SUPPORTING INFORMATION

Synthesis of Deoxybenzoins From β-Alkoxy Styrenes and Arylboronic Acids *via* Palladium-Catalyzed Regioselective Heck-Arylation Reactions

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1. Experimental Section: General Information

All the reactions were carried out using oven dried glasswares. Solvents were evaporated with the help of rotary evaporator. Thin layer chromatography was performed using pre-coated plates obtained from E. Merck (TLC silica gel 60 F254). TLC plates were visualized by exposure to ultraviolet light (UV). The column chromatography was performed on silica gel (100-200 mesh) using a mixture of ethyl acetate and hexane as an eluent. The NMR spectra were recorded on Bruker Avence 400 and 500 MHz NMR spectrometers. The $CDCl_3$ signals were taken as the reference 7.26 ppm for ^{1}H NMR spectra and 77.0 ppm for ^{13}C NMR spectra in $CDCl_3$. HRMS were analyzed with Agilent Q-TOF 6230. FT-IR spectra were recorded on a Perkin Elmer spectrometer. All the known products were characterized by proton and carbon NMR and compared with literature data. Starting materials were prepared using literature

procedures as stated below.[1-2] Solvents and chemicals were purchased commercially and used without further purification. The palladium catalysts were purchased from Sigma Aldrich.

2. Experimental Procedures:

2.1. General procedure for the Synthesis of α-aryl acetophenones 3a-3o, 4a-4j:

To the solution of β-methoxystyrene (0.5 mmol) in Acetic acid (3 mL), arylboronic acid (0.6 mmol), palladium acetate (5 mol%) and TEMPO (1.0 mmol) were added sequentially at 40 ^{o}C. The reaction mixture was allowed to stir for 4 h. After completion, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with ethyl acetate (2 × 30 mL), washed with water (2 × 20 mL) and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the α-aryl acetophenones.

2.2. Gram scale synthesis of 3a:

To the solution of styryl ether **1a** (1.0 g, 7.45 mmol) in Acetic acid (20 mL), were added 4-methoxyarylboronic acid **2a** (1.36 g, 8.94 mmol), palladium acetate (84 mg, 5 mol%) and TEMPO (2.33 g, 14.91 mmol) at 40 ^{o}C. The reaction mixture was allowed to stir for 4 h. After completion, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL), extracted with ethyl acetate (2 × 100 mL), washed with water (2 × 50 mL) and washed with brine (2 × 30 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the product **3a** (Yield 82%, 1.38 g).

2.3 Synthesis of 5a:

To the solution of 2'-nitrostyrene methyl ether (**1k**) (180 mg, 1.0 mmol) in Acetic acid (5 mL), arylboronic acid **2b** (147 mg, 1.2 mmol), palladium acetate (12 mg, 5 mol%) and TEMPO (314 mg, 2.0 mmol) were added sequentially at 40 ^{o}C. The reaction mixture was allowed to stir for 4 h. After completion, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with ethyl acetate (2 × 50 mL), washed with water (2 × 20 mL) and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4 and concentrated to obtain crude nitro compound, which was subjected to the next step without further purification. Zinc dust (394 mg, 6 mmol) and glacial acetic acid (690 μL, 12 mmol) were taken in a 50 mL RB flask. Ethanol (2 mL) and nitro compound were sequentially added by syringe at ambient temperature. The mixture was stirred at 70 °C for 4 hours. After that the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 20 mL). The combined organic

layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuum. The residue was purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to provide the title compound **5a** (Yield 77%, 150 mg).

2.4. Procedure for the synthesis of fenflumizole (8):

The title compound was prepared using a literature procedure.[3] To the solution of β-methoxystyrene **1l** (1 mmol) in Acetic acid (5 mL), arylboronic acid **2a** (1.2 mmol), palladium acetate (5 mol%) and TEMPO (2.0 mmol) were added sequentially at 40 ^oC. The reaction mixture was allowed to stir for 4 h. After completion, the reaction mixture was quenched with a saturated aqueous solution of $NaHCO_3$ (10 mL), extracted with ethyl acetate (2 × 30 mL), washed with water (2 × 20 mL) and washed with brine (2 × 15 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the α-aryl acetophenone **6** (yield 79%, 202 mg). To the solution of ketone **6** (150 mg, 0.58 mmol) in DMF (3 mL) was added DABCO (20 mol%) and stirred at 90 ^oC for 24 h in air. After completion of the reaction, the mixture was cooled to room temperature, extracted with ethyl acetate (2 × 50 mL), washed with water (2 × 25 mL) and washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the 1,2-diketone **7** (Yield 90%, 142 mg). To the solution of 1,2-diketone (**7**) (0.35 mmol) and 2,4-difluorobenzaldehyde (0.53 mmol) in AcOH (3 mL) and NH_4OAc (1.0 mmol) was added at rt. Then, the reaction mixture was heated at 100 °C for 3 h. After completion of the reaction, the reaction mixture was added to ice-cold water and extracted with ethyl acetate (2 × 50 mL), and washed with brine (2 × 20 mL), dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (100-200 mesh) using hexane/ethyl acetate to afford the 76% yield of fenflumizole (**8**).

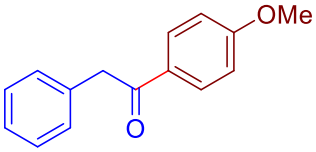
2.5. Procedure for the synthesis of oxaprozin (10):

The title compound was prepared using a literature procedure.[4] To a solution of the ketone **3b** (88 mg, 1.0 eq.) in the methyl 3-cyanopropanoate (20 eq.) were added TfOH (6 eq.), oxone (1.1 eq.) and iodine (0.7 eq.). The reaction mixture was allowed to stir for 6 h at 70 °C. After completion of the reaction, a solution of aqueous Na_2SO_3 and aqueous $NaHCO_3$ were added and the mixture was extracted with EtOAc. A combined organic layer wash with brine was performed and it was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (100−200 mesh) using ethyl acetate and petroleum ether as an eluent to afford ester **9** (yield 81%, 111 mg). The ester **9** (90 mg, 1.0 eq) was dissolved in ethanol (1.5 ml). LiOH (4 eq.) was dissolved in H_2O (1.5 ml). Subsequently, both reaction mixtures were combined and stirred at rt for

12 h. After completion of the reaction, 1M HCl was added and the mixture was extracted with EtOAc. A combined organic layer wash with brine was performed and it was dried over anhydrous Na_2SO_4. The crude product was purified by column chromatography on silica gel (100−200 mesh) using ethyl acetate and petroleum ether as an eluent to afford oxaprozin **10** (yield 88%, 75 mg).

3. Analytical data for the Products:

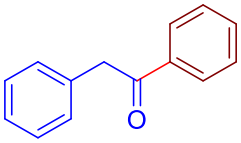
1-(4-methoxyphenyl)-2-phenylethan-1-one (3a)[1]:



3a

The title compound was obtained as a colourless solid. Yield 90% (101 mg), mp 78−80 °C. R_f (5% EtOAc/Hexane): 0.45. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 – 7.88 (m, 2H), 7.23 (dd, *J* = 10.0, 4.6 Hz, 2H), 7.19 – 7.13 (m, 3H), 6.86 – 6.82 (m, 2H), 4.14 (s, 2H), 3.76 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.1, 163.4, 134.9, 130.8, 129.5, 129.3, 128.5, 126.7, 113.7, 55.4, 45.2.

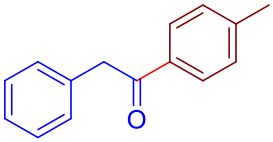
1,2-diphenylethan-1-one (3b)[1]:



3b

The title compound was obtained as a colourless solid. Yield 90% (88 mg), mp 132−134 °C. R_f (10% EtOAc/Hexane): 0.5. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.57 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.47 (dd, *J* = 10.5, 4.8 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.27 (m, 3H), 4.31 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 136.4, 134.4, 133.0, 129.3, 128.5, 128.5, 128.4, 126.7, 45.3.

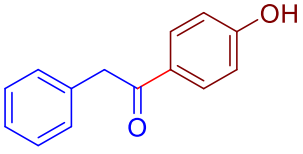
2-phenyl-1-(p-tolyl)ethan-1-one (3c)[1]:



3c

The title compound was obtained as a colourless solid. Yield 84% (88 mg), mp 109−111 °C. R_f (5% EtOAc/Hexane): 0.34. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 2H), 7.26 – 7.22 (m, 2H), 7.18 (dt, *J* = 7.9, 4.0 Hz, 5H), 4.18 (s, 2H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.3, 143.9, 134.7, 134.0, 129.4, 129.3, 128.7, 128.6, 126.7, 45.3, 21.6.

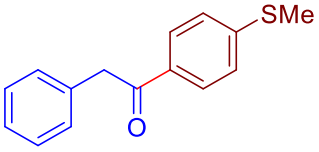
1-(4-hydroxyphenyl)-2-phenylethan-1-one (3d)[5]:



3d

The title compound was obtained as a colourless solid. Yield 81% (86 mg), mp 150−152 °C. R_f (20% EtOAc/Hexane): 0.26. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.33 (dd, *J* = 10.0, 4.6 Hz, 2H), 7.30 – 7.26 (m, 4H), 6.90 – 6.85 (m, 2H), 4.26 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.9, 160.5, 134.7, 131.3, 129.3, 128.6, 126.8, 115.4, 45.2.

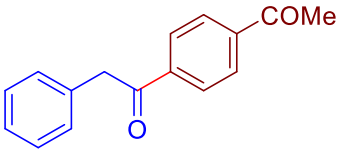
1-(4-(methylthio)phenyl)-2-phenylethan-1-one (3e)[1]:



3e

The title compound was obtained as a yellow solid, mp 96−98 °C. R_f (5% EtOAc/Hexane): 0.4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.32 (dd, *J* = 10.0, 4.7 Hz, 2H), 7.27 – 7.24 (m, 8H), 4.24 (s, 2H), 2.51 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.65, 146.03, 134.67, 132.82, 129.36, 129.05, 128.67, 126.85, 124.99, 77.25, 77.00, 76.75, 45.36, 14.72.

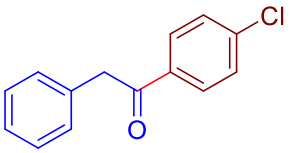
1-(4-acetylphenyl)-2-phenylethan-1-one (3f)[1]:



3f

The title compound was obtained as a colourless solid. Yield 78% (93 mg), mp 138−140 °C. R_f (10% EtOAc/Hexane): 0.3. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.10 – 8.05 (m, 2H), 8.04 – 7.99 (m, 2H), 7.38 – 7.30 (m, 2H), 7.27 – 7.25 (m, 3H), 4.31 (s, 2H), 2.63 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.4, 197.0, 140.1, 139.6, 133.9, 129.3, 128.7, 128.7, 128.4, 127.0, 45.8, 26.8.

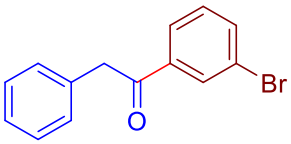
1-(4-chlorophenyl)-2-phenylethan-1-one (3g)[1]:



3g

The title compound was obtained as a colourless liquid. Yield 80% (92 mg). R_f (5% EtOAc/Hexane): 0.32. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.6 Hz, 1H), 7.42 (d, *J* = 8.6 Hz, 1H), 7.33 (t, *J* = 7.3 Hz, 1H), 7.28 – 7.24 (m, 2H), 4.26 (s, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.4, 139.6, 134.8, 134.1, 130.0, 129.3, 128.9, 128.7, 127.0, 45.5.

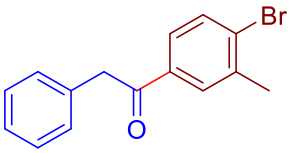
1-(3-bromophenyl)-2-phenylethan-1-one (3h)[1]:



3h

The title compound was obtained as a light yellow solid. Yield 78% (107 mg), mp 83−85 °C. R_f (5% EtOAc/Hexane): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.70 – 7.61 (m, 1H), 7.34 – 7.29 (m, 3H), 7.28 – 7.22 (m, 3H), 4.24 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.1, 138.2, 135.9, 133.8, 131.5, 130.1, 129.3, 128.7, 127.0, 127.0, 122.9, 45.4.

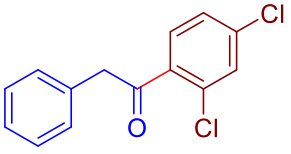
1-(4-bromo-3-methylphenyl)-2-phenylethan-1-one (3i):



3i

The title compound was obtained as a yellow liquid. Yield 72% (104 mg). R_f (5% EtOAc/Hexane): 0.3. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 1H), 7.28 – 7.18 (m, 3H), 7.18 – 7.16 (m, 1H), 7.14 (s, 1H), 4.14 (s, 2H), 2.34 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.8, 138.5, 135.5, 134.2, 132.6, 130.7, 130.6, 129.3, 128.6, 127.3, 126.9, 45.4, 22.9. HRMS (ESI): m/z $[M + Na]^+$ calculated for : $C_{15}H_{13}BrNaO$: 311.0047; found: 311.0063. IR:(KBr) ν_{max} 2992, 1675, 1609, 1257, 1103, 926, 814, 733, 699, 545 cm^{-1}.

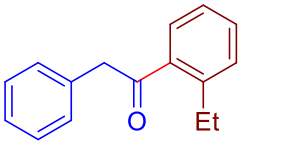
1-(2,4-dichlorophenyl)-2-phenylethan-1-one (3j)[6]:



3j

The title compound was obtained as a light-yellow liquid. Yield 74% (98 mg). R_f (5% EtOAc/Hexane): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 1.9 Hz, 2H), 7.54 (t, *J* = 1.9 Hz, 1H), 7.35 (t, *J* = 7.4 Hz, 2H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.23 (m, 2H), 4.23 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.0, 138.9, 135.6, 133.3, 132.8, 129.9, 129.3, 128.8, 128.1, 127.2, 126.9, 45.5.

1-(2-ethylphenyl)-2-phenylethan-1-one (3k):

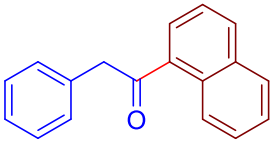


3k

The title compound was obtained as a colourless liquid. Yield 68% (76 mg). R_f (5% EtOAc/Hexane): 0.38. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 – 7.62 (m, 1H), 7.38 (td, *J* = 7.7, 1.4 Hz, 1H), 7.33 – 7.29 (m, 2H), 7.27 – 7.21 (m, 5H), 4.19 (s, 2H), 2.75 (q, *J* = 7.5 Hz, 2H), 1.13 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 201.9, 144.2,

137.8, 134.3, 131.2, 130.3, 129.5, 128.5, 128.1, 126.8, 125.5, 48.8, 26.8, 15.9. HRMS (ESI): m/z $[M + H]^+$ calculated for : $C_{16}H_{17}O$: 225.1279; found: 225.1285. IR:(KBr) ν_{max} 2988, 1673, 1609, 1282, 1119, 928, 803, 776, 684, 576 cm^{-1}.

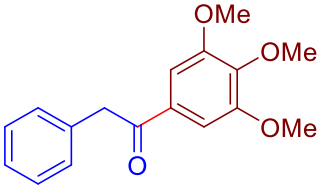
1-(naphthalen-1-yl)-2-phenylethan-1-one[1]:



3l

The title compound was obtained as a colourless solid. Yield 82% (100 mg), mp 60−62 °C. R_f (5% EtOAc/Hexane): 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 – 8.45 (m, 1H), 7.87 (dd, *J* = 12.2, 4.9 Hz, 2H), 7.77 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.50 – 7.37 (m, 3H), 7.26 – 7.18 (m, 4H), 7.18 – 7.13 (m, 1H), 4.28 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.4, 135.5, 134.5, 133.9, 132.7, 130.3, 129.4, 128.6, 128.3, 127.9, 127.8, 126.9, 126.4, 125.7, 124.2, 48.8.

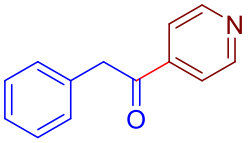
2-phenyl-1-(3,4,5-trimethoxyphenyl)ethan-1-one[7]:



3m

The title compound was obtained as a colourless solid. Yield 75% (107 mg), mp 92−94 °C. R_f (10% EtOAc/Hexane): 0.27. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 (ddd, *J* = 7.1, 4.4, 1.6 Hz, 2H), 7.22 – 7.14 (m, 5H), 4.17 (s, 2H), 3.83 (s, 3H), 3.81 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 152.9, 142.5, 134.8, 131.6, 129.2, 128.7, 126.9, 106.2, 60.8, 56.2, 45.6.

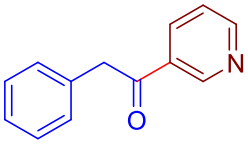
2-phenyl-1-(pyridin-4-yl)ethan-1-one (3m)[8]:



3n

The title compound was obtained as a yellow solid. Yield 38% (37 mg), mp 102−104 °C. R_f (30% EtOAc/Hexane): 0.6. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.40 – 8.34 (m, 2H), 7.64 – 7.60 (m, 1H), 7.47 – 7.41 (m, 2H), 7.23 – 7.12 (m, 1H), 7.10 – 7.01 (m, 1H), 6.95 – 6.91 (m, 1H), 6.88 – 6.84 (m, 1H), 3.93 (s, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.1, 167.1, 165.6, 149.8, 149.3, 141.4, 137.5, 132.5, 131.7, 129.9, 128.6, 127.7, 127.3, 126.1, 122.1, 120.5, 44.5, 39.6, 39.4, 39.1, 38.9, 38.7, 38.5, 38.3.

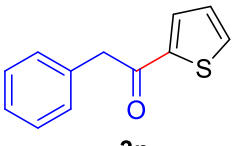
2-phenyl-1-(pyridin-3-yl)ethan-1-one (3n)[9]:



3o

The title compound was obtained as a yellow solid. Yield 35% (34 mg), mp 87−89 °C. R_f (20% EtOAc/Hexane): 0.35. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.22 (dd, J = 2.3, 0.8 Hz, 1H), 8.75 (dd, J = 4.8, 1.7 Hz, 1H), 8.27 – 8.23 (m, 1H), 7.39 (ddd, J = 8.0, 4.8, 0.9 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.28 – 7.23 (m, 3H), 4.29 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.3, 153.4, 150.0, 135.8, 133.4, 131.7, 129.3, 128.7, 127.1, 123.6, 45.7.

2-phenyl-1-(thiophen-2-yl)ethan-1-one (3o)[9]:

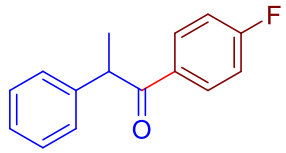


3p

The title compound was obtained as a yellow oil. Yield 30% (30 mg). R_f (10% EtOAc/Hexane): 0.24. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 3.8, 1.1 Hz, 1H), 7.63 (dd, J = 5.0, 1.1 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 4.20 (s, 2H). **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 190.4, 143.8, 134.2, 133.9, 132.6, 129.3, 128.6, 128.1, 126.9, 46.2.

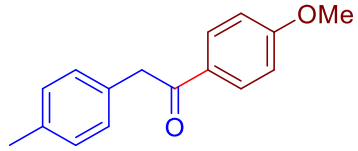
1-(4-fluorophenyl)-2-phenylpropan-1-one (3l)[10]:



3q

The title compound was obtained as a light-yellow liquid. Yield 61% (69 mg). R_f (5% EtOAc/Hexane): 0.2. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 – 7.93 (m, 2H), 7.31 – 7.24 (m, 4H), 7.22 – 7.17 (m, 1H), 7.02 (t, *J* = 8.7 Hz, 2H), 4.62 (q, *J* = 6.8 Hz, 1H), 1.52 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 198.6, 165.3 (d, *J* = 252.5 Hz), 141.3, 131.3 (d, *J* = 8.75 Hz), 129.0, 126.9, 115.5 (d, *J* = 21.45 Hz), 47.9, 19.4.

