No Photocatalyst Required – Versatile, Visible Light Mediated Transformations with Polyhalomethanes

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Supporting Information

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1 General Methods

Unless otherwise noted, all commercially available compounds were used as provided without further purification.

NMR spectra were recorded on a Bruker Avance 300 (300.13 MHz), Varian MERCURY plus (300.08 MHz), Bruker Avance III 400 MHz (400.13 MHz) and Varian MERCURY plus (399.95 MHz) using the solvent peak as internal reference ($CDCl_3$: δ H 7.26; δ C 77.0; DMSO-d_6: δ H 2.50; δ C 39.5). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), sept (septet), m (multiplet)); coupling constants (J) are given in Hertz (Hz). High resolution mass was recorded on an Agilent Q-TOF 6540 UHD, Finnigan MAT95 or Bruker APEX II. All reactions were monitored by thin-layer chromatography using Merck silica gel plates 60 F_{254}; visualization was accomplished with UV light and/or appropriate staining. Standard flash chromatography procedures (SiO_2, size 40–63 µm) or standard chromatography procedures (SiO_2, size 63-200 µm) were followed.

Irradiation was performed with eight OSRAM® OSLON LD H9GP deep blue LEDs (455 nm, radiometric power 630 mW) or with nine Philips LUXEON® Rebel royal blue LEDs (455 nm, radiometric power 740 mW) attached to a heat sink. The LEDs were operated at 700 mA. Alternatively, the reactions were irradiated with a 30 cm 1 W blue LED stripe mounted on the inside of a beaker to surround the corresponding Schlenk tube. For "white light" irradiation a fluorescent light bulb (OSRAM DULUX Superstar, 22 W, 6500K, 1370 lm) was used. Emission spectra were recorded with an AVANTES AVASPEC-3648 fiber optic spectrometer.
IR spectra following the course of the reaction were recorded on a Mettler Toledo ReactIR™.

All reactions were carried out under a protective atmosphere of dry nitrogen using oven-dried glassware unless otherwise stated.

1,2,3,4-Tetrahydroisoquinoline derivatives were prepared according to known protocols.[1]

$CBrCl_3$ was distilled under Ar using a Vigreux column and then stored under argon in a flask which was additionally covered with aluminium foil (light protection).

NMR yields were determined using either of the following internal NMR standards (trichloroethylene (1H, 6.45 ppm), bromoform (1H, 6.82 ppm) or dibromomethane (2H, 4.93 ppm)). The standards were added using a microliter syringe after irradiation or after work-up. The accurate value of the injection was controlled by balancing the syringe`s weight before and after the addition of the standard. The yields were corrected according to this value.

[1] For the synthesis of *N*-Aryl-1,2,3,4-tetrahydroisoquinolines see: a) Li, Z.; Li, C.-J. *J. Am. Chem. Soc.* **2005**, *127*, 6968. b) Kwong, F. Y.; Klapars, A.; Buchwald, S. L. *Org. Lett.* **2002**, *4*, 581. For the preparation of *N*-Alkyl-1,2,3,4-tetrahydroisoqinolines see: c) Kessar, S. V.; Kulkarni, S. K.; Jain, R.; Trehan, S.; Magadi, S. K.; Das, J.; Kaur, G.; Singh, K. N.; Lata, S.; Dhir, A. Novel Monoamine Re-Uptake Inhibitors. PCT WO/2009/118765, Oct 1, 2009. d) Smissman, E. E.; Reid, J. R.; Walsh, D. A.; Borchardt, R. T. *J. Med. Chem.* **1976**, *19*, 127. *N*-Boc-1,2,3,4-tetrahydroisoquinoline **xxx** was prepared according to: e) Schrittwieser, J. H.; Resch, V.; Wallner, S.; Lienhart, W.-D.; Sattler, J. H.; Resch, J.; Macheroux, P.; Kroutil, W. *J. Org. Chem.* **2011**, *76*, 6703.

2 General Procedures

Procedure A: In an oven-dried Schlenk tube equipped with a magnetic stir bar 1,2,3,4-tetrahydroisoquinoline (THIQ) (0.25 mmol, 1.0 equiv) was dissolved in the indicated solvent. Bromotrichloromethane was added under nitrogen and the tube was then irradiated with blue LEDs for the indicated time at room temperature. The yield was determined by NMR using bromoform as internal standard.

Procedure B: In an oven-dried Schlenk tube equipped with a magnetic stir bar THIQ (0.25 mmol, 1.0 equiv) was dissolved in the indicated solvent (0.5 mL). Bromotrichloromethane (0.375 mmol, 1.5 equiv) was added under nitrogen and the tube was then irradiated with blue LEDs for 30 min at room temperature. The yield was determined by NMR using bromoform as internal standard.

Procedure C: (Standard Conditions) In an oven-dried Schlenk tube equipped with a magnetic stir bar the THIQ derivate (0.25 mmol, 1.0 equiv) was dissolved in acetonitrile (0.5 mL). Bromotrichloromethane (0.375 mmol, 1.5 equiv) was added under nitrogen and the tube was then irradiated with blue LEDs for 30 min at room temperature. The yield was determined by NMR using bromoform as internal standard.

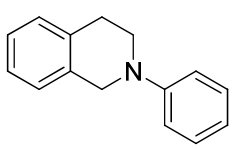
Procedure D: In an oven-dried Schlenk tube equipped with a magnetic stir bar THIQ (0.25 mmol, 1.0 equiv) was dissolved in the indicated solvent. Bromotrichloromethane was added under nitrogen and the tube was then irradiated with blue LEDs for 30 min at room temperature. After irradiation the reaction flask was covered with aluminum foil, extra solvent, the nucleophile and, if required, base was added and the reaction mixture was stirred at room temperature overnight. If needed, short work-up was performed prior to determining the yield by NMR using dibromomethane as internal standard.

For amine (THIQ) substrates the color rapidly changes from a colourless to a deep bluish solution which then vanishes to a light brown solution with the termination of the reaction.

3 Experimental Data

3.1 Experimental Data of THIQ Starting Material[1]

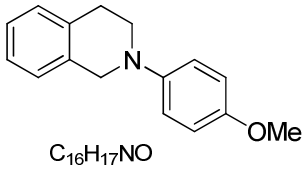
2-Phenyl-1,2,3,4-tetrahydroisoquinoline (1)



$C_{15}H_{15}N$
209.12 g/mol

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.28 (m, 2H), 7.23-7.15 (m, 4H), 7.04-6.98 (m, 2H), 6.89-6.82 (m, 1H), 4.44 (s, 2H), 3.59 (t, J = 5.9 Hz, 2H), 3.01 (t, J = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 150.6, 134.9, 134.5, 129.2, 128.6, 126.6, 126.4, 126.1, 118.7, 115.2, 50.8, 46.6, 29.2.

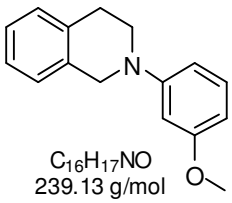
2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (S1)



$C_{16}H_{17}NO$
239.13 g/mol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.21-7.10 (m, 4H), 7.02-6.95 (m, 2H), 6.90-6.83 (m, 2H), 4.30 (s, 2H), 3.78 (s, 3H), 3.45 (t, J = 5.9 Hz, 2H), 2.99 (t, J = 5.8 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 153.5, 145.4, 134.6, 134.5, 128.7, 126.5, 126.3, 125.9, 118.0, 114.6, 55.6, 52.7, 48.5, 29.1.

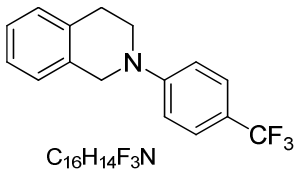
2-(3-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (S2)



$C_{16}H_{17}NO$
239.13 g/mol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.25 – 7.11 (m, 5H), 6.61 (dd, J = 8.2, 2.0 Hz, 1H), 6.53 (t, J = 2.0 Hz, 1H), 6.41 (dd, J = 8.1, 2.0 Hz, 1H), 4.42 (s, 2H), 3.82 (s, 3H), 3.57 (t, J = 5.9 Hz, 2H), 2.99 (t, J = 5.8 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3): δ 160.7, 151.8, 134.9, 134.4, 129.8, 128.4, 126.5, 126.3, 126.0, 107.8, 103.2, 101.4, 55.1, 50.5, 46.3, 29.1.

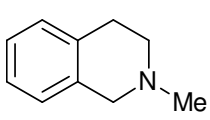
2-(4-(Trifluoromethyl)phenyl)-1,2,3,4-tetrahydroisoquinoline (S3)



$C_{16}H_{14}F_3N$
277.11 g/mol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55-7.48 (m, 2H), 7.25-7.16 (m, 4H), 6.98-6.91 (m, 2H), 4.49 (s, 2H), 3.64 (t, J = 5.9 Hz, 2H), 3.00 (t, J = 5.9 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 152.1, 134.9, 133.8, 128.3, 126.7, 126.5, 126.5 (q, $^3J_{CF}$ = 3.8 Hz), 126.4, 125.0 (q, $^1J_{CF}$ = 270.3 Hz), 119.1 (q, $^2J_{CF}$ = 32.8 Hz), 113.0, 49.4, 45.2, 29.0. ^{19}F NMR (282 MHz, $CDCl_3$): δ -61.5.

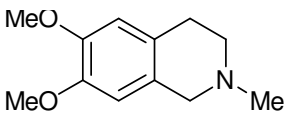
2-Methyl-1,2,3,4-tetrahydroisoquinoline (S4)



$C_{10}H_{13}N$
147.10 g/mol

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.08 (m, 3H), 7.05-6.99 (m, 1H), 3.59 (s, 2H), 2.93 (t, *J* = 5.9 Hz, 2H), 2.69 (t, *J* = 6.0 Hz, 2H), 2.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 134.8, 133.8, 128.7, 126.4, 126.1, 125.6, 58.1, 53.0, 46.2, 29.3.

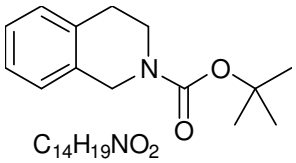
6,7-Dimethoxy-2-methyl-1,2,3,4-tetrahydroisoquinoline (S5)



$C_{12}H_{17}NO_2$
207.13 g/mol

^{1}H NMR (300 MHz, $CDCl_3$): δ 6.58 (s, 1H), 6.50 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.49 (s, 2H), 2.83 (t, *J* = 5.9 Hz, 2H), 2.64 (t, *J* = 5.9 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 147.6, 147.2, 126.7, 125.8, 111.5, 109.4, 57.7, 56.00, 55.96, 53.1, 46.2, 28.9.

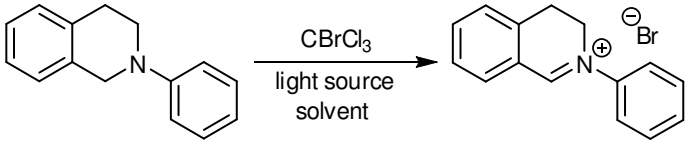
***tert*-Butyl-3,4-dihydroisoquinoline-2(1*H*)-carboxylate (S6)**



$C_{14}H_{19}NO_2$
233.14 g/mol

^{1}H NMR (300 MHz, $CDCl_3$): δ 7.22-7.07 (m, 4H), 4.58 (s, 2H), 3.65 (t, *J* = 5.9 Hz, 2H), 2.84 (t, *J* = 5.9 Hz, 2H), 1.50 (s, 9H).

3.2 Screening for best conditions



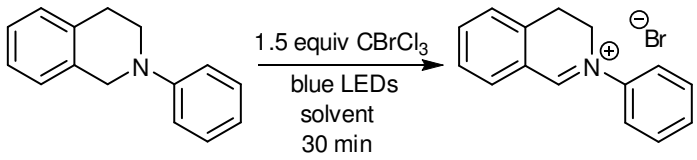
according to **General Procedure A:**

Table S1:

n (mmol) of THIQ	$CBrCl_3$	solvent	light source	temperature	time	yield (NMR)[a]
0.25	3.0 equiv	acetonitrile	blue LEDs	rt	30 min	91
0.25	1.0 equiv	acetonitrile	blue LEDs	rt	30 min	97
0.25	1.0 equiv	acetonitrile	blue LEDs	rt	60 min	99
0.25	1.5 equiv	acetonitrile	blue LEDs	rt	30 min	quant.
0.25	1.5 equiv	acetonitrile	22 W bulb	rt	30 min	quant.
0.25	1.5 equiv	acetonitrile	sunlight	rt	30 min	91
0.25	1.5 equiv	acetonitrile	green LEDs	rt	30 min	14
0.25	1.5 equiv	acetonitrile	no light	70 °C	30 min	23
0.25	1.5 equiv	toluene	no light	100 °C	30 min	decomposition
2.50 (large scale)	1.5 equiv	acetonitrile	blue LEDs	rt	30 min	95

a) using bromoform ($C\underline{H}Br_3$) as internal standard.

3.3 Solvents



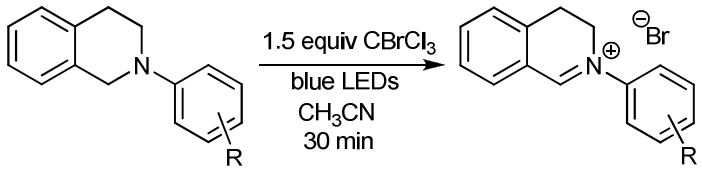
according to **General Procedure B:**

Table S2:

solvent	**yield (NMR)**[a]
acetonitrile (CH_3CN)	100
H_2O	98
1,4-dioxane	96
toluene	100
MTBE	100
ethanol	100
acetone	27
DMSO	100
DMF	100
THF	74
ethyl acetate (EE)	95
$CHCl_3$	100
dichloromethane (DCM)	99
hexanes	71
cyclohexane	88
ethyl methyl ketone	54
Et_2O	82
benzene	99

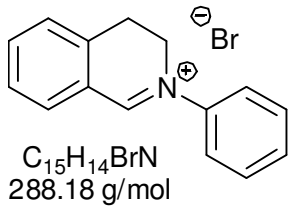
a) using bromoform as internal standard.

3.4 Substrate Scope



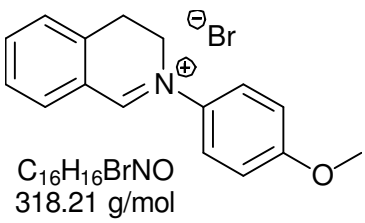
according to **General Procedure C = Standard Conditions** (NMR spectra see p.S39 sqq.)

2-Phenyl-3,4-dihydroisoquinolinium bromide (2)[2]



according to **general procedure C**: 100% yield (NMR)
^{1}H NMR (300 MHz, DMSO-d_6): δ 9.63 (s, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.95-7.82 (m, 3H), 7.76 – 7.57 (m, 5H), 4.60 (t, *J* = 7.7 Hz, 2H), 3.43 (t, *J* = 8.0 Hz, 2H). ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.46 (d, *J* = 7.5 Hz, 1H), 8.06 – 7.98 (m, 2H), 7.72 (td, *J* = 7.6, 1.1 Hz, 1H), 7.58 – 7.42 (m, 4H), 7.38 (d, *J* = 7.6 Hz, 1H), 4.58 (t, *J* = 7.9 Hz, 2H), 3.50 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.2, 142.9, 138.4, 137.1, 134.8, 130.9, 130.0, 128.3, 128.3, 125.5, 122.7, 50.7, 24.8.

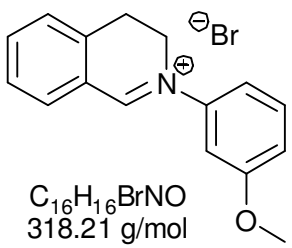
2-(4-Methoxyphenyl)-3,4-dihydroisoquinolinium bromide (3)



according to **general procedure C**: 95% yield (NMR)
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.28 (s, 1H), 8.42 (d, *J* = 7.5 Hz, 1H), 8.02 (d, *J* = 9.0 Hz, 2H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.9 Hz, 2H), 4.56 (t, *J* = 7.9 Hz, 2H), 3.77 (s, 3H), 3.47 (t, *J* = 7.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.2, 161.5, 138.3, 136.3, 135.8, 134.9, 128.7, 127.9, 125.5, 124.3, 115.3, 55.7, 51.7, 25.9. HR MS (EI) ($C_{16}H_{16}NO^+$; [M^+]): calcd.: 238.1226, found: 238.1225

[2] For literature reference NMR data, please see: a) Li, Z.; MacLeod, P. D.; Li, C.-J. *Tetrahedron Asymm.* **2006**, *17*, 590 and supporting information of b) Boess, E.; Sureshkumar, D.; Sud, A.; Wirtz, C.; Farès, C.; Klussmann, M. *J. Am. Chem. Soc.* **2011**, *133*, 8106.

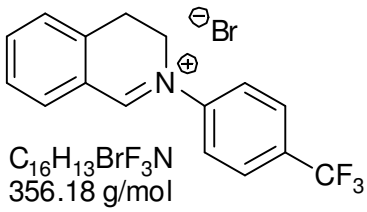
2-(3-Methoxyphenyl)-3,4-dihydroisoquinolinium bromide (4)



according to **general procedure C**: 94% yield (NMR)

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.32 (s, 1H), 8.45 (d, *J* = 7.6 Hz, 1H), 7.76 – 7.64 (m, 2H), 7.46 – 7.31 (m, 4H), 6.96 (dd, *J* = 8.3, 1.8 Hz, 1H), 4.58 (t, *J* = 7.9 Hz, 2H), 3.91 (s, 3H), 3.47 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 165.8, 160.8, 143.2, 138.7, 136.7, 136.3, 130.8, 128.7, 127.9, 125.4, 118.3, 114.2, 107.8, 56.7, 51.8, 25.9. HR MS (EI) ($C_{16}H_{16}NO^+$ [M^+]): calcd.: 238.1226, found: 238.1228

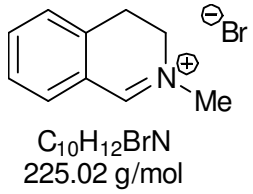
2-(4-(Trifluoromethyl)phenyl)-3,4-dihydroisoquinolinium bromide (5)



according to **general procedure C:** 100% yield (NMR)

^{1}H NMR (300 MHz, $CDCl_3$): δ 10.45 (s, 1H), 8.37 (d, *J* = 7.2 Hz, 1H), 8.27 (d, *J* = 8.5 Hz, 2H), 7.72 (m, 3H), 7.39 (m, 2H), 4.63 (t, *J* = 7.9 Hz, 2H), 3.52 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 167.2, 144.8, 139.3, 137.0, 136.5, 132.7 (q, $^2J_{CF}$ = 33.8 Hz), 128.8, 128.2, 127.4 (q, $^3J_{CF}$ = 3.7 Hz), 125.7, 123.9, 123.0 (q, $^1J_{CF}$ = 271.5 Hz), 52.1, 26.1. ^{19}F NMR (282 MHz, $CDCl_3$): δ -63.3. HR MS (EI) ($C_{16}H_{13}F_3N^+$ [M^+]): calcd.: 276.0995, found: 276.0993

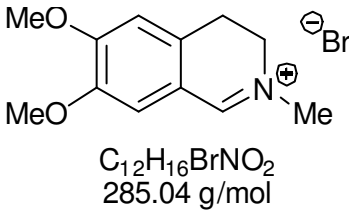
2-Methyl-3,4-dihydroisoquinolinium bromide (6)



according to **general procedure C**: 85% yield (NMR)

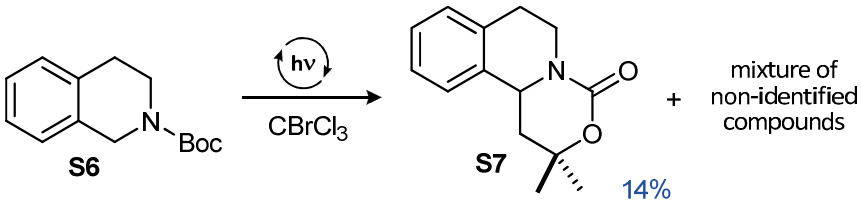
^{1}H NMR (300 MHz, $CDCl_3$): δ 10.34 (s, 1H), 8.05 (d, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 4.18 (t, *J* = 8.1 Hz, 2H), 4.11 (s, 3H), 3.39 (t, *J* = 8.1 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 167.6, 138.0, 135.5, 134.6, 128.7, 128.2, 124.7, 50.7, 48.3, 25.5. LR MS (ESI) ($C_{10}H_{12}N^+$ [M^+]): calcd.: 146.1, found: 146.1

6,7-Dimethoxy-2-methyl-3,4-dihydroisoquinolinium bromide (7)



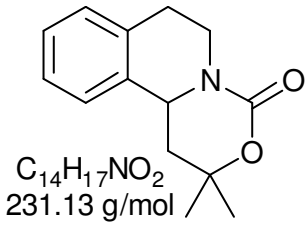
according to **general procedure C**: 98% yield (NMR)
^{1}H NMR (300 MHz, $CDCl_3$): δ 9.93 (s, 1H), 7.55 (s, 1H), 6.81 (s, 1H), 4.03 (t, *J* = 8.3 Hz, 2H), 3.93 (s, 6H), 3.84 (s, 3H), 3.25 (t, *J* = 8.3 Hz, 2H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 165.4, 157.3, 148.7, 131.7, 117.2, 115.6, 110.8, 56.8, 56.7, 50.0, 47.5, 25.4. HR MS (ESI) ($C_{12}H_{17}NO_2^+$ $[M+H]^+$): calcd.: 206.1176, found: 206.1184.

Cyclization of Boc substrate S6



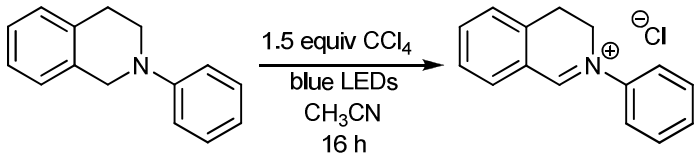
In an oven-dried Schlenk tube equipped with a magnetic stir bar *tert*-Butyl 3,4-Dihydro-2(1*H*)-isoquinolinecarboxylate (0.25 mmol, 1 equiv) was dissolved in acetonitrile (0.5 mL). Bromotrichloromethane (0.375 mmol, 1.5 equiv) was added and the resulting mixture was degassed *via* three pump-freeze-thaw cycles. The tube was then irradiated with blue LEDs for 1 h at room temperature. The reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (15 mL) and extracted with ethyl acetate (3 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the desired product in 14% yield.

2,2-dimethyl-1,2,6,7-tetrahydro-[1,3]oxazino[4,3-a]isoquinolin-4(11b*H*)-one (S7)



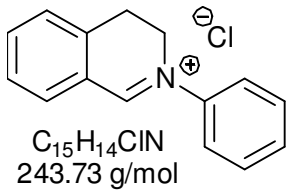
^{1}H NMR (300 MHz, $CDCl_3$):δ7.27 – 7.08 (m, 4H), 4.83 (dd, *J* = 11.7, 5.2 Hz, 1H), 4.67 – 4.56 (m, 1H), 3.13 – 3.01 (m, 2H), 2.82 – 2.71 (m, 1H), 2.46 (dd, *J* = 13.7, 5.2 Hz, 1H), 1.87 (dd, *J* = 13.3, 12.2 Hz, 1H), 1.54 (s, 3H), 1.46 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$):δ 152.8, 136.0, 134.8, 129.3, 126.9, 126.6, 124.7, 76.5, 51.6, 42.0, 40.7, 29.6, 28.8, 25.2.

3.5 CCl_4 as Oxidant



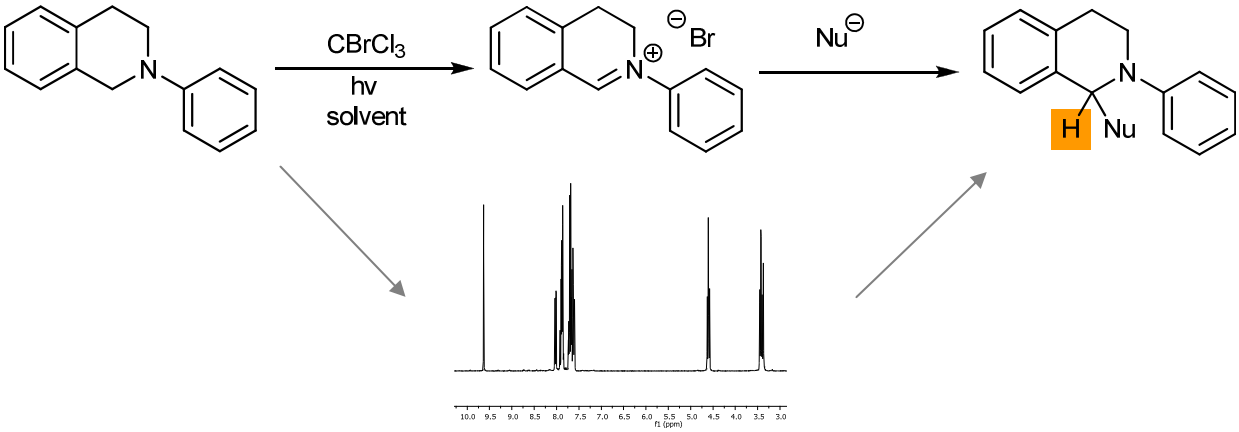
In an oven-dried Schlenk tube equipped with a magnetic stir bar THIQ (0.25 mmol, 1.0 equiv) was dissolved in acetonitrile (0.5 mL). Tetrachloromethane (0.375 mmol, 1.5 equiv) was added under nitrogen. After three freeze- pump-thaw cycles the tube was then irradiated with blue LEDs for 16 h at room temperature. The yield was determined by NMR using an internal standard.

2-Phenyl-3,4-dihydroisoquinolinium chloride (S8)



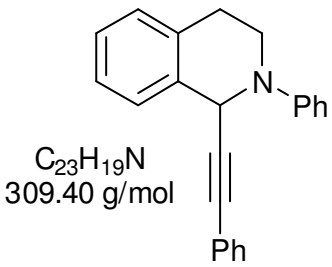
according to **procedure** (*vide supra* CH 3.5): 100% yield (NMR) ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.49 (s, 1H), 8.47 (d, *J* = 7.6 Hz, 1H), 8.07 – 7.98 (m, 2H), 7.69 (td, *J* = 7.6, 1.3 Hz, 1H), 7.54 – 7.32 (m, 5H), 4.60 (t, *J* = 7.9 Hz, 2H), 3.47 (t, *J* = 8.0 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 166.7, 142.2, 138.7, 136.9, 136.1, 131.1, 130.3, 128.7, 127.9, 125.5, 122.6, 51.4, 25.8. HR MS ($C_{15}H_{14}N^+$ [M^+]): calcd.: 208.1121, found: 208.1123

3.6 Addition of Nucleophiles – Scope of Reaction



NMR yield determined according to ^{1}H NMR signal of marked proton.

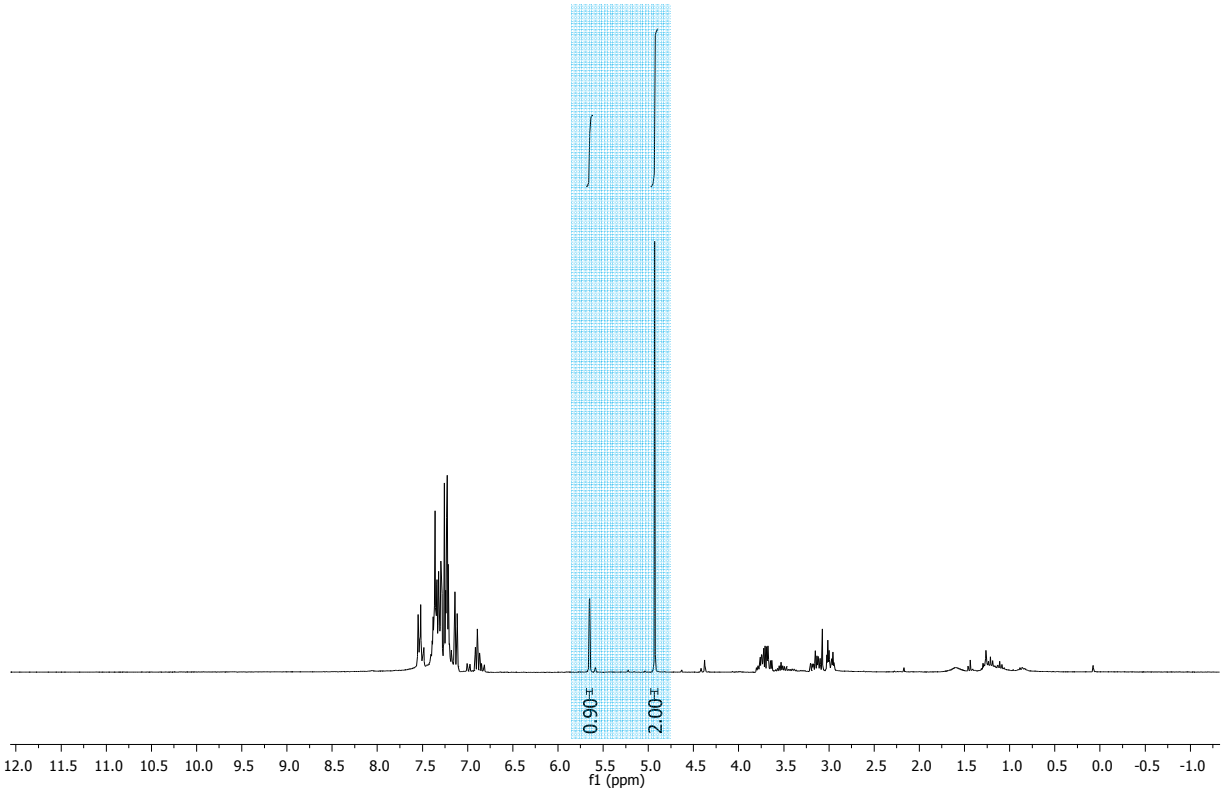
2-Phenyl-1-(phenylethynyl)-1,2,3,4-tetrahydroisoquinoline (13)



$C_{23}H_{19}N$
309.40 g/mol

according to **general procedure D:** 94% yield

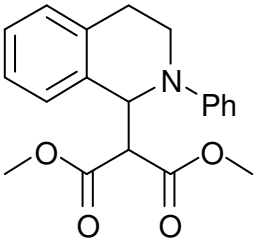
Procedure used 1,2,3,4-tetrahydroisoquinoline (52 mg, 0.25 mmol, 1.0 equiv), bromotrichloromethane (38 µL, 0.375 mmol, 1.5 equiv), acetonitrile (0.5 mL). After irradiation: 0.5 mL CH_3CN, triethylamine (0.18 mL, 1.25 mmol, 5 equiv), phenylacetylene (0.14 mL, 1.25 mmol, 5.0 equiv), Cu(I)Br (5.4 mg, 0.038 mmol, 0.15 equiv) were added. The reaction was stirred at room temperature over night. After filtration through a short plug of silica the solvent was removed under reduced pressure. The residue was dissolved in 1 mL $CDCl_3$ and NMR standard (CH_2Br_2) was added. The yield was determined by NMR.



