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Electronic Supplementary Information for:

Visible Light-Mediated Formal Alkylation and [4+1]-Cycloaddition Strategies of Silyl Enol Ethers with Aryldiazoacetates

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Table of Contents

1. Materials and Methods

All reactions were carried out under air, in oven dried glassware with magnetic stirring, unless otherwise noted. All reagents employed in this work were purchased from Sigma-Aldrich/ Merck or Oakwood and used as such without further purification. All solvents employed in the reactions were distilled from appropriate drying agents prior to use. Organic solutions were concentrated under reduced pressure on an IKA rotary evaporator RV-10 Control. Reactions were monitored by thin-layer chromatography (TLC) on Silica gel 60 F_{254} plastic plates (Merck). Chromatograms were visualized by fluorescence quenching with UV light at 254 nm and/or by staining with a *para*-anisaldehyde stain solution. Flash column chromatography was performed using Merck silica gel 60 (particle size 35-70μm). ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on Bruker AV – 250, 400 and 500. Chemical shifts (δ) are given in parts per million, referenced to the residual peak of $CDCl_3$, $\delta = 7.26$ (^{1}H NMR) and $\delta = 77.16$ (^{13}C{^{1}H} NMR) as internal references. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, sext. = sextuplet, sept. = septuplet, m = multiplet, br s = broad singlet. High-resolution mass spectra were recorded on Q Exactive Orbitrap spectrometer working with an electrospray ionization (ESI). Infrared spectra were performed on the Agilent Cary 630 FTIR spectrometer. Melting points were measured on Metler Toledo MP50 Melting Point System and are uncorrected.

2. Experimental Procedures and Characterization of Compounds

2.1. Diazo Compounds 1

The following diazo compounds **1** and iodonium ylide **1z’** were employed in our work (Figure S1). Ethyl diazoacetate **1y** was purchased from Sigma-Aldrich and used directly from the bottle. All other diazo compounds **1** were synthesized in our laboratory (as described below, *cf.* **General Procedures A1-3** and **B**).

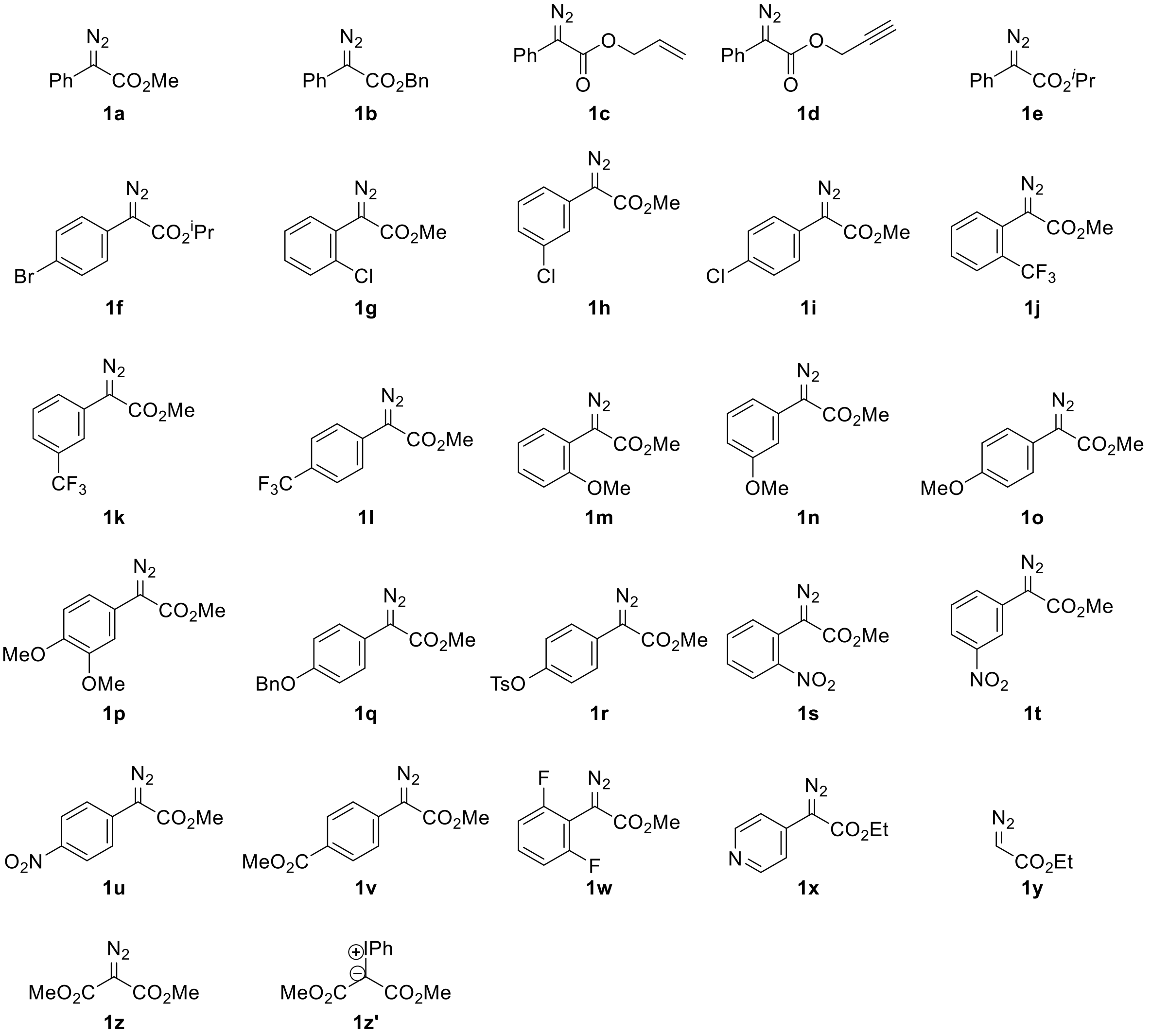
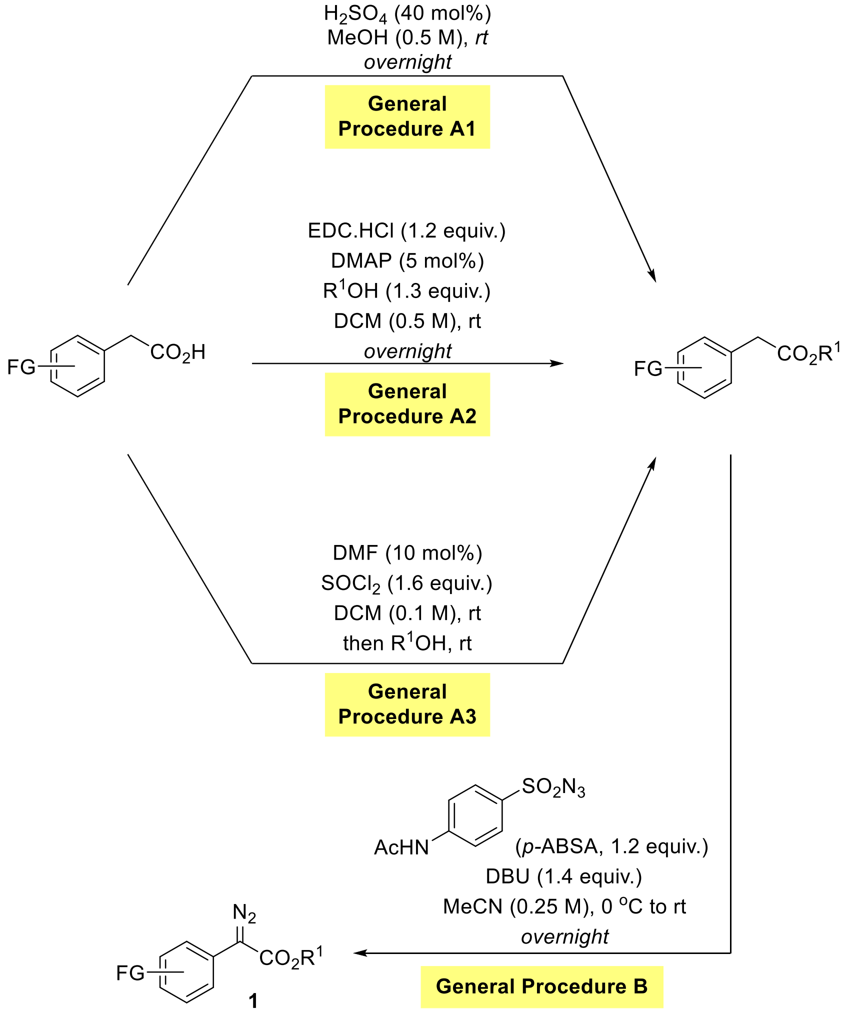


Figure S1. Diazo compounds **1a** - **1z** (and iodonium ylide **1z’**) employed in this work.

2.1.1. Synthesis of Diazo Compounds 1



Scheme S1: Synthetic routes employed for the synthesis of aryldiazoacetates **1**.

<u>General Procedure A1, Fischer Esterification:</u> Under air, at room temperature, a round bottom flask is charged with the carboxylic acid (1 equiv.), and MeOH (0.5 M in relation to the starting carboxylic acid). Then, H_2SO_4 (40 mol%) is added, and the resulting mixture is allowed to stir at room temperature overnight. Then, the reaction is neutralized with a saturated aqueous solution of $NaHCO_3$ and extracted with DCM (3x). The combined organic phases are dried ($MgSO_4$), and then utilized for the next step without any further purification.

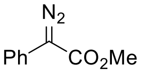
<u>General Procedure A2, Steglich Esterification:</u> Under air, at room temperature, a round bottom flask is charged with the carboxylic acid (1 equiv.), DMAP (5 mol %), EDC.HCl (1.2

equiv.), and dry DCM (0.5 M in relation to the starting carboxylic acid). The mixture is stirred for 15 minutes, and R^1OH (1.3 equiv.) is added dropwise. The resulting mixture is allowed to stir overnight. Then, the reaction is washed with water (3x) and washed with a saturated aqueous solution of $NaHCO_3$ (1x). The combined organic phases are dried ($MgSO_4$), filtered and concentrated under reduced pressure. In general, the product is obtained clean and can be used in the next step without any purification step.

General Procedure A3: Under N_2, a round bottom flask is charged with the carboxylic acid (1 equiv.), DMF (10 mol%) and dry DCM (0.1 M in relation to the starting carboxylic acid). The mixture is cooled down to 0 ºC. Then, $SOCl_2$ (1.6 equiv.) is added dropwise. The reaction is monitored by TLC. Upon complete consumption of the starting carboxylic acid, R^1OH (excess) is added dropwise. The reaction is stirred at room temperature, while being followed by TLC. Upon complete consumption of the intermediate acyl chloride, the reaction is quenched with a saturated aqueous solution of $NaHCO_3$, extracted with DCM (3x), and dried ($MgSO_4$). The combined organic phases are filtered and concentrated under reduced pressure. The residue obtained generally contains the desired ester sufficiently clean and is used as such in the next step without any purification.

General Procedure B, Regitz Diazo Transfer: Under air, at room temperature, a round bottom flask is charged with the previously prepared alkyl ester (1 equiv.), *p*-ABSA (1.2 equiv.), and dry MeCN (0.25 M in relation to the alkyl ester). Then, the temperature of the reaction mixture is lowered to 0 °C, and DBU (1.4 equiv.) is added dropwise. The reaction mixture is allowed to stir overnight with the reaction mixture slowly warming up to room temperature. Then, DCM is added, and the resulting organic layer is washed with a saturated aqueous solution of NH_4Cl, dried ($MgSO_4$), and concentrated under reduced pressure. Finally, the resulting residue is purified by flash column chromatography to afford the desired diazo compound in the stated yield.

Methyl 2-diazo-2-phenylacetate[1] (**1a)**

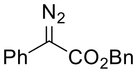


The **General Procedure B** is performed with methyl 2-phenylacetate (375 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL) Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange oil that crystallizes in the fridge: 352 mg, 80% yield.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.50 – 7.47 (m, 2H), 7.42 – 7.36 (m, 2H), 7.22 – 7.16 (m, 1H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.7, 129.0, 125.9, 125.6, 124.1, 52.1.

Benzyl 2-diazo-2-phenylacetate[1] **(1b)**



The **General Procedure A2** is performed with phenylacetic acid (340 mg, 2.5 mmol, 1 equiv.), EDC.HCl (576 mg, 3 mmol, 1.2 equiv), DMAP (15 mg, 0.125 mmol, 5 mol%), BnOH (340 µL, 3.25 mmol, 1.3 equiv.) and DCM (5 mL). Then, **General Procedure B** is performed with benzyl 2-phenylacetate (565 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 350 mg, 55% yield (for 2 steps).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.51 – 7.49 (m, 2H), 7.42 – 7.34 (m, 7H), 7.21 – 7.17 (m, 1H), 5.33 (s, 2H).

^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.1, 136.0, 129.1, 128.8, 128.5, 128.3, 126.0, 125.6, 124.2, 66.6.

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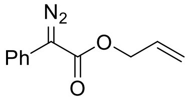
[1] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: M. L. Stivanin, A. A. G. Fernandes, A. F. da Silva, C. Y. Okada Jr, I. D. Jurberg, *Adv. Synth. Catal.*, 2020, **362**, 1106 – 1111.

Allyl 2-diazo-2-phenylacetate[2] **(1c)**

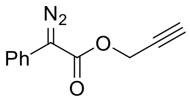


The **General Procedure A2** is performed with phenylacetic acid (1.36 g, 10 mmol, 1 equiv.), EDC.HCl (2.3 g, 12 mmol, 1.2 equiv), DMAP (61 mg, 0.5 mmol, 5 mol%), allyl alcohol (1.36 mL, 20 mmol, 2 equiv.) and DCM (20 mL). Then, the **General Procedure B** is performed with allyl 2-phenylacetate (1.76 g, 10 mmol, 1 equiv.), *p*-ABSA (2.88 g, 12 mmol, 1.2 equiv.), DBU (2.1 mL, 14 mmol, 1.4 equiv.), and MeCN (40 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange oil: 1.11 g, 55% yield (for 2 steps).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.51 – 7.46 (m, 2H), 7.42 – 7.35 (m, 2H), 7.22 – 7.15 (m, 1H), 6.06 – 5.91 (m, 1H), 5.36 (dq, *J* = 17.0 Hz, *J* = 1.4Hz, 1H), 5.28 (dq, *J* = 10.3 Hz, *J* = 1.4 Hz, 1H), 4.77 (dt, *J* = 5.6Hz, *J* = 1.4 Hz, 2H).

^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.0, 132.2, 129.1, 126.0, 125.6, 124.2, 118.5, 65.6.

Prop-2-yn-1-yl 2-diazo-2-phenylacetate[2] **(1d)**



The **General Procedure A2** is performed with phenylacetic acid (1.5 g, 11 mmol, 1 equiv.), EDC.HCl (2.53 g, 13.2 mmol, 1.2 equiv), DMAP (67 mg, 0.55 mmol, 5 mol%), propargyl alcohol (1.3 mL, 22 mmol, 2 equiv.), and DCM (22 mL). Then, the **General Procedure B** is performed with prop-2-yn-1-yl 2-phenylacetate (1.34 g, 7.7 mmol, 1 equiv.), *p*-ABSA (2.22 g, 9.24 mmol, 1.2 equiv.), DBU (1.6 mL, 10.8 mmol, 1.4 equiv.), and MeCN (30 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange oil: 1.16 g, 53% yield (for 2 steps).

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.49 – 7.47 (m, 2H), 7.41 – 7.38 (m, 2H), 7.22 – 7.19 (m, 1H), 4.88 (d, *J* = 2.5 Hz, 2H), 2.51 (t, *J* = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 164.4, 129.1, 126.2, 125.2, 124.2, 77.8, 75.3, 52.4.

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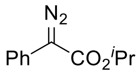
[2] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: S. Thurow, A. A. G. Fernandes, Y. Quevedo-Acosta, M. F. de Oliveira, M. G. de Oliveira, I. D. Jurberg, *Org. Lett.*, 2019, **21**, 6909–6913.

Isopropyl 2-diazo-2-phenylacetate[2] (1e)

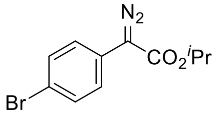


The **General Procedure A3** is performed with phenylacetic acid (340 mg, 2.5 mmol, 1 equiv.), DMF (20 μL, 0.25 mmol, 10 mol%), dry DCM (25 mL), $SOCl_2$ (290 μL, 4 mmol, 1.6 equiv.) and ^{i}PrOH (2 mL, 28.6 mmol, 11.4 equiv.). Then, the **General Procedure B** is performed with isopropyl 2-phenylacetate (445 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 μL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL) Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 164 mg, 32% yield (2 steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.49 – 7.48 (m, 2H), 7.39 – 7.37 (m, 2H), 7.19 – 7.16 (m, 1H), 5.21 (hept, *J* = 6.2 Hz, 1H), 1.33 (d, *J* = 6.2 Hz, 6H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.0, 129.0, 126.0, 125.8, 124.1, 68.8, 22.2.

Isopropyl 2-(4-bromophenyl)-2-diazoacetate[1] (1f)

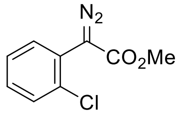


The **General Procedure A3** is performed with 4-bromophenylacetic acid (538 mg, 2.5 mmol, 1 equiv.), DMF (20 μL, 0.25 mmol, 10 mol%), dry DCM (25 mL), $SOCl_2$ (290 μL, 4 mmol, 1.6 equiv.) and ^{i}PrOH (2 mL, 28.6 mmol, 11.4 equiv.). Then, the **General Procedure B** is performed with isopropyl 2-phenylacetate (617 mg, 2.4 mmol, 1 equiv.), *p*-ABSA (691 mg, 2.88 mmol, 1.2 equiv.), DBU (510 μL, 3.4 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 430 mg, 61% (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.49 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 2H), 5.20 (hept, *J* = 6.3 Hz, 1H), 1.32 (d, *J* = 6.3 Hz, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 164.6, 132.1, 125.5, 125.2, 119.3, 69.1, 22.2.

Methyl 2-(2-chlorophenyl)-2-diazoacetate[1] **(1g)**

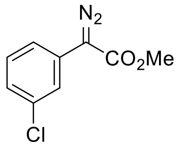


The **General Procedure A1** is performed with (2-chloro)-phenylacetic acid (426 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(2-chlorophenyl)acetate (463 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 404 mg, 77 % yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 (dd, *J* = 7.8 Hz, *J* = 1.8 Hz, 1H), 7.39 (d, *J* = 7.8 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 3.82 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.1, 133.9, 132.4, 130.2, 129.8, 127.3, 124.0, 52.4.

Methyl 2-(3-chlorophenyl)-2-diazoacetate[3] **(1h)**



The **General Procedure A1** is performed with (3-chloro)-phenylacetic acid (852 mg, 5 mmol, 1 equiv.), H_2SO_4 (100 µL, 2 mmol, 40 mol%) and MeOH (10 mL). Then, the **General Procedure B** is performed with methyl 2-(3-chlorophenyl)acetate (777 mg, 4.2 mmol, 1 equiv.), *p*-ABSA (1.2 g, 5 mmol, 1.2 equiv.), DBU (880 µL, 5.88 mmol, 1.4 equiv.), and MeCN (20 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 850 mg, 81% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.54 (t, *J* = 1.8 Hz, 1H), 7.33 (dt, *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.15 (dt, *J* = 7.6 Hz, *J* = 1.8 Hz, 1H), 3.87 (s, 3H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.2, 135.2, 130.2, 127.9, 125.9, 123.8, 121.7, 52.3.

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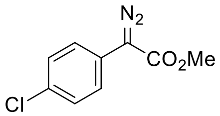
[3] ^{1}H and $^{13}C\{^1H\}$ NMR spectra are in good agreement with the literature. See: H. Keipour, T. Ollevier, *Org. Lett.*, 2017, **19**, 5736–5739.

Methyl 2-(4-chlorophenyl)-2-diazoacetate[1] **(1i)**

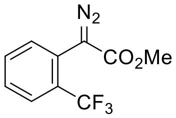


The **General Procedure A1** is performed with (4-chloro)-phenylacetic acid (428 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(4-chlorophenyl)acetate (426 mg, 2.3 mmol, 1 equiv.), *p*-ABSA (662 mg, 2.76 mmol, 1.2 equiv.), DBU (480 µL, 3.22 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 417 mg, 79% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, *J* = 9.0 Hz, 2H), 7.35 (d, *J* = 9.0 Hz, 2H), 3.87 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.5, 131.7, 129.3, 125.2, 124.3, 52.3.

Methyl 2-diazo-2-(2-(trifluoromethyl)phenyl)acetate (1j)



The **General Procedure A1** is performed with 2-(2-(trifluoromethyl)phenyl)-acetic acid (510 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-*(*2-(trifluoromethyl)phenyl)acetate (523 mg, 2.4 mmol, 1 equiv.), *p*-ABSA (690 mg, 2.88 mmol, 1.2 equiv.), DBU (510 µL, 3.4 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow oil: 445 mg, 73% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.75 (d, *J* = 7.9 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.52 – 7.49 (m, 1H), 3.82 (s, 3H).

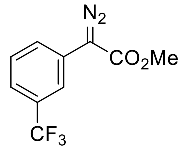
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.4, 134.6, 132.4, 130.2 (q, *J* = 30 Hz), 129.6, 127.0 (q, *J* = 5.0 Hz), 123.9 (q, *J* = 271.3 Hz), 123.7 (q, *J* = 2.5 Hz), 52.5.

^{19}F{^{1}H} NMR (470 MHz, $CDCl_3$) δ: -61.65.

IR (ATR, cm^{-1}): 3003, 2956, 2956, 2906, 1699, 1152, 1109.

HRMS (ESI+): Calcd. for $[C_{10}H_7F_3N_2O_2 + H]^+$: 245.0532, found: 245.0534.

Methyl 2-diazo-2-(3-(trifluoromethyl)phenyl)acetate[4] (1k)



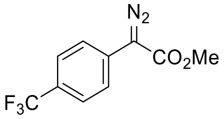
The **General Procedure A1** is performed with 2-(3-(trifluoromethyl)phenyl)-acetic acid (510 mg, 2.5 mmol, 1 equiv), H_2SO_4 (50 µL, 1.2 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(3-(trifluoromethyl)phenyl)acetate (523 mg, 2.4 mmol, 1 equiv.), *p*-ABSA (690 mg, 2.88 mmol, 1.2 equiv.), DBU (510 µL, 3.4 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 554 mg, 91% yield (2 steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.79 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 3.89 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.1, 131.6 (q, *J* = 32.5 Hz), 129.5, 127.2, 126.8, 124.1 (q, *J* = 270.0 Hz), 122.5 (q, *J* = 4.5 Hz), 120.6 (q, *J* = 4.5 Hz), 52.4.

^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ: -62.89.

Methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate[1] (1l)



The **General Procedure A1** is performed with 2-(4-(trifluoromethyl)phenyl)-acetic acid (326 mg, 1.6 mmol, 1 equiv.), H_2SO_4 (34 µL, 0.64 mmol, 40 mol%), and MeOH (3.5 mL). Then, the **General Procedure B** is performed with methyl 2-(4-(trifluoromethyl)phenyl)acetate (318 mg, 1.46 mmol, 1 equiv.), *p*-ABSA (420 mg, 1.75 mmol, 1.2 equiv.), DBU (305 µL, 2.04 mmol, 1.4 equiv.), and MeCN (6.5 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 329 mg, 84% yield (2 steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.64 – 7.40 (m, 4H), 3.89 (s, 3H).

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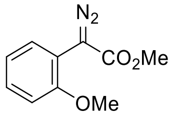
[4] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: R. Sambasivan, Z. T. Ball, *J. Am. Chem. Soc.*, 2010, **132**, 9289–9291.

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.0, 130.2 (q, *J* = 1.2 Hz), 127.7 (q, *J* = 32.9 Hz), 126.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 268.5 Hz), 123.6, 52.4.

$^{19}F\{^1H\}$ NMR (564 MHz, $CDCl_3$) δ: -62.48.

Methyl 2-diazo-2-(2-methoxyphenyl)acetate[5] (1m)

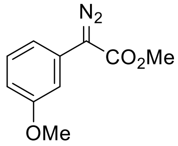


The **General Procedure A1** is performed with (2-methoxy)-phenylacetic acid (415 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl *2*-(2-methoxyphenyl)acetate (450 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange oil: 256 mg, 50% yield (2 steps).

^1H NMR (600 MHz, $CDCl_3$) δ: 7.55 (dd, *J* = 7.8 Hz, *J* = 1.7 Hz, 1H), 7.28 – 7.25 (m, 1H), 7.02 (td, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 6.90 (dd, *J* = 7.8 Hz, *J* = 1.2 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.8, 155.7, 130.4, 128.8, 121.3, 113.8, 111.1, 55.7, 52.1.

Methyl 2-diazo-2-(3-methoxyphenyl)acetate[1] (1n)



The **General Procedure A1** is performed with (3-methoxy)-phenylacetic acid (415 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%) and MeOH (5 mL). The **General Procedure B** is performed with methyl 2-(3-methoxyphenyl)acetate (432 mg, 2.4 mmol, 1 equiv.), *p*-ABSA (690 mg, 2.88 mmol, 1.2 equiv.), DBU (510 µL, 3.4 mmol, 1.4 equiv.), and MeCN (10 mL) Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange oil: 198 mg, 39% yield (2 steps).

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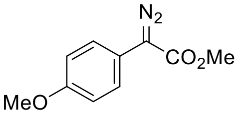
[5] ^1H and $^{13}C\{^1H\}$ NMR spectra are in good agreement with the literature. See: W.-W. Chan, S.-H. Yeung, Z. Zhou, A. S. C. Chan, W.-Y. Yu, *Org. Lett.*, 2010, **12**, 604–607.

^{1}H NMR (400 MHz, CDCl$_3$) δ: 7.28 (t, *J* = 8.0 Hz, 1H), 7.16 (t, *J* = 2.3 Hz, 1H), 6.98 (ddd, *J* = 8.0 Hz, *J* = 2.3, *J* = 0.8 Hz, 1H), 6.72 (ddd, *J* = 8.0 Hz, *J* = 2.3 Hz, *J* = 0.8 Hz, 1H), 3.86 (s, 3H), 3.81 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.5, 160.1, 129.9, 127.0, 116.0, 111.5, 109.7, 55.3, 52.0.

Methyl 2-diazo-2-(4-methoxyphenyl)acetate[1] (1o)

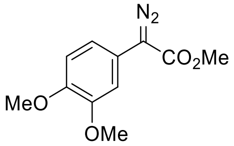


The **General Procedure A1** is performed with (4-methoxy)-phenylacetic acid (415 mg, 2.5 mmol, 1 equiv.), H$_2$SO$_4$ (50 µL, 1 mmol, 40 mol%) and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(4-methoxyphenyl)acetate (450 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL) Purification by flash column chromatography (SiO$_2$, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a dark orange/ red solid: 240 mg, 47% yield (2 steps).

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.38 (d, *J* = 8.8 Hz, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 3.81 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.3, 158.2, 126.1, 117.0, 114.8, 55.5, 52.1.

Methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate[6] (1p)



The **General Procedure A1** is performed with 2-(3,4-dimethoxyphenyl)acetic acid (490 mg, 2.5 mmol, 1 equiv.), H$_2$SO$_4$ (50 µL, 1 mmol, 40 mol%) and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(3,4-dimethoxyphenyl)acetate (525 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO$_2$,

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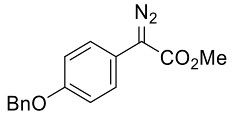
[6] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: A. F. da Silva, M. A. S. Afonso, R. A. Cormanich, I. D. Jurberg, *Chem. Eur. J.*, 2020, **26**, 5648-5653.

gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an orange solid: 371 mg, 63% yield (2 steps).

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.18 (d, *J* = 2.0 Hz, 1H), 6.89 (d, *J* = 8.5 Hz, 1H), 6.86 (dd, *J* = 8.5 Hz, *J* = 2.0 Hz, 1H), 3.90 (s, 3H), 3.88 (s, 3H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.3, 149.6, 147.5, 117.5, 116.6, 111.8, 108.5, 56.1, 56.0, 52.1.

Methyl 2-(4-(benzyloxy)phenyl)-2-diazoacetate[7] (1q)



Under air, a round bottom flask is charged with methyl 2-(4-hydroxyphenyl)acetate (415 mg, 2.5 mmol, 1 equiv.), K_2CO_3 (690 mg, 5 mmol, 2 equiv.), benzyl bromide (420 μL, 3.5 mmol, 1.4 equiv.) and acetone (5 mL, 0.5 M in relation to the starting ester). The mixture is stirred and heated to reflux (60 ^{o}C) overnight. Then, the reaction is allowed to cool down to room temperature; is quenched with water, extracted with DCM (3x), and dried ($MgSO_4$). Then, the combined organic phases are filtered and concentrated under reduced pressure. The residue contains the product sufficiently clean, and it is used as such in the next step without further purification. Then, the **General Procedure B** is performed with methyl 2-(4-(benzyloxy)phenyl)-acetate (500 mg, 1.95 mmol, 1 equiv.), *p*-ABSA (562 mg, 2.34 mmol, 1.2 equiv.), DBU (410 µL, 2.7 mmol, 1.4 equiv.), and MeCN (8 mL) Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a dark orange solid: 330 mg, 47% yield (2 steps).

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.44 – 7.42 (m, 2H), 7.40 – 7.37 (m, 4H), 7.34 – 7.31 (m, 1H), 7.02 (d, *J* = 8.5, 2H), 5.07 (s, 2H), 3.85 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.3, 157.4, 136.9, 128.8, 128.2, 127.6, 126.1, 117.3, 115.7, 70.3, 52.1.

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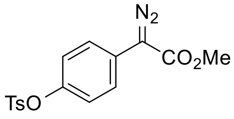
[7] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: G. S. Sinclair, R. Tran, J. Tao, W. S. Hopkins, G. K. Murphy, *Eur. J. Org. Chem.*, 2016, **2016**, 4603-4606.

Methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate[8] (1r)

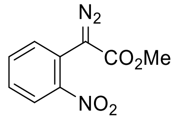


Under air, at room temperature, a round bottom flask is charged with methyl 2-(4-hydroxyphenyl)acetate (481 mg, 2.9 mmol, 1 equiv.), Et_3N (445 µL, 3.2 mmol, 1.1 equiv.) and dry DCM (6 mL, 0.5 M in relation to the starting the ester). The mixture is stirred for 5 minutes; then, *p*-TsCl (610 mg, 3.2 mmol, 1.1 equiv.) is added. The reaction is allowed to stir at room temperature overnight. Then, the reaction is washed with water (3x), and washed with a saturated aqueous solution of $NaHCO_3$ (1x). The combined organic phases are dried ($MgSO_4$), filtered and concentrated under reduced pressure. The obtained residue contains the desired tosylated intermediate sufficiently clean and is used as such in the next step without further purification. Then, the **General Procedure B** is performed with methyl 2-(4-(tosyloxy)phenyl)acetate (928 mg, 2.9 mmol, 1 equiv.), *p*-ABSA (840 mg, 3.5 mmol, 1.2 equiv.), DBU (610 µL, 4.1 mmol, 1.4 equiv.), and MeCN (12 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as an orange solid: 803 mg, 80% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.70 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.85 (s, 3H), 2.45 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.4, 147.5, 145.6, 132.4, 130.0, 128.7, 124.9 (x2), 123.2, 52.3, 21.9.

Methyl 2-diazo-2-(2-nitrophenyl)acetate[9] (1s)



The **General Procedure A1** is performed with 2-(2-nitrophenyl)acetic acid (453 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%) and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(2-nitrophenyl)acetate (488 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column

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[8] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: J. Tao, R. Tran, M. Richard, G. K. Murphy, *J. Am. Chem. Soc.*, 2013, **135**, 16312-16315.

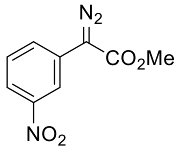
[9] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: L. S. Munaretto, C. Y. dos Santos, R. D. C. Gallo, C. Y. Okada Jr, V. M. Deflon, I. D. Jurberg, *Org. Lett.*, 2021, **23**, 9292–9296.

chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 445 mg, 81% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.05 (dd, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H), 7.65 (td, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.55 (dd, *J* = 8.0, *J* = 1.5 Hz, 1H), 7.49 – 7.46 (m, 1H), 3.82 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.2, 147.4, 133.4, 131.3, 129.0, 125.8, 121.1, 52.6.

Methyl 2-diazo-2-(3-nitrophenyl)acetate[10] (1t)

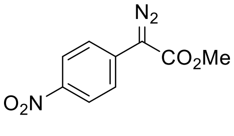


The **General Procedure A1** is performed with 2-(3-nitrophenyl)acetic acid (453 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(3-nitrophenyl)acetate (488 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 396 mg, 72% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.36 (t, *J* = 2.0 Hz, 1H), 8.02 (ddd, *J* = 8.0 Hz, *J* = 2.0 Hz, *J* = 1.0 Hz, 1H), 7.84 (ddd, *J* = 8.0 Hz, *J* = 2.0 Hz, *J* = 1.0 Hz, 1H), 7.55 (t, *J* = 8.0 Hz, 1H), 3.91 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 164.8, 148.9, 130.0, 129.2, 128.6, 120.5, 118.3, 52.5.

Methyl 2-diazo-2-(4-nitrophenyl)acetate[5] (1u)



The **General Procedure A1** is performed with 2-(4-nitrophenyl)acetic acid (453 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%), and MeOH (5 mL). Then, the **General Procedure B** is performed with methyl 2-(4-nitrophenyl)acetate (488 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash

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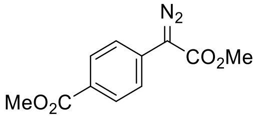
[10] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: L. S. Munaretto, R. D. C. Gallo, L. P. M. O. Leão, I. D. Jurberg, *Org. Biomol. Chem.*, 2022, **20**, 6178-6182.

column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 394 mg, 71% yield

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.24 (d, *J* = 9.0 Hz, 2H), 7.67 (d, *J* = 9.0 Hz, 2H), 3.91 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 164.3, 145.2, 134.0, 124.5, 123.3, 52.6.

Methyl 4-(1-diazo-2-methoxy-2-oxoethyl)benzoate[11] (1v)

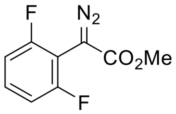


The **General Procedure A1** is performed with 4-(carboxymethyl)benzoic acid (540 mg, 3 mmol, 1 equiv.), H_2SO_4 (64 µL, 1.2 mmol, 40 mol%), and MeOH (6 mL). Then, the **General Procedure B** is performed with methyl 4-(2-methoxy-2-oxoethyl)benzoate (562 mg, 2.7 mmol, 1 equiv.), *p*-ABSA (780 mg, 3.24 mmol, 1.2 equiv.), DBU (567 µL, 3.8 mmol, 1.4 equiv.), and MeCN (11 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as an orange solid: 227 mg, 32% yield (2 steps).

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.03 (d, *J* = 8.7 Hz, 2H), 7.56 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H), 3.88 (s, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 166.8, 164.9, 131.2, 130.3, 127.2, 123.1, 52.3, 52.2.

Methyl 2-diazo-2-(2,6-difluorophenyl)acetate[12] (1w)



The **General Procedure A1** is performed with 2-(2,6-difluorophenyl)acetic acid (430 mg, 2.5 mmol, 1 equiv.), H_2SO_4 (50 µL, 1 mmol, 40 mol%) and MeOH (5 mL). The **General Procedure B** is performed with methyl 2-(2,6-difluorophenyl)acetate (446 mg, 2.4 mmol, 1 equiv.), *p*-ABSA (691 mg, 2.88 mmol, 1.2

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[11] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: F. Ye, C. Wang, Y. Zhang, J. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11625-11628.

[12] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: R. D. C. Gallo, M. Duarte, A. F. da Silva, C. Y. Okada Jr, V. M. Deflon, I. D. Jurberg, *Org. Lett.*; 2021, **23**, 8916-8920.

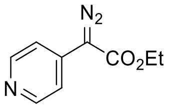
equiv.), DBU (500 µL, 3.36 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 97:3 Hex:AcOEt) affords the title compound as a yellow solid: 45 mg, 9% yield (2 steps).

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.36 – 7.33 (m, 1H), 6.99 – 6.95 (m, 2H), 3.84 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 165.1, 160.7 (dd, *J* = 249.8 Hz, *J* = 5.3 Hz), 131.1 (t, *J* = 10.5 Hz), 111.9 (dd, *J* = 20.3 Hz, *J* = 3.8 Hz), 103.6 (t, *J* = 18.8 Hz), 52.6.

^{19}F{^{1}H} NMR (564 MHz, $CDCl_3$) δ: -108.96.

Ethyl 2-diazo-2-(pyridin-4-yl)acetate[11] (1x)

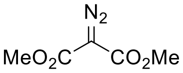


The **General Procedure B** is performed with ethyl 2-(pyridin-4-yl)acetate (413 mg, 2.5 mmol, 1 equiv.), *p*-ABSA (720 mg, 3 mmol, 1.2 equiv.), DBU (523 µL, 3.5 mmol, 1.4 equiv.), and MeCN (10 mL). Purification by flash column chromatography (SiO_2, 80:20:2 Hex:AcOEt:Et_3N) affords the title compound as a yellow solid: 195 mg, 41% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.52 – 8.51 (m, 2H), 7.41 – 7.40 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 163.7, 150.0, 135.8, 117.3, 61.6, 14.6.

Dimethyl 2-diazomalonate[13] (1z)



The **General Procedure B** is performed with dimethyl malonate (230 µL, 2 mmol, 1 equiv.), *p*-ABSA (576 mg, 2.4 mmol, 1.2 equiv.), DBU (420 µL, 2.8 mmol, 1.4 equiv.), and MeCN (8 mL). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a light-yellow oil: 161 mg, 51% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 3.82 (s, 6H).

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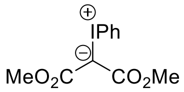
[13] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: I. D. Jurberg, H. M. L. Davies, *Chem. Sci.*, 2018, **9**, 5112-5118.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) ***(1C cannot be unambiguously assigned)*** **δ:** 161.6, 52.6.

Dimethyl 2-(phenyl-λ^3-iodaneylidene)malonate[14] (1z')



Under a nitrogen atmosphere, an oven-dried round bottom flask is charged with dimethyl malonate (343 µL, 3 mmol, 1 equiv.), dry MeCN (10 mL, 0.3 M in relation to the dimethyl malonate), and KOH (1 g, 18 mmol, 6 equiv.). Then, the reaction mixture is cooled down to 0 °C and stirred for 5 min.. At this stage, a white suspension is observed, and then $PhI(OAc)_2$ (1.06 g, 3.3 mmol, 1.1 equiv.) is added in one portion at 0 °C. The reaction is allowed to stir for 2 hours with the temperature raising to room temperature. Then, the reaction is quenched with water and stirred for additional 5 min.. The solid formed is filtered off in a Büchner funnel and washed with water (2x), then with Et_2O (1x). The solvent must be thoroughly removed after each wash. The title product is obtained as a white solid: 559 mg, 56% yield. (*Important:* The title product could be stored dry and protected from light at -20 °C (freezer) for 1-2 days, but it is highly advisable to be used when freshly prepared. This compound was found to rapidly decompose when in contact with different solvents. The NMR spectra were obtained immediately after the product was dissolved in d_6-DMSO)

^1H NMR (400 MHz, d_6-DMSO) δ: 7.75 – 7.72 (m, 2H), 7.53 – 7.49 (m, 1H), 7.48 – 7.42 (m, 2H), 3.50 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, d_6-DMSO) ***(1C cannot be unambiguously assigned)*** **δ:** 165.6, 131.1, 130.9, 130.2, 116.0, 51.0.

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[14] ^1H and $^{13}C\{^1H\}$ NMR spectra are in good agreement with the literature. See: R. F. J. Epping, M. M. Hoeksma, E. O. Bobylev, S. Mathew, B. de Bruin, *Nature Chem.*, 2022, **14**, 550-557.

2.2. Silyl Enol Ethers 2 and Silyl Dienol Ethers 5

The following silyl enol ethers **2** and silyl dienol ethers **5** were employed in our work (Figure S2). Compounds **2a**, **2e** – **2h**, **5a**, and **5c** were purchased from Sigma-Aldrich, Ambeed or TCI and used directly from their bottles. All other silyl enol ethers were synthesized in our laboratory (as described below, *cf.* **General Procedure C**).

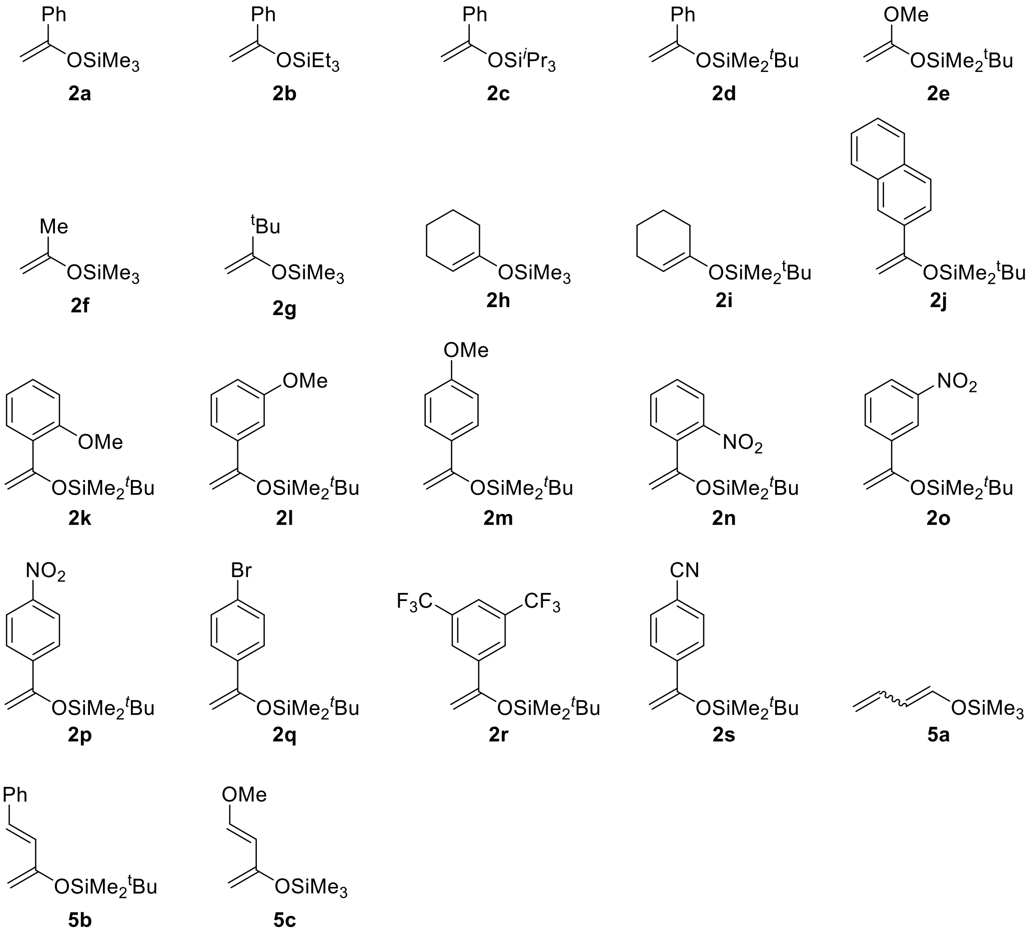
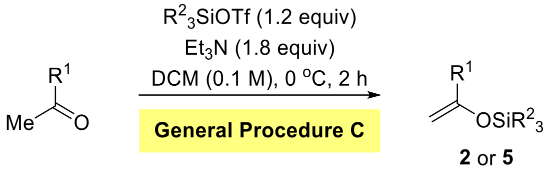


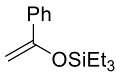
Figure S2. Silyl enol ethers **2a – 2s** and silyl dienol ethers **5a – 5c** employed in this work.

2.2.1. Synthesis of Silyl Enol Ethers 2 and Silyl Dienol Ethers 5



General Procedure C:[15] Under a nitrogen atmosphere, at room temperature, an oven-dried round bottom flask is charged with a ketone (1 equiv.), dry DCM (0.1 M in relation to the ketone), and Et$_3$N (1.8 equiv). Then, the reaction mixture is stirred for 30 min at room temperature. Then, the reaction mixture is cooled down to 0 °C and R$^2_3$SiOTf (1.2 equiv) is added dropwise; and the reaction mixture is allowed to stir at this temperature for 2 h. Then, the reaction is quenched with NaHCO$_3$ (2 equiv.) at 0 °C and stirred for a few minutes at this temperature. Then, the temperature is allowed to raise to room temperature and MgSO$_4$ is added. The solids are filtered off; and the reaction is concentrated under reduced pressure. The resulting crude residue is purified by flash column chromatography using Et$_3$N-deactivated silica to provide corresponding silyl enol ethers in pure form.

Triethyl((1-phenylvinyl)oxy)silane[16] **(2b)**



The **General Procedure C** is performed with acetophenone (240 mg, 2 mmol, 1 equiv), Et$_3$N (500 μL, 3.6 mmol, 1.8 equiv), and TESOTf (542 μL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et$_3$N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 309 mg, 66% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.64 – 7.62 (m, 2H), 7.35 – 7.28 (m, 3H), 4.89 (d, J = 1.5 Hz, 1H), 4.44 (d, J = 1.5 Hz, 1H), 1.02 (t, J = 7.8 Hz, 9H), 0.78 (q, J = 7.8 Hz, 6H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 156.0, 137.8, 128.3, 128.2, 125.4, 90.5, 6.9, 5.1.

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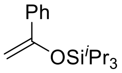
[15] Adapted from: W. Dong, Z. Ye, W. Zhao, *Angew. Chem. Int. Ed.*, 2022, **61**, e202117413.

[16] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: J.-F. Zhao, B.-H. Tan, T.-P. Loh, *Chem. Sci.*, 2011, **2**, 349-352.

Triisopropyl((1-phenylvinyl)oxy)silane[16] (2c)

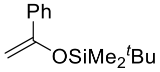


The **General Procedure C** is performed with acetophenone (240 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TIPSOTf (645 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography on Et_3N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 403 mg, 73% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.66 – 7.64 (m, 2H), 7.35 – 7.27 (m, 3H), 4.86 (d, *J* = 2.0 Hz, 1H), 4.42 (d, *J* = 2.0 Hz, 1H), 1.34 – 1.27 (m, 3H), 1.14 (d, *J* = 7.5 Hz, 18H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 156.3, 138.1, 128.2 (x2), 125.4, 90.1, 18.3, 12.9.

tert-Butyldimethyl((1-phenylvinyl)oxy)silane[16] (2d)

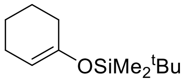


The **General Procedure C** is performed with acetophenone (240 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 384 mg, 82% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.63 – 7.61 (m, 2H), 7.35 – 7.27 (m, 3H), 4.90 (d, *J* = 1.5 Hz, 1H), 4.43 (d, *J* = 1.5 Hz, 1H), 1.01 (s, 9H), 0.22 (s, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 156.1, 137.9, 128.3, 128.2, 125.4, 91.0, 26.0, 18.5, -4.5.

tert-Butyl(cyclohex-1-en-1-yloxy)dimethylsilane[17] (2i)



The **General Procedure C** is performed with cyclohexanone (207 µL, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a yellowish oil: 234 mg, 55% yield.

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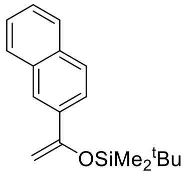
[17] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: H. P. Caldora, Z. Zhang, M. J. Tilby, O. Turner, D. Leonori, *Angew. Chem. Int. Ed.*, 2023, **62**, e202301656.

^{1}H NMR (400 MHz, CDCl$_3$) δ: 4.87 – 4.85 (m, 1H), 2.02 – 1.97 (m, 4H), 1.68 – 1.62 (m, 2H), 1.53 – 1.49 (m, 2H), 0.92 (s, 9H), 0.12 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ: 150.7, 104.5, 30.0, 25.9, 24.0, 23.3, 22.5, 18.2, -4.2.

tert-Butyldimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane[18] (2j)

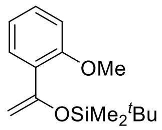


The **General Procedure C** is performed with 1-(naphthalen-2-yl)ethan-1-one (340 mg, 2 mmol, 1 equiv.), Et$_3$N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography on Et$_3$N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 540 mg, 95% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 8.10 (s, 1H), 7.86 – 7.85 (m, 1H), 7.83 – 7.82 (m, 1H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.72 (dd, *J* = 8.4 Hz, *J* = 1.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 5.06 (d, *J* = 1.8 Hz, 1H), 4.56 (d, *J* = 1.8 Hz, 1H), 1.07 (s, 9H), 0.26 (s, 6H).

^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 156.1, 135.2, 133.4, 133.3, 128.7, 127.7 (x2), 126.3, 126.2, 124.5, 123.6, 92.0, 26.1, 18.6, -4.4.

tert-Butyl((1-(2-methoxyphenyl)vinyl)oxy)dimethylsilane[19] (2k)



The **General Procedure C** is performed with 2’-methoxyacetophenone (300 mg, 2 mmol, 1 equiv.), Et$_3$N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et$_3$N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 316 mg, 60% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.54 (dd, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 7.26 (ddd, *J* = 8.2 Hz, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 6.94 (td, *J* = 7.5 Hz, *J* = 1.4 Hz, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 4.99 (s, 1H), 4.66 (s, 1H), 3.86 (s, 3H), 0.97 (s, 9H), 0.16 (s, 6H).

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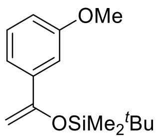
[18] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: H. Y. Bae, D. Höfler, P. S. J. Kaib, P. Kasaplar, C. K. De, A. Döhring, S. Lee, K. Kaupmees, I. Leito, B. List, *Nature Chem.*, 2018, **10**, 888 - 894.

[19] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: I. Khan, B. G. Reed-Berendt, R. L. Melen, L. C. Morrill, *Angew. Chem. Int. Ed.*, 2018, **57**, 12356 - 12359.

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 157.1, 153.5, 129.3, 129.2, 127.3, 120.2, 111.1, 96.6, 55.5, 26.0, 18.4, -4.5.

***tert*-Butyl((1-(3-methoxyphenyl)vinyl)oxy)dimethylsilane[15] (2l)**

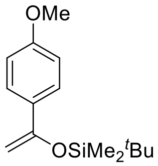


The **General Procedure C** is performed with 3'-methoxyacetophenone (300 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 450 mg, 85% yield.

^1H NMR (400 MHz, $CDCl_3$) δ: 7.30 – 7.21 (m, 3H), 6.90 – 6.87 (m, 1H), 4.94 (d, *J* = 1.8 Hz, 1H), 4.47 (d, *J* = 1.8 Hz, 1H), 3.86 (s, 3H), 1.05 (s, 9H), 0.26 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.6, 155.9, 139.5, 129.2, 118.0, 114.0, 110.9, 91.4, 55.3, 26.0, 18.5, -4.5.

***tert*-Butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane[19] (2m)**

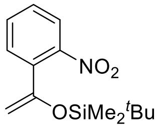


The **General Procedure C** is performed with 4'-methoxyacetophenone (300 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a colorless oil: 475 mg, 90% yield.

^1H NMR (400 MHz, $CDCl_3$) δ: 7.55 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 4.77 (d, *J* = 1.3 Hz, 1H), 4.33 (d, *J* = 1.3 Hz, 1H), 3.82 (s, 3H), 1.00 (s, 9H), 0.21 (s, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 159.8, 155.9, 130.6, 126.7, 113.5, 89.4, 55.4, 26.0, 18.5, -4.5.

tert-Butyldimethyl((1-(2-nitrophenyl)vinyl)oxy)silane (2n)



The **General Procedure C** is performed with 2'-nitroacetophenone (330 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography on triethylamine deactivated silica (100% Hex) to provide the title compound as a colorless oil: 335 mg, 60% yield.

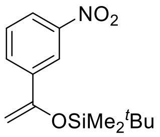
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.72 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.50 (m, 2H), 7.44 – 7.40 (m, 1H), 4.63 (d, *J* = 2.0 Hz, 1H), 4.54 (d, *J* = 2.0 Hz, 1H), 0.87 (s, 9H), 0.17 (s, 6H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 154.6, 148.7, 134.3, 132.2, 130.5, 129.0, 124.1, 94.8, 25.7, 18.3, -5.0.

IR (ATR, cm^{-1}): 2932, 2859, 1533, 1319, 1256, 1003.

HRMS (ESI+): Calcd. for $[C_{14}H_{21}NO_3Si + Na]^+$: 302.1183 found:302.1185.

tert-Butyldimethyl((1-(3-nitrophenyl)vinyl)oxy)silane (2o)



The **General Procedure C** is performed with 3'-nitroacetophenone (330 mg, 2 mmol, 1 equiv.), Et_3N (500 µL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 µL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a yellow oil: 553 mg, 99% yield.

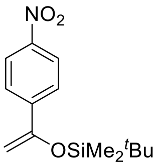
^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.46 (t, *J* = 2.5 Hz, 1H), 8.14 (ddd, *J* = 10.0 Hz, *J* = 2.5 Hz, *J* = 1.5 Hz, 1H), 7.92 (ddd, *J* = 10.0 Hz, *J* = 2.5 Hz, *J* = 1.5 Hz, 1H), 7.50 (t, *J* = 10.0 Hz, 1H), 5.02 (d, *J* = 2.8 Hz, 1H), 4.57 (d, *J* = 2.8 Hz, 1H), 1.02 (s, 9H), 0.24 (s, 6H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 153.8, 148.5, 139.7, 131.0, 129.2, 122.9, 120.4, 92.9, 25.9, 18.4, -4.5.

IR (ATR, cm^{-1}): 2931, 2859, 1530, 1343, 1255, 1015.

HRMS (ESI+): Calcd. for $[C_{14}H_{21}NO_3Si + H]^+$: 280.1363, found: 280.1363.

***tert*-Butyldimethyl((1-(4-nitrophenyl)vinyl)oxy)silane (2p)**



The **General Procedure C** is performed with 4’-nitroacetophenone (330 mg, 2 mmol, 1 equiv.), Et_3N (500 μL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 μL, 2.4 mmol, 1.2 equiv.) in DCM (20 mL). The crude residue was purified by flash column chromatography on Et_3N- deactivated silica (100% Hex) to provide the title compound as a white solid: 285 mg, 51% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.18 (d, *J* = 9.0 Hz, 2H), 7.74 (d, *J* = 9.0 Hz, 2H), 5.05 (d, *J* = 2.3 Hz, 1H), 4.61 (d, *J* = 2.3 Hz, 1H), 1.00 (s, 9H), 0.23 (s, 6H).

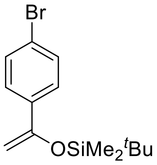
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 154.2, 147.6, 144.1, 126.0, 123.6, 94.6, 25.9, 18.5, -4.5.

M.P.: 70 – 71 °C.

IR (ATR, cm^{-1}): 2955, 2931, 2859, 1533, 1361, 1319, 1257, 1004.

HRMS (ESI+): Calcd. for $[C_{14}H_{21}NO_3Si + H]^+$: 280.1363, found: 280.1364.

((1-(4-bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane[20] (2q)



The **General Procedure C** is performed with 4’-bromoacetophenone (400 mg, 2 mmol, 1 equiv.), Et_3N (500 μL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 μL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a yellow oil: 590 mg, 94% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49 – 7.43 (m, 4H), 4.88 (d, *J* = 1.9 Hz, 1H), 4.44 (d, *J* = 1.9 Hz, 1H), 1.00 (m, 9H), 0.21 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 155.2, 136.9, 131.3, 127.0, 122.3, 91.5, 26.0, 18.5, -4.5.

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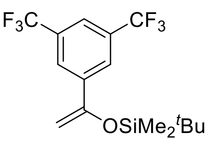
[20] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: B. Lipshutz, R. Moser, K. R. Voigtritter, *Isr. J. Chem.*, 2010, **50**, 691 – 695.

((1-(3,5-Bis(trifluoromethyl)phenyl)vinyl)oxy)(tert-butyl)dimethylsilane (2r)



The **General Procedure C** is performed with 1-(3,5-bis(trifluoromethyl)phenyl)ethan-1-one (512 mg, 2 mmol, 1 equiv.), Et$_3$N (500 μL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 μL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography on Et$_3$N-deactivated silica (100% Hex) to the title compound as a colorless oil: 370 mg, 50% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 8.04 (s, 2H), 7.79 (s, 1H), 5.04 (d, *J* = 2.5 Hz, 1H), 4.61 (d, *J* = 2.5 Hz, 1H), 1.01 (s, 9H), 0.24 (s, 6H).

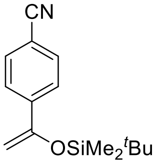
^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 153.3, 140.0, 131.7 (q, *J* = 33.0 Hz), 125.3 (q, *J* = 4.5 Hz), 123.5 (q, *J* = 271.5 Hz), 121.8 (hept, *J* = 3.8 Hz), 93.4, 25.8, 18.4, -4.6.

^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ: -63.07.

IR (ATR, cm^{-1}): 2956, 2863, 1711, 1277, 1128.

HRMS (ESI+): Calcd. for [$C_{16}H_{20}F_6OSi$ + H]$^{+}$: 371.1260, found: 371.1263.

4-(1-((*tert*-Butyldimethylsilyl)oxy)vinyl)benzonitrile[21] (2s)



The **General Procedure C** is performed with 4'-cyanoacetophenone (290 mg, 2 mmol, 1 equiv.), Et$_3$N (500 μL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 μL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography on triethylamine deactivated silica (100% Hex) to provide the title compound as a white solid: 347 mg, 67% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.69 (d, *J* = 8.6 Hz, 2H), 7.61 (d, *J* = 8.6 Hz, 2H), 5.00 (d, *J* = 2.2 Hz, 1H), 4.57 (d, *J* = 2.2 Hz, 1H), 0.99 (s, 9H), 0.22 (s, 6H).

^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 154.3, 142.2, 132.1, 125.8, 119.0, 111.6, 93.8, 25.9, 18.4, -4.6.

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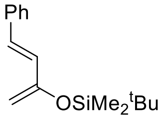
[21] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: D. Spinnato, B. Schweitzer-Chaput, G. Goti, M. Ošeka, P. Melchiorre, P.; *Angew. Chem. Int. Ed.*, 2020, **59**, 9485-9490.

(*E*)-*tert*-Butyldimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane[22] (5b)



The **General Procedure C** is performed with (*E*)-4-phenylbut-3-en-2-one (292 mg, 2 mmol, 1 equiv.), Et_3N (500 μL, 3.6 mmol, 1.8 equiv), and TBSOTf (551 μL, 2.4 mmol, 1.2 equiv) in DCM (20 mL). The crude residue was purified by flash column chromatography using Et_3N-deactivated silica (100% Hex) to provide the title compound as a yellow oil: 515 mg, 99% yield.

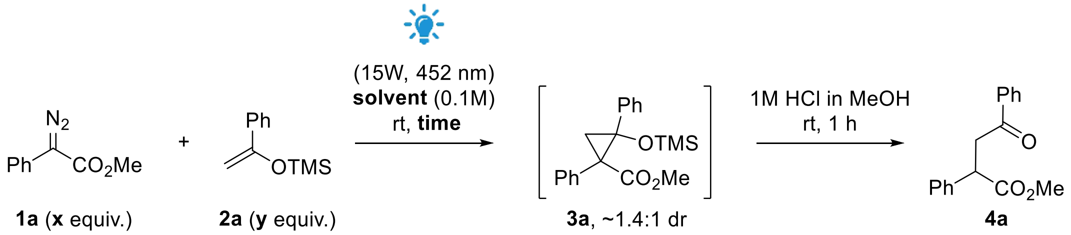
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 – 7.45 (m, 2H), 7.39 – 7.35 (m, 2H), 7.30 – 7.26 (m, 1H), 6.91 (d, *J* = 15.7 Hz, 1H), 6.63 (d, *J* = 15.7 Hz, 1H), 4.50 (s, 1H), 4.47 (s, 1H), 1.08 (s, 9H), 0.27 (s, 6H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 155.4, 137.0, 129.4, 128.7, 127.8, 126.9, 126.7, 96.9, 26.0, 18.5, -4.5.

3. Optimization Studies

3.1. Formal Alkylation of Silyl Enol Ether 2a with Aryldiazoacetate 1a.

Table S1. Reactions performed in 0.2-mmol scale of the limiting reagent. [a]Estimated by ^{1}H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield. [c]Reaction performed under ambient light, at 40 °C.



Entry	x	y	**solvent** (0.1M)	**time** (h)	Yield **4a** (%)[a]
1	1	1	DCM	12	44
2	1	1	$CHCl_3$	12	21
3	1	1	1,2-DCE	12	29
4	1	1	AcOEt	12	22
5	1	1	MeCN	12	24
6	1	1	toluene	12	23
7	2	1	DCM	12	54
8	3	1	DCM	12	71
9	4	1	DCM	12	71
10	1	2	DCM	12	66

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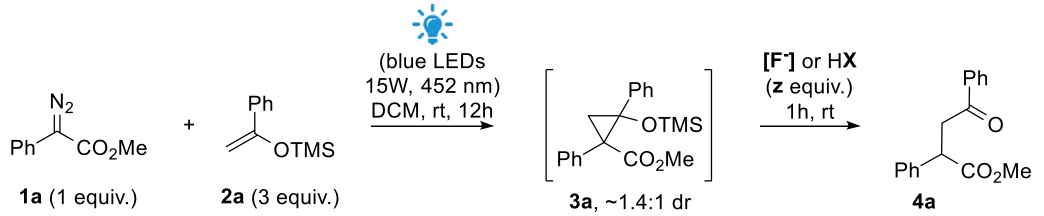
[22] ^{1}H and ^{13}C{^{1}H} NMR spectra are in good agreement with the literature. See: T. Aono, H. Sasagawa, K. Fuchibe, J. Ichikawa, *Org. Lett.*, 2015, **17**, 5736 – 5739.

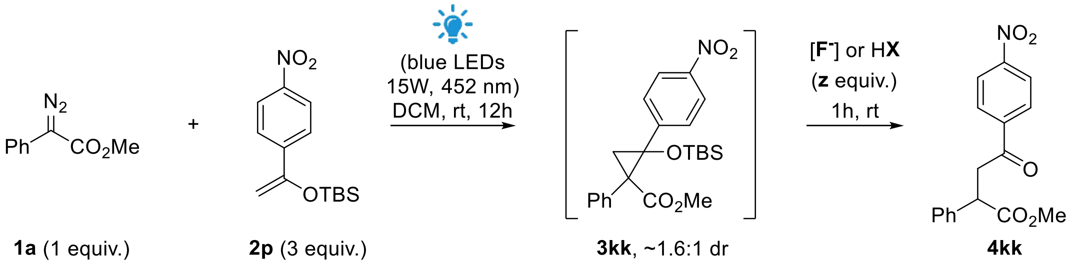
11	**1**	**3**	**DCM**	**12**	**72/ 67**[b]
12	1	4	DCM	12	70
13	1	3	DCM	6	52
14	1	3	DCM	24	72
15[c]	1	3	DCM	12	0

Table S2. Reactions performed in 0.2-mmol scale of the limiting reagent **1a**. [a]Estimated by ^{1}H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.



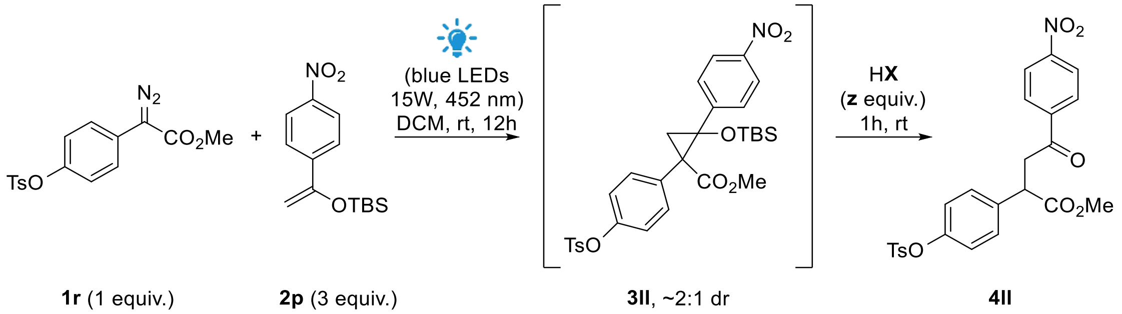
Entry	**[F$^-$]** or H**X** (**z** equiv.**)**	observation	yield **4a** (%)[a]
1	-	cyclopropane **3a** is the major compound observed, 1.4:1 dr	-
2	70% $(HF)_x$.pyr (15)	keeping glass vial as reaction vessel	60
3	70% $(HF)_x$.pyr (15)	changing from glass vial to plastic Falcon tube as reaction vessel	73
4	CsF (3)	cyclopropane **3a** is the major compound observed, 1.4:1 dr	-
5	TBAF (3)	-	65
6	AcOH (3)	cyclopropane **3a** is the major compound observed, 1.4:1 dr	-
7	TFA (3)	-	73
8	*p*TSA.H_2O (3)	-	72
9	**1M HCl in MeOH (5)**	No ketal is observed	**72/ 67**[b]
10	1M HCl in EtOH (5)	No transesterification occurs, no ketal is observed	73
11	1M HCl in dioxane (5)	-	72

Table S3. Optimization of ring-opening of more resistant cyclopropane **3kk**. Reactions performed in 0.2-mmol scale of the limiting reagent **1a**. [a]Estimated by ^1H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Desired product could not be isolated by flash column chromatography because it has the same R_f of the 4'-nitroacetophenone by-product derived from the desilylation of **2p**.

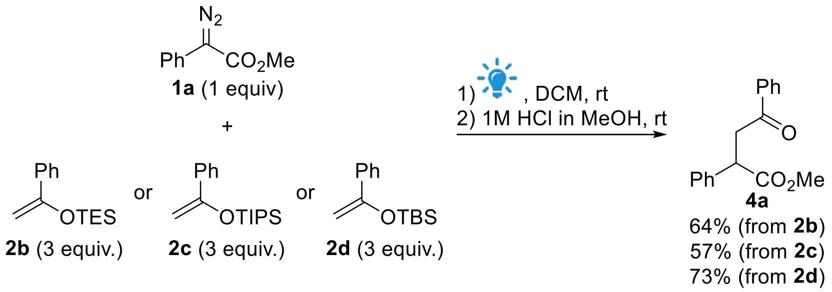


Entry	[F⁻] or HX (z equiv.)	obervations	yield **3kk** (%)[a]	yield **4kk** (%)[a]
1	70% $(HF)_x$.pyr (15)	Changing reaction vessel from glass vial to plastic falcon tube	41:22	-
2	TBAF (1)	**3kk** is not observed at the end of the reaction	-	13
3	TBAF (1.5)	degradation, **3kk** is not observed at the end of the reaction	-	-
4	TBAF (2)	degradation, **3kk** is not observed at the end of the reaction	-	-
5	1M HCl in MeOH (5)	-	42:27	-
6	1M HCl in MeOH (5), 24h	other compounds are observed in relation to reaction performed in 1h	26:16	-
7	TFA (3)	~ dirty reaction	30:19	-
8	*p*TsOH.H_2O (3)		45:28	-
9	**TfOH (1)**	**3kk** is not observed at the end of the reaction	**-**	**60/ -[b]**
10	TfOH (3)	**3kk** is not observed at the end of the reaction	-	62

Table S4. Optimization of ring-opening of more resistant cyclopropane **3ll**. Reactions performed in 0.2-mmol scale of the limiting reagent **1r**. [a]Estimated by ^1H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.



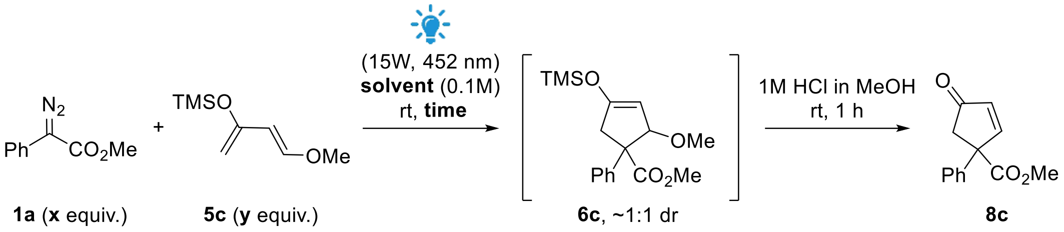
Entry	HX (z equiv.)	obervations	yield **3ll** (%)[a]	yield **4ll** (%)
1	1M HCl in MeOH (5)	No ring-opening from **3ll** to **4ll** is observed	41:19	-
2	12M HCl in H_2O (60)	No ring-opening from **3ll** to **4ll** is observed	40:18	-
3	**TfOH (1)**	**3ll** is completely consumed	**-**	**63[a]/ 60[b]**



Scheme S2. Evaluation of other silyl groups in the formal alkylation protocol.

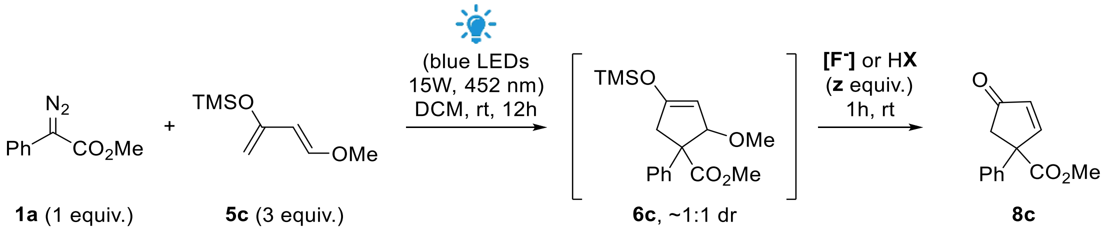
3.2. Formal [4+1]-Cycloaddition of Danishefky's Diene 5c with Aryldiazoacetate 1a.

Table S5. Reactions performed in 0.2-mmol scale of the limiting reagent. [a]Estimated by ^{1}H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield. [c]Reaction performed under ambient light, at 40 °C.



Entry	**x**	**y**	**solvent** (0.1M)	**time** (h)	yield **8c** (%)[a]
1	1	1	DCM	12	38
2	1	1	$CHCl_3$	12	< 5
3	1	1	1,2-DCE	12	13
4	1	1	AcOEt	12	17
5	1	1	MeCN	12	28
6	1	1	toluene	12	19
7	2	1	DCM	12	42
8	3	1	DCM	12	18
9	4	1	DCM	12	33
10	1	2	DCM	12	61
11	**1**	**3**	**DCM**	**12**	**70/ 69[b]**
12	1	4	DCM	12	70
13	1	3	DCM	6	63
14	1	3	DCM	24	70
15[c]	1	3	DCM	12	0

Table S6. Reactions performed in 0.2-mmol scale of the limiting reagent **1a**. [a]Estimated by ^{1}H NMR from the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal standard. [b]Isolated yield.

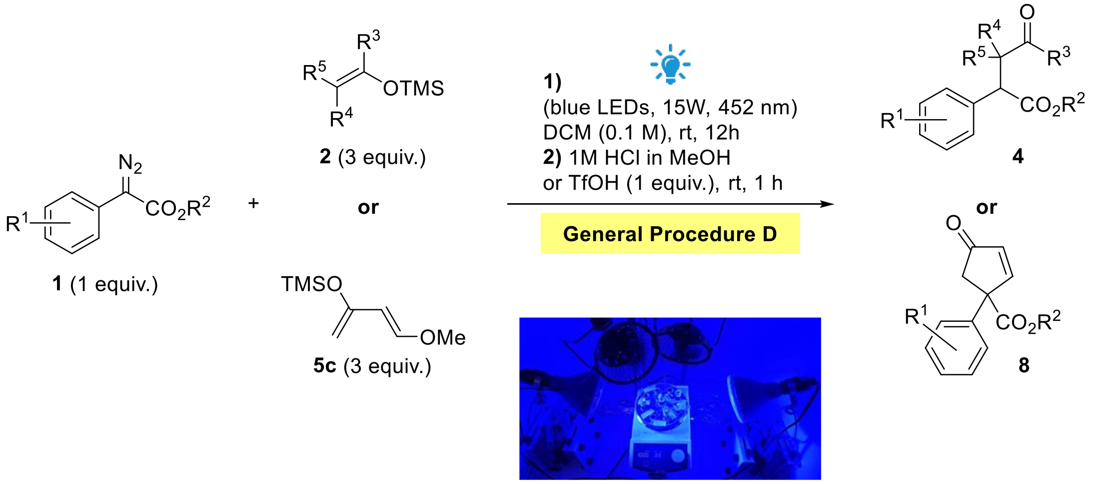


Entry	**[F$^-$]** or H**X** (**z** equiv.)	observation	yield **8c** (%)[a]
1	-	intermediate **6c** is observed as the major compound of interest, 1:1 dr	< 10
2	TBAF (3)	-	51
3	AcOH (3)	-	65

4	TFA (3)	-	67
5	*p*TSA.H_2O (3)	-	70
6	**1M HCl in MeOH (5)**	No ketal is observed	**70/ 69**[b]
7	1M HCl in EtOH (5)	No transesterification occurs, no ketal is observed	70
8	1M HCl in dioxane (5)	-	69

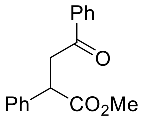
4. Scope of Key Transformations

4.1. Synthesis of γ-Keto Esters 4 and 2-Cyclopentenones 8



General Procedure D: Under air, at room temperature, a 4 mL-glass vial is charged with aryldiazoacetate **1** (0.2 mmol, 1 equiv.), DCM (0.1 M, 2 mL) and silyl enolether **2** (0.6 mmol, 3 equiv.) or Danishefsky's diene **5c** (0.6 mmol, 3 equiv.). The reaction mixture is irradiated by blue light (2 lamps, 15W each, λ_{max} = 452 nm) approximately placed at a 10 - 15 cm-distance, while being stirred at room temperature (*ca.* 30 - 35 °C) for 12h. At this point, the blue light sources are turned off and a 1M solution of HCl in MeOH (1 mL) or TfOH (1 equiv.) is added. Then, the resulting reaction mixture is allowed to stir at room temperature under ambient light for an additional 1h. Finally, the reaction is quenched with a saturated aqueous solution of $NaHCO_3$, extracted with DCM (3x), dried ($MgSO_4$), filtered and concentrated under reduced pressure. The residue obtained is purified by flash column chromatography to afford the desired product **4** or **8** in the stated yield.

Methyl 4-oxo-2,4-diphenylbutanoate[23] (4a)



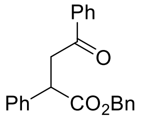
The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 μL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex - 95:5 Hex:AcOEt) affords the title compound as a white solid: 36 mg, 67% yield.

This reaction was also performed in a 1-mmol scale in relation to aryldiazoacetate **1a** (176 mg, 1 mmol, 1 equiv.) as identically described above to produce the title compound **4a** as a white solid: 134 mg, 50% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 – 7.97 (m, 2H), 7.56 (tt, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.37 – 7.33 (m, 4H), 7.32 – 7.27 (m, 1H), 4.31 (dd, *J* = 10.5 Hz, *J* = 4.0 Hz, 1H), 3.96 (dd, *J* = 18.0 Hz, *J* = 10.5 Hz, 1H), 3.70 (s, 3H), 3.28 (dd, *J* = 18.0 Hz, *J* = 4.0 Hz, 1H).

$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 197.8, 174.0, 138.5, 136.5, 133.5, 129.1, 128.8, 128.2, 128.0, 127.7, 52.5, 46.5, 43.0.

Benzyl 4-oxo-2,4-diphenylbutanoate[24] (4b)



The **General Procedure D** is performed with benzyl 2-diazo-2-phenylacetate **1b** (50 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 μL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 43 mg, 63% yield.

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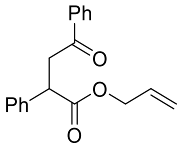
[23] ^{1}H and $^{13}C\{^1H\}$ NMR data are in good agreement with the literature. See: F. Zhao, N. Li, T. Zhang, Z.-Y. Han, S.-W. Luo, L.-Z. Gong, *Angew. Chem. Int. Ed.*, 2017, **56**, 3247-3251.

[24] ^{1}H and $^{13}C\{^1H\}$ NMR data are in good agreement with the literature. See: Q. Liu, R.-G. Wang, H.-J. Song, Y.-X. Liu, Q.-M. Wang, *Adv. Synth. Catal.*, 2020, **362**, 4391–4396.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.99 – 7.97 (m, 2H), 7.57 (tt, *J* = 7.2 Hz, *J* = 1.2 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.37 – 7.33 (m, 4H), 7.31 – 7.27 (m, 4H), 7.24 – 7.22 (m, 2H), 5.18 (d, *J* = 12.6 Hz, 1H), 5.13 (d, *J* = 12.6 Hz, 1H), 4.39 (dd, *J* = 10.8 Hz, *J* = 4.2 Hz, 1H), 3.98 (dd, *J* = 18.0 Hz, *J* = 10.8 Hz, 1H), 3.31 (dd, *J* = 18.0 Hz, *J* = 4.2 Hz, 1H).

^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 197.7, 173.3, 138.3, 136.6, 136.0, 133.4, 129.0, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 127.7, 66.8, 46.6, 42.8.

Allyl 4-oxo-2,4-diphenylbutanoate[25] (**4c**)

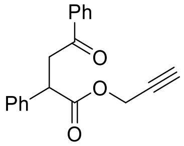


The **General Procedure D** is performed with allyl 2-diazo-2-phenylacetate **1c** (40 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO$_2$, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a colorless oil: 41 mg, 70% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.98 – 7.96 (m, 2H), 7.56 (tt, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.38 – 7.33 (m, 4H), 7.31 – 7.27 (m, 1H), 5.89 – 5.81 (m, 1H), 5.21 (ddt, *J* = 17.0 Hz, *J* = 1.5 Hz, *J* = 1.0 Hz, 1H), 5.16 (ddt, *J* = 10.5 Hz, *J* = 1.5 Hz, *J* = 1.0 Hz, 1H), 4.64 (ddt, *J* = 13.5 Hz, *J* = 5.5Hz, *J* = 1.0 Hz, 1H), 4.58 (ddt, *J* = 13.5 Hz, *J* = 6.0 Hz, *J* = 1.0 Hz, 1H), 4.33 (dd, *J* = 10.3 Hz, *J* = 4.3 Hz, 1H), 3.96 (dd, *J* = 18.0 Hz, *J* = 10.3 Hz, 1H), 3.29 (dd, *J* = 18.0 Hz, *J* = 4.3 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.7, 173.2, 138.5, 136.6, 133.5, 132.1, 129.0, 128.8, 128.2, 128.0, 127.7, 118.1, 65.7, 46.6, 42.9.

Prop-2-yn-1-yl 4-oxo-2,4-diphenylbutanoate (**4d**)



The **General Procedure D** is performed with prop-2-yn-1-yl 2-diazo-2-phenylacetate **1d** (40 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and

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[25] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: A. M. Davies, S. S. Londhe, E. R. Smith, J. A. Tunge, *Org. Lett.*, 2023, **25**, 8634-8639.

1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a colorless oil: 30 mg, 51% yield.

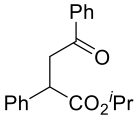
^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 – 7.96 (m, 2H), 7.58 – 7.55 (m, 1H), 7.47 – 7.44 (m, 2H), 7.38 – 7.33 (m, 4H), 7.32 – 7.28 (m, 1H), 4.73 (dd, *J* = 15.5 Hz, *J* = 2.5 Hz, 1H), 4.67 (dd, *J* = 15.5 Hz, *J* = 2.5 Hz, 1H), 4.34 (dd, *J* = 10.2 Hz, *J* = 4.1 Hz, 1H), 3.94 (dd, *J* = 18.0 Hz, *J* = 10.2 Hz, 1H), 3.31 (dd, *J* = 18.0 Hz, *J* = 4.1 Hz, 1H), 2.42 (t, *J* = 2.5 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 197.5, 172.7, 137.9, 136.5, 133.5, 129.1, 128.8, 128.3, 128.0, 127.8, 77.6, 75.1, 52.8, 46.4, 43.0.

IV (ATR, cm^{-1}): 3286, 3031, 2918, 2132, 1738, 1864, 1152.

HRMS (ESI+): Calcd. for $[C_{19}H_{16}O_3 + Na]^+$: 315.0992, found: 315.0992.

Isopropyl 4-oxo-2,4-diphenylbutanoate[26] (4e)



The **General Procedure D** is performed with isopropyl 2-diazo-2-phenylacetate **1e** (41 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:$CHCl_3$) affords the title compound as a yellow oil: 31 mg, 52% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.98 – 7.96 (m, 2H), 7.56 (tt, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 7.46 – 7.44 (m, 2H), 7.35 – 7.32 (m, 4H), 7.29 – 7.27 (m, 1H), 5.02 (hept, *J* = 6.2 Hz, 1H), 4.25 (dd, *J* = 10.4 Hz, *J* = 4.1 Hz, 1H), 3.93 (dd, *J* = 18.0 Hz, *J* = 10.4 Hz, 1H), 3.24 (dd, *J* = 18.0 Hz, *J* = 4.1 Hz, 1H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 197.9, 172.9, 138.8, 136.7, 133.4, 129.0, 128.7, 128.2, 127.9, 127.5, 68.5, 46.9, 42.9, 21.9, 21.6.

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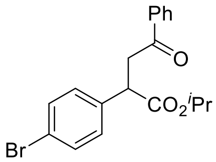
[26] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: G. N. Gururaja, S. M. Mobin, I. N. N. Namboothiri, *Eur. J. Org. Chem.*, 2011, **2011**, 2048-2052.

Isopropyl 2-(4-bromophenyl)-4-oxo-4-phenylbutanoate (**4f**)



The **General Procedure D** is performed with isopropyl 2-(4-bromophenyl)-2-diazoacetate **1f** (57 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a light yellow solid: 42 mg, 56% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 – 7.95 (m, 2H), 7.57 (tt, *J* = 7.3 Hz, *J* = 1.5 Hz, 1H), 7.47 – 7.44 (m, 4H), 7.23 (d, *J* = 8.5Hz, 2H), 5.00 (hept, *J* = 6.3 Hz, 1H), 4.21 (dd, *J* = 9.9 Hz, *J* = 4.5 Hz, 1H), 3.88 (dd, *J* = 17.9 Hz, *J* = 9.9 Hz, 1H), 3.24 (dd, *J* = 17.9 Hz, *J* = 4.5 Hz, 1H), 1.27 (d, *J* = 6.3 Hz, 3H), 1.10 (d, *J* = 6.2 Hz, 3H).

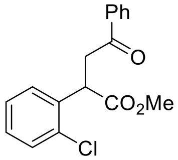
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ: 197.5, 172.5, 137.8, 136.6, 133.5, 132.1, 129.7, 128.8, 128.2, 121.5, 68.8, 46.4, 42.6, 21.9, 21.6.

M.P.: 73 – 75 °C.

IR (ATR, cm^{-1}): 2979. 2932, 1724, 1685, 1170, 1102.

HRMS (ESI+): Calcd. For $[C_{19}H_{19}BrO_3+H]^+$: 375.0590, found:375.0586.

Methyl 2-(2-chlorophenyl)-4-oxo-4-phenylbutanoate[23] **(4g)**

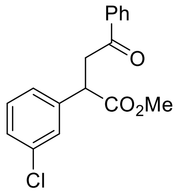


The **General Procedure D** is performed with methyl 2-diazo-2-(2-chlorophenyl)acetate **1g** (42 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and a 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a colorless oil: 29 mg, 48% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.91 – 7.89 (m, 2H), 7.50 – 7.47 (m, 1H), 7.39 – 7.36 (m, 2H), 7.34 – 7.32 (m, 1H), 7.28 – 7.26 (m, 1H), 7.19 – 7.14 (m, 2H), 4.76 (dd, *J* = 9.8 Hz, *J* = 4.1 Hz, 1H), 3.82 (dd, *J* = 18.2 Hz, *J* = 9.8 Hz, 1H), 3.65 (s, 3H), 3.20 (dd, *J* = 18.2 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 197.4, 173.5, 136.5 (x2), 133.9, 133.5, 130.2, 129.2, 128.9, 128.8, 128.3, 127.4, 52.6, 43.5, 41.6.

Methyl 2-(3-chlorophenyl)-4-oxo-4-phenylbutanoate[23] (4h)

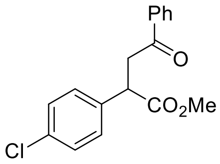


The **General Procedure D** is performed with methyl 2-(3-chlorophenyl)-2-diazoacetate **1h** (42 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 31 mg, 51% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.98 – 7.96 (m, 2H), 7.57 (tt, *J* = 7.5 Hz, *J* = 1.2 Hz, 1H), 7.47 – 7.45 (m, 2H), 7.35 (s, 1H), 7.29 – 7.23 (m, 3H), 4.28 (dd, *J* = 10.1 Hz, *J* = 4.2 Hz, 1H), 3.93 (dd, *J* = 18.0 Hz, *J* = 10.1 Hz, 1H), 3.71 (s, 3H), 3.27 (dd, *J* = 18.0 Hz, *J* = 4.2 Hz, 1H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 197.3, 173.4, 140.4, 136.4, 134.8, 133.6, 130.3, 128.8, 128.2 (x2), 128.0, 126.3, 52.7, 46.2, 42.7.

Methyl 2-(4-chlorophenyl)-4-oxo-4-phenylbutanoate[23] (4i)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-chlorophenyl)acetate **1i** (42 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a light yellow solid: 41 mg, 68% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.98 – 7.95 (m, 2H), 7.57 (tt, *J* = 7.5 Hz, *J* = 1.8 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.33 – 7.28 (m, 4H), 4.29 (dd, *J* = 9.9 Hz, *J* = 4.4 Hz, 1H), 3.91 (dd, *J* = 18.0 Hz, *J* = 9.9 Hz, 1H), 3.70 (s, 3H), 3.28 (dd, *J* = 18.0 Hz, *J* = 4.4 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 197.4, 173.7, 136.9, 136.4, 133.7, 133.6, 129.4, 129.2, 128.8, 128.2, 52.6, 45.9, 42.7.

Crystallography data for 4i (CCDC 2384541)[27]

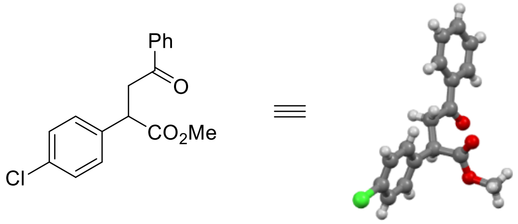


Table S7. Crystal data and structure refinement.

Empirical formula	$C_{17}H_{15}ClO_3$	
Formula weight	302.74	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P c a 21	
Unit cell dimensions	a = 10.8616(7) Å	a= 90°.
	b = 17.3612(11) Å	b= 90°.
	c = 8.0514(4) Å	g = 90°.
Volume	1518.26(16) Å^3	
Z	4	
Density (calculated)	1.324 Mg/m^3	
Absorption coefficient	0.258 mm^{-1}	
F(000)	632	
Crystal size	0.500 x 0.320 x 0.070 mm^3	
Theta range for data collection	2.212 to 26.397°.	
Index ranges	-13<=h<=13, -21<=k<=21, -10<=l<=10	
Reflections collected	22340	
Independent reflections	3096 [R(int) = 0.0863]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3096 / 1 / 191	
Goodness-of-fit on F^2	1.068	
Final R indices [I>2sigma(I)]	R1 = 0.0490, wR2 = 0.1051	
R indices (all data)	R1 = 0.0770, wR2 = 0.1220	
Absolute structure parameter	0.10(10)	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.154 and -0.228 e.Å^{-3}	

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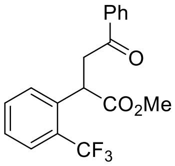
[27] CCDC 2384541 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.

Methyl 4-oxo-4-phenyl-2-(2-(trifluoromethyl)phenyl)butanoate (4j)



The **General Procedure D** is performed with methyl 2-diazo-2-(2-(trifluoromethyl)phenyl)acetate **1j** (49 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a colorless oil: 30 mg, 45% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 – 7.95 (m, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.58 – 7.54 (m, 3H), 7.47 – 7;44 (m, 2H), 7.43 – 7.39 (m, 1H), 4.75 (dd, *J* = 11.0 Hz, *J* = 3.0 Hz, 1H), 3.89 (dd, *J* = 18.0 Hz, 11.0 Hz, 1H), 3.72 (s, 3H), 3.19 (dd, *J* = 18.0 Hz, *J* = 3.0 Hz, 1H).

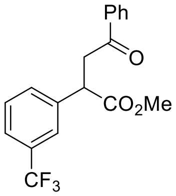
$^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ: 197.0, 173.5, 137.3, 136.3, 133.5, 132.5, 129.0, 128.8, 128.7 (q, *J* = 30.0 Hz), 128.3, 127.7, 126.6 (q, *J* = 5.6 Hz), 124.3 (q, *J* = 272.5 Hz), 52.7, 43.5, 42.1 (q, *J* = 2.5 Hz).

$^{19}F\{^1H\}$ NMR (470 MHz, $CDCl_3$) δ: -59.07.

IR (ATR, cm^{-1}): 2954, 1735, 1690.

HRMS (ESI+): Calcd. for $[C_{18}H_{15}F_3O_3 + H]^+$: 337.1046, found: 337.1046.

Methyl 4-oxo-4-phenyl-2-(3-(trifluoromethyl)phenyl)butanoate (4k)



The **General Procedure D** is performed with methyl 2-diazo-2-(3-(trifluoromethyl)phenyl)acetate **1k** (49 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a light yellow solid: 36 mg, 54% yield.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.99 – 7.95 (m, 2H), 7.62 – 7.54 (m, 4H), 7.50 – 7.43 (m, 3H), 4.38 (dd, *J* = 9.9 Hz, *J* = 4.3 Hz, 1H), 3.97 (dd, *J* = 18.0 Hz, *J* = 9.9 Hz, 1H), 3.72 (s, 3H), 3.30 (dd, *J* = 18.0 Hz, *J* = 4.3 Hz, 1H).

$^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$) δ: 197.2, 173.4, 139.5, 136.3, 133.7, 131.5, 131.4 (q, *J* = 32.2 Hz), 129.5, 128.8, 128.2, 124.8 (q, *J* = 8.4 Hz), 124.7 (d, *J* = 8.6 Hz), 124.1 (q, *J* = 270.9 Hz), 52.7, 46.3, 42.7.

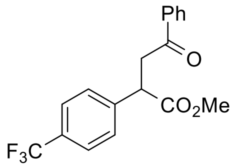
^{19}F{^{1}H} NMR (235 MHz, CDCl$_3$) δ: -62.59.

M.P.: 62 – 64 °C.

IR (ATR, cm^{-1}): 2953, 2919, 2850, 1735, 1685.

HRMS (ESI+): Calcd. for $[C_{18}H_{15}F_3O_3 + H]^+$: 337.1046, found: 337.1042.

Methyl 4-oxo-4-phenyl-2-(4-(trifluoromethyl)phenyl)butanoate[28] (4l)



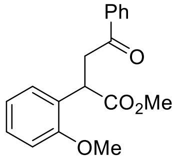
The **General Procedure D** is performed with methyl 2-diazo-2-(4-(trifluoromethyl)phenyl)acetate **1l** (49 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO$_2$, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a light-yellow oil: 36 mg, 54% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.98 – 7.96 (m, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.58 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.49 – 7.45 (m, 4H), 4.39 (dd, *J* = 9.7 Hz, *J* = 4.5 Hz, 1H), 3.95 (dd, *J* = 18.0 Hz, *J* = 9.7 Hz, 1H), 3.71 (s, 3H), 3.31 (dd, *J* = 18.0 Hz, *J* = 4.5 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.2, 173.3, 142.5, 136.4, 133.7, 130.1 (q, *J* = 32.5 Hz), 128.8, 128.5, 128.2, 126.0 (q, *J* = 3.8 Hz), 124.2 (q, *J* = 270.0 Hz), 52.7, 46.3, 42.6.

^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$) δ: -62.61.

Methyl 2-(2-methoxyphenyl)-4-oxo-4-phenylbutanoate (4m)



The **General Procedure D** is performed with methyl 2-diazo-2-(2-methoxyphenyl)acetate **1m** (41 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and1M HCl in MeOH (1mL). Purification by flash column chromatography (SiO$_2$, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 29 mg, 49% yield.

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[28] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: S. Meninno, C. Volpe, A. Lattanzi, *Adv. Synth. Catal.*, 2016, **358**, 2845-2848.

^{1}H NMR (250 MHz, CDCl$_3$) δ: 7.96 – 7.92 (m, 2H), 7.52 (tt, *J* = 7.3 Hz, *J* = 1.8 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.23 – 7.20 (m, 2H), 6.94 – 6.84 (m, 2H), 4.67 (dd, *J* = 9.7 Hz, *J* = 4.2 Hz, 1H), 3.85 (dd, *J* = 18.0 Hz, *J* = 9.7 Hz, 1H), 3.80 (s, 3H), 3.66 (s, 3H), 3.16 (dd, *J* = 18.0 Hz, *J* = 4.2 Hz, 1H).

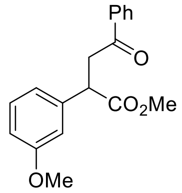
^{13}C NMR (62.5 MHz, CDCl$_3$) δ: 198.2, 174.4, 156.8, 136.8, 133.2, 129.0, 128.7 (x2), 128.3, 127.4, 121.0, 111.1, 55.6, 52.3, 41.6, 40.7.

M.P.: 62 - 64 °C.

IR (ATR, cm^{-1}): 2951, 2844, 1733, 1677.

HRMS (ESI+): Calcd. for [$C_{18}H_{18}O_4$ + H]$^+$: 299.1278, found: 299.1277.

Methyl 2-(3-methoxyphenyl)-4-oxo-4-phenylbutanoate[29] (4n)



The **General Procedure D** is performed with methyl 2-diazo-2-(3-methoxyphenyl)acetate **1n** (41 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO$_2$, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 27 mg, 45% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.99 – 7.96 (m, 2H), 7.56 (tt, *J* = 7.3 Hz, *J* = 1.3 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.26 (t, *J* = 8.0 Hz, 1H), 6.94 (dt, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H), 6.90 (t, *J* = 2.5 Hz, 1H), 6.84 (ddd, *J* = 8.0 Hz, *J* = 2.5 Hz, *J* = 1.1 Hz, 1H), 4.29 (dd, *J* = 10.4 Hz, *J* = 4.0 Hz, 1H), 3.95 (dd, *J* = 18.0 Hz, *J* = 10.4 Hz, 1H), 3.81 (s, 3H), 3.70 (s, 3H), 3.27 (dd, *J* = 18.0 Hz, *J* = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.8, 173.9, 160.1, 140.0, 136.5, 133.5, 130.1, 128.8, 128.2, 120.3, 113.8, 113.1, 55.4, 52.5, 46.5, 43.0.

M.P.: 98 – 101 °C.

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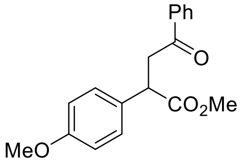
[29] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: W. Li, Y. Yang, Z. Tang, X. Yu, J. Lin, Y. Jin, *J. Org. Chem.*, 2022, **87**, 13352-13362.

Methyl 2-(4-methoxyphenyl)-4-oxo-4-phenylbutanoate[29] (4o)

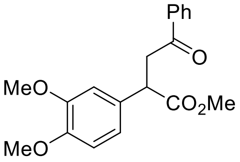


The **General Procedure D** is performed with methyl 2(4-methoxyphenyl)2-diazoacetate **1o** (41 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt - 9:1 Hex:AcOEt) affords the title compound as a white solid: 34 mg, 57% yield.

^{1}H NMR (250 MHz, $CDCl_3$) δ: 7.99 – 7.95 (m, 2H), 7.59 – 7.52 (m, 1H), 7.48 – 7.42 (m, 2H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 4.25 (dd, *J* = 10.2 Hz, *J* = 4.2 Hz, 1H), 3.92 (dd, *J* = 18.0 Hz, *J* = 10.2 Hz, 1H), 3.79 (s, 3H), 3.69 (s, 3H), 3.26 (dd, *J* = 18.0 Hz, *J* = 4.2 Hz, 1H).

^{13}C{^{1}H} NMR (62.5 MHz, $CDCl_3$) δ: 197.8, 174.2, 159.1, 136.5, 133.4, 130.5, 129.0, 128.7, 128.2, 114.4, 55.4, 52.4, 45.6, 43.0.

Methyl 2-(3,4-dimethoxyphenyl)-4-oxo-4-phenylbutanoate (4p)



The **General Procedure D** is performed with methyl 2-diazo-2-(3,4-dimethoxyphenyl)acetate **1p** (47 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a light-yellow solid: 39 mg, 59% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.98 – 7.96 (m, 2H), 7.56 (tt, *J* = 7.2 Hz, *J* = 1.4 Hz, 1H), 7.47 – 7.43 (m, 2H), 6.90 – 6.86 (m, 2H), 6.83 (d, *J* = 8.2 Hz, 1H), 4.23 (dd, *J* = 10.4 Hz, *J* = 4.1 Hz, 1H), 3.92 (dd, *J* = 18.0 Hz, *J* = 10.4 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.70 (s, 3H), 3.27 (dd, *J* = 18.0 Hz, *J* = 4.1 Hz, 1H).

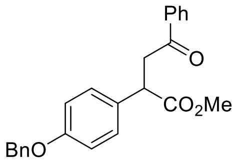
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 197.9, 174.2, 149.3, 148.6, 136.6, 133.4, 130.9, 128.7, 128.2, 120.0, 111.6, 111.1, 56.1, 56.0, 52.5, 46.1, 43.1.

M.P.: 76 - 77 °C.

IR (ATR, cm^{-1}): 3001, 2950, 2836, 1731, 1683, 1515.

HRMS (ESI+): Calcd. for $[C_{19}H_{20}O_5 + H]^+$: 329.1384, found: 329.1386.

Methyl 2-(4-(benzyloxy)phenyl)-4-oxo-4-phenylbutanoate (4q)



The **General Procedure D** is performed with methyl 2-(4-(benzyloxy)phenyl)-2-diazoacetate **1q** (56 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a colorless oil: 39 mg, 52% yield.

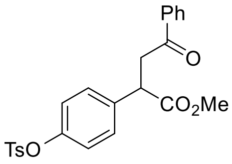
^{1}H NMR (600 MHz, $CDCl_3$) δ: 7.97 – 7.96 (m, 2H), 7.56 (tt, *J* = 7.4 Hz, *J* = 1.5 Hz, 1H), 7.47 – 7.42 (m, 4H), 7.40 – 7.37 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.96 (d, *J* = 8.7 Hz, 2H), 5.05 (s, 2H), 4.25 (dd, *J* = 10.2 Hz, *J* = 4.1 Hz, 1H), 3.92 (dd, *J* = 18.0 Hz, *J* = 10.2 Hz, 1H), 3.69 (s, 3H), 3.26 (dd, *J* = 18.0 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) ***(1C could not be unambiguously assigned)*** **δ:** 197.9, 174.2, 158.4, 137.0, 136.6, 133.5, 130.8, 129.1, 128.8, 128.2 (x2), 127.6, 115.4, 70.2, 52.5, 45.7, 43.0.

IR (ATR, cm^{-1}): 2951, 2923, 2868, 1732, 1683, 1510, 1223, 1131, 1003.

HRMS (ESI+): Calcd. for $[C_{24}H_{22}O_4 + H]^+$: 375.1591, found: 375.1592.

Methyl 4-oxo-4-phenyl-2-(4-(tosyloxy)phenyl)butanoate (4r)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate **1r** (69 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:$CHCl_3$ – 85:15 Hex:$CHCl_3$) affords the title compound as a white solid: 48 mg, 55% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 – 7.94 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.57 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.48 – 7.44 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.7 Hz, 2H), 6.97 (d, *J* = 8.7 Hz, 2H), 4.27 (dd, *J* = 10.0 Hz, *J* = 4.3 Hz, 1H), 3.88 (dd, *J* = 18.0 Hz, *J* = 10.0 Hz, 1H), 3.69 (s, 3H), 3.25 (dd, *J* = 18.0 Hz, *J* = 4.3 Hz, 1H), 2.46 (s, 3H).

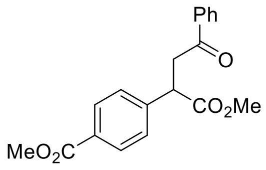
^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 197.4, 173.6, 149.1, 145.6, 137.4, 136.4, 133.6, 132.7, 130.0, 129.3, 128.8, 128.6, 128.2, 123.0, 52.6, 45.9, 42.8, 21.9.

M.P.: 100 - 103°C.

IR (ATR, cm^{-1}): 3058, 1732, 1685, 1569, 1348.

HRMS (ESI+): Calcd. for [$C_{24}H_{22}O_6S$ + H]$^+$: 439.1210, found: 439.1209.

Methyl 4-(1-methoxy-1,4-dioxo-4-phenylbutan-2-yl)benzoate (4v)



The **General Procedure D** is performed with methyl 4-(1-diazo-2-methoxy-2-oxoethyl)benzoate **1v** (47 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 36 mg 55% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.02 (d, *J* = 8.5 Hz, 2H), 7.98 – 7.96 (m, 2H), 7.57 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.47 – 7.42 (m, 4H), 4.38 (dd, *J* = 10.0 Hz, *J* = 4.4 Hz, 1H), 3.95 (dd, *J* = 18.0 Hz, *J* = 10.0 Hz, 1H), 3.91 (s, 3H), 3.70 (s, 3H), 3.30 (dd, *J* = 18.0 Hz, *J* = 4.4 Hz, 1H).

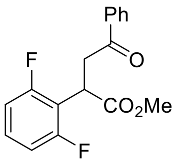
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.3, 173.4, 166.9, 143.6, 136.4, 133.6, 130.4, 129.7, 128.8, 128.3, 128.1, 52.7, 52.3, 46.5, 42.6.

M.P.: 97 - 99°C.

IR (ATR, cm^{-1}): 2990, 2954, 1732, 1716, 1677.

HRMS (ESI+): Calcd. for [$C_{19}H_{18}O_5$ + H]$^+$: 327.1227, found: 327.1227.

Methyl 2-(2,6-difluorophenyl)-4-oxo-4-phenylbutanoate (4w)



The **General Procedure D** is performed with methyl 2-diazo-2-(2,6-difluorophenyl)acetate **1w** (42 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a colorless oil: 29 mg, 48% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.00 – 7.98 (m, 2H), 7.56 (tt, *J* = 7.5 Hz, *J* = 1.3 Hz, 1H), 7.47 – 7.44 (m, 2H), 7.27 – 7.21 (m, 1H), 6.93 – 6.88 (m, 2H), 4.89 (dd, *J* = 8.5 Hz, *J* = 5.2 Hz, 1H), 4.11 (dd, *J* = 17.9 Hz, *J* = 8.5 Hz, 1H), 3.70 (s, 3H), 3.19 (dd, *J* = 17.9 Hz, *J* = 5.2 Hz, 1H).

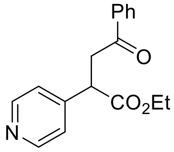
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.1, 172.2, 161.3 (dd, *J* = 247.5 Hz, *J* = 7.9 Hz), 136.6, 133.4, 129.2 (t, *J* = 10.6 Hz), 128.7, 128.3, 115.5 (t, *J* = 18.8 Hz), 111.7 (dd, *J* = 20.0 Hz, *J* = 5.2 Hz), 52.8, 39.6, 35.2 (t, *J* = 3.1 Hz).

^{19}F{^{1}H} NMR (470 MHz, CDCl$_3$) δ: -113.49.

IR (ATR, cm^{-1}): 2954, 1740, 1686, 1470, 1234, 1000.

HRMS (ESI+): Calcd. for: $[C_{17}H_{15}F_2O_3]^+$: 305.0984, found: 305.0981.

Ethyl 4-oxo-4-phenyl-2-(pyridin-4-yl)butanoate (**4x**)



The **General Procedure D** is performed with ethyl 2-diazo-2-(pyridin-4-yl)acetate **1x** (38 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO$_2$, gradient: 8:2:1 Hex:AcOEt:Et$_3$N – 6.5:3.5:1 Hex:AcOEt:Et$_3$N) affords the title compound as a yellow solid: 10 mg, 18% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 8.58 – 8.57 (m, 2H), 7.97 – 7.95 (m, 2H), 7.58 (tt, *J* = 7.2 Hz, *J* = 1.5 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.30 – 7.28 (m, 2H), 4.29 (dd, *J* = 9.7 Hz, *J* = 4.6 Hz, 1H), 4.21 (dq, *J* = 10.8 Hz, *J* = 7.2 Hz, 1H), 4.14 (dq, *J* = 10.8 Hz, *J* = 7.2 Hz, 1H), 3.92 (dd, *J* = 18.0 Hz, *J* = 9.7 Hz, 1H), 3.29 (dd, *J* = 18.0 Hz, *J* = 4.6 Hz, 1H), 1.22 (t, *J* = 7.2 Hz, 3H).

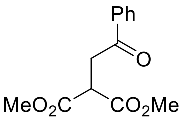
^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 197.0, 172.2, 150.4, 147.5, 136.3, 133.7, 128.9, 128.2, 123.2, 61.7, 46.2, 42.0, 14.2.

IR (ATR, cm^{-1}): 3029, 2982, 1731, 1686, 1599.

M.P.: 50 – 51 °C.

HRMS (ESI+): Calcd. for $[C_{17}H_{17}NO_3 + H]^+$: 284.1281, found: 284.1280.

Dimethyl 2-(2-oxo-2-phenylethyl)malonate[30] (4z)

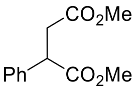


The **General Procedure D** is performed with dimethyl 2-(phenyl-λ^3-iodaneylidene)malonate **1z'** (67 mg, 0.2 mmol, 1 equiv.), trimethyl((1-phenylvinyl)oxy)silane **2a** (123 µL, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a colorless oil: 20 mg, 40% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 – 7.97 (m, 2H), 7.61 – 7.57 (m, 1H), 7.50 – 7.45 (m, 2H), 4.10 (t, *J* = 7.1 Hz, 1H), 3.79 (s, 6H), 3.65 (d, *J* = 7.1 Hz, 2H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 196.6, 169.6, 136.1, 133.7, 128.8, 128.3, 53.0, 47.0, 38.1.

Dimethyl 2-phenylsuccinate[31] (4aa)



The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), *tert*-butyl((1-methoxyvinyl)oxy)dimethylsilane **2e** (140 µL, 0.6 mmol, 3 equiv., 95%), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a white solid: 27 mg, 61% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.35 – 7.31 (m, 2H), 7.29 – 7.26 (m, 3H), 4.10 (dd, *J* = 10.1 Hz, *J* = 5.2 Hz, 1H), 3.68 (s, 3H), 3.67 (s, 3H), 3.21 (dd, *J* = 17.0 Hz, *J* = 10.1 Hz, 1H), 2.67 (dd, *J* = 17.0 Hz, *J* = 5.2 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 173.6, 172.2, 137.8, 129.1, 127.9, 127.8, 52.5, 52.0, 47.2, 37.8.

M.P.: 53 - 55 °C.

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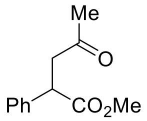
[30] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: P. Chandu, S. Biswas, K. Pal, D. Sureshkumar, *J. Org. Chem.*, 2024, **89**, 3912-3925.

[31] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: M. Luo, Z. Liu, H. Chen, H. Fu, R. Li, X. Zheng, *Journal of Catalysis*, 2024, **433**, 115459.

Methyl 4-oxo-2-phenylpentanoate[32] (4bb)

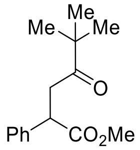


The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), (isopropenyloxy)trimethylsilane **2f** (200 μL, 1 mmol, 5 equiv., ≥ 85%), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt) affords the title compound as a yellow oil: 32 mg, 77% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.34 – 7.30 (m, 2H), 7.29 – 7.24 (m, 3H), 4.11 (dd, *J* = 10.4 Hz, *J* = 4.2 Hz, 1H), 3.66 (s, 3H), 3.40 (dd, *J* = 18.0 Hz, *J* = 10.4 Hz, 1H), 2.72 (dd, *J* = 18.1 Hz, *J* = 4.2 Hz, 1H), 2.18 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 206.4, 173.9, 138.3, 129.0, 127.9, 127.7, 52.5, 47.3, 46.3, 30.1.

Methyl 5,5-dimethyl-4-oxo-2-phenylhexanoate (4cc)



The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), ((3,3-dimethylbut-1-en-2-yl)oxy)trimethylsilane **2g** (132 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5) affords the title compound as a yellow oil: 9 mg, 18% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34 – 7.31 (m, 2H), 7.28 – 7.25 (m, 3H), 4.10 (dd, *J* = 10.4 Hz, *J* = 4.2 Hz, 1H), 3.66 (s, 3H), 3.44 (dd, *J* = 18.1 Hz, *J* = 10.4 Hz, 1H), 2.77 (dd, *J* = 18.1 Hz, *J* = 4.2 Hz, 1H), 1.14 (s, 9H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 213.9, 174.1, 138.6, 129.0, 127.9, 127.6, 52.4, 46.4, 44.1, 41.3, 26.5.

IR (ATR, cm^{-1}): 2958, 2872, 1735, 1705, 1228, 1166.

HRMS (ESI+): Calcd. for $[C_{15}H_{20}O_3 + Na]^+$: 271.1305, found: 271.1306.

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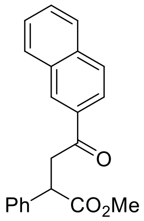
[32] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: X.-Q. Yu, T. Shirai, Y. Yamamoto, N. Miyaura, *Chem. Asian J.*, 2011, **6**, 932-937.

Methyl 4-(naphthalen-2-yl)-4-oxo-2-phenylbutanoate[23] (4ee)



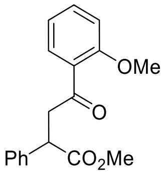
The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), *tert*-butyldimethyl((1-(naphthalen-2-yl)vinyl)oxy)silane **2j** (170 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid: 26 mg, 41% yield.

^{1}H NMR (600 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 8.03 (dd, *J* = 8.6 Hz, *J* = 1.7 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 1H), 7.90 – 7.86 (m, 2H), 7.61 – 7.59 (m, 1H), 7.56 – 7.54 (m, 1H), 7.41 – 7.36 (m, 4H), 7.32 – 7.31 (m, 1H), 4.37 (dd, *J* = 10.3 Hz, *J* = 4.1 Hz, 1H), 4.10 (dd, *J* = 17.8 Hz, *J* = 10.3 Hz, 1H), 3.72 (s, 3H), 3.42 (dd, *J* = 17.8 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ: 197.7, 174.1, 138.6, 135.9, 133.9, 132.6, 130.1, 129.7, 129.1, 128.7, 128.6, 128.0, 127.9, 127.7, 127.0, 123.9, 52.5, 46.6, 43.1.

MP: 58 – 60 °C.