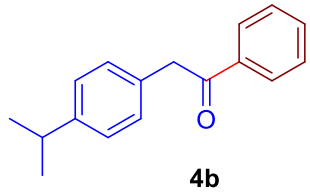
1-(4-methoxyphenyl)-2-(p-tolyl)ethan-1-one (4a)[7]:



4a

The title compound was obtained as a colourless solid. Yield 87% (104 mg), mp 89−91 °C. R_f (5% EtOAc/Hexane): 0.4. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.9 Hz, 2H), 7.16 – 7.11 (m, 4H), 6.92 (d, *J* = 8.9 Hz, 2H), 4.19 (s, 2H), 3.86 (s, 3H), 2.32 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 196.4, 163.3, 136.2, 131.7, 130.8, 129.5, 129.2, 129.1, 113.6, 55.3, 44.8, 20.9.

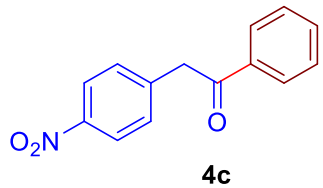
2-(4-isopropylphenyl)-1-phenylethan-1-one (4b):



4b

The title compound was obtained as a colourless solid. Yield 83% (99 mg), mp 85−87 °C. R_f (5% EtOAc/Hexane): 0.45. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.57 – 7.48 (m, 1H), 7.48 – 7.38 (m, 2H), 7.20 – 7.17 (m, 4H), 4.24 (s, 2H), 2.93 – 2.80 (m, 1H), 1.22 (d, *J* = 6.9 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.7, 147.3, 136.5, 133.0, 131.6, 129.5, 129.3, 129.0, 128.5, 128.5, 127.0, 126.6, 126.5, 44.9, 33.6, 23.9. HRMS (ESI): m/z $[M + H]^+$ calculated for : $C_{17}H_{19}O$: 239.1436; found: 239.1463. IR:(KBr) ν_{max} 3034, 1679, 1600, 1249, 1121, 922, 806, 757, 698, 569 cm^{-1}.

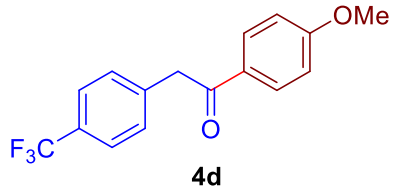
2-(4-nitrophenyl)-1-phenylethan-1-one (4c)[1]:



4c

The title compound was obtained as a yellow solid. Yield 81% (96 mg), mp 132−134 °C. R_f (5% EtOAc/Hexane): 0.25. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.23 – 8.18 (m, 2H), 8.01 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.64 – 7.59 (m, 1H), 7.53 – 7.48 (m, 2H), 7.46 – 7.41 (m, 2H), 4.42 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.9, 147.0, 141.9, 136.1, 133.7, 130.6, 128.8, 128.4, 123.7, 44.9.

1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)ethan-1-one (4d)[11]:

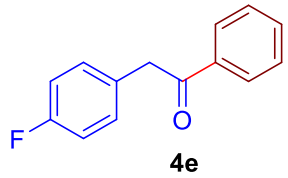


4d

The title compound was obtained as a colourless solid. Yield 79% (116 mg), mp 124−126 °C. R_f (10% EtOAc/Hexane): 0.37. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 2H), 6.98 – 6.93 (m, 2H), 4.30 (s, 2H), 3.88 (s,

3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.1, 163.7, 138.8, 130.7, 129.8, 129.0 (q, *J* = 33.5 Hz), 125.4 (q, *J* = 3.75 Hz), 113.8, 55.4, 44.7.

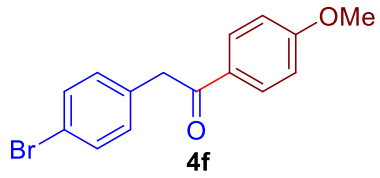
2-(4-fluorophenyl)-1-phenylethan-1-one (4e)[1]:



4e

The title compound was obtained as a colourless liquid. Yield 84% (90 mg). R_f (5% EtOAc/Hexane): 0.26. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.3, 1.2 Hz, 2H), 7.60 – 7.55 (m, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.23 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.06 – 6.99 (m, 2H), 4.27 (s, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 197.3, 161.8 (d, *J* = 242.5 Hz), 136.4, 133.2, 131.0 (d, *J* = 7.5 Hz), 130.1 (d, *J* = 3.75 Hz), 128.6, 128.4, 115.4 (d, *J* = 21.25 Hz), 44.4.

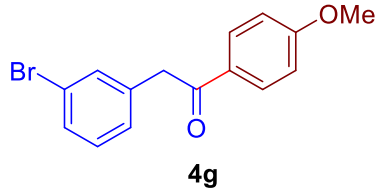
2-(4-bromophenyl)-1-(4-methoxyphenyl)ethan-1-one (4f)[7]:



4f

The title compound was obtained as a light yellow solid. Yield 88% (133 mg), mp 135−137 °C. R_f (5% EtOAc/Hexane): 0.36. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.19 (s, 2H), 3.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.4, 163.5, 133.7, 131.5, 131.1, 130.7, 129.2, 120.7, 113.7, 55.4, 44.3.

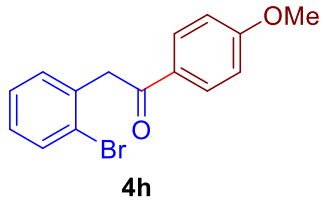
2-(3-bromophenyl)-1-(4-methoxyphenyl)ethan-1-one (4g):



4g

The title compound was obtained as a light yellow solid. Yield 86% (130 mg), mp 118−120 °C. R_f (5% EtOAc/Hexane): 0.32. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.9 Hz, 2H), 7.43 (s, 1H), 7.40 – 7.34 (m, 1H), 7.19 (dd, *J* = 4.1, 1.6 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 4.20 (s, 2H), 3.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 195.3, 163.6, 137.0, 132.4, 130.8, 130.0, 129.9, 129.3, 128.1, 122.5, 113.8, 55.4, 44.5. HRMS (ESI): m/z [M + H]$^+$ calculated for : $C_{15}H_{14}BrO_2$: 305.0177; found: 305. 0195. IR:(KBr) ν_{max} 2963, 1670, 1602, 1254, 990, 845, 745, 702, 668, 555 cm^{-1}.

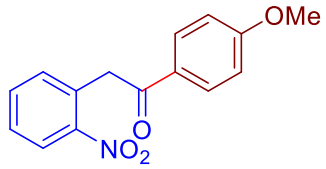
2-(2-bromophenyl)-1-(4-methoxyphenyl)ethan-1-one (4h)[12]:



4h

The title compound was obtained as a colourless solid. Yield 70% (106 mg), mp 66−68 °C. R_f (5% EtOAc/Hexane): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.66 – 7.54 (m, 1H), 7.30 – 7.23 (m, 2H), 7.17 – 7.12 (m, 1H), 6.98 – 6.94 (m, 2H), 4.41 (s, 2H), 3.88 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.9, 163.6, 135.2, 132.7, 131.6, 130.6, 129.6, 128.5, 127.4, 125.0, 113.8, 55.4, 45.3.

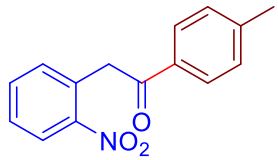
1-(4-methoxyphenyl)-2-(2-nitrophenyl)ethan-1-one (4i)[13]:



4i

The title compound was obtained as a yellow solid. Yield 67% (91 mg), mp 113−115 °C. R_f (20% EtOAc/Hexane): 0.6. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.2 Hz, 1H), 8.03 – 7.97 (m, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 6.95 (dd, *J* = 8.7, 1.3 Hz, 2H), 4.67 (s, 2H), 3.85 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 193.7, 163.6, 148.9, 133.5, 133.3, 130.7, 130.41, 129.3, 128.1, 125.0, 113.7, 55.4, 43.5.

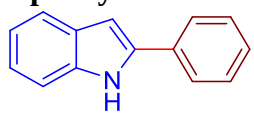
2-(2-nitrophenyl)-1-(p-tolyl)ethan-1-one (4j)[1]:



4j

The title compound was afforded as a yellow solid. Yield 65% (83 mg), mp 78−80 °C. R_f (10% EtOAc/Hexane): 0.35. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 2H), 7.60 (td, *J* = 7.5, 1.1 Hz, 1H), 7.47 (dd, *J* = 11.2, 4.5 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.9 Hz, 2H), 4.71 (s, 2H), 2.43 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.8, 149.0, 144.3, 133.9, 133.5, 133.3, 130.7, 129.3, 128.3, 128.2, 125.1, 43.9, 21.6.

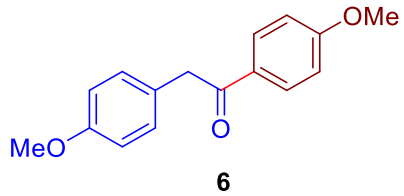
2-phenyl-1H-indole (6a)[1]:



5a

The title compound was afforded as a light yellow solid. Yield 77% (75 mg), mp 180−182 °C. R_f (5% EtOAc/Hexane): 0.45. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.37 (s, 1H), 7.68 – 7.64 (m, 3H), 7.47 – 7.41 (m, 3H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 6.84 (s, 1H).**^{13}C NMR** (150 MHz, $CDCl_3$) δ 137.8, 136.8, 132.3, 129.2, 129.0, 127.7, 125.1, 122.3, 120.6, 120.2, 110.9, 99.9.

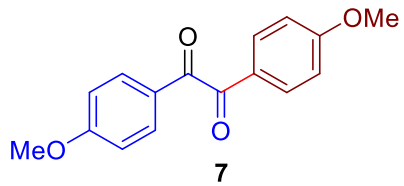
1,2-bis(4-methoxyphenyl)ethan-1-one[14]:



6

The title compound was afforded as a colourless solid. Yield 79% (202 mg), mp 110−112 °C. R_f (5% EtOAc/Hexane): 0.33. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.8 Hz, 2H), 7.18 (d, *J* = 8.5 Hz, 2H), 6.96 – 6.89 (m, 2H), 6.88 – 6.82 (m, 2H), 4.17 (s, 2H), 3.86 (s, 3H), 3.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 163.4, 158.4, 130.8, 130.3, 129.6, 126.9, 114.0, 113.7, 55.4, 55.2, 44.3.

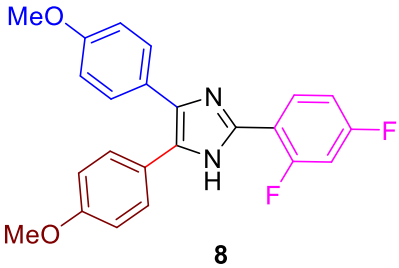
1,2-bis(4-methoxyphenyl)ethane-1,2-dione[15]:



7

The title compound was afforded as a light yellow solid. Yield 90% (142 mg), mp 125−127 °C. R_f (5% EtOAc/Hexane): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 – 7.92 (m, 2H), 6.98 – 6.94 (m, 2H), 3.87 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.4, 164.8, 132.3, 126.2, 114.2, 55.5.

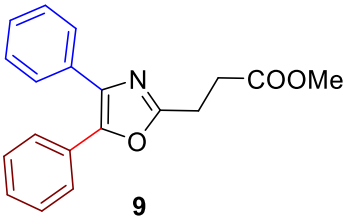
2-(2,4-difluorophenyl)-4,5-bis(4-methoxyphenyl)-1H-imidazole[3]:



8

The title compound was afforded as a colourless liquid. Yield 76% (106 mg). R_f (30% EtOAc/Hexane): 0.4. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.42 – 8.36(m, 1H), 7.47 (d, J = 8.2 Hz, 4H), 7.04 – 6.99 (m, 1H), 6.96 – 6.86 (m, 5H), 3.83 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.8 (d, *J* = 12.6 Hz), 161.3 (d, *J* = 12.5 Hz), 160.5 (d, *J* = 11.6 Hz), 159.0, 158.0 (d, *J* = 11.7 Hz), 139.8, 129.9 (dd, *J* = 9.4, 5.0 Hz), 129.0, 114.0, 112.5 (d, *J* = 21 Hz), 104.2 (t, *J* = 26 Hz), 55.2. HRMS (ESI): m/z $[M + H]^+$ calculated for : $C_{23}H_{19}F_2N_2O_2$: 393.1415; found: 393.1421

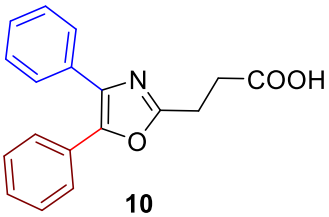
methyl 3-(4,5-diphenyloxazol-2-yl)propanoate[16]:



9

The title compound was afforded as a colourless solid. Yield 81% (111 mg), mp 60−62 °C. R_f (20% EtOAc/Hexane): 0.3. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.60 (m, 2H), 7.60 – 7.52 (m, 2H), 7.40 – 7.28 (m, 6H), 3.74 (s, 3H), 3.19 (t, *J* = 7.6 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 161.6, 135.1, 132.4, 128.9, 128.6, 128.5, 128.4, 128.0, 127.8, 126.4, 51.9, 30.9, 23.5. HRMS (ESI): m/z $[M + H]^+$ calculated for : $C_{19}H_{18}NO_3$: 308.1287; found: 308.1291

3-(4,5-diphenyloxazol-2-yl)propanoic acid[16]:



10

The title compound was afforded as a colourless solid. Yield 88% (75 mg), mp 153−155 °C. R_f (10% MeOH/$CHCl_3$): 0.32. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.16 (s, 1H), 7.66 – 7.60 (m, 2H), 7.59 – 7.54 (m, 2H), 7.40 – 7.28 (m, 6H), 3.21 (t, *J* = 7.4 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 176.6, 161.8, 145.5, 134.8, 132.0, 128.7, 128.6, 128.5, 128.5, 128.1, 127.9, 126.4, 30.8, 23.2. HRMS (ESI): m/z $[M + H]^+$ calculated for : $C_{18}H_{16}NO_3$: 294.1130; found: 294.1133

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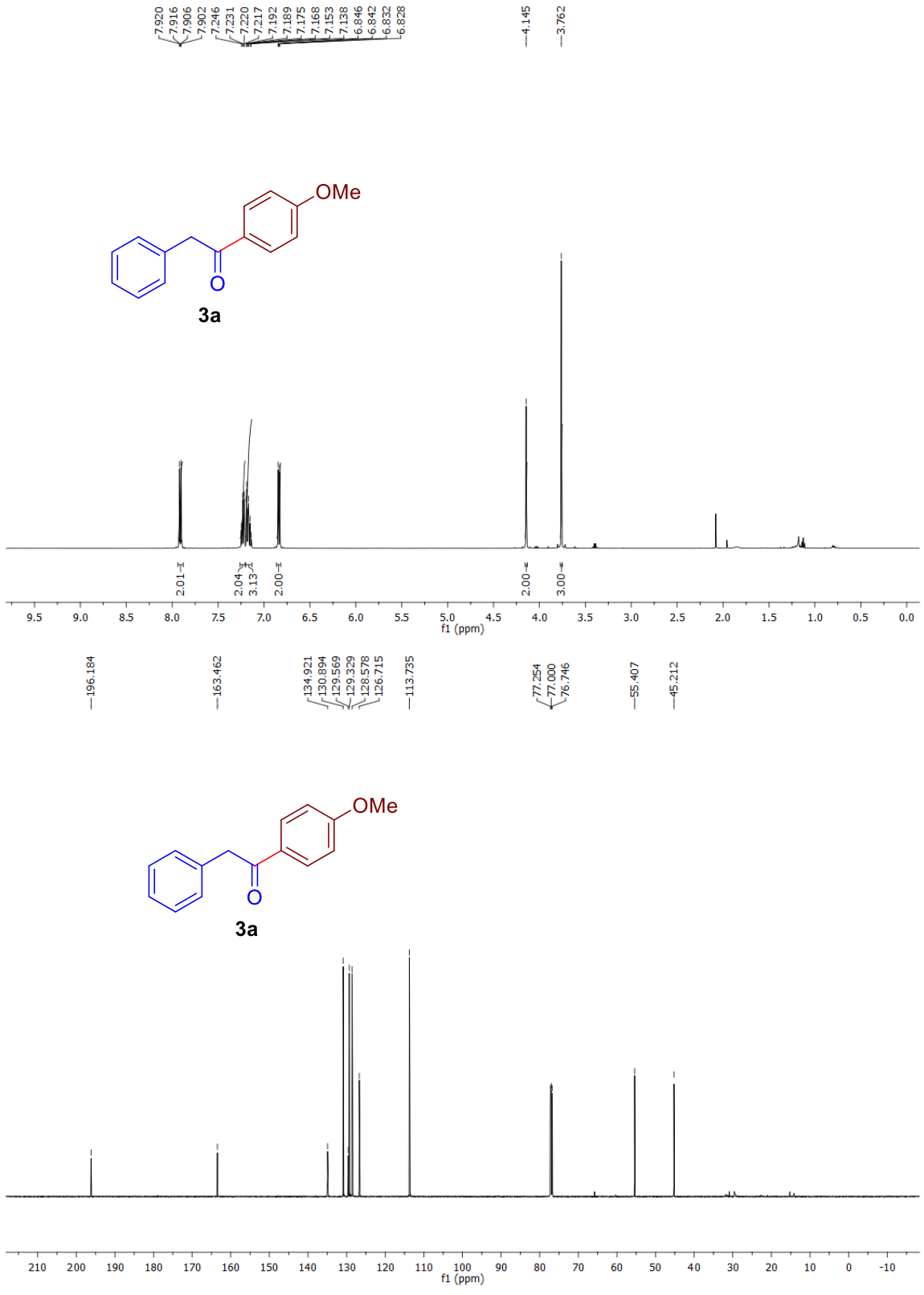

Figure 5.1. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3a**) in $CDCl_3$

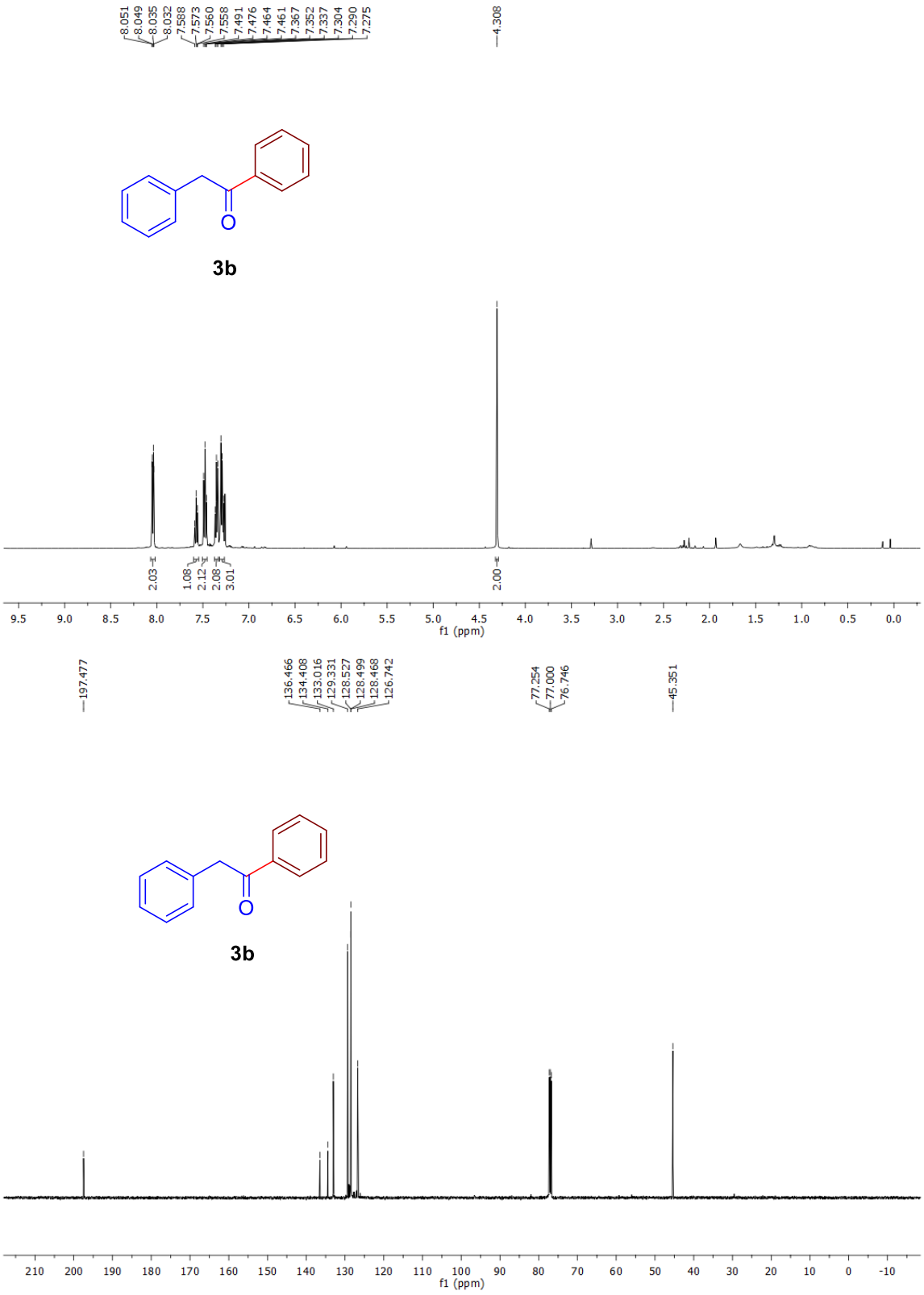

Figure 5.2. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3b**) in $CDCl_3$.