CH_2Br_2 as internal standard (integral (δ 4.93: δ 5.65) =2:1 = 100% yield)

After weighted sample correction of internal standard → 94% yield

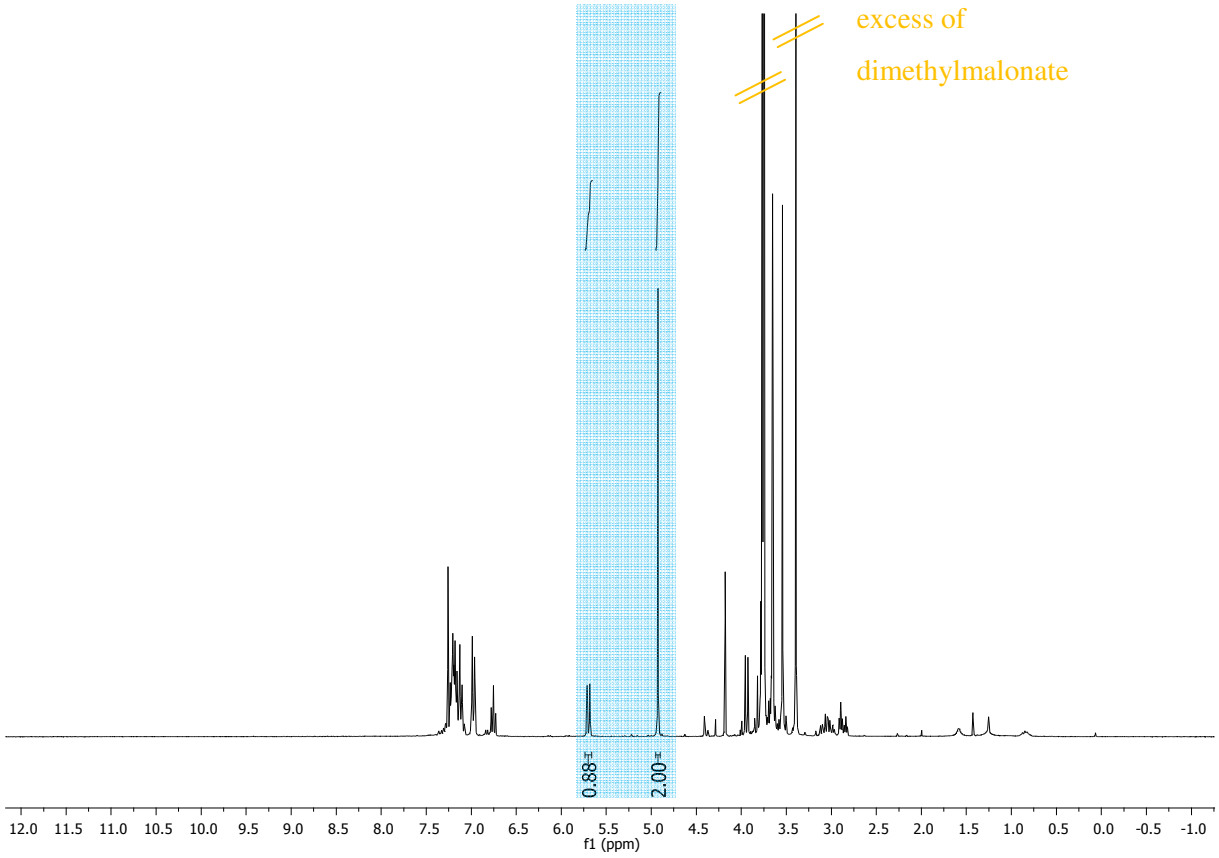
Dimethyl 2-(2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)malonate (10)



$C_{20}H_{21}NO_4$
339.39 g/mol

according to **general procedure D:** 91% yield

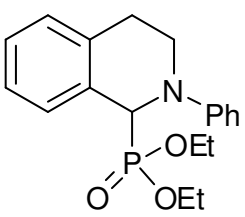
Procedure used 1,2,3,4-tetrahydroisoquinoline (52 mg, 0.25 mmol, 1.0 equiv), bromotrichloromethane (38 µL, 0.375 mmol, 1.5 equiv), acetonitrile (0.5 mL). After irradiation: 0.5 mL CH_3CN, dimethylmalonate (0.145 mL, 1.25 mmol, 5.0 equiv), K_2CO_3 (173 mg, 1.25 mmol, 5.0 equiv) were added. The reaction was stirred at room temperature over night. After filtration through a short plug of silica the solvent was removed under reduced pressure. The residue was dissolved in 1 mL $CDCl_3$ and NMR standard (CH_2Br_2) was added. The yield was determined by NMR.



CH_2Br_2 as internal standard (integral (δ 4.92: δ 5.70) = 2:1 = 100% yield)

After weighted sample correction of internal standard → 91% yield

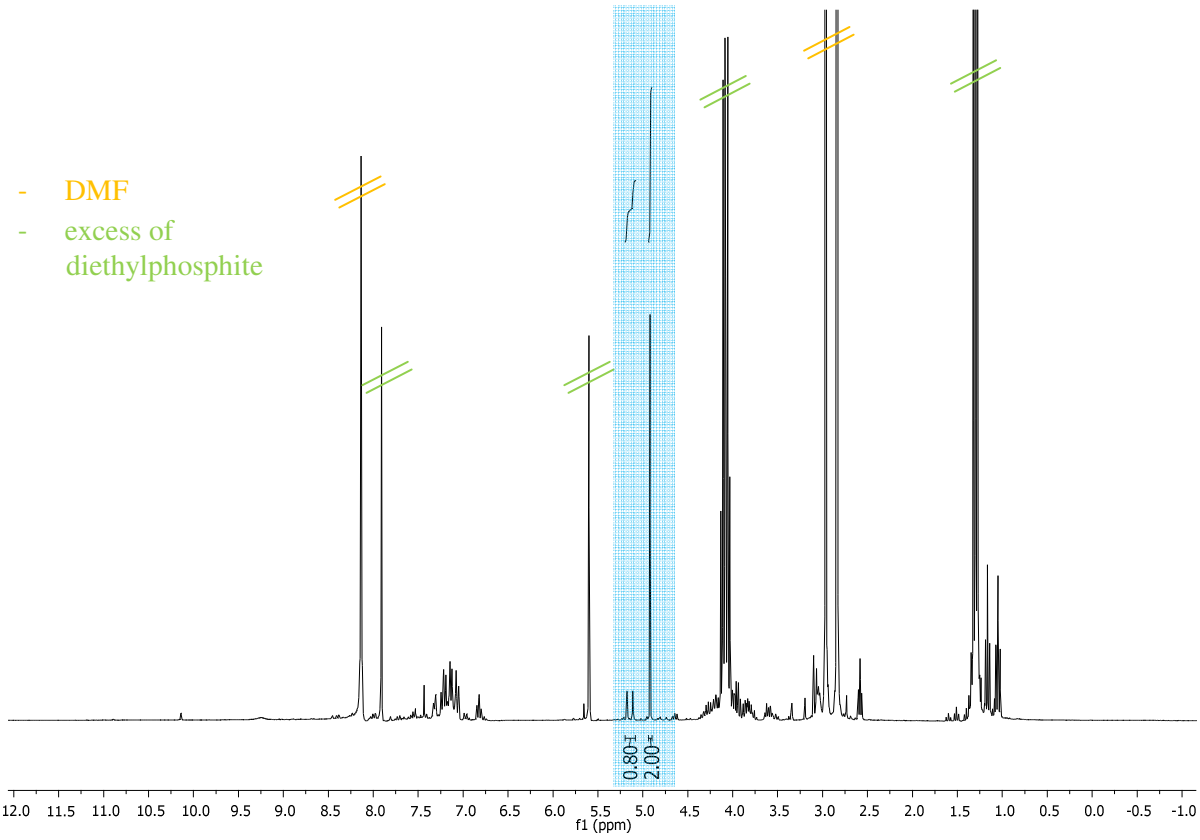
Diethyl 2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-ylphosphonate (8)



$C_{19}H_{24}NO_3P$
345.37 g/mol

according to **general procedure D:** 82% yield

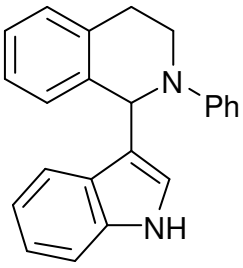
Procedure used 1,2,3,4-tetrahydroisoquinoline (52 mg, 0.25 mmol, 1.0 equiv), bromotrichloromethane (38 µL, 0.375 mmol, 1.5 equiv), DMF (0.5 mL). After irradiation: 0.5 mL DMF, diethylphosphite (0.131 mL, 1.0 mmol, 4.0 equiv) were added. The reaction was stirred at room temperature over night. NMR standard (CH_2Br_2) was added directly to the crude reaction mixture. The yield was determined by NMR.



CH_2Br_2 as internal standard (integral (δ 4.92: δ 5.15) = 2:1 = 100% yield)

After weighted sample correction of internal standard → 82% yield

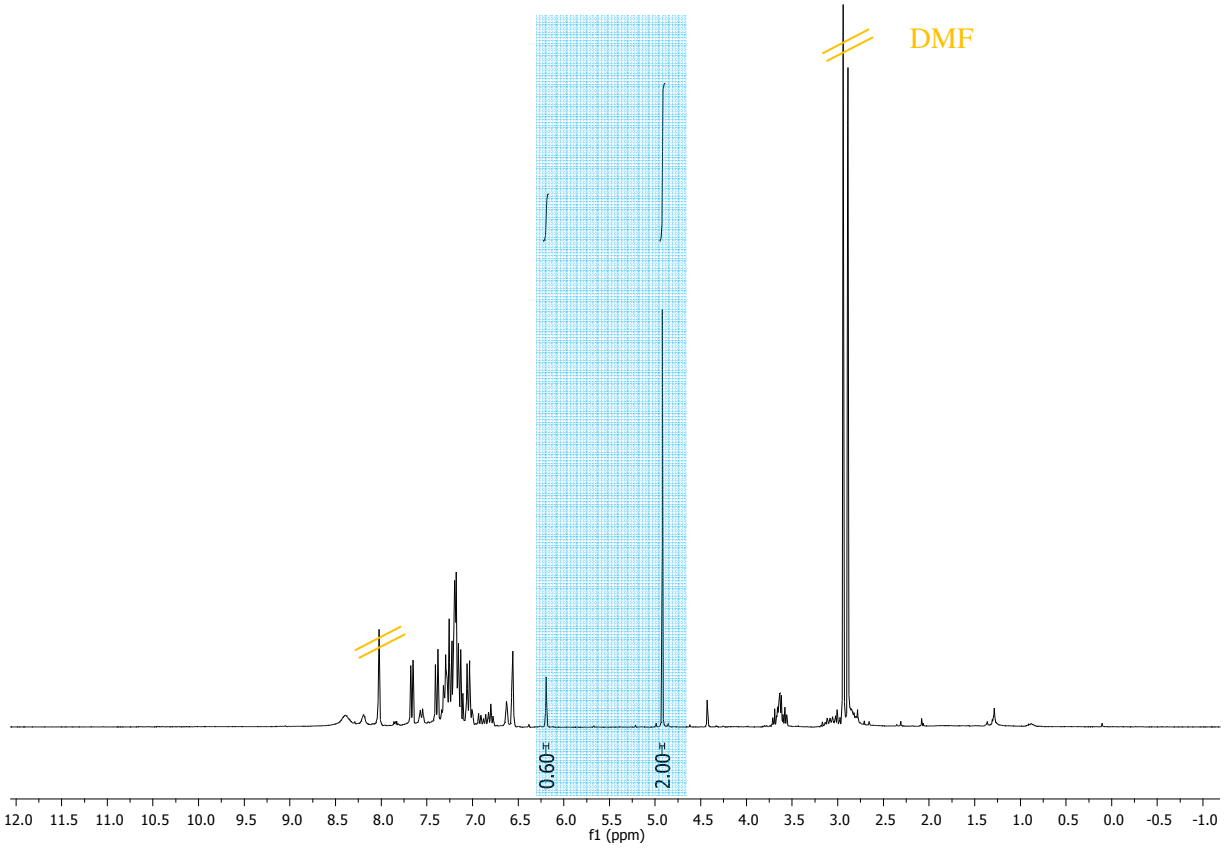
1-(1*H*-indol-3-yl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (11)



$C_{23}H_{20}N_2$
324.42 g/mol

according to **general procedure D:** 60% yield

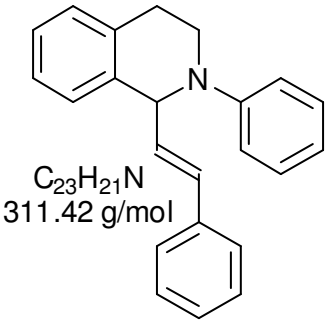
Procedure used 1,2,3,4-tetrahydroisoquinoline (52 mg, 0.25 mmol, 1.0 equiv), bromotrichloromethane (38 µL, 0.375 mmol, 1.5 equiv), DMF (1 mL). Solution was degassed. After irradiation: indole (146 mg, 1.25 mmol, 5.0 equiv), KOtBu (140 mg, 1.25 mmol, 5.0 equiv) were added. The reaction was stirred at room temperature over night. After filtration through a short plug of silica the solvent was removed under reduced pressure. The residue was dissolved in 1 mL $CDCl_3$ and NMR standard (CH_2Br_2) was added. The yield was determined by NMR.



CH_2Br_2 as internal standard (integral (δ 4.92: δ 6.19) = 2:1 = 100% yield)

After weighted sample correction of internal standard → 60% yield

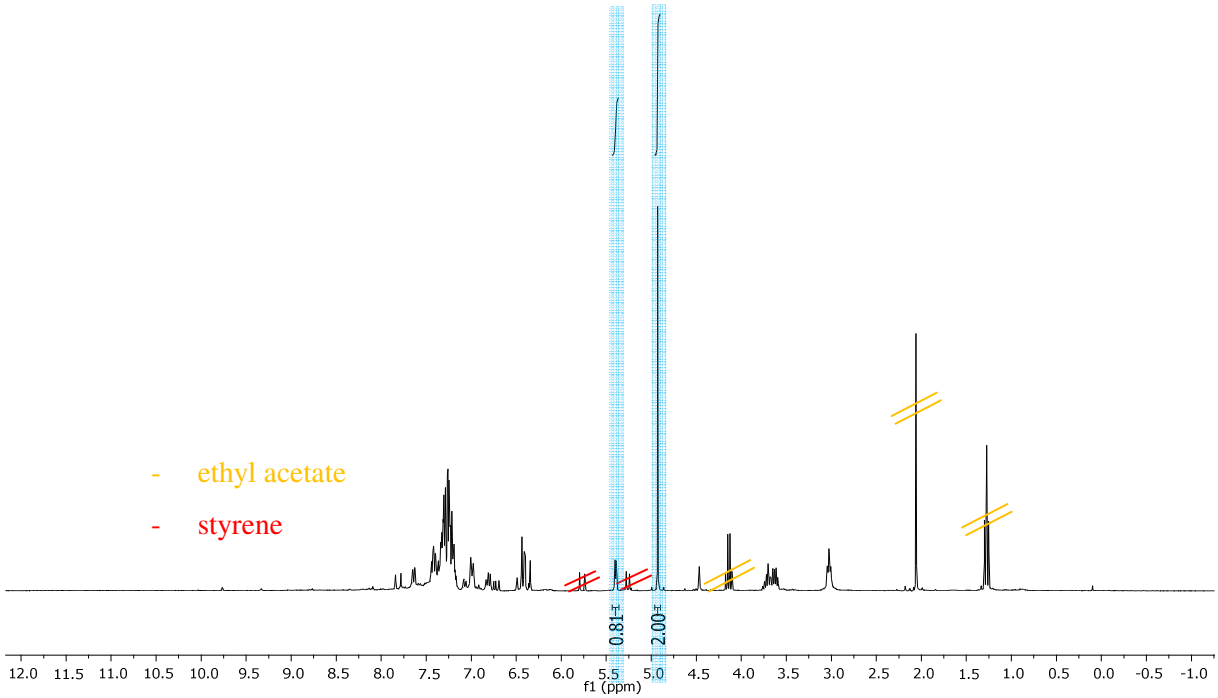
2-Phenyl-1-styryl-1,2,3,4-tetrahydroisoquinoline (15)



according to **general procedure D:** 83% yield

Procedure used 1,2,3,4-tetrahydroisoquinoline (52 mg, 0.25 mmol, 1.0 equiv), bromotrichloromethane (27 µL, 0.275 mmol, 1.1 equiv), DCM (1 mL). Solution was degassed. After irradiation: Potassium *trans*-beta-styryltrifluoroborate(158 mg, 0.75 mmol, 3 equiv) was added. The reaction was stirred at room temperature over night. After extraction with EE and water (2x) the combined organic layers were washed with brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. Finally, the residue was dissolved in 1 mL $CDCl_3$, NMR standard (CH_2Br_2) was added and the yield was determined by NMR.

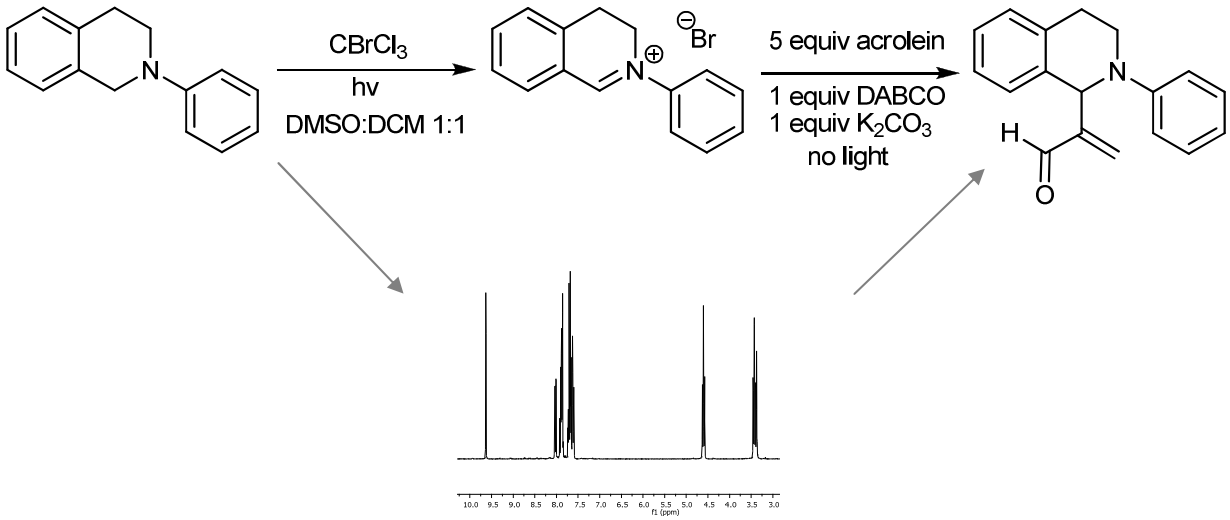
Data for the isolated product: (Reaction was performed with isolated THIQImBr **X** as starting material) ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34-7.15 (m, 11H), 6.97-6.92 (m, 2H), 6.80-6.73 (m, 1H), 6.46 (d, 1H, *J* = 16.2 Hz), 6.36 (dd, 1H, *J* = 15.8, 4.4 Hz), 5.38 (d, 1H, *J* = 4.3 Hz), 3.76-3.53 (m, 2H), 3.09-2.90 (m, 2H). ^{13}C-NMR (75 MHz, $CDCl_3$): δ = 149.5, 136.8, 136.7, 135.7, 130.5, 130.3, 129.2, 128.5, 128.3, 127.5, 127.4, 126.9, 126.5, 126.3, 117.6, 114.1, 61.4, 43.1, 28.3. (NMR spectrum, see p. S50 sqq.)
HRMS (ESI) ($C_{23}H_{21}NH^+$ [M+H$^+$]): calcd.: 312.1747, found: 312.1749



CH_2Br_2 as internal standard (integral (δ 4.93: δ 5.40) = 2:1 = 100% yield)

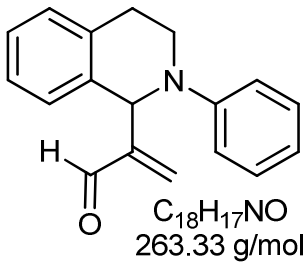
After weighted sample correction of internal standard → 83% yield

3.7 Morita-Baylis-Hilman Type sp³ C-H acroleination of THIQ



In an oven-dried Schlenk tube equipped with a magnetic stir bar the THIQ derivative (0.5 mmol, 1.0 equiv) was dissolved in DMSO:DCM 1:1 (2 mL). Bromotrichloromethane (0.75 mmol, 1.5 equiv) was added under nitrogen and the tube was then irradiated with blue LEDs for 30 min at room temperature. After irradiation K_2CO_3 (0.5 mmol, 1.0 equiv) and DABCO (0.5 mmol, 1.0 equiv) were added. Subsequently, after three freeze-pump-thaw cycles, the flask was covered with aluminum foil, 5 equiv of acrolein were added under N_2 and then the reaction was stirred at room temperature for 24 h. For workup the mixture was then extracted with water and diethylether (25 mL). The layers were separated and the aqueous layer was extracted with diethylether (2×25 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product. (PE:EE 30:1)

2-(2-Phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde (12)[3]



according to **procedure** (vide supra): 77% yield

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.65 (s, 1H), 7.35 – 7.14 (m, 6H), 6.88 – 6.82 (m, 2H), 6.82 – 6.75 (m, 1H), 6.24 (d, *J* = 0.7 Hz, 1H), 6.08 (s, 1H), 5.83 (s, 1H), 3.81 – 3.71 (m, 1H), 3.57 – 3.46 (m, 1H), 3.11 – 2.91 (m, 2H).^{13}C NMR (75 MHz, $CDCl_3$): δ 193.3, 151.2, 148.4, 135.6, 134.9, 134.2, 129.1, 128.3, 127.9, 127.1, 126.3, 117.9, 113.8, 56.8, 43.3, 27.8.

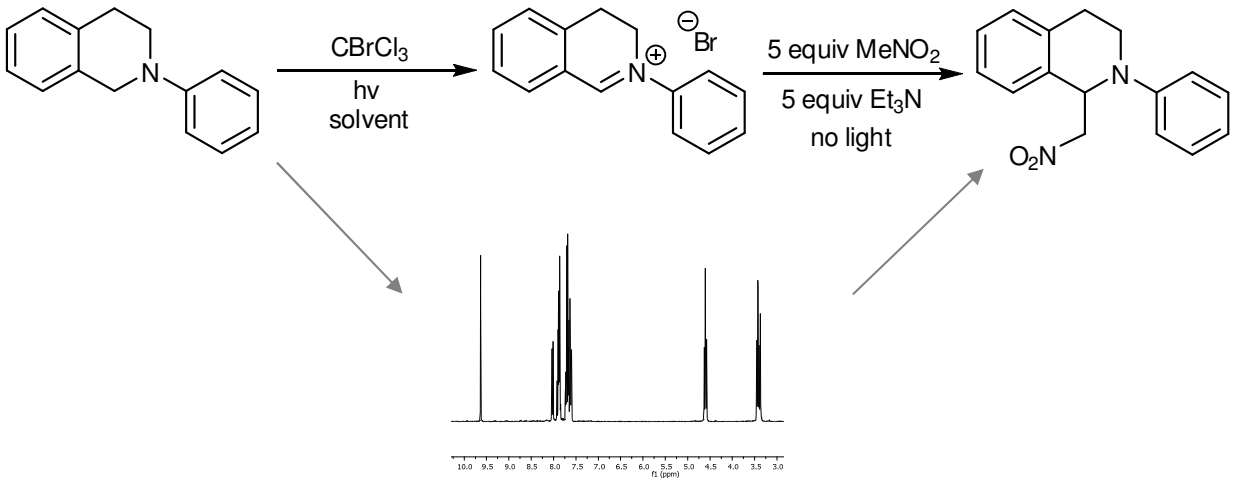
[3] Feng, Z.-J.; Xuan, J.; Xia, X.-D.; Ding, W.; Guo, W. ; Chen, J.-R.; Zou, Y.-Q.; Lu, L.-Q.; Xiao, W.-J. *Org. Biomol. Chem.* **2014**, *12*, 2037.

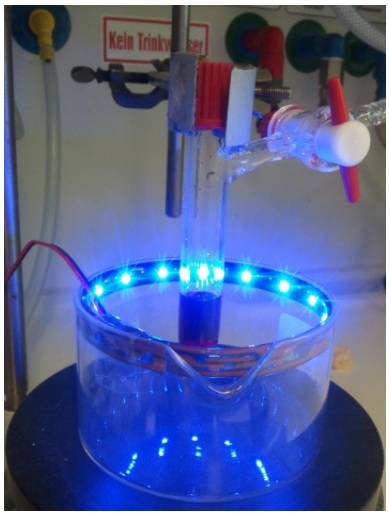
Table S3:

	n (mmol) THIQ	solvent	$CBrCl_3$	LED	time	yield (%)[a]
1[3]	0.5	DMSO:DCM 1:1 (2.0 mL)	3 equiv + cat	blue LEDs	3 h	83 (lit[3])
2[b]	0.5	DMSO:DCM 1:1 (2.0 mL)	1.5 equiv	blue LEDs	30 min	77
3[b]	0.5	CH_3CN (2 mL)	1.5 equiv	blue LEDs	30 min	71

a) Yield of isolated product. b) Entries 2 and 3 (catalyst-free) have been performed in our labs.

3.8 Aza-Henry Reaction





- **Exp. 1)** In an oven-dried Schlenk tube equipped with a magnetic stir bar THIQ (0.244 mmol, 1.0 equiv) and $Ru(bpy)_3Cl_2$ (0.002 mmol, 0.01 equiv) was dissolved in DMF (1 mL). Bromotrichloromethane (3 equiv) was added and the mixture was irradiated by a 30 cm 1 W blue LED strip under nitrogen atmosphere (according to literature[4])

- **Exp. 2)** see Exp. 1, but **without** $Ru(bpy)_3Cl_2$

- **Exp. 3 and 4)** In an oven-dried Schlenk tube equipped with a magnetic stir bar THIQ (0.25 mmol, 1.0 equiv) was dissolved in CH_3CN (0.5 mL or 1 mL). Bromotrichloromethane (1.5 equiv) was added and the mixture was irradiated with a blue LED array under nitrogen atmosphere.

After irradiation the flask was covered with aluminum foil, 5 equiv of $MeNO_2$ and Et_3N were added and then the reaction was stirred at room temperature over night. For workup the mixture was then extracted with a saturated solution of $NaHCO_3$ and EtOAc. The layers were separated and the aqueous layer was extracted with EtOAc (2×). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and concentrated. The residue was purified by silica gel chromatography to afford the desired product.

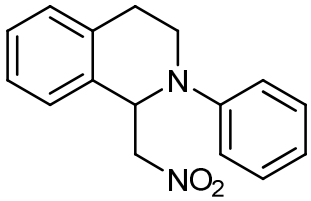
[4] Freeman, D. B.; Furst, L.; Condie, A. G.; Stephenson, C. R. J. *Org. Lett.* **2011**, *14*, 94.

Table S4:

	n (mmol) THIQ	solvent	$CBrCl_3$	LED	time	yield (%)[a]
1	0.244	DMF (1.0 mL)	3 equiv + cat.	Blue 1 W	3 h	95 (lit)[4]
2[b]	0.244	DMF (1.0 mL)	3 equiv	blue 1 W	3 h	97
3[b]	0.25	CH_3CN (0.5 mL)	1.5 equiv	blue LEDs	30 min	98
4[b]	0.25	CH_3CN (1.0 mL)	1.5 equiv	blue LEDs	30 min	100

a) Yield of isolated product. b) Entries 2 to 4 (catalyst-free) have been performed in our labs.

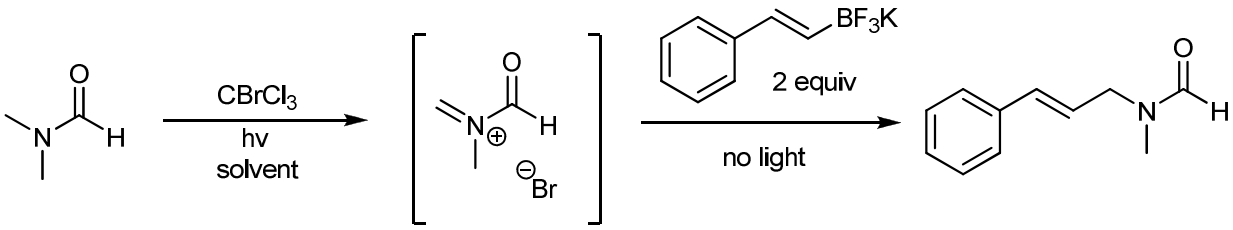
1-(Nitromethyl)-2-phenyl-1,2,3,4-tetrahydroisoquinoline (9)



$C_{16}H_{16}N_2O_2$
268.31 g/mol

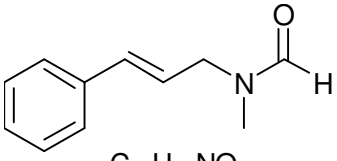
^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34 – 7.10 (m, 6H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H), 5.56 (t, *J* = 7.2 Hz, 1H), 4.88 (dd, *J* = 11.8, 7.8 Hz, 1H), 4.57 (dd, *J* = 11.8, 6.6 Hz, 1H), 3.74 – 3.56 (m, 2H), 3.17 – 3.03 (m, 1H), 2.80 (dt, *J* = 16.4, 5.0 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 135.3, 132.9, 129.5, 129.2, 128.1, 127.0, 126.7, 119.4, 115.1, 78.8, 58.2, 42.1, 26.4.