Methyl 4-(2-methoxyphenyl)-4-oxo-2-phenylbutanoate[33] (4ff)



The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), *tert*-butyl((1-(2-methoxyphenyl)vinyl)oxy)dimethylsilane **2k** (159 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a colorless oil: 28 mg, 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.76 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 1H), 7.46 (td, *J* = 8.5 Hz, *J* = 1.4 Hz, 1H), 7.34 – 7.33 (m, 4H), 7.29 – 7.27 (m, 1H), 6.99 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 8.5 Hz, 1H), 4.27 (dd, *J* = 10.2 Hz, *J* = 4.1 Hz, 1H), 3.92 (dd, *J* = 18.1 Hz, *J* = 10.2 Hz, 1H), 3.88 (s, 3H), 3.69 (s, 3H), 3.37 (dd, *J* = 18.1 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 199.4, 174.2, 159.1, 138.8, 134.0, 130.7, 128.9, 128.1, 127.5, 127.4, 120.8, 111.7, 55.7, 52.4, 48.0, 46.9.

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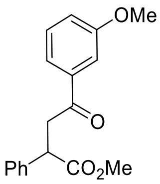
[33] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: W.-J. Zhao, M. Yan, D. Huang, S.-J. Ji, *Tetrahedron*, 2005, **61**, 5585 - 5593.

Methyl 4-(3-methoxyphenyl)-4-oxo-2-phenylbutanoate[23] **(4gg)**

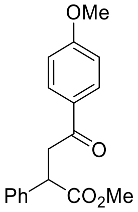


The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), *tert*-butyl((1-(3-methoxyphenyl)vinyl)oxy)dimethylsilane **2l** (159 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a colorless oil: 32 mg, 54% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.56 (d, *J* = 7.7 Hz, 1H), 7.49 (dd, *J* = 2.2 Hz, *J* = 1.8 Hz, 1H), 7.37 – 7.33 (m, 5H), 7.32 – 7.27 (m, 1H), 7.11 (dd, *J* = 8.2 Hz, *J* = 2.2 Hz, 1H), 4.29 (dd, *J* = 10.3 Hz, *J* = 4.1 Hz, 1H), 3.93 (dd, *J* = 18.0 Hz, *J* = 10.3 Hz, 1H), 3.84 (s, 3H), 3.70 (s, 3H), 3.28 (dd, *J* = 18.0 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.6, 174.0, 160.0, 138.5, 137.9, 129.7, 129.1, 128.0, 127.7, 120.9, 120.1, 112.3, 55.6, 52.5, 46.5, 43.1.

Methyl 4-(4-methoxyphenyl)-4-oxo-2-phenylbutanoate[33] **(4hh)**



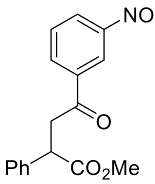
The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), *tert*-butyl((1-(4-methoxyphenyl)vinyl)oxy)dimethylsilane **2m** (159 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid: 42 mg, 71% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 7.95 (d, *J* = 9.0 Hz, 2H), 7.36 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 6.92 (d, *J* = 9.0 Hz, 2H), 4.29 (dd, *J* = 10.0 Hz, *J* = 4.1 Hz, 1H), 3.90 (dd, *J* = 17.9 Hz, *J* = 10.0 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 3.23 (dd, *J* = 17.9 Hz, *J* = 4.1 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 196.3, 174.1, 163.8, 138.7, 130.5, 129.7, 129.0, 128.0, 127.7, 113.9, 55.6, 52.5, 46.6, 42.6.

M.P.: 77 – 79 °C.

Methyl 4-(3-nitrophenyl)-4-oxo-2-phenylbutanoate (4jj)



The **General Procedure D** is performed with methyl 2-diazo-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), ((1-(3-nitrophenyl)vinyl)oxy)(tert-butyl)dimethylsilane **2o** (168 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and TfOH (18 µL, 0.6 mmol, 1 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a colorless oil: 31 mg, 50% yield.

The same reaction was performed again in the same manner as previously described, but this time using TfOH (54 µL, 0.6 mmol, 3 equiv.) and afforded the title compound as a white solid: 33 mg, 53% yield.

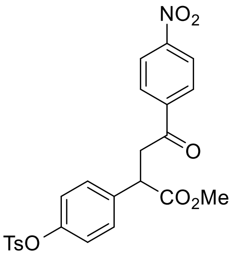
^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.79 (t, *J* = 2.0 Hz, 1H), 8.43 (ddd, *J* = 8.0 Hz, *J* = 2.4 Hz, *J* = 1.2 Hz, 1H), 8.30 (dt, *J* = 8.0 Hz, *J* = 1.4 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 7.40 – 7.29 (m, 5H), 4.34 (dd, *J* = 10.3 Hz, *J* = 4.0 Hz, 1H), 4.00 (dd, *J* = 18.1 Hz, *J* = 10.3 Hz, 1H), 3.71 (s, 3H), 3.28 (dd, *J* = 18.1 Hz, *J* = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 195.7, 173.7, 148.6, 137.9, 137.7, 133.8, 130.1, 129.2, 128.0, 127.9, 127.8, 123.2, 52.6, 46.4, 43.1.

IR (ATR, cm^{-1}): 3087, 3031, 2953, 1732, 1693, 1614, 1530, 1350.

HRMS (ESI+): Calcd. for $[C_{17}H_{15}NO_5 + H]^+$: 314.1023, found: 314.1025.

Methyl 4-(4-nitrophenyl)-4-oxo-2-(4-(tosyloxy)phenyl)butanoate (4ll)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate **1r** (69 mg, 0.2 mmol, 1 equiv.), tert-butyldimethyl((1-(4-nitrophenyl)vinyl)oxy)silane **2p** (168 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and TfOH (18 µL, 0.2 mmol, 1 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 7:3 Hex:AcOEt) affords the title compound as a yellowish solid: 58 mg, 60 % yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.31 (d, *J* = 8.9 Hz, 2H), 8.11 (d, *J* = 8.9 Hz, 2H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 4.28 (dd, *J* = 10.2 Hz, *J* = 4.0 Hz, 1H), 3.93 (dd, *J* = 18.1 Hz, *J* = 10.2 Hz, 1H), 3.70 (s, 3H), 3.24 (dd, *J* = 18.1 Hz, *J* = 4.0 Hz, 1H), 2.46 (s, 3H).

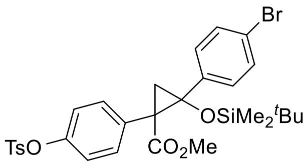
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 196.1, 173.3, 150.7, 149.2, 145.7, 140.7, 136.8, 132.7, 130.0, 129.3, 129.2, 128.6, 124.1, 123.1, 52.8, 45.8, 43.2, 21.9.

M.P.: 99 - 100 °C.

IR (ATR, cm^{-1}): 2955, 2924, 1736, 1695, 1527, 1346, 1179.

HRMS (ESI+): Calcd. for [$C_{24}H_{21}NO_8S$ + H]$^+$: 484.1061, found: 484.1062.

Methyl 2-(4-bromophenyl)-2-((tert-butyldimethylsilyl)oxy)-1-(4-(tosyloxy)phenyl)cyclopropane-1-carboxylate (3mm)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate **1r** (69 mg, 0.2 mmol, 1 equiv.), ((1-(4-bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane **2q** (188 mg, 0.6 mmol, 2 equiv.) and DCM (2 mL). *No treatment with acid was performed*. The crude residue was purified by flash column chromatography using Et$_3$N-deactivated silica (SiO$_2$, gradient: 98:0:2 Hex:AcOEt:Et$_3$N – 92:6:2 Hex:AcOEt:Et$_3$N) affording the title compound as a colorless oil: 85 mg, 68% yield, 1.6:1 dr.

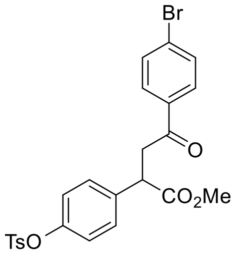
^{1}H NMR (500 MHz, CDCl$_3$) (mixture of diastereosiomers, 1.6:1 dr) δ: 7.98 (d, *J* = 8.0 Hz, 3.2H), 7.75 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.5 Hz, 3.2H), 7.65 (d, *J* = 8.5 Hz, 3.2 H), 7.58 – 7.51 (m, 8.4H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 8.5 Hz, 5.2H), 6.88 (d, *J* = 8.5 Hz, 2H), 3.93 (s, 3H), 3.46 (s, 4.8H), 2.88 (d, *J* = 6.5 Hz, 1.6H), 2.69 (s, 7.8H), 2.65 (d, *J* = 7.0 Hz, 1H), 2.33 (d, *J* = 7.0 Hz, 1H), 1.87 (d, *J* = 6.5 Hz, 1.6H), 1.11 (s, 9H), 0.72 (s, 14.4H), 0.33 (s, 3H), -0.01 (s, 7.8H), -0.14 (s, 4.8H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) (mixture of diastereosiomers, 1.6:1 dr) δ: 170.0, 169.2, 148.9, 148.4, 145.4, 145.3, 138.1, 137.9, 134.8, 134.5, 133.3, 132.8, 132.3, 132.2, 131.2, 130.8, 130.2, 129.9, 129.8, 128.9, 128.6, 128.5, 122.0, 121.7 (x2), 121.3, 66.5, 66.1, 52.6, 52.3, 42.8, 41.6, 25.7, 25.2, 24.1, 21.8, 21.5, 18.0, 17.6, -3.65, -3.99, -4.38.

IR (ATR, cm^{-1}): 2930, 2952, 2857, 1725, 1598, 1505, 1375, 1199, 1178, 1155.

HRMS (ESI+): Calcd. for [$C_{30}H_{35}BrO_6$ SSi + Na]$^+$: 653.1005, found: 653.1002.

Methyl 4-(4-bromophenyl)-4-oxo-2-(4-(tosyloxy)phenyl)butanoate (**4mm**)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate **1r** (69 mg, 0.2 mmol, 1 equiv.), ((1-(4-bromophenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane **2q** (188 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and TfOH (18 μL, 0.2 mmol, 1 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a white solid: 57 mg, 55% yield.

The same reaction was performed again in the same manner as previously described, but this time using TfOH (54 μL, 0.6 mmol, **3 equiv.**) and afforded the title compound as a white solid: 55 mg, 53% yield.

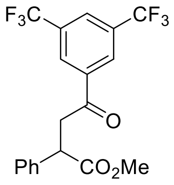
^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 4.25 (dd, *J* = 10.2 Hz, *J* = 4.2 Hz, 1H), 3.84 (dd, *J* = 18.0 Hz, *J* = 10.2 Hz, 1H), 3.69 (s, 3H), 3.19 (dd, *J* = 18.0 Hz, *J* = 4.2 Hz, 1H), 2.46 (s, 3H).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ: 196.4, 173.5, 149.1, 145.6, 137.2, 135.1, 132.7, 132.2, 130.0, 129.7, 129.3, 128.9, 128.6, 123.0, 52.7, 45.8, 42.7, 21.9.

IR (ATR, cm^{-1}): 2952, 1736, 1687, 1587, 1503, 1200, 1179, 1154.

HRMS (ESI+): Calcd. for $[C_{24}H_{21}BrO_6S + H]^+$: 517.0320 found: 517.0316.

Methyl 4-(3,5-bis(trifluoromethyl)phenyl)-4-oxo-2-phenylbutanoate (4nn)



The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), ((1-(3,5-bis(trifluoromethyl)phenyl)vinyl)oxy)(*tert*-butyl)dimethylsilane **2r** (222 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and TfOH (18 μL, 0.2 mmol, 1 equiv.). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt) affords the title compound as a colorless oil: 32 mg, 40% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 8.39 (s, 2H), 8.07 (s, 1H), 7.39 – 7.31 (m, 5H), 4.34 (dd, *J* = 10.2 Hz, *J* = 4.2 Hz, 1H), 3.98 (dd, *J* = 18.3 Hz, *J* = 10.2 Hz, 1H), 3.71 (s, 3H), 3.27 (dd, *J* = 18.3 Hz, *J* = 4.2 Hz, 1H).

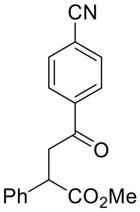
^{13}C{^{1}H} NMR (150 MHz, CDCl$_3$) δ: 195.2, 173.7, 138.0, 137.8, 132.6 (q, *J* = 34.5 Hz), 129.3, 128.3 (q, *J* = 4.5 Hz), 128.1, 127.9, 126.7 (hept, *J* = 3.0 Hz), 123.0 (q, *J* = 271.5 Hz), 52.7, 46.4, 43.1.

^{19}F{^{1}H} NMR (564 MHz, CDCl$_3$) δ: -62.95.

IR (ATR, cm^{-1}): 2961, 2924, 1728, 1699, 1280, 1182, 1169, 1125.

HRMS (ESI+): Calcd. for [$C_{19}H_{14}F_6O_3$ + H]$^+$: 405.0920, found: 405.0921.

Methyl 4-(4-cyanophenyl)-4-oxo-2-phenylbutanoate[29] (4oo)

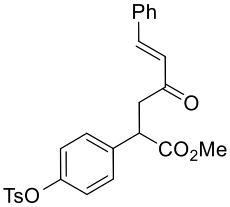


The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), 4-(1-((*tert*-butyldimethylsilyl)oxy)vinyl)benzonitrile **2s** (156 mg, 0.6 mmol, 3 equiv.), DCM (2 mL) and TfOH (18 µL, 0.2 mmol, 1 equiv.). Purification by flash column chromatography (SiO$_2$, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a white solid: 29 mg, 50% yield.

^{1}H NMR (500 MHz, CDCl$_3$) δ: 8.06 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.28 (m, 5H), 4.30 (dd, *J* = 10.3 Hz, *J* = 4.0 Hz, 1H), 3.95 (dd, *J* = 18.1 Hz, *J* = 10.3 Hz, 1H), 3.70 (s, 3H), 3.24 (dd, *J* = 18.1 Hz, *J* = 4.0 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 196.6, 173.7, 139.4, 138.0, 132.7, 129.2, 128.7, 127.9 (x2), 118.0, 116.8, 52.6, 46.4, 43.2.

Methyl (E)-4-oxo-6-phenyl-2-(4-(tosyloxy)phenyl)hex-5-enoate (7b)



The **General Procedure D** is performed with methyl 2-diazo-2-(4-(tosyloxy)phenyl)acetate **1r** (69 mg, 0.2 mmol, 1 equiv.), (*E*)-tert-butyldimethyl((4-phenylbuta-1,3-dien-2-yl)oxy)silane **5b** (156 mg, 0.6 mmol, 3 equiv.) DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO$_2$, gradient: Hex -

95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a light yellow solid: 68 mg, 73% yield.

^{1}H NMR (600 MHz, CDCl$_3$) δ: 7.72 (d, *J* = 7.8 Hz, 2H), 7.56 (d, *J* = 16.2 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.40 – 7.38 (m, 3H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 6.72 (d, *J* = 16.2 Hz, 1H), 4.20 (dd, *J* = 10.0 Hz, *J* = 4.5 Hz, 1H), 3.68 (s, 3H), 3.58 (dd, *J* = 17.7 Hz, *J* = 10.0 Hz, 1H), 2.96 (dd, *J* = 17.7 Hz, *J* = 4.5 Hz, 1H), 2.45 (s, 3H).

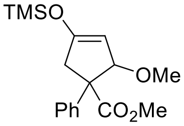
^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) δ: 197.2, 173.5, 149.0, 145.6, 143.5, 137.4, 134.4, 132.6, 130.8, 129.9, 129.2, 129.1, 128.6, 128.5, 125.7, 122.9, 52.6, 45.7, 44.4, 21.8.

M.P.: 114-113 °C.

IR (ATR, cm^{-1}): 3059, 2951, 1733, 1690, 1611, 1599, 1502, 1200, 1178, 1152.

HRMS (ESI+): Calcd. for [$C_{26}H_{24}O_6S$ + H]$^+$: 465.1366, found: 465.1369.

Methyl 2-methoxy-1-phenyl-4-((trimethylsilyl)oxy)cyclopent-3-ene-1-carboxylate (6c)



The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv) and DCM (2 mL). *No treatment with acid was performed.* Upon reaction completion (TLC), the reaction mixture is carefully evaporated under reduced pressure for a prolonged time (to eliminate the excess of the Danishefsky's diene **5c**) and the resulting crude reaction mixture contained the title compound as the major compound, 1:1 dr.

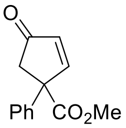
^{1}H NMR (500 MHz, CDCl$_3$) (mixture of diastereoisomers, 1:1 dr) δ: 7.17 – 7.15 (m, 2H), 7.14-7.09 (m, 4H), 7.07 – 7.02 (m, 4H), 4.85 (d, *J* = 2.5 Hz, 1H), 4.82 (td, *J* = 2.3 Hz, *J* = 1.0 Hz, 1H), 4.77 (td, *J* = 2.5 Hz, *J* = 1.0 Hz, 1H), 4.50 (dd, *J* = 2.5 Hz, *J* = 2.3 Hz, 1H), 3.52 – 3.48 (m, 4H), 3.45 (s, 3H), 3.15 (s, 3H), 3.00 (d, *J* = 15.5 Hz, 1H), 2.90 – 2.86 (m, 4H), 2.03 (d, *J* = 16.0 Hz, 1H), 0.08 (s, 9H), 0.00 (s, 9H).

^{13}C{^{1}H} NMR (125 MHz, CDCl$_3$) (mixture of diastereoisomers, 1:1 dr) δ: 175.0, 173.6, 159.6, 159.5, 143.8, 138.3, 128.4, 128.0 (x2), 127.0, 126.9, 126.2, 102.1, 100.4, 88.0, 85.5, 61.1, 61.0, 56.7, 55.3, 52.7, 52.1, 44.1, 40.9, 0.1, 0.0.

IR (ATR, cm^{-1}): 2953, 1729, 1637, 1498, 1449, 1436, 1335, 1300, 1251, 1220, 1167, 1086.

HRMS (ESI+): Calcd. for [$C_{17}H_{24}O_4Si$ + H]$^+$: 321.1517, found: 321.1505.

Methyl 4-oxo-1-phenylcyclopent-2-ene-1-carboxylate[34] (8c)

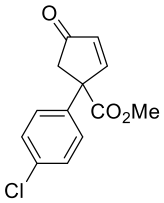


The **General Procedure D** is performed with methyl 2-diazo-2-phenylacetate **1a** (35 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil: 30 mg, 69% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.96 (d, *J* = 5.7 Hz, 1H), 7.38 – 7.34 (m, 2H), 7.30 (tt, *J* = 7.0 Hz, *J* = 1.5 Hz, 1H), 7.22 – 7.19 (m, 2H), 6.34 (d, *J* = 5.7 Hz, 1H), 3.76 (s, 2H), 3.51 (d, *J* = 18.8 Hz, 1H), 2.60 (d, *J* = 18.9 Hz, 1H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 207.1, 172.5, 163.1, 141.0, 134.3, 129.3, 128.0, 126.0, 60.1, 53.3, 47.0.

Methyl 1-(4-chlorophenyl)-4-oxocyclopent-2-ene-1-carboxylate (8d)



The **General Procedure D** is performed with methyl 2-(4-chlorophenyl)-2-diazoacetate **1i** (42 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a pale yellow oil: 33 mg, 66% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92 (d, *J* = 5.6 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.35 (d, *J* = 5.6 Hz, 1H), 3.75 (s, 3H), 3.50 (d, *J* = 18.8 Hz, 1H), 2.54 (d, *J* = 18.8 Hz, 1H).

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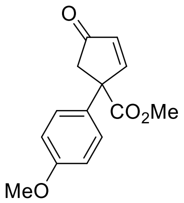
[34] ^{1}H and ^{13}C{^{1}H} NMR data are in good agreement with the literature. See: Q. Gui, J. J. Wang, S. Ng, A. Dancevic, T. B. Wright, P. A. Evans, *Chem. Commun.*, 2019, **55**, 12368-12371.

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ: 206.5, 172.1, 162.4, 139.5, 134.6, 134.1, 129.4, 127.5, 59.6, 53.4, 46.8.

IR (ATR, cm^{-1}): 2956, 1737, 1704, 1164, 1090.

HRMS (ESI+): Calcd. for $[C_{13}H_{11}ClO_3 + H]^+$: 251.0469, found: 251.0471.

Methyl 1-(4-methoxyphenyl)-4-oxocyclopent-2-ene-1-carboxylate[34] (8e)

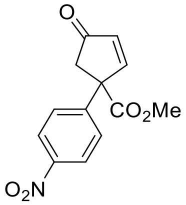


The **General Procedure D** is performed with methyl 2-(4-methoxyphenyl)-2-diazoacetate **1o** (41 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 98:2 Hex:AcOEt – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt) affords the title compound as a light-yellow oil: 29 mg, 59% yield.

^1H NMR (250 MHz, $CDCl_3$) δ: 7.94 (d, *J* = 5.6 Hz, 1H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.31 (d, *J* = 5.6 Hz, 1H), 3.79 (s, 3H), 3.74 (s, 3H), 3.47 (d, *J* = 18.9 Hz, 1H), 2.58 (d, *J* = 18.9 Hz, 1H).

$^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$) δ: 207.3, 172.7, 163.3, 159.2, 134.0, 133.0, 127.2, 114.6, 59.4, 55.5, 53.2, 47.0.

Methyl 1-(4-nitrophenyl)-4-oxocyclopent-2-ene-1-carboxylate (8f)



The **General Procedure D** is performed with methyl 2-(4-nitrophenyl)-2-diazoacetate **1u** (44 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt – 1:1 Hex:AcOEt) affords the title compound as a light-yellow oil: 24 mg, 46% yield.

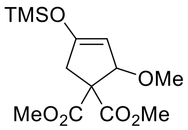
^1H NMR (250 MHz, $CDCl_3$) δ: 8.23 (d, *J* = 8.9 Hz, 2H), 7.94 (d, *J* = 5.7 Hz, 1H), 7.41 (d, *J* = 8.9 Hz, 2H), 6.43 (d, *J* = 5.7 Hz, 1H), 3.77 (s, 3H), 3.56 (d, *J* = 18.8 Hz, 1H), 2.54 (d, *J* = 18.8 Hz, 1H).

$^{13}C\{^1H\}$ NMR (62.5 MHz, $CDCl_3$) δ: 205.6, 171.4, 161.2, 147.9, 147.5, 135.4, 127.3, 124.4, 60.0, 53.7, 46.6.

IR (ATR, cm^{-1}): 2954, 1719, 1492, 1252, 1088.

HRMS (ESI+): Calcd. for $[C_{13}H_{11}NO_5 + H]^+$: 262.0710, found: 262.0707.

Dimethyl 2-methoxy-4-((trimethylsilyl)oxy)cyclopent-3-ene-1,1-dicarboxylate[35] (6h)



The **General Procedure D** is performed with dimethyl 2-(phenyl-λ^3-iodanylidene)malonate **1z'** (67 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6 mmol, 3 equiv) and DCM (2 mL). *No treatment with acid was performed*. Upon reaction completion (TLC), the reaction mixture is carefully evaporated under reduced pressure for a prolonged time (to eliminate the excess of the Danishefsky's diene **5c**) and the resulting crude reaction mixture contained the title compound as the major compound.

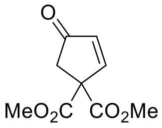
^1H NMR (600 MHz, $CDCl_3$) δ: 4.96 (t, *J* = 1.5 Hz, 1H), 4.75 (dt, *J* = 2.1 Hz, *J* = 1.5 Hz, 1H), 3.744 (s, 3H), 3.739 (s, 3H), 3.36 (dt, *J* = 16.8 Hz, *J* = 2.1 Hz, 1H), 3.32 (s, 3H), 2.50 (dd, *J* = 16.8 Hz, *J* = 2.1 Hz, 1H), 0.23 (s, 9H).

$^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ: 171.7, 169.1, 156.9, 100.7, 86.5, 62.5, 57.5, 52.9, 52.7, 40.1, 0.03.

IR (ATR, cm^{-1}): 2956, 1732, 1687, 1658, 1623, 1595, 1151, 1437, 1238, 1199, 1151, 1095.

HRMS (ESI+): Calcd. for $[C_{13}H_{22}O_6Si + H]^+$: 303.1258, found: 303.1264.

Dimethyl 4-oxocyclopent-2-ene-1,1-dicarboxylate (8h)



The **General Procedure D** is performed with dimethyl 2-(phenyl-λ^3-iodanylidene)malonate **1z'** (67 mg, 0.2 mmol, 1 equiv.), (*E*)-((4-methoxybuta-1,3-dien-2-yl)oxy)trimethylsilane (Danishefsky's Diene) **5c** (120 µL, 0.6

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[35] The same product containing a TBS group replaced by the TMS group has been previously reported. A comparison between the two ^1H NMR spectra show small deviations of chemical shifts (*ca.* 0.2 ppm), and multiplicities of all signals referring to common atoms being virtually identical. Also, both $^{13}C\{^1H\}$ NMR have very similar chemical displacements for common atoms. See: J. Schnaubelt, E. Marks, H.-U. Reissig, *Chem. Ber.*, 1996, **129**, 73-75.

mmol, 3 equiv), DCM (2 mL) and 1M HCl in MeOH (1 mL). Purification by flash column chromatography (SiO_2, gradient: Hex – 95:5 Hex:AcOEt – 9:1 Hex:AcOEt – 8:2 Hex:AcOEt) affords the title compound as a pale yellow oil: 24 mg, 61% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.69 (d, *J* = 5.5 Hz, 1H), 6.29 (d, *J* = 5.5 Hz, 1H), 3.80 (s, 6H), 2.96 (s, 2H).

^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ: 205.3, 168.9, 158.6, 135.3, 61.9, 53.7, 41.5.

IR (ATR, cm^{-1}): 2956, 2919, 1722.

HRMS (ESI+): Calcd. for $[C_9H_{10}O_5 + H]^+$: 199.0601, found: 199.0601.

5. Mechanistic Investigations

5.1. Reaction Profile of [2+1]-Cycloaddition

Each reaction **1a** + **2a** → **3a** was performed twice and the average yields (based on the ^{1}H NMR analysis of the crude reaction mixture using 1,3,5-trimethoxybenzene as internal reference) for two runs considering the sum of both diastereoisomers were plotted against the reaction time (Table S8 and Figure S3).

Table S8. Data obtained for the reaction profile of the reaction **1a** + **2a** → **3a** in different stoichiometries of the reagents (performed in duplicate).

	1:3 1a:2a			1:1 1a:2a			3:1 1a:2a		
Time (h)	**D1 (%)**	**D2 (%)**	**average D1+D2 (%)**	**D1 (%)**	**D2 (%)**	**average D1 + D2 (%)**	**D1 (%)**	**D2 (%)**	**average D1 + D2 (%)**
1	4	3	5.5	6	4	10	4	2	5.5
1	3	1		6	4		3	2	
2	13	10	25.5	14	8	20.5	7	5	13.5
2	16	12		11	8		9	6	
4	30	20	50	22	15	35	15	10	22.5
4	30	20		20	13		13	7	
6	42	30	70	23	15	37	25	16	36
6	41	27		22	14		19	12	

8	40	26	68	24	15	40	30	20	45.5
8	42	28		26	15		25	16	
12	43	28	68	26	15	40.5	32	19	51
12	39	26		26	14		31	20	

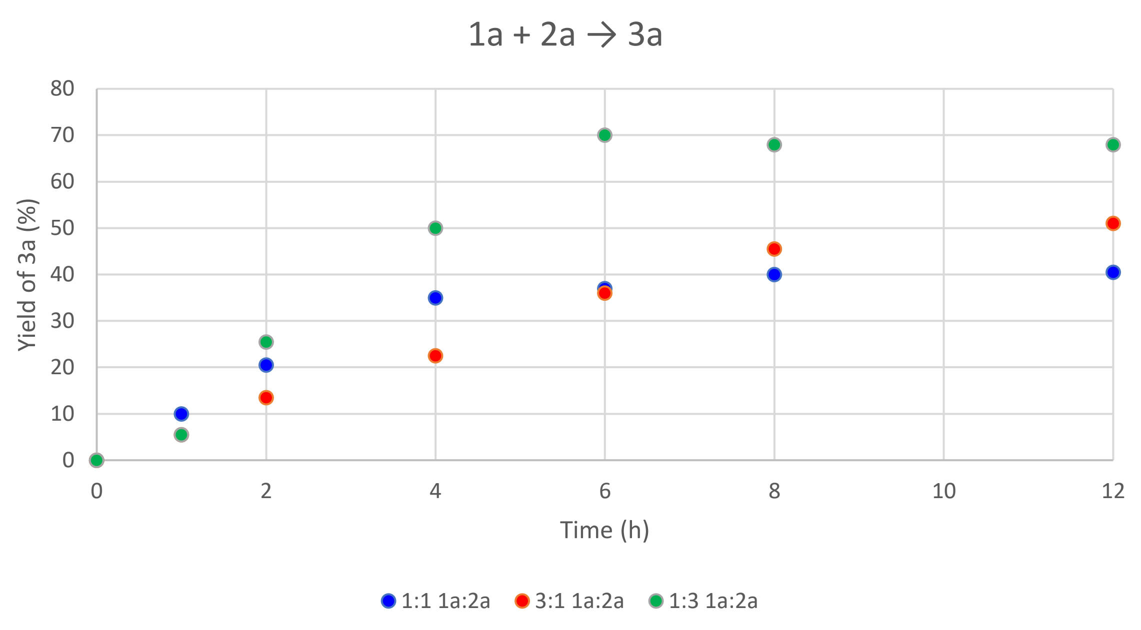

Figure S3: Reaction profiles of reactions **1a** + **2a** → **3a** according with different stoichiometries of the reagents.

5.2. DFT Calculations

Computational details: Transition states were found by a restricted conformational search in dichloromethane using the ALPB implicit solvent model at the GFN2-xTB[36] level in CREST 2.12 software.[37,38] All conformers were reoptimized and had their frequencies calculated at standard temperature and pressure using the M06-2X/6-311++G** level in Gaussian 16.[39] Solvent effects were included using the IEFPCM method with parameters of

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[36] C. Bannwarth, S. Ehlert and S. Grimme, *J. Chem. Theory Comput*., 2019, **15**, 1652–1671.

[37] C. Bannwarth, E. Caldeweyher, S. Ehlert, A. Hansen, P. Pracht, J. Seibert, S. Spicher and S. Grimme, *WIREs Comput. Mol. Sci*., 2021, **11**, e1493.

[38] P. Pracht, F. Bohle and S. Grimme, *Phys. Chem. Chem. Phys.*, 2020, **22**, 7169–7192.

[39] Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R.

dichloromethane. The lack of imaginary frequencies was used to characterize true minima and the observation of a single imaginary frequency to characterize transition states. IRC calculations were performed to further characterize the transition states found. Resulting reactants and products obtained from the IRC calculates were reoptimized to calculate Gibbs free energy barriers. NBO analysis (using the NBO 7.0 program[40,41,42,43,44] interfaced with Gaussian16) were also calculated at the M06-2X/6-311++G** level of theory. The above workflow was run in a development version of Autobench.[45]

5.2.1. Mechanism of [2+1]-Cycloaddition:

Visible light-mediated photolysis of aryldiazoacetates can lead to singlet and/ or triplet carbenes, which are in equilibrium.[46] Experimentally, we investigated our model reaction **1a** + **2a** → **3a** under air *versus* degassing by freeze-pump-thaw, under N_2 or Ar and all three reactions approximately produced the same yield for **3a**, 70% yield (estimated based on ^{1}H NMR of crude reaction mixture using 1,3,5-trimethoxybenzene as internal reference). In addition, when this same reaction was performed in the presence of 1 equiv. of TEMPO, **3a** could still be produced in 50% yield (also estimated yield, as above). These observations suggest that a singlet carbene is the major intermediate involved in such reaction conditions[13,47] (however, the involvement of a triplet carbene cannot be ruled out for **1a** or for other aryldiazoacetates **1** having different aryl groups, Figure S4).

Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

[40] E. D. Glendening, J. K. Badenhoop, A. E. Reed, J. E. Carpenter, J. A. Bohmann, C. M. Morales, P. Karafiloglou, C. R. Landis, F. Weinhold, NBO 7.0; Theoretical Chemistry Institute, University of Wisconsin, Madison, WI, 2018.

[41] F. Weinhold, C. R. Landis, Discovering Chemistry with Natural Bond Orbitals, Wiley-VCH, Hoboken, 2012.

[42] A. E. Reed, R. B. Weinstock, F. Weinhold, *J. Chem. Phys.*, 1985, **83**, 735-746.

[43] J. K. Badenhoop, F. Weinhold, *J. Chem. Phys.*, 1997, **107**, 5406-5421.

[44] J. K. Badenhoop, F. Weinhold, *Int. J. Quantum Chem.*, 1999, **72**, 269-280.

[45] R. A. Cormanich, G. D. da Silva, *J. Chem. Inf. Model.*, 2024, **64**, 3322-3331.

[46] a) J.-L. Wang, I. Likhotvorik, M. S. Platz, *J. Am. Chem. Soc.*, 1999, **121**, 2883-2890. b) Z. Zhu, T. Bally, L. L. Stracener, R. J. McMahon, *J. Am. Chem. Soc.*, 1999, **121**, 2863-2874.

[47] Previous work from other groups have also favored the major involvement of singlet carbenes under these reaction conditions. See for instance: a) S. Jana, C. Pei, C. Empel, R. M. Koenigs, *Angew. Chem. Int. Ed.*, 2021, **60**, 13271-13279. b) G. M. Gallardo, D. J. Ventura, A. S. Petit, *J. Org. Chem.*, 2022, **87**, 6212-6223. c) Y. Zhang, J. Kubicki, J. Wang, M. S. Platz, *J. Phys. Chem. A*, 2008, **112**, 11093-11098.

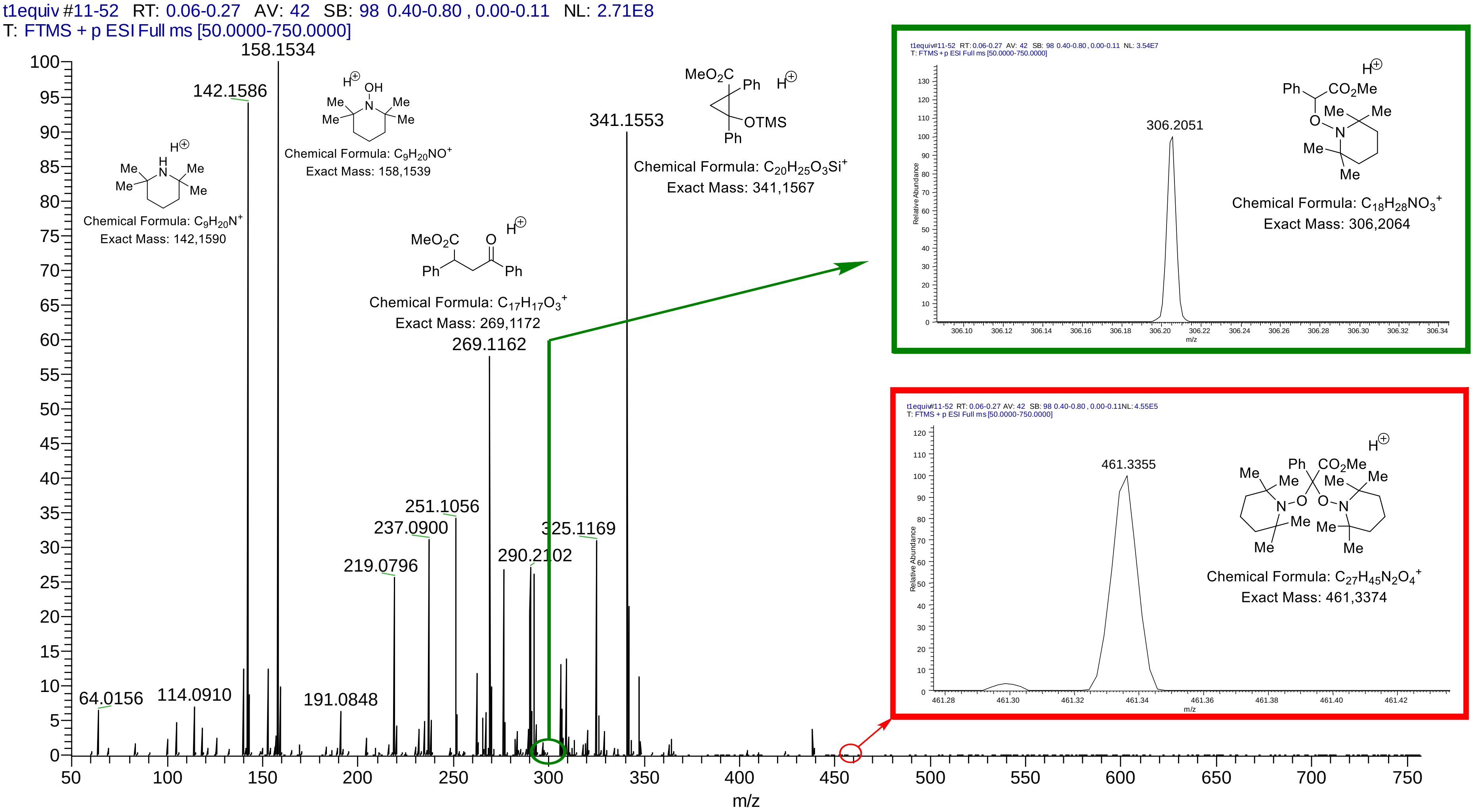
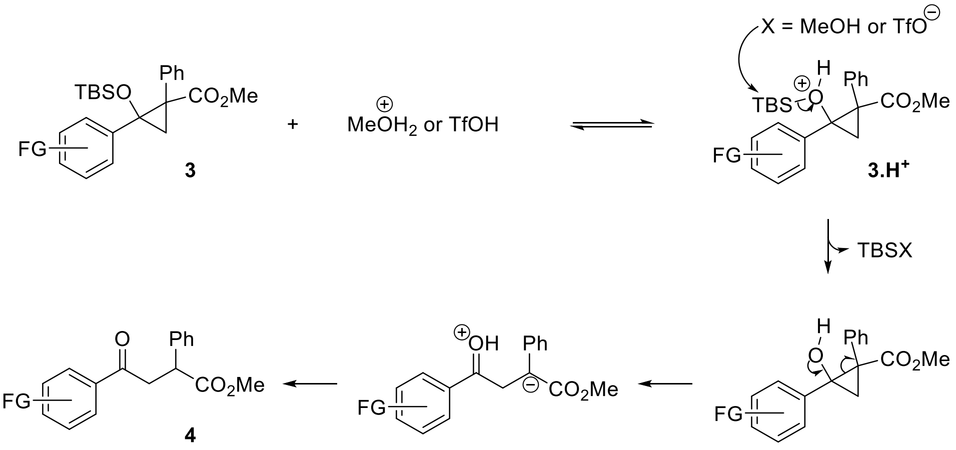


Figure S4. HRMS analysis of the crude reaction mixture of **1a** (1 equiv.) + **2a** (3 equiv.) + TEMPO (1 equiv.) irradiating at 452 nm for 16h. (Using FIA 200 μL/min 1:1 H_2O:MeCN + 0,1 % HCO_2H).

In this context, DFT calculations were performed in order to preliminarily access the overall mechanism of the [2+1]-cycloaddition mechanism. In this context, a transition state was searched for the reaction between a free singlet carbene intermediate (formed from aryldiazoacetate **1a**) and silyl enol ether **2a** to afford the corresponding TMS-protected cyclopropanol intermediate **3a**. The computations consistently transitioned directly to **3a**, with no observable transition state being observed. Although a hypothetical transition state featuring an imaginary frequency could be identified by restricting the distances between the approaching carbene formed from **1a** to **2a**, removing these limitations allowed the system to advance directly to the product without forming a clear transition state. This pattern indicates that the steps leading to **3a** occur without a significant energetic barrier.

5.2.2. Ring-Opening of Silylated TBS-Protected Cyclopropanol Intermediates 3:

The protonation of the silyl-protected cyclopropanol intermediate **3** by either $MeOH_2^+$ (formed from HCl in MeOH) or TfOH leading to **3.H⁺** is tentatively attributed as a key event ultimately leading γ-ketoester **4** (Scheme S3).



Scheme S3: Proposed mechanism for the ring-opening of silyl-protected cyclopropanols **3** leading to γ-ketoesters **4**.

For FG = H, *o*-OMe, *m*-OMe, *p*-OMe, intermediate **3** could be ring-opened to γ-ketoester **4** using a solution of 1M HCl in MeOH. For FG = *p*-Br, 3,5-$(CF_3)_2$, *p*-CN, *m*-NO_2, *p*-NO_2, the use of stronger acid TfOH was required (See Scheme 4 of the manuscript). Our current working hypothesis is that the protonation of intermediate **3** to **3.H⁺** triggers the ring-opening of the cyclopropanol intermediate to afford **4**. We speculate that for a weak electron-poor aryl ring (FG = *m*-OMe) or an electron-neutral aryl ring (FG = H) or an electron-rich aryl ring (FG = *o*-/*p*-OMe) within intermediate **3**, protonation is favored in the presence of a **weaker acid** ($MeOH_2^+$, presumably formed from HCl in MeOH). On the other hand, for electron-poorer aryl rings within **3** (FG = *p*-Br, 3,5-$(CF_3)_2$, *p*-CN, *m*-/*p*-NO_2), protonation does not occur when using a weak acid (*i.e.* 1M HCl in MeOH); and it requires a **stronger acid** (*i.e.* TfOH) to compensate for their lower reactivities. This electronic behavior can be tentatively correlated with the Hammett parameters associated with these functional groups (excluding *ortho*-substituents, whose effects are also a consequence of steric hindrance), thus allowing a possible comparison for the ease of ring-opening of different intermediates (**FG = *p*-OMe, σ = -0.27**/ **FG = H, σ = 0.0**/ **FG = *m*-OMe, σ = 0.10**/ **FG = *p*-Br, σ = 0.26**/ **FG = *m*-CF_3, σ = 0.46**/ **FG = *p*-CN, σ = 0.70**/ **FG = *m*-NO_2, σ = 0.71**/ **FG = *p*-NO_2, σ = 0.81**).[48] (At this time, it is not possible to rule out that other effects could also play a role.)

5.2.3. Mechanism of [4+1]-Cycloaddition:

Calculations were performed to explore three possible pathways for the reaction of the Danishefsky's diene **5c** with the free singlet carbene derived from aryldiazoacetate **1a** to afford intermediate **6c** (Scheme S4). Despite multiple attempts to locate transition states (TS) for the formation of **5c(int1)** and **5c(int3) = 6c**, which included a restricted conformational search using CREST and re-optimization using several DFT functionals and the 6-311++G** basis set, no true transition states could be identified. The calculations consistently converged directly from **5c** to either **5c(int1)** or **5c(int3) = 6c**, bypassing any detectable transition state. Although an artificial transition state with an imaginary frequency could be located when distances between the approaching carbene and **5c** were constrained, releasing these constraints caused the system to proceed directly to the product without forming a distinct transition state. This behavior suggests that the elementary steps leading to the formation of **5c(int1)** and **5c(int3) = 6c** are effectively barrierless.

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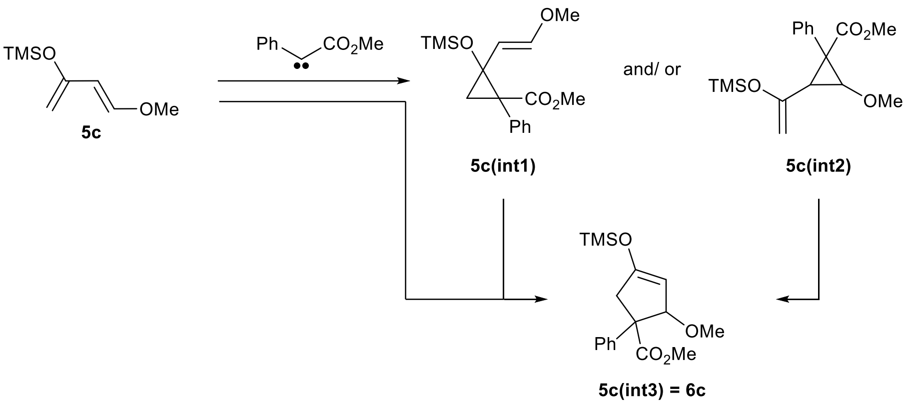
[48] E. V. Anslyn, D. A. Dougherty, *Modern Physical Organic Chemistry*, 2006, University Science Books, *p.* 446.



Scheme S4: Three possible intermediates for the (formal) [4+1]-cycloaddition step, ultimately leading after treatment with HCl in MeOH to the formation of **8c**. **5c(int1)** is generated via a [2+1]-cycloaddition to the silyl enol ether double bond of the Danishefsky's diene; **5c(int2)** is formed through a [2+1]-cycloaddition to the methyl enol ether double bond, and **5c(int3)** results from a concerted [4+1]-cycloaddition with the Danishefsky's diene.

Conversely, a transition state for the formation of **5c(int2)** was successfully identified, and an Intrinsic Reaction Coordinate (IRC) profile was obtained (Figure S5). However, the reaction barrier for this step was found to be quite low, 1.6 kcal mol^{-1} (Figure S6) at the M06-2X/6-311++G** level, indicating that this step is also virtually barrierless. Other DFT functionals also predict a low barrier, ranging from 1.6 to 6.4 kcal mol^{-1}, and a highly exergonic reaction, with $\Delta G°$ values around -60 to -70 kcal mol^{-1}, depending on the functional employed in the calculation (Table S9). Therefore, despite the identification of a transition state for **5c(int2)**, the low energy barrier further indicates that the overall transformation from **5c** to any of the three intermediates mentioned occurs with negligible barriers. This suggests that all three possible pathways, whether proceeding through a [2+1]-cycloaddition with any of the two double bonds available, followed by ring expansion; or via a concerted [4+1]-cycloaddition mechanism are viable alternatives to afford **5c(Int3)** = **6c**.

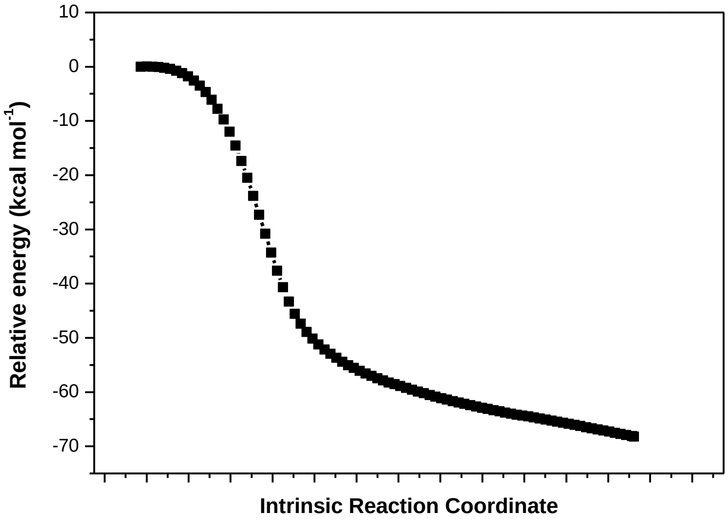
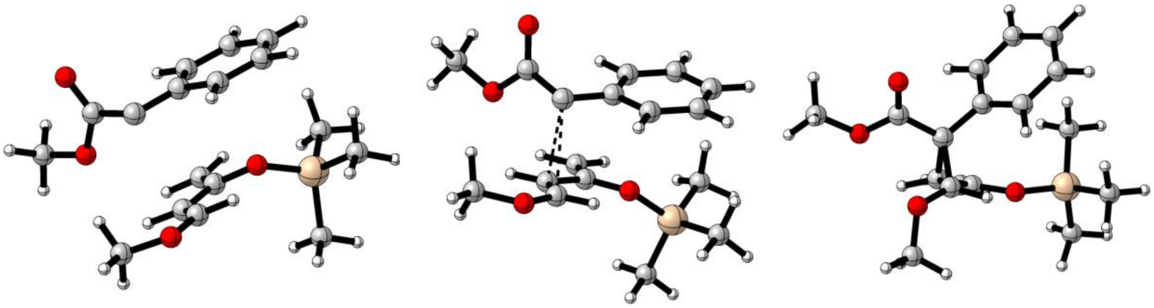


Figure S5: Intrinsic Reaction coordinate calculated at the M06-2X/6-311++G**level for the elementary step of formation of **5c(int2)**.



5c + carbene **0.0** | **5c-TS-5c(int2)** **1.6** | **5c(int2)** **-66.7**

Figure S6: Graphical representations of the reactants, transition state (**TS**) and **5c(int2)** intermeditate for the [2+1]-cycloaddition elementary step found at the M06-2X/6-311++G** level. Energies relative to reactants are given in kcal mol^{-1}.

Table S9: Gibbs free energy (kcal mol^{-1}) relative to reactants calculated at several theoretical levels for the [2+1]-cycloaddition elementary step of formation of **5c(int2)**. Dichloromethane implicit solvent model was used to account for solvent effects and the 6-311++G** basis set was employed in all cases.

	R	**TS**	**P**
BHandH/6-311++G**	**Not found**	**Not found**	**Not found**
ωb97X-D/6-311++G**	**0.0**	**3.7**	**-62.99**
M05-2X/6-311++G**	**0.0**	**3.2**	**-64.4**
M06L/6-311++G**	**0.0**	**2.6**	**-56.3**
M06-2X/6-311++G**	**0.0**	**1.6**	**-66.7**
PBE/6-311++G**	**Not found**	**Not found**	**Not found**
PBE0/6-311++G**s	**0.0**	**6.4**	**-60.9**
M11/6-311++G**	**0.0**	**0.3**	**-70.0**

Table S10: Cartesian coordinates, electronic and Gibbs free energies in hartrees and first harmonic frequency in cm^{-1} obtained for the elementary step of formation of **5c(int2)**, transition state and product calculated at the M06-2X/6-311++G** level in implicit dichloromethane (IEFPCM implicit solvent model).

5c + carbene
Electronic Energy = -1252.145845 hartrees
Gibbs Free Energy = -1251.836652 hartrees
First Harmonic Frequency = 8.6440 cm^{-1}

C	0.163411	-2.088420	1.478365
H	1.159284	-2.333093	1.828496
C	-0.043134	-1.516641	0.283814
H	-1.036953	-1.264577	-0.066799
C	1.058457	-1.190165	-0.626104
C	0.846000	-0.629999	-1.828916
H	-0.166767	-0.409652	-2.142422
H	1.650040	-0.384092	-2.510044
O	-0.770614	-2.435580	2.390190
C	-2.132756	-2.188773	2.062763
H	-2.418286	-2.735766	1.158450
H	-2.718948	-2.542629	2.909417
H	-2.309826	-1.119390	1.910558
O	2.285976	-1.506908	-0.135402
Si	3.842985	-1.407446	-0.797092
C	4.280902	0.379113	-1.153231
H	4.132819	0.998774	-0.263253
H	5.336039	0.451026	-1.438628
H	3.686767	0.805316	-1.965830
C	4.920851	-2.094119	0.564632
H	4.827228	-1.497696	1.477259
H	4.643573	-3.125589	0.802199
H	5.973518	-2.087828	0.263644
C	3.951602	-2.466151	-2.338164
H	3.643690	-3.494374	-2.124159
H	3.327228	-2.087925	-3.151857
H	4.986373	-2.494395	-2.696324
C	-3.375125	1.367606	0.403607
C	-2.284670	2.198617	0.738328
C	-1.266863	2.579116	-0.179370
C	-2.194404	2.665190	2.075194
C	-0.218016	3.379779	0.225921
H	-1.320309	2.234267	-1.206813
C	-1.141200	3.465383	2.479084
H	-2.974848	2.372990	2.769077
C	-0.158384	3.819016	1.552955
H	0.558125	3.665945	-0.474952
H	-1.076145	3.817165	3.502463
H	0.669079	4.447393	1.867536
C	-3.552207	0.911624	-0.949958
O	-4.215149	1.549278	-1.761256
O	-3.035985	-0.302786	-1.194816
C	-3.349937	-0.888202	-2.471188
H	-2.966677	-0.266585	-3.281355
H	-2.858731	-1.858991	-2.471447
H	-4.429317	-1.006147	-2.576555

5c-TS-5c(int2)
Electronic Energy = -1252.138301 hartrees

Gibbs Free Energy = -1251.820511 hartrees **First Harmonic Frequency** = -157.3182 cm^{-1}			
C	-0.735134	-1.777957	1.149740
H	0.049453	-1.400258	1.794063
C	-0.652354	-1.627493	-0.197107
H	-1.430588	-1.994697	-0.849535
C	0.539510	-1.087046	-0.848598
C	0.610737	-0.942125	-2.182342
H	-0.233997	-1.222820	-2.798958
H	1.489566	-0.547207	-2.674954
O	-1.655956	-2.445124	1.844898
C	-2.735604	-3.051142	1.133928
H	-2.354961	-3.788437	0.420350
H	-3.348230	-3.545499	1.885422
H	-3.317862	-2.291128	0.609556
O	1.537494	-0.756384	0.010809
Si	3.218010	-0.665695	-0.205569
C	3.682573	0.799946	-1.276251
H	3.174441	1.707351	-0.936811
H	4.762205	0.973463	-1.208819
H	3.438150	0.646934	-2.330982
C	3.853363	-0.433178	1.534851
H	3.450307	0.482594	1.977746
H	3.568002	-1.274683	2.173240
H	4.945691	-0.359181	1.539826
C	3.820823	-2.270896	-0.956297
H	3.562526	-3.122682	-0.319712
H	3.391825	-2.443683	-1.947224
H	4.910599	-2.248194	-1.062870
C	-1.909542	0.473964	0.714020
C	-0.839946	1.438504	0.692131
C	-0.514681	2.210804	-0.443664
C	-0.122512	1.672363	1.883009
C	0.470762	3.184817	-0.382963
H	-1.056381	2.048405	-1.369391
C	0.861694	2.645673	1.946162
H	-0.371582	1.081371	2.758088
C	1.157020	3.402705	0.811488
H	0.705991	3.777328	-1.260940
H	1.395933	2.823628	2.873480
H	1.924593	4.169037	0.859427
C	-2.957722	0.556620	-0.268684
O	-3.705121	1.537247	-0.229754
O	-3.194303	-0.483868	-1.087459
C	-4.391705	-0.401936	-1.875320
H	-4.366627	0.475201	-2.523252
H	-4.407006	-1.312699	-2.471279
H	-5.271086	-0.353193	-1.230971
5c(int2) **Electronic Energy** = -1252.248990 hartrees **Gibbs Free Energy** = -1251.926458hartrees **First Harmonic Frequency** = 24.4442 cm^{-1}			
C	-1.163867	-1.187046	0.691243
H	-0.319079	-1.230183	1.376561
C	-0.838164	-1.039440	-0.763056
H	-1.556357	-1.474390	-1.447307

C	0.565876	-1.065882	-1.255907
C	0.853605	-1.283820	-2.545009
H	0.051713	-1.427618	-3.258360
H	1.869878	-1.323812	-2.915670
O	-2.275959	-1.922332	1.085430
C	-2.025835	-3.321045	1.112594
H	-1.216700	-3.560431	1.813261
H	-2.945756	-3.801703	1.445731
H	-1.759845	-3.690820	0.115640
O	1.477467	-0.876639	-0.273397
Si	3.170792	-0.742370	-0.290503
C	3.690434	0.686645	-1.381748
H	3.174855	1.605056	-1.085465
H	4.767761	0.855576	-1.278471
H	3.481556	0.505047	-2.439308
C	3.579202	-0.408006	1.499981
H	3.093988	0.510114	1.844368
H	3.245611	-1.230794	2.139610
H	4.659704	-0.292833	1.633767
C	3.925263	-2.358720	-0.862131
H	3.559066	-3.194401	-0.257655
H	3.706294	-2.576863	-1.910794
H	5.014219	-2.317739	-0.750840
C	-1.411439	0.141814	0.034365
C	-0.570858	1.332085	0.400333
C	-0.138241	2.201776	-0.602085
C	-0.249452	1.615200	1.726854
C	0.608910	3.332162	-0.285003
H	-0.383317	1.988254	-1.638448
C	0.499216	2.744123	2.047786
H	-0.588479	0.949906	2.514796
C	0.931282	3.605561	1.042304
H	0.940858	3.998575	-1.074965
H	0.741896	2.952641	3.085073
H	1.514943	4.486015	1.291813
C	-2.859973	0.492667	-0.193861
O	-3.441221	1.340095	0.453842
O	-3.449063	-0.206174	-1.165670
C	-4.848131	0.044127	-1.371919
H	-5.007069	1.085733	-1.654086
H	-5.146362	-0.621313	-2.179266
H	-5.408152	-0.179156	-0.462794

5.3. Quantum Yield

The procedure employed for the measurement of quantum yield was based on the work reported by Xia and co-workers.[49]

5.3.1. Determination of the Photon Flux using $K_3[Fe(C_2O_4)_3]$:

The ferrioxalate actinometer solution measures the decomposition of Fe^{3+} ions to Fe^{2+} ions, which are complexed by 1,10-phenanthroline and monitored by UV/ Vis absorbance at 510 nm. The moles of the complex $Fe(phen)_3^{2+}$ formed are related to moles of photons absorbed.

The solutions were prepared and stored in dark:

1. Potassium ferrioxalate solution: 590 mg of $K_3[Fe(C_2O_4)_3]$ and 280 μL of H_2SO_4 (96%) were added to a 100 mL volumetric flask and filled with water (HPLC grade) until the mark.

2. 0.2% 1,10-phenantroline solution: 200 mg of 1,10-phenanthroline was added to a 100 mL-volumetric flask and filled with water (HPLC grade) until the mark.

3. Buffer solution: 4.94 g of NaOAc and 1 mL of H_2SO_4 (96%) were added to a 100 mL-volumetric flask and filled with water (HPLC grade) until the mark.

Procedure: 1 mL of the actinometer solution was added to a quartz cuvette (l = 10 mm). The cuvette was placed in front of the CW laser light source (Picoquant) and irradiated at $\lambda = 405$ nm, Power = 13.8 mW. This procedure was repeated another time (*i.e.* in a total of 2 replicates), quenching the reactions after different time intervals: 10, 20 and 30 seconds.

The actinometer measurements were performed as follows:

1. After irradiation, the actinometer solution was removed and placed in a 10 mL volumetric flask containing 0.5 mL of 1,10-phenanthroline solution and 2 mL of buffer solution. This flask was filled with water (HPLC grade) until the mark.
2. The UV-Vis spectra of the complexed actinometer samples were recorded for each time interval. The absorbance of the complexed actinometer solution was monitored at 510 nm.

The moles of Fe^{+2} formed for each sample were determined according to the Beer's Law:

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[49] K. Liang, X. Li, D. Wei, C. Jin, C. Liu, C. Xia, *Chem.*, 2023, **9**, 511 – 522.

$$mol\ Fe^{2+} = \frac{V_1 \cdot V_3 \cdot \Delta A(510\ nm)}{10^3 \cdot V_2 \cdot l \cdot \varepsilon(510\ nm)} \quad \text{(Eq. 1)}$$

In Eq. 1, V_1 represents the irradiated volume (1 mL), V_2 represents the aliquot of the irradiated solution taken for the determination of Fe^{2+} ions (1 mL), V_3 represents the final volume after complexation with 1,10-phenanthroline (10 mL), l represents the optical path-length of the irradiation cell (1 cm), $\Delta A(510\ nm)$ represents the optical difference in absorbance between the irradiated solution and the one stored in the dark, $\varepsilon(510\ nm)$ represents the molar absorptivity of the complex $Fe(phen)_3^{2+}$ (11100 $L.mol^{-1}.cm^{-1}$)[50]

The amount of Fe^{2+} formed (in moles) can be plotted as a function of time (in seconds). The slope of the straight line obtained can be correlated with the amount of incident photons (in moles) by unit of time ($q_{n,p}^0$, *i.e.* photon flux) using the following equation:

$$\Phi(\lambda) = \frac{dx/dt}{q_{n,p}^0[1-10^{-A(\lambda)}]} \quad \text{(Eq. 2)}$$

In Eq. 2, dx/dt represents the rate of change of a measurable quantity (here, this is the slope of the plotted curve of mol Fe^{2+} x time, Figure S7), $\Phi(\lambda)$ represents the quantum yield for the formation of Fe^{2+} at 405 nm (1.19),[50] and $A(\lambda)$ represents the absorbance of the actinometer at λ = 405 nm, which was measured by UV/ Vis spectroscopy to be 2.04,[49] using a spectrophotometer HP 8452AX and a quartz cuvette with $l = 1\ cm$ (Figure S8); $q_{n,p}^0$ represents the photon flux, which after replacing the above values in Eq. 2, it can be calculated to be $q_{n,p}^0 = \frac{6 \cdot 10^{-8}}{1.19 \cdot (1-10^{-2.04})} = 5.088 \cdot 10^{-8}\ einsteins \cdot s^{-1}$. (The photon flux was also independently measured in a direct manner using a power meter, and we found the value of $4.70 \cdot 10^{-8}\ einsteins \cdot s^{-1}$, which is reasonably in good agreement with the previous value).

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[50] J. N. Demas, W. D. Bowman, E. F. Zalewski, R. A. Velapoldi, *J. Phys. Chem.*,1981, **85**, 2766 – 2771.

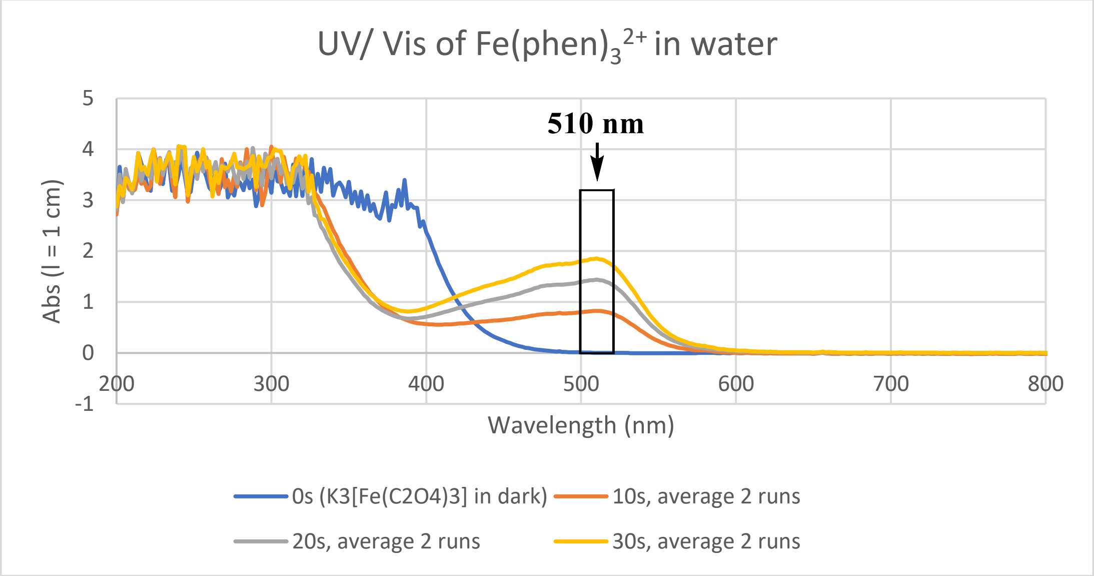


Figure S7. UV-Vis absorption spectra of the solutions of Fe(phen)$_3^{2+}$ in water (derived from the irradiation of the solution of $K_3[Fe(C_2O_4)_3]$ with a CW laser (Picoquant) of λ = 405 nm, Power = 13.8 mW, for 10, 20 and 30 seconds, followed by the treatment with the solution 0.2% 1,10-phen and the buffer solution) using a spectrophotometer HP 8452AX and a cuvette of $l = 1\ cm$. All points plotted represent an average of 2 runs.

Wavelength (nm)	Abs @ 0 s ($K_3[Fe(C_2O_4)_3]$ in dark)	Abs @ 10 s average of 2 runs	Abs @ 20 s average of 2 runs	Abs @ 30 s average of 2 runs
510	0.00363	0.826495	1.439875	1.85727

$$\text{For t} = 0\text{ s}, \qquad mol\ Fe^{2+} \approx 0$$

$$\text{For t} = 10\text{ s}, \qquad mol\ Fe^{2+} = \frac{1 \cdot 10 \cdot (0.826495 - 0.00363)}{1000 \cdot 1 \cdot 1 \cdot 11100} = 7.41 \cdot 10^{-7}$$

$$\text{For t} = 20\text{ s}, \qquad mol\ Fe^{2+} = \frac{1 \cdot 10 \cdot (1.439875 - 0.00363)}{1000 \cdot 1 \cdot 1 \cdot 11100} = 1.29 \cdot 10^{-6}$$

$$\text{For t} = 30\text{ s}, \qquad mol\ Fe^{2+} = \frac{1 \cdot 10 \cdot (1.85727 - 0.00363)}{1000 \cdot 1 \cdot 1 \cdot 11100} = 1.67 \cdot 10^{-6}$$

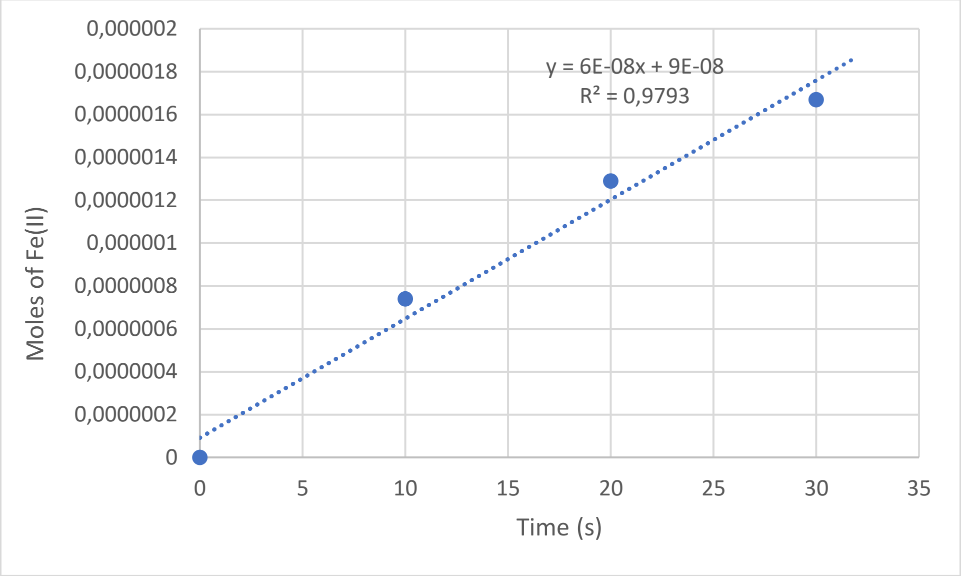
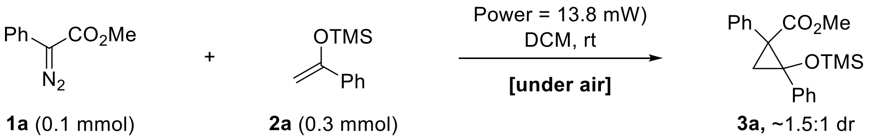
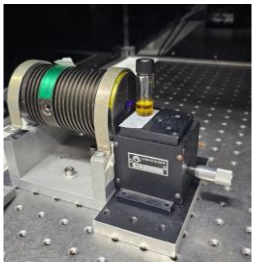


Figure S8. Moles of Fe^{2+} formed during different reaction times irradiating with a laser of λ= 405 nm, Power = 13.8 mW.

5.3.2. Determination of the Quantum Yield of the Reaction 1a + 2a → 3a:

A model reaction was employed according to **General Procedure D** (see page S34) using 0.1 mmol, 1 equiv. of the limiting reagent **1a** and 0.3 mmol, 3 equiv. of silyl enol ether **2a** in 1 mL, 0.1 M of DCM at rt, irradiating with a CW laser (Picoquant, λ = 405 nm, Power = 13.8 mW) during different reaction times of 1 h, 2 h, 3 h and 4 h; and the chemical yield associated with the sum of the diastereoisomers of **3a** for each reaction was measured by ^{1}H NMR of the crude reaction mixture using 1,3,5-trimethoxybenzene as an internal reference (Scheme S5). Each reaction was repeated a second time (*i.e.* 2 replicates were made for each t = 1, 2, 3 and 4 h. Yields reported are an average of 2 runs).





Scheme S5. Model reaction having its quantum yield measured.

Time (h)	1 (12% yield)	2 (23% yield)	3 (38% yield)	4 (50% yield)
Moles of **3a**	0.000012	0.000023	0.000038	0.00005

The moles of **3a** formed per unit of time are related to the number of photons absorbed. The photons absorbed are correlated with the number of incident photons using Eq 2. The absorption $A(405\,nm)$ of the reaction mixture was determined using a spectrophotometer HP 8452AX to be 2.8 using a quartz cuvette of $l = 0.5\,cm$ (Figure S9), which corresponds to an absorbance of 5.6 with a path length of $l = 1\,cm$; therefore $(1 - 10^{-5.6}) \approx 1$. The photon flux $q_{n,p}^{0}$ was previously established for this CW laser light source as $5.088 \cdot 10^{-8}\,einstein \cdot s^{-1}$. This time, we can plot the moles of **3a** x moles of incident photons, which can be calculated by $(1 - 10^{-A(405\,nm)}) \cdot q_{n,p}^{0} \cdot t$ (Figure S10). The slope of the curve obtained is the quantum yield of this transformation, *i.e.* an approximate value of $\mathbf{\Phi = 0.07}$.

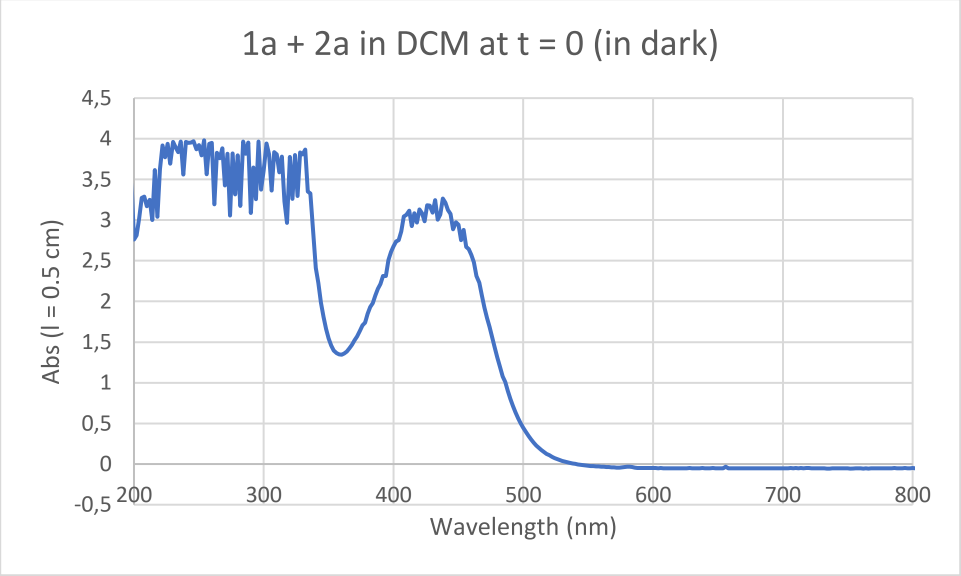


Figure S9. UV/ Vis absorption spectrum measured of the reaction mixture of **1a** + **2a** in DCM at t = 0 (in dark) using a spectrophotometer HP 8452AX and a cuvette of $l = 0.5\,cm$.

Moles of incident photons	0.0001832 (t = 1h)	0.0003663 (t = 2h)	0.0005495 (t = 3h)	0.0007327 (t = 4h)

Moles of **3a**	0.000012	0.000023	0.000038	0.00005

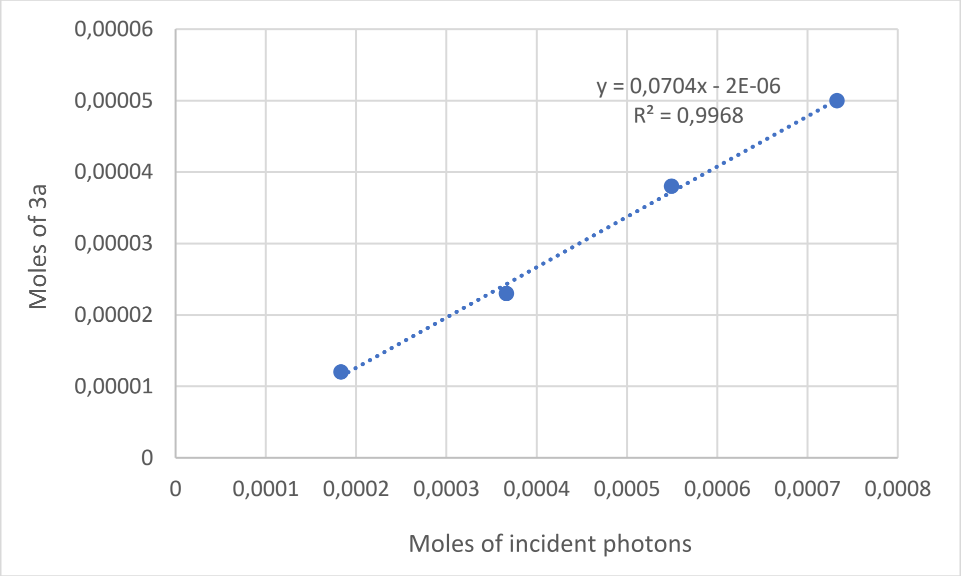
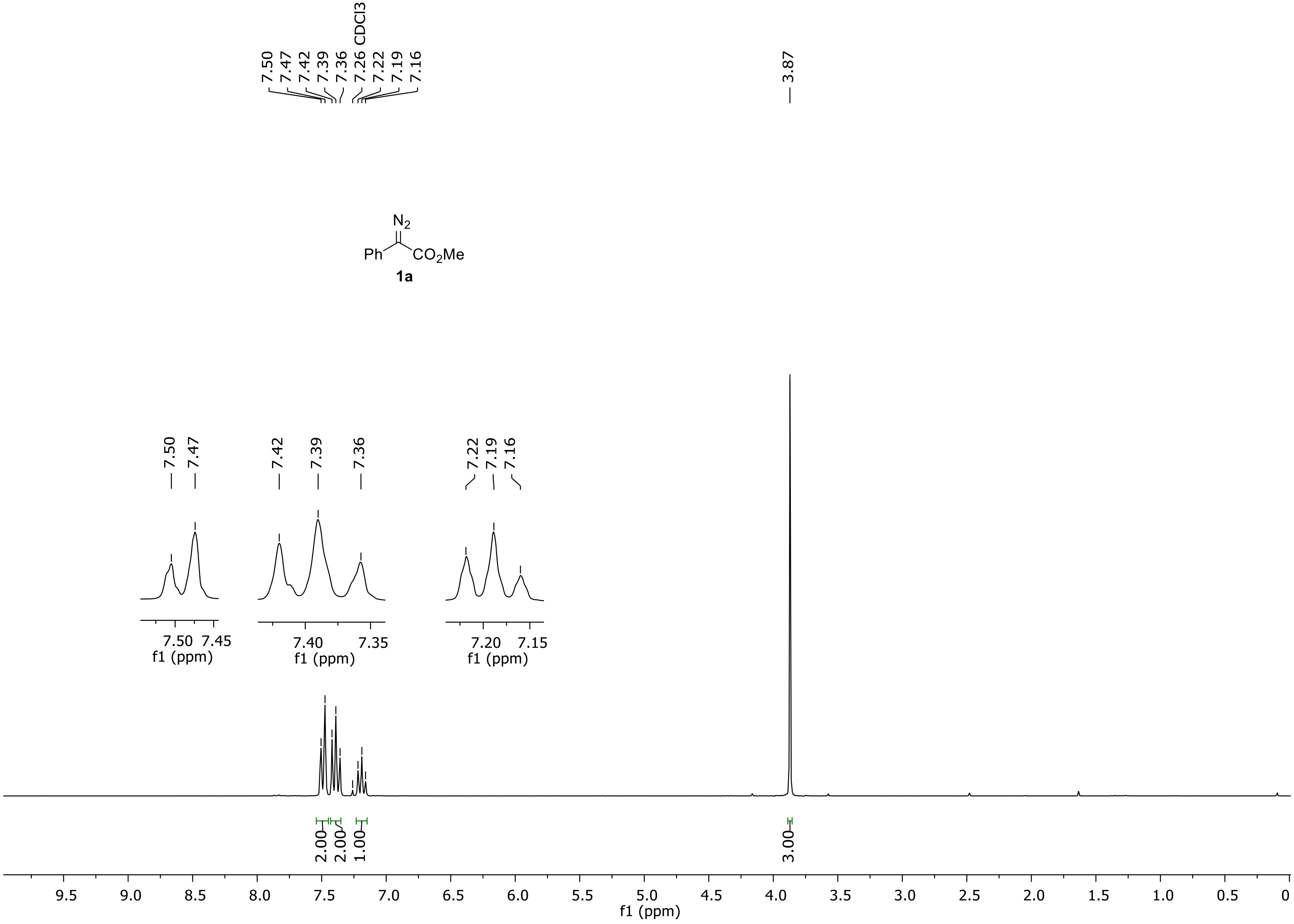


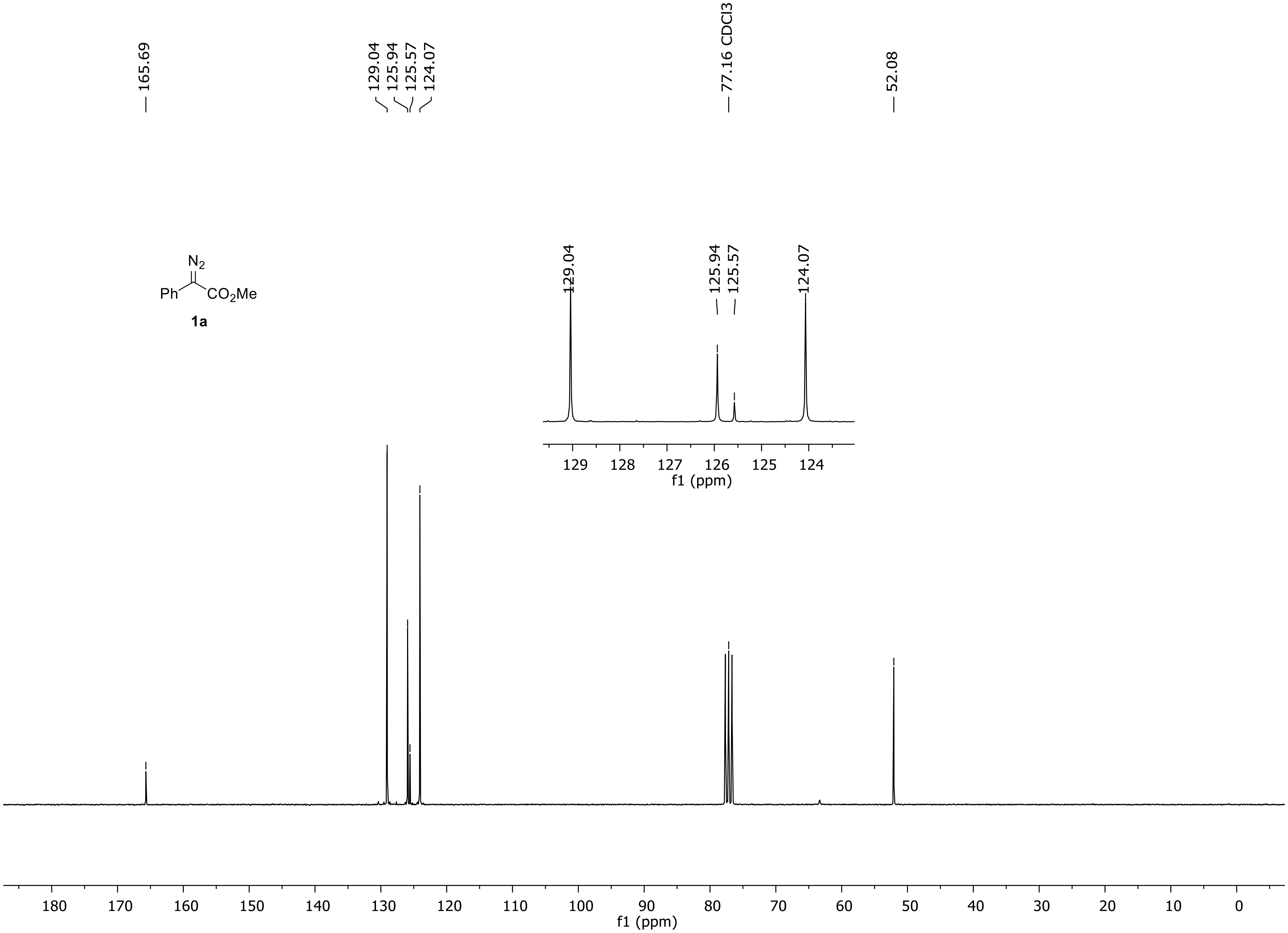
Figure S10. Variation of moles of **3a** formed according with the moles of incident photons using a CW laser (Picoquant) of λ = 405 nm, Power = 13.8 mW.

6. Copies of ^{1}H, ^{13}C{^{1}H} and ^{19}F{^{1}H} NMR Spectra

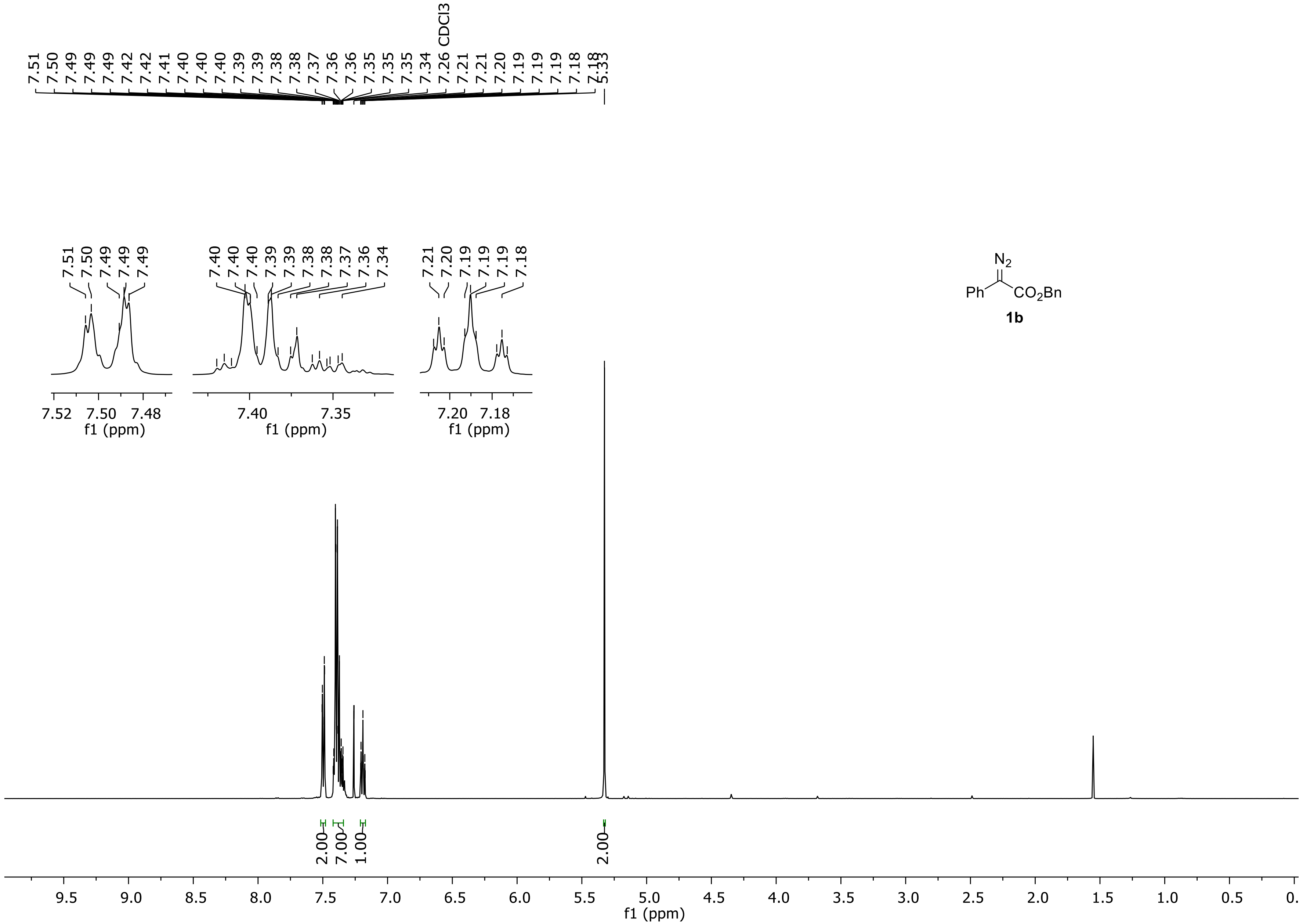
^{1}H NMR of 1a (CDCl$_3$, 250 MHz)



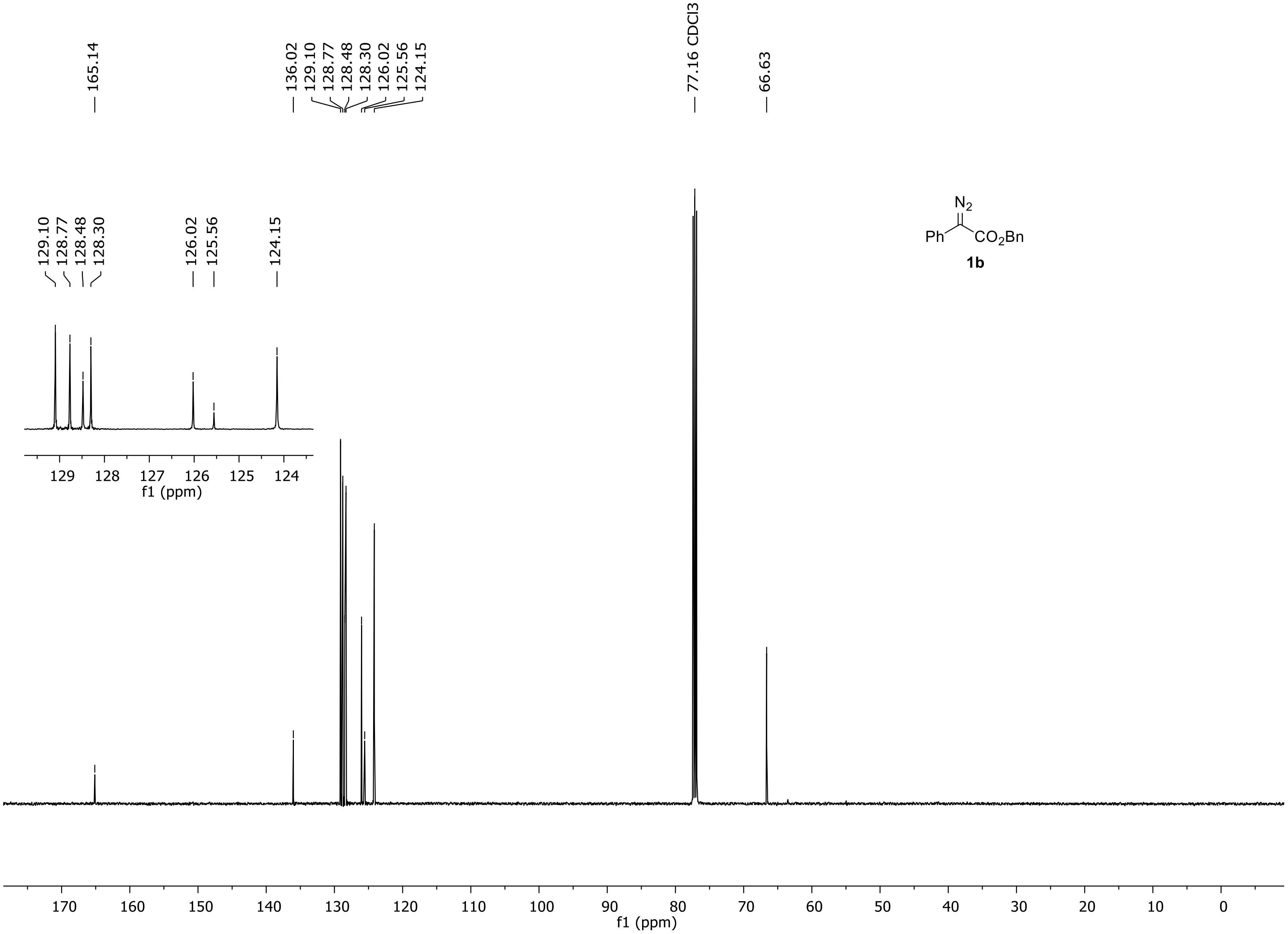
$^{13}C\{^1H\}$ NMR of 1a ($CDCl_3$, 62.5 MHz)



^{1}H NMR of 1b ($CDCl_3$, 500 MHz)



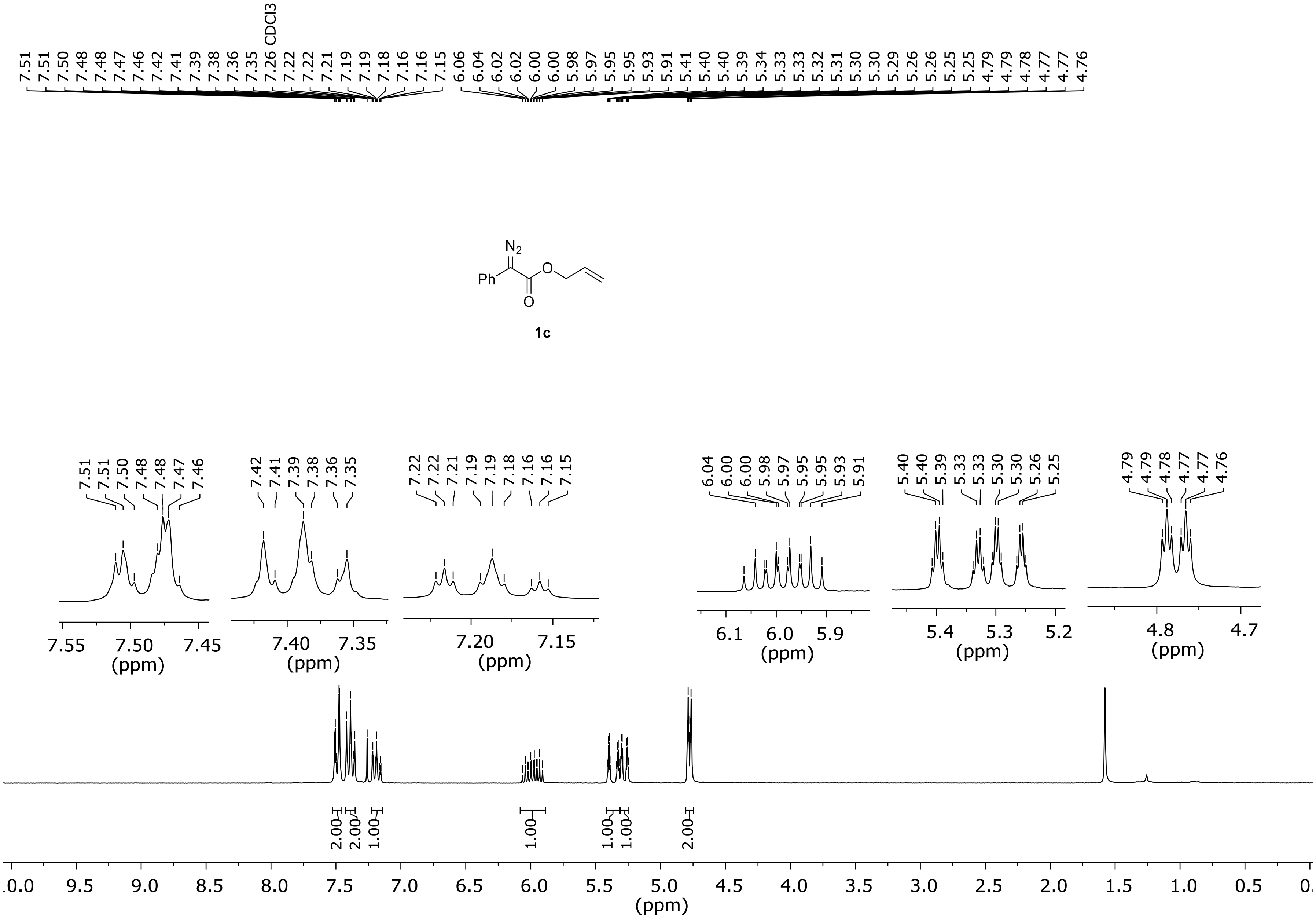
$^{13}C\{^1H\}$ NMR of 1b ($CDCl_3$, 125 MHz)



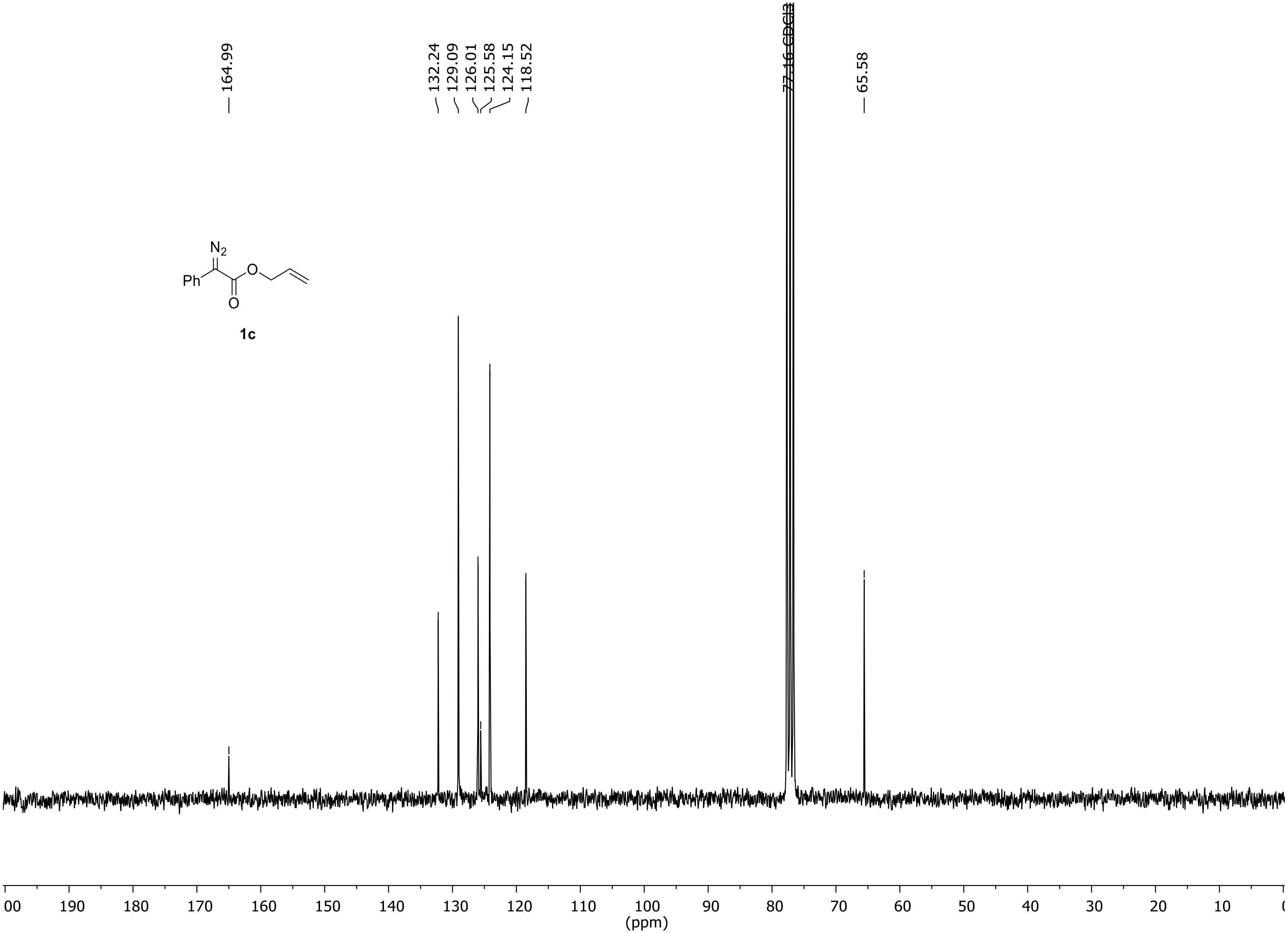
1b

^{1}H NMR of 1c (CDCl$_3$, 250 MHz)

1c

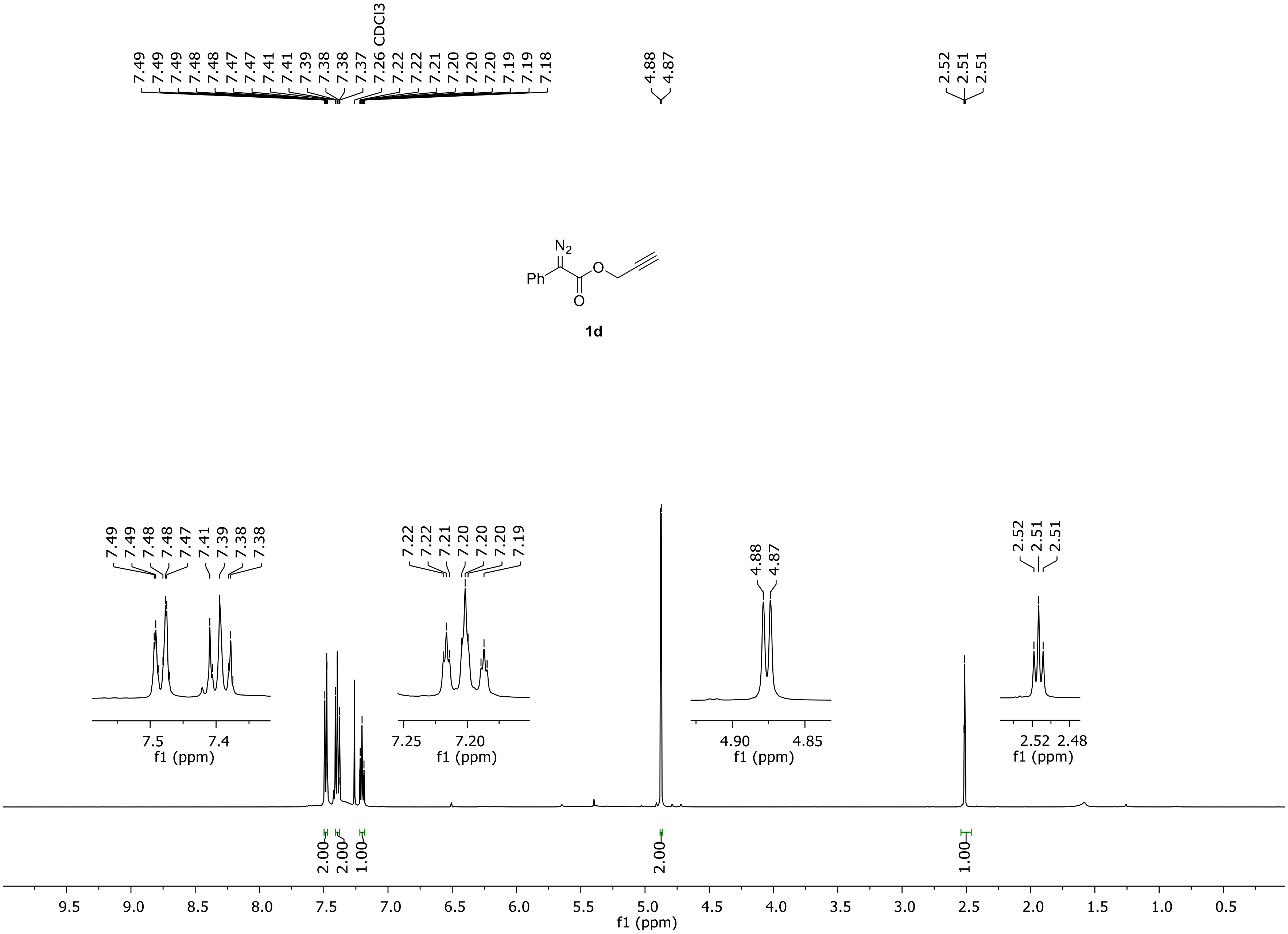


$^{13}C\{^1H\}$ NMR of 1c ($CDCl_3$, 62.5 MHz)



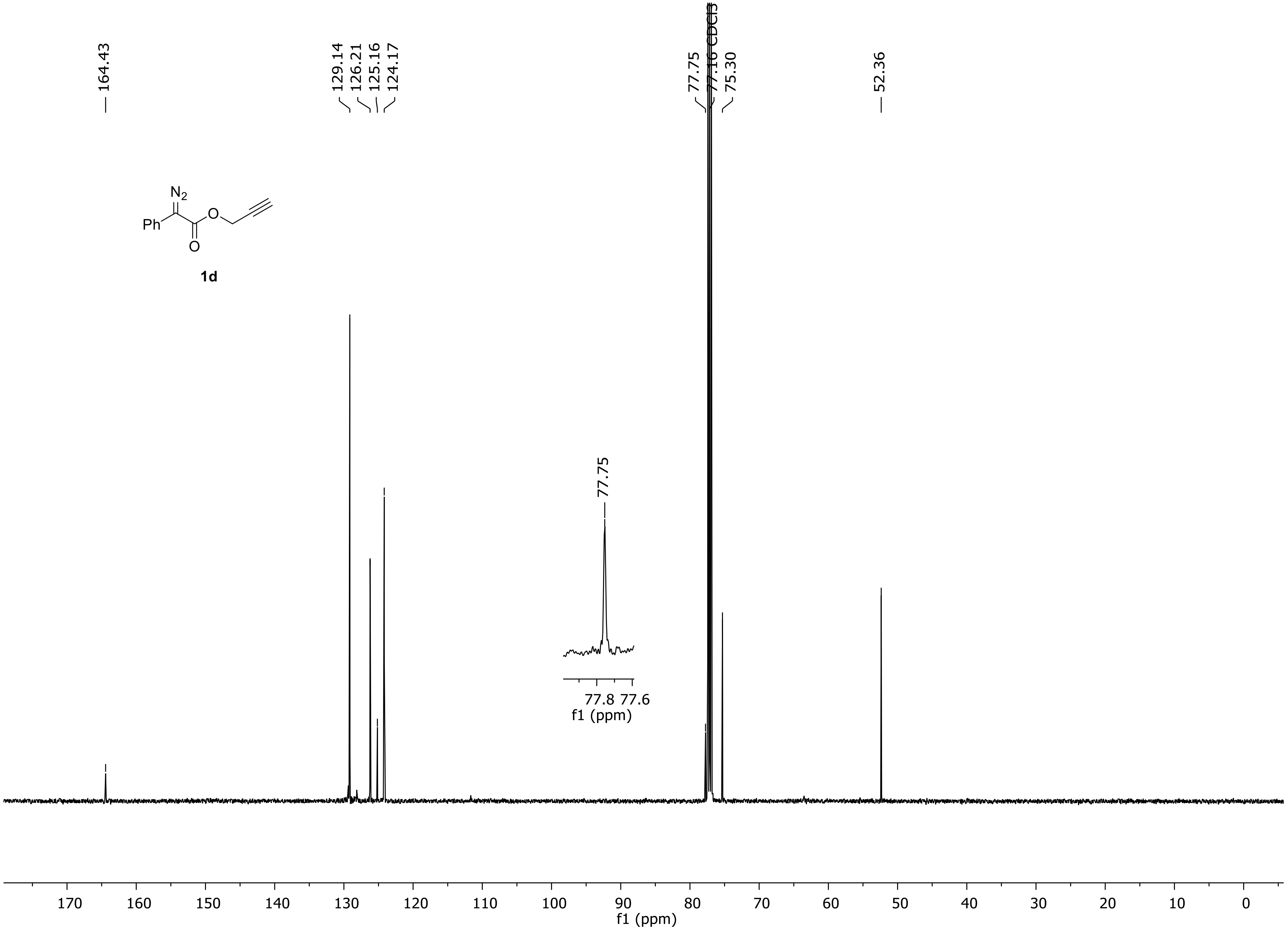
1c

^{1}H NMR of 1d (CDCl$_3$, 500 MHz)



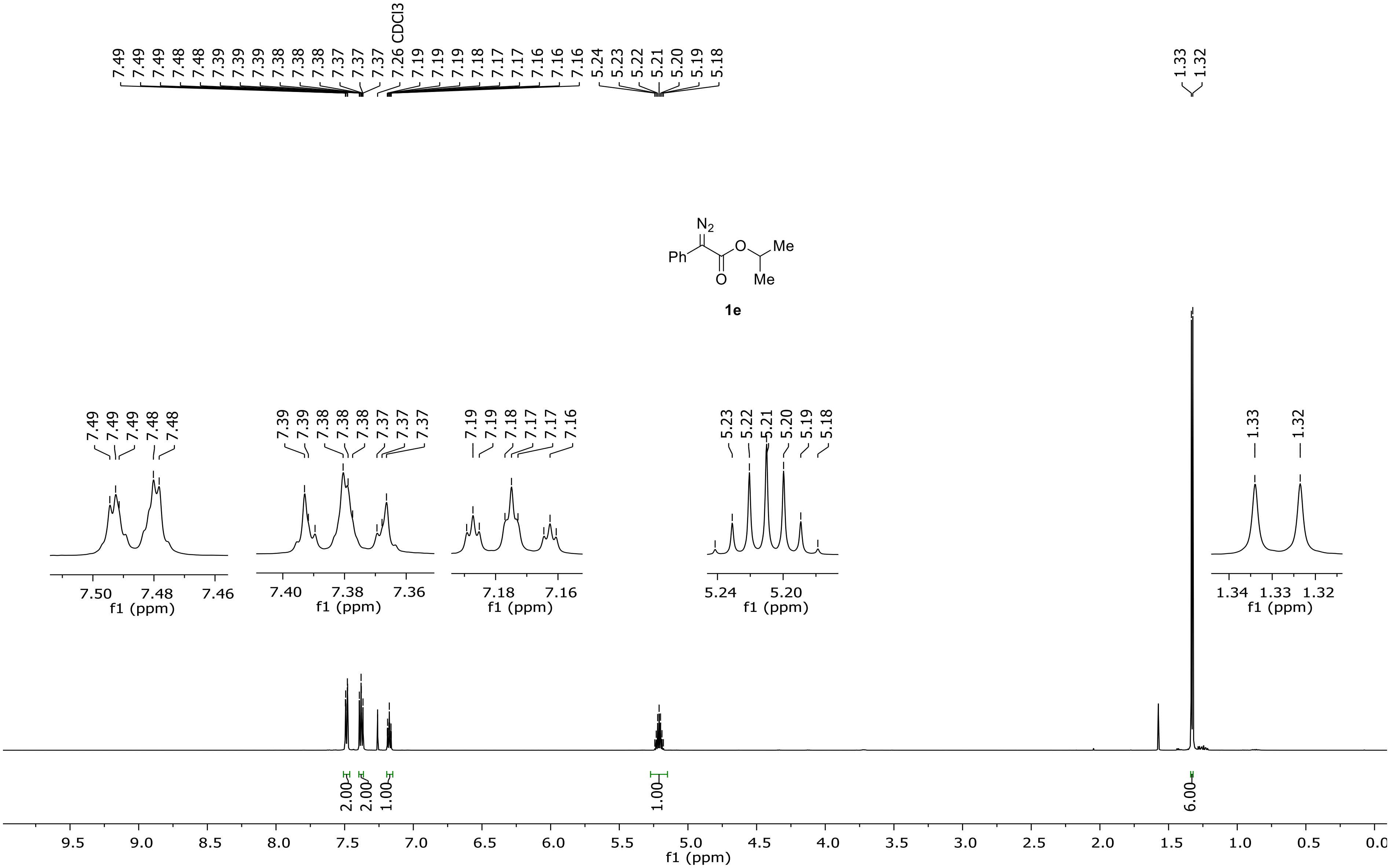
$^{13}C\{^1H\}$ NMR of 1d ($CDCl_3$, 125 MHz)

1d

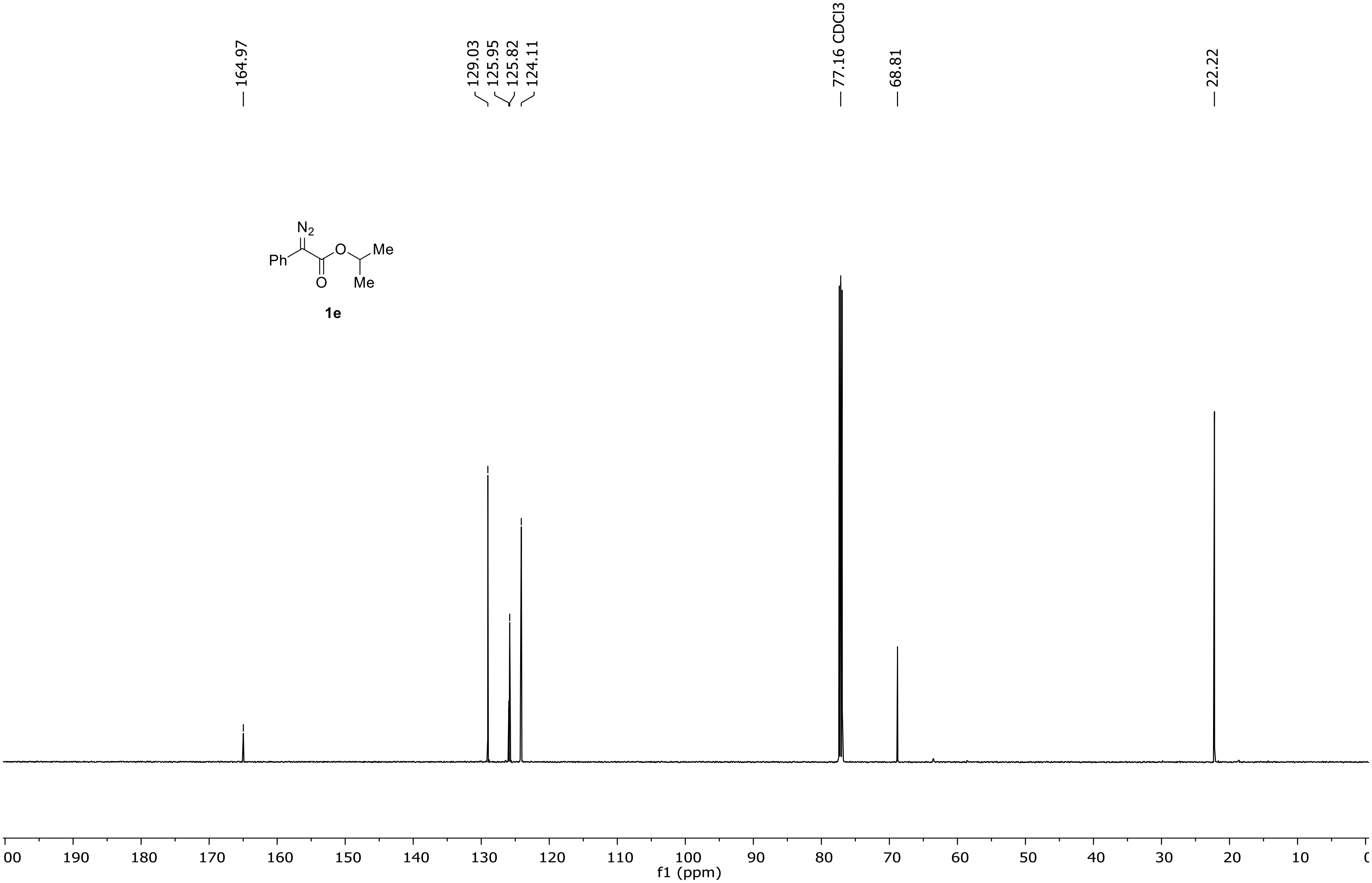


^{1}H NMR of 1e (CDCl$_3$, 600 MHz)

