

## Electronic Supplementary Information

### Rhodium(III)-Catalyzed Synthesis of Trisubstituted Furans *via* Vinylic C-H Bond Activation

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### **General Experimental**

NMR spectra were recorded on a 400 MHz spectrometer in CDCl<sub>3</sub>, Tetramethylsilane (TMS;  $\delta = 0.00$  ppm) served as an internal standard for <sup>1</sup>H NMR. The corresponding residual non-deuterated solvent signal (CDCl<sub>3</sub>;  $\delta = 77.00$  ppm) was used as internal standard for <sup>13</sup>C NMR. IR spectra were measured using a FT-IR spectrometer. Mass spectra were obtained with a Q-TOF Mass Spectrometer (ESI-HRMS). Flash column chromatography was carried out by packing glass columns with commercial silica gel 100 - 200 mesh (commercial suppliers) and thin-layer chromatography was carried out using silica gel GF-254. All catalysts, reagents and reactants were procured from commercial suppliers. All solvents used for work up and chromatographic procedures were purchased from commercial suppliers and used without any further purification.

### **Typical experimental procedure for the synthesis of furan derivative:**

To a pre-dried 8 mL screw cap vial was added  $\alpha,\beta$ -unsaturated ketone derivatives (0.2 mmol, 1equiv.), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9.3 mg, 7.5 mol %), AgSbF<sub>6</sub> (21 mg, 30 mol %), acrylate derivative (0.8 mmol), Piv-OH (20.4 mg, 0.2 mmol), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (48 mg, 0.24 mmol). To this mixture, DCM (2 mL) was added. The vial was tightly capped and placed in a pre-heated (90 °C) metal block. After 48h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and passed through a short silica gel (100-200 mesh size) bed. The organic layer was concentrated under reduced pressure, and the crude product was purified on a silica gel column using ethyl acetate/hexane (0:100 to 5:95) mixture.

### **Experimental procedure for the Scale-up of the synthesis of furan derivative:**

In a 50-mL pressure tube  $\alpha,\beta$ -unsaturated ketone derivatives (4 mmol, 1 equiv.), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (186 mg, 7.5 mol %), Piv-OH (408 mg, 1 equiv.), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (960 mg, 1.2 equiv.), methyl acrylate derivative (160mmol, 4 equiv.), AgSbF<sub>6</sub> (420 mg, 30 mol %). To this mixture DCM (40 mL) was added. This tube was sealed with a screw cap and placed in a pre-heated oil bath at 90 °C and the reaction mixture was stirred at the same temperature for 48 h. After completion of the reaction (monitored by TLC) the reaction mixture was cooled to room temperature and filtered through silica gel bed (100-200 mesh) taken in a short column and concentrated under vacuum. The crude products were purified by flash column chromatography using ethyl acetate and petroleum ether (0:100 to 5:95) to afford 60% (0.55 g) yield.

### **Typical experimental procedure for synthetic transformation of furan product 4aa :**

To a pre-dried 8 mL, screw cap vial was added compound **4aa** (0.25 mmol) and aq. solution of NaOH (5%, 1 mL), the reaction mixture was stirred at 90 °C for 5 min followed by stirring

at rt for 24h. After completion of the reaction (monitored by TLC), 1N HCl was added to the reaction mixture, and pH was adjusted up to 2. Extracted with ethyl acetate (10 mL \* 3 times) then combined organic layer passed through sodium sulphate, the solvent was evaporated, and crude mixture subjected to flash column chromatography to obtain pure product **5** as a white solid.

To a solution of **4aa** (0.25 mmol) in Dry THF (2 mL) in a 10 mL round bottom flask, Suspension of LiAlH<sub>4</sub> in dry THF solution was added dropwise at 0 °C, after addition of LiAlH<sub>4</sub>, the reaction mixture was stirred at rt for overnight. The reaction mixture was then quenched by the addition of water and extracted with ethyl acetate (15 mL \* 3 times). The combined organic layer passed through sodium sulphate, the solvent was evaporated, and the crude mixture was subjected to flash column chromatography to obtain pure product **6**.

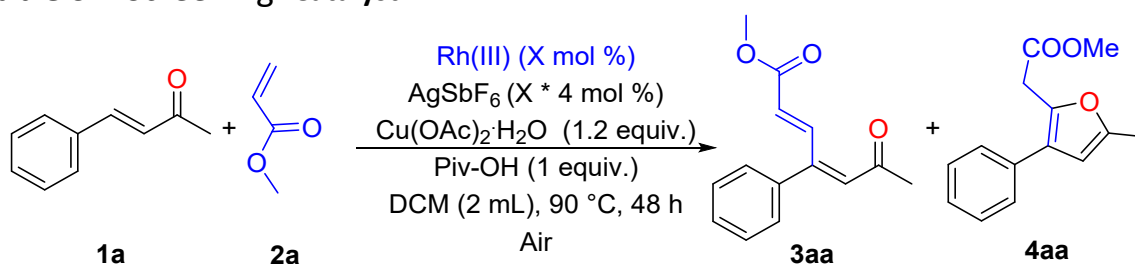
### Mechanistic studies (H/D exchange reaction):

To a pre-dried 8 mL screw cap vial was added enone derivative (0.2 mmol, 1 equiv.), [RhCp\*Cl<sub>2</sub>]<sub>2</sub> (9.3 mg, 7.5 mol %), Cu(OAc)<sub>2</sub>·H<sub>2</sub>O (48 mg, 0.24 mmol), D<sub>2</sub>O (2.0 mmol, 10 equiv.), AgSbF<sub>6</sub> (21.0 mg, 30 mol %). To this mixture DCM (2 mL) was added. The vial was tightly capped and placed in a pre-heated (90 °C) metal block. After 48h, the reaction mixture was cooled to room temperature, diluted with ethyl acetate, and passed through a short silica gel (100-200 mesh size) bed. The organic layer was concentrated under reduced pressure and the crude product was purified on a silica gel column using ethyl acetate/hexane mixture.

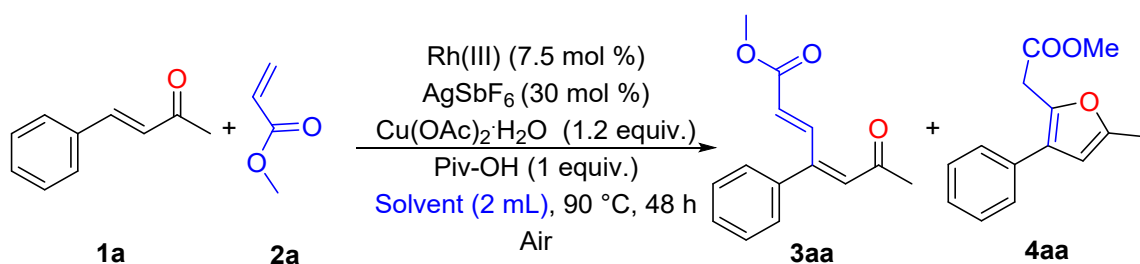
### Optimization:

All reactions were carried out on a 0.2 mmol scale. Yields are based in <sup>1</sup>H NMR using Trimethoxy benzene as an internal standard.

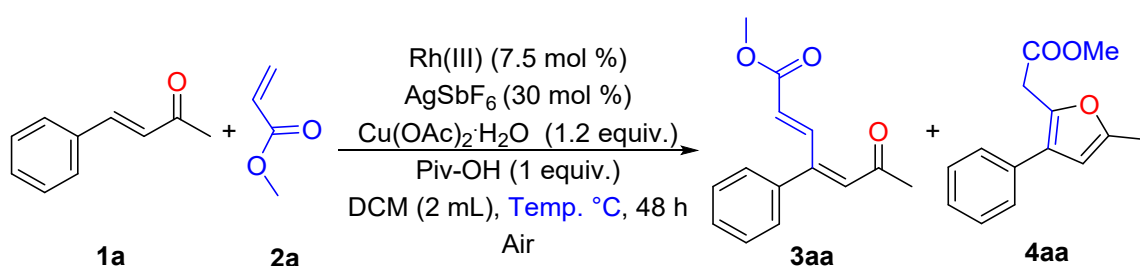
**Table S1: Screening: Catalyst**



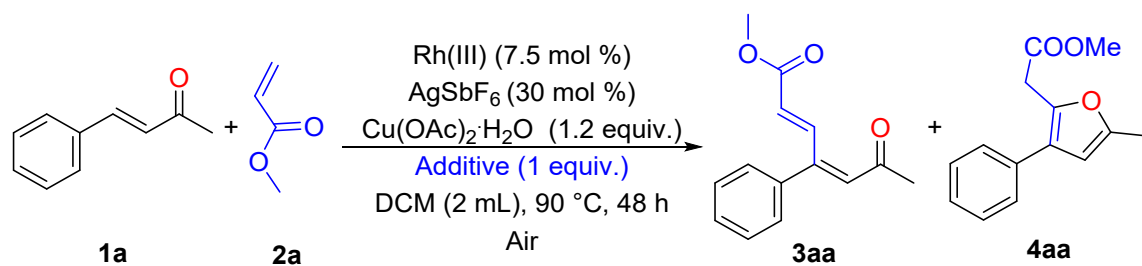
Entry	Catalyst (mol %)	NMR yields 3aa/4aa (%)
1	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (10)	00/58
2	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (7.5)	00/69
3	[RhCp*Cl <sub>2</sub> ] <sub>2</sub> (05)	00/48
4	[Ru( <i>p</i> -cymene)Cl <sub>2</sub> ] <sub>2</sub> (7.5)	20/30
5	[IrCp*Cl <sub>2</sub> ] <sub>2</sub> (7.5)	nd
6	[Cp*Co(CO)I <sub>2</sub> ] (7.5)	nd

**Table S2: Screening: Solvent**

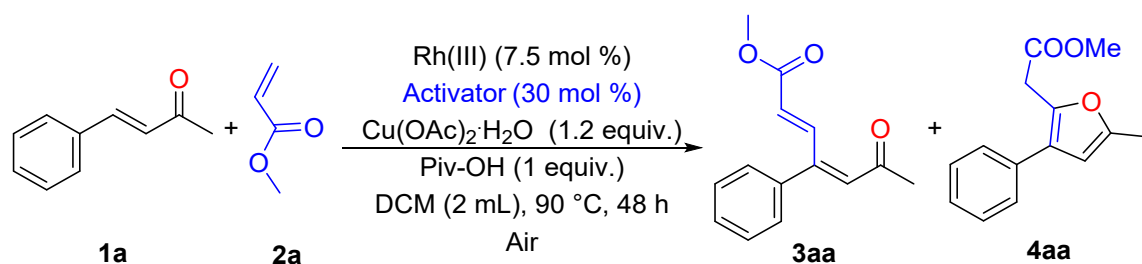
Entry	Solvent (2 mL)	NMR yields 3aa/4aa (%)
1	DCM	00/69
2	EtOAc	nd
3	THF	nd
4	DCE	05/53
5	Toluene	nd
6	TFE	nd
7	1,4-Dioxane	nd
8	HFIP	nd
9	MeOH	nd
10	CHCl <sub>3</sub>	nd
11	DMSO	nd
12	DMF	nd

**Table S3: Screening: Temperature**

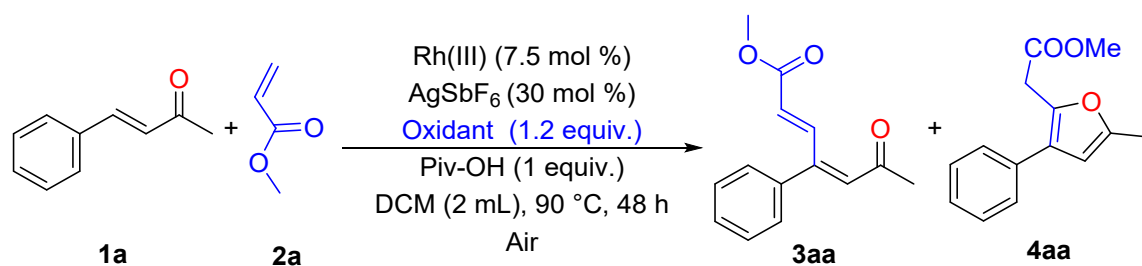
Entry	Temperature (°C)	NMR yields 3aa/4aa (%)
1	r.t.	nd
2	80	10/48
3	90	00/69
4	100	00/48

**Table S4: Screening: Additives**

Entry	Additive (equiv.)	NMR yields 3aa/4aa (%)
1	NaOAc (1)	nd
2	TFA (1)	00/45
3	AcOH (1)	00/59
4	KOAc (1)	nd
5	K <sub>2</sub> CO <sub>3</sub> (1)	nd
6	AdCOOH (1)	00/62
7	Pivalic acid (1)	00/69
8	Pivalic acid (1.5)	00/68
9	Pivalic acid (0.5)	00/56
10	Benzoic acid (1)	nd

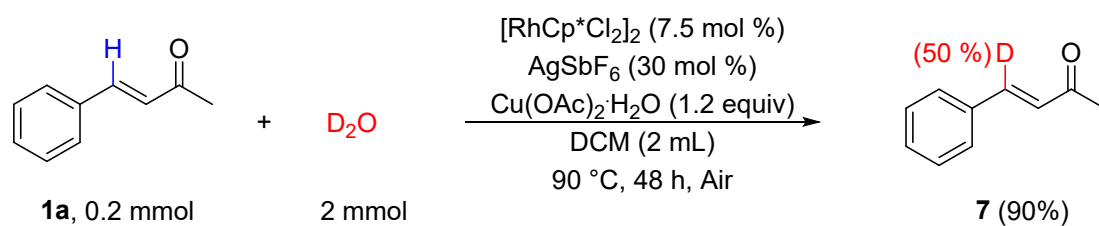
**Table S5: Screening: Activator**

Entry	Activator (30 mol %)	NMR yields 3aa/4aa (%)
1	AgBF <sub>4</sub>	00/49
2	AgPF <sub>6</sub>	nd
3	AgSbF <sub>6</sub>	00/69
4	AgSbF <sub>6</sub> (20 mol %)	00/50
5	AgSbF <sub>6</sub> (40 mol %)	00/65
6	AgNTf <sub>2</sub>	nd
7	AgOAc	nd
8	-	nd

**Table S6: Screening: Oxidants**

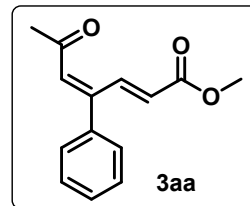
Entry	Oxidants (equiv.)	NMR yields 3aa/4aa (%)
1	CuCO <sub>3</sub> (1.2)	05/11
2	CuOTf (1.2)	nd
3	CuO (1.2)	nd
4	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (1.2)	00/69
5	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (1.5)	00/69
6	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (1.0)	00/60
7	Cu(OAc) <sub>2</sub> ·H <sub>2</sub> O (2.0)	00/68
8	Ag <sub>2</sub> CO <sub>3</sub> (1.2)	nd
9	AgOAc (1.2)	00/30
10	AgSbF <sub>6</sub> (1.2)	nd
11	Cu(acac) <sub>2</sub> (1.2)	nd
12	Zn(OAc) <sub>2</sub> ·2H <sub>2</sub> O	nd
13	Mn(OAc) <sub>2</sub> ·4H <sub>2</sub> O	nd

**Mechanistic studies (H/D exchange reaction):**

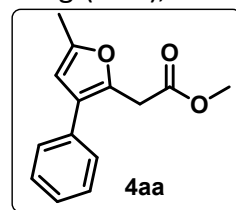


Characterization Data for all Isolated Products

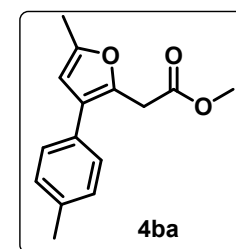
- 1) **Methyl (2E,4E)-6-oxo-4-phenylhepta-2,4-dienoate (3aa).** Yield – 16 mg (35%), yellow liquid;  $R_f$  (10% EtOAc/hexane) 0.25; IR (Neat,  $\text{cm}^{-1}$ ): 1682, 1721.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.81 (s, 3 H), 3.73 (s, 3 H), 5.70 (d,  $J = 15.55$  Hz, 1 H), 6.40 (s, 1 H), 7.13-7.15 (m, 2 H), 7.41-7.44 (m, 3 H), 7.50 (d,  $J = 15.59$  Hz, 1 H).  $^{13}\text{C} \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  30.5, 51.8, 126.8, 128.5, 128.7, 128.8, 135.31, 135.35, 147.0, 148.7, 166.5, 199.5. HRMS (ESI)  $m/z$ : (M+Na)<sup>+</sup> Calculated for  $\text{C}_{14}\text{H}_{14}\text{O}_3\text{Na}$  253.0841, found 253.0838.



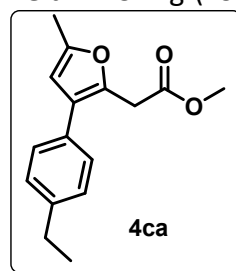
- 2) **Methyl 2-(5-methyl-3-phenylfuran-2-yl)acetate (4aa).** Yield - 29 mg (64%), 550 mg [(4 mmol scale) 60%] yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.4; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.32 (s, 3 H), 3.75 (s, 5 H), 6.14 (s, 1 H), 7.26-7.31 (m, 1 H), 7.38 (d,  $J = 4.22$  Hz, 4 H).  $^{13}\text{C} \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.0, 52.3, 107.5, 124.7, 126.8, 127.6, 128.6, 133.6, 141.3, 151.4, 170.3. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{14}\text{H}_{14}\text{O}_3$  231.1021, found 231.1019.



