaction was carried out in oven-dried round-bottomed flask with magnetic stirring under an argon atmosphere with freshly distilled dry solvents: To a stirred 0 ℃ solution of 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octanol (1 mmol) and pyridine (1.5 mmol) in DCM (3.3 mL) was added dropwise trifluoromethanesulfonic anhydride (1.3 mmol). The resulting reaction mixture was then stirred at rt for several hours until the reaction is complete as indicated by TLC. The reaction mixture was filtered and the filtrate was concentrated in vacuo. Then, the resultant mixture was purified by silica gel column chromatography (PE/EA 45:1) to give pure 2-(perfluorohexyl)ethyl triflate (387 mg, 79%).



Preparation of fluorous-triphenylphosphine (5).

To an oven-dried round-bottomed flask equipped with a magnetic stir bar were added Cs_2CO_3 (3.38 mmol), (4-hydroxyphenyl)-diphenylphosphine (1.69 mmol) in MeCN (15 mL) under Ar. After 10 min, the solution of 2-(perfluorohexyl)ethyl triflate (3.38 mmol) in MeCN (12 mL) was added dropwise and the mixture was kept stirring at rt for 16 h. The mixture was purified by silica gel column chromatography to afford **5** (81%).

Recovery of 5:

F-SPE procedure:

After 5 turns, the reaction mixture was filtrated to obtain the pure product, and the mother liquid was concentrated in vacuo and the residue was dissolved in 5 mL of DCM and MeOH (v/v 1:1). 0.2 mL of the solution was taken and loaded on fluorous silica gel

(FluorousFlash™ SPE cartridge 2 grams, 8 cc tube), then first washed with 15 mL of MeCN-H_2O (v/v: 1:1) to elute the organic-residue. The fluorous catalyst was obtained by eluting fluorous silica gel with 20 mL of THF. The evaporation of the THF filtrates in vacuo to afforded fluorous phosphine (70% yield of **5**), which could be used for the next cycle.

Catalytic performance of the recovered fluorous phosphine:

To a stirred solution of **1a** (0.15 mmol, 19.7 mg, 1 equiv), fluorous phosphine (obtained above) in *i*-PrOH (0.38 mL) was added methyl acrylate (MA) (**2b**, 0.525 mmol, 3.5 equiv). The resulting solution was stirred at rt for 3 h. Then the mixture was concentrated in vacuo and the residue was dissolved in 0.4 mL of $CDCl_3$ to detect the yield (89 % yield).

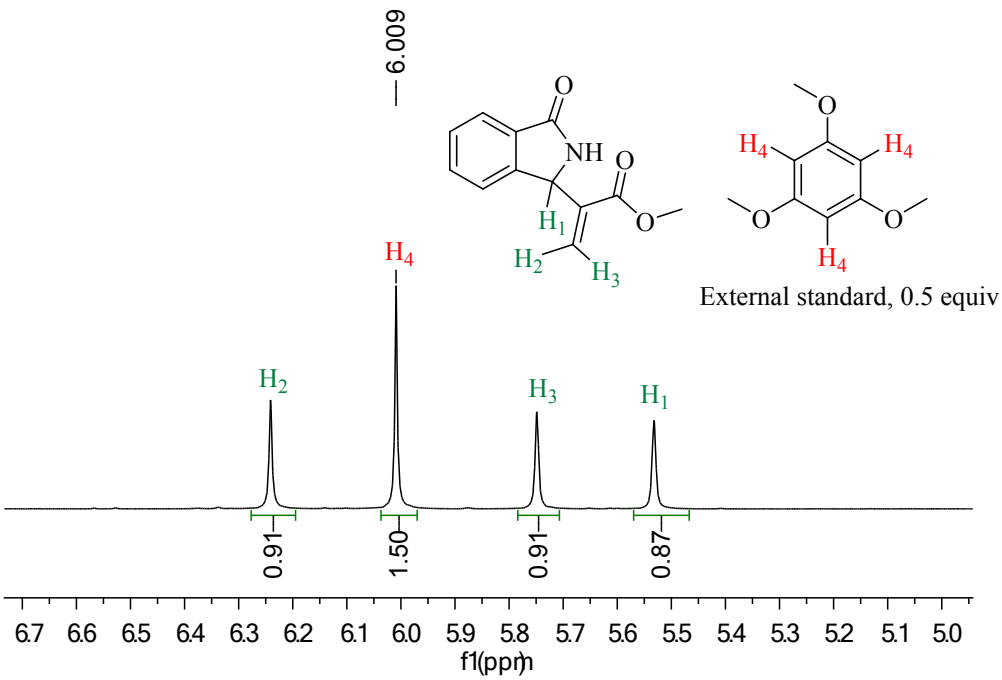
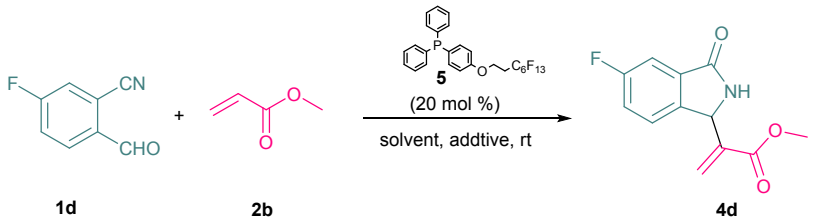


Fig. S1 Catalytic performance of **5a**: ^1H NMR of reaction mixture, the mesitoxybenzene (0.5 equiv) was added followed by adding 0.4 mL $CDCl_3$

IV. Determination of the optimal reaction conditions of MA

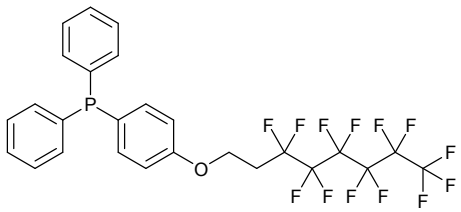


Entry	Solvents	Addtive	T	MA	Yield[d]
1	EA	-	24 h	1.2 eq	trace
2	Anisole	-	24 h	1.2 eq	trace
3[b]	EA	Water	24 h	1.2 eq	< 10%
4[b]	Anisole	Water	24 h	1.2 eq	< 10%
5[b]	EA	Water	24 h	2.4 eq	14%
6[b]	Anisole	Water	24 h	2.4 eq	15%
7[b]	Anisole	Water	24 h	3.5 eq	23%
8	*i*-PrOH	-	3 h	3.5 eq	47%
9	*t*-BuOH	-	3 h	3.5 eq	78%
10[c]	Anisole	*t*-BuOH	12 h	3.5 eq	92% (88%)[e]

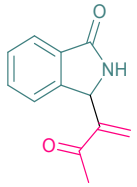
Table S1[a]

[a]Unless otherwise noted, all reactions were conduct with mixtures of 2-cyano-4-fluorobenzaldehyde (**1d**, 0.15 mmol, 1 equiv), methyl acrylate (**2b**, 0.53 mmol, 3.5 equiv) and the catalyst (**5**, 0.03 mmol, 20 mol%) in solvent (0.38 mL) at rt. [b]$V_{solvent}$: V_{Water} = 28 : 1. [c]Anisole: 0.27 mL, *t*-BuOH: 0.11 mL. [d]Deternmined by ^{1}H NMR spectroscopy. [e]Filtration yield.

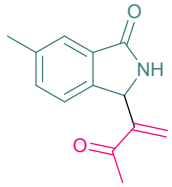
V. Characterization of the products.



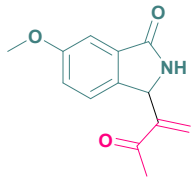
(4-((3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)oxy)phenyl)diphenylphosphane (5): White solid, mp: 48-50 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.23 (m, 12H), 6.88 (d, J = 8.4 Hz, 2H), 4.27 (t, J = 6.8 Hz, 2H), 2.70-2.55 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.8, 137.7 (d, $J_{P\text{-}C}$ = 10.6 Hz), 135.7 (d, $J_{P\text{-}C}$ = 21.3 Hz), 133.5 (d, $J_{P\text{-}C}$ = 19.3 Hz), 128.9 (d, $J_{P\text{-}C}$ = 6.1 Hz), 128.6, 128.5 (d, $J_{P\text{-}C}$ = 4.4 Hz), 114.8 (d, $J_{P\text{-}C}$ = 8.0 Hz), 60.0, 31.3. ^{31}P NMR (162 MHz, $CDCl_3$) -6.43. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.8 (t, J = 10.0 Hz 3F), -113.2 (m, 2F), -121.8 (m, 2F), -122.8 (m, 2F), -123.5 (m, 2F), -126.1 (m, 2F). HRMS: calcd. for $C_{26}H_{19}F_{13}OP^+$ $[M + H]^+$: 625.0949; Found: 625.0960.



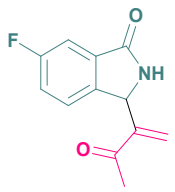
3-(3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3a):[3] White solid, mp: 166-168 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 7.2 Hz, 1H), 7.54 (td, J = 7.6, 1.3 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.56 (d, J = 7.6 Hz, 1H), 6.69 (s, 1H), 6.16 (s, 1H), 5.98 (s, 1H), 5.70 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.20, 171.02, 146.19, 146.02, 132.08, 131.18, 128.47, 126.15, 123.99, 123.66, 55.27, 26.09. HRMS: calcd. for $C_{12}H_{11}NNaO_2$ $[M + Na]^+$: 224.0682; Found: 224.0684.



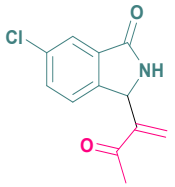
3-(5-methyl-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3b): White solid, mp: 135-137 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.25 (d, J = 7.6 Hz, 1H), 7.22 (s, 1H), 6.13 (s, 1H), 5.99 (s, 1H), 5.66 (s, 1H), 2.44 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.22, 171.18, 146.32, 143.28, 138.53, 133.03, 131.26, 125.93, 124.12, 123.34, 55.11, 26.08, 21.22. HRMS: calcd. for $C_{13}H_{13}NNaO_2$ $[M + Na]^+$: 238.0838; Found: 238.0838.



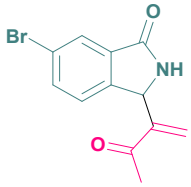
3-(5-methoxy-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3c): White solid, mp: 141-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, J = 2.4 Hz, 1H), 7.27 (s, 1H), 7.25 (s, 1H), 7.08 (dd, J = 8.6, 2.6 Hz, 1H), 6.14 (s, 1H), 5.99 (s, 1H), 5.63 (s, 1H), 3.85 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.25, 170.96, 160.20, 146.27, 138.13, 132.57, 125.93, 124.56, 120.36, 106.53, 55.67, 54.99, 26.13. HRMS: calcd. for $C_{13}H_{13}NNaO_3$ $[M + Na]^+$: 254.0788, Found: 254.0789.



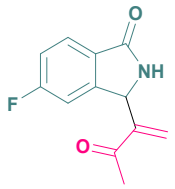
3-(5-fluoro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3d): White solid, mp: 108-110 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.50 (dd, *J* = 7.4, 2.4 Hz, 1H), 7.37 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.23 (td, *J* = 8.8, 2.4 Hz, 1H), 6.18 (s, 1H), 6.03(s, 1H), 5.70 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.12, 170.08 (d, $^{4}J_{C\text{-}F}$ = 3.3 Hz), 162.98 (d, $^{1}J_{C\text{-}F}$ = 248.1 Hz), 145.93, 141.54 (d, $^{4}J_{C\text{-}F}$ = 2.5 Hz), 133.30 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 126.18, 125.32 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 119.58 (d, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 110.59 (d, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 55.15, 26.07. HRMS: calcd. for $C_{12}H_{10}FNNaO_2$ [M + Na]$^{+}$: 242.0588; Found: 242.0591.



3-(5-chloro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3e): White solid, mp: 127-130 °C ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 2, 1H), 7.50 (dd, *J* = 10.8, 2.4 Hz, 1H), 7.32 (d, *J* = 10.8 Hz, 1H), 6.45 (s, 1H), 6.18 (s, 1H), 5.97 (s, 1H), 5.66 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.06, 169.79, 145.77, 144.24, 134.82, 132.95, 132.27, 126.32, 125.02, 124.08, 67.06, 55.21, 26.07. HRMS: calcd. for $C_{12}H_{10}ClNNaO_2$ [M + Na]$^{+}$: 258.0292; Found: 258.0292.

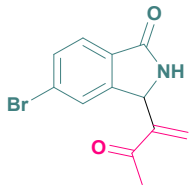


3-(5-broro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3f): White solid, mp: 147-149 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 1.6, 1H), 7.65 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.27 (d, *J* = 8.4 Hz, 1H), 6.88 (s, 1H), 6.18 (s, 1H), 5.99 (s, 1H), 5.66 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.09, 169.62, 145.64, 144.71, 135.09, 133.17, 127.13, 126.40, 125.35, 122.61, 55.23, 26.10. HRMS: calcd. for $C_{12}H_{10}BrNNaO_2$ [M + Na]$^{+}$: 301.9787; Found: 301.9788.

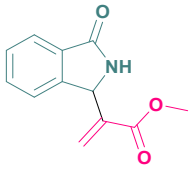


3-(6-fluoro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3g): White solid, mp: 130-132 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.2, 5 Hz, 1H), 7.16 (dd, *J* = 8.6 Hz, 1H), 7.13-7.02 (m, 2H), 6.20 (s, 1H), 6.04(s, 1H), 5.59 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.10, 169.78, 165.35 (d, $^{1}J_{C\text{-}F}$ = 252.3 Hz), 148.44 (d,

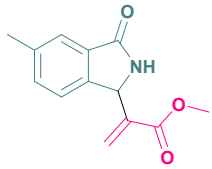
$^3J_{C\text{-}F}$ = 10.0 Hz), 145.75, 127.04 (d, $^4J_{C\text{-}F}$ = 2.2 Hz), 126.42, 126.04 (d, $^3J_{C\text{-}F}$ = 9.8 Hz), 116.36 (d, $^2J_{C\text{-}F}$ = 23.6 Hz), 111.22 (d, $^2J_{C\text{-}F}$ = 24.7 Hz), 54.88 (d, $^4J_{C\text{-}F}$ = 2.6 Hz), 26.08. HRMS: calcd. for $C_{12}H_{10}FNNaO_2$ [M + Na]$^+$: 242.0588; Found: 242.0586.



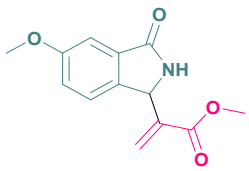
3-(6-broro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)-3-buten-2-one (3h): White solid, mp: 136-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.55 (s, 1H), 7.18 (s, 1H), 6.20 (s, 1H), 6.03 (s, 1H), 5.70 (s, 1H), 2.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.01, 170.14, 147.86, 145.62, 132.01, 130.01, 127.10, 126.97, 126.55, 125.35, 54.95, 26.07. HRMS: calcd. for $C_{12}H_{10}BrNNaO_2$ [M + Na]$^+$: 301.9787; Found: 301.9789.



Methyl 2-(3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4a):[3] White solid, mp: 173-175 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.56 (td, *J* = 7.6, 1.2 Hz, 1H), 7.51-7.44 (m, 2H), 7.01 (s, 1H), 6.32 (s, 1H), 5.81 (d, *J* = 0.8 Hz, 1H), 5.59 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.81, 166.40, 145.46, 137.90, 132.08, 131.37, 128.58, 126.30, 124.03, 123.52, 56.45, 52.36. HRMS: calcd. for $C_{12}H_{11}NNaO_3$ [M + Na]$^+$: 240.0631; Found: 260.0623.

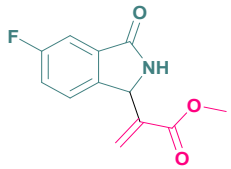


Methyl 2-(5-methyl-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4b): White solid, mp: 165-167 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.39-7.31 (m, 2 H), 7.00 (s, 1 H), 6.30 (s, 1 H), 5.79 (d, *J* = 0.8 Hz, 1 H), 5.54 (s, 1 H), 3.85 (s, 3 H), 2.44 (s, 3 H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 169.94, 165.77, 143.63, 138.53, 138.14, 132.89, 132.16, 126.52, 123.40, 122.96, 56.48, 52.39, 21.09. HRMS: calcd. for $C_{13}H_{13}NNaO_3$ [M + Na]$^+$: 254.0788; Found: 254.0788.

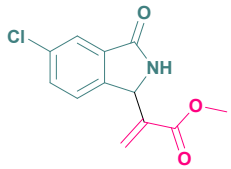


Methyl 2-(5-methoxy-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4c): White solid, mp:146-148 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38-7.30 (m, 2 H), 7.20 (s, 1 H),

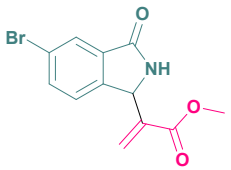
7.11 (dd, J = 8.4, 2.8 Hz, 1 H), 6.29 (s, 1 H), 5.79 (s, 1 H), 5.52 (s, 1 H), 3.86 (s, 3 H), 3.85 (s, 3 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (101 MHz,) 170.68, 166.40, 160.28, 138.02, 137.54, 132.79, 126.04, 124.42, 120.36, 106.61, 56.09, 55.67, 52.36. HRMS: calcd. for $C_{13}H_{13}NNaO_4$ [M + Na]$^+$: 270.0737; Found: 270.0739.



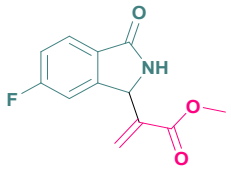
Methyl 2-(5-fluoro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4d): White solid, mp: 140-142 ^{o}C. ^{1}H NMR (400 MHz, d_6-DMSO) δ 9.00 (s, 1H), 7.50-7.38 (m, 3H), 6.24 (s, 1H), 5.92 (s, 1H), 5.51 (s, 1H), 3.71 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 168.62 (d, $^4J_{C\text{-}F}$ = 3.5 Hz), 165.51, 162.47 (d, $^1J_{C\text{-}F}$ = 244.7 Hz), 142.03, 137.94, 134.38 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 127.26, 125.21 (d, $^3J_{C\text{-}F}$ = 8.6 Hz), 119.27 (d, $^2J_{C\text{-}F}$ = 23.5 Hz), 109.67 (d, $^2J_{C\text{-}F}$ = 23.2 Hz), 56.50, 52.25. HRMS: calcd. for $C_{12}H_{10}FNNaO_3$ [M + Na]$^+$: 258.0537; Found: 258.0541.



Methyl 2-(5-chloro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4e): White solid, mp: 143-145 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 1.6 Hz, 1H), 7.53 (dd, J = 8.2, 1.6 Hz, 1H), 7.41 (d, J = 8 Hz, 1H), 6.70 (s, 1H), 6.34 (s, 1H), 5.80 (d, J = 0.8 Hz, 1H), 5.56 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) 168.34, 165.42, 144.92, 137.67, 134.23, 133.38, 131.90, 127.61, 125.08, 122.86, 56.66, 52.25. HRMS: calcd. for $C_{12}H_{10}ClNNaO_3$ [M + Na]$^+$: 274.0241; Found: 274.0241.

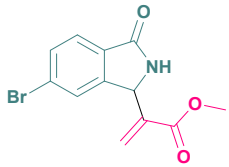


Methyl 2-(5-broro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4f): White solid, mp: 147-148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 1.6 Hz, 1H), 7.67 (dd, J = 8.2, 1.6 Hz, 1H), 7.36 (d, J = 8 Hz, 1H), 7.03 (s, 1H), 6.34 (s, 1H), 5.81 (d, J = 0.8 Hz, 1H), 5.54 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) 169.13, 166.20, 144.08, 137.42, 135.11, 133.41, 127.27, 126.61, 125.18, 122.80, 56.33, 52.47. HRMS: calcd. for $C_{12}H_{10}BrNNaO_3$ [M + Na]$^+$: 317.9736; Found: 317.9740.

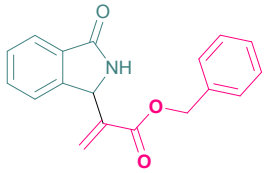


Methyl 2-(6-fluoro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4g): White solid,

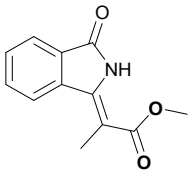
mp: 142-144 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 1H), 7.22-7.15 (m, 2H), 6.53 (s, 1H), 6.35 (s, 1H), 5.84 (d, J = 1.2 Hz, 1H), 5.99 (s, 1H), 5.56 (s, 1H), 3.87 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 168.79, 165.51, 164.61 (d, $^1J_{C\text{-}F}$ = 248.3 Hz), 148.93 (d, $^3J_{C\text{-}F}$ = 10.0 Hz), 137.73, 128.48 (d, $^4J_{C\text{-}F}$ = 1.6 Hz), 127.65, 125.51 (d, $^3J_{C\text{-}F}$ = 9.9 Hz), 116.11 (d, $^2J_{C\text{-}F}$ = 23.5 Hz), 110.48 (d, $^2J_{C\text{-}F}$ = 24.4 Hz), 56.54 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 52.32. HRMS: calcd. for $C_{12}H_{10}FNNaO_3$ [M + Na]$^+$: 258.0537; Found: 258.0539.



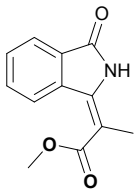
Methyl 2-(6-broro-3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4h): White solid, mp: 146-148 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, J = 7.6 Hz, 1H), 7.68-7.60 (m, 2H), 7.16 (s, 1H), 6.35 (s, 1H), 5.85 (s, 1H), 5.58 (s, 1H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 169.10, 165.72, 148.75, 137.78, 131.96, 131.71, 128.24, 126.47, 125.78, 125.40, 56.84, 52.58. HRMS: calcd. for $C_{12}H_{10}BrNNaO_3$ [M + Na]$^+$: 317.9736; Found: 317.9737.



Benzyl 2-(3-Oxo-2,3-dihydro-1*H*-isoindol-1-yl)acrylate (4i): White solid, mp: 122-124 °C. ^{1}H NMR (400 Hz, $CDCl_3$) δ 7.85 (m, 1H), 7.54 (dt, J = 7.4, 1.5 Hz, 1H), 7.51-7.45 (m ,1H), 7.45-7.41 (m, 1H), 7.40-7.33 (m, 1H), 6.97 (s, 1H), 6.37 (s, 1H), 5.82 (d, J = 0.8 Hz, 1H), 5.60 (s, 1H), 5.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.63, 165.72, 145.33, 137.90, 135.26, 132.07, 131.30, 128.65, 128.57, 128.49, 128.30, 126.67, 124.04, 123.49, 67.17, 56.45. HRMS: calcd. for $C_{18}H_{15}NNaO_3$ [M + Na]$^+$: 316.0944; Found: 316.0952.



Methyl (Z)-2-(3-oxoisoindolin-1-ylidene)propanoate (4a-s1): White solid, ^{1}H NMR (400 Hz, $CDCl_3$) δ 10.24 (s, 1H), 7.94 (s, 1H), 7.92 (s, 1H), 7.70-7.55 (m, 2H), 3.86 (s, 3H), 2.39 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.96, 167.52, 143.24, 136.49, 132.43, 130.78, 130.39, 125.45, 124.02, 104.37, 52.26, 13.40. HRMS: calcd. for $C_{12}H_{11}NNaO_3$ [M + Na]$^+$: 240.0631; Found: 260.0628.

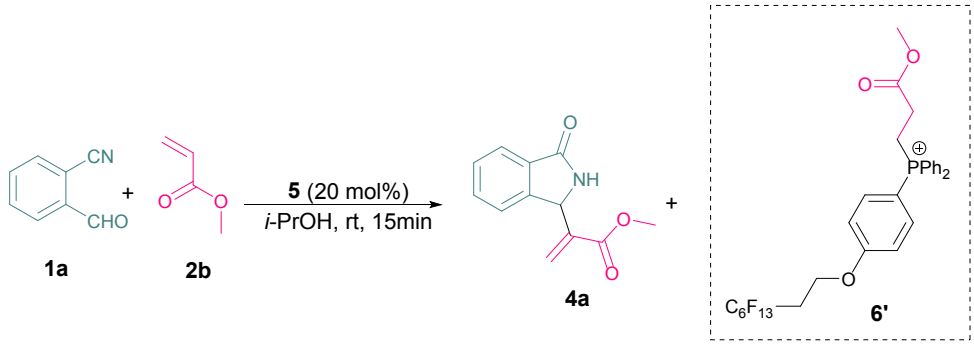


Methyl (E)-2-(3-oxoisoindolin-1-ylidene)propanoate (4a-s2): White solid, ^{1}H NMR (400 Hz, $CDCl_3$) δ 8.83 (s, 1H), 8.41(d, J = 8 Hz, 1H) , 7.87 (d, J = 8 Hz, 1H), 7.66-7.49 (m, 2H), 3.89 (s, 3H), 2.25 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 168.68, 168.33, 140.20, 134.98, 132.88, 130.76, 129.96, 126.16, 123.32, 108.89, 52.16, 16.05. HRMS: calcd. for $C_{12}H_{11}NNaO_3$ $[M + Na]^+$: 240.0631; Found: 260.0630.

VI. Mechanistic study.

Capture of intermediate 6'

To a stirred solution of **1a** (0.3 mmol, 2 equiv), **5** (2 equiv) in *i*-PrOH (0.75 mL) was added methyl acrylate (**2b**, 0.15 mmol, 1 equiv). The resulting reaction mixture was stirred at rt for 15 mins. The intermediate **6'** was captured by ESI-MS as shown in Fig. S2.



Captured by ESI-MS

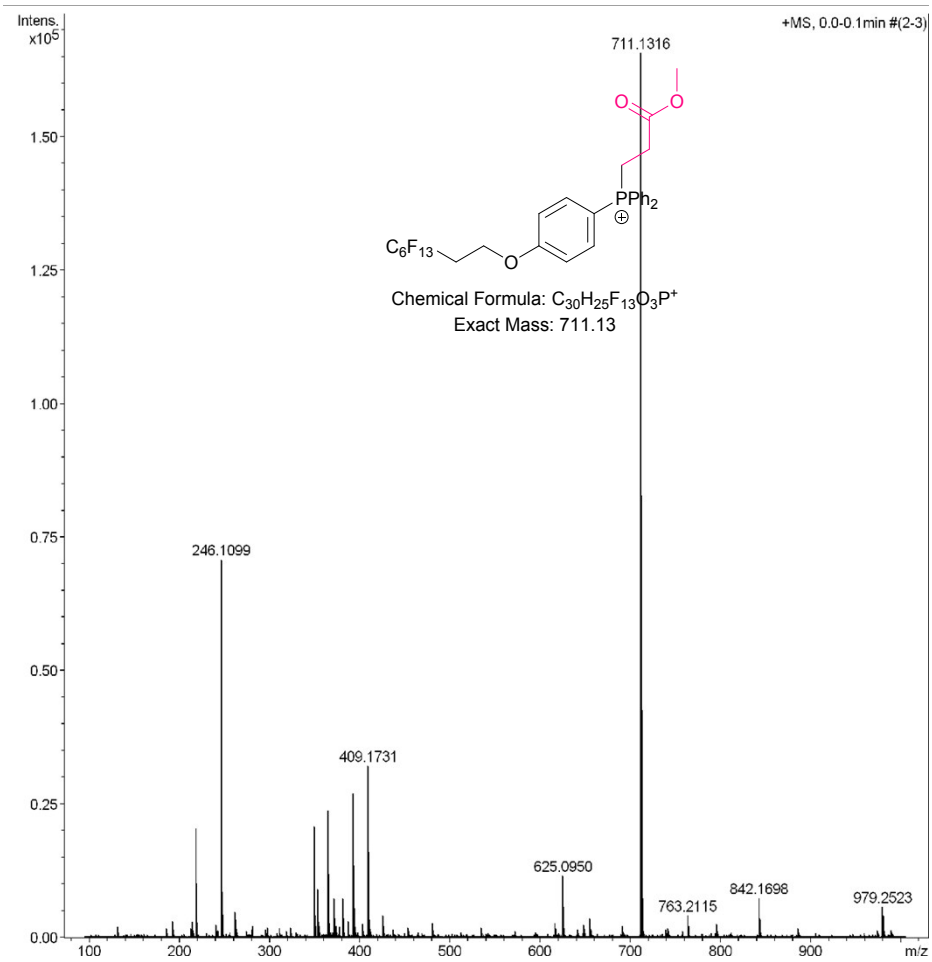


Fig. S2 ESI(+)-MS plot of the reaction: t=15 min.

Besides, the intermediate **6'** was obtained as shown in Fig. S3, A and B. Reaction procedure: To a stirred solution of **5** (0.15 mmol, 1 equiv), *p*-nitrophenol (PNP, 1.8 equiv) and EA (0.5 mL) was added methyl acrylate (**2b**, 3.5 equiv). The resulting reaction mixture was stirred at rt for 3 h.

It should be noted that no obvious change was observed when adding **6'** to the solution of **2a** in *i*-PrOH, even prolonging the reaction time to 24 h (Fig. S3, C).

