

Supporting Information

Tandem synthesis of N-methylated tertiary amines *via* three components coupling of carbonyl compounds, amines, and methanol

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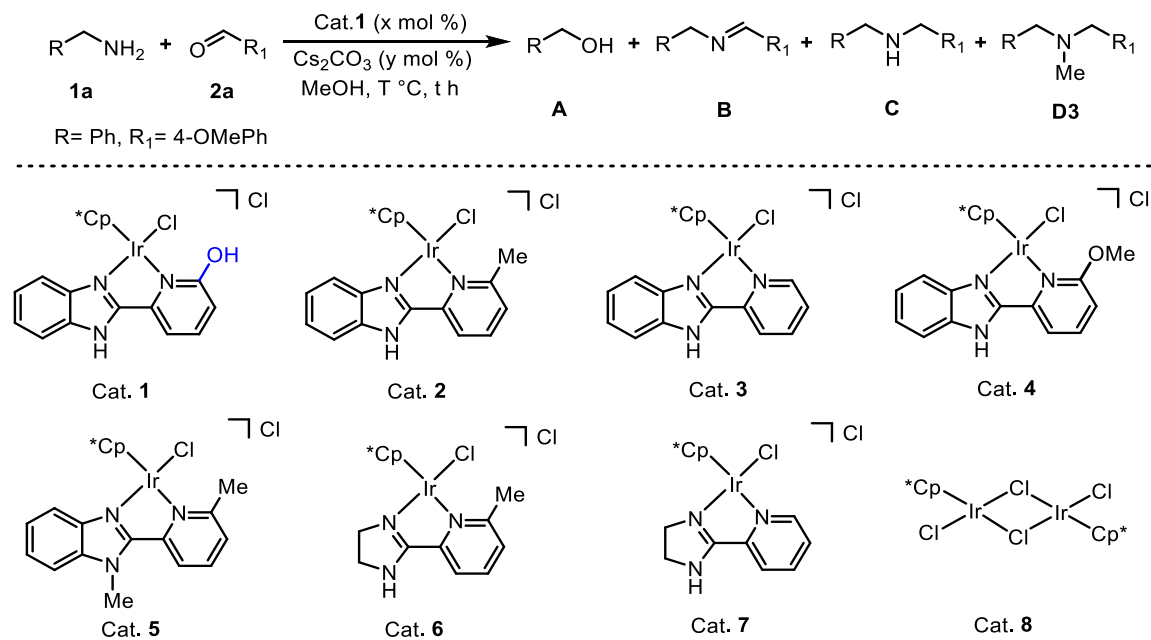
1. Experimental Section

1.1. General Information. Unless noted, all experiments were carried out under argon atmosphere using either standard Schlenk line technique or argon filled Glove box. Glass apparatus were oven dried prior to use. All the alcohols, iridium precursor and other commercially available reagents were purchased from Sigma-Aldrich, Alfa Aesar, SD-fine chemicals, Avra or Spectrochem. Products were purified by column chromatography using silica gel (100-200 mesh) with hexane/ethyl acetate as eluent, based on silica gel coated aluminium TLC plate. ^1H and $^{13}\text{C}\{^1\text{H}\}$ Spectra were recorded using CDCl_3 and $\text{DMSO}-d_6$ solvents in JEOL 400 MHz, 500 MHz, 101 MHz, and 126 MHz spectrometer respectively. All ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR experiments were reported in parts per million (ppm) units and were measured relative to the signals for residual chloroform (7.26 ppm for ^1H and 77.16 ppm for $^{13}\text{C}\{^1\text{H}\}$) and DMSO (2.50 ppm for ^1H and 39.5 ppm for $^{13}\text{C}\{^1\text{H}\}$) in the deuterated solvent, unless otherwise stated and coupling constants (J) were reported in hertz (Hz).

1.2. General procedure

- (A) **Synthesis of Metal Complexes:** The metal complexes **1-8** were synthesized according to literature procedures.¹
- (B) **Synthesis of N-methylated tertiary amine:** To a reaction tube equipped with a magnetic stir bar, amine (0.20 mmol), aldehyde (0.20 mmol), Cat. **1** (0.2 mol %), caesium carbonate (20 mol%), and 1.2 mL of dry methanol were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 16 h. Then, the reaction mixture was cooled to room temperature and the solvent was evaporated. The crude product was purified by column chromatography in EtOAc/hexane to afford corresponding amines **D1-D47**.
- (C) **Preparative Scale Synthesis:** In a reaction tube equipped with a magnetic stir bar, amine (5 mmol), aldehyde (5 mmol), Cat. **1** (0.2 mol %), caesium carbonate (20 mol%), and 5.0 mL of dry methanol were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 16 h. Then, the reaction mixture was cooled to room temperature and the solvent was evaporated. The crude product was purified by column chromatography in EtOAc/hexane to afford corresponding amines.

2. Optimization of Reaction Parameters^a



Entry	Catalyst (mol %)	Base (mol %)	Yield (%) ^b			
			A	B	C	D
1 ^{c, d}	Cat. 1 (0.1)	Cs ₂ CO ₃ (10)	22	0	0	78
2 ^d	Cat. 1 (0.1)	Cs ₂ CO ₃ (10)	9	12	10	69
3 ^d	Cat. 1 (0.2)	Cs ₂ CO ₃ (10)	6	5	12	77
4 ^d	Cat. 1 (0.2)	Cs ₂ CO ₃ (20)	3	3	11	83
5	Cat. 1 (0.2)	Cs₂CO₃ (20)	3	0	0	97
6	Cat. 2 (0.2)	Cs ₂ CO ₃ (20)	7	0	10	83
7	Cat. 3 (0.2)	Cs ₂ CO ₃ (20)	8	0	15	77
8	Cat. 4 (0.2)	Cs ₂ CO ₃ (20)	6	3	12	79
9	Cat. 5 (0.2)	Cs ₂ CO ₃ (20)	11	8	12	69
10	Cat. 6 (0.2)	Cs ₂ CO ₃ (20)	10	5	9	76
11	Cat. 7 (0.2)	Cs ₂ CO ₃ (20)	9	7	13	71

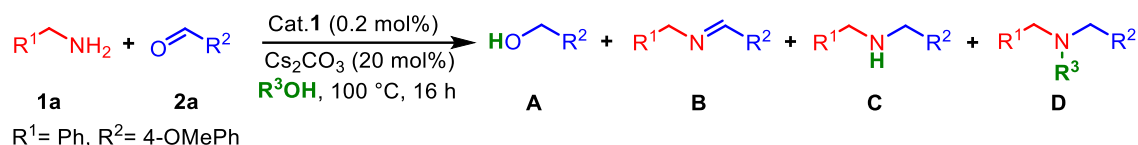
12	Cat. 8 (0.1)	Cs ₂ CO ₃ (20)	10	30	31	29
13	IrCl ₃ .H ₂ O	Cs ₂ CO ₃ (20)	11	62	27	0
14	-	Cs ₂ CO ₃ (20)	0	88	0	0
15	Cat. 1 (0.2)	K ₂ CO ₃ (20)	11	3	0	86
16	Cat. 1 (0.2)	NaOH (20)	12	7	0	81
17	Cat. 1 (0.2)	KO ^t Bu (20)	15	6	0	79
18	Cat. 1 (0.2)	CsOH.H ₂ O (20)	9	7	0	84
19 ^e	Cat. 1 (0.2)	Cs ₂ CO ₃ (20)	6	2	43	49

Reaction Condition: ^aBenzyl amine (**1a**, 0.1 mmol), 4-methoxy benzaldehyde (**2a**, 0.1 mmol), catalyst (x mol %), base (y mol %), MeOH (0.6 mL) at 100 °C for 16 h under Ar atmosphere.

^bNMR yields with 1,3,5- trimethoxybenzene as an internal standard. ^cAt 120 °C. ^dFor 12 h. ^eAt 90 °C.

3. Reaction with Other Alcohols^a

The reaction of benzylamine **1a** (0.1 mmol) was performed with 4-methoxybenzaldehyde **2a** (0.1 mmol) under optimised reaction conditions with three different alcohols; isopropyl alcohol, *tert*-butanol and cyclohexanol but desired tertiary amine was not formed in any of the cases. However, in isopropanol formation of transfer hydrogenated product **C** was observed, while in *tert*-butanol and cyclohexanol, only N-benzyl-1-(4-methoxyphenyl)methanimine (**B**) formation took place. The results are tabulated below-



Entry	R ³ OH	Yield (%) ^b			
		A	B	C	D
1	isopropanol	12	-	88	-
2 ^c	<i>tert</i> -butanol	-	75	-	-
3 ^c	cyclohexanol	-	90	-	-

Reaction Condition: ^aBenzyl amine (**1a**, 0.1 mmol), 4-methoxy benzaldehyde (**2a**, 0.1 mmol), catalyst (0.2 mol %), base (20 mol %), MeOH (0.6 mL) at 100 °C for 16 h under Ar atmosphere.

^bNMR yields with 1,3,5- trimethoxybenzene as an internal standard. ^cStarting material was left.

Benzyl amine (**1a**, 0.2 mmol), 4-methoxybenzaldehyde (**2a**, 0.2 mmol), and Cat. **1** (0.2 mol %), Cs₂CO₃ (20 mol %), and 1.2 mL of dry methanol were taken in oven dried reaction tubes under argon atmosphere. The tubes were then dipped in a preheated oil bath at 100 °C (oil bath temperature) and heated for specified times. The progress of the reactions was monitored by ¹H NMR using 1,3,5-trimethoxybenzene as the internal standard. All the reactions were repeated three times and the average data were plotted as conversion (%) vs time (h).

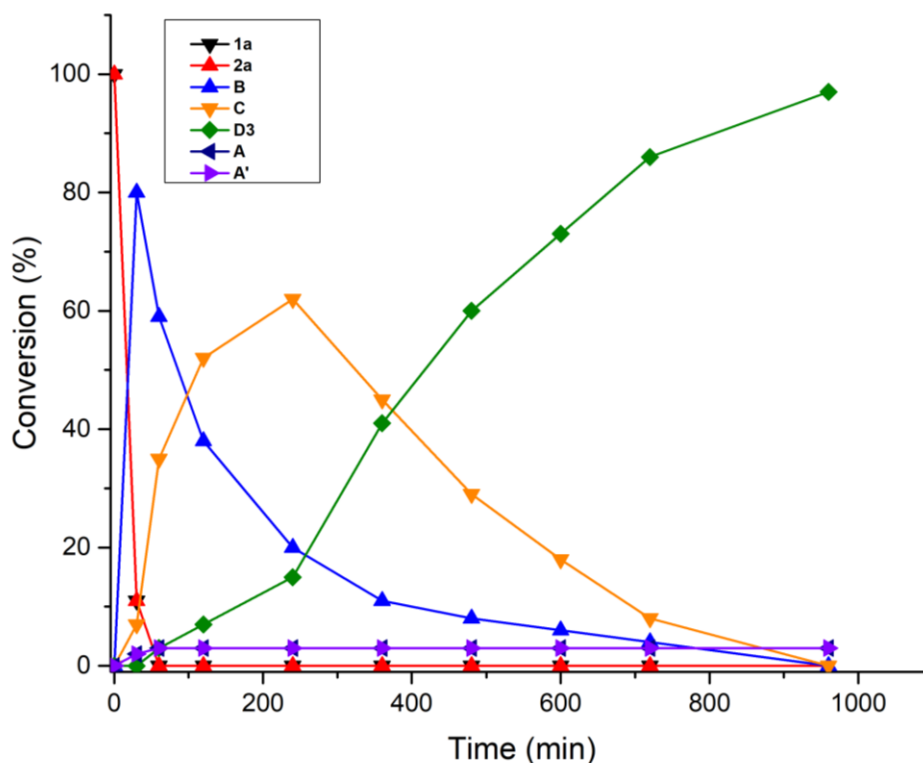
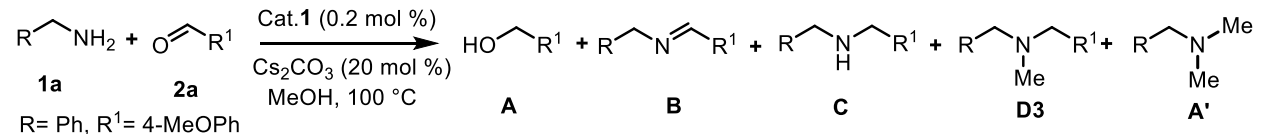
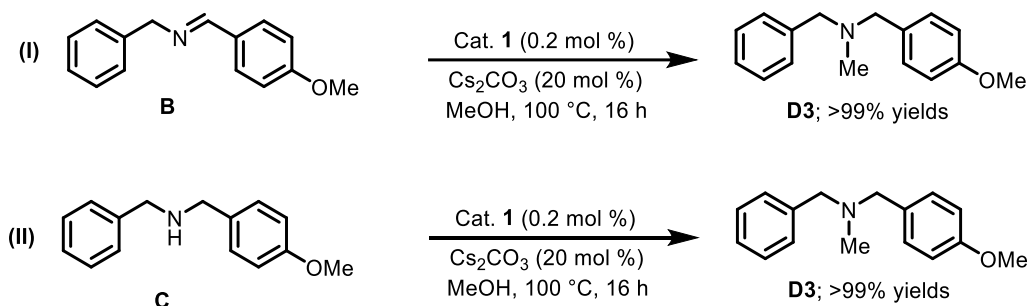


Fig S1. Plot For Time Dependent Product Distribution Studies.

5. Control experiments

5.1. Determination of Intermediates Formed

To a reaction tube equipped with a magnetic stir bar, N-benzyl-1-(4-methoxyphenyl) methanimine (**B**) or N-benzyl-1-(4-methoxyphenyl) methanamine (**C**) (0.2 mmol), Cat. **1** (0.2 mol %), caesium carbonate (20 mol%), and 1.2 mL of dry methanol were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 16 h. Then, the reaction mixture was cooled to room temperature and the solvent was evaporated. The yield of the product was calculated by ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard. The results confirmed that these were the probable intermediates formed during the reaction.

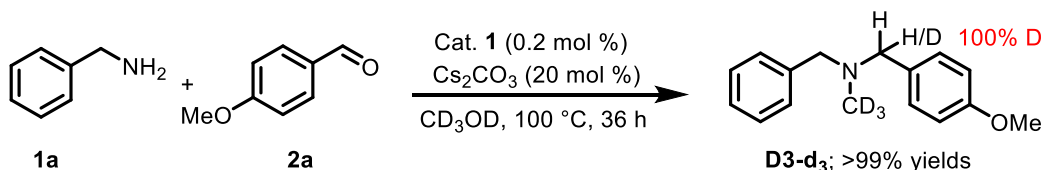


Scheme S1 Determination of Intermediates Formed.

4.2 Deuterium Labelling Experiments

4.2.1 Reaction with CD₃OD

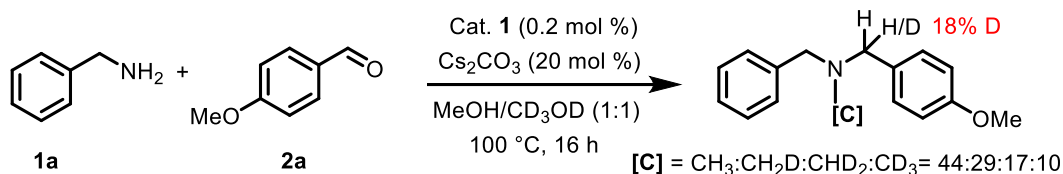
To a reaction tube equipped with a magnetic stir bar, benzylamine (**1a**, 0.20 mmol), 4-methoxy benzaldehyde (**2a**, 0.20 mmol), Cat. **1** (0.2 mol %), caesium carbonate (20 mol%), and 1.2 mL of CD₃OD were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 36 h. Then, the reaction mixture was cooled to room temperature and the solvent was evaporated. The product was confirmed by ¹H NMR which produced only **D3-d₃**.



Scheme S2 Reaction with CD₃OD.

4.2.2 Competitive Reaction

To a reaction tube equipped with a magnetic stir bar, benzylamine (**1a**, 0.20 mmol), 4-methoxy benzaldehyde (**2a**, 0.20 mmol), Cat. **1** (0.2 mol %), caesium carbonate (20 mol%), and 1.2 mL of 1:1 mixture of CH₃OH and CD₃OD were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 16 h. The products were confirmed by ¹H NMR which primarily yielded (**D3**) compared to mixture of its D-labelled analogues.

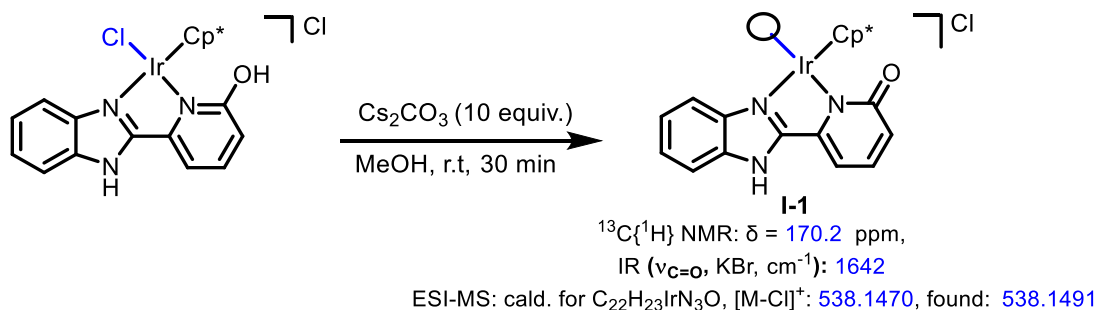


Scheme S3 Competitive Reaction.

4.3 Determination of the Active Catalytic Species

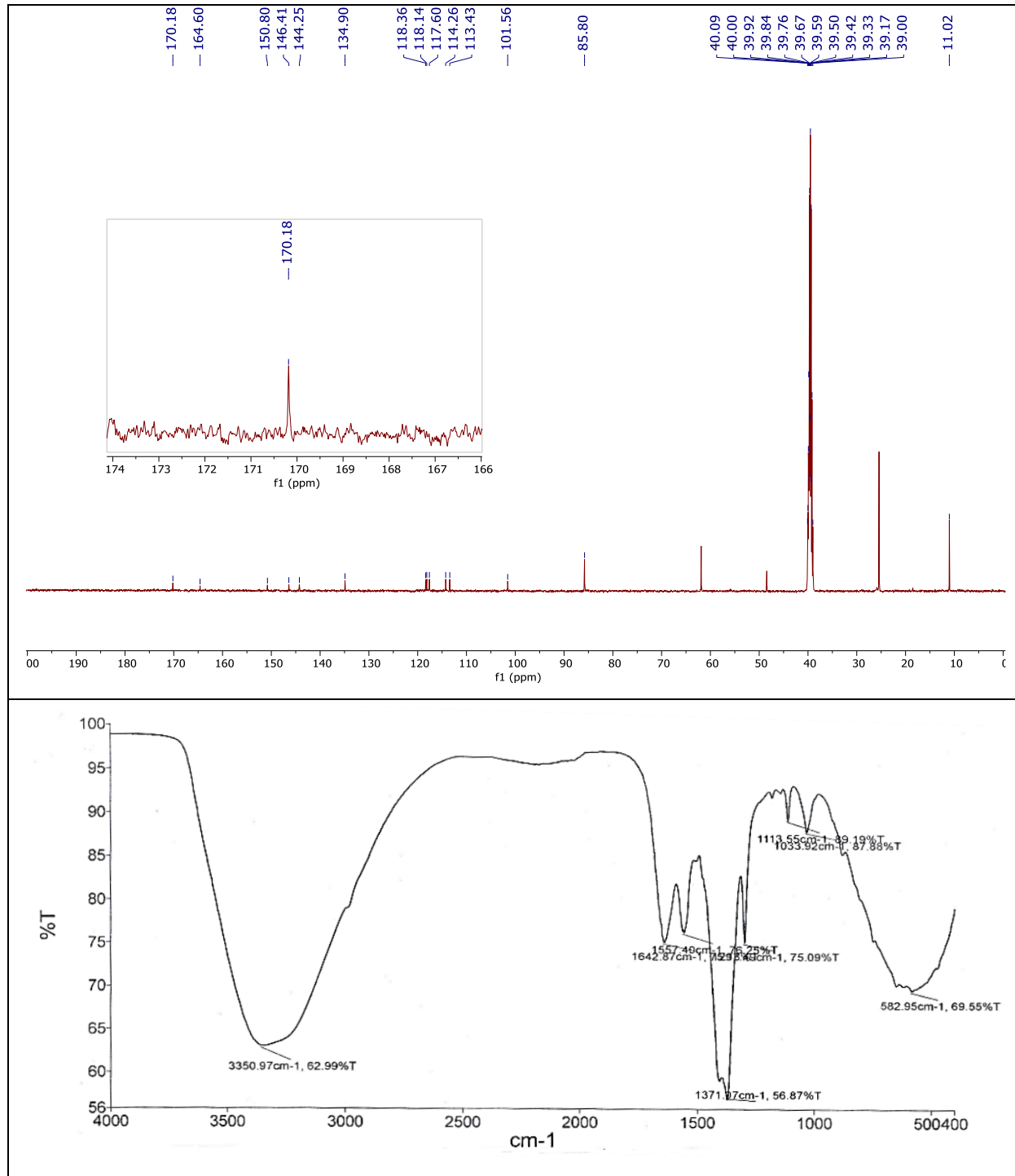
4.3.1 General Procedure for the Synthesis of Ir-pyridonate Species (**I-1**)

In a round bottom flask, Cat. **1** (0.1 mmol), Cs₂CO₃ (1.0 mmol, 10.0 equiv.), and MeOH (0.6 mL) were taken and stirred at room temperature for 30 min under an argon atmosphere. After that, the solvent was removed under vacuum, and then, dry dichloromethane was added to extract the Ir-pyridonate (**I-1**) complex. Next, the solution was filtered under an argon atmosphere, and the filtrate was dried under vacuum and washed with ether to afford (**I-1**) as a dark yellow powder. The compound formation was confirmed by ¹³C{¹H} NMR, IR spectrum which matched with the previously reported data.²



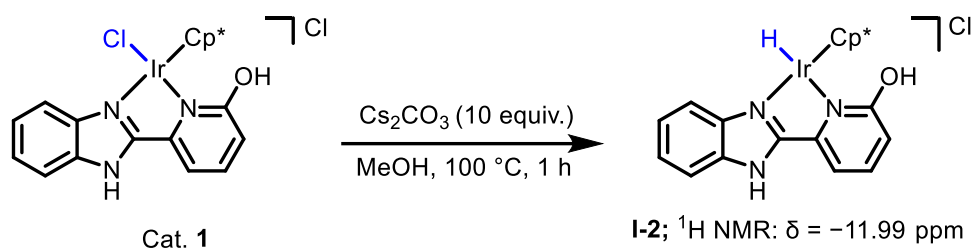
Scheme S4 Synthesis of Ir-pyridonate Species (**I-1**).

¹³C{¹H}-NMR and IR Spectra of Ir-pyridonate (I-1)



4.3.2 General Procedure for the Synthesis of Ir(III)-Hydride (I-2)

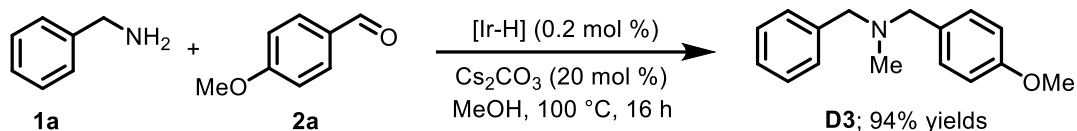
In a reaction tube, Cat. **1** (0.1 mmol), Cs₂CO₃ (1.0 mmol, 10 equiv.), and MeOH (0.6 mL) were taken and heated at 100 °C for 1 h under an argon atmosphere. After that, the mixture was cooled to room temperature, the solvent was removed under vacuum, and then, dry dichloromethane was added to extract the Ir-hydride complex. Next, the solution was filtered under an argon atmosphere, and the filtrate was dried under vacuum to afford [Ir(III)-H] (**I-2**) as a yellow powder. The ¹H NMR spectrum was recorded in DMSO-d₆ which matched with the previously reported data.^{1,3}



Scheme S5 Synthesis of Ir(III)-Hydride (I-2).

4.3.3 General Procedure for the Reactivity Study of Ir-Hydride ([Ir-H])

In a reaction tube equipped with a magnetic stir bar, benzylamine (**1a**, 0.20 mmol), 4-methoxy benzaldehyde (**2a**, 0.20 mmol), **I-2** (0.2 mol %), caesium carbonate (20 mol%), and 1.0 mL of methanol were added under argon atmosphere. The mixture was placed in a preheated oil bath at 100 °C for 16 h. Then, the reaction mixture was cooled to room temperature and the solvent was evaporated. The yield of the product was determined by ¹H NMR with 1,3,5-trimethoxybenzene as an internal standard.



Scheme S6 Reactivity Study of Ir-Hydride ([Ir-H]).

6. Kinetic Isotope Effect (KIE) Studies

Parallel reactions for the synthesis of N-benzyl-1-(4-methoxyphenyl)-N-methylmethanamine from benzylamine (**1a**) and 4-methoxy benzaldehyde (**2a**) were carried out using CH₃OH and CD₃OD under standard conditions for 30 min, 1, 2, 4, 6, 8, 12 and 16 hrs. All the tubes were placed in a preheated oil-baths at 100 °C and the progress of the reaction was analysed by ¹H NMR with 1,3,5-trimethoxybenzene as an internal standard. All the reactions were repeated thrice, and the average data were plotted as final product yields (%) vs time (h). For this tandem transformation, a kinetic isotope effect (KIE) study using CH₃OH and CD₃OD disclosed $k_{C-H}/k_{C-D} = 2.77$.

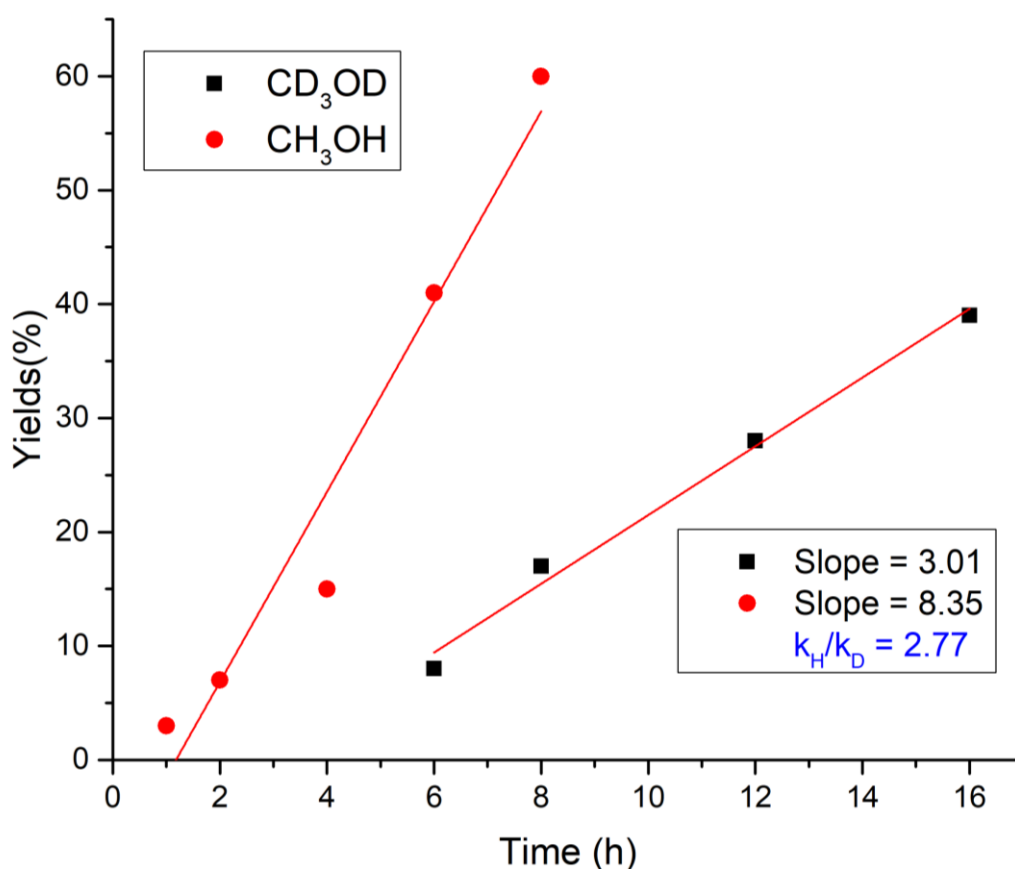
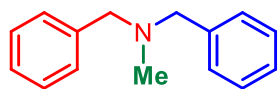


Fig S2. Plot For Kinetic Isotopic Effect.

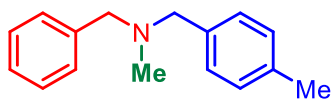
7. Characterization Data of Final Products

N-Benzyl-N-methyl-1-phenylmethanamine (D1)⁴



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 91% yield (38.5 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.39 (d, *J*_{H,H} = 7.3 Hz, 4H), 7.35 (t, *J*_{H,H} = 7.6 Hz, 4H), 7.26 (t, *J*_{H,H} = 7.2 Hz, 2H), 3.54 (s, 4H), 2.20 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 139.5, 129.0, 128.3, 127.0, 62.0, 42.4.

N-Benzyl-N-methyl-1-(p-tolyl)methanamine (D2)⁵



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 92% yield (41.5 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.37 (d, *J*_{H,H} = 7.1 Hz, 2H), 7.32 (t, *J*_{H,H} = 7.5 Hz, 2H), 7.26 (dd, *J*_{H,H} = 7.9, 3.9 Hz, 3H), 7.14 (d, *J*_{H,H} = 7.9 Hz, 2H), 3.51 (s, 2H), 3.50 (s, 2H), 2.34 (s, 3H), 2.18 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 139.5, 136.6, 136.3, 129.1, 129.0, 128.3, 127.0, 61.9, 61.7, 42.3, 21.2.

N-Benzyl-1-(4-methoxyphenyl)-N-methylmethanamine (D3)⁶



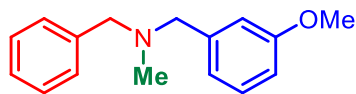
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 93% yield (44.9 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.38-7.25 (m, 7H), 6.89 (d, *J*_{H,H} = 8.6 Hz, 2H), 3.81 (s, 3H), 3.52 (s, 2H), 3.49 (s, 2H), 2.19 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 158.7, 139.5, 131.4, 130.2, 129.0, 128.3, 127.0, 113.7, 61.8, 61.3, 55.3, 42.2.

N-Benzyl-N-methyl-1-(m-tolyl)methanamine (D4)⁷



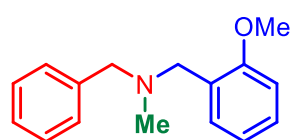
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 91% yield (41.0 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.39-7.32 (m, 4H), 7.28-7.17 (m, 4H), 7.08 (d, *J*_{H,H} = 7.3 Hz, 1H), 3.54 (s, 2H), 3.51 (s, 2H), 2.37 (s, 3H), 2.20 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 139.3, 137.9, 129.8, 129.1, 129.1, 128.3, 128.2, 127.8, 127.0, 126.2, 62.0, 42.4, 21.6.

N-Benzyl-1-(3-methoxyphenyl)-N-methylmethanamine (D5)⁸



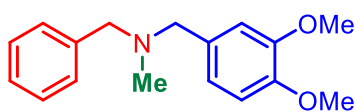
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 90% yield (43.4 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.37 (d, $J_{\text{H,H}}$ = 7.3 Hz, 2H), 7.32 (dd, $J_{\text{H,H}}$ = 8.3, 6.6 Hz, 2H), 7.27-7.22 (m, 2H), 6.96-6.94 (m, 2H), 6.81-6.78 (m, 1H), 3.82 (s, 3H), 3.52 (s, 2H), 3.51 (s, 2H), 2.20 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 159.8, 141.2, 139.5, 129.3, 129.0, 128.3, 127.1, 121.4, 114.4, 112.5, 62.0, 55.3, 42.4.

N-Benzyl-1-(3-methoxyphenyl)-N-methylmethanamine (D6)⁹



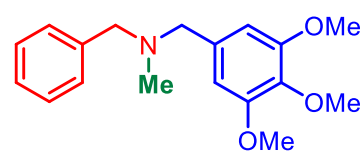
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 87% yield (42.0 mg). **¹H NMR** (500 MHz, CDCl₃) δ 7.52 (dd, $J_{\text{H,H}}$ = 7.5, 1.8 Hz, 1H), 7.45 (d, $J_{\text{H,H}}$ = 7.1 Hz, 2H), 7.37 (t, $J_{\text{H,H}}$ = 7.6 Hz, 2H), 7.31-7.25 (m, 2H), 7.01 (t, $J_{\text{H,H}}$ = 7.4 Hz, 1H), 6.91 (d, $J_{\text{H,H}}$ = 8.3 Hz, 1H), 3.85 (s, 3H), 3.64 (s, 2H), 3.63 (s, 2H), 2.28 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 158.0, 139.7, 130.5, 129.2, 128.3, 128.0, 127.4, 127.0, 120.5, 110.5, 62.4, 55.5, 55.3, 42.5.

N-Benzyl-1-(3,4-dimethoxyphenyl)-N-methylmethanamine (D7)¹⁰



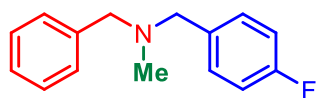
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 95% yield (51.6 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.36-7.30 (m, 4H), 7.26-7.23 (m, 1H), 6.95 (d, $J_{\text{H,H}}$ = 1.8 Hz, 1H), 6.87 (dd, $J_{\text{H,H}}$ = 8.1, 2.0 Hz, 1H), 6.82 (d, $J_{\text{H,H}}$ = 8.1 Hz, 1H), 3.90 (s, 3H), 3.87 (s, 3H), 3.50 (s, 2H), 3.48 (s, 2H), 2.19 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 149.0, 148.1, 139.4, 132.0, 129.0, 128.3, 127.0, 121.1, 112.0, 110.9, 61.8, 61.7, 56.0, 55.9, 42.4.

N-Benzyl-N-methyl-1-(3,4,5-trimethoxyphenyl)methanamine (D8)



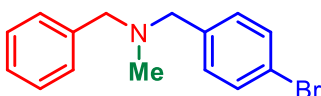
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 93% yield (56.1 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.36 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 6.62 (s, 2H), 3.87 (s, 6H), 3.84 (s, 3H), 3.51 (s, 2H), 3.47 (s, 2H), 2.22 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 153.3, 139.4, 135.3, 129.0, 128.3, 127.1, 105.7, 62.3, 61.8, 61.0, 56.2, 42.6. **ESI-MS**: Calcd. for C₁₈H₂₄NO₃⁺, [M+H]⁺: 302.1751; found: 302.1759.

N-Benzyl-1-(4-fluorophenyl)-N-methylmethanamine (D9)¹¹



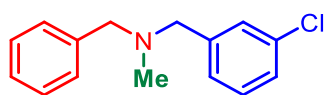
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 89% yield (40.8 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.37 – 7.31 (m, 6H), 7.26 (t, $J_{\text{H,H}}$ = 6.9 Hz, 1H), 7.01 (t, $J_{\text{H,H}}$ = 8.7 Hz, 2H), 3.52 (s, 2H), 3.48 (s, 2H), 2.18 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 162.0 (d, $J_{\text{C,F}}$ = 242.5 Hz), 139.3, 135.2, 130.4 (d, $J_{\text{C,F}}$ = 7.5 Hz), 129.0 (d, $J_{\text{C,F}}$ = 5.0 Hz), 128.3 (d, $J_{\text{C,F}}$ = 5.0 Hz), 127.0 (d, $J_{\text{C,F}}$ = 10.0 Hz), 115.1 (d, $J_{\text{C,F}}$ = 21.2 Hz), 61.9, 61.1, 42.3.

N-Benzyl-1-(4-bromophenyl)-N-methylmethanamine (D10)⁷



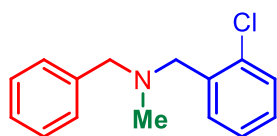
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 90% yield (52.2 mg). **¹H NMR** (400 MHz, CDCl₃): δ = 7.47 (d, $J_{\text{H,H}}$ = 8.5 Hz, 2H), 7.39-7.33 (m, 4H), 7.29-7.26 (m, 3H), 3.54 (s, 2H), 3.49 (s, 2H), 2.20 (s, 3H). **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 139.2, 138.6, 131.4, 130.6, 129.0, 128.4, 127.1, 120.8, 62.0, 61.2, 42.3.

N-Benzyl-1-(3-chlorophenyl)-N-methylmethanamine (D11)⁷



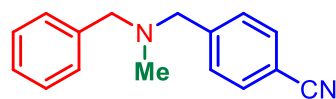
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 85% yield (41.8 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.39-7.32 (m, 5H), 7.27-7.21 (m, 4H), 3.53 (s, 2H), 3.49 (s, 2H), 2.19 (s, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 141.8, 139.2, 134.3, 129.6, 129.0, 129.0, 128.4, 127.2, 127.2, 127.1, 62.1, 61.3, 42.4.

