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Supporting Information

N-hydroxyphthalimidyl diazoacetate (NHPI-DA): a modular methylene linchpin for the C–H alkylation of indoles

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1. **General Information**

Materials: Indoles were either synthesised using the procedures described in the literature[1-18] or purchased from commercial sources, e.g.; Sigma Aldrich, Fluorochem and TCI Chemicals etc. NHPI-DA (**7a**) was prepared according to the procedure developed by our group.[19] Alternatively, it can be purchased from Key Organics (CAS: 816437-80-6; Product Number: SO-3001). Catalysts, $[Ru(Pheox)(CH_3CN)_4]PF_6$ (**13**) and Fe[TPP]Cl were synthesized using the procedures described in the literature.[20] Other catalysts and ligands used in this work, were purchased from aforementioned commercial sources. Dry solvents were obtained by passing them through activated alumina columns. When appropriate, degassing of anhydrous solvent was performed by bubbling argon for 30 minutes under sonication. The solvents used in column chromatography, petroleum ether, pentane, dichloromethane, methanol and ethyl acetate, were purchased from commercial suppliers in HPLC grade and used without further purification.

Chromatography: Thin layer chromatography (TLC) was carried out on 0.25 mm E. Merck silica plates (60F – 254) using UV light (λ = 254 nm) as visualizing agent and a vanillin, phosphomolybdic acid (PMA) or $KMnO_4$ solution and heat as developing agents, as specified. Flash column chromatography on SiO_2 was performed using E. Merck silica oil (60 Å, particle size 0.043–0.063mm).

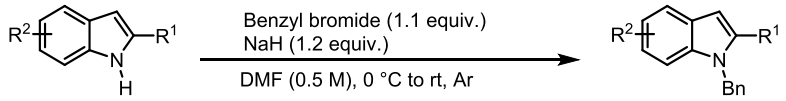
Characterization: NMR spectra for the characterization of compounds were recorded at room temperature on a Bruker instrument 400 MHz (^{1}H) and at 101 MHz (^{13}C) and 376 MHz (^{19}F), or 500 MHz (^{1}H) and at 126 MHz (^{13}C). Chemical shifts (δ) are reported in ppm, using the residual solvent peak in $CDCl_3$ (δ_H = 7.26 and δ_C = 77.16 ppm), coupling constants (*J*) are given in hertz (Hz). Data are reported as follows: chemical shift, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, br: broad, m: multiplet), coupling constants and integration. Carbon multiplicities were assigned by DEPT and edited HSQC techniques.

High-resolution mass spectra (HRMS) were determined with a Bruker Daltonics microTOF Mass Spectrometer using an ESI ion source. Melting points (m.p.) of solid samples were measured by a Melting-point apparatus (Stuart SMP 50).

Experimental details: Reactions were performed in common pyrex round bottom flasks, microwave vials 2 - 8 mL (VWR or Biotage®), or 5 - 20 ml flat bottom vials (Cronus, SMILabHut Ltd. or VWR®) crimped on top with 20 mm Sil/PTFE Septa. Reaction temperatures were maintained using Thermowatch-controlled silicone oil baths, dry ice-acetone, water-ice baths or an Immersion Cooler (Julabo-FT902) equipped with temperature controller. Slow additions were performed using Landgraf HLL LA-30 or Harvard Apparatus Pump11Elite syringe pumps.

2. Preparation of starting materials

General procedure A: Benzyl protection of indoles

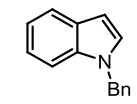


1a,q,s-v,aa
5.0 mmol

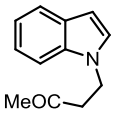
10a,q,s-v,aa

To a solution of the relevant indole (5.0 mmol, 1.0 equiv.) in DMF (10.0 mL) was added sodium hydride (60 % dispersion in mineral oil; 0.24 g, 6.0 mmol, 1.2 equiv.) and the mixture was stirred for 1 h at room temperature. The resulting suspension was cooled in an ice bath and benzyl bromide (0.94 g, 5.5 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred overnight. Upon completion, the reaction was quenched with water (30.0 mL) and EtOAc (30.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2x20.0 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:2 to 95:5) to afford benzyl protected 1-*H* indoles **10a,q,s-v,aa**.

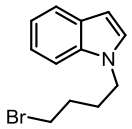
The following indoles were synthesized according to the procedures reported in the literature. All the data are in accordance with the literature.[1-18]



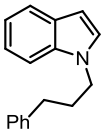
10a
synthesized using procedure A *ref. 1*



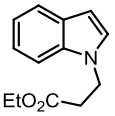
10c
synthesized following *ref. 15*



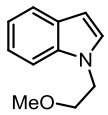
10d
synthesized following *ref. 11*



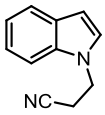
10e
synthesized following *ref. 14*



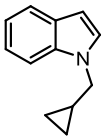
10f
synthesized following *ref. 10*



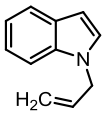
10g
synthesized following *ref. 12*



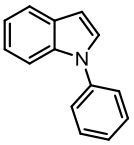
10h
synthesized following *ref. 9*



10i
synthesized following *ref. 13*



10j
synthesized following *ref. 8*



10k
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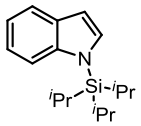
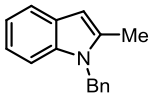
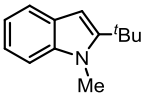


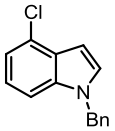
10l
synthesized following *ref. 2*



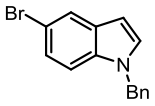
10q
synthesize following procedure A *ref. 2*



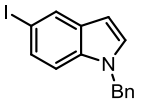
10r
synthesized using *ref. 17a,b*



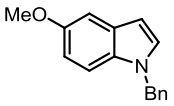
10s
synthesized using procedure A *ref. 5*



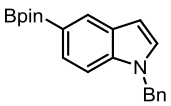
10t
synthesized using procedure A *ref. 2*



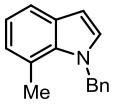
10u
synthesized using procedure A *ref. 4*



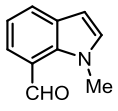
10v
synthesized using procedure A *ref. 3*



10w
synthesized using procedure A *ref. 16*

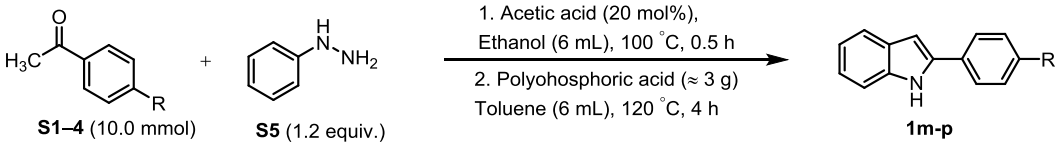


10aa
synthesized using procedure A *ref. 6*

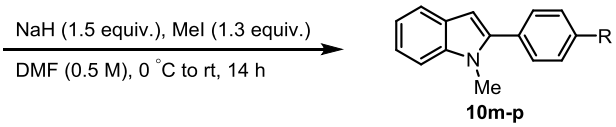


10ab
synthesized following *ref. 7a,b*

General procedure B: Synthesis of 1-methyl-2-aryl-1H-indole by Fischer-Indole synthesis[18a]



S1–4 (10.0 mmol) + **S5** (1.2 equiv.) → **1m-p**



10m-p

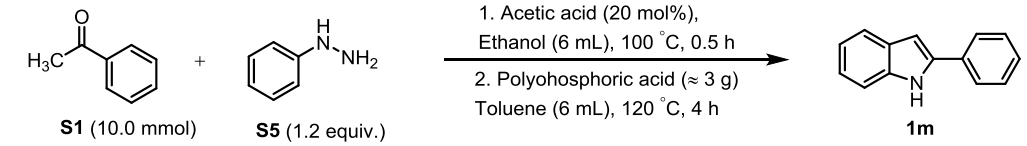
A round-bottomed flask was charged with acetophenone **S1-4** (10.0 mmol, 1.0 equiv.), phenylhydrazine **S5** (1.3 g, 12 mmol, 1.2 equiv.), acetic acid (0.12 g, 2.0 mmol, 20 mol%), and ethanol (6.0 mL). The resulting mixture was refluxed at 100 ˚C for 30 min. Upon completion (as detected by TLC), the reaction mixture was cooled to room temperature and ethanol was

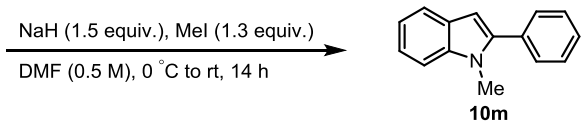
evaporated under reduced pressure. The crude was recrystallized from hexane/EtOAc to obtain the hydrazone in quantitative yield.

Polyphosphoric acid (~ 3 g) was added to a solution of hydrazone (10 mmol, 1.0 equiv.) in toluene (6.0 mL). The resulting mixture was refluxed at 120 °C for 4 h. Upon completion, (as monitored by TLC) the reaction mixture was quenched with water (50.0 mL) and EtOAc (30.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2×20.0 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:5 to 9:1) to afford 2-aryl-1*H*-indole **1m-p** in 40 to 60% yield.

In the next step, 2-aryl-1*H*-indole **1m-p** (5.0 mmol, 1.0 equiv.) was added to a stirred suspension of sodium hydride (60 % dispersion in mineral oil; 0.30 g, 7.5 mmol, 1.5 equiv.) in DMF (10.0 mL) at 0 ˚C under argon. The heterogeneous mixture was stirred at 0 °C for 15 min, and another 30 min at room temperature. The mixture was then cooled to 0 °C and iodomethane (0.92 g, 6.5 mmol, 1.3 equiv.) was added dropwise. The resulting mixture was slowly warmed to room temperature and stirring was continued overnight. Upon completion, the mixture was poured into water (30.0 mL) and diethyl ether (25.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2x25.0 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 99:1 to 98:2) to afford 1-methyl-2-aryl-1*H*-indole **10m-p**.

*Synthesis of 1-methyl-2-phenyl-1H-indole (**10m**)*





General procedure B was applied using acetophenone (**S1**; 1.2 g, 10 mmol, 1.0 equiv.), phenyl hydrazine (**S5**; 1.3 g, 12 mmol, 1.2 equiv.), acetic acid (0.12 g, 2.0 mmol, 0.20 equiv.), polyphosphoric acid (≈ 3.0 g), and ethanol (6.0 mL) for 4 h at 120 ˚C. Next, 2-phenyl-1*H*-indole (**1m**; 0.97 g, 5.0 mmol, 1.0 equiv.), iodomethane (0.92 g, 6.5 mmol, 1.3 equiv.) and sodium hydride (0.30 g, 7.5 mmol, 1.5 equiv.) were stirred in DMF (10.0 mL) at 0 ˚C to room temperature for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 99:1 to 98:2) to afford compound **10m** (0.83 g, 4.0 mmol, 82%).

Appearance: white solid.

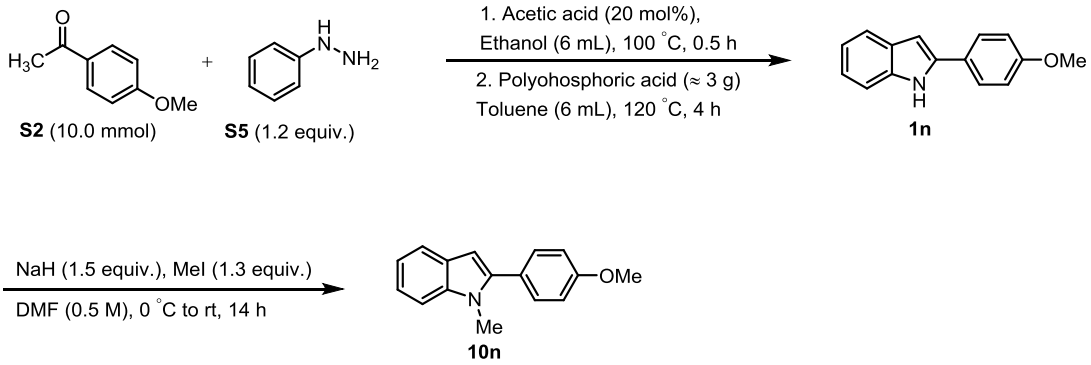
TLC: R_f = 0.5 (Petroleum ether/EtOAc = 98:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.49 – 7.35 (m, 3H), 7.31 – 7.26 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.18 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 1H), 6.60 (d, *J* = 0.9 Hz, 1H), 3.78 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.6, 138.3, 132.8, 129.4, 128.6, 127.9, 127.9, 121.7, 120.5, 119.9, 109.7, 101.6, 31.3.

All the data are in accordance with the literature.[18b]

*Synthesis of 2-(4-methoxyphenyl)-1-methyl-1H-indole (**10n**)*



General procedure B was applied using 1-(4-methoxyphenyl)ethan-1-one (**S2**; 1.5 g, 10 mmol, 1.0 equiv.), phenyl hydrazine (**S5;** 1.3 g, 12 mmol, 1.2 equiv.), acetic acid (0.12 g, 2.0 mmol, 20 mol%), polyphosphoric acid (~ 3 g), and ethanol (6.0 mL) for 4 h at 120 °C. Next, 2-(4-methoxyphenyl)-1*H*-indole (**1n**; 1.1 g, 5.0 mmol, 1.0 equiv.), iodomethane (0.92 g, 6.5 mmol, 1.3 equiv.) and sodium hydride (0.30 g, 7.5 mmol, 1.5 equiv.) were stirred in DMF (10.0 mL) at 0 °C to room temperature for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 99:1 to 98:2) to afford compound **10n** (0.91 g, 3.8 mmol, 77%).

Appearance: white solid.

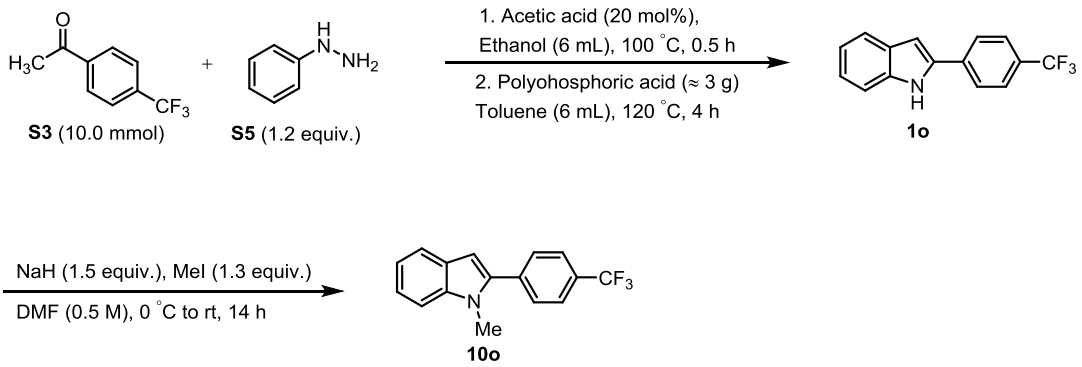
TLC: R_f = 0.45 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (d, *J* = 7.8 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.40 – 7.36 (m, 1H), 7.29 – 7.24 (m, 1H), 7.17 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 7.07 – 7.01 (m, 2H), 6.54 (d, *J* = 0.8 Hz, 1H), 3.89 (s, 3H), 3.75 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 159.4, 141.4, 138.1, 130.7, 127.9, 125.2, 121.4, 120.3, 119.8, 113.9, 109.6, 100.9, 55.4, 31.2.

All the data are in accordance with the literature.[18b]

*Synthesis of 1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indole (**10o**)*



General procedure B was applied using 1-(4-(trifluoromethyl)phenyl)ethan-1-one (**S3**; 1.9 g, 10 mmol, 1.0 equiv.), phenyl hydrazine (**S5**; 1.3 g, 12 mmol,1.2 equiv.), acetic acid (0.12 g, 2.0 mmol, 20 mol%), polyphosphoric acid (~ 3 g), and ethanol (6.0 mL) for 4 h at 120 °C. Next, 2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**1o**; 1.3 g, 5.0 mmol, 1.0 equiv.), iodomethane (0.92 g, 6.5 mmol, 1.3 equiv.) and sodium hydride (0.30 g, 7.5 mmol, 1.5 equiv.) were stirred in DMF (10.0 mL) at 0 °C to room temperature for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 99:1 to 98:2) to afford compound **10o** (0.93 g, 3.4 mmol, 68%).

Appearance: white solid.

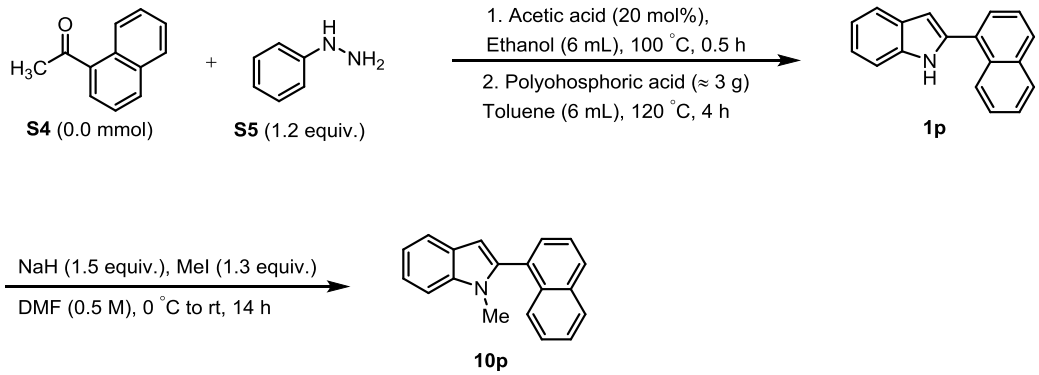
TLC: R_f = 0.55 (Petroleum ether/EtOAc = 98:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.76 (d, *J* = 7.7 Hz, 2H), 7.70 (dt, *J* = 7.9, 1.0 Hz, 1H), 7.68 – 7.64 (m, 2H), 7.45 – 7.41 (m, 1H), 7.33 (ddd, *J* = 8.3, 7.0, 1.2 Hz, 1H), 7.22 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.67 (d, *J* = 0.9 Hz, 1H), 3.79 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.9, 138.7, 136.4, 130.9 (q, J_{C-F} = 270 Hz), (130.2 (q, J_{C-F} = 33 Hz), 129.5, 127.8, 125.6 (q, J_{C-F} = 3.8 Hz), 122.4, 120.8, 120.2, 109.9, 102.8, 31.4.

All the data are in accordance with the literature.[18b]

*Synthesis of 1-methyl-2-(naphthalen-1-yl)-1H-indole (**10p**)*



General procedure B was applied using 1-(naphthalen-1-yl)ethan-1-one (**S4**; 1.7 g, 10 mmol, 1.0 equiv.), phenyl hydrazine (**S5**; 1.3 g, 12 mmol, 1.2 equiv.), acetic acid (0.12 g, 2.0 mmol, 20 mol%), polyphosphoric acid (~ 3 g), and ethanol (6.0 mL) for 4 h at 120 °C. Next, 2-

(naphthalen-1-yl)-1H-indole (**1p**; 1.2 g, 5.0 mmol, 1.0 equiv.), iodomethane (0.92 g, 6.5 mmol, 1.3 equiv.) and sodium hydride (0.30 g, 7.5 mmol, 1.5 equiv.) were stirred in DMF (10.0 mL) at 0 ˚C to room temperature for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 99:1 to 98:2) to afford compound **10p** (0.67 g, 2.6 mmol, 52%).

Appearance: white solid.

TLC: R_f = 0.45 (Petroleum ether/EtOAc = 98:2, UV-active and stains in vanillin).

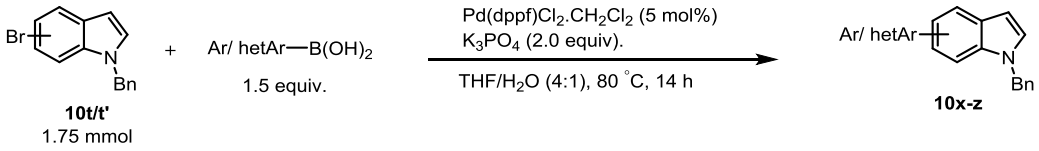
m.p. = 74.3 – 77.6 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.00 – 7.86 (m, 2H), 7.71 (dd, *J* = 7.9, 1.1 Hz, 2H), 7.61 – 7.50 (m, 3H), 7.47 – 7.40 (m, 2H), 7.33 – 7.27 (m, 1H), 7.24 – 7.17 (m, 1H), 6.64 (s, 1H), 3.50 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.4, 137.7, 133.5, 132.9, 130.5, 128.9, 128.9, 128.3, 128.1, 126.6, 126.1 (2Ar C–H), 125.2, 121.6, 120.5, 119.8, 109.5, 103.1, 30.8.

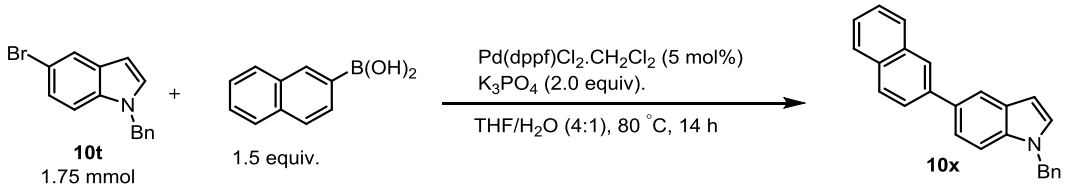
All the data are in accordance with the literature.[18c]

General procedure C: Synthesis of 5- or 6- substituted indoles using Suzuki coupling



A microwave vial was charged with 1-benzyl-5-bromo-1*H*-indole or 1-benzyl-6-bromo-1*H*-indole (**10t**/**t'**; 1.75 mmol, 1.00 equiv.), aryl or heteroaryl-boronic acid (2.6 mmol, 1.5 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ (72 mg, 0.087 mmol, 5.0 mol%), and K_3PO_4 (0.74 g, 3.5 mmol, 2.0 equiv.), followed by addition of THF (4.0 mL) and water (1.0 mL). The vial was degassed for 5 min, and heated at 80 °C for 14 h. Upon completion, water (15.0 mL) and EtOAc (15.0 mL) were added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2x15.0 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:2 to 9:1) to afford compound **10x-z.**

*Synthesis of 1-benzyl-5-(naphthalen-2-yl)-1H-indole (**10x**)*



General procedure C was applied using 1-benzyl-5-bromo-1*H*-indole (**10t**; 0.50 g, 1.7 mmol, 1.0 equiv.), naphthalen-2-ylboronic acid (0.45 g, 2.6 mmol, 1.5 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ (72 mg, 0.087 mmol, 5.0 mol%), and K_3PO_4 (0.74 g, 3.5 mmol, 2.0 equiv.) in THF/water (4:1) at 80 °C for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:2 to 95:5) to afford compound **10x** (0.53 g, 1.6 mmol, 92%).

Appearance: white solid.

TLC: R_f = 0.65 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

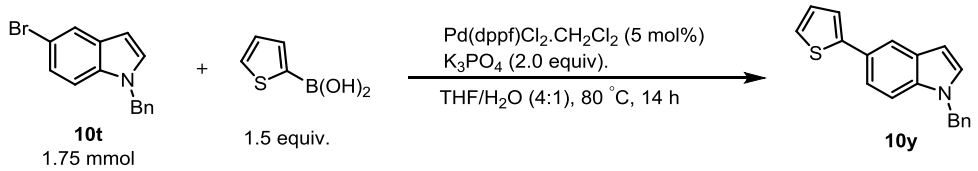
m.p. = 120.5 – 124.8 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.08 (s, 1H), 8.00 (s, 1H), 7.93 – 7.81 (m, 4H), 7.58 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.53 – 7.42 (m, 2H), 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 2H), 7.19 (d, *J* = 3.1 Hz, 1H), 7.18 – 7.14 (m, 2H), 6.64 (d, *J* = 3.1 Hz, 1H), 5.38 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.8, 137.4, 135.9, 133.8, 132.9, 132.1, 129.3, 129.0, 128.8, 128.1, 128.0, 127.7, 127.6, 126.7, 126.2, 126.0, 125.5, 125.4, 121.8, 119.8, 110.0, 102.1, 50.2.

HRMS (ESI-TOF) calc'd for $C_{25}H_{19}NNa$ $[M+Na]^+$: 356.1410, found: 356.1405.

*Synthesis of 1-benzyl-5-(thiophen-2-yl)-1H-indole (**10 y**)*



General procedure C was applied using 1-benzyl-5-bromo-1*H*-indole (**10t**; 0.50 g, 1.7 mmol, 1.0 equiv.), thiophen-2-ylboronic acid (0.34 g, 2.6 mmol, 1.5 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ (72 mg, 0.087 mmol, 5.0 mol%), and K_3PO_4 (0.74 g, 3.5 mmol, 2.0 equiv.) in THF/water (4:1) at 80 °C for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:2 to 95:5) to afford compound **10y** (0.39 g, 1.3 mmol, 77%).

Appearance: pink solid.

TLC: R_f = 0.45 (Petroleum ether/EtOAc = 98:2, UV-active and stains in vanillin).

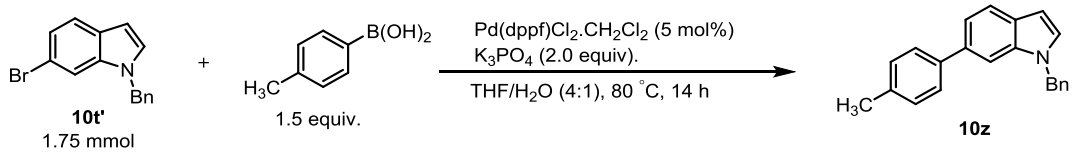
m.p. = 78.9 – 81.3 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 (d, *J* = 1.7 Hz, 1H), 7.45 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.38 – 7.24 (m, 5H), 7.22 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.16 – 7.10 (m, 3H), 7.07 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.58 (dd, *J* = 3.1, 0.8 Hz, 1H), 5.33 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 146.1, 137.3, 135.9, 129.2, 129.1, 128.8, 127.8, 127.7, 126.7, 126.4, 123.5, 122.0, 120.8, 118.5, 110.0, 102.1, 50.2.

HRMS (ESI-TOF) calc'd for $C_{19}H_{15}NSNa$ $[M+Na]^+$: 312.0817, found: 312.0814.

*Synthesis of 1-benzyl-6-(p-tolyl)-1H-indole (**10z**)*



General procedure C was applied using 1-benzyl-6-bromo-1*H*-indole (**10t'**; 0.50 g, 1.75 mmol, 1.0 equiv.), *p*-tolylboronic acid (0.35 g, 2.6 mmol, 1.5 equiv.), $Pd(dppf)Cl_2.CH_2Cl_2$ (72 mg, 0.087

mmol, 5.0 mol%), and K_3PO_4 (0.74 g, 3.5 mmol, 2.0 equiv.) in THF/water (4:1) at 80 °C for 14 h. The crude was purified by flash chromatography on SiO_2 (petroleum ether/EtOAc = 98:2 to 95:5) to afford compound **10z** (0.45 g, 1.5 mmol, 88%).

Appearance: white solid.

TLC: R_f = 0.65 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

m.p. = 102.1 – 104.6 °C

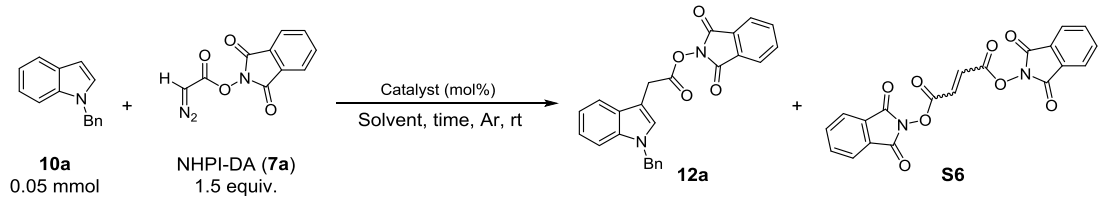
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.69 (d, *J* = 8.2 Hz, 1H), 7.52 – 7.50 (d, *J* = 8.1 Hz, 2H), 7.47 (s, 1H), 7.37 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.34 – 7.26 (m, 3H), 7.23 (d, *J* = 7.8 Hz, 2H), 7.17 – 7.13 (m, 3H), 6.57 (d, *J* = 3.2, 0.8 Hz, 1H), 5.37 (s, 2H), 2.39 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.6, 137.4, 136.9, 136.2, 135.3, 129.3, 128.7, 128.7, 127.8, 127.6, 127.2, 126.8, 121.0, 119.4, 107.9, 101.6, 50.0, 21.0.

HRMS (ESI-TOF) calc'd for $C_{22}H_{19}NNa$ $[M+Na]^+$: 320.1410, found: 320.1404.

3. Optimization Studies

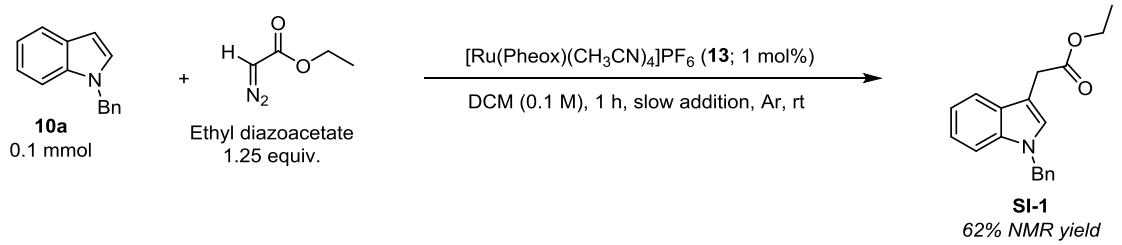
3.1 Ru(II)-Pheox catalyzed C–H functionalization of indole using NHPI-DA (7a)



Entry	Catalyst (mol%)	Solvent (M)	Time	Yield **12a** (%)	Yield **S6** (%)[a]
1	$Rh_2(OAc)_4$ (2 mol%)	DCE (0.05 M)	12 h	38	8
2	$Rh_2(OAc)_4$ (2 mol%)	DCE (0.05 M)	12 h	30	3
3	$Rh_2(piv)_4$ (2 mol%)	DCE (0.05 M)	12 h	36	11
4	$Rh_2(TPA)_4$ (2 mol%)	DCE (0.05 M)	12 h	23	12
5	$Rh_2(esp)_2$ (2 mol%)	DCE (0.05 M)	12 h	33	13
6	$Cu(OTf)_2$ (10 mol%)	DCE (0.05 M)	12 h	12	6
7	CuI (10 mol%)	DCE (0.05 M)	12 h	4	3
8	$[Cu(CH_3CN)_4]PF_6$ (10 mol%)	DCM (0.05 M)	12 h	33	5
9	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L1** (10 %)	DCM (0.05 M)	12 h	24	1
10	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L2** (10 %)	DCM (0.05 M)	12 h	27	3
11	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L3** (10 %)	DCM (0.05 M)	12 h	23	3
12	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L5** (10 %)	DCM (0.05 M)	12 h	35	3
13[b]	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L5** (10 %)	DCM (0.05 M)	12 h	33	3
14[c]	$Cu(OTf)_2.C_6H_6$ (5 mol%) + **L5** (10 %)	DCM (0.05 M)	12 h	23	3
15	Fe[TPP]Cl (10 mol%)	DCE (0.05 M)	24 h	<1	5
16	Fe**L4** (10 mol%)	DCE (0.05 M)	24 h	30	6
17	$[Ru(p\text{-cymene})_2Cl_2]$ (1 mol%)	DCM (0.05 M)	12 h	56	12
18	$[Ru(Pheox)(CH_3CN)_4]PF_6$ (**13**; 1 mol%)	DCM (0.05 M)	12 h	87	–
19[d,e]	$[Ru(Pheox)(CH_3CN)_4]PF_6$ (**13**; 1 mol%)	DCM (0.1 M)	2 h	95	–
20[d]	$[Ru(Pheox)(CH_3CN)_4]PF_6$ (**13**; 1 mol%)	DCM (0.1 M)	0.25 h	95	–

Yields were determined by ^{1}H-NMR using 1,1,2,2-tetrachloroethane as internal standard. [a] Poor mass balance was obtained due to low solubility of **S6**. [b] 30 min addition of **7a**; [c] 60 °C; [d] 1.25 equiv. of **7a**; [e] 15 min addition of **7a**. L1 = (S)-Ph-BOX; **L2** = 2,2'-bibyridine; **L3** = 1,10-phenanthroline; **L4** = phthalocyanine; **L5** = 4,4'-di-tert-butyl-2,2'-bipyridine; TPP = tetraphenyl porphyrin; Pheox = 4,4-dimethyl-2-phenyloxazolin-2'-yl.

3.2 Ru(II)-Pheox catalyzed C–H functionalization of indole using ethyl diazoacetate



A flame-dried vial was charged with a stirring bar and *N*-benzyl indole (**10a**; 21 mg, 0.10 mmol, 1.0 equiv.). The vial was evacuated and refilled with argon (three cycles), followed by the addition of a solution of Ru(II)-Pheox (**13**; 0.6 mg, 1.0 µmol, 1 mol%) in dry DCM (0.5 mL). The mixture was stirred for 5 min at room temperature and a solution of ethyl diazoacetate (18.0 mg, 0.12 mmol, 1.25 equiv.) in dry DCM (0.5 mL) was added slowly over a period of 15 min. The resulting mixture was stirred for another 45 min at room temperature. Upon completion, DCM was evaporated under reduced pressure and the crude ^{1}H-NMR of the insertion product **SI-1** was recorded using 1,1,2,2- tetrachloroethane as internal standard.

^{1}H-NMR yield: 62%

The crude ^{1}H-NMR data is in accordance with the literature.[21]

4. Scope Studies of Ru(II)-catalyzed C–H insertion on indoles

General procedure D: Ru(II)-Pheox catalyzed C–H insertion of indoles at the C3-position

A flame-dried vial was charged with a stirring bar and *N*-protected indole **10a-ab** (0.2-0.3 mmol, 1.0 equiv.). The vial was evacuated and refilled with argon (three cycles), followed by the addition of a solution of Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol 1 mol%) in dry DCM (1.0 mL). The mixture was stirred for 5 min at room temperature and a solution of NHPI-diazo compound (**7a**; 1.25 equiv.) in dry DCM was added in one portion (or via slow addition by a syringe pump as indicated in specific cases). The resulting mixture was stirred for the specified time at room temperature. Upon completion, DCM was evaporated under reduced pressure and the crude was purified by flash chromatography on SiO_2 to afford NHPI-ester of indoles **12a-ac**.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-1H-indol-3-yl)acetate (**12a**)*

General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-benzyl-1*H*-indole (**10a**; 41 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 15 min at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12a** (76 mg, 0.18 mmol, 93%).

Appearance: white solid.

m.p. = 143.8 – 146.1 °C.

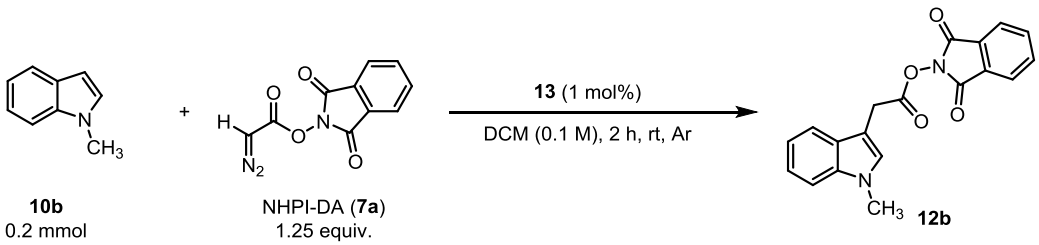
TLC: R_f = 0.41 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 – 7.87 (m, 2H), 7.79 – 7.77 (m, 2H), 7.69 (d, *J* = 8 Hz, 1H), 7.33 – 7.22 (m, 5H), 7.21 – 7.13 (m, 4H), 5.32 (s, 2H), 4.16 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 137.3, 136.5, 134.7, 129.0, 128.8, 127.7 (2Ar C-H), 127.5, 126.9, 124.0, 122.3, 119.8, 118.9, 109.9, 105.0, 50.2, 28.1.

HRMS (ESI-TOF) calc'd for $C_{25}H_{18}N_2O_4Na$ $[M+Na]^+$: 433.1158, found: 433.1152.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-methyl-1H-indol-3-yl)acetate (**12b**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-methyl-1*H*-indole (**10b**; 26 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 2 h at room temperature under argon. The diazo compound was added slowly over a period of 1 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12b** (55 mg, 0.16 mmol, 82%).

Appearance: brown solid.

TLC: R_f = 0.41 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

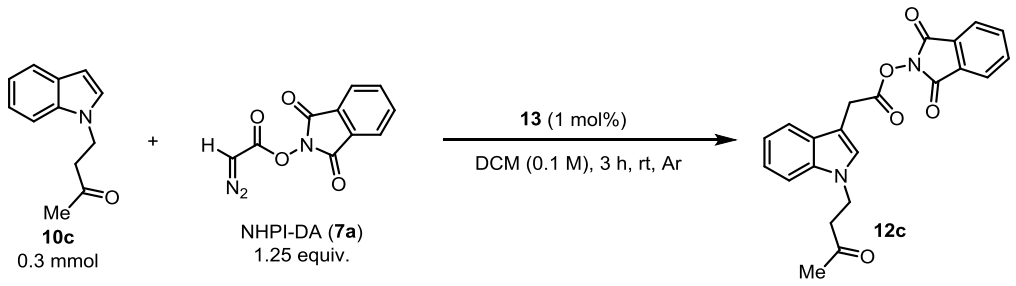
m.p. = 112.2 – 115.9 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 – 7.87 (m, 2H), 7.80 – 7.77 (m, 2H), 7.67 (d, *J* = 8 Hz, 1H), 7.34 (d, *J* = 8 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.20 – 7.16 (m, 2H), 4.16 (s, 2H), 3.79 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.1, 162.0, 136.8, 134.8, 128.8, 128.1, 127.3, 124.0, 122.0, 119.5, 118.7, 109.4, 104.1, 32.9, 28.0.

HRMS (ESI-TOF) calc'd for $C_{19}H_{14}N_2O_4Na$ $[M+Na]^+$: 357.0845, found: 357.0846.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(3-oxobutyl)-1H-indol-3-yl)acetate (**12c**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 4-(1H-indol-1-yl)butan-2-one (**10c**; 0.56 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 6:4) to afford compound **12c** (0.10 g, 0.27 mmol, 90%).

Appearance: brown oil.

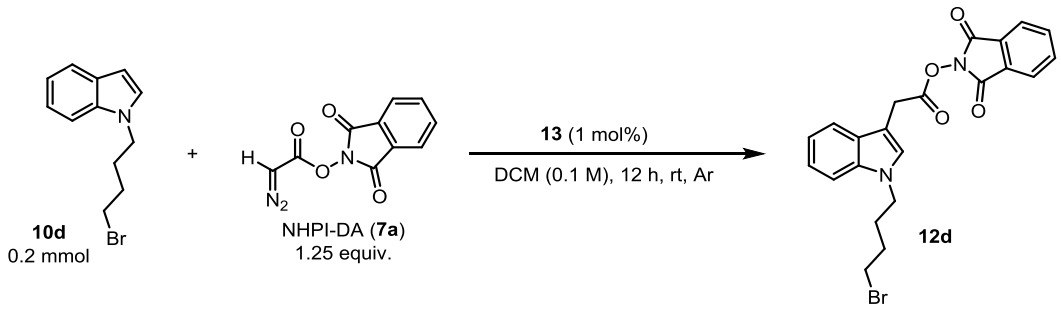
TLC: R_f = 0.5 (Petroleum ether/EtOAc = 6:4, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.85 (m, 2H), 7.81 – 7.75 (m, 2H), 7.64 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.33 (dt, *J* = 8.3, 1.0 Hz, 1H), 7.27 – 7.21 (m, 2H), 7.17 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.41 (t, *J* = 6.7 Hz, 2H), 4.12 (d, *J* = 0.9 Hz, 2H), 2.96 (t, *J* = 6.7 Hz, 2H), 2.12 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 206.1, 167.9, 161.9, 135.9, 134.7, 129.0, 127.6, 127.3, 123.9, 122.2, 119.7, 119.0, 109.3, 104.9, 43.5, 40.6, 30.4, 28.0.

HRMS (ESI-TOF) calc'd for $C_{22}H_{18}N_2O_5Na$ $[M+Na]^+$: 413.1108, found: 413.1103.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(4-bromobutyl)-1H-indol-3-yl)acetate (**12d**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-(4-bromobutyl)-1*H*-indole (**10d**; 50 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude

was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12d** (68 mg, 0.15 mmol, 75%).

Appearance: yellow solid.

TLC: R_f = 0.65 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

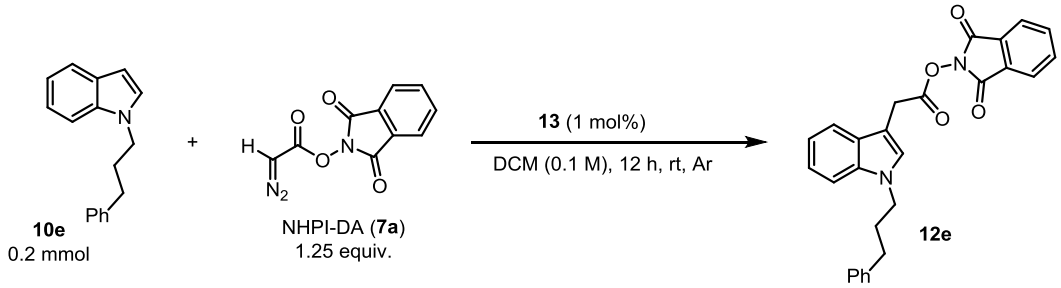
m.p. = 139.1 – 141.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 7.66 (d, *J* = 8 Hz, 1H), 7.35 (d, *J* = 8 Hz, 1H), 7.27 – 7.23 (m, 2H), 7.19 (t, *J* = 8 Hz, 1H), 4.18 – 4.14 (m, 4H), 3.40 (t, *J* = 6 Hz, 2H), 2.06 – 1.99 (m, 2H), 1.90 – 1.83 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 136.1, 134.7, 128.9, 127.5, 126.8, 123.9, 122.1, 119.6, 118.9, 109.4, 104.7, 45.5, 33.0, 29.9, 28.7, 28.1.

HRMS (ESI-TOF) calc'd for $C_{22}H_{19}BrN_2O_4Na$ $[M+Na]^+$: 477.0420, found: 477.0423.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(3-phenylpropyl)-1H-indol-3-yl)acetate (**12e**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-(3-phenylpropyl)-1*H*-indole (**10e**; 47 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12e** (68 mg, 0.15 mmol, 78%).

Appearance: white foam.

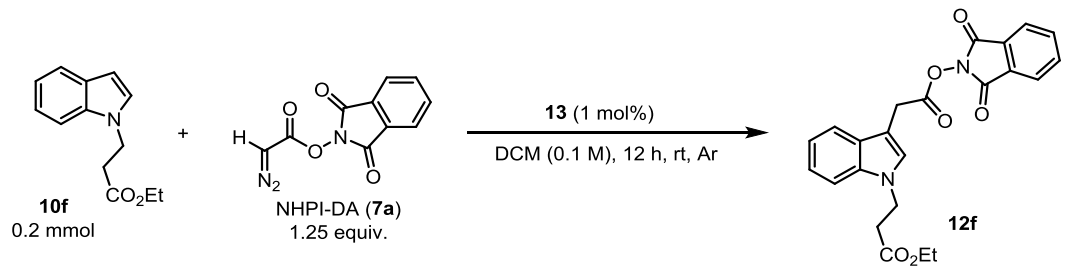
TLC: R_f = 0.4 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 – 7.86 (m, 2H), 7.80 – 7.76 (m, 2H), 7.67 (d, *J* = 8 Hz, 1H), 7.32 – 7.16 (m, 9H), 4.17 (s, 2H), 4.14 (t, *J* = 6 Hz, 2H), 2.67 (t, *J* = 8 Hz, 2H), 2.23 – 2.26 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.1, 162.0, 140.9, 136.1, 134.8, 128.8, 128.5, 128.4, 127.4, 127.1, 126.1, 124.0, 121.9, 119.5, 118.8, 109.6, 104.2, 45.6, 32.9, 31.5, 28.0.

HRMS (ESI-TOF) calc'd for $C_{27}H_{22}N_2O_4Na$ $[M+Na]^+$: 461.1471, found: 461.1476.

*Synthesis of ethyl 3-(3-(2-((1,3-dioxoisoindolin-2-yl)oxy)-2-oxoethyl)-1H-indol-1-yl)propanoate (**12f**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), ethyl 3-(1*H*-indol-1-yl)propanoate (**10f**; 43 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 6:4) to afford compound **12f** (54 mg, 0.13 mmol, 65%).

Appearance: puffy white solid.

TLC: R_f = 0.51 (Petroleum ether/EtOAc = 6:4, UV-active and stains in vanillin).

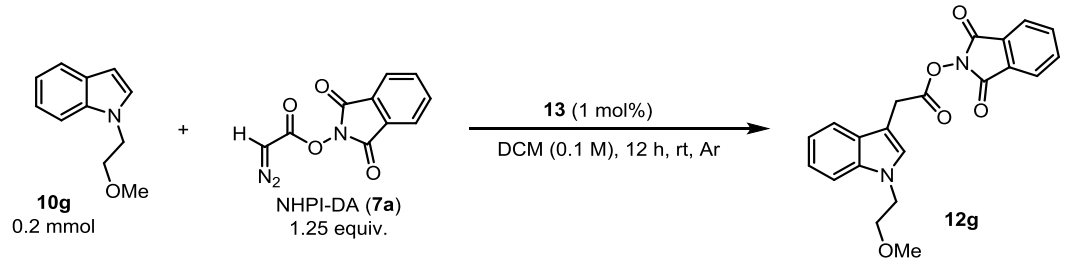
m.p. = 106.2 – 108.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 – 7.85 (m, 2H), 7.80 – 7.77 (m, 2H), 7.66 (d, *J* = 8 Hz, 1H), 7.37 – 7.34 (m, 1H), 7.28 (m, 1H), 7.20 (t, *J* = 8 Hz, 1H), 4.46 (t, *J* = 6 Hz, 2H), 4.14 (m, 4H), 2.84 (t, *J* = 6 Hz, 2H), 1.12 (t, *J* = 8 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 171.1, 167.8, 161.9, 135.9, 134.7, 128.9, 127.6, 127.1, 123.9, 122.2, 119.7, 118.9, 109.3, 104.9, 60.9, 41.8, 35.0, 28.0, 14.0.

HRMS (ESI-TOF) calc'd for $C_{23}H_{20}N_2O_6Na$ $[M+Na]^+$: 443.1213, found: 443.1218.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(2-methoxyethyl)-1H-indol-3-yl)acetate (**12g**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-(2-methoxyethyl)-1*H*-indole (**10g**; 35 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12g** (59 mg, 0.16 mmol, 78%).

Appearance: brown solid.

TLC: R_f = 0.53 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

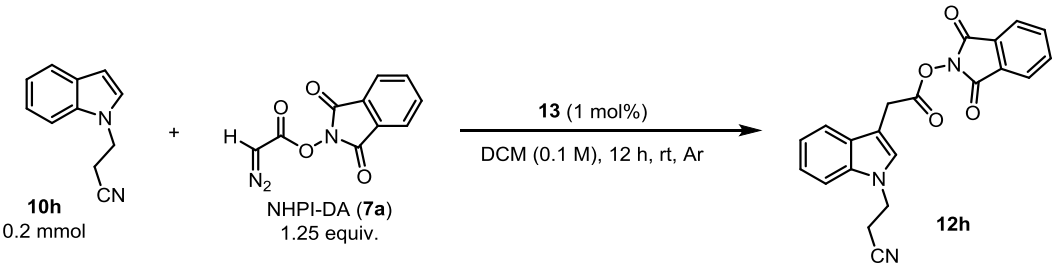
m.p. = 186.5 – 188.9 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.85 (m, 2H), 7.79 – 7.75 (m, 2H), 7.66 (d, *J* = 8 Hz, 1H), 7.36 (d, *J* = 8 Hz, 1H), 7.29 (s, 1H), 7.27 – 7.24 (m, 1H), 7.19 (t, *J* = 8 Hz, 1H), 4.29 (t, *J* = 6 Hz, 2H), 4.15 (s, 2H), 3.73 (t, *J* = 6 Hz, 2H), 3.32 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 136.3, 134.7, 128.9, 127.6, 127.5, 123.9, 122.0, 119.5, 118.8, 109.4, 104.6, 71.4, 59.1, 46.1, 28.1.

HRMS (ESI-TOF) calc'd for $C_{21}H_{18}N_2O_5Na$ $[M+Na]^+$: 401.1107, found: 401.1114.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(2-cyanoethyl)-1H-indol-3-yl)acetate (**12h**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 3-(1*H*-indol-1-yl)propanenitrile (**10h**; 34 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 7:3 to 1:1) to afford compound **12h** (51 mg, 0.14 mmol, 69%).

Appearance: white solid.

TLC: R_f = 0.48 (Petroleum ether/EtOAc = 1:1, UV-active and stains in vanillin).

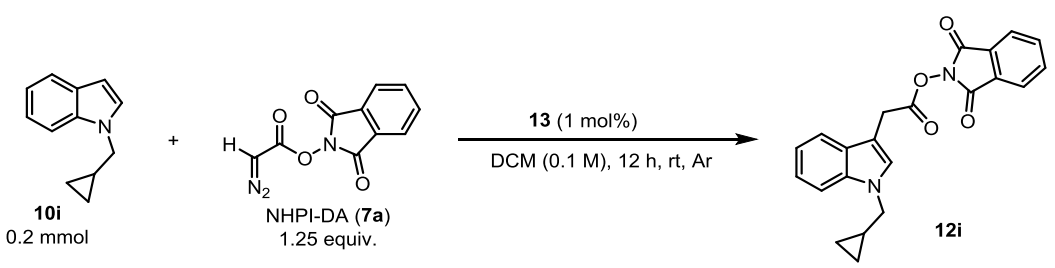
m.p. = 133.3 – 136.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 – 7.85 (m, 2H), 7.80 – 7.76 (m, 2H), 7.68 (d, *J* = 8 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.26 (s, 1H), 7.23 – 7.19 (m, 1H), 4.41 (t, *J* = 6 Hz, 2H), 4.13 (d, *J* = 1.0 Hz, 2H), 2.81 (t, *J* = 6 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.7, 161.9, 135.6, 134.8, 128.9, 127.8, 126.5, 123.9, 122.8, 120.4, 119.3, 117.1, 108.9, 106.3, 42.1, 28.0, 19.1.

HRMS (ESI-TOF) calc'd for $C_{21}H_{15}N_3O_5Na$ $[M+Na]^+$: 396.0954, found: 396.0951.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(cyclopropylmethyl)-1H-indol-3-yl)acetate (**12i**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-(cyclopropylmethyl)-1*H*-indole (**10i**; 34 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2

mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12i** (60 mg, 0.16 mmol, 80%).

Appearance: brown solid.

TLC: R_f = 0.42 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

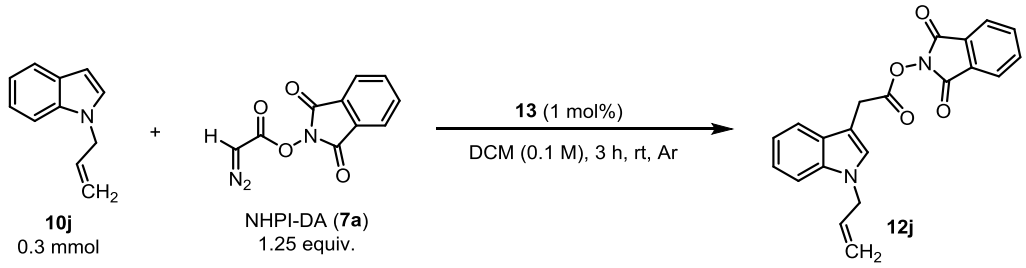
m.p. = 178.5 – 181.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.86 (m, 2H), 7.80 – 7.75 (m, 2H), 7.67 (d, *J* = 8 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.27 – 7.23 (m, 1H), 7.20 – 7.16 (m, 1H), 4.18 (d, *J* = 1 Hz, 2H), 3.98 (d, *J* = 8 Hz, 2H), 1.33 – 1.23 (m, 1H), 0.67 – 0.62 (m, 2H), 0.41 – 0.37 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.1, 162.0, 136.3, 134.8, 128.8, 127.3, 126.7, 124.0, 121.9, 119.5, 118.8, 109.6, 104.2, 50.0, 28.1, 11.2, 4.2.

HRMS (ESI-TOF) calc'd for $C_{22}H_{18}N_2O_4Na$ $[M+Na]^+$: 397.1158, found: 397.1159.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-allyl-1H-indol-3-yl)acetate (**12j**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-allyl-1*H*-indole (**10j**; 47 mg, 0.3 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 6:4) to afford compound **12j** (96 mg, 0.26 mmol, 89%).

Appearance: Foamy solid.

TLC: R_f = 0.45 (Petroleum ether/EtOAc = 6:4, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.85 (m, 2H), 7.80 – 7.74 (m, 2H), 7.66 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.27 – 7.21 (m, 2H), 7.18 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.05 – 5.95 (m, 1H), 5.21 (dq, *J* = 10.2, 1.4 Hz, 1H), 5.12 (dq, *J* = 17.1, 1.6 Hz, 1H), 4.72 (dt, *J* = 5.4, 1.6 Hz, 2H), 4.16 (d, *J* = 0.9 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.0, 161.9, 136.3, 134.7, 133.3, 128.9, 127.6, 127.1, 124.0, 122.1, 119.7, 118.8, 117.5, 109.8, 104.7, 48.9, 28.0.

HRMS (ESI-TOF) calc'd for $C_{21}H_{16}N_2O_4Na$ $[M+Na]^+$: 383.1002, found: 383.1004.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-phenyl-1H-indol-3-yl)acetate (**12k**)*

General procedure D was applied using NHPI-DA (**7a**; 72 mg, 0.31 mmol, 1.25 equiv.), 1-phenyl-1*H*-indole (**10k**; 48 mg, 0.25 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.5 mg, 2.5 µmol, 1.0 mol%) in DCM (2.5 mL) for 2 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12k** in (76 mg, 0.19 mmol, 77%).

Appearance: yellow solid.

m.p. = 240.2 – 243.6 °C

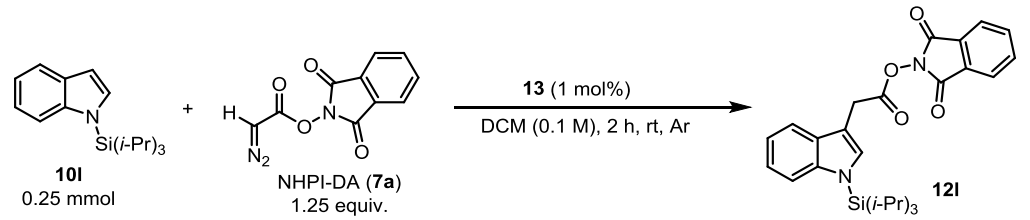
TLC: Rf = 0.55 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.87 (m, 2H), 7.81 – 7.77 (m, 2H), 7.73 – 7.71 (m, 1H), 7.58 – 7.56 (m, 1H), 7.53 – 7.50 (m, 5H), 7.39 – 7.34 (m, 1H), 7.29 – 7.22 (m, 2H), 4.22 (d, *J* = 0.9 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) = 167.7, 161.9, 139.6, 136.0, 134.7, 129.6, 128.9, 128.2, 127.1, 126.5, 124.3, 123.9, 122.9, 120.5, 118.9, 110.7, 106.9, 28.0.

HRMS (ESI-TOF) calc'd for $C_{24}H_{16}N_2O_4Na$ $[M+Na]^+$: 419.1002; found: 419.1000.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-(triisopropylsilyl)-1H-indol-3-yl)acetate (**12l**)*



General procedure D was applied using NHPI-DA (**7a**; 72 mg, 0.31 mmol, 1.25 equiv.), 1-(triisopropylsilyl)-1*H*-indole (**10l**; 68 mg, 0.25 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.5 mg, 2.5 µmol, 1.0 mol%) in DCM (2.5 mL) for 2 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12l** (96 mg, 0.20 mmol, 81%).

Appearance: yellow solid.

TLC: R_f = 0.55 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

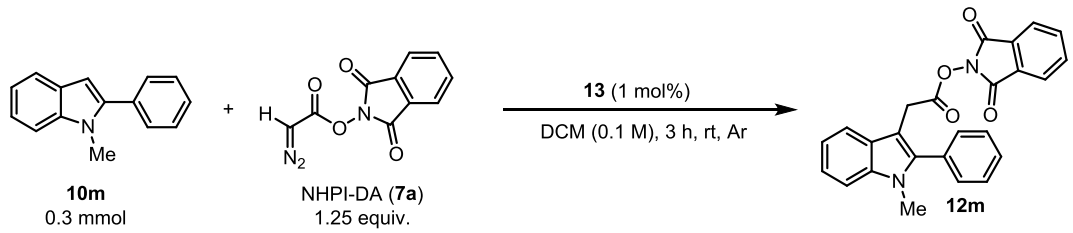
m.p. = 127.9 – 130.6 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.86 (m, 2H), 7.79 – 7.74 (m, 2H), 7.66 – 7.62 (m, 1H), 7.53 – 7.49 (m, 1H), 7.38 (s, 1H), 7.21 – 7.16 (m, 2H), 4.16 (s, 2H), 1.76 (m, 3H), 1.17 (d, *J* = 8 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) = 167.9, 161.9, 141.1, 134.6, 130.3, 130.3, 129.0, 123.9, 121.8, 119.9, 118.4, 114.1, 108.0, 28.1, 18.1, 12.8.

HRMS (ESI-TOF) calc'd for $C_{27}H_{32}N_2O_4SiNa$ $[M+Na]^+$: 499.2023, found: 499.2024.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-methyl-2-phenyl-1H-indol-3-yl)acetate (**12m**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-methyl-2-phenyl-1*H*-indole (**10m**; 62 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12m** (86 mg, 0.21 mmol, 70%).

Appearance: light-yellow solid.

TLC: R_f = 0.62 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

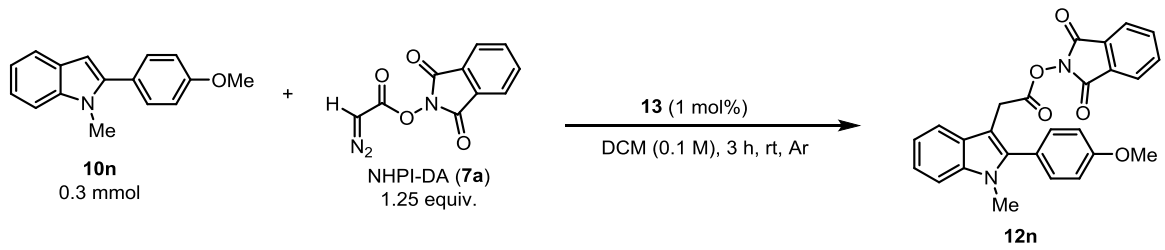
m.p. = 148.9 – 151.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (pm) = 7.89 – 7.84 (m, 2H), 7.79 – 7.73 (m, 3H), 7.58 – 7.52 (m, 2H), 7.51 – 7.46 (m, 3H), 7.37 (dt, *J* = 8.1, 0.9 Hz, 1H), 7.30 (ddd, *J* = 8.2, 7.0, 1.3 Hz, 1H), 7.23 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 4.02 (s, 2H), 3.64 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.3, 161.9, 140.0, 137.2, 134.7, 130.7, 130.7, 129.0, 128.7, 128.7, 127.3, 123.9, 122.3, 120.1, 119.0, 109.5, 103.2, 31.0, 27.9.

HRMS (ESI-TOF) calc'd for $C_{25}H_{18}N_2O_4Na$ $[M+Na]^+$: 433.1159; found: 433.1152.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(2-(4-methoxyphenyl)-1-methyl-1H-indol-3-yl)acetate (**12n**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 2-(4-methoxyphenyl)-1-methyl-1*H*-indole (**10n**; 71 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 7:3) to afford compound **12n** (82 mg, 0.19 mmol, 62%).

Appearance: white solid.

TLC: R_f = 0.46 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

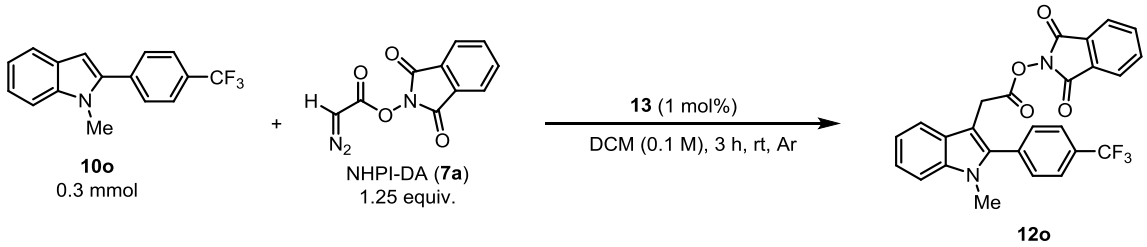
m.p. = 141.1 – 143.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.86 (m, 2H), 7.79 – 7.71 (m, 3H), 7.44 – 7.39 (m, 2H), 7.35 (dt, *J* = 8.2, 1.0 Hz, 1H), 7.31 – 7.26 (m, 1H), 7.22 (ddd, *J* = 8.0, 6.9, 1.2 Hz, 1H), 7.09 – 7.05 (m, 2H), 4.01 (s, 2H), 3.90 (s, 3H), 3.63 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.4, 161.9, 159.9, 139.9, 137.0, 134.7, 131.9, 129.0, 127.3, 123.9, 122.9, 122.1, 120.0, 118.8, 114.2, 109.5, 102.9, 55.4, 30.9, 28.0.

HRMS (ESI-TOF) calc'd for $C_{26}H_{20}N_2O_5Na$ $[M+Na]^+$: 463.1264, found: 463.1265.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-methyl-2-(4-(trifluoromethyl)phenyl)-1H-indol-3-yl)acetate (**12o**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.25 mmol, 1.25 equiv.), 1-methyl-2-(4-(trifluoromethyl)phenyl)-1*H*-indole (**10o**; 83 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12o** (59 mg, 0.12 mmol, 44%).

Appearance: white solid.

TLC: R_f = 0.62 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

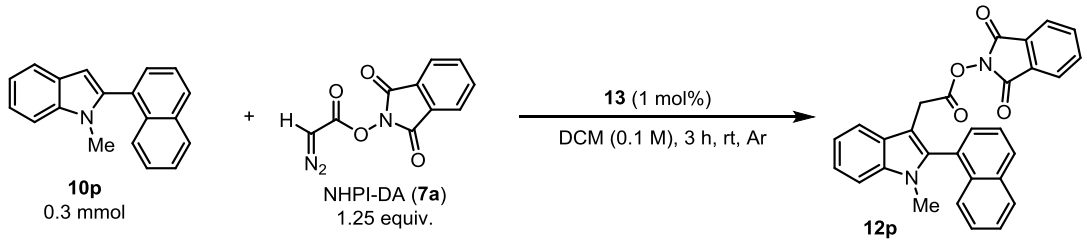
m.p. = 126.9 – 129.7 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.84 (m, 2H), 7.84 – 7.80 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.74 (m, 3H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.39 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.33 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.25 (m, 1H), 4.01 (s, 2H), 3.65 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.1, 161.9, 138.2, 137.4, 134.7, 134.5, 131.0, 130.9 (q, $^2J_{C\text{-}F}$ = 32 Hz), 128.9, 127.2, 125.8 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 125.4 (q, $^1J_{C\text{-}F}$ = 271 Hz), 123.9, 122.9, 120.4, 119.1, 109.7, 104.1, 31.1, 27.8.

HRMS (ESI-TOF) calc'd for $C_{26}H_{17}F_3N_2O_4Na$ $[M+Na]^+$: 501.1032, found: 501.1029.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-methyl-2-(naphthalen-1-yl)-1H-indol-3-yl)acetate (**12p**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-methyl-2-(naphthalen-1-yl)-1*H*-indole (**10p**; 77 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12p** (0.13 g, 0.28 mmol, 93%).

Appearance: brown solid.

TLC: R_f = 0.57 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

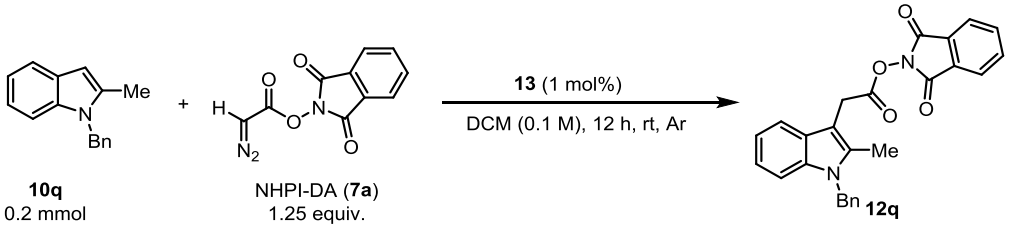
m.p. = 74.3 – 77.8 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.02 (m, 1H), 7.97 (dd, *J* = 8.6, 1.3 Hz, 1H), 7.84 (m, 3H), 7.77 – 7.73 (m, 2H), 7.67 – 7.62 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.41 (m, 2H), 7.35 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.29 (m, 1H), 4.01 (d, *J* = 16.9 Hz, 1H), 3.84 (d, *J* = 16.8 Hz, 1H), 3.46 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.0, 161.9, 138.2, 137.2, 134.7, 133.6, 133.1, 130.1, 129.7, 129.0, 128.4, 128.2, 127.3, 127.0, 126.3, 125.7, 125.5, 123.9, 122.2, 120.1, 119.1, 109.5, 104.5, 30.8, 28.0.

HRMS (ESI-TOF) calc'd for $C_{29}H_{20}N_2O_4Na$ $[M+Na]^+$: 483.1315, found: 483.1307.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-2-methyl-1H-indol-3-yl)acetate (**12q**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-benzyl-2-methyl-1*H*-indole (**10q**; 44 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12q** (64 mg, 0.15 mmol, 76%).

Appearance: white solid.

m.p. = 180.1 – 182.9 °C

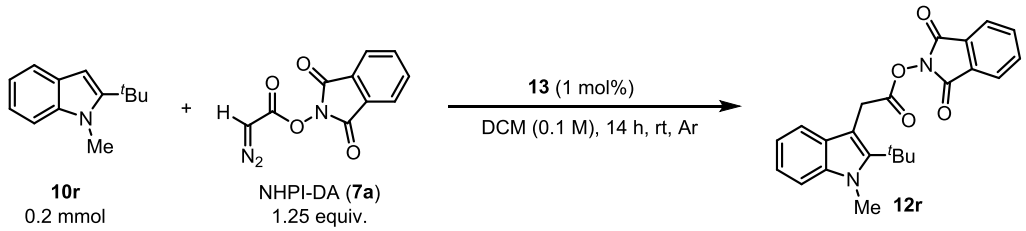
TLC: R_f = 0.52 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 – 7.84 (m, 2H), 7.78 – 7.74 (m, 2H), 7.67 – 7.64 (m, 1H), 7.29 – 7.20 (m, 4H), 7.19 – 7.23 (m, 2H), 6.99 (d, *J* = 8 Hz, 2H), 5.34 (s, 2H), 4.13 (s, 2H), 2.40 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.8, 161.8, 137.5, 136.4, 135.1, 134.6, 128.9, 128.8, 127.5, 127.3, 125.9, 123.9, 121.4, 119.8, 117.9, 109.2, 102.0, 46.6, 27.4, 10.4.

HRMS (ESI-TOF) calc'd for $C_{26}H_{20}N_2O_4Na$ $[M+Na]^+$: 447.1315, found: 447.1316.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(2-(tert-butyl)-1-methyl-1H-indol-3-yl)acetate (**12r**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 2-(tert-butyl)-1-methyl-1*H*-indole (**10r**; 37 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 14 h at room temperature under argon. The diazo compound was added slowly over a period of 12 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12r** (30 mg, 0.08 mmol, 38%).

Appearance: pale-yellow solid.

m.p. = 197.2 – 199.7 °C.

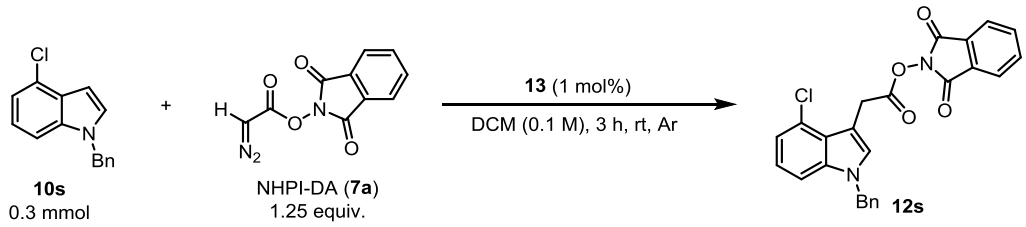
TLC: R_f = 0.57 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.88 – 7.83 (m, 2H), 7.79 – 7.74 (m, 2H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.9 Hz, 1H), 7.22 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.16 (ddd, *J* = 8.1, 6.9, 1.3 Hz, 1H), 4.38 (s, 2H), 3.91 (s, 3H), 1.62 (s, 9H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.8, 162.0, 144.6, 137.5, 134.7, 128.9, 128.5, 123.9, 121.9, 119.7, 117.6, 108.8, 100.6, 34.5, 33.6, 31.2, 28.9.

HRMS (ESI-TOF) calc'd for $C_{23}H_{22}N_2O_4Na$ $[M+Na]^+$: 413.1471, found: 413.1469.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-4-chloro-1H-indol-3-yl)acetate (**12s**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-4-chloro-2-methyl-1*H*-indole (**10s**; 73 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12s** (96 mg, 0.22 mmol, 72%).

Appearance: off-white solid.

TLC: R_f = 0.6 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

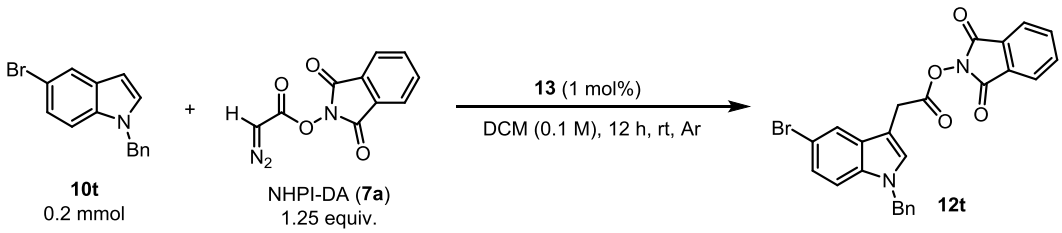
m.p. = 139.7 – 142.4 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.87 (m, 2H), 7.76 (m, 2H), 7.33 – 7.23 (m, 4H), 7.14 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.12 – 7.02 (m, 4H), 5.27 (s, 2H), 4.45 (d, *J* = 0.9 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.5, 161.9, 137.8, 136.7, 134.7, 129.1, 128.9, 128.9, 127.8, 126.8, 126.3, 124.5, 123.9, 122.8, 120.6, 108.8, 105.4, 50.4, 29.3.

HRMS (ESI-TOF) calc'd for $C_{25}H_{17}ClN_2O_4Na$ $[M+Na]^+$: 467.0769, found: 467.0766.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-bromo-1H-indol-3-yl)acetate (**12t**)*



General procedure D was applied using NHPI-DA (**7a**; 57 mg, 0.25 mmol, 1.25 equiv.), 1-benzyl-5-bromo-2-methyl-1*H*-indole (**10t**; 60 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12t** (68 mg, 0.14 mmol, 70%).

Appearance: white solid.

TLC: R_f = 0.55 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

m.p. = 165.3 – 168.6 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.86 (m, 2H), 7.81 – 7.76 (m, 3H), 7.33 – 7.26 (m, 5H), 7.14 – 7.09 (m, 3H), 5.29 (s, 2H), 4.10 (d, *J* = 0.8 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.6, 161.8, 136.7, 135.1, 134.7, 129.3, 128.9, 128.8, 128.7, 127.8, 126.7, 125.2, 124.0, 121.5, 113.2, 111.4, 104.6, 50.3, 27.9.

HRMS (ESI-TOF) calc'd for $C_{25}H_{17}BrN_2O_4Na$ $[M+Na]^+$: 511.0245, found: 511.0240.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-iodo-1H-indol-3-yl)acetate (**12u**)*

General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-benzyl-5-iodo-2-methyl-1*H*-indole (**10u**; 69 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 2 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12u** (71 mg, 0.13 mmol, 66%).

Appearance: white solid.

TLC: R_f = 0.65 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

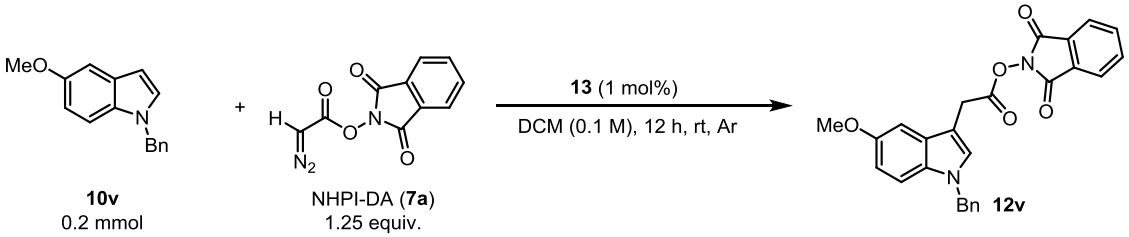
m.p. = 157.2 – 159.8 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.00 (d, *J* = 1.2 Hz, 1H), 7.91 – 7.86 (m, 2H), 7.81 – 7.77 (m, 2H), 7.45 (d, *J* = 8 Hz, 1H), 7.33 – 7.27 (m, 3H), 7.24 (s, 1H), 7.11 (d, *J* = 8 Hz, 2H), 7.05 (d, *J* = 8 Hz, 1H), 5.28 (s, 2H), 4.10 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) **=** 167.6, 161.8, 136.7, 135.6, 134.7, 130.6, 130.1, 128.9, 128.8, 128.3, 127.8, 127.8, 126.7, 124.0, 111.4, 104.4, 83.3, 50.3, 27.8.

HRMS (ESI-TOF) calc'd for $C_{25}H_{17}IN_2O_4Na$ $[M+Na]^+$: 559.0125, found: 559.0124.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-methoxy-1H-indol-3-yl)acetate (**12v**)*



General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-benzyl-5-methoxy-2-methyl-1*H*-indole (**10v**; 50 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12v** (63 mg, 0.14 mmol, 72%).

Appearance: white solid.

TLC: R_f = 0.37 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

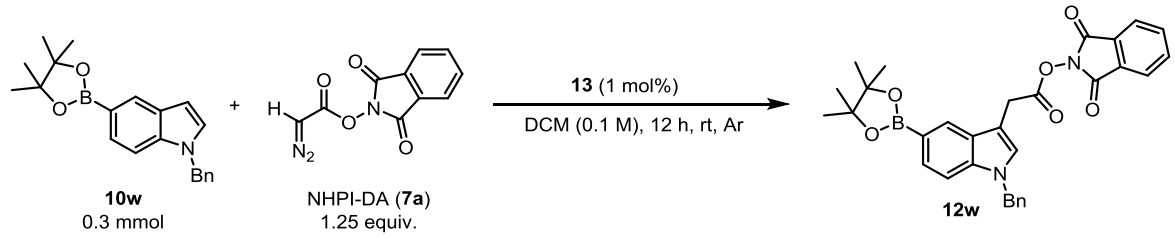
m.p. = 153.3 – 155.1 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.90 – 7.86 (m, 2H), 7.80 – 7.75 (m, 2H), 7.32 – 7.75 (m, 3H), 7.22 (s, 1H), 7.16 – 7.11 (m, 4H), 6.87 (dd, *J* = 8.9, 2.4 Hz, 1H), 5.27 (s, 2H), 4.13 (d, *J* = 2.4 Hz, 2H), 3.90 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 154.4, 137.3, 134.7, 131.7, 128.9, 128.7, 128.1, 128.0, 127.6, 126.7, 123.9, 112.7, 110.8, 104.5, 100.3, 55.8, 50.3, 28.1.

HRMS (ESI-TOF) calc'd for $C_{26}H_{20}N_2O_5Na$ $[M+Na]^+$: 463.1264, found: 463.1271.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indol-3-yl)acetate (**12w**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1*H*-indole (**10w**; 0.10 g, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 12 h at room temperature under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12w** (90 mg, 0.18 mmol, 60%).

Appearance: white solid.

TLC: R_f = 0.65 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

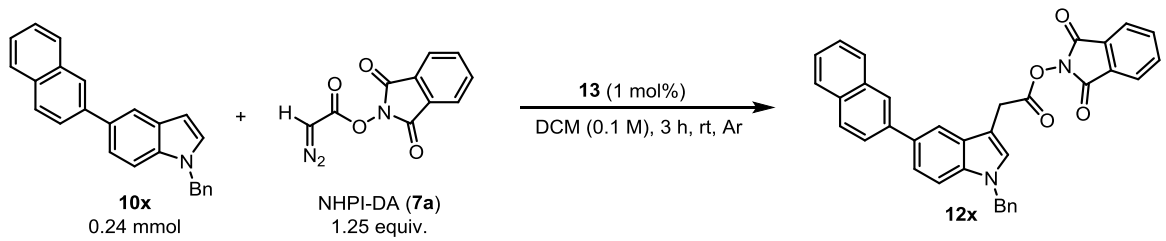
m.p. = 190.9 – 193.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.17 (s, 1H), 7.88 (m, 2H), 7.80 – 7.74 (m, 2H), 7.66 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.33 (s, 1H), 7.32 – 7.22 (m, 4H), 7.11 (dd, *J* = 8.1, 1.5 Hz, 2H), 5.32 (s, 2H), 4.20 (s, 2H), 1.37 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 138.4, 137.2, 134.7, 129.0, 128.8, 128.4, 127.6, 127.6, 127.5, 126.8, 126.3, 123.9, 109.3, 105.8, 83.5, 50.1, 27.8, 24.9.

HRMS (ESI-TOF) calc'd for $C_{31}H_{29}BN_2O_4Na$ $[M+Na]^+$: 559.2016, found: 559.2017.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-(naphthalen-2-yl)-1H-indol-3-yl)acetate (**12x**)*



General procedure D was applied using NHPI-DA (69 mg, 0.30 mmol, 1.25 equiv.), 1-benzyl-5-(naphthalen-2-yl)-1*H*-indole (**10y**; 80 mg, 0.24 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.4 mg, 2.4 µmol, 1.0 mol%) in DCM (2.4 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12x** (97 mg, 0.18 mmol, 75%).

Appearance: yellow solid.

TLC: R_f = 0.48 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

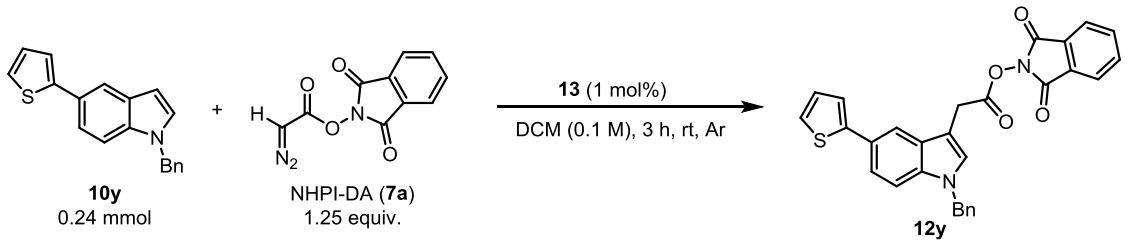
m.p. = 76.4 – 80.5 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.15 (d, *J* = 1.2 Hz, 1H), 8.02 (dd, *J* = 1.8, 0.7 Hz, 1H), 7.95 – 7.91 (m, 2H), 7.90 – 7.84 (m, 4H), 7.79 – 7.74 (m, 2H), 7.60 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.53 – 7.44 (m, 2H), 7.37 (dd, *J* = 8.6, 0.7 Hz, 1H), 7.36 – 7.27 (m, 4H), 7.20 – 7.17 (m, 2H), 5.35 (s, 2H), 4.23 (d, *J* = 0.9 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 168.0, 161.9, 139.6, 137.2, 136.1, 134.7, 133.9, 133.2, 132.3, 129.0, 128.9, 128.3, 128.3, 128.2, 128.2, 127.8, 127.6, 126.9, 126.3, 126.1, 125.7, 125.5, 124.0, 122.4, 117.7, 110.4, 105.5, 50.3, 28.1.

HRMS (ESI-TOF) calc'd for $C_{35}H_{24}N_2O_4Na$ $[M+Na]^+$: 559.1628, found: 559.1624.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-5-(thiophen-2-yl)-1H-indol-3-yl)acetate (**12y**)*



General procedure D was applied using NHPI-DA (**7a**; 69 mg, 0.30 mmol, 1.25 equiv.), 1-benzyl-5-(thiophen-2-yl)-1*H*-indole (**10y**; 69 mg, 0.24 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.4 mg, 2.4 µmol, 1.0 mol%) in DCM (2.4 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12y** (55 mg, 0.11 mmol, 47%).

Appearance: greenish solid.

TLC: R_f = 0.55 (Petroleum ether/EtOAc = 8:2, UV-active and stains in vanillin).

m.p. = 151.7 – 153.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.89 (m, 3H), 7.81 – 7.75 (m, 2H), 7.48 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.33 – 7.31 (m, 2H), 7.30 – 7.28 (m, 2H), 7.28 – 7.24 (m, 2H), 7.23 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.17 – 7.12 (m, 2H), 7.08 (dd, *J* = 5.1, 3.6 Hz, 1H), 5.32 (s, 2H), 4.18 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.8, 161.9, 145.8, 137.0, 136.1, 134.7, 129.0, 128.9, 128.4, 128.1, 127.9, 127.8, 126.8, 126.7, 124.0, 123.7, 122.3, 121.4, 116.3, 110.3, 105.5, 50.3, 28.0.