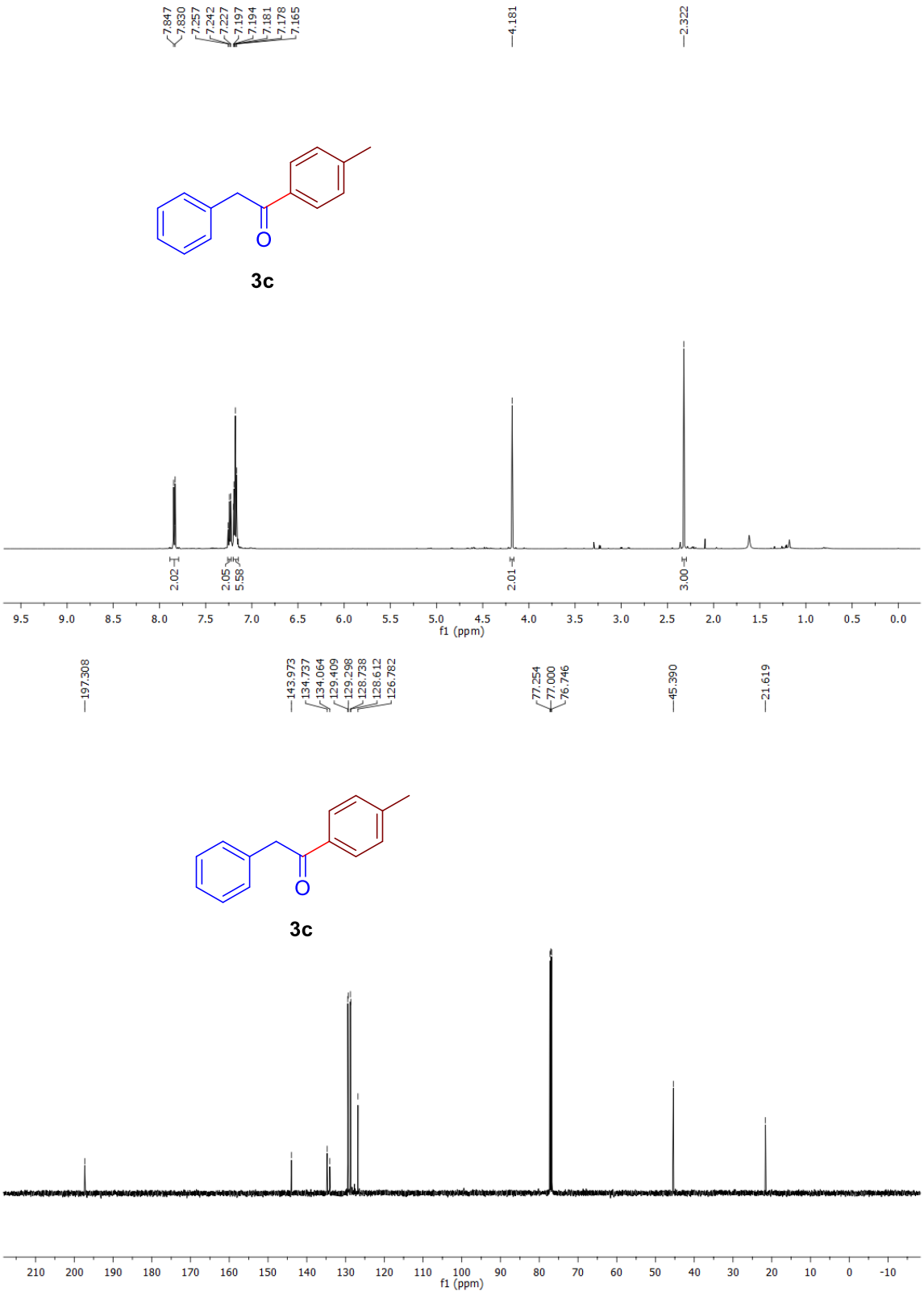

Figure 5.3. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3c**) in $CDCl_3$.

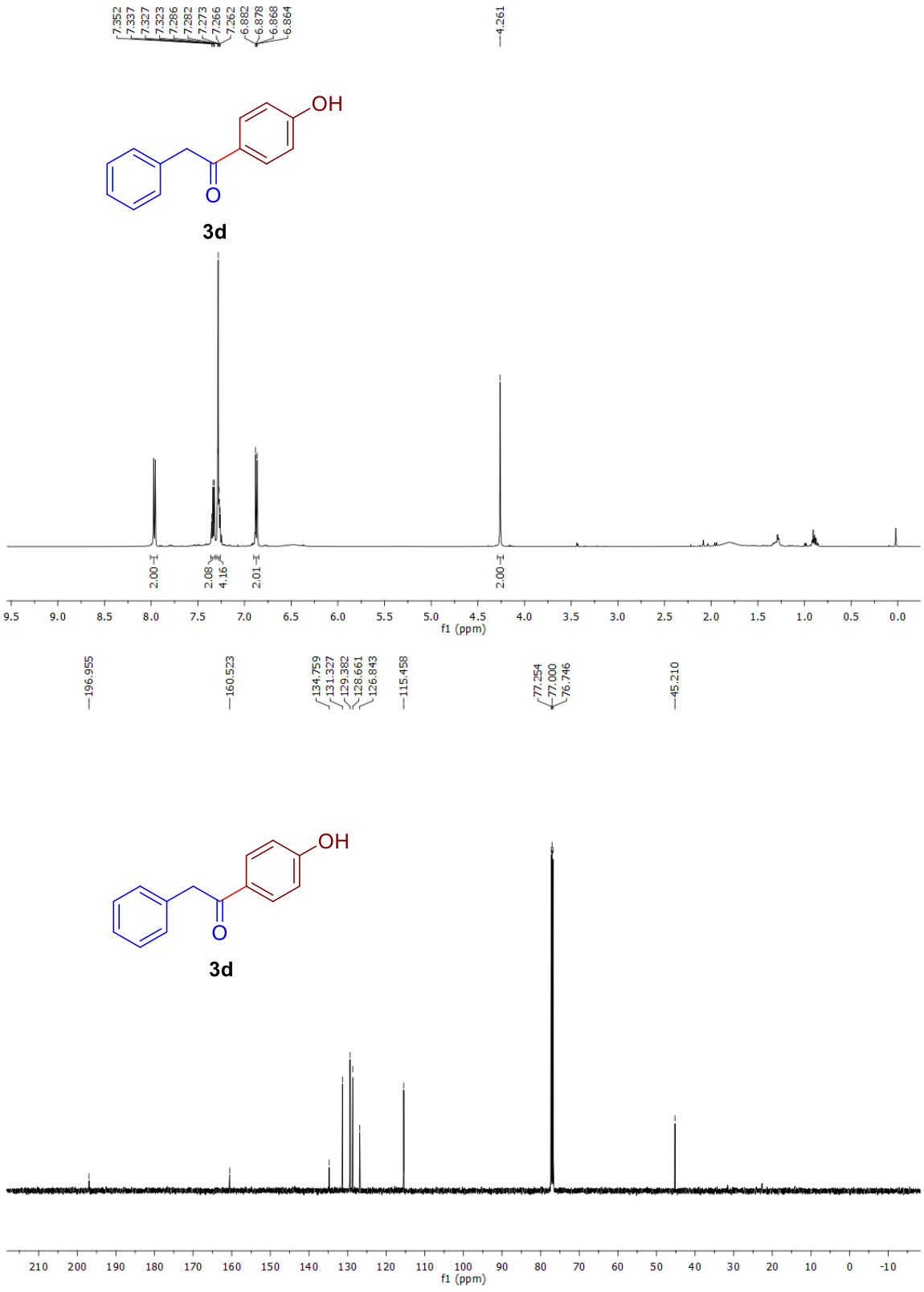

Figure 5.4. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3d**) in $CDCl_3$.

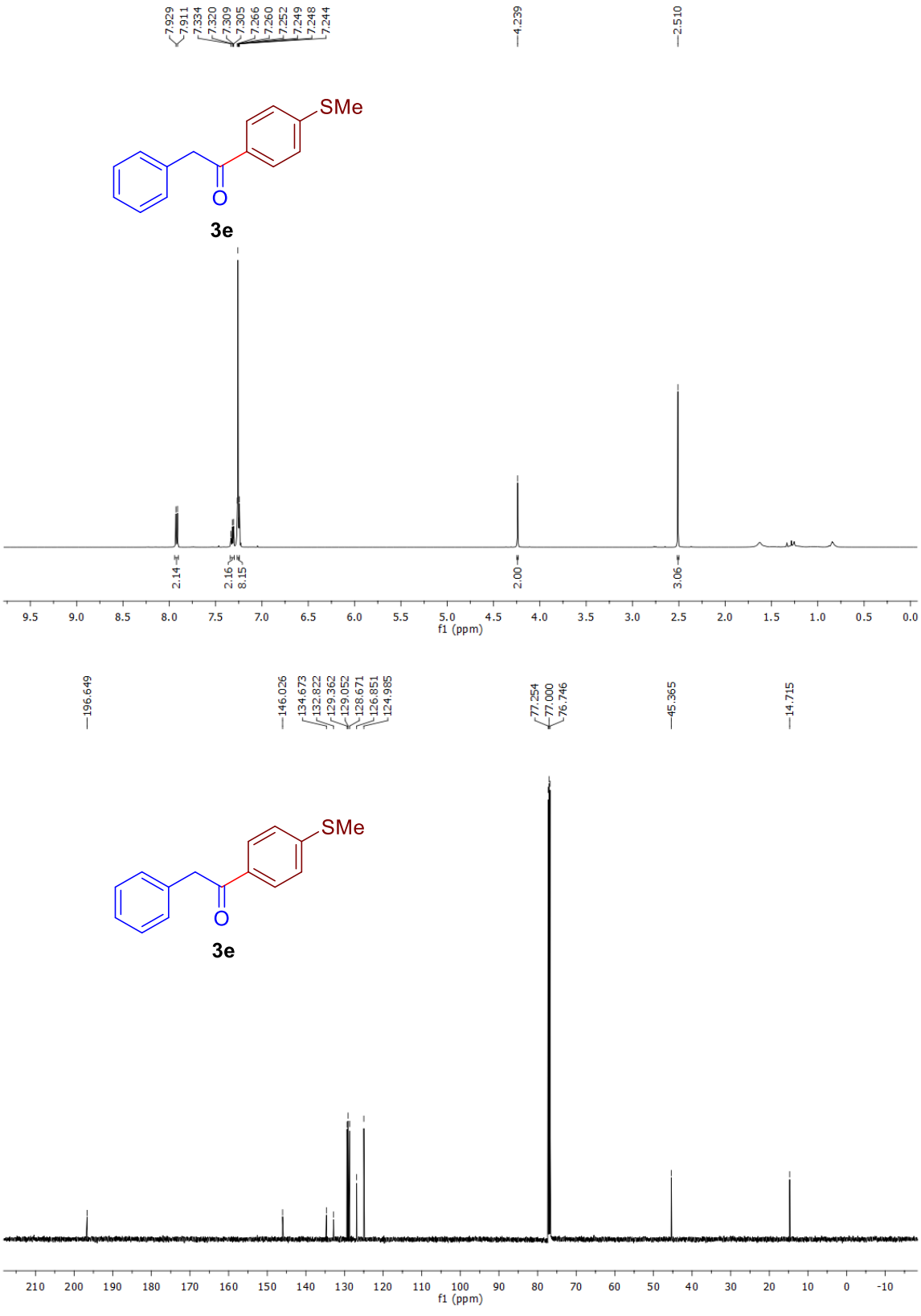

Figure 5.5. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3e**) in $CDCl_3$.

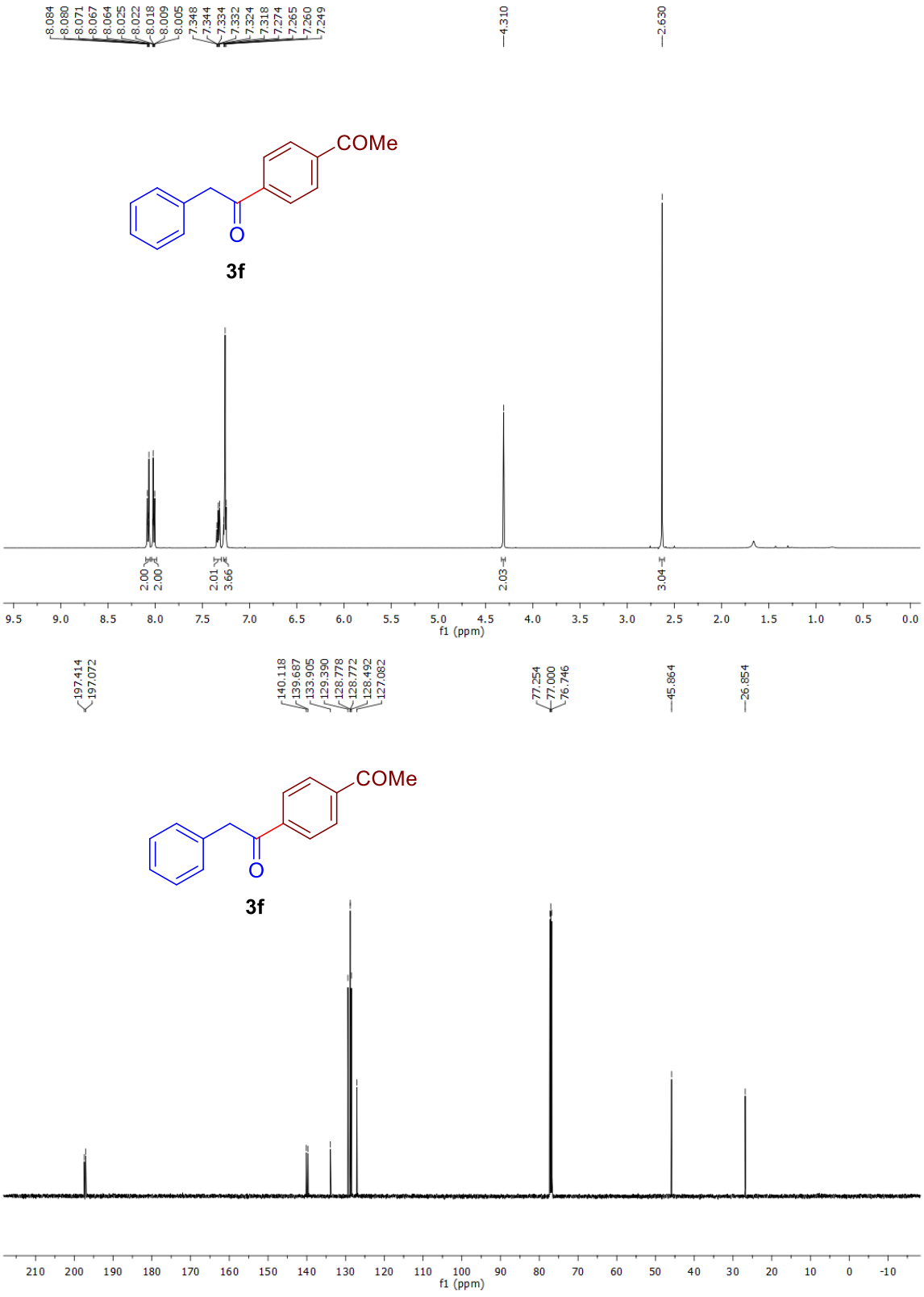

Figure 5.6. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3f**) in $CDCl_3$.

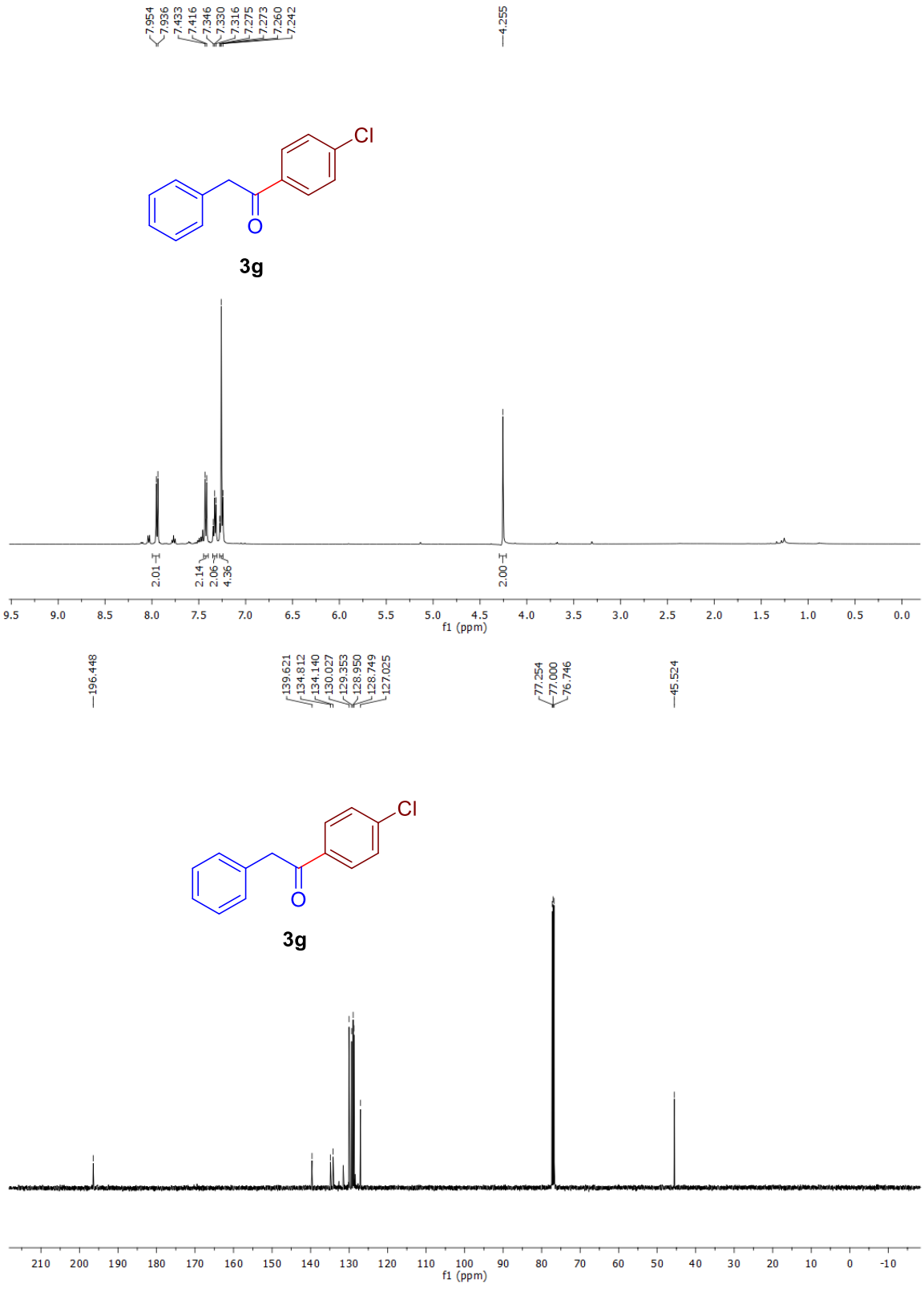

Figure 5.7. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3g**) in $CDCl_3$.