N-Benzyl-1-(2-chlorophenyl)-N-methylmethanamine (D12)¹²



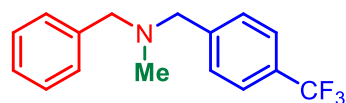
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 80% yield (39.3 mg). **¹H NMR** (400 MHz, CDCl₃): δ = 7.56 (dd, $J_{\text{H,H}}$ = 7.6, 1.9 Hz, 1H), 7.41-7.29 (m, 5H), 7.24 (td, $J_{\text{H,H}}$ = 7.0, 1.6 Hz, 2H), 7.17 (td, $J_{\text{H,H}}$ = 7.6, 1.8 Hz, 1H), 3.65 (s, 2H), 3.59 (s, 2H), 2.21 (s, 3H). **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 139.4, 137.1, 134.4, 130.8, 129.5, 129.0, 128.4, 128.1, 127.1, 126.7, 62.4, 58.6, 42.4.

N-Benzyl-1-(4-cyanophenyl)-N-methylmethanamine (D13)¹³



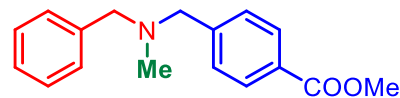
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 87% yield (41.1 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.62-7.59 (m, 2H), 7.49 (d, *J*_{H,H} = 8.0 Hz, 2H), 7.37-7.31 (m, 4H), 7.29-7.25 (m, 1H), 3.56 (s, 2H), 3.55 (s, 2H), 2.19 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 145.5, 138.9, 132.2, 129.4, 128.9, 128.5, 127.3, 119.1, 110.8, 62.2, 61.3, 42.5.

N-Benzyl-N-methyl-1-(4-(trifluoromethyl)phenyl)methanamine (D14)¹⁰



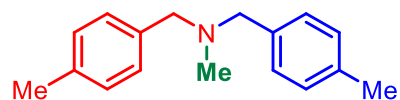
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 86% yield (48.0 mg). ¹H NMR (500 MHz, CDCl₃) δ 7.58 (d, *J*_{H,H} = 8.1 Hz, 2H), 7.50 (d, *J*_{H,H} = 7.9 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.28 – 7.25 (m, 1H), 3.57 (s, 2H), 3.55 (s, 2H), 2.20 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ = 143.8, 139.1, 129.4 (q, *J*_{C-F} = 32 Hz), 129.1, 129.0, 128.5, 127.2, 125.3 (q, *J*_{C-F} = 4.0 Hz), 124.4 (q, *J*_{C-F} = 271 Hz), 62.1, 61.4, 42.4.

N-Benzyl-1-(2-chlorophenyl)-N-methylmethanamine (D15)¹⁴



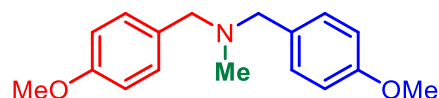
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 86% yield (46.3 mg). ¹H NMR (500 MHz, CDCl₃): δ = 8.01 (d, *J*_{H,H} = 8.0 Hz, 2H), 7.45 (d, *J*_{H,H} = 8.1 Hz, 2H), 7.35 (dt, *J*_{H,H} = 14.9, 7.4 Hz, 4H), 7.27-7.24 (m, 1H), 3.91 (s, 3H), 3.56 (s, 2H), 3.54 (s, 2H), 2.19 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 167.2, 145.1, 139.1, 129.7, 129.0, 128.8, 128.4, 127.2, 62.1, 61.6, 52.1, 42.4.

N-Methyl-N-(4-methylbenzyl)-1-(p-tolyl)methanamine (D16)¹⁵



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 96% yield (46.0 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.27 (d, *J*_{H,H} = 7.9 Hz, 4H), 7.15 (d, *J*_{H,H} = 7.8 Hz, 4H), 3.50 (s, 4H), 2.36 (s, 6H), 2.19 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 136.5, 136.4, 129.0, 61.6, 42.2, 21.2.

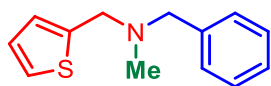
N-(4-Methoxybenzyl)-1-(4-methoxyphenyl)-N-methylmethanamine (D17)¹⁵



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 97% yield (52.6 mg). ¹H NMR

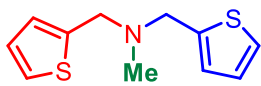
(500 MHz, CDCl₃): δ = 7.28-7.26 (m, 4H), 6.87 (d, $J_{\text{H,H}}$ = 8.7 Hz, 4H), 3.80 (s, 6H), 3.45 (s, 4H), 2.15 (d, $J_{\text{H,H}}$ = 1.5 Hz, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 158.7, 131.5, 130.2, 113.7, 61.1, 55.3, 42.1.

N-Benzyl-N-methyl-1-(thiophen-2-yl)methanamine (D18)¹⁶



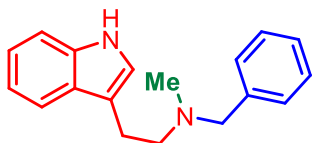
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 89% yield (38.7 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.43 (d, $J_{\text{H,H}}$ = 7.1 Hz, 2H), 7.39 (t, $J_{\text{H,H}}$ = 7.5 Hz, 2H), 7.31-7.27 (m, 2H), 7.01-6.97 (m, 2H), 3.81 (s, 2H), 3.60 (s, 2H), 2.30 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 142.9, 139.1, 129.0, 128.3, 127.1, 126.4, 125.7, 124.9, 61.2, 56.1, 42.2.

N-Methyl-1-(thiophen-2-yl)-N-(thiophen-2-ylmethyl)methanamine (D19)¹⁵



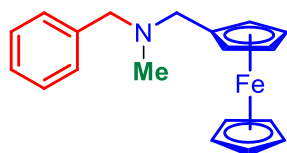
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 87% yield (38.9 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.26 (d, $J_{\text{H,H}}$ = 3.9 Hz, 2H), 6.97-6.94 (m, 4H), 3.79 (s, 4H), 2.33 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 142.3, 126.5, 126.0, 125.1, 55.3, 42.1.

N-Benzyl-2-(1H-indol-3-yl)-N-methylethan-1-amine (D20)¹⁷



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 89% yield (47.1 mg). ¹H NMR (500 MHz, CDCl₃): δ = 8.09 (bs, 1H), 7.58 (d, $J_{\text{H,H}}$ = 7.9 Hz, 1H), 7.40 – 7.32 (m, 5H), 7.28 (dd, $J_{\text{H,H}}$ = 13.5, 6.6 Hz, 1H), 7.21 (t, $J_{\text{H,H}}$ = 7.4 Hz, 1H), 7.13 (t, $J_{\text{H,H}}$ = 7.5 Hz, 1H), 6.99 (d, $J_{\text{H,H}}$ = 2.3 Hz, 1H), 3.65 (s, 2H), 3.05-3.02 (m, 2H), 2.82-2.78 (m, 2H), 2.37 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 139.1, 136.3, 129.3, 128.4, 127.7, 127.1, 122.0, 121.6, 119.3, 119.0, 114.6, 111.2, 62.4, 58.1, 42.3, 23.4.

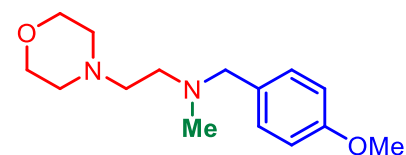
1-[(N-Benzyl-N-methylamino)methyl]ferrocene (D21)



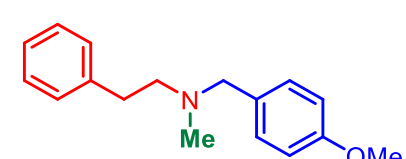
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 87% yield (60.8 mg). ¹H NMR (500 MHz, CDCl₃): δ = 7.27-7.25 (m, 4H), 7.22-7.20 (m, 1H), 4.14 (s, 2H), 4.08 (s, 2H), 4.04 (s, 5H), 3.40 (s, 4H), 2.09 (s, 3H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ =

139.4, 129.1, 128.3, 127.0, 83.3, 70.3, 68.6, 68.1, 61.1, 57.0, 41.8. **ESI-MS:** Calcd. for $C_{19}H_{22}FeN_3^+$, $[M+H]^+$: 320.1096; found: 320.1108.

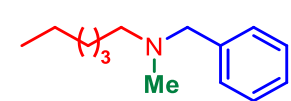
N-(4-Methoxybenzyl)-N-methyl-2-morpholinoethan-1-amine (D22)

 Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 79% yield (41.8 mg). **1H NMR** (400 MHz, $CDCl_3$): δ = 7.20 (d, $J_{H,H}$ = 8.5 Hz, 2H), 6.83 (d, $J_{H,H}$ = 8.6 Hz, 2H), 3.77 (s, 3H), 3.70-3.66 (m, 4H), 3.44 (s, 2H), 2.49 (s, 4H), 2.44-2.39 (m, 4H), 2.21 (s, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): δ = 158.8, 131.0, 130.2, 113.7, 67.0, 62.2, 57.1, 55.3, 54.2, 54.1, 42.7. **ESI-MS:** Calcd. for $C_{15}H_{25}N_2O_2^+$, $[M+H]^+$: 265.1911; found: 265.1911.

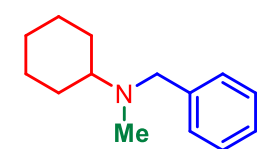
N-(4-Methoxybenzyl)-N-methyl-2-phenylethan-1-amine (D23)¹⁸

 Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 90% yield (40.6 mg). **1H NMR** (500 MHz, $CDCl_3$): δ = 7.32 (t, $J_{H,H}$ = 7.8 Hz, 2H), 7.28-7.20 (m, 5H), 6.89 (d, $J_{H,H}$ = 8.6 Hz, 2H), 3.83 (s, 3H), 3.55 (s, 2H), 2.87 (dd, $J_{H,H}$ = 9.5, 6.5 Hz, 2H), 2.71-2.65 (m, 2H), 2.31 (s, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): δ = 158.7, 140.6, 131.0, 130.2, 128.8, 128.6, 128.4, 126.0, 114.0, 113.7, 61.6, 59.1, 55.3, 42.1, 33.9.

N-Benzyl-N-methylhexan-1-amine (D24)¹⁹

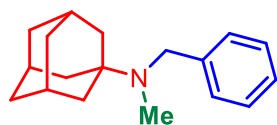
 Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 89% yield (36.6 mg). **1H NMR** (500 MHz, $CDCl_3$): δ = 7.35-7.31 (m, 4H), 7.26 (td, $J_{H,H}$ = 5.5, 5.0, 2.5 Hz, 1H), 3.50 (s, 2H), 2.40-2.37 (m, 2H), 2.21 (s, 3H), 1.53 (q, $J_{H,H}$ = 7.8 Hz, 2H), 1.36-1.28 (m, 6H), 0.91 (t, $J_{H,H}$ = 6.8 Hz, 3H). **$^{13}C\{^1H\}$ NMR** (126 MHz, $CDCl_3$): δ = 139.5, 129.2, 128.3, 126.9, 62.5, 57.8, 42.4, 32.0, 27.5, 27.3, 22.8, 14.2.

N-Benzyl-N-methylcyclohexanamine (D25)²⁰

 Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 82% yield (33.3 mg). **1H NMR** (500 MHz, $CDCl_3$): δ = 7.32 (td, $J_{H,H}$ = 8.6, 6.5 Hz, 4H), 7.26-7.21 (m, 1H), 3.58 (s, 2H), 2.48-2.42 (m, 1H), 2.20 (s, 3H), 1.93-1.87 (m, 2H), 1.81 (dt, $J_{H,H}$ = 12.6, 3.4 Hz, 2H), 1.64 (ddd, $J_{H,H}$ = 11.5,

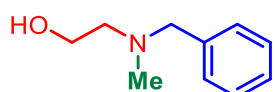
4.8, 2.2 Hz, 1H), 1.36-1.19 (m, 4H), 1.17-1.07 (m, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 140.3, 129.0, 128.3, 126.9, 62.7, 58.0, 37.8, 28.8, 26.6, 26.2.

(3s,5s,7s)-N-Benzyl-N-methyladamantan-1-amine (D26)



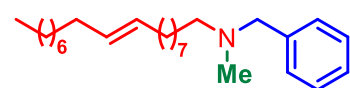
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 83% yield (42.4 mg). ^1H NMR (500 MHz, CDCl_3): δ = 7.35 (d, $J_{\text{H,H}}$ = 7.4 Hz, 2H), 7.30 (t, $J_{\text{H,H}}$ = 7.5 Hz, 2H), 7.22 (t, $J_{\text{H,H}}$ = 7.2 Hz, 1H), 3.57 (s, 2H), 2.14 (s, 3H), 2.13 (s, 3H), 1.81 (d, $J_{\text{H,H}}$ = 3.0 Hz, 6H), 1.72-1.63 (m, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz CDCl_3): δ = 142.0, 128.8, 128.2, 126.5, 54.2, 53.6, 39.0, 37.1, 33.4, 29.9. **ESI-MS**: Calcd. for $\text{C}_{18}\text{H}_{26}\text{N}^+$, $[\text{M}+\text{H}]^+$: 256.2060; found: 256.2064.

2-(Benzyl(methyl)amino)ethan-1-ol (D27)²¹



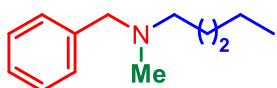
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 85% yield (28.1 mg). ^1H NMR (500 MHz, CDCl_3): δ = 7.36-7.26 (m, 5H), 3.62-3.60 (m, 2H), 3.56 (s, 2H), 2.60-2.58 (m, 2H), 2.22 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 138.6, 129.1, 128.4, 127.3, 62.4, 58.4, 58.4, 41.6.

N-Benzyl-N-methyloleylamine (D28)²²



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 85% yield (65.6 mg). ^1H NMR (500 MHz, CDCl_3): δ = 7.34 (d, $J_{\text{H,H}}$ = 4.6 Hz, 4H), 7.26 (td, $J_{\text{H,H}}$ = 4.8, 2.5 Hz, 1H), 5.42 (t, $J_{\text{H,H}}$ = 3.5 Hz, 1H), 5.38 (t, $J_{\text{H,H}}$ = 4.9 Hz, 1H), 3.50 (s, 2H), 2.38 (t, $J_{\text{H,H}}$ = 7.3 Hz, 2H), 2.21 (s, 3H), 2.05 (q, $J_{\text{H,H}}$ = 6.6 Hz, 3H), 2.00 (d, $J_{\text{H,H}}$ = 5.3 Hz, 1H), 1.57-1.50 (m, 2H), 1.33-1.27 (m, 22H), 0.91 (t, $J_{\text{H,H}}$ = 6.8 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 139.4, 130.0, 130.0, 129.2, 128.3, 126.9, 62.5, 57.8, 42.4, 32.7, 32.1, 29.9, 29.8, 29.8, 29.7, 29.7, 29.5, 29.5, 29.4, 29.3, 27.6, 27.6, 27.4, 22.8, 22.7, 14.3.

N-benzyl-N-methylpentan-1-amine (D29)²³

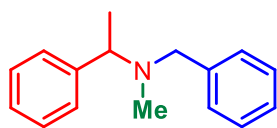


D29

Purified by column chromatography on silica gel (ethyl acetate/hexane); Brown oil; 85% yield (65.6 mg). ^1H NMR (400 MHz, CDCl_3): δ = 7.35-7.22 (m, 5H), 3.49 (s, 2H), 2.36 (t, $J_{\text{H,H}}$ = 7.3 Hz, 2H), 2.19 (s, 3H), 1.56-

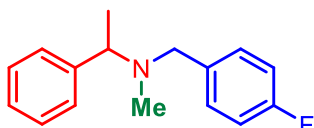
1.49 (m, 2H), 1.34-1.27 (m, 6H), 0.90 (t, $J_{\text{H,H}} = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): $\delta = 139.2, 129.2, 128.3, 127.0, 62.4, 57.6, 42.3, 29.8, 27.1, 22.7, 14.2$.

N-Benzyl-N-methyl-1-phenylethan-1-amine (D30)²⁴



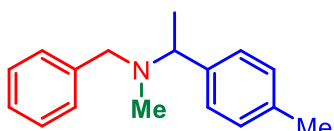
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 82% yield (36.9 mg). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.44$ (d, $J_{\text{H,H}} = 7.7$ Hz, 2H), 7.40-7.31 (m, 6H), 7.30-7.23 (m, 2H), 3.68 (q, $J_{\text{H,H}} = 6.8$ Hz, 1H), 3.62 (d, $J_{\text{H,H}} = 13.4$ Hz, 1H), 3.34 (d, $J_{\text{H,H}} = 13.2$ Hz, 1H), 2.17 (s, 3H), 1.46 (d, $J_{\text{H,H}} = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta = 144.3, 140.2, 128.9, 128.3, 127.8, 126.9, 126.8, 63.4, 59.0, 38.5, 18.5$.

N-(4-Fluorobenzyl)-N-methyl-1-phenylethan-1-amine (D31)



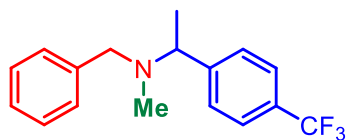
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 80% yield (38.9 mg). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.42$ (d, $J_{\text{H,H}} = 7.8$ Hz, 2H), 7.37 (t, $J_{\text{H,H}} = 7.6$ Hz, 2H), 7.33-7.24 (m, 3H), 7.04-6.97 (m, 2H), 3.66 (q, $J_{\text{H,H}} = 6.7$ Hz, 1H), 3.56 (d, $J_{\text{H,H}} = 13.3$ Hz, 1H), 3.29 (d, $J_{\text{H,H}} = 13.1$ Hz, 1H), 2.15 (s, 3H), 1.45 (d, $J_{\text{H,H}} = 6.4$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta = 162.0$ (d, $J_{\text{C,F}} = 244.4$ Hz), 144.1, 135.8, 130.3 (d, $J_{\text{C,F}} = 8.8$ Hz), 128.4, 127.8, 127.0, 115.1 (d, $J_{\text{C,F}} = 21.4$ Hz), 63.4, 58.2, 38.3, 18.5. **ESI-MS**: Calcd. for $\text{C}_{16}\text{H}_{19}\text{FN}^+$, $[\text{M}+\text{H}]^+$: 244.1496; found: 244.1488.

N-(4-Methylbenzyl)-N-methyl-1-phenylethan-1-amine (D32)²⁵



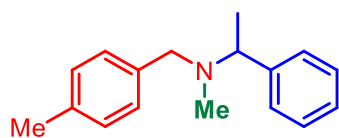
Purified by column chromatography on silica gel (ethyl acetate/hexanes); Colorless oil; 58% yield (27.8 mg). ^1H NMR (500 MHz, CDCl_3): $\delta = 7.33$ -7.21 (m, 7H), 7.15 (d, $J_{\text{H,H}} = 7.7$ Hz, 2H), 3.62 (q, $J_{\text{H,H}} = 6.7$ Hz, 1H), 3.58 (d, $J_{\text{H,H}} = 13.3$ Hz, 1H), 3.29 (d, $J_{\text{H,H}} = 13.3$ Hz, 1H), 2.34 (s, 3H), 2.13 (s, 3H), 1.41 (d, $J_{\text{H,H}} = 6.8$ Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): $\delta = 136.5, 129.0, 128.9, 128.3, 127.8, 126.8, 63.0, 58.9, 38.5, 21.2, 18.6$.

N-(4-Trifluoromethylbenzyl)-N-methyl-1-phenylethan-1-amine (D33)



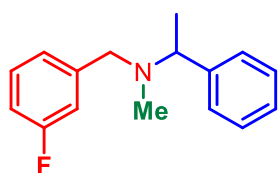
Purified by column chromatography on silica gel (ethyl acetate/hexanes); Colorless oil; 40% yield (23.5 mg). **¹H NMR** (400 MHz, CDCl₃): δ = 7.58 (d, *J*_{H,H} = 8.4 Hz, 2H), 7.52 (d, *J*_{H,H} = 8.2 Hz, 2H), 7.34-7.19 (m, 5H), 3.68 (q, *J*_{H,H} = 6.7 Hz, 1H), 3.54 (d, *J*_{H,H} = 13.4 Hz, 1H), 3.33 (d, *J*_{H,H} = 13.3 Hz, 1H), 2.12 (s, 3H), 1.41 (d, *J*_{H,H} = 6.7 Hz, 3H). **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 148.8, 139.8, 129.4 (q, *J*_{C,F} = 32 Hz), 128.8, 128.4, 128.0, 127.0, 125.3 (q, *J*_{C,F} = 4 Hz), 124.4 (q, *J*_{C,F} = 270 Hz), 62.9, 59.1, 38.4, 18.2. **ESI-MS**: Calcd. for C₁₇H₁₉F₃N⁺, [M+H]⁺: 294.1464; found: 294.1472.

N-Methyl-N-(4-methylbenzyl)-1-phenylethan-1-amine (D34)²⁶



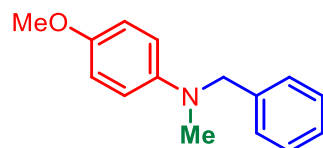
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 65% yield (31.1 mg). **¹H NMR** (400 MHz, CDCl₃): δ = 7.43 (d, *J*_{H,H} = 7.7 Hz, 2H), 7.37 (d, *J*_{H,H} = 7.4 Hz, 2H), 7.27 (s, 1H), 7.24 (d, *J*_{H,H} = 7.9 Hz, 2H), 7.14 (d, *J*_{H,H} = 7.7 Hz, 2H), 3.66 (q, *J*_{H,H} = 6.8 Hz, 1H), 3.58 (d, *J*_{H,H} = 13.3 Hz, 1H), 3.31 (d, *J*_{H,H} = 13.1 Hz, 1H), 2.36 (s, 3H), 2.16 (s, 3H), 1.45 (d, *J*_{H,H} = 6.4 Hz, 3H). **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 144.3, 137.1, 136.4, 129.0, 128.8, 128.3, 127.8, 126.9, 63.2, 58.7, 38.4, 21.2, 18.5.

N-(3-Fluorobenzyl)-N-methyl-1-phenylethan-1-amine (D35)



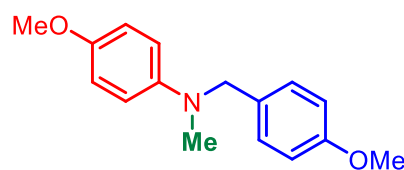
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 50% yield (24.3 mg). **¹H NMR** (400 MHz, CDCl₃): δ = 7.42 (d, *J*_{H,H} = 7.5 Hz, 2H), 7.36 (t, *J*_{H,H} = 7.4 Hz, 2H), 7.29 – 7.23 (m, 2H), 7.12 – 7.07 (m, 2H), 6.92 (td, *J*_{H,H} = 8.4, 2.6 Hz, 1H), 3.65 (q, *J*_{H,H} = 6.7 Hz, 1H), 3.58 (d, *J*_{H,H} = 13.5 Hz, 1H), 3.32 (d, *J*_{H,H} = 13.5 Hz, 1H), 2.16 (s, 3H), 1.45 (d, *J*_{H,H} = 6.7 Hz, 3H). **¹³C{¹H} NMR** (101 MHz, CDCl₃): δ = 163.2 (d, *J*_{C,F} = 243 Hz), 144.2, 143.2 (d, *J*_{C,F} = 7 Hz), 129.7 (d, *J*_{C,F} = 8 Hz), 128.4, 127.8, 127.1, 124.3, 115.5 (d, *J*_{C,F} = 21 Hz), 113.7 (d, *J*_{C,F} = 21 Hz), 63.5, 58.5, 38.6, 18.6. **ESI-MS**: Calcd. for C₁₆H₁₉FN⁺, [M+H]⁺: 244.1496; found: 244.1470

4-Methoxy-N-(4-methoxybenzyl)-N-methylaniline (D36)¹⁹



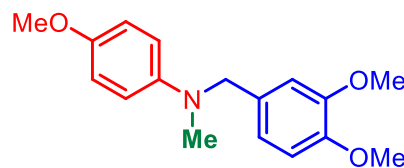
Purified by column chromatography on silica gel (ethyl acetate/hexanes); Colorless oil; 45% yield (20.5 mg). ^1H NMR (400 MHz, CDCl_3): δ = 7.34-7.29 (m, 2H), 7.25 (d, J = 7.4 Hz, 3H), 6.85-6.80 (m, 2H), 6.77-6.73 (m, 2H), 4.43 (s, 2H), 3.76 (s, 3H), 2.92 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 151.9, 145.0, 139.4, 128.6, 127.2, 127.0, 114.9, 114.7, 58.1, 55.9, 39.2.

4-Methoxy-N-(4-methoxybenzyl)-N-methylaniline (D37)²⁷



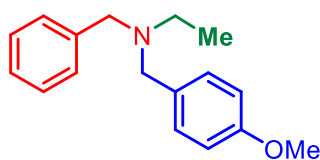
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 58% yield (29.8 mg). ^1H NMR (400 MHz, CDCl_3): δ = 7.17-7.14 (m, 2H), 6.86-6.81 (m, 4H), 6.77-6.74 (m, 2H), 4.35 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H), 2.87 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 158.7, 151.9, 145.0, 131.2, 128.5, 115.0, 114.8, 114.0, 57.6, 55.9, 55.4, 39.0.

4-Methoxy-N-(4-methoxybenzyl)-N-methylaniline (D38)²⁸



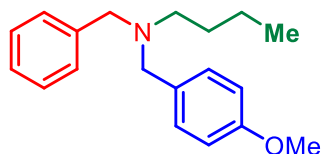
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 62% yield (35.6 mg). ^1H NMR (400 MHz, CDCl_3): δ = 6.84-6.76 (m, 7H), 4.34 (s, 2H), 3.86 (s, 3H), 3.82 (s, 3H), 3.76 (s, 3H), 2.87 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 152.1, 149.2, 148.1, 131.8, 119.4, 115.2, 114.8, 111.2, 110.5, 58.2, 56.1, 56.0, 55.9, 39.1.

N-Benzyl-N-(4-methoxybenzyl)ethanamine (D39)⁷



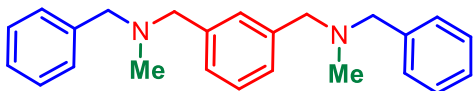
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 85% yield (43.4 mg). ^1H NMR (400 MHz, CDCl_3): δ = 7.37 (d, $J_{\text{H,H}}$ = 7.2 Hz, 2H), 7.29 (dt, $J_{\text{H,H}}$ = 13.0, 5.8 Hz, 4H), 7.21 (t, $J_{\text{H,H}}$ = 7.2 Hz, 1H), 6.86-6.83 (m, 2H), 3.79 (s, 3H), 3.54 (s, 2H), 3.50 (s, 2H), 2.48 (q, $J_{\text{H,H}}$ = 7.0 Hz, 2H), 1.05 (t, $J_{\text{H,H}}$ = 7.2 Hz, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz CDCl_3): δ = 158.6, 130.0, 128.9, 128.3, 126.8, 113.7, 77.4, 77.2, 77.1, 76.9, 57.7, 57.2, 55.4, 47.0, 12.0.

N-Benzyl-N-(4-methoxybenzyl)butan-1-amine (D40)



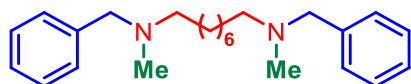
Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 83% yield (47.0 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.38 (d, $J_{\text{H,H}}$ = 7.2 Hz, 2H), 7.34-7.27 (m, 4H), 7.26-7.21 (m, 1H), 6.89-6.84 (m, 2H), 3.81 (s, 3H), 3.55 (s, 2H), 3.50 (s, 2H), 2.44-2.39 (m, 2H), 1.54-1.46 (m, 2H), 1.31 (dq, $J_{\text{H,H}}$ = 14.5, 7.3 Hz, 2H), 0.85 (t, $J_{\text{H,H}}$ = 7.3 Hz, 3H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 158.6, 140.3, 132.2, 130.0, 128.9, 128.2, 126.8, 113.7, 58.3, 57.7, 55.4, 53.1, 29.4, 20.6, 14.2. **ESI-MS**: Calcd. for C₁₉H₂₆NO⁺, [M+H]⁺: 284.2009; found: 284.2007

1, 1'-(1, 3-Phenylene)bis(N-benzyl-N-methylmethanamine) (D41)



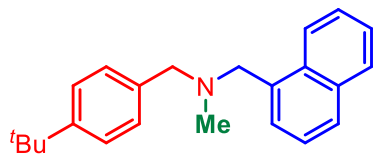
Purified by column chromatography on silica gel (ethyl acetate/hexanes); Colorless oil; 92% yield (63.4 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.42-7.39 (m, 5H), 7.36 (ddd, $J_{\text{H,H}}$ = 8.7, 5.2, 2.1 Hz, 4H), 7.33 – 7.26 (m, 5H), 3.57 (dd, $J_{\text{H,H}}$ = 5.8, 2.3 Hz, 8H), 2.23 (d, $J_{\text{H,H}}$ = 2.5 Hz, 6H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 139.3, 139.2, 129.7, 129.1, 128.3, 128.2, 127.8, 127.0, 62.0, 61.9, 42.3. **ESI-MS**: Calcd. for C₂₄H₂₉N₂⁺, [M+H]⁺: 345.2325; found: 345.2318

N1, N8-dibenzyl-N1, N8-dimethyloctane-1,8-diamine (D42)



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 84% yield (59.2 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 7.30 (d, J = 4.5 Hz, 8H), 7.26-7.21 (m, 2H), 3.47 (s, 4H), 2.34 (t, $J_{\text{H,H}}$ = 7.3 Hz, 4H), 2.17 (s, 6H), 1.52-1.47 (m, 4H), 1.28 (d, $J_{\text{H,H}}$ = 2.8 Hz, 8H). **¹³C{¹H} NMR** (126 MHz, CDCl₃): δ = 139.4, 129.2, 128.3, 126.9, 62.4, 57.7, 42.4, 29.7, 27.5. **ESI-MS**: Calcd. for C₂₄H₃₇N₂⁺, [M+H]⁺: 353.2951; found: 353.2949.

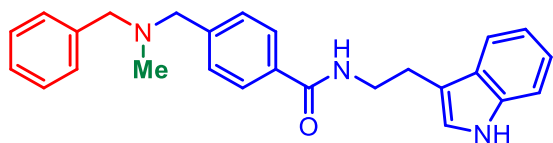
N-(4-(Tert-butyl)benzyl)-N-methyl-1-(naphthalen-1-yl)methanamine (D43)²⁹



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 87% yield (55.2 mg). **¹H NMR** (500 MHz, CDCl₃): δ = 8.28-8.26 (m, 1H), 7.87 (dd, $J_{\text{H,H}}$ = 7.7, 2.0 Hz, 1H), 7.79 (d, $J_{\text{H,H}}$ = 8.1 Hz, 1H), 7.51 (ddd, $J_{\text{H,H}}$ = 6.8, 3.9, 2.2 Hz, 3H), 7.45-7.41 (m, 1H), 7.37 (d, $J_{\text{H,H}}$ = 8.5 Hz, 2H), 7.32 (d, $J_{\text{H,H}}$ = 8.1 Hz, 2H), 3.96 (s, 2H), 3.61 (s, 2H), 2.24 (s, 3H), 1.35 (s,

9H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 150.0, 136.4, 135.2, 134.0, 132.7, 128.9, 128.5, 128.0, 127.5, 125.8, 125.7, 125.2, 125.0, 62.2, 60.6, 42.5, 34.6, 31.6.

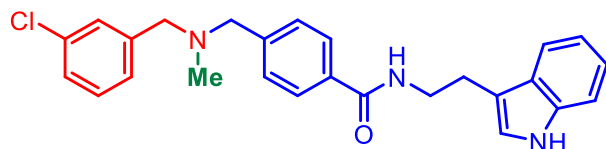
N-[2-(1H-Indol-3-yl)ethyl]-4-[[benzyl(methyl)amino]methyl]benzamide (D44)³⁰



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 80% yield (63.6 mg). ^1H NMR (400 MHz, CDCl_3): δ = 8.31 (s,

1H), 7.64 (dd, $J_{\text{H,H}}$ = 8.1, 3.5 Hz, 3H), 7.40 – 7.30 (m, 7H), 7.28 – 7.25 (m, 1H), 7.21 (t, $J_{\text{H,H}}$ = 7.7 Hz, 1H), 7.13 (t, $J_{\text{H,H}}$ = 7.5 Hz, 1H), 7.04 (d, $J_{\text{H,H}}$ = 2.4 Hz, 1H), 6.28 (t, $J_{\text{H,H}}$ = 5.8 Hz, 1H), 3.80 (q, $J_{\text{H,H}}$ = 6.4 Hz, 2H), 3.52 (d, $J_{\text{H,H}}$ = 5.4 Hz, 4H), 3.09 (t, $J_{\text{H,H}}$ = 6.7 Hz, 2H), 2.17 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3): δ = 167.6, 143.3, 139.1, 136.6, 133.5, 129.07, 128.4, 127.5, 127.2, 127.0, 122.4, 122.3, 119.7, 118.9, 113.1, 111.5, 62.0, 61.5, 42.4, 40.4, 25.4.

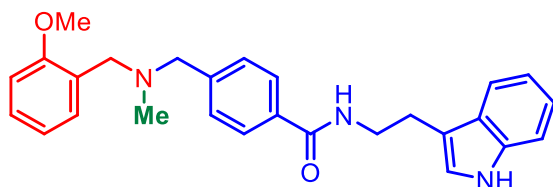
N-[2-(1H-Indol-3-yl)ethyl]-4-[[3-chlorobenzyl(methyl)- amino]methyl]benzamide (D45)³⁰



Purified by column chromatography on silica gel (ethyl acetate/hexanes); Colorless oil; 73% yield (63.1 mg). ^1H NMR (500 MHz, CDCl_3):

δ = 8.30 (s, 1H), 7.64 (dd, $J_{\text{H,H}}$ = 8.3, 2.3 Hz, 3H), 7.39-7.33 (m, 4H), 7.22 (dd, $J_{\text{H,H}}$ = 6.7, 3.8 Hz, 4H), 7.13 (s, 1H), 7.05 (d, $J_{\text{H,H}}$ = 2.3 Hz, 1H), 6.28 (s, 1H), 3.84-3.76 (m, 2H), 3.53 (s, 2H), 3.47 (s, 2H), 3.09 (t, $J_{\text{H,H}}$ = 6.6 Hz, 2H), 2.16 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (126 MHz, CDCl_3): δ = 167.5, 142.9, 141.4, 136.6, 134.3, 133.6, 129.7, 129.0, 128.9, 127.4, 127.3, 127.0, 122.3, 122.3, 119.6, 118.9, 113.1, 111.5, 61.6, 61.3, 42.4, 40.4, 25.4.

N-[2-(1H-Indol-3-yl)ethyl]-4-[[2-methoxybenzyl(methyl)-amino]methyl]benzamide(D46)³⁰

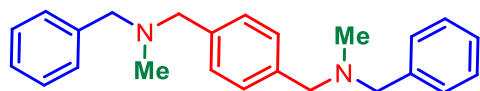


Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 59% yield (50.4 mg). ^1H NMR (400 MHz, CDCl_3): δ = 8.23 (s,

1H), 7.62 (dd, $J_{\text{H,H}}$ = 10.0, 7.7 Hz, 3H), 7.41-7.34 (m, 4H), 7.23-7.16 (m, 2H), 7.11 (t, $J_{\text{H,H}}$ = 7.4 Hz, 1H), 7.03 (d, $J_{\text{H,H}}$ = 2.1 Hz, 1H), 6.93 (t, $J_{\text{H,H}}$ = 7.5 Hz, 1H), 6.85 (d, $J_{\text{H,H}}$ = 8.1 Hz, 1H), 6.21 (d, $J_{\text{H,H}}$ = 6.1 Hz, 1H), 3.78 (d, $J_{\text{H,H}}$ = 4.2 Hz, 5H), 3.58 (d, $J_{\text{H,H}}$ = 6.2 Hz, 4H), 3.08 (t, $J_{\text{H,H}}$ = 6.7 Hz, 2H), 2.19 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz,

CDCl₃): δ = 167.5, 157.9, 136.6, 133.5, 130.7, 129.2, 128.4, 127.5, 127.2, 126.9, 122.4, 122.3, 120.5, 119.7, 118.9, 113.2, 111.4, 110.6, 61.7, 55.5, 55.2, 42.3, 40.3, 25.4.

1,1'-(1,4-phenylene)bis(N-benzyl-N-methylmethanamine) (D47)³¹



Purified by column chromatography on silica gel (ethyl acetate/hexane); Colorless oil; 93% yield (64.1 mg). ¹H

NMR (500 MHz, CDCl₃): δ = 7.40 (d, *J* = 7.0 Hz, 4H), 7.37- 7.33 (m, 8H), 7.29-7.25 (m, 2H), 3.55 (s, 4H), 3.54 (s, 4H), 2.21 (s, 6H). ¹³C{¹H} NMR (126 MHz, CDCl₃): δ = 139.5, 138.1, 129.1, 129.0, 128.3, 127.0, 62.0, 61.7, 42.4, 29.8.