3.9 Amidoalkylation of DMF



In an oven-dried Schlenk tube equipped with a magnetic stir bar bromotrichloromethane (0.375 mmol, 1 equiv) was dissolved in DMF (1.0 mL) and the mixture was degassed *via* three pump-freeze-thaw cycles. The tube was then irradiated with blue LEDs for 3 h at room temperature. The LEDs were removed and potassium styryltrifluoroborate (0.75 mmol, 2.0 equiv) was added. The Schlenk tube was covered with aluminium foil and the resulting mixture was stirred at room temperature overnight. The reaction mixture was quenched with a saturated aqueous solution of NH_4Cl (10 mL) and extracted with diethyl ether (3 x 15 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The residue was purified by flash column chromatography to afford the desired product.

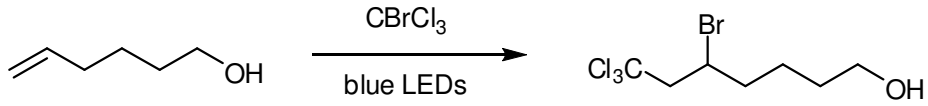
***N*-cinnamyl-N-methylformamide (16)**



$C_{11}H_{13}NO$
175.10 g/mol

^{1}H NMR (300 MHz, $CDCl_3$, two rotamers): δ 8.17/8.11 (s, 1H), 7.41-7.21 (m, 5H), 6.56/6.54 (d, *J* = 15.8 Hz, 1H), 6.12/6.07 (dt, *J* = 15.9, 6.6 Hz, 1H), 4.11/4.00 (dd, *J* = 6.6, 1.2 Hz, 2H), 2.95/2.89 (s, 3H).

3.10 ATRA Reactions



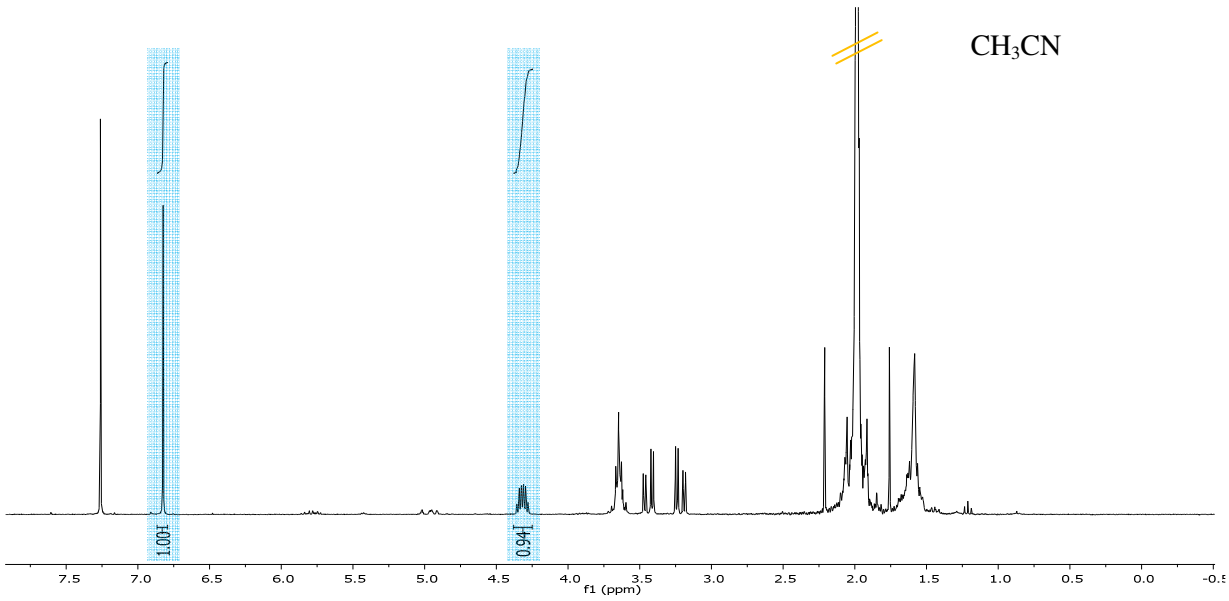
In an oven-dried Schlenk tube equipped with a magnetic stir bar 5-hexen-1-ol (2 mmol, 1.0 equiv) and bromotrichloromethane (4 mmol, 2 equiv) was dissolved in acetonitrile (4.0 mL) under an atmosphere of nitrogen. The tube was then irradiated with blue LEDs for 24 h at room temperature. The yield (92%) was determined by NMR with internal standard.

Table S5:

	5-hexen-1-ol (mmol)	$CBrCl_3$ (mmol)	catalyst	solvent (mL)	conc. (mol/l)	light source	yield
1	2	4	----	CH_3CN (4)	0.5	blue LEDs	92% [a]
2	2	4	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+ PF_6^-$	DMF (0.82) H_2O (3.3)	0.49	1 W blue LED stripe	87% (lit)[b]
3	1	2	$[Ir\{dF(CF_3)ppy\}_2(dtbbpy)]^+ PF_6^-$	DMF (0.41) H_2O (1.65)	0.49	1 W blue LED stripe	87% (lit)[b]
4	1	1.2	$Ru(bpy)_3Cl_2$	DMSO (2)	0.5	1 W blue LED stripe	95% (lit)[b]

a) NMR yield b) Isolated yield out of literature[5] (entries 2 and 3 are reported exactly like this in ref.5a and 5b).

[5] a) Wallentin, C.-J.; Nguyen, J. D.; Finkbeiner, P.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2012**, *134*, 8875; b) D. Nguyen, J. D.; Tucker, J. W.; Konieczynska, M. D.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2011**, *133*, 4160.



$CHBr_3$ as internal standard (integral (δ 6.82: δ 4.32) = 1:1 = 100% yield)

After weighted sample correction of internal standard → 92% yield

3.11 React-IR Experiments

Before the measurements:

Preparation of three solutions in a Schlenk tube:

1) Acetonitrile (CH_3CN)
2) 0.25 mmol of THIQ in 0.5 mL CH_3CN
3) 0.25 mmol of THIQ iminium bromide in 0.5 mL CH_3CN

Then all spectra of the three solutions were measured with Mettler Toledo ReactIR™.

Clean spectra of THIQ and THIQImBr were obtained by subtraction of the spectrum of pure CH_3CN as background.

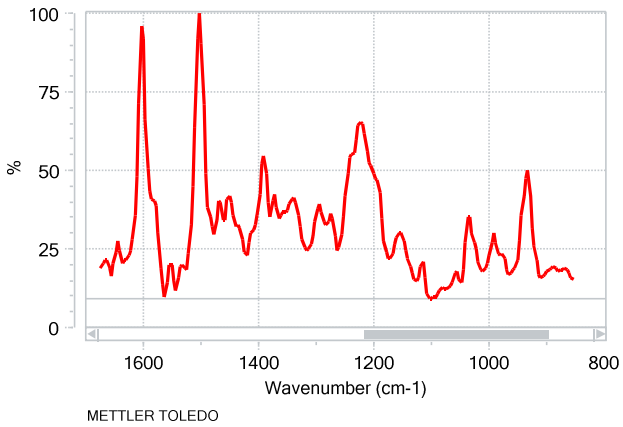


Figure S1: Spectrum of THIQ (starting material = red).

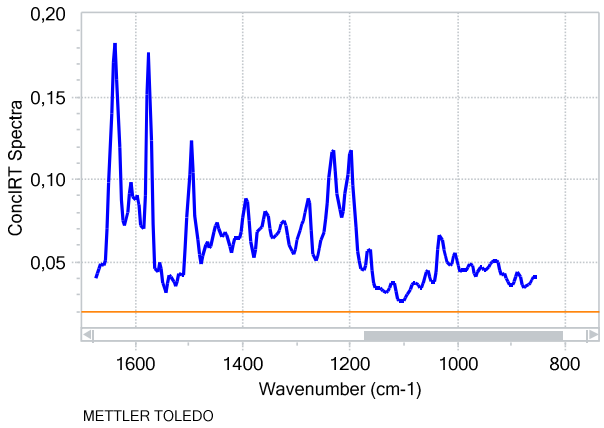


Figure S2: Spectrum of THIQImBr (product = blue).

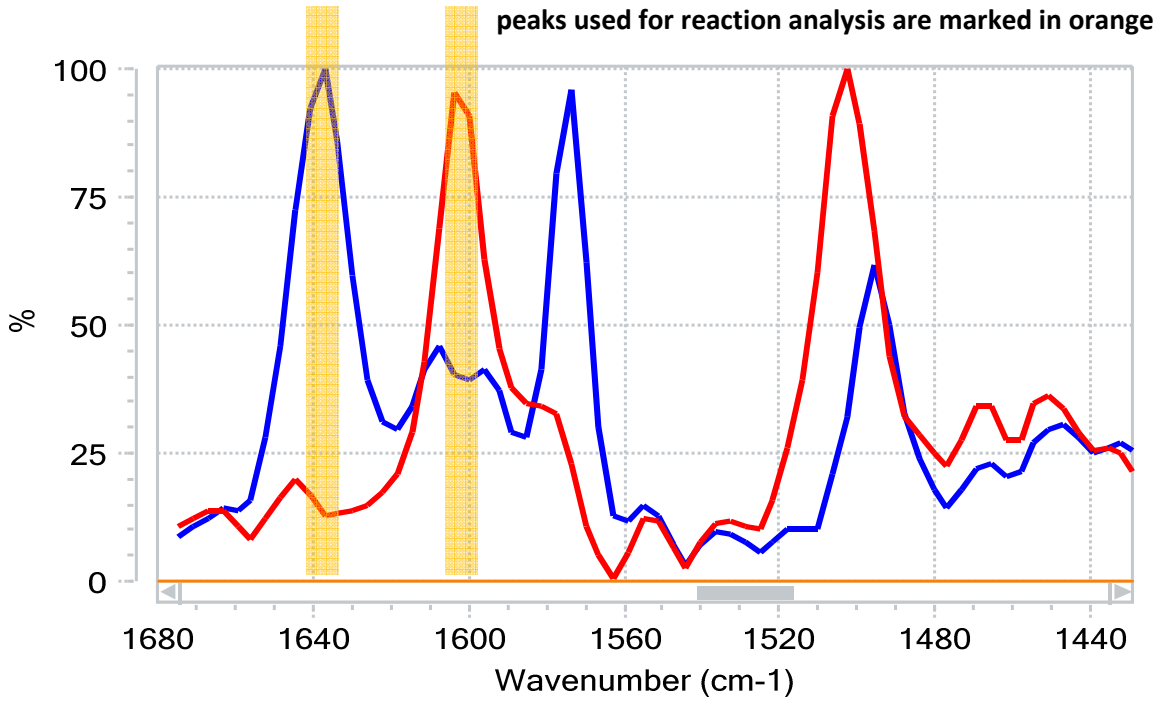


Figure S3: Overlapping spectra of starting material (red) and product (blue).

The marked two wavelength at 1604 cm^{-1} and 1640 cm^{-1} were determined to be indicative for the reaction progress.

The reaction was performed under standard conditions and controlled with the Mettler Toledo ReactIR™ sensor directly dipping in the reaction solution.

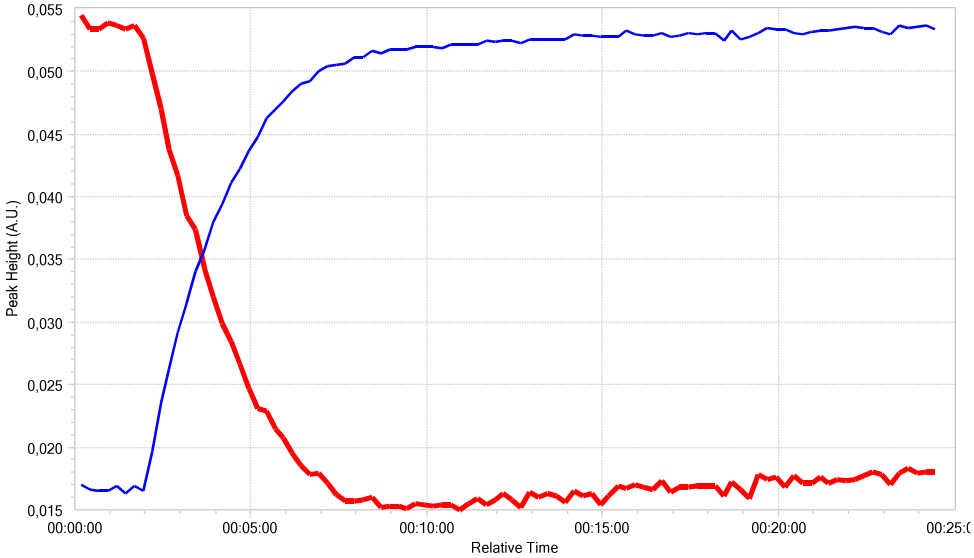


Figure S4: Reaction progress (decrease of starting material at 1604 cm^{-1} and product formation at 1641 cm^{-1} (fast reaction which is nearly finished after 12 min).

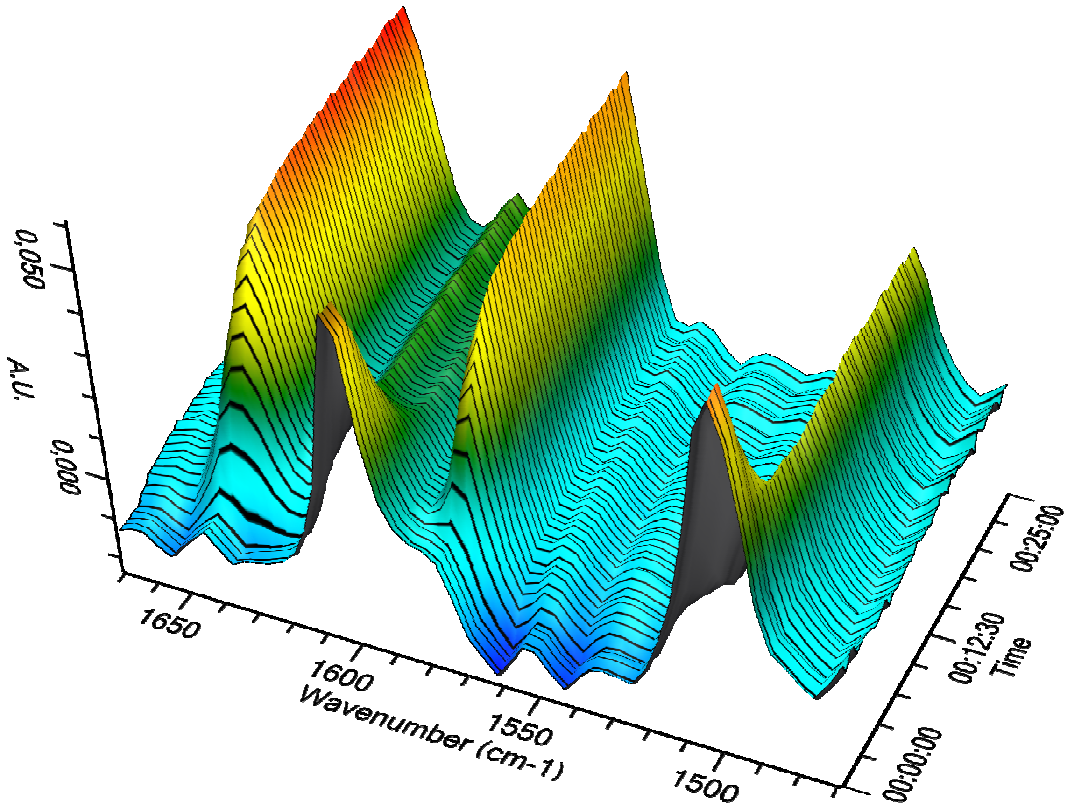
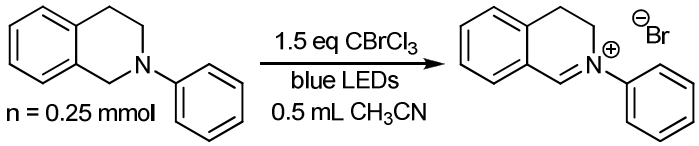


Figure S5: Reaction development over the time (3D-Plot)

3.12 Reaction Course as a Function of Light



Reaction was performed in the presence of 0.25 mmol of trichloroethylene as internal standard to allow for direct NMR yield determination.[6]

Table S6: Irradiation and results of the corresponding NMR measurements

0 min	no light	NMR yield determined (0%)
30 min	no light	NMR yield determined (17%)
	30 s irradiation with blue LEDs	
30 min 30 sec	no light	NMR yield determined (41%)
45 min 30 sec	no light	NMR yield determined (41%)
	1 min 30 s irradiation with blue LEDs	
47 min	no light	NMR yield determined (61%)
62 min	no light	NMR yield determined (62%)
	5 min irradiation with blue LEDs	
67 min	no light	NMR yield determined (73%)

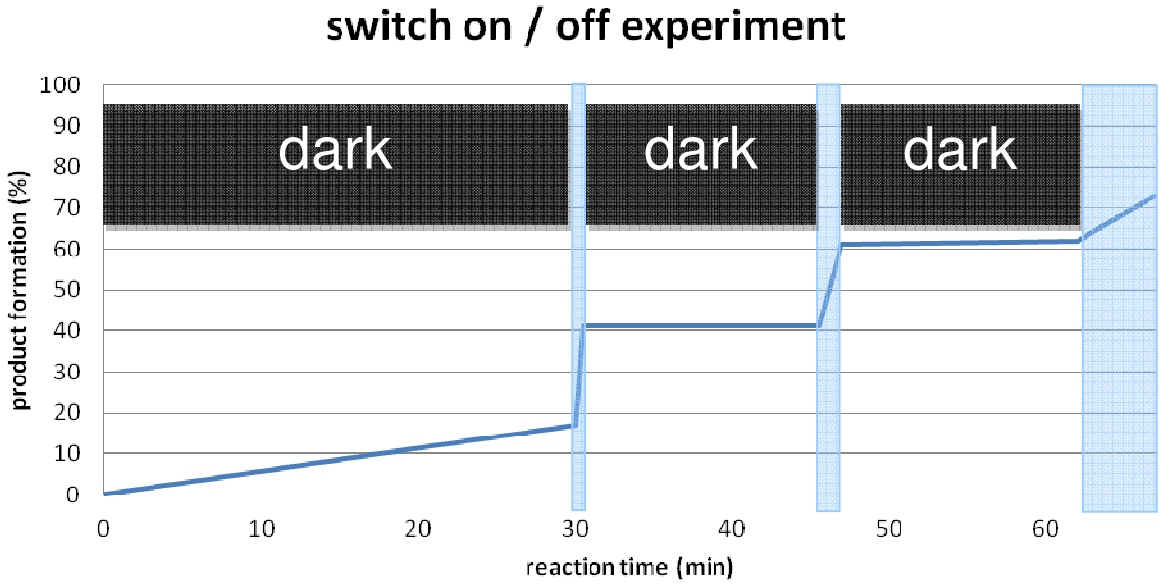


Figure S6: Reaction progress during periods of irradiation and darkness.

This experiment shows that, if a radical chain mechanism is operative, the corresponding chain might only be very short as only during irradiation periods significant reaction progress is observed.

[6] The alternative use of bromoform as NMR standard would require addition of the standard *after* irradiation which was not compatible with our reaction set-up, allowing for immediate NMR measurements.

To get a closer insight to the dark reaction at the beginning (first 30 min in the dark) we performed several experiments with no irradiation:

Reaction time	Yield
16 h (no light)	11%
24 h (no light)	12%
72 h (no light)	11%

3.12.1 UV/Vis Spectra of THIQ in the Presence of $CBrCl_3$

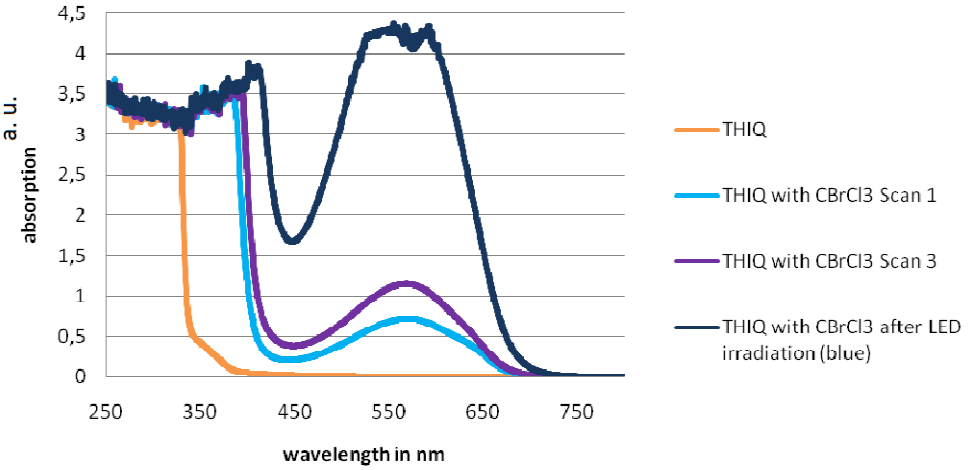


Figure S7: UV/Vis Spectra of pure THIQ and in the presence of $CBrCl_3$
scan 1 and *3*: light exposition only from spectrometer light for measurement
scan (blue): spectra after short irradiation with blue LEDs; formation of deeply blue colored solution (possibly charge-transfer complex formation).

3.13 UV–Filter

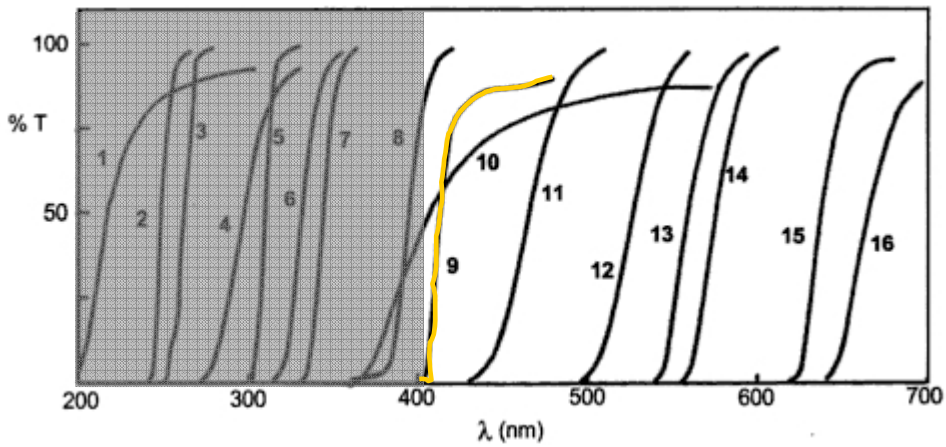


Figure S8: Comparison of commonly used cut-off filters with their wavelength profile.[7]

Number 9 shows the transmission curve of a $NaNO_2$ cut-off filter solution[7] (conc.: 75% w/v).
➔ light with $\lambda \leq 400$ nm is blocked

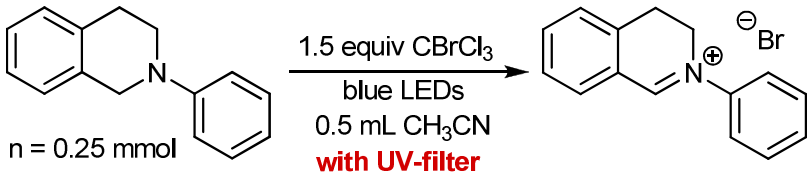
[7] Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. *Handbook of Photochemistry, 3rd Edition*, CRC Press, Boca Raton, **2006,** 596.

3.13.1 UV Filter Test

A Schlenk tube was equipped with a stripe of white office paper (containing an optical brightener). The upper half of the Schlenk tube was covered with aluminium foil to avoid fluorescence with scattered light. The left photography shows the strong fluorescence of the paper by irradiation with UV-light (366 nm) through pure water. The right picture shows the same experiment using a saturated solution of $NaNO_2$ as cut-off filter. No fluorescence can be detected which clearly illustrates the effectiveness of this cut-off filter.

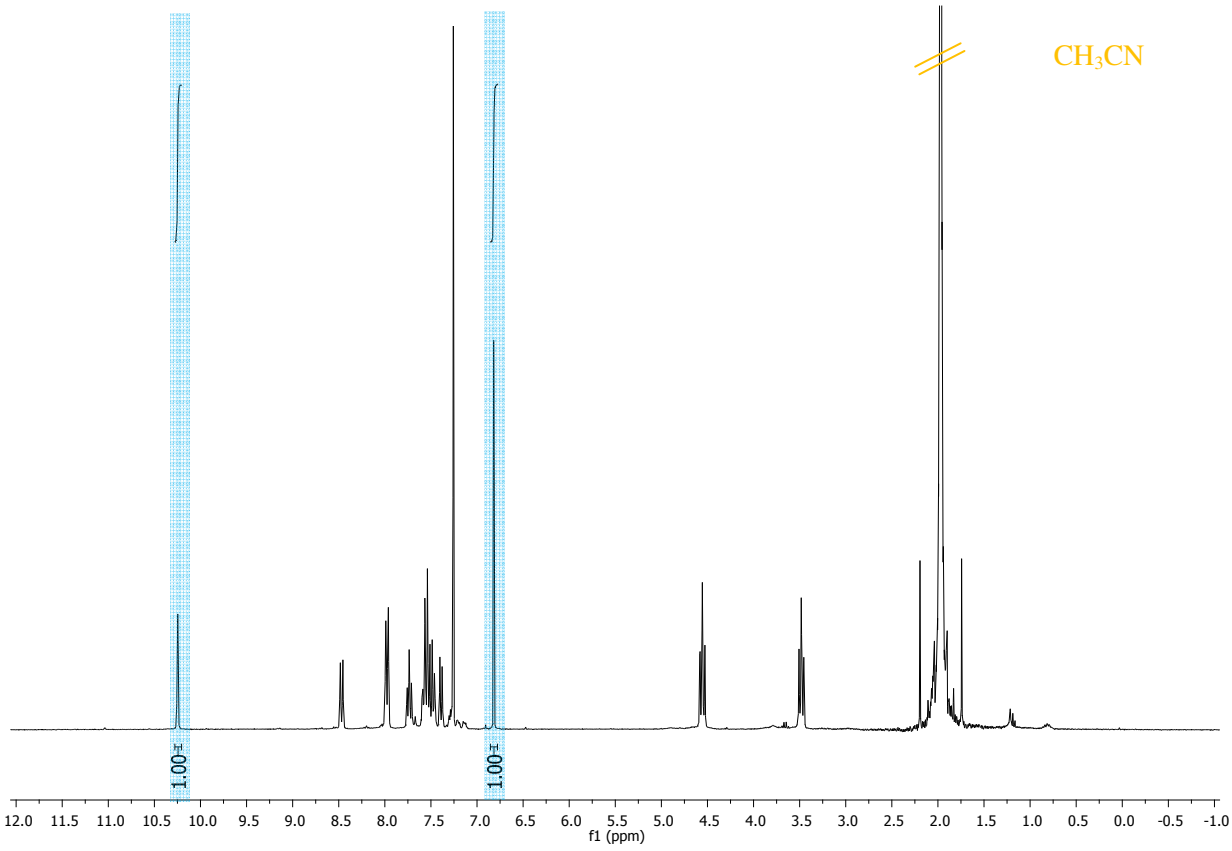
Figure S9: Comparison of white paper (with optical brightener) with irradiation (λ = 366 nm, TLC detection UV lamp used) through water (left side) or through a saturated solution of $NaNO_2$ as cut-off filter (< 400 nm).

3.13.2 Iminium Bromide Formation with UV-Filter



According to **general procedure C** but with additional UV filter:

Figure S10: Iminium formation with blue LED irradiation through a $NaNO_2$-cut-off filter (only $\lambda \geq 400$ nm).



$CHBr_3$ as internal standard (integral (δ 6.82: δ 10.25) = 1:1 = 100% yield)

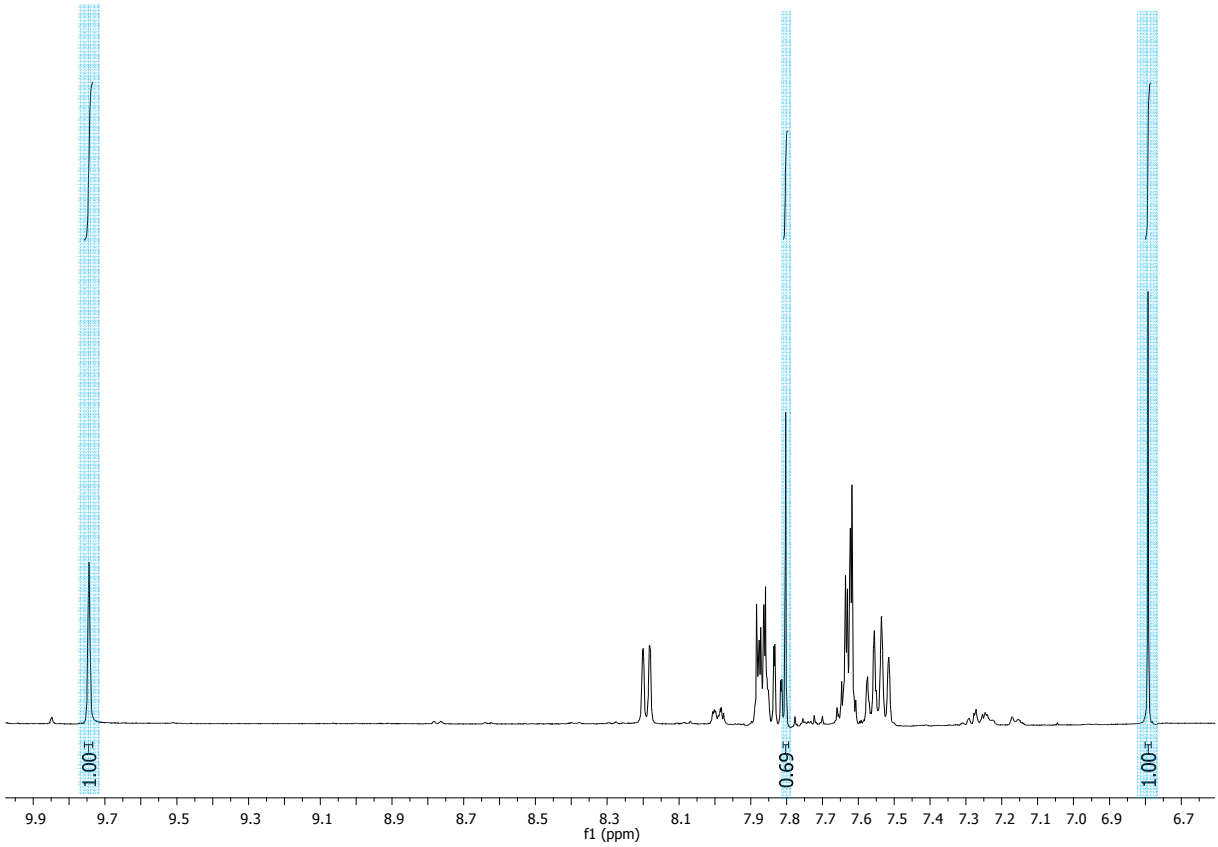
After weighted sample correction of internal standard → 100% yield

Figure S11: Crude NMR of iminium formation with UV cut-off filter (indicative signal at 10.25 ppm).