HRMS (ESI-TOF) calc'd for $C_{29}H_{20}N_2O_4SNa$ $[M+Na]^+$: 515.1035, found: 515.1045.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-6-(p-tolyl)-1H-indol-3-yl)acetate (**12z**)*

General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-6-(*p*-tolyl)-1*H*-indole (**10z**; 89 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12z** (0.12 g, 0.25 mmol, 84%).

Appearance: white solid.

TLC: R_f = 0.6 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

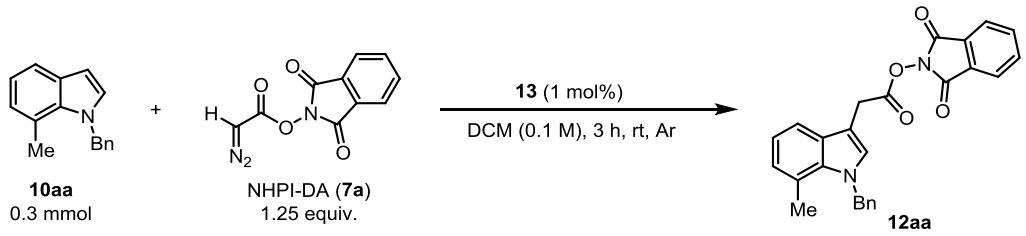
m.p. = 124.8 – 126.1 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.86 (m, 2H), 7.80 – 7.75 (m, 2H), 7.73 (dd, *J* = 8.2, 0.8 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.47 – 7.42 (m, 2H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.25 – 7.23 (m, 2H), 7.20 – 7.15 (m, 2H), 5.35 (s, 2H), 4.18 (d, *J* = 0.7 Hz, 2H), 2.40 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 139.4, 137.2, 137.1, 136.4, 135.9, 134.7, 129.4, 129.0, 128.8, 128.1, 127.7, 127.3, 126.9, 126.8, 124.0, 119.7, 119.1, 108.2, 105.0, 50.1, 28.1, 21.1.

HRMS (ESI-TOF) calc'd for $C_{32}H_{24}N_2O_4Na$ $[M+Na]^+$: 523.1628, found: 523.1626.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(1-benzyl-7-methyl-1H-indol-3-yl)acetate (**12aa**)*



General procedure D was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-7-methyl-1*H*-indole (**10aa**; 66 mg, 0.30 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12aa** (94 mg, 0.22 mmol, 74%).

Appearance: white solid.

TLC: R_f = 0.6 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

m.p. = 157.1 – 159.8 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.91 – 7.85 (m, 2H), 7.80 – 7.75 (m, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.31 – 7.23 (m, 3H), 7.21 (s, 1H), 7.09 – 7.05 (m, 1H), 6.97 – 6.89 (m, 3H), 5.57 (s, 2H), 4.16 (d, *J* = 0.9 Hz, 2H), 2.52 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 167.9, 161.9, 139.4, 135.3, 134.7, 129.4, 129.0, 128.9, 128.7, 127.3, 125.5, 125.2, 123.9, 121.3, 120.1, 116.8, 105.1, 52.3, 28.0, 19.5.

HRMS (ESI-TOF) calc'd for $C_{26}H_{20}N_2O_4Na$ $[M+Na]^+$: 447.1315; found: 447.1316.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(7-formyl-1-methyl-1H-indol-3-yl)acetate (**12ab**)*

General procedure D was applied using NHPI-DA (**7a**; 58 mg, 0.25 mmol, 1.25 equiv.), 1-methyl-1*H*-indole-7-carbaldehyde (**10ab**; 32 mg, 0.20 mmol, 1.0 equiv.) and Ru(II)-Pheox (**13**; 1.2 mg, 2.0 µmol, 1.0 mol%) in DCM (2.0 mL) for 3 h at room temperature under argon. The diazo compound was added slowly over a period of 2 h by a syringe pump. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 7:3) to afford compound **12ab** (37 mg, 0.10 mmol, 51%).

Appearance: brown solid.

TLC: R_f = 0.35 (Petroleum ether/EtOAc = 7:3, UV-active and stains in vanillin).

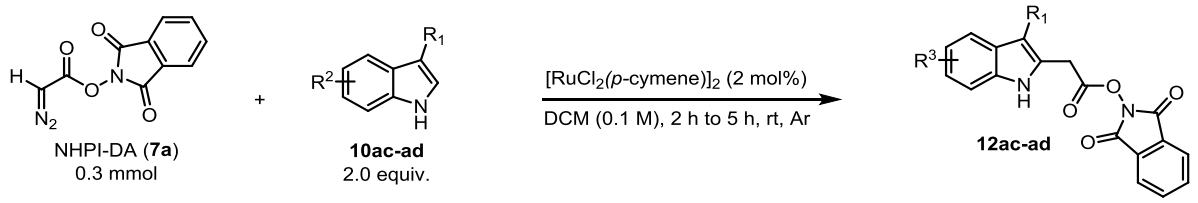
m.p. = 148.9 – 151.7 °C

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 10.22 (s, 1H), 7.91 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.89 – 7.87 (m, 2H), 7.80 – 7.78 (m, 2H), 7.75 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.21 (s, 1H), 4.14 (d, *J* = 0.9 Hz, 2H), 4.13 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 191.0, 167.7, 161.9, 134.8, 134.0, 131.8, 130.8, 130.4, 128.9, 125.8, 124.0, 123.2, 119.1, 105.5, 39.1, 27.8.

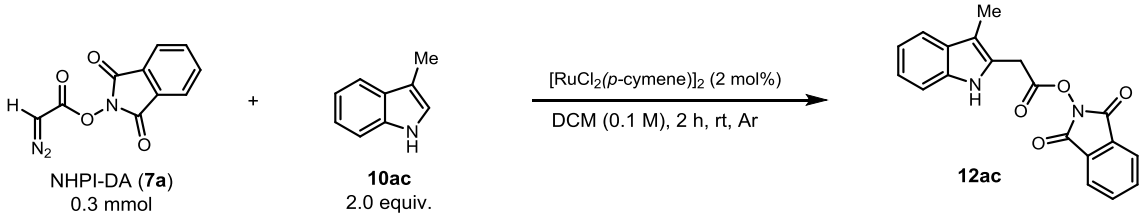
HRMS (ESI-TOF) calc'd for $C_{20}H_{14}N_2O_5Na$ $[M+Na]^+$: 385.0794, found: 357.0774.

General procedure E: Ru(II)- catalyzed C–H insertion of indoles at the C2 position



A flame-dried vial was charged with a stirring bar, unprotected indole (0.60 mmol, 2.0 equiv.), and $[RuCl_2(p\text{-cymene})]_2$ (3.7 mg, 6.0 µmol, 2.0 mol%). The vial was evacuated and refilled with argon (three cycles), followed by the addition of dry DCM (1.0 mL). Next, a solution of NHPI-diazo compound (**7a**; 69 mg, 0.30 mmol, 1.0 equiv.) in DCM (2.0 mL) was added to the mixture of the indole and the catalyst in one shot at room temperature. After complete addition, the resulting mixture was allowed to stir until full conversion of the diazo compound (as monitored by TLC). Upon completion of the reaction, DCM was evaporated under reduced pressure and the crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 8:2 to 6:4) to afford NHPI-ester of indoles **12ac-ad**.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(3-methyl-1H-indol-2-yl)acetate (**12ac**)*



General procedure E was applied using NHPI-DA (**7a**; 69 mg, 0.30 mmol, 1.0 equiv.), 3-methyl-1*H*-indole (**10ac**; 79 mg, 0.60 mmol, 2.0 equiv.) and $[RuCl_2(p\text{-cymene})]_2$ (3.6 mg, 6.0 µmol, 2.0 mol%) in DCM (3.0 mL) for 2 h at room temperature under argon. The diazo compound, dissolved in DCM (2.0 mL), was added in one portion. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12ac** (79 mg, 0.24 mmol, 79%).

Appearance: yellow solid.

TLC: R_f = 0.51 (pentane/EtOAc = 7:3, UV-active and stains in vanillin).

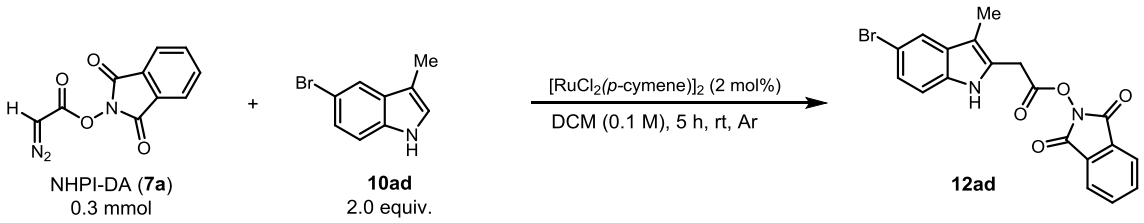
m.p. = 154.8 – 157.6 °C.

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.50 (s, 1H), 7.92 – 7.87 (m, 2H), 7.82 – 7.77 (m, 2H), 7.54 (d, *J* = 7.8 Hz, 1H), 7.36 – 7.34 (m, 1H), 7.19 (ddd, *J* = 8.1, 7.0, 1.3 Hz, 1H), 7.12 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 4.15 (s, 2H), 2.32 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 166.7, 161.8, 135.9, 135.0, 128.8, 128.6, 124.1, 123.4, 122.3, 119.4, 118.7, 110.9, 110.4, 29.1, 8.5.

HRMS (ESI-TOF) calc'd for $C_{19}H_{14}N_2O_4Na$ $[M+Na]^+$: 357.0846, found: 357.0844.

*Synthesis of 1,3-dioxoisoindolin-2-yl 2-(5-bromo-3-methyl-1H-indol-2-yl)acetate (**12ad**)*



General procedure E was applied using NHPI-DA (**7a**; 69 mg, 0.30 mmol, 1.0 equiv.), 5-bromo-3-methyl-1*H*-indole (**10ad**; 0.13 g, 0.60 mmol, 2.0 equiv.) and $[RuCl_2(p\text{-cymene})]_2$ (3.6 mg, 6.0 µmol, 2 mol%) in DCM (3.0 mL) for 5 h at room temperature under argon. The diazo compound, dissolved in DCM (2.0 mL), was added in one portion. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **12ad** (75 mg, 0.18 mmol, 60%).

Appearance: yellow solid.

TLC: R_f = 0.48 (pentane/EtOAc = 7:3, UV-active and stains in vanillin).

m.p. = 171.8 – 173.5 °C.

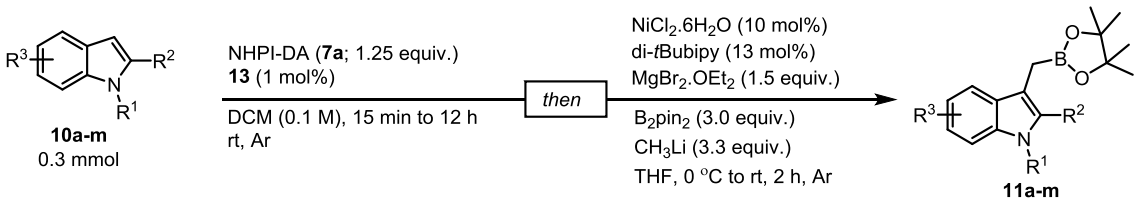
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 8.63 (s, 1H), 7.92 – 7.86 (m, 2H), 7.83 – 7.78 (m, 2H), 7.64 (d, *J* = 1.7 Hz, 1H), 7.26 – 7.24 (m, 1H), 7.21 (d, *J* = 8.5, 1H), 4.13 (s, 2H), 2.26 (s, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 166.5, 161.8, 135.0, 134.5, 130.4, 128.7, 125.0, 124.8, 124.2, 121.3, 112.7, 112.3, 110.0, 29.1, 8.5.

HRMS (ESI-TOF) calc'd for $C_{19}H_{13}BrN_2O_4Na$ $[M+Na]^+$: 434.9951, found: 434.9948.

5. Diversification of redox-active ester products

General Procedure E: One pot methylborylation of indoles

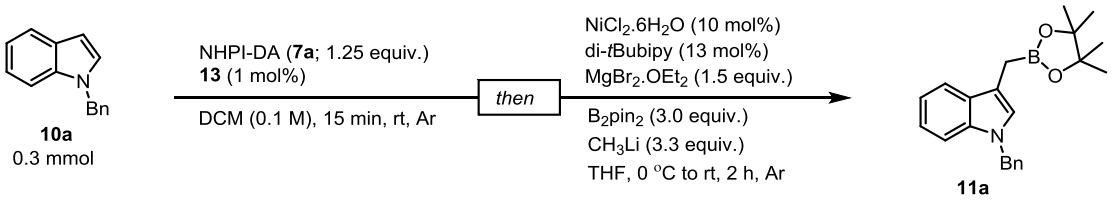


The procedure has been adapted from the one reported by Baran.[22]

General procedure D was applied for the synthesis of redox-active ester of indoles using indole **10a-m**; (0.30 mmol, 1.0 equiv.), NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 15 min to 12 h at room temperature under argon. Upon completion, DCM was removed under reduced pressure and $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.) was added to the crude NHPI-ester. The vial was closed with a screw cap fitted with a Teflon septa, followed by evacuation and refilling with argon (three cycles). Anhydrous THF (1.2 mL) was added and the mixture was sonicated until no granular $MgBr_2.OEt_2$ was observed (*c.a.* 2-3 min).

A light-green coloured suspension of $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (di-*t*Bubipy; 10.5 mg, 0.04 µmol, 0.13 equiv.) in THF (0.6 mL; prepared from 2-3 h stirring under argon) was added to the vial containing the redox-active ester and $MgBr_2.OEt_2$ via a syringe. The resulting mixture was stirred vigorously for 5 min until no visible solid was observed on the bottom of the vial. In a separate flask, a suspension of $[B_2pin_2Me]Li$ was prepared by dropwise addition of methyl lithium (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) to a solution of bis(pinacolato)diboron (0.8 mL in dry THF; 0.23 g, 0.90 mmol, 3.0 equiv.) at 0 °C. The resulting mixture was slowly warmed to room temperature and stirred for 1 h). Then, this suspension of $[B_2pin_2Me]Li$ (1.6 mL in THF) was added to the vial containing the redox-active ester, which is pre-cooled in an ice bath, in one portion (colour change was observed from pale-green to dark brown). After stirring for 1 h at 0 °C, followed by 1 h stirring at room temperature, the reaction mixture was quenched with 0.1 M HCl (5.0 mL) and diethyl ether (5.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with diethyl ether (2×5.0 mL). The combined organic layer was washed with brine (10.0 mL) and dried over Na_2SO_4. The crude oil was purified by flash chromatography on SiO_2 (pentane/EtOAc = 100:0 to 98:2) to afford C_3-methyl borylated indoles **11a-m**.

*Synthesis of 1-benzyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11a**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-1*H*-indole (**10a**; 62 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1 mol%) in DCM (3.0 mL) for 15 min at room temperature under argon to obtain the crude redox-active ester of **10a**. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11a** (53 mg, 0.15 mmol, 51%).

Appearance: colourless oil.

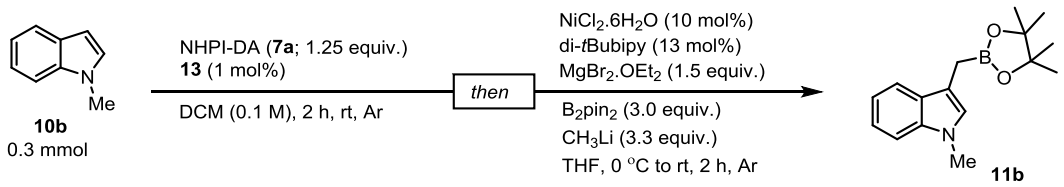
TLC: R_f = 0.55 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.64 – 7.62 (m, 1H), 7.33 – 7.20 (m, 4H), 7.18 – 7.07 (m, 4H), 7.02 (s, 1H), 5.27 (s, 2H), 2.34 (s, 2H), 1.27 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 138.0, 136.6, 129.1, 128.6, 127.4, 126.8, 126.0, 121.4, 119.3, 118.5, 110.8, 109.3, 83.4, 49.8, 24.8.

HRMS (ESI-TOF) calc'd for $C_{22}H_{26}BNO_2Na$ $[M+Na]^+$: 370.1948, found: 370.1953.

*Synthesis of 1-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11b**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-methyl-1*H*-indole (**10b**; 39 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 2 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11b** (40 mg, 0.15 mmol, 49%).

Appearance: colourless oil.

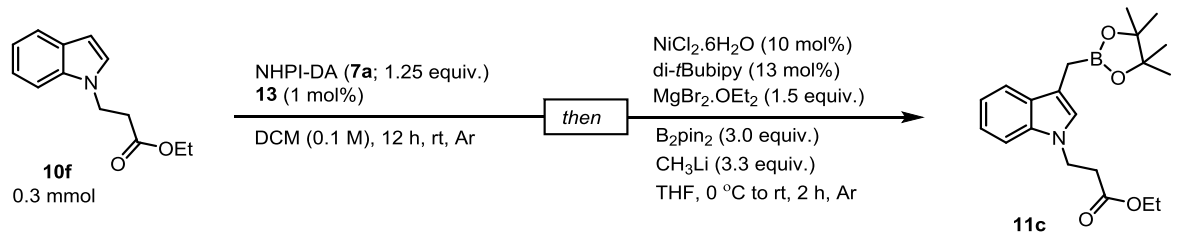
TLC: R_f = 0.5 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.59 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.22 – 7.18 (m, 1H), 7.08 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 6.93 (s, 1H), 3.73 (s, 3H), 2.34 (s, 2H), 1.28 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 136.9, 128.8, 126.6, 121.2, 119.2, 118.2, 110.1, 108.8, 83.4, 32.5, 24.8.

HRMS (ESI-TOF) calc'd for $C_{16}H_{22}BNO_2Na$ $[M+Na]^+$: 294.1635, found: 294.1610.

*Synthesis of 1-(4-bromobutyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11c**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), ethyl 3-(1*H*-indol-1-yl)propanoate (**10f**; 65 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 12 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 98:2 to 95:5) to afford **11c** (44 mg, 0.12 mmol, 41%).

Appearance: colourless oil.

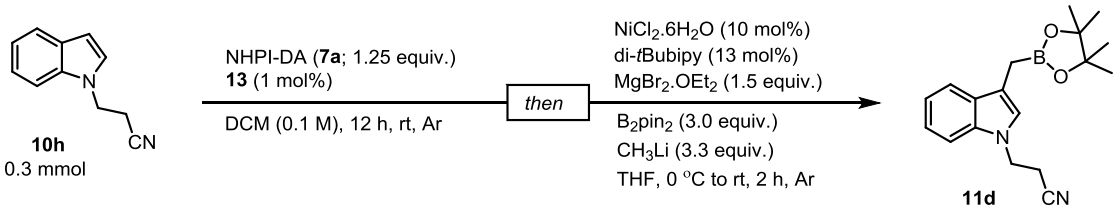
TLC: R_f = 0.65 (Pentane/EtOAc = 9:1, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 (d, *J* = 7.8 Hz, 1H), 7.28 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.16 (m, 1H), 7.07 (td, *J* = 7.5, 7.0, 1.0 Hz, 1H), 6.99 (s, 1H), 4.39 (t, *J* = 7.1 Hz, 2H), 4.12 (q, *J* = 7.2 Hz, 2H), 2.79 (t, *J* = 7.1 Hz, 2H), 2.29 (s, 2H), 1.26 (s, 12H), 1.21 (t, *J* = 7.1 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 171.4, 136.0, 129.1, 125.4, 121.4, 119.3, 118.5, 110.8, 108.8, 83.4, 60.8, 41.6, 35.2, 24.8, 14.1.

HRMS (ESI-TOF) calc'd for $C_{20}H_{28}BNO_4Na$ $[M+Na]^+$: 380.2007 ; found: 380.2009.

*Synthesis of 3-(3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indol-1-yl)propanenitrile (**11d**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 3-(1*H*-indol-1-yl)propanenitrile (**10h**; 51 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 12 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford **11d** (47 mg, 0.15 mmol, 51%).

Appearance: colourless oil.

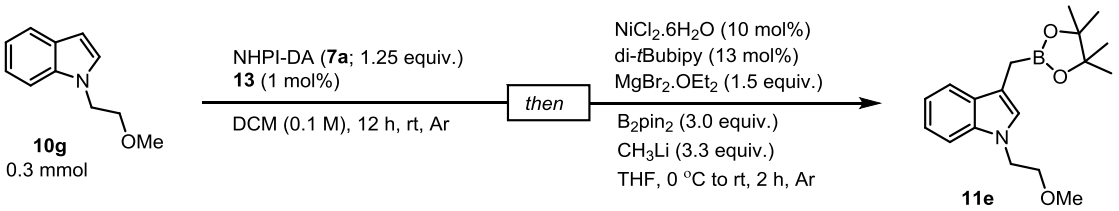
TLC: R_f = 0.45 (Pentane/EtOAc = 8:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.62 – 7.60 (m, 1H), 7.25 – 7.20 (m, 2H), 7.12 (ddd, *J* = 7.9, 5.6, 2.4 Hz, 1H), 7.02 (s, 1H), 4.38 (t, *J* = 7.0 Hz, 2H), 2.77 (t, *J* = 7.0 Hz, 2H), 2.30 (s, 2H), 1.27 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 135.6, 129.5, 124.9, 122.0, 119.7, 119.2, 117.4, 112.2, 108.3, 83.5, 41.9, 24.8, 19.1.

HRMS (ESI-TOF) calc'd for $C_{18}H_{23}BN_2O_2Na$ $[M+Na]^+$: 333.1744, found: 333.1741.

*Synthesis of 1-(2-methoxyethyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11e**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-(2-methoxyethyl)-1*H*-indole (**10g**; 53 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 12 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, .099 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was

purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:2 to 95:5) to afford **11e** (55 mg, 0.17 mmol, 58%).

Appearance: colourless oil.

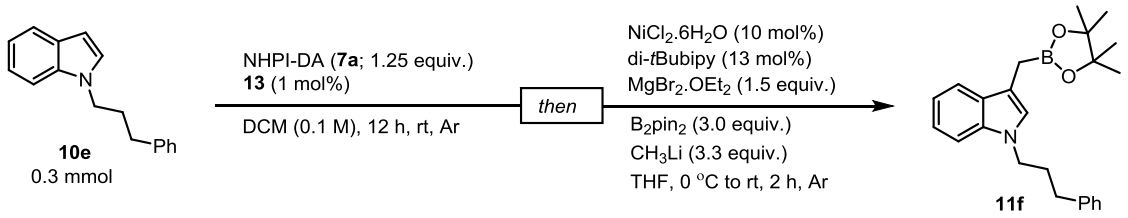
TLC: R_f = 0.6 (Pentane/EtOAc = 9:1, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.59 (dt, *J* = 7.9, 0.9 Hz, 1H), 7.29 (d, *J* = 8.2 Hz, 1H), 7.20 – 7.15 (m, 1H), 7.07 (ddd, *J* = 7.9, 7.0, 1.0 Hz, 1H), 7.03 (s, 1H), 4.23 (t, *J* = 5.8 Hz, 2H), 3.69 (t, *J* = 5.9 Hz, 2H), 3.32 (s, 3H), 2.33 (s, 2H), 1.27 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 136.4, 129.0, 126.0, 121.2, 119.3, 118.3, 110.5, 108.9, 83.3, 71.7, 59.0, 45.9, 24.8.

HRMS (ESI-TOF) calc'd for $C_{18}H_{26}BNO_3Na$ $[M+Na]^+$: 338.1901, found: 338.1900.

*Synthesis of 1-(3-phenylpropyl)-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11f**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-(3-phenylpropyl)-1*H*-indole (**10e**; 70 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol 1.0 mol%) in DCM (3.0 mL) for 12 h at room temperature under argon to obtain the crude. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 98:2 to 95:5) to affoed **11f** (47 mg, 0.12 mmol, 42%).

Appearance: colourless oil.

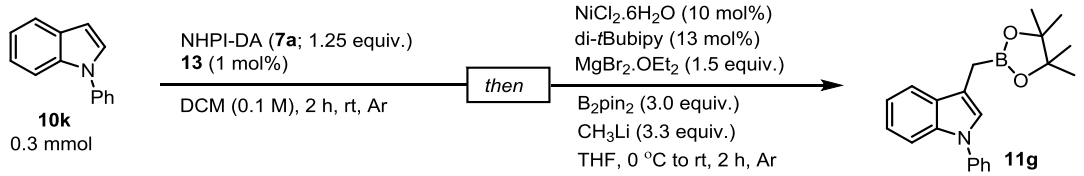
TLC: R_f = 0.55 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.62 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.33 – 7.28 (m, 2H), 7.25 – 7.16 (m, 5H), 7.09 (ddd, *J* = 8.0, 6.8, 1.2 Hz, 1H), 7.01 (s, 1H), 4.09 (t, *J* = 7.0 Hz, 2H), 2.65 (t, *J* = 8.0 Hz, 2H), 2.34 (s, 2H), 2.21 – 2.14 (m, 2H), 1.29 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.2, 136.2, 129.0, 128.4 (4 Ar CH), 126.0, 125.5, 121.1, 119.3, 118.2, 110.2, 109.1, 83.4, 45.4, 33.0, 31.6, 24.9.

HRMS (ESI-TOF) calc'd for $C_{24}H_{30}BNO_2Na$ $[M+Na]^+$: 398.2266, found: 398.2268.

*Synthesis of 1-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11g**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-phenyl-1*H*-indole (**10k**; 58 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 2 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 95:5) to afford **11g** (38 mg, 0.11 mmol, 38%).

Appearance: colourless oil.

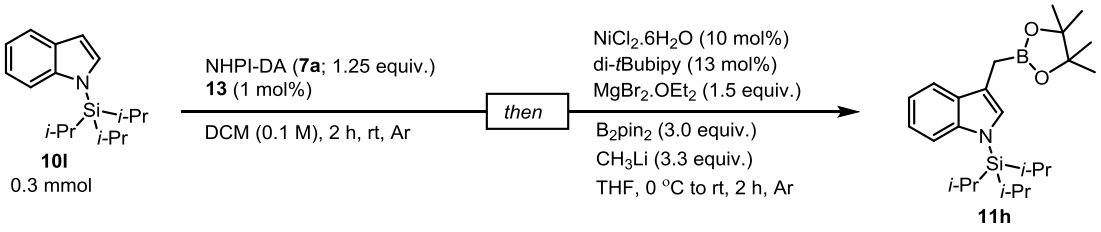
TLC: R_f = 0.51 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.67 – 7.64 (m, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.47 (m, 4H), 7.35 – 7.28 (m, 1H), 7.26 (s, 1H), 7.21 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.15 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 2.38 (s, 2H), 1.29 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 140.2, 135.9, 130.0, 129.5, 125.7, 125.5, 124.0, 122.2, 119.5, 119.4, 112.9, 110.2, 83.5, 24.9.

HRMS (ESI-TOF) calc'd for $C_{21}H_{24}BNO_2Na$ $[M+Na]^+$: 356.1792, found: 356.1782.

*Synthesis of 3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1-(triisopropylsilyl)-1H-indole (**11h**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-(triisopropylsilyl)-1*H*-indole (**10l**; 82 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 2 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was

purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11h** (71 mg, 0.17 mmol, 57%).

Appearance: colourless oil.

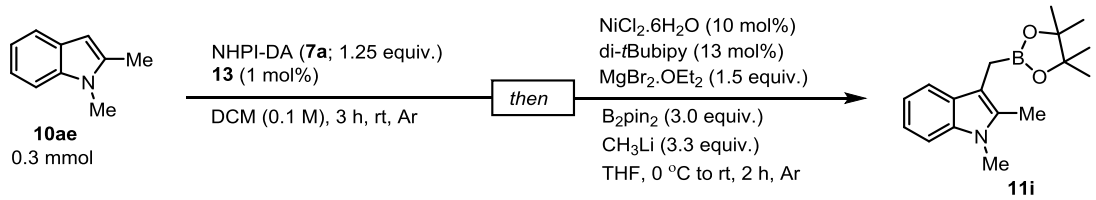
TLC: R_f = 0.67 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (d, *J* = 6.4 Hz, 1H), 7.44 (d, *J* = 7.8 Hz, 1H), 7.17 (s, 1H), 7.13 – 7.07 (m, 2H), 2.29 (s, 2H), 1.67 (hept, *J* = 7.7 Hz, 3H), 1.26 (s, 12H), 1.15 (d, *J* = 7.7, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.1, 132.1, 128.8, 121.0, 118.9, 118.8, 113.6, 113.1, 83.2, 24.9, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{24}H_{40}BNO_2SiNa$ $[M+Na]^+$: 436.2813, found: 436.2812.

*Synthesis of 1,2-dimethyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11i**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1,2-dimethyl-1*H*-indole (**10ae**; 43 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11i** (30 mg, 0.10 mmol, 35%).

Appearance: colourless oil.

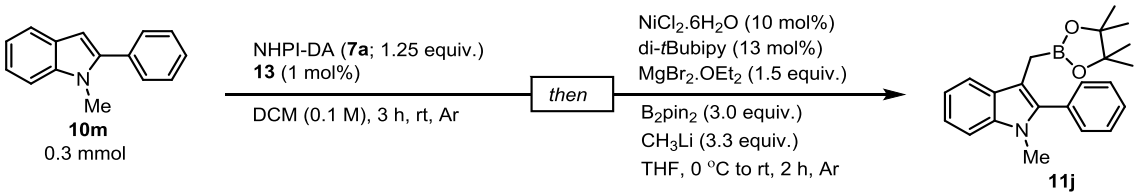
TLC: R_f = 0.5 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.51 (d, *J* = 8.0, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.13 – 7.09 (m, 1H), 7.03 (td, *J* = 7.5, 7.1, 1.0 Hz, 1H), 3.64 (s, 3H), 2.35 (s, 3H), 2.26 (s, 2H), 1.23 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 136.5, 132.1, 128.2, 120.2, 118.3, 118.2, 108.2, 106.7, 83.3, 29.5, 24.8, 10.5.

HRMS (ESI-TOF) calc'd for $C_{17}H_{24}BNO_2Na$ $[M+Na]^+$: 308.1792, found: 308.1795.

*Synthesis of 1-methyl-2-phenyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11j**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-methyl-2-phenyl-1*H*-indole (**10m**; 62 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 95:5) to afford **11j** (34 mg, 0.1 mmol, 33%).

Appearance: white solid.

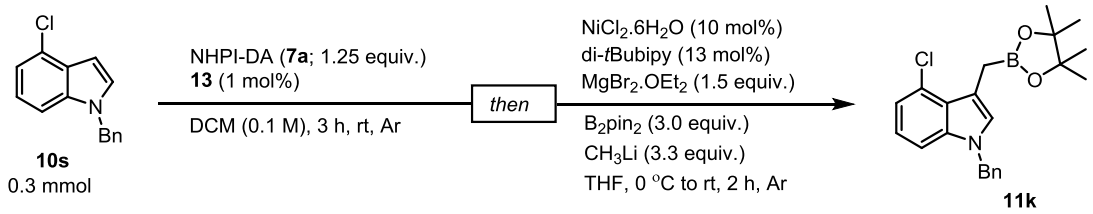
TLC: R_f = 0.5 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.63 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.51 – 7.46 (m, 4H), 7.43 – 7.38 (m, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.23 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.13 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 3.62 (s, 3H), 2.31 (s, 2H), 1.17 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 137.3, 132.4, 130.8, 130.6, 128.4, 128.3, 128.2, 127.6, 121.4, 119.3, 118.7, 109.1, 83.2, 31.0, 24.8.

HRMS (ESI-TOF) calc'd for $C_{22}H_{26}BNO_2Na$ $[M+Na]^+$: 370.1948, found: 370.1954.

*Synthesis of 1-benzyl-4-chloro-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11k**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-4-chloro-1*H*-indole (**10s**; 72 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11k** (48 mg, 0.13 mmol, 42%).

Appearance: colourless oil.

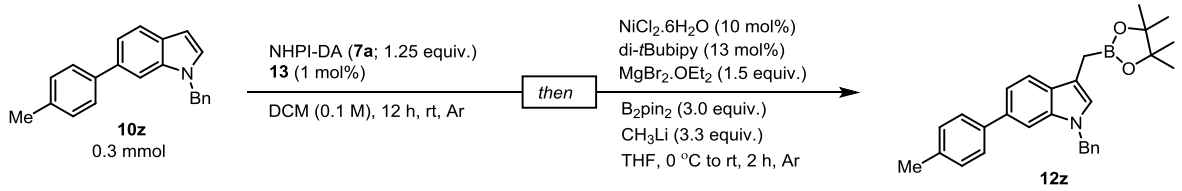
TLC: R_f = 0.55 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.33 – 7.22 (m, 3H), 7.12 – 7.05 (m, 3H), 7.01 – 6.95 (m, 3H), 5.23 (s, 2H), 2.65 (m, 2H), 1.27 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 138.0, 137.4, 128.7, 127.6, 127.4, 126.8, 126.8, 125.4, 121.9, 119.6, 111.8, 108.3, 83.3, 50.0, 24.9.

HRMS (ESI-TOF) calc'd for $C_{22}H_{25}BNO_2ClNa$ $[M+Na]^+$: 404.1559, found: 404.1503.

*Synthesis of 1-benzyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-6-(p-tolyl)-1H-indole (**11l**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-6-(p-tolyl)-1*H*-indole (**10z**; 89 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.5 mg, 40.0 µmol, 13.0 mol%), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) at 0 °C to room temperature for 2 h. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **12z** (60 mg, 0.14 mmol, 46%).

Appearance: colourless oil.

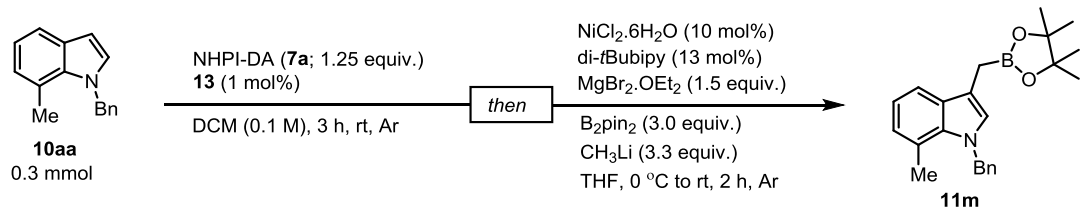
TLC: R_f = 0.5 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 (dd, *J* = 8.2, 0.7 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.40 (s, 1H), 7.34 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.31 – 7.20 (m, 5H), 7.16 – 7.13 (m, 2H), 7.02 (s, 1H), 5.31 (s, 2H), 2.39 (s, 3H), 2.35 (s, 2H), 1.27 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 139.8, 137.9, 137.1, 136.1, 135.0, 129.3, 128.7, 128.3, 127.4, 127.3, 126.8, 126.5, 119.5, 118.4, 110.9, 107.7, 83.4, 49.8, 24.8, 21.1.

HRMS (ESI-TOF) calc'd for $C_{29}H_{32}BNO_2Na$ $[M+Na]^+$: 460.2418, found: 460.2425.

*Synthesis of 1-benzyl-7-methyl-3-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)-1H-indole (**11m**)*



General procedure E was applied using NHPI-DA (**7a**; 87 mg, 0.37 mmol, 1.25 equiv.), 1-benzyl-7-methyl-1*H*-indole (**10aa**; 66 mg, 0.30 mmol, 1.0 equiv.), and Ru(II)-Pheox (**13**; 1.7 mg, 3.0 µmol, 1.0 mol%) in DCM (3.0 mL) for 3 h at room temperature under argon to obtain the crude redox-active ester. Then, $NiCl_2.6H_2O$ (7 mg, 0.03 mmol, 0.1 equiv.), 4,4'-di-*tert*-butyl-2,2'-bipyridine (10.47 mg, 0.04 mmol, 0.13 equiv.), $MgBr_2.OEt_2$ (0.12 g, 0.45 mmol, 1.5 equiv.), B_2pin_2 (0.23 g, 0.90 mmol, 3.0 equiv.), and MeLi (0.82 mL, 1.2 M in Et_2O, 0.99 mmol, 3.3 equiv.) were added and stirred in THF (2.0 mL) for 2 h at 0 °C to room temperature. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford **11m** (43 mg, 0.12 mmol, 40%).

Appearance: colourless oil.

TLC: R_f = 0.48 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

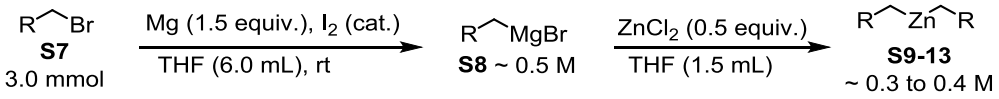
^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, *J* = 7.9 Hz, 1H), 7.29 – 7.19 (m, 3H), 7.01 – 6.97 (m, 1H), 6.96 – 6.91 (m, 3H), 6.86 (d, *J* = 8.0, 1H), 5.53 (s, 2H), 2.50 (s, 3H), 2.32 (s, 2H), 1.26 (s, 12H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 140.2, 135.3, 130.1, 128.7, 127.9, 127.1, 125.5, 124.3, 120.7, 118.9, 117.3, 110.9, 83.3, 51.9, 24.8, 19.5.

HRMS (ESI-TOF) calc'd for $C_{23}H_{28}BNO_2Na$ $[M+Na]^+$: 384.2109, found: 384.2112.

Synthesis of alkyl indole derivatives

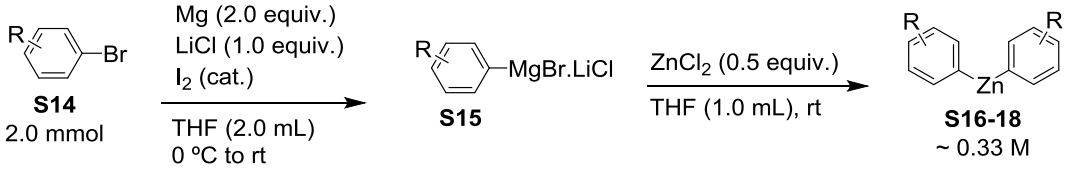
General Procedure F: Preparation of dialkyl zinc reagents



The procedure has been adapted from the one reported by Baran.[23]

A flame-dried microwave vial was charged with Mg turnings (0.10 g, 4.5 mmol, 1.5 equiv.) and I_2 (8 mg, 0.03 mmol, 0.01 equiv.). In a separate flame-dried vial, alkyl bromide **S7** (3.0 mmol, 1.0 equiv.) was dissolved in anhydrous THF (6.0 mL) to make a 0.5 M solution. A small portion of the alkyl bromide solution (*ca.* 1.0 mL) was added to the mixture of Mg and I_2. The vial was stirred while heated gently with a heat gun until the dark brown colour disappeared. The rest of the alkyl bromide solution (5.0 mL) was added dropwise while the vial was heated with a heat gun. After 1 h, the resulting solution of the freshly prepared Grignard reagent **S8** (without titrating) was added dropwise to a separate flame-dried microwave vial containing $ZnCl_2$ (1.0 M in THF, 0.20 g, 1.5 mmol. 0.50 equiv.). Dialkyl zinc **S9-13** was obtained in quantitative yield as a gray solution which was used without further titration.

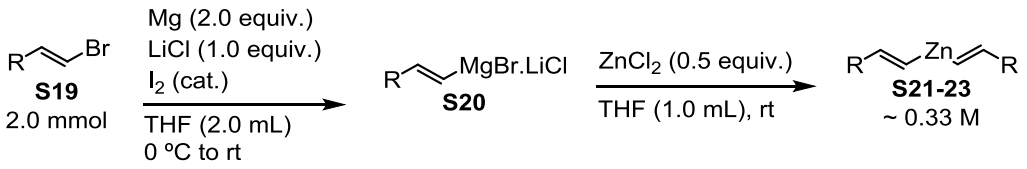
General Procedure G: Preparation of diaryl zinc reagents



The procedure has been adapted from the one reported by Wang.[24]

A flame-dried microwave vial was charged with Mg turnings (0.97 g, 4.0 mmol, 2.0 equiv.), LiCl (85 mg, 2.0 mmol, 1.0 equiv.) and I_2 (5.0 mg, 0.02 mmol, 0.01 equiv.). The vial was sealed, evacuated and refilled with argon (three times). Anhydrous THF (2.0 mL) was added to the vial and the mixture was stirred at room temperature for 5 min. The mixture was cooled to 0 °C in an ice bath and aryl bromide **S14** (2.0 mmol, 1.0 equiv.) was added dropwise. After 5 min the mixture was removed from the ice bath and allowed to stir at room temperature for 1 h. In a separate vial $ZnCl_2$ (0.14 g, 1.0 mmol, 0.50 equiv.) was weighed and heated under vacuum for 5 min with a heat gun. After cooling down the vial, anhydrous THF (1.0 mL) was added under argon and the mixture was allowed to stir at room temperature for 5 min. Then freshly prepared arylMgBr·LiCl **S15** (2.0 mL, 1 M in THF, 2.0 mmol, 1.0 equiv.) was added dropwise to the solution of $ZnCl_2$ to obtain diaryl zinc **S16-18** in THF (c = 0.33 M), which was used without further titration.

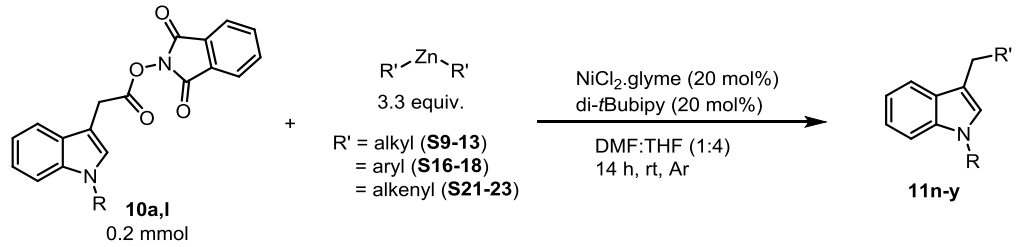
General Procedure H: Preparation of dialkenyl zinc reagents



The procedure has been adapted from the one reported by Wang.[24]

A flame-dried microwave vial was charged with Mg turnings (97 mg, 4 mmol, 2.0 equiv.), LiCl (85 mg, 2.0 mmol, 1.0 equiv.) and I_2 (5.0 mg, 0.02 mmol, 0.01 equiv.). The vial was sealed, evacuated and refilled with argon (three times). Anhydrous THF (2.0 mL) was added to the vial and the mixture was stirred at room temperature for 5 min. The mixture was then cooled in an ice bath and alkenyl bromide **S19** (2.0 mmol, 1.0 equiv.) was added dropwise. After 5 min the mixture was removed from the ice bath and allowed to stir at room temperature for 1 h. A separate vial was charged with $ZnCl_2$ (0.14 g, 1.0 mmol, 0.50 equiv.) and heated under vacuum for 5 min with a heat gun. After cooling down the vial, anhydrous THF (1.0 mL) was added under argon and the mixture was allowed to stir at room temperature for 5 min. Then freshly prepared alkenylMgBr·LiCl **S20** (2.0 mL, 1 M in THF, 2.0 mmol, 1.0 equiv.) was added dropwise to the solution of $ZnCl_2$ to obtain dialkenyl zinc **S21-23** in THF (c = 0.33 M), which was used without further titration.

General procedure I: Ni-catalyzed decarboxylative Negishi coupling of redox-active ester of indoles

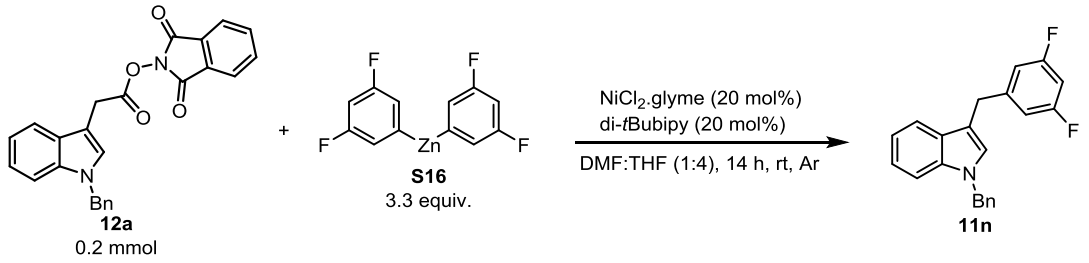


The procedure has been adapted from the one reported by Baran.[23]

A flame-dried vial was charged with a stirring bar, redox-active ester **10a/l** (0.20 mmol, 1.0 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.) and 4,4'-di-*tert*-butyl-2,2'-bipyridine (di-*t*Bubipy; 11 mg, 40 µmol, 0.20 equiv.). The vial was evacuated and refilled with argon (three cycles), followed by addition of dry DMF (0.5 mL). The resulting mixture was sonicated for 2 to 3 min, followed by stirring at room temperature for 5 to 10 min until no solid residue was observed. Then, dialkyl/diaryl/dialkenyl zinc **S9-13,16-18,21-23** (2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.) was added to the mixture in one portion and the mixture was stirred at room temperature for 14 h. The reaction was quenched with 0.1 M HCl (5.0 mL) and EtOAc (5.0 mL) was added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2x5 mL). The combined organic layer was washed with brine (5.0 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The crude was purified by flash

chromatography on SiO_2 (pentane/EtOAc or DCM/MeOH = 99:1 to 95:5) to afford compound **11n-y**.

*Synthesis of 1-benzyl-3-(3,5-difluorobenzyl)-1H-indole (**11n**)*



General procedure I was applied using redox-active ester **12a** (82 mg, 0.20 mmol, 1.0 equiv.), bis(3,5-difluorophenyl)zinc (**S16**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11n** (37 mg, 0.11 mmol, 56%).

Appearance: colourless oil.

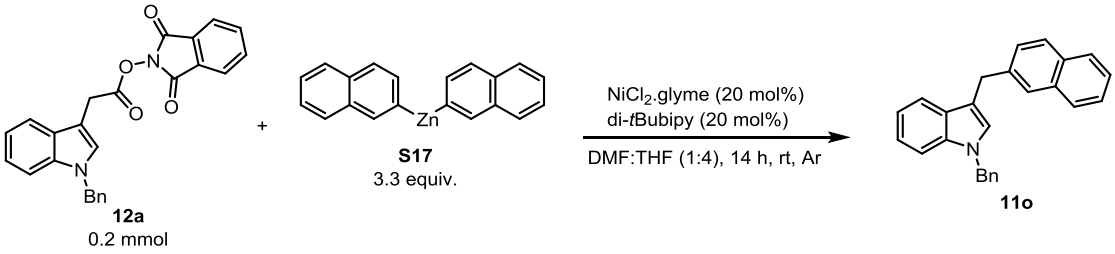
TLC: R_f = 0.6 (pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47 (d, *J* = 7.9, 1H), 7.34 – 7.26 (m, 4H), 7.21 – 7.17 (m, 1H), 7.15 – 7.07 (m, 3H), 6.93 (s, 1H), 6.84 – 6.75 (m, 2H), 6.63 (tt, *J* = 9.0, 2.4 Hz, 1H), 5.30 (s, 2H), 4.10 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 164.3 (dd, $J_{C\text{-}F}$ = 247.3, 13.4 Hz), 145.6 (t, $J_{C\text{-}F}$ = 8.8 Hz), 137.5, 136.9, 128.8, 127.8, 127.6, 126.8, 126.7, 122.1, 119.4, 119.1, 113.1, 111.4 (dd, $J_{C\text{-}F}$ = 18.1, 6.4 Hz), 109.8, 101.6 (t, $J_{C\text{-}F}$ = 25.1 Hz), 50.0, 31.4.

HRMS (ESI-TOF) calc'd for $C_{22}H_{17}F_2NNa$ $[M+Na]^+$: 356.1221, found: 356.1215.

*Synthesis of 1-benzyl-3-(naphthalen-2-ylmethyl)-1H-indole (**11o**)*



General procedure I was applied using redox-active ester **12a** (82 mg, 0.20 mmol, 1.0 equiv.), di(naphthalen-2-yl)zinc (**S17**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11o** (50 mg, 0.14 mmol, 72%).

Appearance: colourless oil.

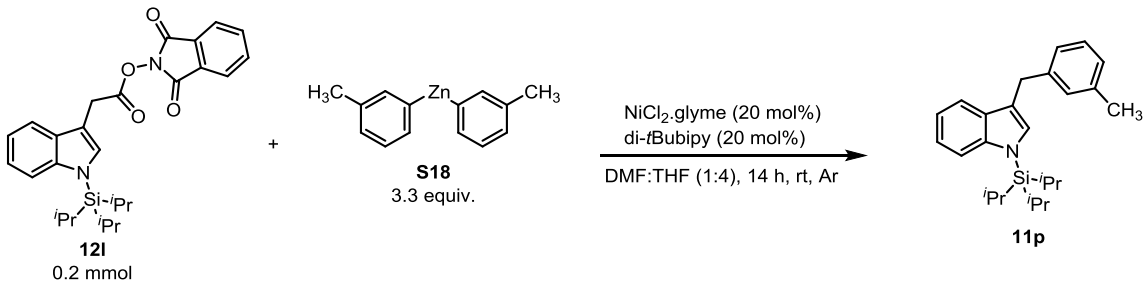
TLC: R_f = 0.6 (pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.82 – 7.79 (m, 1H), 7.78 – 7.73 (m, 3H), 7.57 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.47 – 7.40 (m, 3H), 7.33 – 7.23 (m, 4H), 7.17 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 1H), 7.14 – 7.10 (m, 2H), 7.07 (ddd, *J* = 8.0, 7.0, 1.1 Hz, 1H), 6.89 (s, 1H), 5.28 (s, 2H), 4.29 (s, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 138.8, 137.7, 136.9, 133.6, 132.1, 128.7, 128.2, 127.9, 127.6, 127.6 (3 Ar CH), 127.5, 126.7, 126.7, 125.8, 125.2, 121.8, 119.4, 119.1, 114.8, 109.7, 49.9, 31.8.

HRMS (ESI-TOF) calc'd for $C_{26}H_{21}NNa$ $[M+Na]^+$: 370.1566, found: 370.1560.

*Synthesis of 3-(3-methylbenzyl)-1-(triisopropylsilyl)-1H-indole (**11p**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), *m*-tolyl(*p*-tolyl)zinc (**S18**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 0.04 mmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11p** (50 mg, 0.13 mmol, 66%).

Appearance: colourless oil.

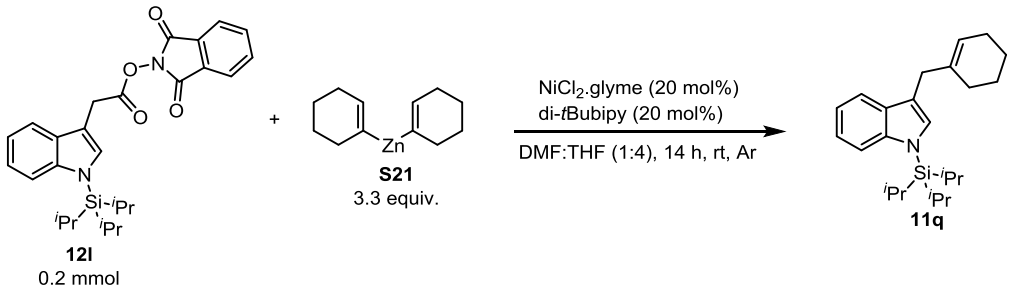
TLC: R_f = 0.7 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.52 – 7.47 (m, 2H), 7.19 – 7.11 (m, 2H), 7.11 – 7.05 (m, 3H), 7.03 – 6.98 (m, 2H), 4.09 (s, 2H), 2.31 (s, 3H), 1.69 (hept, *J* = 7.6 Hz, 3H), 1.15 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.5, 141.2, 137.7, 131.1, 129.4, 129.4, 128.1, 126.5, 125.6, 121.3, 119.3, 119.0, 117.2, 113.9, 31.5, 21.4, 18.2, 12.8.

HRMS (ESI-TOF) calc'd for $C_{25}H_{35}NSiNa$ $[M+Na]^+$: 400.2431, found: 400.2427.

*Synthesis of 3-(cyclohex-1-en-1-ylmethyl)-1-(triisopropylsilyl)-1H-indole (**11q**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), cyclohex-1-en-1-yl(cyclohex-2-en-1-yl)zinc (**S21**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11q** (49 mg, 0.13 mmol, 67%).

Appearance: colourless oil.

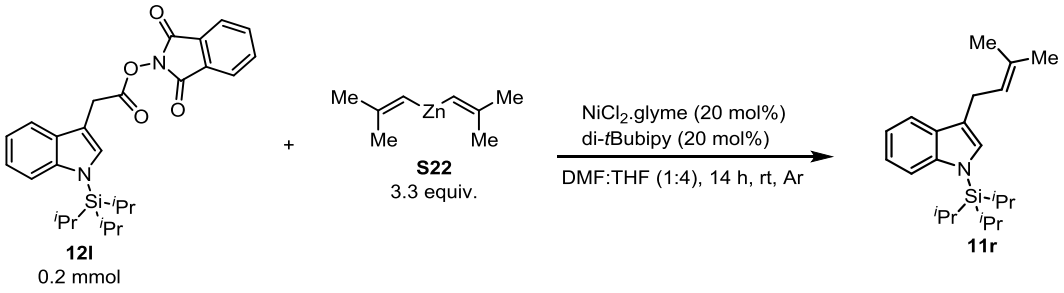
TLC: R_f = 0.5 (pentane/EtOAc = 97:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.60 – 7.56 (m, 1H), 7.49 – 7.45 (m, 1H), 7.15 – 7.07 (m, 2H), 7.00 (s, 1H), 5.57 – 5.53 (m, 1H), 3.39 (s, 2H), 2.05 – 1.91 (m, 4H), 1.69 (h, *J* = 7.5 Hz, 3H), 1.63 – 1.51 (m, 4H), 1.15 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.4, 136.9, 131.4, 129.1, 121.8, 121.1, 119.2, 119.0, 116.2, 113.8, 34.1, 28.2, 25.3, 23.1, 22.6, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{24}H_{37}NSiNa$ $[M+Na]^+$: 390.2588; found: 390.2589.

*Synthesis of 3-(3-methylbut-2-en-1-yl)-1-(triisopropylsilyl)-1H-indole (**11r**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), bis(2-methylprop-1-en-1-yl)zinc (**S22**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11r** (42 mg, 0.12 mmol, 62%).

Appearance: colourless oil.

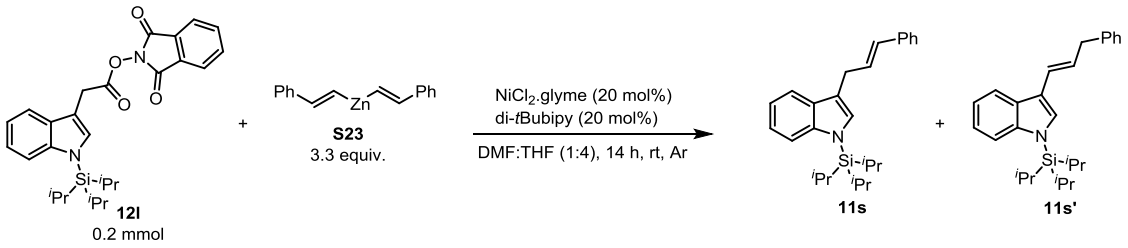
TLC: R_f = 0.5 (Pentane/EtOAc = 97:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.57 – 7.54 (m, 1H), 7.49 – 7.44 (m, 1H), 7.12 (pd, *J* = 7.0, 1.4 Hz, 2H), 6.97 (s, 1H), 5.46 – 5.41 (m, 1H), 3.45 (d, *J* = 7.3 Hz, 2H), 1.79 – 1.75 (m, 6H), 1.73 – 1.63 (m, 3H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.5, 131.8, 131.1, 128.0, 123.3, 121.2, 119.1, 118.8, 117.6, 113.9, 25.7, 24.3, 18.2, 17.9, 12.9.

HRMS (ESI-TOF) calc'd for $C_{22}H_{35}NSiNa$ $[M+Na]^+$: 364.2460, found: 364.2452.

*Synthesis of 3-cinnamyl-1-(triisopropylsilyl)-1H-indole (**11s**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), di((*E*)-styryl)zinc (**S23**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compounds **11s**,**s'** (61 mg, 0.16 mmol, 79%) as inseparable mixture (25:4).

Appearance: colourless oil.

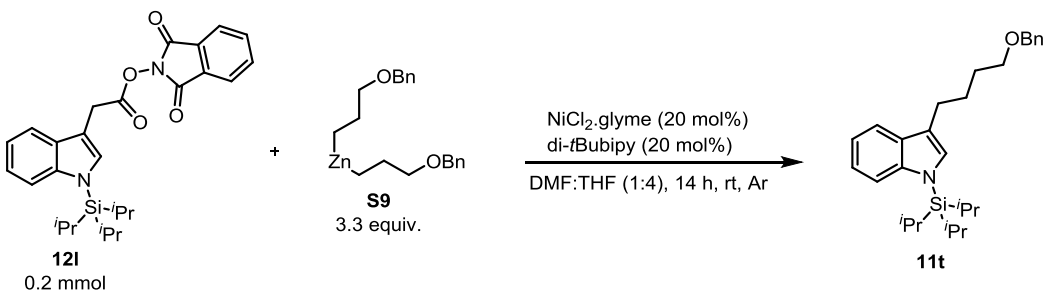
TLC: R_f = 0.5 (pentane/EtOAc = 97:3, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.51 – 7.48 (m, 1H), 7.38 – 7.35 (m, 2H), 7.31 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 7.17 – 7.13 (m, 1H), 7.11 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.06 (d, *J* = 1.0 Hz, 1H), 6.56 – 6.43 (m, 2H), 3.69 (d, *J* = 5.8 Hz, 1H), 1.76 – 1.64 (m, 3H), 1.15 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.5, 137.8, 131.0, 130.3, 129.6, 128.7, 128.4, 126.8, 126.1, 121.4, 119.3, 118.9, 116.1, 113.9, 29.1, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{26}H_{35}NSiNa$ $[M+Na]^+$: 412.2405, found: 412.2400.

*Synthesis of 3-(4-(benzyloxy)butyl)-1-(triisopropylsilyl)-1H-indole (**11t**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), bis(3-(benzyloxy)propyl)zinc (**S9**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11t** (76 mg, 0.17 mmol, 87%).

Appearance: colourless oil.

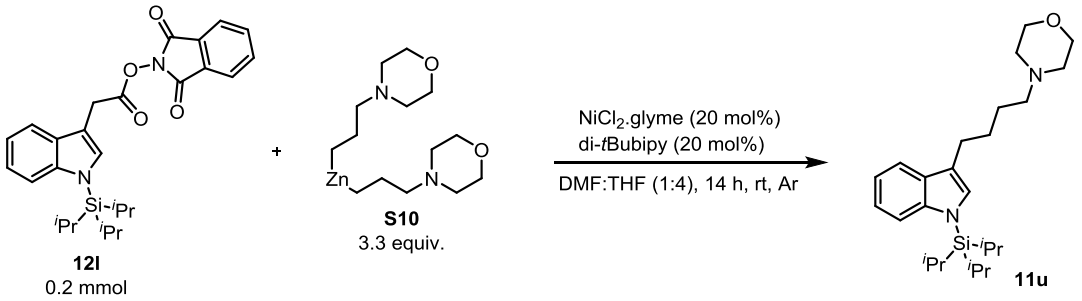
TLC: R_f = 0.55 (Petroleum ether/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.59 – 7.55 (m, 1H), 7.47 (*J* = 7.0, 1.3 Hz, 1H), 7.38 – 7.27 (m, 5H), 7.11 (pd, *J* = 7.0, 1.4 Hz, 2H), 6.99 (s, 1H), 4.50 (s, 2H), 3.52 (t, *J* = 6.4 Hz, 2H), 2.77 (t, *J* = 8.0 Hz, 2H), 1.86 – 1.77 (m, 2H), 1.77 – 1.63 (m, 5H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.4, 138.7, 131.1, 128.3, 128.0, 127.6, 127.4, 121.2, 119.0, 118.7, 118.3, 113.9, 72.8, 70.4, 29.6, 26.5, 25.0, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{28}H_{41}NOSiNa$ $[M+Na]^+$: 458.2849, found: 458.2835.

*Synthesis of 4-(4-(1-(triisopropylsilyl)-1H-indol-3-yl)butyl)morpholine (**11u**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), bis(3-morpholinopropyl)zinc (**S10**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (DCM/methanol = 98:1 to 98:2) to afford compound **11u** (51 mg, 0.12 mmol, 61%).

Appearance: colourless oil.

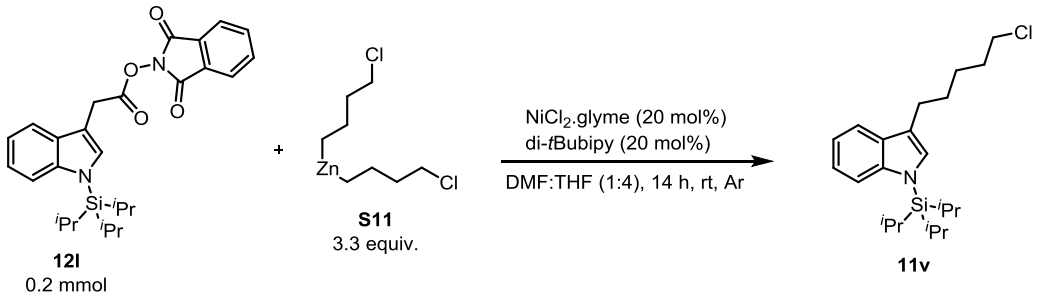
TLC: R_f = 0.5 (DCM/Methanol = 98:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.59 – 7.55 (m, 1H), 7.48 – 7.45 (m, 1H), 7.11 (pd, *J* = 7.0, 1.4 Hz, 2H), 6.98 (s, 1H), 3.71 (t, *J* = 4.7 Hz, 4H), 2.79 (m, t, *J* = 8.0 Hz, 2H), 2.43 – 2.37 (m, 6H), 1.78 – 1.64 (m, 5H), 1.63 – 1.55 (m, 2H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.4, 131.0, 128.0, 121.2, 119.1, 118.7, 118.2, 113.9, 66.9, 58.9, 53.7, 27.8, 26.3, 25.1, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{25}H_{43}N_2OSi$ $[M+H]^+$: 415.3139, found: 415.3137.

*Synthesis of 3-(5-chloropentyl)-1-(triisopropylsilyl)-1H-indole (**11v**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), bis(4-chlorobutyl)zinc (**S11**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11v** (37 mg, 0.1 mmol, 49%).

Appearance: colourless oil.

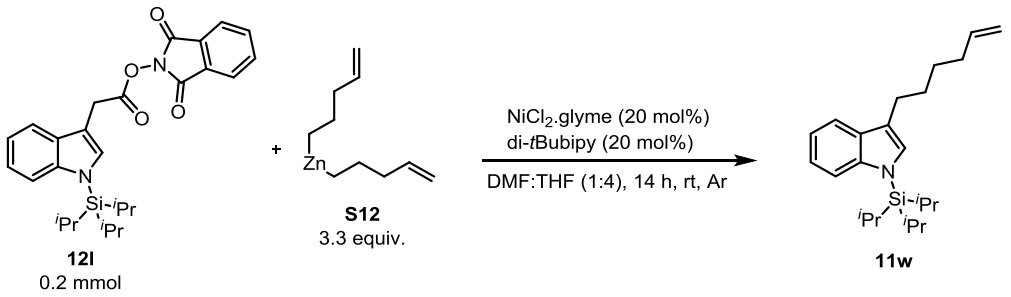
TLC: R_f = 0.65 (pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.59 – 7.54 (m, 1H), 7.49 – 7.45 (m, 1H), 7.12 (pd, *J* = 7.0, 1.4 Hz, 2H), 6.99 (s, 1H), 3.53 (t, *J* = 6.7 Hz, 2H), 2.76 (t , *J* = 8.0 Hz, 2H), 1.86 – 1.78 (m, 2H), 1.78 – 1.63 (m, 5H), 1.57 – 1.48 (m, 2H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.4, 131.0, 128.0, 121.2, 119.1, 118.6, 118.1, 113.9, 45.2, 32.5, 29.2, 26.8, 25.0, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{22}H_{36}ClNSiNa$ $[M+Na]^+$: 400.2197, found: 400.2162.

*Synthesis of 3-(hex-5-en-1-yl)-1-(triisopropylsilyl)-1H-indole (**11w**)*



General procedure I was applied using redox-active ester **10l** (95.2 mg, 0.20 mmol, 1.0 equiv.), di(pent-4-en-1-yl)zinc (**S12**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11w** (38 mg, 0.11 mmol, 54%).

Appearance: colourless oil.

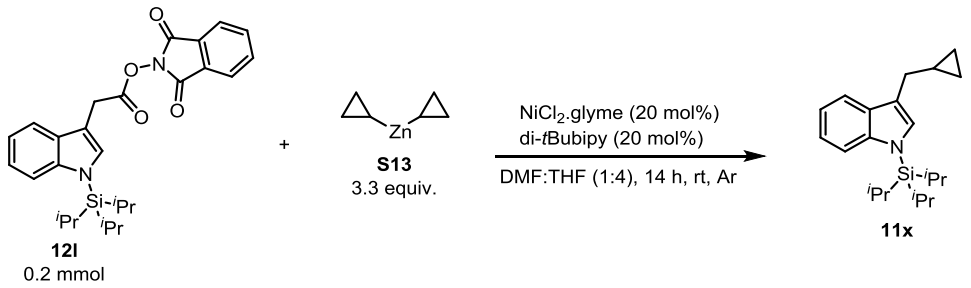
TLC: R_f = 0.6 (pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.60 – 7.55 (m, 1H), 7.49 – 7.45 (m, 1H), 7.15 – 7.08 (m, 2H), 6.99 (s, 1H), 5.87 – 5.77 (m, 1H), 5.03 – 4.92 (m, 2H), 2.75 (t, *J* = 7.3 Hz, 2H), 2.14 – 2.07 (m, 2H), 1.77 – 1.63 (m, 5H), 1.53 – 1.45 (m, 2H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.4, 139.1, 131.1, 127.9, 121.2, 119.0, 118.7, 118.4, 114.2, 113.9, 33.6, 29.4, 28.8, 25.0, 18.2, 12.9.

HRMS (ESI-TOF) calc'd for $C_{23}H_{37}NSiNa$ $[M+Na]^+$: 378.2587, found: 378.2587.

*Synthesis of 3-(cyclopropylmethyl)-1-(triisopropylsilyl)-1H-indole (**11x**)*



General procedure I was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), dicyclopropylzinc (**S13**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol, 0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11x** (24 mg, 0.07 mmol, 37%).

Appearance: colourless oil.

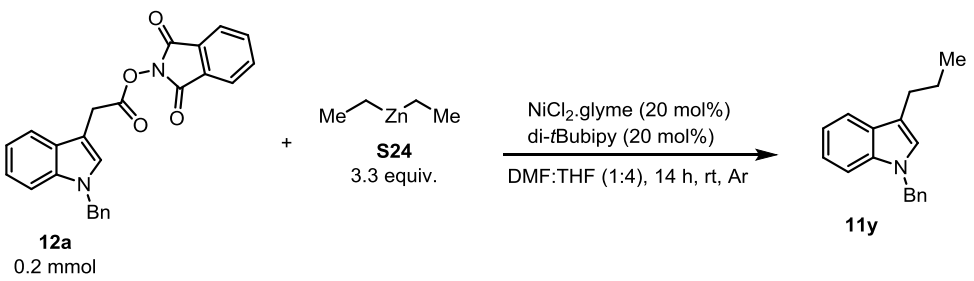
TLC: R_f = 0.65 (pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 – 7.57 (m, 1H), 7.49 – 7.46 (m, 1H), 7.16 – 7.08 (m, 3H), 2.70 (d, *J* = 8.0 Hz, 2H), 1.70 (h, *J* = 7.5 Hz, 3H), 1.15 (d, *J* = 7.5 Hz, 18H), 1.12 – 1.07 (m, 1H), 0.55 – 0.49 (m, 2H), 0.23 – 0.18 (m, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 141.3, 131.3, 128.2, 121.2, 119.1, 118.8, 118.0, 113.9, 29.8, 18.2, 12.9, 11.0, 4.8.

HRMS (ESI-TOF) calc'd for $C_{21}H_{33}NSiNa$ $[M+Na]^+$: 350.2274, found: 350.2276.

*Synthesis of 1-benzyl-3-propyl-1H-indole (**11y**)*



General procedure I was applied using redox-active ester **10a** (82 mg, 0.20 mmol, 1.0 equiv.), diethyl zinc (**S24**; 2.0 mL, 0.33 M in THF, 0.66 mmol, 3.3 equiv.), $NiCl_2$.glyme (8.7 mg, 40 µmol,

0.20 equiv.), and 4,4'-di-*tert*-butyl-2,2'-bipyridine (11 mg, 40 µmol, 0.20 equiv.) in DMF (0.5 mL) at room temperature for 14 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1) to afford compound **11y** (24 mg, 0.1 mmol, 50%).

Appearance: colourless oil.

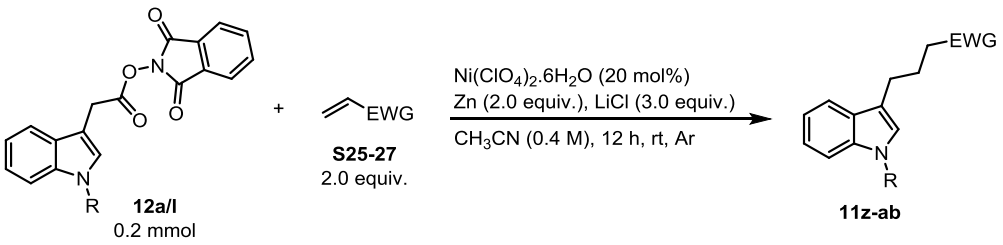
TLC: R_f = 0.55 (Pentane/EtOAc = 98:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.65 – 7.62 (m, 1H), 7.33 – 7.24 (m, 4H), 7.19 – 7.15 (m, 1H), 7.14 – 7.09 (m, 3H), 6.89 (s, 1H), 5.28 (s, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.03 (t, *J* = 7.3 Hz, 3H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 137.9, 136.7, 128.7, 128.3, 127.5, 126.7, 125.4, 121.6, 119.2, 118.7, 116.2, 109.5, 49.8, 27.3, 23.4, 14.2.

All the data are in accordance with the literature.[25]

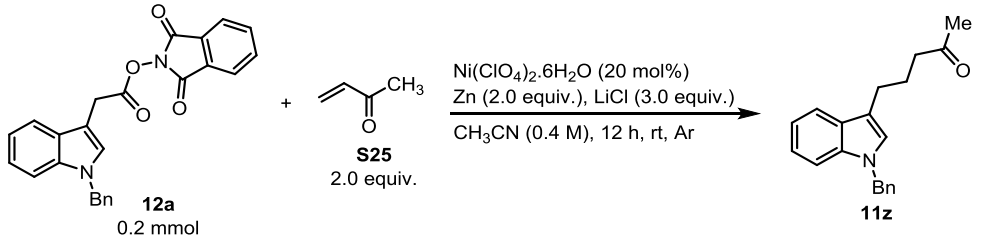
General procedure J: Decarboxylative Giese reaction of redox-active ester of indoles



The procedure has been adapted from the one reported by Baran.[26]

A flame dried vial was charged with a stirring bar, redox-active ester (**12a**/**l**, 0.20 mmol, 1.0 equiv.), $Ni(ClO_4)_2.6H_2O$ (15 mg, 40 µmol, 0.20 equiv.), zinc dust (26 mg, 0.30 mmol, 2.0 equiv.), and lithium chloride (25 mg, 0.60 mmol, 3.0 equiv.). The vial was evacuated and refilled with argon (three times), followed by addition of anhydrous acetonitrile (0.5 mL). Michael acceptor (0.40 mmol, 2.0 equiv.) was added via a syringe and the mixture was stirred at room temperature. After 12 h, the solid residue was filtered off through a Celite pad (*c.a.* 3 to 4 cm length). The filtrate was diluted with distilled H_2O (5.0 mL) and saturated aqueous NH_4Cl solution (5.0 mL) and EtOAc (10.0 mL) were added. The organic layer was separated and the aqueous layer was extracted with EtOAc (2×10.0 mL). The combined organic layer was washed with brine (10.0 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 8:2) to afford the coupling products **11z-ab**.

*Synthesis of 5-(1-benzyl-1H-indol-3-yl)pentan-2-one (**11z**)*



General procedure J was applied using redox-active ester **12a** (82 mg, 0.20 mmol, 1.0 equiv.), $Ni(ClO_4)_2.6H_2O$ (15 mg, 40 µmol, 0.20 equiv.), zinc dust (26 mg, 0.30 mmol, 2.0 equiv.), lithium chloride (25 mg, 0.60 mmol, 3.0 equiv.), and but-3-en-2-one (**S25**; 28 mg, 0.40 mmol, 2.0 equiv.) in acetonitrile (0.5 mL) at room temperature for 12 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1) to afford compound **11z** (33 mg, 0.11 mmol, 56%).

Appearance: greenish oil.

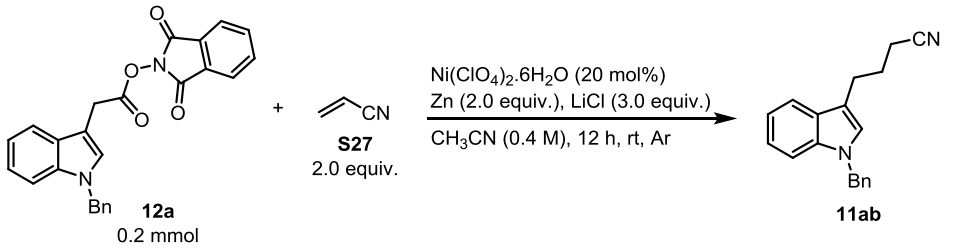
TLC: R_f = 0.4 (Pentane/EtOAc = 8:2, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.61 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.17 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.14 – 7.08 (m, 3H), 6.91 (s, 1H), 5.28 (s, 2H), 2.78 (t, *J* = 8.0Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H), 2.11 (s, 3H), 2.00 (p, *J* = 7.4 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 209.1, 137.8, 136.7, 128.7, 128.1, 127.5, 126.8, 125.6, 121.7, 119.1, 118.9, 115.0, 109.6, 49.9, 43.3, 30.0, 24.4, 24.3.

HRMS (ESI-TOF) calc'd for $C_{20}H_{21}NONa$ $[M+Na]^+$: 314.1515, found: 314.1510.

*Synthesis of 4-(1-benzyl-1H-indol-3-yl)butanenitrile (**11aa**)*



General procedure J was applied using redox-active ester **12a** (82 mg, 0.20 mmol, 1.0 equiv.), $Ni(ClO_4)_2.6H_2O$ (15 mg, 40 µmol, 0.20 equiv.), zinc dust (26 mg, 0.30 mmol, 2.0 equiv.), lithium chloride (21 mg, 0.60 mmol, 3.0 equiv.), and acrylonitrile (**S27**; 28 mg, 0.40 mmol, 2.0 equiv.) in acetonitrile (0.5 mL) at room temperature for 12 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 9:1 to 8:2) to afford compound **11ab** (24 mg, 80 µmol, 44%).

Appearance: greenish oil.

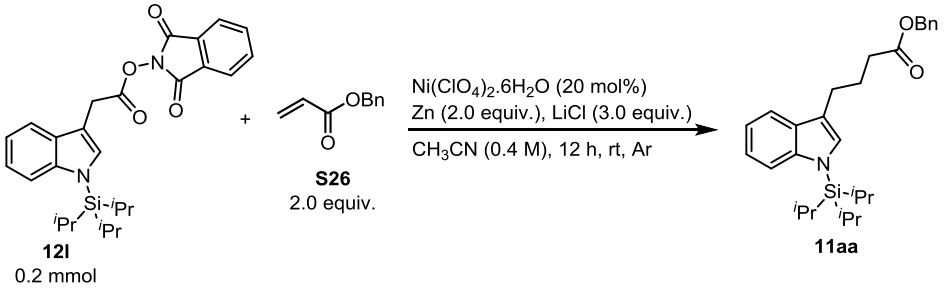
TLC: R_f = 0.45 (Petroleum ether/EtOAc = 3:1, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.58 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.23 (m, 4H), 7.19 – 7.15 (m, 1H), 7.13 – 7.08 (m, 3H), 6.95 (s, 1H), 5.27 (s, 2H), 2.94 (t, *J* = 7.2 Hz, 2H), 2.33 (t, *J* = 7.1 Hz, 2H), 2.05 (p, *J* = 7.1 Hz, 2H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 137.6, 136.9, 128.8, 127.8, 127.7, 126.8, 126.1, 122.0, 119.8, 119.2, 118.9, 113.1, 109.9, 50.0, 25.9, 23.9, 16.6.

HRMS (ESI-TOF) calc'd for $C_{19}H_{18}N_2Na$ [M+Na]$^+$: 297.1362, found: 297.1387.

*Synthesis of benzyl 4-(1-(triisopropylsilyl)-1H-indol-3-yl)butanoate (**11ab**)*



General procedure J was applied using redox-active ester **12l** (95 mg, 0.20 mmol, 1.0 equiv.), $Ni(ClO_4)_2.6H_2O$ (15 mg, 40 µmol, 0.20 equiv.), zinc dust (26 mg, 0.30 mmol, 2.0 equiv.), lithium chloride (25 mg, 0.60 mmol, 3.0 equiv.), and benzyl acrylate (**S26**; 65 mg, 0.40 mmol, 2.0 equiv.) in acetonitrile (0.5 mL) at room temperature for 12 h under argon. The crude was purified by flash chromatography on SiO_2 (pentane/EtOAc = 99:1 to 98:2) to afford compound **11aa** (48 mg, 0.11 mmol, 53%).

Appearance: colourless oil.

TLC: R_f = 0.4 (Pentane/EtOAc = 95:5, UV-active and stains in vanillin).

^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.56 – 7.53 (m, 1H), 7.48 – 7.45 (m, 1H), 7.40 – 7.29 (m, 5H), 7.15 – 7.06 (m, 2H), 6.98 (s, 1H), 5.12 (s, 2H), 2.83 (t, *J* = 8.0 Hz, 2H), 2.42 (t, *J* = 7.4 Hz, 2H), 2.07 (p, *J* = 7.4 Hz, 2H), 1.66 (h, *J* = 7.5 Hz, 3H), 1.12 (d, *J* = 7.5 Hz, 18H).

^{13}C-NMR (101 MHz, $CDCl_3$) δ (ppm) = 173.6, 141.4, 136.1, 130.9, 128.5, 128.4, 128.2, 128.2, 121.3, 119.2, 118.7, 117.1, 113.9, 66.1, 33.9, 25.3, 24.5, 18.2, 12.8.

HRMS (ESI-TOF) calc'd for $C_{28}H_{39}NO_2SiNa$ [M+Na]$^+$: 472.2462, found: 472.2632.