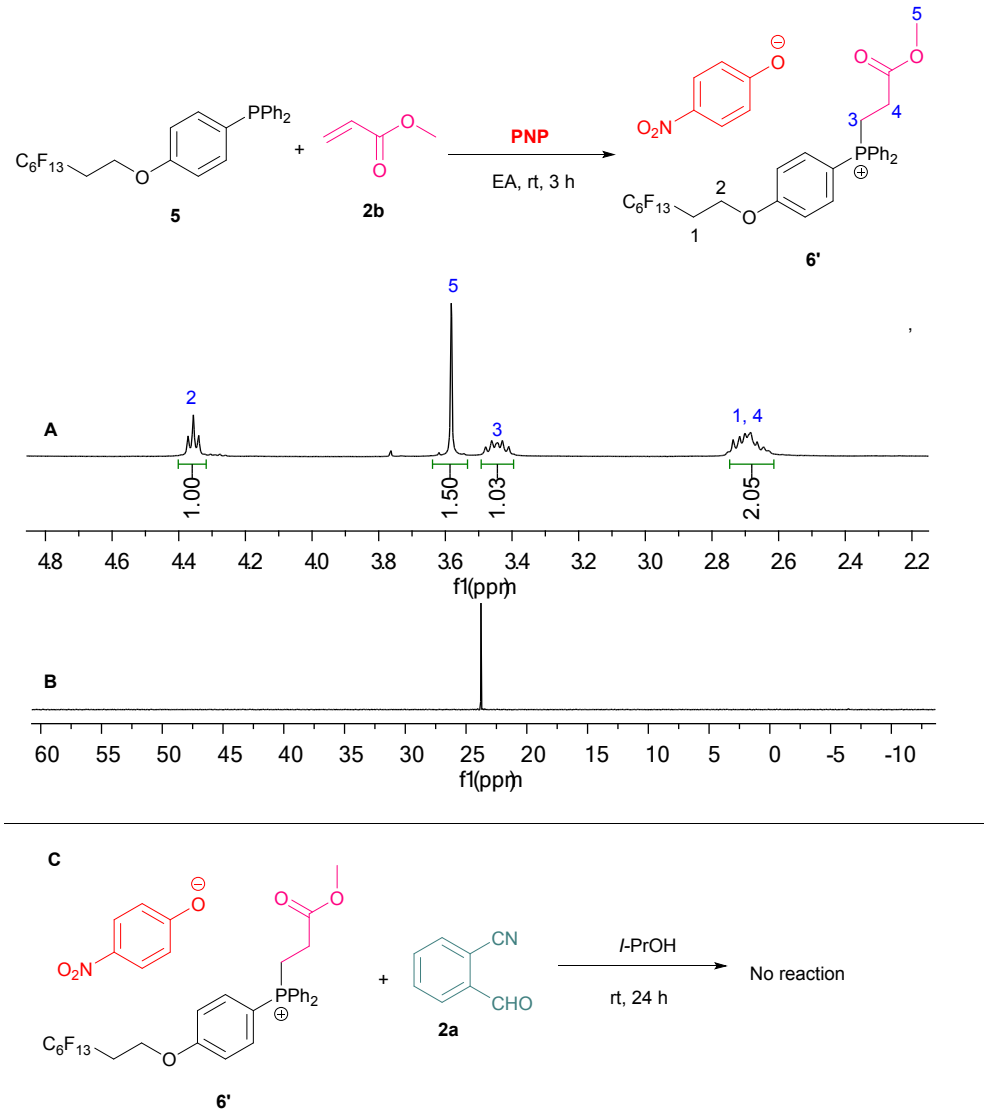


Fig. S3: A) ^{1}H NMR spectrum of 6'; B) ^{31}P NMR spectrum of 6'; C) Further investigation of its reactivity.

Capture of intermediate 7

To a stirred solution of **1a** (0.15 mmol, 1 equiv), **5** (1 equiv) in EA (0.38 mL) was added methyl acrylate (**2b**, 0.15 mmol, 1 equiv). The resulting reaction mixture was stirred at rt for 5 mins. The intermediate **7** was markedly captured by ESI-MS as shown in Fig. S4.

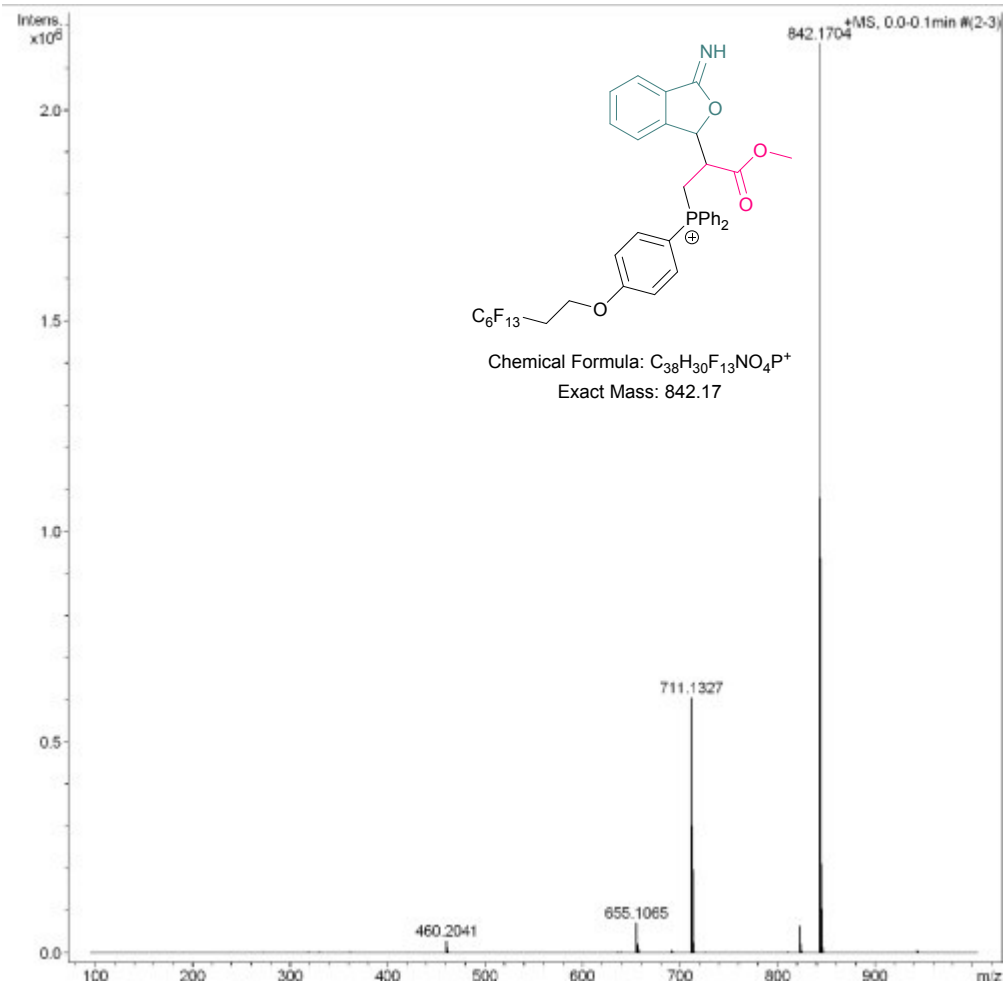
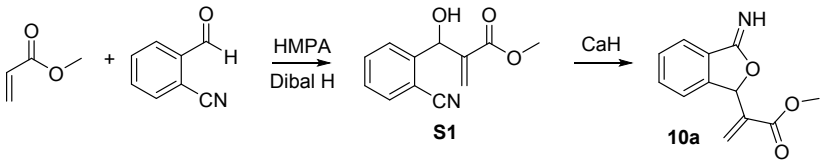


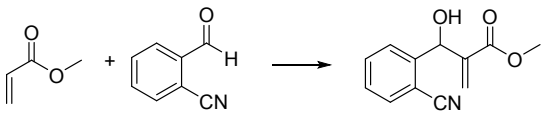
Fig. S4 ESI(+)-MS plot of the reaction: t=5 min.

Control experiment

1. Synthesis of possible intermediate 10

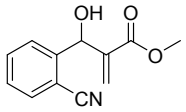


Scheme S1 Synthetic route of possible intermediate **10a**



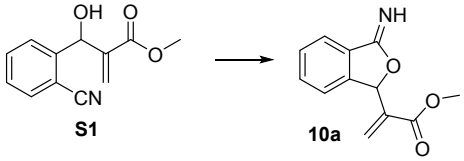
S1

To a stirred solution of HMPA (0.391 mL, 2.25 mmol) in THF (8 mL) was dropped a solution of DIBAL H (1.65 mmol) in hexane (1 M, 1.65 mL) at 0 °C. After 0.5 h, methyl propynoate (0.133 mL, 1.50 mmol) was added. The reaction mixture was stirred for 1 h, and then butyraldehyde (0.265 mL, 3.00 mmol) was added. The mixture was allowed to warm to rt and stirred for 15 h at the same temperature. The resulting solution was then treated with 5 mL of 1 N HCl solution, and extracted with 100 mL of ether. The organic layer was successively washed with 1 N HC1 solution (10 mL×3) and saturated $NaHCO_3$ solution (10 mL×1). The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc : PE = 1 : 5 v/v) to give compound **S1** 207 mg as oil (13%).



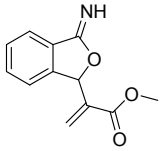
s1

Methyl 2-((2-cyanophenyl)(hydroxy)methyl)acrylate (S1): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.89 (m, 1H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.51 (m, 2H), 6.40 (d, *J* = 1.2 Hz, 1H), 6.30 (s, 1H), 5.95 (s, 1H), 3.82 (d, *J* = 2.4 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 165.3, 148.4, 136.4, 134.3, 129.5, 127.6, 125.8, 125.3, 122.8, 78.7, 52.3; IR (KBr, cm^{-1}) v 3203, 1709, 1630; HRMS：calcd. for $C_{13}H_{13}NNaO_3$ $[M + Na]^+$ 240.0631, found 240.0623.



S1 **10a**

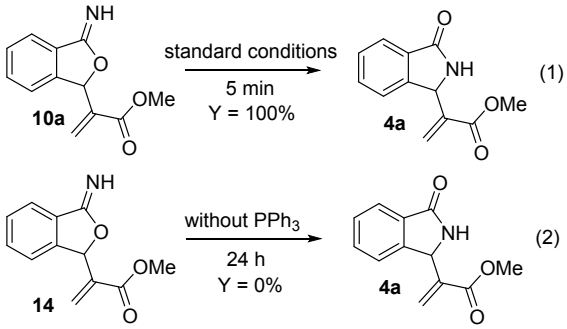
To a stirred solution of compound **S1** (200 mg, 0.92 mmol) in THF (4.6 mL), CaH (39 mg, 0.92 mmol) was added in batches at -78 ^{o}C under Ar atmosphere. The reaction mixture was stirred at the same temperature for 1 h, and then quenched by saturated NH_4Cl solution, and extracted with 50 mL of ether. The organic layer was successively washed with H_2O (10 mL×3) and brine (10 mL×1). The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc : PE = 1 : 3 v/v) to give compound **10a** 181 mg as oil (90 %).



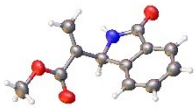
Methyl 2-(3-imino-1,3-dihydroisobenzofuran-1-yl)acrylate (10a):
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 6.6 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.57 – 7.53 (m, 2H), 6.51 (s, 1H), 6.33 (s, 1H), 6.12 (s, 1H), 3.84 (s, 3H); ^{13}C NMR (150 MHz,

$CDCl_3$) δ 170.3, 167.0, 154.6, 147.5, 135.1, 129.9, 129.5, 127.6, 125.9, 125.8, 79.1, 52.4; HRMS：calcd. for $C_{13}H_{13}NNaO_3$ $[M + Na]^+$ 240.0631, found 240.0633.

2. Control experiment:



To gain some insight of the tandem reaction, two control experiments were carried out. The imidate **10a** was converted into isoindolinone **4a** quantitatively within 5 min in presence of 0.2 equiv. of PPh_3 [Eq. (1)], while no reaction happened in the absence of PPh_3 [Eq. (2)], indicating that imidate **10** may be a possible intermediate in the formation of final product **3** or **4**.



VII. Crystal structure of 4a.

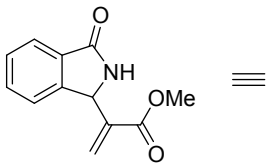


Fig. S5 ORTEP drawing (30%) of the crystal structure of compound **4a**.

Table S2. The single crystal date of compound 4a

Identification code	exp_11203
Empirical formula	C12H11NO3
Formula weight	217.22
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1

a/Å	4.1648(3)
b/Å	10.9613(6)
c/Å	12.0440(7)
α /°	105.854(5)
β /°	90.015(6)
γ /°	94.640(6)
Volume/Å3	527.04(6)
Z	2
ρ calcg/cm3	1.369
μ /mm-1	0.824
F (000)	228.0
Crystal size/mm3	? × ? × ?
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.632 to 144.658
Index ranges	-5 ⩽ h ⩽ 3, -13 ⩽ k ⩽ 13, -14 ⩽ l ⩽ 14
Reflections collected	7998
Independent reflections	2037 [Rint = 0.0266, Rsigma = 0.0224]
Data/restraints/parameters	2037/0/154
Goodness-of-fit on F2	1.030
Final R indexes [I>=2σ (I)]	R1 = 0.0420, wR2 = 0.1076
Final R indexes [all data]	R1 = 0.0548, wR2 = 0.1181
Largest diff. peak/hole / e Å-3	0.15/-0.17

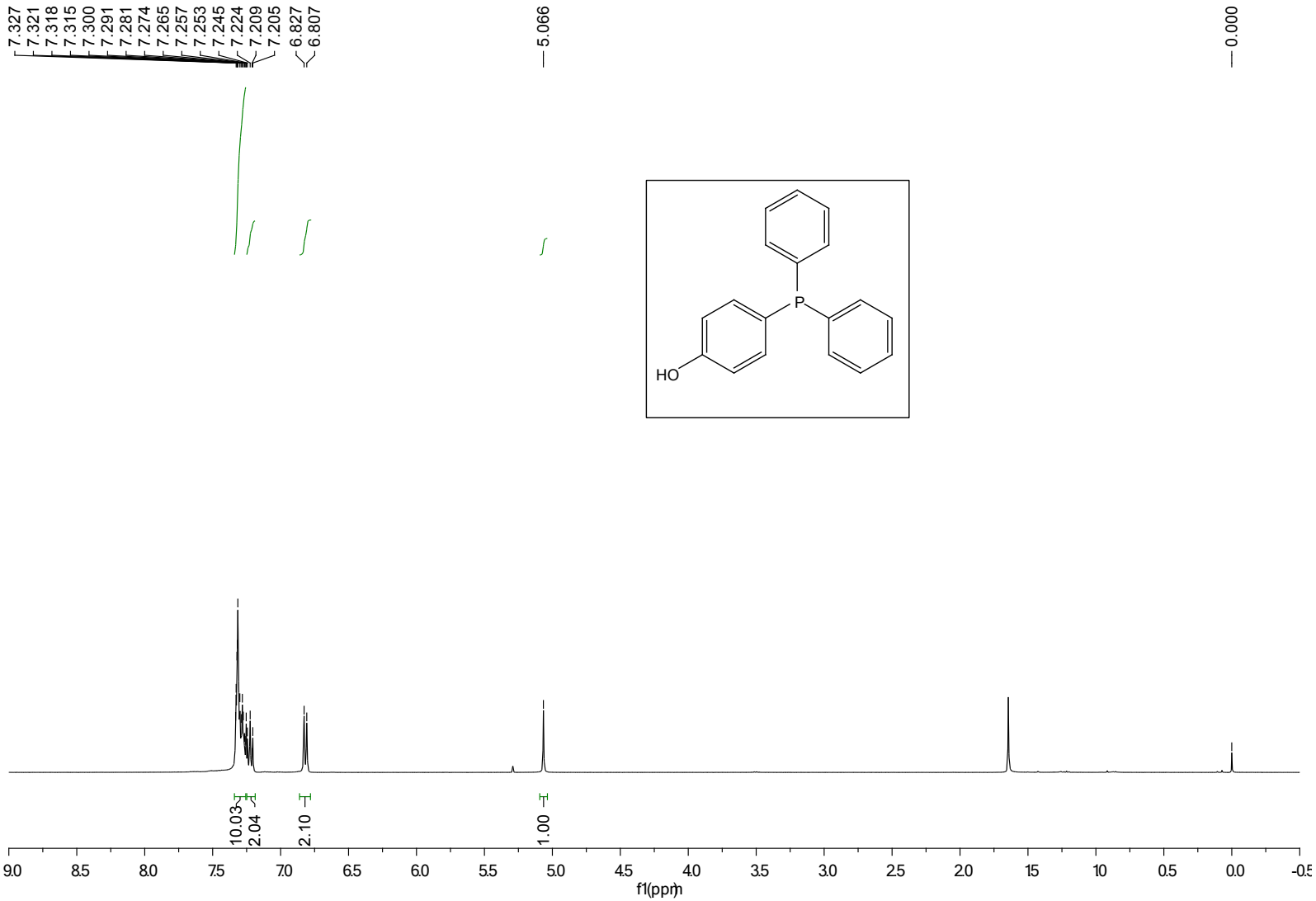
VIII. Reference

1 a) F. Sieber, P. J. Wentworth, J. D. Toker, A. D. Wentworth, W. A. Metz, N. N. Reed and K. D. Janda, *J. Org. Chem.*, 1999, **64**, 5188-5192; b) D. E. Bergbreiter and Y. C. Yang, *J. Org. Chem.*, 2010, **75**, 873–878.

2 T. Bríza, J. Kvícala, P. Mysík, O. Paleta, J. Cermák, *Synlett* 2001, 685-687.

3 Y. S. Song, C. H. Lee and K. J. Lee, *J. Heterocycl. Chem.*, 2003, **40**, 939-941.

IX. NMR spectra of the products.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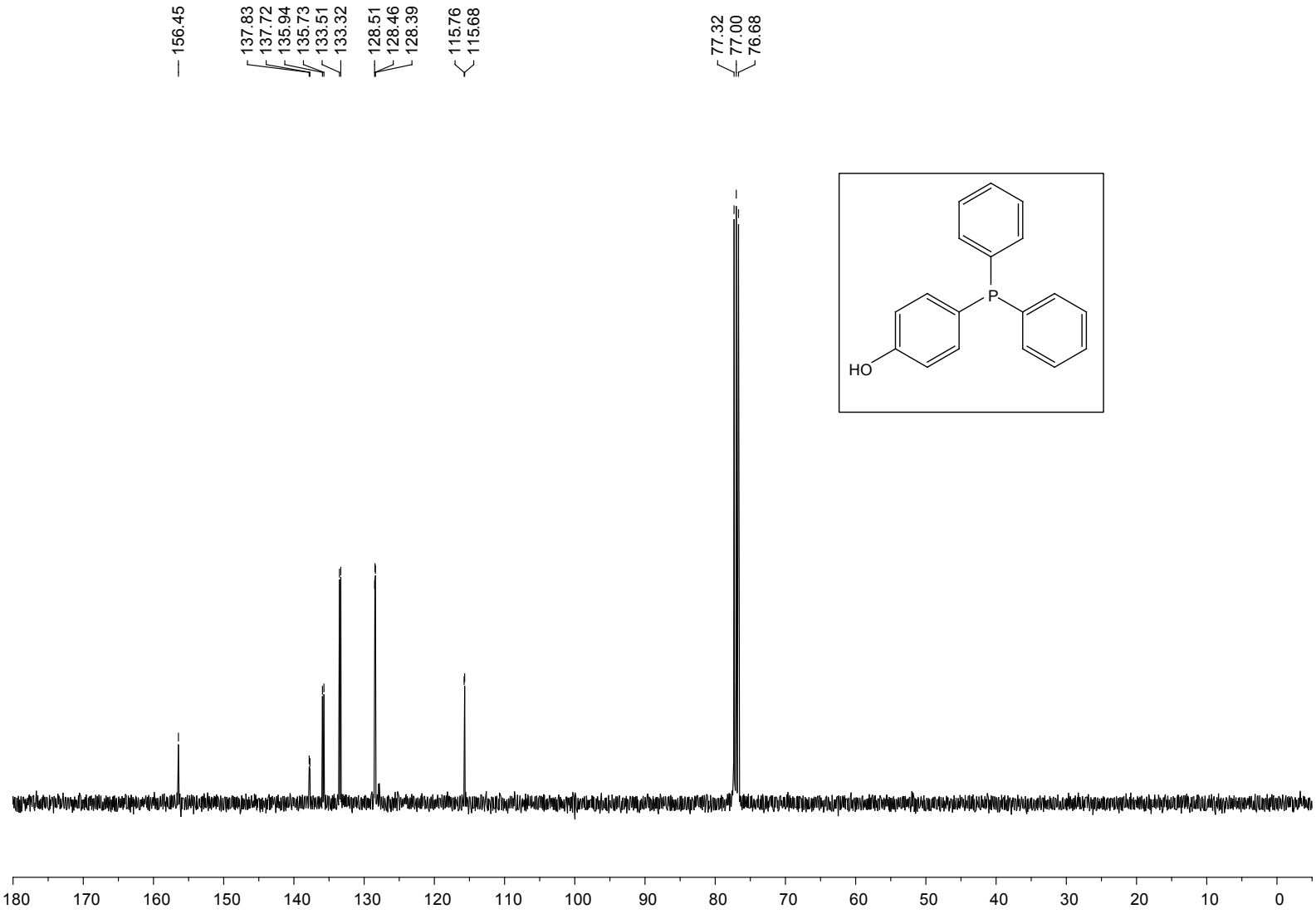
7.321
7.318
7.315
7.300
7.291
7.281
7.274
7.265
7.257
7.253
7.245
7.224
7.209
7.205
6.827
6.807
5.066
0.000
P
HO
10.03
2.04
2.10
1.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)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137.83
137.72
135.94
135.73
133.51
133.32
128.51
128.46
128.39
115.76
115.68
77.32
77.00
76.68
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80
70
60
50
40
30
20
10
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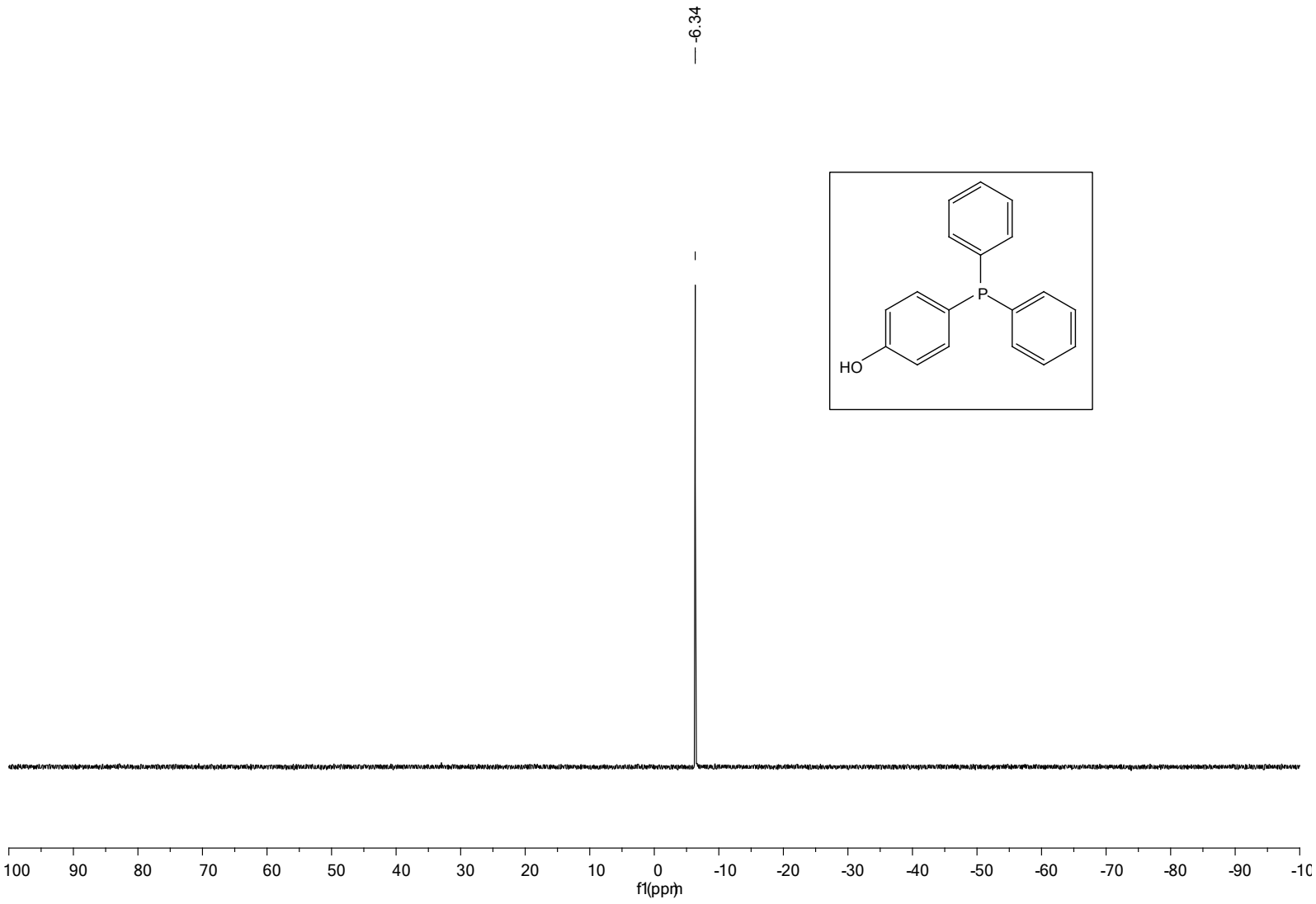
-6.34
P
HO
100
90
80
70
60
50
40
30
20
10
0
-10
-20
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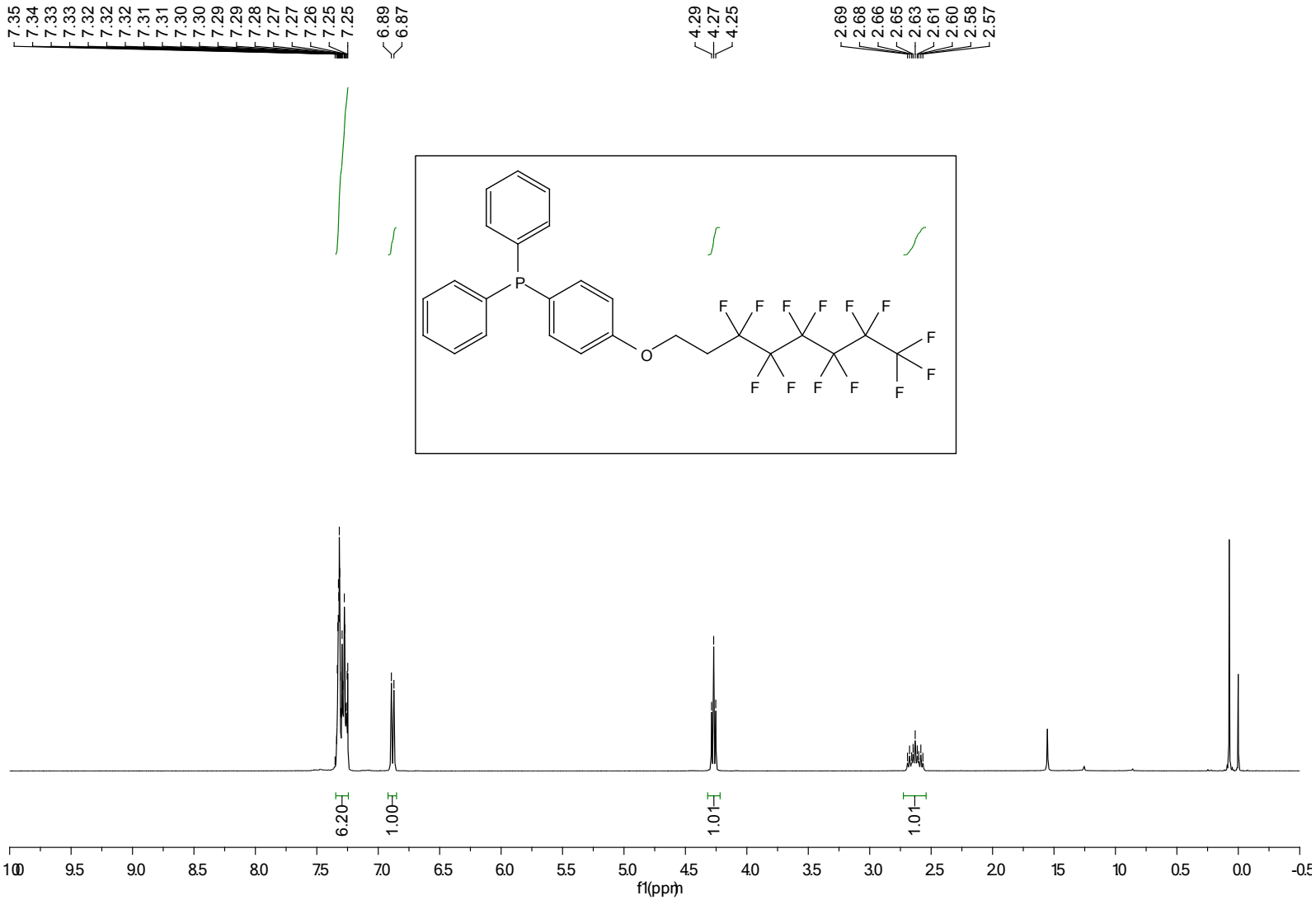
-40
-50
-60
-70
-80
-90
f1(ppm)