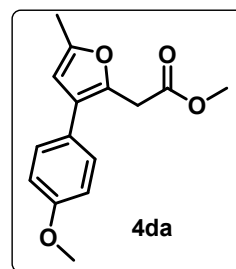
- 3) **Methyl 2-(5-methyl-3-(p-tolyl)furan-2-yl)acetate (4ba).** Yield - 26 mg (53%), brown liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1743.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 2.35 (s, 3 H), 3.72 (s, 2 H), 3.73 (s, 3 H), 6.11 (s, 1 H), 7.18 (d,  $J = 7.95$  Hz, 2 H), 7.26 (d,  $J = 7.89$  Hz, 2 H).  $^{13}\text{C} \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 21.1, 33.0, 52.3, 107.5, 124.6, 127.5, 129.3, 130.7, 136.4, 141.0, 151.2, 170.4. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_3$  245.1178, found 245.1176.



- 4) **Methyl 2-(3-(4-ethylphenyl)-5-methylfuran-2-yl)acetate (4ca).** Yield – 25 mg (49%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.35; IR (Neat,  $\text{cm}^{-1}$ ): 1743.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.25 (t,  $J = 7.60$  Hz, 3 H), 2.31 (s, 3 H), 2.66 (q,  $J = 7.60$  Hz, 2 H), 3.73 (s, 2 H), 3.74 (s, 3 H), 6.12 (s, 1 H), 7.22 (d,  $J = 7.94$  Hz, 2 H), 7.30 (d,  $J = 8.06$  Hz, 2 H).  $^{13}\text{C} \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 15.5, 28.5, 33.0, 52.3, 107.5, 124.6, 127.6, 128.1, 130.9, 141.0, 142.8, 151.2, 170.4. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_3$  259.1334, found 259.1336.

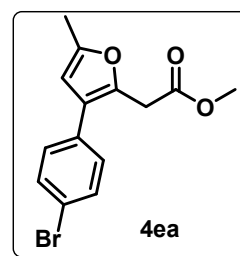


- 5) **Methyl 2-(3-(4-methoxyphenyl)-5-methylfuran-2-yl)acetate (4da).** Yield - 24 mg (46%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.35; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 3.71 (s, 2 H), 3.74 (s, 3 H), 3.82 (s, 3 H), 6.10 (s, 1 H), 6.90-6.94 (m, 2 H), 7.29-7.32 (m, 2 H).  $^{13}\text{C} \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.0, 52.3, 55.3, 107.5, 114.1, 124.3, 126.1, 128.7, 140.7, 151.2, 158.5, 170.5. HRMS (ESI)  $m/z$ : (M+Na)<sup>+</sup> Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_4$  283.0946, found 283.0942.

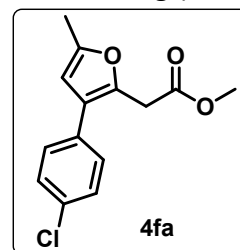




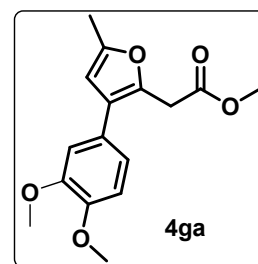
- 6) **Methyl 2-(3-(4-bromophenyl)-5-methylfuran-2-yl)acetate (4ea)**. Yield - 31 mg (50%), pale yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 3.70 (s, 2 H), 3.74 (s, 3 H), 6.10 (s, 1 H), 7.23-7.26 (m, 2 H), 7.48-7.51 (m, 2 H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.0, 52.4, 107.2, 120.7, 123.7, 129.2, 131.7, 132.5, 141.5, 151.7, 170.1. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{14}\text{H}_{13}\text{BrO}_3$  309.0126, found 309.0124.



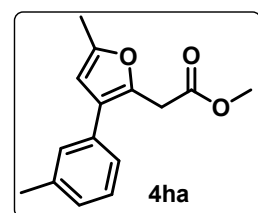
- 7) **Methyl 2-(3-(4-chlorophenyl)-5-methylfuran-2-yl)acetate (4fa)**. Yield - 24 mg (44%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 3.70 (s, 2 H), 3.74 (s, 3 H), 6.10 (s, 1 H), 7.29-7.32 (m, 2 H), 7.33-7.36 (m, 2 H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.0, 52.4, 107.3, 123.7, 128.84, 128.89, 132.1, 132.6, 141.5, 151.6, 170.2. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{14}\text{H}_{13}\text{ClO}_3$  265.0631, found 265.0613.



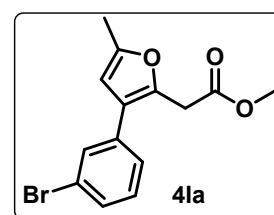
- 8) **Methyl 2-(3-(3,4-dimethoxyphenyl)-5-methylfuran-2-yl)acetate (4ga)**. Yield - 23 mg (40%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.3; IR (Neat,  $\text{cm}^{-1}$ ): 1741.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 3.72 (s, 2 H), 3.74 (s, 3 H), 3.893 (s, 3 H), 3.898 (m, 3 H), 6.11 (s, 1 H), 6.88 (d,  $J = 8.27$  Hz, 1 H), 6.92 (dd,  $J = 8.19, 1.81$  Hz, 1 H), 6.96 (d,  $J = 1.72$  Hz, 1 H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.1, 52.3, 55.8, 55.9, 107.5, 111.1, 111.4, 119.9, 124.6, 126.4, 140.8, 148.0, 148.9, 151.3, 170.4. HRMS (ESI)  $m/z$ : (M+Na)<sup>+</sup> Calculated for  $\text{C}_{16}\text{H}_{18}\text{O}_5$  Na 313.1052, found 313.1050.



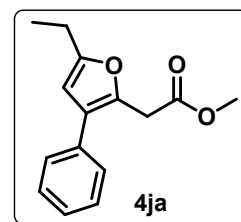
- 9) **Methyl 2-(5-methyl-3-(*m*-tolyl)furan-2-yl)acetate (4ha)**. Yield - 22.5 mg (46%), pale yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.4; IR (Neat,  $\text{cm}^{-1}$ ): 1742.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 2.37 (s, 3 H), 3.73 (s, 2 H), 3.74 (s, 3 H), 6.12 (s, 1 H), 7.09 (d,  $J = 7.47$  Hz, 1 H), 7.17 (d,  $J = 7.66$  Hz, 2 H), 7.26 (t,  $J = 7.28$  Hz, 1 H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 21.4, 33.0, 52.3, 107.5, 124.71, 124.77, 127.5, 128.4, 128.5, 133.5, 138.2, 141.2, 151.3, 170.4. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_3$  245.1178, found 245.1178.



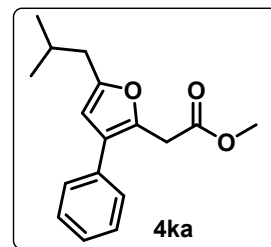
- 10) **Methyl 2-(3-(3-bromophenyl)-5-methylfuran-2-yl)acetate (4ia)**. Yield - 27 mg (43%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.4; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.30 (s, 3 H), 3.72 (s, 2 H), 3.75 (s, 3 H), 6.11 (d,  $J = 0.58$  Hz, 1 H), 7.24 (t,  $J = 7.89$  Hz, 1 H), 7.31 (dt,  $J = 7.75, 1.40$  Hz, 1 H), 7.40 (dt,  $J = 7.86, 1.81$  Hz, 1 H), 7.53 (t,  $J = 1.78$  Hz, 1 H).  $^{13}\text{C } \{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.0, 52.4, 107.2, 122.7, 123.5, 126.1, 129.7, 130.1, 130.6, 135.7, 141.8, 151.7, 170.1. HRMS (ESI)  $m/z$ : (M+H)<sup>+</sup> Calculated for  $\text{C}_{14}\text{H}_{13}\text{BrO}_3$  309.0126, found 309.0128.



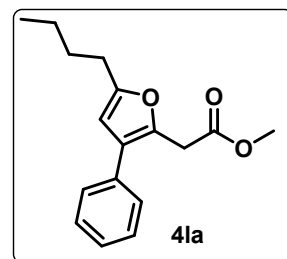
**11) Methyl 2-(5-ethyl-3-phenylfuran-2-yl)acetate (4ja).** Yield – 26 mg (53%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.3; IR (Neat,  $\text{cm}^{-1}$ ): 1743.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.26 (t,  $J = 7.56$  Hz, 3 H), 2.66 (q,  $J = 7.56$  Hz, 2 H), 3.74 (s, 3 H), 3.75 (s, 2 H), 6.15 (s, 1 H), 7.26-7.30 (m, 1 H), 7.38-7.39 (m, 4 H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  11.9, 21.3, 33.0, 52.3, 105.9, 124.5, 126.7, 127.6, 128.6, 133.7, 141.2, 157.1, 170.4. HRMS (ESI)  $m/z$ : (M+H) $^+$  Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_3$  245.1178, found 245.1176.



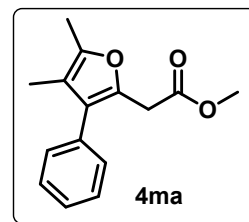
**12) Methyl 2-(5-isobutyl-3-phenylfuran-2-yl)acetate (4ka).** Yield – 36.5 mg (63%), pale yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.45; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.97 (d,  $J = 6.73$  Hz, 6 H), 1.99 (septet,  $J = 6.78$  Hz, 1 H), 2.50 (d,  $J = 7.00$  Hz, 2 H), 3.74 (s, 3 H), 3.76 (s, 2 H), 6.16 (s, 1 H), 7.26-7.31 (m, 1 H), 7.36-7.41 (m, 4 H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  22.3, 27.8, 33.1, 37.1, 52.2, 107.6, 124.4, 126.7, 127.6, 128.6, 133.7, 141.2, 154.9, 170.3. HRMS (ESI)  $m/z$ : (M+H) $^+$  Calculated for  $\text{C}_{17}\text{H}_{21}\text{O}_3$  273.1491, found 273.1495.



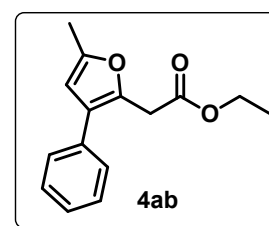
**13) Methyl 2-(5-butyl-3-phenylfuran-2-yl)acetate (4la).** Yield – 34 mg (59%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1743.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.90-0.93 (m, 3 H), 1.33-1.38 (m, 4 H), 1.63-1.71 (m, 2 H), 2.62 (t,  $J = 7.75$  Hz, 2 H), 3.74 (s, 3 H), 3.75 (s, 2 H), 6.15 (s, 1 H), 7.26-7.31 (m, 1 H), 7.36-7.40 (m, 4 H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  14.0, 22.4, 27.6, 27.9, 31.4, 33.1, 52.3, 106.5, 124.4, 126.7, 127.6, 128.6, 133.7, 141.1, 155.9, 170.4. HRMS (ESI)  $m/z$ : (M+Na) $^+$  Calculated for  $\text{C}_{18}\text{H}_{20}\text{O}_3\text{Na}$  309.1467, found 309.1464.



**14) Methyl 2-(4,5-dimethyl-3-phenylfuran-2-yl)acetate (4ma).** Yield – 9 mg (19%), pale yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.3; IR (Neat,  $\text{cm}^{-1}$ ): 1743.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.89 (s, 3 H), 2.24 (s, 3 H), 3.60 (s, 2 H), 3.71 (s, 3 H), 7.27-7.32 (m, 3 H), 7.39 (t,  $J = 7.50$  Hz, 2 H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  9.0, 11.5, 32.6, 52.2, 114.3, 125.6, 126.8, 128.4, 129.2, 133.3, 141.1, 146.8, 170.4. HRMS (ESI)  $m/z$ : (M+H) $^+$  Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_3$  245.1178, found 245.1177.

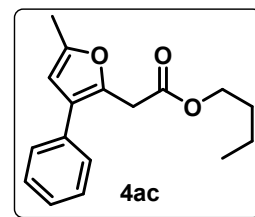


**15) Ethyl 2-(3-phenylfuran-2-yl)acetate (4ab).** Yield – 22 mg (45%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1742.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.27 (t,  $J = 7.21$  Hz, 3 H), 2.31 (s, 3 H), 3.72 (s, 2 H), 4.20 (q,  $J = 7.07$  Hz, 2 H), 6.14 (s, 1 H), 7.26-7.31 (m, 1 H), 7.35-7.39 (m, 4 H).  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 14.1, 33.3, 61.2, 107.4, 124.6, 126.7, 127.6, 128.6, 133.7, 141.5, 151.3, 169.9. HRMS (ESI)  $m/z$ : (M+Na) $^+$  Calculated for  $\text{C}_{15}\text{H}_{16}\text{O}_3\text{Na}$  267.0997, found 267.0998.



**16) Butyl 2-(3-phenylfuran-2-yl)acetate (4ac).**

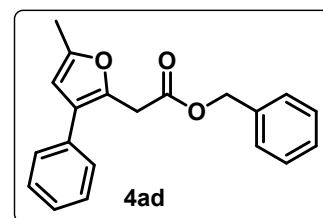
Yield - 28 mg (52%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.45; IR (Neat,  $\text{cm}^{-1}$ ): 1744.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  0.92 (t,  $J = 7.40$  Hz, 3 H), 1.37 (sextet,  $J = 7.55$  Hz, 2 H), 1.62 (quintet,  $J = 6.67$  Hz, 2 H), 2.31 (s, 3 H), 3.72 (s, 2 H), 4.15 (t,  $J = 6.57$  Hz, 2 H), 6.14 (s, 1 H), 7.26-7.30 (m, 1 H), 7.36-7.40 (m, 4 H).



$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 13.6, 19.0, 30.5, 33.3, 65.0, 107.4, 124.5, 126.7, 127.6, 128.6, 133.7, 141.5, 151.2, 170.0. HRMS (ESI)  $m/z$ :  $(\text{M}+\text{Na})^+$  Calculated for  $\text{C}_{17}\text{H}_{20}\text{O}_3$  Na 295.1310, found 295.1310.

**17) Benzyl 2-(3-phenylfuran-2-yl)acetate (4ad).**

Yield - 27 mg (45%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.5; IR (Neat,  $\text{cm}^{-1}$ ): 1741.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.32 (s, 3 H), 3.79 (s, 2 H), 5.20 (s, 2 H), 6.15 (s, 1 H), 7.27-7.29 (m, 1 H), 7.32-7.38 (m, 9 H).

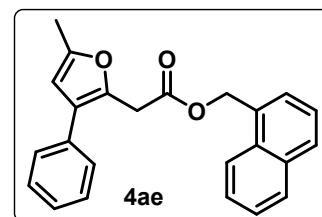


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 33.2, 66.8, 107.5, 124.8, 126.7, 127.6, 128.1, 128.2, 128.5, 128.6, 133.6, 135.7, 141.2, 151.4, 169.7. HRMS (ESI)  $m/z$ :  $(\text{M}+\text{Na})^+$  Calculated for  $\text{C}_{20}\text{H}_{18}\text{O}_3\text{Na}$  329.1154, found 329.1151.

**18) Naphthalen-1-yl 2-(3-phenylfuran-2-yl)acetate (4ae).**

Yield - 21 mg (30%), yellow liquid;  $R_f$  (5% EtOAc/hexane) 0.3; IR (Neat,  $\text{cm}^{-1}$ ): 1745.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.39 (d,  $J = 0.57$  Hz, 3 H), 4.10 (s, 2 H), 6.23 (d,  $J = 0.81$  Hz, 1 H), 7.28 (dd,  $J = 7.57$ , 0.88 Hz, 1 H), 7.32 (tt,  $J = 7.25$ , 1.99 Hz, 1 H), 7.41-7.51 (m, 7 H), 7.74 (d,  $J = 8.29$  Hz, 1 H), 7.78-7.80 (m, 1 H), 7.86 (dd,  $J = 7.32$ , 1.59 Hz, 1 H).

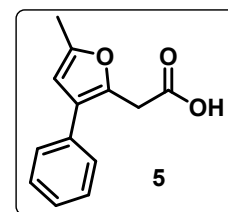


$^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.6, 33.5, 107.8, 118.0, 121.1, 125.2, 125.3, 126.1, 126.45, 126.47, 126.6, 127.0, 127.8, 127.9, 128.8, 133.6, 134.6, 140.8, 146.5, 151.7, 168.3. HRMS (ESI)  $m/z$ :  $(\text{M}+\text{Na})^+$  Calculated for  $\text{C}_{23}\text{H}_{18}\text{O}_3\text{Na}$  365.1154, found 365.1152.