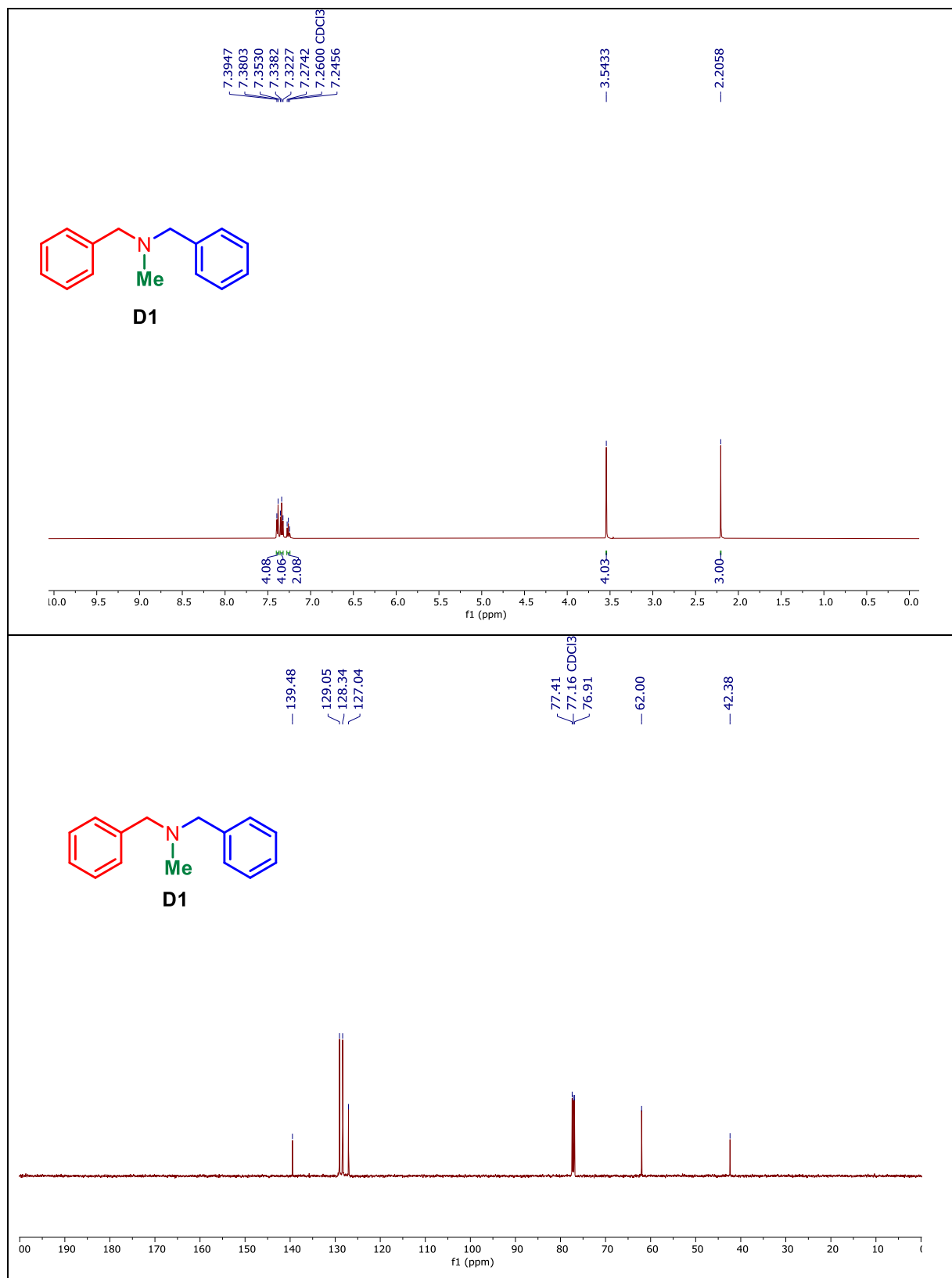
8. References

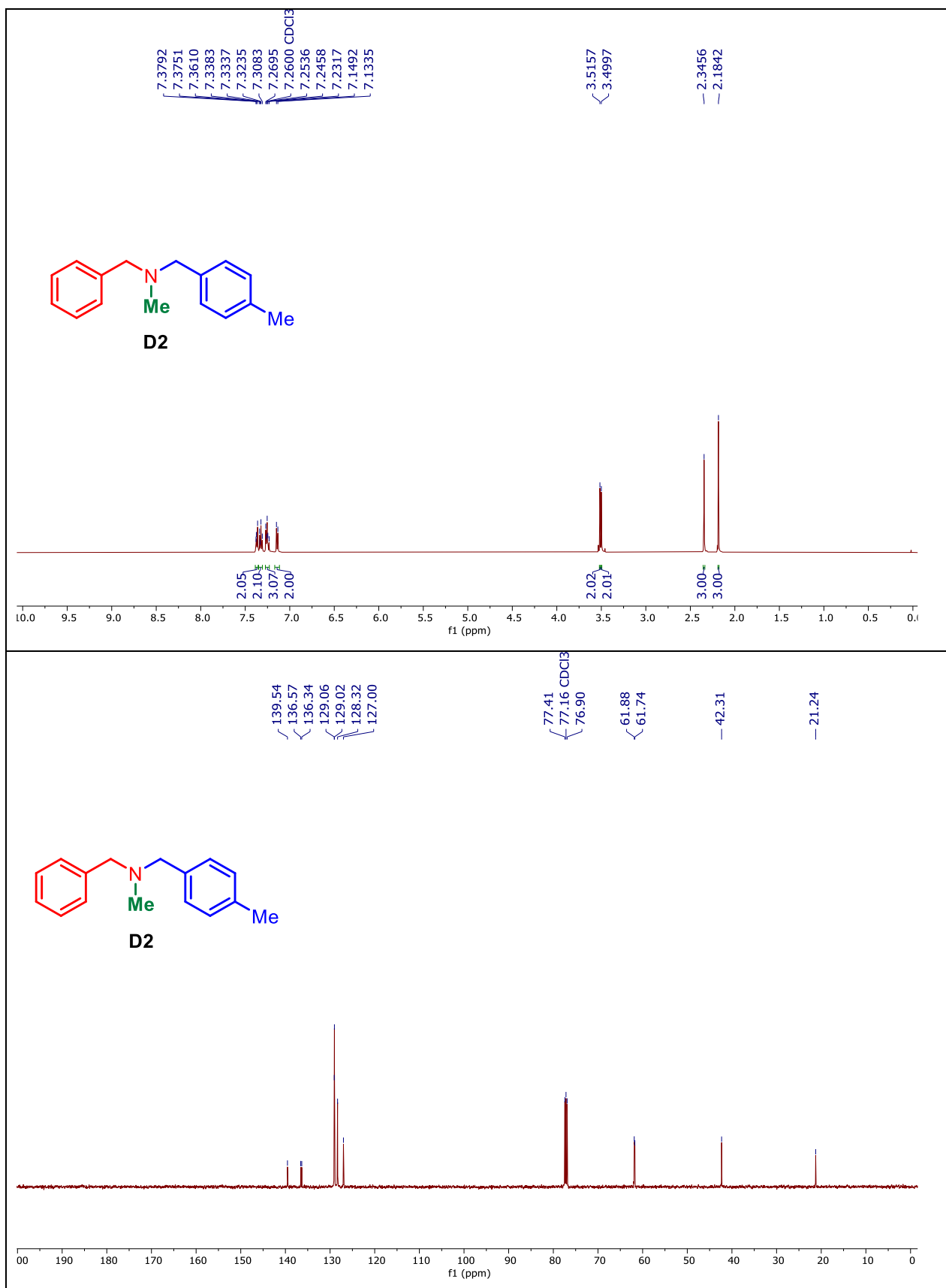
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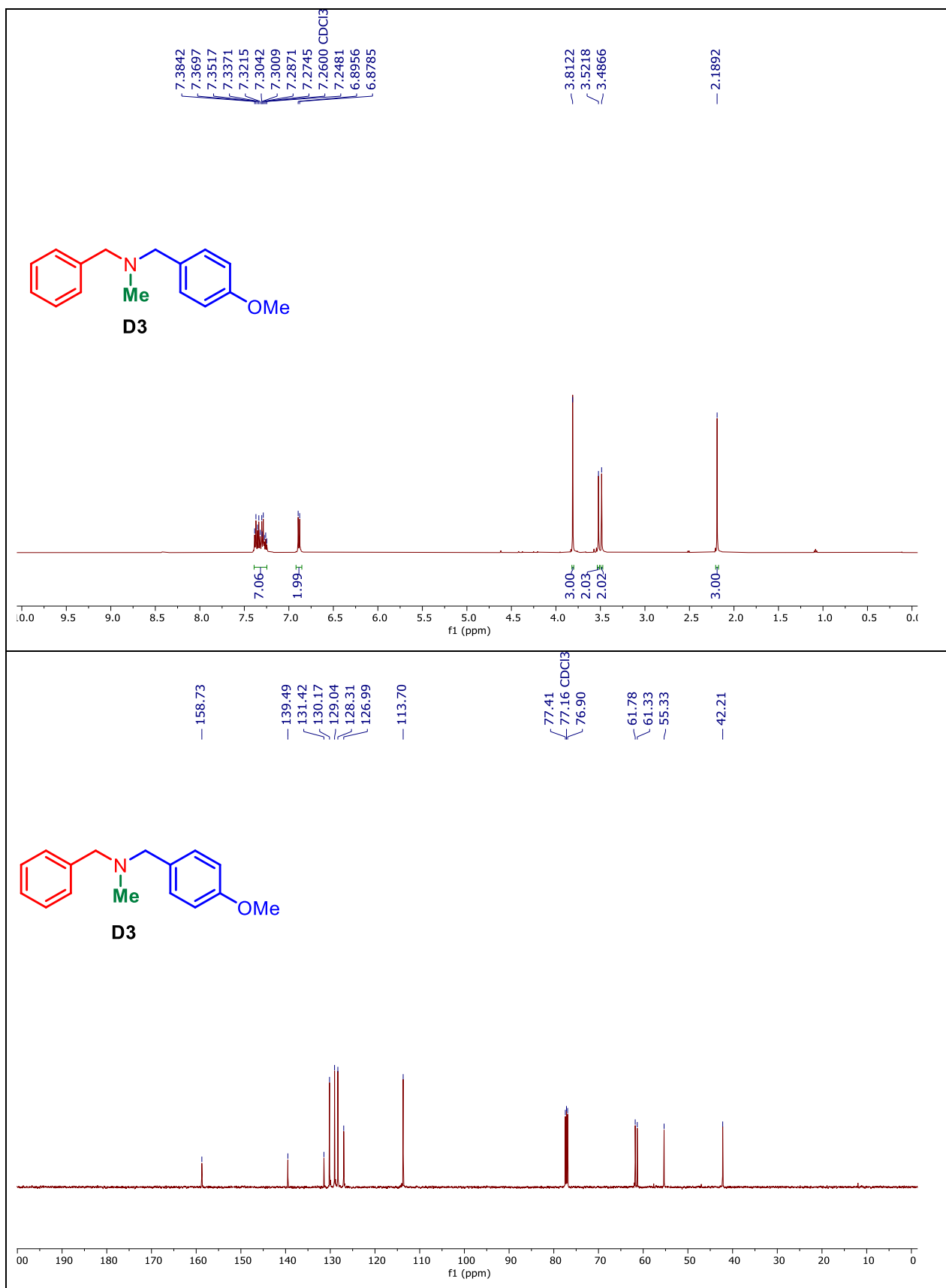
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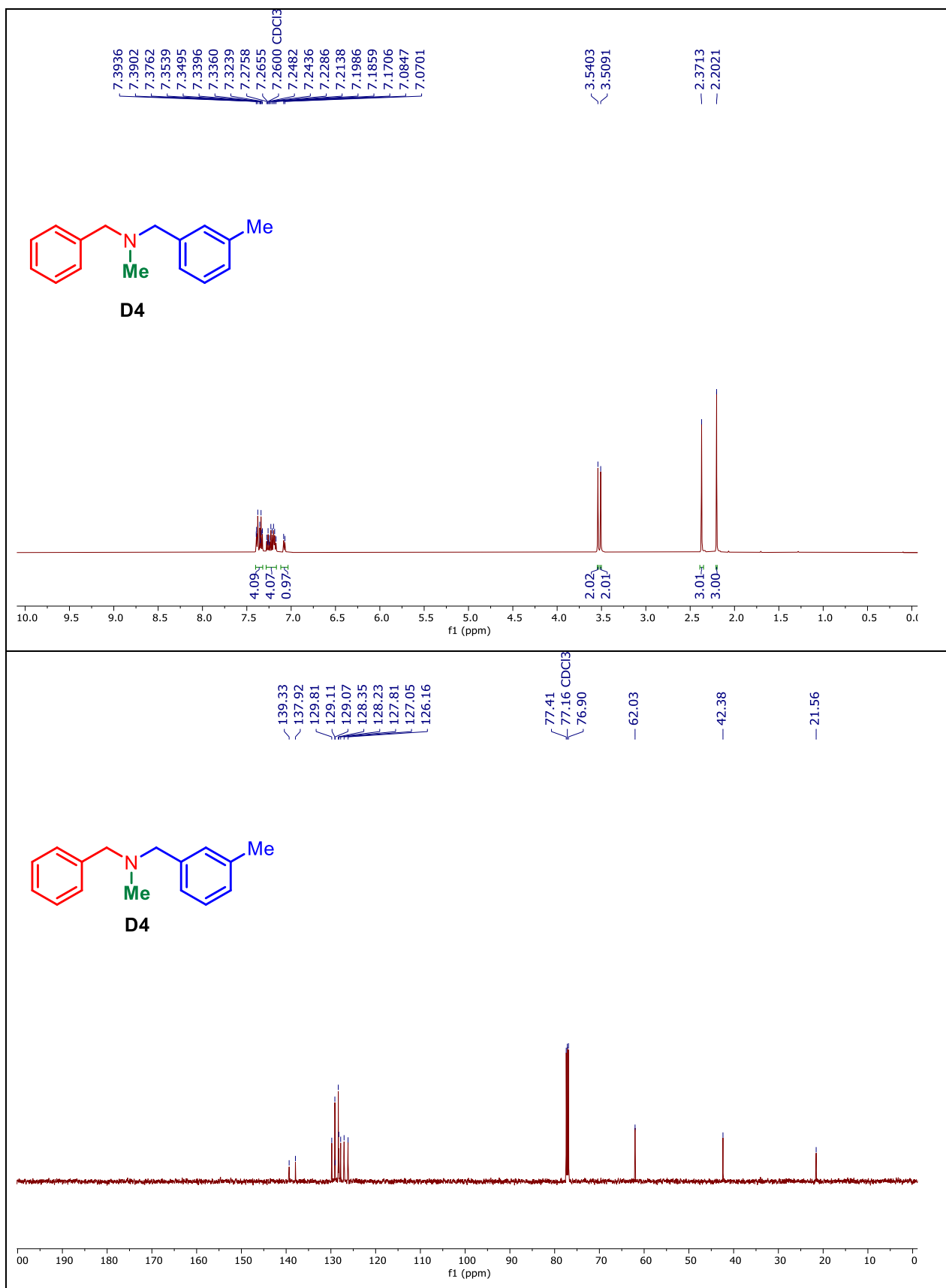
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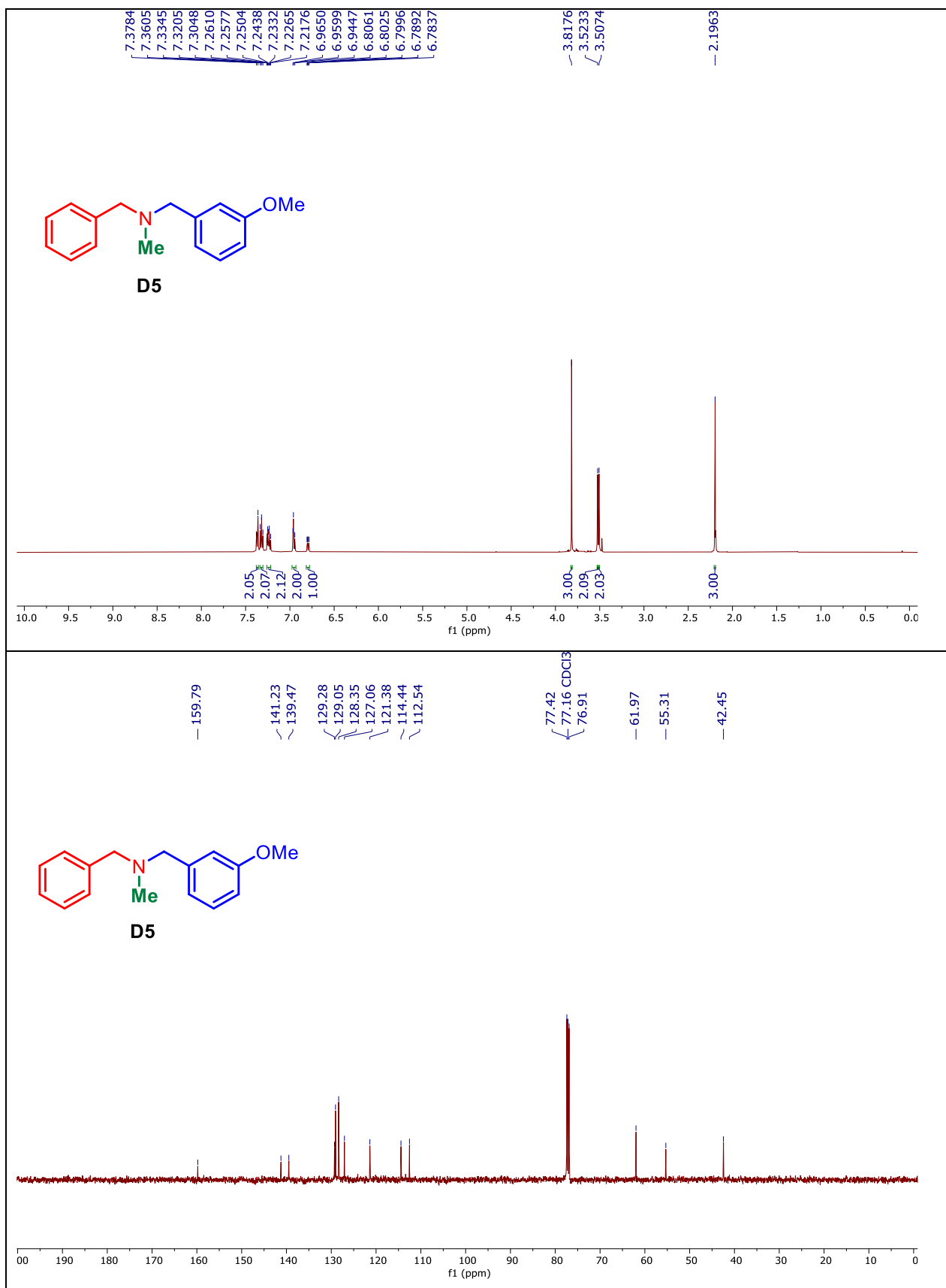
9. Copies of ^1H and ^{13}C NMR of the Tertiary Amines