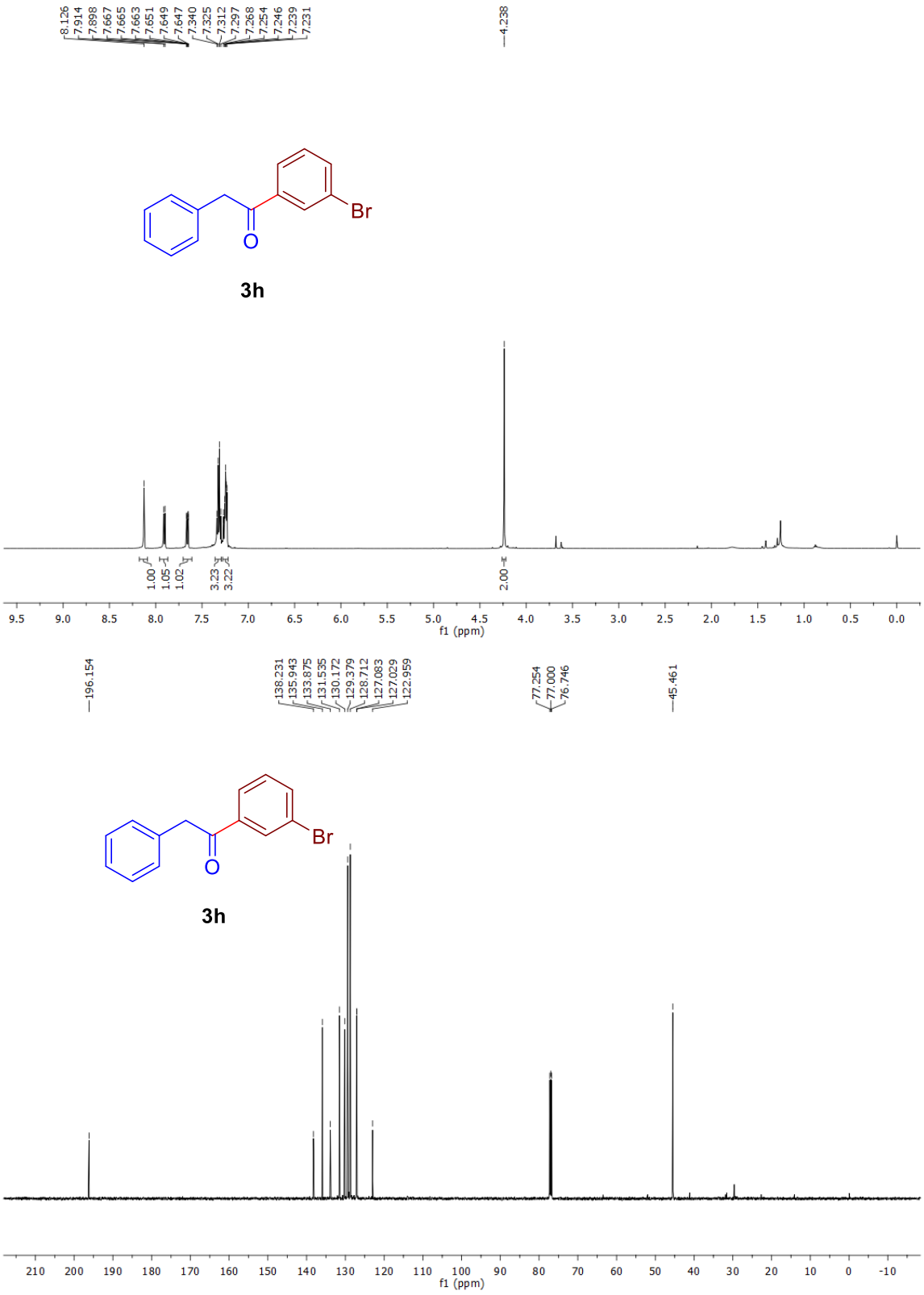

Figure 5.8. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3h**) in $CDCl_3$.

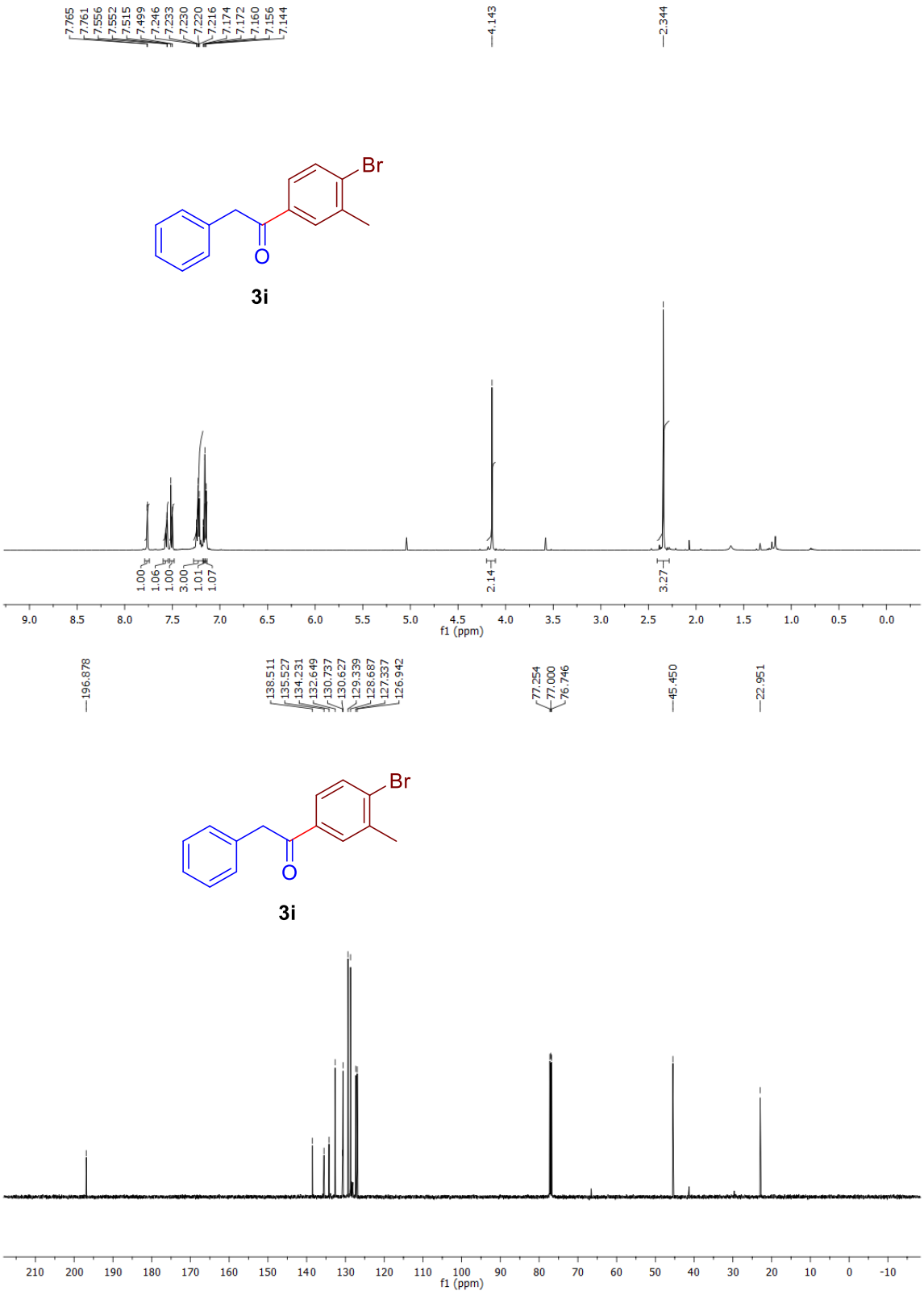

Figure 5.9. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3i**) in $CDCl_3$.

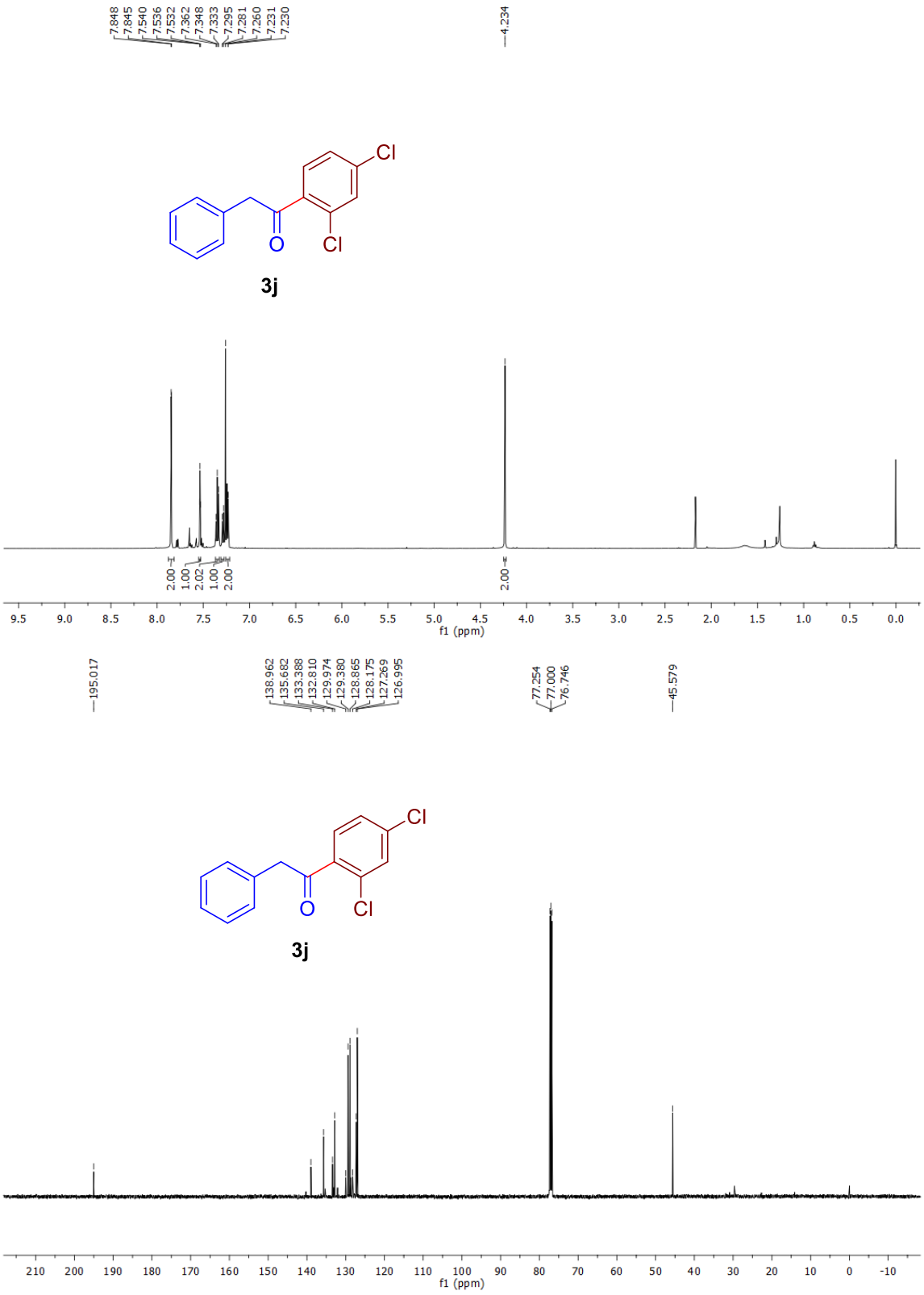

Figure 5.10. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3j**) in $CDCl_3$.

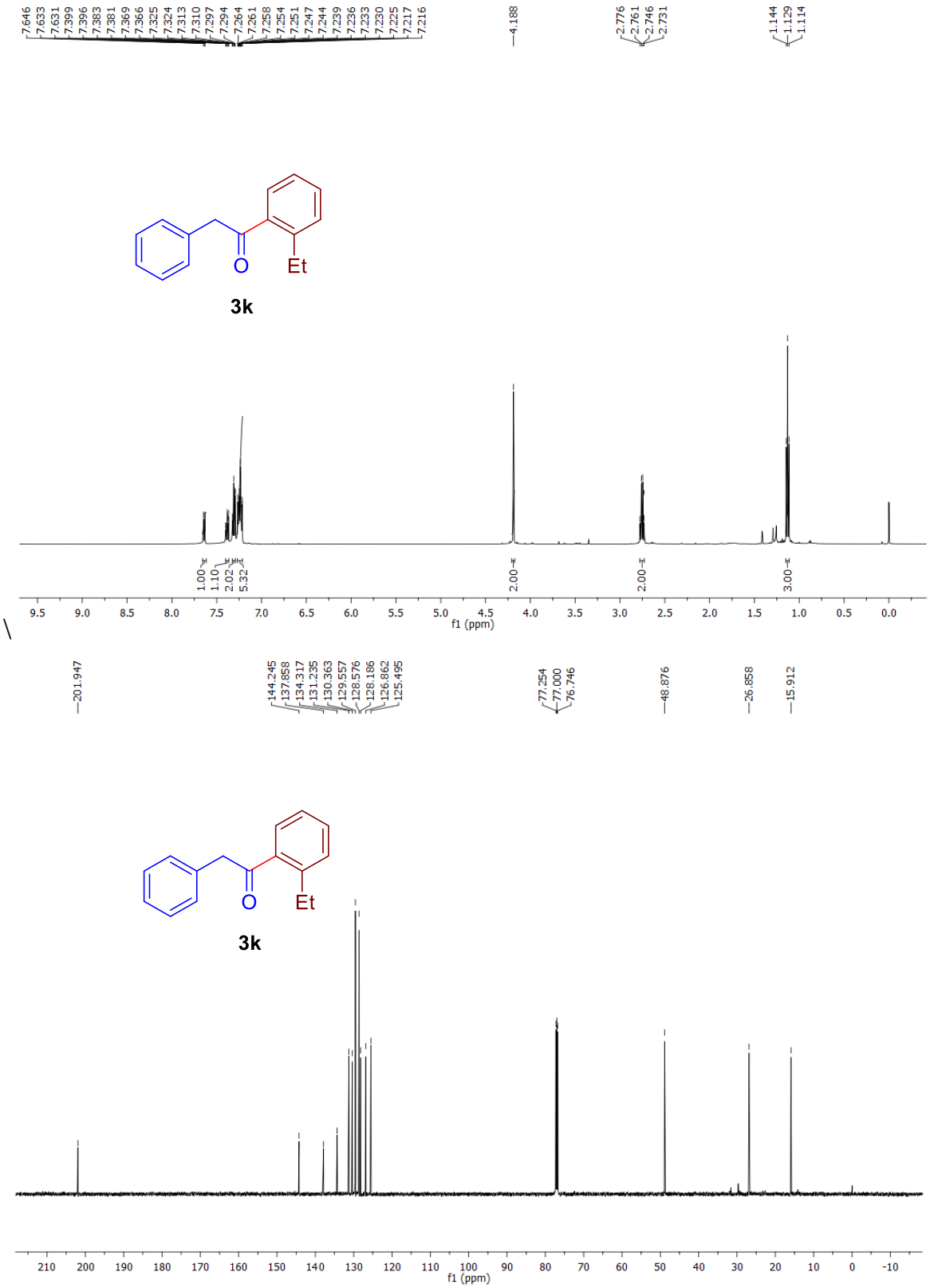

Figure 5.11. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3k**) in $CDCl_3$.

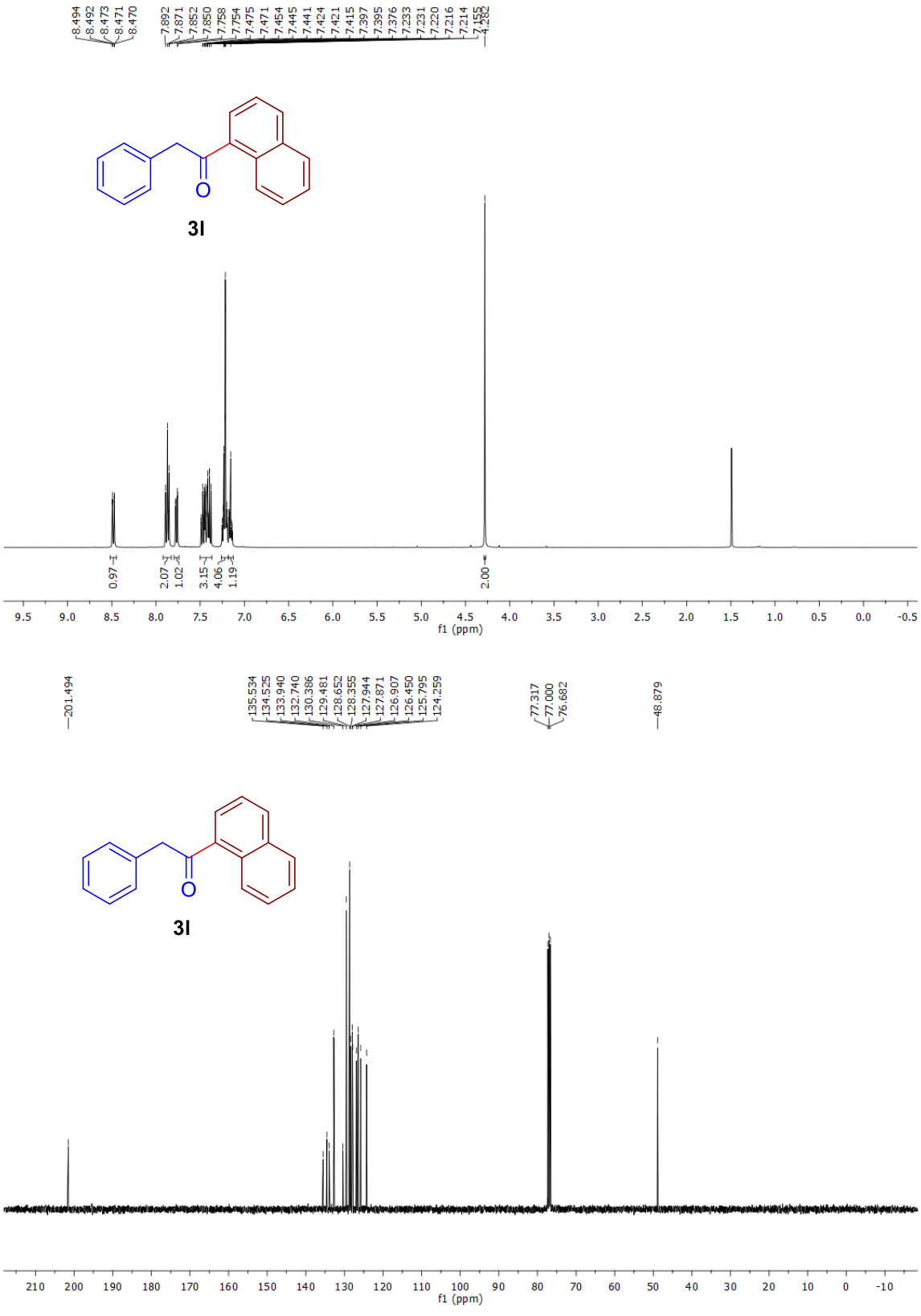

Figure 5.12. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**3l**) in $CDCl_3$

