Supplementary Information

Cobalt catalyzed *meta* selective C–H activation of diverse classes of arenes

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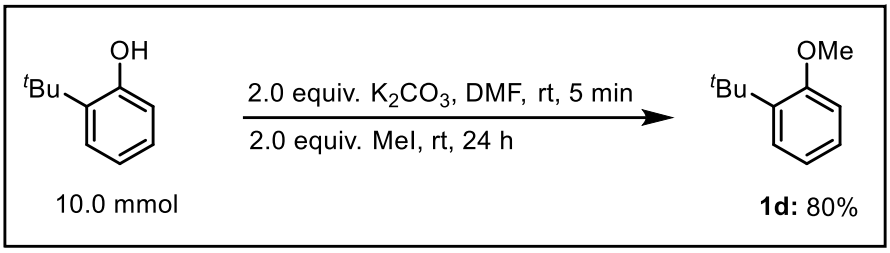
General Information:

All commercially available chemicals were used as received unless otherwise indicated. Pinacolborane (HBPin) and bis(pinacolato)diboron (B_2pin_2) were procured from Sigma-Aldrich. Cobalt(II) acetate, anhydrous, was procured from Thermo Fisher Scientific. Anhydrous KO^{t}Bu was procured from TCI. Tetrahydrofuran (THF) was refluxed over sodium/benzophenone ketyl, distilled and degassed twice before borylation. Column chromatography was performed on flash silica gel (ACME). Thin layer chromatography was performed on 0.25 mm thick aluminum-backed silica gel plates purchased from Merck and visualized with ultraviolet light (λ = 254 nm).

^{1}H, ^{13}C, and ^{11}B spectra were recorded on Bruker 400 and 800 MHz NMR spectrometer. The boron bearing carbon atom was not observed due to quadrupolar relaxation. All coupling constants are apparent *J* values measured at the indicated field strengths in Hertz (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, br s = broad singlet, br m = broad multiplet, dt = doublet of triplet, td = triplet of doublet, ddd = doublet of doublets of doublets, p = pentate, sept = septet). High-resolution mass spectra (HRMS) were obtained using a Waters GCT Premier instrument run on electron ionization (EI) direct probe or a Waters QTOF Ultima instrument run on electrospray ionization (ESI+). GC/MS (Agilent Technology) was obtained and for the analysis RAM temperature was used 50 ^{o}C for each sample.

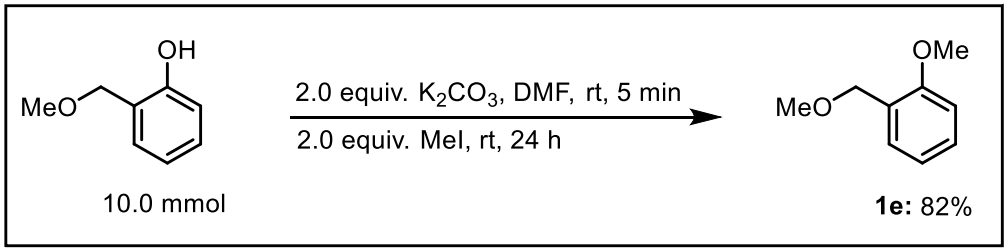
Preparation of starting materials:

Preparation of 2-(tert-butyl)anisole (1d):



In a 100 ml round bottom flask, 2-(tert-butyl)phenol (1.5 g, 10.0 mmol) and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 1.31 g (80%) of the 2-(tert-butyl)anisole (**1d**) as oil. Spectral data are in accordance with the reported data.[1]

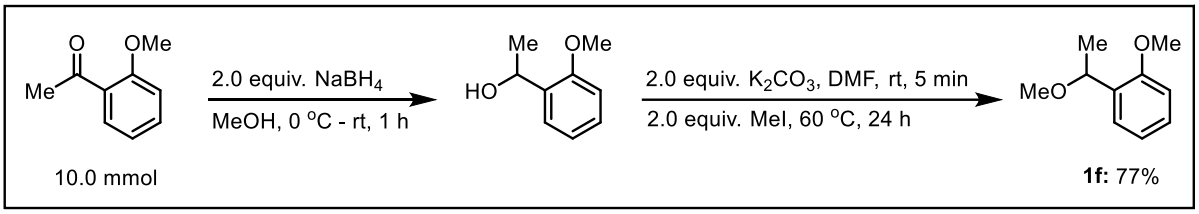
Preparation of 2-(methoxymethyl)anisole (1e):



In a 100 ml round bottom flask, 2-(methoxymethyl)phenol (1.38 g, 10.0 mmol) and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column

chromatography (5% ethyl acetate in hexane as eluent) to afford 1.25 g (82%) of the 2-(methoxymethyl)anisole (**1e**) as oil. Spectral data are in accordance with the reported data.[2]

Preparation of 1-methoxy-2-(1-methoxyethyl)benzene (1f):



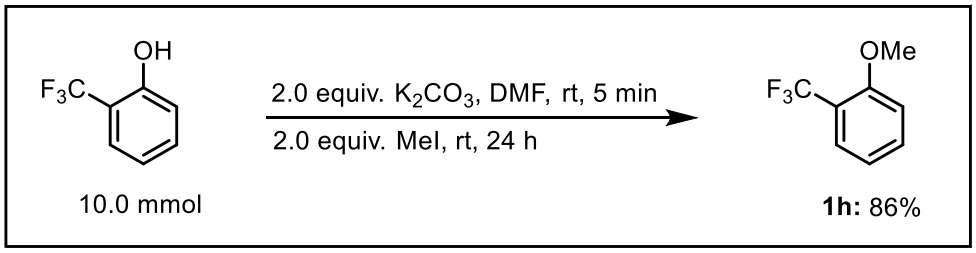
Step I:

In a 100 ml round bottom flask, 1-(2-methoxyphenyl)ethan-1-one (1.5 g, 10.0 mmol) was dissolved in MeOH and placed the flask in an ice-bath. $NaBH_4$ (760 mg, 2.0 equiv.) was added portion wise into the flask with vigorous stirring. After addition the reaction mixture was stirred for another 1 h at room temperature. The completion of the reaction was confirmed by checking the TLC and the MeOH was evaporated under reduced pressure to get a white paste. Then ice-cold water was poured slowly into it and work up was done with EtOAc. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The next step was set up with the crude material without further purification.

Step II:

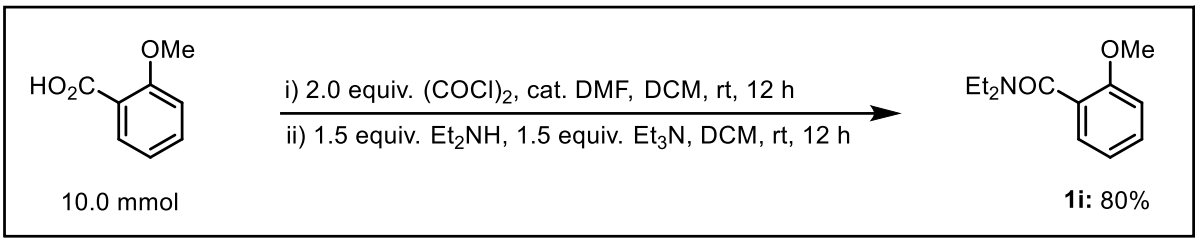
In a 100 ml round bottom flask, crude 1-(2-methoxyphenyl)ethan-1-ol and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred at 60 °C for 24 h. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 1.28 g (77%) of the 1-methoxy-2-(1-methoxyethyl)benzene (**1f**) as oil. Spectral data are in accordance with the reported data.[3]

Preparation of 2-(trifluoromethyl)anisole (1h):



In a 100 ml round bottom flask, 2-(trifluoromethyl)phenol (1.62 g, 10.0 mmol) and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 1.51 g (86%) of the 2-(trifluoromethyl)anisole (**1h**) as oil. Spectral data are in accordance with the reported data.[4]

Preparation of N,N-diethyl-2-methoxybenzamide (1i):



Step-I:

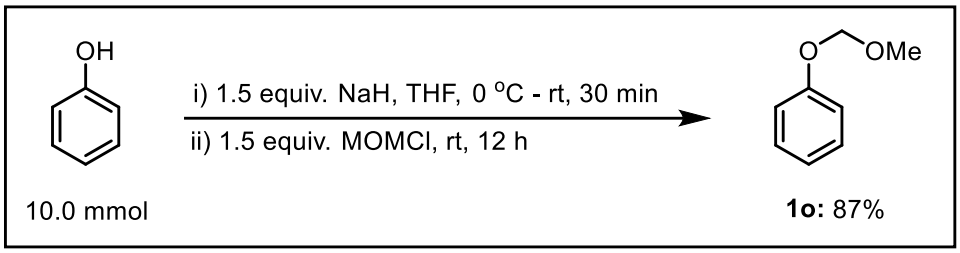
In a 100 mL round-bottom flask, 2-methoxybenzoic acid (1.52 g, 10.0 mmol) was dissolved in dry DCM (30 mL) and catalytic amount of DMF was added into it. The reaction mixture was cooled to 0 ºC and stirred for 5 minutes. Then $(COCl)_2$ (1.4 mL, 2.0 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II:

To a solution of diethylamine (2.4 mL, 1.5 equiv.) and Et_3N (2.8 mL, 2.0 equiv.) in dry DCM (30 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (50 mL) was added and the organic layer was

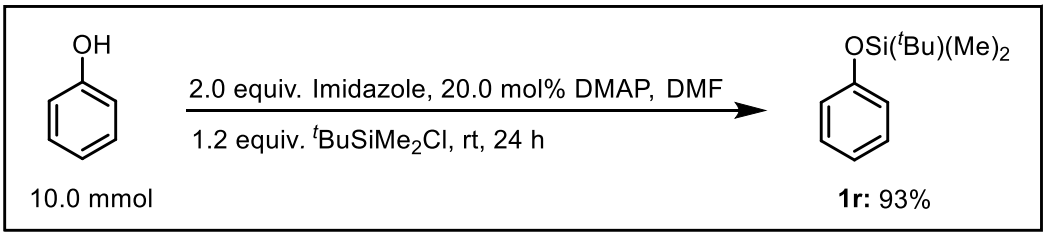
separated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution followed by water (50 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (25% ethyl acetate in hexane as eluent) to afford 1.66 g (80%) of the N,N-diethyl-2-methoxybenzamide (**1i**) as white solid. Spectral data are in accordance with the reported data.[5]

Preparation of 1-(methoxymethoxy)benzene (1o):



In a 100 ml round bottom flask, phenol (940 mg, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, chloromethyl methyl ether (1.2 ml, 1.5 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for overnight. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 1.2 g (87%) of the 1-(methoxymethoxy)benzene (**1o**) as oil. Spectral data are in accordance with the reported data.[6]

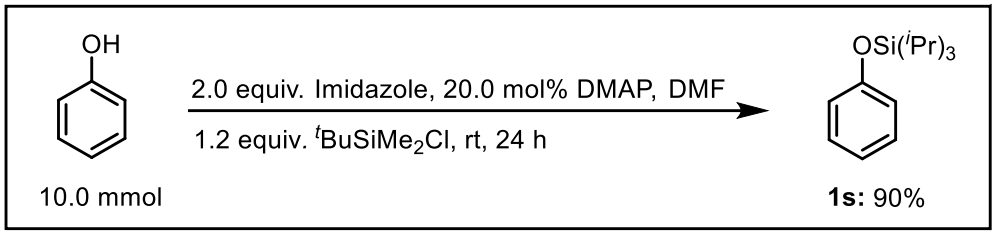
Preparation of tert-butyldimethyl(phenoxy)silane (1r):



In a 100 ml round-bottomed flask, phenol (940 mg, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of tert-butylchlorodimethylsilane (TBDMSCl) (2.1 g, 12.0

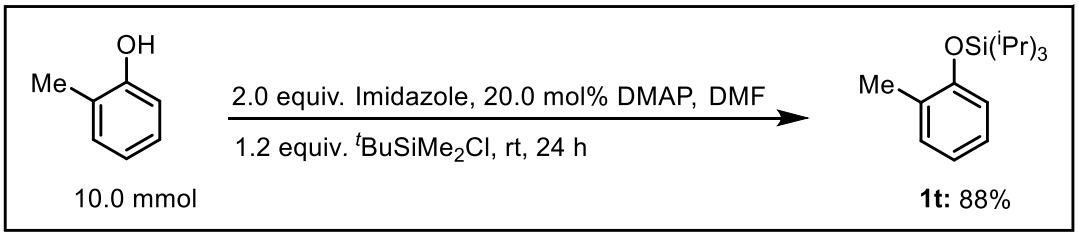
mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (2% ethyl acetate in hexane as eluent) to afford 1.9 g (93%) tert-butyldimethyl(phenoxy)silane (**1r**) as oil. Spectral data are in accordance with the reported data.[7]

Preparation of triisopropyl(phenoxy)silane (1s):



In a 100 ml round-bottomed flask, phenol (940 mg, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (TIPSCl) (2.5 ml, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (2% ethyl acetate in hexane as eluent) to afford 2.25 g (90%) triisopropyl(phenoxy)silane (**1s**) as oil. Spectral data are in accordance with the reported data.[7]

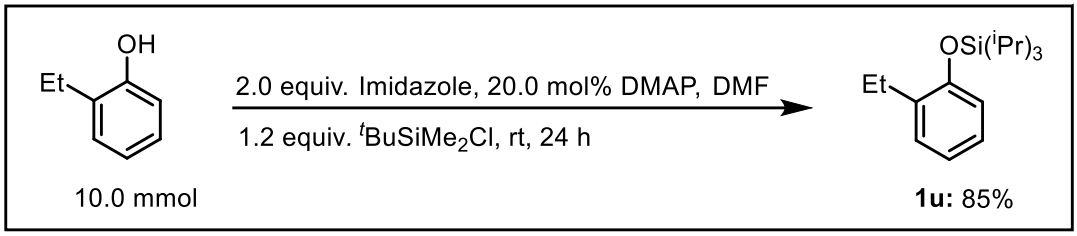
Preparation of triisopropyl(o-tolyloxy)silane (1t):



In a 100 ml round-bottomed flask, o-cresol (1.1 g, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry

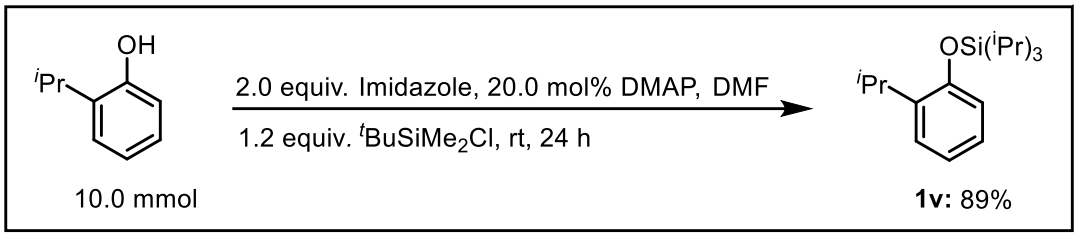
DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (TIPSCl) (2.5 ml, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 2.3 g (88%) triisopropyl(o-tolyloxy)silane (**1t**) as oil. Spectral data are in accordance with the reported data.[7]

Preparation of (2-ethylphenoxy)triisopropylsilane (1u):



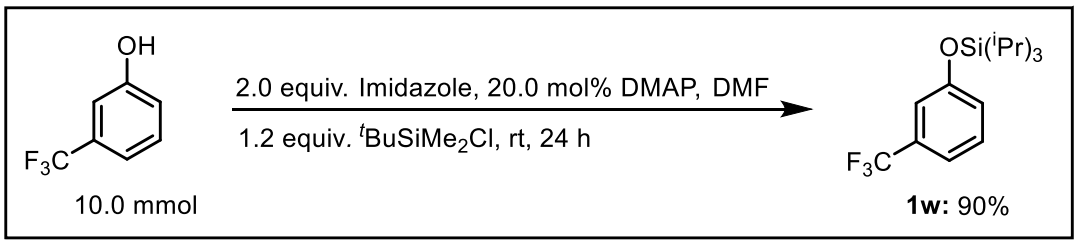
In a 100 ml round-bottomed flask, 2-ethylphenol (1.22 g, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (TIPSCl) (2.5 ml, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 2.36 g (85%) (2-ethylphenoxy)triisopropylsilane (**1u**) as oil. Spectral data are in accordance with the reported data.[7]

Preparation of triisopropyl(2-isopropylphenoxy)silane (1v):



In a 100 ml round-bottomed flask, 2-isopropylphenol (1.36 g, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (TIPSCl) (2.5 ml, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 2.6 g (89%) triisopropyl(2-isopropylphenoxy)silane (**1v**) as oil. Spectral data are in accordance with the reported data.[7]

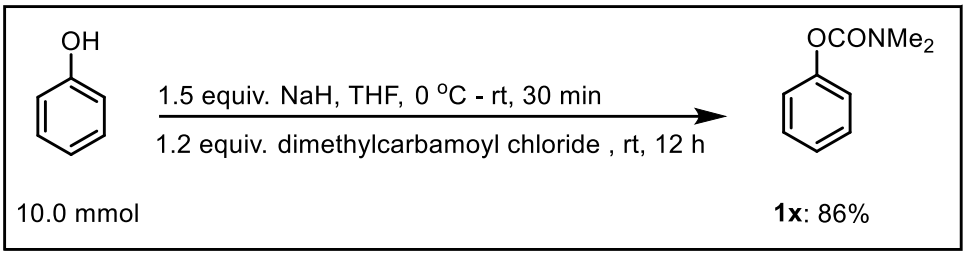
Preparation of triisopropyl(3-(trifluoromethyl)phenoxy)silane (1w):



In a 100 ml round-bottomed flask, 3-(trifluoromethyl)phenol (1.62 g, 10.0 mmol), imidazole (1.36 g, 20.0 mmol, 2.0 equiv.), 4-Dimethylaminopyridine (DMAP) (244 mg, 2.0 mmol, 20 mol%) and 20 mL dry DMF was added. Then the raection mixture was stirred for 5 minutes at room temperature followed by dropwise addition of triisopropylsilyl chloride (TIPSCl) (2.5 ml, 12.0 mmol, 1.2 equiv.). The reaction mixture was stirred at the same temperature for additional 24 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude

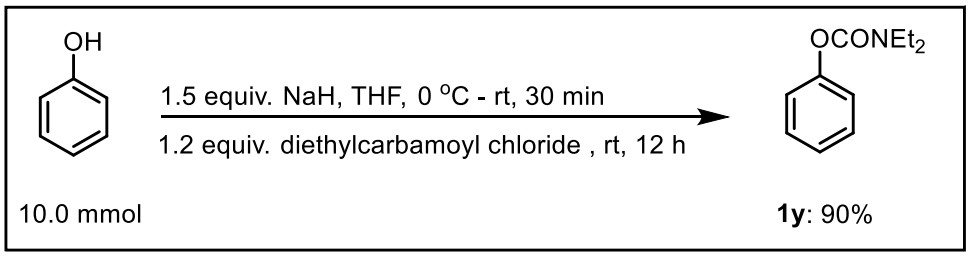
mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 2.87 g (90%) triisopropyl(3-(trifluoromethyl)phenoxy)silane (**1w**) as oil. Spectral data are in accordance with the reported data.[7]

Preparation of phenyl dimethylcarbamate (1x):



In a 100 ml round bottom flask, phenol (940 mg, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, dimethylcarbamoyl chloride (1.1 ml, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.42 g (86%) of the phenyl dimethylcarbamate (**1x**) as oil. Spectral data are in accordance with the reported data.[8]

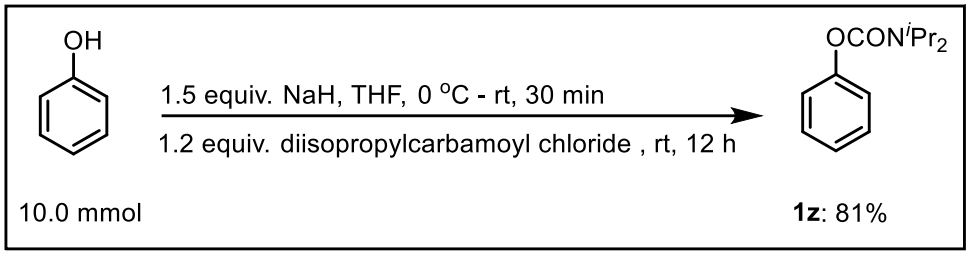
Preparation of phenyl diethylcarbamate (1y):



In a 100 ml round bottom flask, phenol (940 mg, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, diethylcarbamoyl chloride (1.5 ml, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it

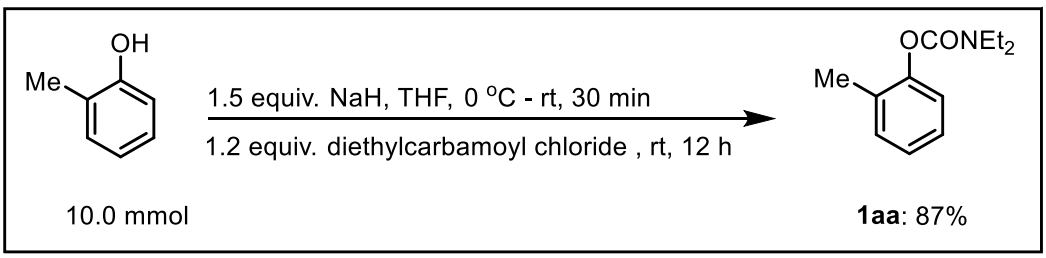
and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.74 g (90%) of the phenyl diethylcarbamate (**1y**) as oil. Spectral data are in accordance with the reported data.[8]

Preparation of phenyl diisopropylcarbamate (1z):



In a 100 ml round bottom flask, phenol (940 mg, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, diisopropylcarbamoyl chloride (1.96 g, 1.2 equiv.) was added dropwise (by solubilizing it in dry THF) at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.79 g (81%) of the phenyl diisopropylcarbamate (**1z**) as oil. Spectral data are in accordance with the reported data.[8]

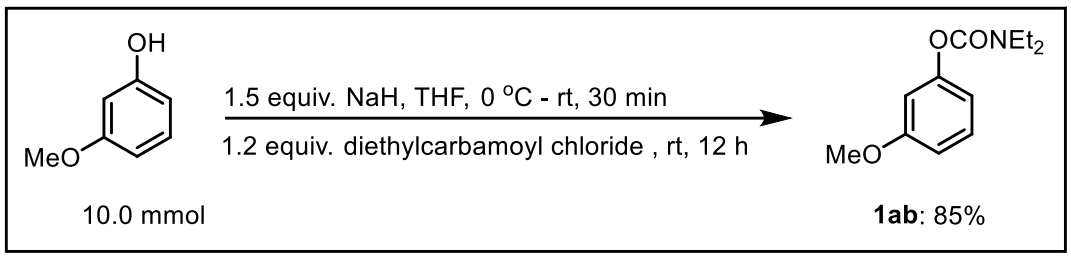
Preparation of o-tolyl diethylcarbamate (1aa):



In a 100 ml round bottom flask, o-cresol (1.1 g, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to

stir for 30 min at room temperature. Then, diethylcarbamoyl chloride (1.5 ml, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.8 g (87%) of the *o*-tolyl diethylcarbamate (**1aa**) as oil. Spectral data are in accordance with the reported data.[8]

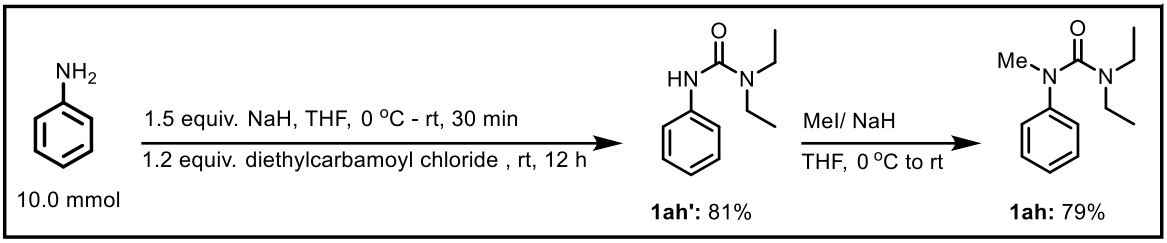
Preparation of 3-methoxyphenyl diethylcarbamate (1ab):



In a 100 ml round bottom flask, 3-methoxyphenol (1.24 g, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, diethylcarbamoyl chloride (1.5 ml, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.9 g (85%) of the 3-methoxyphenyl diethylcarbamate (**1ab**) as oil. Spectral data are in accordance with the reported data.[8]

Anilines:

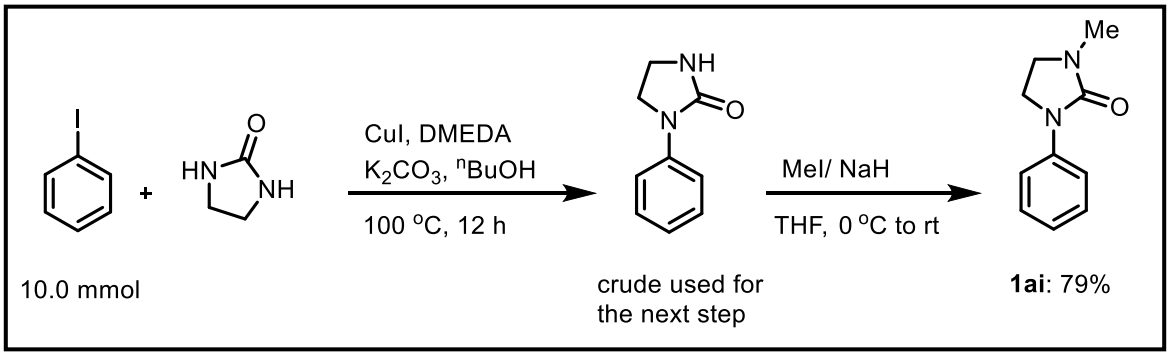
Preparation of 1,1-Diethyl-3-methyl-3-phenylurea (1ah):



Step-1: In a 100 ml round bottom flask, aniline (930 mg, 10.0 mmol) was dissolved in dry THF (30 ml) under argon atmosphere. The flask was placed in an ice-bath and NaH (60% dispersion in mineral oil, 600 mg, 1.5 equiv.) was added portion wise into it. The reaction was allowed to stir for 30 min at room temperature. Then, diethylcarbamoyl chloride (1.5 ml, 1.2 equiv.) was added dropwise at 0 °C and the reaction was stirred at room temperature for 12 h. After completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with water (100 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.6 g (81%) of the *1,1-diethyl-3-phenylurea* (**1ah'**) as oil. Spectral data are in accordance with the reported data.[9]

Step-2: A 100 mL round bottom flask was charged with 1,1-diethyl-3-phenylurea (1ah': 960 mg, 5.0 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (480 mg, 50 % dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 °C and methyl iodide (623 µL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h, the reaction mixture was diluted with ice water and extracted with ethyl acetate (3 x 30 mL) and dried over Na_2SO_4. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (20% ethyl acetate in hexane as eluent) gave 815 mg (79%) of the *1,1-diethyl-3-methyl-3-phenylurea* (**1ah**) as oil. Spectral data are in accordance with the reported data.[9]

*Preparation of 1-methyl-3-phenylimidazolidin-2-one (**1ai**):*

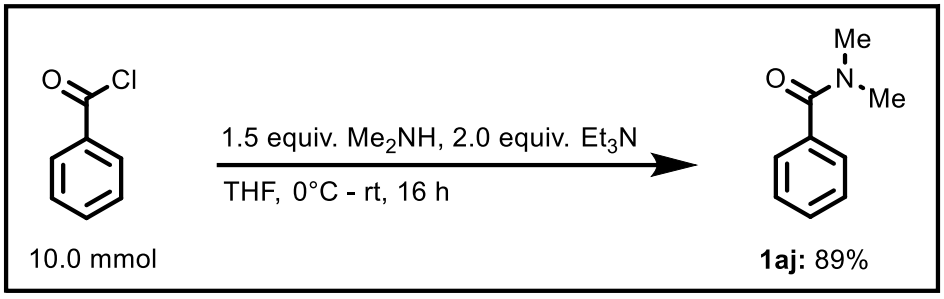


Step-1: A 100 mL round-bottom flask was charged with iodobenzene (2.0 g, 10 mmol), 2-imidazolidinone (4.3 g, 5 equiv.), CuI (190.6 mg, 0.1 equiv.), DMEDA (N,Ndimehtylethylenediamine) (264.5 mg, 0.3 equiv.), and K_2CO_3 (4.1 g, 3 equiv.). The reaction mixture was refluxed in n-butanol (40 mL) at 100 ºC for 12 h. The crude reaction mixture was poured into a 10 % w/w NH_4Cl aqueous solution and the organic layer was extracted with DCM (3 x 25 mL). Then the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure and the crude mixture was used in the next step without further purification. Crude reaction mixture showed full completion of the reaction (checked by TLC).

Step-2: A 100 mL round bottom flask was charged with crude 1-(2-chlorophenyl)imidazolidin-2-one obtained from step-1in dry DMF (25 ml) under an argon atmosphere at 0 °C. NaH (960 mg, 50 % dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 ºC and methyl iodide (1.3 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h, the reaction mixture was diluted with ice water and extracted with ethyl acetate (3 x 30 mL) and dried over Na_2SO_4. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel (30% ethyl acetate in hexane as eluent) gave 1.37 g (79%) of the *1-methyl-3-phenylimidazolidin-2-one* (**1ai**) as white solid. Spectral data are in accordance with the reported data.[8]

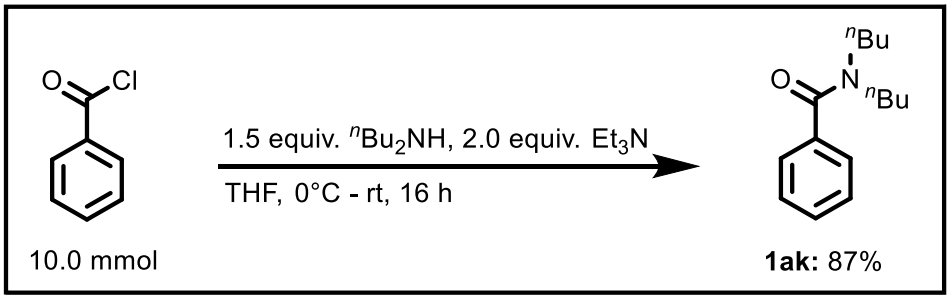
Aromatic Amides:

Preparation of N,N-dimethylbenzamide (1aj):



In a 100 ml round bottom flask, dimethylamine (2.0 M in THF) (7.5 mL, 1.5 equiv.), Et_3N (2.8 mL, 2.0 equiv.) was added in dry THF (30 ml) under argon atmosphere. The reaction mixture was cooled to 0 ^oC and stirred for 5 minutes. Then benzoyl chloride (1.3 mL, 10 mmol) was added dropwise to the reaction mixture at 0 ^oC and the reaction was stirred at room temperature for 16 h. After completion the reaction was quenched with cold water. EtOAc (50 ml) was added to it and the organic layer was separated and the aqueous layer was extracted with EtOAc (50 ml) for two times. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution and then with water (50 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (30% ethyl acetate in hexane as eluent) to afford 1.32 g (89%) of the *N,N*-dimethylbenzamide (**1aj**) as oil. Spectral data are in accordance with the reported data.[8]

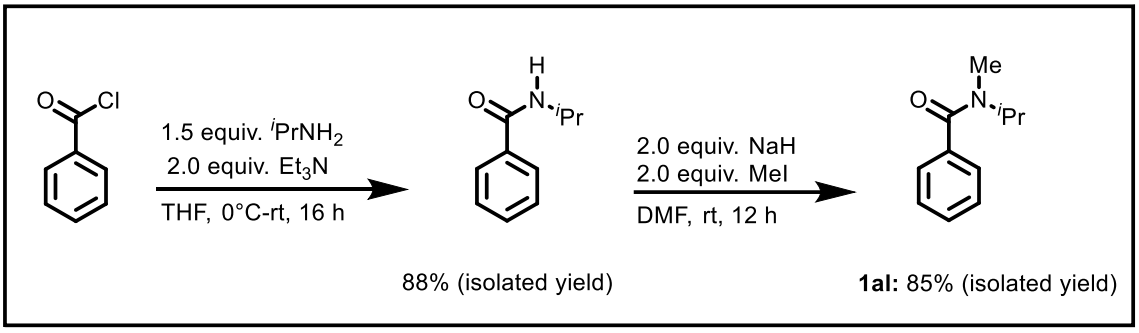
Preparation of N,N-dibutylbenzamide (1ak):



In a 100 ml round bottom flask, dibutylamine (2.5 mL, 1.5 equiv.), Et_3N (2.8 mL, 2.0 equiv.) was added in dry THF (30 ml) under argon atmosphere. The reaction mixture was cooled to 0 ^oC and stirred for 5 minutes. Then benzoyl chloride (1.3 mL, 10 mmol) was added dropwise to the reaction mixture at 0 ^oC and the reaction was stirred at room temperature for 16 h. After completion the reaction was quenched with cold water. EtOAc (50 ml) was added to it and the

organic layer was separated and the aqueous layer was extracted with EtOAc (50 ml) for two times. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution and then with water (50 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 2.0 g (87%) of the *N,N-dibutylbenzamide* (**1ak**) as oil. Spectral data are in accordance with the reported data.[10]

Preparation of N-isopropyl-N-methylbenzamide (1al):

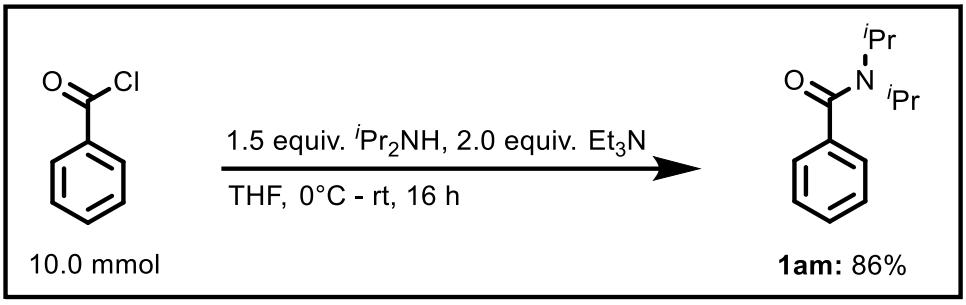


Step-I: A 100 mL round-bottom flask was charged with a solution of isopropylamine (1.3 mL, 1.5 equiv.), Et_3N (2.8 mL, 2.0 equiv.) and dry THF (25 mL). The reaction mixture was cooled to 0 ºC and stirred for 5 minutes. Then benzoyl chloride (1.3 mL, 10 mmol) was added dropwise to the reaction mixture at 0 ºC and stirred at room temperature for 16 h. Then the reaction was quenched with water (50 mL), the organic layer was separated and the aqueous layer was extracted with EtOAc (3 x 40 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution followed by brine (40 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.43 g (88%) of the *N*-isopropylbenzamide as white solid. Spectral data are in accordance with the reported data.

Step-II: A 100 mL round bottom flask was charged with *N*-isopropylbenzamide (816.1 mg, 5 mmol) in dry DMF (20 ml) under an argon atmosphere at 0 °C. NaH (436.4 mg, 55 % dispersion in mineral oil, 2.0 equiv.) was added. The reaction was then stirred for 15 minutes at 0 ºC and methyl iodide (0.62 mL, 2 equiv.) was added. Then the reaction mixture was warmed to room temperature and stirred for 12 h. After 12 h, the reaction mixture was diluted with ice water and extracted with ethyl acetate (3 x 30 mL) and dried over Na_2SO_4. Organic extract was evaporated under reduced pressure and chromatographic separation with silica gel

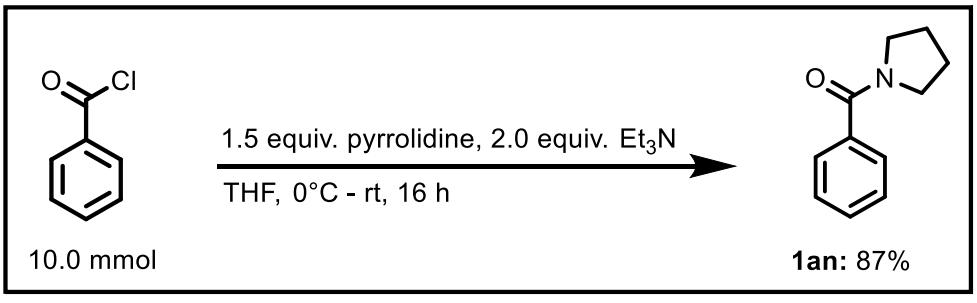
(10% ethyl acetate in hexane as eluent) gave 752 mg (85%) of the *N*-isopropyl-*N*-methylbenzamide (**1al**) as oil. Spectral data are in accordance with the reported data.[8]

Preparation of N,N-diisopropylbenzamide (1am):



In a 100 ml round bottom flask, diisopropylamine (2.2 mL, 1.5 equiv.), Et_3N (2.8 mL, 2.0 equiv.) was added in dry THF (30 ml) under argon atmosphere. The reaction mixture was cooled to 0 ºC and stirred for 5 minutes. Then benzoyl chloride (1.3 mL, 10 mmol) was added dropwise to the reaction mixture at 0 ºC and the reaction was stirred at room temperature for 16 h. After completion the reaction was quenched with cold water. EtOAc (50 ml) was added to it and the organic layer was separated and the aqueous layer was extracted with EtOAc (50 ml) for two times. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution and then with water (50 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (15% ethyl acetate in hexane as eluent) to afford 1.76 g (86%) of the *N,N-diisopropylbenzamide* (**1am**) as white solid. Spectral data are in accordance with the reported data.[8]

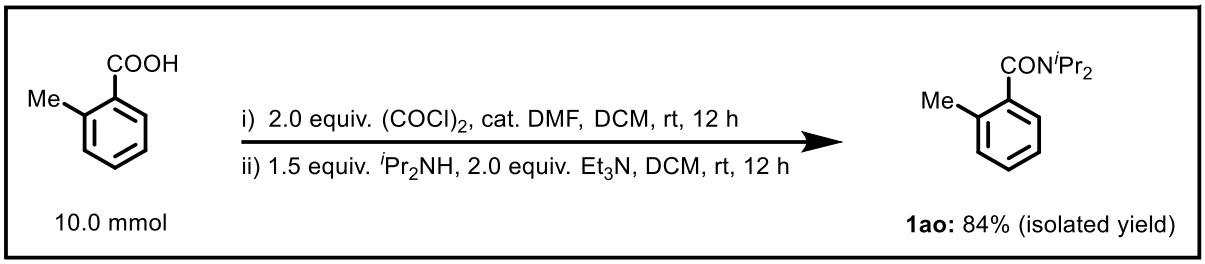
Preparation of phenyl(pyrrolidin-1-yl)methanone (1aj):



In a 100 ml round bottom flask, dibutylamine (1.2 mL, 1.5 equiv.), Et_3N (2.8 mL, 2.0 equiv.) was added in dry THF (30 ml) under argon atmosphere. The reaction mixture was cooled to 0 ºC and stirred for 5 minutes. Then benzoyl chloride (1.3 mL, 10 mmol) was added dropwise to the reaction mixture at 0 ºC and the reaction was stirred at room temperature for 16 h. After

completion the reaction was quenched with cold water. EtOAc (50 ml) was added to it and the organic layer was separated and the aqueous layer was extracted with EtOAc (50 ml) for two times. The organic layer was washed with saturated aqueous $NaHCO_3$ (50 mL) solution and then with water (50 ml) for two times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (40% ethyl acetate in hexane as eluent) to afford 1.5 g (87%) of the *phenyl(pyrrolidin-1-yl)methanone* (**1an**) as oil. Spectral data are in accordance with the reported data.[10]

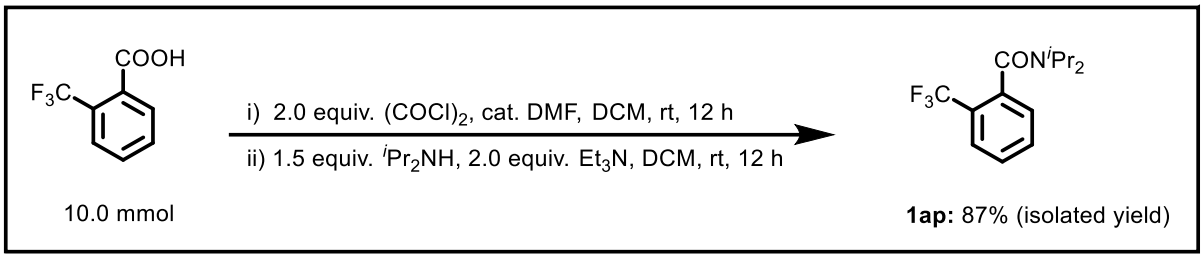
Preparation of N,N-diisopropyl-2-methylbenzamide (1ao):



Step-I: A 100 mL round-bottom flask was charged with 2-methylbenzoic acid (1.36 g, 10 mmol), dry DCM (25 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 ^oC and stirred for 5 minutes. Then $(COCl)_2$ (1.4 mL, 2.0 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II: To a solution of diisopropylamine (2.2 mL, 1.5 equiv.) and Et_3N (2.8 mL, 2.0 equiv.) in dry DCM (25 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (50 mL) was added and the organic layer was separated and the aqueous layer was extracted with DCM (3 x 40 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (40 mL) solution followed by water (40 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 1.8 g (84%) of the *N,N*-diisopropyl-2-methylbenzamide (**1ao**) as off white solid. Spectral data are in accordance with the reported data.[8]

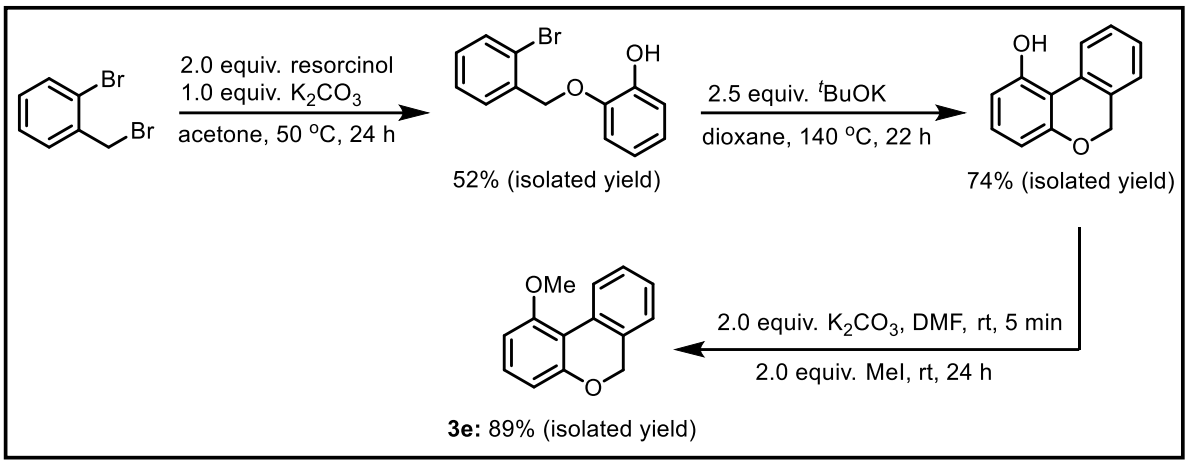
Preparation of N,N-diisopropyl-2-(trifluoromethyl)benzamide (1ap):



Step-I: A 100 mL round-bottom flask was charged with 2-methoxybenzoic acid (1.5 g, 10 mmol), dry DCM (25 mL) and catalytic amount of DMF. The reaction mixture was cooled to 0 ºC and stirred for 5 minutes. Then $(COCl)_2$ (1.4 mL, 2.0 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 12 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride quantitatively which was used directly without further purification for the next step.

Step-II: To a solution of diisopropylamine (2.2 mL, 1.5 equiv.) and Et_3N (2.8 mL, 2.0 equiv.) in dry DCM (25 mL), acid chloride (1.0 equiv.) was added dropwise at 0 °C and the reaction mixture was stirred at room temperature for 12 h. Then water (50 mL) was added and the organic layer was separated and the aqueous layer was extracted with DCM (3 x 40 mL). The combined organic layer was washed with saturated aqueous $NaHCO_3$ (40 mL) solution followed by water (40 mL). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 2.4 g (87%) of the *N,N*-diisopropyl-2-(trifluoromethyl)benzamide (**1ap**) as off white solid. Spectral data are in accordance with the reported data.[8]

Preparation of 1-methoxy-6H-benzo[c]chromene (3e):

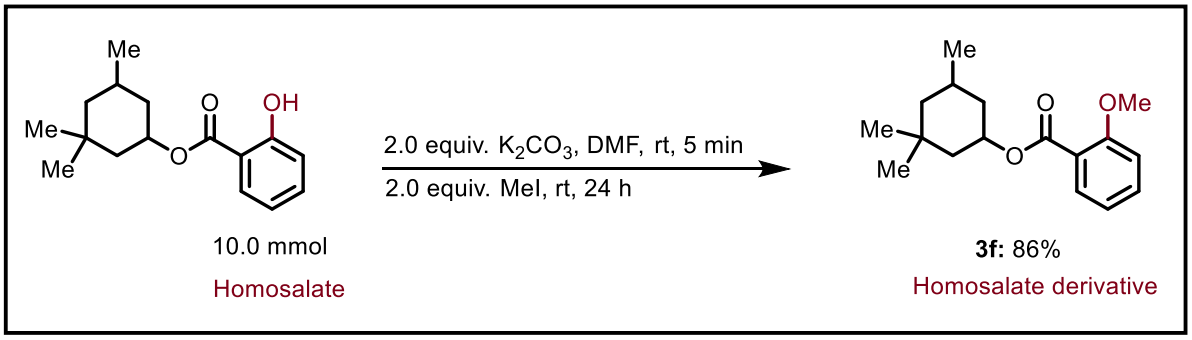


Step I: An oven dried 100 mL round bottom flask was charged with resorcinol (4.95 g, 30.0 mmol), K_2CO_3 (2.07 g, 1.0 equiv.) and acetone (75.0 mL). This mixture was stirred at room temperature for 30 minutes. 2-Bromobenzyl bromide (3.75 g, 15.0 mmol) was added to the mixture and placed into preheated oil bath at 50 °C for 23 h 30 minutes. Upon total consumption of 2-bromobenzyl bromide (checked by TLC), the reaction mixture was cooled to room temperature, poured into aqueous 2N NaOH (75 mL) and extracted with ethyl acetate (50 mL x 3). The combined organic layer was washed with brine (40 mL) and dried over anhydrous Na_2SO_4. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (10% ethyl acetate in hexane as eluent) gave 2.17 g (52%) of 3-((2-bromobenzyl)oxy)phenol as white solid. Spectral data are in accordance with the reported data.[7]

Step II: In an argon-filled glove box, an oven dried 15 mL pressure tube was charged with 3-((2-bromobenzyl)oxy)phenol (2.09g, 7.5 mmol), ^{t}BuOK (2.1 g, 2.5 equiv.), sealed with a rubber septum and taken out from the glove box. Dioxane (10.0 mL) was added to the mixture, capped with a teflon pressure cap and stirred at room temperature for 5 minutes. The pressure tube was placed in a preheated silicon oil bath at 140 °C and stirred for 22 h. After cooling to room temperature, the reaction mixture was quenched with 2N HCl (50 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer was washed with brine (40 mL) and dried over anhydrous Na_2SO_4. The organic extract was concentrated under reduced pressure and chromatographic separation with silica gel (40% dichloromethane in hexane as eluent) gave 1.11 g (74%) of 6H-benzo[c]chromen-1-ol as white solid. Spectral data are in accordance with the reported data.[7]

Step III: In a dry 100 mL round-bottomed flask 6H-benzo[c]chromen-1-ol (960 mg, 5 mmol), In a 100 ml round bottom flask, phenol (940 mg, 10.0 mmol) and K_2CO_3 (1.38 g, 2.0 equiv.) was dissolved in dry DMF (20 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (625 µL, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. After completion (judged by TLC), the reaction mixture was diluted with cold water (30 mL) and extracted with ethyl acetate (30 mL x 3). The combined organic layer washed with cold water (30 mL x 3), brine (50 mL) and dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (2% ethyl acetate in hexane as eluent) to afford 943 mg (89%) of 1-methoxy-6H-benzo[c]chromene (**3e**) as oil. Spectral data are in accordance with the reported data.[11]

Preparation of 3,3,5-trimethylcyclohexyl 2-methoxybenzoate (3f):



In a 100 ml round bottom flask, phenol (2.6 g, 10.0 mmol) and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (3% ethyl acetate in hexane as eluent) to afford 2.38 g (86%) of the anisole (**3f**) as oil.

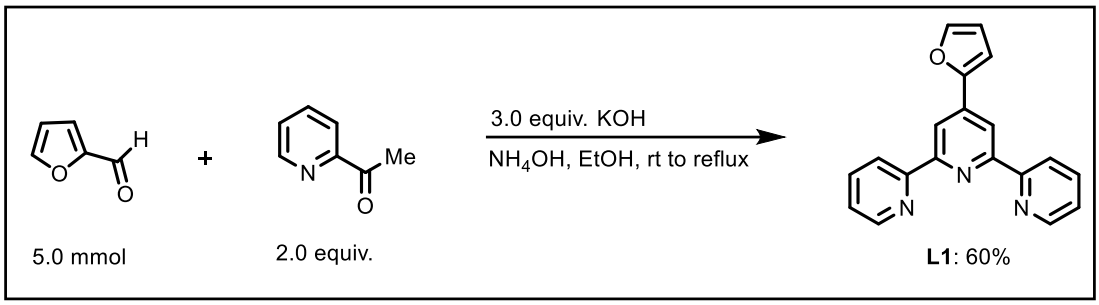
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, J = 8.0, 2.0 Hz, 1H), 7.45 – 7.41 (m, 1H), 6.97 – 6.93 (m, 2H), 5.18 – 5.10 (m, 1H), 3.88 (s, 3H), 2.11 (d, J = 12.0 Hz, 1H), 1.84 – 1.72 (m, 2H), 1.38 – 1.35 (m, 1H), 1.22 (t, J = 11.6 Hz, 1H), 0.99 – 0.92 (m, 10H), 0.82 (t, J = 12.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7, 159.0, 133.1, 131.2, 120.9, 120.0, 112.0, 71.4, 55.9, 47.6, 44.0, 40.4, 33.0, 32.3, 27.1, 25.5, 22.3.

HRMS (ESI) *m/z* calculated for $C_{17}H_{25}O_3$ $[M+H]^+$ 277.1804, found 277.1811.

Synthesis of ligands

*Preparation of **L1**:*



1-(pyridin-2-yl)ethan-1-one (1.21 g, 10.0 mmol) was added to a solution of furan-2-carbaldehyde (480 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(furan-2-yl)-2,2':6',2"-terpyridine (**L1**) (898 mg, 60%) as white powder.

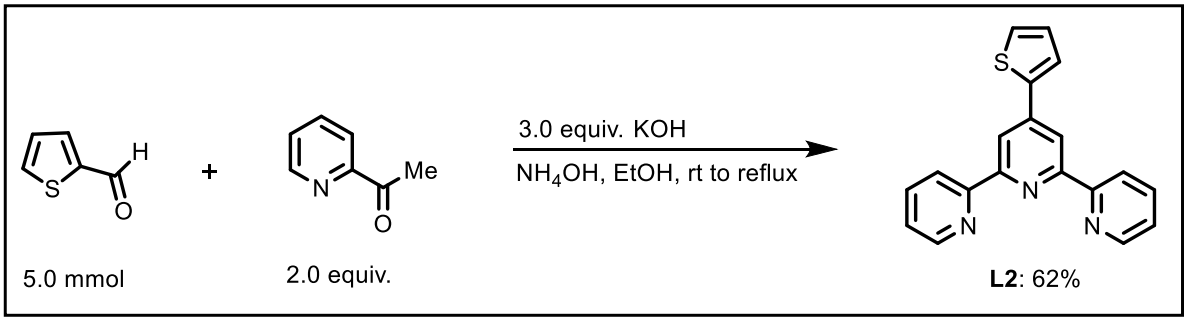
Spectral data of L1:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 – 8.70 (m, 4H), 8.64 – 8.61 (m, 2H), 7.88 – 7.83 (m, 2H), 7.58 (d, J = 1.6 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.10 (t, J = 3.2 Hz, 1H), 6.56 – 6.54 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 155.9, 151.9, 149.1, 143.6, 139.5, 136.8, 123.8, 121.2, 115.1, 112.1, 109.1.

HRMS (ESI) *m/z* calcd for $C_{19}H_{14}N_3O$ $[M+H]^+$ 300.1137, found 300.1152.

*Preparation of **L2**:*



1-(pyridin-2-yl)ethan-1-one (1.21 g, 10.0 mmol) was added to a solution of thiophene-2-carbaldehyde (560.7 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(thiophen-2-yl)-2,2':6',2''-terpyridine (**L2**) (978 mg, 62%) as white powder.

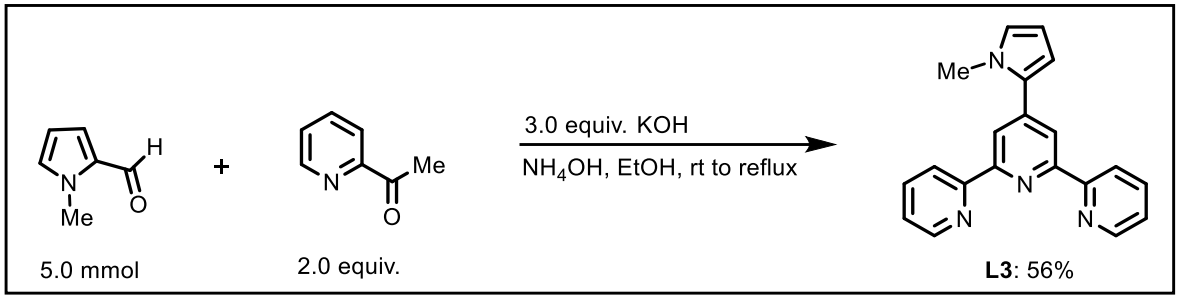
Spectral data of L2:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.71 – 8.66 (m, 4H), 8.60 (d, *J* = 8.0 Hz, 2H), 7.82 (td, *J* = 7.6, 1.6 Hz, 2H), 7.74 (d, *J* = 3.2 Hz, 1H), 7.41 (d, *J* = 5.2 Hz, 1H), 7.30 (dd, *J* = 6.8, 5.2 Hz, 2H), 7.14 (dd, *J* = 4.8, 4.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 155.9, 149.0, 143.3, 141.8, 136.7, 128.2, 127.0, 125.7, 123.8, 121.2, 117.0.

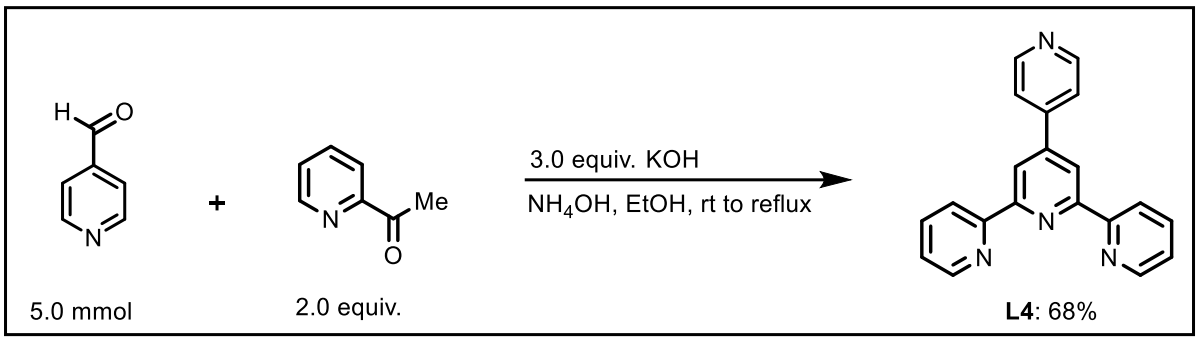
HRMS (ESI) *m/z* calcd for $C_{19}H_{14}N_3S$ $[M+H]^+$ 316.0908, found 316.0921.

*Preparation of **L3**:*



1-(pyridin-2-yl)ethan-1-one (1.21 g, 10.0 mmol) was added to a solution of 1-methyl-1H-pyrrole-2-carbaldehyde (545.6 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(1-methyl-1H-pyrrol-2-yl)-2,2':6',2''-terpyridine (**L3**) (875 mg, 56%) as white powder. Spectral data are in accordance with the reported data.[12]

*Preparation of **L4**:*



1-(pyridin-2-yl)ethan-1-one (1.21 g, 10.0 mmol) was added to a solution of isonicotinaldehyde (535.6 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(pyridin-4-yl)-2,2':6',2"-terpyridine (**L4**) (1.05 g, 68%) as white powder.

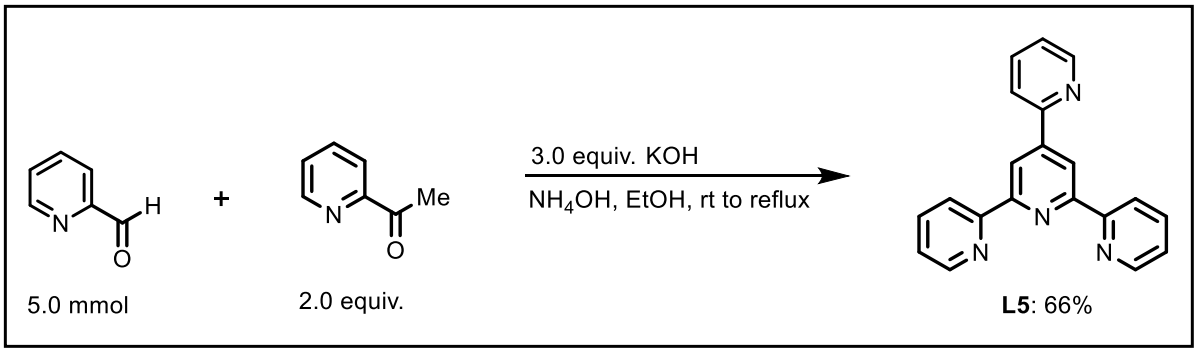
Spectral data of L4:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 – 8.69 (m, 6H), 8.63 (d, J = 7.6 Hz, 2H), 7.85 (td, J = 8.0, 2.0 Hz, 2H), 7.74 (dd, J = 4.4, 1.2 Hz, 2H), 7.37 – 7.30 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 155.6, 150.5, 149.1, 147.3, 145.8, 136.9, 124.0, 121.6, 121.3, 118.5.

HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_4$ $[M+H]^+$ 311.1297, found 311.1283.

*Preparation of **L5**:*



1-(pyridin-2-yl)ethan-1-one (1.21 g, 10.0 mmol) was added to a solution of picolinaldehyde (535.6 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and

recrystallized from hot MeOH afforded 6'-(pyridin-2-yl)-2,2':4',2"-terpyridine (**L5**) (1.02 g, 66%) as white powder.

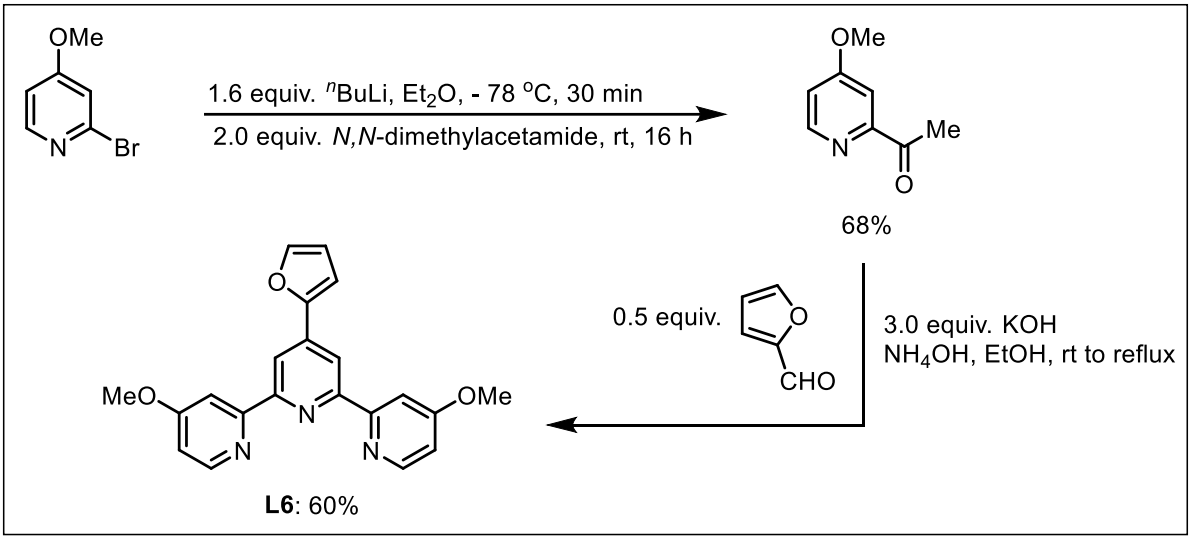
Spectral data of L5:

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.09 (s, 2H), 8.77 – 8.71 (m, 3H), 8.62 (d, *J* = 8.0 Hz, 2H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.84 – 7.75 (m, 3H), 7.29 (t, *J* = 6.0 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 156.0, 154.9, 149.9, 149.1, 148.5, 136.7, 136.7, 123.7, 123.6, 121.2, 121.1, 118.5.

HRMS (ESI) *m/z* calcd for $C_{20}H_{15}N_4$ $[M+H]^+$ 311.1297, found 311.1288.

*Preparation of **L6**:*



Step I: Under cooling to -78°C, *n*-butyllithium (a 2.5 M solution in hexane, 13 mL) was added dropwise to a solution of 2-bromo-4-methoxypyridine (3.76 g, 20.0 mmol) in diethyl ether (60 mL) over 20 minutes, and then the resultant mixture was stirred for 30 minutes. *N,N*-dimethyl acetamide (3.7 mL, 2.0 equiv.) was added dropwise to the reaction solution, and the mixture was gradually warmed to room temperature, and stirred for 16 hours at room temperature. Saturated ammonium chloride solution was added to the reaction, which was then extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After workup with ethyl acetate (100 ml x 3) and water (100 ml) the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (ethyl acetate-hexane), to obtain 1-(4-methoxypyridin-2-yl)ethan-1-one (2.06 g, 68%) as light-yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, *J* = 5.6 Hz, 1H), 7.52 (d, *J* = 2.8 Hz, 1H), 6.93 (dd, *J* = 5.6, 2.8 Hz, 1H), 3.86 (s, 3H), 2.67 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 199.9, 166.4, 155.4, 150.0, 113.8, 106.7.

HRMS (ESI) *m/z* calcd for $C_8H_{10}NO_2$ $[M+H]^+$ 152.0712, found 152.0726.

Step II: 1-(4-methoxypyridin-2-yl)ethan-1-one (1.51 g, 10.0 mmol) was added to a solution of furan-2-carbaldehyde (480 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(furan-2-yl)-4,4''-dimethoxy-2,2':6',2''-terpyridine (**L6**) (1.08 g, 60%) as white powder.

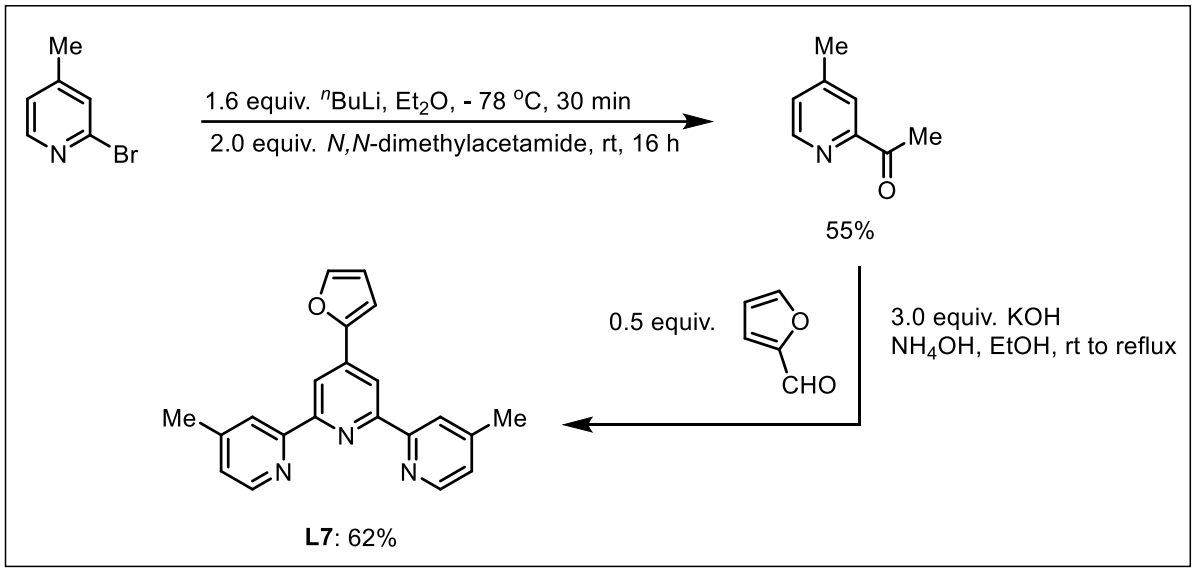
Spectral data of L6:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.69 (s, 2H), 8.55 (d, J = 5.6 Hz, 2H), 8.16 (d, J = 2.8 Hz, 2H), 7.57 (d, J = 1.2 Hz, 1H), 7.09 (d, J = 3.2 Hz, 1H), 6.87 (dd, J = 5.6, 2.8 Hz, 2H), 6.55 (dd, J = 3.6, 2.0 Hz, 1H), 3.96 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 157.7, 155.5, 151.8, 150.3, 143.5, 139.3, 115.3, 112.0, 109.9, 109.1, 107.0, 55.1.

HRMS (ESI) *m/z* calcd for $C_{21}H_{18}N_3O_3$ $[M+H]^+$ 360.1348, found 360.1355.

*Preparation of **L7**:*



Step I: Under cooling to -78°C, n-butyllithium (a 2.5 M solution in hexane, 13 mL) was added dropwise to a solution of 2-bromo-4-methylpyridine (3.44 g, 20.0 mmol) in diethyl ether (60 mL) over 20 minutes, and then the resultant mixture was stirred for 30 minutes. *N,N*-dimethyl acetamide (3.7 mL, 2.0 equiv.) was added dropwise to the reaction solution, and the mixture was gradually warmed to room temperature, and stirred for 16 hours at room temperature. Saturated ammonium chloride solution was added to the reaction, which was then extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After workup with ethyl acetate (100 ml x 3) and water (100 ml) the solvent was removed under reduced

pressure and the crude residue was purified by silica gel column chromatography (ethyl acetate-hexane), to obtain 1-(4-methylpyridin-2-yl)ethan-1-one (1.49 g, 55%) as light-yellow oil. Spectral data are in accordance with the reported data.[13]

Step II: 1-(4-methylpyridin-2-yl)ethan-1-one (1.35 g, 10.0 mmol) was added to a solution of furan-2-carbaldehyde (480 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(furan-2-yl)-4,4''-dimethyl-2,2':6',2''-terpyridine (**L7**) (1.01 g, 62%) as white powder.

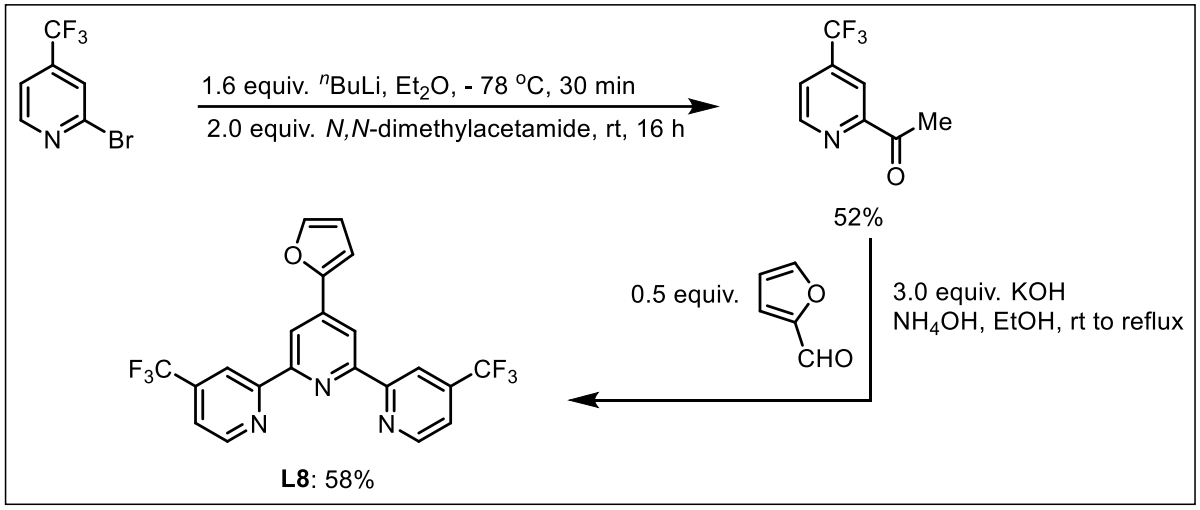
Spectral data of L7:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 2H), 8.57 (d, *J* = 4.8 Hz, 2H), 8.41 (s, 2H), 7.56 (d, *J* = 1.2 Hz, 1H), 7.15 (d, *J* = 4.4 Hz, 2H), 7.09 (d, *J* = 3.2 Hz, 1H), 6.54 (dd, *J* = 3.2, 1.6 Hz, 1H), 2.48 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 155.9, 151.9, 148.9, 147.9, 143.6, 139.4, 124.8, 122.0, 115.2, 112.0, 109.0, 76.7, 21.3.

HRMS (ESI) *m/z* calculated for $C_{21}H_{18}N_3O$ $[M+H]^+$ 328.1450, found 328.1442.

*Preparation of **L8**:*



Step I: Under cooling to -78°C, n-butyllithium (a 2.5 M solution in hexane, 13 mL) was added dropwise to a solution of 2-bromo-4-(trifluoromethyl)pyridine (4.52 g, 20.0 mmol) in diethyl ether (60 mL) over 20 minutes, and then the resultant mixture was stirred for 30 minutes. *N,N*-dimethyl acetamide (3.7 mL, 2.0 equiv.) was added dropwise to the reaction solution, and the mixture was gradually warmed to room temperature, and stirred for 16 hours at room temperature. Saturated ammonium chloride solution was added to the reaction, which was then

extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After workup with ethyl acetate (100 ml x 3) and water (100 ml) the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (ethyl acetate-hexane), to obtain 1-(4-(trifluoromethyl)pyridin-2-yl)ethan-1-one (1.97 g, 52%) as light-yellow oil. Spectral data are in accordance with the reported data.[14]

Step II: 1-(4-(trifluoromethyl)pyridin-2-yl)ethan-1-one (1.89 g, 10.0 mmol) was added to a solution of furan-2-carbaldehyde (480 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(furan-2-yl)-4,4''-bis(trifluoromethyl)-2,2':6',2''-terpyridine (**L8**) (1.26 g, 58%) as light-yellow powder.

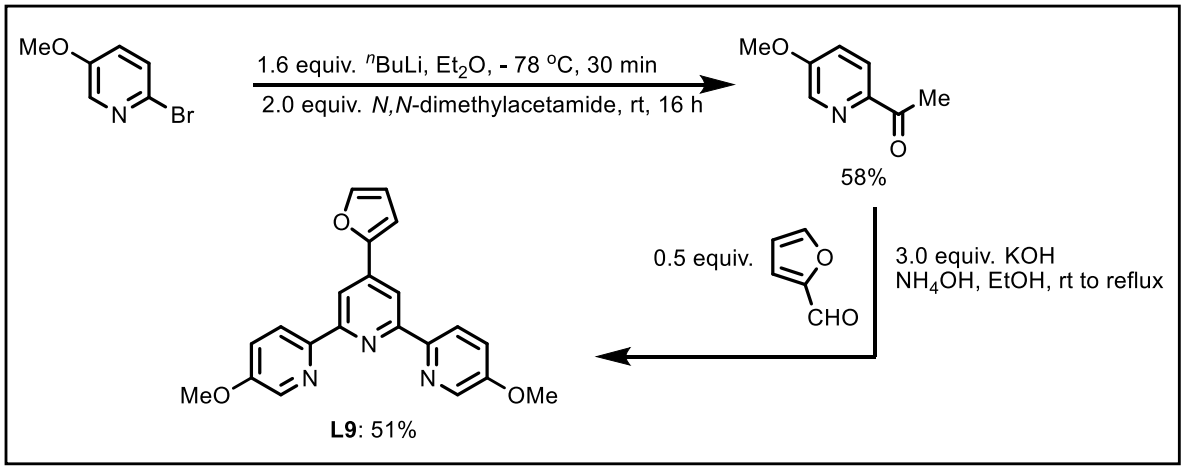
Spectral data of L8:

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (d, J = 4.8 Hz, 2H), 8.65 (d, J = 12.0 Hz, 4H), 7.50 – 7.47 (m, 3H), 7.01 (d, J = 3.6 Hz, 1H), 6.48 – 6.47 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 154.9, 151.4, 150.1, 144.1, 139.9, 139.6, 119.4, 117.0, 116.1, 112.3, 109.7.

HRMS (ESI) *m/z* calculated for $C_{21}H_{12}F_6N_3O$ $[M+H]^+$ 436.0885, found 436.0868.

*Preparation of **L9**:*



Step I: Under cooling to -78°C, n-butyllithium (a 2.5 M solution in hexane, 13 mL) was added dropwise to a solution of 2-bromo-5-methoxypyridine (3.76 g, 20.0 mmol) in diethyl ether (60 mL) over 20 minutes, and then the resultant mixture was stirred for 30 minutes. *N,N*-dimethyl acetamide (3.7 mL, 2.0 equiv.) was added dropwise to the reaction solution, and the mixture was gradually warmed to room temperature, and stirred for 16 hours at room temperature.

Saturated ammonium chloride solution was added to the reaction, which was then extracted with ethyl acetate. The organic layer was dried over anhydrous sodium sulfate. After workup with ethyl acetate (100 ml x 3) and water (100 ml) the solvent was removed under reduced pressure and the crude residue was purified by silica gel column chromatography (ethyl acetate-hexane), to obtain 1-(5-methoxypyridin-2-yl)ethan-1-one (1.75 g, 58%) as light-yellow oil.

Step II: 1-(4-(trifluoromethyl)pyridin-2-yl)ethan-1-one (1.89 g, 10.0 mmol) was added to a solution of furan-2-carbaldehyde (480 mg, 5.0 mmol) in EtOH (30 mL). KOH pellets (840 mg, 15.0 mmol) and aq. NH_3 (25 mL, 30% solution) were then added to the solution. The solution was stirred at 90 °C for 4 h. The solvent was reduced to 20 mL and saturated with H_2O (100 mL). The off-white solid was filtered, washed with H_2O (30 ml) and EtOH (30 ml). The precipitate was collected and recrystallized from hot MeOH afforded 4'-(furan-2-yl)-5,5''-dimethoxy-2,2':6',2''-terpyridine (**L9**) (916 mg, 51%) as light-yellow powder.

Reaction Developments

Reaction Optimization for the *meta* selective borylation of arenes with *in situ* pre-catalyst activation:

The course of reaction without any activator:

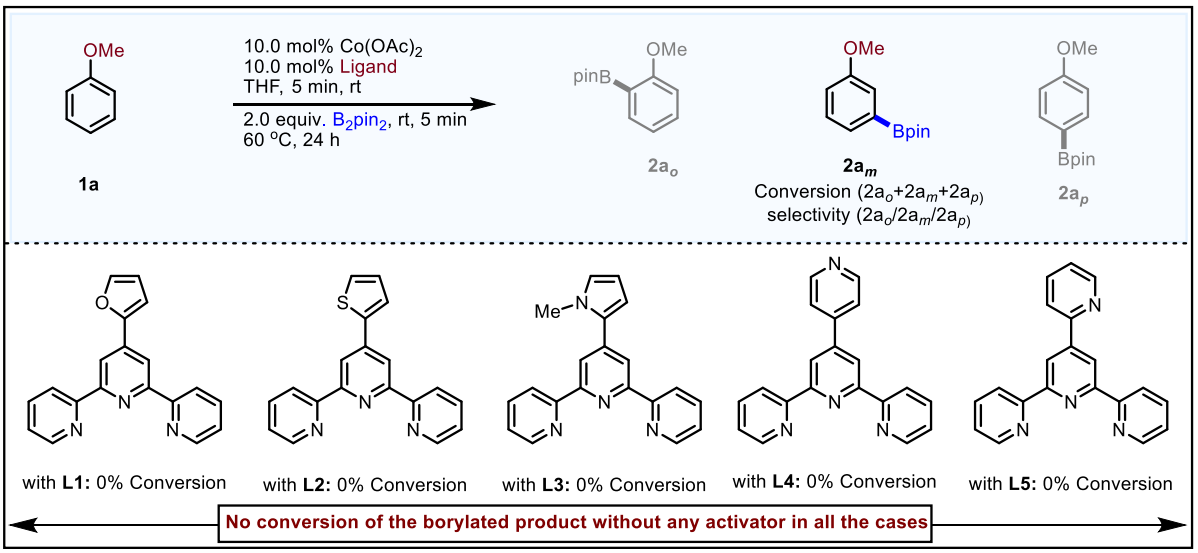


Figure S1: The course of reaction without any activator with various heteroarene appended TPY ligands.

General procedure without activator: In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (1.8 mg, 10.0 mol%), ligand (10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (50.8 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Then

substrate (0.1 mmol) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. In all the cases we observed no conversion of the corresponding borylated product. Hence, without any activator, active catalyst is not generated.

Incorporation of activators and their effects:

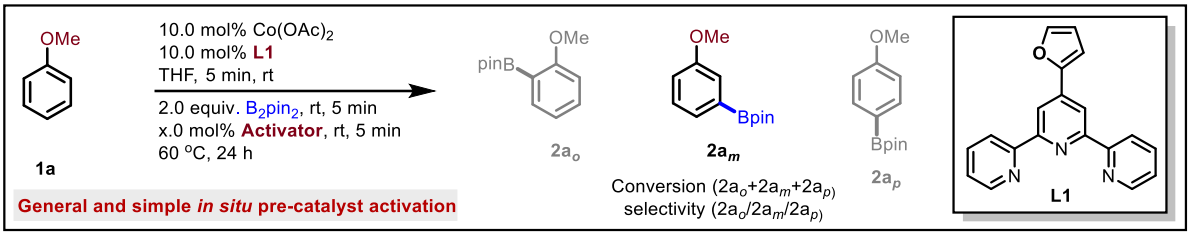


Table S1: Effect of non-organometallic activators and further screenings:

entry	Activator	Loading	conversion	*o:m:p*
1	Without Activator		0%	
2.	KO^{t}Bu	10 mol%	0%	
3.	KO^{t}Bu	20 mol%	0%	
4.	KO^{t}Bu	30 mol%	73%	0:91:9
5.	**KO^{t}Bu**	**40 mol%**	**78%**	**0:91:9**
8.	NaO^{t}Bu	40 mol%	61%	0:90:10
9.	LiO^{t}Bu	40 mol%	51%	0:88:12
10.	KOMe	40 mol%	58%	0:90:10
11.	KOPiv	40 mol%	25%	0:91:9

Further screening with other ligands:

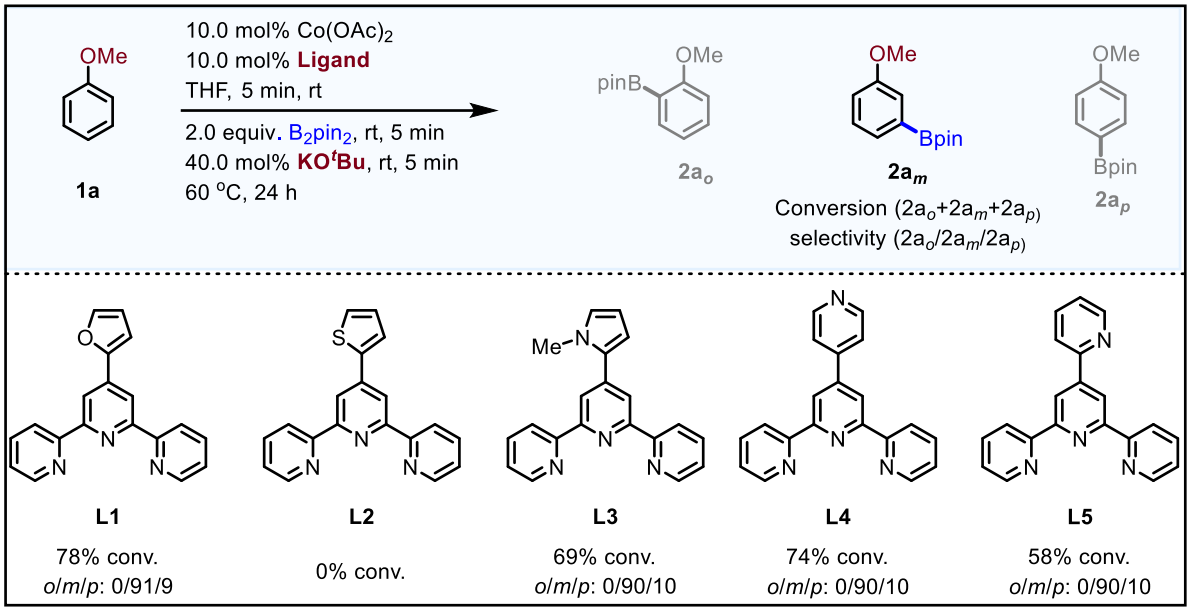


Figure S2: Further screening with various heteroarene appended TPY ligands in presence of activator.

General procedure with activator: In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (1.8 mg, 10.0 mol%), ligand L1 (3.6 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (25.4 – 50.8 mg, 1.0 – 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (1.1 – 4.5 mg, 10.0 – 40.0 mol%) was added. Finally stirring for another 5 minutes *substrate* (0.1 mmol) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard.

Further modification of the ligand scaffold:

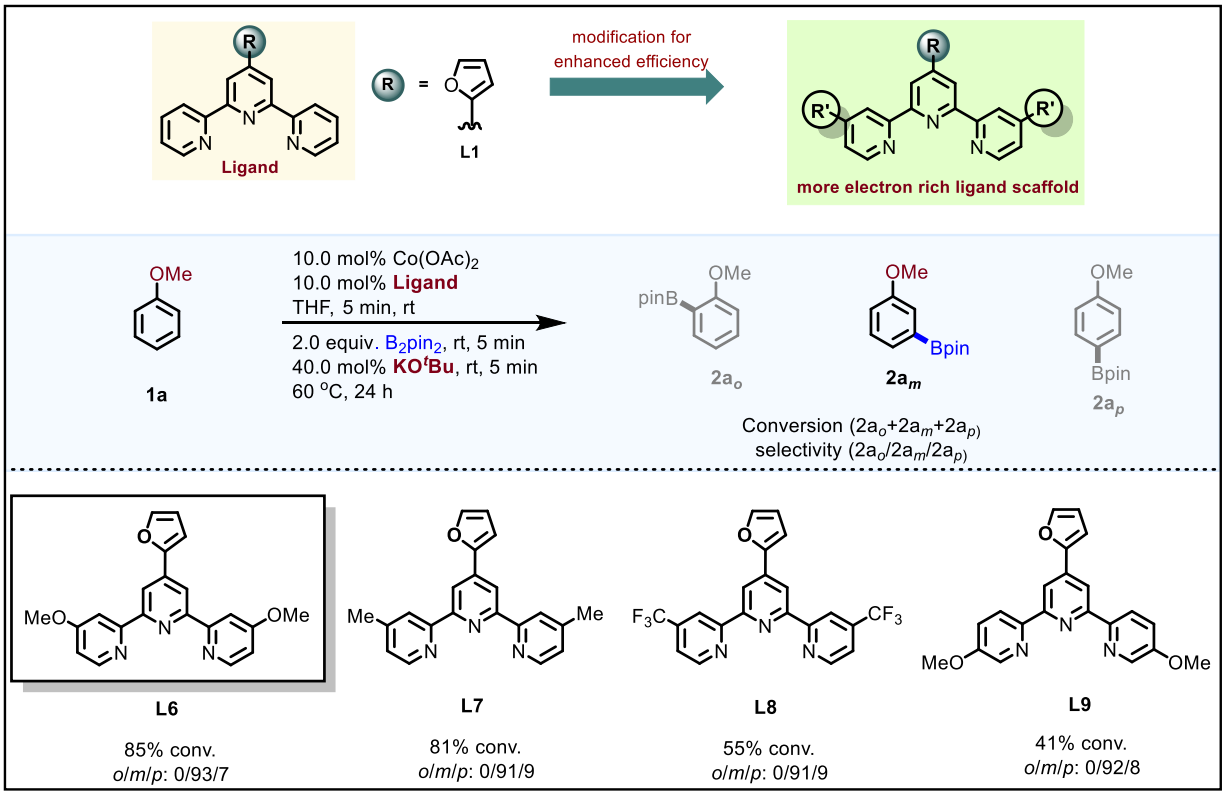


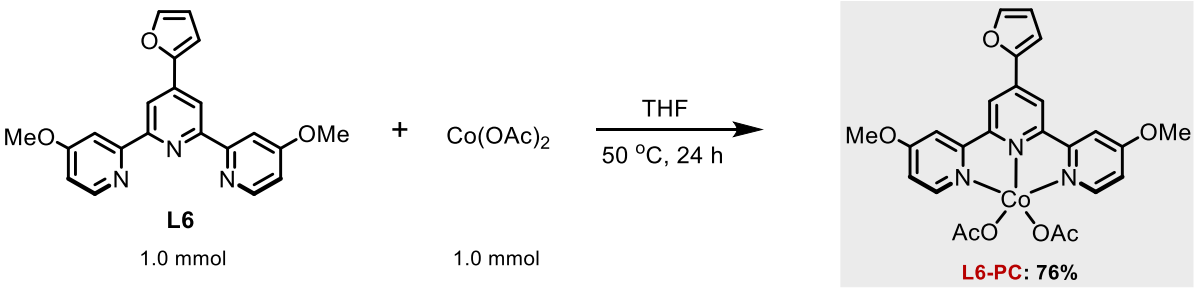
Figure S3: Further modification of the ligand scaffold and their effects on the course of the reaction.

Table S2: Further optimization with the optimized ligand **L6**:

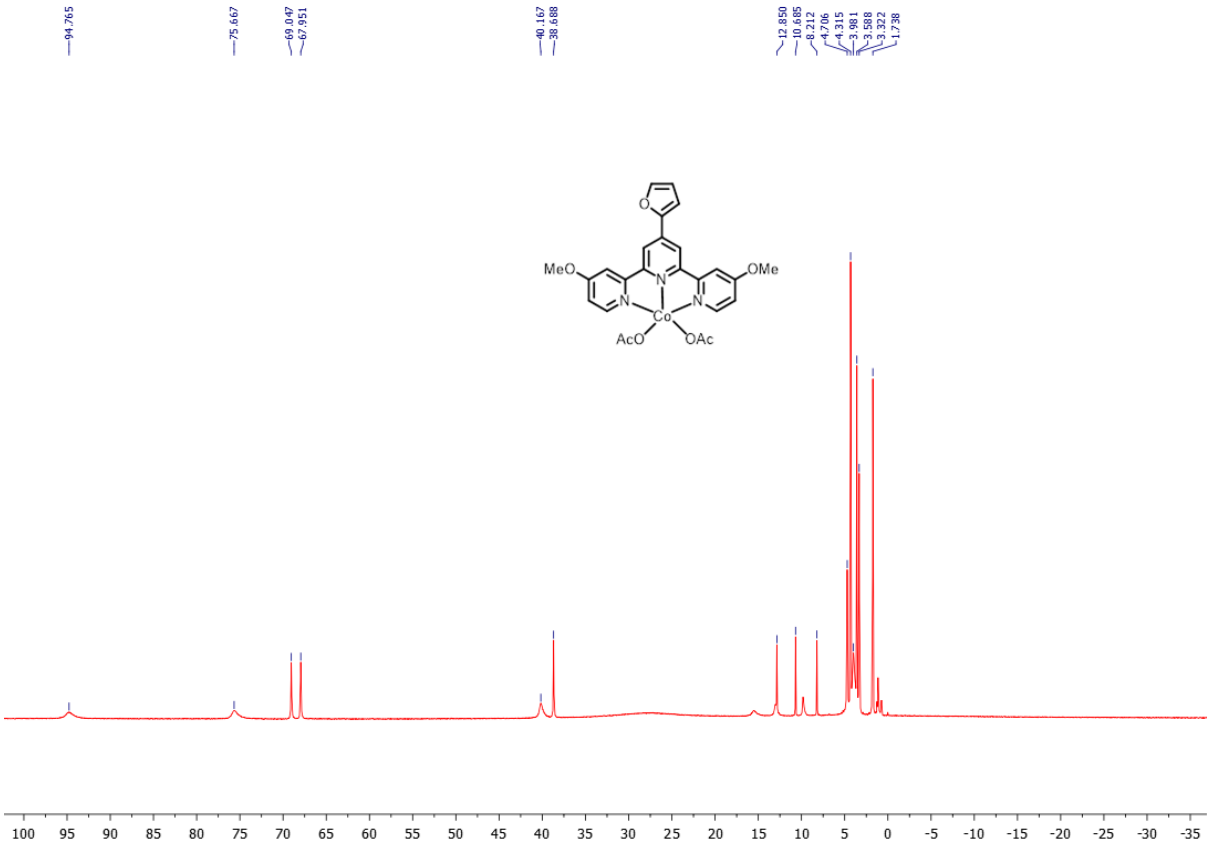
Entry	Ligand	KO^{t}Bu (Loading)	B_2pin_2	Temperature	Conversion	*o:m:p*
1	L6	40.0 mol%	1.0 equiv	60 °C	65%	0:93:7
2.	L6	40.0 mol%	1.2 equiv.	60 °C	70%	0:93:7
3.	L6	40.0 mol%	1.5 equiv.	60 °C	73%	0:93:7
4.	L6	40.0 mol%	2.0 equiv.	60 °C	85%	0:93:7
5.	L6	40.0 mol%	2.0 equiv.	40 °C	75%	0:93:7
6.	L6	40.0 mol%	2.0 equiv.	50 °C	79%	0:93:7
7.	L6	30.0 mol%	2.0 equiv.	60 °C	82%	0:93:7
8.	L6	35.0 mol%	2.0 equiv.	60 °C	85%	0:93:7
9.	L6	40.0 mol%	4.0 equiv. HBpin	60 °C	0%	0:93:7

Reaction Procedure: Same as General procedure with activator.

Preparation of Cobalt Pre-catalyst: In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with anhydrous $Co(OAc)_2$ (177 mg, 1.0 mmol), ligand L6 (359.4, 1.0 mmol) and dry THF (3.0 mL) sequentially. The microreactor was capped with a teflon pressure cap and stirred at 50 °C for 24 h, during which a light-brown precipitate formed. The resulting solid was collected by filtration, washed several times with anhydrous *n*-hexane, and dried under vacuum for 24 h to afford the light-brown powder pre-catalyst **L6-PC**.



We have taken the NMR in $CDCl_3$-CD_3OD (1:1) and the ^1H NMR spectra is following,



^1H NMR spectra of **L6-PC** (25 °C, 400 MHz, $CDCl_3$:CD_3OD (1:1))

Keeping the NMR tube inside the glove box fridge at -20 °C for several days, we got corresponding crystals (although the quality was not very good) and recorded the XRD data for further confirming the pre-catalyst formation.

checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_JD_26112025_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_JD_26112025_0m

Bond precision: C-C = 0.0380 A Wavelength=0.71073

Cell: a=10.704(4) b=28.119(10) c=10.033(3)
alpha=90 beta=114.242(8) gamma=90
Temperature: 150 K

	Calculated	Reported
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Hall group	C -2yc	C -2yc
Moiety formula	C25 H23 Co N3 O7, C H Cl3	C25 H23 Co N3 O7, C H Cl3
Sum formula	C26 H24 Cl3 Co N3 O7	C26 H24 Cl3 Co N3 O7
Mr	655.76	655.76
Dx,g cm-3	1.582	1.582
Z	4	4
Mu (mm-1)	0.965	0.965
F000	1340.0	1340.0
F000'	1343.70	
h,k,lmax	10,28,10	10,28,10
Nref	2924[1469]	2272
Tmin,Tmax		
Tmin'		

Correction method= Not given

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R(reflections)= 0.0865( 1863)                    wR2(reflections)=
                                                 0.2548( 2272)
S = 1.048                  Npar= 366
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The following ALERTS were generated. Each ALERT has the format
      test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
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Alert level A

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THETM01_ALERT_3_A  The value of sine(theta_max)/wavelength is less than 0.550
           Calculated sin(theta_max)/wavelength =    0.5023
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Author Response: The crystal exhibited weak diffraction quality and did not yield stabl refinement at higher resolution; therefore, the data were truncated at a resolution corresponding to sin theta by lemda equal to 0.55.

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PLAT090_ALERT_3_A Poor Data / Parameter Ratio (Zmax > 18) ........       3.87 Note
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Author Response: The crystal diffracted weakly and was also air-sensitive, which limite data quality and reduced the number of observed reflections.

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PLAT213_ALERT_2_A Atom C7              has ADP max/min Ratio .....        7.6 oblate
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Author Response: The oblate ADP of atom C7 arises from weak diffraction and limited high-resolution data.

Alert level B

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PLAT341_ALERT_3_B Low Bond Precision on  C-C Bonds ...............      0.038 Ang.
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Author Response: This alert comes due to the disorder in the five member ring.