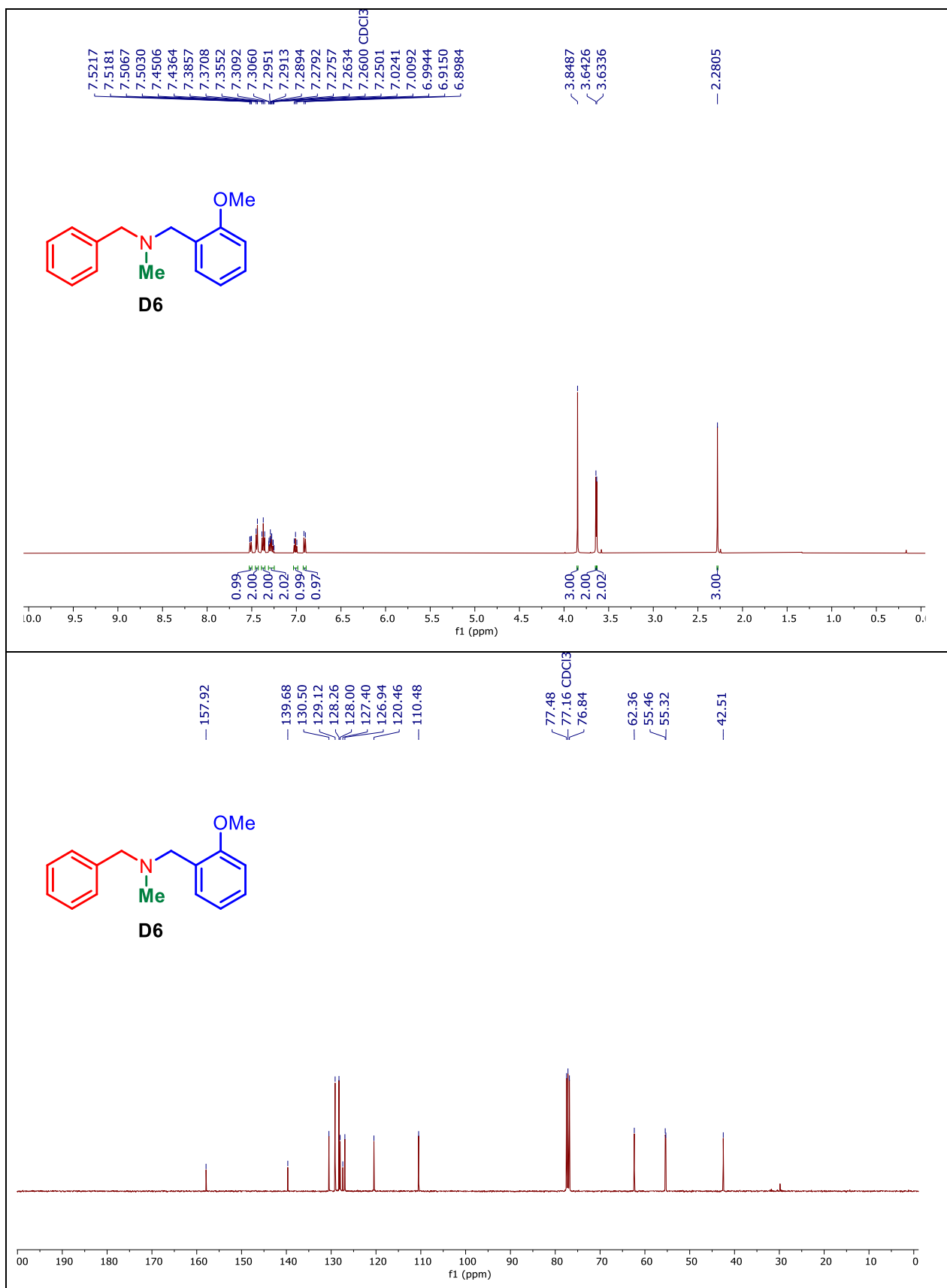


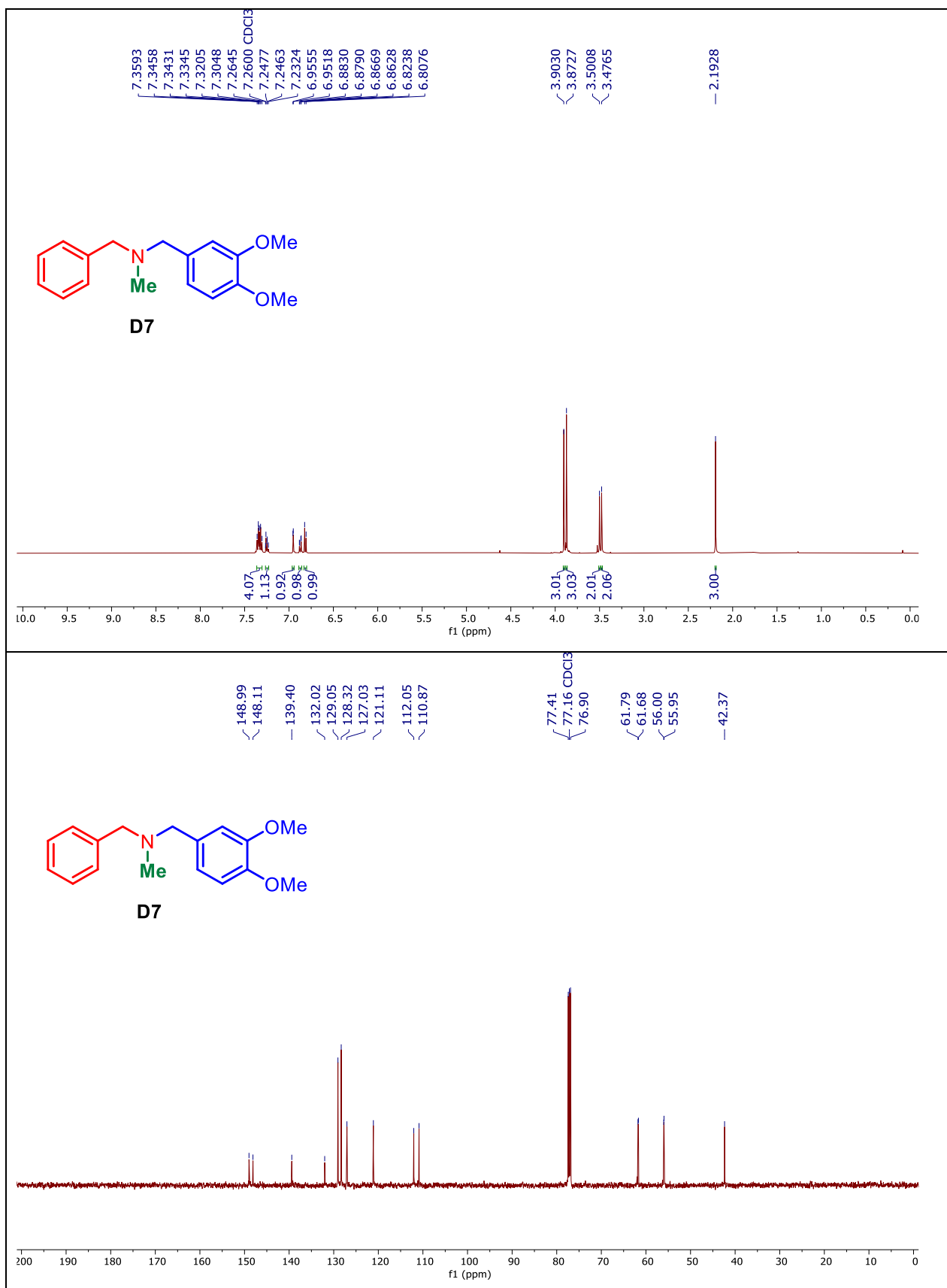


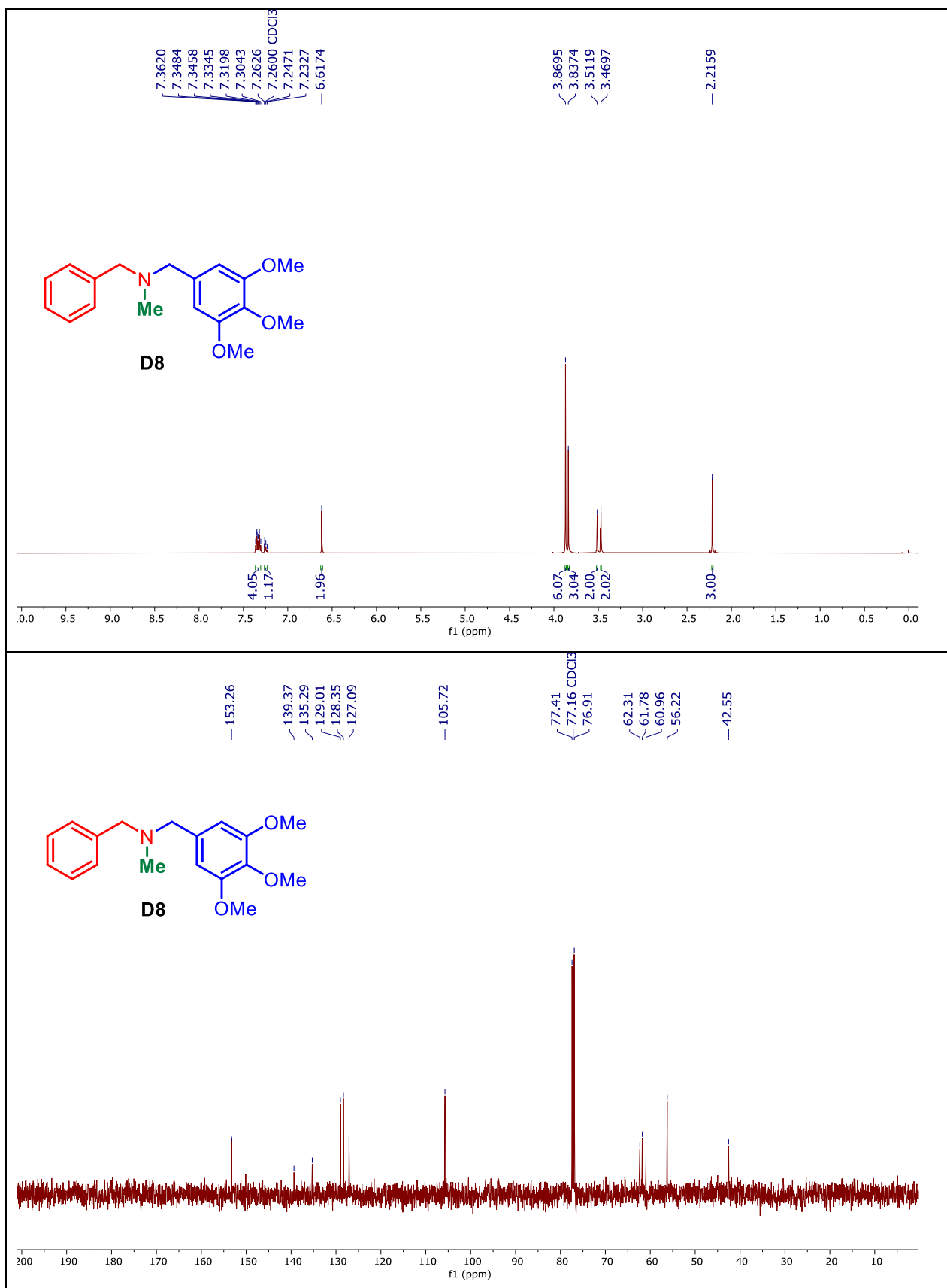


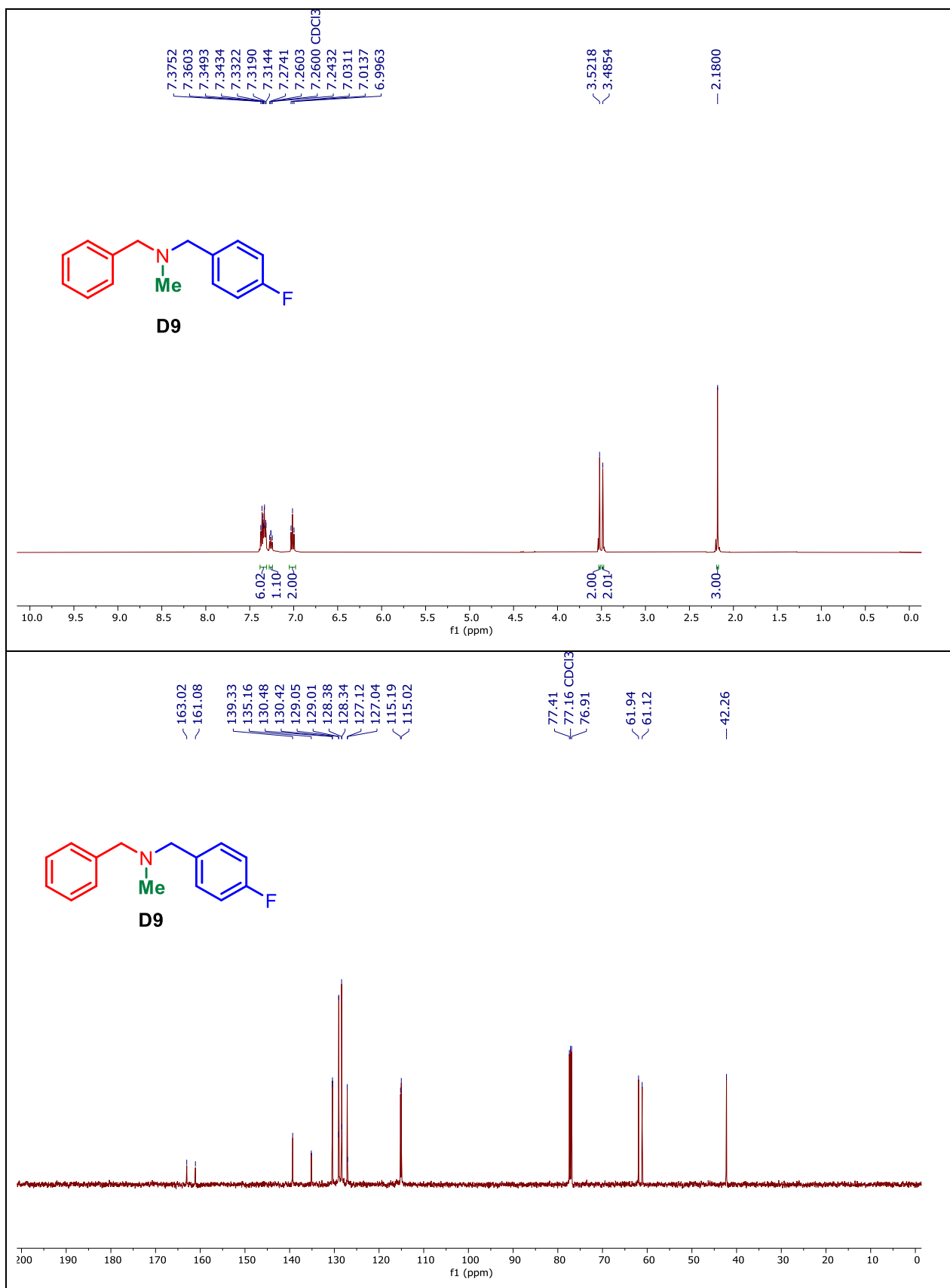


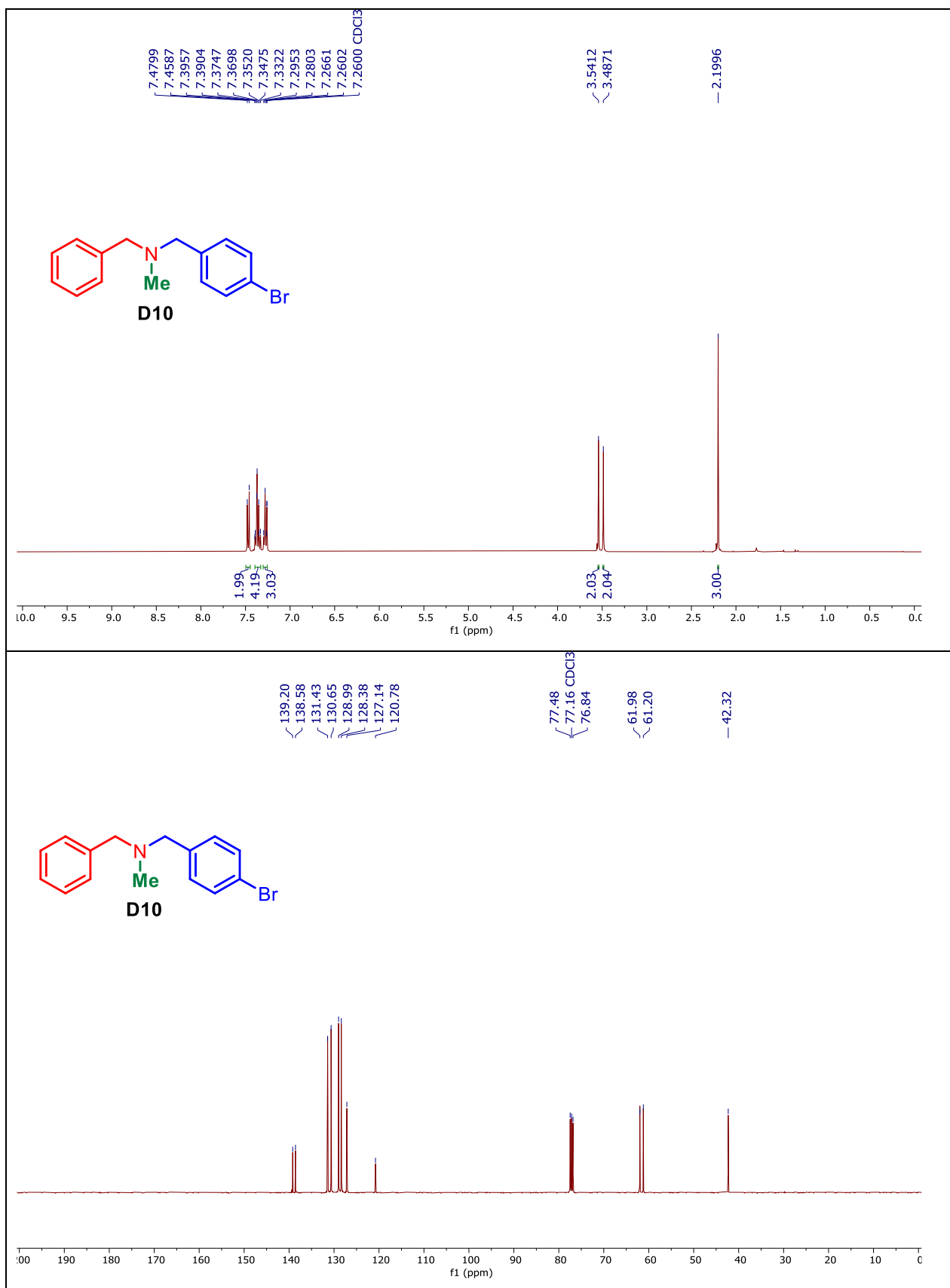


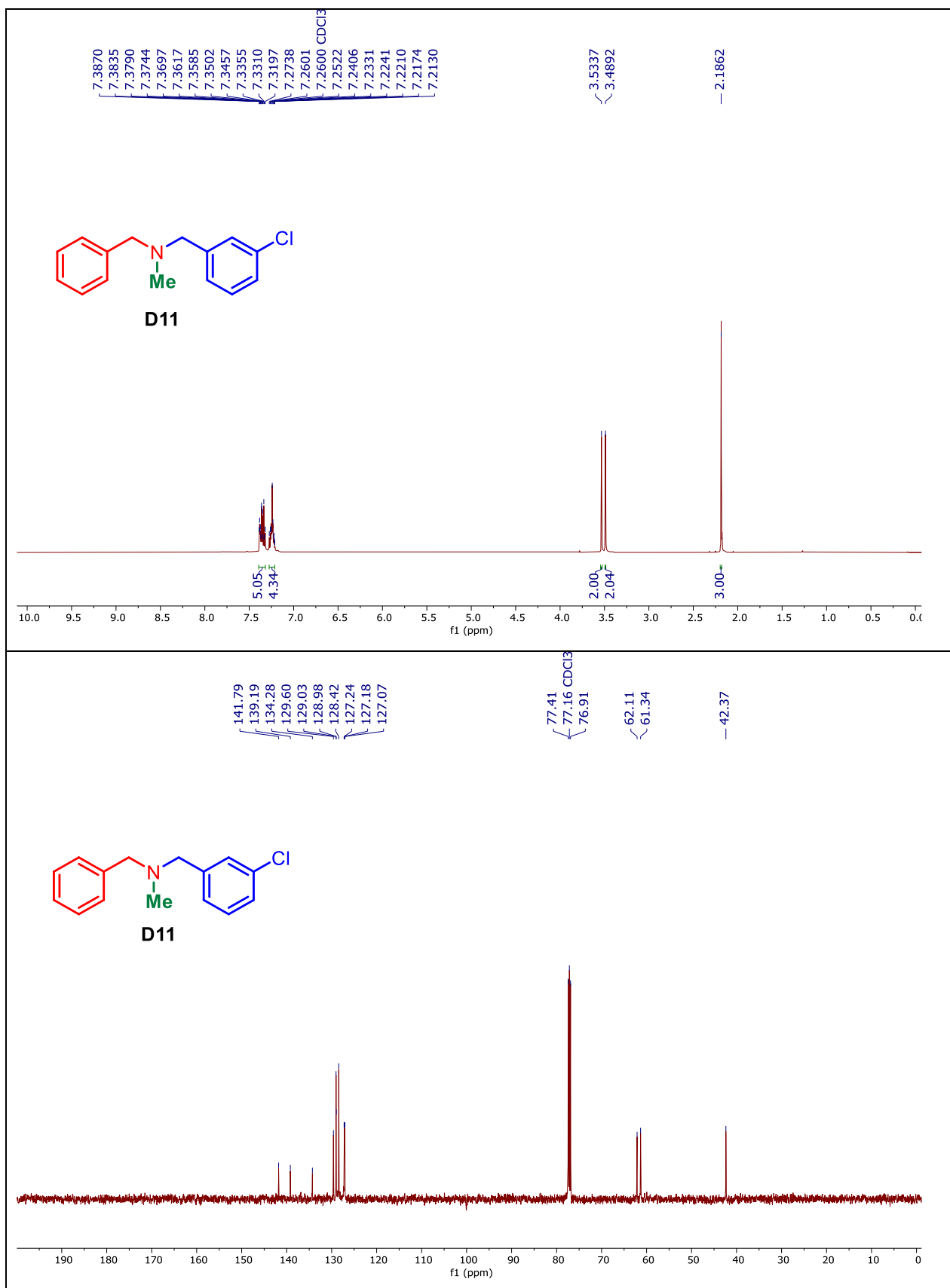


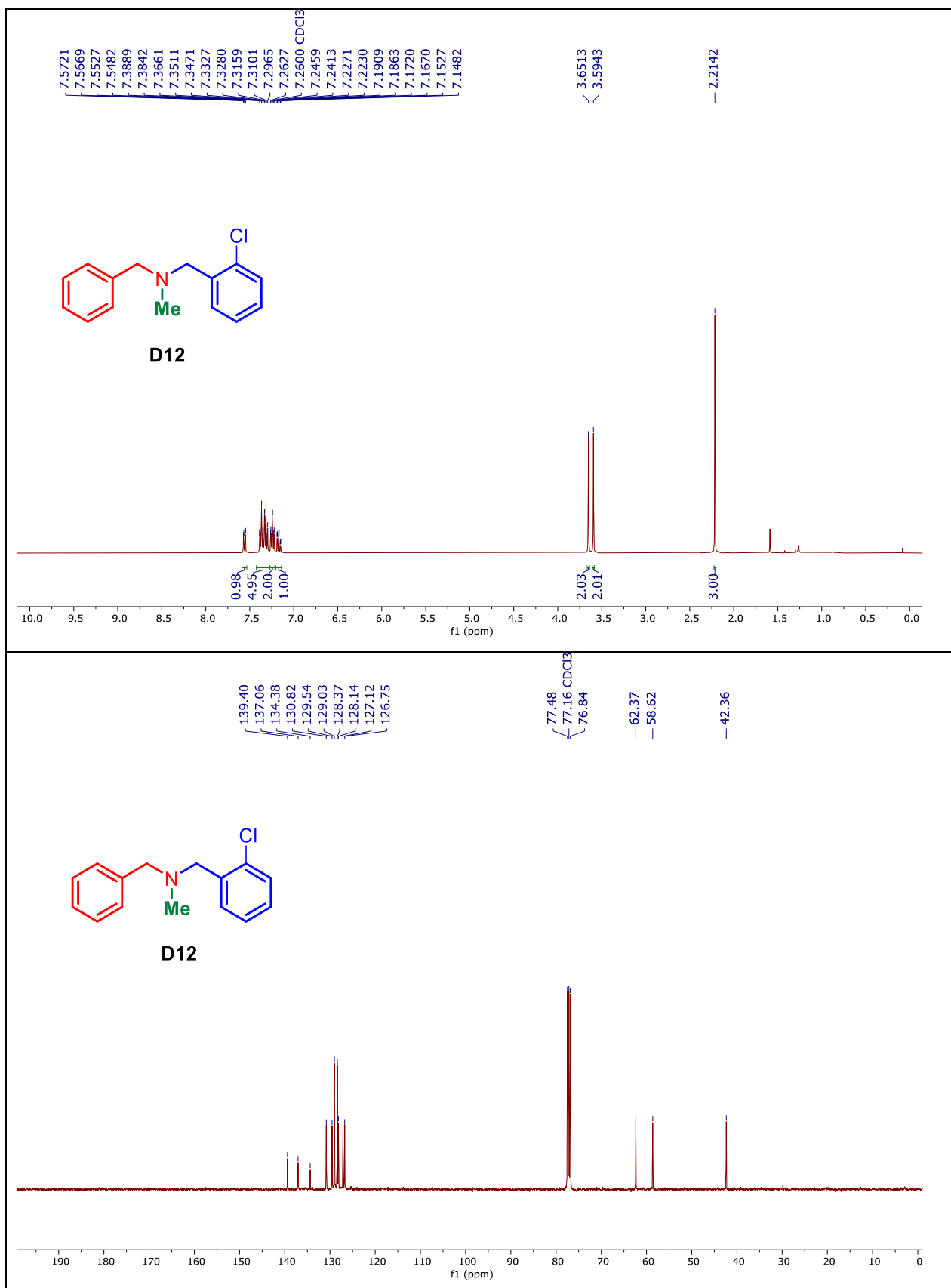


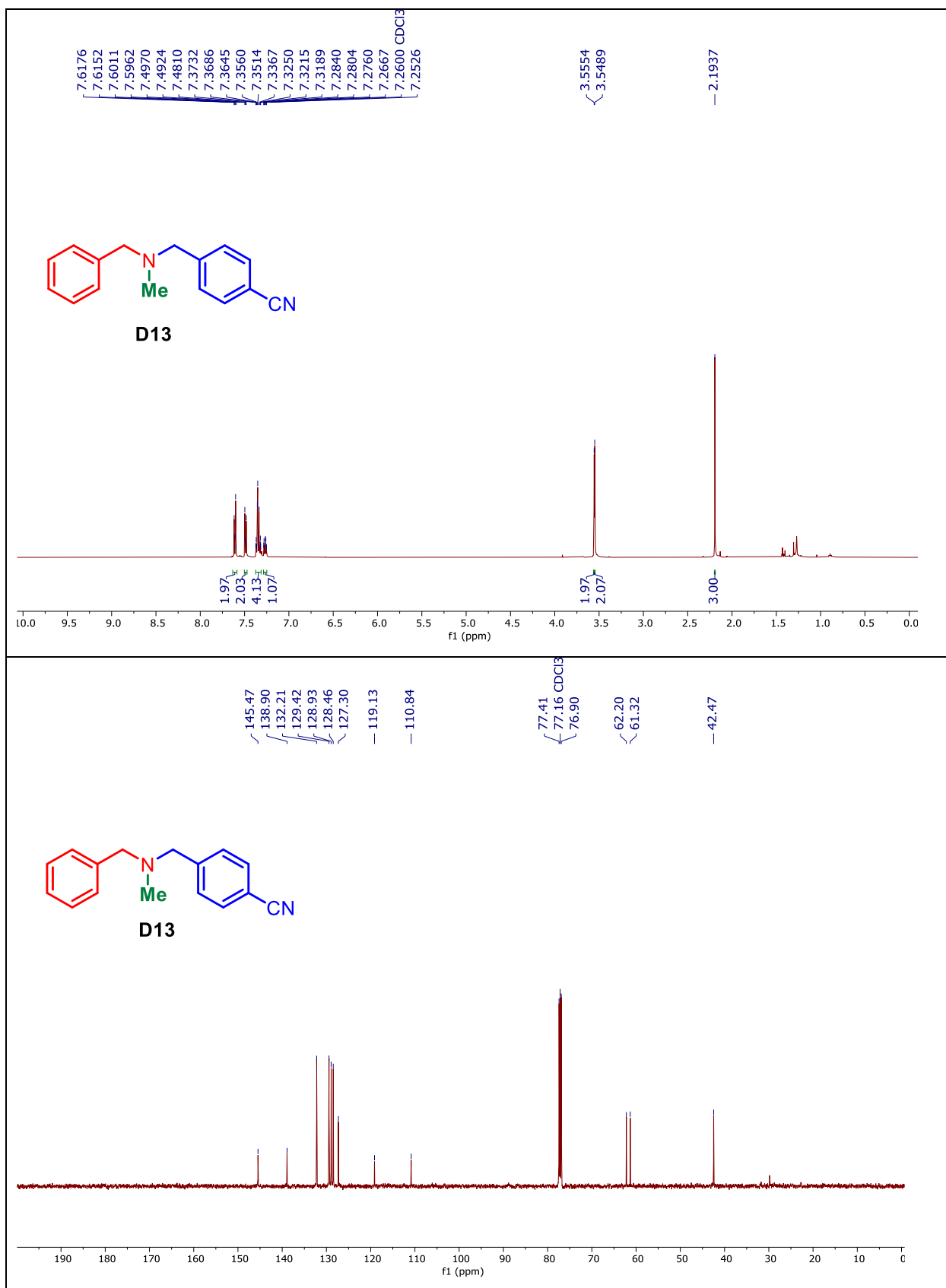


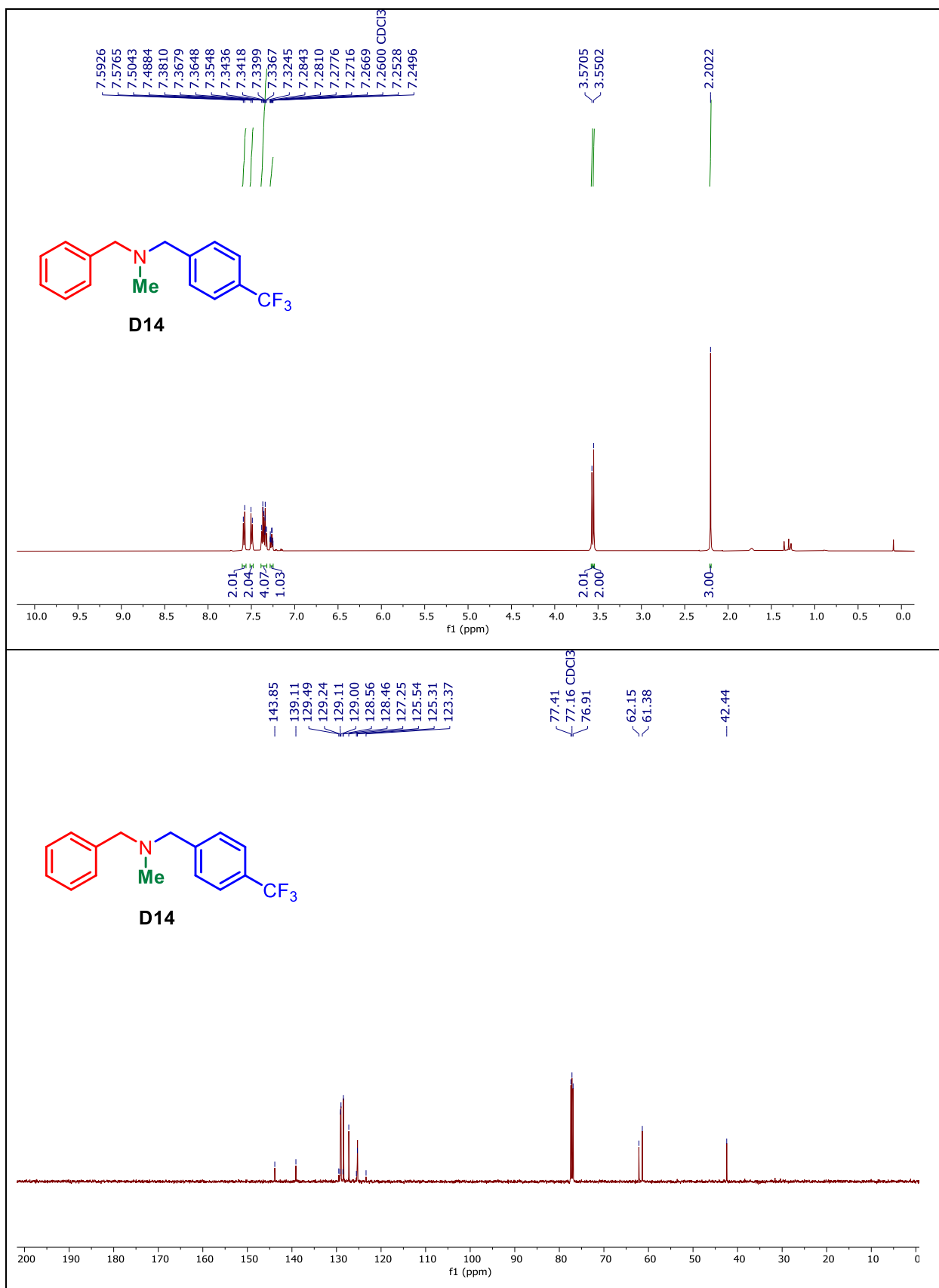


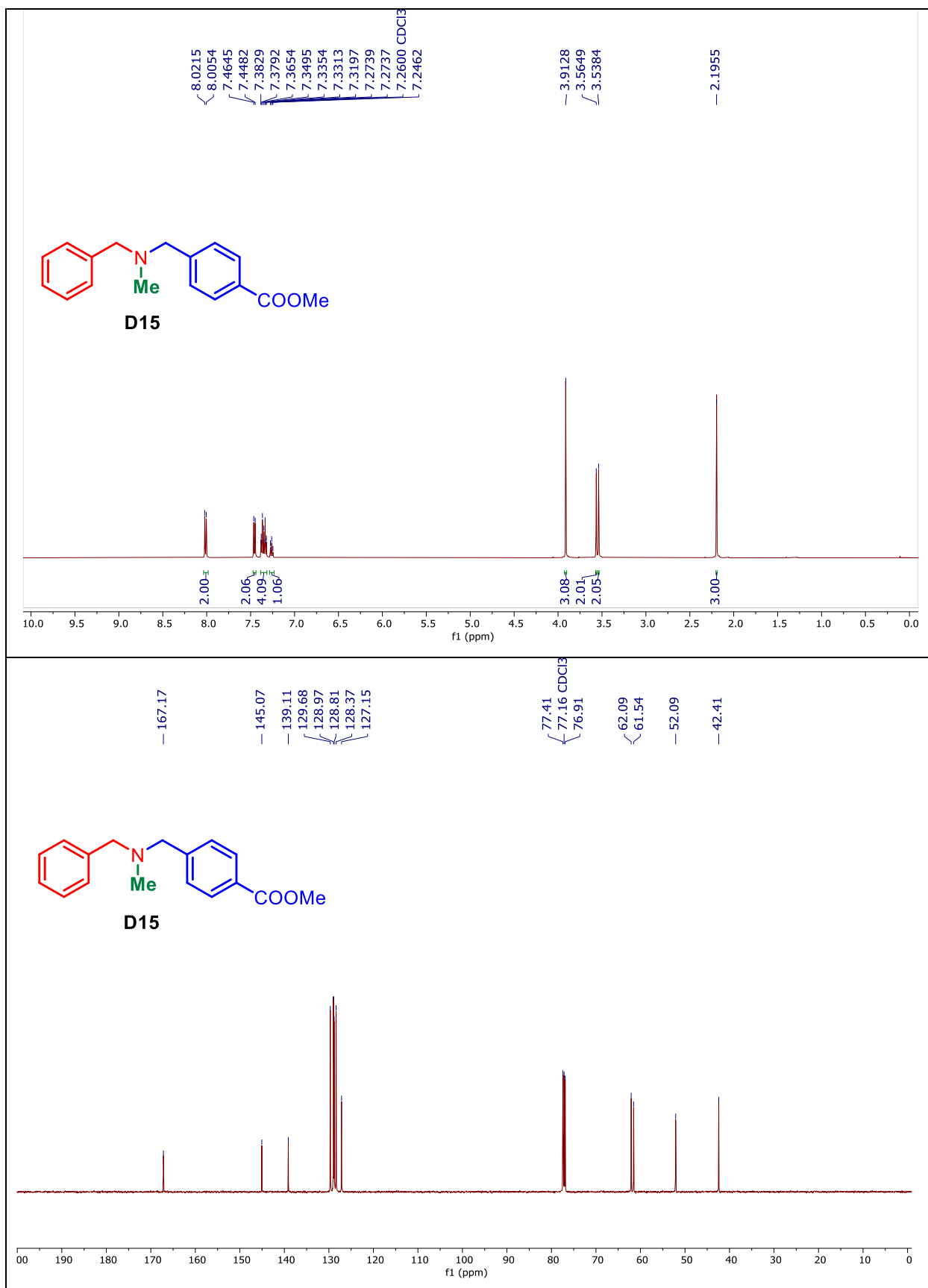


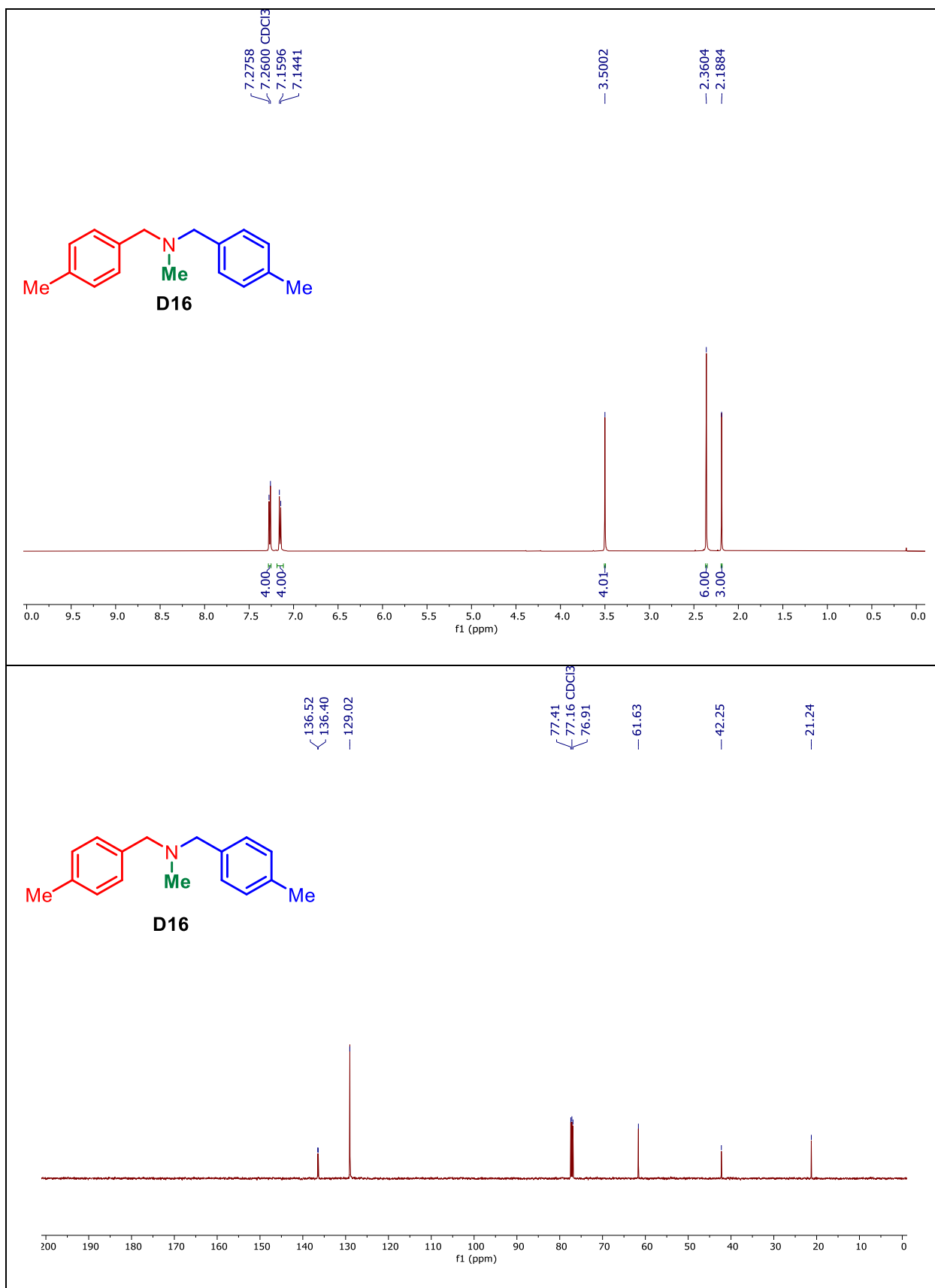


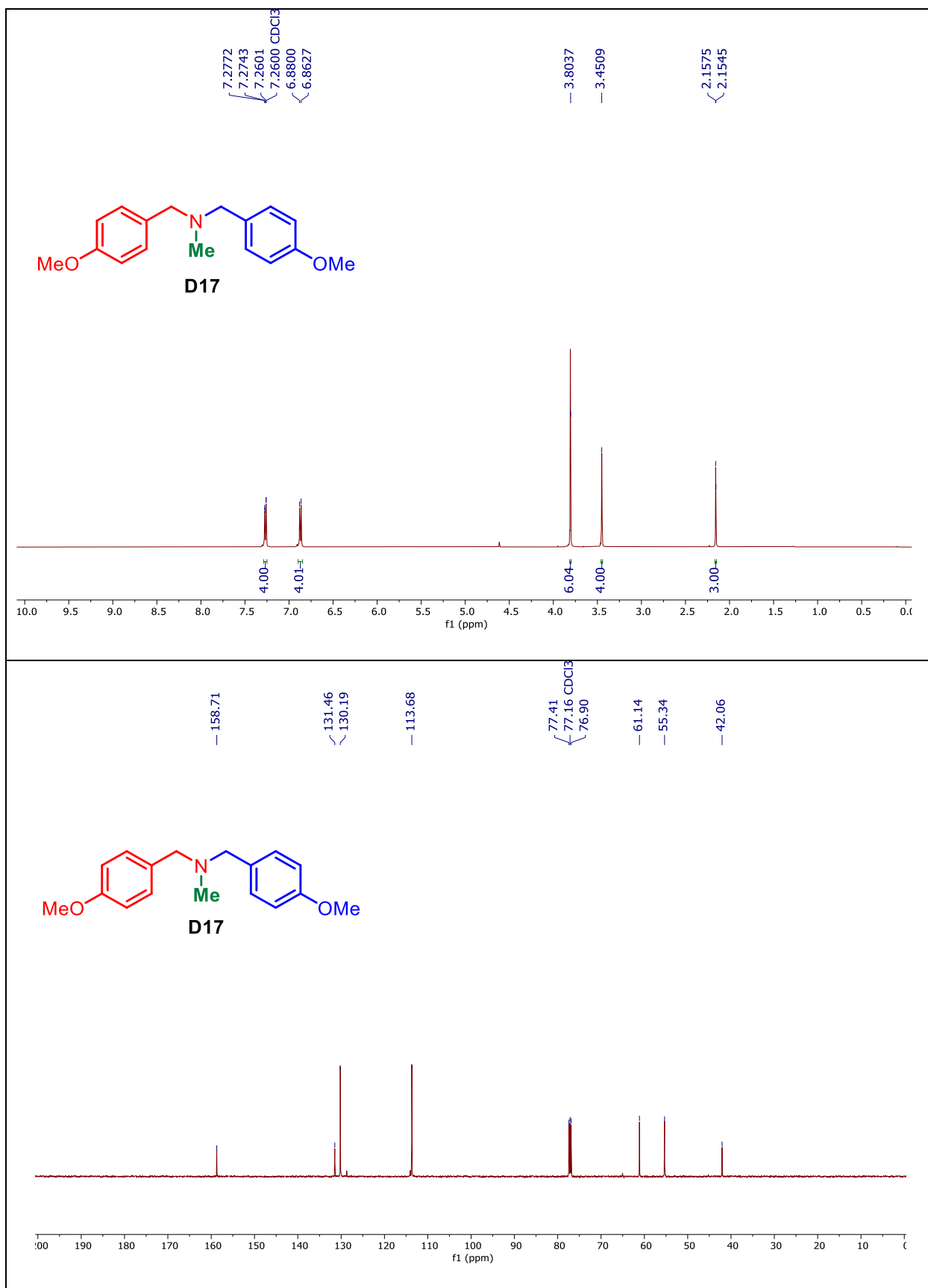


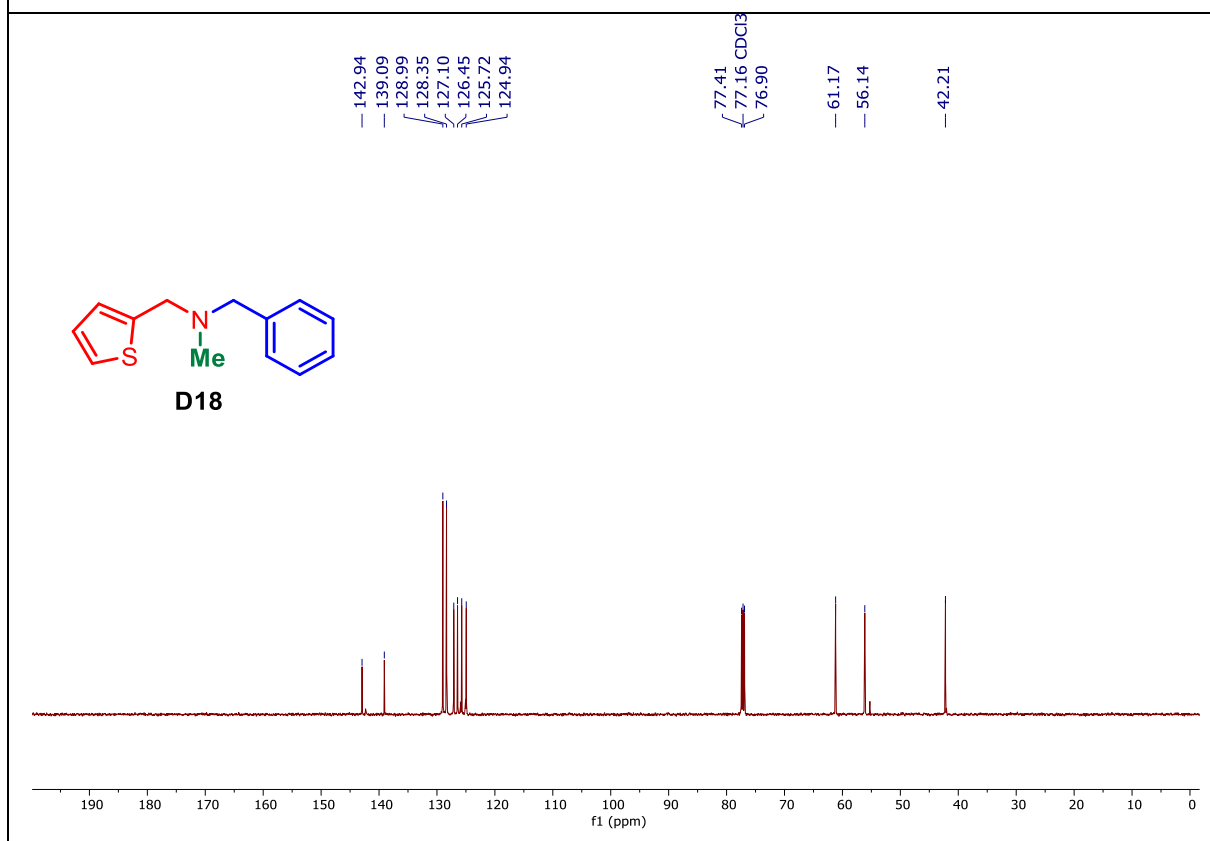
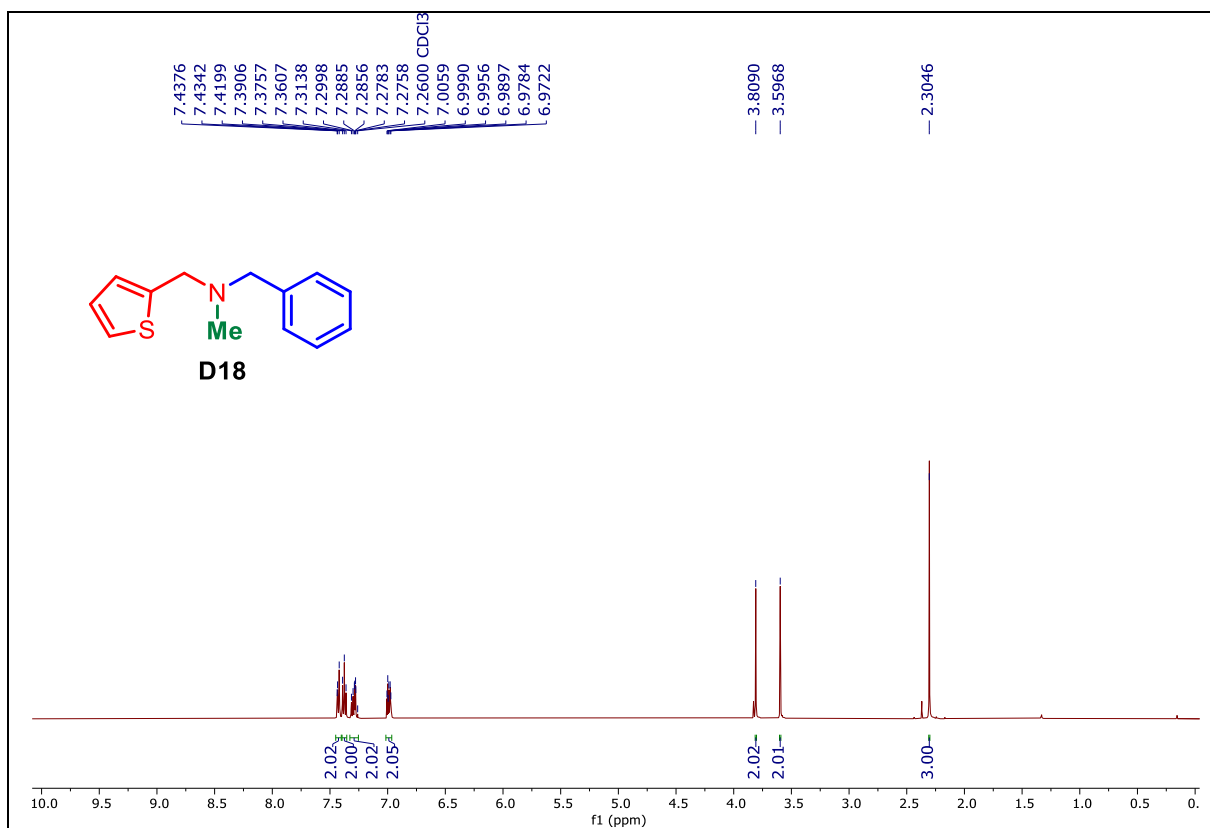