The crude NMR (figure S11) shows quantitative conversion in 30 min to the THIQ iminium bromide in the presence of the UV-filter. This clearly excludes any UV-light promoted pathway.

3.14 Chloroform Formation during the Reaction

For a closer insight into the reaction mechanism the proposed formation of $CHCl_3$ during the reaction was examined by performing of the reaction according to **general procedure C, but** with acetonitrile-d_3 as solvent (for an overview of the applicability of different solvents, see SI, CH3.3, table 2).



Trichloroethylene as internal standard (integral (δ 6.79 : δ 7.80 : δ 9.75) = 1:1:1 = 100% yield)

After weighted sample correction of internal standard → 100% yield (iminium), 69% yield ($CHCl_3$)

Identity of the shifted chloroform peak (@ 7.80 ppm) was confirmed via co-addition of $CHCl_3$ to the NMR tube after the first measurement; the signal increased considerably.

Figure S12: Crude NMR of iminium formation (9.75 ppm) in CD_3CN as solvent showing $CHCl_3$ formation during the visible light promoted reaction with $CBrCl_3$.

The formation of significant amounts of chloroform (see provides additional evidence for the (dual) role of $CBrCl_3$ according to our proposed reaction mechanism (initial activation, CCl_3• as hydrogen atom acceptor).

3.15 Iodine-Starch Test

The oxidative power of $CBrCl_3$ under visible irradiation was examined using the iodine starch test reaction.

Conditions:
Preparation of the KI-solution (1 molar):
1.66 g potassium iodide was dissolved in 10 mL distilled water.

Preparation of the starch solution:
1 g of soluble starch was suspended in 50 mL distilled water. The suspension was shortly heated to 100 °C, followed by hot filtration.

According to tables S7A- S7C 1 mL of the solvent (water *or* KI solution) was mixed as stated with $CBrCl_3$ in a test tube. The mixture was then irradiated with blue LEDs *or* stored in the dark for the time indicated. Subsequently, the respective additives were added to the reaction mixture (according to tables S7A-S7C). Finally, three drops taken out of each of these prepared mixtures were added to 0.2 mL of the starch solution and the potential change in color was observed (change to blue: positive result ✓).

Table S7A: Overview of experiments without light

	solvent (1 mL)	**$CBrCl_3$ (38 µL)**	**light**	**reaction time**	**additive**	**result**
1	H_2O	yes	no	5 min	I_2	✓
2	H_2O	no	no	5 min	Br_2	×
3	KI-solution	yes	no	5 min	-	×
4	KI + starch solution	yes	no	5 min	-	×
5	KI-solution	no	no	5 min	Br_2	×

Without light only entry 1 with iodine as additive showed a positive result. Potassium iodide solution with $CBrCl_3$ led to negative test results in the dark. Bromine alone or even in the presence of potassium iodide solution also provided negative results. Although Bromine should be able to oxidize iodide to iodine, no positive result was observed, as potentially an excess of bromine (table S7A, entry 5) seems to destroy the iodine starch complex (see also table S7B, entry 12).

Table S7B illustrates that potassium iodide solution, $CBrCl_3$ **and** light are essential to get positive test results (entry 6, 8 and 11). All other combinations showed negative iodine starch test results. Entry 12 should be positive, but as mentioned before (and demonstrated in the "blind" test without light, see table S7A, entry 5) bromine seems to destroy the iodine starch complex.

Table S7B: Overview of experiments with light

	solvent (1 mL)	$CBrCl_3$ (38 µL)	light	reaction time	additive	result
6	KI-solution	yes	yes	5 min	-	✓
7	KI-solution	no	yes	5 min	-	×
8	-	yes	yes	5 min	then KI	✓*
9	-	yes	yes	5 min	-	×
10	H_2O	yes	yes	5 min	-	×
11	KI-solution	yes	yes	5 min	I_2	✓
12	KI-solution	yes	yes	5 min	Br_2 vapor	×

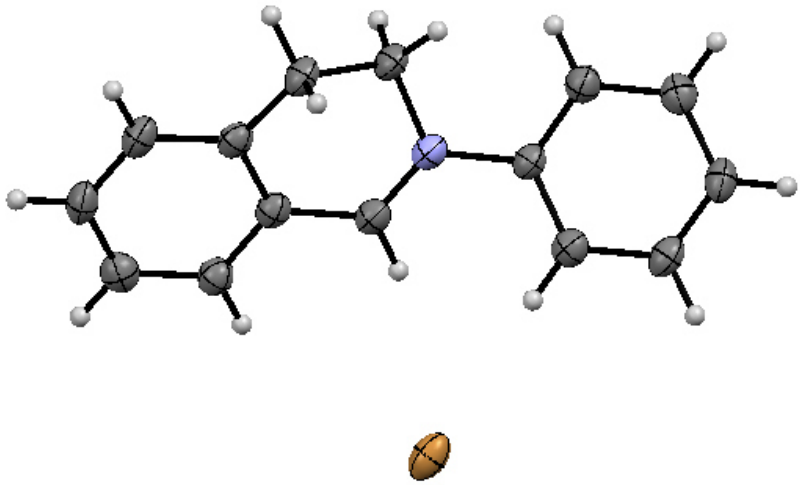
* Slightly bluish after drop addition of starch solution, after shaking slightly orange.

Even extended reaction time in the dark did not lead to a positive result (table S7C, entry 13); this indicates that the involvement of a significant background reaction without light can be excluded. To further prove that all reagents are stable after in the dark without altering their reactivity, half of the solution out of entry 13 was then illuminated with blue light for 5 min (table S7C, entry 14) to show the expected positive result.

Table S7C: Combined experiments

	solvent (1 mL)	$CBrCl_3$ (38 µL)	light	reaction time	additive	result
13	KI-solution	yes	no	30 min	-	×
14	**rxn 13** divided in 2 parts after 30 min stirring in dark, then 5 min hv **@14**					✓

3.16 X-ray Structure of THIQ Iminium Bromide 2[8]



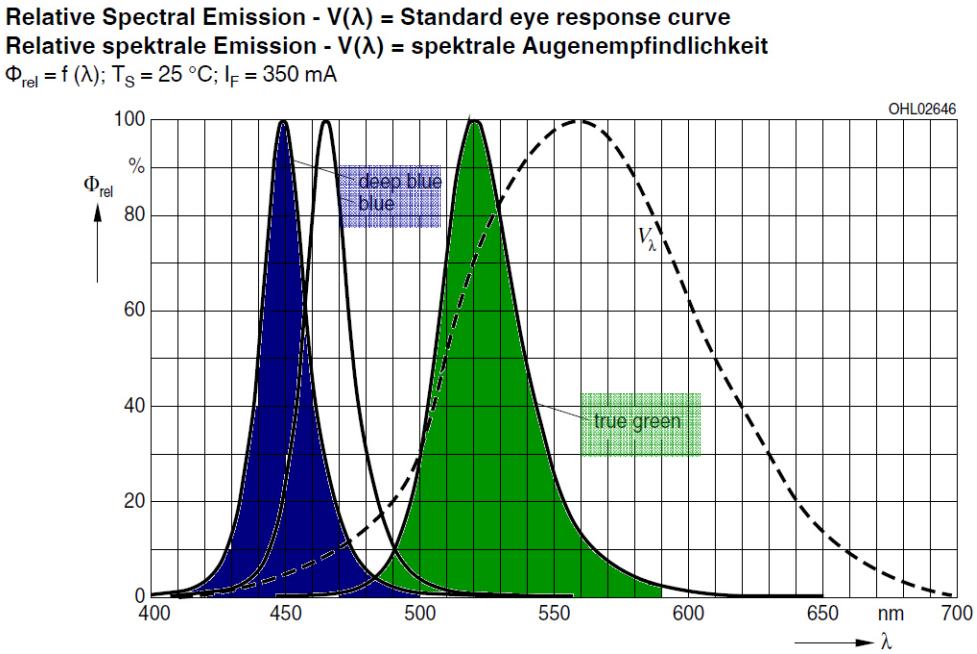
CRYSTAL DATA

Reference Code JFF_110 // K099; 11/2011; measurement temperature 293 (2) K; $\lambda = 1.54184$ Å; cell setting: orthorhombic; space group P bca; a = 19.3180 (5) Å $\alpha = 90.00$ (5)° b = 7.1849 (2) Å $\beta = 90.00$ (3)° c = 19.6634 (5) Å $\gamma = 90.00$ (4)°; V = 22729.22 (11) Å^3; Z = 8; $\rho_{cal.}$ 1.403 Mg/m^3; absorption coefficient 3.908 mm^{-1}; F(000) 1168; crystal size: .13 x .07 x .04 mm; $\vartheta = 4.50°$ to 75.38°; $-23 \leq h \leq 22$, $-8 \leq k \leq 9$, $-24 \leq l \leq 18$; total number of measured reflections 9376; number of unique reflections 2769 [R(int) = 0.0284]; absorption correction; max. and min. transmissions 0.700 and 0.852; Goodness-of-fit based on F^2 1.104; refined parameters [$I>2\sigma(I)$] $R^1 = 0.0440$, $wR^2 = 0.1266$; R^1 (all data) = 0.0477, wR^2 (all data) = 0.1307; difference in electron density 0.088 eÅ^{-3}.

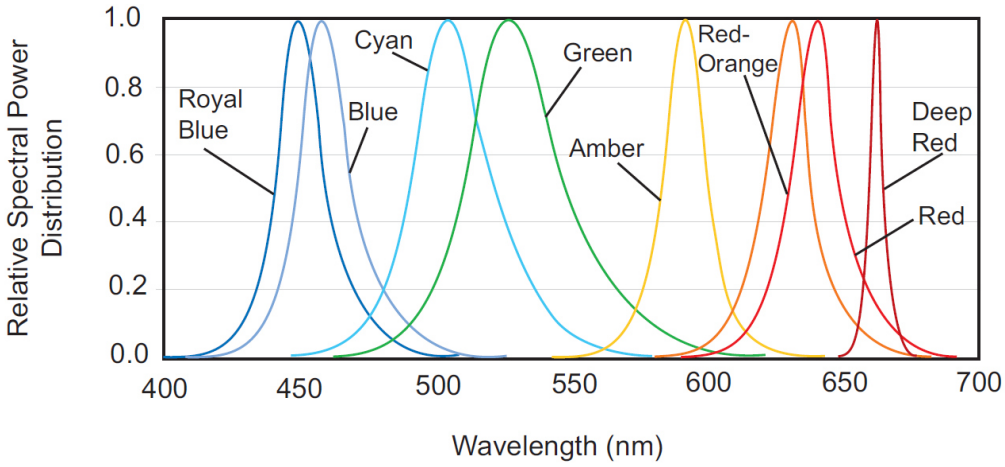
[8] CCDC 993641 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

3.17 Emission Characteristics of Used LEDs

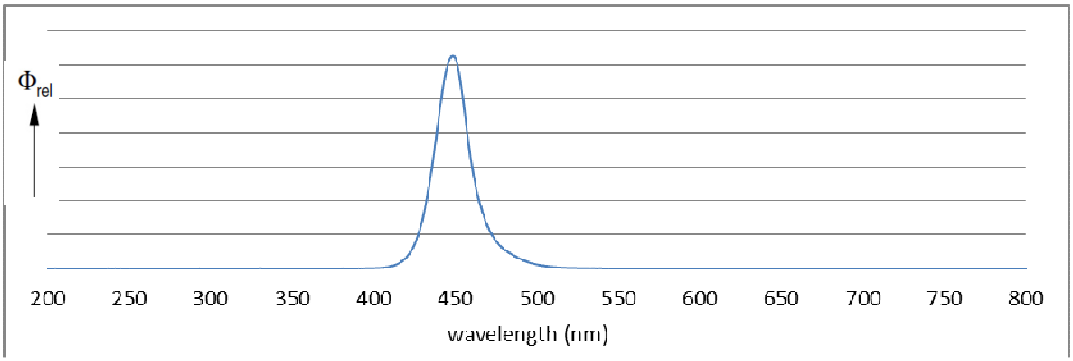
OSRAM Oslon Technical Datasheet:



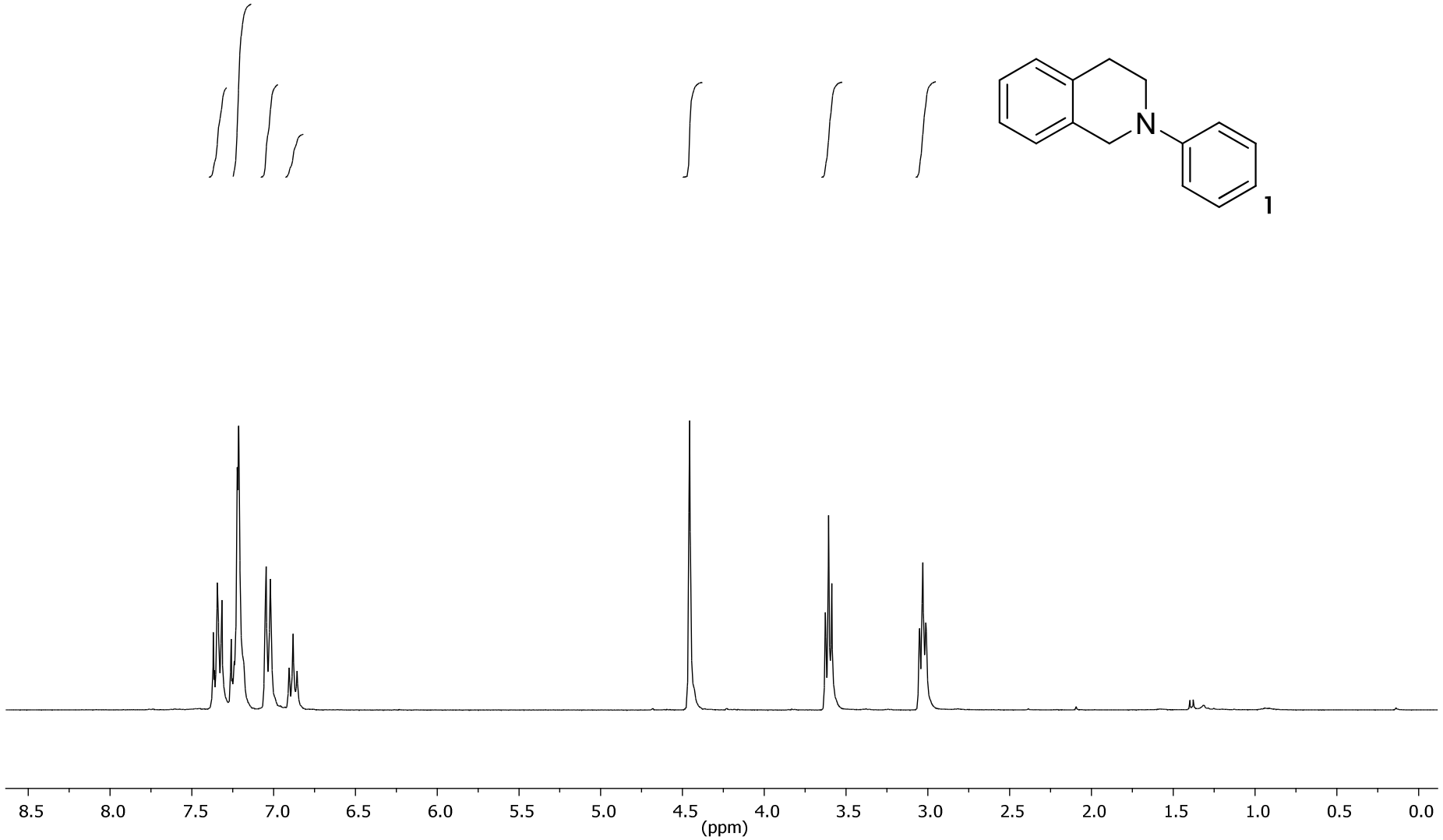
Philips Luxeon Technical Datasheet:

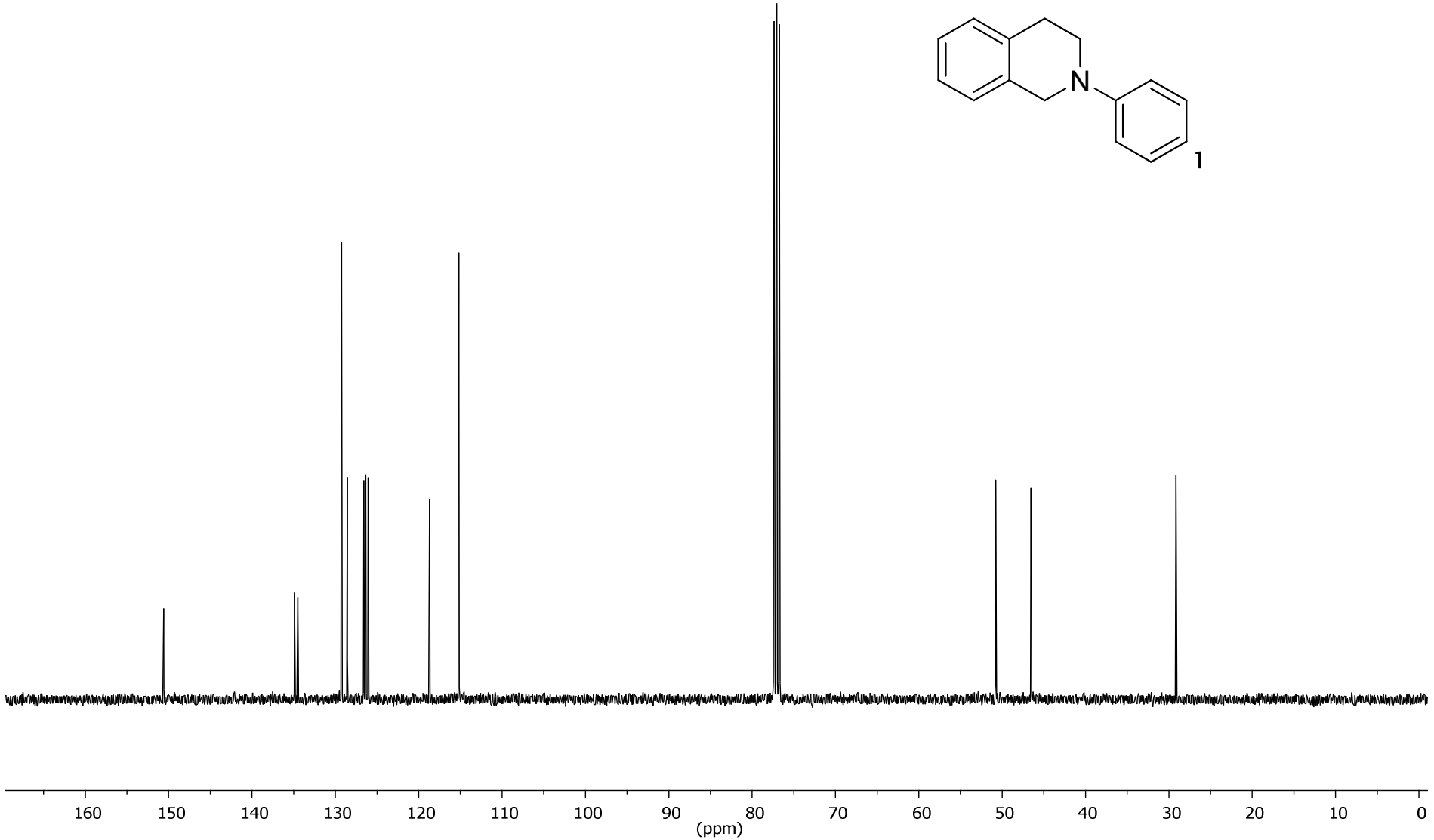


Qualitative Emission Spectra of OSRAM Olson Deep Blue (recorded with an AVASPEC-3648 fiber optic spectrometer, Avantes)