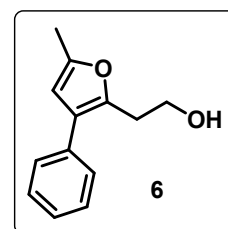
**19) 2-(5-methyl-3-phenylfuran-2-yl)acetic acid (5).**

Yield - 53.5 mg (99%), White solid; M.P. 116 °C,  $R_f$  (30% EtOAc/hexane) 0.3; IR (Neat,  $\text{cm}^{-1}$ ): 1712.

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  2.32 (s, 3 H), 3.78 (s, 2 H), 6.15 (s, 1 H), 7.27-7.30 (m, 1 H), 7.36-7.39 (m, 4 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 32.9, 107.6, 125.2, 126.7, 126.9, 127.6, 128.7, 133.4, 140.6, 151.6, 176.3. HRMS (ESI)  $m/z$ :  $(\text{M}+\text{K})^+$  Calculated for  $\text{C}_{13}\text{H}_{12}\text{O}_3\text{K}$  255.0424, found 255.0421.

**20) 2-(5-methyl-3-phenylfuran-2-yl)ethan-1-ol (6).**

Yield - 40 mg (79%), reddish brown liquid; IR (Neat,  $\text{cm}^{-1}$ ): 3355, 2922.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  1.73 (s, 1 H), 2.31 (d,  $J = 0.44$  Hz, 3 H), 3.01 (t,  $J = 6.21$  Hz, 2 H), 3.93 (t,  $J = 6.36$  Hz, 2 H), 6.12 (d,  $J = 0.85$  Hz, 1 H), 7.24-7.28 (m, 1 H), 7.35-7.40 (m, 4 H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  13.5, 30.3, 61.5, 107.4, 123.5, 126.5, 127.7, 128.5, 134.0, 146.4, 150.7. HRMS (ESI)  $m/z$ :  $(\text{M}+\text{H})^+$  Calculated for  $\text{C}_{13}\text{H}_{15}\text{O}_2$  203.1072, found 203.1071.

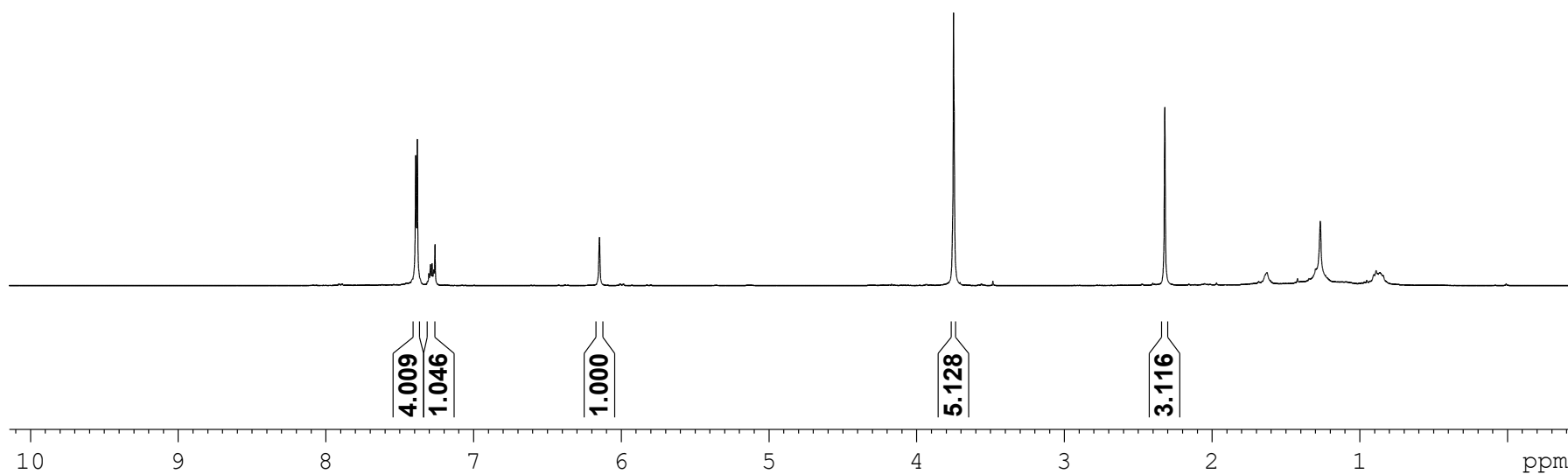
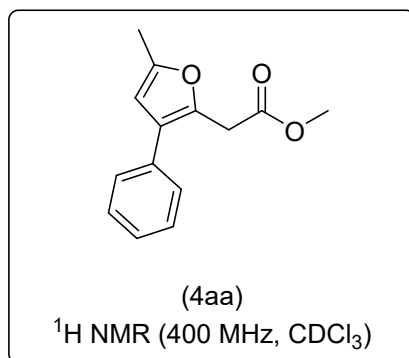