Alert level C

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STRVA01_ALERT_4_C           Flack test results are ambiguous.
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          From the CIF: _refine_ls_abs_structure_Flack_su    0.090
PLAT029_ALERT_3_C _diffrn_measured_fraction_theta_full value Low .      0.965 Why?
PLAT053_ALERT_1_C Minimum Crystal Dimension Missing (or Error) ...     Please Check
PLAT054_ALERT_1_C Medium  Crystal Dimension Missing (or Error) ...     Please Check
PLAT055_ALERT_1_C Maximum Crystal Dimension Missing (or Error) ...     Please Check
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range        3.4 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1  H   Uiso(max)/Uiso(min) Range        4.2 Ratio
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PLAT244_ALERT_4_C Low    'Solvent' Ueq as Compared to Neighbors of        C26 Check
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=    0.502         50 Report
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                1  3  2,   3  9  2,  -5 25  2,   7  1  3,   2  2  3,   8  2  3,
                7  3  3,   6  0  4,   7  1  4,   6  2  4,   7  5  4,   2  8  4,
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Alert level G

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PLAT003_ALERT_2_G Number of Uiso or U(i,j)  Restrained non-H-Atoms         40 Report
PLAT083_ALERT_2_G SHELXL Second Parameter in WGHT  Unusually Large       56.19 Why ?
PLAT111_ALERT_2_G ADDSYM Detects New (Pseudo) Centre of Symmetry .         80 %Fit
PLAT113_ALERT_2_G ADDSYM Suggests Possible Pseudo/New  Space-group       C2/c Check
             Check Model Parameter Symmetry for Reflection Data Support
PLAT171_ALERT_4_G The CIF-Embedded .res File Contains EADP Records          1 Report
PLAT174_ALERT_4_G The CIF-Embedded .res File Contains FLAT Records          1 Report
PLAT177_ALERT_4_G The CIF-Embedded .res File Contains DELU Records          1 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          1 Report
PLAT186_ALERT_4_G The CIF-Embedded .res File Contains ISOR Records          1 Report
PLAT187_ALERT_4_G The CIF-Embedded .res File Contains RIGU Records          1 Report
PLAT398_ALERT_2_G Deviating  C-O-C   Angle From 120 for O1        .       105.4 Degree
PLAT794_ALERT_5_G Tentative Bond Valency for Co1       (II)      .        1.97 Info
PLAT802_ALERT_4_G CIF Input Record(s) with more than 80 Characters          2 Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints .............        910 Note
PLAT883_ALERT_1_G Absent Datum for _atom_sites_solution_primary ..     Please Do !
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still         66% Note
PLAT910_ALERT_3_G Missing FCF Reflection(s) Below Theta(Min)[Deg]=       2.21 Note
               0  2  0,
PLAT915_ALERT_3_G No Flack x Check Done: Low Friedel Pair Coverage          59 %
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity ...........        3.0 Low
PLAT965_ALERT_2_G The SHELXL WEIGHT Optimisation has not Converged     Please Check
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value ...........      2.579 Note
             Predicted wR2: Based on SigI**2  9.85 or SHELX Weight 24.32
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          2 Info
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  3 ALERT level A = Most likely a serious problem - resolve or explain
  1 ALERT level B = A potentially serious problem, consider carefully
 10 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 22 ALERT level G = General information/check it is not something unexpected