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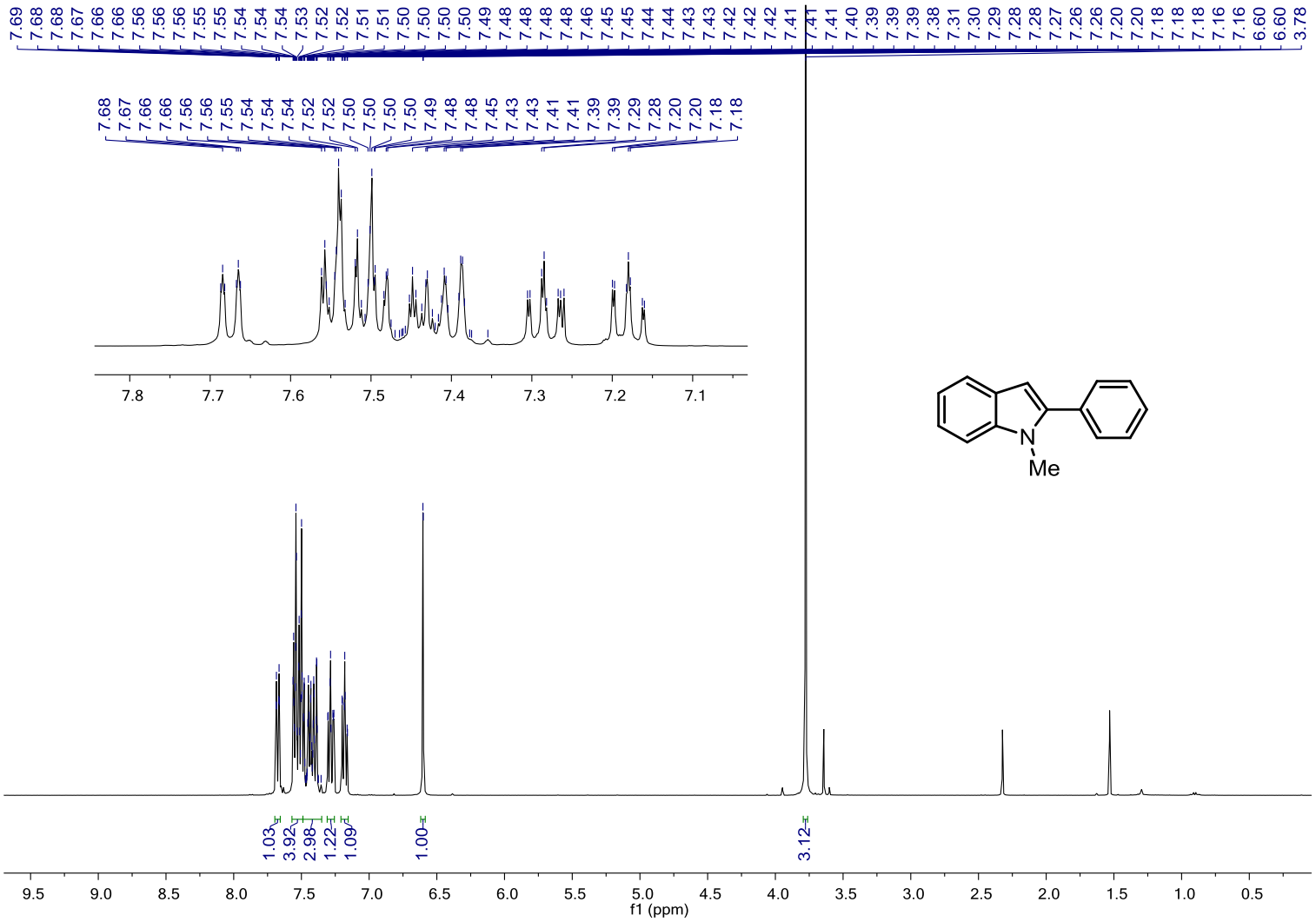
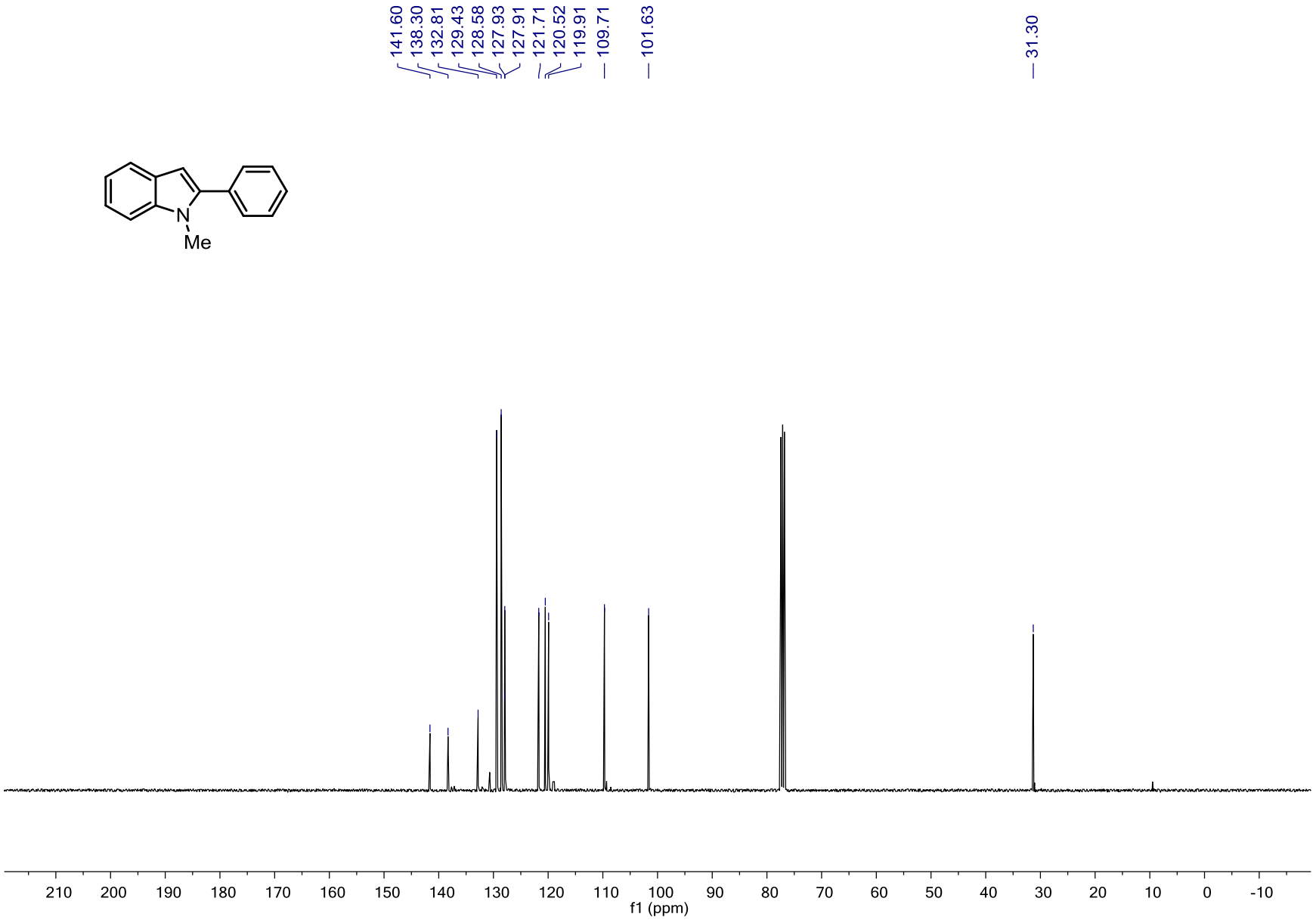
7. NMR spectra of synthesiszed compounds

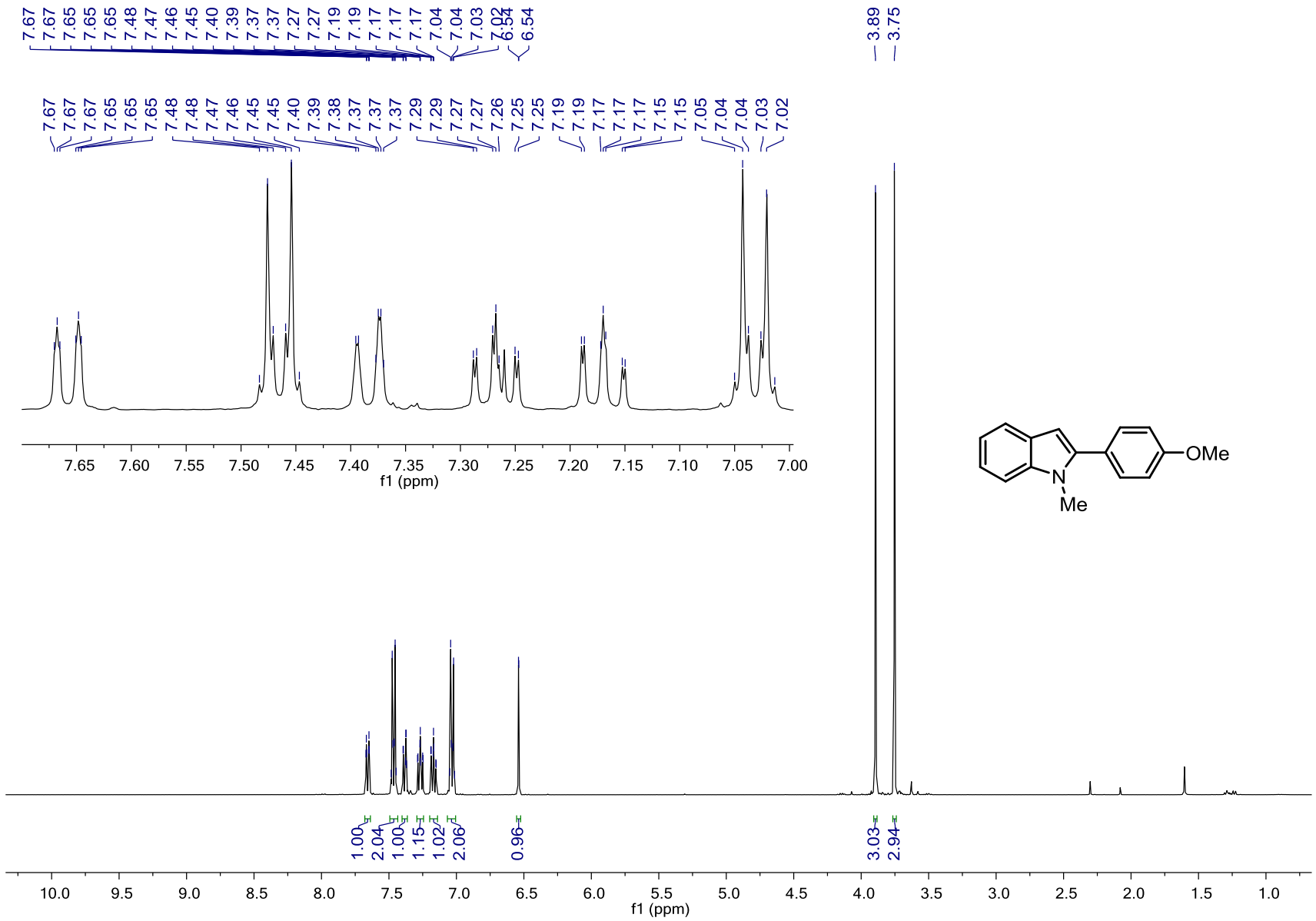
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **10m***



*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **10m***



*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **10n***



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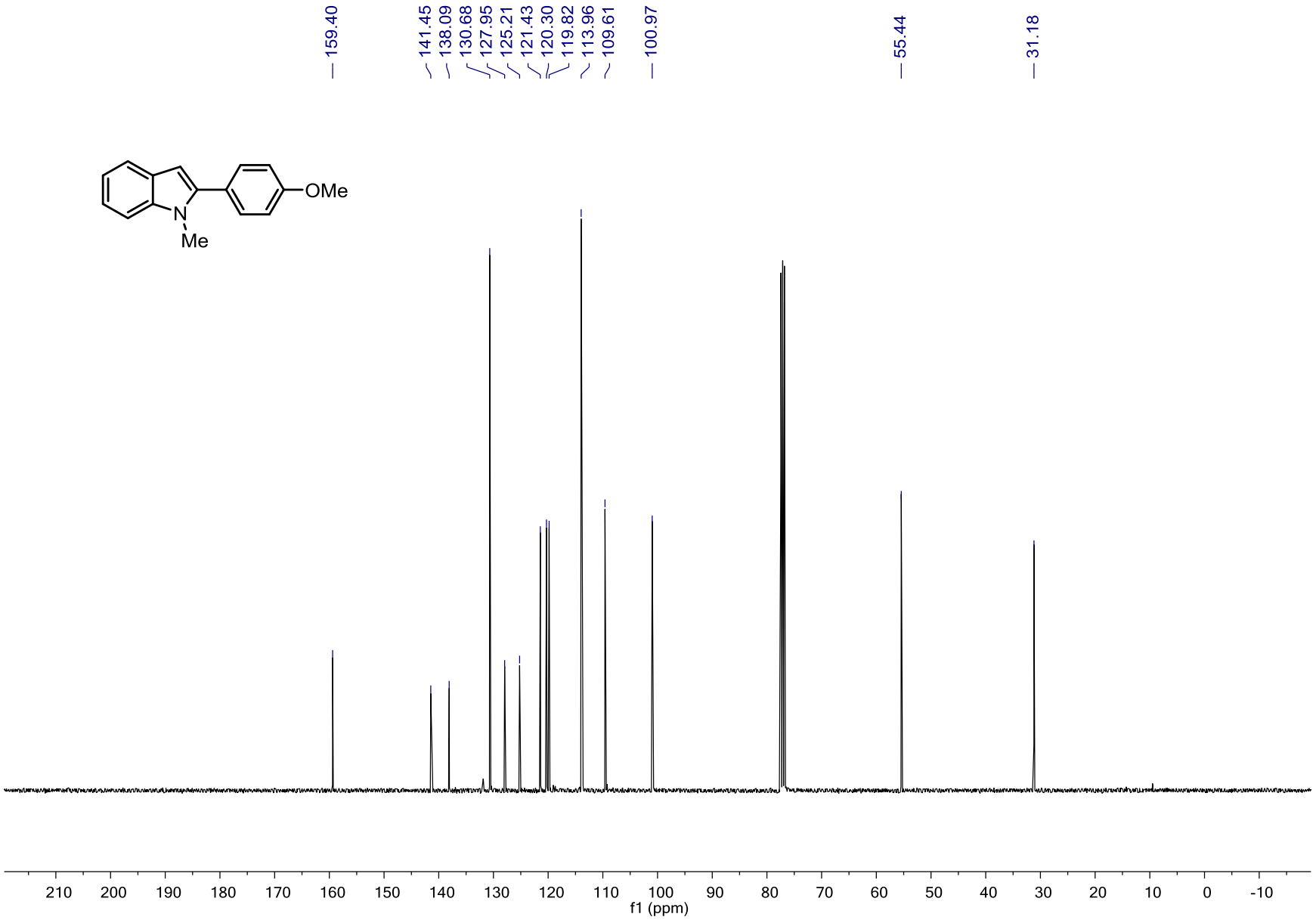
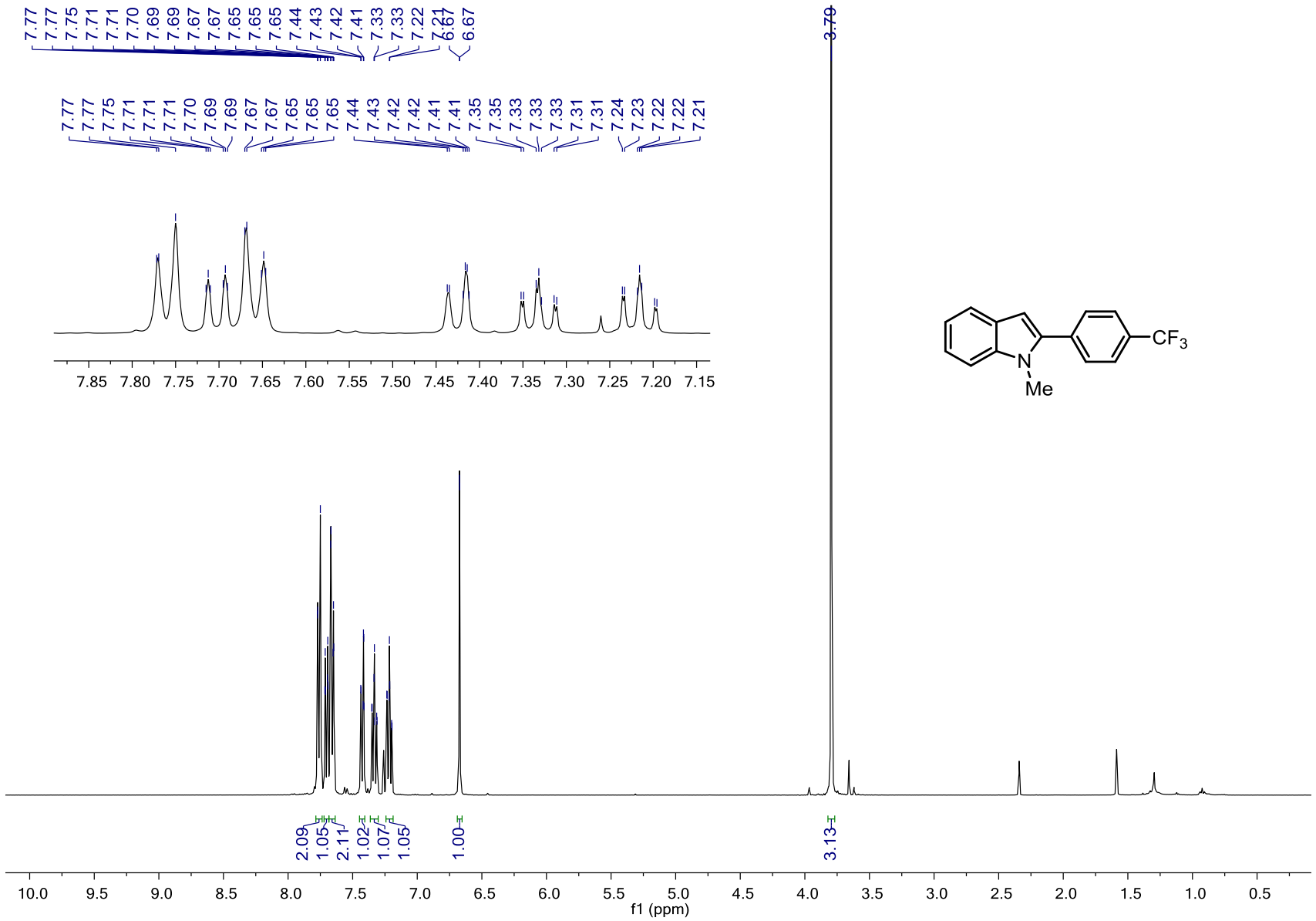
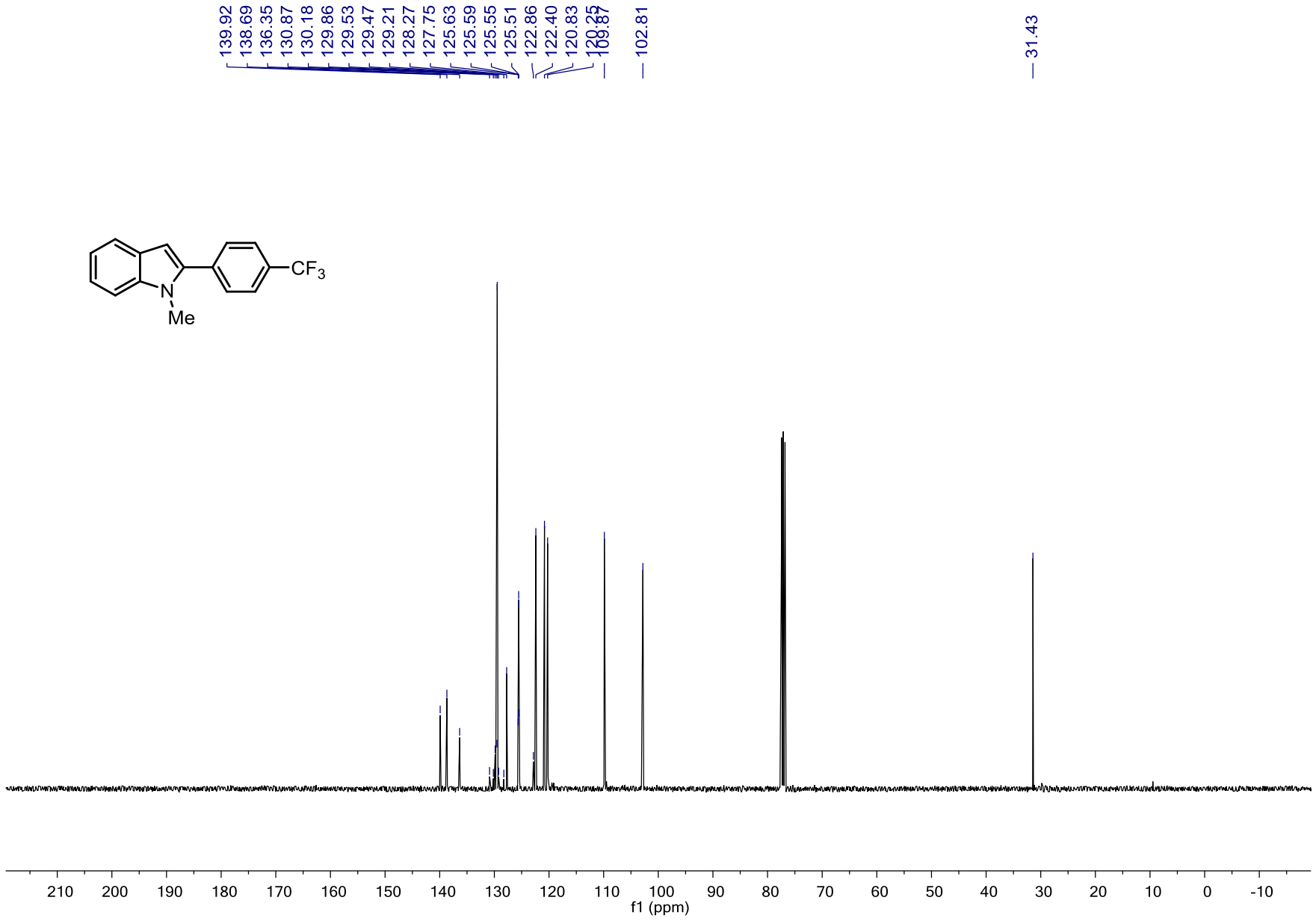


*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **10o***



*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **10p***



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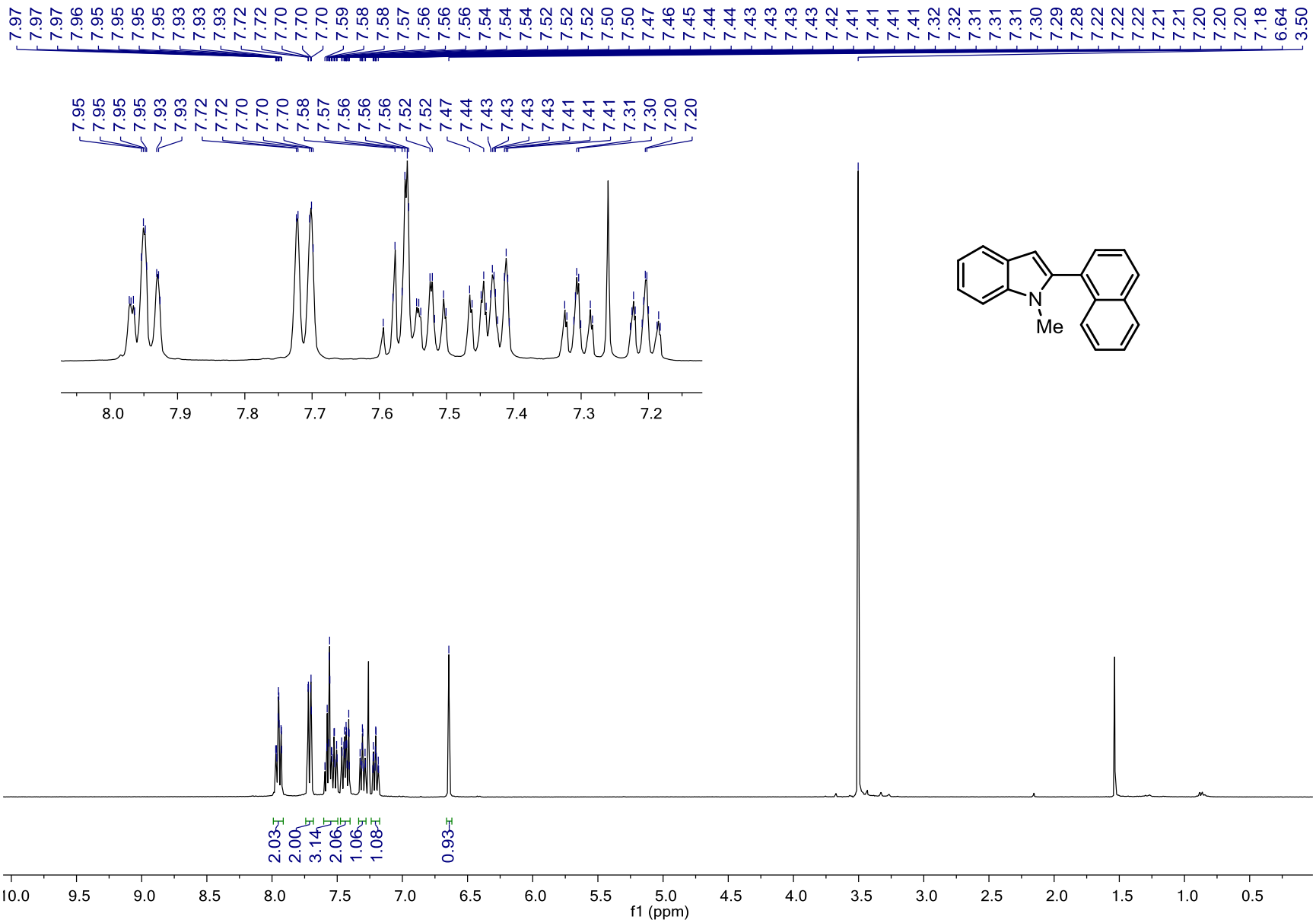

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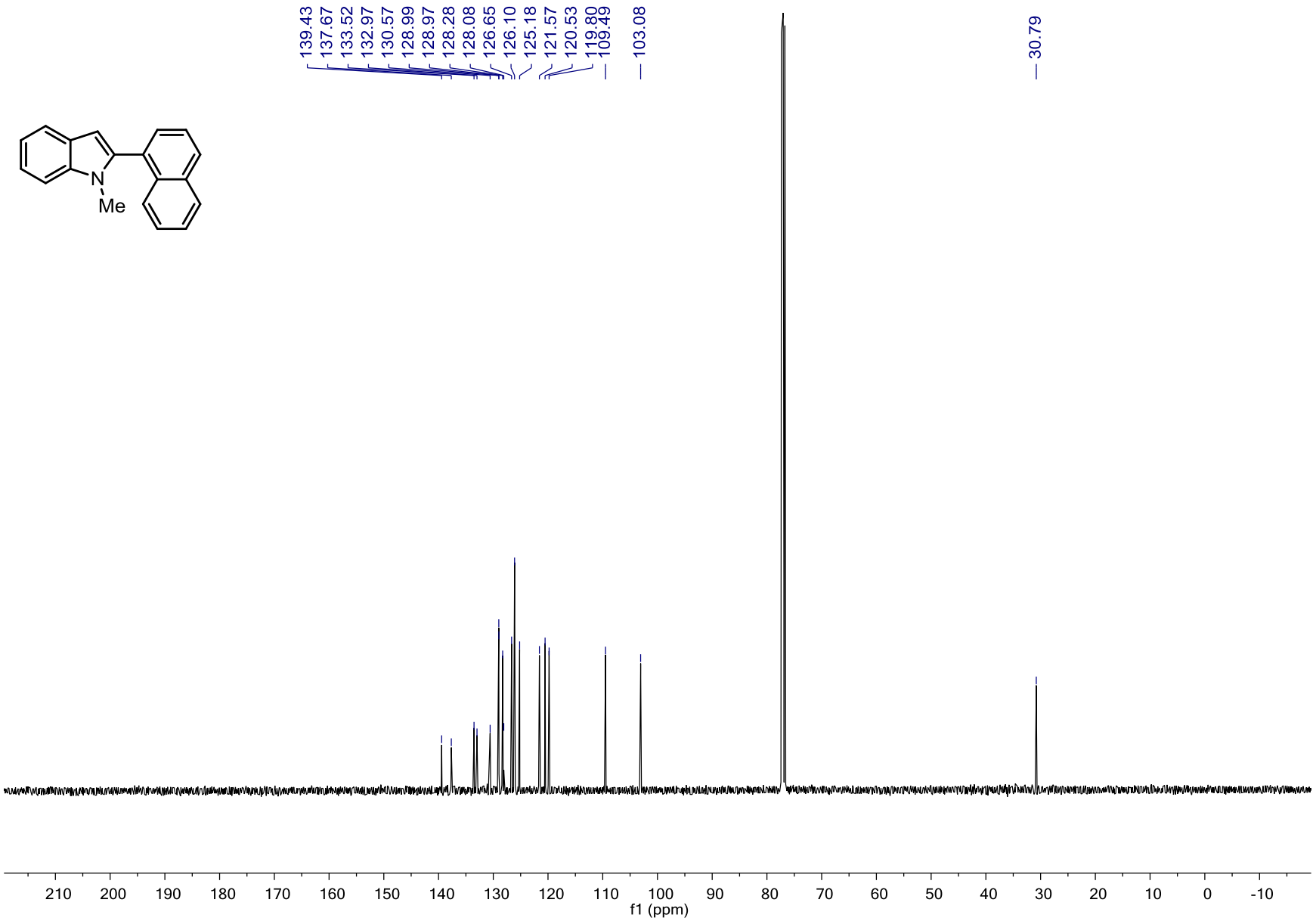
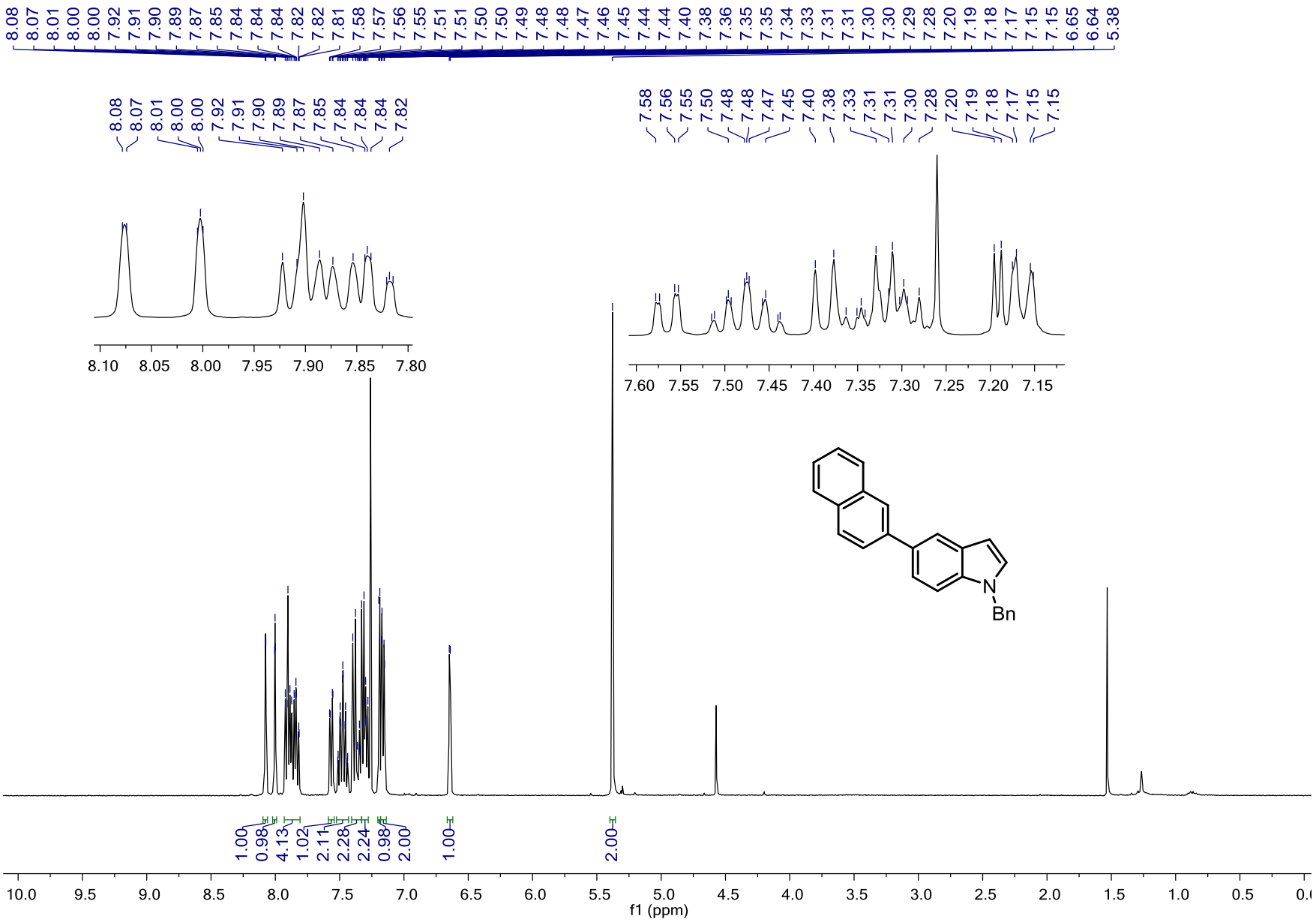


*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **10x***



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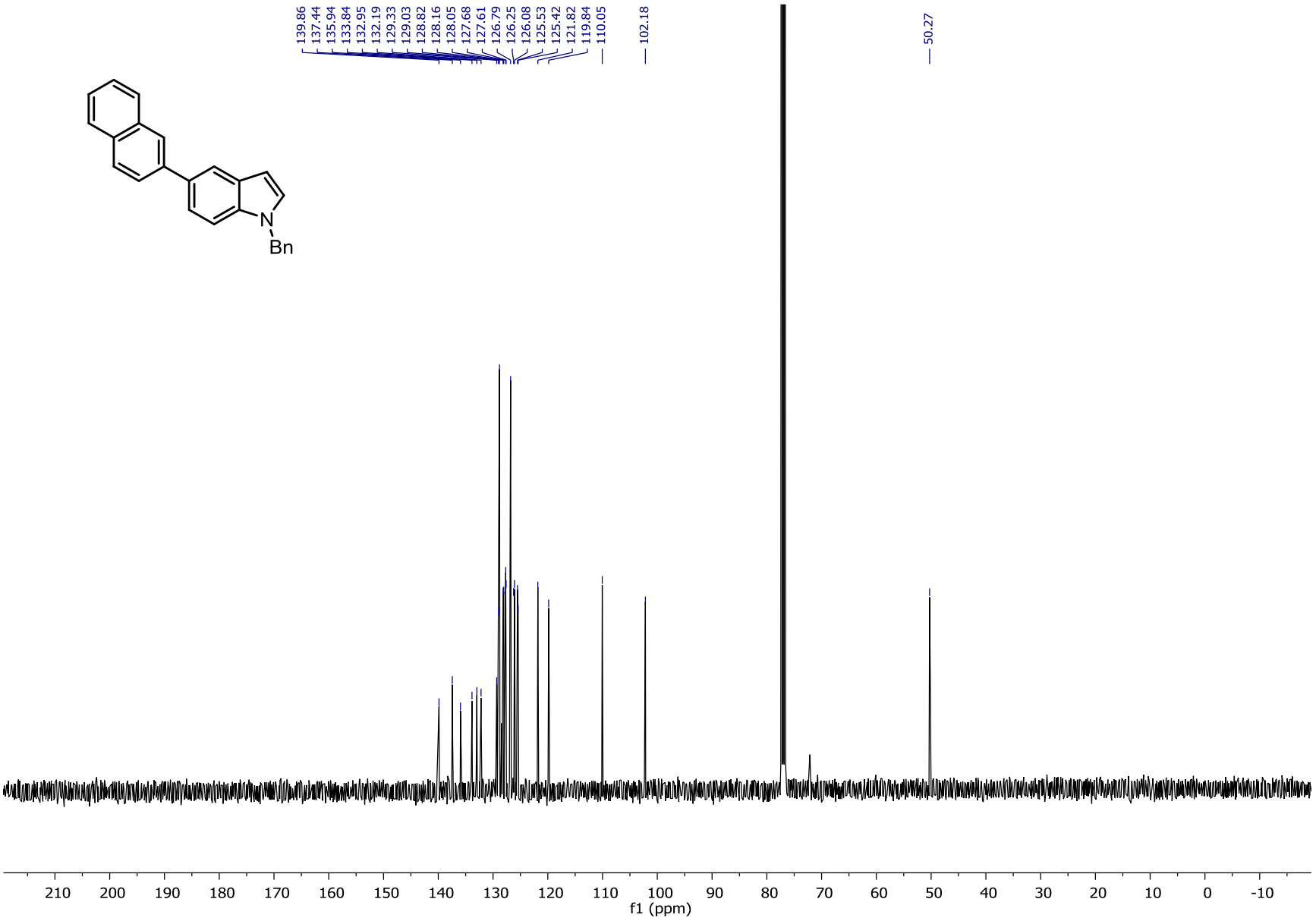
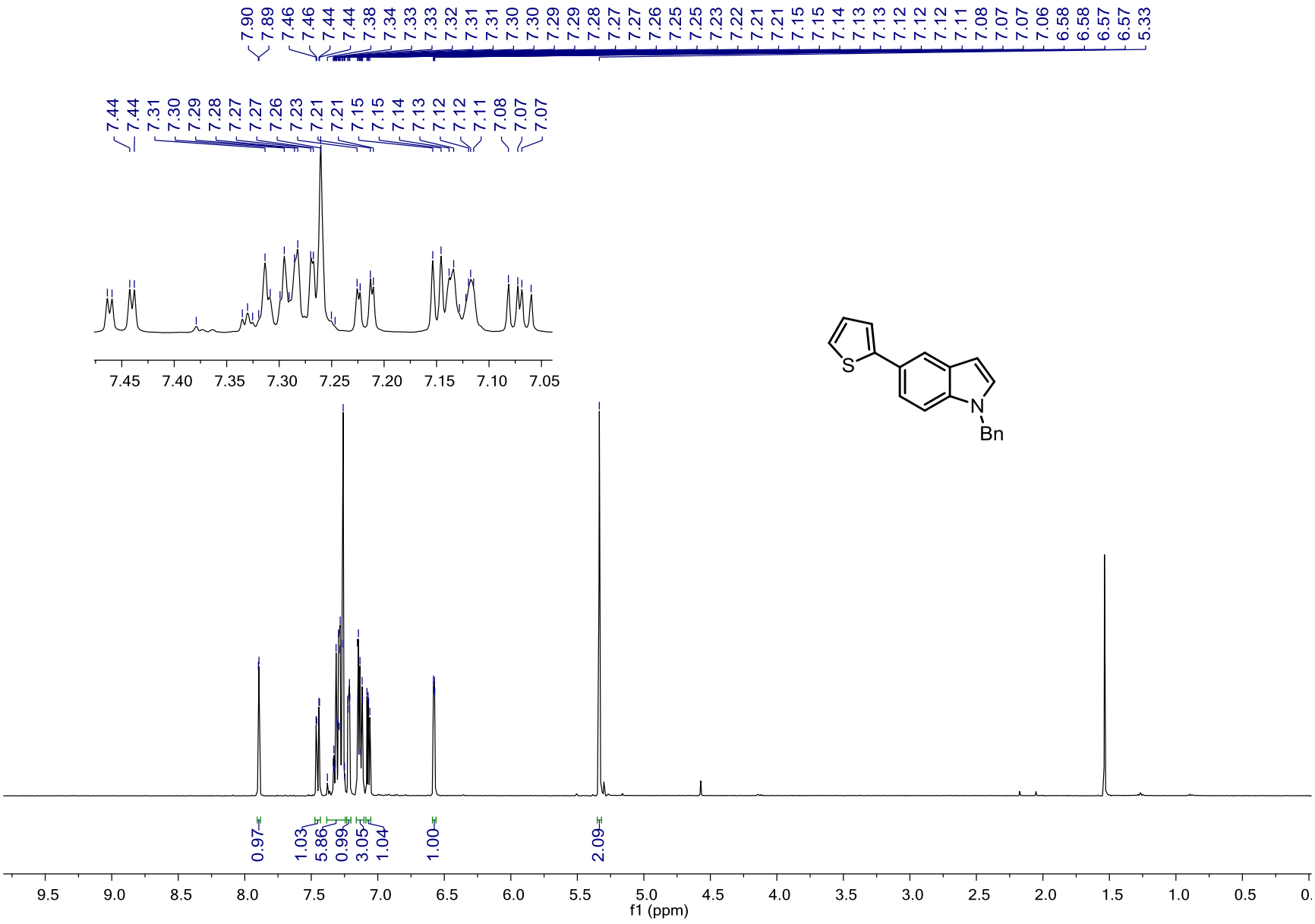


*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **10y***



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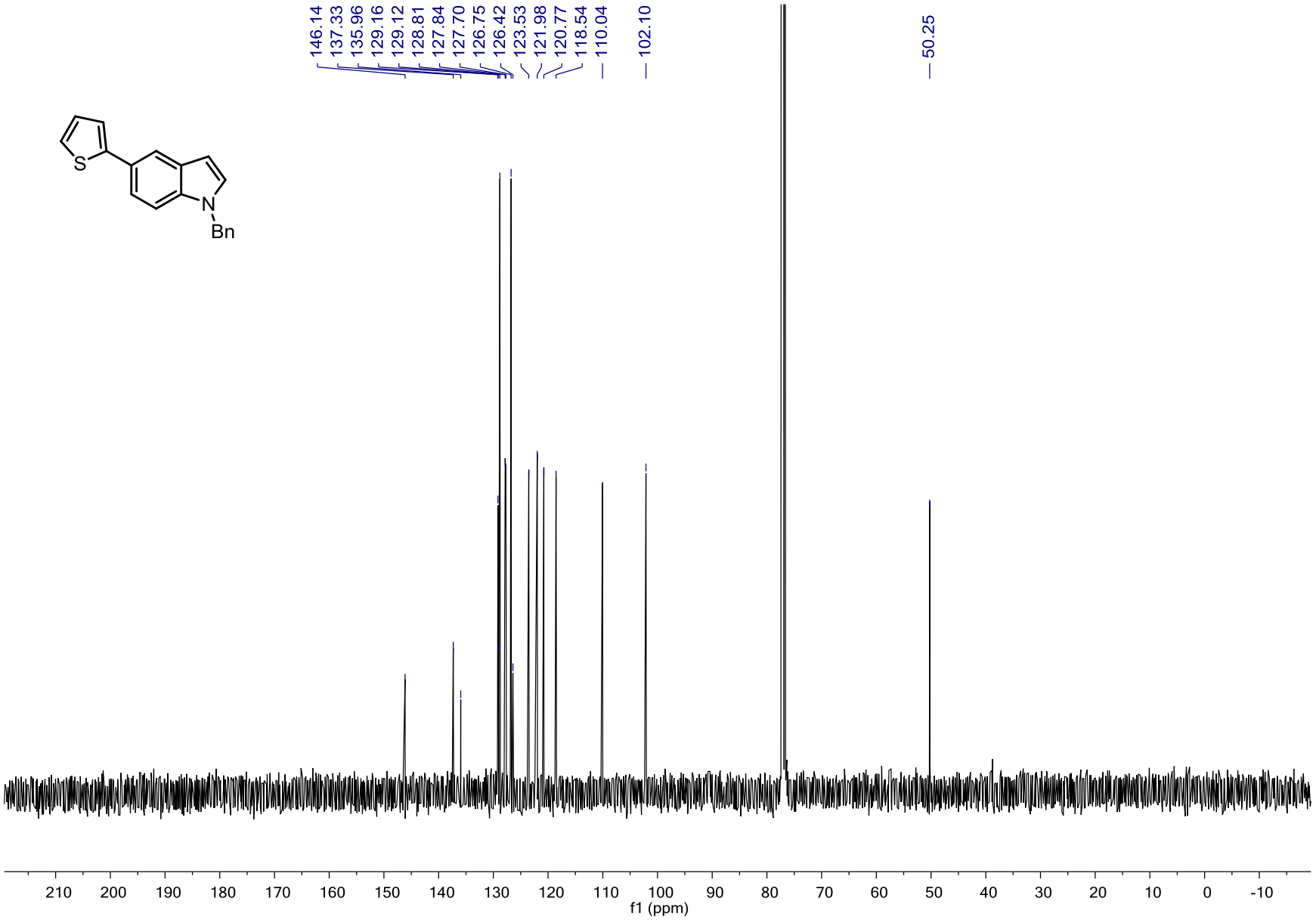

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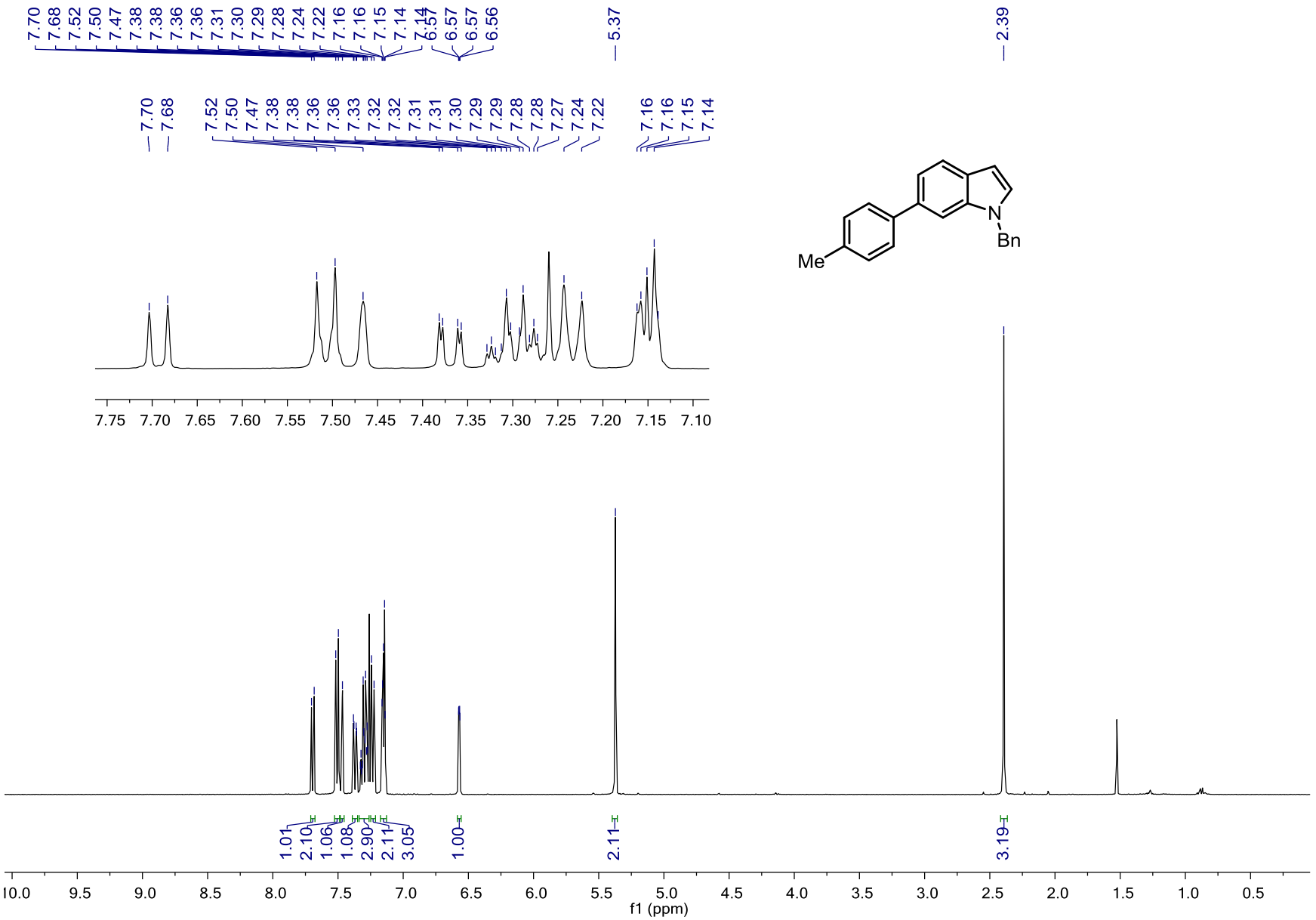

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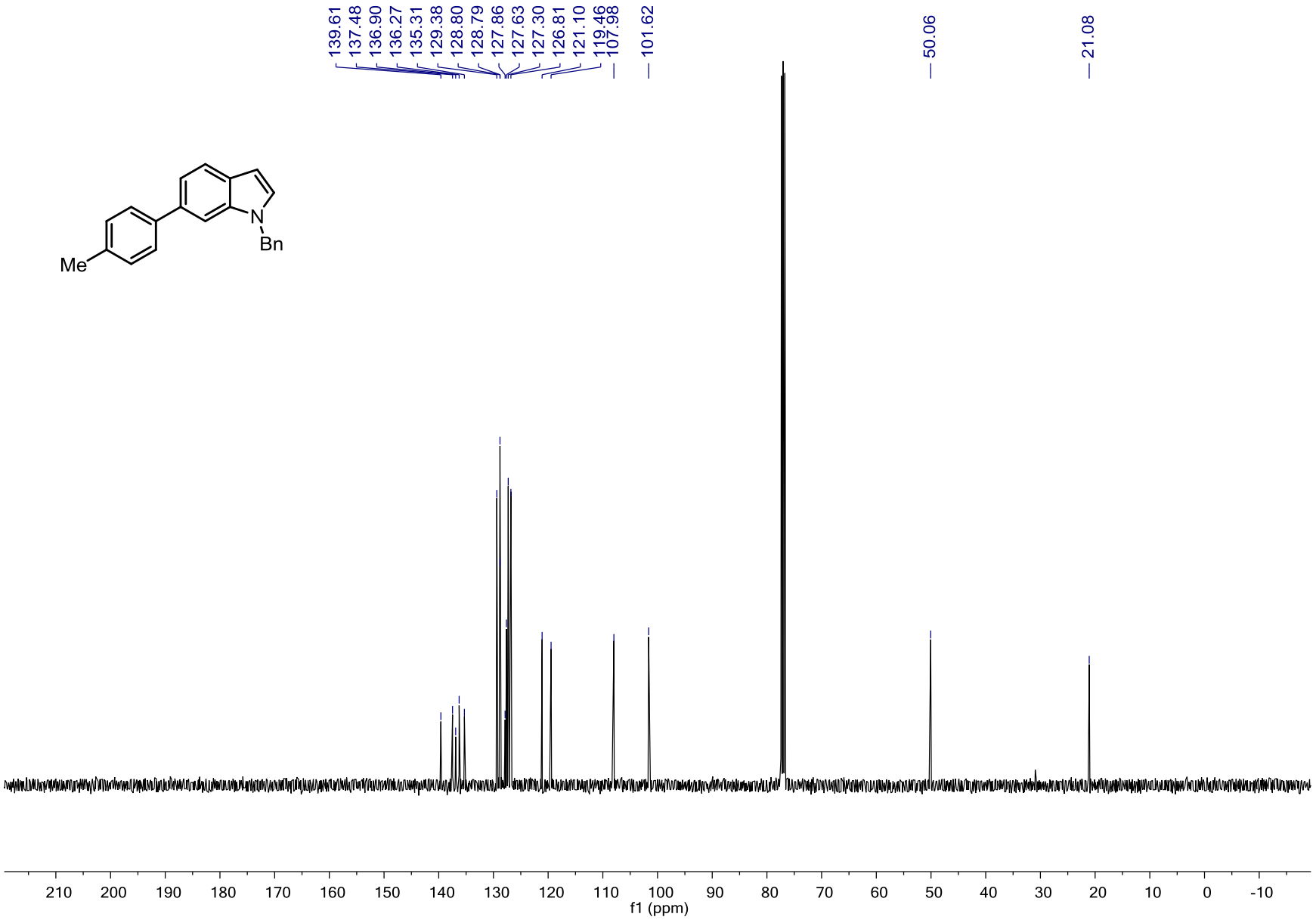
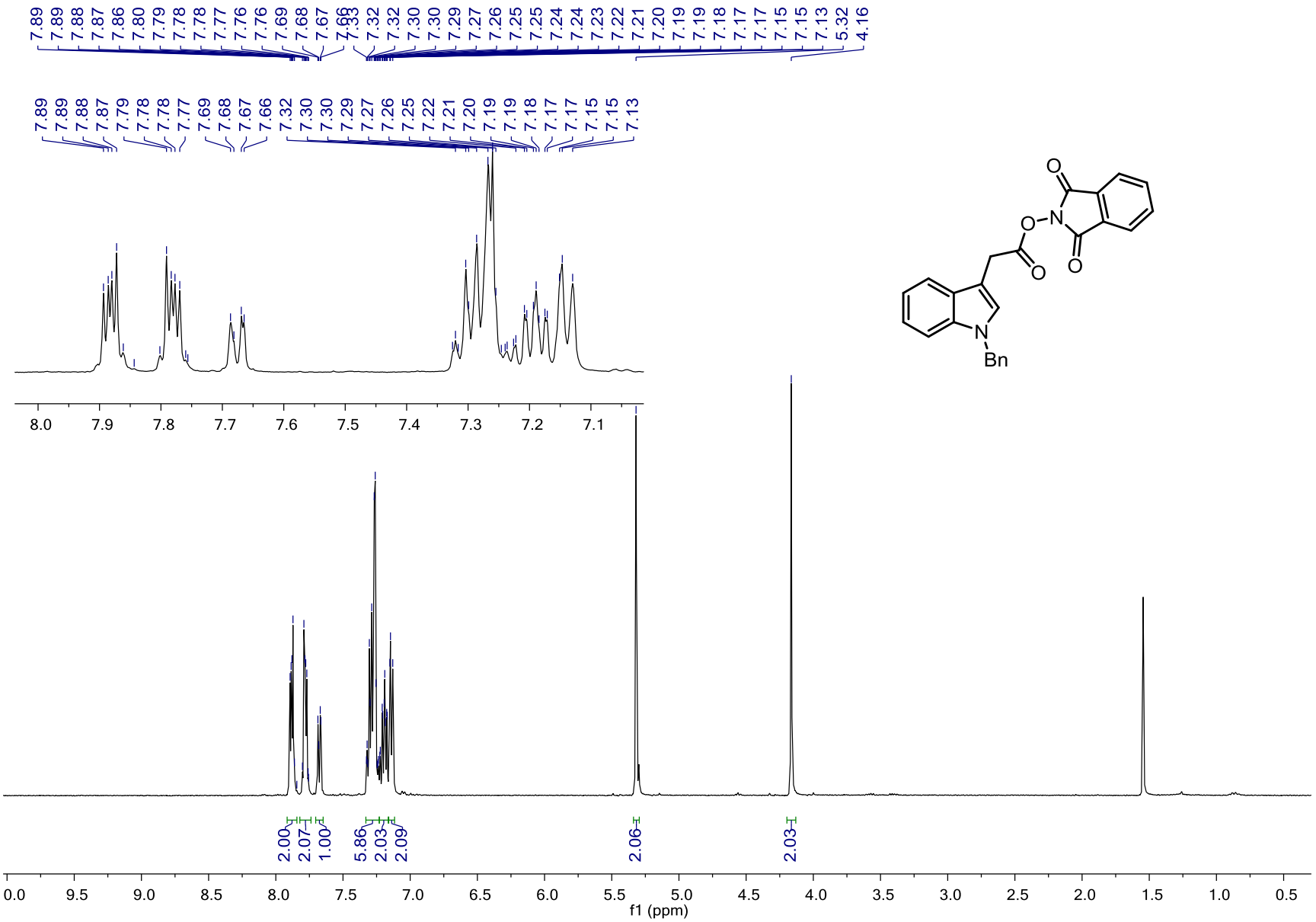


*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12a***



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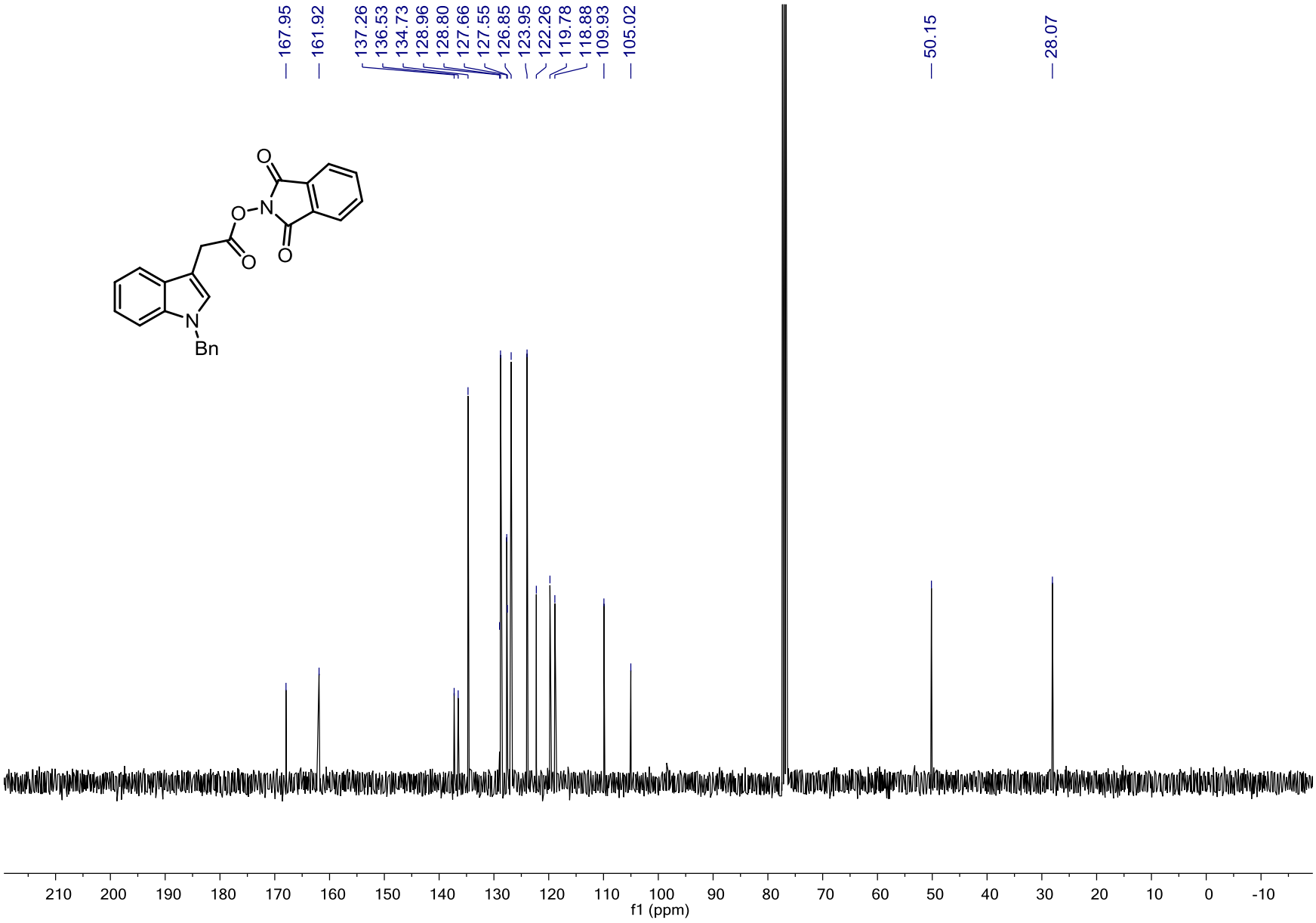
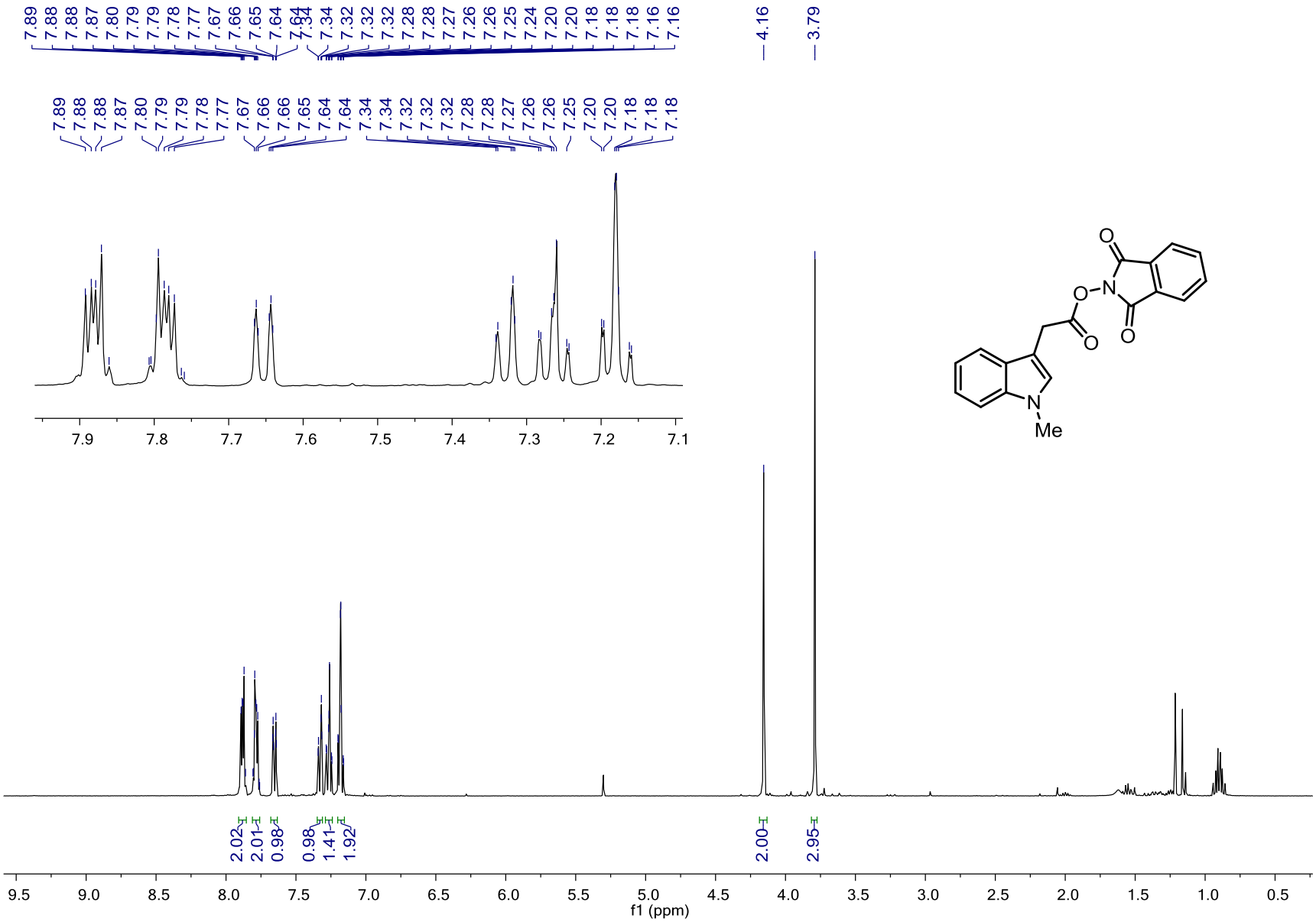


*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12b***



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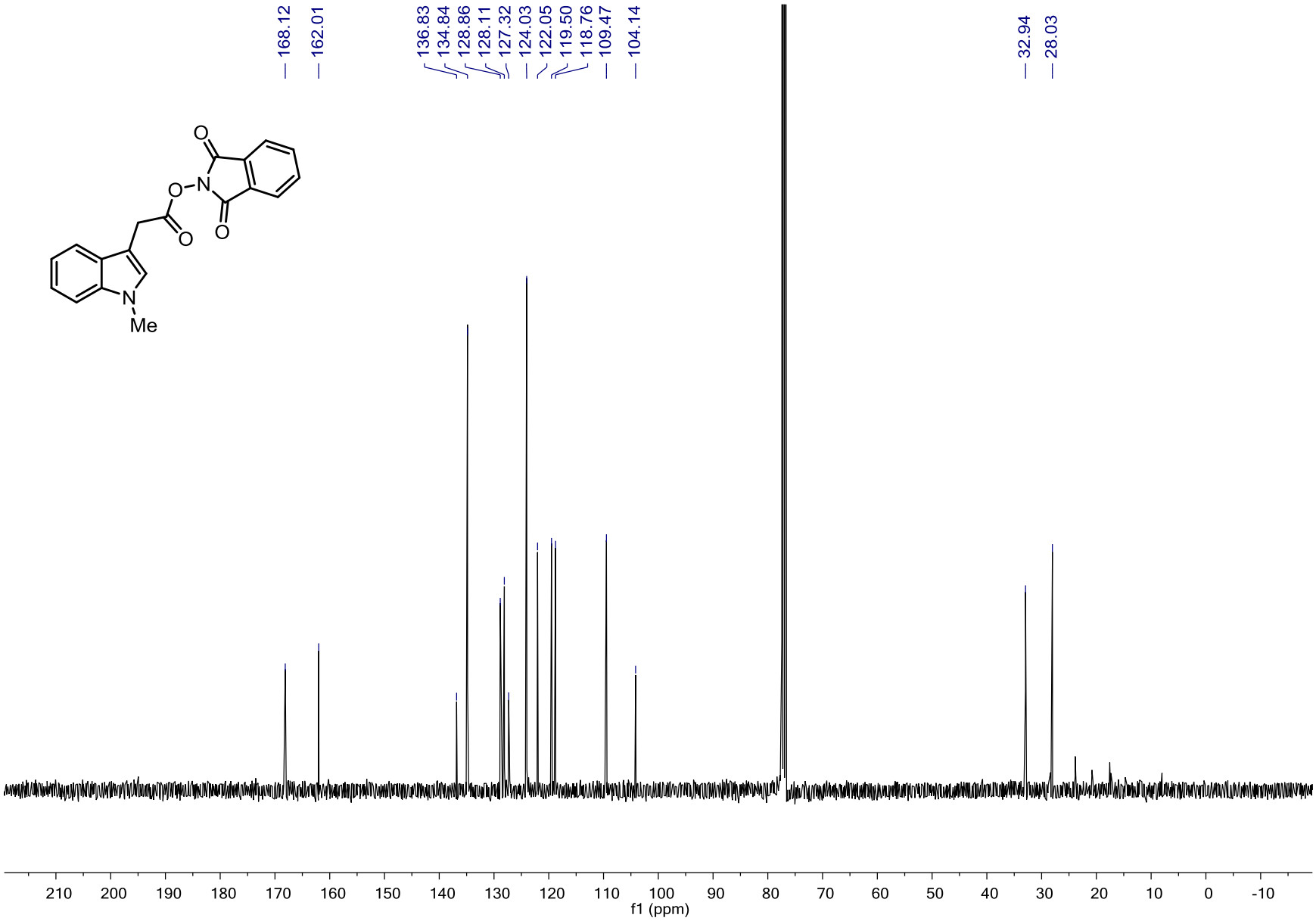
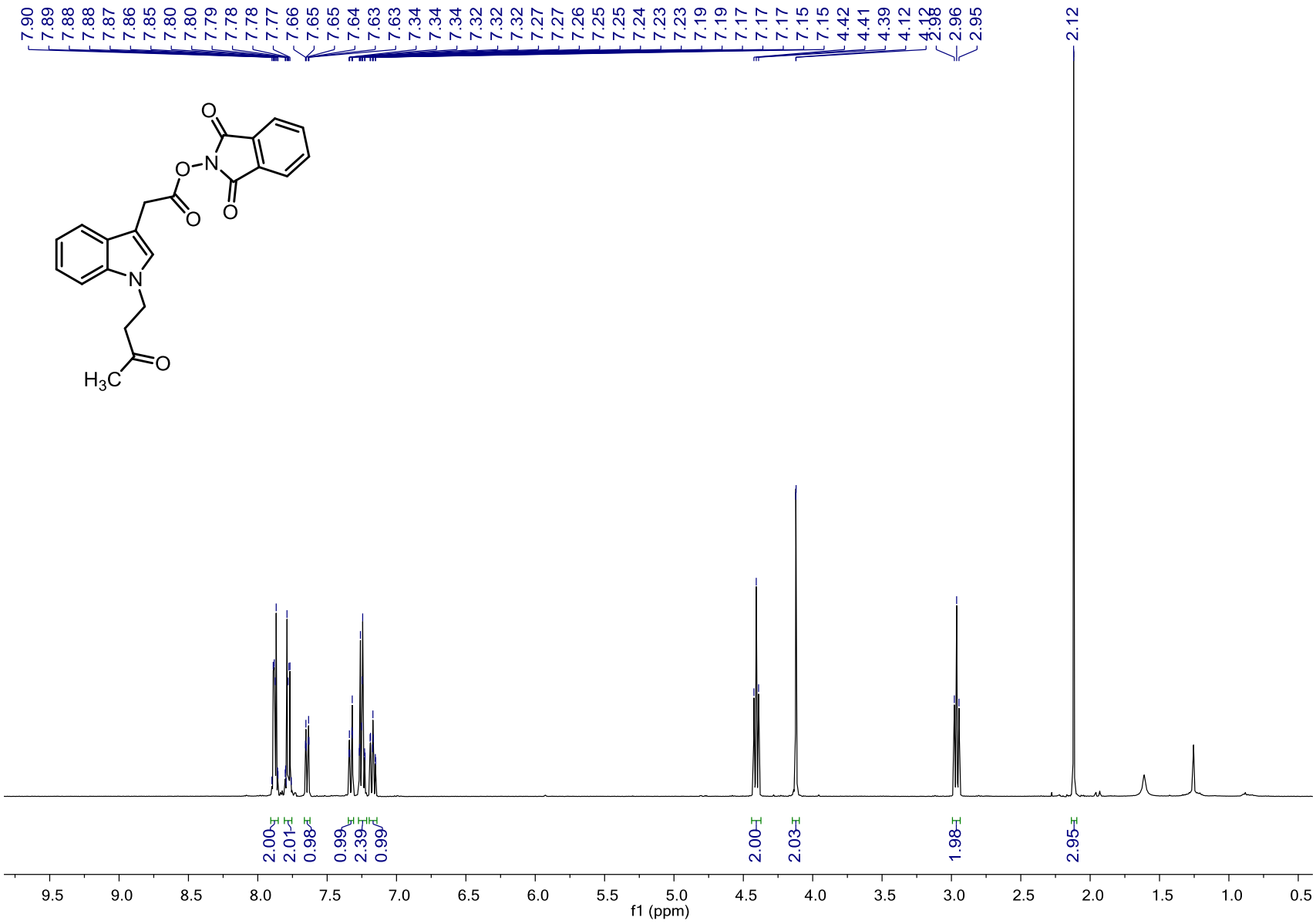
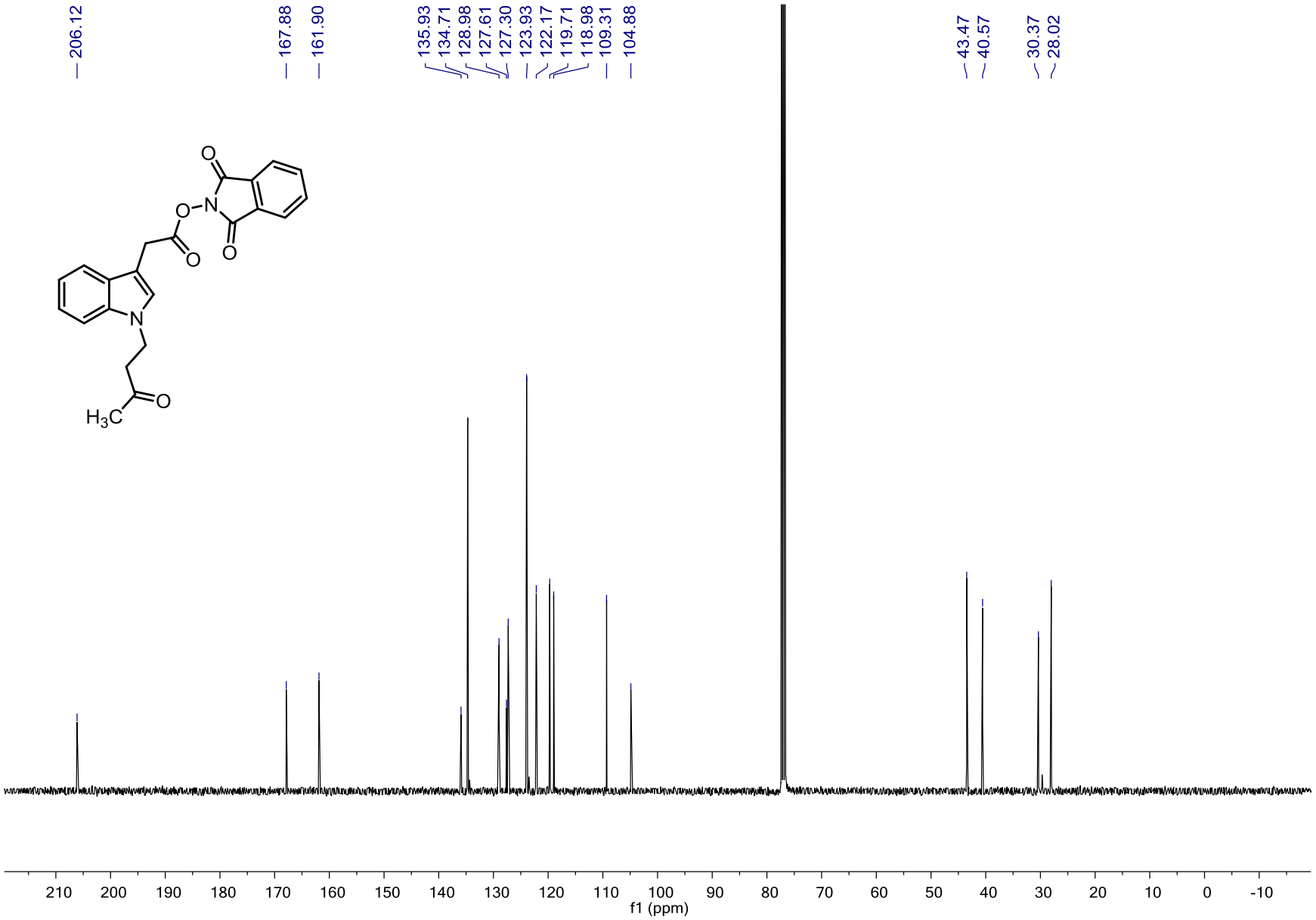


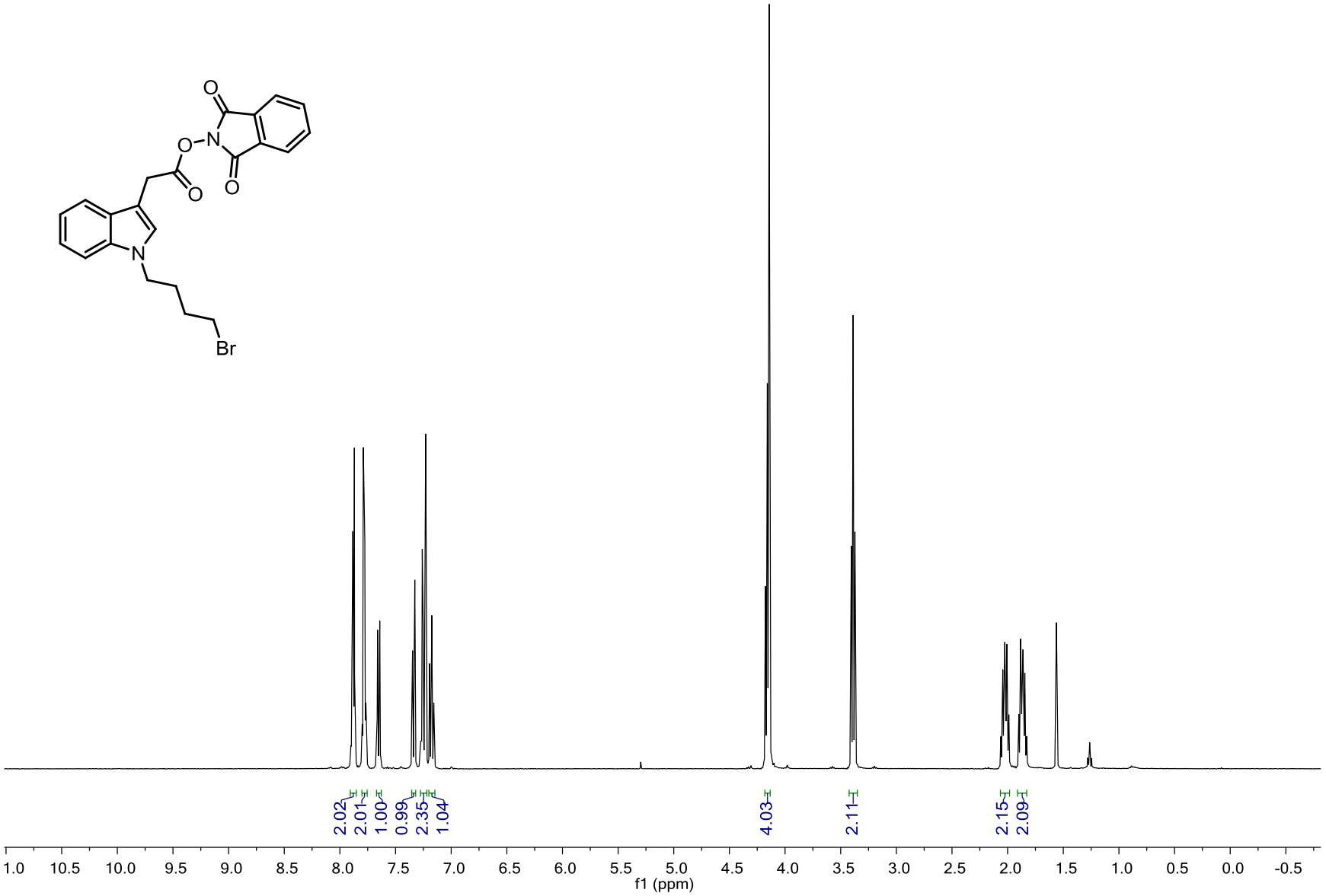
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12c***



*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12c***



*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12d***



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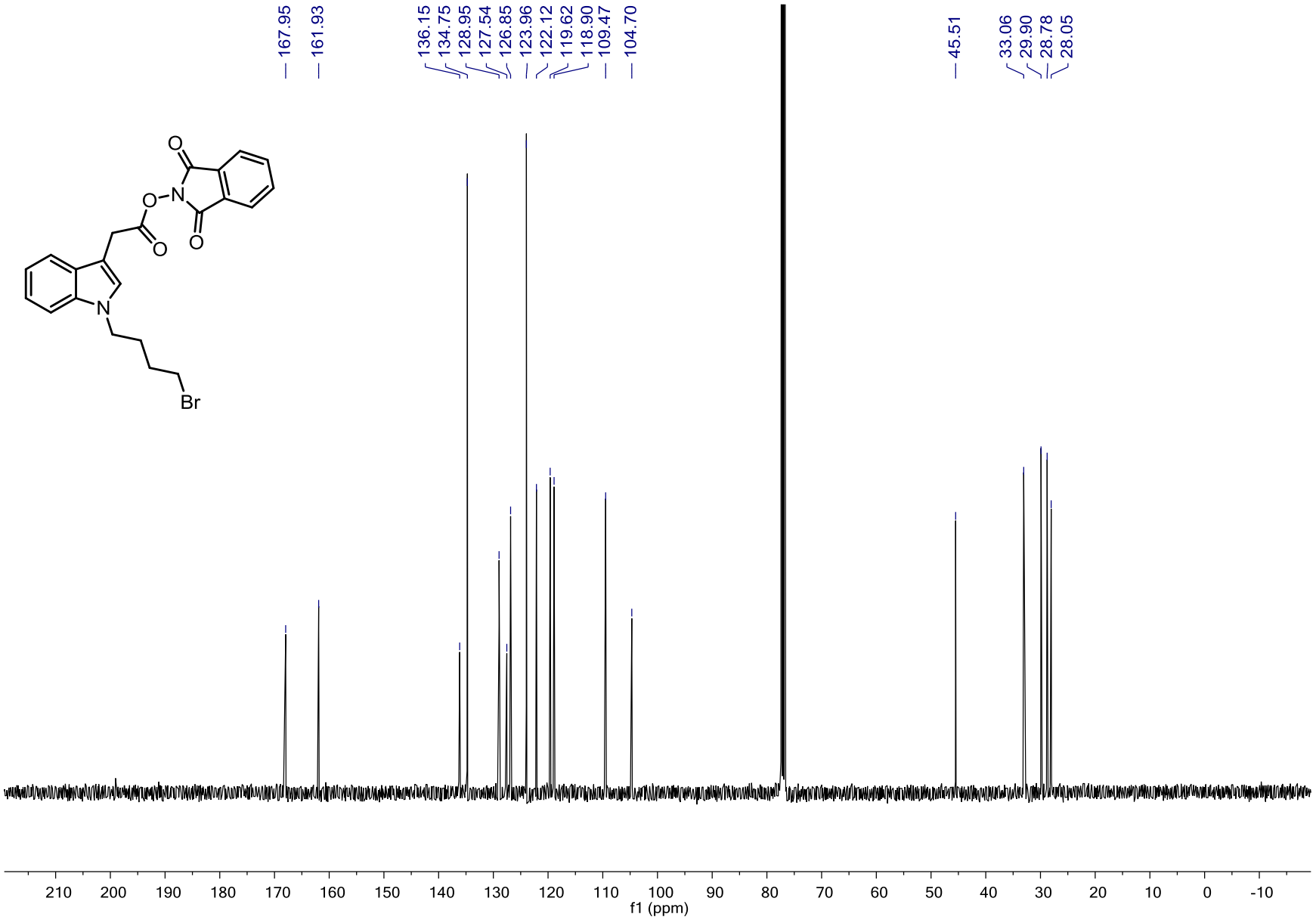
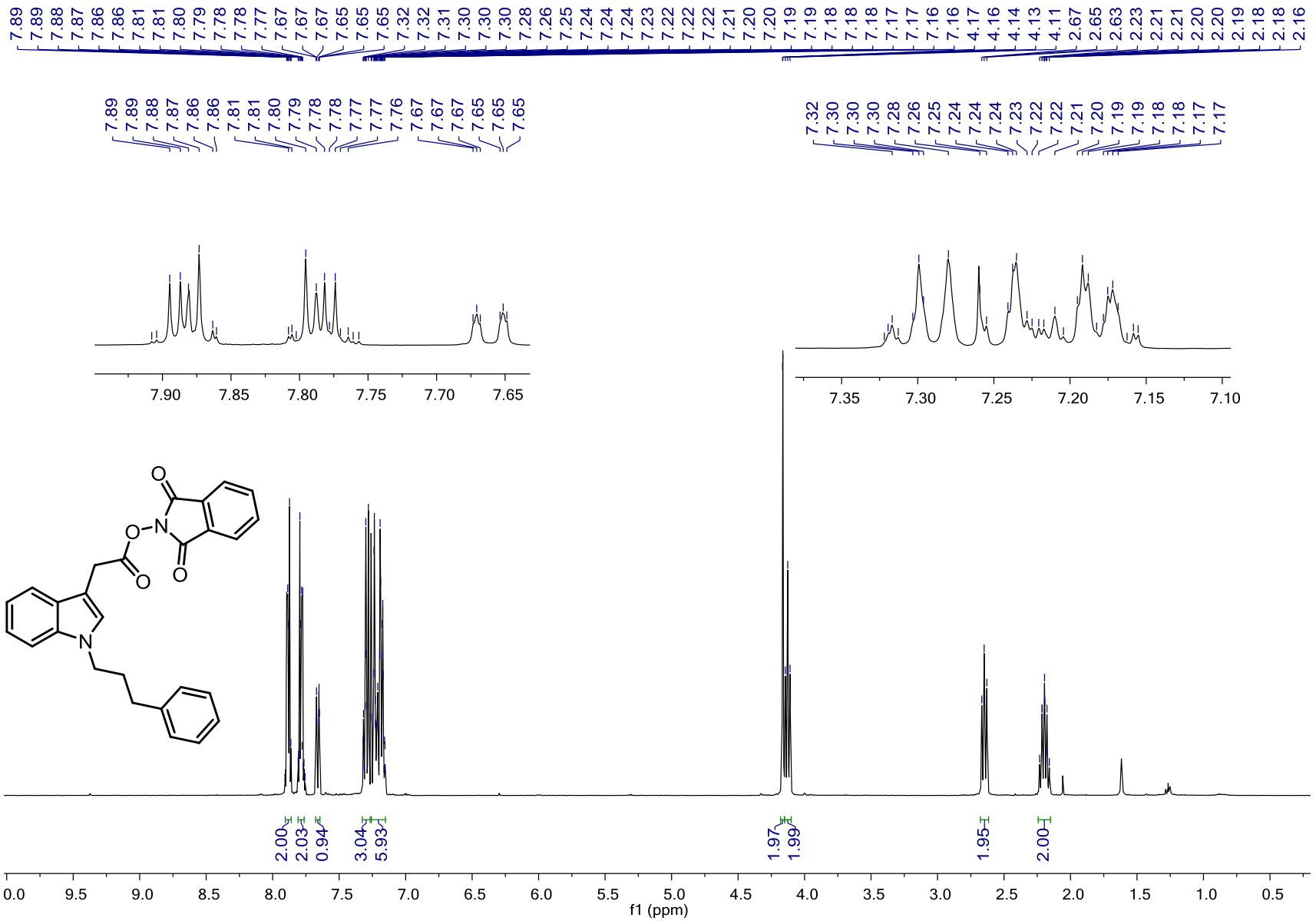
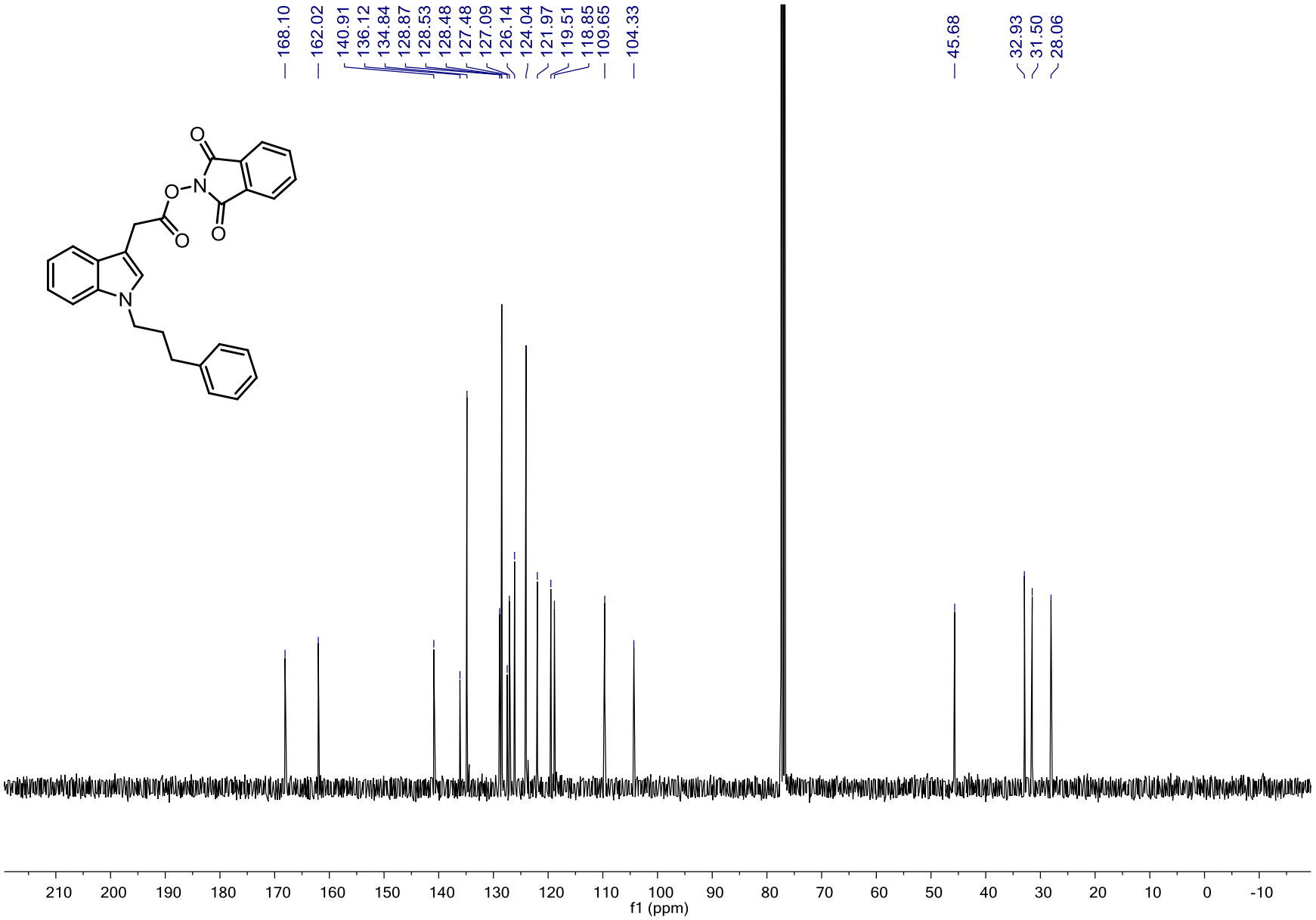