4 NMR Spectra of Substrates and Products

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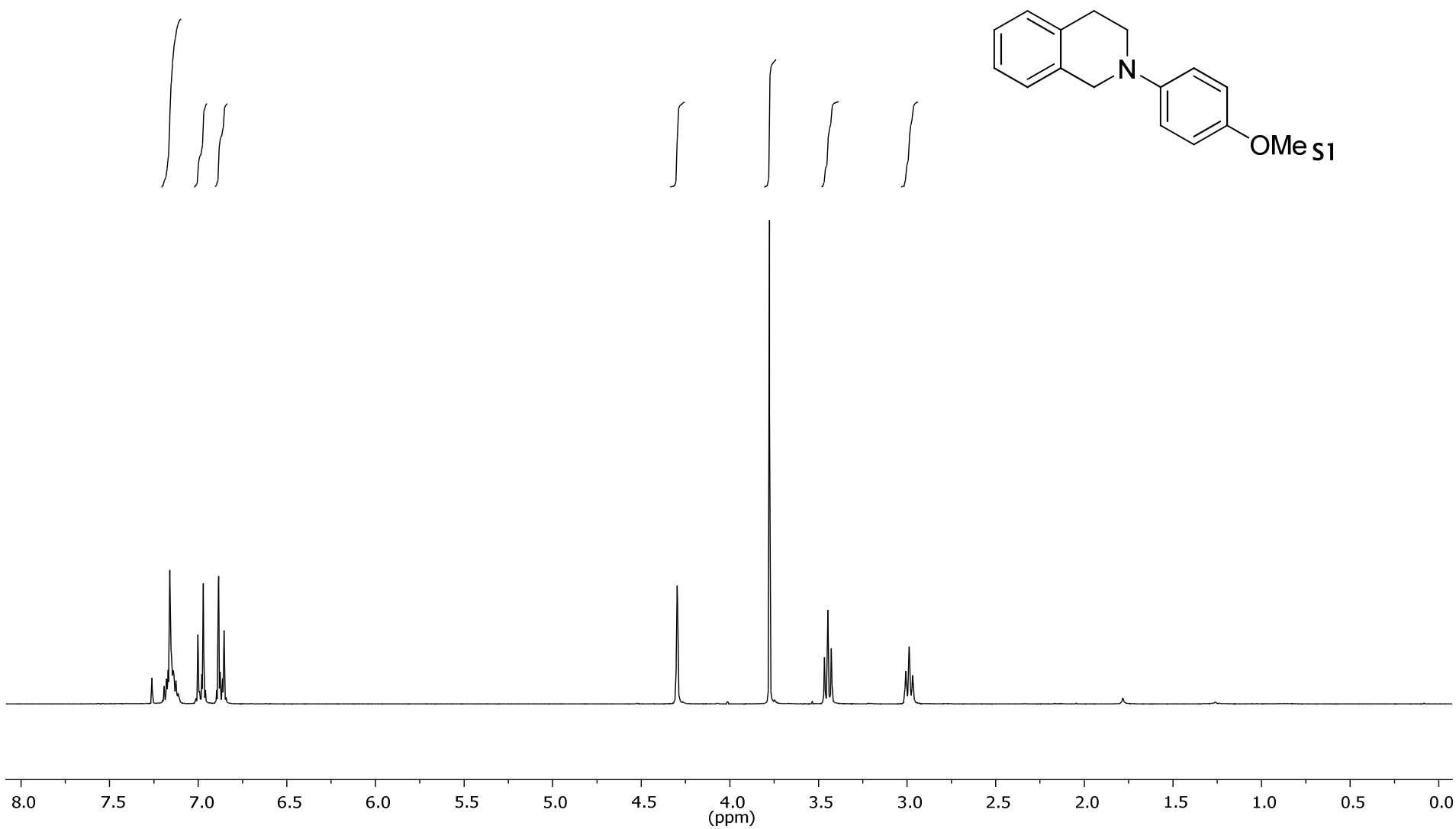
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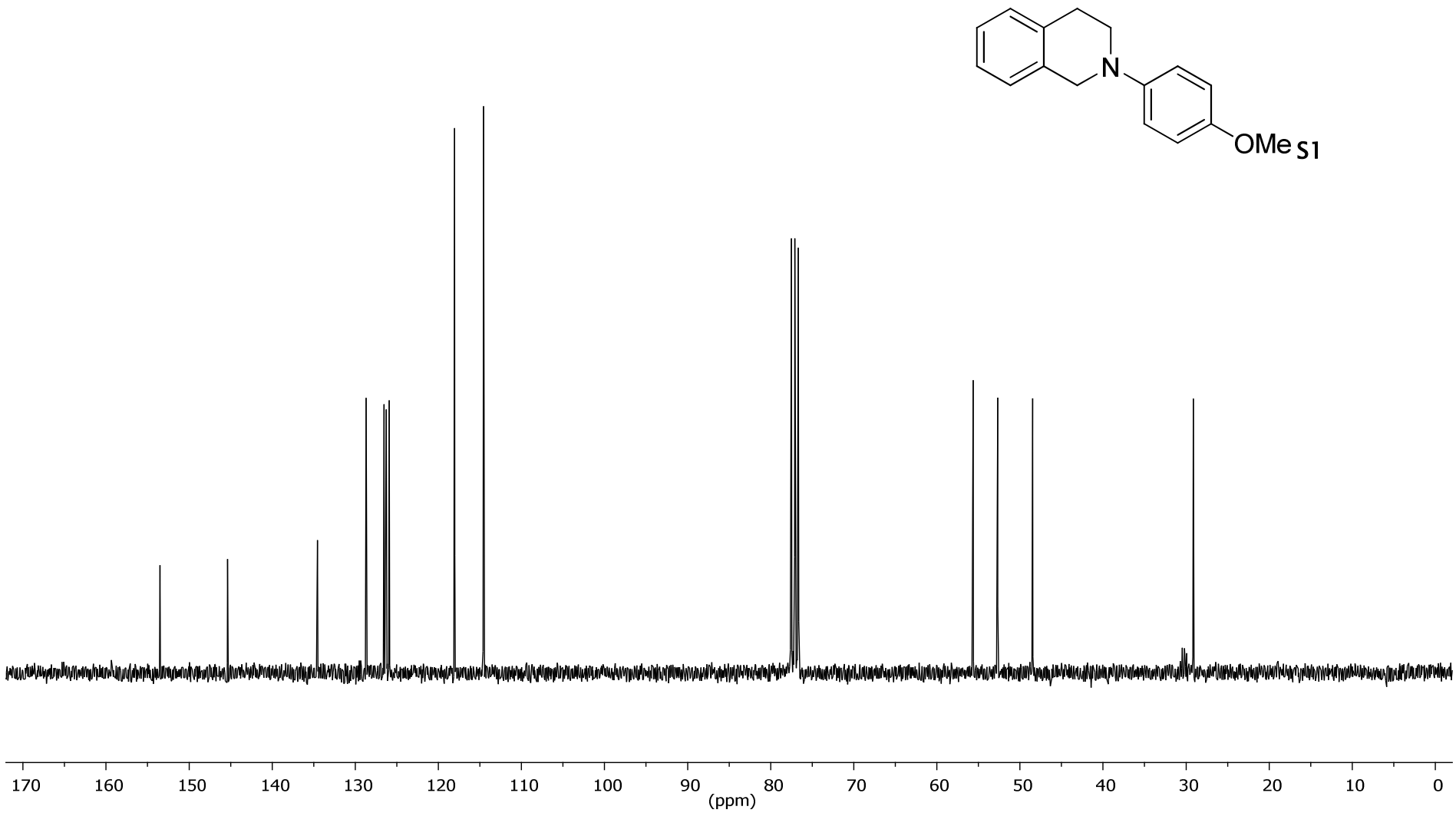
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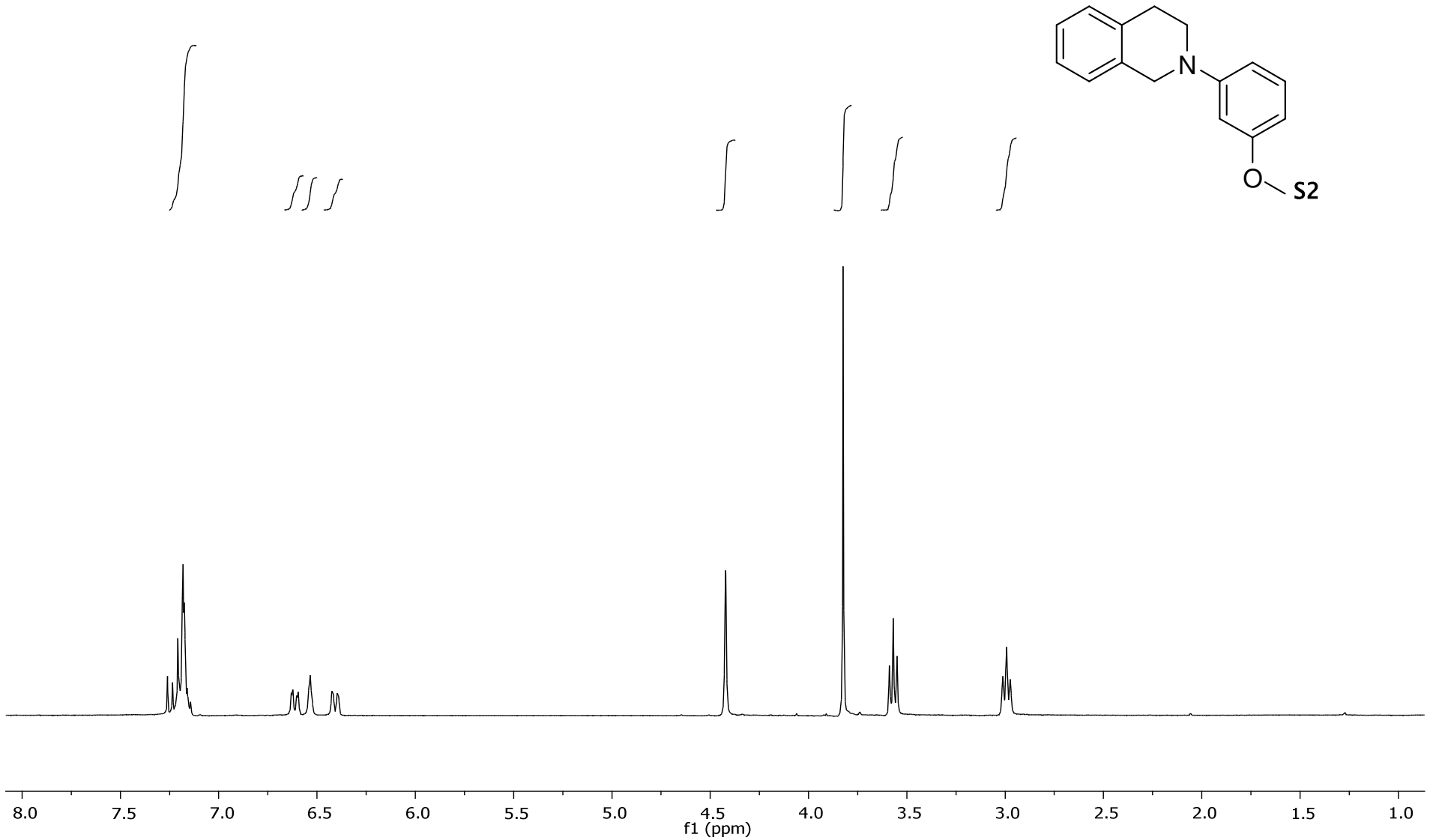
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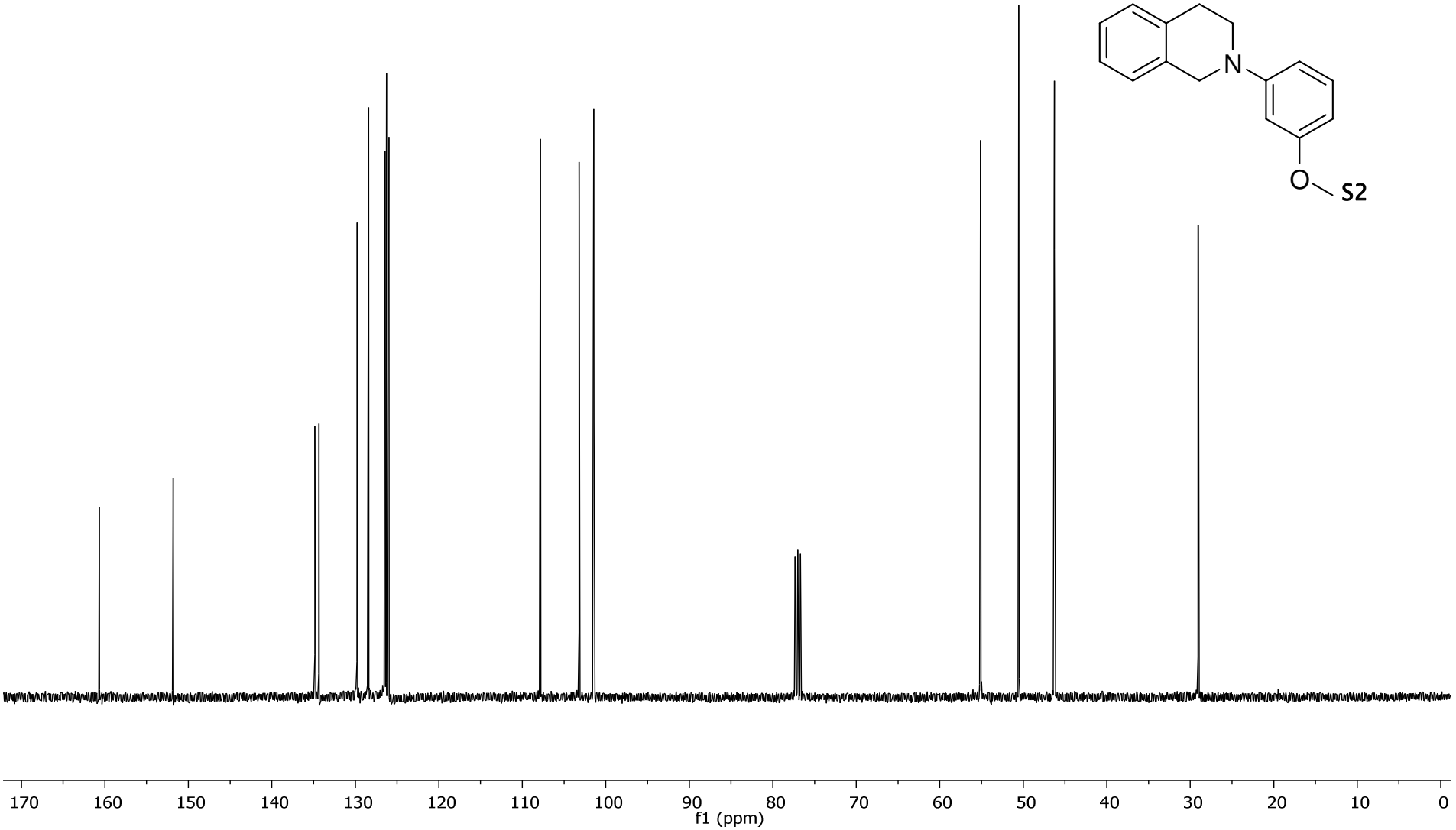
f1 (ppm)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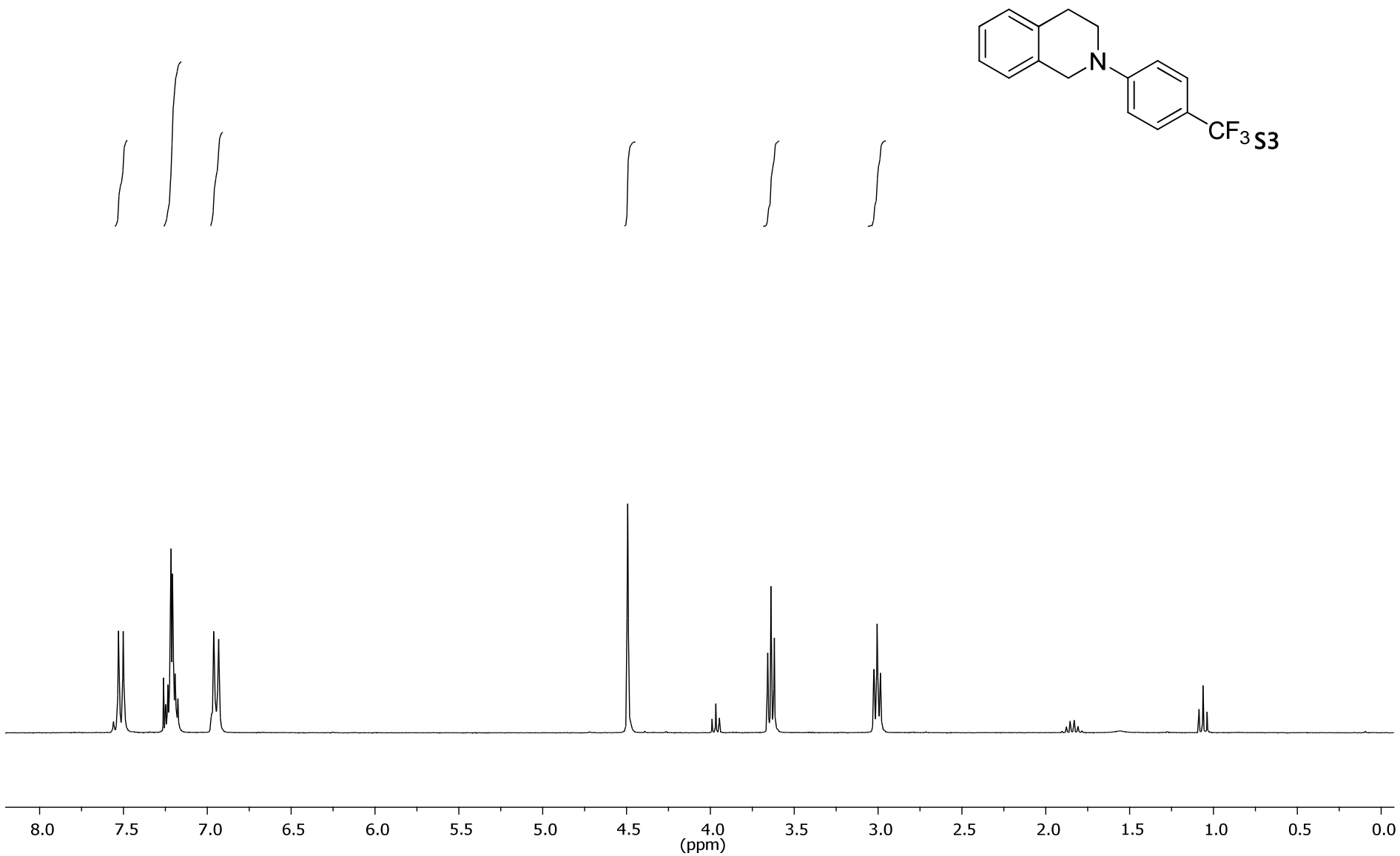
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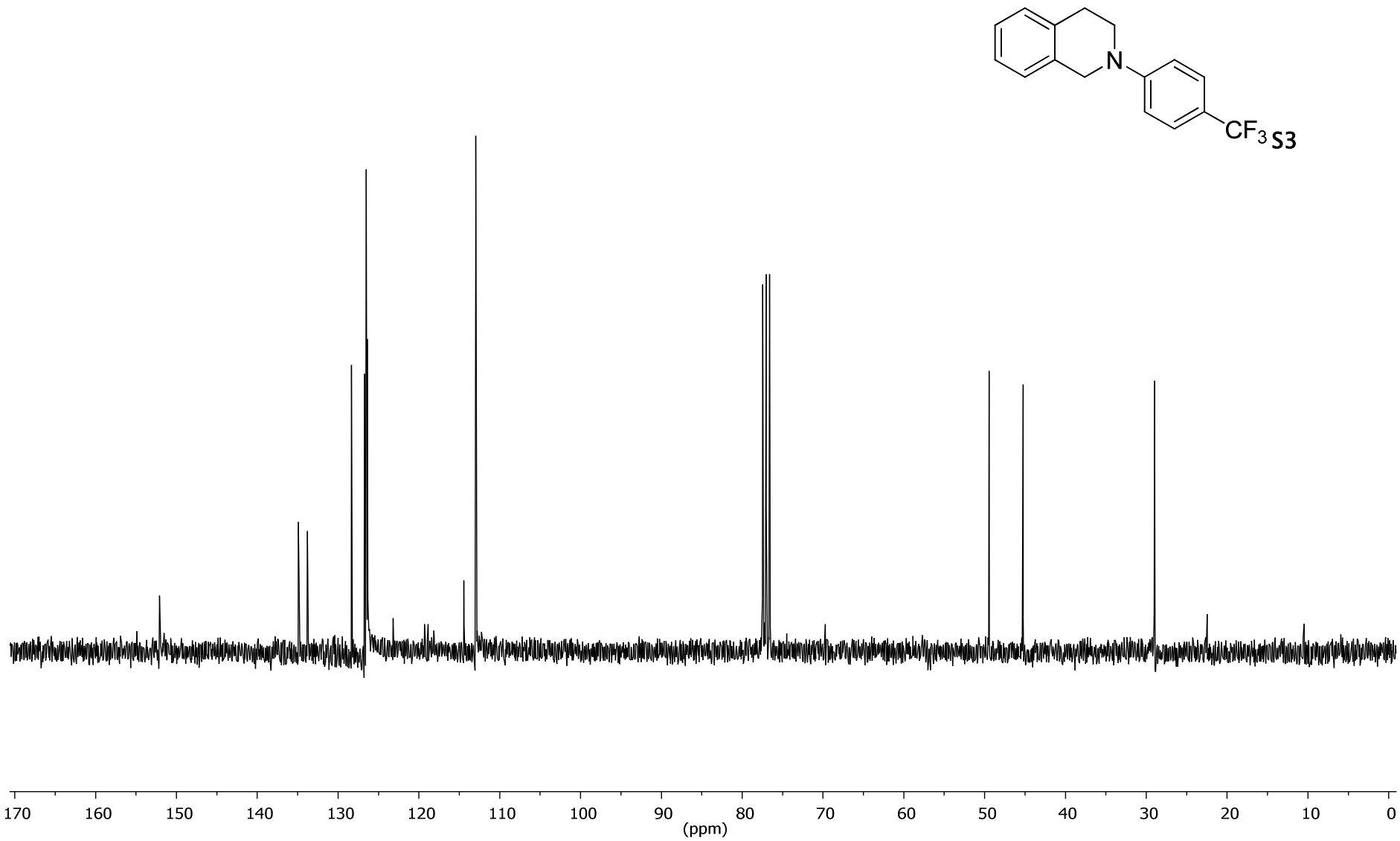