  4 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
 10 ALERT type 2 Indicator that the structure model may be wrong or deficient
 11 ALERT type 3 Indicator that the structure quality may be low
  9 ALERT type 4 Improvement, methodology, query or suggestion
  2 ALERT type 5 Informative message, check
```

It is advisable to attempt to resolve as many as possible of the alerts in all categories. Often the minor alerts point to easily fixed oversights, errors and omissions in your CIF or refinement strategy, so attention to these fine details can be worthwhile. It is up to the individual to critically assess their own results and, if necessary, seek expert advice.

PLATON version of 26/09/2025; check.def file version of 20/09/2025

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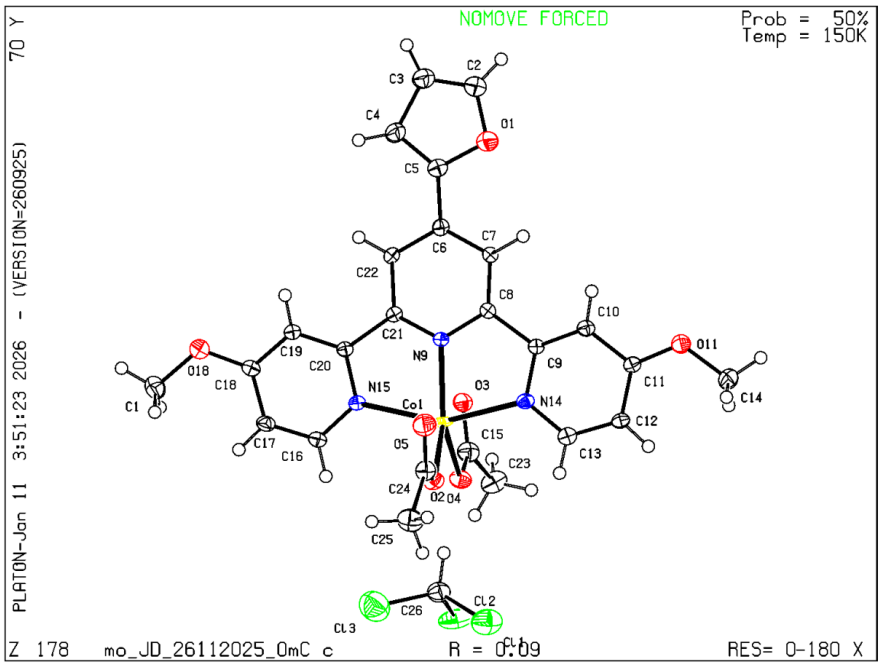
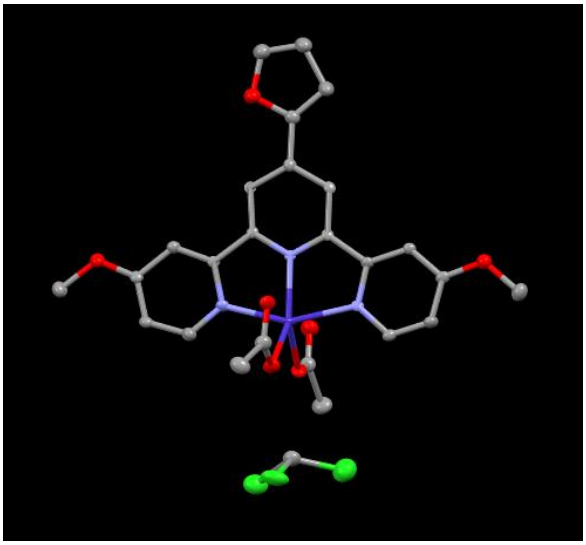
duplicate check

No duplication found

Datablock mo_JD_26112025_0m - ellipsoid plot





CCDC Number: 2521880

Superior reaction outcome with pre-catalyst L6-PC:

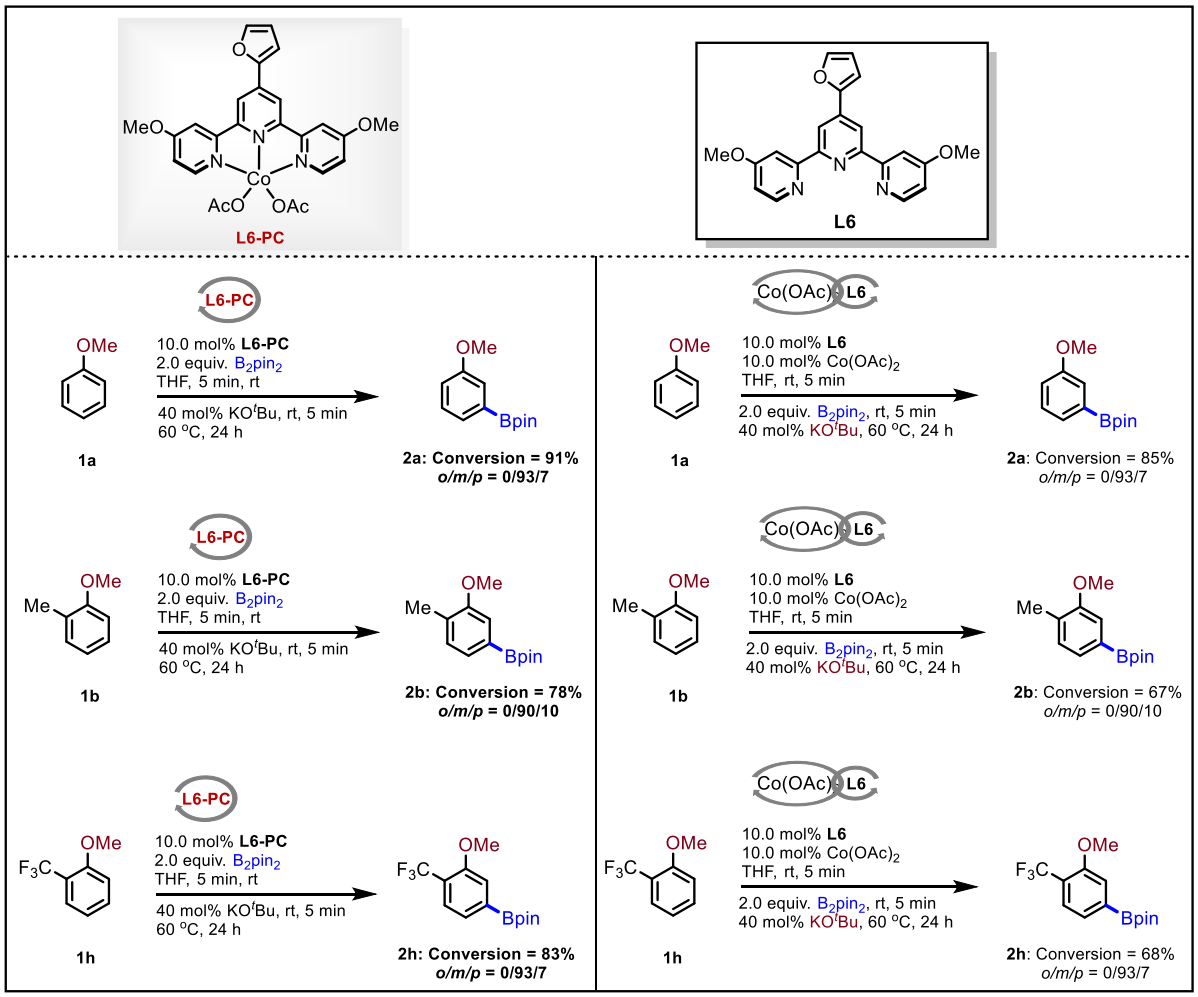
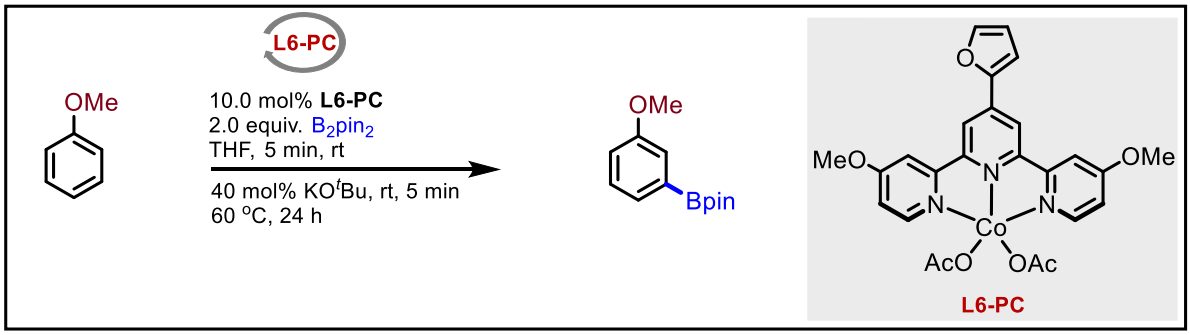


Figure S4: Comparison between the catalytic activity of **L6-PC** and **L6**/$Co(OAc)_2$.

Optimized reaction conditions:

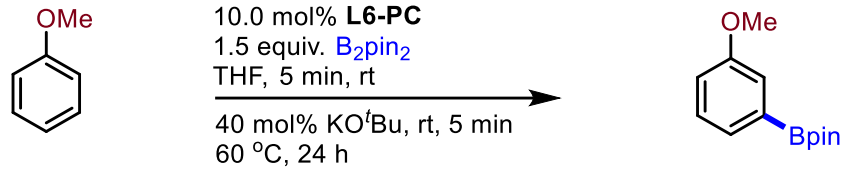


In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (5.4 mg, 10.0 mol%), B_2pin_2 (50.8 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (4.5 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, substrate (0.1 mmol) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot

was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. For NMR Conversion, the reaction was then diluted with chloroform and filtered through a thin pad of silica gel under air. The resulting mixture was concentrated in vacuo and then analyzed by ^{1}H using trimethoxybenzene as internal standard.

Substrate Scope: Substrate scope for the *meta* C-H borylation of diverse classes of arenes

*meta-Borylation of anisole (**2a**):*



1a: 0.2 mmol

2a: 83%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, anisole (**1a:** 0.2 mmol, 21.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 38.8 mg (83%) of the *meta*-borylated product (**2a**) as gummy liquid.

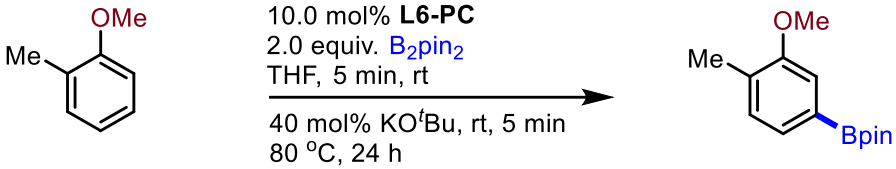
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.40 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.30 (t, J = 8.0 Hz, 1H), 7.01 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 3.83 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (200 MHz, $CDCl_3$): δ 159.0, 128.9, 127.2, 118.6, 117.9, 83.8, 55.2, 24.8.

^{11}B NMR (256 MHz, $CDCl_3$): 30.8.

HRMS (ESI) *m/z* calculated for $C_{13}H_{20}BO_3$ $[M+H]^+$ 235.1505, found 235.1518.

*meta-Borylation of 2-methylanisole (**2b**):*



1b: 0.2 mmol

2b: 78%
o/m/p = 0/90/10

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 2-methylanisole (**1b:** 0.2 mmol, 24.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 38.7 mg (78%) of the *meta*-borylated product (**2b**) as gummy liquid.

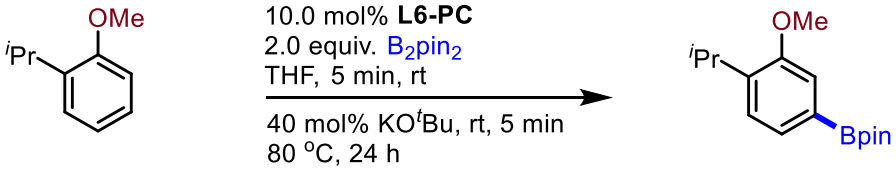
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 (d, J = 7.2 Hz, 1H), 7.24 (s, 1H), 7.15 (d, J = 7.2 Hz, 1H), 3.88 (s, 3H), 2.25 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 130.2, 127.2, 115.3, 83.6, 55.3, 24.8, 16.5.

^{11}B NMR (128 MHz, $CDCl_3$) δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_3$ $[M+H]^+$ 249.1662, found 249.1665.

*meta-Borylation of 1-isopropyl-2-methoxybenzene (**2c**):*



1c: 0.2 mmol

2c: 72%
o/m/p = 0/92/8

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-isopropyl-2-methoxybenzene (**1c:** 0.2 mmol, 30.0 mg) was

added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 39.8 mg (72%) of the *meta*-borylated product (**2c**) as gummy liquid.

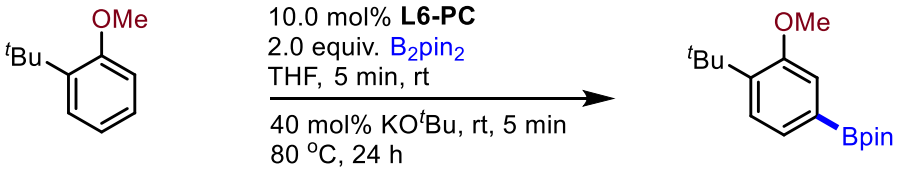
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, J = 7.6 Hz, 1H), 7.27 (s, 1H), 7.23 (d, J = 7.6 Hz, 1H), 3.88 (s, 3H), 3.38 – 3.31 (m, 1H), 1.34 (s, 12H), 1.21 (d, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 140.6, 127.5, 125.5, 115.9, 83.6, 55.4, 26.8, 24.8, 22.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{16}H_{26}BO_3$ $[M+H]^+$ 277.1975, found 277.1968.

*meta-Borylation of 1-(tert-butyl)-2-methoxybenzene (**2d**):*



1d: 0.2 mmol

2d: 75%
o/m/p = 0/96/4

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-(tert-butyl)-2-methoxybenzene (**1d:** 0.2 mmol, 32.8 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 43.5 mg (75%) of the *meta*-borylated product (**2d**) as gummy liquid.

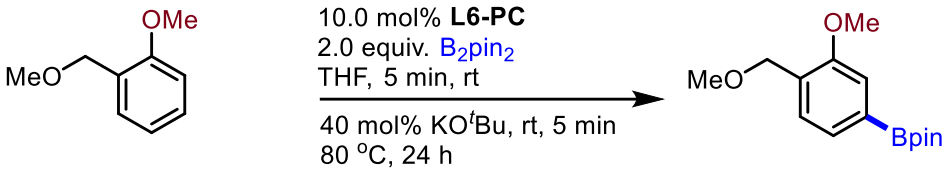
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.6 Hz, 1H), 7.30 – 7.28 (m, 2H), 3.89 (s, 3H), 1.37 (s, 9H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.0, 141.7, 127.2, 126.1, 117.1, 83.7, 55.1, 35.0, 29.6, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calculated for $C_{17}H_{28}BO_3$ $[M+H]^+$ 291.2132, found 291.2129.

*meta-Borylation of 1-methoxy-2-(methoxymethyl)benzene (**2e**):*



1e: 0.2 mmol

2e: 81%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-methoxy-2-(methoxymethyl)benzene (**1e:** 0.2 mmol, 30.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 45.1 mg (81%) of the *meta*-borylated product (**2e**) as gummy liquid.

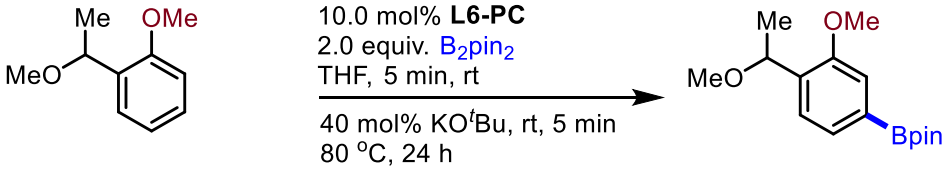
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.2 Hz, 1H), 7.37 (d, J = 7.2 Hz, 1H), 7.28 (s, 1H), 4.52 (s, 2H), 3.88 (s, 3H), 3.41 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 129.8, 127.9, 127.2, 115.5, 83.7, 69.5, 58.3, 55.4, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): 30.8.

HRMS (ESI) *m/z* calculated for $C_{15}H_{24}BO_4$ $[M+H]^+$ 279.1768, found 279.1759.

*meta-Borylation of 1-methoxy-2-(1-methoxyethyl)benzene (**2f**):*



1f: 0.2 mmol

2f: 85%
o/m/p = 0/99/1

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-methoxy-2-(1-methoxyethyl)benzene (**1f:** 0.2 mmol, 33.2 mg)

was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 49.7 mg (85%) of the *meta*-borylated product (**2f**) as gummy liquid.

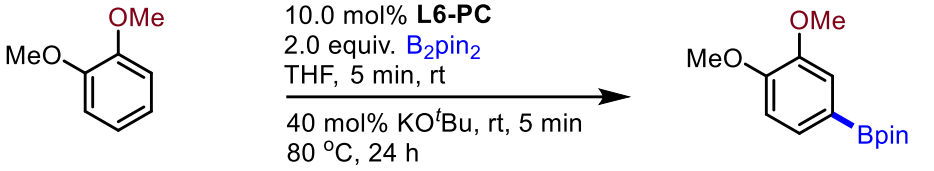
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 7.6 Hz, 1H), 7.29 (s, 1H), 4.76 (q, J = 6.4 Hz, 1H), 3.87 (s, 3H), 3.25 (s, 3H), 1.37 (d, J = 6.4 Hz, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.1, 135.2, 127.6, 125.2, 115.8, 83.7, 73.3, 56.5, 55.3, 24.8, 22.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{16}H_{26}BO_4$ $[M+H]^+$ 293.1924, found 293.1931.

*meta-Borylation of 1,2-dimethoxybenzene (**2g**):*



1g: 0.2 mmol

2g: 94%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1,2-dimethoxybenzene (**1g:** 0.2 mmol, 27.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 49.7 mg (94%) of the *meta*-borylated product (**2g**) as gummy liquid.

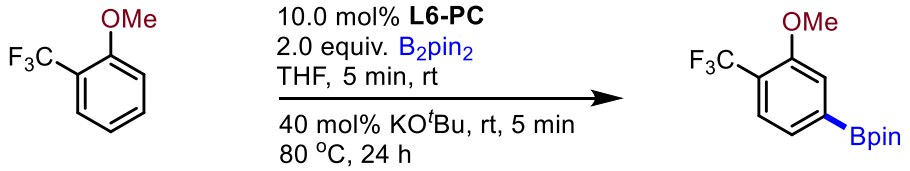
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.6, 1.2 Hz, 1H), 7.28 (d, J = 1.2 Hz, 1H), 6.87 (d, J = 8.0 Hz, 1H), 3.91 (s, 3H), 3.88 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.5, 148.2, 128.4, 116.5, 110.4, 83.4, 55.6, 55.5, 24.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.4.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_4$ $[M+H]^+$ 265.1611, found 265.1619.

*meta-Borylation of 1-methoxy-2-(trifluoromethyl)benzene (**2h**):*



1h: 0.2 mmol

2h: 81%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-methoxy-2-(trifluoromethyl)benzene (**1h:** 0.2 mmol, 35.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 48.9 mg (81%) of the *meta*-borylated product (**2h**) as gummy liquid.

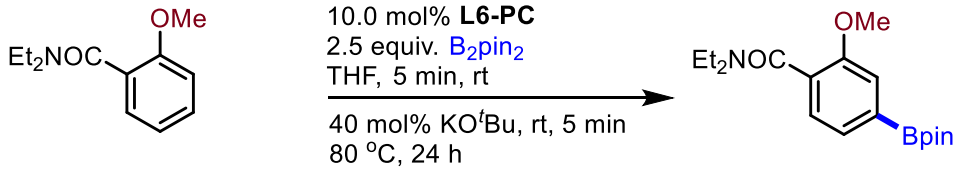
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.40 (s, 1H), 3.94 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.8, 126.4, 126.3 (q, J = 5.3 Hz), 123.6 (q, J = 270.8 Hz), 121.0 (q, J = 30.4 Hz), 117.5, 84.3, 56.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{19}BF_3O_3$ $[M+H]^+$ 303.1379, found 303.1386.

*meta-Borylation of N,N-diethyl-2-methoxybenzamide (**2i**):*



1i: 0.2 mmol

2i: 73%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst

produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, *N,N*-diethyl-2-methoxybenzamide (**1i:** 0.2 mmol, 41.5 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (20% EtOAc in hexane as eluent) gave 48.6 mg (73%) of the *meta*-borylated product (**2i**) as gummy liquid.

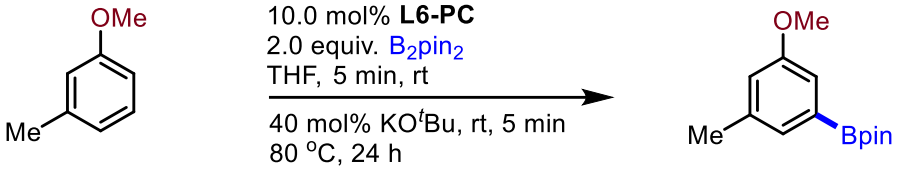
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 1H), 7.25 (s, 1H), 7.12 (d, J = 7.2 Hz, 1H), 3.80 (s, 3H), 3.54 – 3.45 (m, 18H), 3.05 (q, J = 6.8 Hz, 2H), 1.30 (s, 12H), 0.95 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.7, 154.4, 129.3, 127.3, 126.7, 116.3, 83.9, 55.4, 42.7, 38.8, 24.4, 13.7, 12.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.3.

HRMS (ESI) *m/z* calculated for $C_{18}H_{29}BNO_4$ $[M+H]^+$ 334.2190, found 334.2181.

*meta-Borylation of 1-methoxy-3-methylbenzene (**2j**):*



1j: 0.2 mmol

2j: 86%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-methoxy-3-methylbenzene (**1j:** 0.2 mmol, 24.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 42.7 mg (86%) of the *meta*-borylated product (**2j**) as gummy liquid.

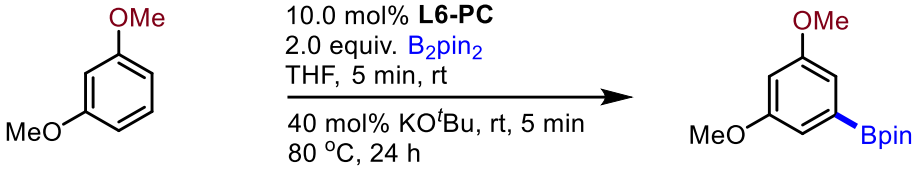
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (s, 1H), 7.15 (d, *J* = 2.4 Hz, 1H), 6.84 (s, 1H), 3.82 (s, 3H), 2.34 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 138.9, 128.0, 118.7, 115.6, 83.7, 55.2, 24.8, 21.2.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_3$ $[M+H]^+$ 249.1662, found 249.1652.

*meta-Borylation of 1,3-dimethoxybenzene (**2k**):*



1k: 0.2 mmol

2k: 85%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1,3-dimethoxybenzene (**1k:** 0.2 mmol, 27.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 44.9 mg (85%) of the *meta*-borylated product (**2k**) as gummy liquid.

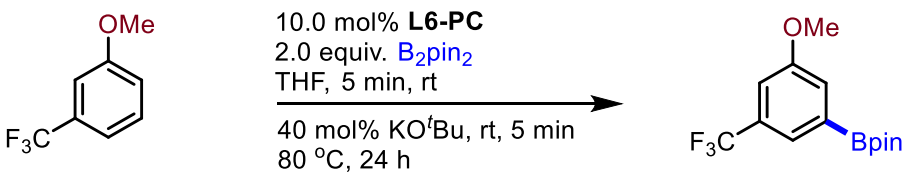
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.94 (d, *J* = 2.4 Hz, 2H), 6.55 (t, *J* = 2.4 Hz, 1H), 3.80 (s, 6H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.3, 111.5, 104.4, 83.8, 55.3, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_4$ $[M+H]^+$ 265.1611, found 265.1629.

*meta-Borylation of 1-methoxy-3-(trifluoromethyl)benzene (**2l**):*



1l: 0.2 mmol

2l: 81%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-methoxy-3-(trifluoromethyl)benzene (**1l:** 0.2 mmol, 35.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 48.9 mg (81%) of the *meta*-borylated product (**2l**) as gummy liquid.

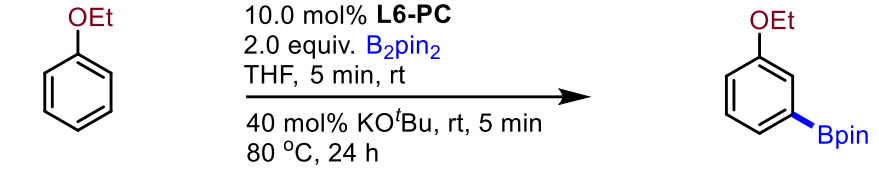
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 1H), 7.48 (d, J = 2.4 Hz, 1H), 7.21 (s, 1H), 3.86 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.2, 131.4 (q, J = 31.6 Hz), 124.0 (q, J = 270.9 Hz), 123.5 (q, J = 3.6 Hz), 122.53 (d, J = 0.7 Hz), 114.1 (d, J = 3.7 Hz), 84.3, 55.5, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{19}BF_3O_3$ $[M+H]^+$ 303.1379, found 303.1371.

*meta-Borylation of ethoxybenzene (**2m**):*



1m: 0.2 mmol

2m: 83%
o/m/p = 0/91/9

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, ethoxybenzene (**1m:** 0.2 mmol, 24.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with

silica gel (2% EtOAc in hexane as eluent) gave 41.2 mg (83%) of the *meta*-borylated product (**2m**) as gummy liquid.

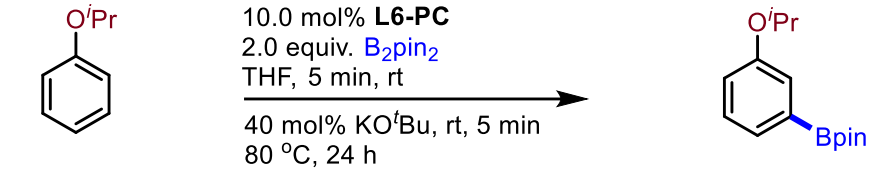
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.38 (d, J = 7.2 Hz, 1H), 7.32 (d, J = 2.4 Hz, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.00 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 4.08 – 4.05 (m, 2H), 1.40 (t, J = 7.2 Hz, 3H), 1.34 (s, 12H).

^{13}C NMR (200 MHz, $CDCl_3$): δ 158.34 128.9, 127.0, 119.5, 118.4, 83.8, 63.3, 24.8, 14.9.

^{11}B NMR (128 MHz, $CDCl_3$): 30.8.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_3$ $[M+H]^+$ 249.1662, found 249.1651.

*meta-Borylation of isopropoxybenzene (**2n**):*



1n: 0.2 mmol

2n: 78%
o/m/p = 0/91/9

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, isopropoxybenzene (**1n:** 0.2 mmol, 27.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 40.9 mg (78%) of the *meta*-borylated product (**2n**) as gummy liquid.

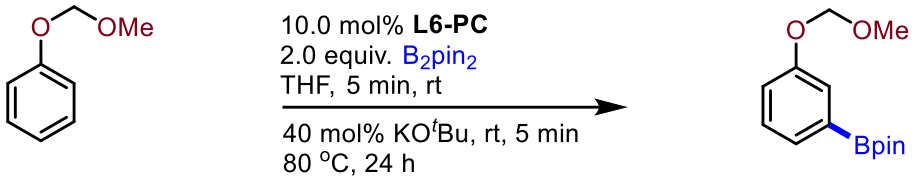
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, J = 7.2 Hz, 1H), 7.33 (d, J = 2.4 Hz, 1H), 7.27 (t, J = 8.0, 2H), 7.00 – 6.96 (m, 1H), 4.63 – 4.57 (m, 1H), 1.34 – 1.32 (m, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 128.9, 127.0, 121.4, 119.6, 83.7, 69.8, 24.8, 22.1.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{15}H_{24}BO_3$ $[M+H]^+$ 263.1819, found 263.1811.

*meta-Borylation of (methoxymethoxy)benzene (**2o**):*



1o: 0.2 mmol

2o: 82%
o/m/p = 0/92/8

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, (methoxymethoxy)benzene (**1o:** 0.2 mmol, 27.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 43.3 mg (82%) of the *meta*-borylated product (**2o**) as gummy liquid.

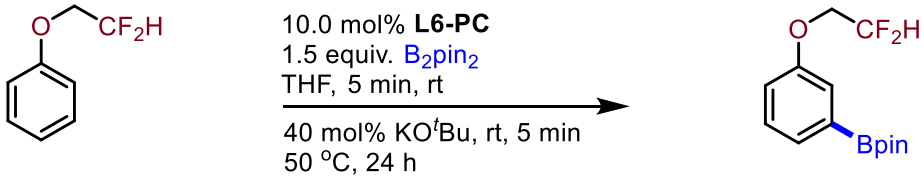
^{1}H NMR (400 MHz, $CDCl_3$): 7.47 – 7.45 (m, 2H), 7.30 (t, J = 8.0 Hz, 1H), 7.14 (ddd, J = 8.0, 2.4, 0.8 Hz, 1H), 5.20 (s, 2H), 3.48 (s, 3H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.6, 128.95, 128.3, 121.9, 119.5, 94.3, 83.8, 56.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_4$ $[M+H]^+$ 265.1611, found 265.1623.

*meta-Borylation of (2,2-difluoroethoxy)benzene (**2p**):*



1o: 0.2 mmol

2o: 70%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, (2,2-difluoroethoxy)benzene (**1p:** 0.2 mmol, 31.6 mg) was added

to it. The microreactor was capped with a teflon pressure cap and stirred at 50 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 39.8 mg (70%) of the *meta*-borylated product (**2p**) as gummy liquid.

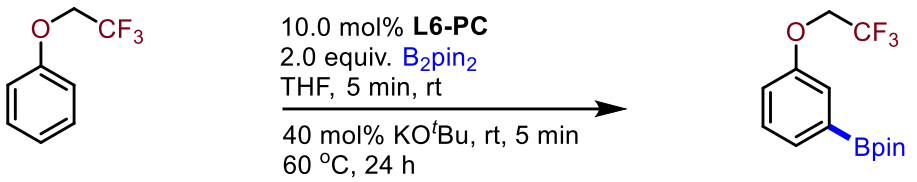
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.2 Hz, 1H), 7.33 – 7.30 (m, 2H), 7.04 (ddd, J = 8.4, 2.8, 0.8 Hz, 1H), 6.06 (tt, J = 55.2, 4.4 Hz, 1H), 4.22 (td, J = 13.2, 4.4 Hz, 2H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 129.2, 128.4, 119.4, 118.5, 113.8 (t, J = 239.2 Hz), 84.0, 67.3 (t, J = 29.3 Hz, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}BF_2O_3$ $[M+H]^+$ 285.1474, found 285.1469.

*meta-Borylation of (2,2,2-trifluoroethoxy)benzene (**2q**):*



1o: 0.2 mmol

2o: 72%
o/m/p = 0/95/5

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, (2,2,2-trifluoroethoxy)benzene (**1q:** 0.2 mmol, 35.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 43.5 mg (72%) of the *meta*-borylated product (**2q**) as gummy liquid.

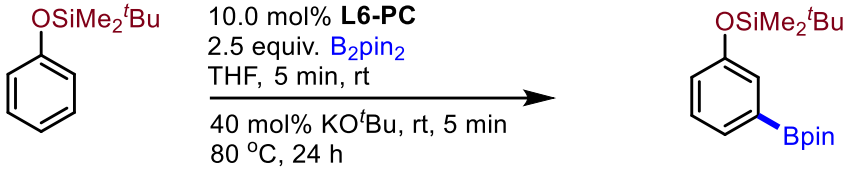
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 7.2 Hz, 1H), 7.35 – 7.31 (m, 2H), 7.07 (ddd, J = 8.4, 2.8, 0.8 Hz, 1H), 4.38 (q, J = 8.4 Hz, 2H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 129.3, 128.9, 123.4 (q, J = 276.1 Hz), 119.6, 118.8, 84.0, 65.8 (q, J = 35.4 Hz), 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calculated for $C_{14}H_{19}BF_3O_3$ $[M+H]^+$ 303.1379, found 303.1363.

*meta-Borylation of tert-butyldimethyl(phenoxy)silane (**2r**):*



1r: 0.2 mmol

2r: 68%
o/m/p = 0/95/5

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, tert-butyldimethyl(phenoxy)silane (**1r:** 0.2 mmol, 41.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 45.5 mg (68%) of the *meta*-borylated product (**2r**) as gummy liquid.

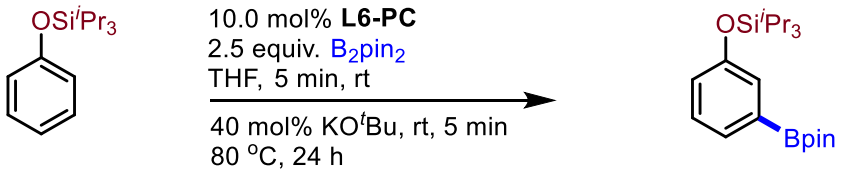
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, J = 7.2 Hz, 1H), 7.29 (s, 1H), 7.25 (t, J = 8.0, 1H), 6.95 (dd, J = 8.0, 1.2 Hz, 1H), 1.35 (s, 12H), 1.01 (s, 9H), 0.22 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 128.8, 127.7, 126.1, 122.8, 83.7, 25.7, 24.8, 18.1, -4.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{18}H_{32}BO_3Si$ $[M+H]^+$ 335.2214, found 335.2221.

*meta-Borylation of triisopropyl(phenoxy)silane (**2s**):*



1s: 0.2 mmol

2s: 65%
o/m/p = 0/94/6

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, triisopropyl(phenoxy)silane (**1s:** 0.2 mmol, 50.1 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 48.9 mg (65%) of the *meta*-borylated product (**2s**) as gummy liquid.

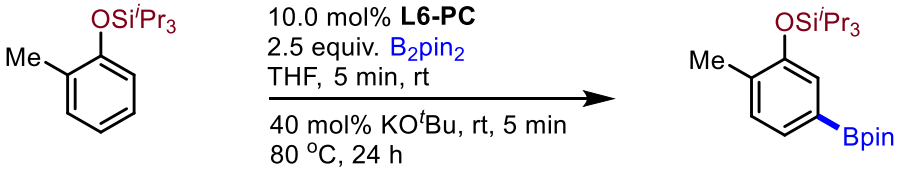
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 7.6 Hz, 1H), 7.32 (d, J = 2.0 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 6.99 – 6.94 (m, 1H), 1.34 (s, 12H), 1.31 – 1.27 (m, 3H), 1.11 (d, J = 7.2 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.5, 128.7, 127.3, 125.9, 122.4, 83.7, 24.8, 17.9, 12.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{21}H_{38}BO_3Si$ $[M+H]^+$ 377.2683, found 377.2677.

*meta-Borylation of triisopropyl(o-tolyloxy)silane (**2t**):*



1t: 0.2 mmol

2t: 64%
o/m/p = 0/91/9

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, triisopropyl(o-tolyloxy)silane (**1t:** 0.2 mmol, 52.9 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 50.0 mg (64%) of the *meta*-borylated product (**2t**) as gummy liquid.

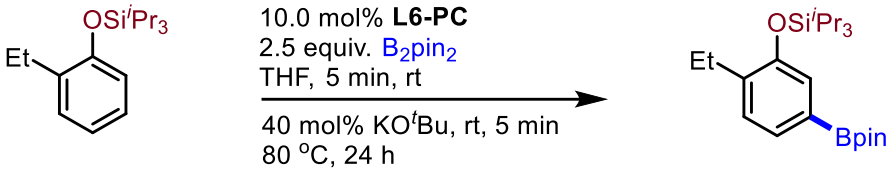
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 7.2 Hz, 1H), 7.19 (s, 1H), 7.12 (d, J = 7.2 Hz, 1H), 2.26 (s, 3H), 1.34 – 1.30 (m, 15H), 1.12 (d, J = 7.2 Hz, 18H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.8, 132.0, 130.4, 127.2, 123.8, 83.5, 24.8, 18.1, 17.3, 13.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{22}H_{40}BO_3Si$ $[M+H]^+$ 391.2840, found 391.2852.

*meta-Borylation of (2-ethylphenoxy)triisopropylsilane (**2u**):*



1u: 0.2 mmol

2u: 62%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, (2-ethylphenoxy)triisopropylsilane (**1u:** 0.2 mmol, 55.7 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 50.6 mg (62%) of the *meta*-borylated product (**2u**) as gummy liquid.

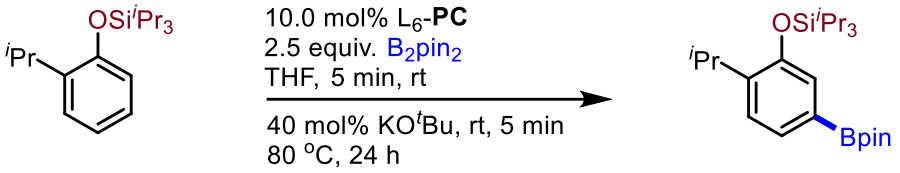
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (dd, J = 7.2, 0.4 Hz, 1H), 7.20 (s, 1H), 7.15 (d, J = 7.6 Hz, 1H), 2.67 (q, J = 7.6 Hz, 2H), 1.34 – 1.30 (m, 15H), 1.20 (t, J = 7.6 Hz, 3H), 1.13 (d, J = 7.2 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.5, 137.9, 128.9, 127.4, 123.9, 83.6, 25.0, 24.1, 18.3, 14.3, 13.2.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calculated for $C_{23}H_{42}BO_3Si$ $[M+H]^+$ 405.2996, found 405.2988.

*meta-Borylation of triisopropyl(2-isopropylphenoxy)silane (**2v**):*



1v: 0.2 mmol

2v: 58%
o/m/p = 0/93/7

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, triisopropyl(2-isopropylphenoxy)silane (**1v:** 0.2 mmol, 58.5 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 48.5 mg (58%) of the *meta*-borylated product (**2v**) as gummy liquid.

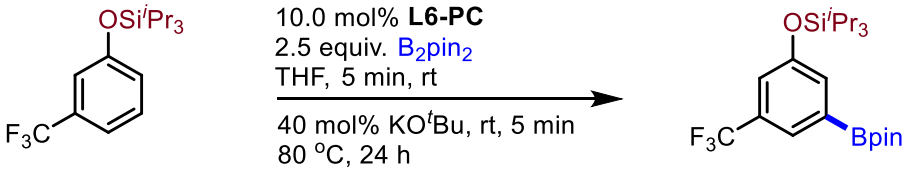
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (d, J = 7.6 Hz, 1H), 7.21 – 7.19 (m, 2H), 3.43 – 3.36 (m, 1H), 1.34 – 1.31 (m, 15H), 1.20 (d, J = 6.8 Hz, 6H), 1.13 (d, J = 7.6 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 144.1, 128.6, 125.2, 114.8, 83.1, 50.1, 25.0, 24.8, 18.0, 13.2.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.7.

HRMS (ESI) *m/z* calculated for $C_{24}H_{44}BO_3Si$ $[M+H]^+$ 419.3153, found 419.3161.

*meta-Borylation of triisopropyl(3-(trifluoromethyl)phenoxy)silane (**2w**):*



1w: 0.2 mmol

2w: 65%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally

stirring for another 5 minutes, triisopropyl(3-(trifluoromethyl)phenoxy)silane (**1w:** 0.2 mmol, 63.7 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 57.8 mg (65%) of the *meta*-borylated product (**2w**) as gummy liquid.

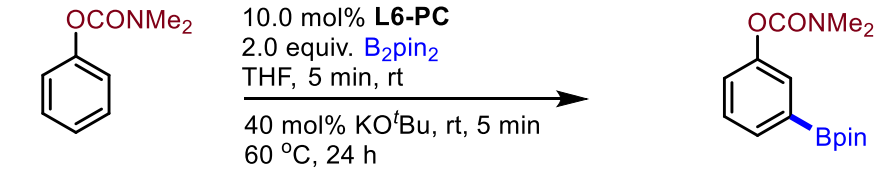
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63 (s, 1H), 7.45 (d, J = 2.0 Hz, 1H), 7.16 (s, 1H), 1.35 (s, 12H), 1.30 – 1.26 (m, 3H), 1.11 (d, J = 7.2 Hz, 18H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.0, 131.4 (d, J = 31.8 Hz), 129.4, 125.5, 123.9 (d, J = 3.8 Hz), 122.8, 119.0 (d, J = 3.6 Hz), 84.4, 25.0, 18.0, 12.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

HRMS (ESI) *m/z* calculated for $C_{22}H_{37}BF_3O_3Si$ $[M+H]^+$ 445.2557, found 445.2571.

*meta-Borylation of phenyl dimethylcarbamate (**2x**):*



1x: 0.2 mmol

2x: 77%
o/m/p = 0/97/3