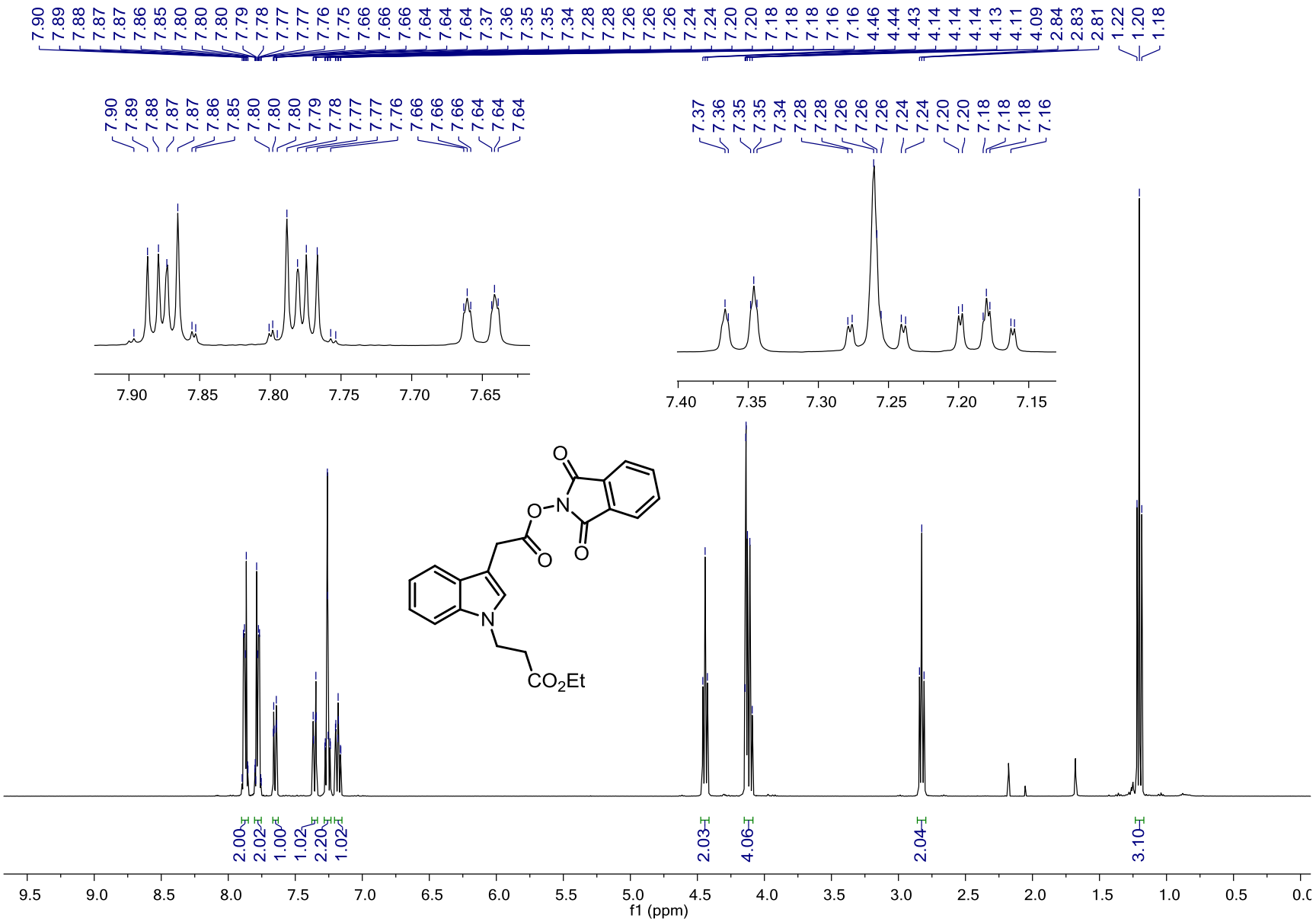
^{1}H-NMR (400 MHz, $CDCl_3$) for compound ***12e***



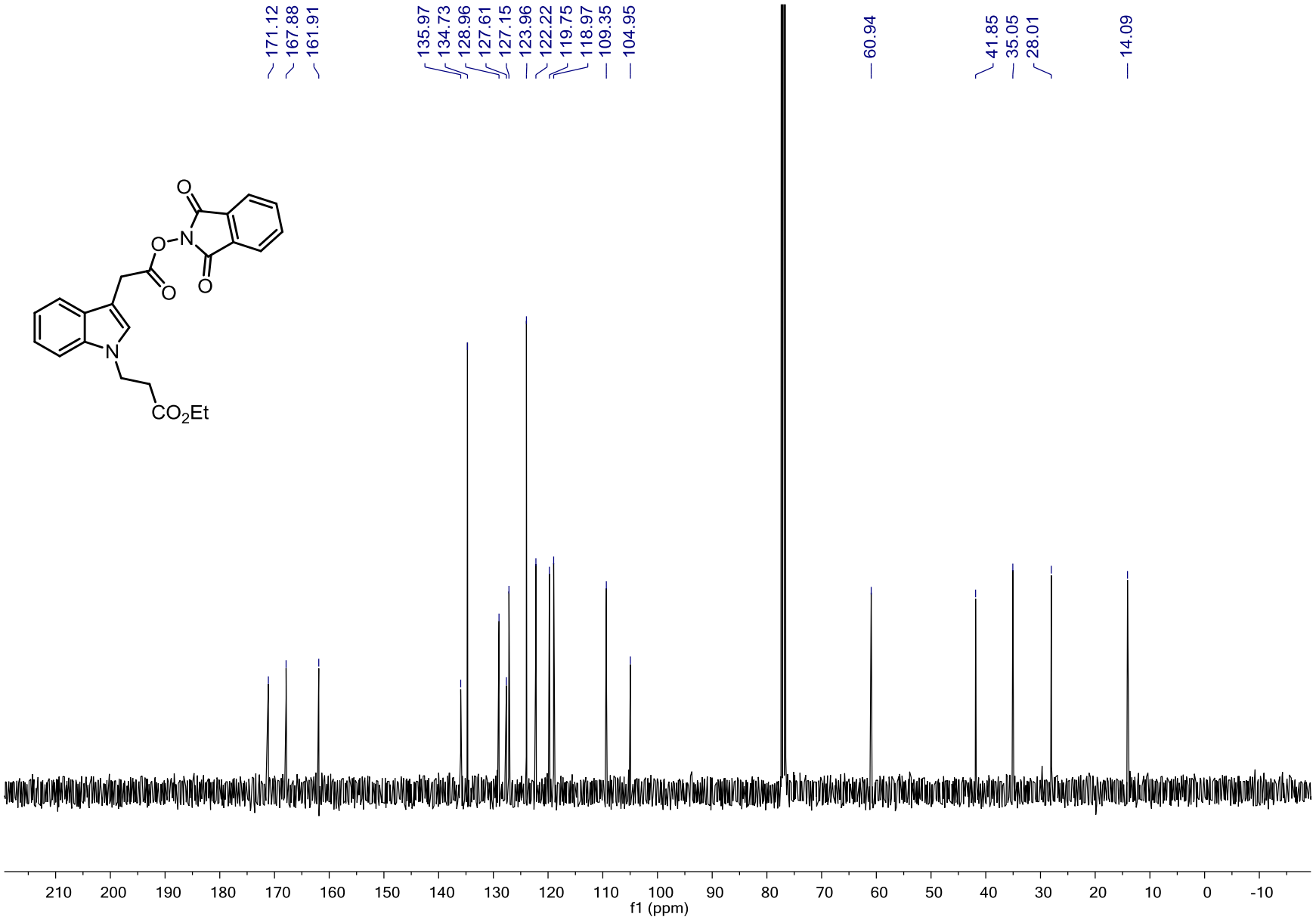
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12e***



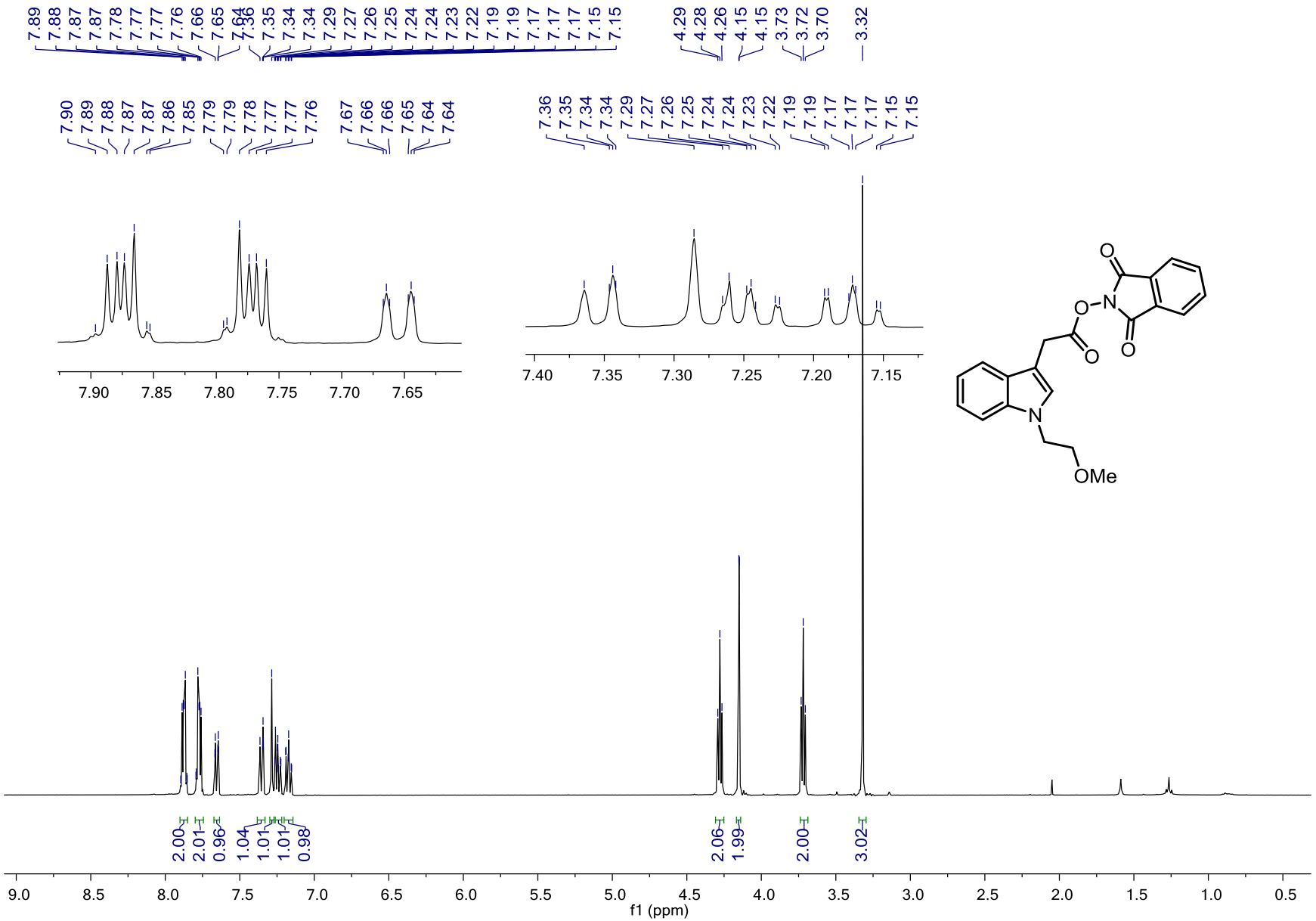
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12f***



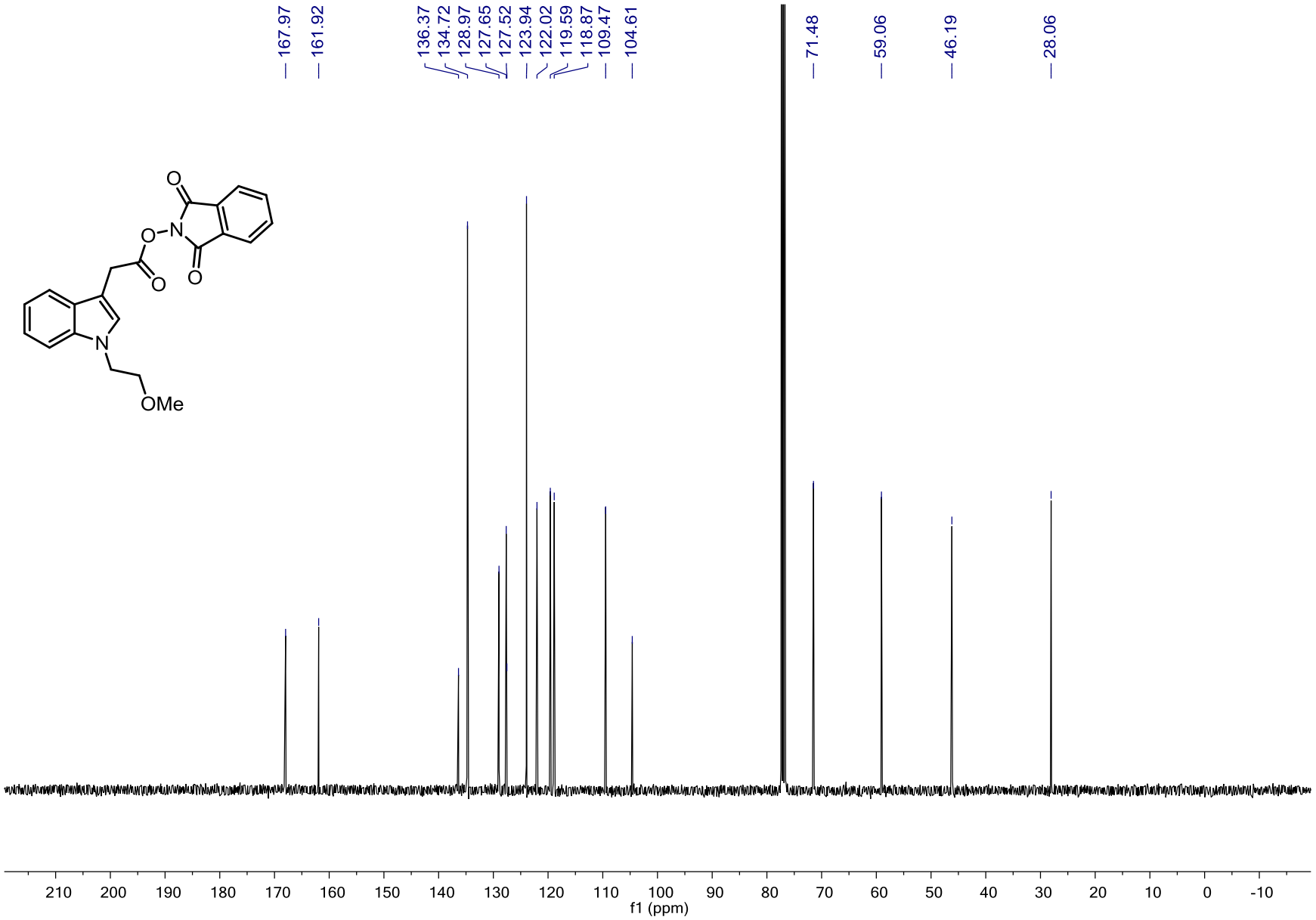
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12f***



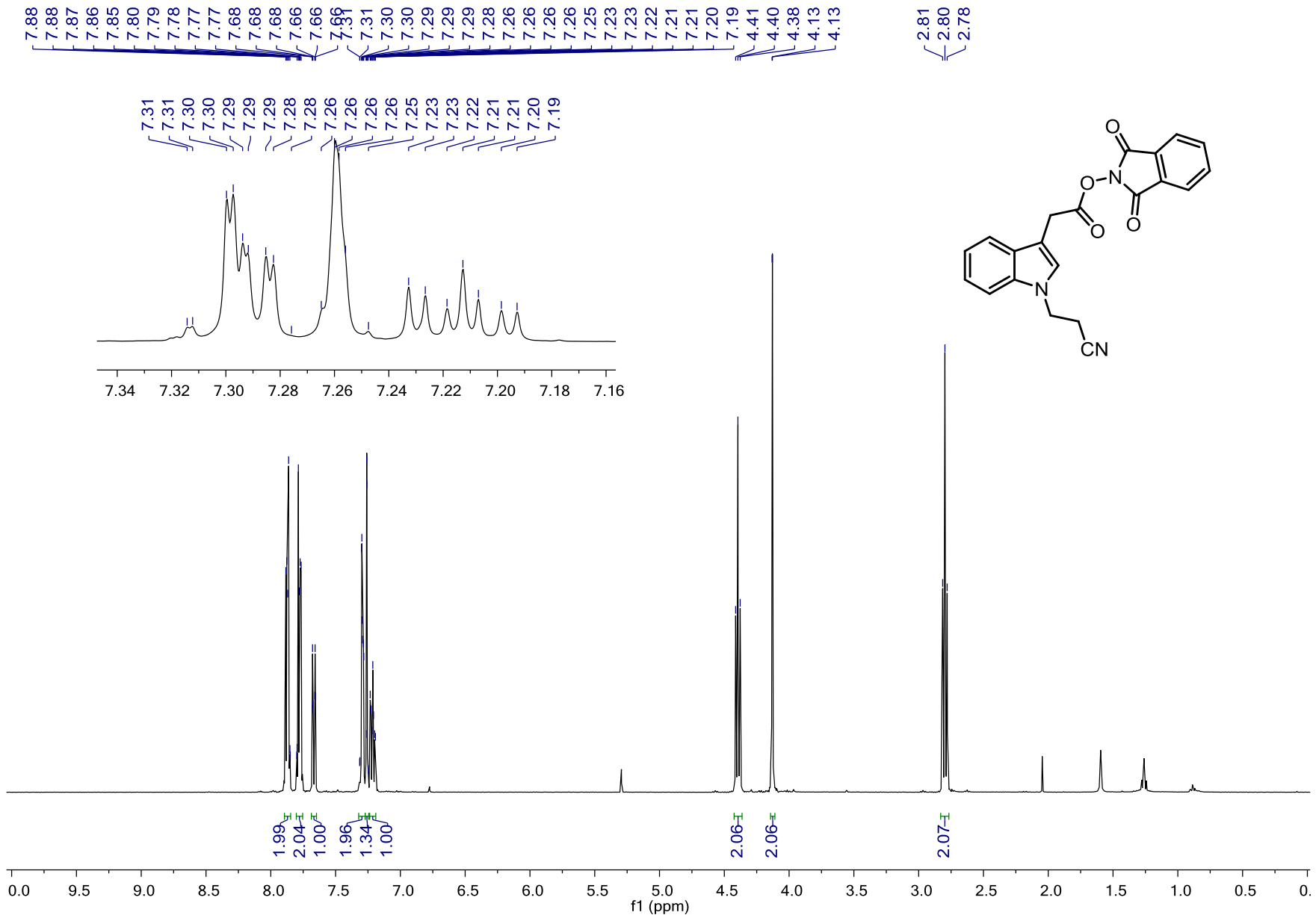
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12g***



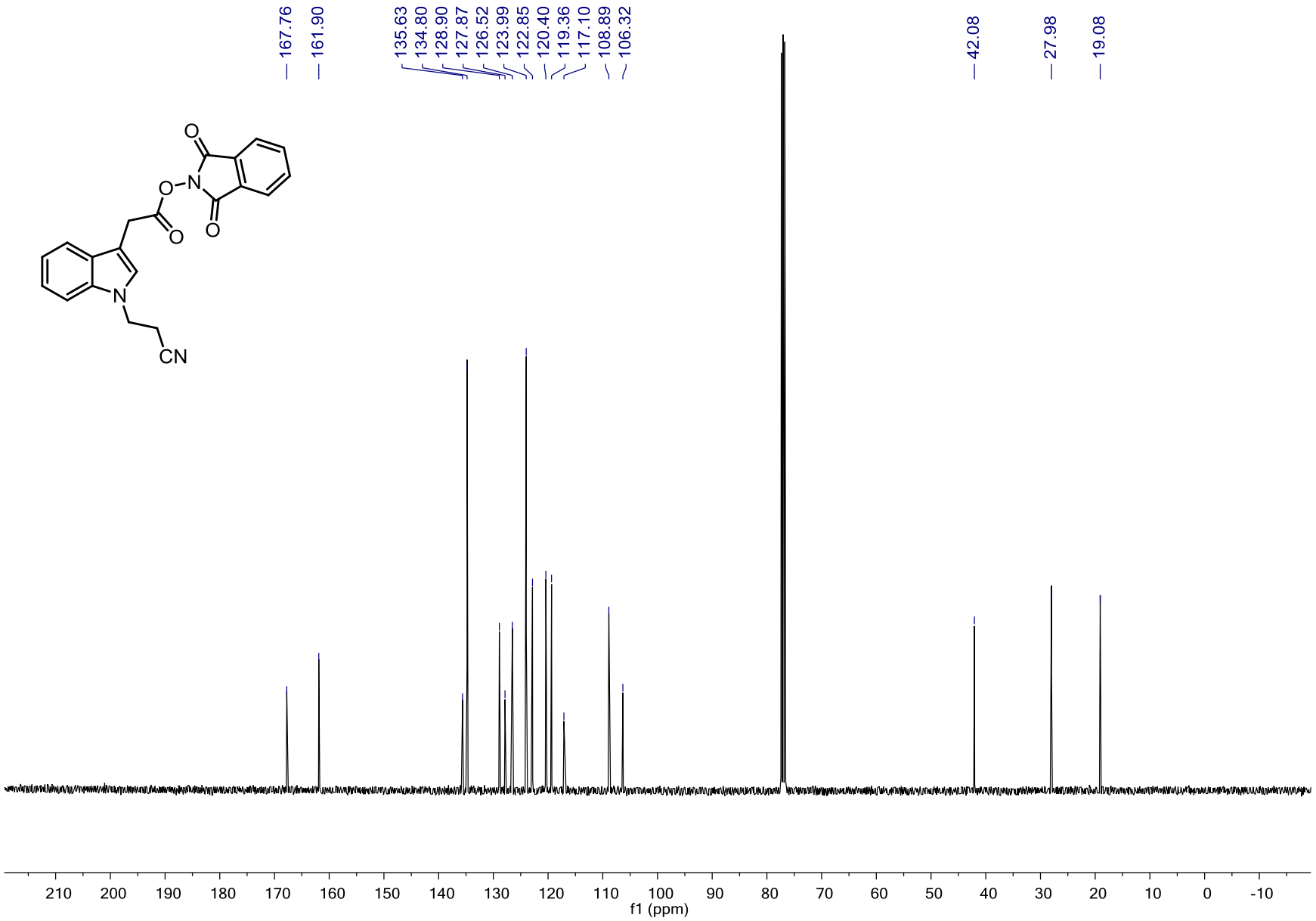
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12g***



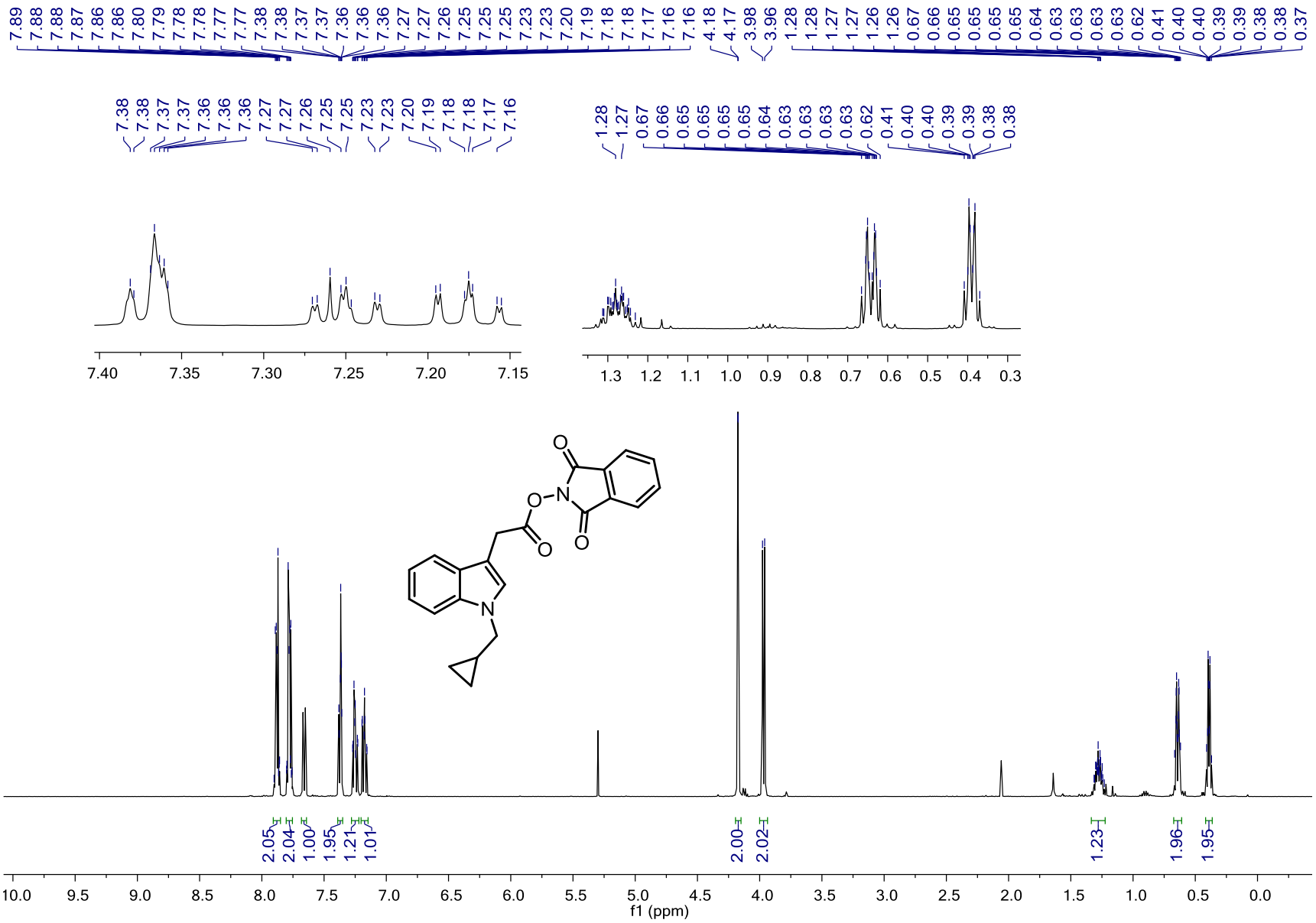
^{1}H-NMR (400 MHz, $CDCl_3$) for compound ***12h***



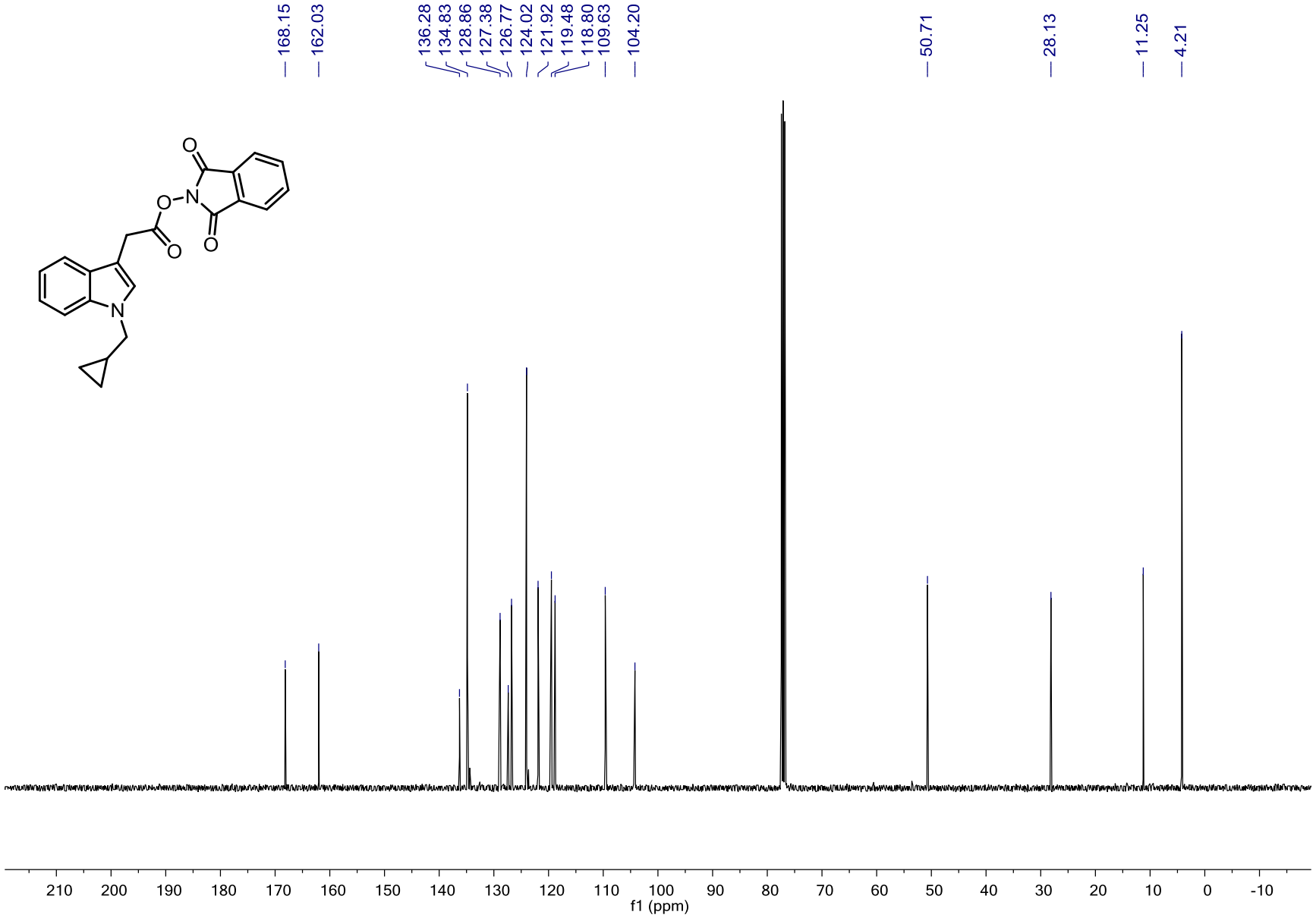
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12h***



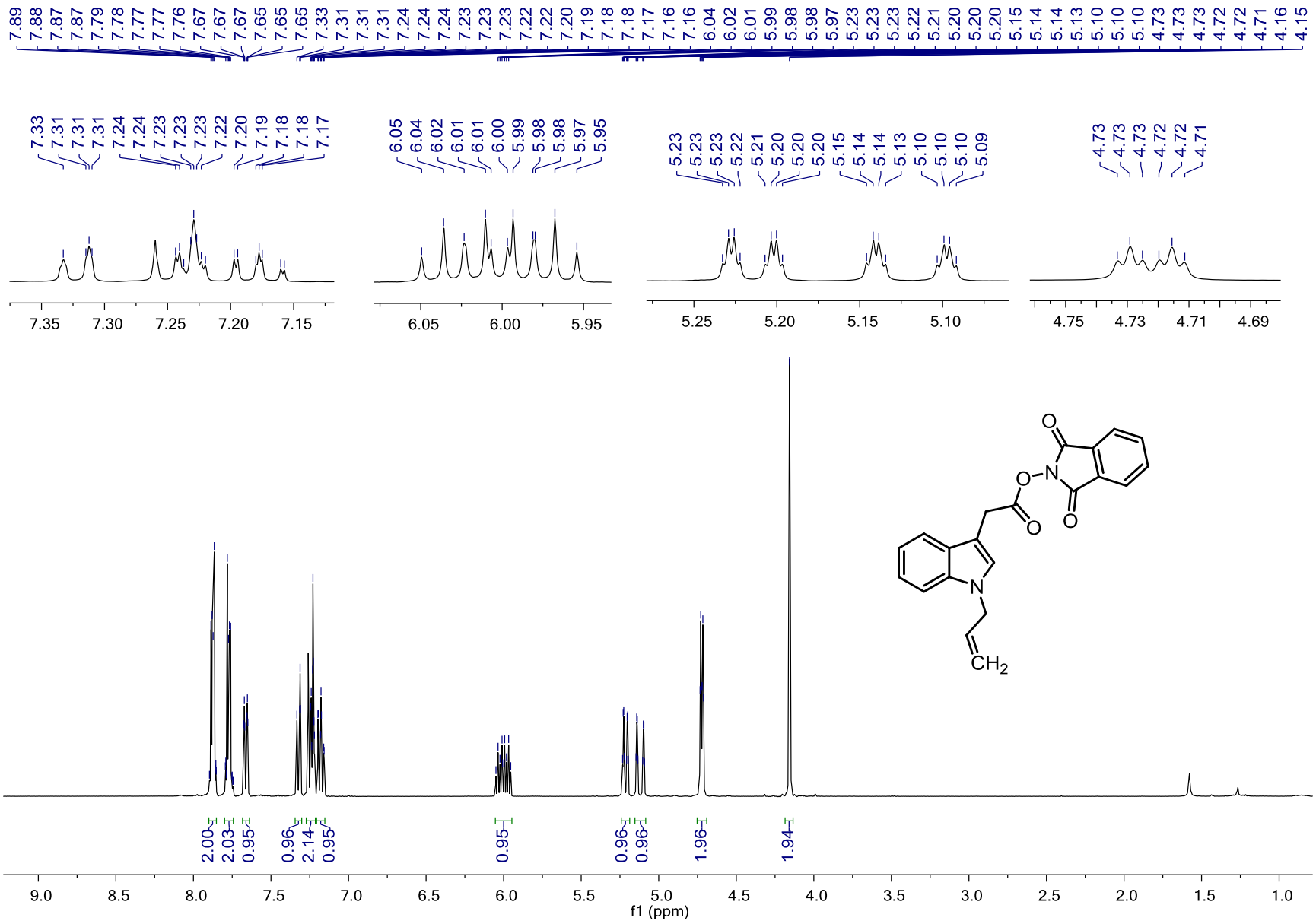
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12i***



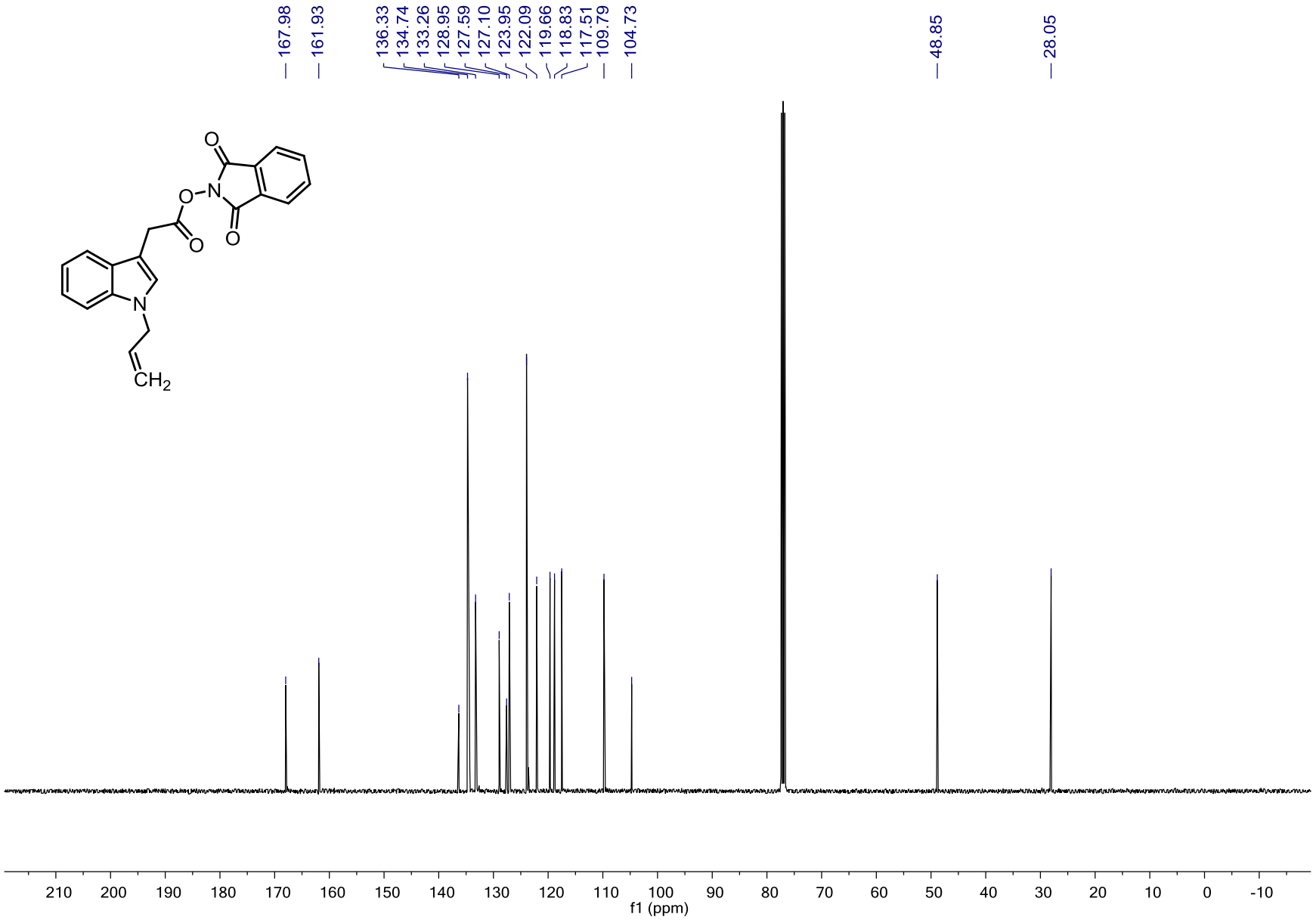
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12i***



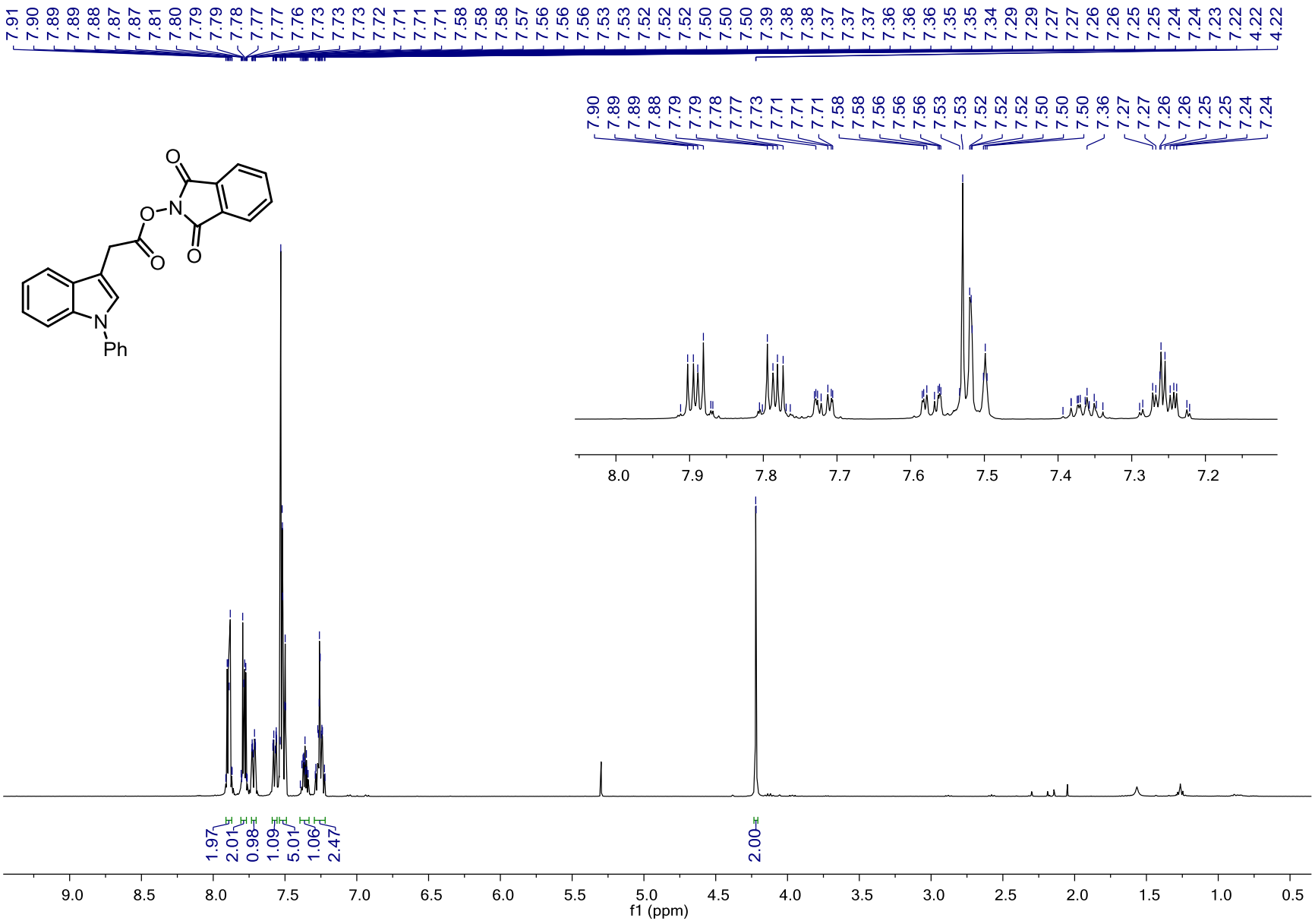
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12j***



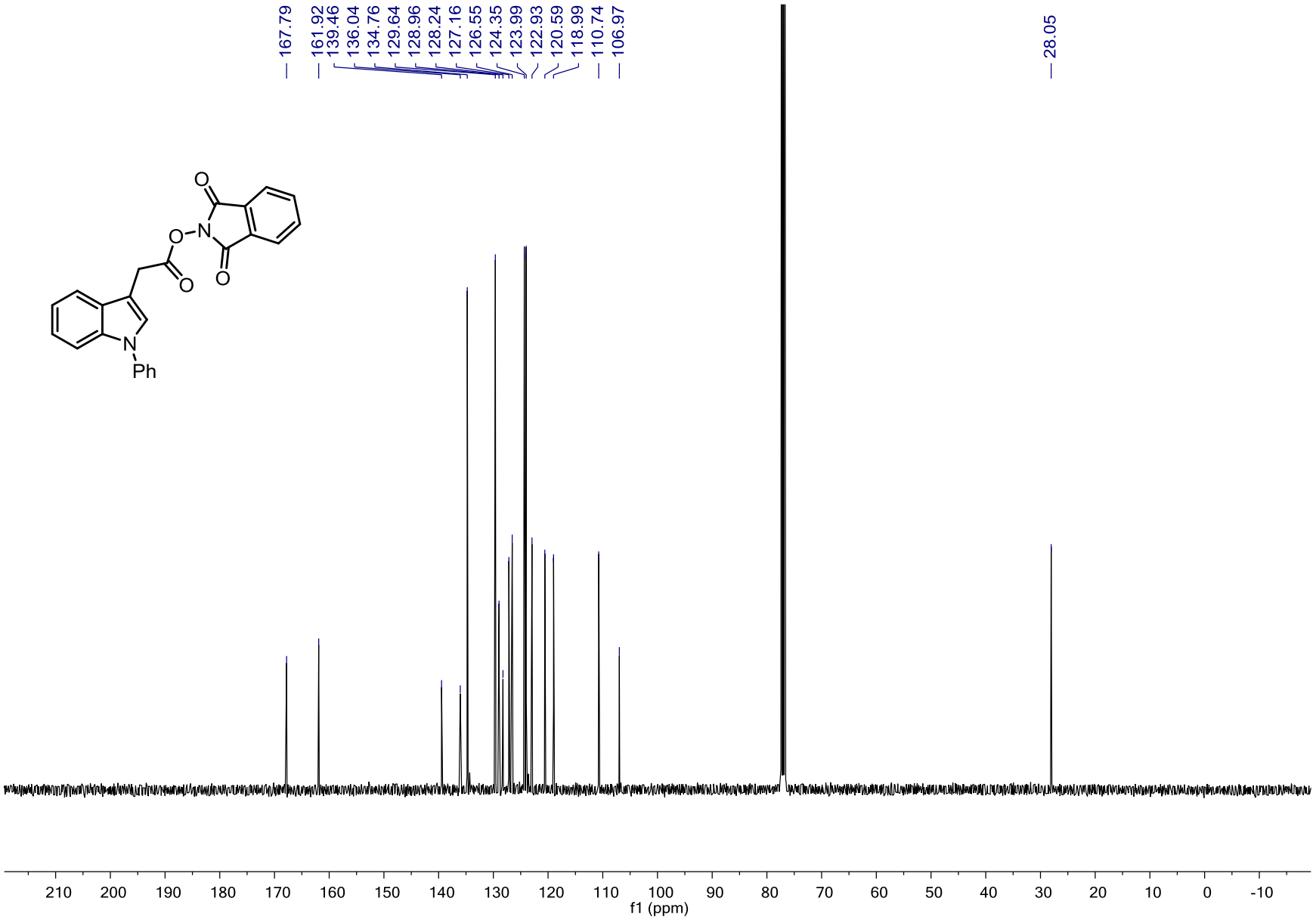
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12j***



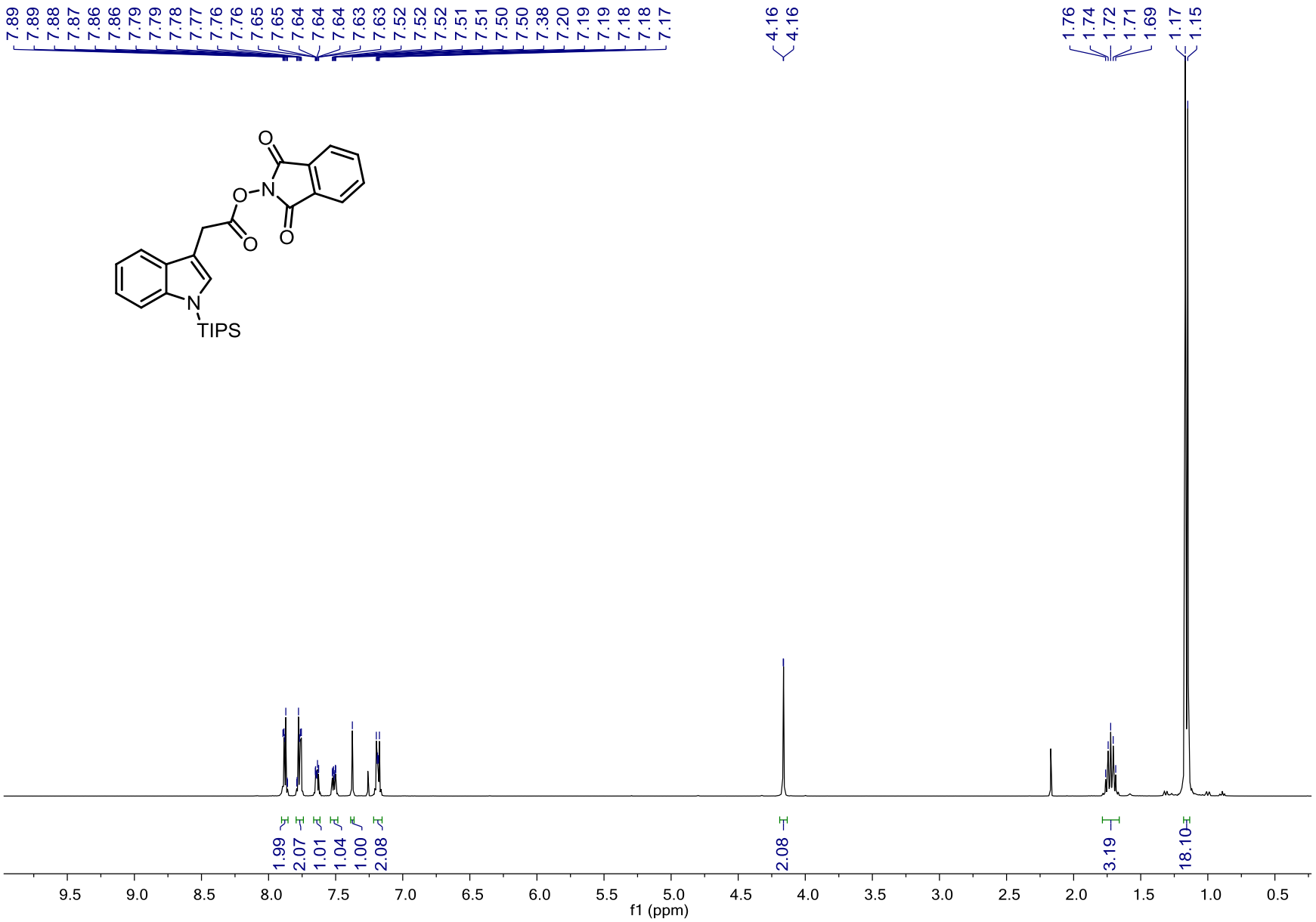
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12k***



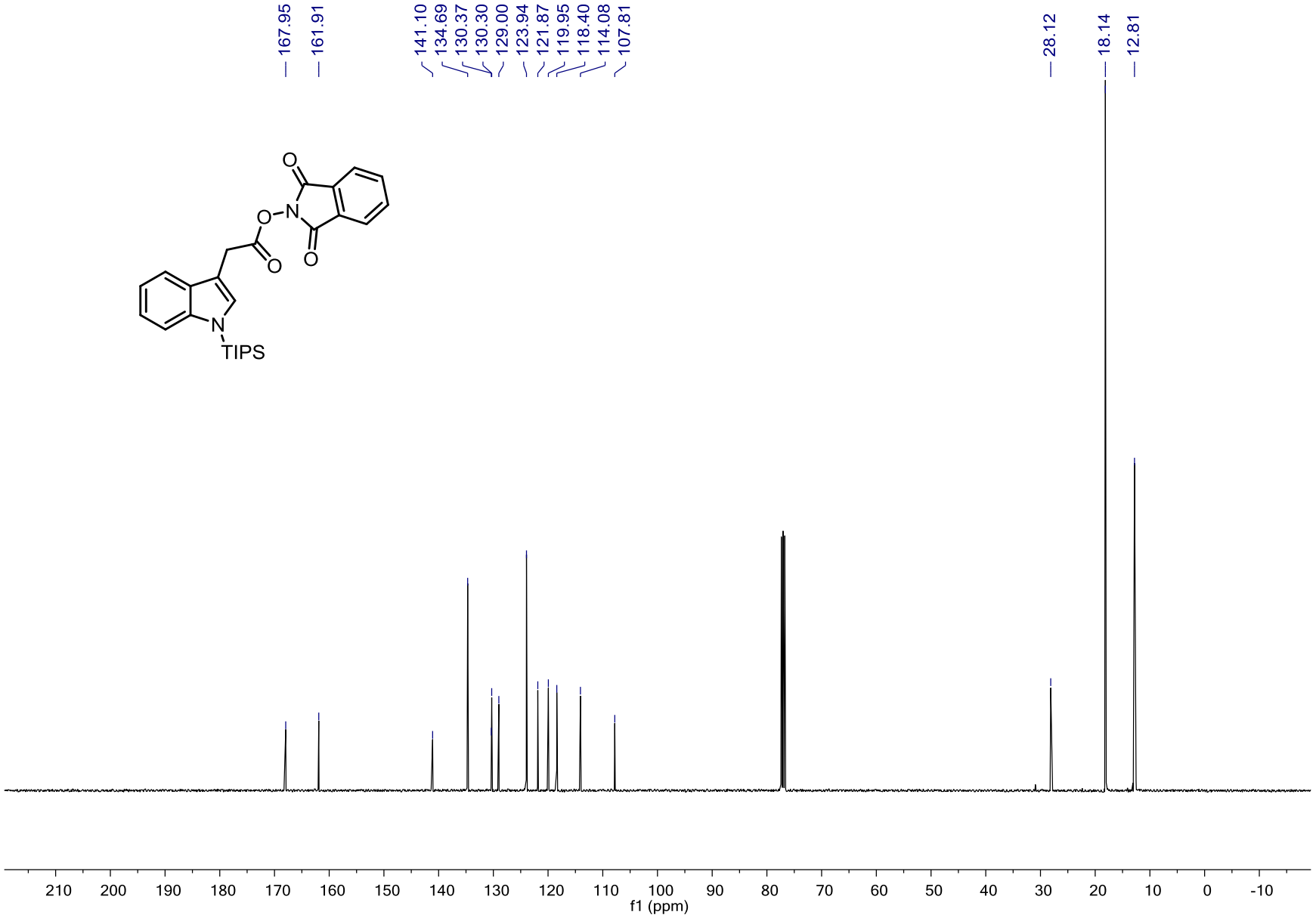
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12k***



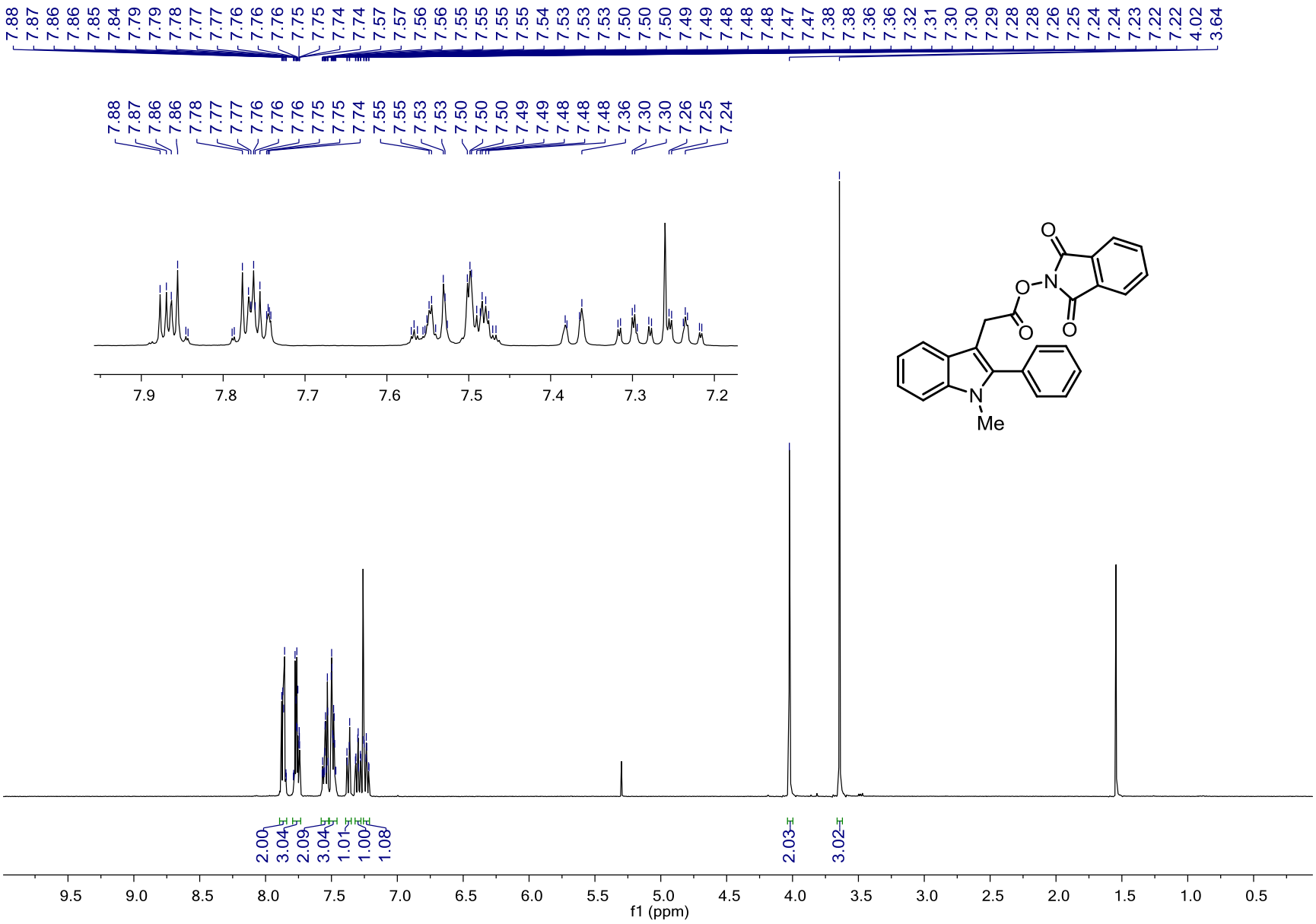
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12l***



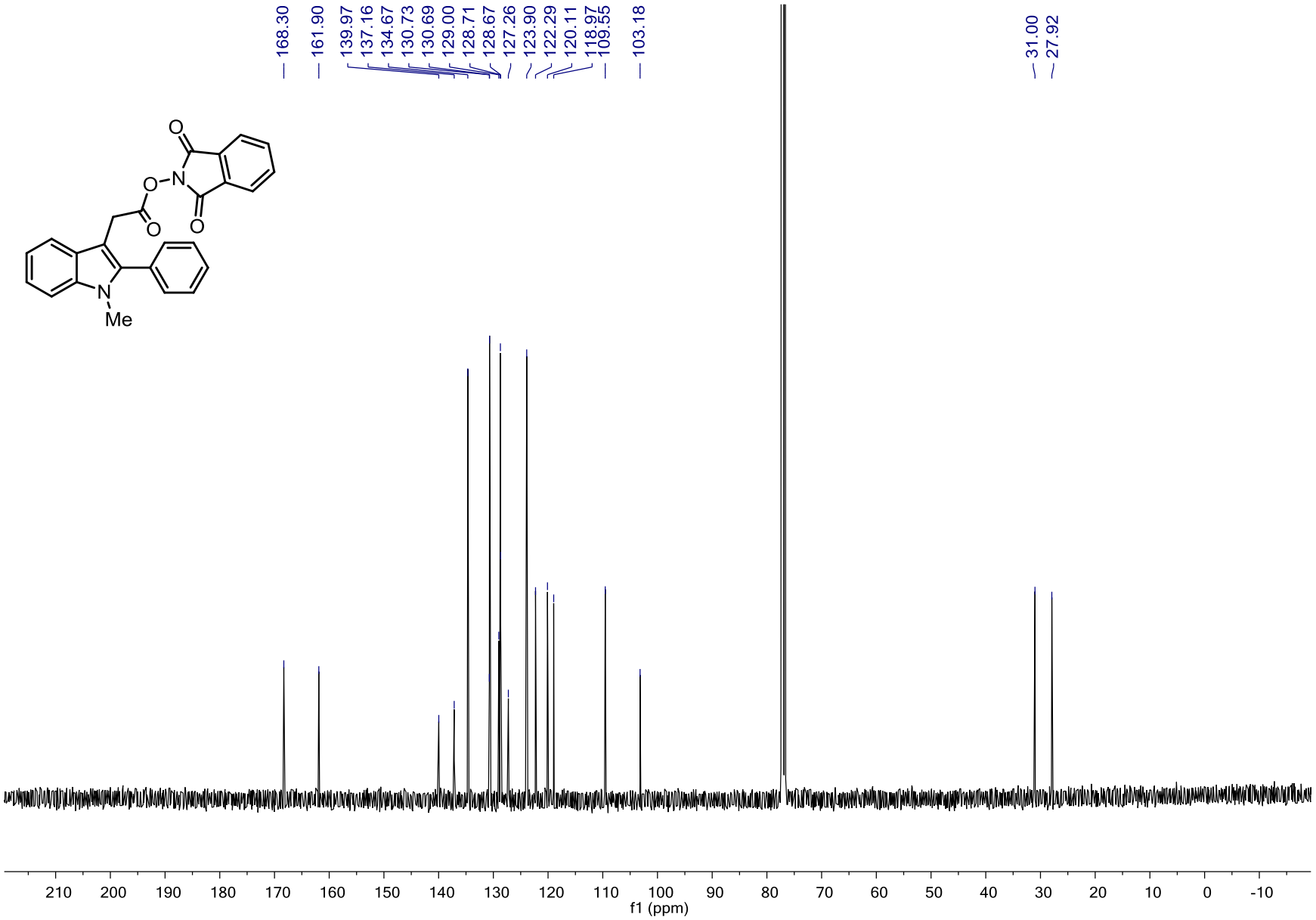
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12l***



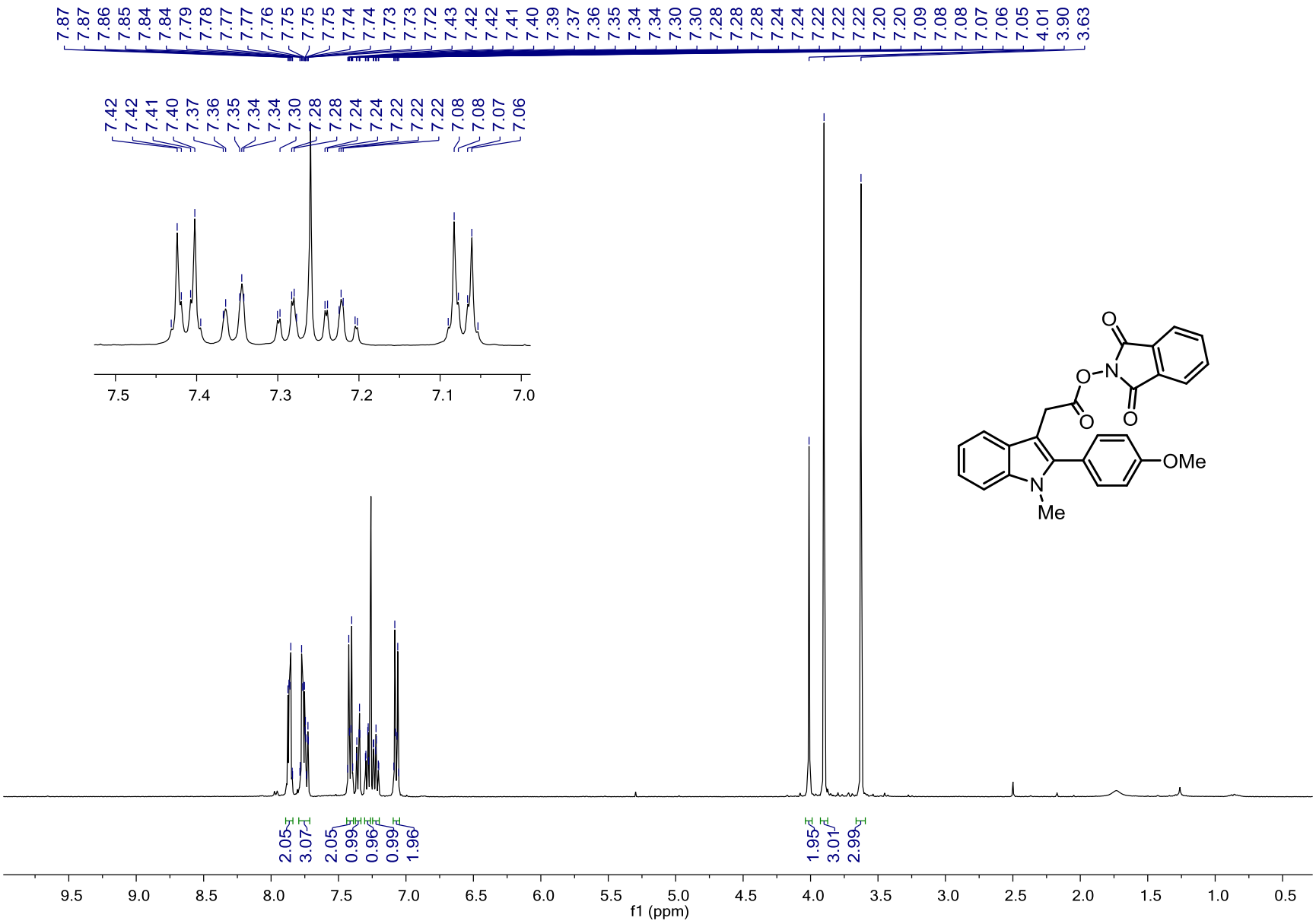
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12m***



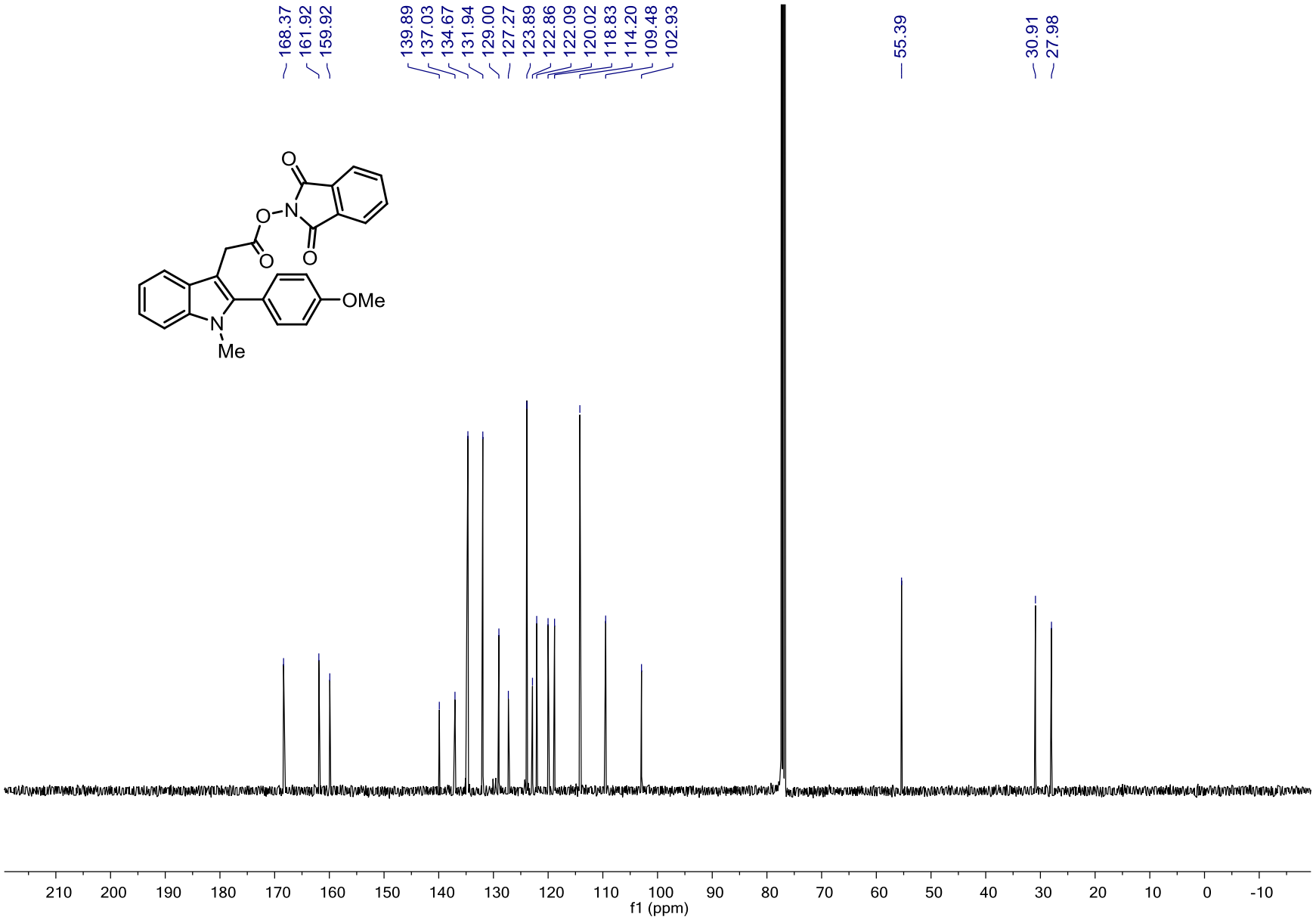
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12m***



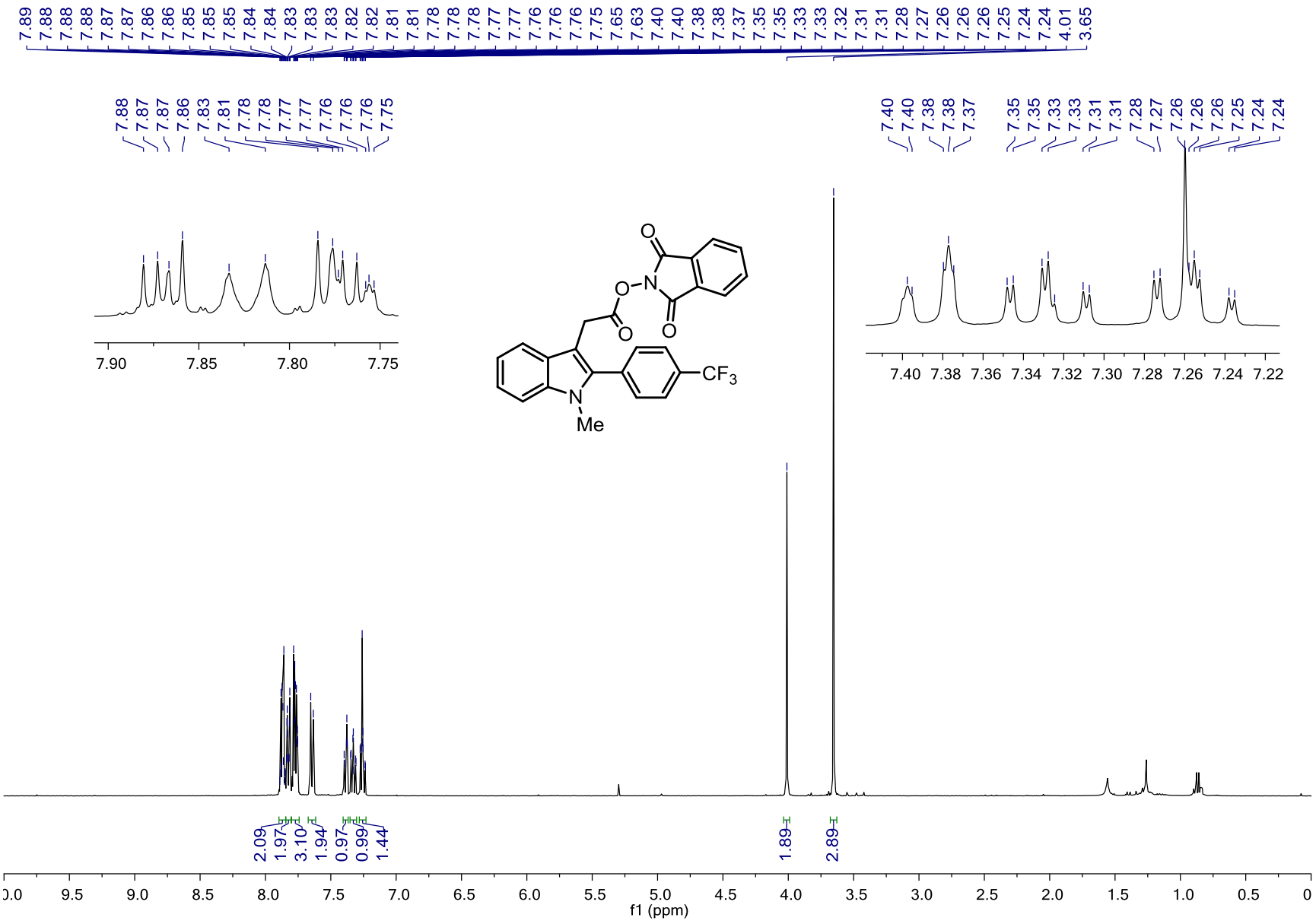
^{1}H-NMR (400 MHz, $CDCl_3$) for compound ***12n***



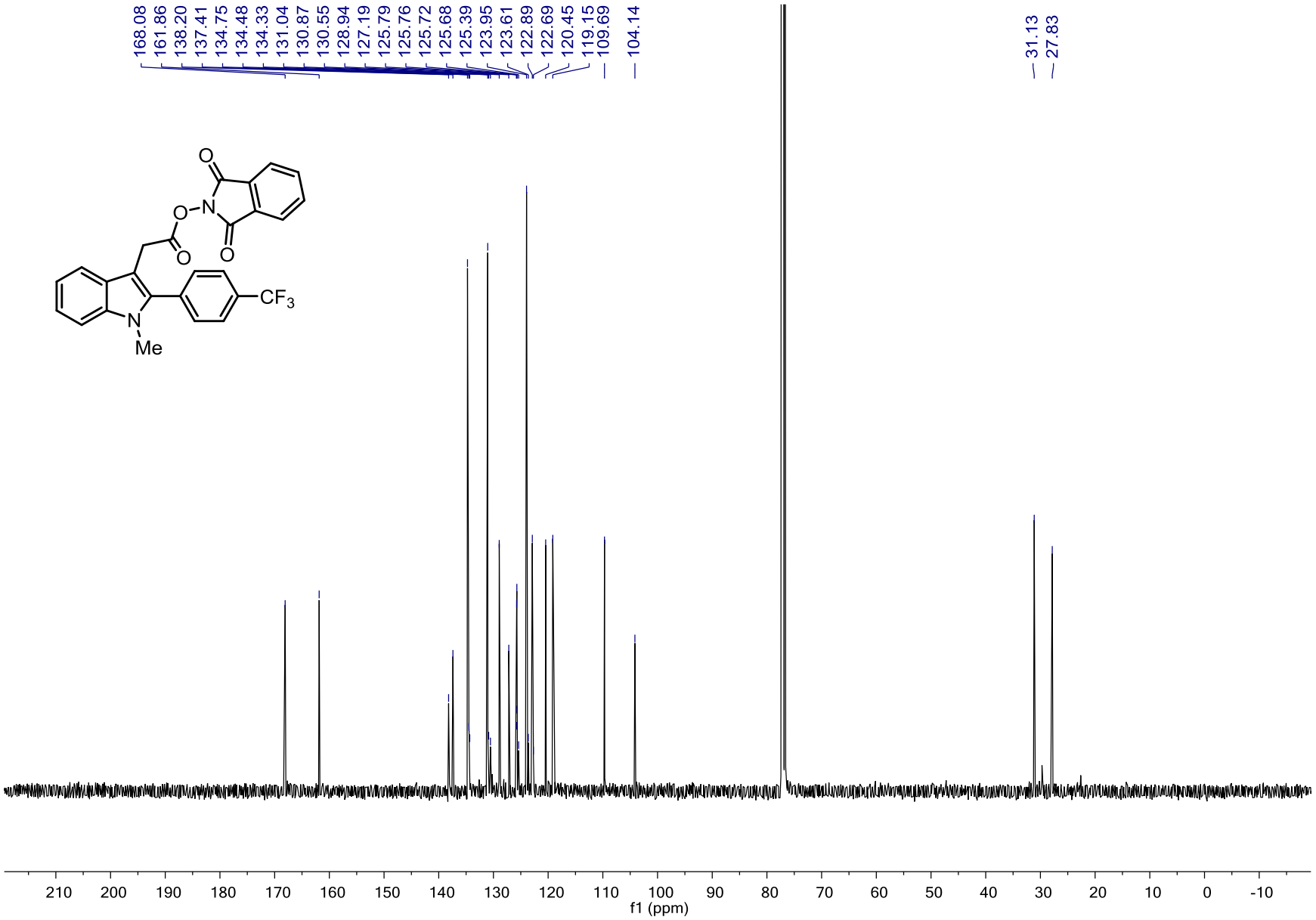
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12n***



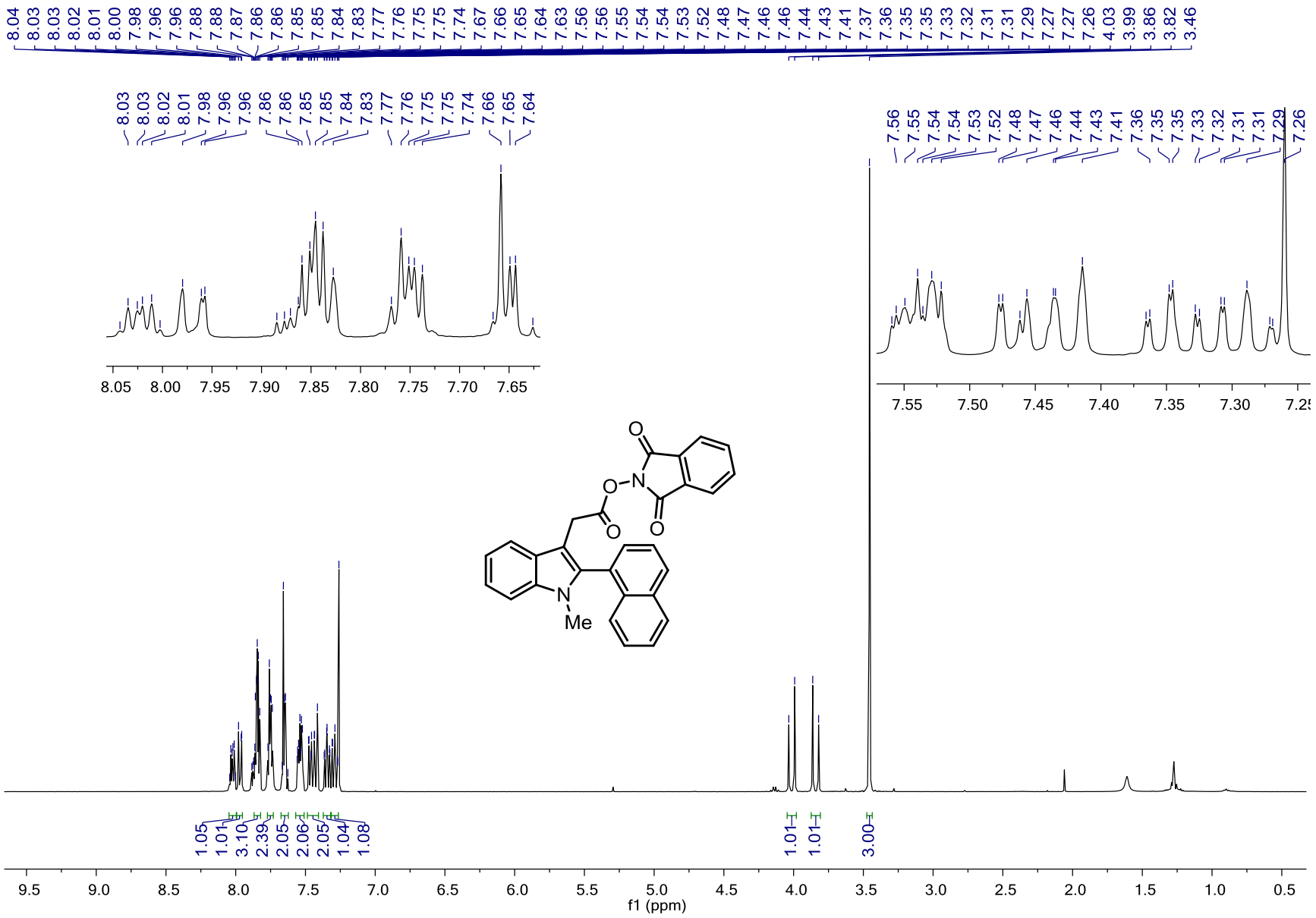
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12o***