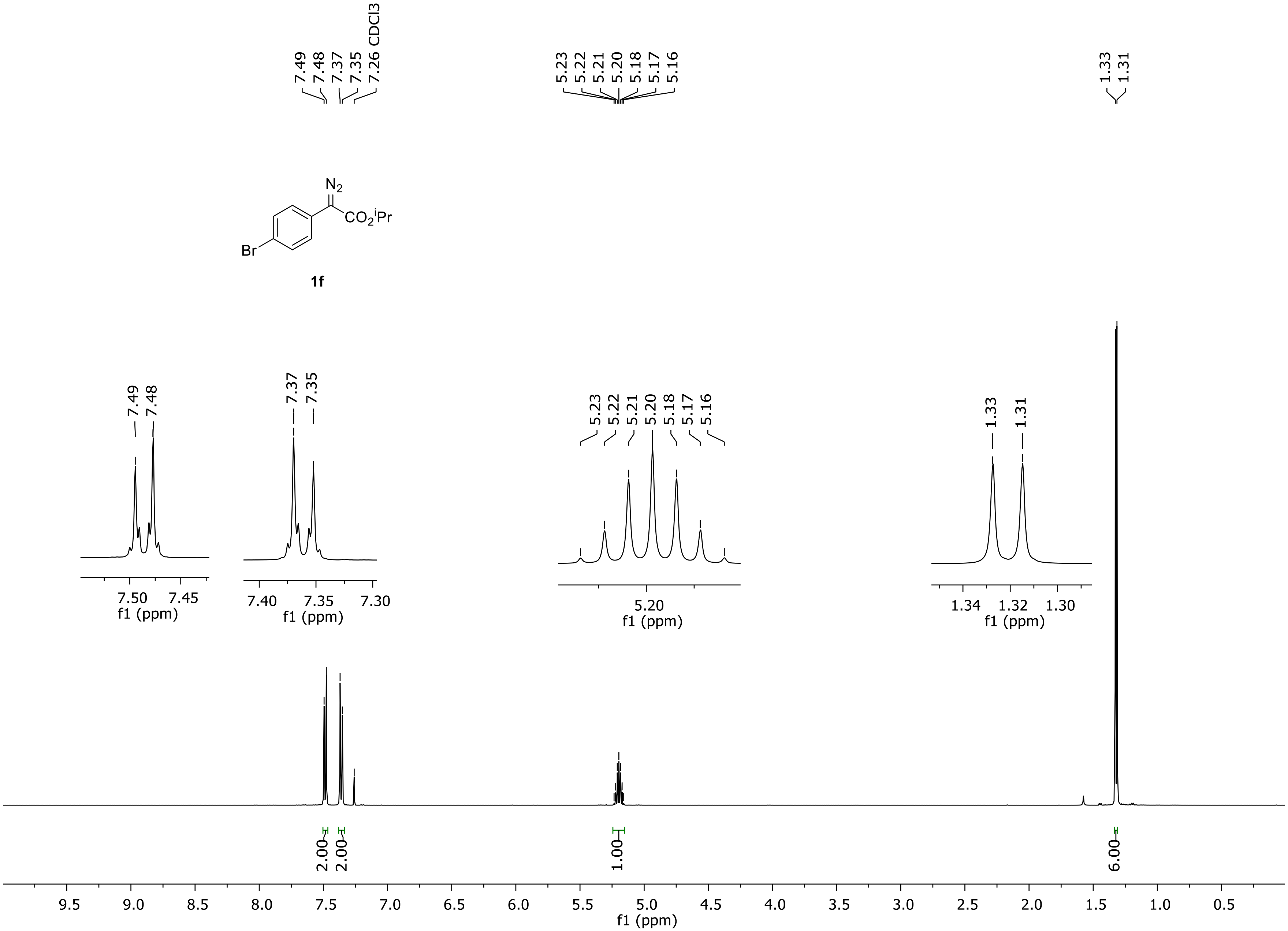
1e



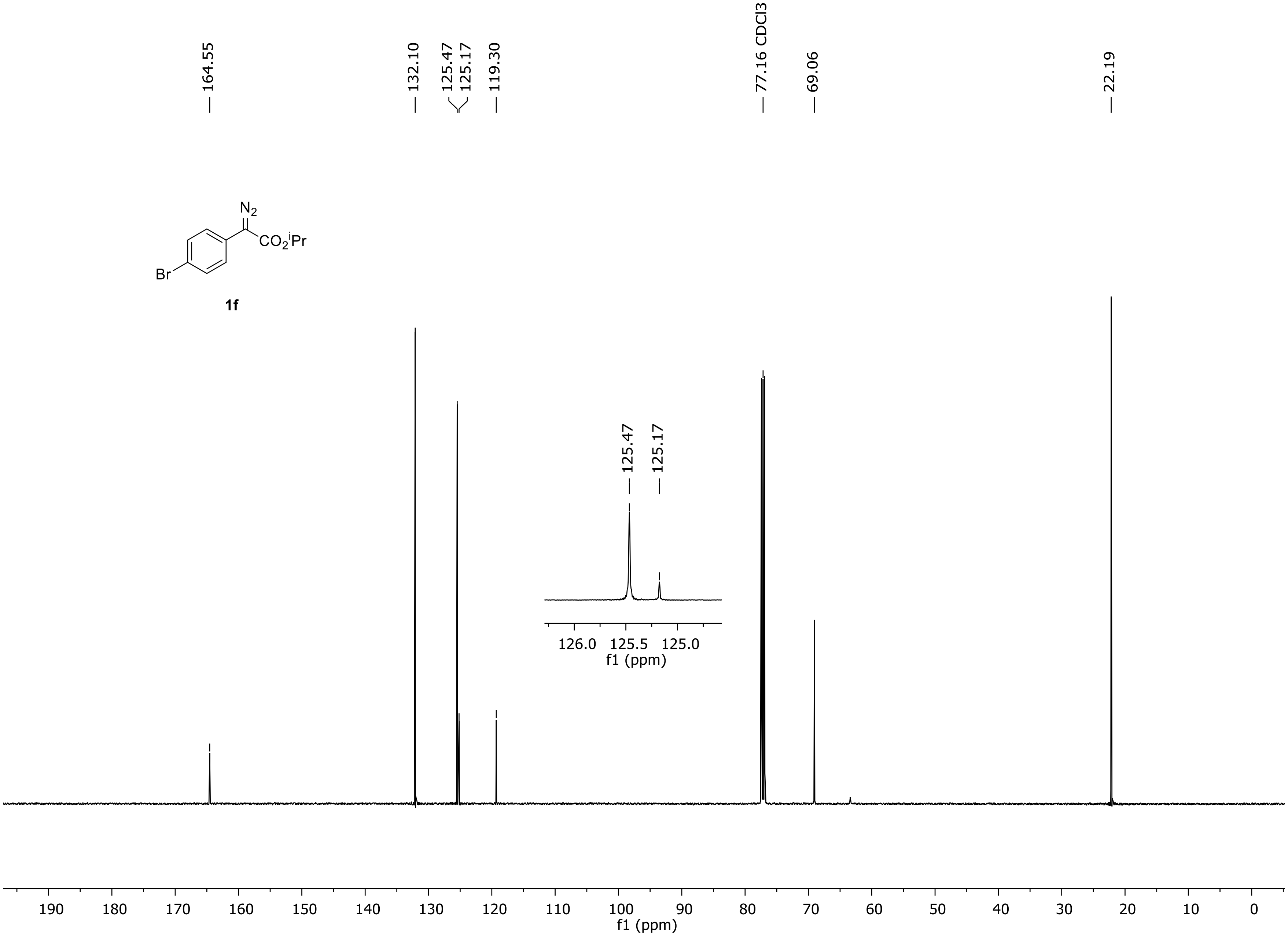
$^{13}C\{^1H\}$ NMR of 1e ($CDCl_3$, 150 MHz)



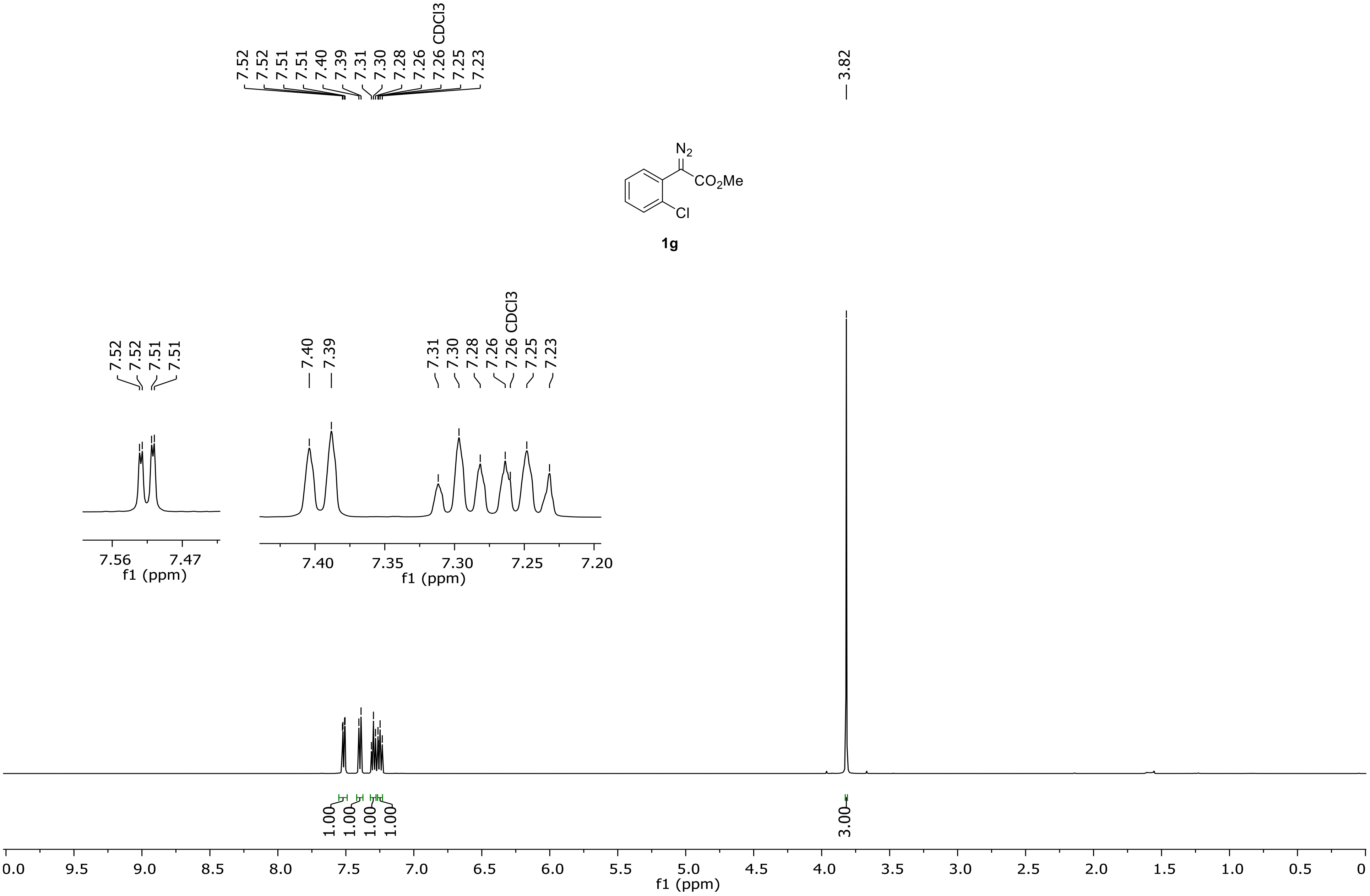
^{1}H NMR of 1f ($CDCl_3$, 500 MHz)



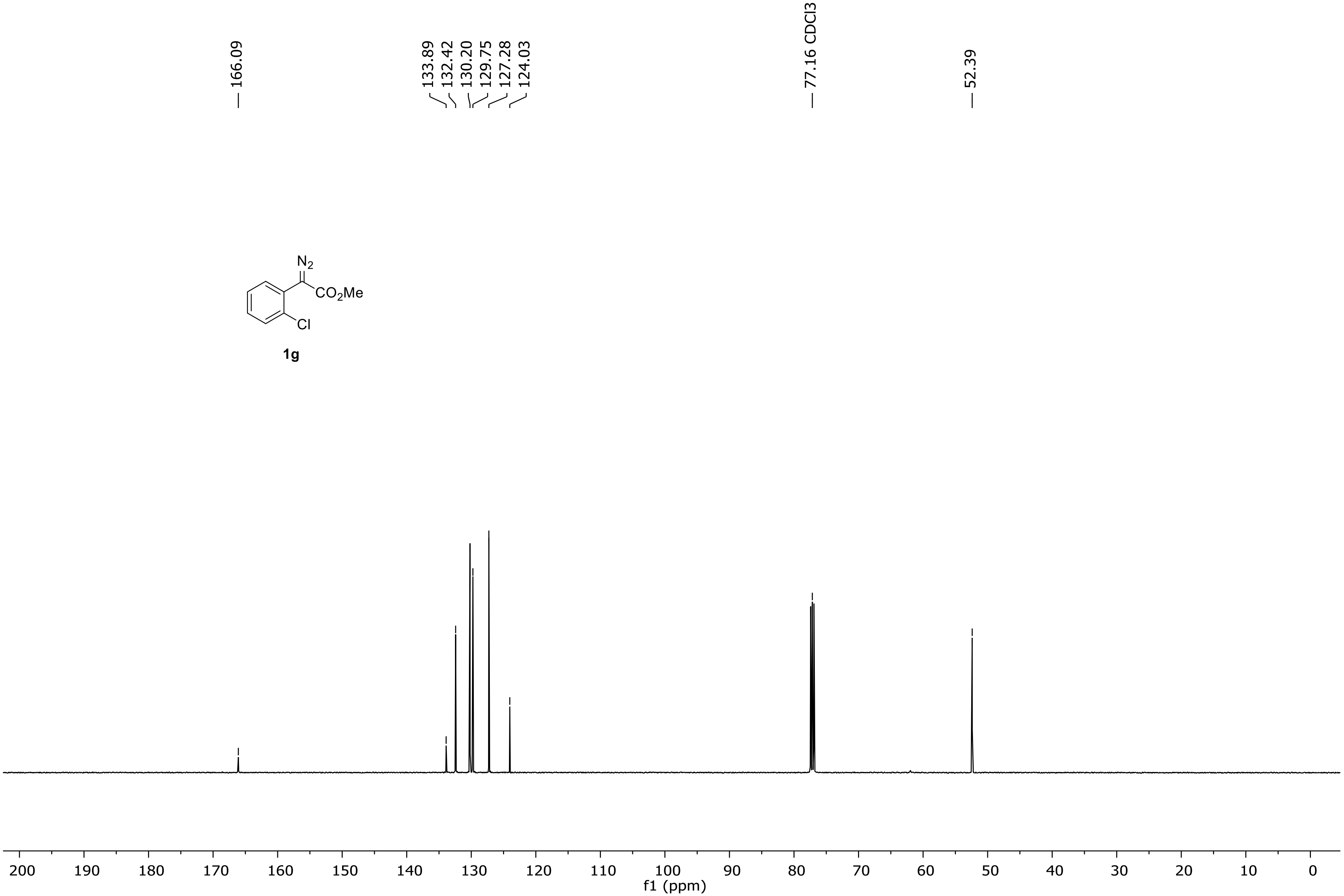
$^{13}C\{^1H\}$ NMR of 1f ($CDCl_3$, 125 MHz)



^{1}H NMR of 1g ($CDCl_3$, 500 MHz)

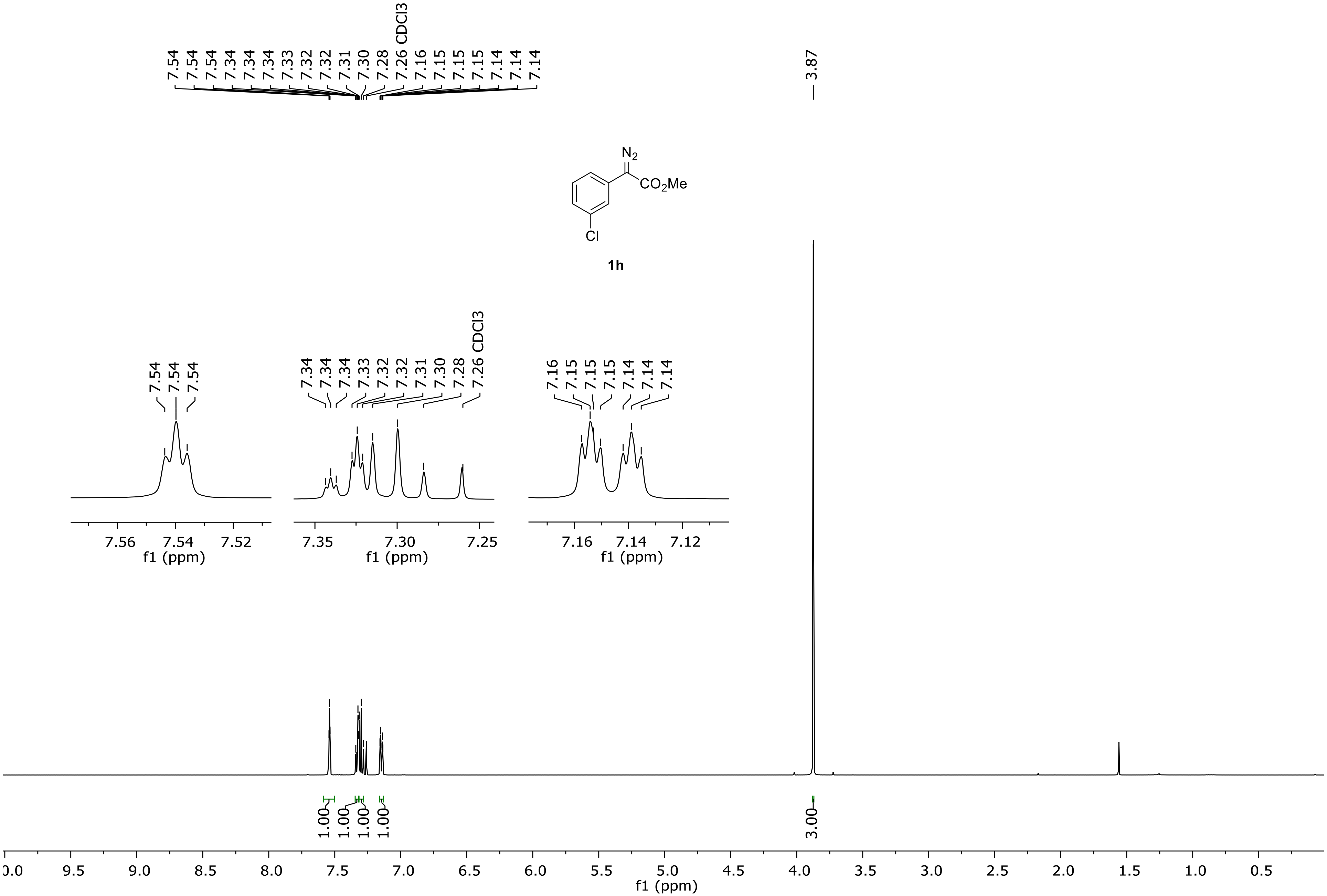


$^{13}C\{^{1}H\}$ NMR of 1g ($CDCl_3$, 125 MHz)

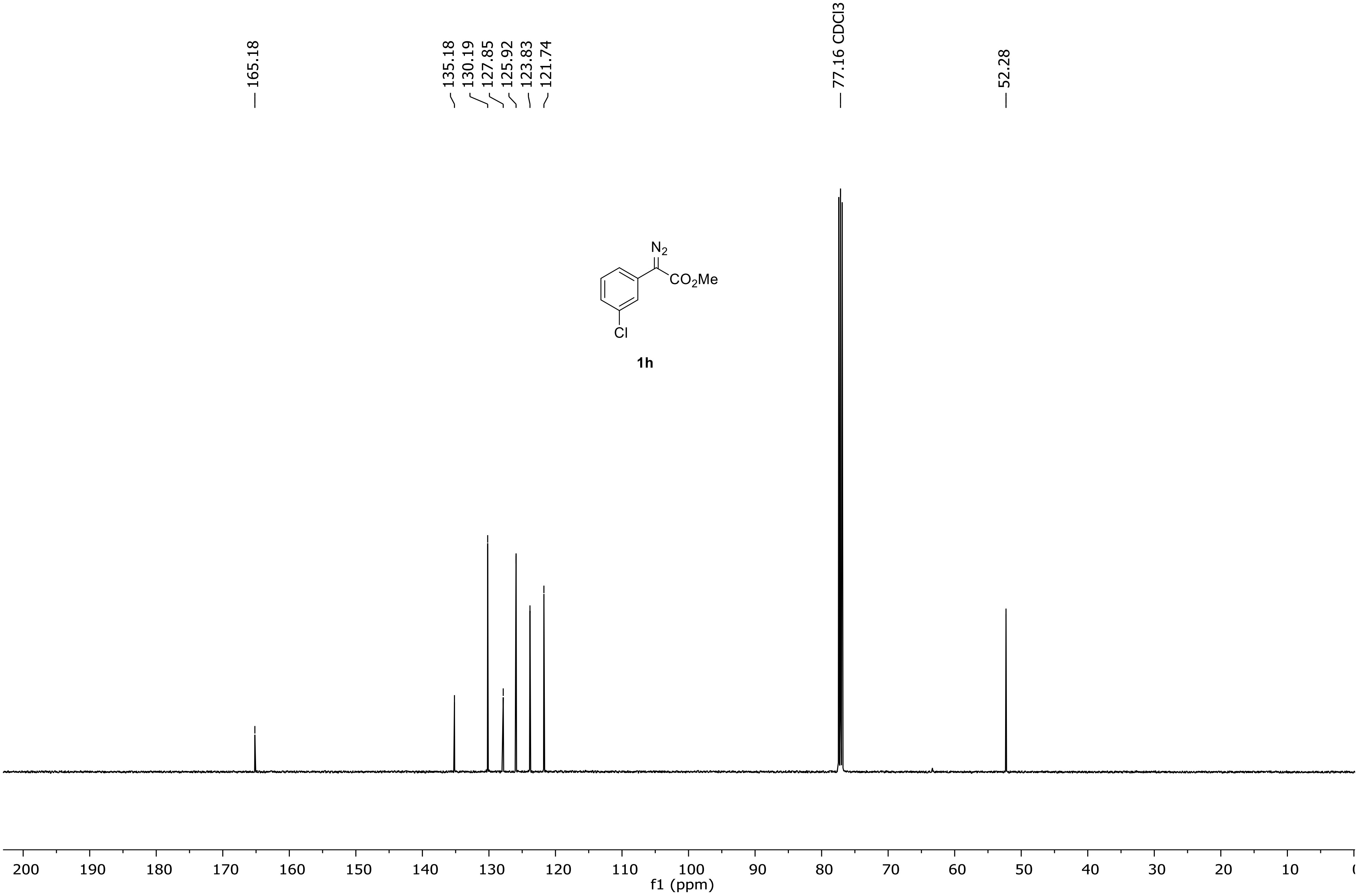


^{1}H NMR of 1h ($CDCl_3$, 500MHz)

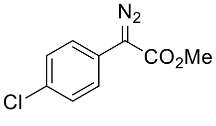
1h



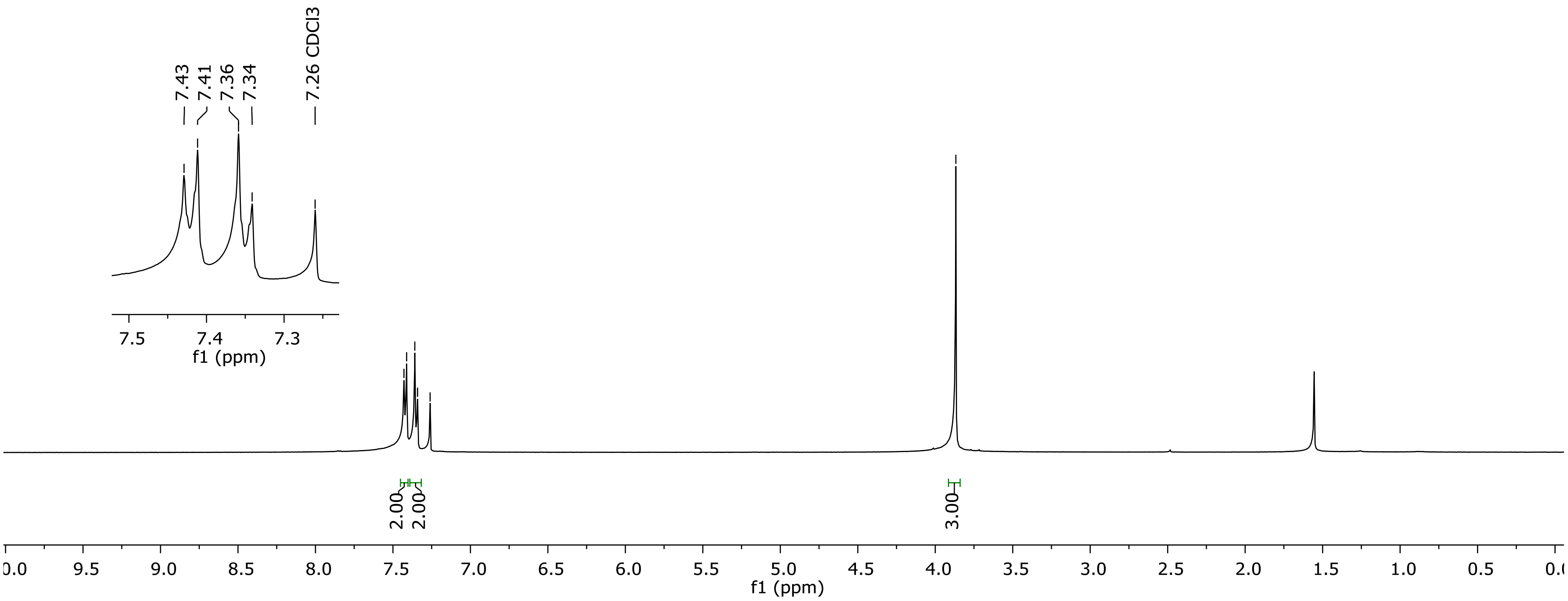
$^{13}C\{^1H\}$ NMR of 1h ($CDCl_3$, 125 MHz)



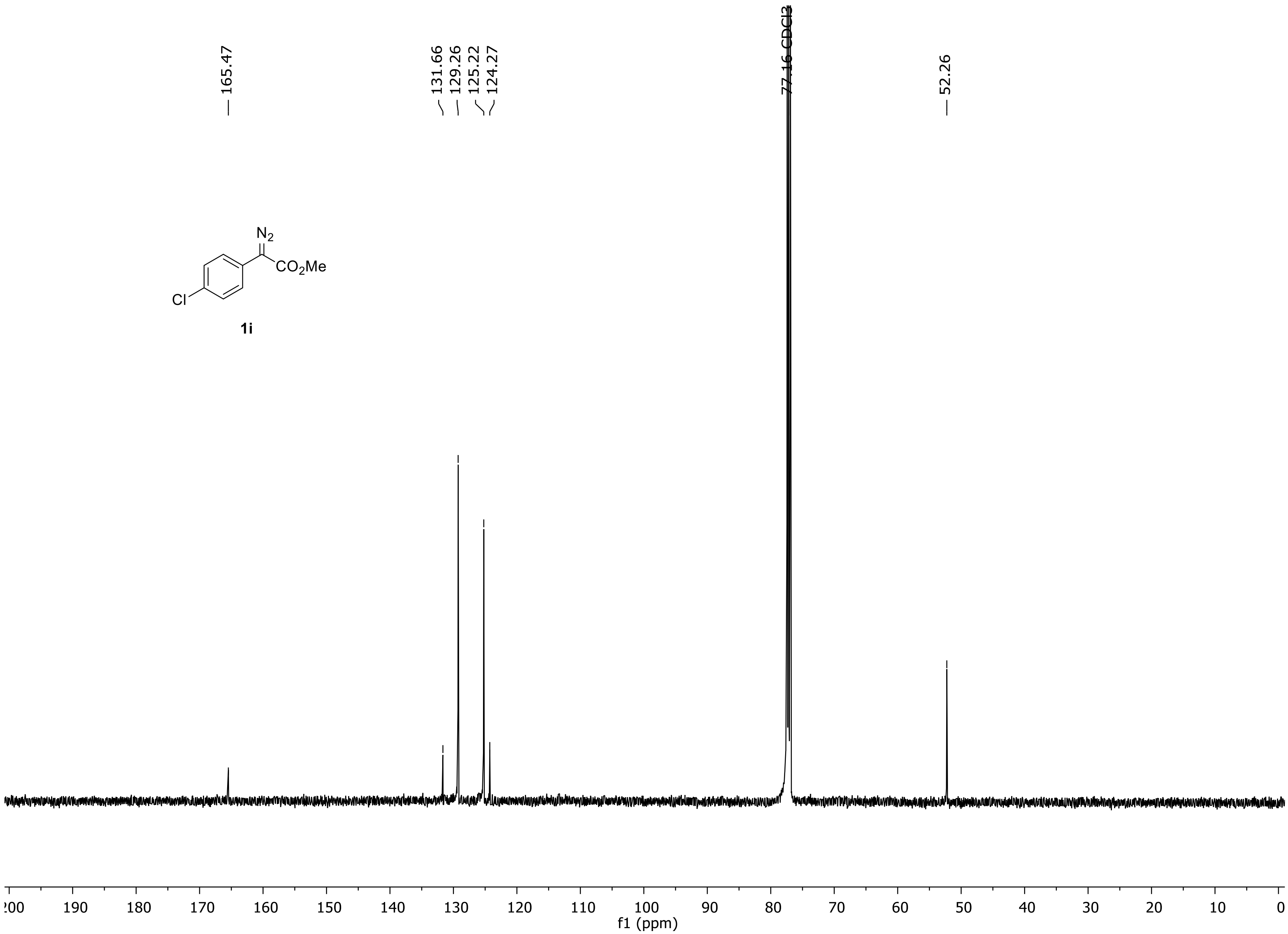
^{1}H NMR of 1i ($CDCl_3$, 500 MHz)



1i

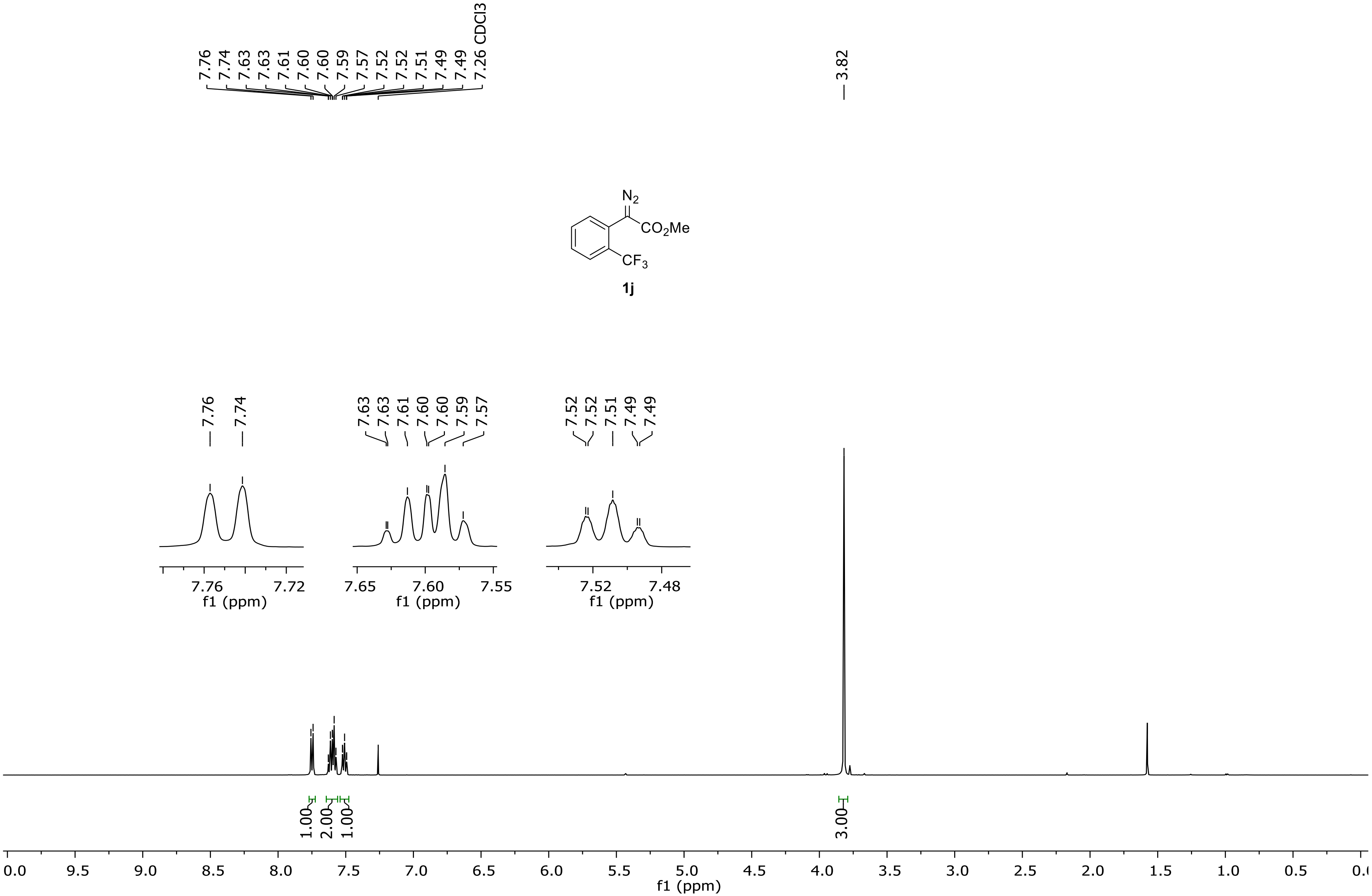


$^{13}C\{^{1}H\}$ NMR of 1i ($CDCl_3$, 125 MHz)

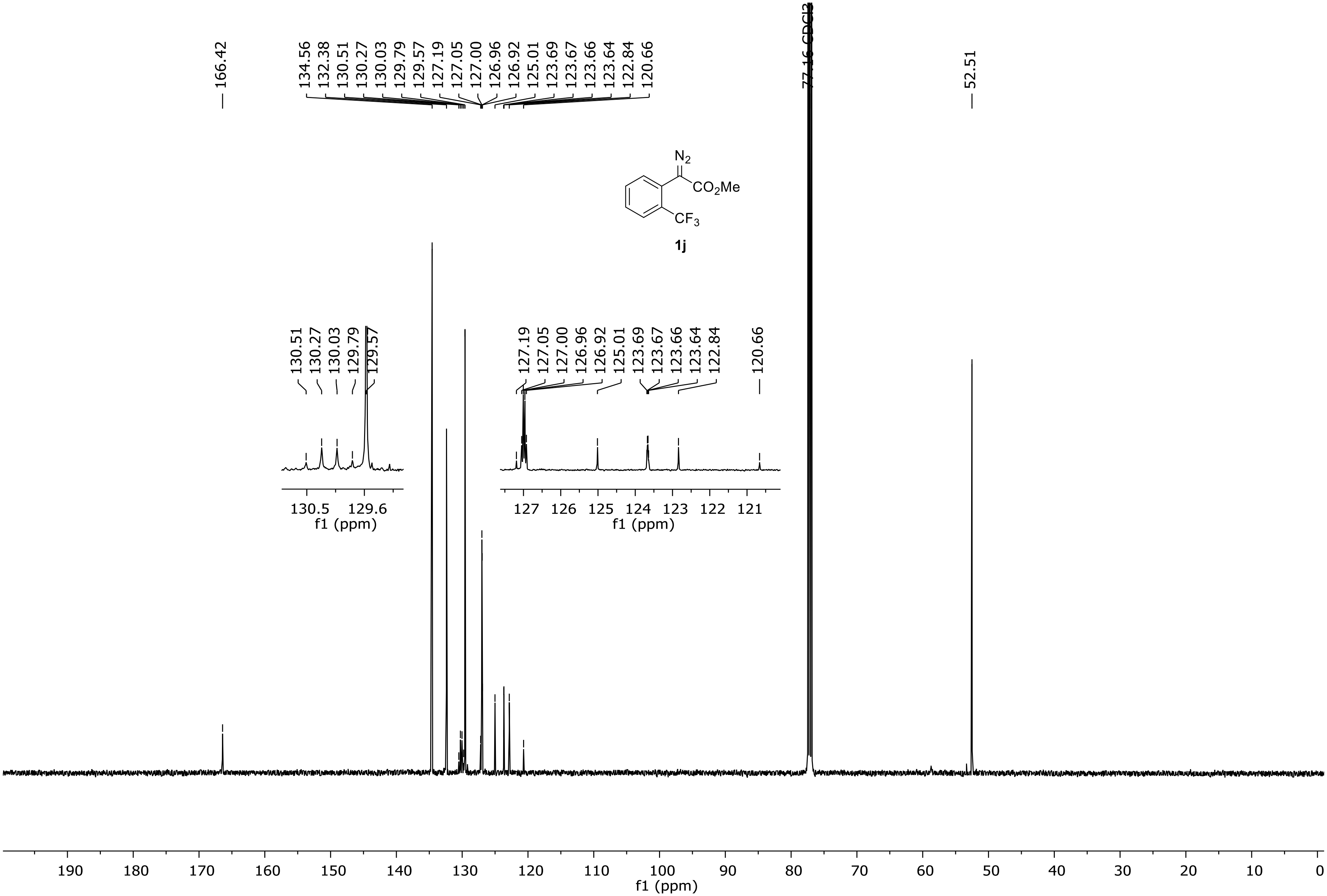


1i

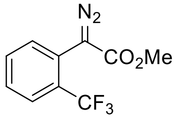
^{1}H NMR of 1j (CDCl$_3$, 500 MHz)



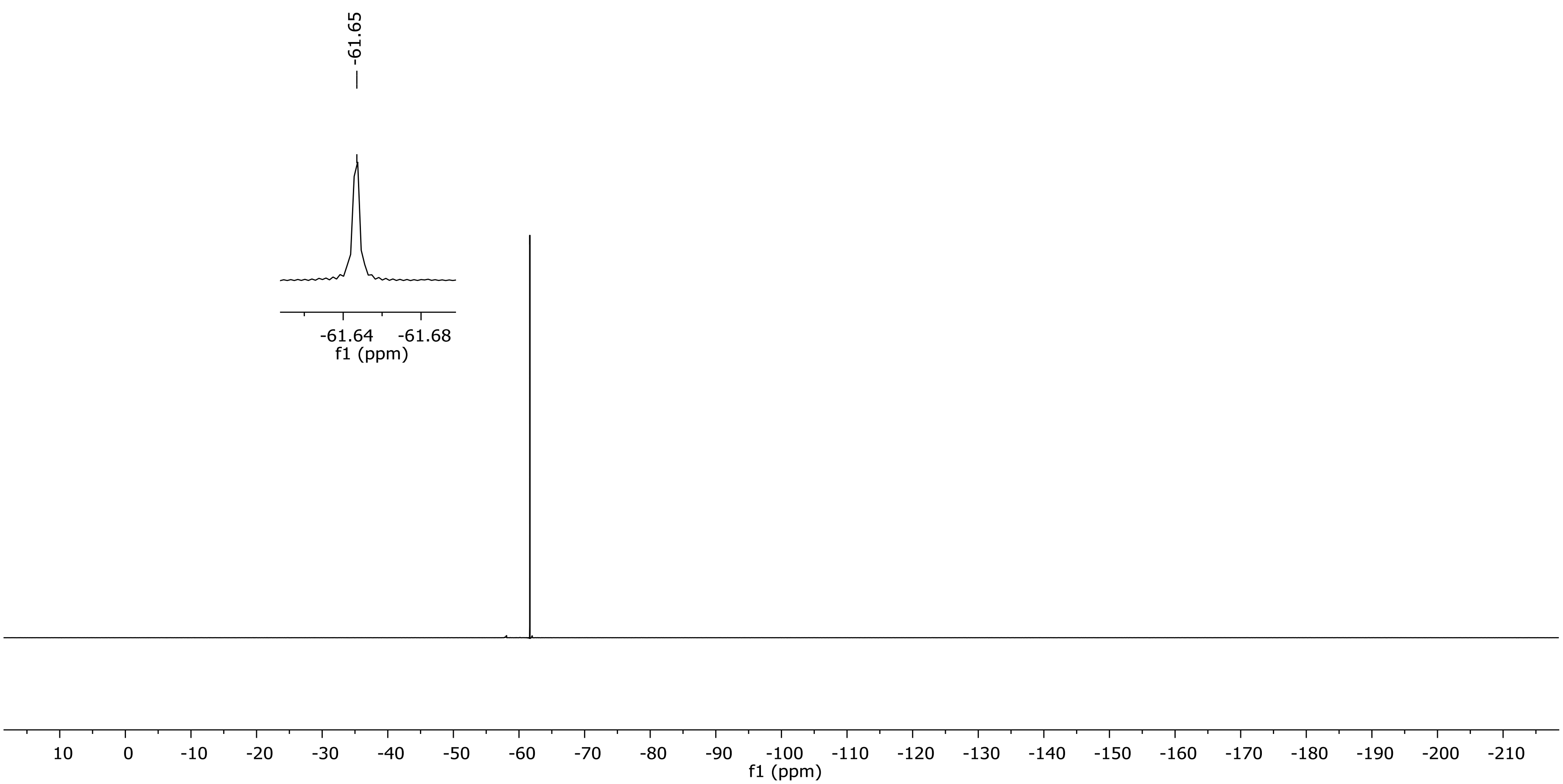
$^{13}C\{^1H\}$ NMR of 1j ($CDCl_3$, 125 MHz)



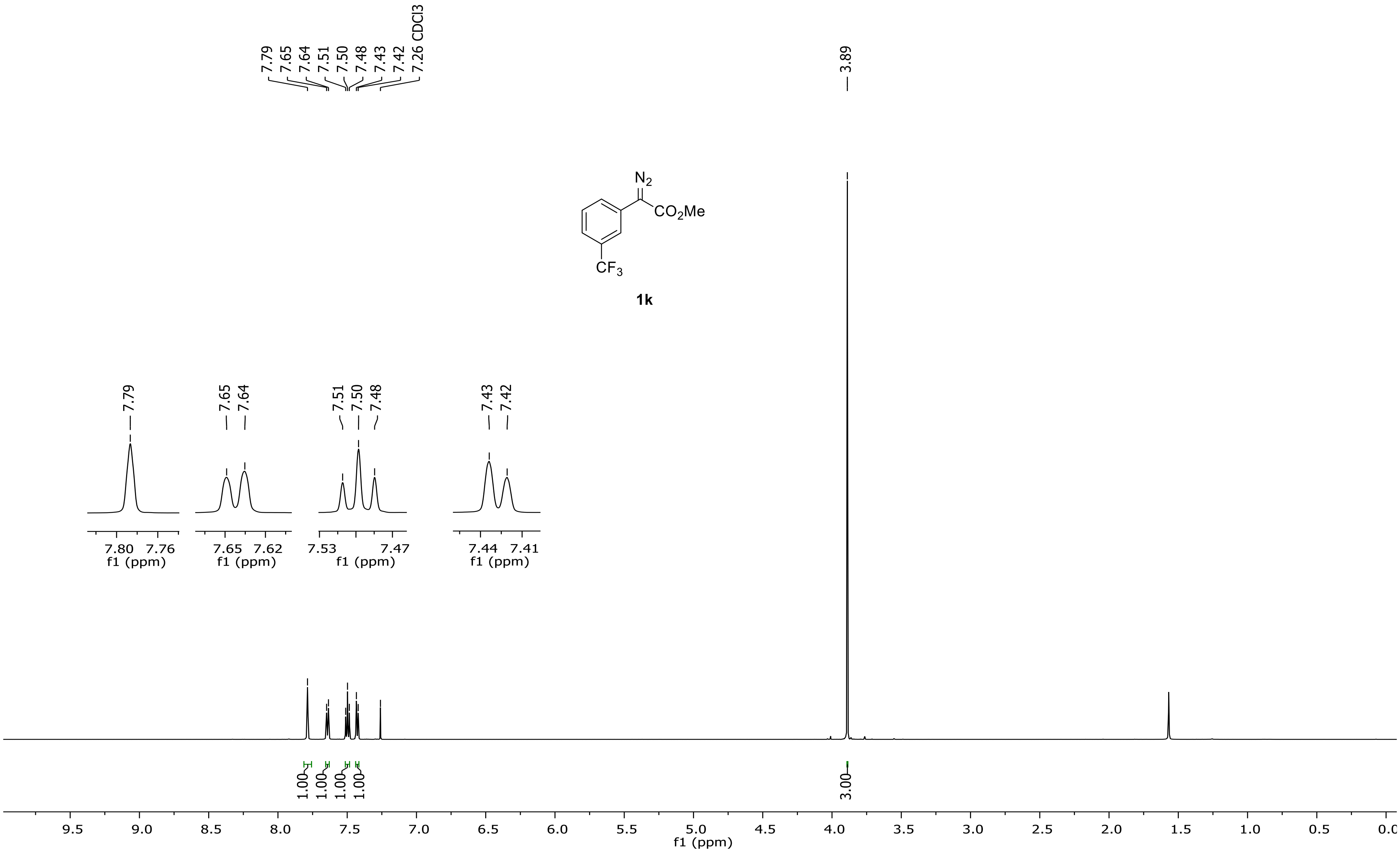
$^{19}F\{^1H\}$ NMR of 1j ($CDCl_3$, 470 MHz)



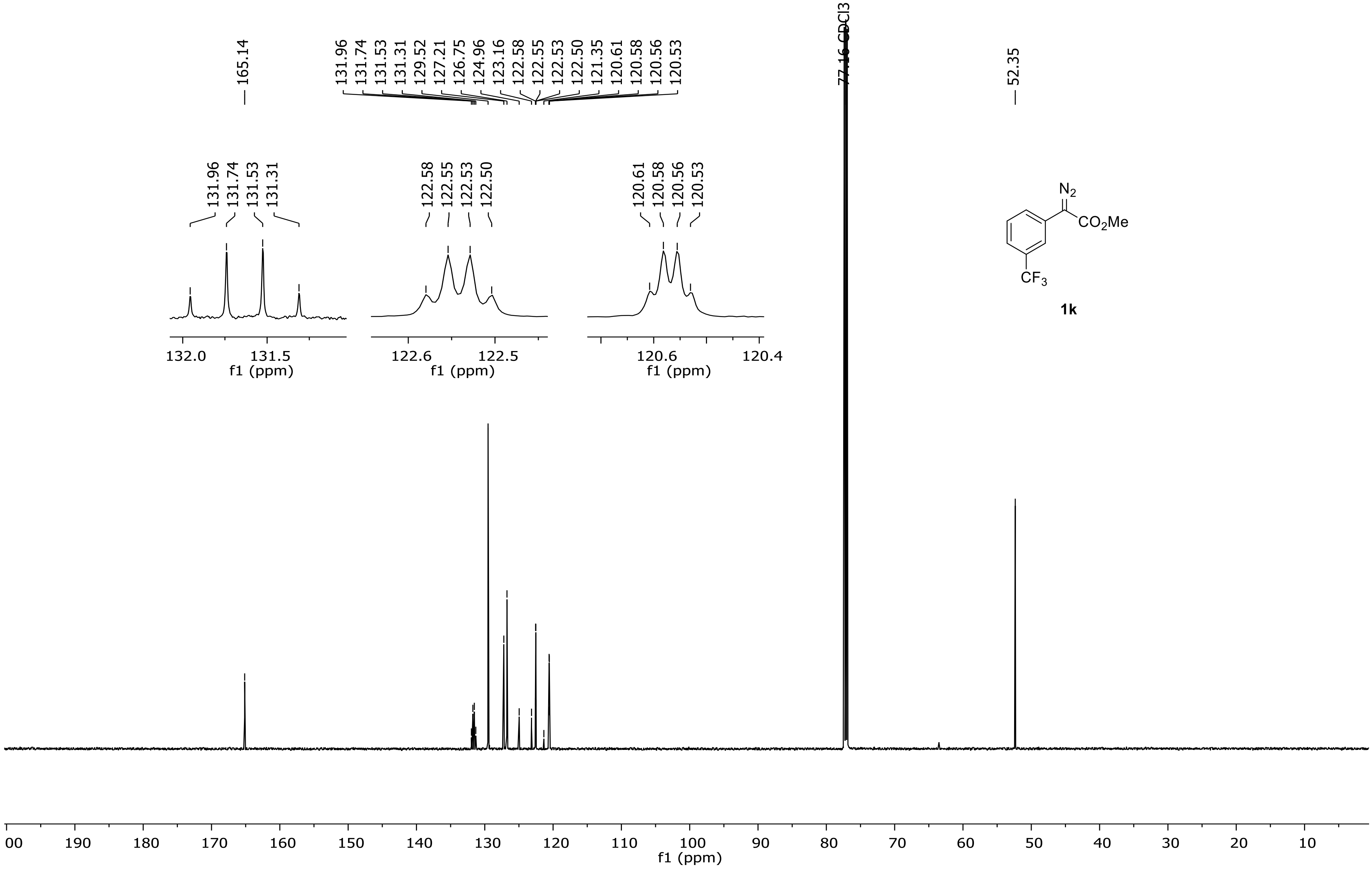
1j



^{1}H NMR of 1k (CDCl$_3$, 600 MHz)

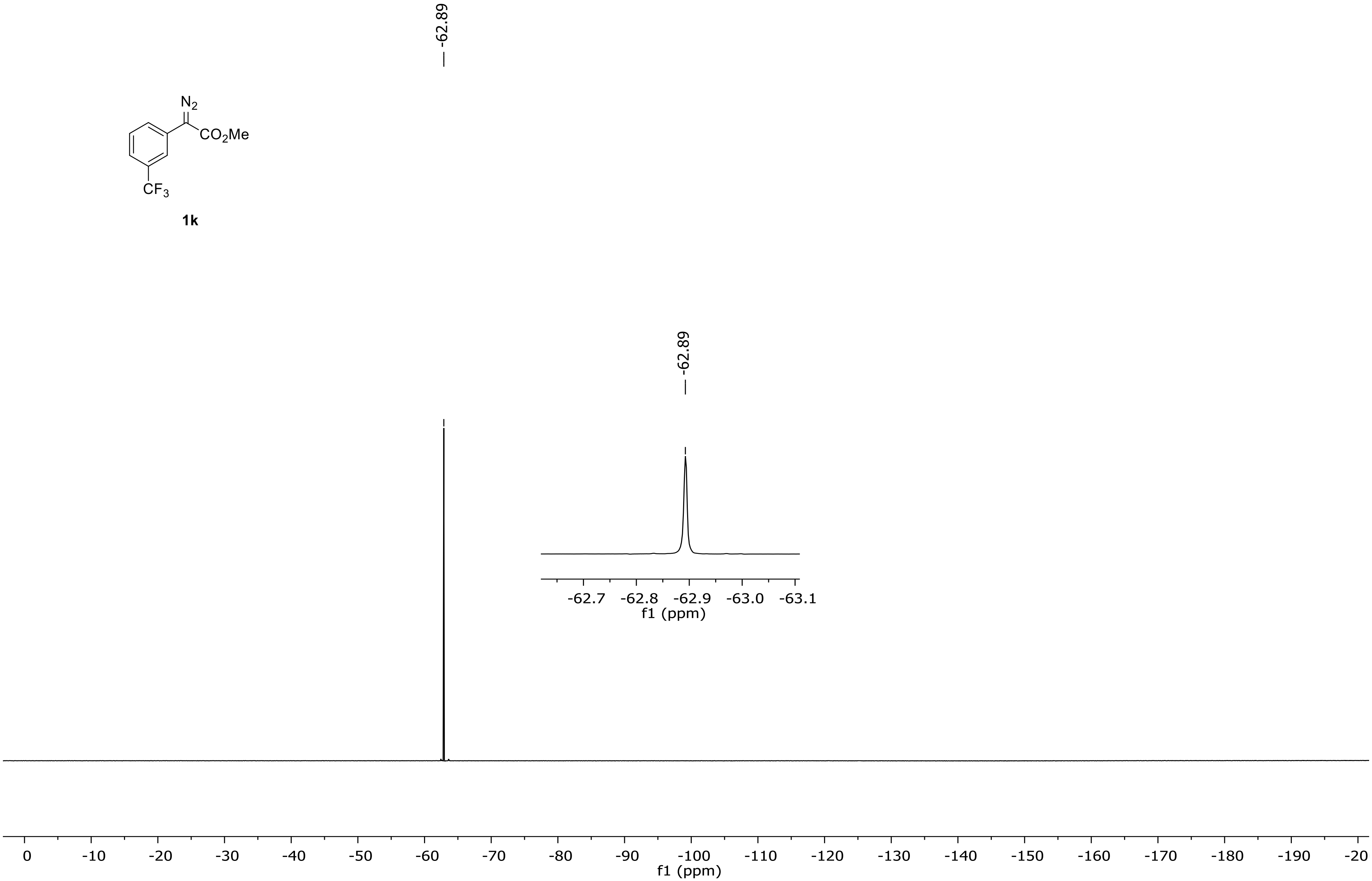


$^{13}C\{^1H\}$ NMR of 1k ($CDCl_3$, 150 MHz)



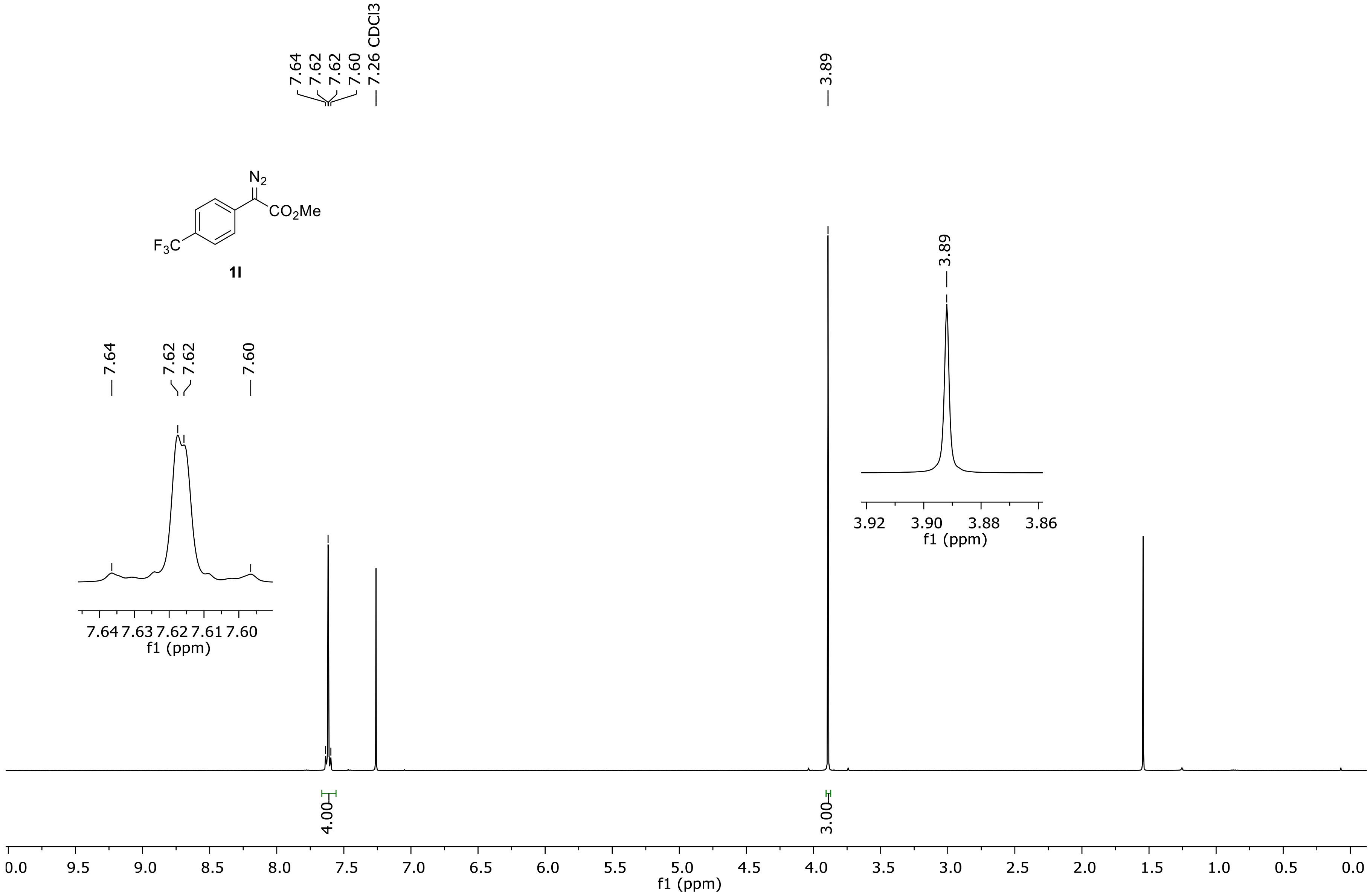
1k

$^{19}F\{^1H\}$ NMR of 1k ($CDCl_3$, 564 MHz)

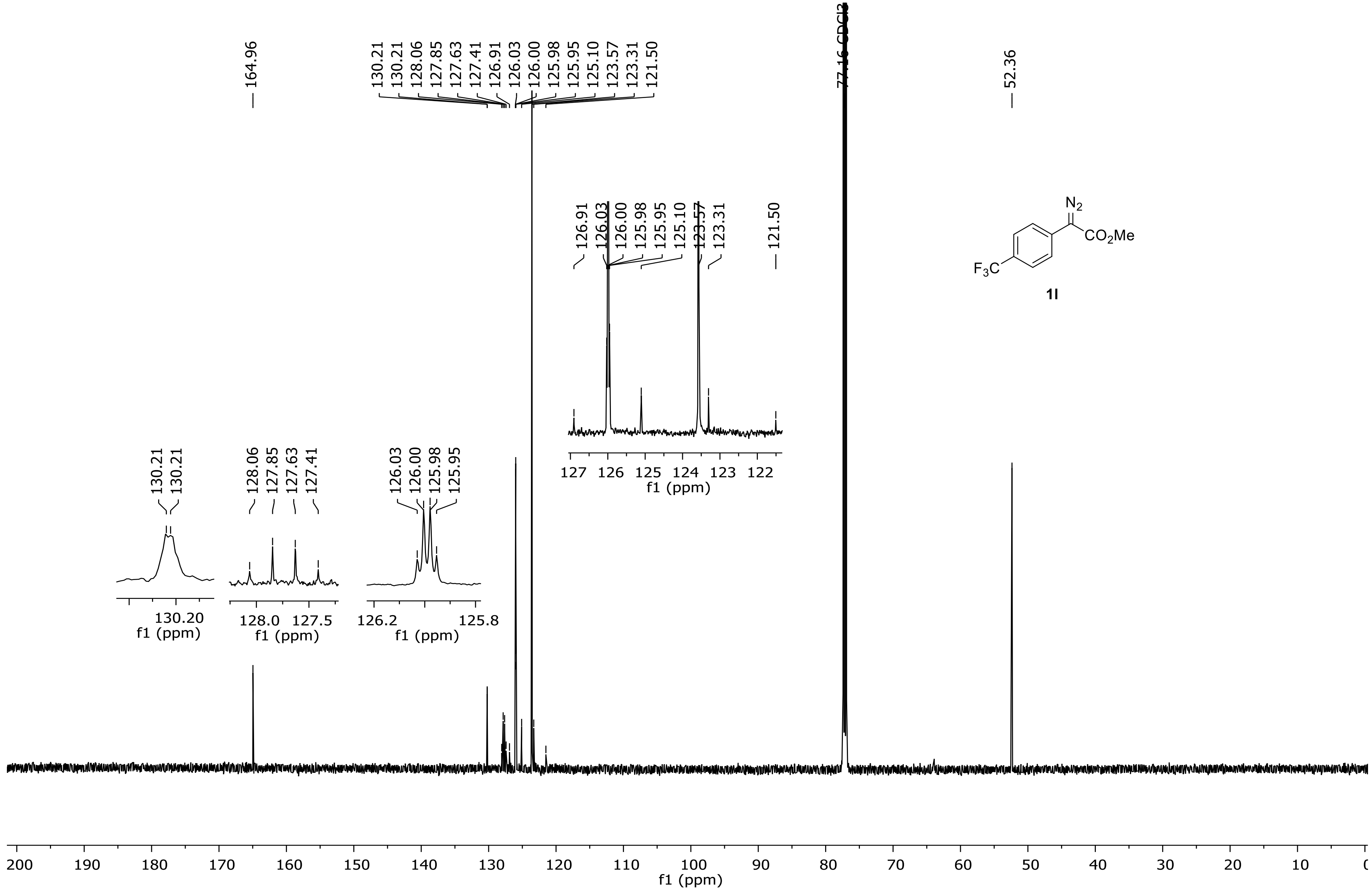


1k

^{1}H NMR of 1l (CDCl$_3$, 600 MHz)

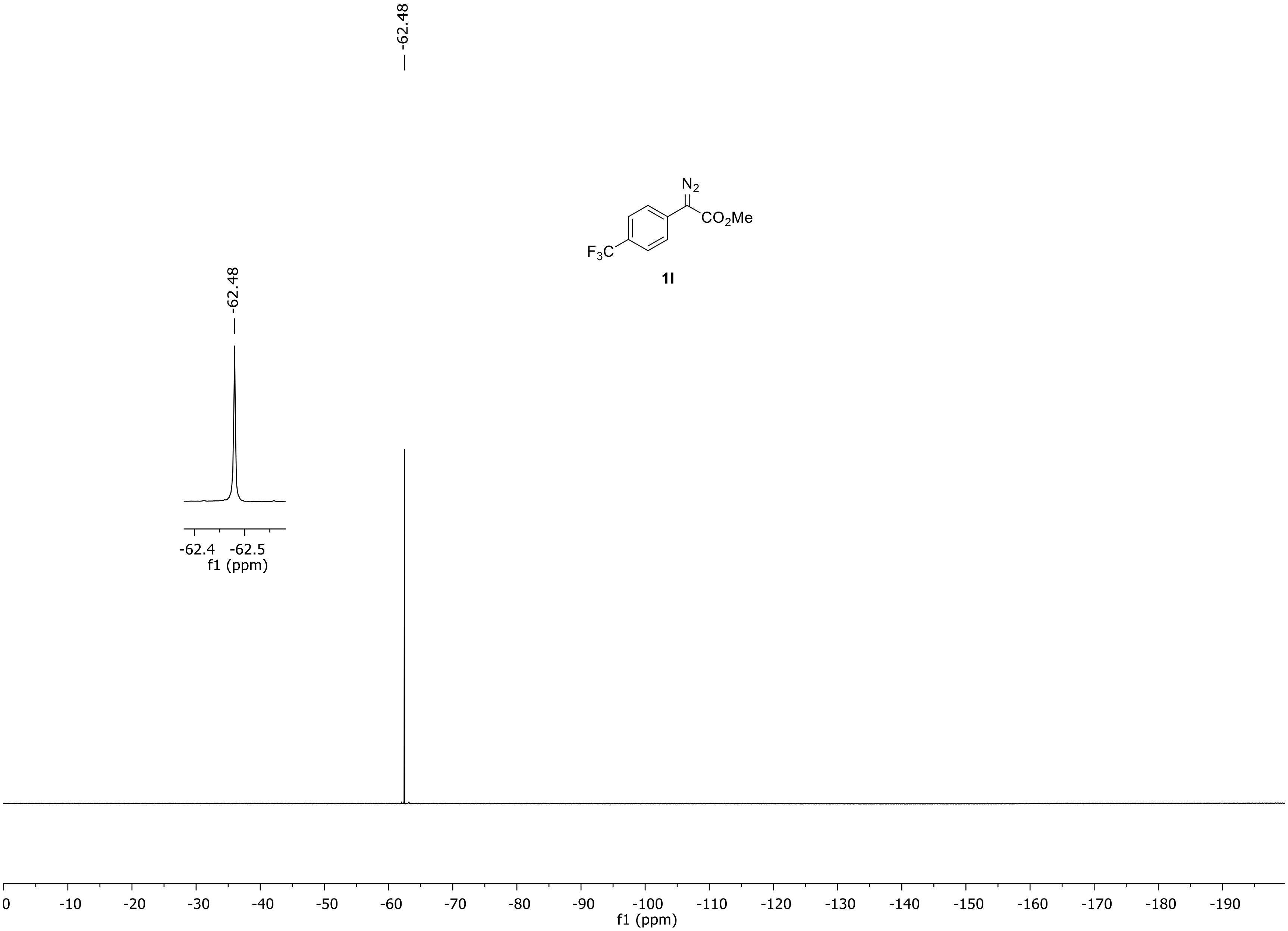


$^{13}C\{^1H\}$ **NMR of 1l ($CDCl_3$, 150 MHz)**

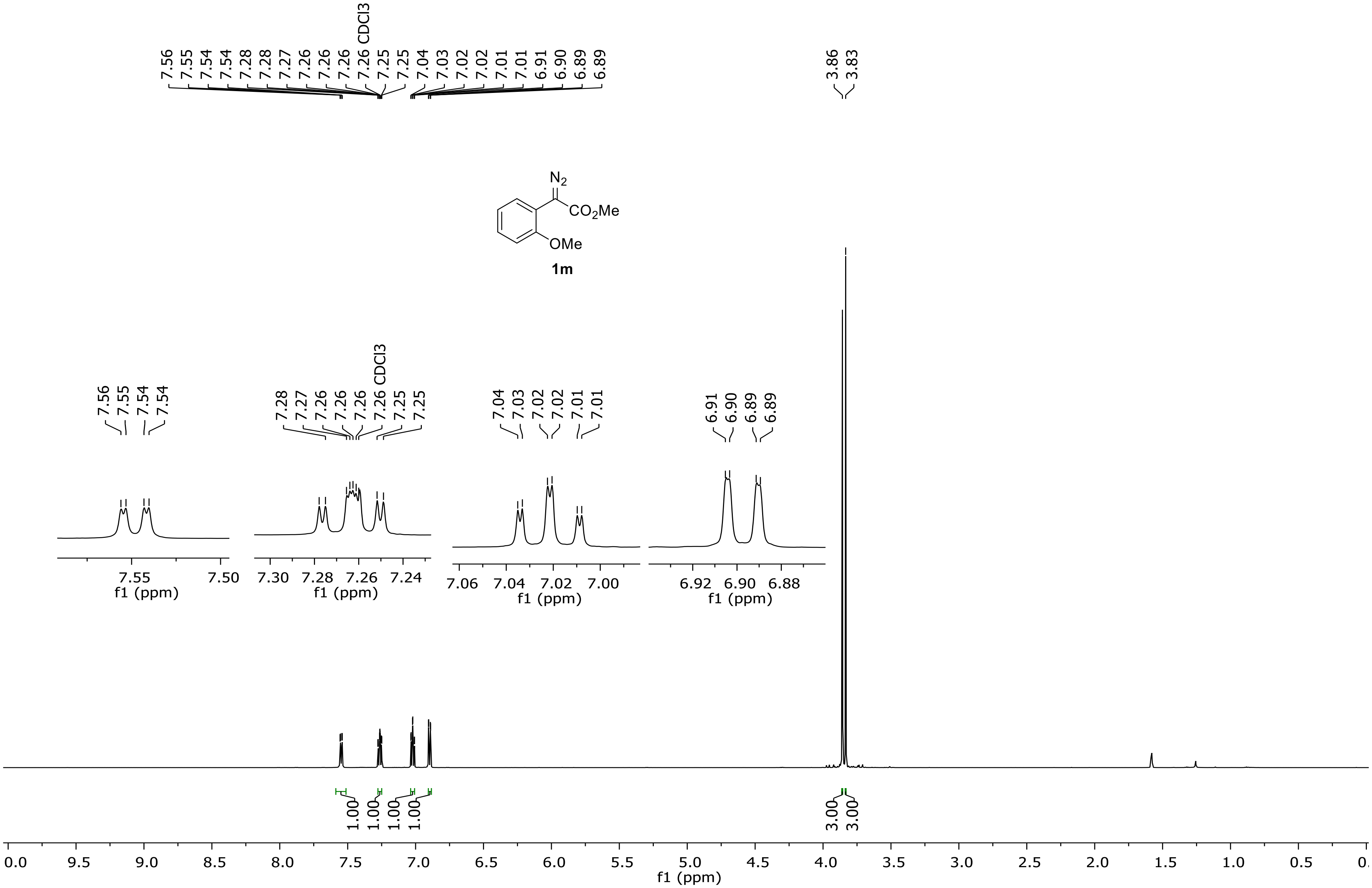


1l

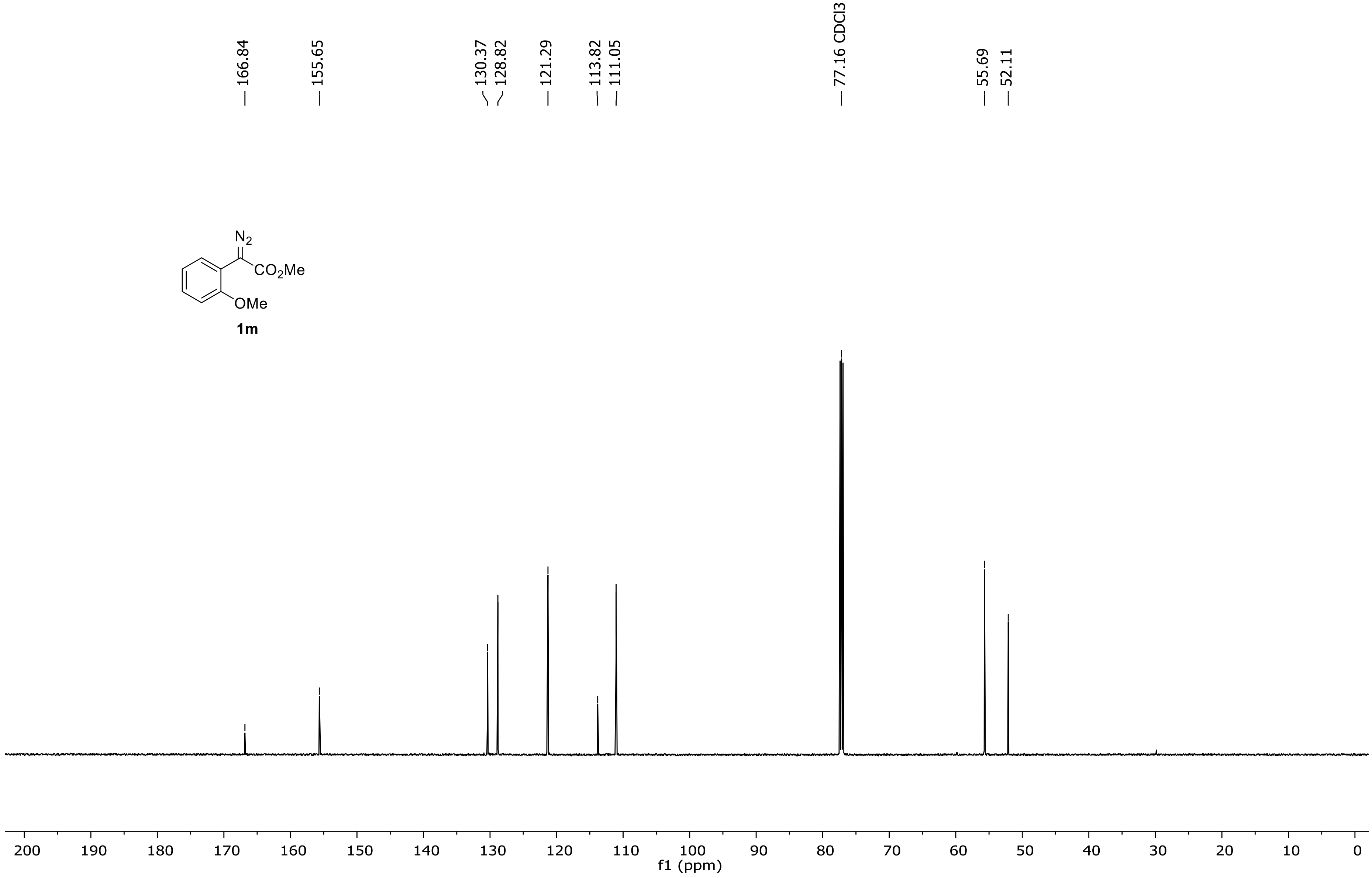
$^{19}F\{^{1}H\}$ NMR of 1l ($CDCl_3$, 564 MHz)



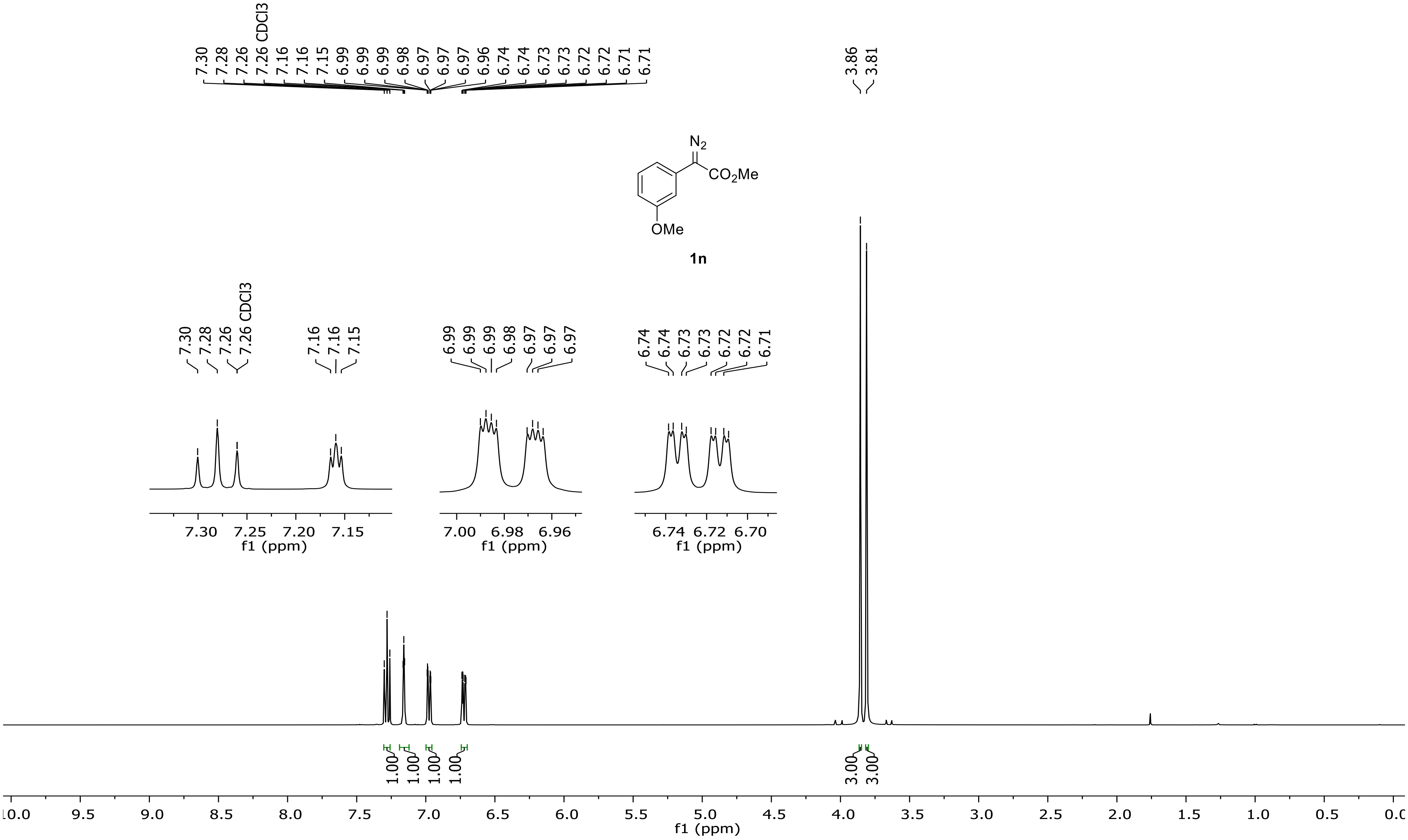
^{1}H NMR of 1m (CDCl$_3$, 600 MHz)



$^{13}C\{^1H\}$ NMR of 1m ($CDCl_3$, 150 MHz)

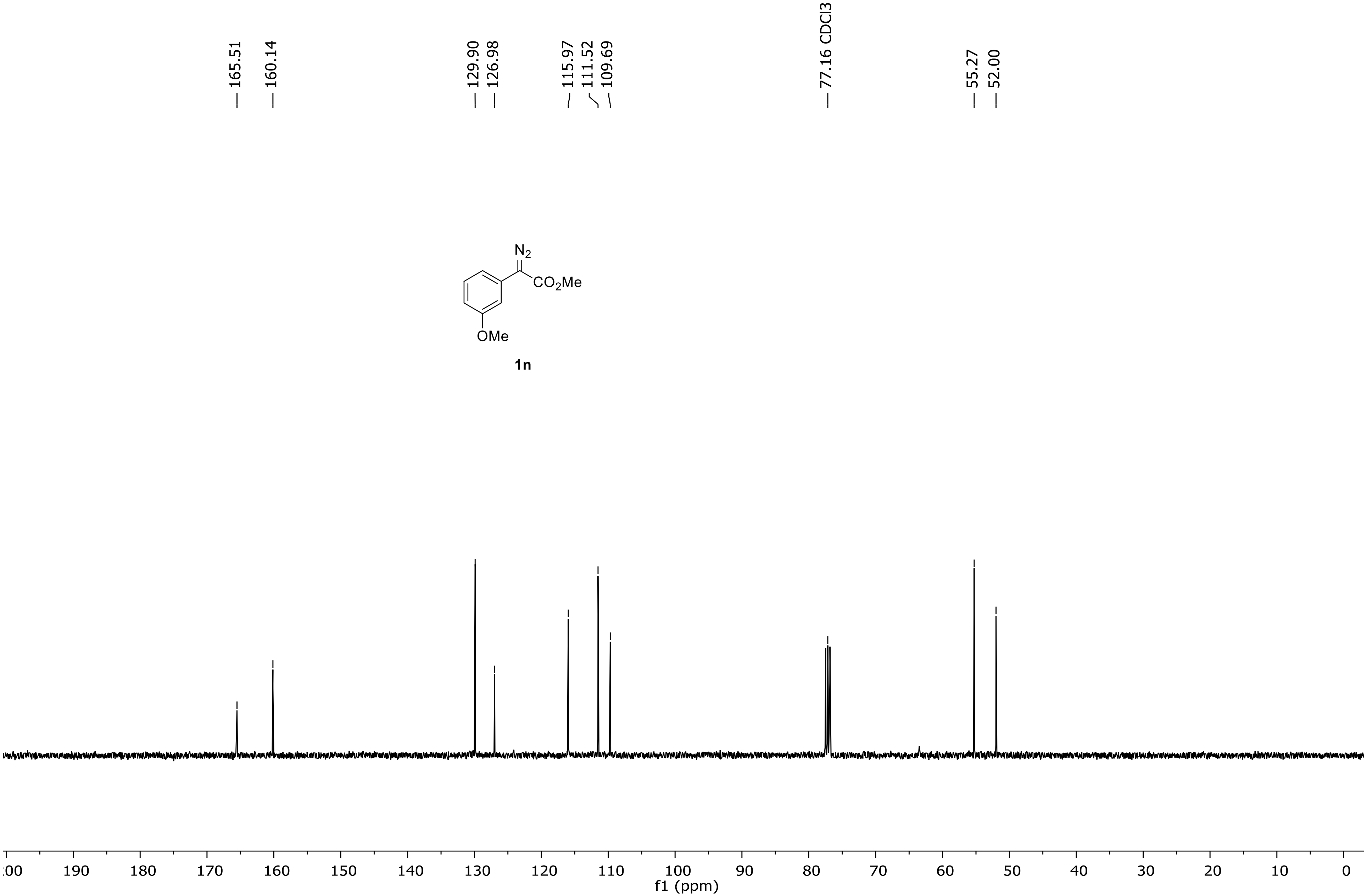


^{1}H NMR of 1n ($CDCl_3$, 400 MHz)

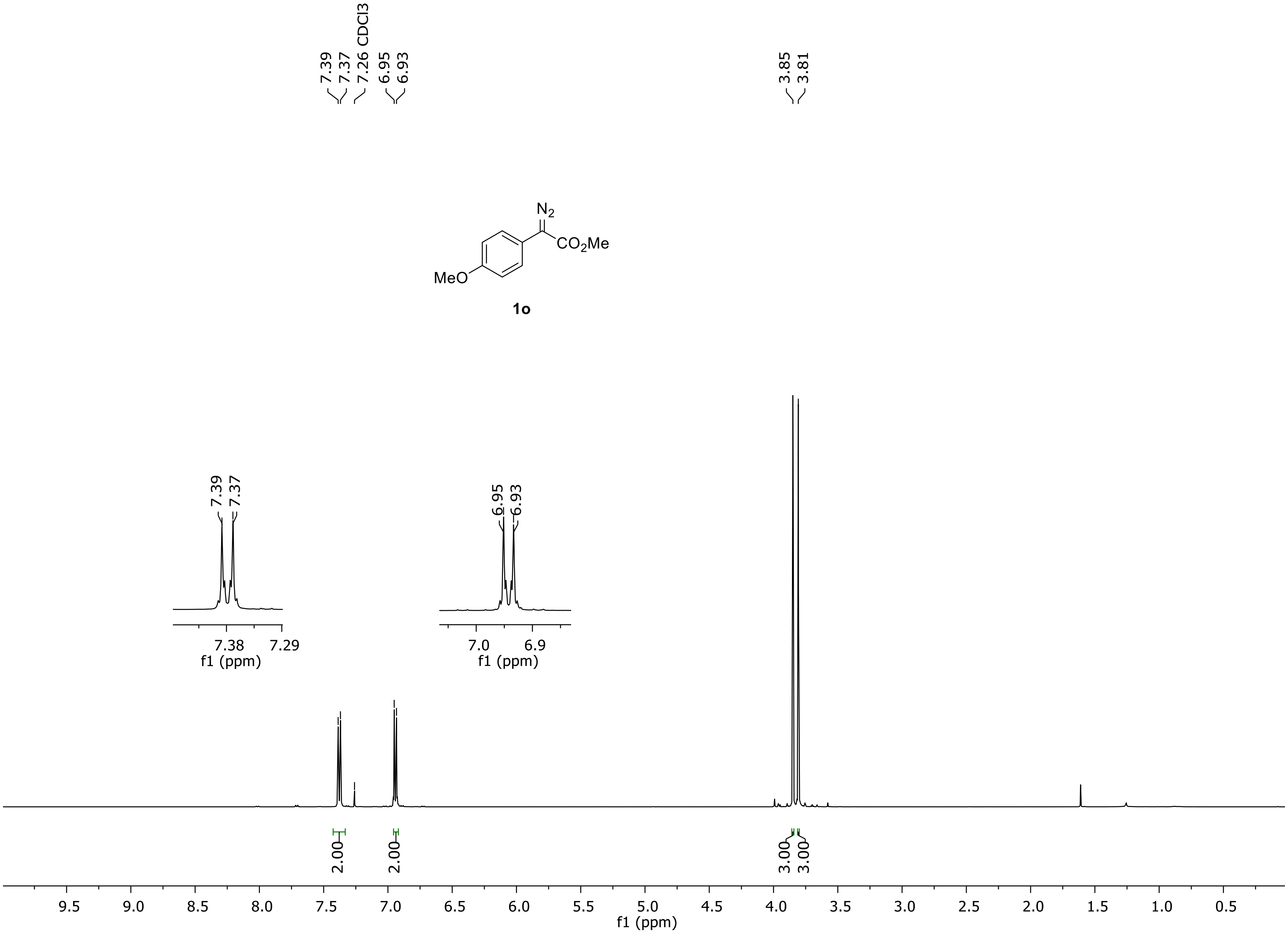


$^{13}C\{^1H\}$ NMR of 1n ($CDCl_3$, 100 MHz)

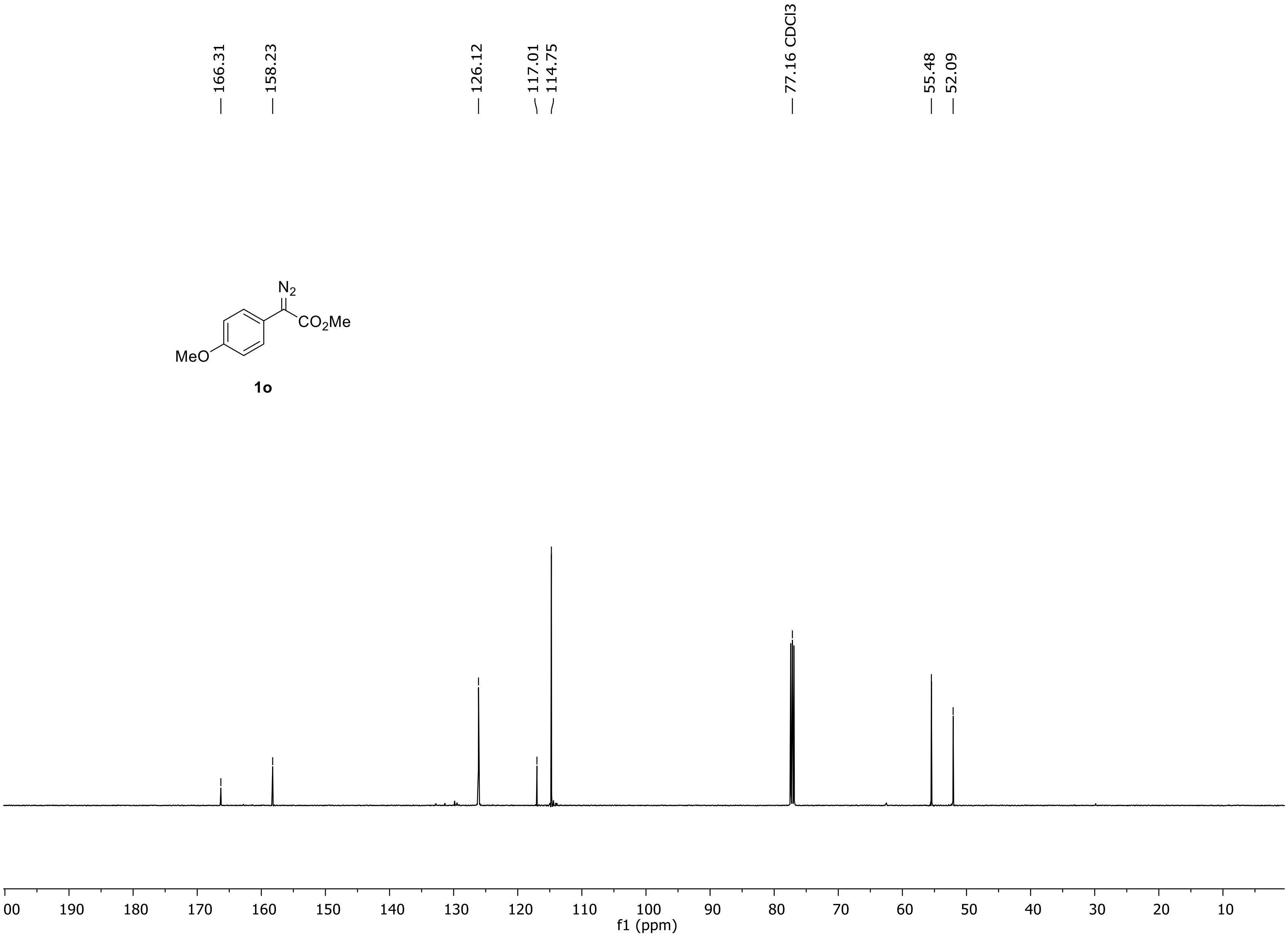
1n



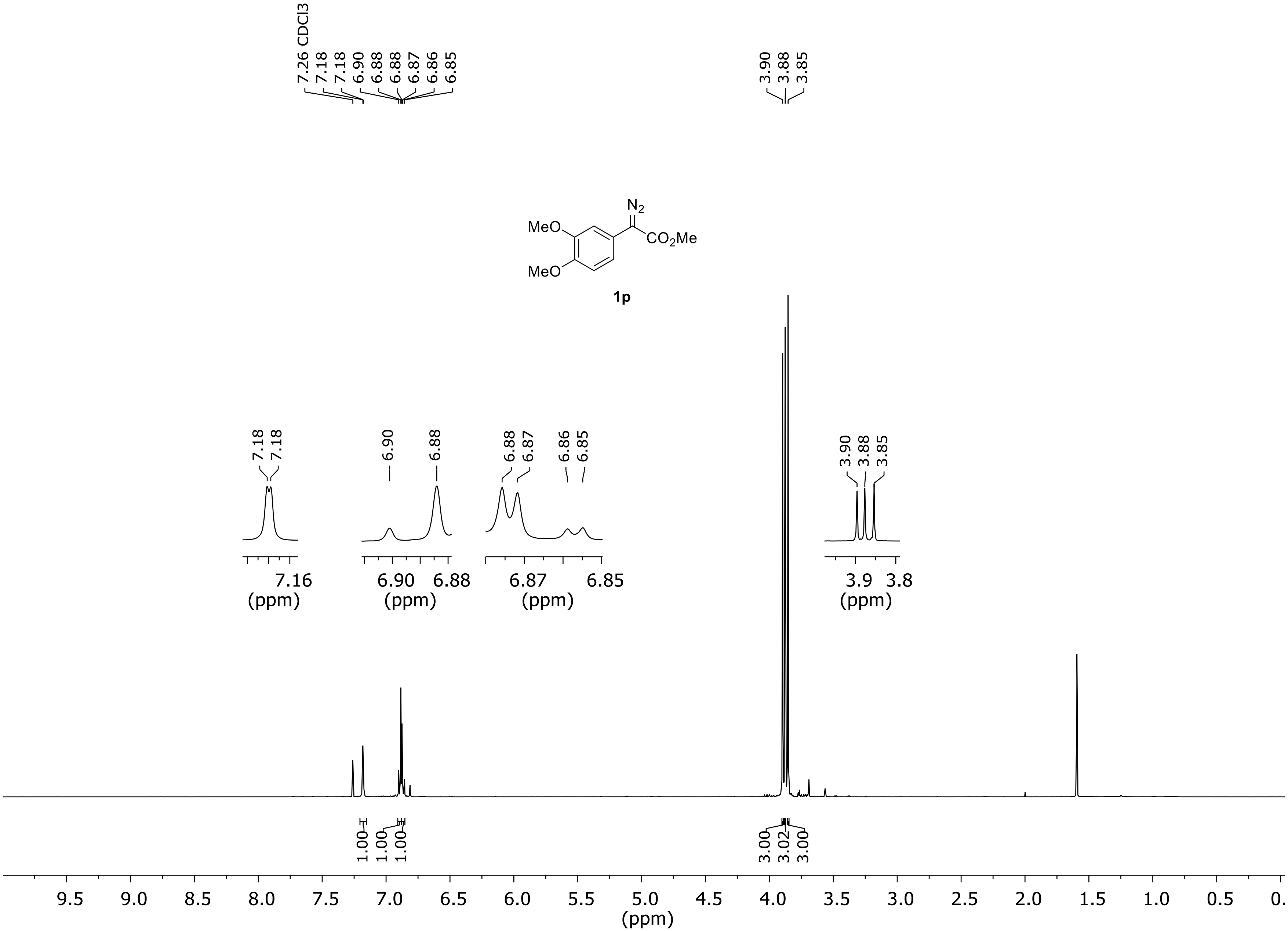
^{1}H NMR of 1o ($CDCl_3$, 500 MHz)



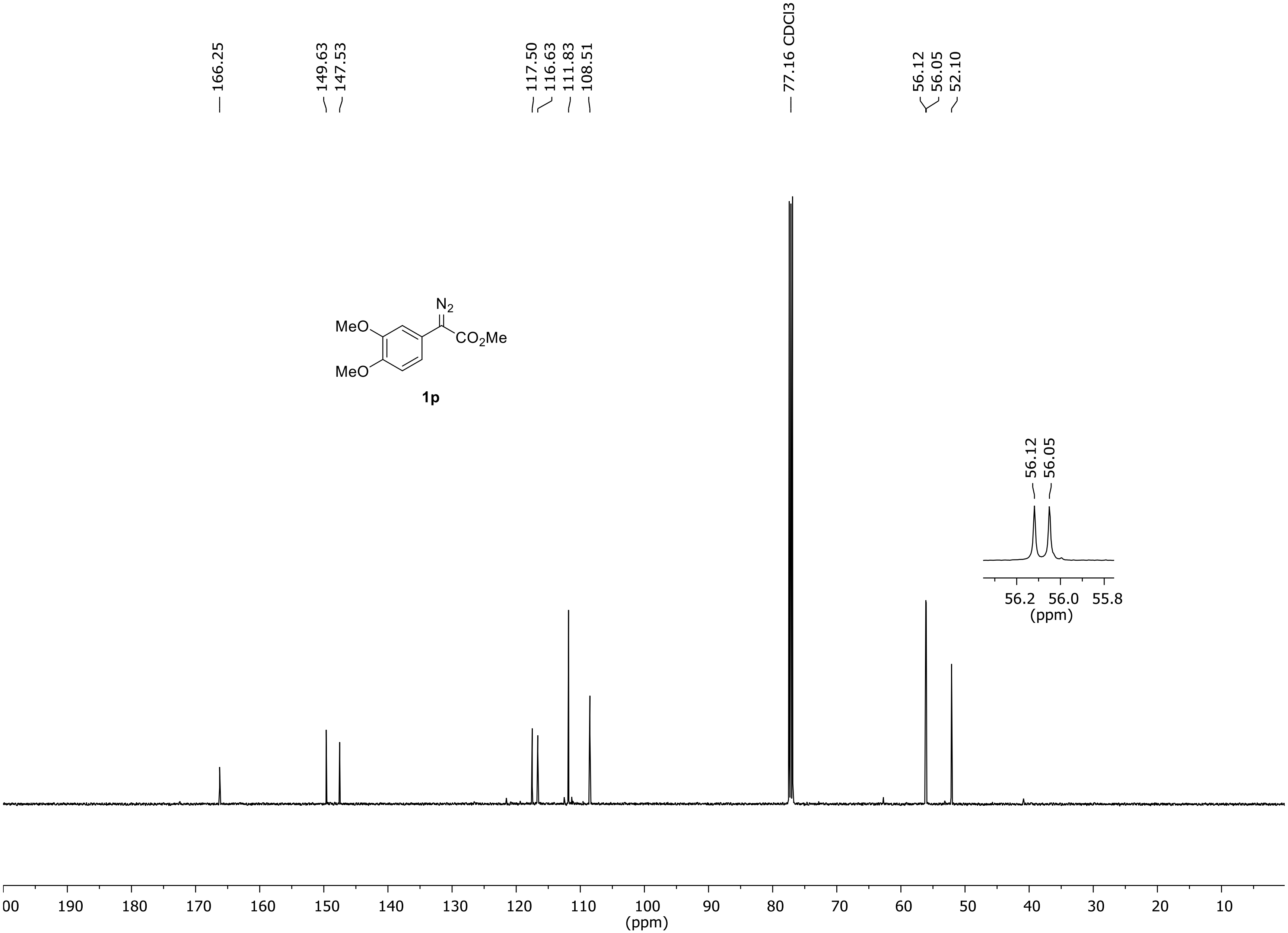
$^{13}C\{^1H\}$ NMR of 1o ($CDCl_3$, 125 MHz)



^{1}H NMR of 1p ($CDCl_3$, 500 MHz)

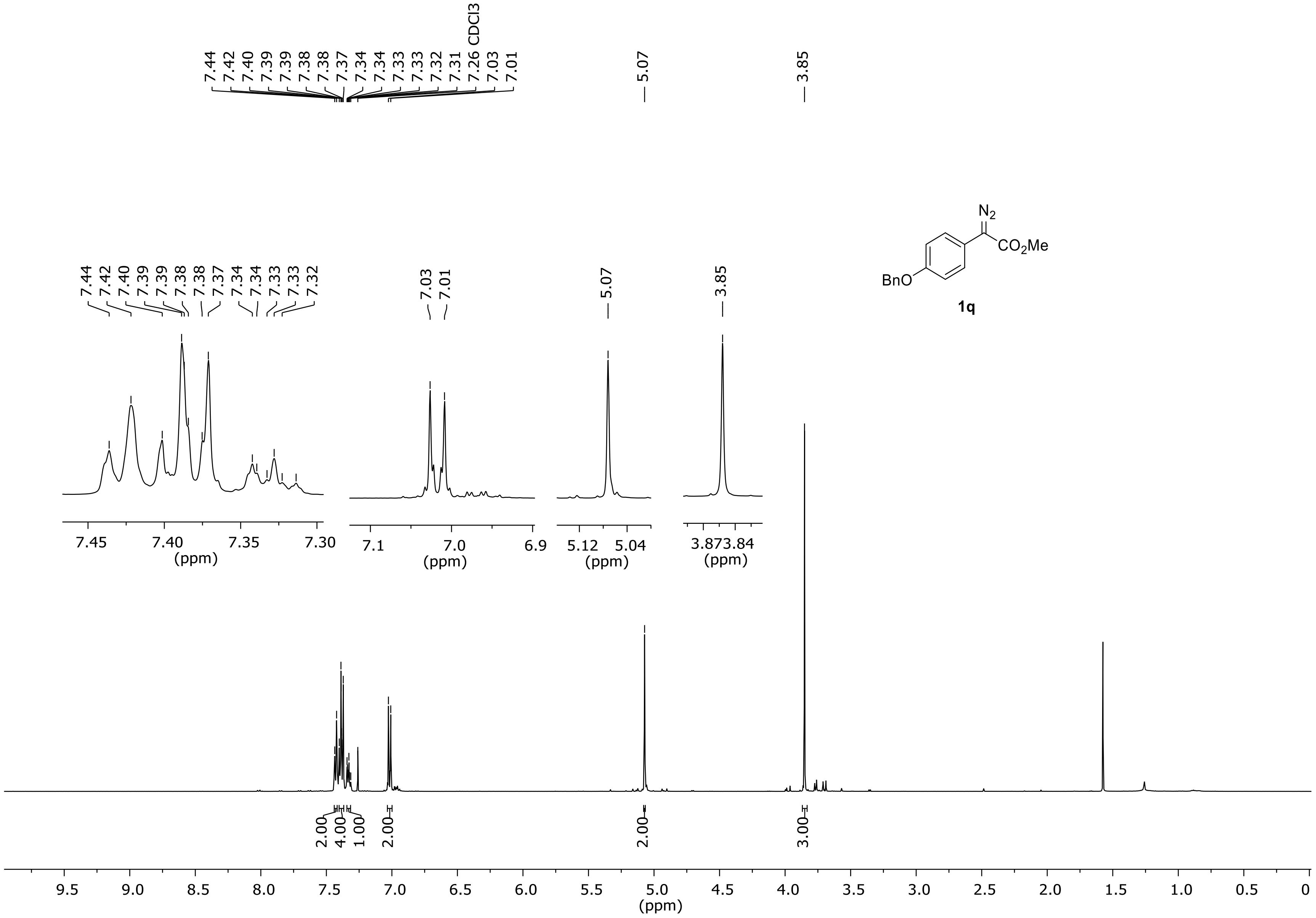


$^{13}C\{^{1}H\}$ NMR of 1p ($CDCl_3$, 125 MHz)

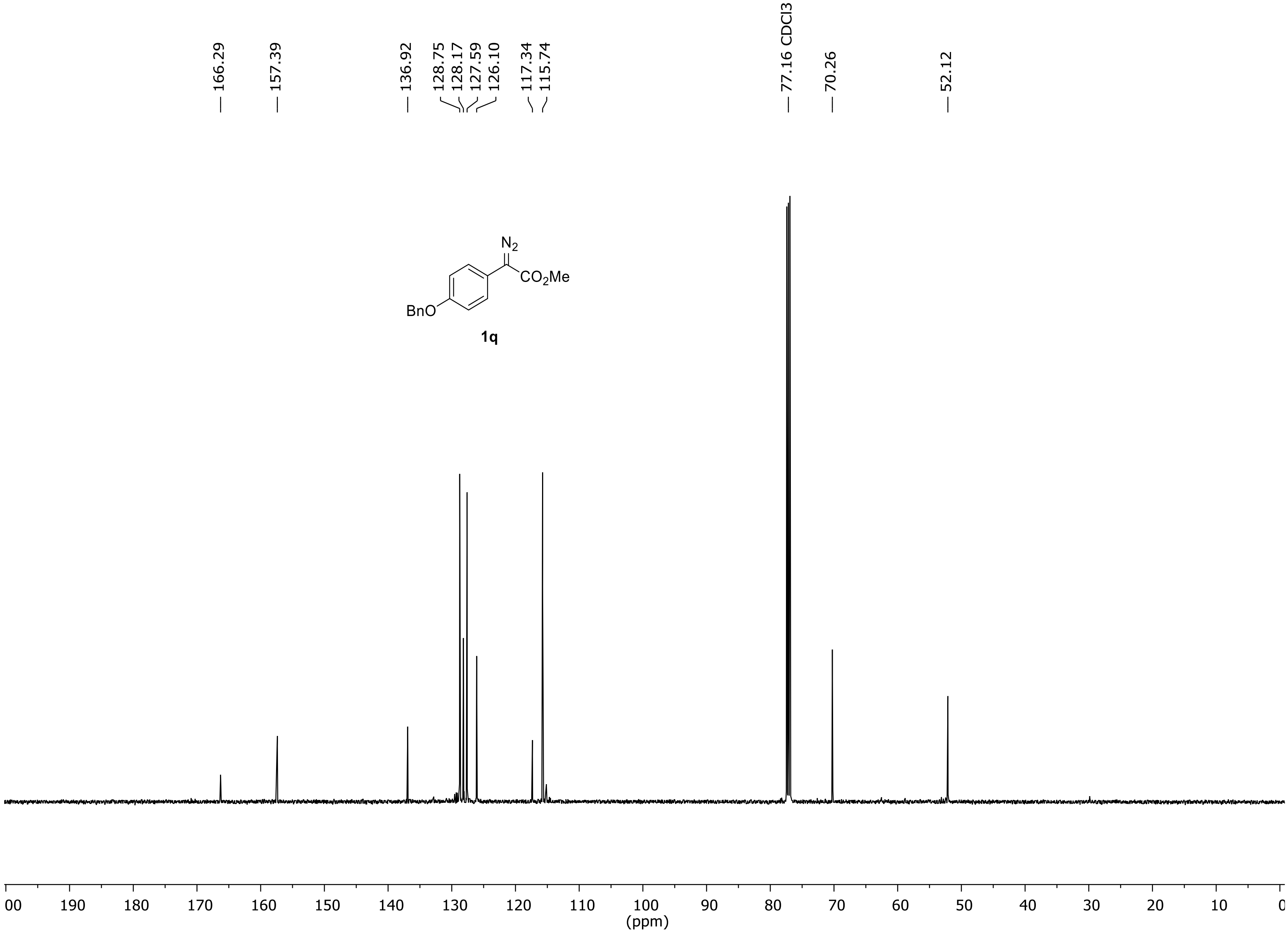


^{1}H NMR of 1q (CDCl$_3$, 500 MHz)

1q

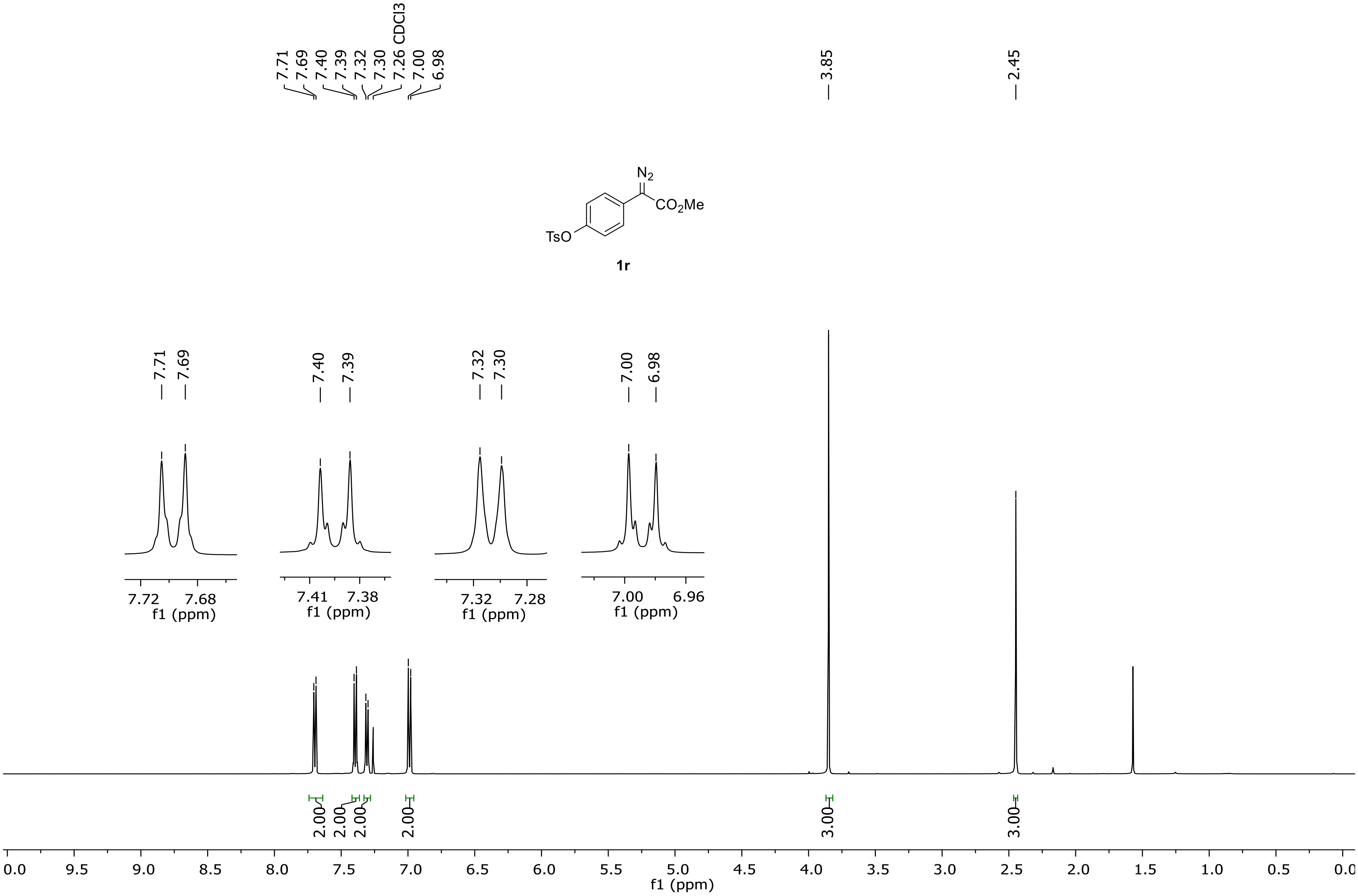


$^{13}C\{^1H\}$ NMR of 1q ($CDCl_3$, 126 MHz)

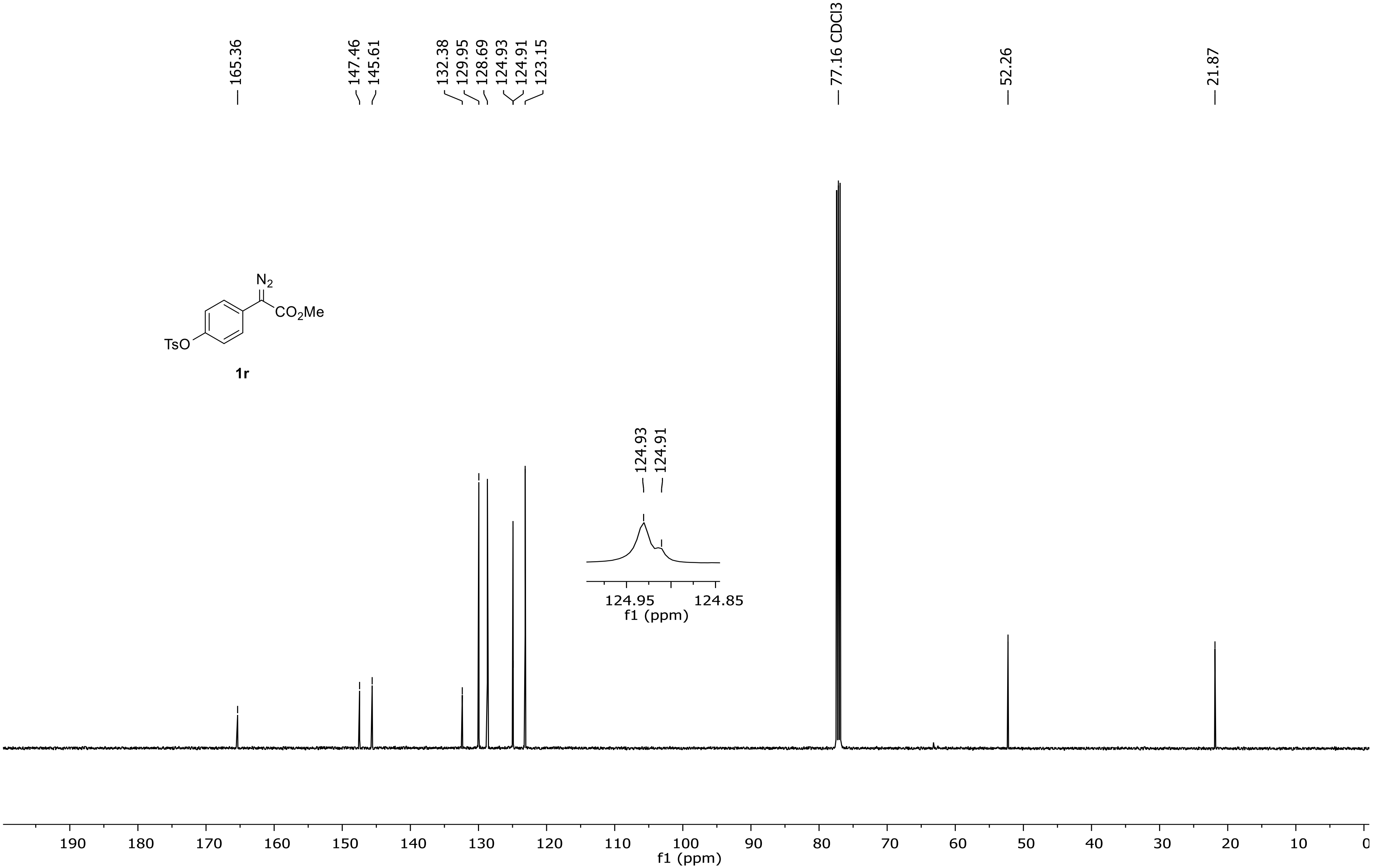


^{1}H NMR of 1r ($CDCl_3$, 500 MHz)