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, phenyl dimethylcarbamate (**1x:** 0.2 mmol, 33.0 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 44.8 mg (77%) of the *meta*-borylated product (**2x**) as gummy liquid.

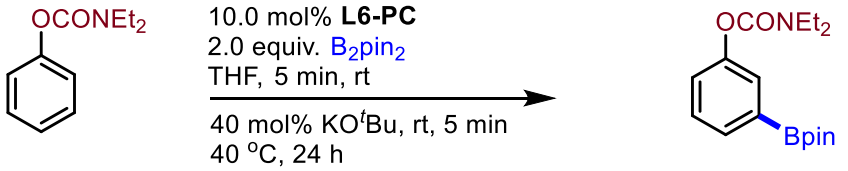
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.2 Hz, 1H), 7.53 (d, J = 1.6 Hz, 1H), 7.35 (t, J = 7.2 Hz, 1H), 7.21 (ddd, J = 7.6, 2.4, 1.2 Hz, 1H), 3.07 (s, 3H), 2.99 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.9, 151.0, 131.4, 128.7, 127.6, 124.7, 83.8, 36.6, 36.3, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7.

HRMS (ESI) *m/z* calculated for $C_{15}H_{23}BNO_4$ $[M+H]^+$ 292.1720, found 292.1711.

*meta-Borylation of phenyl diethylcarbamate (**2y**):*



1y: 0.2 mmol

2y: 82%
o/m/p = 0/98/2

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, phenyl diethylcarbamate (**1y:** 0.2 mmol, 38.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 40 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 52.4 mg (82%) of the *meta*-borylated product (**2y**) as gummy liquid.

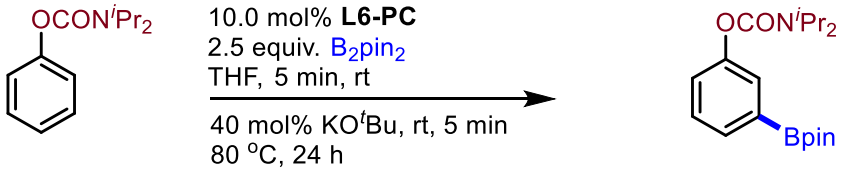
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.6 Hz, 1H), 7.53 (d, J = 2.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.22 (ddd, J = 7.6, 2.4, 0.8 Hz, 1H), 3.43 – 3.37 (m, 4H), 1.33 (s, 12H), 1.26 – 1.18 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.3, 151.1, 131.4, 128.7, 127.6, 124.8, 83.9, 42.2, 41.8, 24.8, 14.2, 13.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{17}H_{27}BNO_4$ $[M+H]^+$ 320.2033, found 320.2049.

*meta-Borylation of phenyl diisopropylcarbamate (**2z**):*



1z: 0.2 mmol

2z: 65%
o/m/p = 0/99/1

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, phenyl diisopropylcarbamate (**1z:** 0.2 mmol, 44.3 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 45.1 mg (65%) of the *meta*-borylated product (**2z**) as gummy liquid.

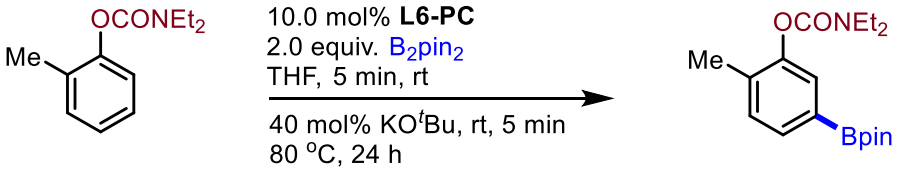
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 7.2 Hz, 1H), 7.52 (d, J = 1.6 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.23 – 7.20 (m, 1H), 4.08 – 4.0 (m, 2H), 1.33 (brs, 24H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 150.9, 131.4, 128.7, 127.7, 125.0, 83.9, 46.8, 46.0, 25.0, 24.8, 24.5, 21.5, 20.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{19}H_{31}BNO_4$ $[M+H]^+$ 348.2346, found 348.2333.

*meta-Borylation of o-tolyl diethylcarbamate (**2aa**):*



1aa: 0.2 mmol

2aa: 66%
o/m/p = 0/82/18

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, o-tolyl diethylcarbamate (**1aa:** 0.2 mmol, 41.5 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with

silica gel (5% EtOAc in hexane as eluent) gave 44.0 mg (66%) of the *meta*-borylated product (**2aa**) as gummy liquid.

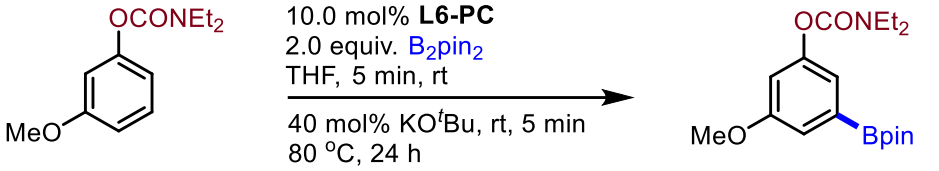
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, J = 7.6 Hz, 1H), 7.47 (s, 1H), 7.21 (d, J = 7.6 Hz, 1H), 3.47 – 3.36 (m, 4H), 2.23 (s, 3H), 1.32 (s, 12H), 1.26 (brs, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 149.6, 134.1, 131.8, 130.5, 128.2, 42.1, 41.8, 24.8, 16.5, 14.2, 13.4.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

HRMS (ESI) *m/z* calculated for $C_{18}H_{29}BNO_4$ $[M+H]^+$ 334.2190, found 334.2179.

*meta-Borylation of 3-methoxyphenyl diethylcarbamate (**2ab**):*



1ab: 0.2 mmol

2ab: 72%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 3-methoxyphenyl diethylcarbamate (**1ab:** 0.2 mmol, 44.7 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 50.3 mg (72%) of the *meta*-borylated product (**2ab**) as gummy liquid.

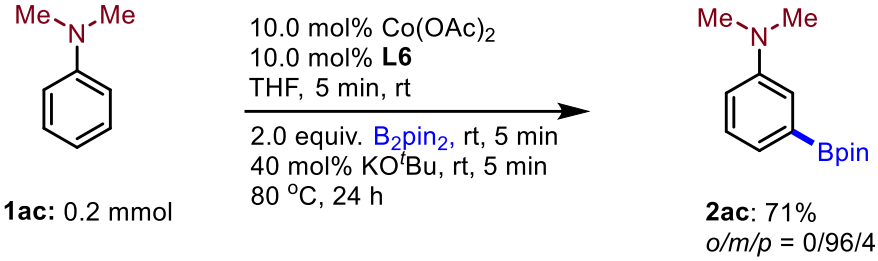
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.79 (t, *J* = 2.4 Hz, 1H), 3.81 (s, 3H), 3.39 (q, *J* = 7.2 Hz, 4H), 1.32 (s, 12H), 1.23 – 1.17 (m, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.9, 154.2, 152.0, 120.0, 116.2, 111.5, 83.9, 55.5, 42.1, 41.8, 24.8, 14.2, 13.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{18}H_{29}BNO_5$ $[M+H]^+$ 350.2139, found 350.2151.

*meta-Borylation of N,N-dimethylaniline (**2ac**):*



1ac: 0.2 mmol

2ac: 71%
o/m/p = 0/96/4

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^tBu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes *N,N*-dimethylaniline (**1ac:** 0.2 mmol, 24.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 35.1 mg (71%) of the *meta*-borylated product (**2ac**) as gummy oil.

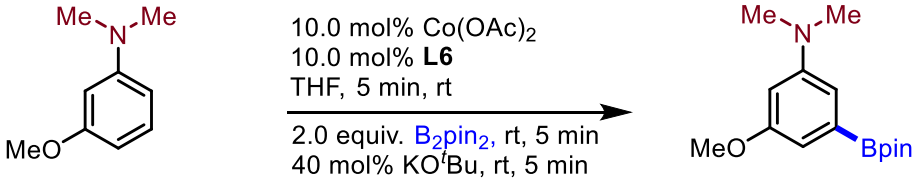
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.26 (t, J = 8.0 Hz, 1H), 7.20 – 7.19 (m, 2H), 6.87 (dd, J = 8.0, 2.4 Hz, 1H), 2.97 (s, 6H), 1.34 (s, 12H).

^{13}C NMR (200 MHz, $CDCl_3$): δ 150.1, 128.5, 123.2, 118.6, 115.8, 83.6, 40.8, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): 30.8.

HRMS (ESI) *m/z* calculated for $C_{14}H_{23}BNO_2$ $[M+H]^+$ 248.1822, found 248.1819.

*meta-Borylation of 3-methoxy-N,N-dimethylaniline (**2ad**):*



1ad: 0.2 mmol

2ad: 81%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ*

generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes 3-methoxy-*N,N*-dimethylaniline (**1ad:** 0.2 mmol, 30.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 44.9 mg (81%) of the *meta*-borylated product (**2ad**) as gummy oil.

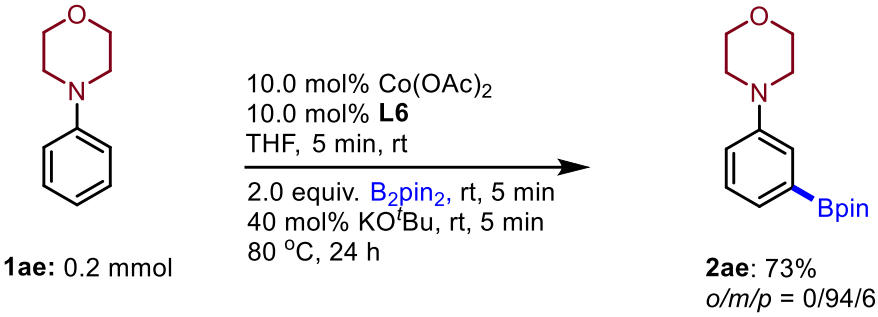
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.85 (d, J = 2.0 Hz, 1H), 6.73 (d, J = 2.0 Hz, 1H), 6.39 (t, J = 2.4 Hz, 1H), 3.82 (s, 3H), 2.95 (s, 6H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 160.1, 151.6, 112.2, 106.3, 102.8, 83.6, 55.2, 40.6, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{15}H_{25}BNO_3$ $[M+H]^+$ 278.1927, found 278.1937.

*meta-Borylation of 4-phenylmorpholine (**2ae**):*



1ae: 0.2 mmol

2ae: 73%
o/m/p = 0/94/6

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes 4-phenylmorpholine (**1ae:** 0.2 mmol, 32.6 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 42.2 mg (73%) of the *meta*-borylated product (**2ae**) as gummy oil.

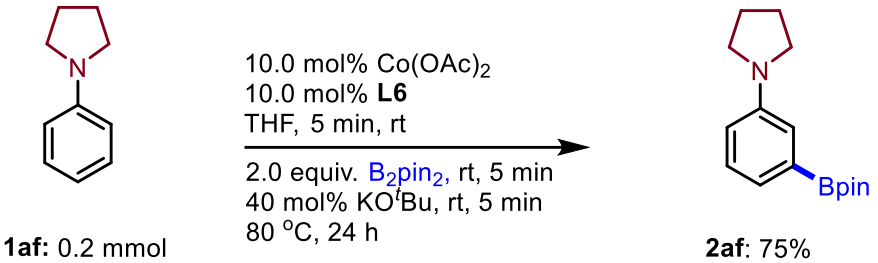
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 2.4 Hz, 1H), 7.35 (d, *J* = 7.2 Hz, 1H), 7.29 (t, *J* = 8.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.2 Hz, 1H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.19 (t, *J* = 4.8 Hz, 4H), 1.34 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.6, 128.6, 126.5, 121.8, 118.7, 83.7, 66.9, 49.4, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{16}H_{25}BNO_3$ $[M+H]^+$ 290.1927, found 290.1933.

*meta-Borylation of 1-phenylpyrrolidine (**2af**):*



1af: 0.2 mmol

2af: 75%
o/m/p = 0/94/6

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes 1-phenylpyrrolidine (**1af:** 0.2 mmol, 29.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 40.9 mg (75%) of the *meta*-borylated product (**2af**) as gummy oil.

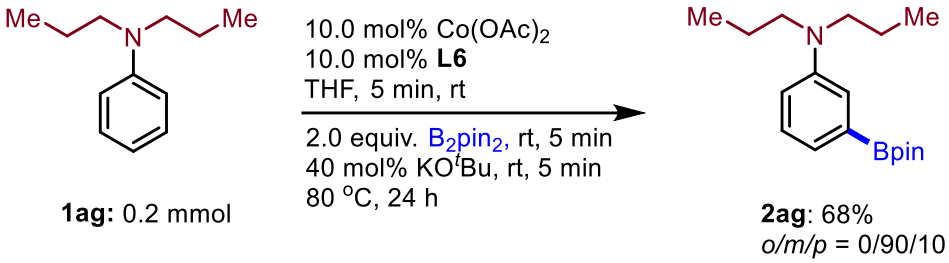
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 2.4 Hz, 1H), 6.71 – 6.68 (m, 1H), 3.34 (t, *J* = 6.4 Hz, 4H), 2.03 – 1.99 (m, 4H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.4, 128.5, 121.8, 117.6, 114.6, 83.5, 47.6, 25.4, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI) *m/z* calculated for $C_{16}H_{25}BNO_2$ $[M+H]^+$ 274.1978, found 274.1989.

*meta-Borylation of N,N-dipropylaniline (**2ag**):*



1ag: 0.2 mmol

2ag: 68%
o/m/p = 0/90/10

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^tBu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes N,N-dipropylaniline (**1ag:** 0.2 mmol, 35.5 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 41.2 mg (68%) of the *meta*-borylated product (**2ag**) as gummy oil.

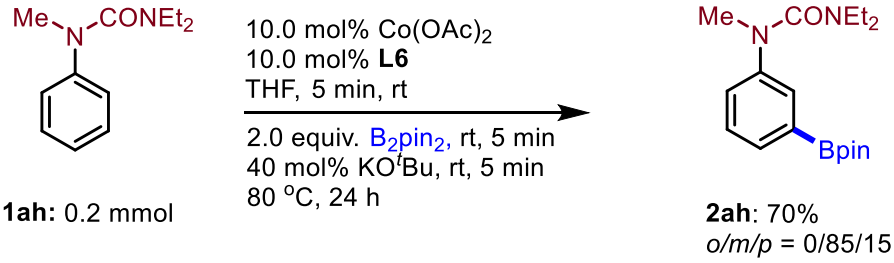
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21 (t, J = 7.6 Hz, 1H), 7.11 – 7.08 (m, 2H), 6.76 (d, J = 6.8 Hz, 1H), 3.26 (t, J = 7.2 Hz, 4H), 1.61 (q, J = 7.6 Hz, 4H), 1.34 (s, 12H), 0.93 (t, J = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 128.5, 121.8, 118.0, 115.0, 83.5, 52.7, 24.8, 20.4, 11.5.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI) *m/z* calculated for $C_{18}H_{31}BNO_2$ $[M+H]^+$ 304.2448, found 304.2433.

*meta-Borylation of 1,1-diethyl-3-methyl-3-phenylurea (**2ah**):*



1ah: 0.2 mmol

2ah: 70%
o/m/p = 0/85/15

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0

equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes 1,1-diethyl-3-methyl-3-phenylurea (**1ah:** 0.2 mmol, 41.3 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 46.5 mg (70%) of the *meta*-borylated product (**2ah**) as gummy oil.

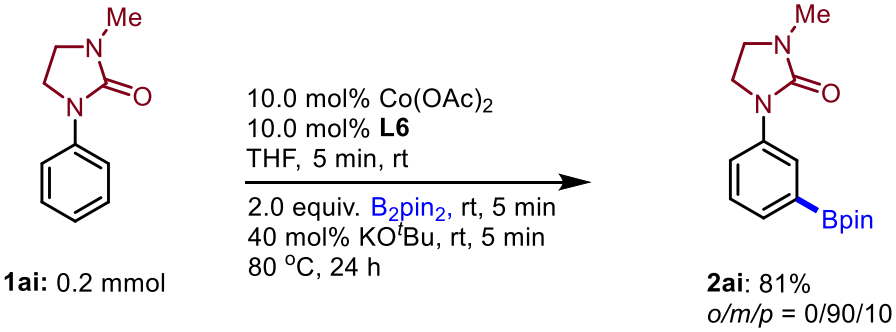
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 – 7.52 (m, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.15 (dd, J = 7.6, 0.8 Hz, 1H), 3.16 (s, 3H), 3.09 (q, J = 7.2 Hz, 4H), 1.33 (s, 12H), 0.91 (t, J = 7.2 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8, 146.8, 130.7, 130.0, 128.7, 126.7, 83.9, 41.9, 39.8, 24.8, 12.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.8.

HRMS (ESI) *m/z* calculated for $C_{18}H_{30}BN_2O_3$ $[M+H]^+$ 333.2349, found 333.2361.

*meta-Borylation of 1-methyl-3-phenylimidazolidin-2-one (**2ai**):*



1ai: 0.2 mmol

2ai: 81%
o/m/p = 0/90/10

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with $Co(OAc)_2$ (3.6 mg, 10.0 mol%), ligand **L6** (7.2 mg, 10.0 mol%) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Then B_2pin_2 (101.6 mg, 2.0 equiv.) was added to it and stirred for another 5 minutes. Addition of B_2pin_2 to the *in situ* generated catalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes 1-methyl-3-phenylimidazolidin-2-one (**1ai:** 0.2 mmol, 35.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversions and selectivities (*o/m/p = 0/90/10*) were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel ($CHCl_3$ with 2% NEt_3 as eluent) gave

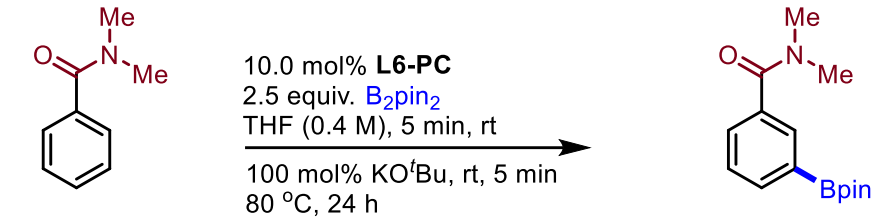
49.0 mg (81%) of the mixture of *meta* and *para* borylated product (*m/p* = 80/20) (**2ai**) as gummy oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.93 (m, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 2.0 Hz, 1H), 7.54 (d, *J* = 8.8 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 3.85 – 3.81 (m, 2H), 3.45 – 3.41 (m, 2H), 2.86 (s, 3H), 1.31 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calculated for $C_{16}H_{24}BN_2O_3$ $[M+H]^+$ 303.1880, found 303.1871.

*meta-Borylation of N,N-dibutylbenzamide (**2aj**):*



1aj: 0.2 mmol

2aj: 77%
o/m/p = 0/98/2

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N,N-dibutylbenzamide* (**1aj:** 0.2 mmol, 28.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 41.3 mg (77%) of the *meta*-borylated product (**2aj**) as gummy liquid.

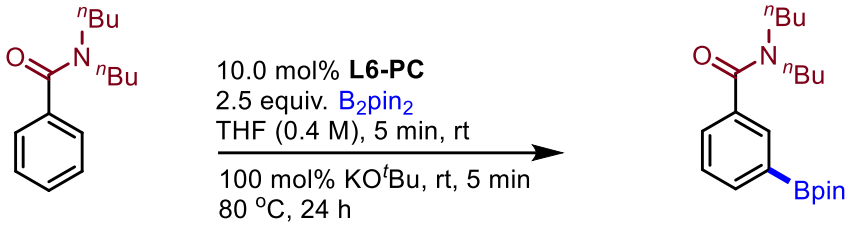
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.80 (m, 2H), 7.48 (td, J= 7.6 Hz, J = 1.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 3.08 (s, 3H), 2.95 (s, 3H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 135.7, 135.6, 133.0, 129.6, 127.7, 83.9, 39.5, 35.2, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.4.

HRMS (ESI) *m/z* calculated for $C_{15}H_{23}BNO_3$ $[M+H]^+$ 276.1771, found 276.1769.

*meta-Borylation of N-isopropyl-N-methylbenzamide (**2ak**):*



1ak: 0.2 mmol

2ak: 80%
o/m/p = 0/98/2

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N-isopropyl-N-methylbenzamide* (**1ak:** 0.2 mmol, 46.7 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 57.5 mg (80%) of the *meta*-borylated product (**2ak**) as gummy liquid.

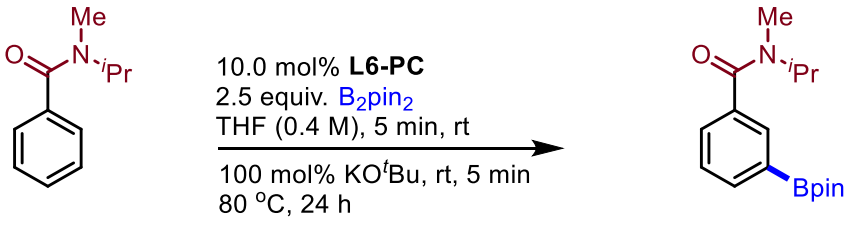
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 – 7.78 (m, 2H), 7.46 – 7.43 (m, 1H), 7.40 – 7.36 (m, 1H), 3.47 (t, J = 7.6 Hz, 2H), 3.16 (t, J = 7.2 Hz, 2H), 1.67 – 1.60 (m, 2H), 1.54 – 1.47 (m, 2H), 1.42 – 1.39 (m, 2H), 1.34 (s, 12H), 1.18 – 1.08 (m, 2H), 0.97 (t, J = 7.2 Hz, 3H), 0.78 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 136.7, 135.3, 132.5, 129.2, 127.7, 83.9, 48.8, 44.5, 30.9, 29.7, 24.8, 20.4, 19.7, 14.0, 13.6.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.1.

HRMS (ESI) *m/z* calculated for $C_{21}H_{35}BNO_3$ $[M+H]^+$ 360.2710, found 360.2729.

*meta-Borylation of N,N-dimethylbenzamide (**2al**):*



1al: 0.2 mmol

2al: 75%
o/m/p = 0/98/2

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N,N*-dimethylbenzamide (**1al:** 0.2 mmol, 41.5 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 50.0 mg (75%) of the *meta*-borylated product (**2al**) as gummy liquid.

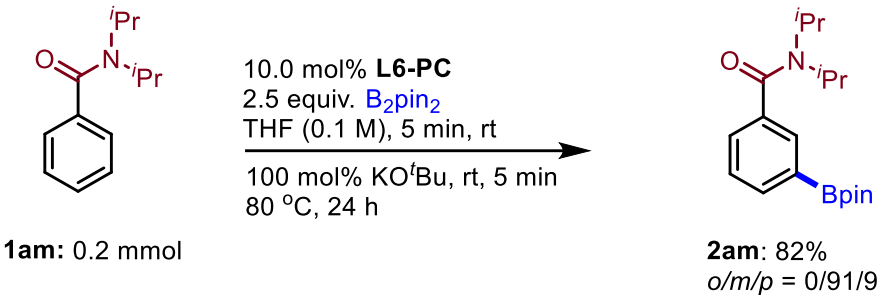
^{1}H NMR (800 MHz, $CDCl_3$): δ 7.80 – 7.78 (m, 2H), 7.42 – 7.40 (m, 1H), 7.36 (t, J = 7.2 Hz, 1H), 4.93 (s, 0.44H), 3.92 (s, 0.57H), 2.91 (s, 1.77H), 2.73 (s, 1.28H), 1.31 (s, 12H), 1.19 – 1.17 (m, 3H), 1.12 – 1.11 (m, 3H). (due to rotamer)

^{13}C NMR (200 MHz, $CDCl_3$): δ 171.5, 171.1, 136.6, 136.4, 135.4, 135.3, 132.7, 132.4, 129.4, 128.6, 127.6, 83.9, 49.7, 44.3, 30.6, 25.9, 24.8, 20.3, 19.2. (due to rotamer)

^{11}B NMR (256 MHz, $CDCl_3$): δ 30.3.

HRMS (ESI) *m/z* calculated for $C_{17}H_{27}BNO_3$ $[M+H]^+$ 304.2084, found 304.2091.

*meta-Borylation of N,N-diisopropylbenzamide (**2mj**):*



1am: 0.2 mmol

2am: 82%
o/m/p = 0/91/9

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (2.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N,N-diisopropylbenzamide* (**1am:** 0.2 mmol, 41.1 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by

GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 54.3 mg (82%) of the *meta*-borylated product (**2am**) as gummy liquid.

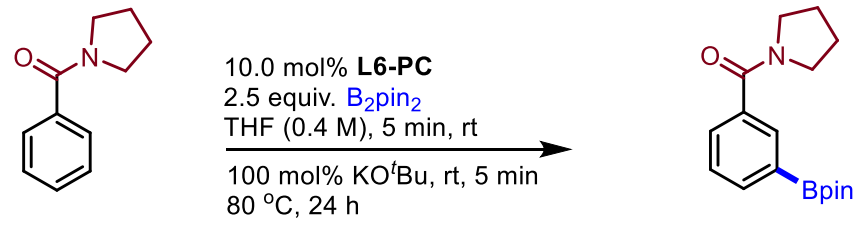
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 – 7.78 (m, 1H), 7.77 – 7.76 (m, 1H), 7.38 – 7.36 (m, 2H), 3.77 (br s, 1H), 3.49 (br s, 1H), 1.58 – 1.43 (m, 2H), 1.34 (s, 12H), 1.24 – 1.05 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.9, 138.3, 134.8, 131.9, 128.1, 127.6, 83.9, 50.8, 45.8, 24.8, 20.7.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.5.

HRMS (ESI) *m/z* calculated for $C_{19}H_{31}BNO_3$ $[M+H]^+$ 332.2397, found 332.2385.

*meta-Borylation of phenyl(pyrrolidin-1-yl)methanone (**2an**):*

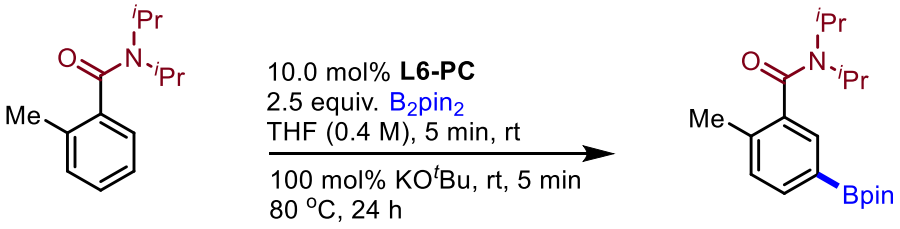


1an: 0.2 mmol

2an: 71%
o/m/p = 0/92/8

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *phenyl(pyrrolidin-1-yl)methanone* (**1an:** 0.2 mmol, 35.0 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 42.8 mg (71%) of the *meta*-borylated product (**2an**) as gummy liquid. Spectral data are in accordance with the previous reported data.[15]

*meta-Borylation of N,N-diisopropyl-2-methylbenzamide (**2ao**):*



1ao: 0.2 mmol

2ao: 68%
o/m/p = 0/83/17

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N,N-diisopropyl-2-methylbenzamide* (**1ao:** 0.2 mmol, 43.9 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 47.0 mg (68%) of the *meta*-borylated product (**2ao**) as gummy liquid.

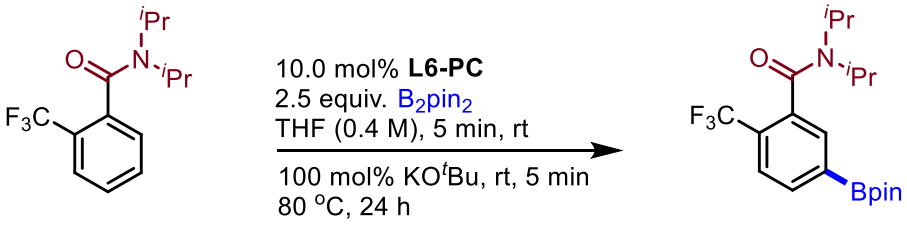
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, J = 7.6, 0.8 Hz, 1H), 7.51 (s, 1H), 7.16 (d, J = 7.6 Hz, 1H), 3.64 (hept, J = 6.4 Hz, 1H), 3.48 (hept, J = 6.8 Hz, 1H), 2.30 (s, 3H), 1.55 (dd, J = 6.8, 2.8 Hz, 6H), 1.30 (d, J = 1.2 Hz, 12H), 1.08 (t, J = 6.8 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 138.0, 136.8, 134.4, 130.9, 129.6, 83.6, 50.7, 45.6, 24.8, 24.6, 20.8, 20.7, 20.6, 20.5, 18.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calculated for $C_{20}H_{33}BNO_3$ $[M+H]^+$ 346.2553, found 346.2531.

*meta-Borylation of N,N-diisopropyl-2-(trifluoromethyl)benzamide (**2ap**):*



1ap: 0.2 mmol

2ap: 65%
o/m/p = 0/89/11

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127 mg, 2.5 equiv.) and dry THF (0.5 mL) sequentially. The reaction

mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (22.4 mg, 100.0 mol%) was added. Finally stirring for another 5 minutes, *N,N-diisopropyl-2-(trifluoromethyl)benzamide* (**1ap:** 0.2 mmol, 54.7 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (30% EtOAc in hexane as eluent) gave 51.9 mg (65%) of the *meta*-borylated product (**2ap**) as gummy liquid.

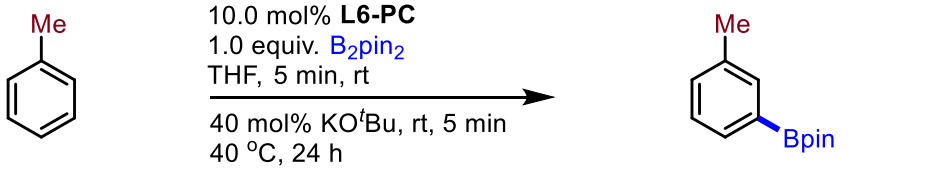
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 7.6 Hz, 1H), 7.67 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 3.59-3.45 (m, 2H), 1.58 (d, J = 6.8 Hz, 3H), 1.52 (d, J = 6.8 Hz, 3H), 1.34 (s, 12H), 1.10 (d, J = 6.4 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.8, 136.0 (q, J = 2.2 Hz), 134.5, 132.4, 128.2 (q, J = 31.6 Hz), 125.7 (q, J = 4.4 Hz), 123.8 (q, J = 272.6 Hz), 84.4, 51.0, 45.8, 24.9, 24.7, 20.7, 20.5, 19.7, 19.6.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.4.

HRMS (ESI) *m/z* calculated for C20H30BF3NO3 $[M+H]^+$ 400.2271, found 400.2266.

*meta-Borylation of toluene (**2aq**):*



1aq: 0.2 mmol

2aq: 99% (Conversion)
o/m/p = 0/70/30

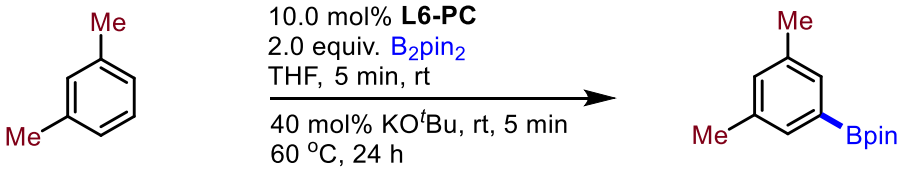
In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (2.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, toluene (**1aq:** 0.2 mmol, 18.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 40 °C for 24 h. After completion (judged by GC-MS), THF was removed under reduced pressure and crude NMR of the reaction mixture was taken. Crude NMR analysis based on ^{1}H-NMR showed 70% of the meta-selective product (**2aq$_m$**) with 99% conversion.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.64 (s, 1H), 7.61 (t, J = 4.8 Hz, 2H), 7.28 – 7.27 (m, 2H), 2.36 (s, 3H), 1.35 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.1.

HRMS (ESI) *m/z* calculated for $C_{13}H_{20}BO_2$ $[M+H]^+$ 219.1556, found 219.1544.

*meta-Borylation of m-xylene (**2ar**):*



1ar: 0.2 mmol

2ar: 85%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**1ar:** 0.2 mmol, 21.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 39.5 mg (85%) of the *meta*-borylated product (**2ar**) as gummy liquid.

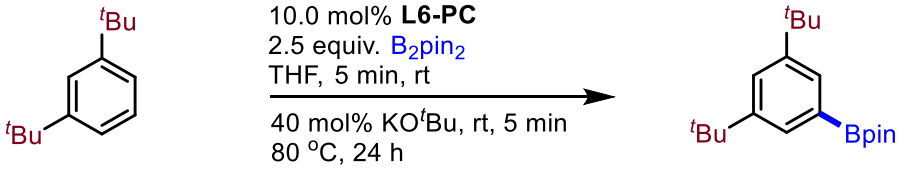
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 2H), 7.11 (s, 1H), 2.33 (s, 6H), 1.35 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 137.1, 133.0, 132.4, 83.7, 24.8, 21.1.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.1.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1713, found 233.1727.

*meta-Borylation of 1,3-di-tert-butylbenzene (**2as**):*



1as: 0.2 mmol

2as: 52%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127.0 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction

mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**1as:** 0.2 mmol, 38.1 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 32.9 mg (52%) of the *meta*-borylated product (**2as**) as gummy liquid.

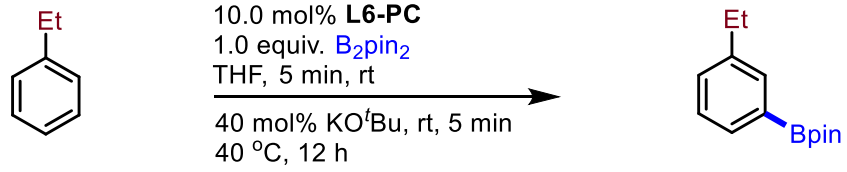
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 2.0 Hz, 2H), 7.57 (t, J = 2.0 Hz, 1H), 1.37 – 1.36 (m, 21H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.8, 128.8, 125.5, 83.5, 34.8, 31.5, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.2.

HRMS (ESI) *m/z* calculated for $C_{20}H_{34}BO_2$ $[M+H]^+$ 317.2652, found 317.2641.

*meta-Borylation of ethylbenzene (**2at**):*



1at: 0.2 mmol

2at: 99% (Conversion)
o/m/p = 0/61/39

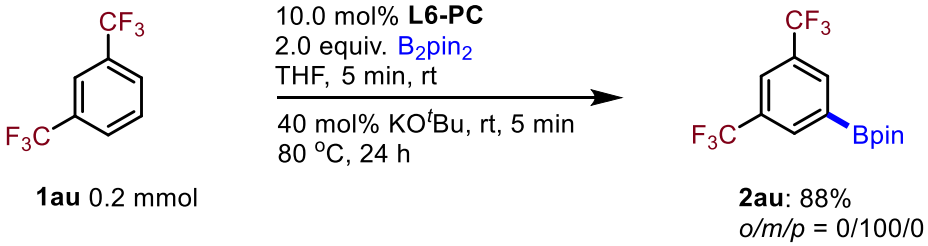
In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (50.8 mg, 1.0 equiv.) and dry THF (2.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, ethylbenzene (**1aq:** 0.2 mmol, 21.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 40 °C for 24 h. After completion (judged by GC-MS), THF was removed under reduced pressure and crude NMR of the reaction mixture was taken. Crude NMR analysis based on ^{1}H-NMR showed 61% of the meta-selective product (**2at**) with 99% conversion.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 – 7.61 (m, 2H), 7.31 – 7.29 (m, 2H), 2.69 – 2.63 (m, 2H), 1.35 (s, 12H), 1.24 (d, J = 2.8 Hz, 3H).

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.1.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_2$ $[M+H]^+$ 233.1713, found 233.1715.

*meta-Borylation of 1,3-bis(trifluoromethyl)benzene (**2au**):*



1au 0.2 mmol

2au: 88%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**1au:** 0.2 mmol, 29.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 47.9 mg (88%) of the *meta*-borylated product (**2au**) as gummy liquid.

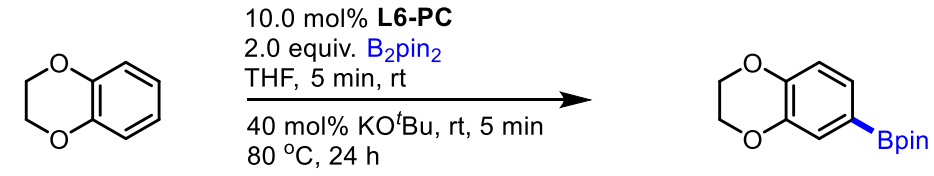