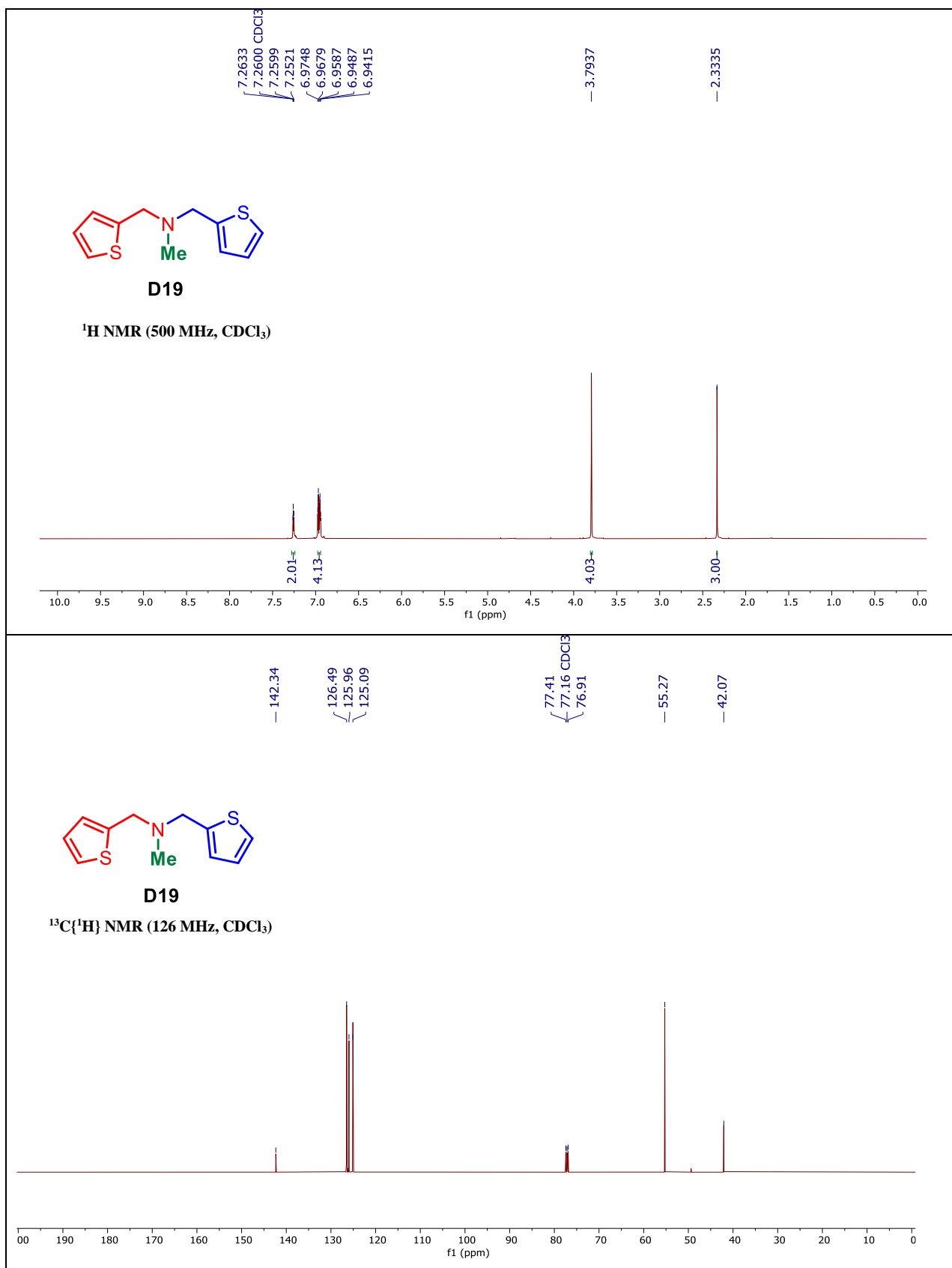


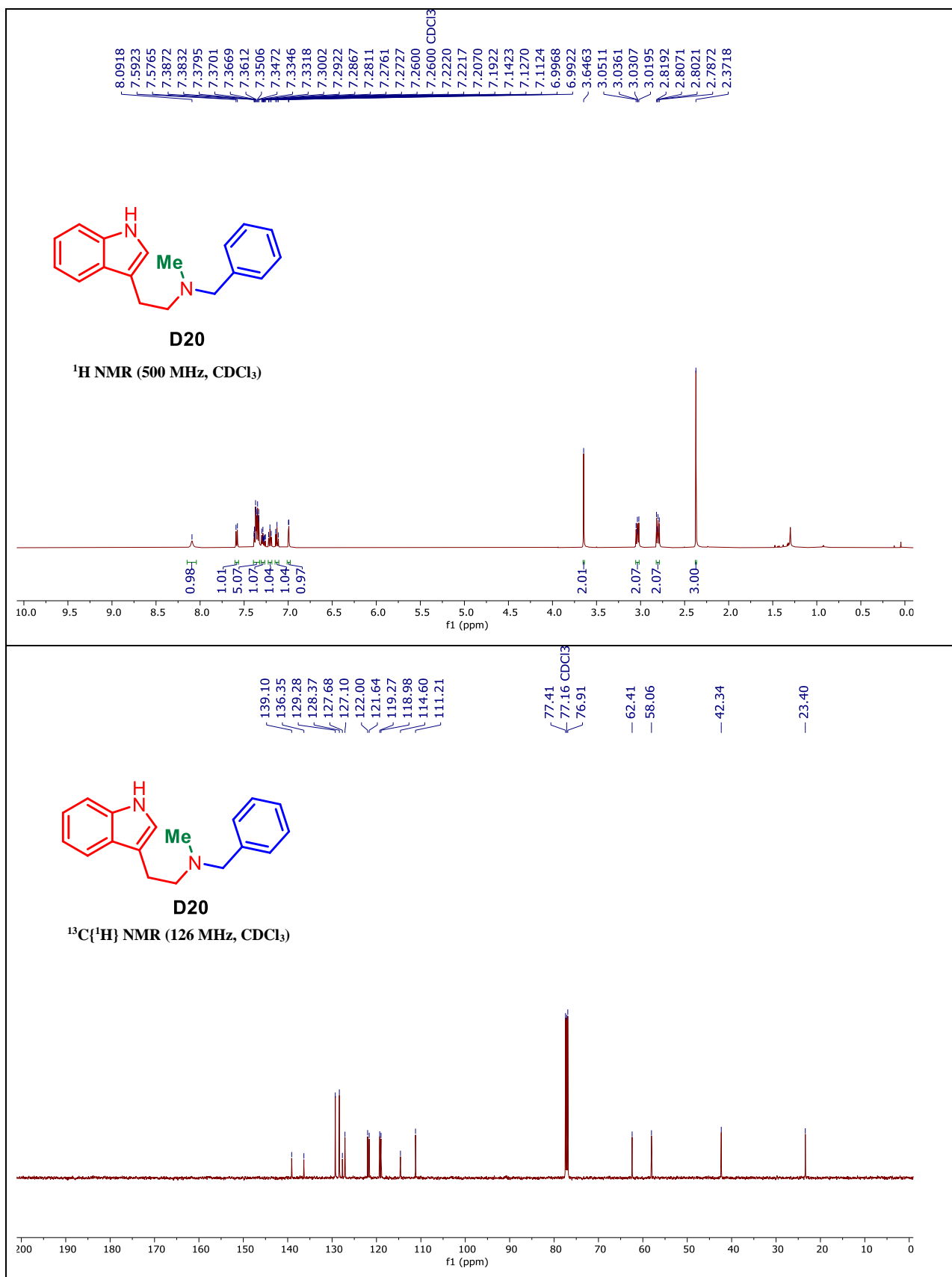


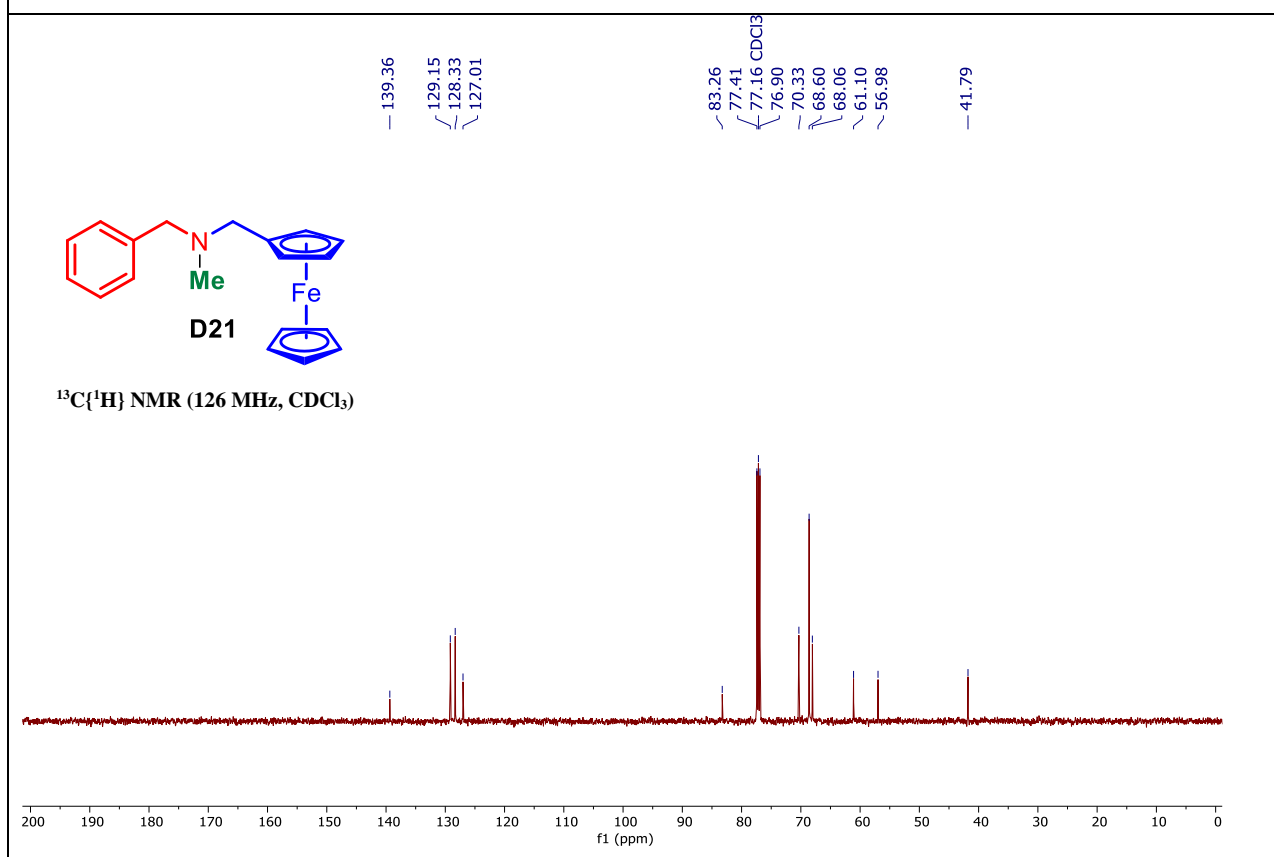
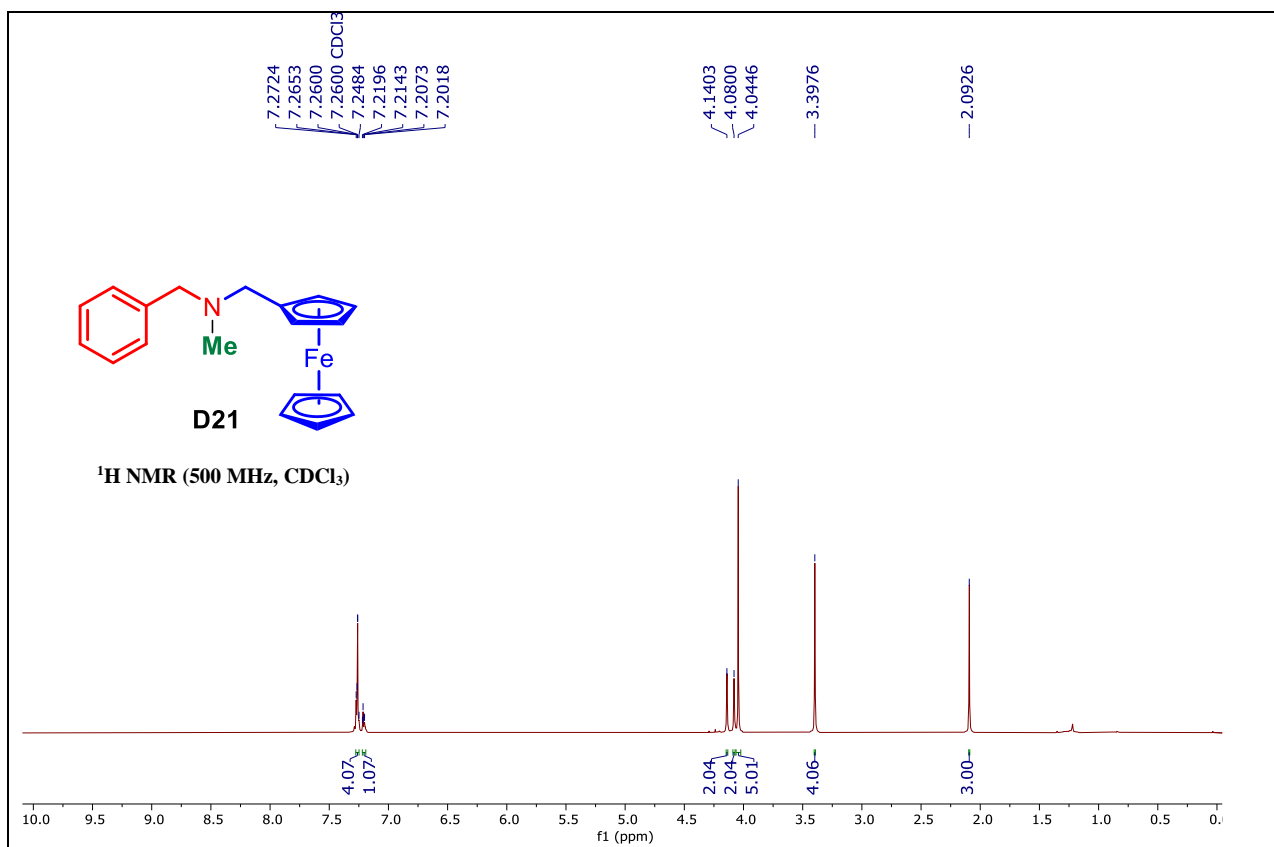


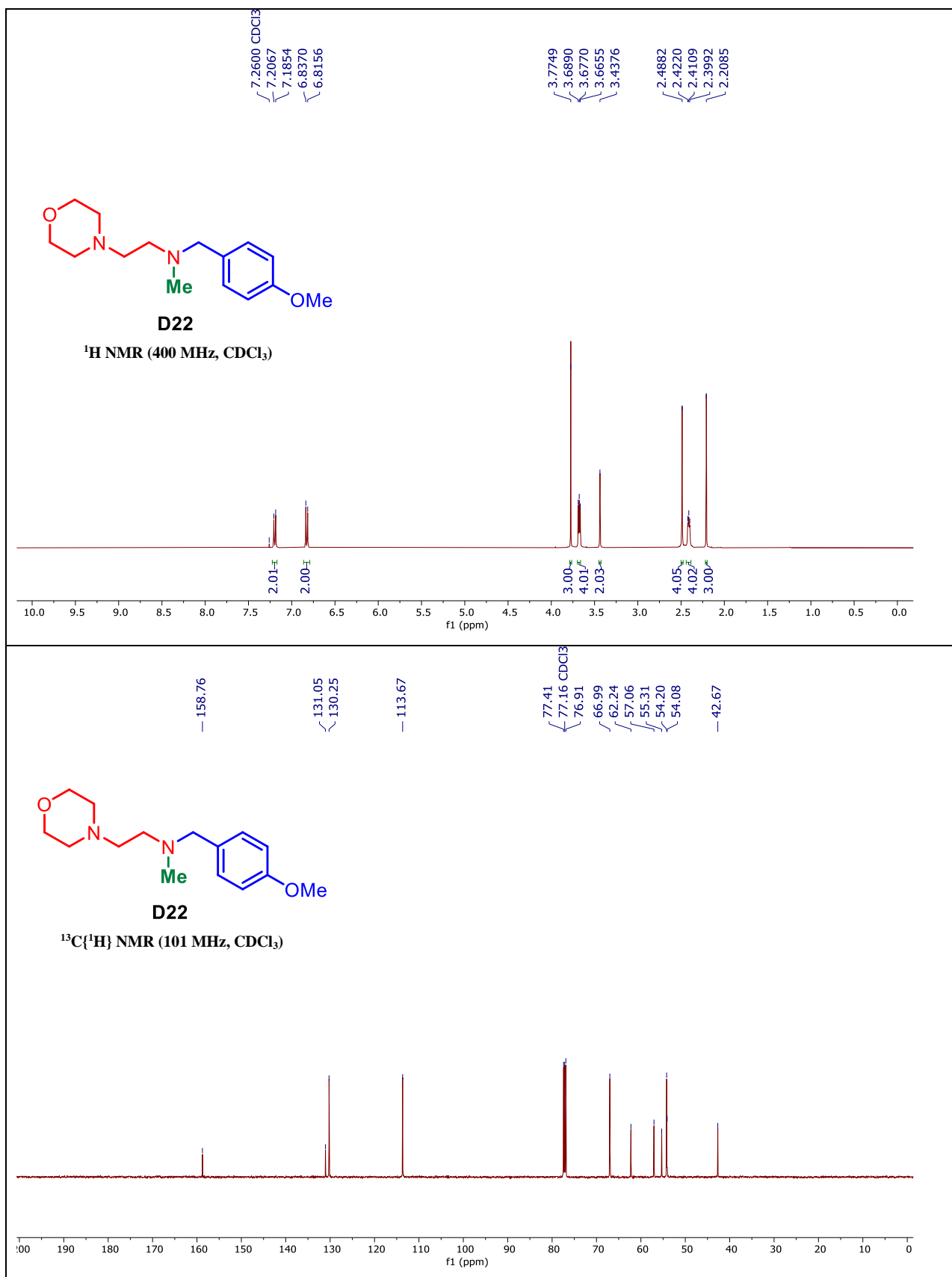


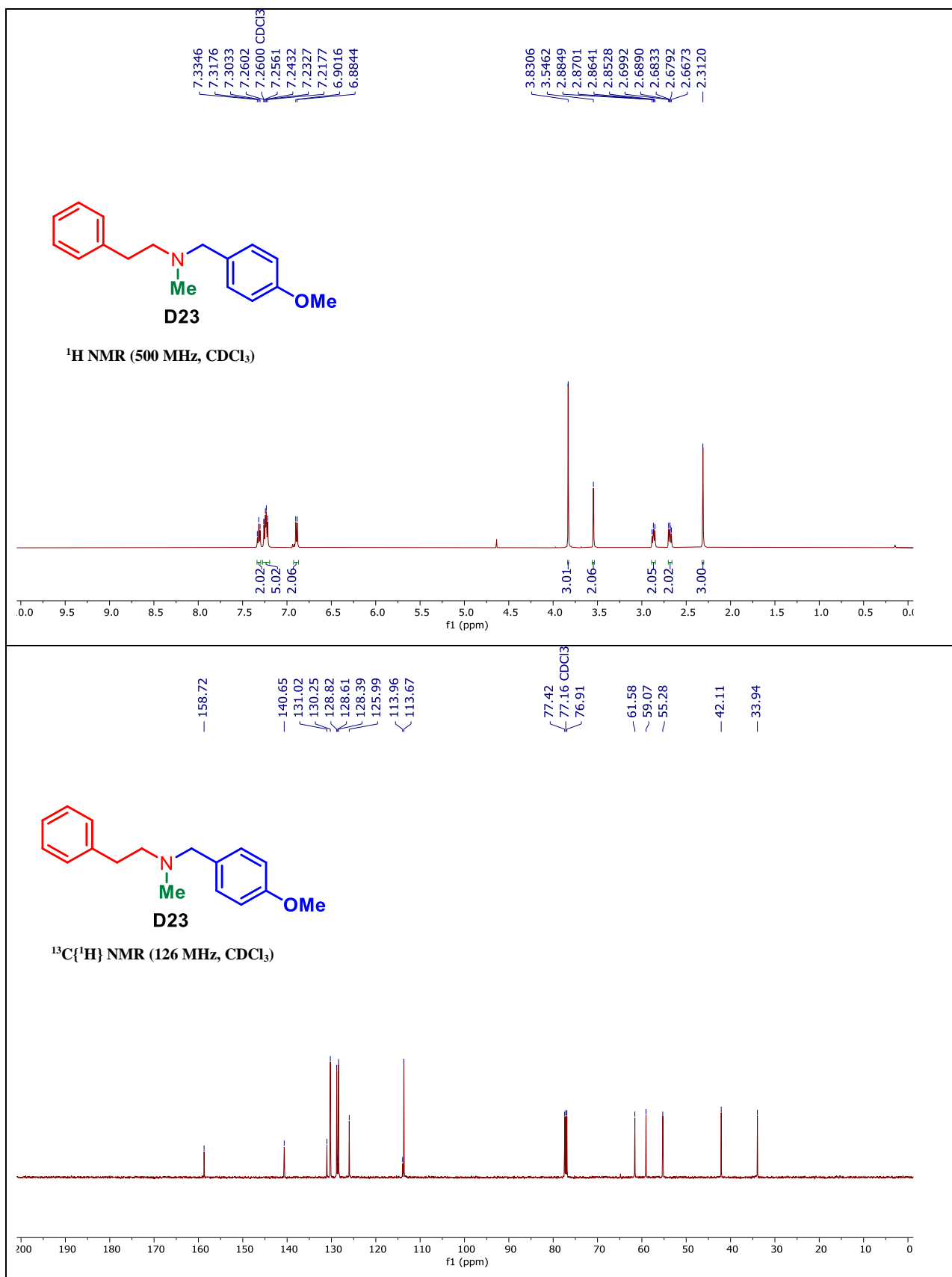


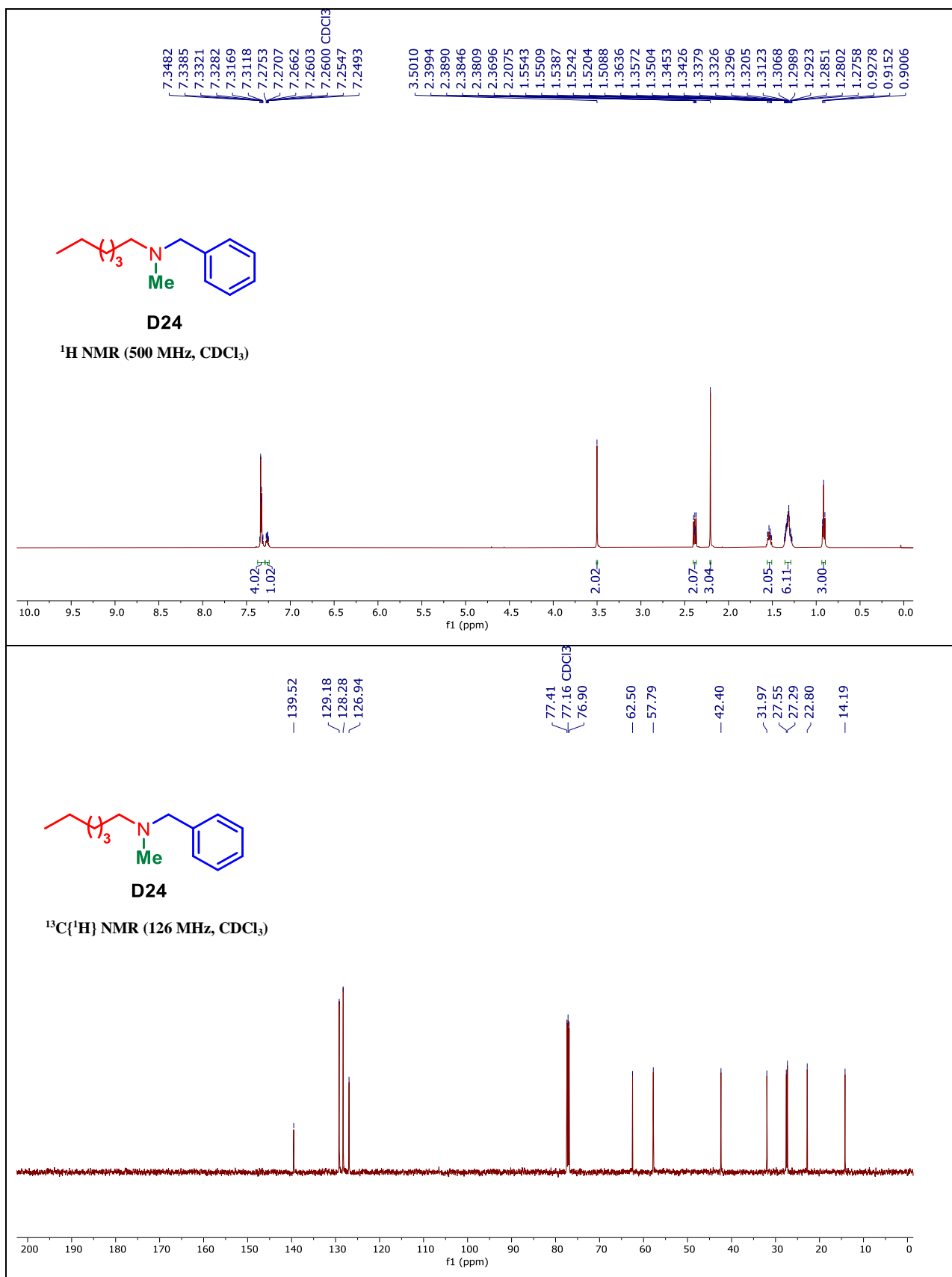


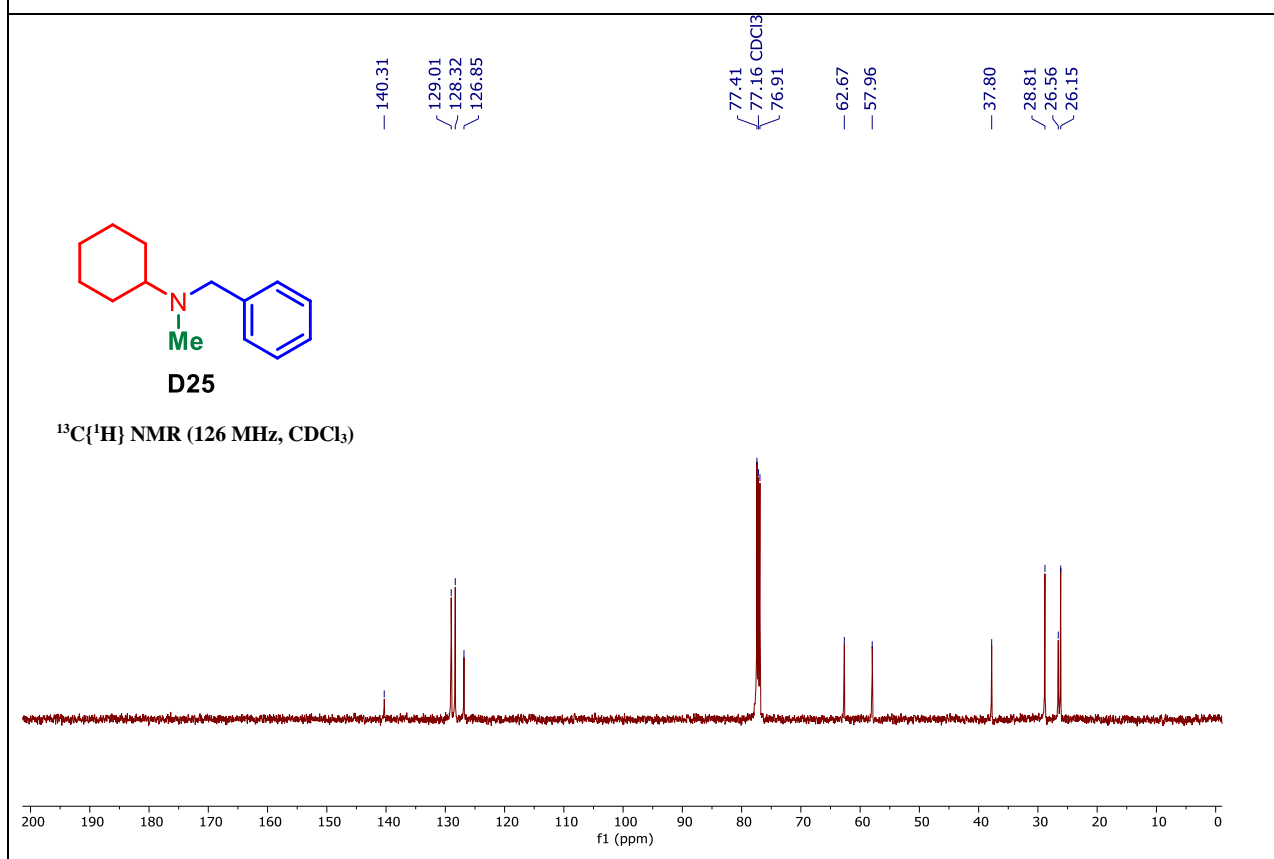
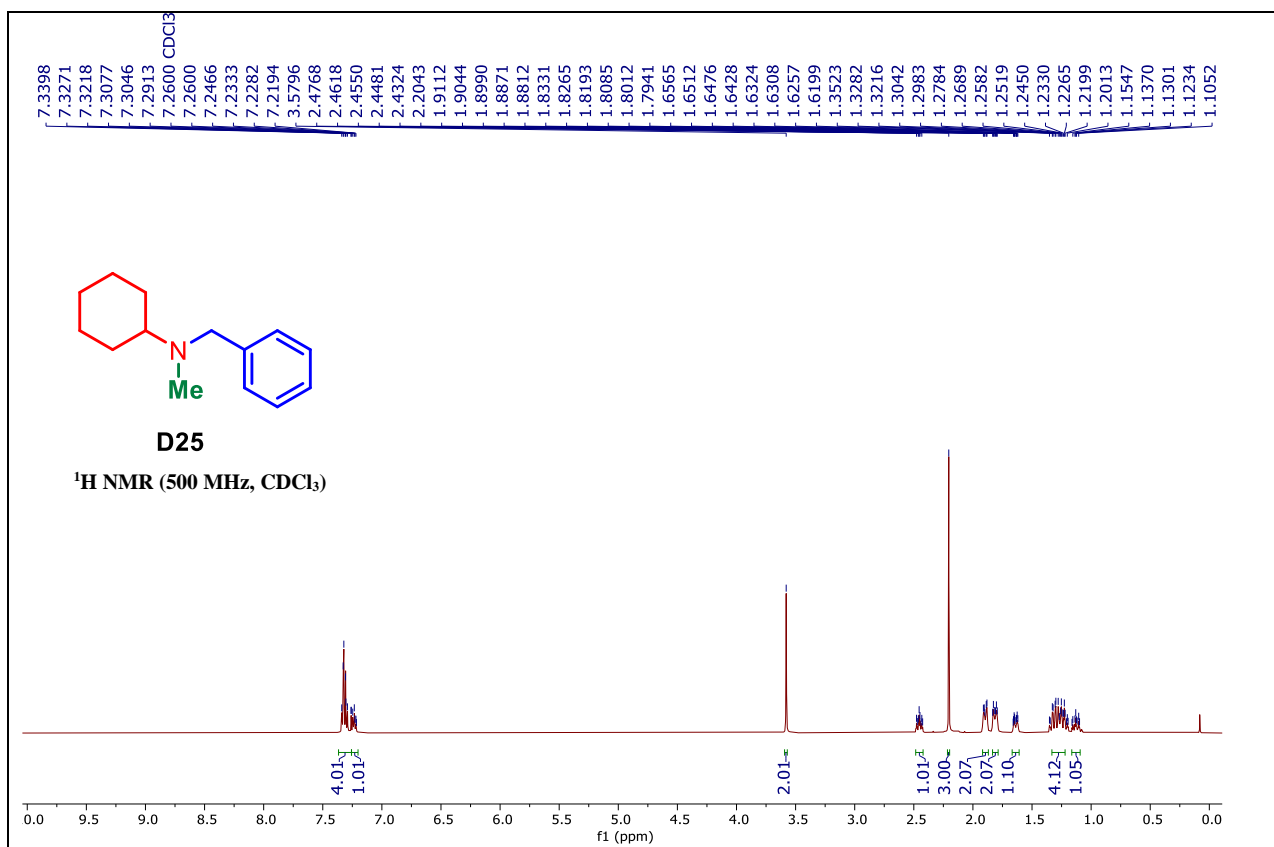