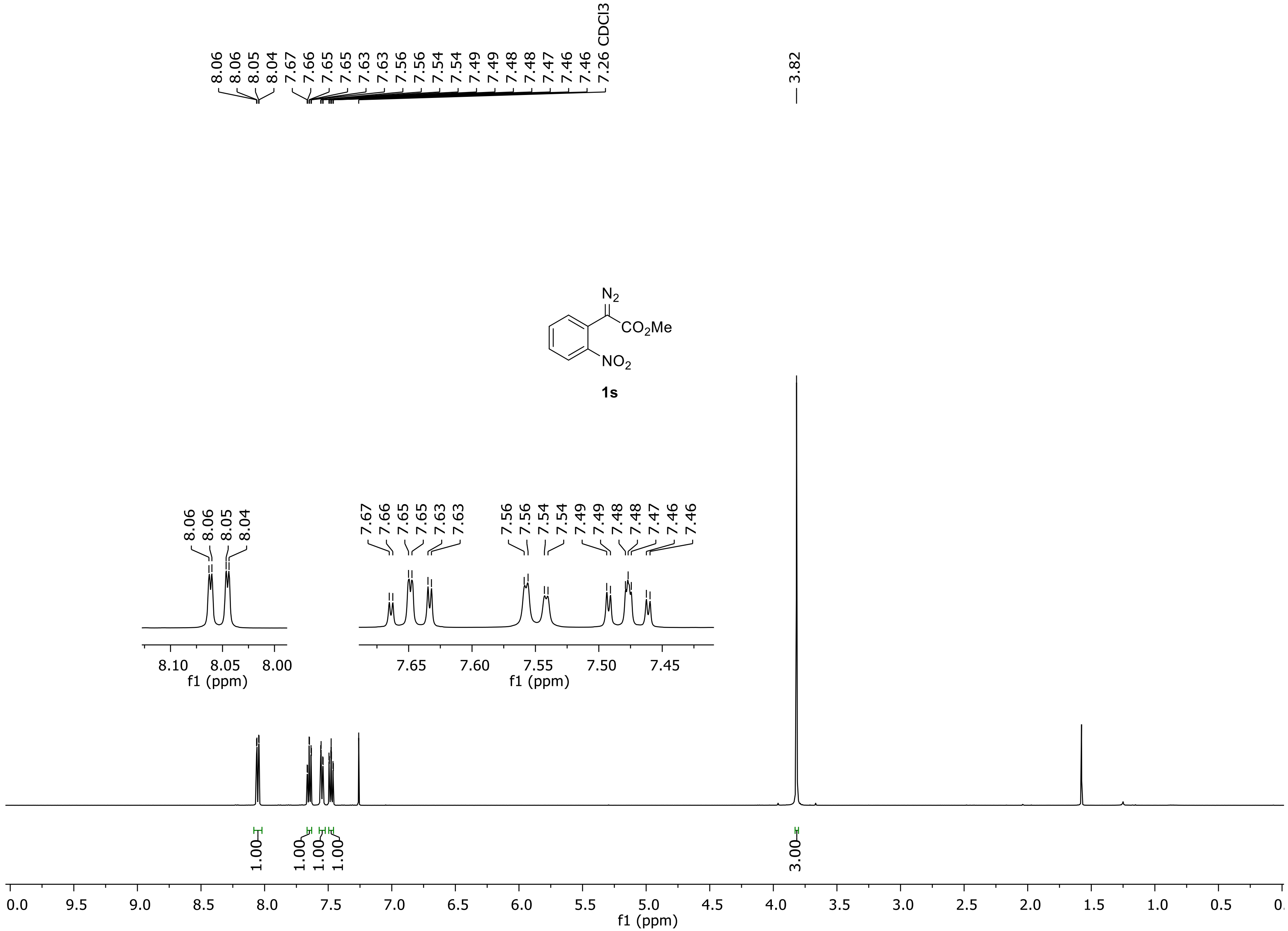
1r



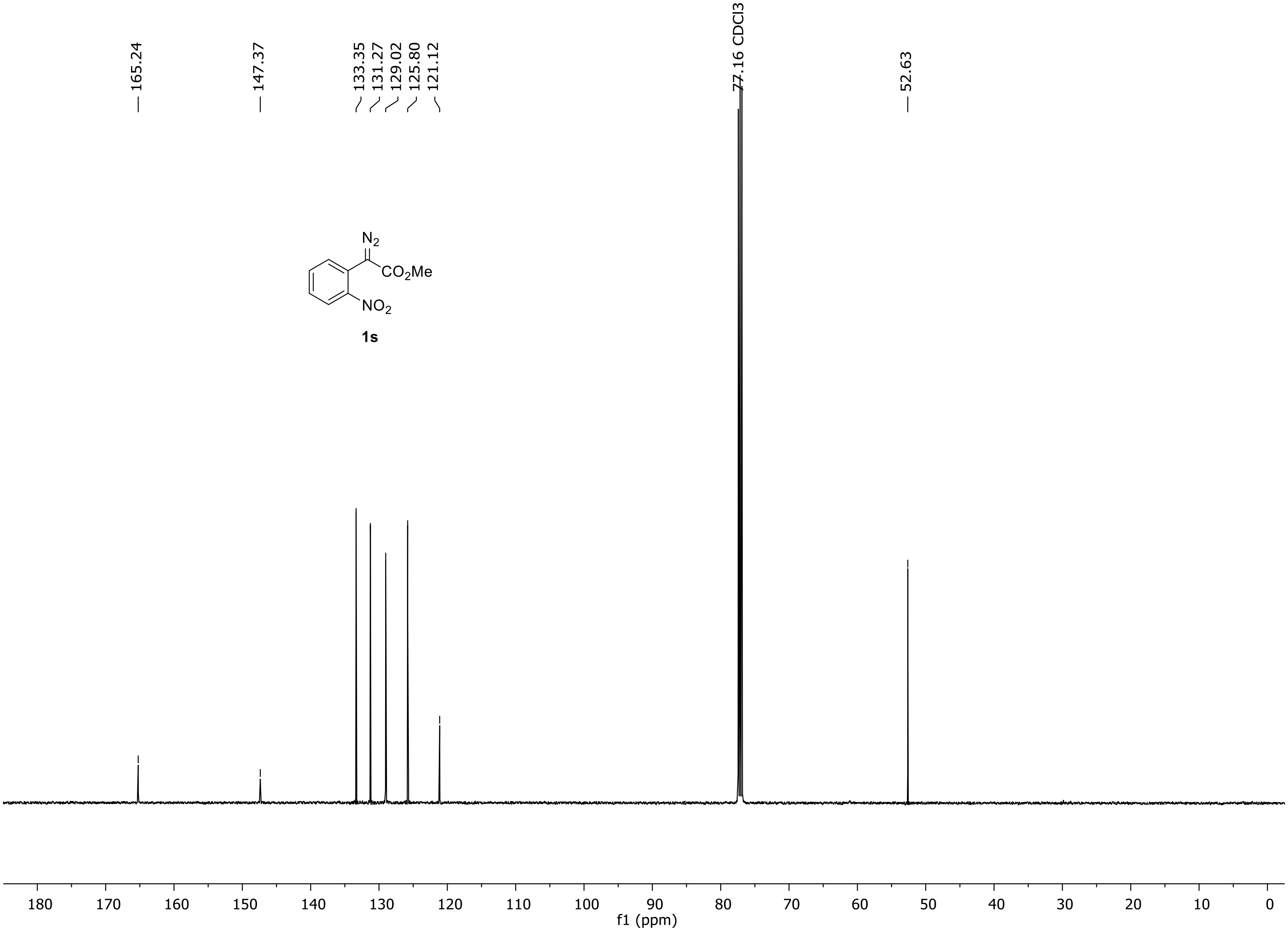
$^{13}C\{^{1}H\}$ NMR of 1r ($CDCl_3$, 125 MHz)



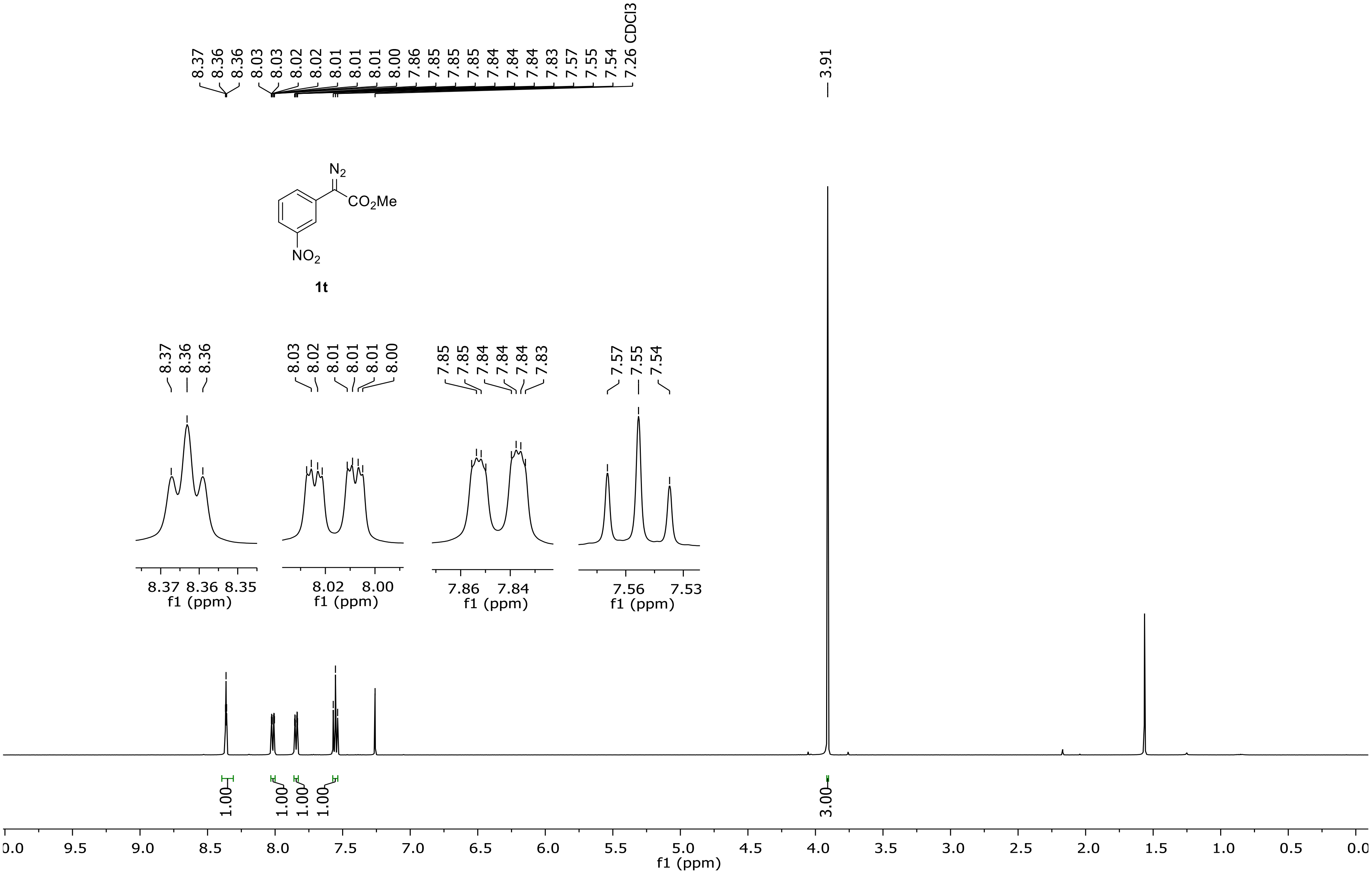
^{1}H NMR of 1s (CDCl$_3$, 500 MHz)



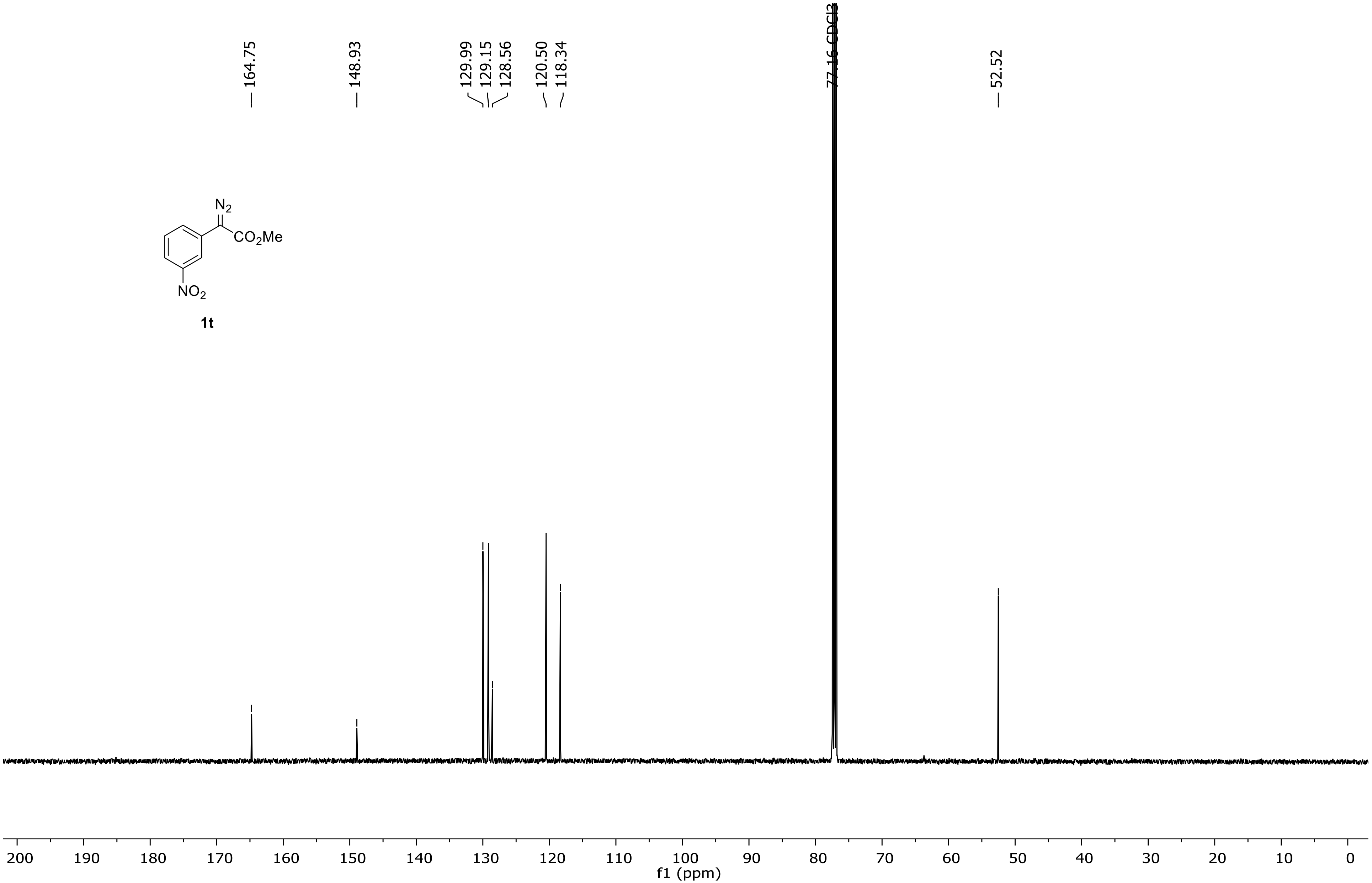
$^{13}C\{^1H\}$ NMR of 1s ($CDCl_3$, 125 MHz)



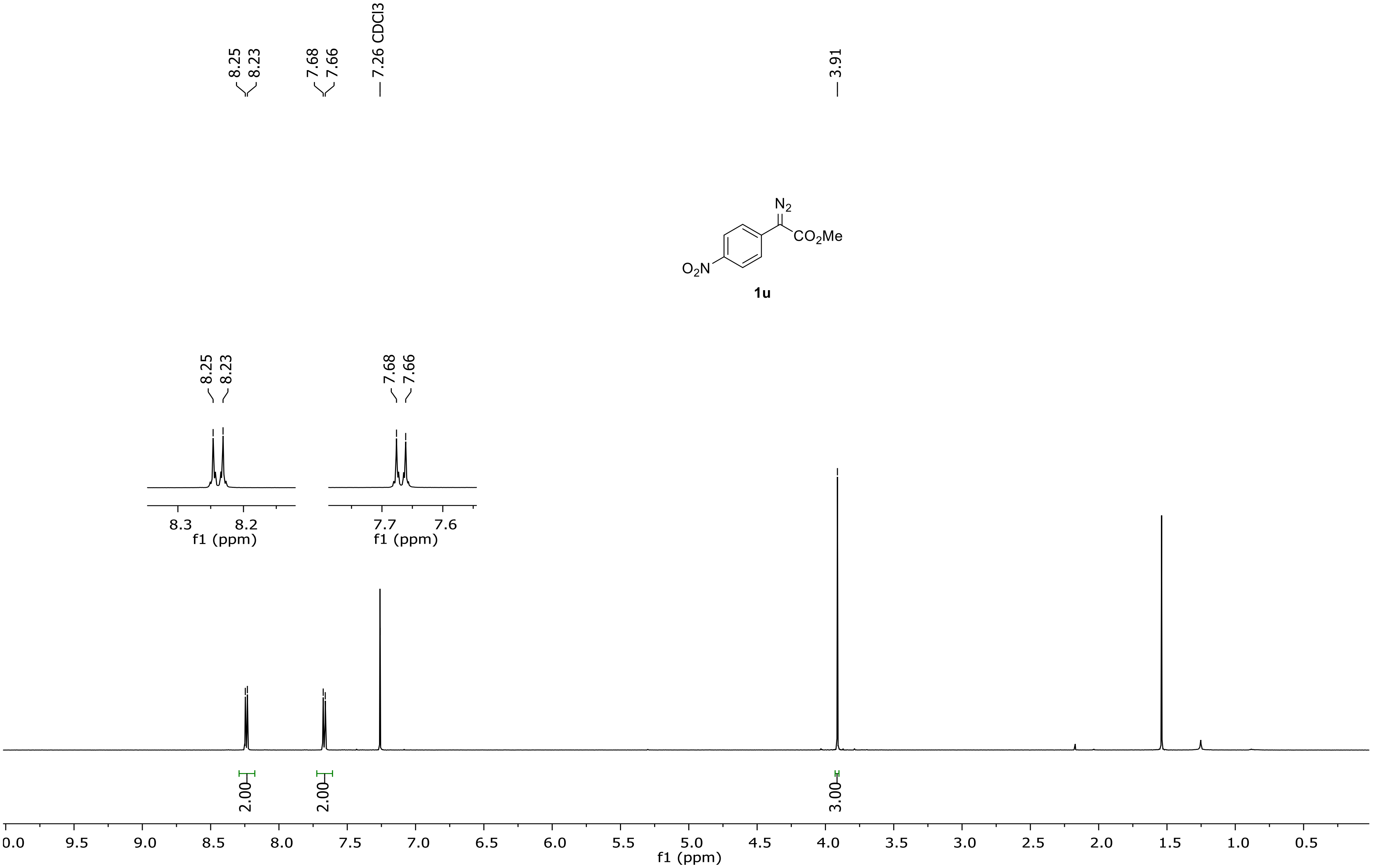
^{1}H NMR of 1t ($CDCl_3$, 500 MHz)



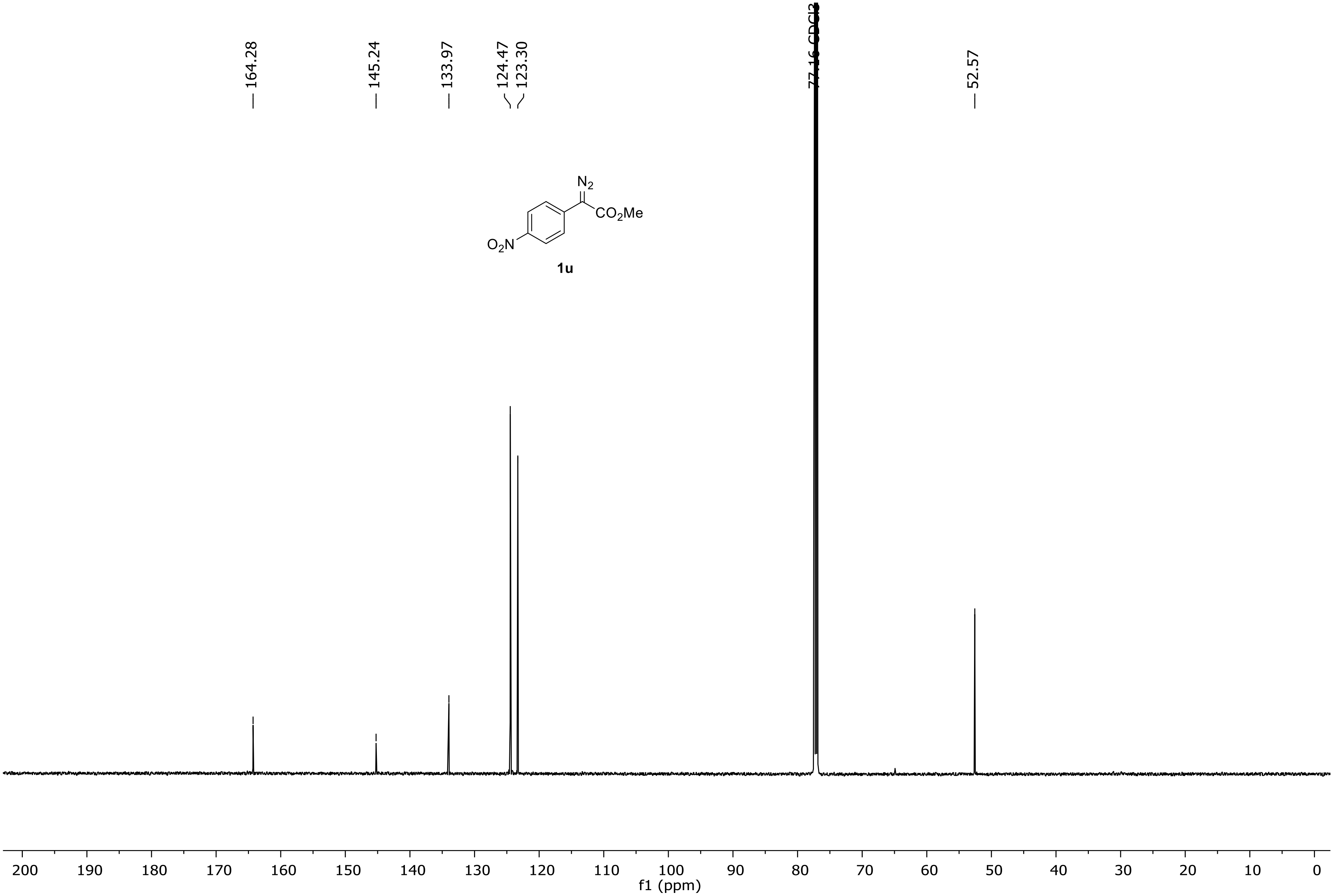
$^{13}C\{^1H\}$ NMR of 1t ($CDCl_3$, 125 MHz)



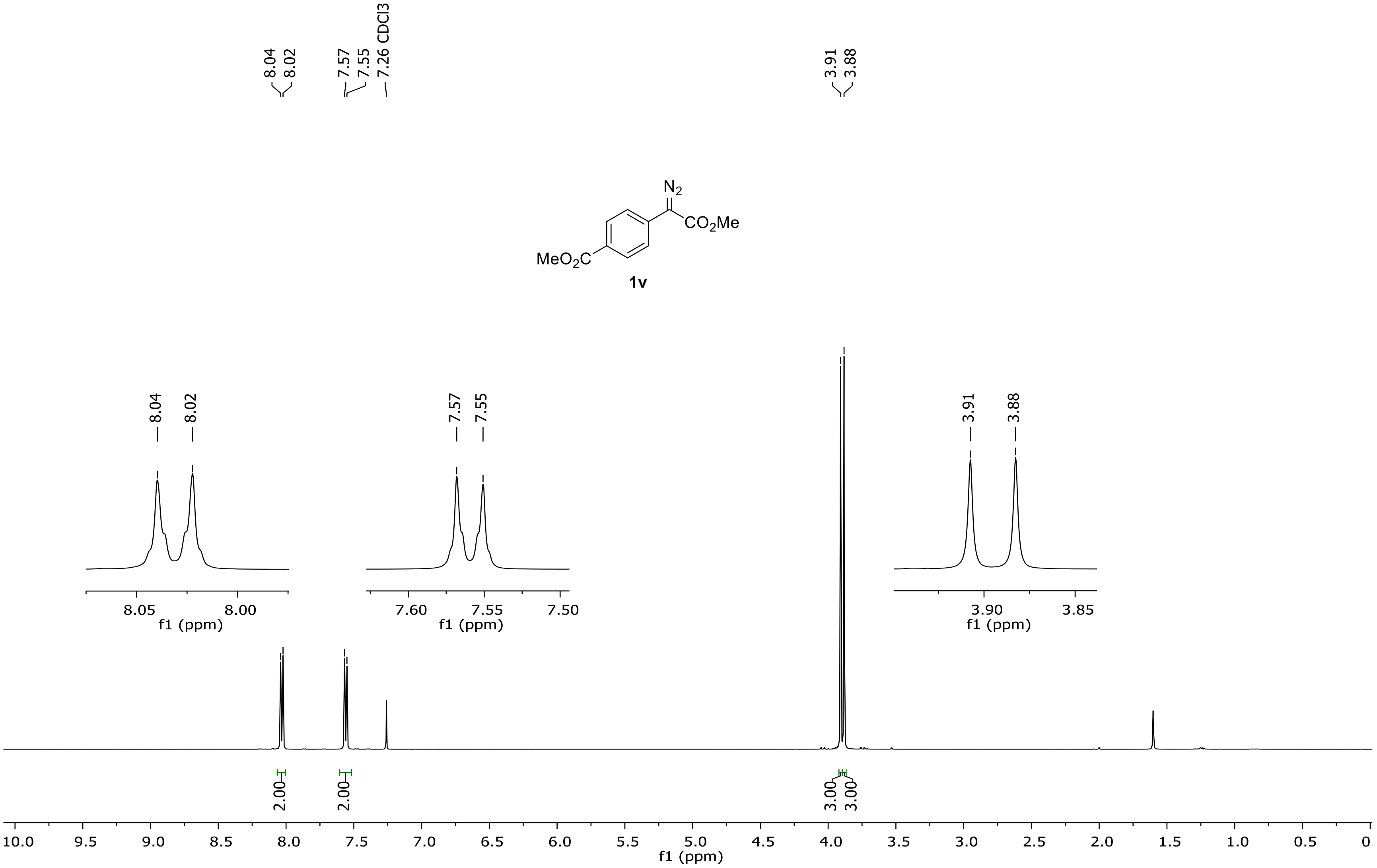
^{1}H NMR of 1u ($CDCl_3$, 600 MHz)



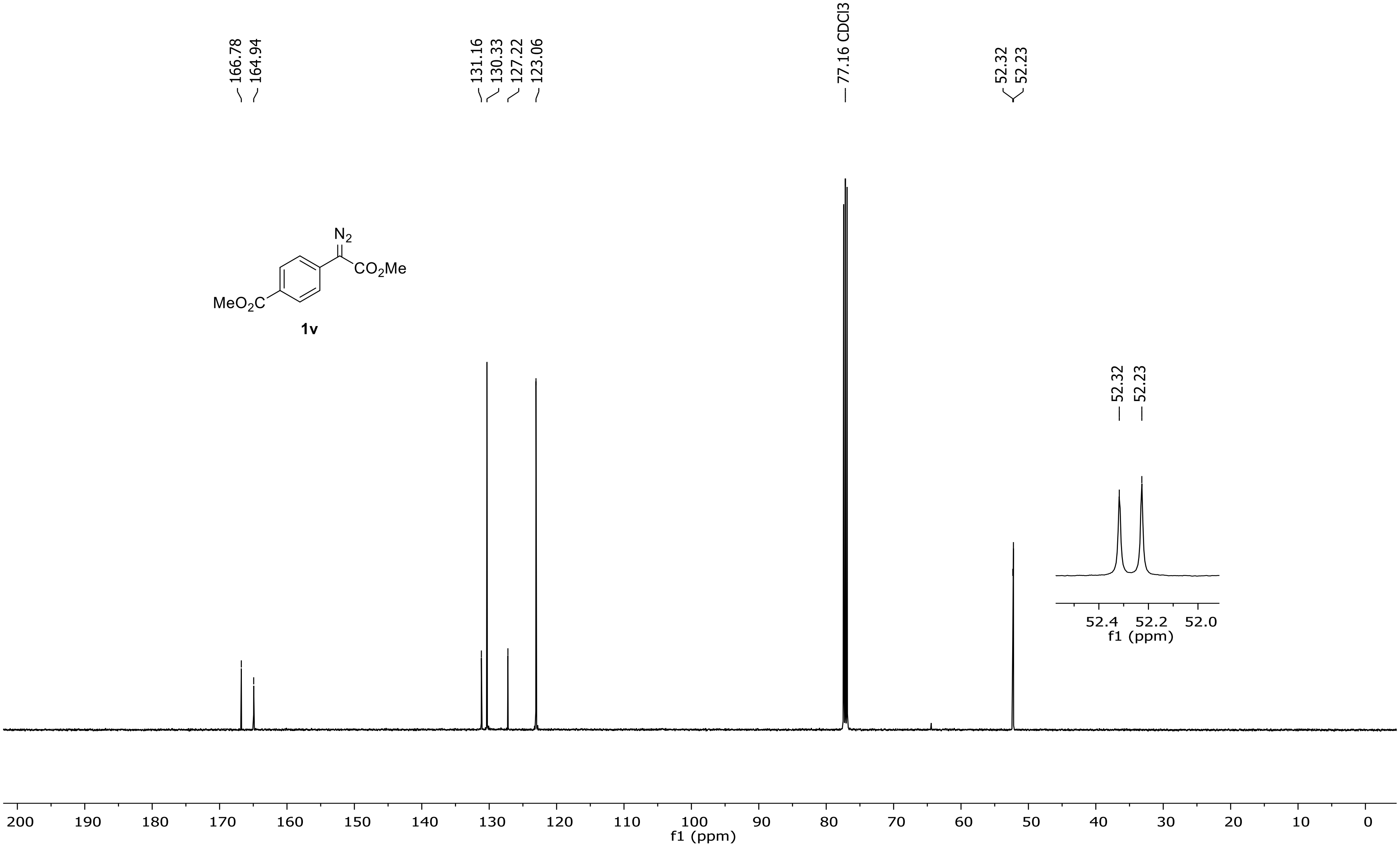
$^{13}C\{^1H\}$ NMR of 1u ($CDCl_3$, 150 MHz)



^{1}H NMR of 1v ($CDCl_3$, 500 MHz)

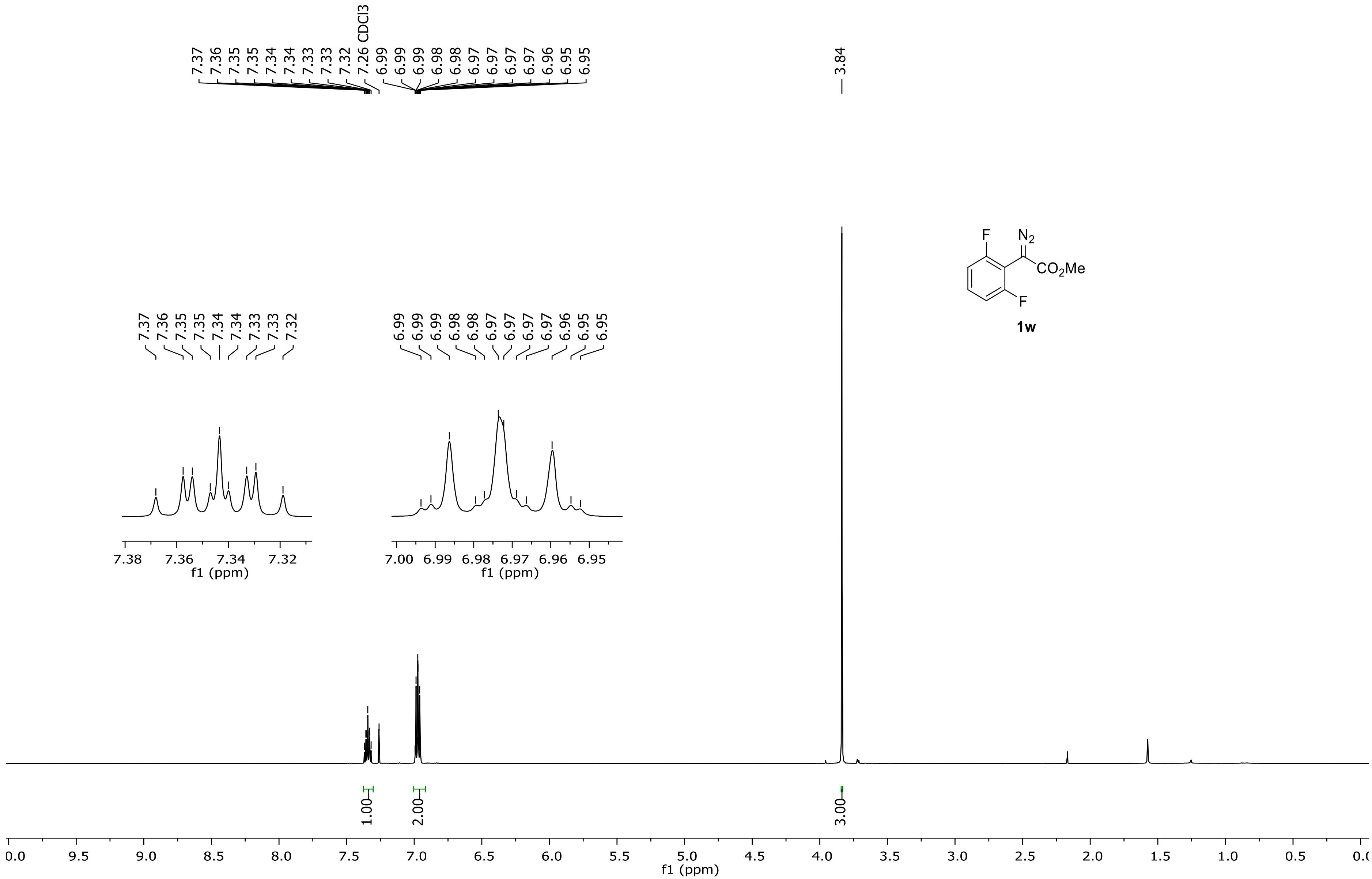


$^{13}C\{^1H\}$ NMR of 1v ($CDCl_3$, 125 MHz)

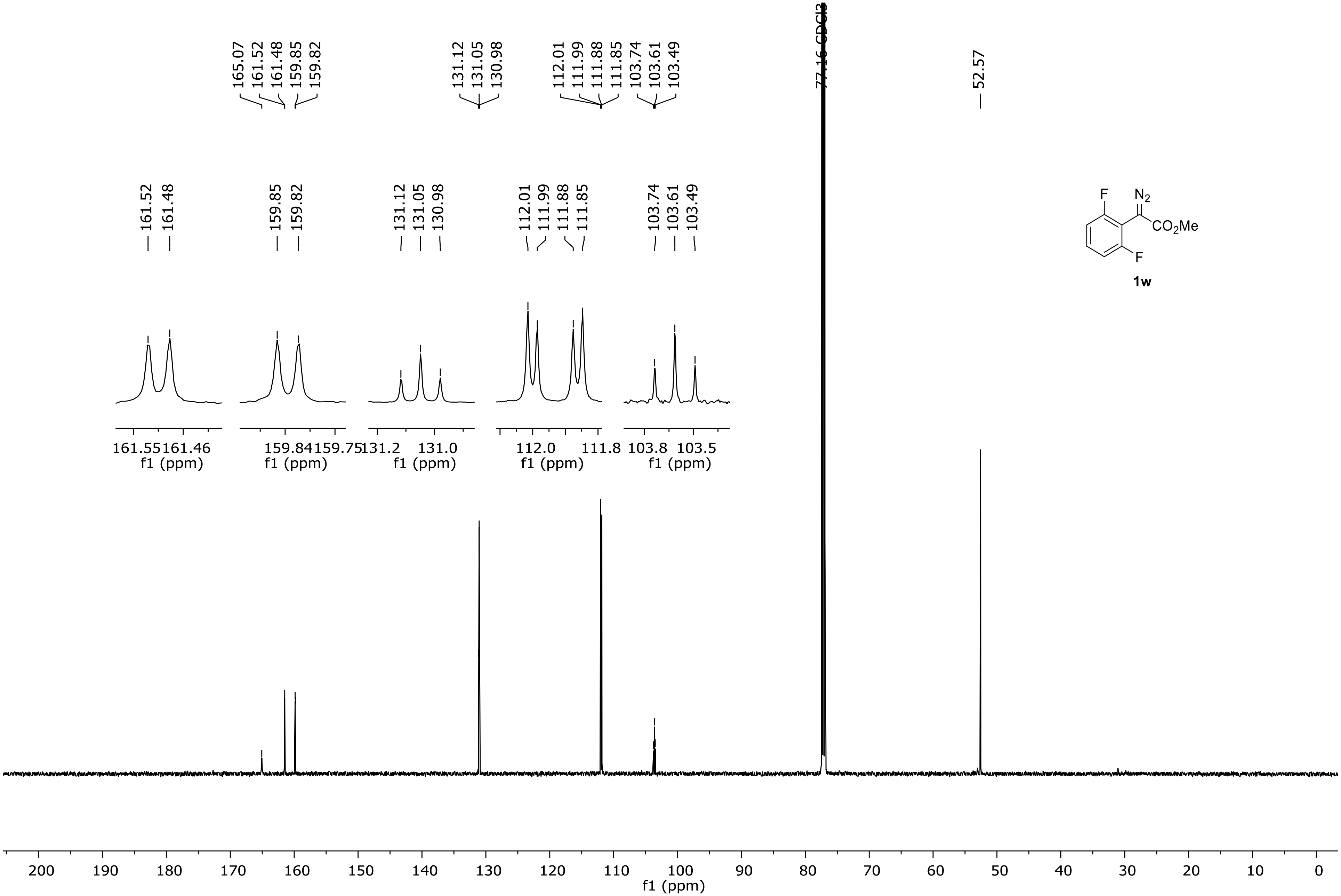


1v

^{1}H NMR of 1w (CDCl$_3$, 600 MHz)



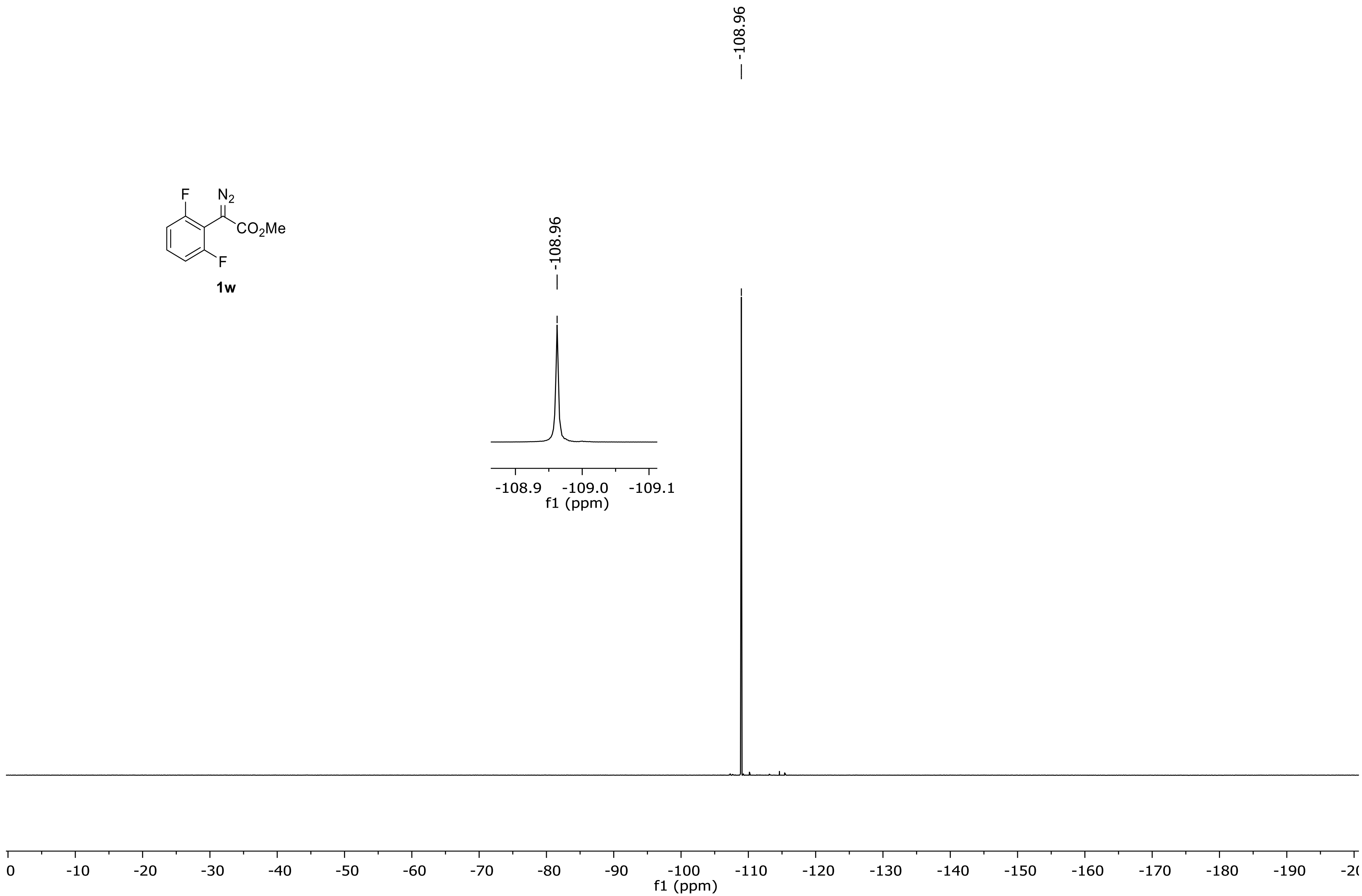
$^{13}C\{^1H\}$ NMR of 1w ($CDCl_3$, 150 MHz)



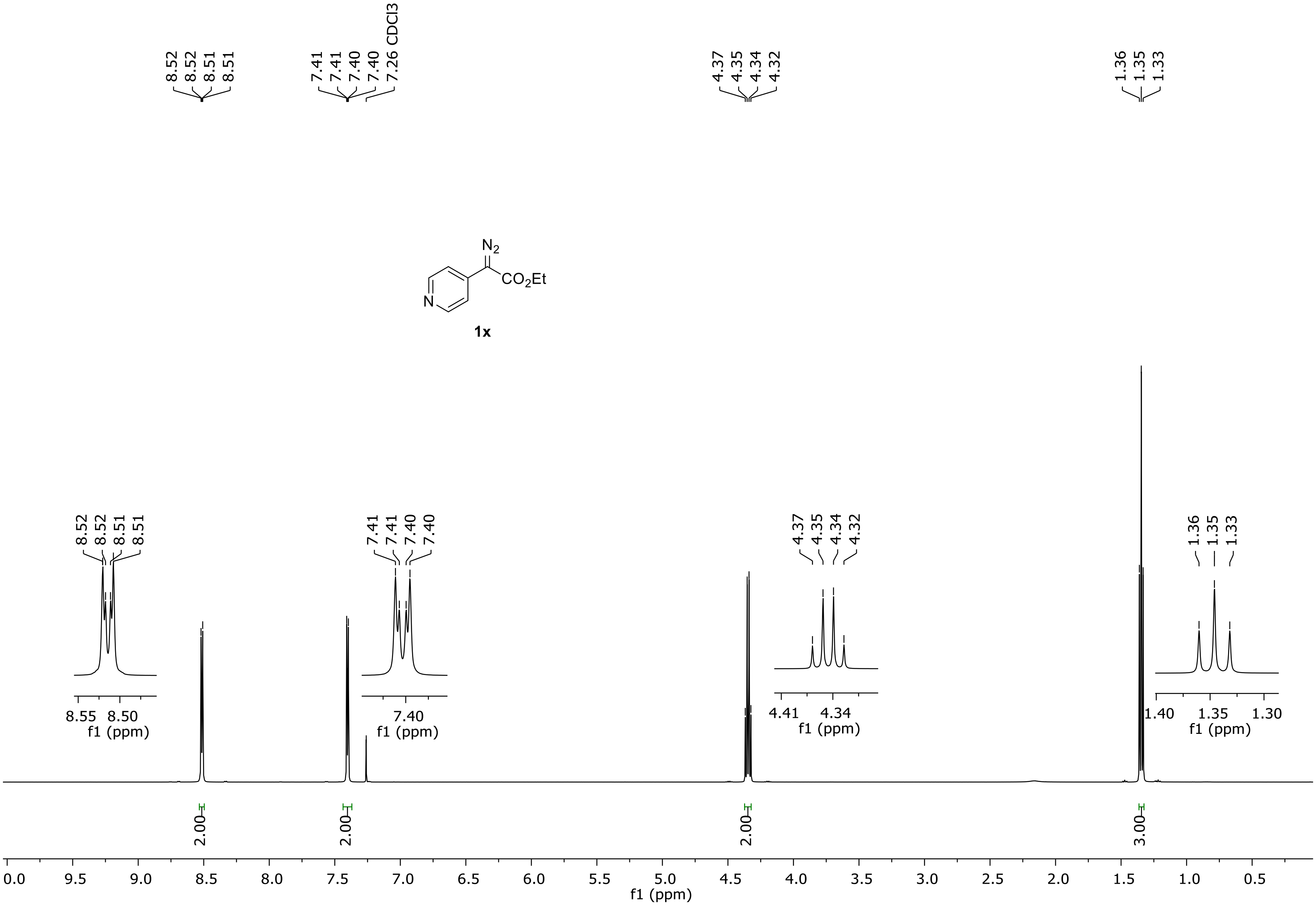
1w

$^{19}F\{^1H\}$ NMR of 1w ($CDCl_3$, 564 MHz)

1w

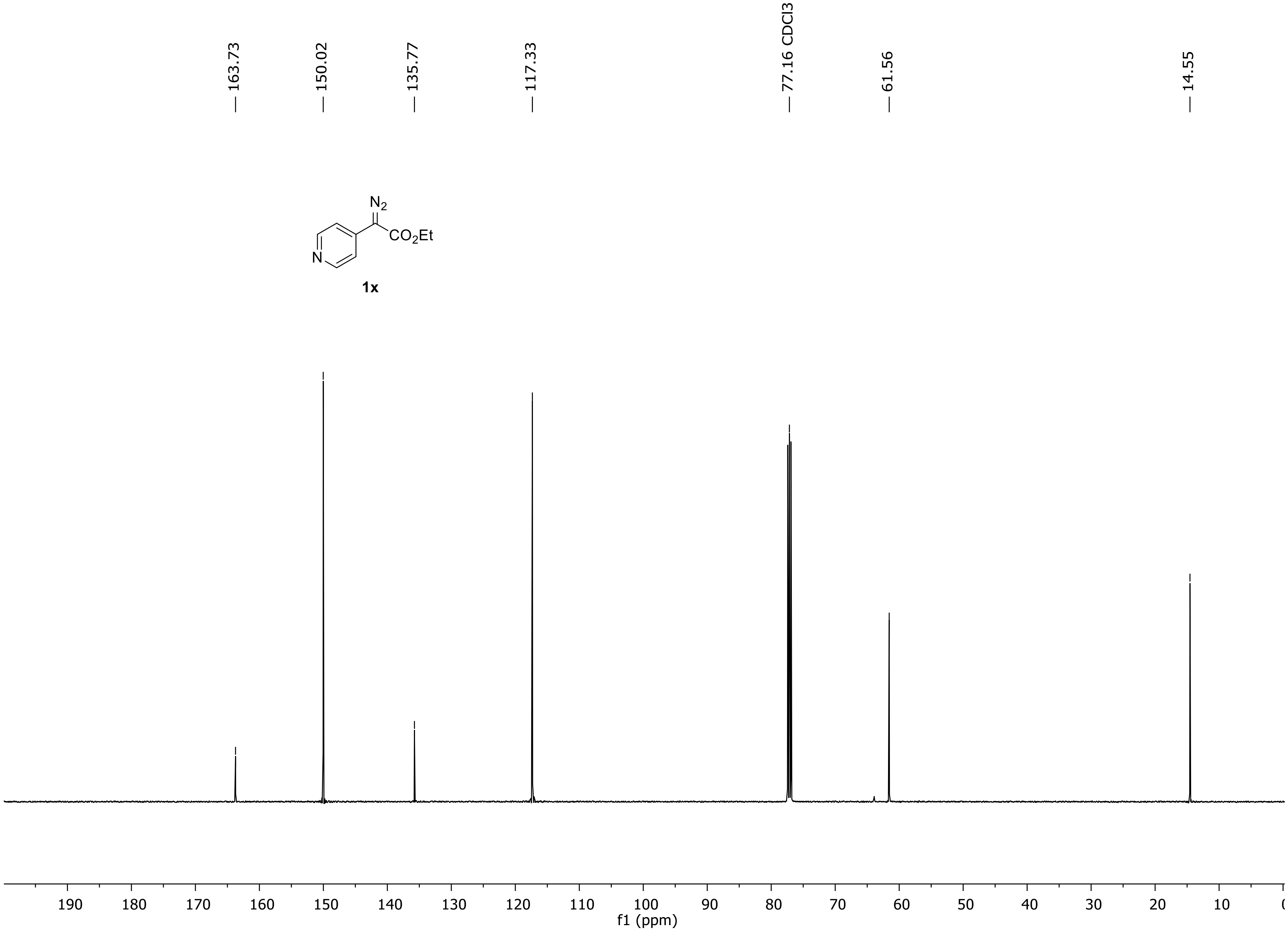


^{1}H NMR of 1x (CDCl$_3$, 500 MHz)

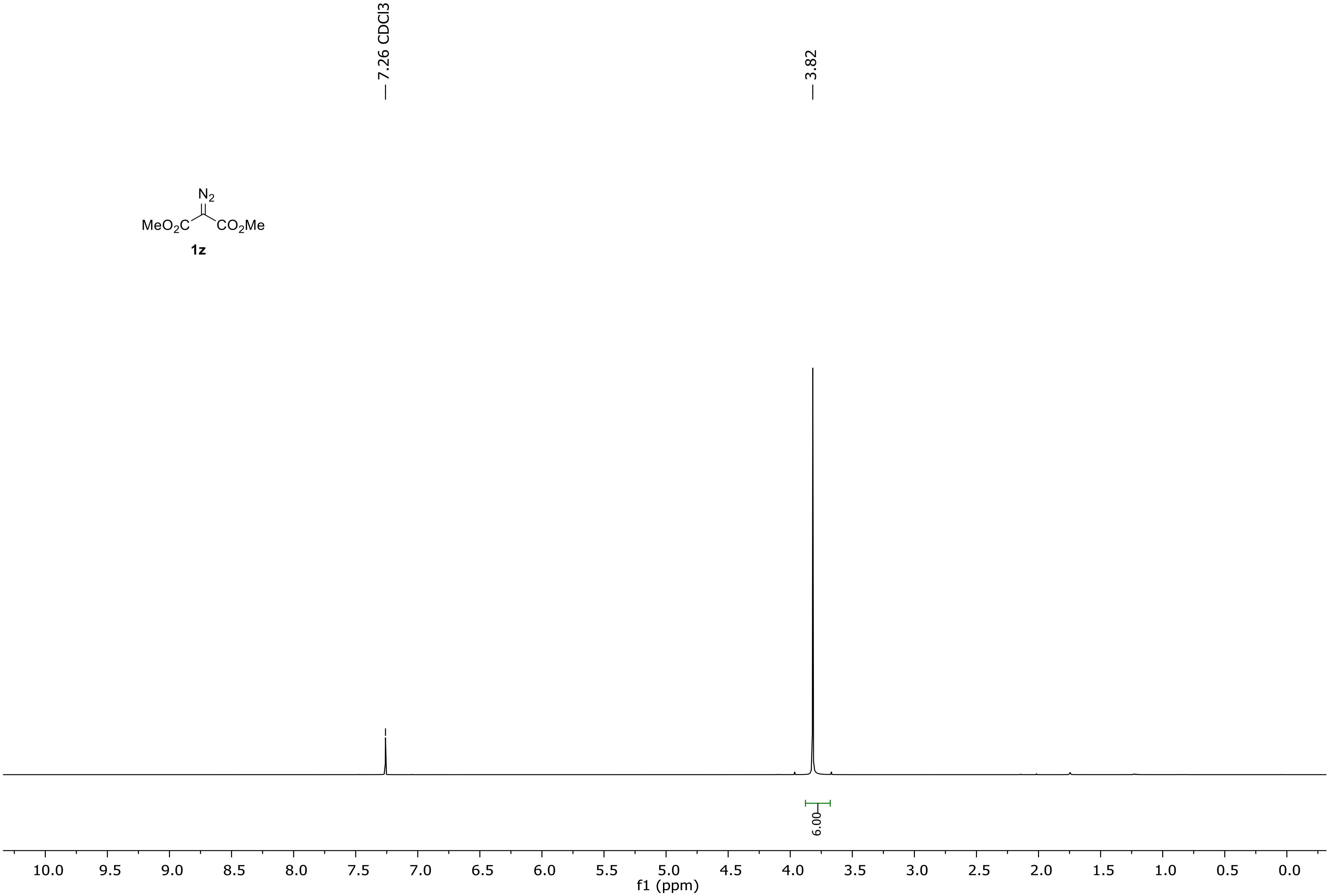


$^{13}C\{^1H\}$ NMR of 1x ($CDCl_3$, 125 MHz)

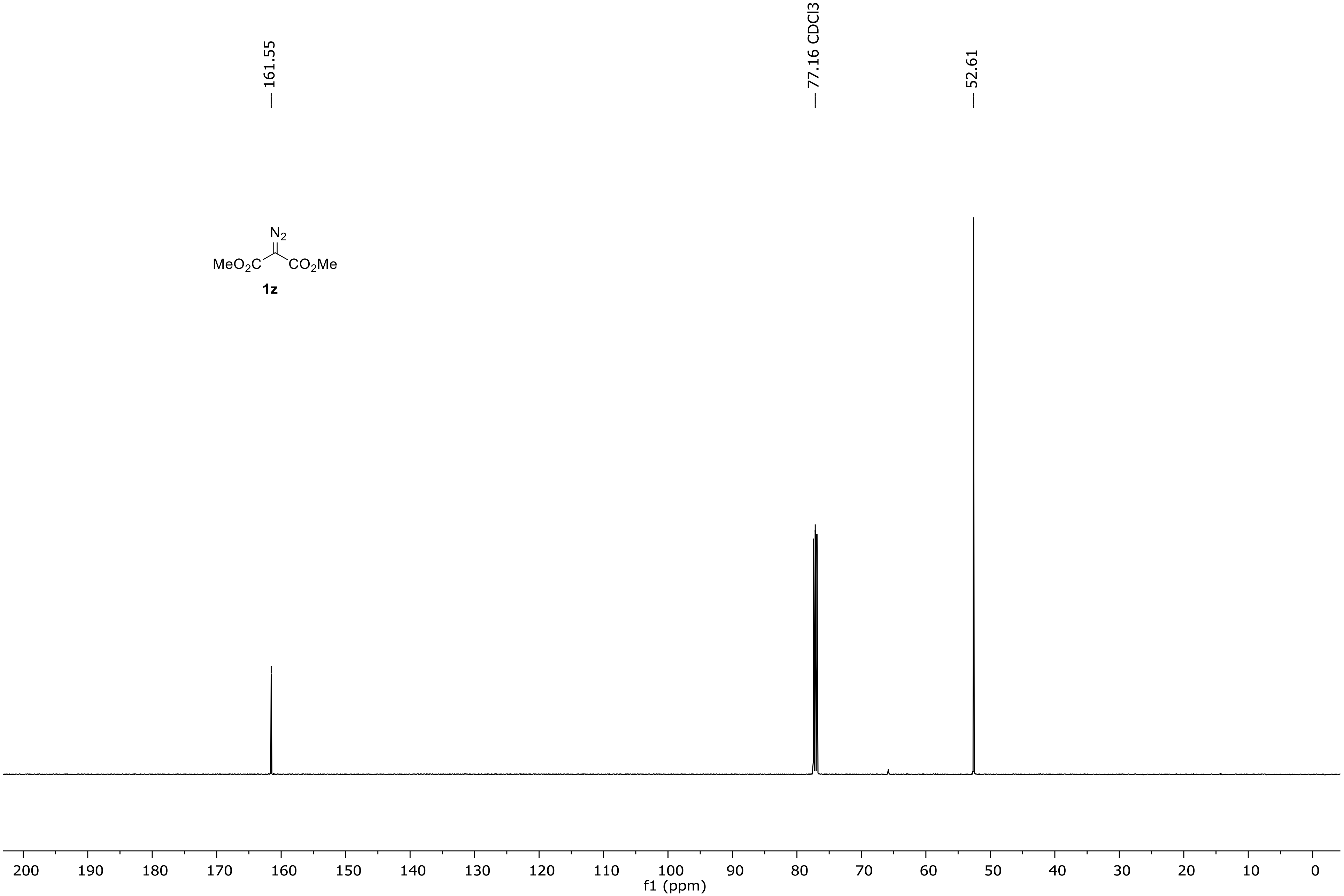
1x



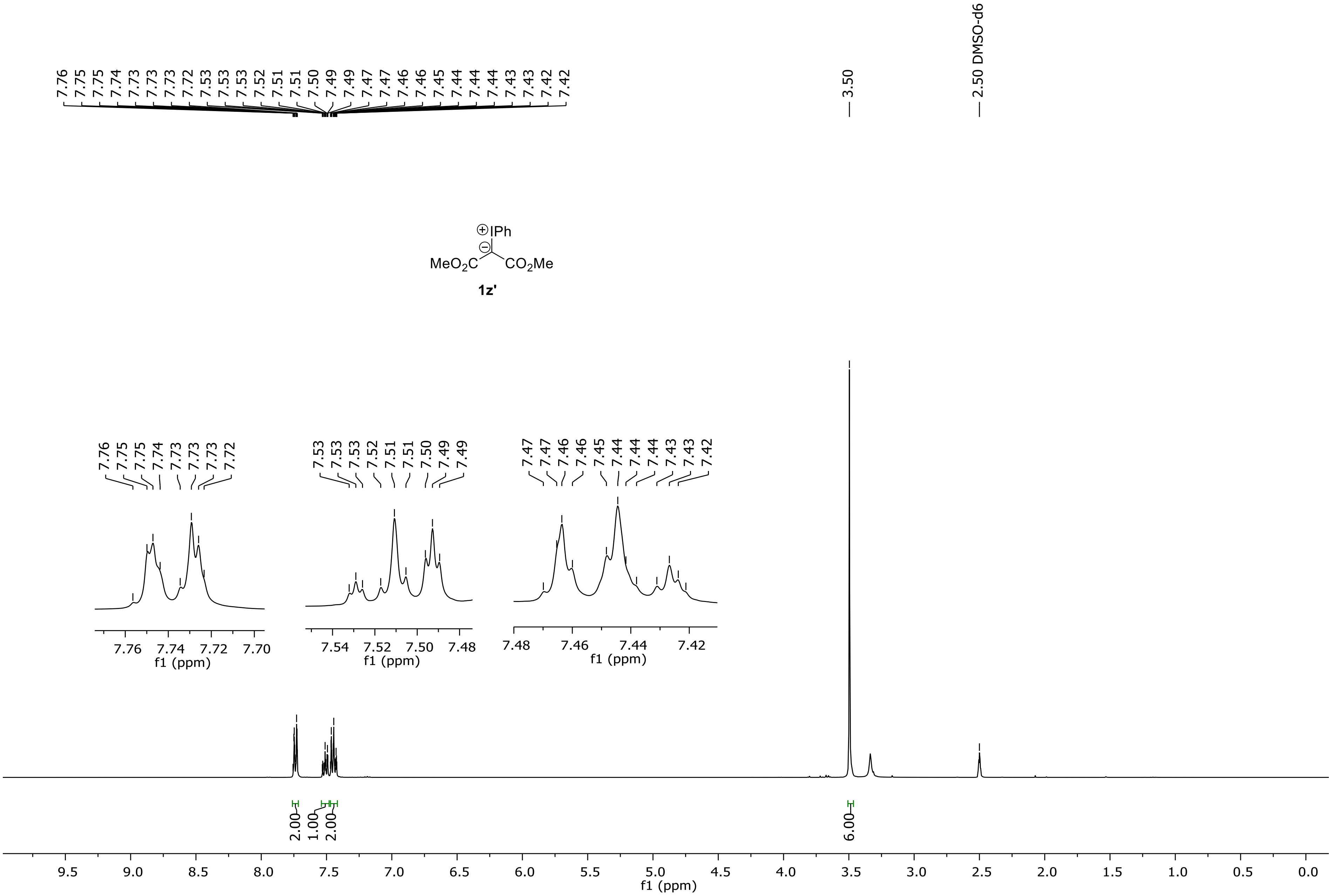
^{1}H NMR of 1z ($CDCl_3$, 500 MHz)



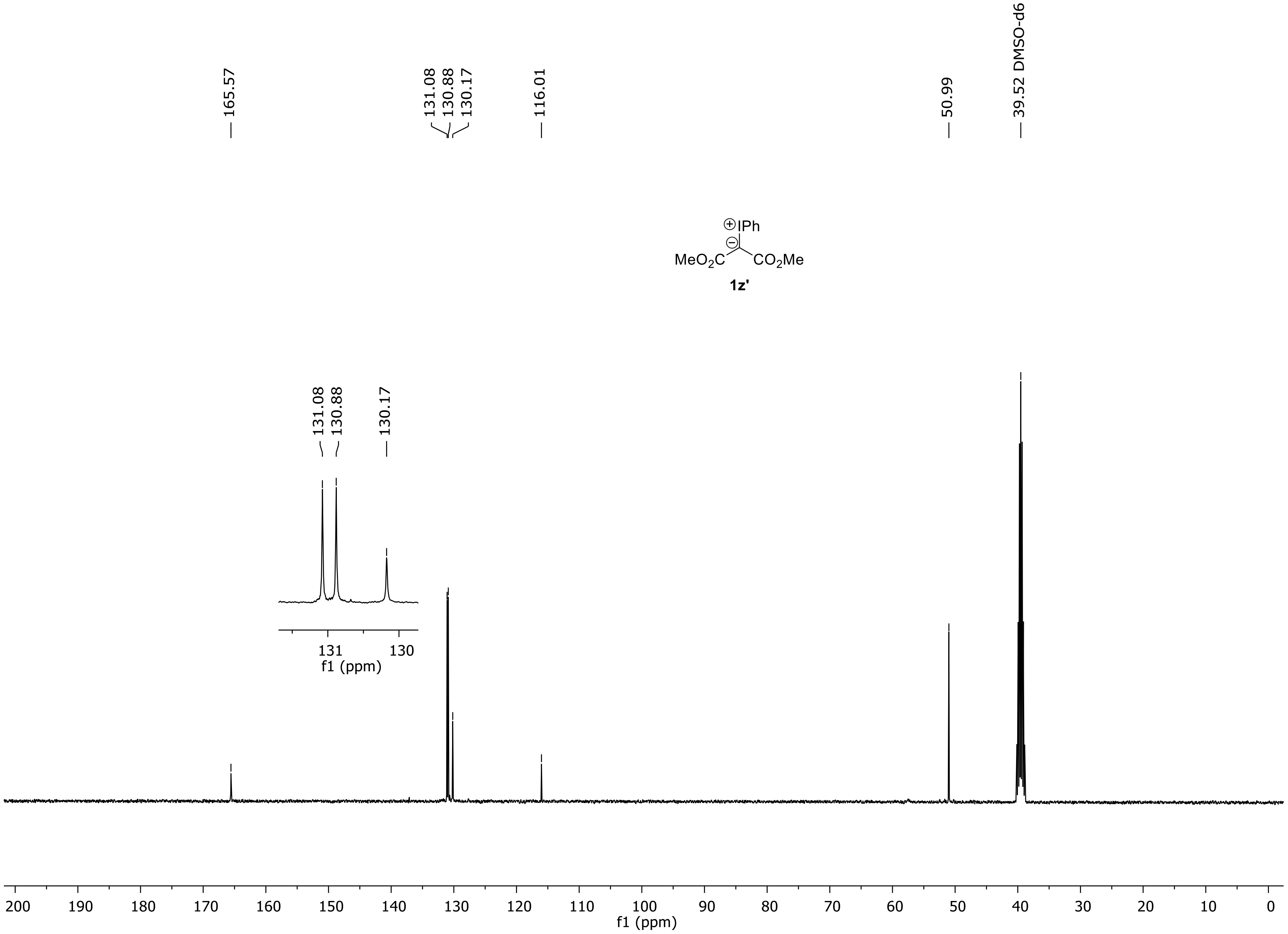
$^{13}C\{^1H\}$ NMR of 1z ($CDCl_3$, 125 MHz)



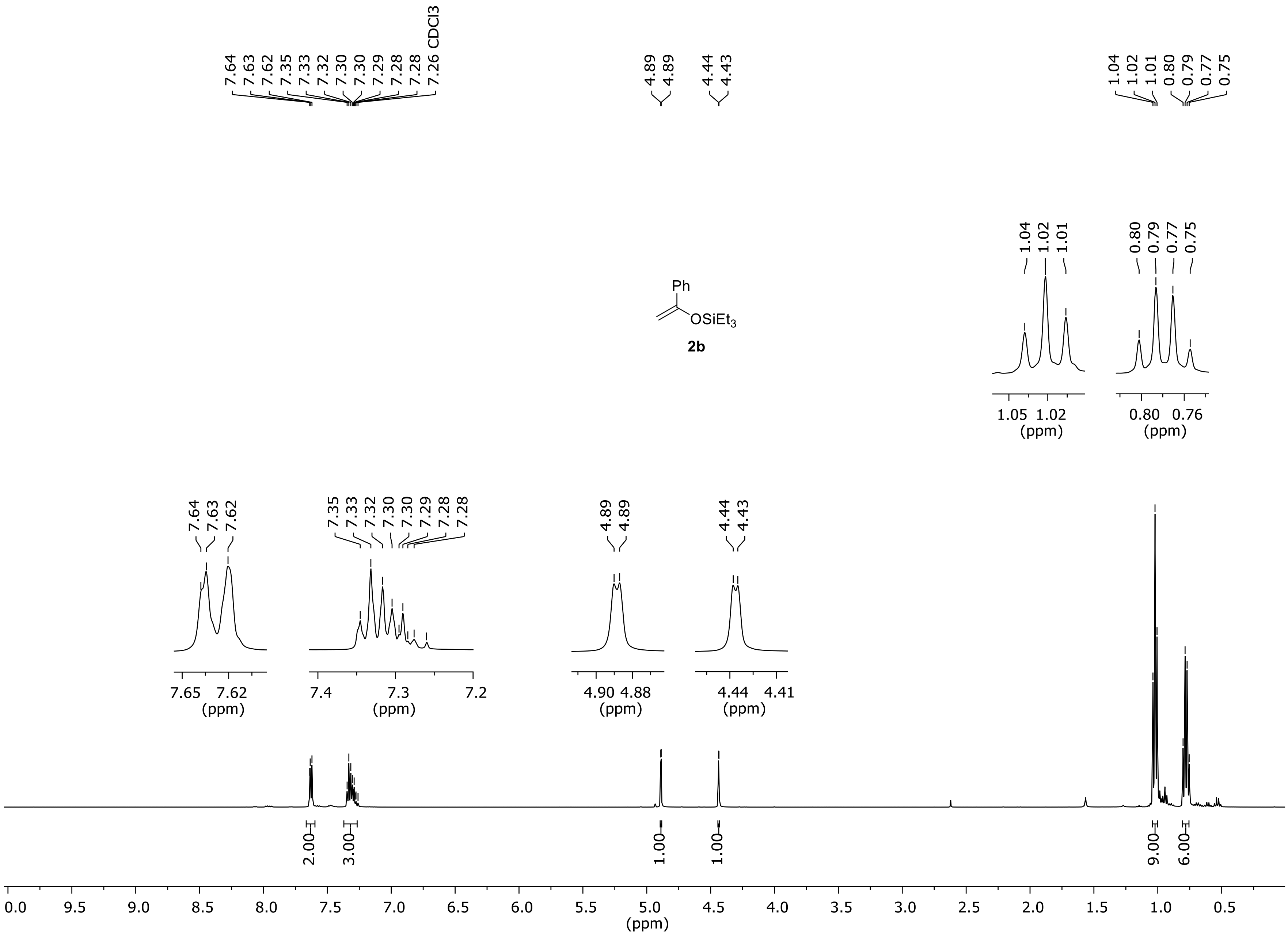
^{1}H NMR of 1z’ (d$_6$-DMSO, 400 MHz)



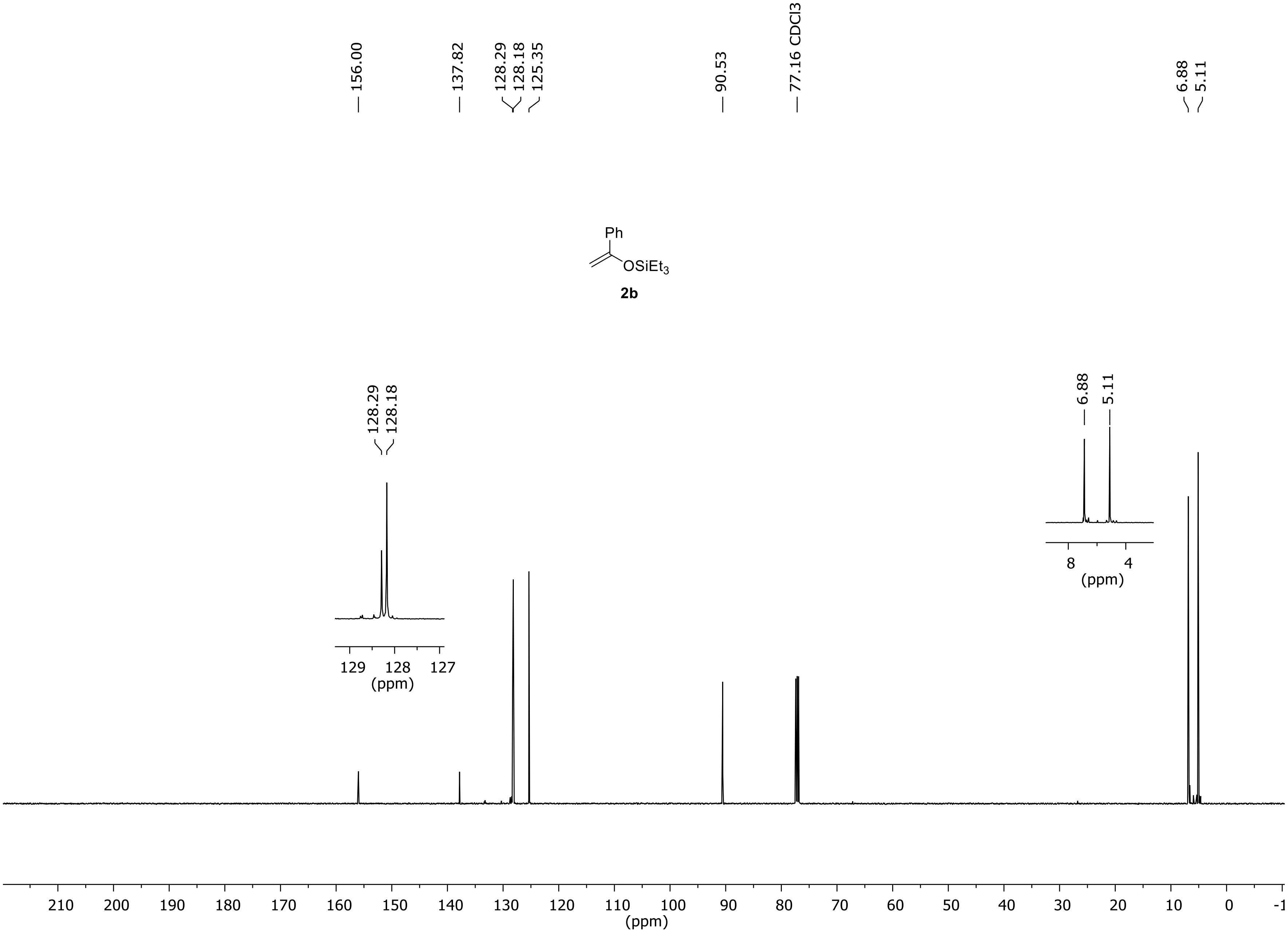
$^{13}C\{^1H\}$ NMR of 1z' (d_6-DMSO, 100 MHz)



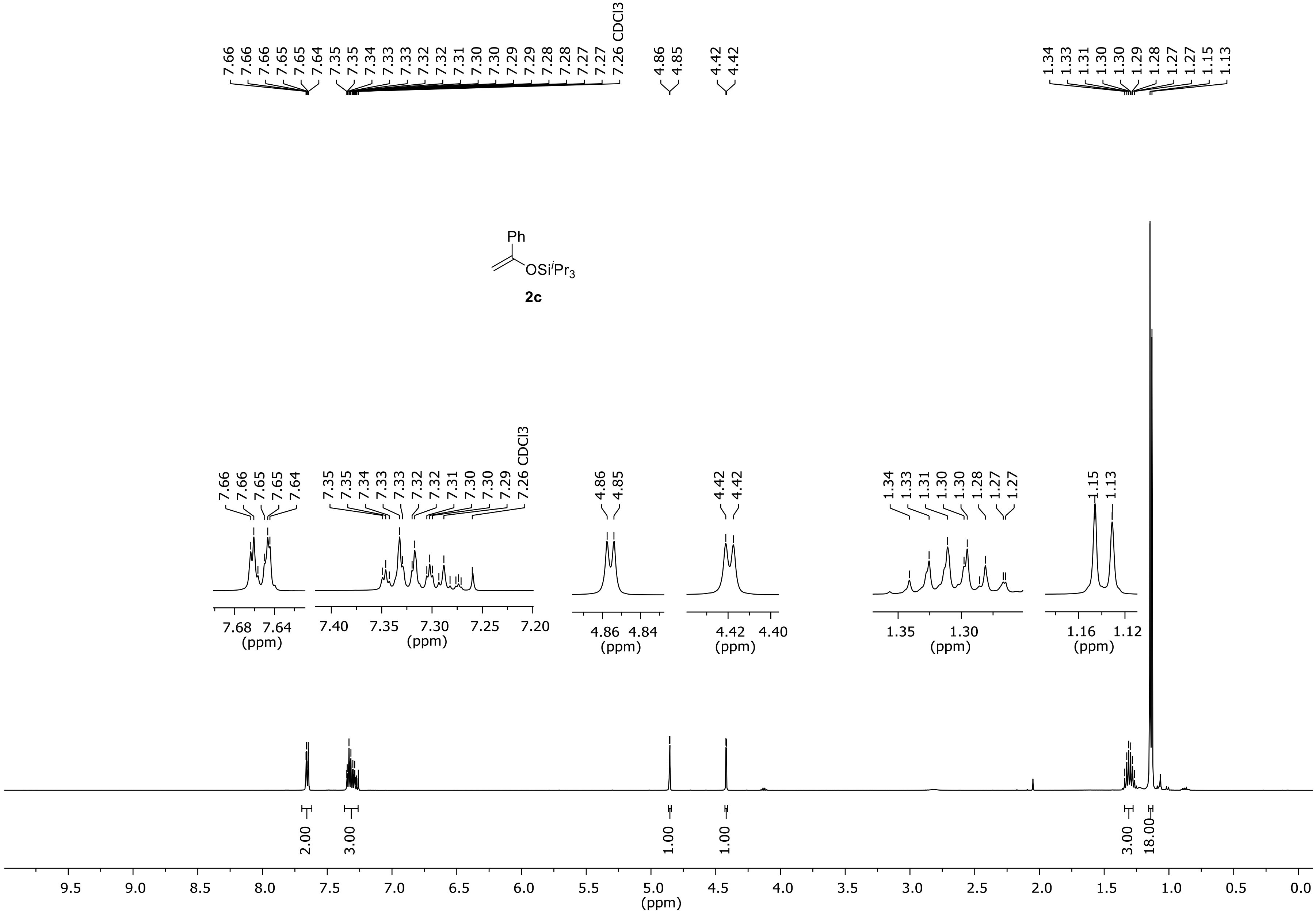
^{1}H NMR of 2b (CDCl$_3$, 500 MHz)



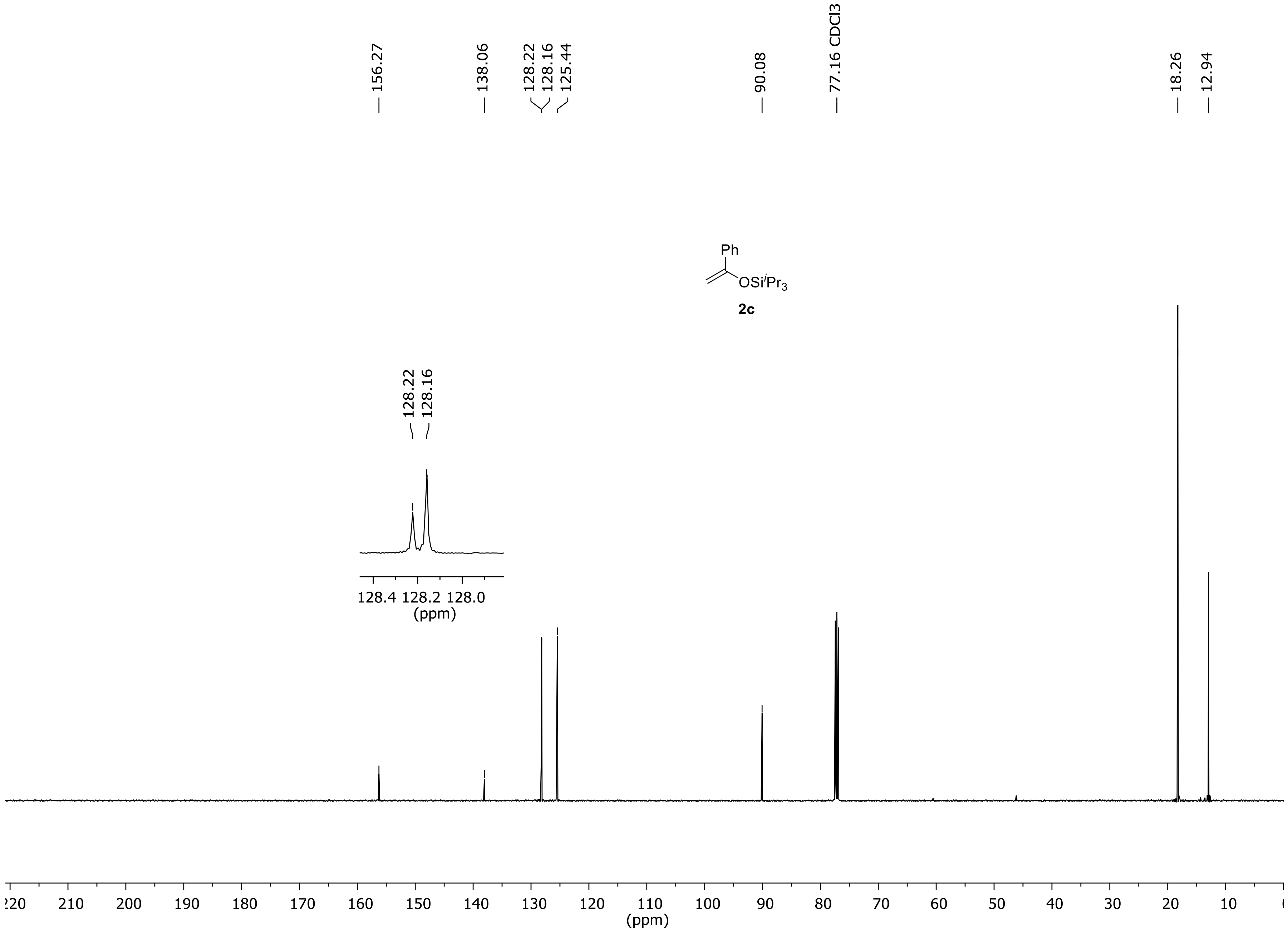
$^{13}C\{^1H\}$ NMR of 2b ($CDCl_3$, 125 MHz)



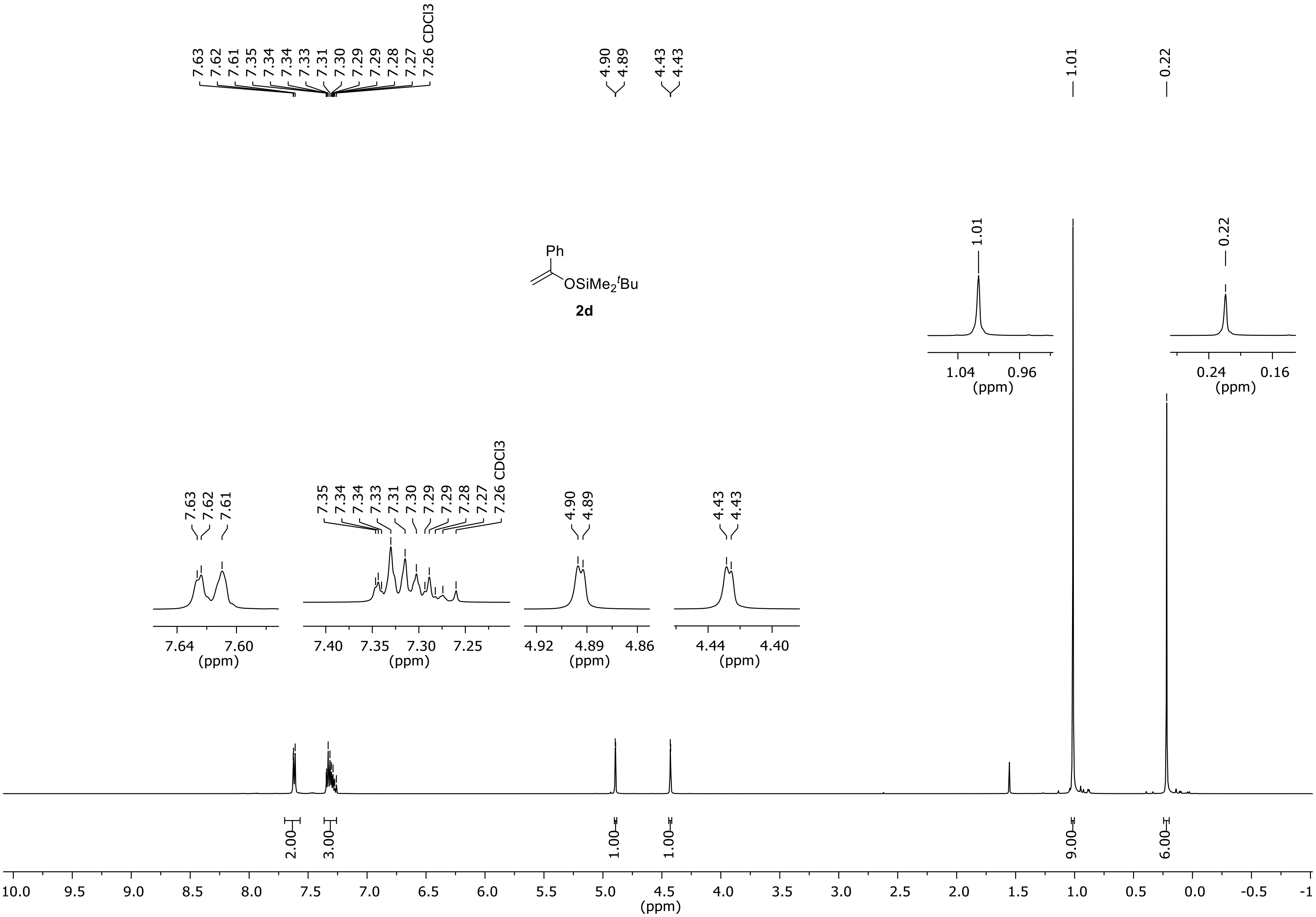
^{1}H NMR of 2c ($CDCl_3$, 500 MHz)



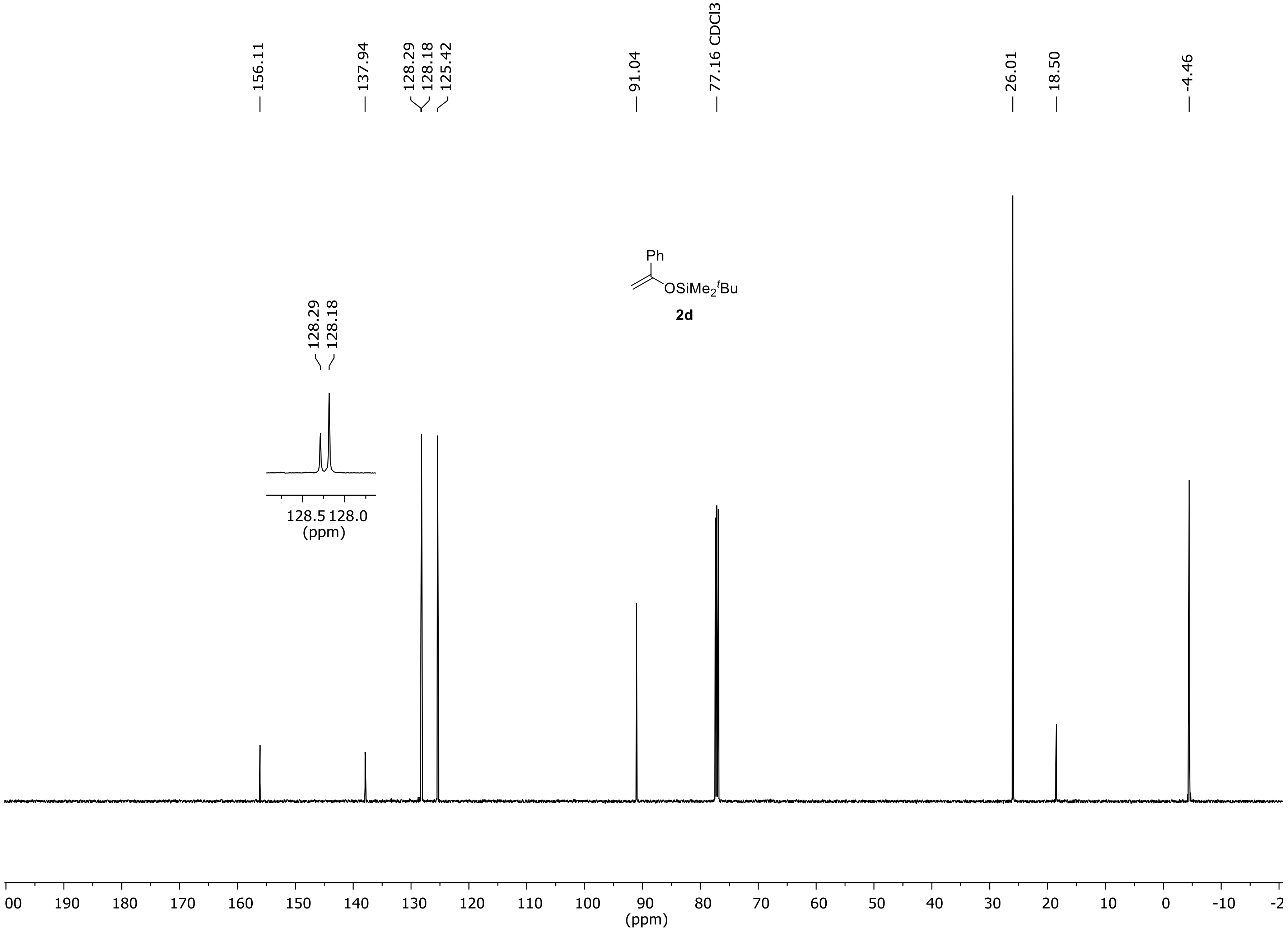
$^{13}C\{^1H\}$ **NMR of 2c ($CDCl_3$, 125 MHz)**



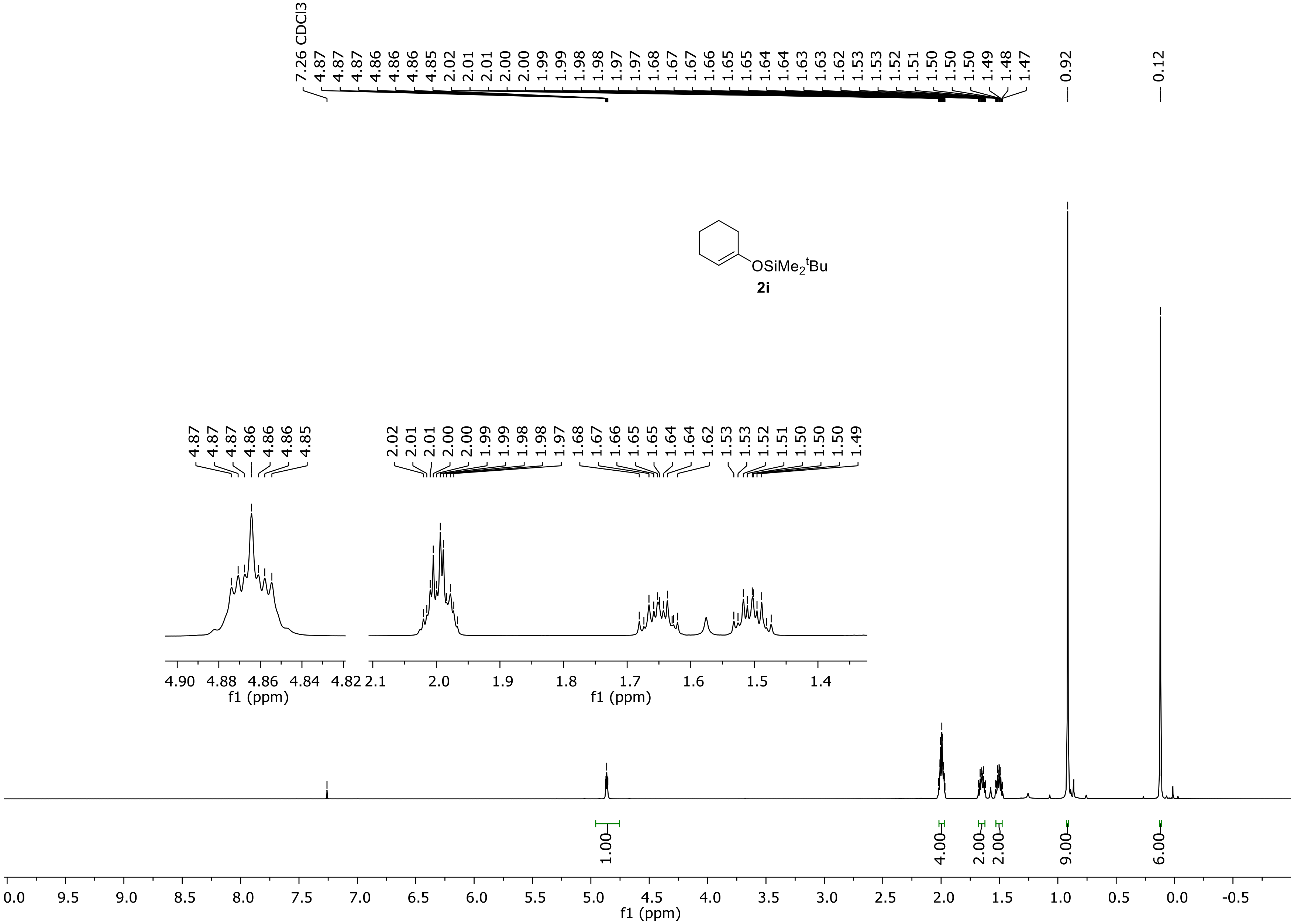
^{1}H NMR of 2d (CDCl$_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 2d ($CDCl_3$, 125 MHz)

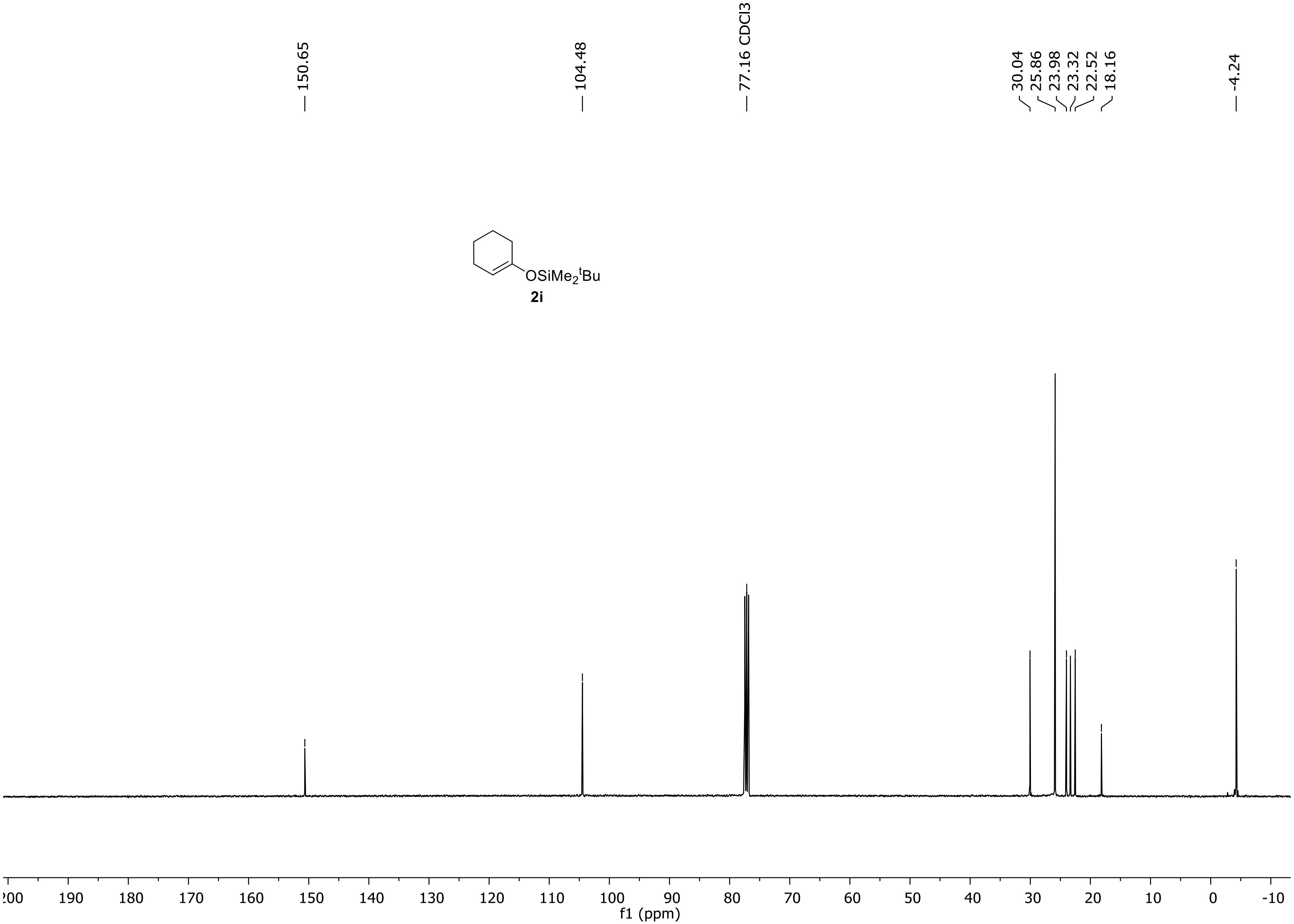


^{1}H NMR of 2i (CDCl$_3$, 400 MHz)



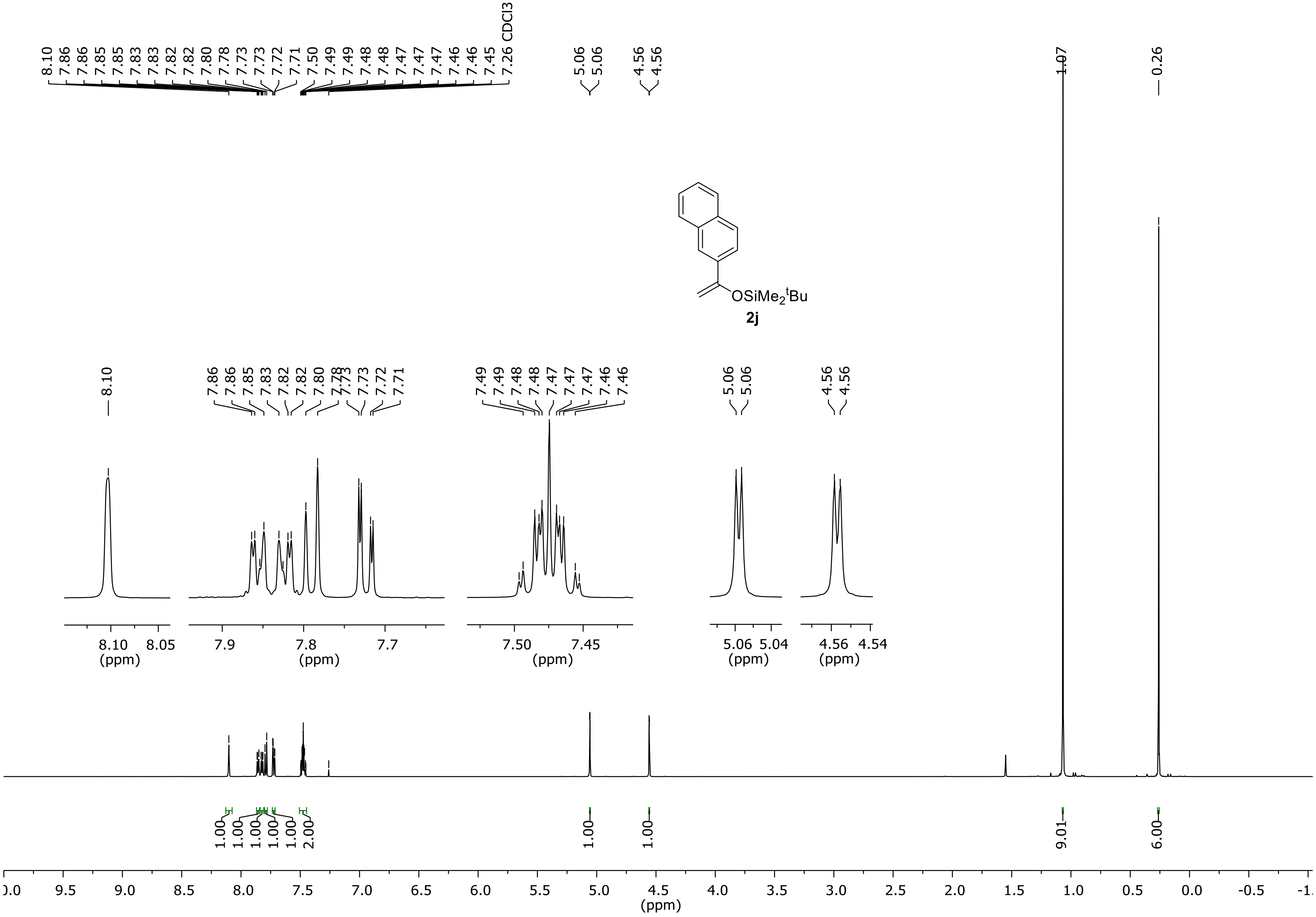
$^{13}C\{^1H\}$ NMR of 2i ($CDCl_3$, 100 MHz)

2i

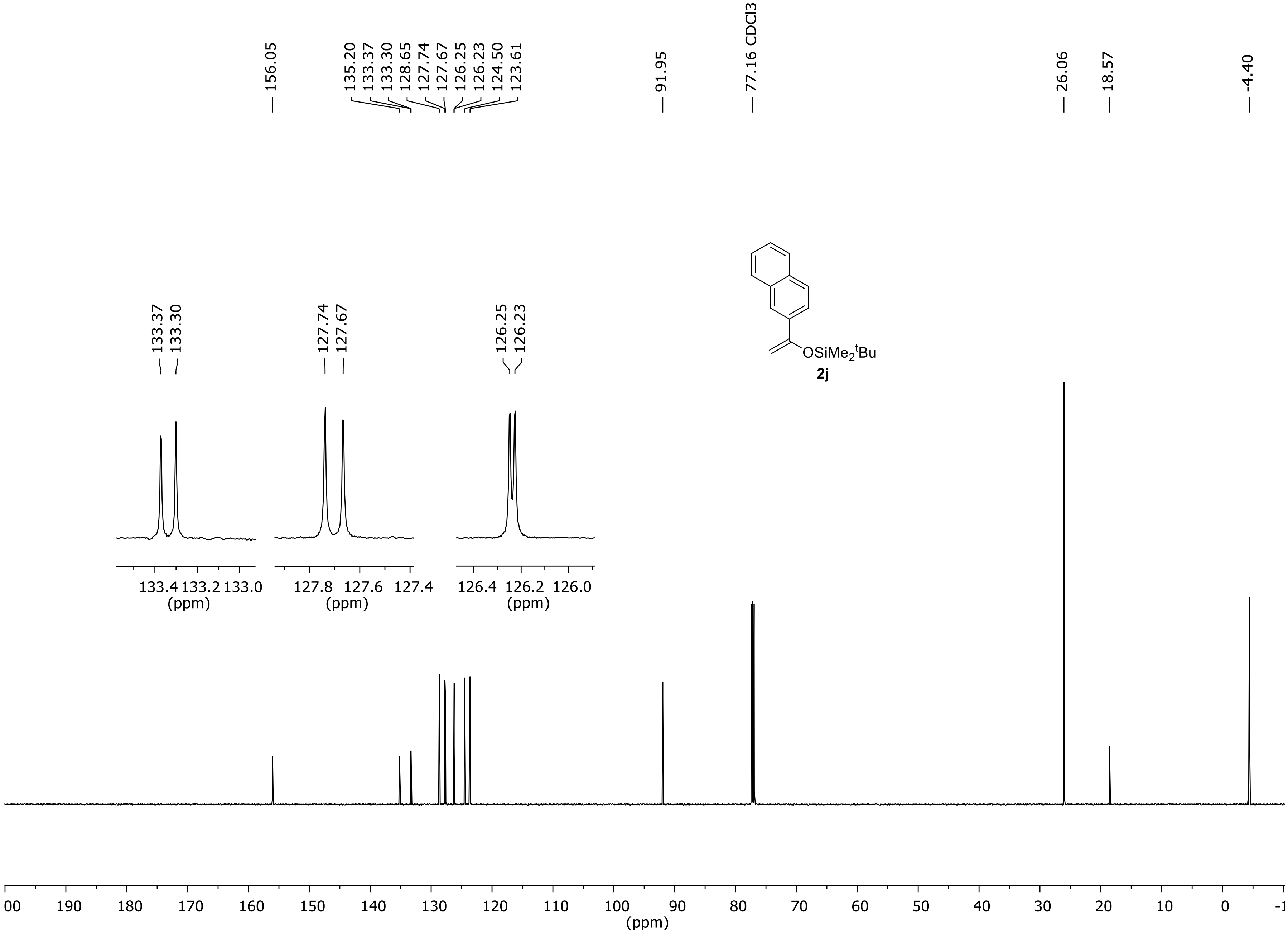


^{1}H NMR of 2j (CDCl$_3$, 600 MHz)

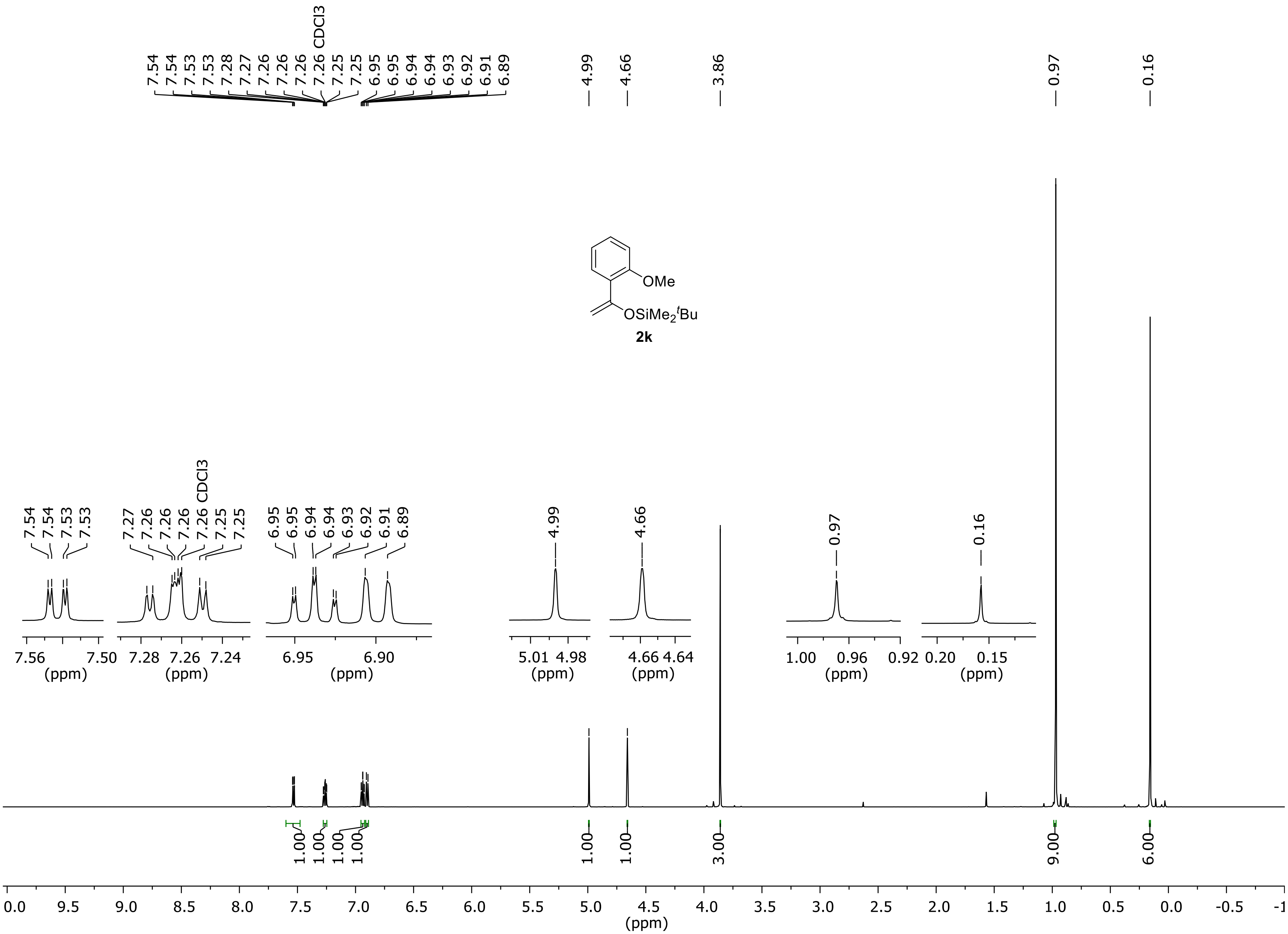
2j



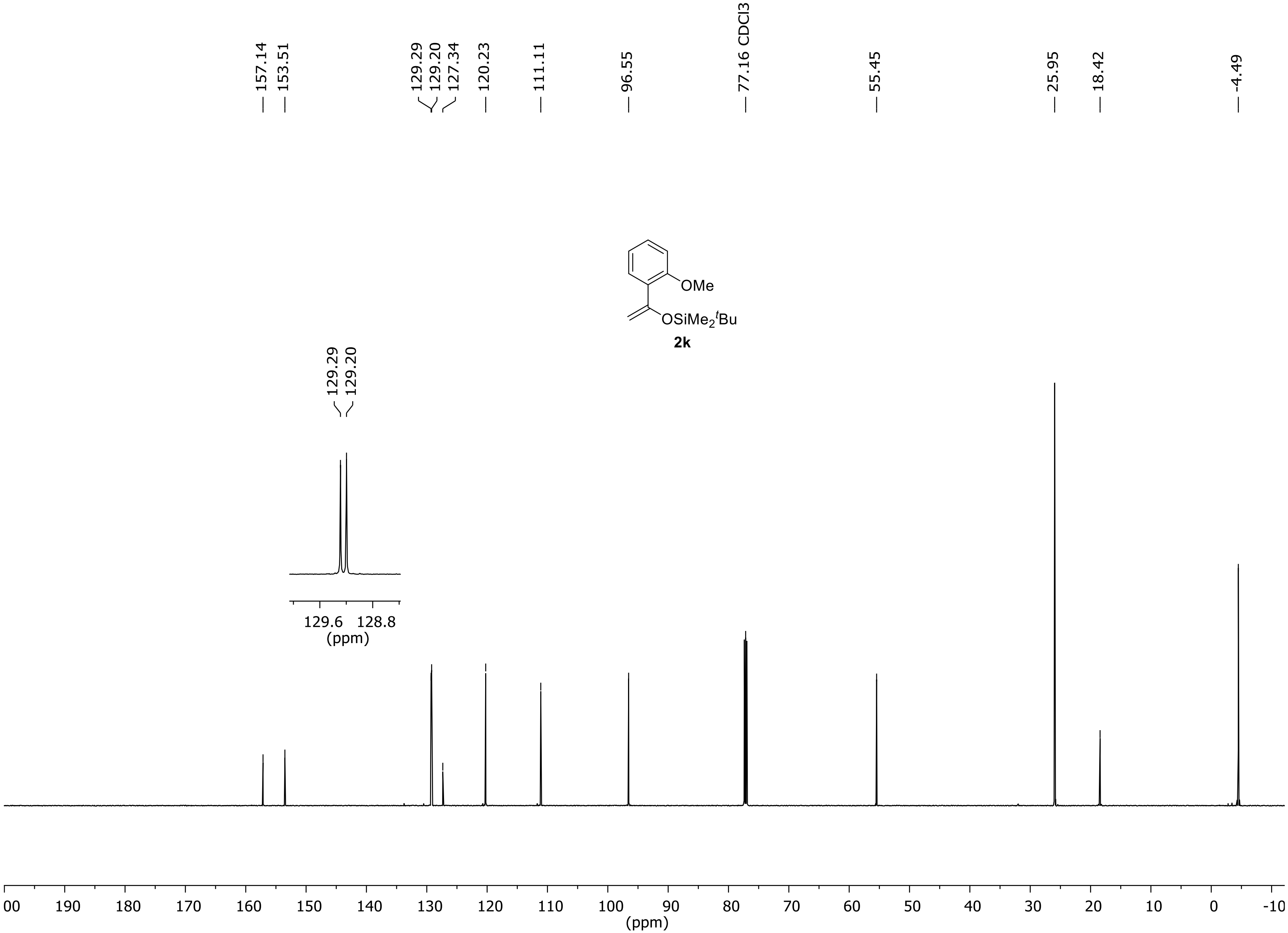
$^{13}C\{^1H\}$ NMR of 2j ($CDCl_3$, 150 MHz)