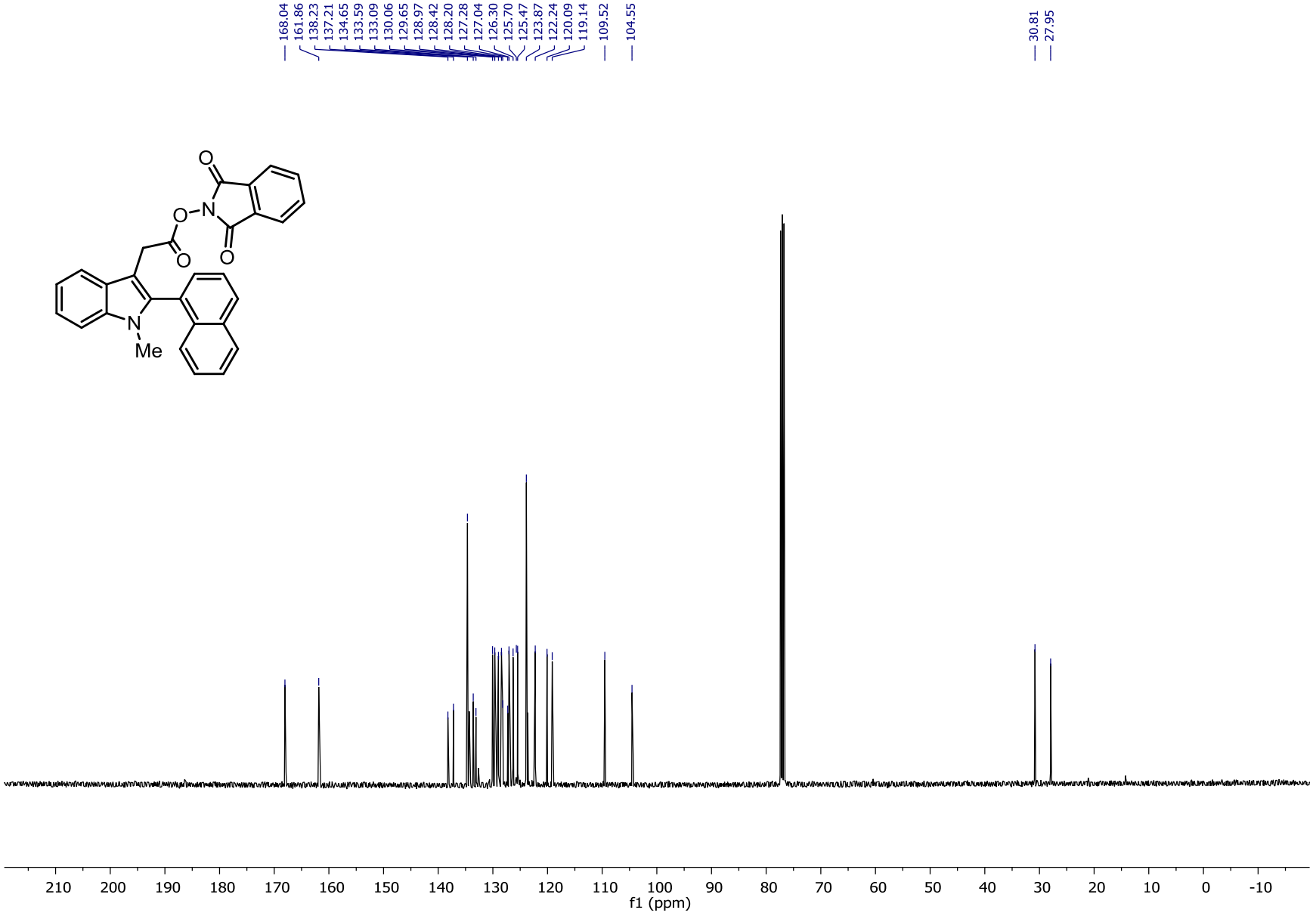
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12o***



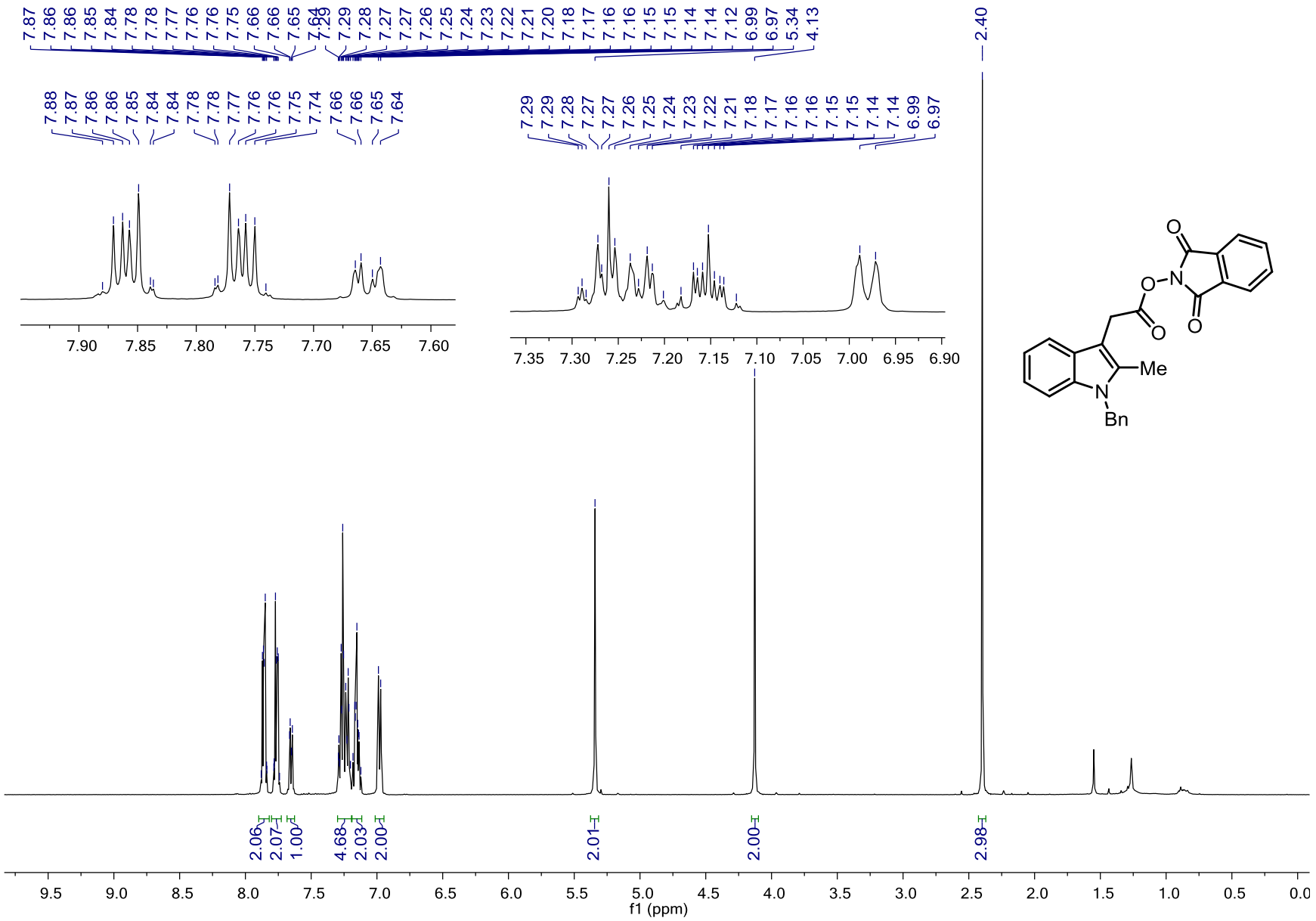
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12p***



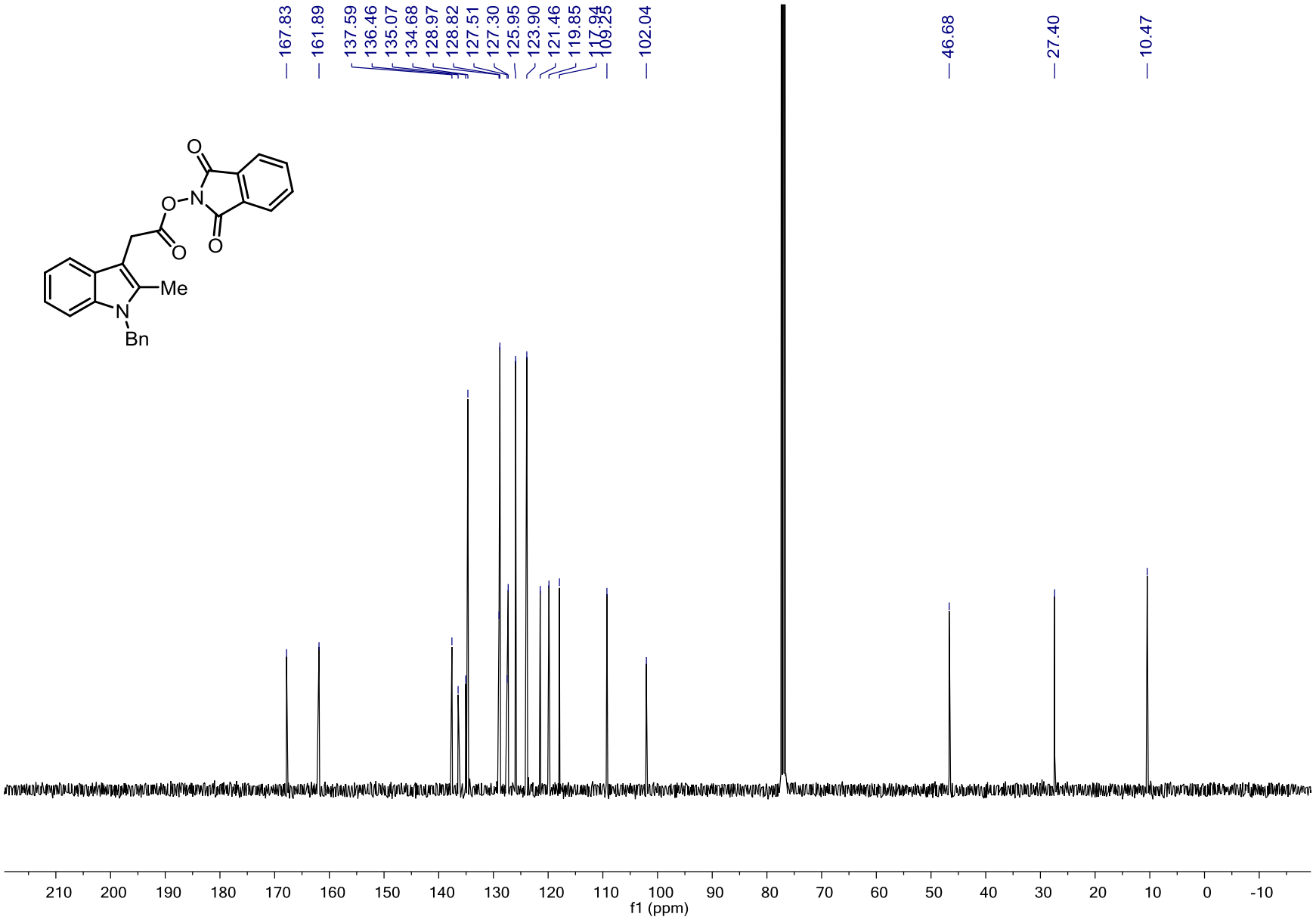
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12p***



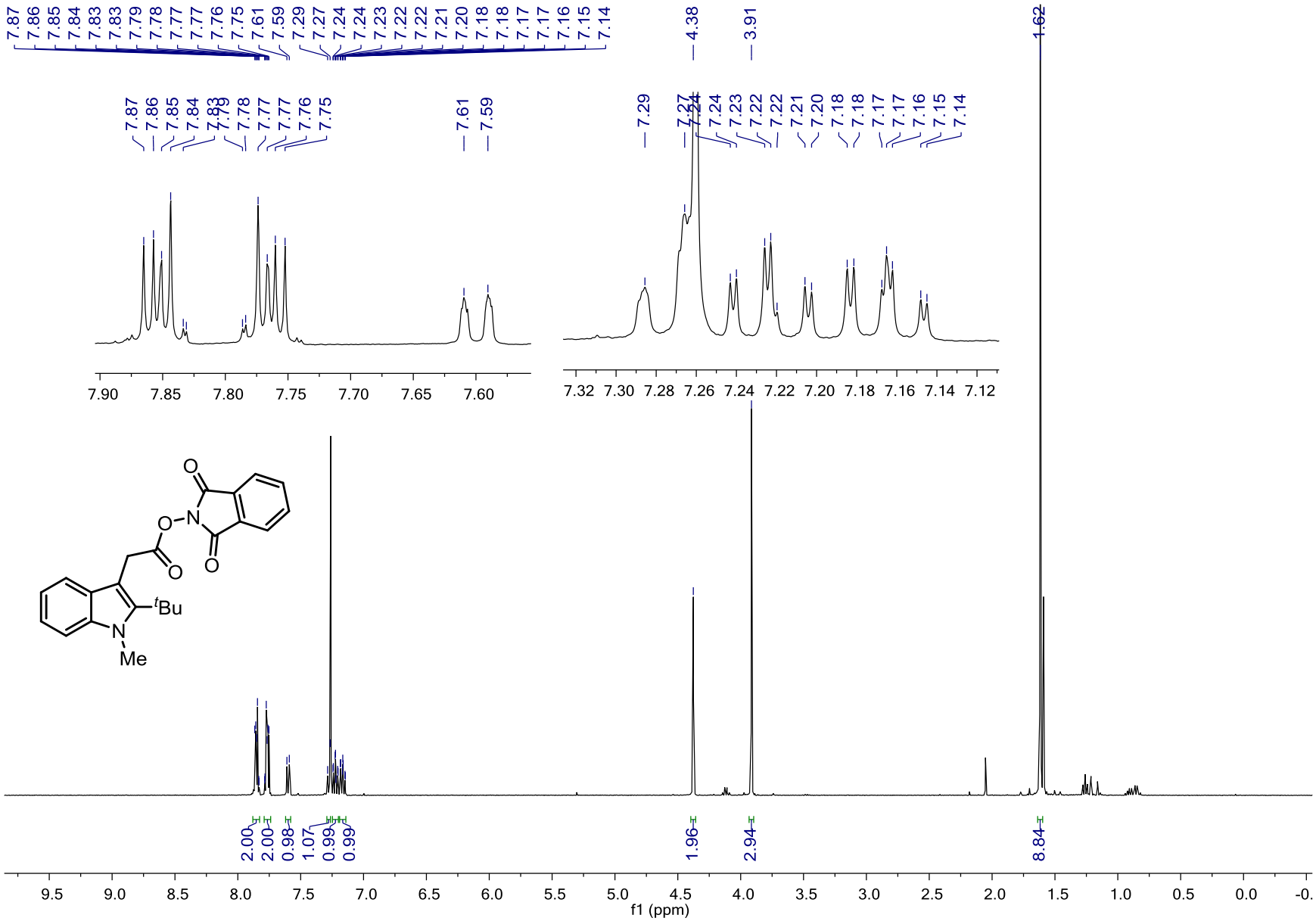
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12q***



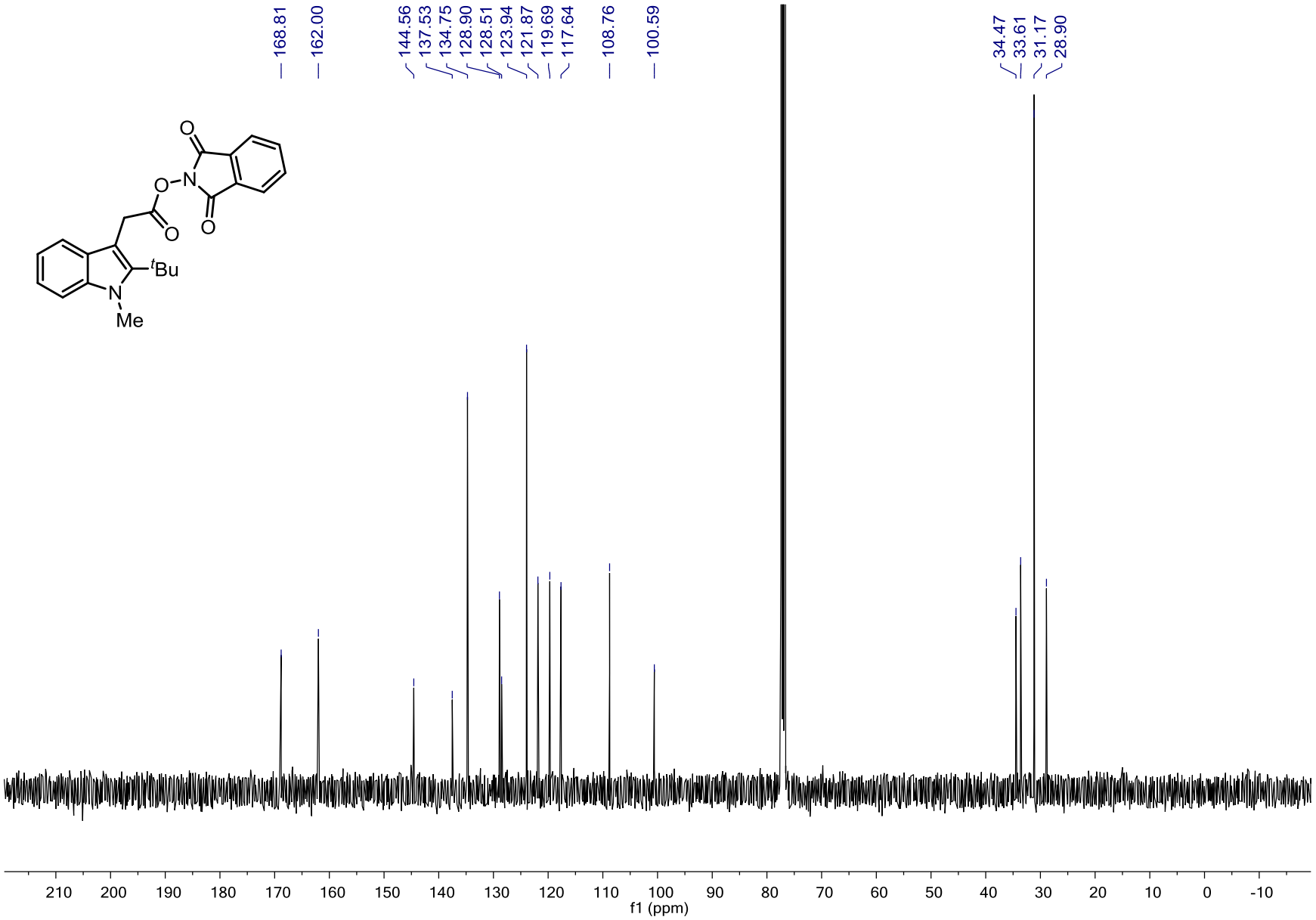
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12q***



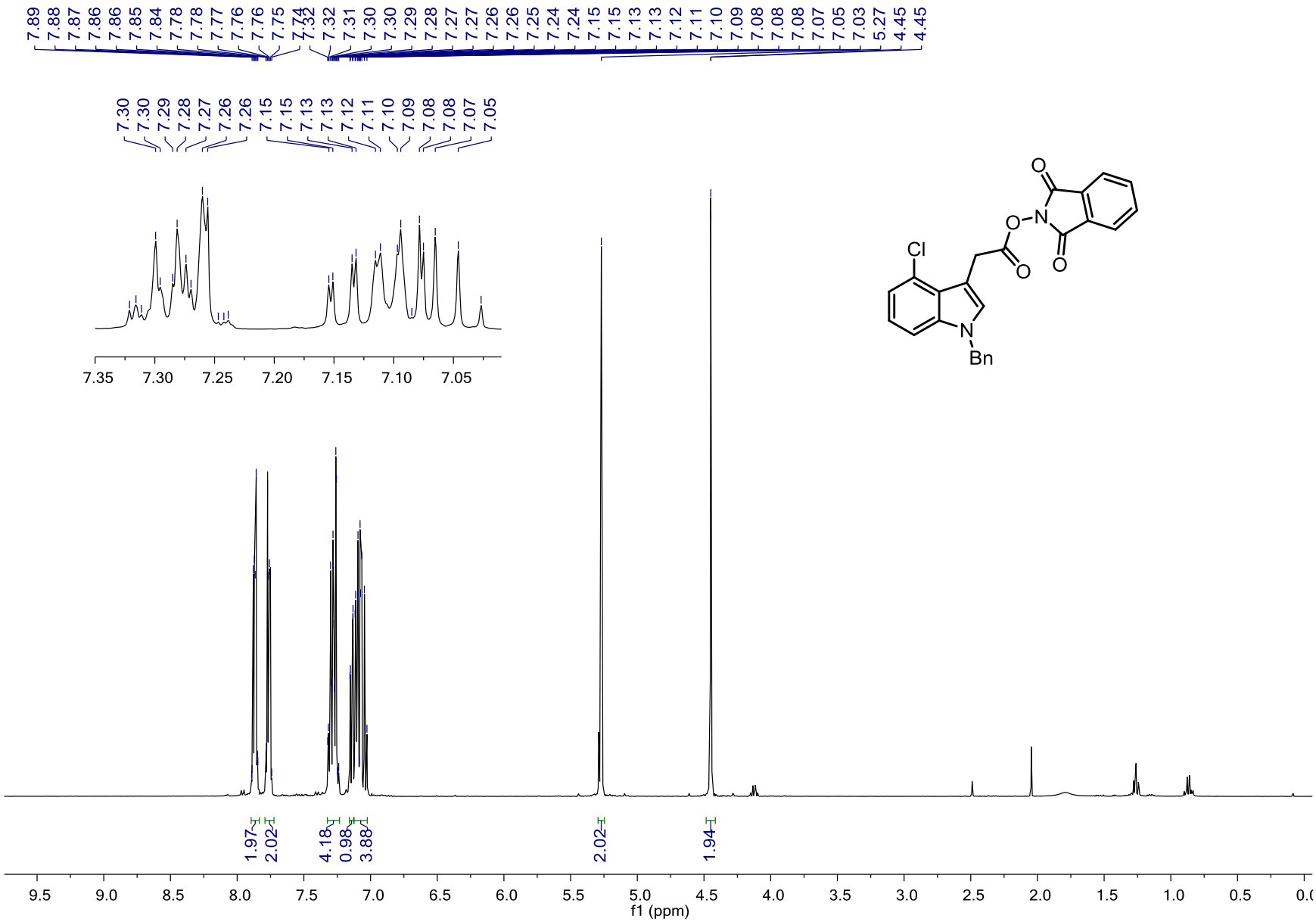
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12r***



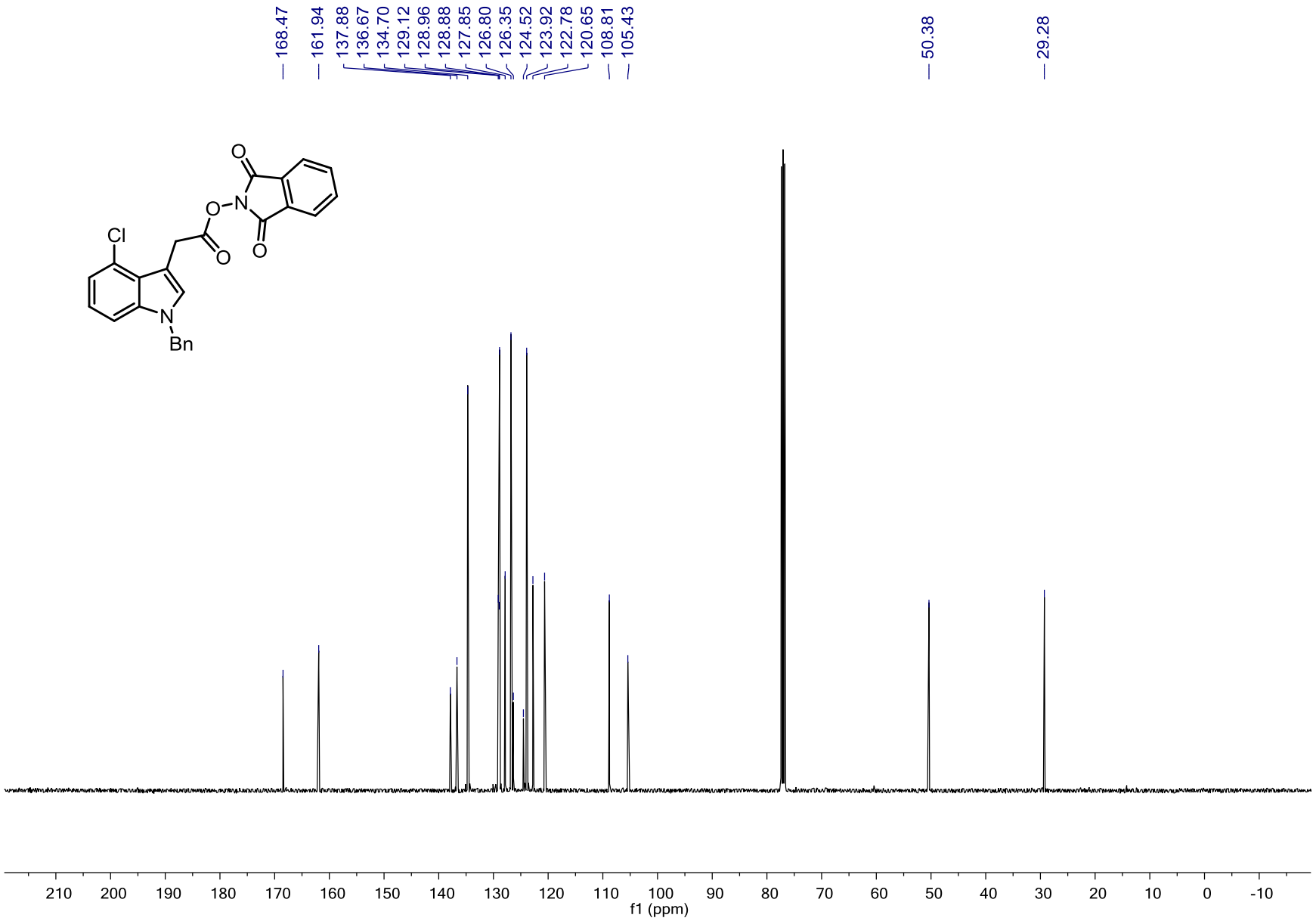
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12r***



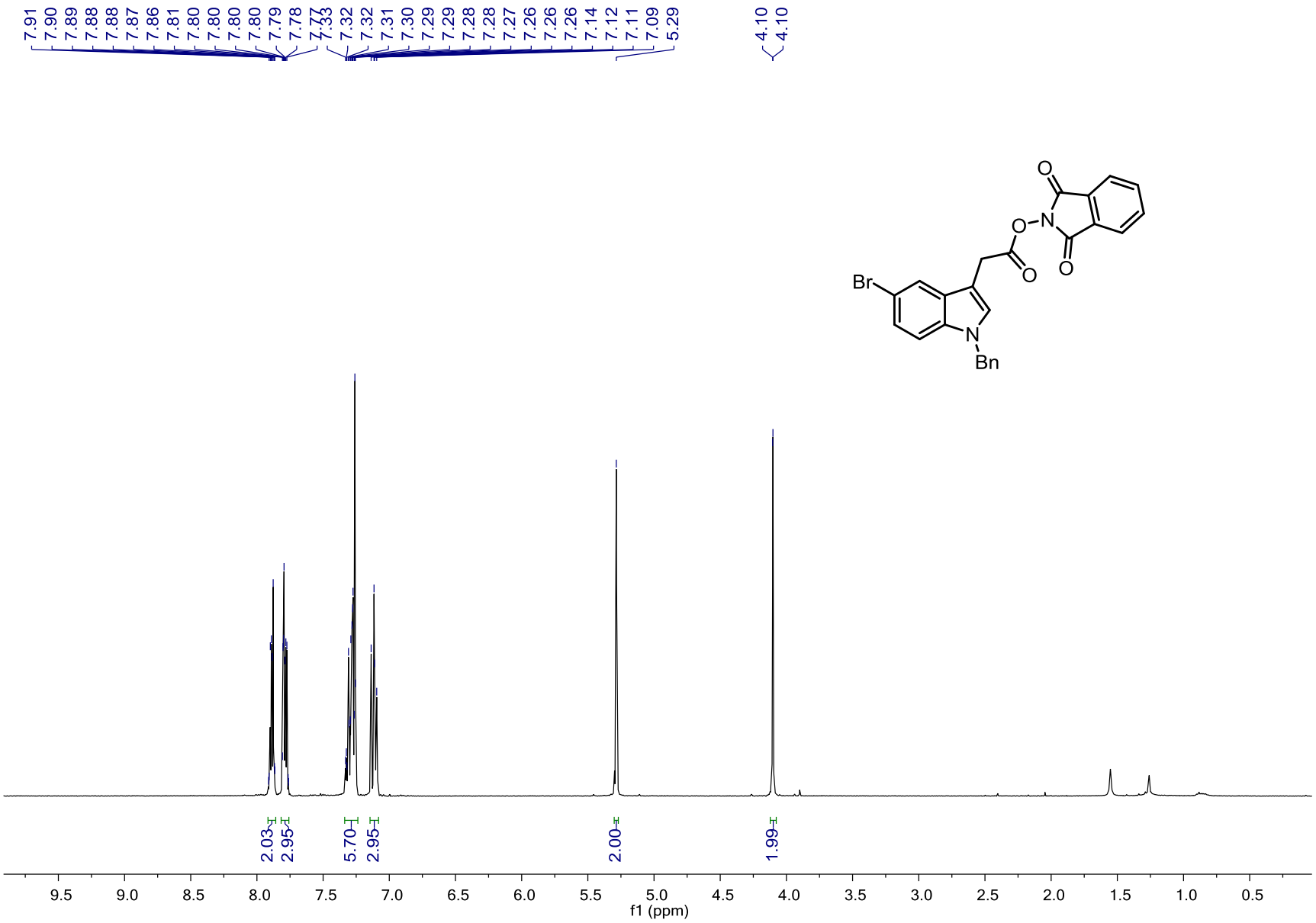
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12s***



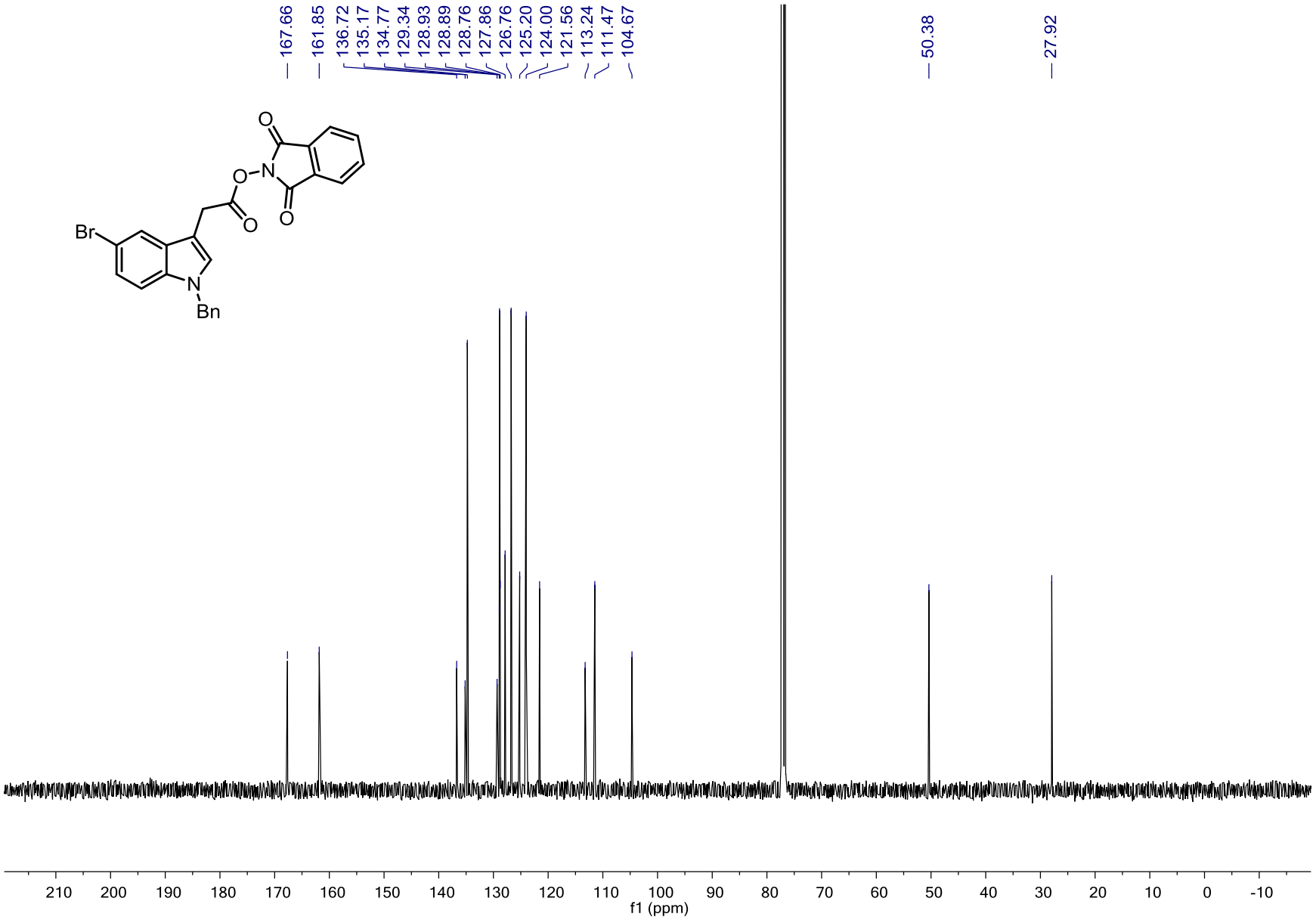
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12s***



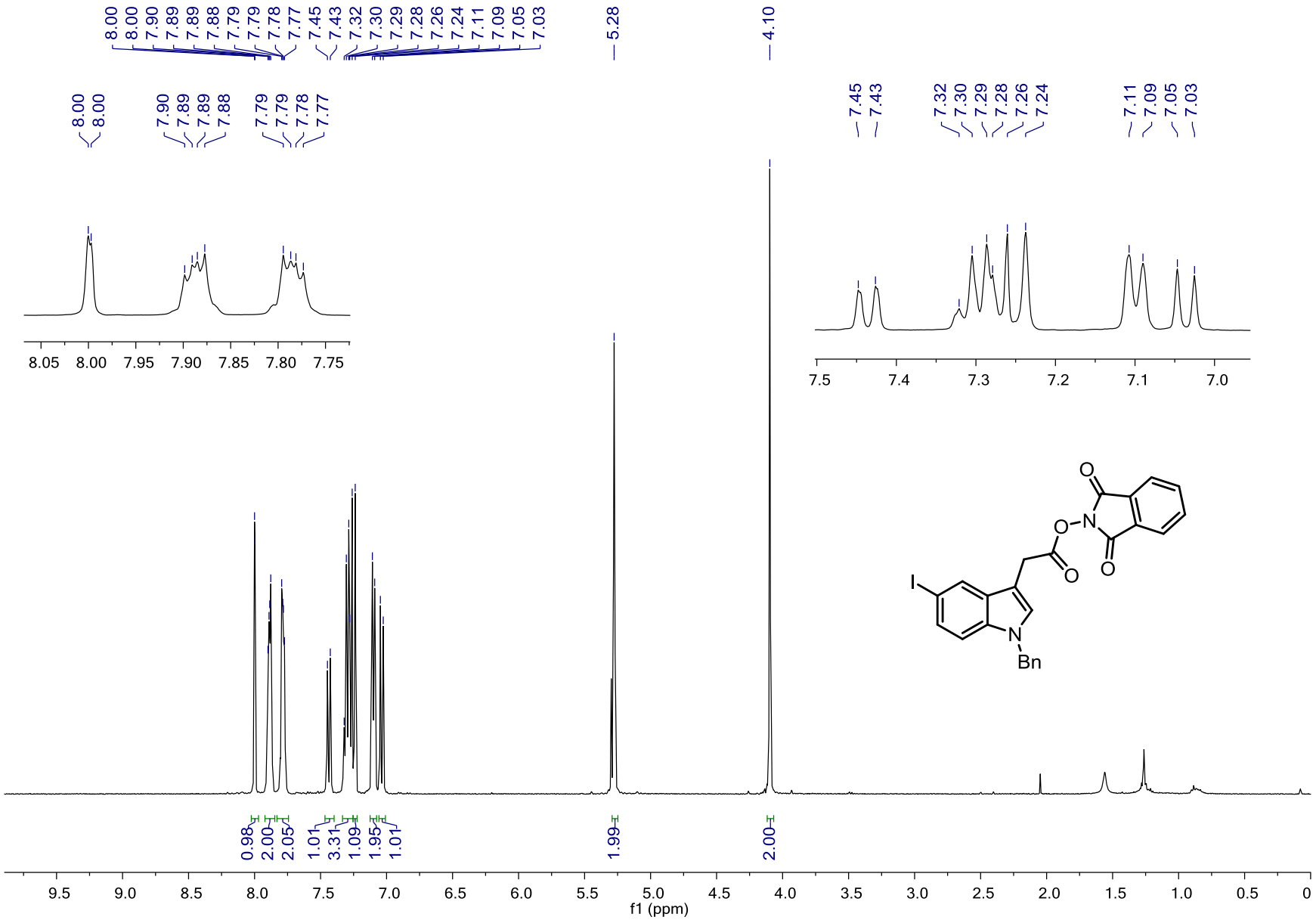
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12t***



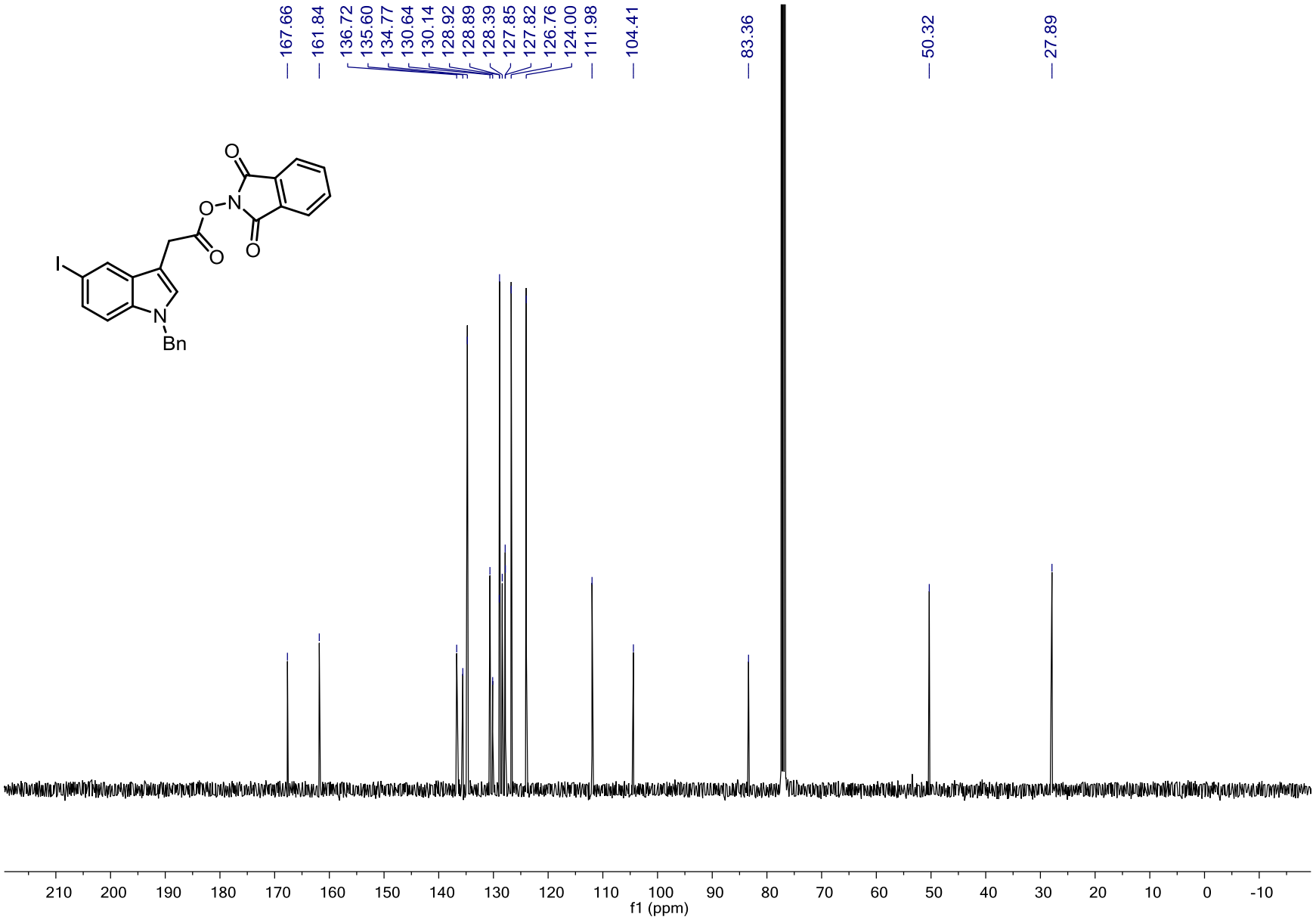
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12t***



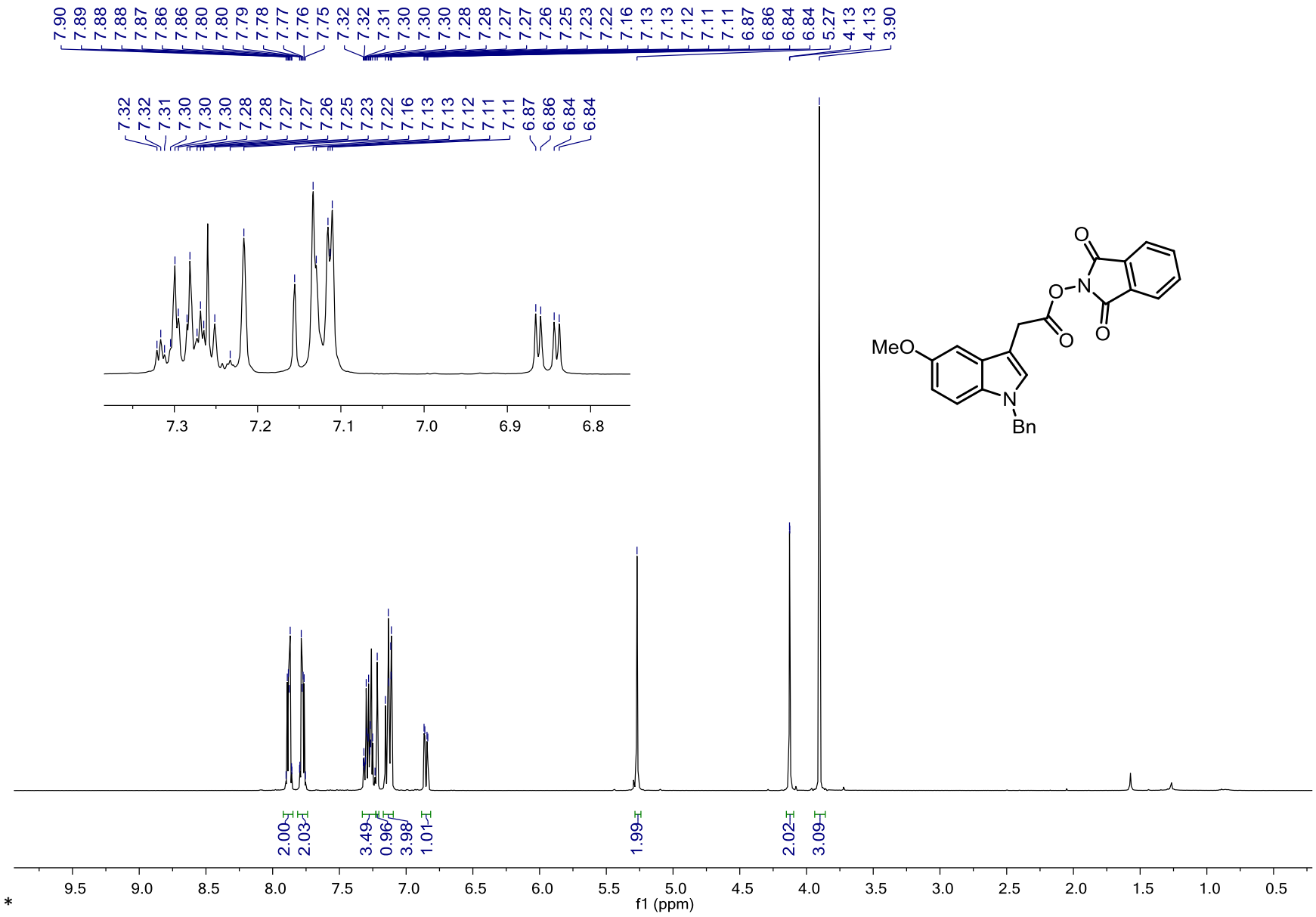
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12u***



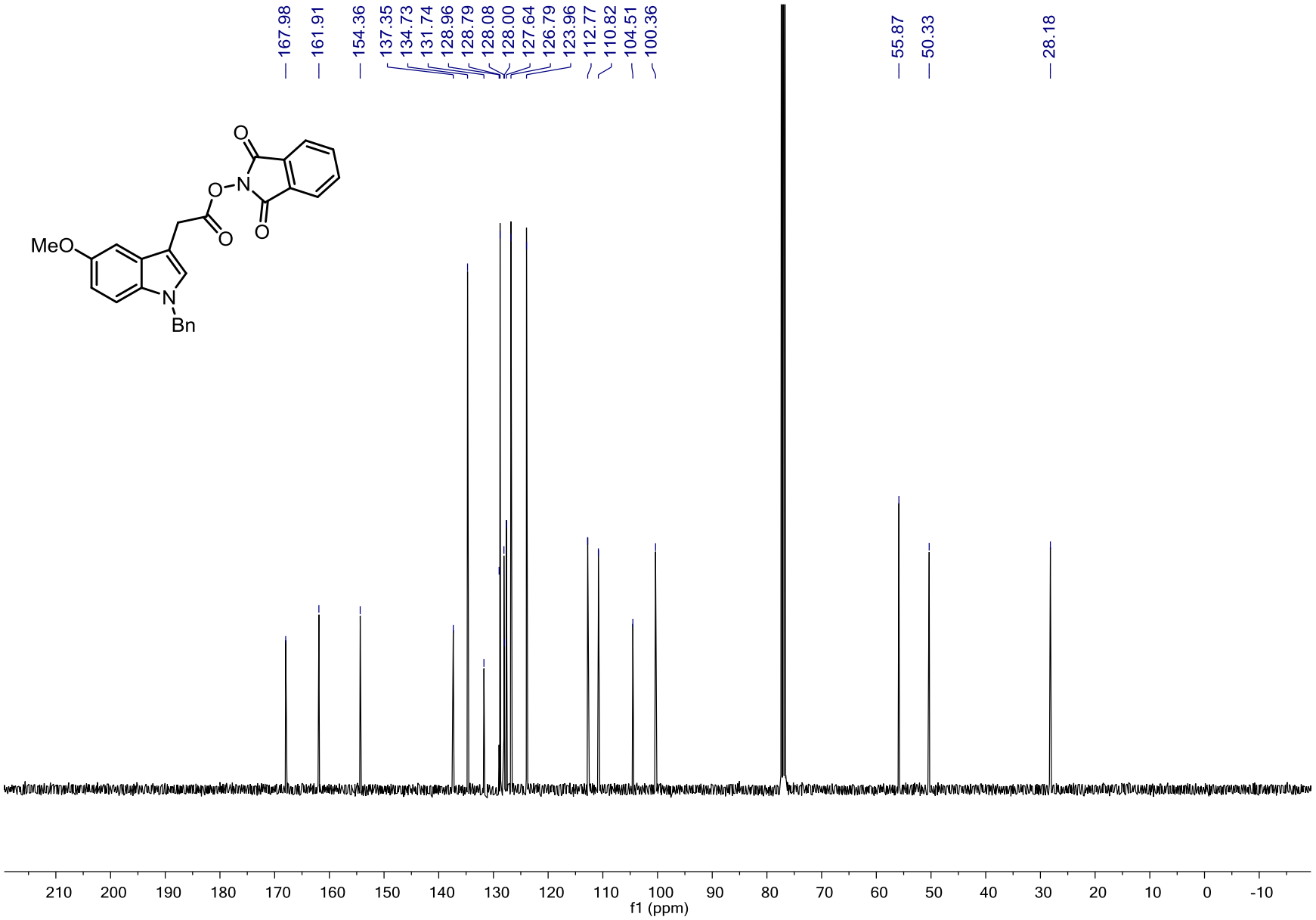
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12u***



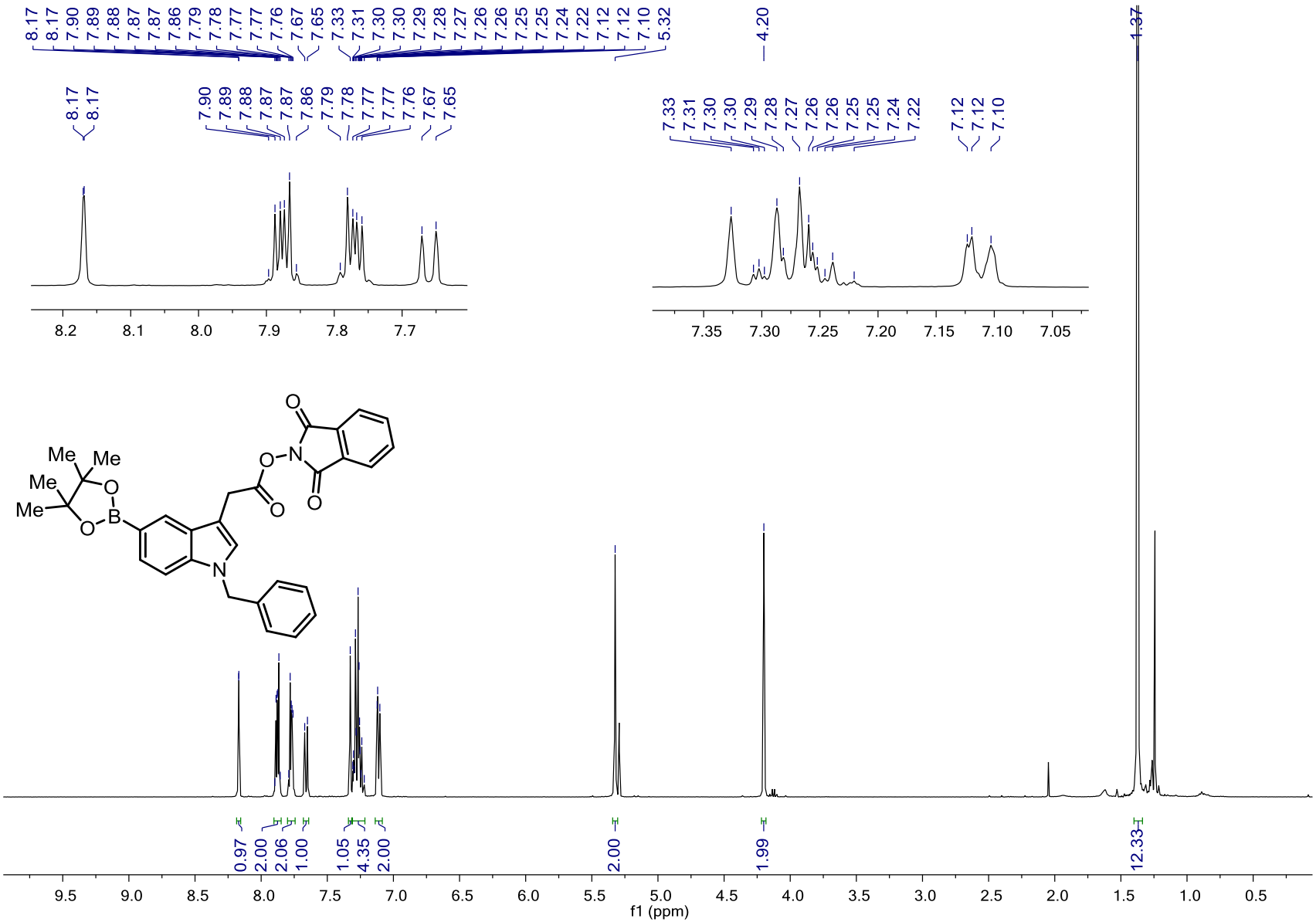
[1]H-NMR (400 MHz, $CDCl_3$) for compound ***12v***



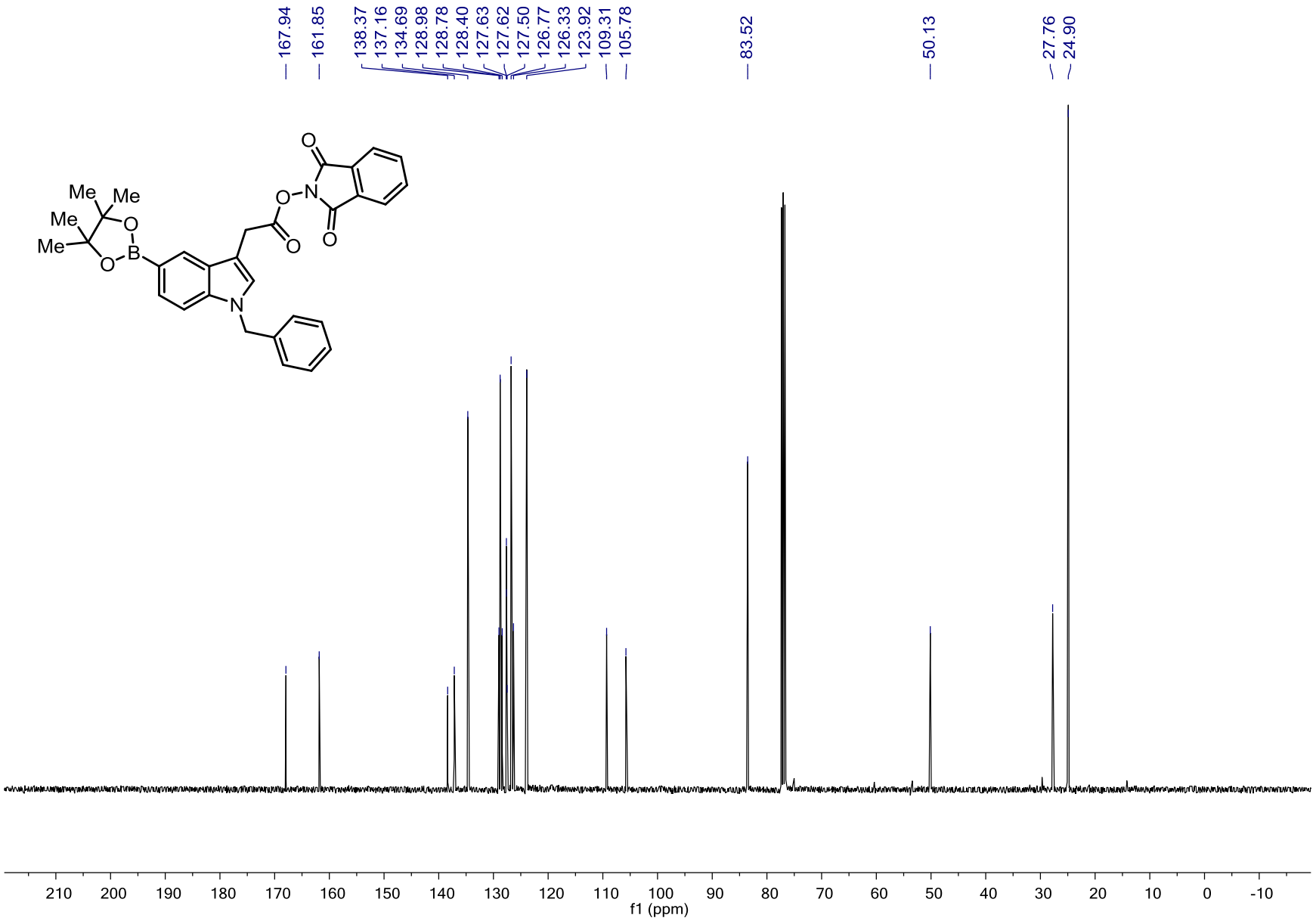
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12v***



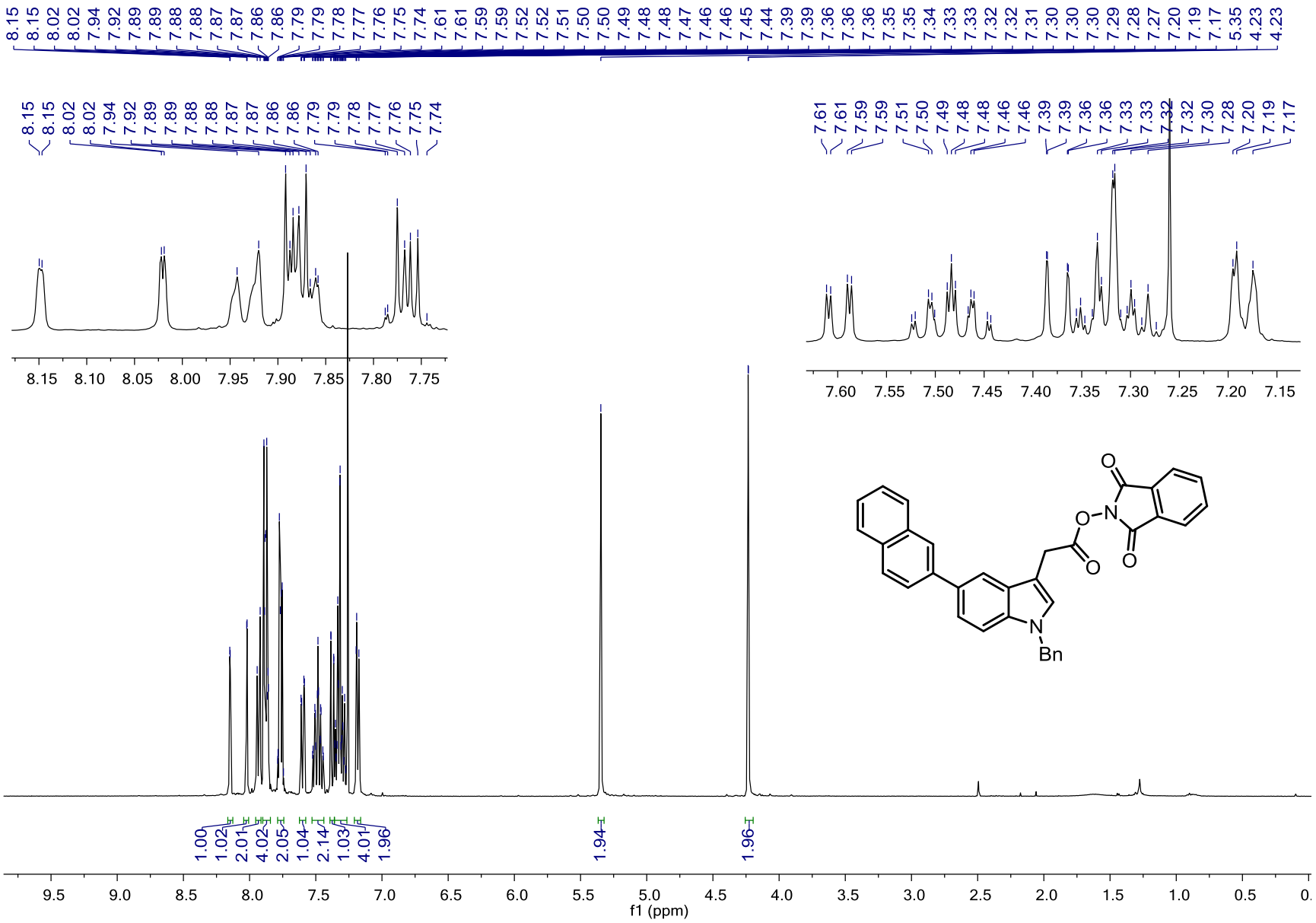
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12w***



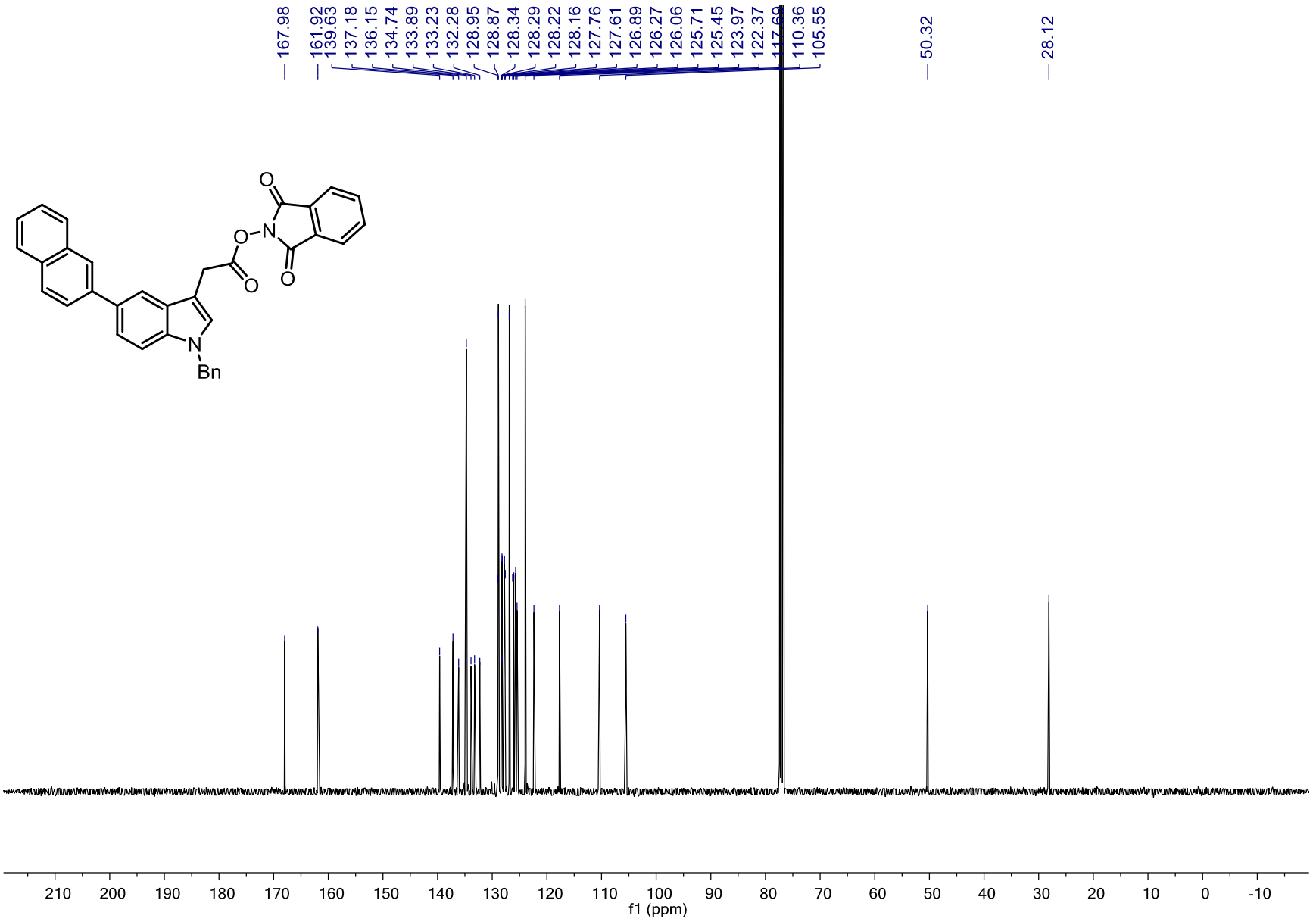
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12w***



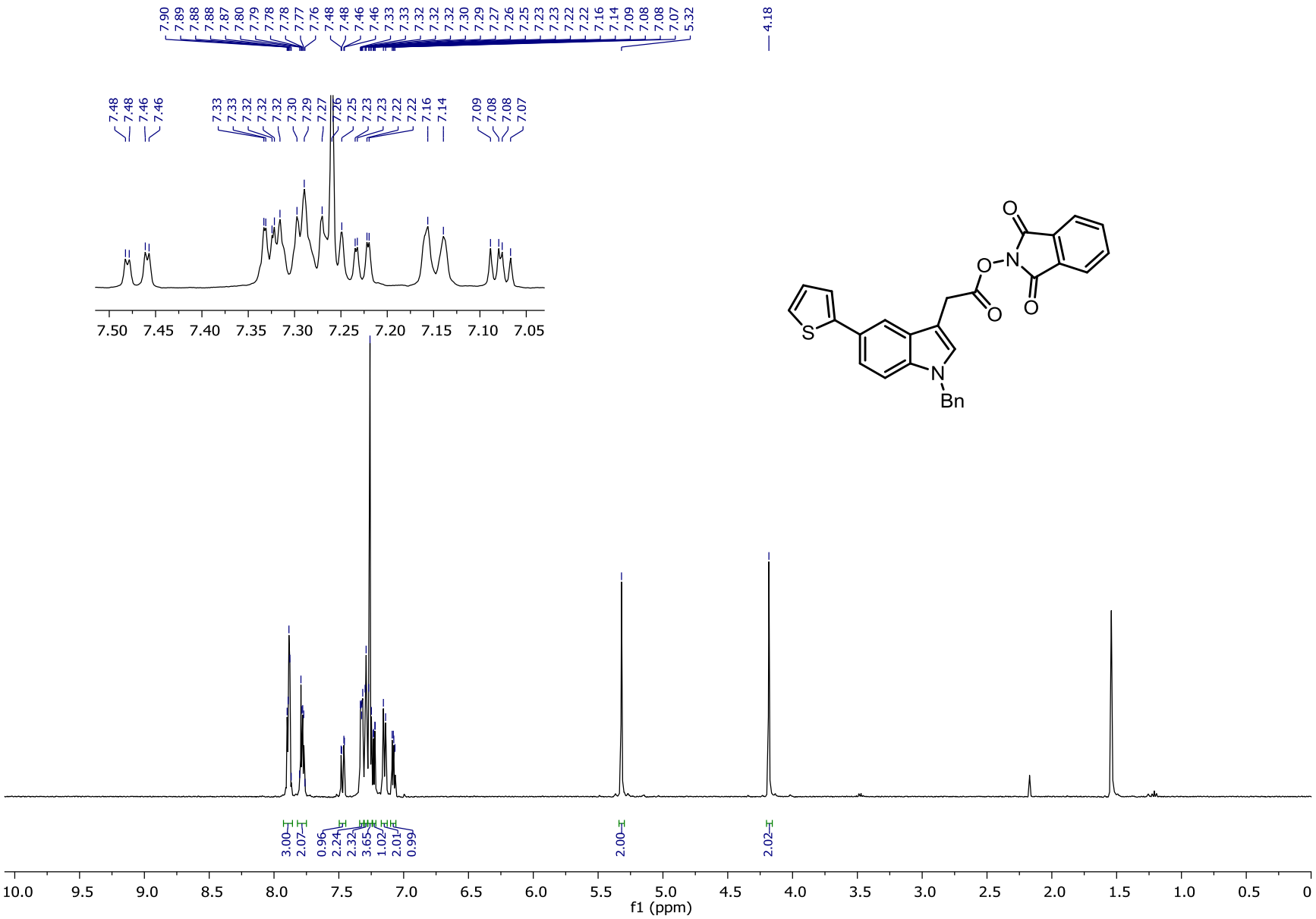
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12x***



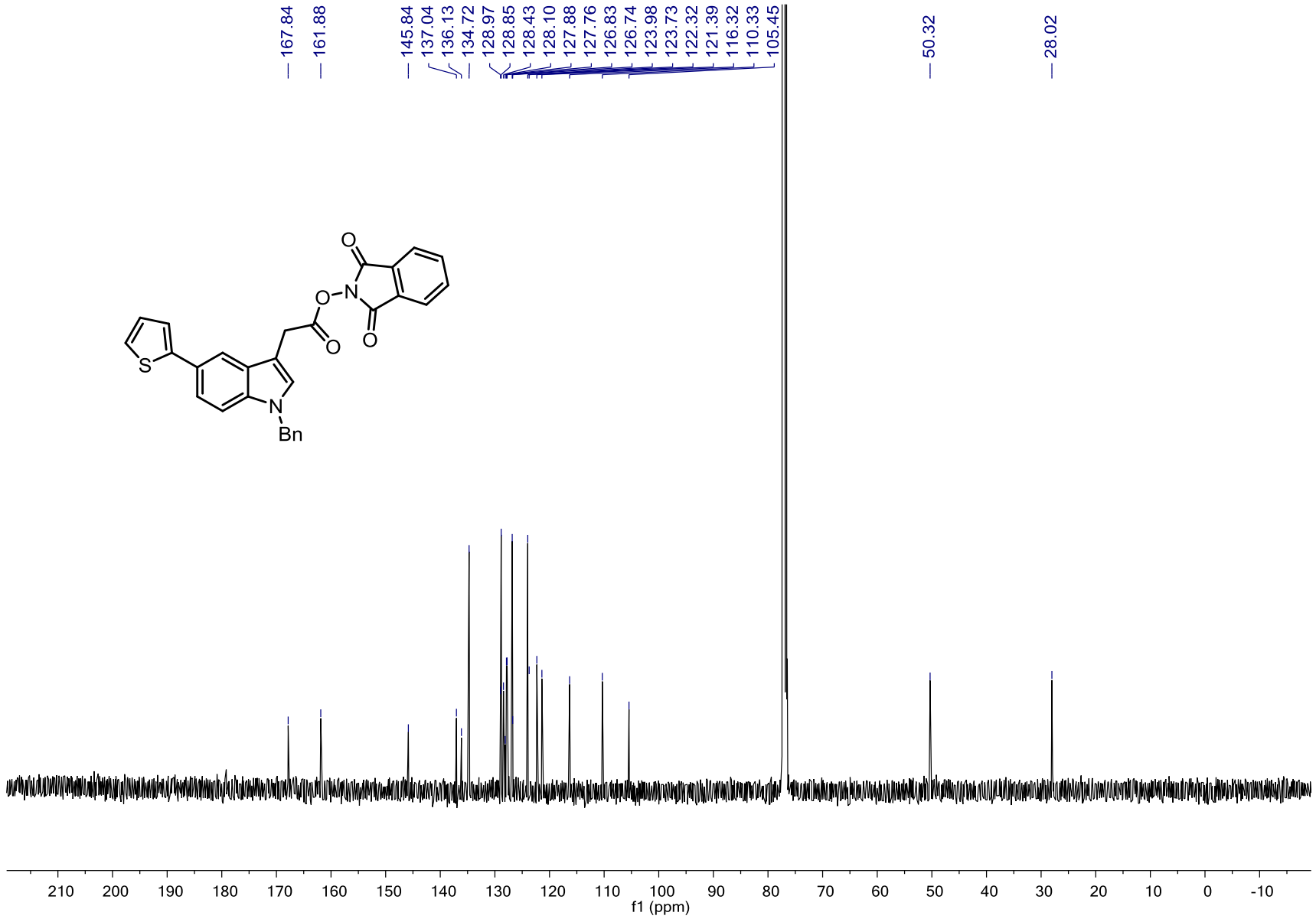
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12x***



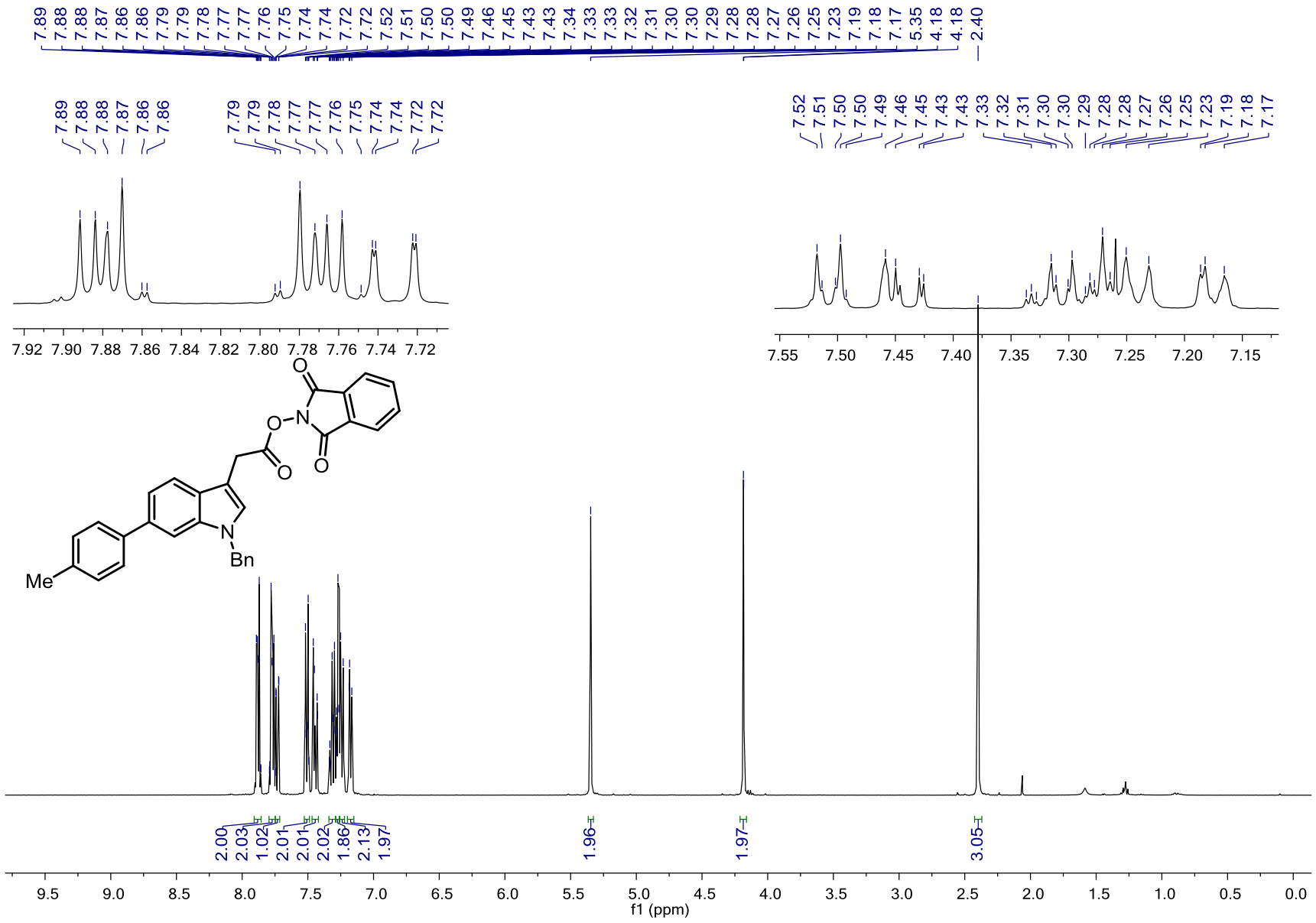
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12y***



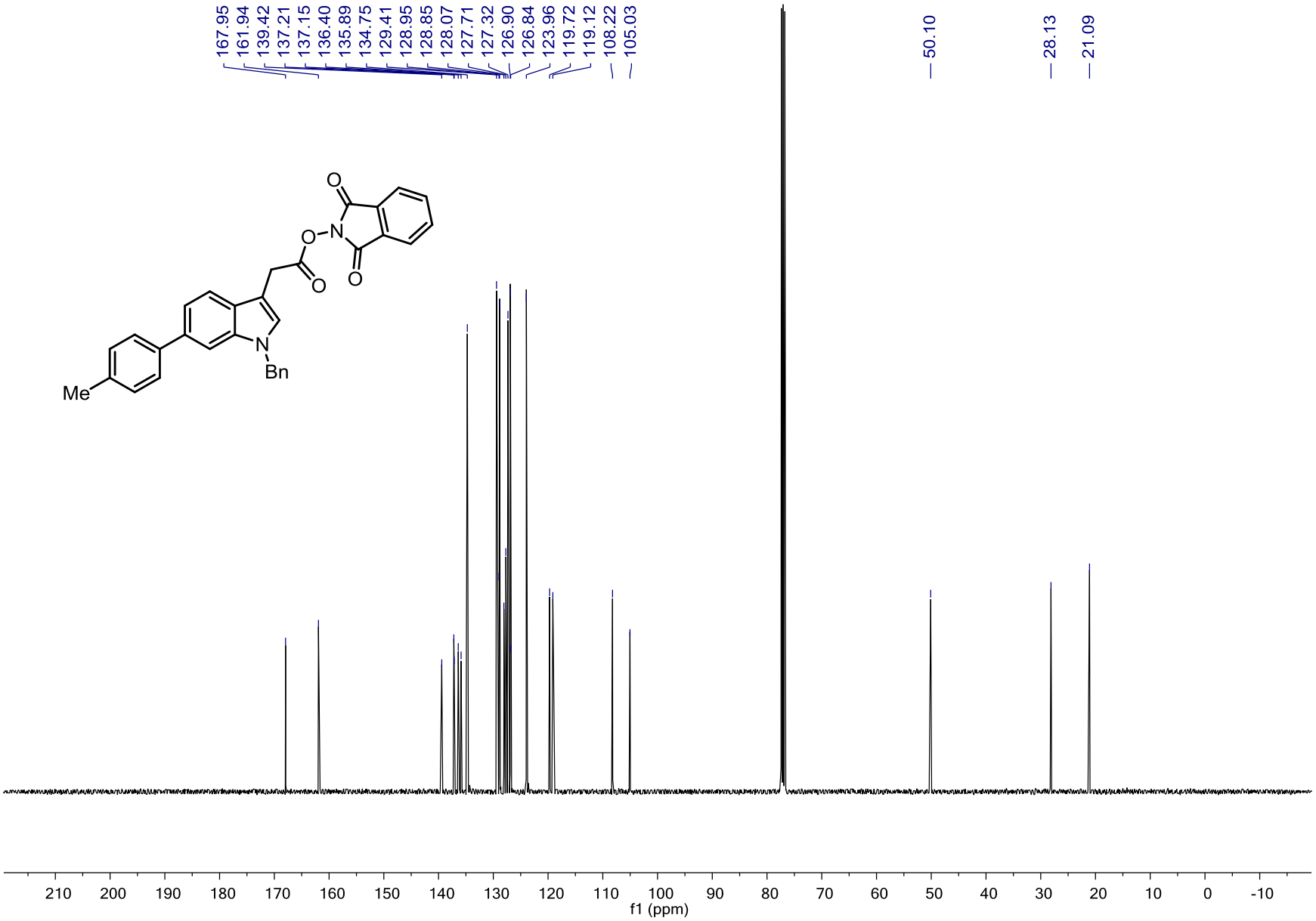
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12y***