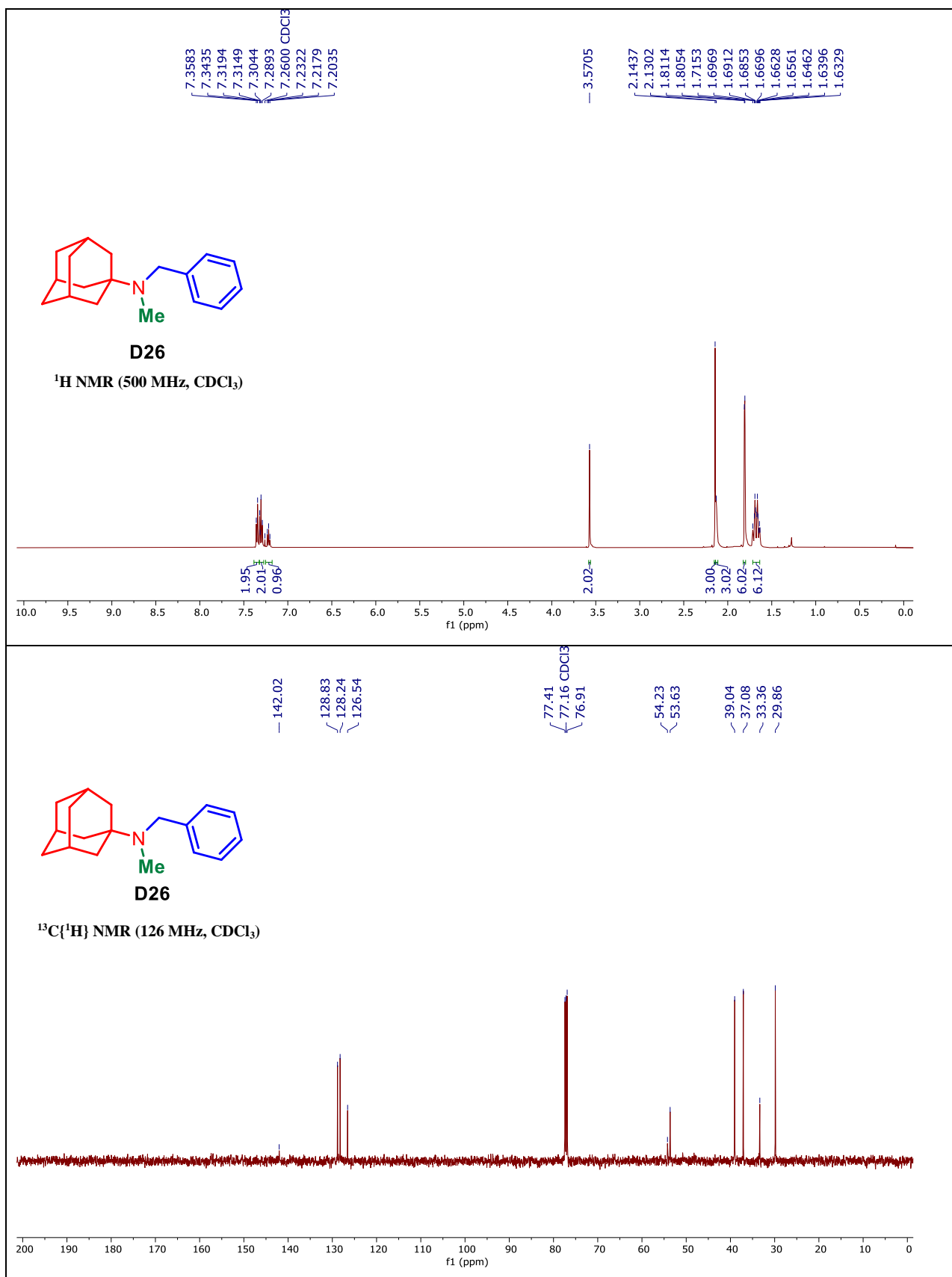


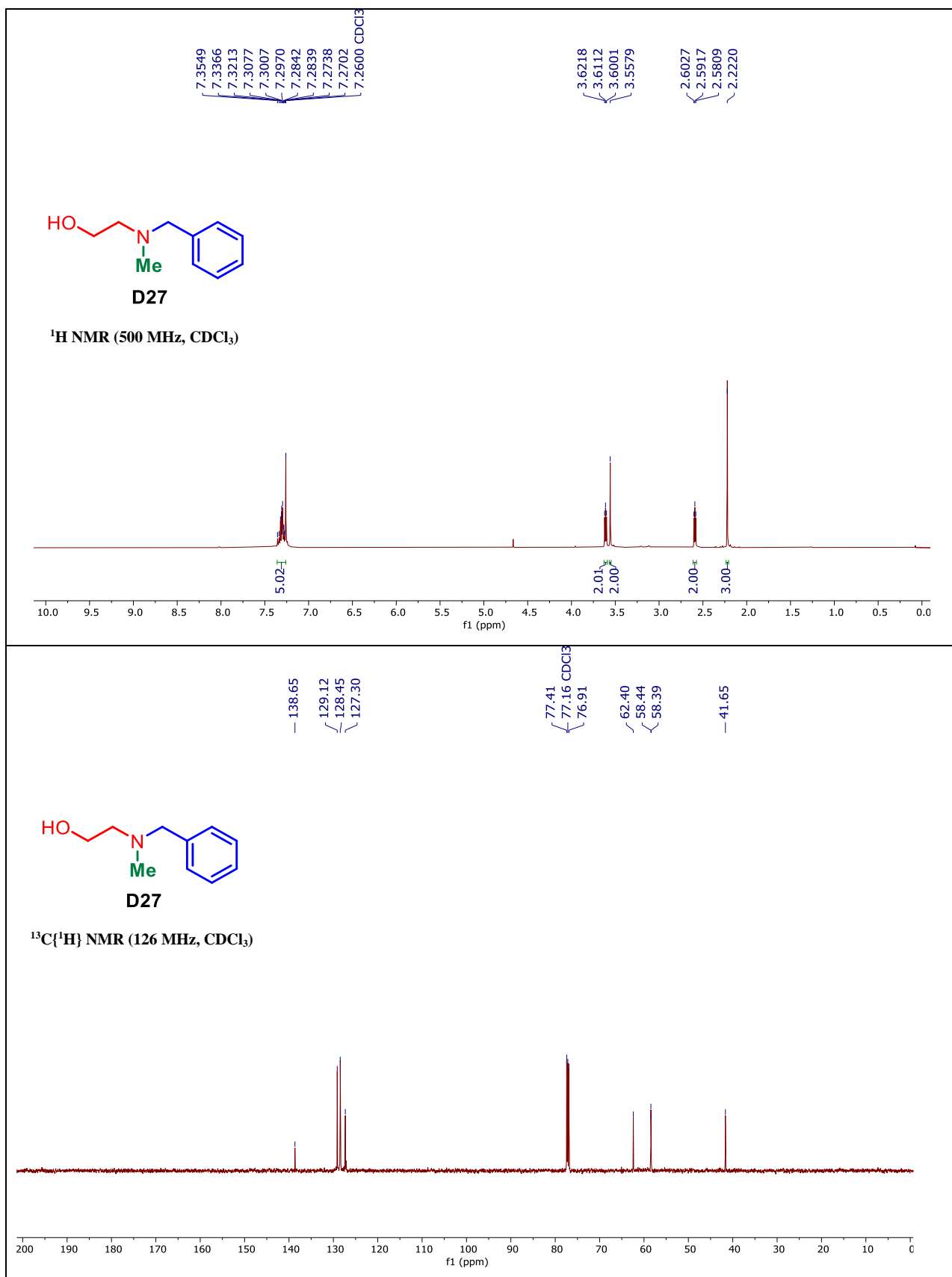


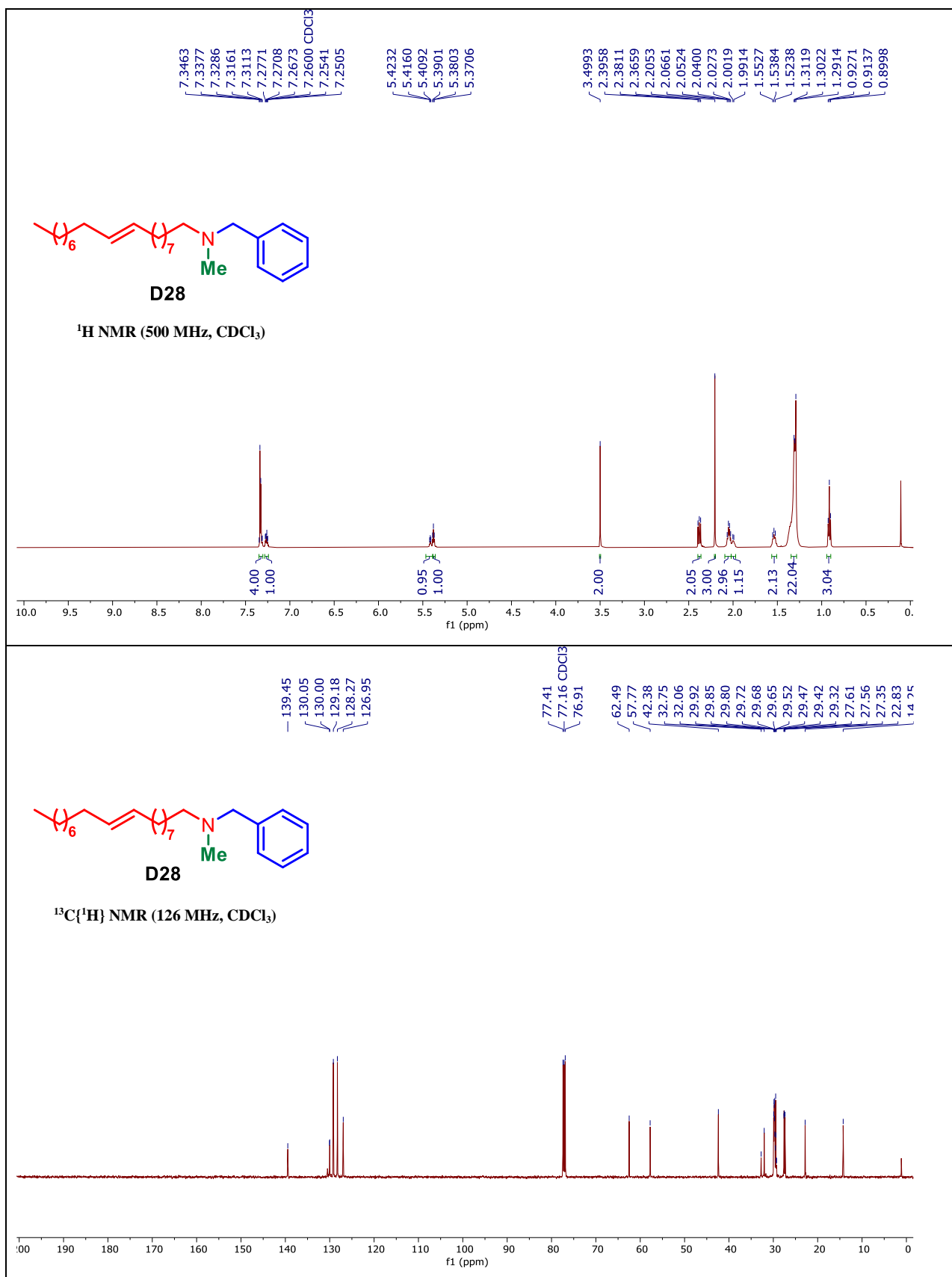


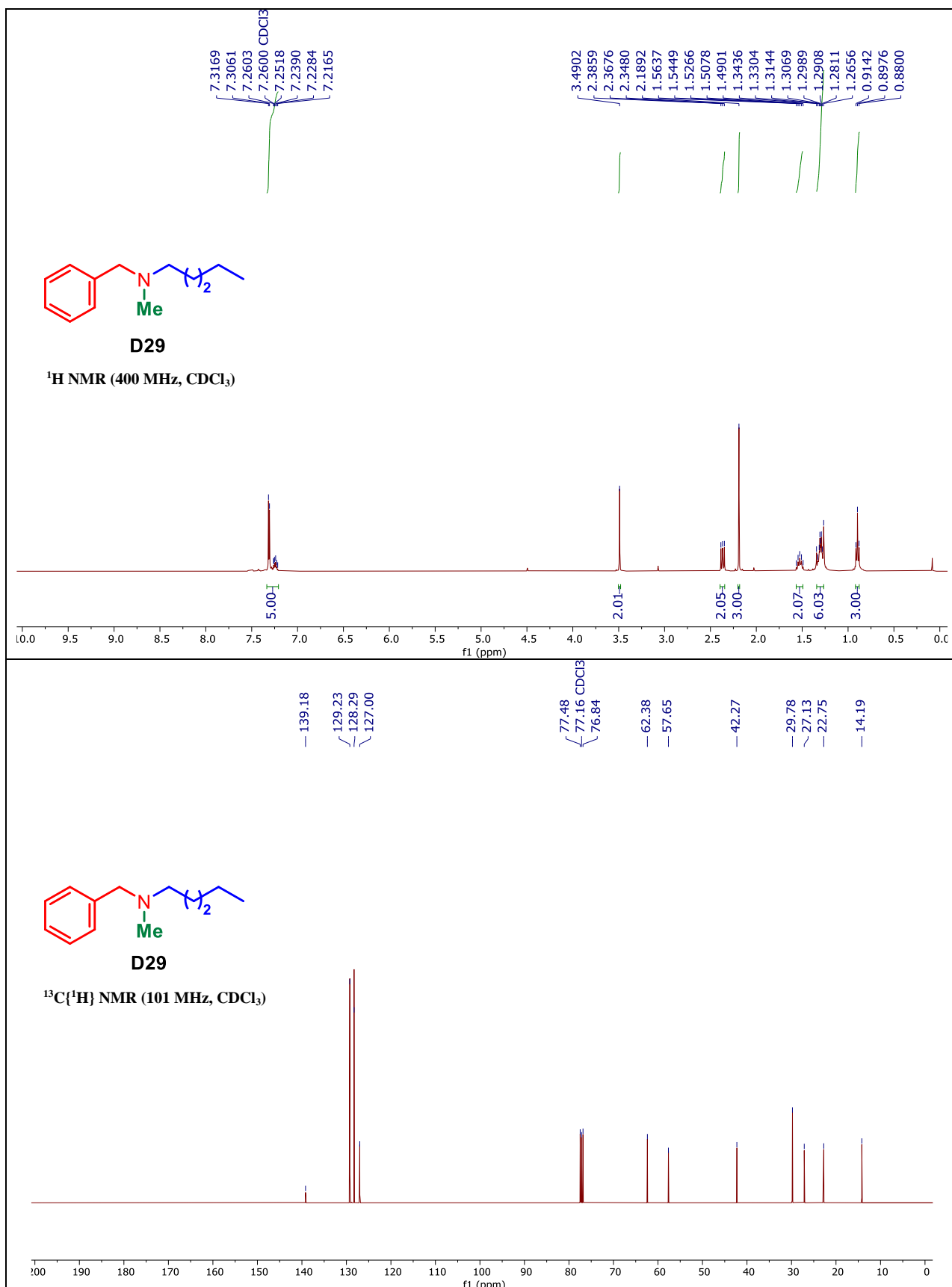


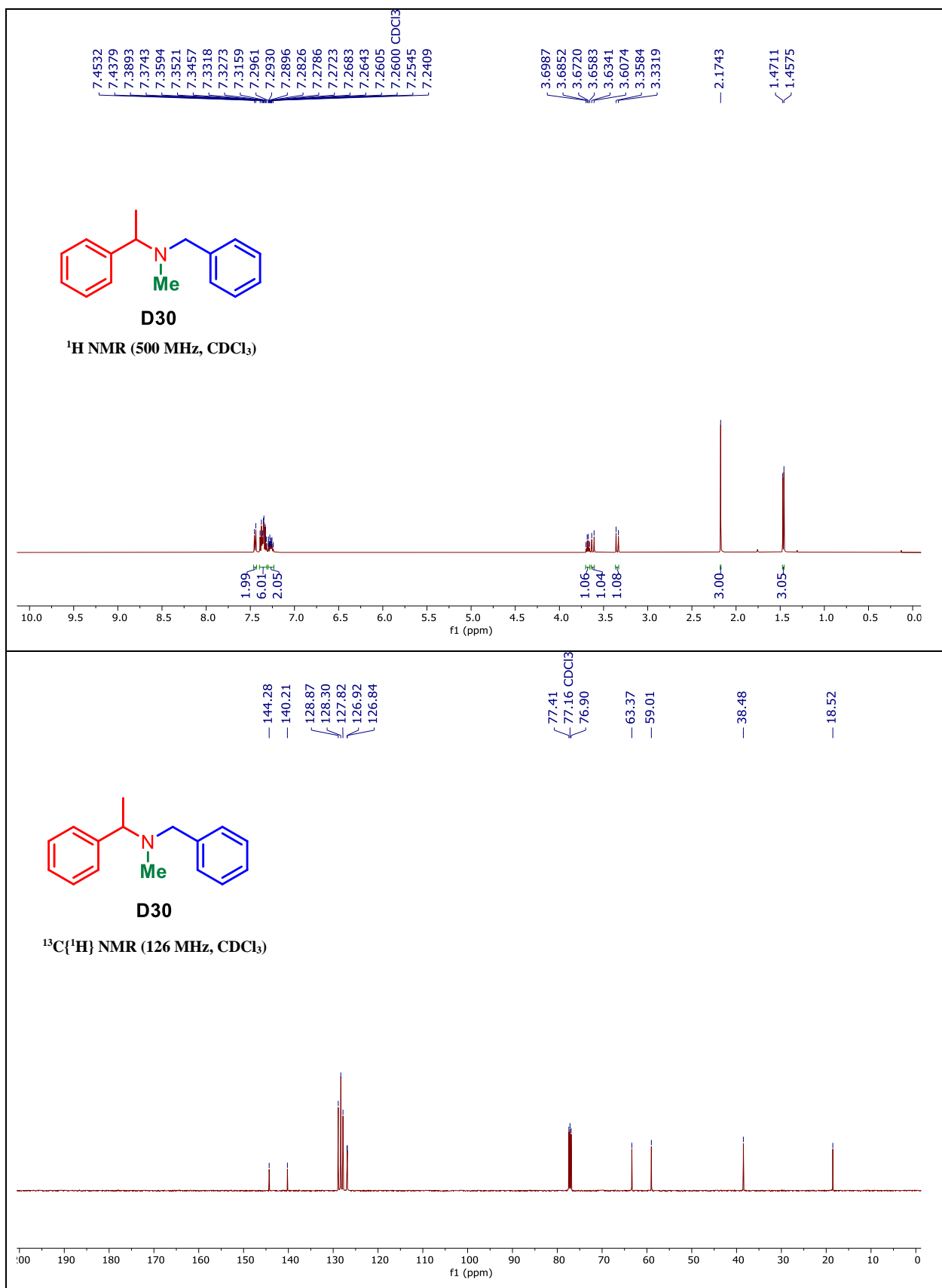


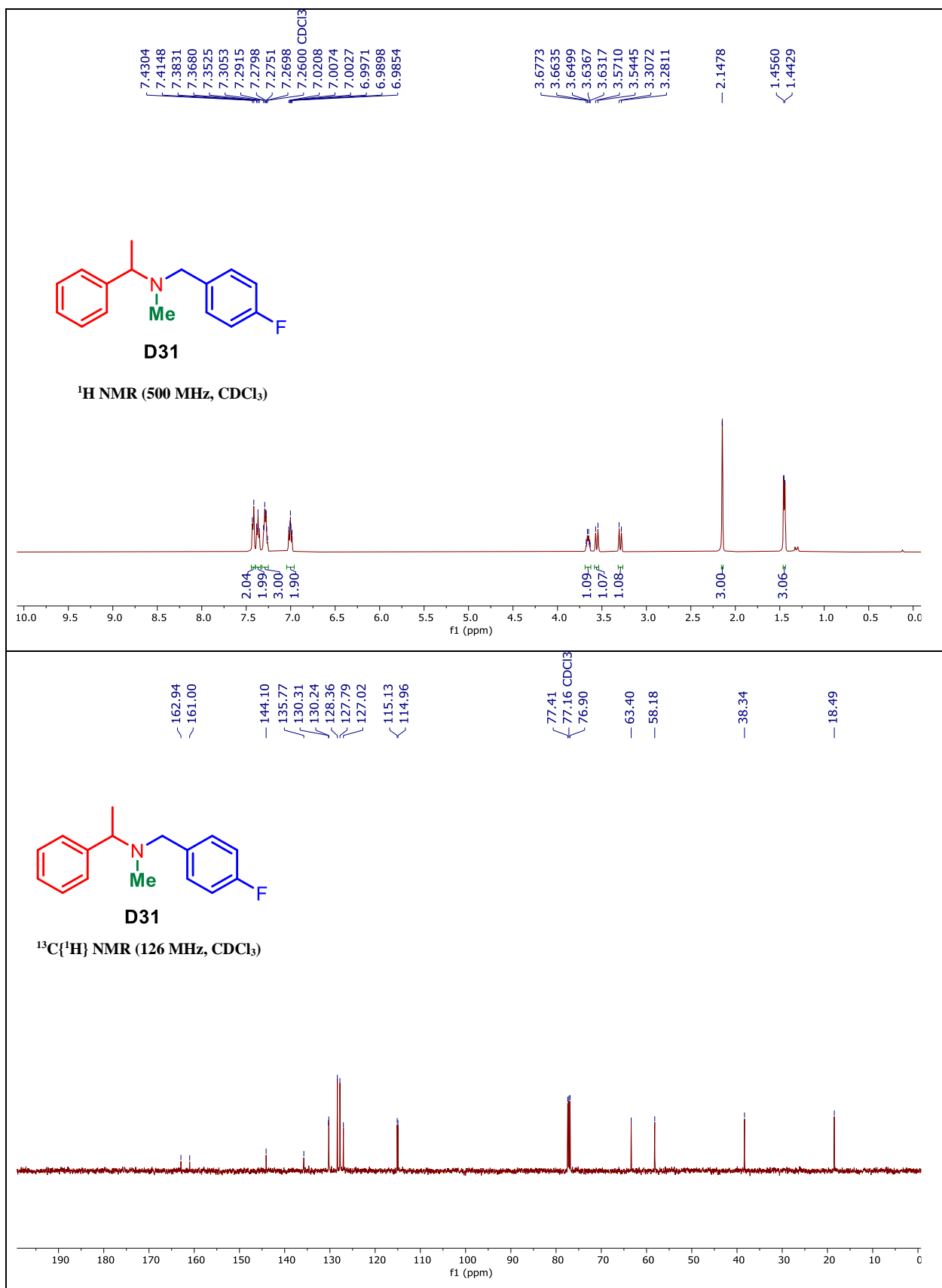


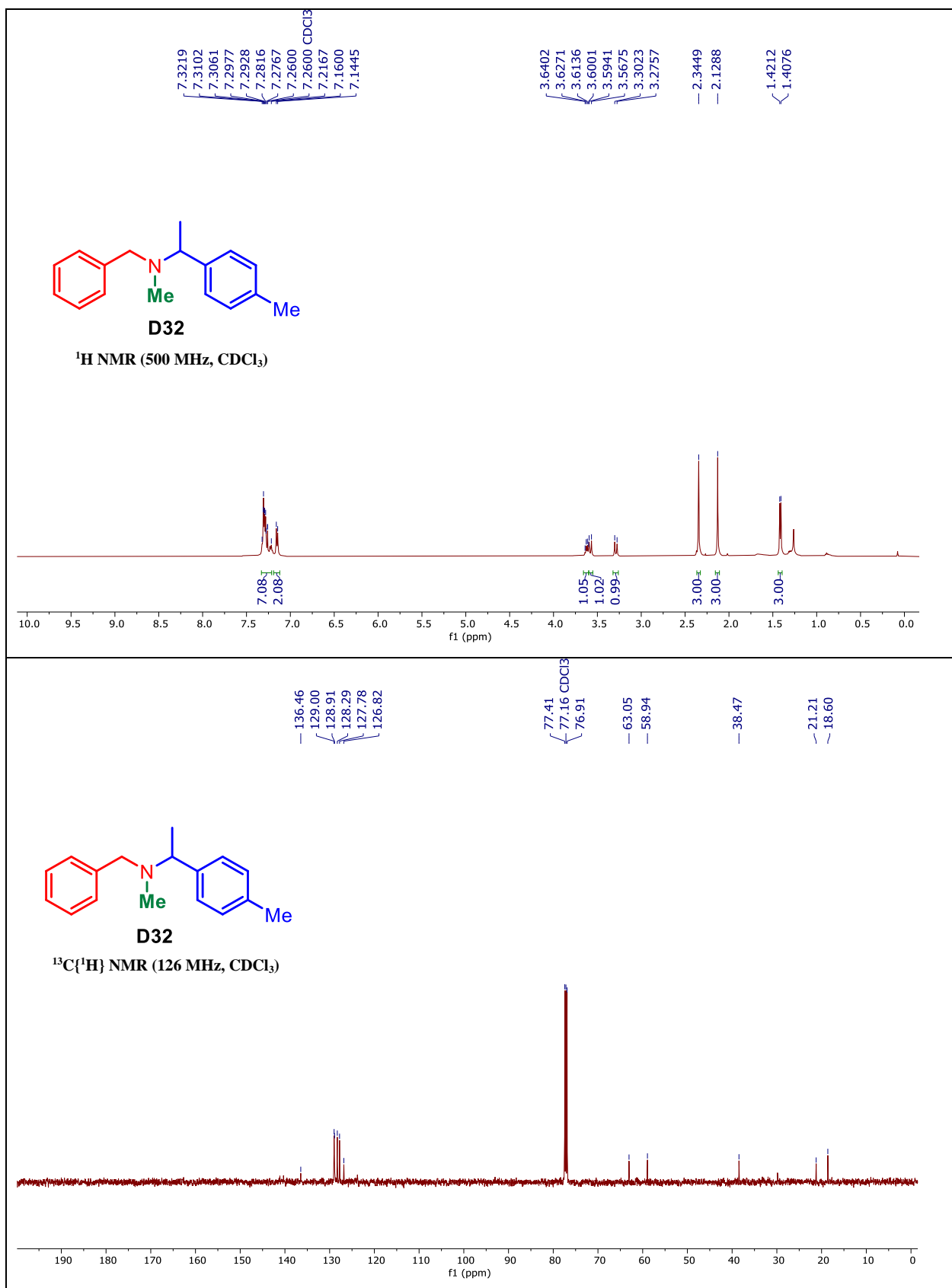


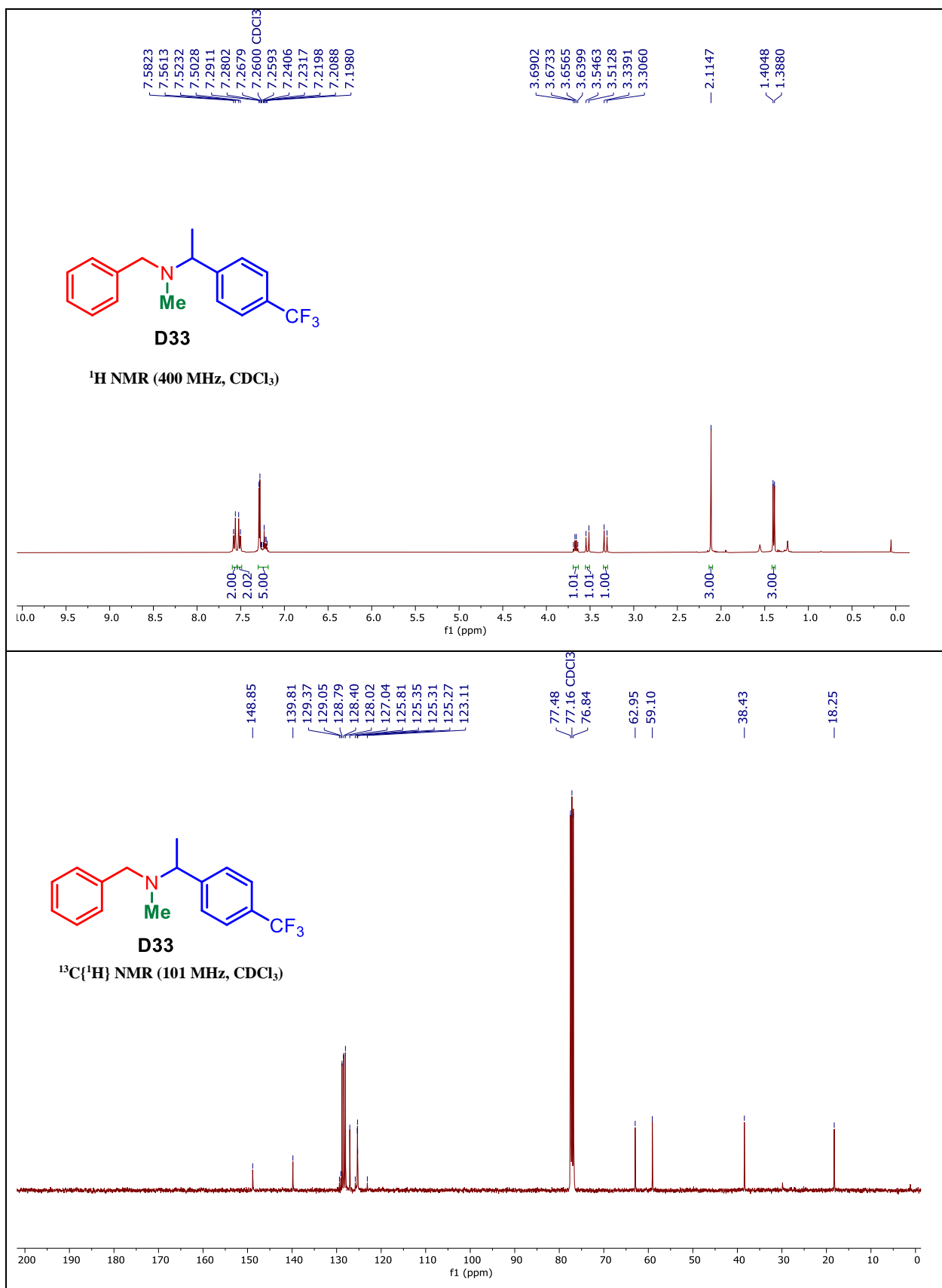


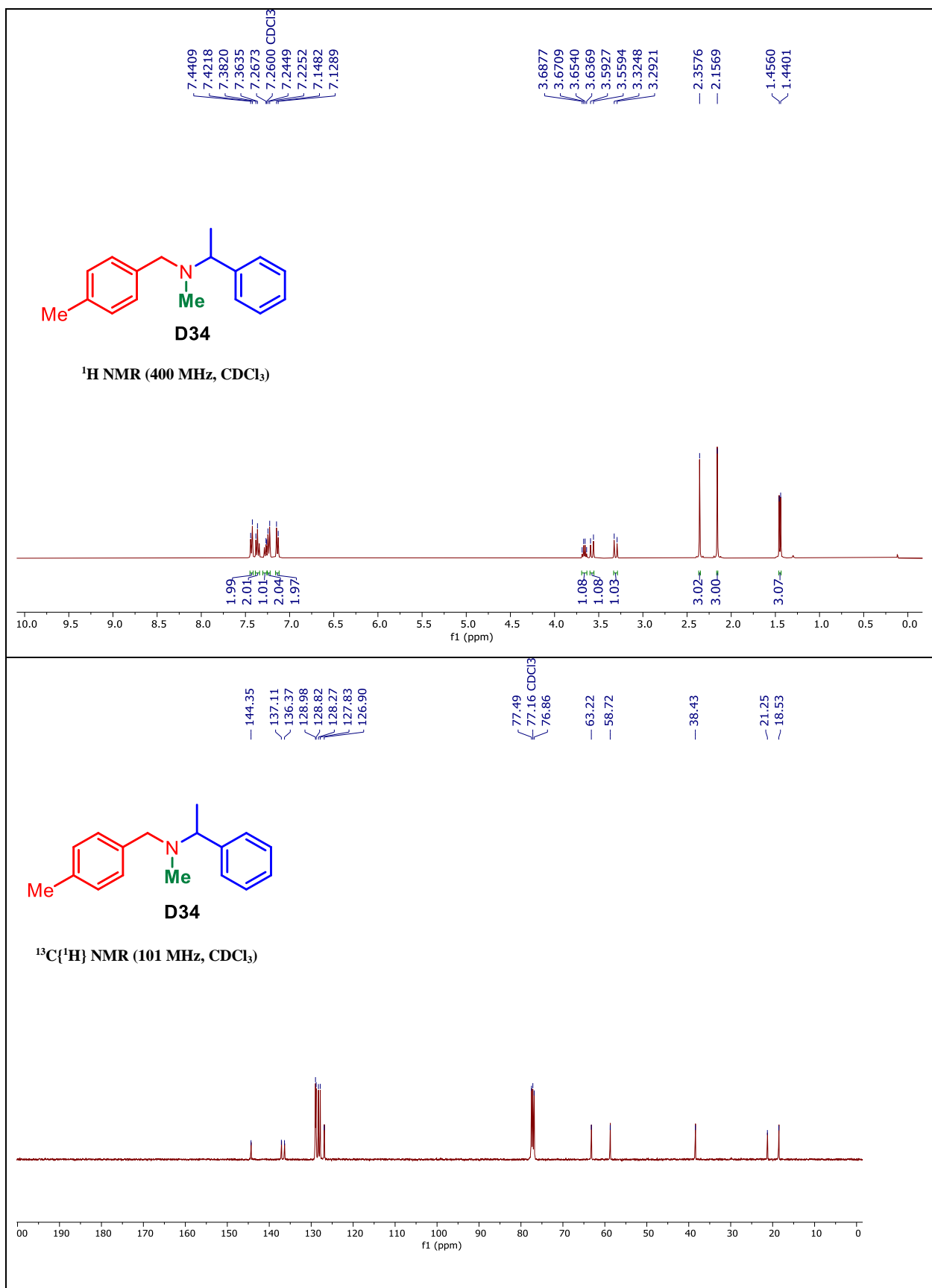


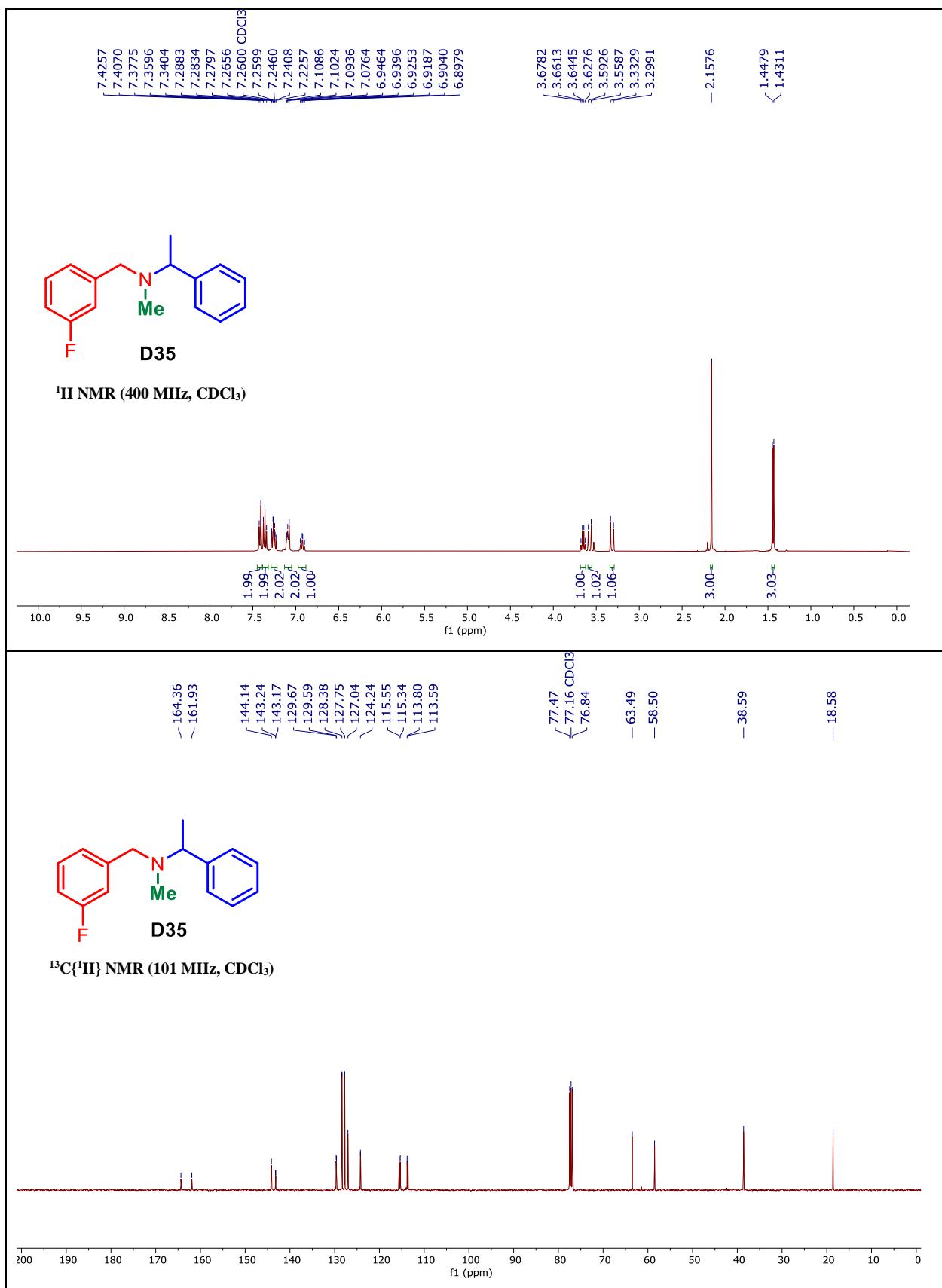


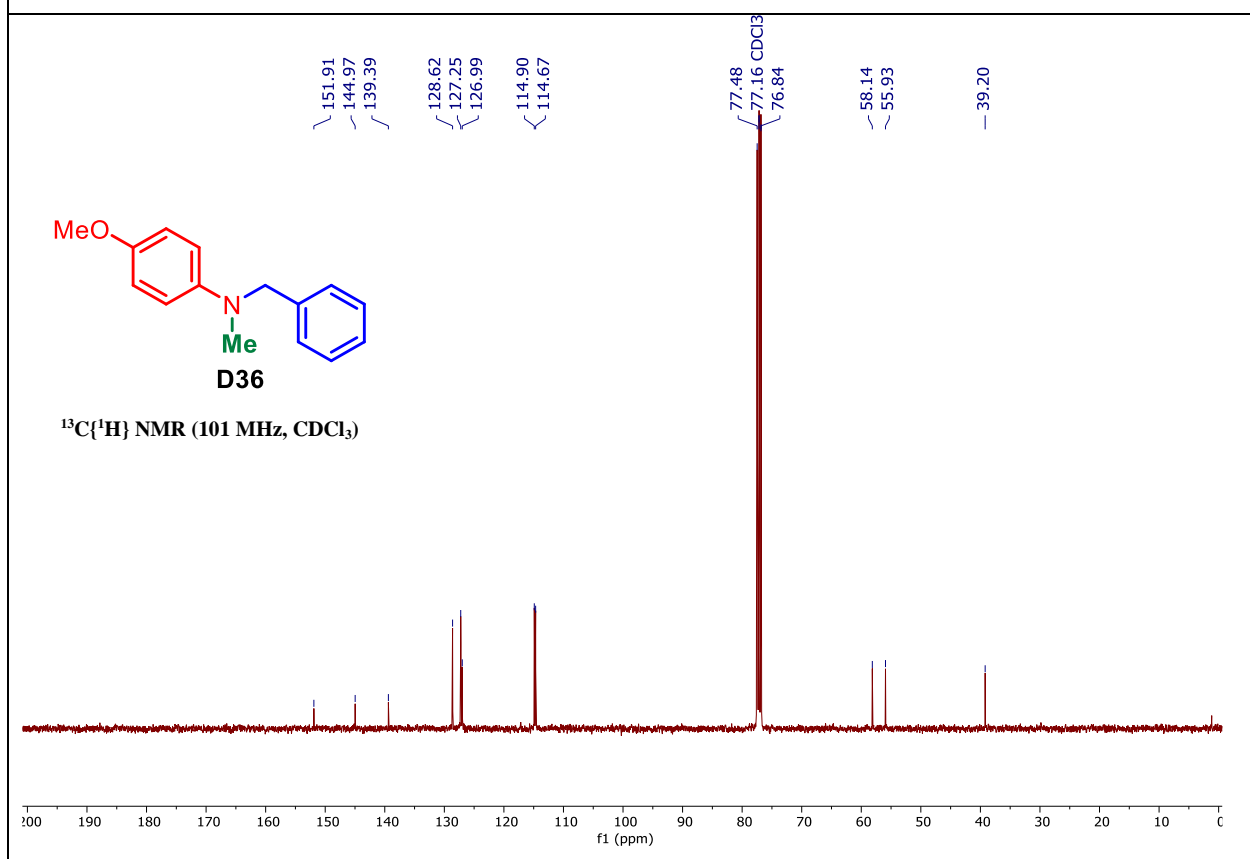
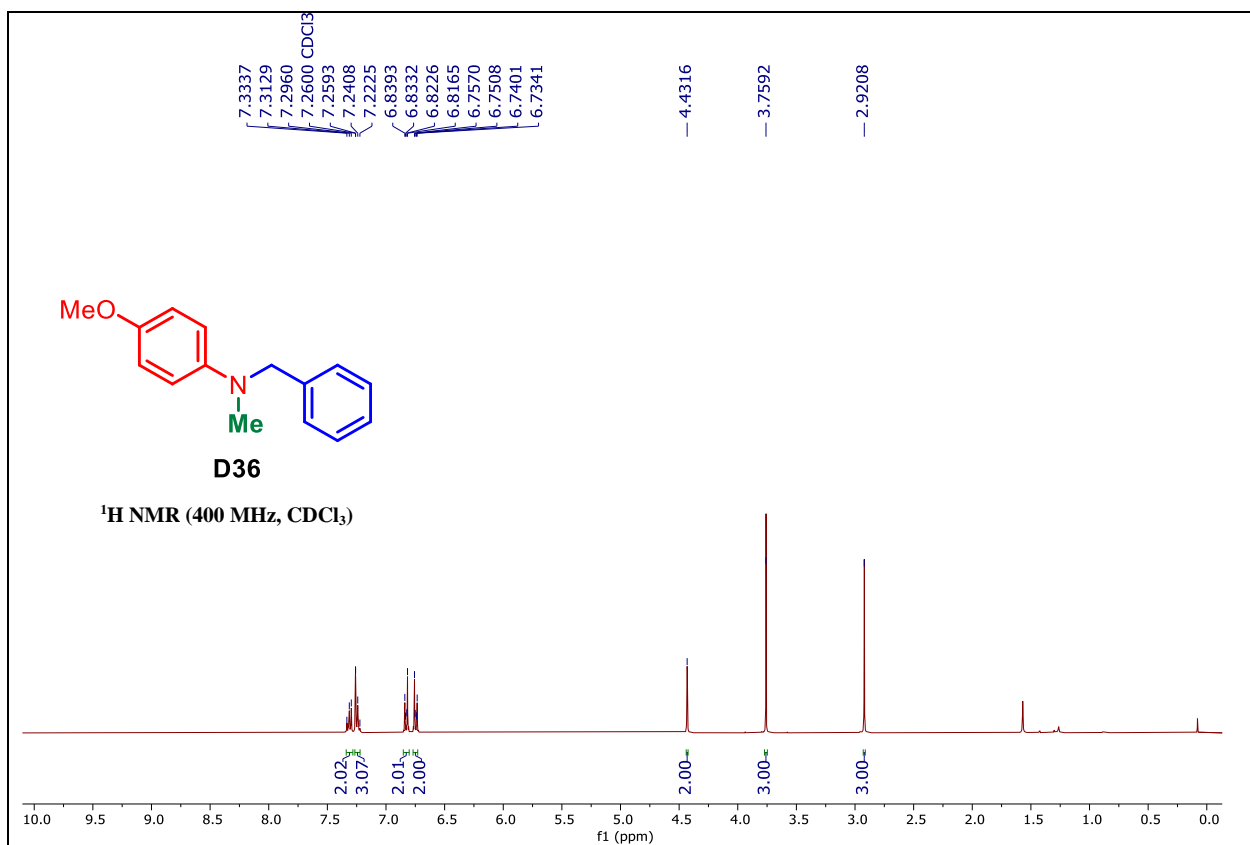