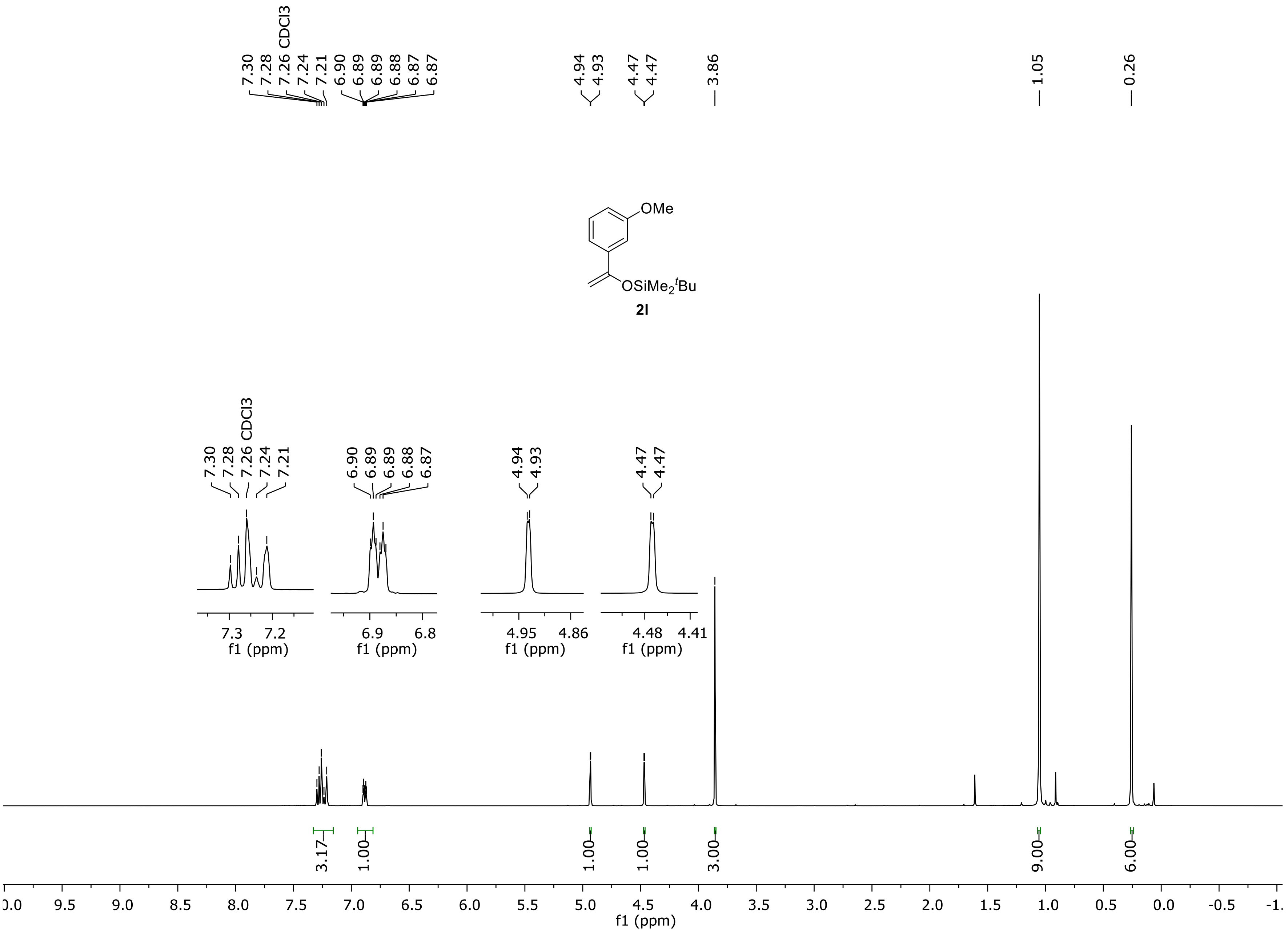
^{1}H NMR of 2k (CDCl$_3$, 600 MHz)



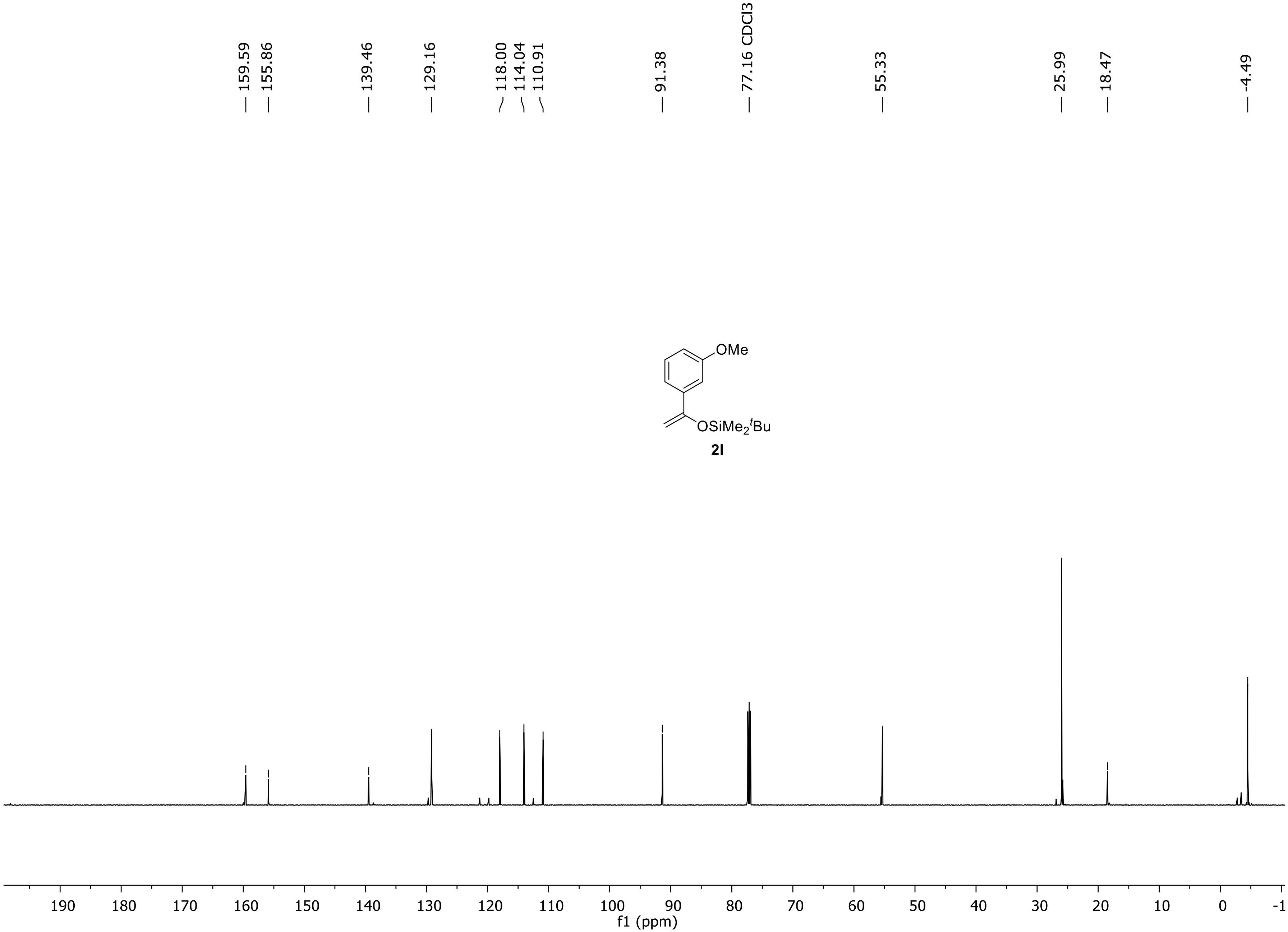
$^{13}C\{^1H\}$ NMR of 2k ($CDCl_3$, 150 MHz)



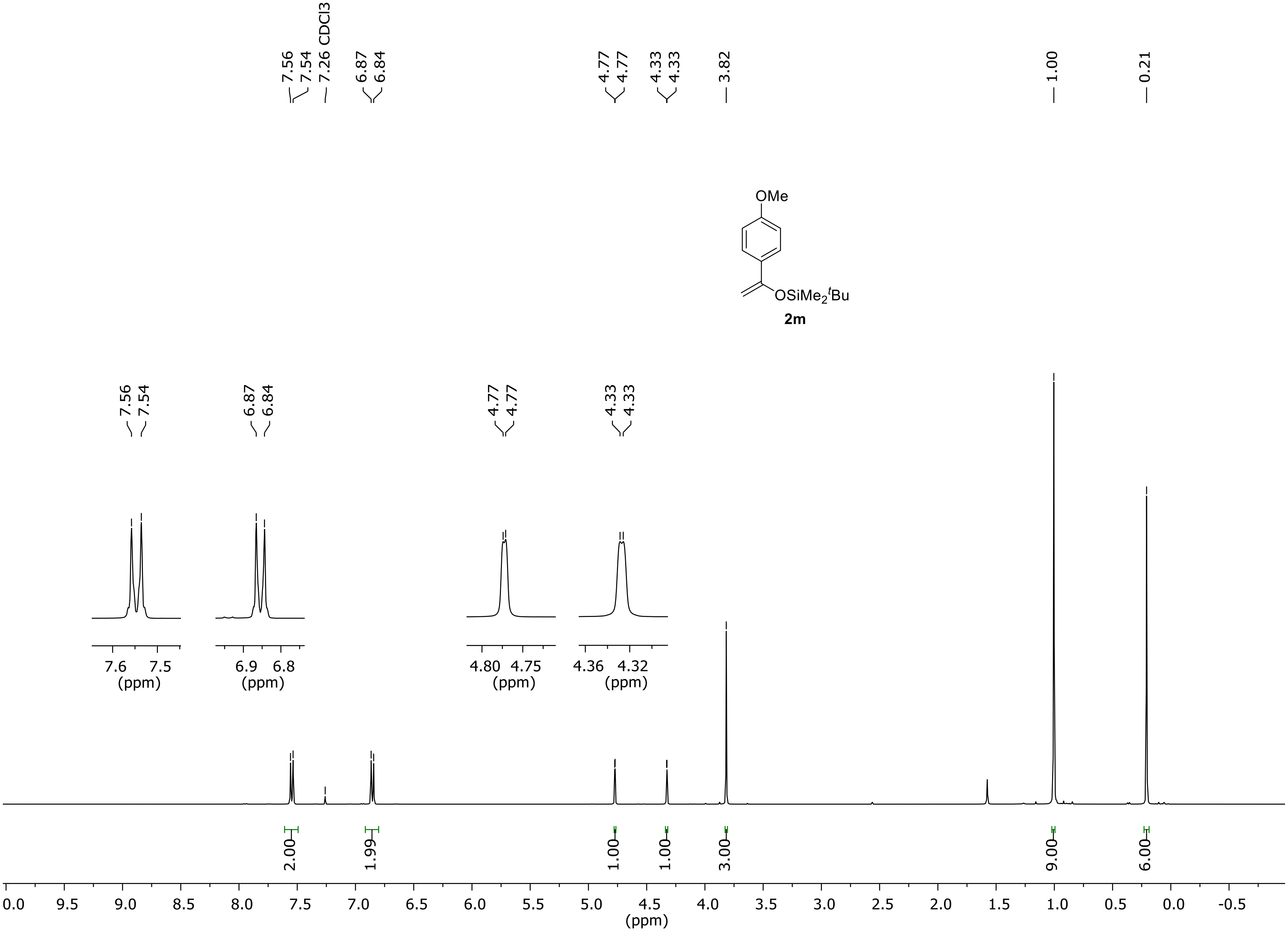
^{1}H NMR of 2l (CDCl$_3$, 400 MHz)



$^{13}C\{^1H\}$ NMR of 2l ($CDCl_3$, 100 MHz)

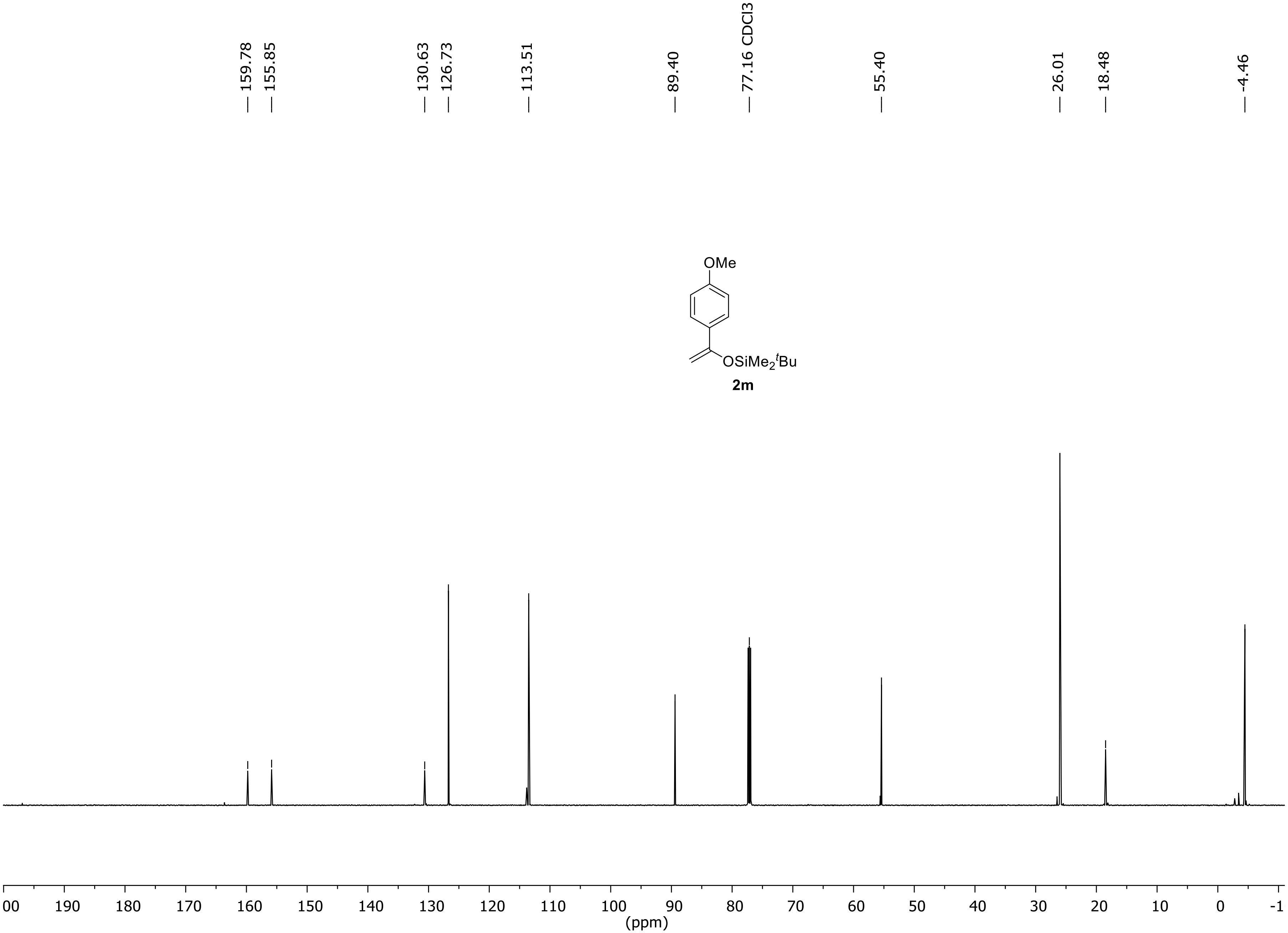


^{1}H NMR of 2m (CDCl$_3$, 500 MHz)

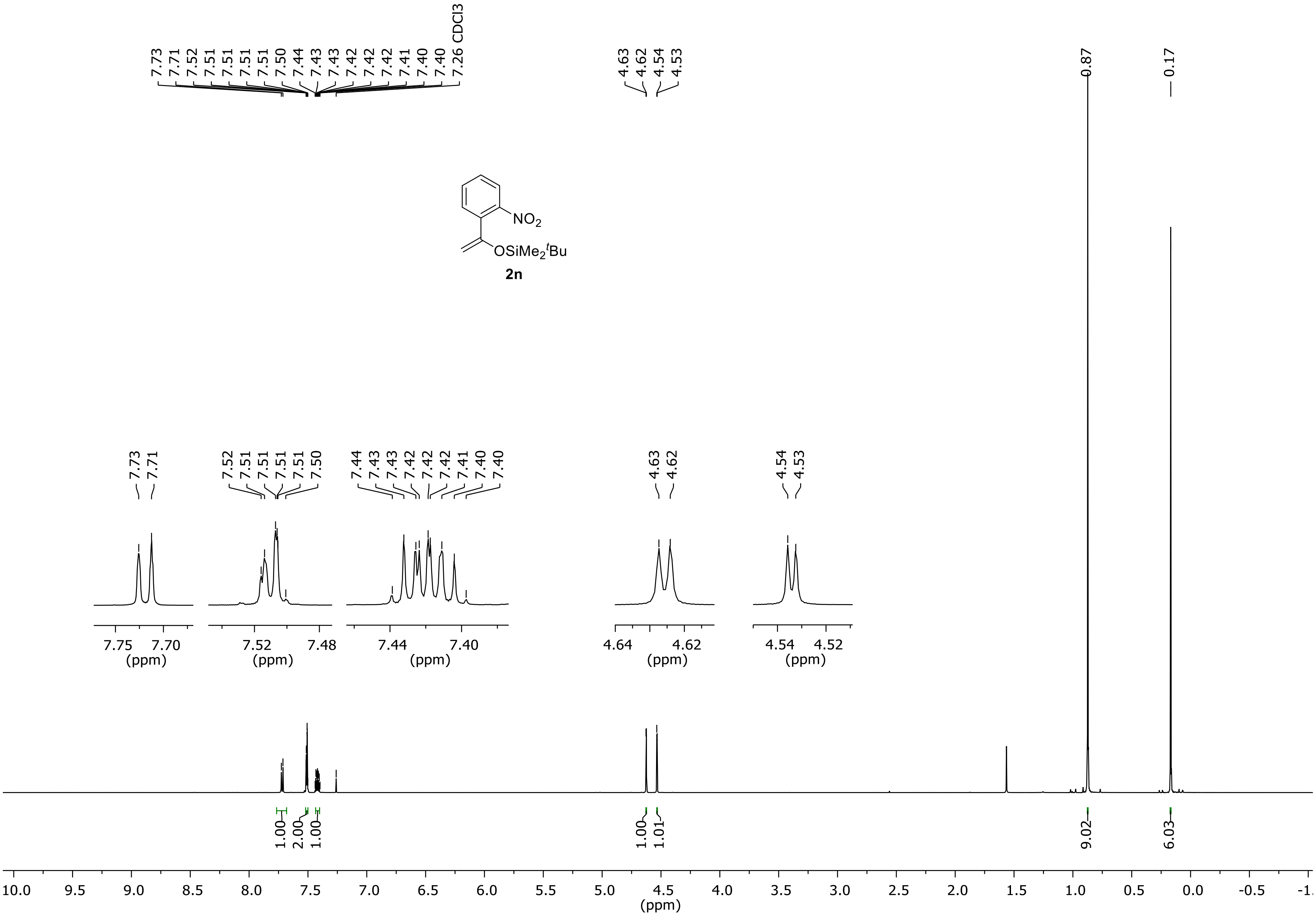


2m

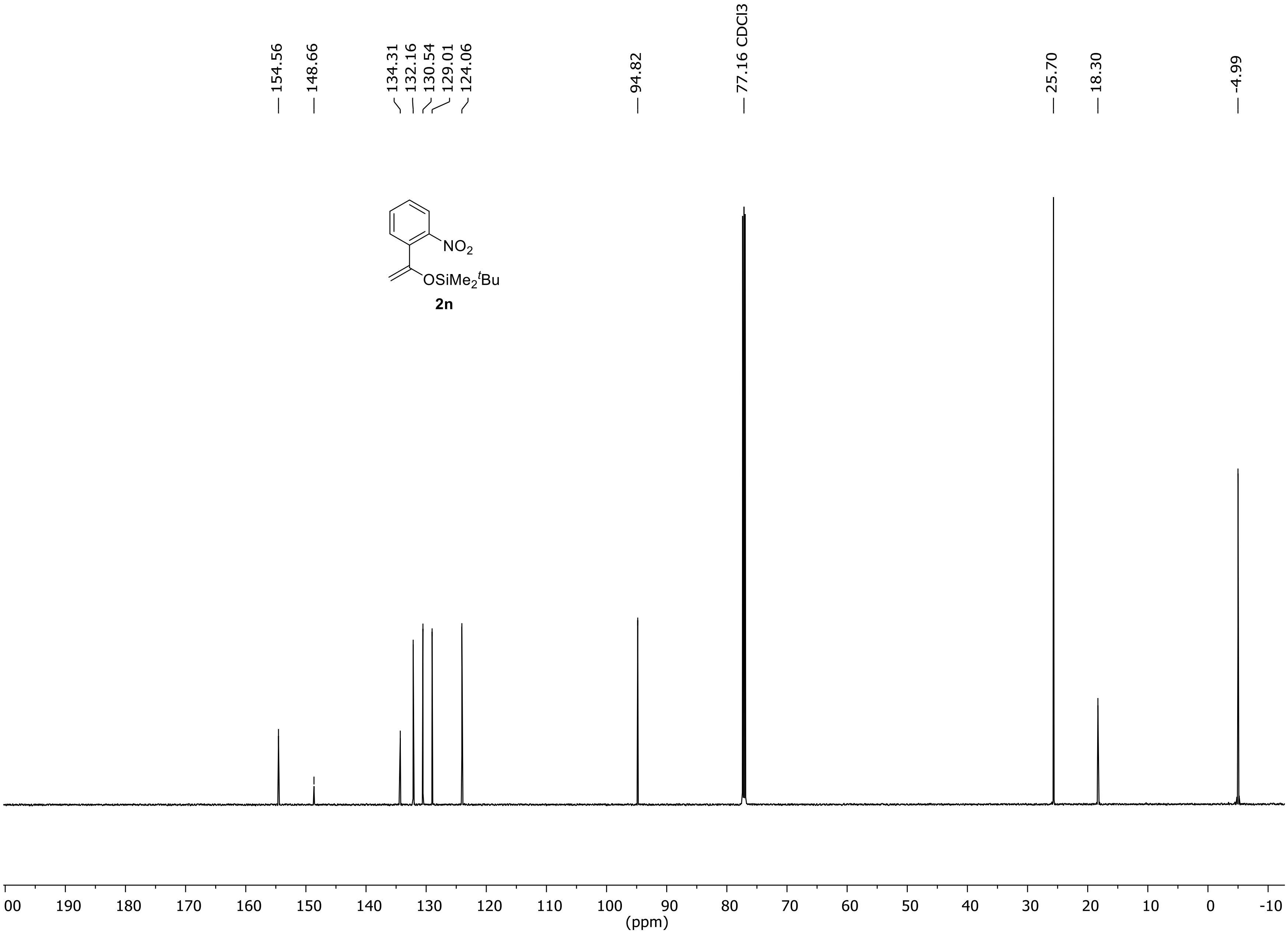
^{13}C{^{1}H} NMR of 2m (CDCl$_3$, 125 MHz)



^{1}H NMR of 2n ($CDCl_3$, 600 MHz)

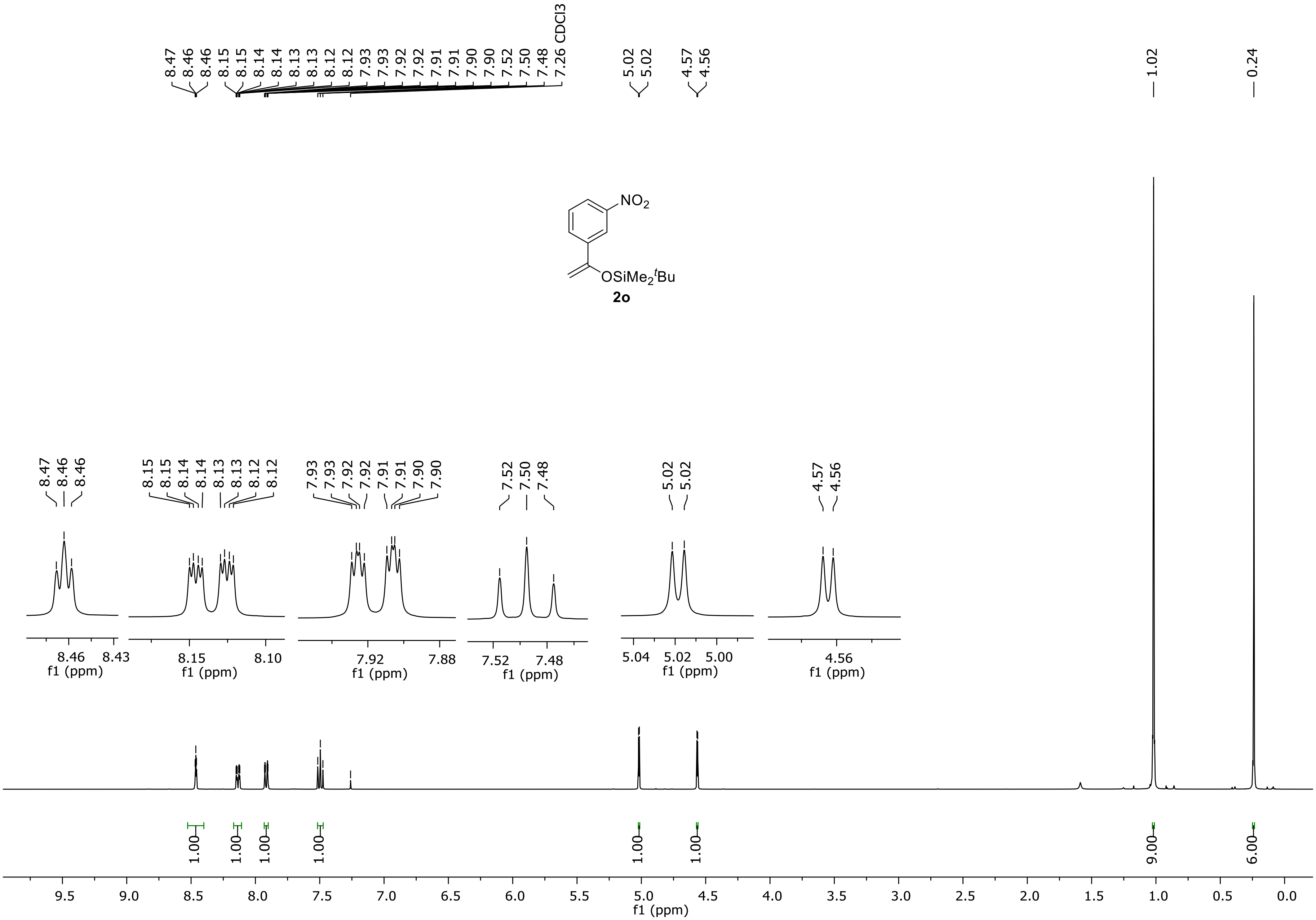


^{13}C{^{1}H} NMR of 2n (CDCl$_3$, 150 MHz)

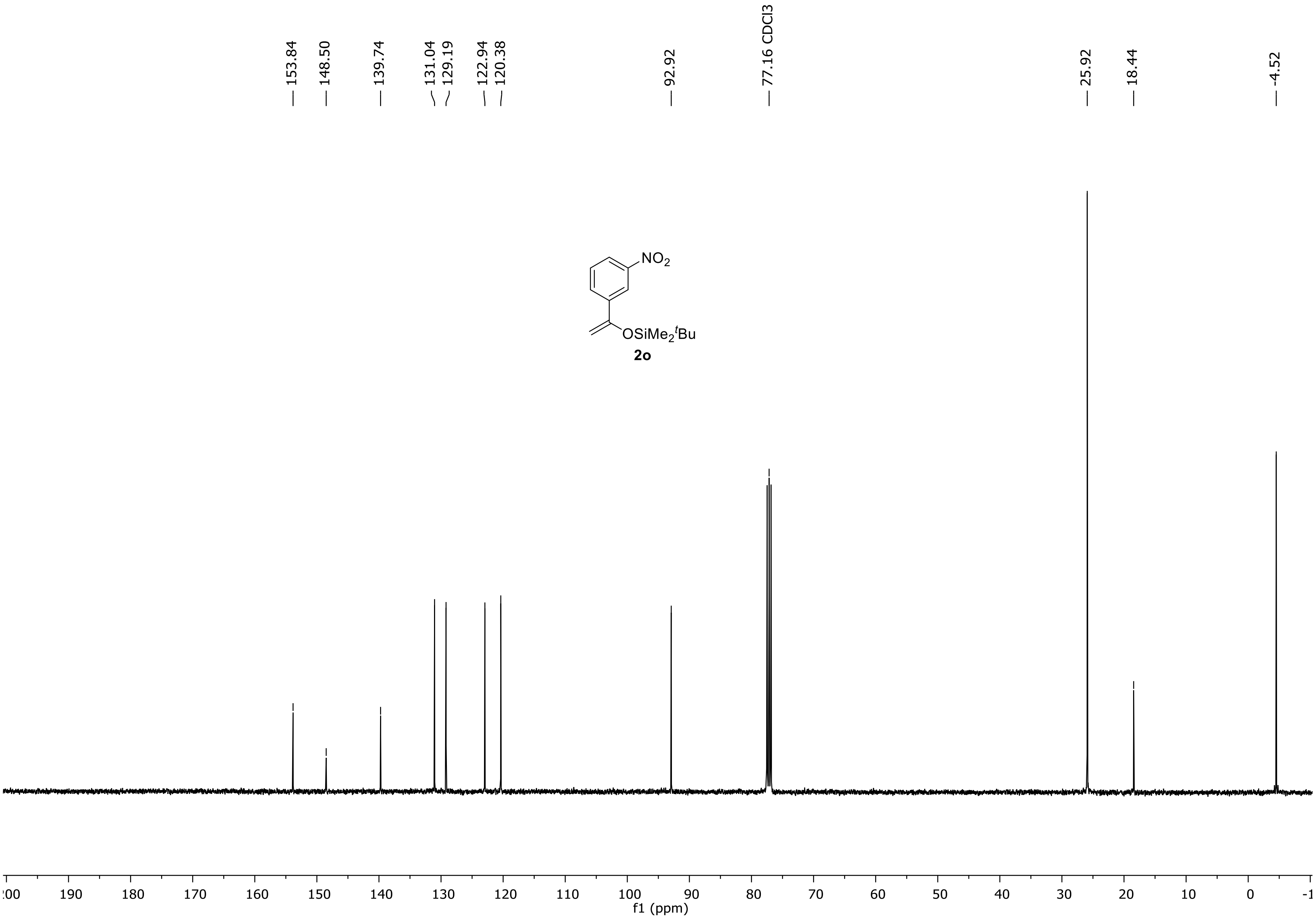


^{1}H NMR of 2o (CDCl$_3$, 500 MHz)

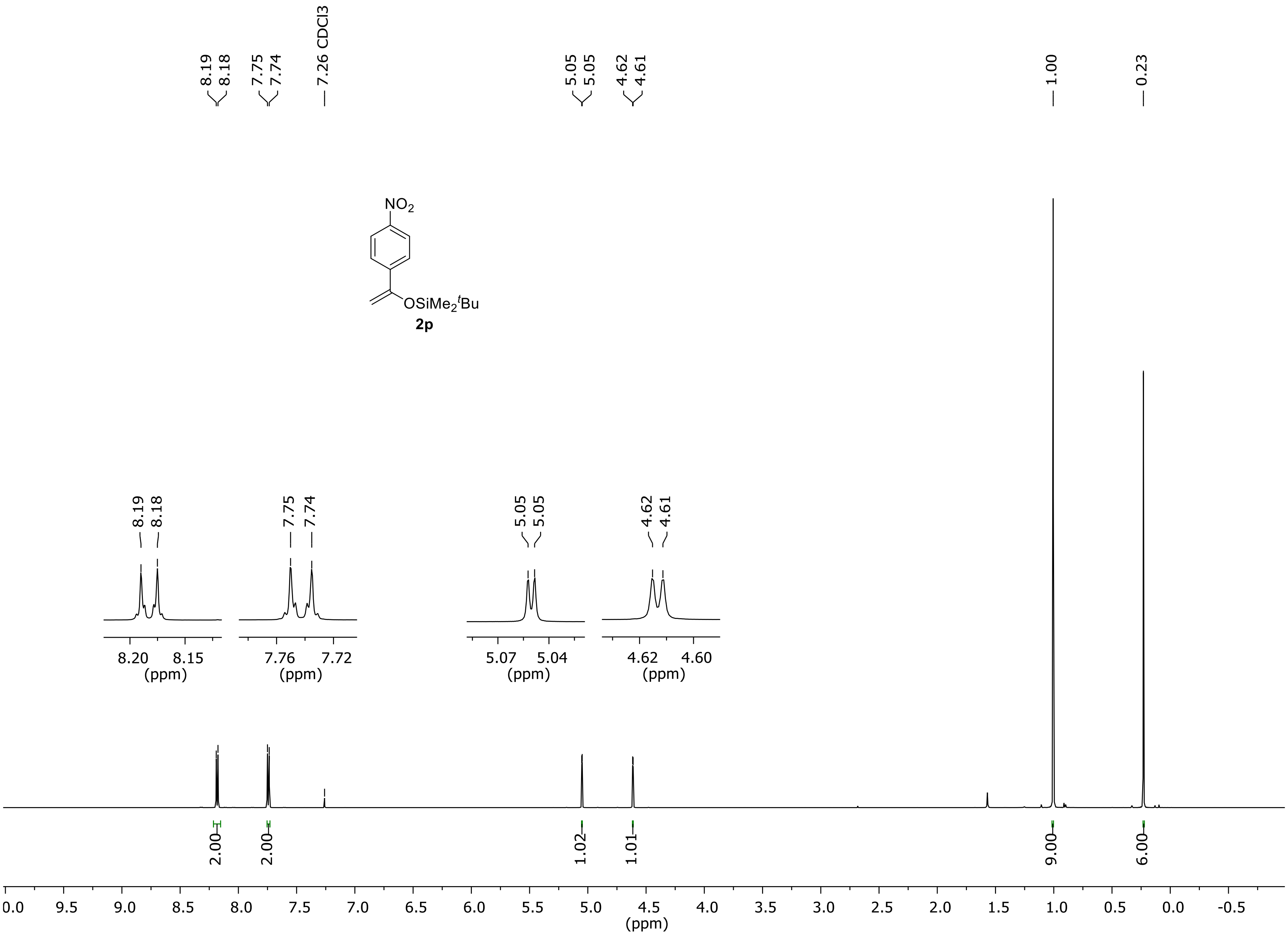
2o



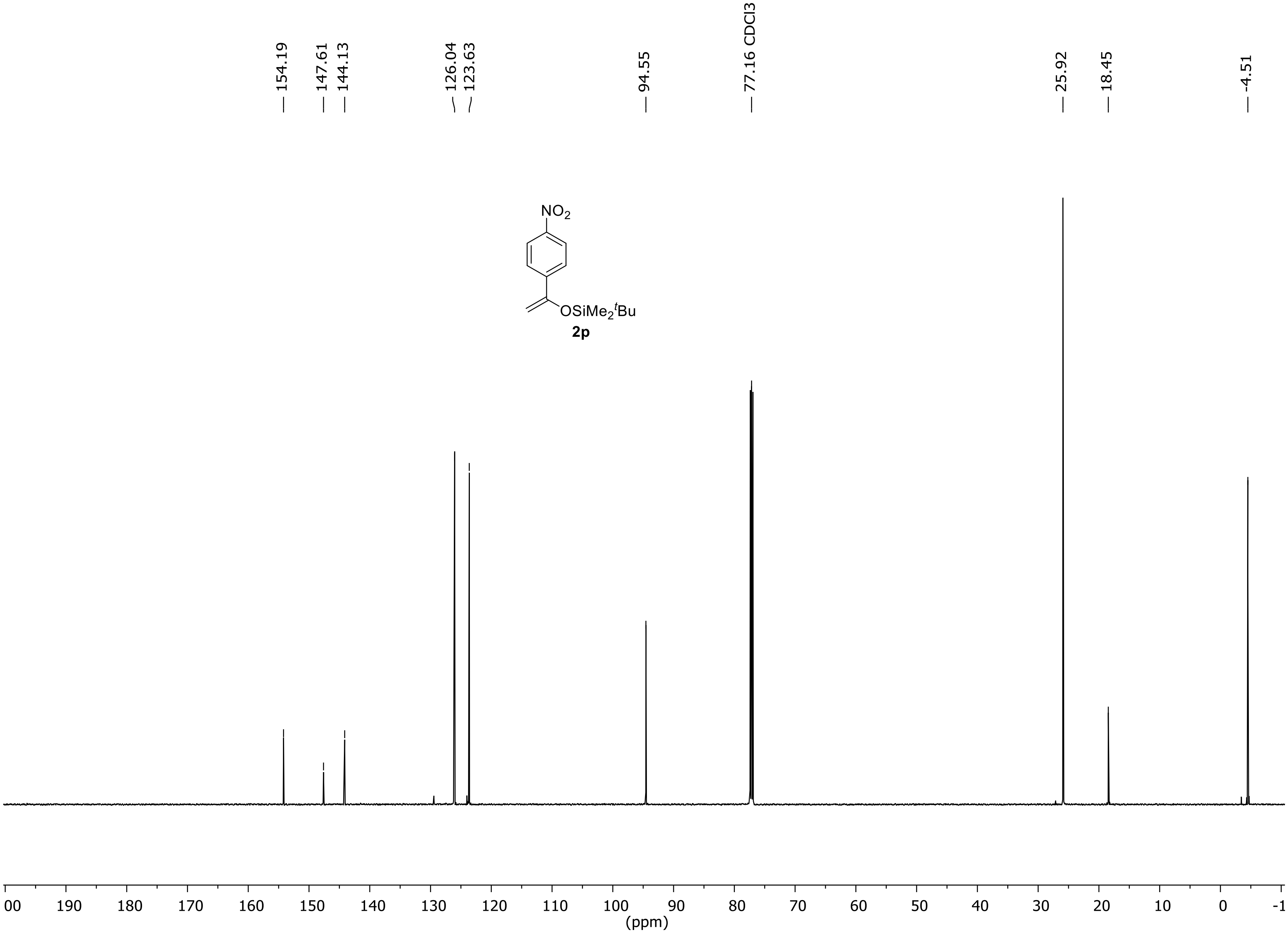
^{13}C{^{1}H} NMR of 2o (CDCl$_3$, 125 MHz)



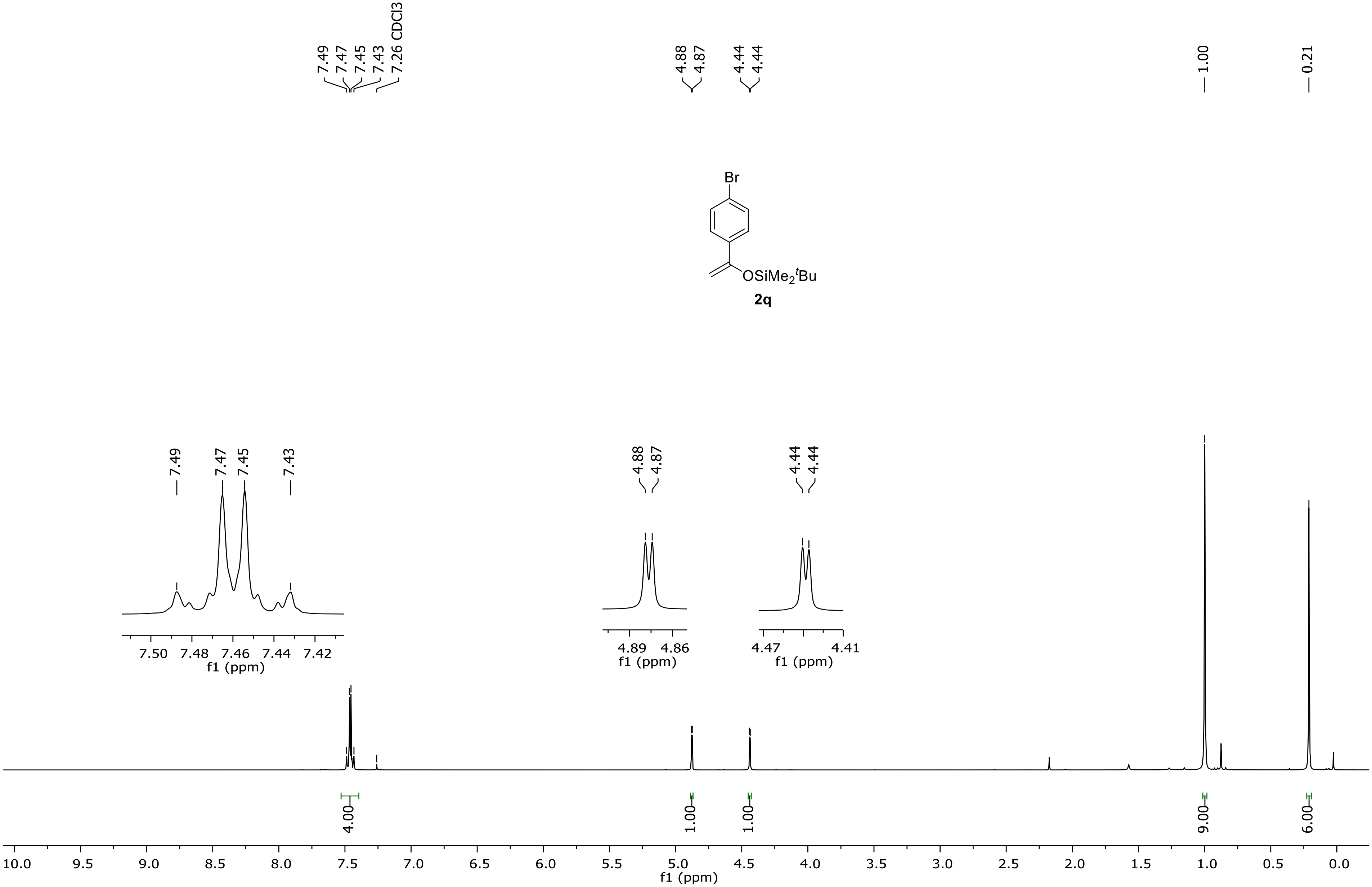
^{1}H NMR of 2p (CDCl$_3$, 600 MHz)



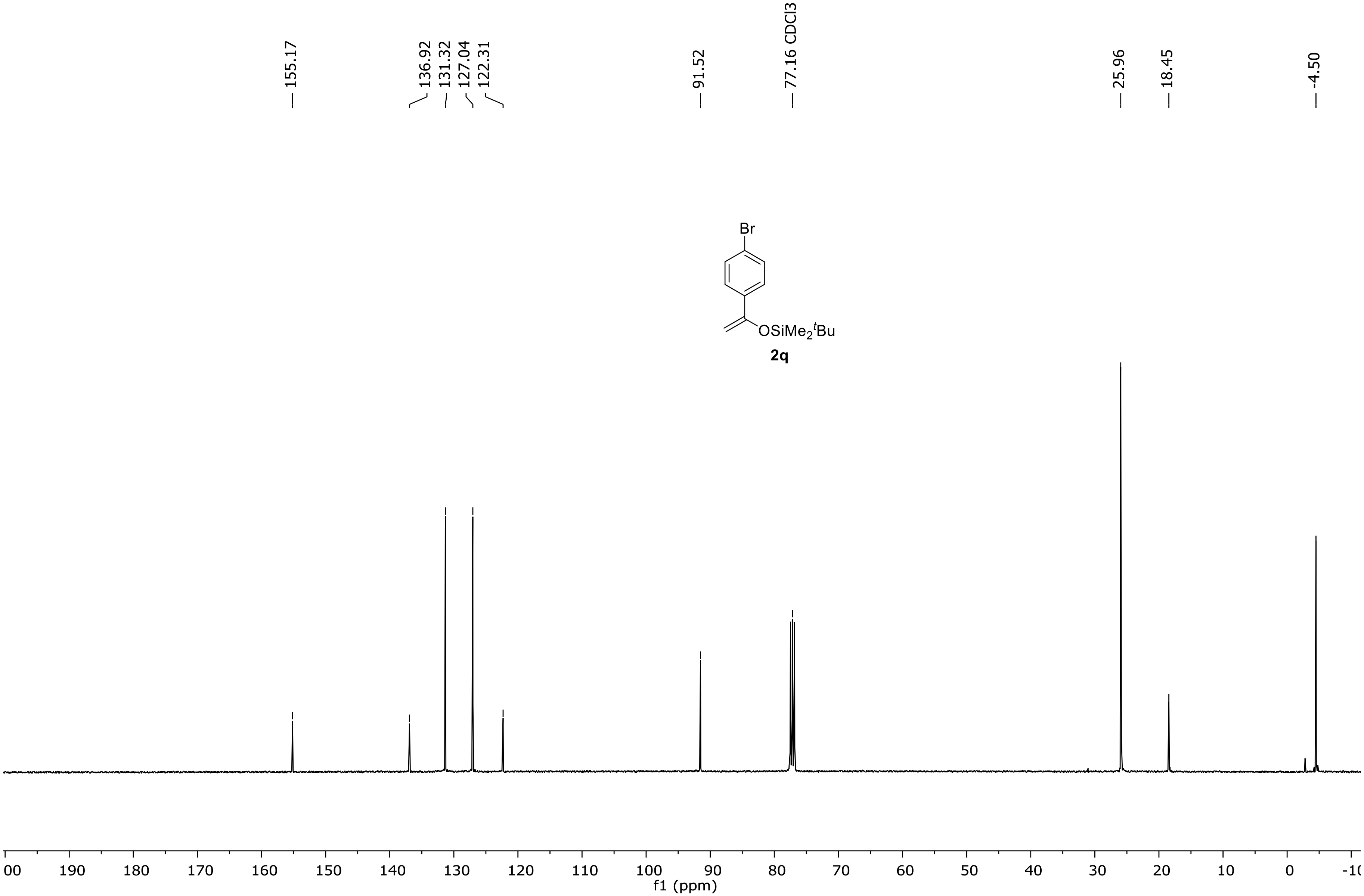
$^{13}C\{^1H\}$ NMR of 2p ($CDCl_3$, 150 MHz)



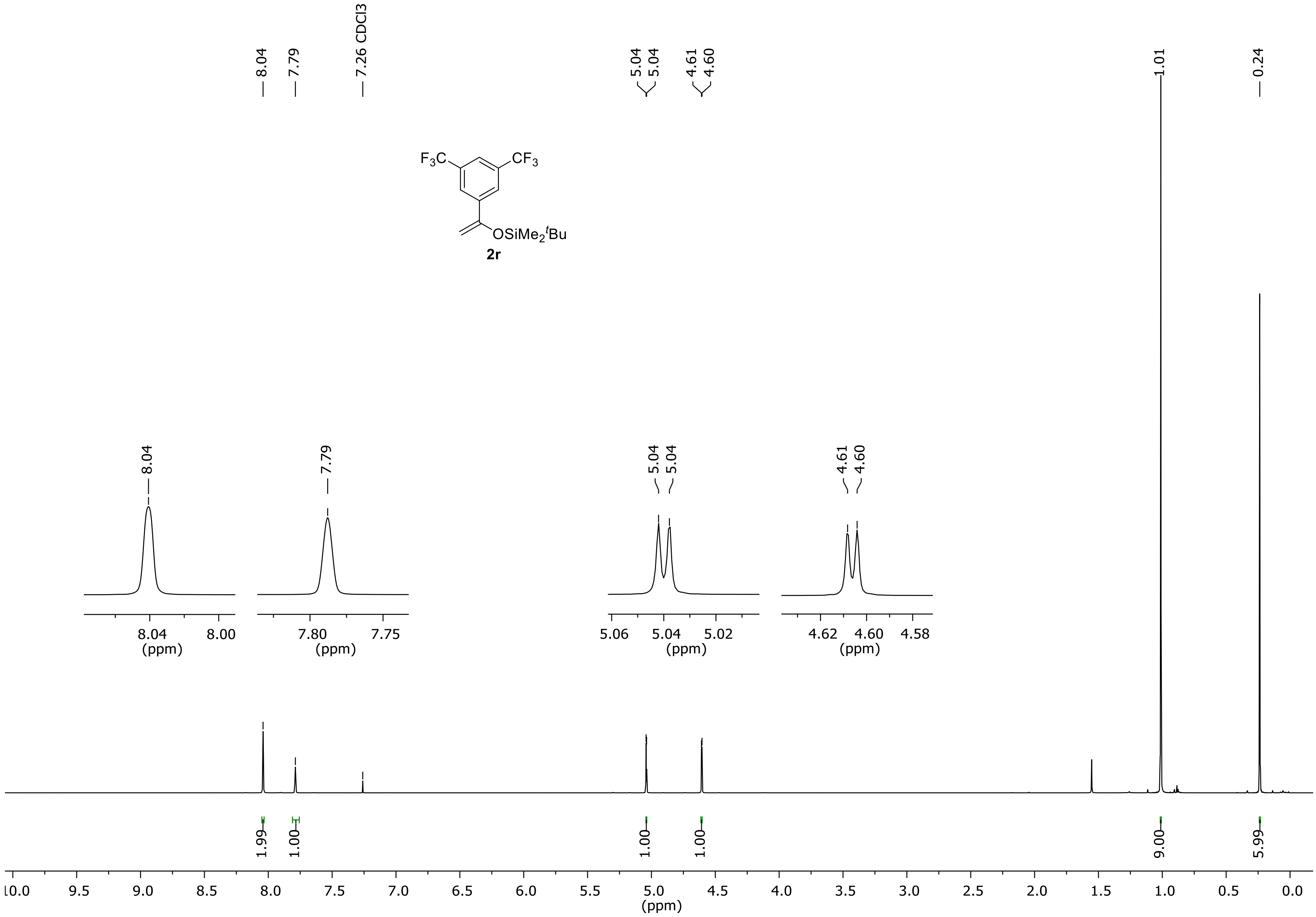
^{1}H NMR of 2q ($CDCl_3$, 400 MHz)



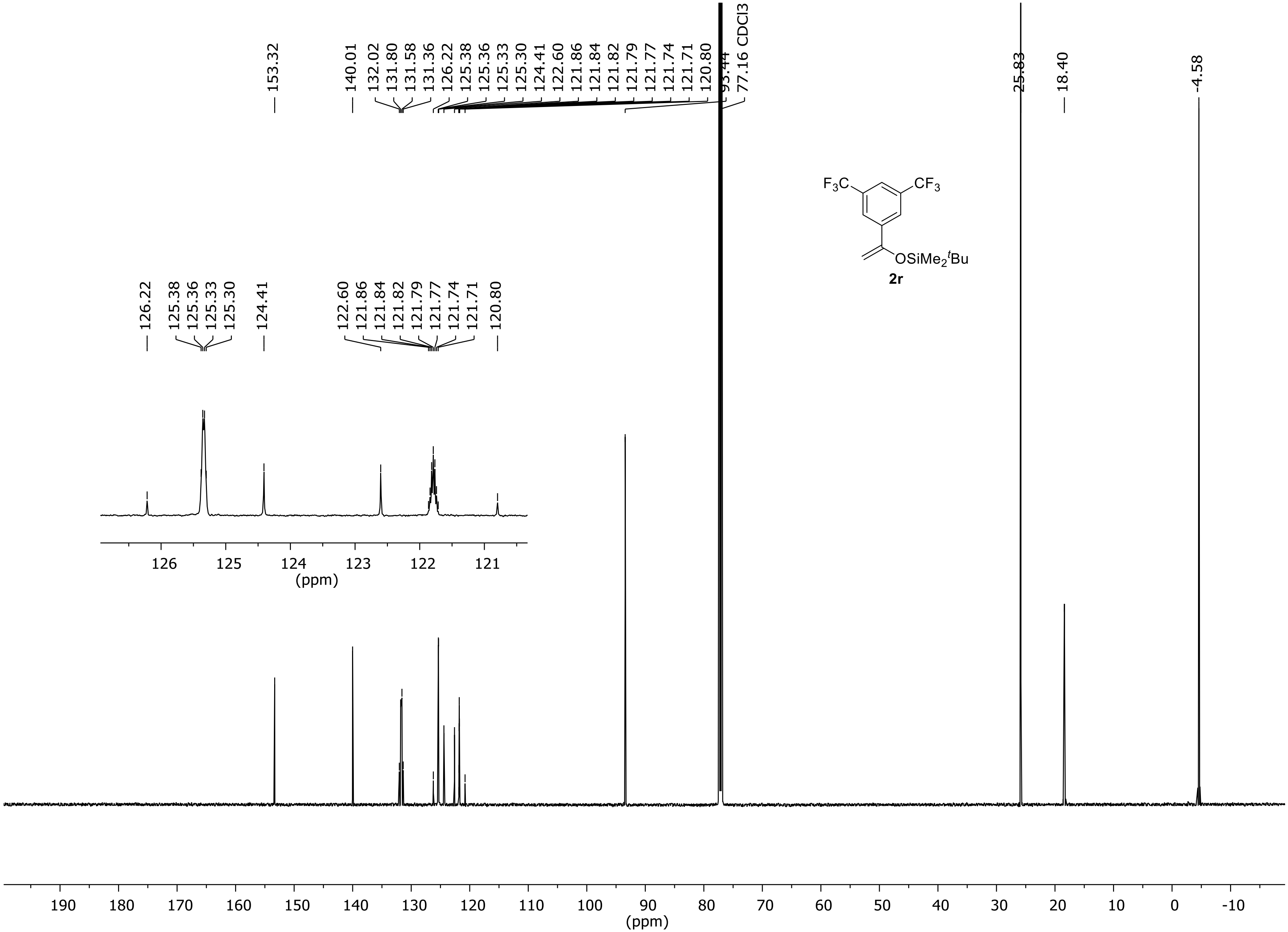
$^{13}C\{^1H\}$ NMR of 2q ($CDCl_3$, 100 MHz)



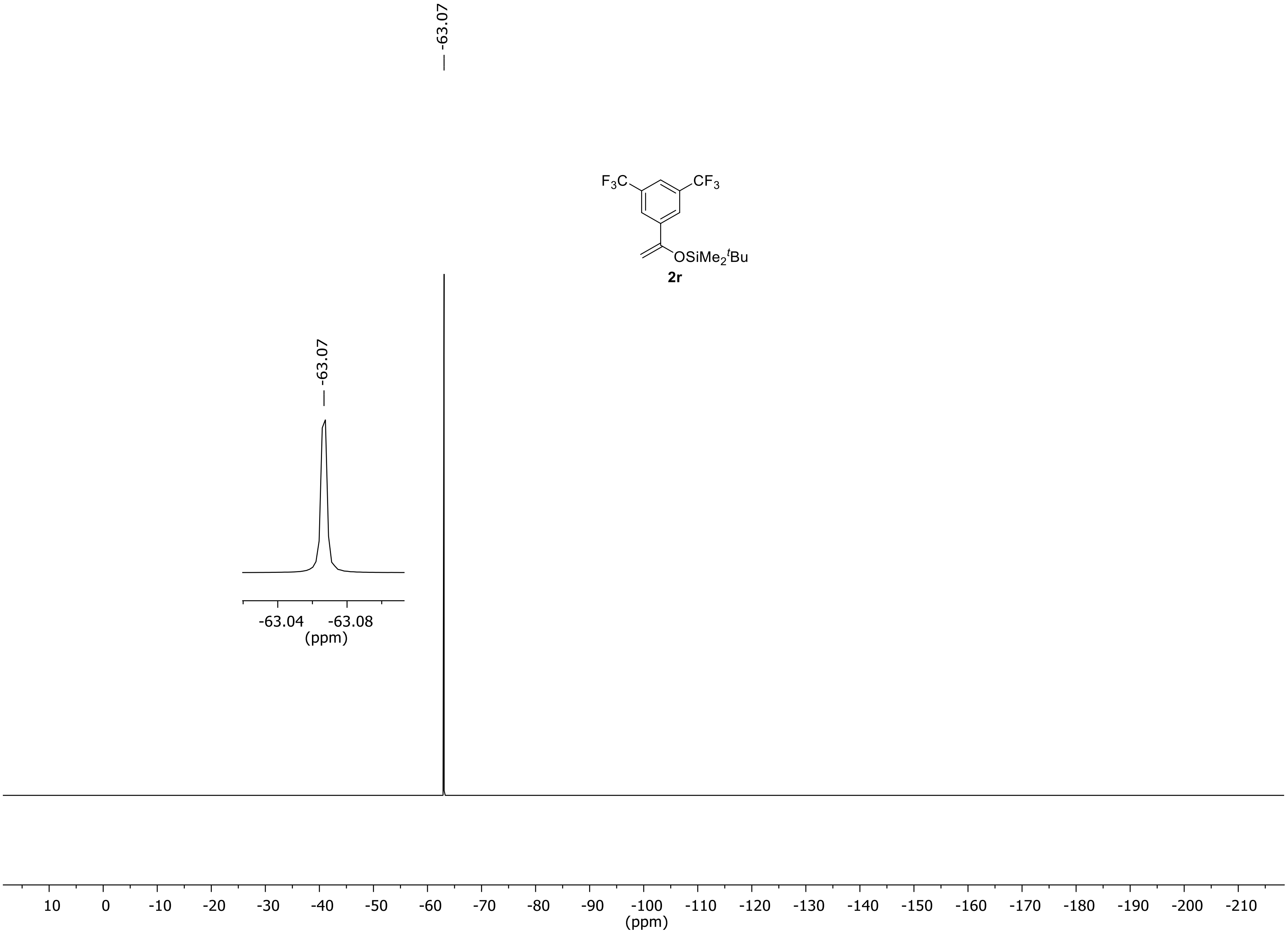
^{1}H NMR of 2r ($CDCl_3$, 600 MHz)



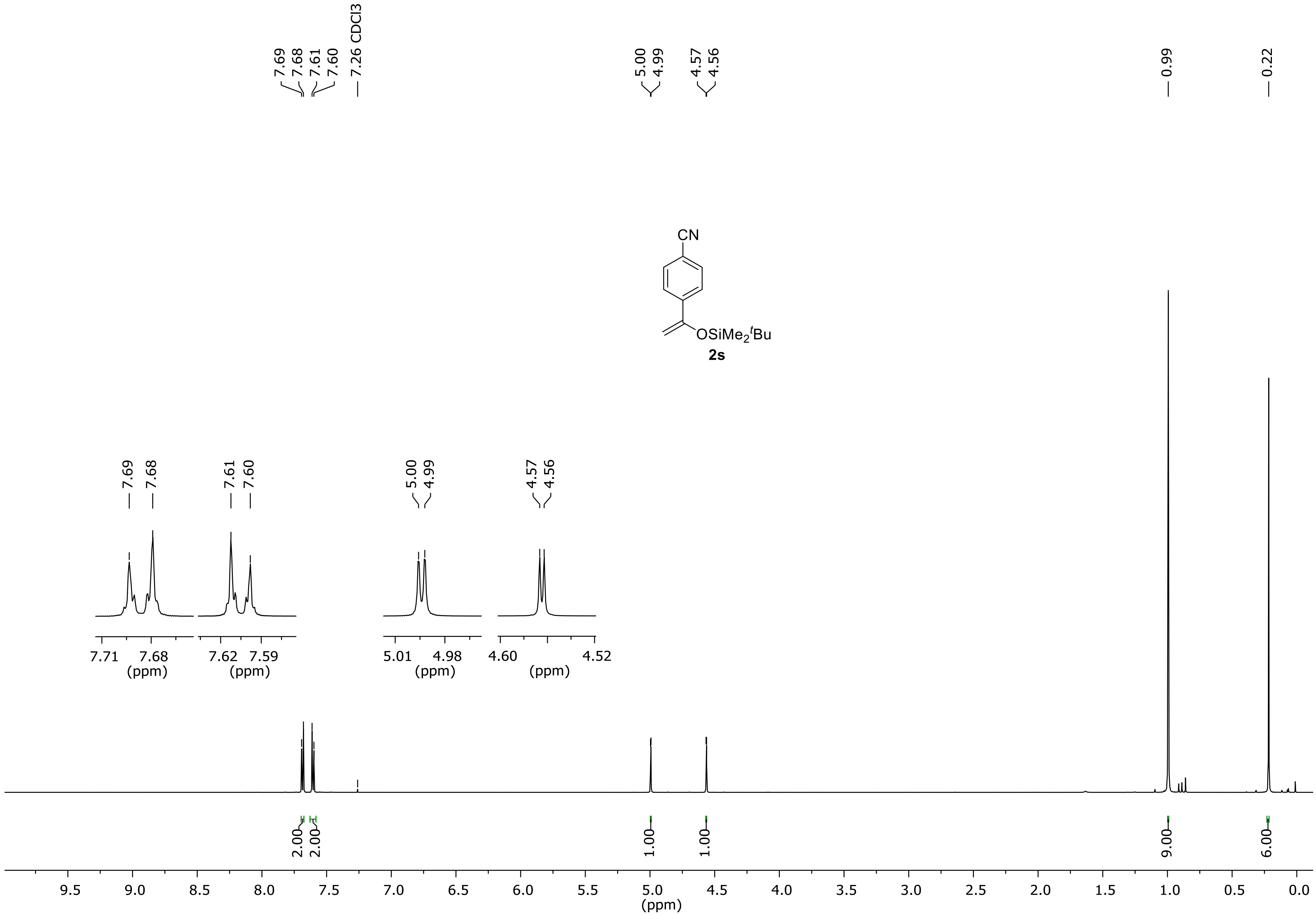
$^{13}C\{^1H\}$ NMR of 2r ($CDCl_3$, 150 MHz)



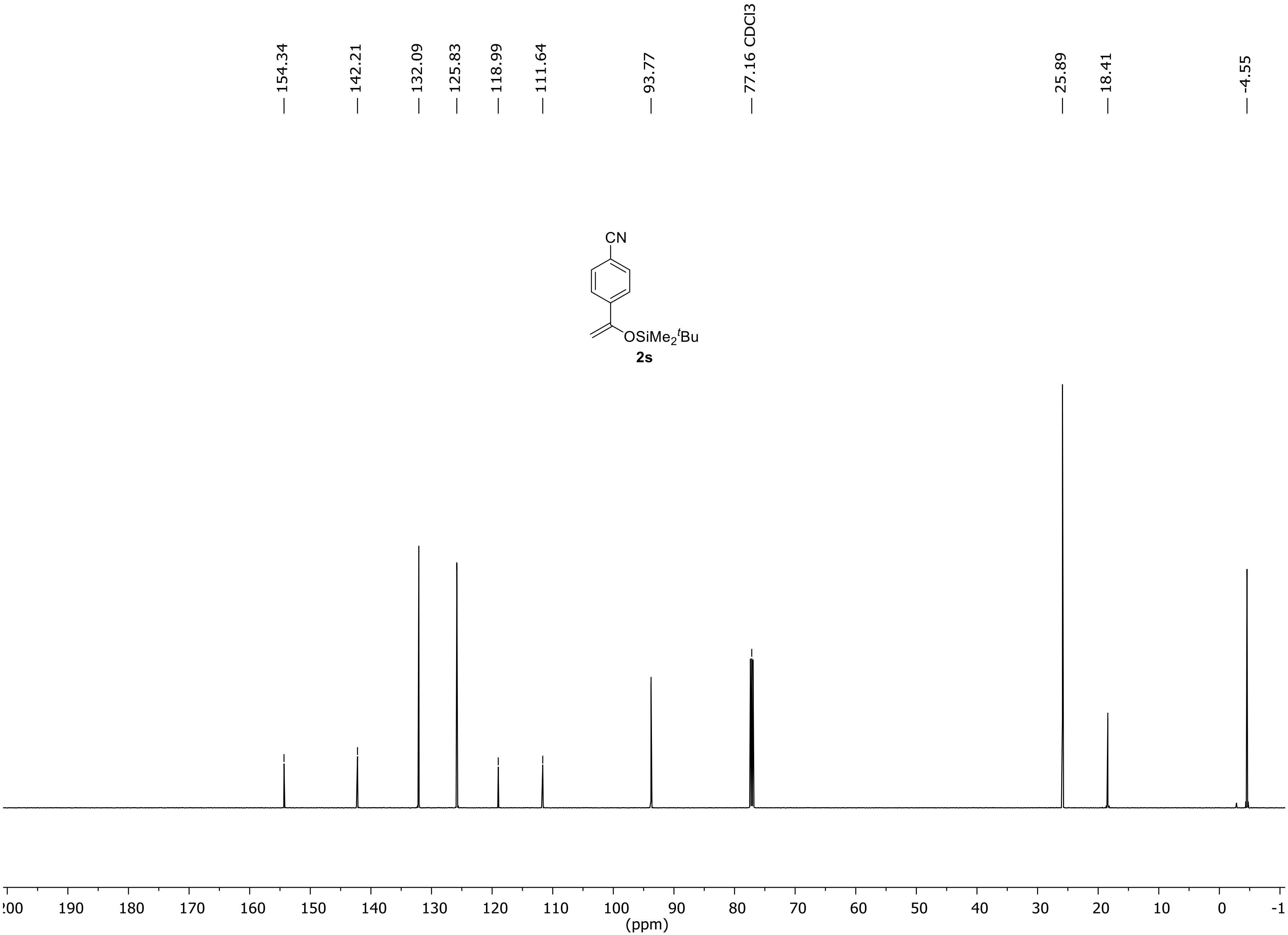
^{19}F{^{1}H} NMR of 2r (CDCl$_3$, 564 MHz)



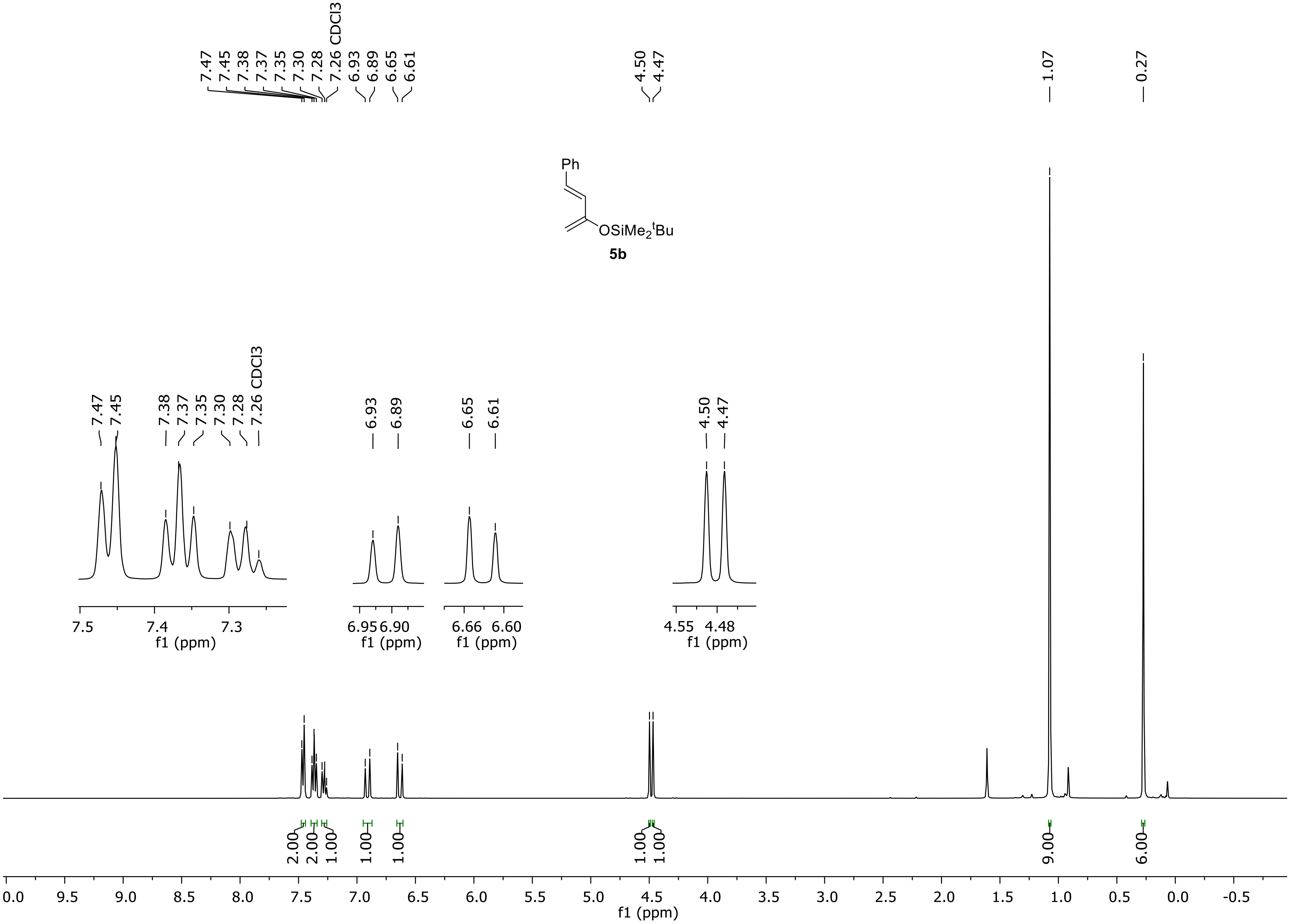
^{1}H NMR of 2s (CDCl$_3$, 600 MHz)



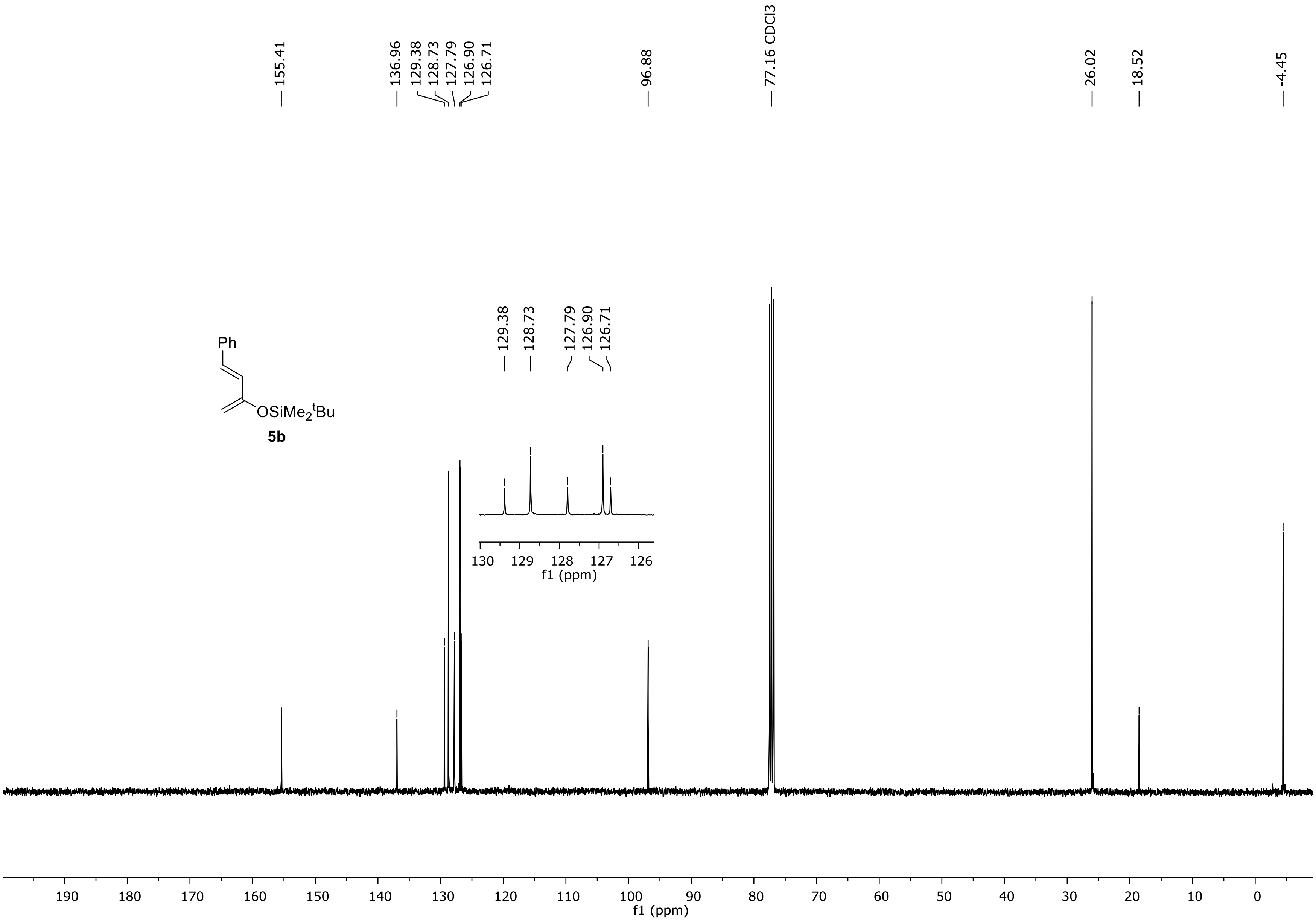
$^{13}C\{^1H\}$ NMR of 2s ($CDCl_3$, 150 MHz)



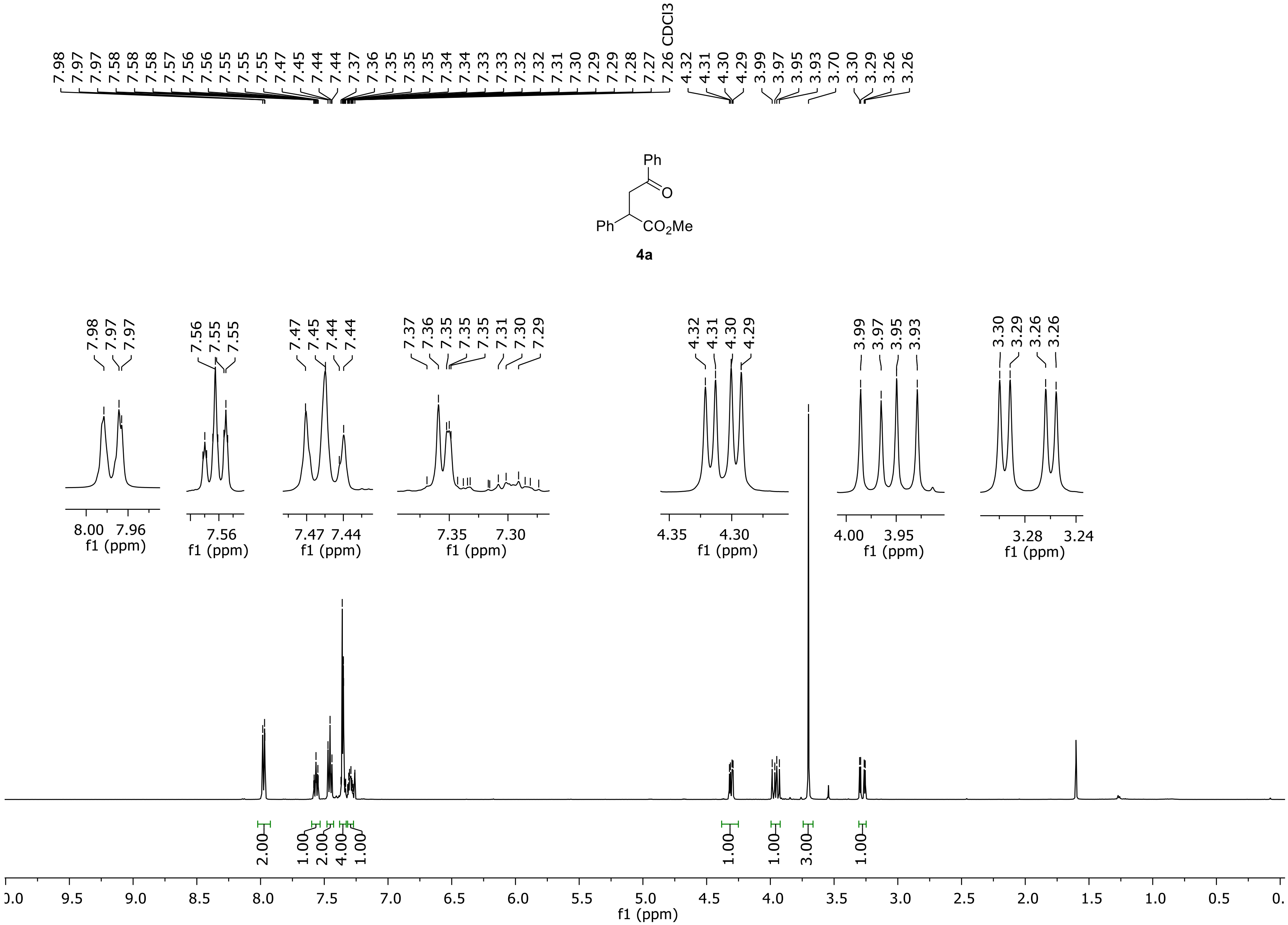
^{1}H NMR of 5b (CDCl$_3$, 400 MHz)



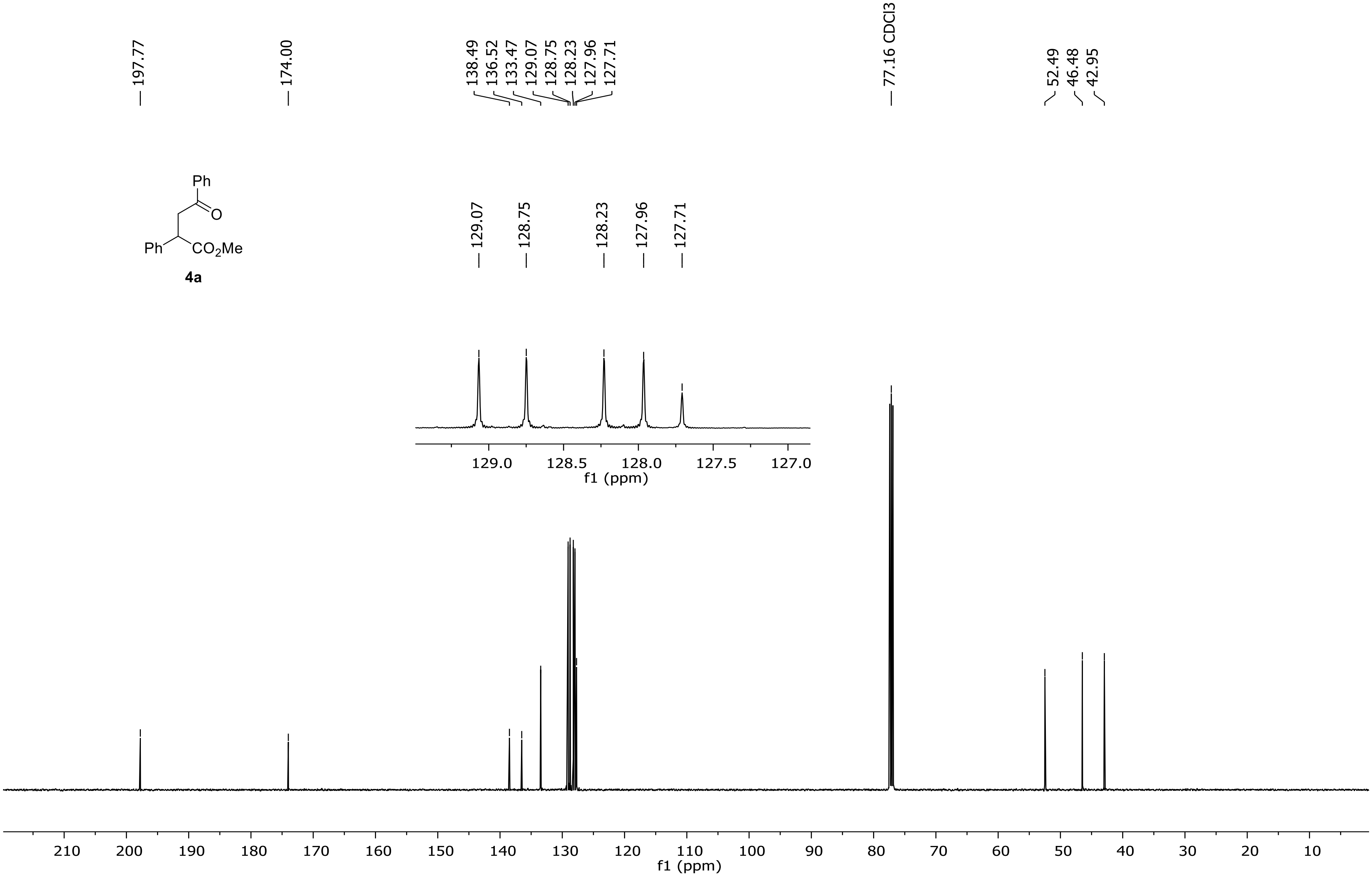
$^{13}C\{^1H\}$ NMR of 5b ($CDCl_3$, 100 MHz)



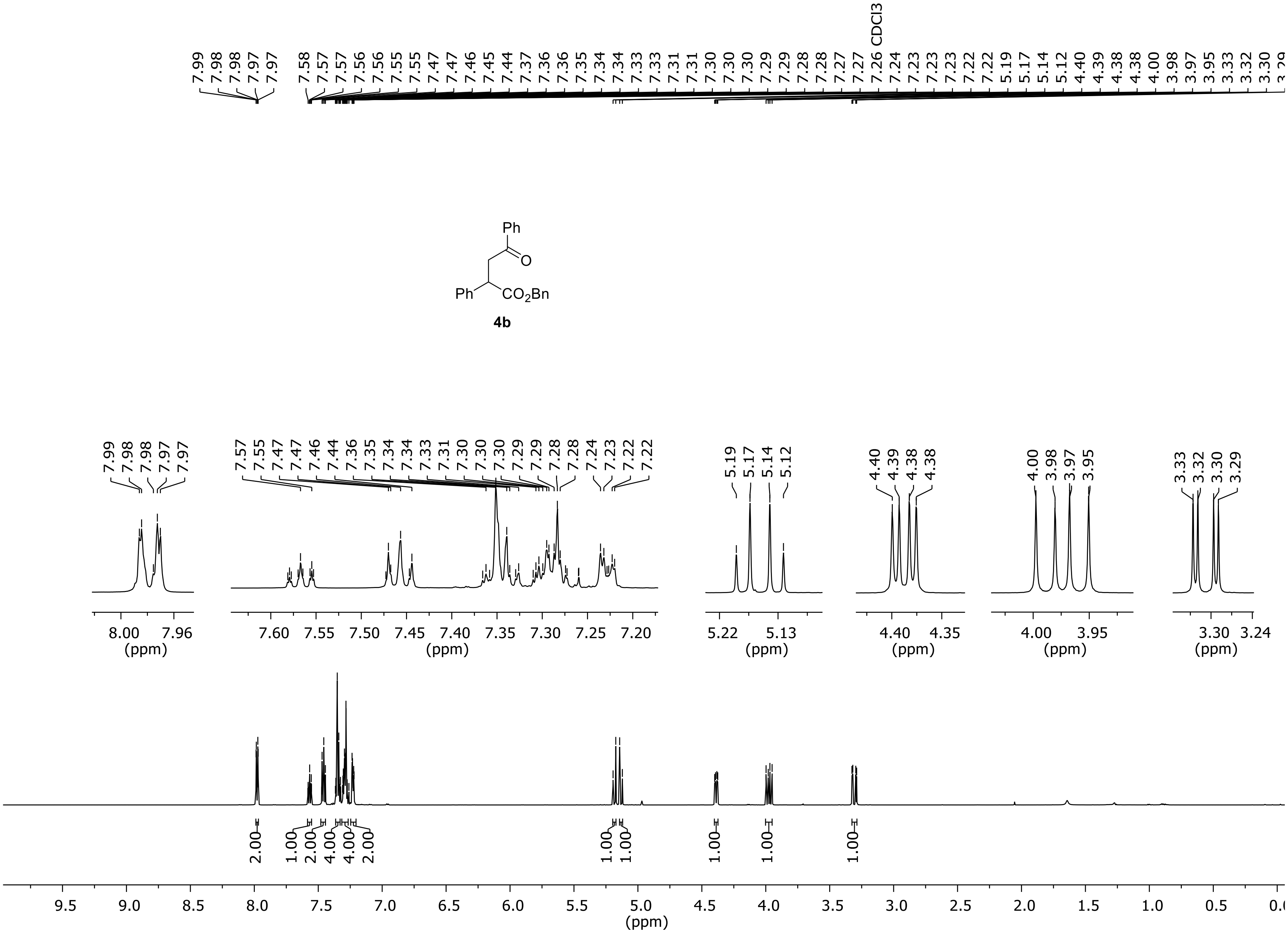
^{1}H NMR of 4a (CDCl$_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 4a ($CDCl_3$, 125 MHz)

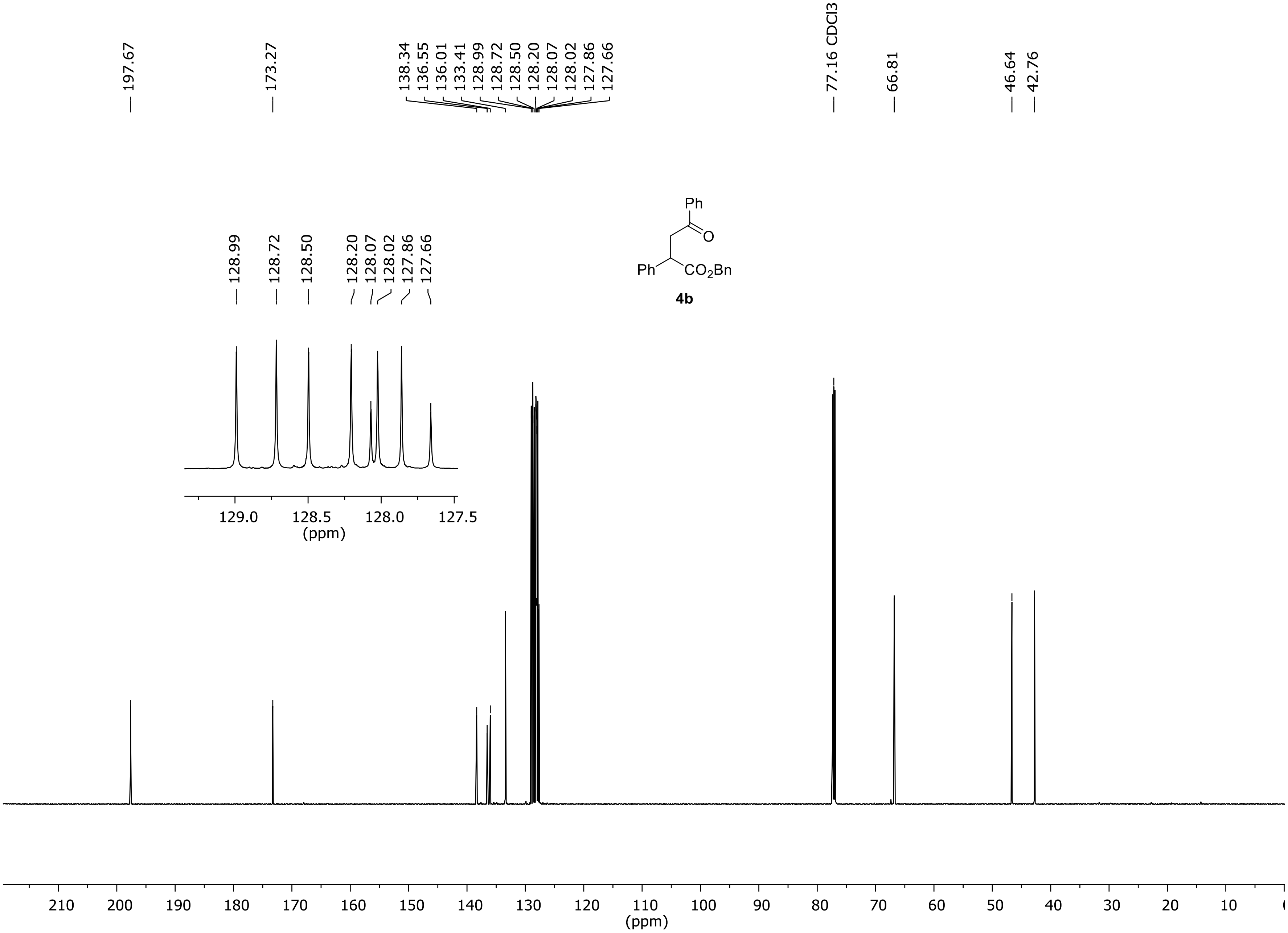

4a

^{1}H NMR of 4b ($CDCl_3$, 600 MHz)

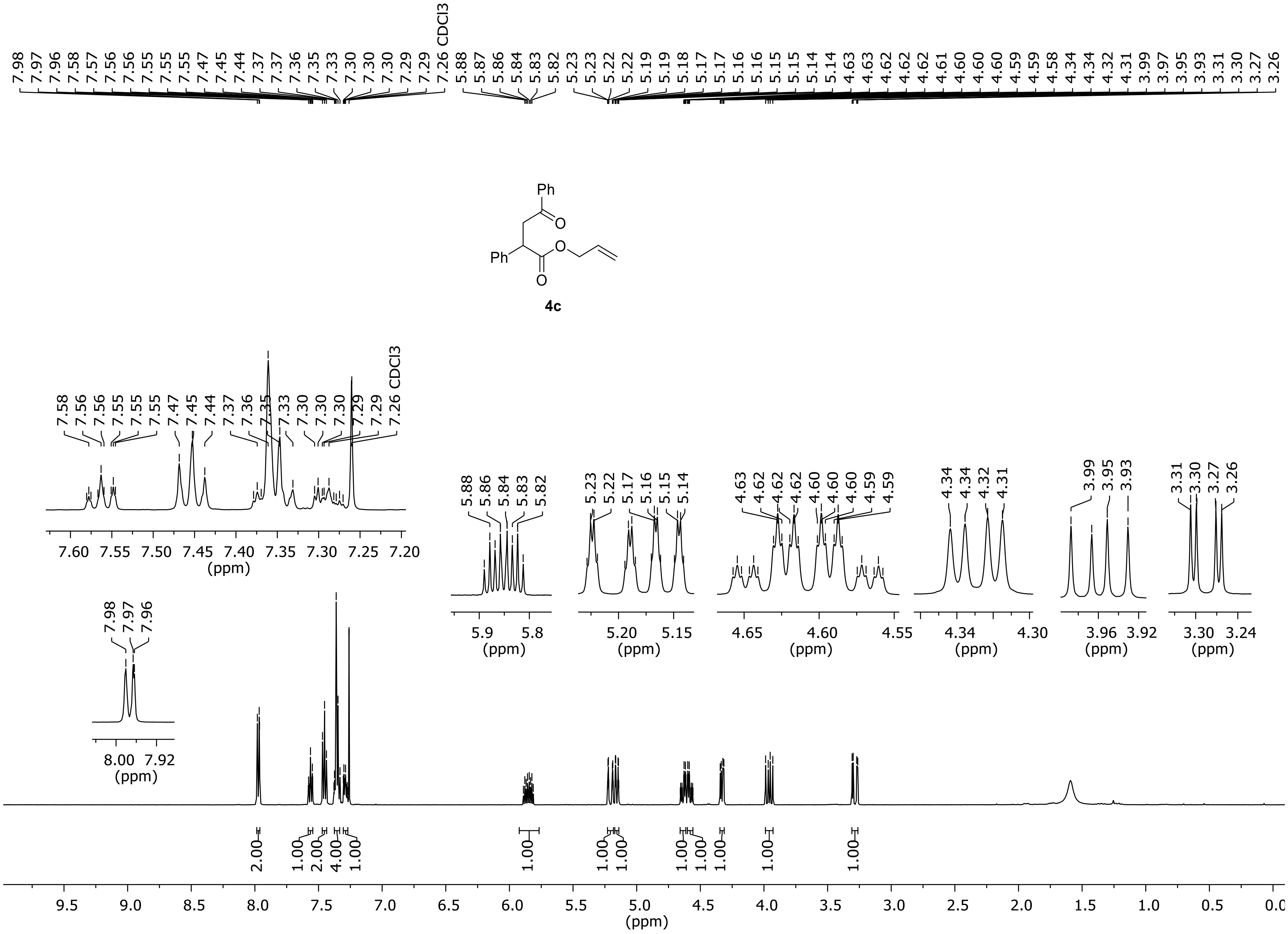


4b

$^{13}C\{^1H\}$ NMR of 4b ($CDCl_3$, 150 MHz)

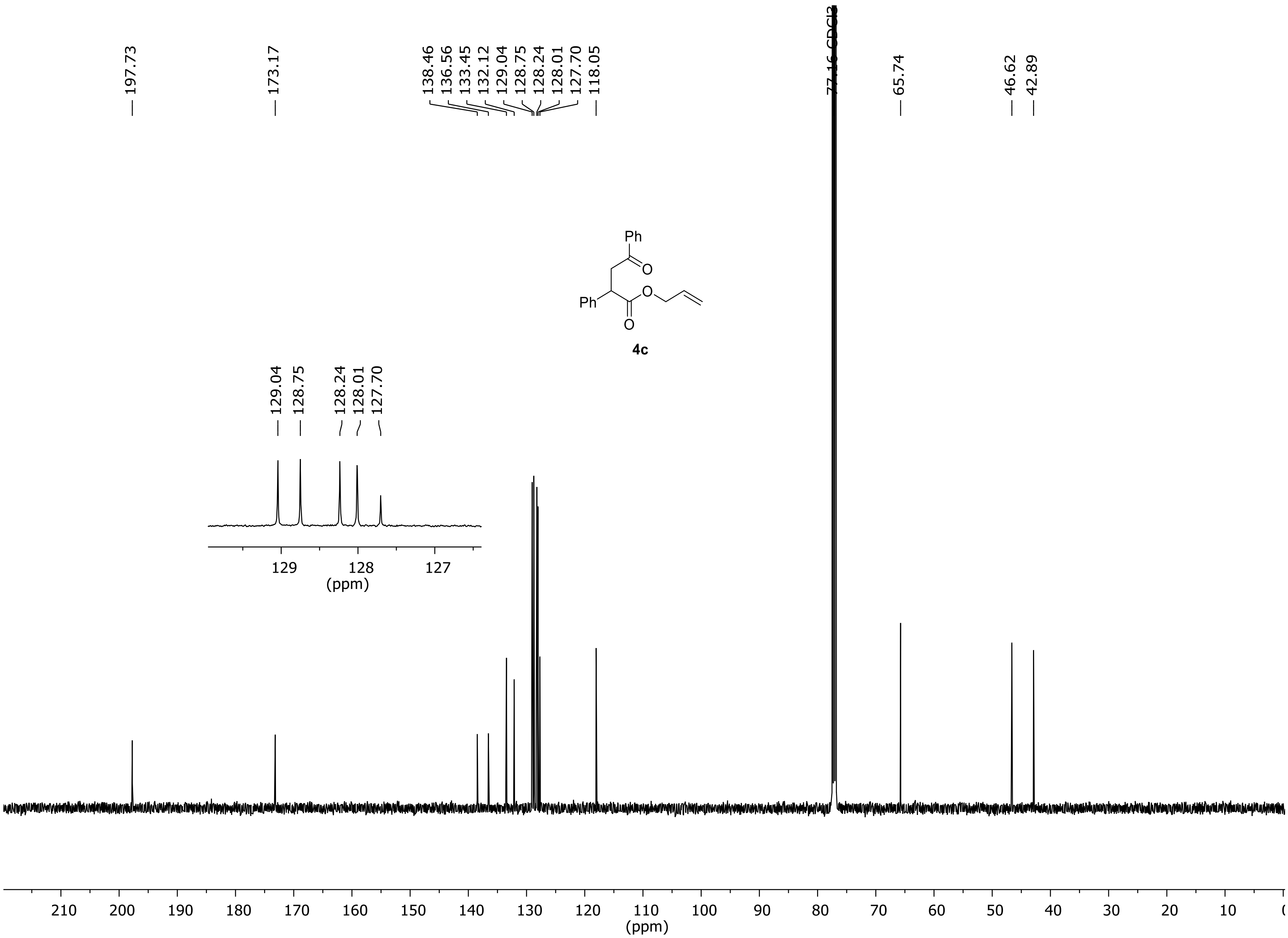


^{1}H NMR of 4c ($CDCl_3$, 500 MHz)

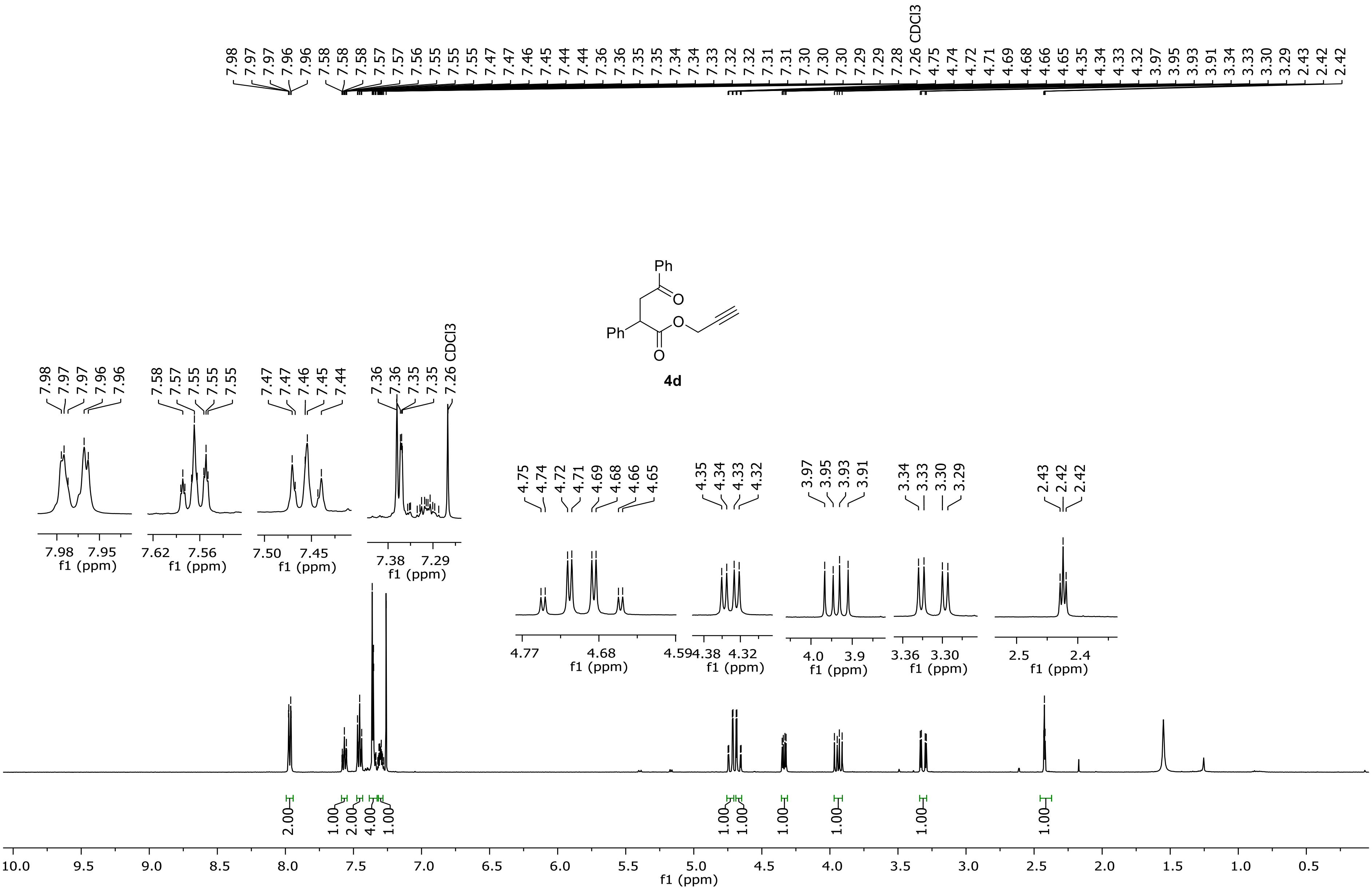


4c

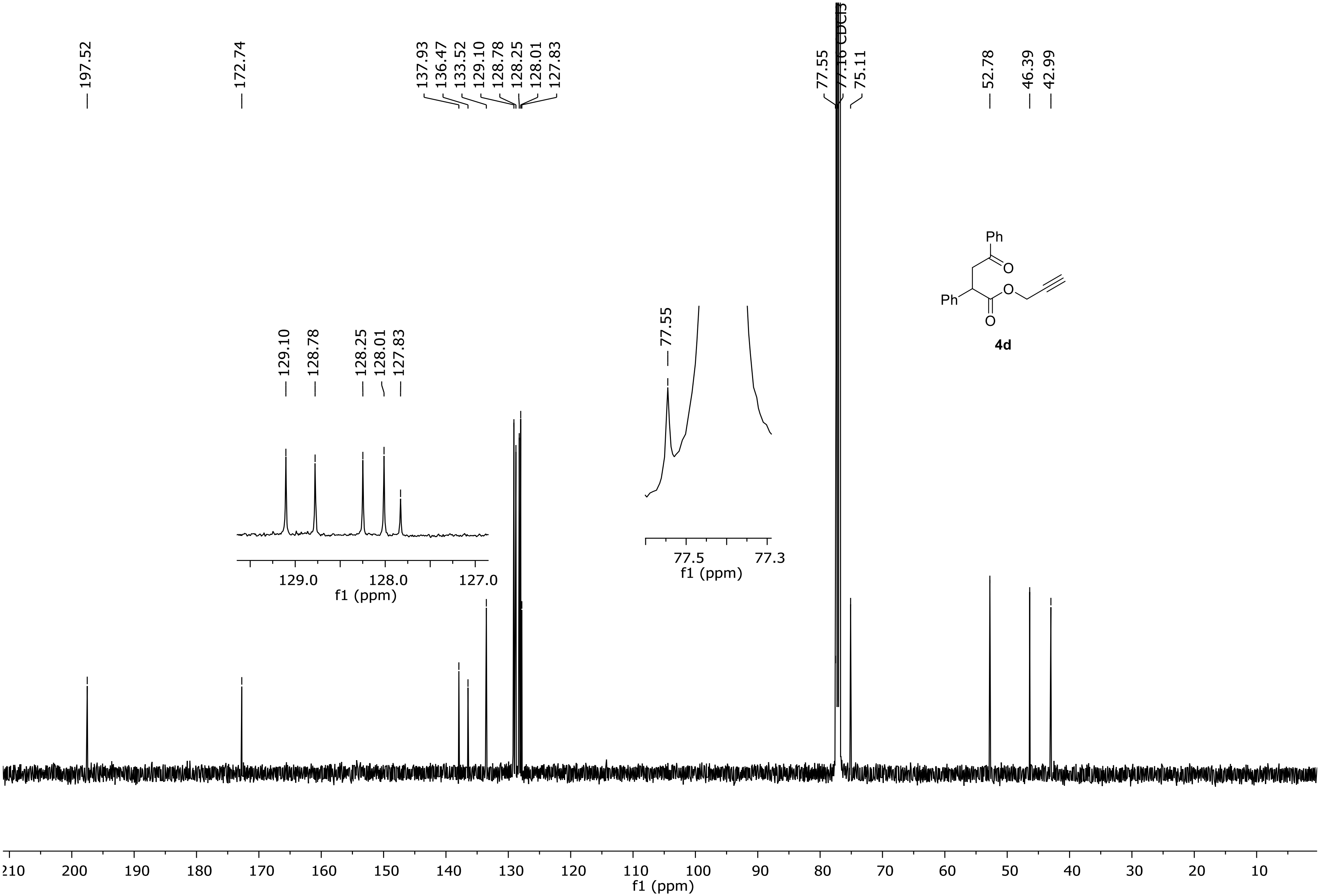
$^{13}C\{^1H\}$ NMR of 4c ($CDCl_3$, 125 MHz)



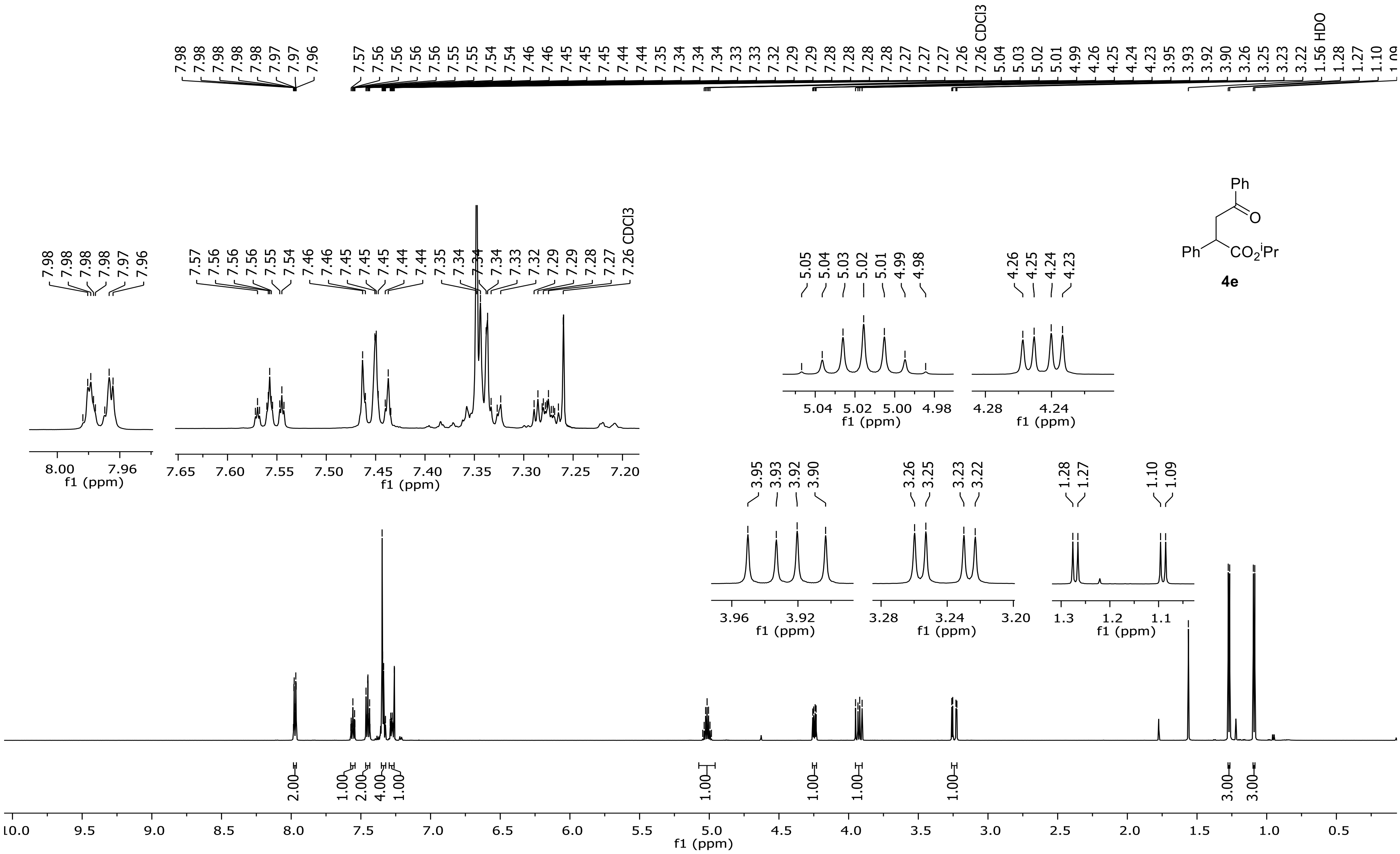
^{1}H NMR of 4d (CDCl$_3$, 500 MHz)


4d

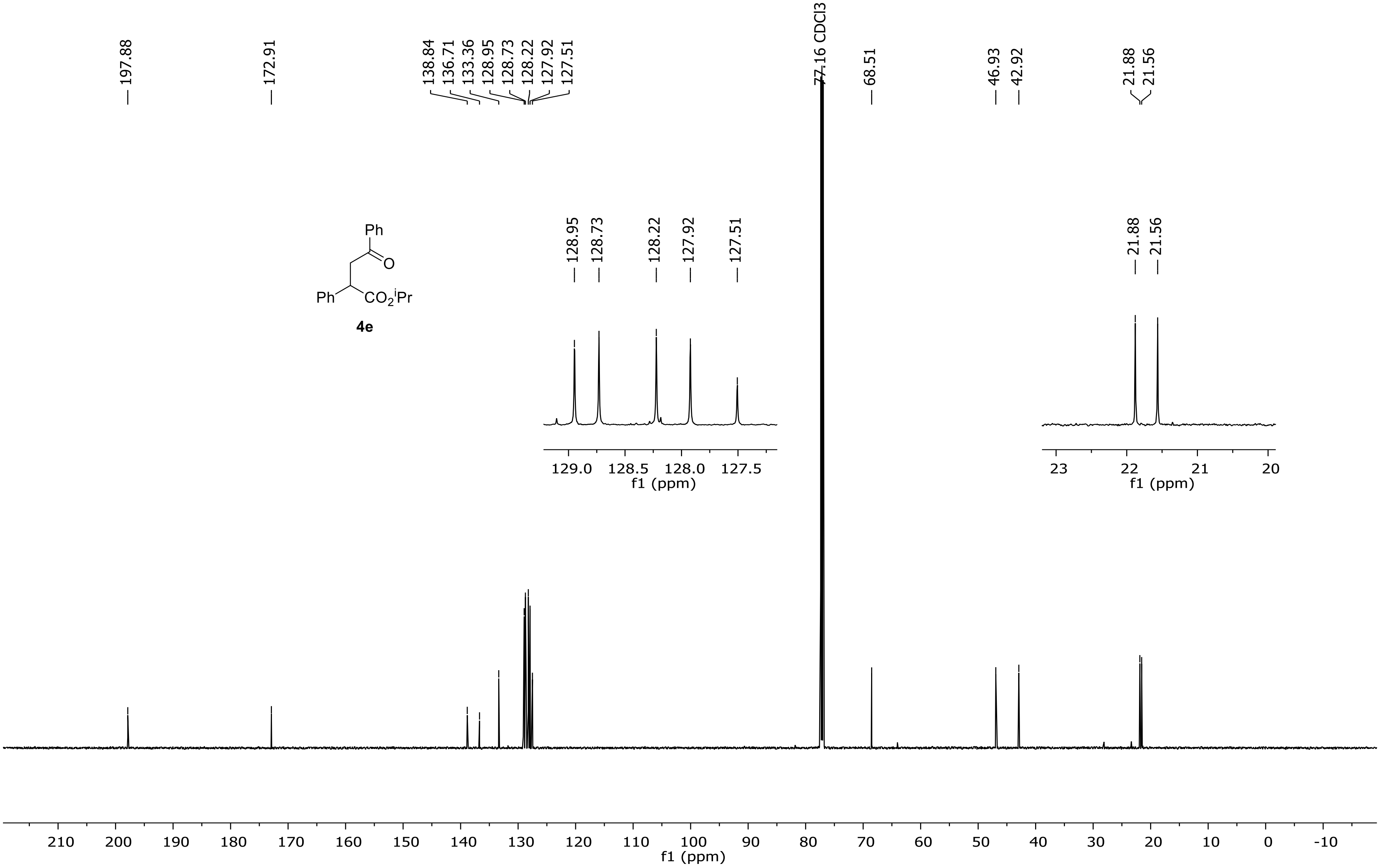
$^{13}C\{^1H\}$ NMR of 4d ($CDCl_3$, 125 MHz)