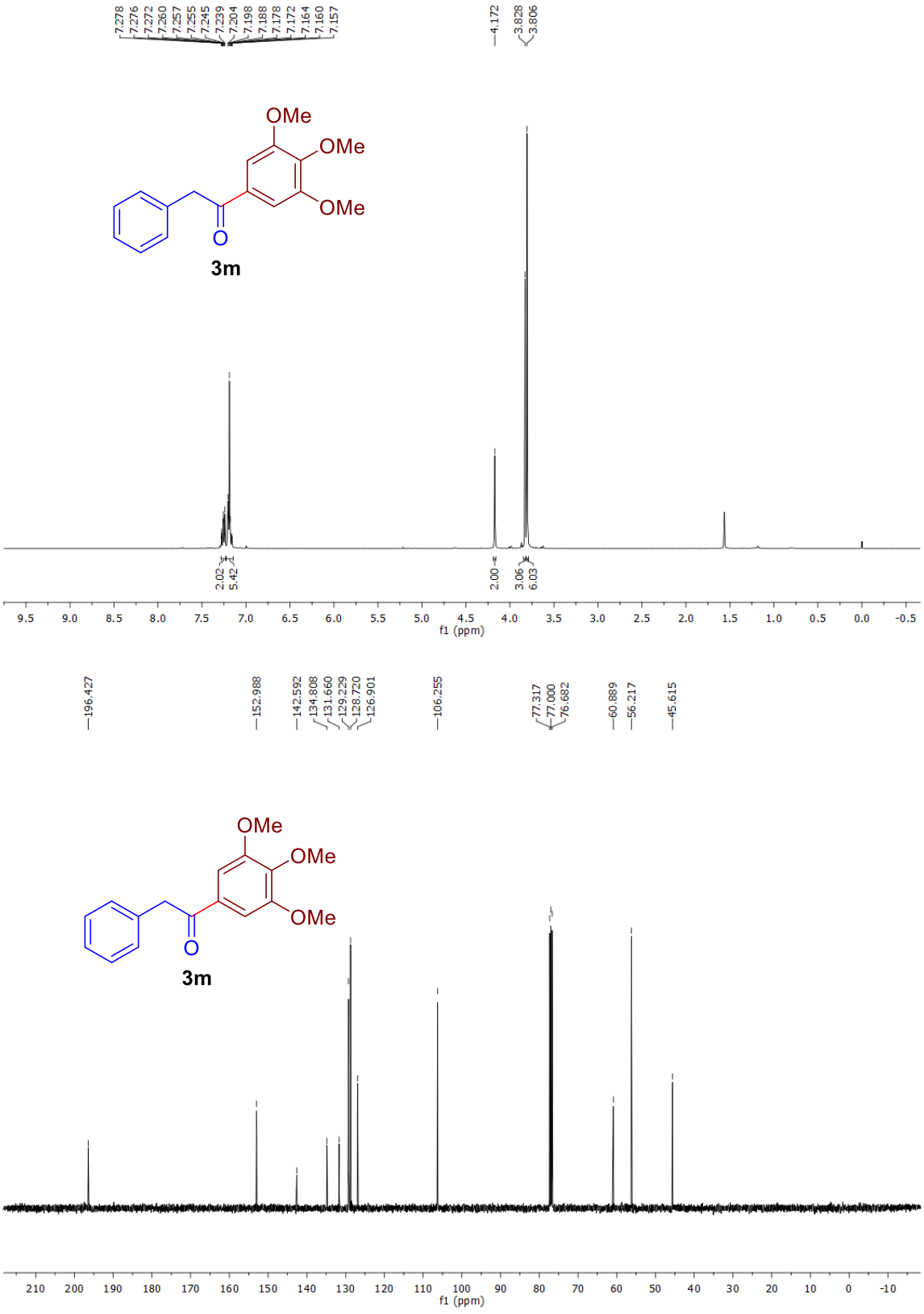

Figure 5.13. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**3m**) in $CDCl_3$

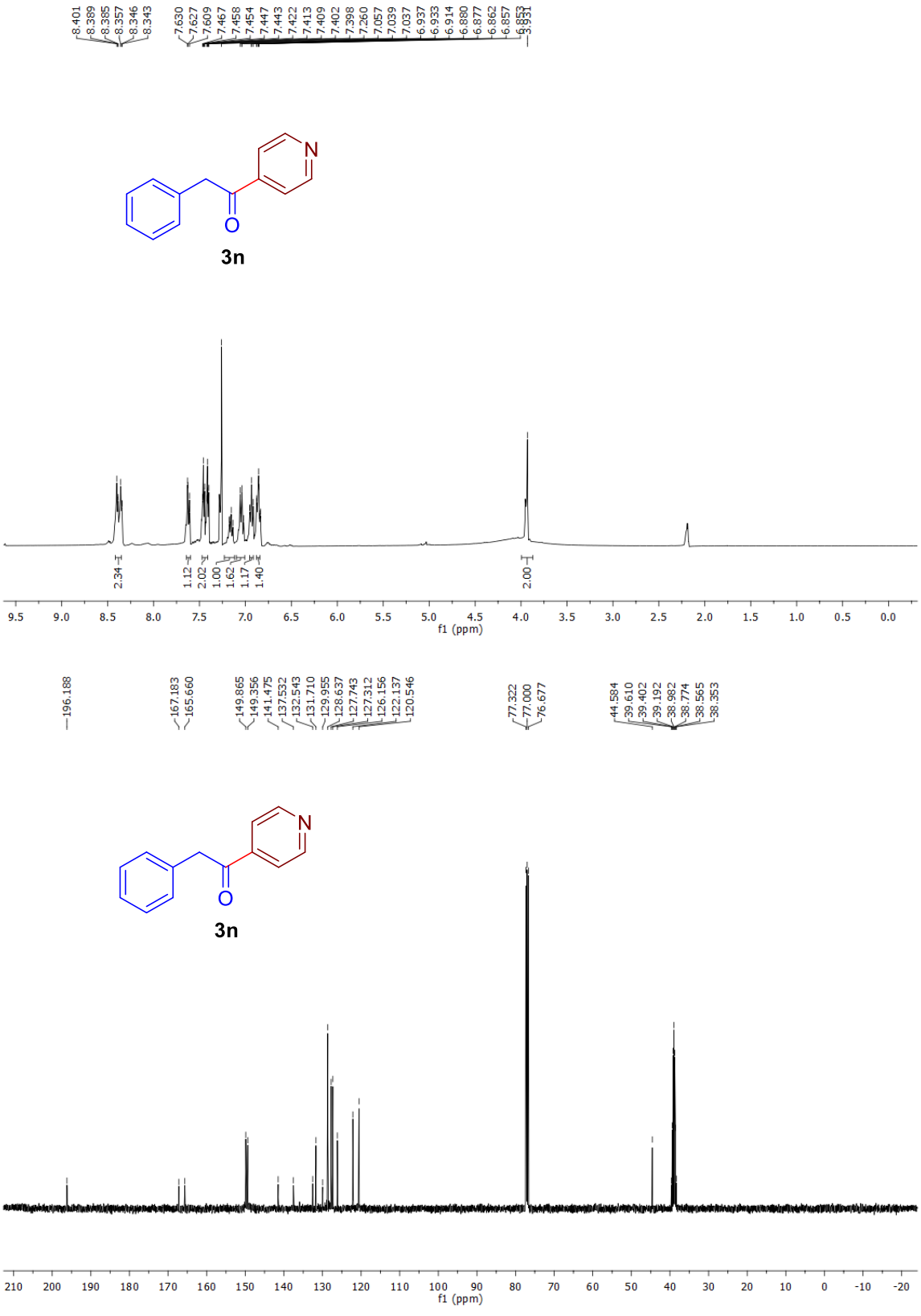

Figure 5.14. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**3n**) in $CDCl_3$ + DMSO-*d*6.

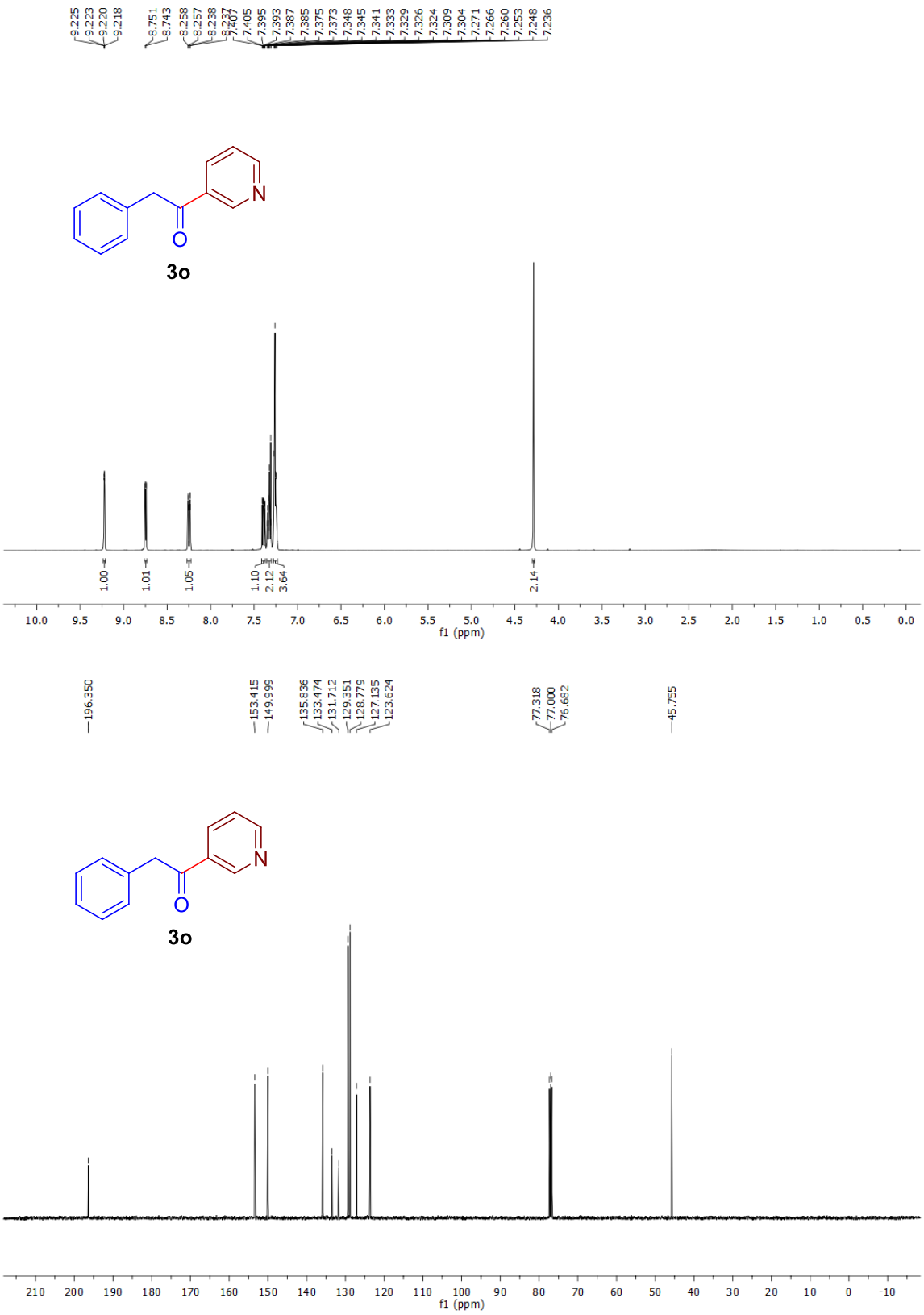

Figure 5.15. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**3o**) in $CDCl_3$.

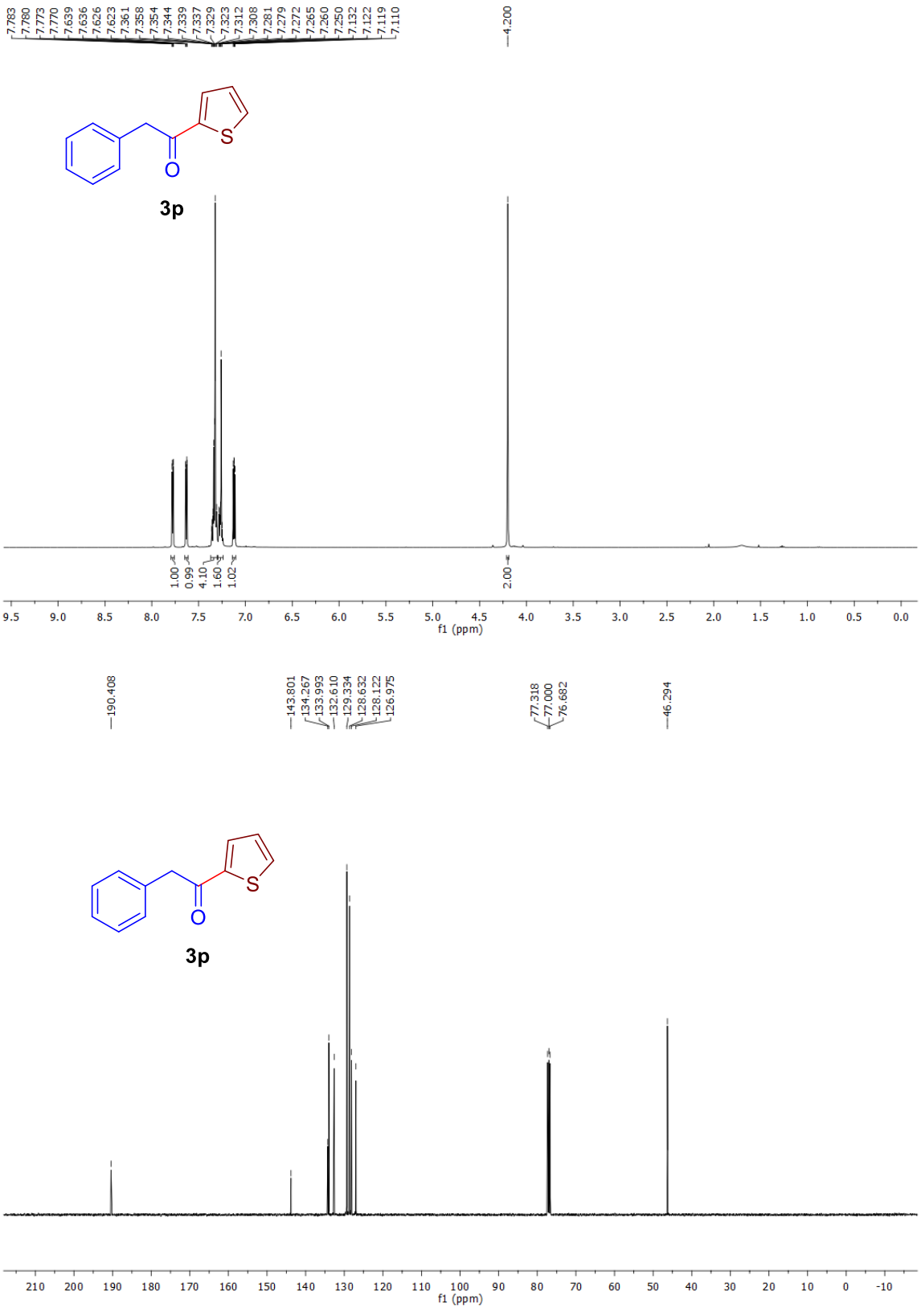

Figure 5.16. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**3p**) in $CDCl_3$.

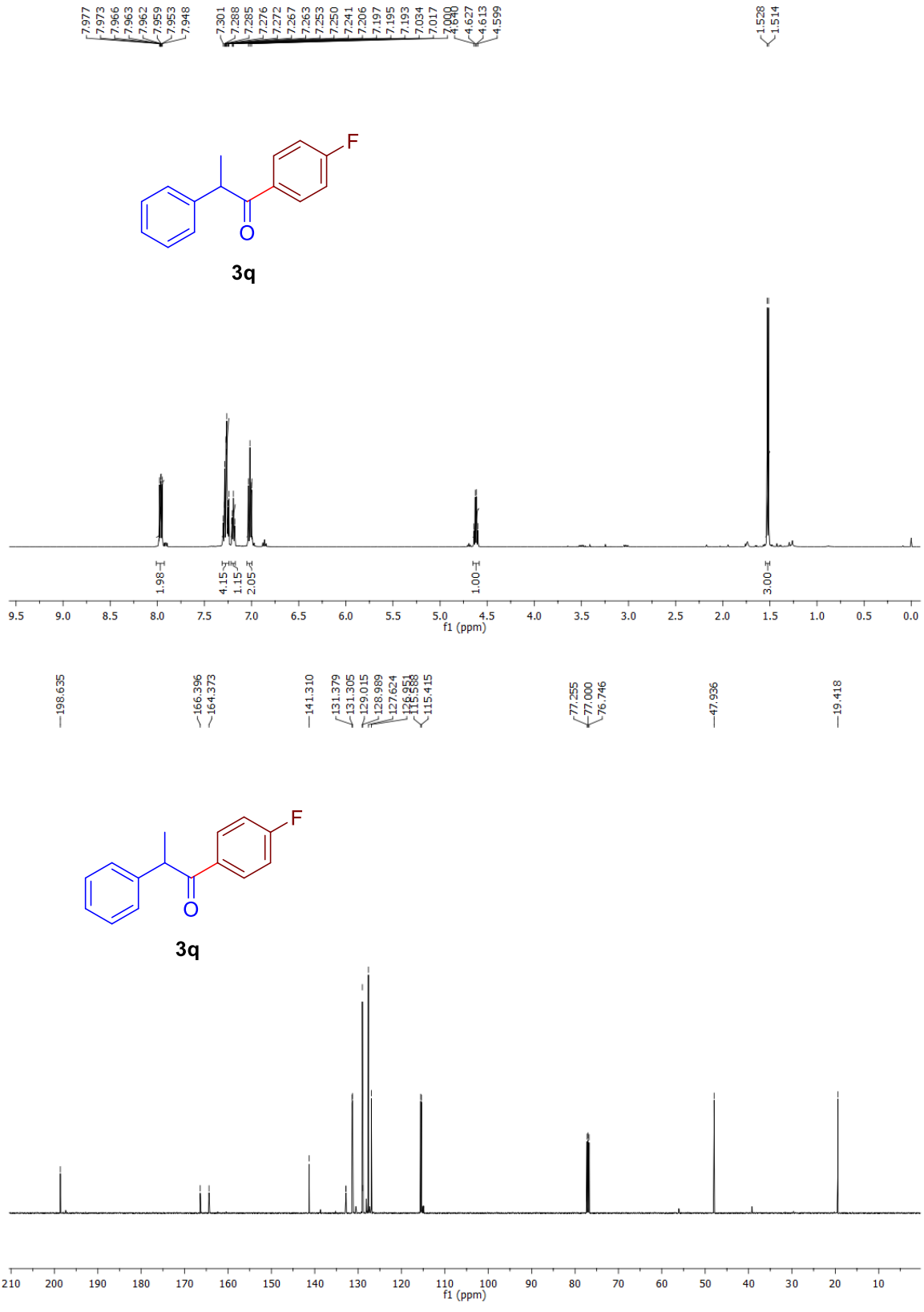

Figure 5.17. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**3q**) in $CDCl_3$.