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2.320



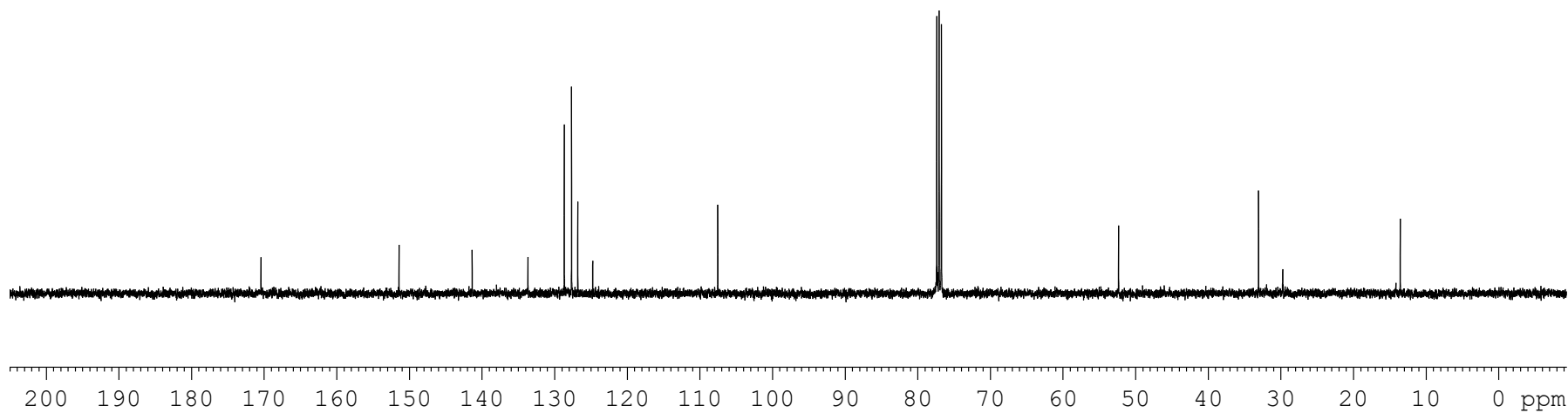
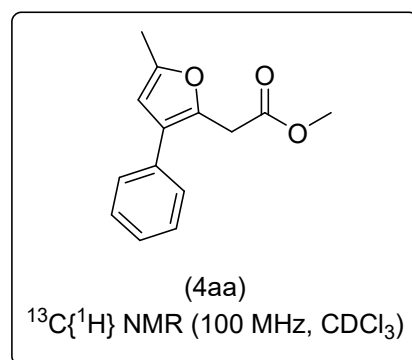
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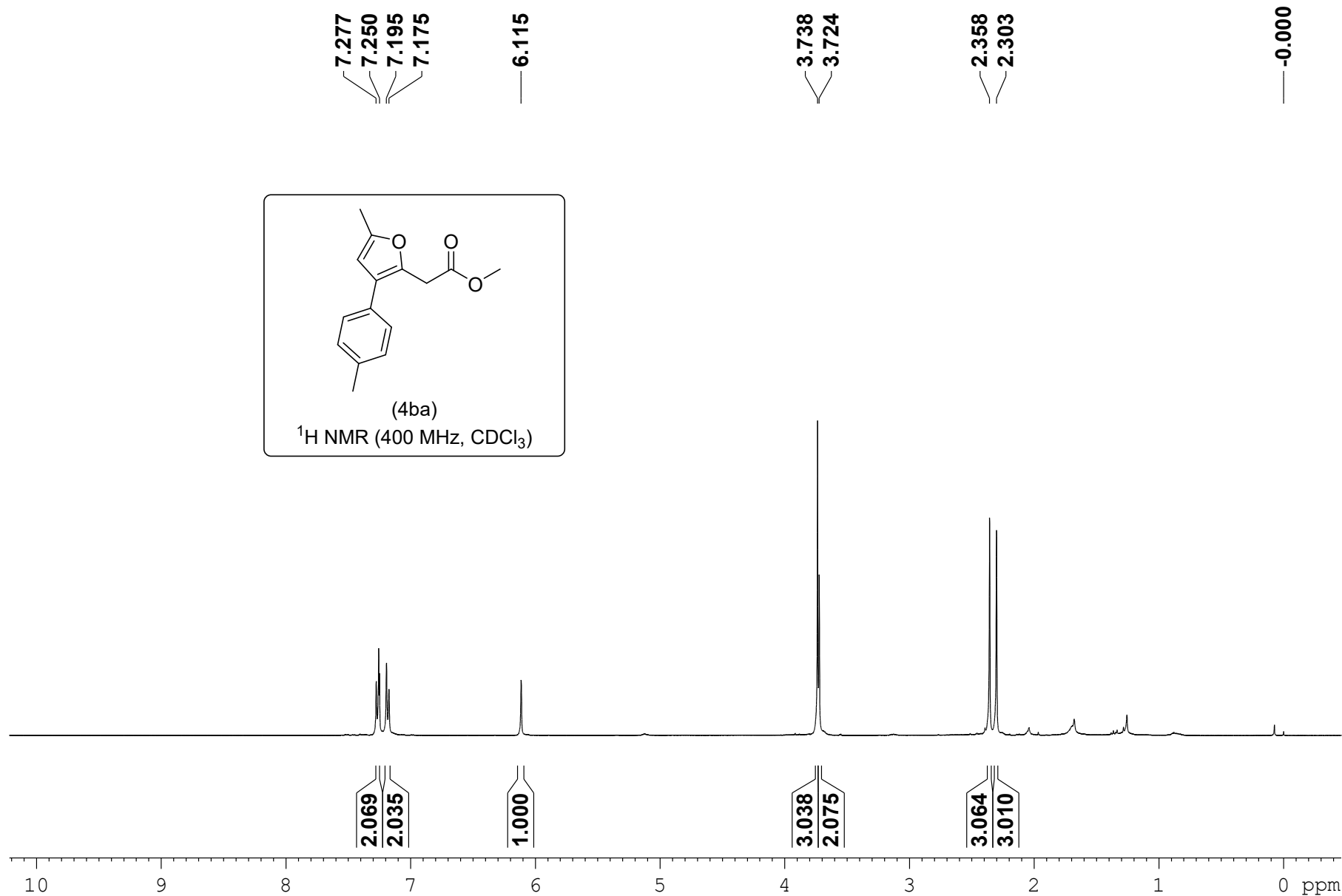
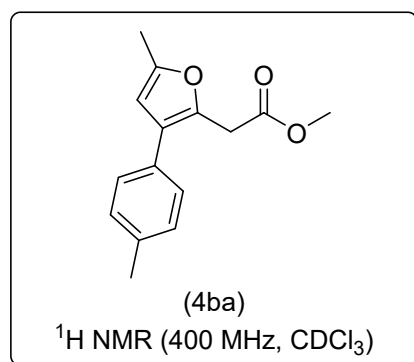
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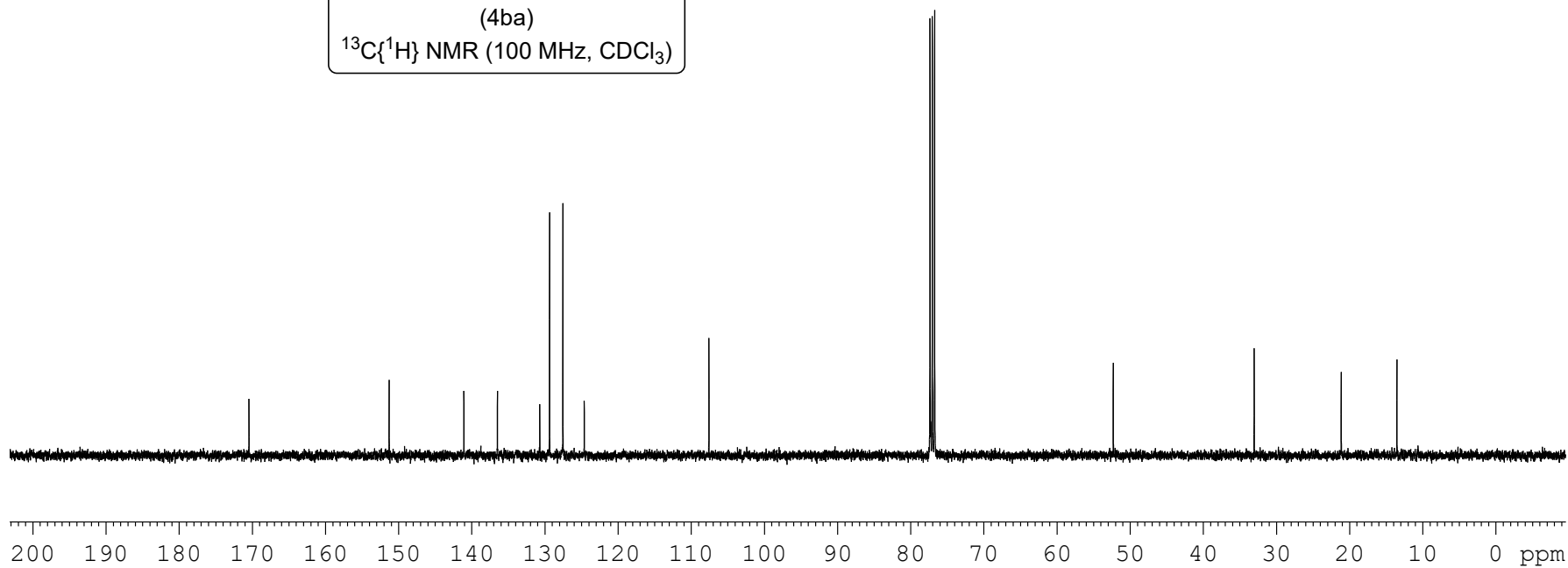
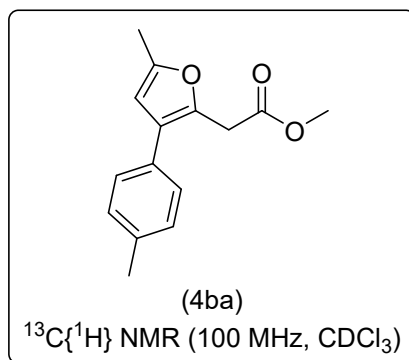
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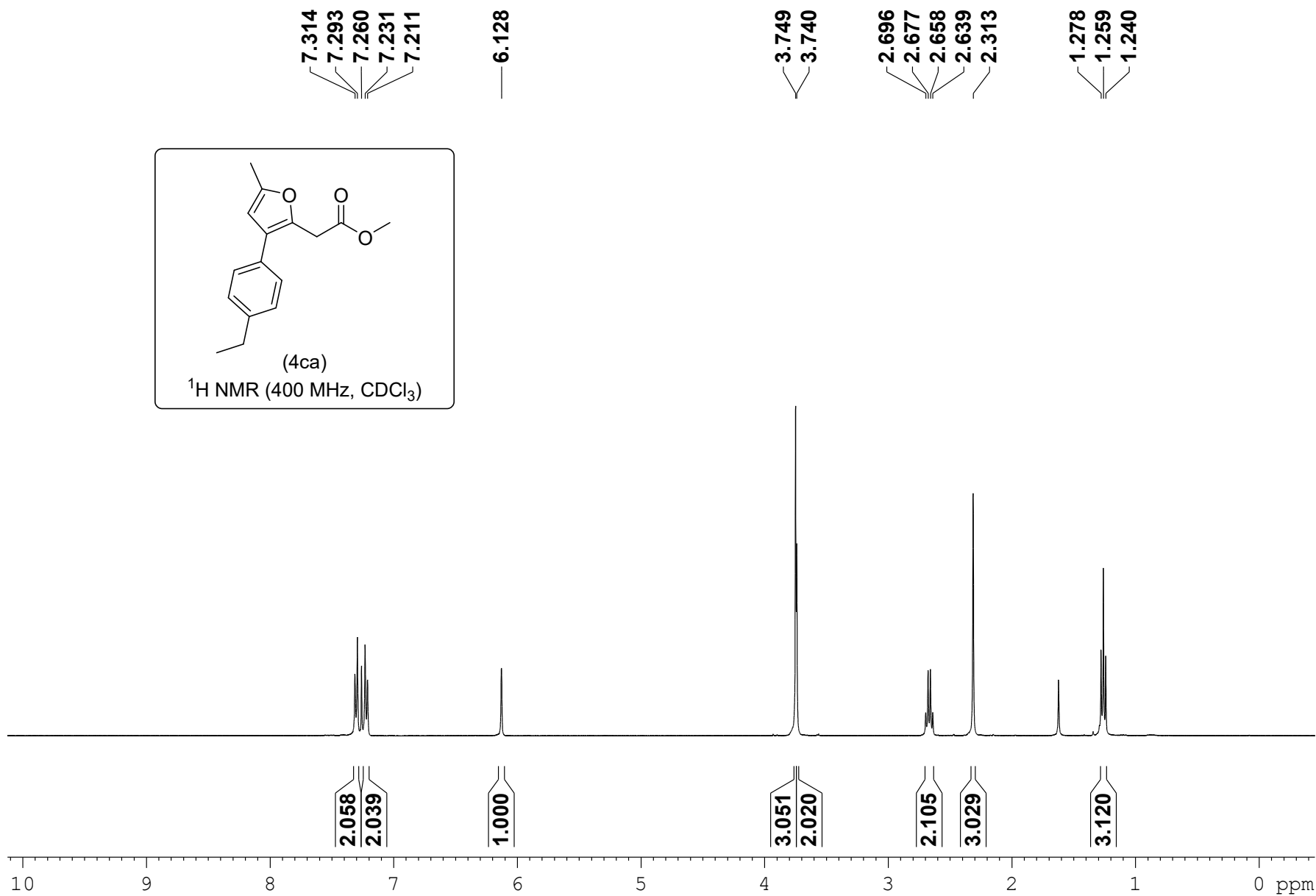
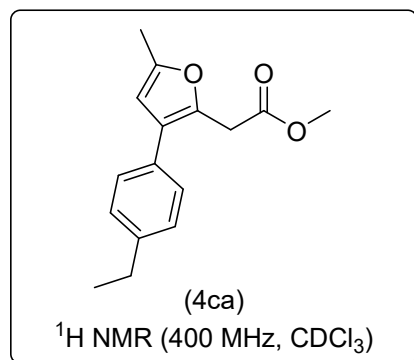
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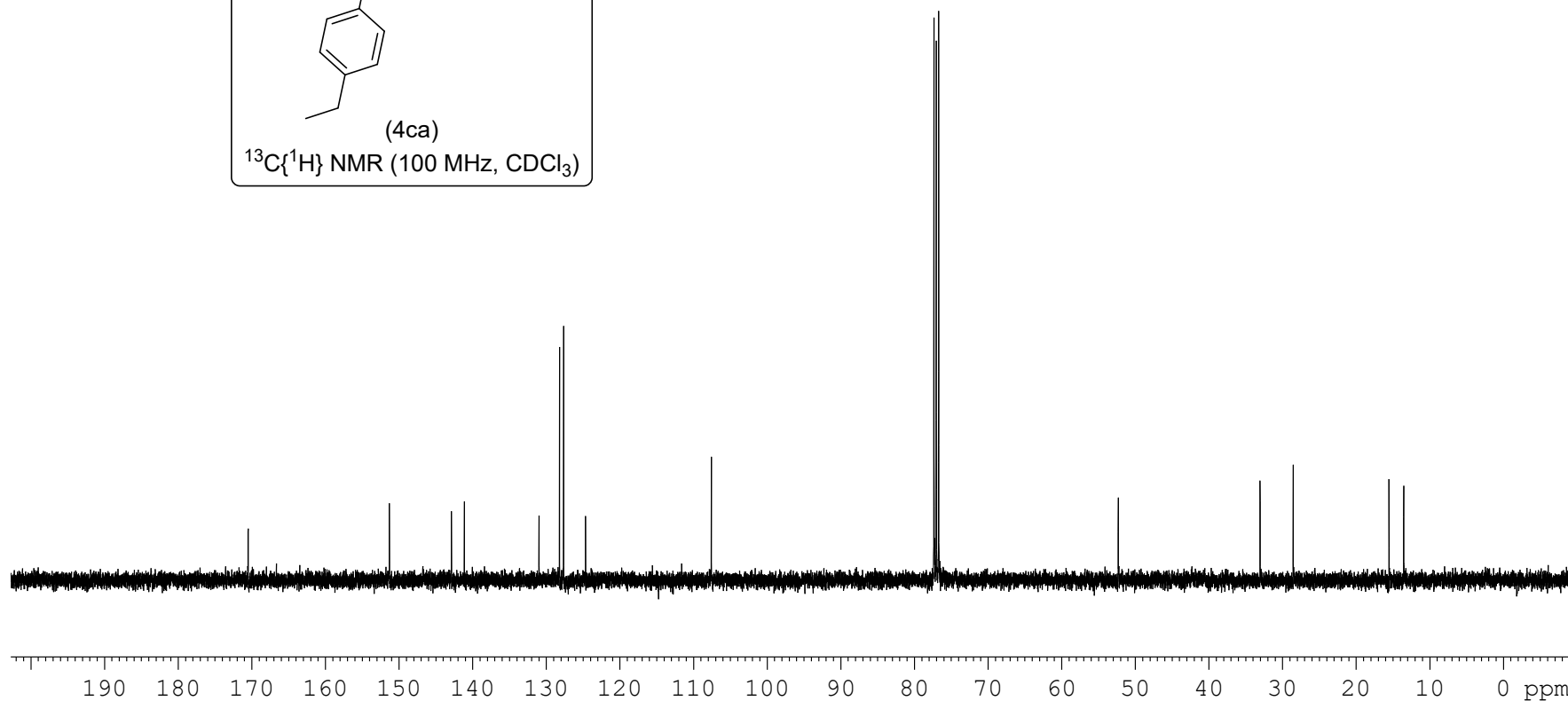
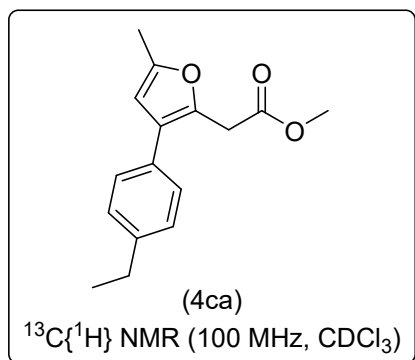
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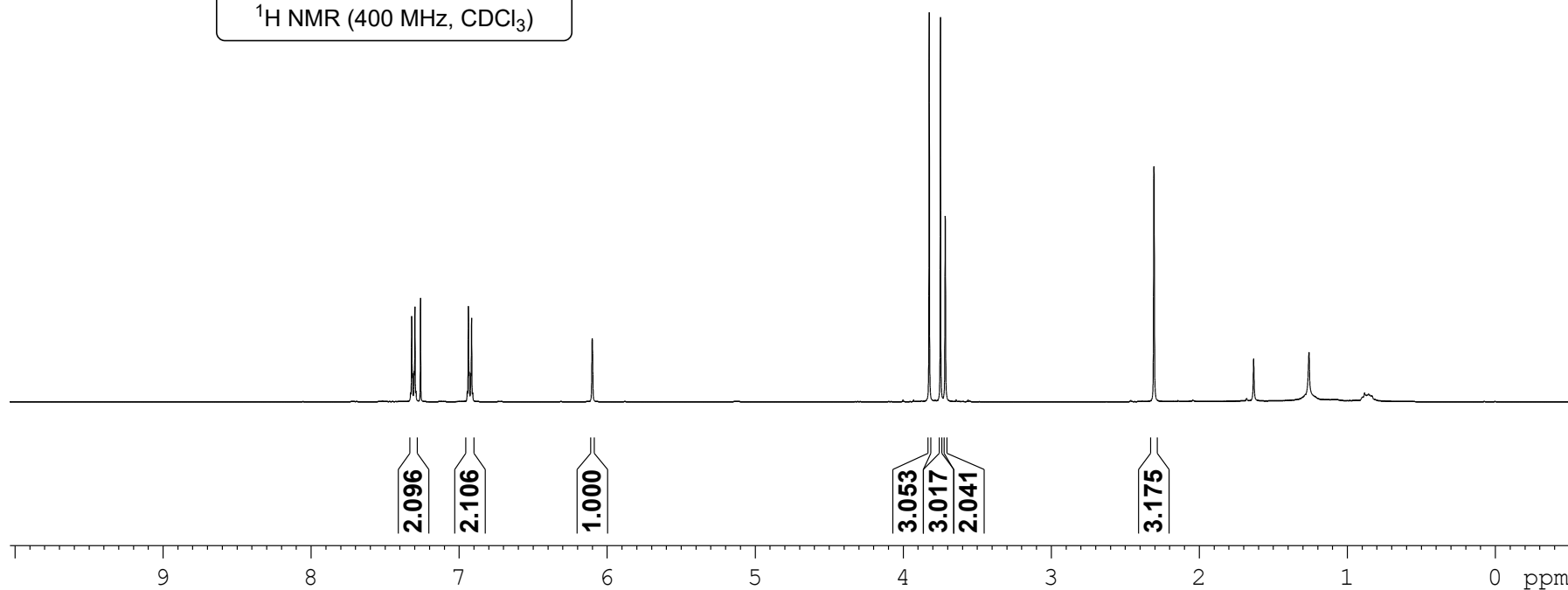
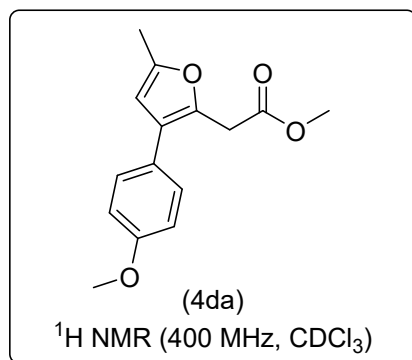
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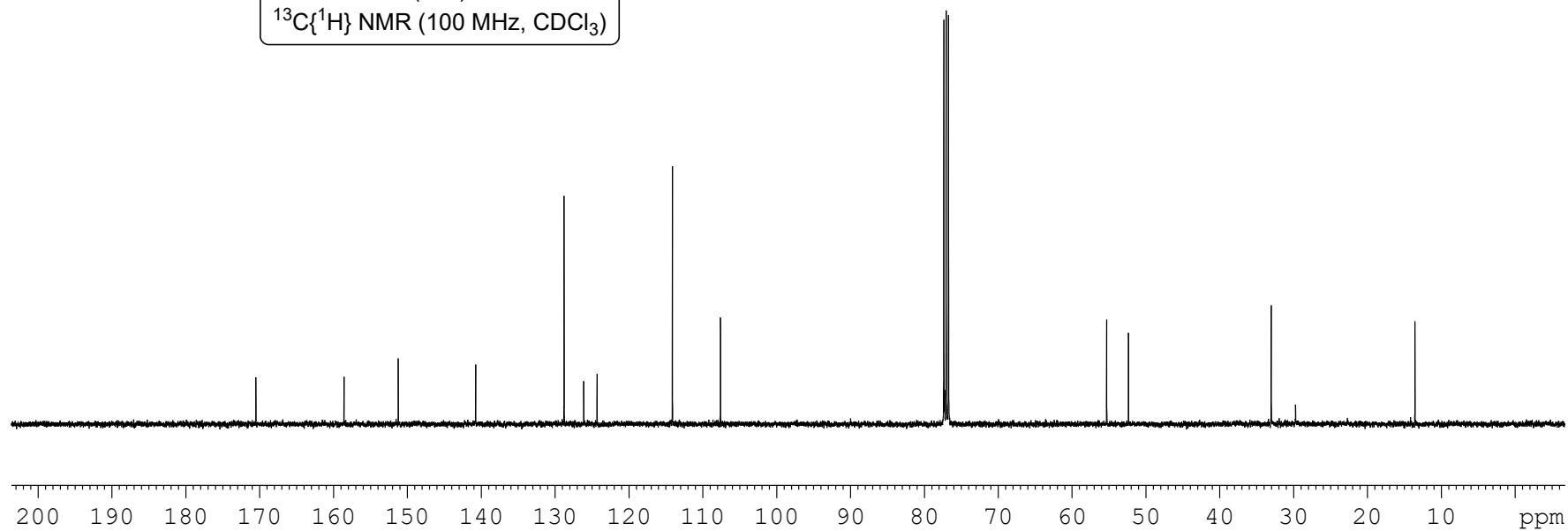
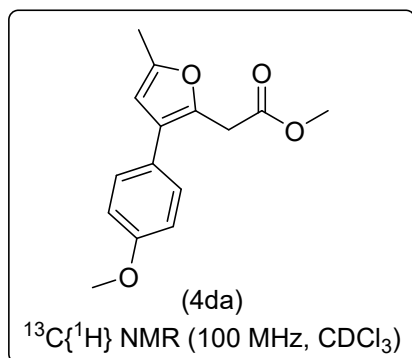
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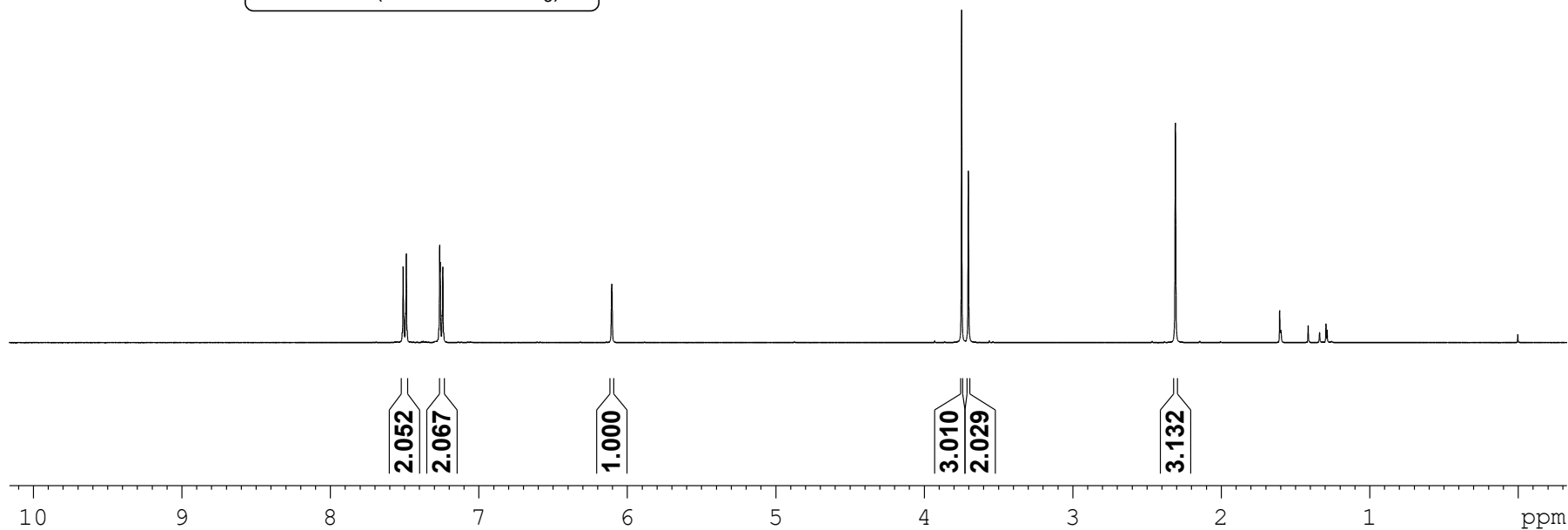