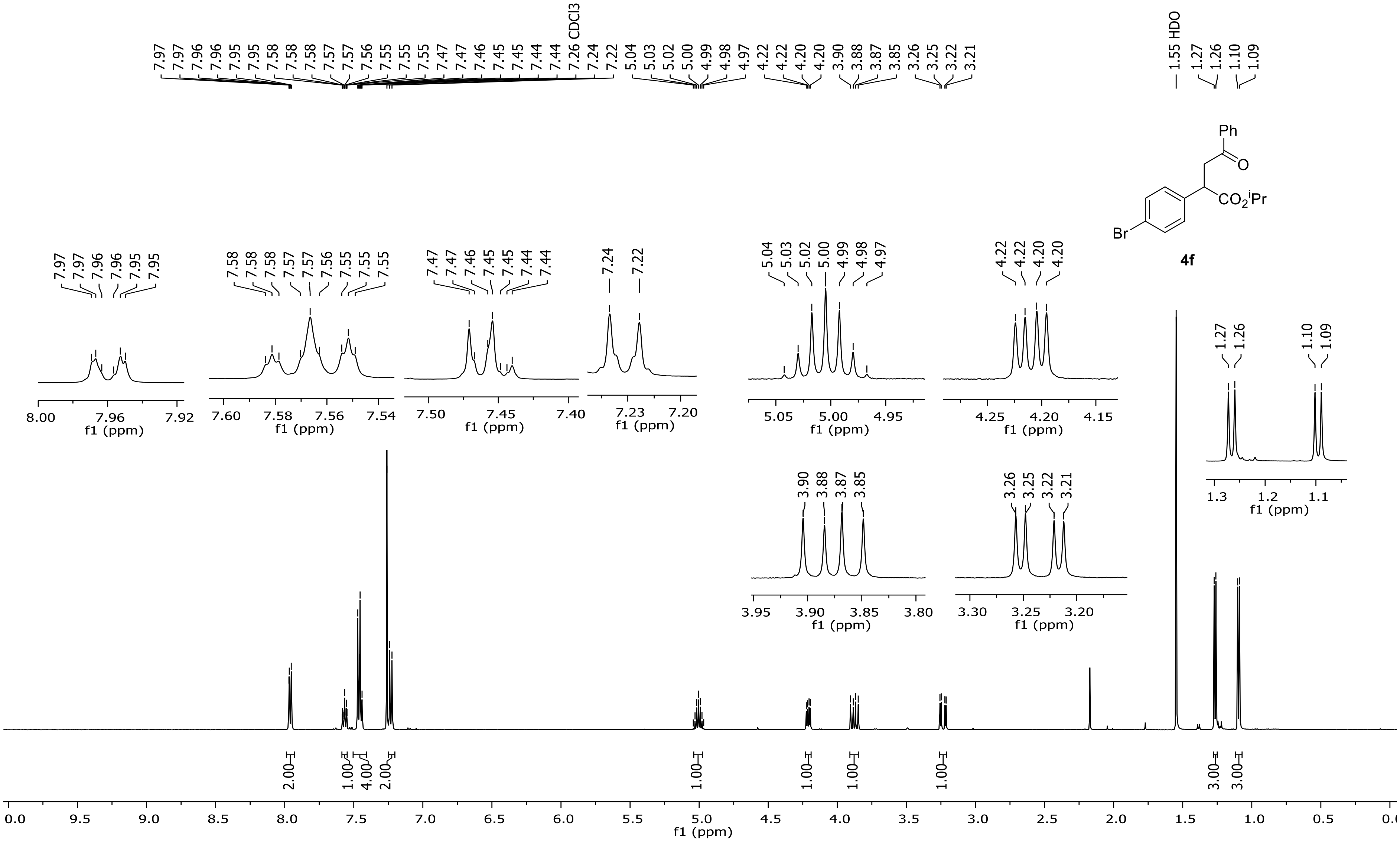
^{1}H NMR of 4e (CDCl$_3$, 600 MHz)



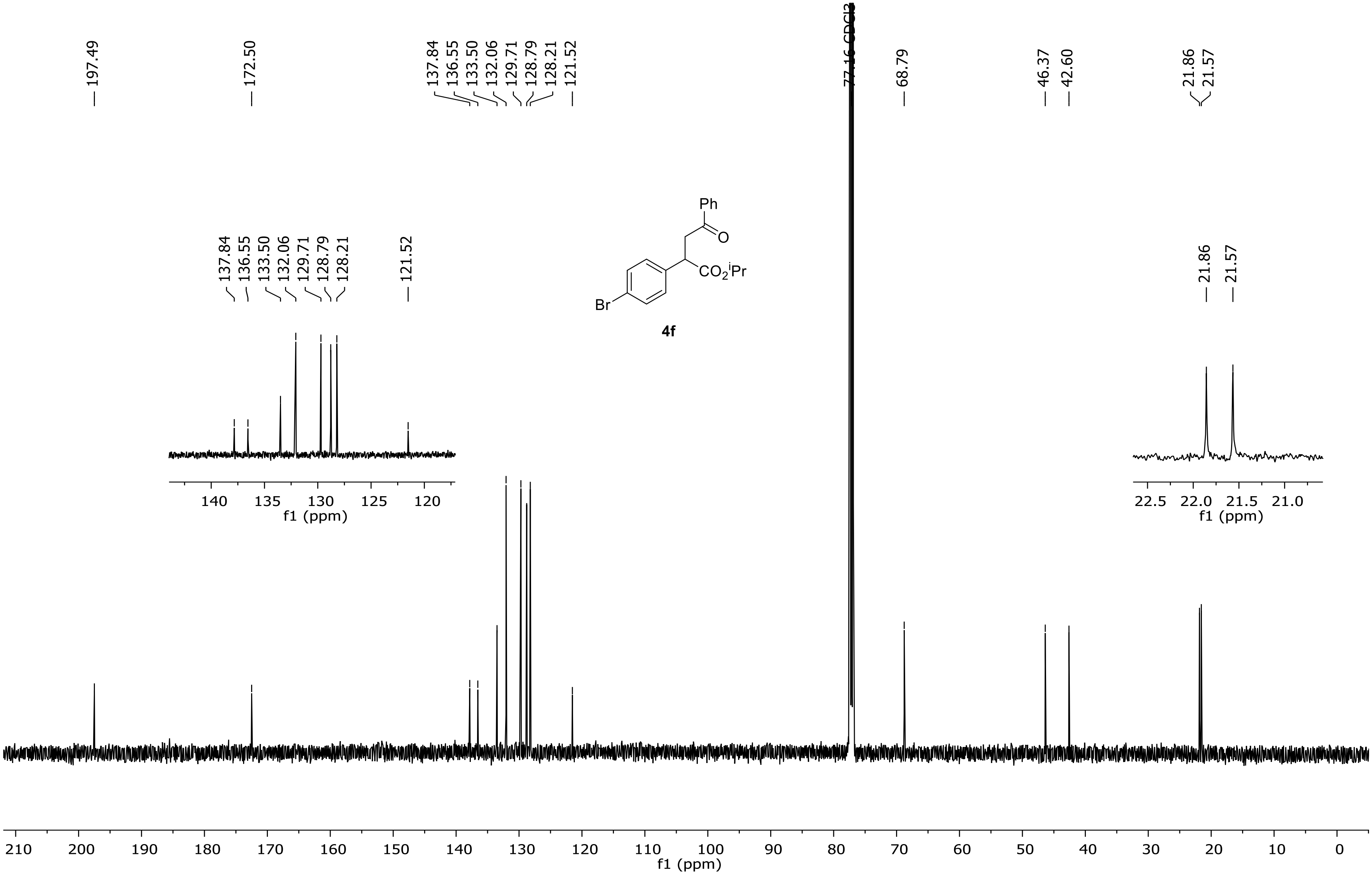
$^{13}C\{^1H\}$ NMR of 4e ($CDCl_3$, 150 MHz)



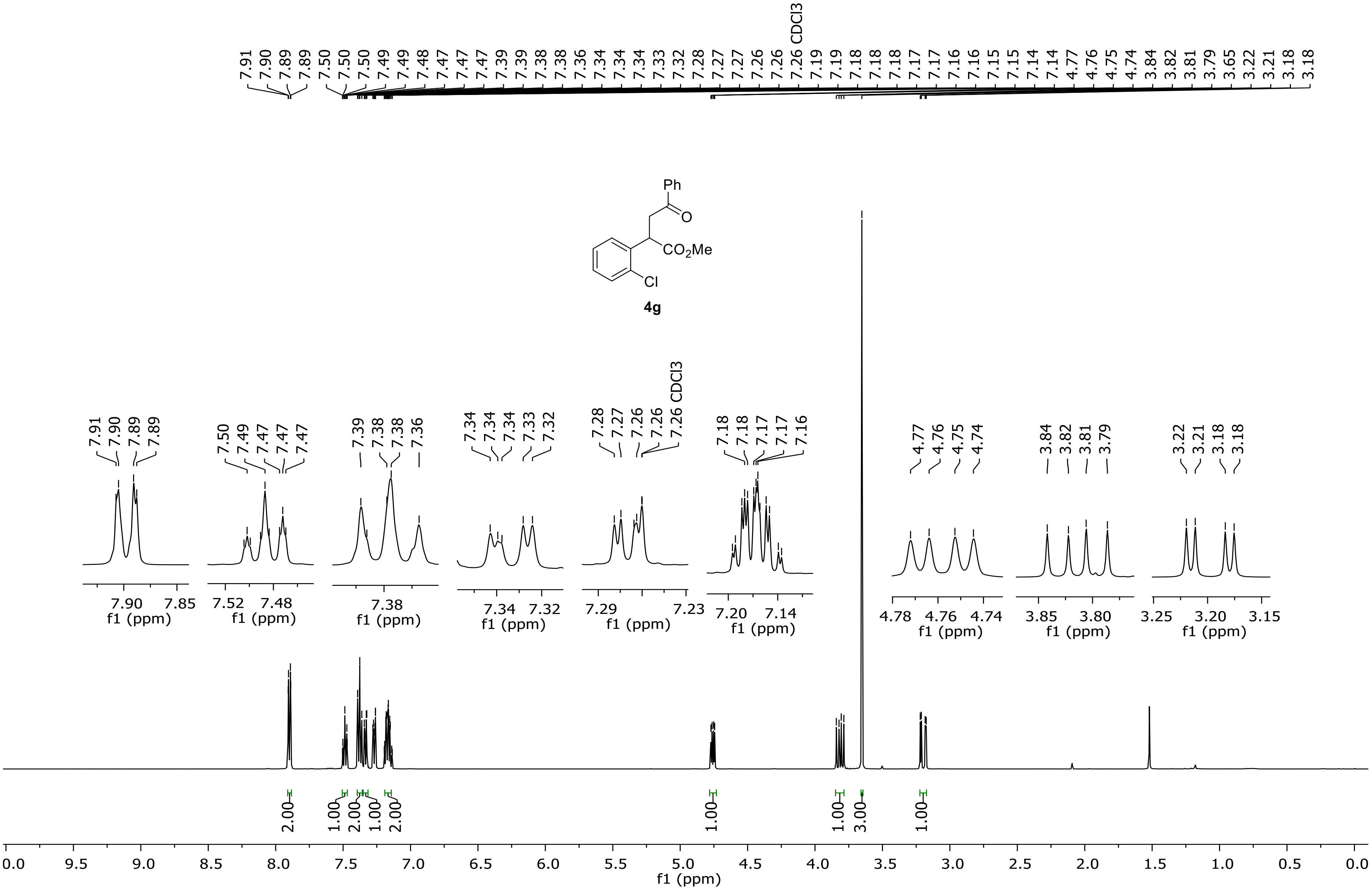
^{1}H NMR of 4f (CDCl$_3$, 500 MHz)



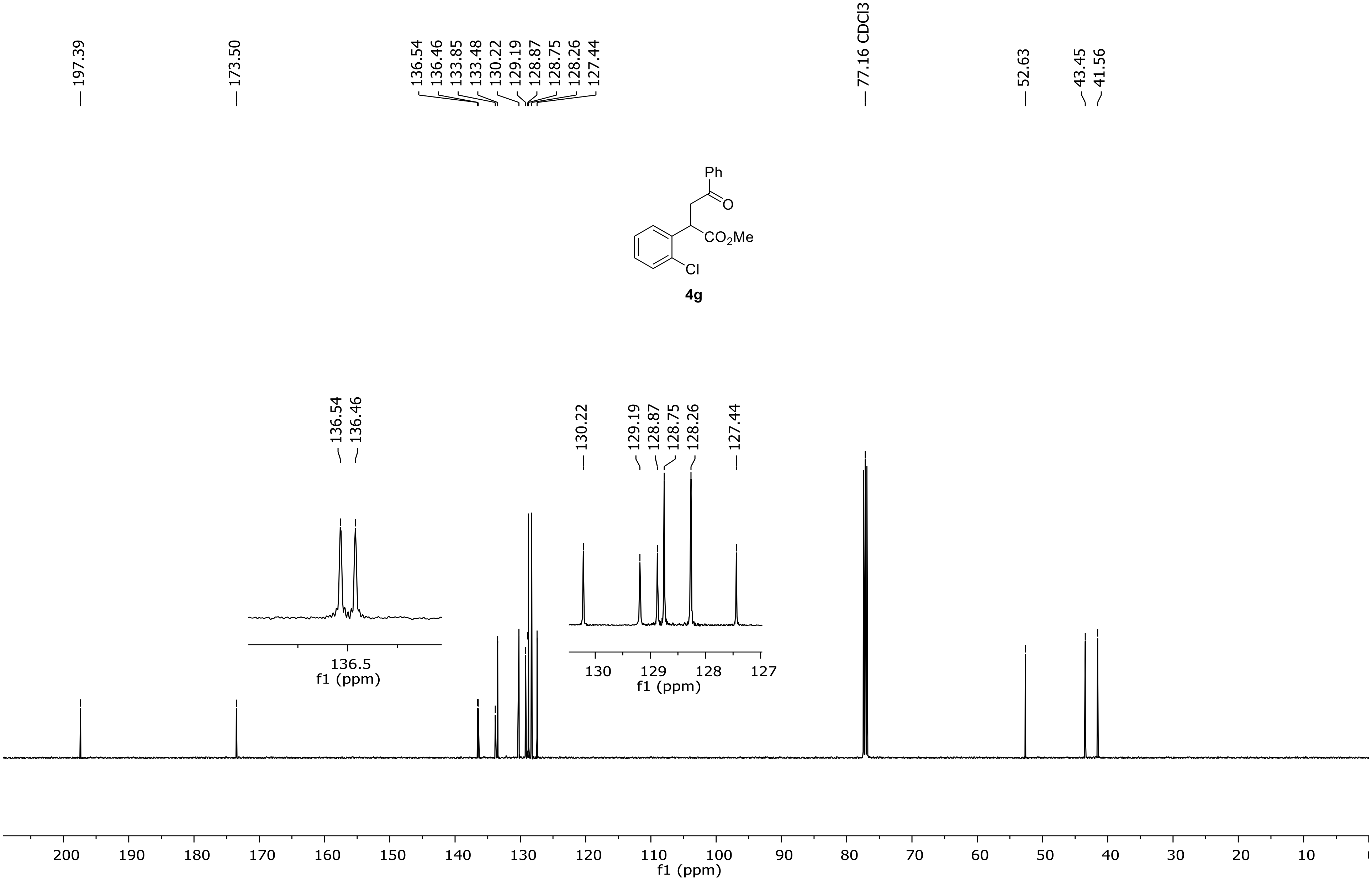
$^{13}C\{^1H\}$ NMR of 4f ($CDCl_3$, 125 MHz)



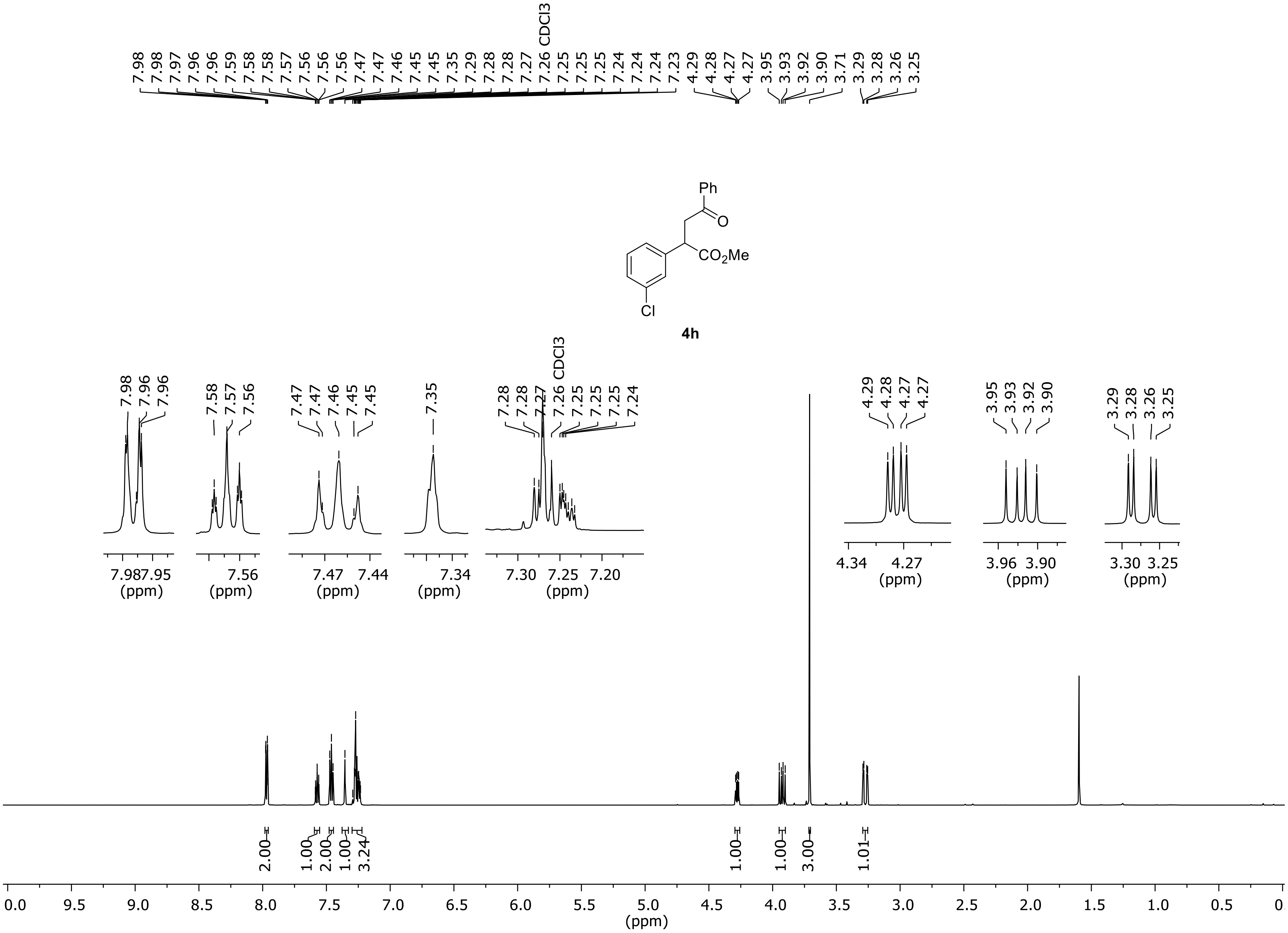
^{1}H NMR of 4g (CDCl$_3$, 500 MHz)



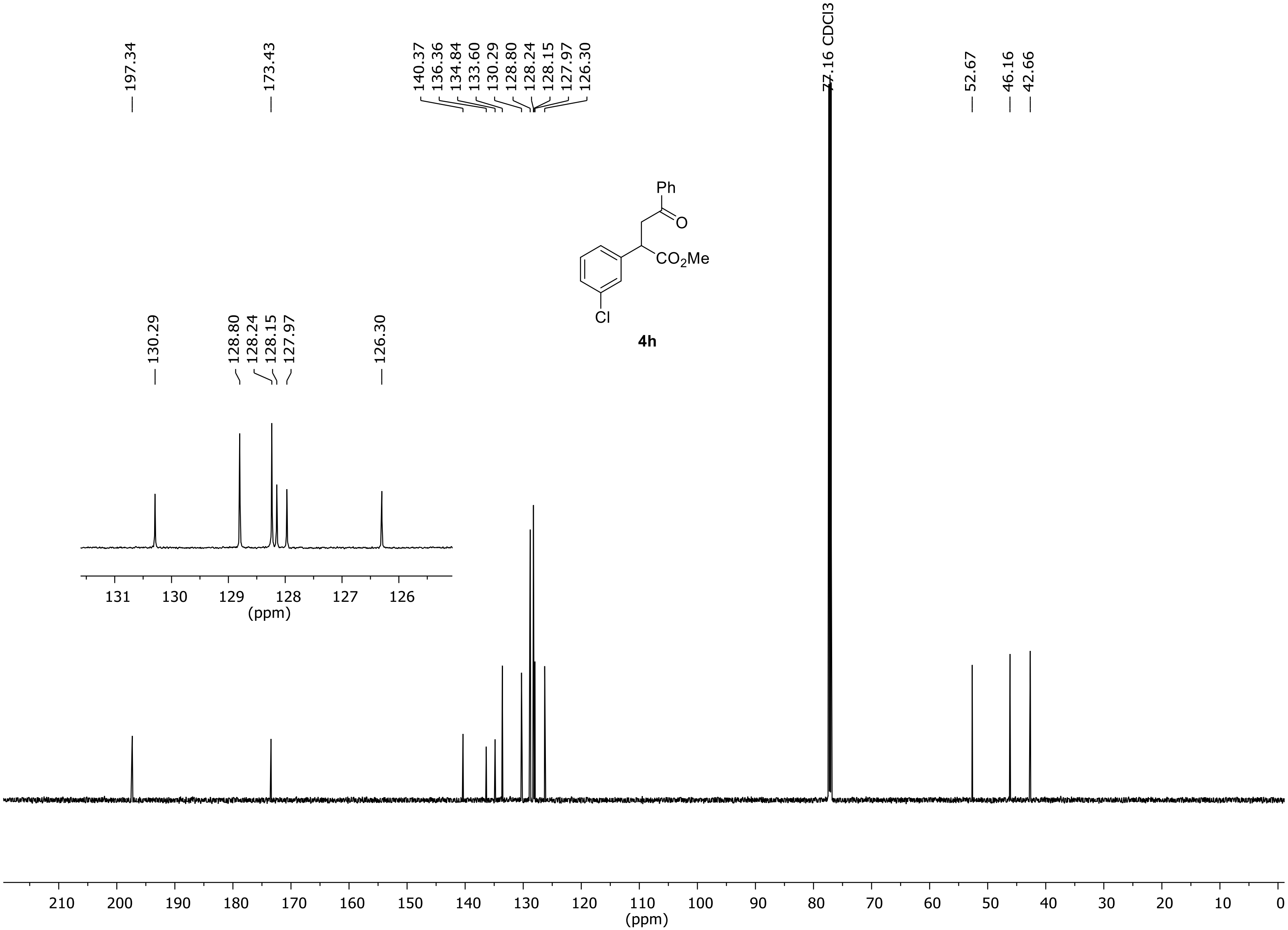
$^{13}C\{^1H\}$ NMR of 4g ($CDCl_3$, 125 MHz)



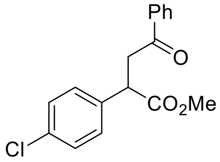
^{1}H NMR of 4h (CDCl$_3$, 600 MHz)


4h

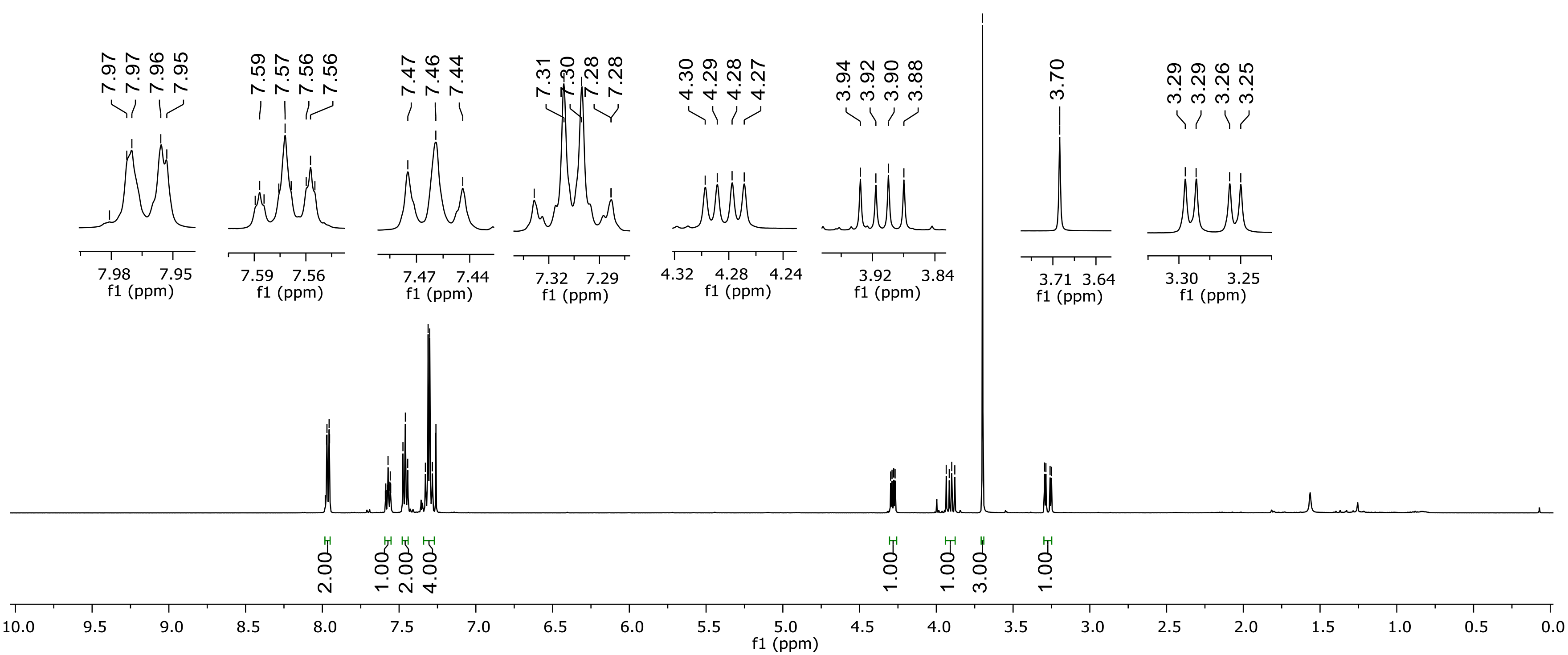
$^{13}C\{^1H\}$ NMR of 4h ($CDCl_3$, 150 MHz)



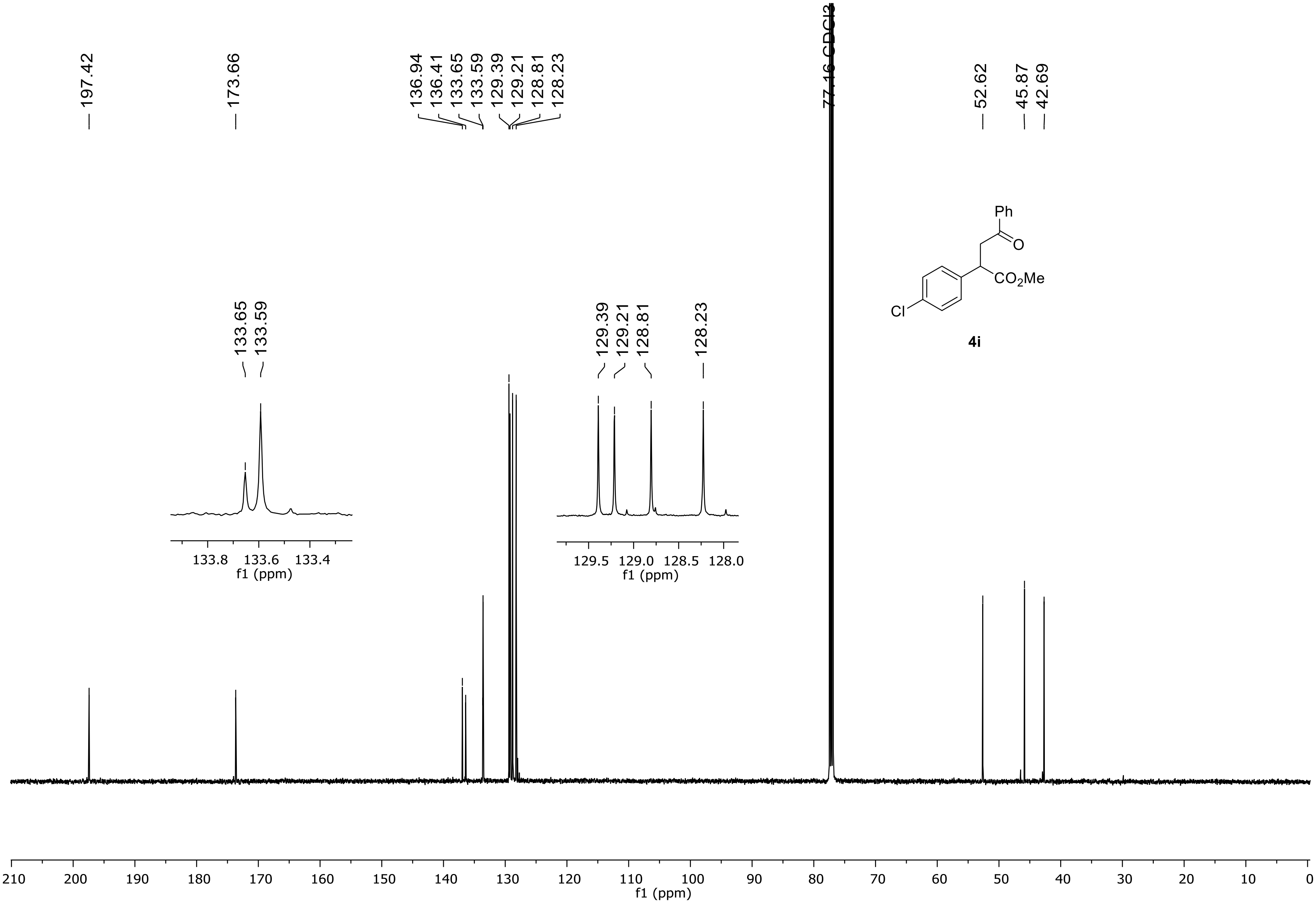
^{1}H NMR of 4i (CDCl$_3$, 500 MHz)



4i

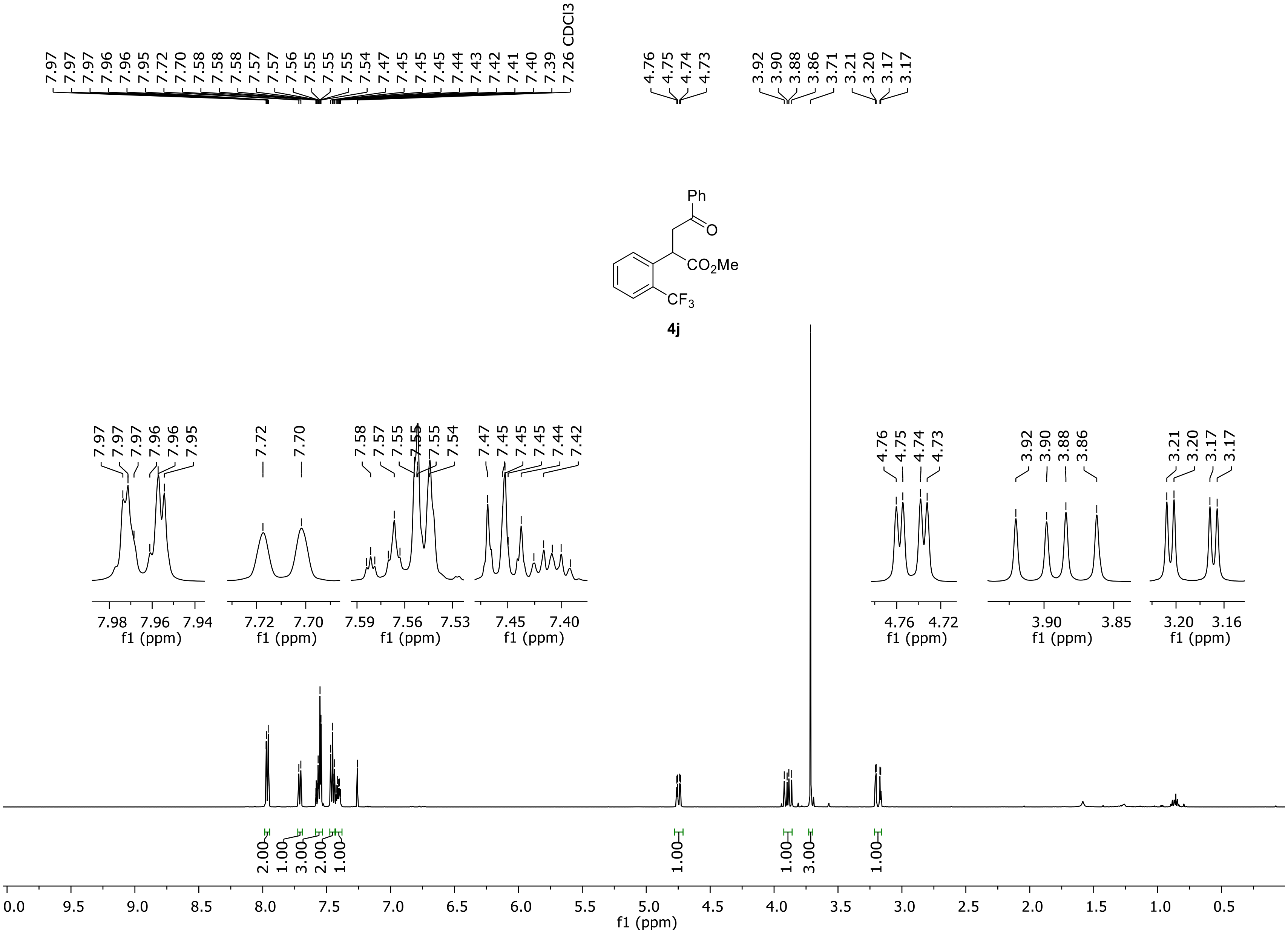


$^{13}C\{^1H\}$ NMR of 4i ($CDCl_3$, 125 MHz)

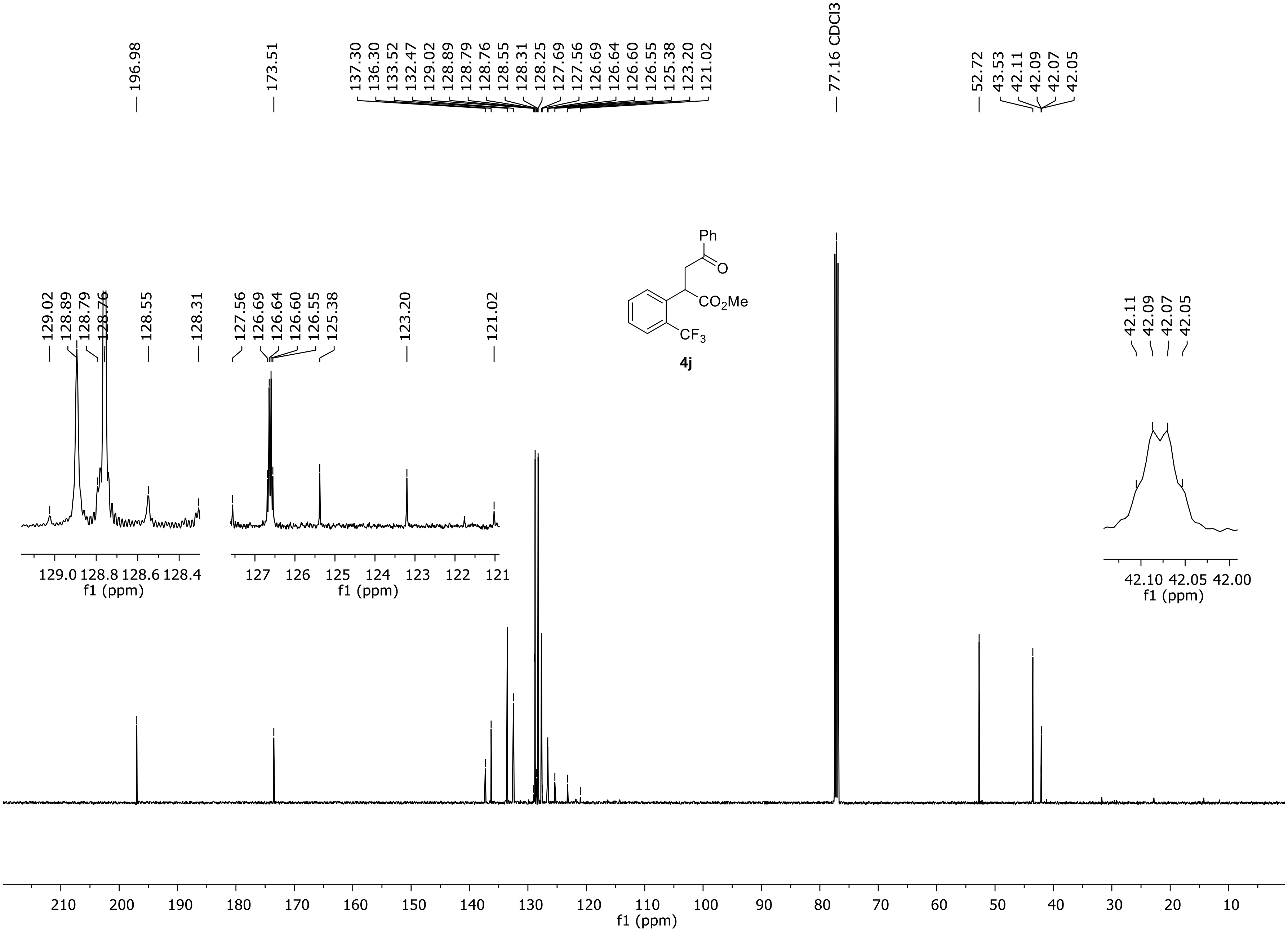


4i

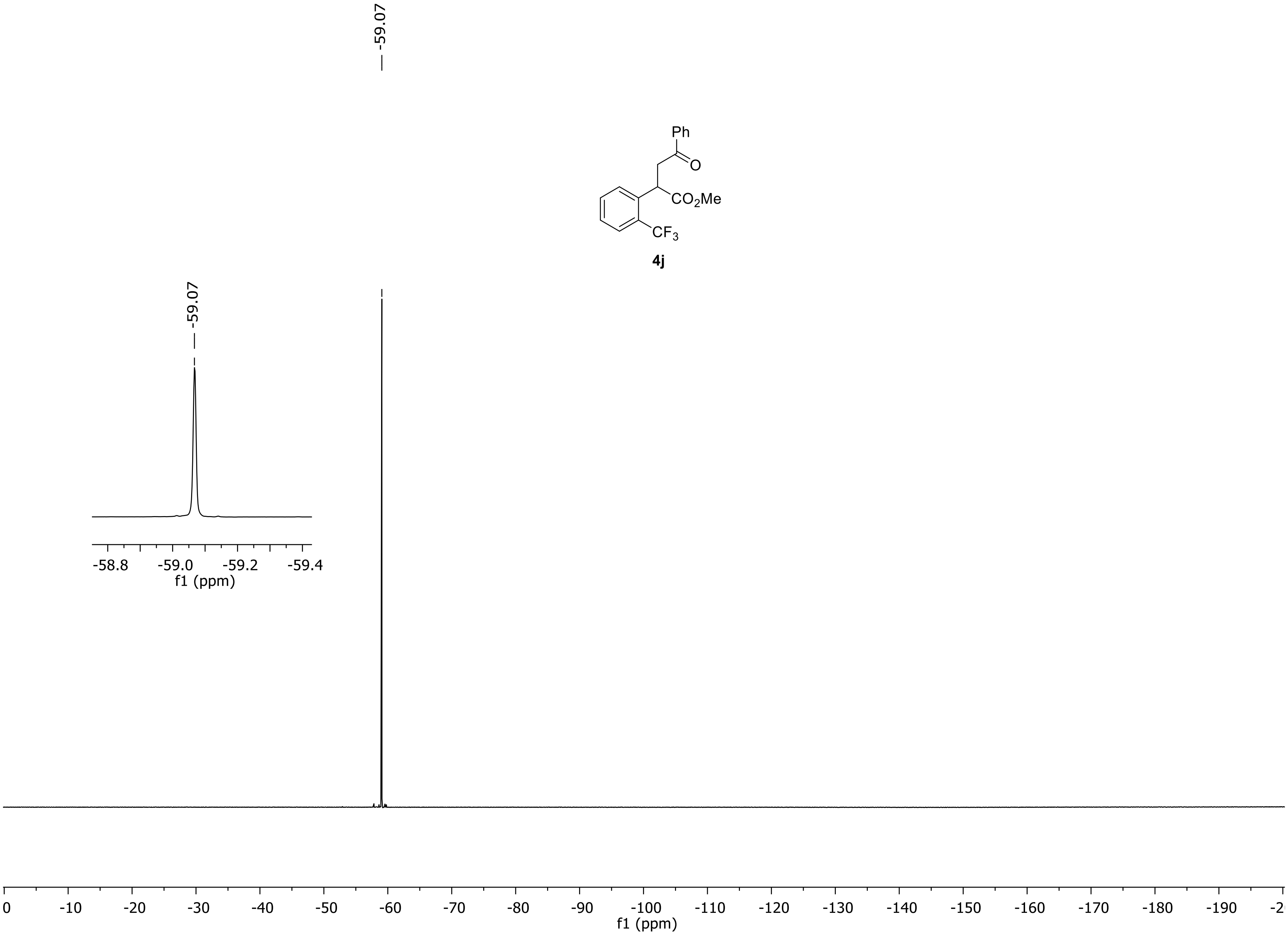
^{1}H NMR of 4j (CDCl$_3$, 500 MHz)



$^{13}C\{^{1}H\}$ NMR of 4j ($CDCl_3$, 125 MHz)

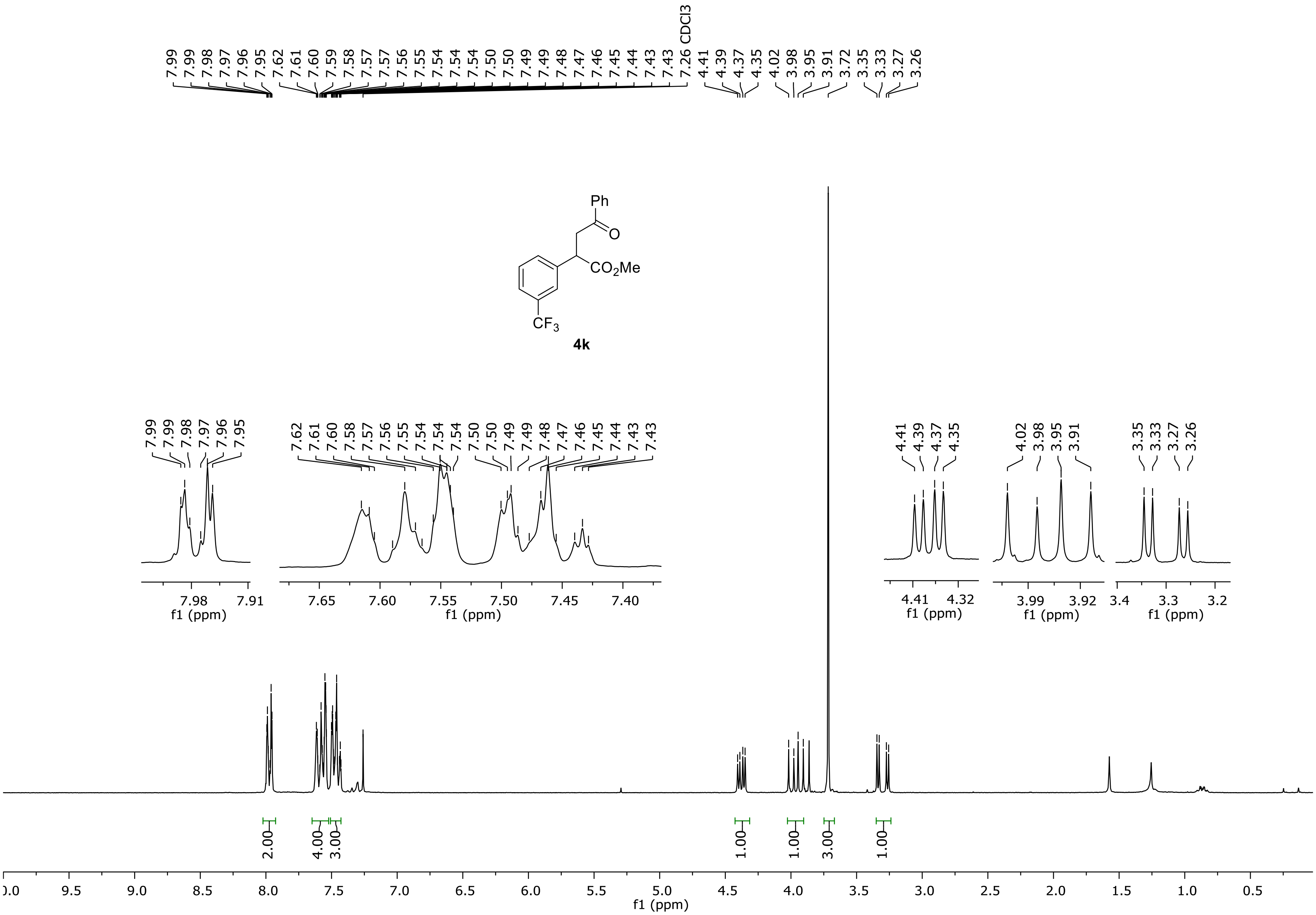


$^{19}F\{^1H\}$ NMR of 4j ($CDCl_3$, 470 MHz)

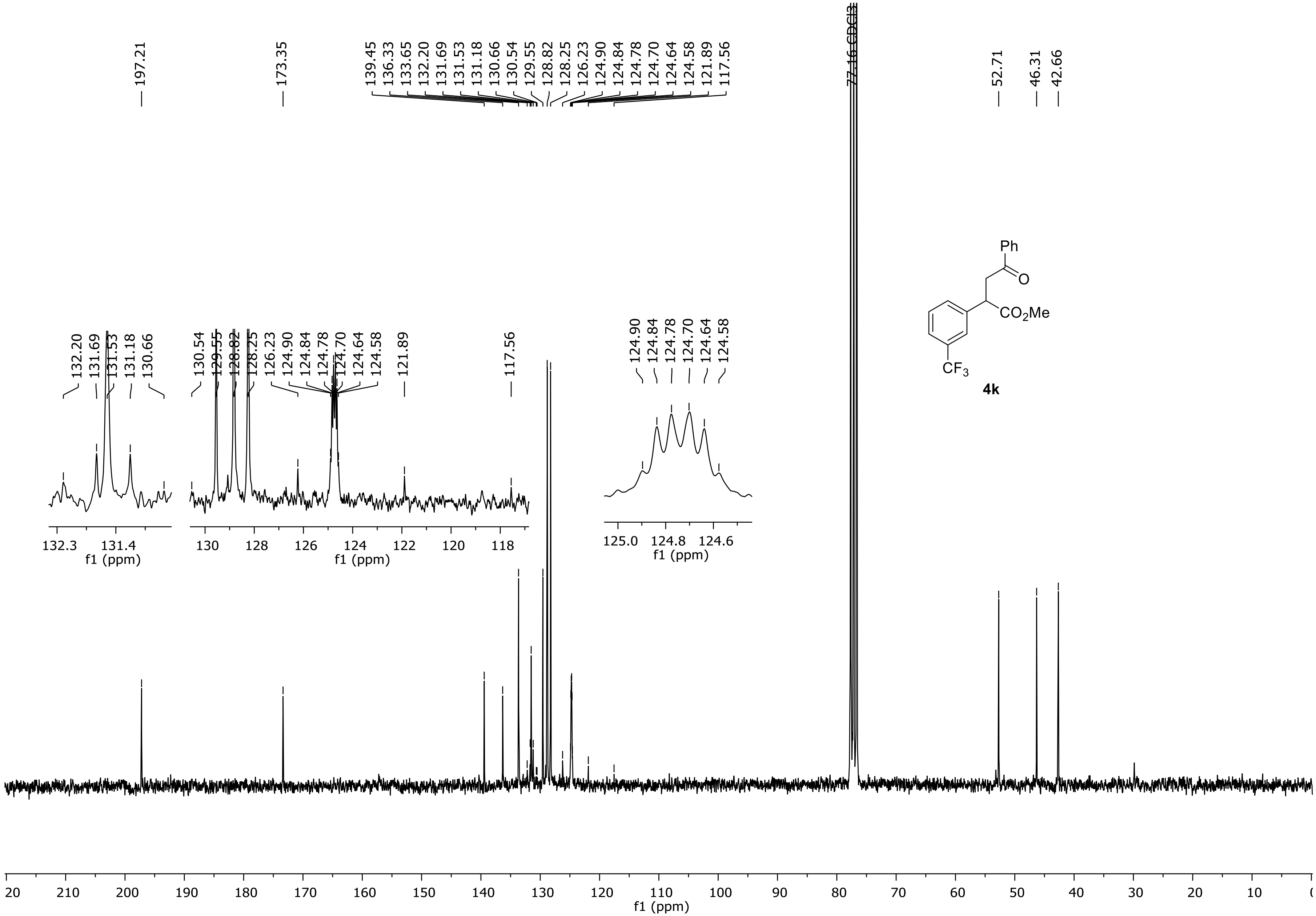


4j

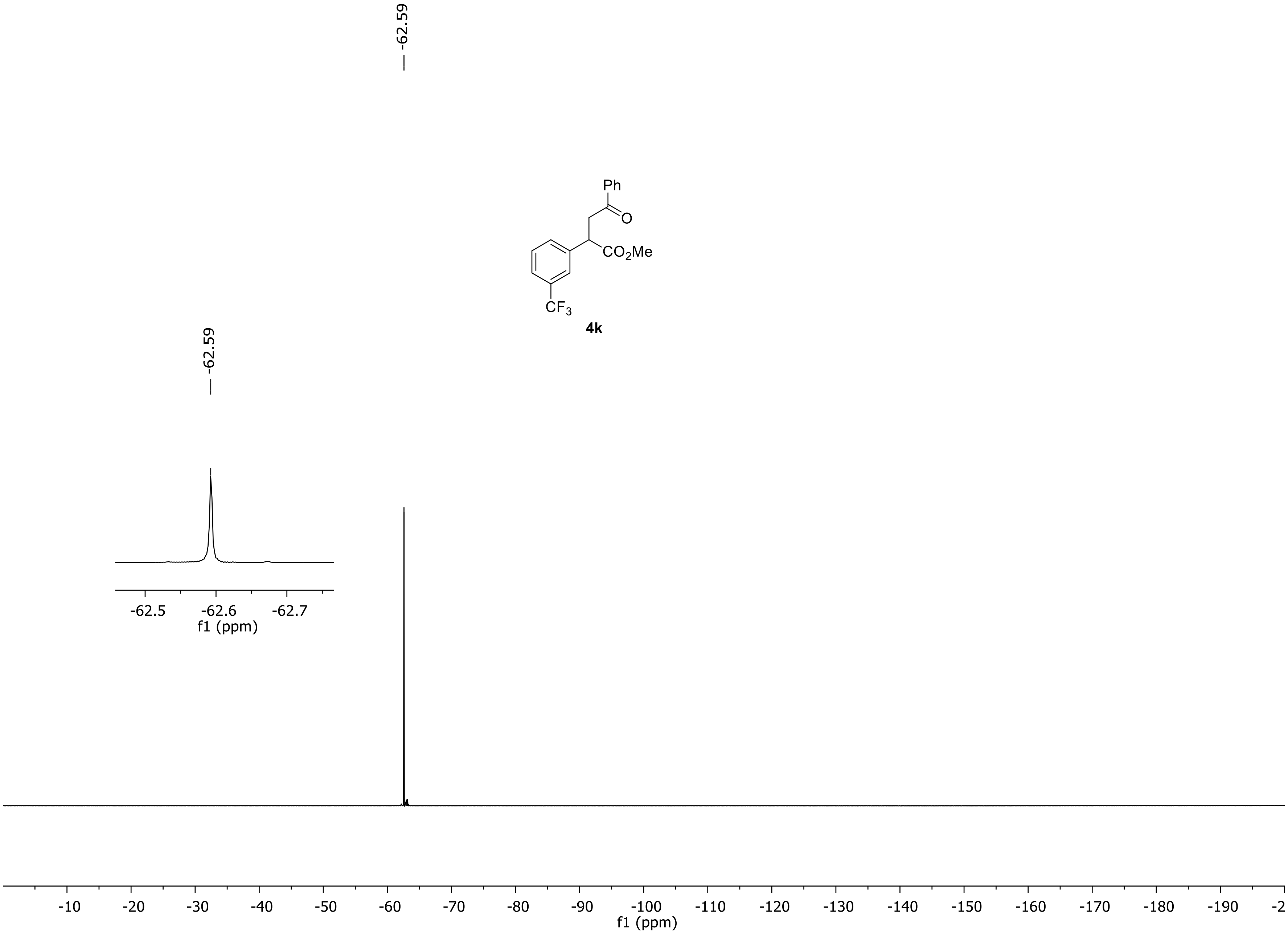
^{1}H NMR of 4k (CDCl$_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 4k ($CDCl_3$, 125 MHz)

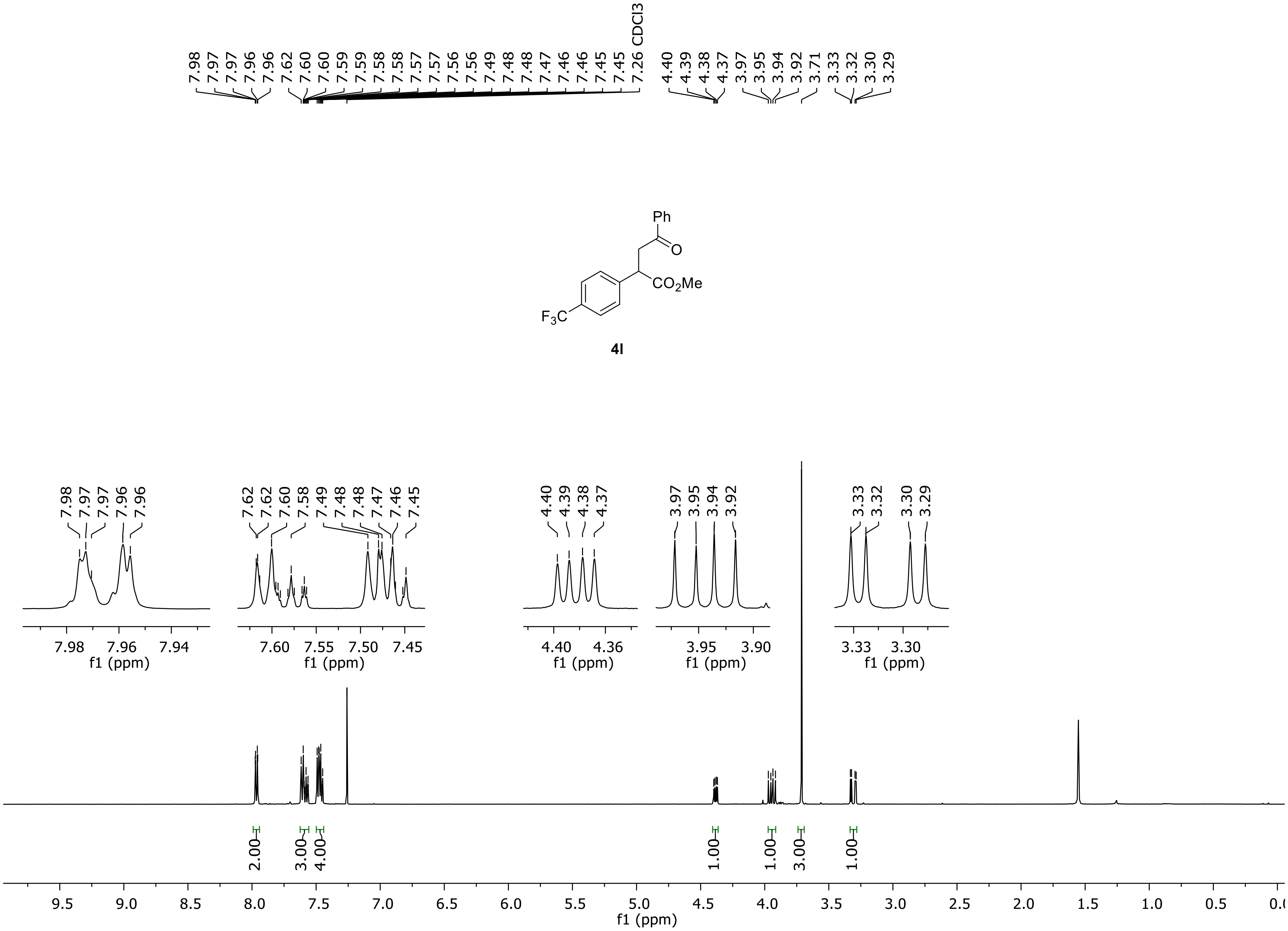


$^{19}F\{^1H\}$ NMR of 4k ($CDCl_3$, 470 MHz)

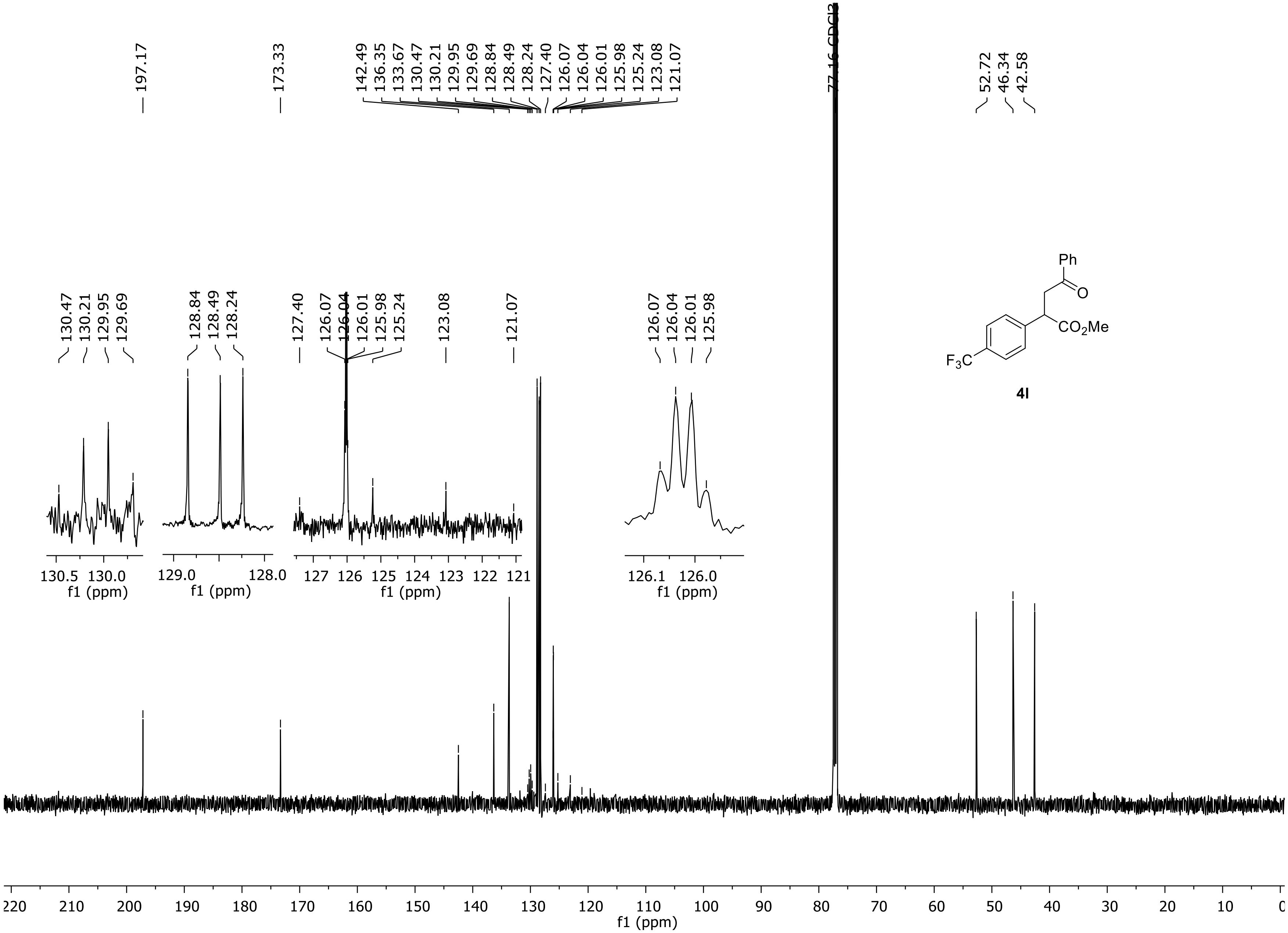


4k

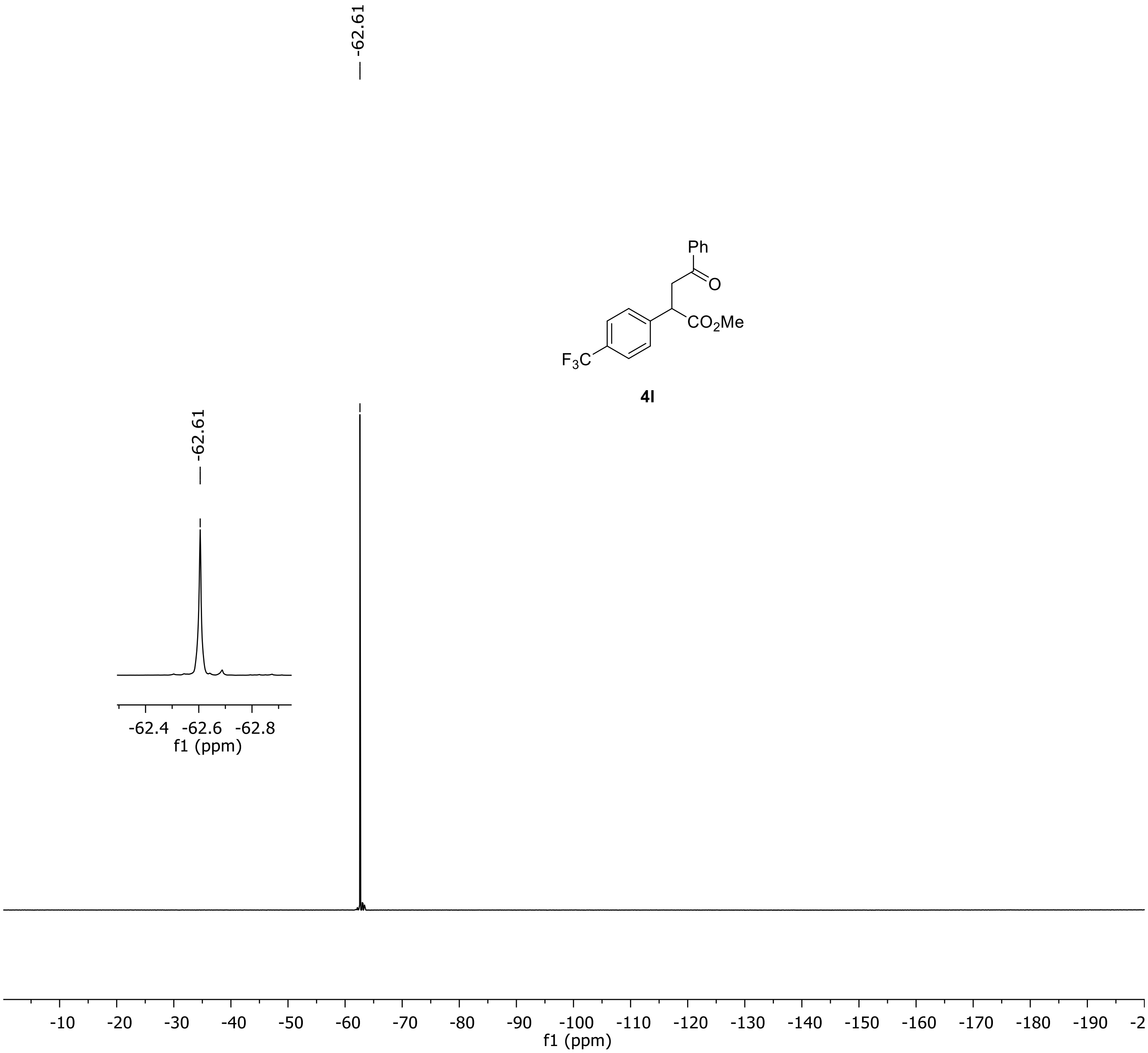
^1H NMR of 4l ($CDCl_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 4l ($CDCl_3$, 125 MHz)

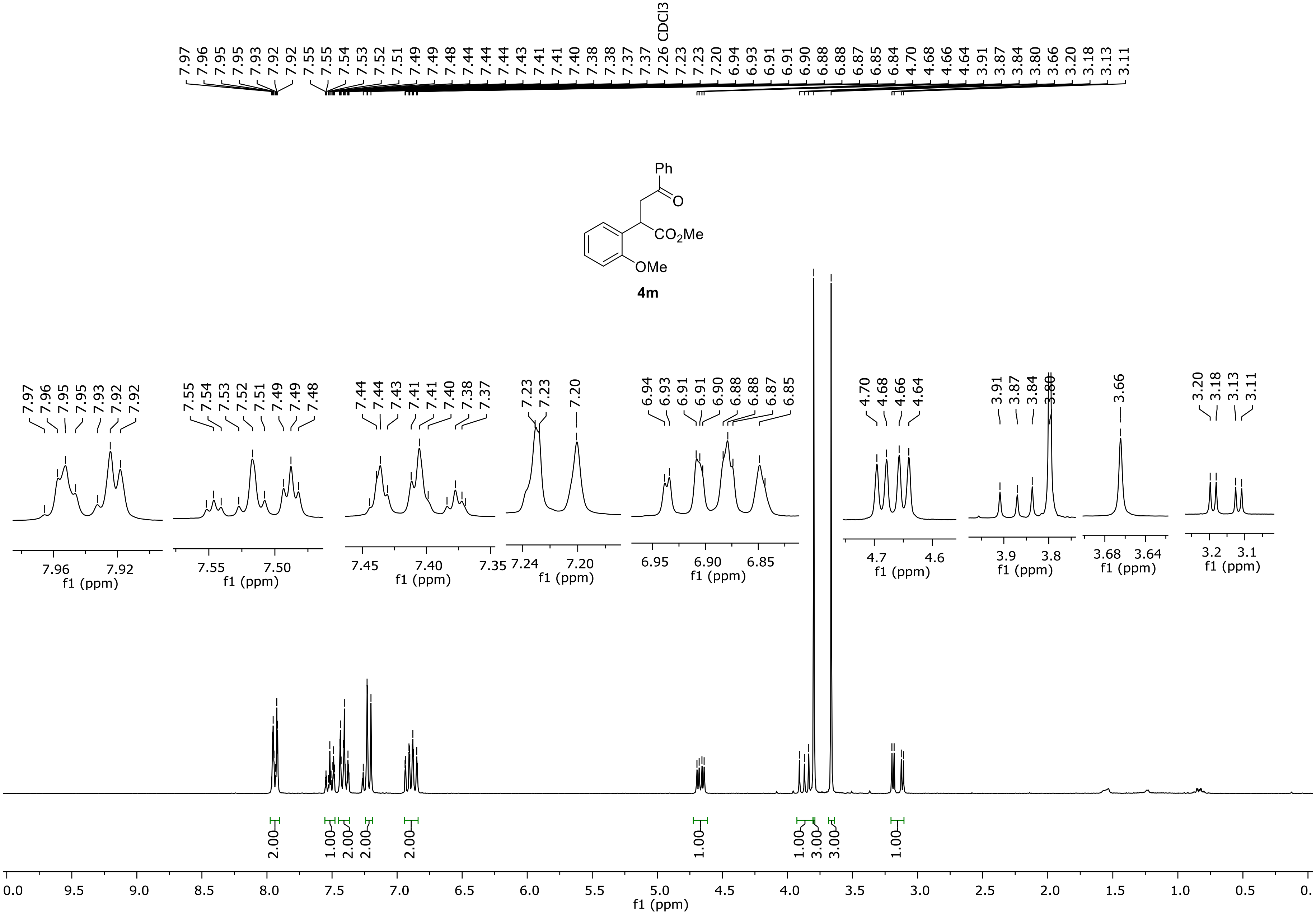


$^{19}F\{^1H\}$ NMR of 4l ($CDCl_3$, 470 MHz)

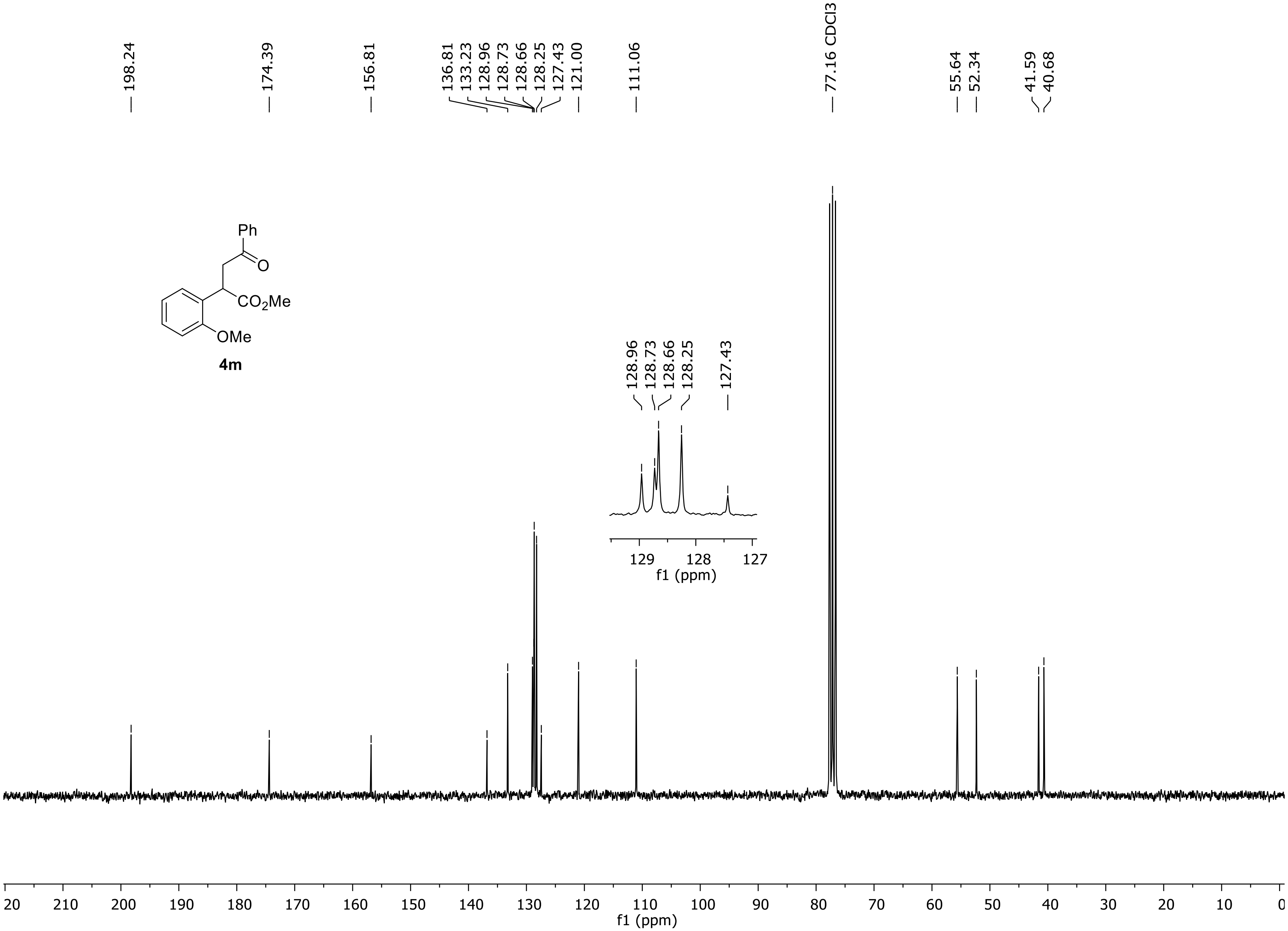


4l

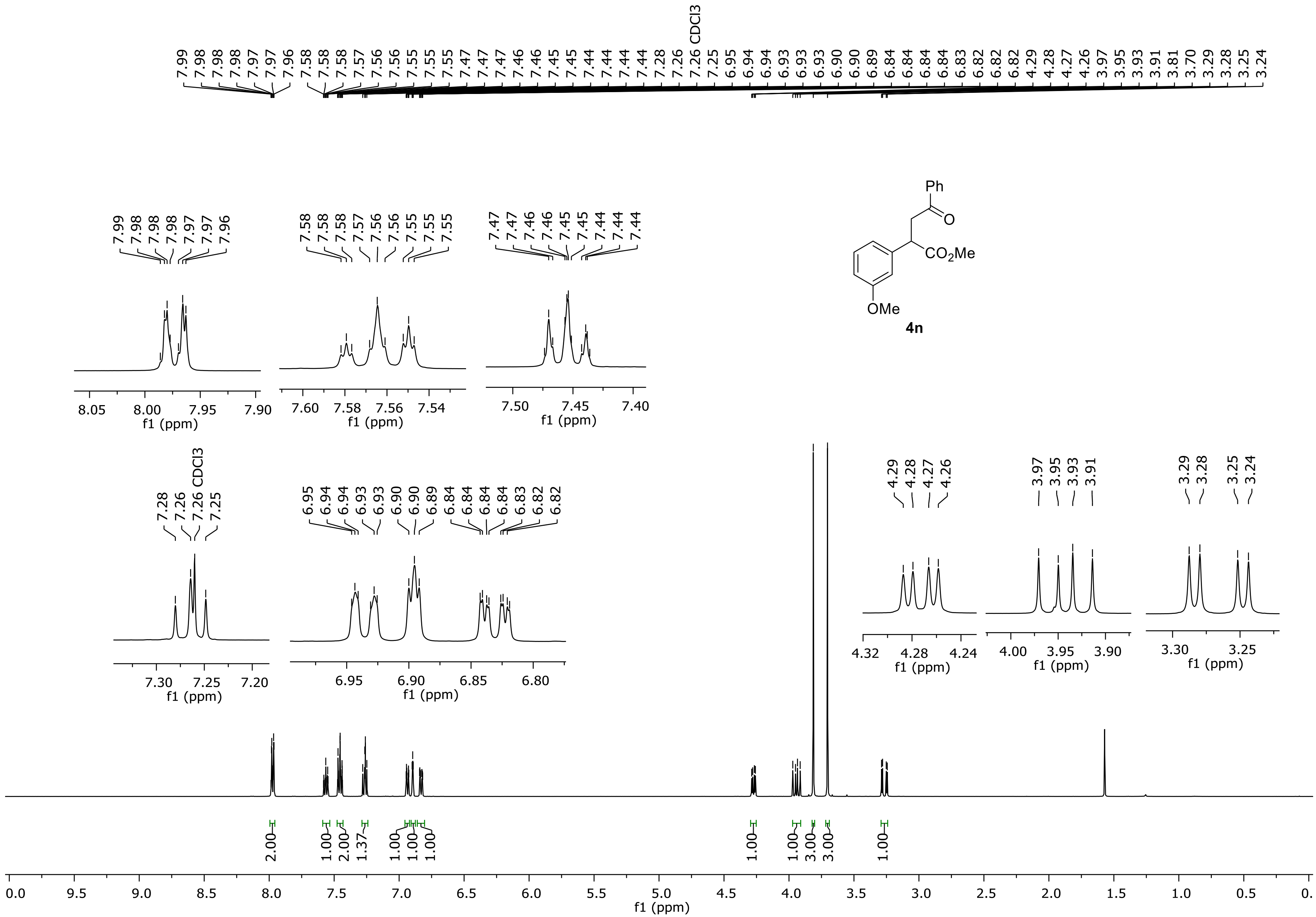
^{1}H NMR of 4m (CDCl$_3$, 250 MHz)



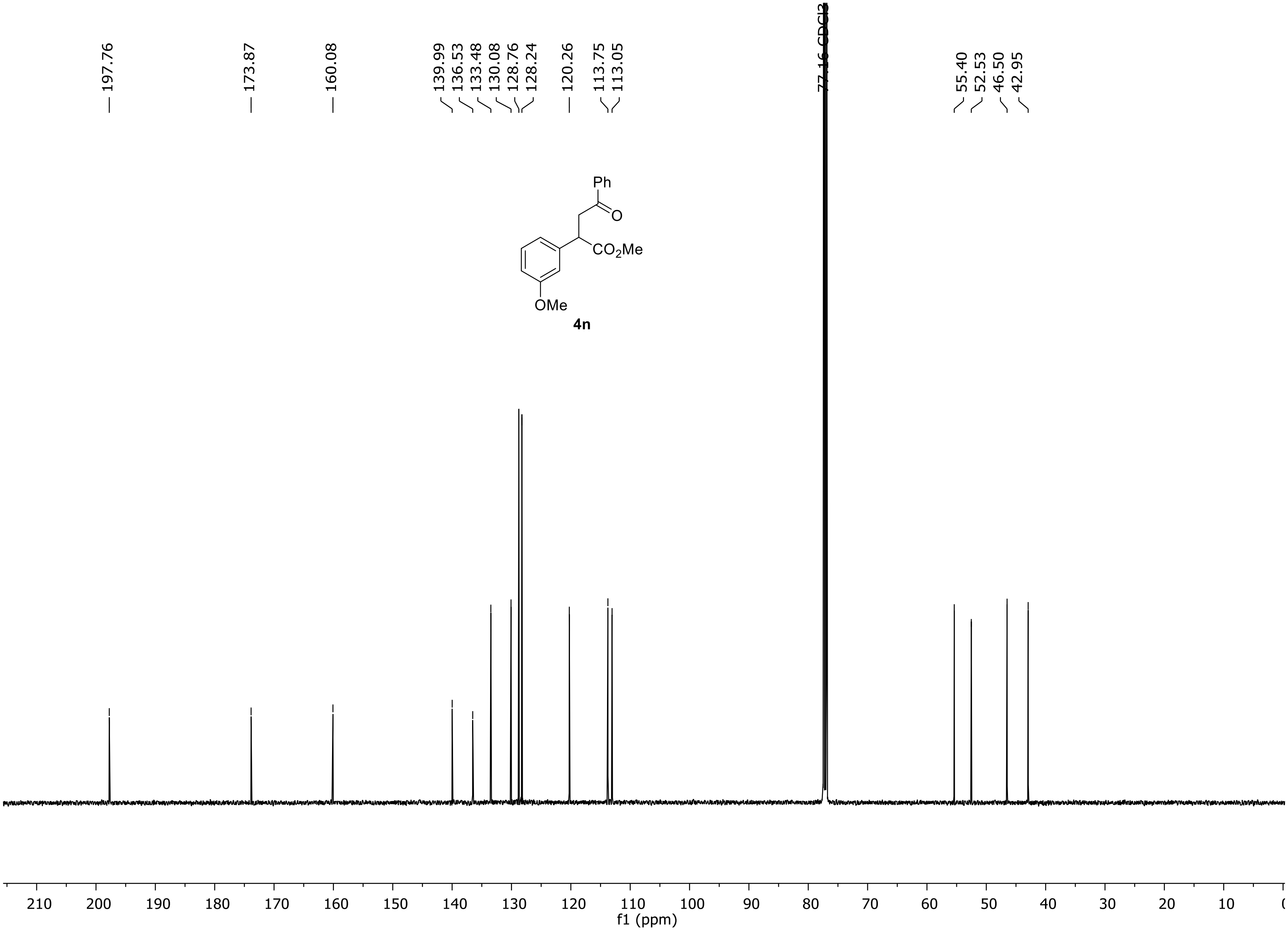
$^{13}C\{^1H\}$ NMR of 4m ($CDCl_3$, 62.5 MHz)



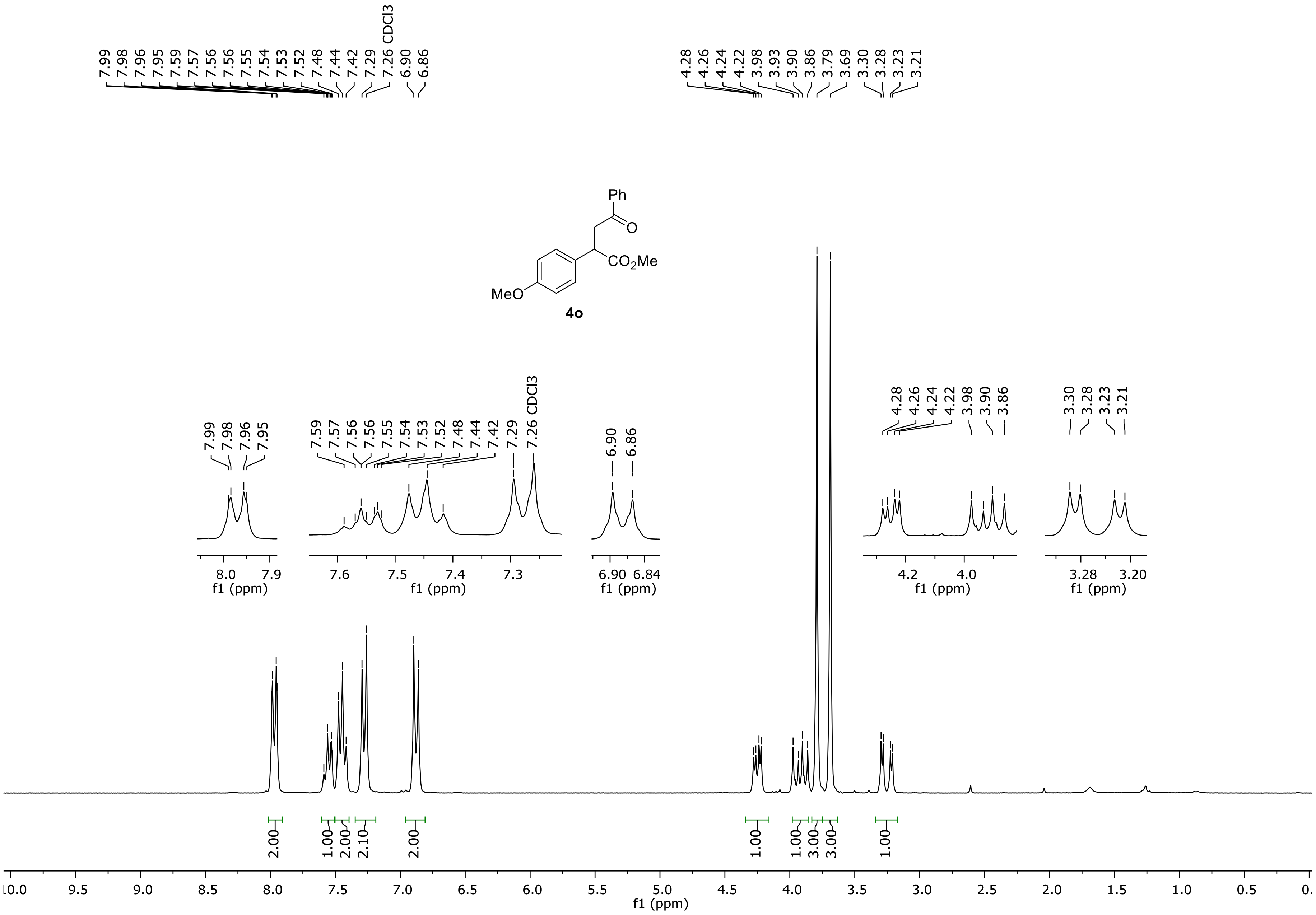
^{1}H NMR of 4n ($CDCl_3$, 500 MHz)



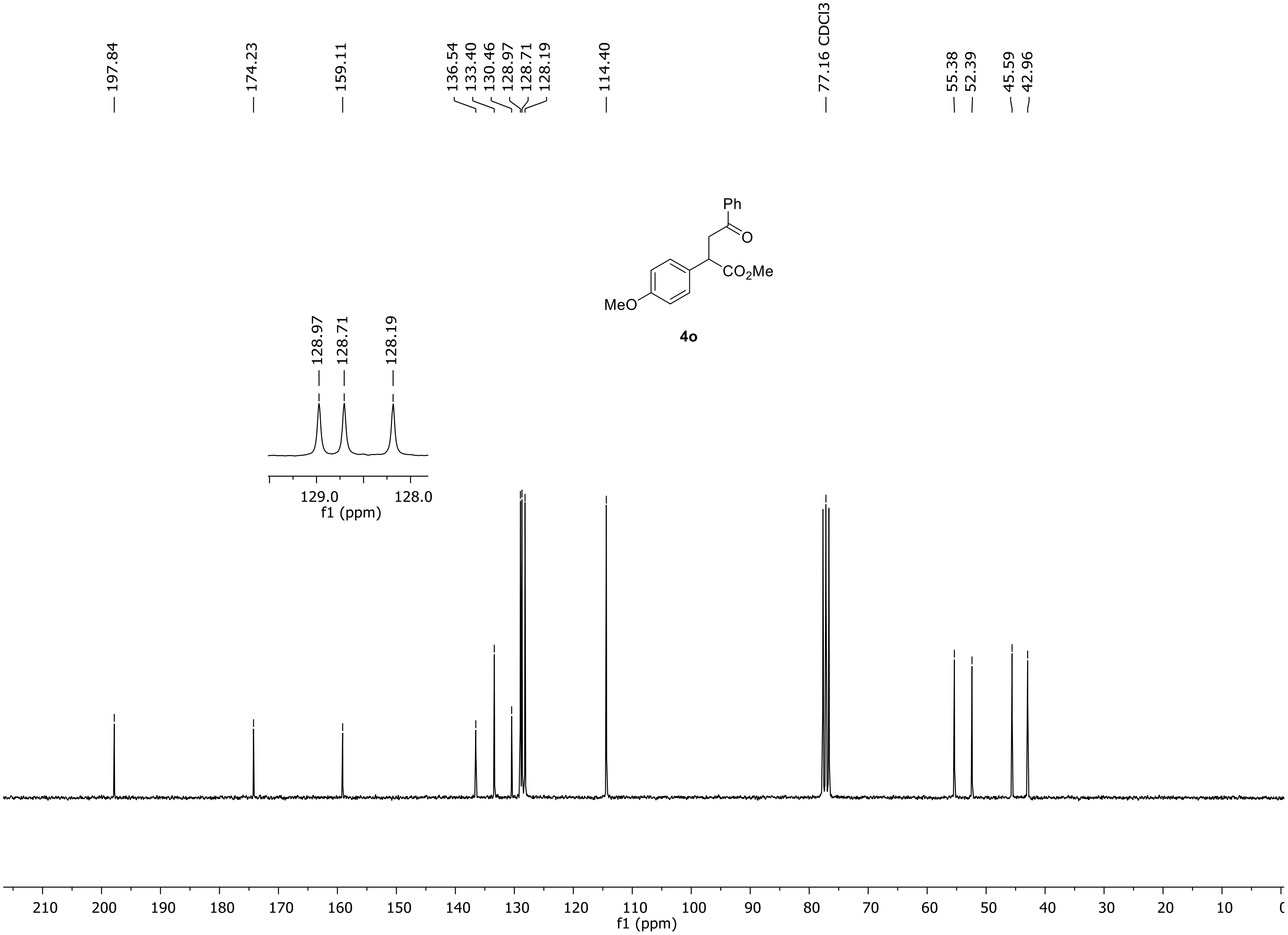
$^{13}C\{^{1}H\}$ **NMR of 4n (CDCl$_3$, 125 MHz)**



^{1}H NMR of 4o ($CDCl_3$, 250 MHz)

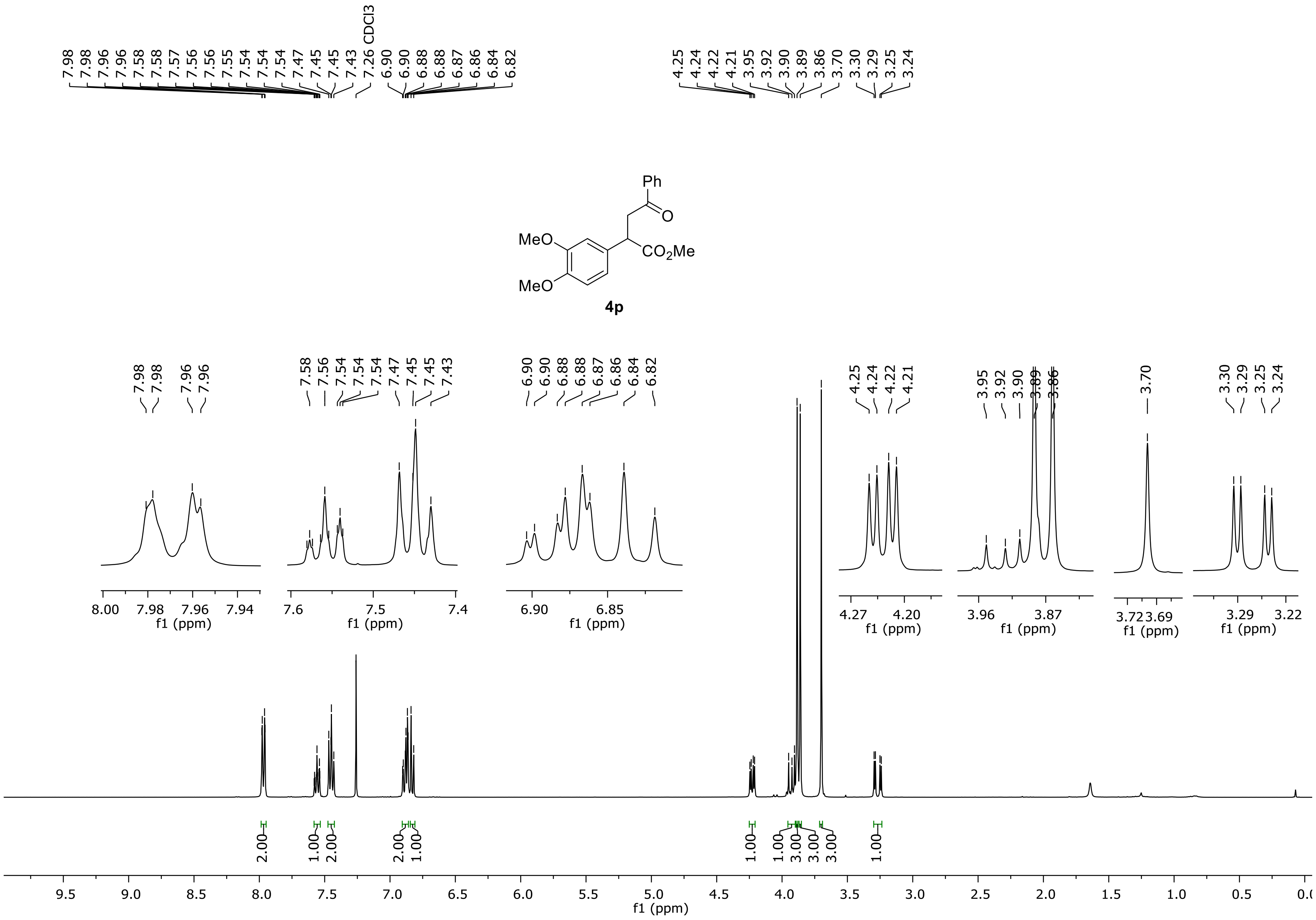


$^{13}C\{^1H\}$ NMR of 4o ($CDCl_3$, 62.5 MHz)

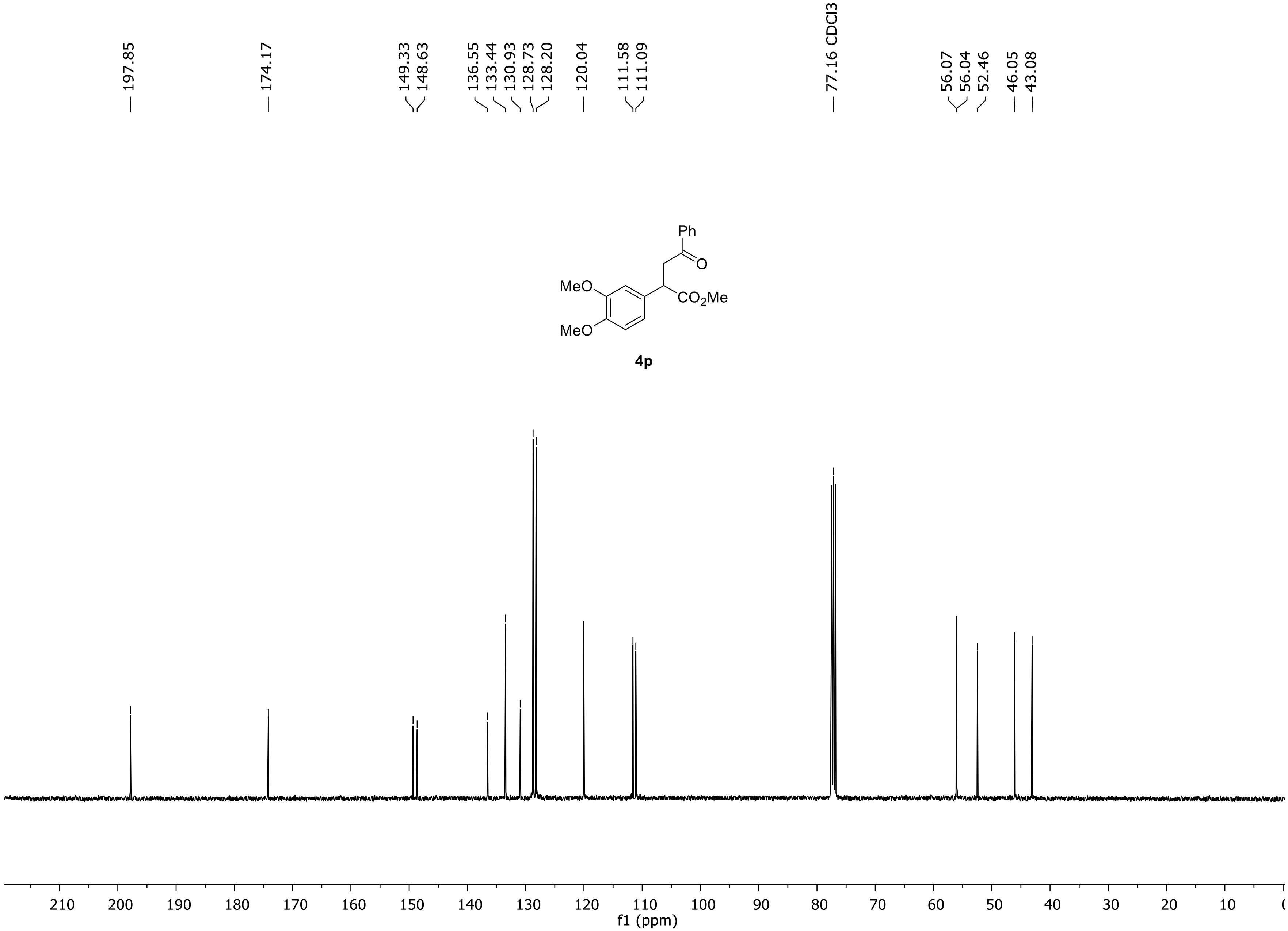


4o

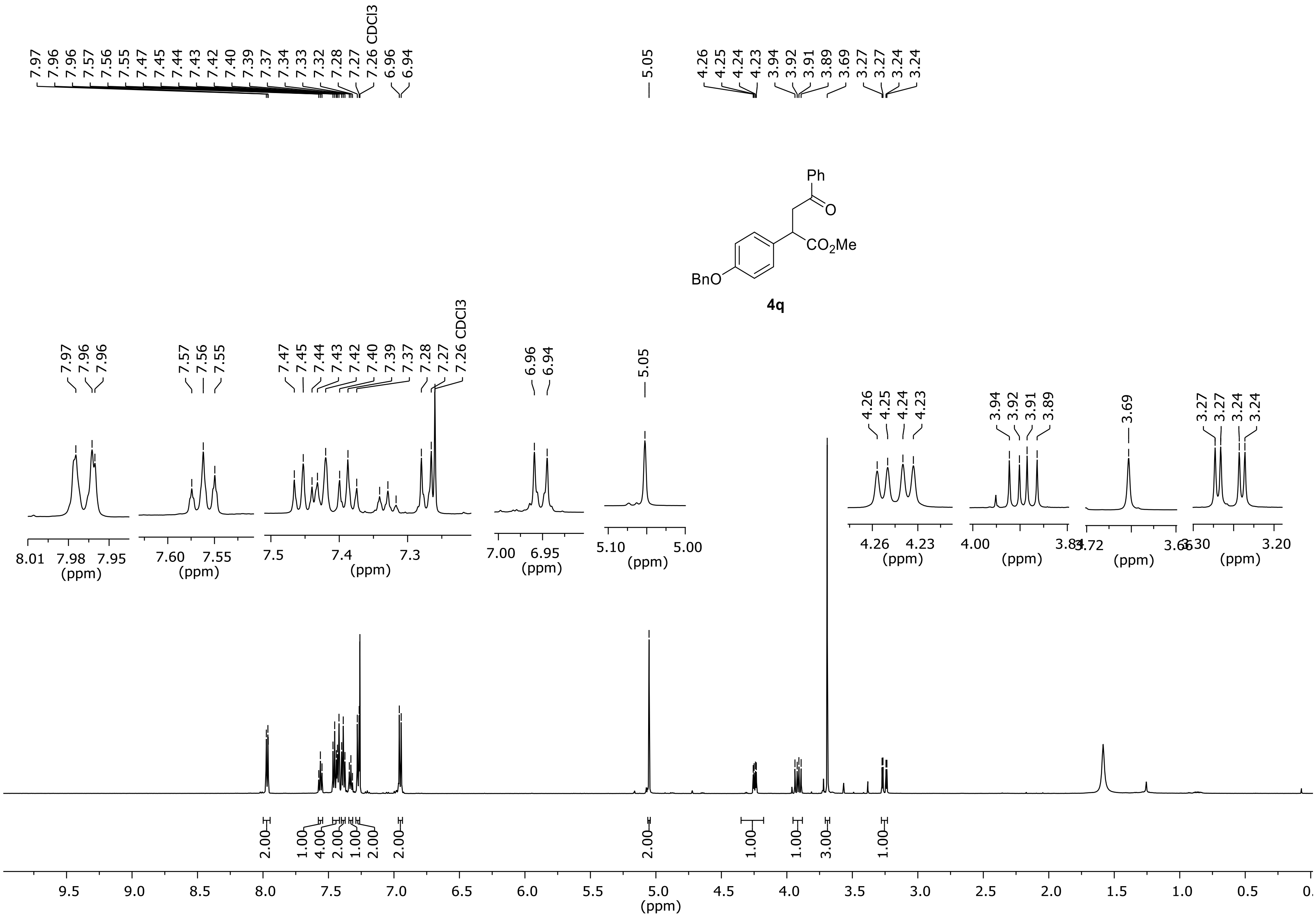
^{1}H NMR of 4p ($CDCl_3$, 400 MHz)



$^{13}C\{^1H\}$ NMR of 4p ($CDCl_3$, 100 MHz)

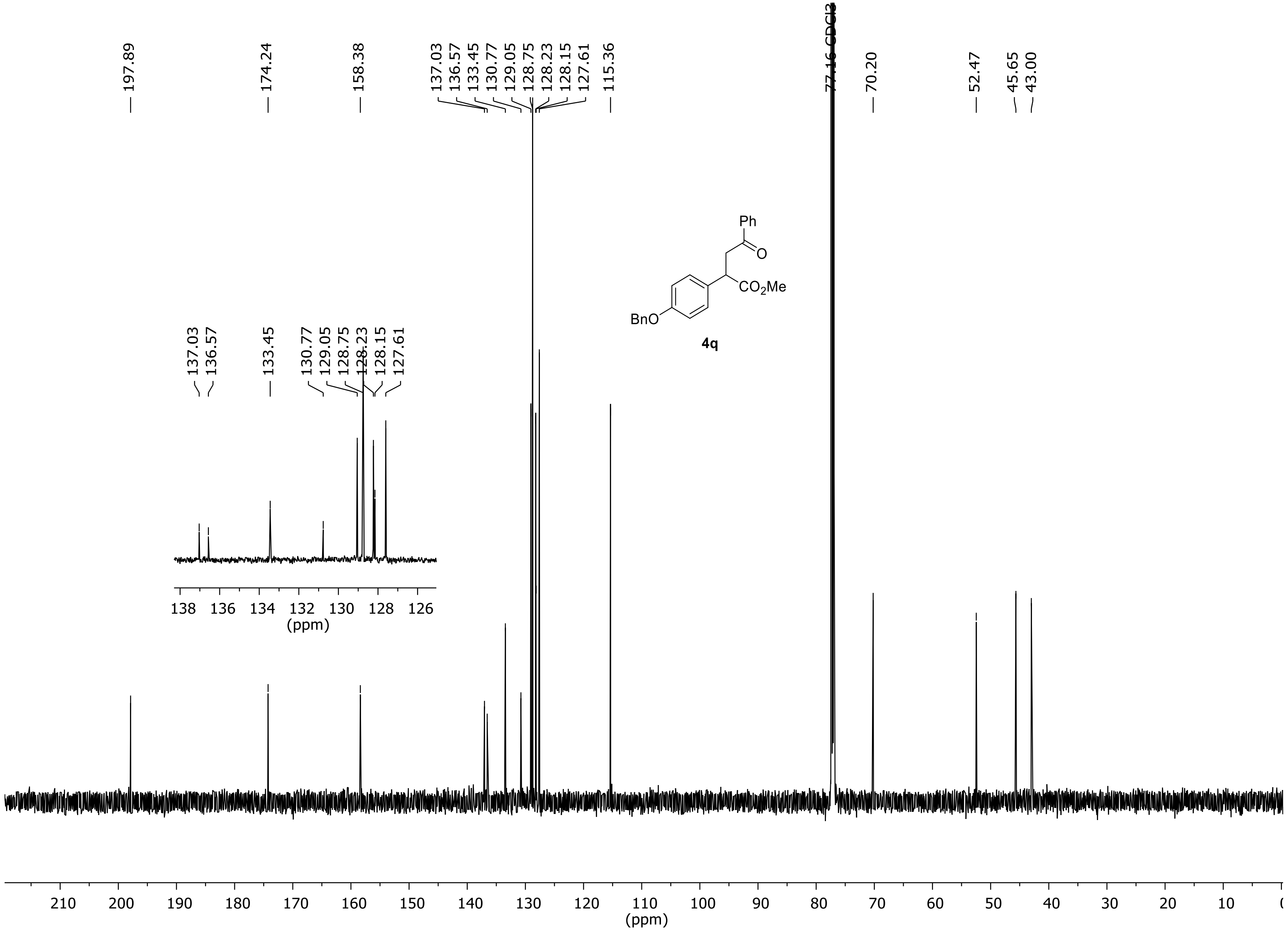


^{1}H NMR of 4q (CDCl$_3$, 600 MHz)

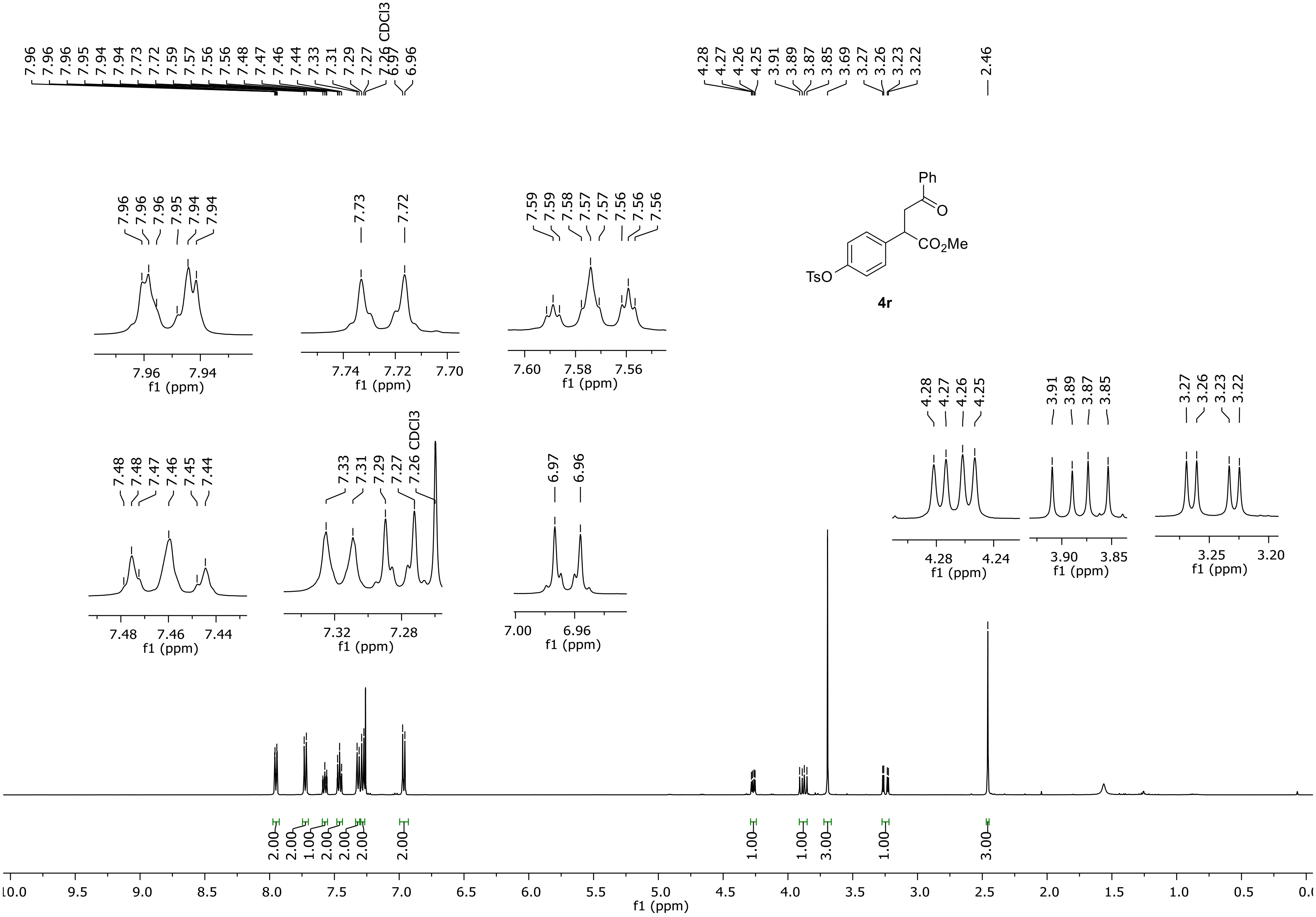


4q

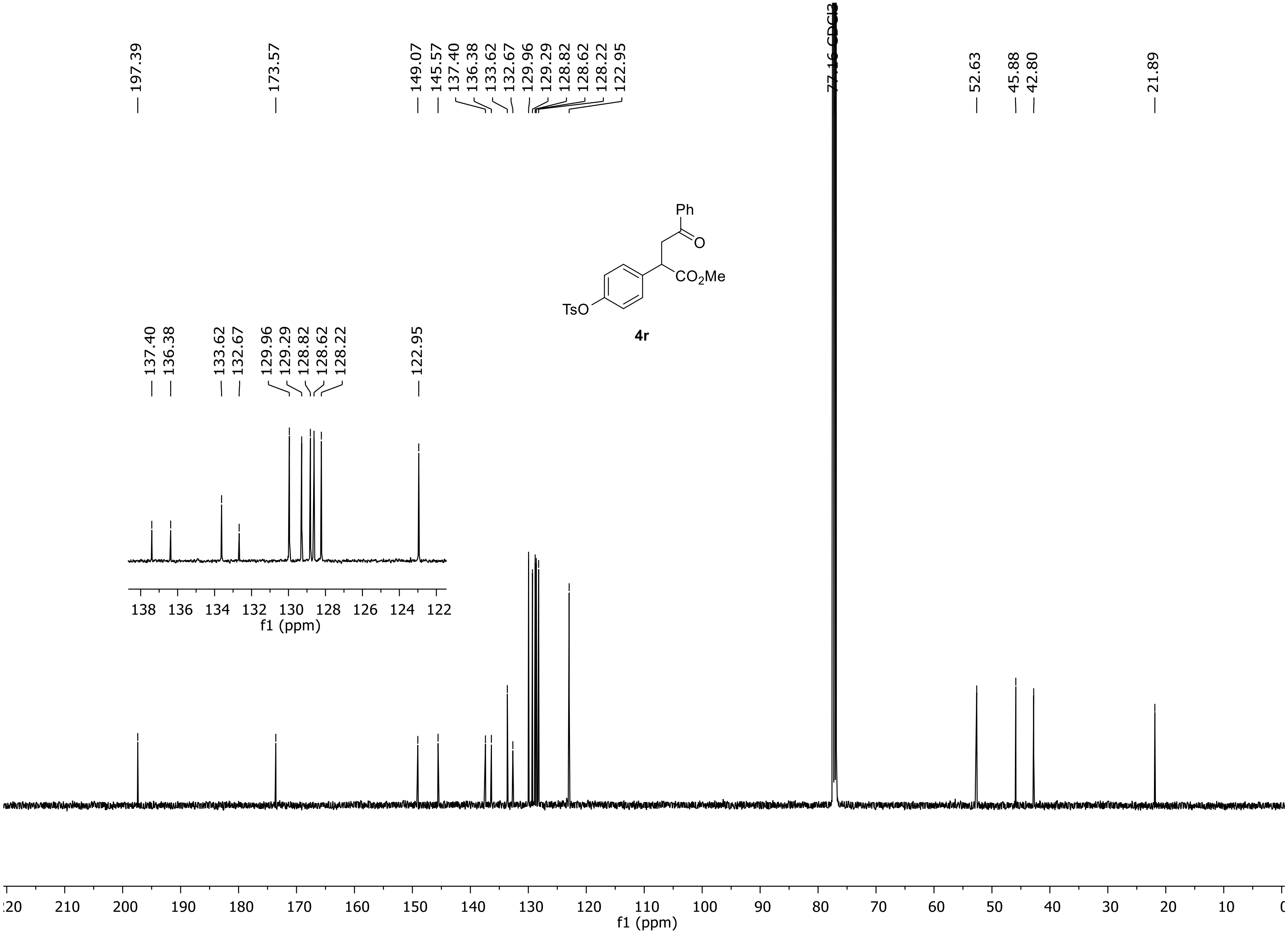
$^{13}C\{^1H\}$ NMR of 4q ($CDCl_3$, 150 MHz)