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (s, 2H), 7.94 (s, 1H), 1.37 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6 (m), 130.9 (q, J = 32.9 Hz), 124.7 (m), 123.5 (q, J = 270.8 Hz), 84.8, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.2.

HRMS (ESI) *m/z* calculated for $C_{14}H_{16}BF_6O_2$ $[M+H]^+$ 341.1148, found 341.1133.

*meta-Borylation of 2,3-dihydrobenzo[b][1,4]dioxine (**2av**):*



1av: 0.2 mmol

2av: 74%
o/m/p = 0/100/0

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**1av:** 0.2 mmol, 27.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h,

50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 38.8 mg (74%) of the *meta*-borylated product (**2av**) as gummy liquid.

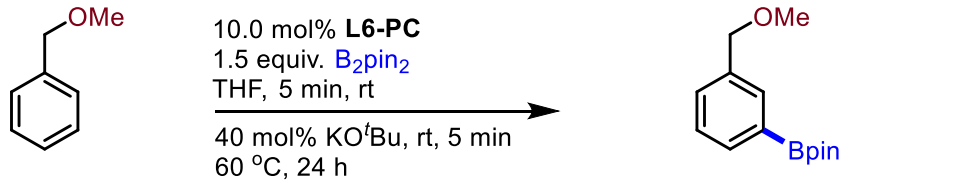
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.28 (m, 2H), 6.85 (d, J = 8.0 Hz, 1H), 4.28 – 4.22 (m, 4H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 143.2, 128.3, 123.7, 116.8, 83.6, 64.6, 64.1, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7.

HRMS (ESI) *m/z* calculated for $C_{14}H_{20}BO_4$ $[M+H]^+$ 263.1455, found 263.1449.

*meta-Borylation of (methoxymethyl)benzene (**2aw**):*



1aw: 0.2 mmol

2aw: 99% (Conversion)
o/m/p = 0/57/43

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (76.2 mg, 1.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**1aw:** 0.2 mmol, 24.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After completion (judged by GC-MS), THF was removed under reduced pressure and crude NMR of the reaction mixture was taken. Crude NMR analysis based on ^{1}H-NMR showed 57% of the meta isomer (**2aw**) with 99% conversion.

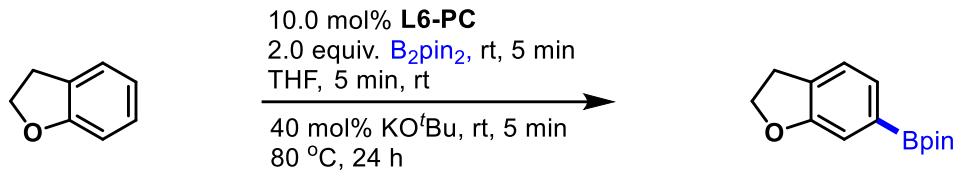
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (s, 1H), 7.74 (d, J = 7.2 Hz, 1H), 7.45 (d, J = 7.6 Hz, 1H), 7.36 (t, J = 7.6, 1H), 4.46 (s, 2H), 3.38 (s, 3H), 1.34 (s, 12H).

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calculated for $C_{14}H_{22}BO_3$ $[M+H]^+$ 249.1662, found 249.1656.

Synthetic Application:

*meta-Borylation of 2,3-dihydrobenzofuran (**4a**):*



3a: 0.2 mmol

4a: 58%
(m/others = 0/81/19)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3a:** 0.2 mmol, 24.0 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 28.6 mg (58%) of the *meta*-borylated product (**4a**) as gummy liquid.

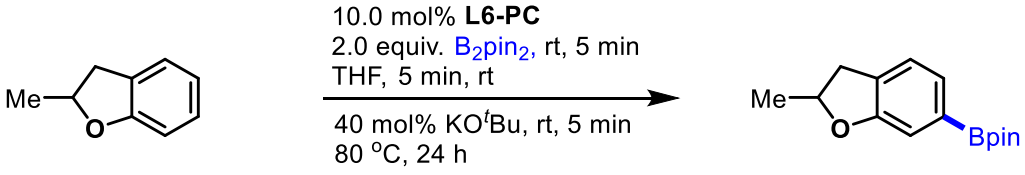
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, J = 7.2 Hz, 1H), 7.20 (t, J = 3.6 Hz, 2H), 4.53 (t, J = 8.8 Hz, 2H), 3.20 (t, J = 8.4 Hz, 2H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 130.5, 127.2, 124.4, 114.8, 83.7, 70.7, 29.9, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for C_8H_8O $[M+H]^+$ 120.0575, found 120.0588.

*meta-Borylation of 2-methyl-2,3-dihydrobenzofuran (**4b**):*



3b: 0.2 mmol

4b: 55%
(m/others = 0/85/15)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3b:** 0.2 mmol, 26.8 mg) was added to it. The

microreactor was capped with a teflon pressure cap and stirred at 80 ºC for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 28.6 mg (55%) of the *meta*-borylated product (**4b**) as gummy liquid.

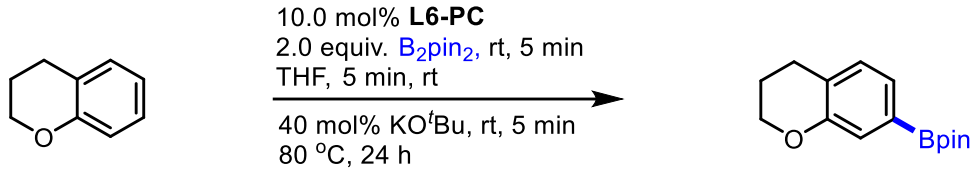
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (d, J = 7.6 Hz, 1H), 7.16 (d, J = 6.8 Hz, 2H), 4.93 – 4.87 (m, 1H), 3.35 – 3.28 (m, 1H), 2.83 – 2.78 (m, 1H), 1.44 (d, J = 6.4 Hz, 3H), 1.33 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 159.2, 130.6, 127.1, 124.5, 114.8, 83.7, 79.1, 37.3, 24.8, 21.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for $C_9H_{10}O$ $[M+H]^+$ 134.0732, found 134.0730.

*meta-Borylation of chromane (**4c**):*



3c: 0.2 mmol

4c: 71%
(m/others = 0/88/12

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3c:** 0.2 mmol, 26.8 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 ºC for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (2% EtOAc in hexane as eluent) gave 36.9 mg (71%) of the *meta*-borylated product (**4c**) as gummy liquid.

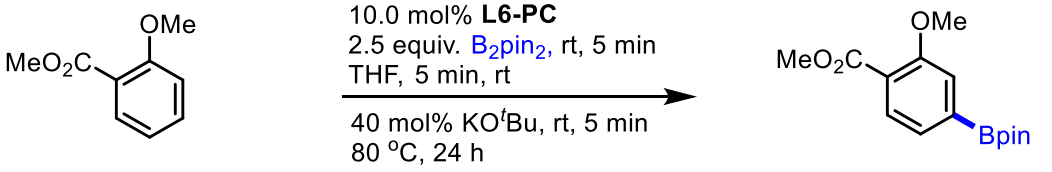
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 – 7.23 (m, 2H), 7.04 (d, J = 7.2 Hz, 1H), 4.18 – 4.15 (m, 2H), 2.79 (t, J = 6.8 Hz, 2H), 2.00 – 1.98 (m, 2H), 1.32 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.6, 129.3, 126.2, 122.9, 116.2, 83.6, 66.4, 25.1, 24.8, 22.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ 31.0.

HRMS (ESI) *m/z* calcd for $C_9H_{10}O$ $[M+H]^+$ 134.0732, found 134.0741.

*meta-Borylation of methyl 2-methoxybenzoate (**4d**):*



3d: 0.2 mmol

4d: 46%
(m/others = 0/99/1)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3d:** 0.2 mmol, 33.2 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (10% EtOAc in hexane as eluent) gave 26.9 mg (46%) of the *meta*-borylated product (**4d**) as gummy liquid.

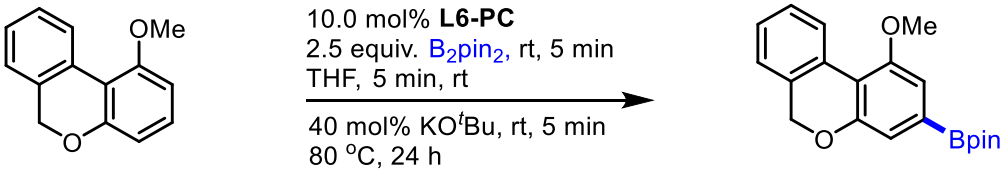
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.6 Hz, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.38 (s, 1H), 3.94 (s, 3H), 3.88 (s, 3H), 1.35 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.8, 158.2, 130.7, 126.4, 122.3, 117.6, 84.2, 56.0, 52.0, 24.8.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.9.

HRMS (ESI) *m/z* calcd for $C_9H_{10}O_3$ $[M+H]^+$ 166.0630, found 166.0623.

*meta-Borylation of 1-methoxy-6H-benzo[c]chromene (**4e**):*



3e: 0.2 mmol

4e: 54%
(m/others = 0/100/0)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127.0 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3e:** 0.2 mmol, 42.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h,

50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 38.8 mg (54%) of the *meta*-borylated product (**4e**) as gummy liquid.

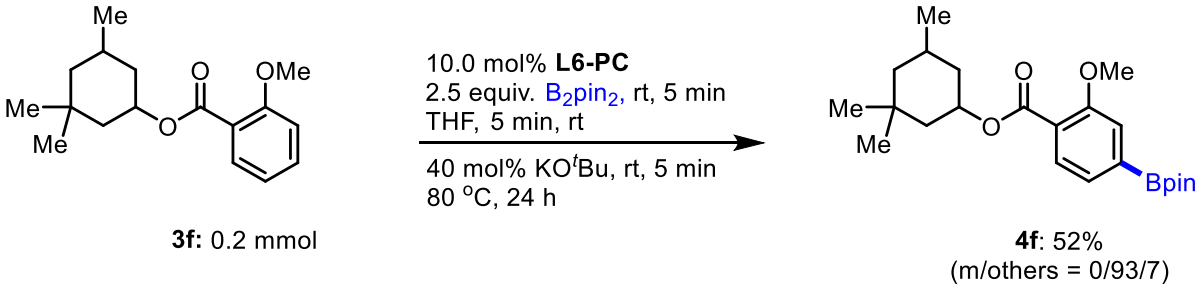
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (d, J = 7.6 Hz, 1H), 7.35 (td, J = 7.6, 1.2 Hz, 1H), 7.29 – 7.25 (m, 2H), 7.18 – 7.13 (m, 2H), 7.06 (s, 1H), 4.98 (s, 2H), 3.99 (s, 3H), 1.36 (s, 12H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.2, 156.2, 132.5, 128.9, 128.0, 127.3, 126.9, 124.3, 116.5, 115.5, 110.4, 83.9, 68.8, 55.8, 24.9.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7.

HRMS (ESI) *m/z* calcd for $C_{14}H_{12}O_2$ $[M+H]^+$ 212.0837, found 212.0845.

*meta-Borylation of 3,3,5-trimethylcyclohexyl 2-methoxybenzoate (**4f**):*



3f: 0.2 mmol

4f: 52%
(m/others = 0/93/7)

In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (127.0 mg, 2.5 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, m-xylene (**3f:** 0.2 mmol, 55.3 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 35.2 mg (52%) of the *meta*-borylated product (**4f**) as gummy liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.6 Hz, 1H), 7.39 – 7.36 (m, 2H), 3.93 (s, 3H), 2.11 (d, J = 12.0 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.63 (br s, 2H), 1.35 (s, 12H), 1.23 (d, J = 3.2 Hz, 3H), 0.98 (d, J = 7.2 Hz, 6H), 0.93 (d, J = 6.4 Hz, 2H).

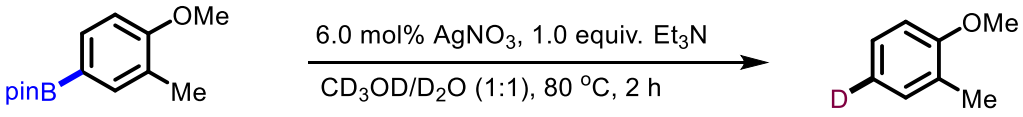
^{13}C NMR (100 MHz, $CDCl_3$): δ 165.8, 158.2, 130.3, 126.4, 123.4, 117.7, 84.1, 71.6, 56.1, 47.6, 43.9, 40.4, 33.0, 32.3, 27.2, 25.5, 24.8, 22.3.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7.

HRMS (ESI) *m/z* calcd for $C_{17}H_{24}O_3$ $[M+H]^+$ 276.1725, found 276.1739.

Synthetic Transformations:

Meta-Bpin to deuteration:



2b **5a:** 90%

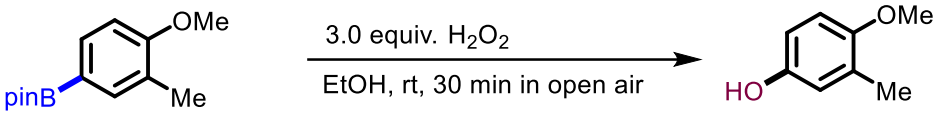
An oven dried 5.0 mL Wheaton microreactor was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg), $AgNO_3$ (2.0 mg, 6.0 mol%), Et_3N (20.2 mg, 1.0 equiv.), MeOD (0.5 mL)/D_2O (0.5 mL) and stirred at 80 °C for 2 hours under air atmosphere. After cooling down to room temperature, the mixture was extracted with ethyl acetate (10 mL x 3). The combined organic layers were washed with saturated brines, dried with Na_2SO_4, concentrated under vacuum. The residue was purified by silica gel chromatography (3% ethyl acetate in hexane) to give **5a** (22.2 mg, 90%) as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, J = 7.2 Hz, 1H), 6.87 (d, J = 7.2 Hz, 1H), 6.84 (s, 1H), 3.84 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.7, 130.6, 126.6, 126.5 (t, J = 24.1 Hz), 120.1, 109.8, 55.2, 16.2.

HRMS (ESI) *m/z* calcd for $C_8H_{10}DO$ $[M+H]^+$ 124.0873, found 124.0882.

Meta-Bpin to hydroxylation:



2b **5b:** 87%

An oven dried 25.0 mL round bottom flask was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg) in 2 ml EtOH. The flask was placed in an ice bath and to the stirred solution, H_2O_2 (30%, 0.6 mmol) was added dropwise for 5 min. The reaction was allowed to stir at room temperature for another 30 min and then quenched with water (5 ml), extracted with ethyl acetate (10 mL x 3) and washed with water (10 ml). The combined organic layers were washed with saturated brine solution, dried with

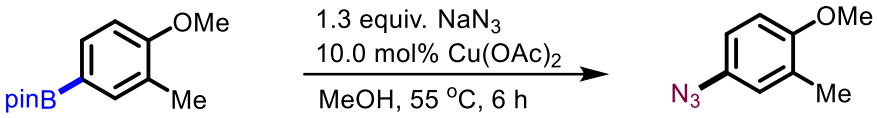
Na_2SO_4, concentrated under vacuum. The residue was purified by silica gel chromatography (5% ethyl acetate in hexane) to give **5b** (24.0 mg, 90%) as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 6.37 (dd, *J* = 8.0, 2.4 Hz, 1H), 6.25 (br s, 1H), 3.75 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 154.6, 130.8, 118.5, 106.5, 98.8, 55.2, 15.3.

HRMS (ESI) *m/z* calcd for $C_8H_{11}O_2$ $[M+H]^+$ 139.0759, found 139.0747.

Meta-Bpin to azidation:



2b **5c:** 92%

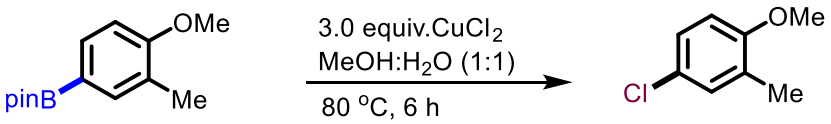
An oven dried 5.0 mL Wheaton microreactor was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg), $Cu(OAc)_2$ (3.6 mg, 10 mol%), NaN_3 (17.0 mg, 1.3 mmol), MeOH (1.5 mL) were stirred at 55 °C for 6 h under air condition (monitored by TLC). After the completion of the reaction, add 10 ml H_2O and extracted with EtOAc (10 mL x 3). The combined organic layers were washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (3% ethyl acetate in hexane) to give **5c** (30.0 mg, 92%) as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 7.6 Hz, 1H), 6.58 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.47 (d, *J* = 2.0 Hz, 1H), 3.82 (s, 3H), 2.20 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 138.4, 131.1, 123.4, 110.2, 101.4, 55.3, 15.7.

HRMS (ESI) *m/z* calcd for $C_8H_{10}N_3O$ $[M+H]^+$ 164.0824, found 164.0817.

Meta-Bpin to chlorination:



2b **5d:** 89%

An oven dried 5.0 mL Wheaton microreactor was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg), $CuCl_2$ (80.7 mg, 3.0 equiv., 0.6 mmol), MeOH (1.5 mL) and water (1.5 mL) and stirred at 80 °C for 6 h. After 6 h, the reaction mixture was cooled to room temperature, diluted with water (5 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation.

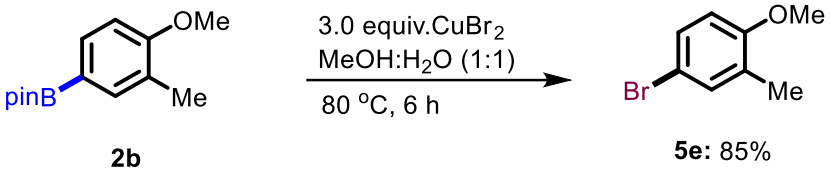
The residue was purified by silica gel chromatography (3% ethyl acetate in hexane) to give **5d** (27.9 mg, 89%) as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.04 (d, *J* = 7.6 Hz, 1H), 6.85 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.81 (d, *J* = 1.6 Hz, 1H), 3.82 (s, 3H), 2.18 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 131.8, 131.1, 125.1, 120.1, 110.6, 55.4, 15.7.

HRMS (ESI) *m/z* calcd for $C_8H_{10}ClO$ $[M+H]^+$ 157.0420, found 157.0425.

Meta-Bpin to bromination:



2b **5e:** 85%

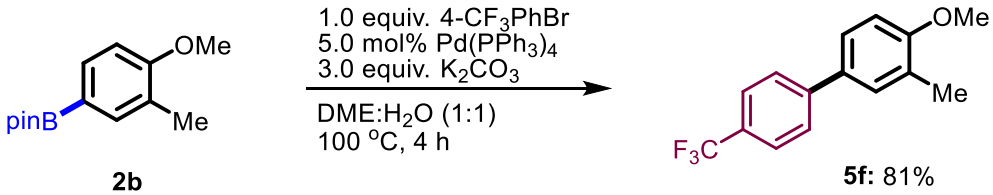
An oven dried 5.0 mL Wheaton microreactor was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg), CuBr2 (134.0 mg, 3.0 equiv., 0.6 mmol), MeOH (1.5 mL) and water (1.5 mL) and stirred at 80 °C for 6 h. After 6 h, the reaction mixture was cooled to room temperature, diluted with water (5 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (3% ethyl acetate in hexane) to give **5e** (34.2 mg, 85%) as colourless liquid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (br s, 2H), 6.95 (s, 1H), 3.82 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 131.5, 125.6, 123.1, 119.5, 113.4, 55.5, 15.8.

HRMS (ESI) *m/z* calcd for $C_8H_{10}BrO$ $[M+H]^+$ 200.9915, found 200.9928.

Meta-Bpin to arylation:



2b **5f:** 81%

In an argon filled glove box, a 5.0 mL Wheaton microreactor was charged with 2-(3-methoxy-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2b:** 0.2 mmol, 49.6 mg), $Pd(PPh_3)_4$ (11.6 mg, 2.5 mol%), K_2CO_3 (82.8 mg, 2.0 equiv., 0.4 mmol) and bromobenzene (31.4 mg, 1.0 equiv., 0.2 mmol). The microreactor was taken out from the glove box, DME (1.0 mL) and water (0.5 mL) were added. The microreactor was degassed well and placed in a preheated aluminium block at 100 °C and heated for 4 h. After 4 h, the reaction mixture was cooled to

room temperature, diluted with water (10 mL) and extracted with ethyl acetate (10 mL x 3). The combined organic layer was washed with saturated brine solution, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. The residue was purified by silica gel chromatography (5% ethyl acetate in hexane) to give **5f** (43.1 mg, 81%) as gummy liquid.

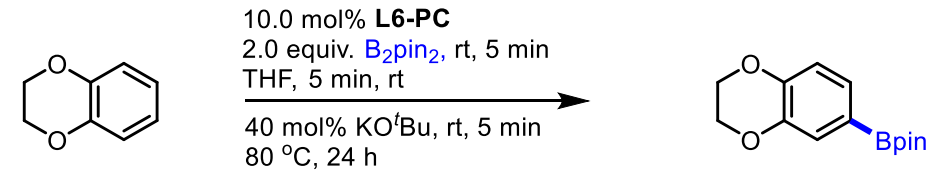
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (s, 4H), 7.23 (d, J = 7.6 Hz, 1H), 7.10 (dd, J = 7.6, 1.6 Hz, 1H), 7.03 (d, J = 1.2 Hz, 1H), 3.91 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 158.1, 145.0, 138.7, 131.1, 129.1 (q, J = 32.2 Hz), 127.3, 126.9, 125.6 (q, J = 3.7 Hz), 124.3 (q, J = 270 Hz), 119.2, 108.9, 55.4, 16.0.

HRMS (ESI) *m/z* calcd for $C_{15}H_{14}F_3O$ $[M+H]^+$ 267.0997, found 267.0988.

Gram Scale Synthesis:

*Gram scale synthesis of **2av**:*

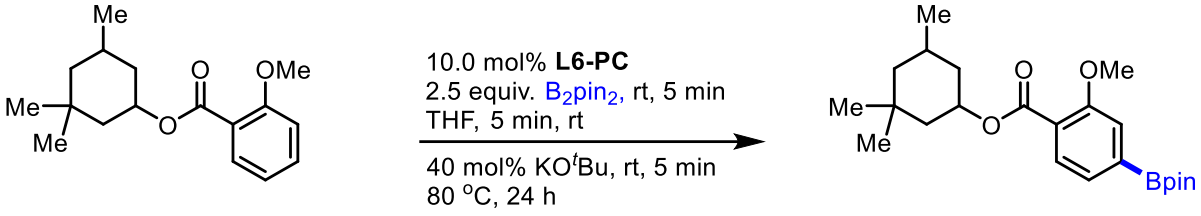


1av: 7.5 mmol

2av: 63% (**1.24 g**)
o/m/p = 0/100/0

In an argon-filled glove box, a 48 mL pressure tube charged with **L6-PC** (401.2 mg, 10.0 mol%), B_2pin_2 (3.81 g, 2.0 equiv.) and dry THF (20.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (337.5 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 2,3-dihydrobenzo[b][1,4]dioxine (**1av:** 1.02 g, 7.5 mmol) was added to it. The pressure tube was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 1.24 g (63%) of the *meta*-borylated product (**2av**) as gummy liquid.

*Gram scale synthesis of **4f**:*

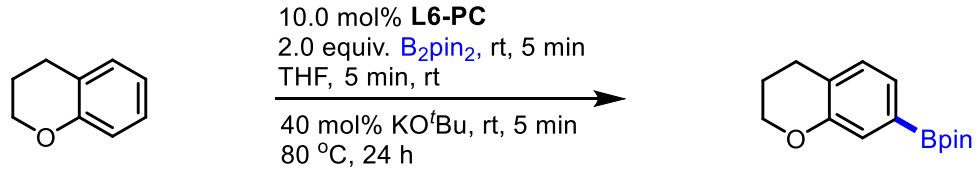


3f: 7.5 mmol

4f: 40% (**1.23 g**)
o/m/p = 0/88/12

In an argon-filled glove box, a 48 mL pressure tube charged with **L6-PC** (401.2 mg, 10.0 mol%), B_2pin_2 (4.76 g, 2.5 equiv.) and dry THF (20.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (337.5 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 3,3,5-trimethylcyclohexyl 2-methoxybenzoate (**3f:** 2.07 g, 7.5 mmol) was added to it. The pressure tube was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 1.23 g (40%) of the *meta*-borylated product (**4f**) as gummy liquid.

*Gram scale synthesis of **4c**:*



3c: 7.5 mmol

4c: 60% (**1.17 g**)
(m/others = 0/83/17

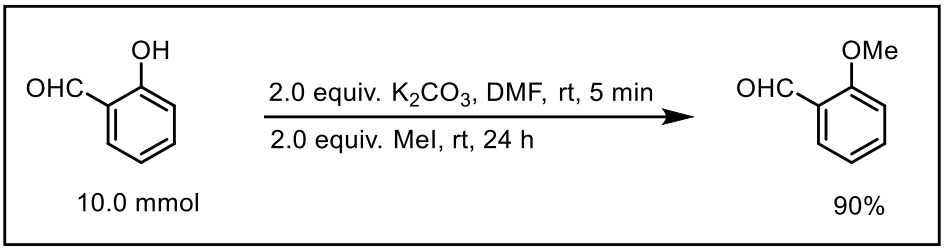
In an argon-filled glove box, a 48 mL pressure tube charged with **L6-PC** (401.2 mg, 10.0 mol%), B_2pin_2 (3.81 g, 2.0 equiv.) and dry THF (20.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (337.5 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, chromane (**3c:** 1.0 g, 7.5 mmol) was added to it. The pressure tube was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (5% EtOAc in hexane as eluent) gave 1.17 g (60%) of the *meta*-borylated product (**4c**) as gummy liquid.

Synthesis of Resorcinol derivative:

Synthesis of propyltriphenylphosphonium bromide salt

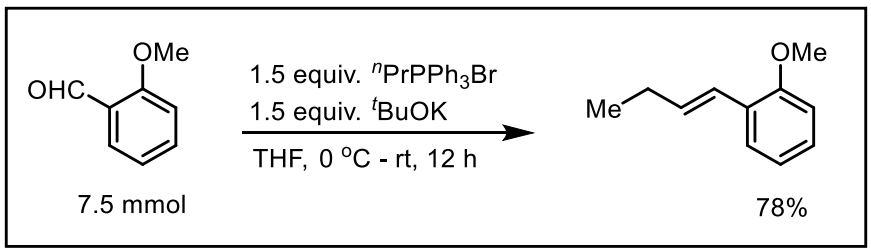
1-bromo-propane (2.46 g, 20.0 mmol) was added dropwise to a solution of triphenylphosphine (4.1 g, 16.0 mmol) in anhydrous toluene (5 mL). The mixture was heated at reflux for 22 hours and, once completed, the solid was filtered and washed several times with hexane. The product was dried in the oven at 100 °C for 12 hours to give propyltriphenylphosphonium bromid salt (4.76 g, 12.3 mmol, 77 % yield) as a white solid.

Step I:



In a 100 ml round bottom flask, 2-hydroxybenzaldehyde (1.22 g, 10.0 mmol) and K_2CO_3 (2.76 g, 2.0 equiv.) was dissolved in dry DMF (30 ml) under argon atmosphere. The mixture was stirred at room temperature for 5 min and then iodomethane (1.25 ml, 2.0 equiv.) was added dropwise into it. After the addition, the reaction mixture was stirred for 24 h at room temperature. The reaction progress was monitored by checking TLC and after completion the reaction was quenched with ice-cold water. EtOAc (100 ml) was added to it and the organic layer was separated. The organic layer was washed with ice-cold water (100 ml) for three times followed by final wash with brine (50 ml). After that, the organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude mass was purified by silica gel column chromatography (5% ethyl acetate in hexane as eluent) to afford 1.22 g (90%) of the 2-methoxybenzaldehyde as oil. Spectral data are in accordance with the reported data.[16]

Step II:



To an oven-dried round-bottom flask equipped with a magnetic stirrer was charged with propyltriphenylphosphonium bromid salt (3.85 g, 10 mmol, 1.5 equiv.), ^{t}BuOK (1.12 g, 10 mmol, 1.5 equiv.) and THF (30 ml) under N_2 atmosphere. The resulting mixture was stirred for 1 h at 0 °C. The yellow suspension was formed and 2-methoxybenzaldehyde (1.02 g, 7.5 mmol,

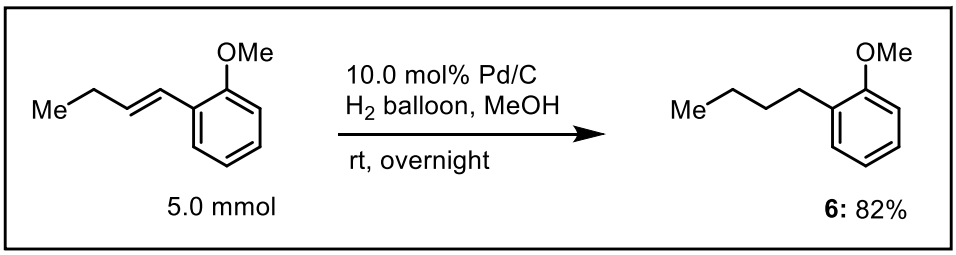
1 equiv.) in anhydrous THF (5 ml) was added slowly into the yellow suspension. Subsequently, the mixture was further stirred at room temperature for overnight. After the completion of the reaction, the resulting mixture was diluted with water (50 mL) and extracted with dichloromethane (3 × 50 mL). The combined organic layer was washed with brine (50 mL) and dried with anhydrous Na_2SO_4. The crude mass was purified by silica gel column chromatography (2% ethyl acetate in hexane as eluent) to afford 949 mg (78%) of the 1-(but-1-en-1-yl)-2-methoxybenzene as light-yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 – 7.27 (m, 2H), 7.00 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.58 (d, *J* = 11.6 Hz, 1H), 5.82 – 5.76 (m, 2H), 3.89 (s, 3H), 2.38 – 2.31 (m, 2H), 1.12 (t, *J* = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 134.5, 129.9, 127.9, 126.4, 123.5, 119.9, 110.3, 55.3, 22.0, 14.4.

HRMS (ESI) *m/z* calcd for $C_{11}H_{15}O$ $[M+H]^+$ 163.1123, found 163.1133.

Step III:



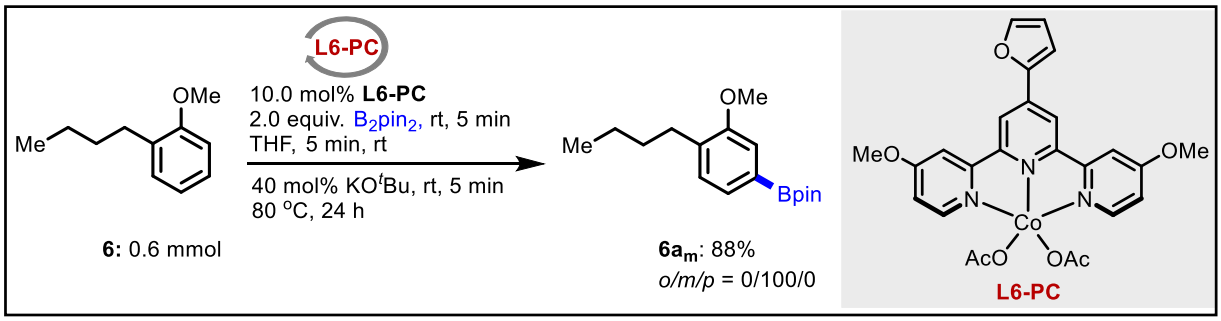
To a solution of 1-(but-1-en-1-yl)-2-methoxybenzene (810 mg, 5.0 mmol) in 15 mL of MeOH was added Pd/C (0.12 g, 10% on carbon). The reaction mixture was stirred under H_2 balloon overnight at room temperature. Then the reaction mixture was filtered through a pad of celite and the solvent was removed in vacuo gave the crude product. The crude mass was purified by silica gel column chromatography (1-2% ethyl acetate in hexane as eluent) to afford 673 mg (82%) of the 1-butyl-2-methoxybenzene (**6**) as colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 – 7.15 (m, 2H), 6.93 – 6.86 (m, 2H), 3.85 (s, 3H), 2.67 – 2.63 (m, 2H), 1.64 – 1.56 (m, 2H), 1.45 – 1.36 (m, 2H), 0.97 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.4, 131.3, 129.7, 126.7, 120.3, 110.2, 55.2, 32.1, 29.8, 22.6, 14.0.

HRMS (ESI) *m/z* calcd for $C_{11}H_{17}O$ $[M+H]^+$ 165.1279, found 165.1272.

Borylation procedure



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (32.1 mg, 10.0 mol%), B_2pin_2 (304.8 mg, 2.0 equiv.) and dry THF (2.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (26.9 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1-butyl-2-methoxybenzene (**6:** 0.6 mmol, 98.4 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 80 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard. After completion (judged by GC-MS), THF was removed under reduced pressure and chromatographic separation with silica gel (1% EtOAc in hexane as eluent) gave 153.6 mg (88%) of the *meta*-borylated product (**6a$_m$**) as gummy liquid.

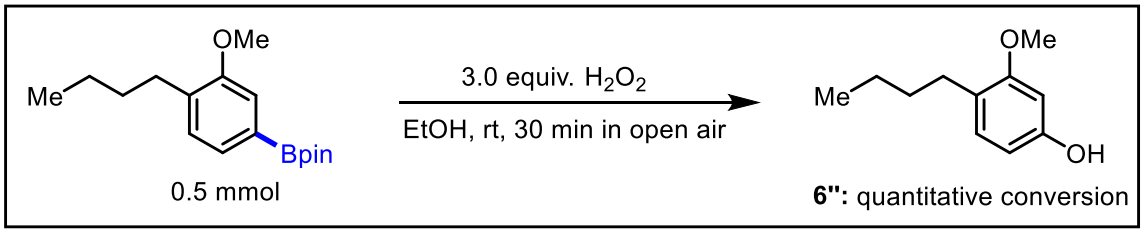
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.2 Hz, 1H), 7.26 (s, 1H), 7.15 (d, J = 7.2 Hz, 1H), 3.87 (s, 3H), 2.65 – 2.61 (m, 2H), 1.58 – 1.54 (m, 2H), 1.40 – 1.34 (m, 15H), 0.92 (t, J = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 157.0, 135.0, 129.3, 127.2, 115.7, 83.6, 55.4, 31.9, 30.0, 24.8, 22.6, 14.0.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.6.