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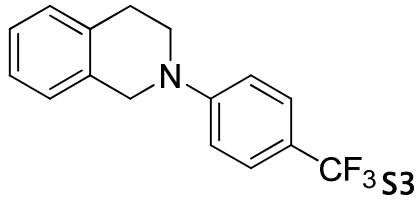
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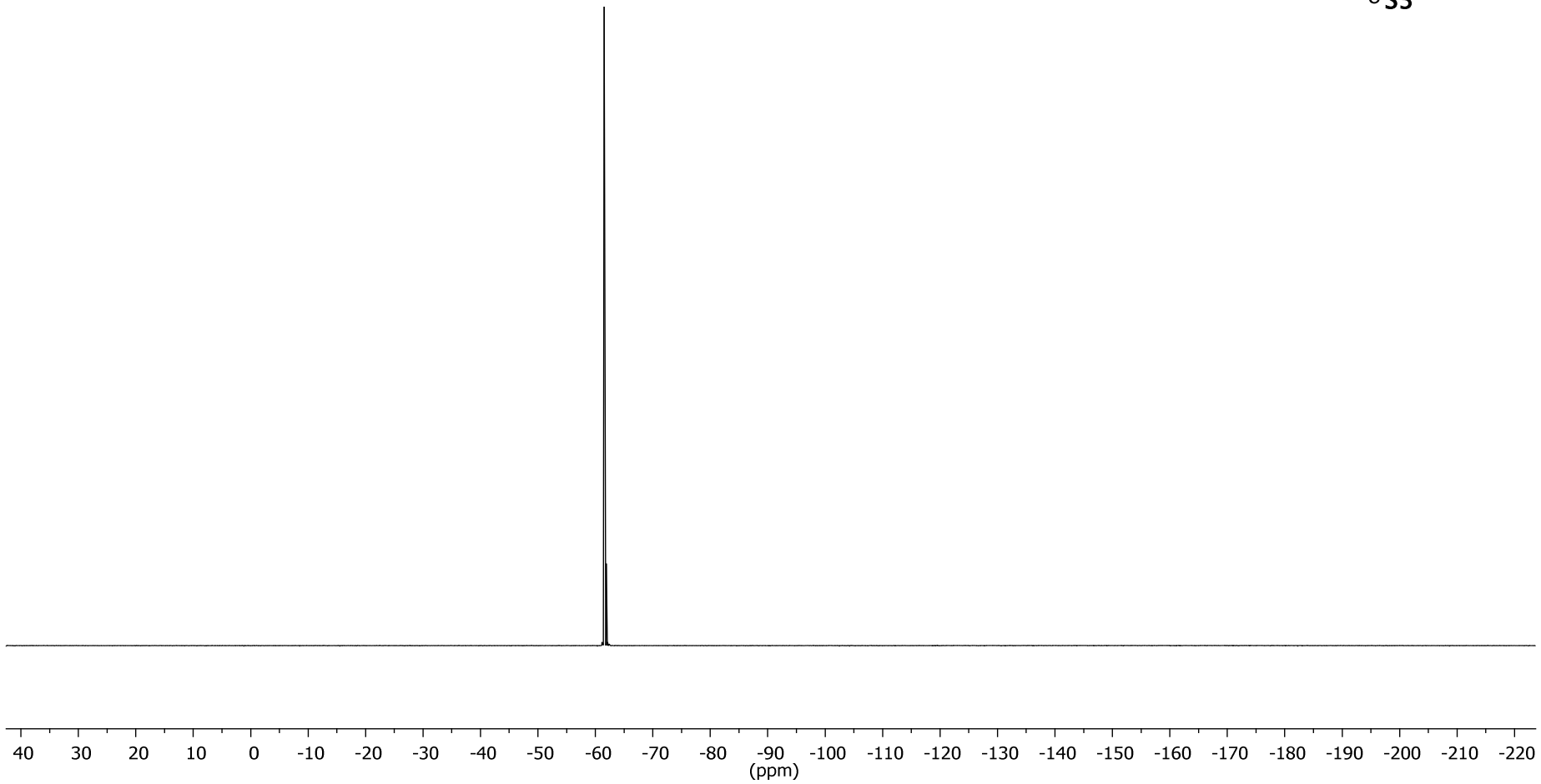
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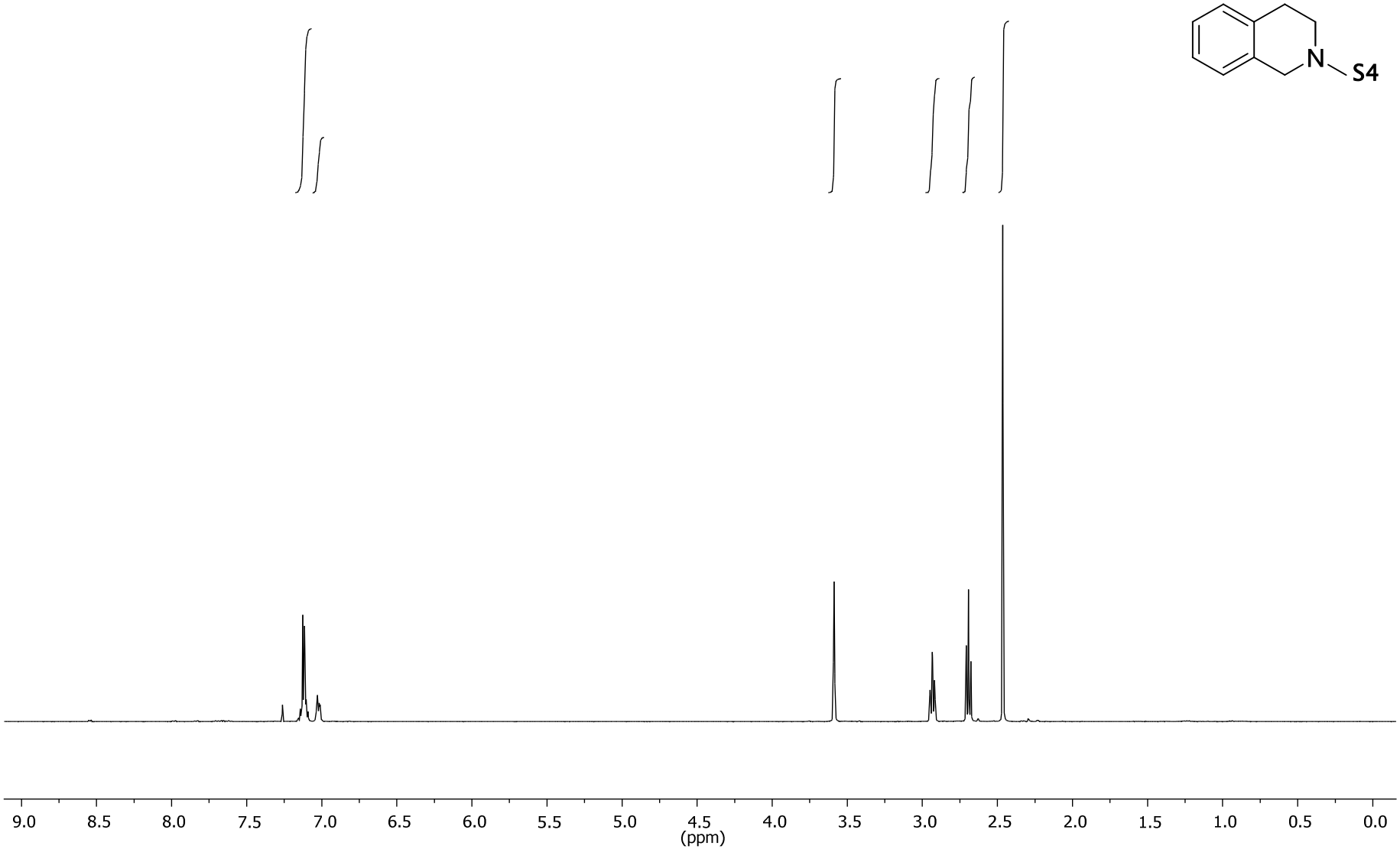
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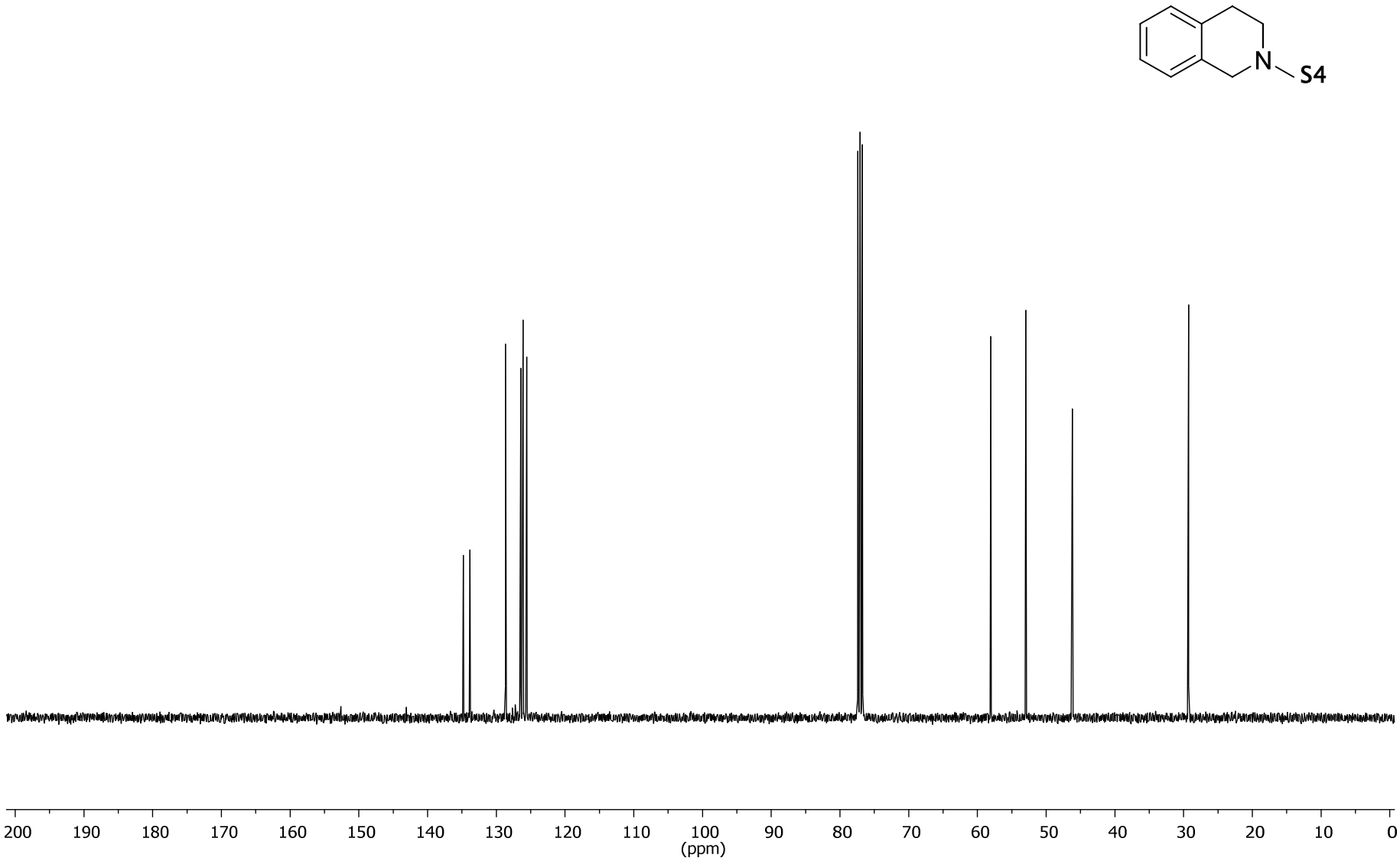
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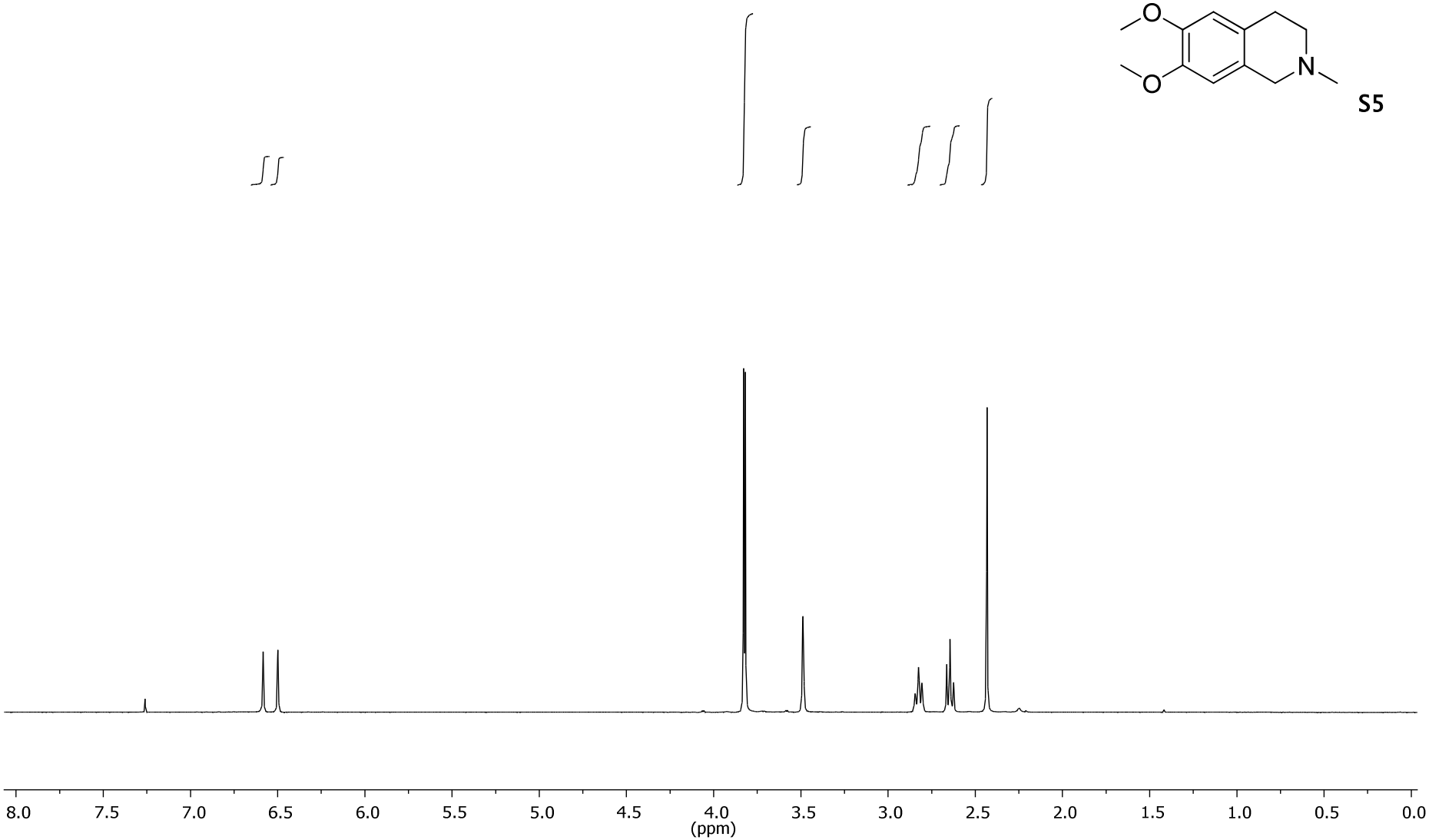
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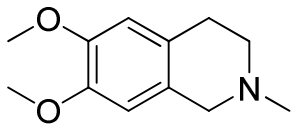
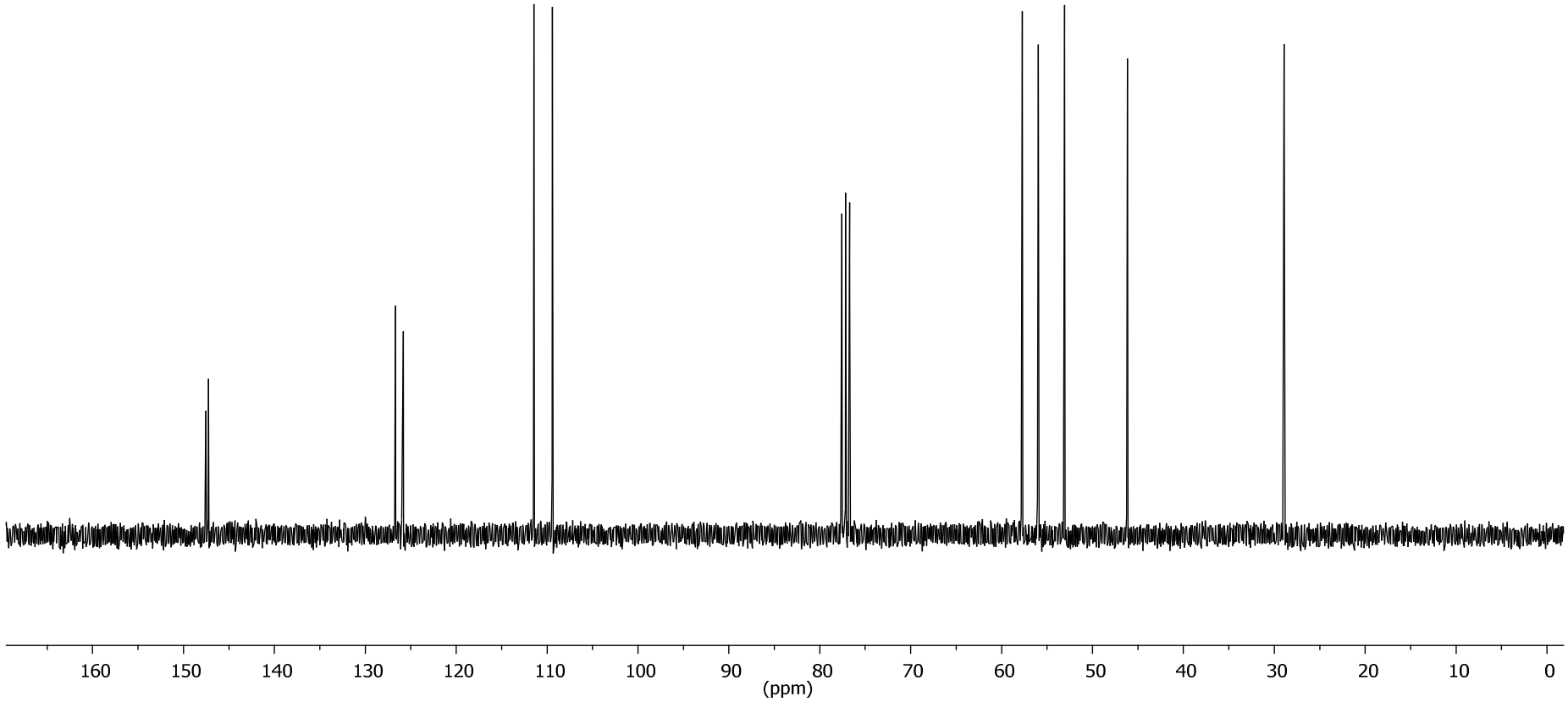
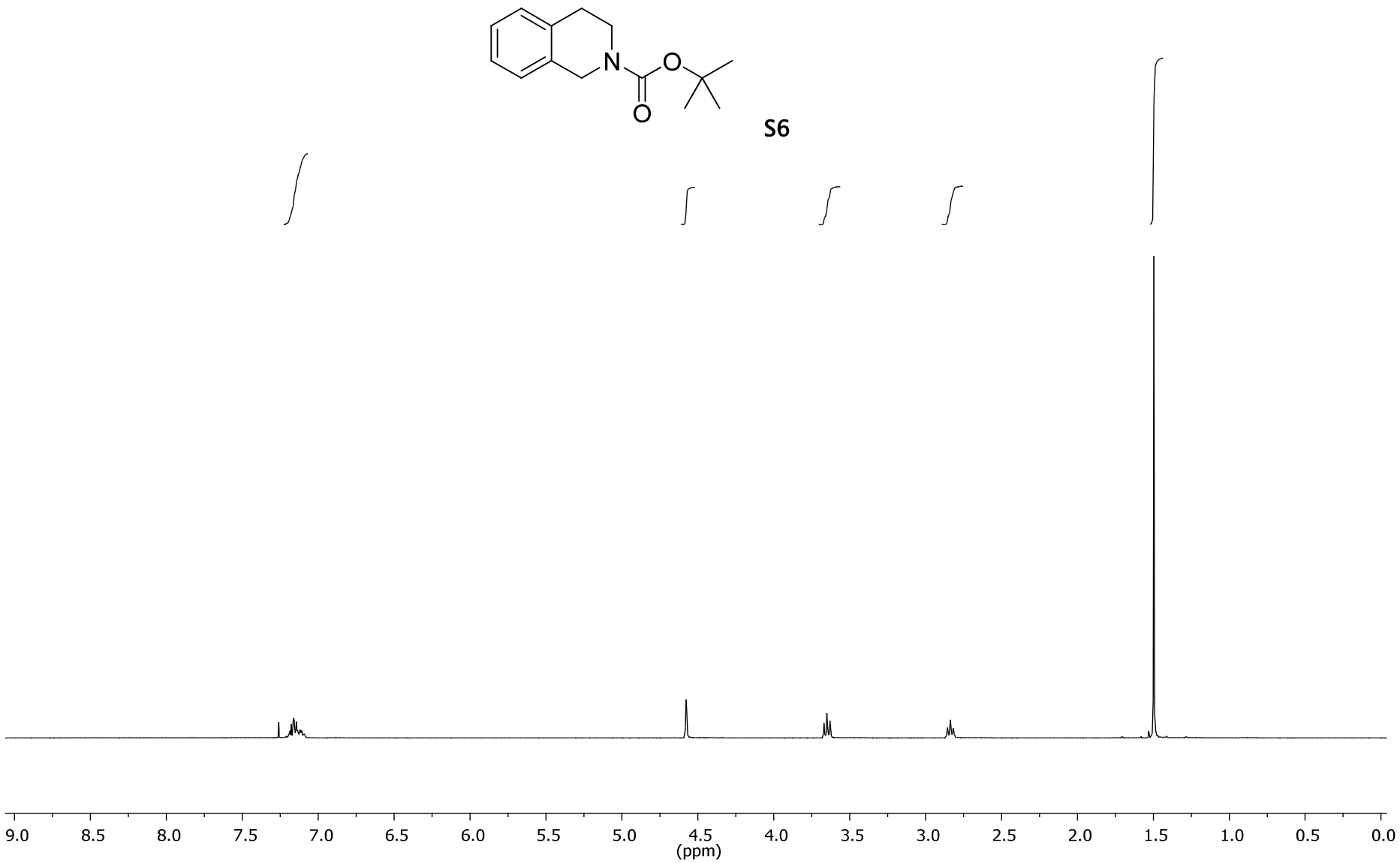
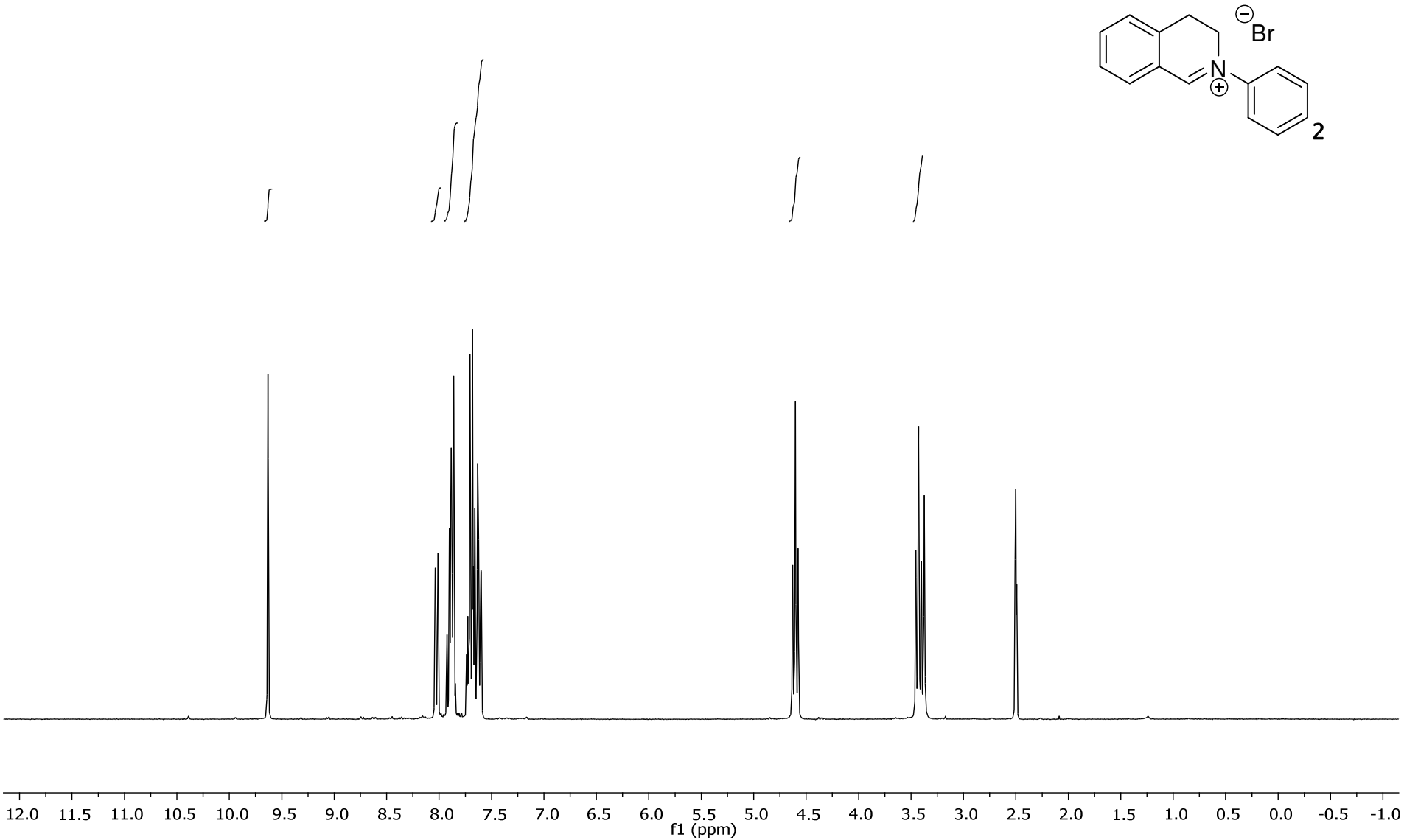
0.0
(ppm)