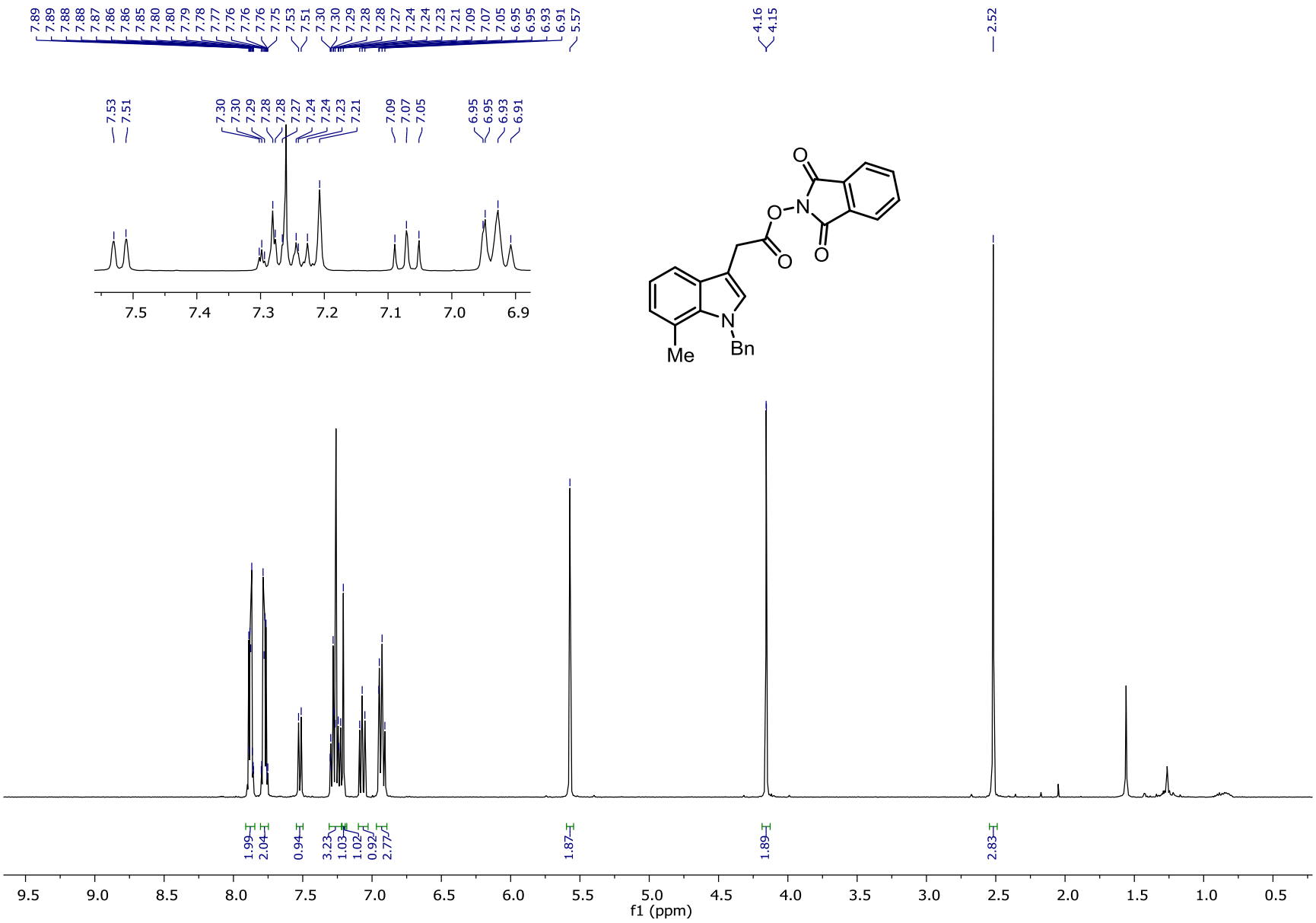
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12z***



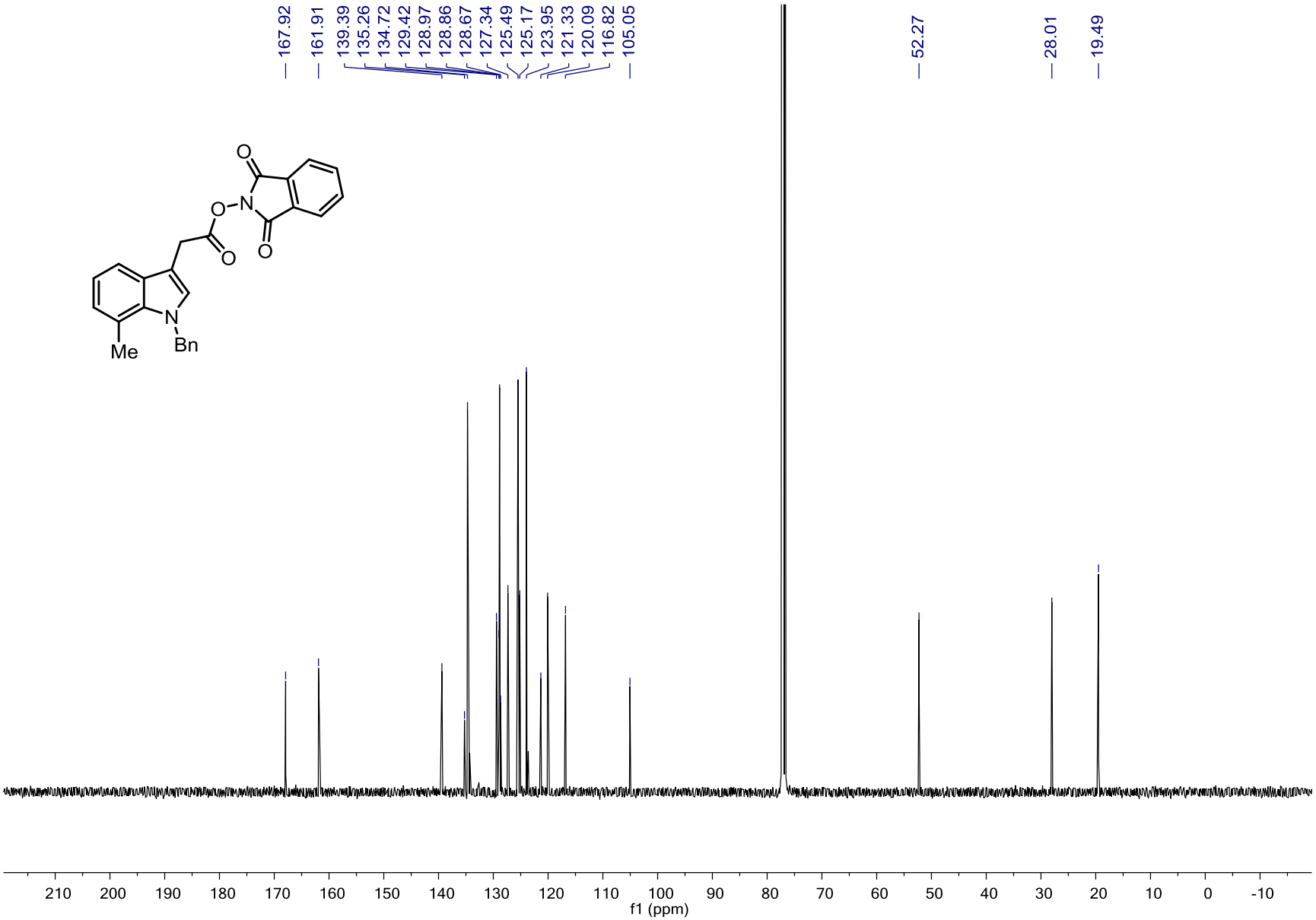
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12z***



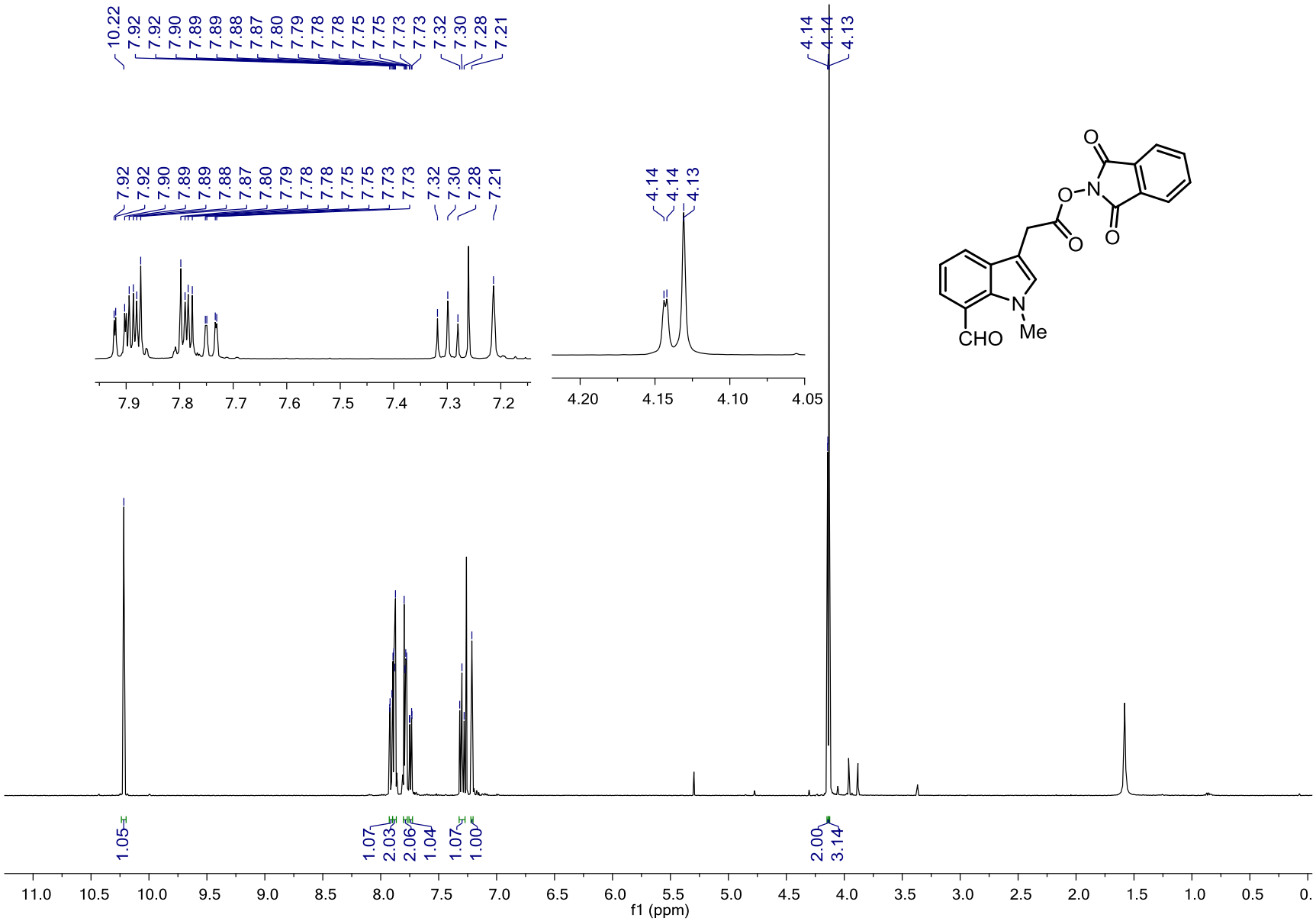
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12aa***



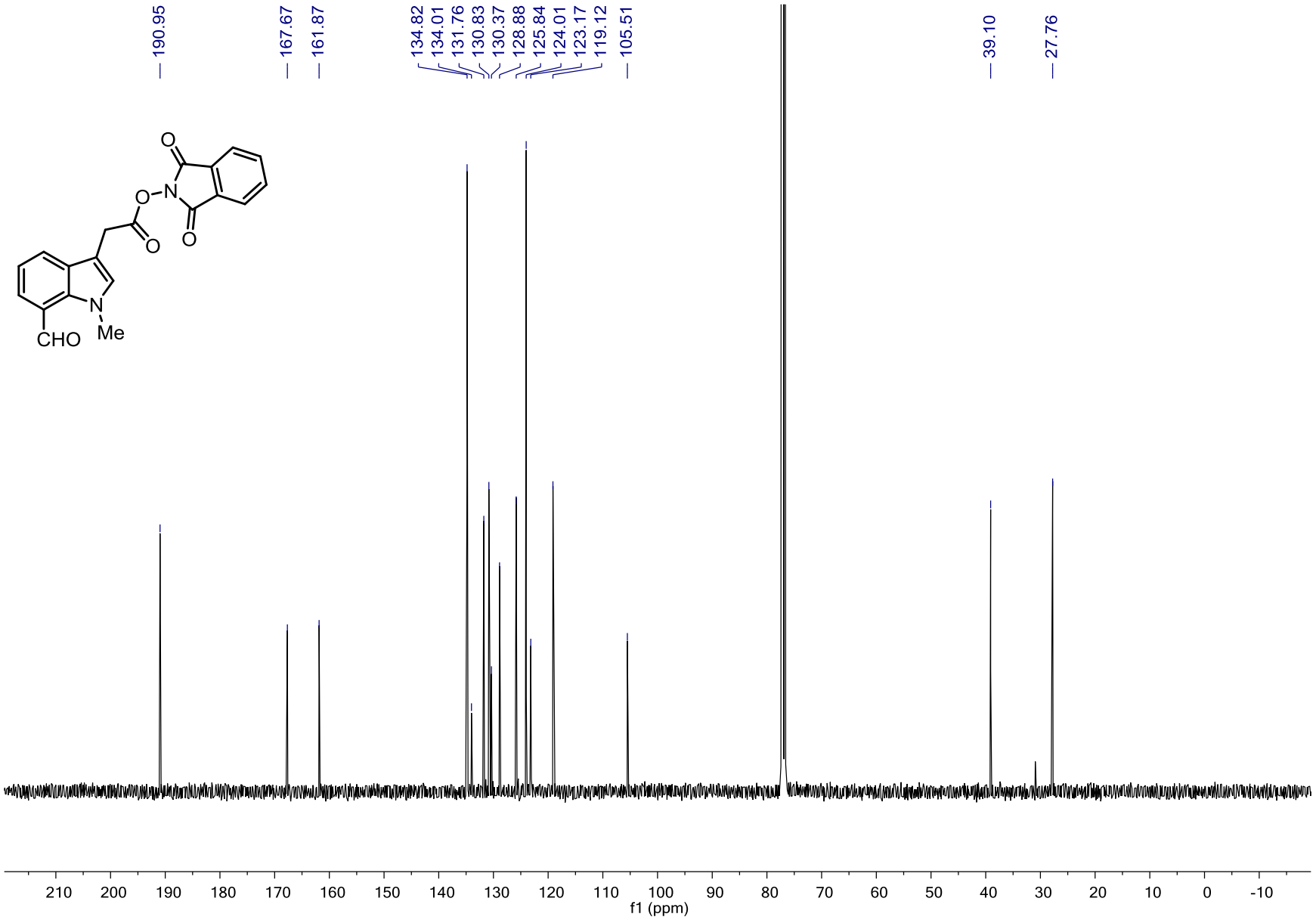
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12aa***



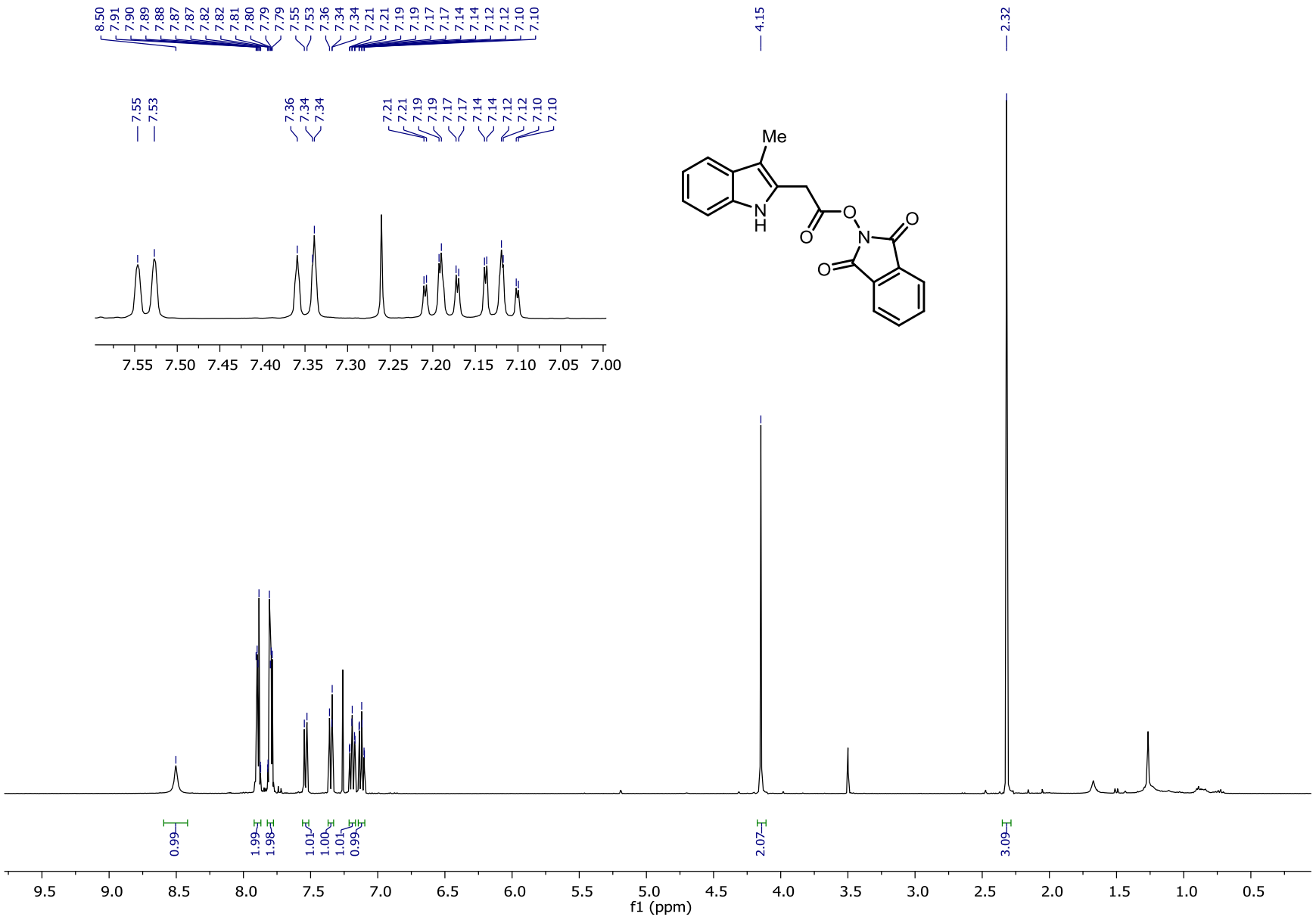
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound 1**2ab***



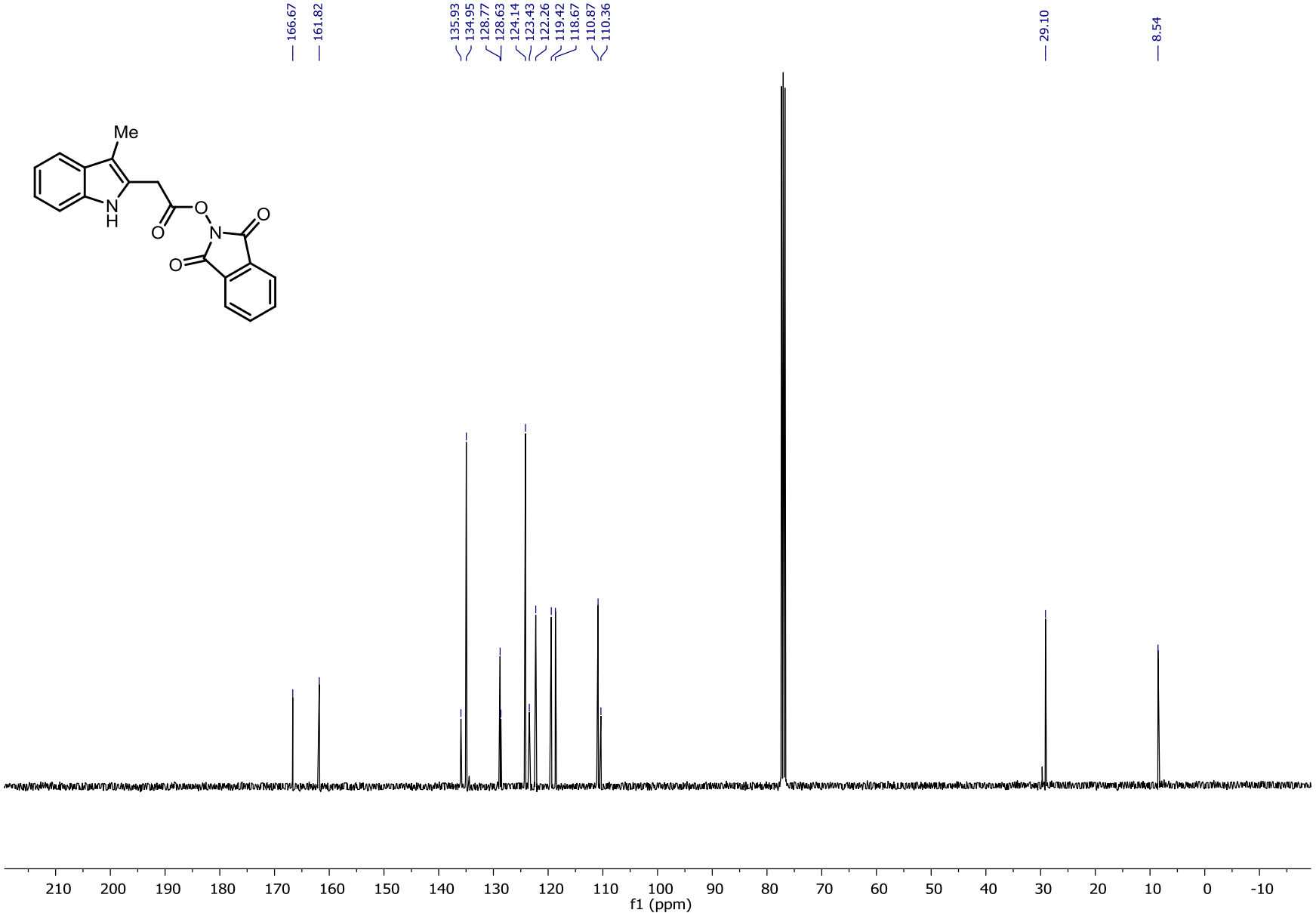
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12ab***



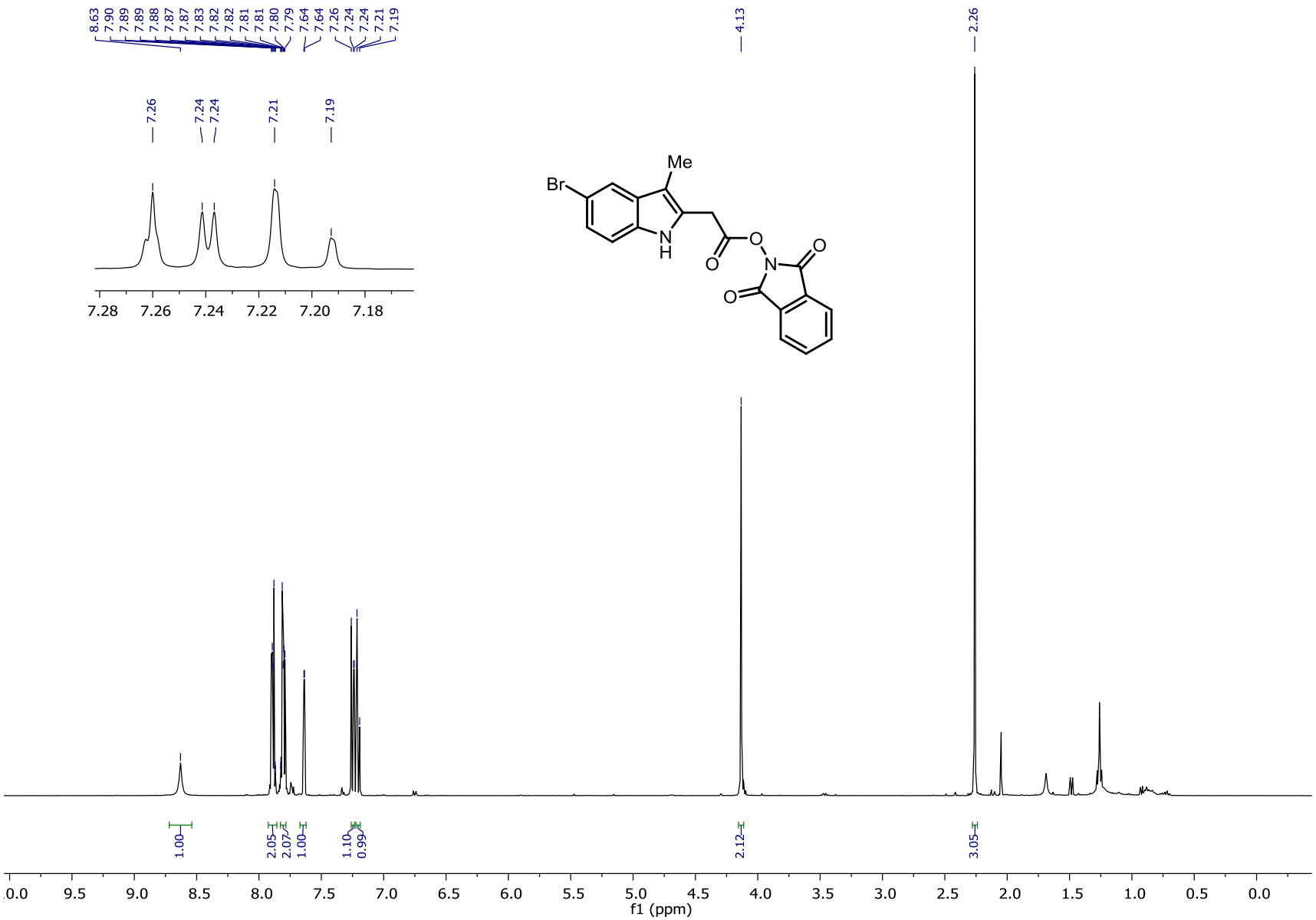
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12ac***



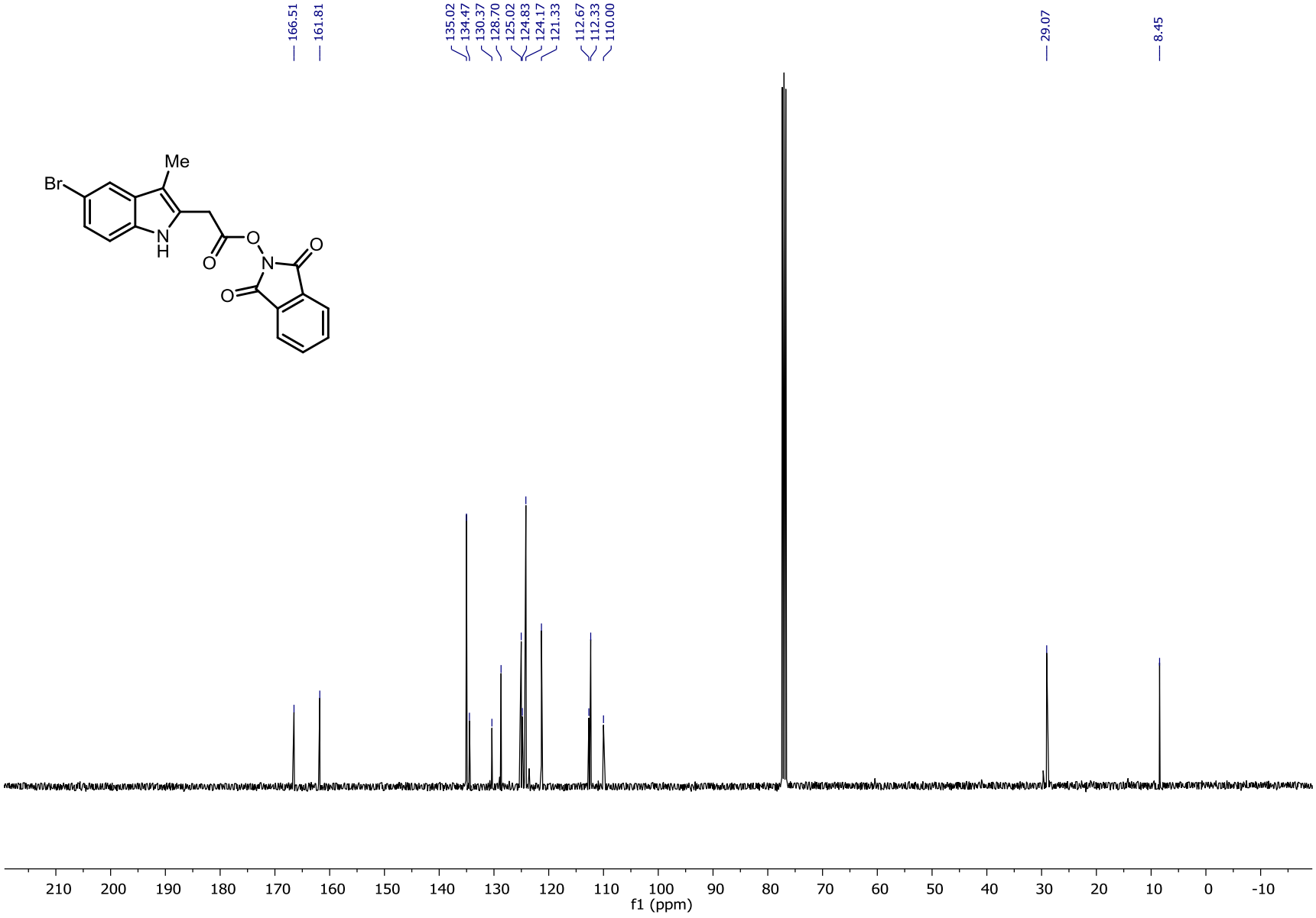
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12ac***



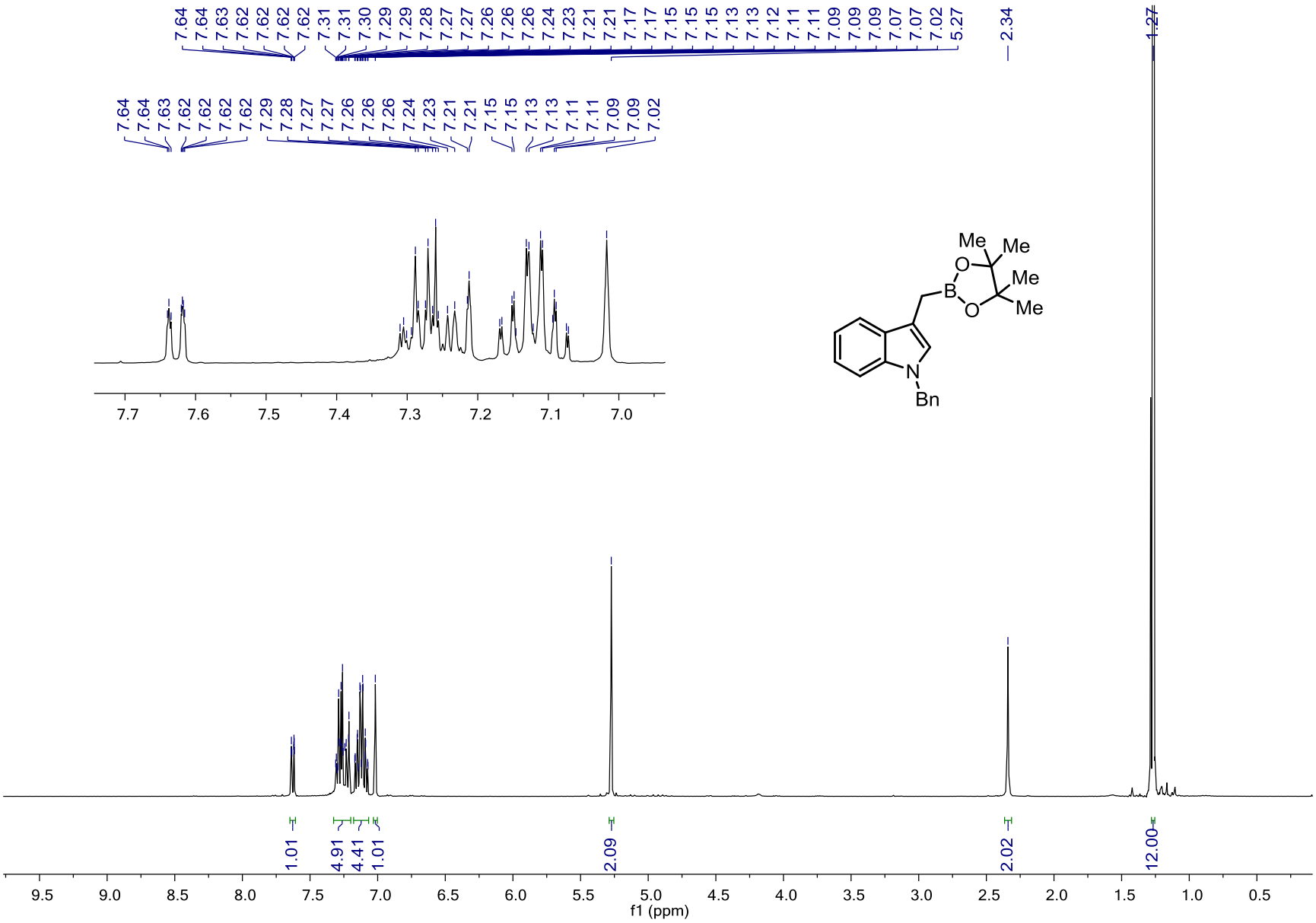
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **12ad***



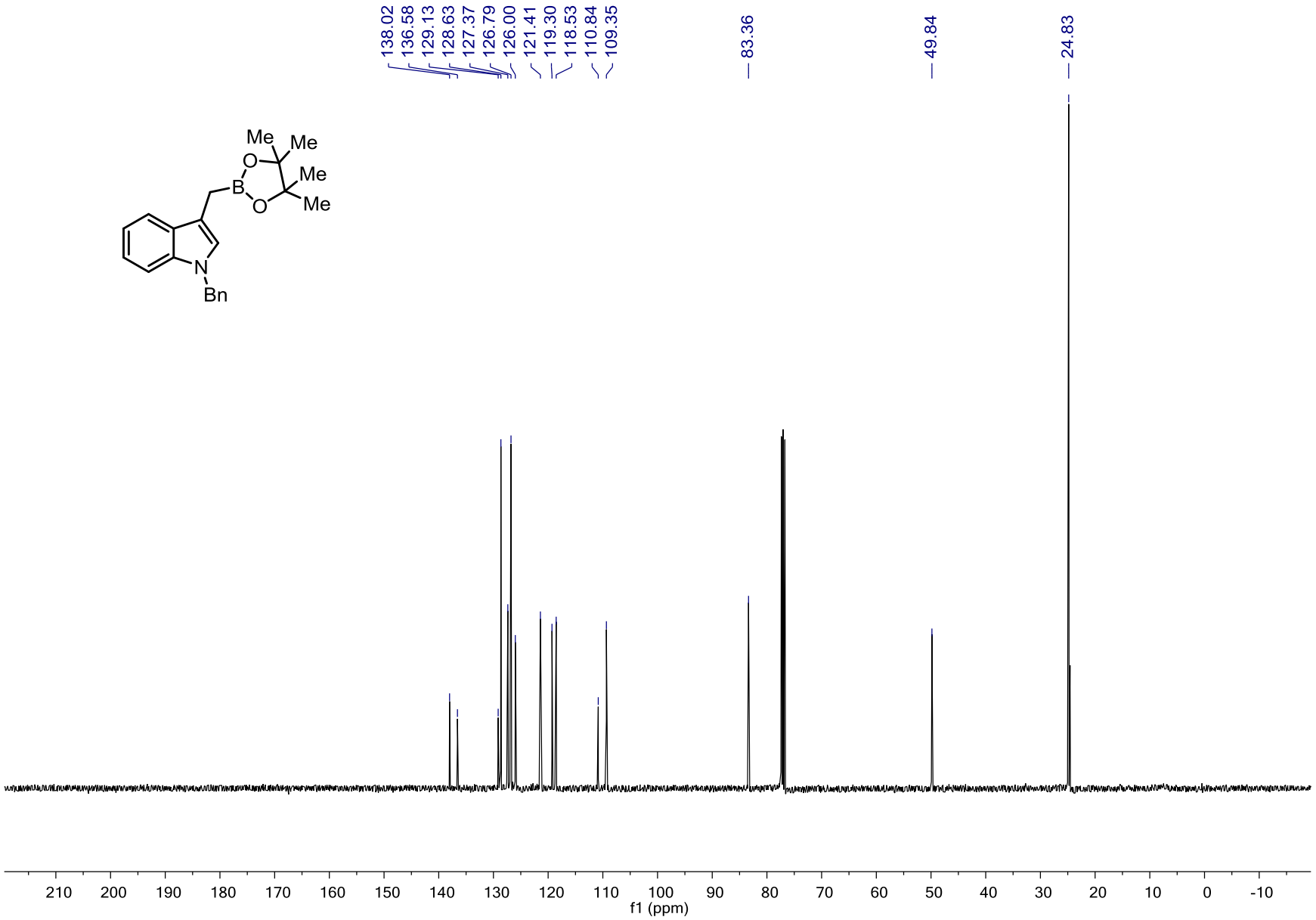
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **12ad***



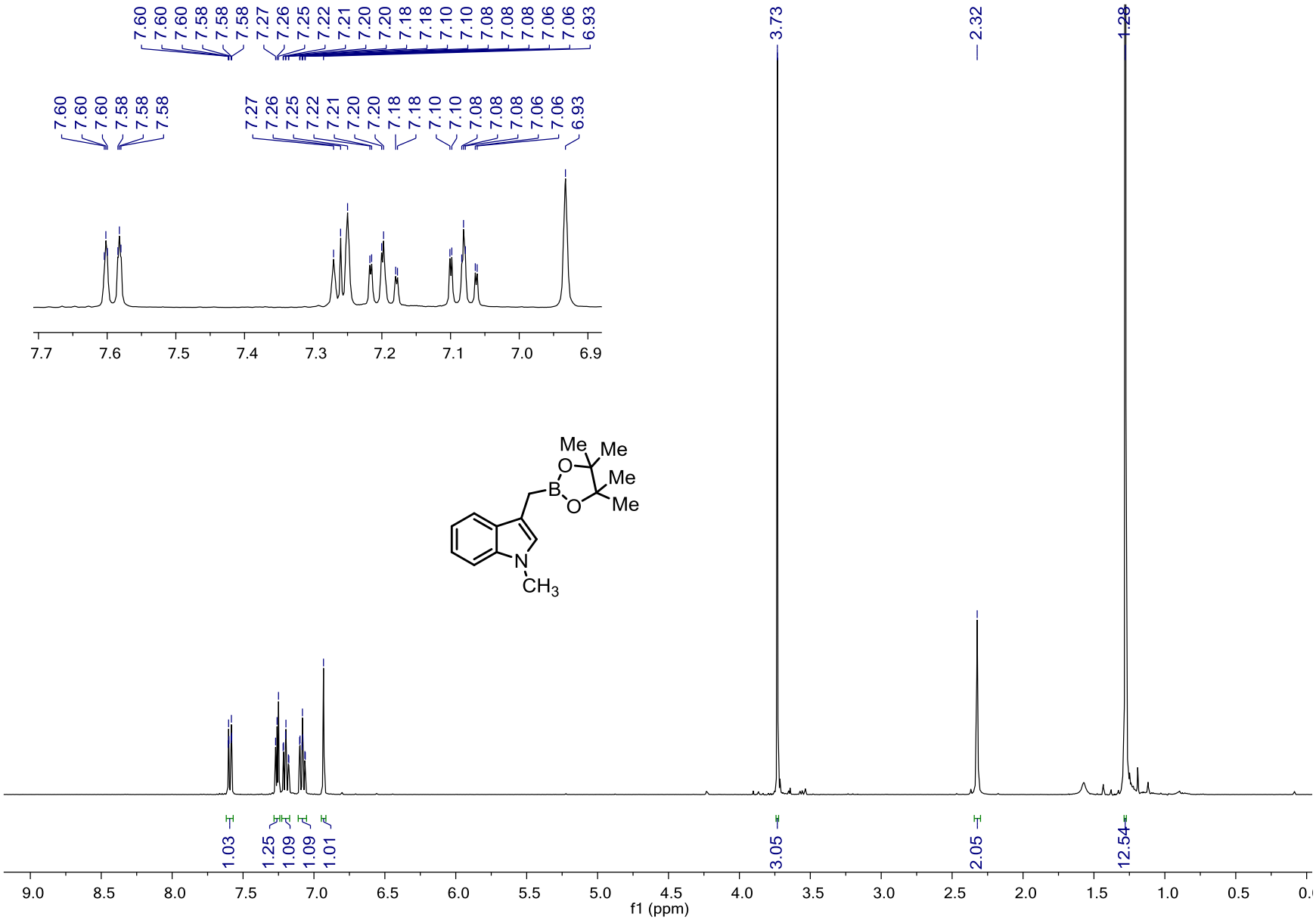
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11a***



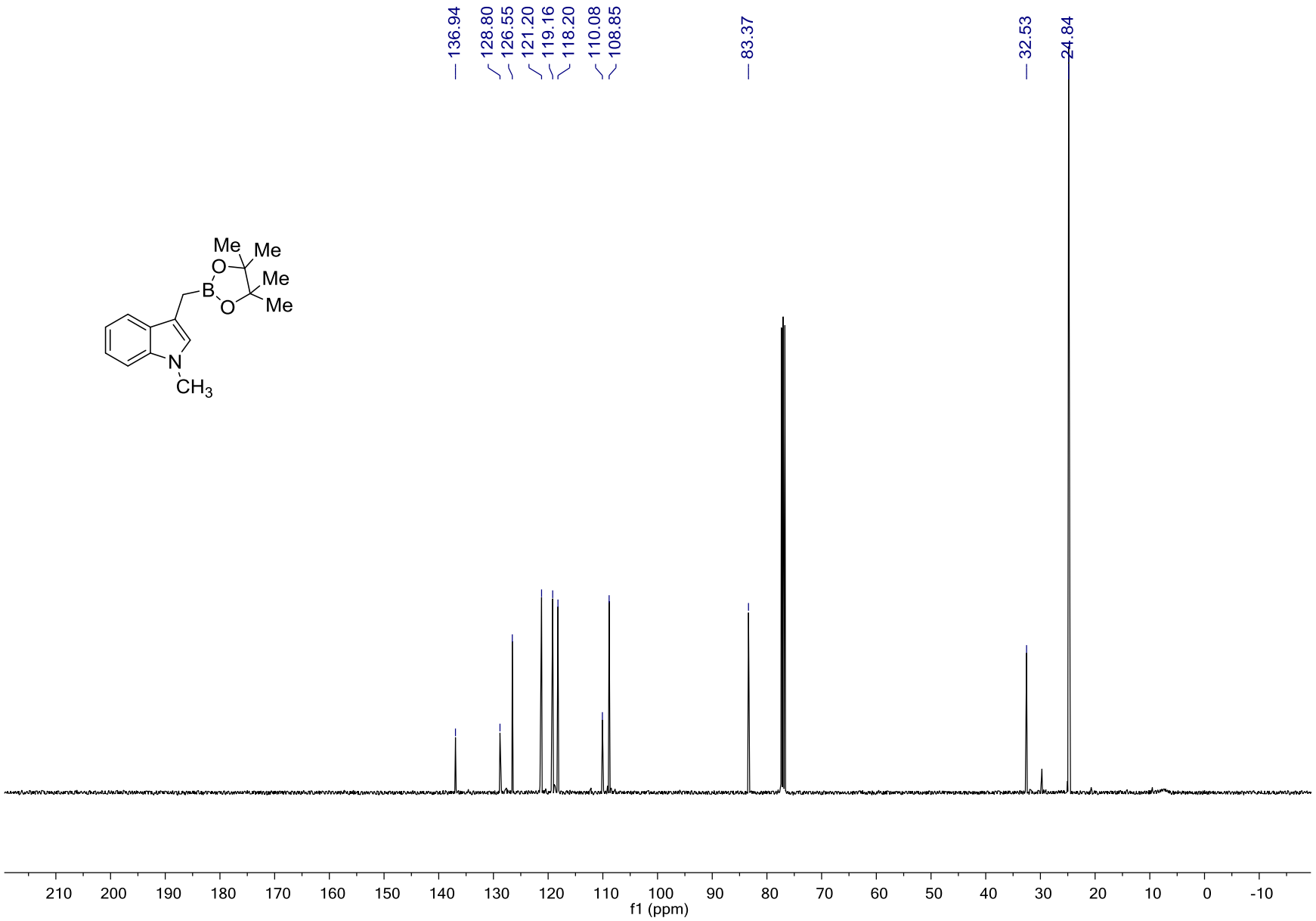
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11a***



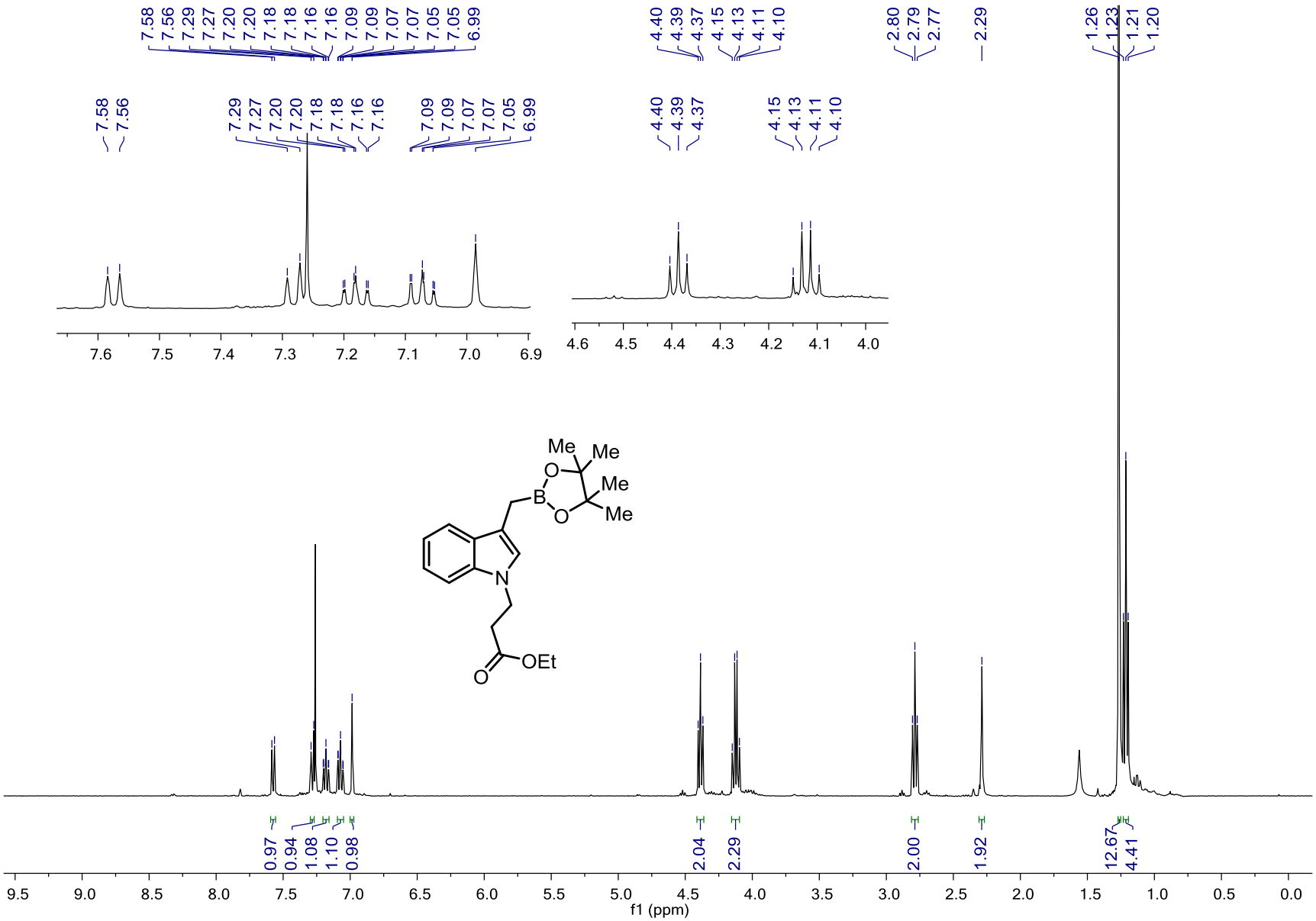
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11b***



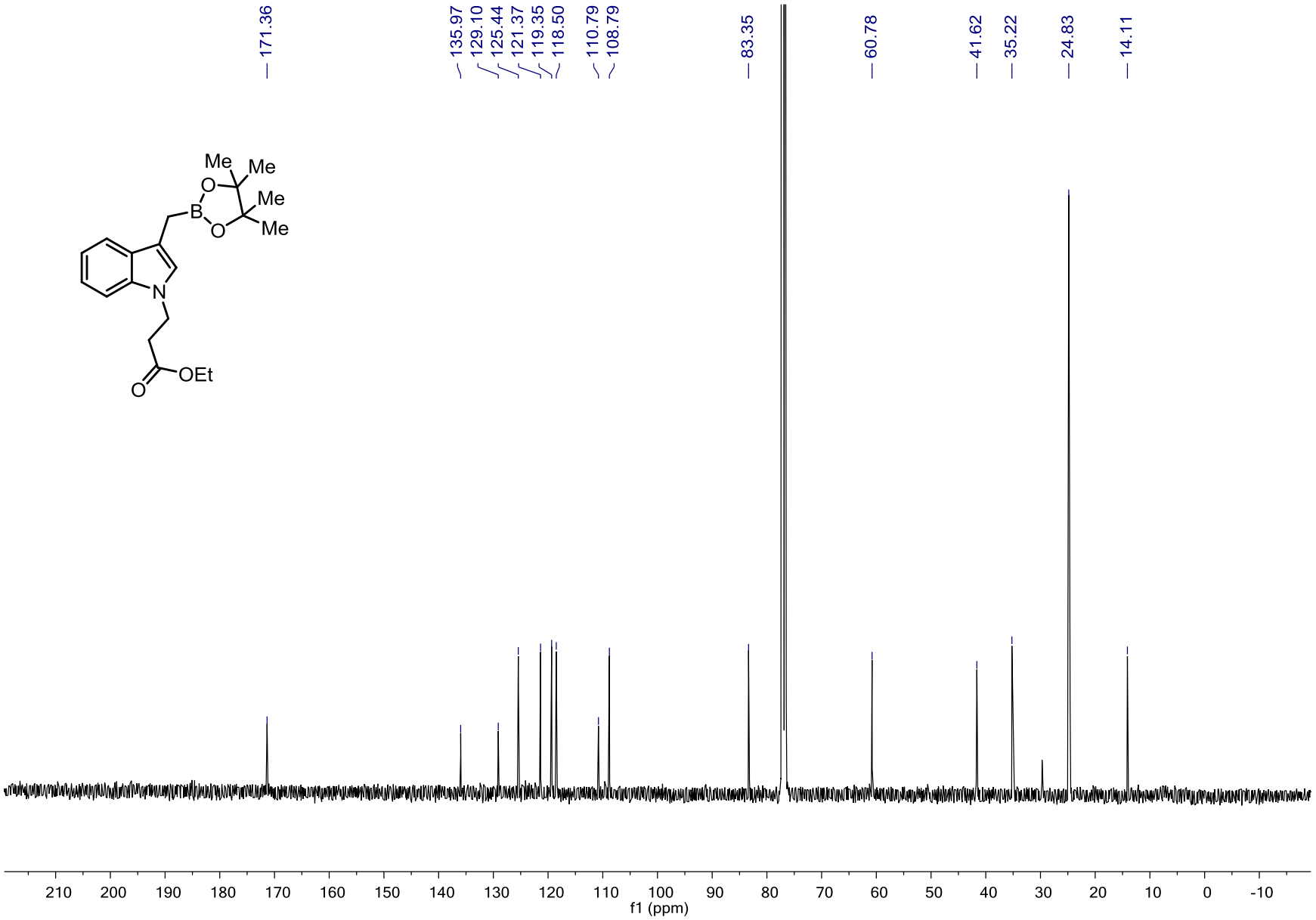
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11b***



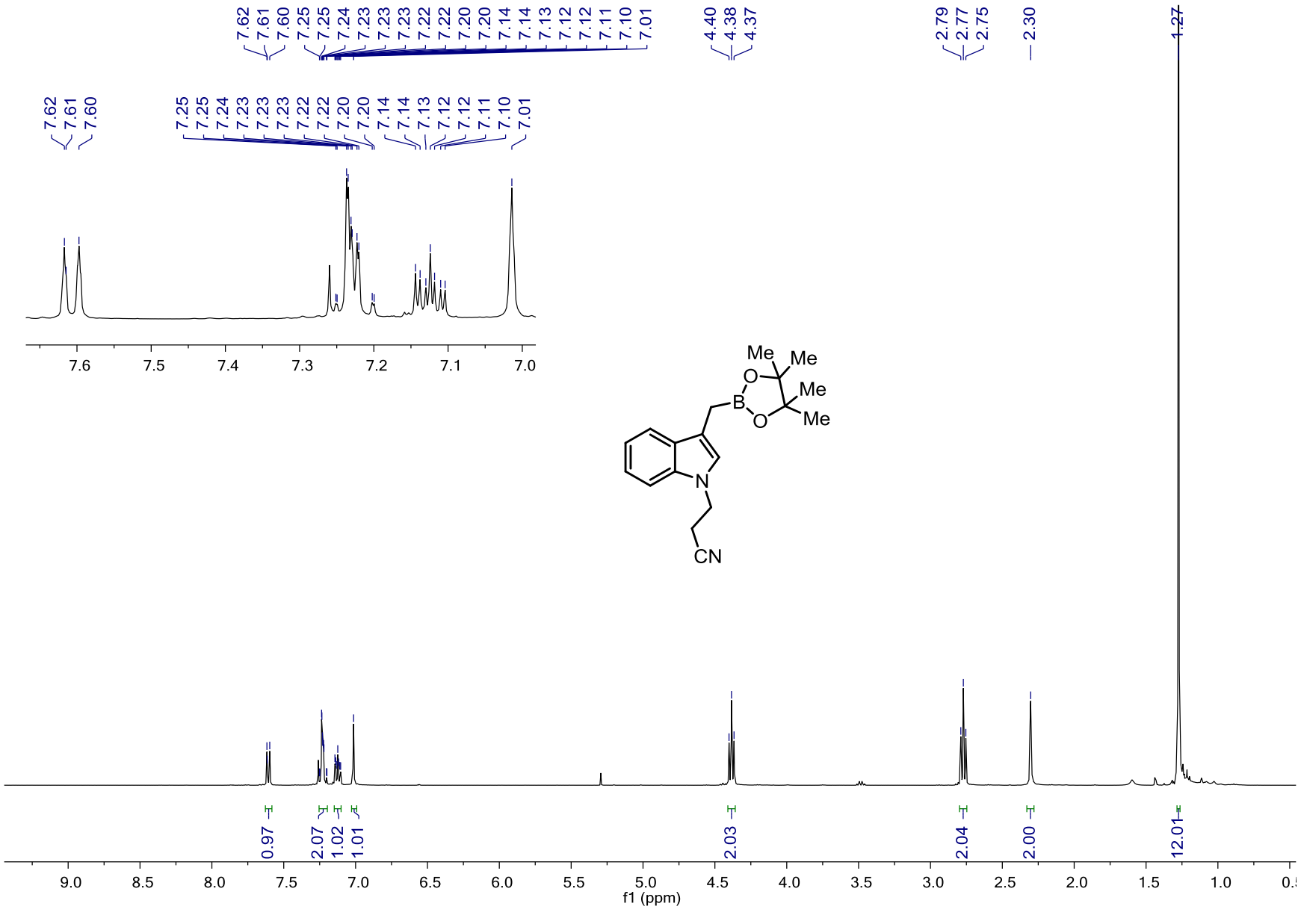
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11c***



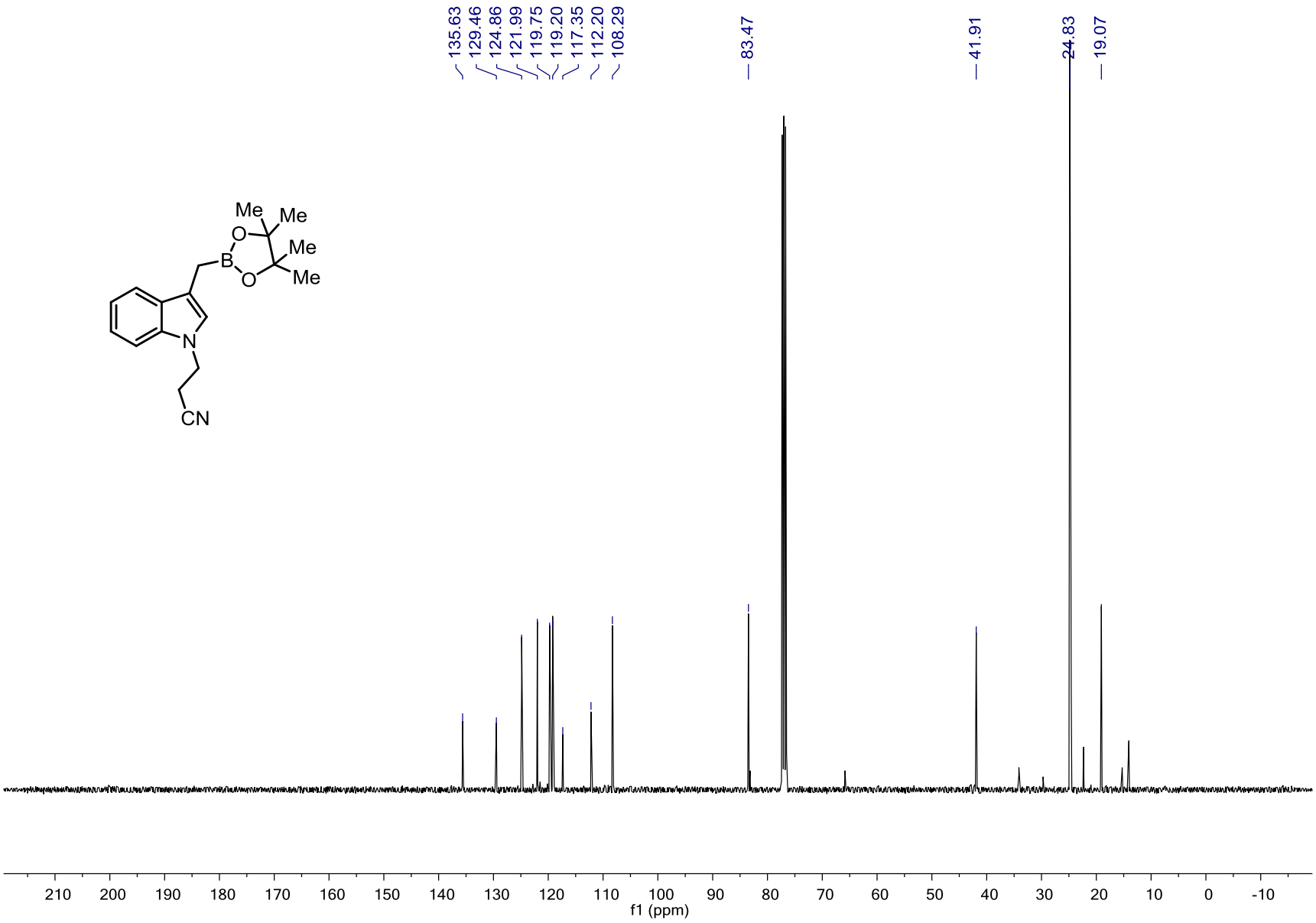
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11c***



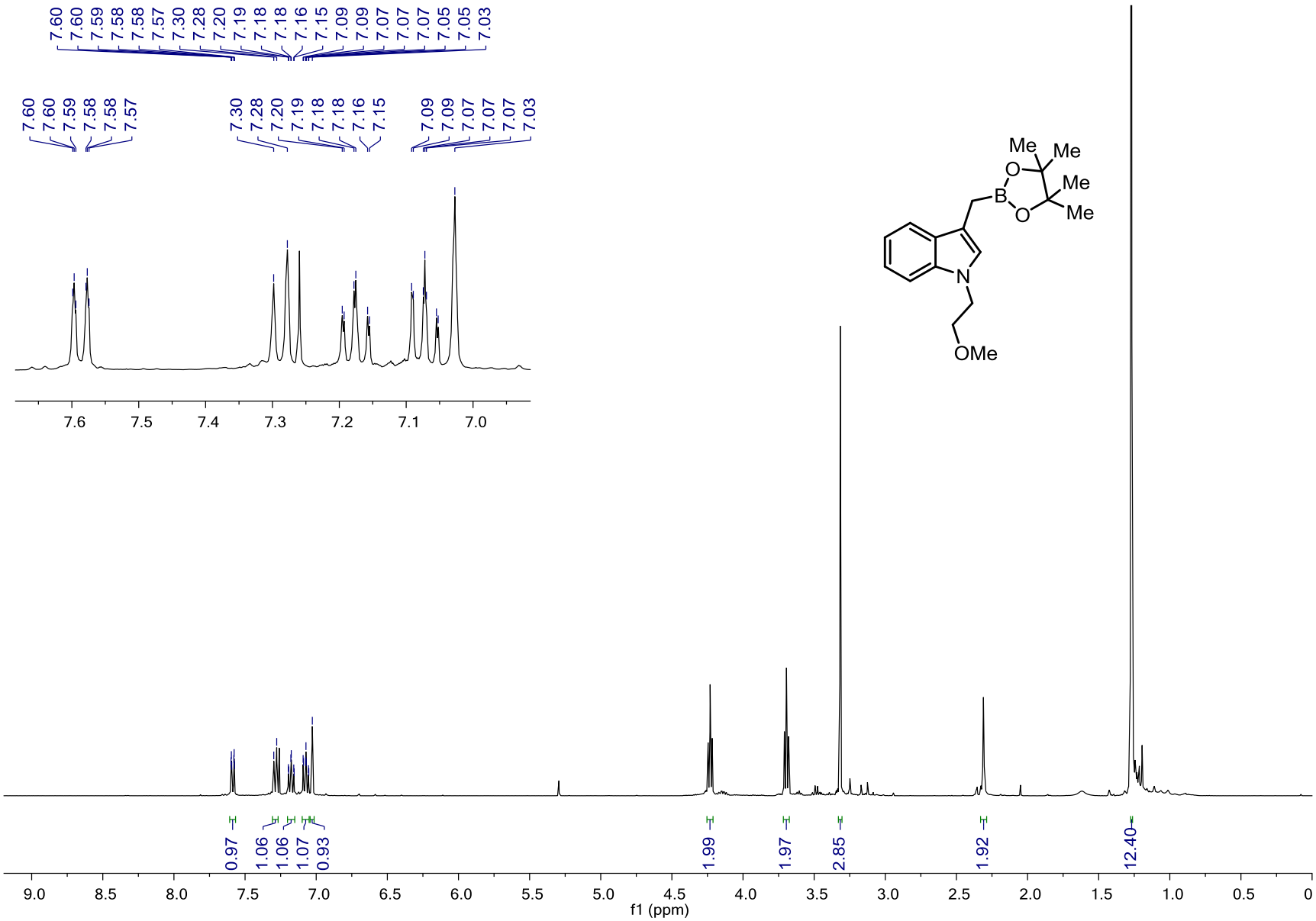
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11d***



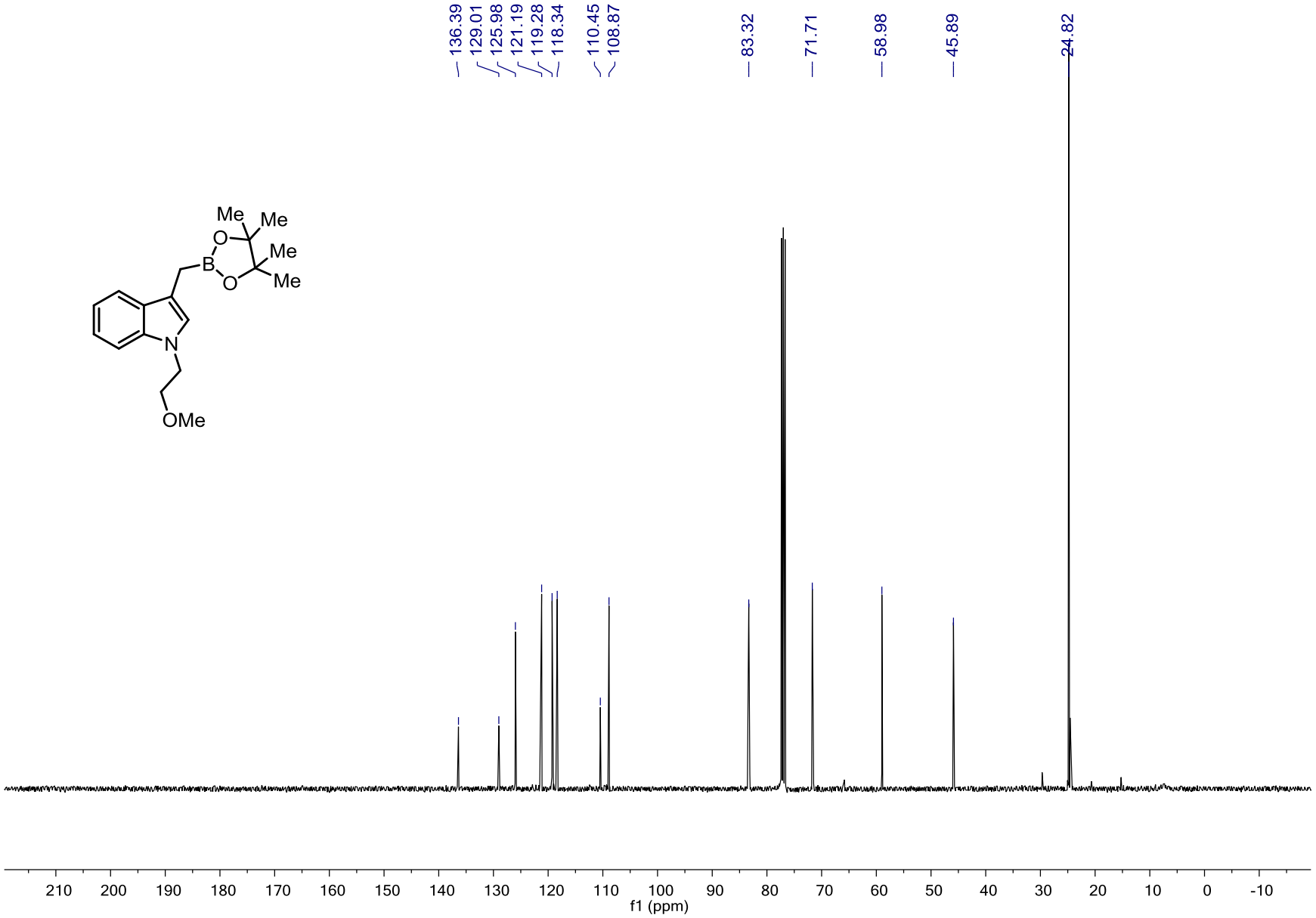
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11d***



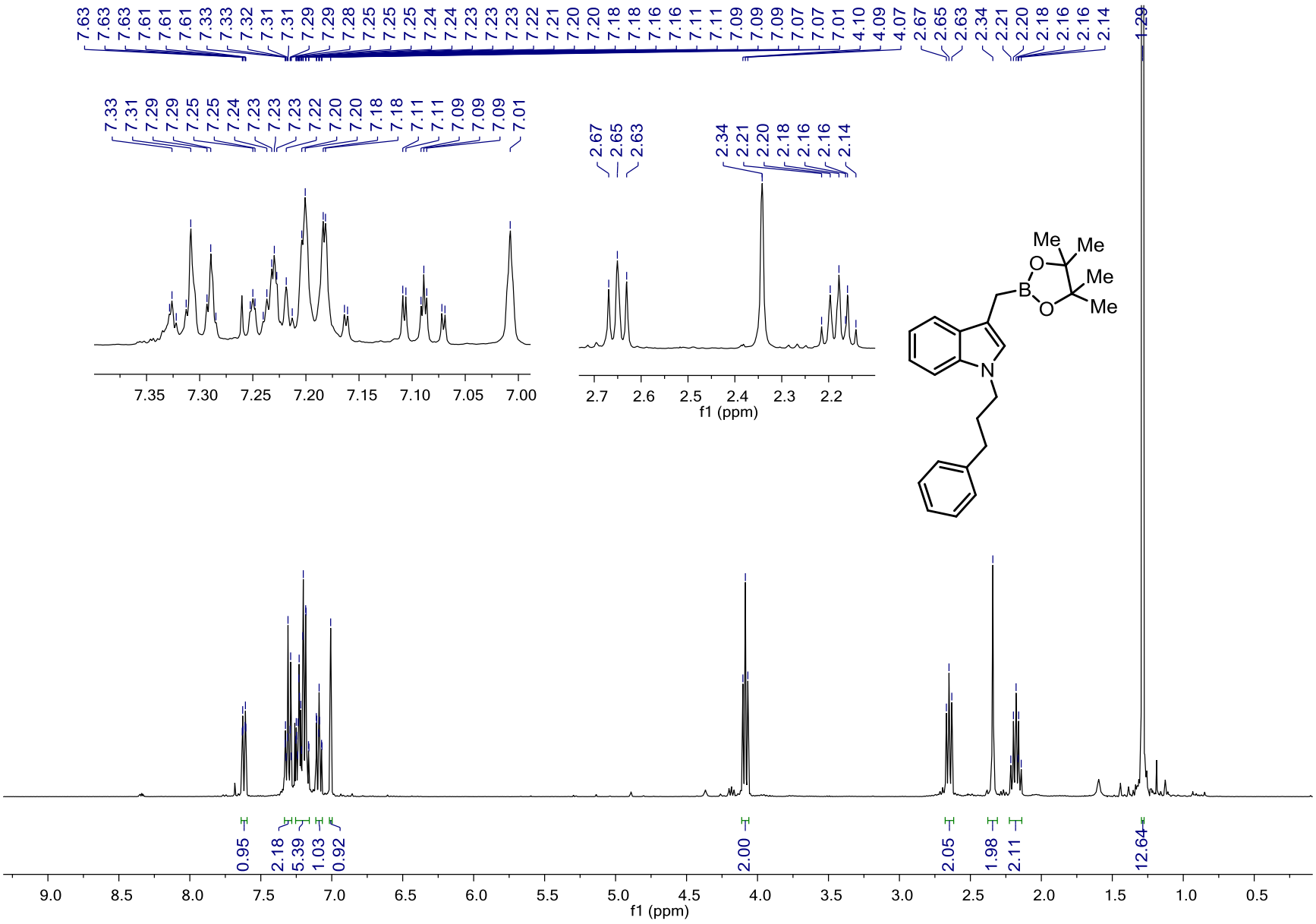
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11e***



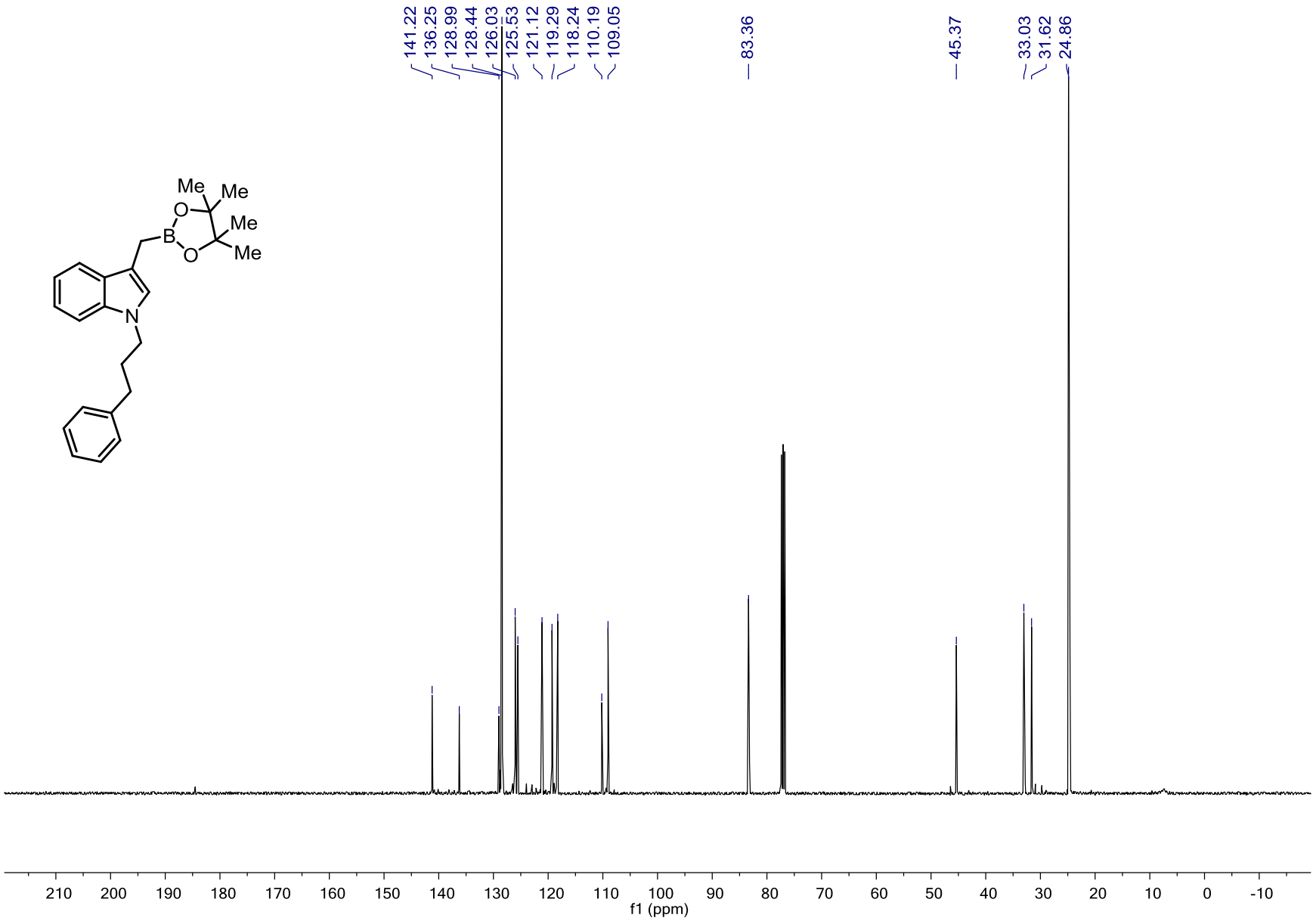
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11e***



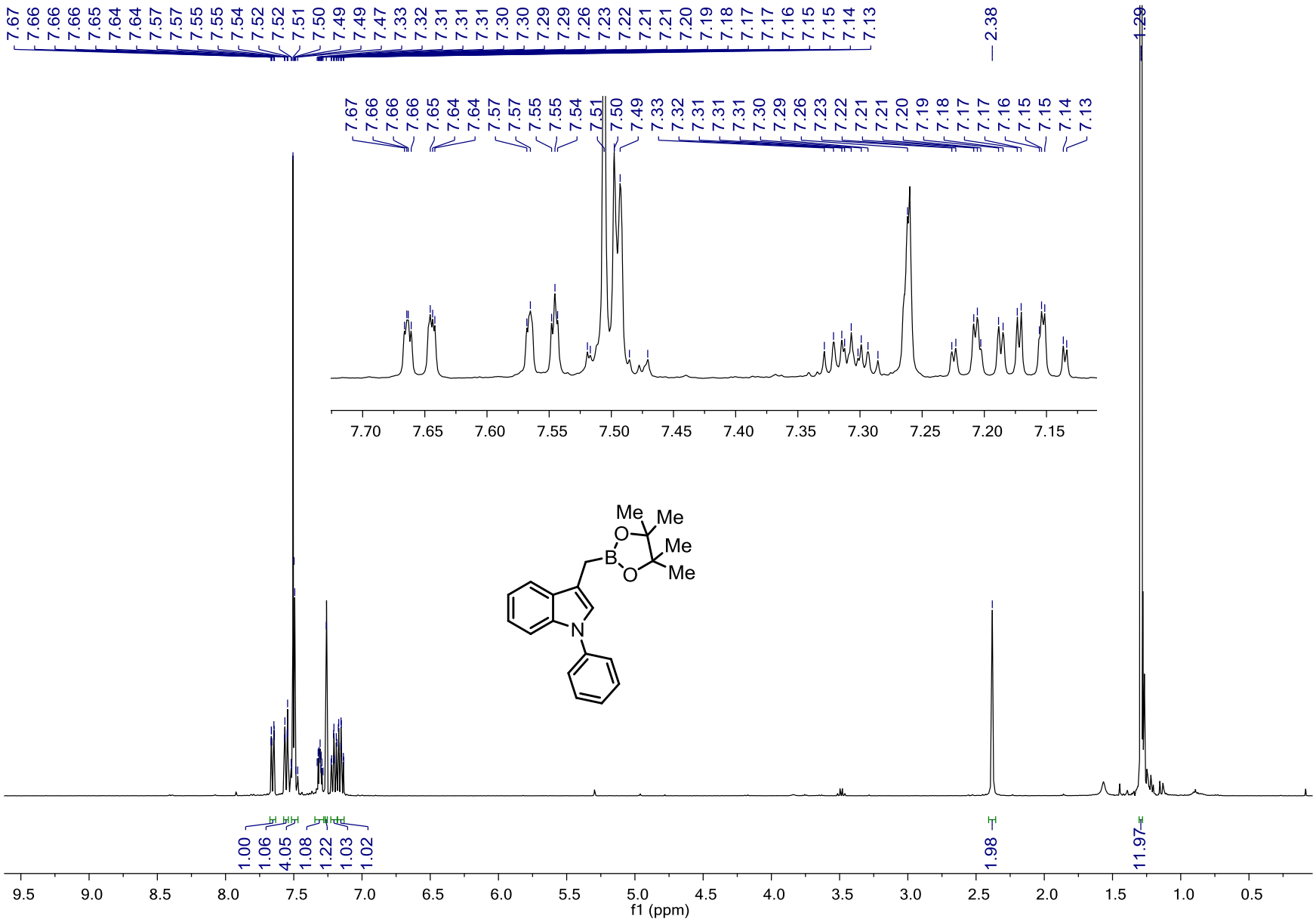
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11f***



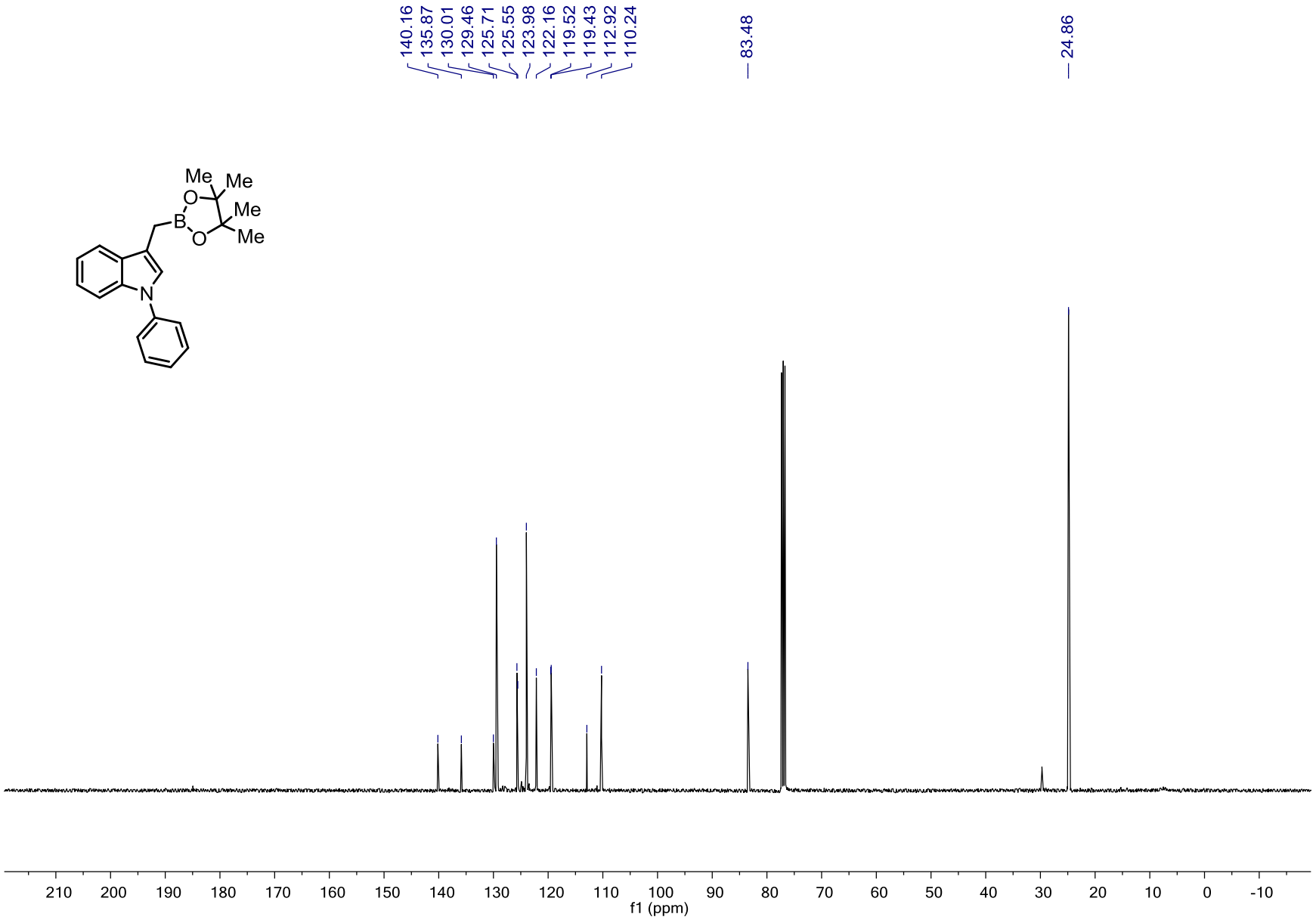
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11f***