HRMS (ESI) *m/z* calcd for $C_{17}H_{28}BO_3$ $[M+H]^+$ 291.2132, found 291.2120.

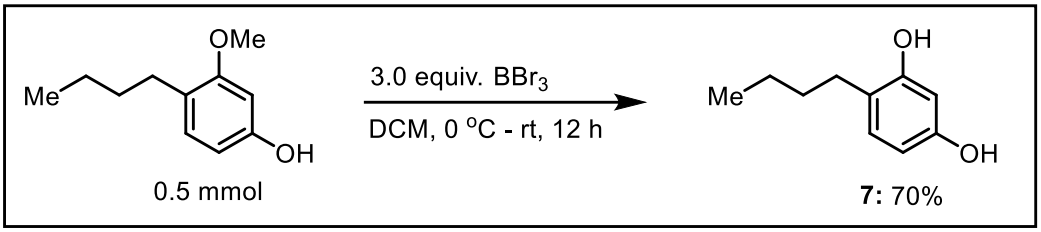
Hydroxylation procedure



An oven dried 25.0 mL round bottom flask was charged with 2-(4-butyl-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6′:** 145.1 mg, 0.5 mmol) in 5 ml EtOH. The flask was placed in an ice bath and to the stirred solution, H_2O_2 (30%, 1.5 mmol) was added dropwise

for 5 min. The reaction was allowed to stir at room temperature for another 30 min and then quenched with water (5 ml), extracted with ethyl acetate (10 mL x 3) and washed with water (10 ml). The combined organic layers were washed with saturated brine solution, dried with Na_2SO_4, concentrated under vacuum. The crude residue was used for the next step without further purification.

Deprotection procedure:



An oven dried 25.0 mL round bottom flask was charged with 4-butyl-3-methoxyphenol (0.5 mmol crude) in 3 ml dry DCM. The flask was cooled to 0 °C and freshly prepared 1.0 M BBr_3 solution in DCM (1.5 ml) was added dropwise. The reaction mixture was allowed to stir at room temperature for overnight and then quenched with water (5 ml), extracted with DCM (10 ml x 3) and washed with water (10 ml). The combined organic layers were washed with saturated brine solution, dried with Na_2SO_4, concentrated under vacuum. The crude mass was purified by silica gel column chromatography (20% ethyl acetate in hexane as eluent) to afford 58.2 mg (70%) of the 4-butylbenzene-1,3-diol (**7**) as brown gummy liquid.

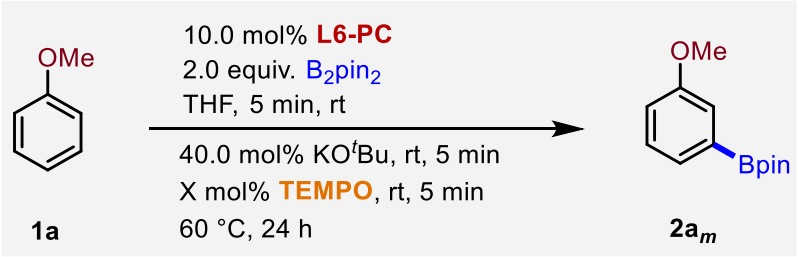
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.91 (d, J = 8.0 Hz, 1H), 6.37 – 6.33 (m, 2H), 2.49 (t, J = 7.6 Hz, 2H), 1.56 – 1.48 (m, 2H), 1.36 – 1.31 (m, 2H), 0.91 (t, J = 7.6 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.2, 154.1, 130.7, 121.4, 107.6, 103.0, 32.1, 28.9, 22.5, 13.9.

HRMS (ESI) *m/z* calcd for $C_{10}H_{15}O_2$ $[M+H]^+$ 167.1072, found 167.1081.

Mechanistic Investigations

TEMPO Quenching Studies:



In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (5.4 mg, 10.0 mol%), B_2pin_2 (50.8 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (4.5 mg, 40.0 mol%) was added. After stirring for another 5 min at room temperature (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO) was added (X mol%). Finally stirring for another 5 minutes, anisole (**1a:** 0.1 mmol, 10.8 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS) using dodecane as internal standard.

Table S3: TEMPO Quenching Study:

Loading of TEMPO (in mol%)	Conversion	*meta/others*	Loading of TEMPO (in mol%)	Conversion	*meta/others*
Without TEMPO	91%	93:7	60.0	<1%	-
10.0	28%	91:9	70.0	0%	-
20.0	20%	92:8	80.0	0%	-
30.0	7%	92:8	90.0	0%	-
40.0	5%	92:8	100.0	0%	-
50.0	<5%	92:8	200.0	0%	-

EPR Studies regarding this: Corresponding X-band EPR spectrum of this deactivation phenomenon was also recorded at 10 K in THF glass. We first prepared a mixture of precatalyst (L6-PC):B_2pin_2:KO^{t}Bu:TEMPO (1:4:4:1; 0.0279 mmol scale) in 0.3 mL dry THF and stirred it for 1 h under argon atmosphere. The EPR spectrum has been shown in **Figure S5**.

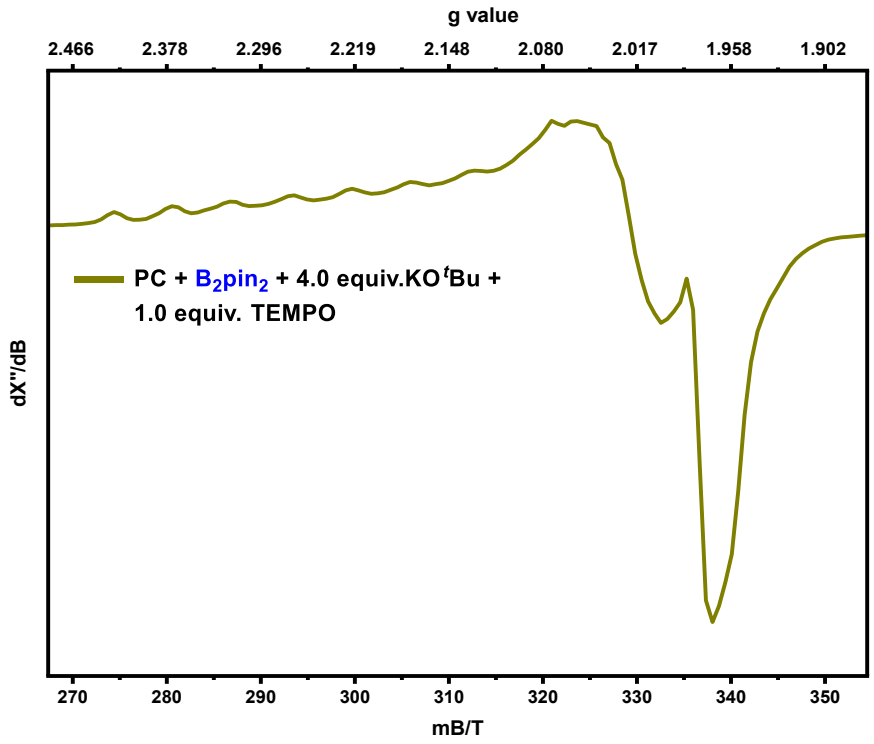
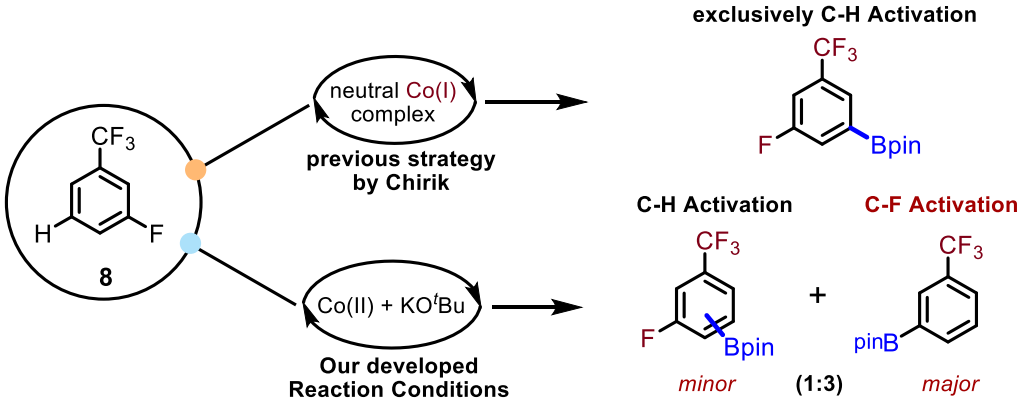
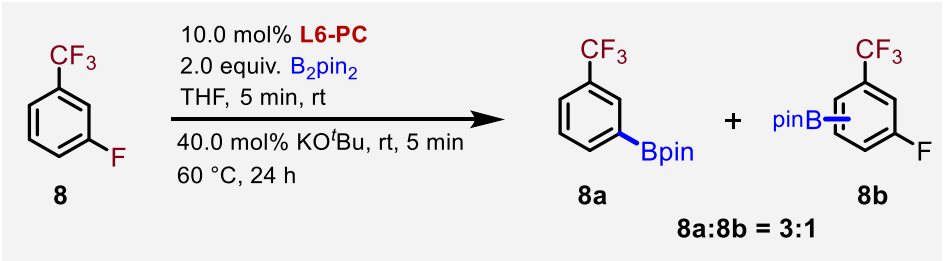


Figure S5: X-band EPR spectrum of (**L6-PC**):B_2pin_2:KO^{t}Bu:TEMPO (1:4:4:1) in THF at 10 K

Competitive Study and concept of Co(I) ate-complex:





In an argon-filled glove box, a 5.0 mL Wheaton microreactor was charged with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally

stirring for another 5 minutes, 1-fluoro-3-(trifluoromethyl)benzene (**8:** 0.2 mmol, 32.8 mg) was added to it. The microreactor was capped with a teflon pressure cap and stirred at 60 °C for 24 h. After 24 h, 50.0 µL of aliquot was withdrawn and conversion and selectivity were checked by gas chromatography (GC/MS). Based on the analysis, major product was defluorinative ipso borylation. Which set this reaction conditions completely different from the previously reported borylation of same substrate by Chirik et al[17].

Determination of Deuterium Kinetic Isotope Effects:

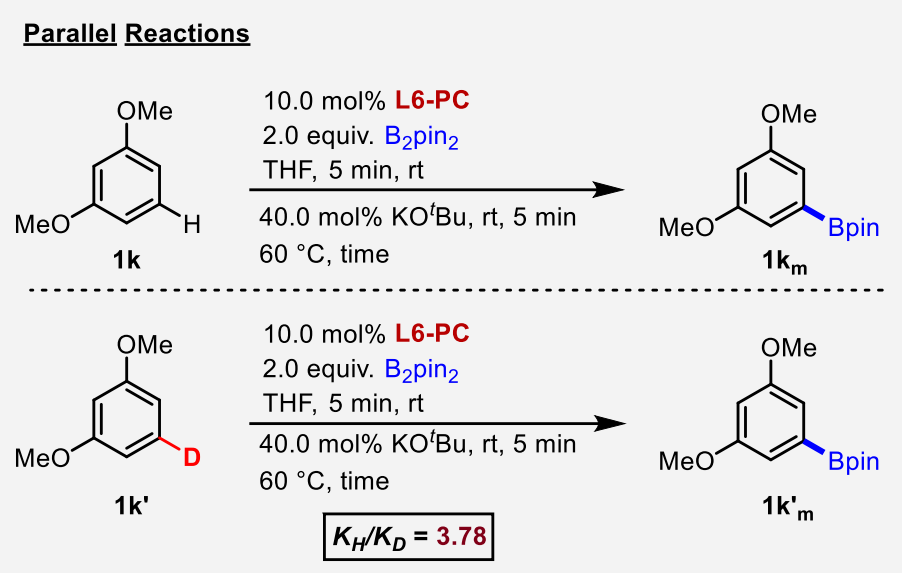


Figure S6: Parallel experiments to assess relative extents of conversion at a common time point in the borylation of 1k and 1k'

In an argon-filled glove box, seven 5.0 mL Wheaton microreactors were charged each with **L6-PC** (10.7 mg, 10.0 mol%), B_2pin_2 (101.6 mg, 2.0 equiv.) and dry THF (1.0 mL) sequentially. The reaction mixture was stirred for 5 minutes at room temperature. Addition of B_2pin_2 to the precatalyst produced a dark purple solution. Thereafter KO^{t}Bu (9.0 mg, 40.0 mol%) was added. Finally stirring for another 5 minutes, 1,3-dimethoxybenzene (**1k:** 0.2 mmol, 27.6 mg) was added to it.

Again, seven separate vials were also prepared with the afore mentioned procedure with the substrate 1,3-dimethoxybenzene-5-*d* (**1k**': 0.2 mmol, 27.8 mg). The microreactors were capped with a teflon pressure cap and stirred at 60 °C for future measurements. Aliquots of the reaction mixtures were taken and analyzed at different time points (1 to 7 hour). The product conversion was determined by GC-MS using dodecane as an internal standard. The value of K_H/K_D was found to be 3.78 and it indicates that oxidative addition of C-H bond is the rate determining step.

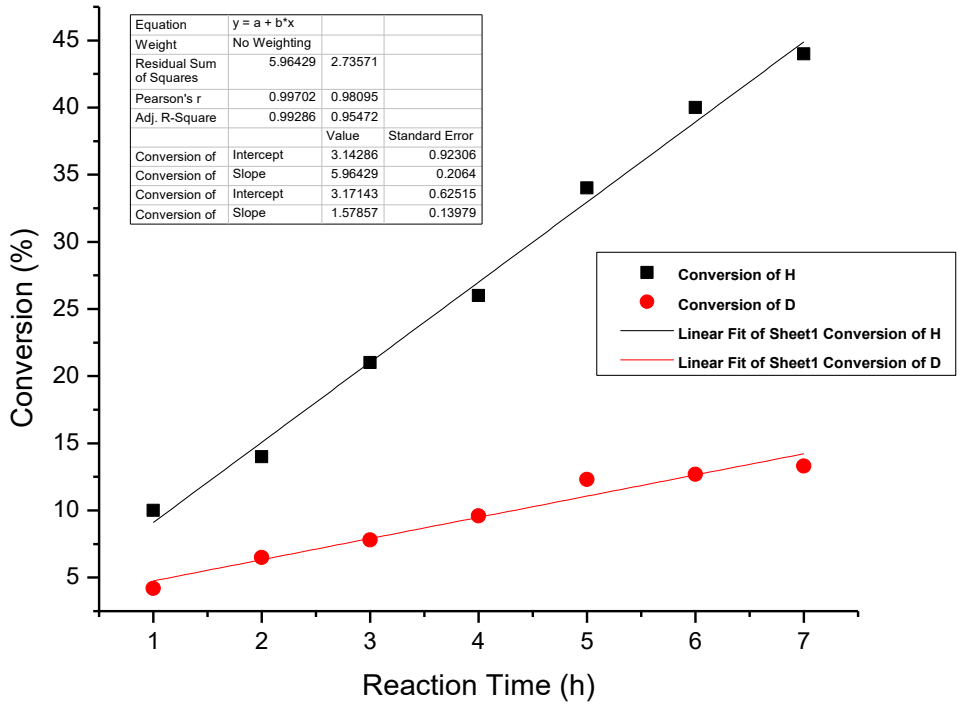


Figure S7: Results of parallel experiments to assess relative extents of conversion at a common time point in the borylation of **1k** and **1k'**

EPR Analyses:

The X-band EPR measurements of the complexes were performed by dissolving them in THF at 10 K. We observed distinct EPR spectrum for these complexes which corroborated the change in oxidation state of the cobalt in the corresponding species. All these experiments were performed in the BRUKER EMXmicroX.

X-band EPR spectrum of precatalyst (**L6-PC**) (15 mg, 0.0279 mmol) was taken after dissolving it in dry THF at 10 K. Next we prepared a mixture of **L6-PC** and B_2pin_2 (1:4; 0.0279 mmol) in 0.3 mL THF and took the EPR measurements at 10 K. Which gave exactly same type of pattern as reported by Chirik et. al.[18]. We prepared a mixture of L6-PC:B_2pin_2:KO^{t}Bu (1:4:4, 0.0279 mmol) in THF (0.3 mL) under argon atmosphere. Its EPR measurements was taken at 10K. We observed a single-line EPR spectrum at g = 1.98, characteristic of a square planar Co(I) complex having ligand centered s = 1/2 spin[19]. All these spectra are shown in **Figure S8**.

Next, we carried out a KO^{t}Bu titration ranging from 1-4 equivalent. Accordingly, we prepared all these samples in the aforementioned way under argon atmosphere and after 1 hour stirring we took EPR spectrum at 10 K. Their EPR spectrum has been shown below in **Figure S9**. From these data it is quite clear that upon 4 equivalent loading of KO^{t}Bu respect to **L6-PC**, a square planar Co(I) complex having ligand centered s = 1/2 spin forms in situ the reaction mixture

which further take part in the C-H oxidative addition with the substrate and continue the catalytic cycle **Figure S10**.

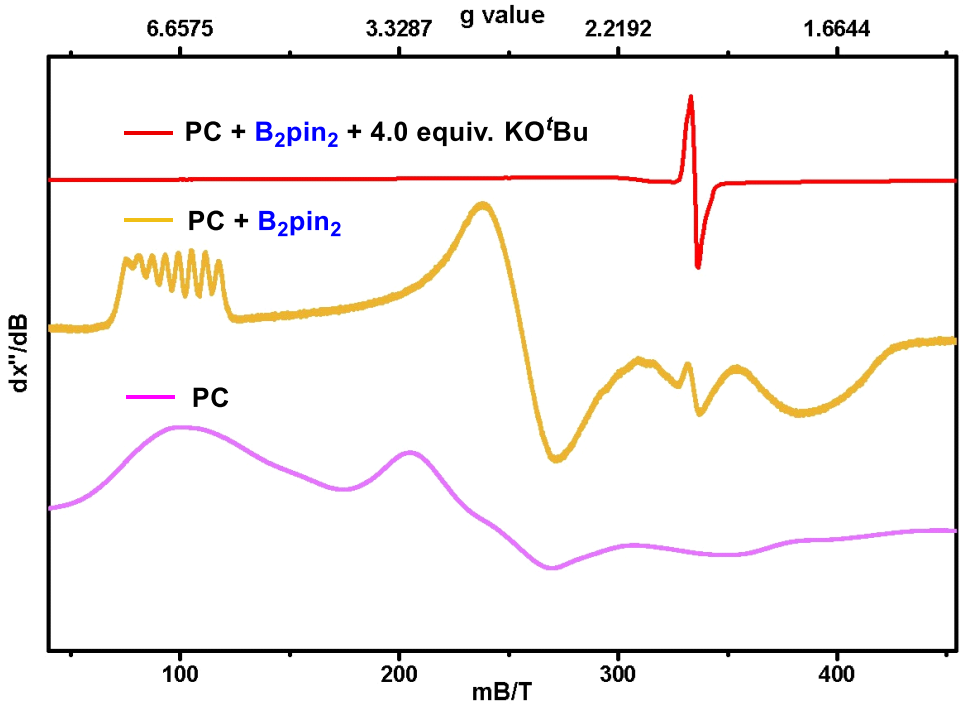


Figure S8: Stacked X-band EPR spectrum of **L6-PC**, **L6-PC**:B_2pin_2 (1:4), **L6-PC**:B_2pin_2:KO^{t}Bu (1:4:4) in THF at 10 K

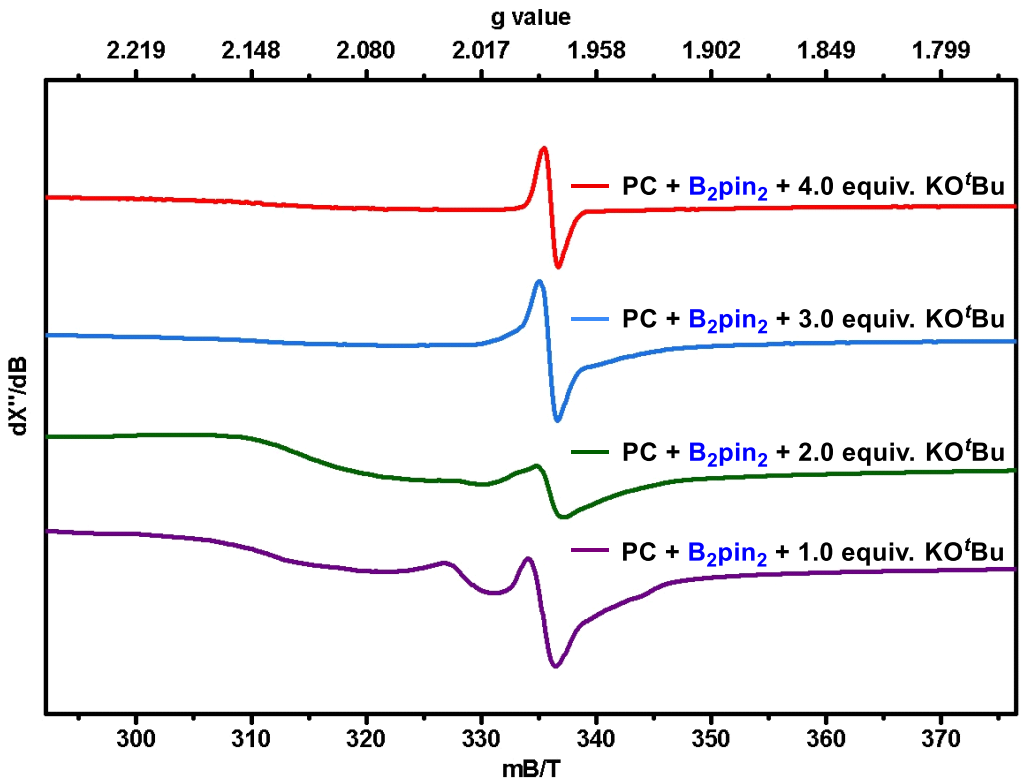


Figure S9: X-band EPR spectrum of **L6-PC**, B_2pin_2 (4 equiv.) and KO^{t}Bu (1 to 4 equiv.) in THF at 10 K

Proposed Reaction Mechanism:

Below is a proposed reaction mechanism for the cobalt catalyzed *meta*-selective C-H functionalization of aromatic arenes. Upon charging of B_2pin_2 and KO^{t}Bu Precatalyst undergoes ligand exchange reaction with intense colour change. Which plausibly leads to the ionic INT1 complex suitable for C-H oxidative addition. After addition of substrate it probably forms the INT2 and transform to INT3 upon releasing of HBpin. This INT3 possibly undergoes oxidative addition with B_2pin_2 and a following by a reductive elimination generates the active catalyst INT1.

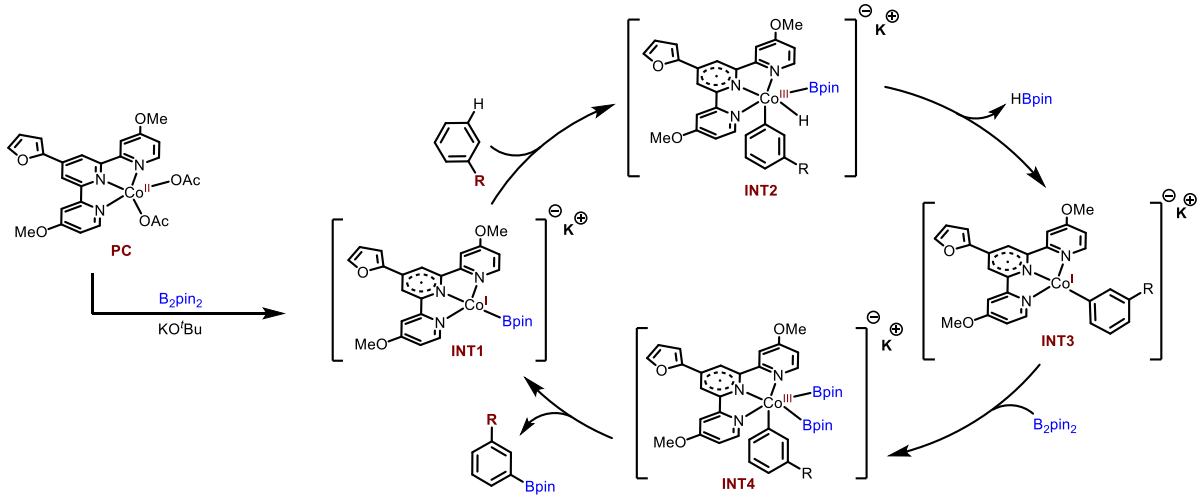


Figure S10: Proposed catalytic cycle

Computational details:

All DFT calculations were carried out with the Gaussian 16 program.[20] The geometry optimizations were conducted using the B3PW91 functional[21,22] including Grimme's dispersion corrections with a Becke-Johnson damping function[23], combined with the SDD basis set[24] for Co, and 6-31G(d) basis set (BS-I) for all other atoms. Single-point energy calculations were performed with the same functional and a mixed basis set (BS-II) of SDD for Co and 6-311+G(d, p) for other atoms with the polarizable continuum model (PCM)[25,26,27] solvation model to simulate the solvent effect of tetrahydrofuran (THF). In this work, discussion is presented using the Gibbs energy. Thermal correction and entropy contribution to the Gibbs energy were evaluated at 296.15 K and 1 atm, where the translational entropy in solution was corrected by the method of Whiteside et al[28].

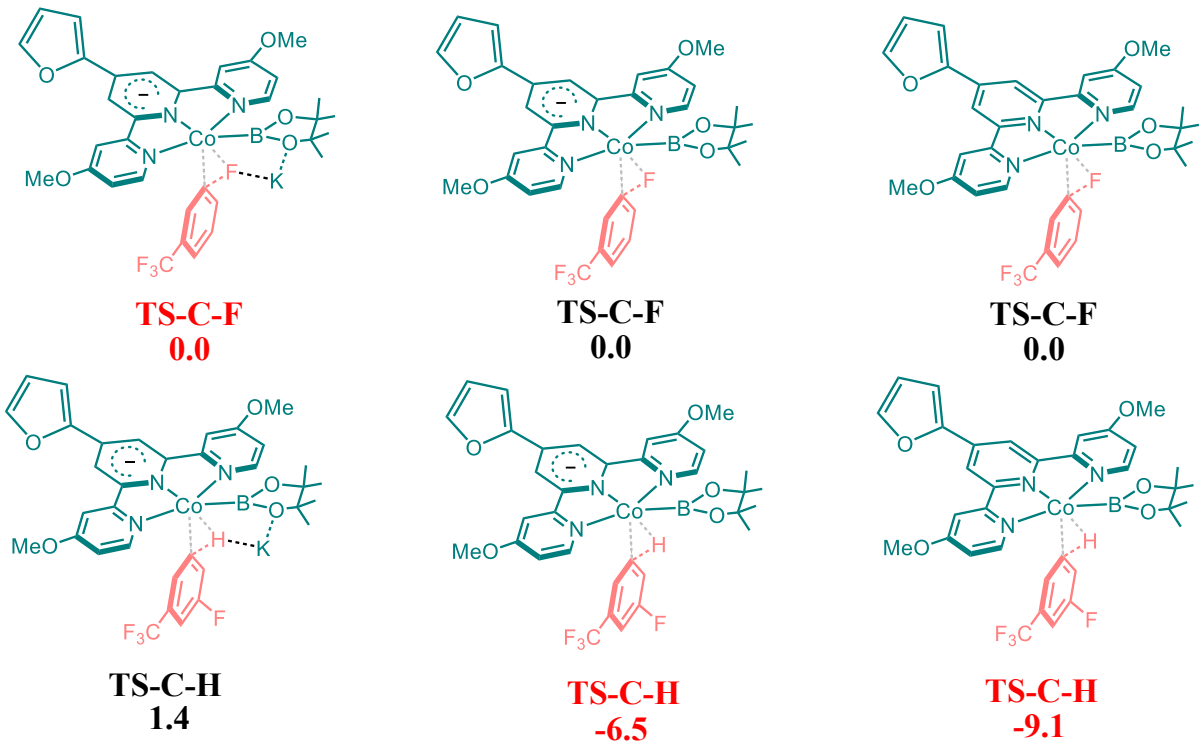


Figure S11. The relative Gibbs energy of the transition state ($\Delta\Delta G^{\circ\neq}$) for C–F and C–H bond activation of substrate **8** catalyzed by ate-complex $[(L6)Co^{I}(Bpin)]^{-}K^{+}$, $[(L6)Co^{I}(Bpin)]^{-}$ and neutral complex $[(L6)Co^{I}(Bpin)]$.

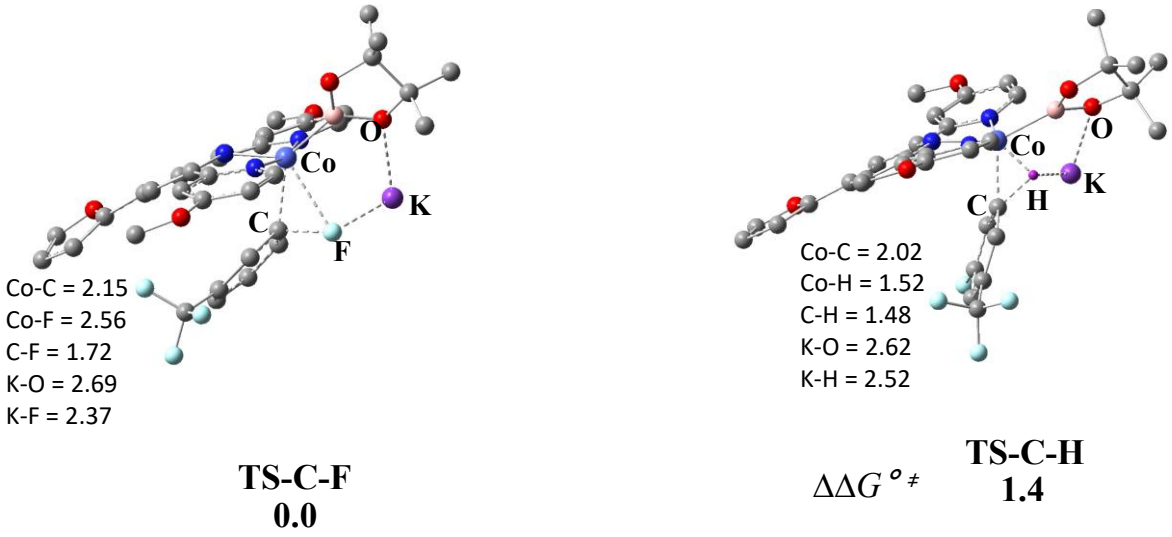


Figure S12. The geometric structure of the transition state ($\Delta\Delta G^{\circ\neq}$) of C–F and C–H bond activation of substrate **8**.

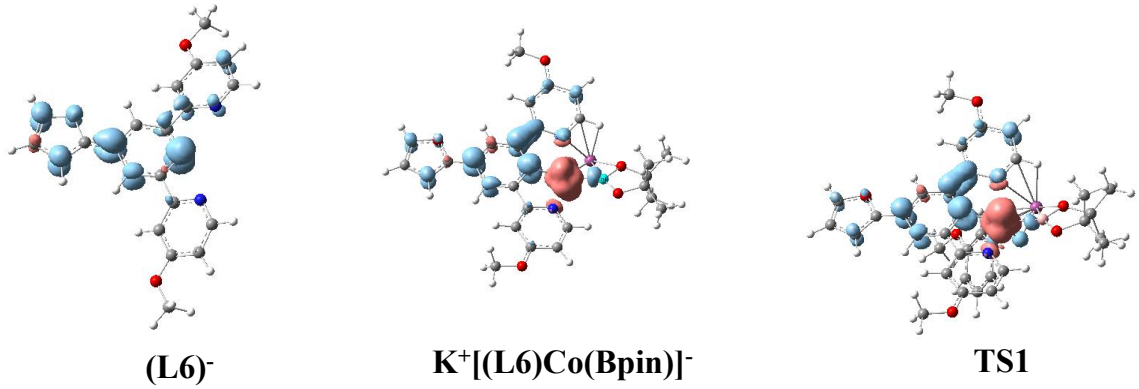


Figure S13. Spin density of **(L6)**$^{-}$, active species **K**$^{+}$**[(L6)Co(Bpin)]**$^{-}$, and **TS1**.

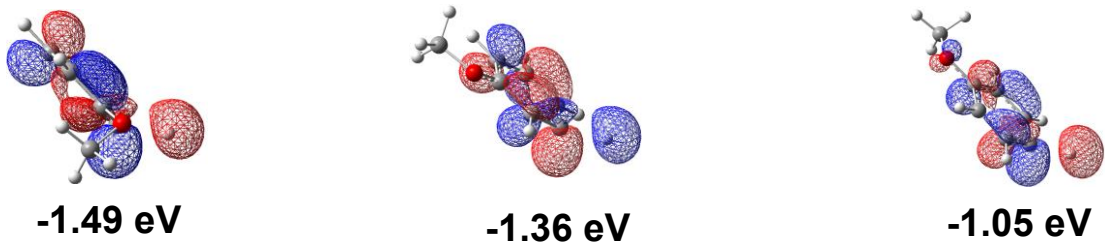


Figure S14. The σ* orbital of *ortho*, *meta* and *para* C-H bond of anisole fragment in transition states and corresponding energy level.

Table S4. The relative Gibbs energy of transition state ($\Delta\Delta G^{\circ\neq}$) for $[(L6)Co^{I}(Bpin)]^{-}K^{+}$ catalyzed C–H activation of diverse classes of arenes (R=Me, OMe, NMe_2 and amide).

R	TS-o	TS-m	TS-p	Cal. ((o/m/p))	Exp. (o/m/p)
Me	6.2	0	0.5	0/80/20	0/70/30
OMe	6.6	0	1.8	0/96/4	0/93/7
NMe_2	7.2	0	3.3	0/99/1	0/96/4
Amide	6.2	0	3.4	0/99/1	0/98/2

Table S5.
Coordinates and energies:

82
TS-o(Me), b3pw91/BS-II = -2628.963832 au

C	1.652772	-2.837170	-0.563020
H	2.724503	-2.682638	-0.603801
C	1.116504	-4.084146	-0.807592
H	1.747378	-4.933829	-1.042050
C	-0.279126	-4.237320	-0.743961
C	-1.054750	-3.120888	-0.466514
H	-2.135166	-3.168579	-0.433388
C	-0.430123	-1.884442	-0.248347
C	-1.156194	-0.636028	-0.107729
C	-2.545873	-0.446555	-0.179814
H	-3.234135	-1.276683	-0.263927
C	-3.029706	0.882813	-0.151540
C	-2.134193	1.945904	-0.093558
H	-2.496888	2.968049	-0.086389
C	-0.740770	1.686887	-0.038291
C	0.334119	2.607805	-0.060753
C	0.199735	4.020244	-0.166101
H	-0.793662	4.438237	-0.270144
C	1.321637	4.817885	-0.134860
C	2.597956	4.217106	0.016950
H	3.487987	4.830647	0.084821
C	2.655066	2.839993	0.082480
H	3.613654	2.345417	0.215091
Co	1.536714	0.081472	0.030991
N	0.929358	-1.746810	-0.262759
N	-0.312442	0.391671	0.001929
N	1.597047	2.025028	0.017102
B	1.843909	0.279372	-1.905258
O	0.823361	0.048617	-2.815800
O	2.917130	0.918262	-2.602900
C	1.240933	0.429397	-4.136408
C	2.381373	1.445969	-3.839195
C	1.736105	-0.835218	-4.837042
C	0.047704	1.012815	-4.875414
C	3.486494	1.501352	-4.879574
C	1.861660	2.848347	-3.529832
H	2.610748	-1.247886	-4.322603
H	1.996980	-0.651222	-5.885262
H	0.942417	-1.587558	-4.802957
H	-0.703788	0.232772	-5.033365
H	0.343929	1.407065	-5.854854
H	-0.417762	1.813174	-4.296160
H	4.248402	2.228384	-4.575758
H	3.090879	1.819704	-5.850785
H	3.968489	0.527845	-5.007999
H	1.053662	2.811074	-2.793649
H	1.498704	3.353840	-4.431248
H	2.671073	3.443725	-3.096419
H	2.783313	-0.026529	1.003828
C	1.903512	-0.066950	2.100978
C	2.272623	-1.194833	2.874415
C	1.415977	1.054923	2.802489
C	2.078558	-1.192120	4.260977
C	1.219479	1.041159	4.179460
H	1.144525	1.951922	2.258881
C	1.541771	-0.093336	4.922170
H	0.804879	1.919820	4.669673
H	1.395464	-0.115896	5.999229
K	4.653989	0.012953	-0.992684
O	1.322795	6.170955	-0.236771
C	0.071122	6.806287	-0.377844
H	-0.442682	6.478626	-1.291808
H	-0.576898	6.609497	0.486844
H	0.278042	7.876173	-0.440722
O	-0.758460	-5.478518	-0.976886
C	-2.161294	-5.655571	-0.924716
H	-2.557904	-5.402552	0.066735
H	-2.668307	-5.046726	-1.684189
H	-2.338245	-6.712646	-1.128482
C	-4.458068	1.138894	-0.197436
C	-5.221981	2.278242	-0.152569
O	-5.285138	0.054541	-0.307267
C	-6.585151	1.867354	-0.240183
H	-4.854972	3.290596	-0.061787
C	-6.563743	0.508655	-0.331914
H	-7.462159	2.499830	-0.233262
H	-7.329104	-0.247806	-0.415801
H	2.367402	-2.075022	4.830204
C	2.915942	-2.404444	2.258444
H	3.567332	-2.112516	1.422304
H	3.522265	-2.946875	2.993106
H	2.180732	-3.106967	1.851996

82
TS-m(Me), b3pw91/BS-II = -2628.971562 au

C	2.123486	-2.821228	-0.182434

H	3.158187	-2.522323	-0.048663
C	1.780770	-4.150132	-0.320246
H	2.530817	-4.932507	-0.304724
C	0.423318	-4.478307	-0.492904
C	-0.513688	-3.455268	-0.496248
H	-1.572193	-3.648425	-0.612226
C	-0.087036	-2.129639	-0.329206
C	-0.969455	-0.981531	-0.340694
C	-2.349262	-0.964224	-0.608064
H	-2.908162	-1.873265	-0.785651
C	-2.994356	0.292651	-0.652419
C	-2.257243	1.460007	-0.469730
H	-2.743417	2.428127	-0.520274
C	-0.862790	1.376905	-0.224785
C	0.086048	2.423103	-0.121116
C	-0.217889	3.809163	-0.220757
H	-1.250148	4.101435	-0.366441
C	0.791809	4.740844	-0.131594
C	2.125235	4.302190	0.070870
H	2.930141	5.019859	0.172514
C	2.346766	2.940942	0.145583
H	3.354616	2.571801	0.323818
Co	1.575850	0.060338	0.041531
N	1.235823	-1.814076	-0.188039
N	-0.284027	0.145537	-0.121820
N	1.402556	2.000398	0.042173
B	1.870941	0.257398	-1.900036
O	0.927215	-0.173452	-2.819164
O	2.816087	1.076702	-2.592235
C	1.273678	0.278749	-4.137740
C	2.201467	1.491724	-3.835130
C	2.000711	-0.869678	-4.835618
C	-0.005268	0.628210	-4.881241
C	3.285957	1.752326	-4.865848
C	1.425200	2.771797	-3.533377
H	2.934489	-1.112317	-4.316828
H	2.228244	-0.637782	-5.882080
H	1.361668	-1.757339	-4.807135
H	-0.593985	-0.279702	-5.046127
H	0.214877	1.076641	-5.857410
H	-0.617428	1.321394	-4.300384
H	3.895315	2.609121	-4.556364
H	2.846363	1.990636	-5.841059
H	3.942859	0.886234	-4.988328
H	0.629397	2.582254	-2.807588
H	0.984997	3.201882	-4.439509
H	2.104203	3.506620	-3.089849
H	2.822522	-0.080628	1.020571
C	1.964377	-0.087283	2.078994
C	1.834577	-1.320394	2.748499
C	2.000122	1.066034	2.886316
C	1.676726	-1.416730	4.131414
H	1.827974	-2.245669	2.178949
C	1.849834	0.985540	4.267629
H	2.117177	2.043930	2.430407
C	1.684187	-0.245759	4.897512
H	1.855776	1.898955	4.860013
H	1.565747	-0.300778	5.977873
K	4.664811	0.440681	-0.980923
O	0.627056	6.084923	-0.220544
C	-0.687172	6.559926	-0.414564
H	-1.113645	6.183319	-1.354263
H	-1.343609	6.271040	0.417204
H	-0.614163	7.648115	-0.458841
O	0.140687	-5.791991	-0.639861
C	-1.216969	-6.150677	-0.809348
H	-1.818385	-5.857688	0.060737
H	-1.640496	-5.693099	-1.712703
H	-1.230385	-7.236862	-0.911162
C	-4.422292	0.369986	-0.903895
C	-5.321595	1.404764	-0.968893
O	-5.082657	-0.806189	-1.133208
C	-6.595879	0.829845	-1.253087
H	-5.101282	2.452824	-0.824644
C	-6.391387	-0.513663	-1.342075
H	-7.537137	1.348533	-1.372471
H	-7.035779	-1.357430	-1.536712
C	1.474093	-2.759570	4.784111
H	0.435884	-2.886216	5.118254
H	1.697054	-3.577137	4.090110
H	2.113259	-2.879801	5.667287

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TS-p(Me), b3pw91/BS-II = -2628.970605 au

C	2.117947	-2.826259	-0.191413
H	3.154592	-2.534164	-0.057705
C	1.766950	-4.152108	-0.337150
H	2.512219	-4.939127	-0.326664
C	0.407585	-4.471055	-0.511071
C	-0.523240	-3.442259	-0.507161
H	-1.582938	-3.628207	-0.623951
C	-0.088306	-2.120469	-0.333214
C	-0.963729	-0.966342	-0.341207

C	-2.342971	-0.940153	-0.608334
H	-2.907941	-1.845445	-0.785850
C	-2.980060	0.321185	-0.652078
C	-2.234948	1.483360	-0.469910
H	-2.714608	2.454726	-0.521339
C	-0.841116	1.391414	-0.225633
C	0.114695	2.431290	-0.125249
C	-0.180081	3.819504	-0.225375
H	-1.210736	4.118676	-0.368449
C	0.836085	4.744303	-0.140344
C	2.167243	4.296969	0.059173
H	2.977113	5.009362	0.158462
C	2.379666	2.934305	0.135345
H	3.385236	2.558436	0.313017
Co	1.590025	0.058727	0.033880
N	1.236296	-1.813672	-0.191443
N	-0.270633	0.155696	-0.121446
N	1.428974	1.999966	0.035094
B	1.866290	0.249016	-1.911385
O	0.916641	-0.189887	-2.820668
O	2.801587	1.069649	-2.615057
C	1.248608	0.259689	-4.143743
C	2.173921	1.477674	-3.853640
C	1.973994	-0.887706	-4.845012
C	-0.038865	0.601366	-4.876099
C	3.247785	1.739593	-4.895094
C	1.394919	2.755349	-3.548857
H	2.913673	-1.124764	-4.334334
H	2.190719	-0.657967	-5.894237
H	1.339123	-1.778040	-4.807877
H	-0.625009	-0.309616	-5.033040
H	0.170065	1.048172	-5.855472
H	-0.648672	1.293281	-4.291277
H	3.856226	2.599965	-4.593886
H	2.798216	1.972857	-5.866979
H	3.907299	0.875950	-5.020914
H	0.606262	2.564335	-2.815713
H	0.945143	3.181099	-4.452340
H	2.074750	3.494051	-3.113073
H	2.847136	-0.085601	0.997606
C	1.998603	-0.092714	2.067419
C	1.883751	-1.320601	2.748182
C	2.030465	1.061032	2.876223
C	1.745720	-1.384063	4.131665
C	1.891455	0.993696	4.257840
H	2.130009	2.039170	2.416161
C	1.743312	-0.229970	4.919899
H	1.887802	1.917054	4.836631
K	4.668576	0.431814	-1.025547
O	0.680229	6.089464	-0.230429
C	-0.631199	6.572993	-0.421995
H	-1.062477	6.197830	-1.360089
H	-1.287599	6.289738	0.411754
H	-0.551040	7.660611	-0.468075
O	0.116866	-5.781933	-0.666622
C	-1.243014	-6.131215	-0.838076
H	-1.842396	-5.840429	0.034134
H	-1.663986	-5.665059	-1.738238
H	-1.263033	-7.216593	-0.947140
C	-4.407527	0.407998	-0.902692
C	-5.300518	1.448444	-0.964950
O	-5.075234	-0.763595	-1.134251
C	-6.578420	0.881981	-1.249846
H	-5.073758	2.494792	-0.818246
C	-6.382265	-0.462565	-1.341878
H	-7.516539	1.406705	-1.367575
H	-7.031939	-1.301935	-1.537955
H	1.627555	-2.356338	4.609481
H	1.870639	-2.253123	2.191704
C	1.619071	-0.300152	6.417670
H	1.113024	-1.219088	6.733934
H	2.602618	-0.285710	6.908256
H	1.050454	0.549581	6.813002

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TS-o(OMe), b3pw91/BS-II = -2704.172931 au

C	1.687471	-2.398667	-1.275026
H	2.735672	-2.179926	-1.452293
C	1.211998	-3.676295	-1.489874
H	1.865345	-4.478486	-1.812997
C	-0.172153	-3.913797	-1.297565
C	-0.986979	-2.858599	-0.951284
H	-2.055651	-2.978439	-0.826032
C	-0.431185	-1.562449	-0.782333
C	-1.196656	-0.384867	-0.569713
C	-2.601729	-0.253497	-0.451134
H	-3.246768	-1.122864	-0.457067
C	-3.152911	1.028194	-0.336525
C	-2.321517	2.159715	-0.354084
H	-2.738344	3.156886	-0.278657
C	-0.924894	1.971611	-0.467085
C	0.103999	2.960044	-0.530260
C	-0.105713	4.357901	-0.499779

H	-1.121413	4.728264	-0.443298
C	0.980898	5.208770	-0.536108
C	2.283844	4.660789	-0.598695
H	3.147634	5.314249	-0.627768
C	2.413772	3.290193	-0.640345
H	3.394180	2.826978	-0.692391
Co	1.426690	0.520654	-0.496212
N	0.939511	-1.351840	-0.891779
N	-0.409876	0.721022	-0.547431
N	1.378632	2.435491	-0.617445
B	2.714391	0.459312	-1.975820
O	2.539404	1.059671	-3.210693
O	3.941538	-0.281073	-2.017881
C	3.430992	0.459569	-4.167622
C	4.614069	-0.005408	-3.269402
C	2.678844	-0.708931	-4.804586
C	3.795463	1.492911	-5.220500
C	5.321794	-1.265749	-3.737944
C	5.623494	1.107828	-2.997024
H	2.416149	-1.463392	-4.055930
H	3.259057	-1.184651	-5.603057
H	1.745807	-0.329487	-5.230841
H	2.900495	1.764447	-5.788440
H	4.537420	1.094398	-5.922686
H	4.191846	2.403961	-4.765978
H	6.139013	-1.519102	-3.051021
H	5.759751	-1.121977	-4.732052
H	4.634365	-2.114028	-3.781661
H	5.114436	2.015942	-2.660033
H	6.216436	1.348089	-3.885535
H	6.315371	0.787613	-2.208357
H	2.636803	0.567505	0.406516
C	1.694604	0.474933	1.542036
C	1.966349	-0.647836	2.347129
C	1.381085	1.650297	2.259567
C	1.904886	-0.622749	3.741509
C	1.294183	1.689475	3.646970
H	1.168675	2.560661	1.710458
C	1.558159	0.548316	4.404453
H	1.016048	2.618935	4.138762
H	1.502231	0.570188	5.489447
K	4.450917	-1.024904	0.440803
O	0.913357	6.562692	-0.514739
C	-0.371818	7.143658	-0.455920
H	-0.977370	6.863425	-1.328112
H	-0.902714	6.848697	0.459174
H	-0.216540	8.223973	-0.453080