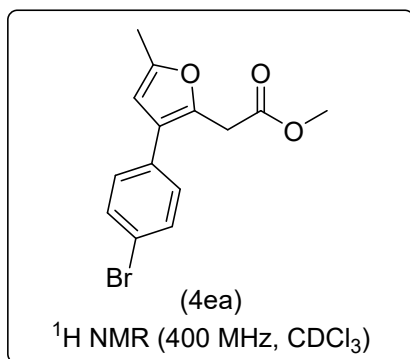
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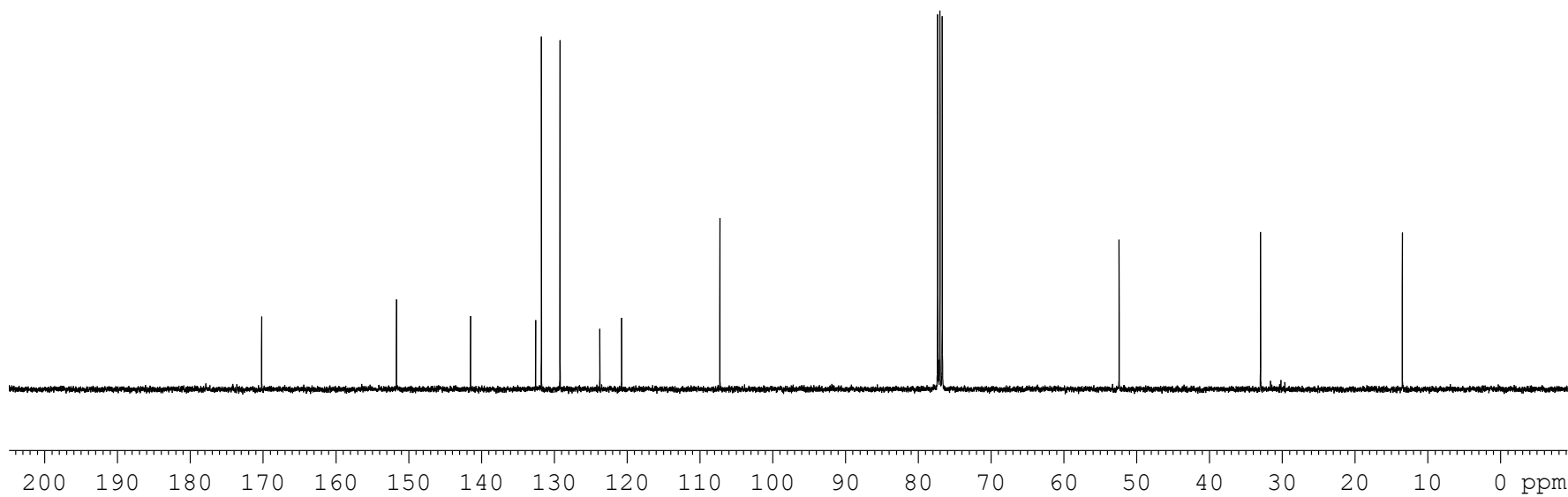
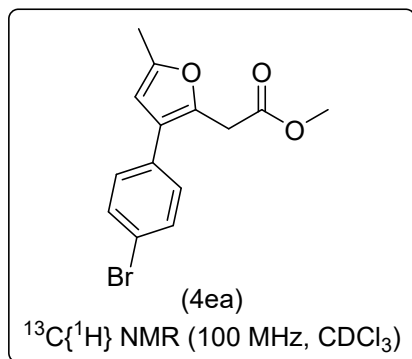
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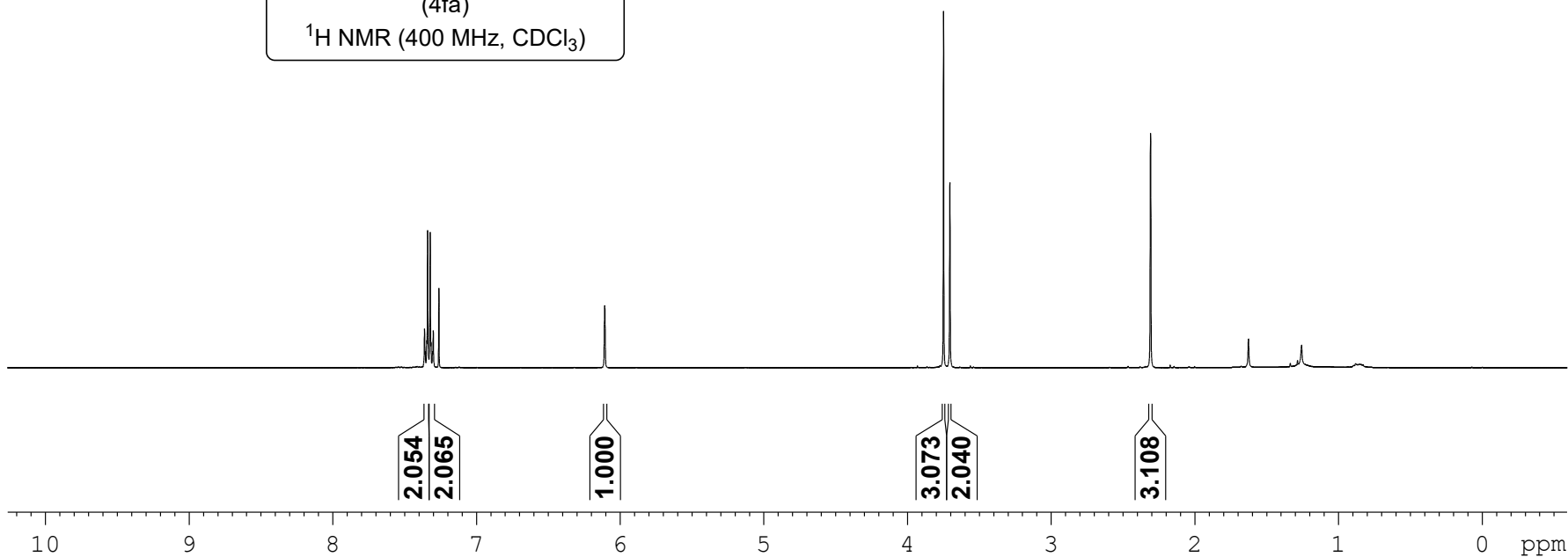
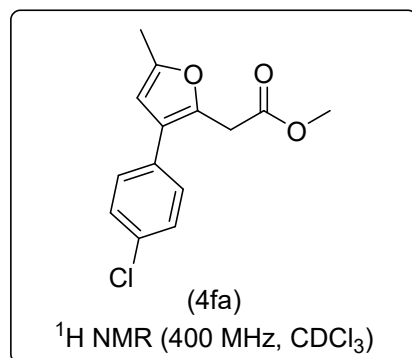
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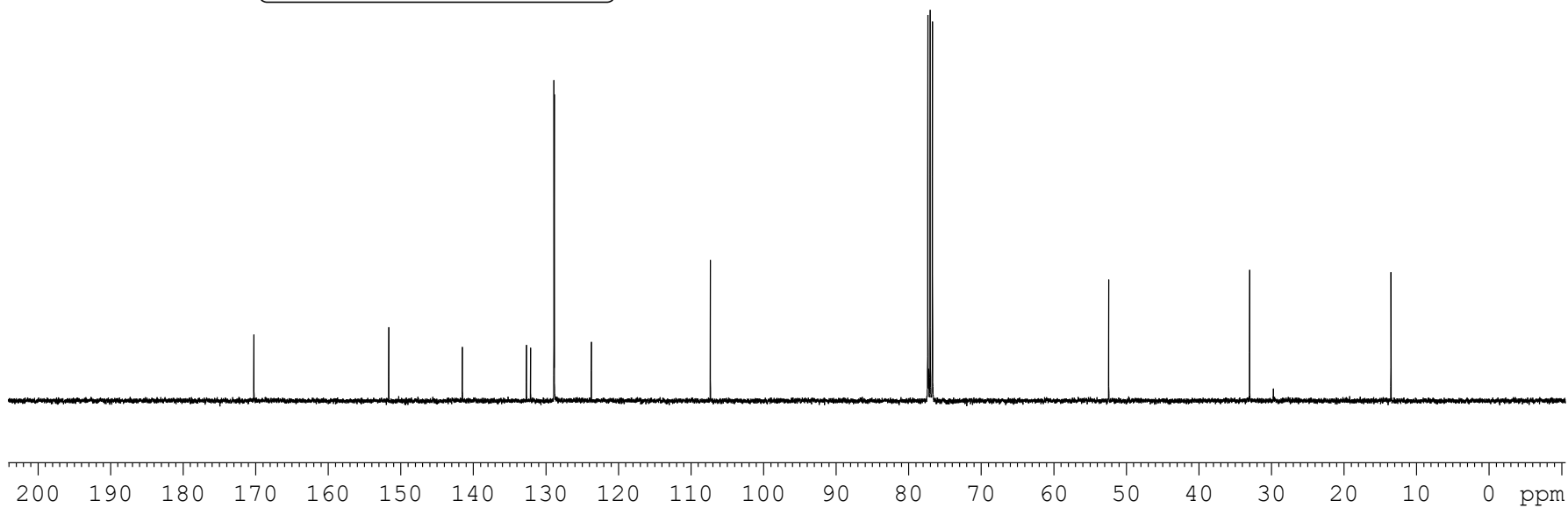
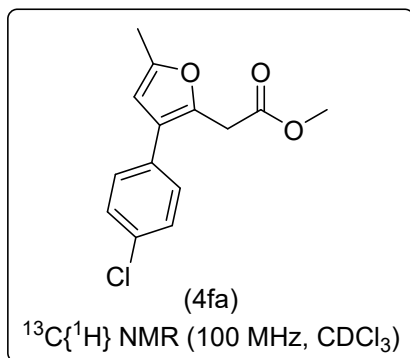
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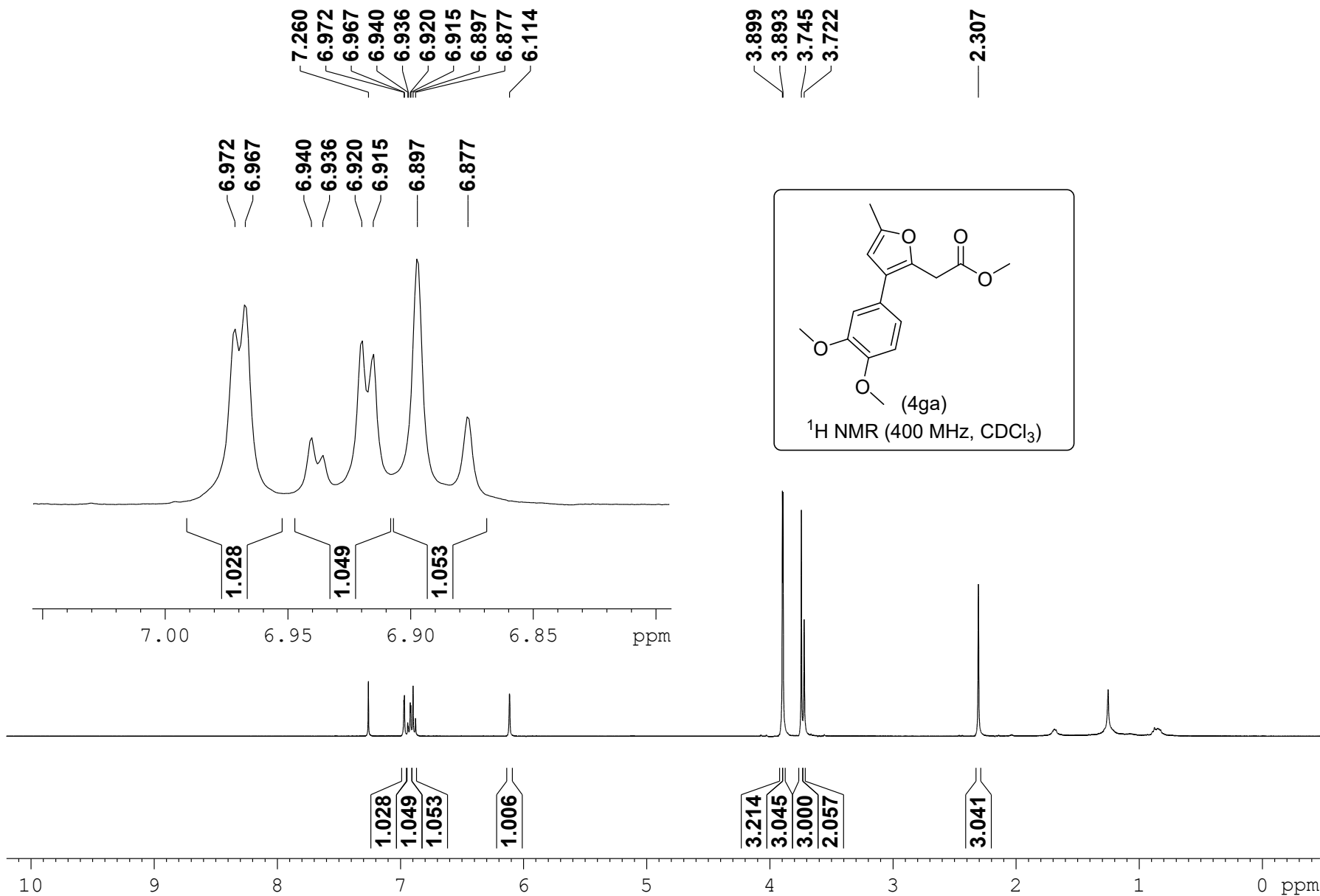
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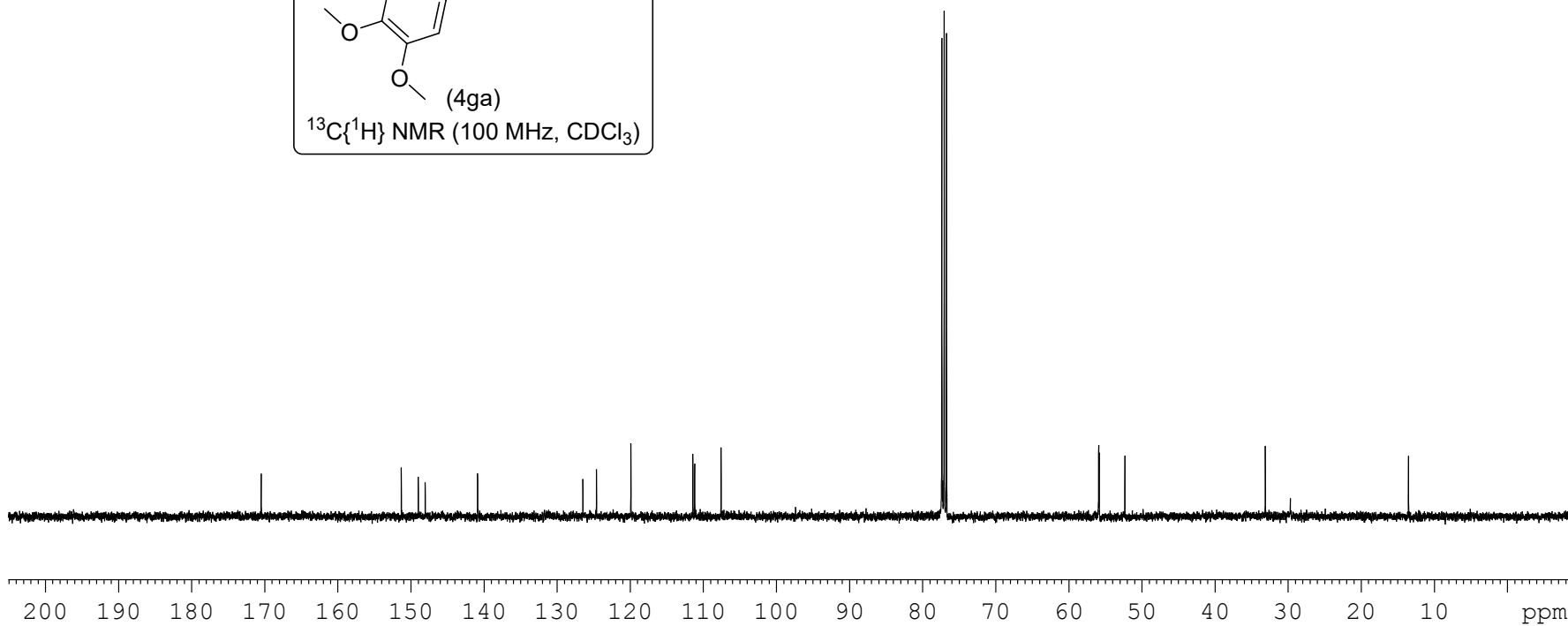
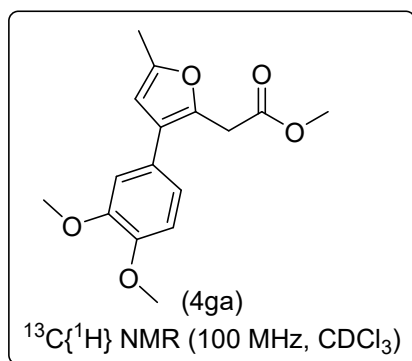
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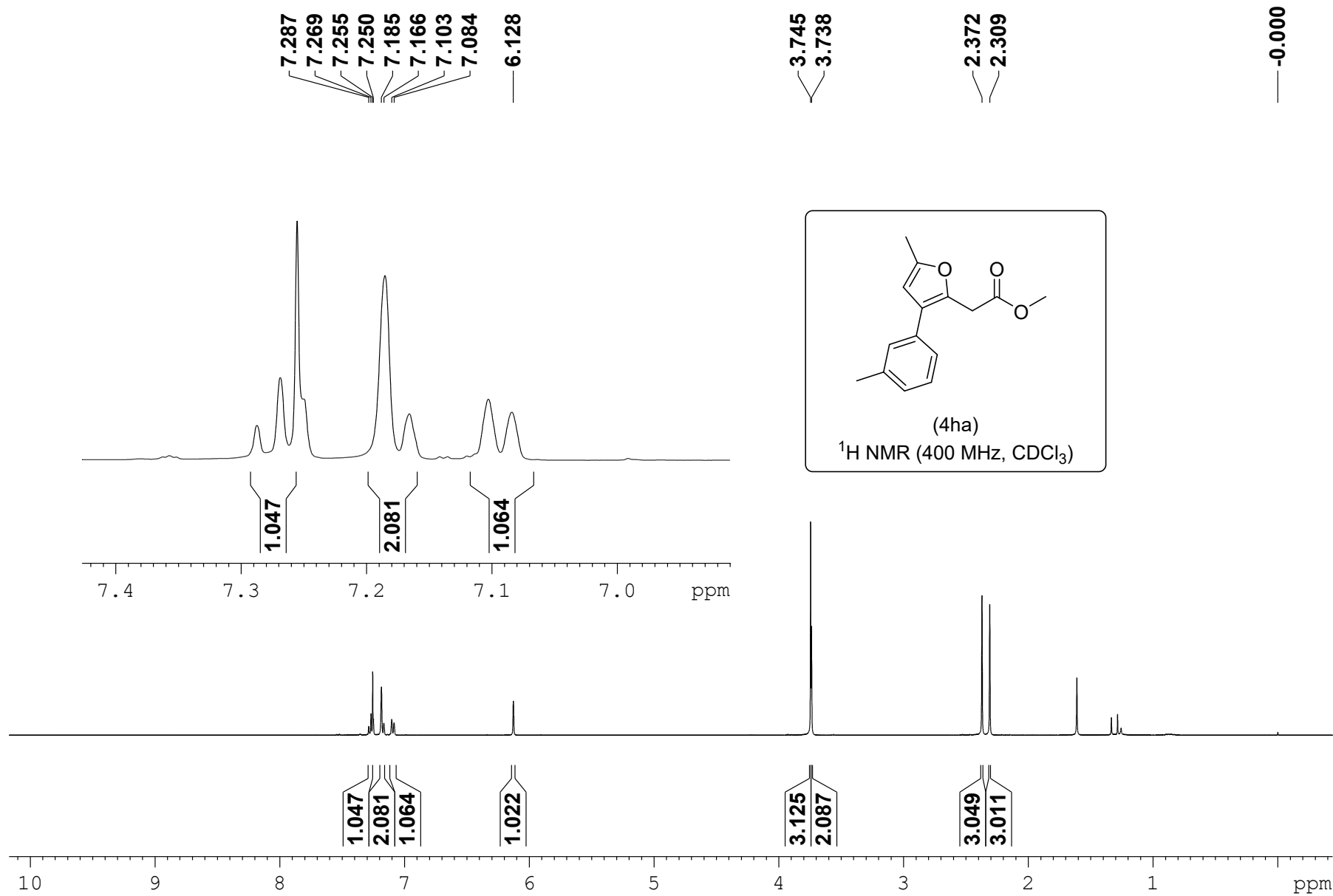
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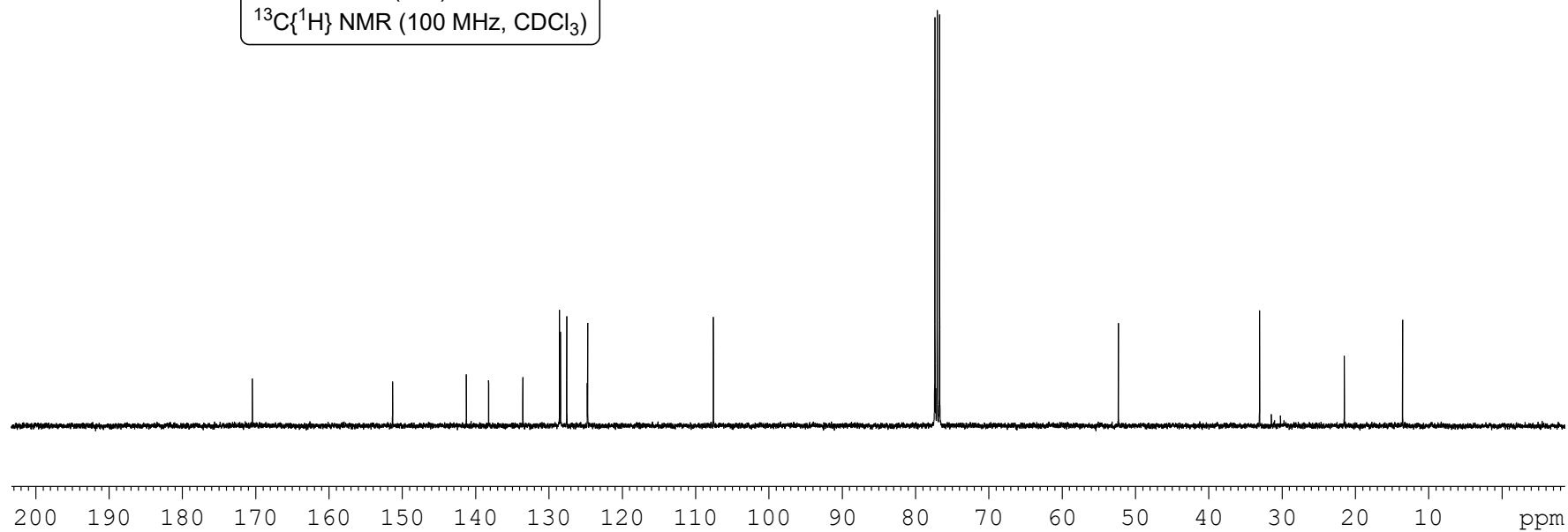
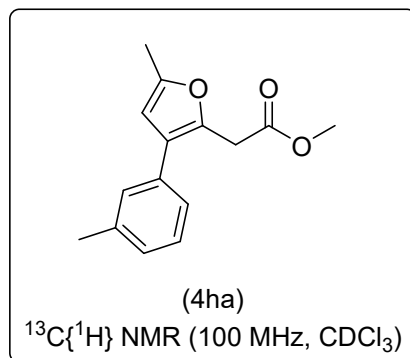
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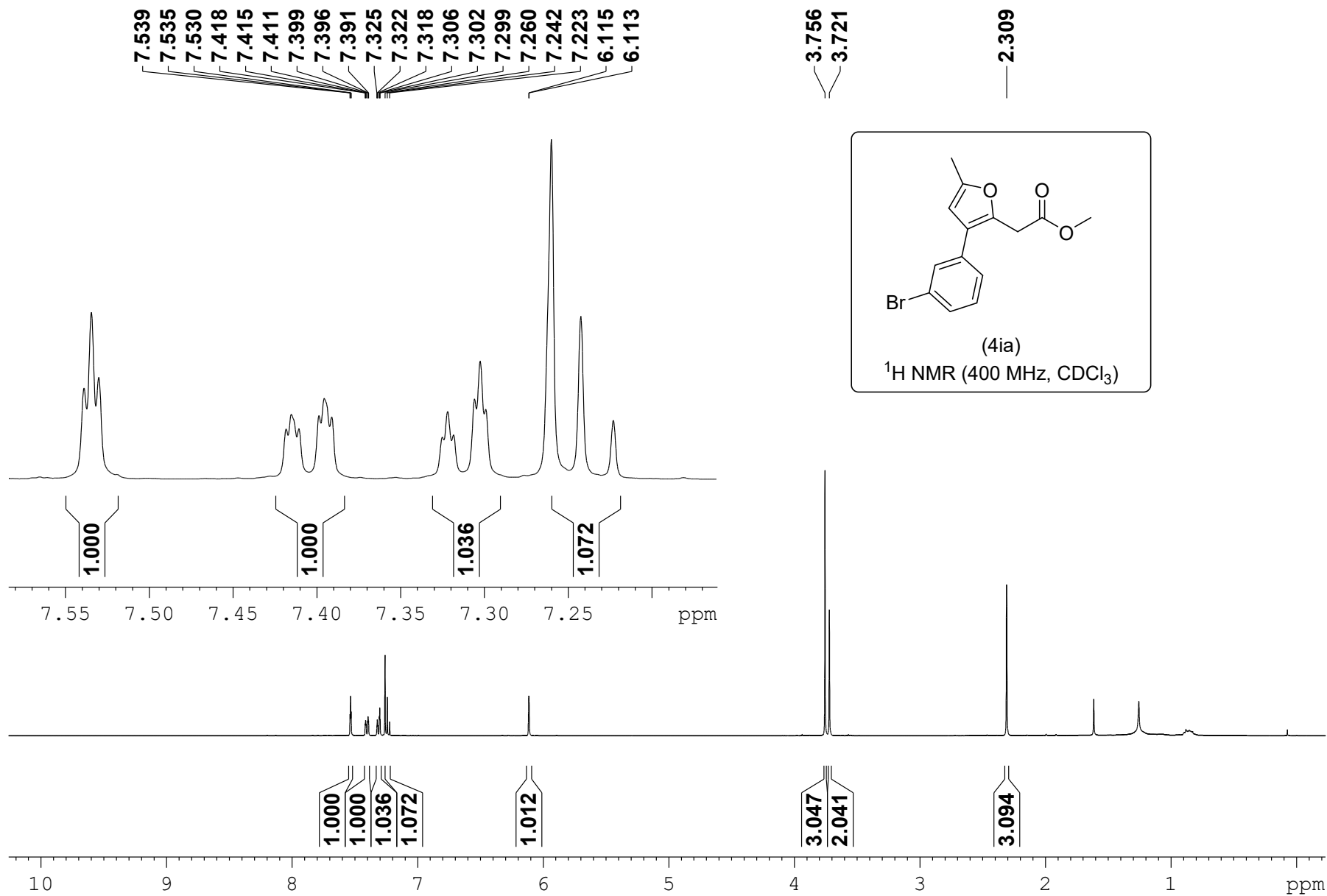
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— 33.058