7.35
7.34
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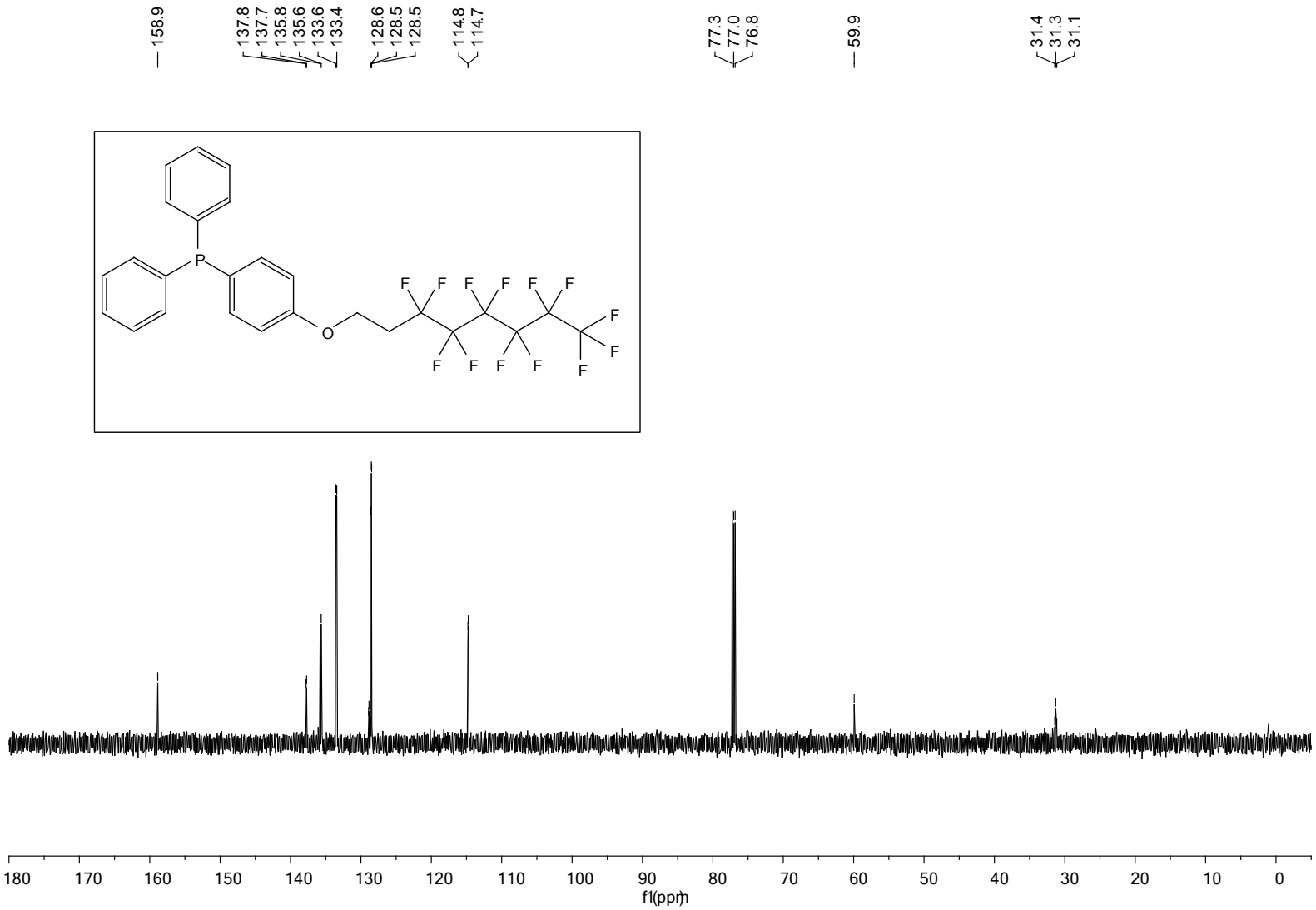
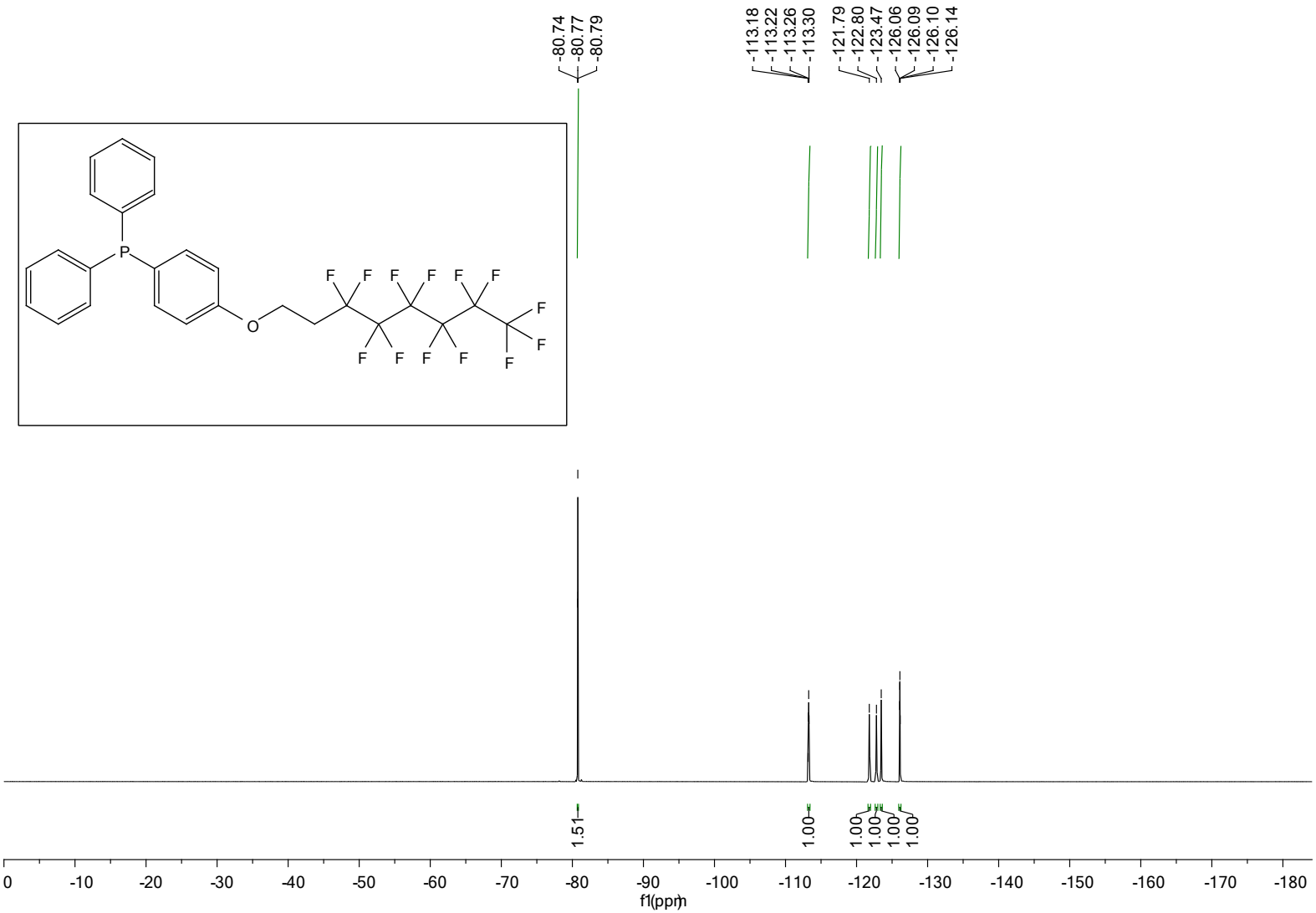
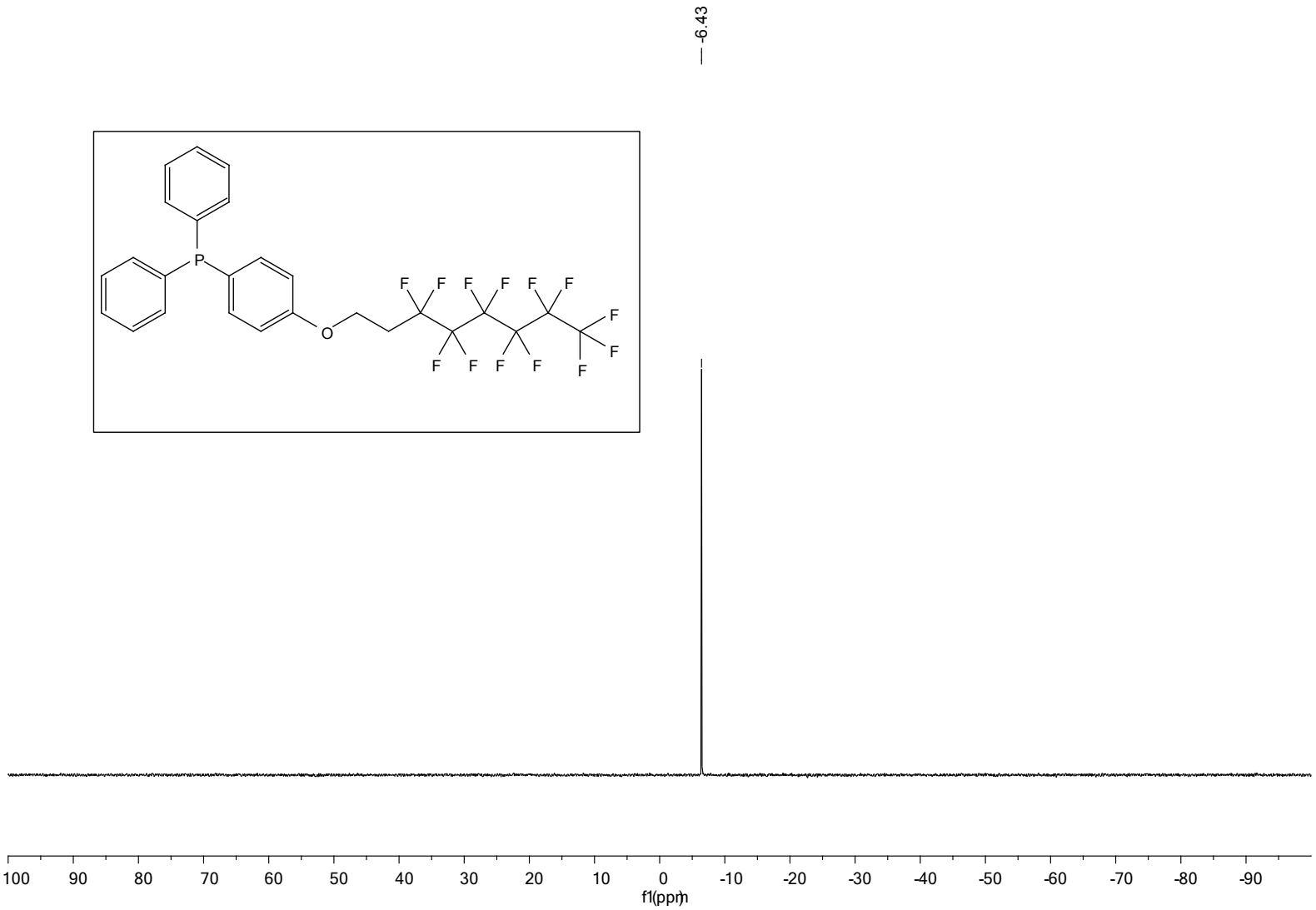
7.28
7.27
7.27
7.26
7.25
7.25
6.89
6.87
4.29
4.27
4.25
2.69
2.68
2.66
2.65
2.63
2.61
2.60
2.58
2.57
P
O
F
6.20
1.00
1.01
1.01
f1(ppm)


158.9
137.8
137.7
135.8
135.6
133.6
133.4
128.6
128.5
128.5
114.8
114.7
77.3
77.0
76.8
59.9
31.4
31.3
31.1
P
O
F
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)


-80.74
-80.77
-80.79
-113.18
-113.22
-113.26
-113.30
-121.79
-122.80
-123.47
-126.06
-126.09
-126.10
-126.14
P
O
F
1.51
1.00
1.00
1.00
1.00
1.00
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
f1(ppm)


-6.43
P
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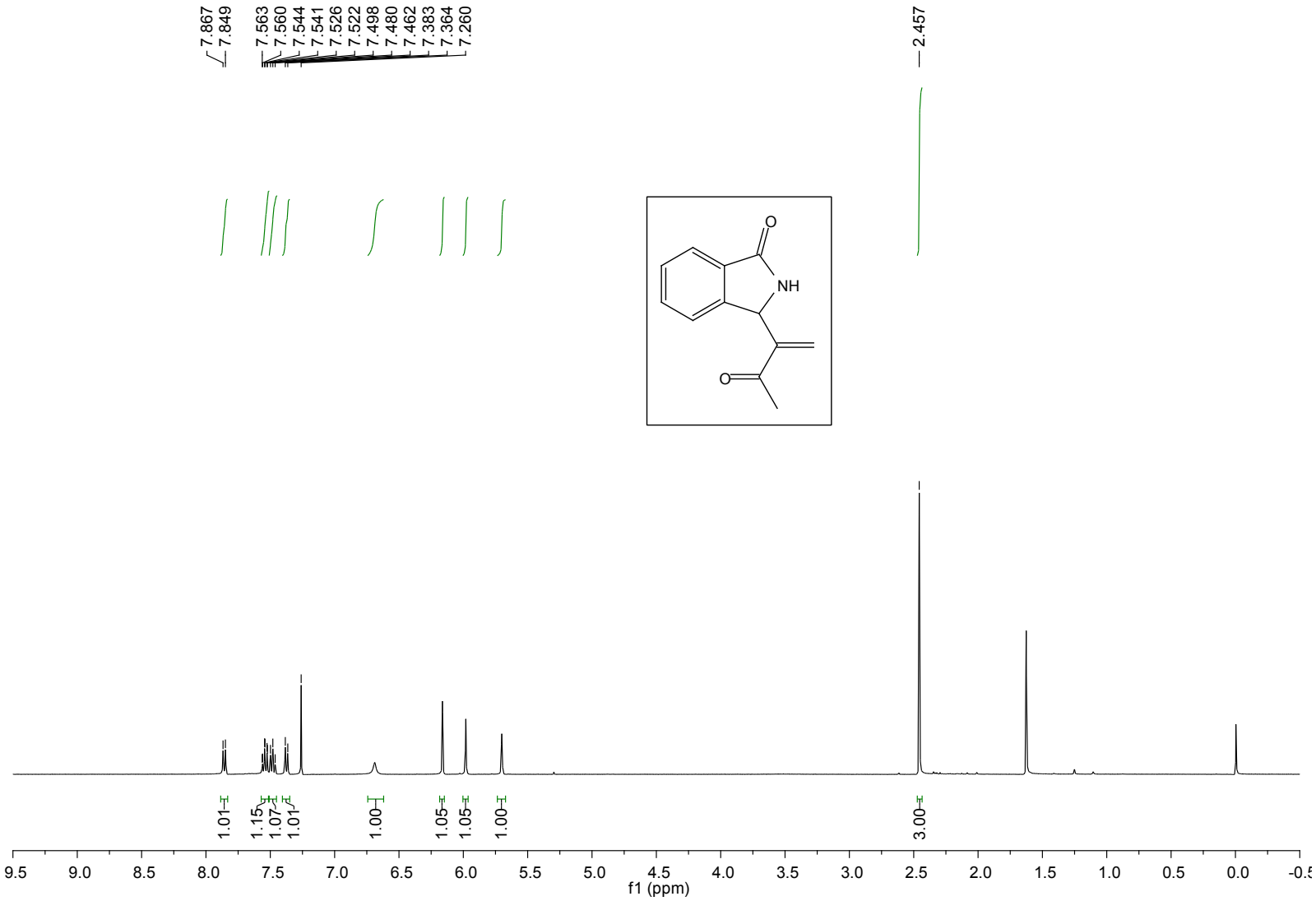
F
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
f1(ppm)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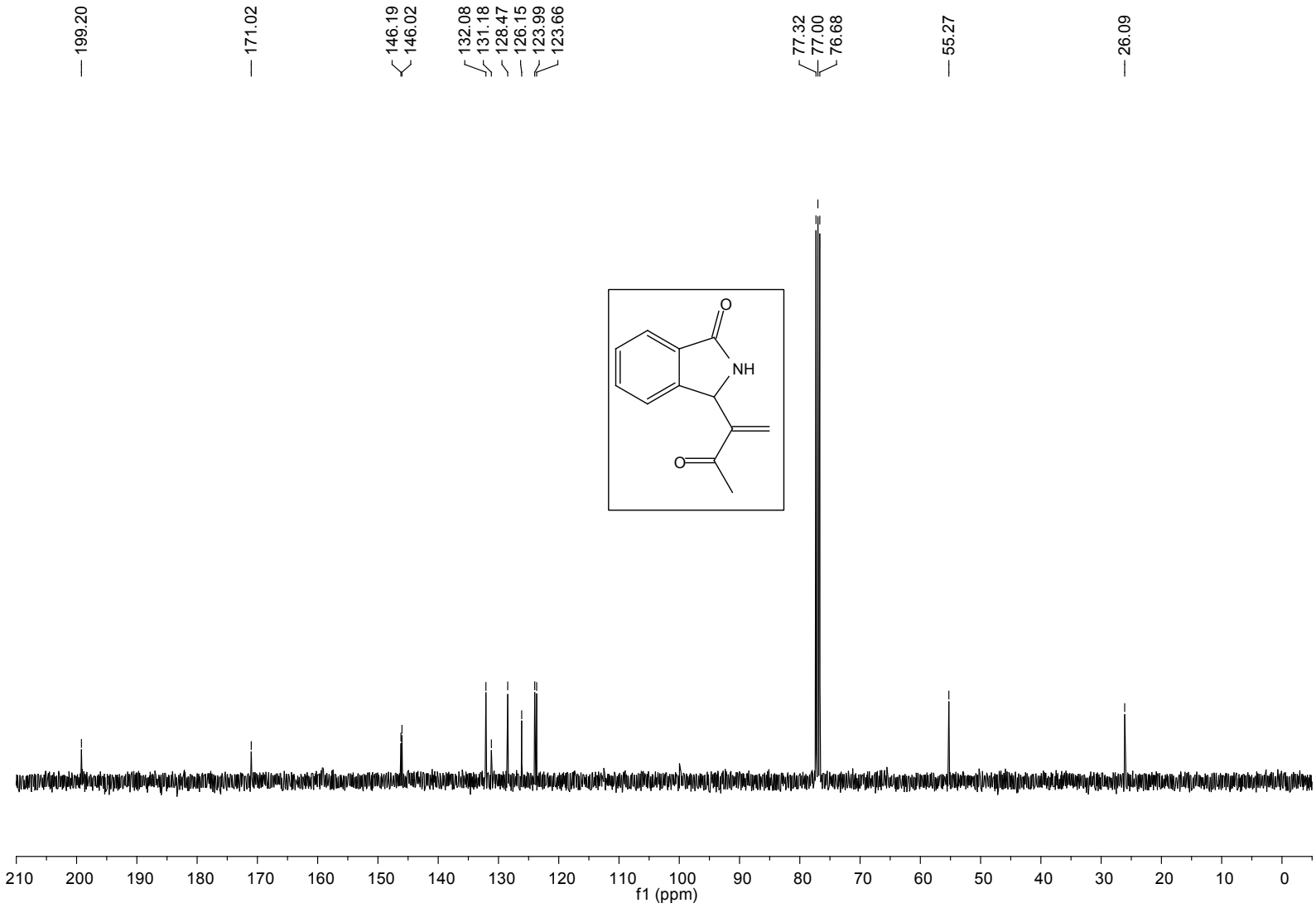
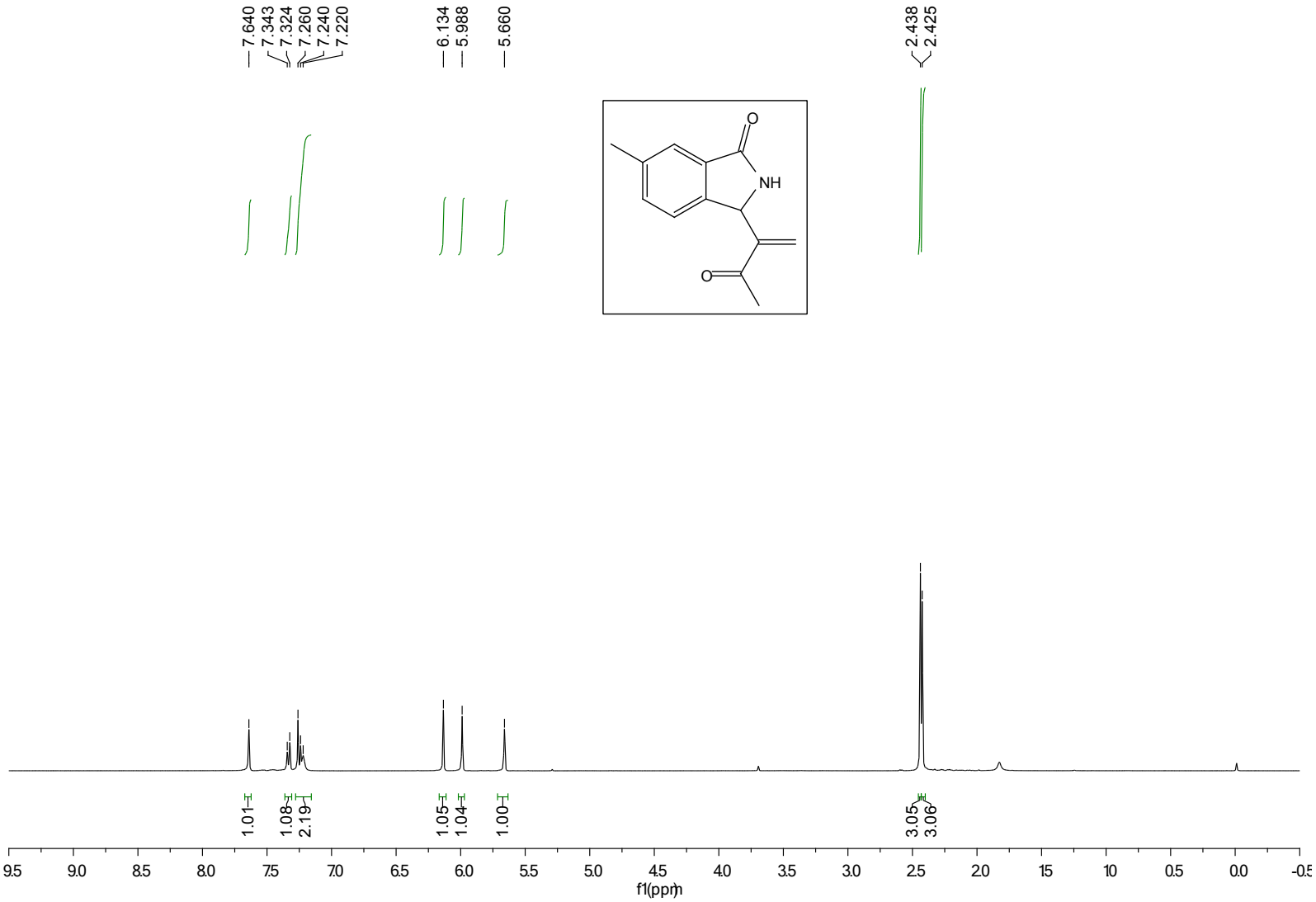
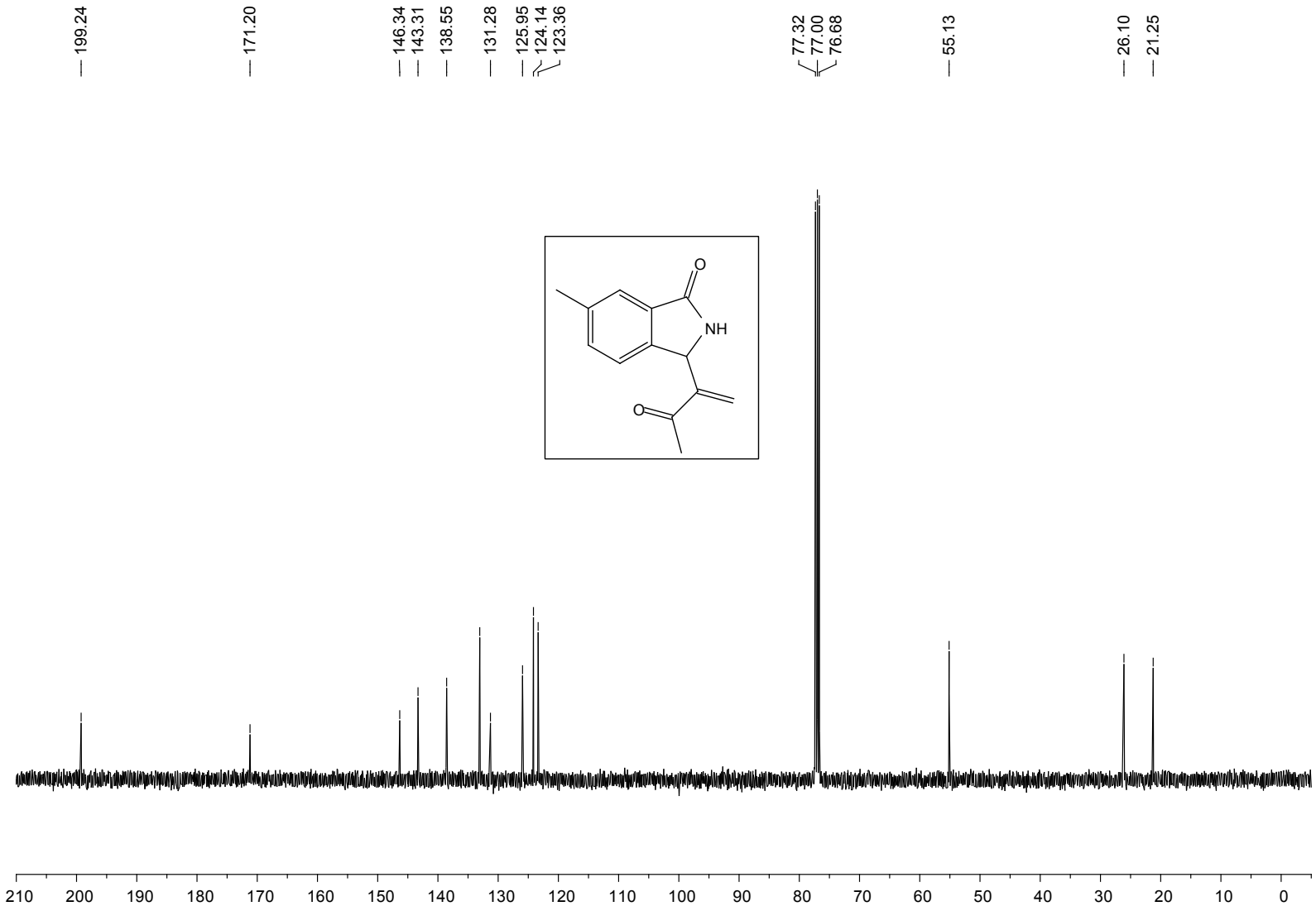
7.563
7.560
7.544
7.541
7.526
7.522
7.498
7.480
7.462
7.383
7.364
7.260
2.457
O
NH
O
1.01
1.15
1.07
1.01
1.00
1.05
1.05
1.00
3.00
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