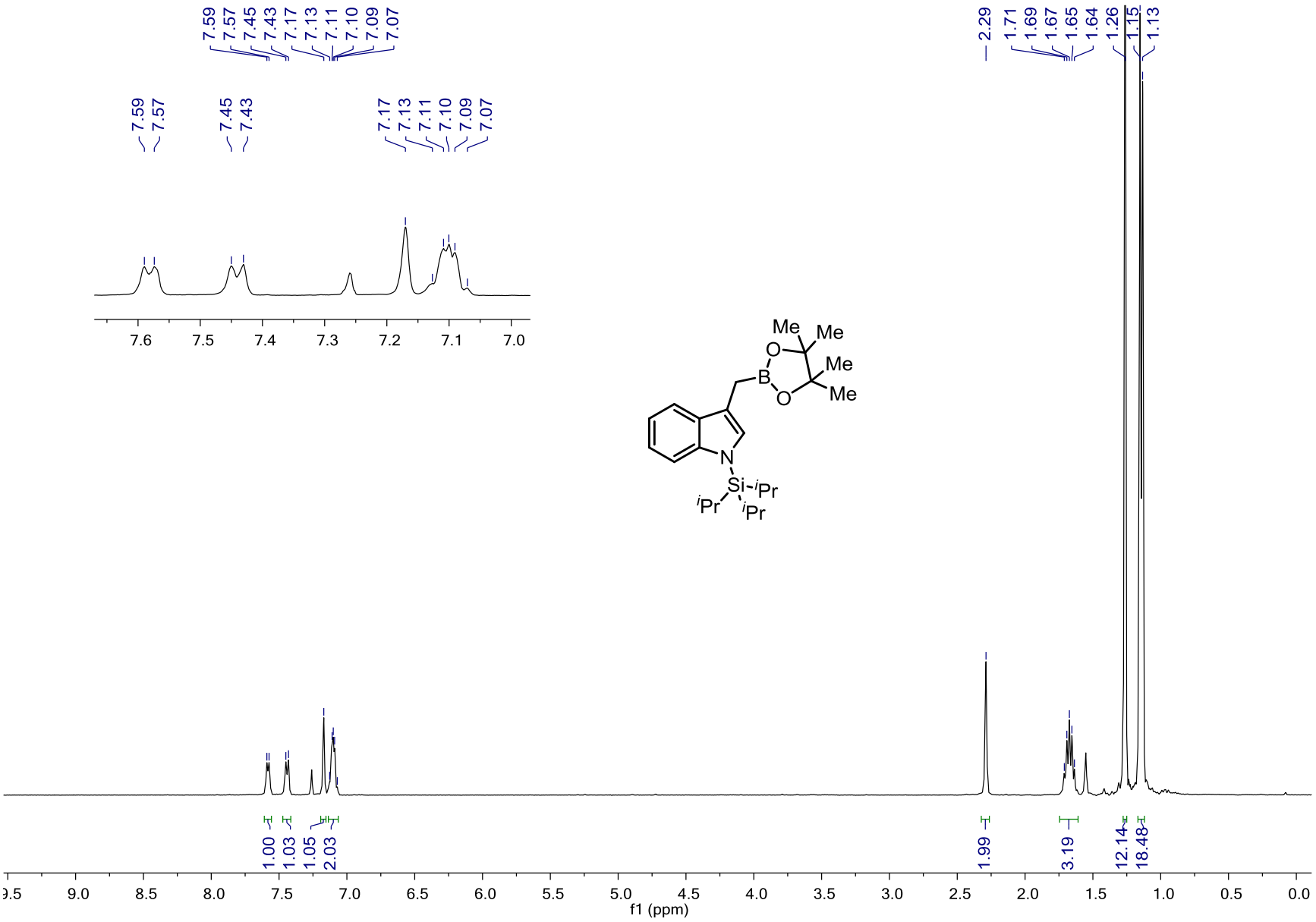
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11g***



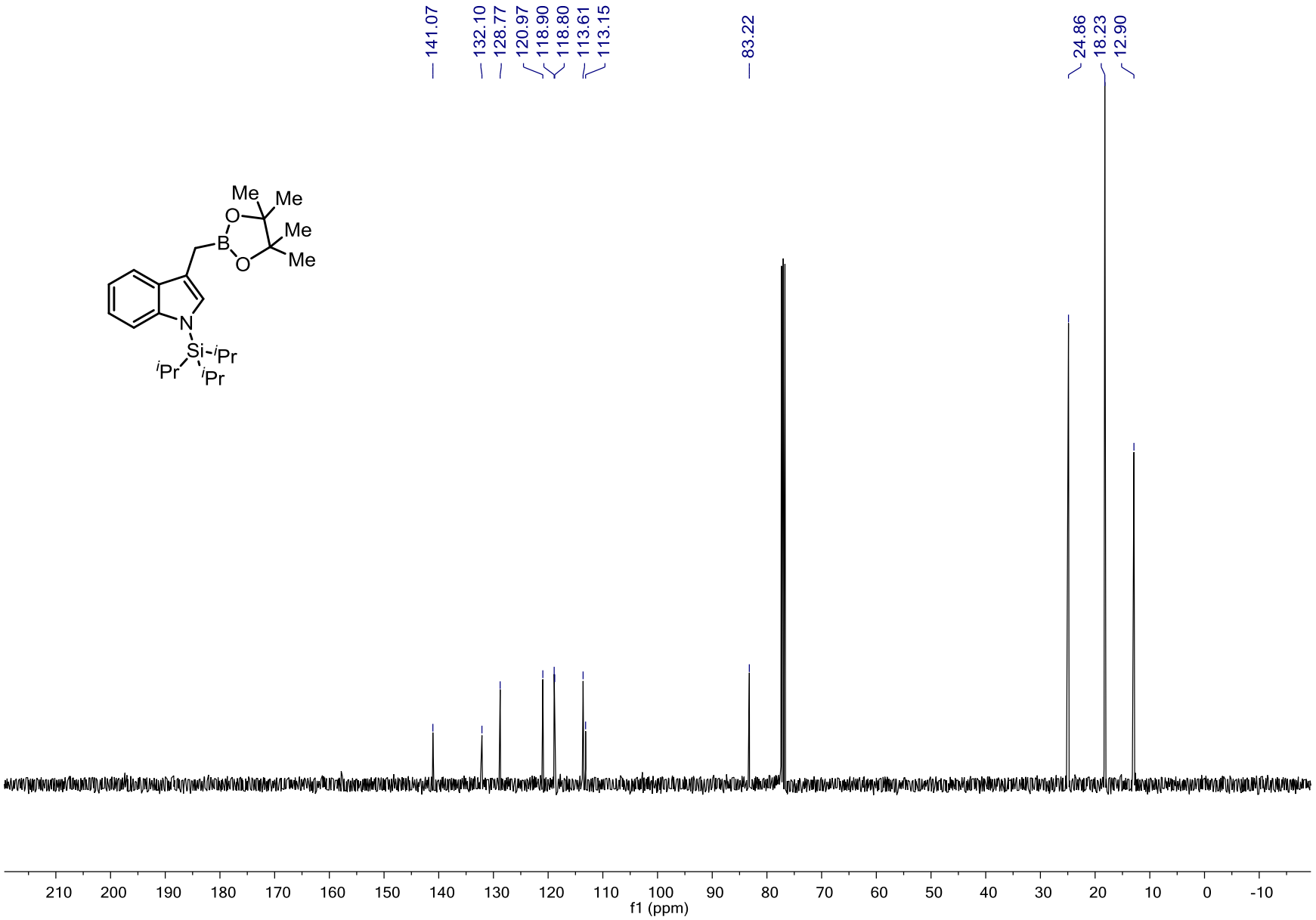
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11g***



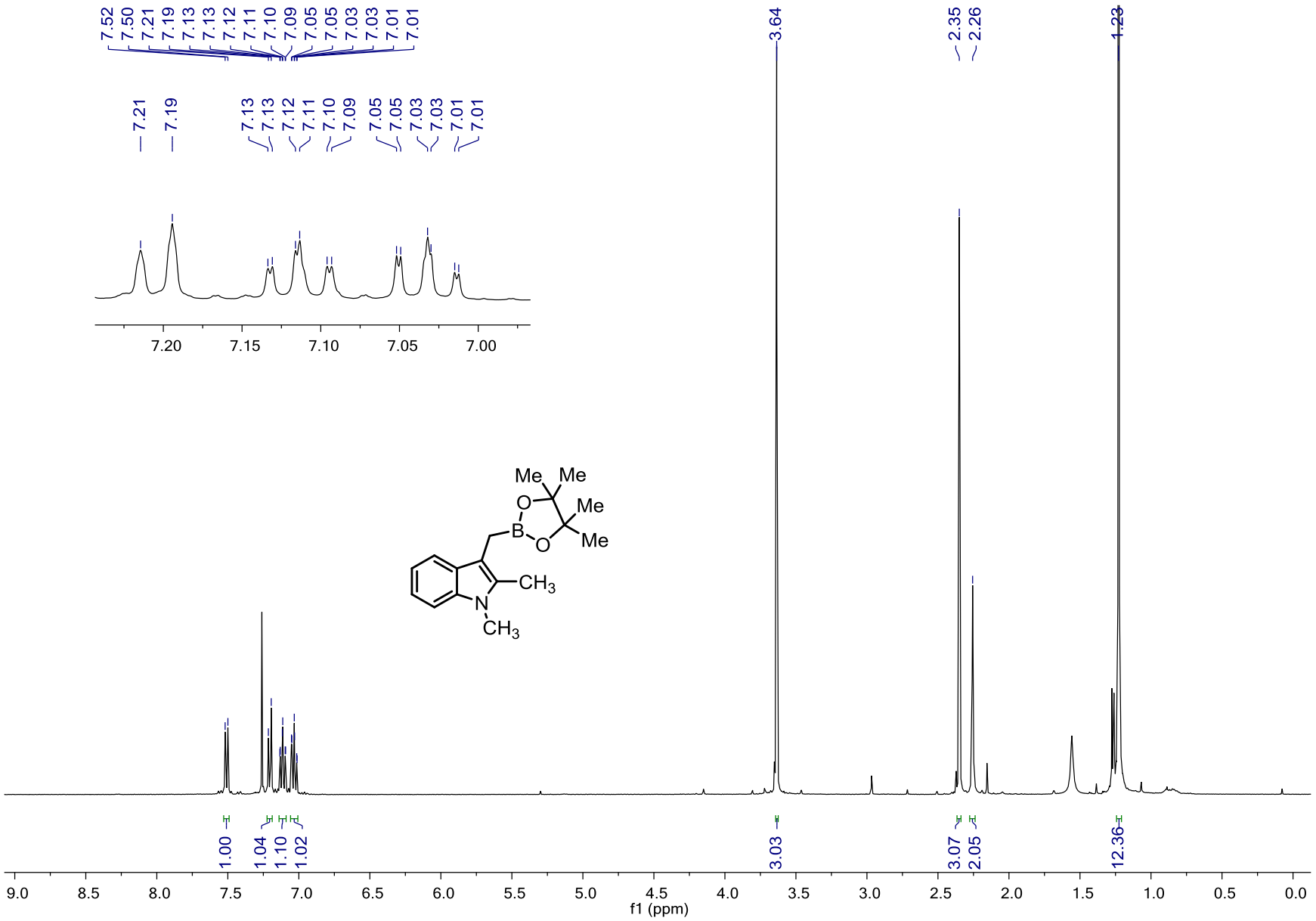
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11h***



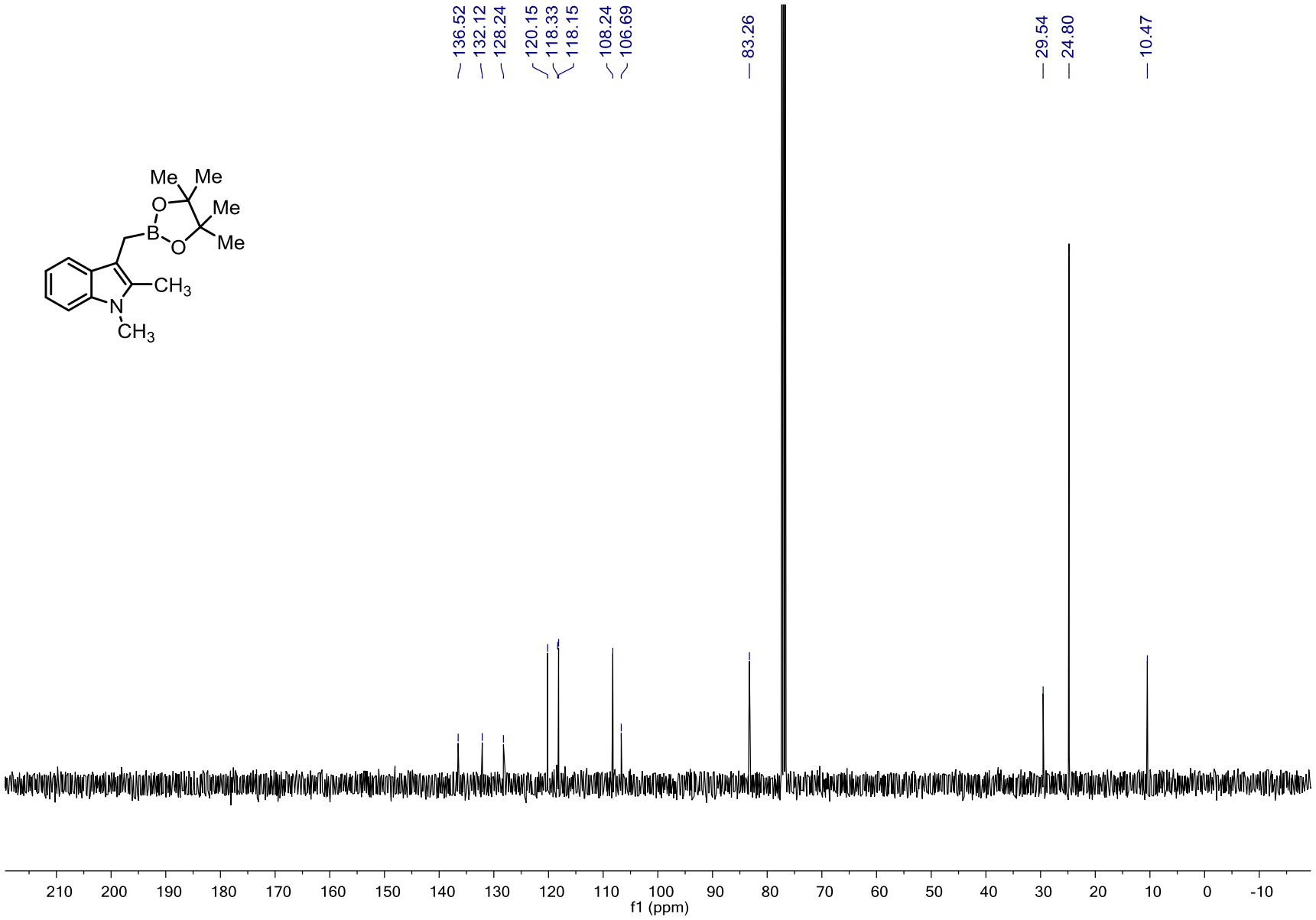
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11h***



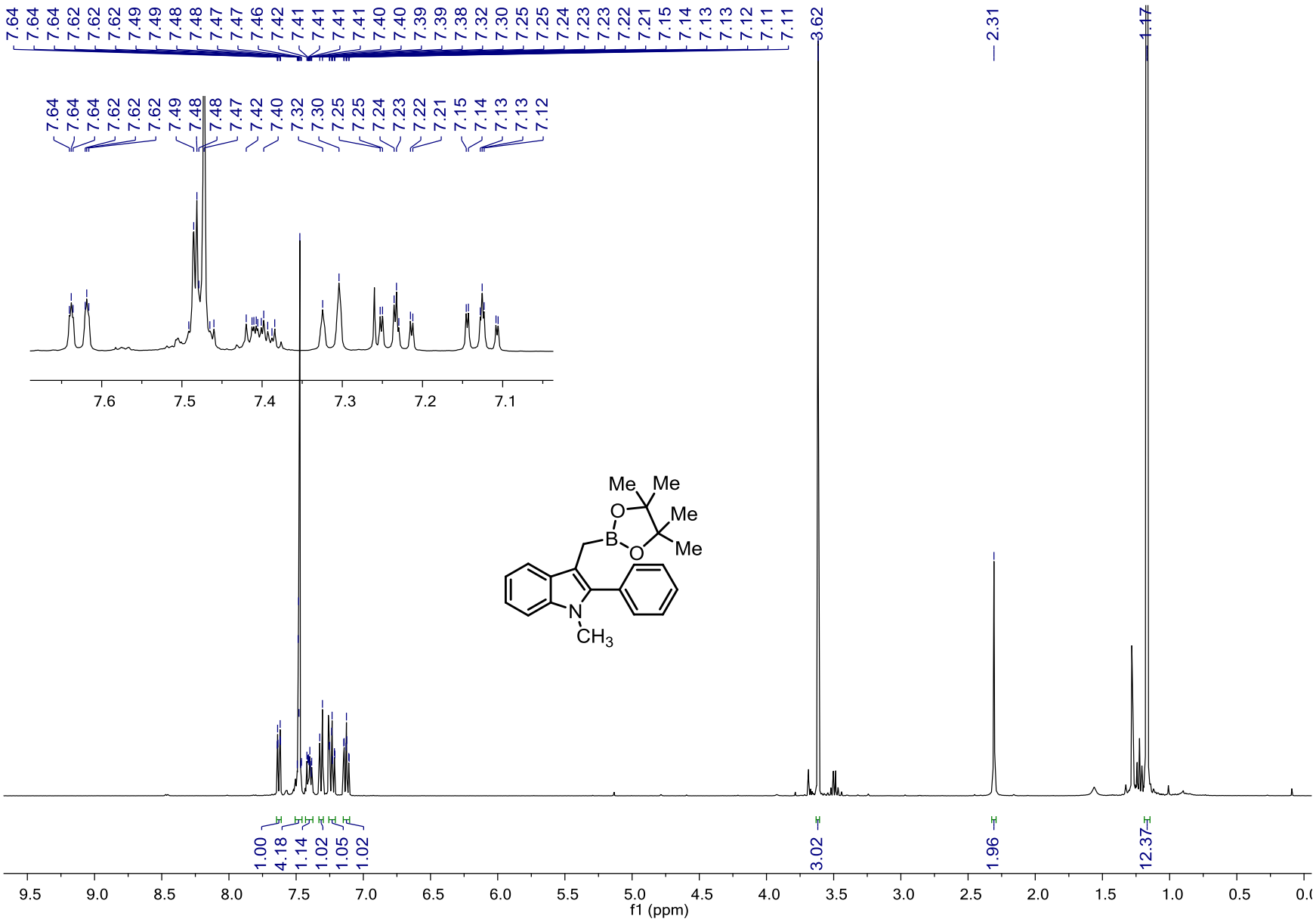
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11i***



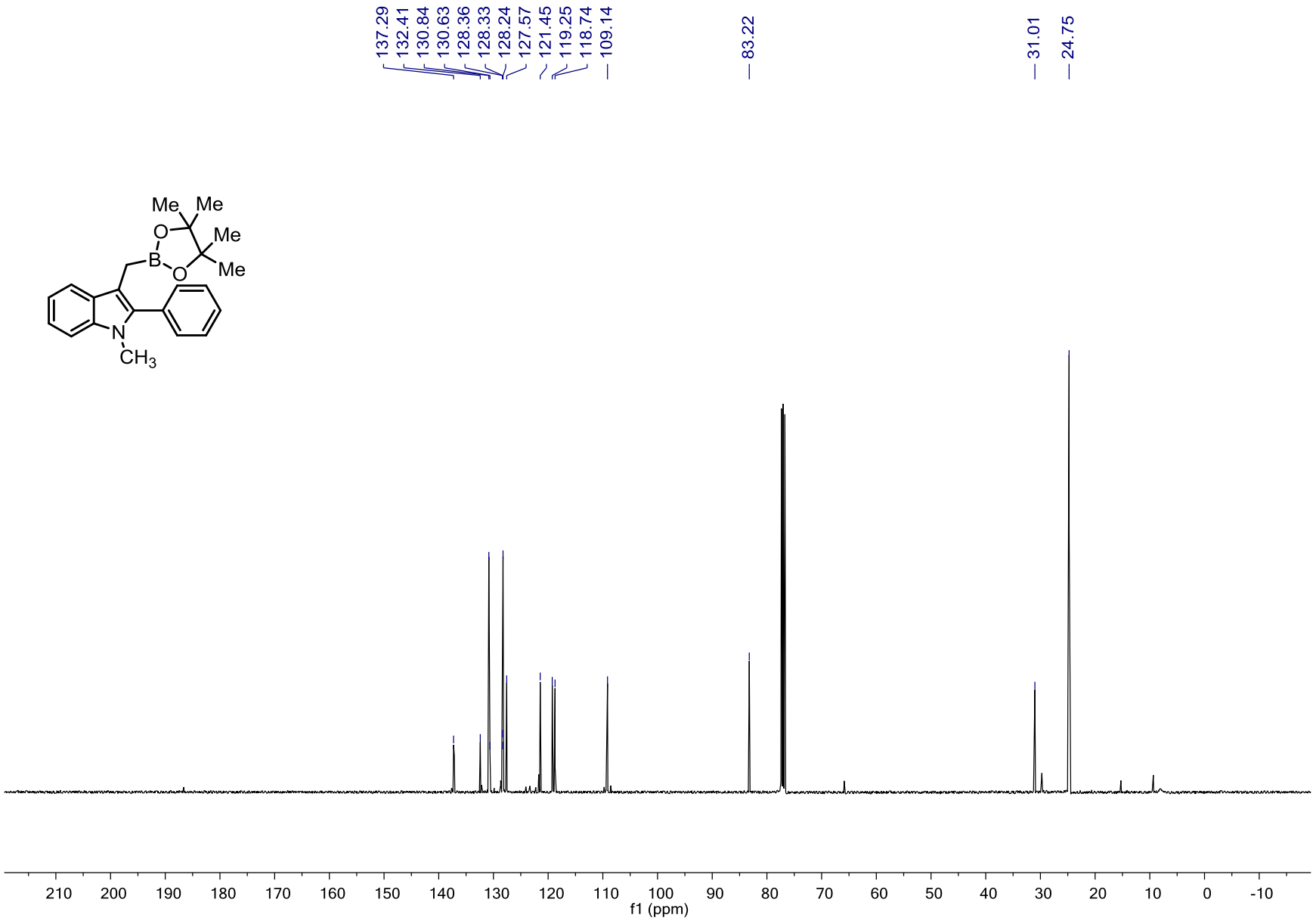
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11i***



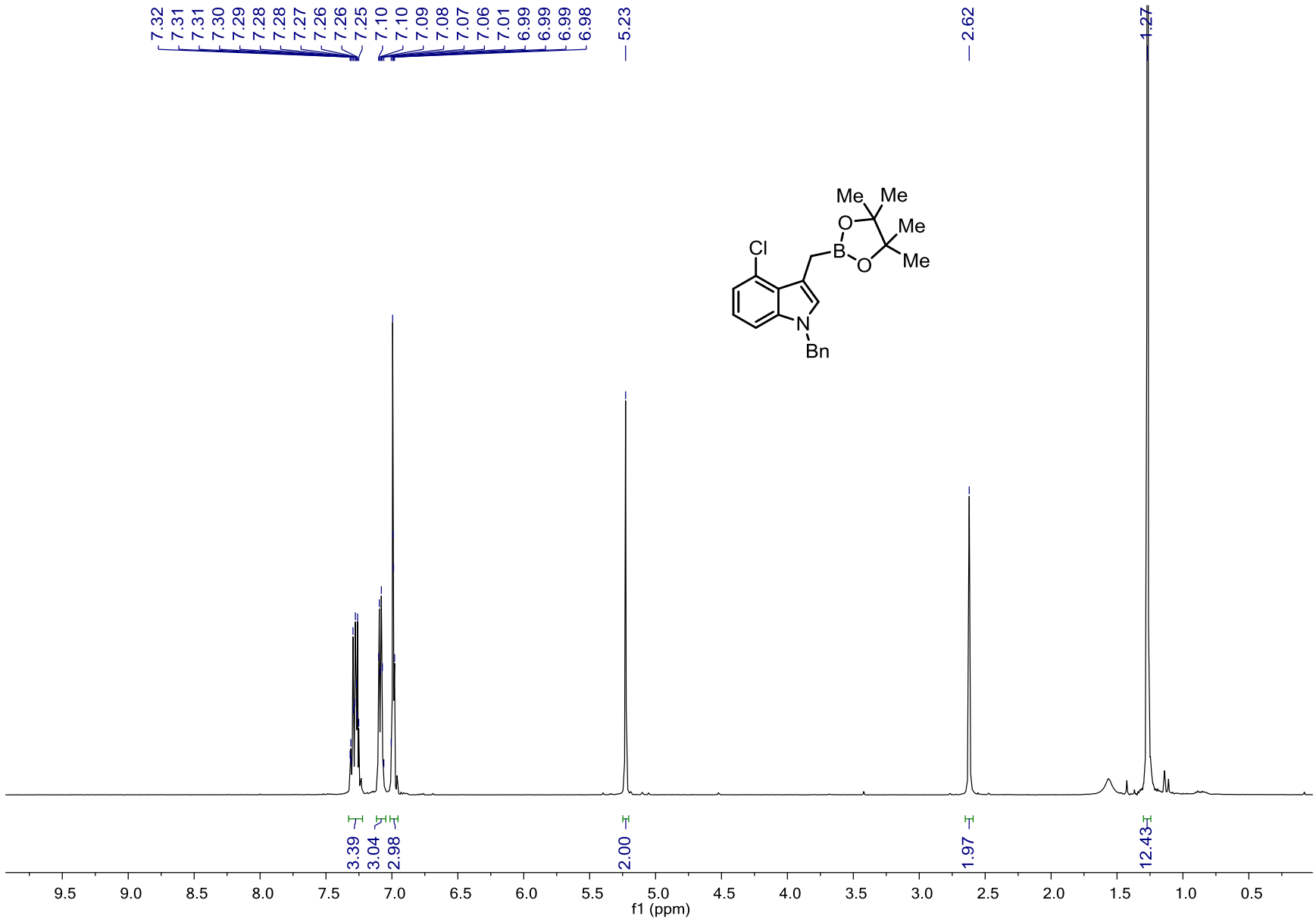
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11j***



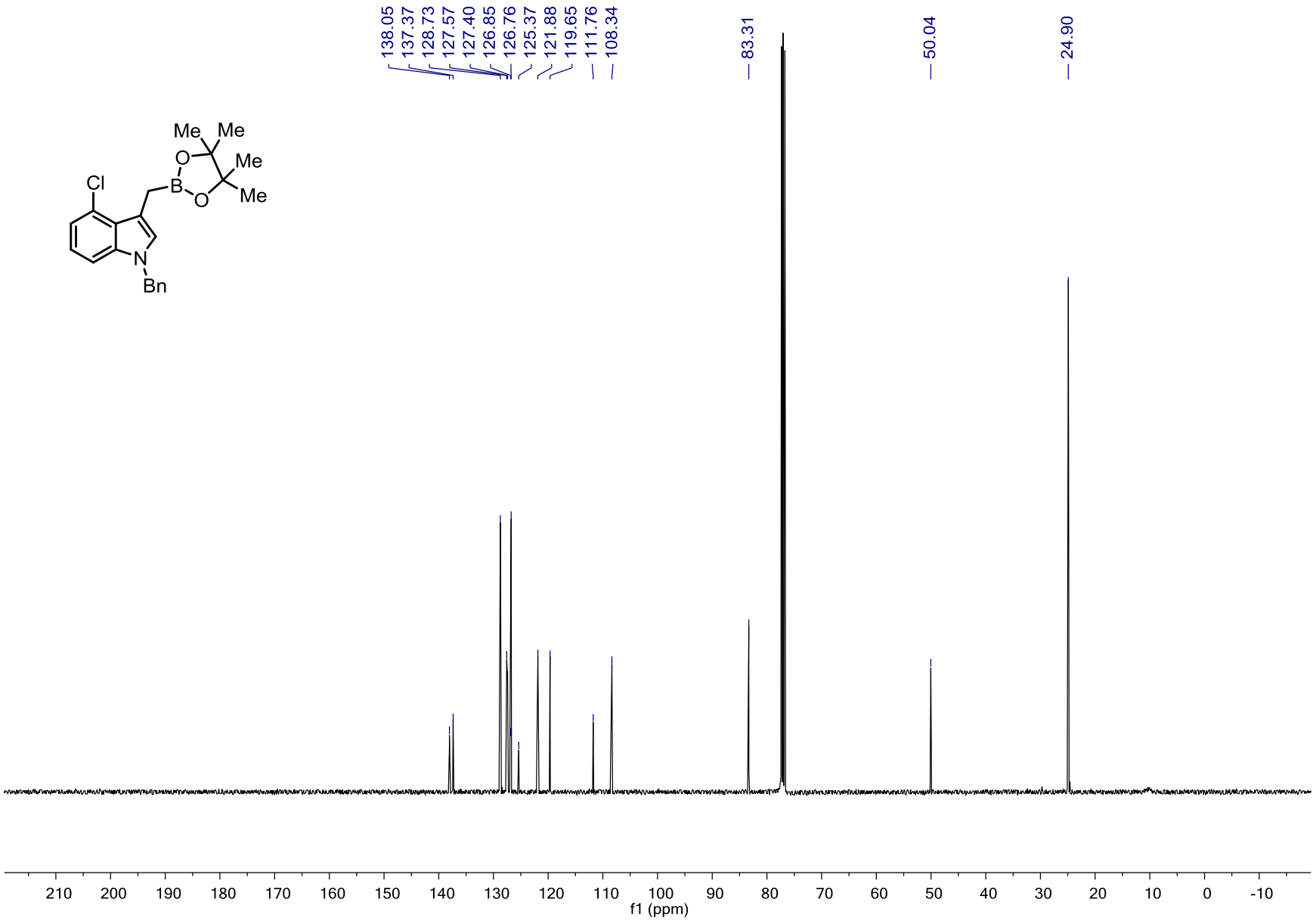
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11j***



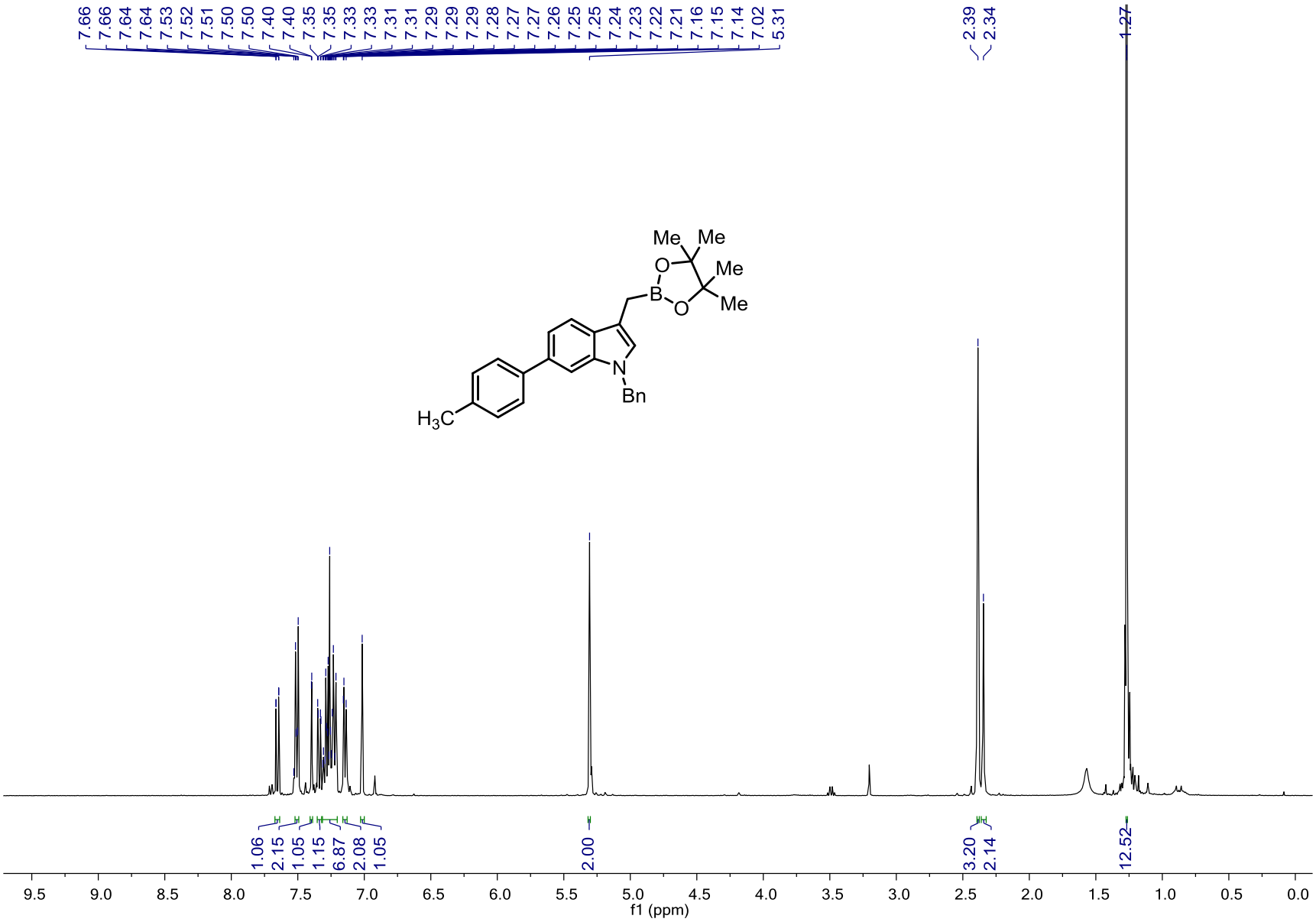
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11k***



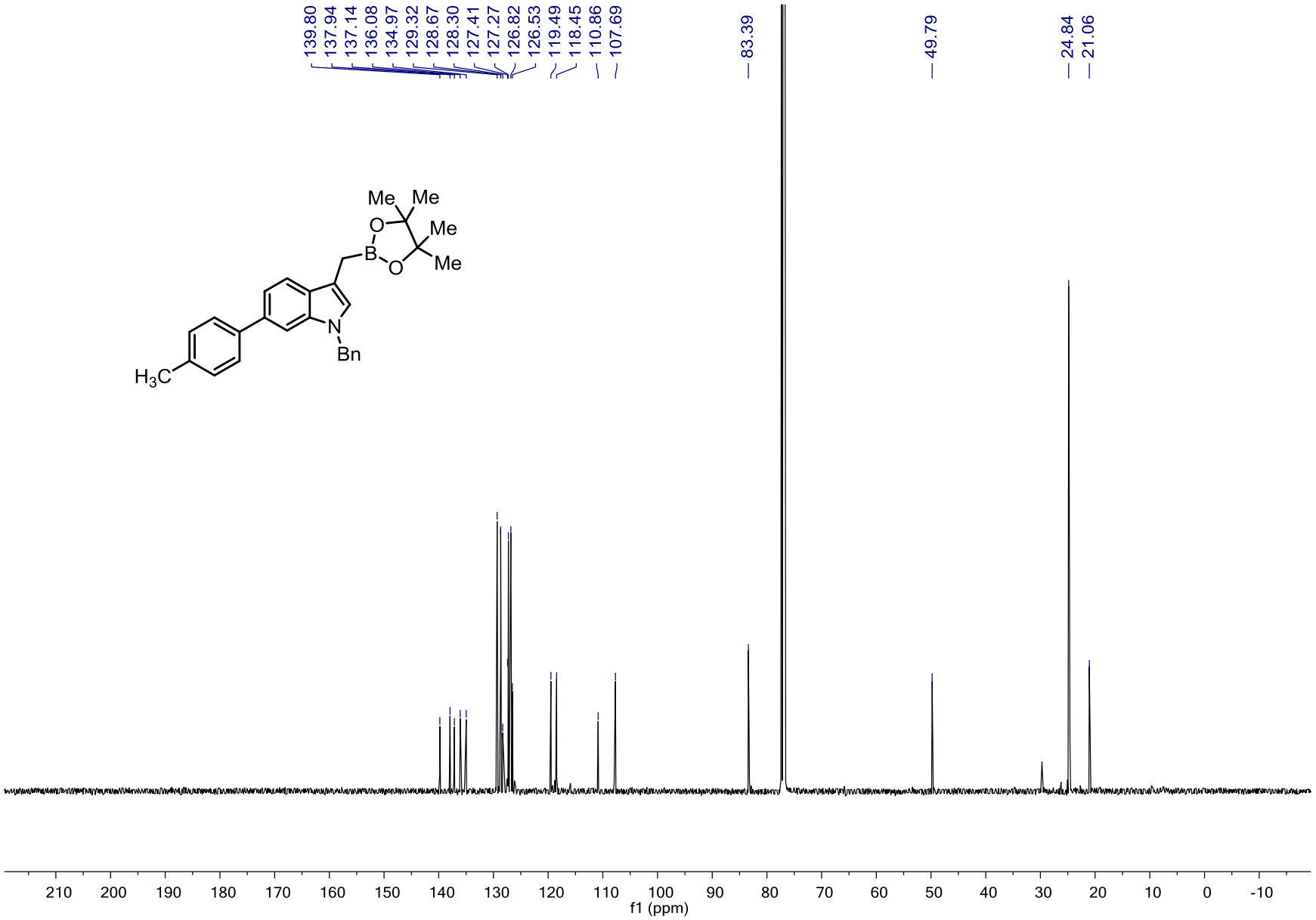
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11k***



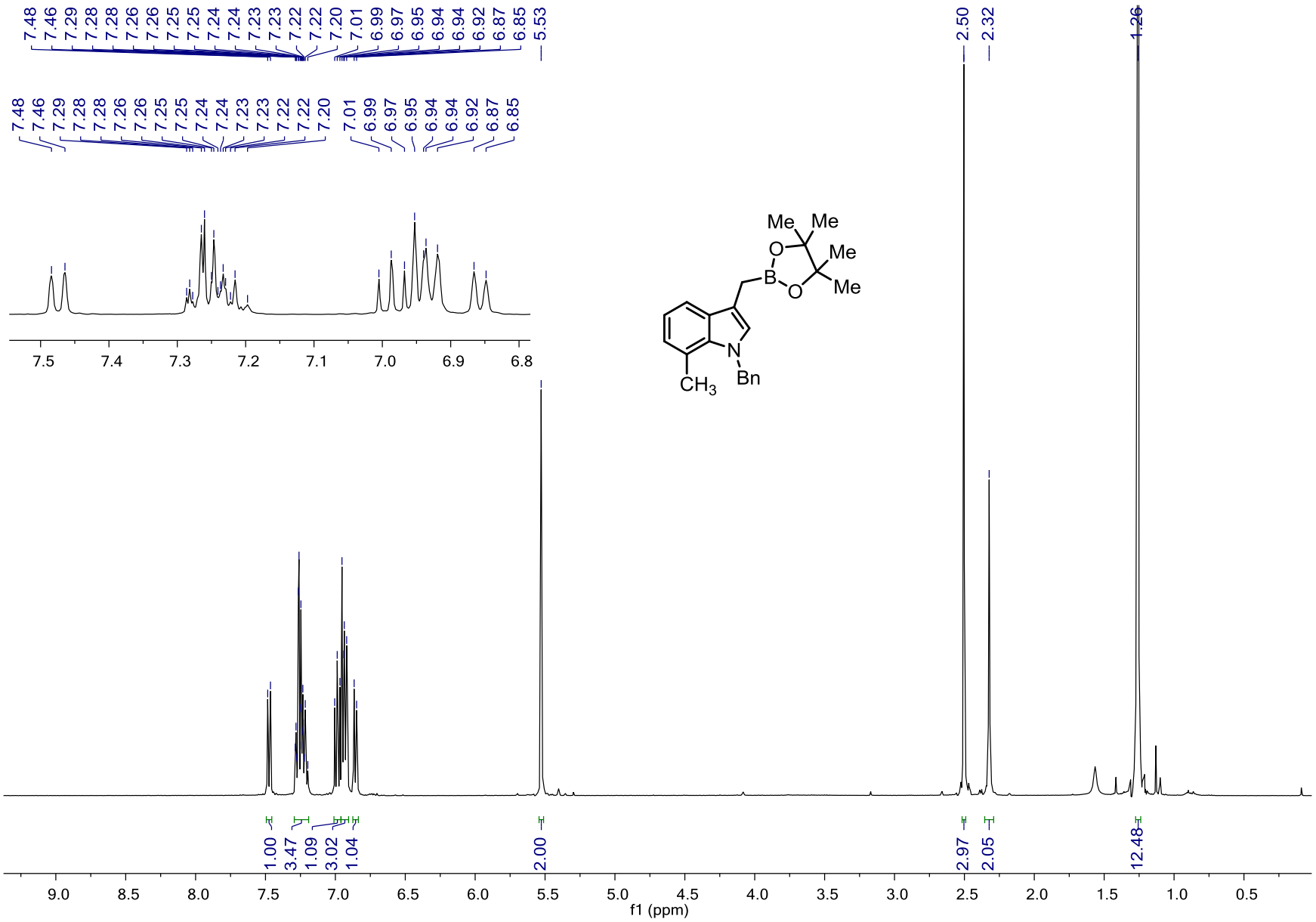
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11l***



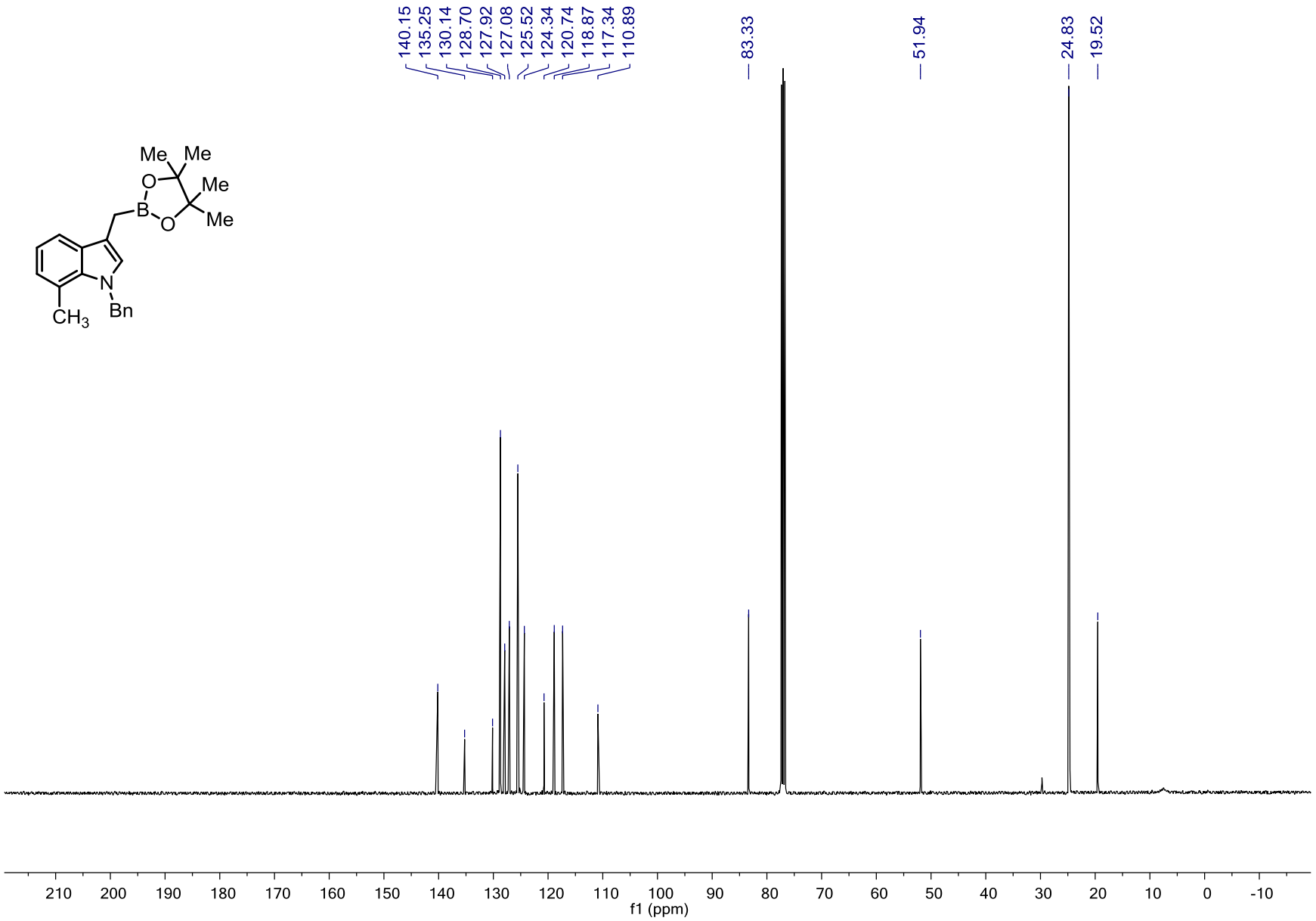
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11l***



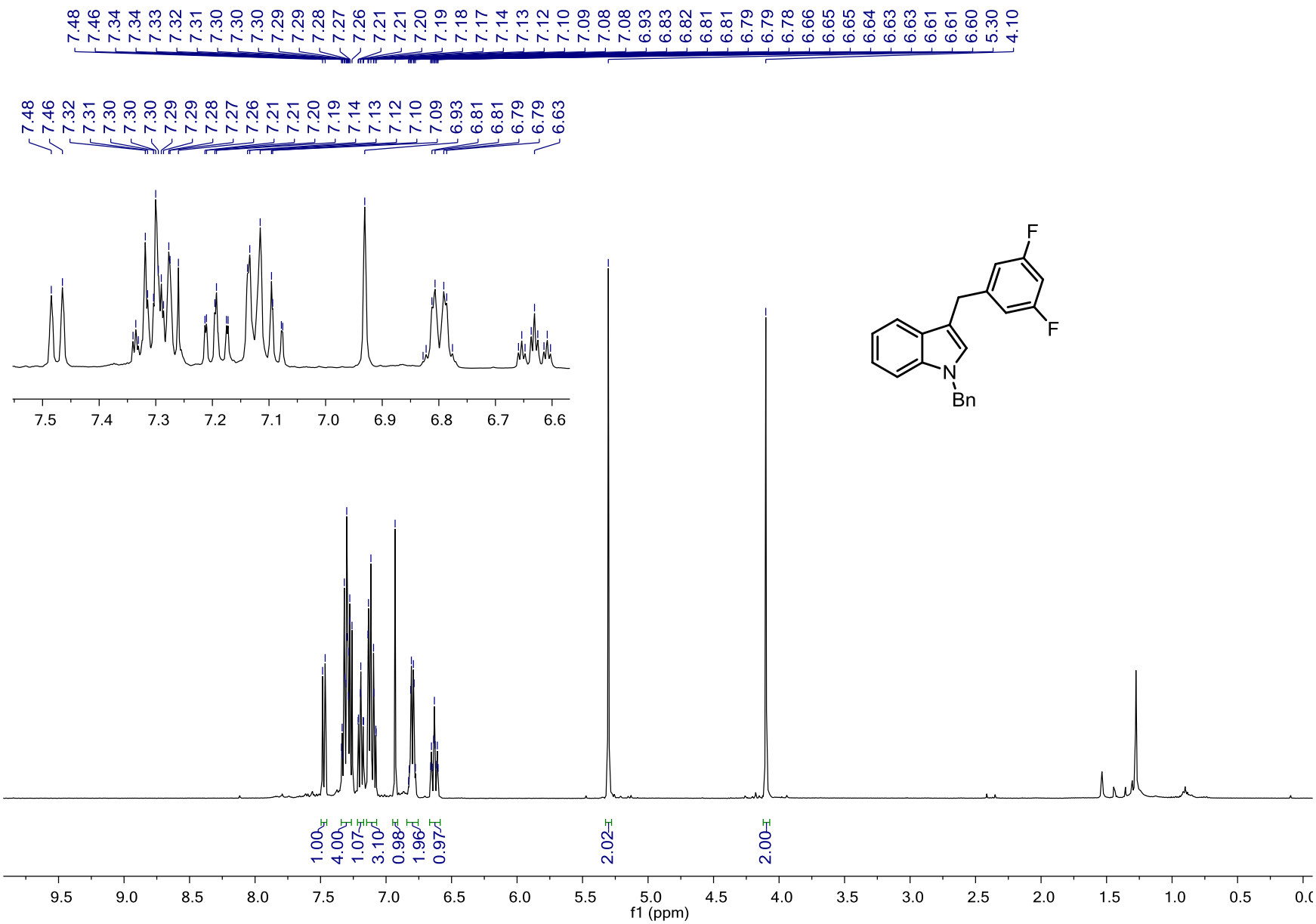
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11m***



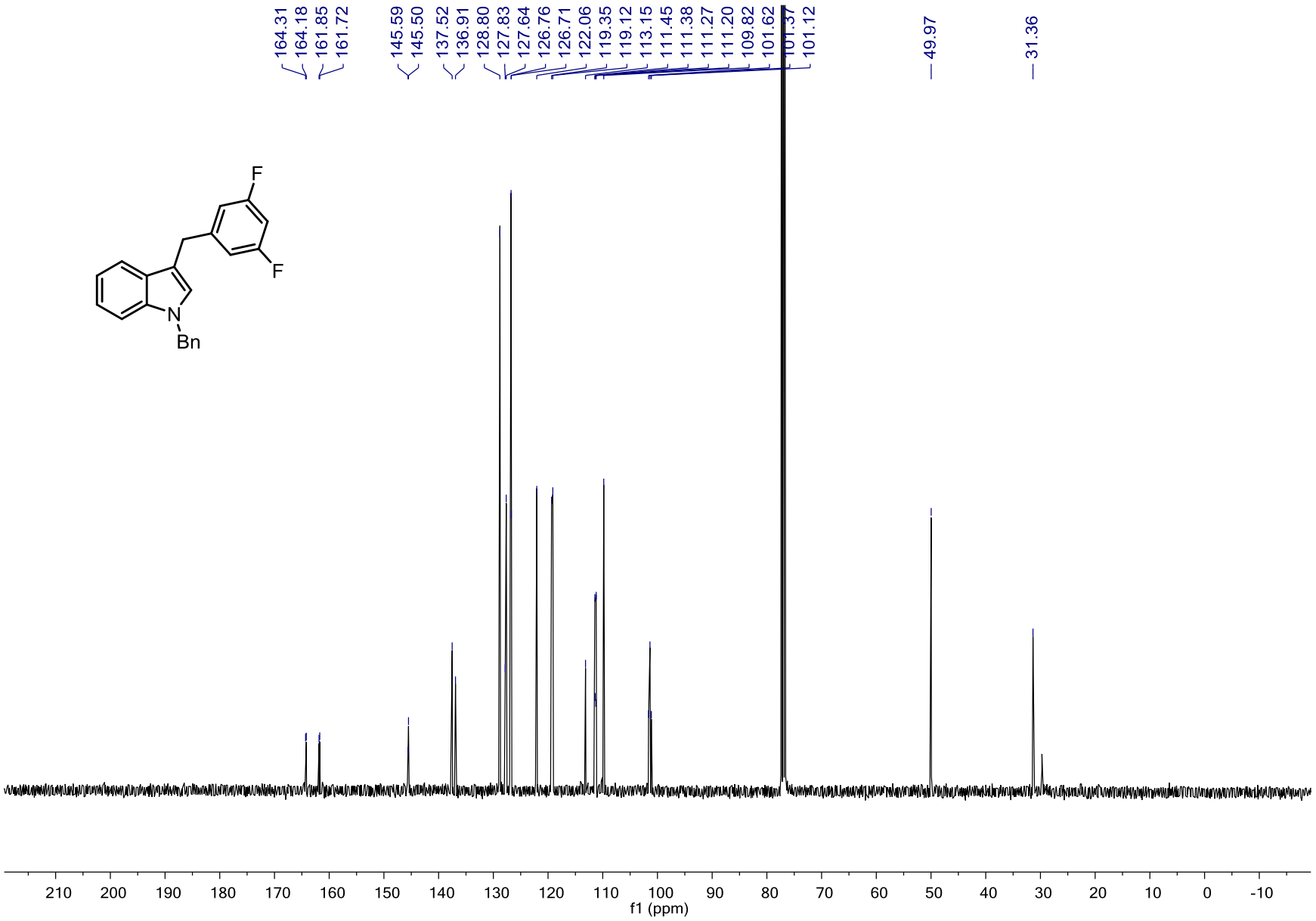
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11m***



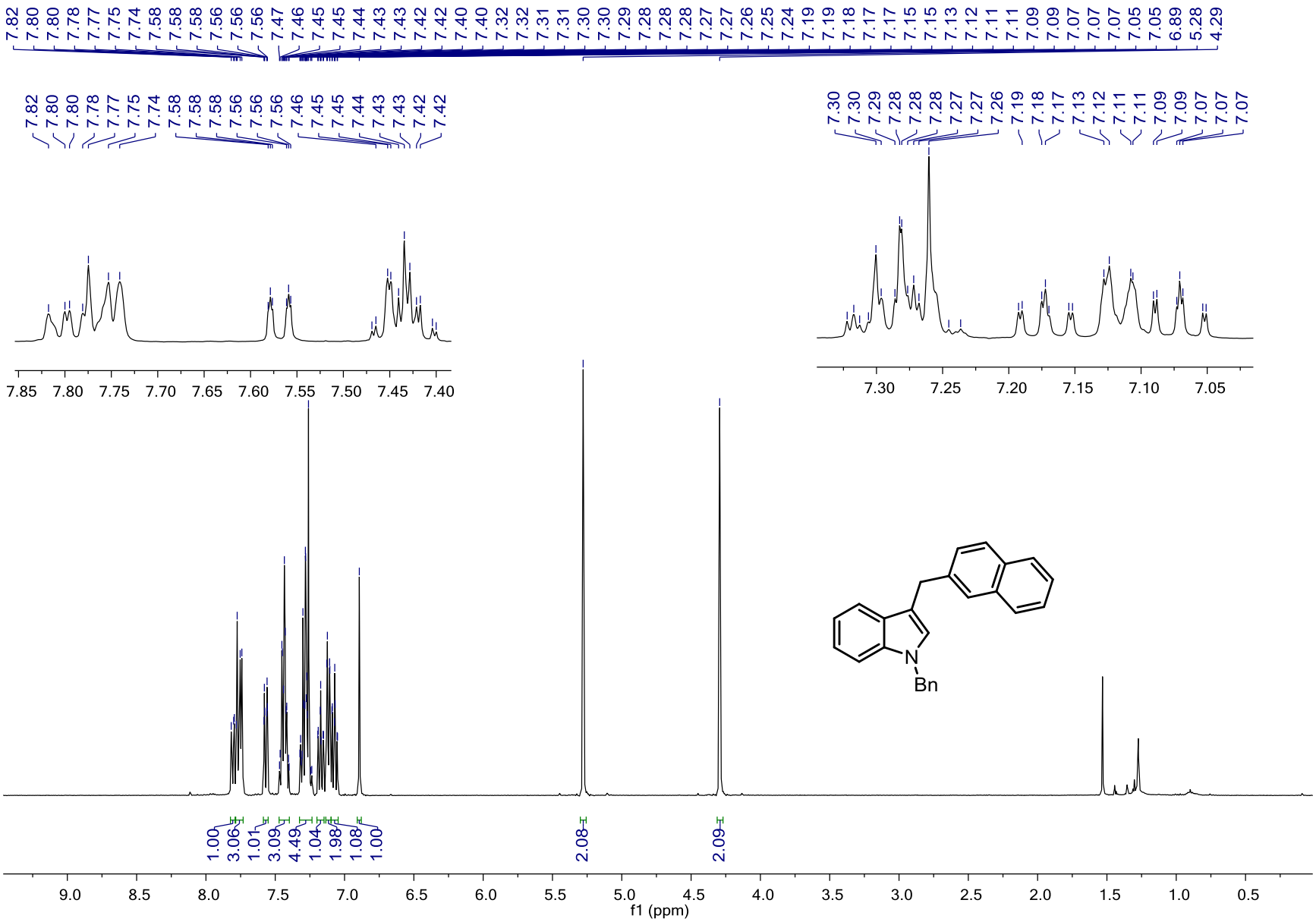
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11n***



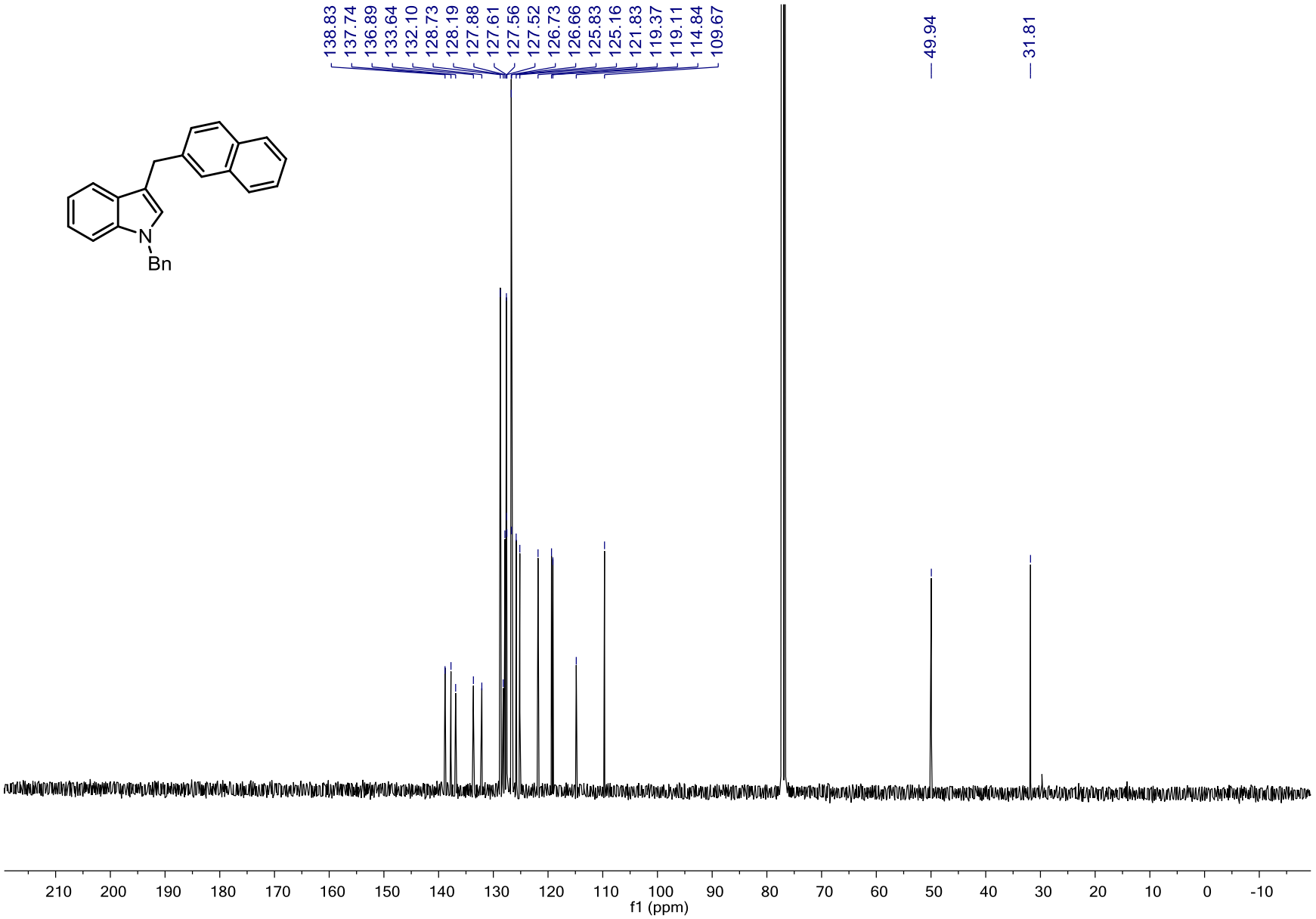
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11n***



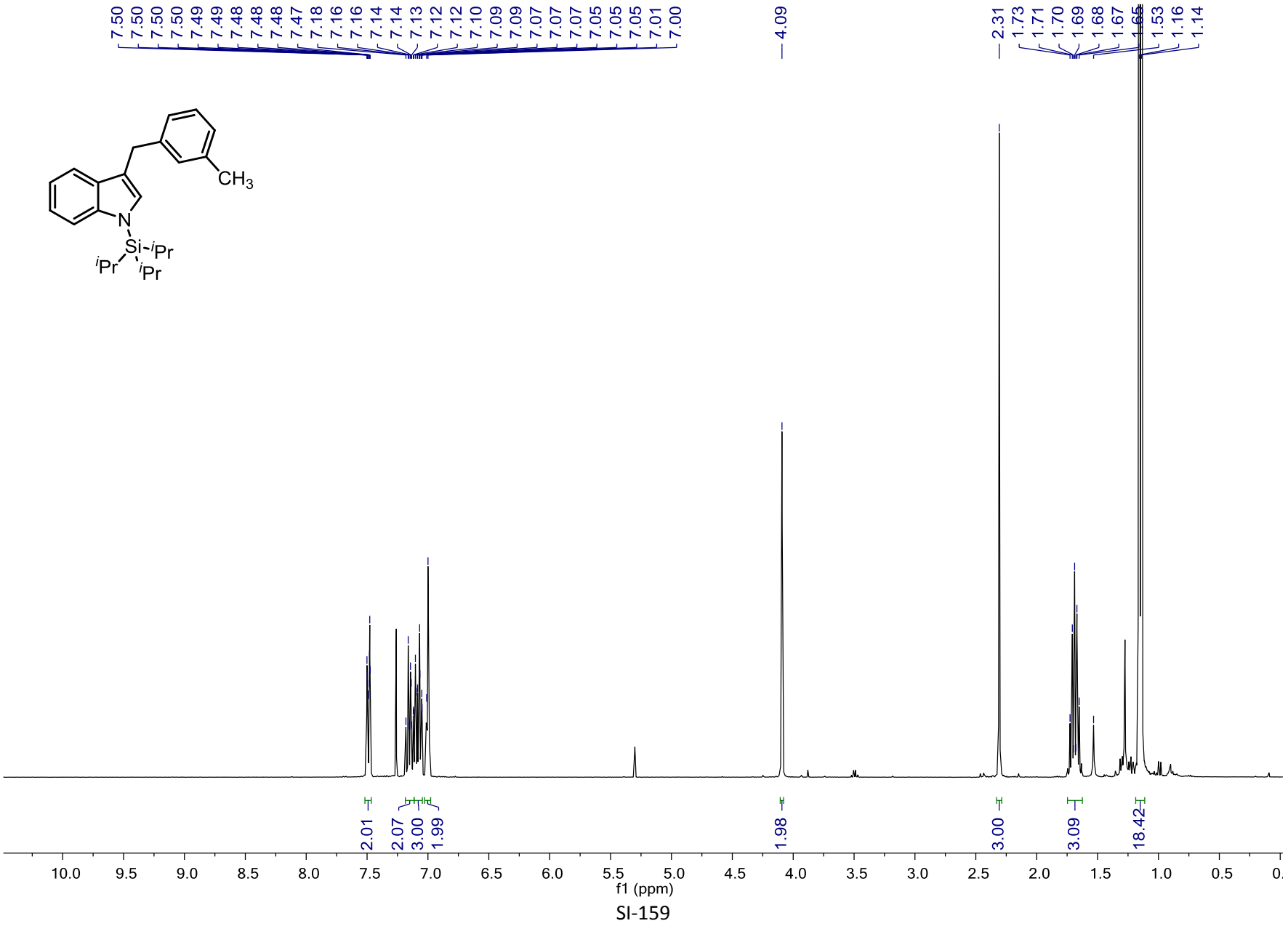
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11o***



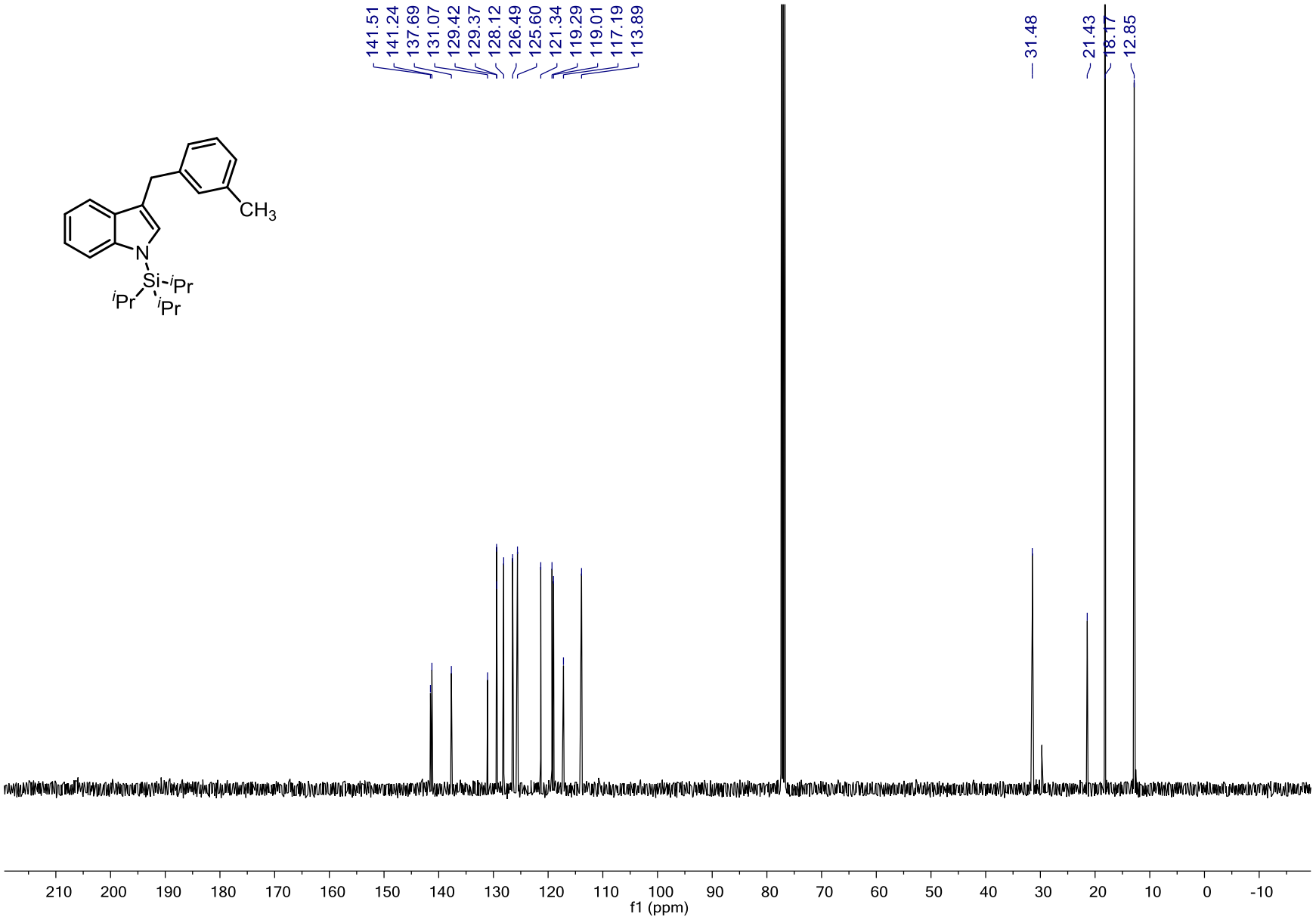
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11o***



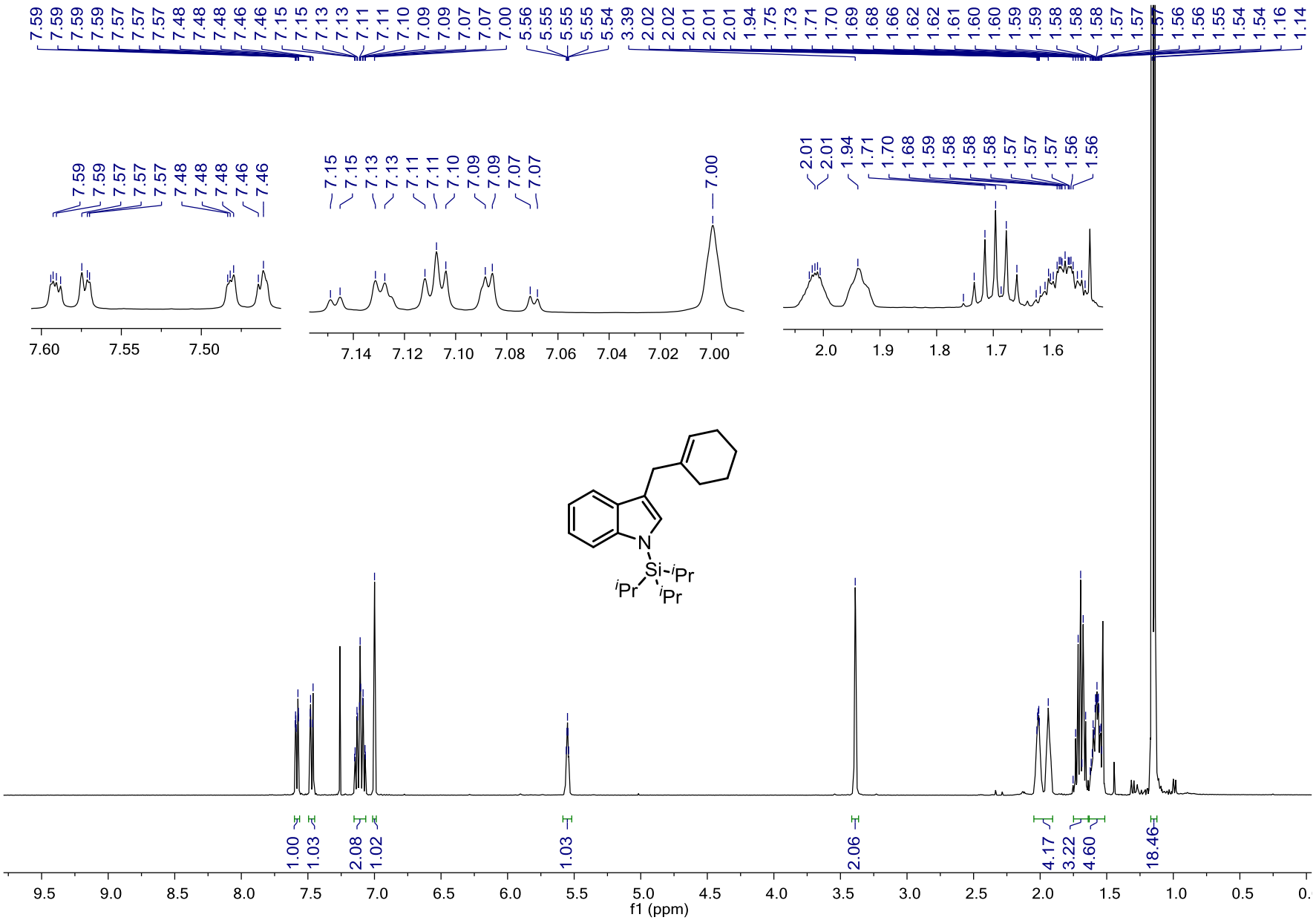
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11p***



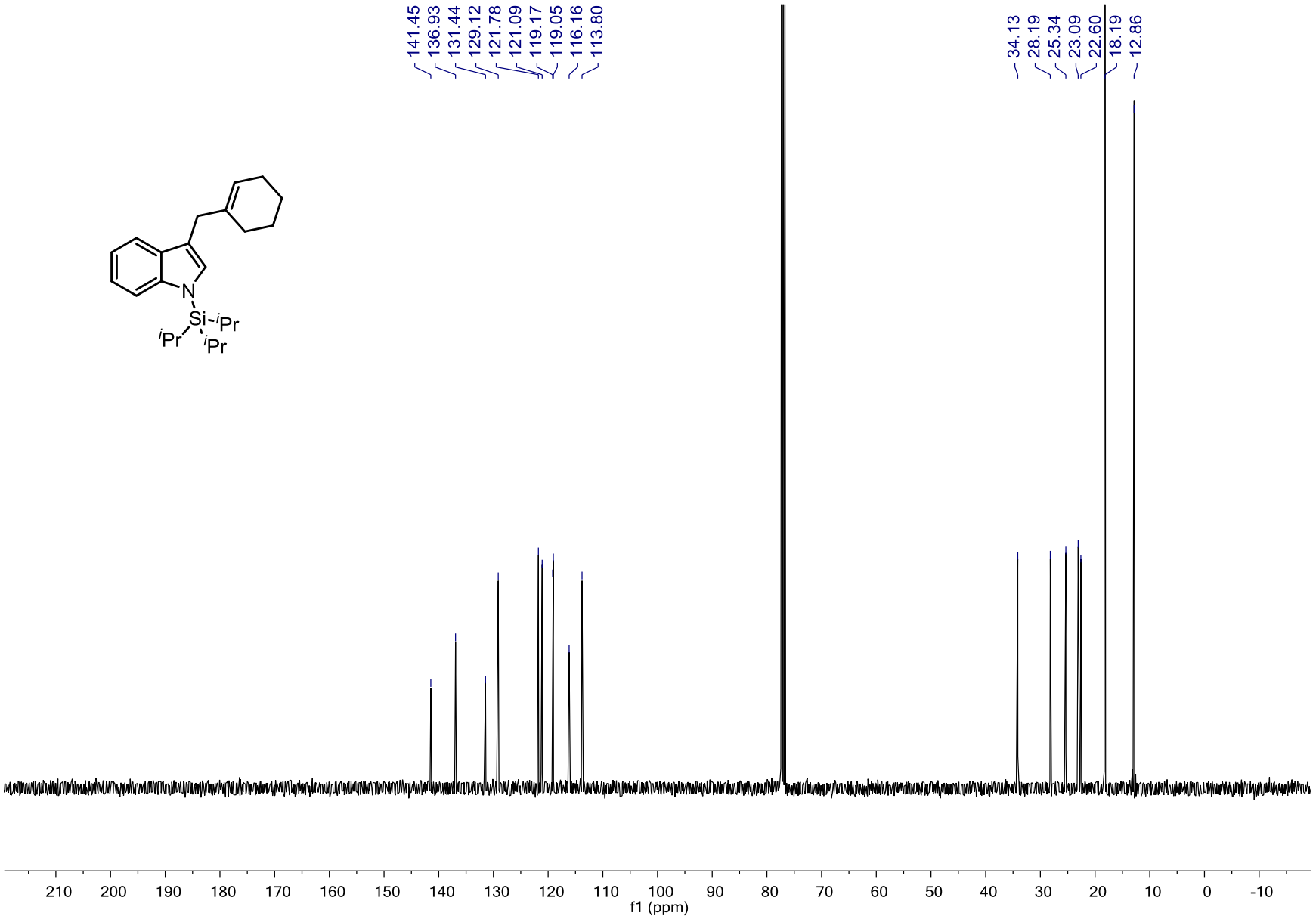
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11p***



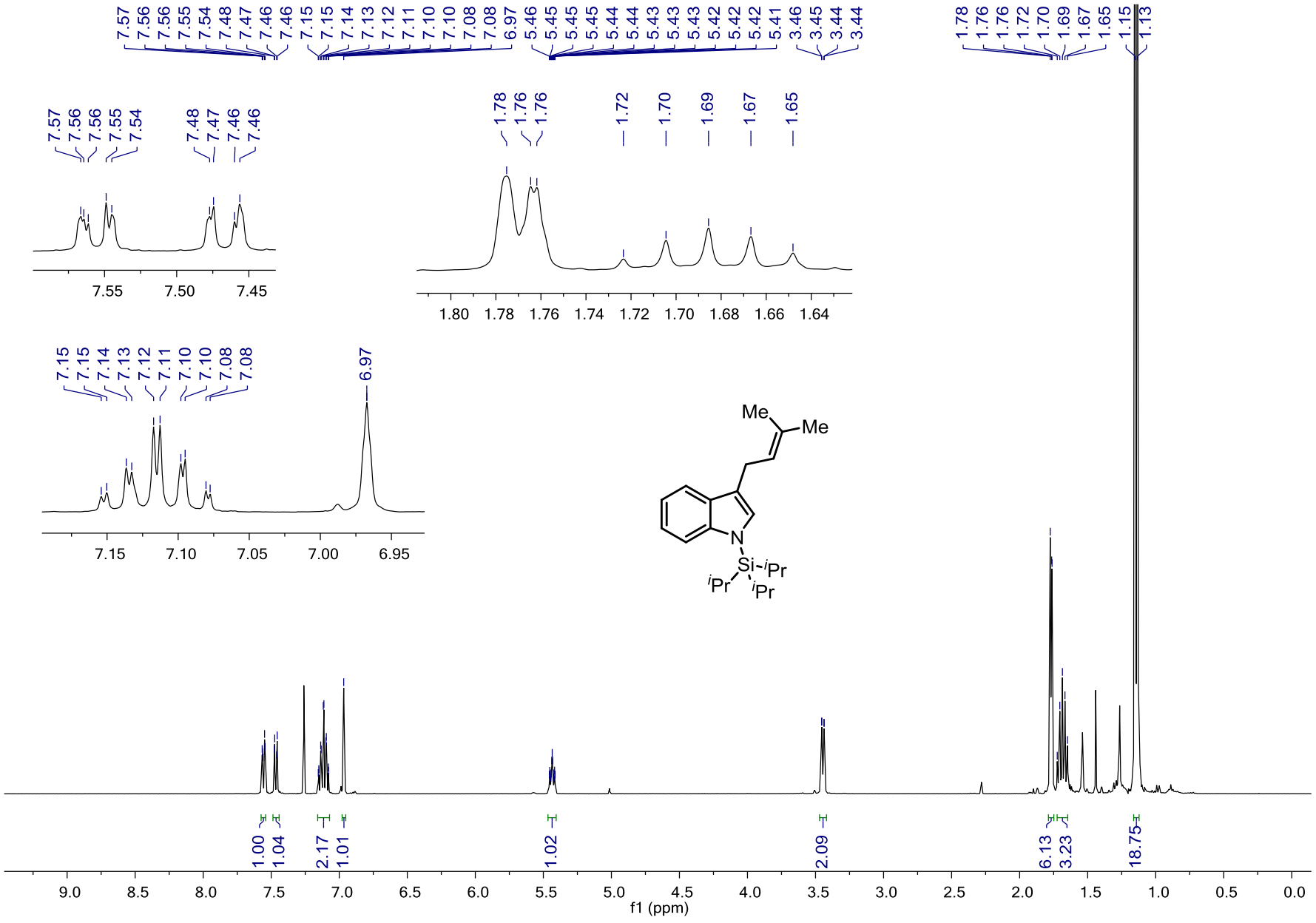
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11q***



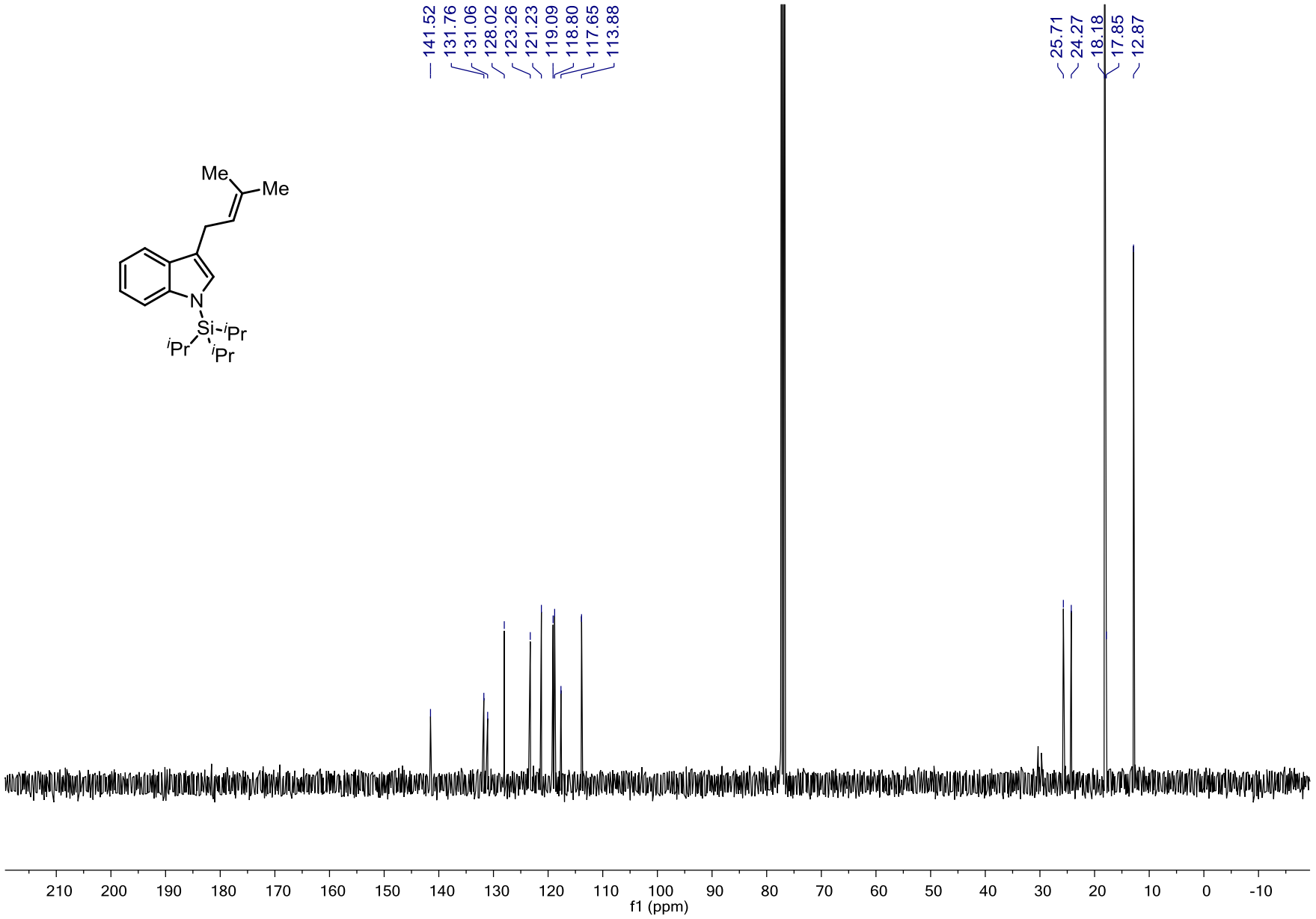
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11q***