— 21.499

— 13.543





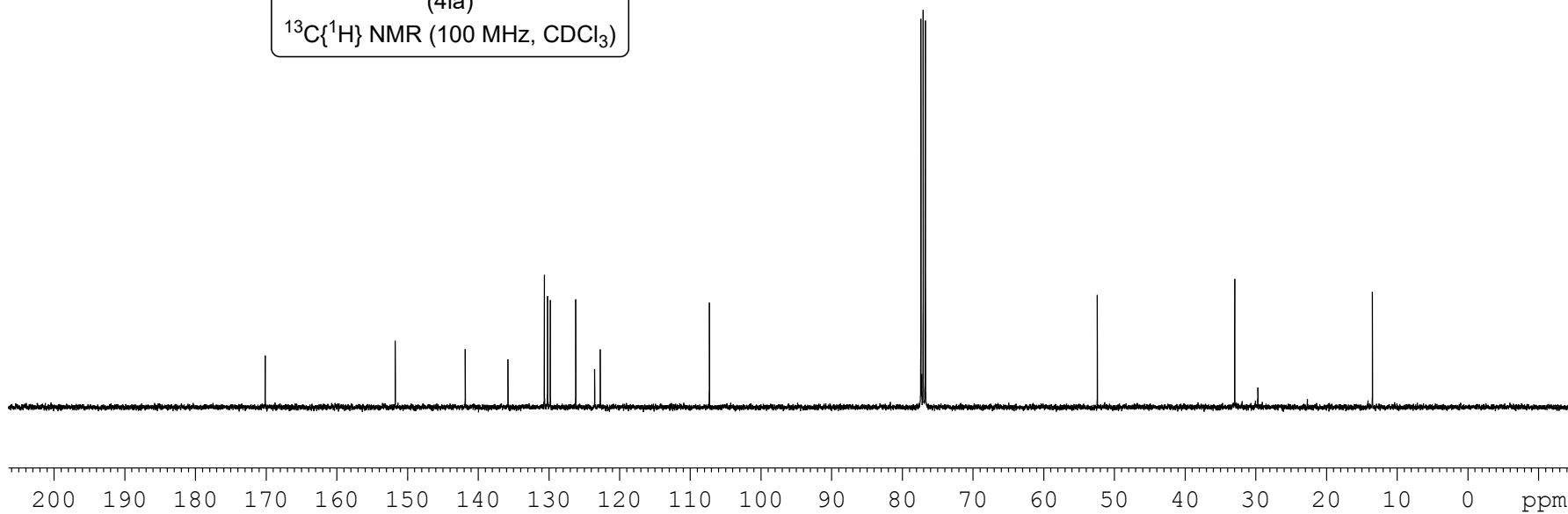
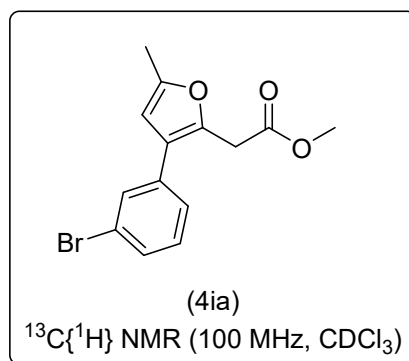
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 — 123.521  
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 — 107.287

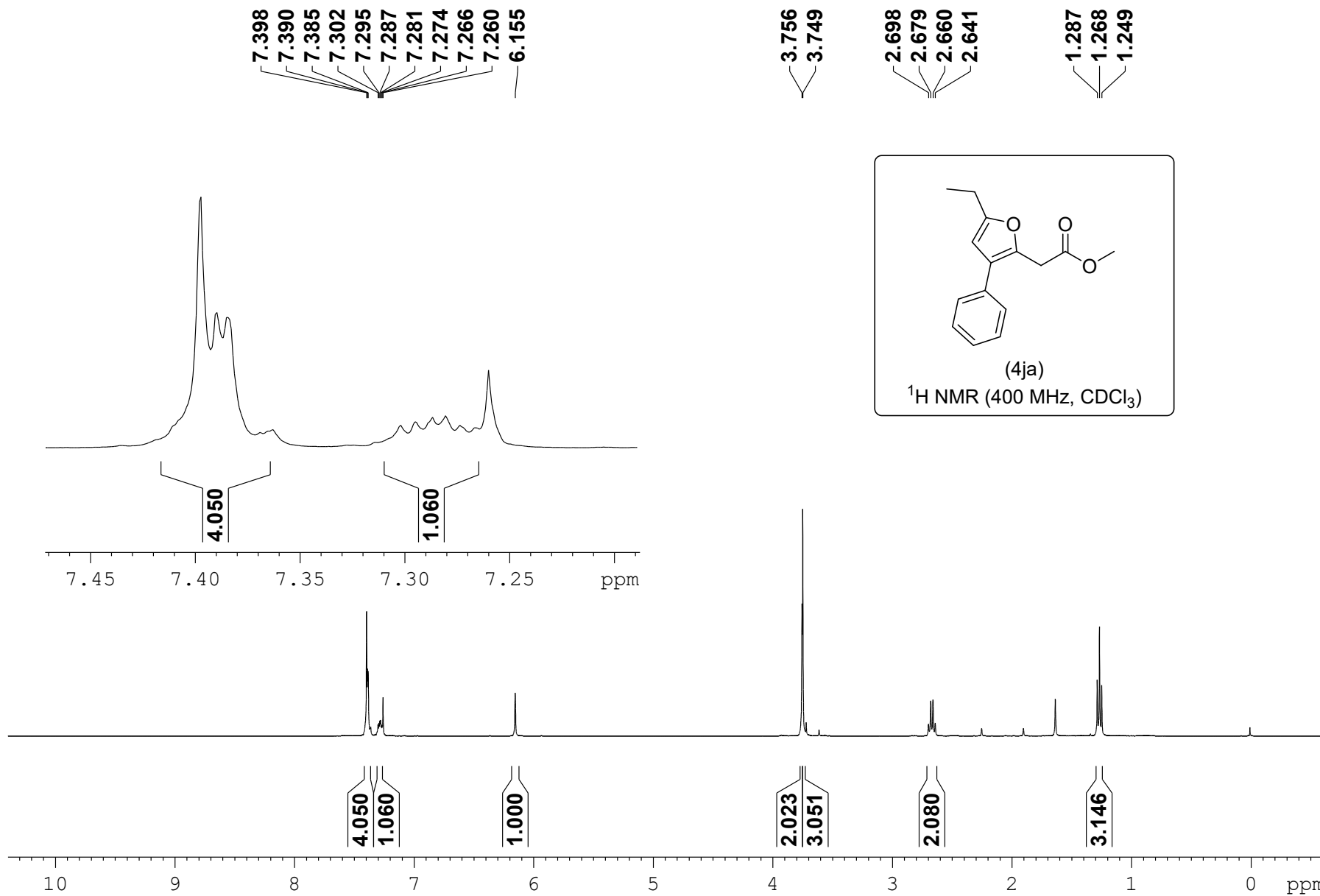
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— 52.441