199.20
171.02
146.19
146.02
132.08
131.18
128.47
126.15
123.99
123.66
77.32
77.00
76.68
55.27
26.09
O
NH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.640
7.343
7.324
7.260
7.240
7.220
6.134
5.988
5.660
2.438
2.425
O
NH
O
1.01
1.08
2.19
1.05
1.04
1.00
3.05
3.06
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)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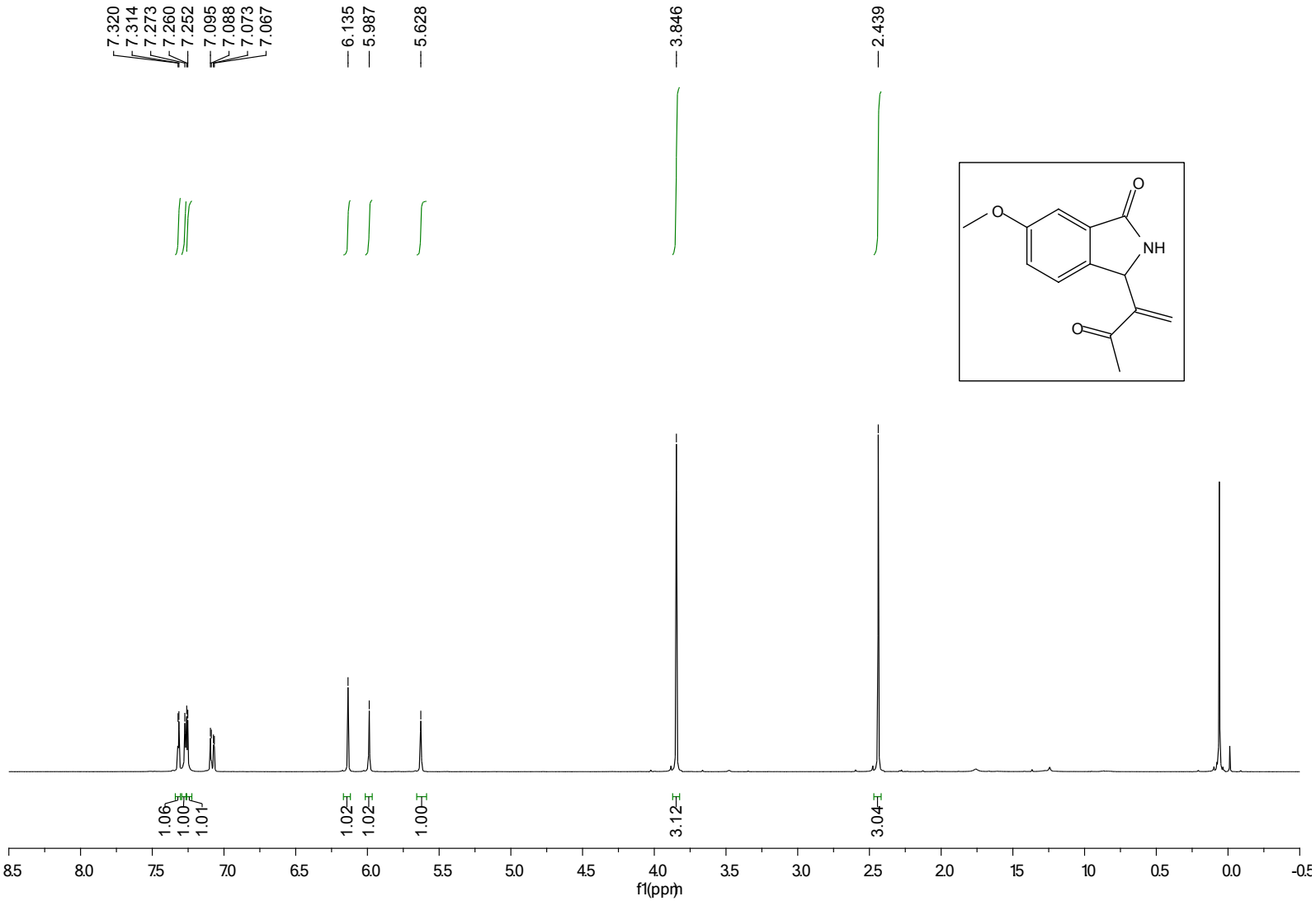
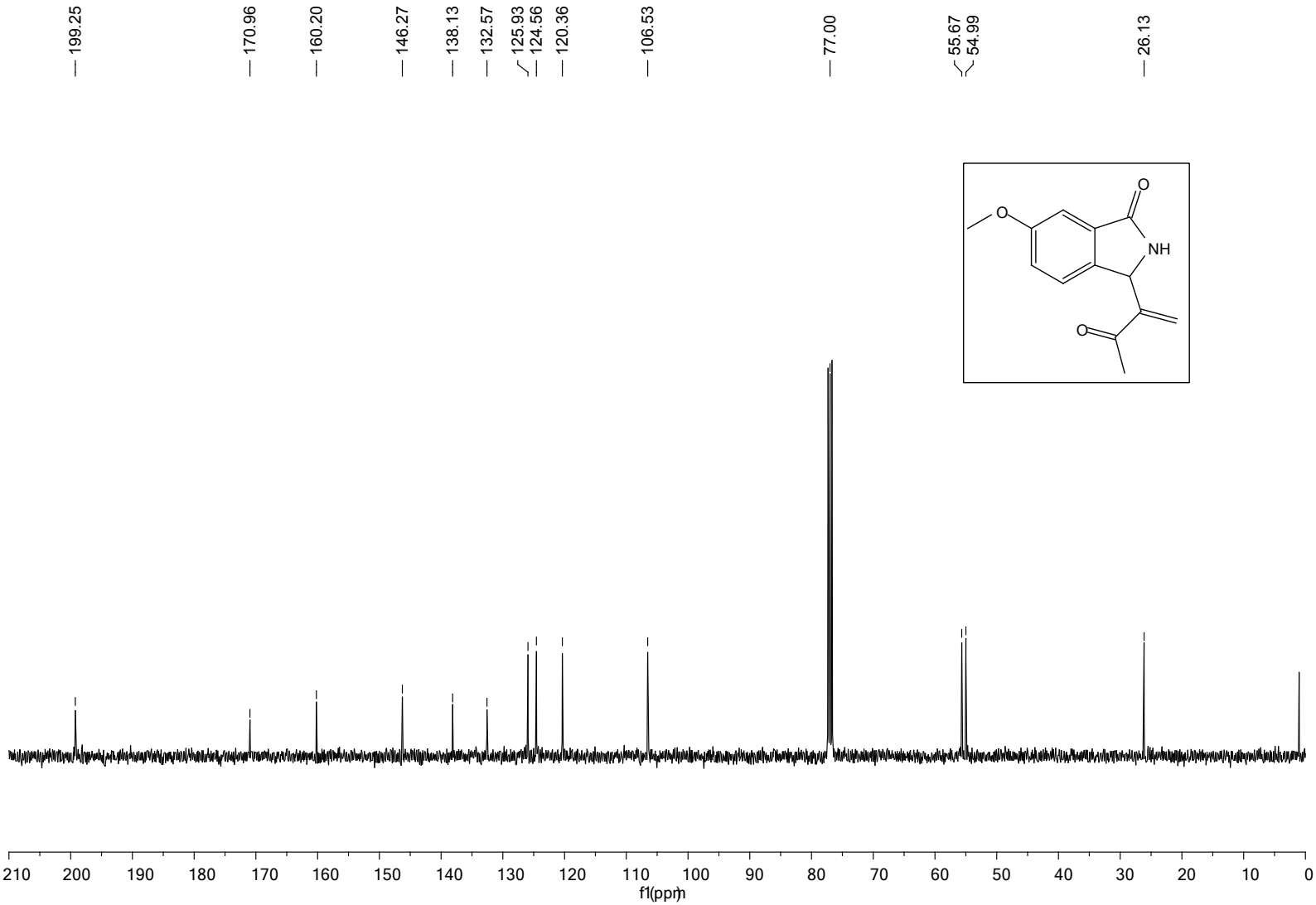
146.34
143.31
138.55
131.28
125.95
124.14
123.36
77.32
77.00
76.68
55.13
26.10
21.25
O
NH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.320
7.314
7.273
7.260
7.252
7.095
7.088
7.073
7.067
6.135
5.987
5.628
3.846
2.439
O
O
NH
O
1.06
1.00
1.01
1.02
1.02
1.00
3.12
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)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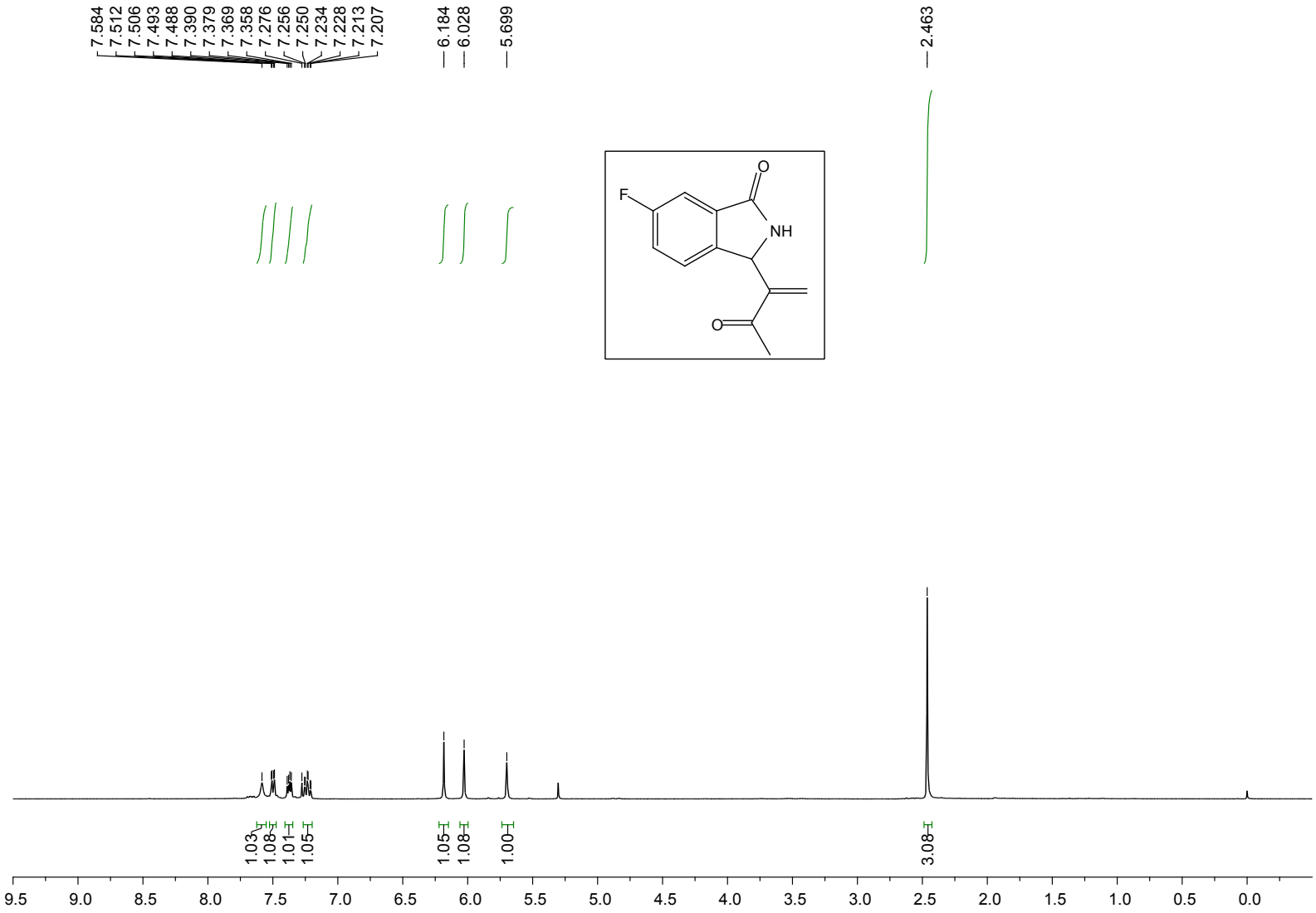
170.96
160.20
146.27
138.13
132.57
125.93
124.56
120.36
106.53
77.00
55.67
54.99
26.13
O
NH
O
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)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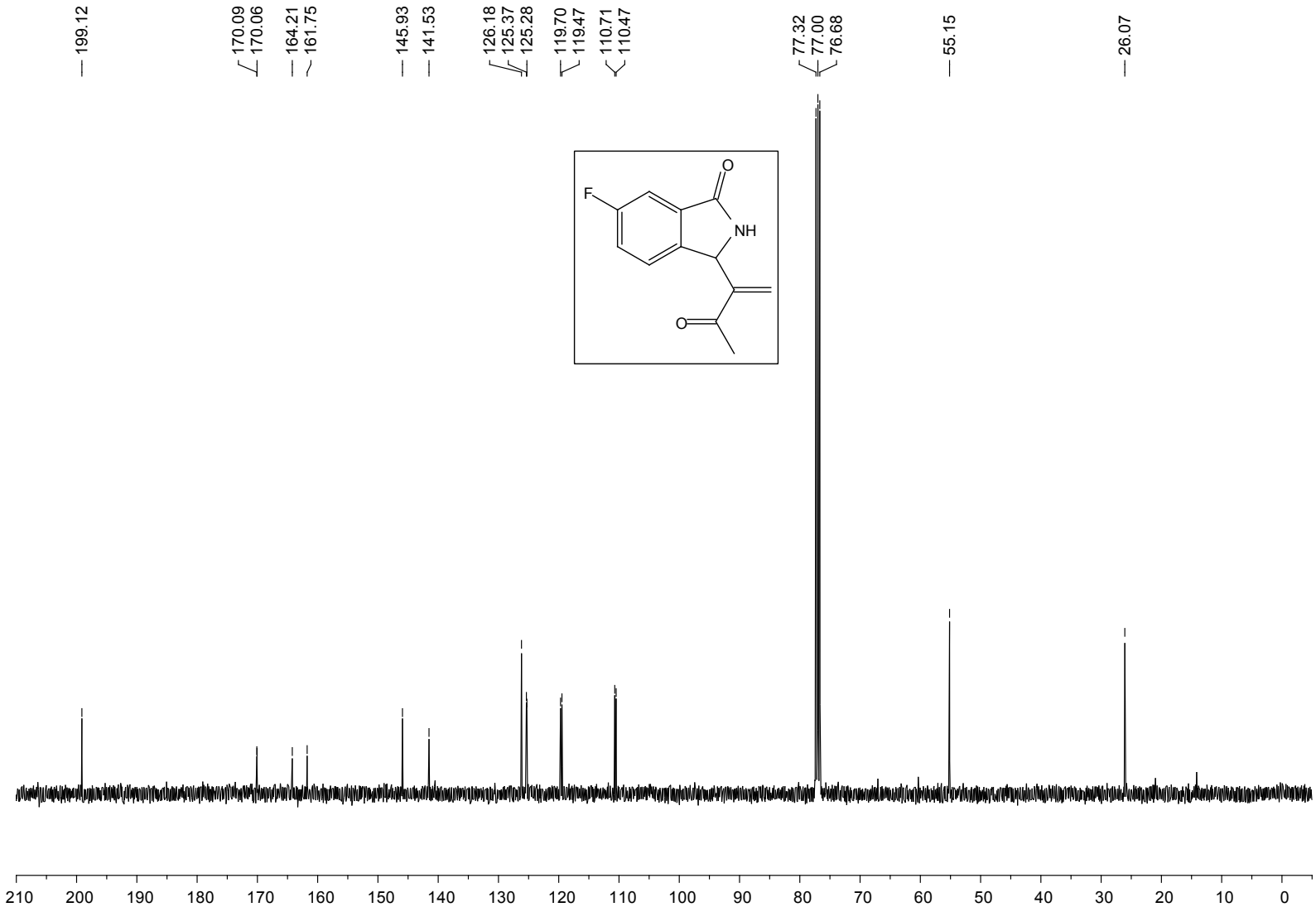
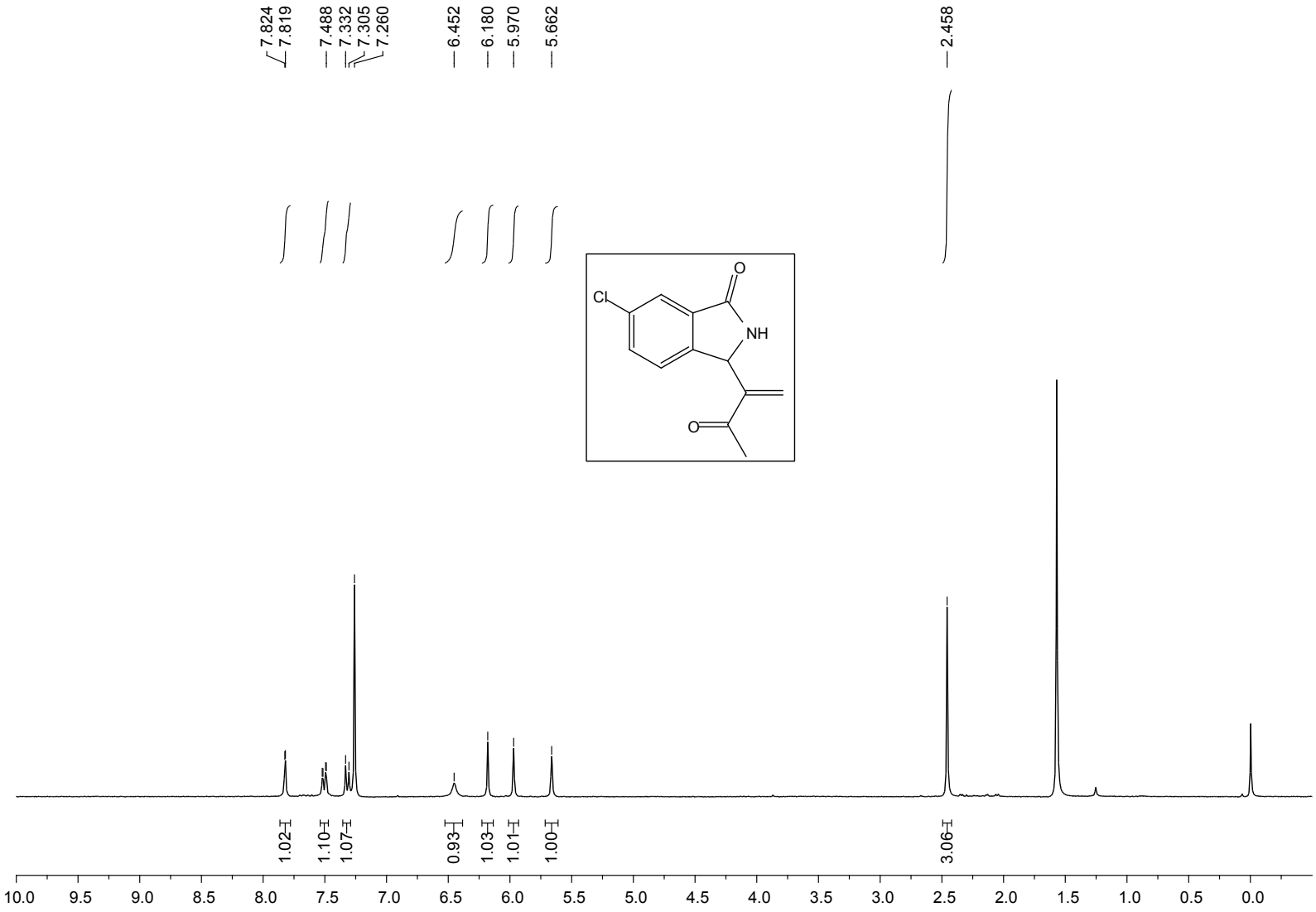
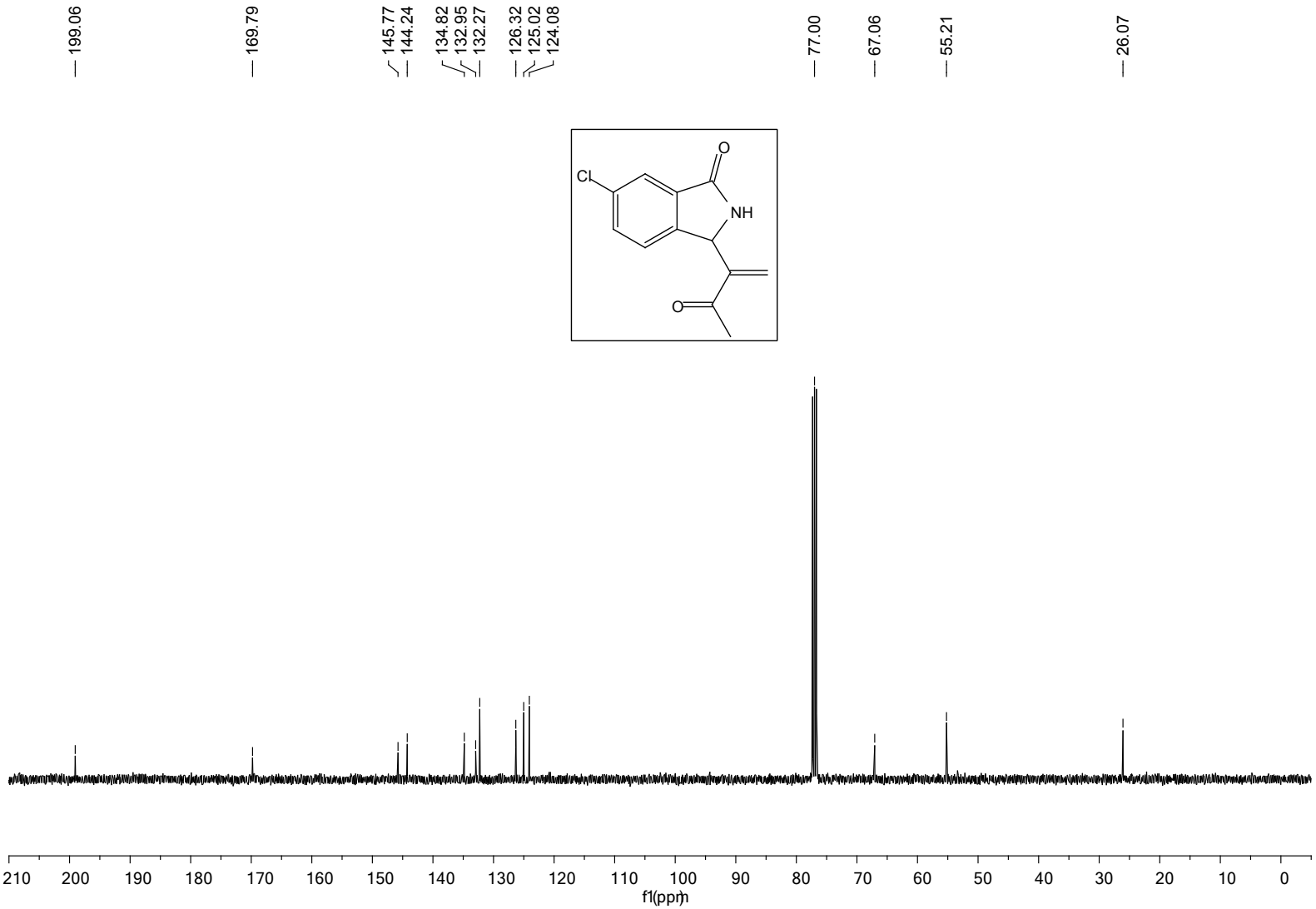
7.512
7.506
7.493
7.488
7.390
7.379
7.369
7.358
7.276
7.256
7.250
7.234
7.228
7.213
7.207
6.184
6.028
5.699
2.463
F
O
NH
O
1.03
1.08
1.01
1.05
1.05
1.08
1.00
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


199.12
170.09
170.06
164.21
161.75
145.93
141.53
126.18
125.37
125.28
119.70
119.47
110.71
110.47
77.32
77.00
76.68
55.15
26.07
F
O
NH
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.824
7.819
7.488
7.332
7.305
7.260
6.452
6.180
5.970
5.662
2.458
Cl
O
NH
O
1.02
1.10
1.07
0.93
1.03
1.01
1.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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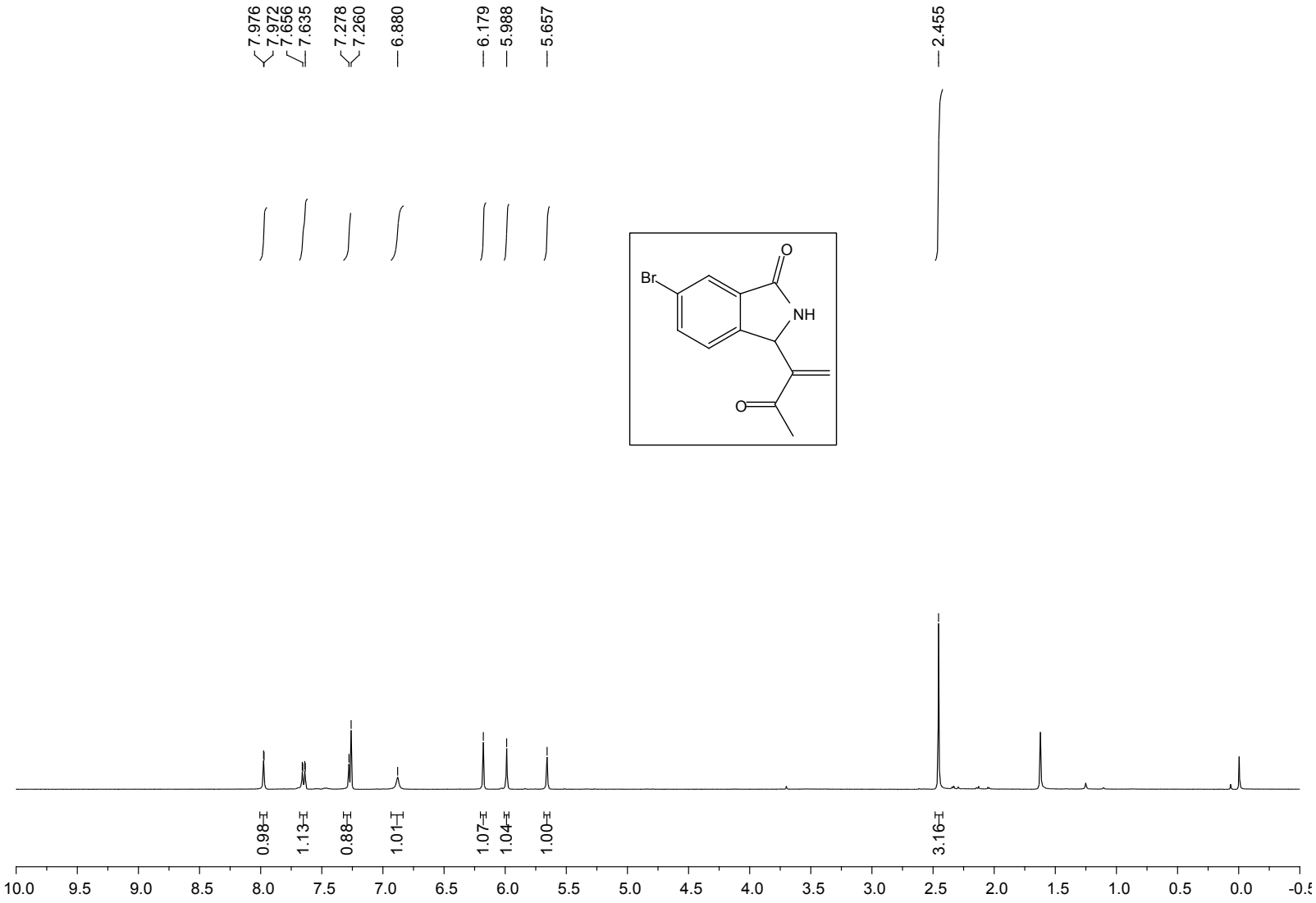
144.24
134.82
132.95
132.27
126.32
125.02
124.08
77.00
67.06
55.21
26.07
Cl
O
NH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)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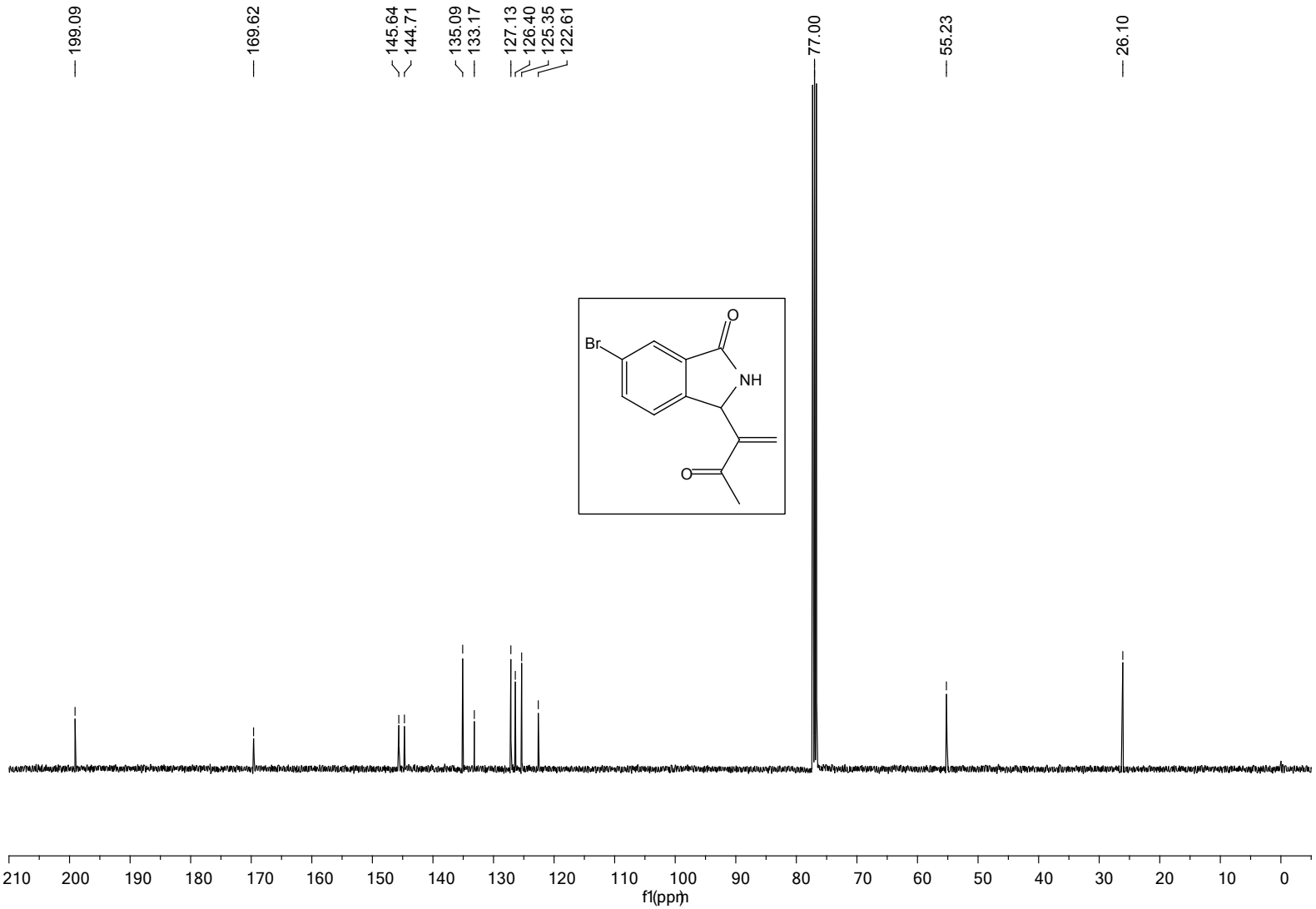
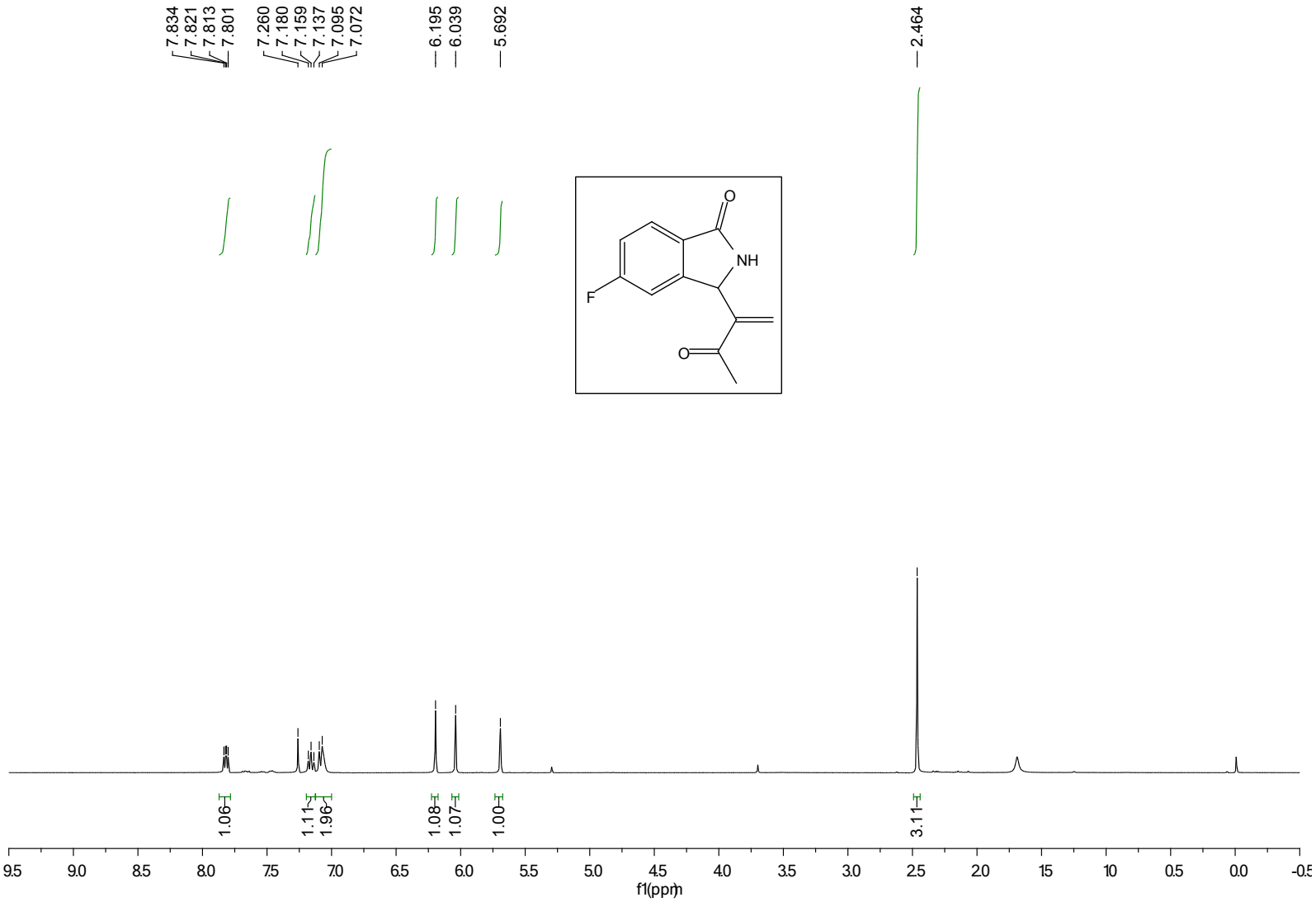
7.972
7.656
7.635
7.278
7.260
6.880
6.179
5.988
5.657
2.455
Br
O
NH
O
0.98
1.13
0.88
1.01
1.07
1.04
1.00
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