O	-0.582349	-5.192733	-1.489507
C	-1.960694	-5.454966	-1.332469
H	-2.297880	-5.223915	-0.313036
H	-2.561354	-4.876714	-2.047010
H	-2.091357	-6.521162	-1.526025
C	-4.589830	1.196439	-0.208667
C	-5.404656	2.292234	-0.073818
O	-5.362846	0.067548	-0.214261
C	-6.744172	1.806556	0.006893
H	-5.085962	3.323977	-0.035116
C	-6.658203	0.450706	-0.083650
H	-7.647930	2.389879	0.117701
H	-7.384784	-0.347510	-0.072841
H	2.133029	-1.529969	4.296833
O	2.377945	-1.846874	1.751144
C	1.417661	-2.893216	1.865315
H	0.454121	-2.565999	1.465468
H	1.786952	-3.730925	1.271326
H	1.299307	-3.202323	2.911141

83

TS-m(OMe), b3pw91/BS-II = -2704.180879 au

C	1.519640	-3.014347	-1.084156
H	2.526296	-2.806002	-1.449085
C	0.922371	-4.231728	-1.335254
H	1.426455	-5.018402	-1.885808
C	-0.412386	-4.413293	-0.891513
C	-1.061842	-3.363190	-0.273250
H	-2.106646	-3.432396	0.002600
C	-0.369711	-2.149155	-0.043590
C	-0.984963	-0.965468	0.493507
C	-2.204543	-0.945063	1.170744
H	-2.750161	-1.866265	1.344083
C	-2.716551	0.250346	1.674225
C	-1.949232	1.433072	1.466842
H	-2.294067	2.377790	1.872169
C	-0.750779	1.356291	0.796896
C	0.140612	2.507110	0.579448
C	-0.271053	3.837574	0.723745
H	-1.298692	4.055181	0.984879
C	0.654119	4.853711	0.502859
C	1.958431	4.510259	0.114466
H	2.688334	5.289188	-0.077208
C	2.268612	3.170725	-0.029687
H	3.251938	2.846982	-0.358957
Co	1.704605	0.037187	0.144019

N	0.949042	-2.007383	-0.397520
N	-0.259106	0.188383	0.297182
N	1.394571	2.183682	0.206408
B	3.467920	-0.077101	-0.854097
O	4.146792	0.949124	-1.513346
O	4.297130	-1.252045	-0.940802
C	5.242740	0.409079	-2.271815
C	5.584972	-0.886420	-1.480877
C	4.718916	0.120188	-3.678606
C	6.360379	1.438468	-2.328343
C	6.117305	-2.033673	-2.323489
C	6.513009	-0.624751	-0.293980
H	3.924683	-0.632172	-3.649704
H	5.512947	-0.224038	-4.350777
H	4.291812	1.040607	-4.087461
H	6.023369	2.313075	-2.893742
H	7.246391	1.030940	-2.829769
H	6.645429	1.774686	-1.328361
H	6.324215	-2.903100	-1.687999
H	7.053571	-1.753888	-2.820281
H	5.394881	-2.335115	-3.085360
H	6.128422	0.192884	0.323757
H	7.530810	-0.376469	-0.612938
H	6.573083	-1.528443	0.325828
H	2.898930	-0.048608	1.071138
C	1.890121	-0.056056	2.171414
C	1.303858	-1.164642	2.804370
C	2.257778	1.025113	2.999486
C	1.050008	-1.188178	4.181906
C	2.002240	1.005638	4.363704
H	2.726368	1.898315	2.552265
C	1.400808	-0.098061	4.978493
H	2.273069	1.863569	4.976433
K	3.373504	-2.530859	1.192103
O	0.390039	6.175358	0.617863
C	-0.916962	6.551457	1.003071
H	-1.662099	6.219896	0.268343
H	-1.175954	6.145253	1.989568
H	-0.914438	7.641617	1.049160
O	-0.960564	-5.623532	-1.158354
C	-2.299232	-5.830534	-0.757384
H	-2.414403	-5.710553	0.328133
H	-2.980964	-5.138648	-1.269172
H	-2.544245	-6.856068	-1.038725
C	-3.956890	0.296860	2.404797
C	-4.659726	1.311279	3.013839
O	-4.641811	-0.878811	2.570120
C	-5.830848	0.722141	3.577325
H	-4.373674	2.352508	3.056057
C	-5.770139	-0.604745	3.279722
H	-6.613857	1.222429	4.130717
H	-6.411550	-1.448373	3.484134
H	0.889117	-1.990580	2.225390
H	1.212774	-0.089512	6.046332
O	0.447160	-2.322122	4.648044
C	0.018588	-2.323890	5.991028
H	-0.671842	-1.494101	6.192476
H	-0.501609	-3.271752	6.143546
H	0.865321	-2.262106	6.689401

83

TS-p(OMe), b3pw91/BS-II = -2704.177918 au

C	1.600614	-3.014101	-1.097597
H	2.619839	-2.796686	-1.420101
C	1.025008	-4.235552	-1.377490
H	1.558536	-5.016056	-1.908687
C	-0.327522	-4.427987	-0.994296
C	-1.011271	-3.385224	-0.402400
H	-2.067150	-3.463456	-0.175290
C	-0.339717	-2.165110	-0.138733
C	-0.988626	-0.987305	0.367775
C	-2.251190	-0.971975	0.964505
H	-2.806852	-1.894262	1.095435
C	-2.799552	0.219674	1.434581
C	-2.023408	1.405718	1.284672
H	-2.398961	2.347317	1.669061
C	-0.783967	1.335133	0.692616
C	0.111455	2.492873	0.529081
C	-0.312641	3.819549	0.673376
H	-1.351129	4.029643	0.894358
C	0.615421	4.843130	0.505014
C	1.936705	4.511147	0.167964
H	2.669853	5.295998	0.016975
C	2.259417	3.175050	0.019337
H	3.257083	2.860468	-0.274030
Co	1.708364	0.036564	0.123917
N	0.993980	-2.012959	-0.433262
N	-0.258533	0.171704	0.219797
N	1.381607	2.180616	0.205405
B	3.516155	-0.058377	-0.787889
O	4.215870	0.978751	-1.408493
O	4.358220	-1.226746	-0.849261
C	5.344088	0.452031	-2.127397

C	5.663831	-0.847413	-1.333518
C	4.878282	0.170464	-3.555973
C	6.456118	1.489057	-2.132178
C	6.238886	-1.983743	-2.162701
C	6.541040	-0.588349	-0.107916
H	4.088992	-0.587582	-3.564123
H	5.700680	-0.163003	-4.198821
H	4.460986	1.091059	-3.974451
H	6.135518	2.365960	-2.703528
H	7.363851	1.091404	-2.601675
H	6.699588	1.819103	-1.119217
H	6.426540	-2.856777	-1.526187
H	7.192280	-1.692925	-2.618900
H	5.550178	-2.284247	-2.955498
H	6.125331	0.221457	0.499977
H	7.568861	-0.329608	-0.383438
H	6.583330	-1.496562	0.506784
H	2.883371	-0.046611	1.070846
C	1.886590	-0.056387	2.172194
C	1.233962	-1.131755	2.814579
C	2.305532	0.987524	3.011272
C	1.005553	-1.156561	4.187543
C	2.079825	0.990877	4.388329
H	2.814752	1.842377	2.569547
C	1.430862	-0.092385	4.987782
H	2.412212	1.838582	4.979435
K	3.360268	-2.513132	1.240839
O	0.339494	6.161928	0.626161
C	-0.985605	6.526751	0.956433
H	-1.695068	6.200170	0.185084
H	-1.286590	6.107642	1.925483
H	-0.991299	7.616289	1.015259
O	-0.854167	-5.641559	-1.289732
C	-2.209988	-5.857073	-0.957470
H	-2.380494	-5.743180	0.121492
H	-2.868739	-5.165809	-1.499351
H	-2.435519	-6.882387	-1.255452
C	-4.090090	0.261558	2.073440
C	-4.840011	1.273900	2.626566
O	-4.780206	-0.916697	2.190083
C	-6.046979	0.680746	3.103561
H	-4.562527	2.316535	2.687119
C	-5.958727	-0.646325	2.814047
H	-6.870495	1.178434	3.597204
H	-6.609386	-1.492545	2.973503
H	0.797539	-1.934431	2.217075
H	0.465844	-1.976187	4.655597
O	1.168144	-0.201651	6.323034
C	1.519961	0.888072	7.142509
H	1.202427	0.623431	8.153208
H	2.604846	1.066110	7.140903
H	1.008646	1.809898	6.832233

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TS-o(NMe_2), b3pw91/BS-II = -2723.627099 au

C	0.361196	-2.540959	0.956681
H	0.530306	-2.211318	1.976139
C	-0.102749	-3.819778	0.711635
H	-0.357758	-4.491349	1.523522
C	-0.345554	-4.208115	-0.643667
C	-0.129583	-3.295848	-1.650158
H	-0.330607	-3.527711	-2.689397
C	0.331008	-1.979558	-1.327641
C	0.477947	-0.913961	-2.226647
C	0.194739	-0.869832	-3.610901
H	-0.123005	-1.763273	-4.134698
C	0.277927	0.349046	-4.293577
C	0.638712	1.518780	-3.596364
H	0.654288	2.479276	-4.097389
C	0.978242	1.428574	-2.233885
C	1.458283	2.453969	-1.373610
C	1.797297	3.760844	-1.790779
H	1.636681	4.030299	-2.827325
C	2.347939	4.641090	-0.885061
C	2.584374	4.197666	0.439376
H	3.019164	4.873253	1.167131
C	2.255495	2.908116	0.771142
H	2.452613	2.535006	1.770836
Co	1.588461	0.078399	0.089236
N	0.659884	-1.637558	-0.000031
N	0.940813	0.221225	-1.594634
N	1.665419	2.030983	-0.072511
B	3.383088	-0.006257	-0.703539
O	4.232434	1.070017	-0.871497
O	3.861967	-1.091655	-1.463162
C	5.048516	0.843161	-2.037531
C	5.104691	-0.715402	-2.105831
C	4.317566	1.463808	-3.224729
C	6.389891	1.526487	-1.829266
C	5.108333	-1.296935	-3.509559
C	6.240375	-1.309062	-1.276318
H	3.347923	0.987759	-3.394475
H	4.911837	1.399719	-4.142680

H	4.126668	2.516889	-2.999913
H	6.236254	2.608176	-1.770100
H	7.068149	1.322658	-2.665943
H	6.868150	1.204598	-0.900795
H	5.150582	-2.391668	-3.462500
H	5.982577	-0.952593	-4.073283
H	4.203485	-1.016011	-4.052222
H	6.234342	-0.905268	-0.259997
H	7.218505	-1.108183	-1.724934
H	6.121634	-2.398706	-1.218932
H	2.724662	0.077950	1.080752
C	1.759991	-0.037328	2.120823
C	2.375547	-0.999931	2.952067
C	0.825563	0.826874	2.717167
C	2.022875	-1.102890	4.302748
C	0.458065	0.705197	4.055274
H	0.333456	1.571401	2.100278
C	1.054569	-0.267950	4.852667
H	-0.306800	1.359589	4.465938
H	0.778209	-0.374686	5.898253
K	2.979344	-3.125387	-0.208802
O	2.714566	5.920814	-1.154398
C	2.497967	6.384951	-2.468021
H	3.075522	5.802402	-3.199352
H	1.434104	6.341387	-2.738324
H	2.834975	7.423042	-2.484555
O	-0.785121	-5.485172	-0.813776
C	-1.107246	-5.879632	-2.129216
H	-1.895268	-5.244401	-2.555074
H	-0.226771	-5.841167	-2.786962
H	-1.464312	-6.908823	-2.061457
C	-0.019212	0.420552	-5.710899
C	-0.003078	1.440483	-6.630222
O	-0.394089	-0.736255	-6.339715
C	-0.390024	0.876618	-7.883142
H	0.255217	2.471528	-6.435569
C	-0.614569	-0.445362	-7.648432
H	-0.487977	1.389066	-8.830401
H	-0.921955	-1.274184	-8.267858
H	2.503324	-1.841132	4.937443
N	3.383612	-1.877266	2.392369
C	3.499826	-3.167875	3.054633
H	4.158641	-3.820024	2.462799
H	3.942191	-3.120080	4.064367
H	2.514135	-3.636930	3.128051
C	4.690005	-1.218856	2.337893
H	5.407041	-1.868239	1.820133
H	4.618072	-0.281636	1.780643
H	5.085484	-1.001454	3.344413

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TS-m(NMe_2), b3pw91/BS-II = -2723.632986 au

C	1.736014	-3.012706	-1.083187
H	2.752395	-2.766300	-1.392932
C	1.209759	-4.262407	-1.337299
H	1.778567	-5.036212	-1.840980
C	-0.139536	-4.495455	-0.963484
C	-0.869757	-3.464947	-0.407556
H	-1.923767	-3.579306	-0.187214
C	-0.247344	-2.212884	-0.168459
C	-0.934658	-1.055672	0.328769
C	-2.197789	-1.080611	0.927405
H	-2.738161	-2.015895	1.027747
C	-2.762566	0.082978	1.442364
C	-2.013285	1.290707	1.318631
H	-2.400609	2.211856	1.738975
C	-0.780814	1.262152	0.709088
C	0.089804	2.442991	0.568862
C	-0.364106	3.756169	0.736659
H	-1.407947	3.938663	0.957079
C	0.542726	4.802830	0.592420
C	1.871785	4.505639	0.255258
H	2.588877	5.308748	0.124591
C	2.224572	3.179947	0.082586
H	3.230768	2.892382	-0.209321
Co	1.738779	0.036851	0.132881
N	1.084882	-2.019864	-0.450742
N	-0.232757	0.123747	0.203455
N	1.366997	2.164154	0.244403
B	3.575139	-0.020221	-0.721388
O	4.285763	1.030045	-1.305612
O	4.433246	-1.177595	-0.753247
C	5.452966	0.523389	-1.975687
C	5.753927	-0.777505	-1.176276
C	5.056762	0.245964	-3.425854
C	6.549661	1.575242	-1.922411
C	6.380897	-1.900282	-1.986109
C	6.571852	-0.515153	0.089006
H	4.279096	-0.522476	-3.475177
H	5.912193	-0.071917	-4.032466
H	4.646655	1.163933	-3.857051
H	6.243953	2.451701	-2.502544
H	7.483537	1.192986	-2.351744

H	6.741274	1.901476	-0.897181
H	6.551383	-2.775221	-1.347371
H	7.349888	-1.593834	-2.396972
H	5.732625	-2.204303	-2.811012
H	6.116989	0.282799	0.684397
H	7.606588	-0.238261	-0.138819
H	6.601654	-1.427739	0.698014
H	2.904361	-0.040678	1.088673
C	1.896954	-0.062044	2.180429
C	1.203903	-1.141889	2.755356
C	2.348158	0.950969	3.042991
C	0.907624	-1.220515	4.132137
C	2.074239	0.886864	4.405791
H	2.891575	1.800684	2.635287
C	1.366528	-0.177909	4.959445
H	2.407868	1.688645	5.062518
K	3.401467	-2.506989	1.320691
O	0.237841	6.112552	0.737773
C	-1.094445	6.441971	1.076303
H	-1.797522	6.117089	0.298386
H	-1.385326	5.995938	2.036327
H	-1.123147	7.529632	1.158388
O	-0.615330	-5.737355	-1.227703
C	-1.964955	-5.995584	-0.902226
H	-2.151135	-5.856896	0.171421
H	-2.644314	-5.346383	-1.470109
H	-2.147950	-7.037121	-1.171772
C	-4.039691	0.073558	2.108734
C	-4.808660	1.051607	2.695890
O	-4.685796	-1.129859	2.226774
C	-5.982041	0.410848	3.195128
H	-4.565908	2.102472	2.762496
C	-5.856687	-0.908309	2.884296
H	-6.809210	0.873580	3.715924
H	-6.474877	-1.778064	3.046422
H	0.762068	-1.878951	2.090482
H	1.160378	-0.177591	6.023451
N	0.180930	-2.297579	4.643209
C	-0.618617	-3.067486	3.708274
H	0.013792	-3.588130	2.979686
H	-1.171485	-3.830886	4.261296
H	-1.332752	-2.446446	3.146781
C	-0.368223	-2.163475	5.975930
H	-0.902637	-3.080808	6.235120
H	0.432661	-2.033660	6.711586
H	-1.064985	-1.313846	6.072713

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TS-p(NMe_2), b3pw91/BS-II = -2723.627531 au

C	1.609419	-3.012515	-1.117825
H	2.628789	-2.795330	-1.439645
C	1.032025	-4.232667	-1.400178
H	1.564071	-5.012039	-1.934529
C	-0.320364	-4.424899	-1.016384
C	-1.001607	-3.384592	-0.417360
H	-2.057383	-3.461605	-0.188947
C	-0.327612	-2.167079	-0.148182
C	-0.971215	-0.993563	0.373887
C	-2.217676	-0.986635	1.003011
H	-2.766560	-1.912109	1.140871
C	-2.754279	0.198959	1.501723
C	-1.984430	1.388251	1.341399
H	-2.349522	2.325312	1.746566
C	-0.761626	1.325850	0.715400
C	0.129058	2.485645	0.543390
C	-0.293695	3.810862	0.703801
H	-1.328829	4.018203	0.942600
C	0.631165	4.836119	0.528490
C	1.947188	4.507532	0.168551
H	2.677719	5.293945	0.013028
C	2.268341	3.172750	0.004667
H	3.261977	2.860674	-0.304779
Co	1.719155	0.033078	0.106297
N	1.004681	-2.013173	-0.448906
N	-0.245944	0.167826	0.217834
N	1.393864	2.176596	0.196510
B	3.531444	-0.064606	-0.789242
O	4.245385	0.973003	-1.393485
O	4.366575	-1.238090	-0.849427
C	5.378755	0.444236	-2.102183
C	5.680286	-0.863002	-1.313804
C	4.929207	0.175855	-3.538521
C	6.497460	1.473972	-2.085473
C	6.259492	-1.996606	-2.143861
C	6.543191	-0.617910	-0.075168
H	4.135441	-0.577180	-3.561931
H	5.757526	-0.158107	-4.173488
H	4.522841	1.102038	-3.955467
H	6.189944	2.356931	-2.654716
H	7.408632	1.073694	-2.546039
H	6.729821	1.795355	-1.067139
H	6.433095	-2.875505	-1.511460
H	7.220658	-1.708299	-2.585141

H	5.579518	-2.286907	-2.947921
H	6.123887	0.189277	0.533771
H	7.575711	-0.362236	-0.335613
H	6.573204	-1.531144	0.532818
H	2.904755	-0.045906	1.038529
C	1.903704	-0.058651	2.154726
C	1.226831	-1.107980	2.803346
C	2.322835	0.986987	2.994219
C	0.963936	-1.111496	4.173220
C	2.067809	1.009520	4.360267
H	2.846831	1.834454	2.554783
C	1.388131	-0.050633	4.993882
H	2.397505	1.868940	4.934573
K	3.347106	-2.514164	1.244555
O	0.356364	6.154081	0.663641
C	-0.963113	6.515000	1.018923
H	-1.685319	6.193833	0.257130
H	-1.247541	6.087924	1.989535
H	-0.968815	7.604067	1.086480
O	-0.849658	-5.636100	-1.318360
C	-2.205799	-5.850067	-0.987392
H	-2.376150	-5.742464	0.092319
H	-2.862867	-5.153597	-1.524679
H	-2.434246	-6.872902	-1.291742
C	-4.022765	0.230852	2.183192
C	-4.755642	1.235397	2.772911
O	-4.706221	-0.950499	2.311174
C	-5.944439	0.634168	3.284390
H	-4.478613	2.278093	2.834482
C	-5.863669	-0.689549	2.977888
H	-6.752059	1.124790	3.810418
H	-6.507415	-1.538763	3.149170
H	0.782089	-1.912238	2.213243
H	0.386996	-1.932198	4.586899
N	1.153468	-0.051146	6.370086
C	0.159711	-0.968540	6.882449
H	-0.838825	-0.819275	6.437619
H	0.460192	-2.006534	6.699548
H	0.079826	-0.839829	7.964655
C	1.296834	1.201008	7.079049
H	1.069341	1.040186	8.135716
H	2.328732	1.564290	7.019575
H	0.633081	1.995036	6.696019

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TS-o(Amide), b3pw91/BS-II =
-2836.982230 au

C	1.438881	-3.058138	-1.135761
H	2.425149	-2.857416	-1.556049
C	0.825145	-4.275408	-1.346732
H	1.295459	-5.066890	-1.919752
C	-0.485388	-4.448207	-0.830590
C	-1.097432	-3.391100	-0.187911
H	-2.126748	-3.454636	0.142424
C	-0.391883	-2.174492	-0.009348
C	-0.978354	-0.986062	0.545124
C	-2.173559	-0.952397	1.271340
H	-2.718442	-1.868118	1.473680
C	-2.656907	0.248698	1.781396
C	-1.904950	1.431635	1.517748
H	-2.236420	2.385082	1.912457
C	-0.738409	1.340702	0.795917
C	0.116786	2.493052	0.457225
C	-0.321332	3.816923	0.526471
H	-1.324236	4.033389	0.870312
C	0.548291	4.829868	0.131759
C	1.807921	4.480518	-0.373869
H	2.486885	5.254561	-0.714621
C	2.154904	3.143944	-0.406993
H	3.117067	2.813099	-0.784589
Co	1.713024	0.035351	0.118704
N	0.910801	-2.042635	-0.428653
N	-0.260589	0.163152	0.314393
N	1.346644	2.166106	0.019185
B	3.454296	-0.099200	-0.932151
O	4.224252	0.945607	-1.454354
O	4.158392	-1.315814	-1.225070
C	5.200844	0.432347	-2.375531
C	5.419301	-1.025730	-1.864599
C	4.570832	0.486112	-3.767322
C	6.436003	1.318089	-2.324978
C	5.664616	-2.056220	-2.956313
C	6.510584	-1.137327	-0.799588
H	3.676006	-0.142135	-3.813002
H	5.269901	0.169987	-4.549381
H	4.263984	1.516227	-3.971209
H	6.180840	2.320315	-2.683516
H	7.232960	0.921956	-2.965248
H	6.819304	1.414121	-1.305820
H	5.792472	-3.049563	-2.510631
H	6.574957	-1.822512	-3.520401
H	4.824757	-2.104721	-3.652412
H	6.348833	-0.421834	0.011919
H	7.509418	-0.967268	-1.214791

H	6.499568	-2.150342	-0.376904
H	2.926861	-0.038895	1.020601
C	1.909969	-0.062141	2.154531
C	1.349908	-1.226425	2.727628
C	2.201318	0.984542	3.060467
C	1.075321	-1.348923	4.088783
C	1.891101	0.876933	4.421144
C	1.350227	-0.289899	4.950360
K	3.419309	-2.531260	1.013510
O	0.260908	6.149397	0.170890
C	-0.979025	6.532813	0.732123
H	-1.821765	6.154245	0.138927
H	-1.073244	6.178151	1.766194
H	-0.989994	7.623847	0.718287
O	-1.050332	-5.659310	-1.057109
C	-2.369772	-5.855281	-0.592460
H	-2.433687	-5.726799	0.496408
H	-3.070684	-5.162748	-1.076710
H	-2.633784	-6.881310	-0.854139
C	-3.865299	0.307975	2.564845
C	-4.530075	1.330724	3.200136
O	-4.553406	-0.860481	2.763227
C	-5.681107	0.755145	3.816383
H	-4.229315	2.368164	3.229844
C	-5.646157	-0.573105	3.520448
H	-6.433344	1.264559	4.402975
H	-6.286080	-1.409707	3.756159
H	1.001990	-2.026154	2.073343
H	1.125385	-0.360811	6.011032
H	0.610097	-2.257996	4.465680
H	2.076621	1.733706	5.064099
C	2.748003	2.326667	2.657685
O	2.092860	3.346167	2.859382
N	4.014325	2.376243	2.136520
C	4.922723	1.260622	2.069513
H	4.502357	0.409013	2.607294
H	5.110333	0.980664	1.025924
H	5.878303	1.527866	2.543310
C	4.561317	3.651188	1.733268
H	3.764778	4.392723	1.778708
H	5.379282	3.953097	2.403328
H	4.953877	3.586266	0.711023

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TS-m(Amide), b3pw91/BS-II = -2836.985576 au

C	1.697498	-2.976513	-1.131503
H	2.706024	-2.727273	-1.459528
C	1.145871	-4.209049	-1.413891
H	1.686723	-4.966489	-1.970663
C	-0.186248	-4.451175	-0.993485
C	-0.879535	-3.443830	-0.348908
H	-1.923092	-3.554778	-0.080803
C	-0.229844	-2.218545	-0.074721
C	-0.865553	-1.090484	0.553910
C	-1.958420	-1.185321	1.410537
H	-2.412041	-2.150919	1.608679
C	-2.418364	-0.059817	2.099766
C	-1.751619	1.178558	1.853110
H	-2.056291	2.073385	2.385650
C	-0.682987	1.214337	0.990244
C	0.142840	2.407710	0.755004
C	-0.302348	3.714687	0.984086
H	-1.319472	3.880931	1.316189
C	0.574717	4.770835	0.751959
C	1.864015	4.490027	0.271795
H	2.555697	5.301820	0.075047
C	2.208568	3.169793	0.046722
H	3.184258	2.893496	-0.344594
Co	1.750102	0.026508	0.152525
N	1.079066	-2.009238	-0.428580
N	-0.221010	0.108676	0.333409
N	1.381410	2.144276	0.287261
B	3.605276	-0.098223	-0.650995
O	4.391474	0.905854	-1.216979
O	4.400698	-1.298957	-0.626732
C	5.563576	0.330716	-1.821804
C	5.758171	-0.972258	-0.992365
C	5.226037	0.052983	-3.286607
C	6.708803	1.326173	-1.726074
C	6.363605	-2.137548	-1.757646
C	6.528970	-0.733899	0.306873
H	4.413067	-0.675346	-3.366394
H	6.092961	-0.316919	-3.845477
H	4.886092	0.984299	-3.749100
H	6.478529	2.208082	-2.332231
H	7.641978	0.890161	-2.102364
H	6.865096	1.657917	-0.696688
H	6.457250	-3.011010	-1.101034
H	7.366186	-1.888397	-2.124156
H	5.741032	-2.419721	-2.609722
H	6.088345	0.093682	0.871527
H	7.586094	-0.513147	0.125130
H	6.483816	-1.637864	0.927602

H	2.923429	-0.065463	1.108390
C	1.910505	-0.068431	2.175837
C	1.317710	-1.204962	2.738076
C	2.250923	0.958071	3.078392
C	1.072098	-1.344856	4.102962
C	1.984131	0.851236	4.442085
H	2.723655	1.861180	2.696988
C	1.401026	-0.303014	4.971724
H	2.248691	1.669961	5.108231
K	3.314726	-2.768040	1.414894
O	0.276138	6.076407	0.939973
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H	-1.047669	7.477892	1.506673
O	-0.687740	-5.670021	-1.302234
C	-2.015445	-5.944944	-0.903844
H	-2.129854	-5.862538	0.185101
H	-2.727338	-5.267452	-1.393116
H	-2.217994	-6.970922	-1.215283
C	-3.456158	-0.157710	3.089940
C	-3.967164	0.720569	4.020599
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C	-4.955276	0.007790	4.763506
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89

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C	0.062462	-2.154288	-0.328988
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H	3.471830	2.586338	0.194427
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H	2.979223	-0.086131	0.959567

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C	1.850010	-0.216398	6.338732
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H	-0.303026	-1.250924	5.278634
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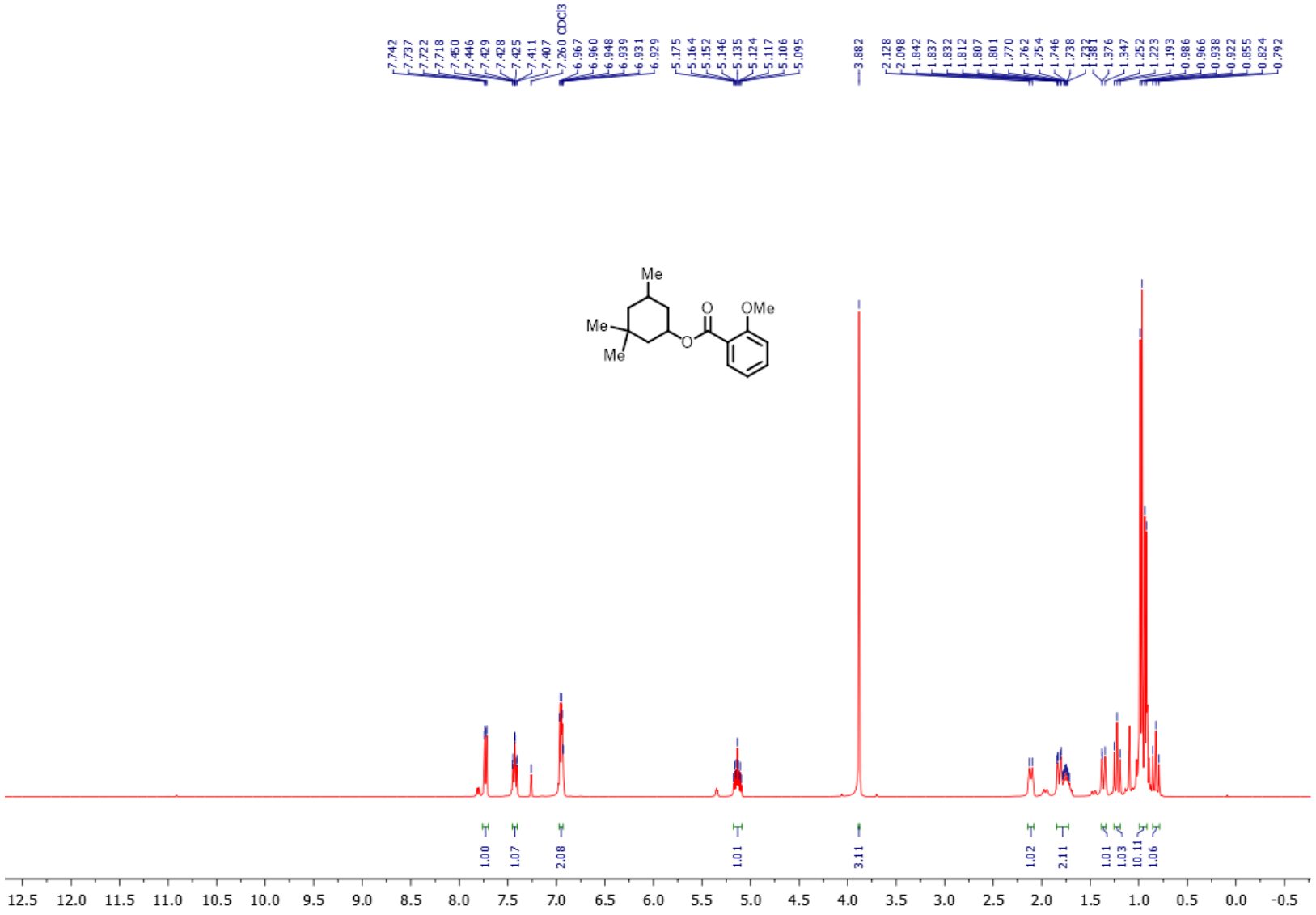
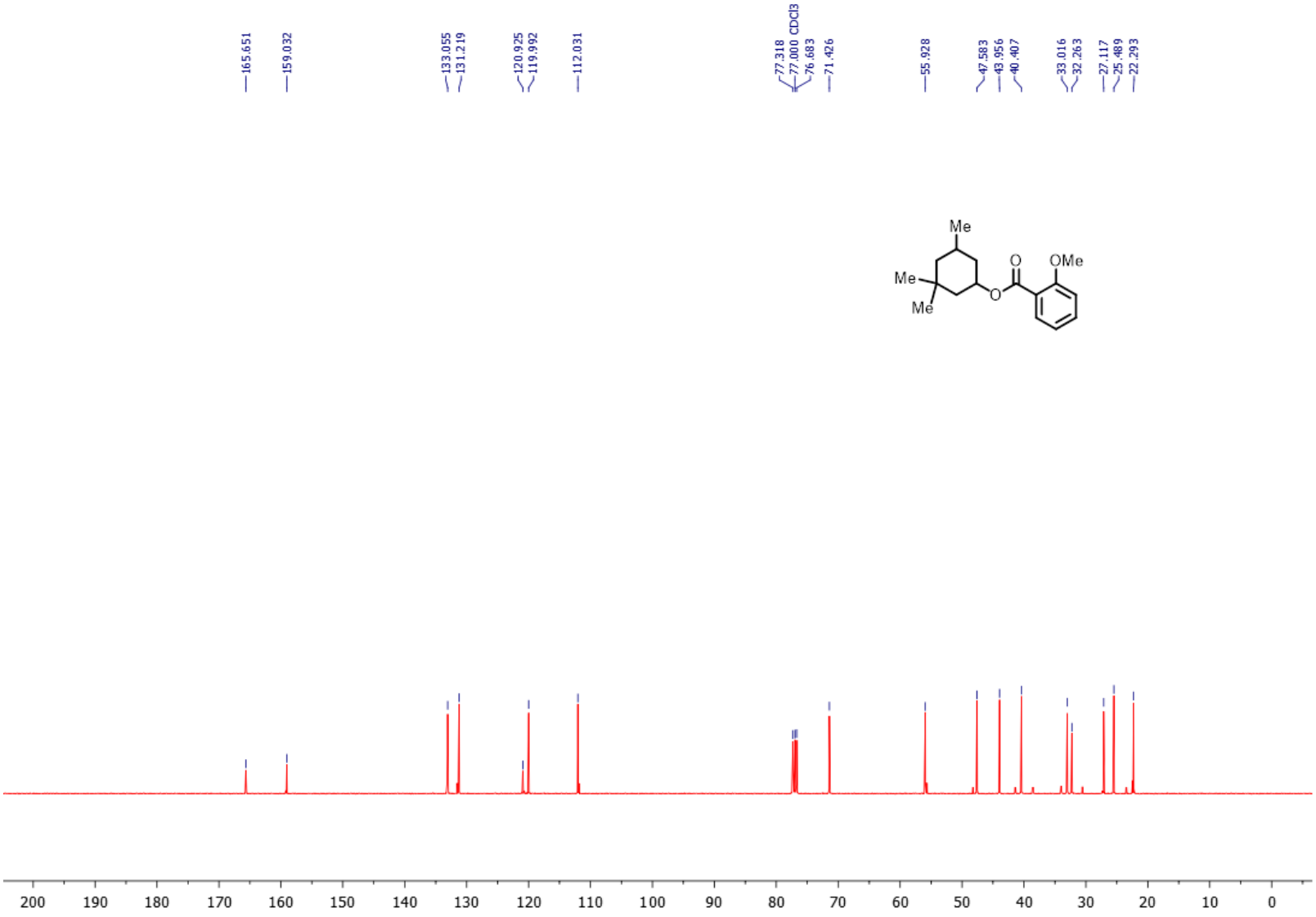
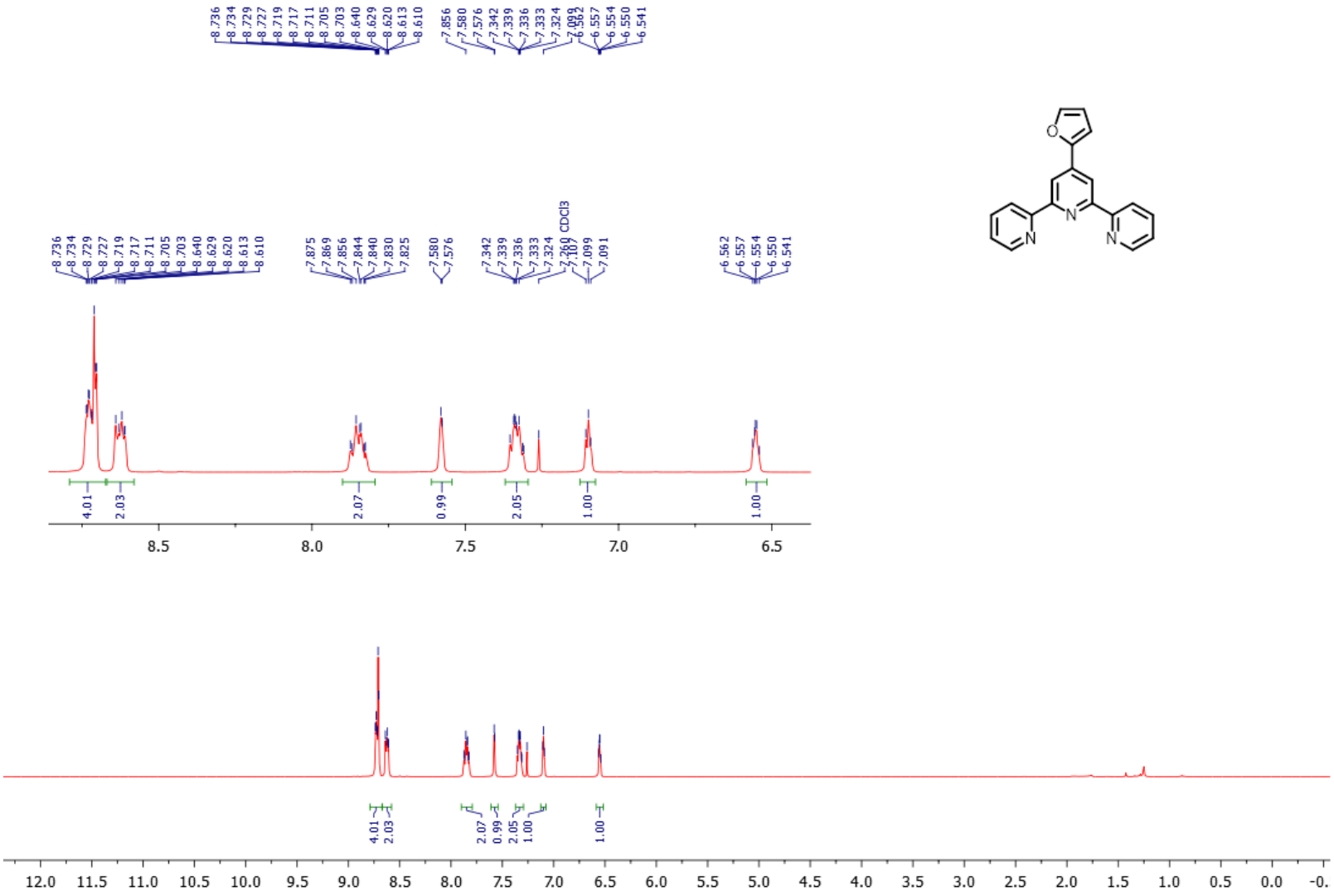


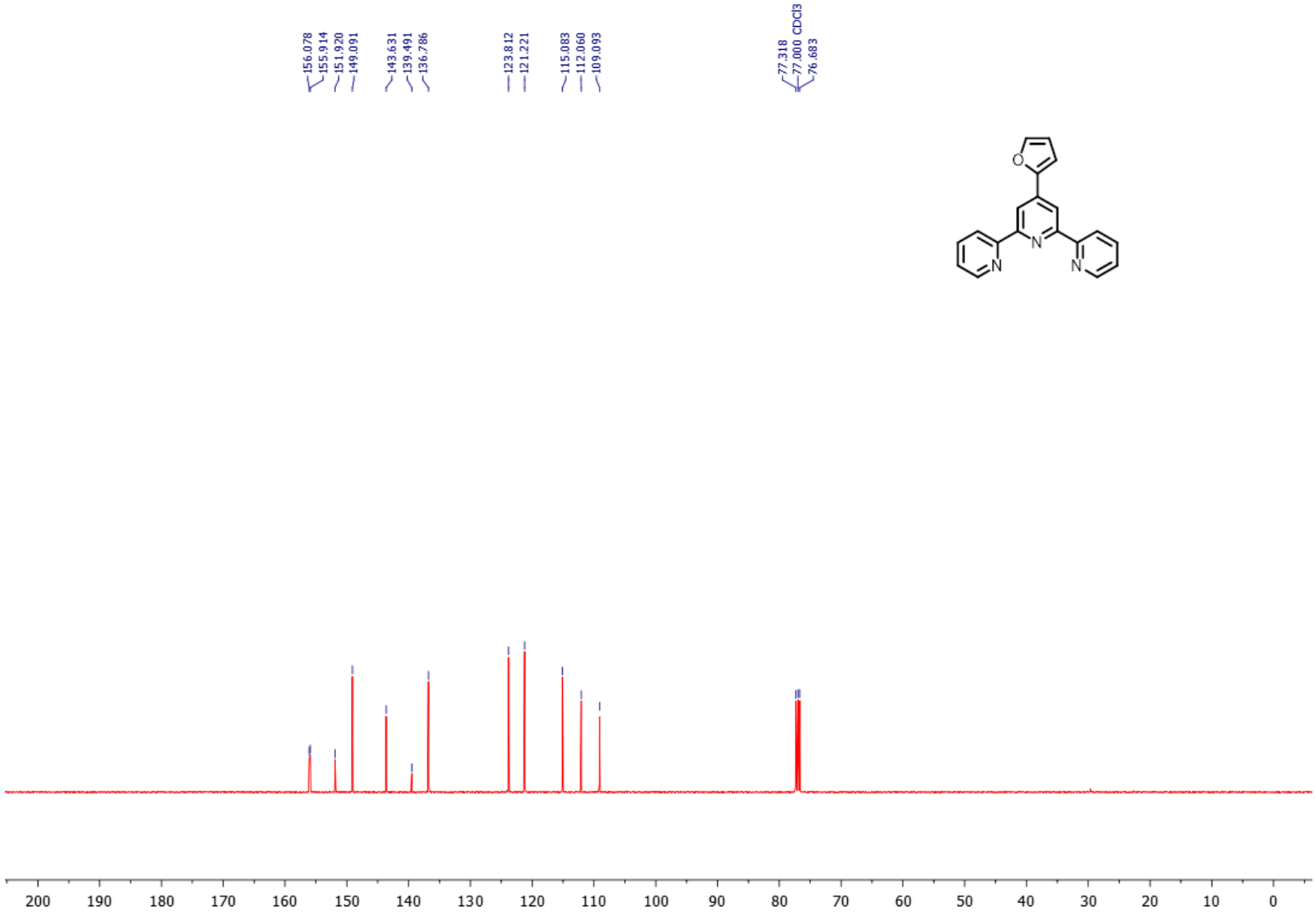
^{1}H NMR spectra of **3f** (25 ^{o}C, 400 MHz, $CDCl_3$)



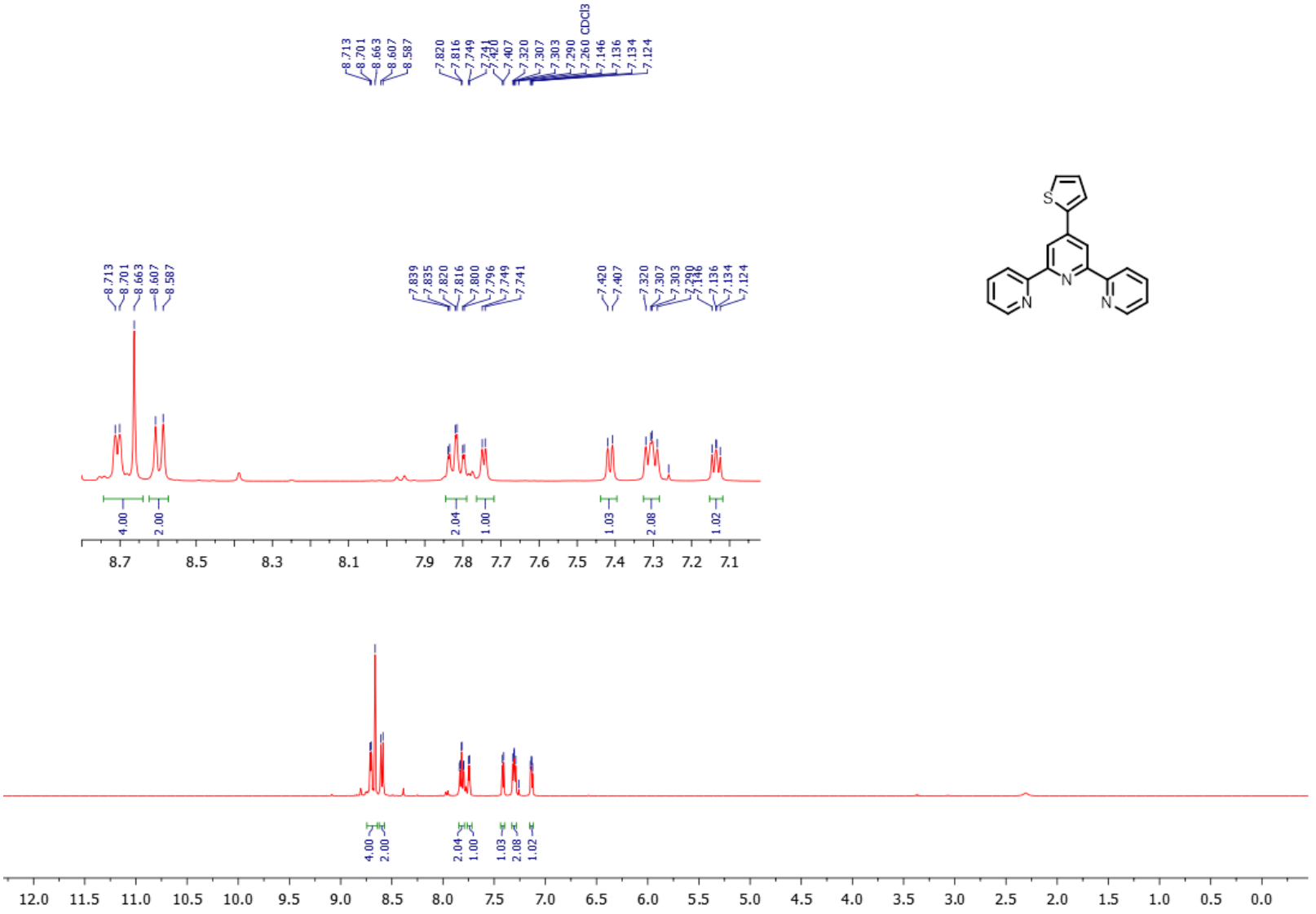
^{13}C NMR spectra of **3f** (25 °C, 100 MHz, $CDCl_3$)



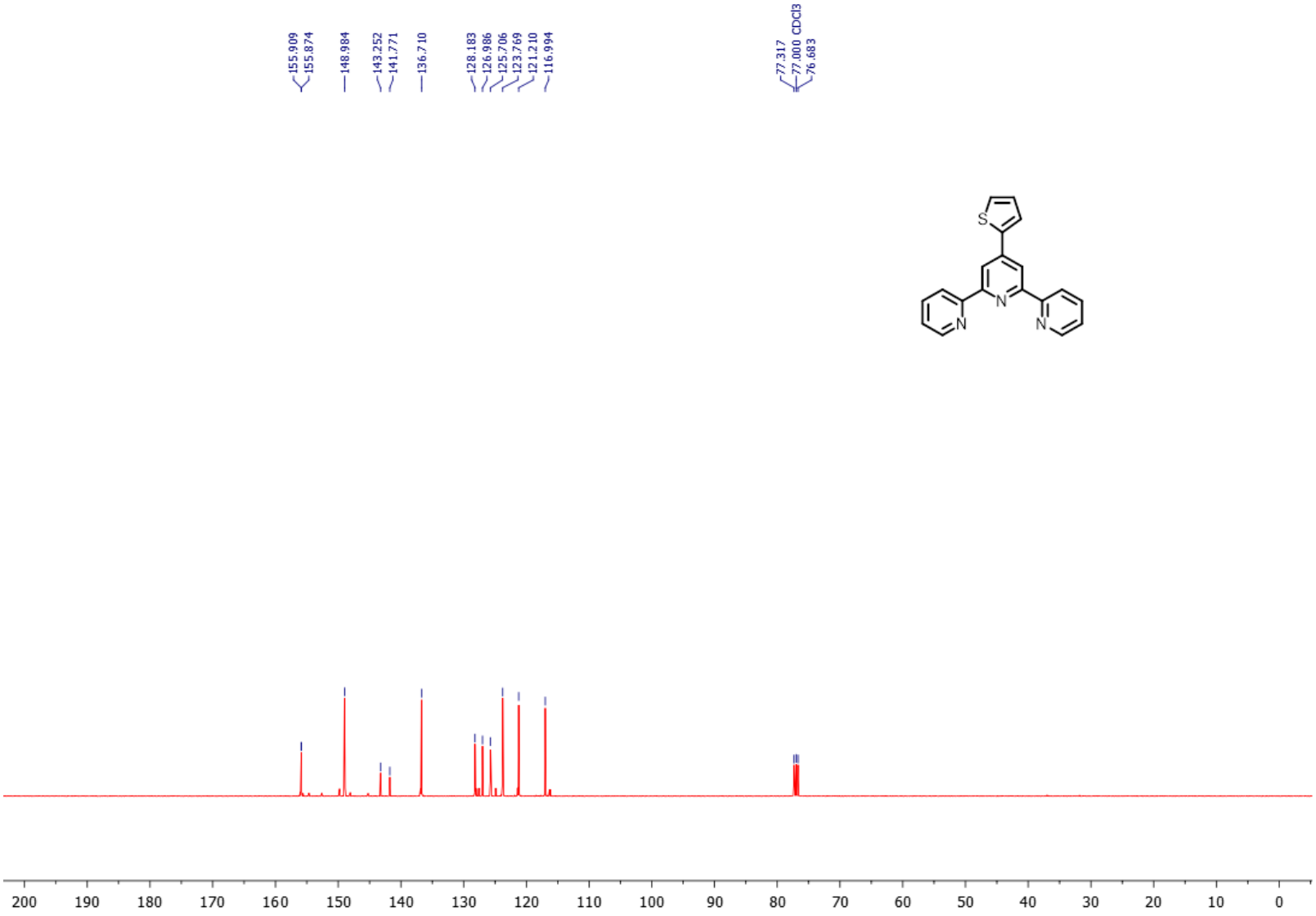
^{1}H NMR spectra of **L1** (25 °C, 400 MHz, $CDCl_3$)



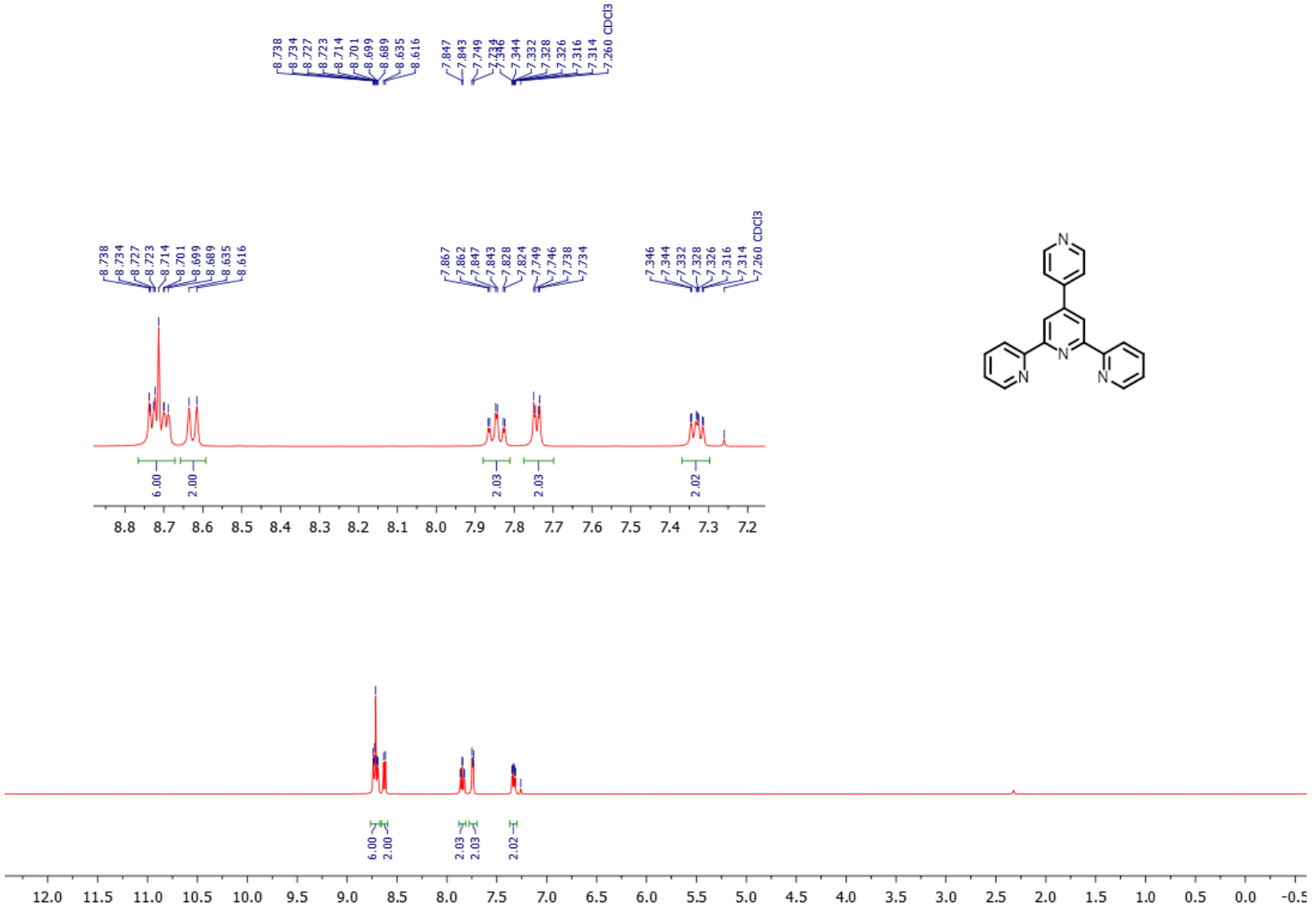
^{13}C NMR spectra of **L1** (25 °C, 100 MHz, $CDCl_3$)