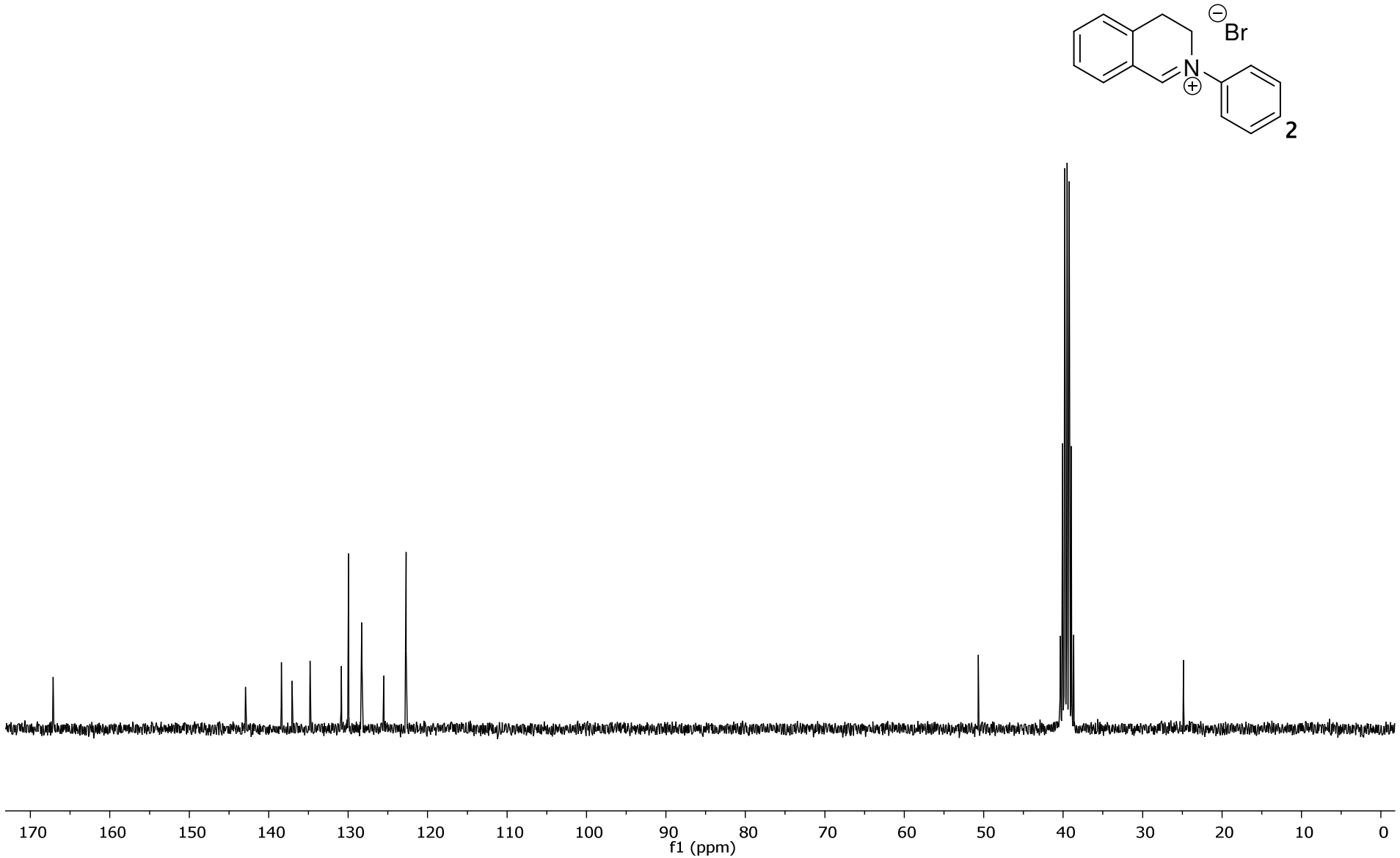


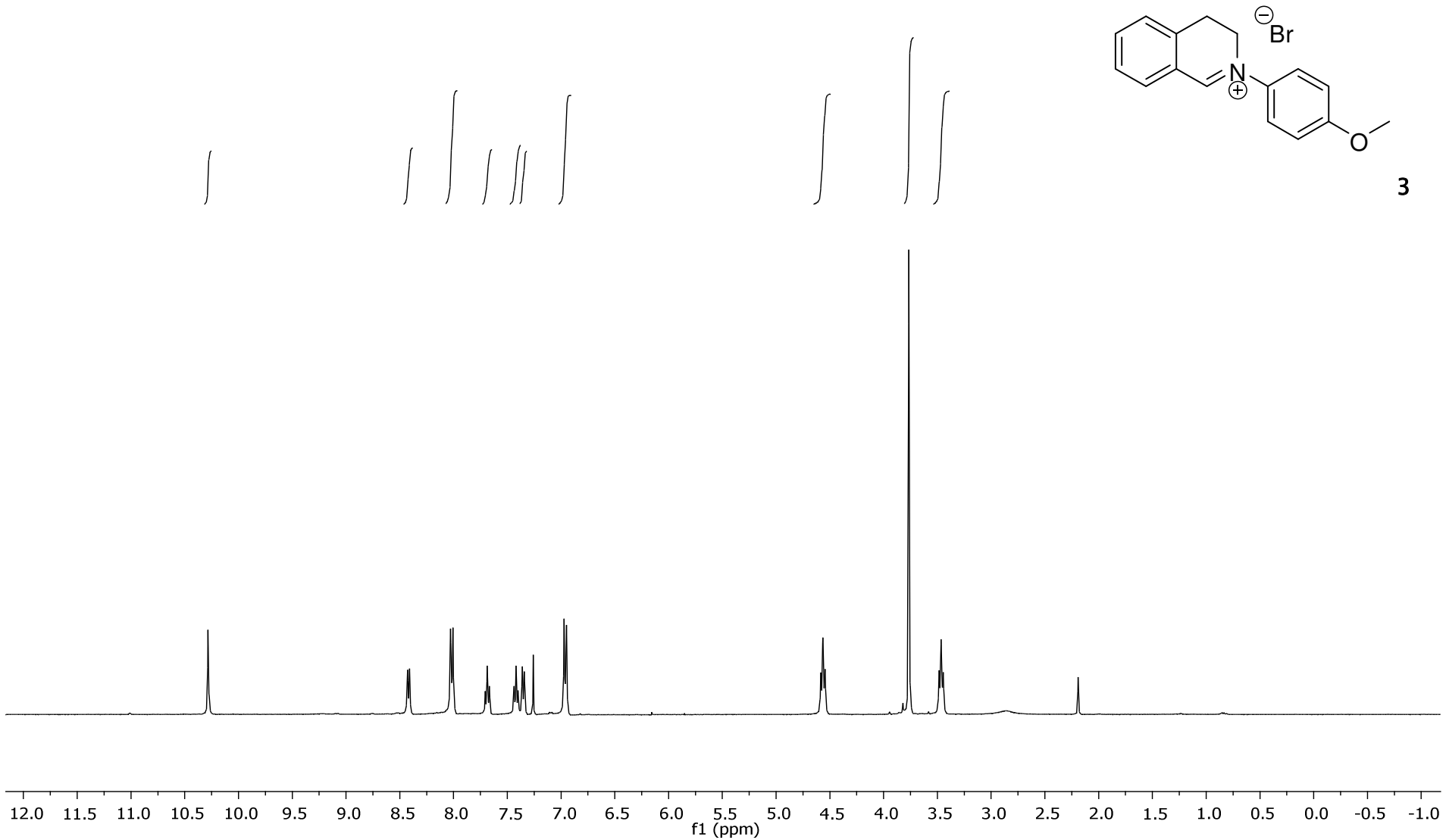
S5

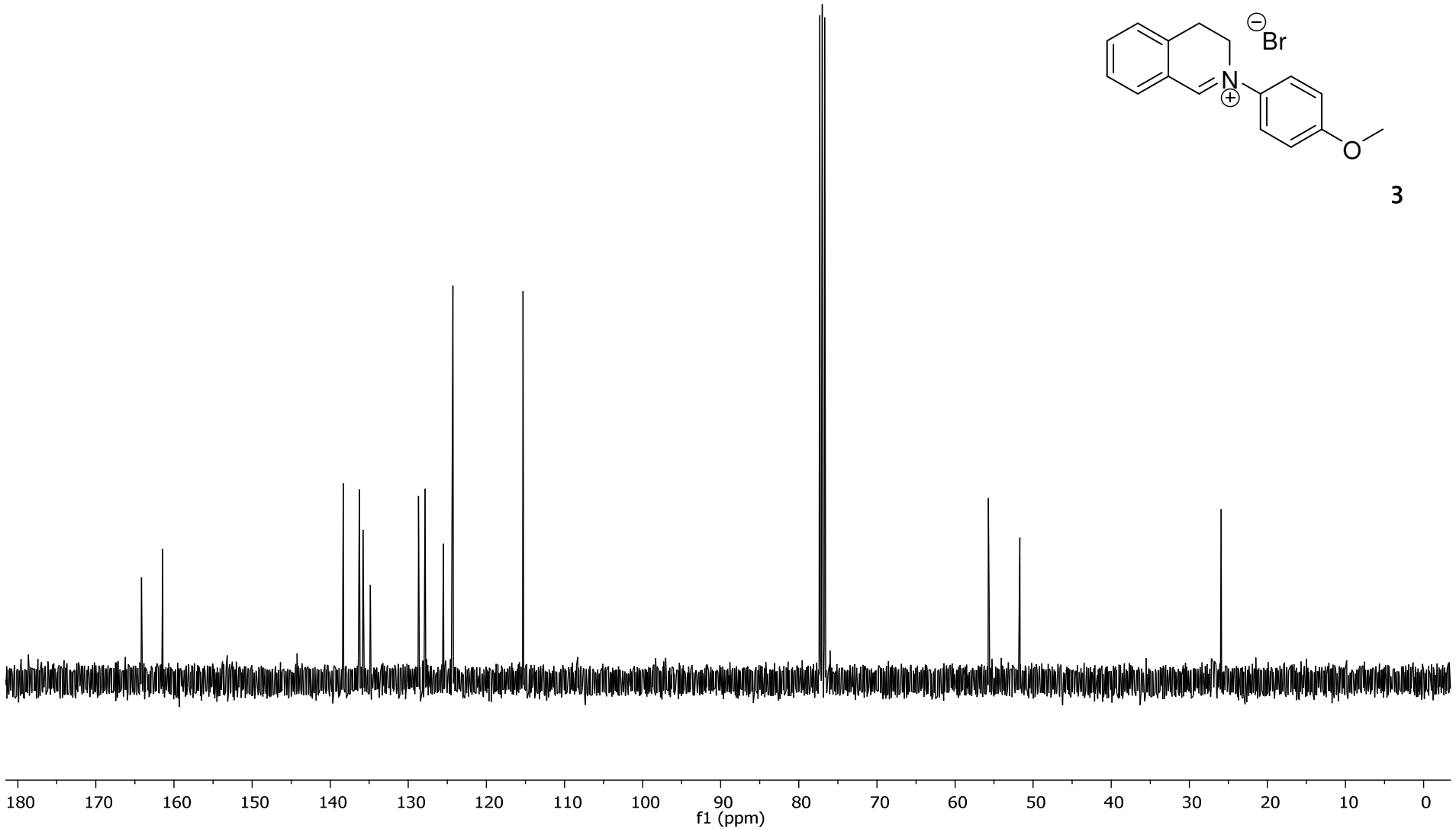


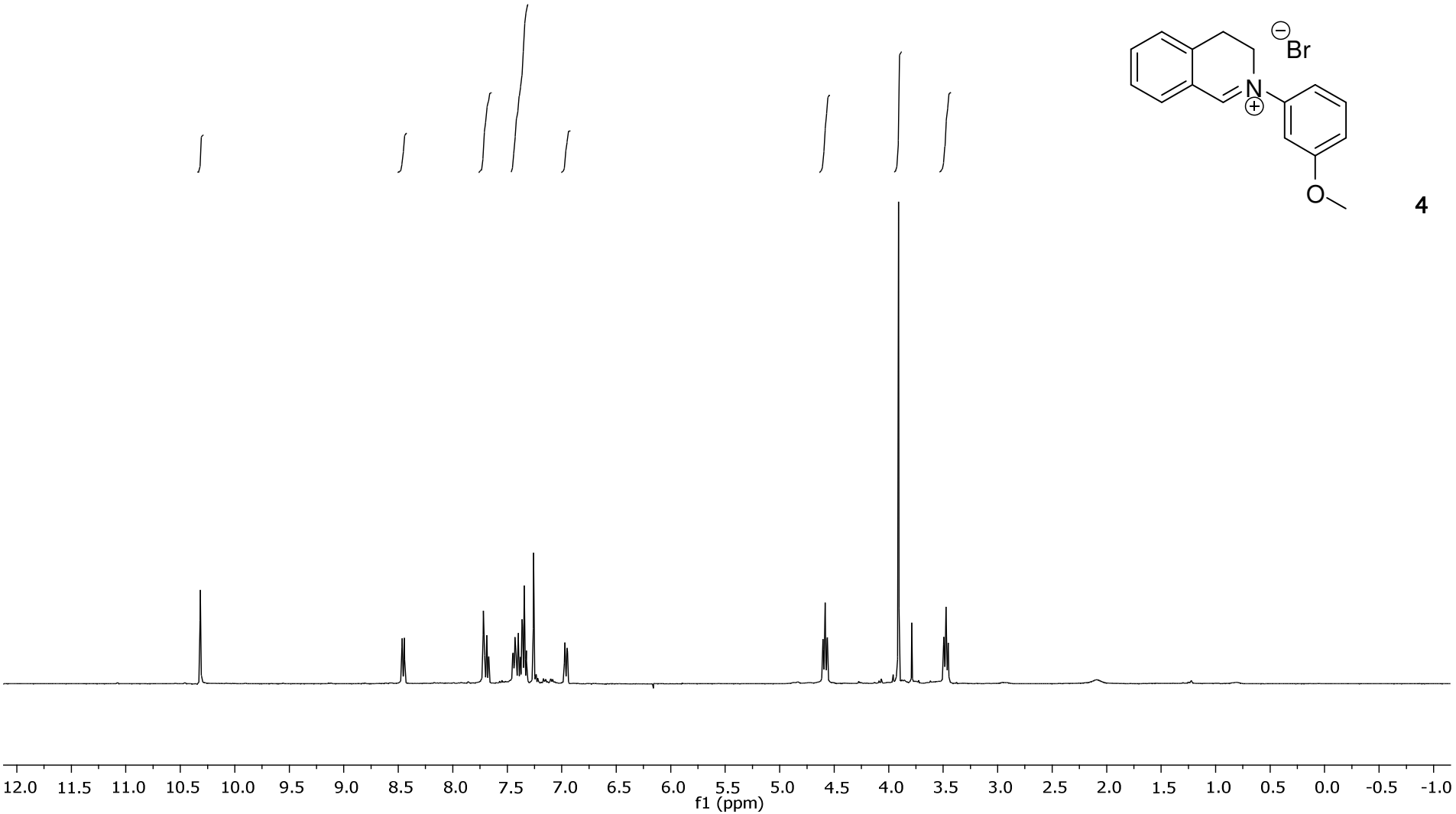

N
O
O
S6
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

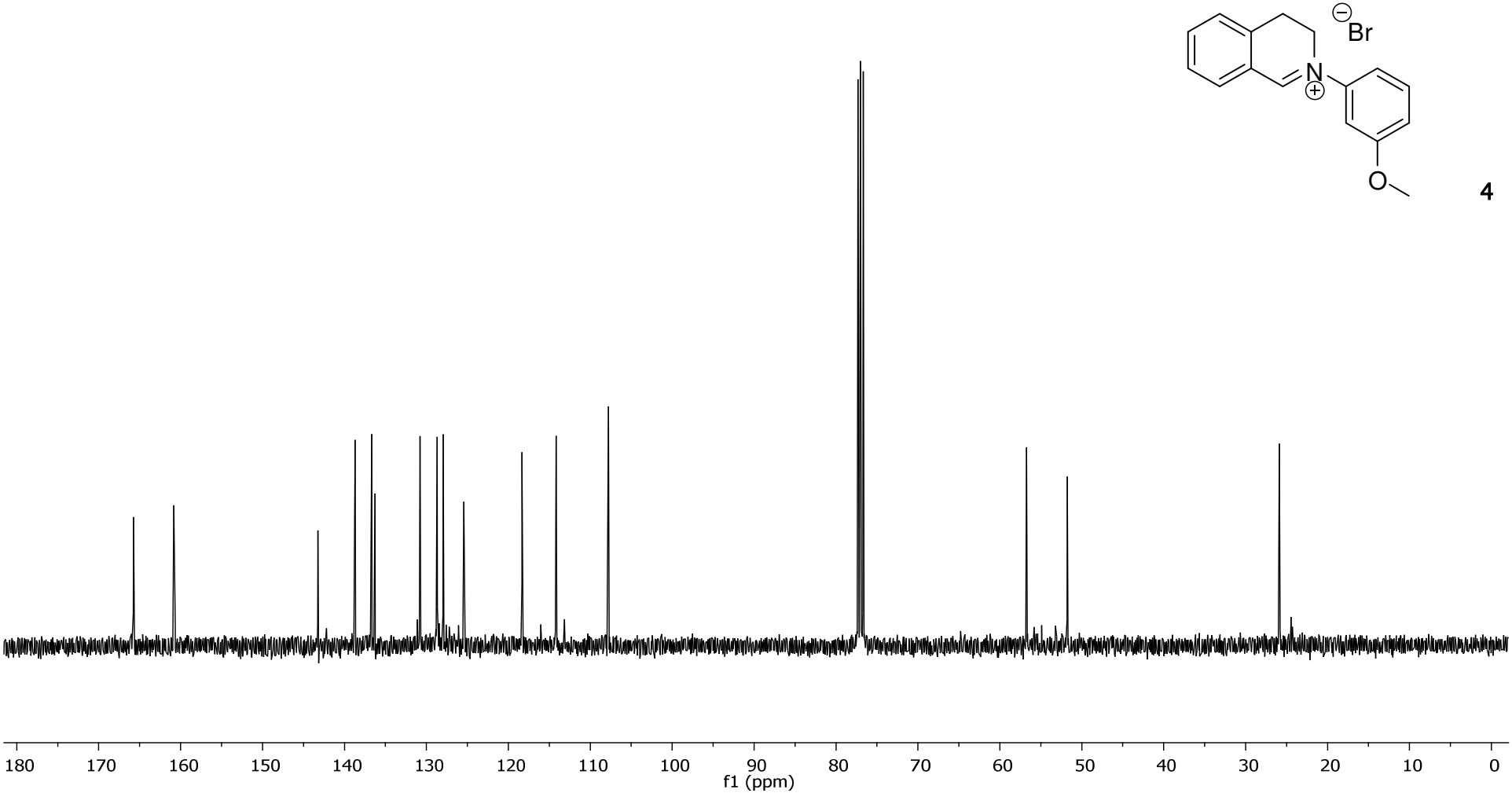

Br
N
2
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

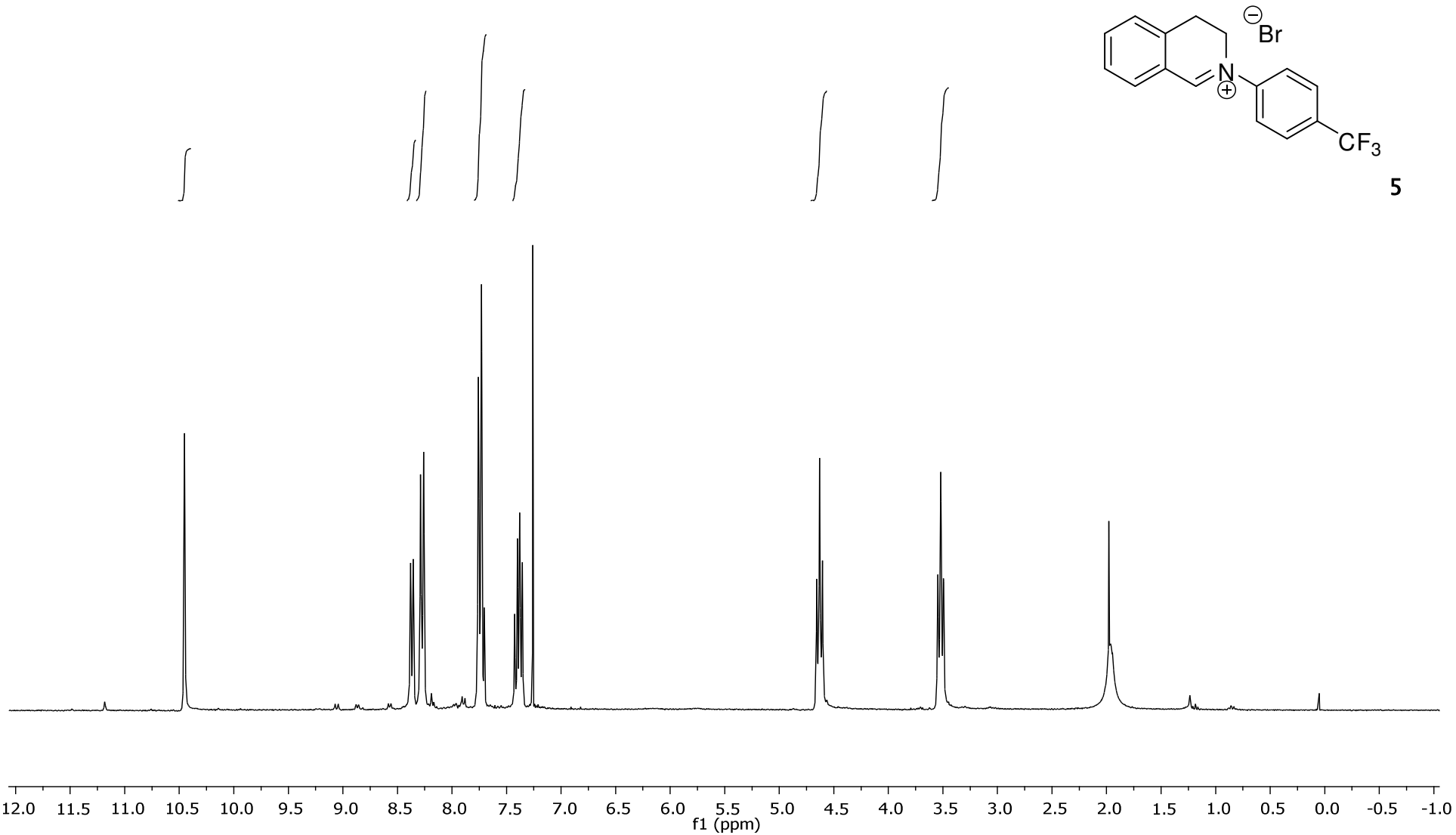

Br
N
2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

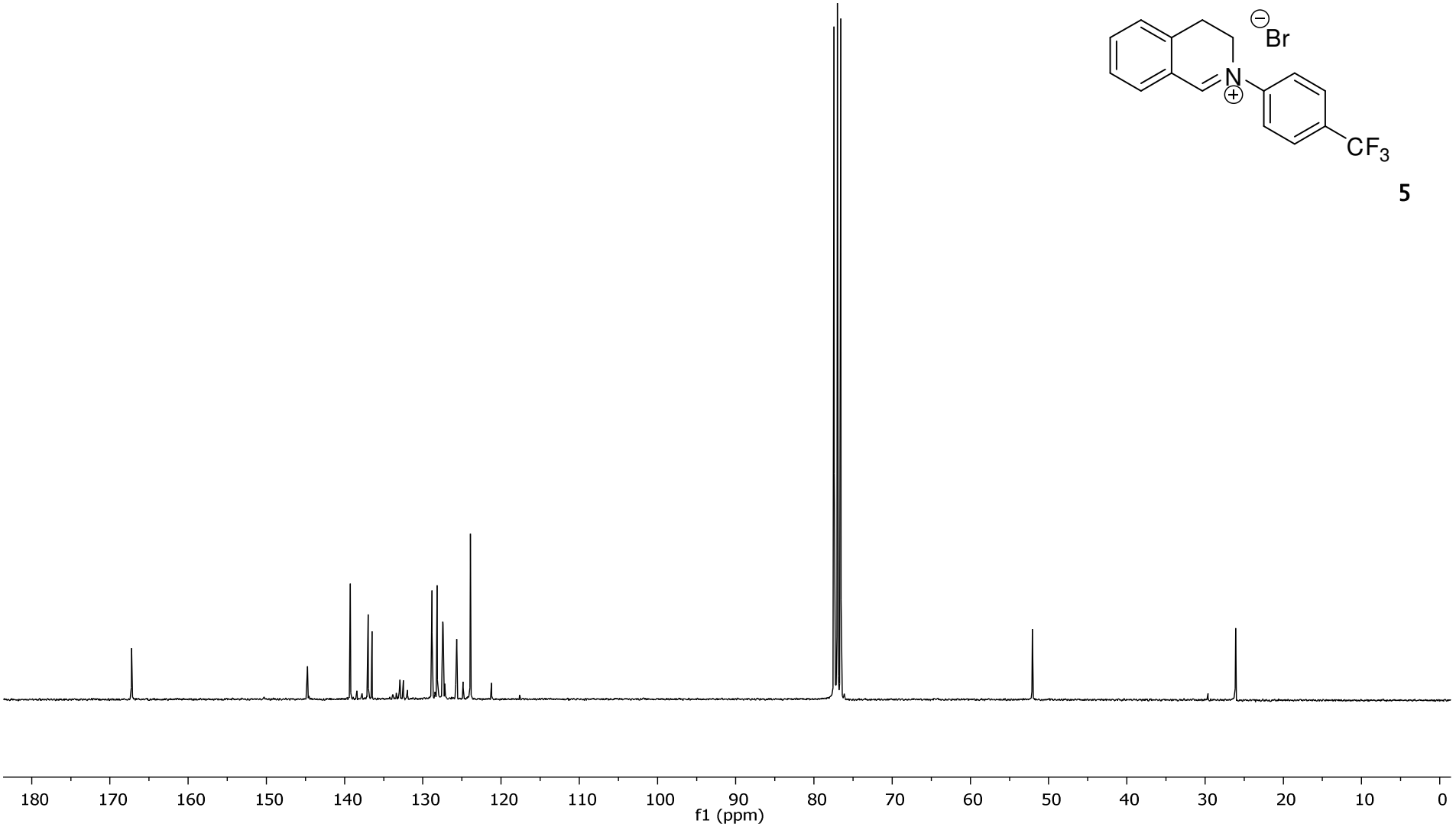

Br
N
O
3
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

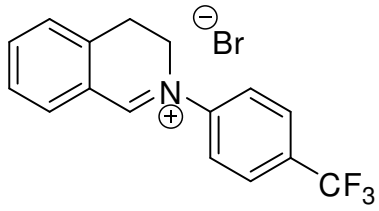

Br
N
O
3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Br
N
O
4
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


Br
N
O
4
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

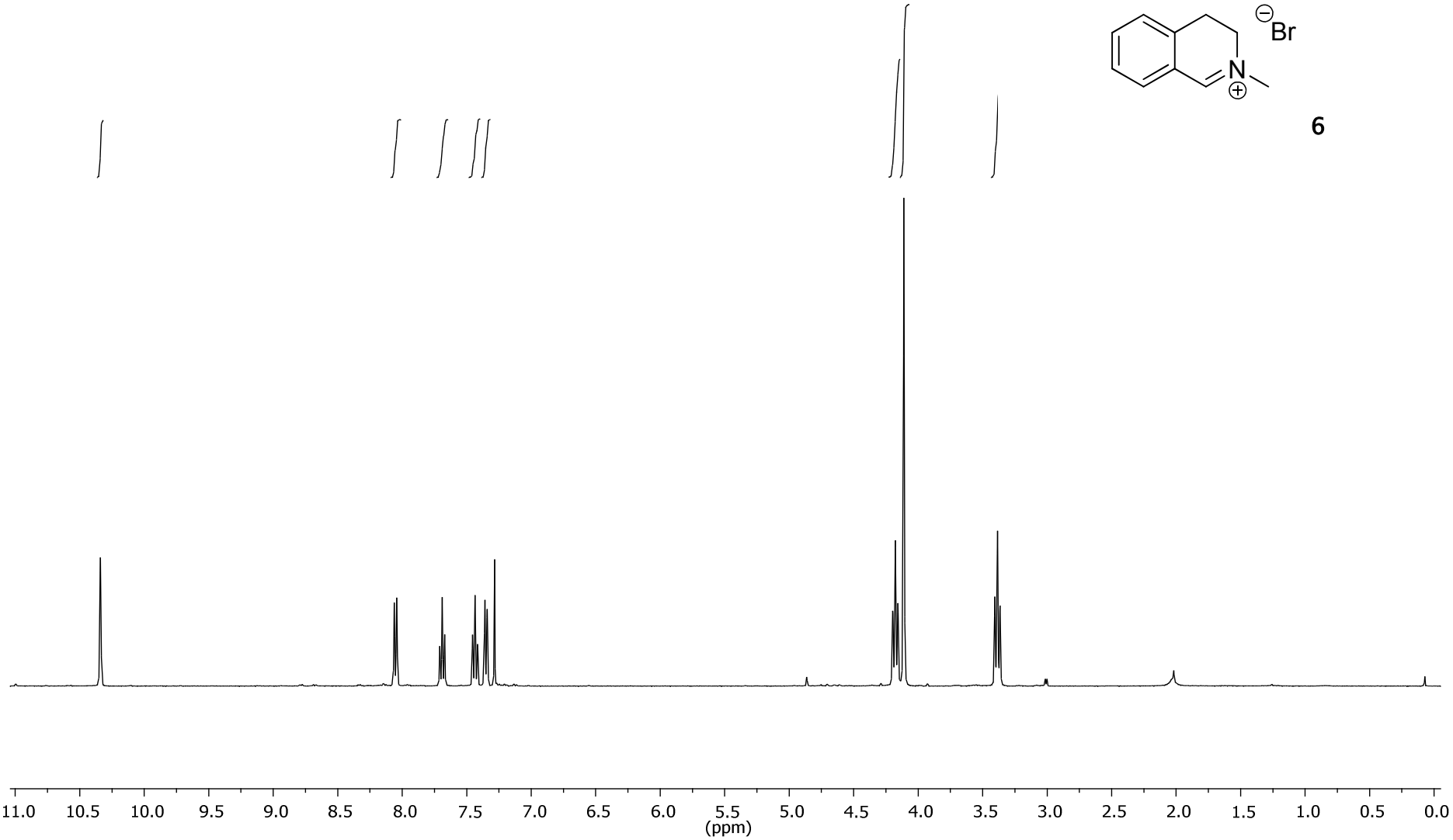

Br
N
CF3
5
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

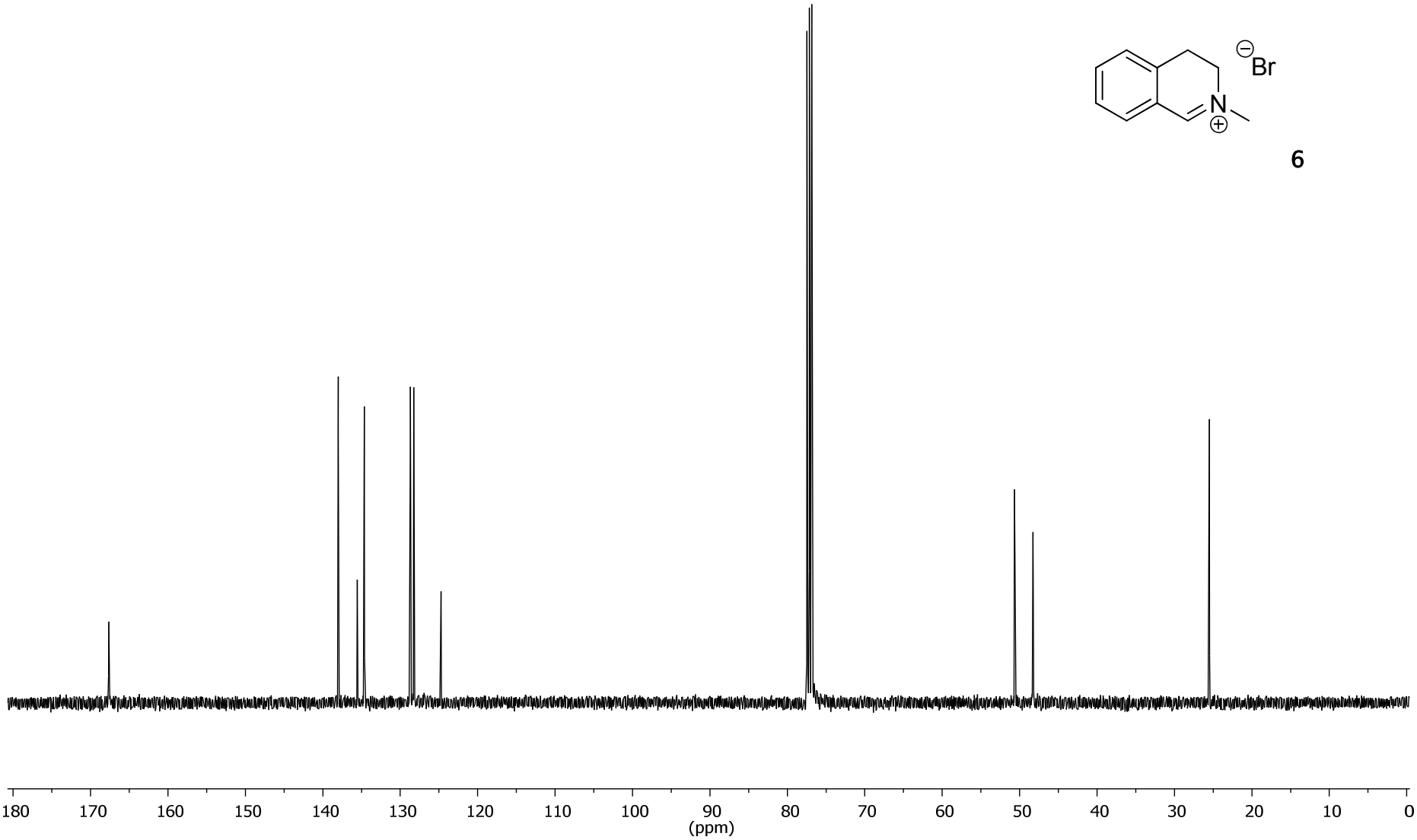

Br
N
CF3
5
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

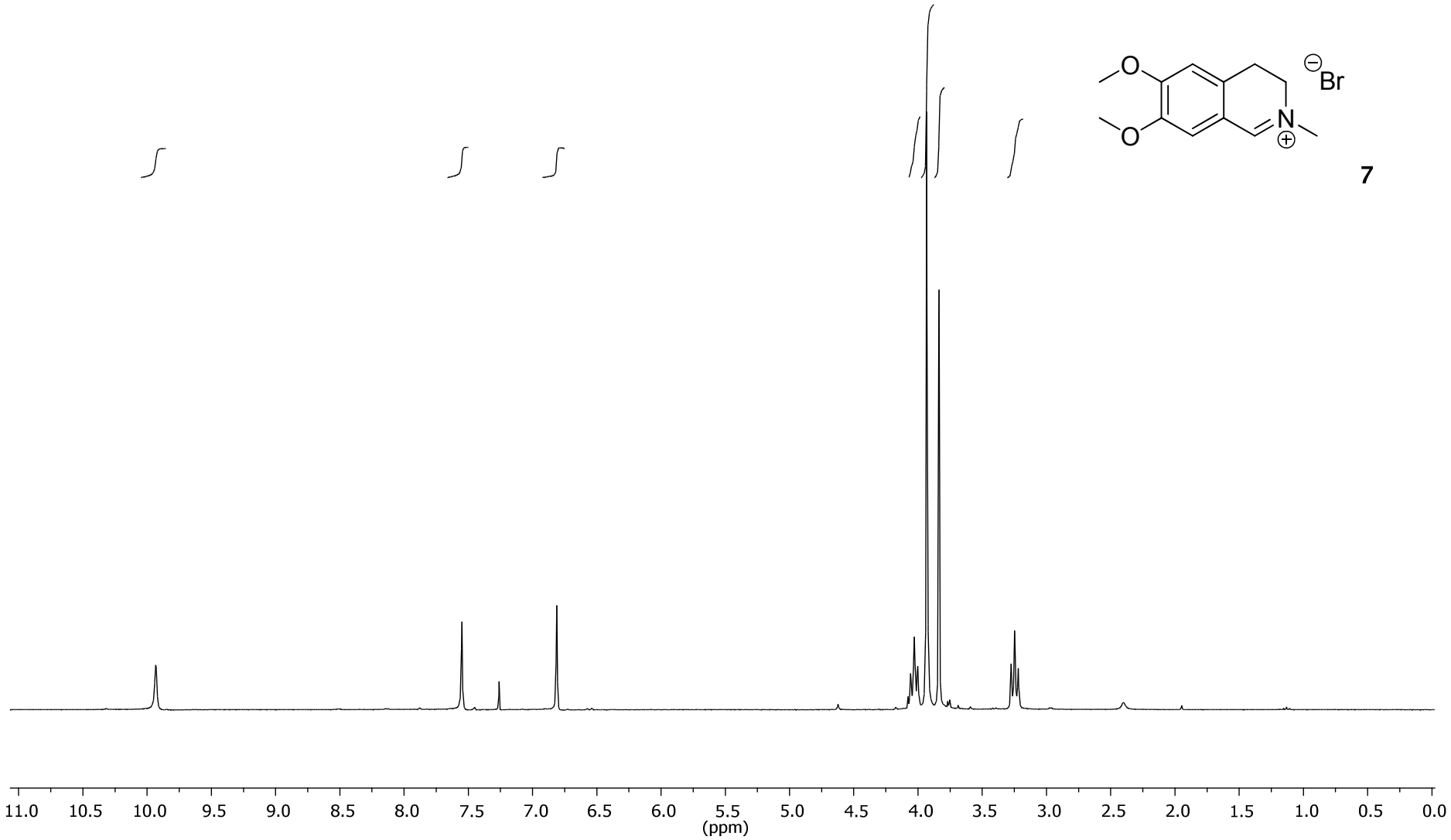

Br
N
CF3

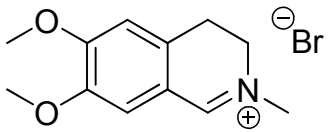
5

-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
-220
f1 (ppm)