199.09
169.62
145.64
144.71
135.09
133.17
127.13
126.40
125.35
122.61
77.00
55.23
26.10
Br
O
NH
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)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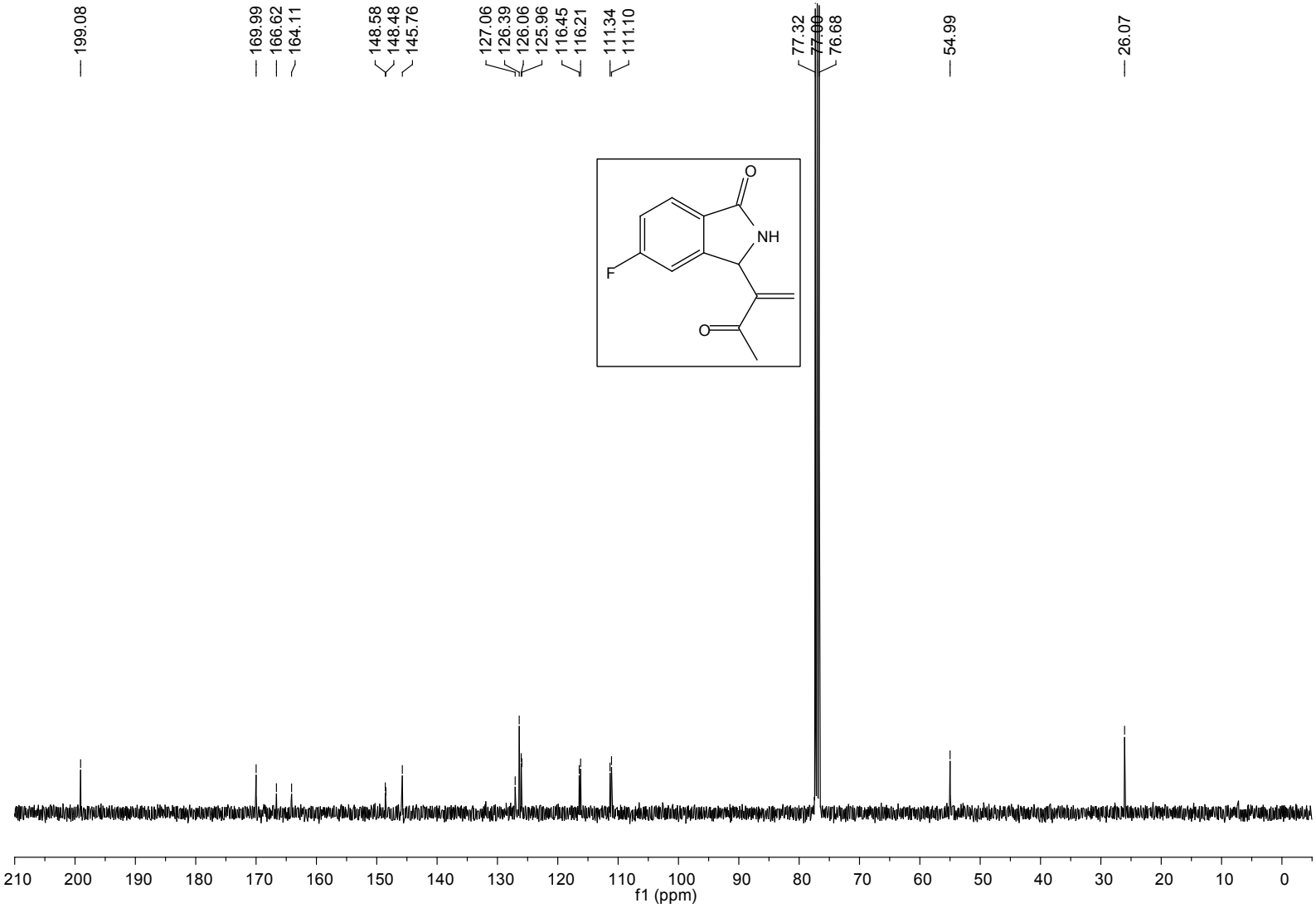
7.813
7.801
7.260
7.180
7.159
7.137
7.095
7.072
6.195
6.039
5.692
2.464
O
NH
F
O
1.06
1.11
1.96
1.08
1.07
1.00
3.11
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)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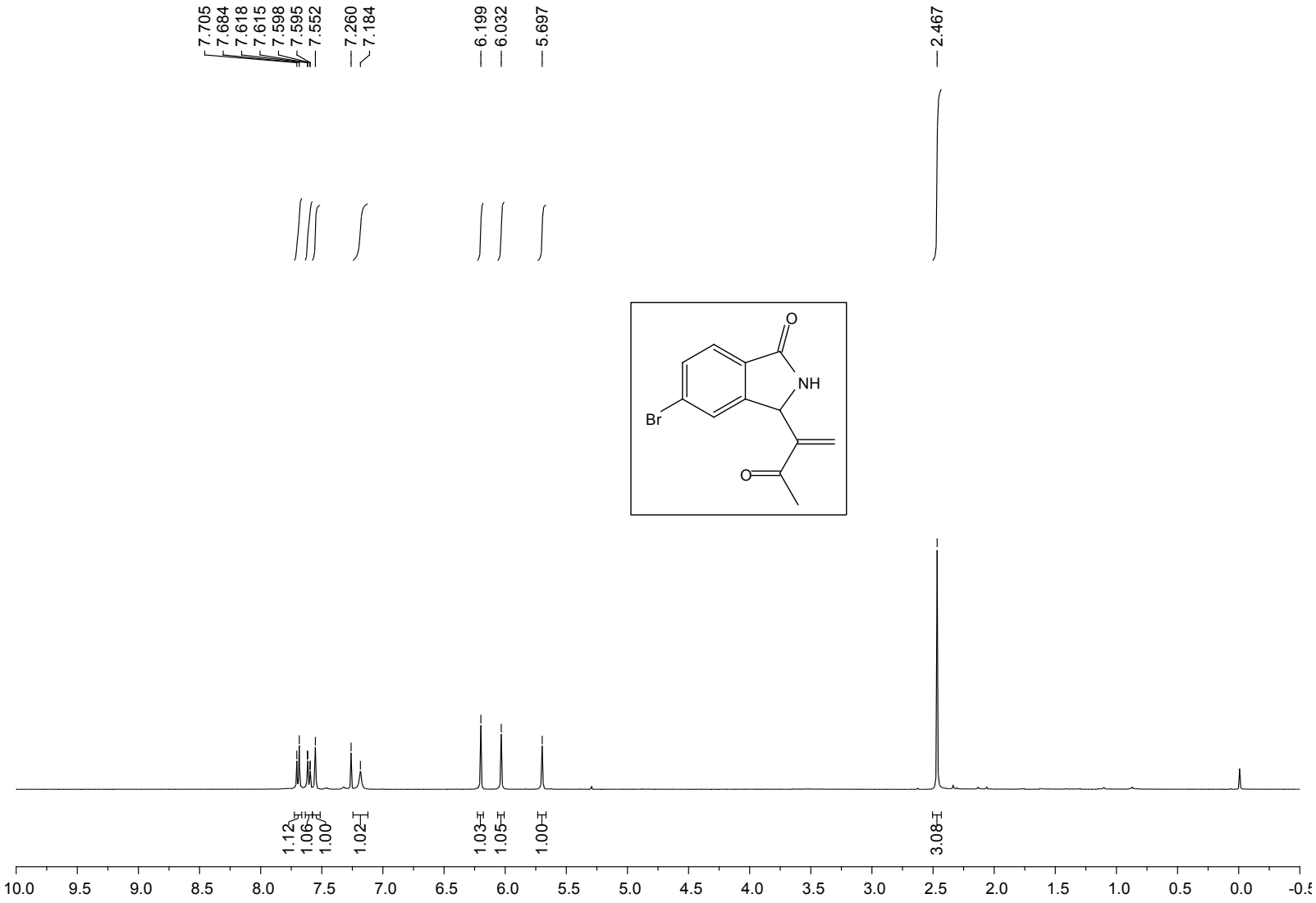
166.62
164.11
148.58
148.48
145.76
127.06
126.39
126.06
125.96
116.45
116.21
111.34
111.10
77.32
77.00
76.68
54.99
26.07
O
NH
F
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.615
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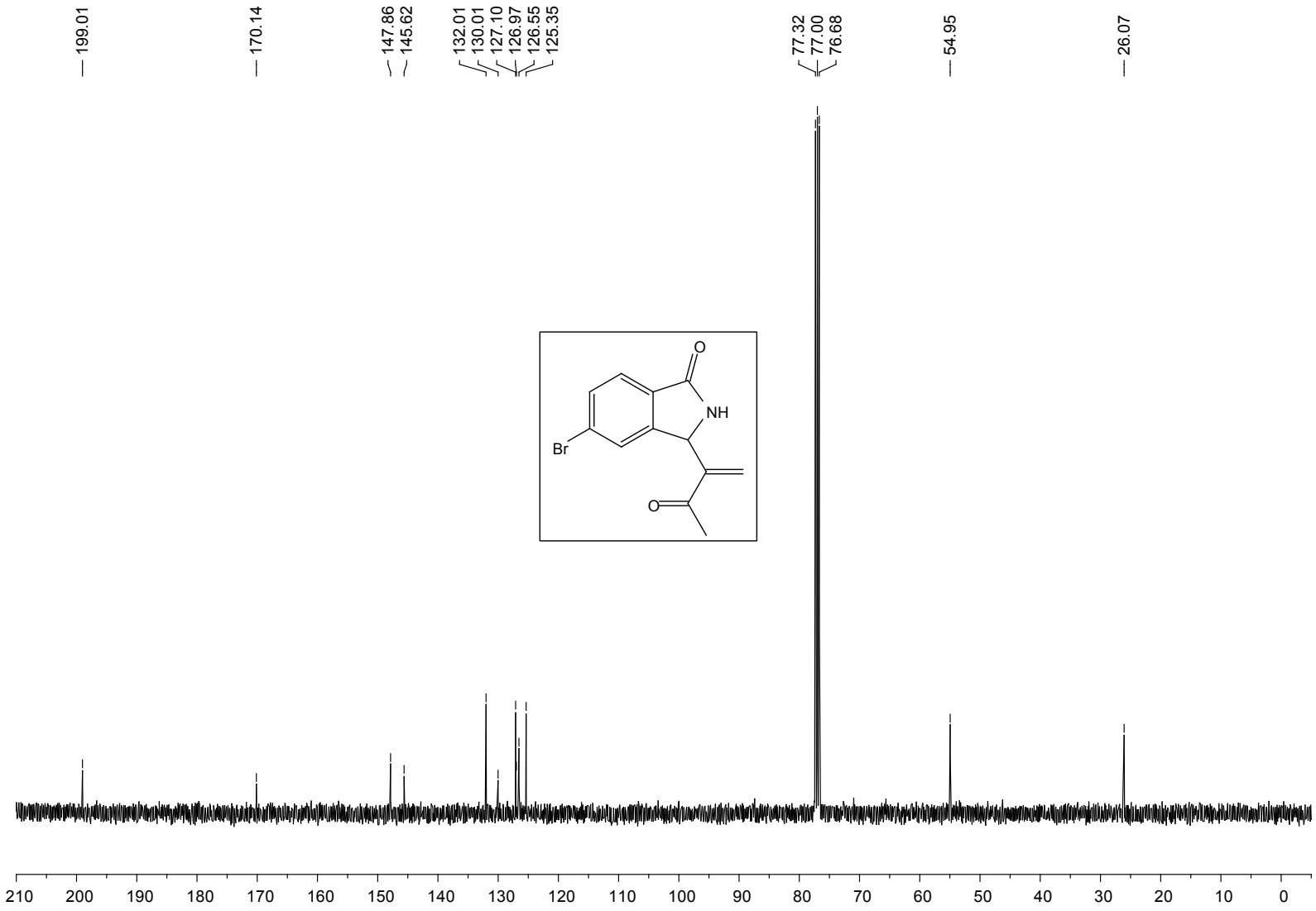
7.595
7.552
7.260
7.184
6.199
6.032
5.697
2.467
O
NH
Br
O
1.12
1.06
1.00
1.02
1.03
1.05
1.00
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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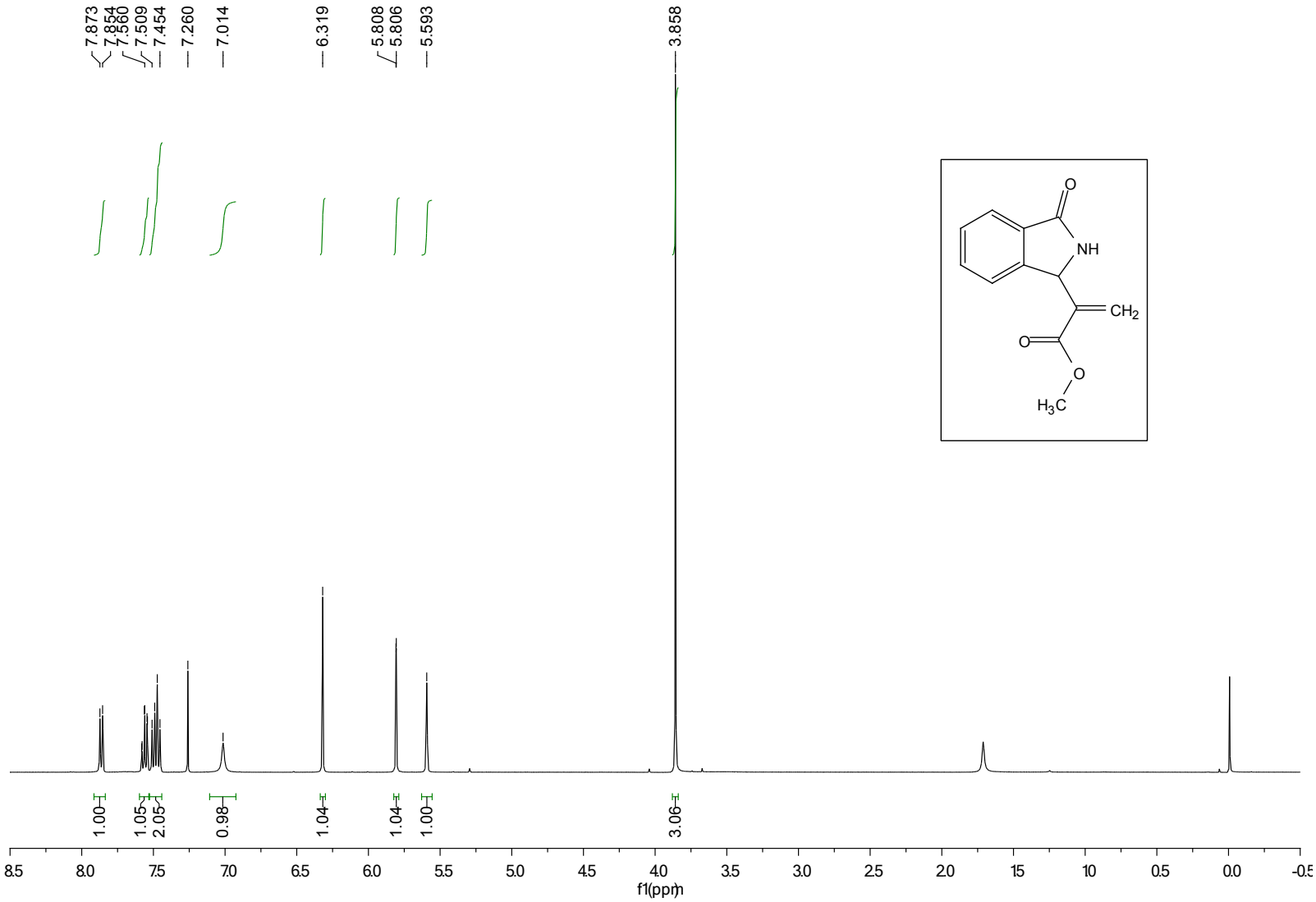
145.62
132.01
130.01
127.10
126.97
126.55
125.35
77.32
77.00
76.68
54.95
26.07
O
NH
Br
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0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6.319
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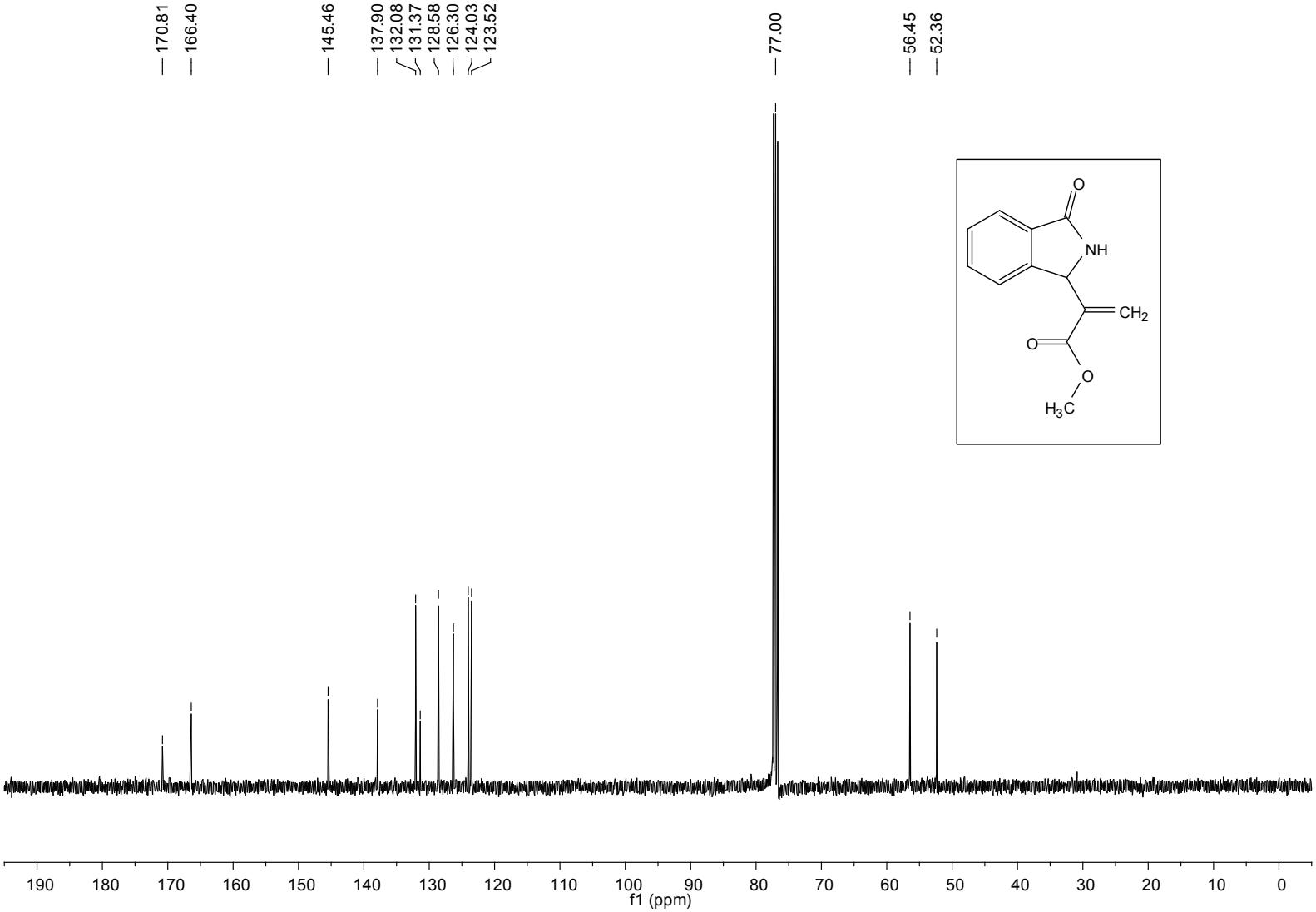
5.806
5.593
3.858
1.00
1.05
2.05
0.98
1.04
1.04
1.00
3.06
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)
O
NH
CH2
O
O
H3C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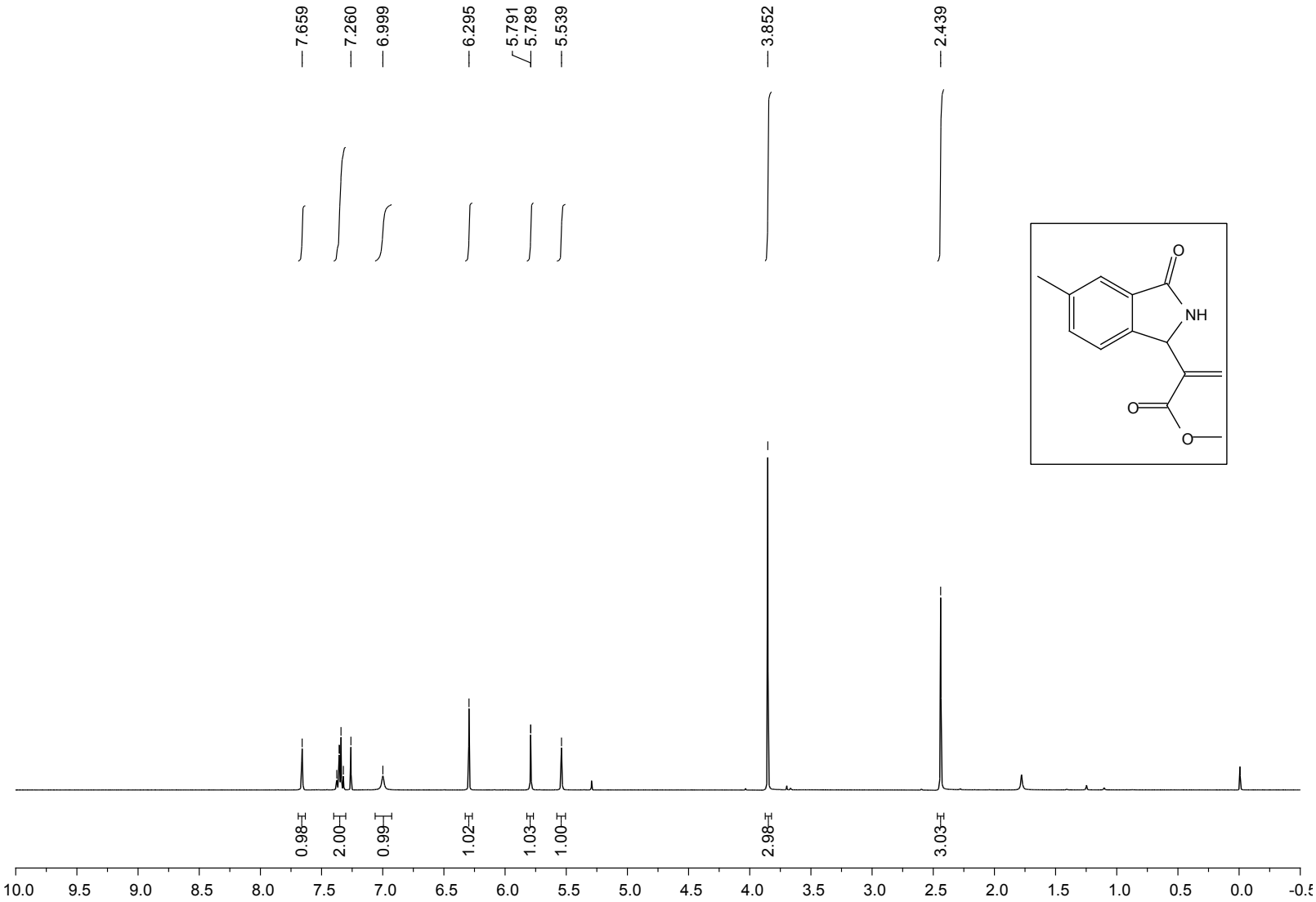
166.40
145.46
137.90
132.08
131.37
128.58
126.30
124.03
123.52
77.00
56.45
52.36
O
NH
CH2
O
O
H3C
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.999
6.295
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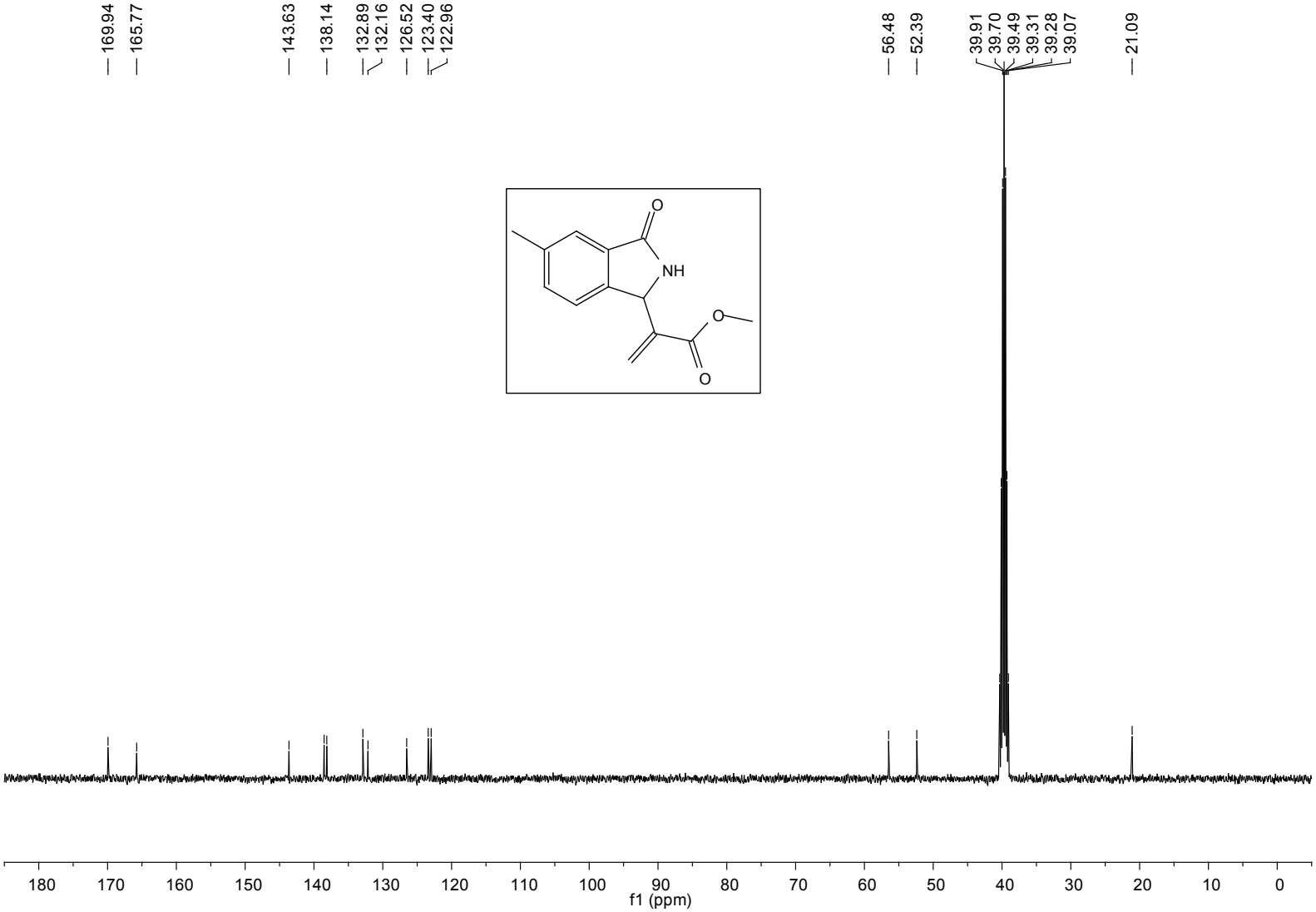
5.789
5.539
3.852
2.439
0.98
2.00
0.99
1.02
1.03
1.00
2.98
3.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
O
NH
O
O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165.77
143.63
138.14
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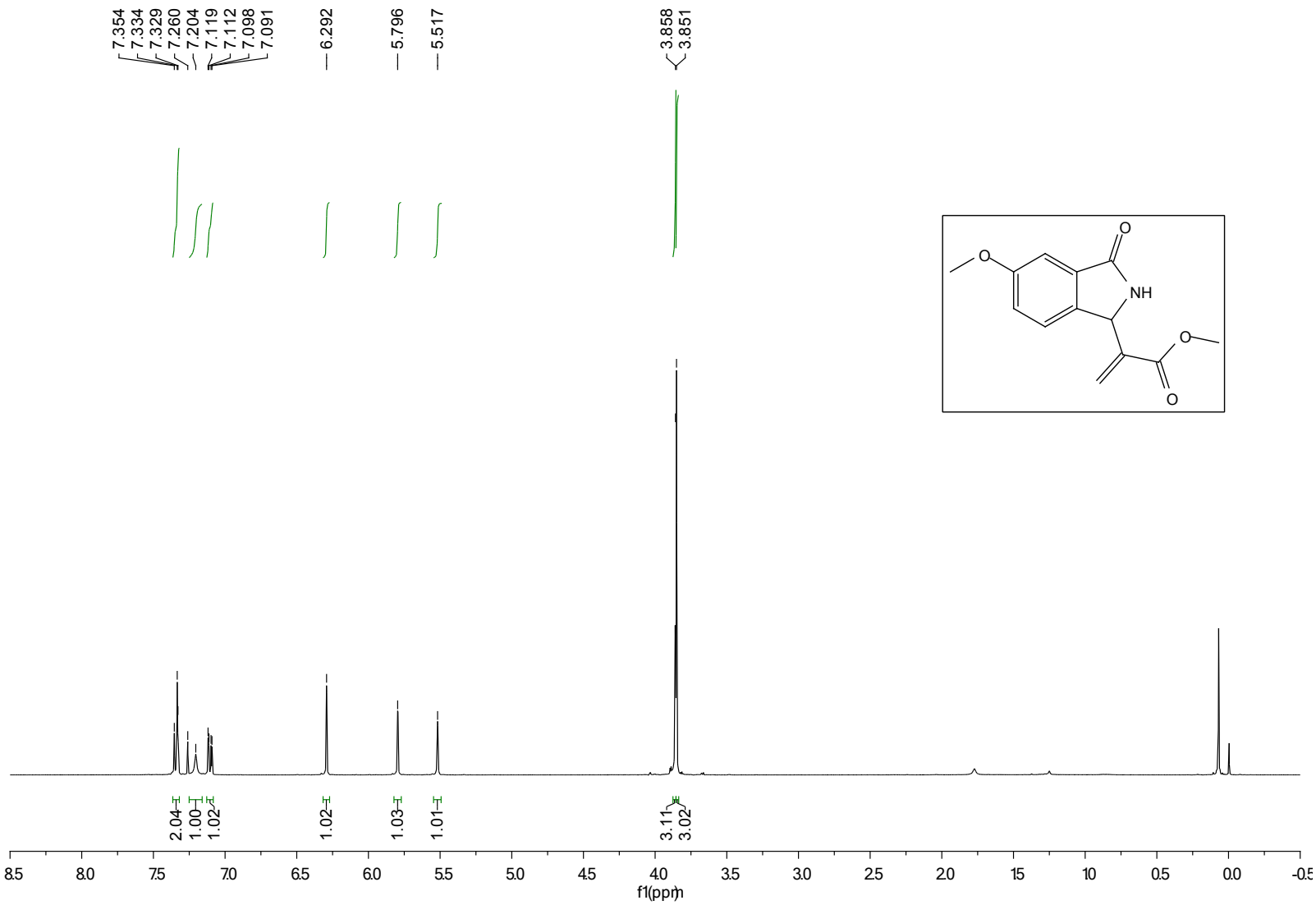
132.16
126.52
123.40
122.96
56.48
52.39
39.91
39.70
39.49
39.31
39.28
39.07
21.09
O
NH
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.329
7.260
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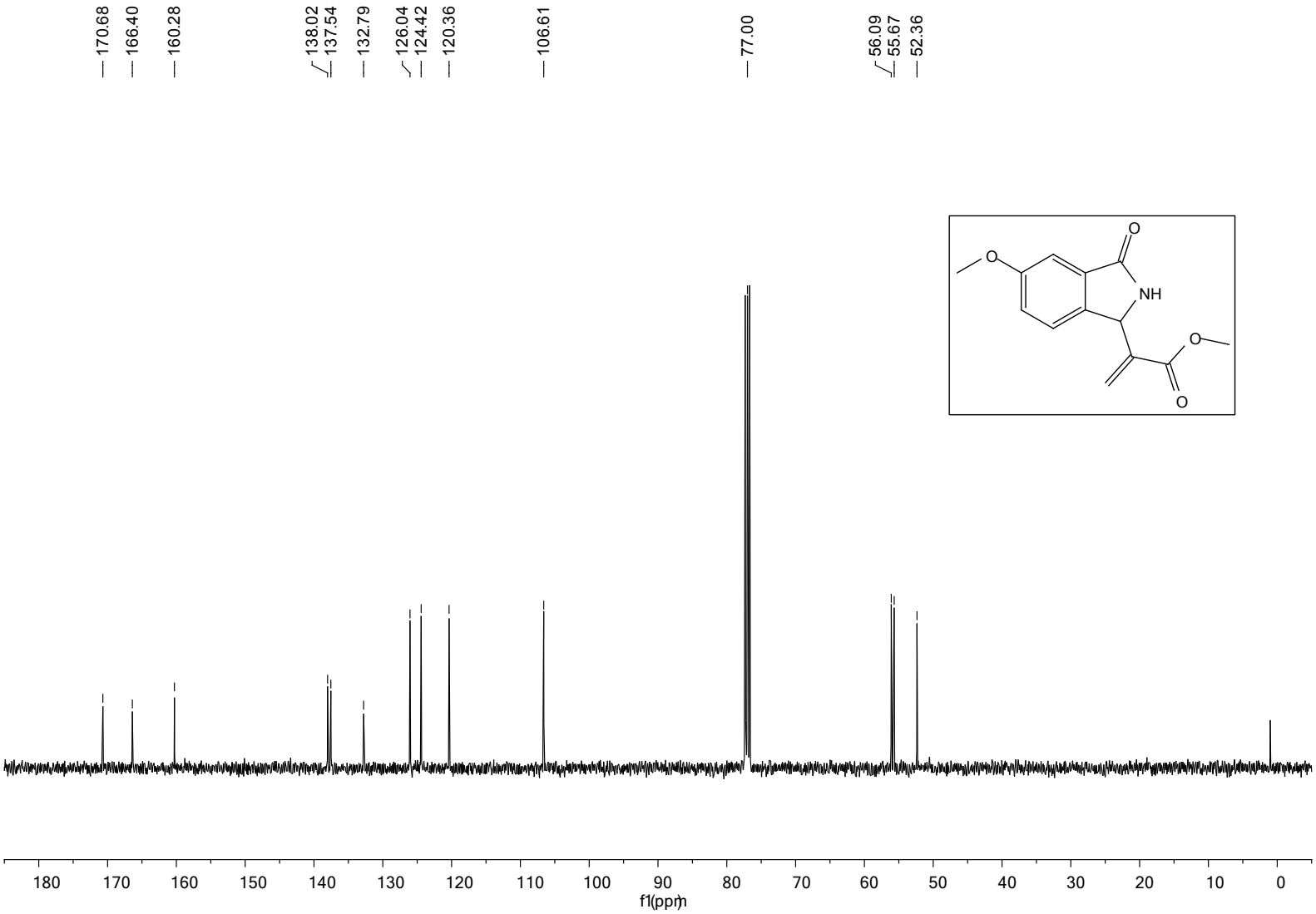
7.119
7.112
7.098
7.091
6.292
5.796
5.517
3.858
3.851
2.04
1.00
1.02
1.02
1.03
1.01
3.11
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1(ppm)
O
O
NH
O
O