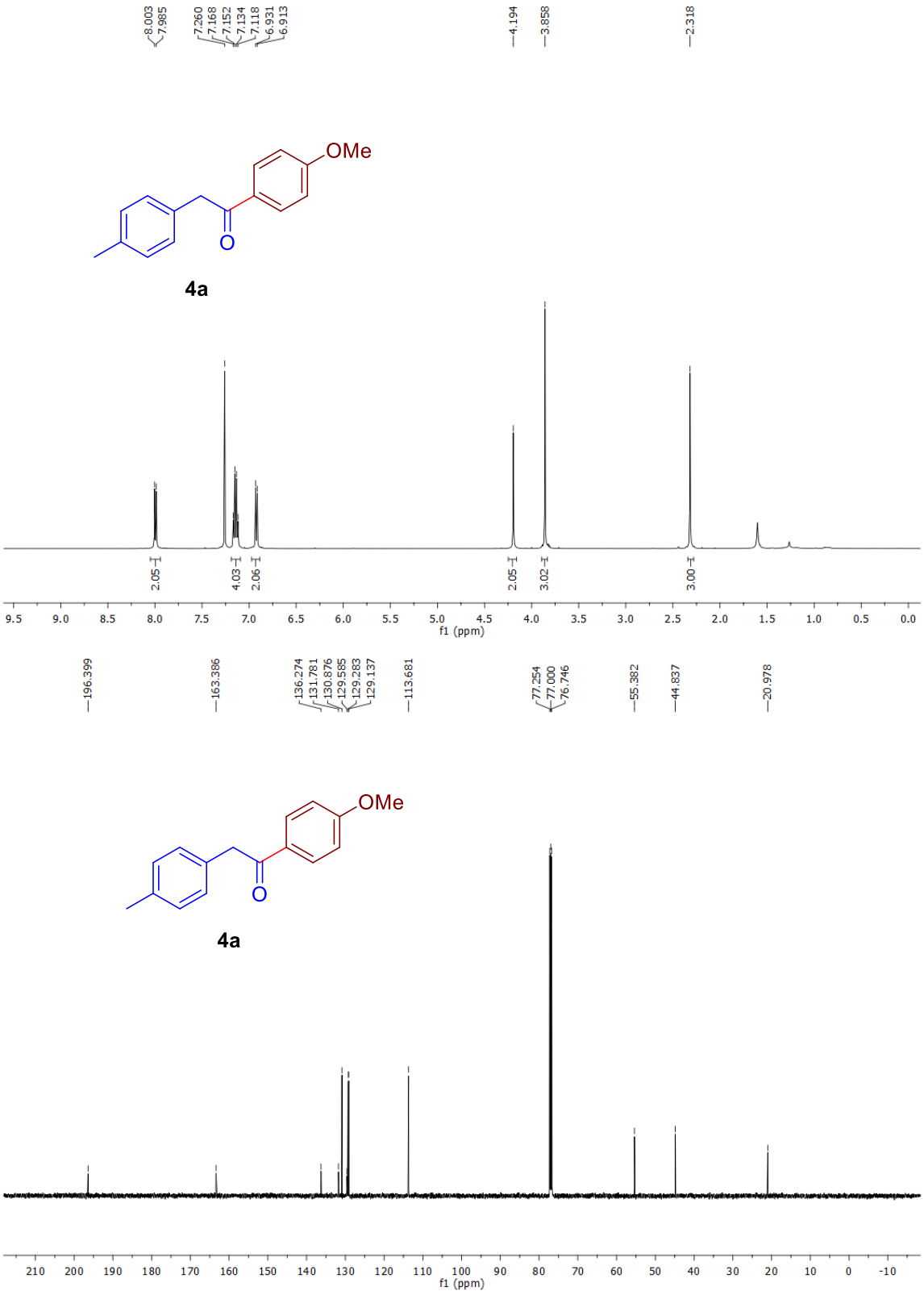

Figure 5.18. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4a**) in $CDCl_3$.

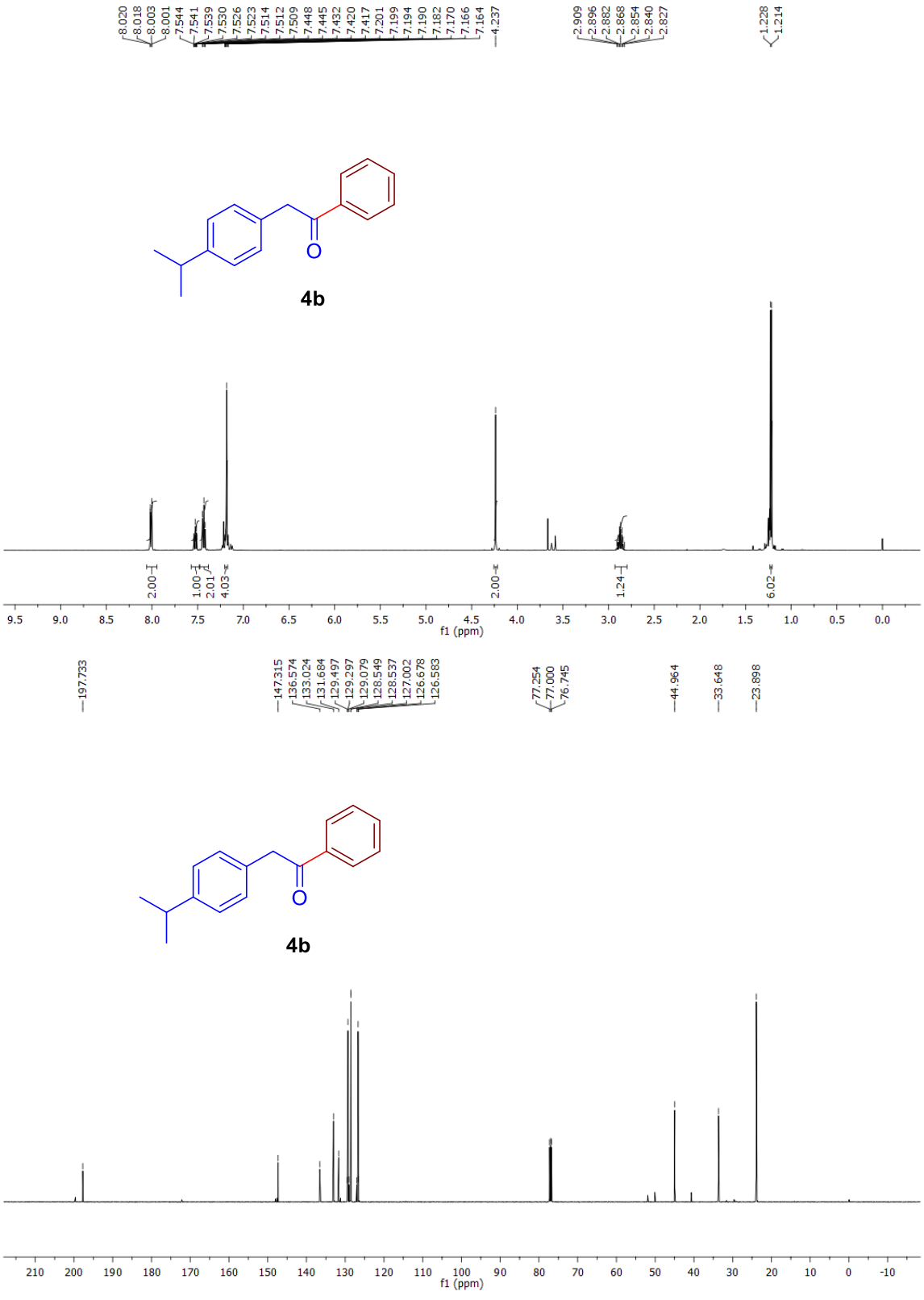

Figure 5.19. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4b**) in $CDCl_3$.

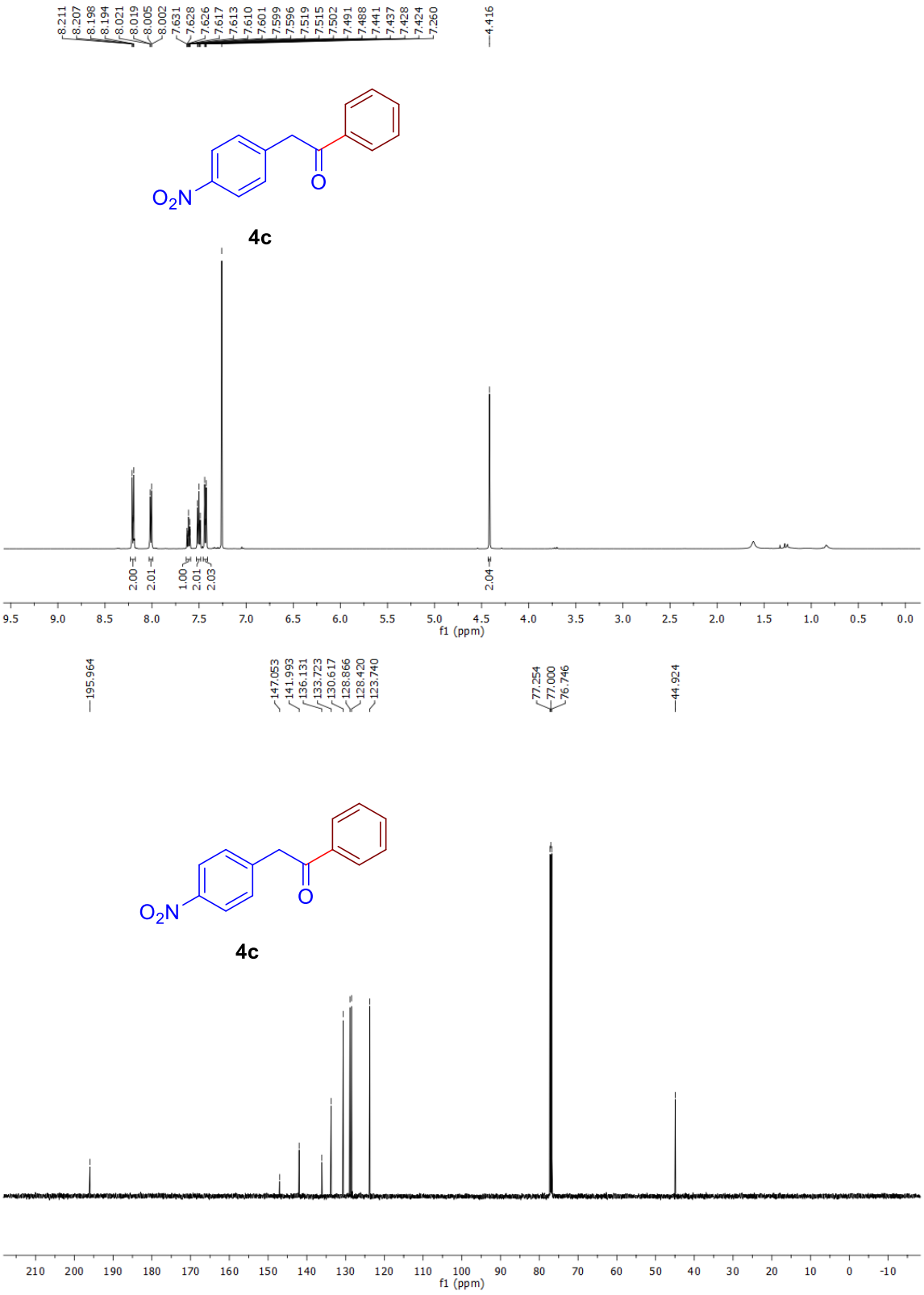

Figure 5.20. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4c**) in $CDCl_3$.

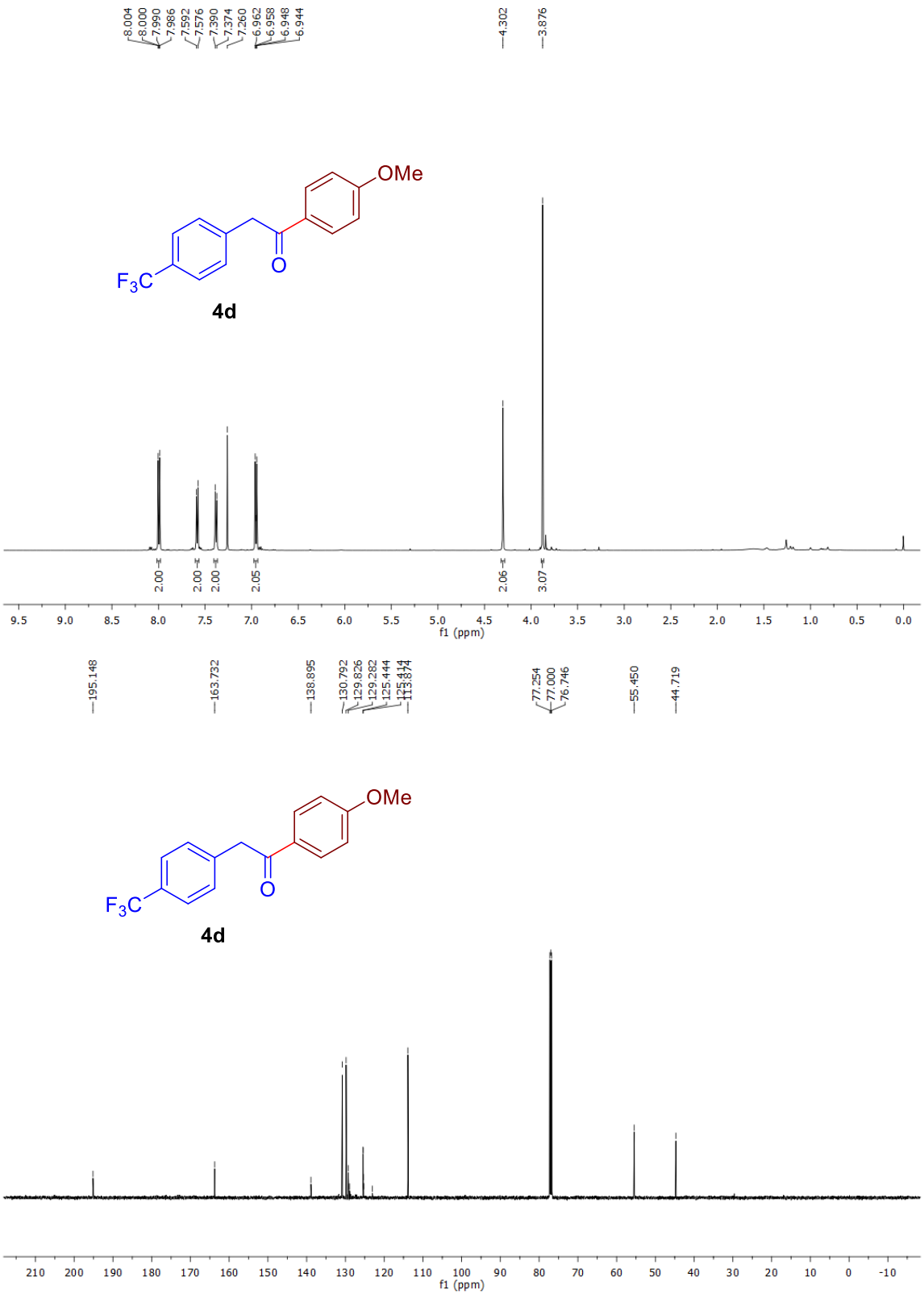

Figure 5.21. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4d**) in $CDCl_3$.

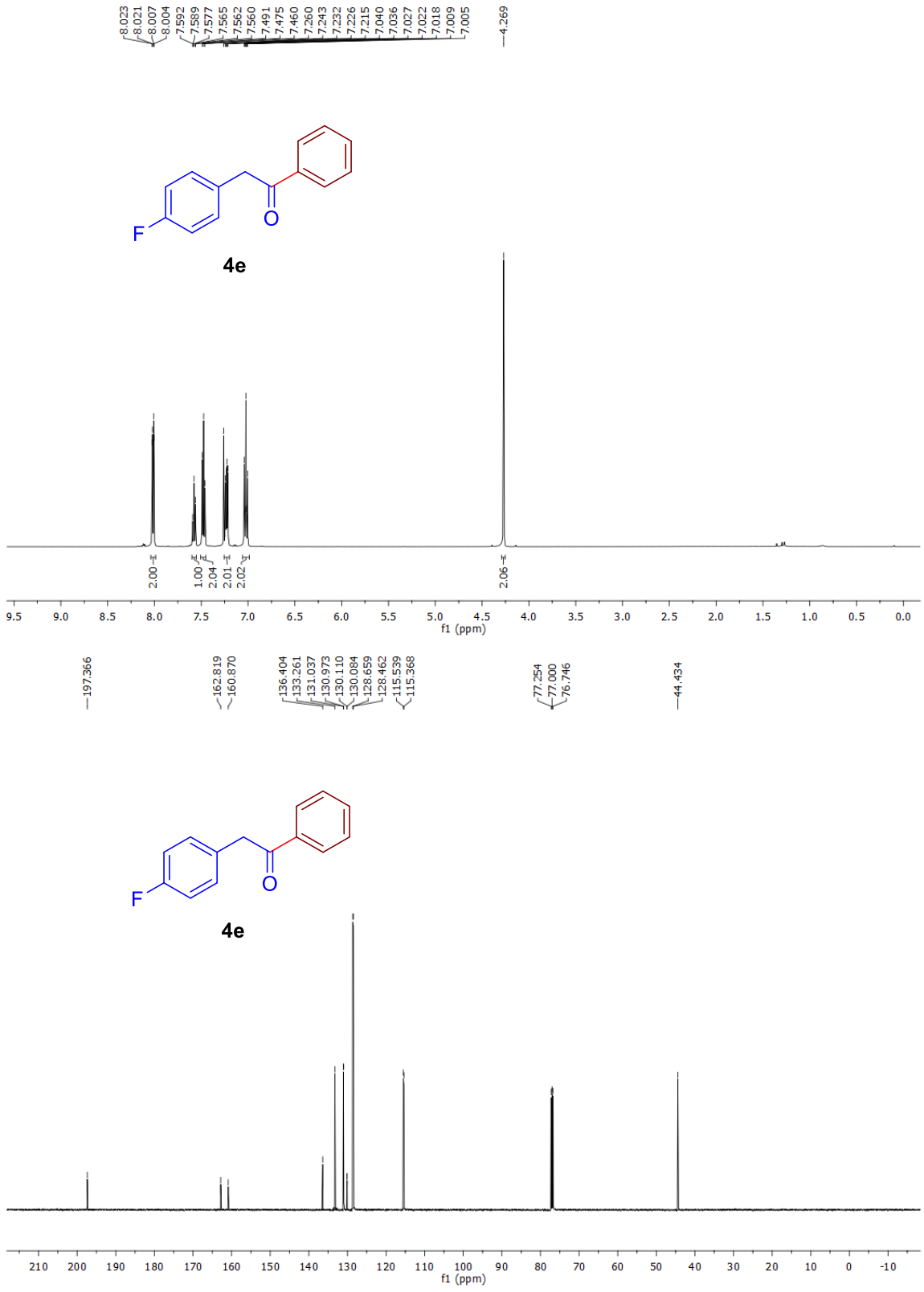

Figure 5.22. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4e**) in $CDCl_3$.

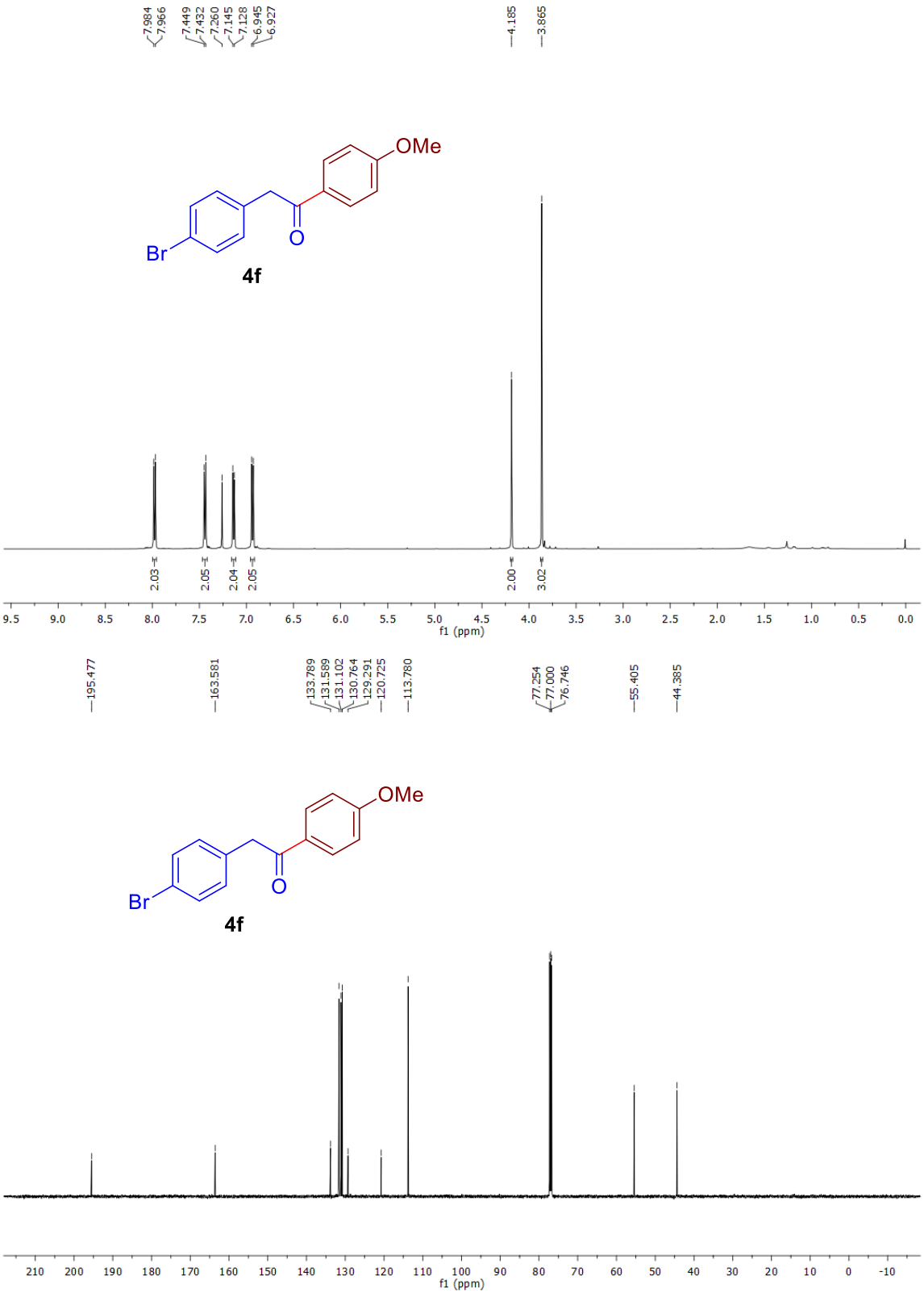

Figure 5.23. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4f**) in $CDCl_3$.