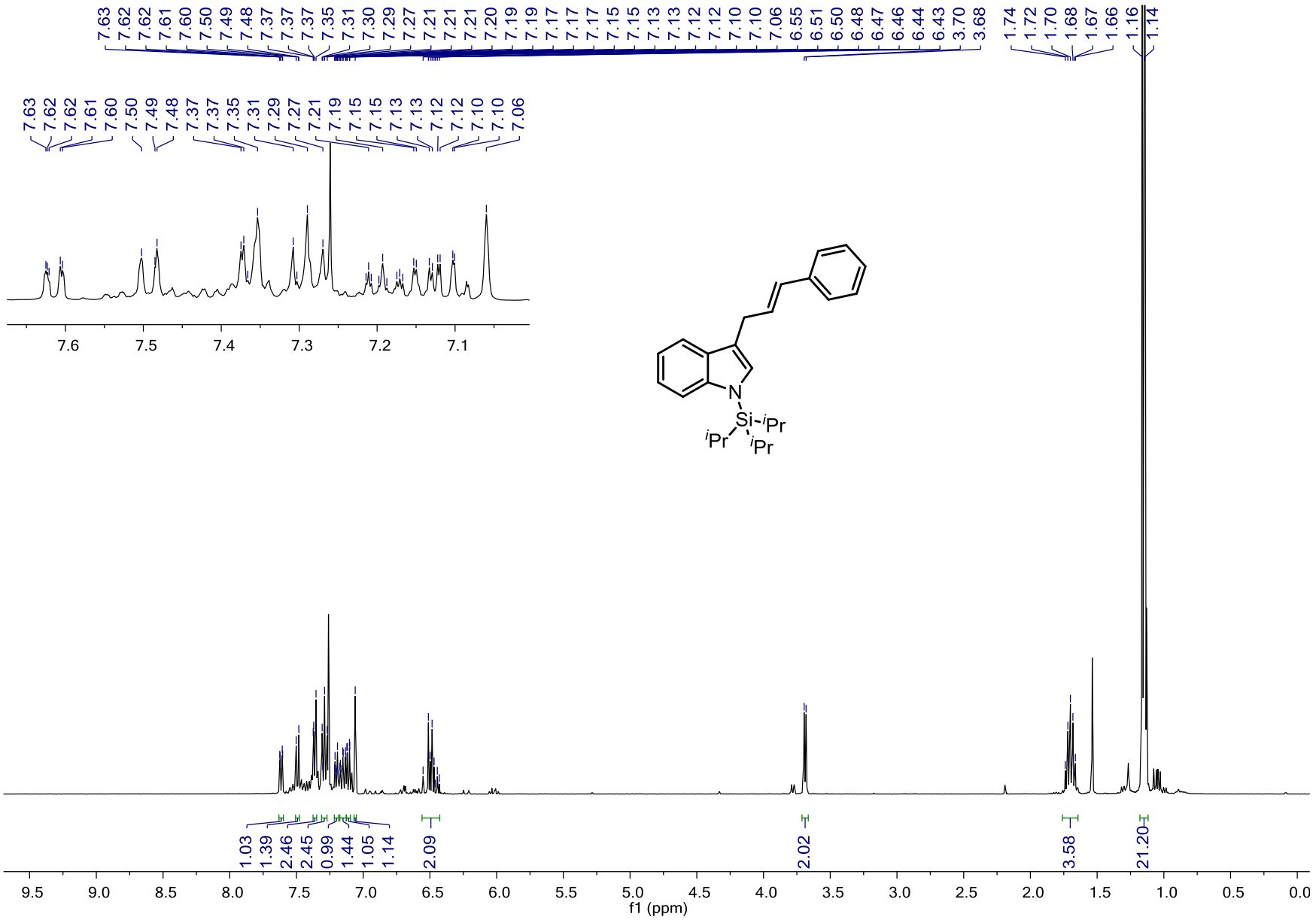
*[1]H-NMR (400 MHz, $CDCl_3$) for compound **11r***



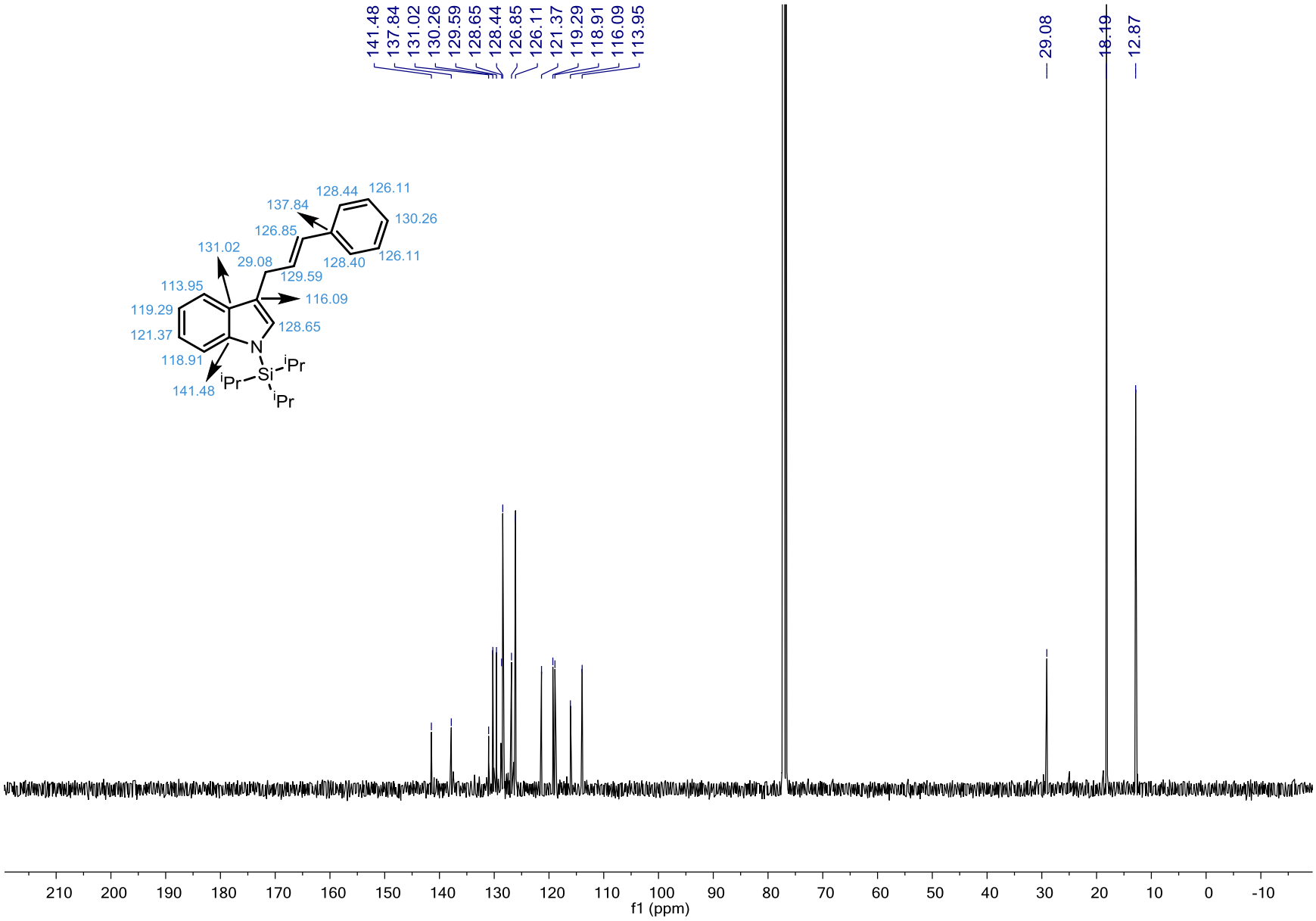
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11r***



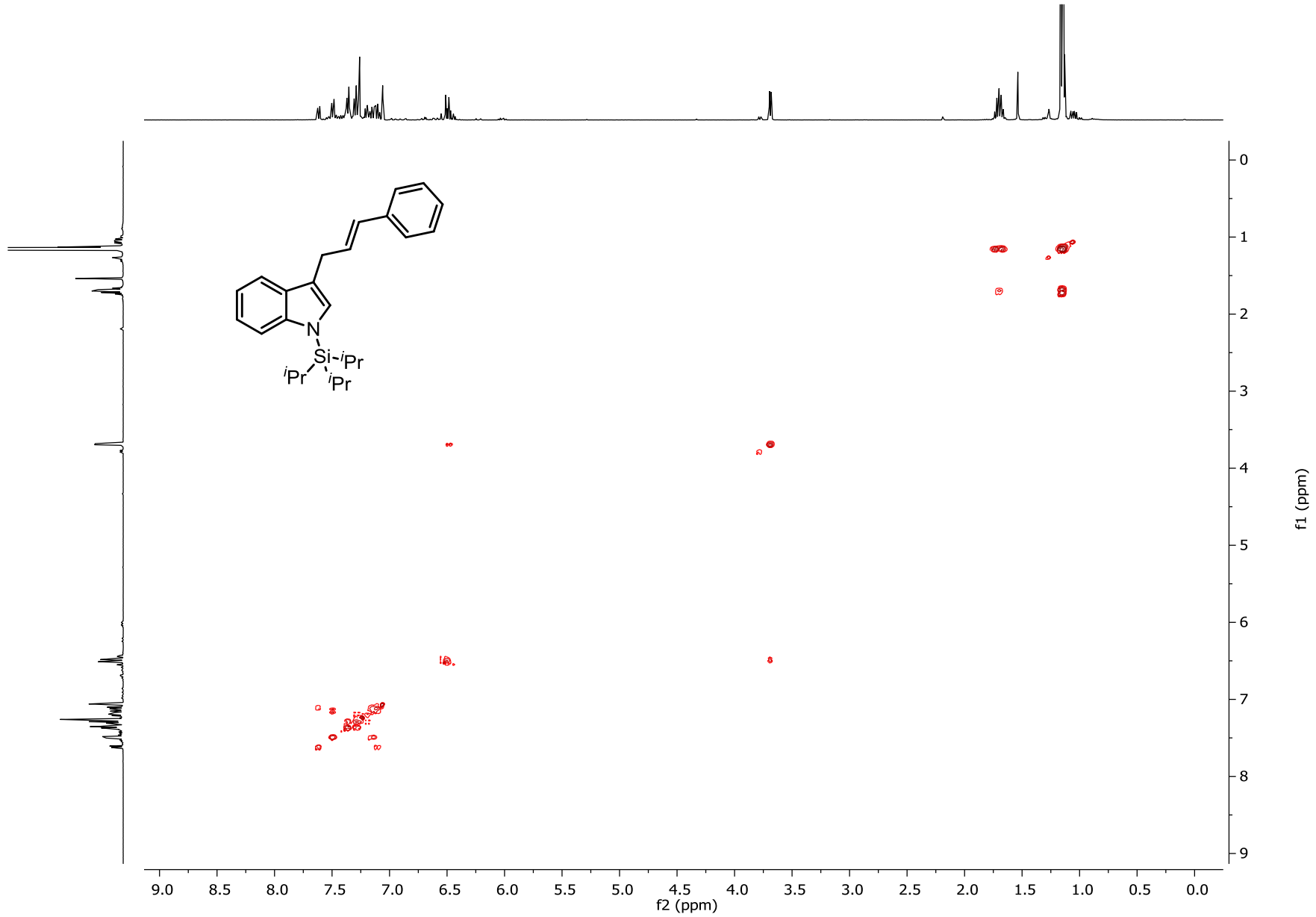
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11s***



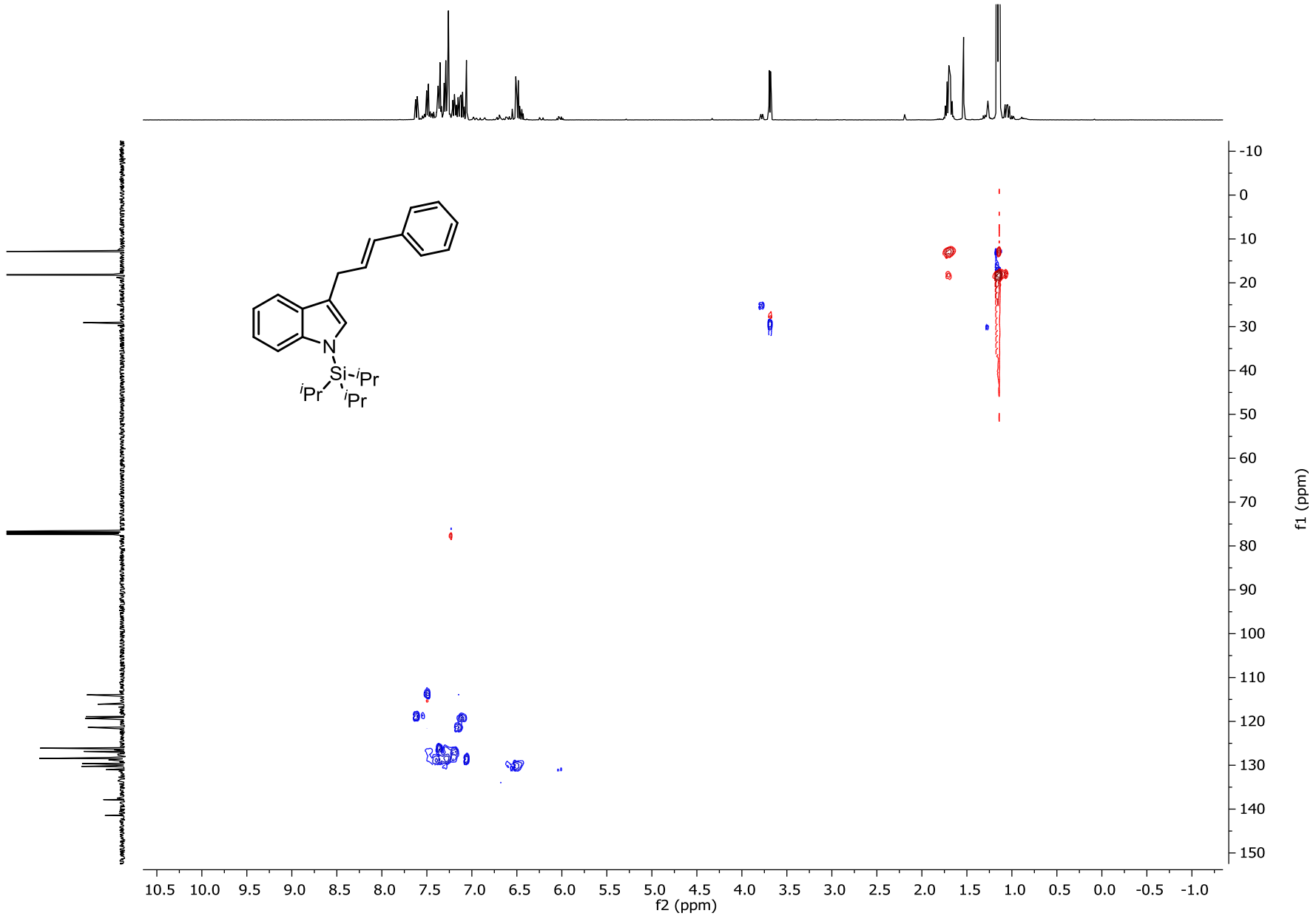
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11s***



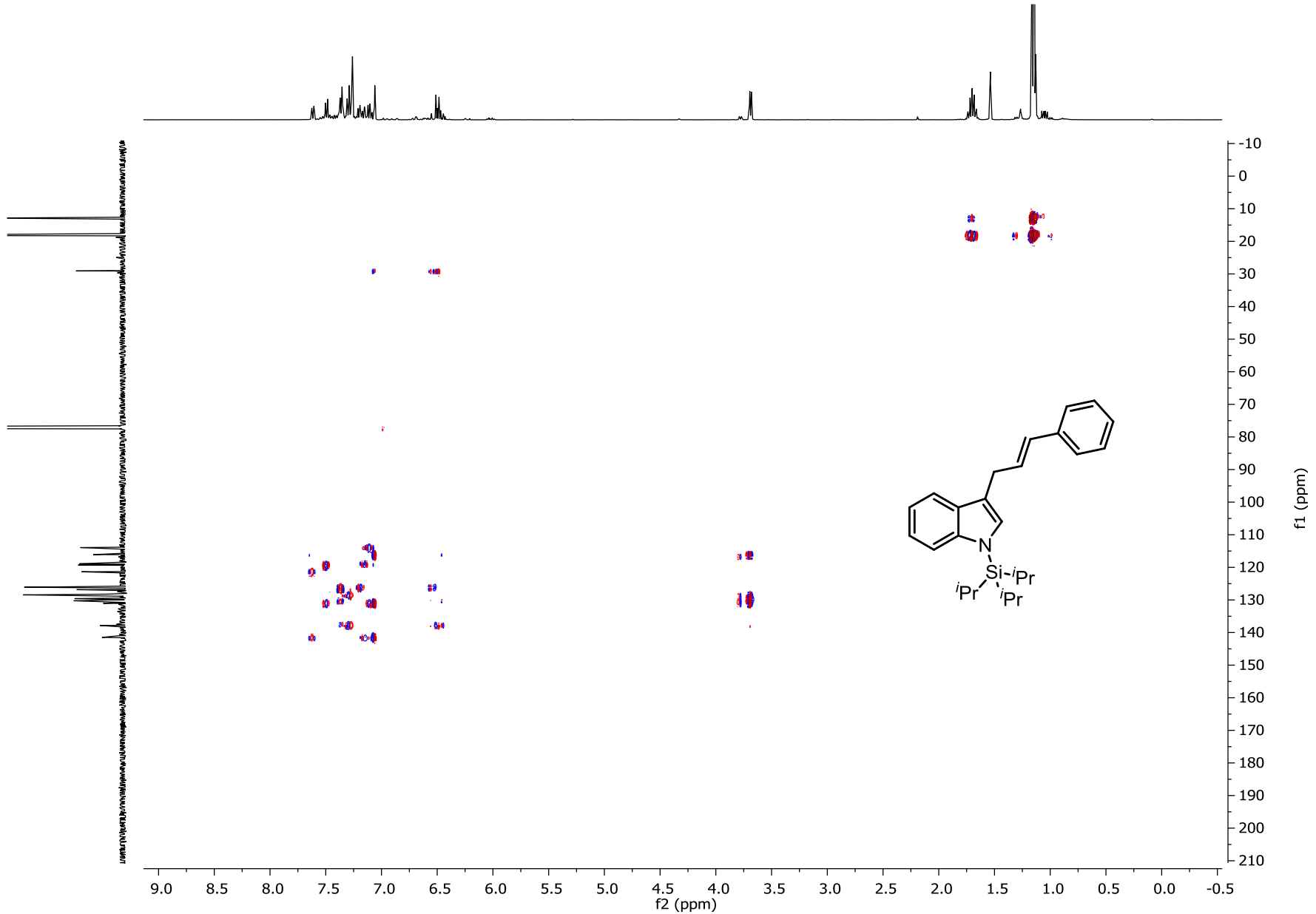
*COSY NMR (400 MHz, $CDCl_3$) for compound **11s***



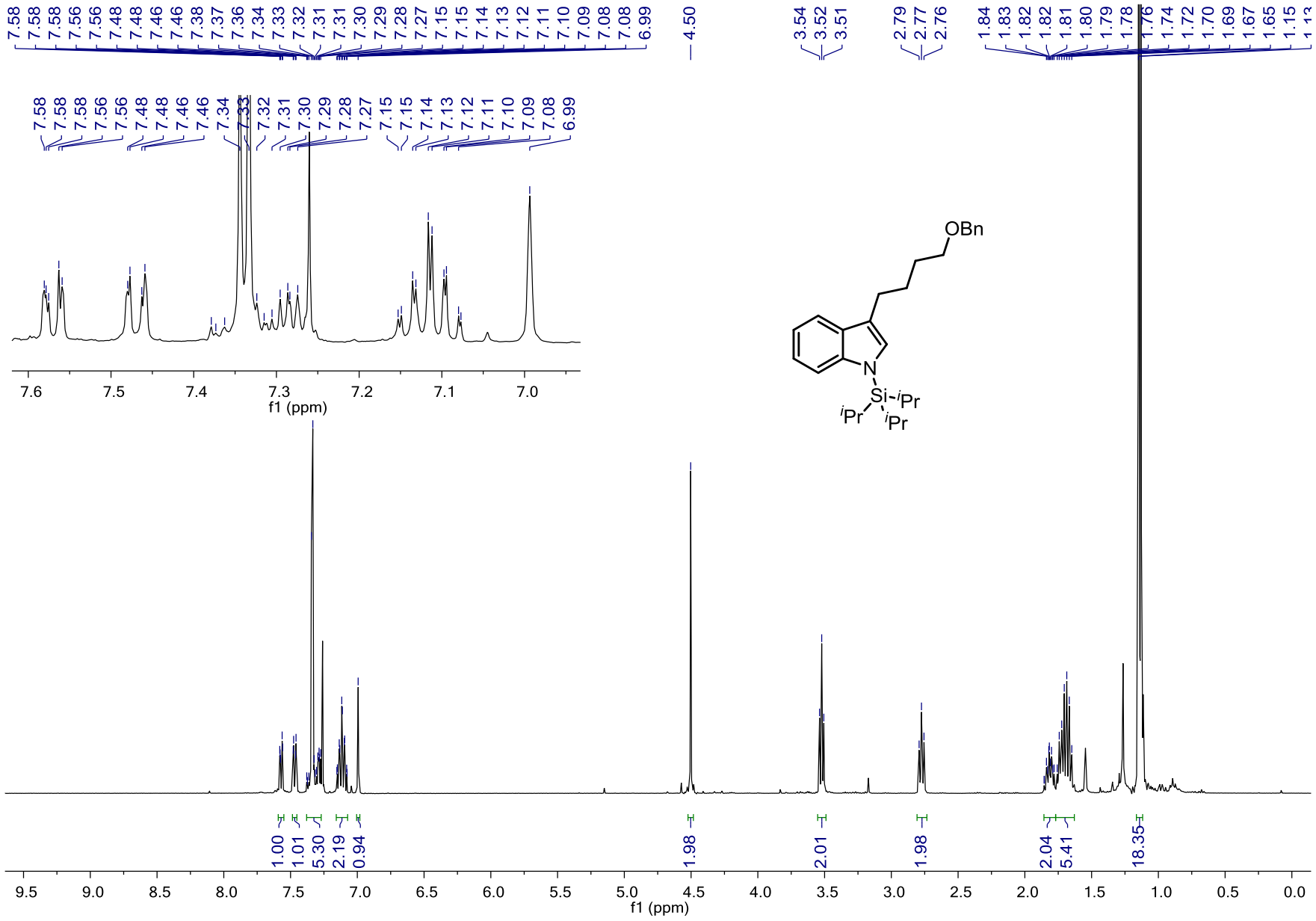
*HSQC NMR (400 MHz, $CDCl_3$) for compound **11s***



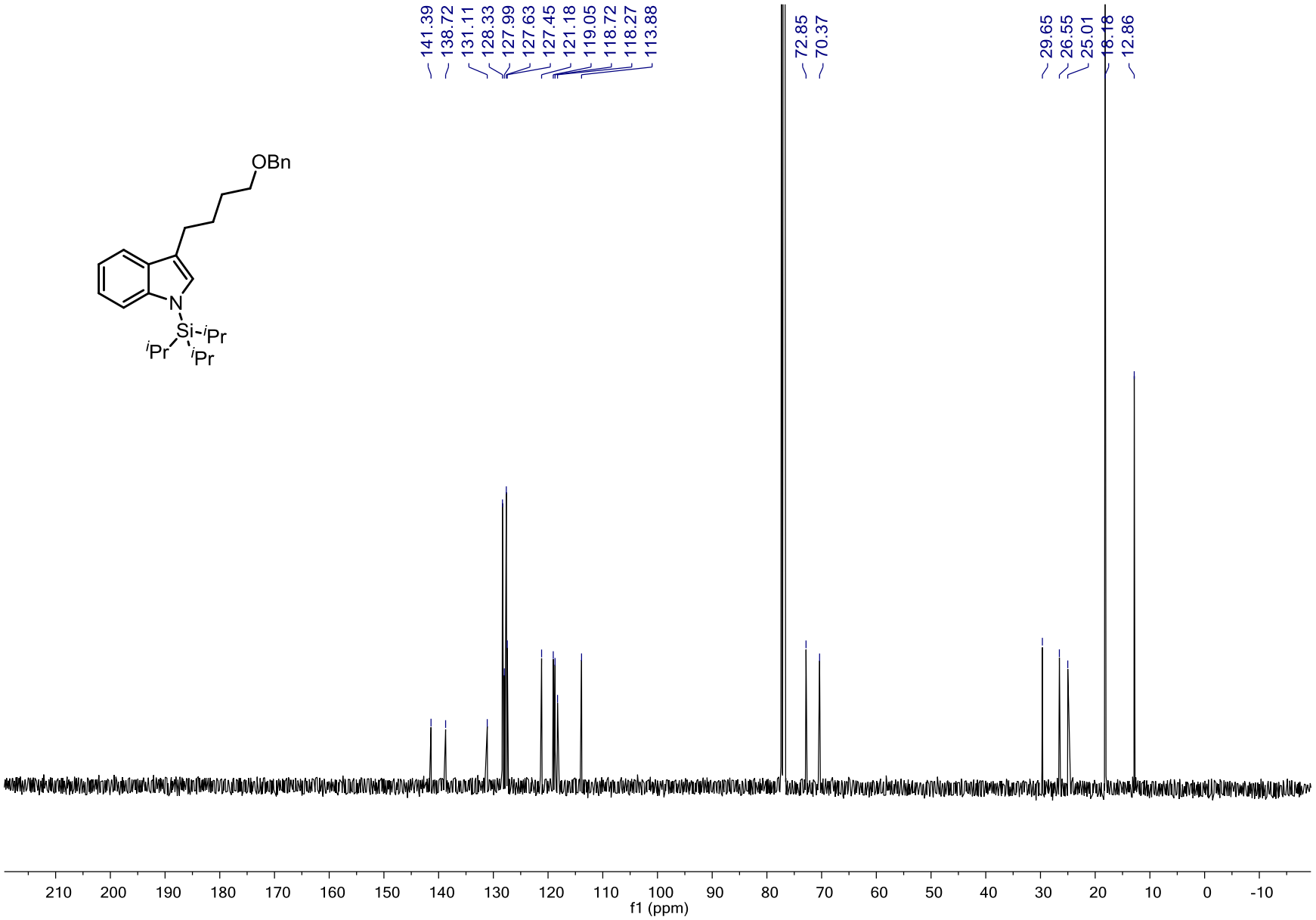
*HMBC NMR (400 MHz, $CDCl_3$) for compound **11s***



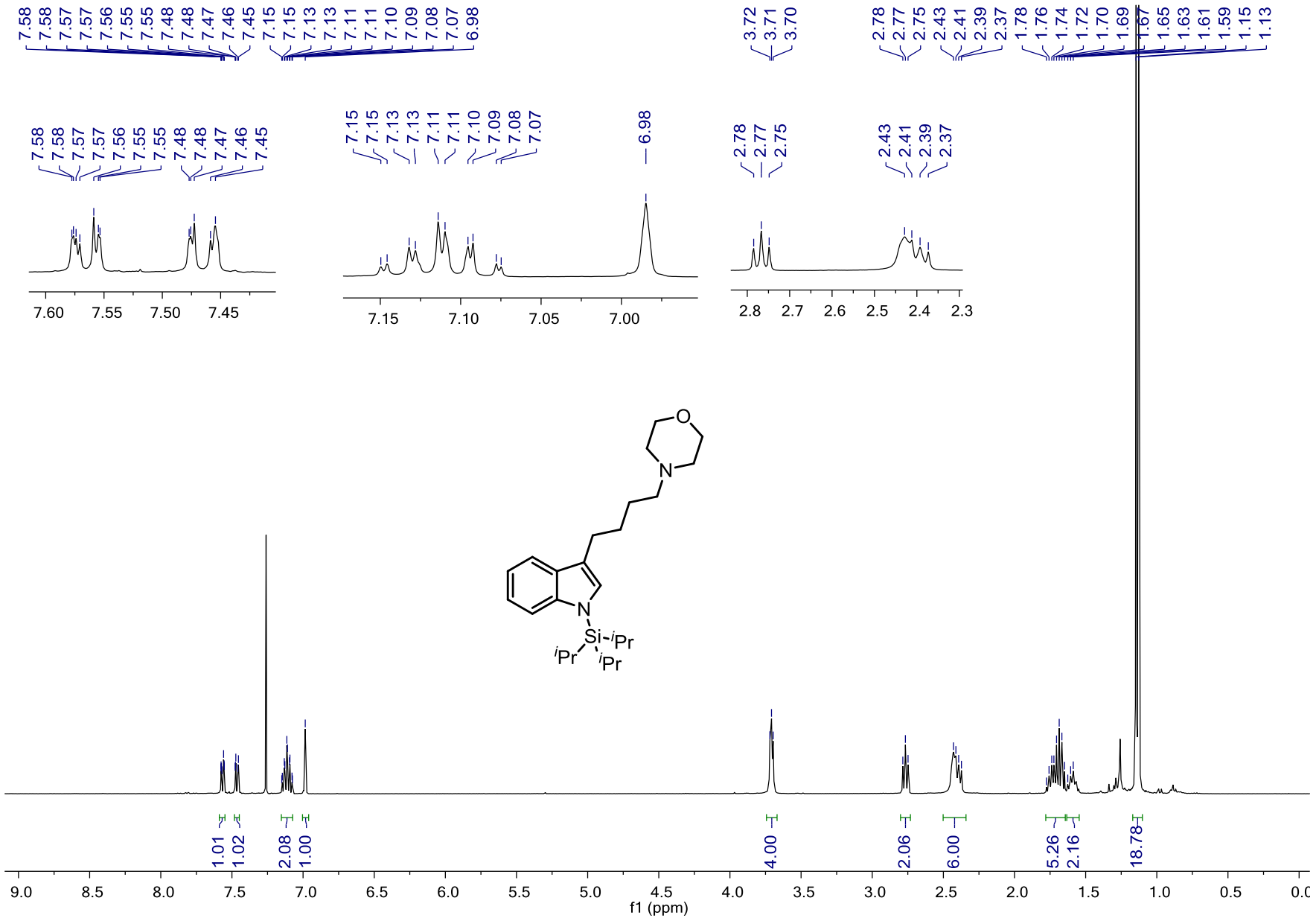
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11t***



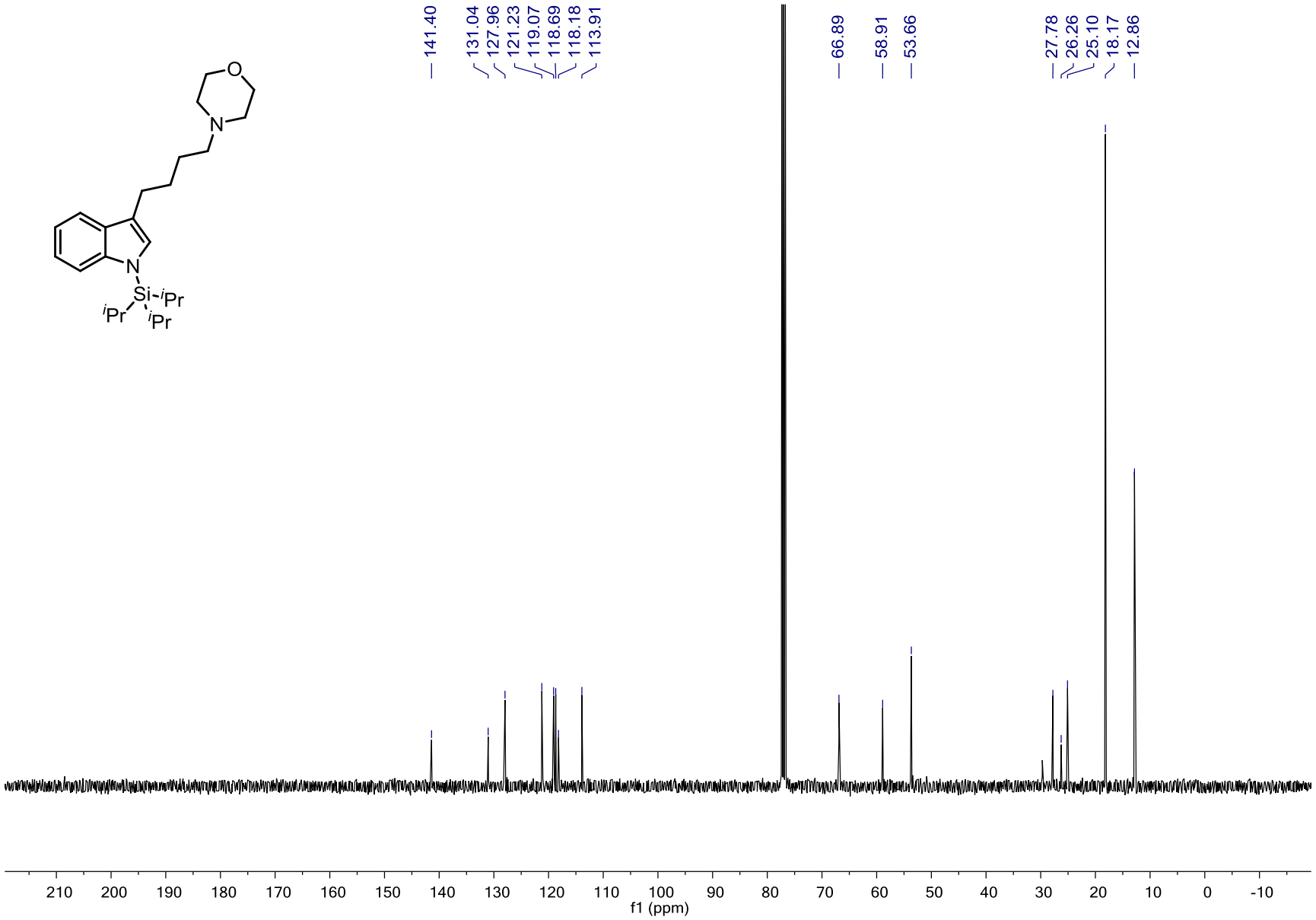
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11t***



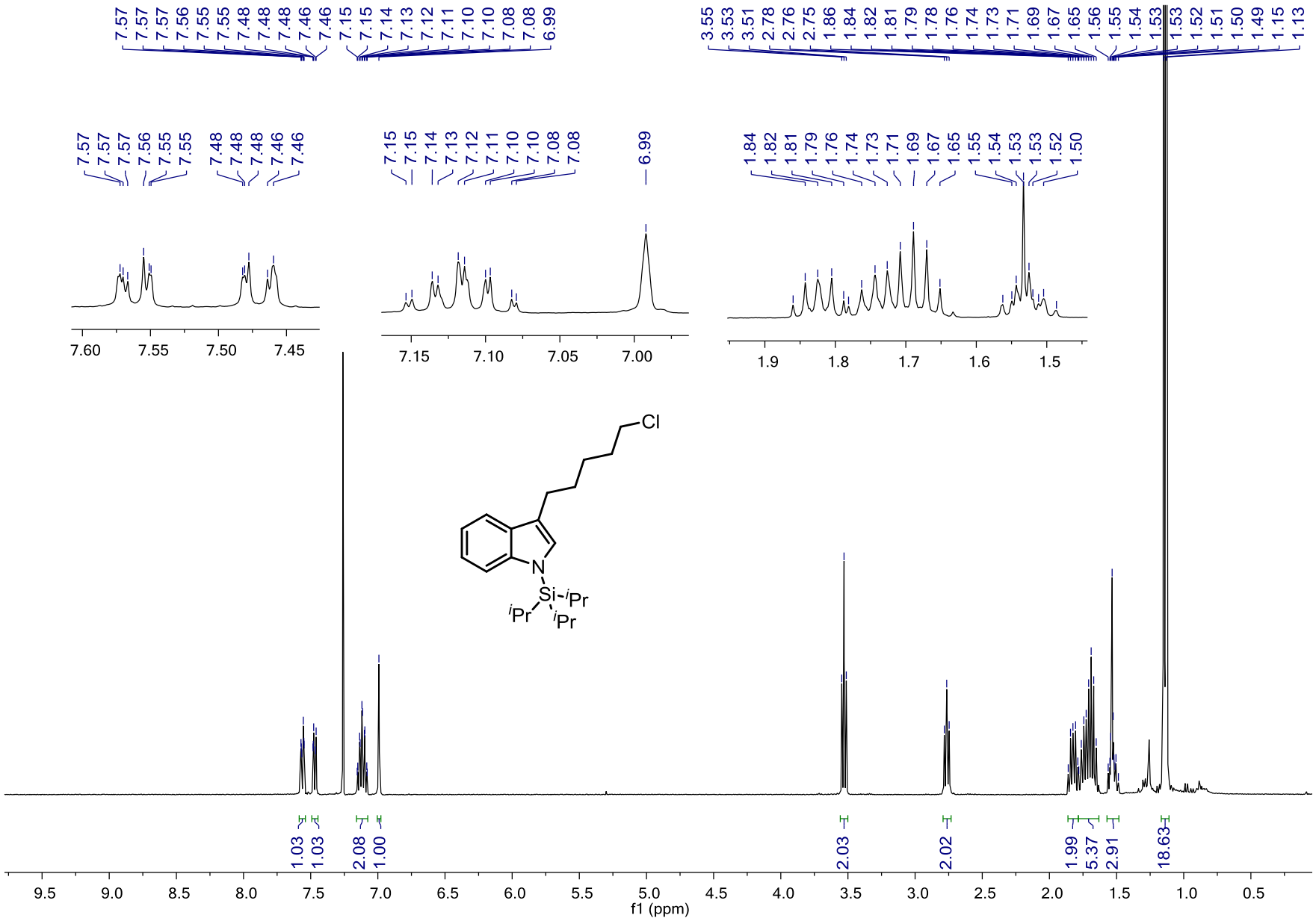
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11u***



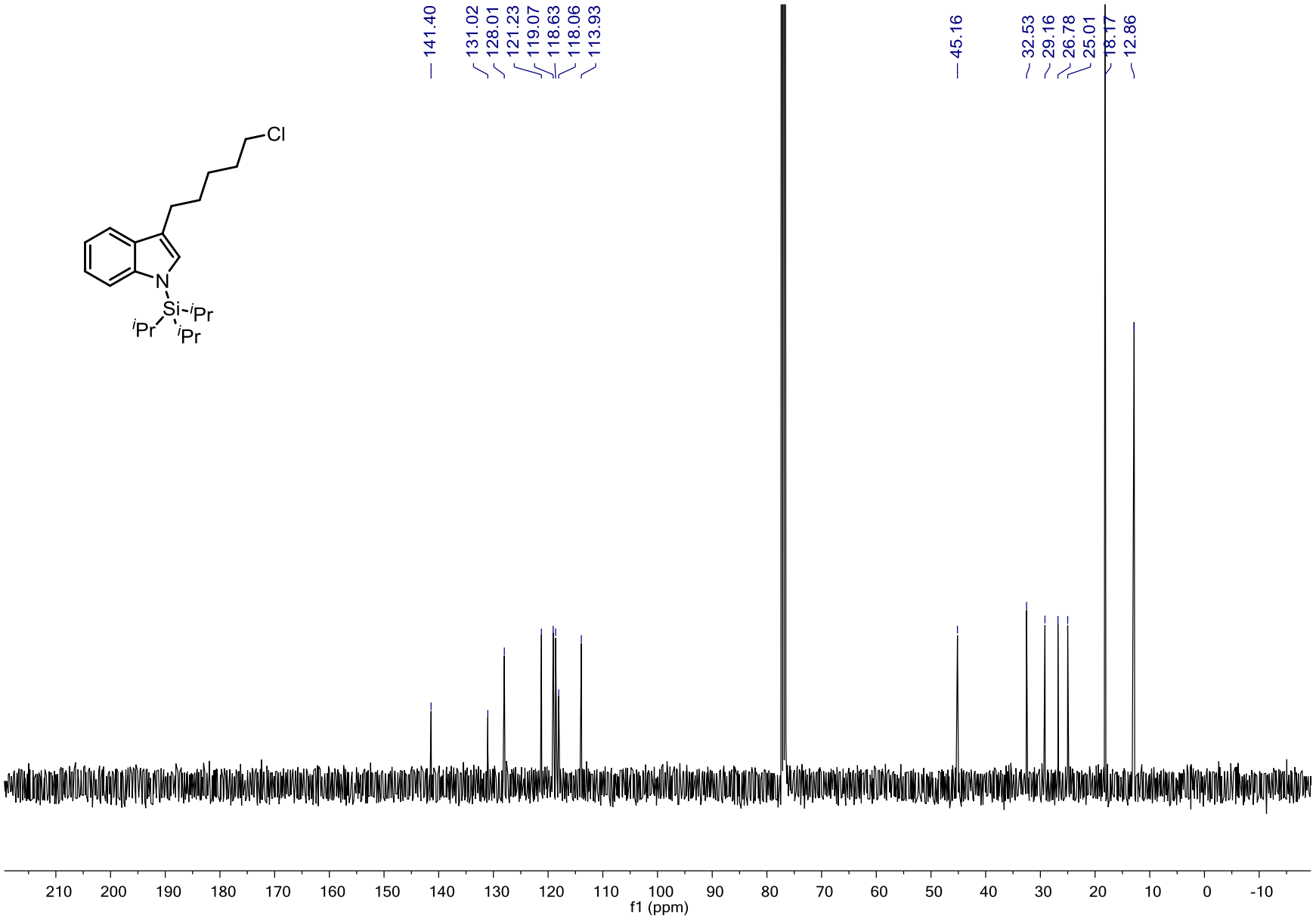
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11u***



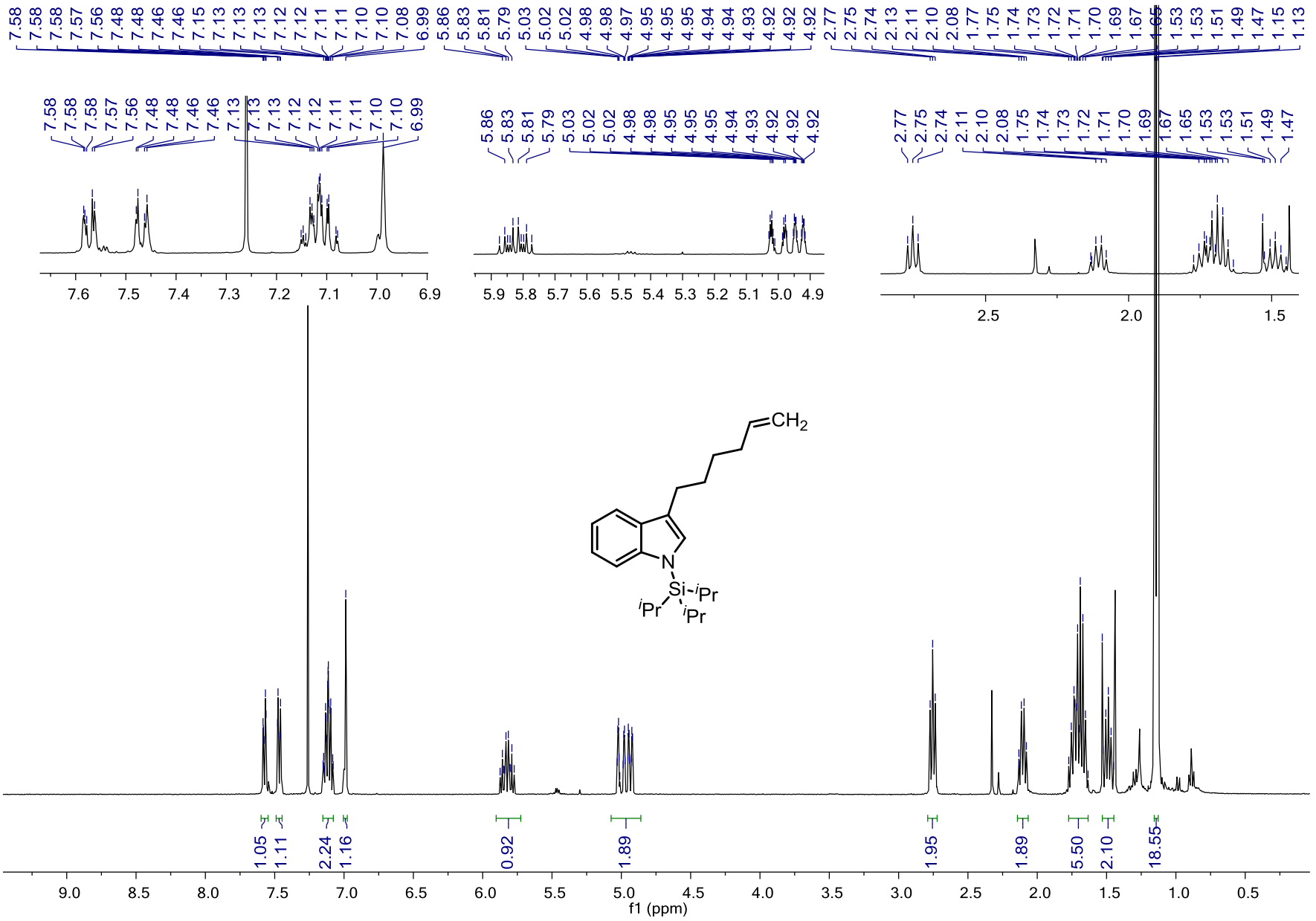
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11v***



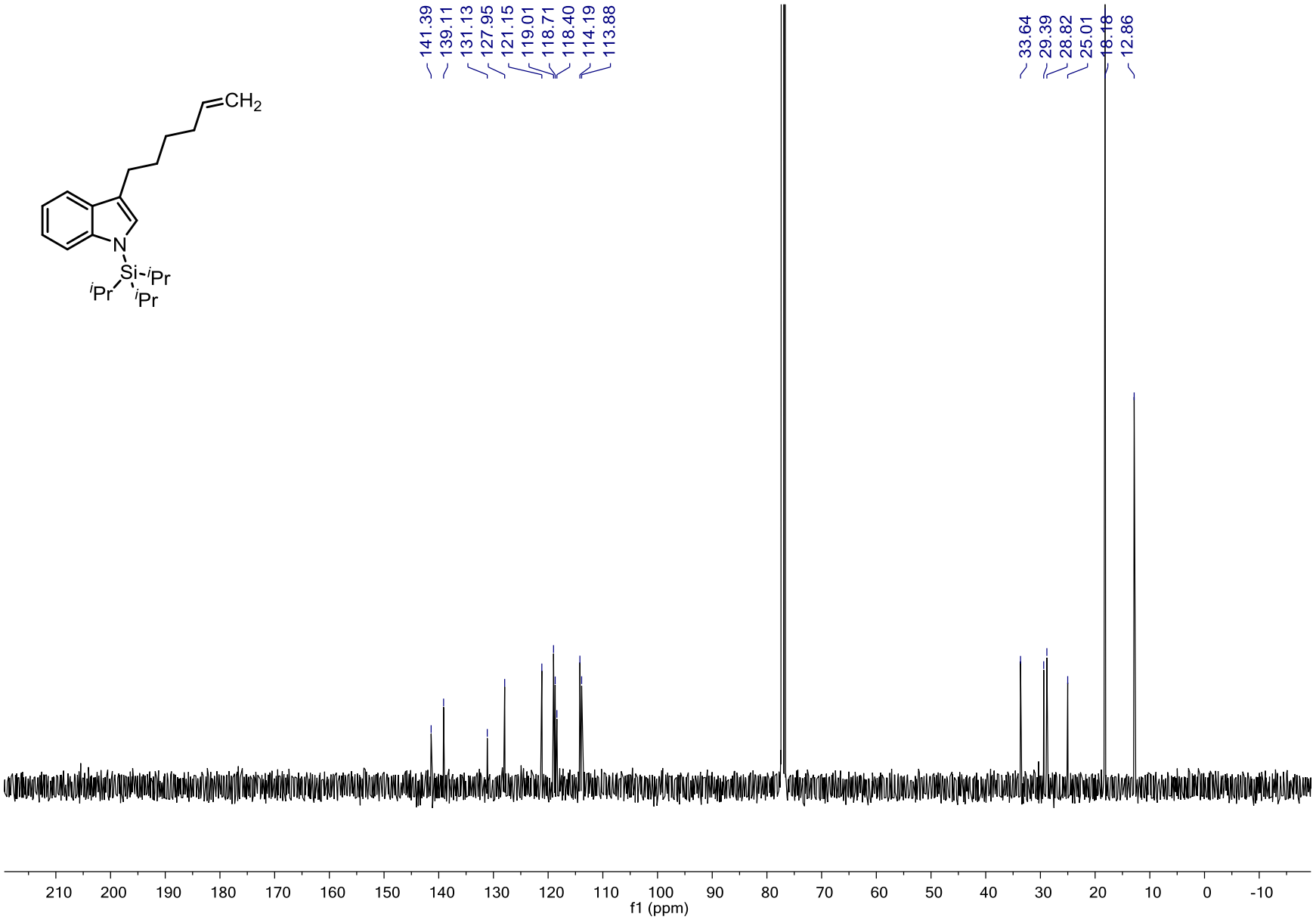
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11v***



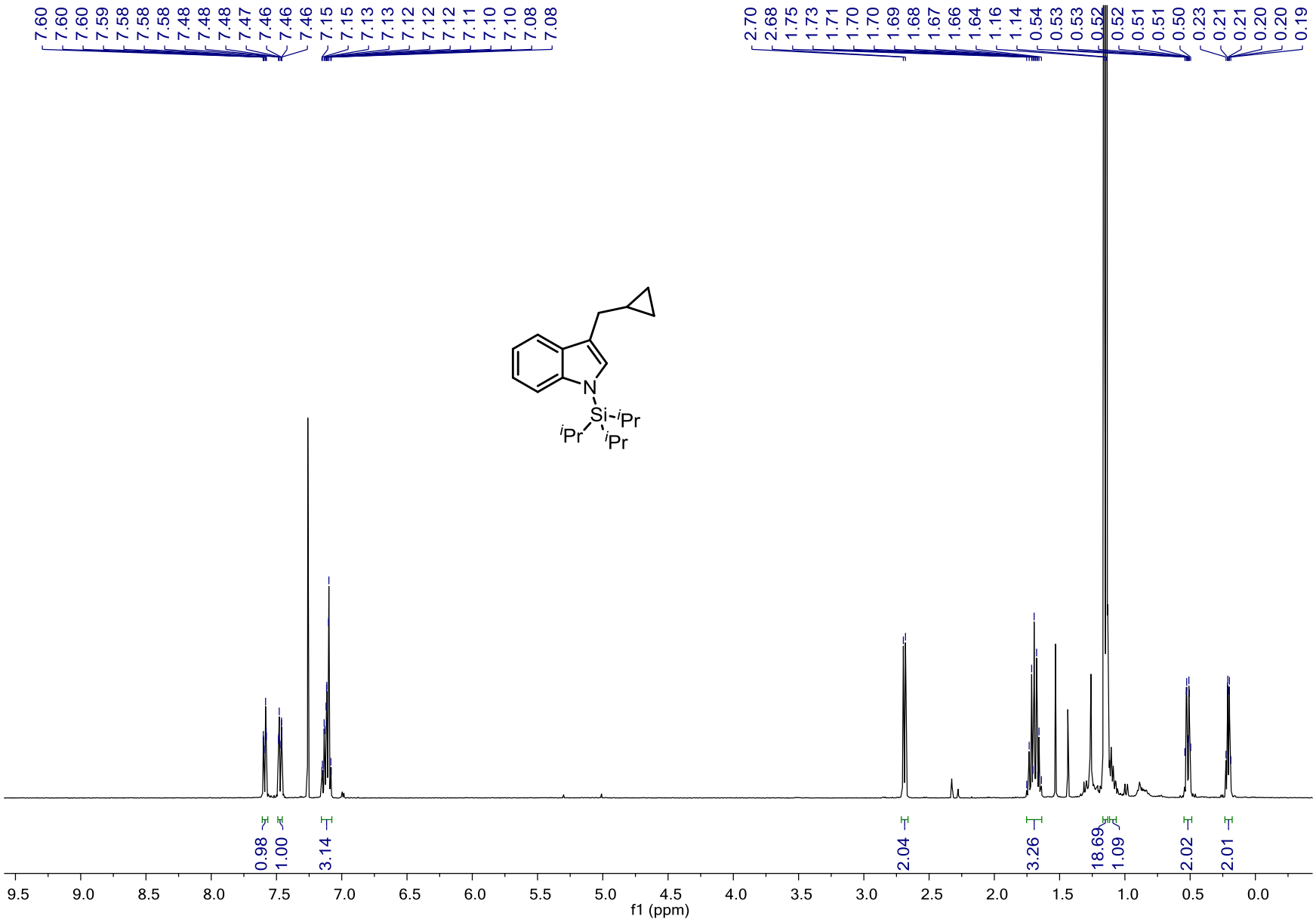
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11w***



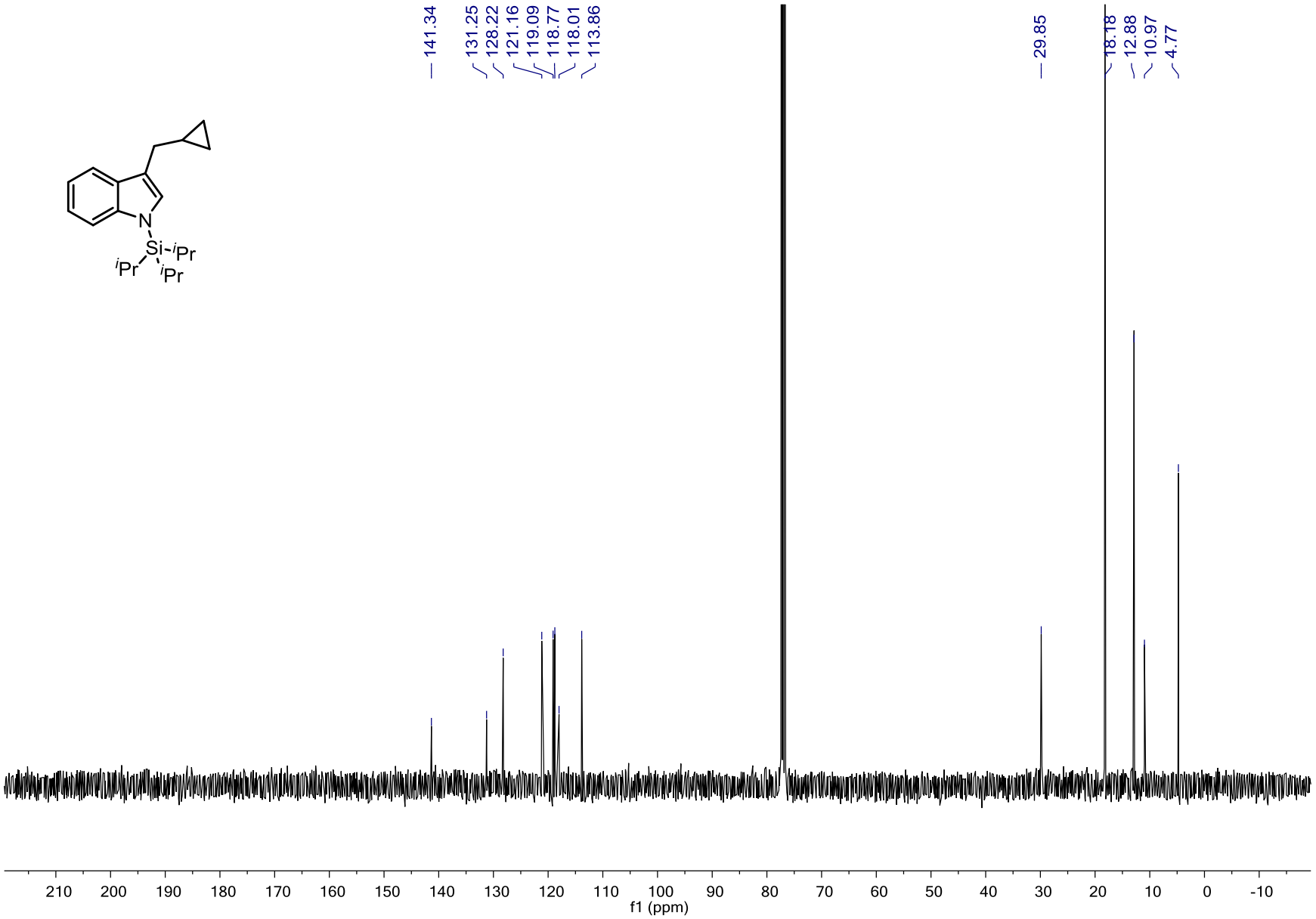
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11w***



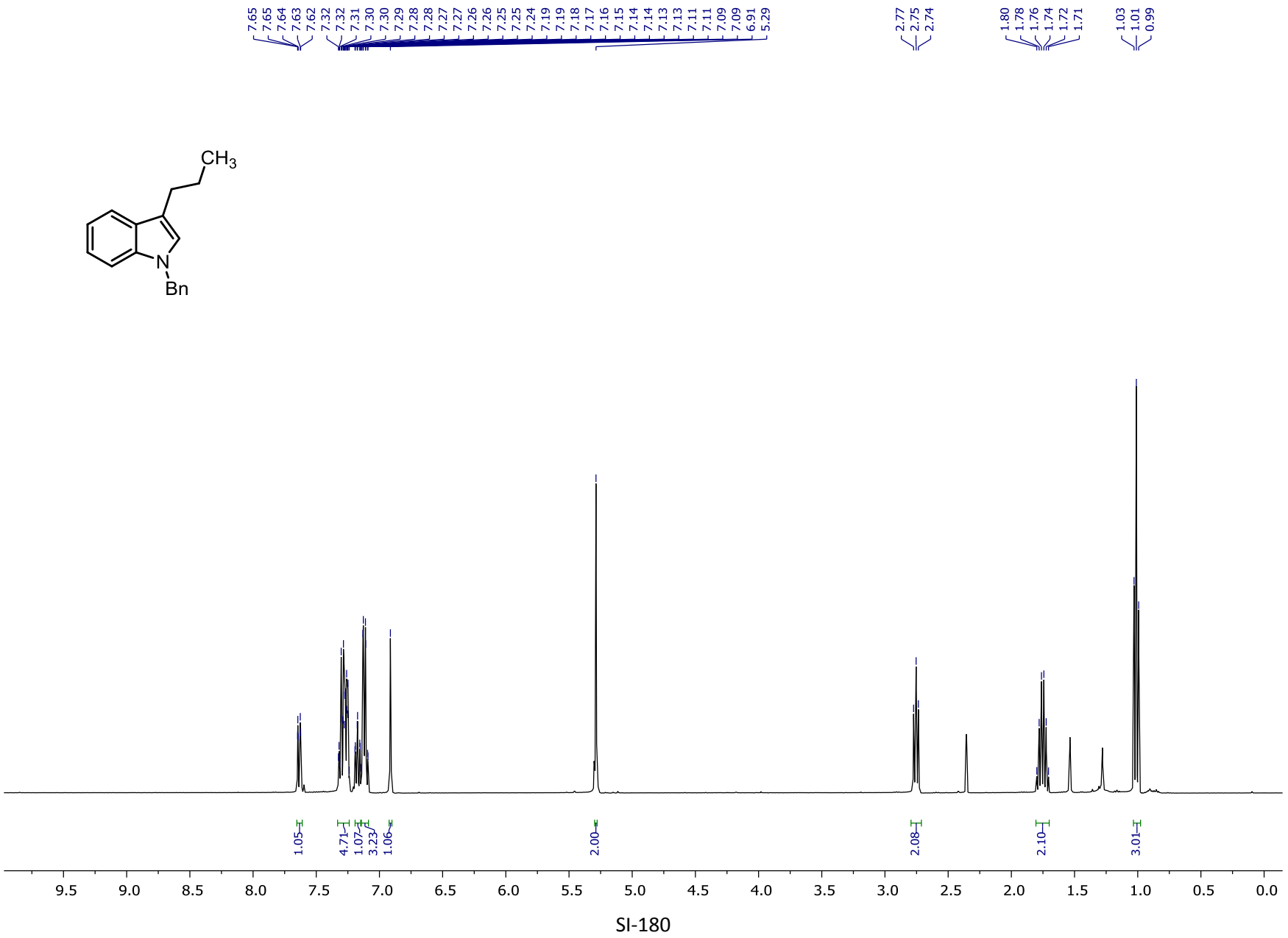
*[1]H-NMR (400 MHz, $CDCl_3$) for compound **11x***



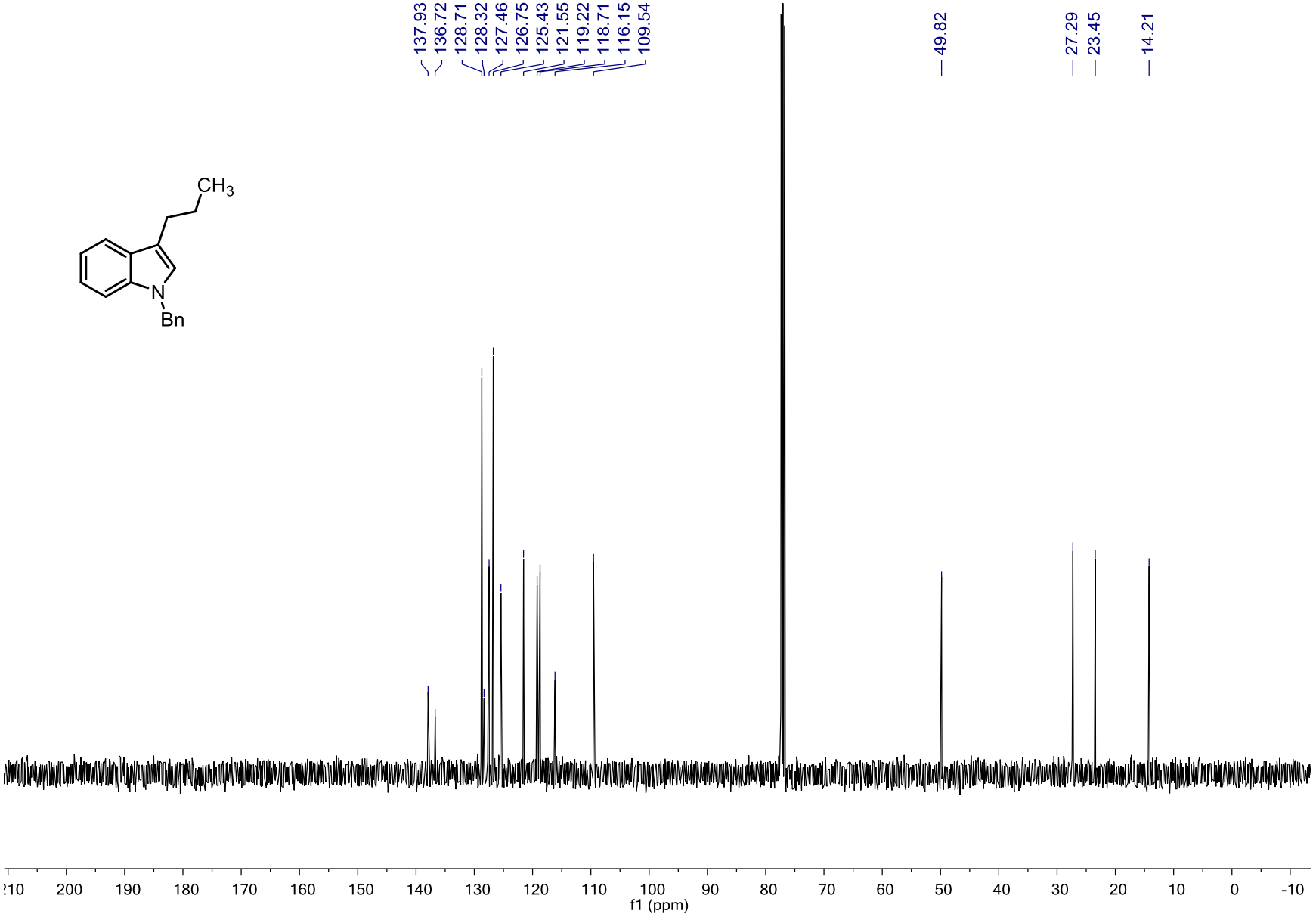
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11x***



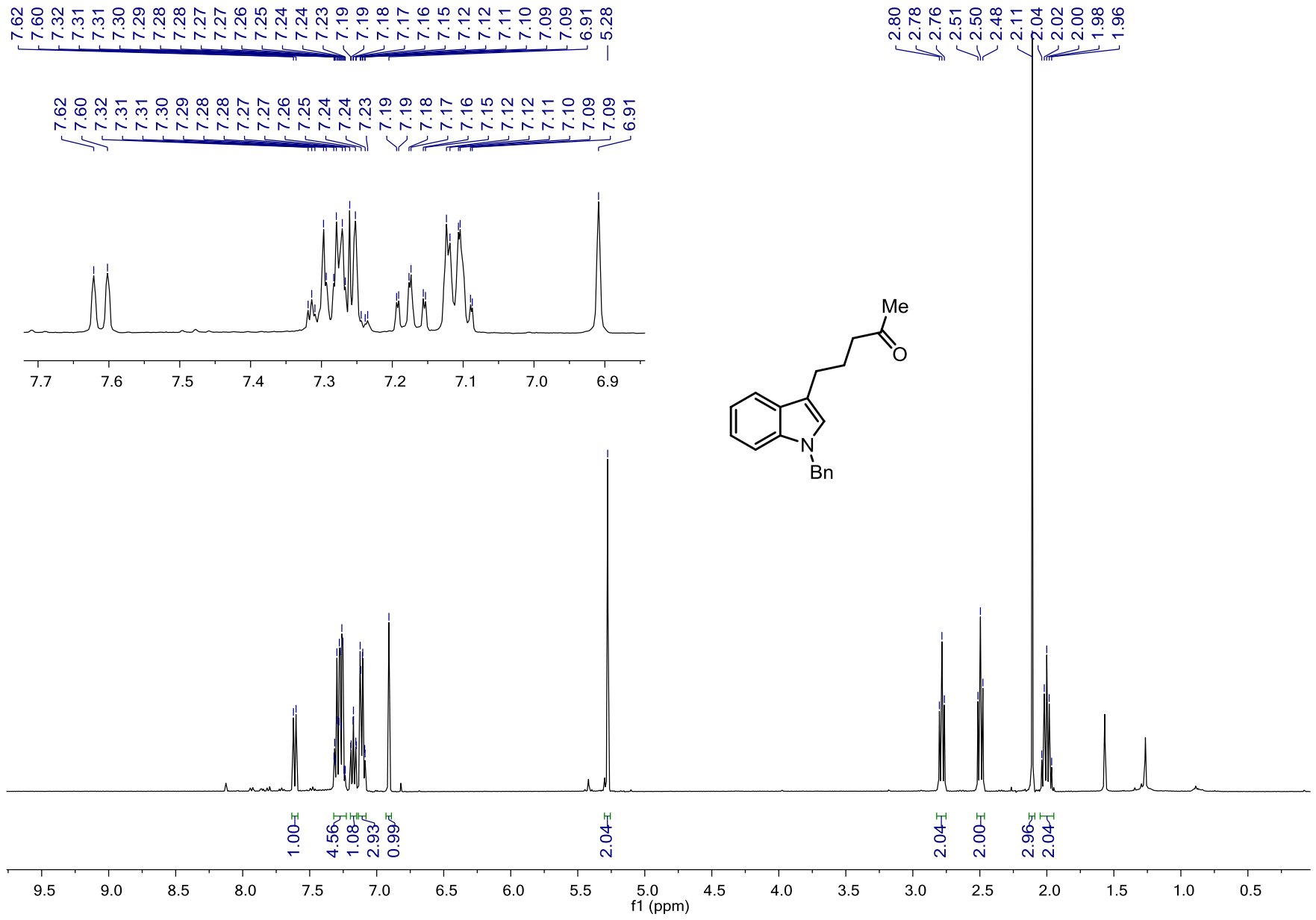
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11y***



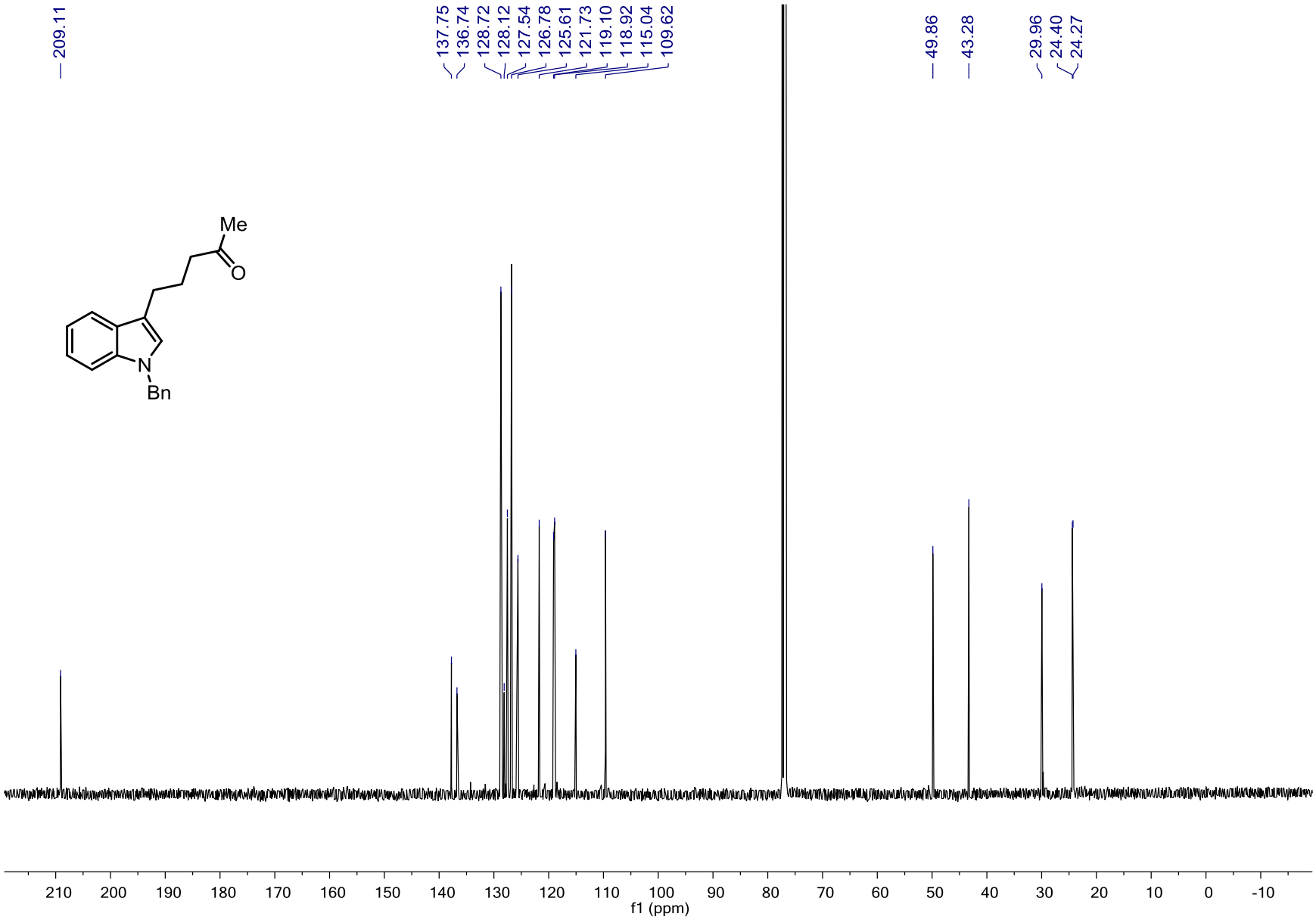
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11y***



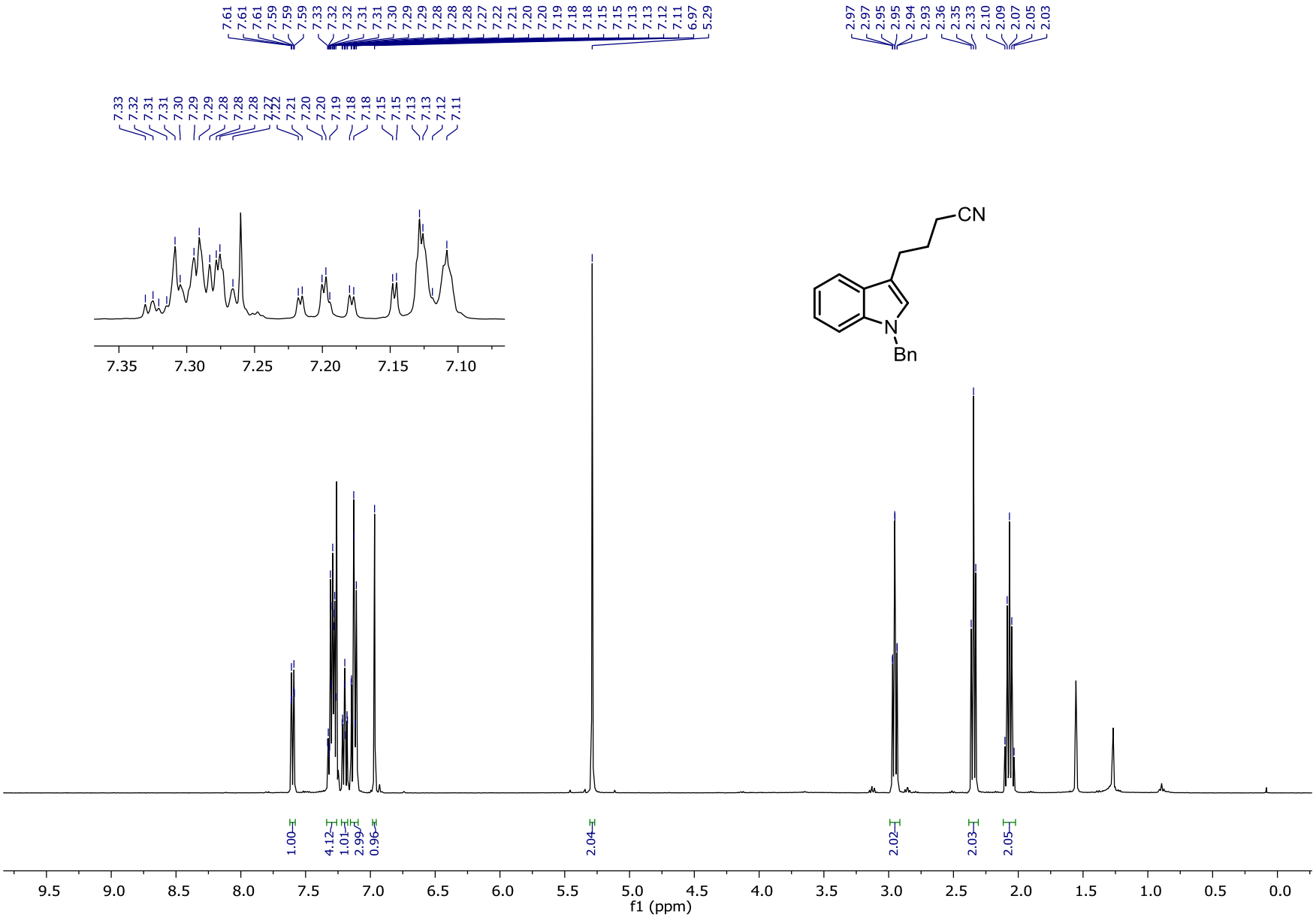
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11z***



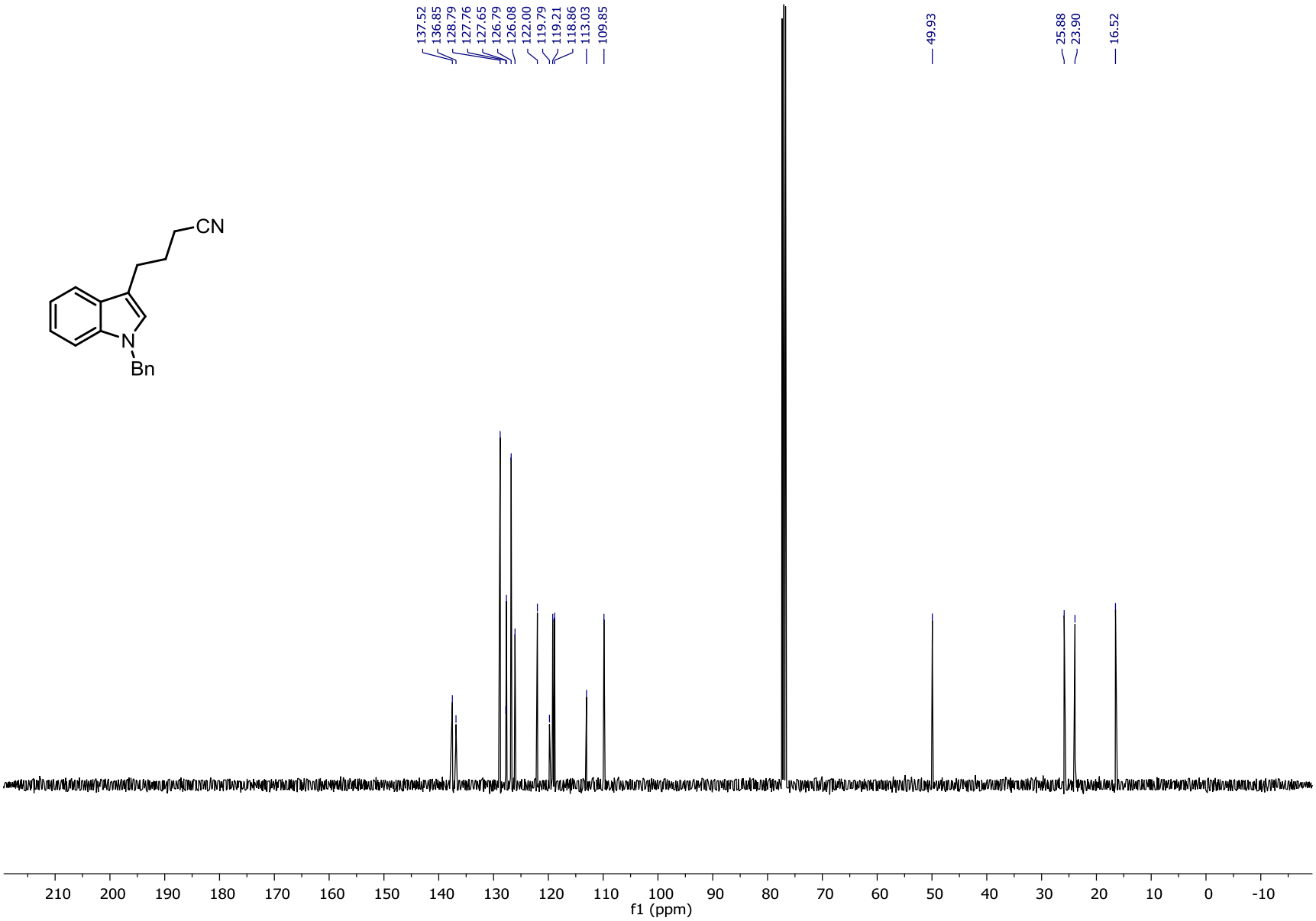
*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11z***



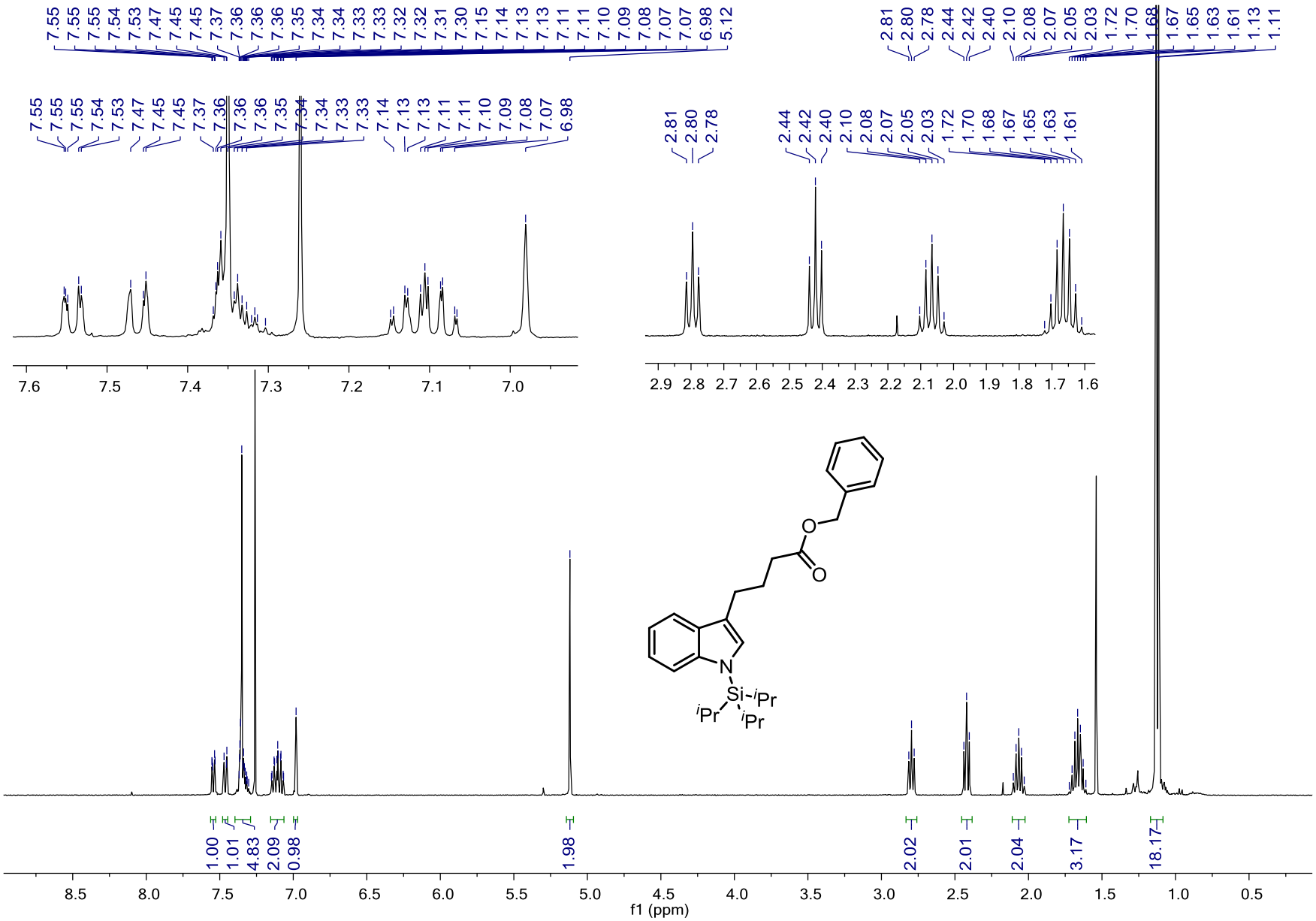
*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11aa***



*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11aa***



*^{1}H-NMR (400 MHz, $CDCl_3$) for compound **11ab***



*^{13}C-NMR (101 MHz, $CDCl_3$) for compound **11ab***