170.68
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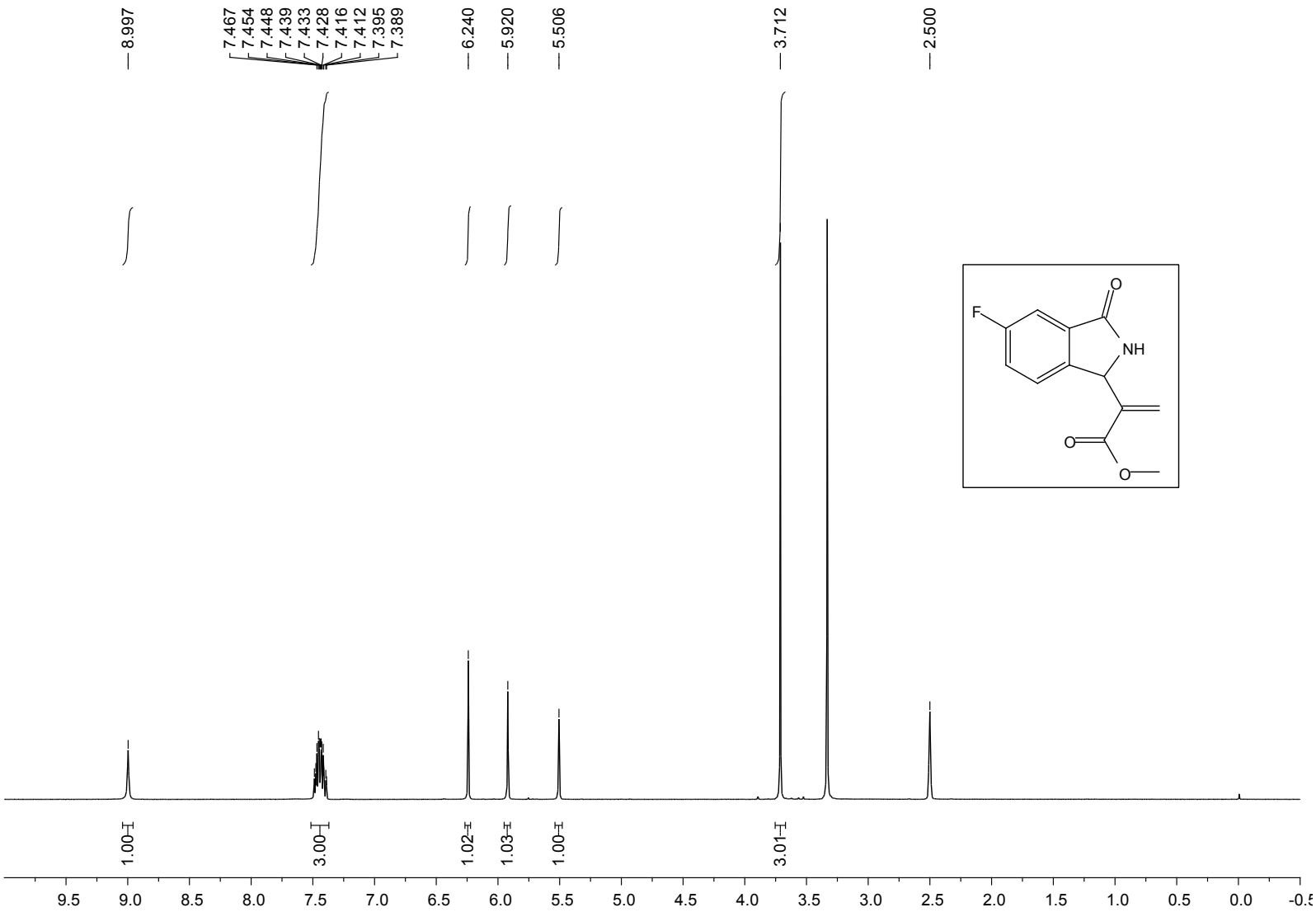
137.54
132.79
126.04
124.42
120.36
106.61
77.00
56.09
55.67
52.36
O
O
NH
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)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7.439
7.433
7.428
7.416
7.412
7.395
7.389
6.240
5.920
5.506
3.712
2.500
1.00
3.00
1.02
1.03
1.00
3.01
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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2.5
2.0
1.5
1.0
0.5
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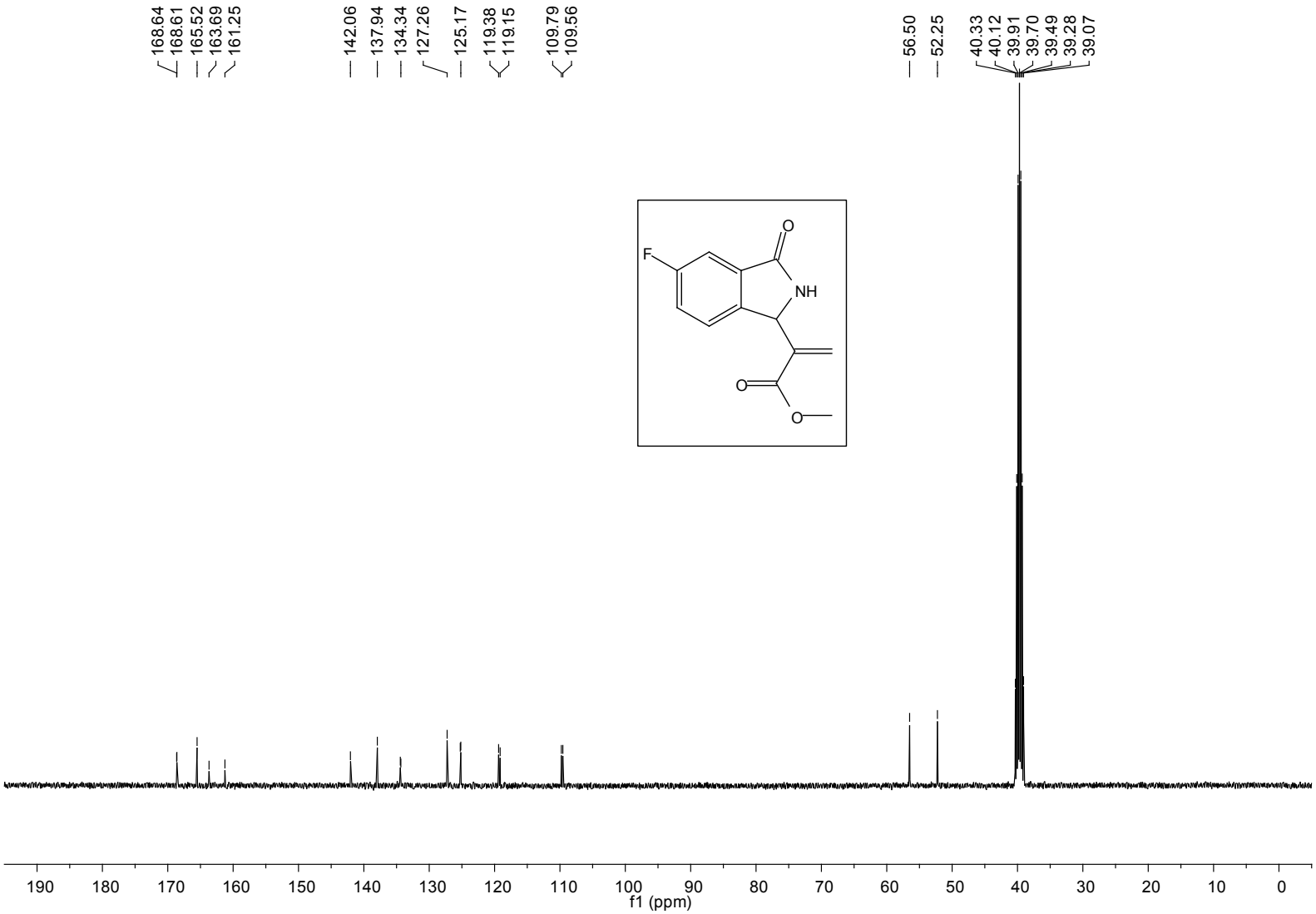
F
O
NH
O
O