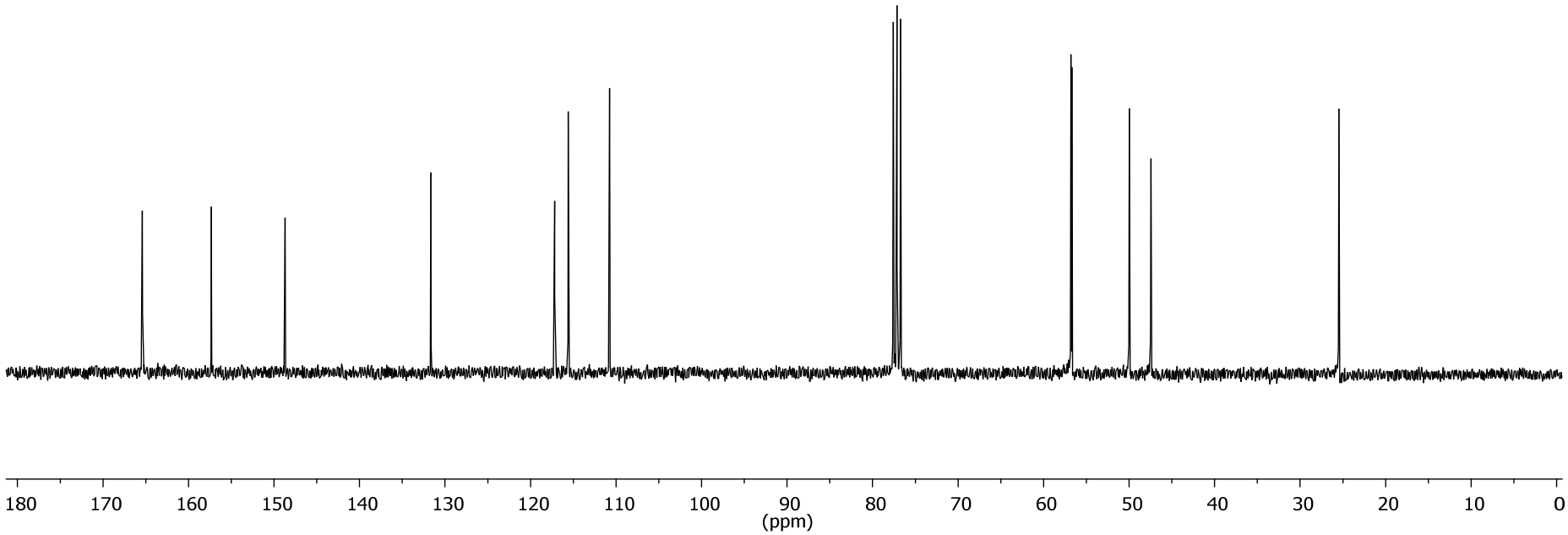

Br
N
6
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

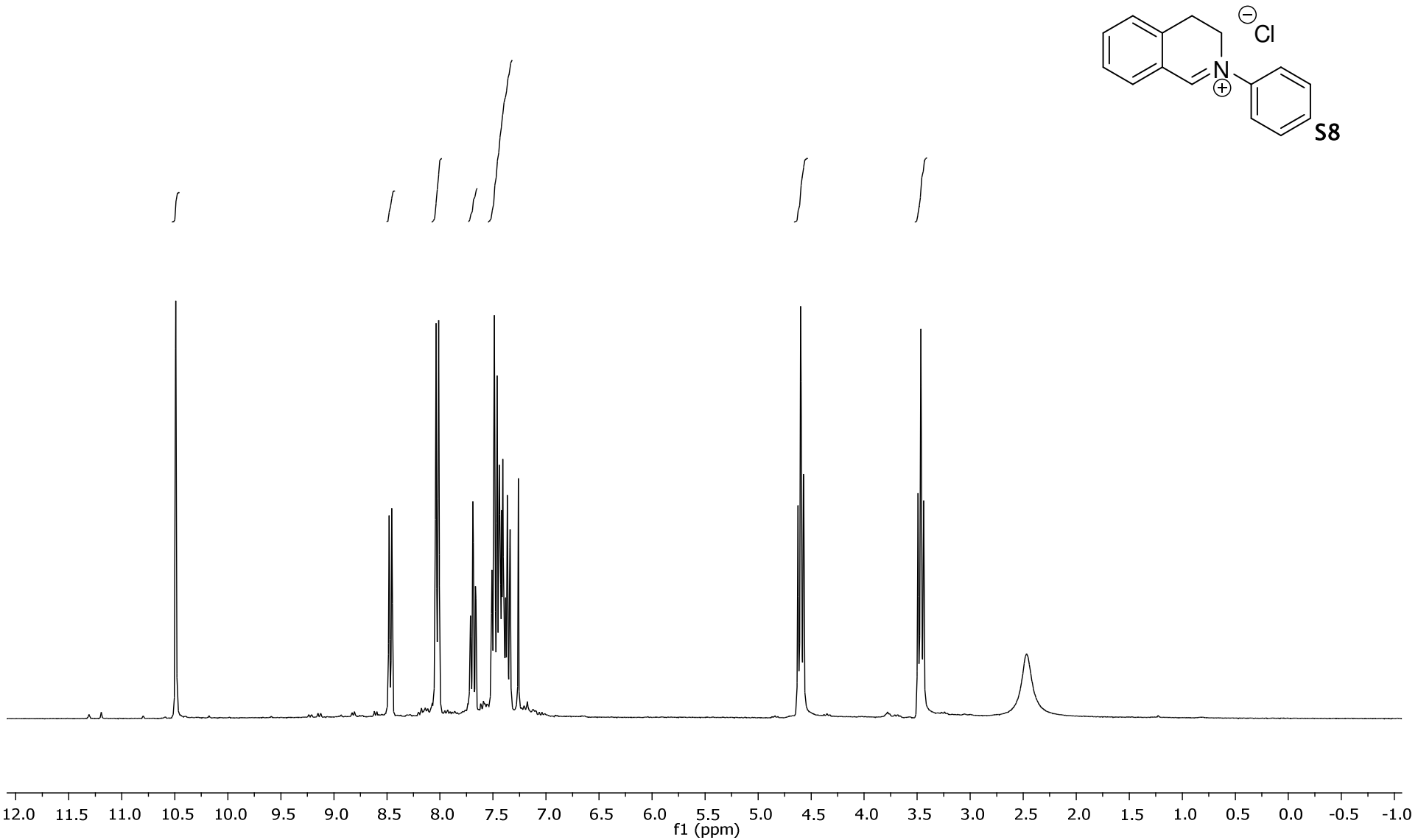

Br
N
6
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

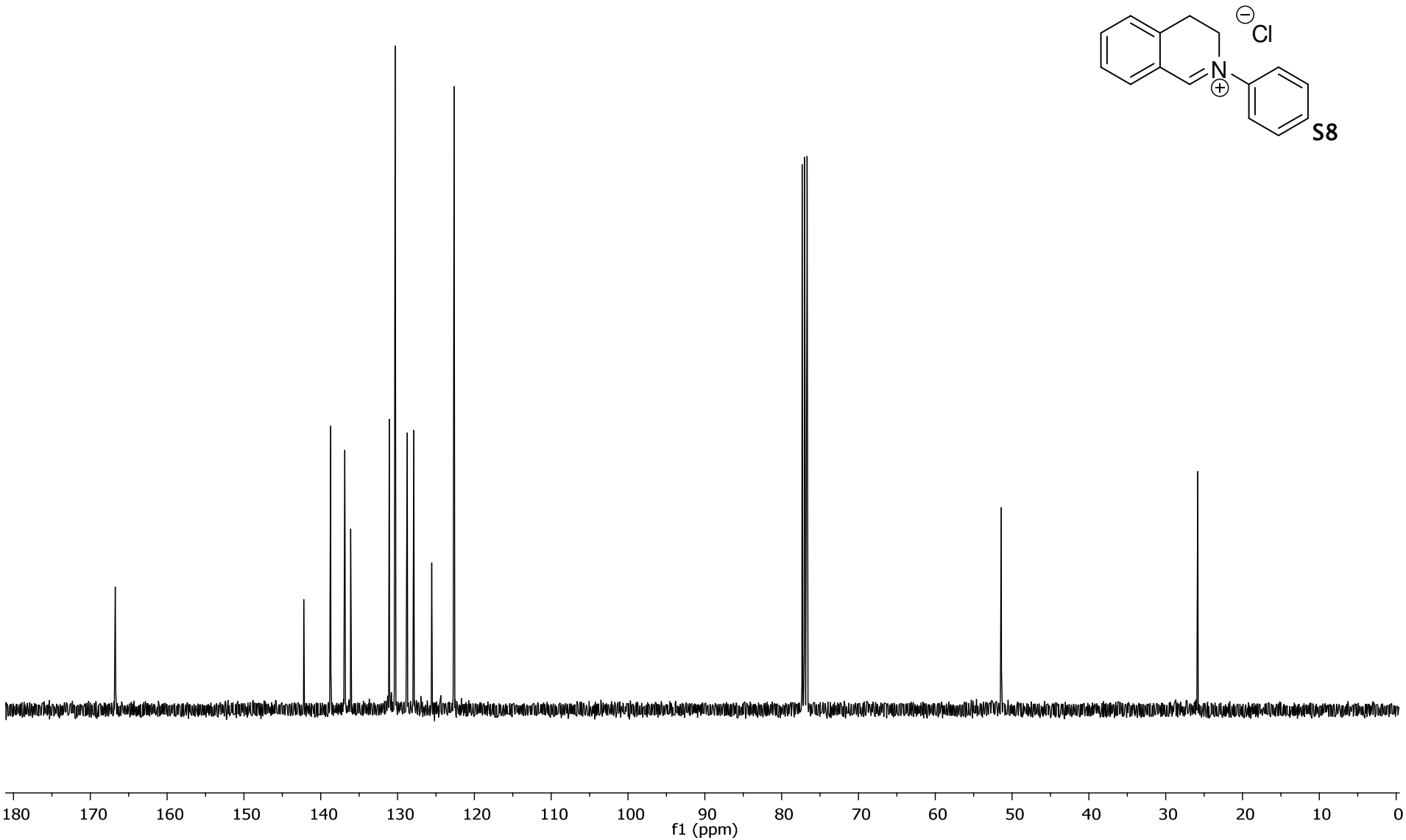

O
O
Br
N
7
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

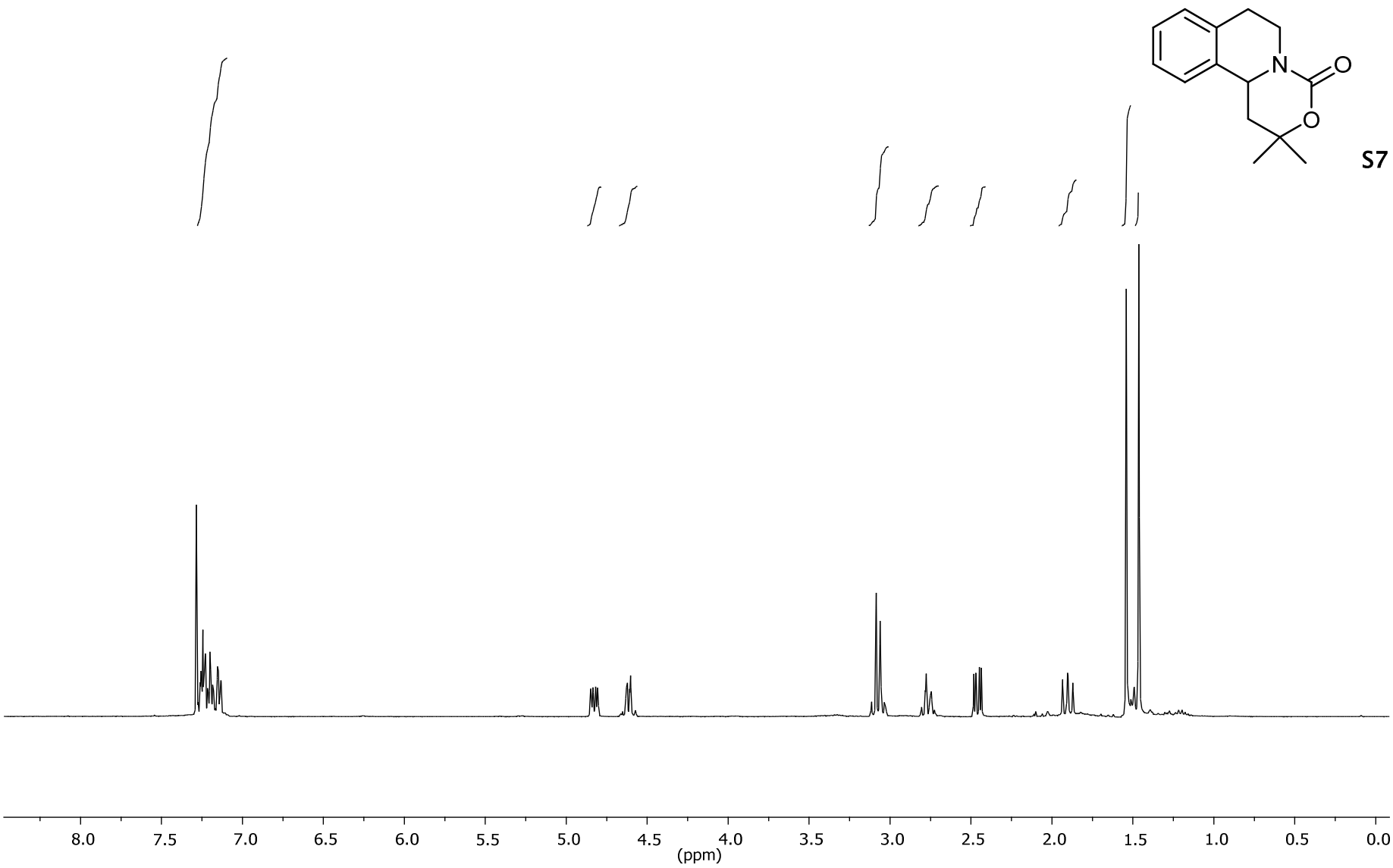

O
O
N
Br

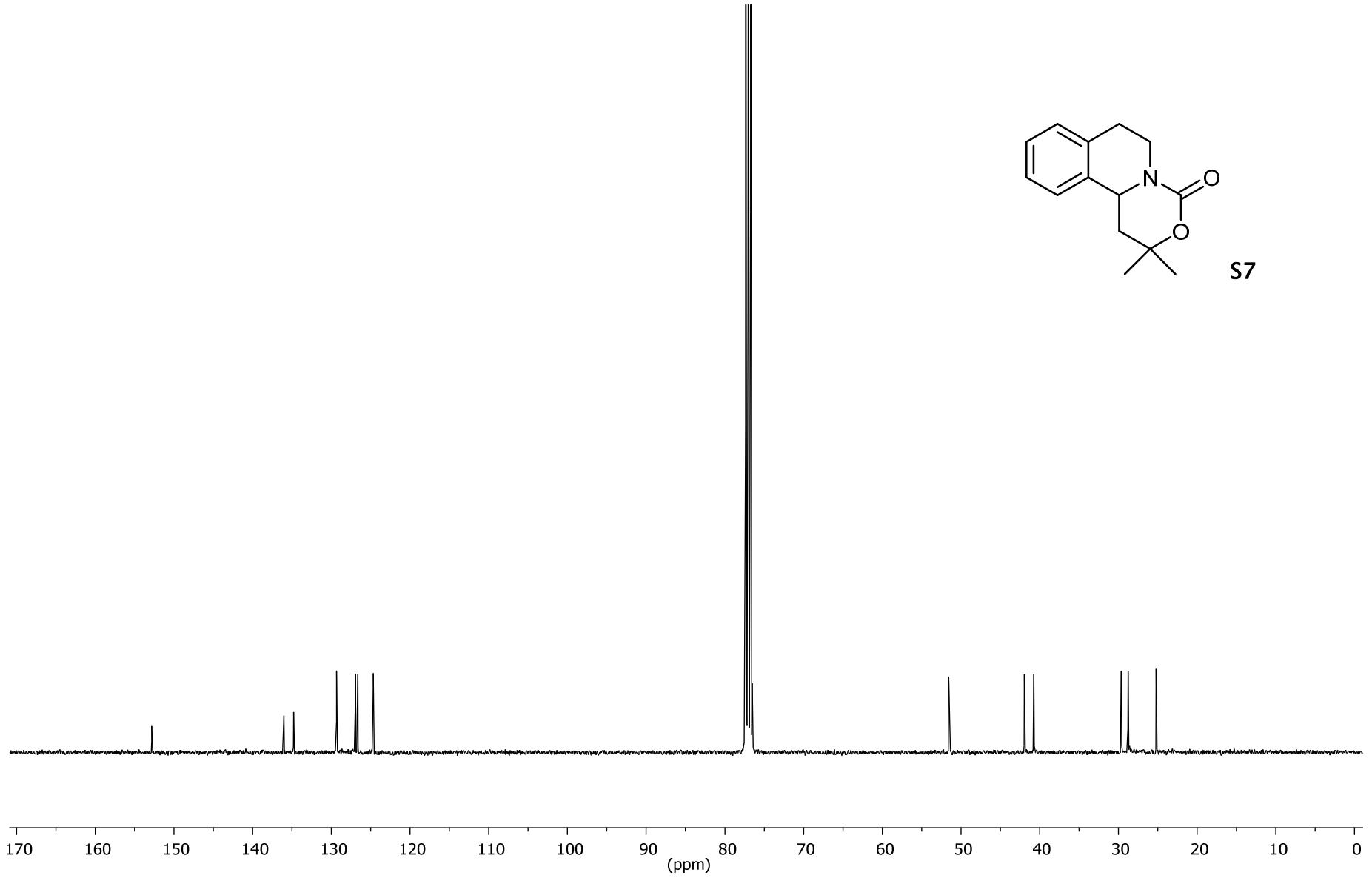
7


180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

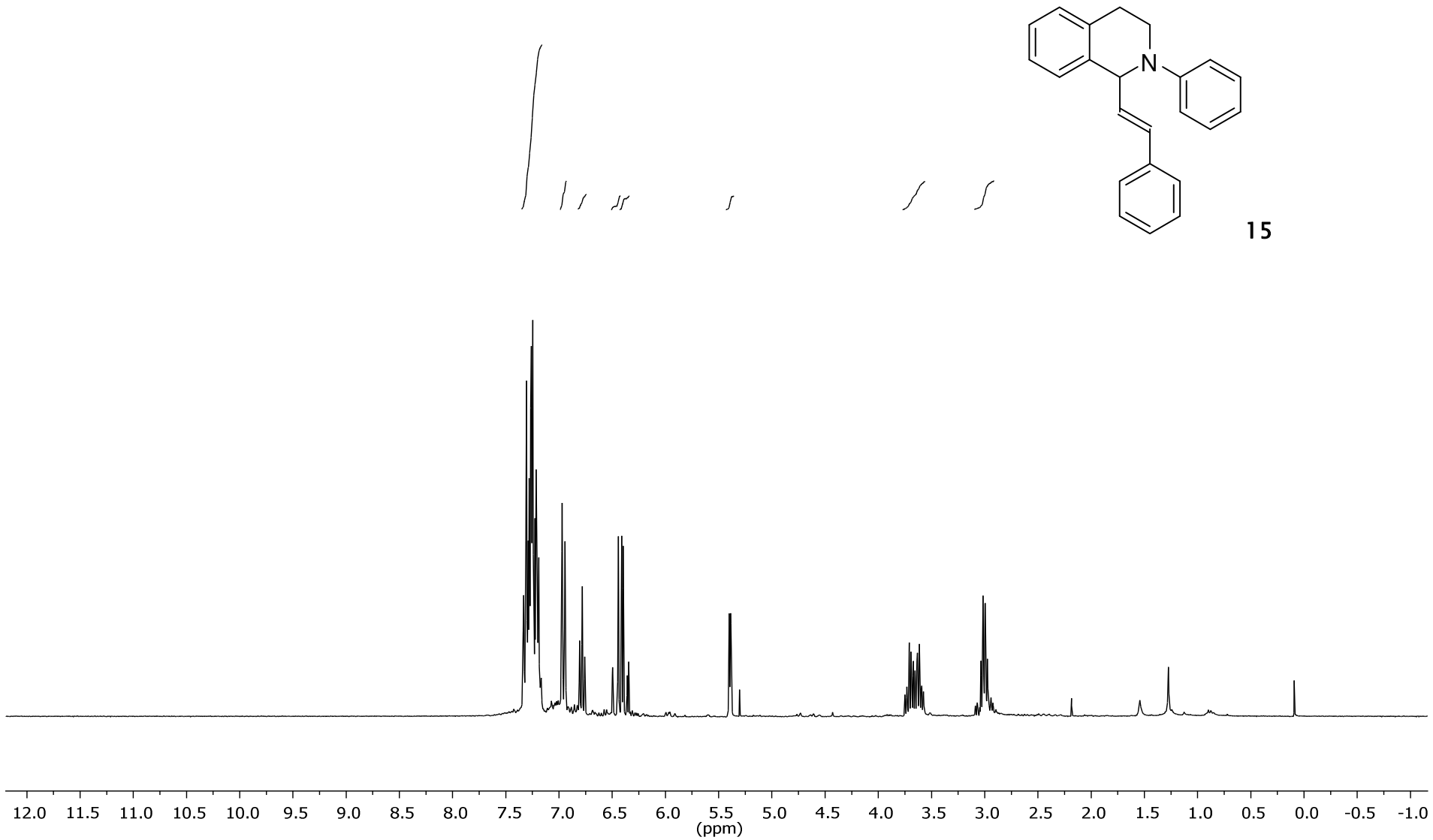

Cl
N
S8
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

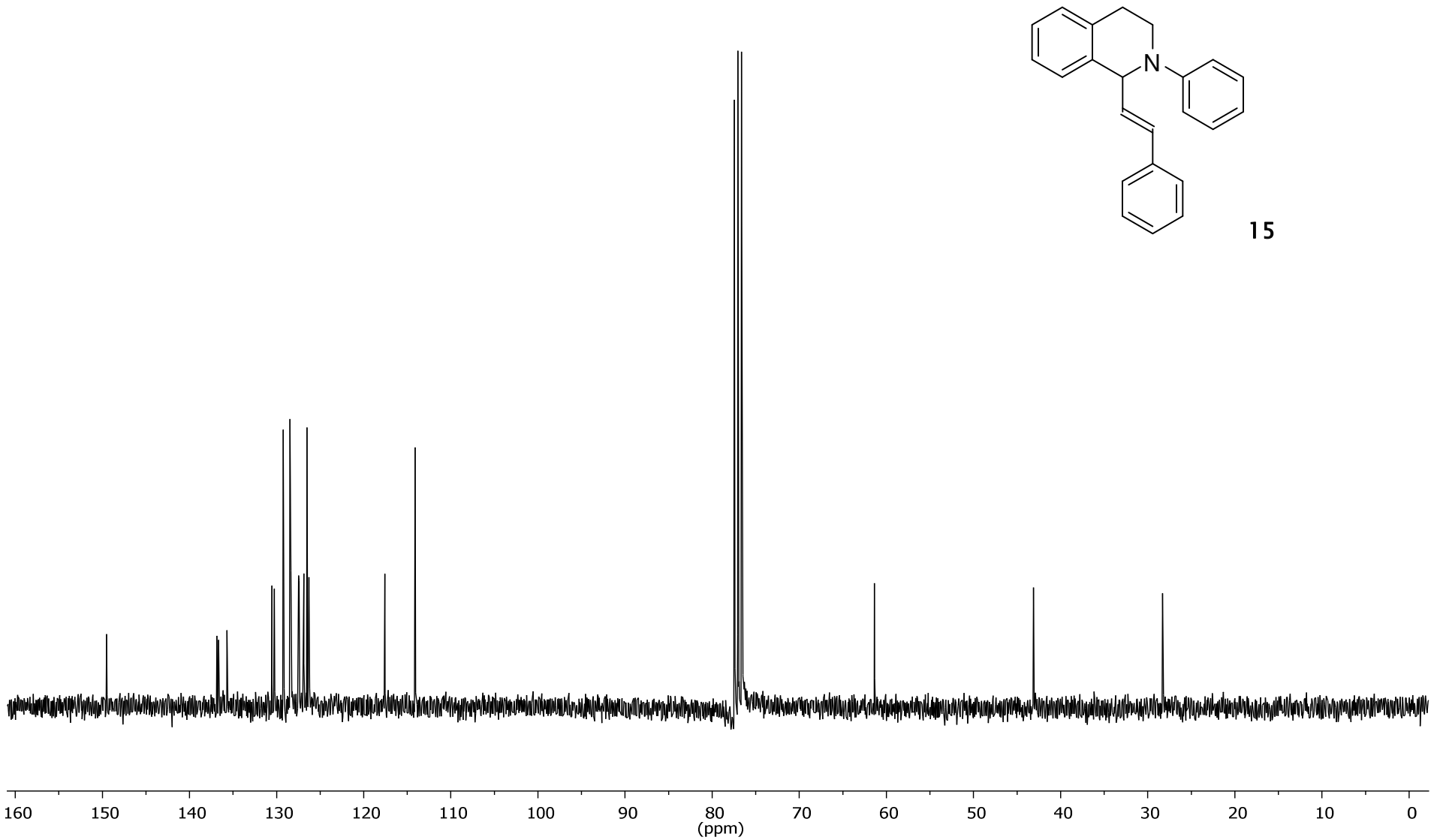

Cl
N
S8
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

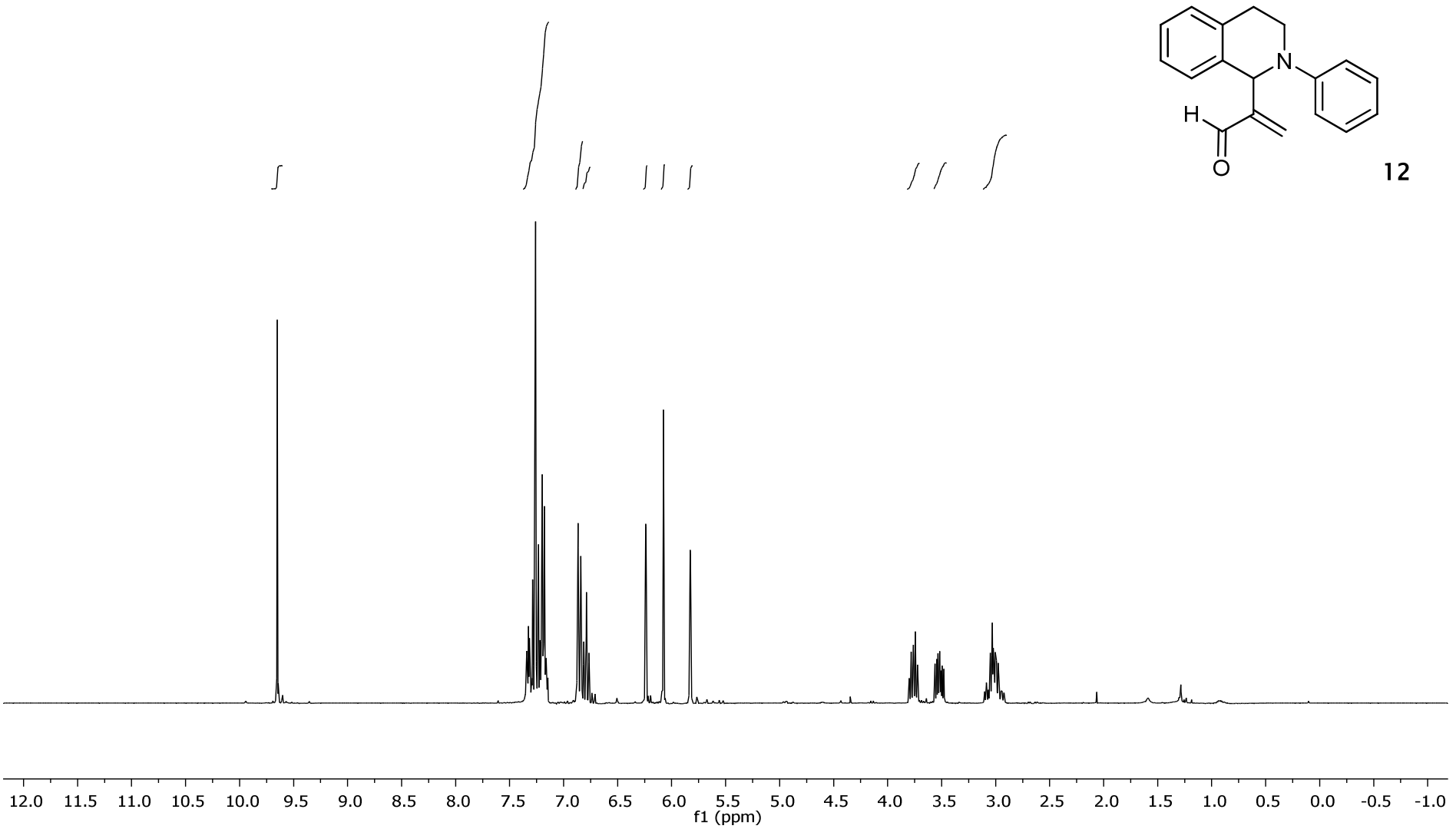

N
O
O
S7
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
(ppm)

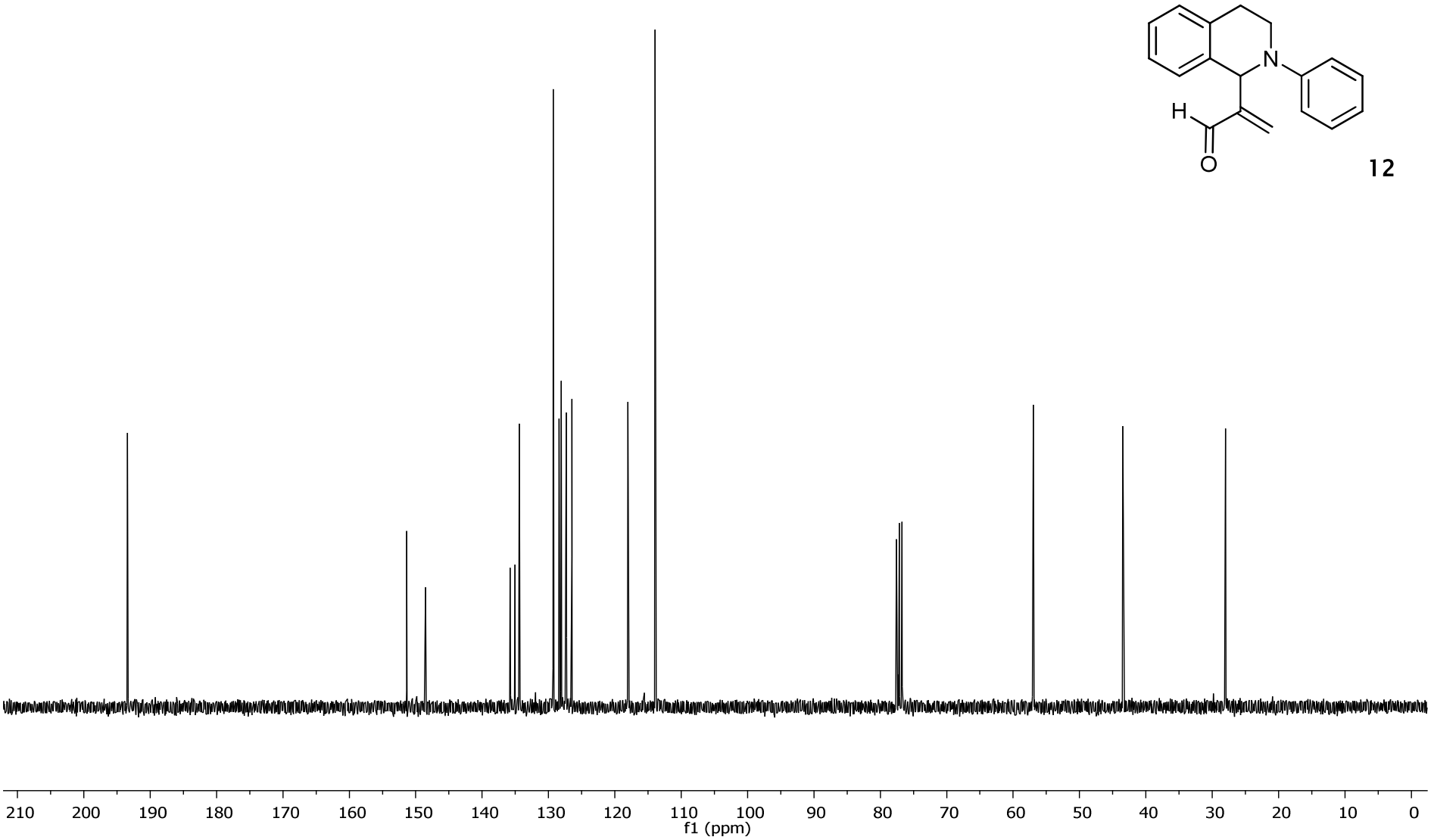


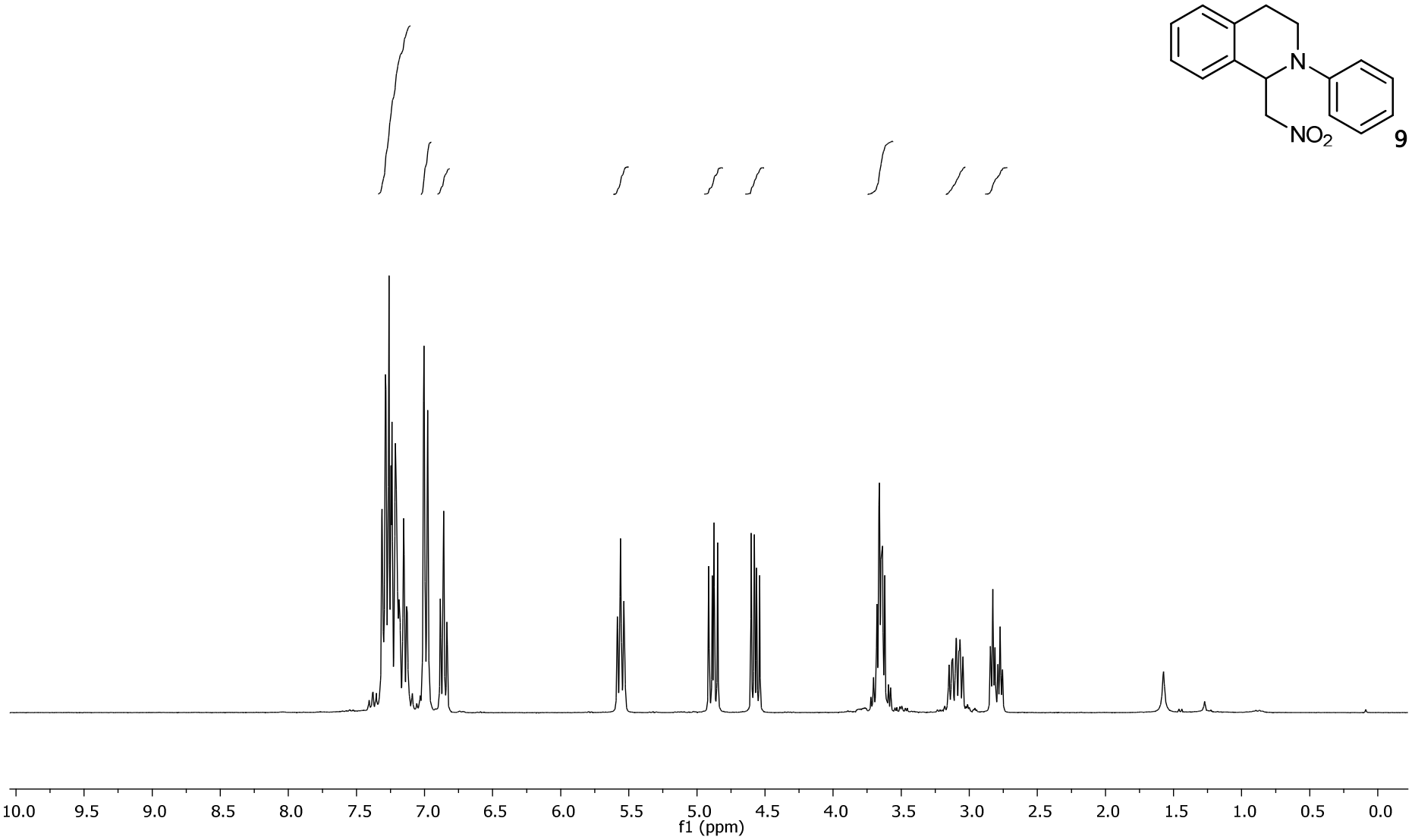
S7

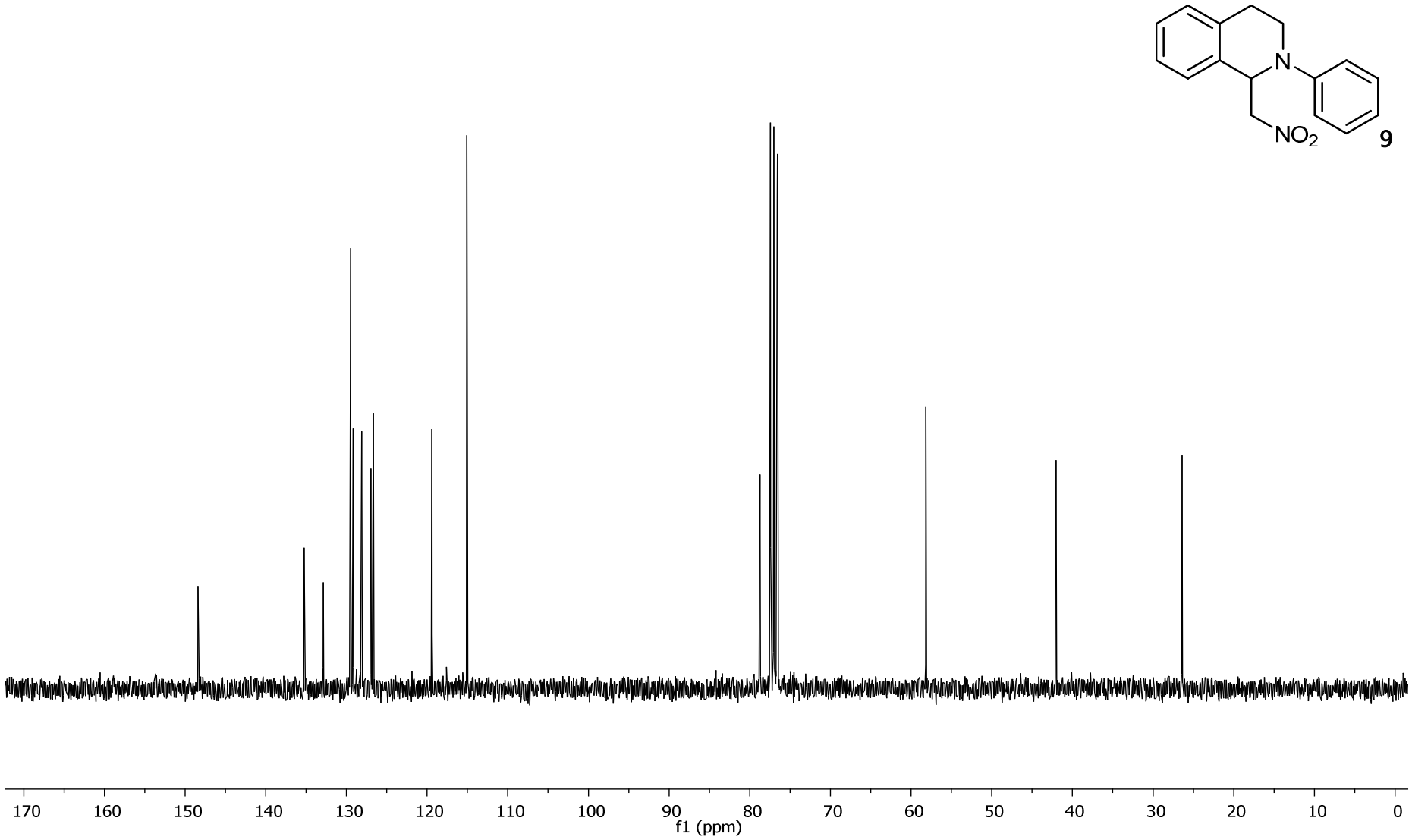

N
15
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
(ppm)

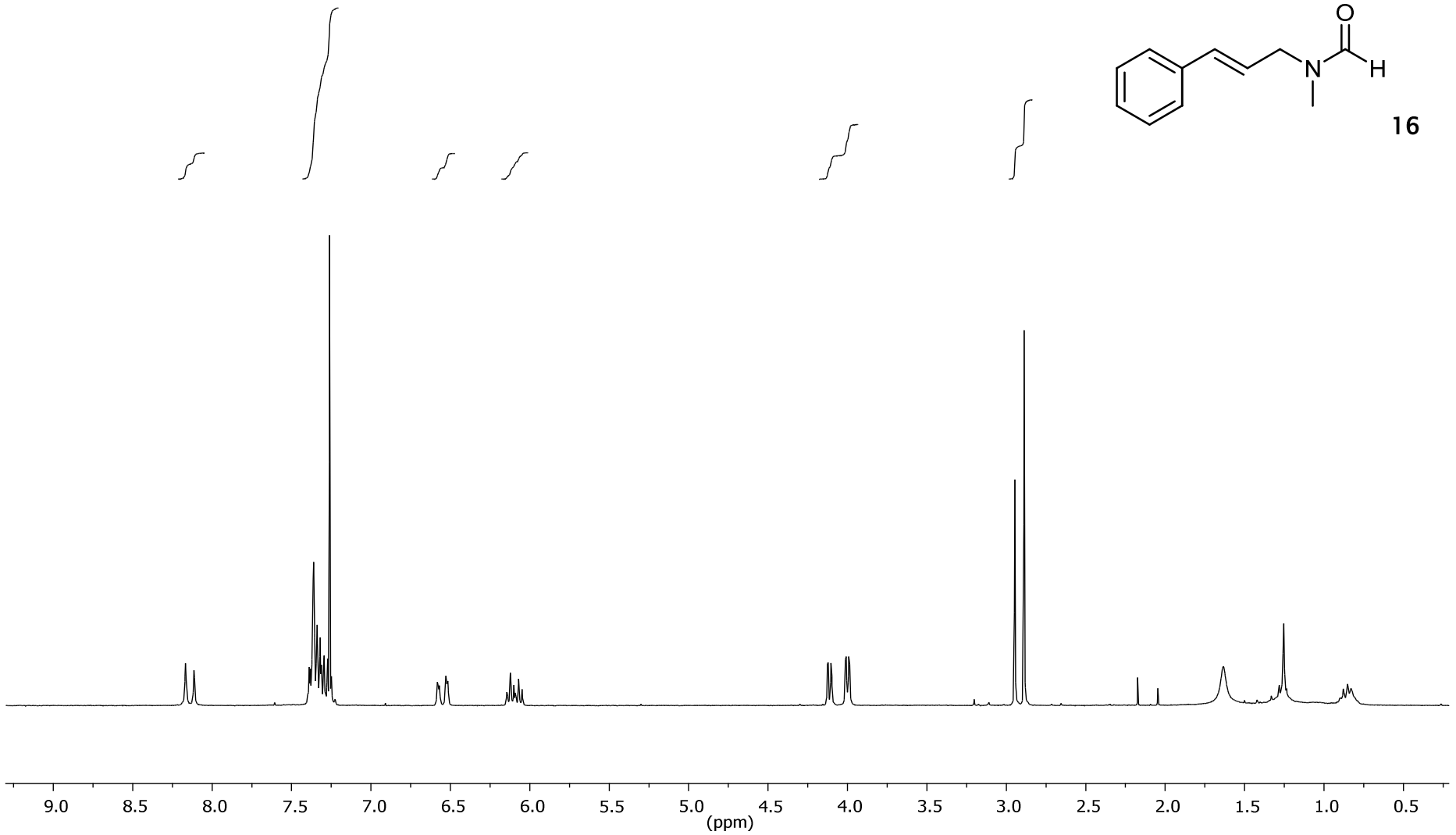

N
15
160
150
140
130
120
110
100
90
80
(ppm)
70
60
50
40
30
20
10
0


N
H
O
12
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


N
H
O
12
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


N
NO2
9
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


N
NO2
9
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
N
H
16
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
(ppm)