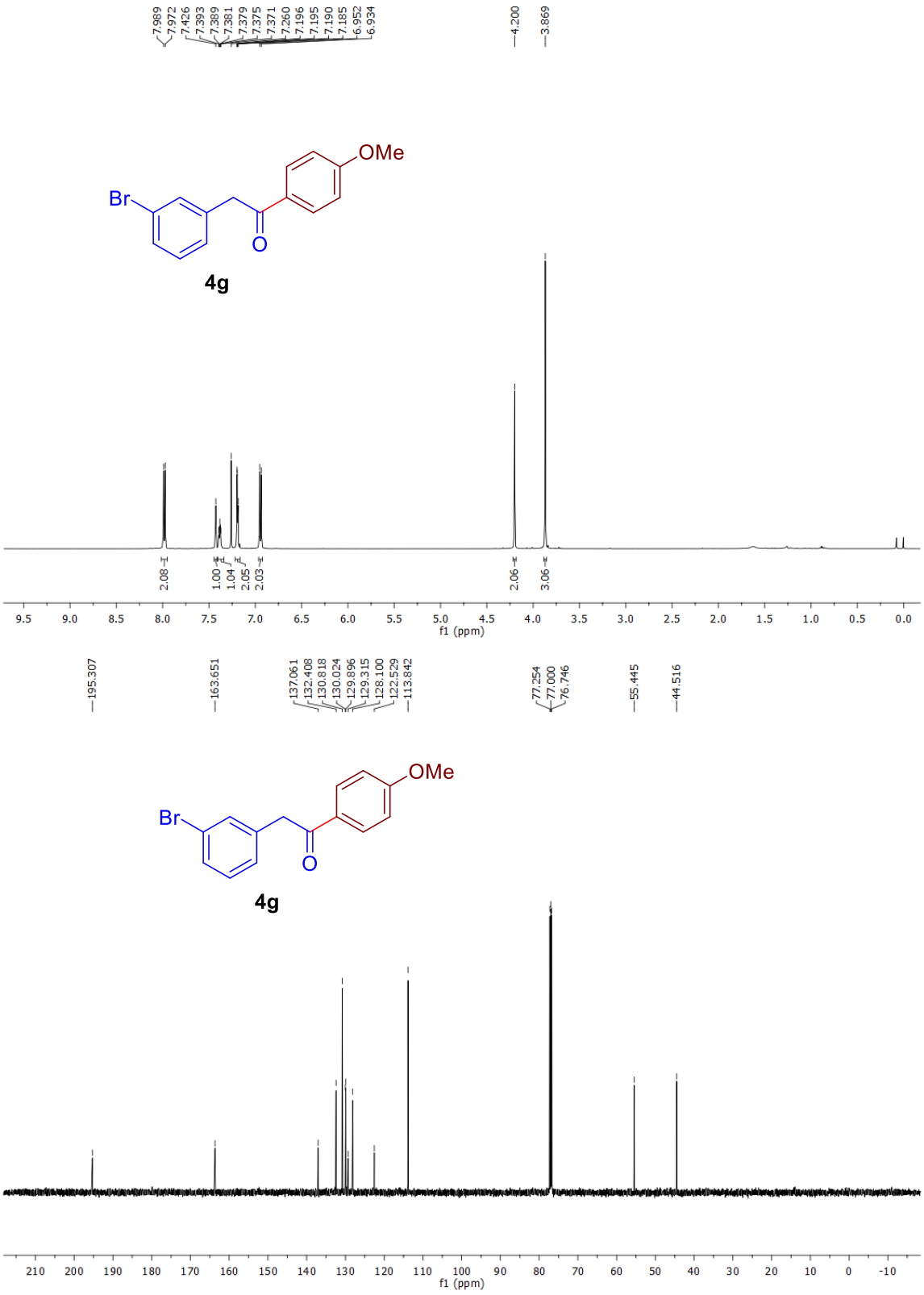

Figure 5.24. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4g**) in $CDCl_3$.

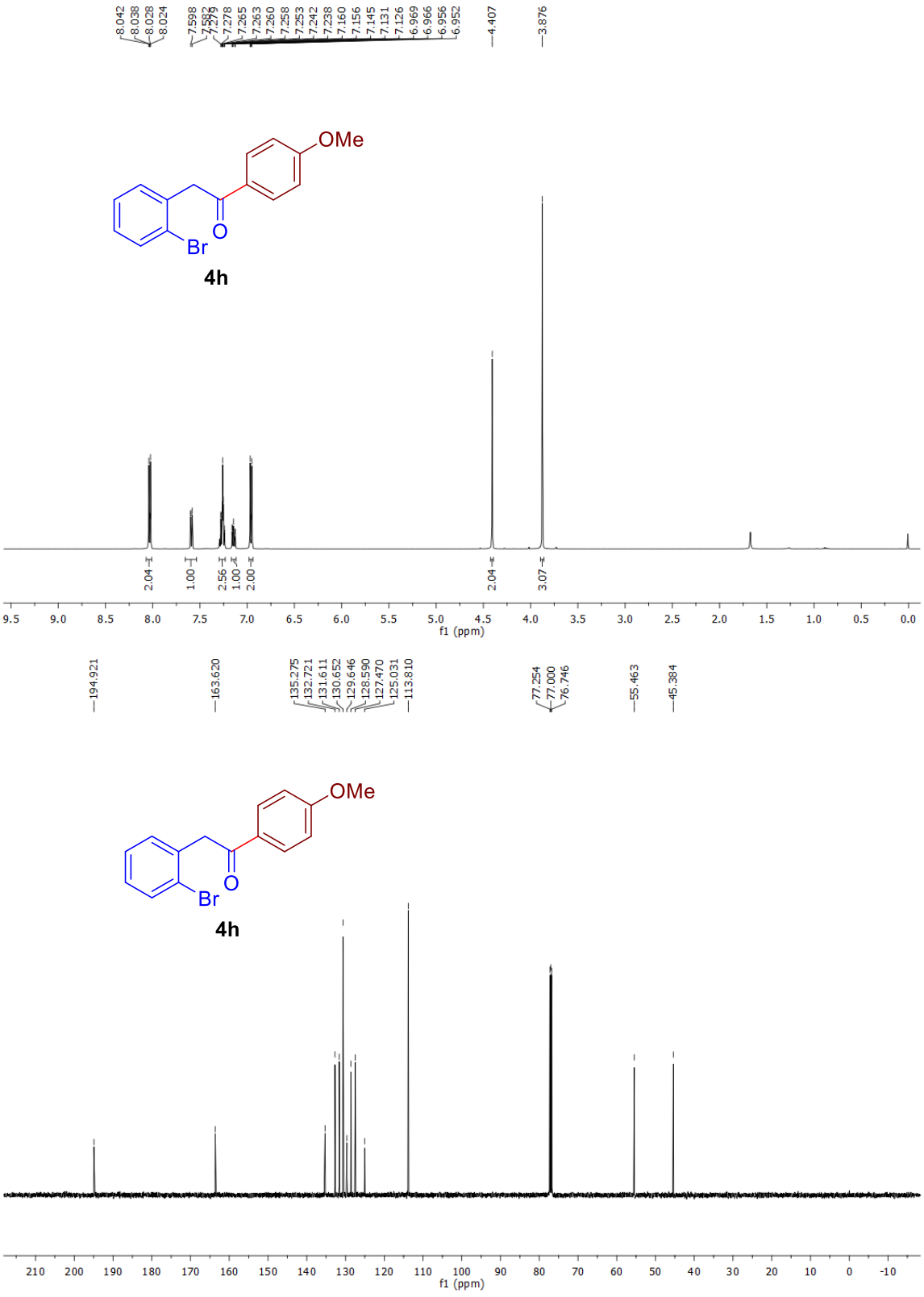

Figure 5.25. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4h**) in $CDCl_3$.

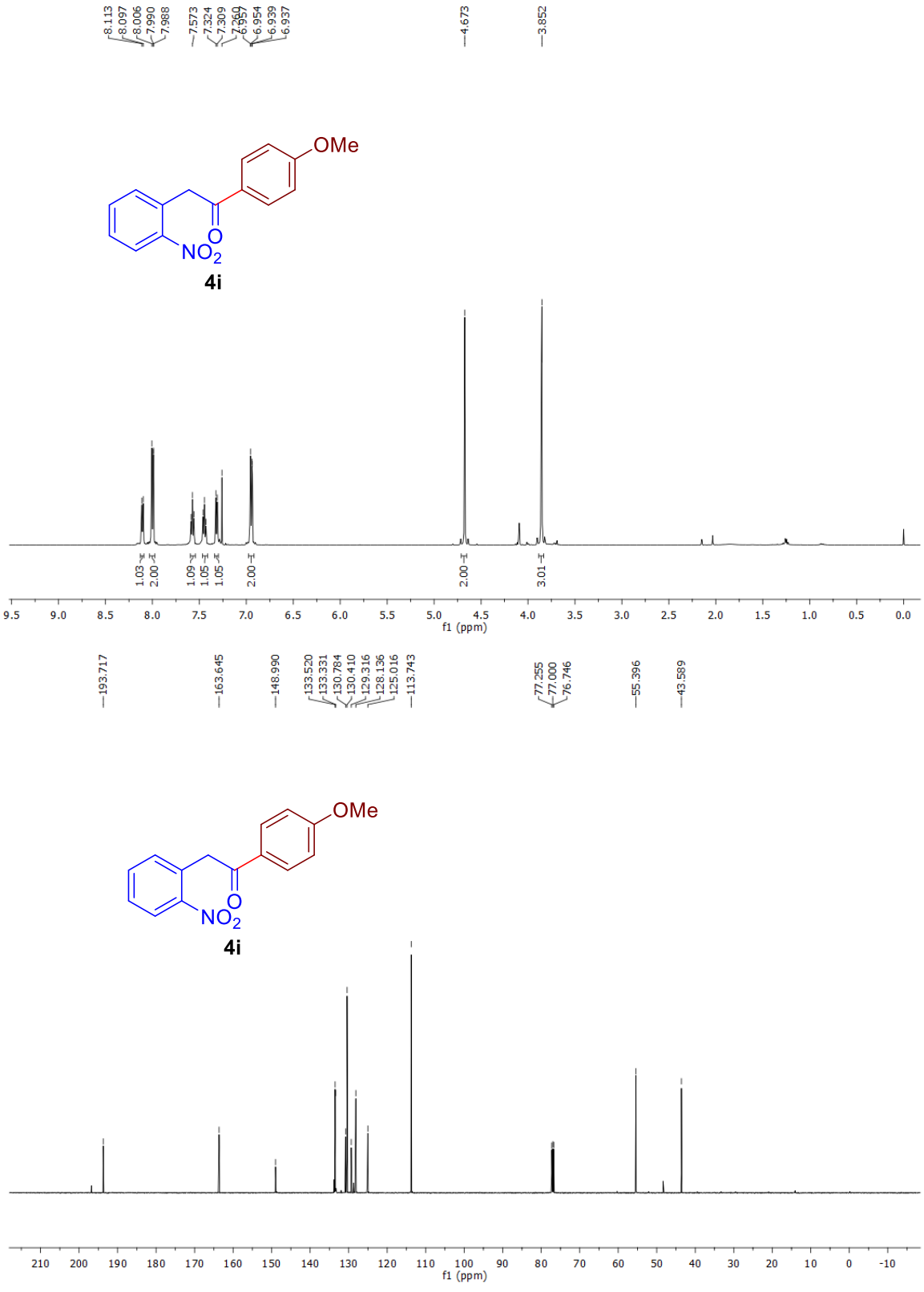

Figure 5.26. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4i**) in $CDCl_3$.

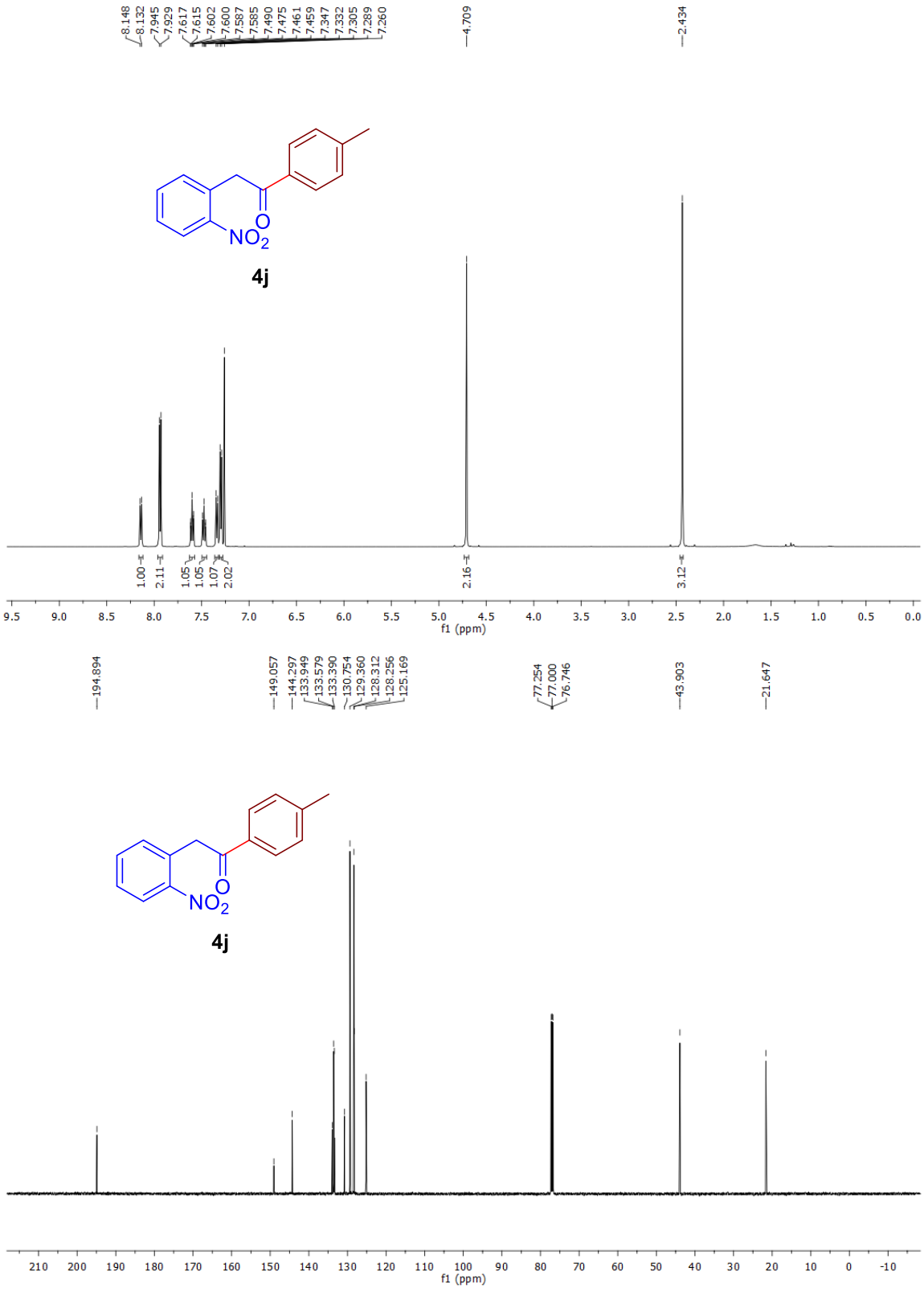

Figure 5.27. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) Spectra of (**4j**) in $CDCl_3$.