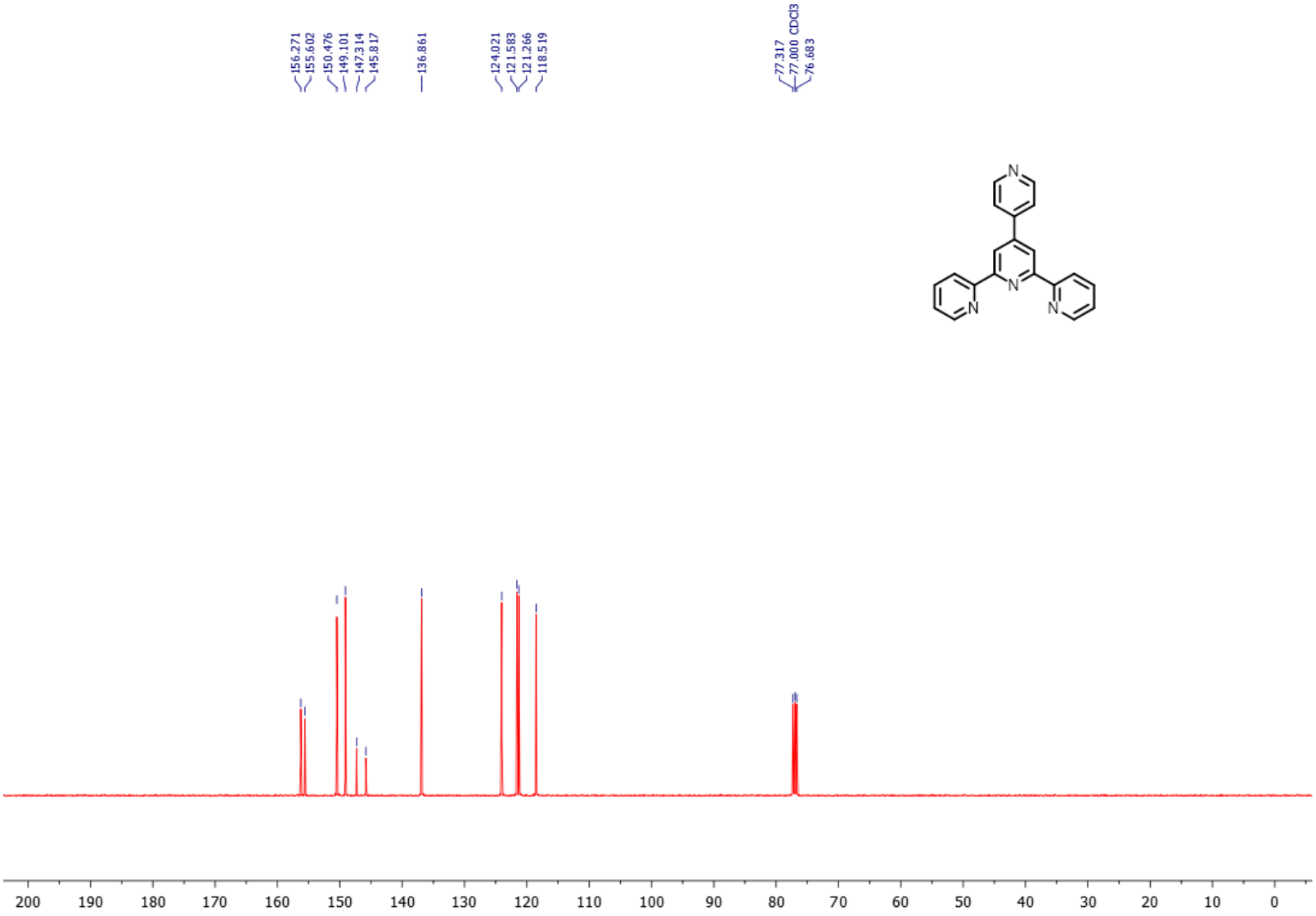
^{1}H NMR spectra of **L2** (25 ^{o}C, 400 MHz, $CDCl_3$)



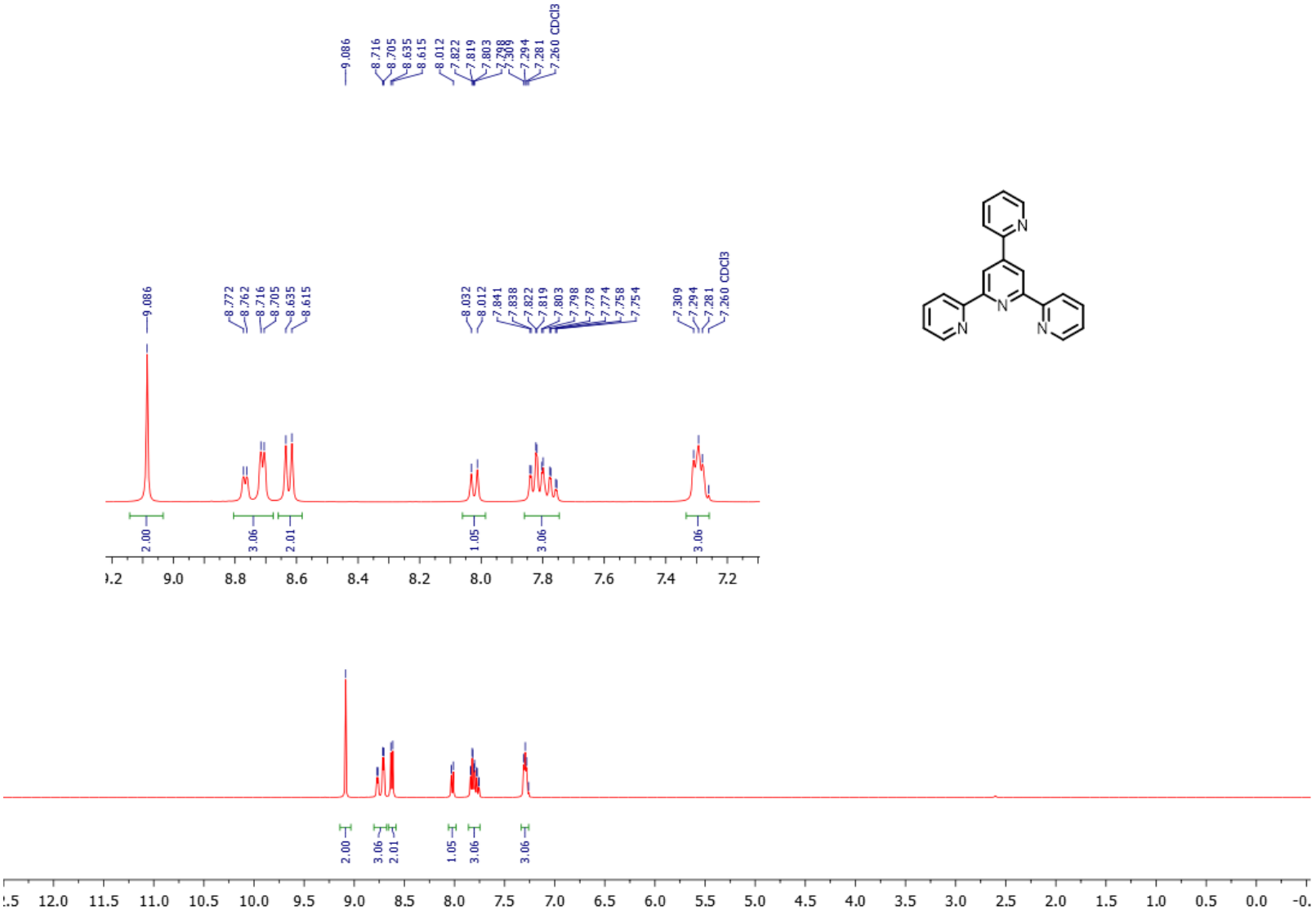
^{13}C NMR spectra of **L2** (25 ºC, 100 MHz, $CDCl_3$)



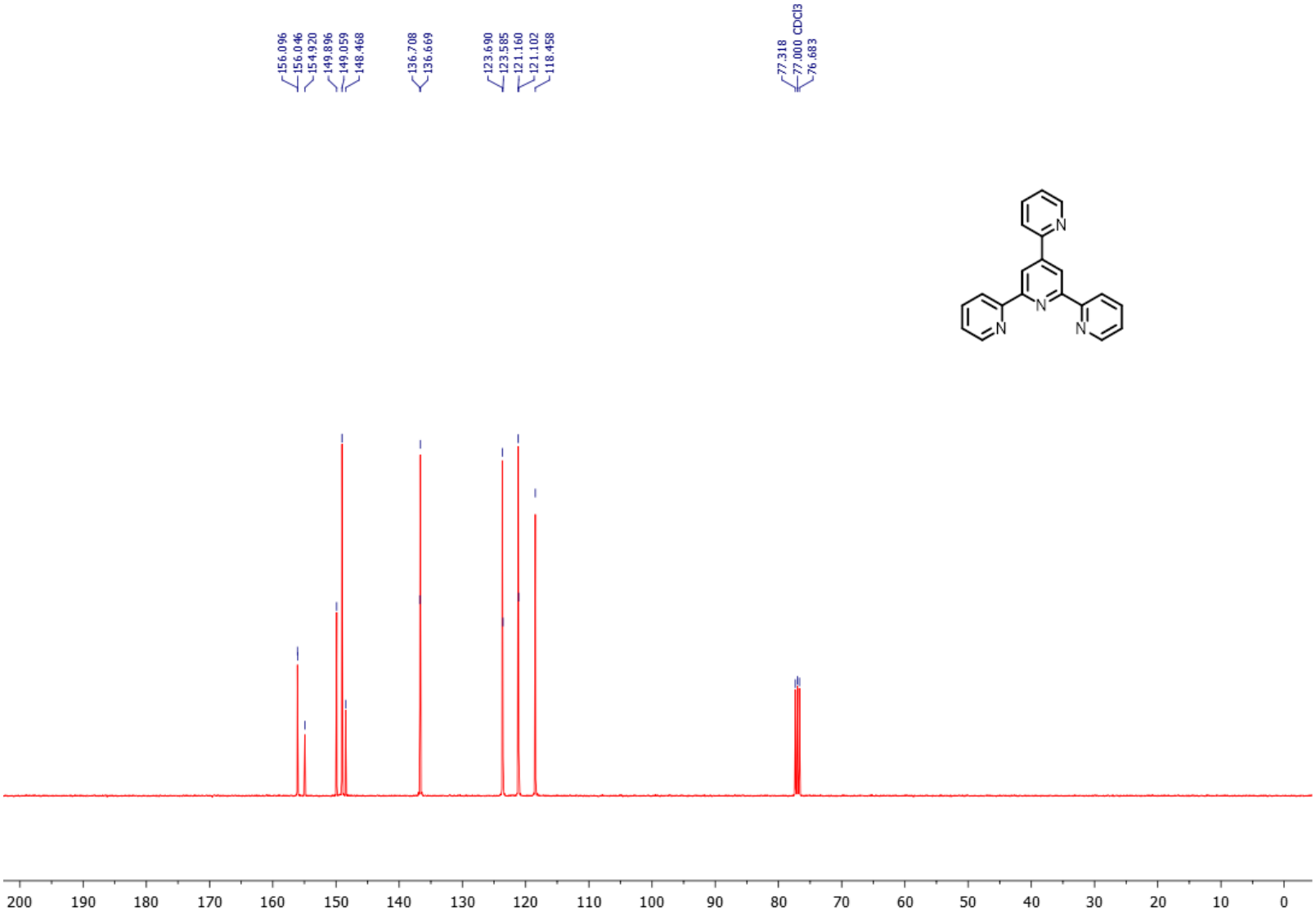
^{1}H NMR spectra of **L4** (25 °C, 400 MHz, $CDCl_3$)



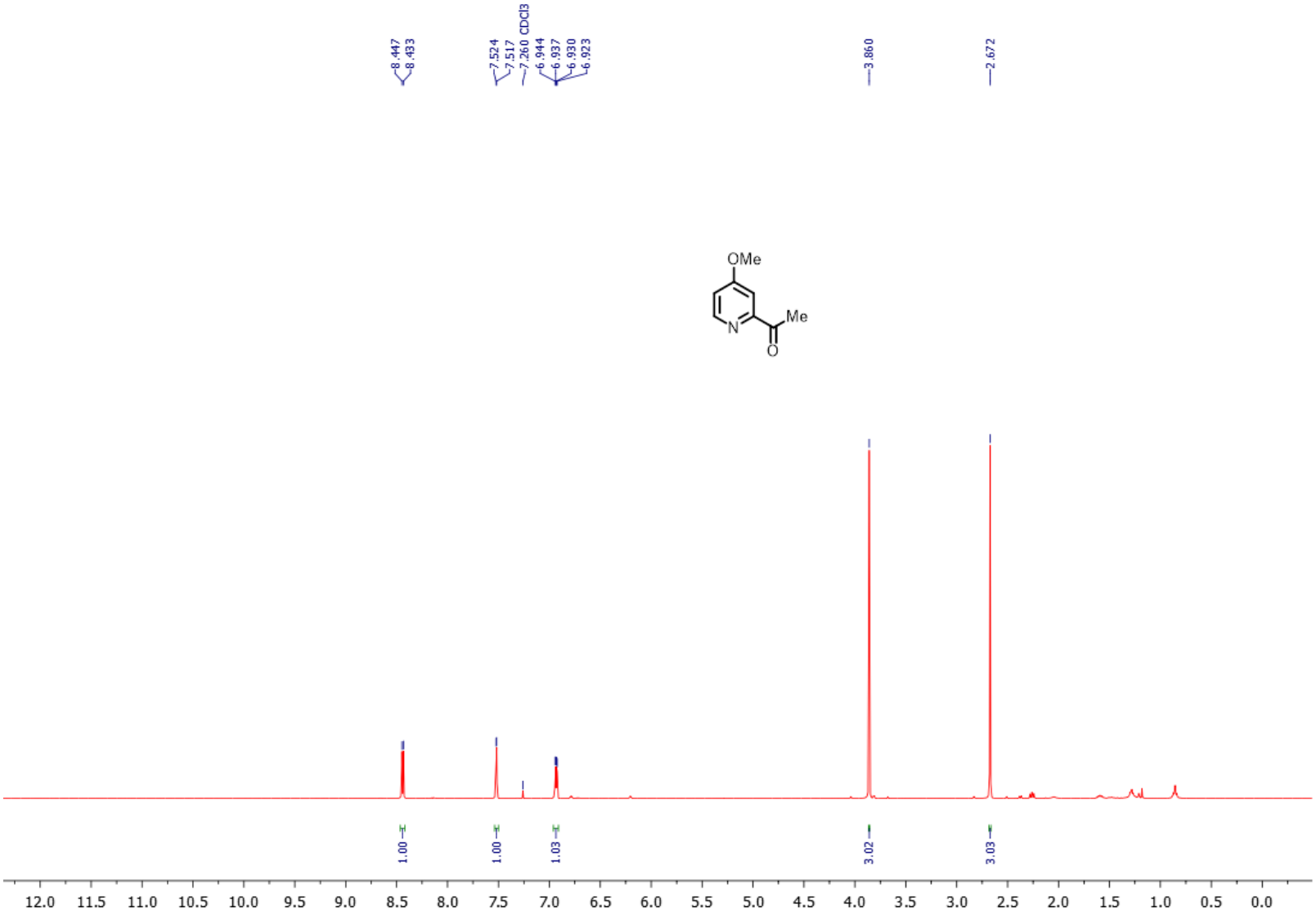
^{13}C NMR spectra of **L4** (25 °C, 100 MHz, $CDCl_3$)



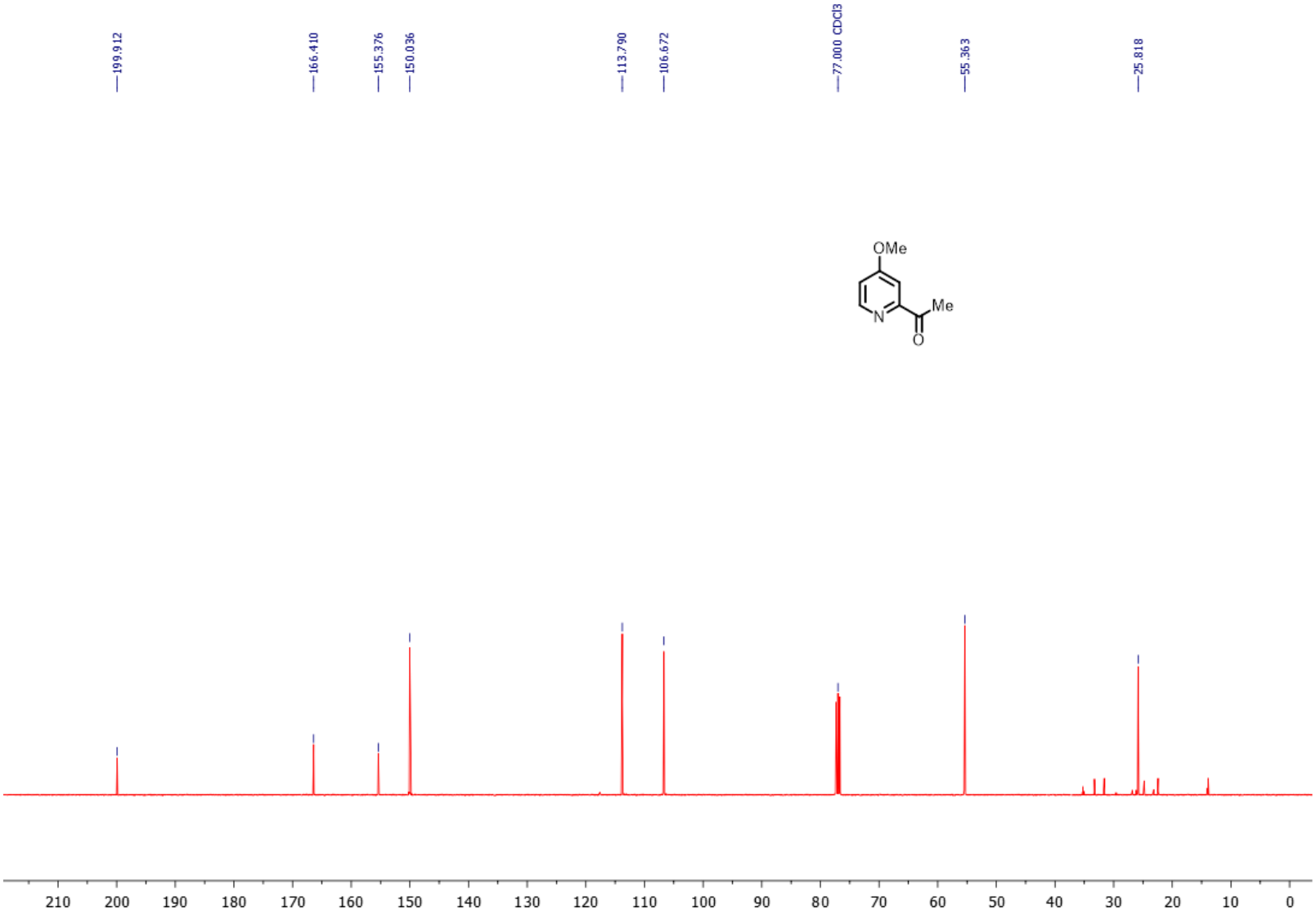
^{1}H NMR spectra of **L5** (25 °C, 400 MHz, $CDCl_3$)



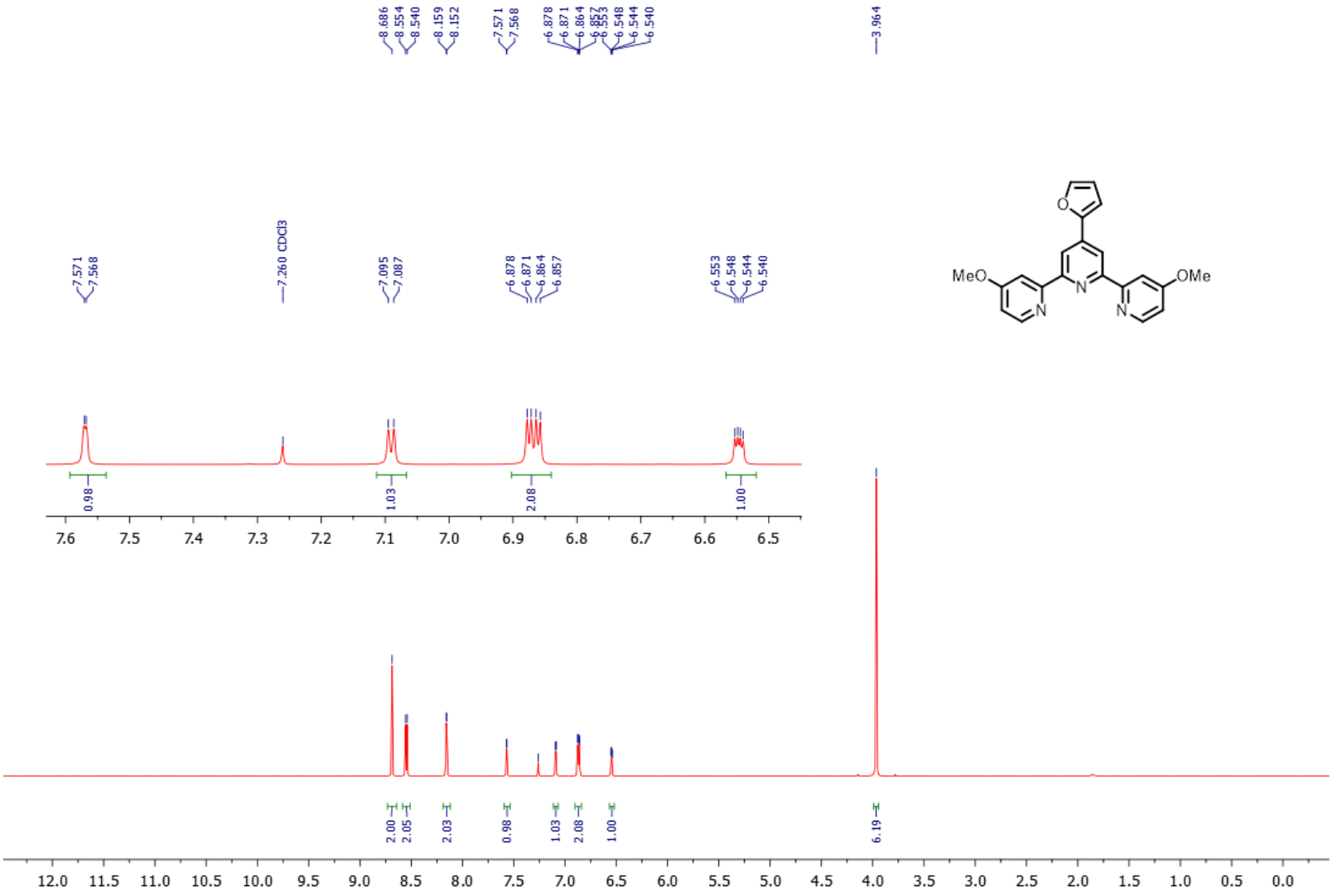
^{13}C NMR spectra of **L5** (25 °C, 100 MHz, $CDCl_3$)



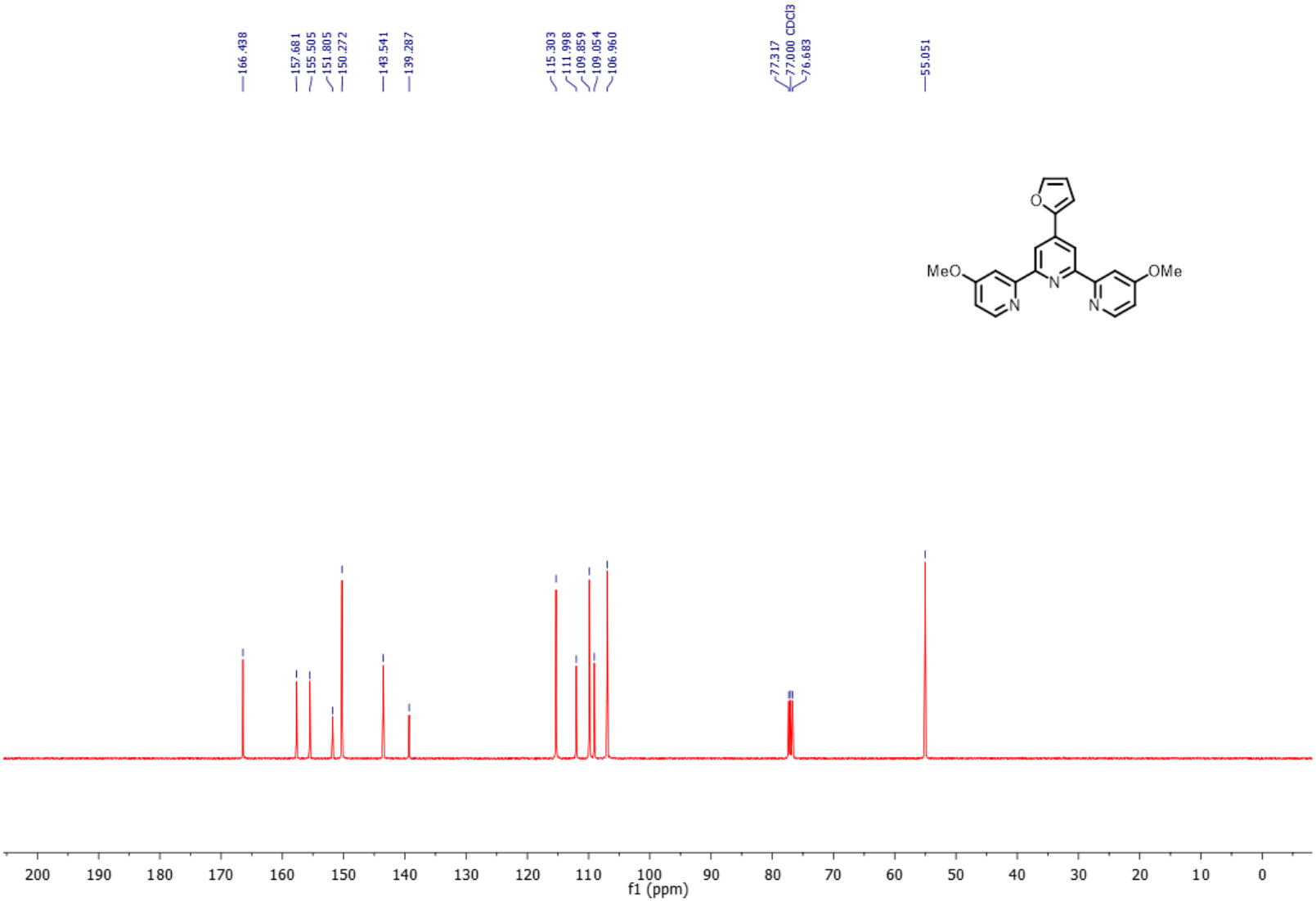
^{1}H NMR spectra of **1-(4-methoxypyridin-2-yl)ethan-1-one** (25 °C, 400 MHz, $CDCl_3$)



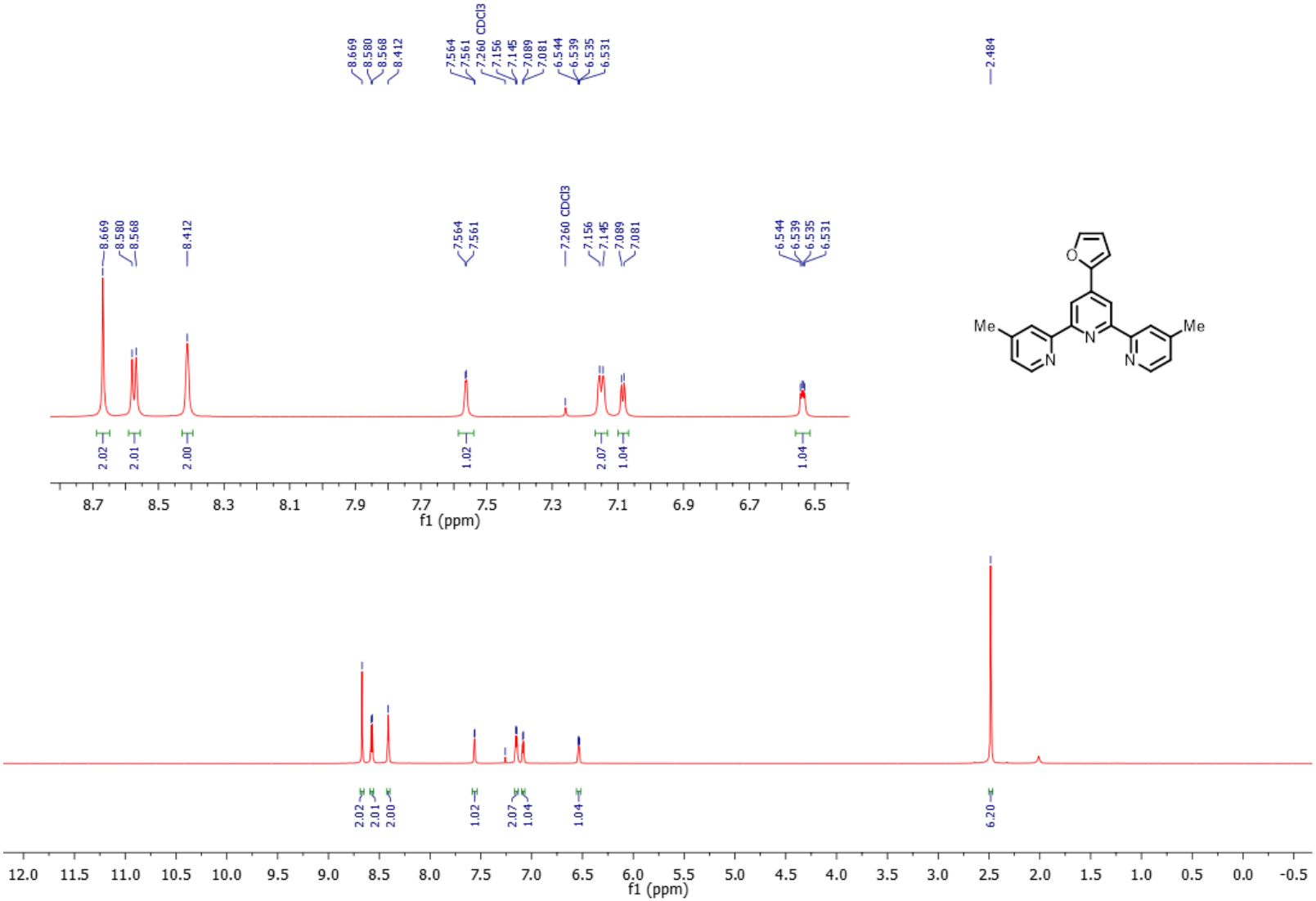
^{13}C NMR spectra of **1-(4-methoxypyridin-2-yl)ethan-1-one** (25 ^{o}C, 100 MHz, $CDCl_3$)



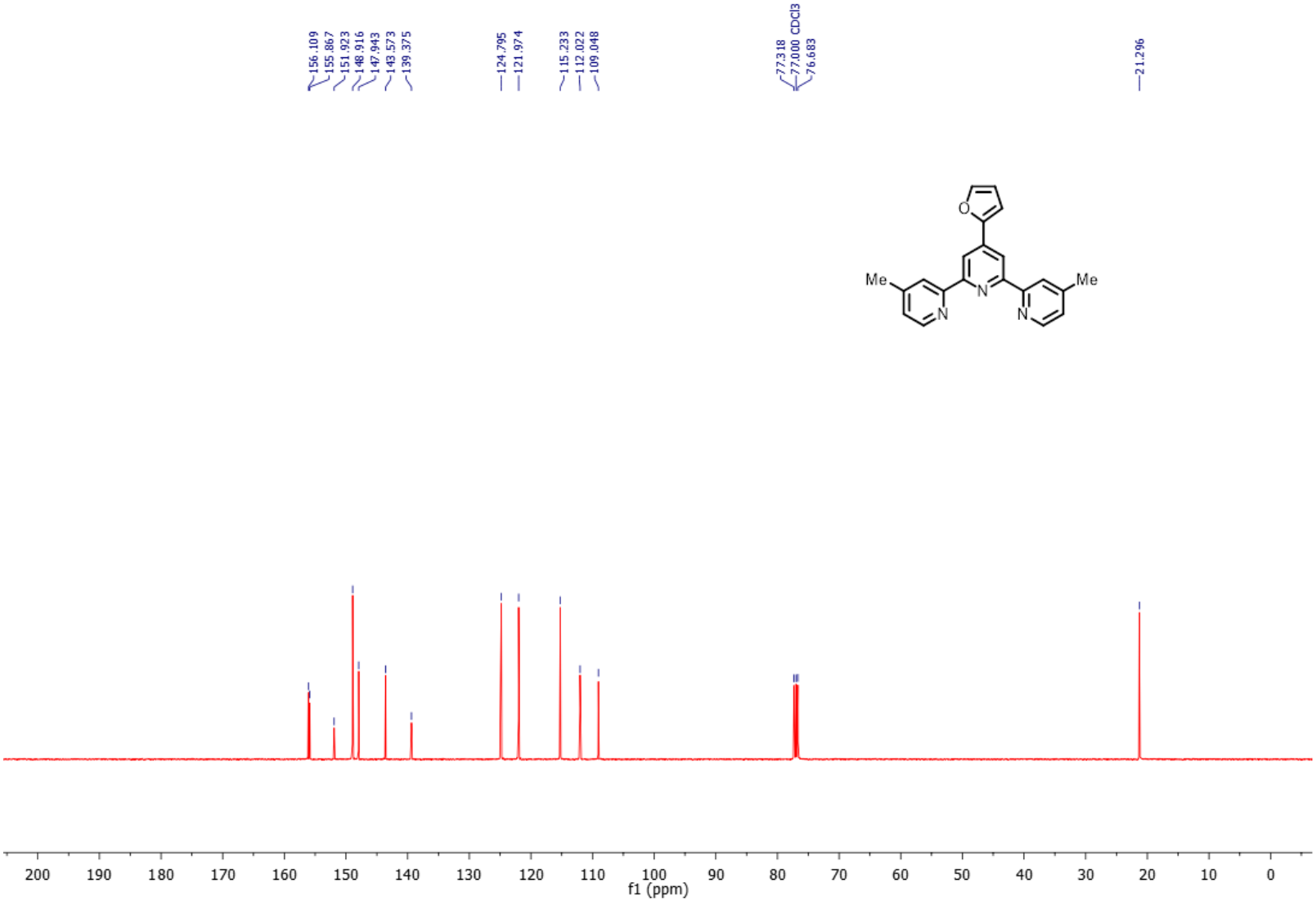
^{1}H NMR spectra of **L6** (25 °C, 400 MHz, $CDCl_3$)



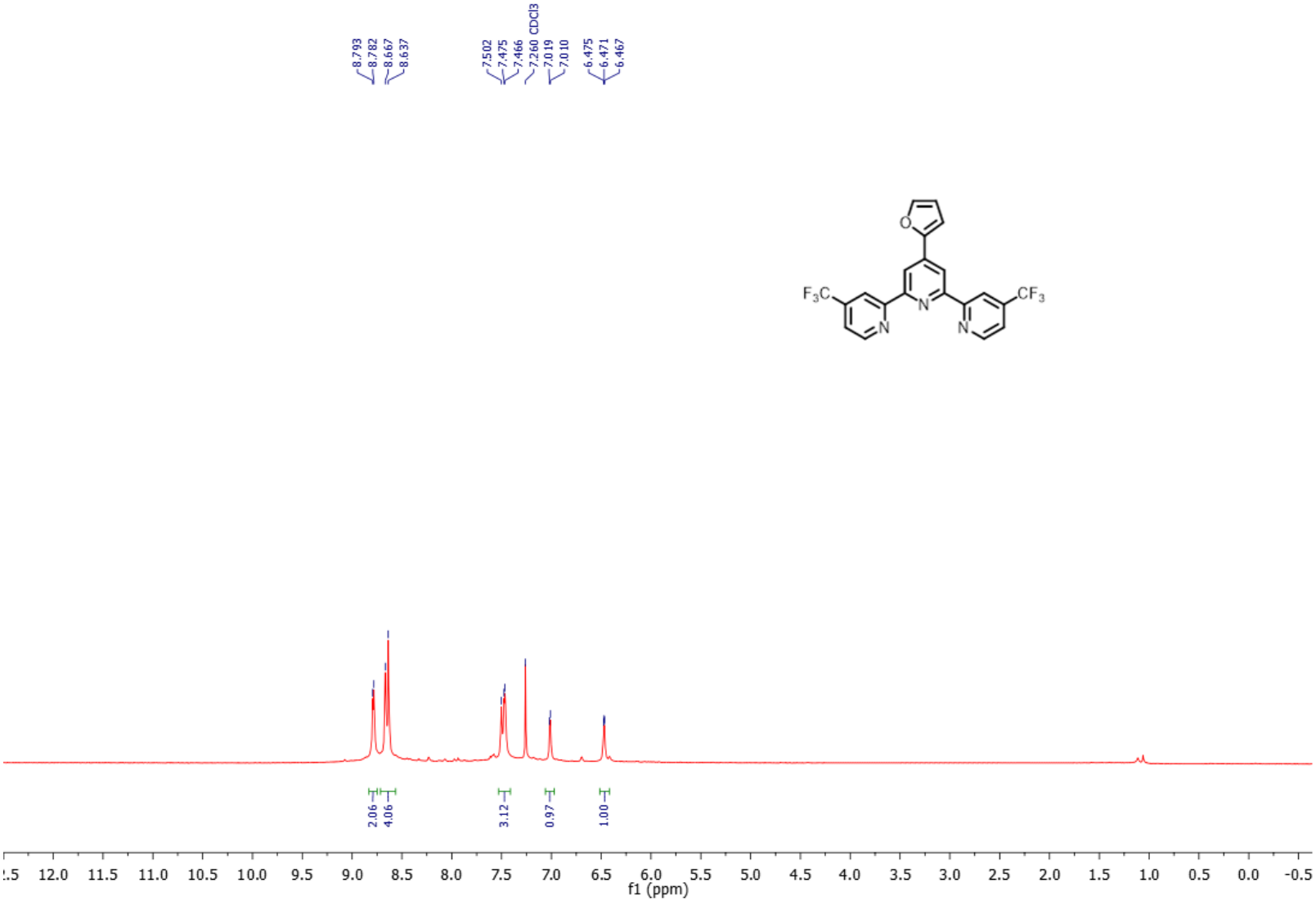
^{13}C NMR spectra of **L6** (25 °C, 100 MHz, $CDCl_3$)



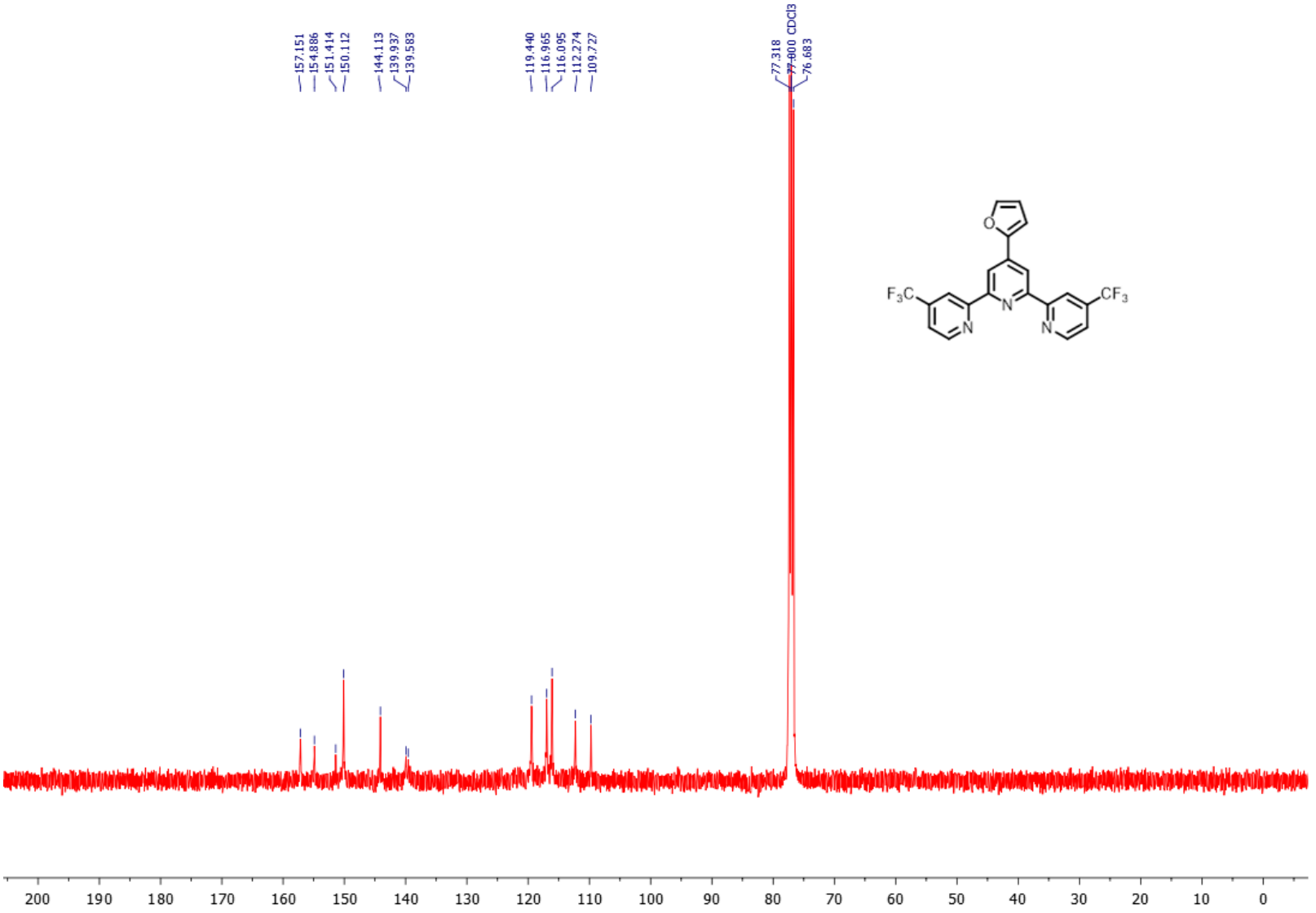
^{1}H NMR spectra of **L7** (25 °C, 400 MHz, $CDCl_3$)



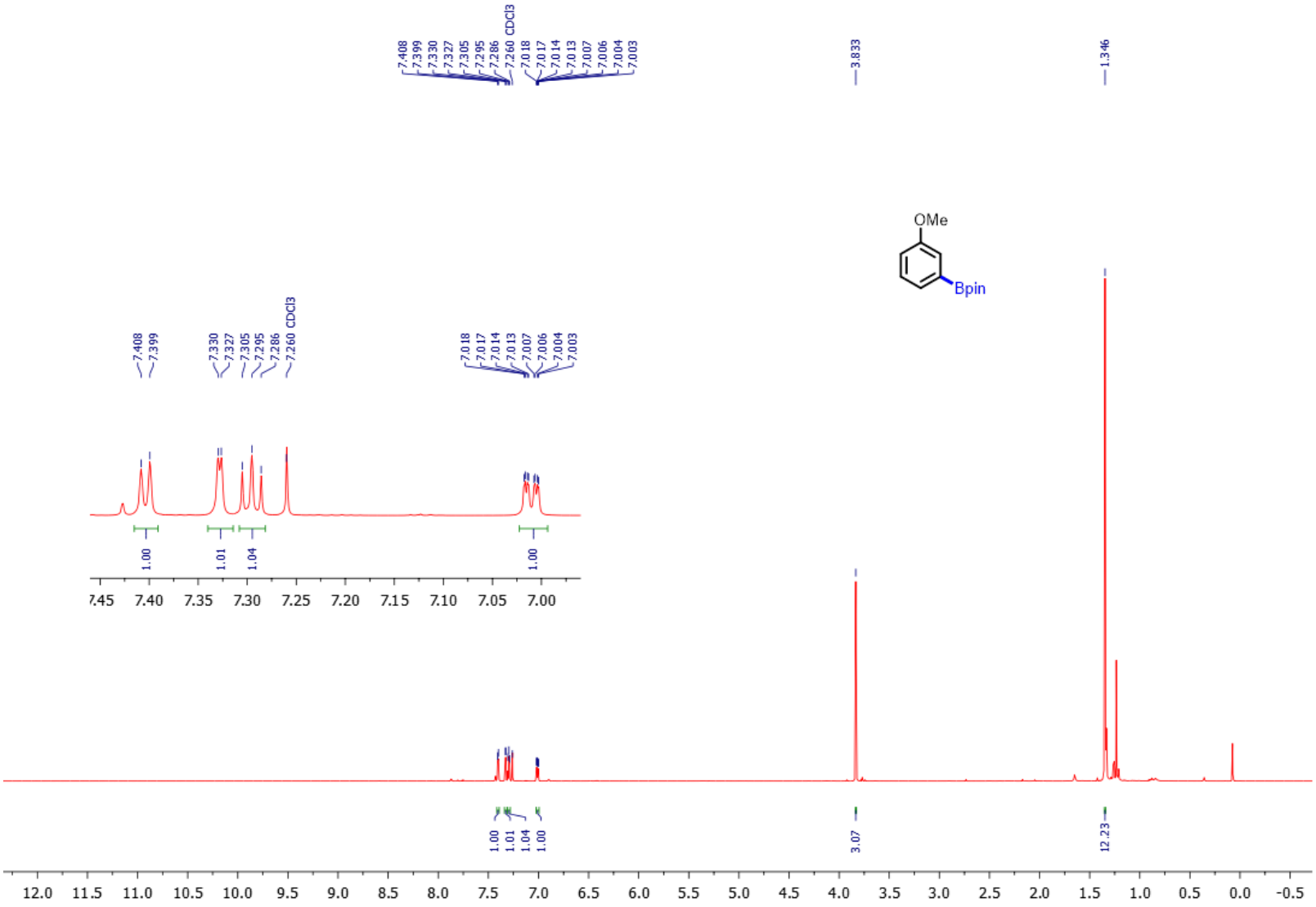
^{13}C NMR spectra of **L7** (25 °C, 100 MHz, $CDCl_3$)



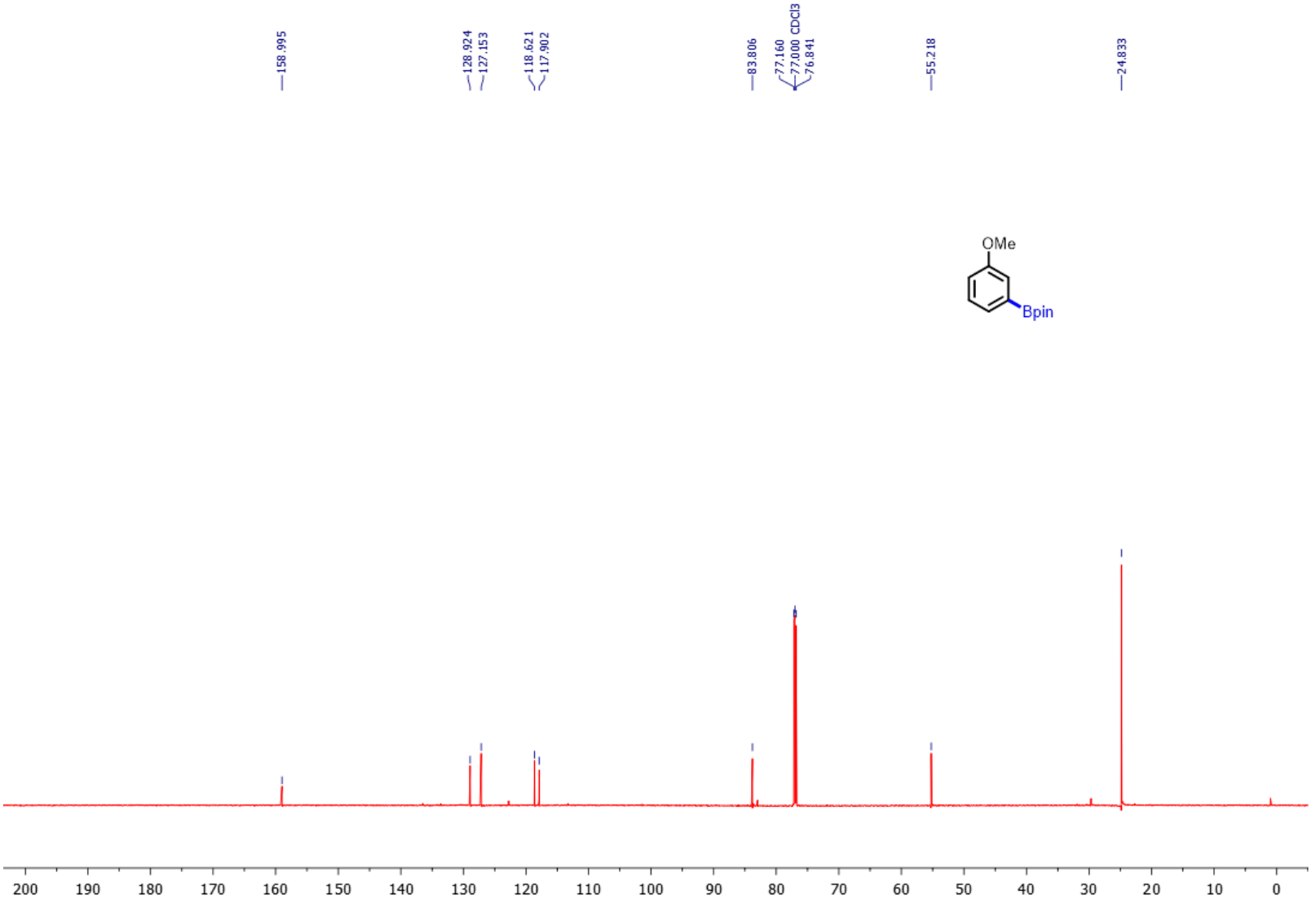
^{1}H NMR spectra of **L8** (25 °C, 400 MHz, $CDCl_3$)



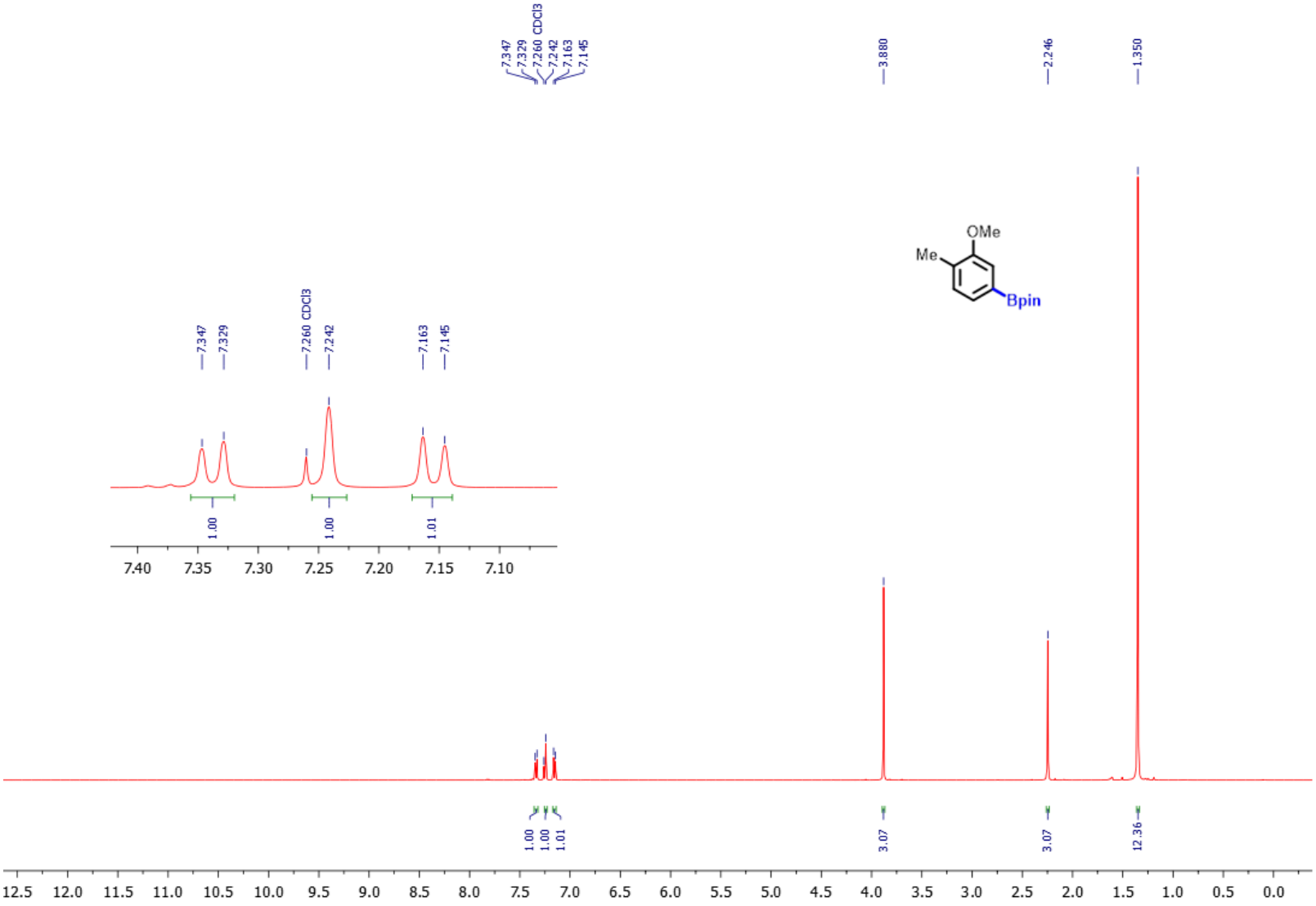
^{13}C NMR spectra of **L8** (25 °C, 100 MHz, $CDCl_3$)



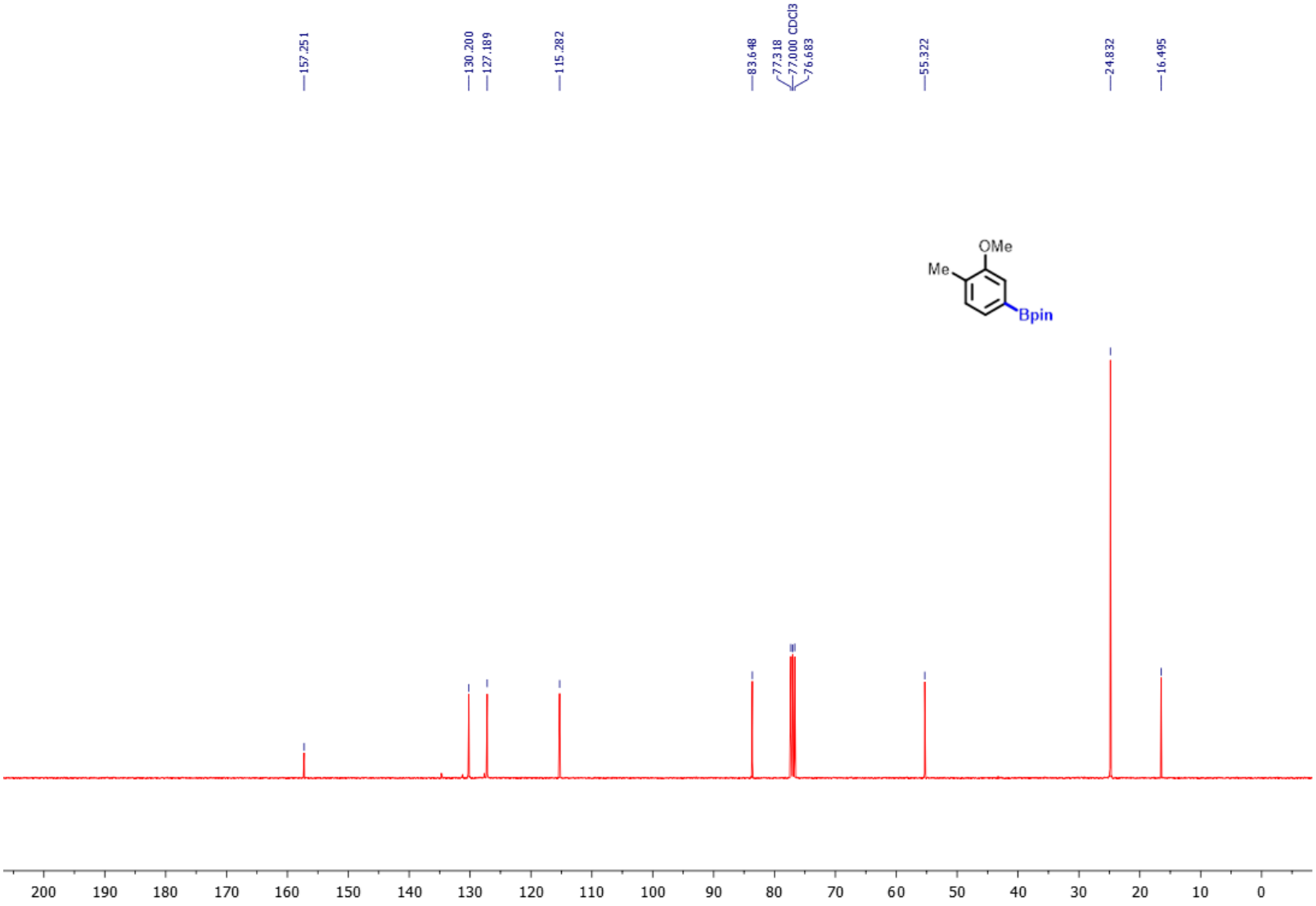
^{1}H NMR spectra of **2a** (25 °C, 800 MHz, $CDCl_3$)



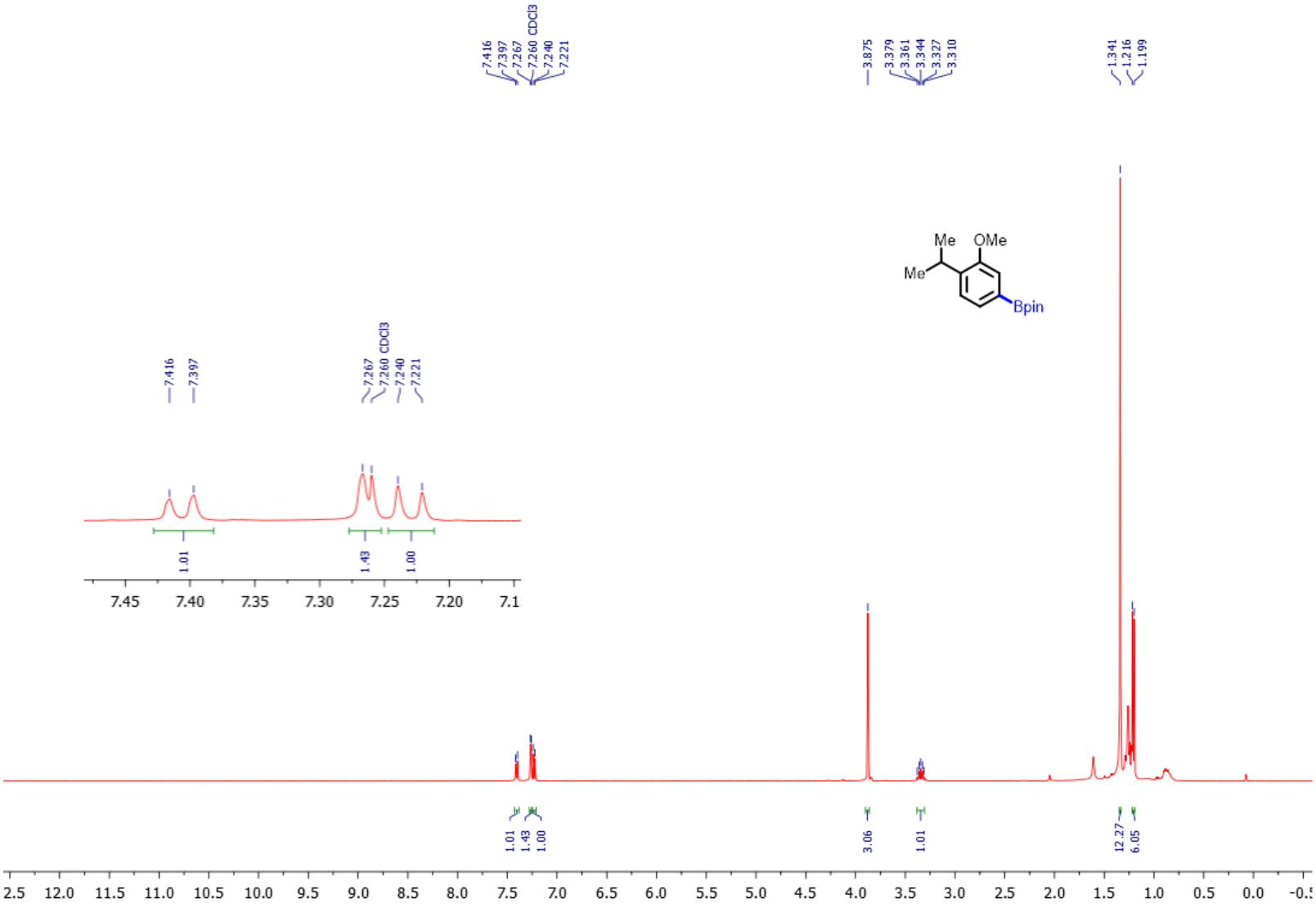
^{13}C NMR spectra of **2a** (25 °C, 200 MHz, $CDCl_3$)



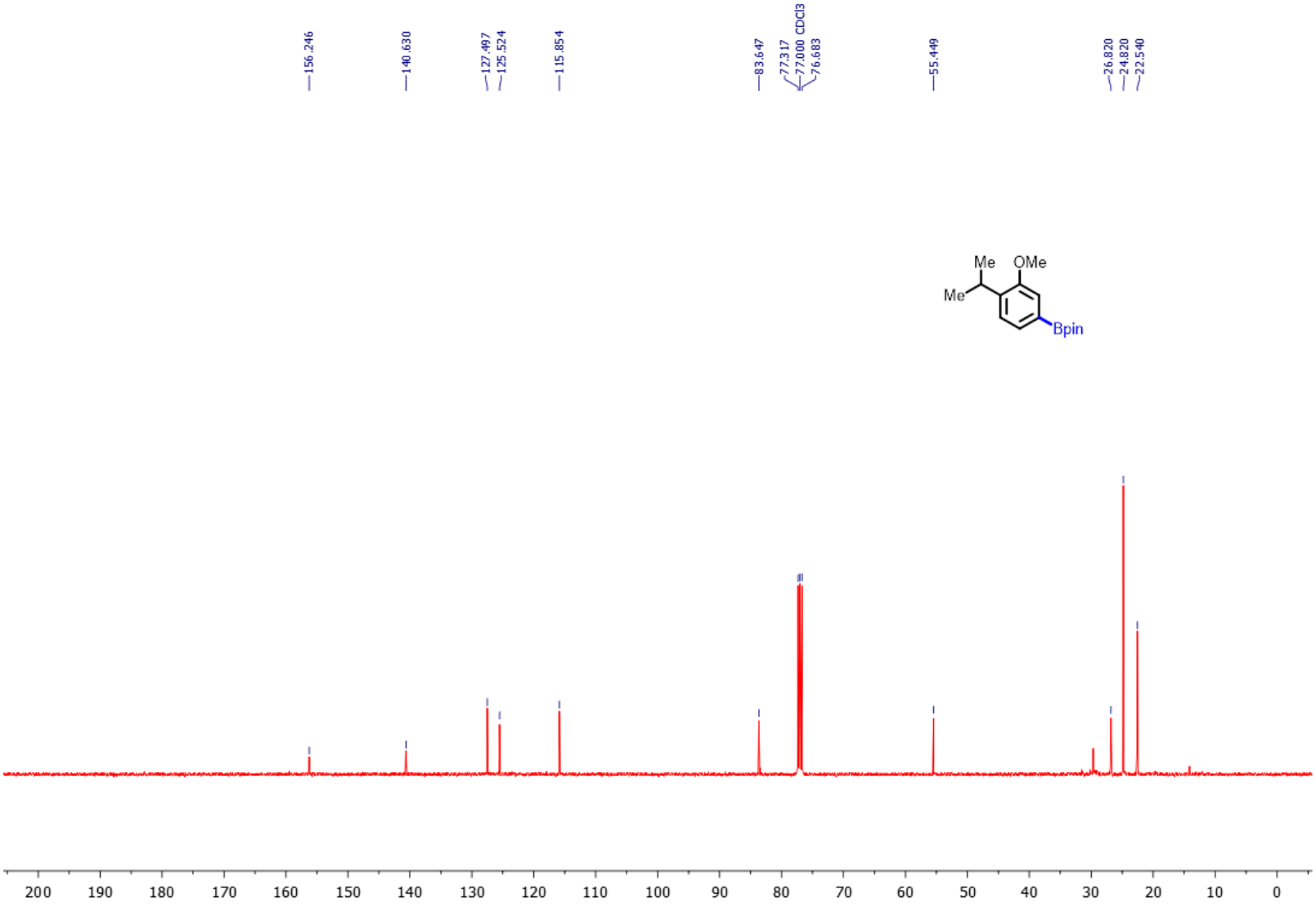
^{1}H NMR spectra of **2b** (25 °C, 400 MHz, $CDCl_3$)



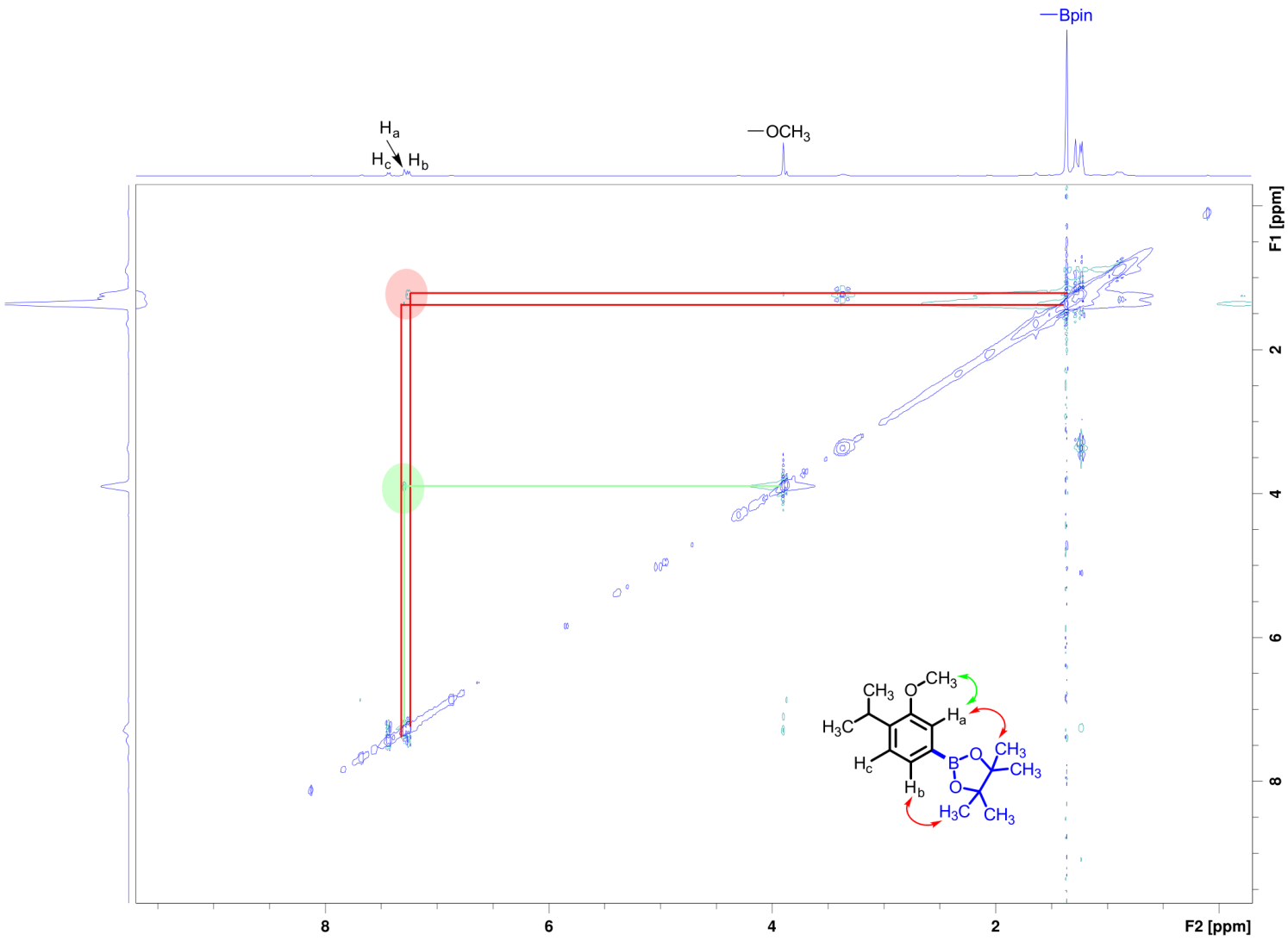
^{13}C NMR spectra of **2b** (25 °C, 100 MHz, $CDCl_3$)



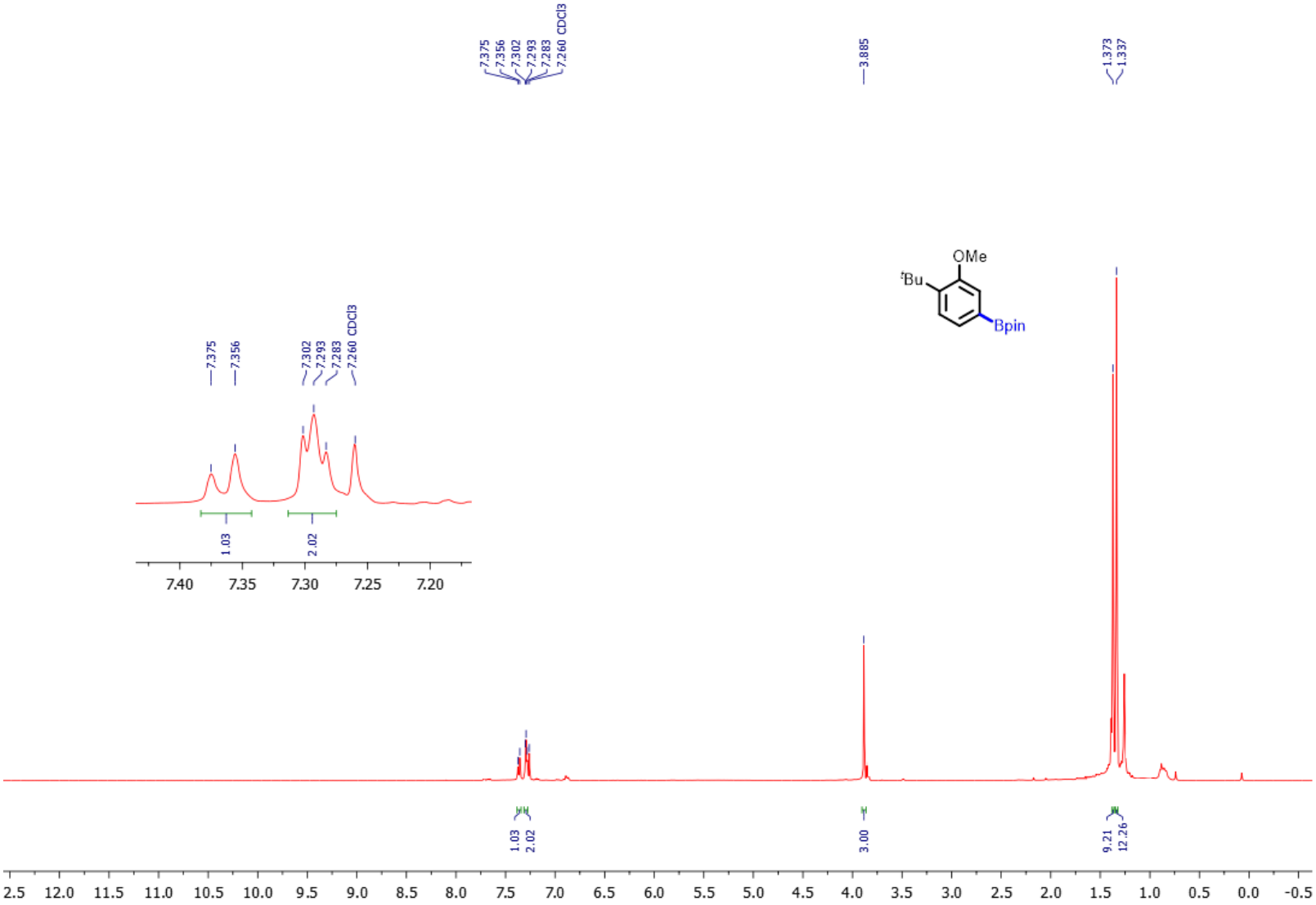
^{1}H NMR spectra of **2c** (25 ^{o}C, 400 MHz, $CDCl_3$)



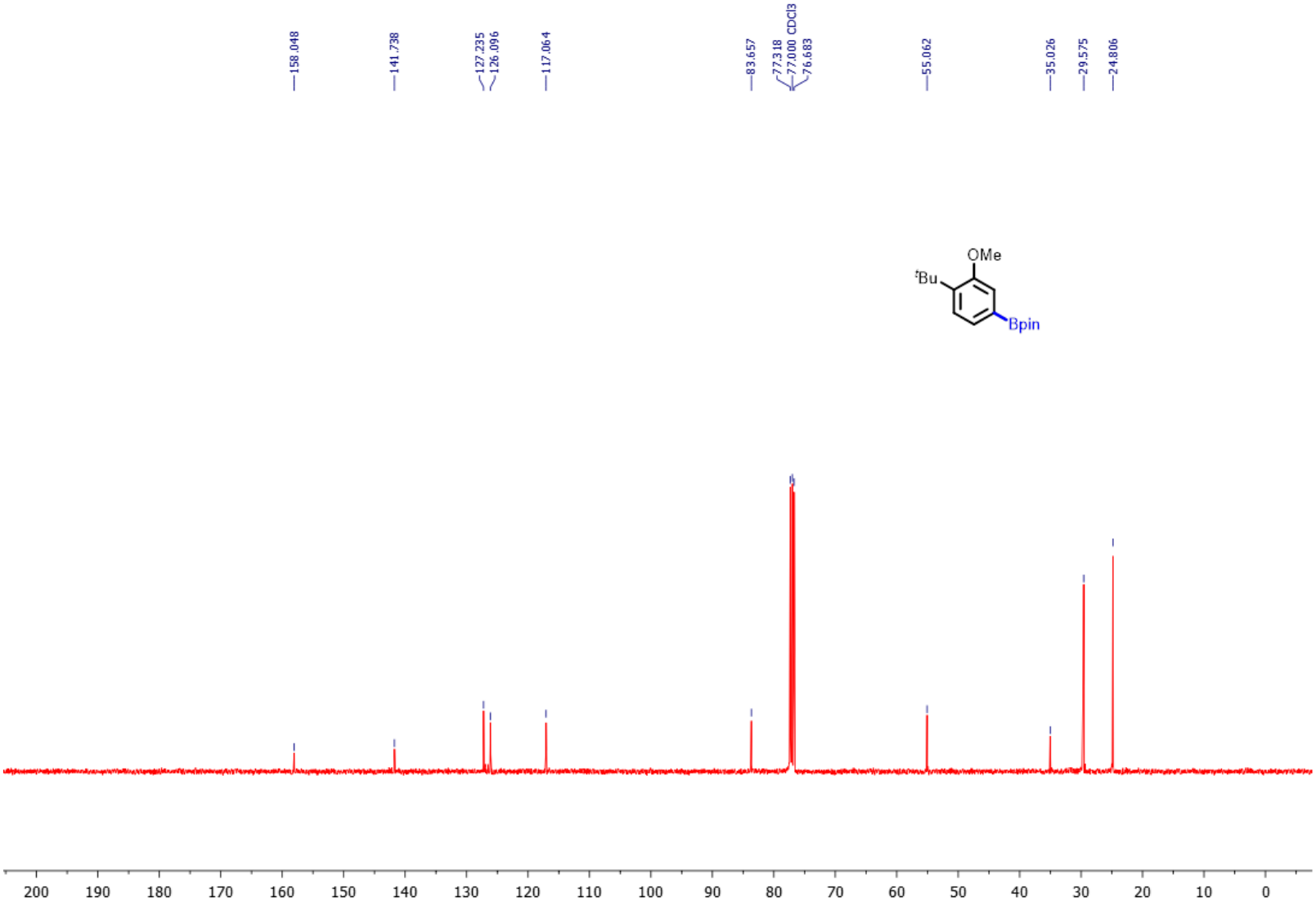
^{13}C NMR spectra of **2c** (25 °C, 100 MHz, $CDCl_3$)



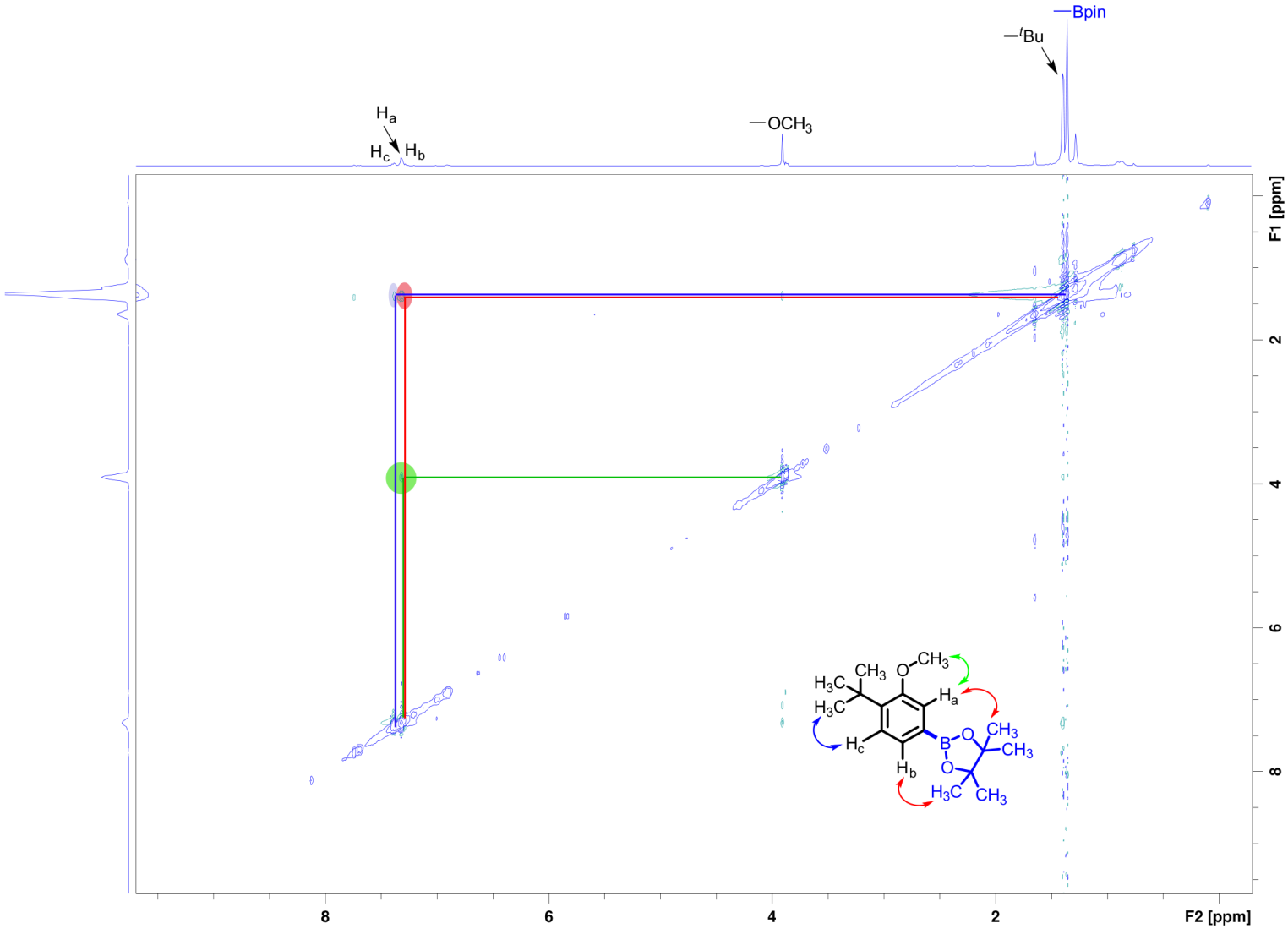
2D NOESY spectra of **2c** (25 °C, 400 MHz, $CDCl_3$)



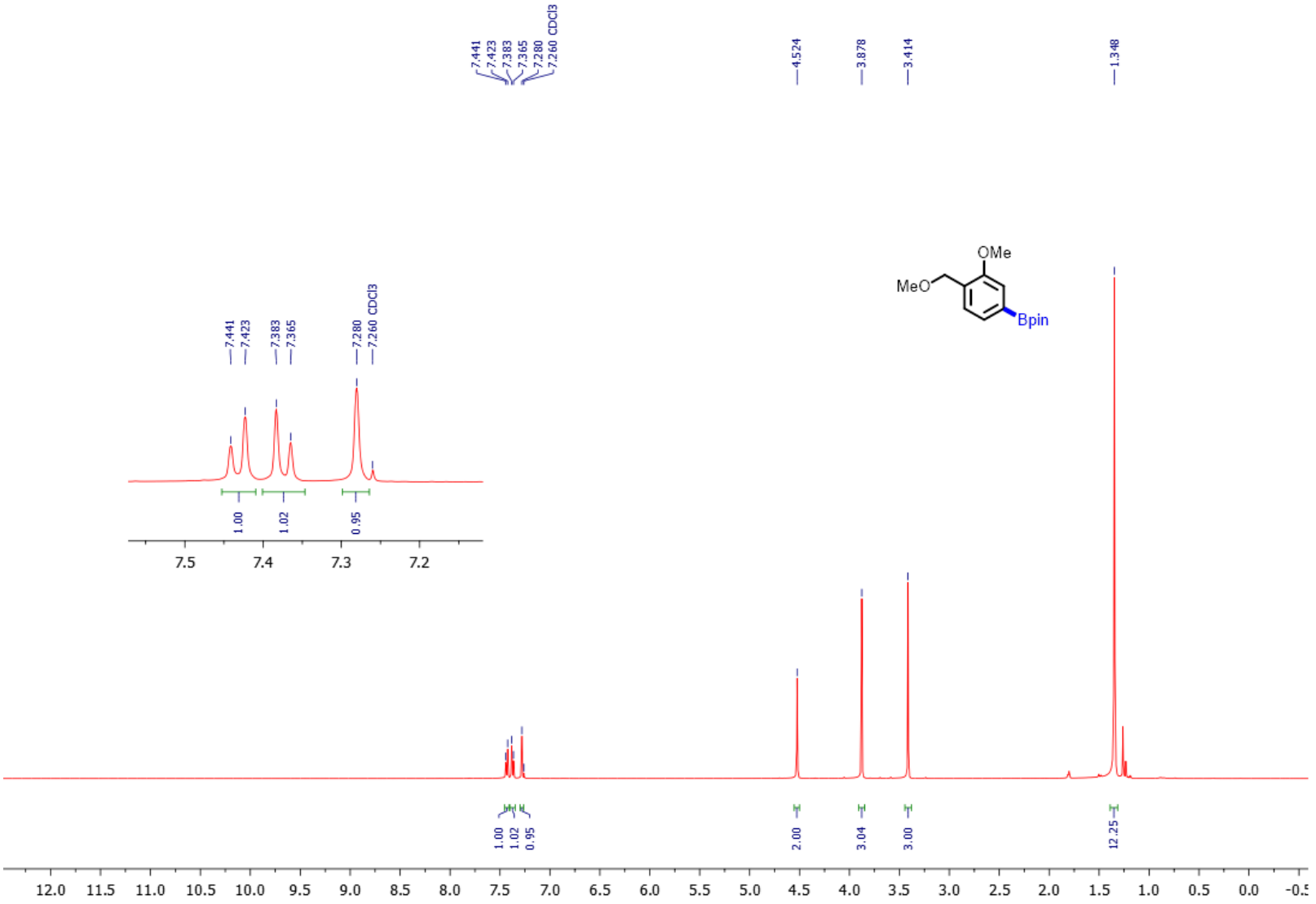
^{1}H NMR spectra of **2d** (25 °C, 400 MHz, $CDCl_3$)



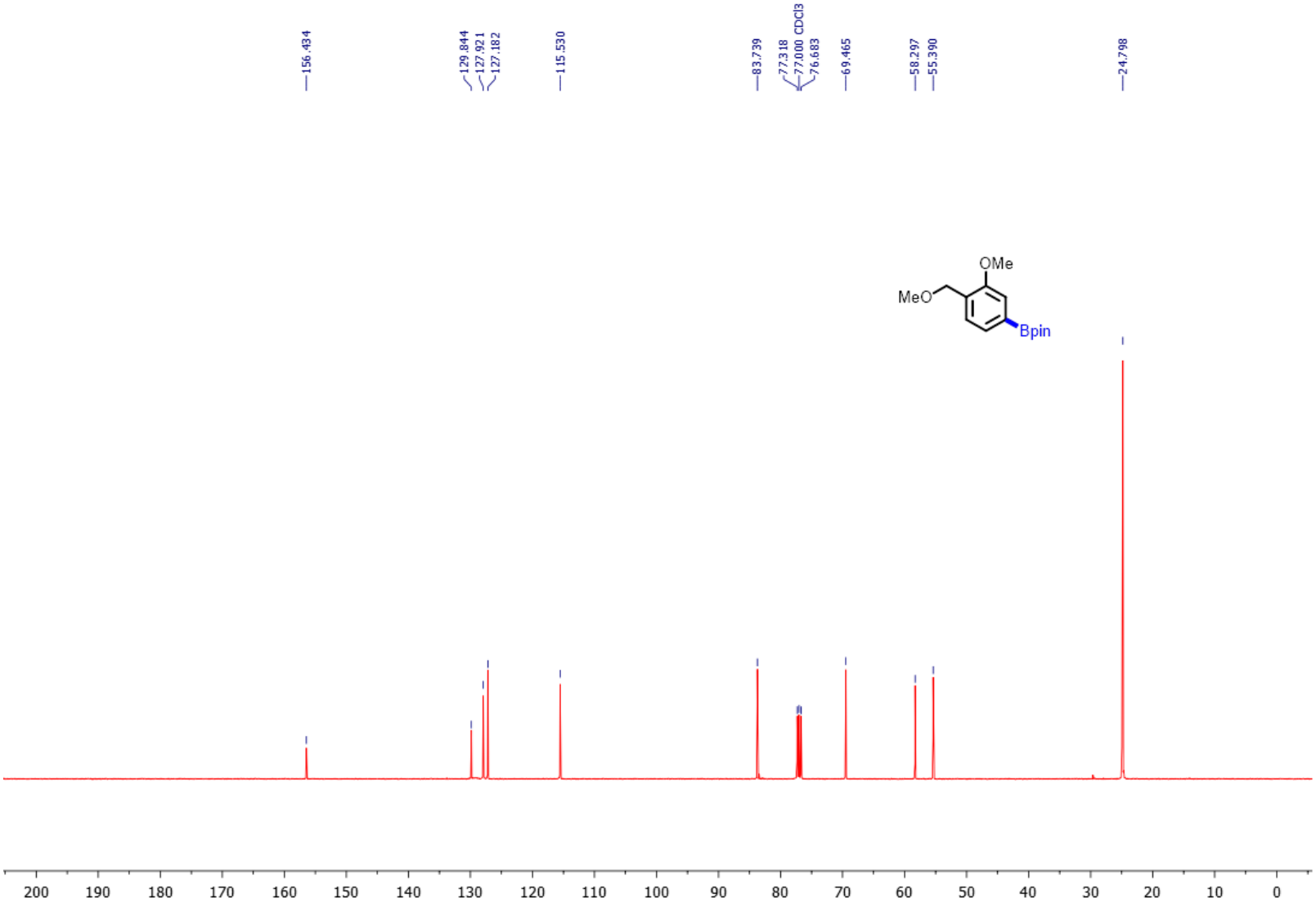
^{13}C NMR spectra of **2d** (25 °C, 100 MHz, $CDCl_3$)



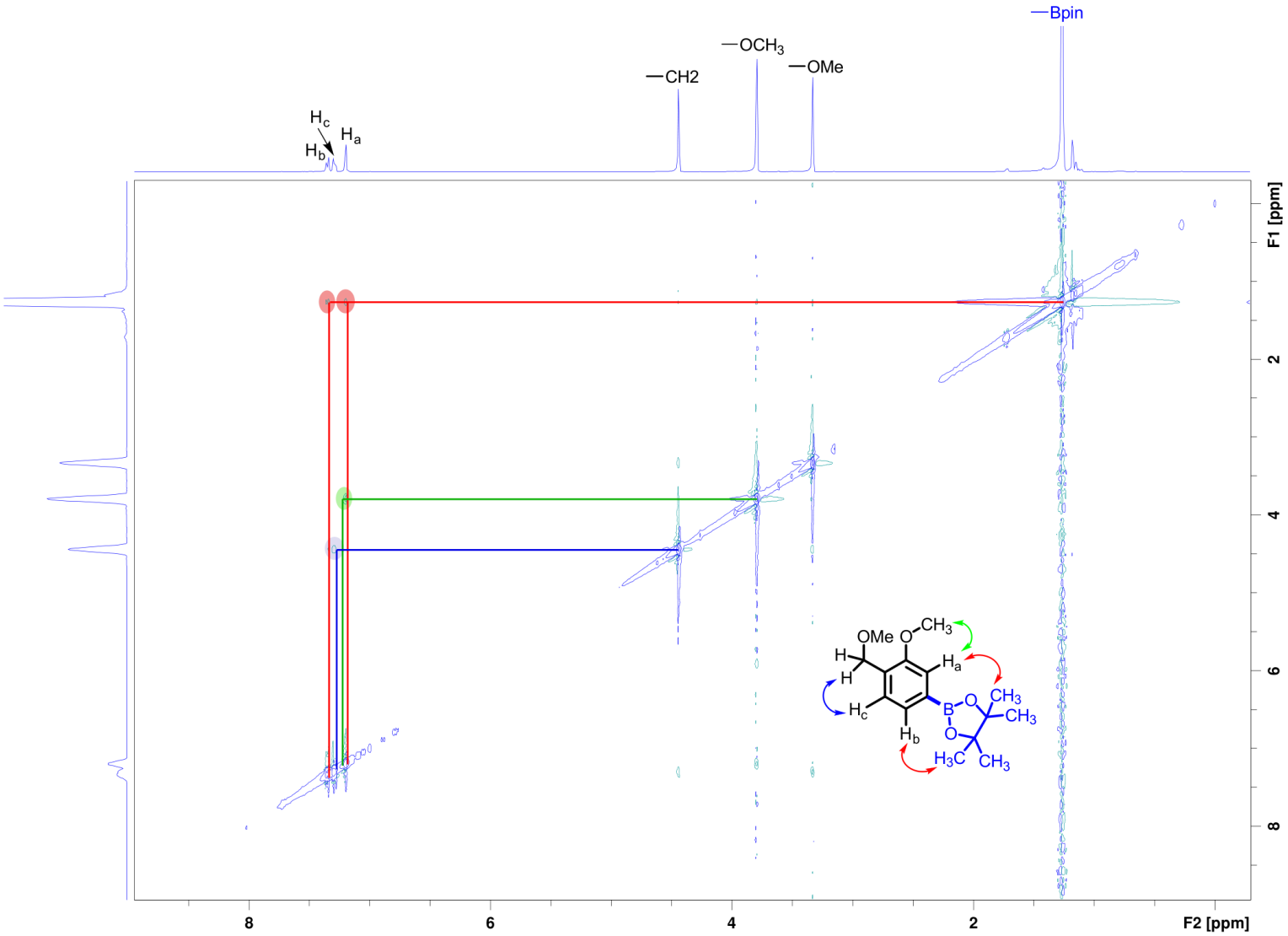
2D NOESY spectra of **2d** (25 ºC, 400 MHz, $CDCl_3$)



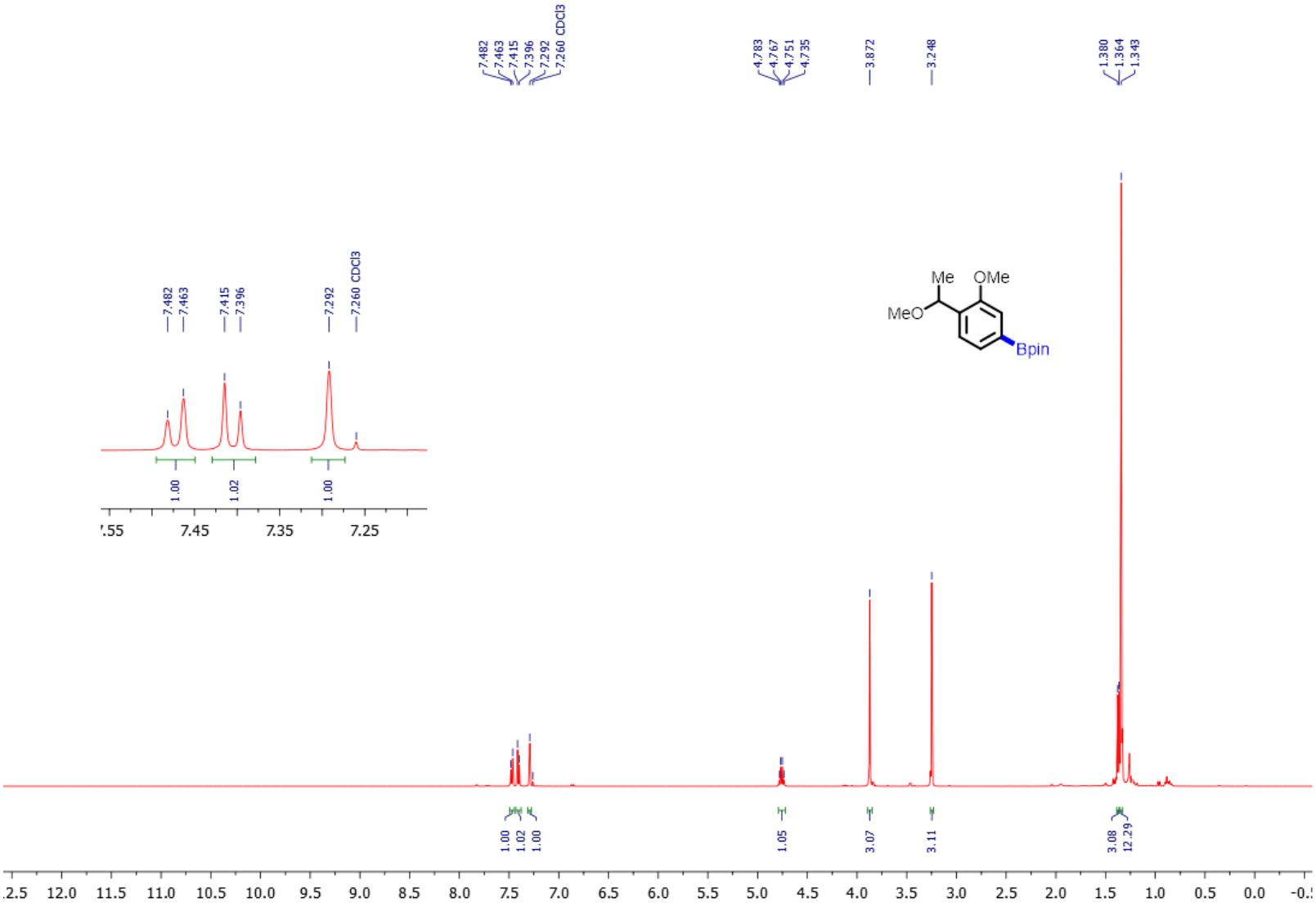
^{1}H NMR spectra of **2e** (25 °C, 400 MHz, $CDCl_3$)



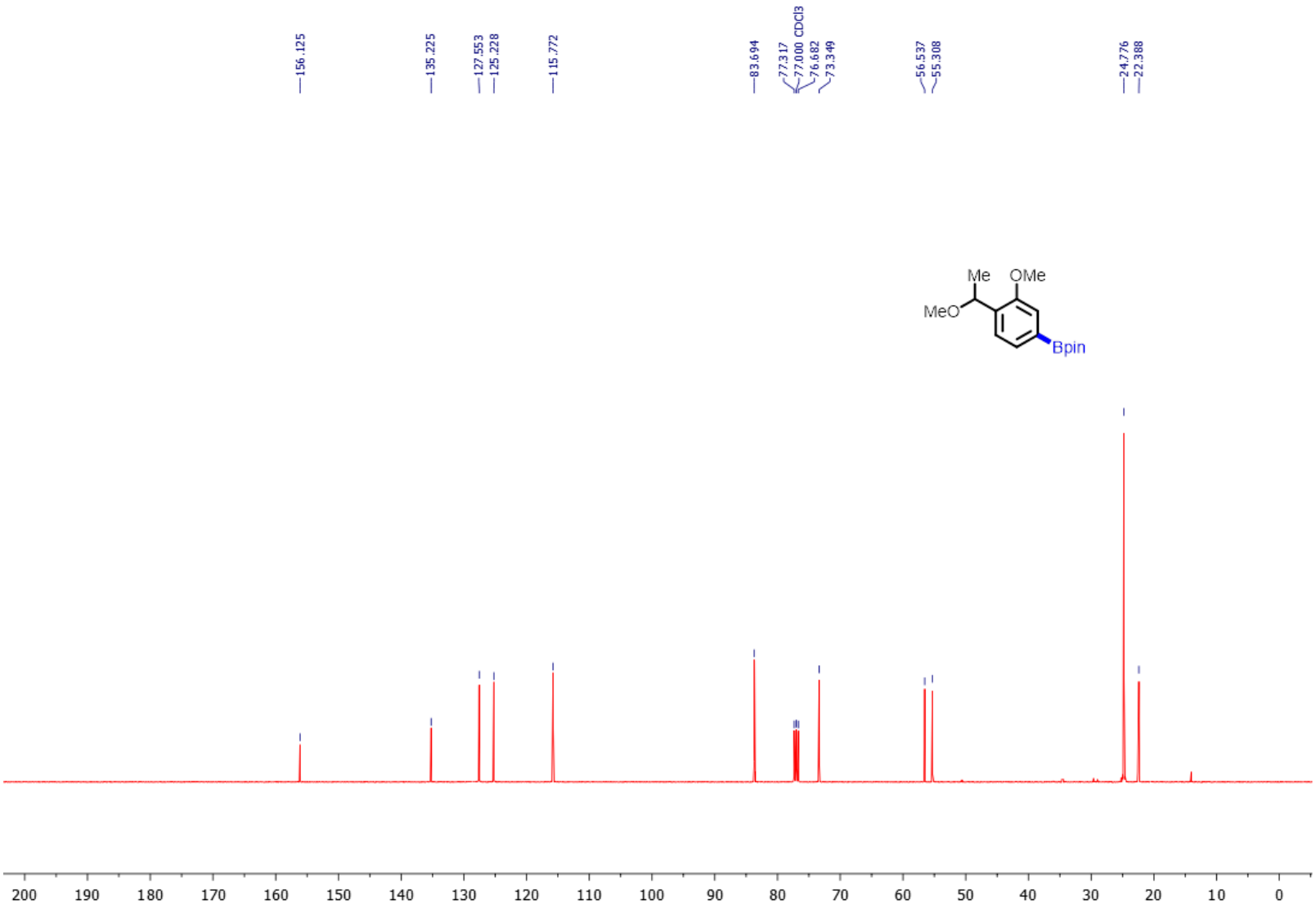
^{13}C NMR spectra of **2e** (25 °C, 100 MHz, $CDCl_3$)



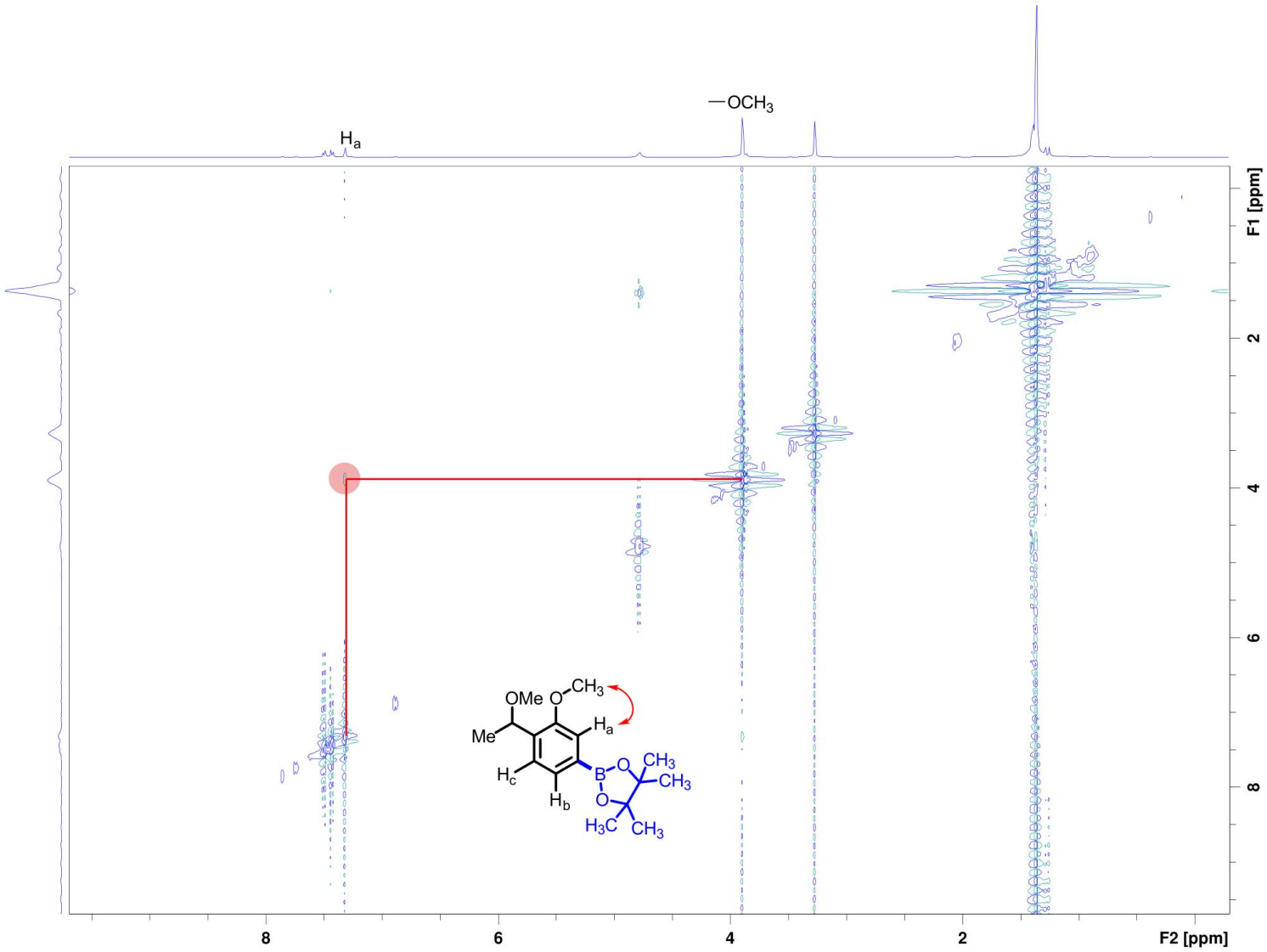
2D NOESY spectra of **2e** (25 °C, 400 MHz, $CDCl_3$)



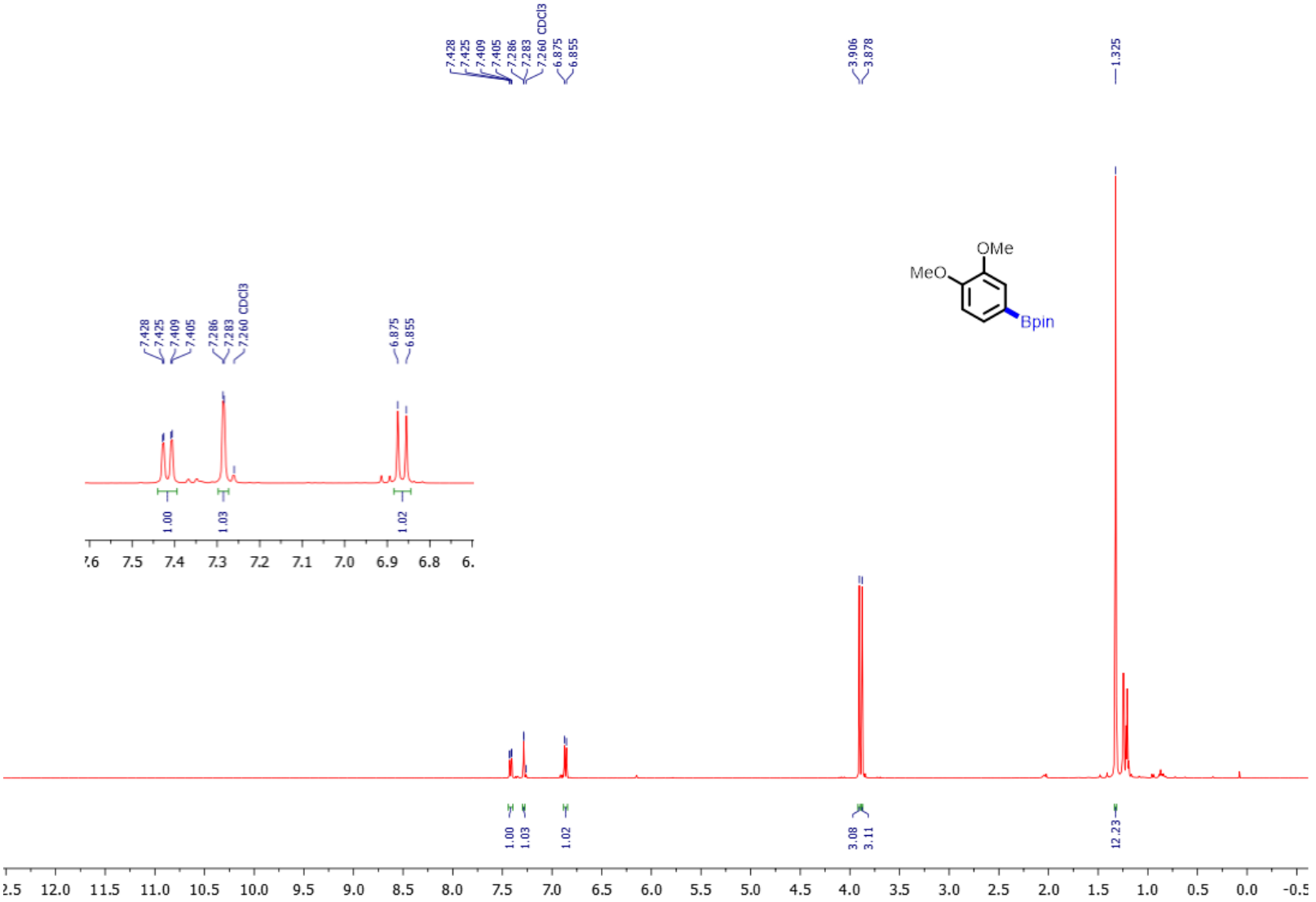
^{1}H NMR spectra of **2f** (25 °C, 400 MHz, $CDCl_3$)



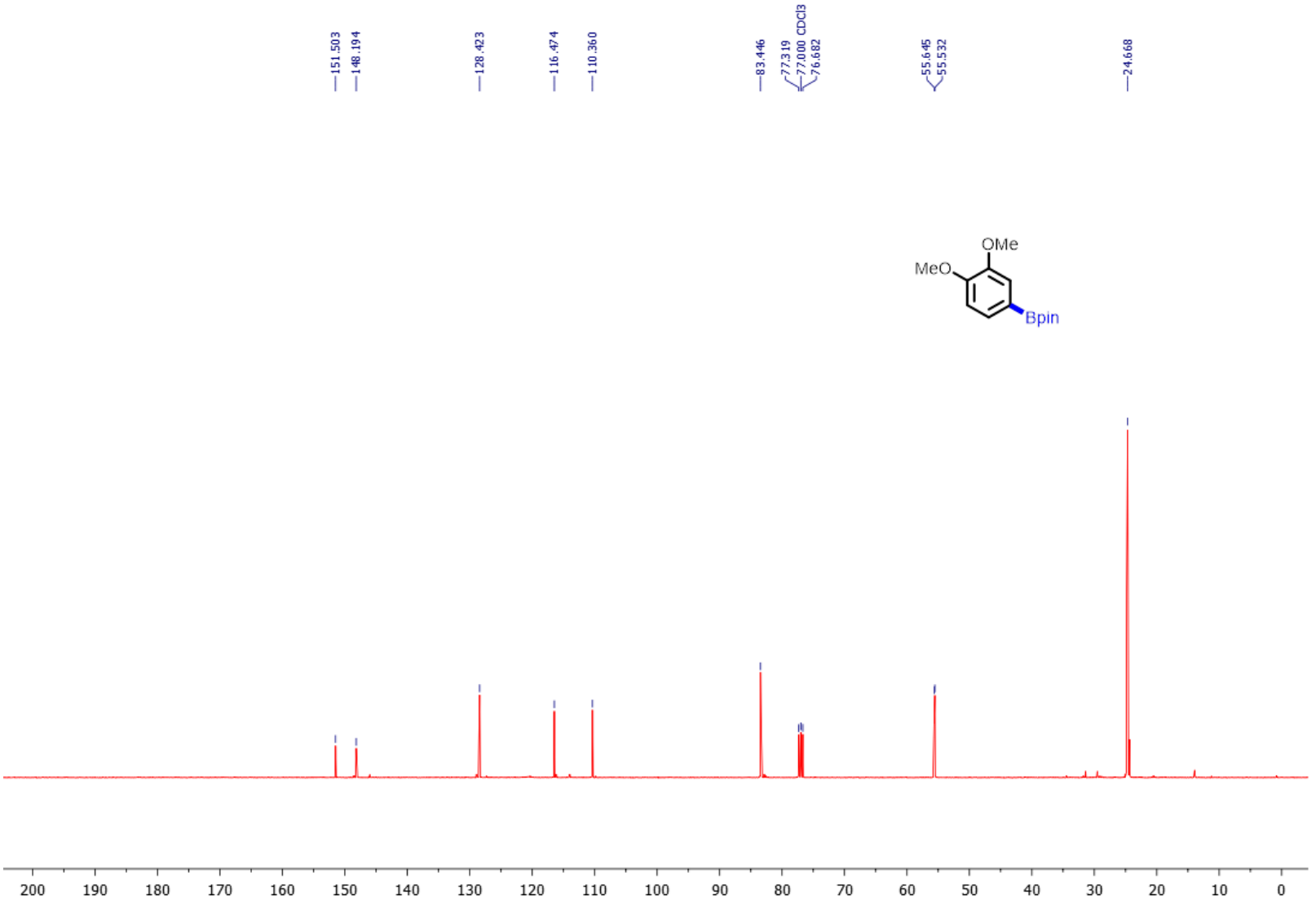
^{13}C NMR spectra of **2f** (25 °C, 100 MHz, $CDCl_3$)



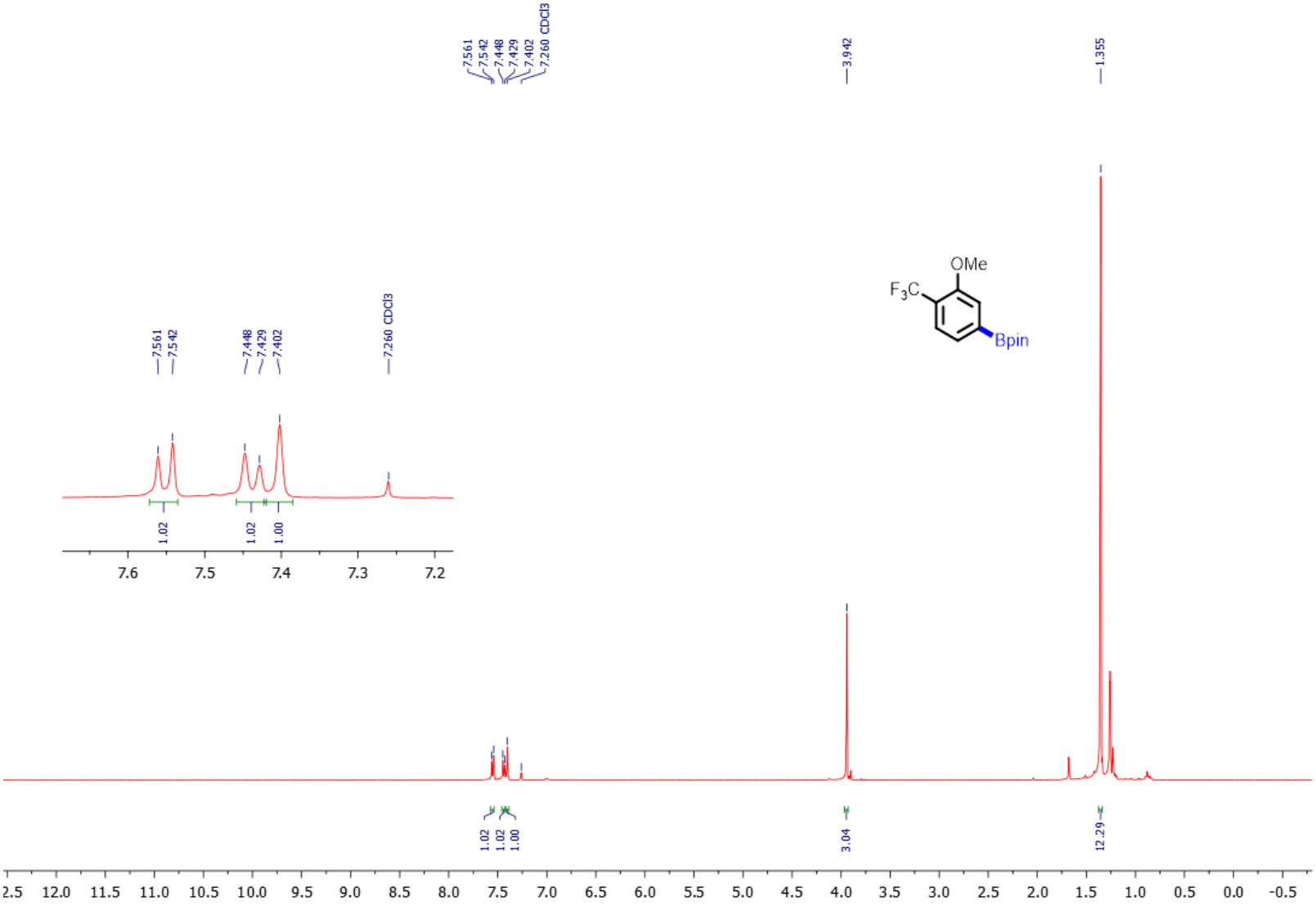
2D NOESY spectra of **2f** (25 °C, 400 MHz, $CDCl_3$)



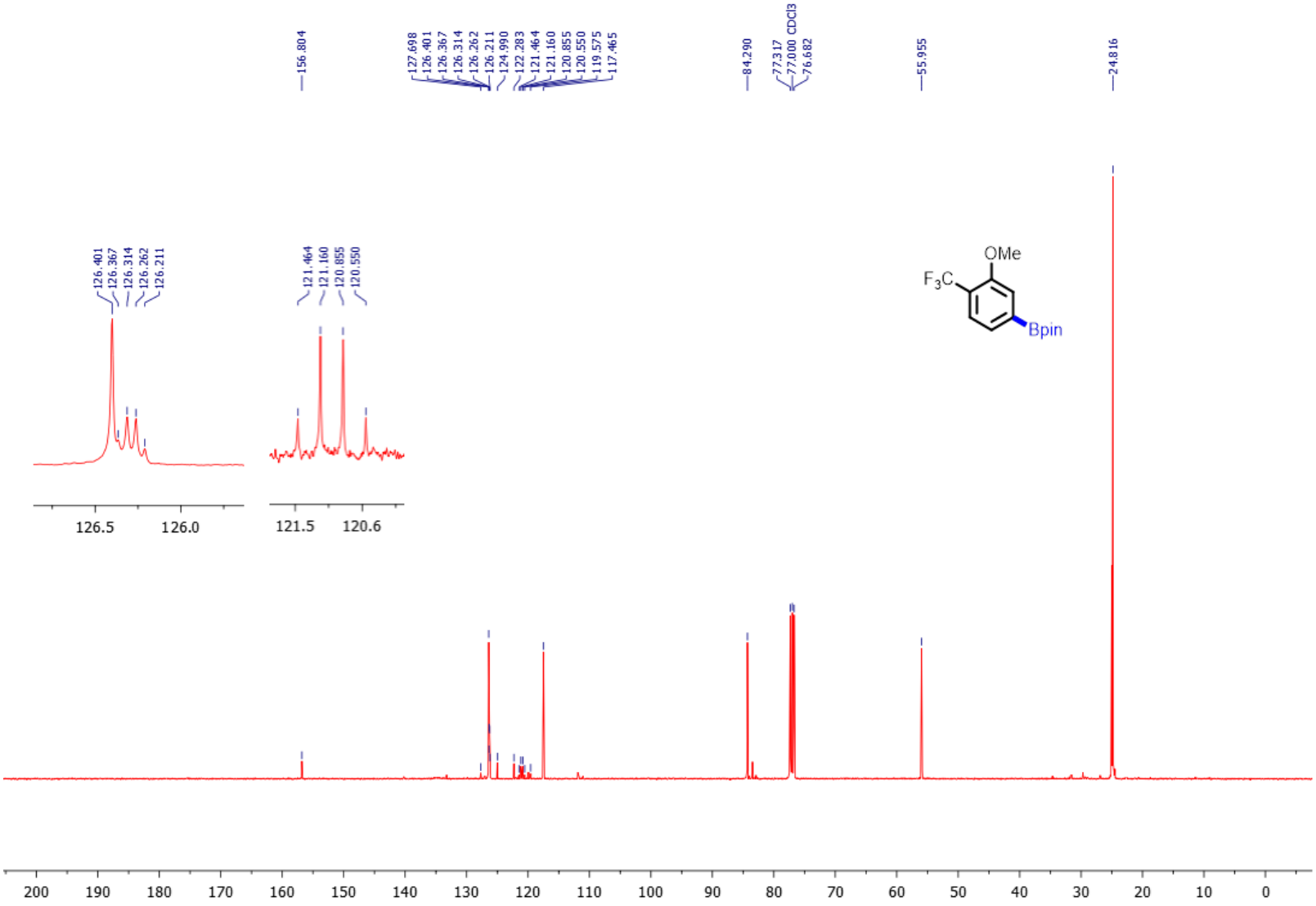
^{1}H NMR spectra of **2g** (25 °C, 400 MHz, $CDCl_3$)



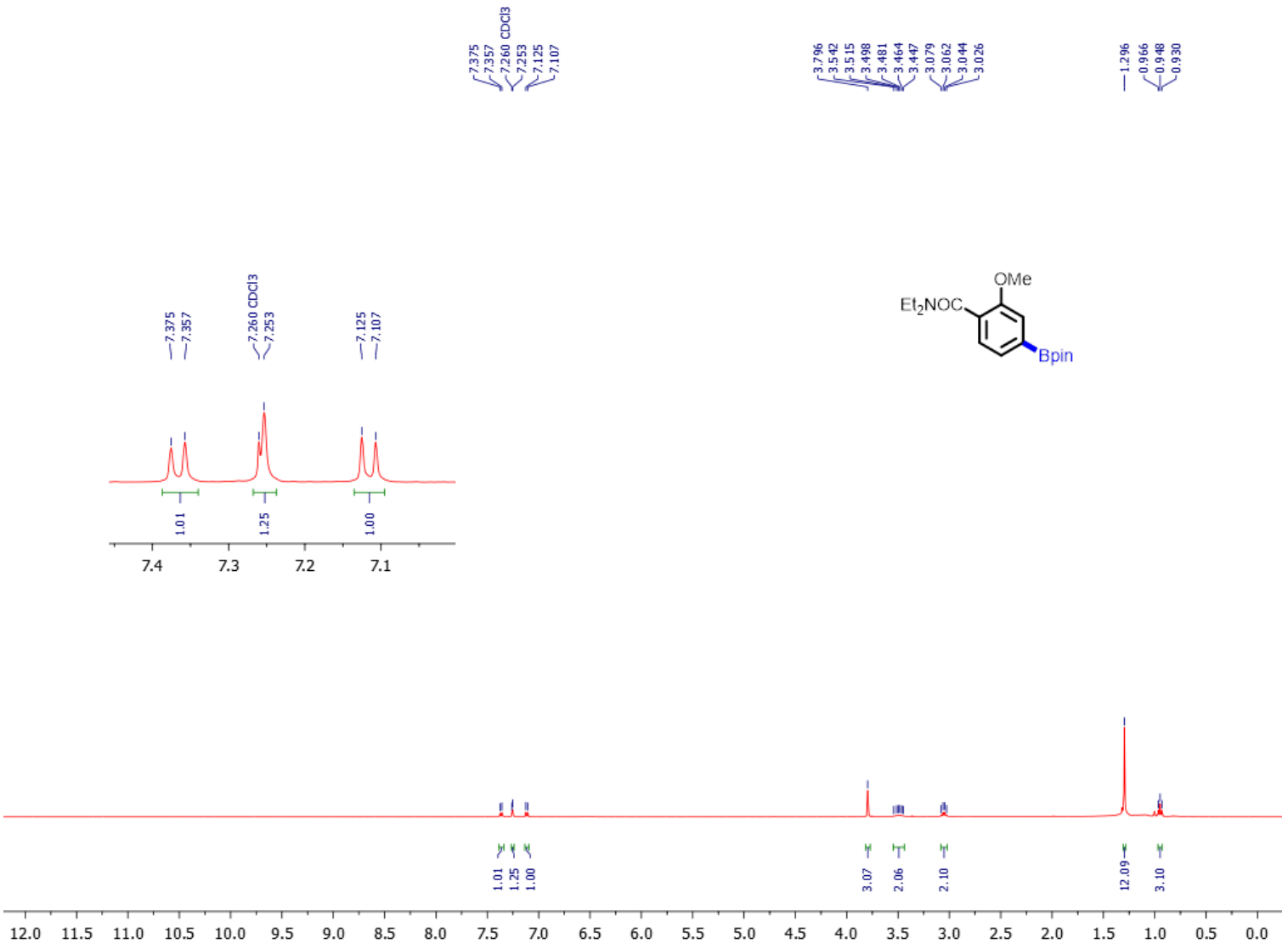
^{13}C NMR spectra of **2g** (25 °C, 100 MHz, $CDCl_3$)



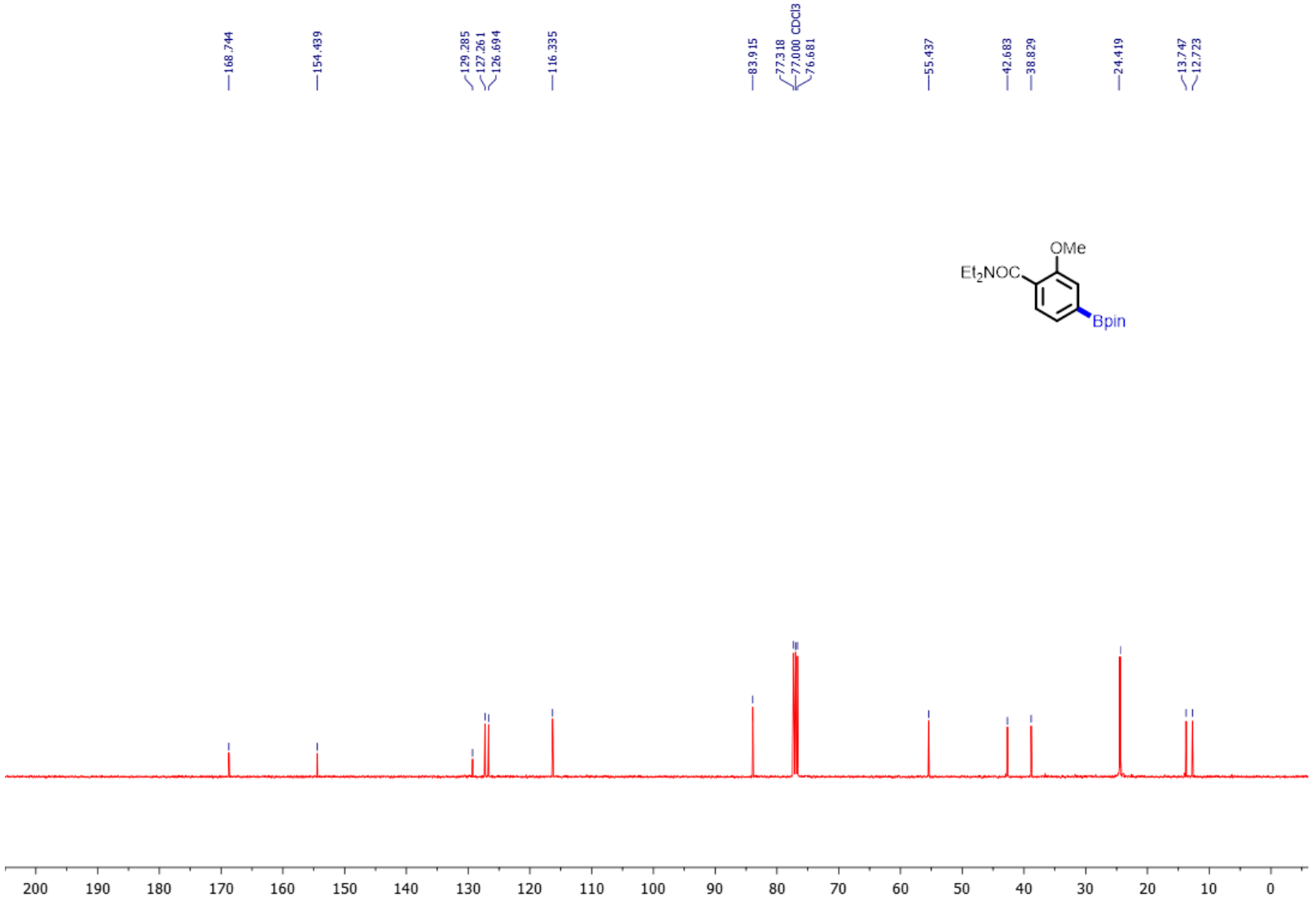
^{1}H NMR spectra of **2h** (25 °C, 400 MHz, $CDCl_3$)



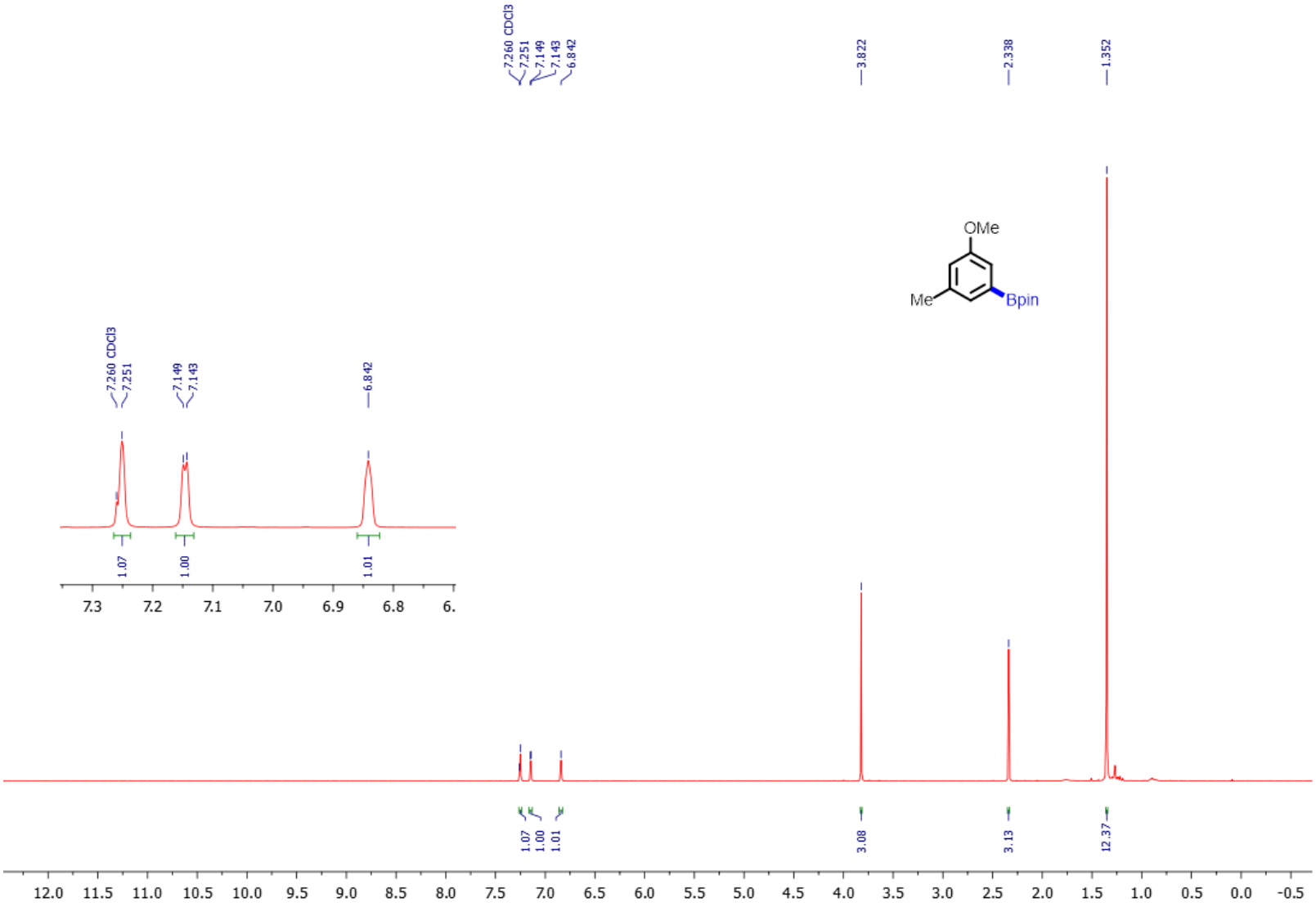
^{13}C NMR spectra of **2h** (25 °C, 100 MHz, $CDCl_3$)



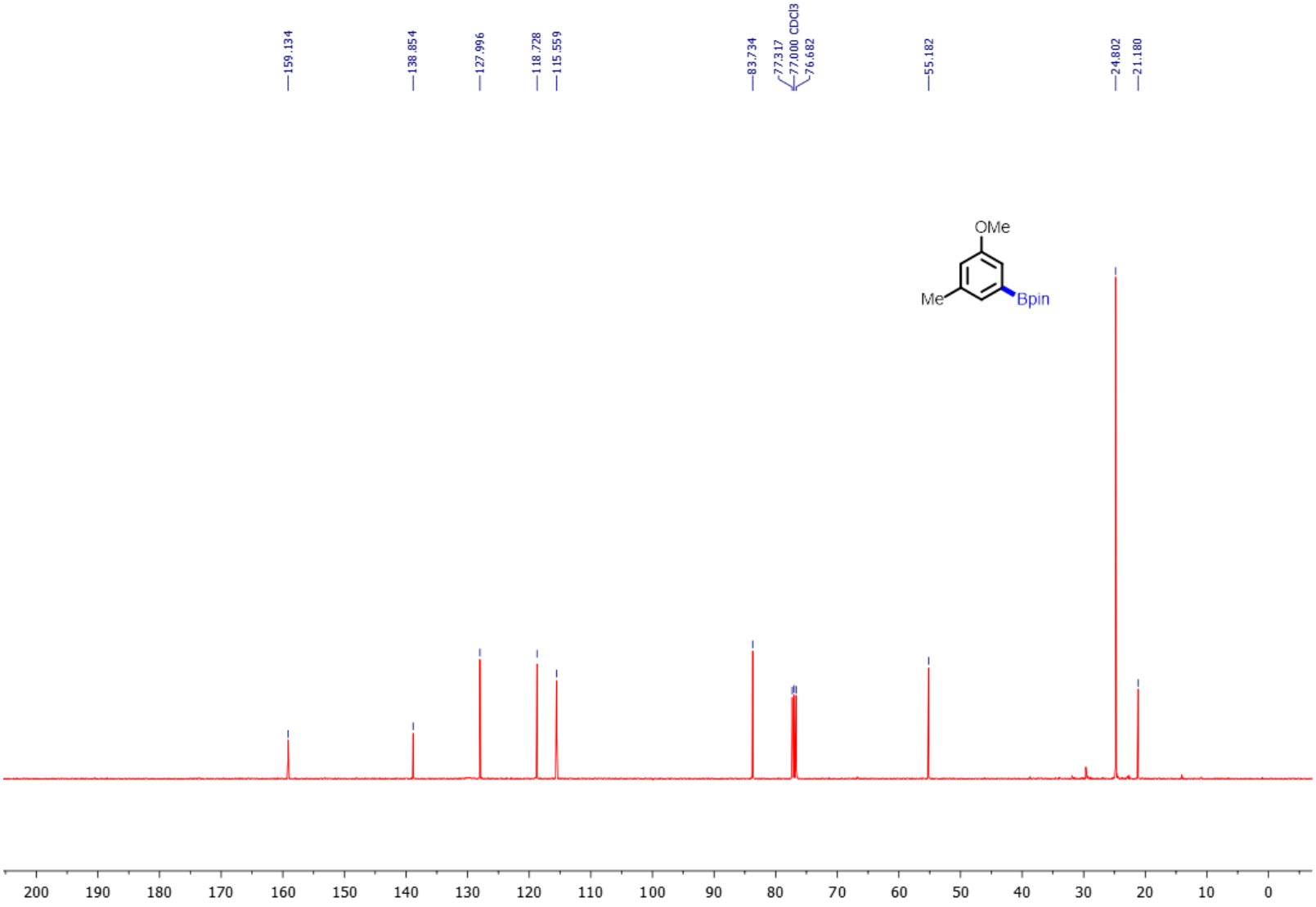
^{1}H NMR spectra of **2i** (25 ºC, 400 MHz, $CDCl_3$)



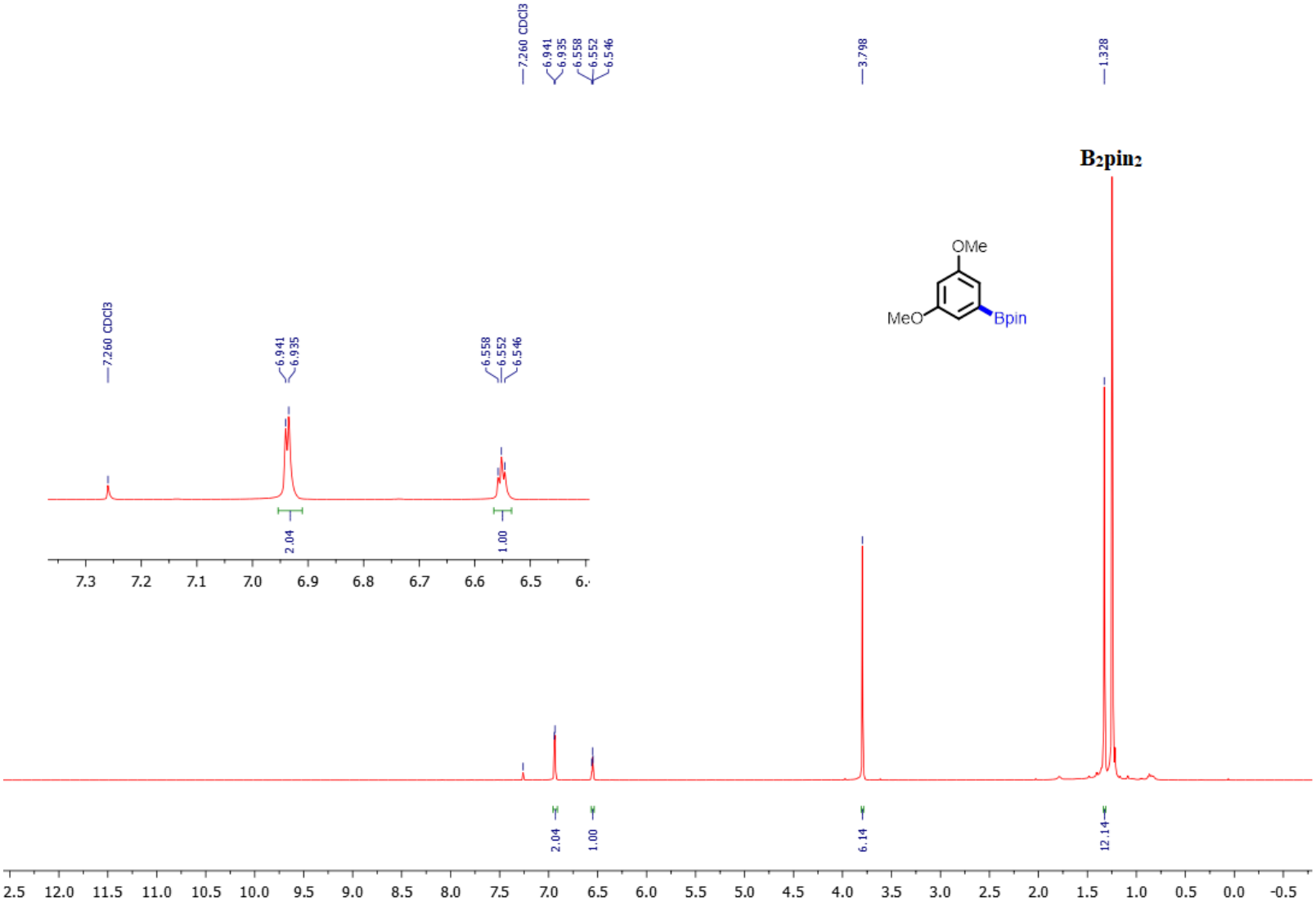
^{13}C NMR spectra of **2i** (25 °C, 100 MHz, $CDCl_3$)



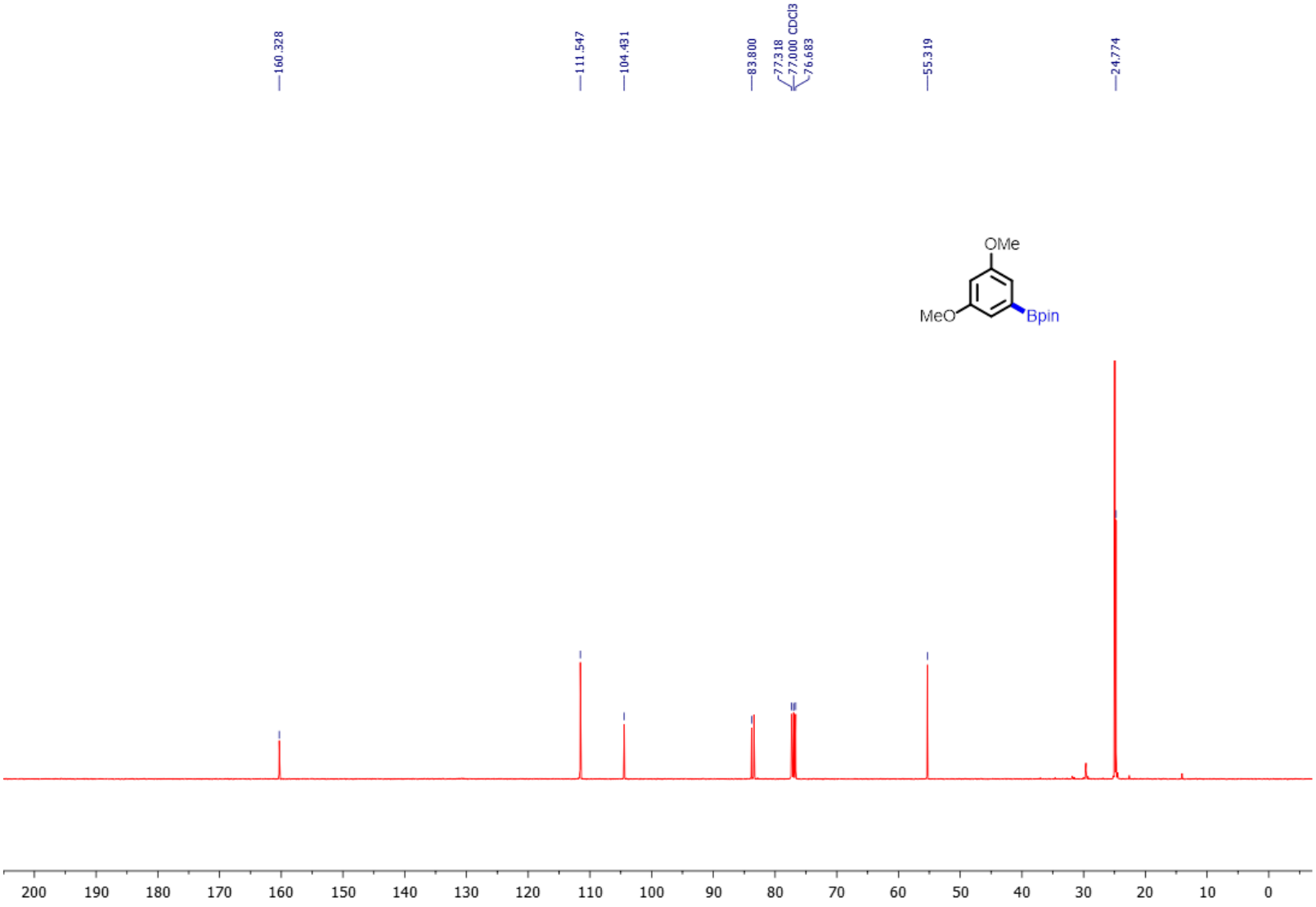
^{1}H NMR spectra of **2j** (25 °C, 400 MHz, $CDCl_3$)



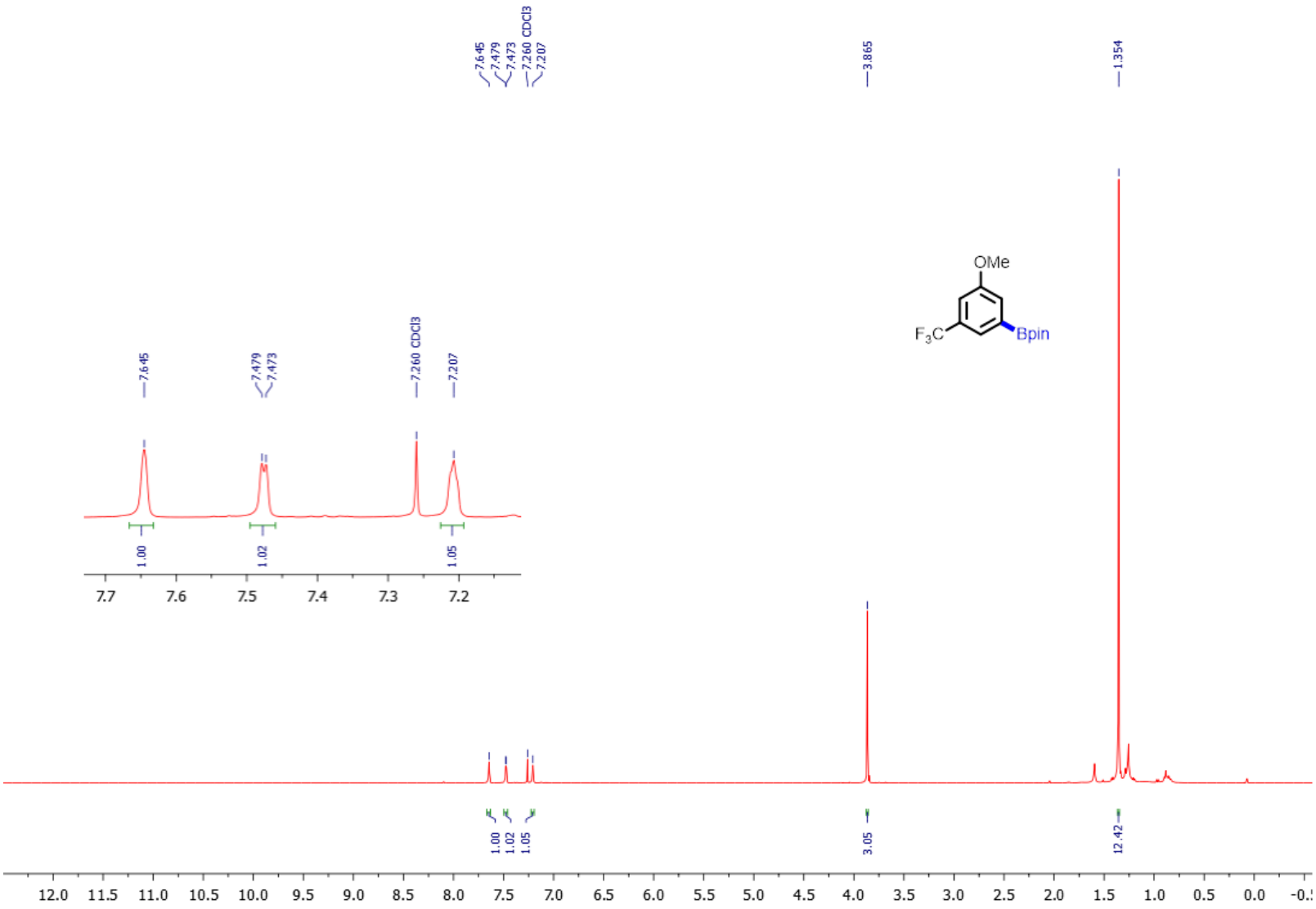
^{13}C NMR spectra of **2j** (25 °C, 100 MHz, $CDCl_3$)



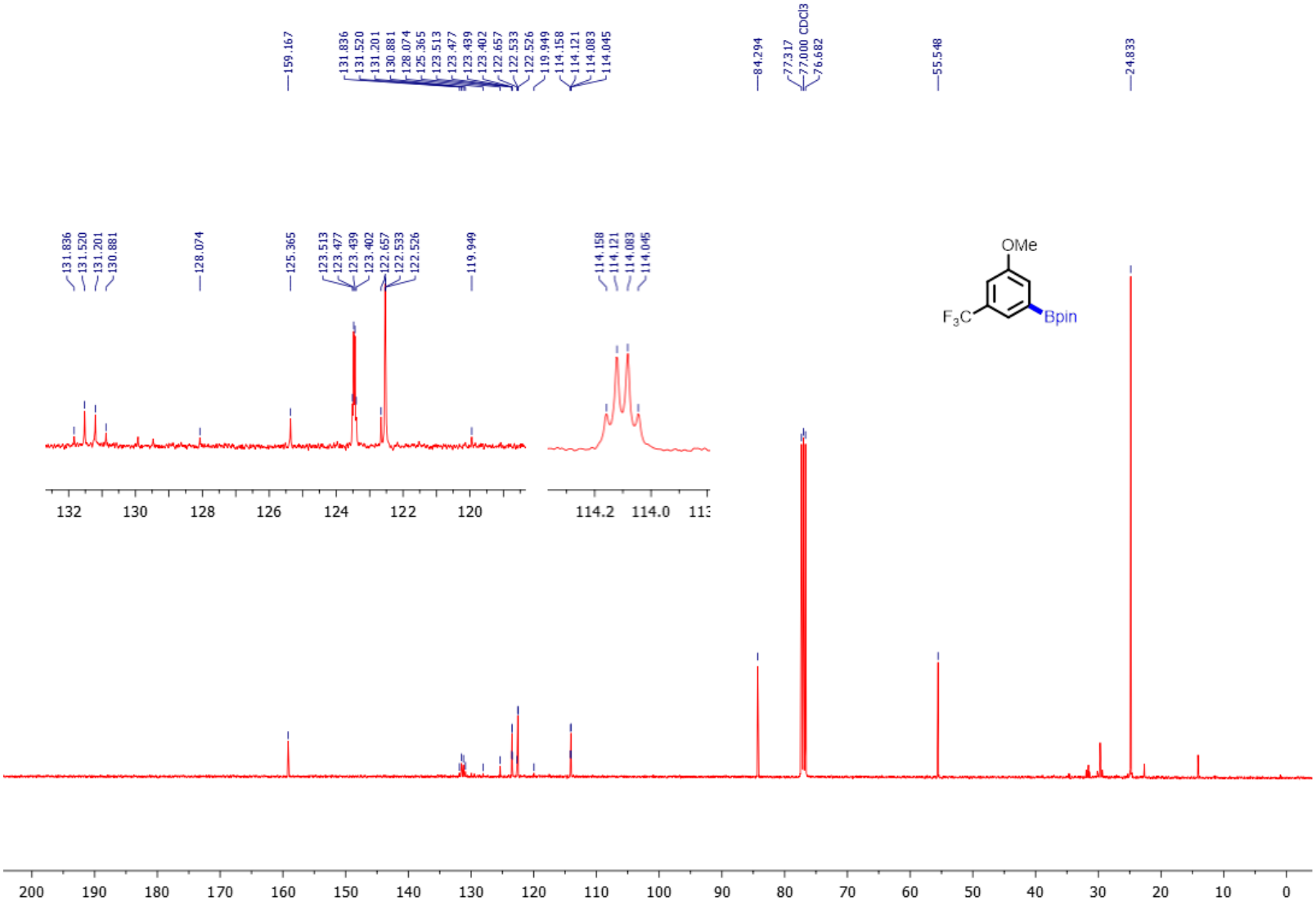
^{1}H NMR spectra of **2k** (25 °C, 400 MHz, $CDCl_3$)



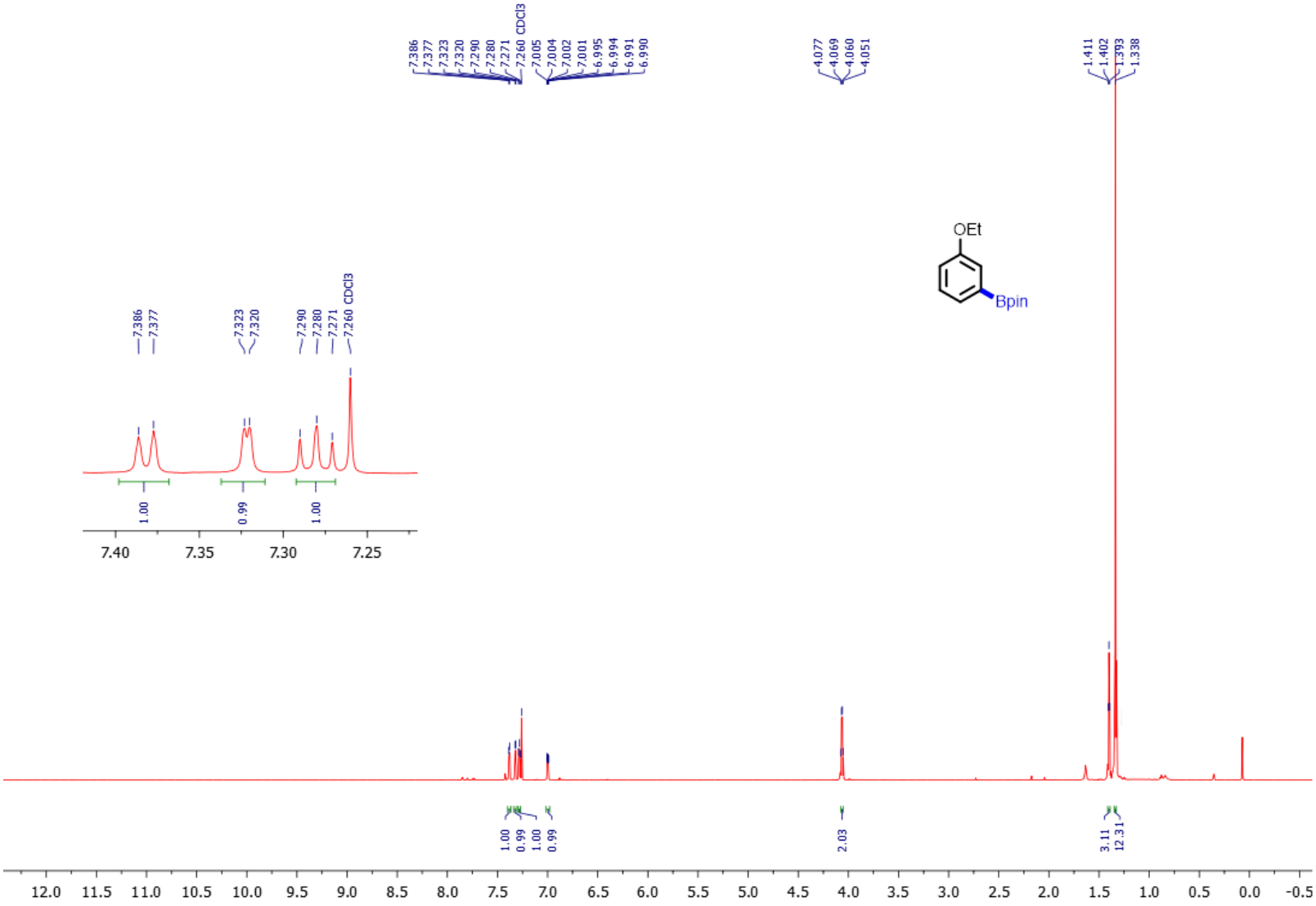
^{13}C NMR spectra of **2k** (25 °C, 100 MHz, $CDCl_3$)



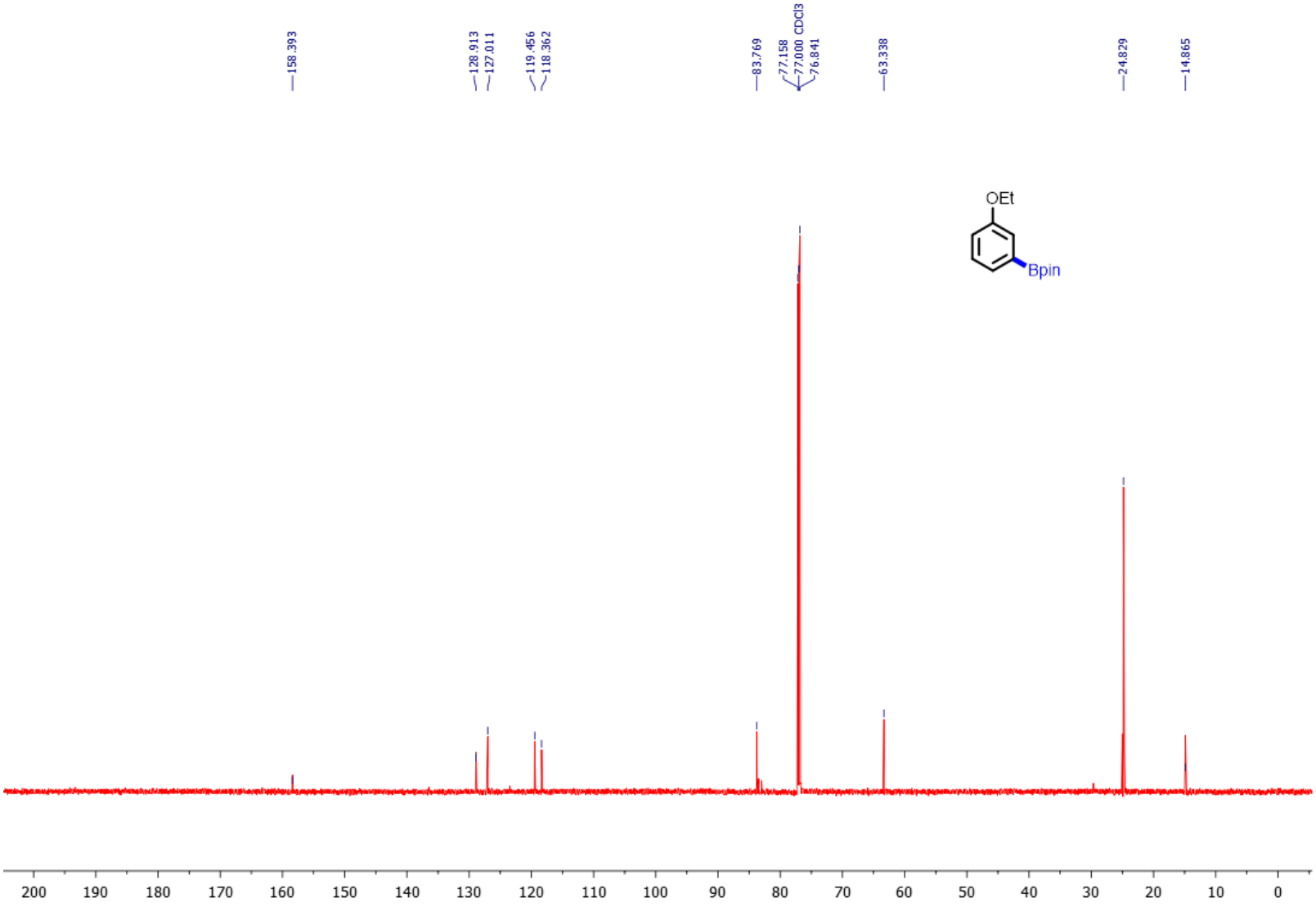
^{1}H NMR spectra of **2l** (25 ºC, 400 MHz, $CDCl_3$)



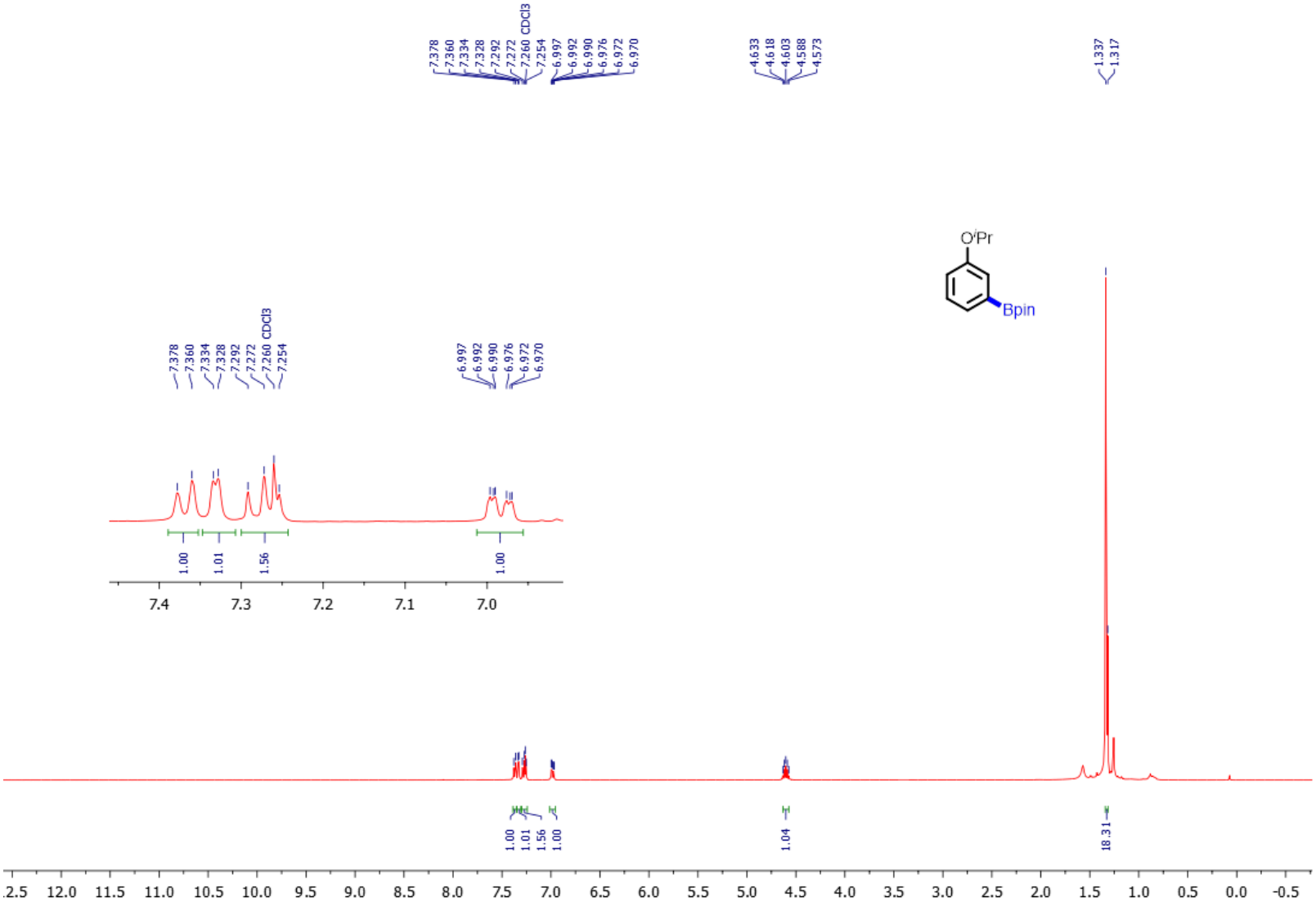
^{13}C NMR spectra of **2l** (25 °C, 100 MHz, $CDCl_3$)



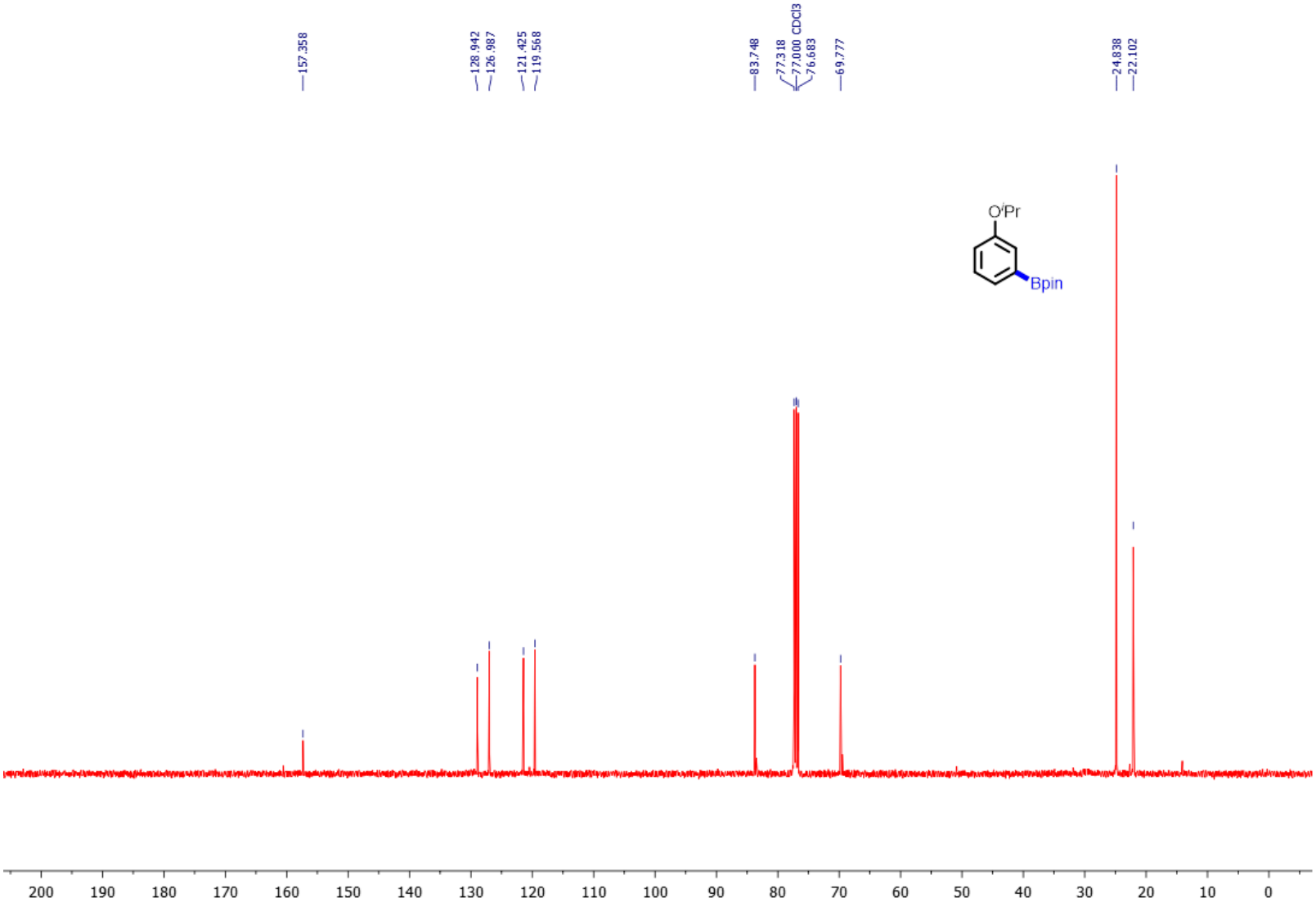
^{1}H NMR spectra of **2m** (25 °C, 800 MHz, $CDCl_3$)



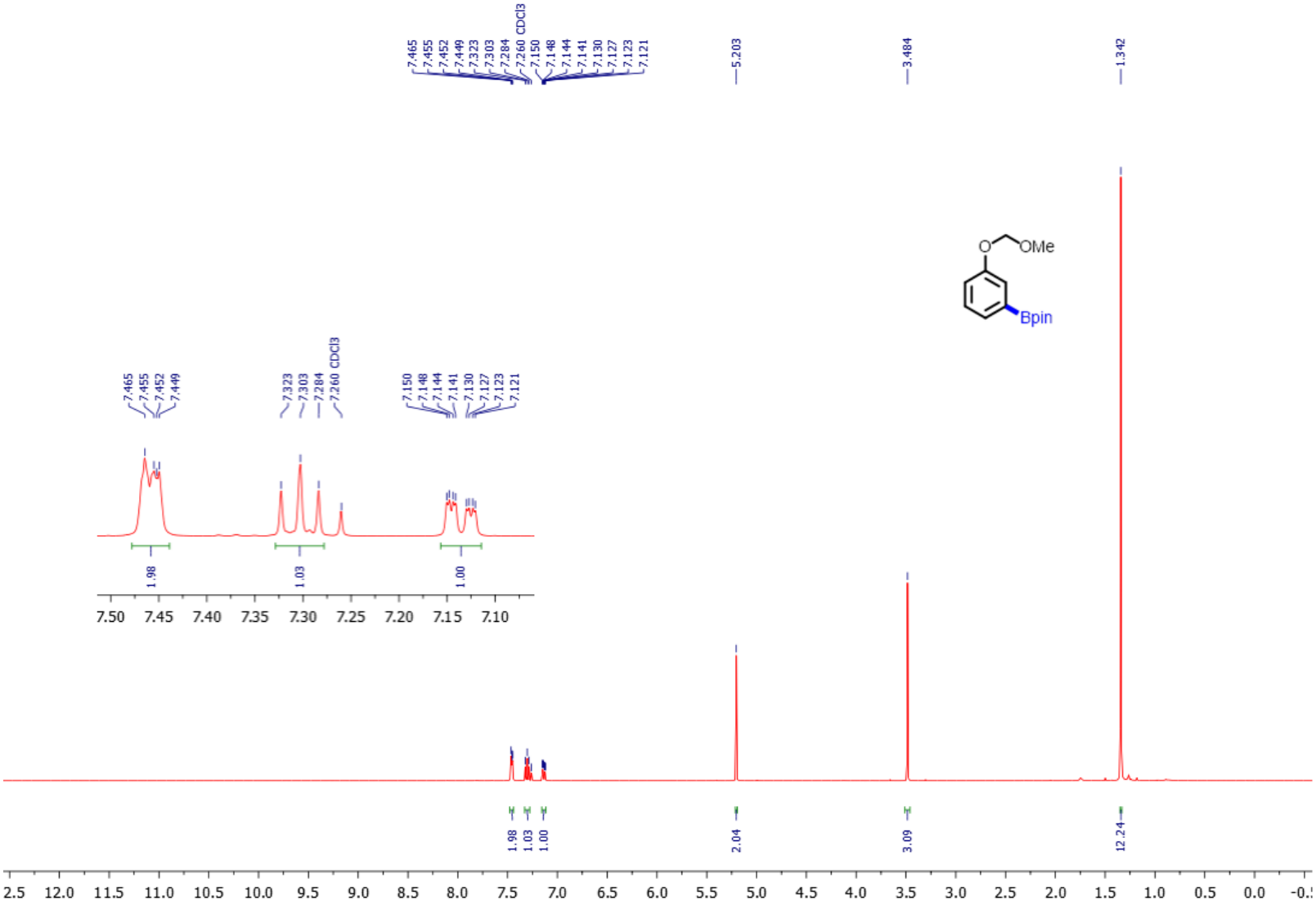
^{13}C NMR spectra of **2m** (25 ^{o}C, 200 MHz, $CDCl_3$)



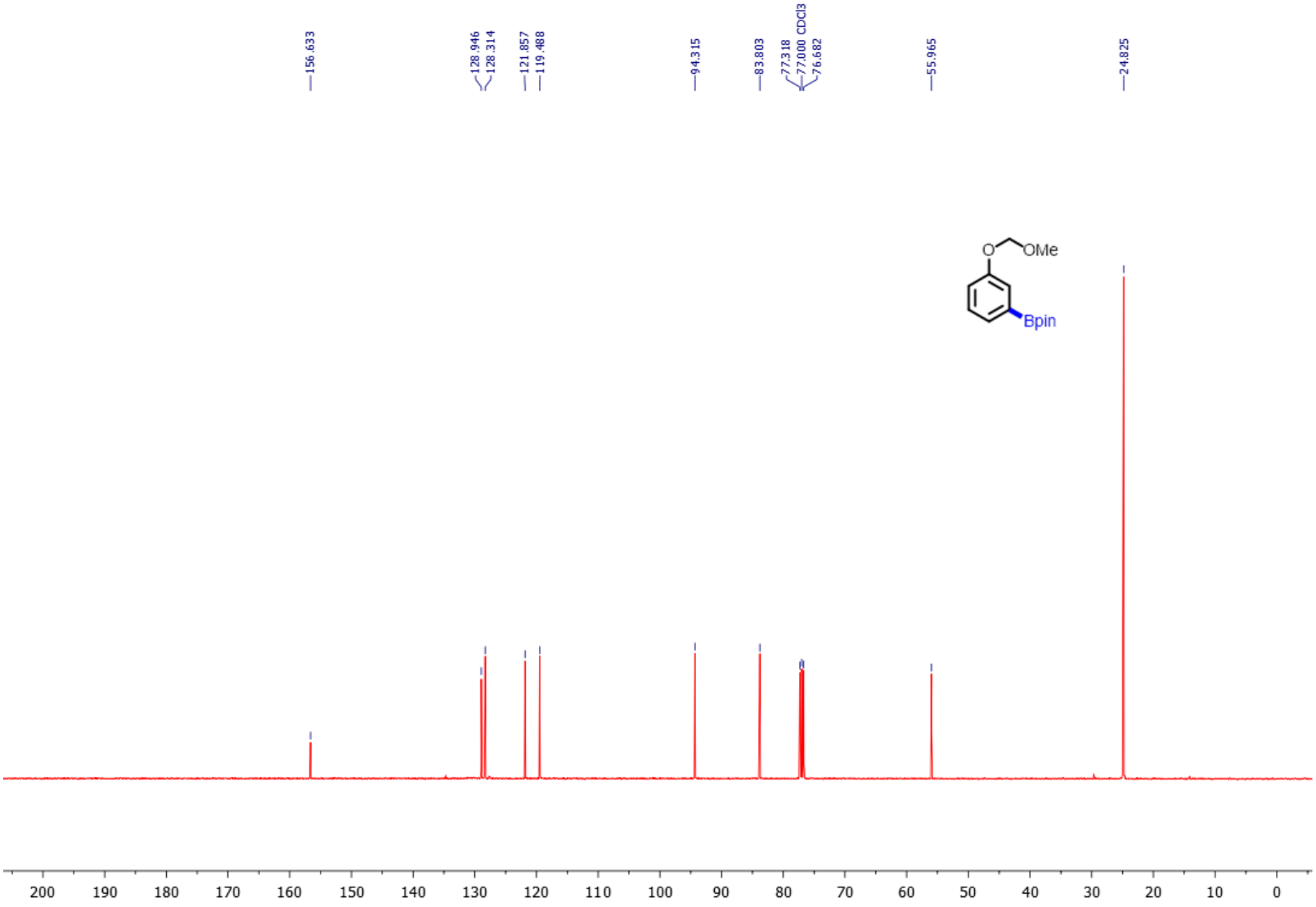
^{1}H NMR spectra of **2n** (25 °C, 400 MHz, $CDCl_3$)



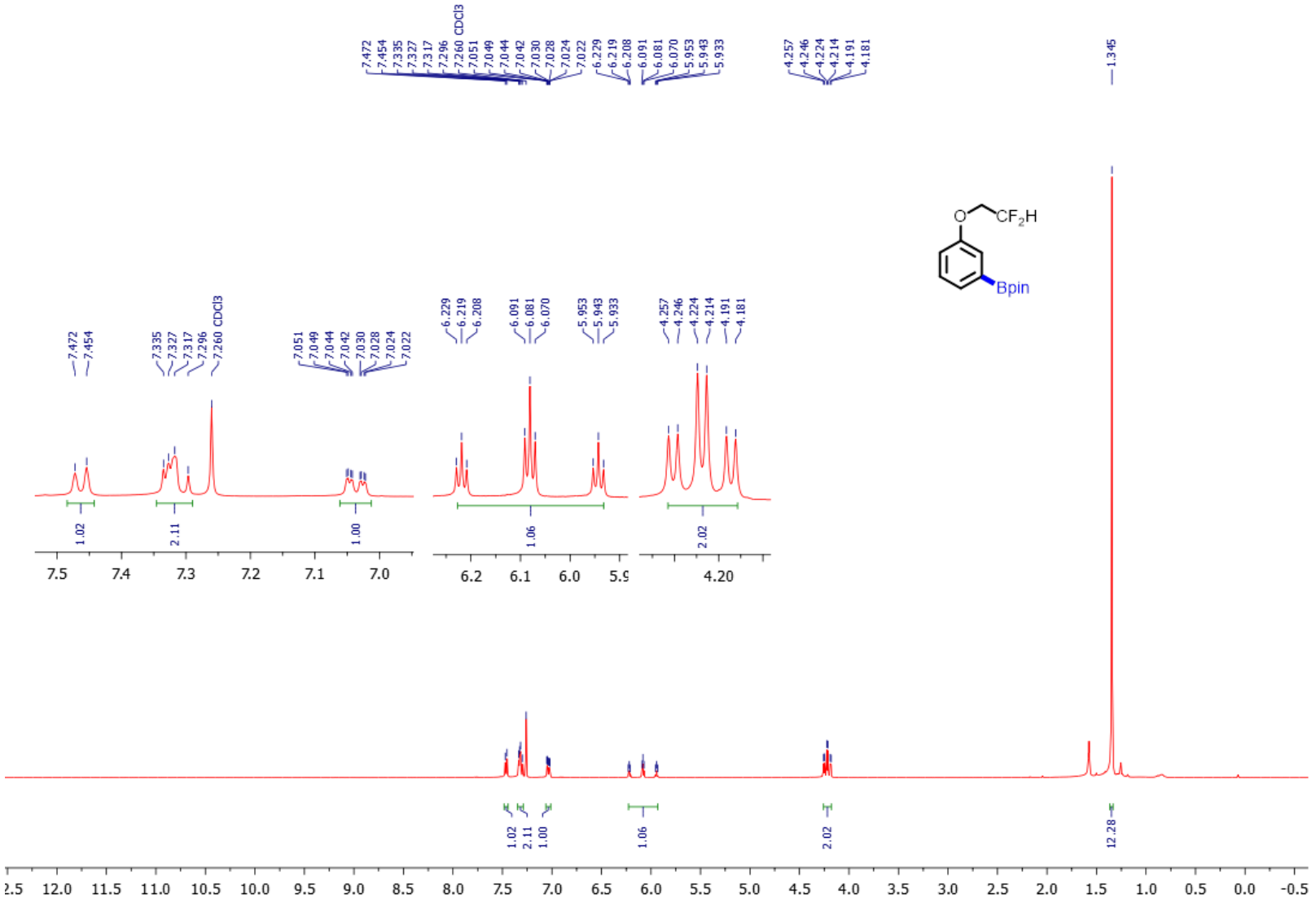
^{13}C NMR spectra of **2n** (25 °C, 100 MHz, $CDCl_3$)



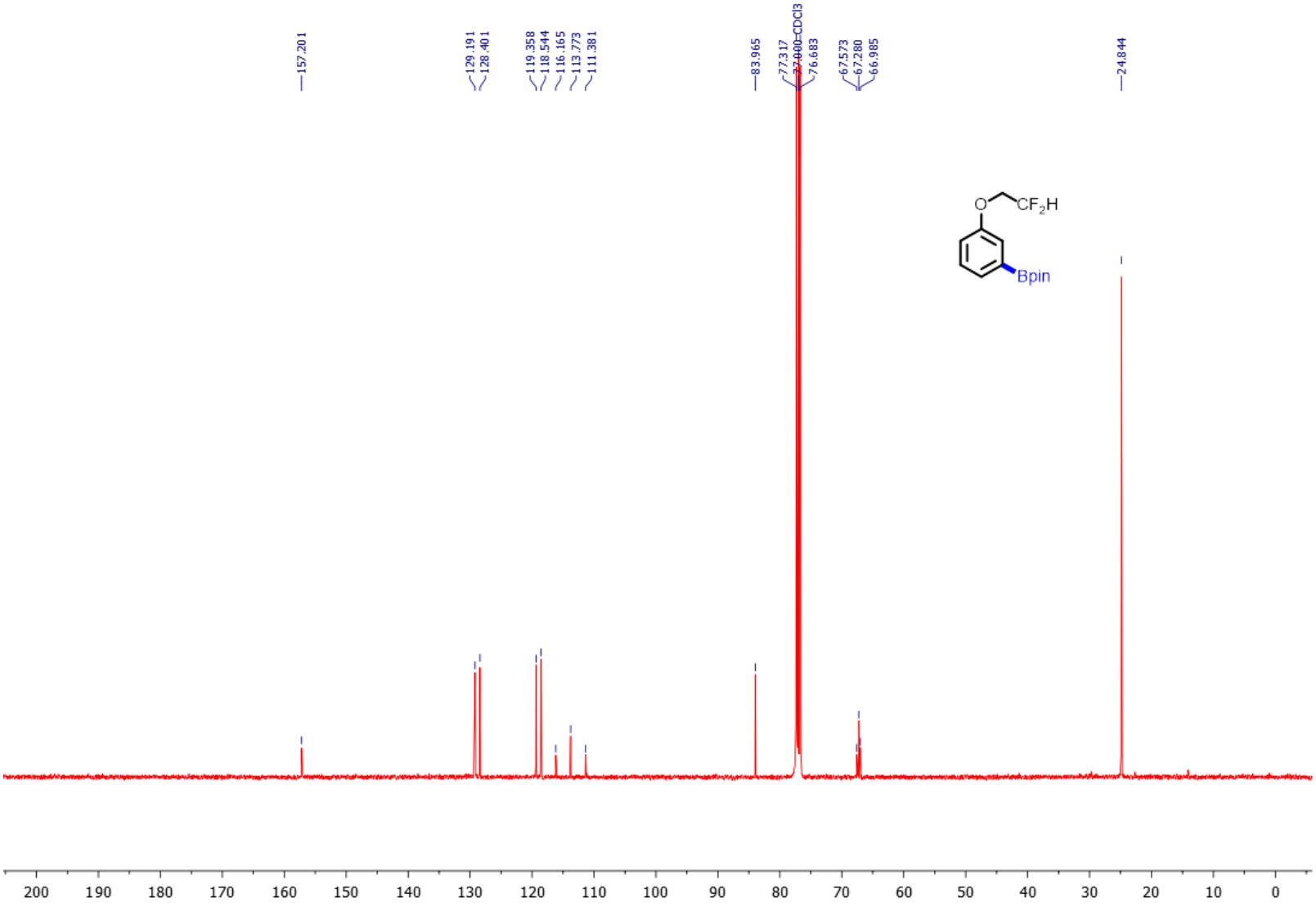
^{1}H NMR spectra of **2o** (25 °C, 400 MHz, $CDCl_3$)



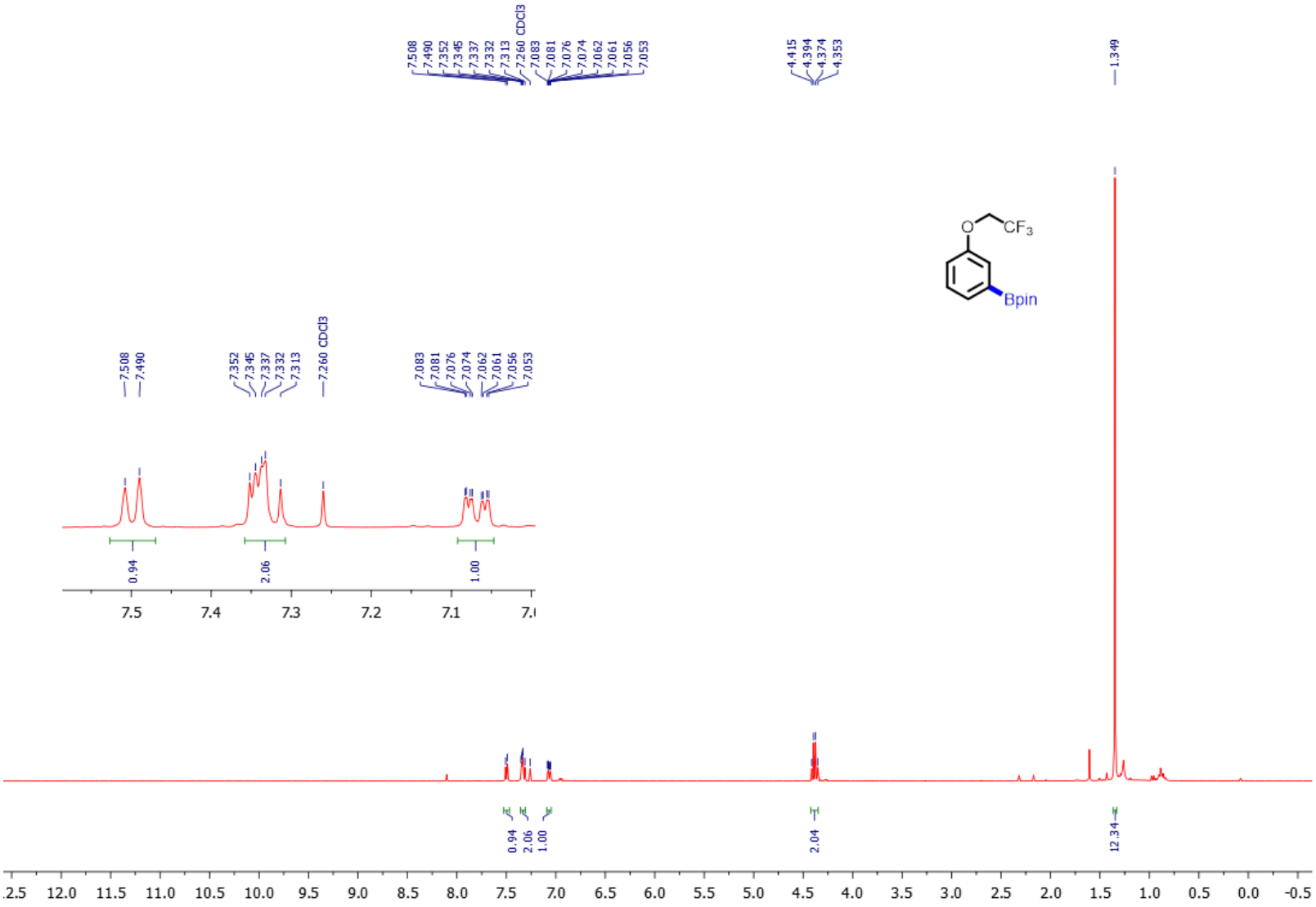
^{13}C NMR spectra of **2o** (25 °C, 100 MHz, $CDCl_3$)



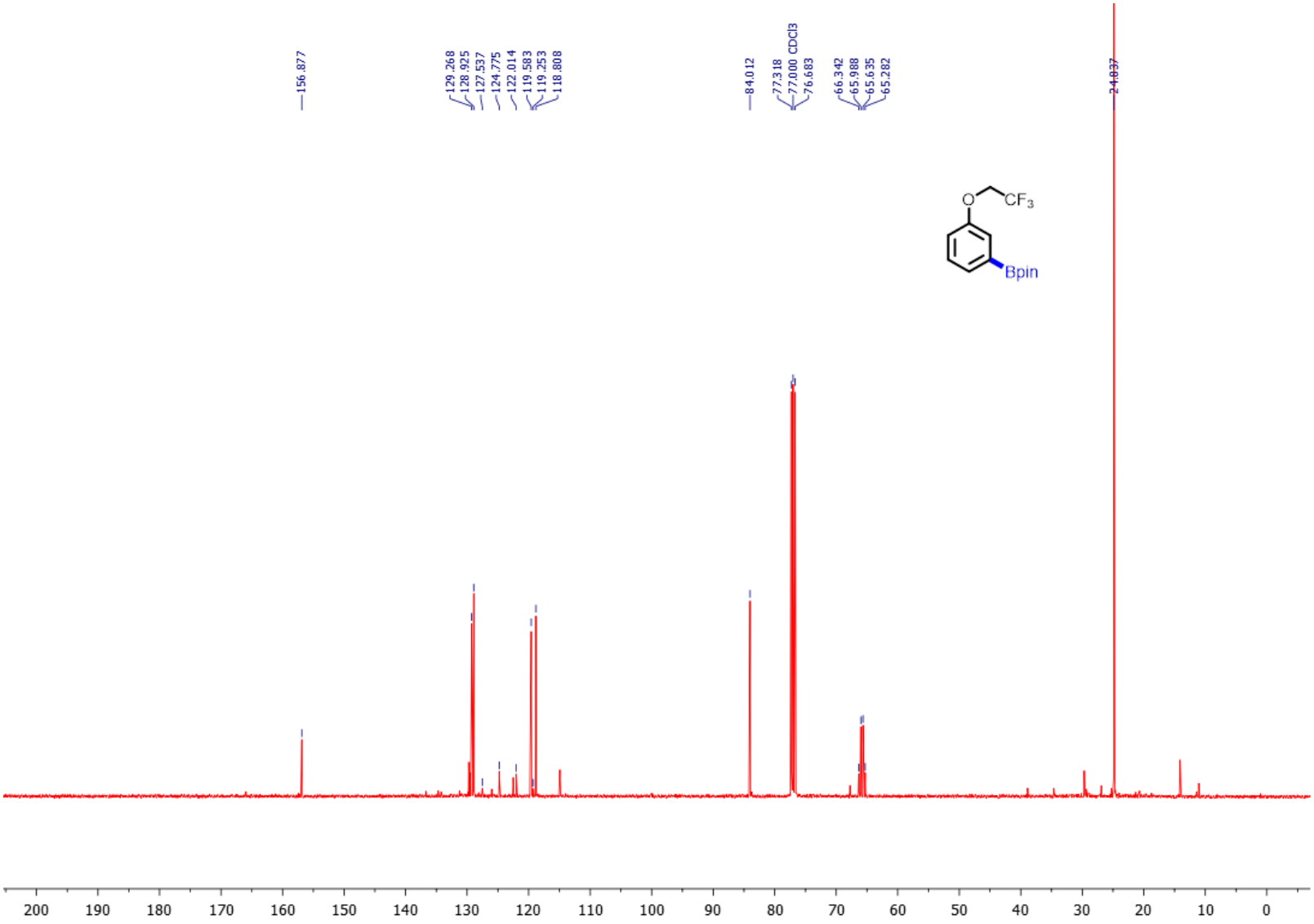
^{1}H NMR spectra of **2p** (25 °C, 400 MHz, $CDCl_3$)



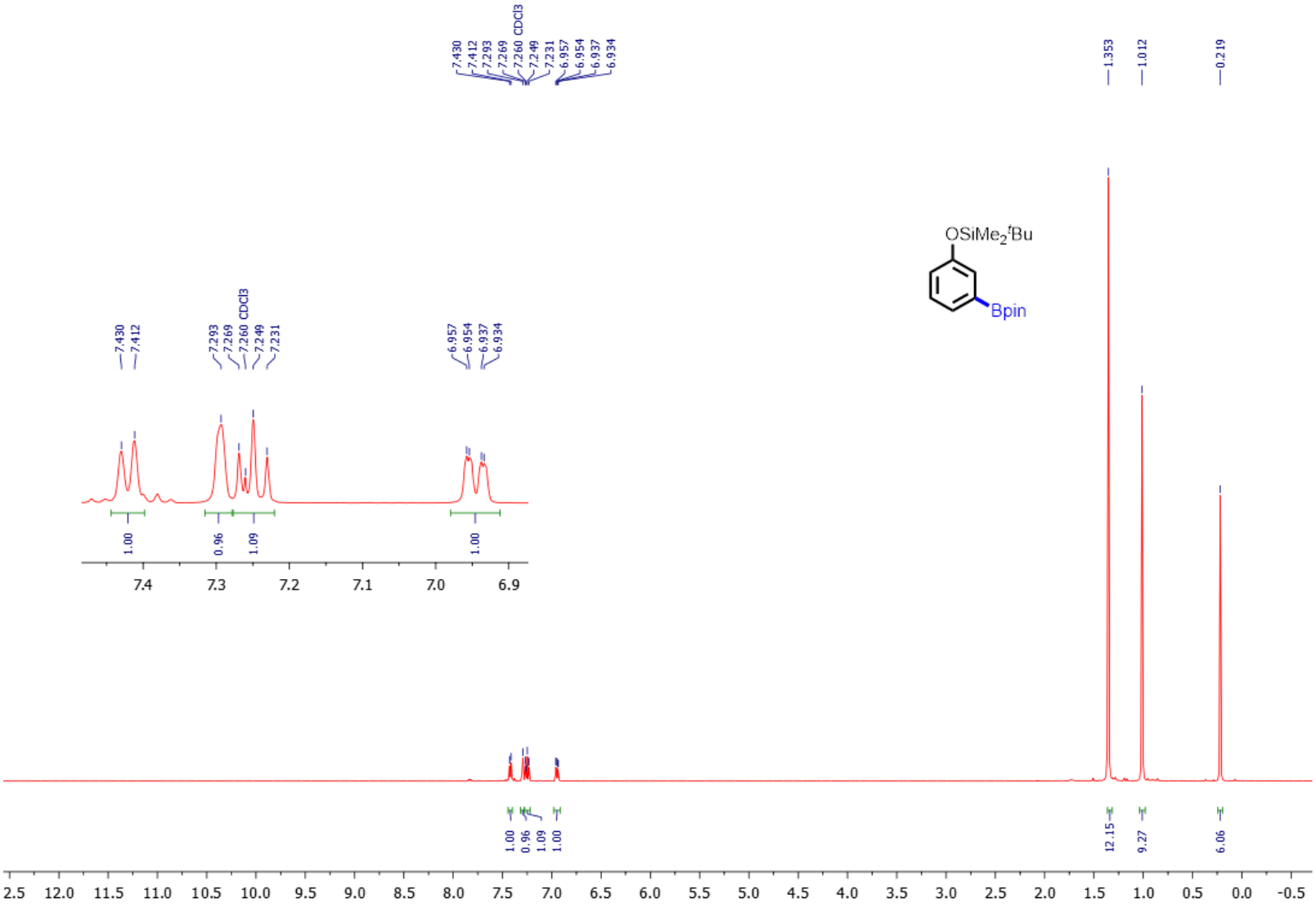
^{13}C NMR spectra of **2p** (25 °C, 100 MHz, $CDCl_3$)



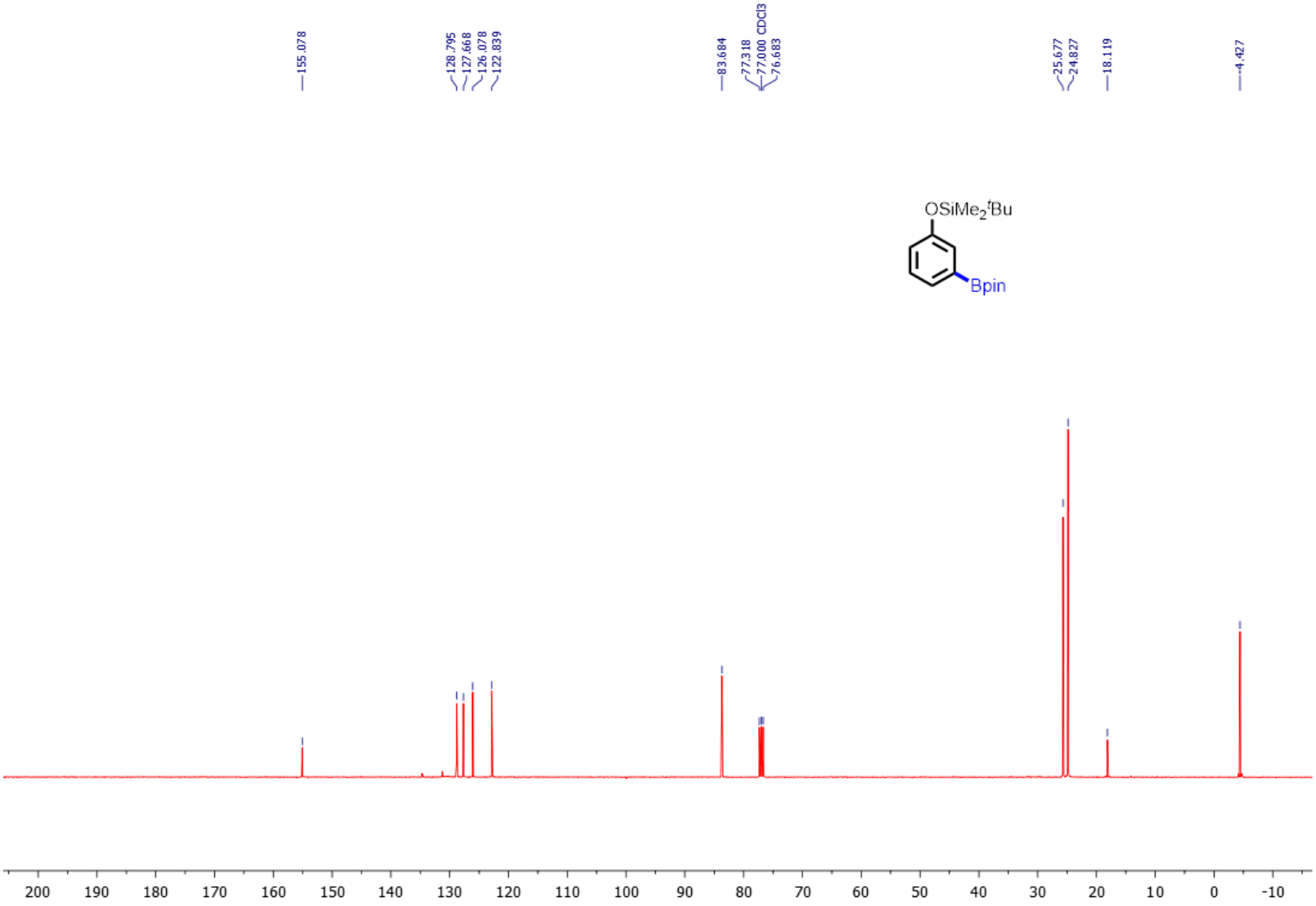
^{1}H NMR spectra of **2q** (25 °C, 400 MHz, $CDCl_3$)



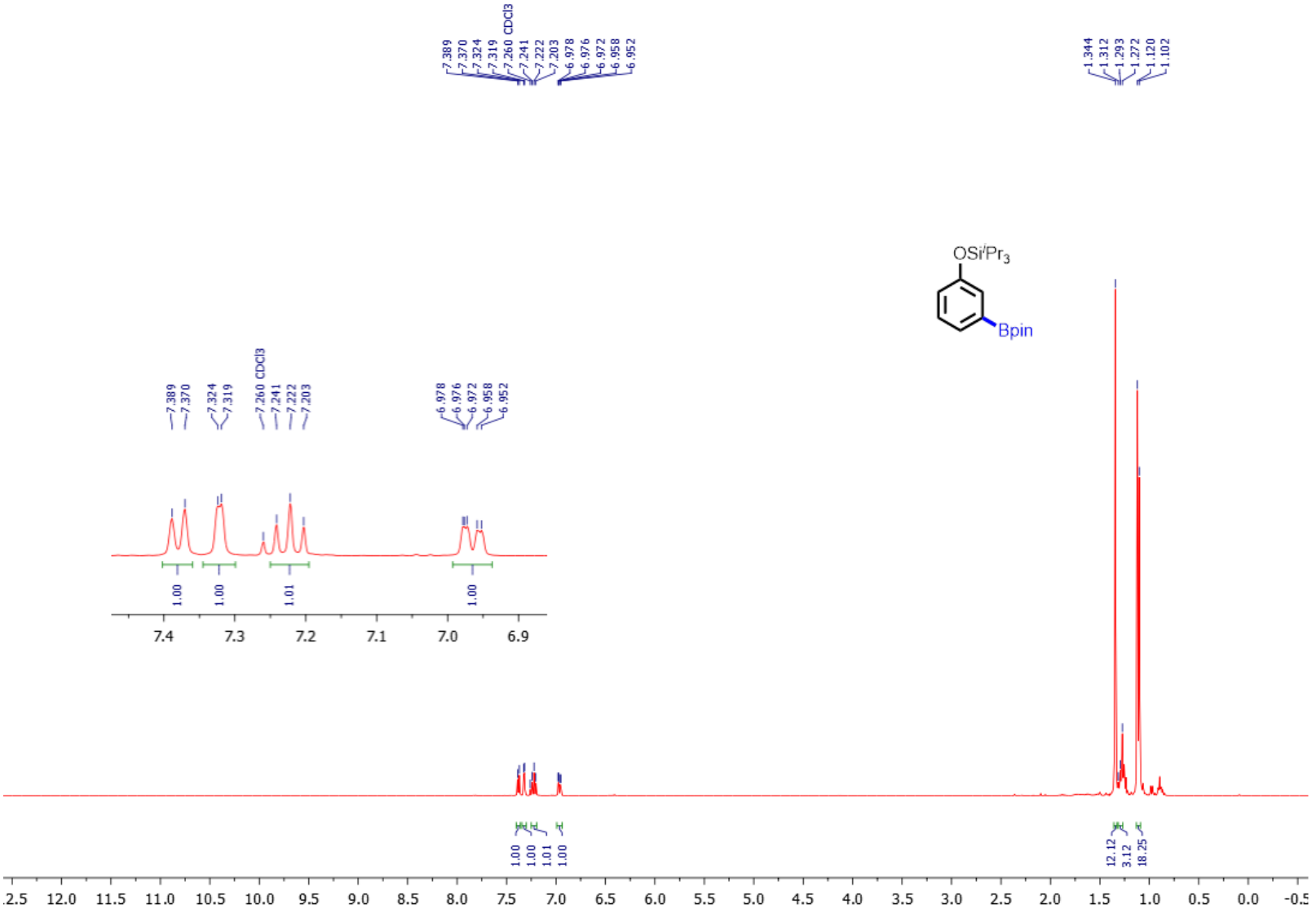
^{13}C NMR spectra of **2q** (25 °C, 100 MHz, $CDCl_3$)



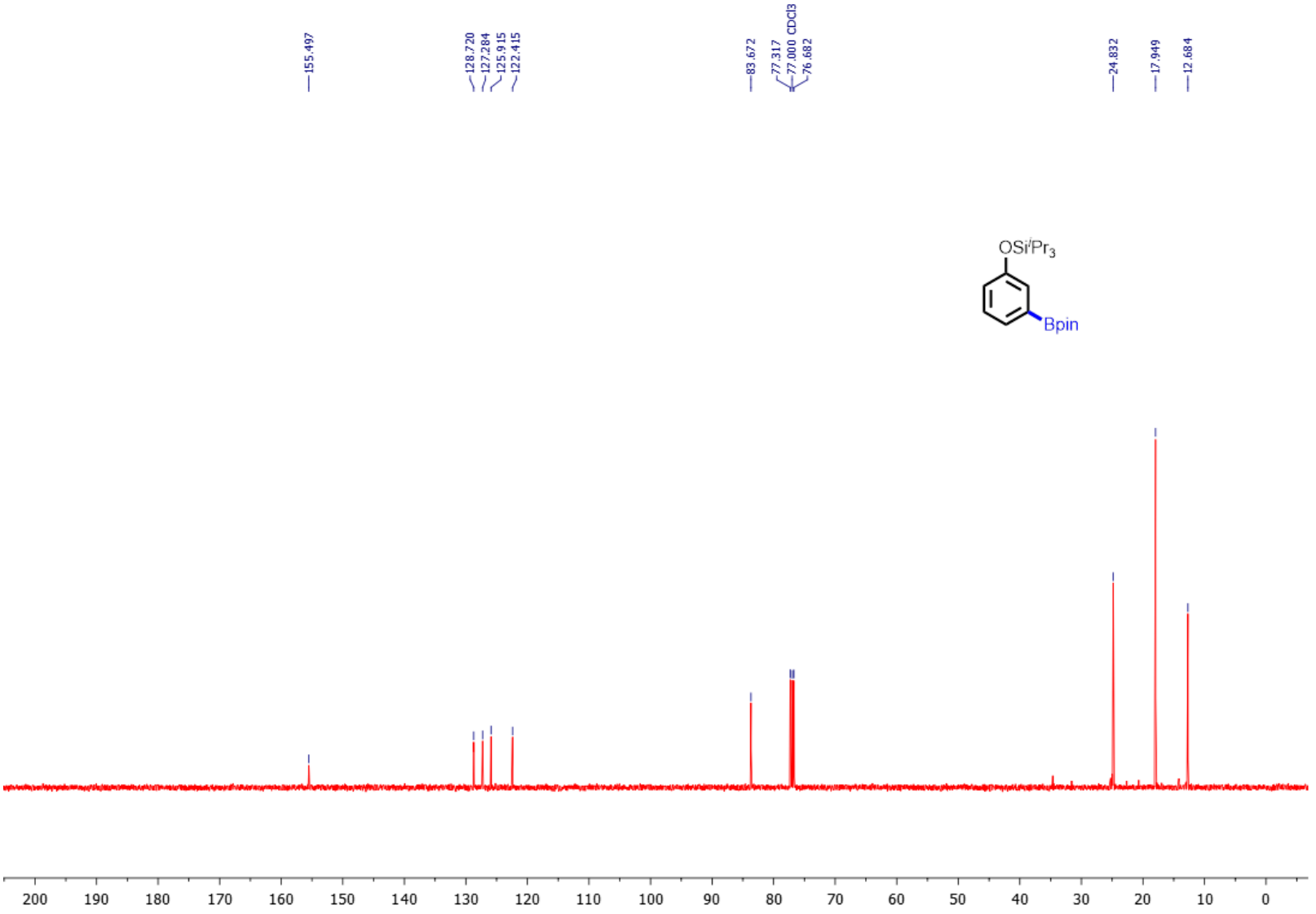
^{1}H NMR spectra of **2r** (25 °C, 400 MHz, $CDCl_3$)



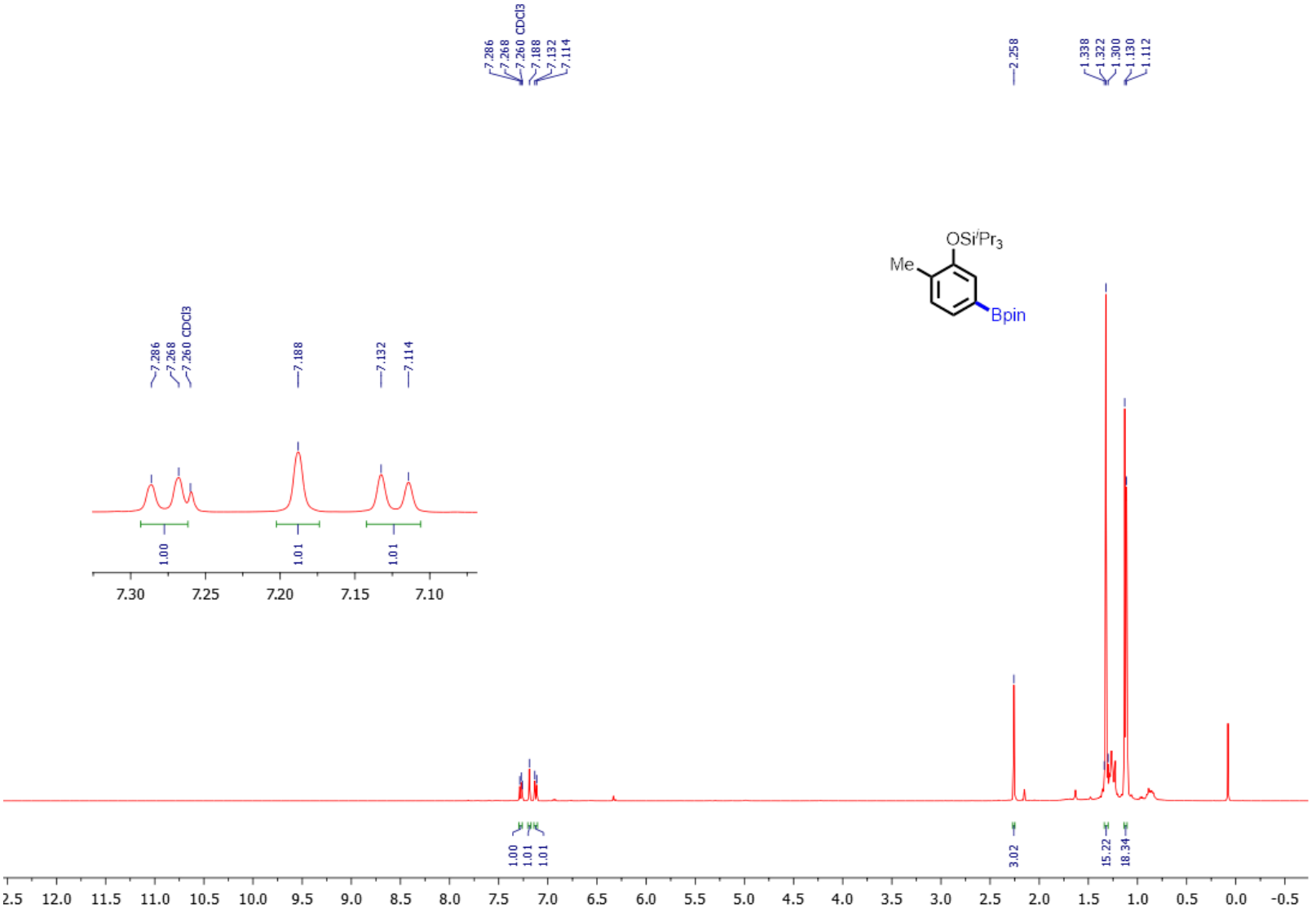
^{13}C NMR spectra of **2r** (25 °C, 100 MHz, $CDCl_3$)



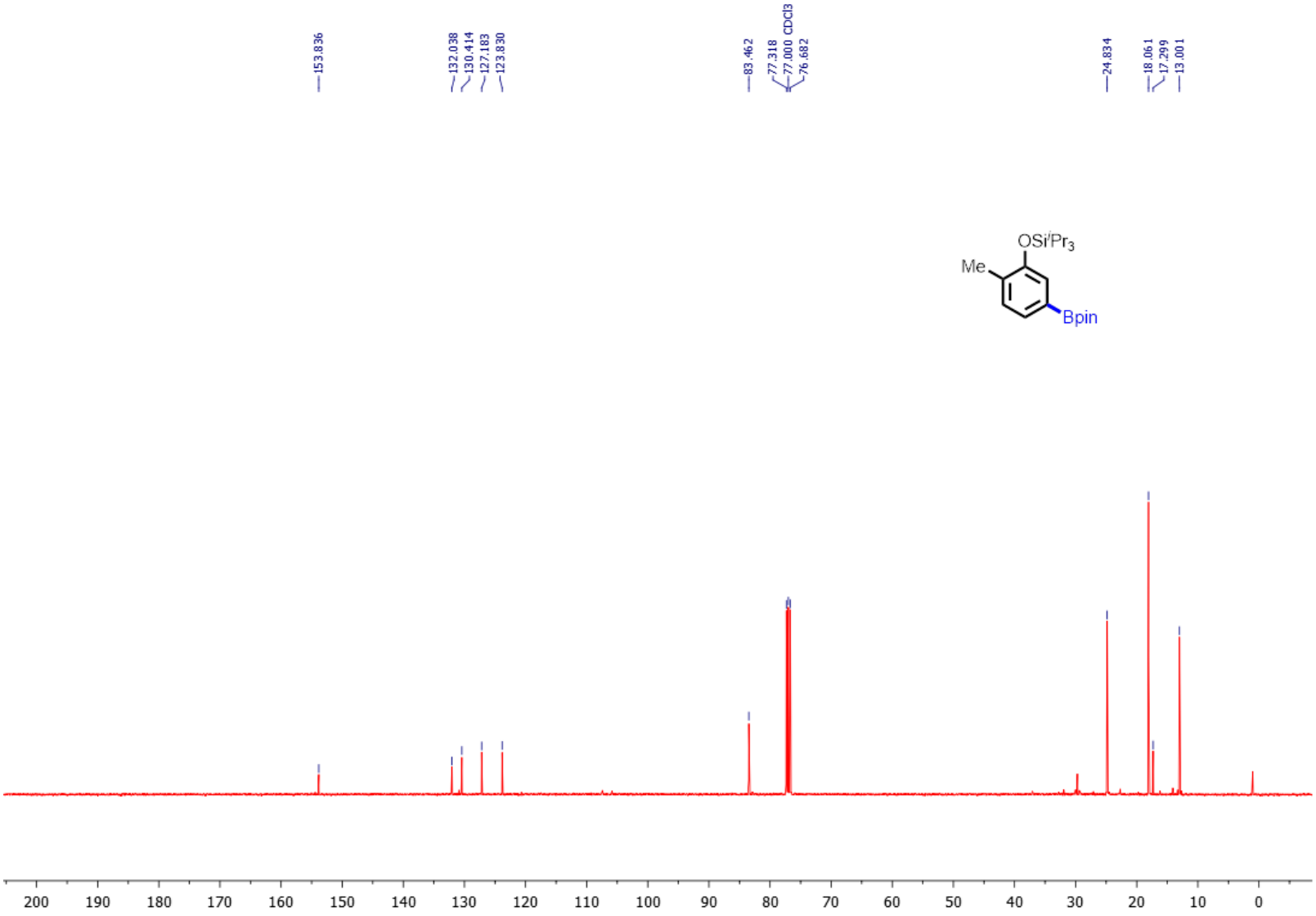
^{1}H NMR spectra of **2s** (25 °C, 400 MHz, $CDCl_3$)



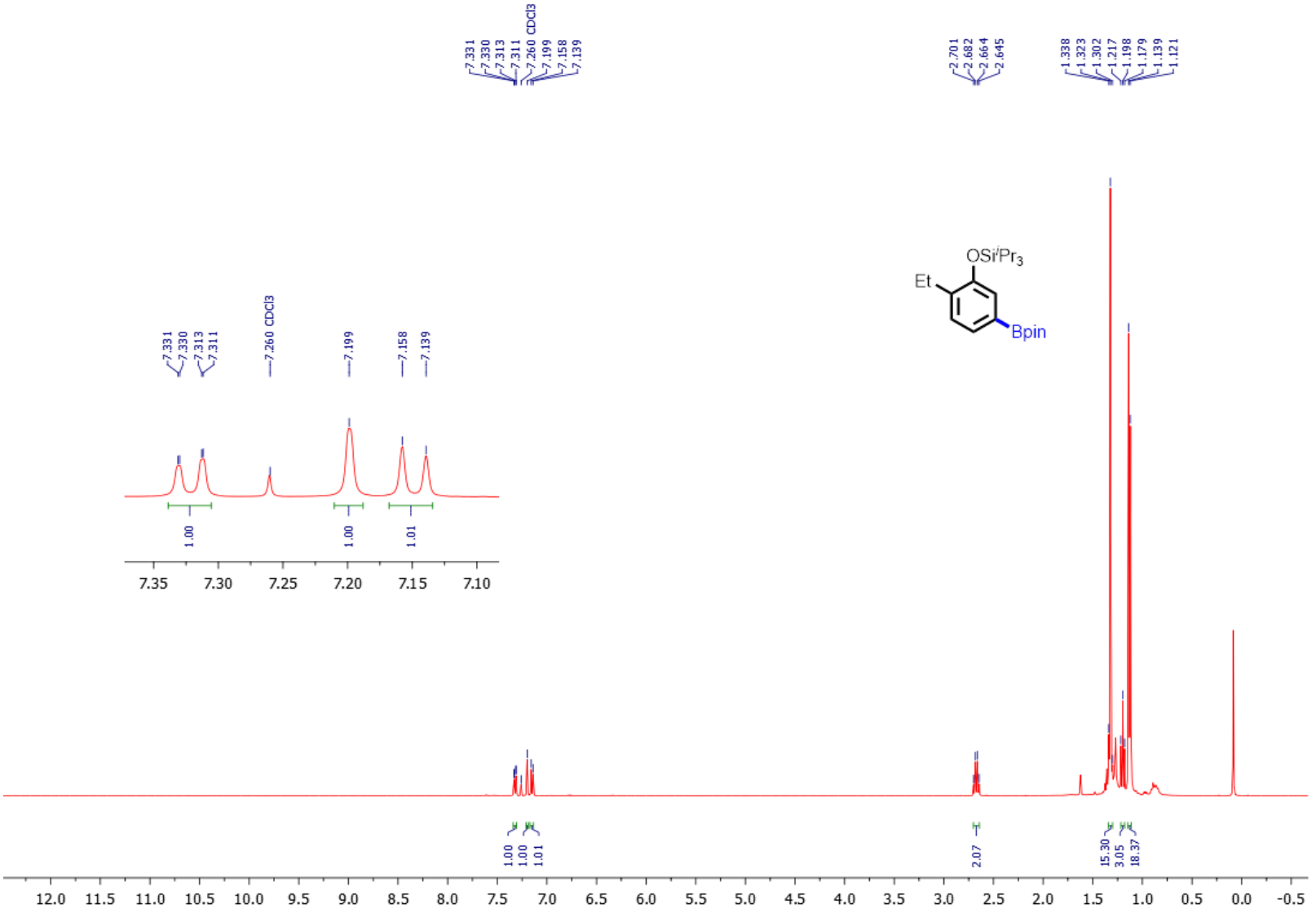
^{13}C NMR spectra of **2s** (25 °C, 100 MHz, $CDCl_3$)



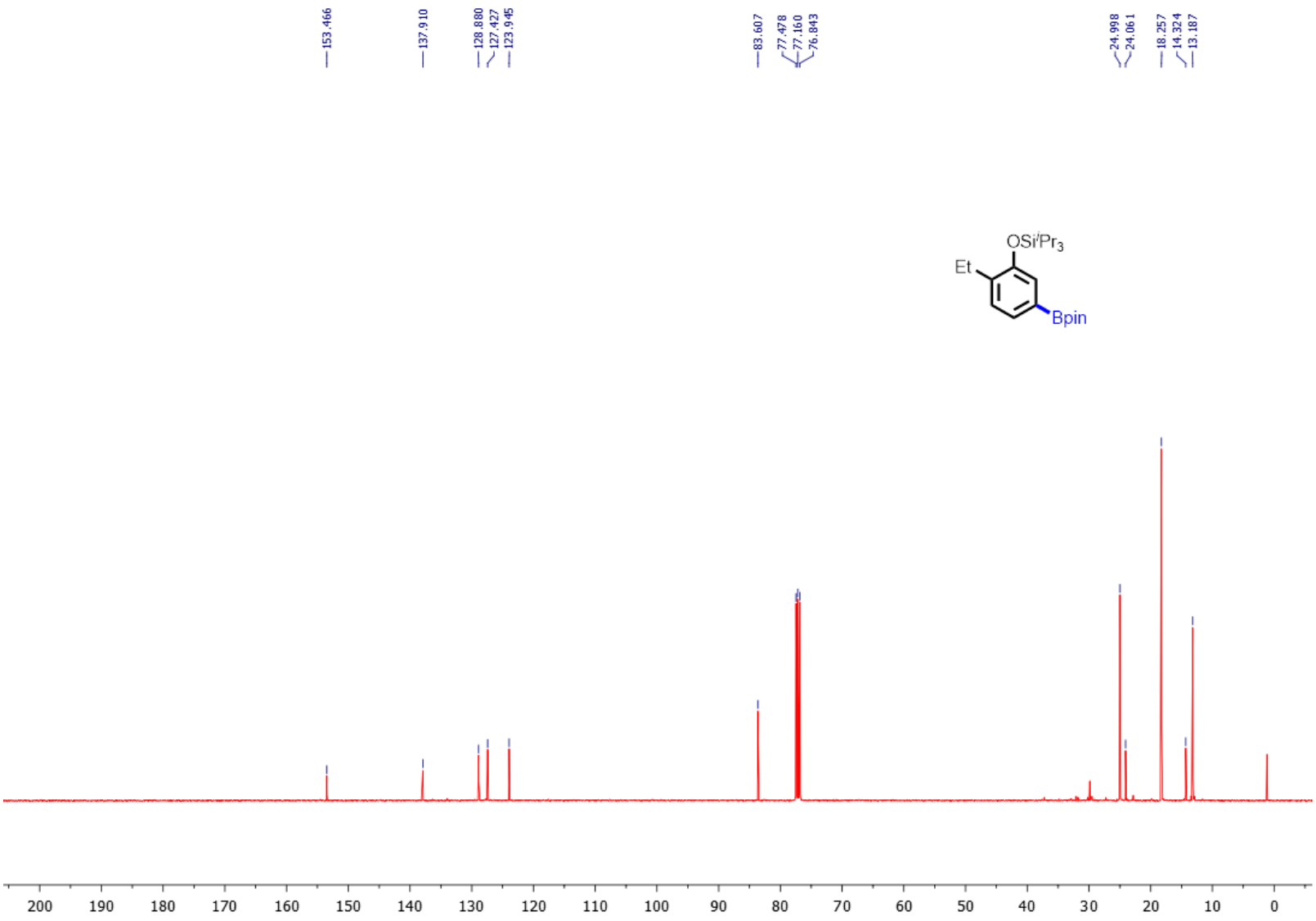
^{1}H NMR spectra of **2t** (25 °C, 400 MHz, $CDCl_3$)



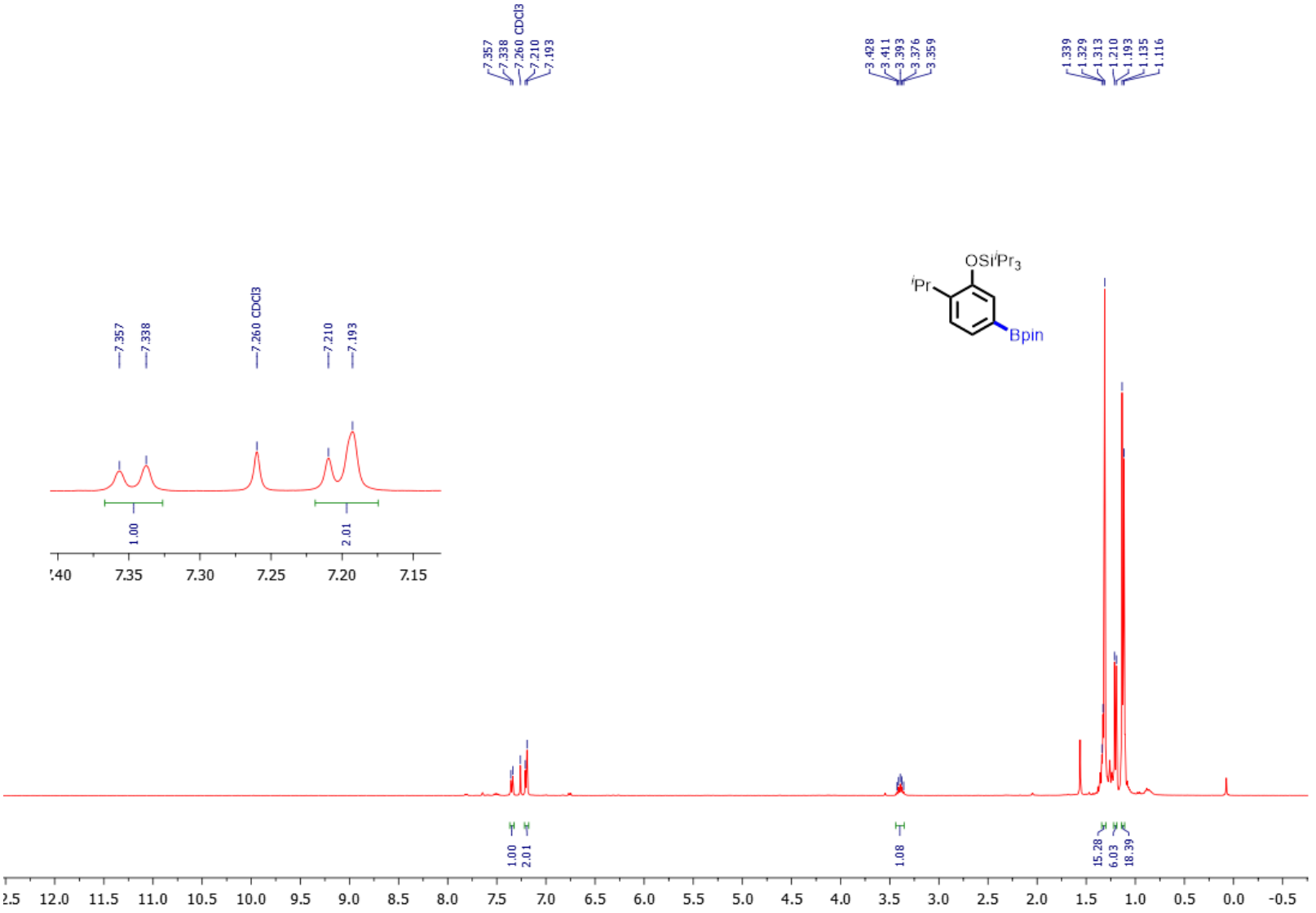
^{13}C NMR spectra of **2t** (25 °C, 100 MHz, $CDCl_3$)



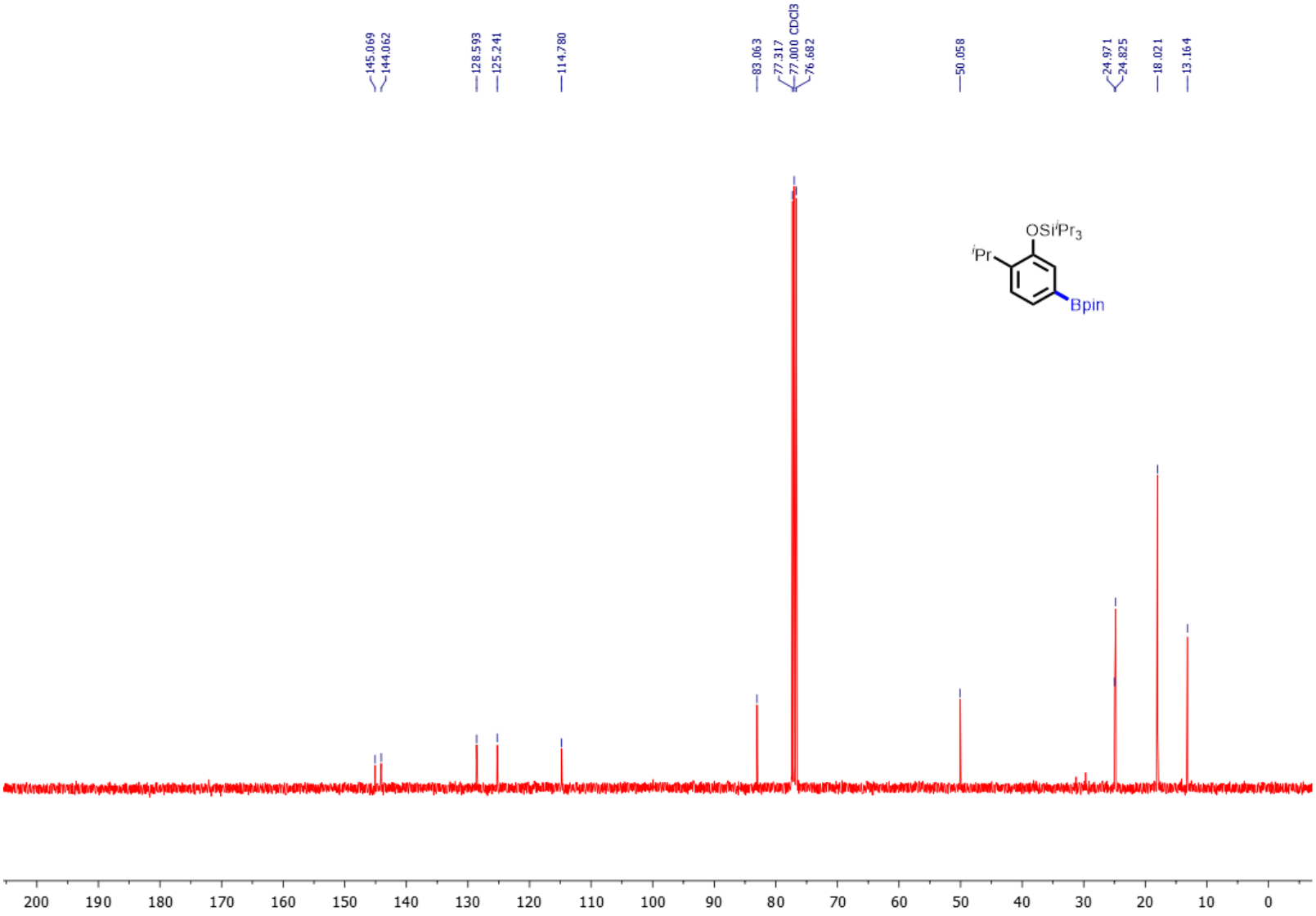
^{1}H NMR spectra of **2u** (25 °C, 400 MHz, $CDCl_3$)



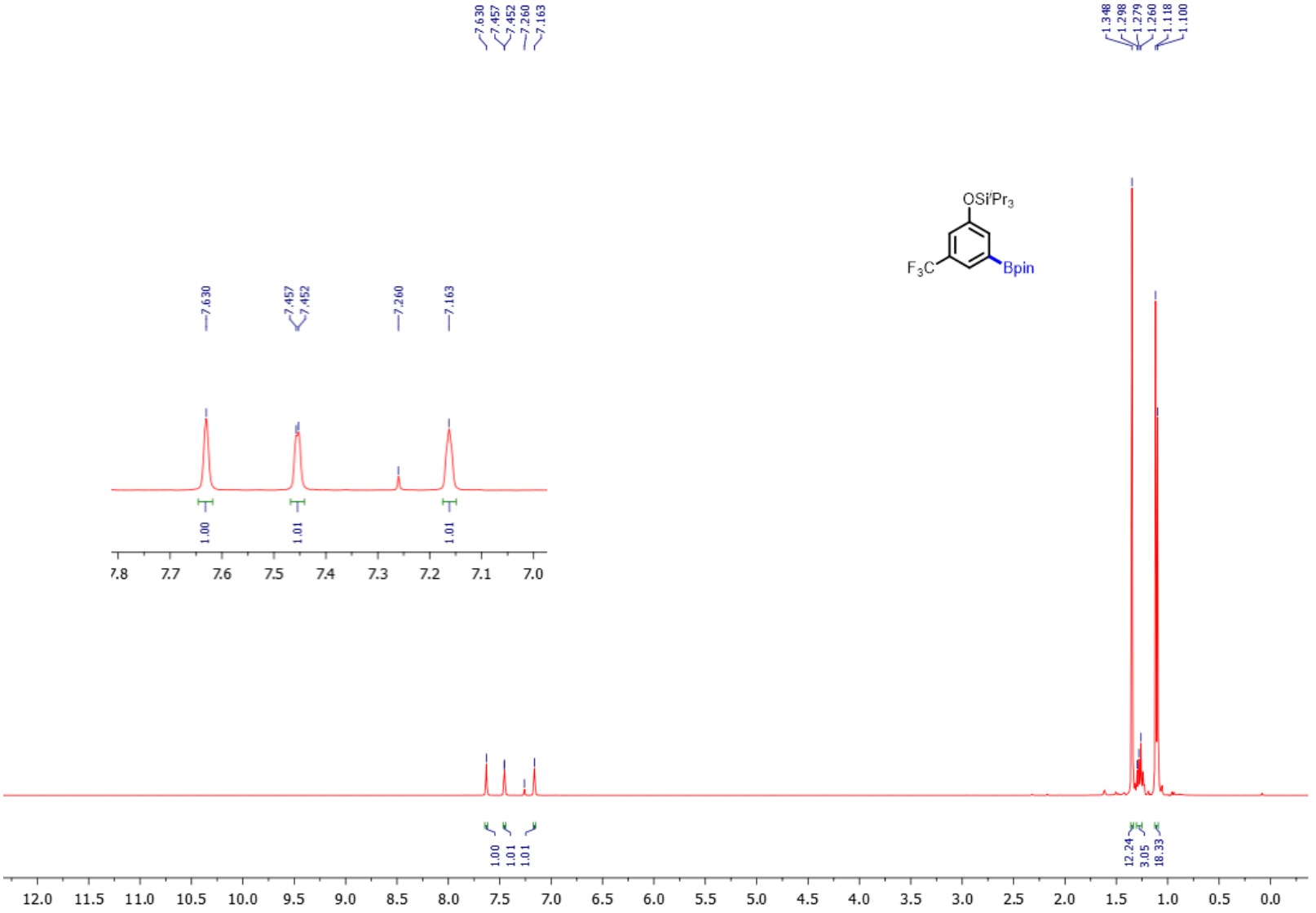
^{13}C NMR spectra of **2u** (25 °C, 100 MHz, $CDCl_3$)



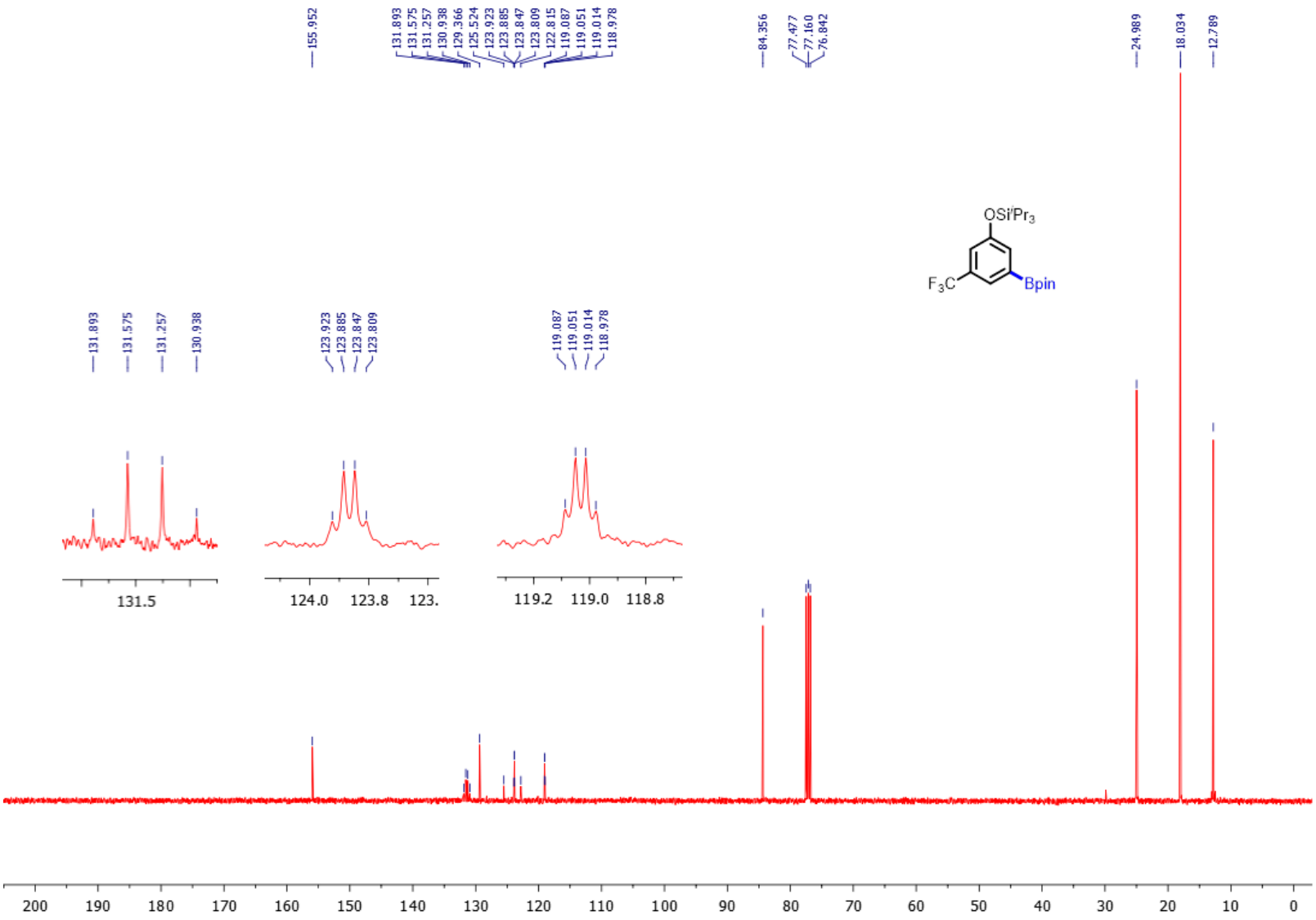
^{1}H NMR spectra of **2v** (25 °C, 400 MHz, $CDCl_3$)



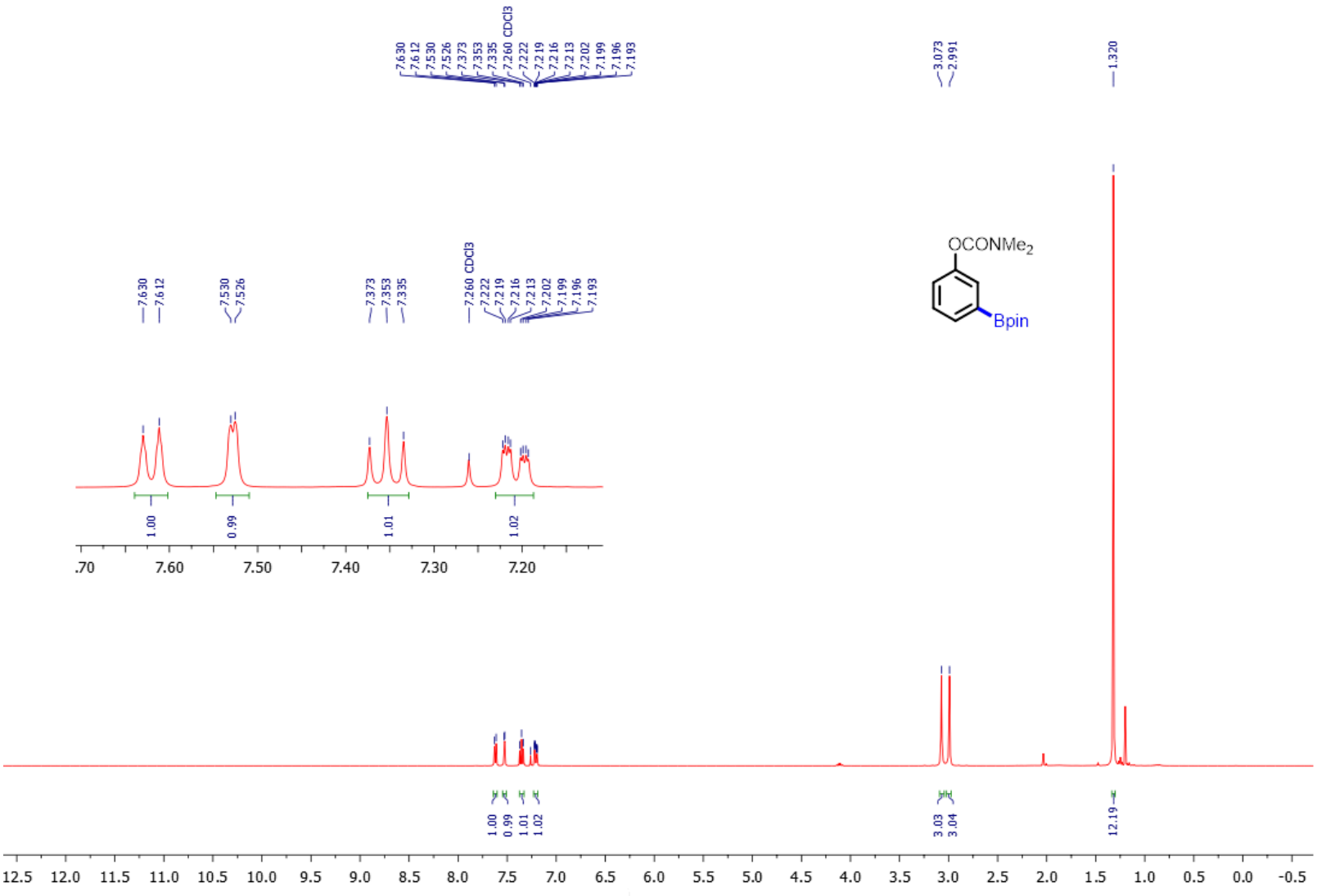
^{13}C NMR spectra of **2v** (25 °C, 100 MHz, $CDCl_3$)



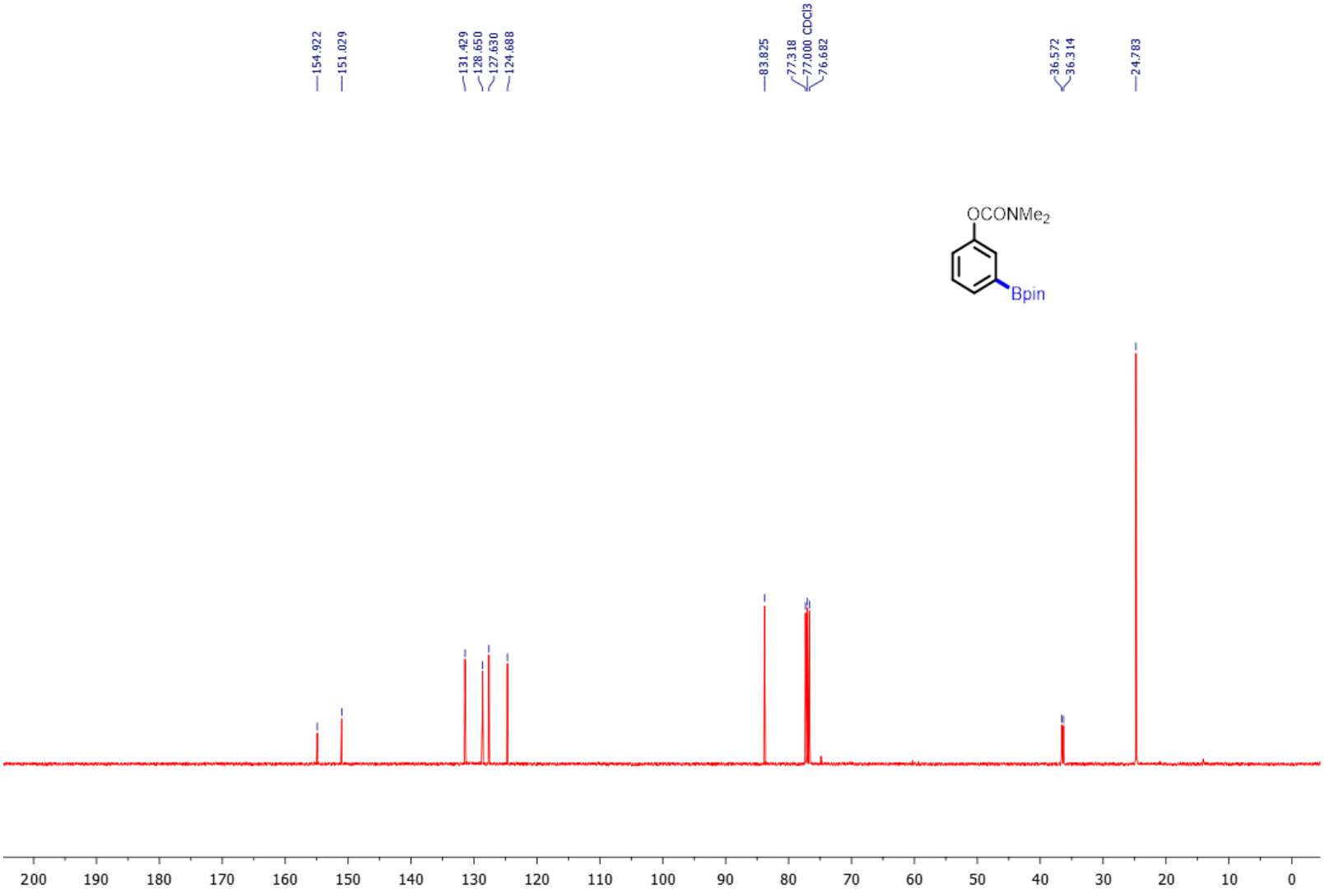
^{1}H NMR spectra of **2w** (25 ^{o}C, 400 MHz, $CDCl_3$)



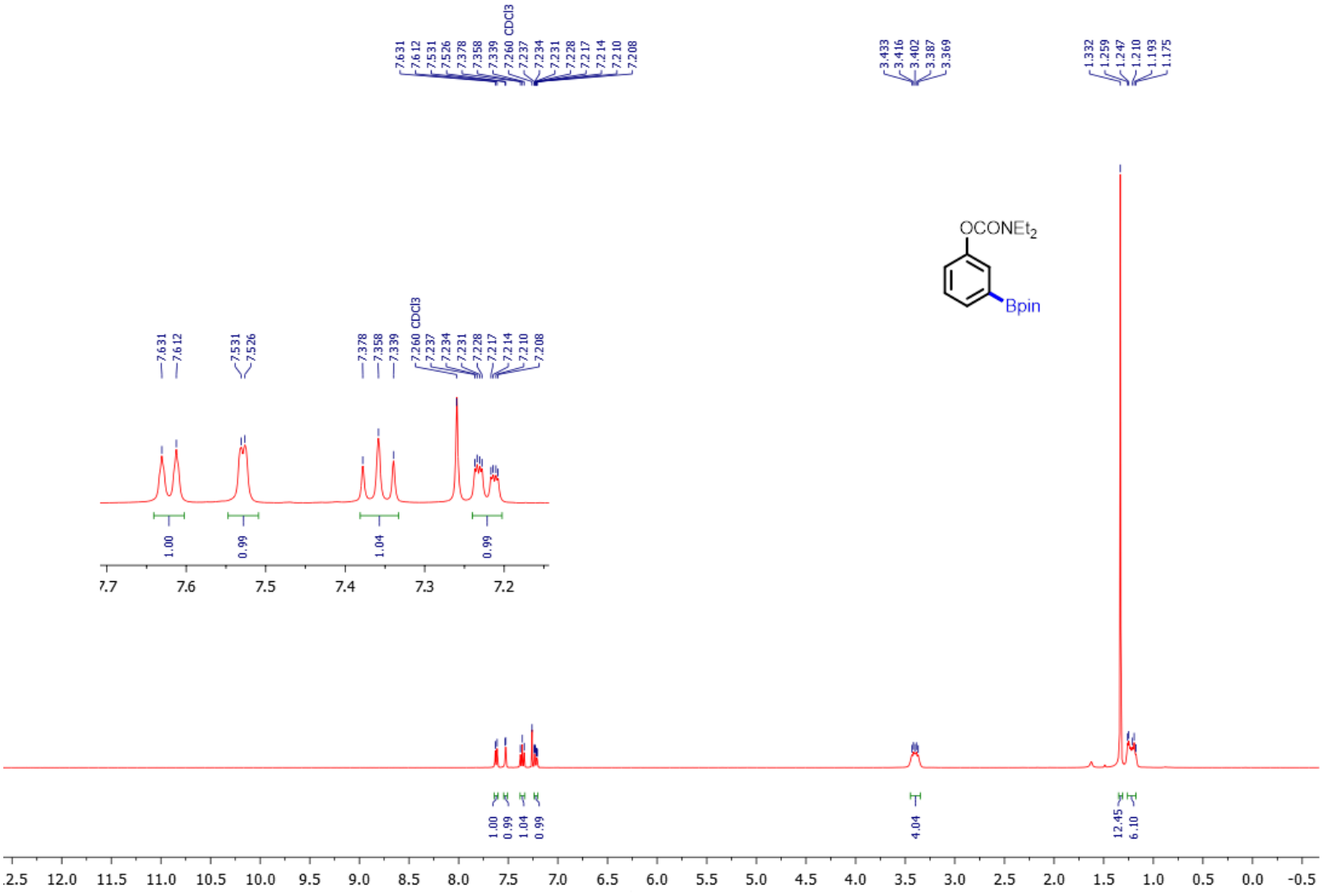
^{13}C NMR spectra of **2w** (25 °C, 100 MHz, $CDCl_3$)



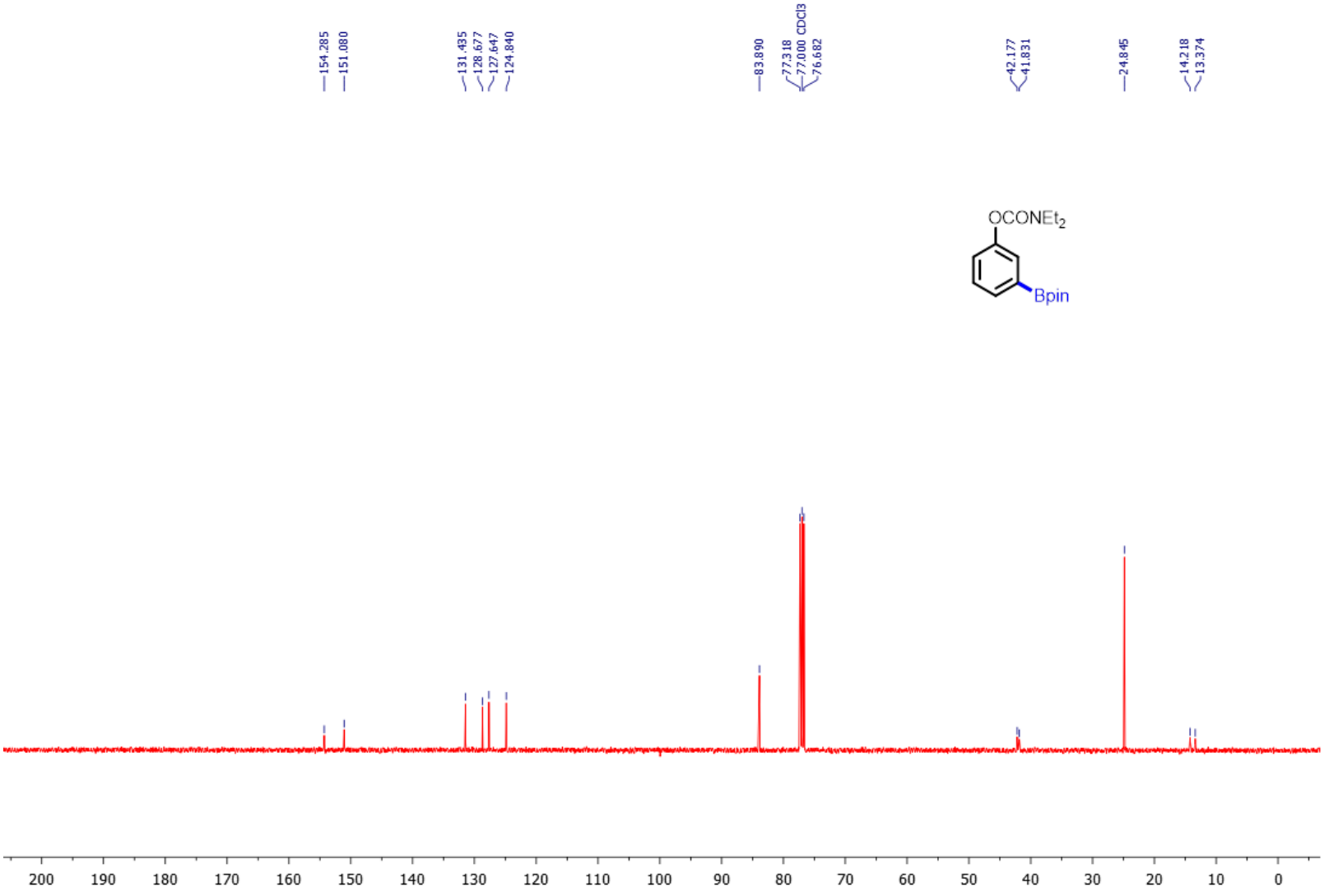
^{1}H NMR spectra of **2x** (25 °C, 400 MHz, $CDCl_3$)



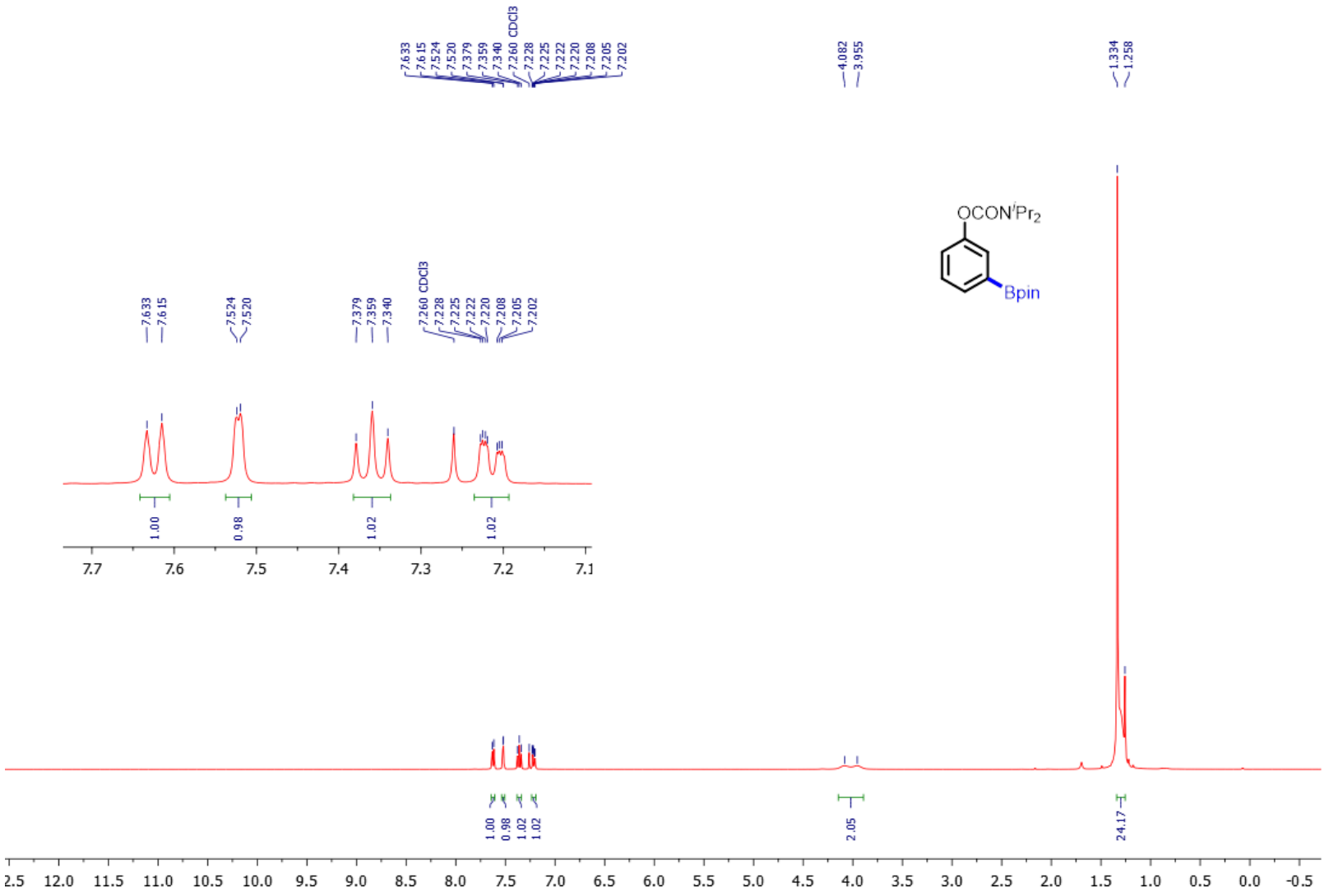
^{13}C NMR spectra of **2x** (25 °C, 100 MHz, $CDCl_3$)



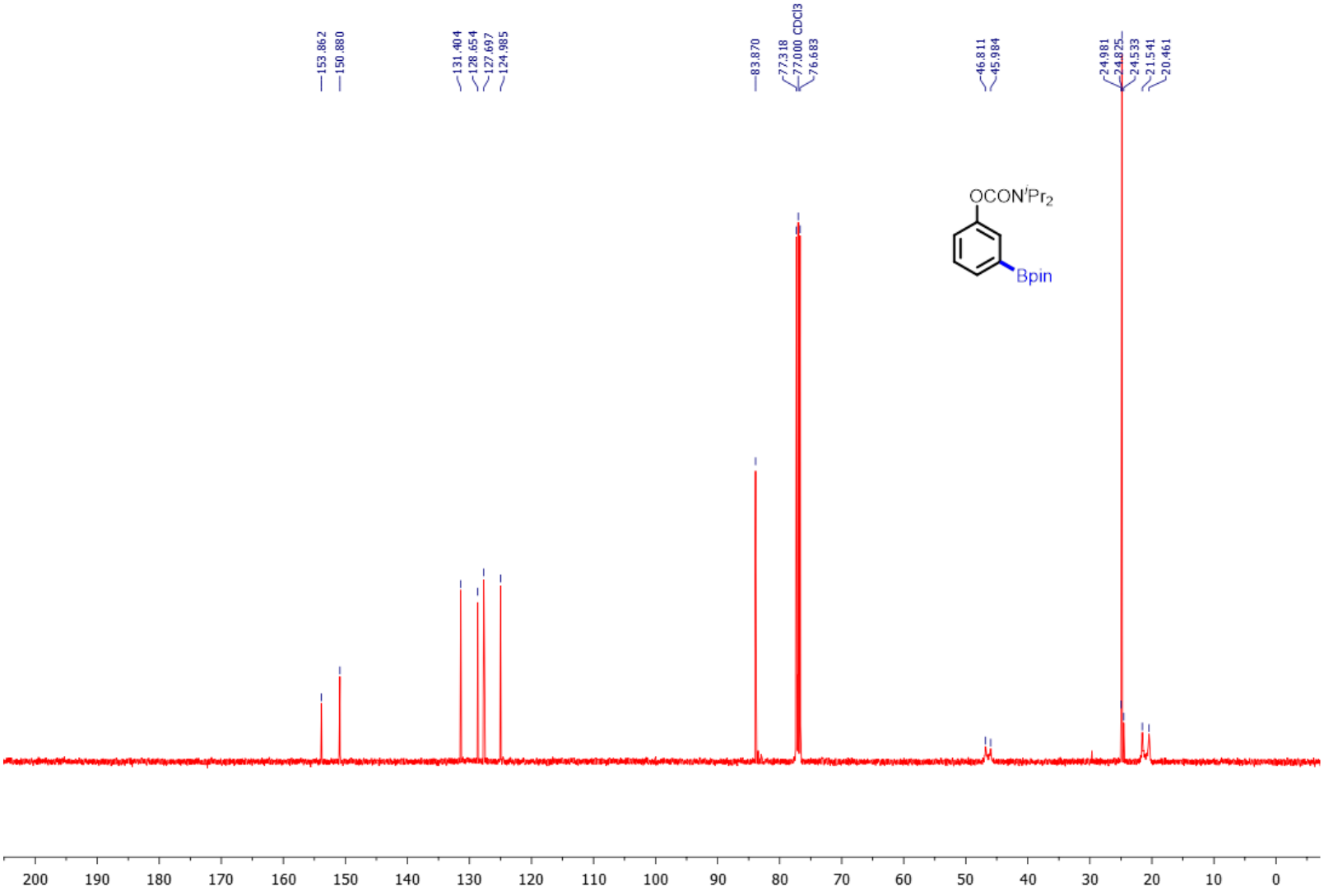
^{1}H NMR spectra of **2y** (25 °C, 400 MHz, $CDCl_3$)



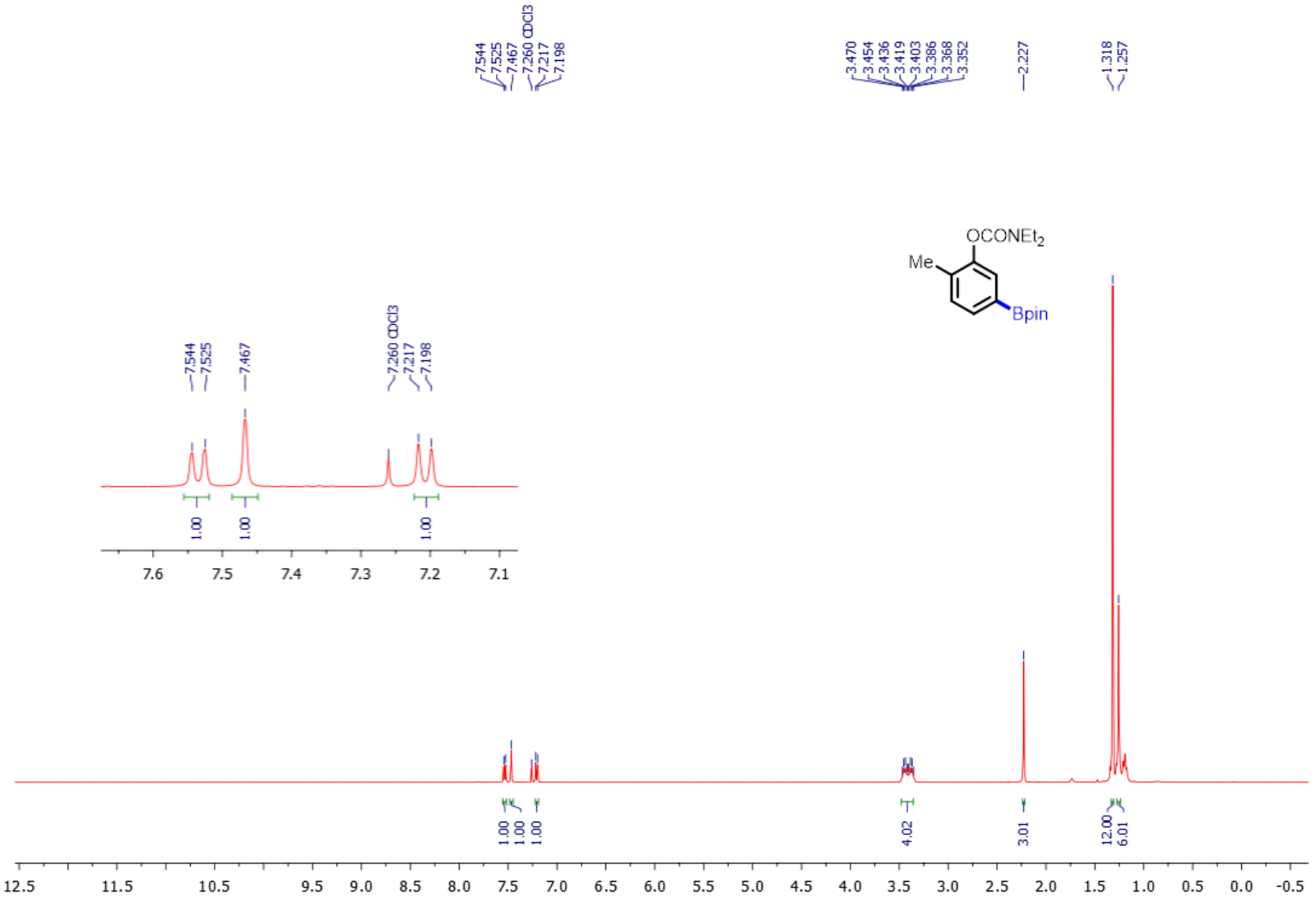
^{13}C NMR spectra of **2y** (25 °C, 100 MHz, $CDCl_3$)



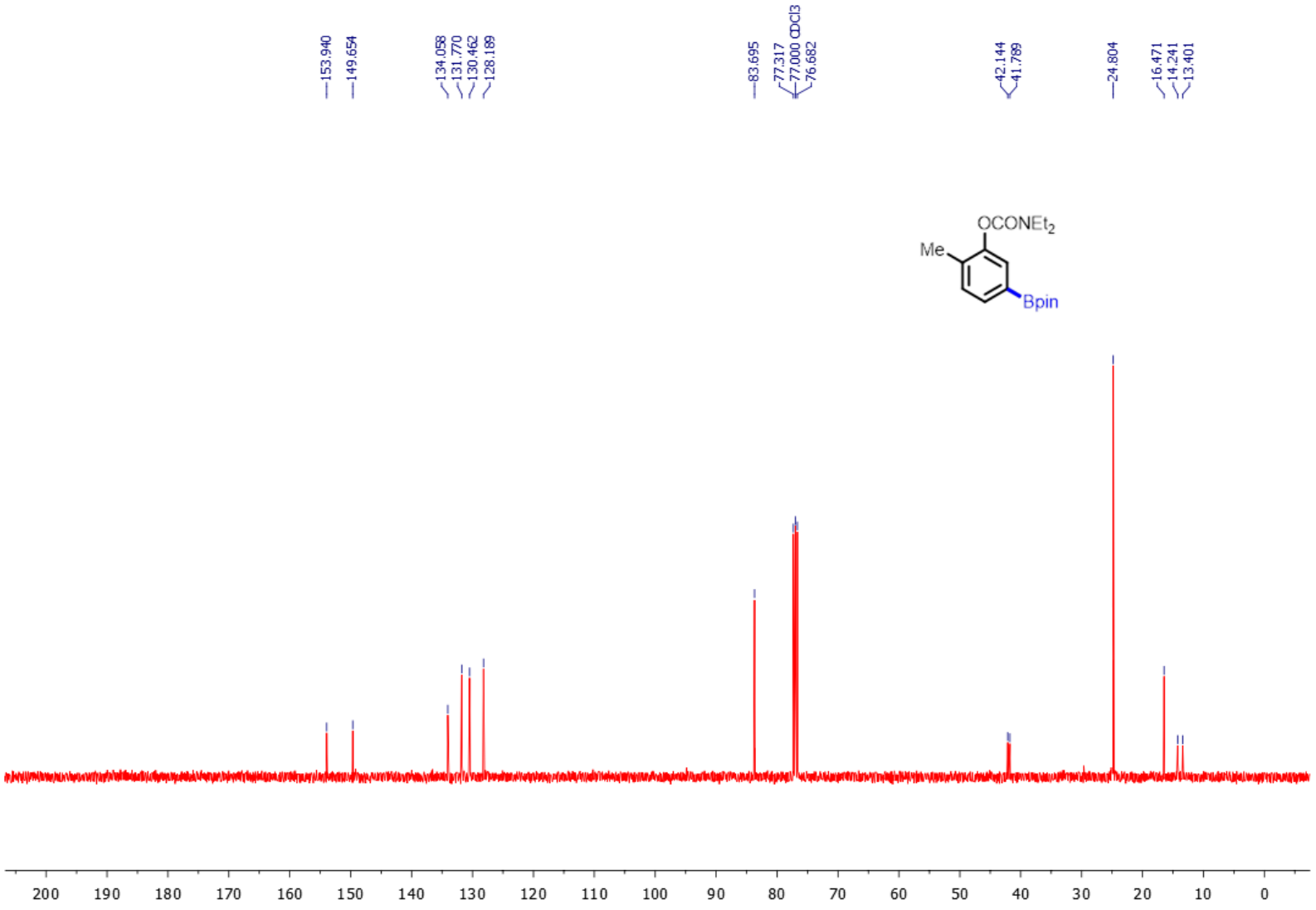
^{1}H NMR spectra of **2z** (25 °C, 400 MHz, $CDCl_3$)



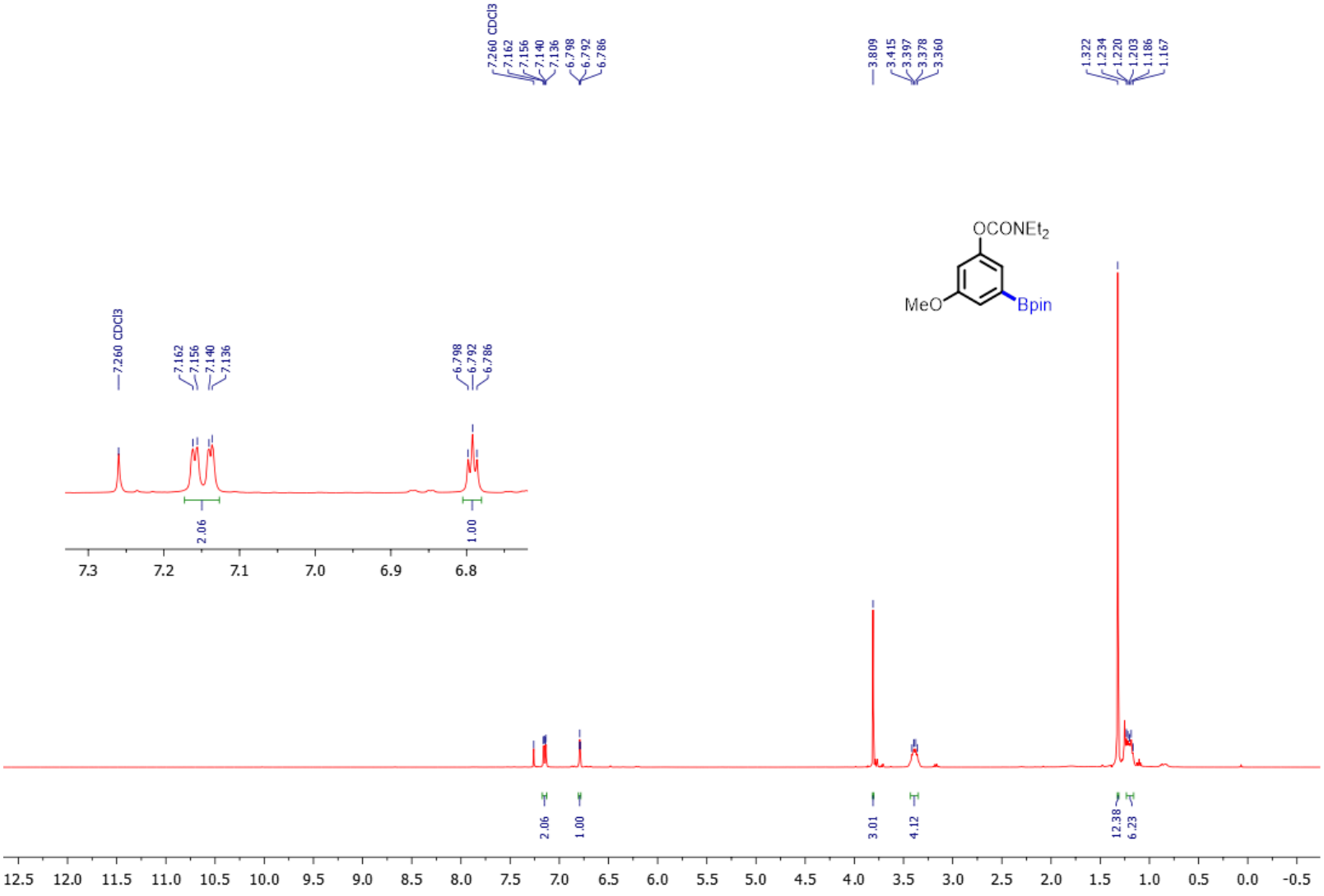
^{13}C NMR spectra of **2z** (25 °C, 100 MHz, $CDCl_3$)



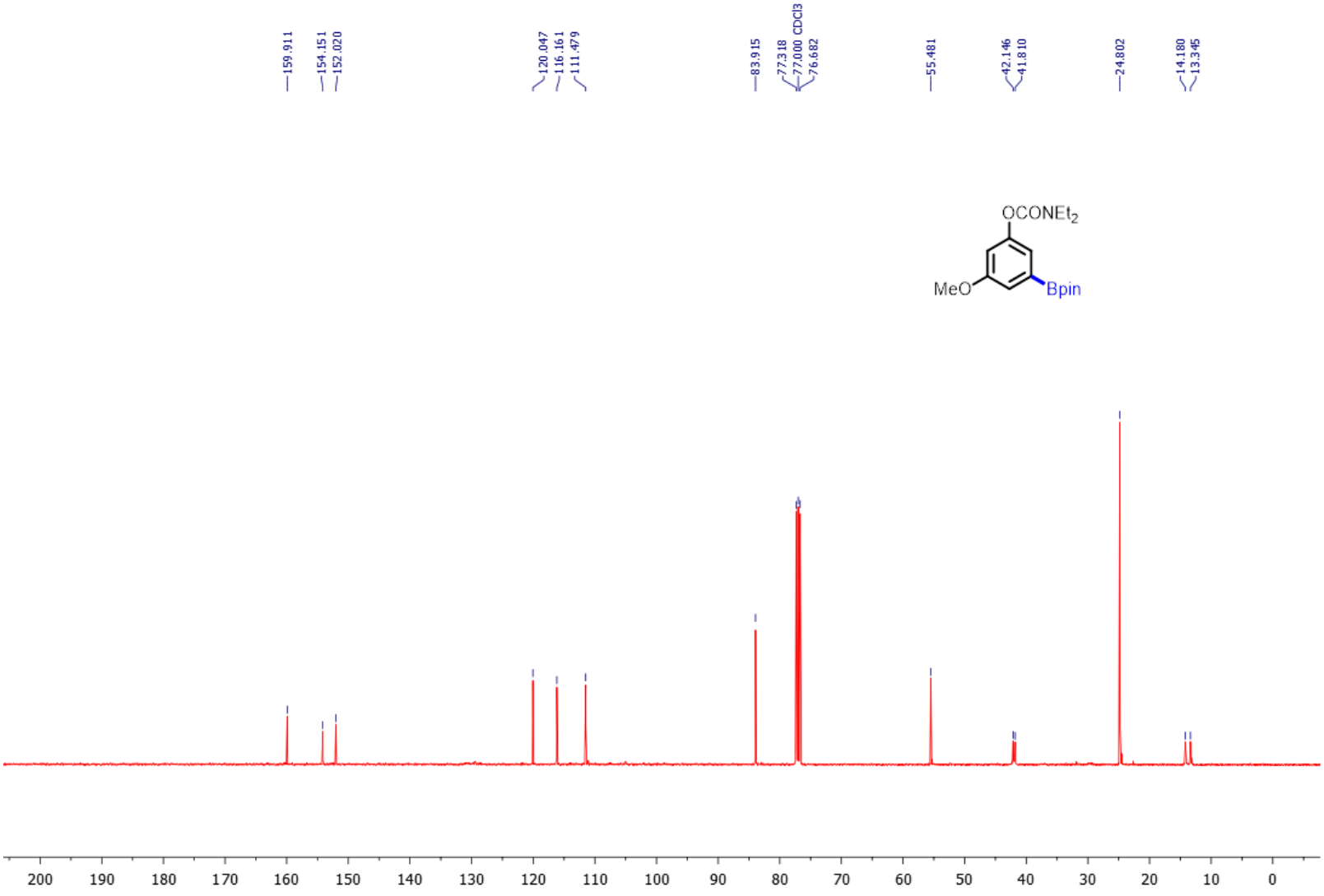
^{1}H NMR spectra of **2aa** (25 ºC, 400 MHz, $CDCl_3$)



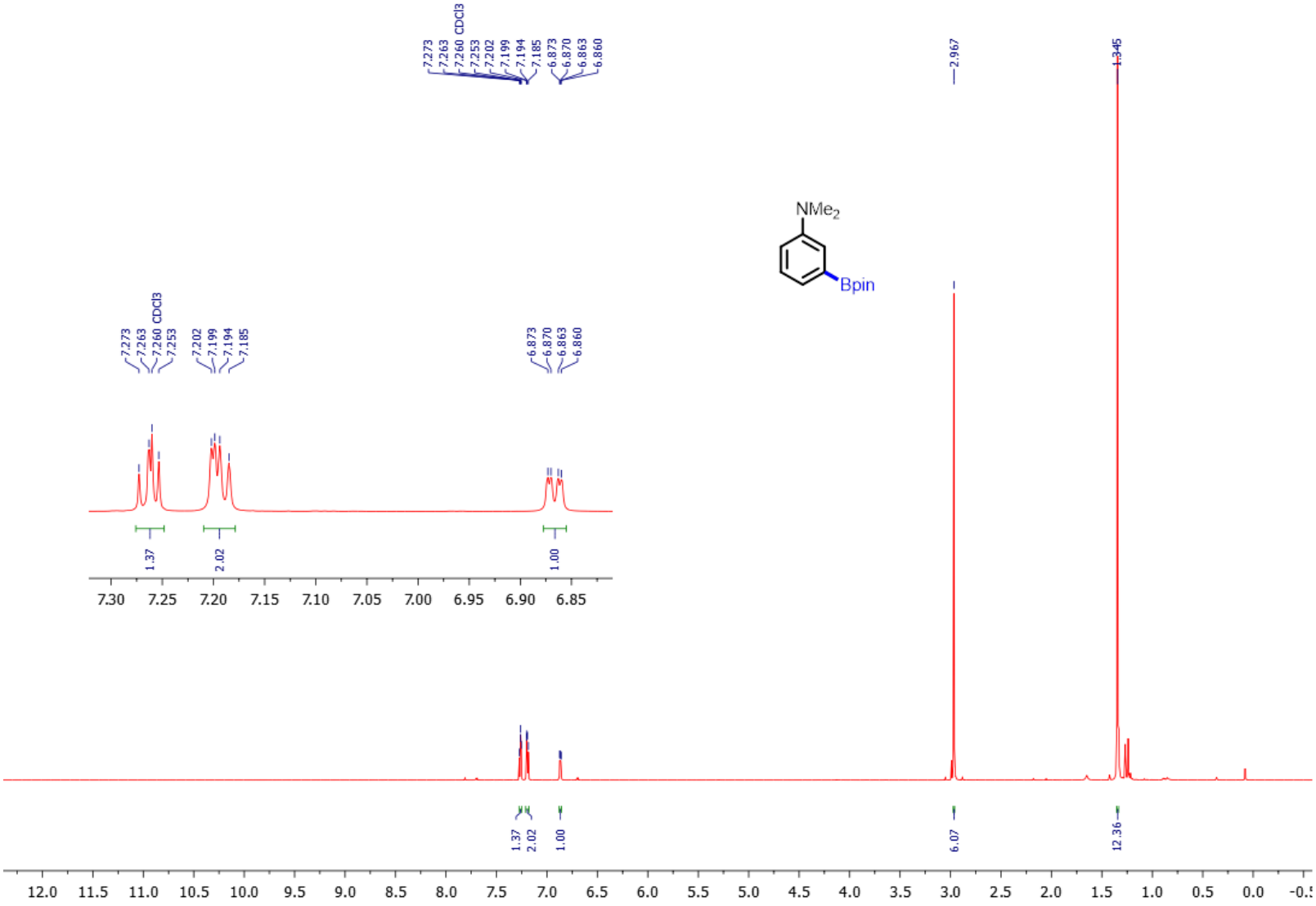
^{13}C NMR spectra of **2aa** (25 °C, 100 MHz, $CDCl_3$)



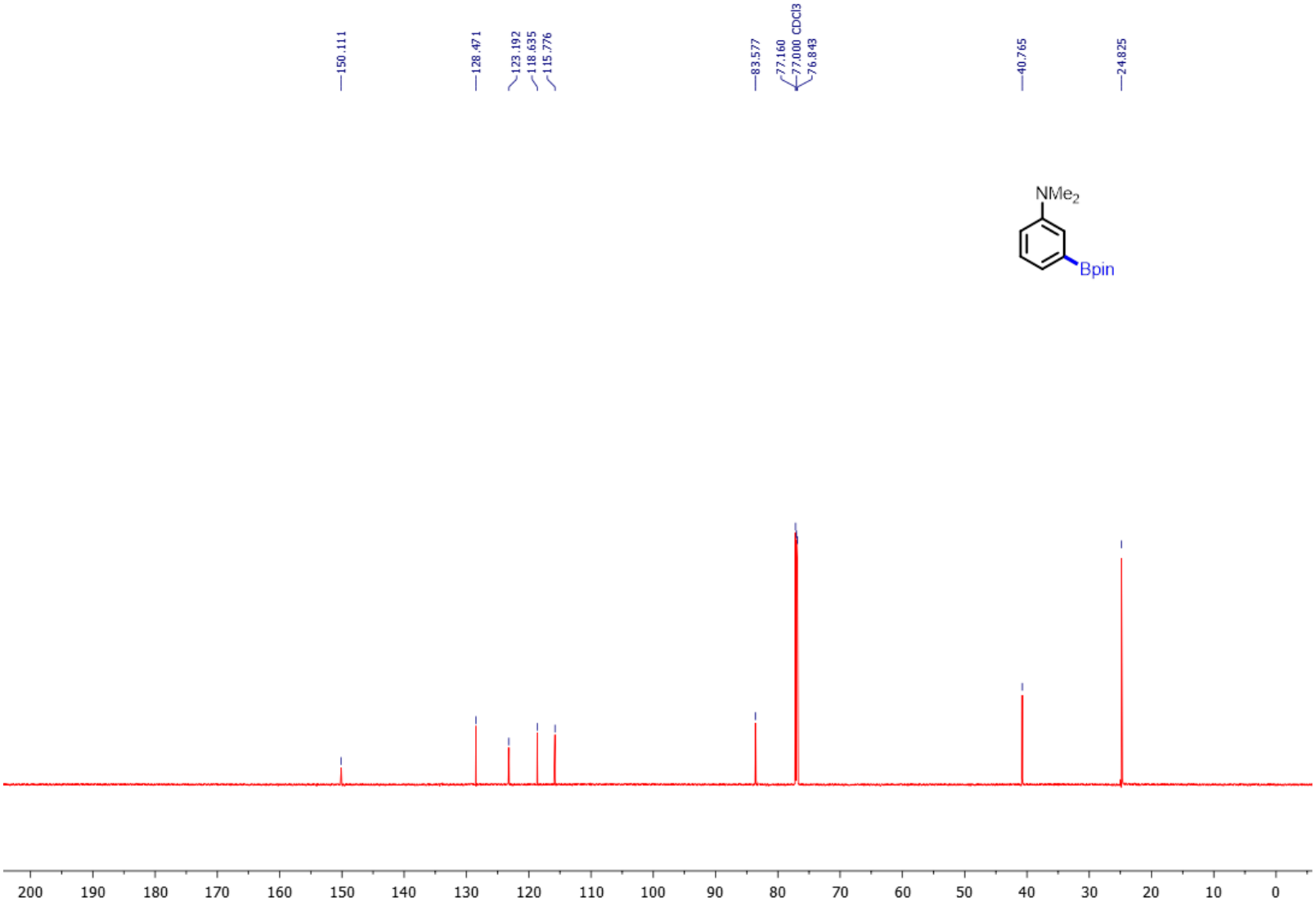
^{1}H NMR spectra of **2ab** (25 ºC, 400 MHz, $CDCl_3$)



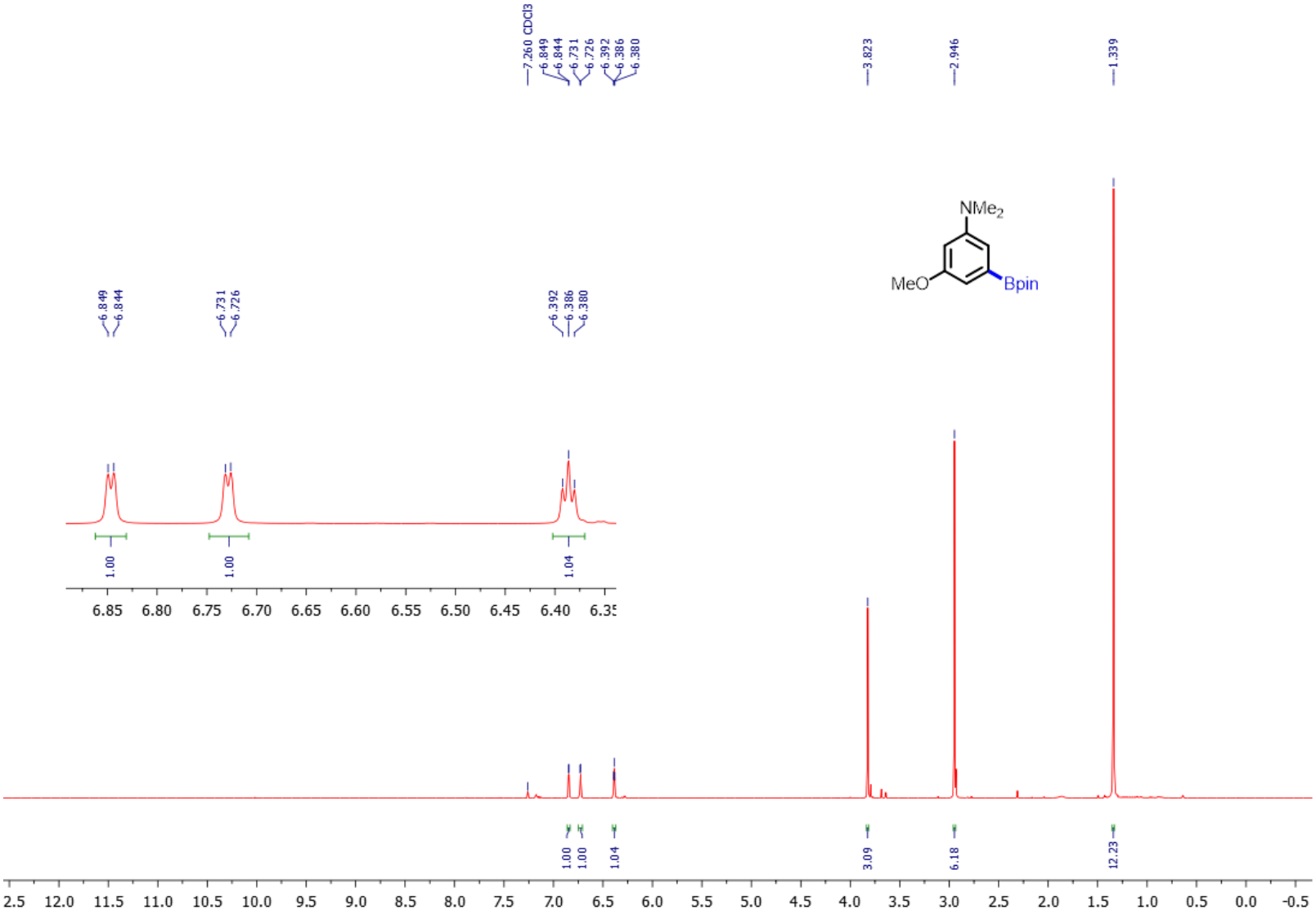
^{13}C NMR spectra of **2ab** (25 ºC, 100 MHz, $CDCl_3$)



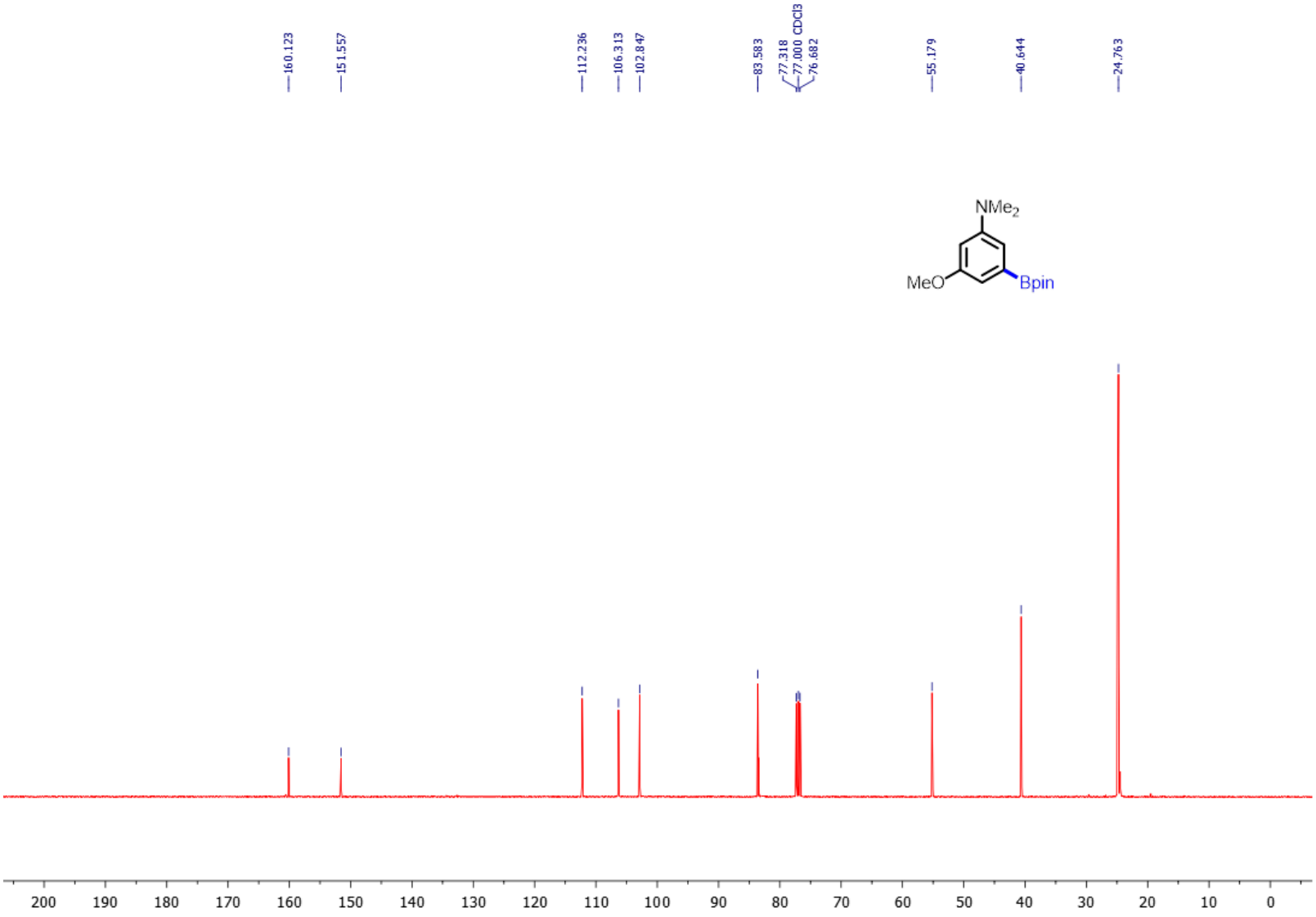
^{1}H NMR spectra of **2ac** (25 ºC, 400 MHz, $CDCl_3$)



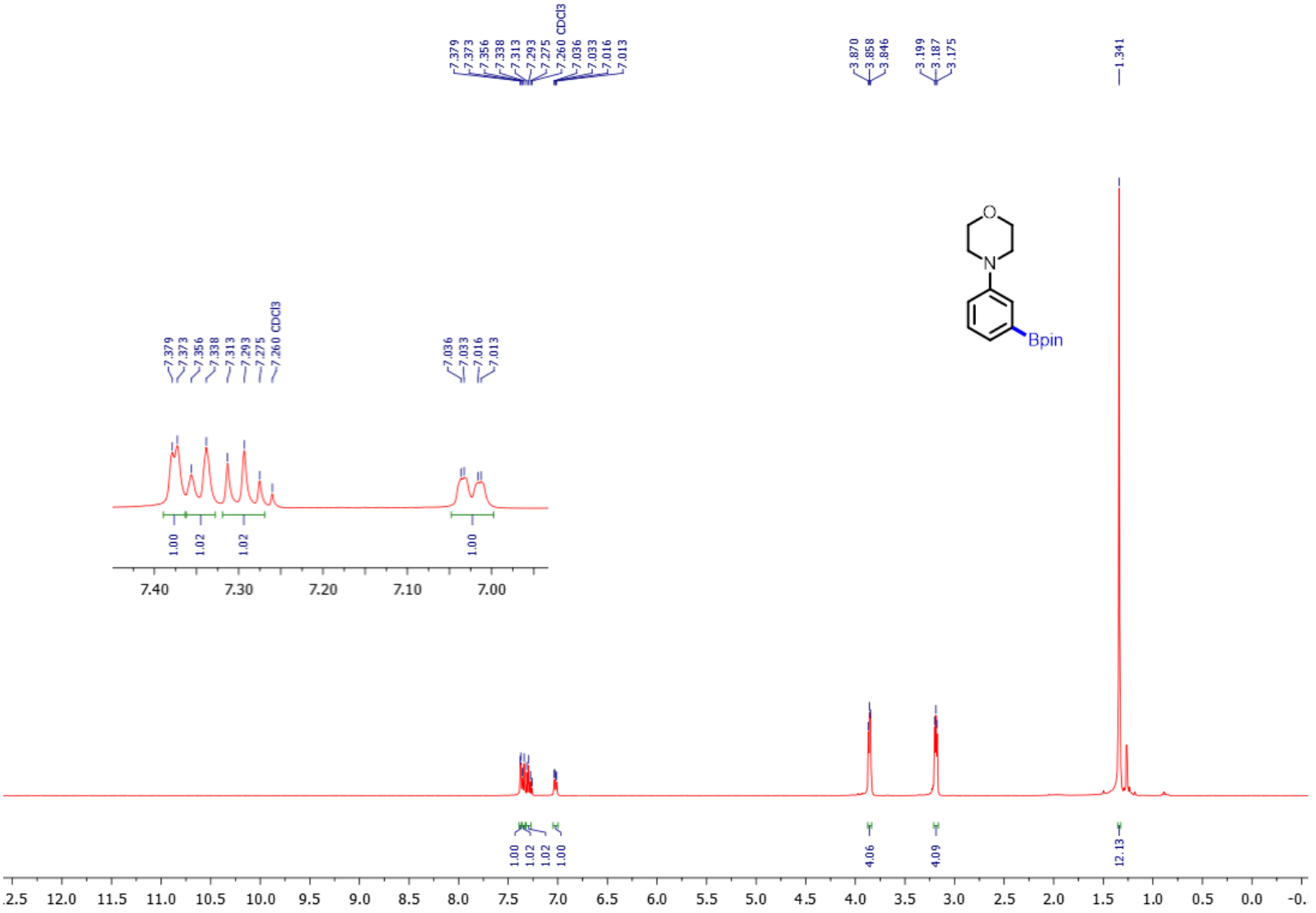
^{13}C NMR spectra of **2ac** (25 °C, 100 MHz, $CDCl_3$)



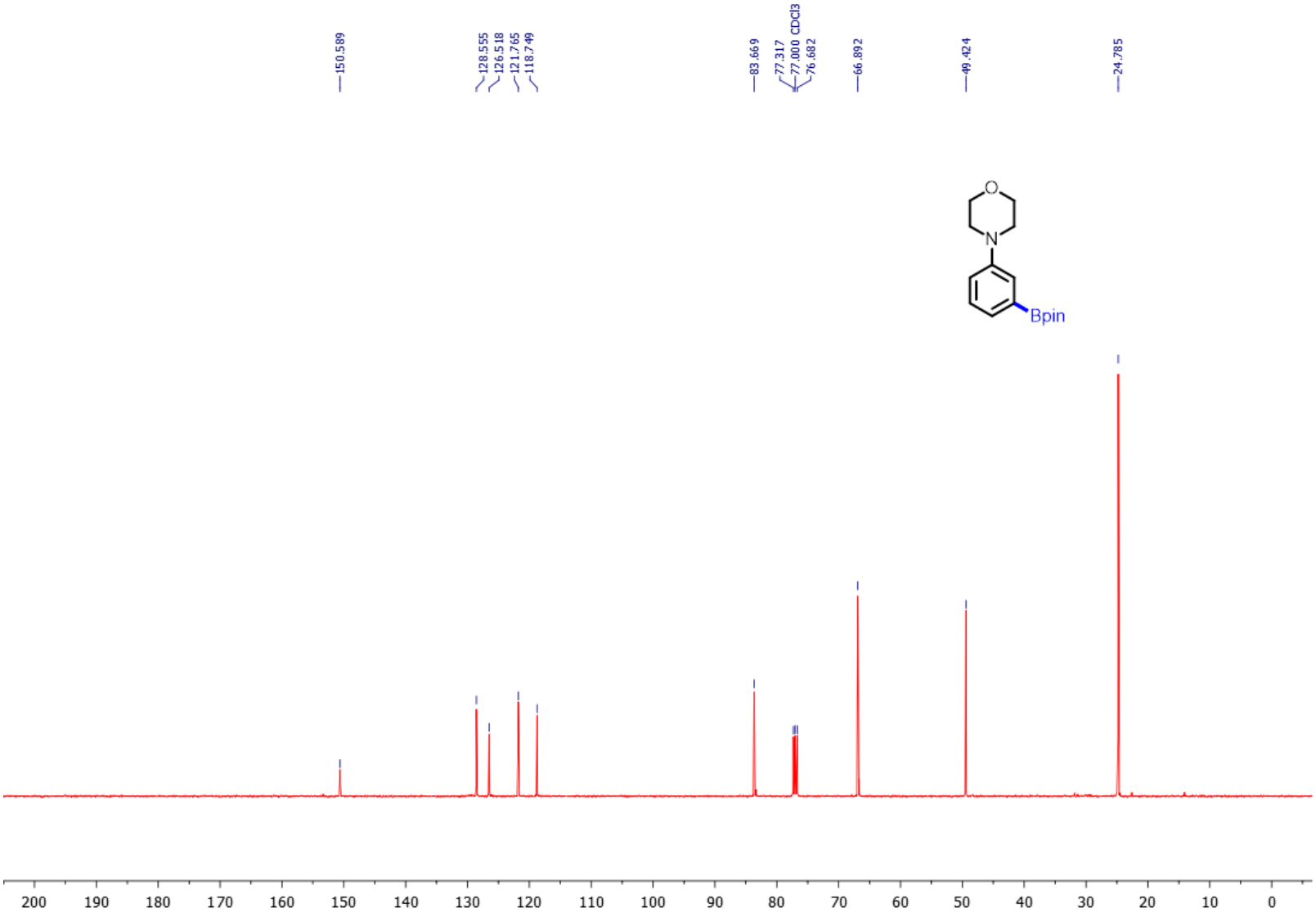
^{1}H NMR spectra of **2ad** (25 ºC, 400 MHz, $CDCl_3$)



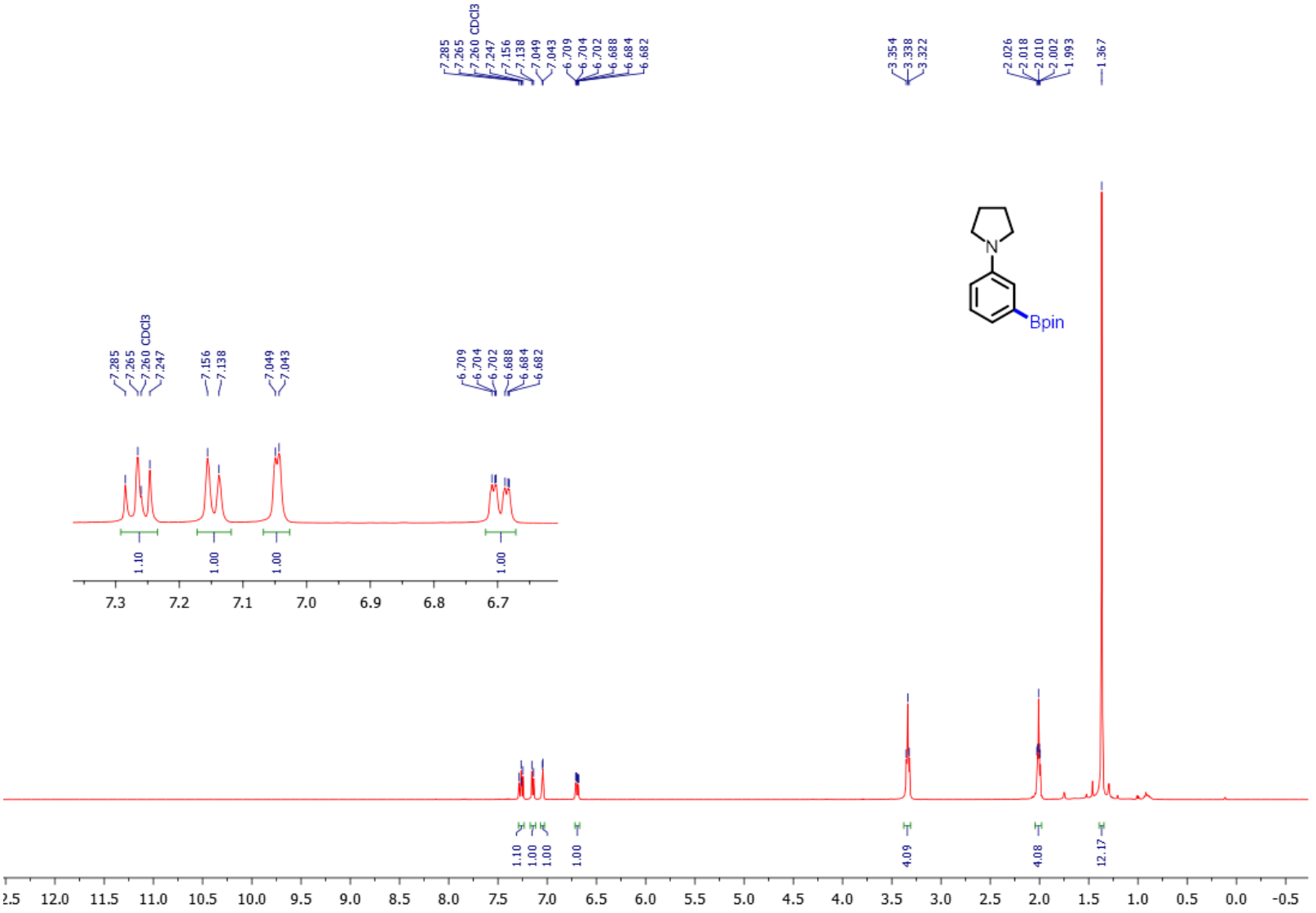
^{13}C NMR spectra of **2ad** (25 ºC, 100 MHz, $CDCl_3$)



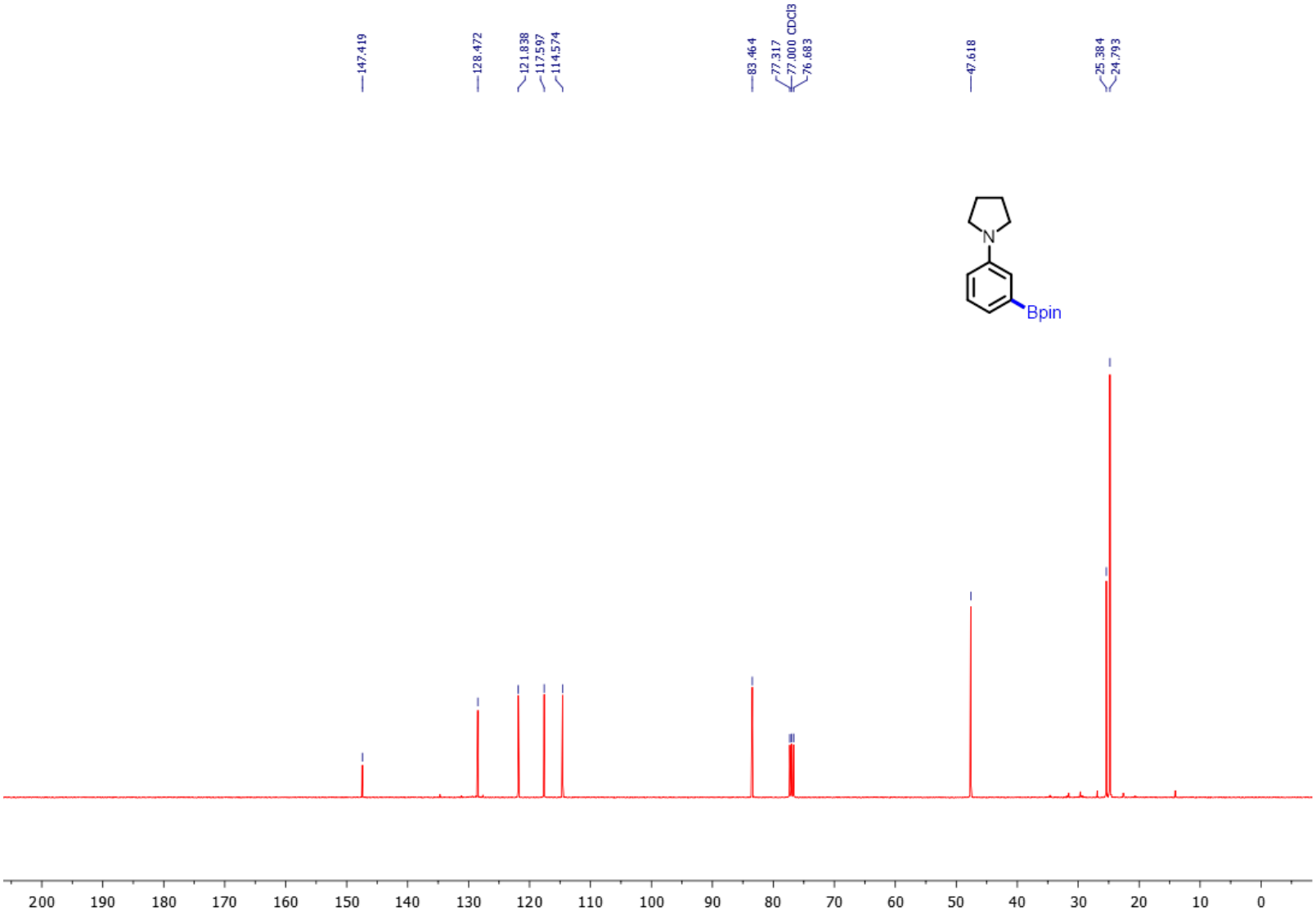
^{1}H NMR spectra of **2ae** (25 ºC, 400 MHz, $CDCl_3$)



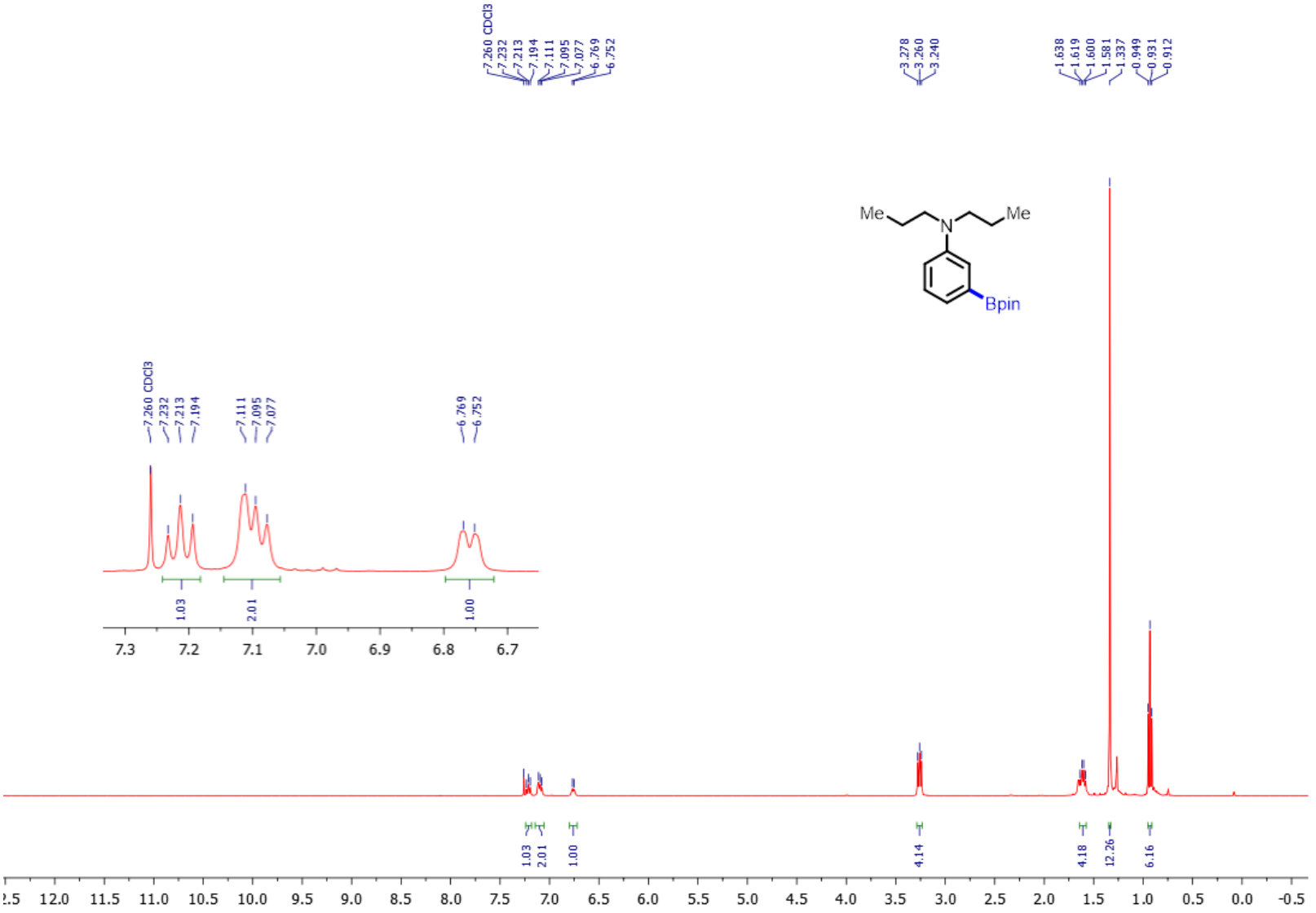
^{13}C NMR spectra of **2ae** (25 °C, 100 MHz, $CDCl_3$)



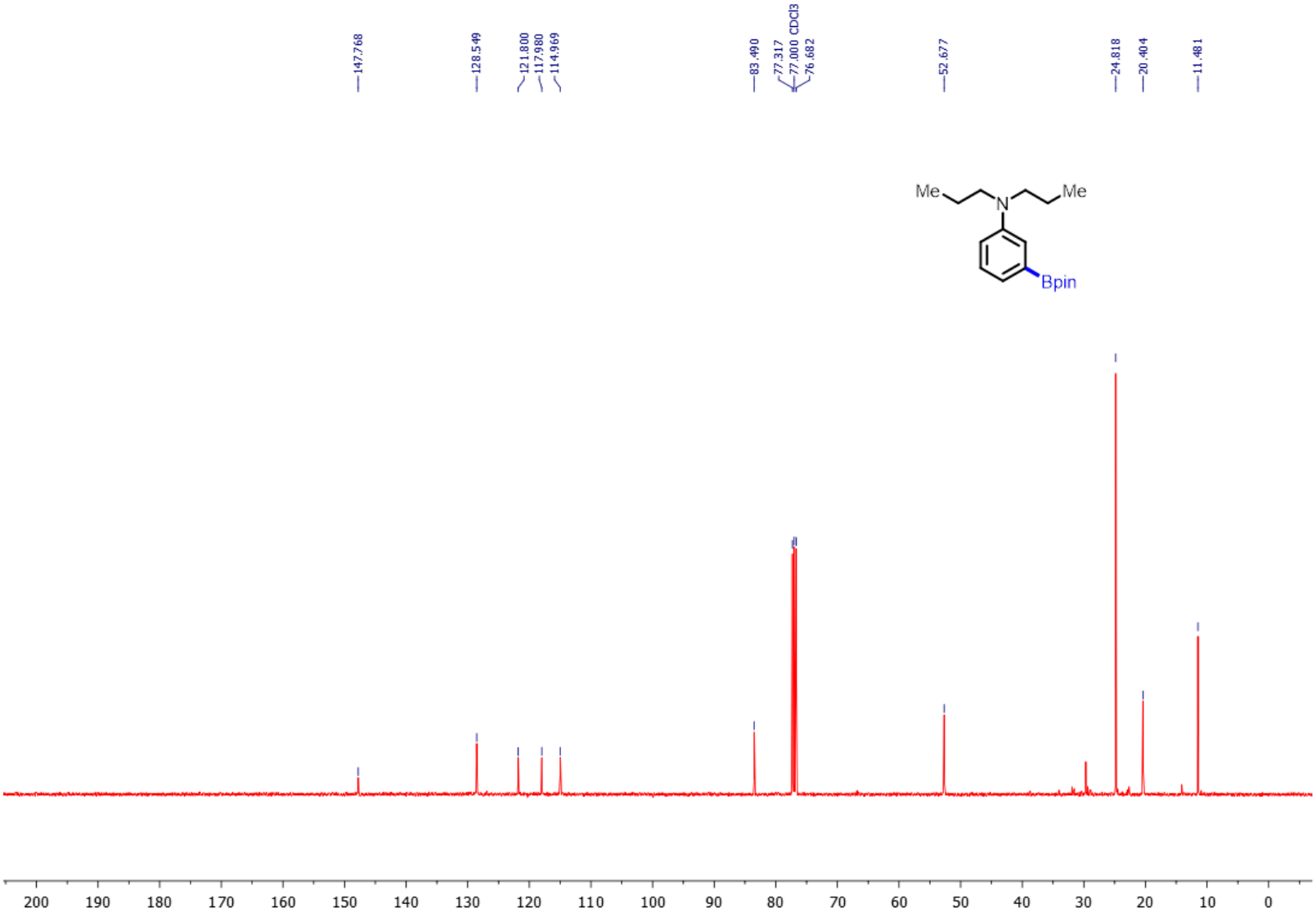
^{1}H NMR spectra of **2af** (25 °C, 400 MHz, $CDCl_3$)



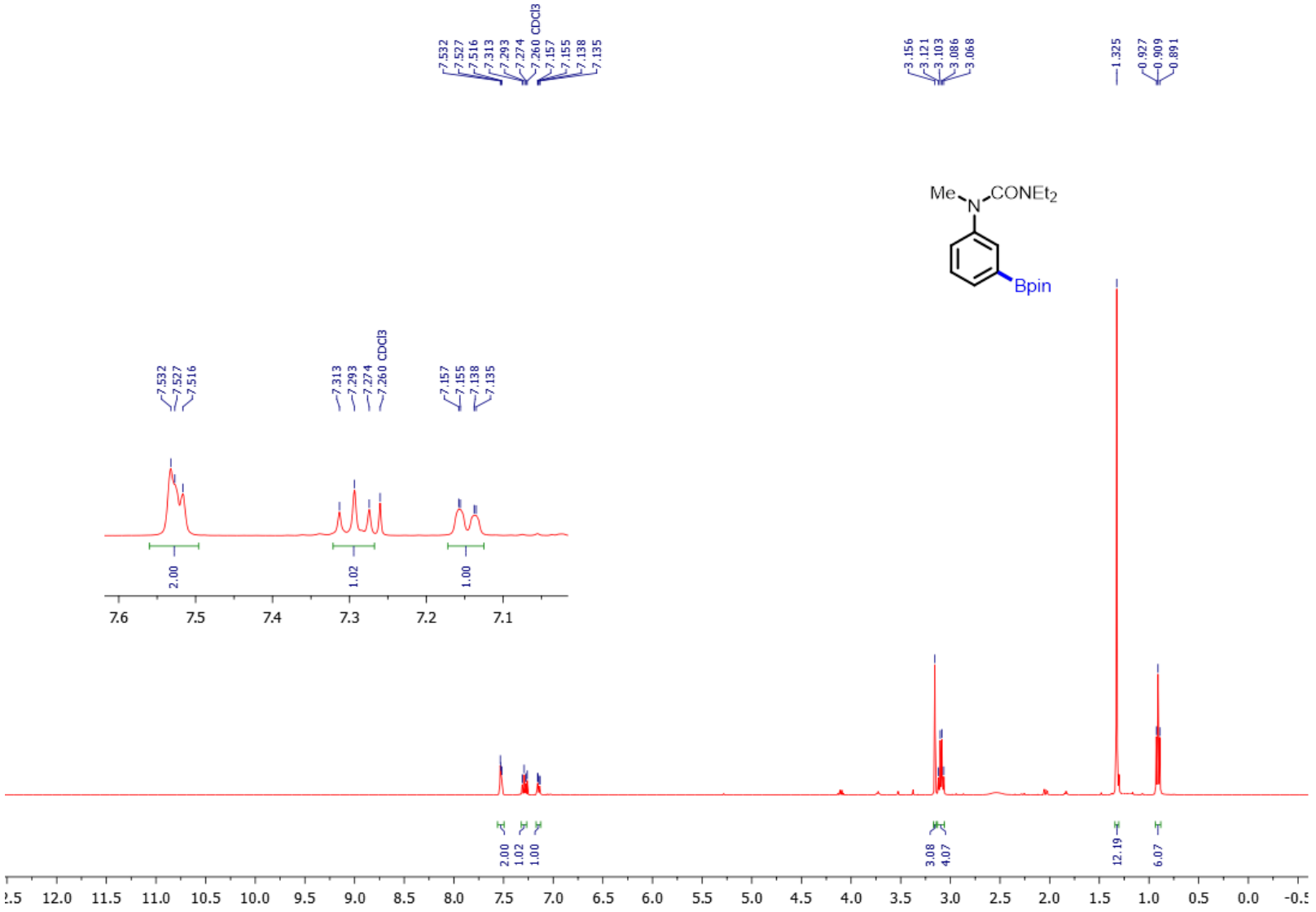
^{13}C NMR spectra of **2af** (25 ^{o}C, 100 MHz, $CDCl_3$)



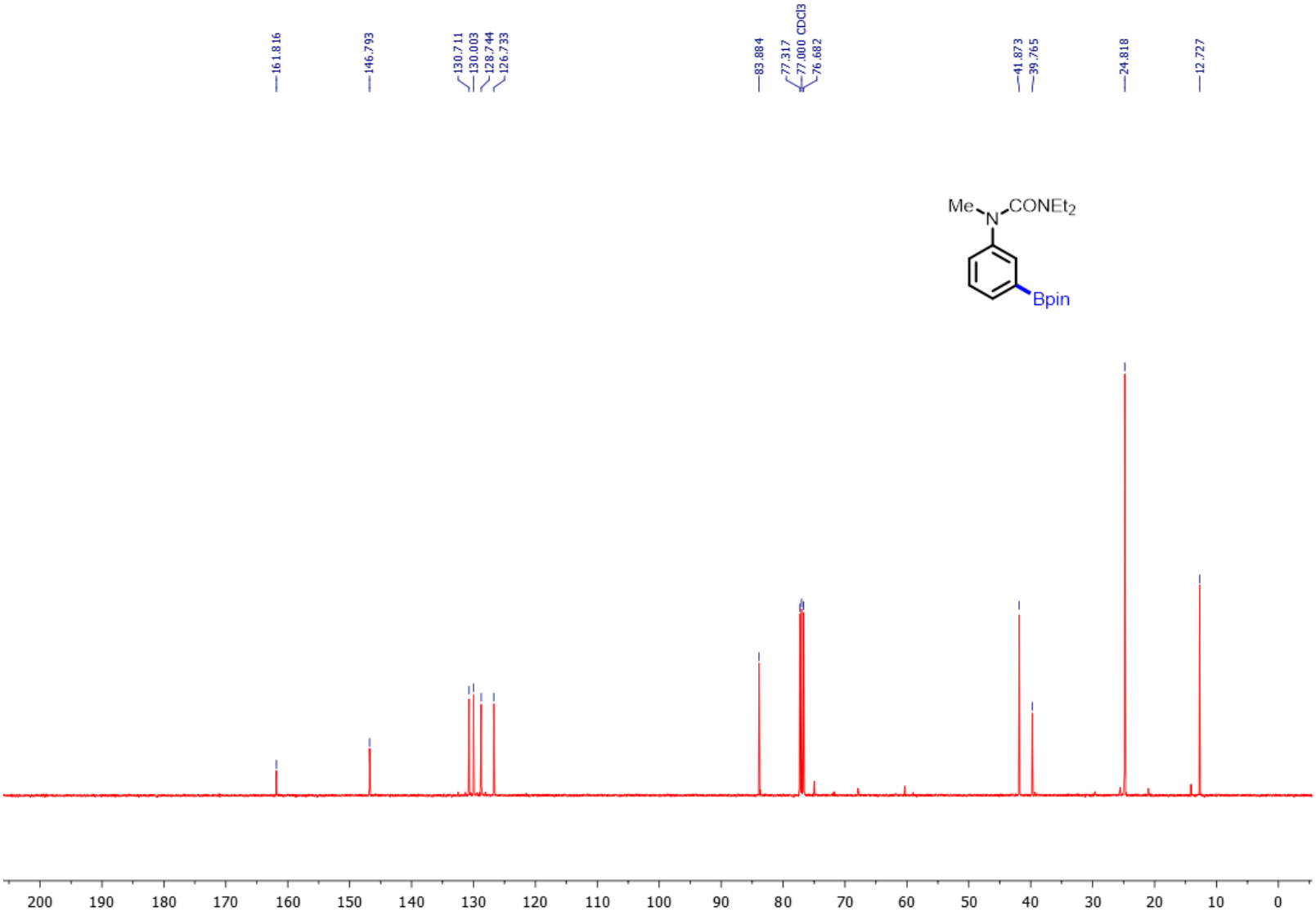
[1]H NMR spectra of **2ag** (25 ºC, 400 MHz, $CDCl_3$)



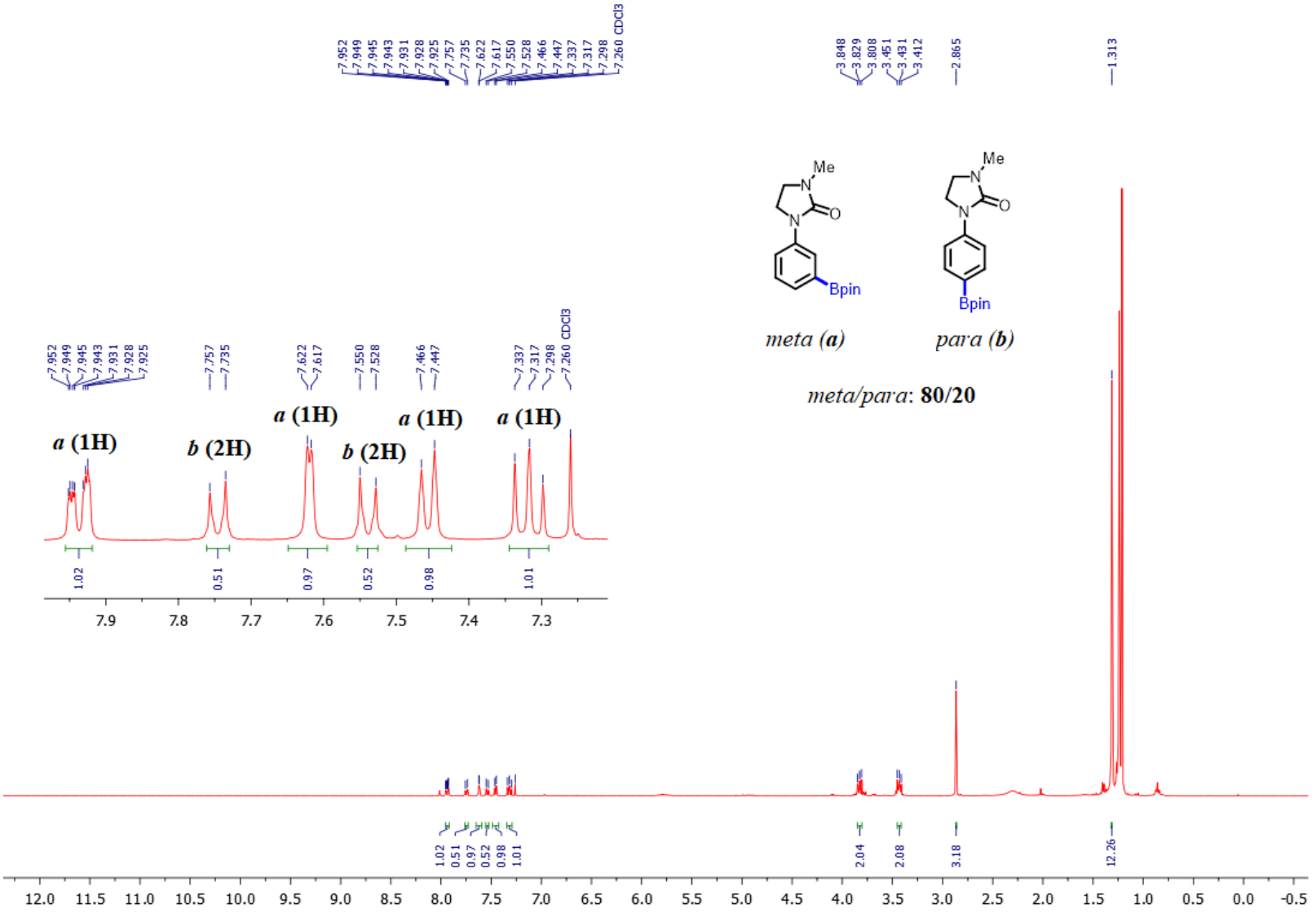
^{13}C NMR spectra of **2ag** (25 °C, 100 MHz, $CDCl_3$)



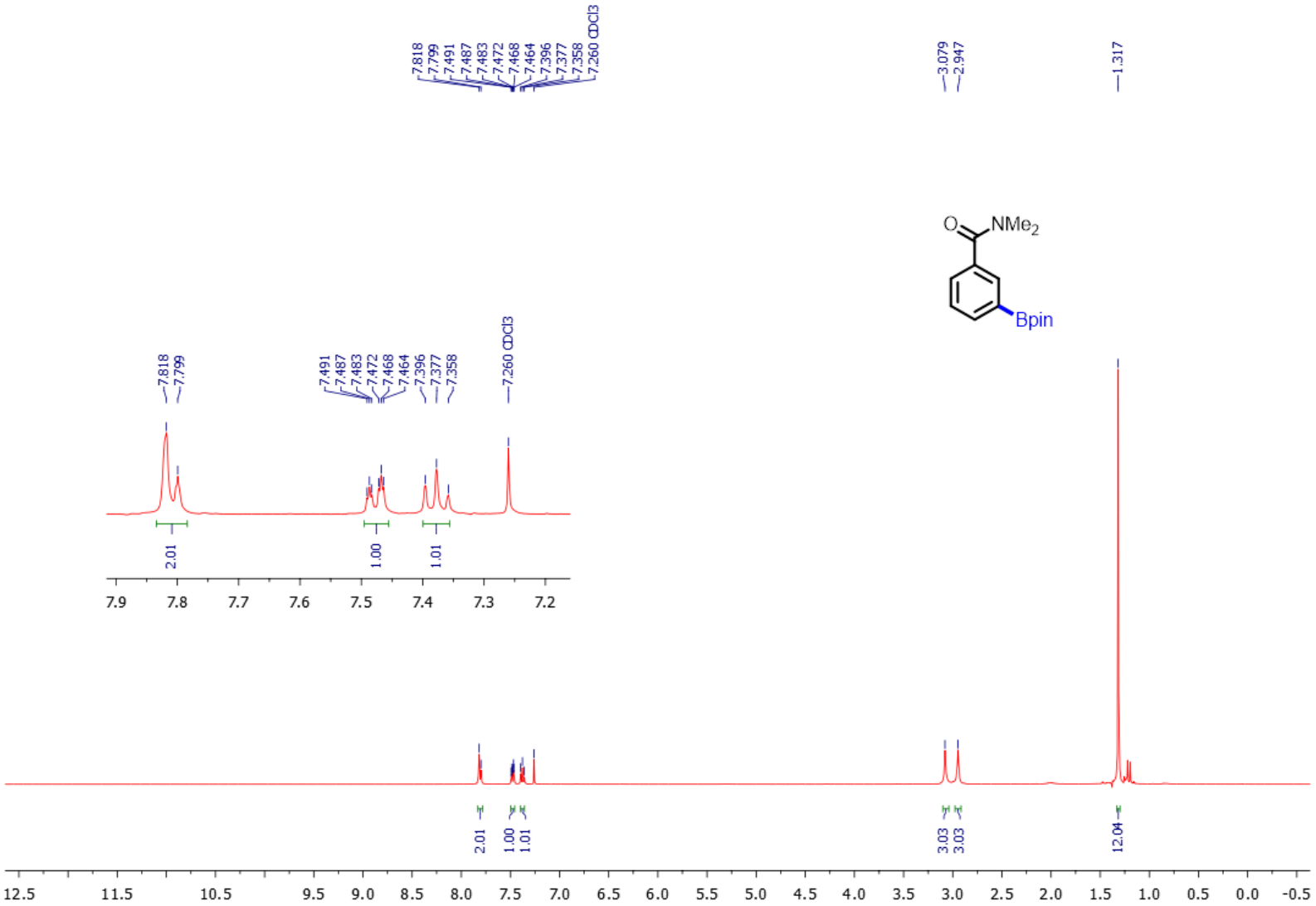
^{1}H NMR spectra of **2ah** (25 ºC, 400 MHz, $CDCl_3$)



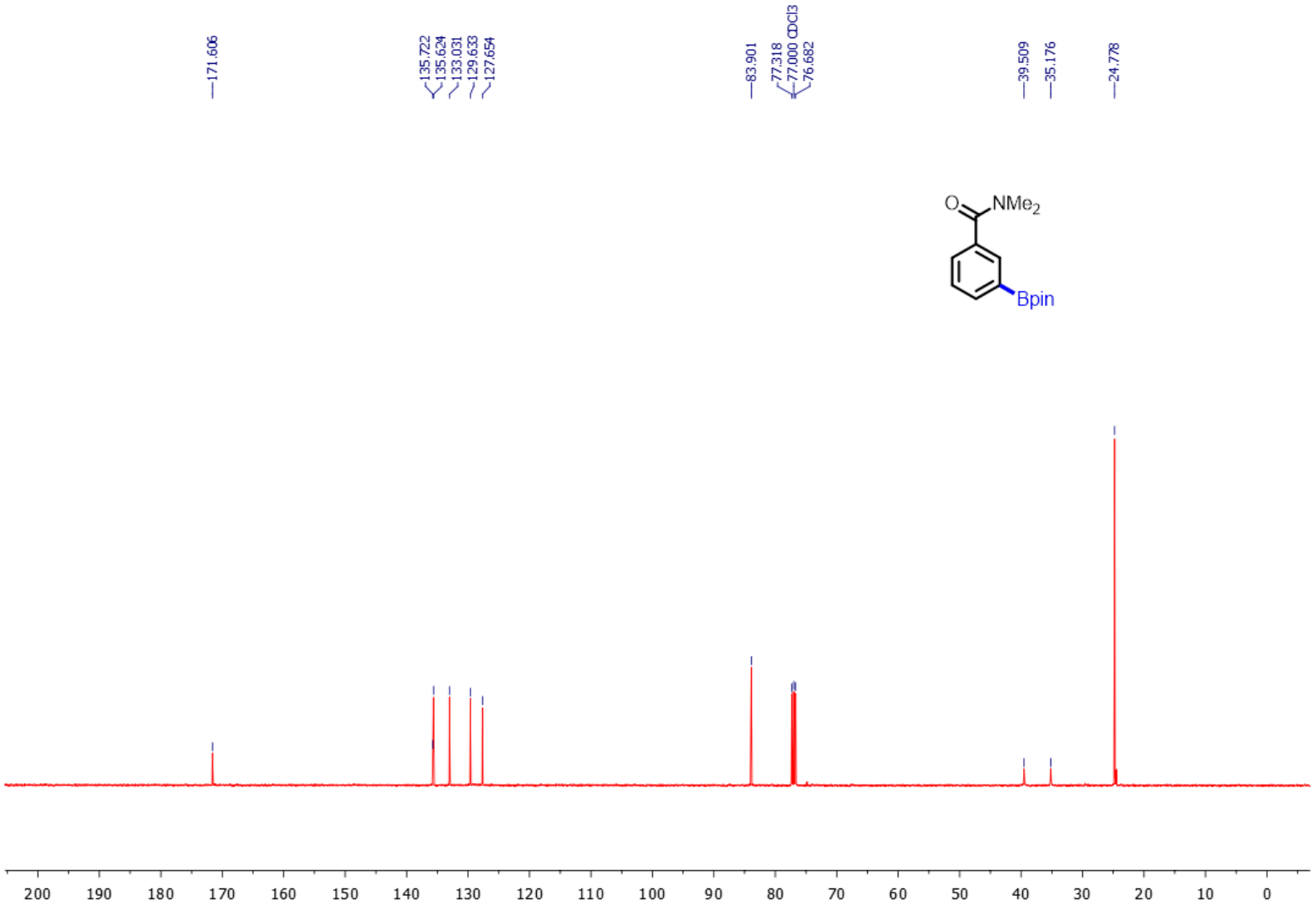
^{13}C NMR spectra of **2ah** (25 ºC, 100 MHz, $CDCl_3$)



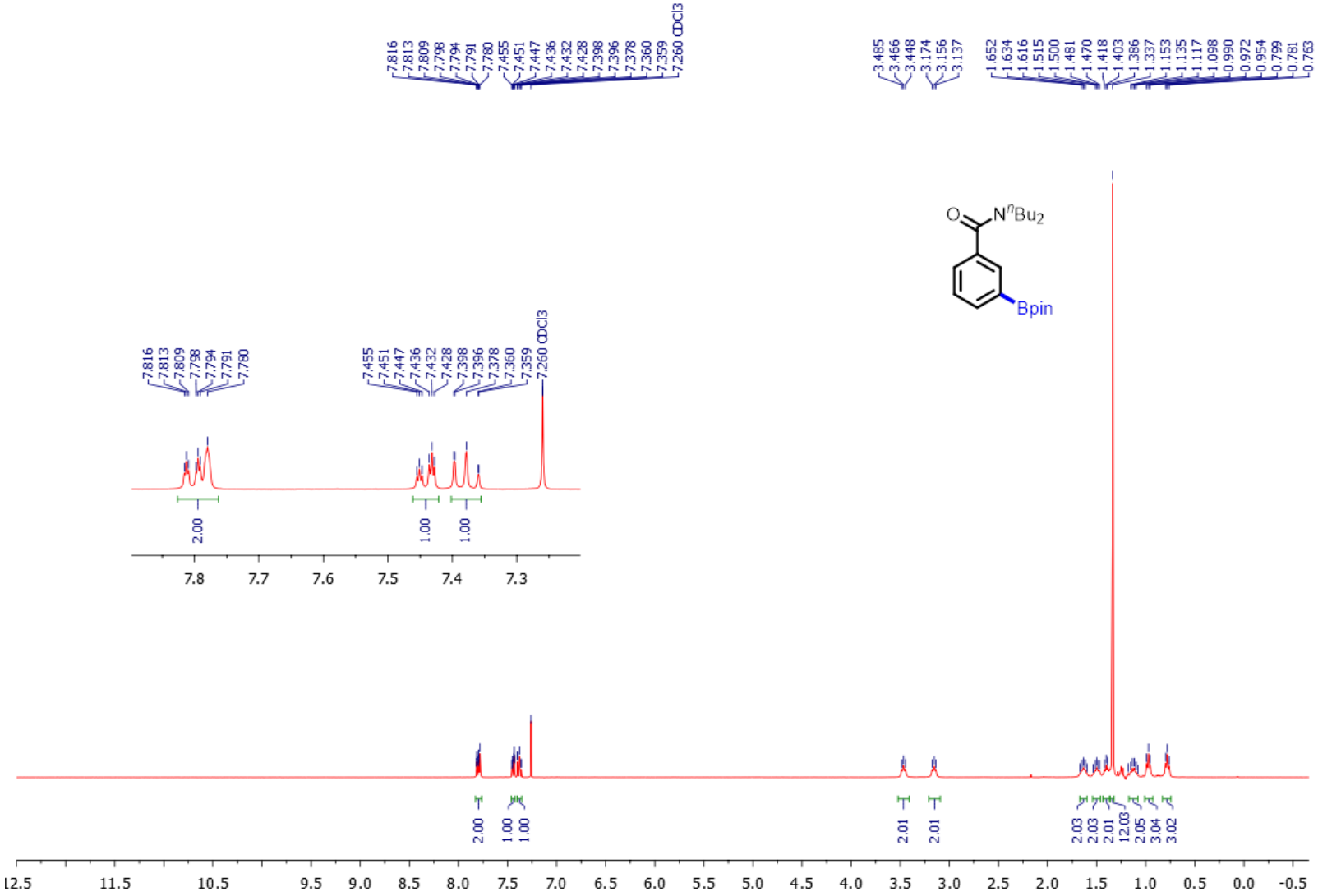
^{1}H NMR spectra of **2ai** (25 °C, 400 MHz, $CDCl_3$)



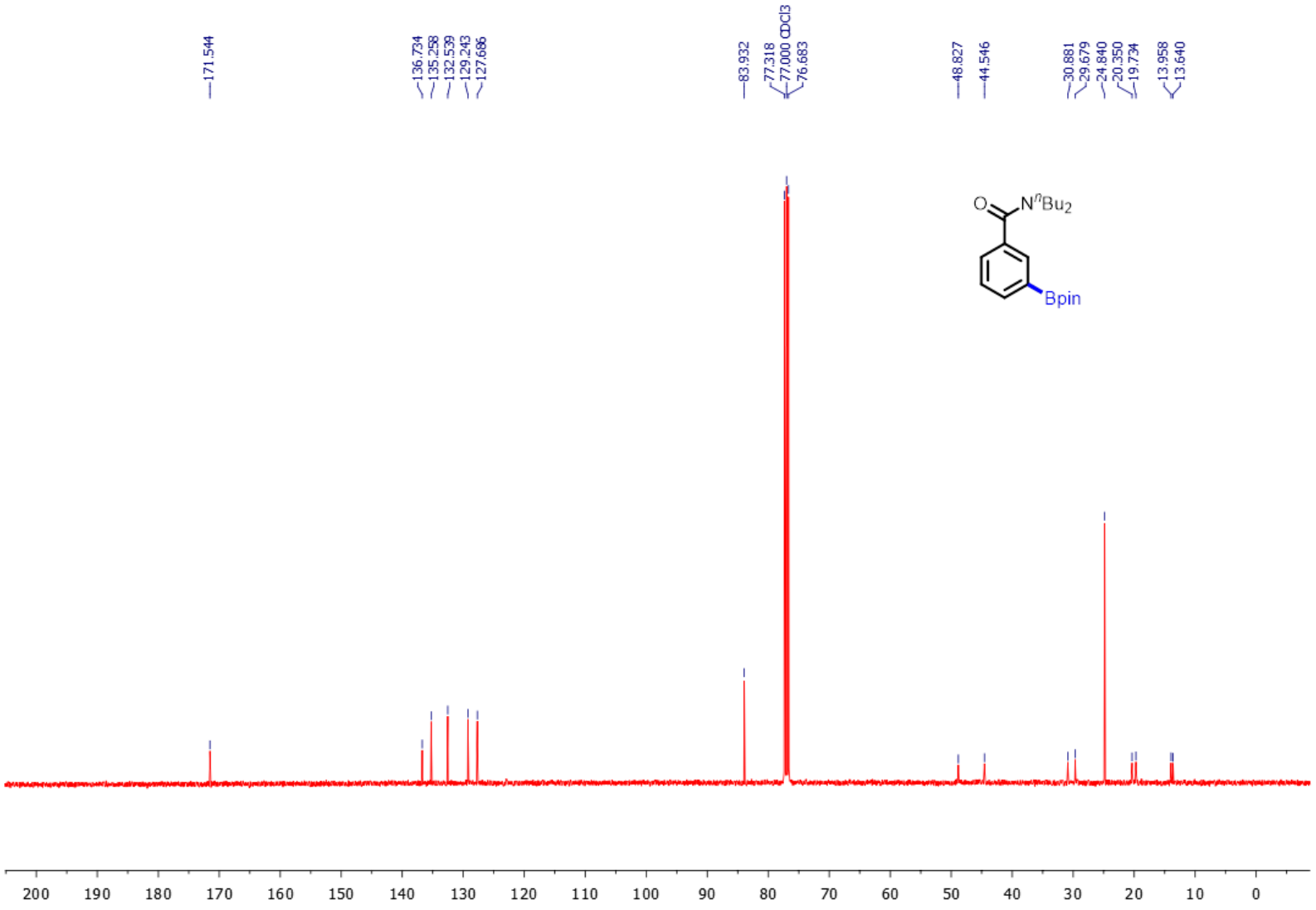
^{1}H NMR spectra of **2aj** (25 °C, 400 MHz, $CDCl_3$)



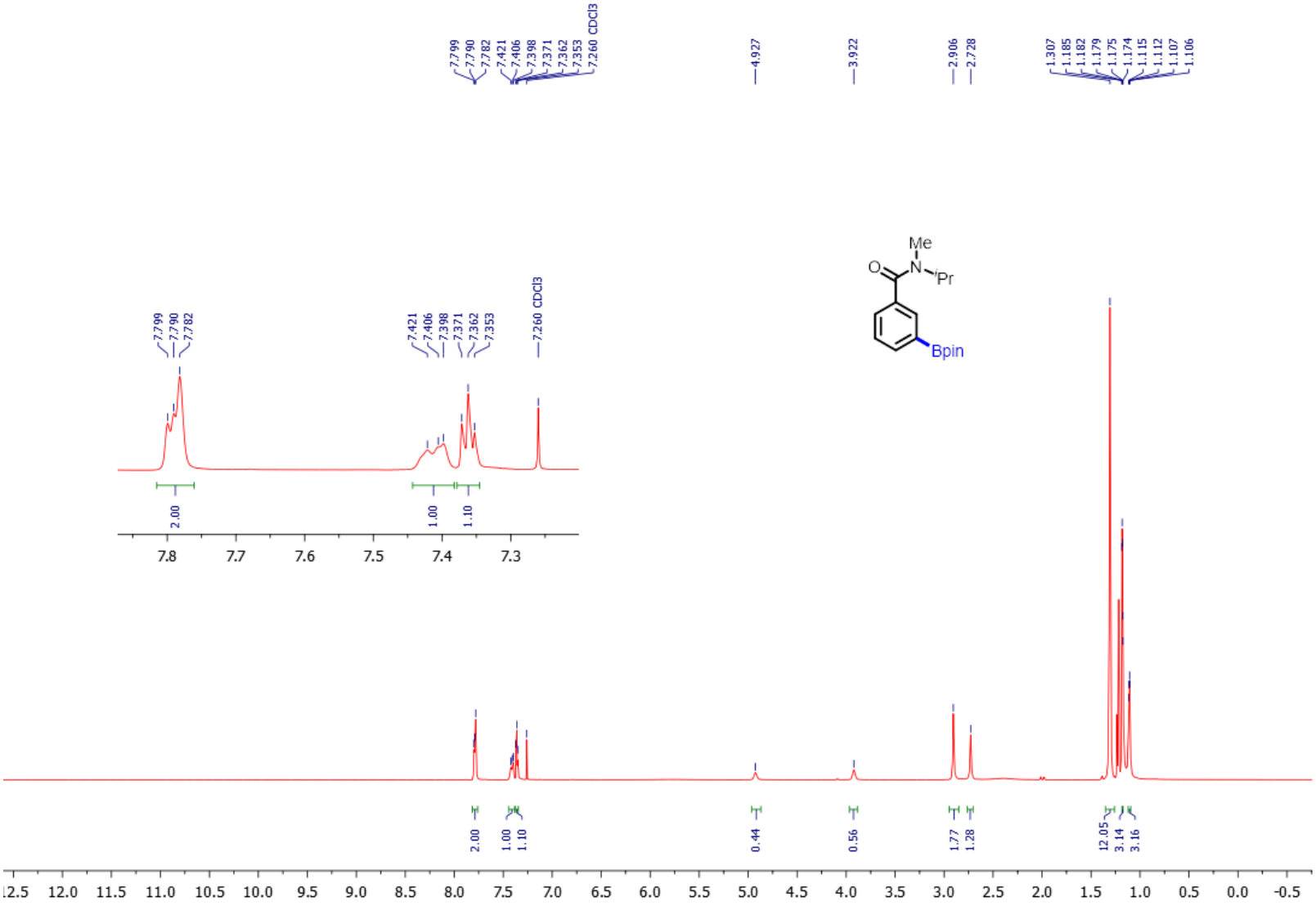
^{13}C NMR spectra of **2aj** (25 ^{o}C, 100 MHz, $CDCl_3$)



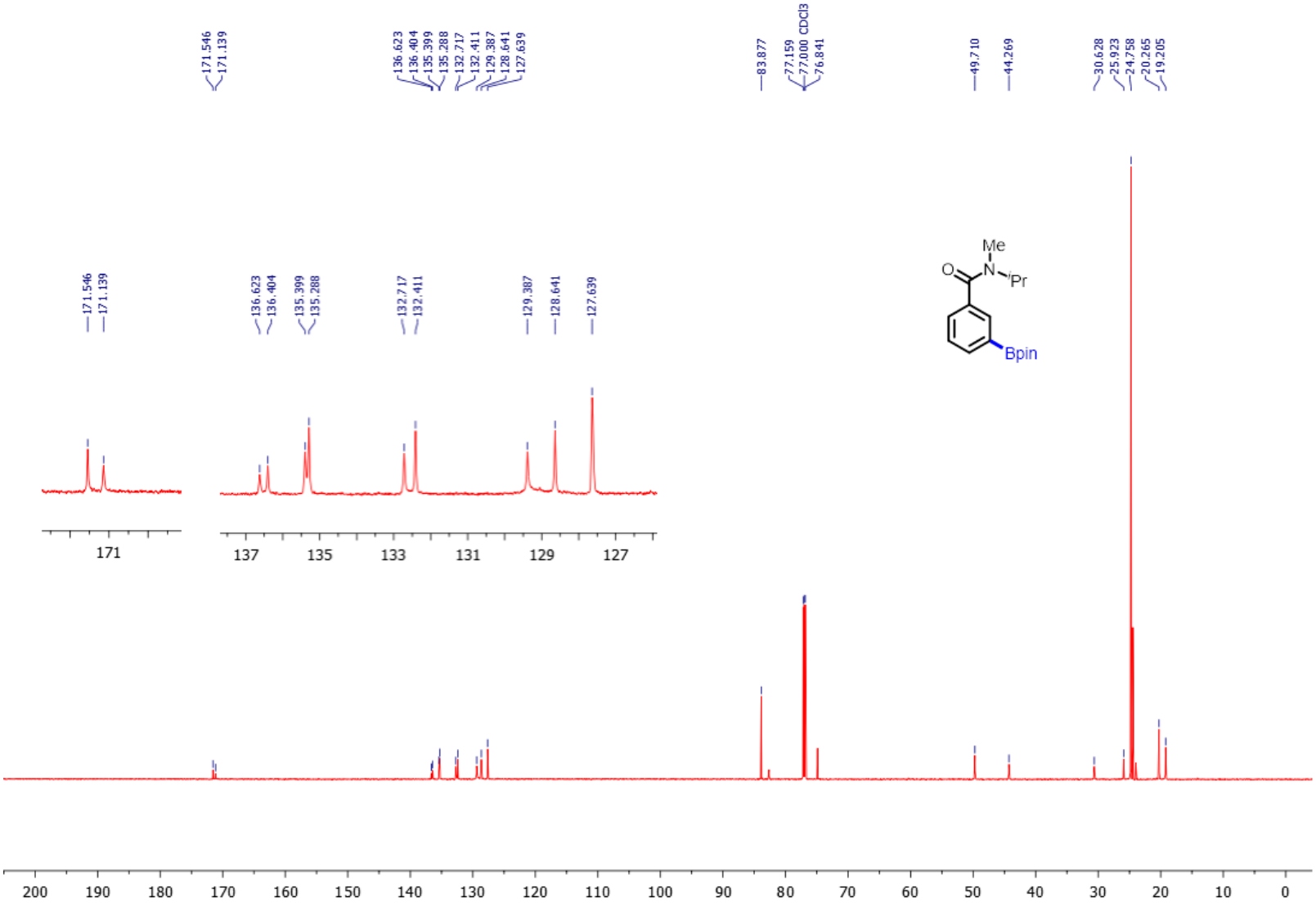
^{1}H NMR spectra of **2ak** (25 ^{o}C, 400 MHz, $CDCl_3$)



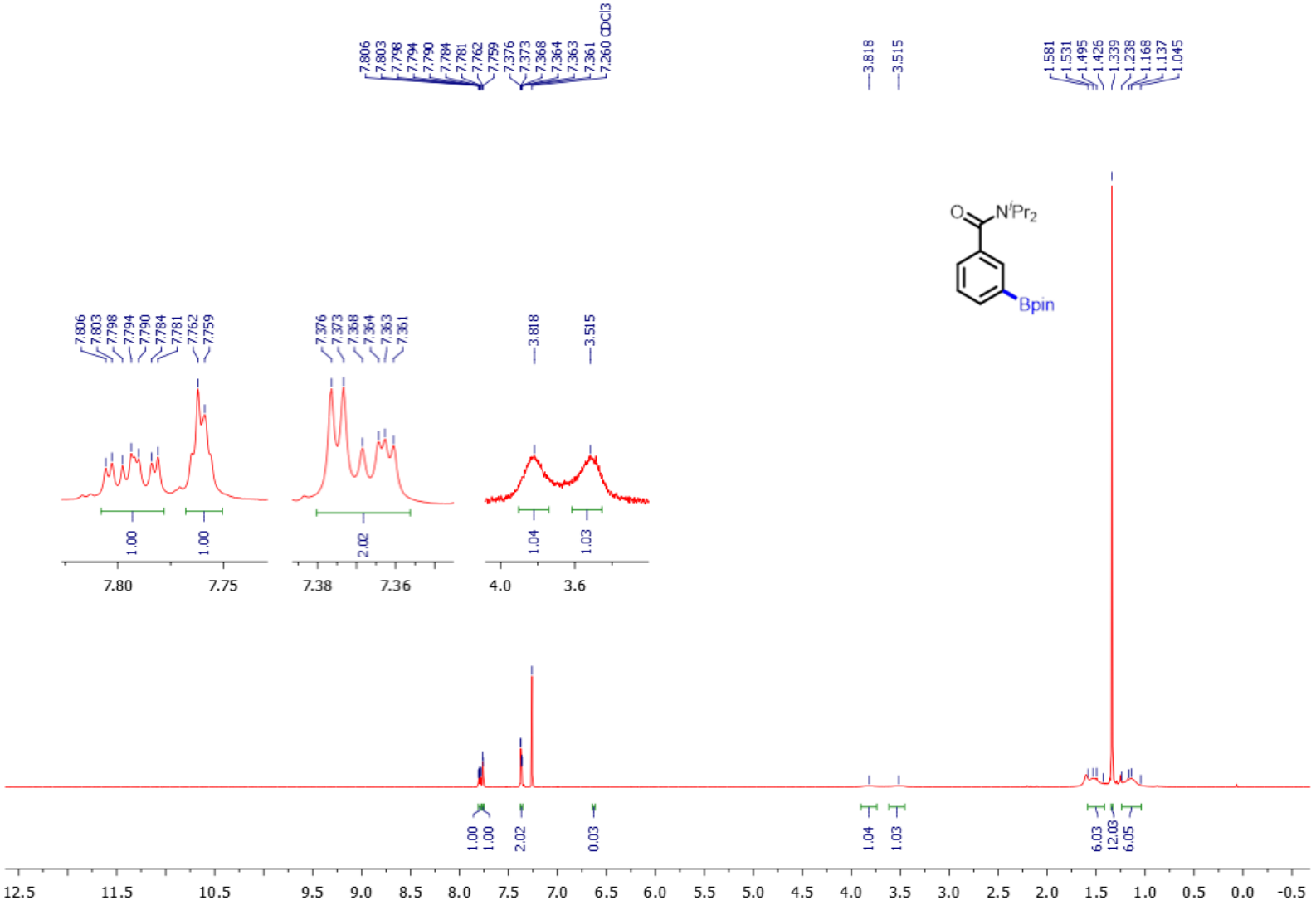
^{13}C NMR spectra of **2ak** (25 ºC, 100 MHz, $CDCl_3$)



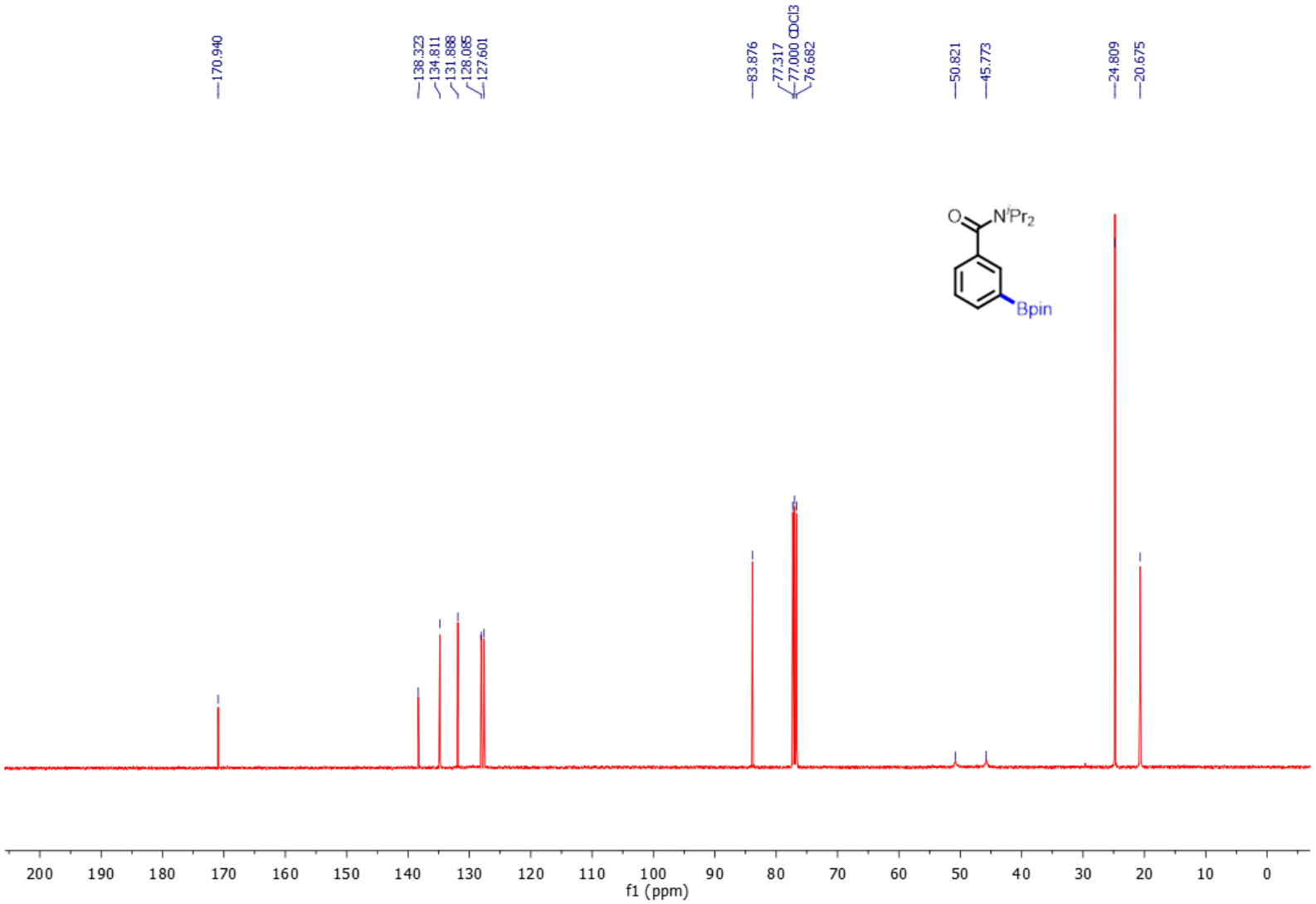
^{1}H NMR spectra of **2al** (25 °C, 400 MHz, $CDCl_3$)



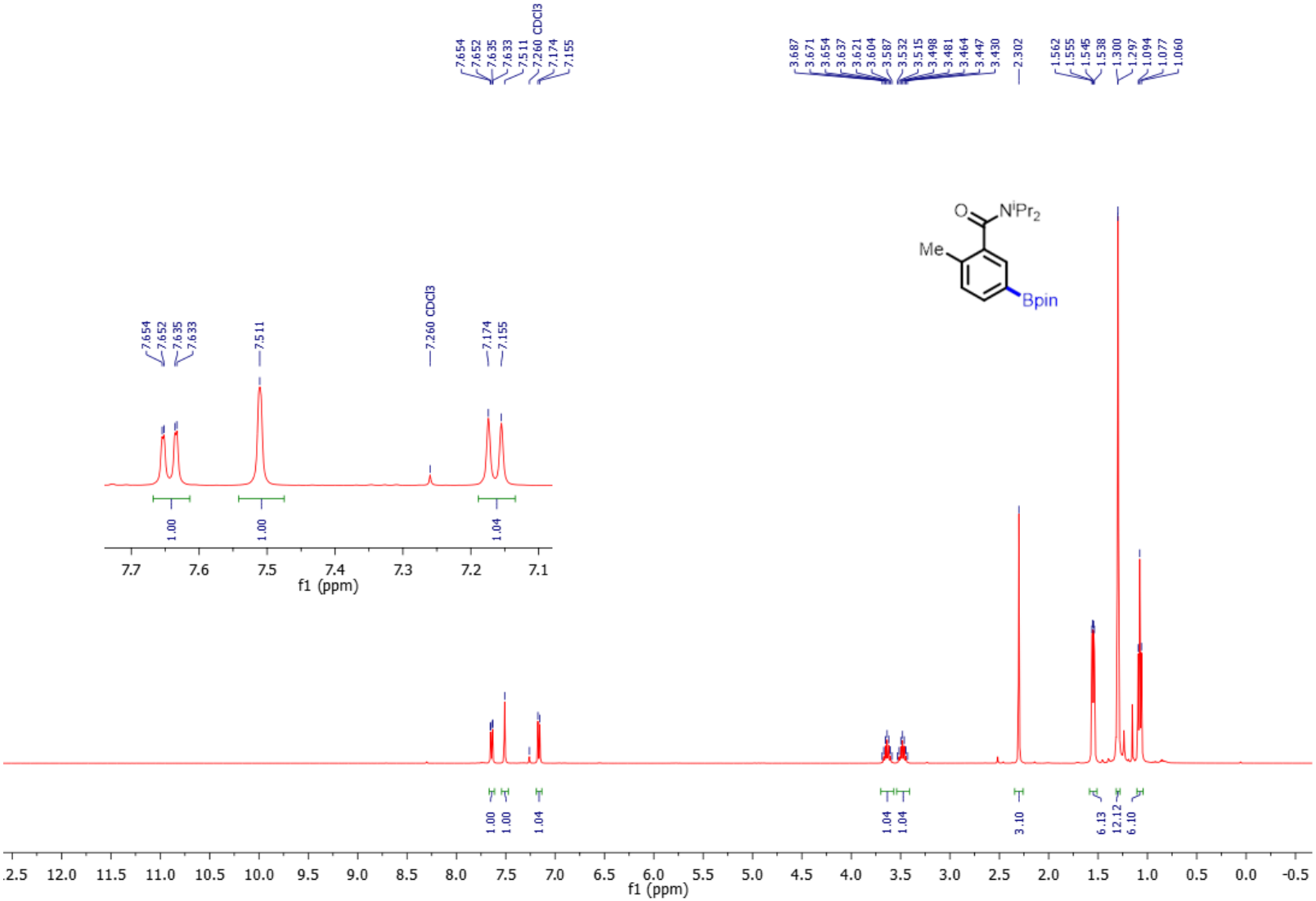
^{13}C NMR spectra of **2al** (25 °C, 100 MHz, $CDCl_3$)



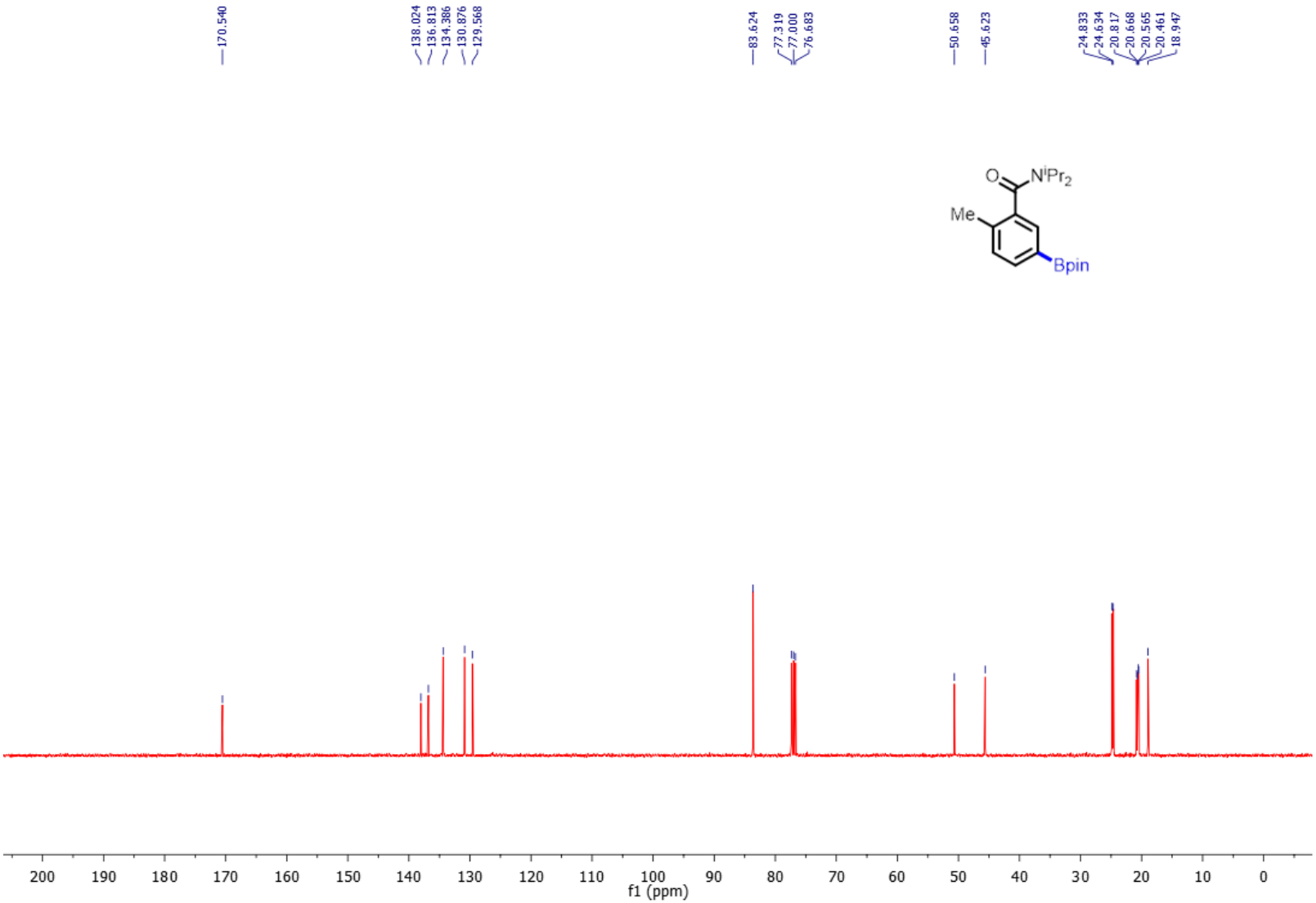
^{1}H NMR spectra of **2am** (25 °C, 400 MHz, $CDCl_3$)



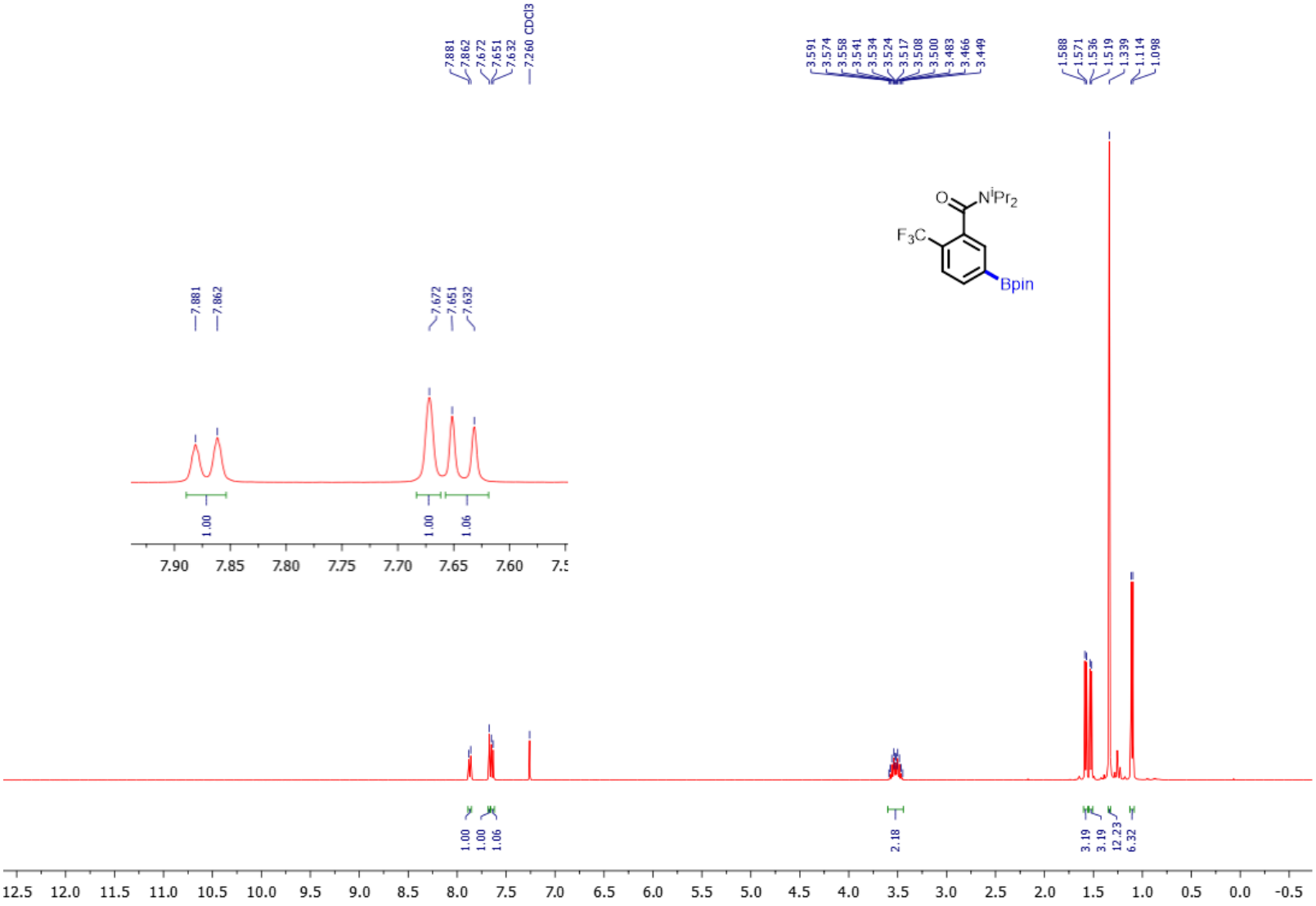
^{13}C NMR spectra of **2am** (25 °C, 100 MHz, $CDCl_3$)



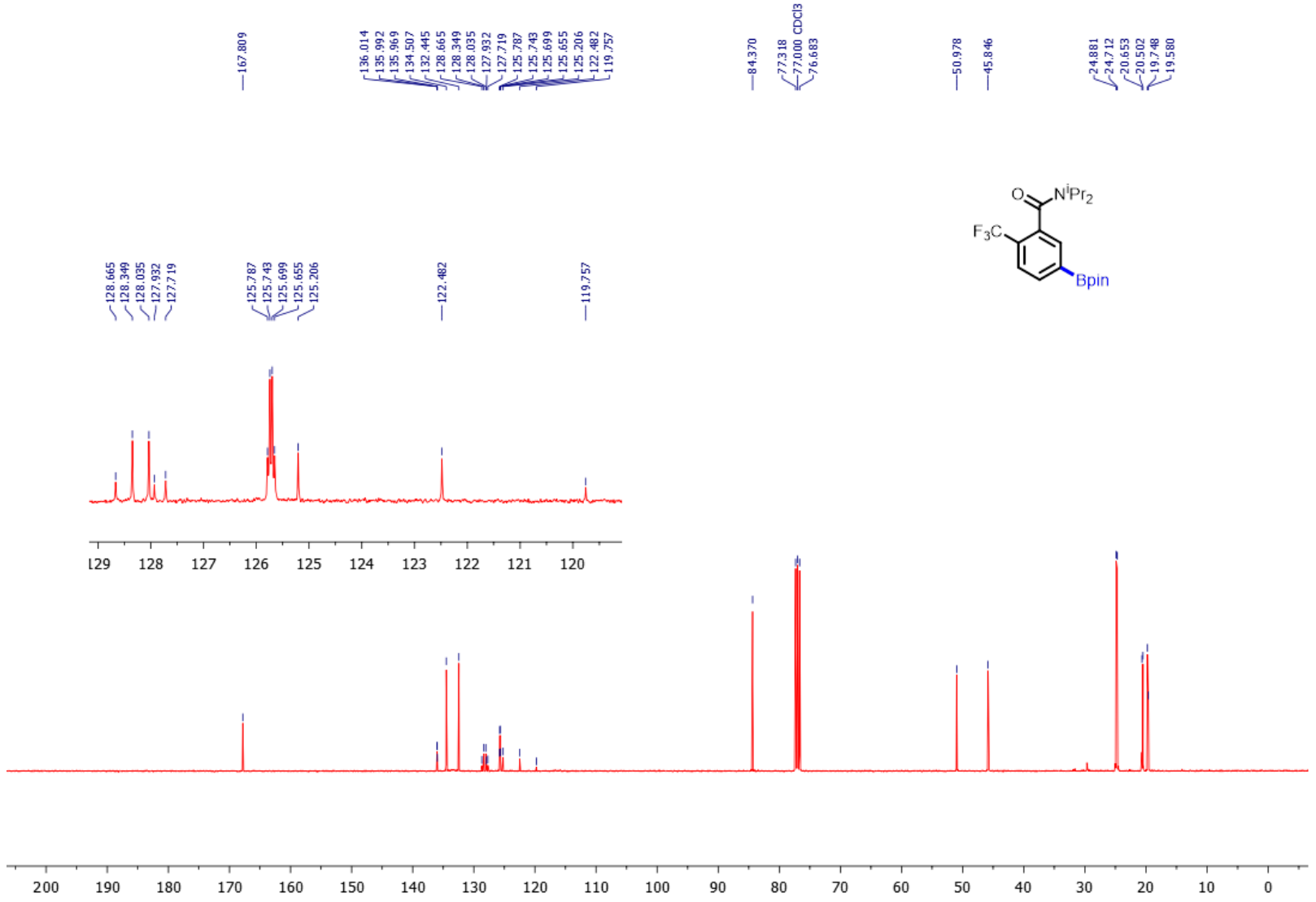
^{1}H NMR spectra of **2ao** (25 ºC, 400 MHz, $CDCl_3$)



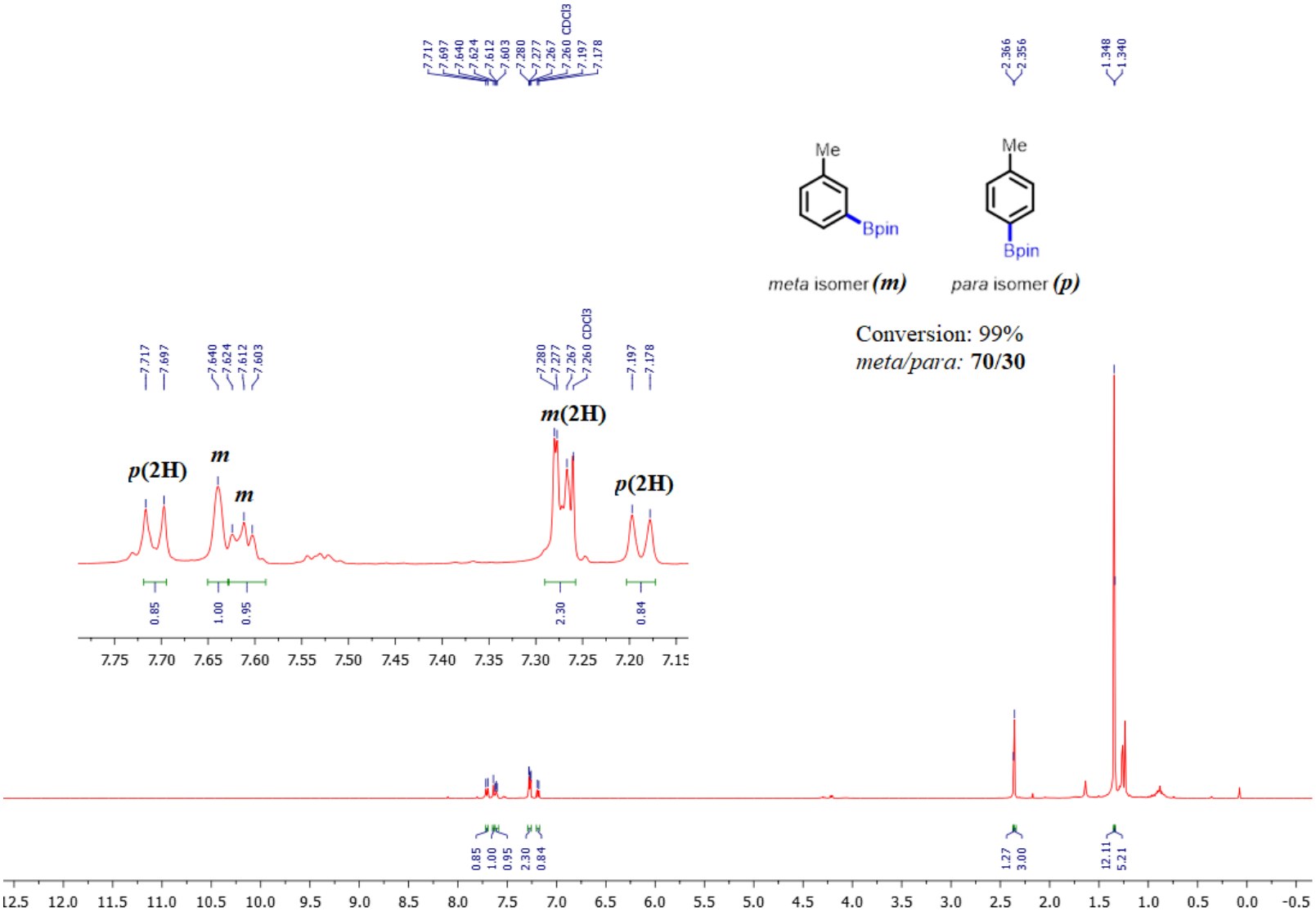
^{13}C NMR spectra of **2ao** (25 °C, 100 MHz, $CDCl_3$)



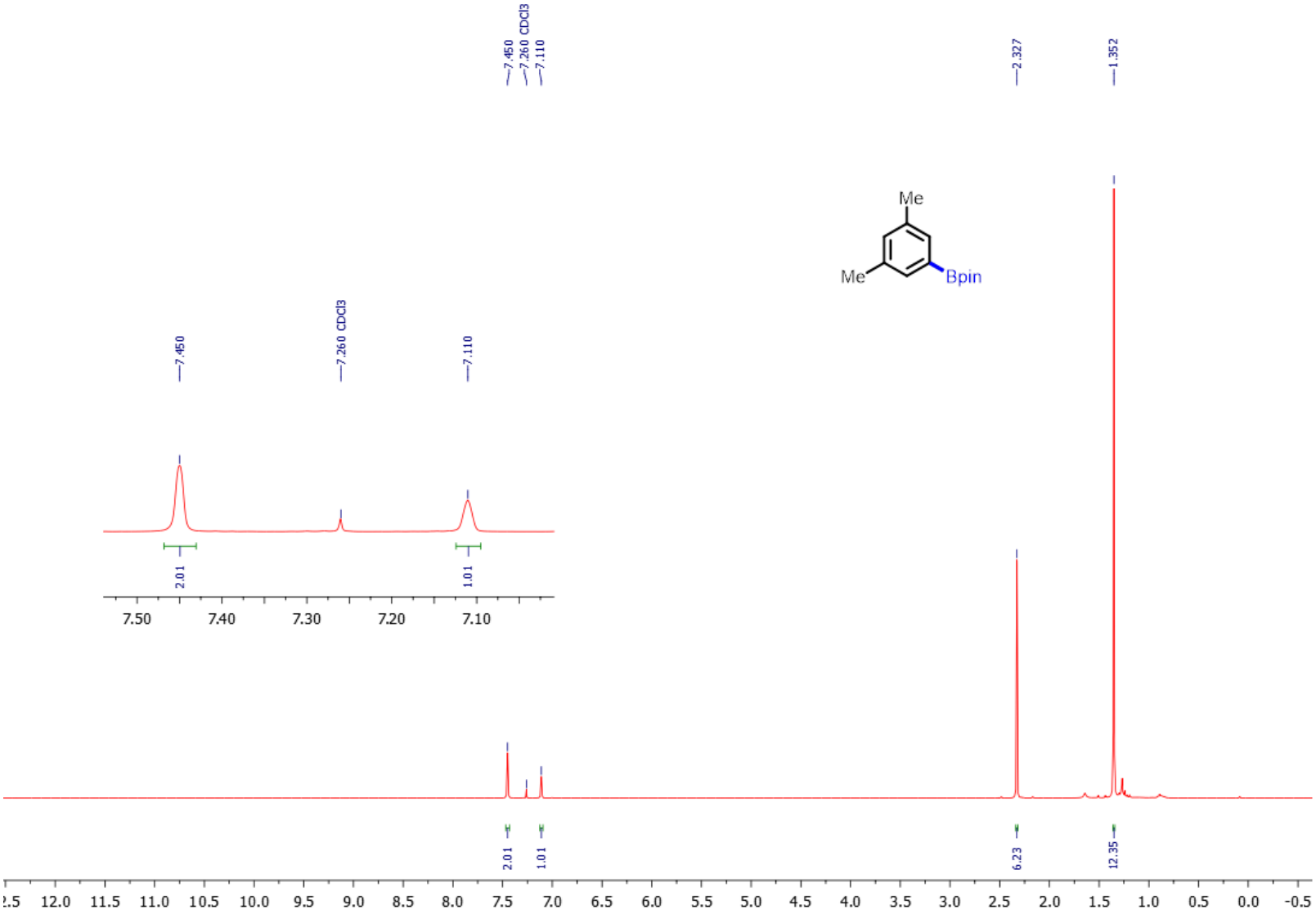
^{1}H NMR spectra of **2ap** (25 ºC, 400 MHz, $CDCl_3$)



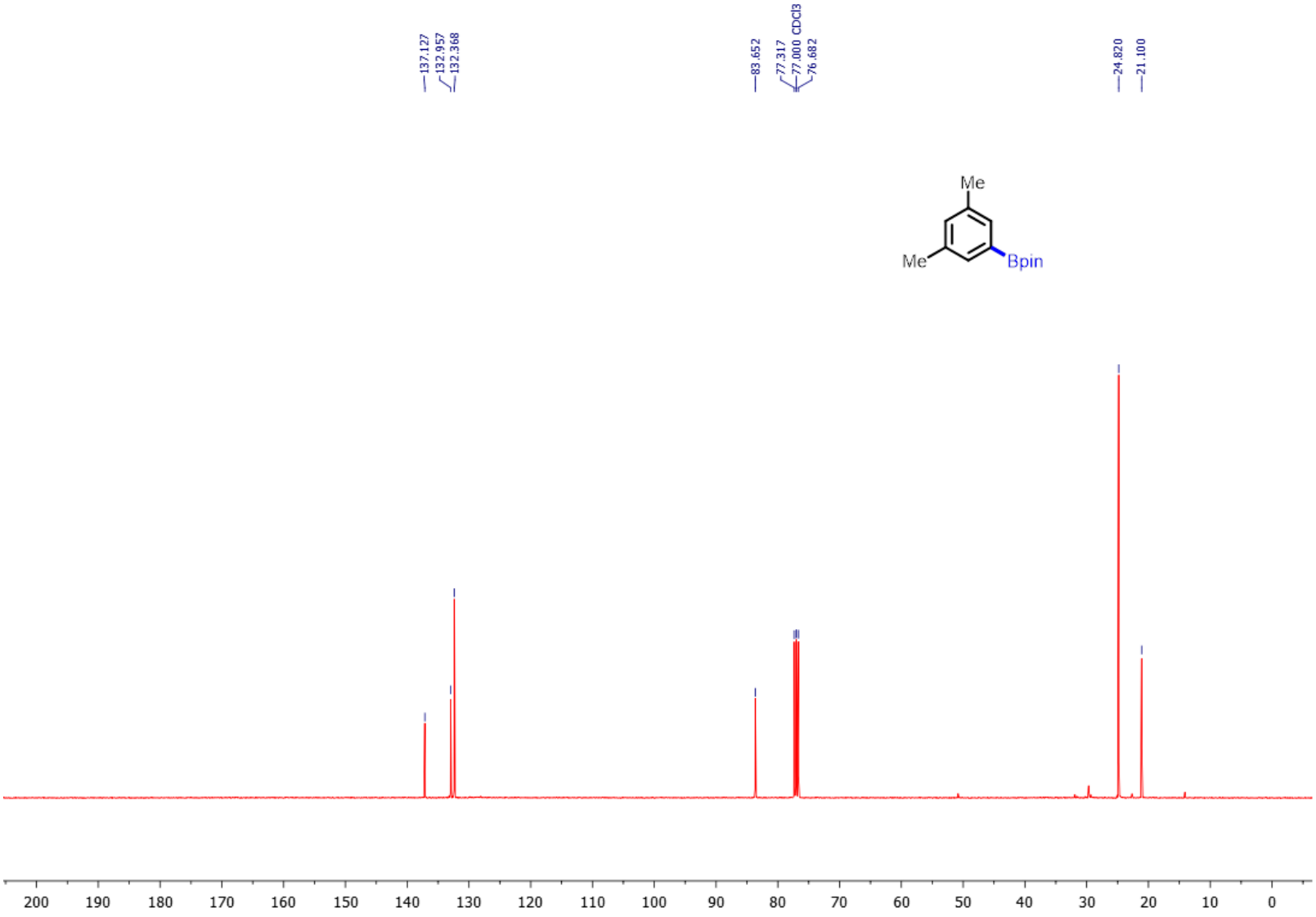
^{13}C NMR spectra of **2ap** (25 ºC, 100 MHz, $CDCl_3$)



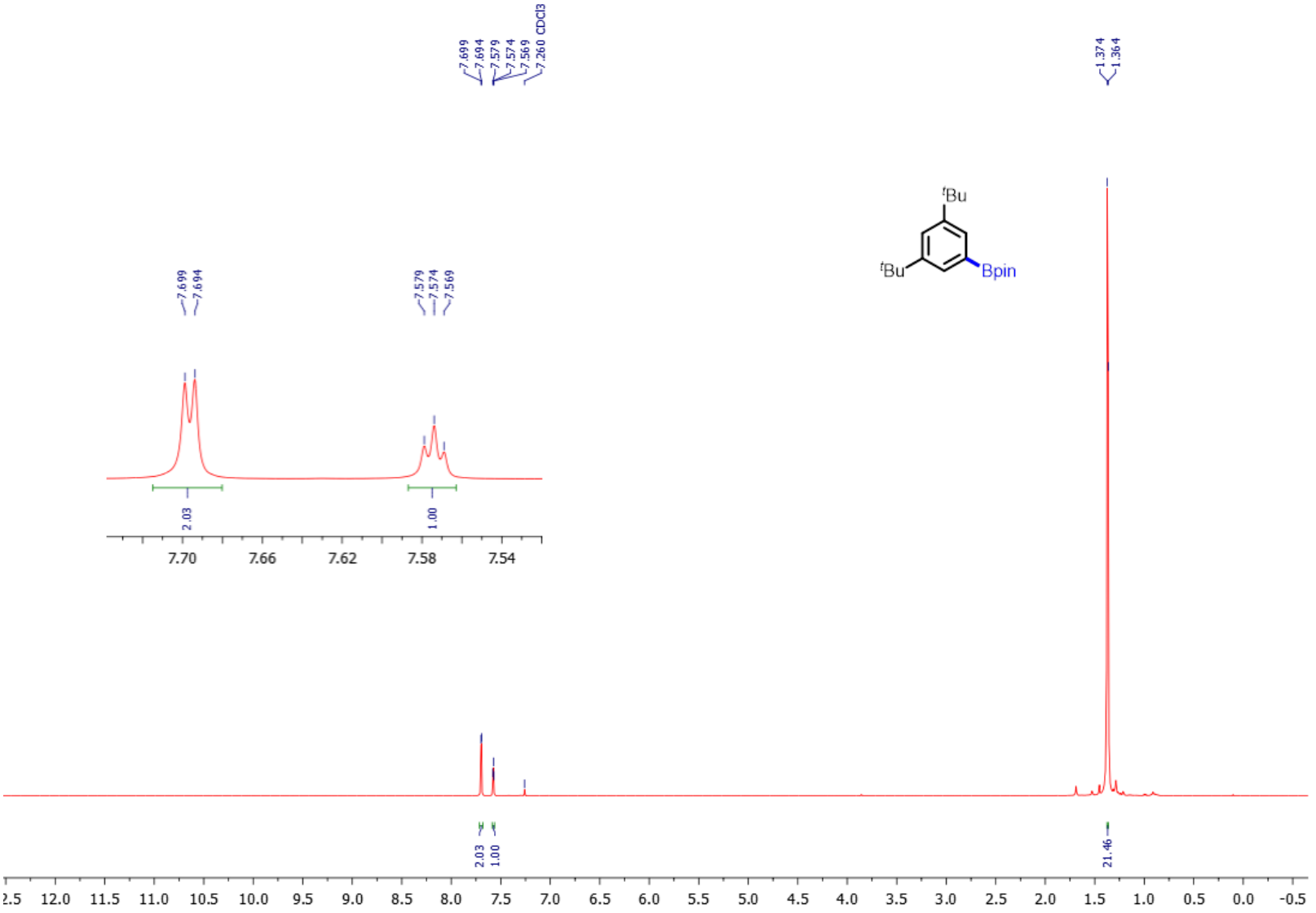
Crude ^{1}H NMR spectra of **2aq** (25 °C, 400 MHz, $CDCl_3$)



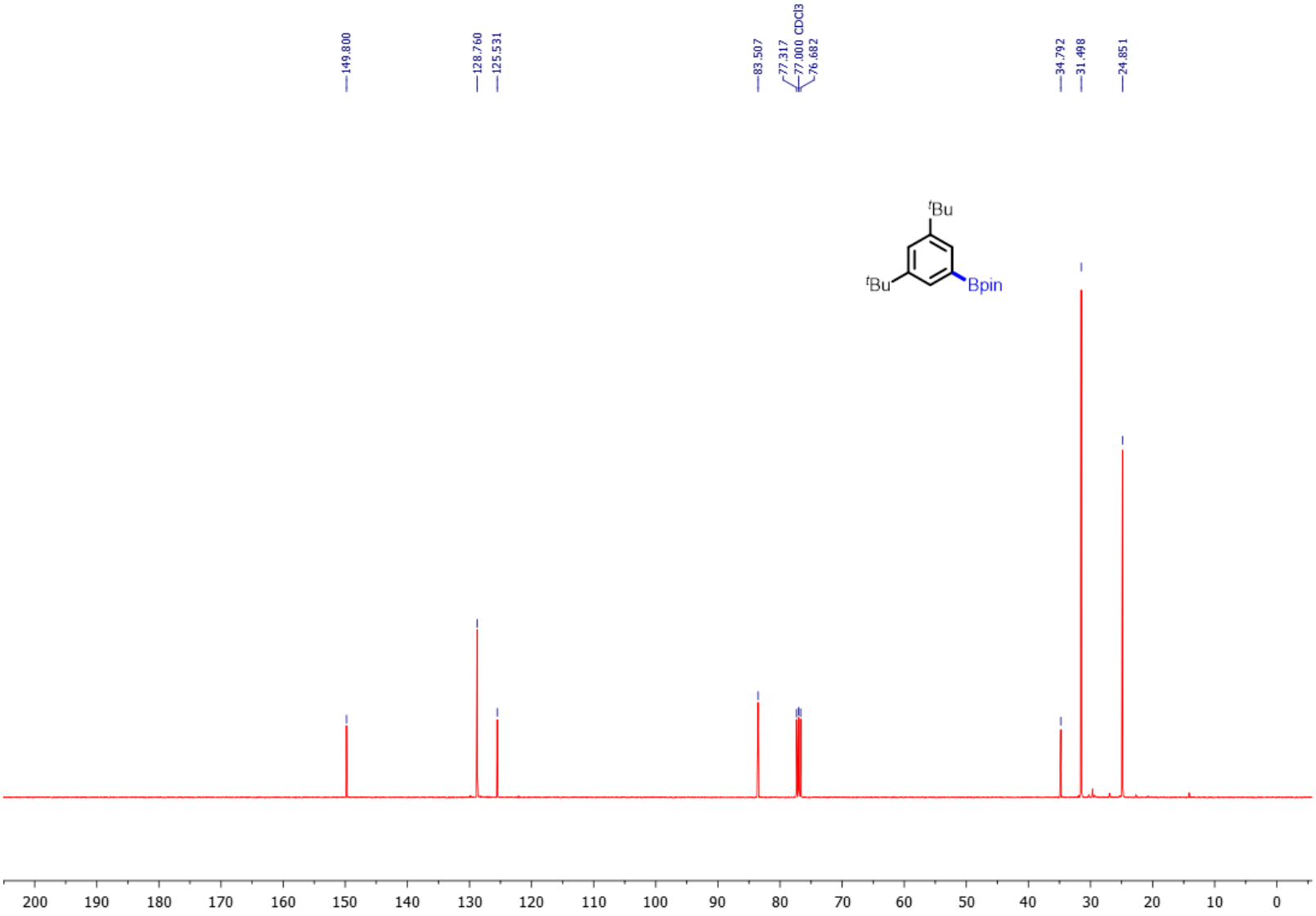
^{1}H NMR spectra of **2ar** (25 °C, 400 MHz, $CDCl_3$)



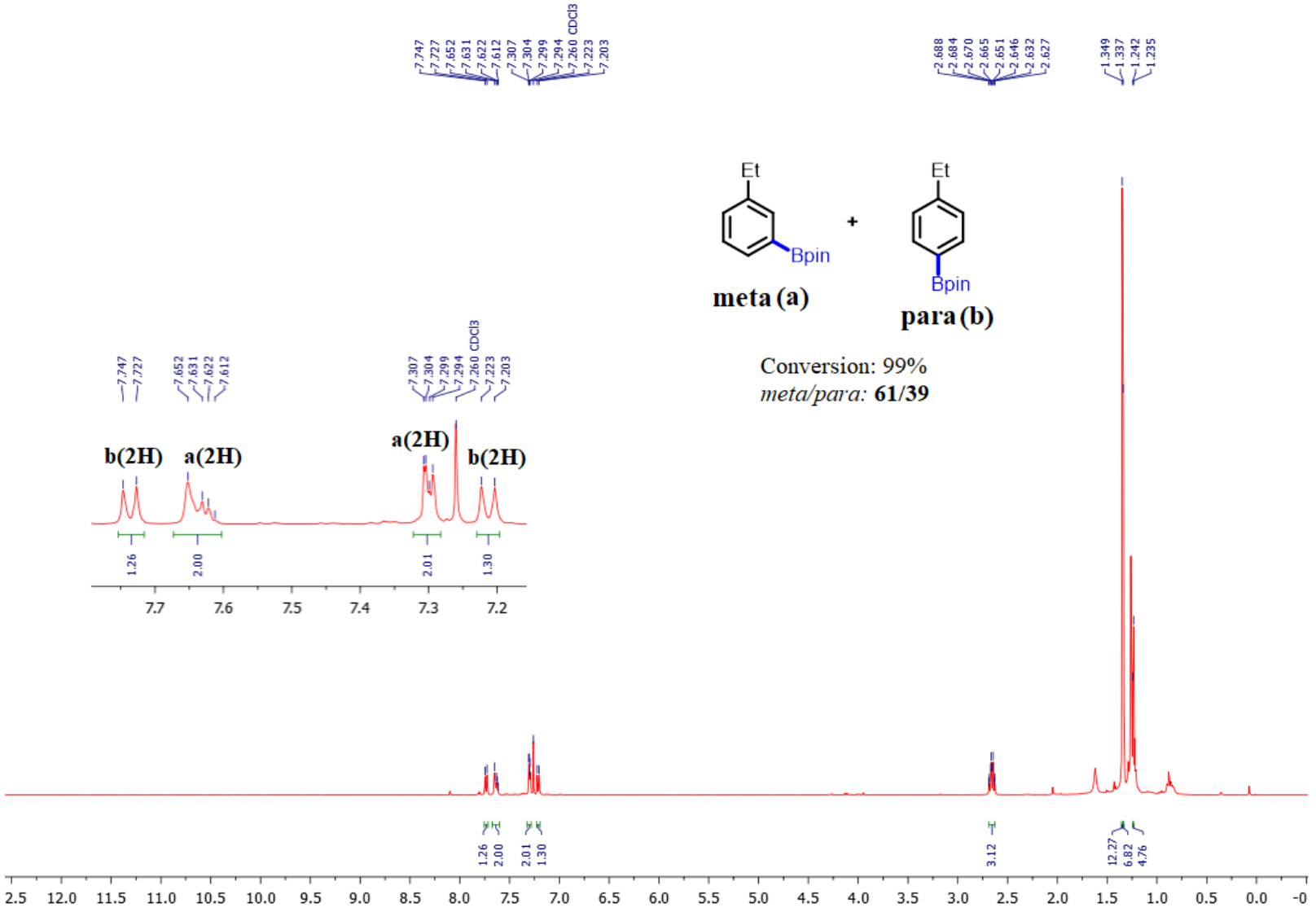
^{13}C NMR spectra of **2ar** (25 °C, 100 MHz, $CDCl_3$)



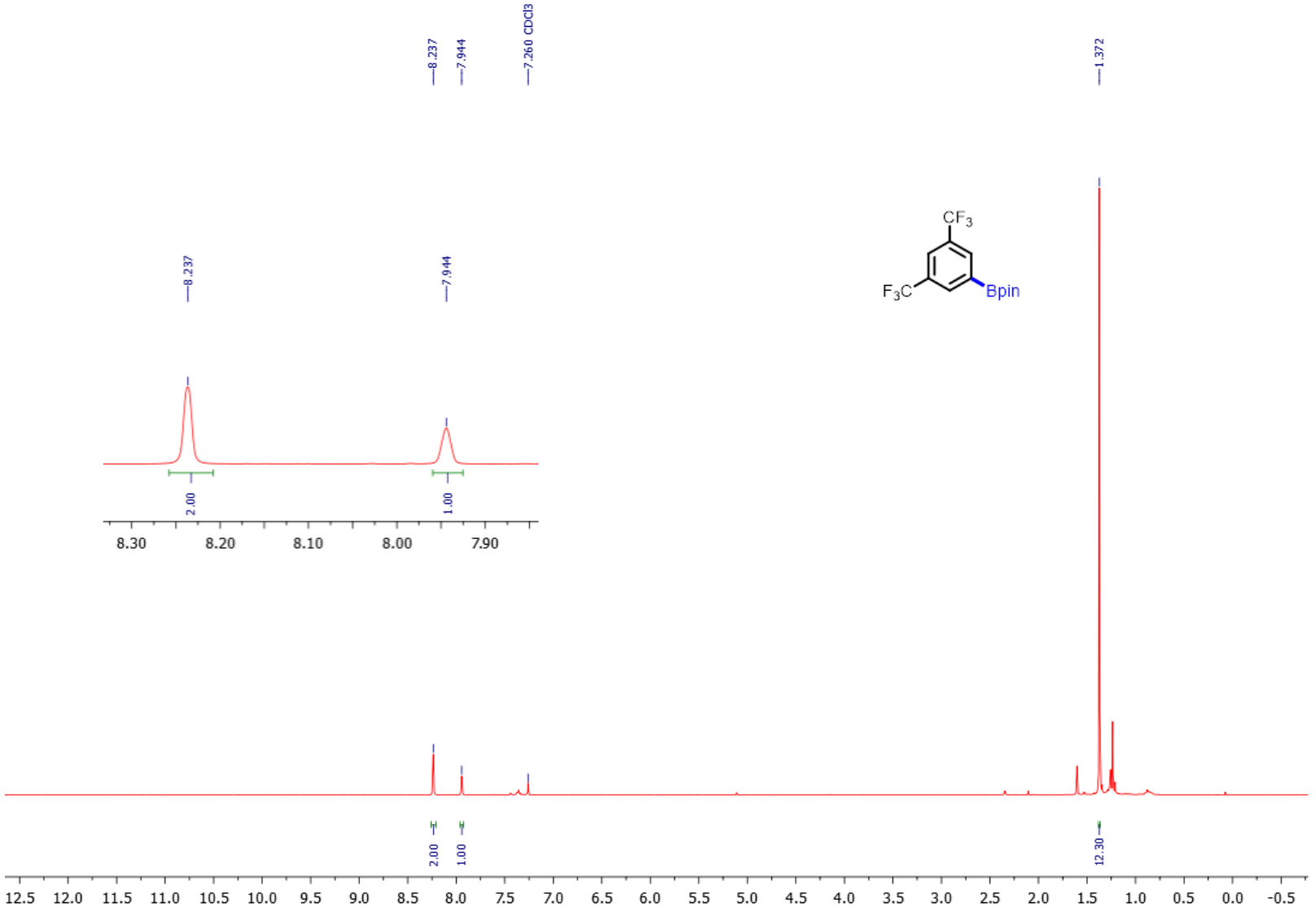
^{1}H NMR spectra of **2as** (25 °C, 400 MHz, $CDCl_3$)



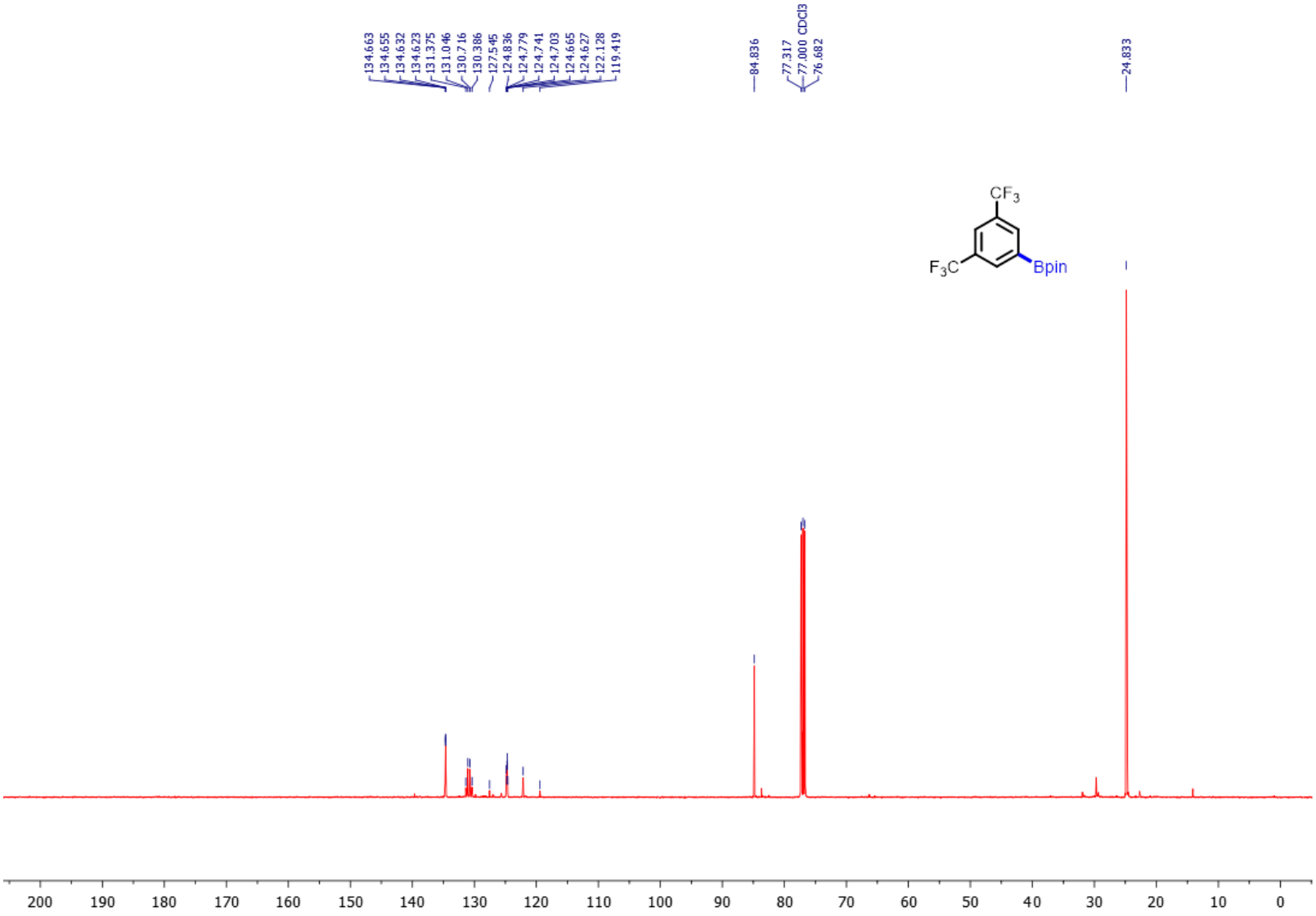
^{13}C NMR spectra of **2as** (25 ºC, 100 MHz, $CDCl_3$)



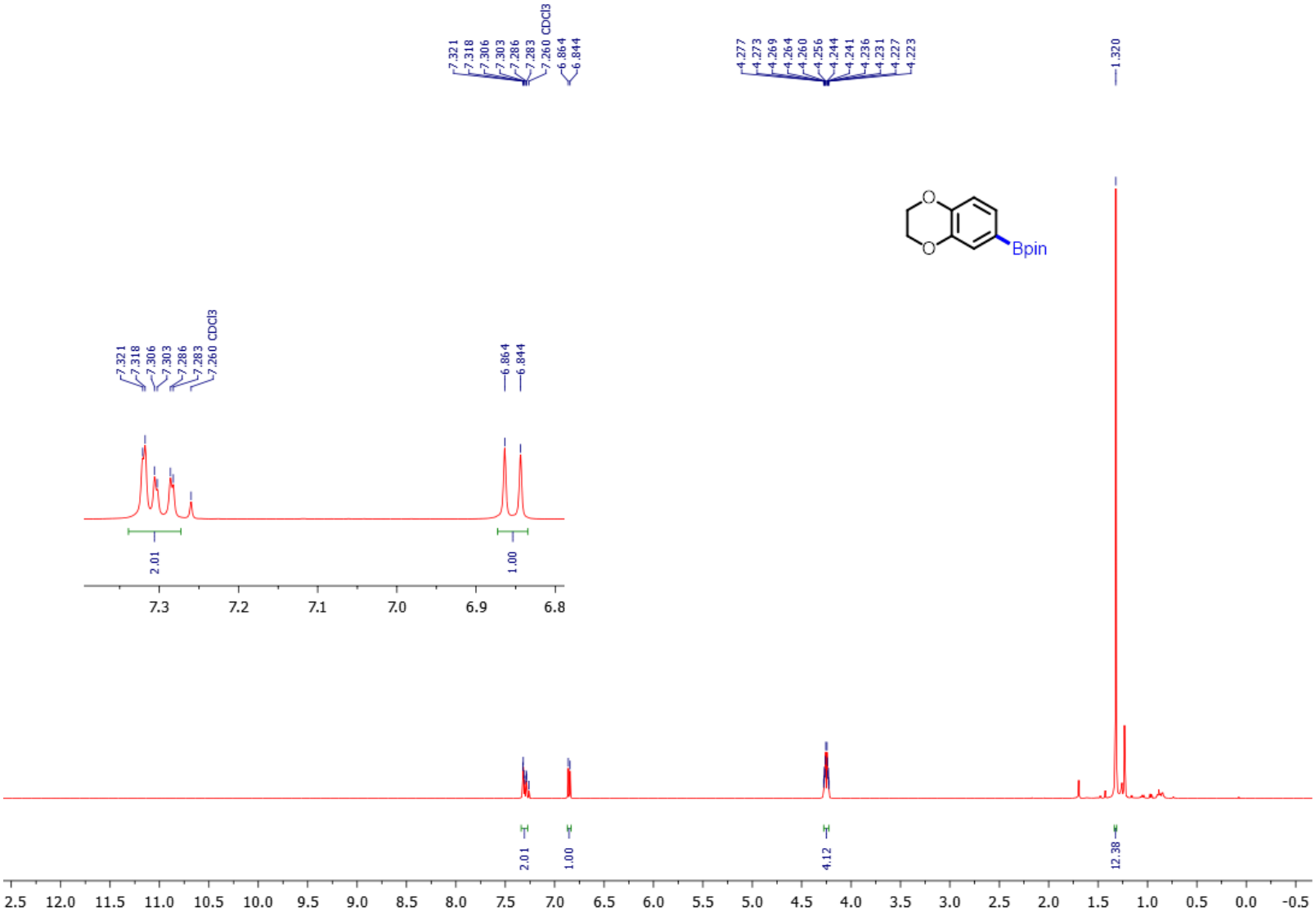
Crude ^{1}H NMR spectra of **2at** (25 °C, 400 MHz, $CDCl_3$)



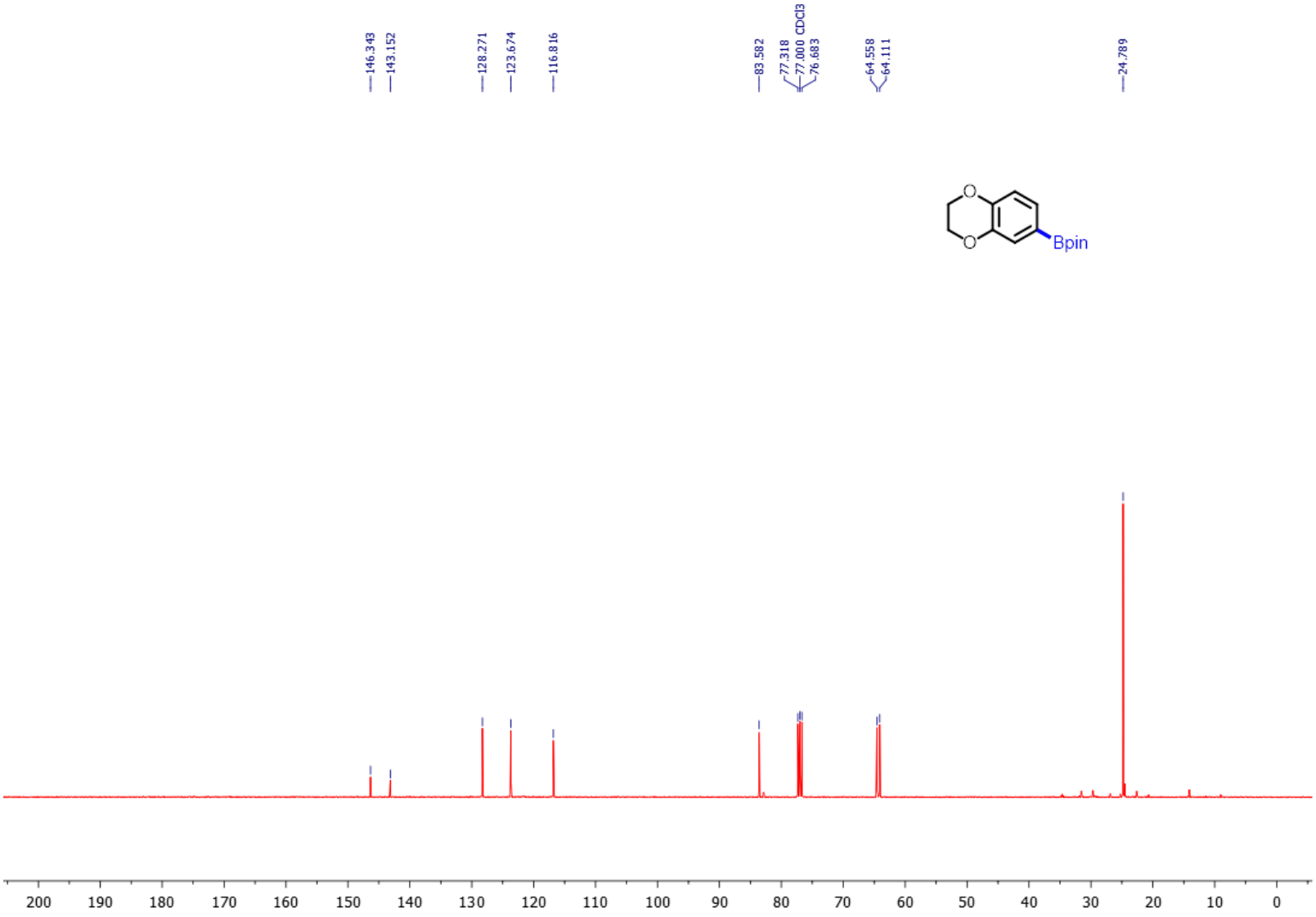
^{1}H NMR spectra of **2au** (25 ºC, 400 MHz, $CDCl_3$)



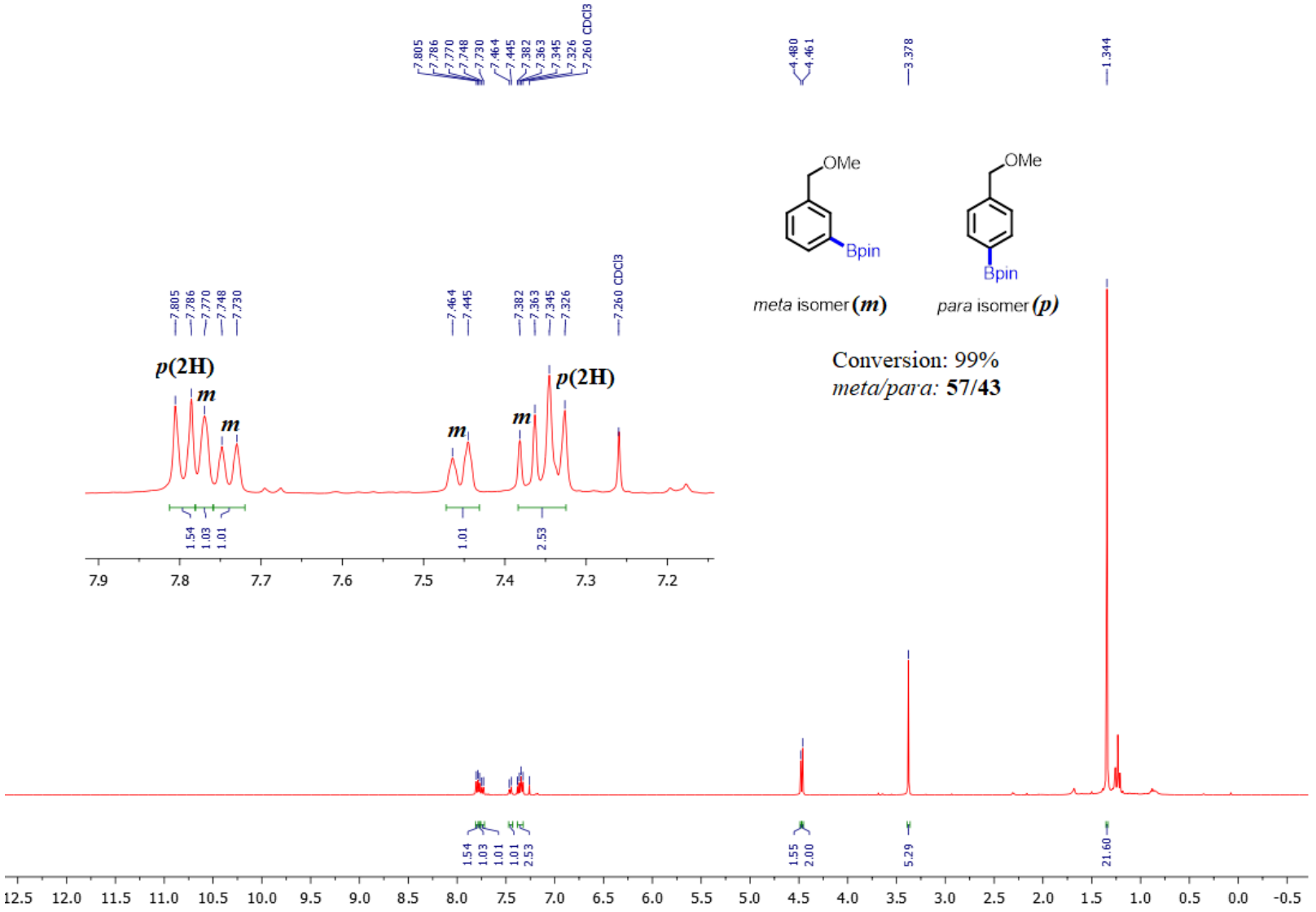
^{13}C NMR spectra of **2au** (25 °C, 100 MHz, $CDCl_3$)



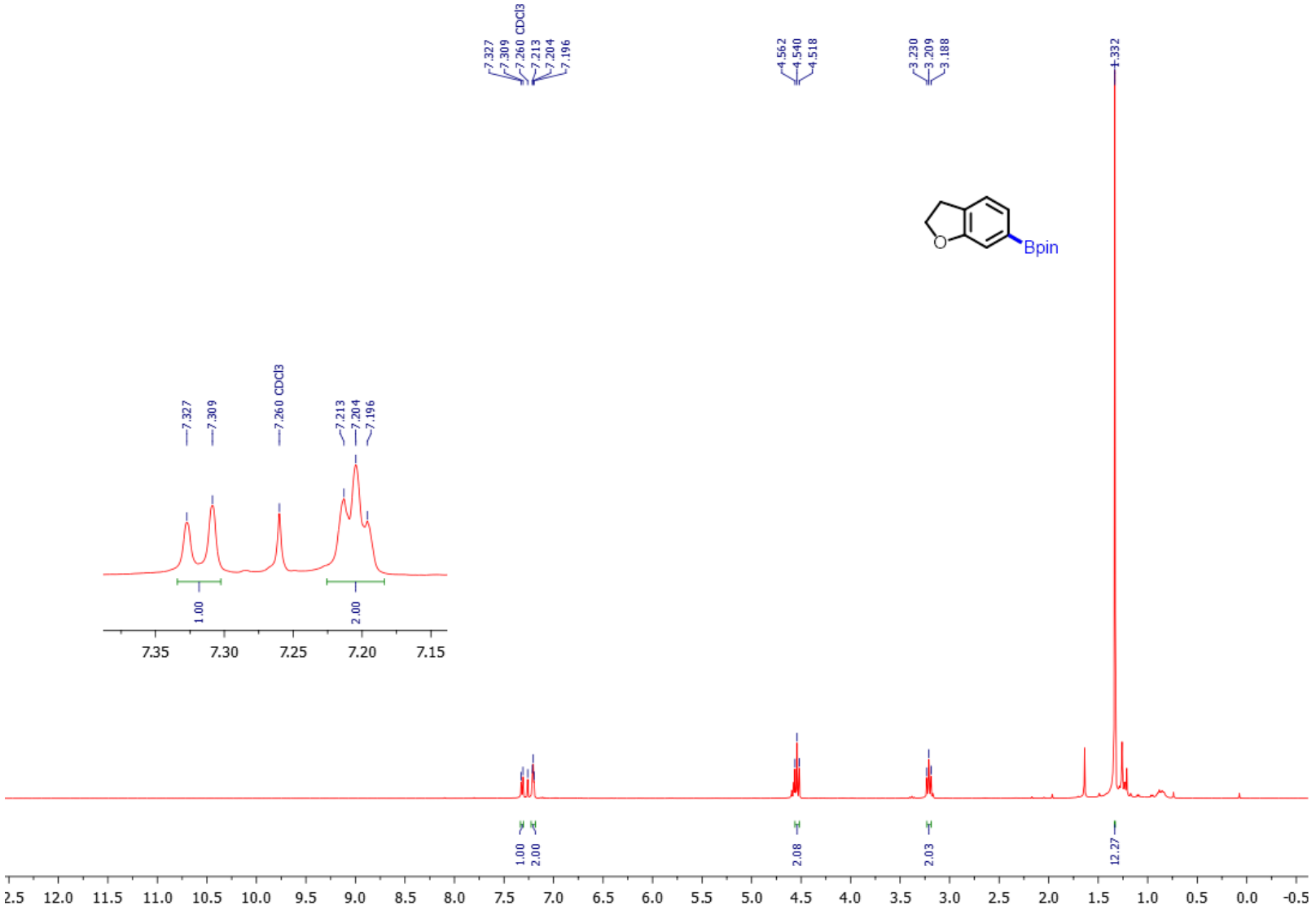
^{1}H NMR spectra of **2av** (25 ºC, 400 MHz, $CDCl_3$)



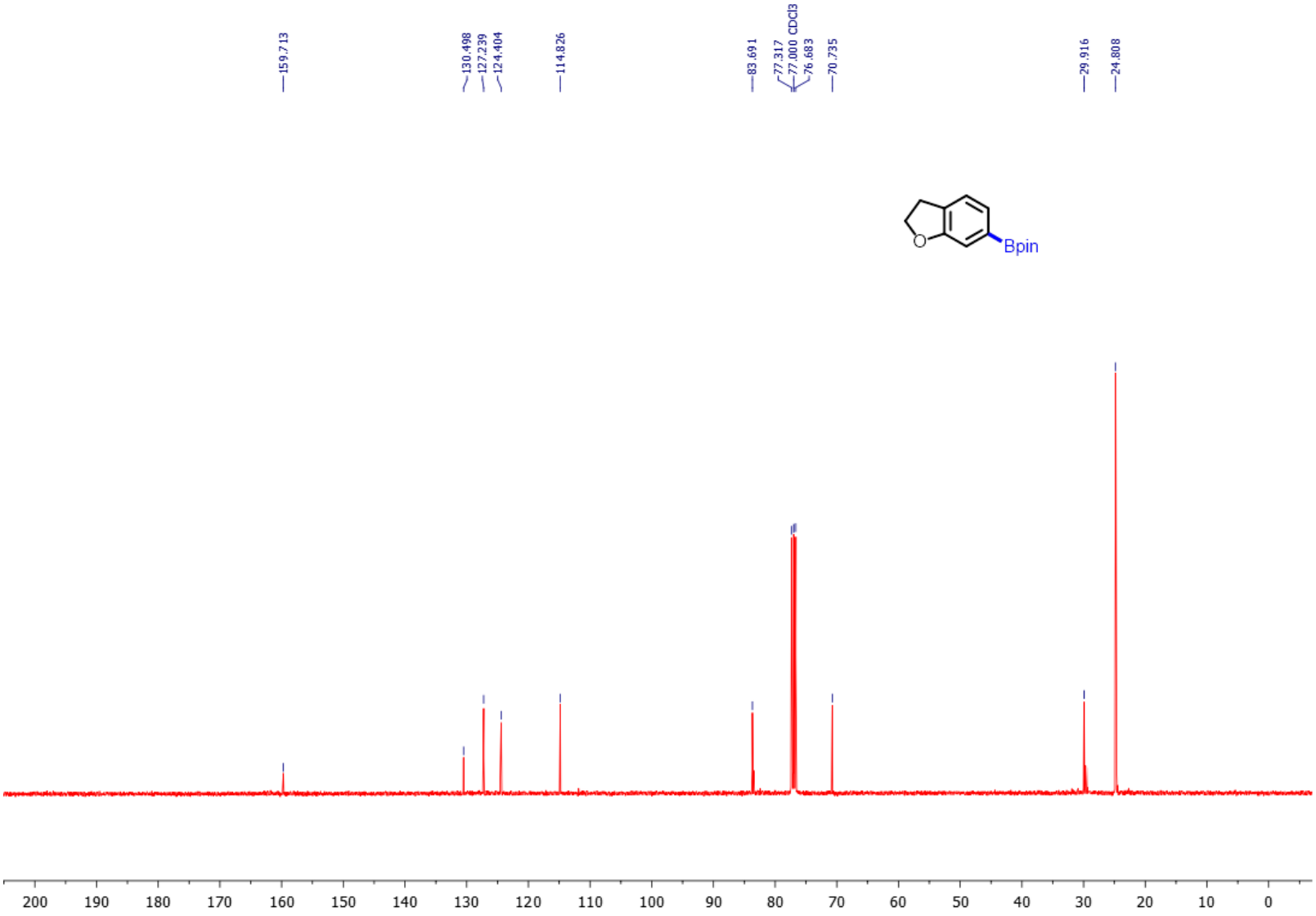
^{13}C NMR spectra of **2av** (25 °C, 100 MHz, $CDCl_3$)



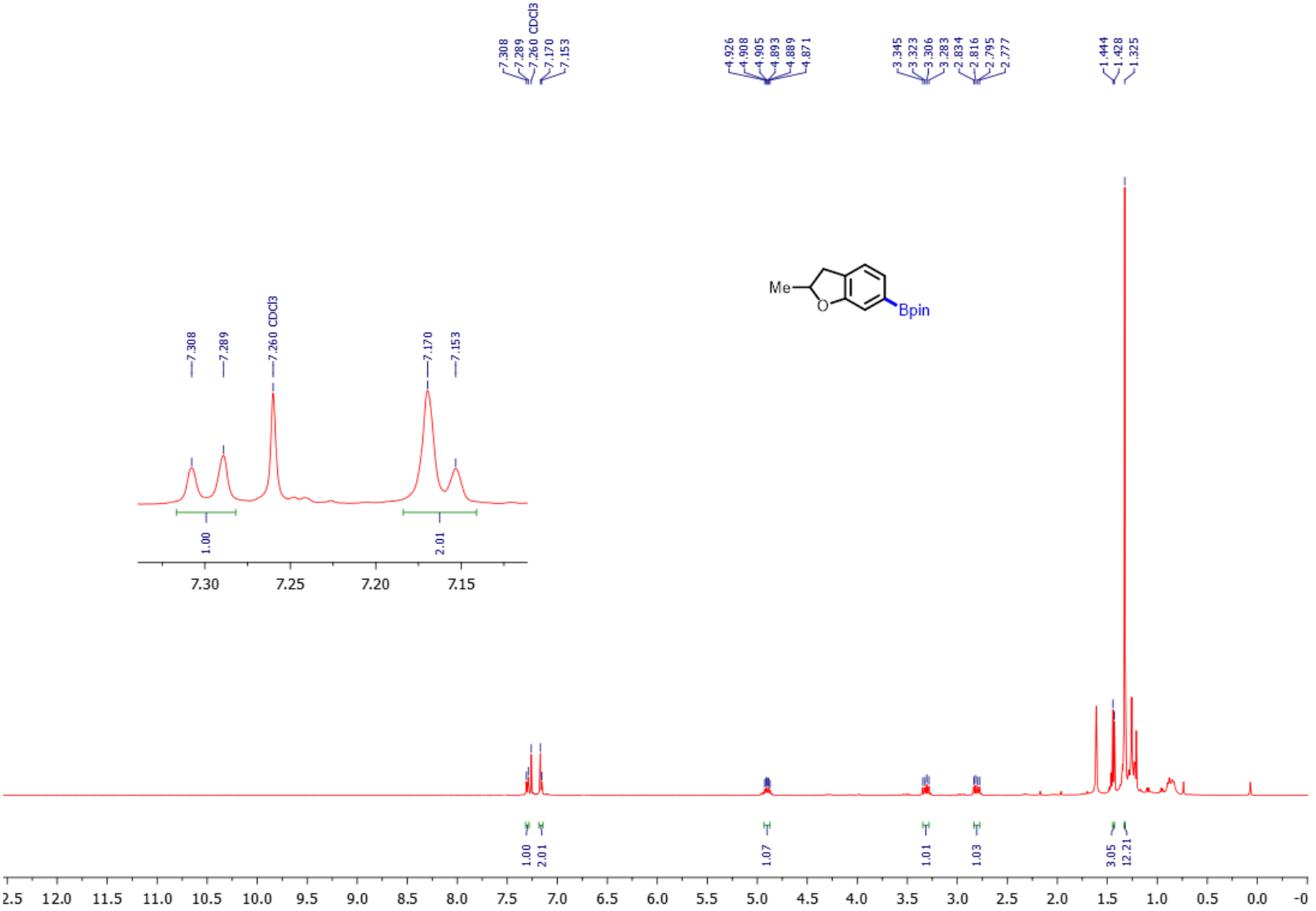
Crude ^{1}H NMR spectra of **2aw** (25 °C, 400 MHz, $CDCl_3$)



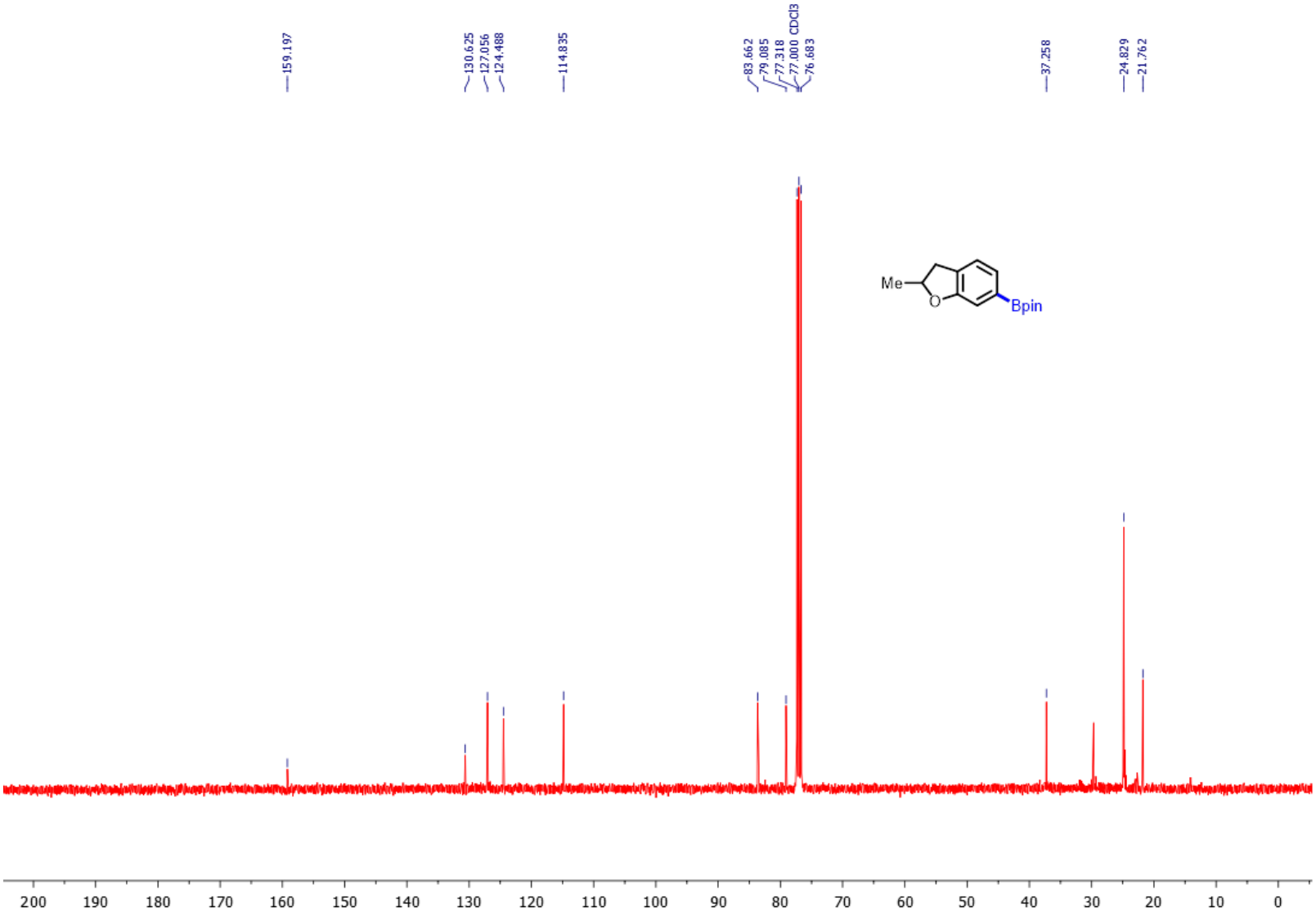
^{1}H NMR spectra of **4a** (25 °C, 400 MHz, $CDCl_3$)



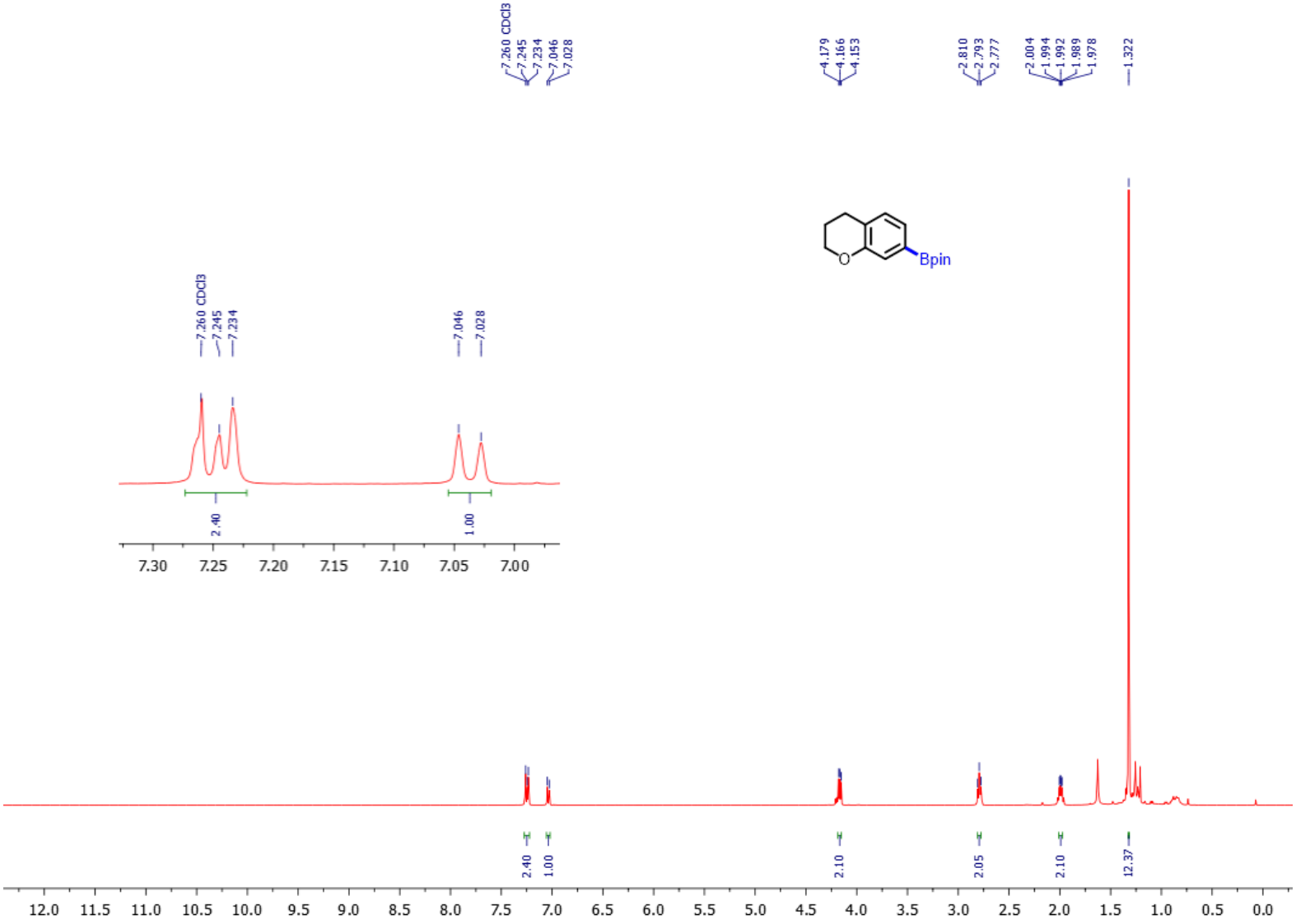
^{13}C NMR spectra of **4a** (25 °C, 100 MHz, $CDCl_3$)



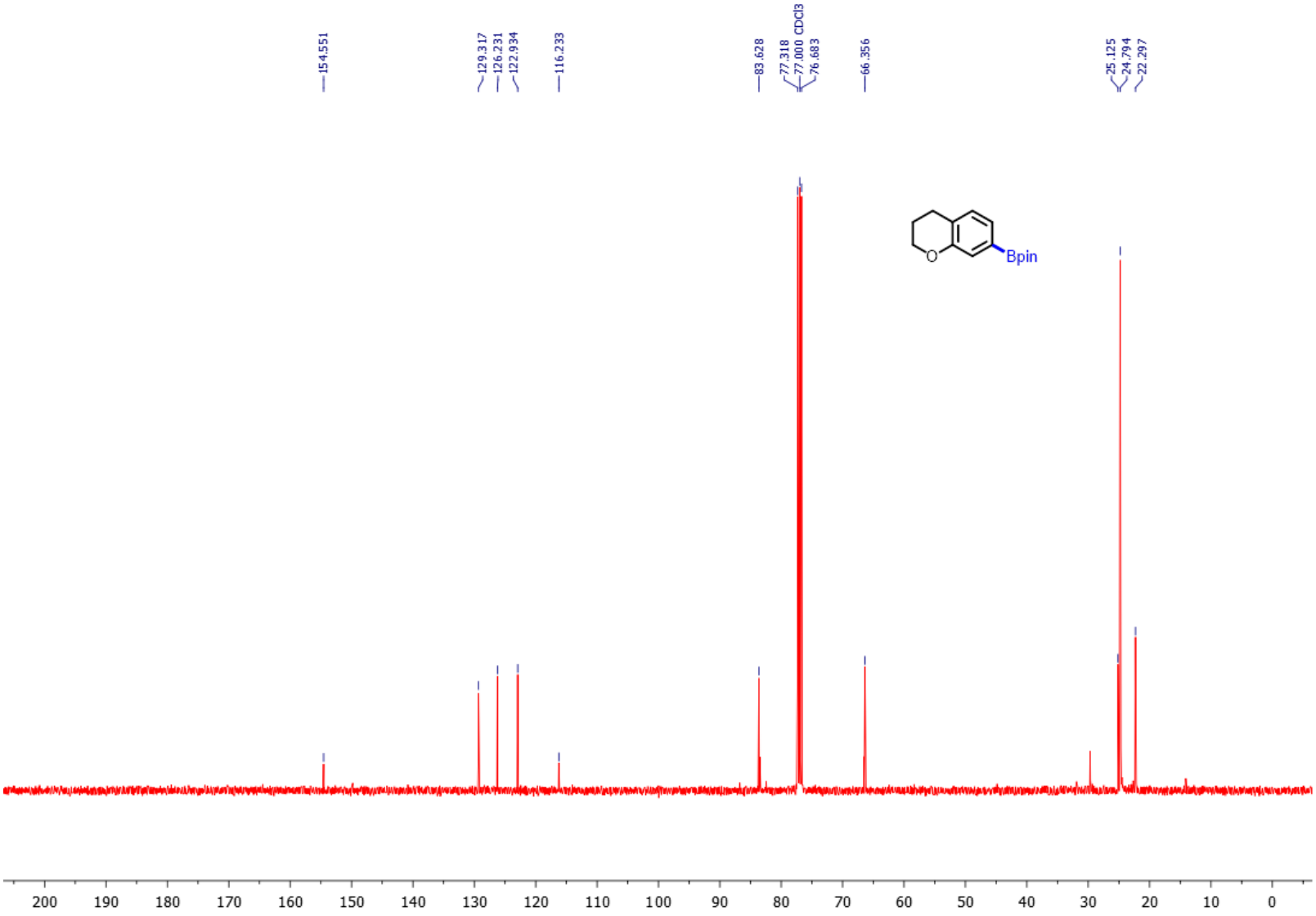
^{1}H NMR spectra of **4b** (25 °C, 400 MHz, $CDCl_3$)



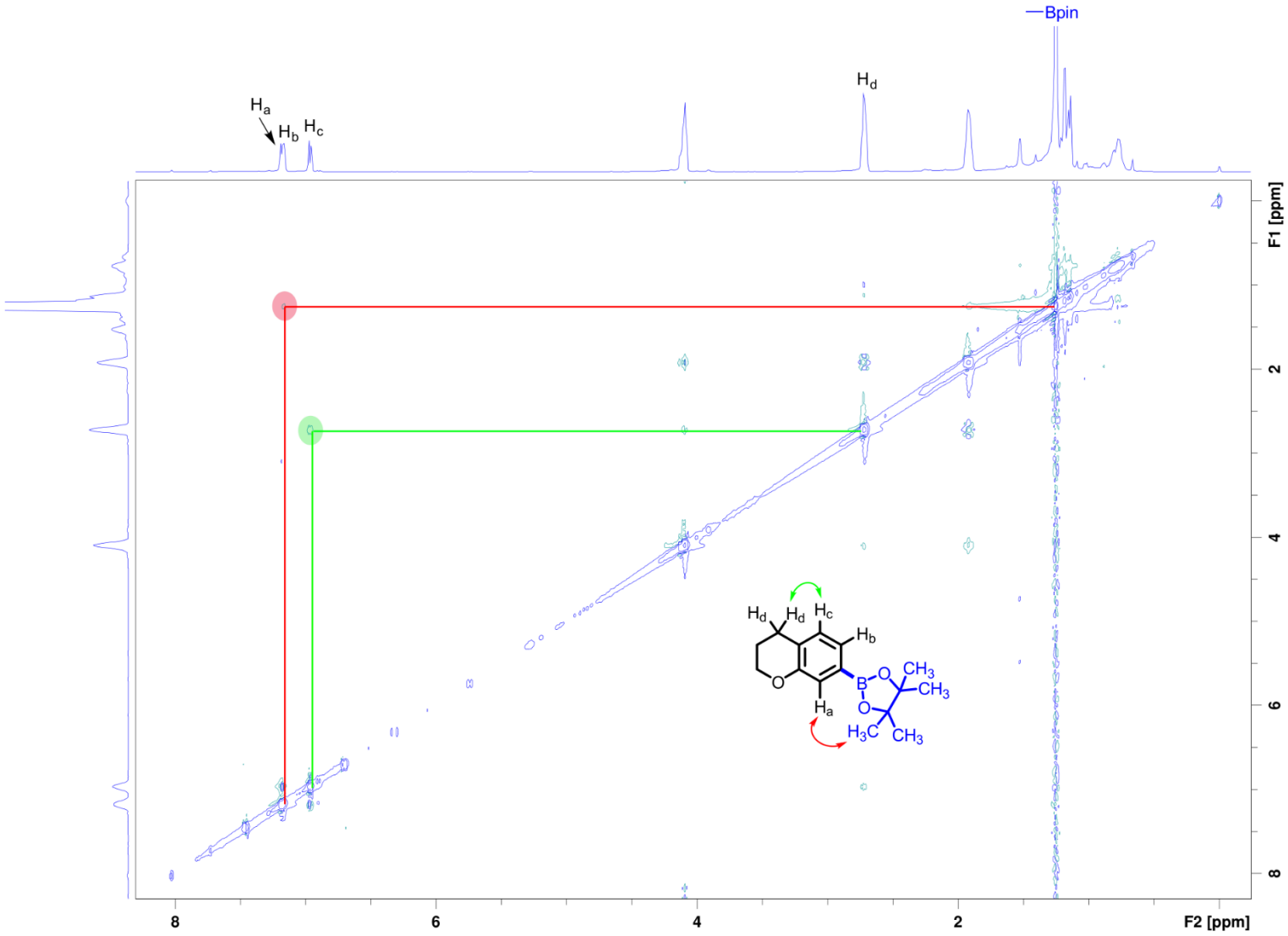
^{13}C NMR spectra of **4b** (25 °C, 100 MHz, $CDCl_3$)



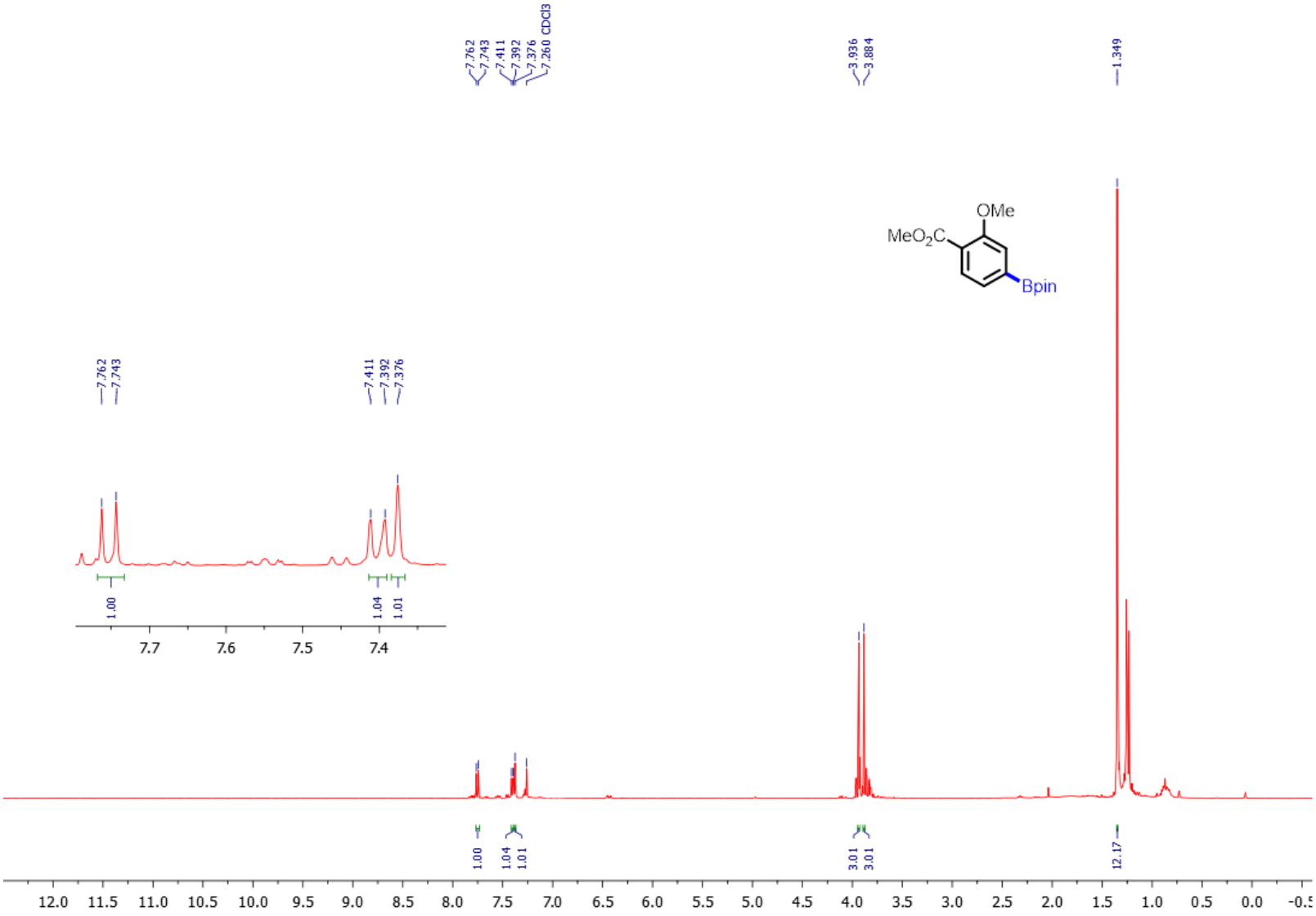
^{1}H NMR spectra of **4c** (25 °C, 400 MHz, $CDCl_3$)



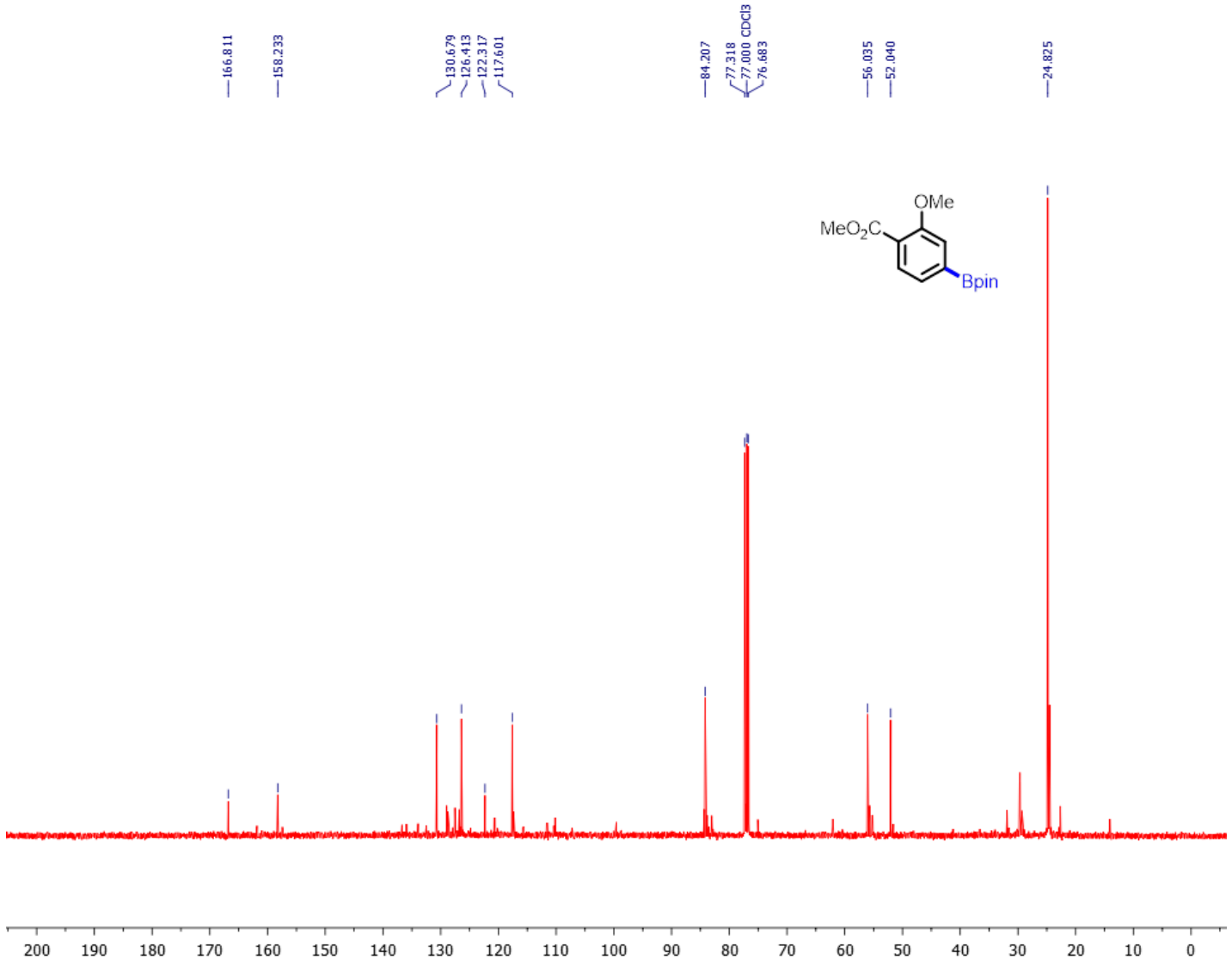
^{13}C NMR spectra of **4c** (25 °C, 100 MHz, $CDCl_3$)



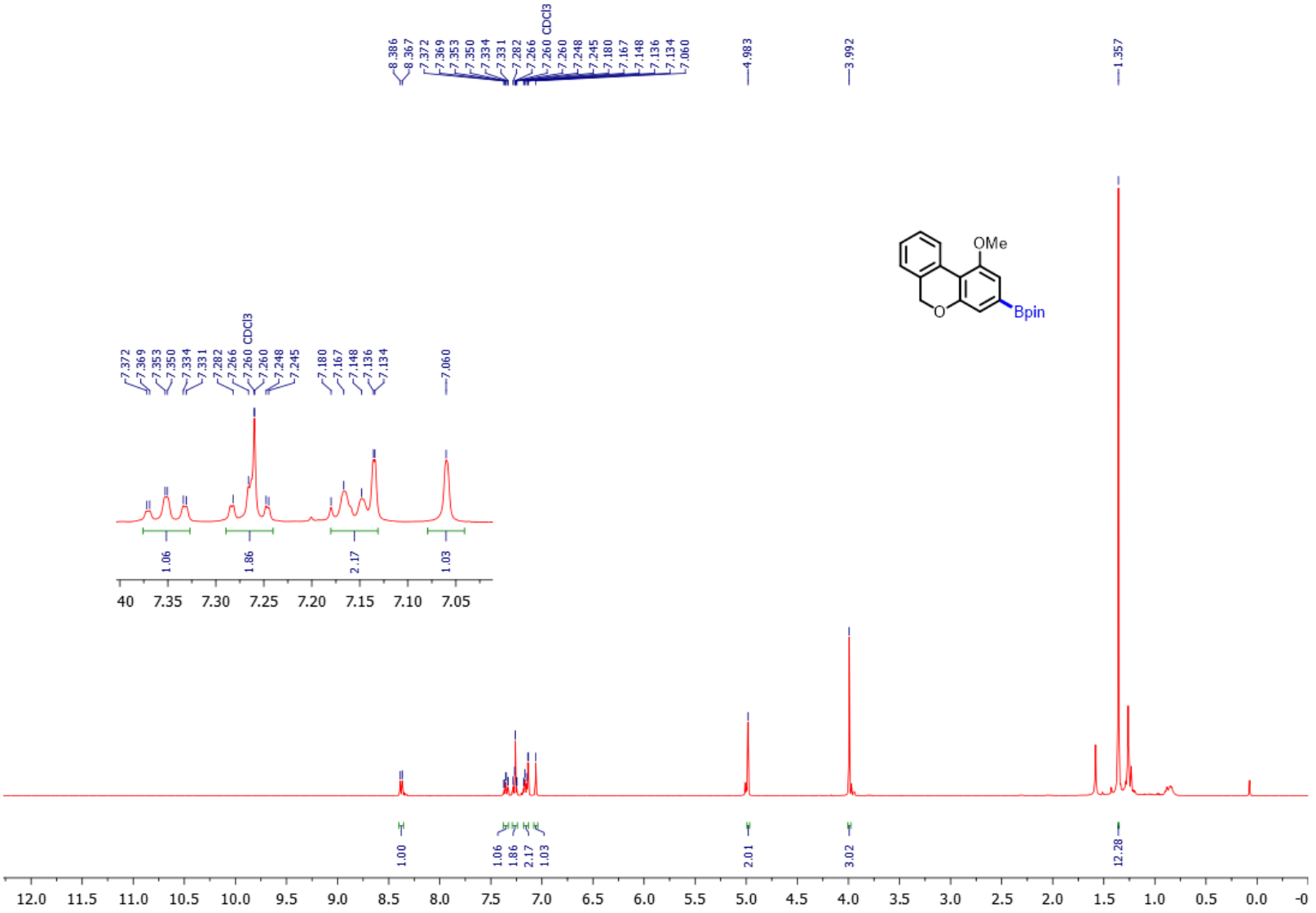
2D NOESY spectra of **4c** (25 ºC, 400 MHz, $CDCl_3$)



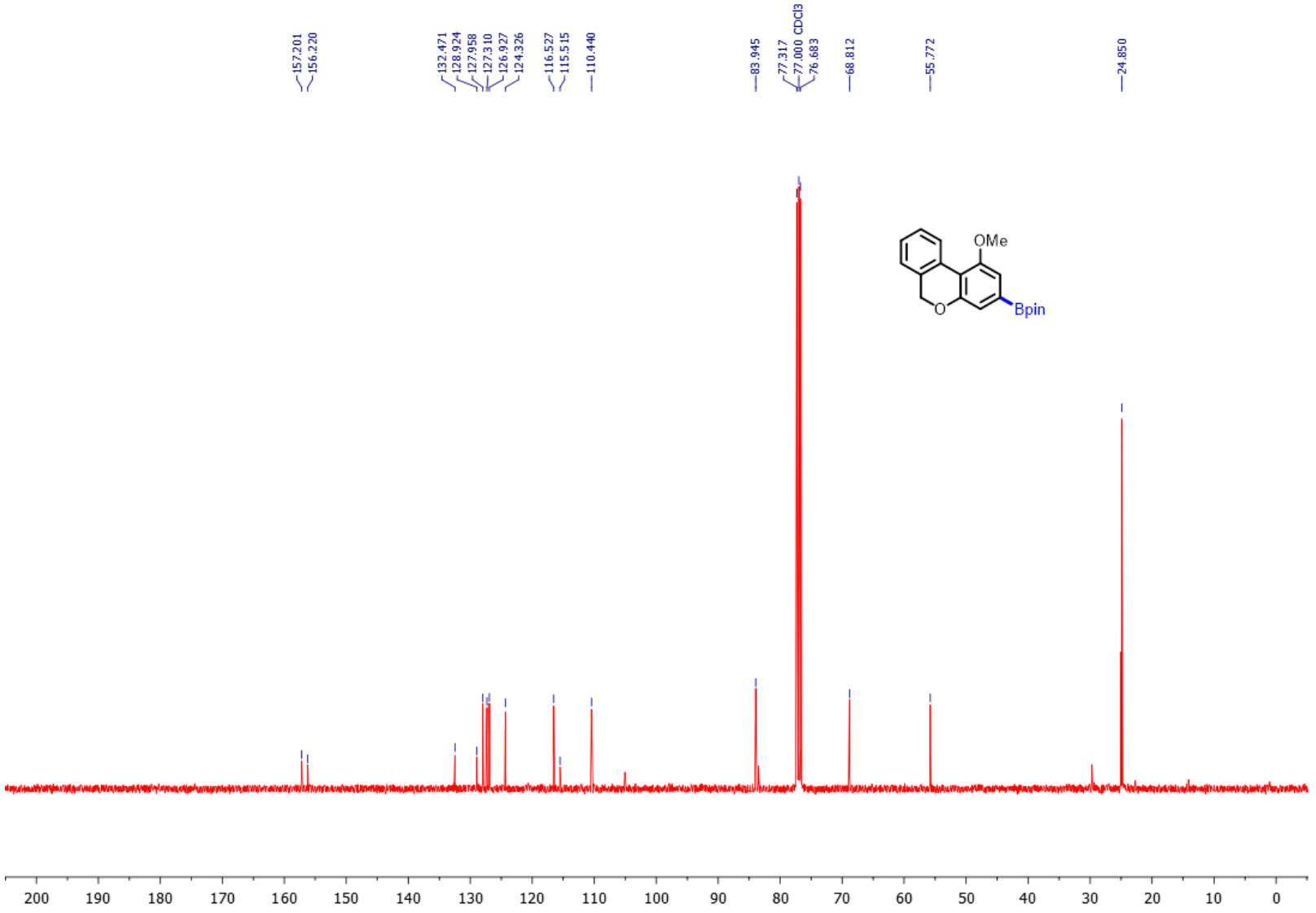
^{1}H NMR spectra of **4d** (25 °C, 400 MHz, $CDCl_3$)



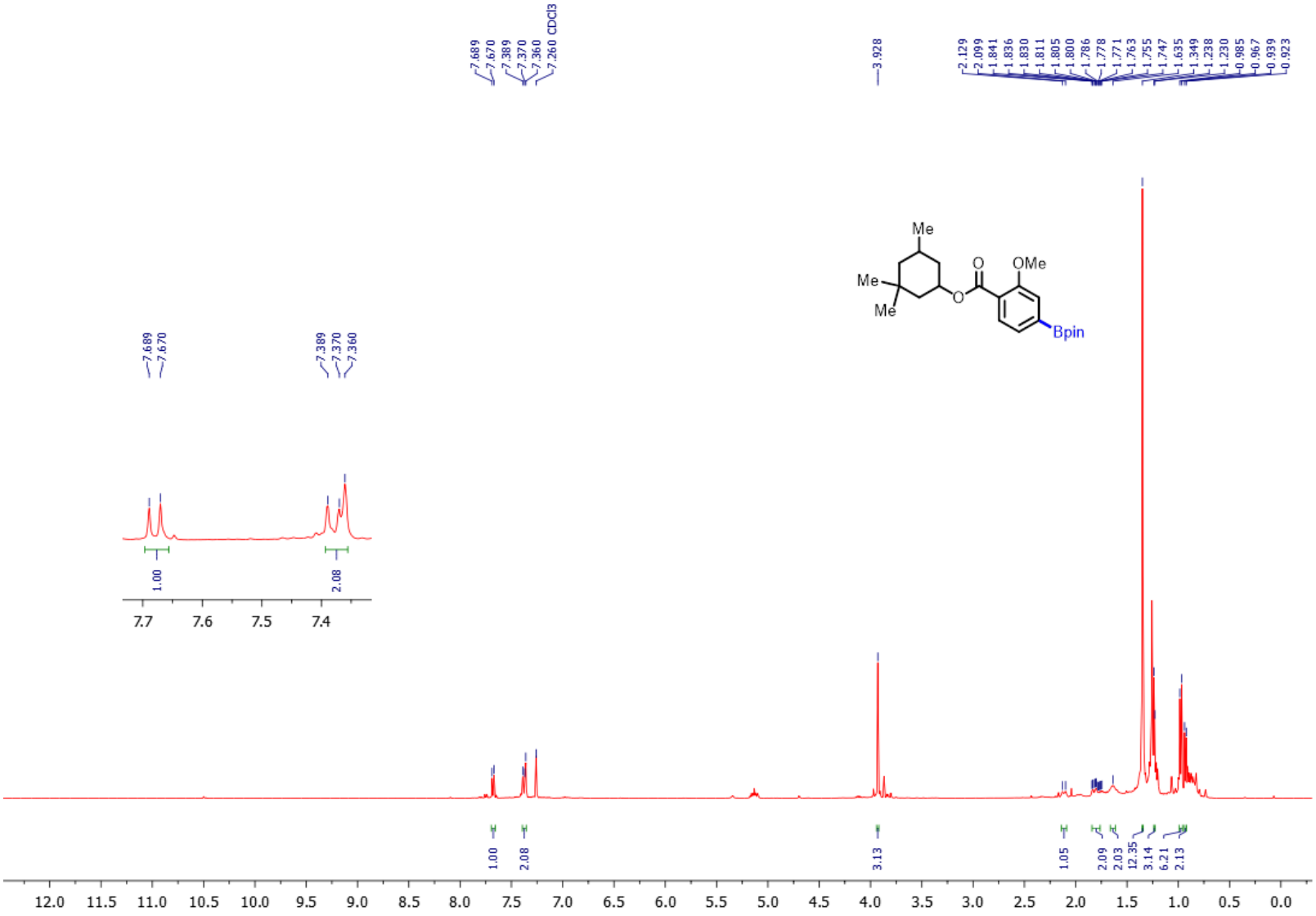
^{13}C NMR spectra of **4d** (25 °C, 100 MHz, $CDCl_3$)



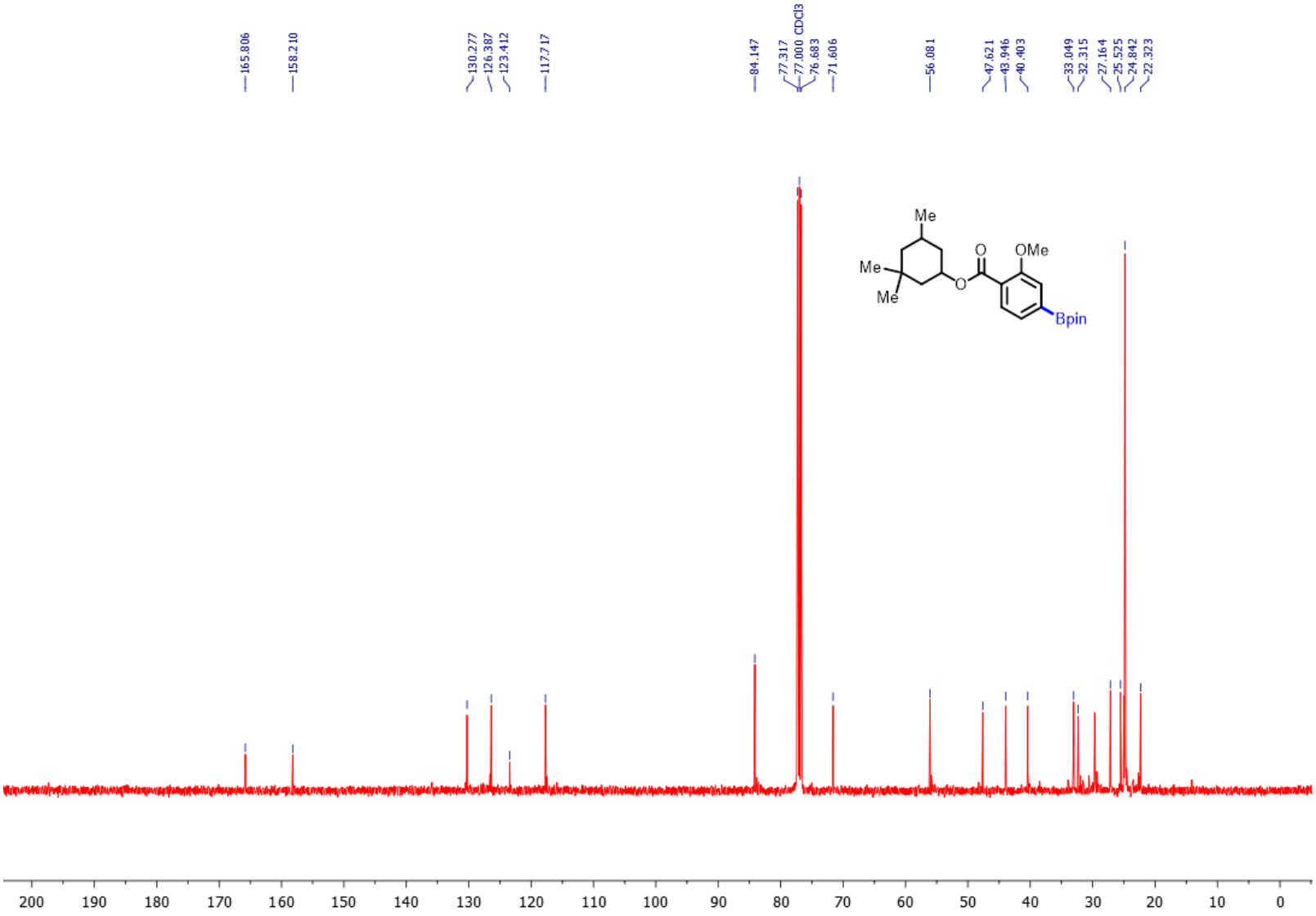
^{1}H NMR spectra of **4e** (25 °C, 400 MHz, $CDCl_3$)



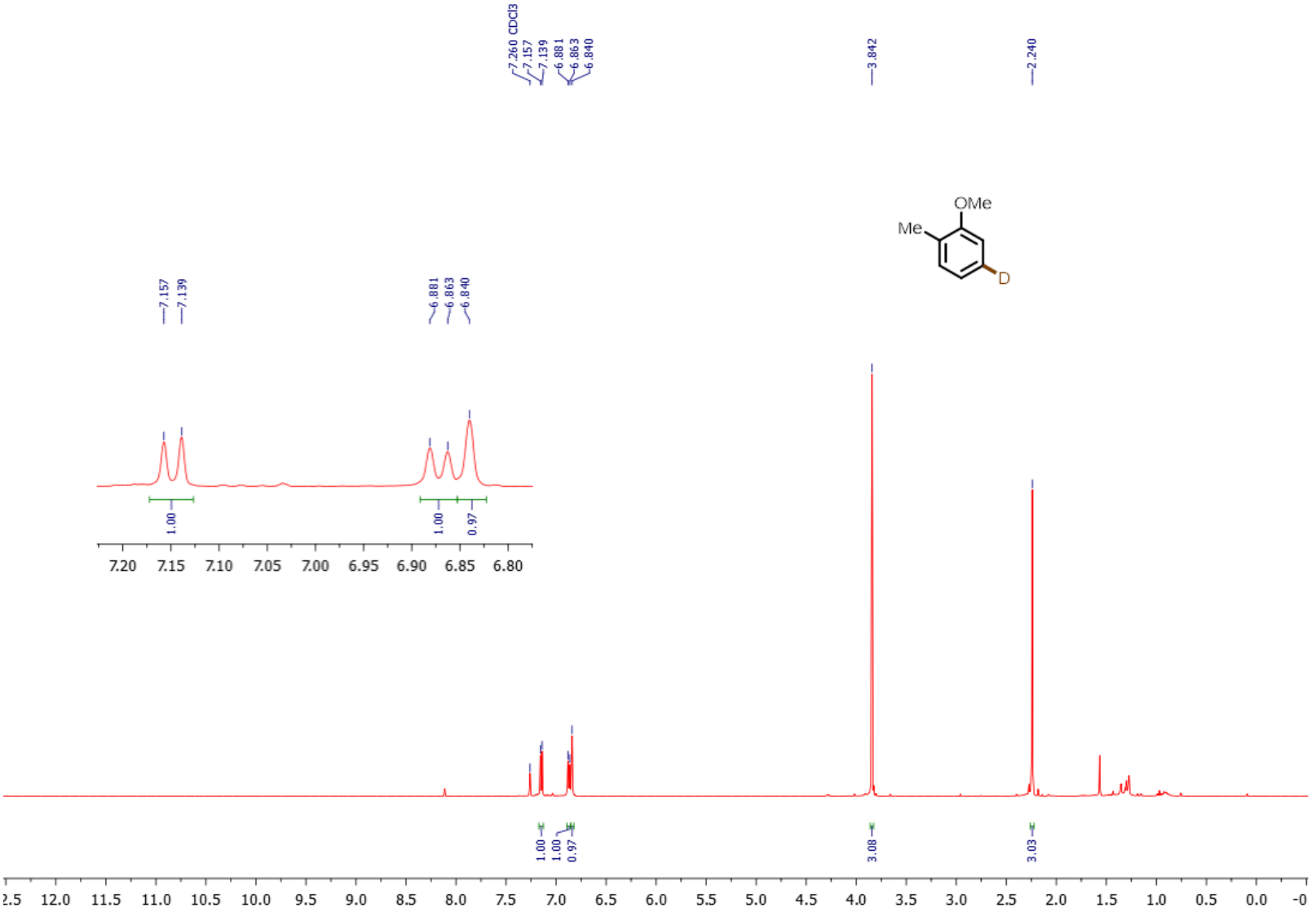
^{13}C NMR spectra of **4e** (25 °C, 100 MHz, $CDCl_3$)



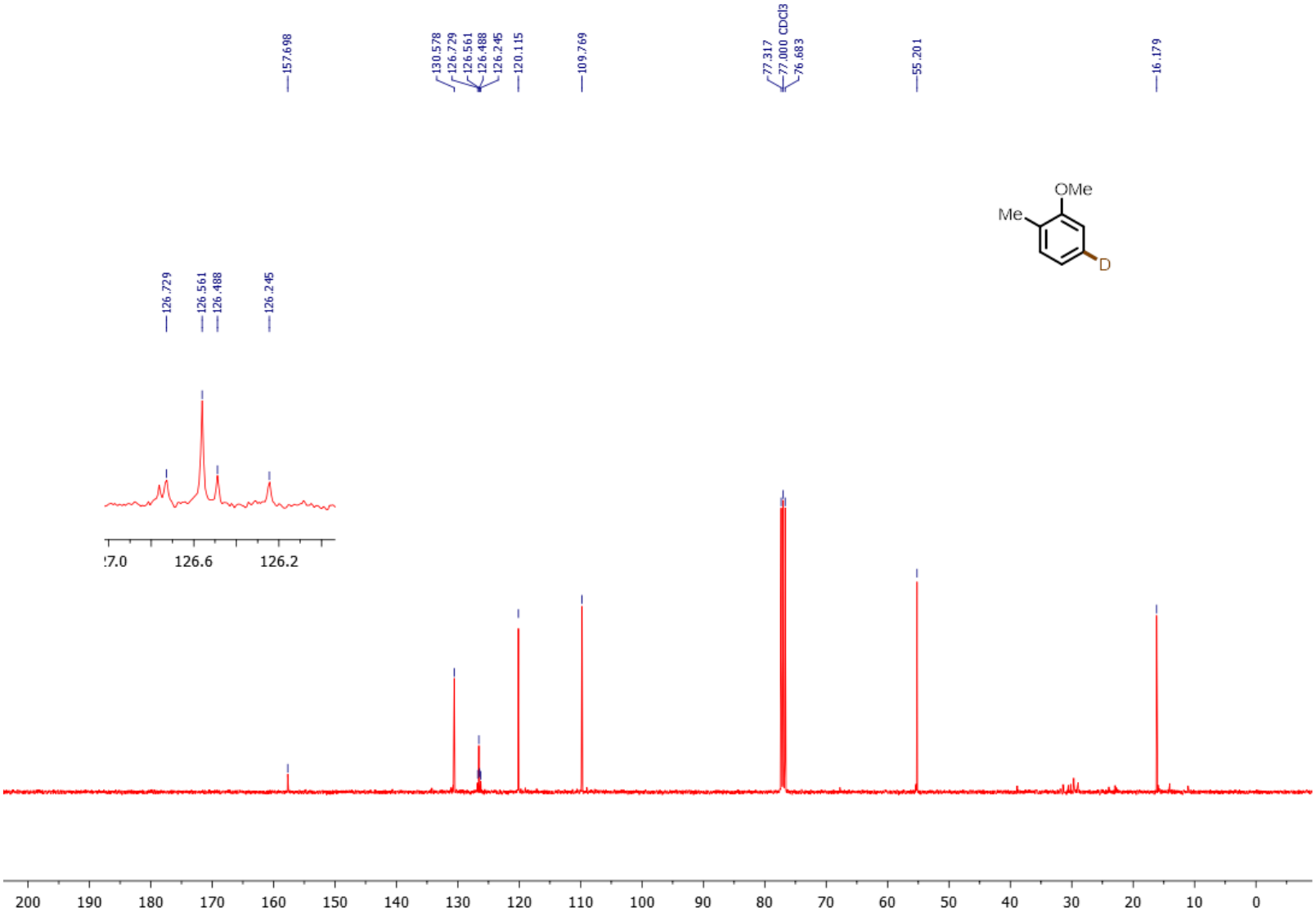
^{1}H NMR spectra of **4f** (25 °C, 400 MHz, $CDCl_3$)



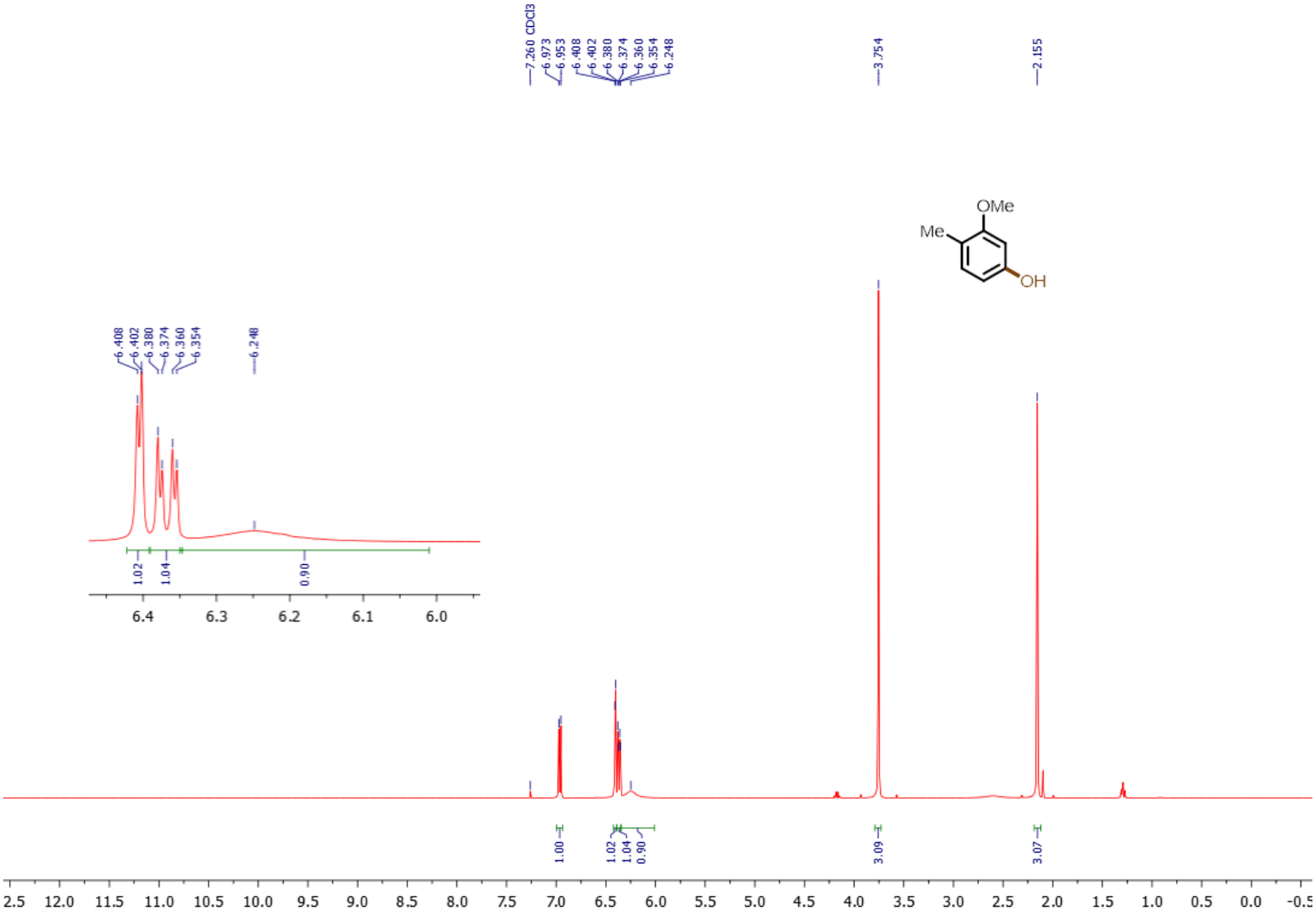
^{13}C NMR spectra of **4f** (25 °C, 100 MHz, $CDCl_3$)



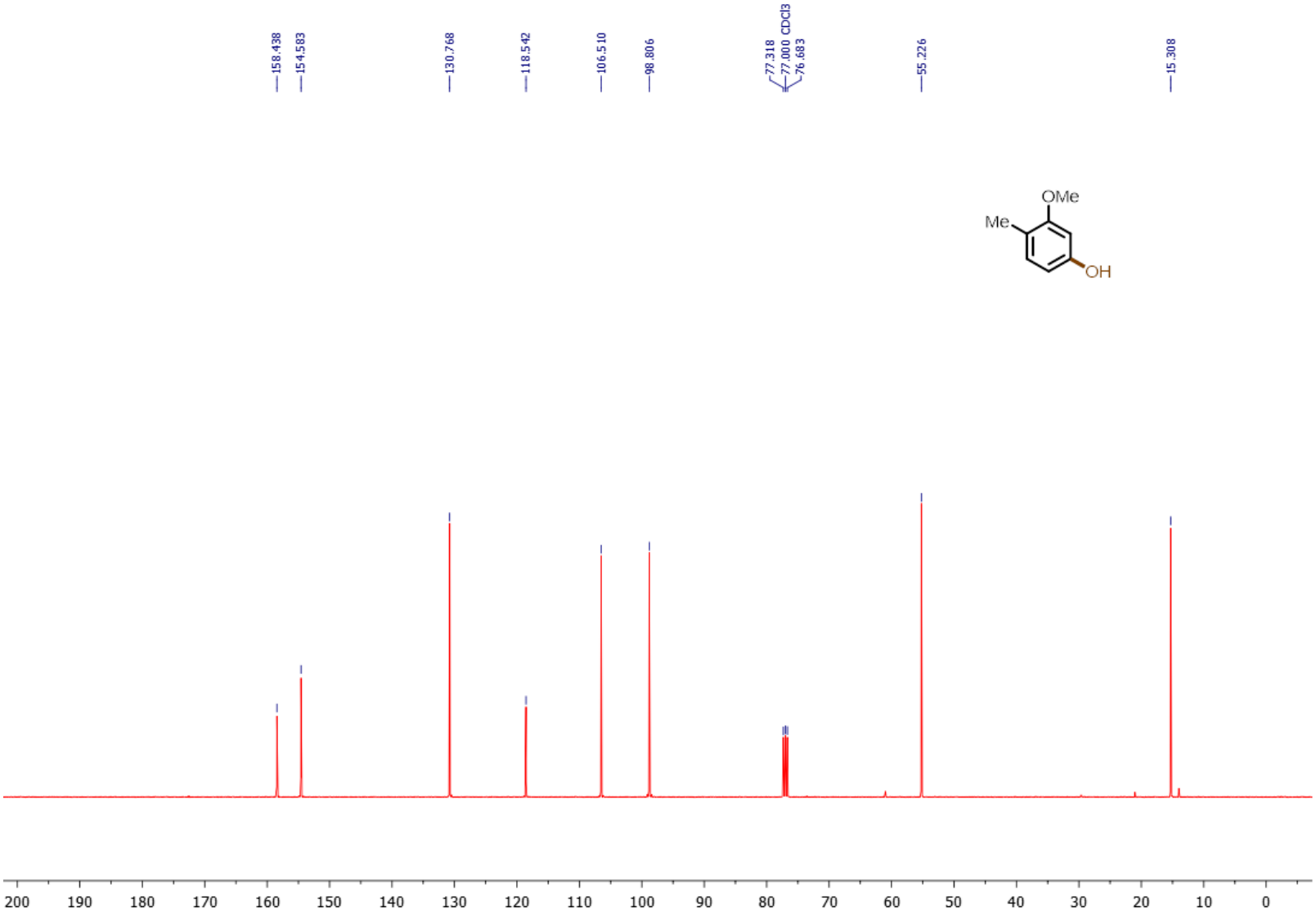
^{1}H NMR spectra of **5a** (25 °C, 400 MHz, $CDCl_3$)



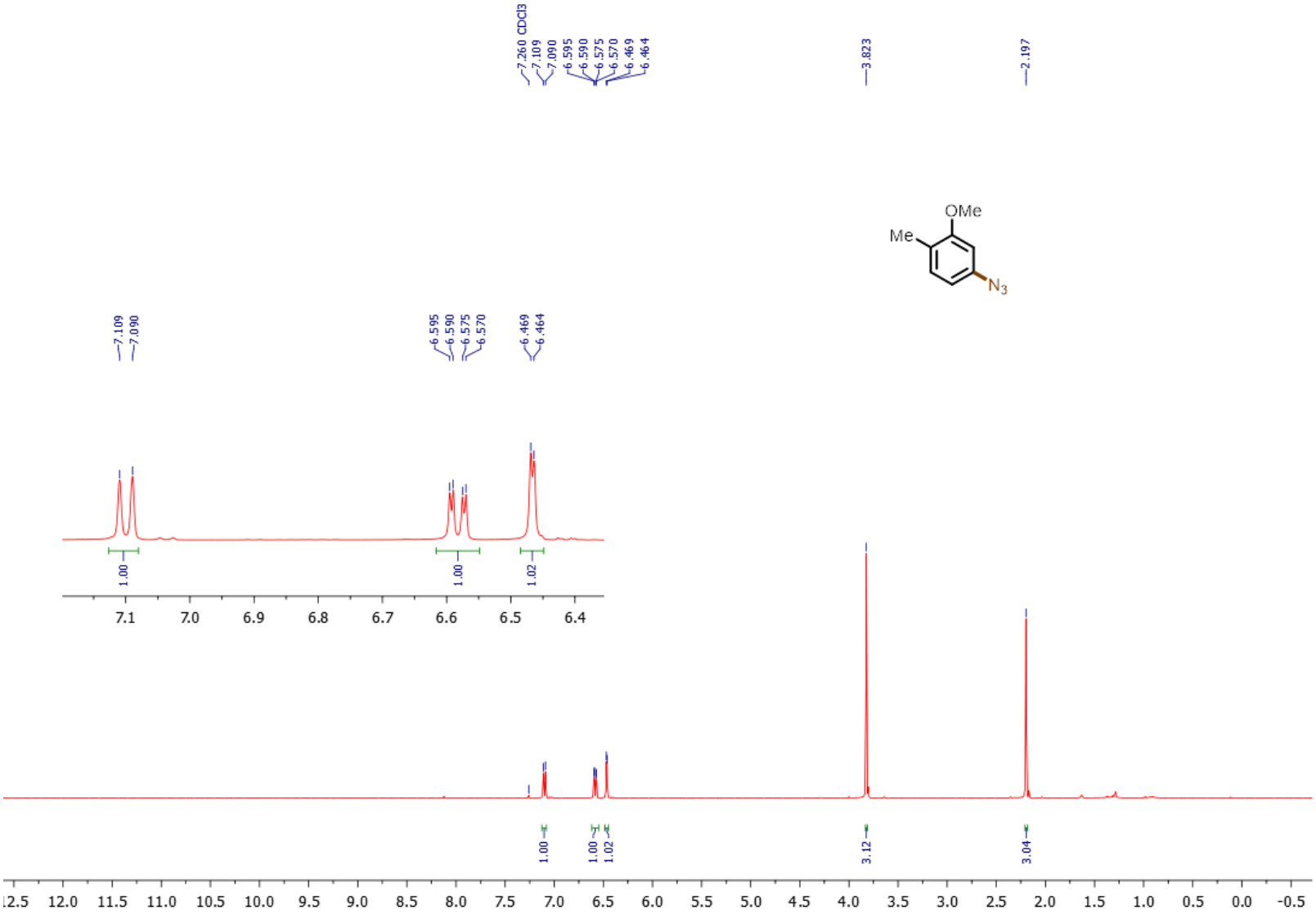
^{13}C NMR spectra of **5a** (25 °C, 100 MHz, $CDCl_3$)



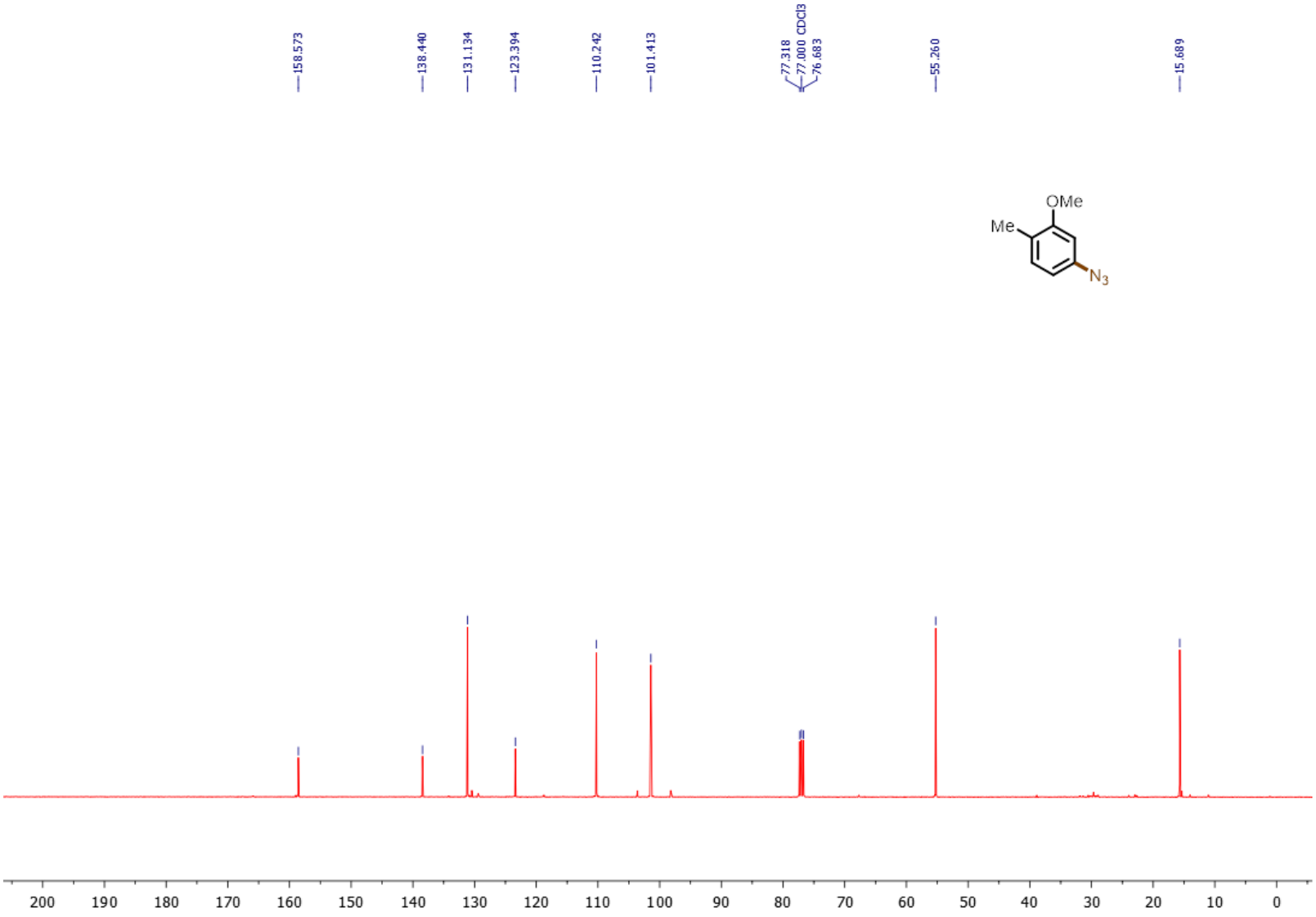
^{1}H NMR spectra of **5b** (25 °C, 400 MHz, $CDCl_3$)



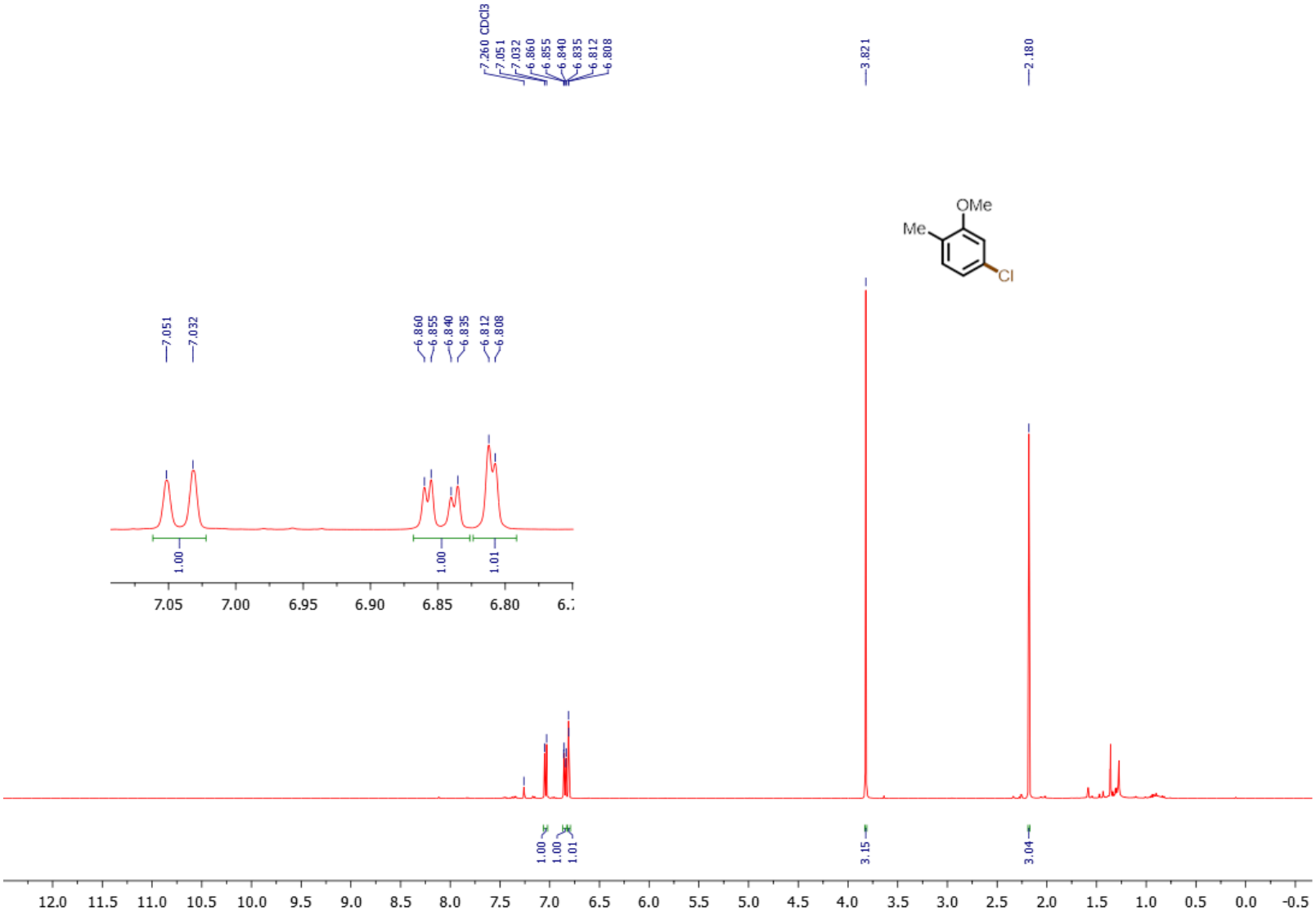
^{13}C NMR spectra of **5b** (25 °C, 100 MHz, $CDCl_3$)



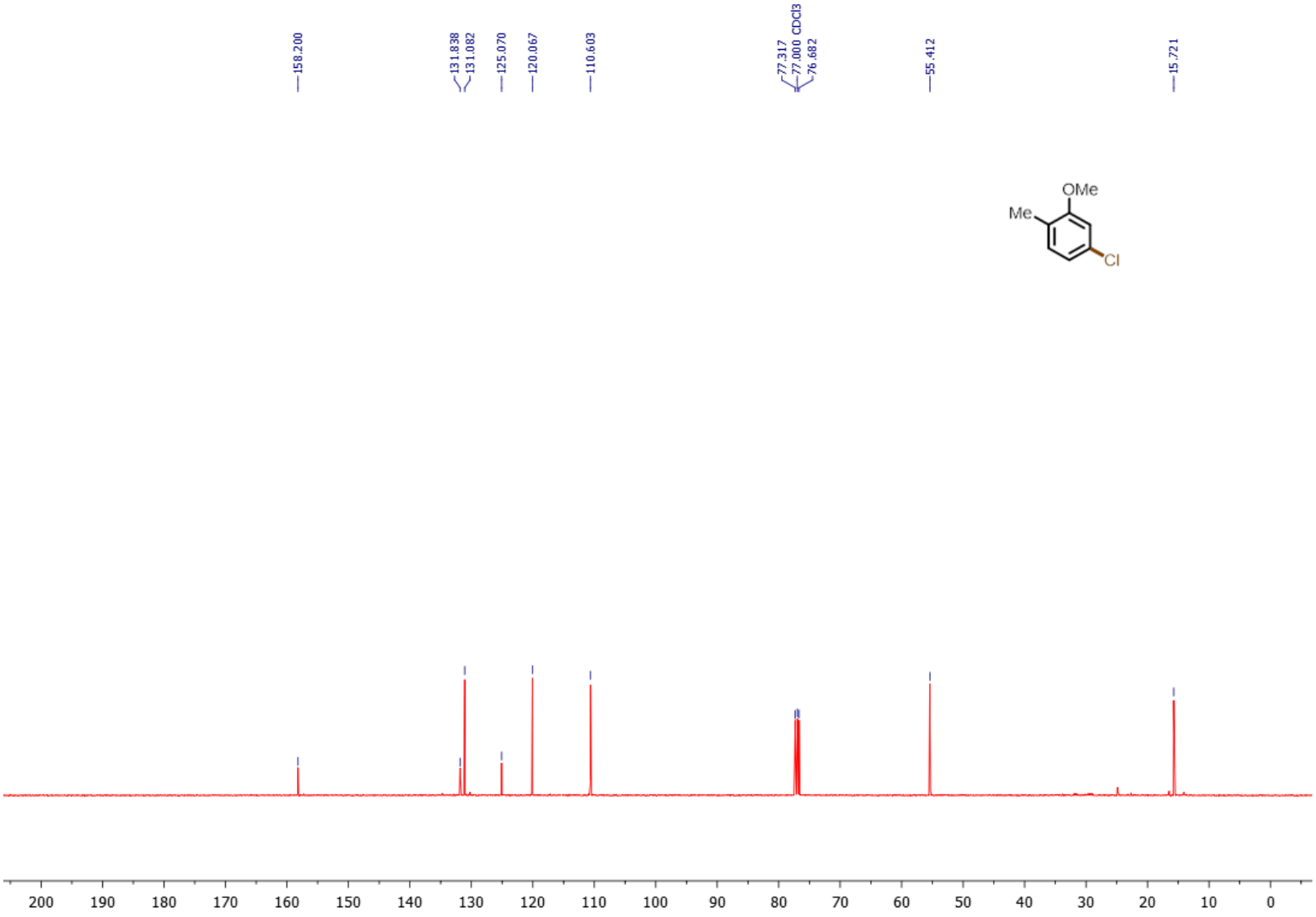
^{1}H NMR spectra of **5c** (25 ^{o}C, 400 MHz, $CDCl_3$)



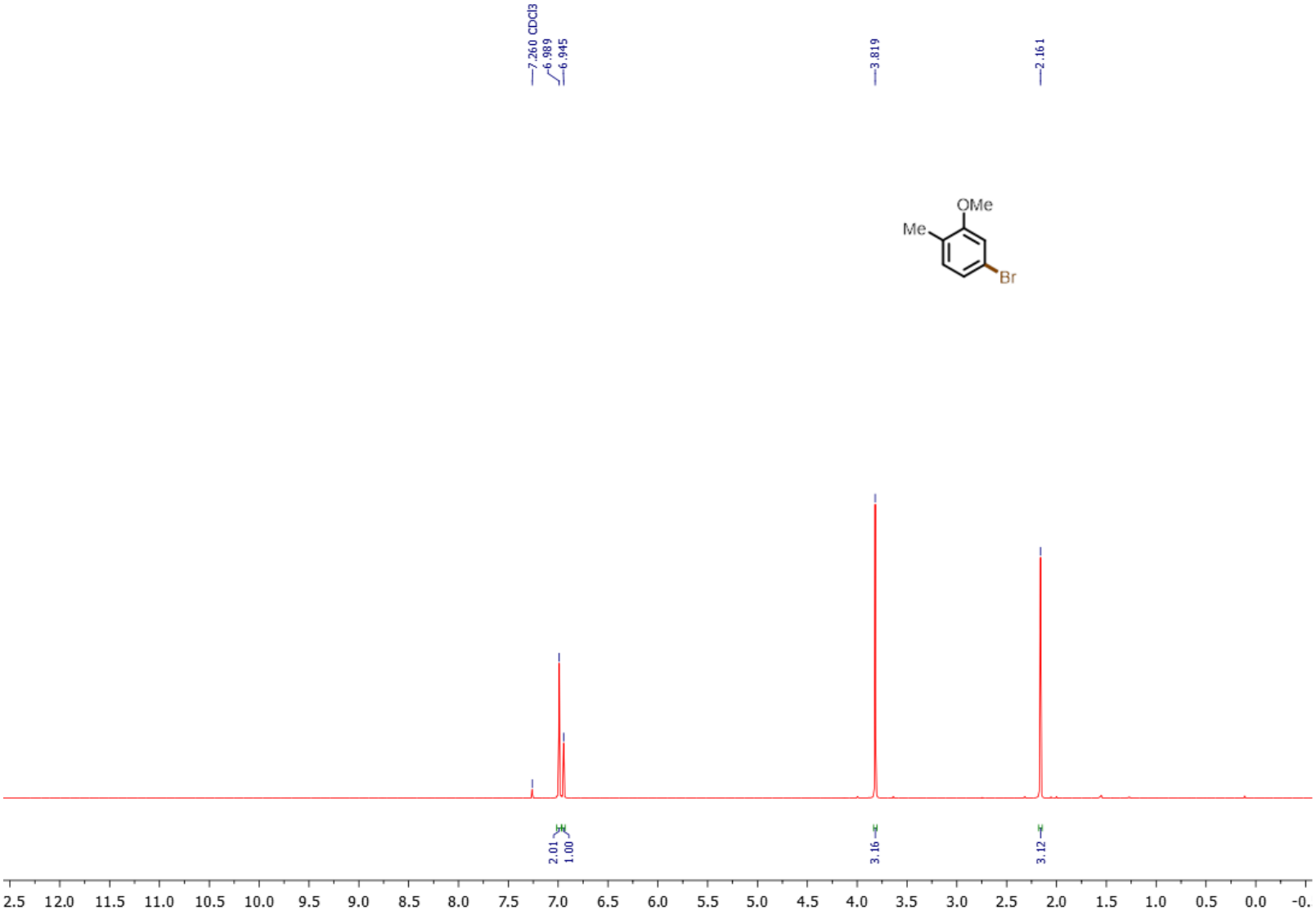
^{13}C NMR spectra of **5c** (25 °C, 100 MHz, $CDCl_3$)



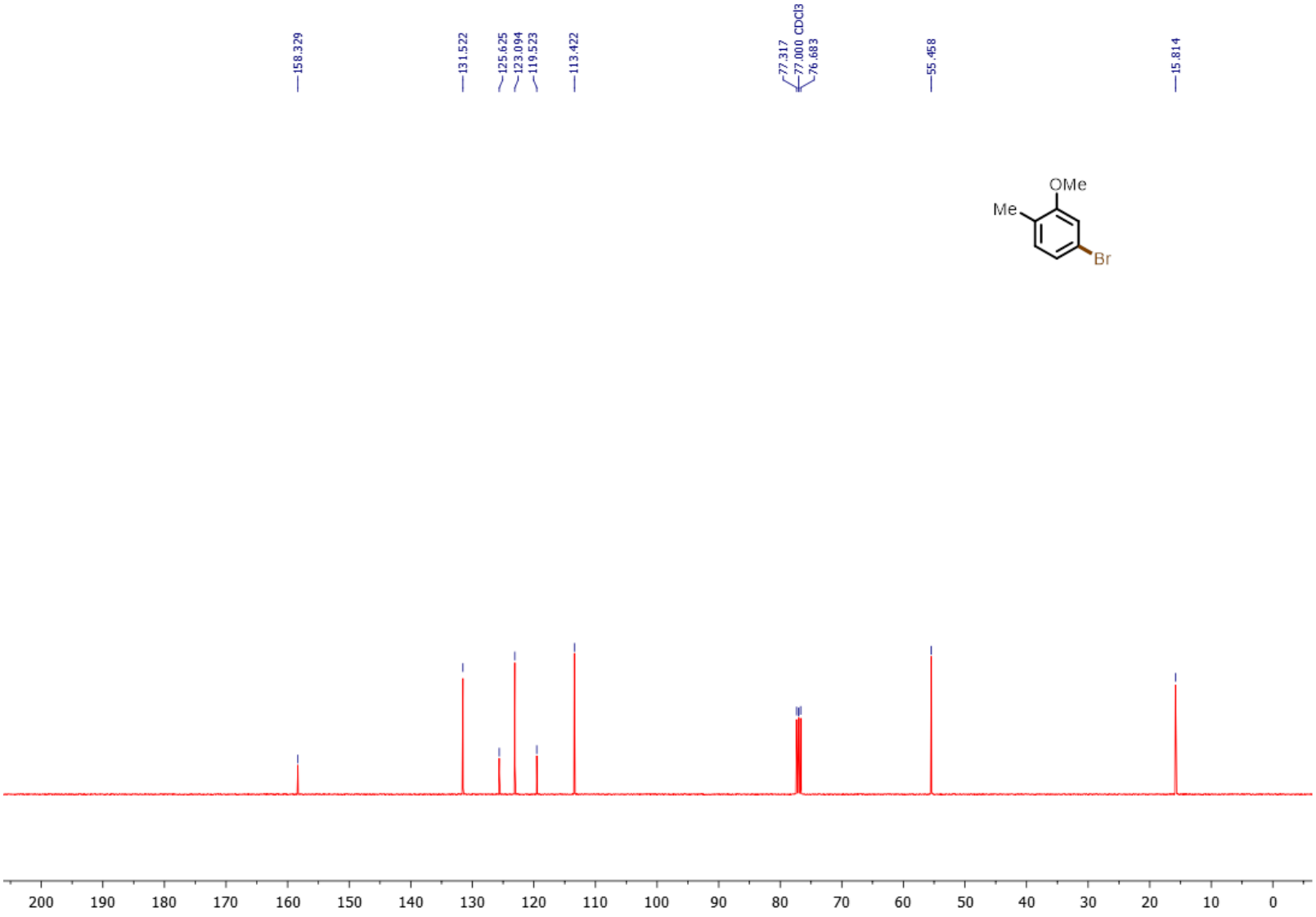
^{1}H NMR spectra of **5d** (25 °C, 400 MHz, $CDCl_3$)



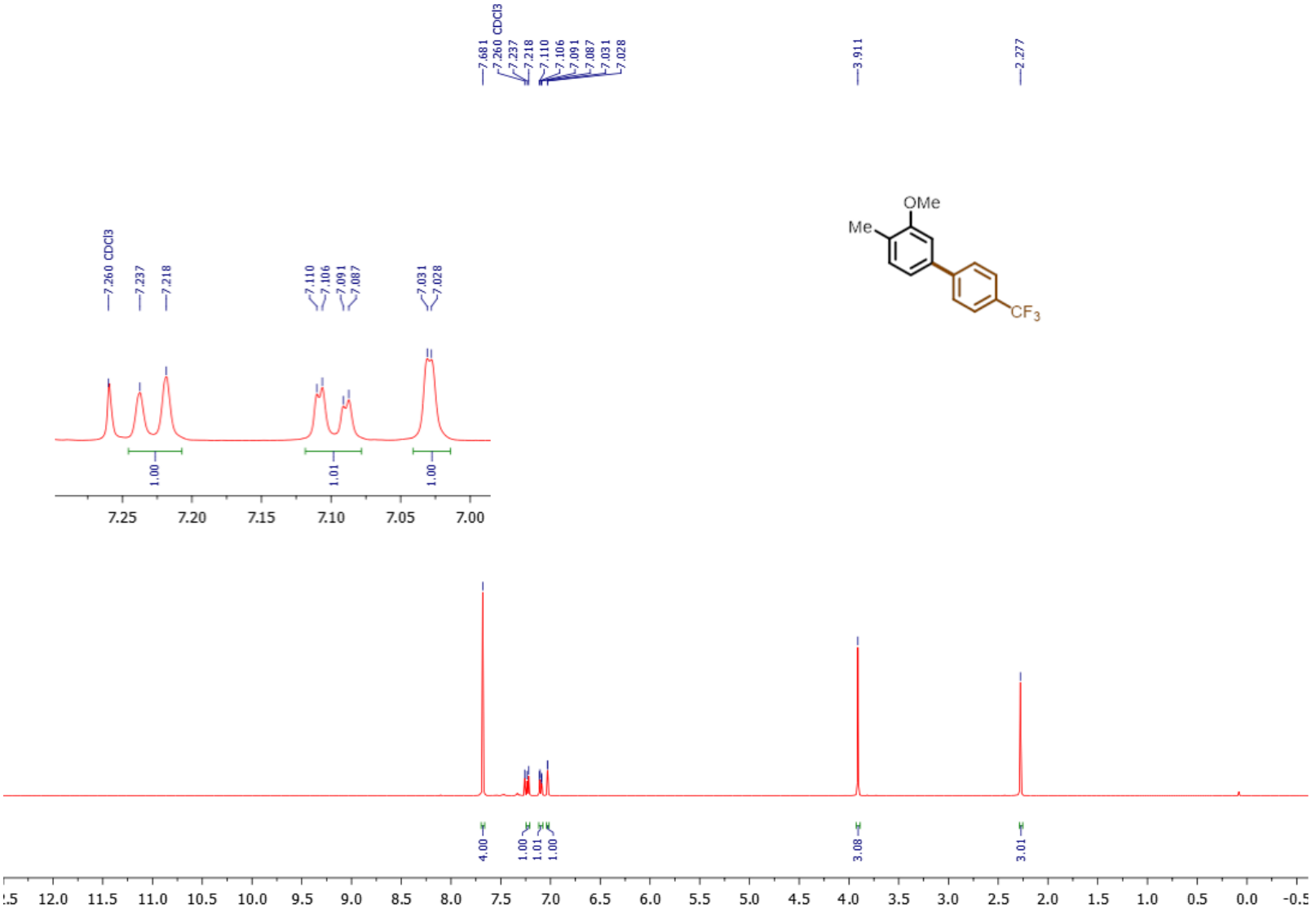
^{13}C NMR spectra of **5d** (25 °C, 100 MHz, $CDCl_3$)



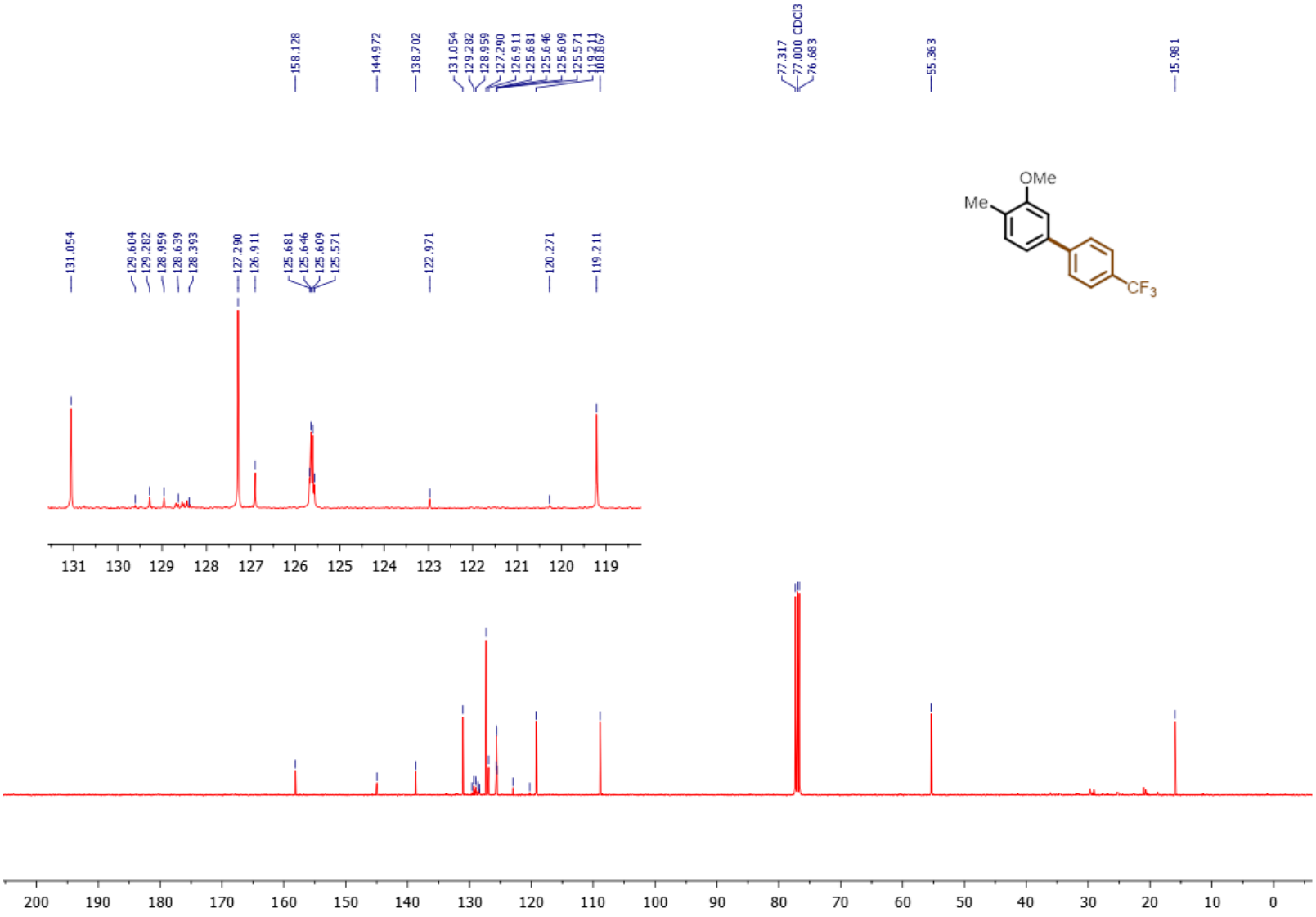
^{1}H NMR spectra of **5e** (25 °C, 400 MHz, $CDCl_3$)



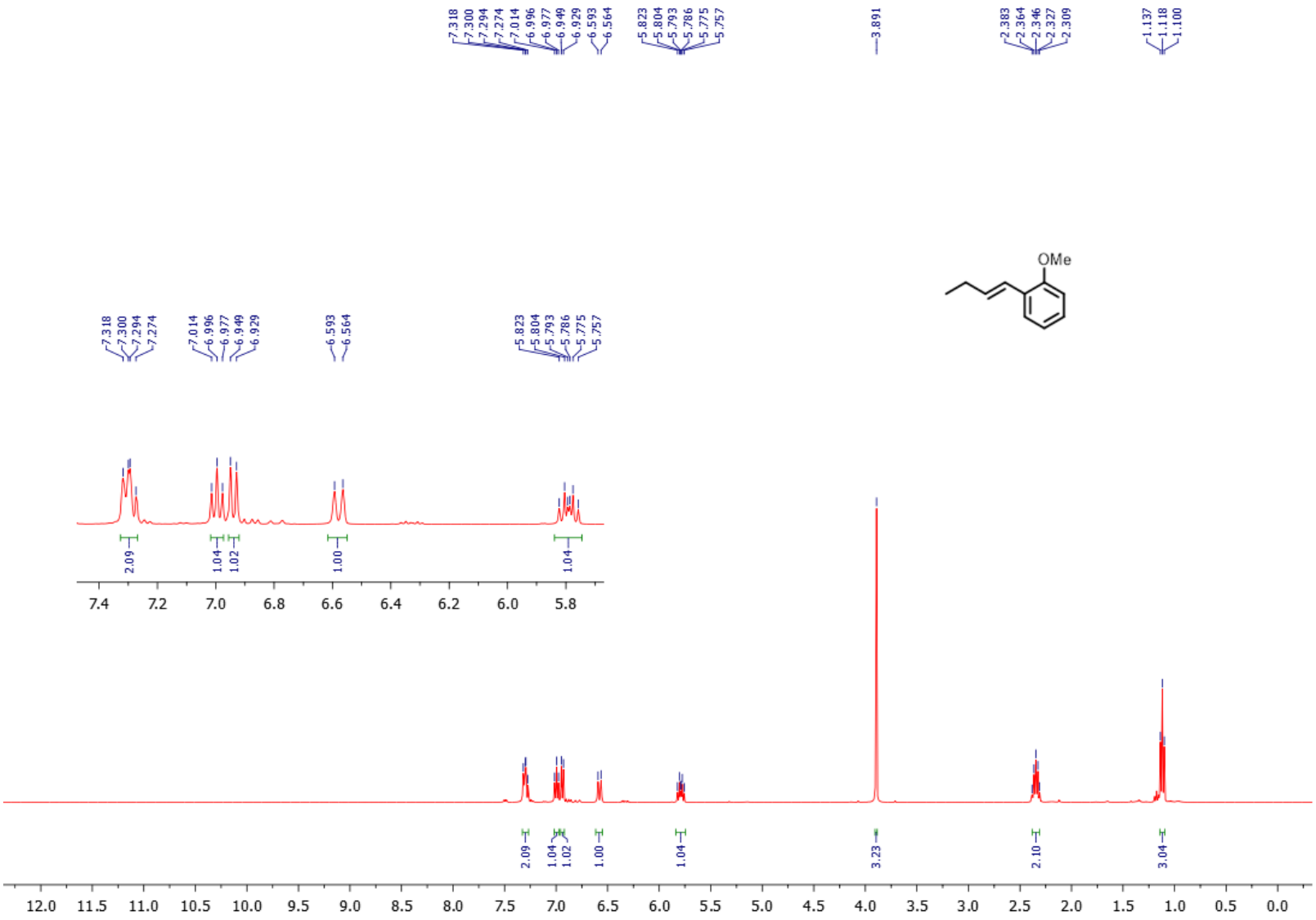
^{13}C NMR spectra of **5e** (25 °C, 100 MHz, $CDCl_3$)



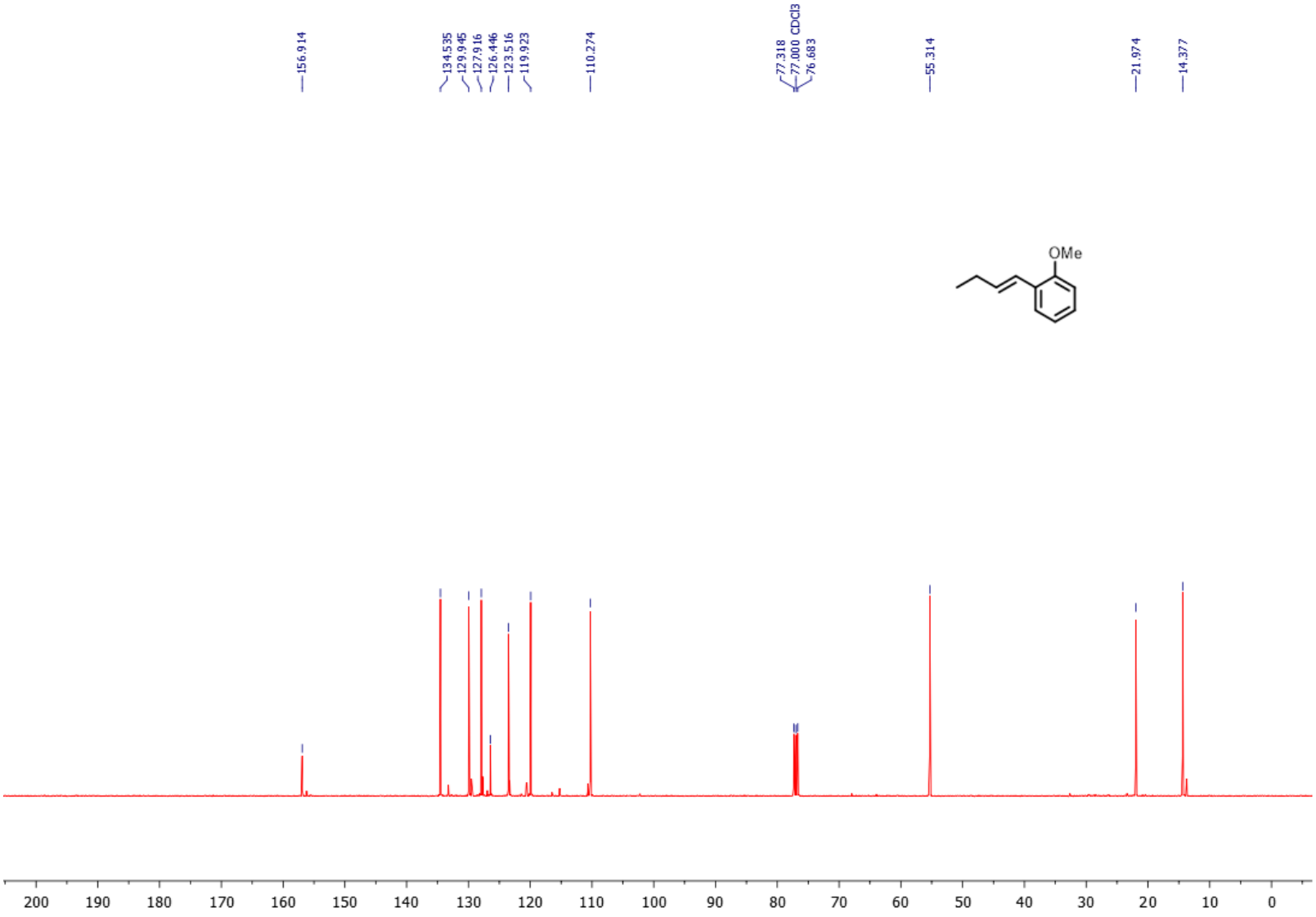
^{1}H NMR spectra of **5f** (25 °C, 400 MHz, $CDCl_3$)



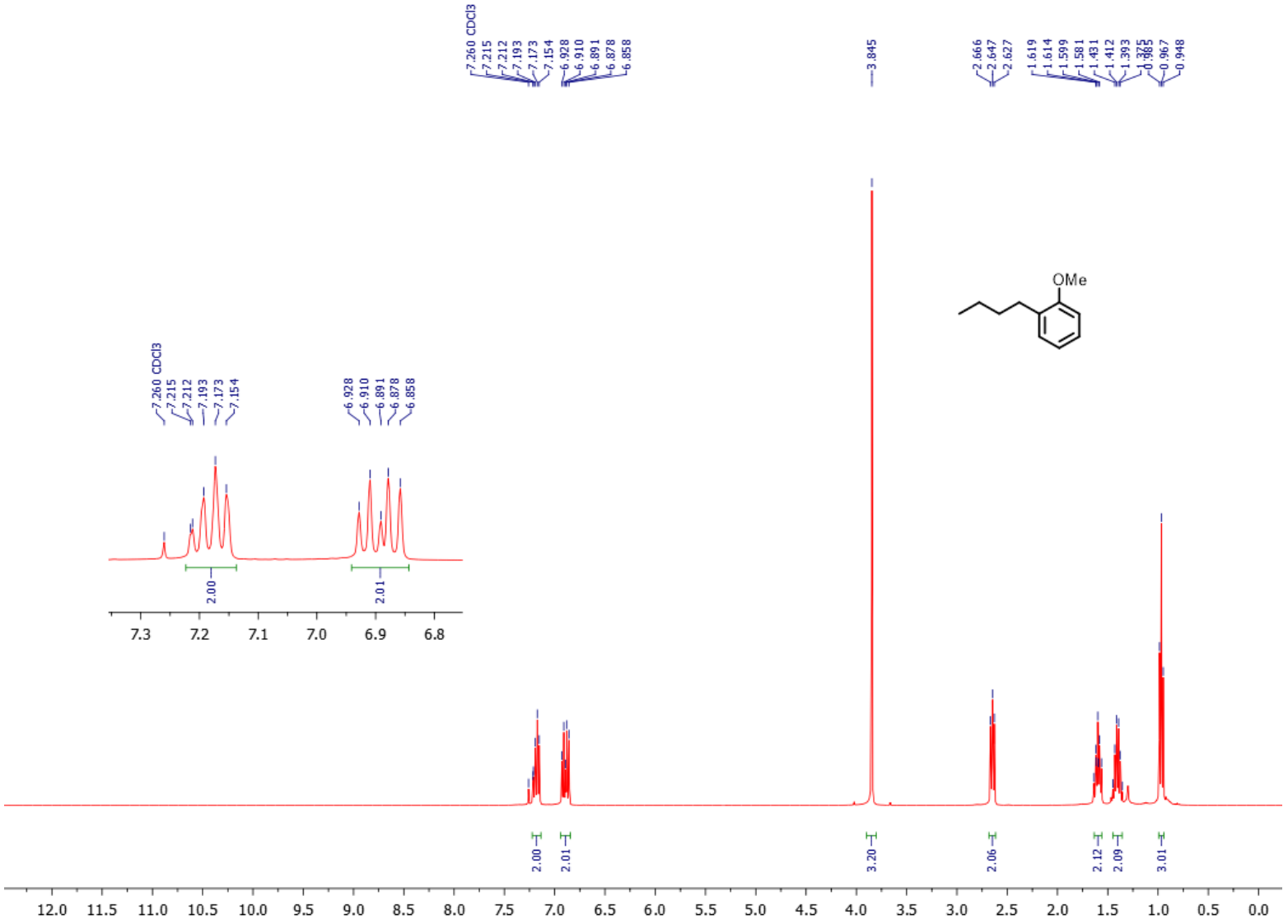
^{13}C NMR spectra of **5f** (25 °C, 100 MHz, $CDCl_3$)



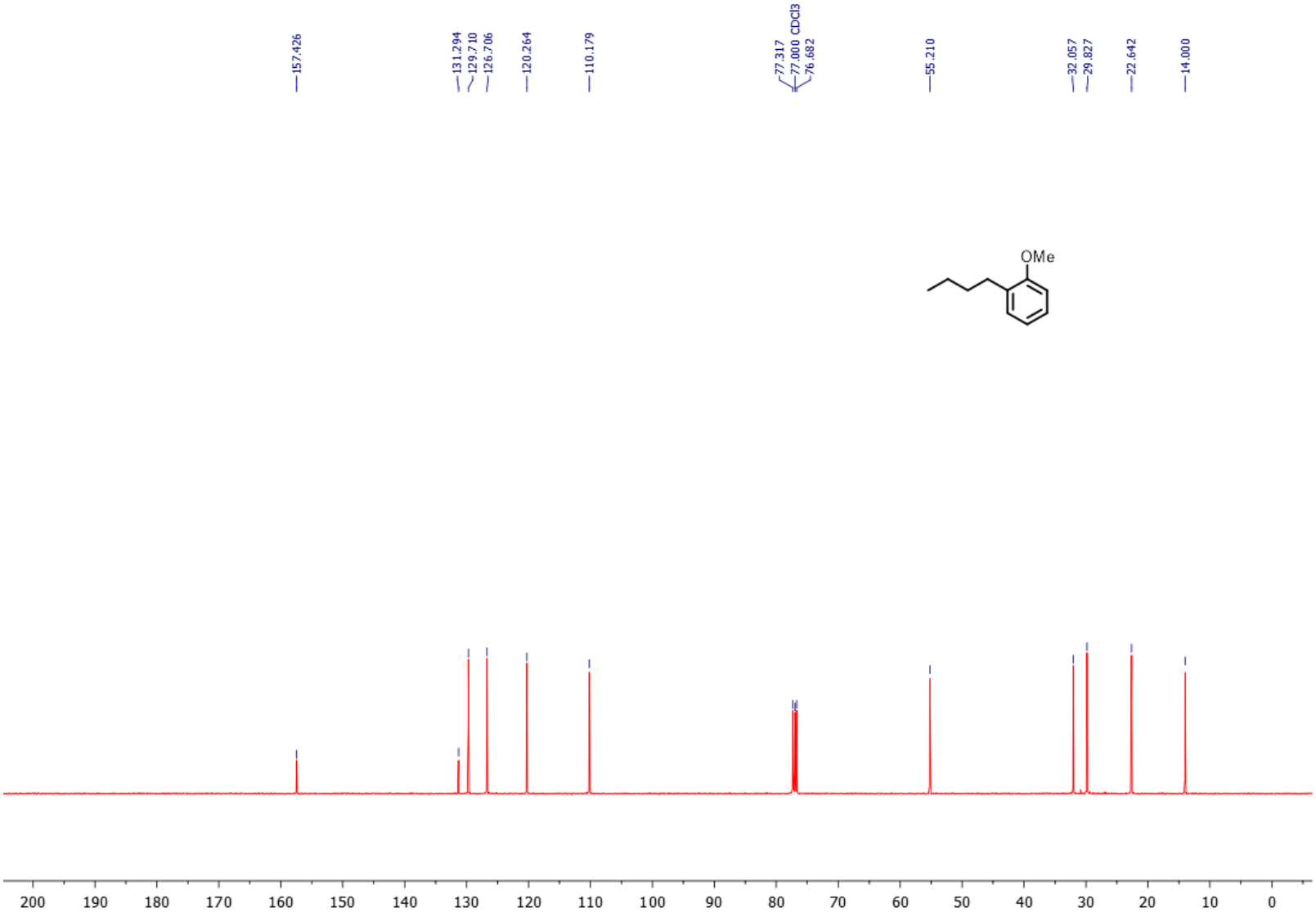
^{1}H NMR spectra of **1-(but-1-en-1-yl)-2-methoxybenzene** (25 ºC, 400 MHz, $CDCl_3$)



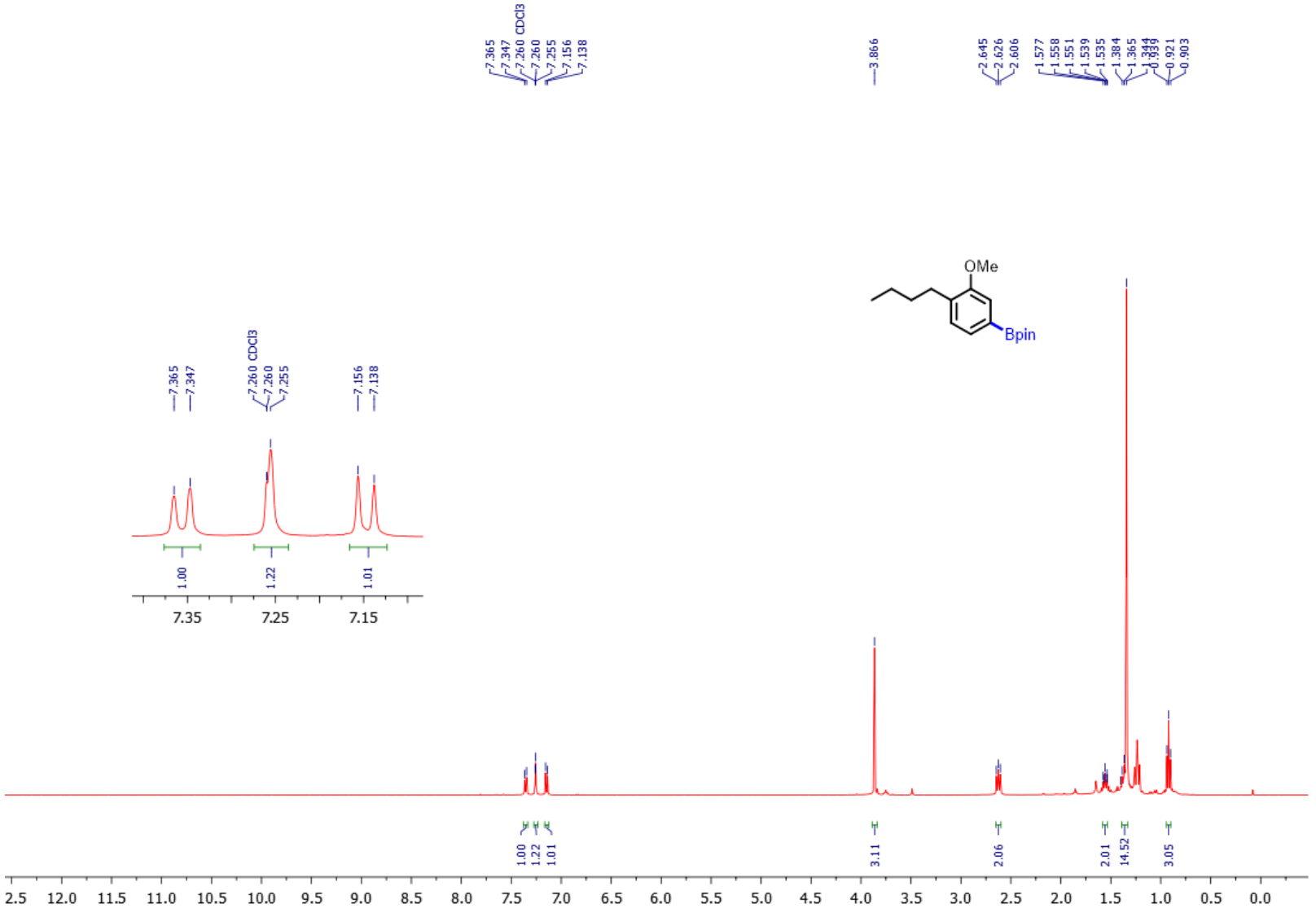
^{13}C NMR spectra of **1-(but-1-en-1-yl)-2-methoxybenzene** (25 ^{o}C, 100 MHz, $CDCl_3$)



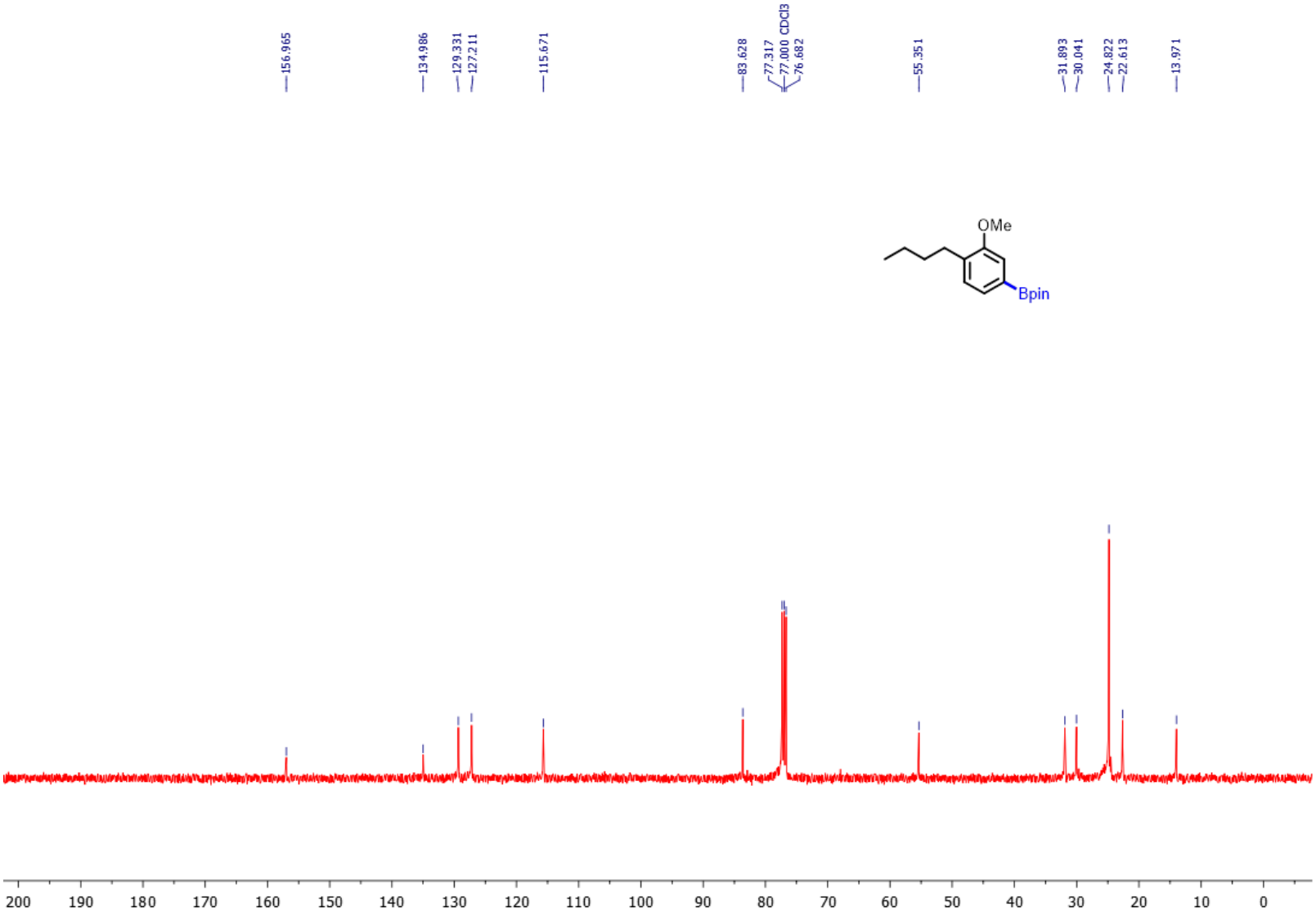
^{1}H NMR spectra of **6** (25 ^{o}C, 400 MHz, $CDCl_3$)



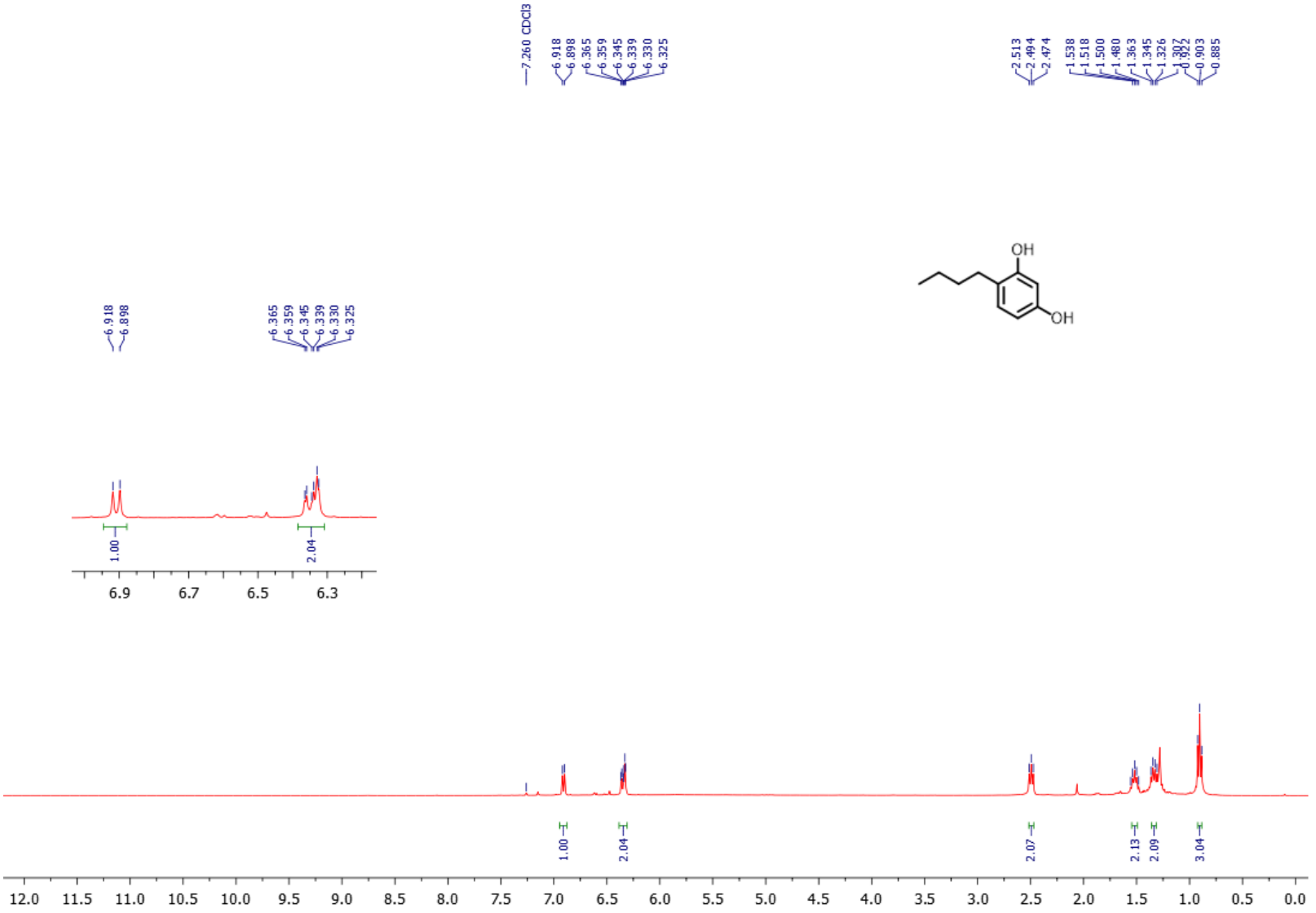
^{13}C NMR spectra of **6** (25 ºC, 100 MHz, $CDCl_3$)



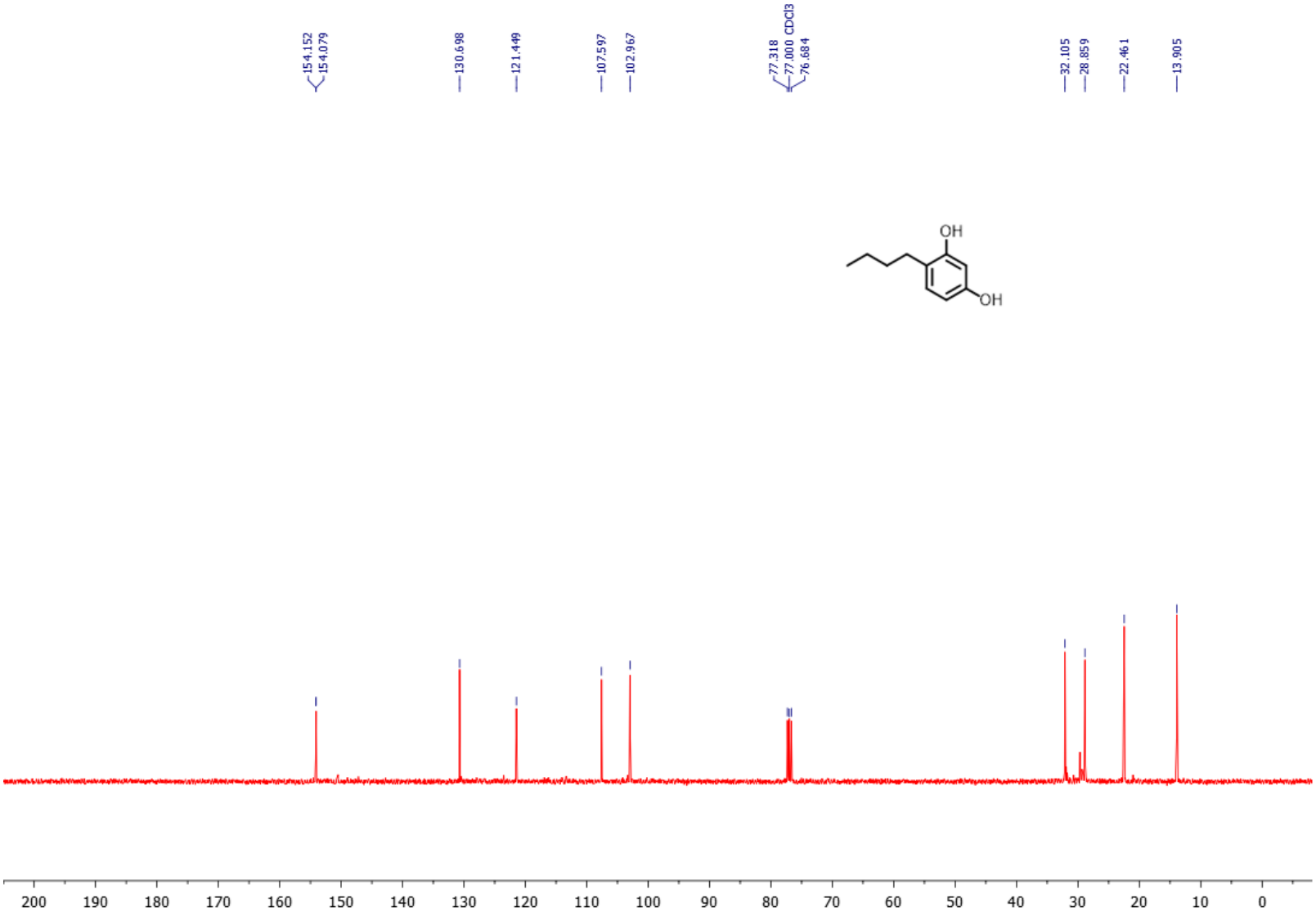
^{1}H NMR spectra of **6a*m*** (25 ºC, 400 MHz, $CDCl_3$)



^{13}C NMR spectra of **6a*m*** (25 ºC, 100 MHz, $CDCl_3$)



^{1}H NMR spectra of **7** (25 ^{o}C, 400 MHz, $CDCl_3$)



^{13}C NMR spectra of **7** (25 ºC, 100 MHz, $CDCl_3$)

1. V. Sukowski, M. van Borselen, S. Mathew, M. A. S. Fernandez-Ibanez, *O*-ligand promoted *meta*-C–H arylation of anisole derivatives via palladium/norbornene catalysis. *Angew. Chem. Int. Ed.* **61**, e202201750 (2022).

2. Y. Li, C. Topf, X. Cui, K. Junge, M. Beller, Lewis Acid Promoted Ruthenium(II)-Catalyzed Etherifications by Selective Hydrogenation of Carboxylic Acids/Esters. *Angew. Chem., Int. Ed.*, **54**, 5196−5200 (2015).

3. Y. Zhang, P. K. Sahoo, P. Ren, Y. Qin, R. Cauwenbergh, P. Nimmegeers, G. SivaRaman,; S. Van Passel, A. Guidetti, S. Das, Transition Metal-Free Approach for Late-Stage Benzylic C(sp^3)−H Etherifications and Esterifications. Chem. Commun., **58**, 11454− 11457 (2022).

4. S. Bhadra, W. I. Dzik, L. J. Goossen, Decarboxylative Etherification of Aromatic Carboxylic Acids. *J. Am. Chem. Soc.*, **134**, 9938–9941 (2012).

5. K. Vamshikrishna, P. Srihari, Total synthesis of (+)-varitriol and (+)-6′-*epi*-varitriol. *Tetrahedron*, **68**, 1540–1546 (2012).

6. Z. Cai, S. Li, Y. Gao, G. Li, Rhodium (II)-Catalyzed Aryl C− H Carboxylation of 2-Pyridylphenols with CO_2. *Adv. Synth. Catal*. **360**, 4005−4011 (2018).

7. S. Guria, M. M. M. Hassan, J. Ma, S. Dey, Y. Liang, B. Chattopadhyay, A tautomerized ligand enabled meta selective C–H borylation of phenol, *Nat. Commun.*, **14**, 6906 (2023).

8. J. Das, M. E. Hoque, M. M. M. Hassan, S. Guria, S. Dey, J. Ma, Z. Deng, Y. Liang, B. Chattopadhyay, Iridium catalyzed regiodivergent functionalization of all three C–H bonds of arenes by a single ligand. *Nat. Commun*. (2025) (doi.org/10.1038/s41467-025-67138-0).

9. J. Vaith, D. Rodina, G. C. Spaulding, S. M. Paradine, Pd Catalyzed Heteroannulation Using N-Arylureas as a Sterically Undemanding Ligand Platform. *J. Am. Chem. Soc*. **144**, 6667−6673 (2022).

10. M. E. Hoque, M. M. M. Hassan, B. Chattopadhyay, Remarkably Efficient Iridium Catalysts for Directed C(sp^2)–H and C(sp^3)–H Borylation of Diverse Classes of Substrates. *J. Am. Chem. Soc.* **143**, 5022-5037 (2021).

11. L.-C. Campeau, M. Parisien, A. Jean, K. Fagnou, Catalytic Direct Arylation with Aryl Chlorides, Bromides, and Iodides: Intramolecular Studies Leading to New Intermolecular Reactions. *J. Am. Chem. Soc*. **128**, 581−590 (2006).

12. A. Maron, A. Szlapa, T. Klemens, S. Kula, B. Machura, S. Krompiec, J. G. Małecki, A. ´Switlicka-Olszewska, K. Erfurt, A. Chrobok, Tuning the photophysical properties of 4′-substituted terpyridines – an experimental and theoretical study. *Org. Biomol. Chem*. **14**, 3793–3808 (2016).

13. E. C. Constable, F. Heirtzler, M. Neuburger, M. Zehnder, Steric Control of Directional Isomerism in Dicopper(I) Helicates of Asymmetrically Substituted 2,2′:6′,2″:2″,6‴-Quaterpyridine Derivatives. *J. Am. Chem. Soc.* **119**, 24, 5606–5617 (1997).

14. R. Rabbani, E. Masson, Probing Interactions between Hydrocarbons and Auxiliary Guests inside Cucurbit[8]Uril. *Org. Lett.* **19**, 4303−4306 (2017).

15. R. Bisht, E. Hoque, B. Chattopadhyay, Amide Effect in C–H Activation: Noncovalent Interactions with L-Shaped Ligand for meta Borylation of Aromatic Amides. *Angew. Chem. Int. Ed.* **57**, 15762-15766 (2018).

16. A. S. Singh, B. M. Bhanage, J. M. Nagarkar, Reductive carbonylation of aryl and heteroaryl iodides using $Pd(acac)_2$/dppm as an efficient catalyst. *Tetrahedron Lett.* **52**, 2383-2386 (2011).

17. T. P. Pabst, P. J. Chirik, Development of Cobalt Catalysts for the meta-Selective $C(sp^2)$−H Borylation of Fluorinated Arenes. *J. Am. Chem. Soc*. **144**, 6465–6474 (2022).

18. N. G. Léonard, M. J. Bezdek, P. J. Chirik, Cobalt-Catalyzed $C(sp^2)$−H Borylation with an Air-Stable, Readily Prepared Terpyridine Cobalt(II) Bis(acetate) Precatalyst. *Organometallics* **36**, 142–150 (2017).

19. B. Goswami, M. Khatua, R. Chatterjee, Kamal, S. Samanta, Amine Functionalized Pincer-like Azo-aromatic Complexes of Cobalt and Their Catalytic Activities in the Synthesis of Quinoline via Acceptor less Dehydrogenation of Alcohols. *Organometallics* **42**, 1854–1868 (2023).

20. M. J. Frisch, G. W. T., H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. B. Scalmani, V. G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams -Young, D.; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J.,, Gaussian 16, Revision C.01, Gaussian, Inc.: Wallingford CT,. **2019**.

21. A. D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A.,* **38** (6), 3098-3100 (1988).

22. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation. *Phys. Rev. B.,* **46** (11), 6671-6687 (1992).

23. S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.,* **132** (15) (2010).

24. D. Andrae, U. H., H. S. M. Dolg, H. Preub, Energy-adjusted ab initio pseudopotentials for the second and third row transition elements. *Theor. Chim. Acta.,* **77**, 123–141 (1990).

25. M. Cossi, V. B., B. Mennucci, J. Toma, Ab initio study of ionic solutions by a polarizable continuum

dielectric model. *Chem. Phys. Lett.,* **286**, 253–260 (1998).

26. E. Cancès, B. Mennucci, J. Tomasi, A new integral equation formalism for the polarizable continuum model: Theoretical background and applications to isotropic and anisotropic dielectrics. *J. Chem. Phys.,* **107** (8), 3032-3041 (1997).

27. B. Mennucci, J. Tomasi, Continuum solvation models: a new approach to the problem of solute's charge distribution and cavity boundaries. *J. Chem. Phys.,* **106** (12), 5151-5158 (1997).

28. M. Mammen, E. I. Shakhnovich, J. M. Deutch, G. M. Whitesides, Estimating the entropic cost of self-assembly of multiparticle hydrogen-bonded aggregates based on the cyanuric acid melamine lattice. *J. Org. Chem.,* **63**, 3821–3830 (1998).