^{1}H NMR of 4r (CDCl$_3$, 500 MHz)

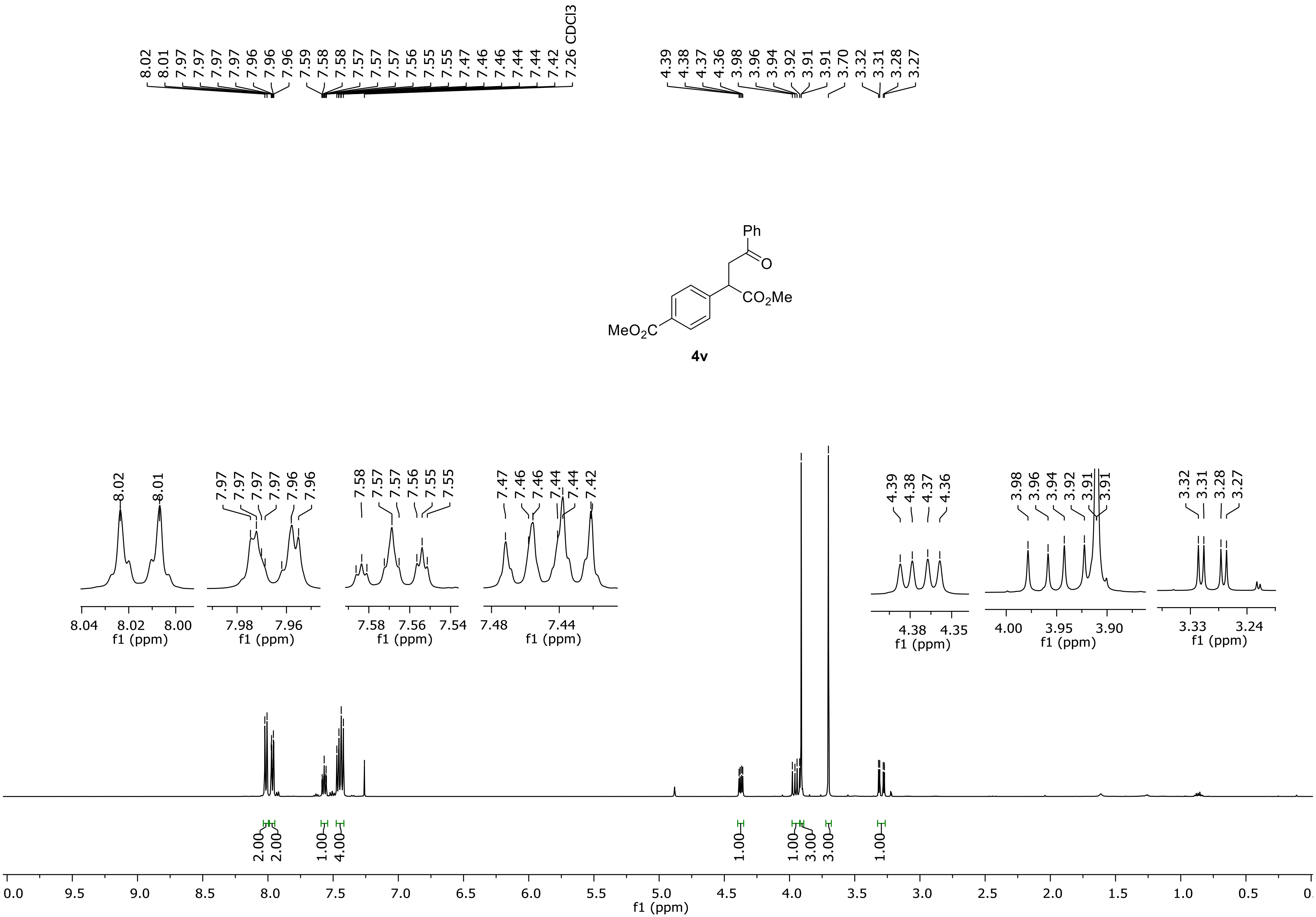


$^{13}C\{^1H\}$ NMR of 4r ($CDCl_3$, 125 MHz)

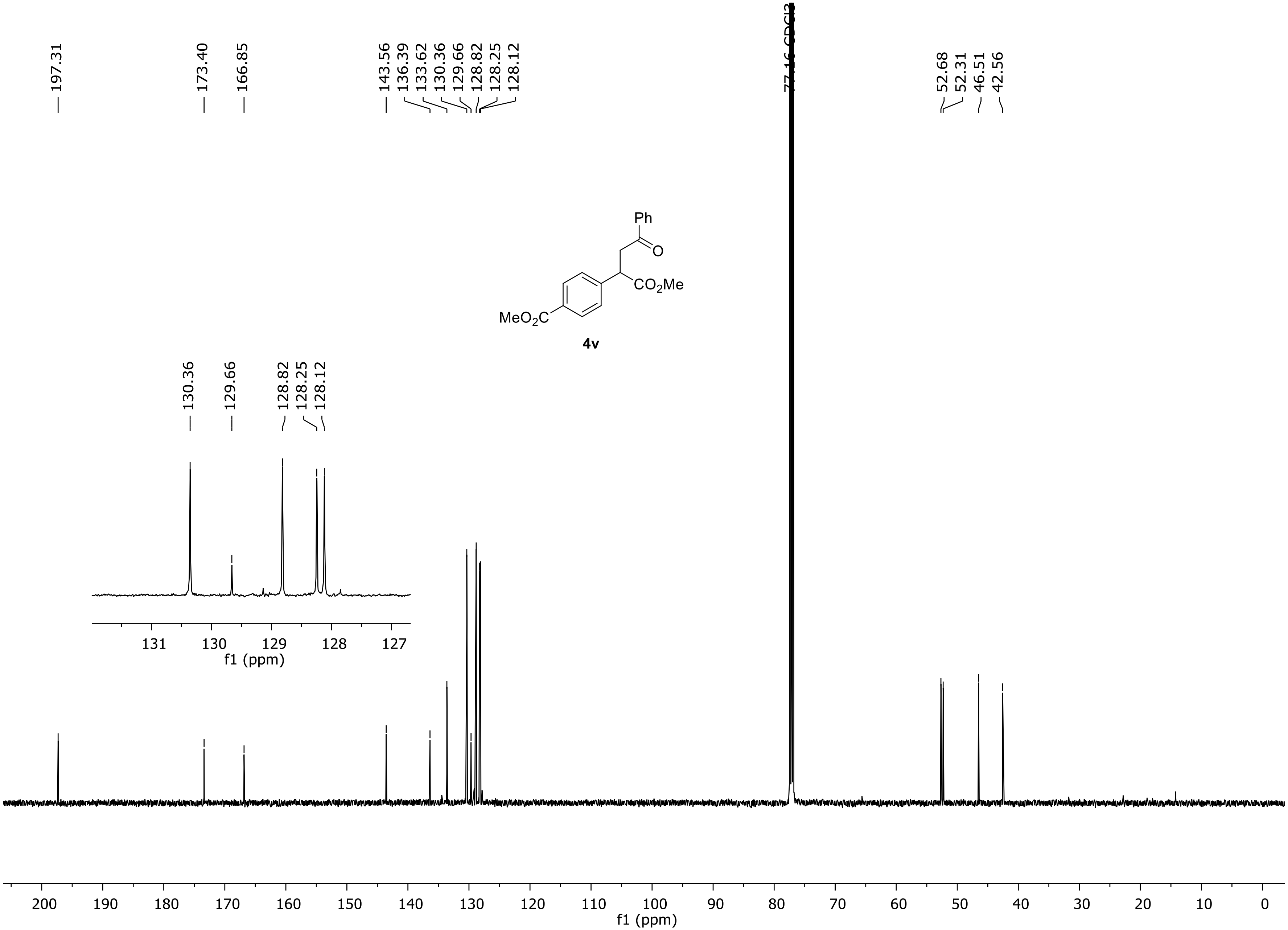


4r

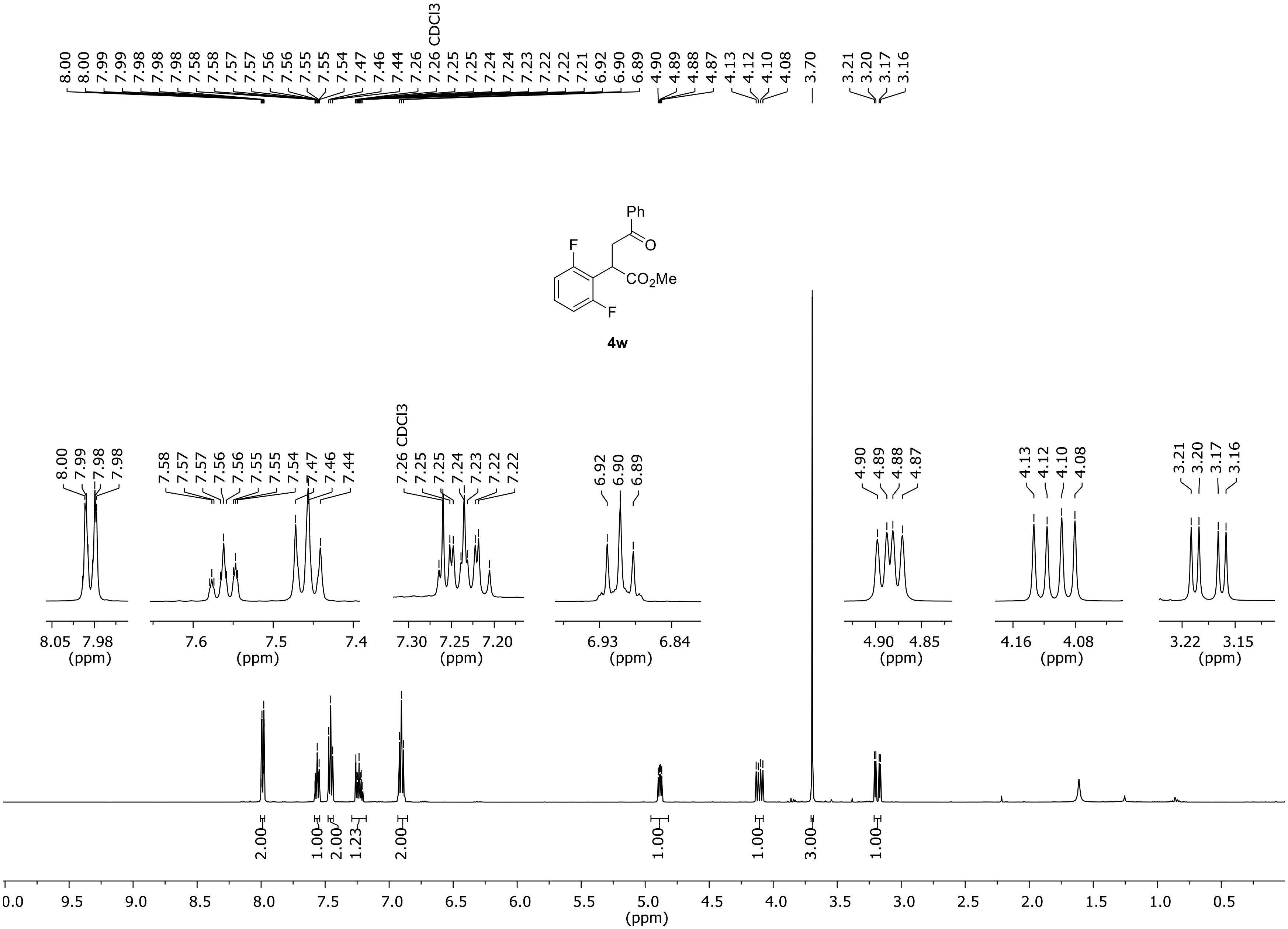
^{1}H NMR of 4v (CDCl$_3$, 500 MHz)



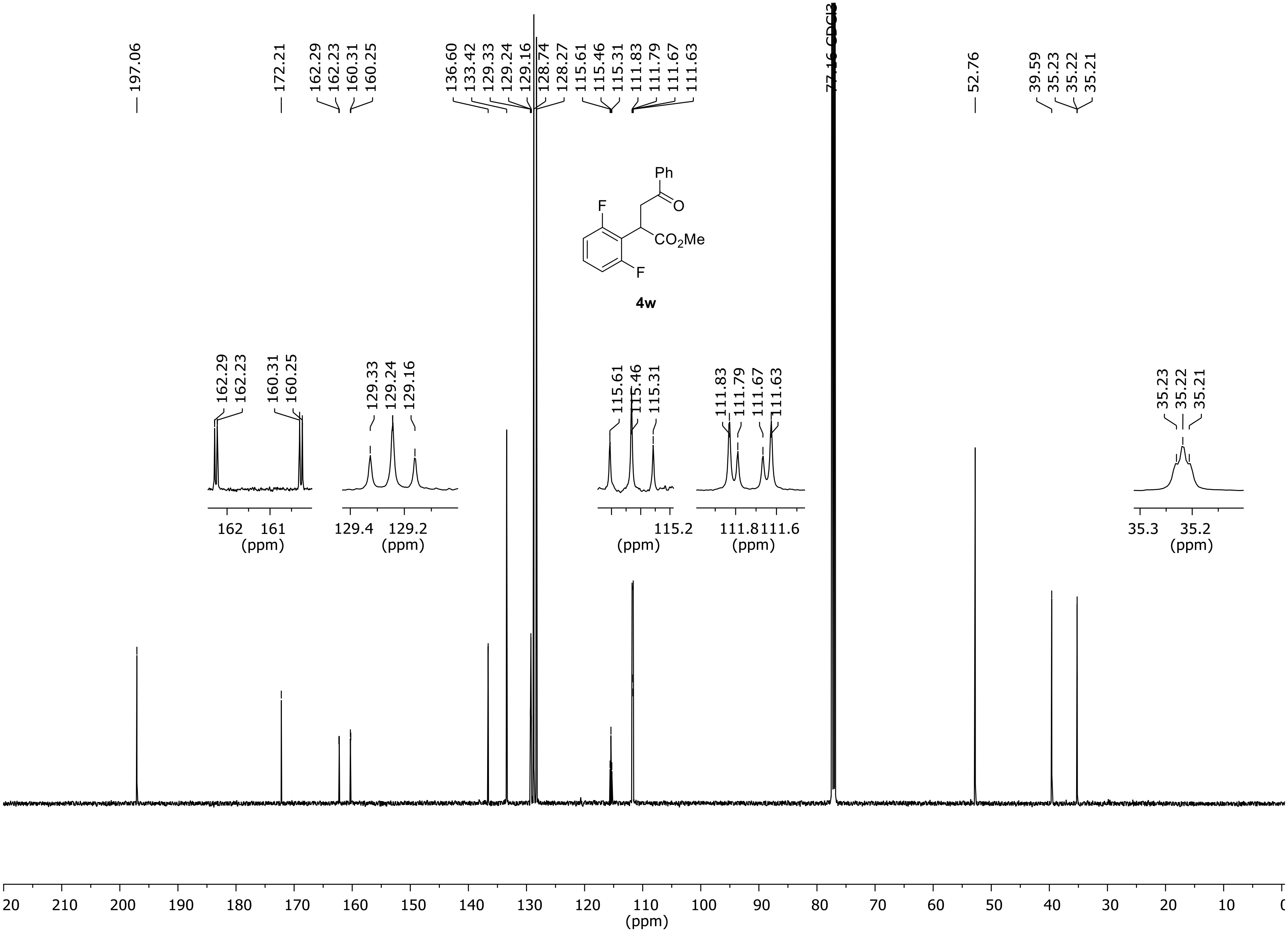
$^{13}C\{^1H\}$ NMR of 4v ($CDCl_3$, 125 MHz)



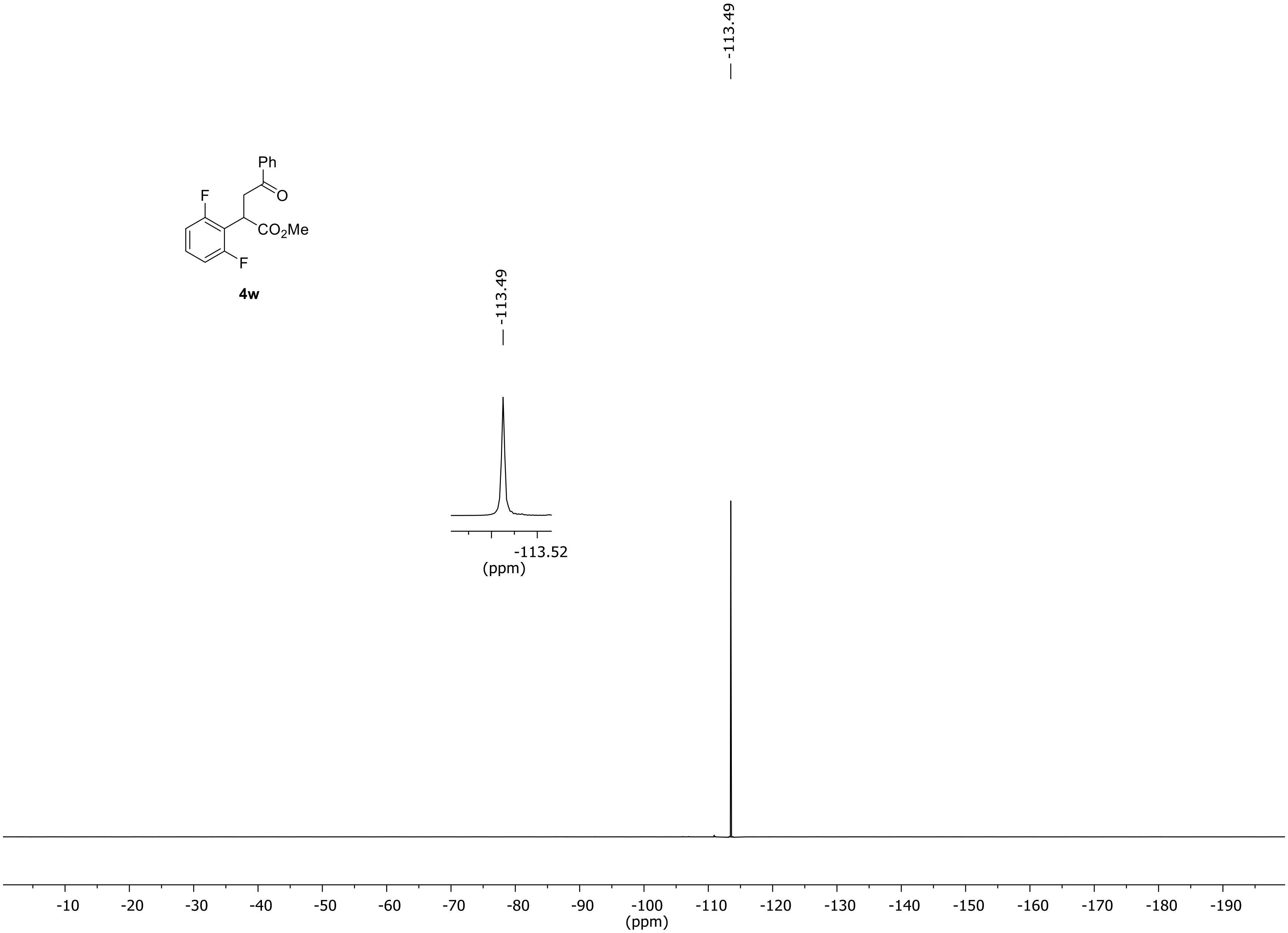
^{1}H NMR of 4w (CDCl$_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 4w ($CDCl_3$, 125 MHz)

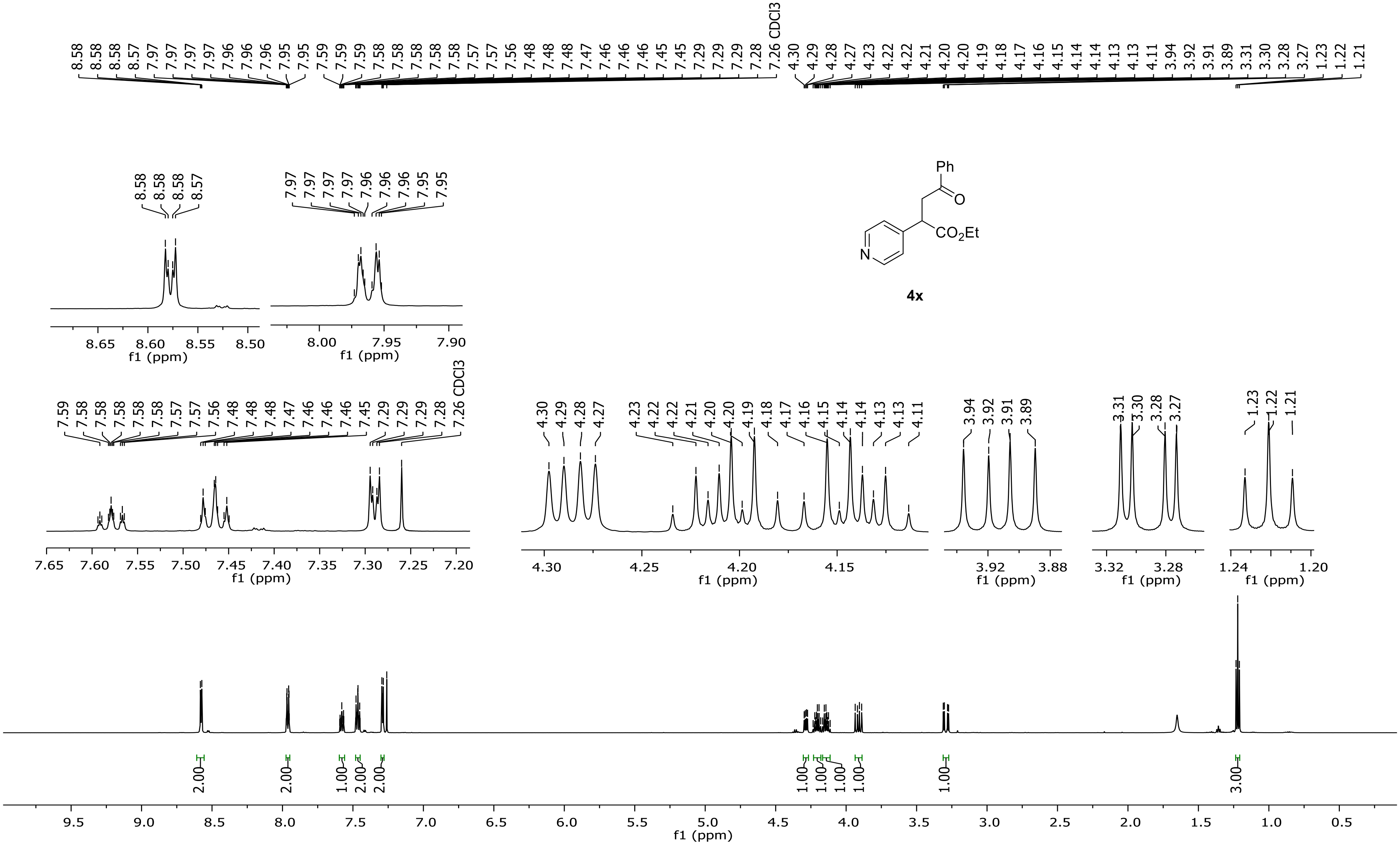


$^{19}F\{^1H\}$ NMR of 4w ($CDCl_3$, 470 MHz)



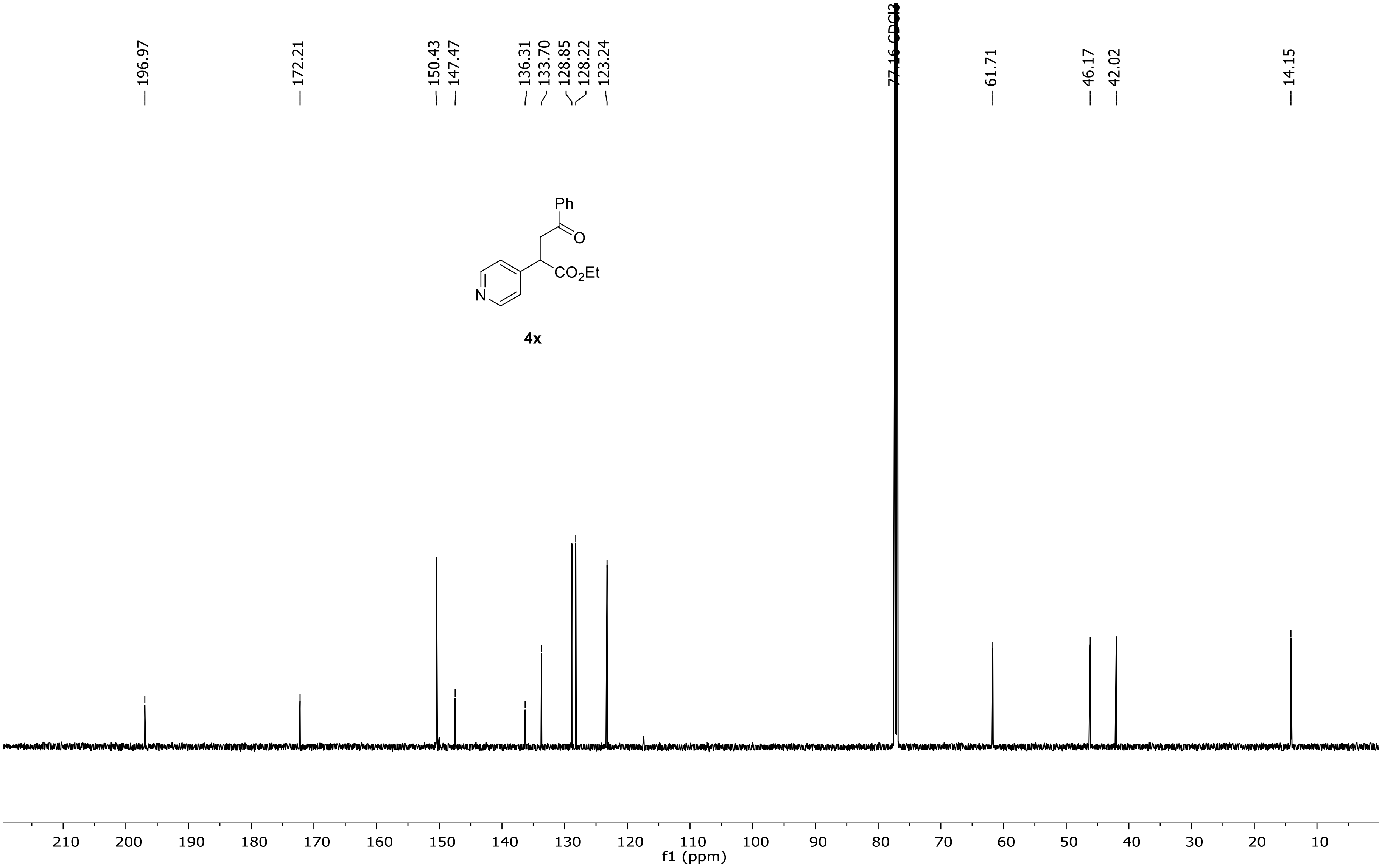
4w

^{1}H NMR of 4x (CDCl$_3$, 600 MHz)

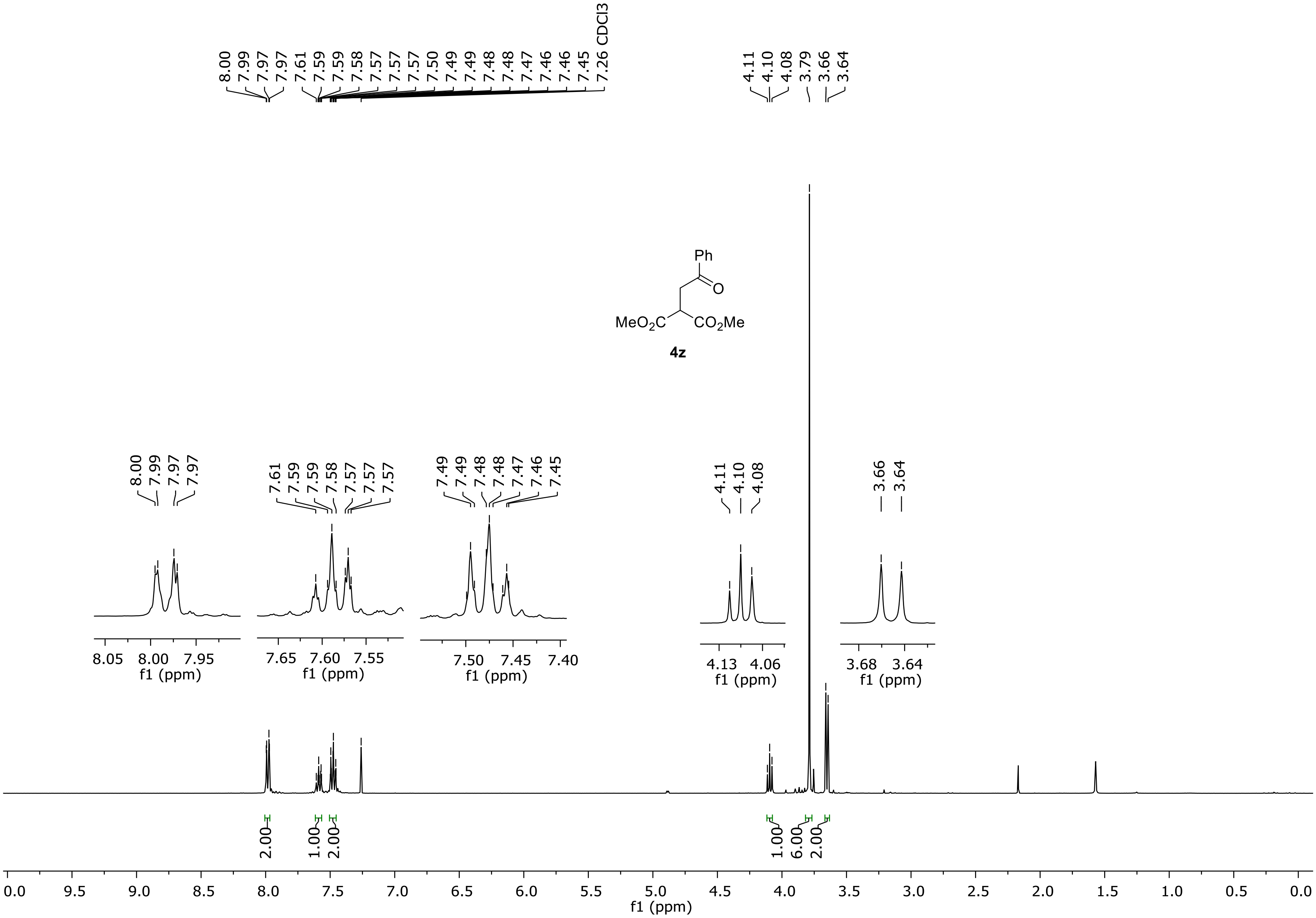


4x

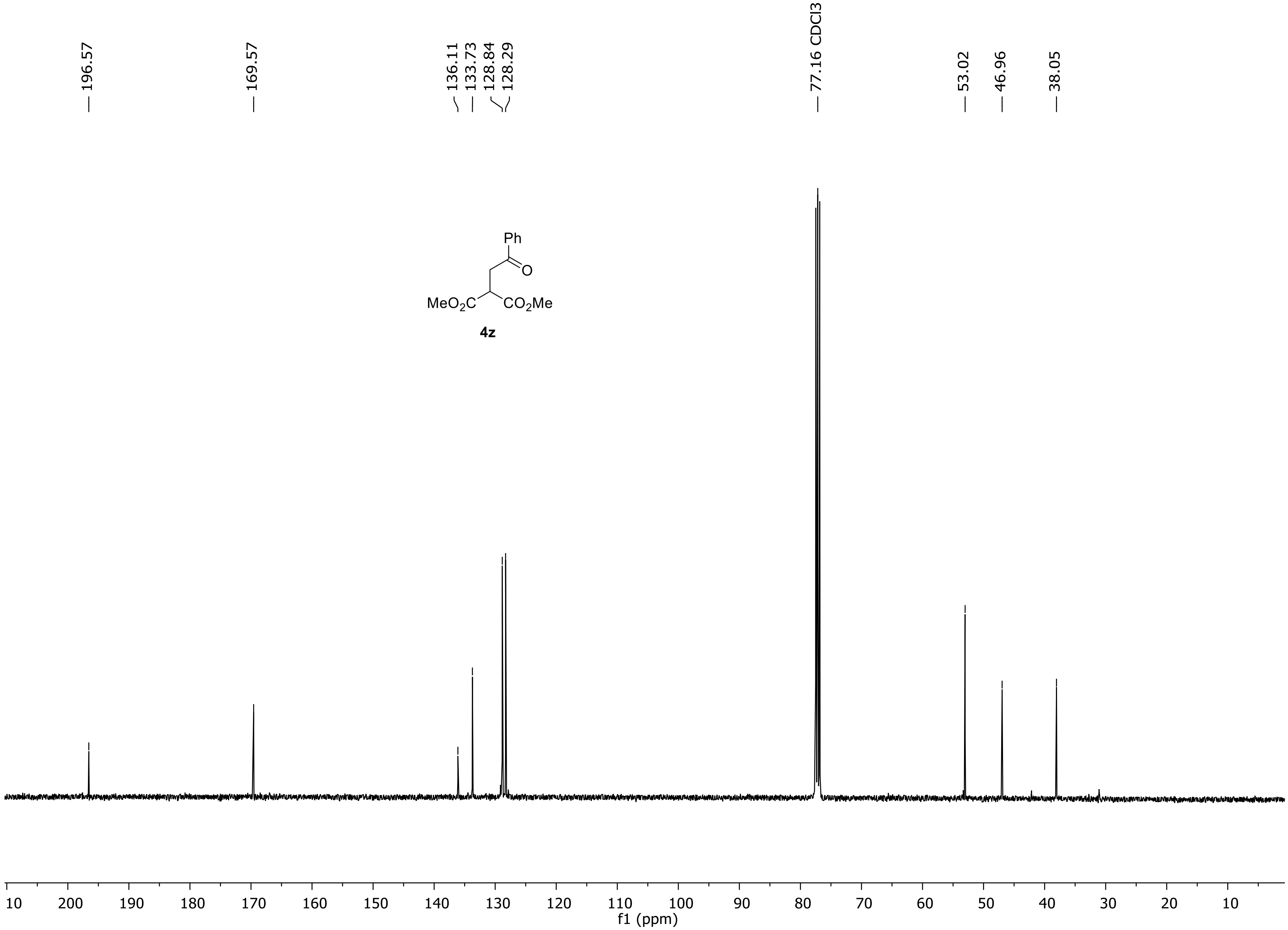
$^{13}C\{^1H\}$ NMR of 4x ($CDCl_3$, 125 MHz)



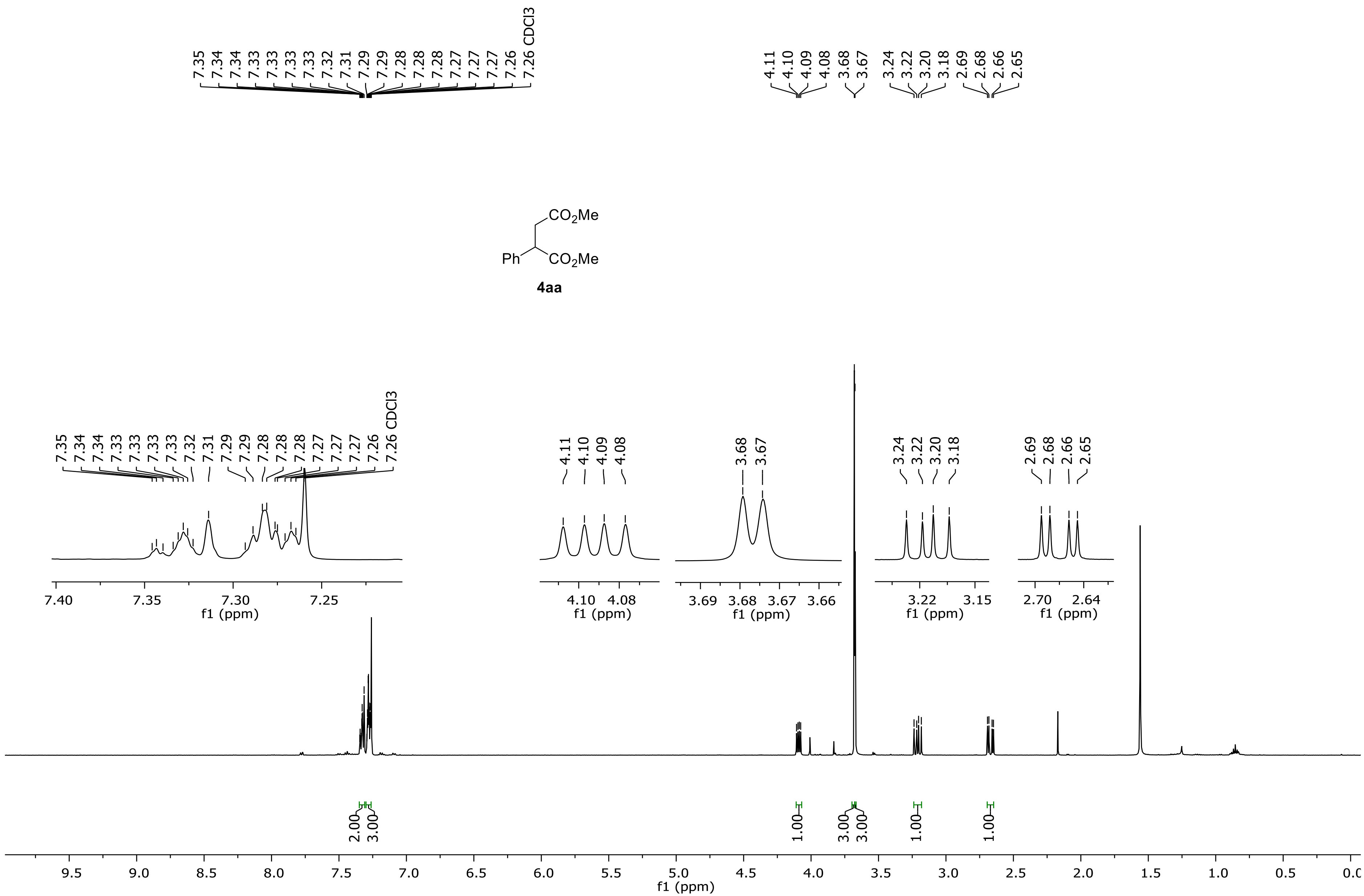
^{1}H NMR of 4z (CDCl$_3$, 400 MHz)



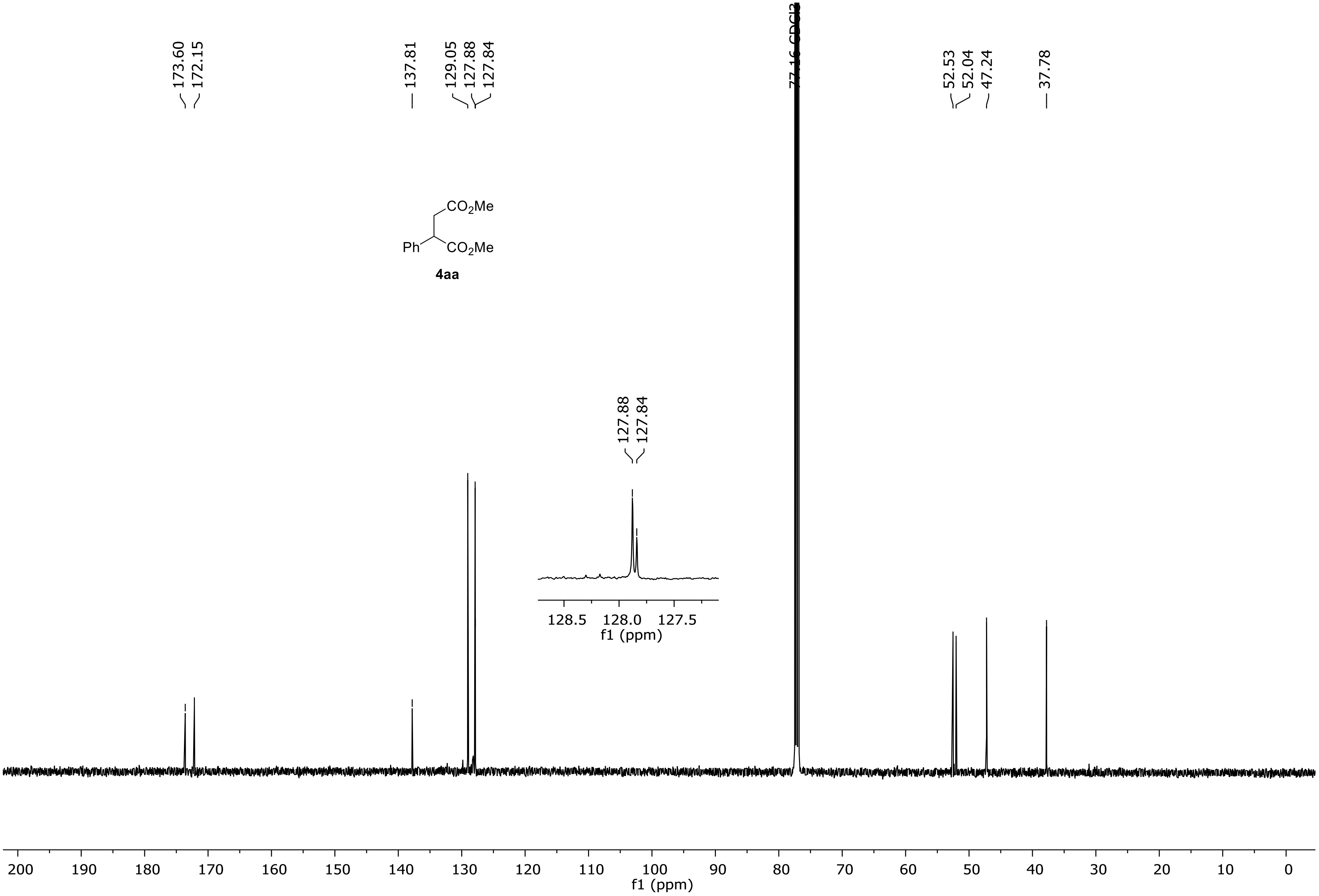
$^{13}C\{^1H\}$ NMR of 4z ($CDCl_3$, 100 MHz)



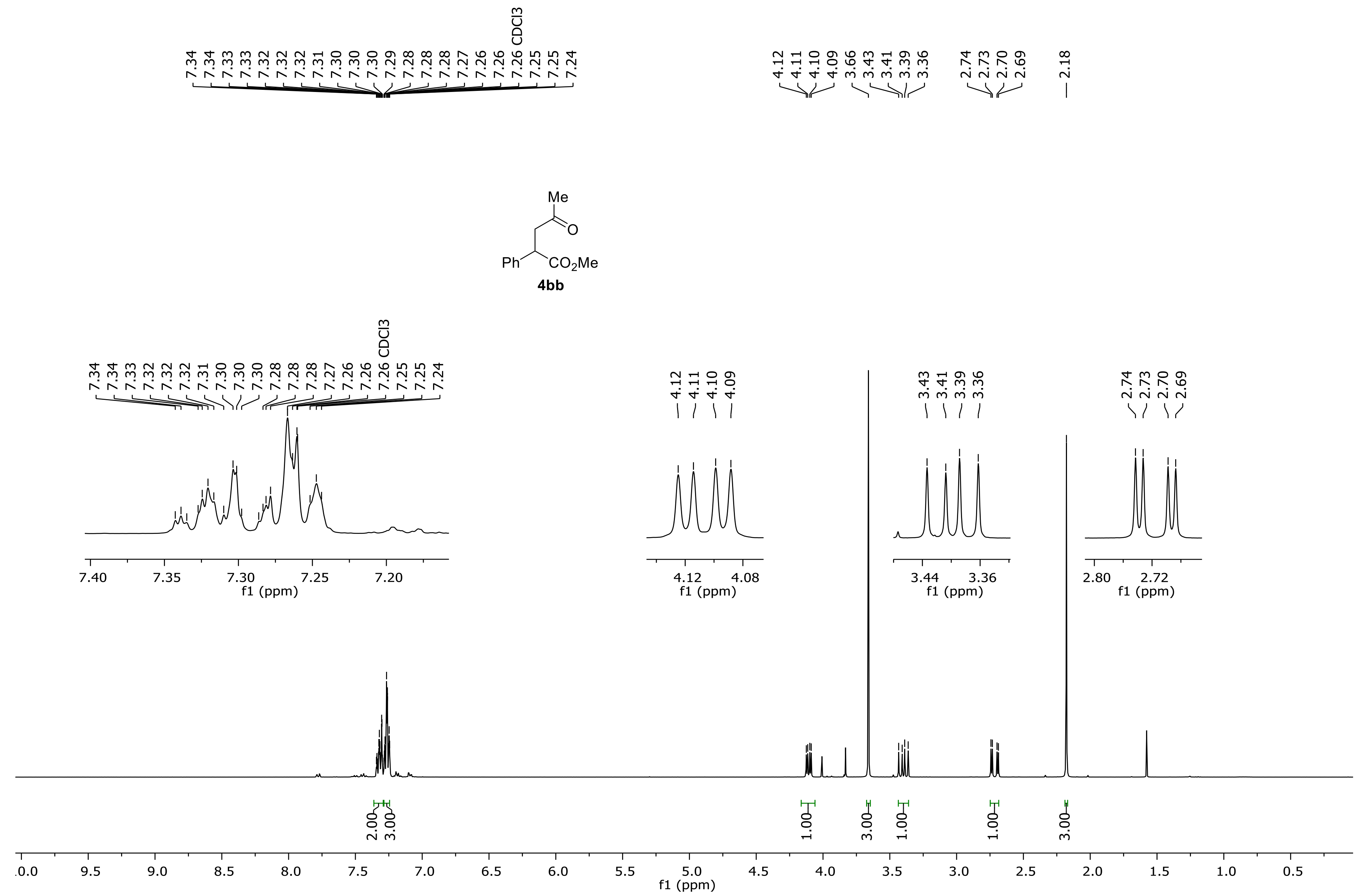
^{1}H NMR of 4aa (CDCl$_3$, 500 MHz)



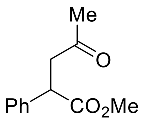
$^{13}C\{^1H\}$ NMR of 4aa ($CDCl_3$, 125 MHz)



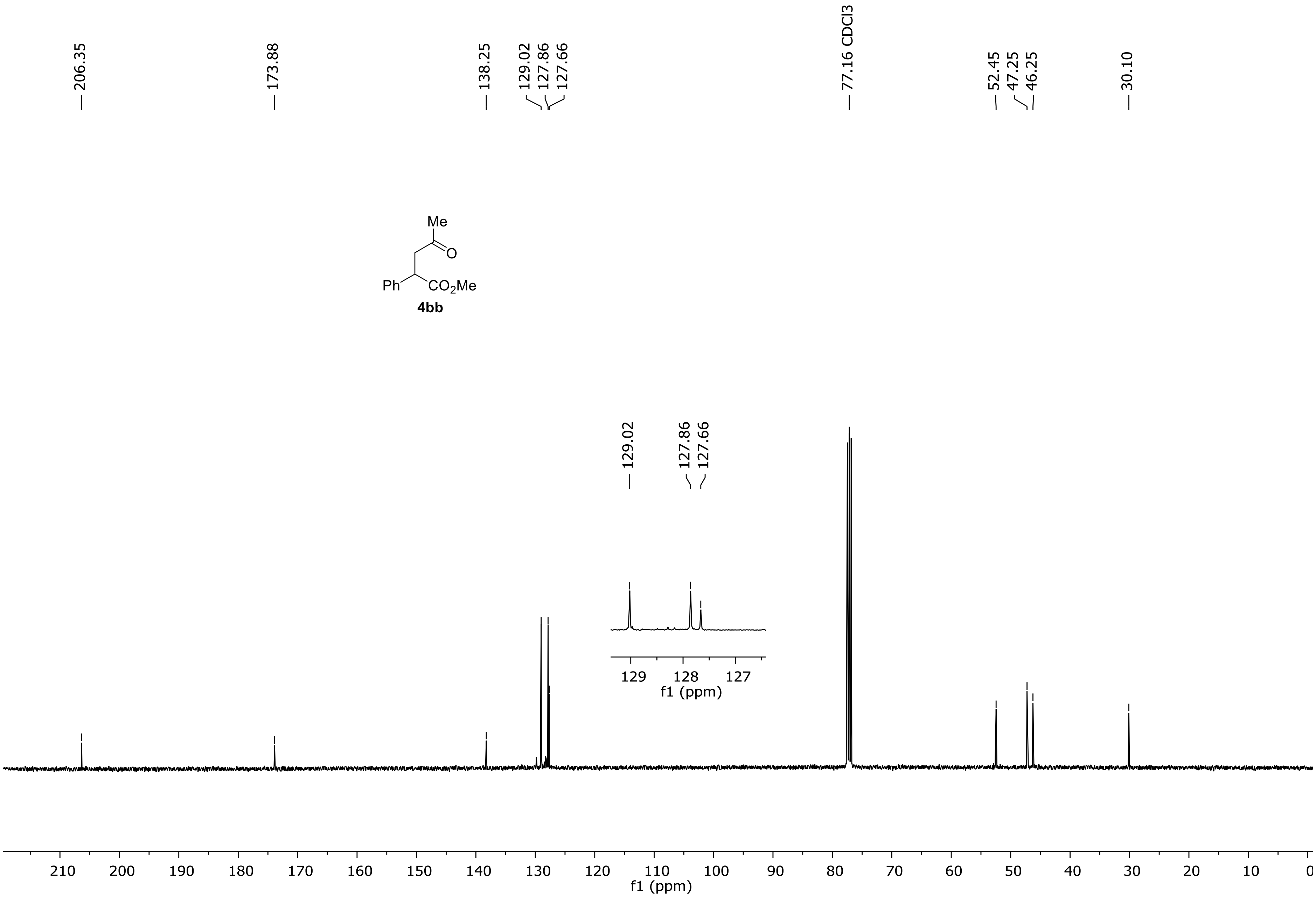
^{1}H NMR of 4bb ($CDCl_3$, 400 MHz)



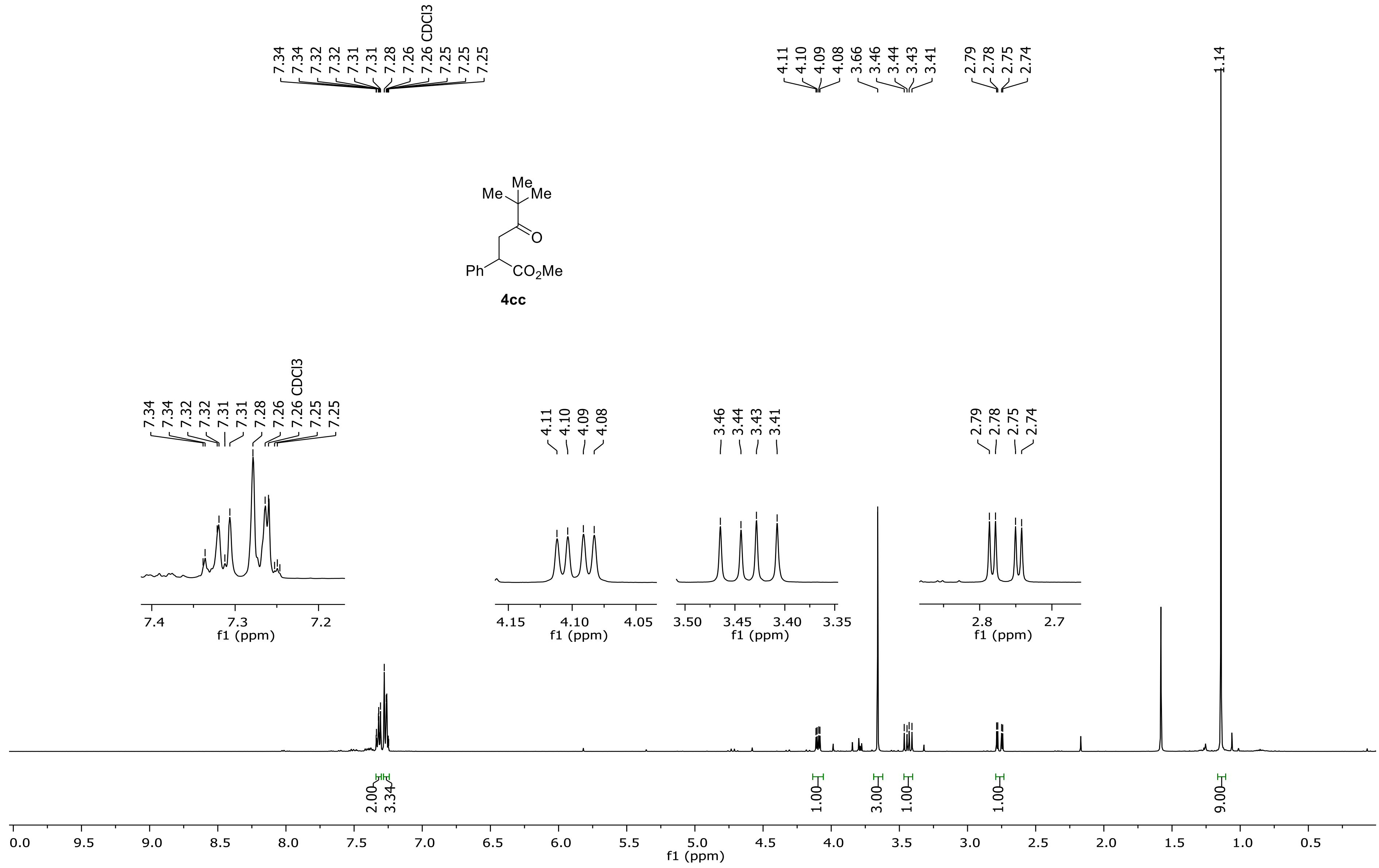
$^{13}C\{^1H\}$ **NMR of 4bb (CDCl$_3$, 100 MHz)**



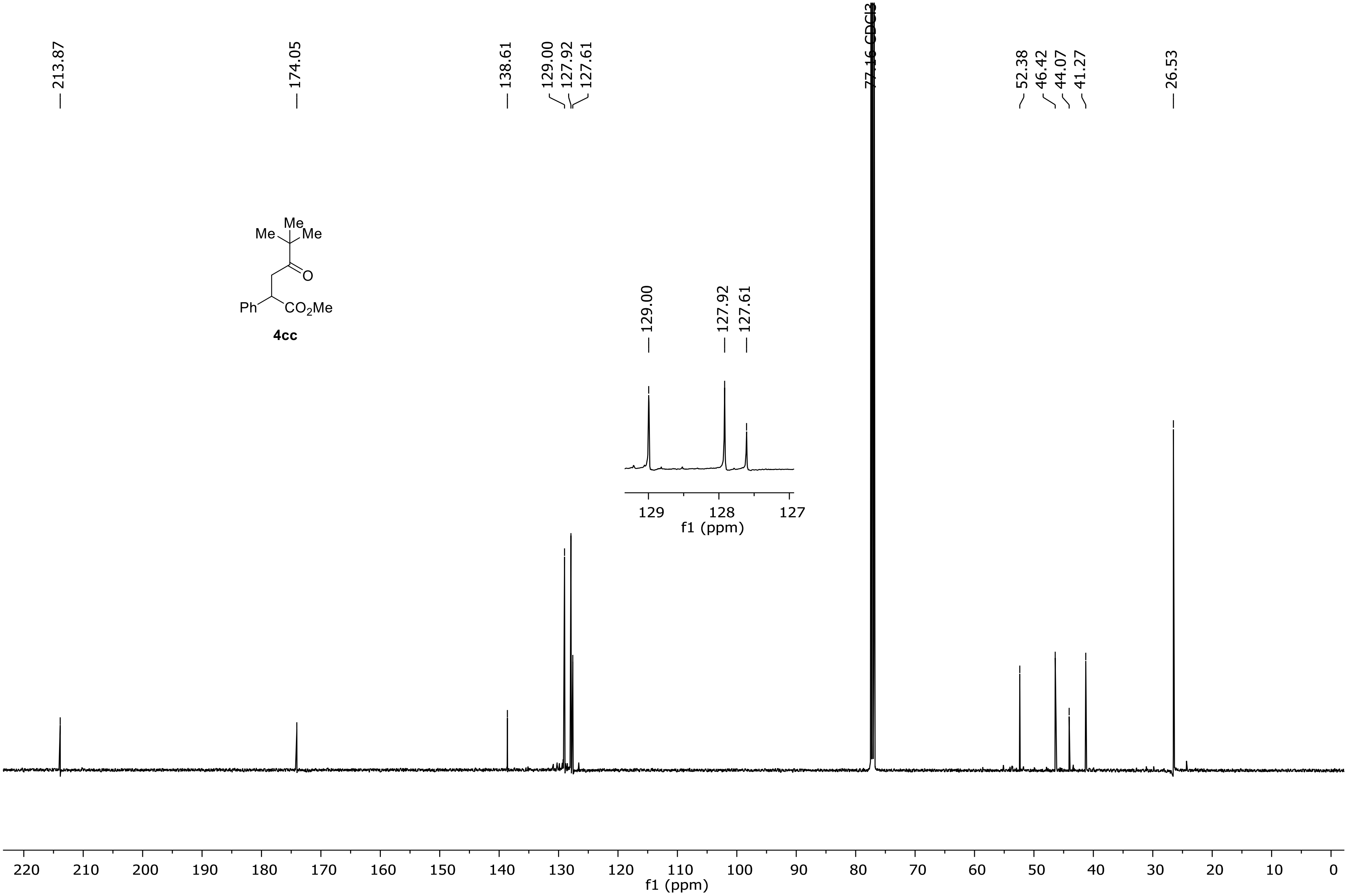
4bb



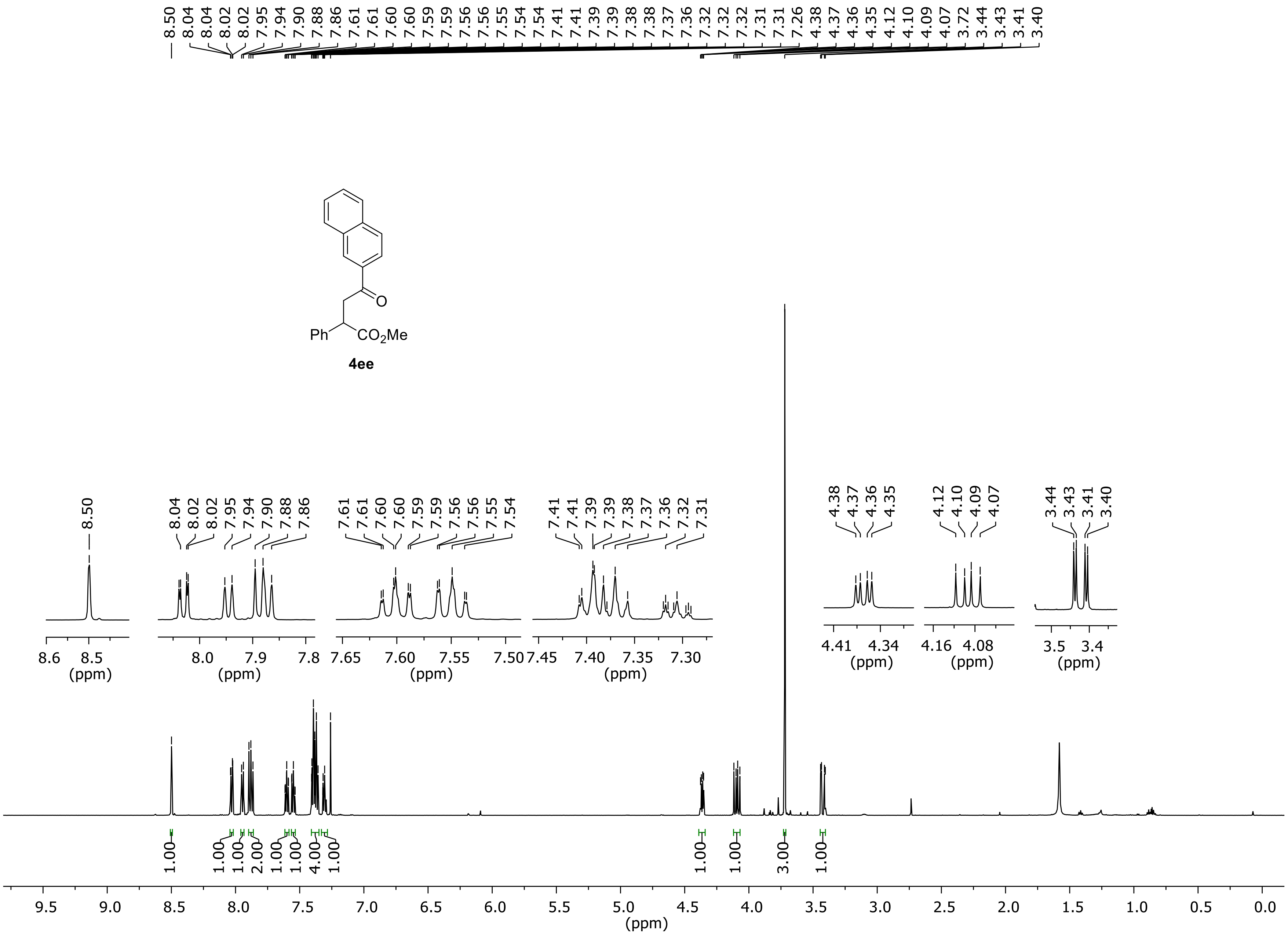
^{1}H NMR of 4cc ($CDCl_3$, 500 MHz)


4cc

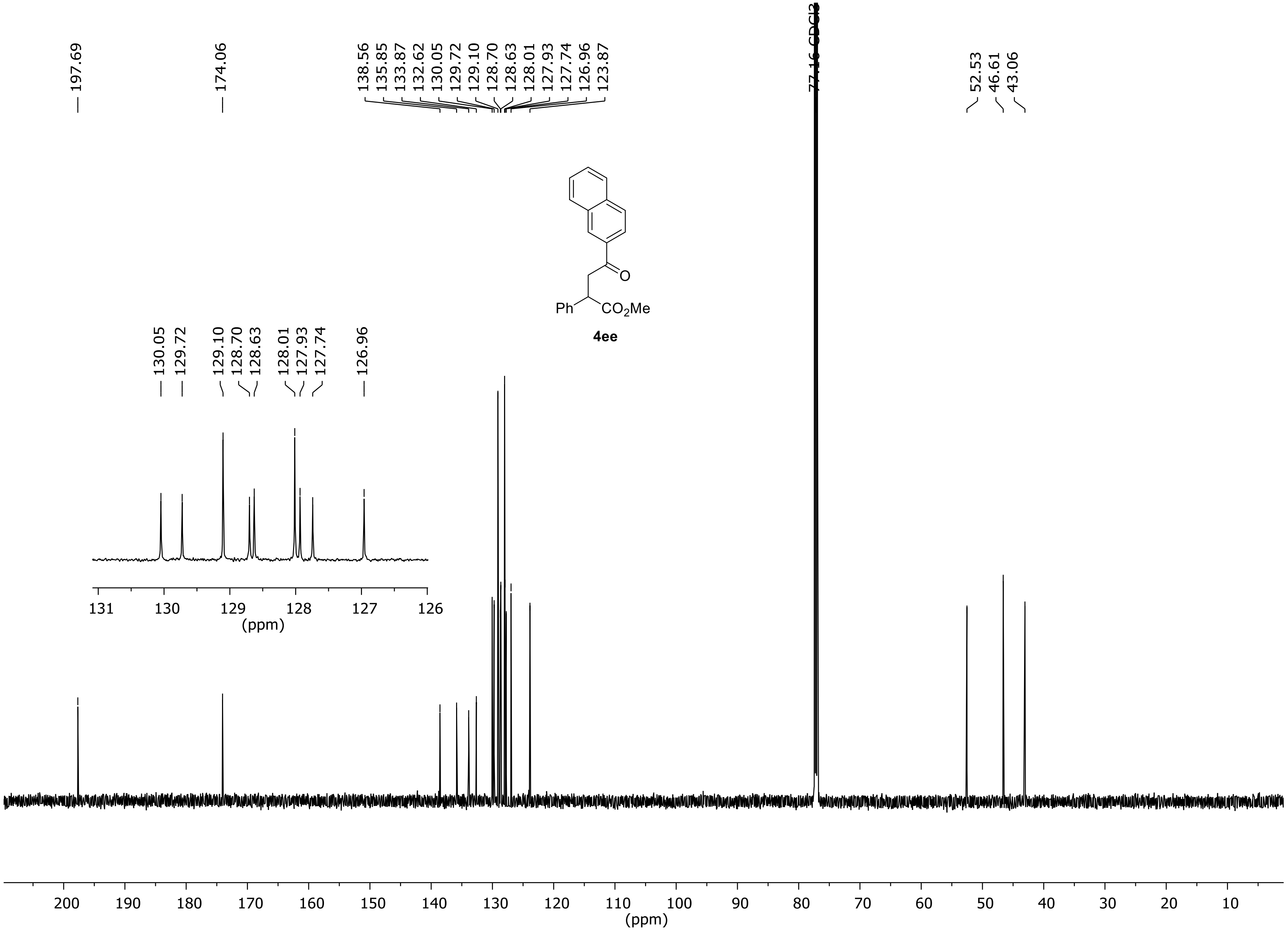
$^{13}C\{^1H\}$ NMR of 4cc ($CDCl_3$, 125 MHz)



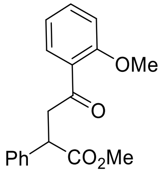
^{1}H NMR of 4ee (CDCl$_3$, 600 MHz)



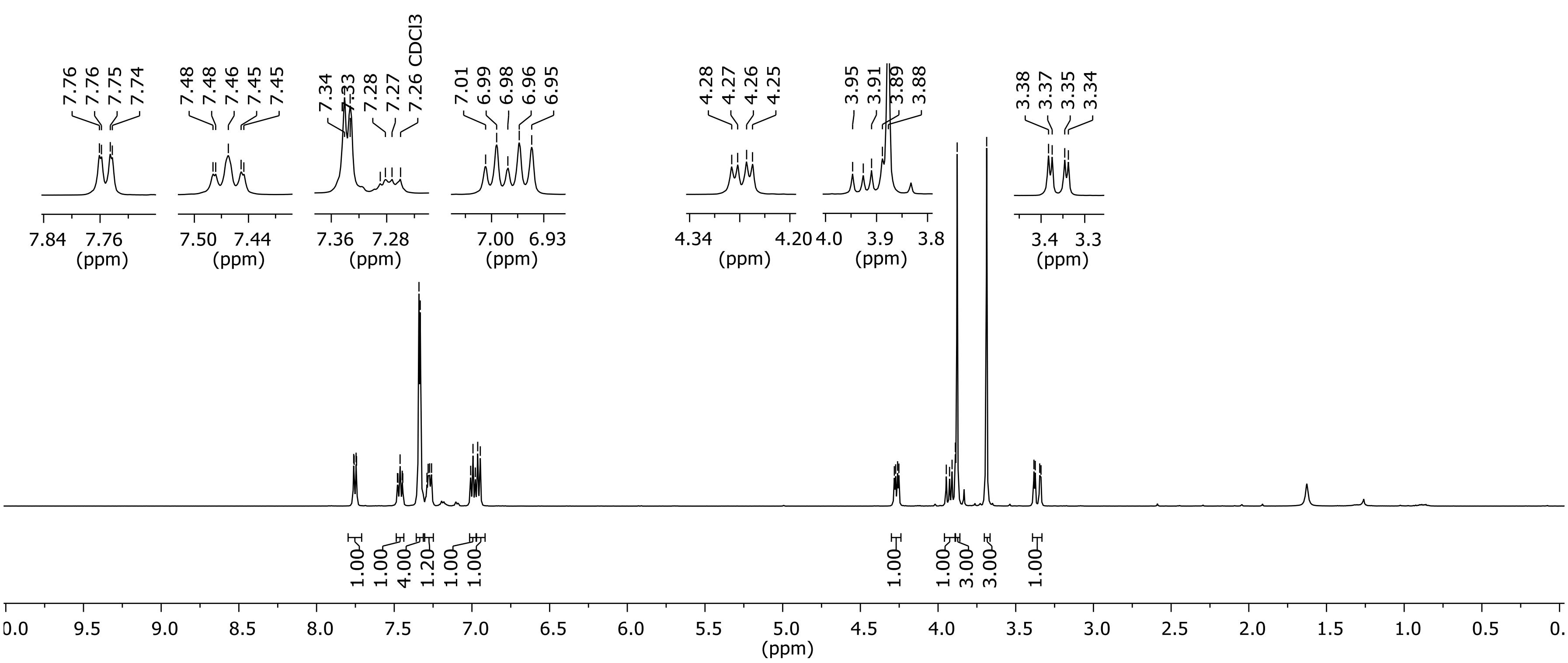
$^{13}C\{^1H\}$ NMR of 4ee ($CDCl_3$, 150 MHz)



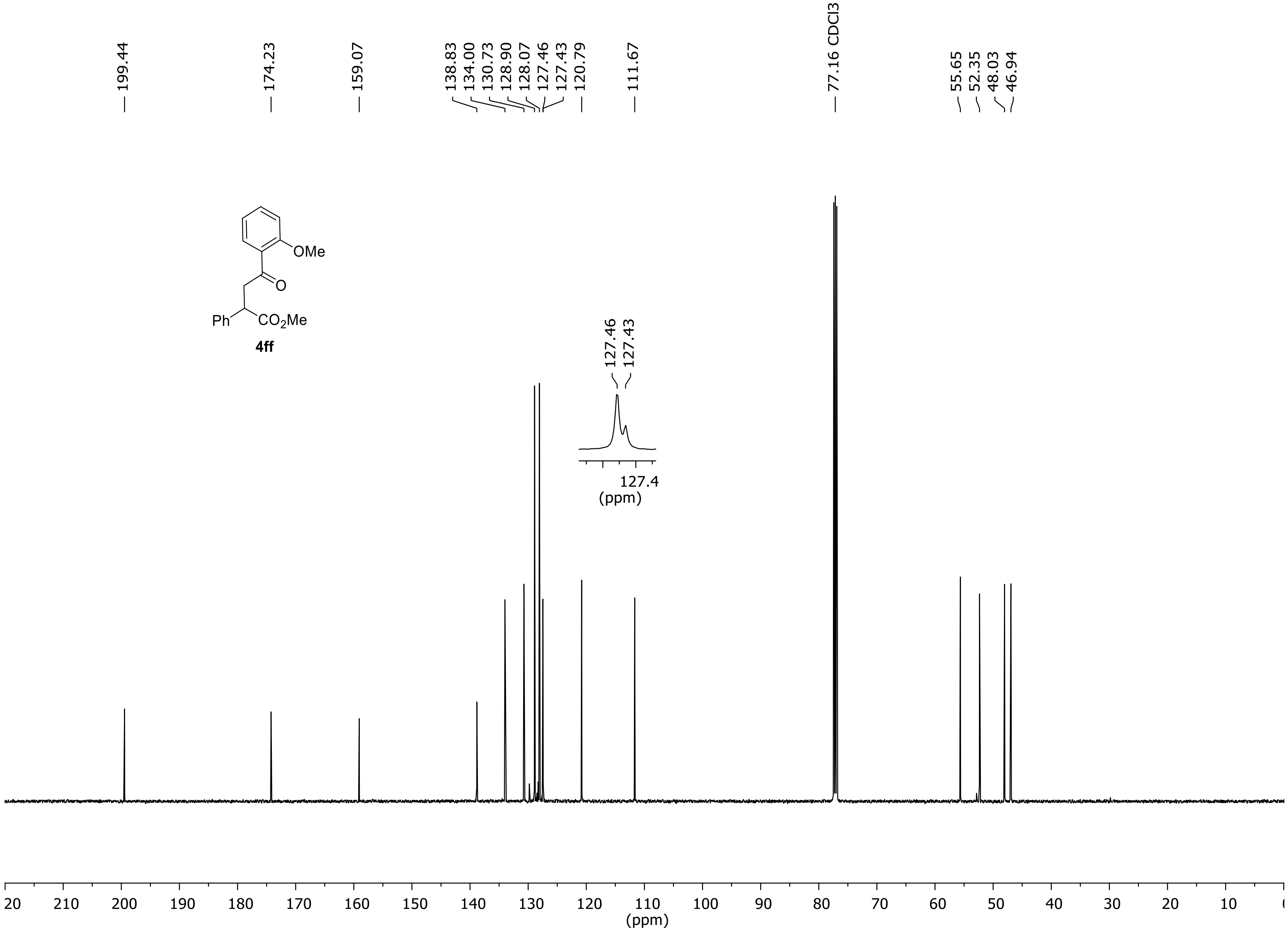
^{1}H NMR of 4ff (CDCl$_3$, 500 MHz)



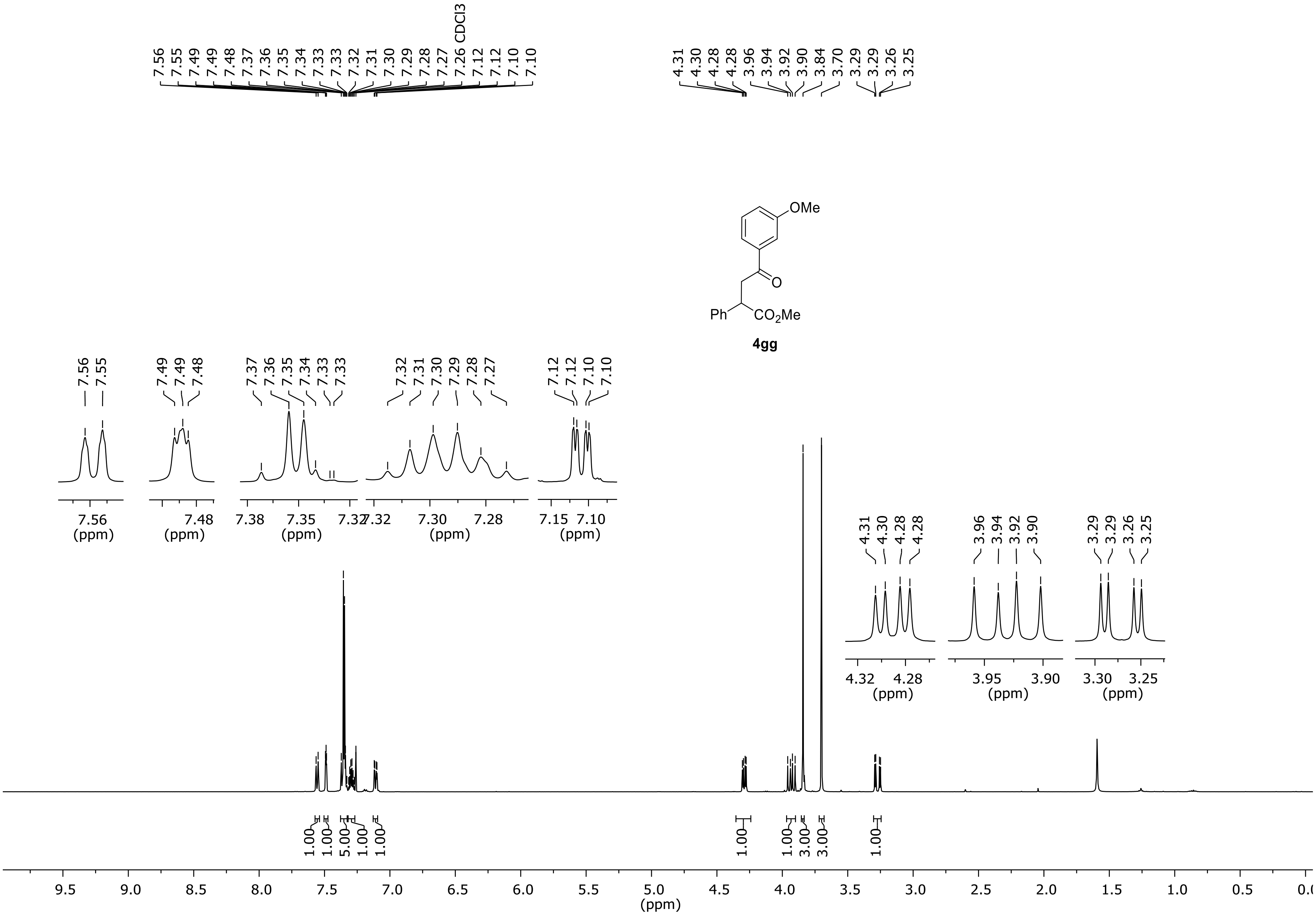
4ff



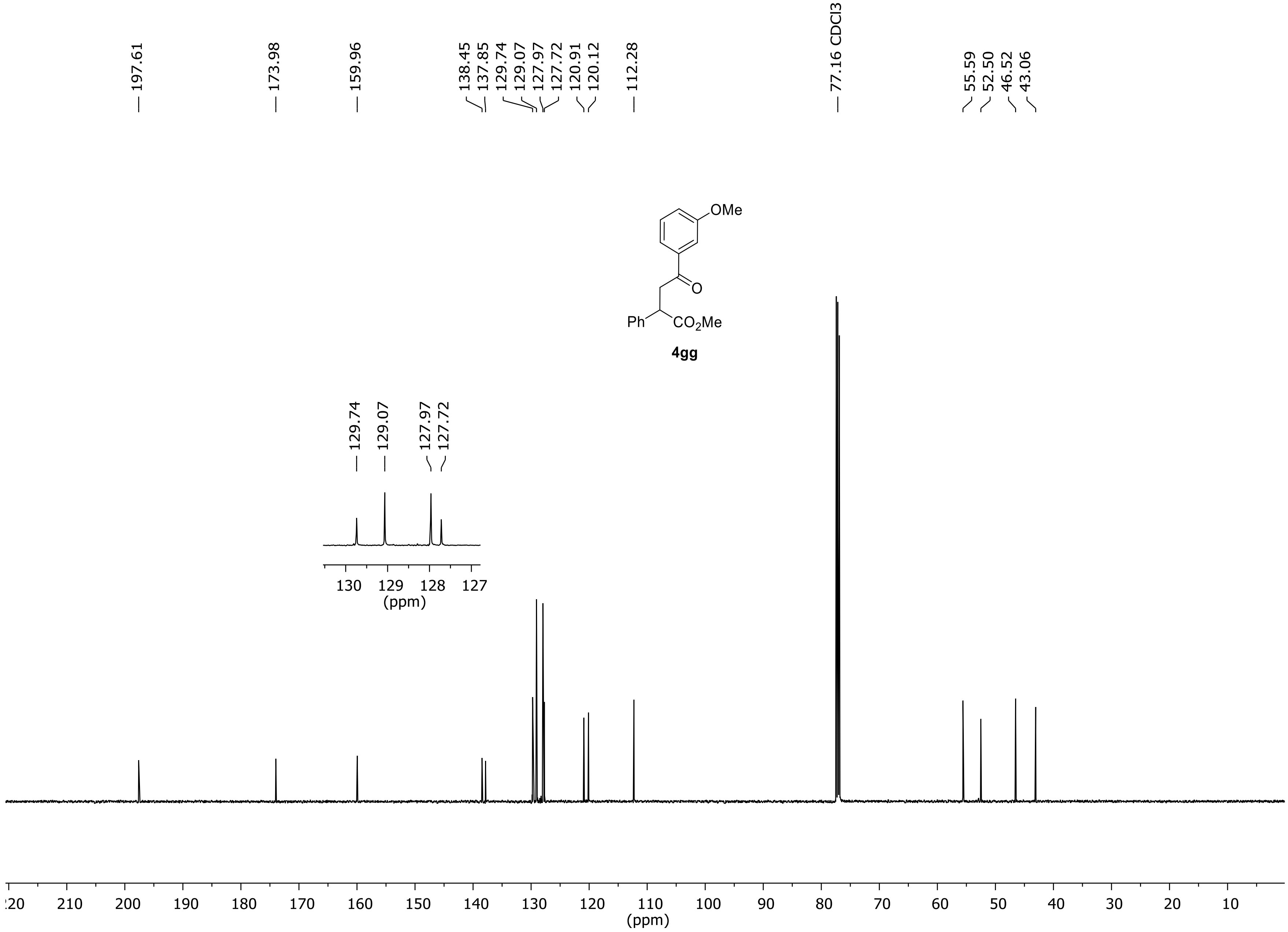
$^{13}C\{^1H\}$ NMR of 4ff ($CDCl_3$, 125 MHz)



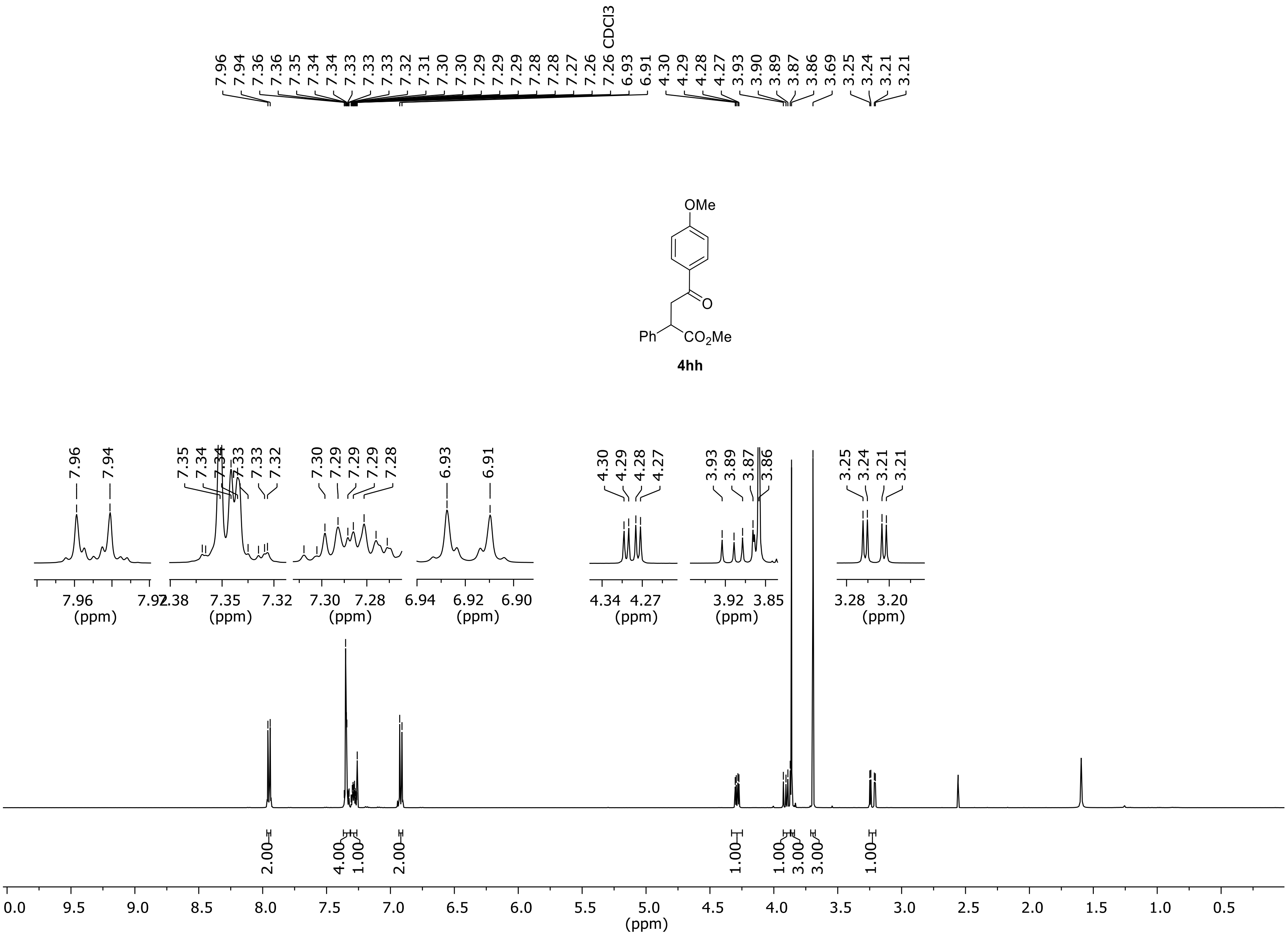
^{1}H NMR of 4gg ($CDCl_3$, 500 MHz)



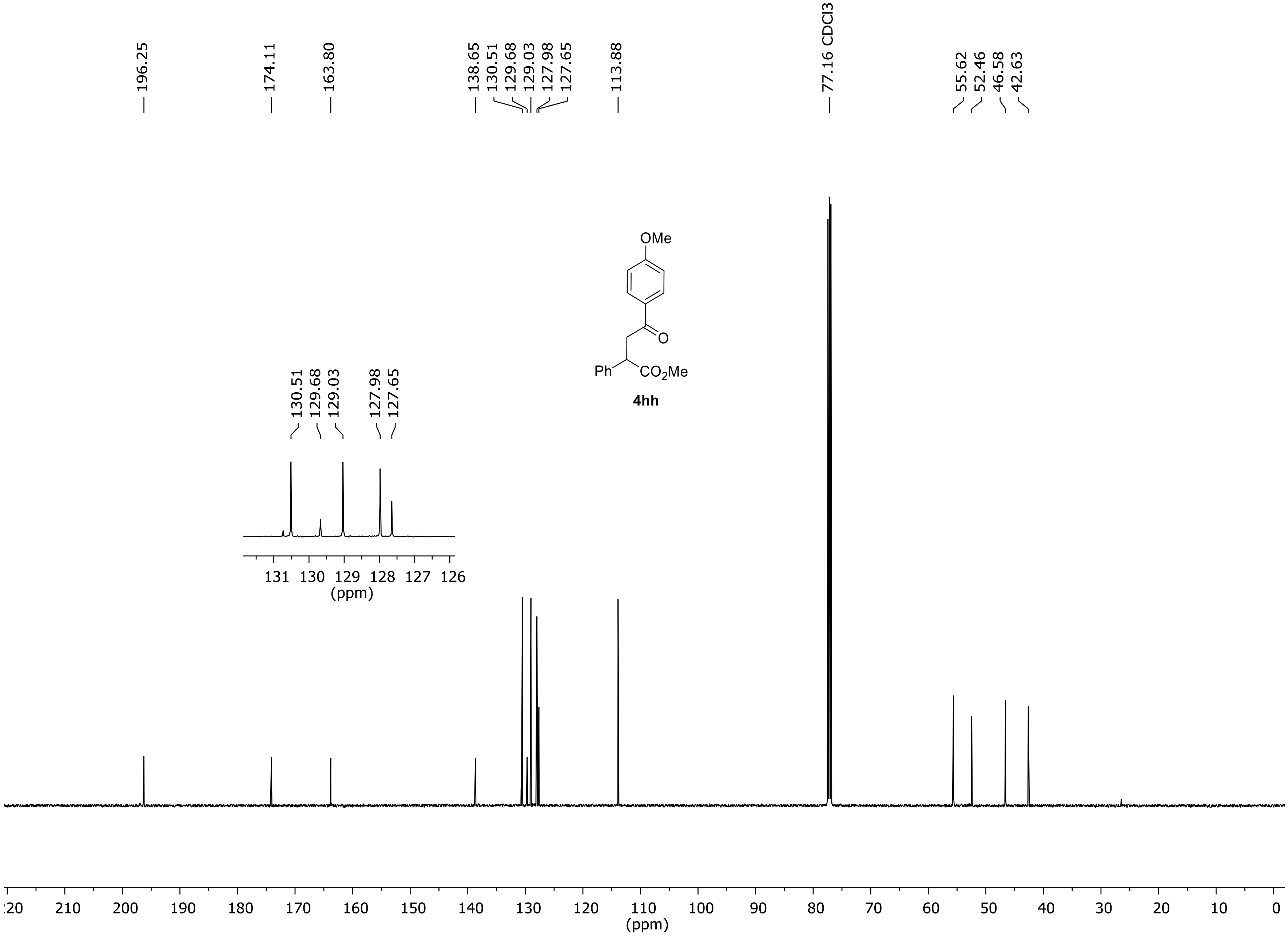
$^{13}C\{^{1}H\}$ NMR of 4gg ($CDCl_3$, 125 MHz)



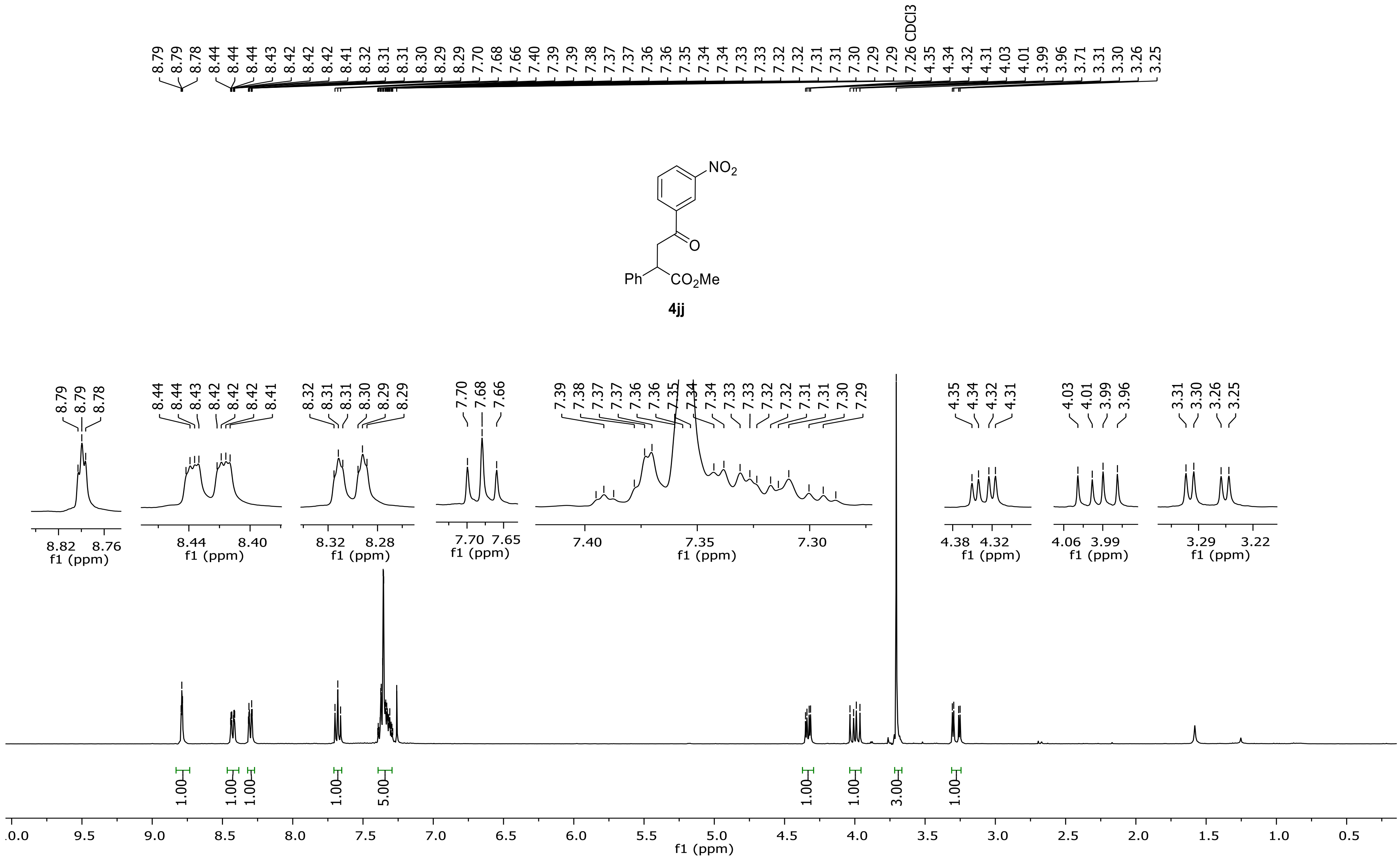
^{1}H NMR of 4hh (CDCl$_3$, 500 MHz)



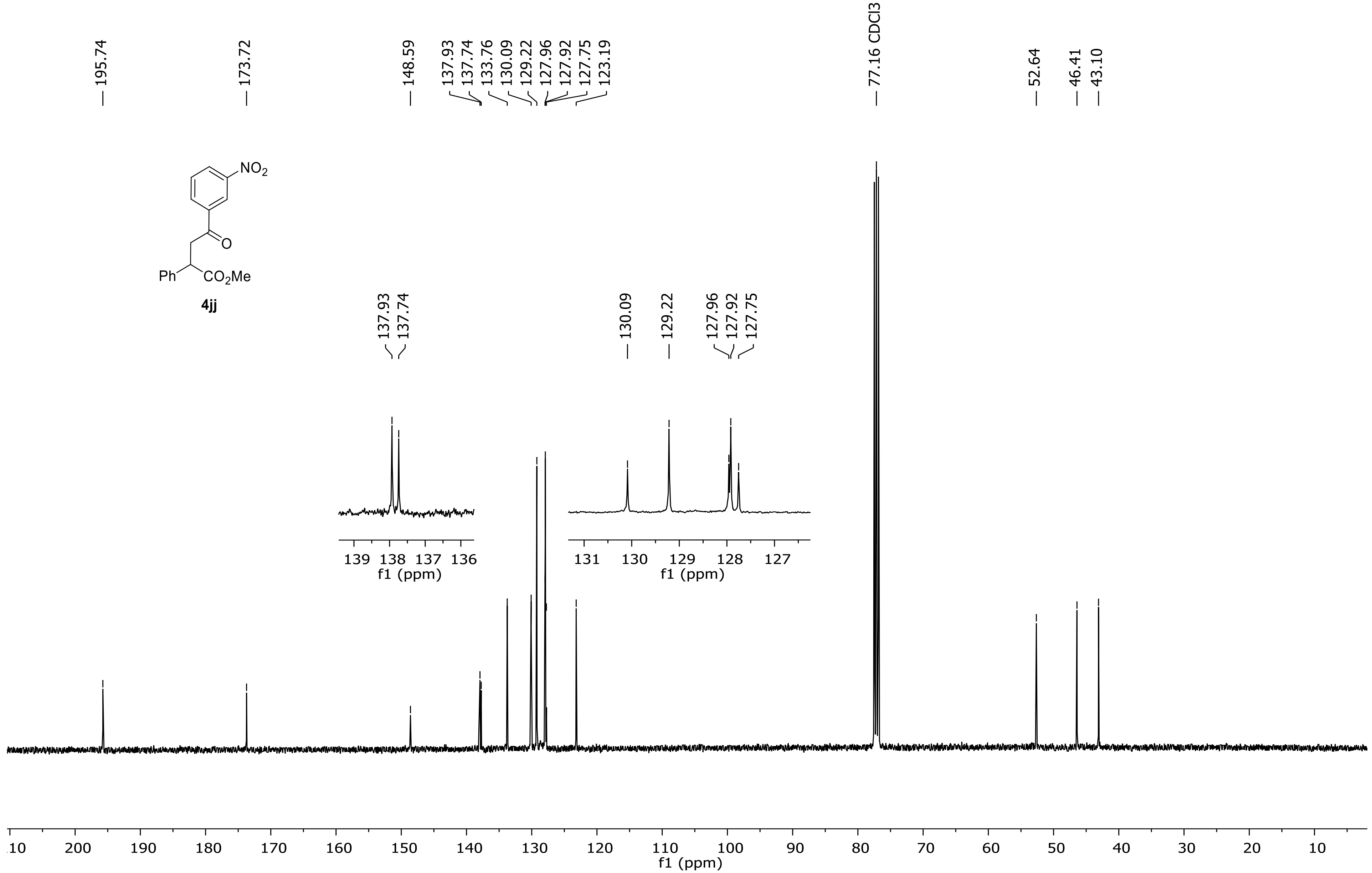
$^{13}C\{^1H\}$ NMR of 4hh (CDCl$_3$, 125 MHz)



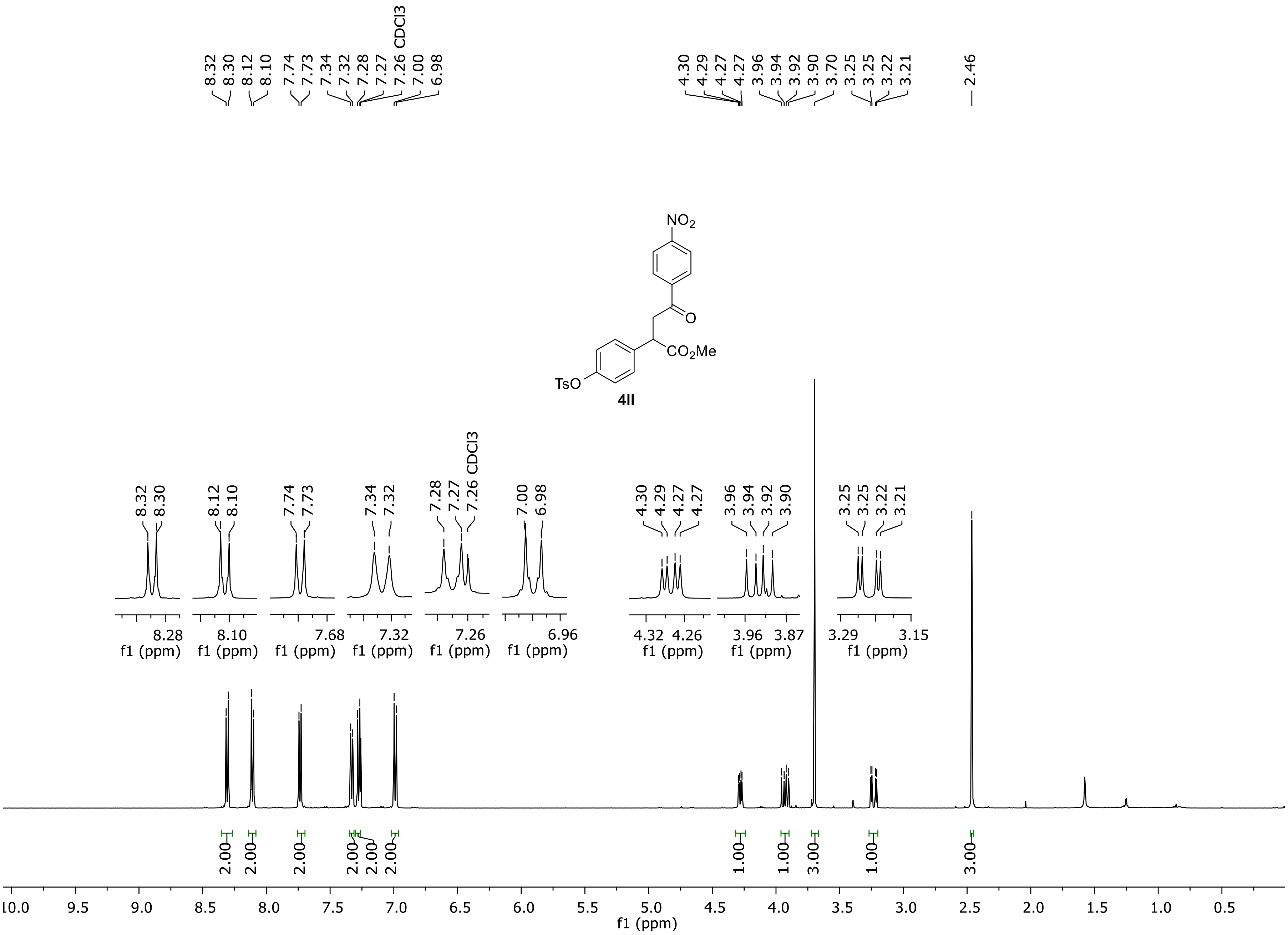
^{1}H NMR of 4jj (CDCl$_3$, 400 MHz)



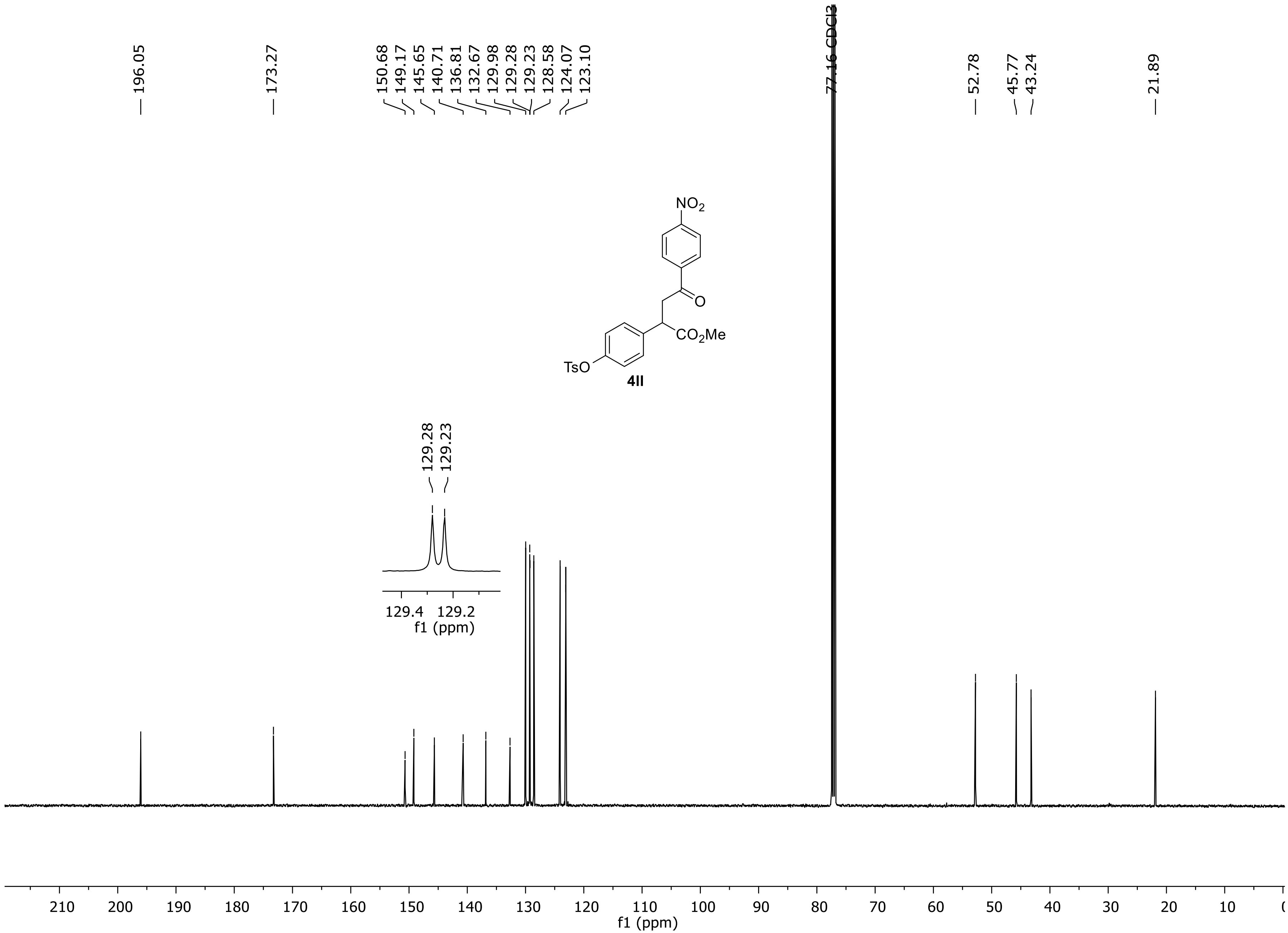
$^{13}C\{^1H\}$ NMR of 4jj ($CDCl_3$, 100 MHz)



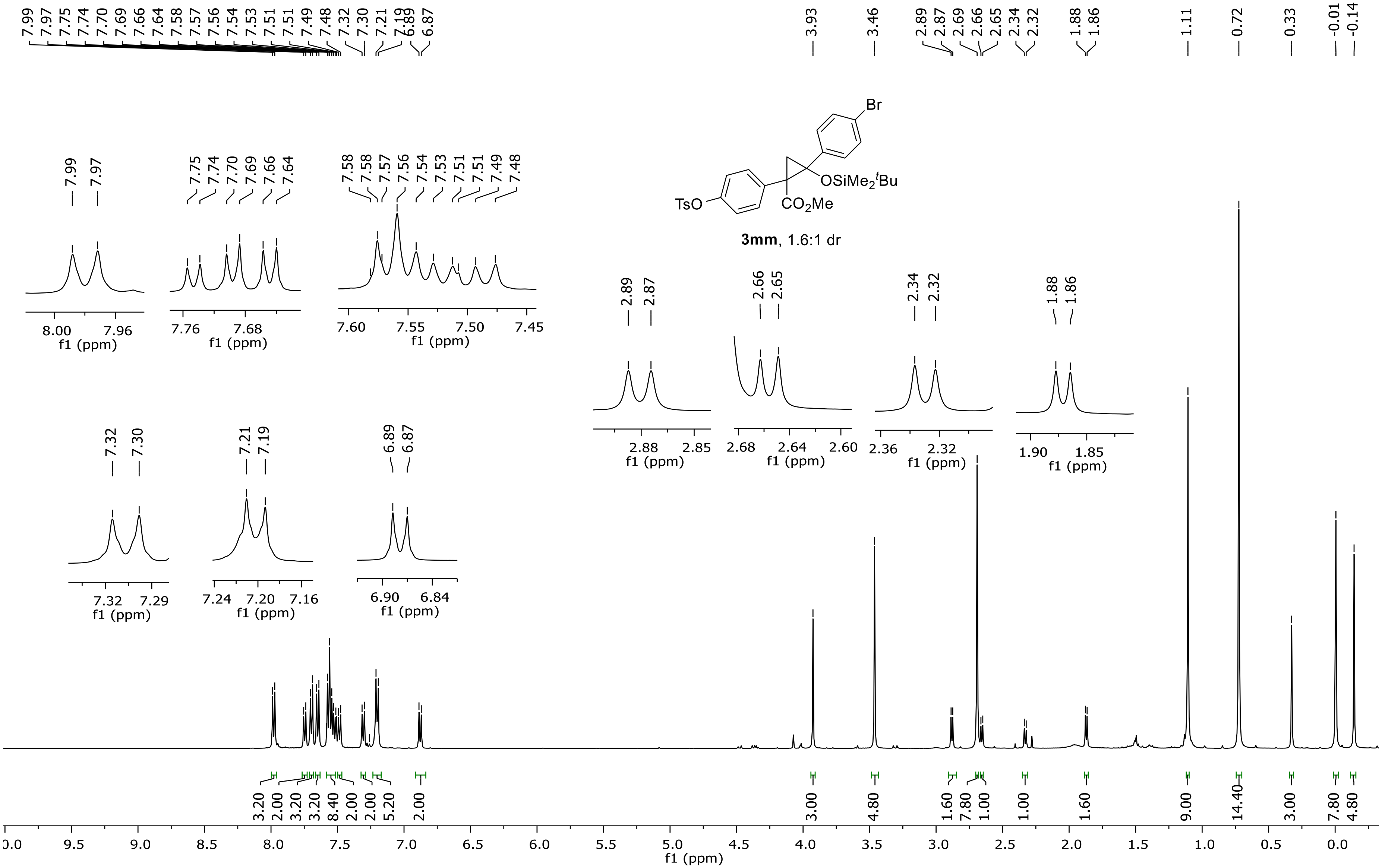
^{1}H NMR of 4ll ($CDCl_3$, 500 MHz)



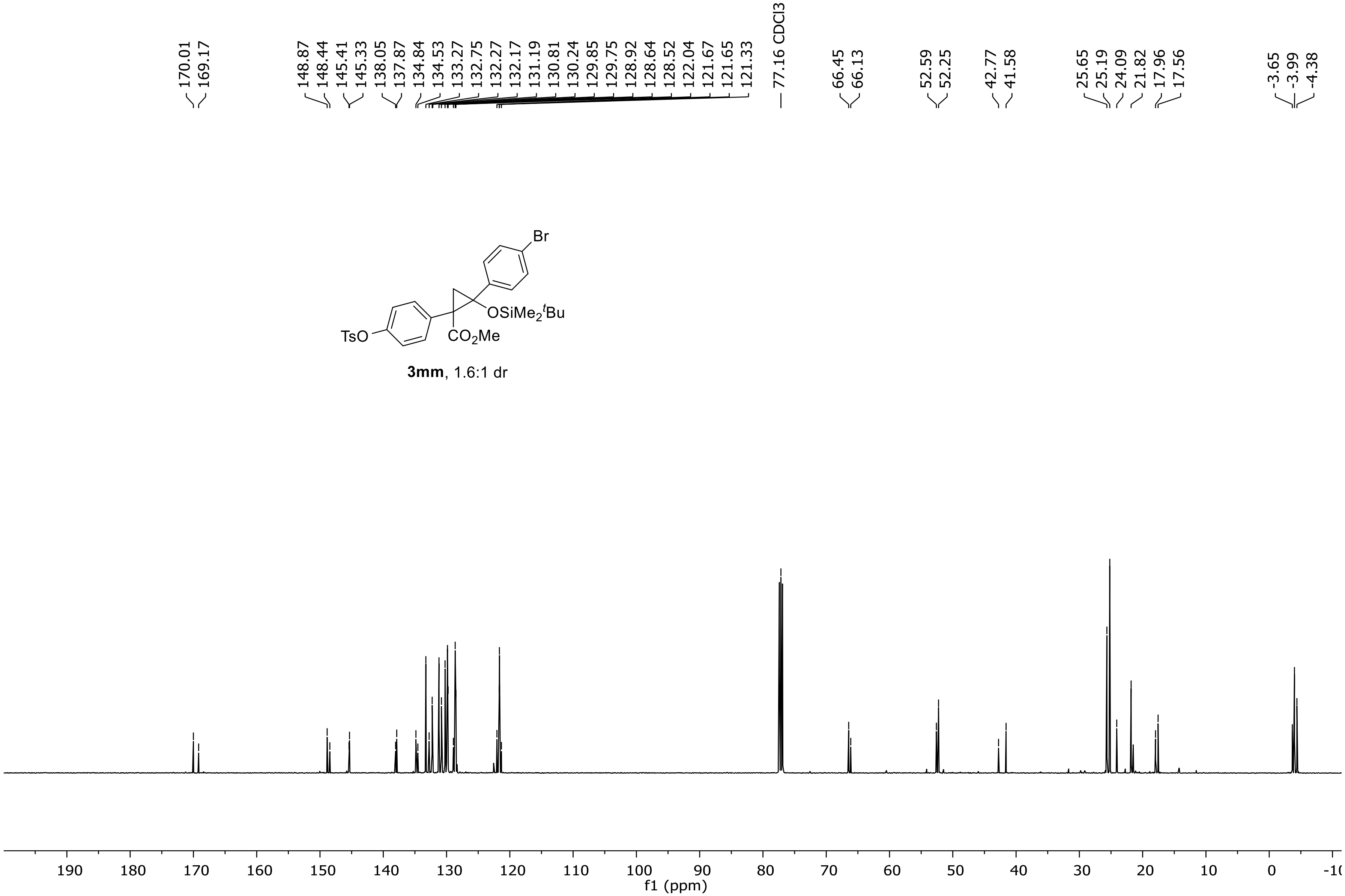
$^{13}C\{^1H\}$ NMR of 4ll ($CDCl_3$, 125 MHz)