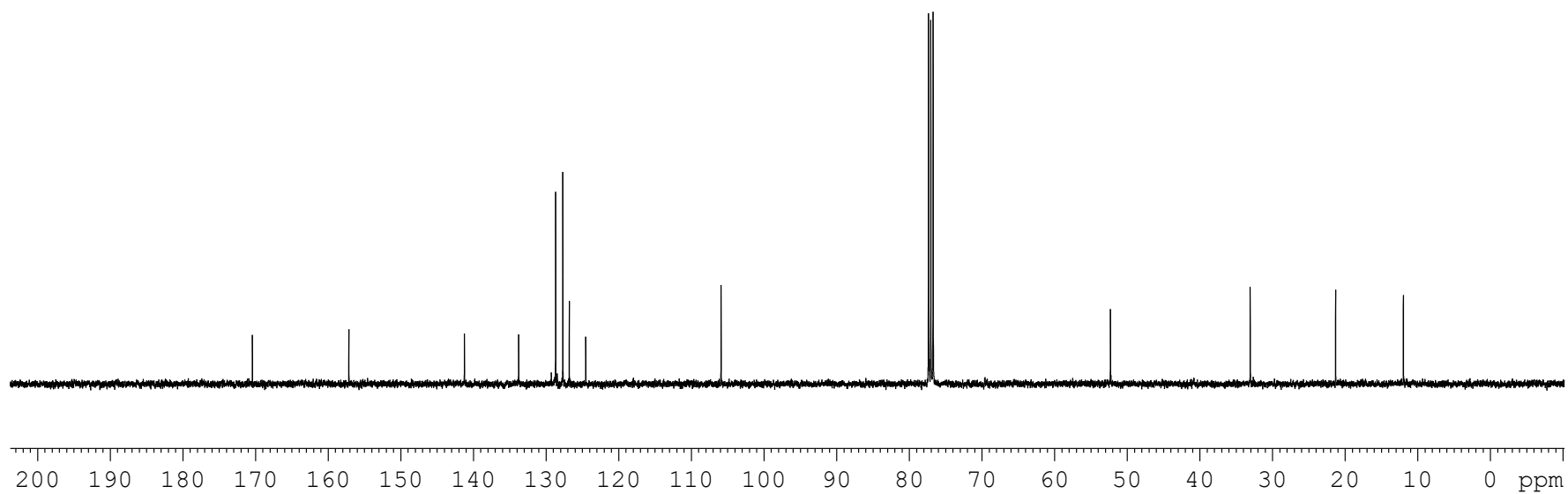
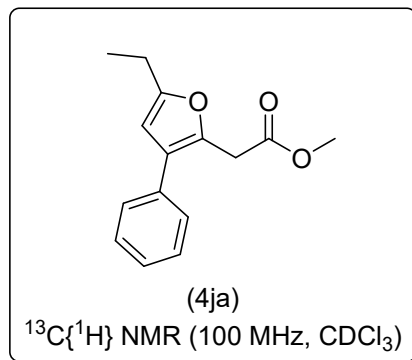
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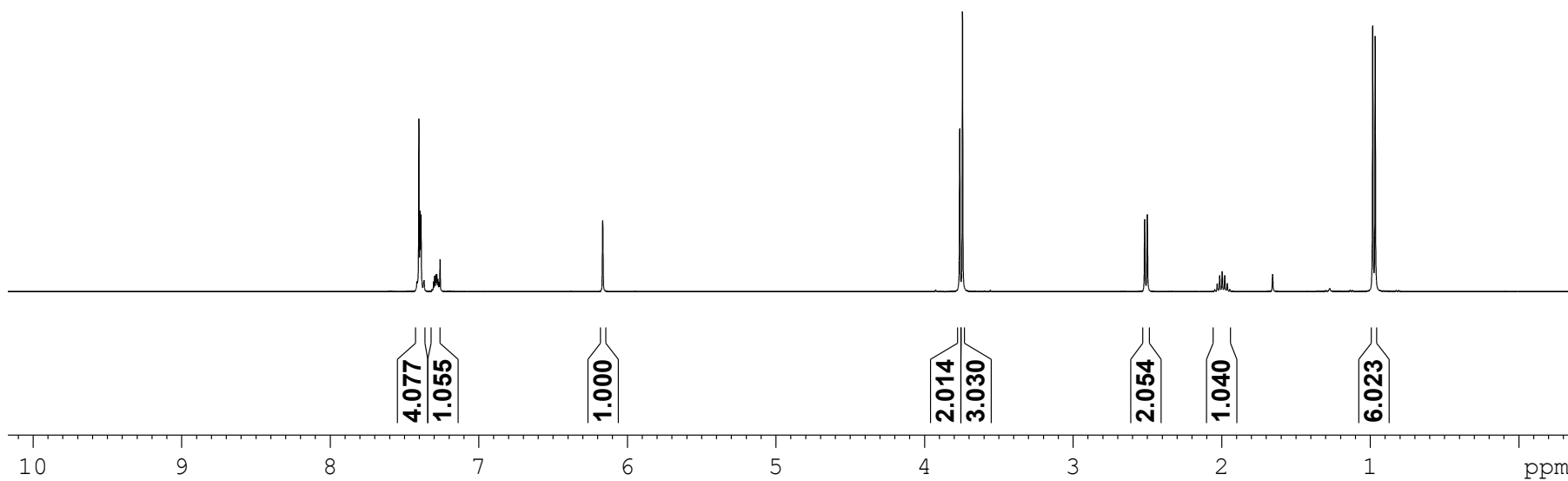
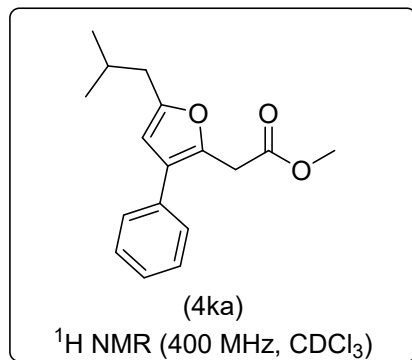
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 — 77.042  
 — 76.724  
 — 52.313  
 — 33.075  
 — 21.318  
 — 11.988



7.415  
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7.395  
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3.745

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—170.382

—154.948

—141.299

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—76.748

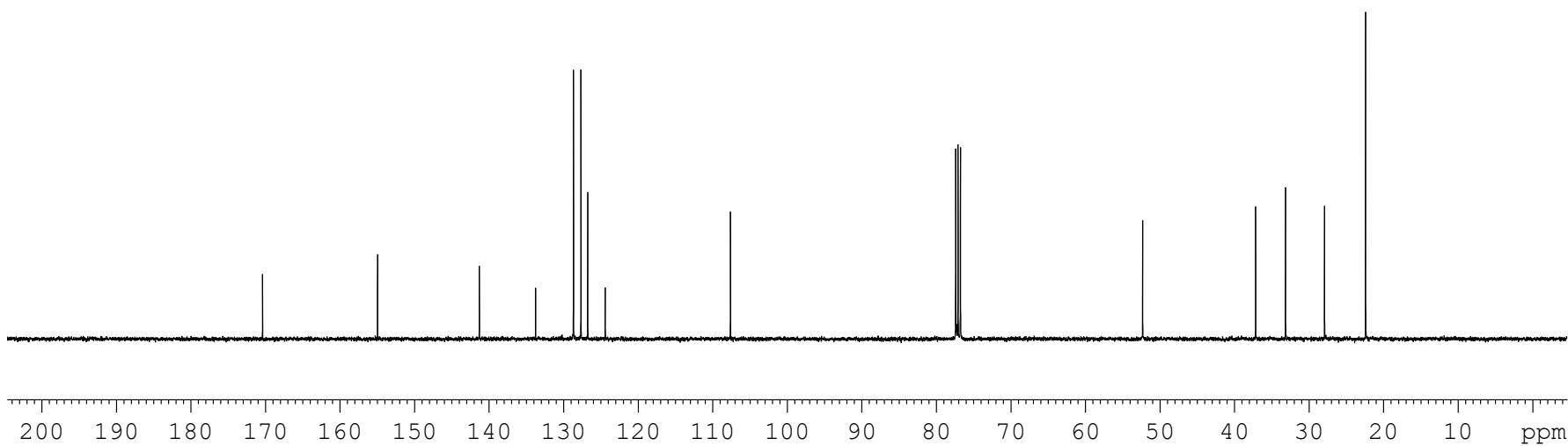
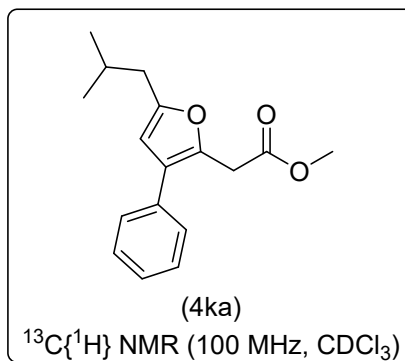
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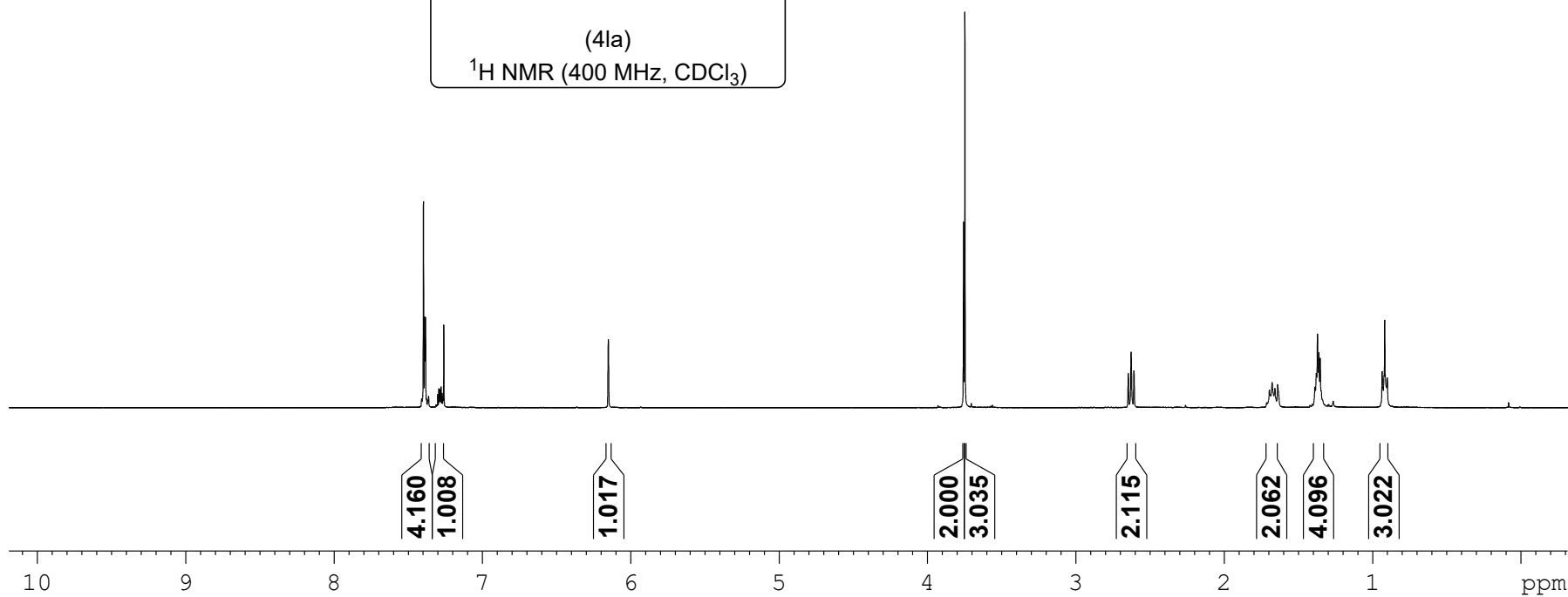
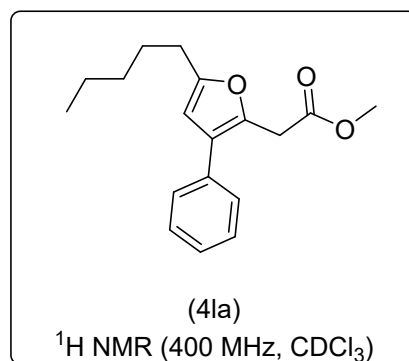
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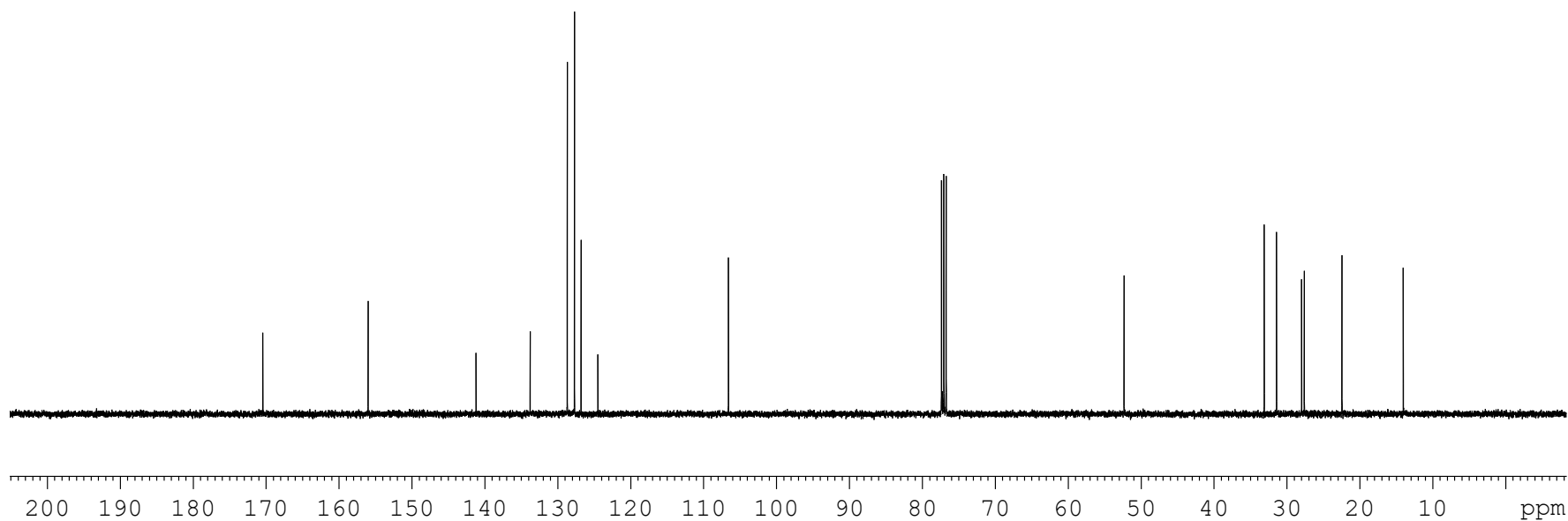
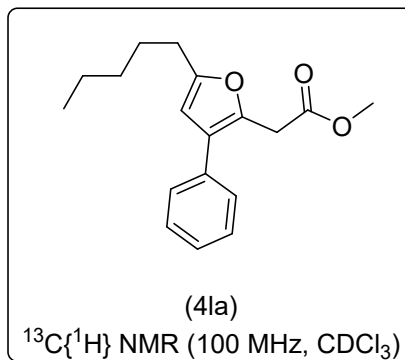


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7.265  
7.260  
6.151

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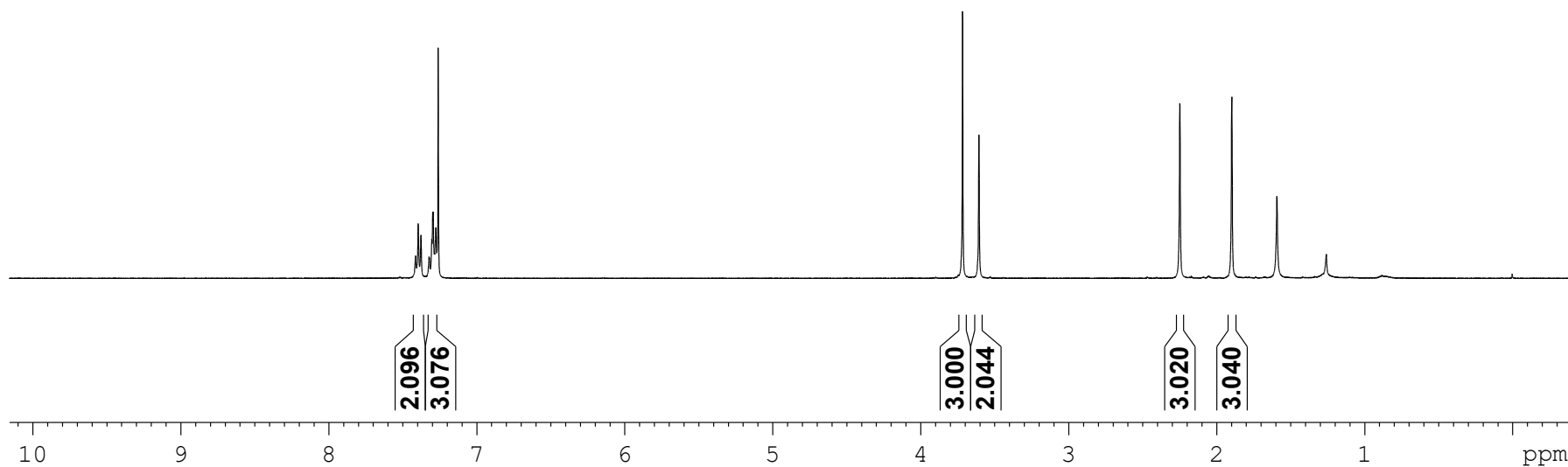
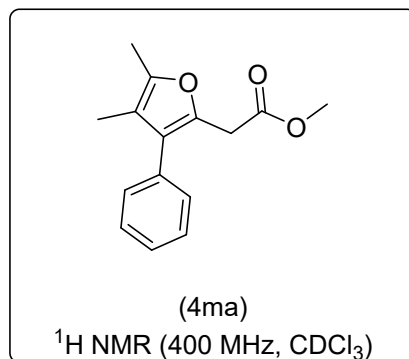
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- 126.760
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- 106.553
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- 33.108
- 31.426
- 27.978
- 27.610
- 22.447
- 14.037