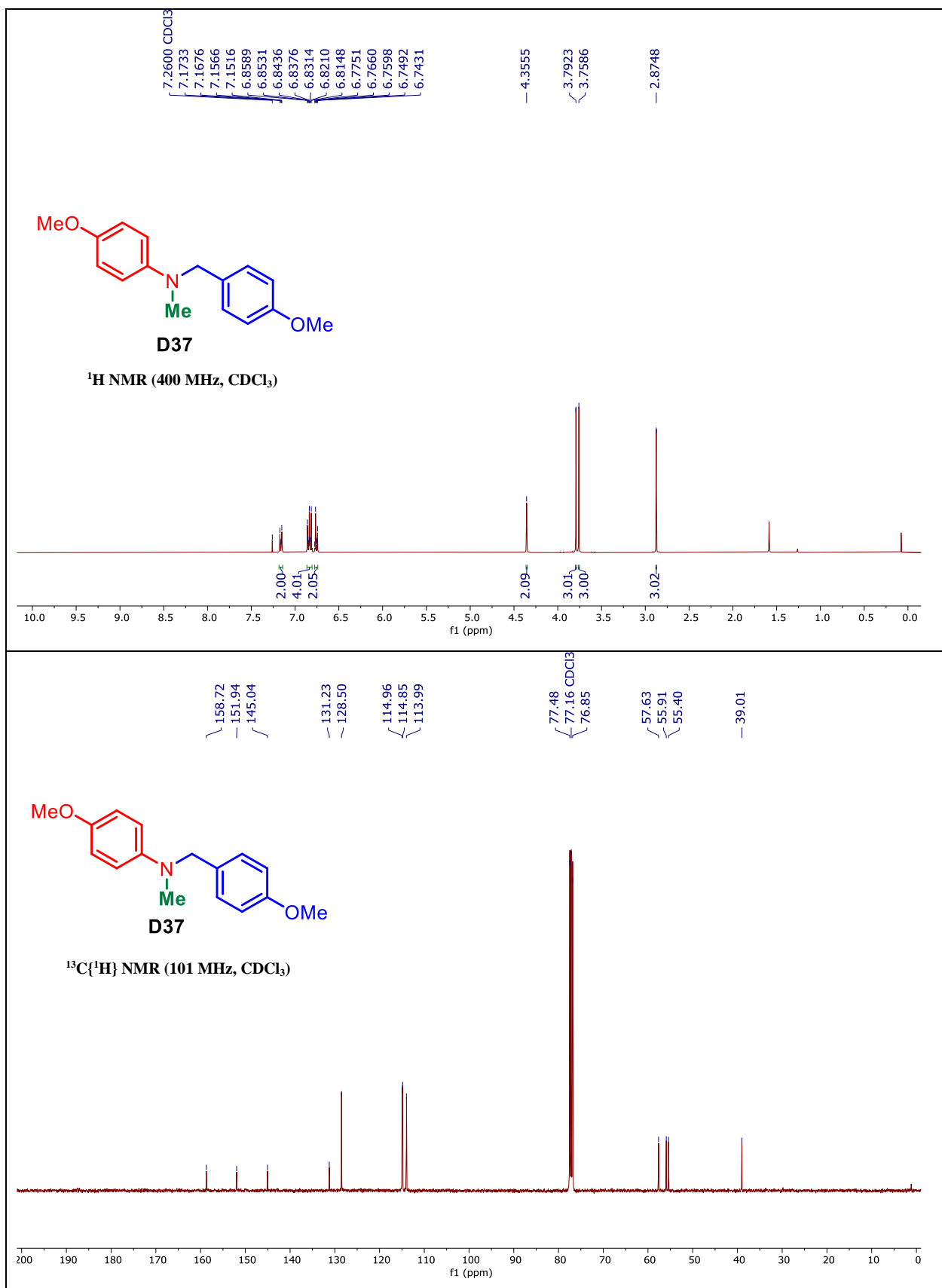


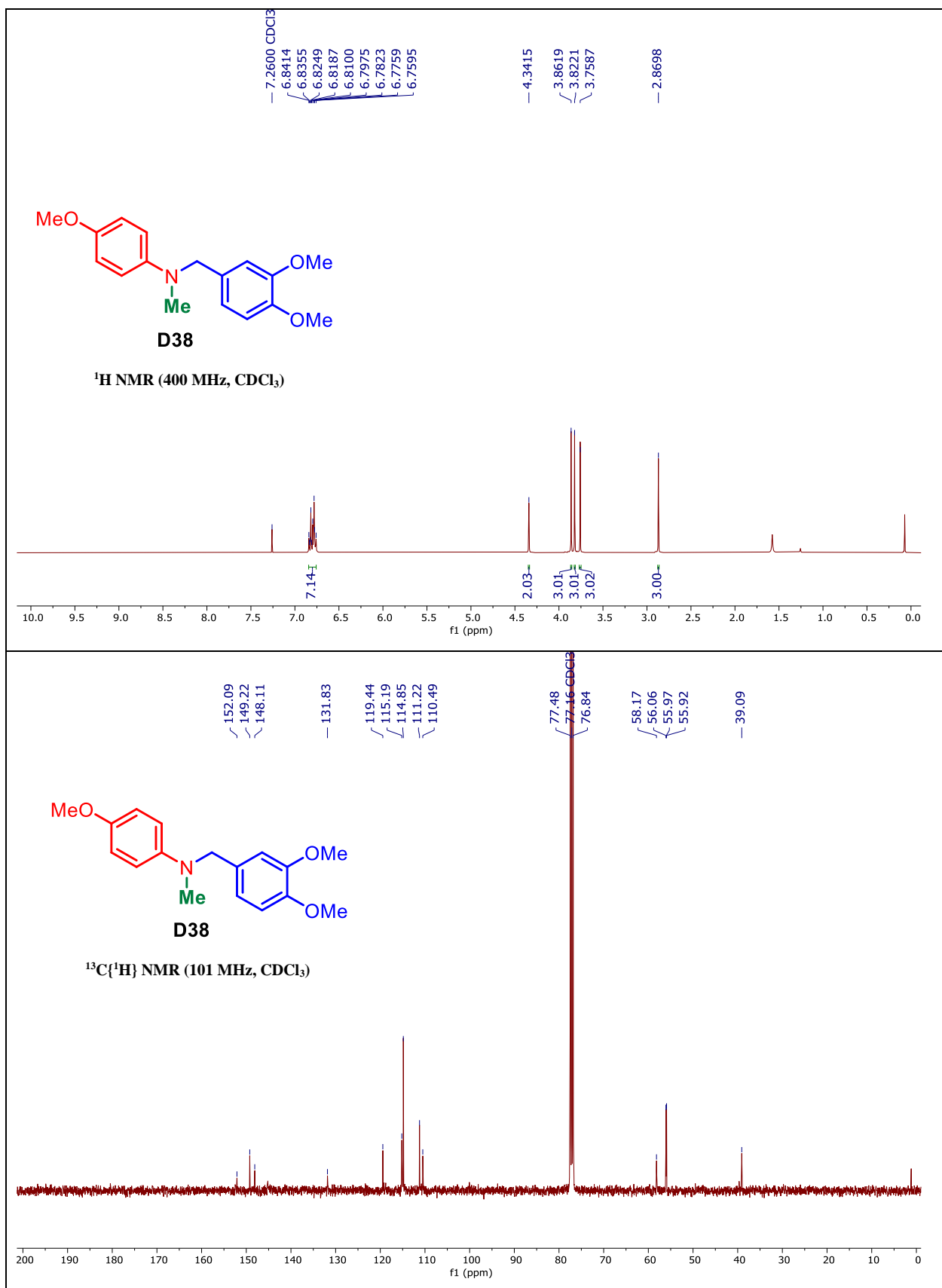


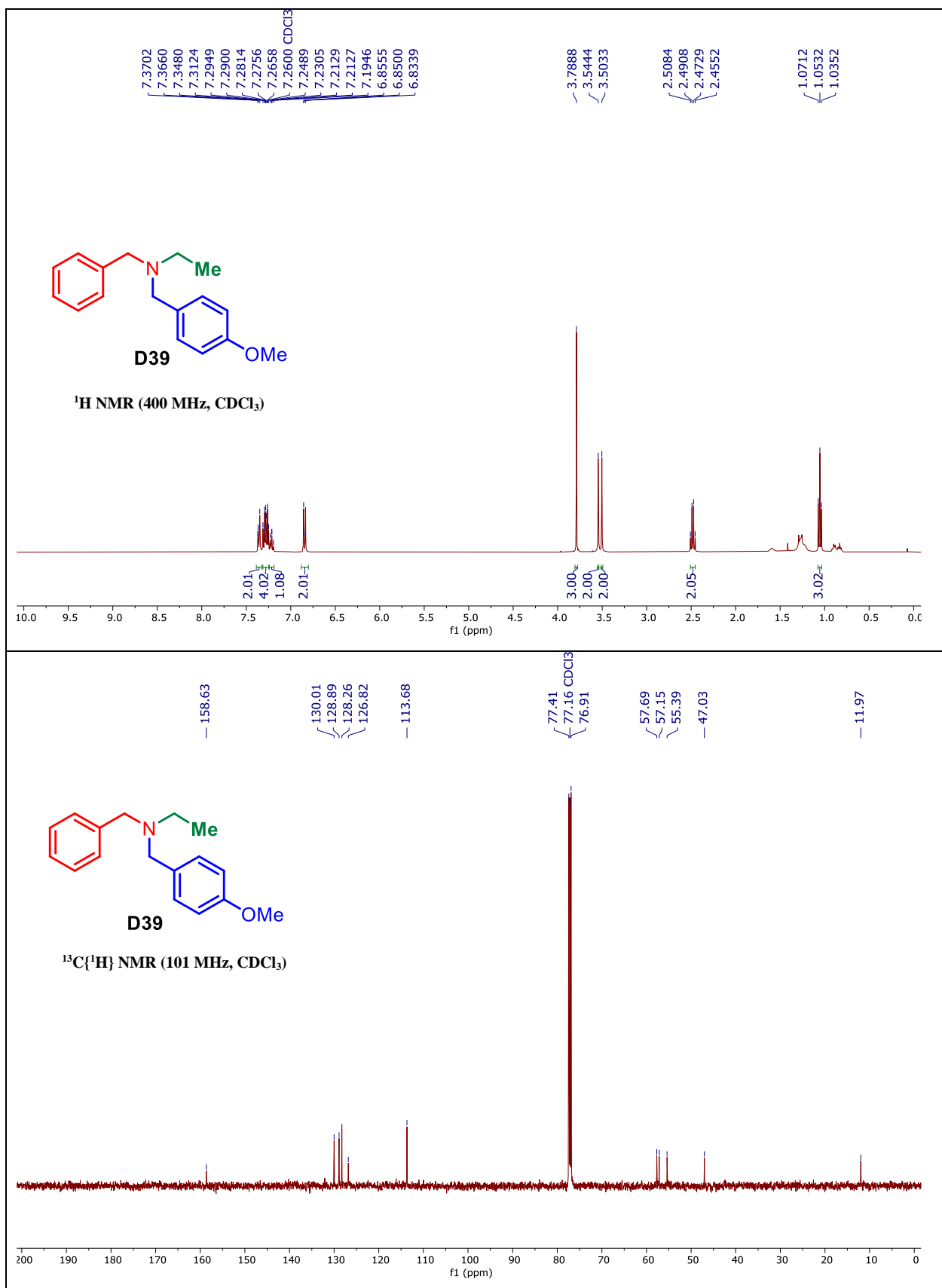


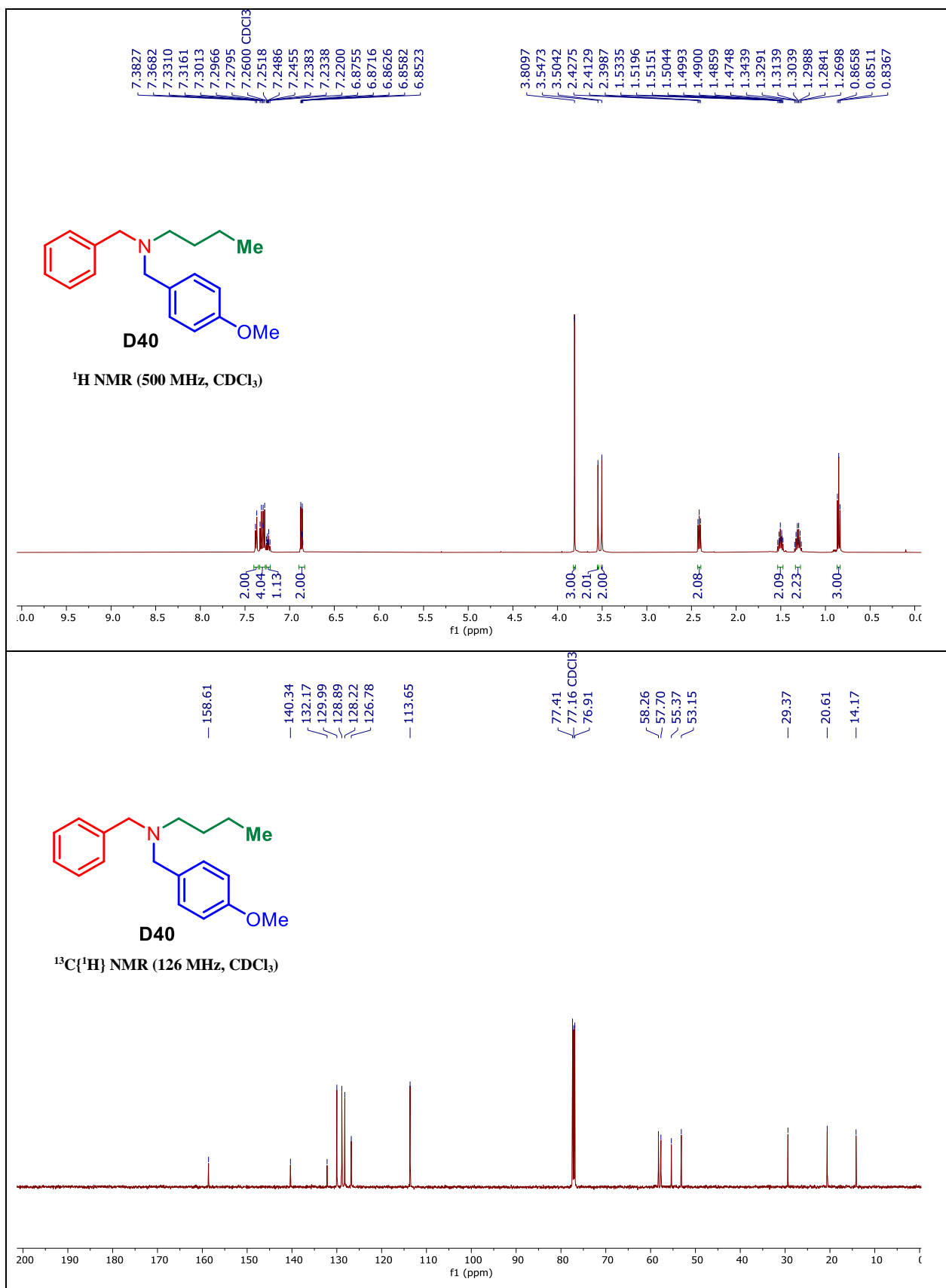


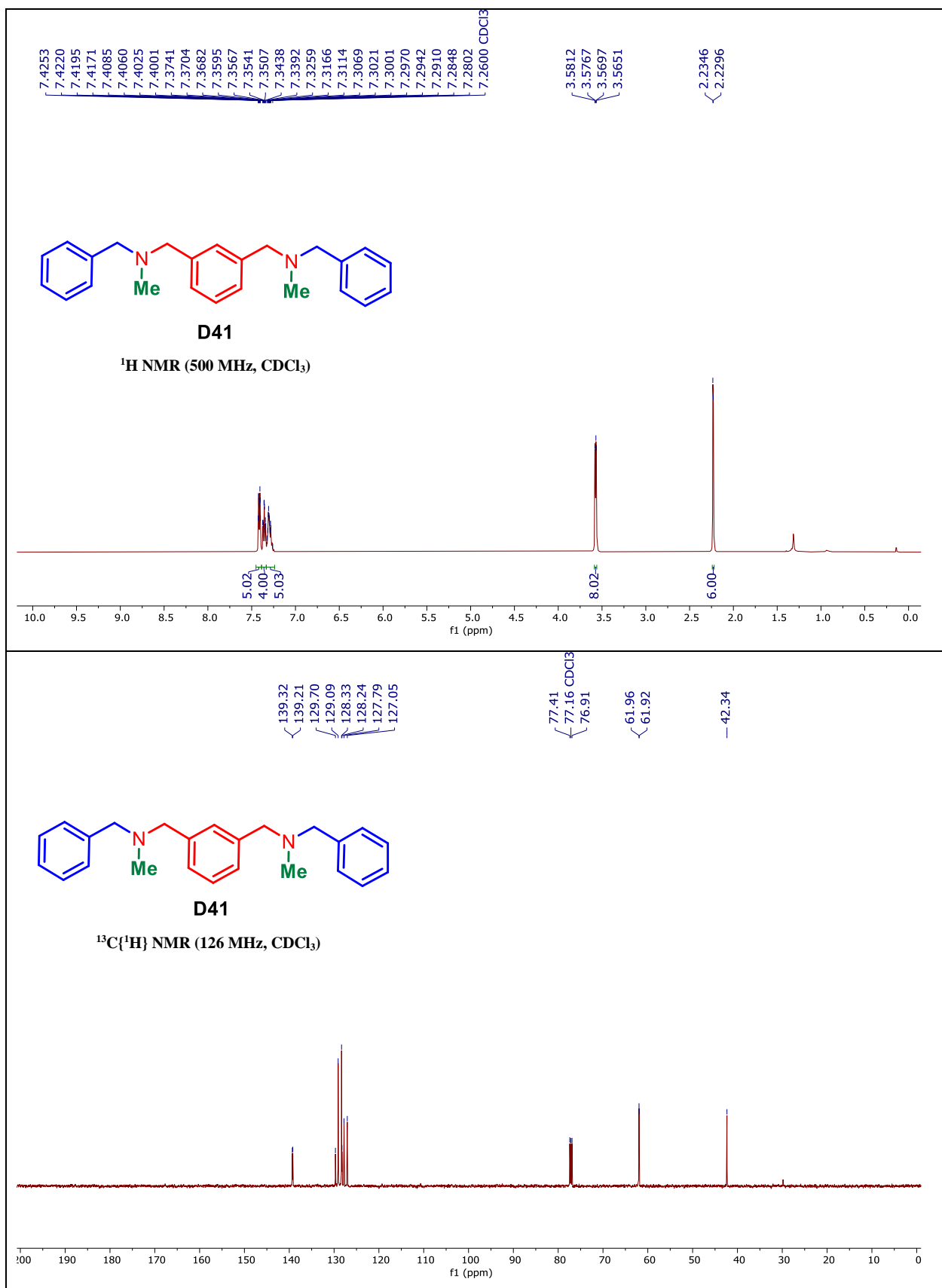


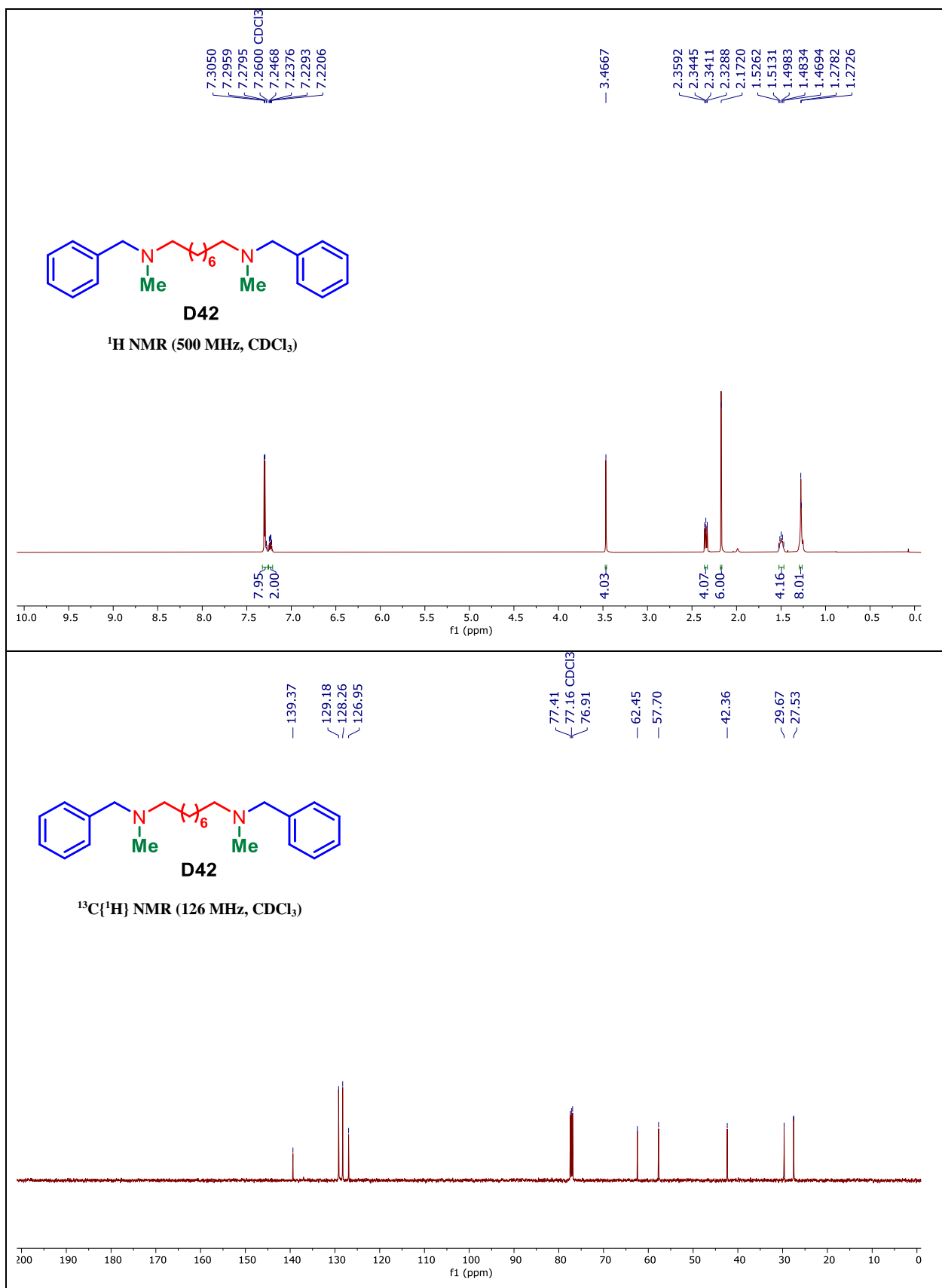


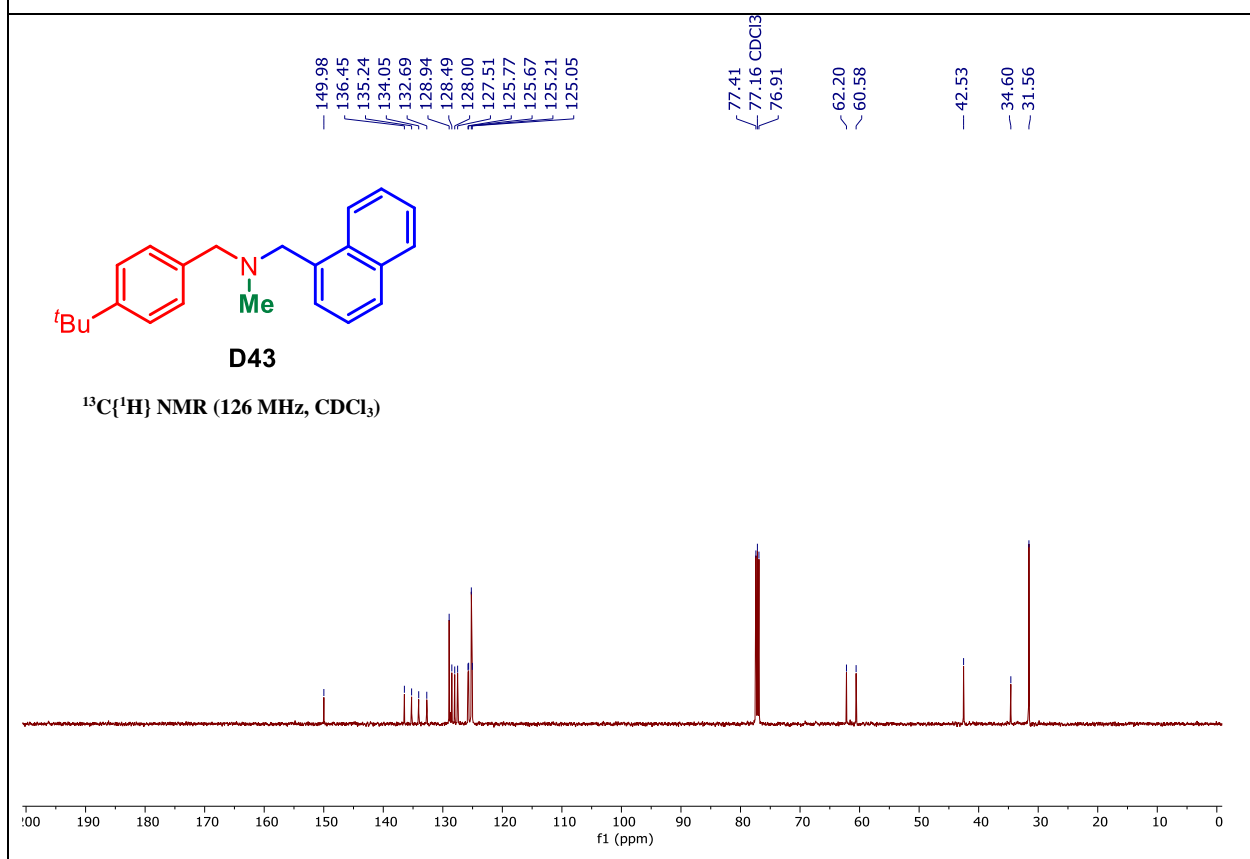
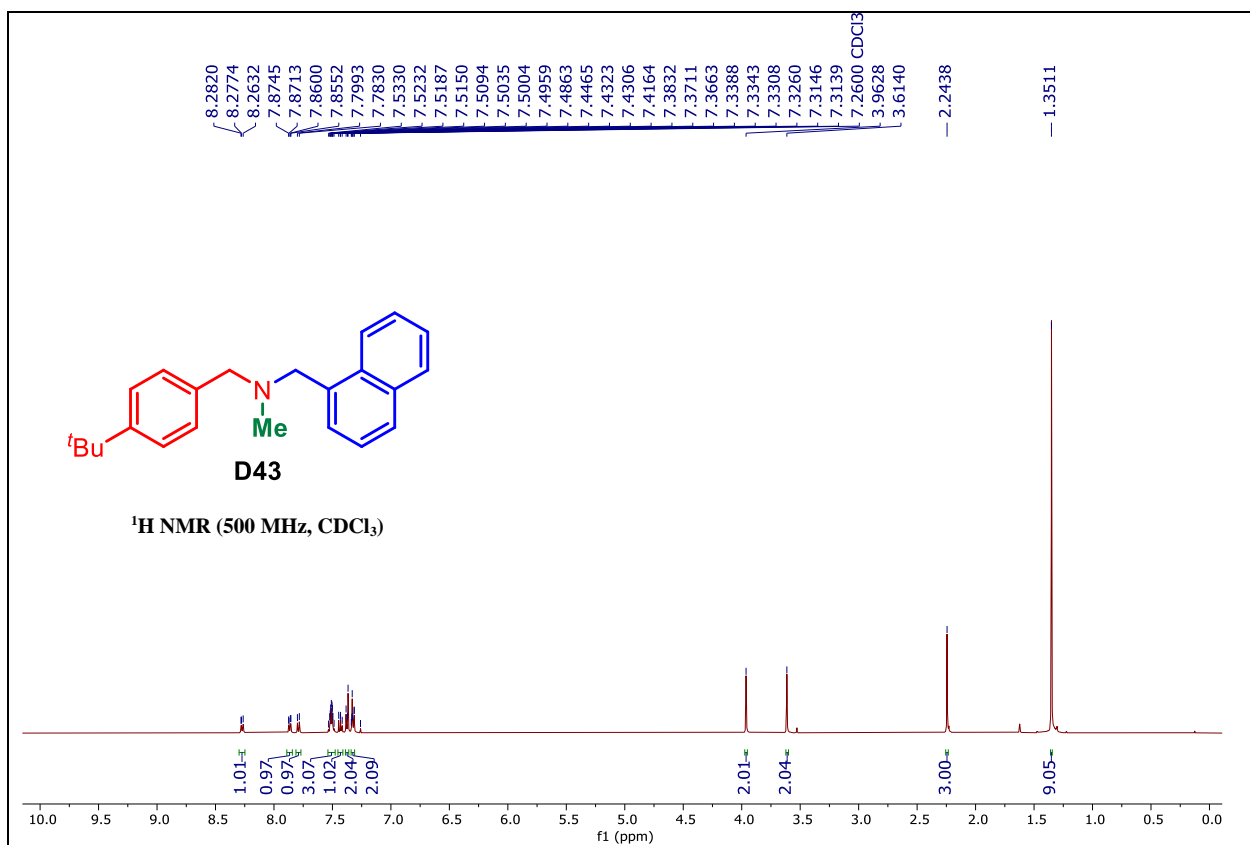


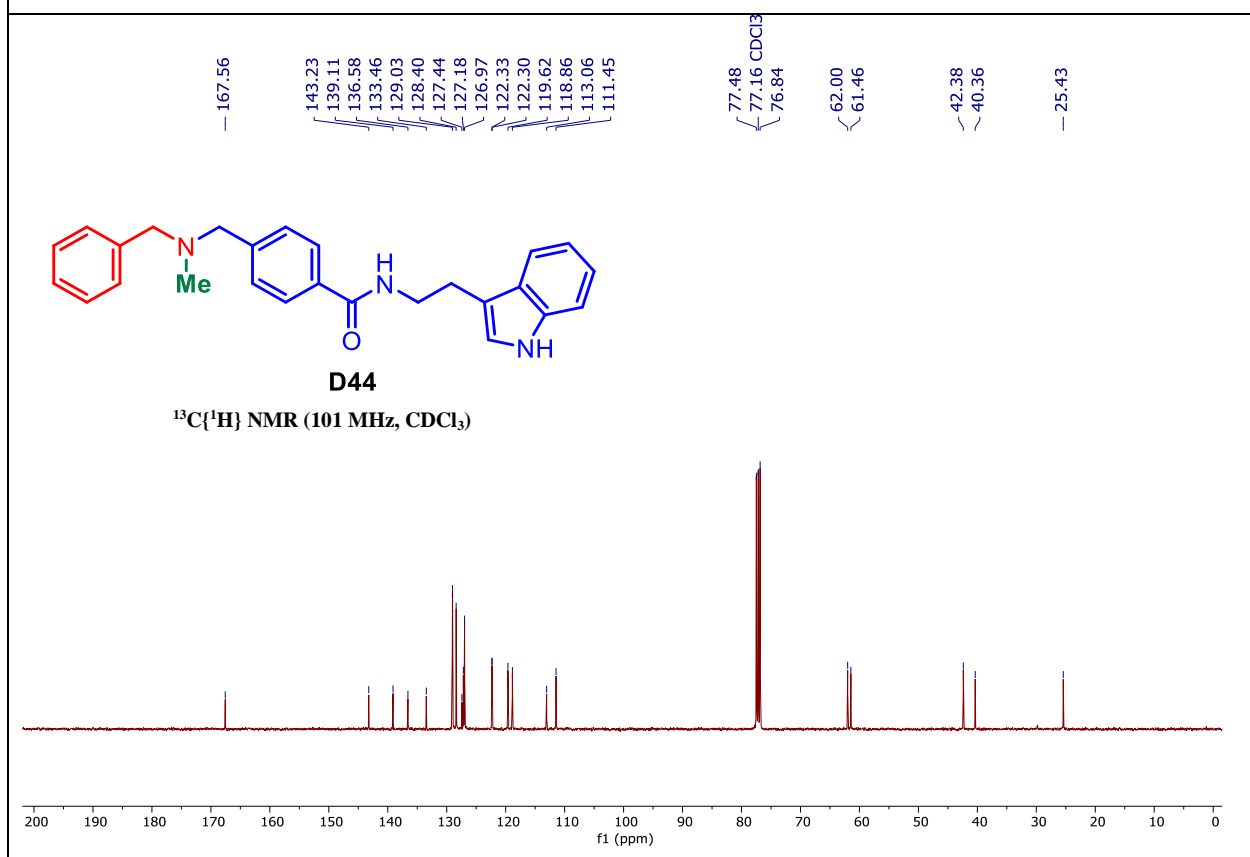
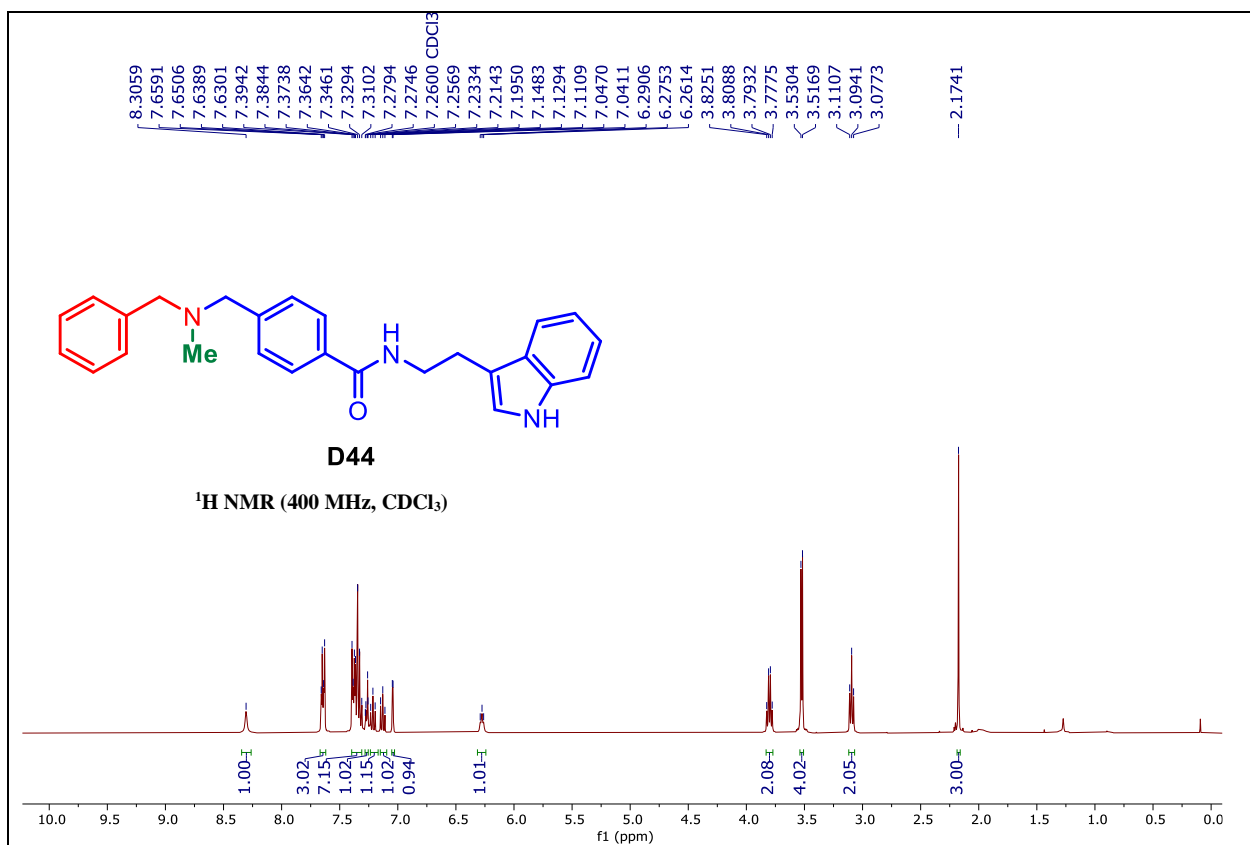