^{1}H NMR of 3mm (CDCl$_3$, 500 MHz)

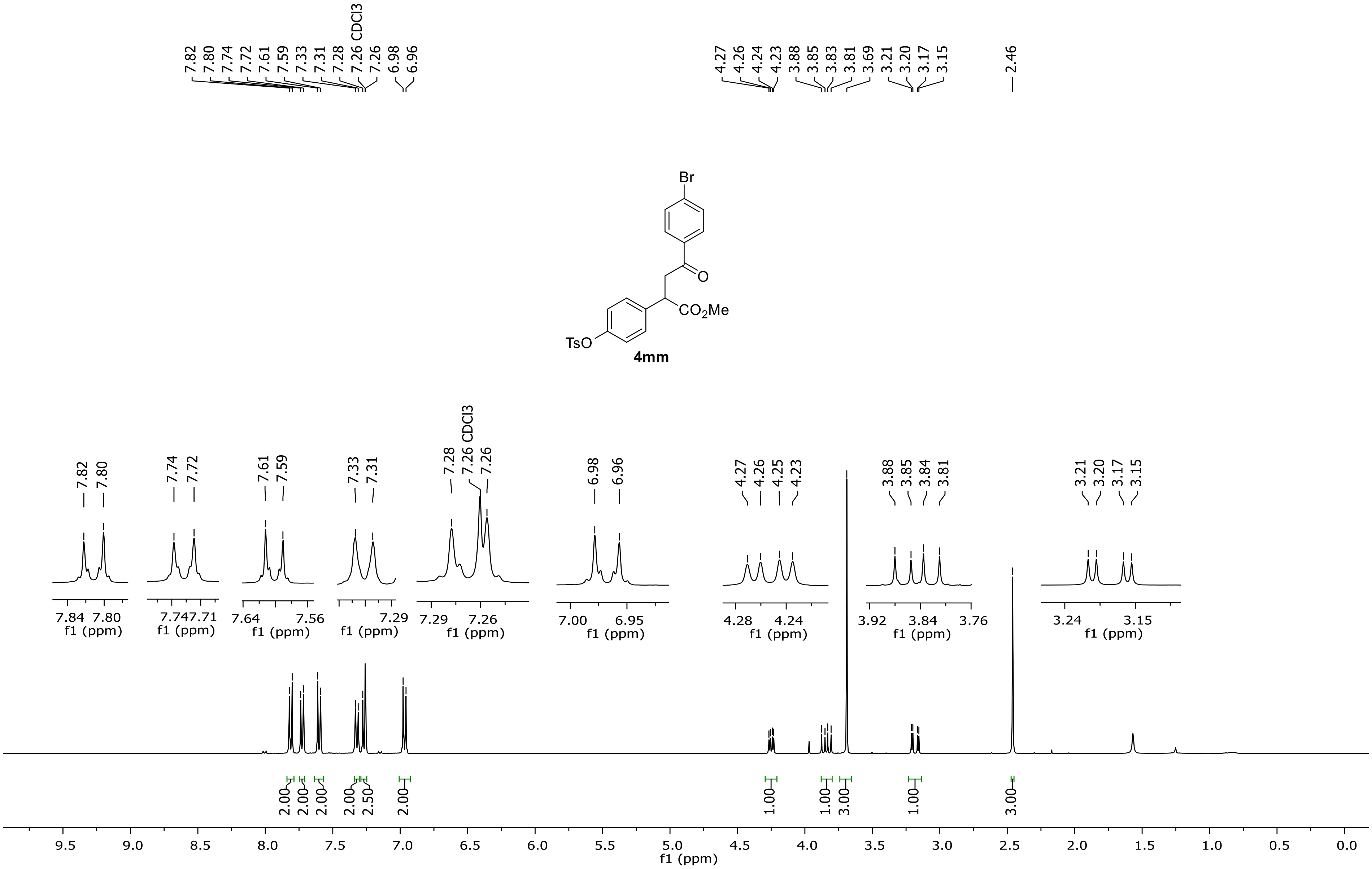

3mm, 1.6:1 dr

$^{13}C\{^1H\}$ NMR of 3mm ($CDCl_3$, 125 MHz)



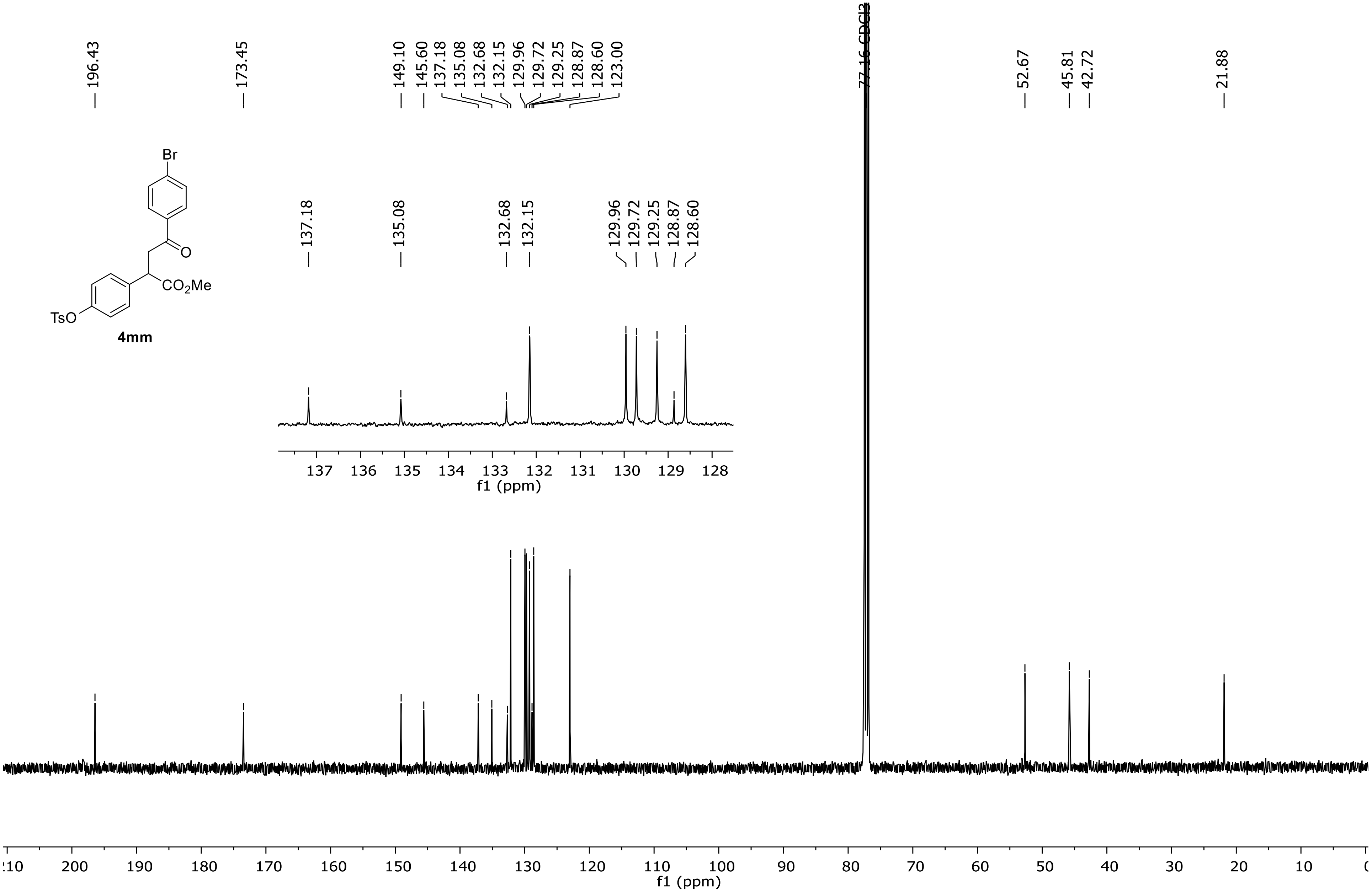
3mm, 1.6:1 dr

^{1}H NMR of 4mm ($CDCl_3$, 500 MHz)

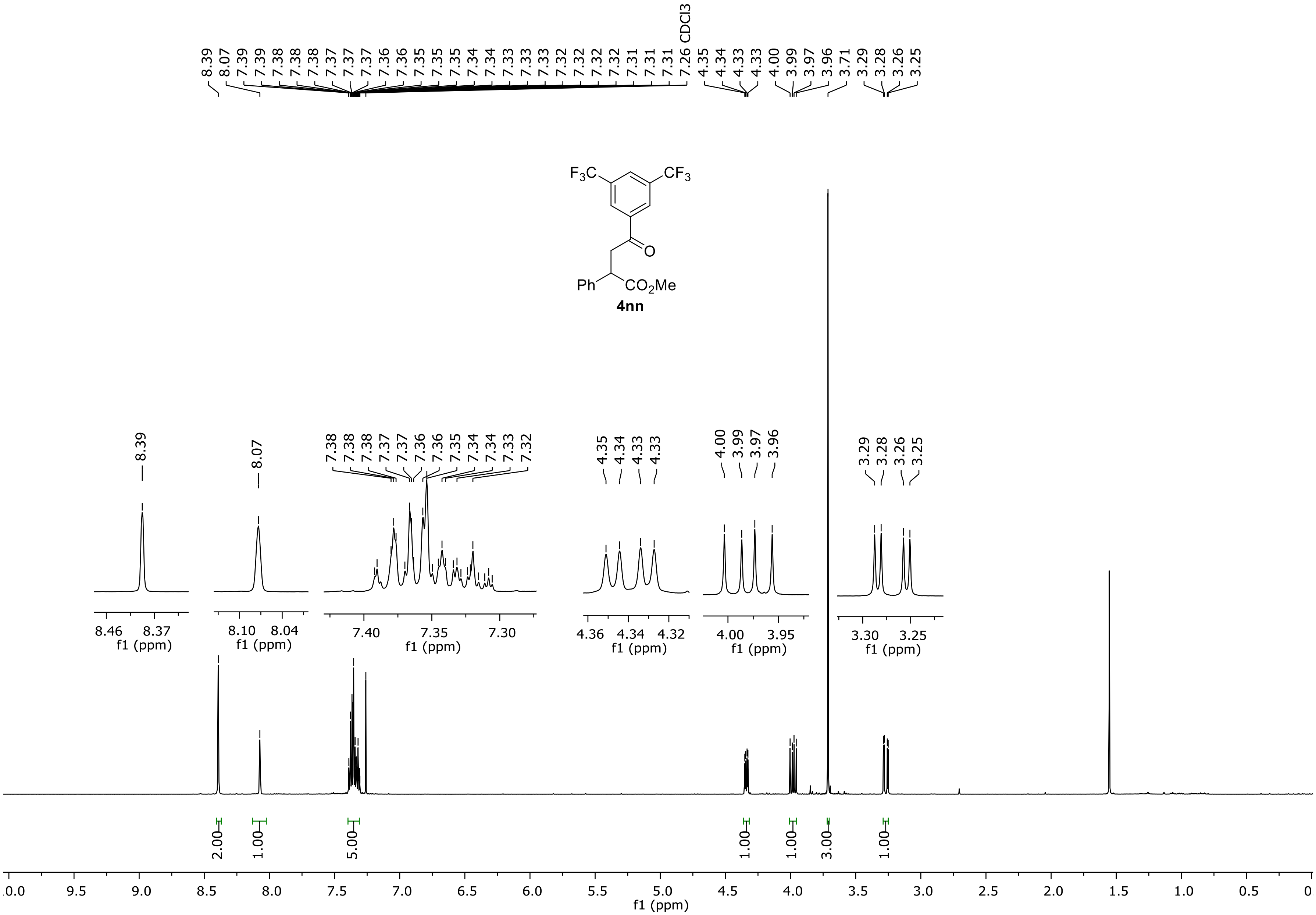


4mm

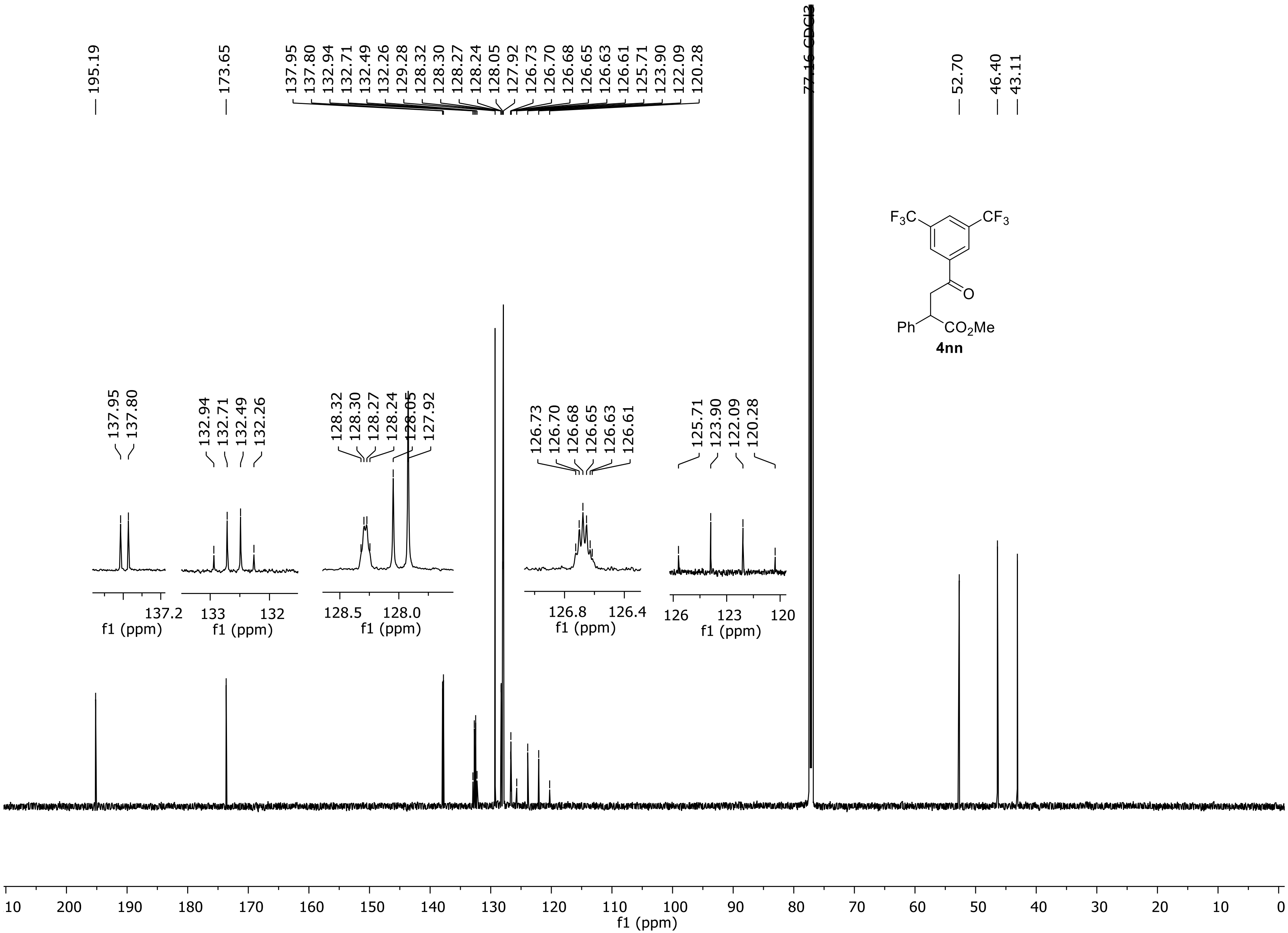
$^{13}C\{^1H\}$ NMR of 4mm ($CDCl_3$, 125 MHz)



^{1}H NMR of 4nn (CDCl$_3$, 600 MHz)

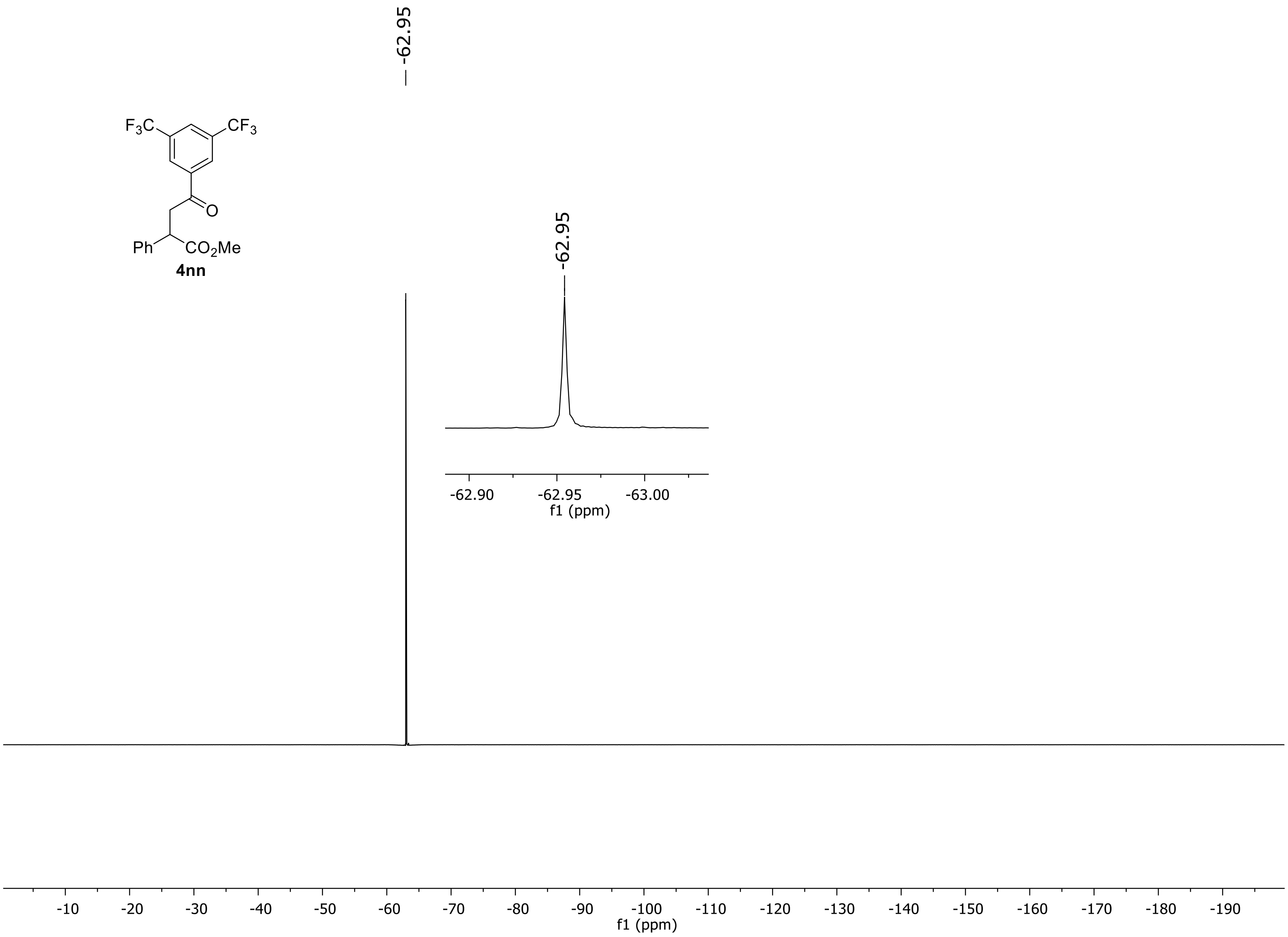


$^{13}C\{^{1}H\}$ NMR of 4nn ($CDCl_3$, 150 MHz)

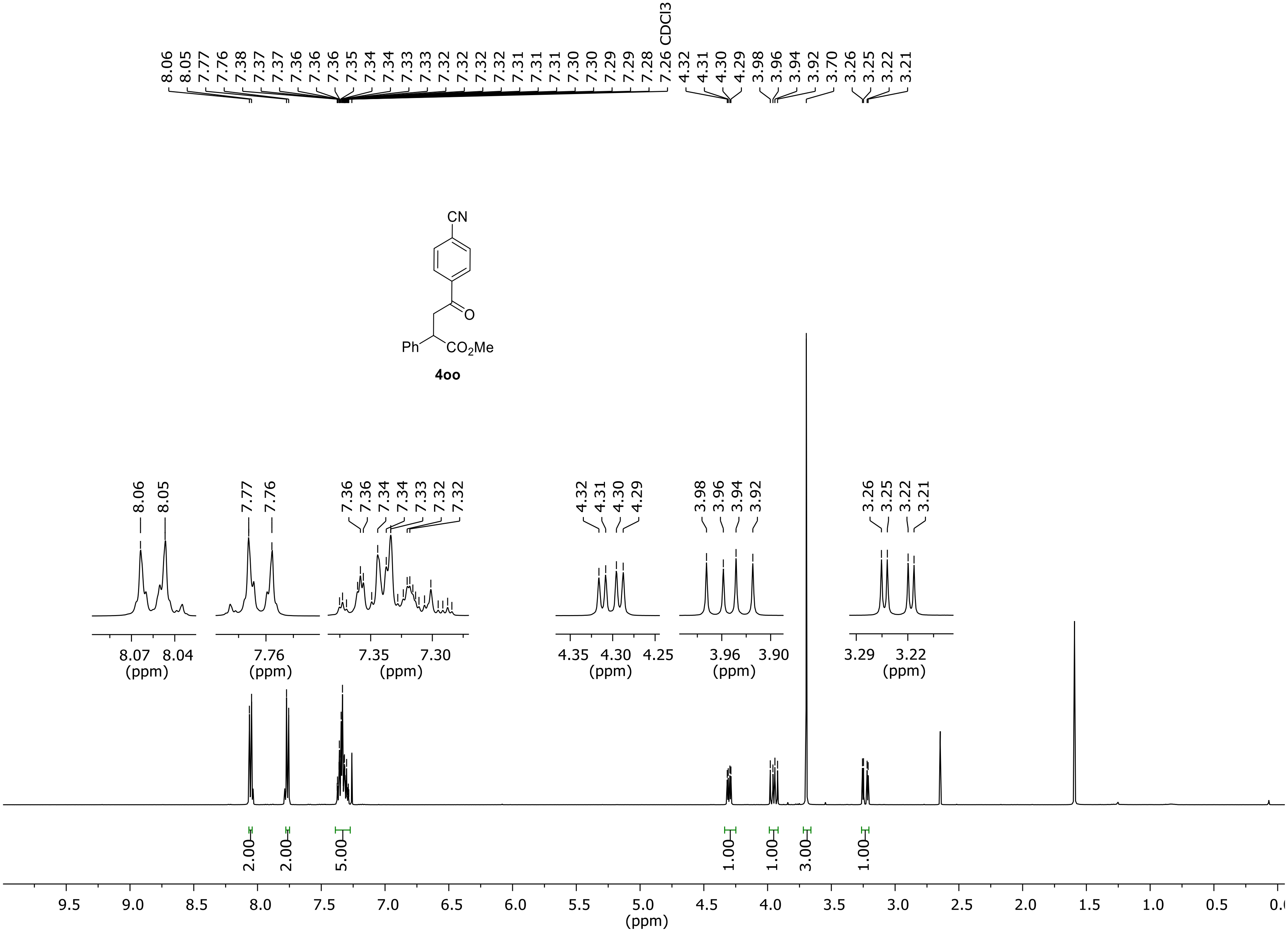


$^{19}F\{^{1}H\}$ NMR of 4nn ($CDCl_3$, 564 MHz)

4nn

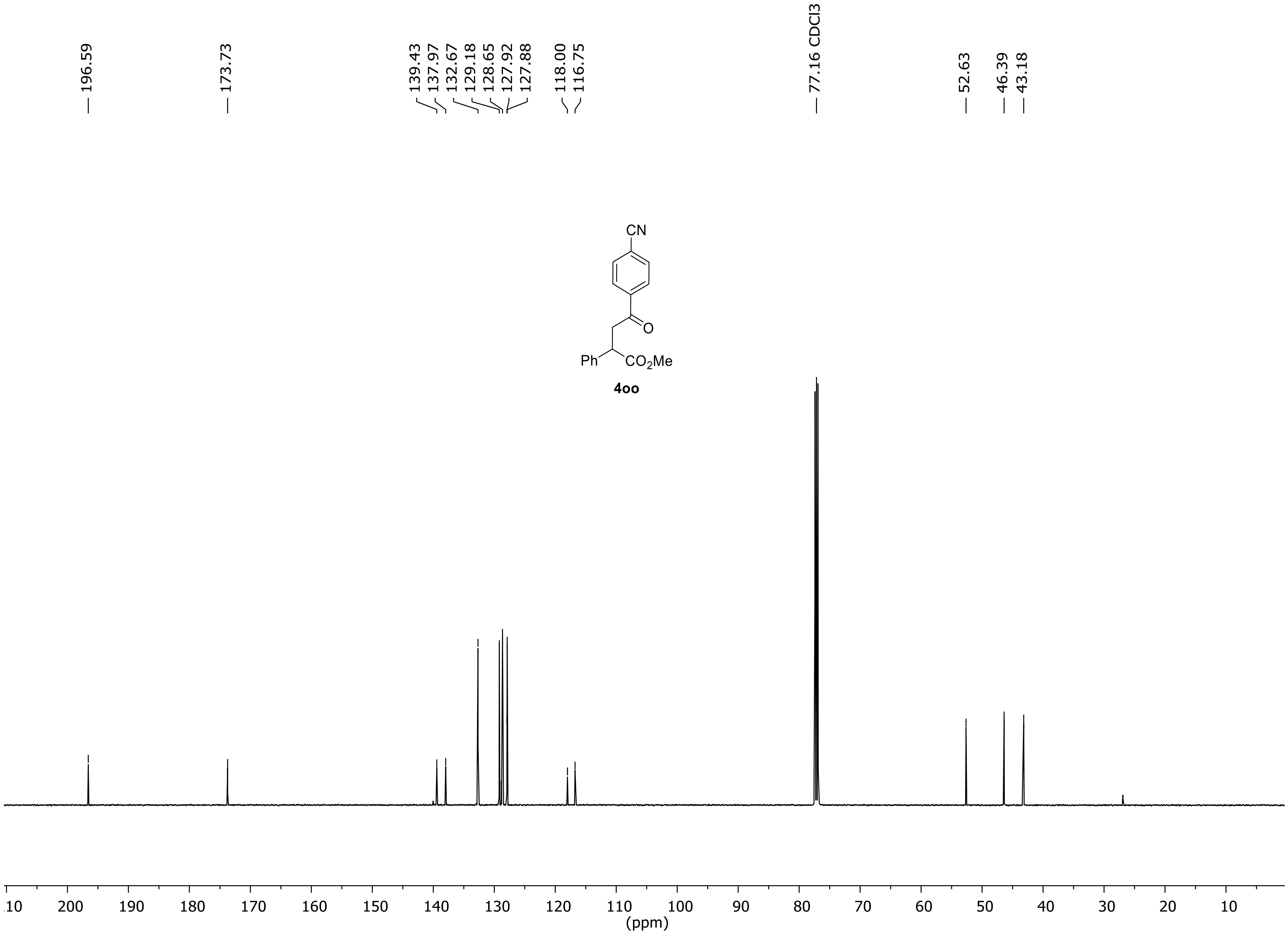


^{1}H NMR of 4oo (CDCl$_3$, 600 MHz)

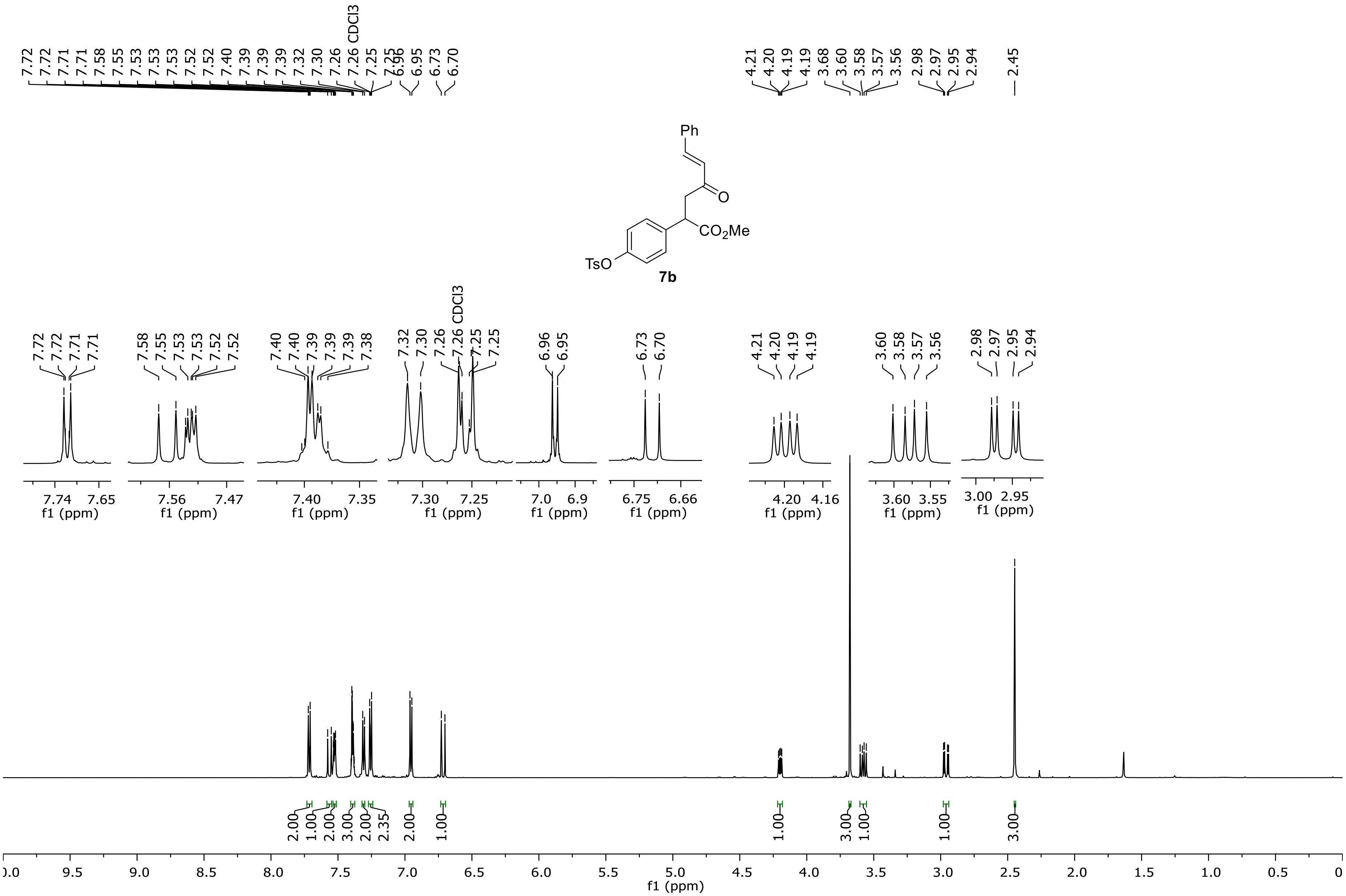


4oo

$^{13}C\{^1H\}$ NMR of 4oo ($CDCl_3$, 150 MHz)

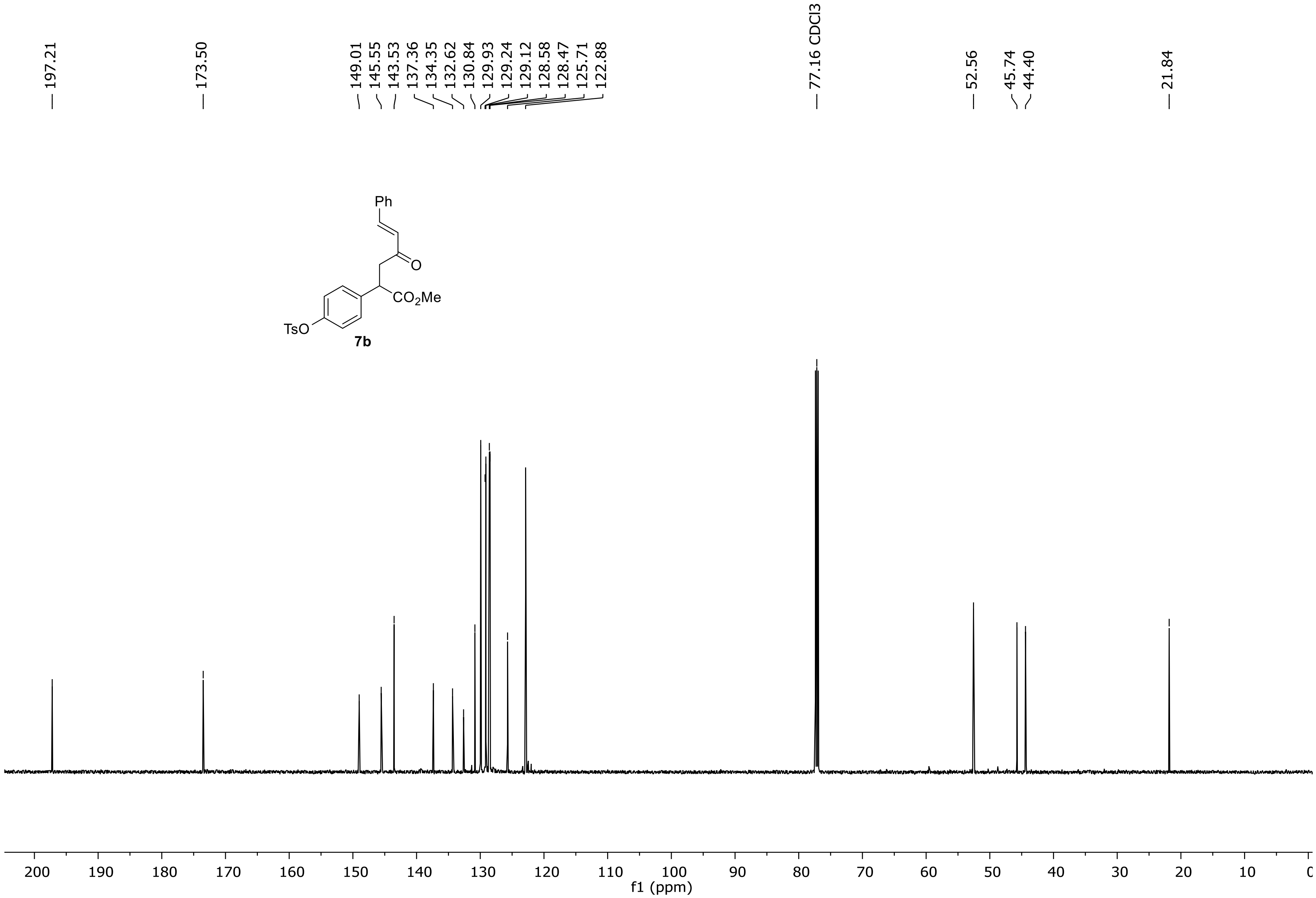


^1H NMR of 7b ($CDCl_3$, 600 MHz)

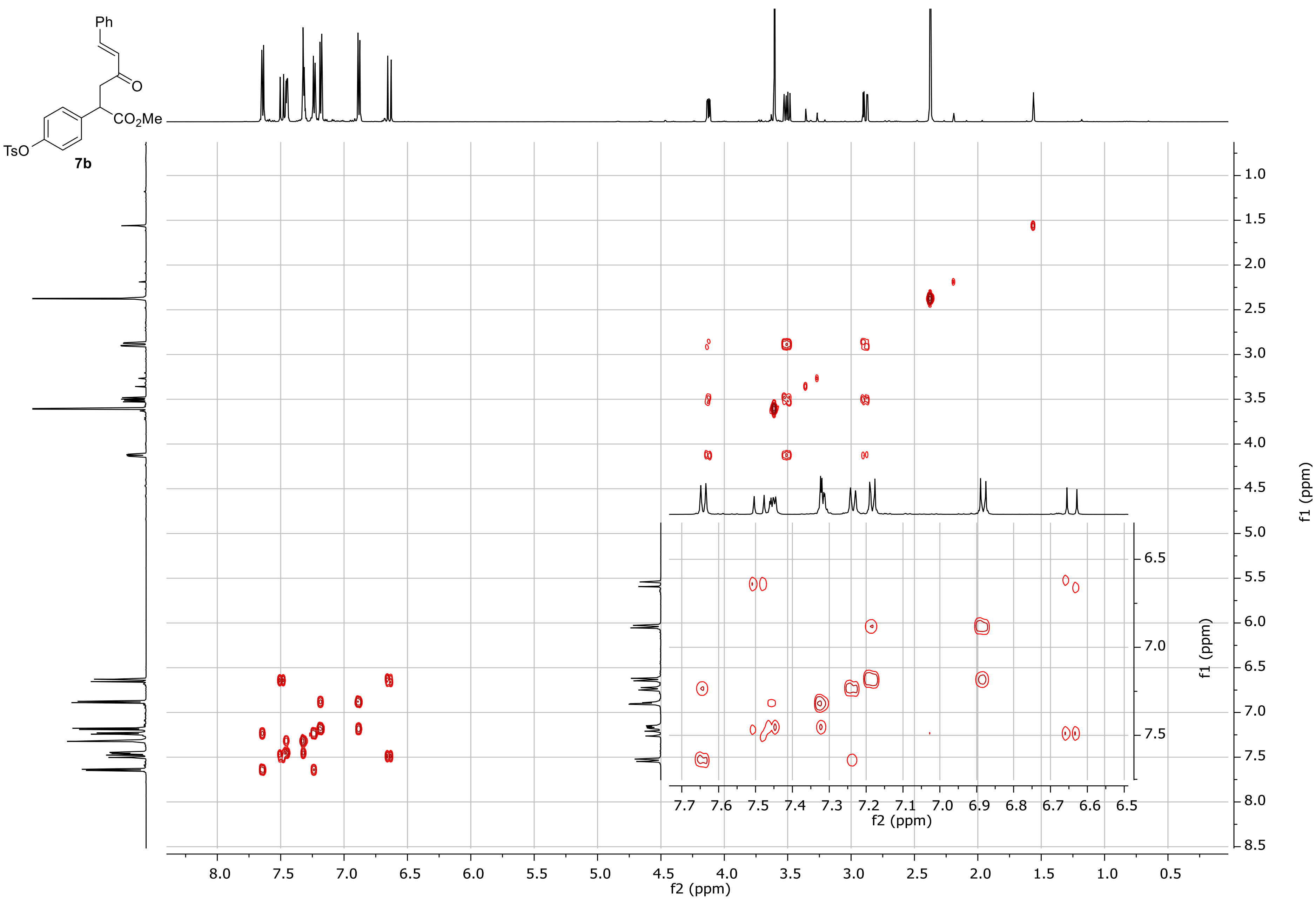


7b

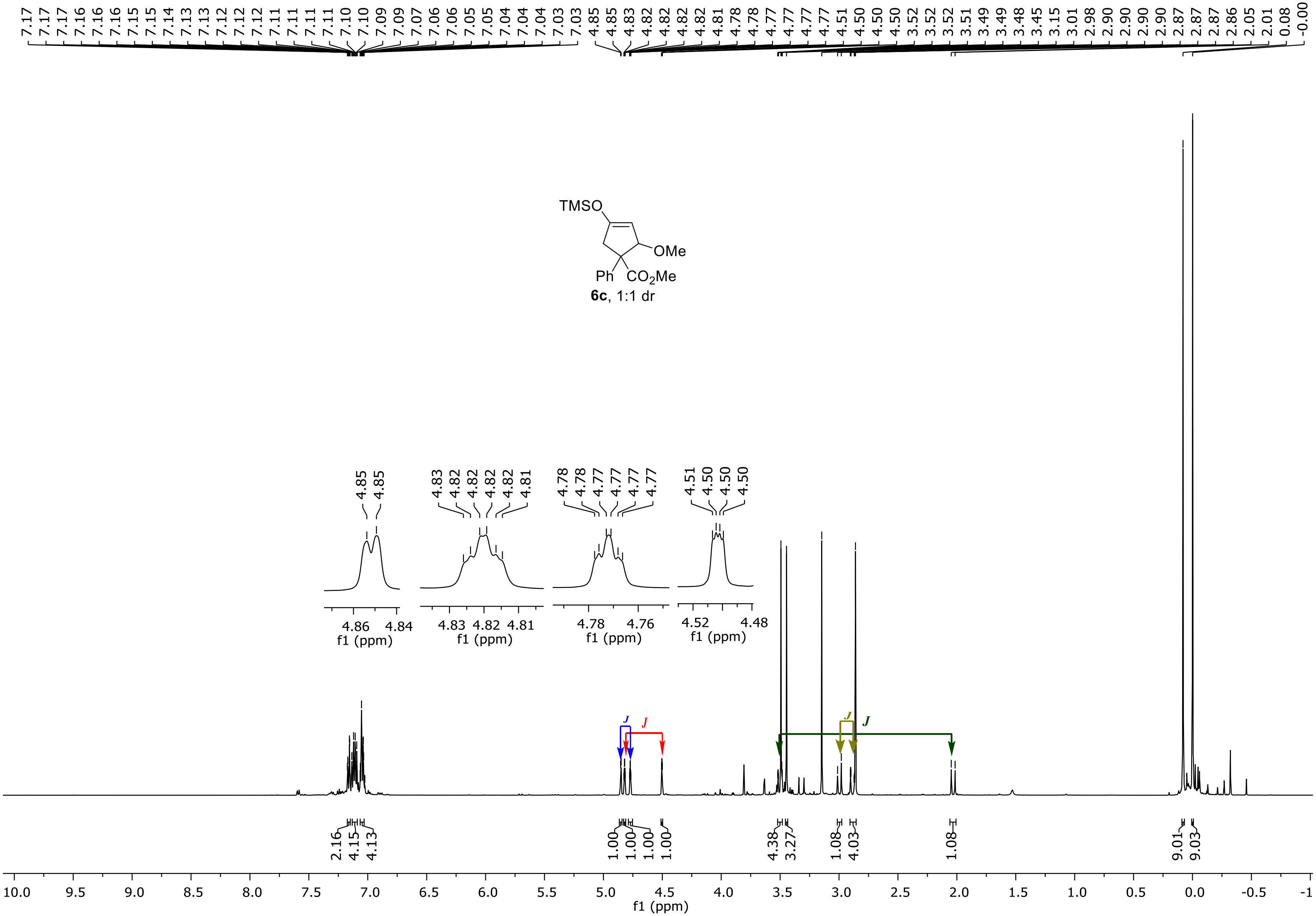
$^{13}C\{^1H\}$ NMR of 7b ($CDCl_3$, 150 MHz)



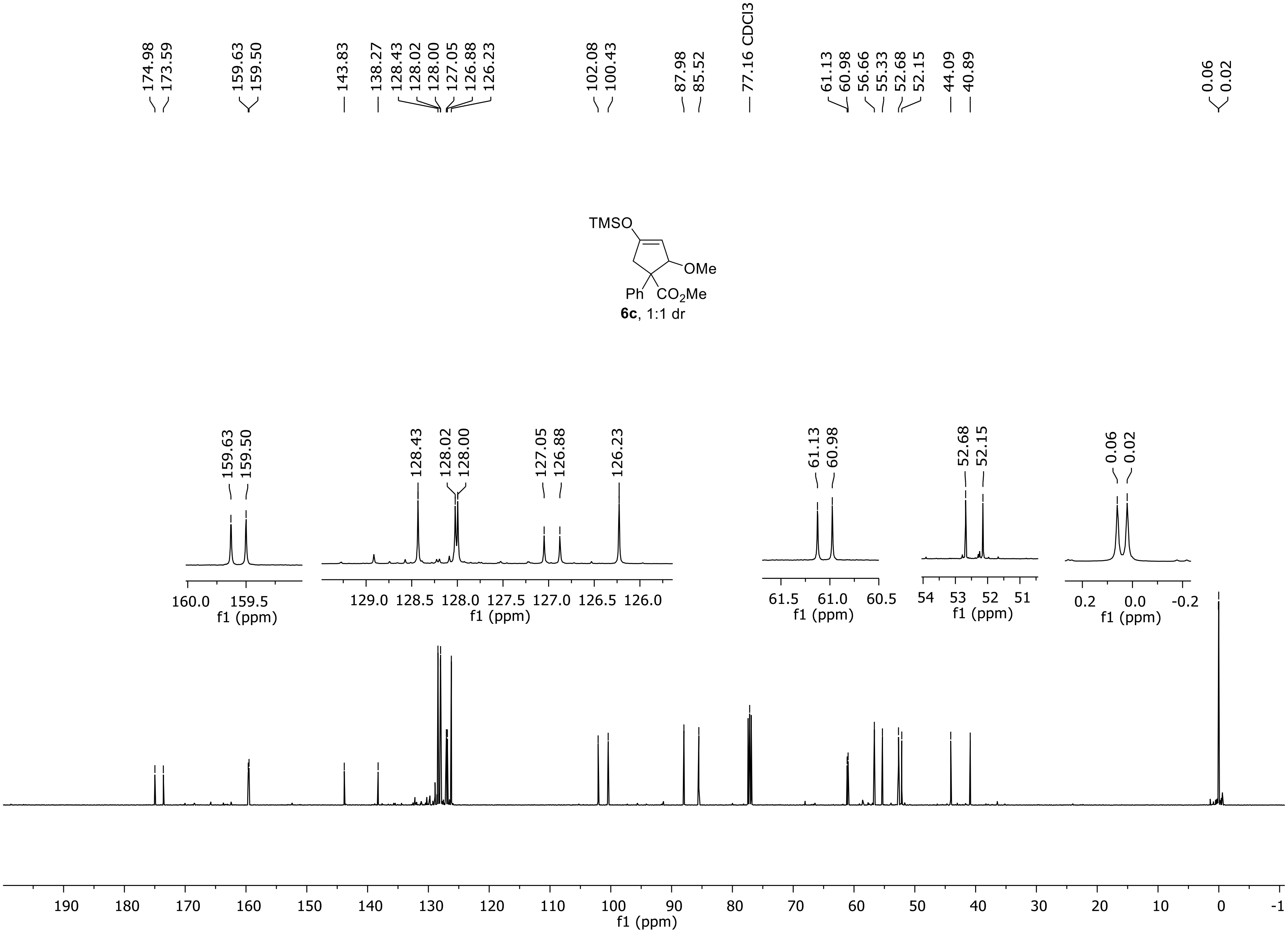
COSY NMR of 7b ($CDCl_3$, 600 MHz)



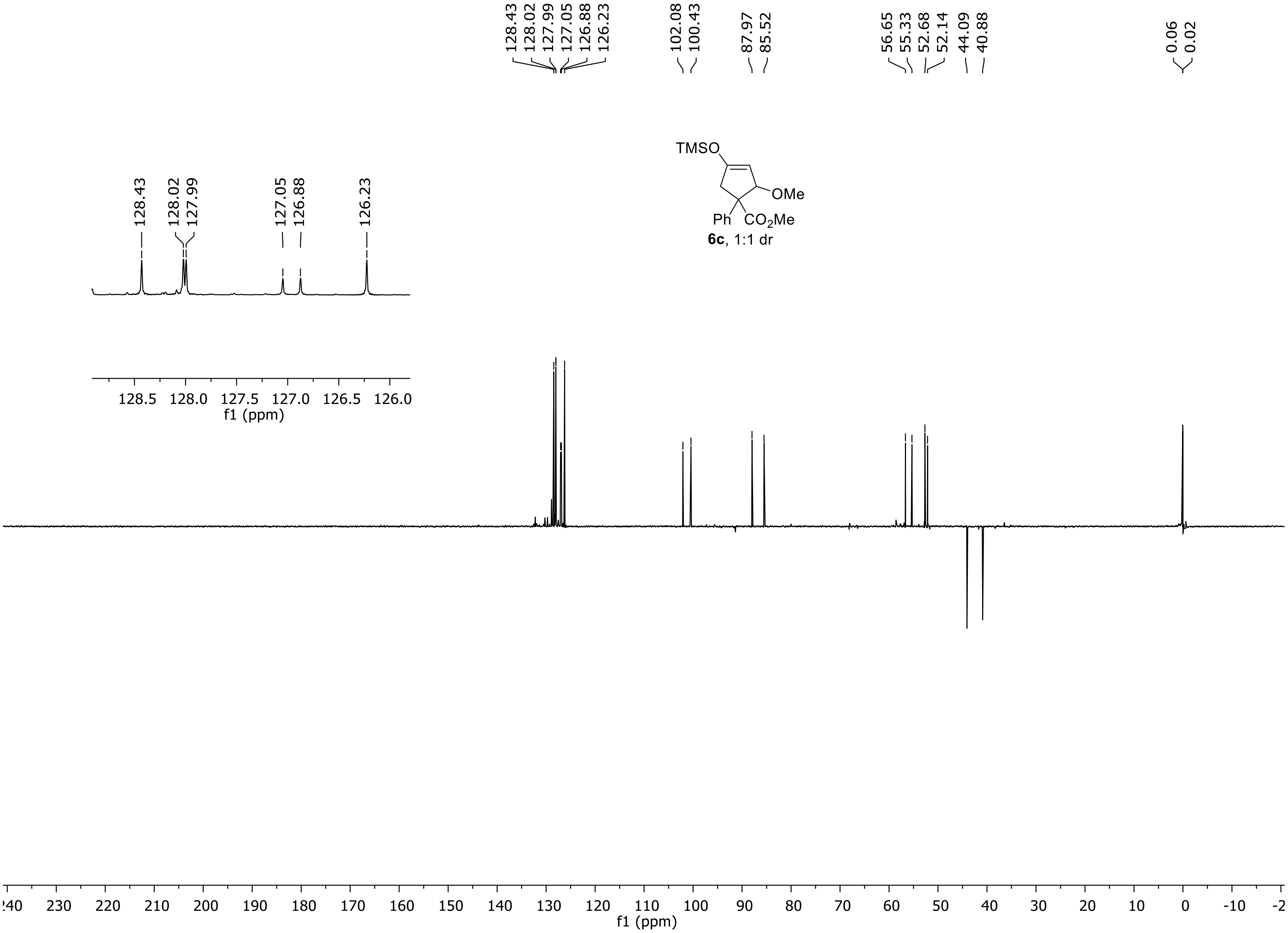
^{1}H NMR of 6c - crude mixture ($CDCl_3$, 500 MHz)



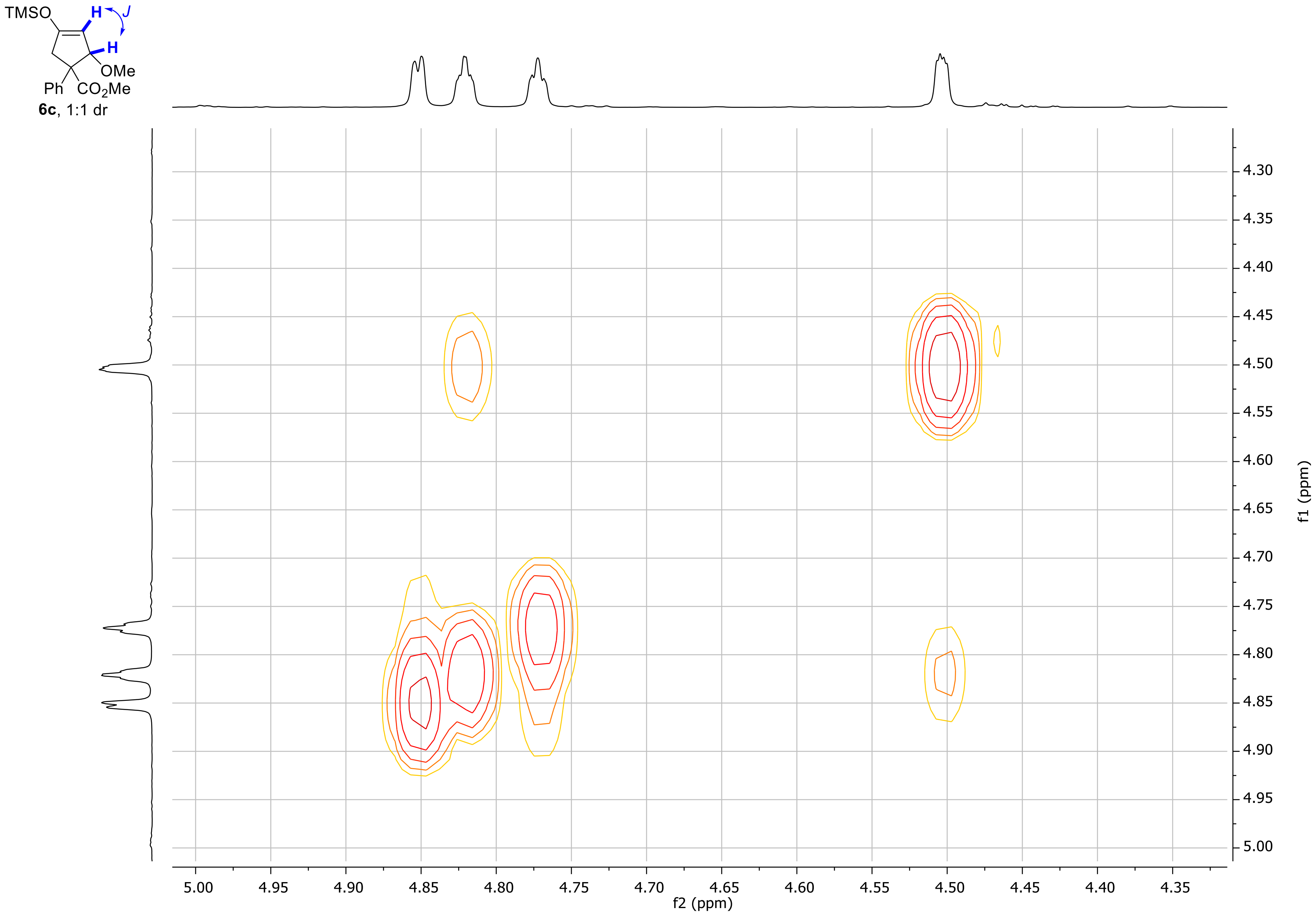
$^{13}C\{^1H\}$ NMR of 6c - crude mixture ($CDCl_3$, 125 MHz)



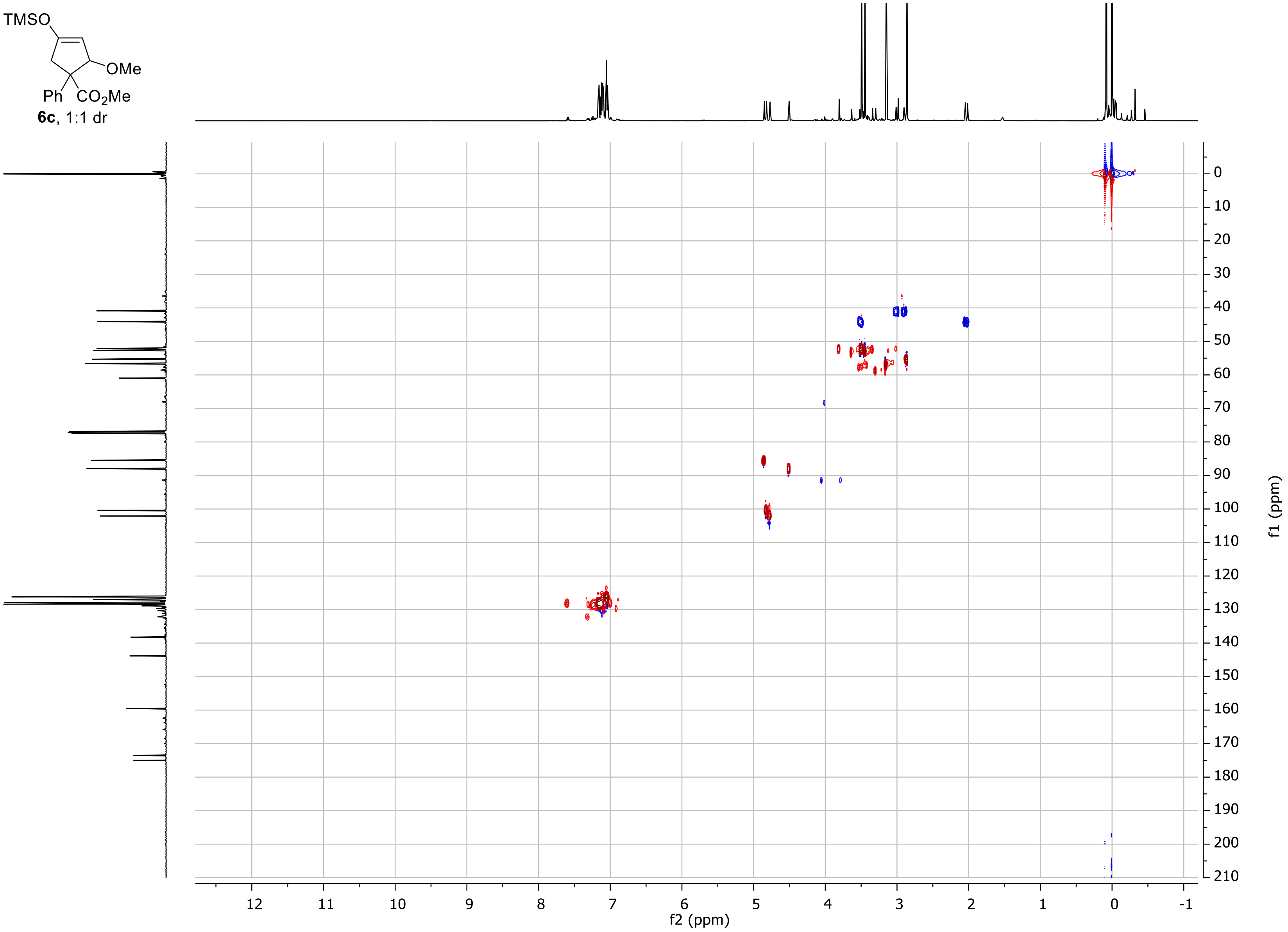
DEPT135 NMR of 6c - crude mixture (CDCl$_3$, 500 MHz)



COSY NMR of 6c - crude mixture (CDCl$_3$, 500 MHz)

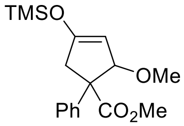


HSQC NMR of 6c - crude mixture (CDCl$_3$, 500 MHz)

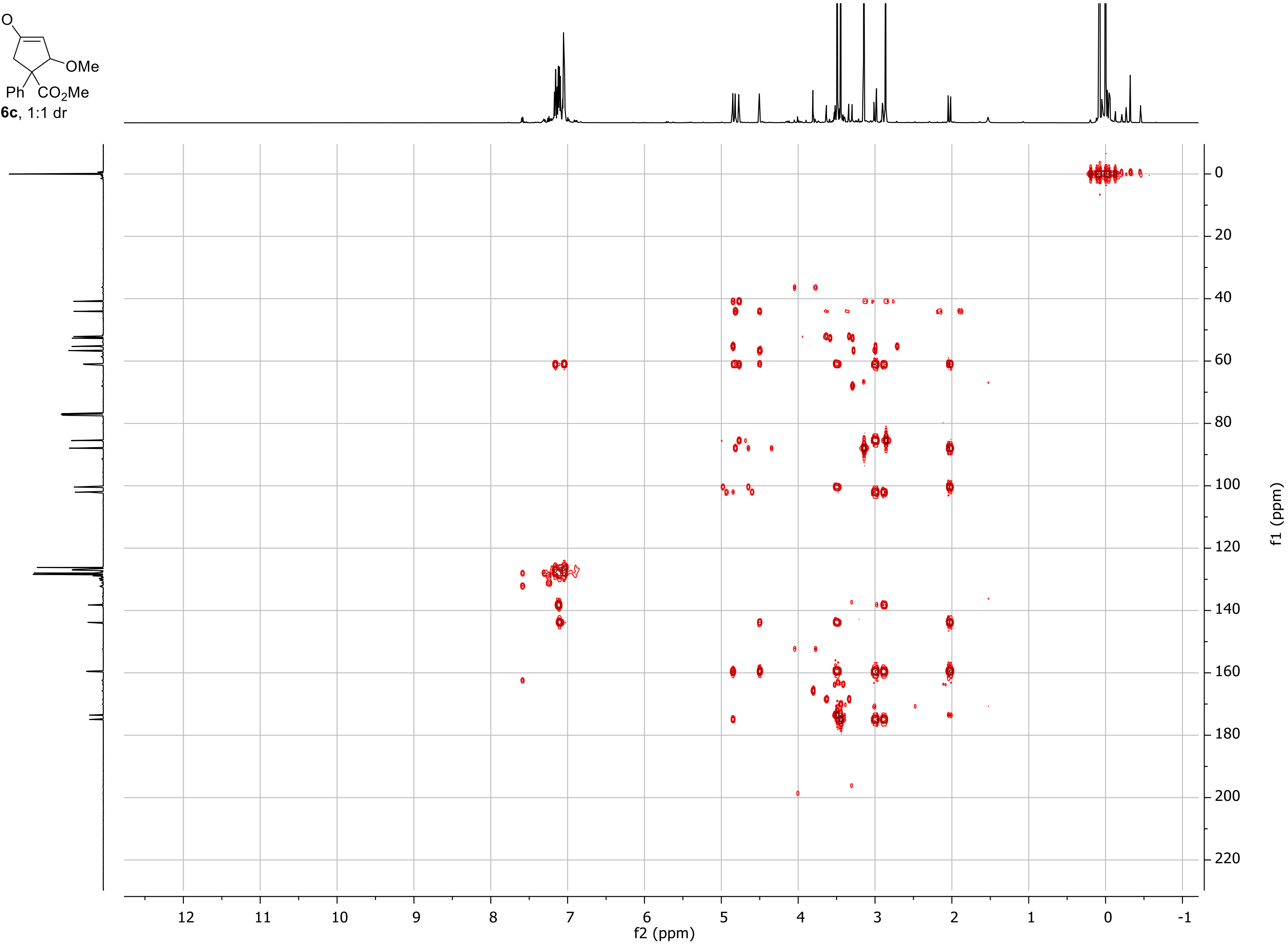


6c, 1:1 dr

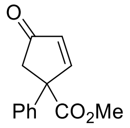
HMBC NMR of 6c - crude mixture (CDCl₃, 500 MHz)



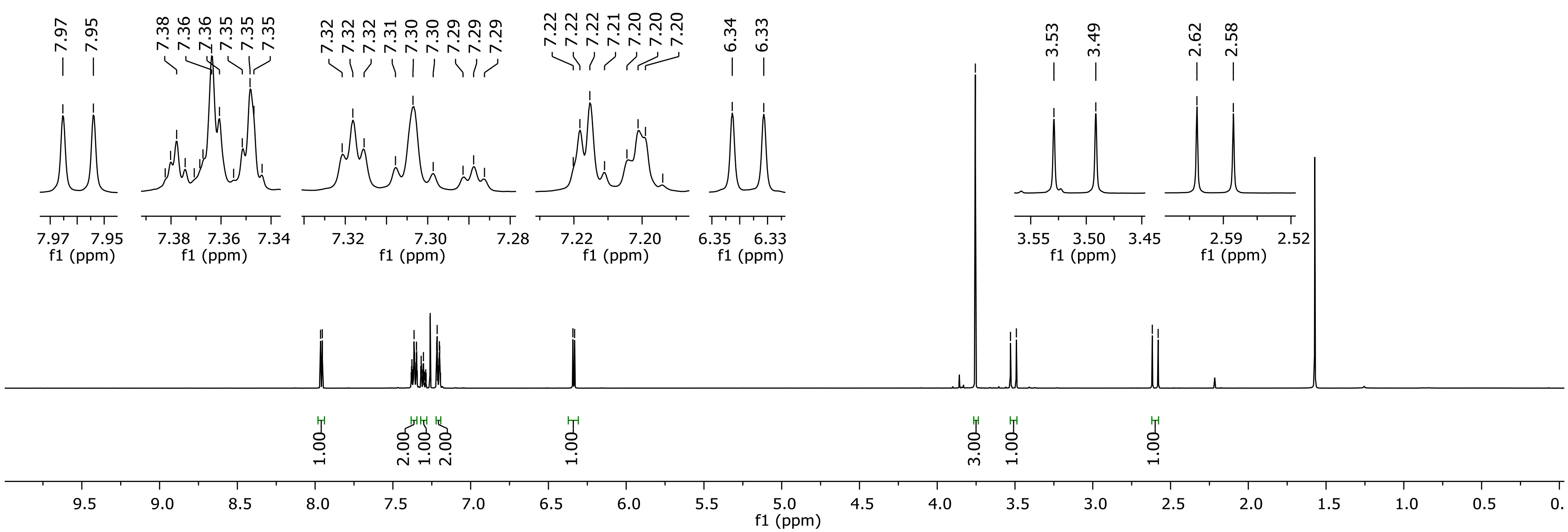
6c, 1:1 dr



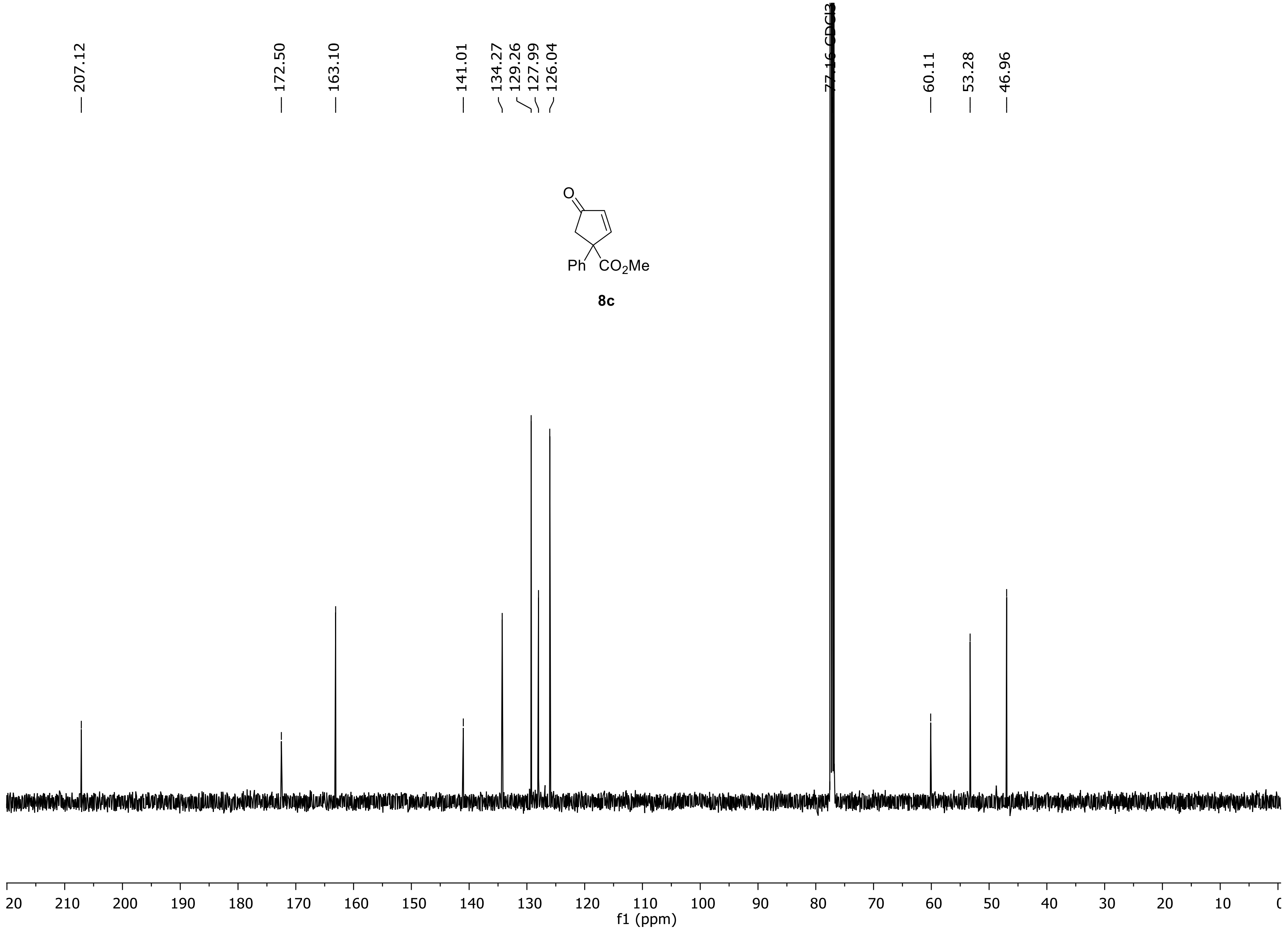
^{1}H NMR of 8c (CDCl$_3$, 500 MHz)



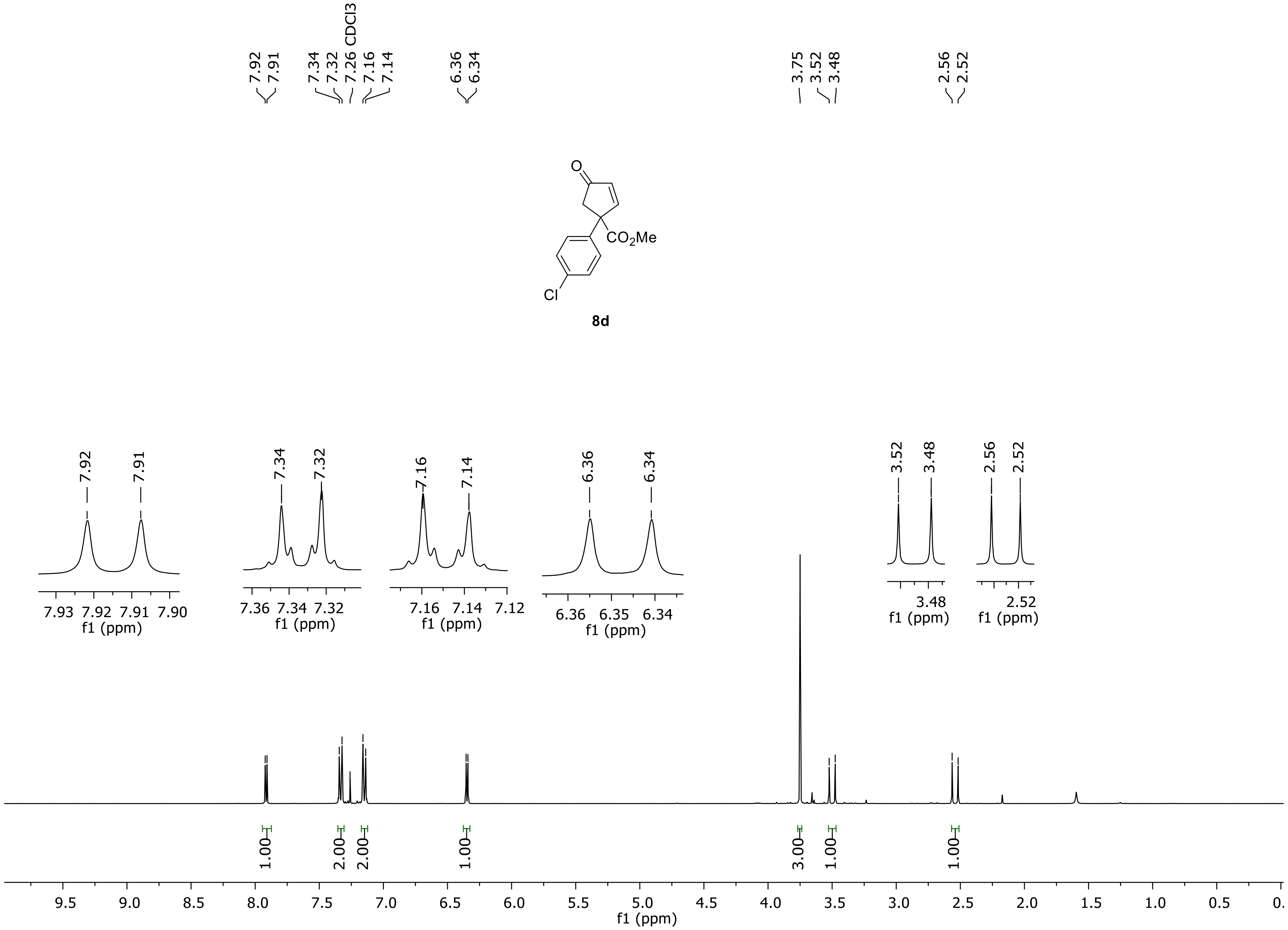
8c



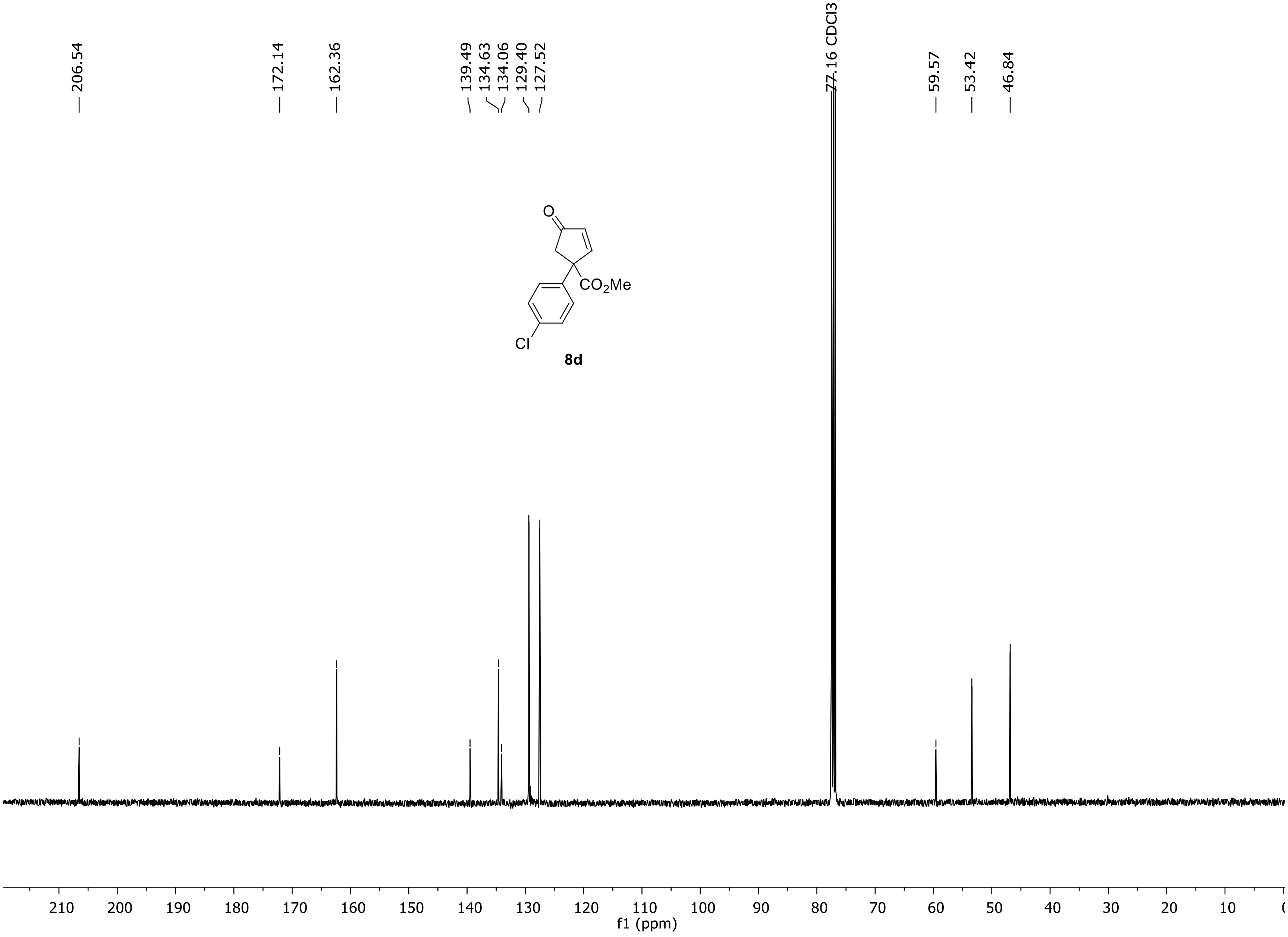
$^{13}C\{^1H\}$ NMR of 8c ($CDCl_3$, 125 MHz)



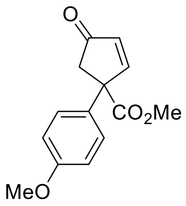
^{1}H NMR of 8d ($CDCl_3$, 400 MHz)



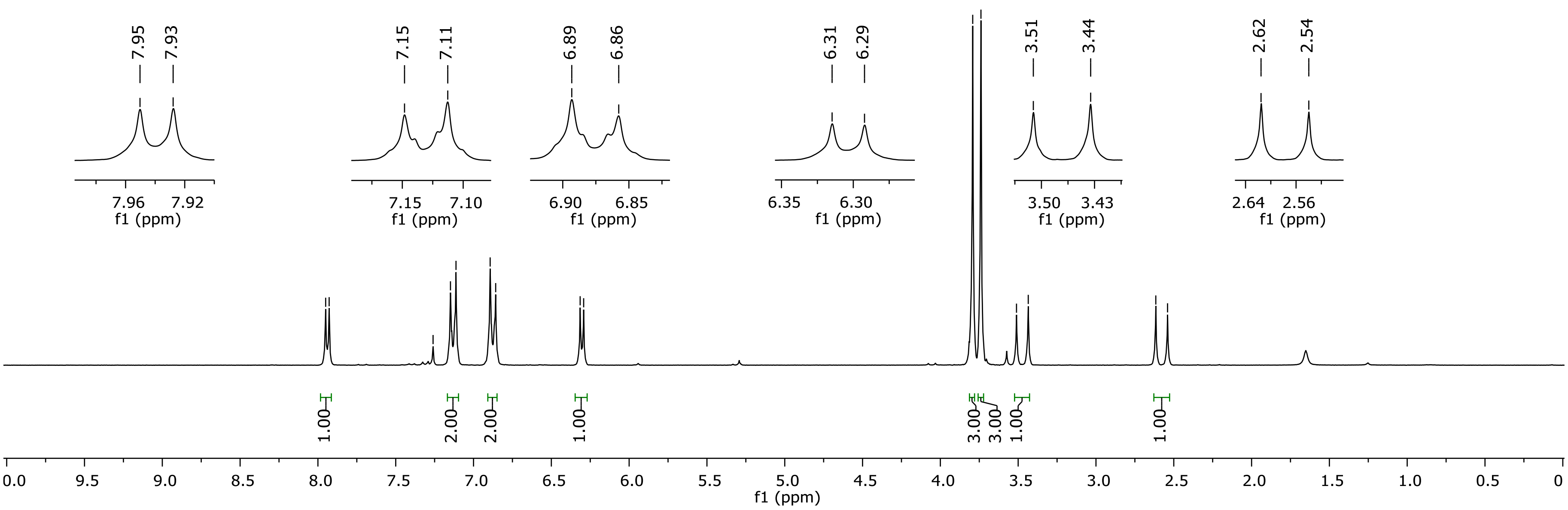
$^{13}C\{^1H\}$ NMR of 8d ($CDCl_3$, 100 MHz)



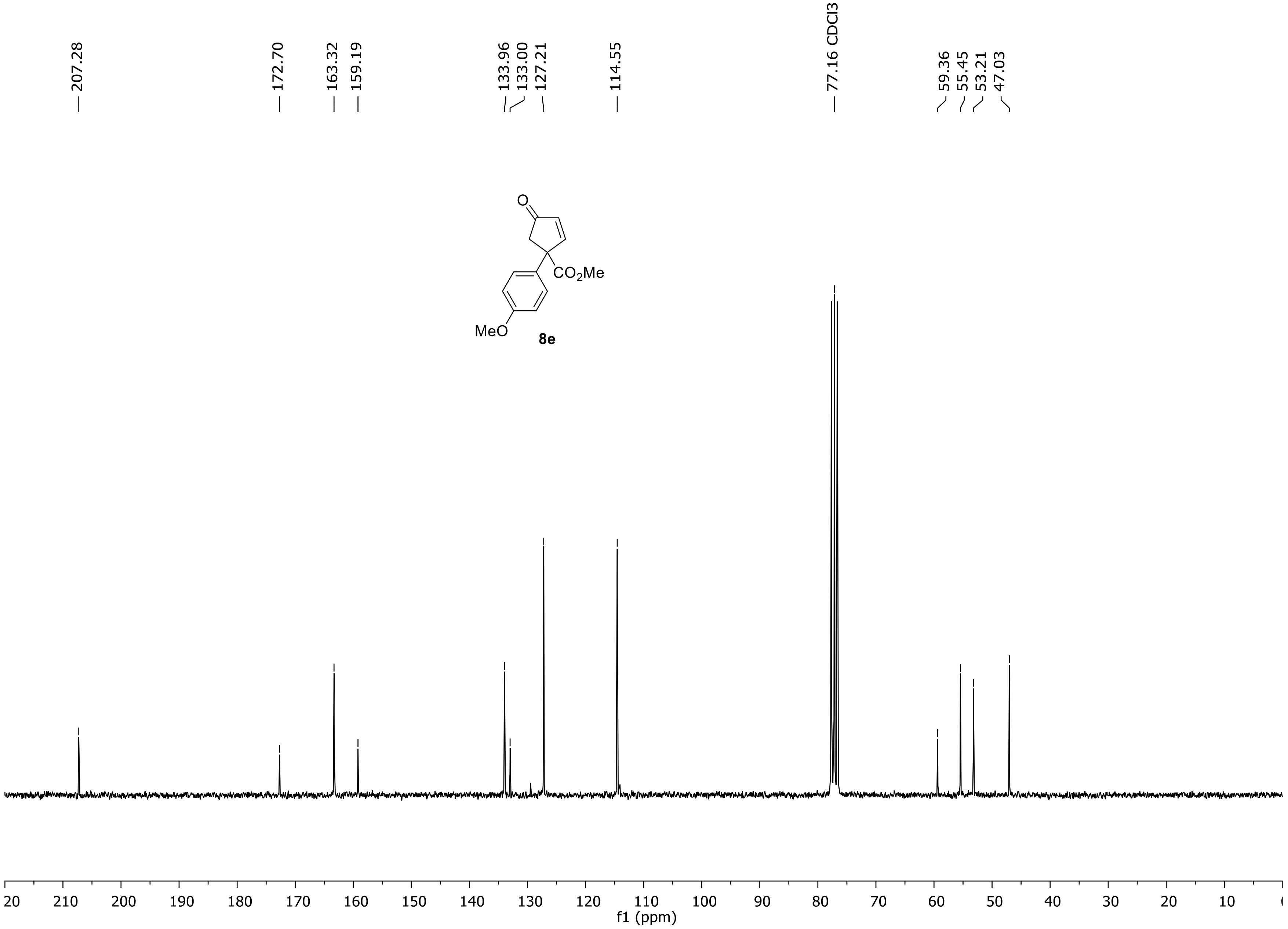
^{1}H NMR of 8e ($CDCl_3$, 250 MHz)



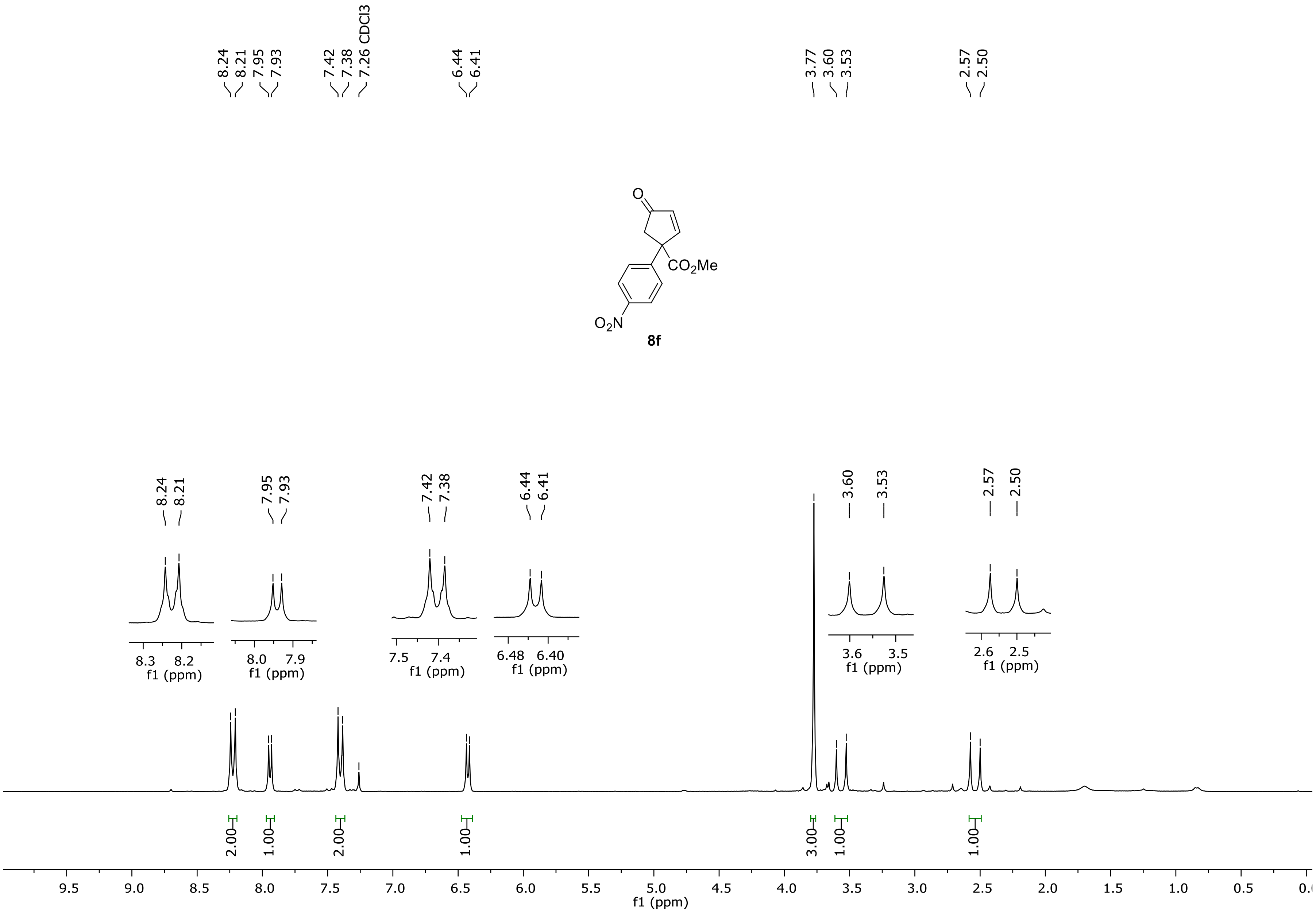
8e



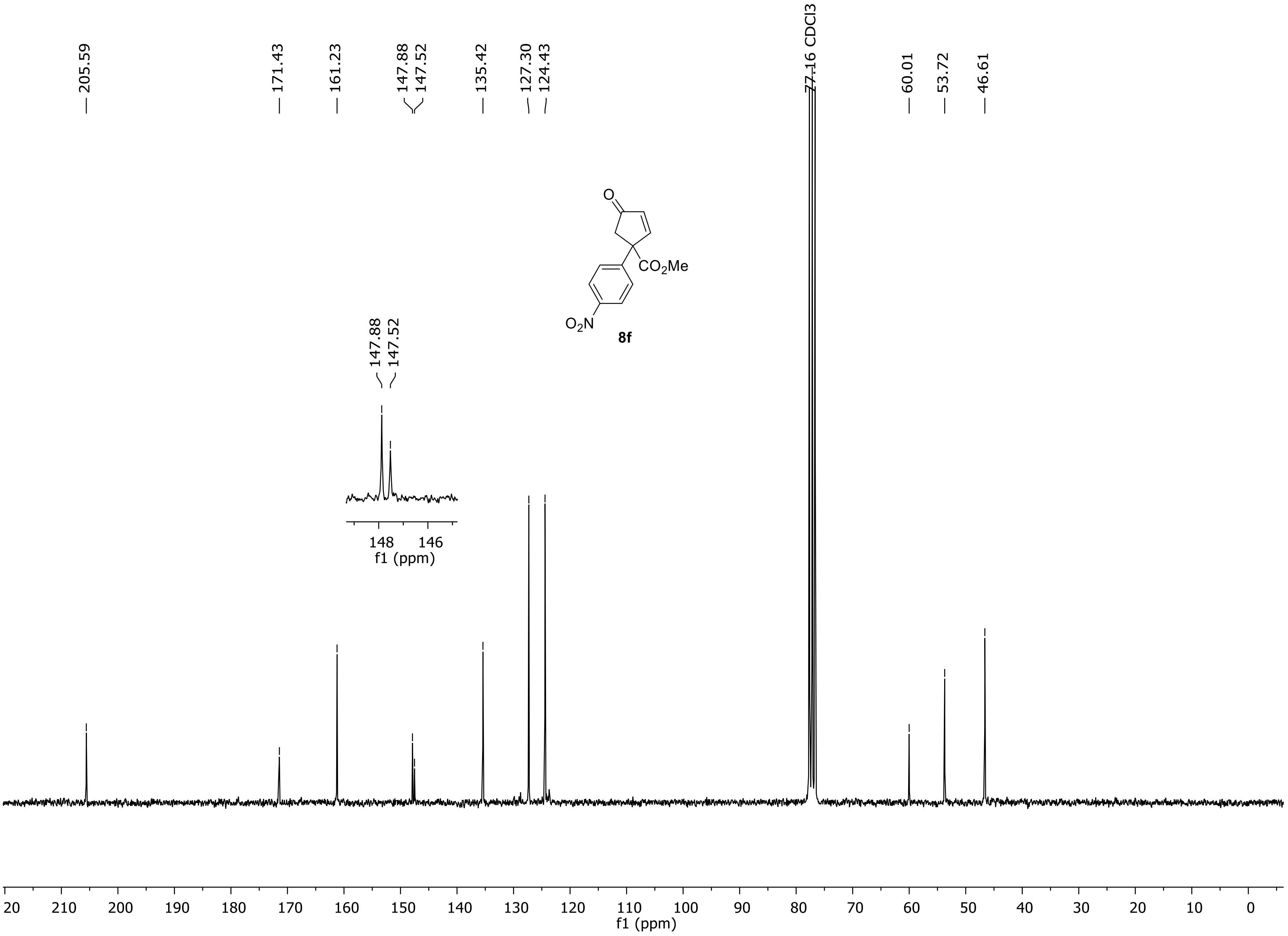
$^{13}C\{^1H\}$ **NMR of 8e ($CDCl_3$, 62.5 MHz)**



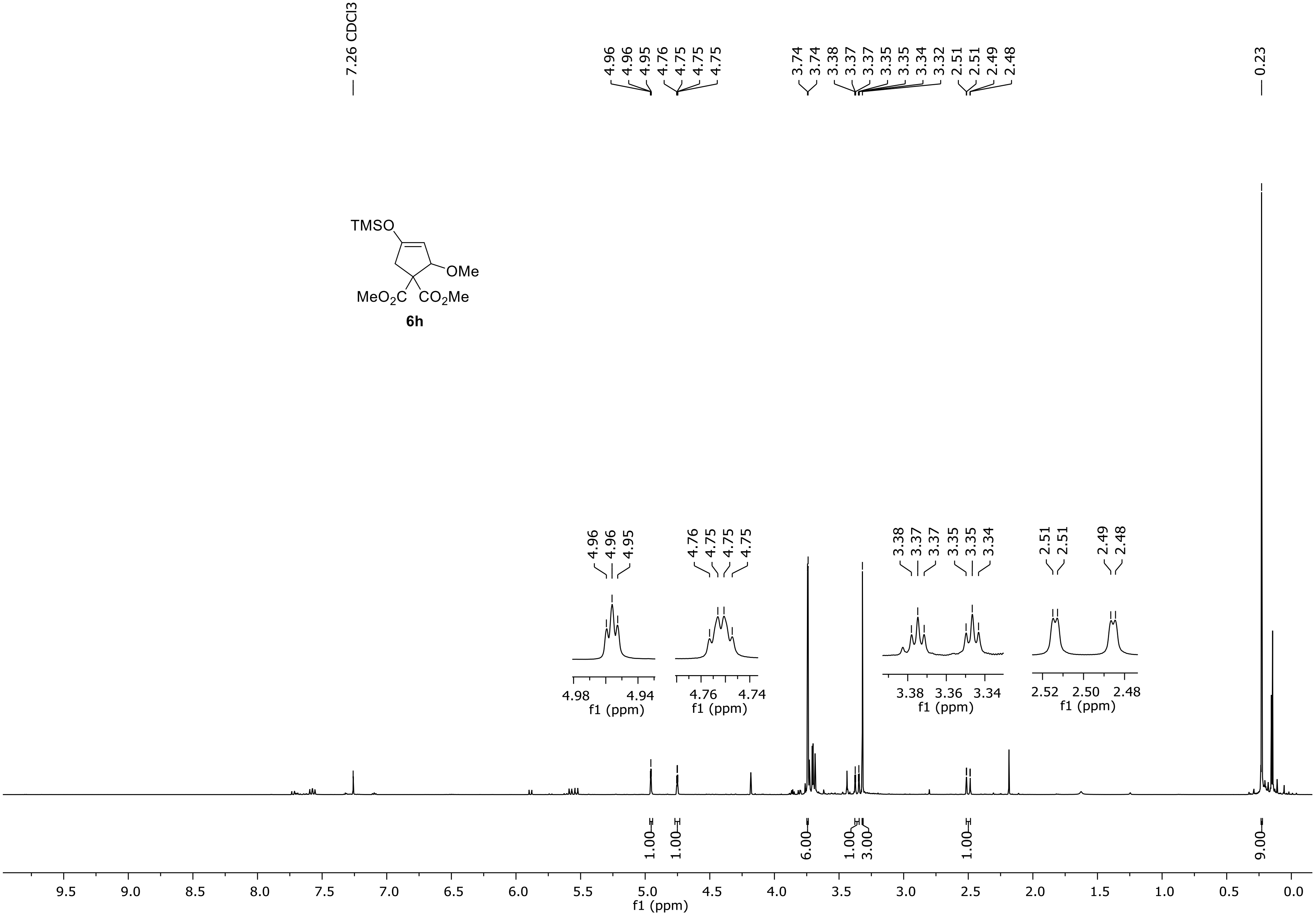
^{1}H NMR of 8f (CDCl$_3$, 250 MHz)



$^{13}C\{^{1}H\}$ **NMR of 8f (CDCl$_3$, 62.5 MHz)**

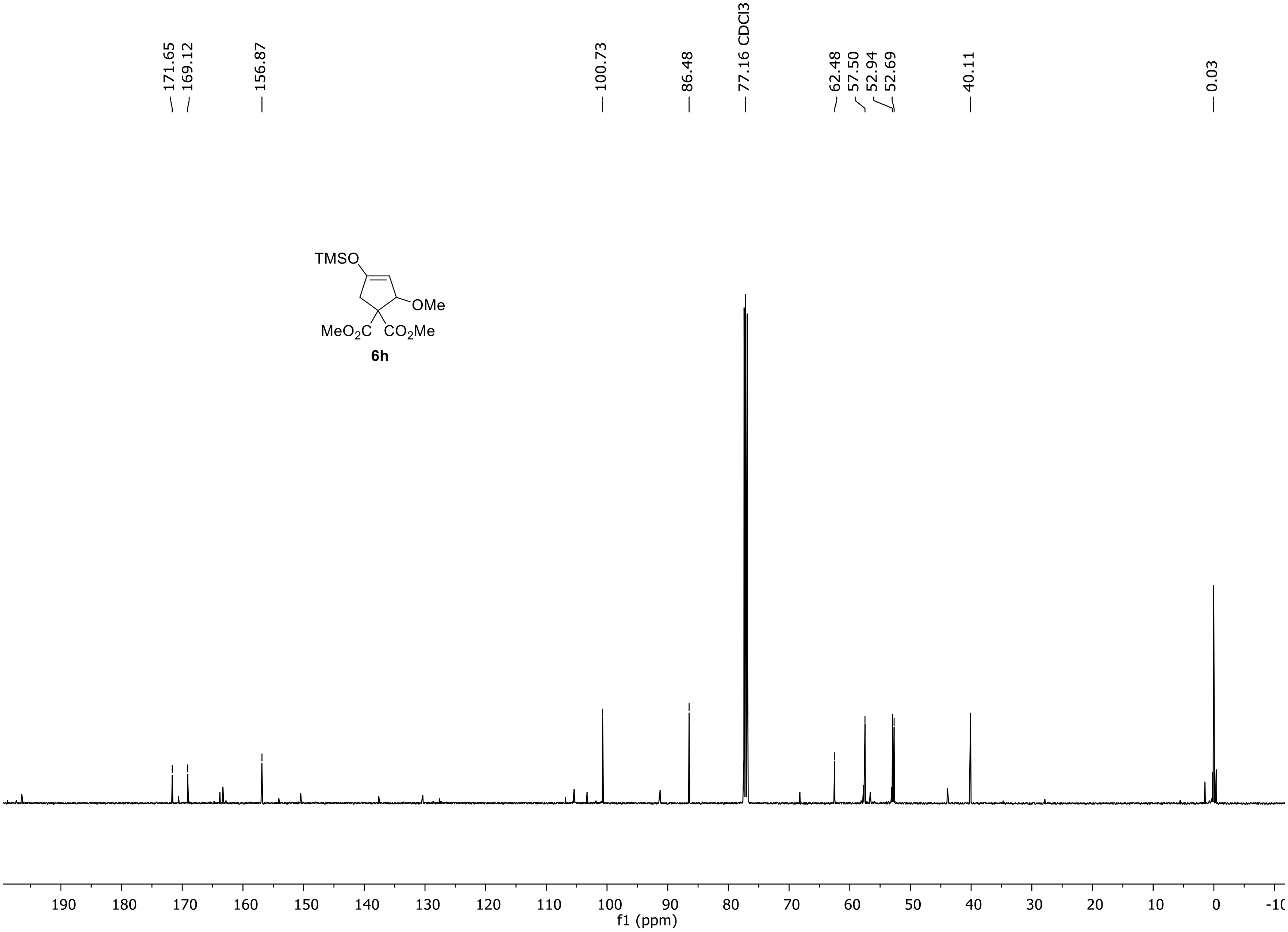


^{1}H NMR of 6h - crude mixture ($CDCl_3$, 600 MHz)

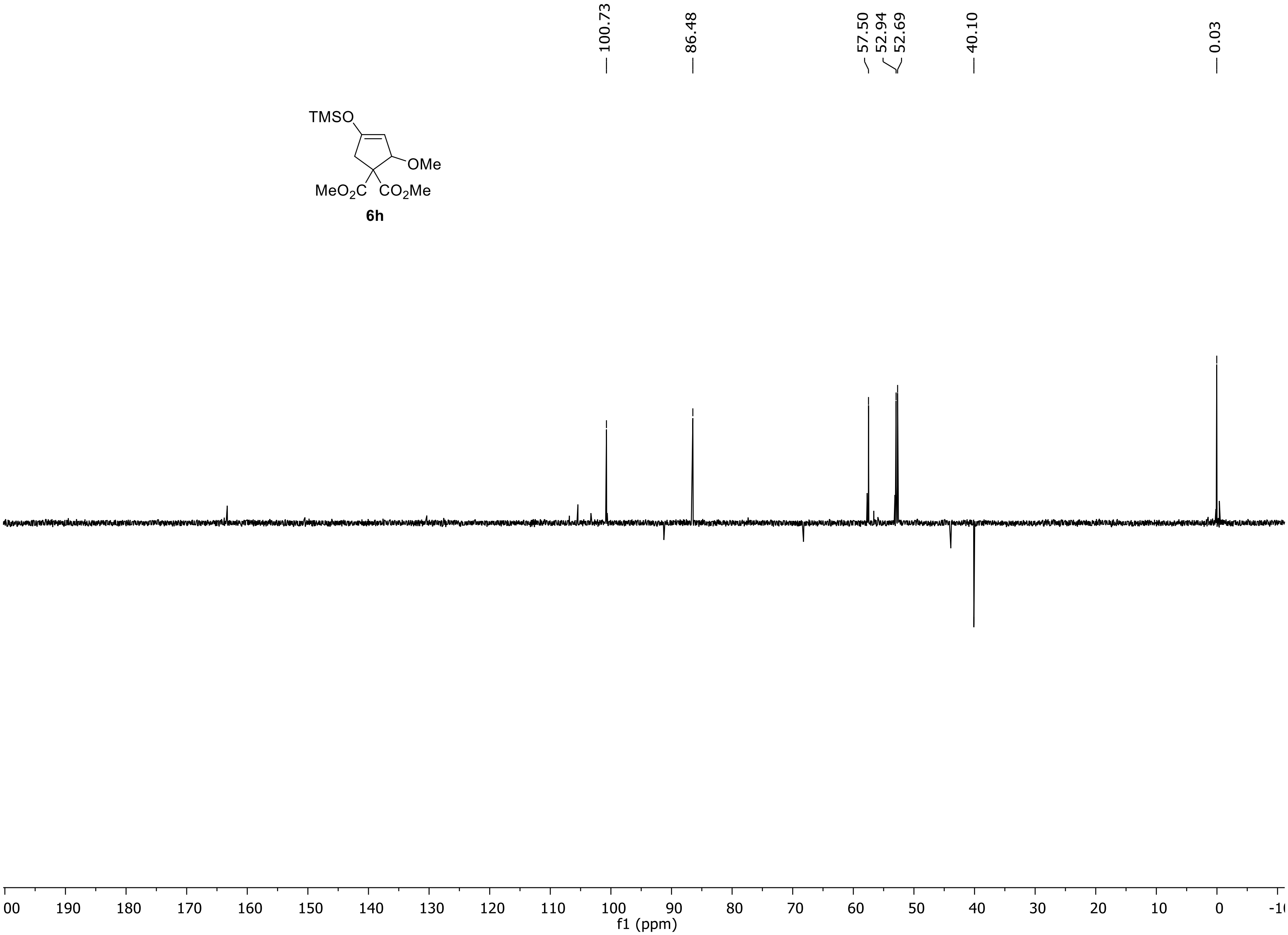


6h

$^{13}C\{^1H\}$ NMR of 6h - crude mixture ($CDCl_3$, 150 MHz)



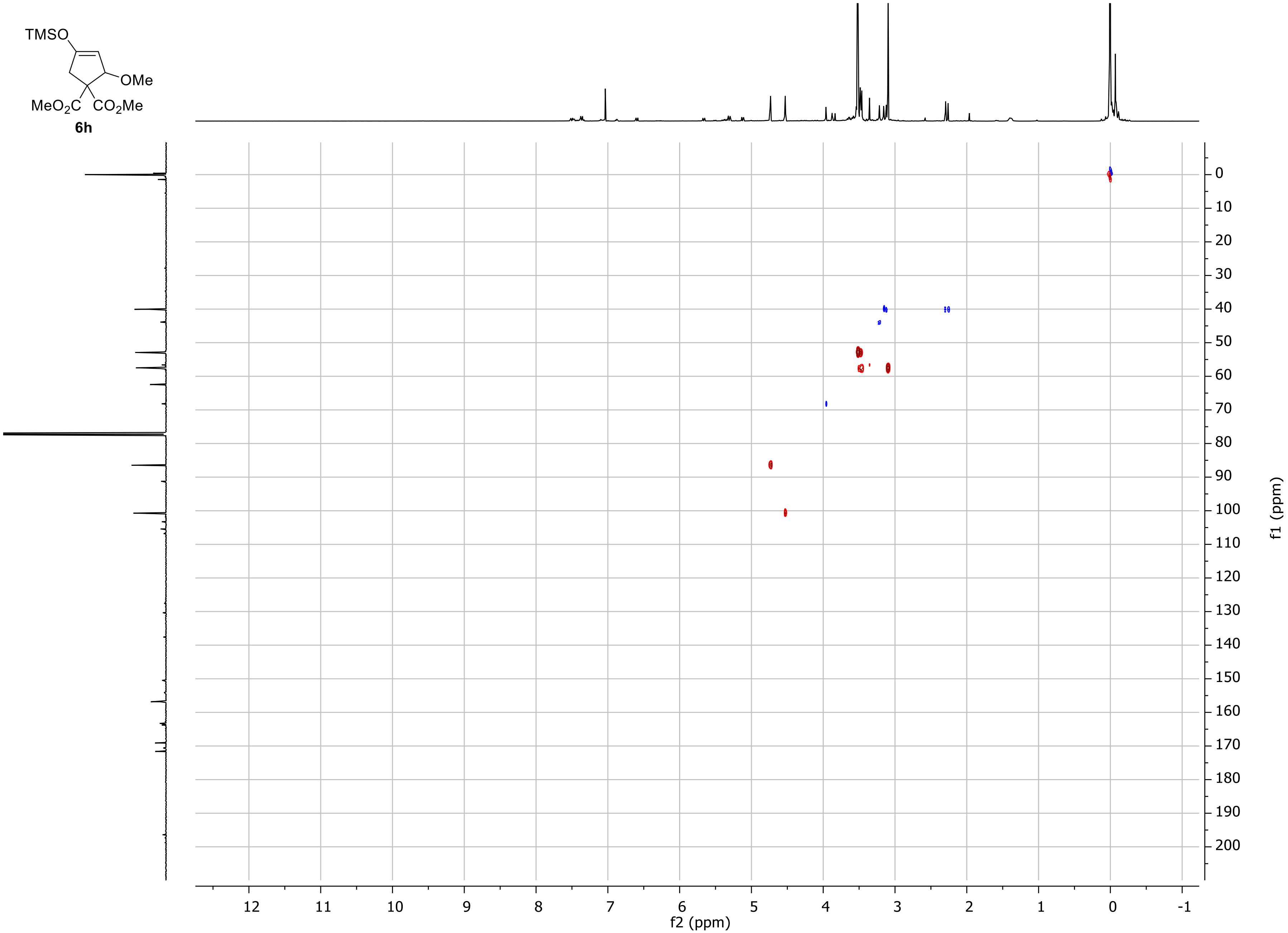
DEPT135 of 6h - crude mixture ($CDCl_3$, 600MHz)



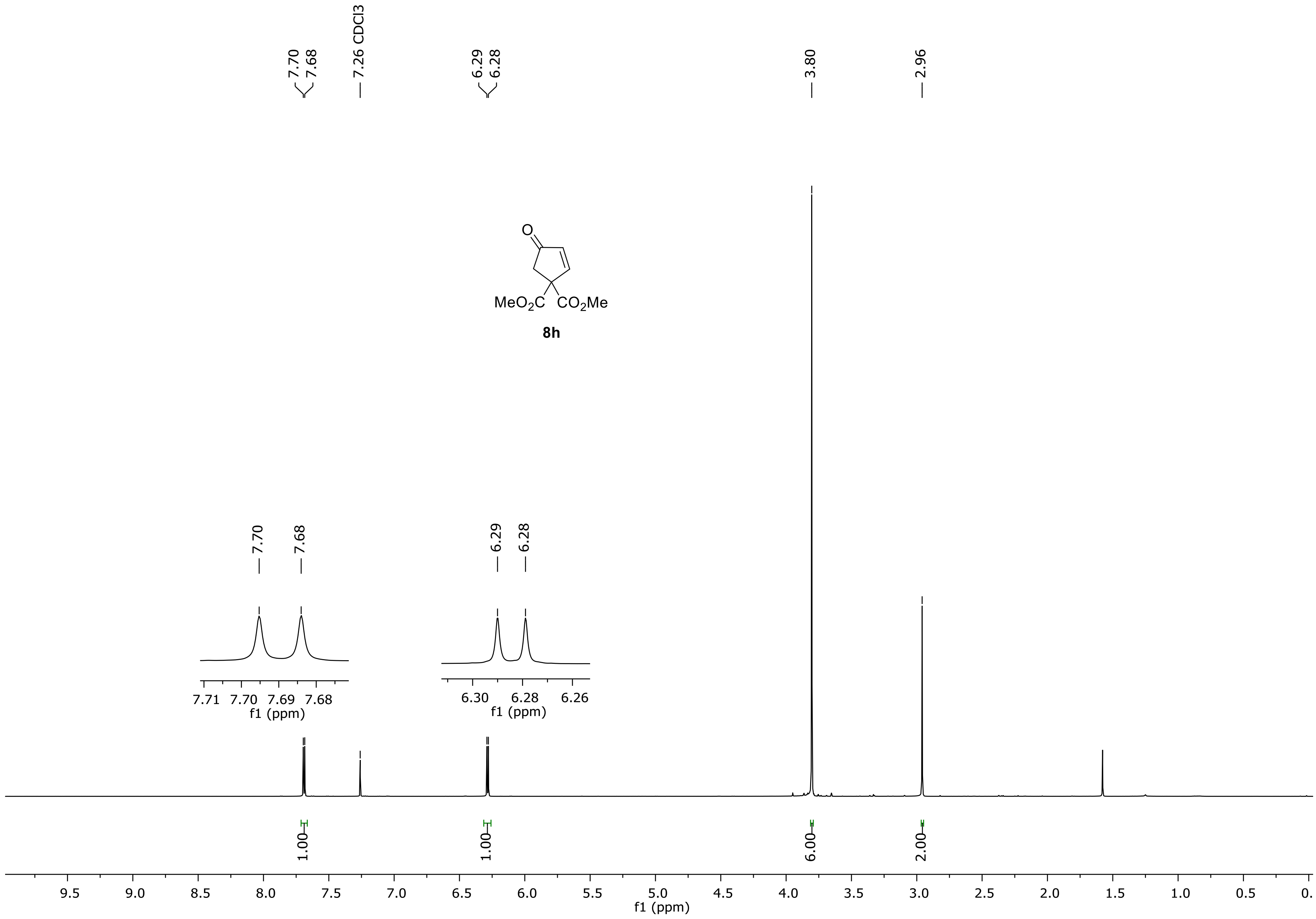
6h

HSQC of 6h - crude mixture ($CDCl_3$, 600 MHz)

6h



^{1}H NMR of 8h (CDCl$_3$, 500 MHz)



$^{13}C\{^1H\}$ NMR of 8h ($CDCl_3$, 125 MHz)