168.64
168.61
165.52
163.69
161.25
142.06
137.94
134.34
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119.15
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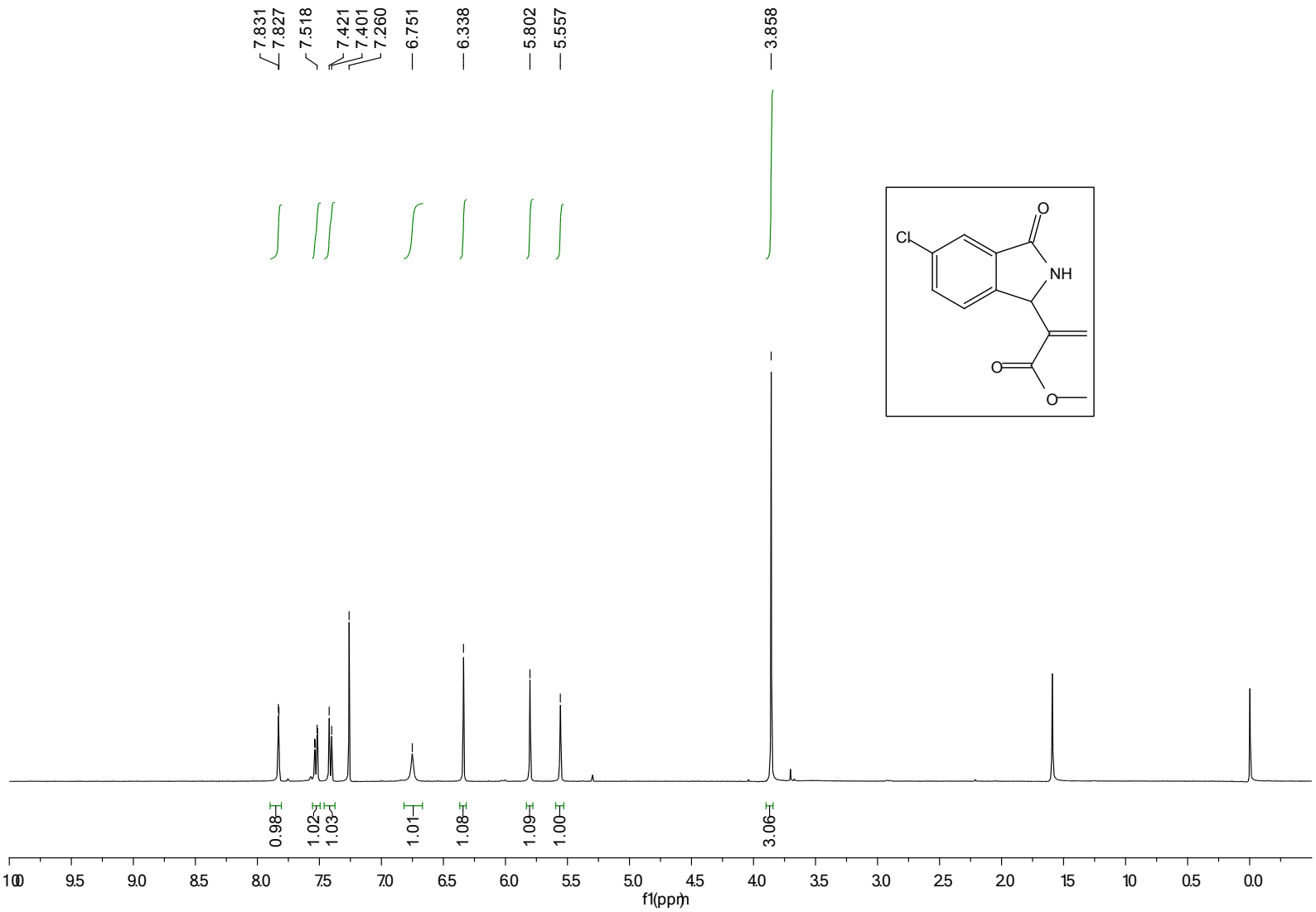
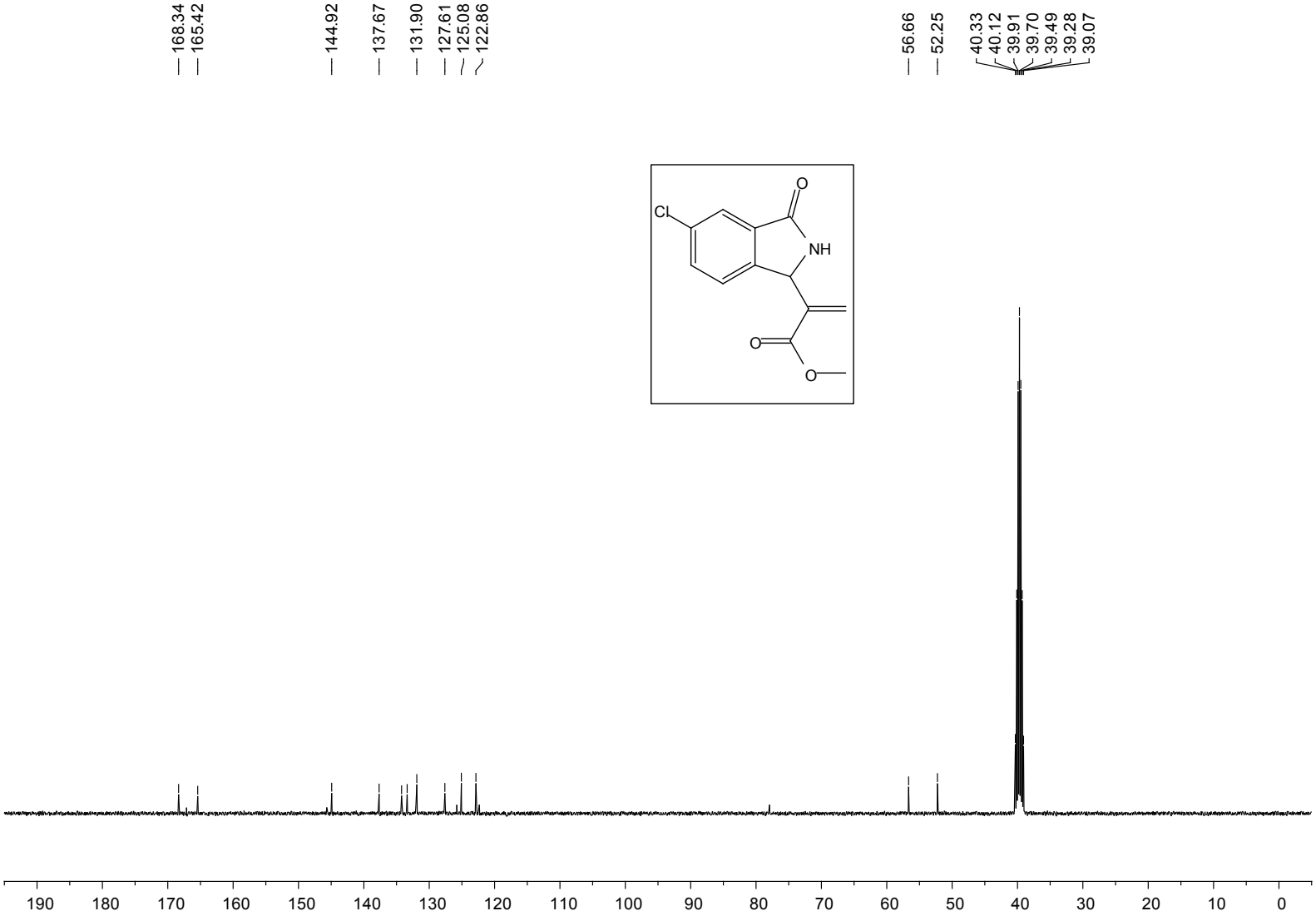
109.56
56.50
52.25
40.33
40.12
39.91
39.70
39.49
39.28
39.07
F
O
NH
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.831
7.827
7.518
7.421
7.401
7.260
6.751
6.338
5.802
5.557
3.858
Cl
O
NH
O
O
0.98
1.02
1.03
1.01
1.08
1.09
1.00
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1(ppm)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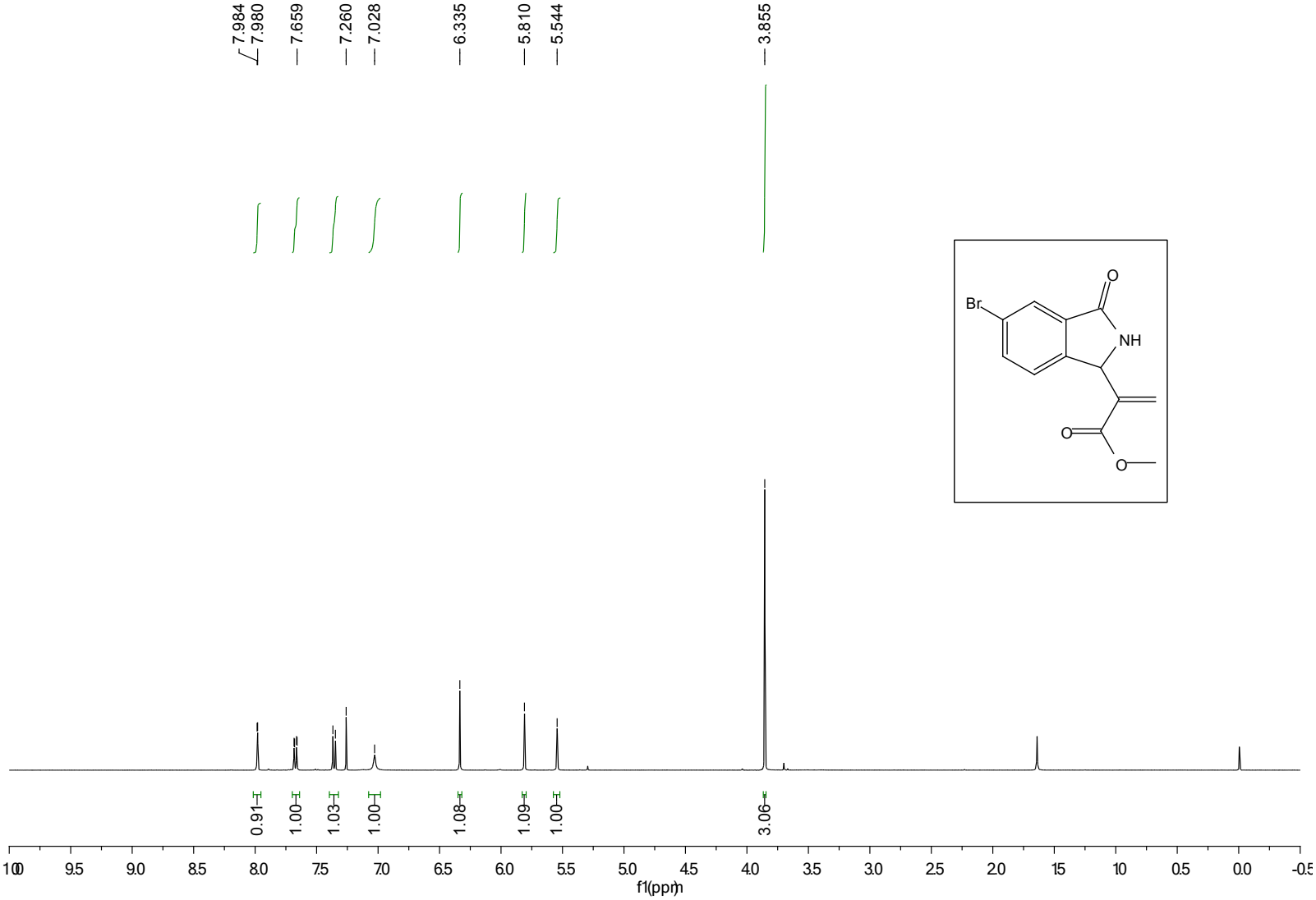
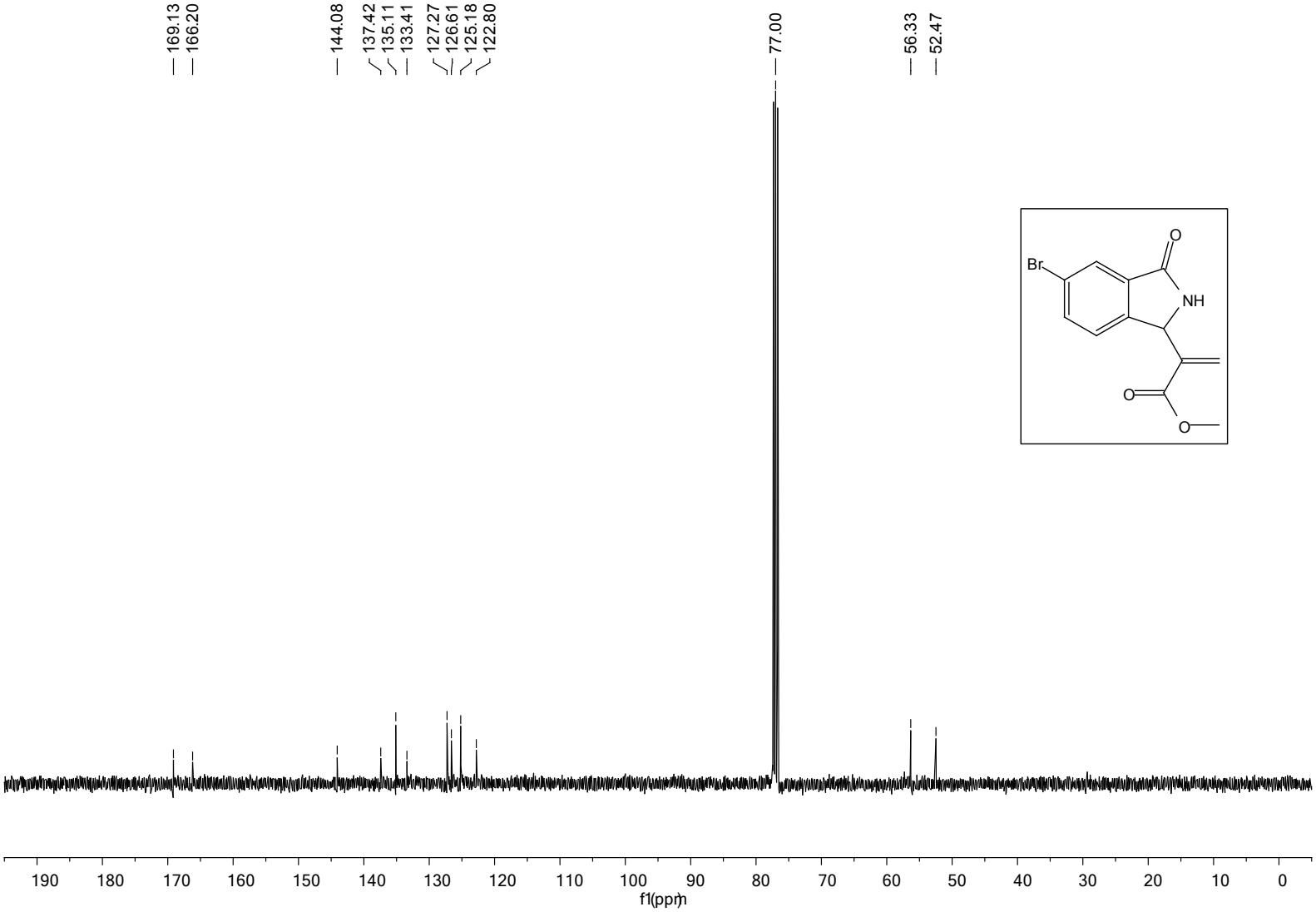
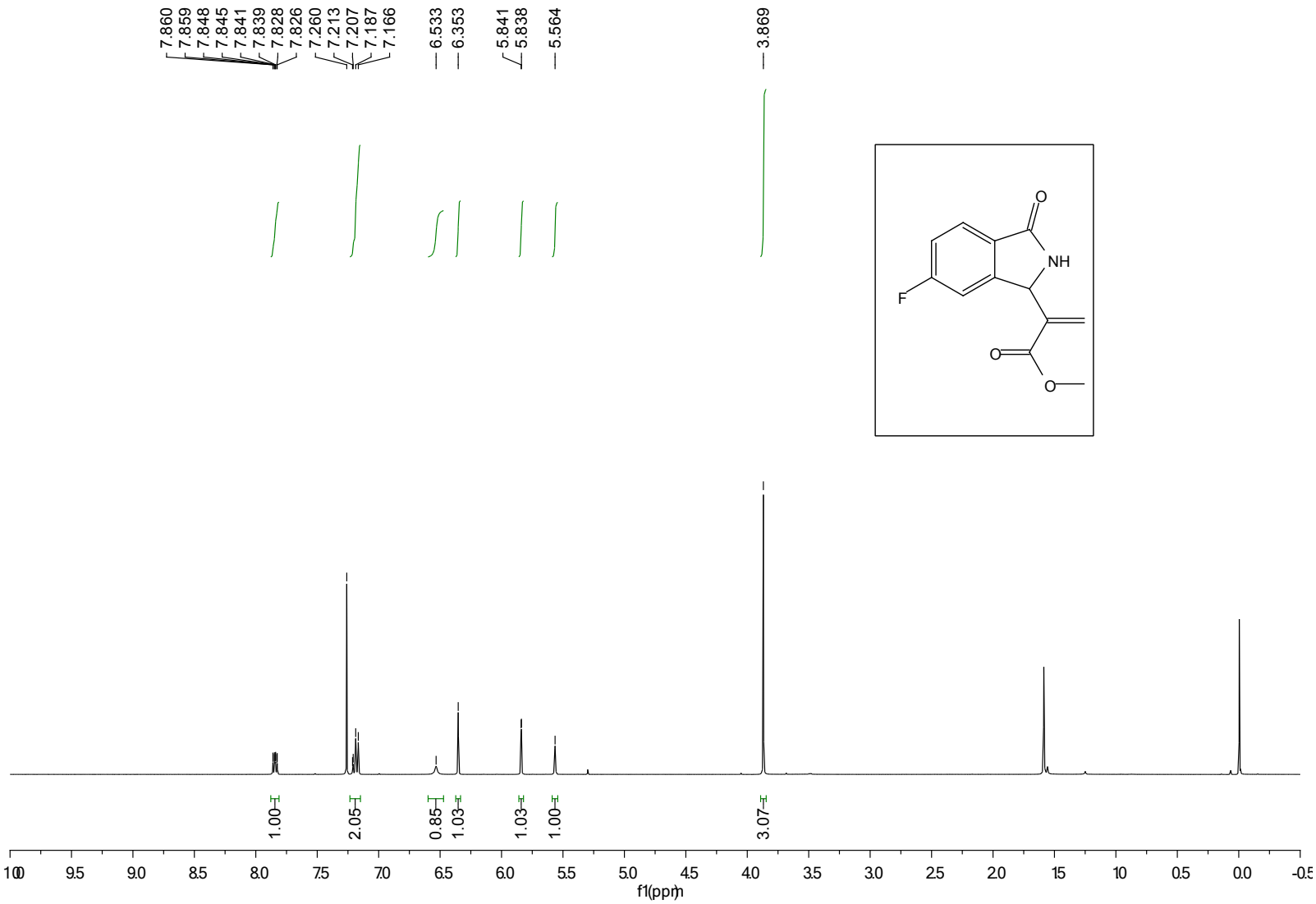
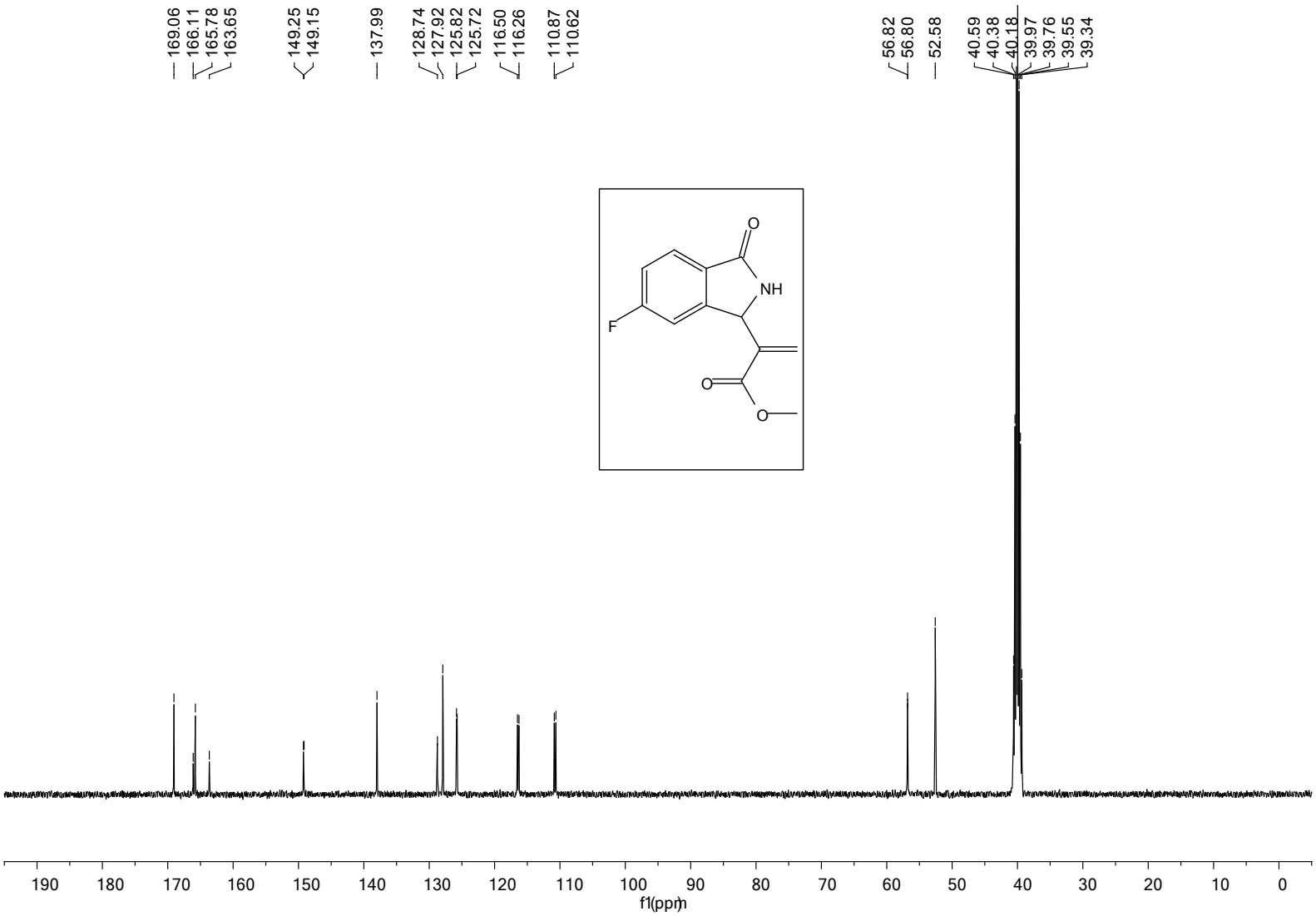
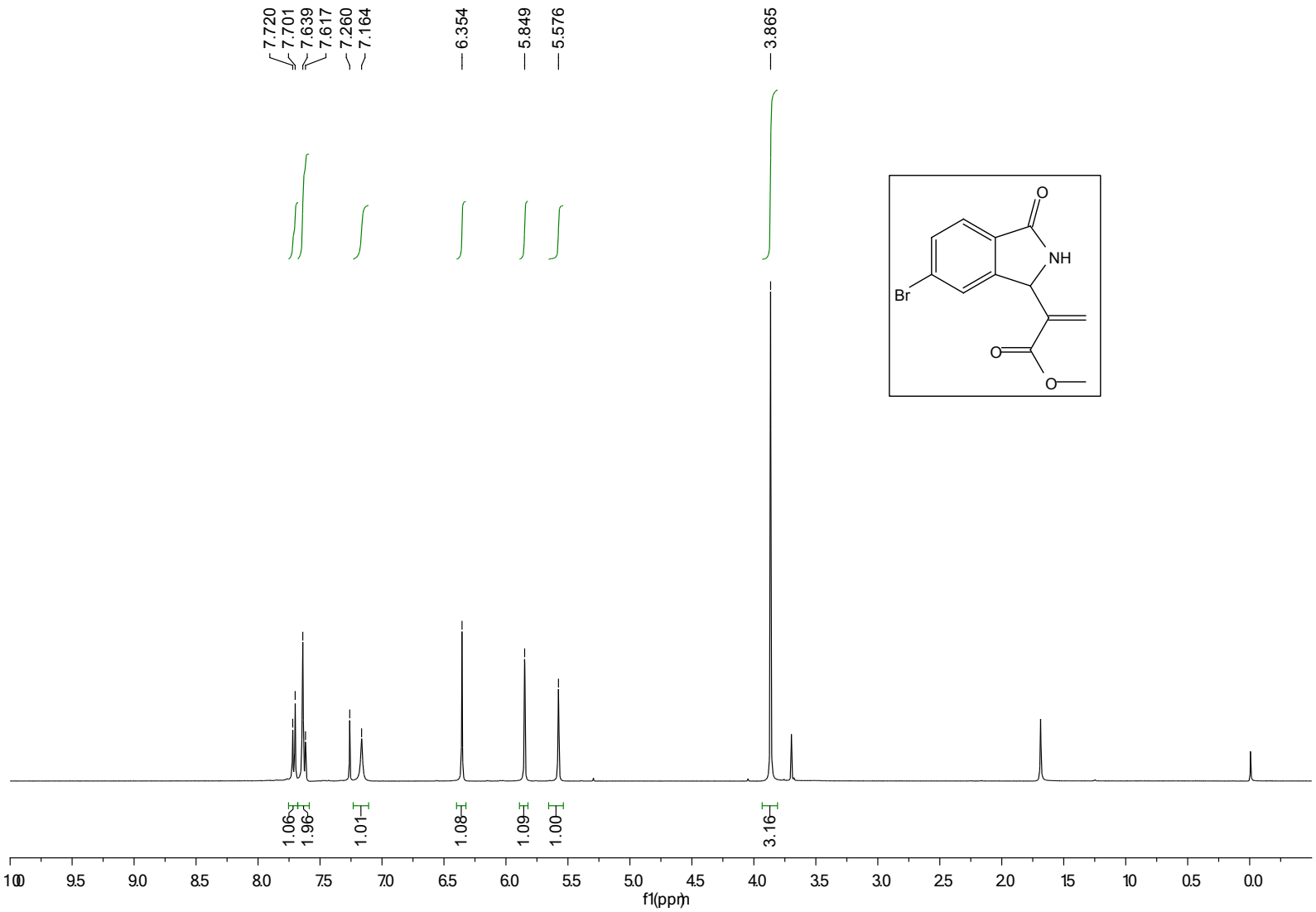
165.42
144.92
137.67
131.90
127.61
125.08
122.86
56.66
52.25
40.33
40.12
39.91
39.70
39.49
39.28
39.07
Cl
O
NH
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

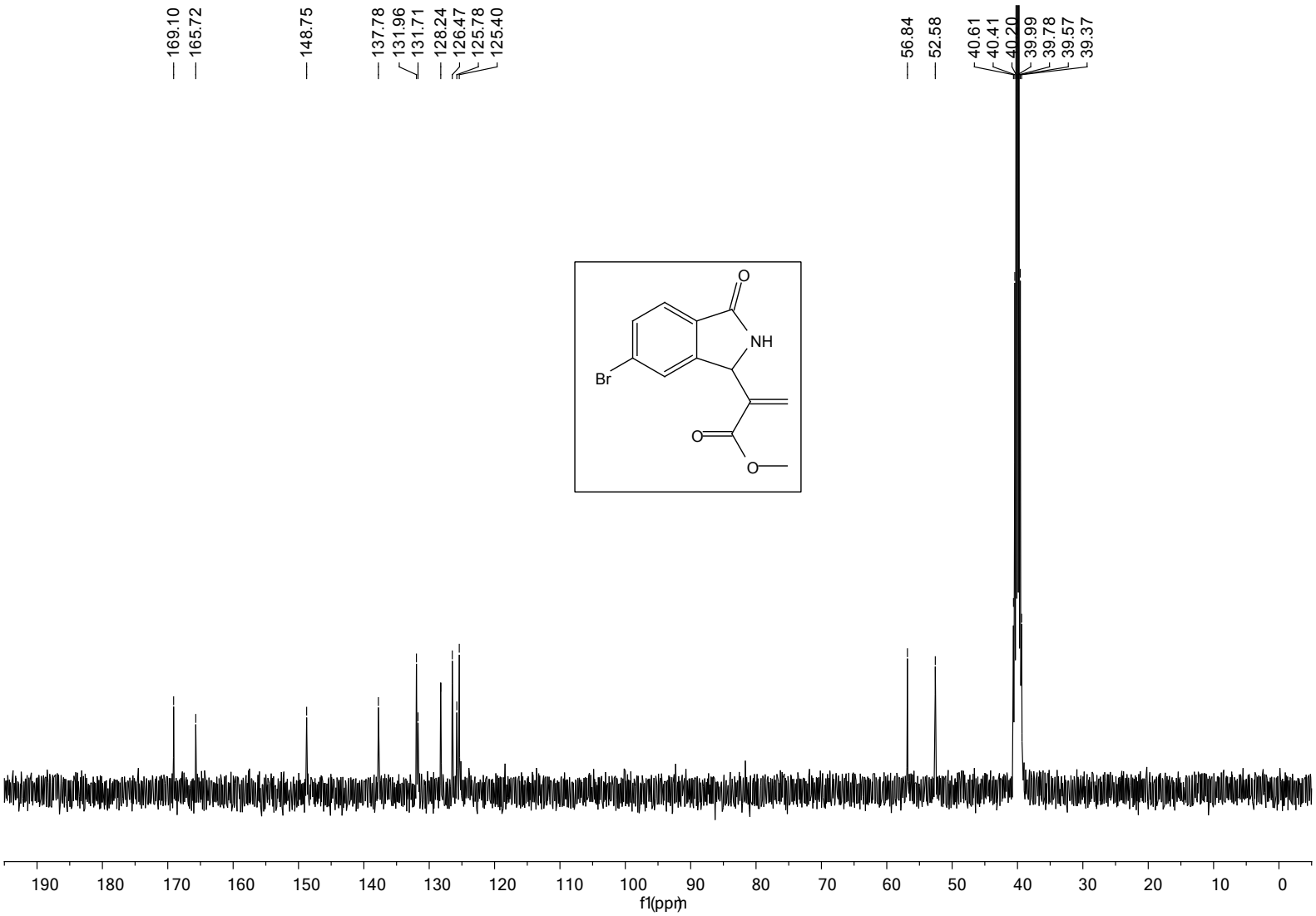

7.984
7.980
7.659
7.260
7.028
6.335
5.810
5.544
3.855
Br
O
NH
O
O
0.91
1.00
1.03
1.00
1.08
1.09
1.00
3.06
f1(ppm)

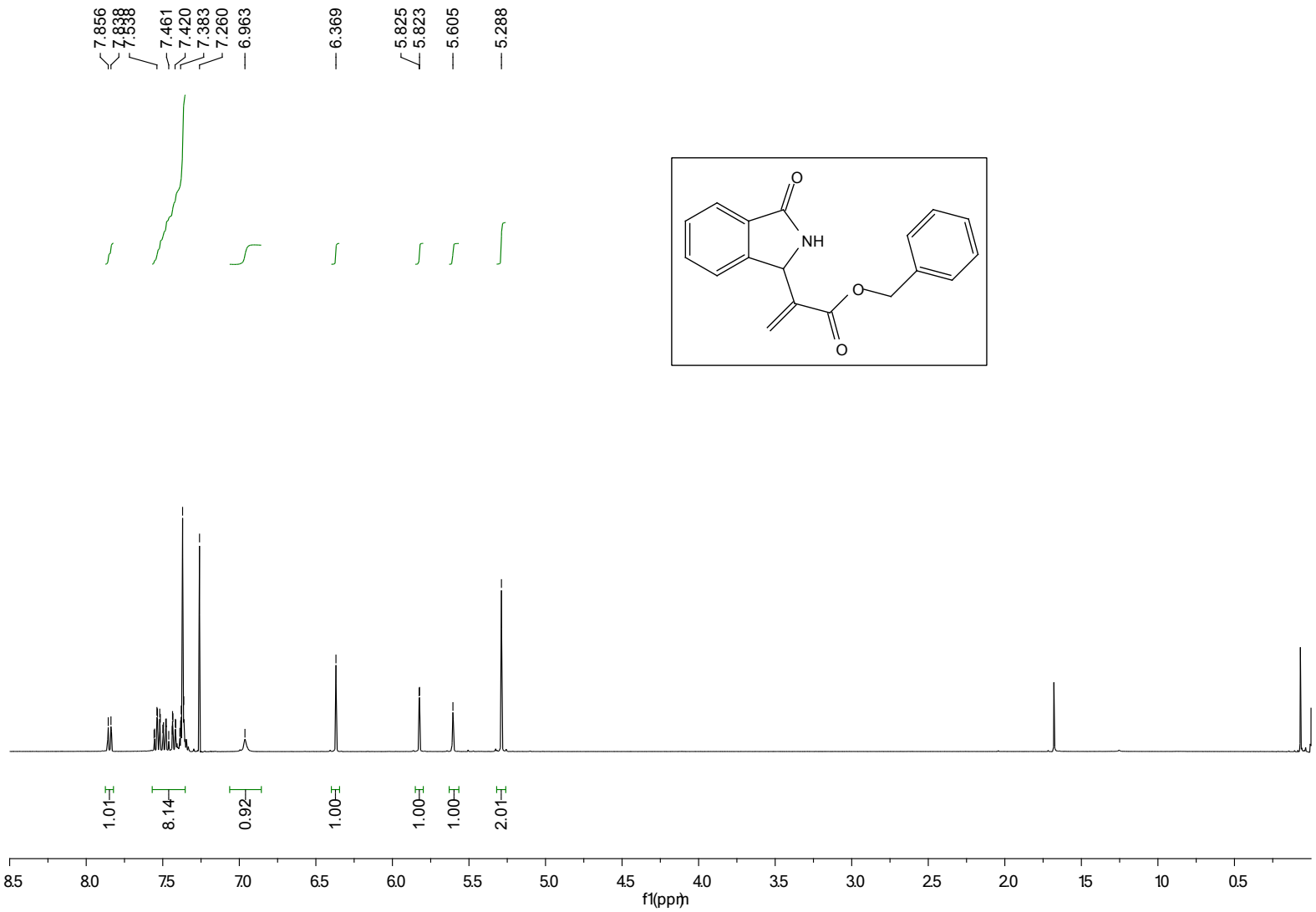

169.13
166.20
144.08
137.42
135.11
133.41
127.27
126.61
125.18
122.80
77.00
56.33
52.47
Br
O
NH
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)

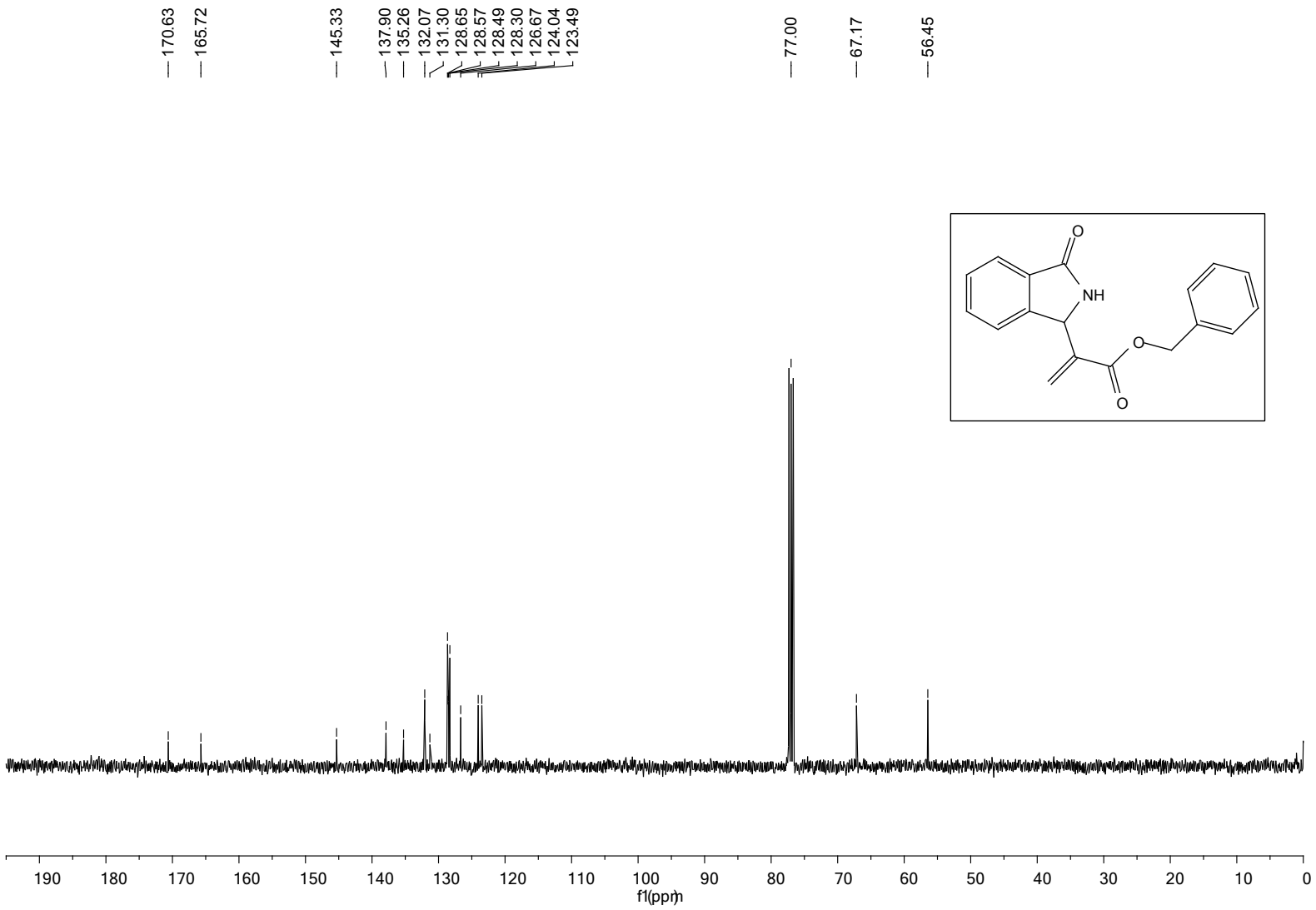

7.860
7.859
7.848
7.845
7.841
7.839
7.828
7.826
7.260
7.213
7.207
7.187
7.166
6.533
6.353
5.841
5.838
5.564
3.869
O
NH
F
O
O
1.00
2.05
0.85
1.03
1.03
1.00
3.07
f1(ppm)

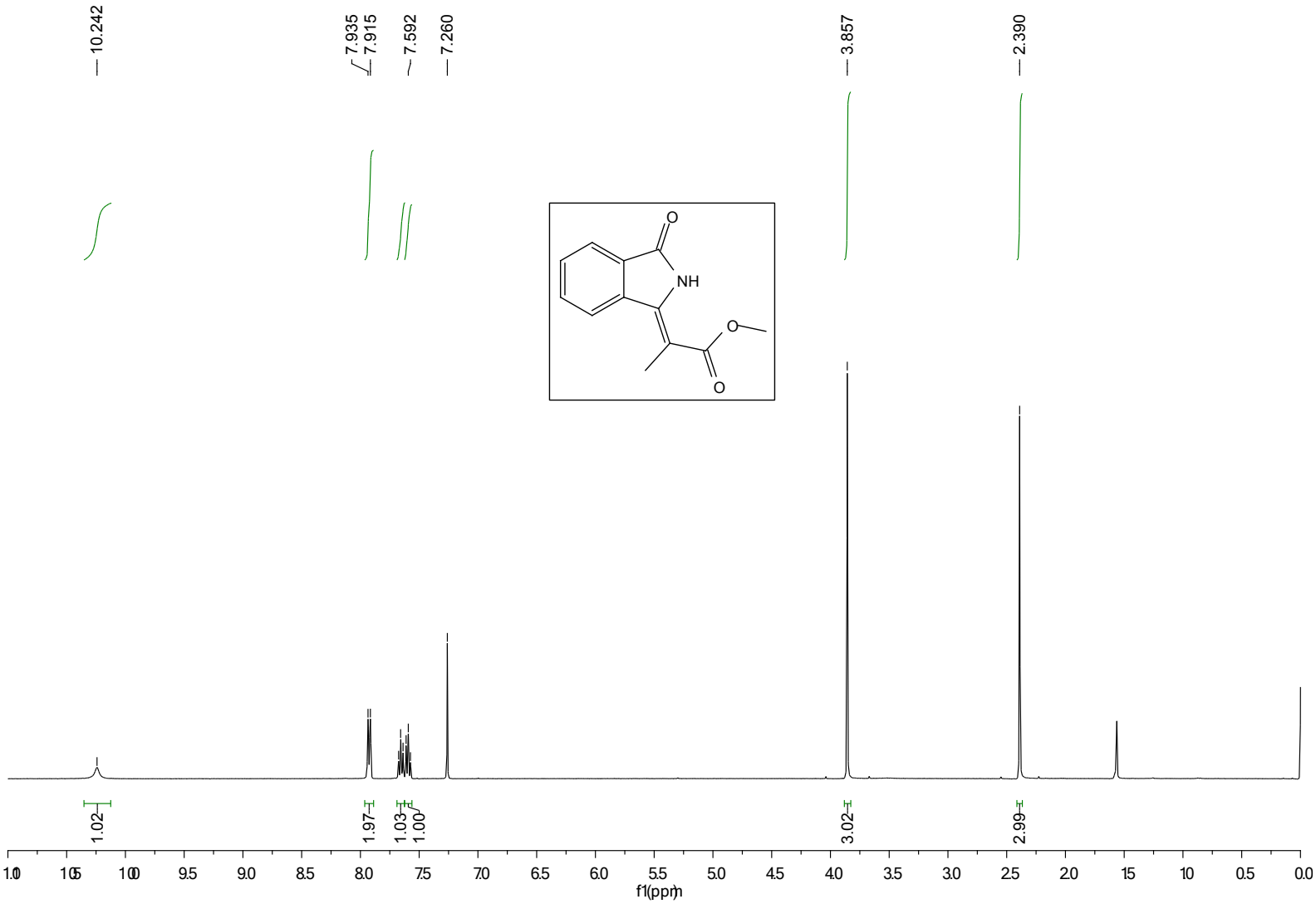

169.06
166.11
165.78
163.65
149.25
149.15
137.99
128.74
127.92
125.82
125.72
116.50
116.26
110.87
110.62
56.82
56.80
52.58
40.59
40.38
40.18
39.97
39.76
39.55
39.34
O
NH
F
O
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1(ppm)