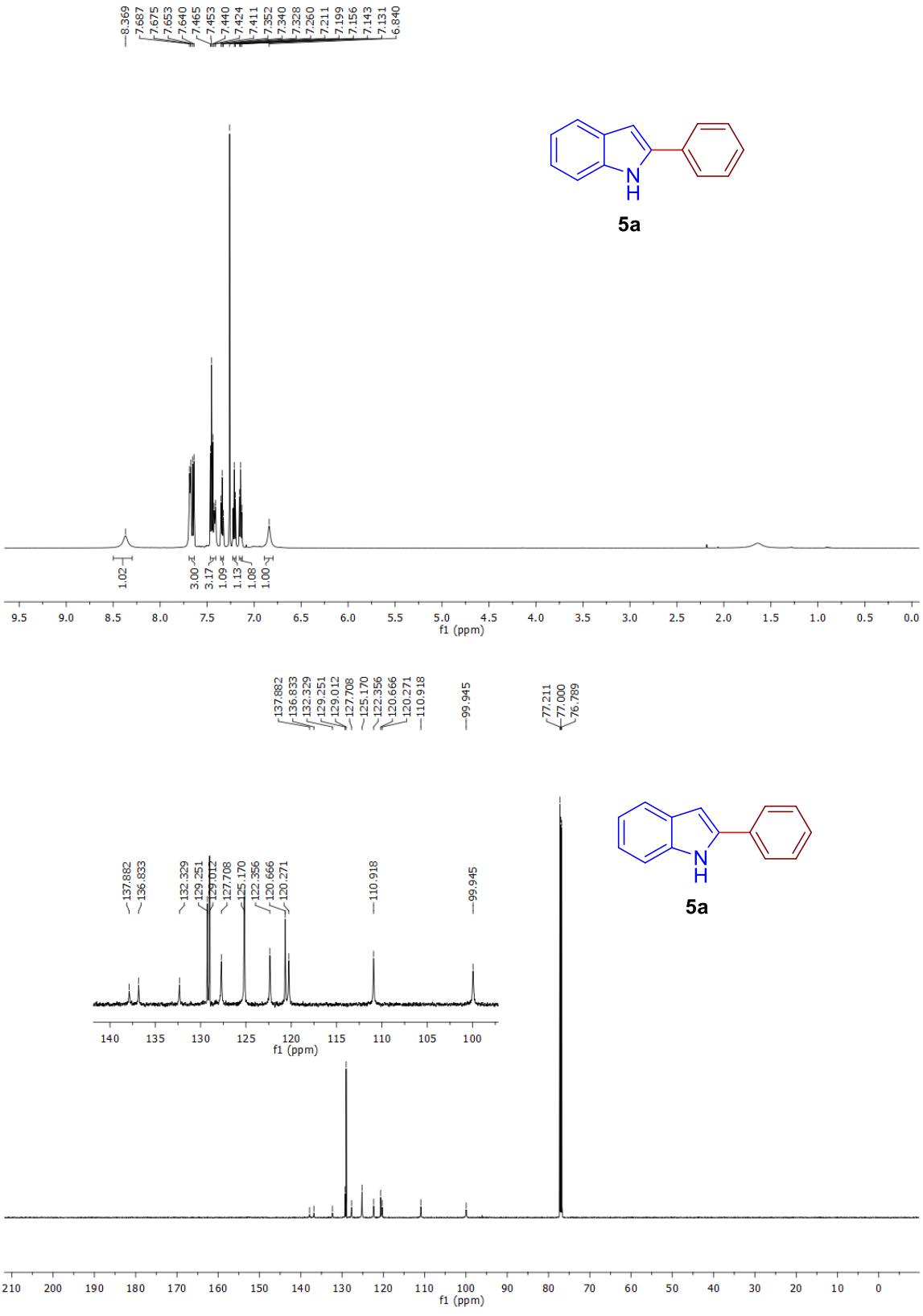

Figure 5.28. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Spectra of (**5a**) in $CDCl_3$

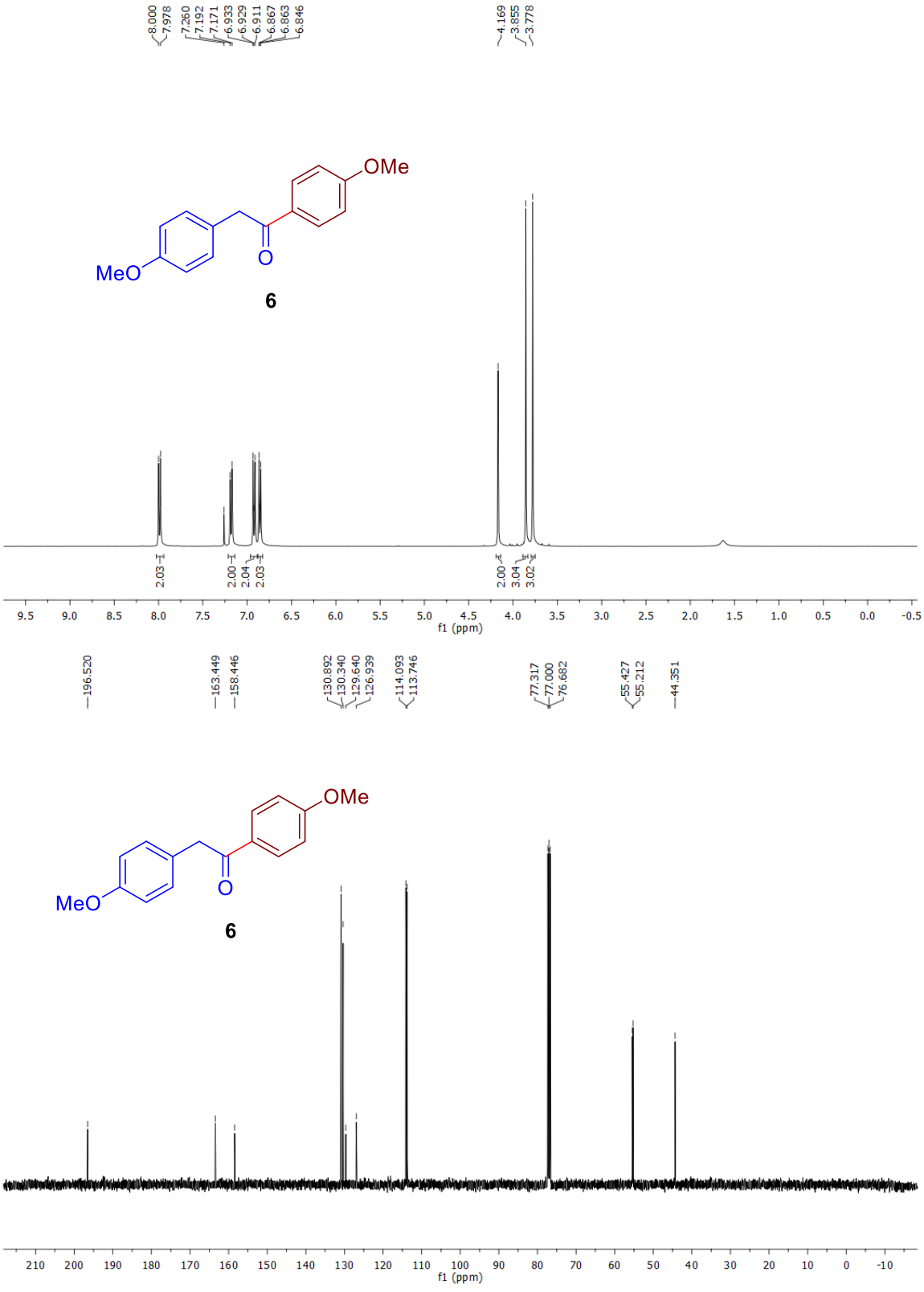

Figure 5.29. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**6**) in $CDCl_3$

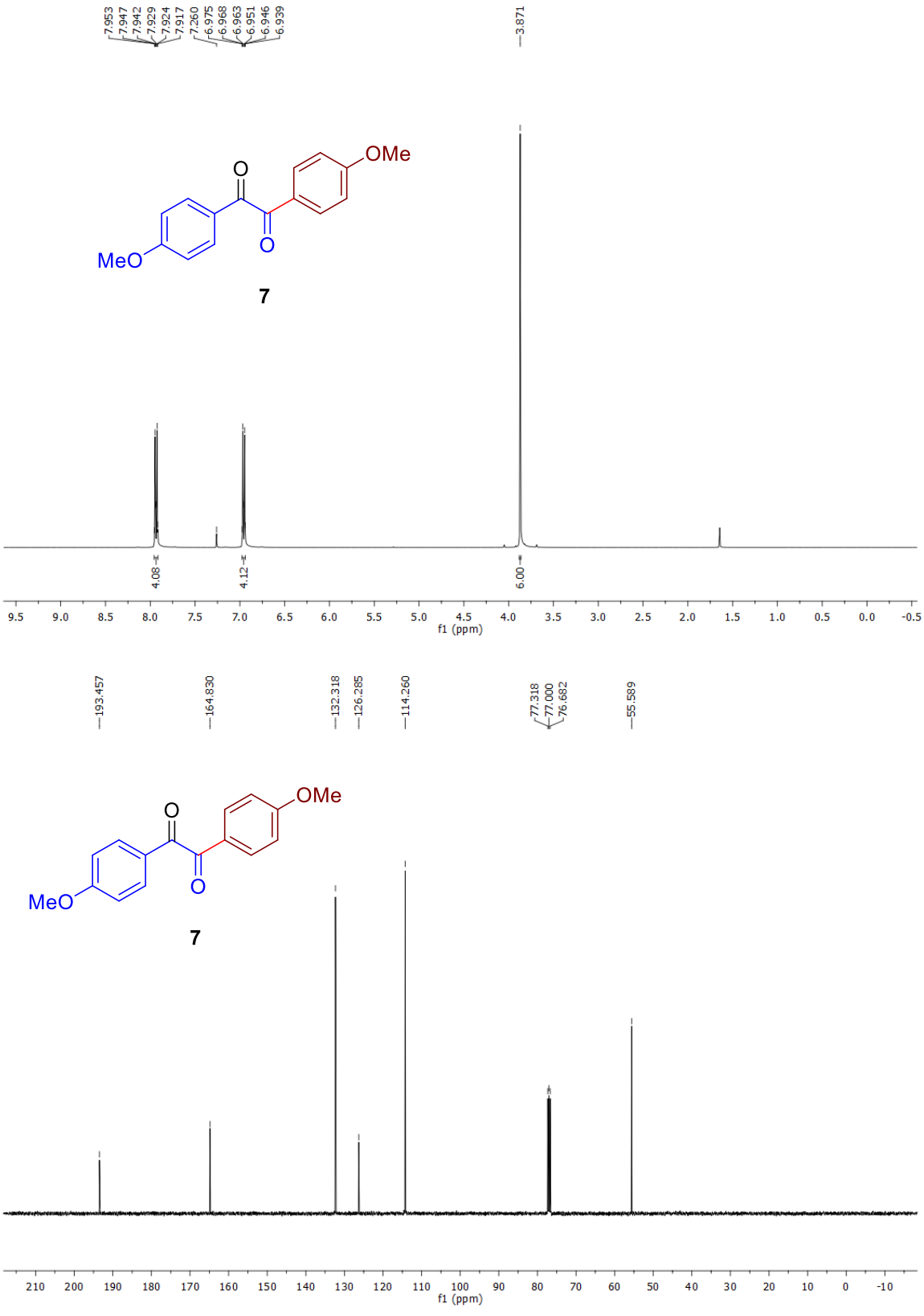

Figure 5.30. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**7**) in $CDCl_3$

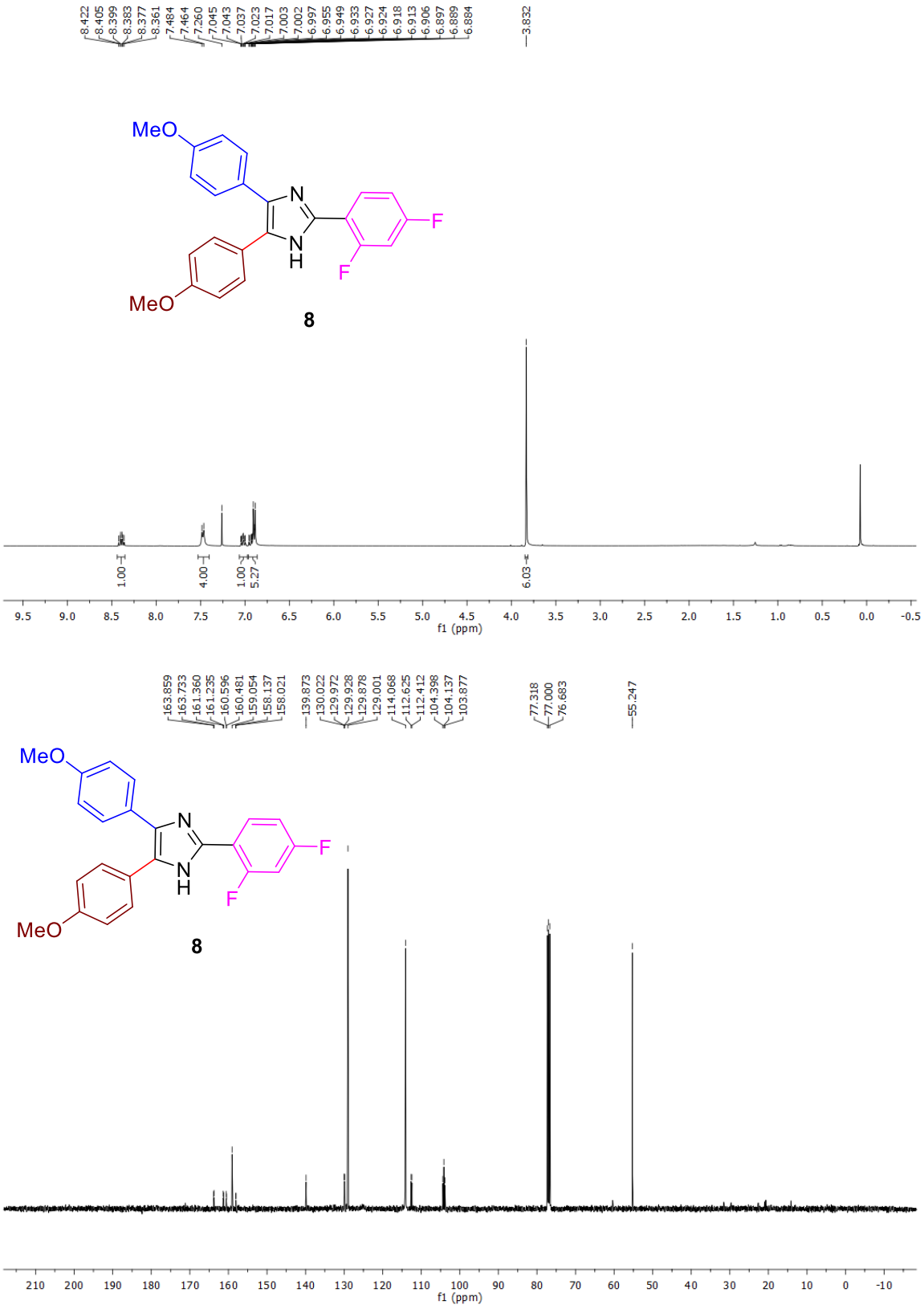

Figure 5.31. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**8**) in $CDCl_3$

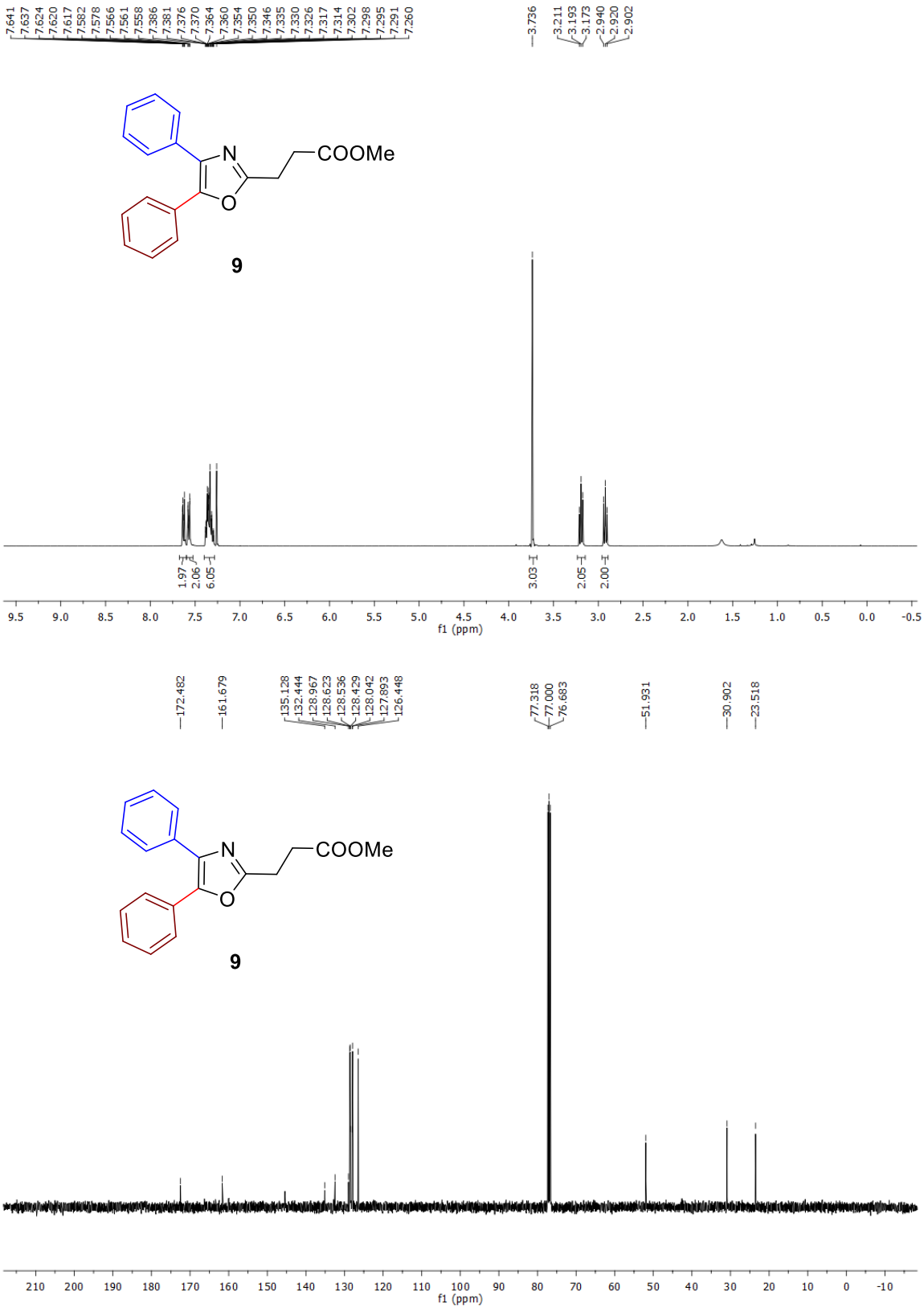

Figure 5.32. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**9**) in $CDCl_3$

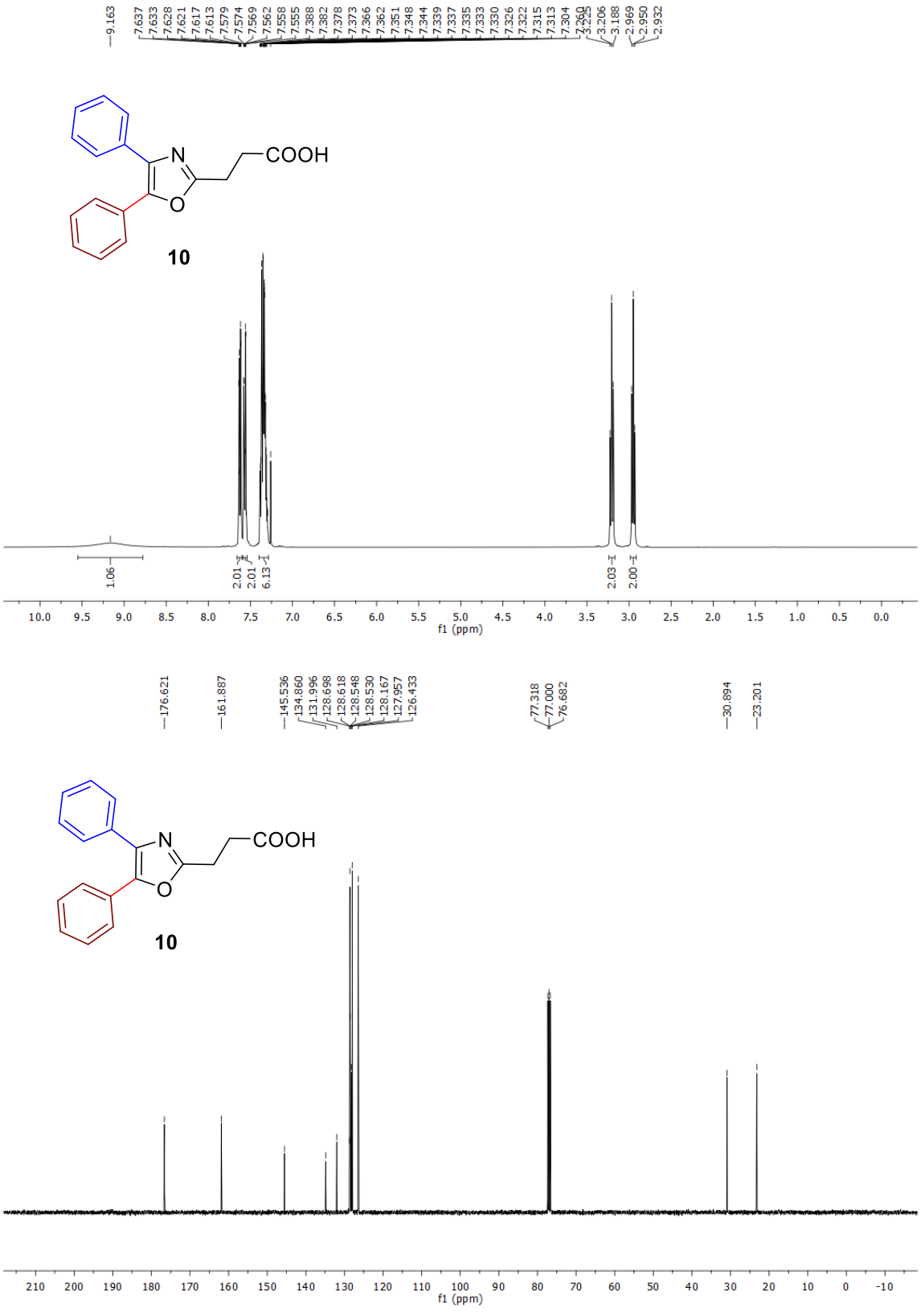

Figure 5.33. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) Spectra of (**10**) in $CDCl_3$