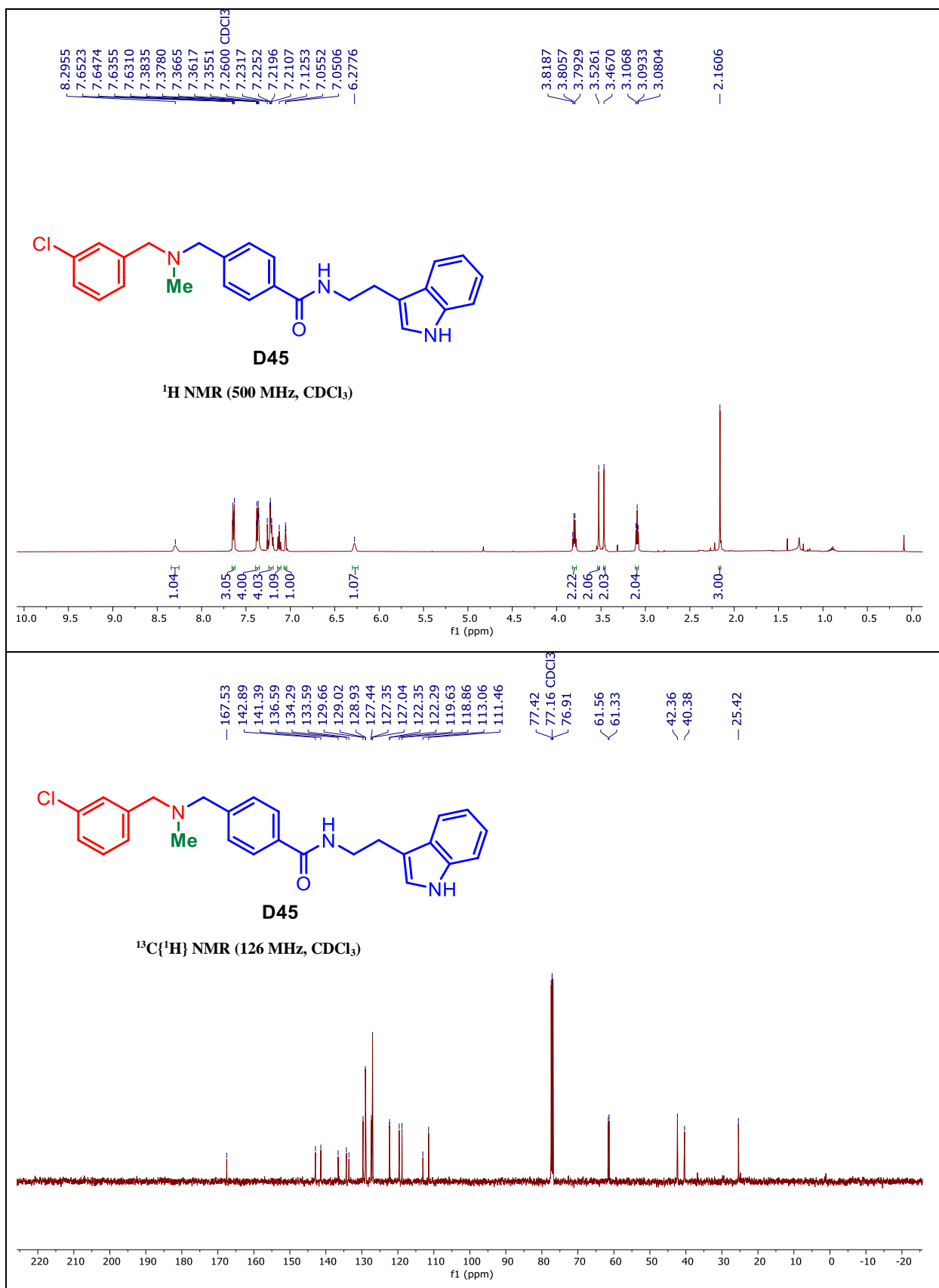


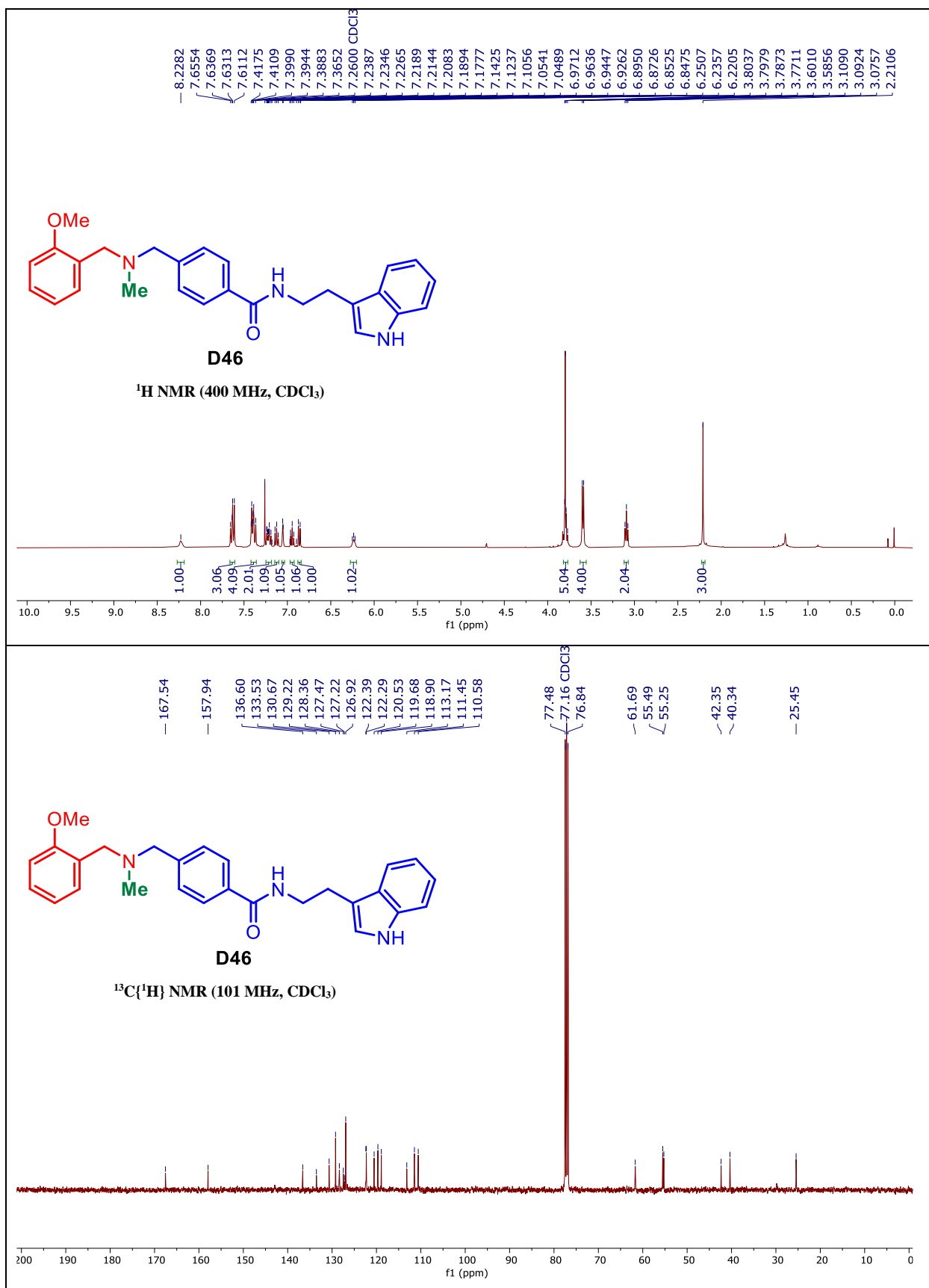


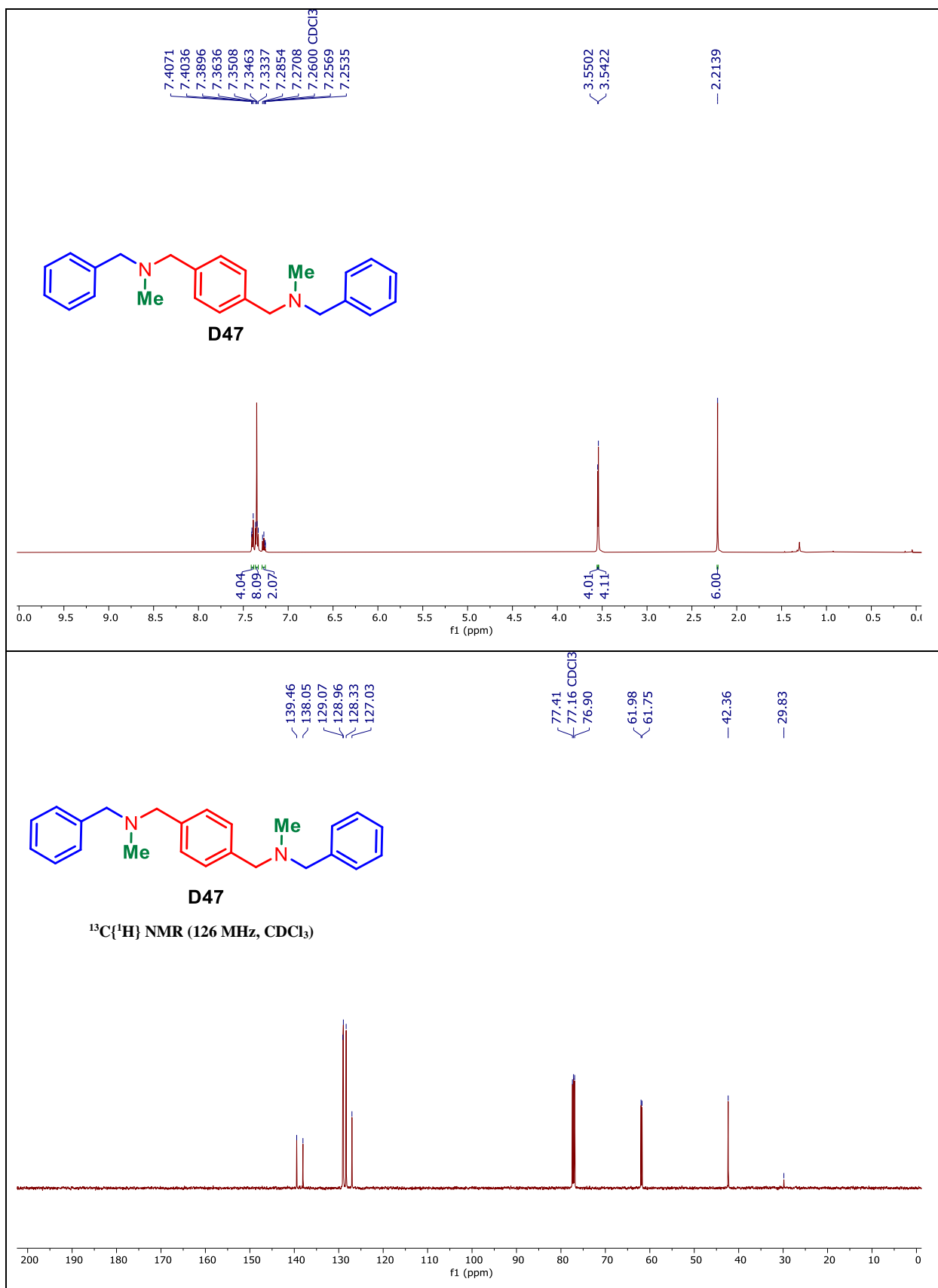




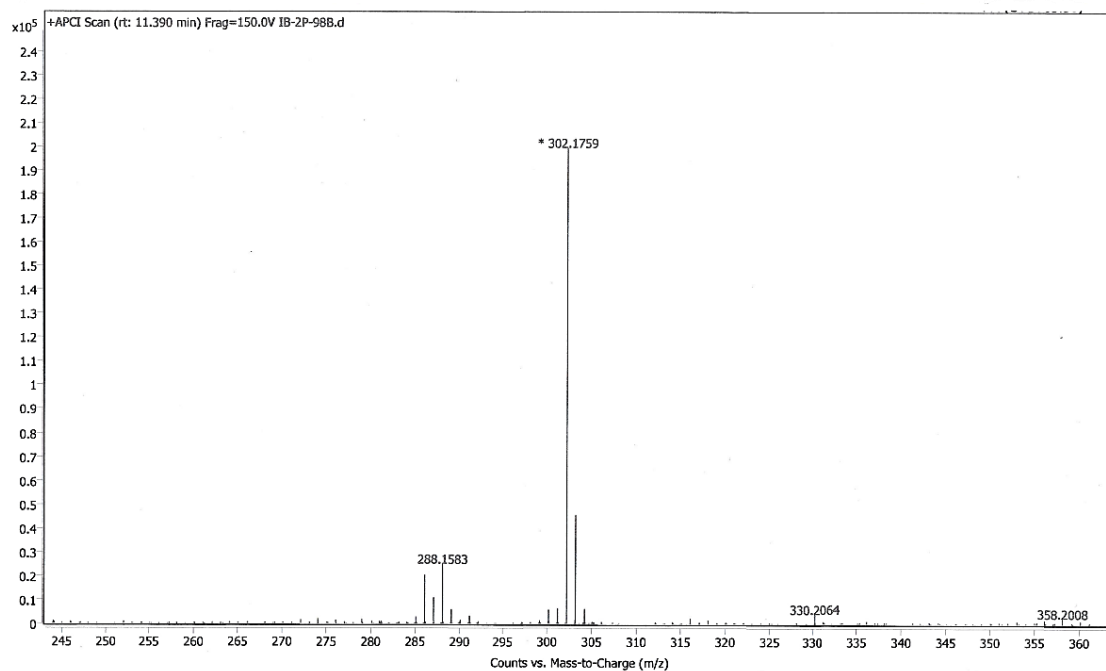




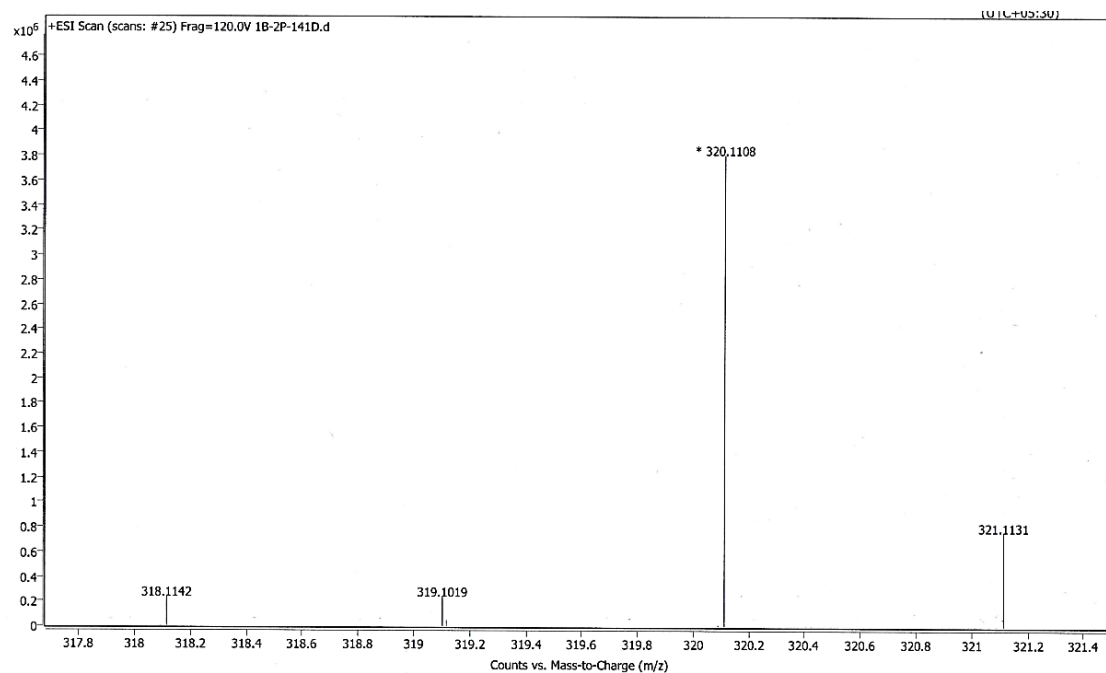




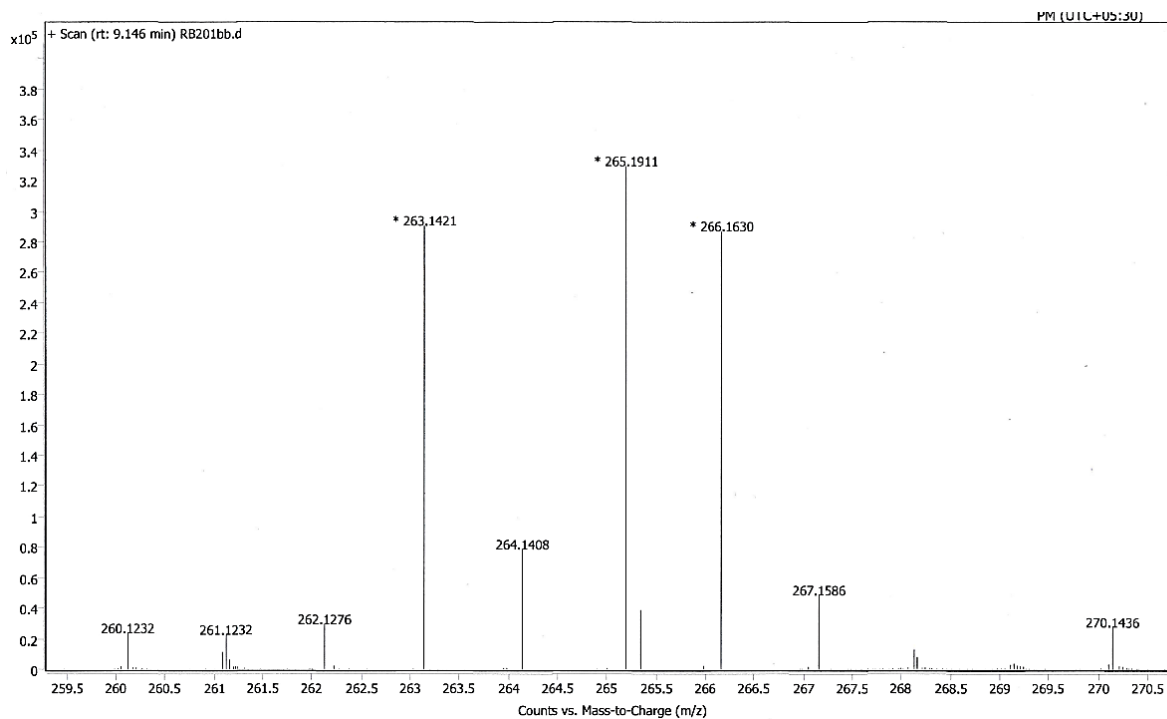
10.HRMS Spectra of the Newly Reported Compounds



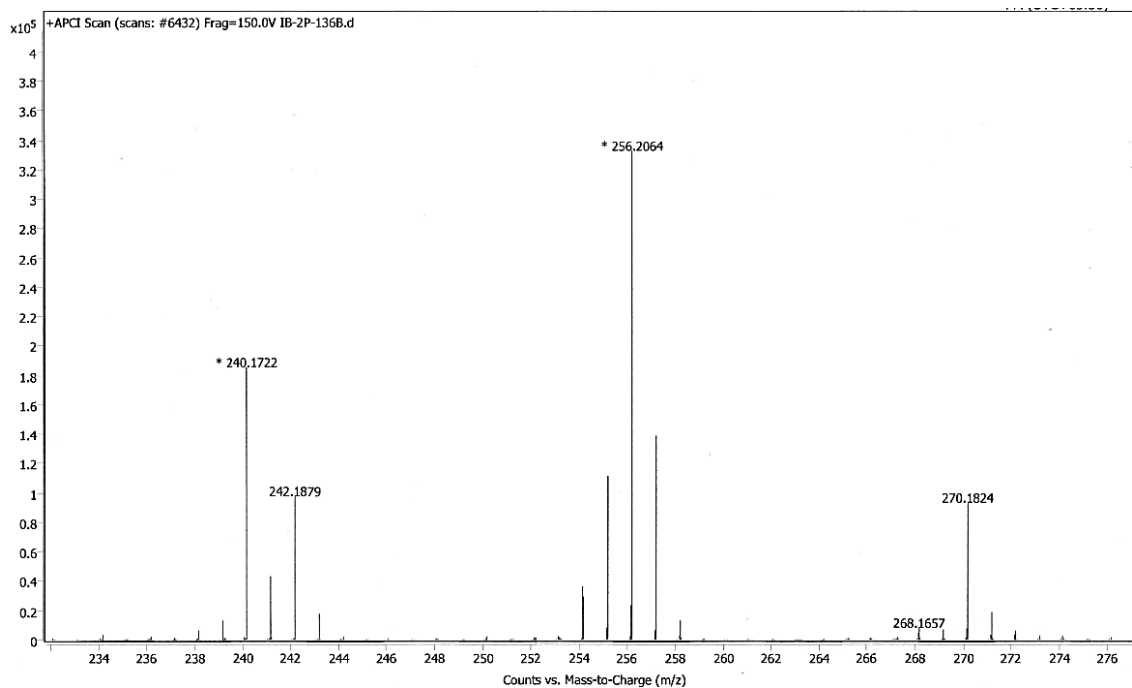
HRMS data for compound **D8**



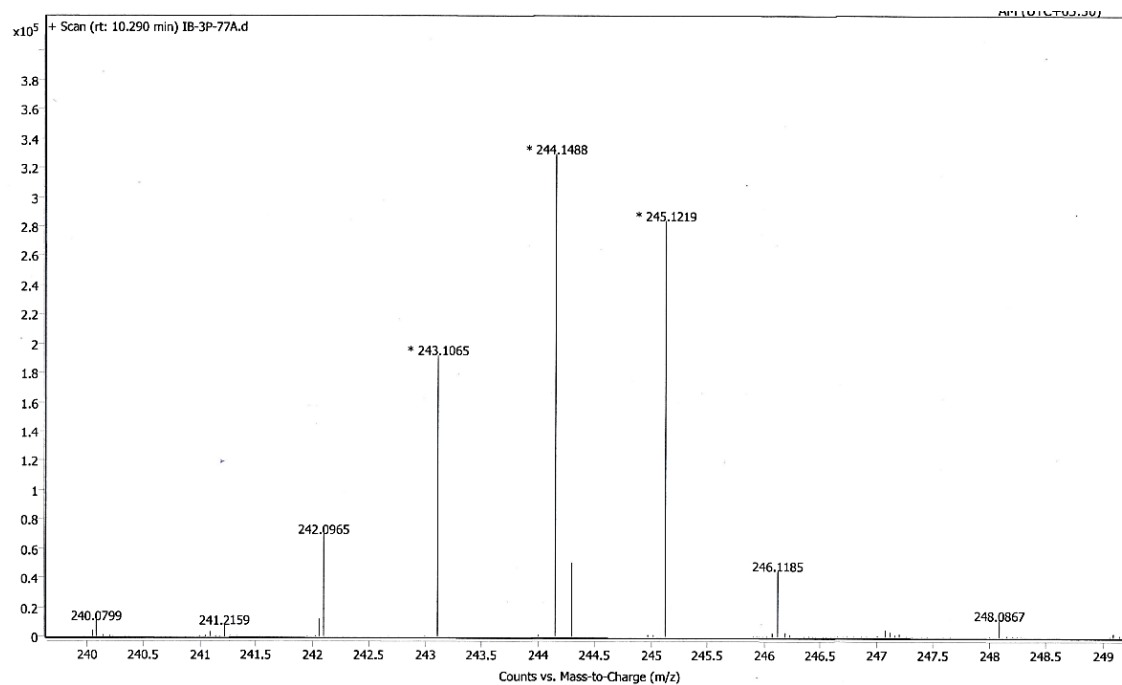
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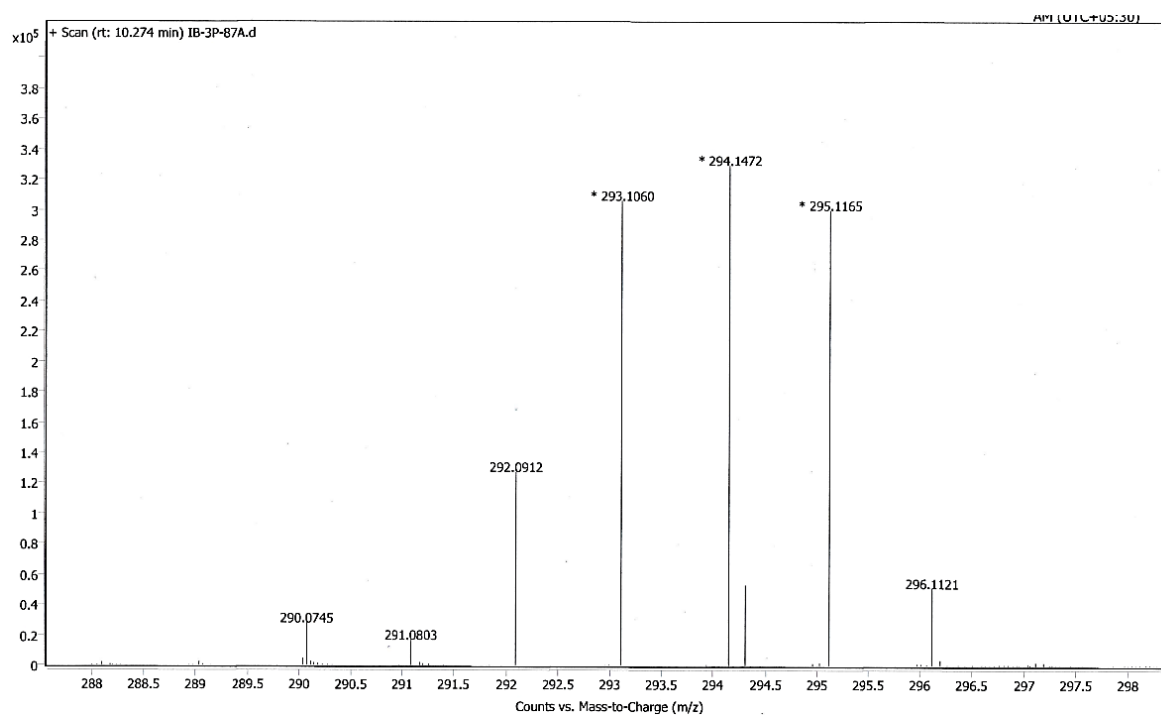
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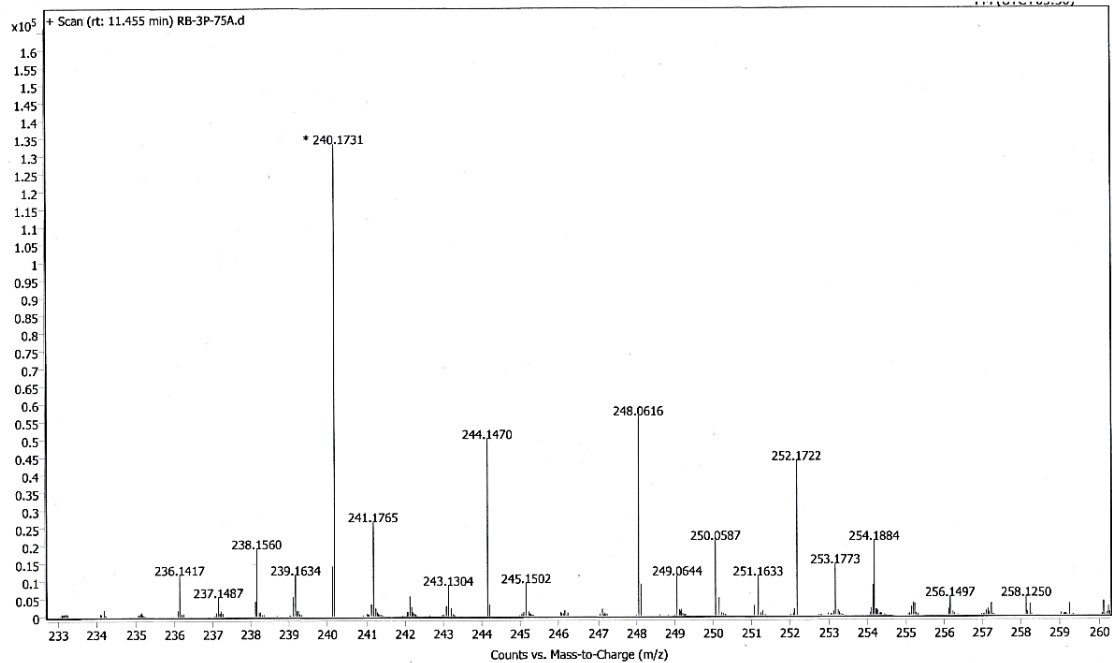
HRMS data for compound **D26**



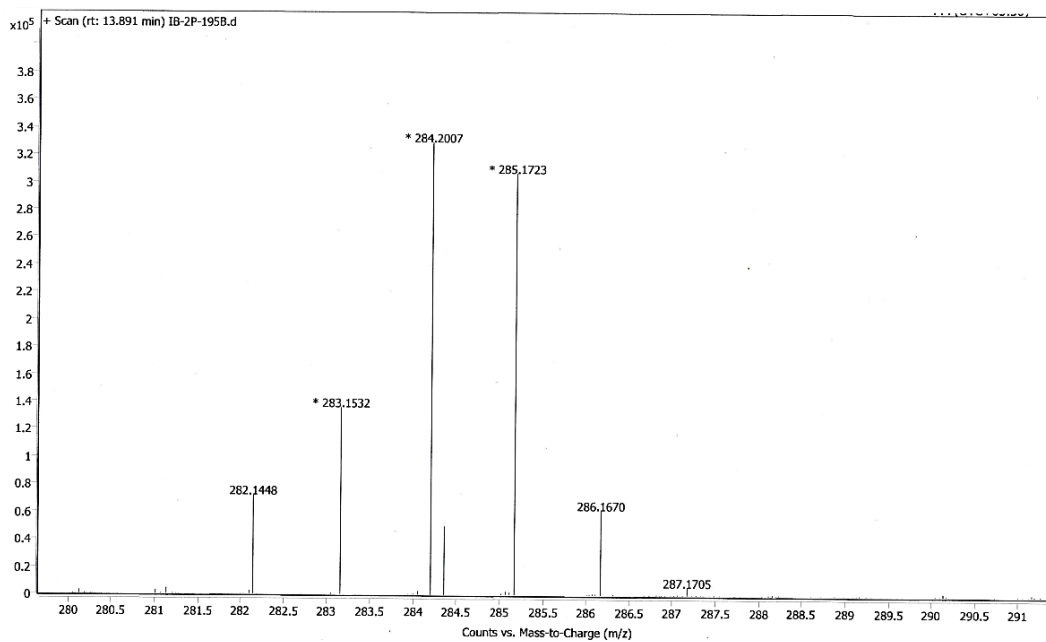
HRMS data for compound **D30**



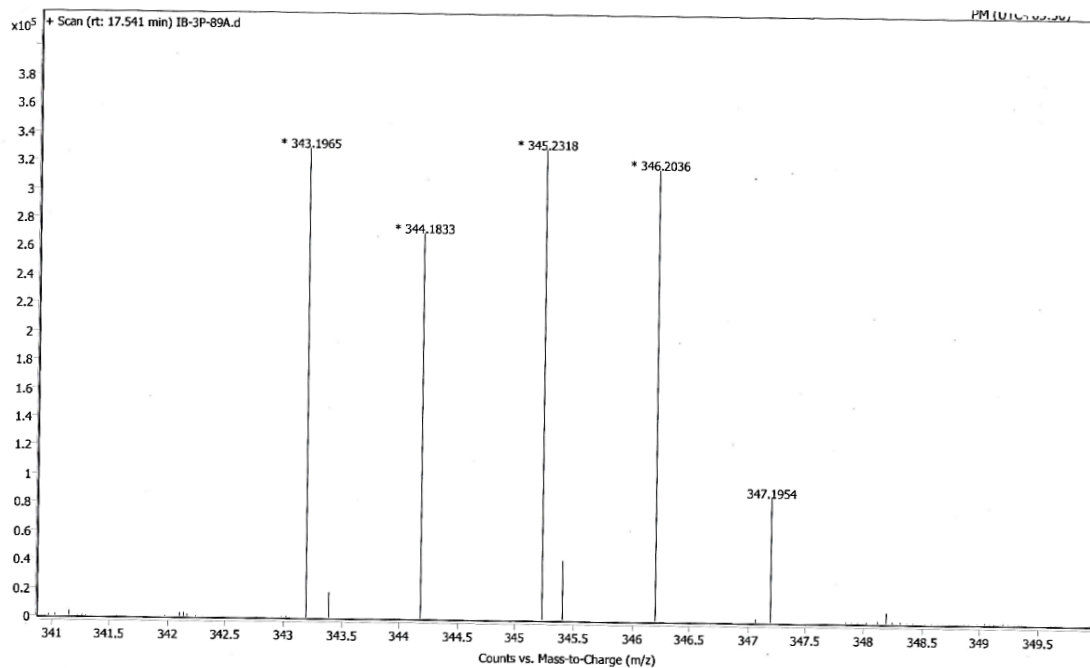
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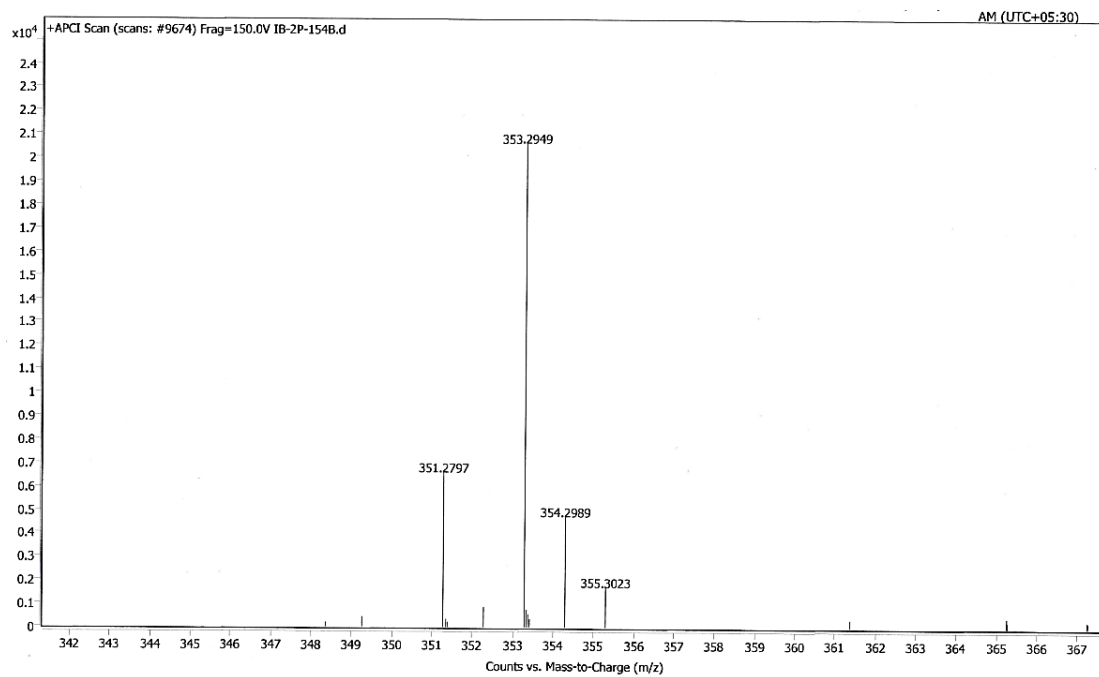
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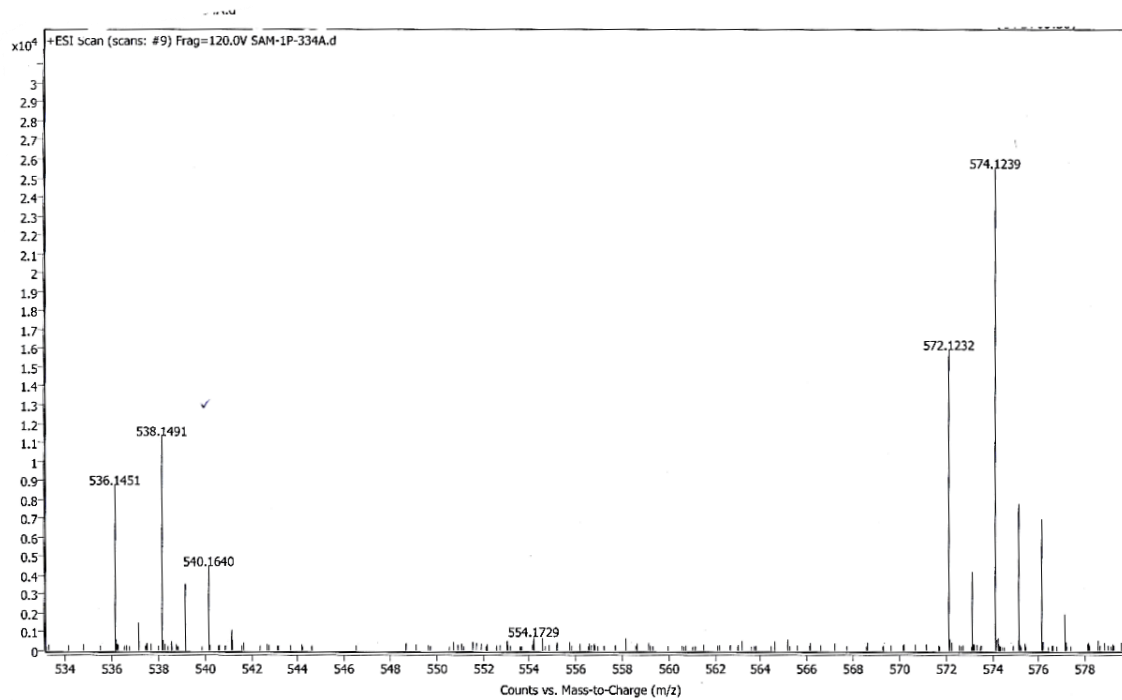
HRMS data for compound D39



HRMS data for compound **D40**



HRMS data for compound **D41**



HRMS data for I-1