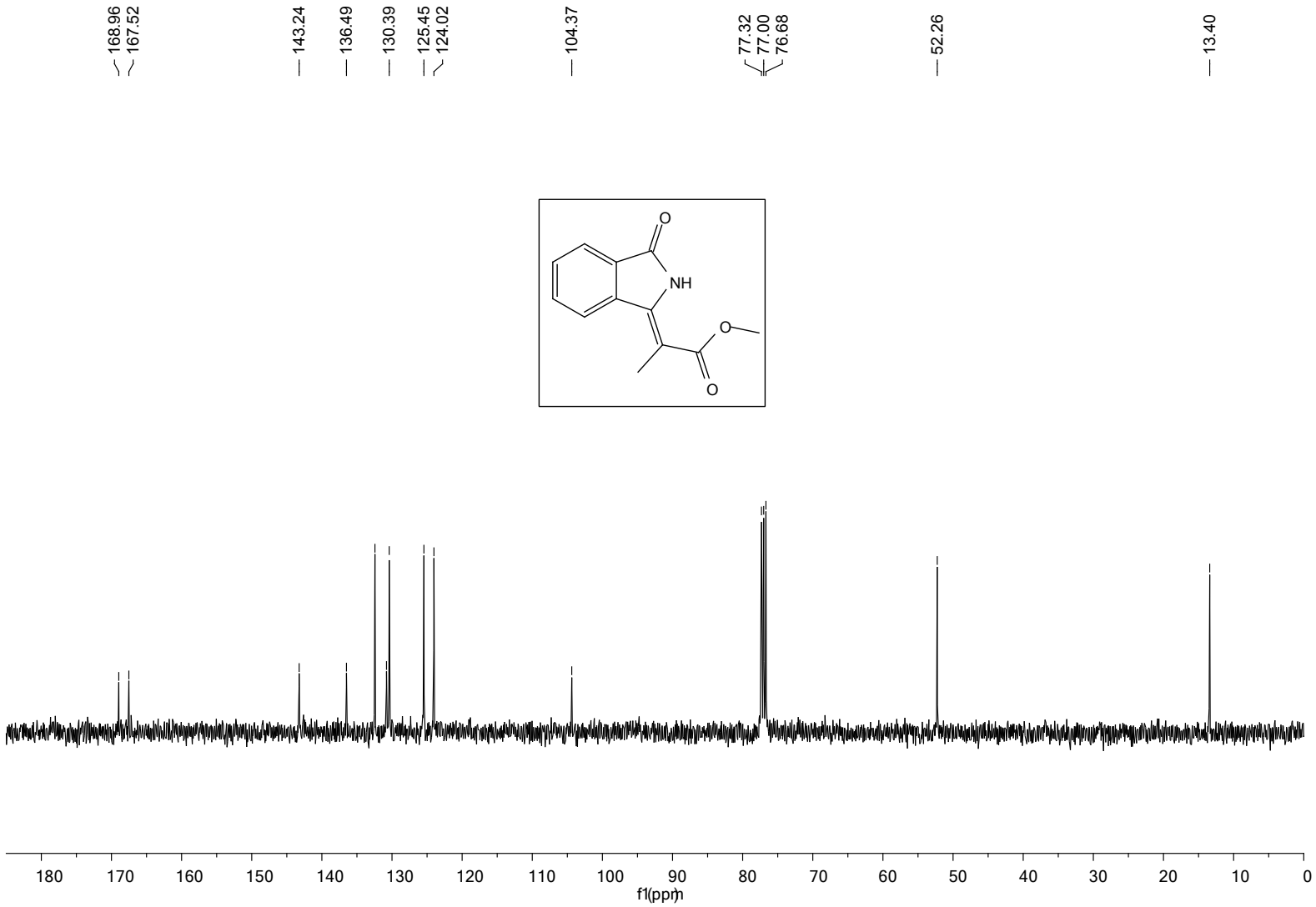

7.720
7.701
7.639
7.617
7.260
7.164
6.354
5.849
5.576
3.865
1.06
1.96
1.01
1.08
1.09
1.00
3.16
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1(ppm)
O
NH
Br
O
O

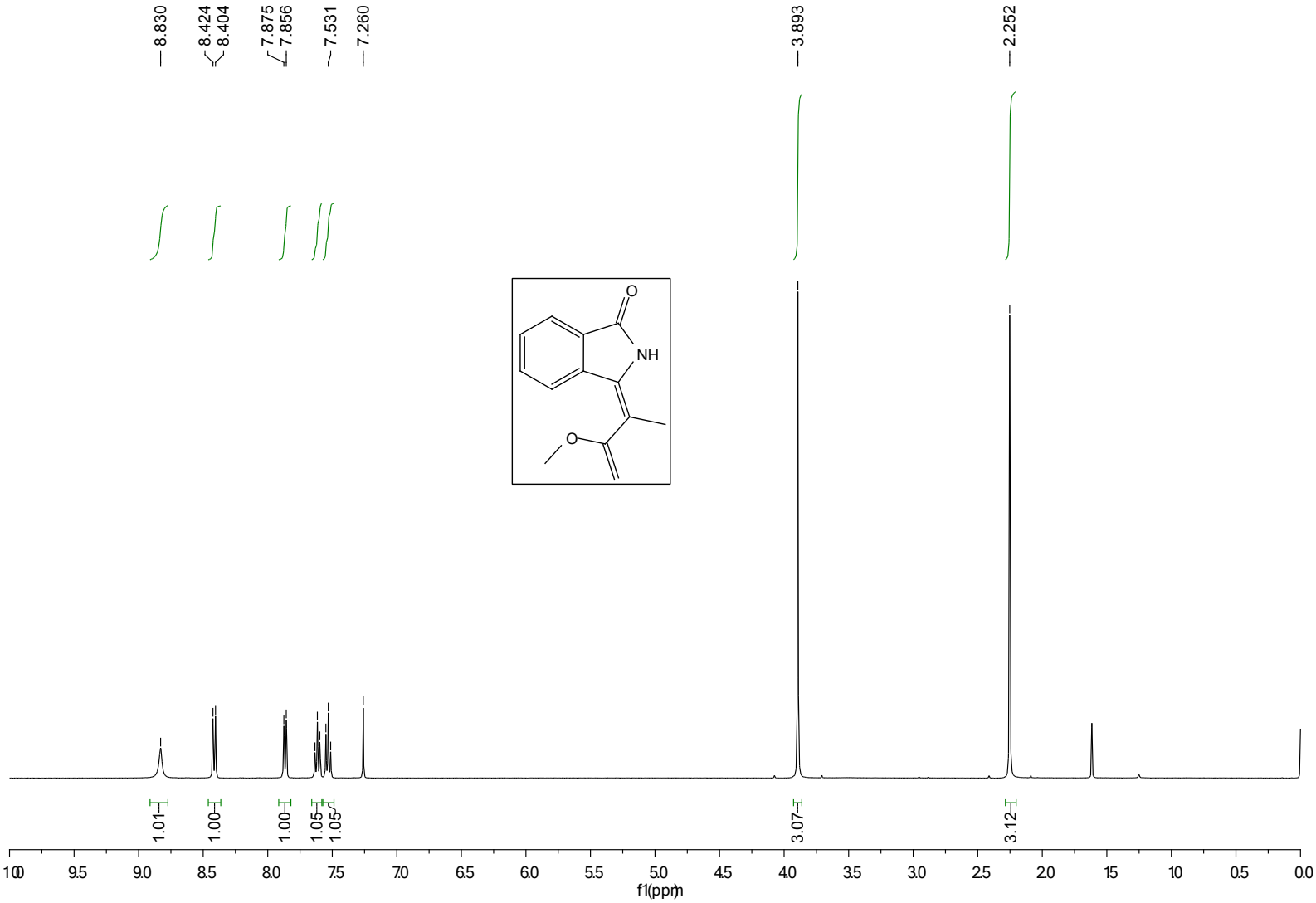

169.10
165.72
148.75
137.78
131.96
131.71
128.24
126.47
125.78
125.40
56.84
52.58
40.61
40.41
40.20
39.99
39.78
39.57
39.37
O
NH
Br
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)

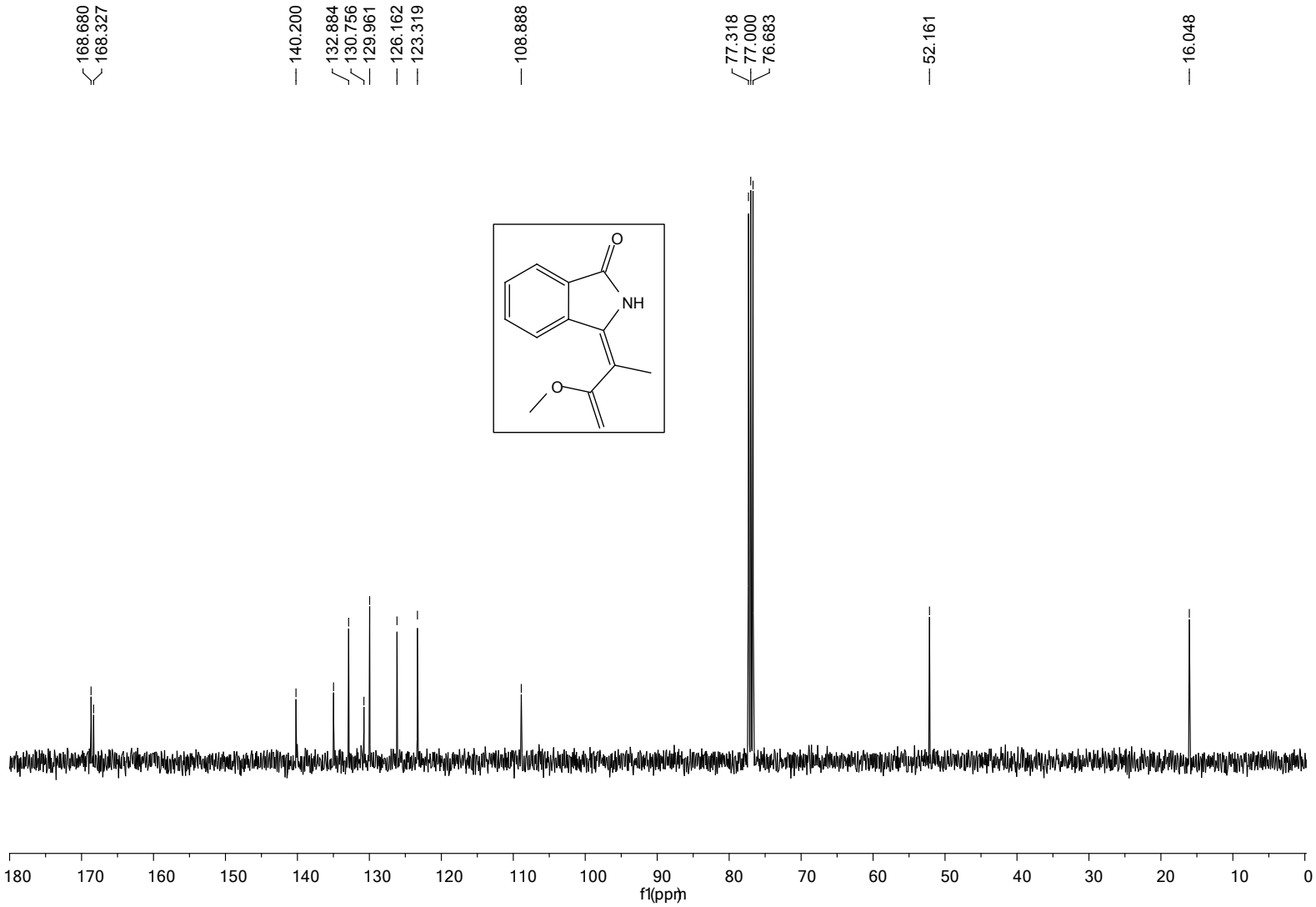

7.856
7.838
7.538
7.461
7.420
7.383
7.260
6.963
6.369
5.825
5.823
5.605
5.288
O
NH
O
O
1.01
8.14
0.92
1.00
1.00
1.00
2.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1(ppm)

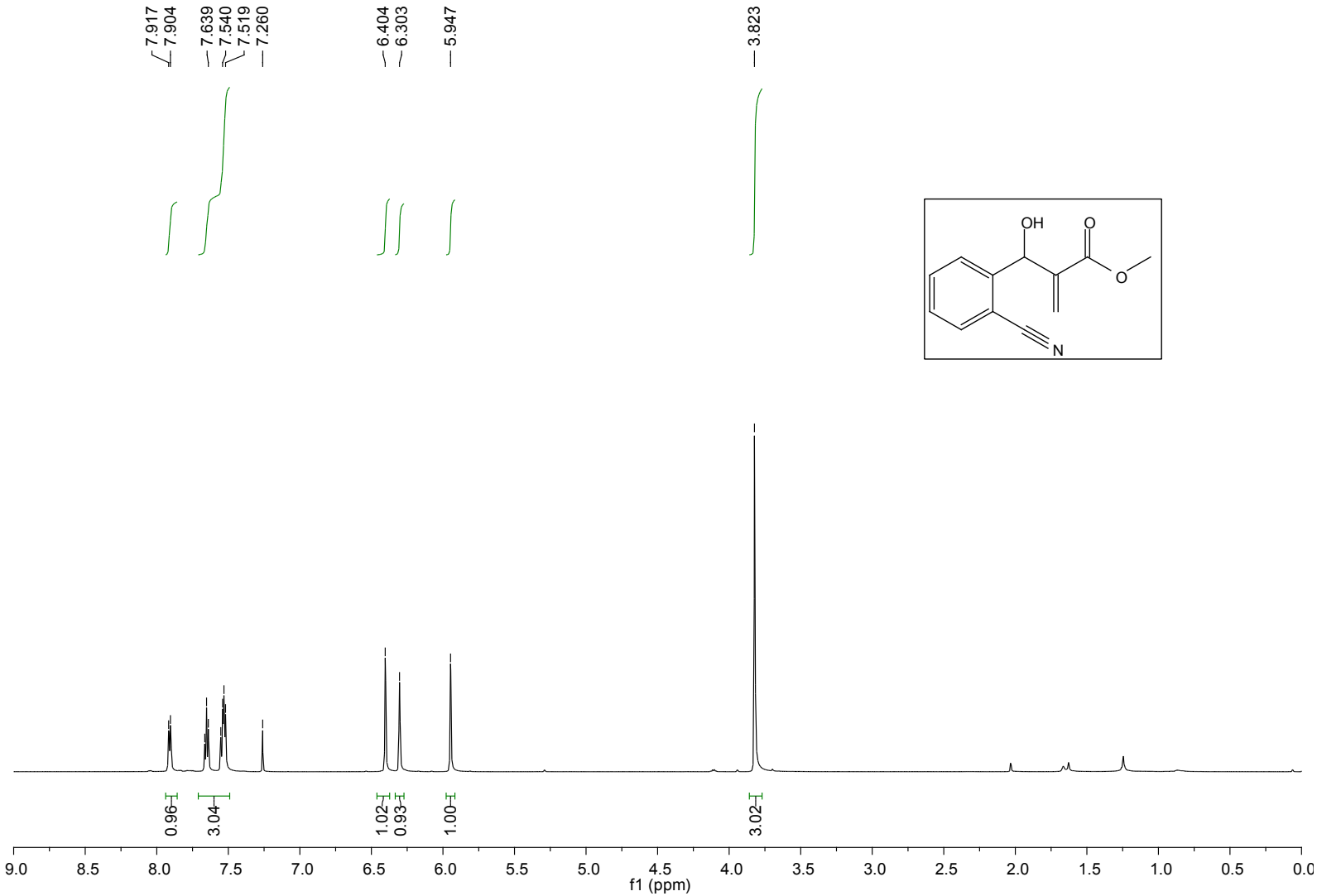

170.63
165.72
145.33
137.90
135.26
132.07
131.30
128.65
128.57
128.49
128.30
126.67
124.04
123.49
77.00
67.17
56.45
O
NH
O
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)

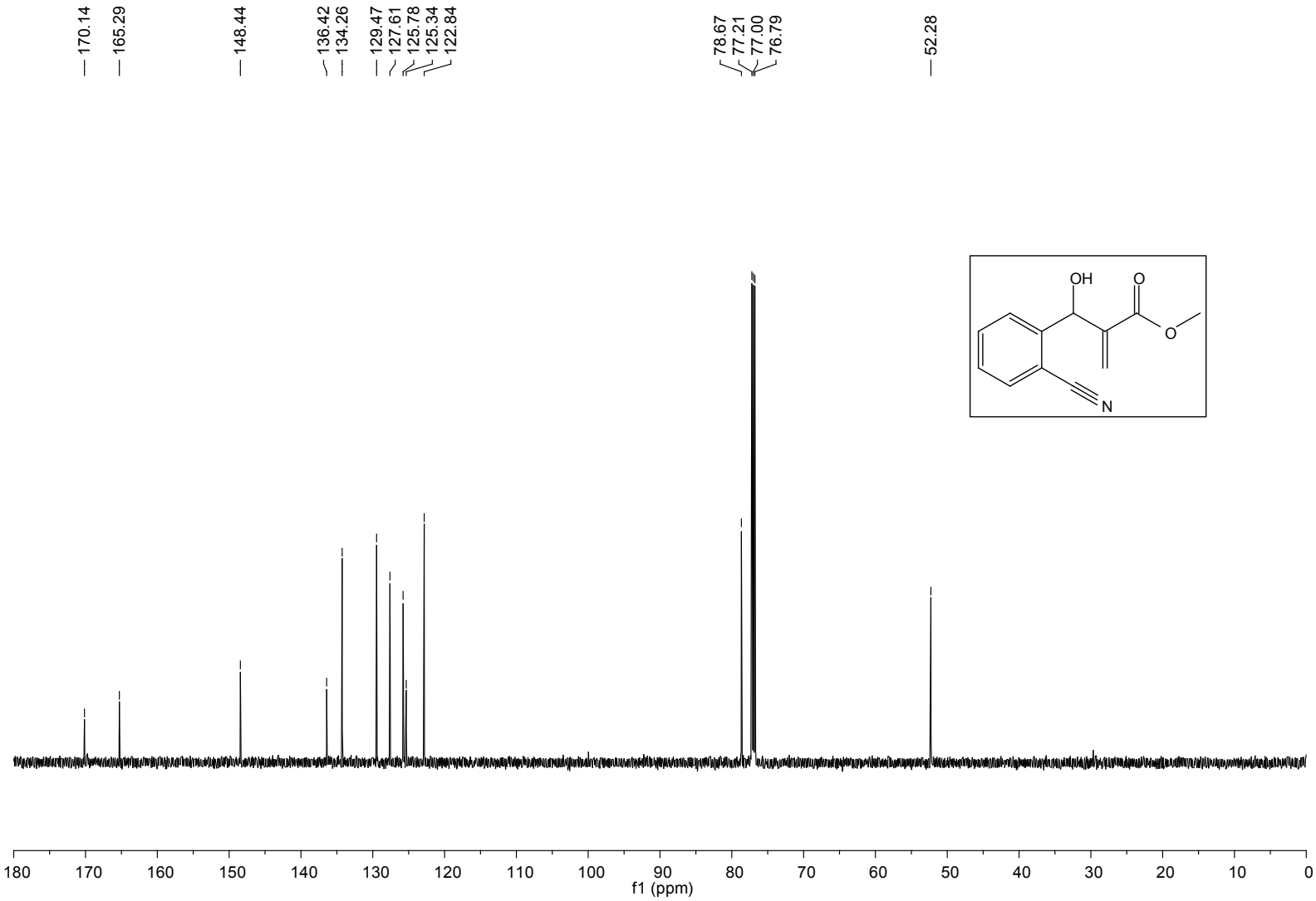

10.242
7.935
7.915
7.592
7.260
3.857
2.390
O
NH
O
O
1.02
1.97
1.03
1.00
3.02
2.99
f1(ppm)

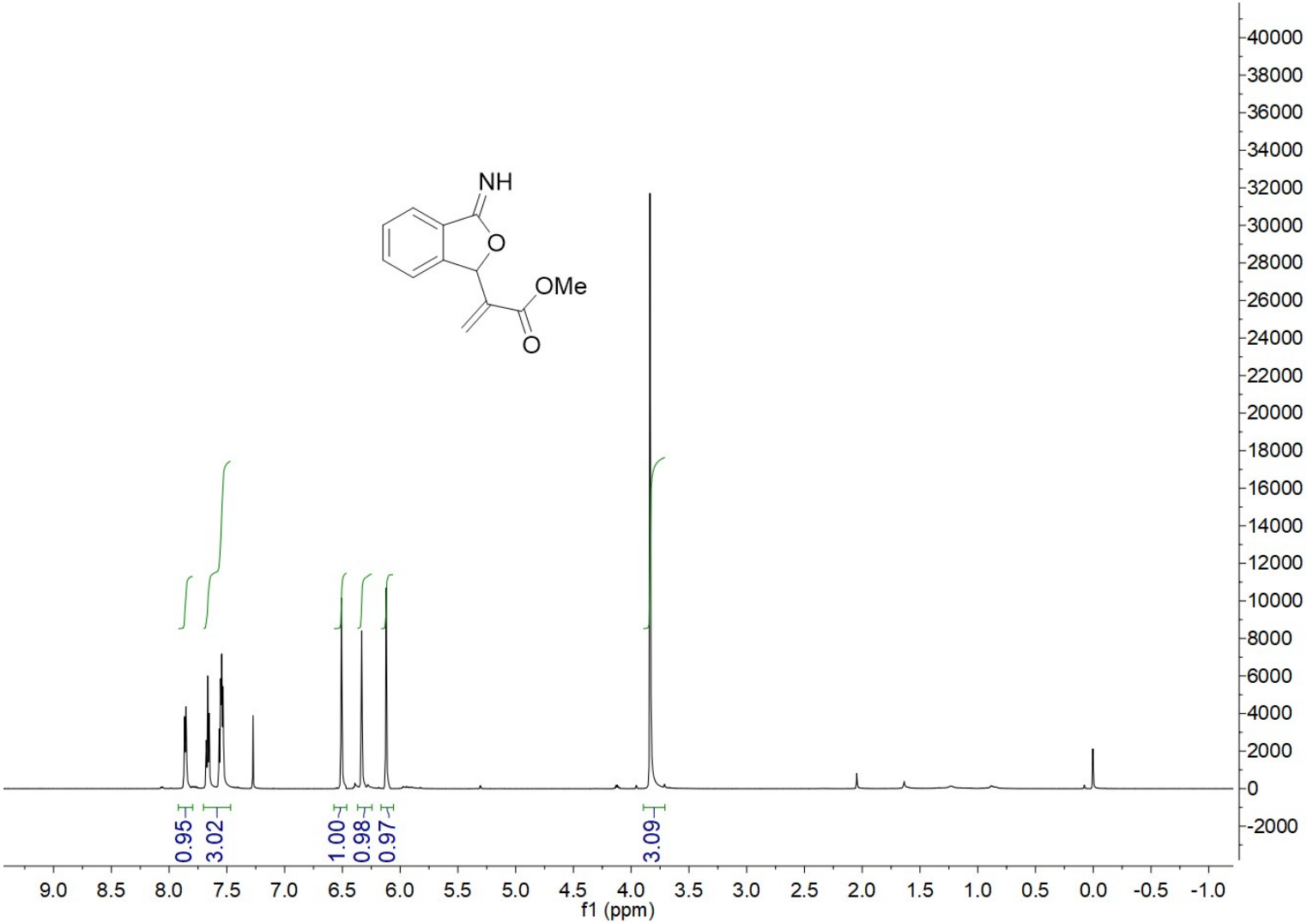

168.96
167.52
143.24
136.49
130.39
125.45
124.02
104.37
77.32
77.00
76.68
52.26
13.40
O
NH
O
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)

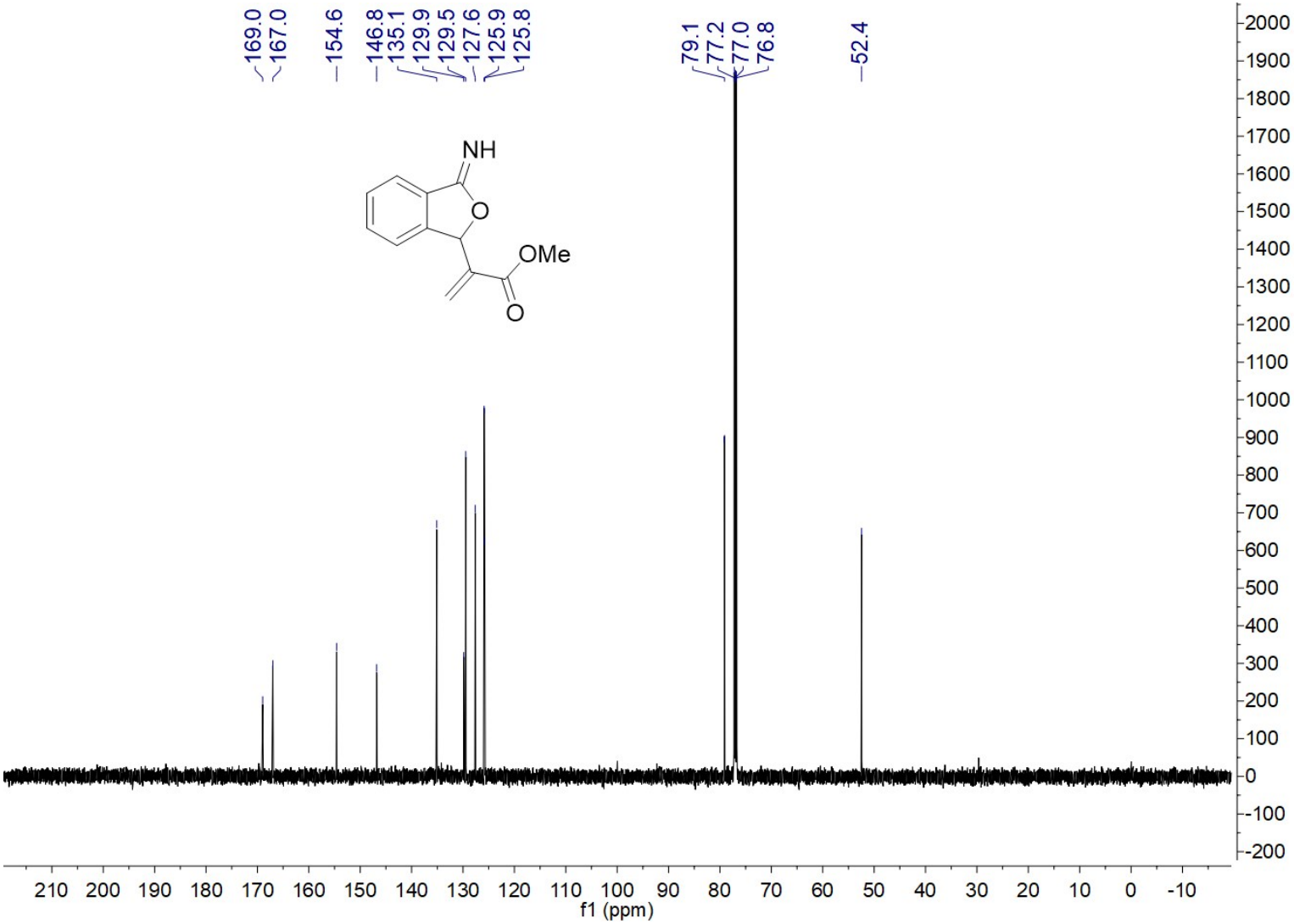

8.830
8.424
8.404
7.875
7.856
7.531
7.260
3.893
2.252
O
NH
O
1.01
1.00
1.00
1.05
1.05
3.07
3.12
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1(ppm)


168.680
168.327
140.200
132.884
130.756
129.961
126.162
123.319
108.888
77.318
77.000
76.683
52.161
16.048
O
NH
O
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1(ppm)


7.917
7.904
7.639
7.540
7.519
7.260
6.404
6.303
5.947
3.823
OH
O
O
N
0.96
3.04
1.02
0.93
1.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


170.14
165.29
148.44
136.42
134.26
129.47
127.61
125.78
125.34
122.84
78.67
77.21
77.00
76.79
52.28
OH
O
O
N
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


NH
O
OMe
O
0.95
3.02
1.00
0.98
0.97
3.09
f1 (ppm)


169.0
167.0
154.6
146.8
135.1
129.9
129.5
127.6
125.9
125.8
79.1
77.2
77.0
76.8
52.4
NH
O
OMe
O
f1 (ppm)