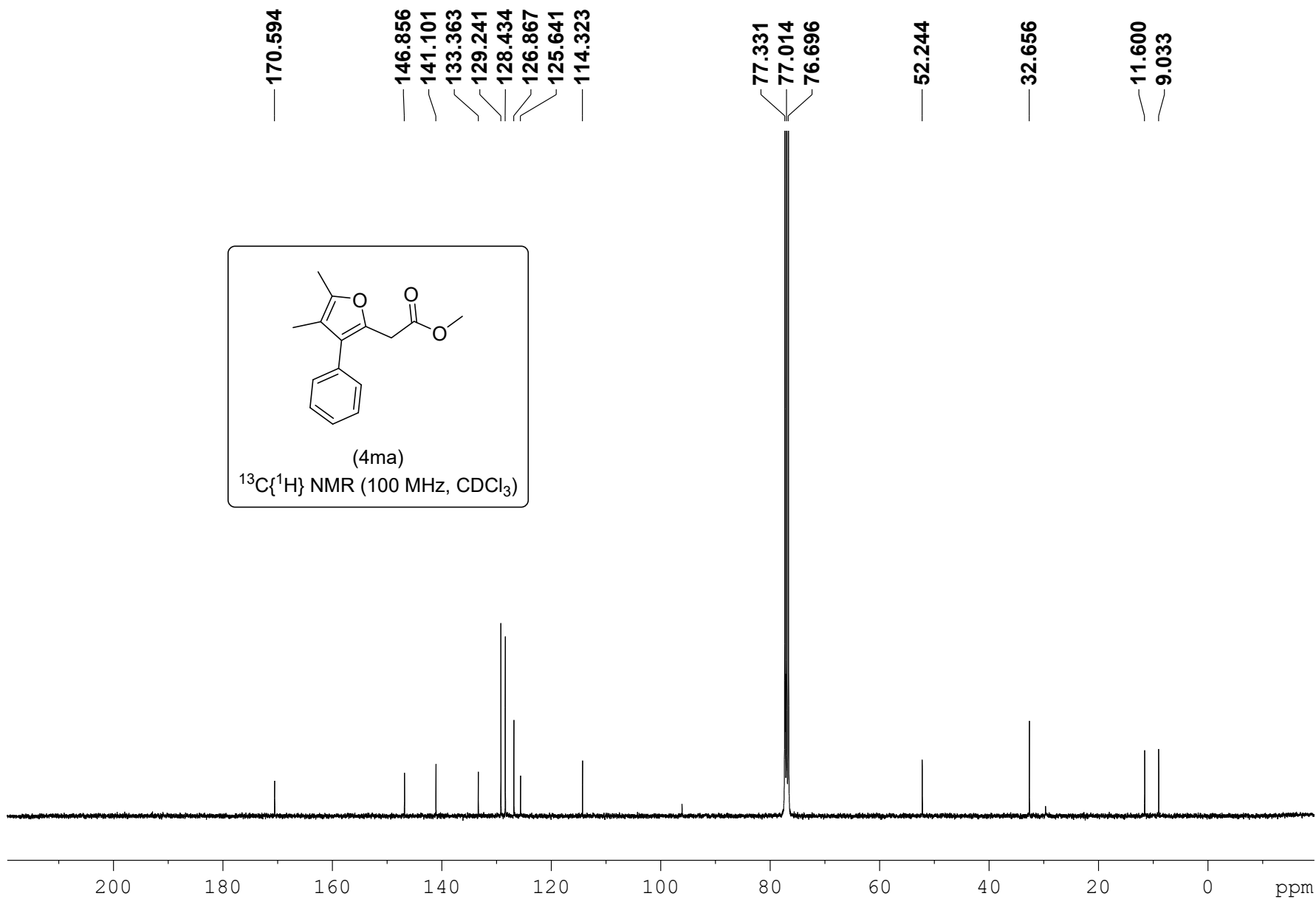


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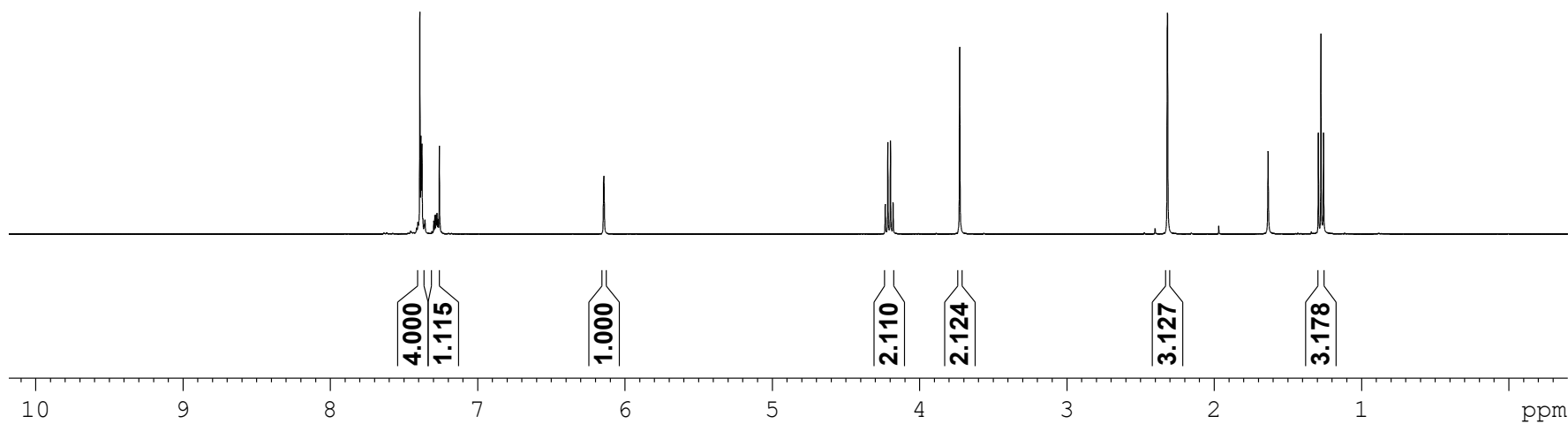
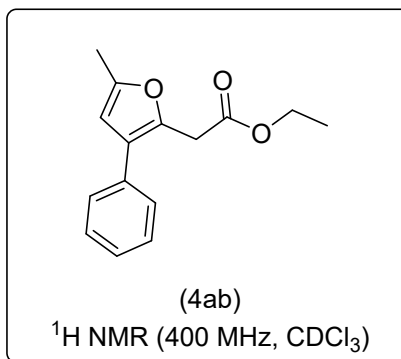


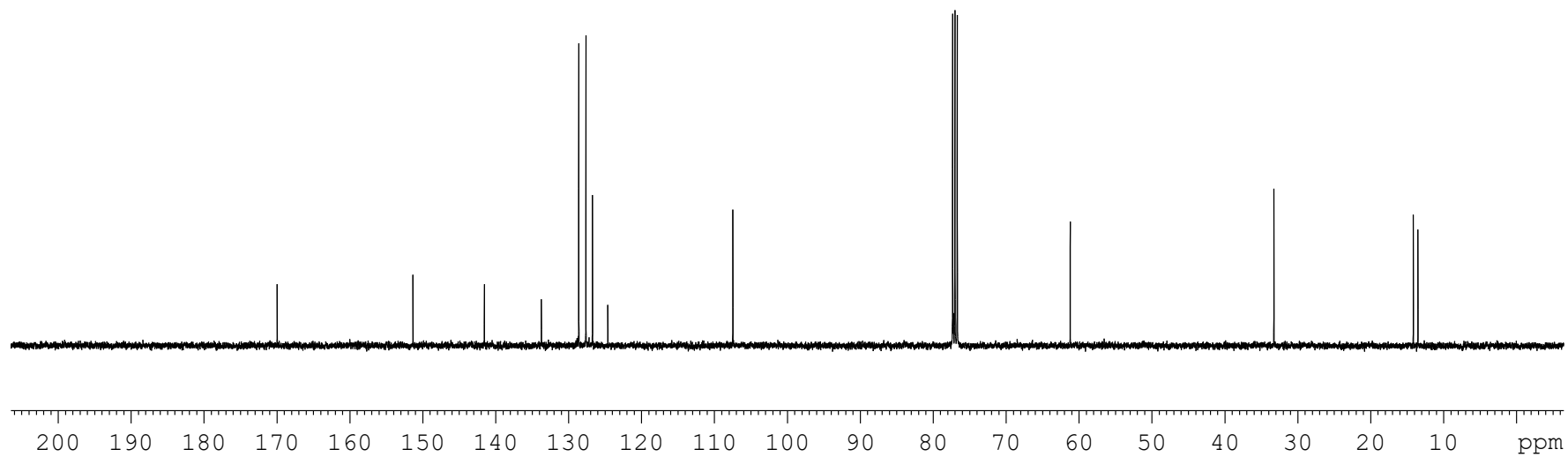
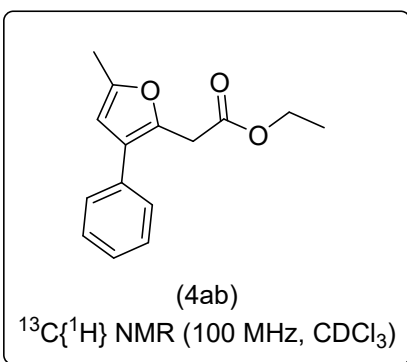
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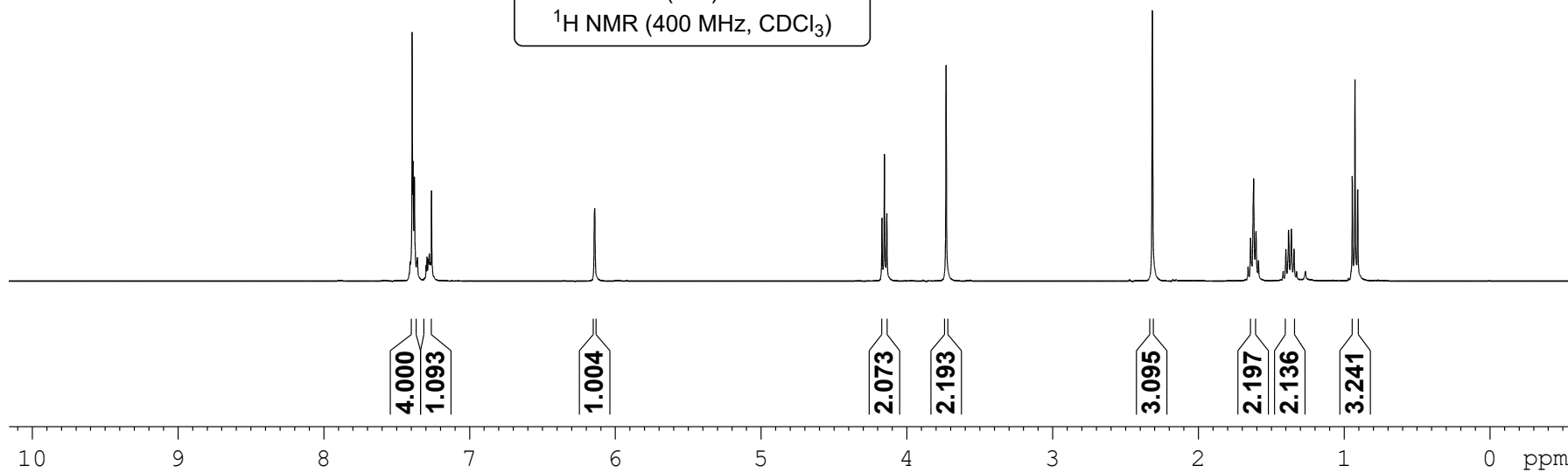
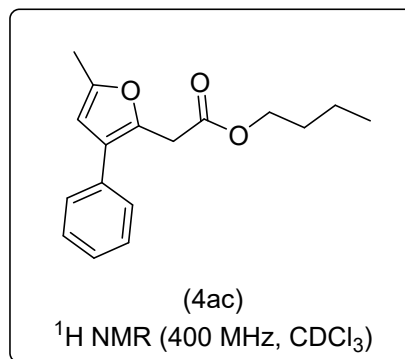




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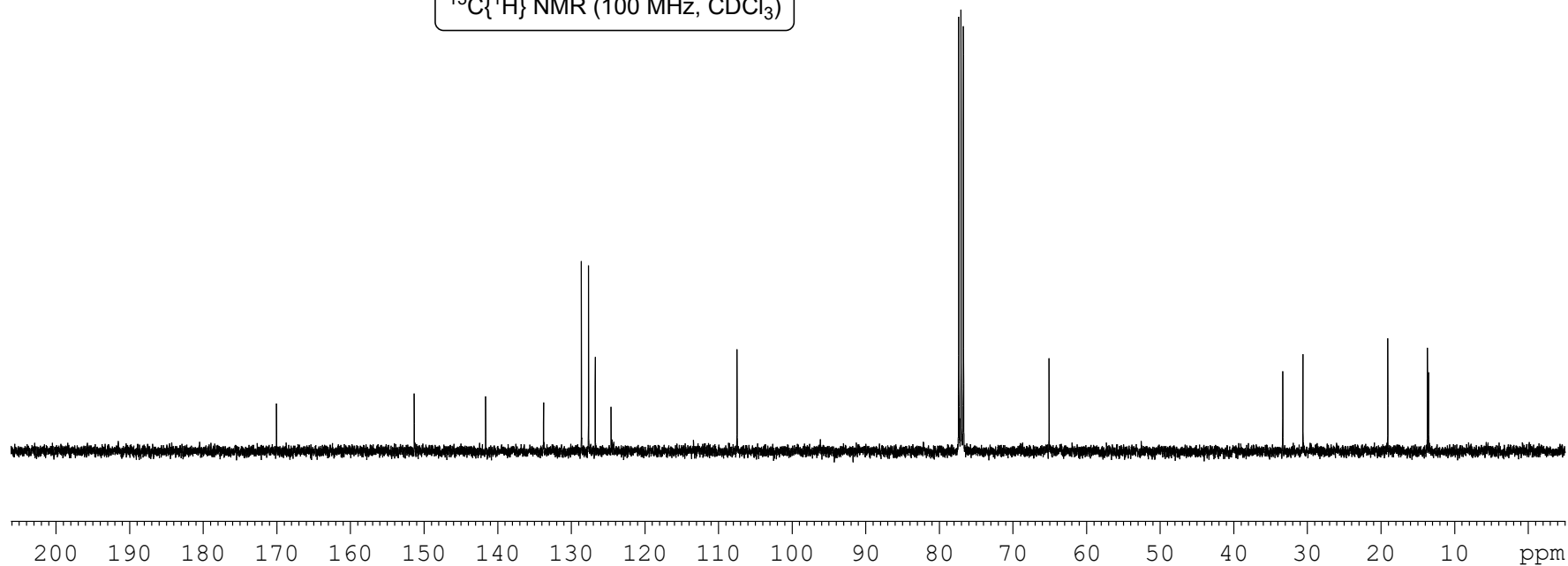
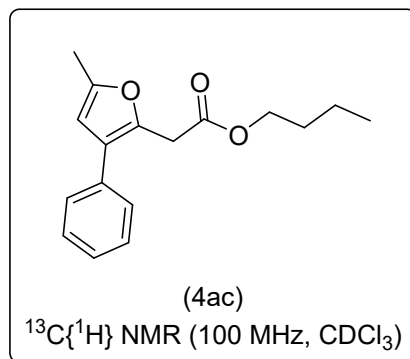
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1.343  
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0.906





— 170.006  
— 151.288  
— 141.593  
— 133.757  
— 128.616  
— 127.653  
— 126.731  
— 124.588  
— 107.471  
  
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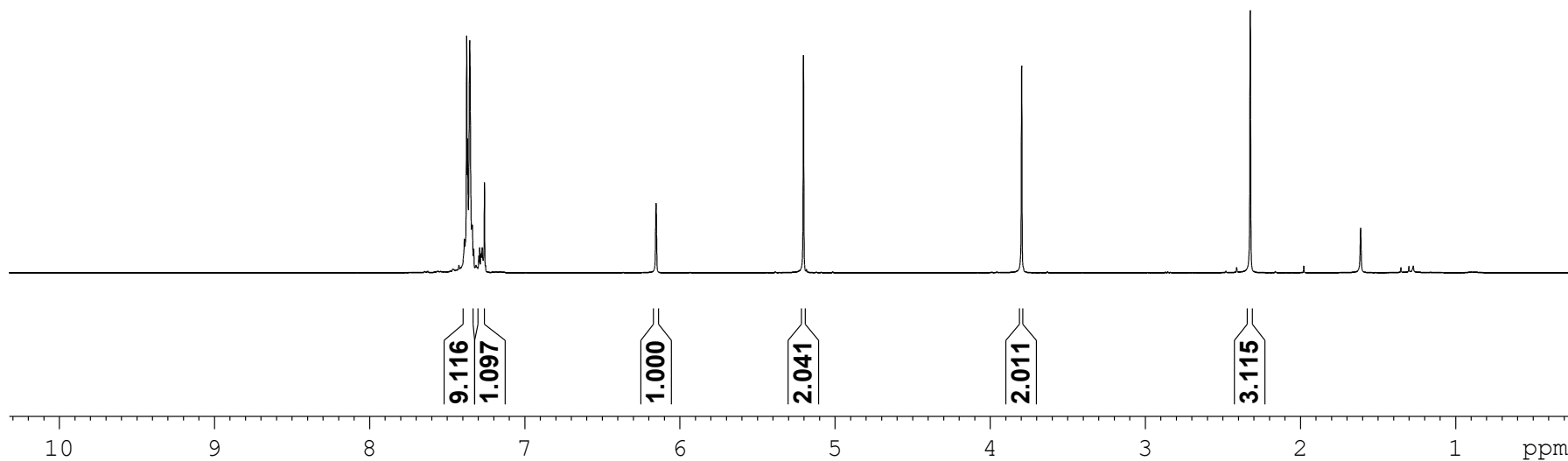
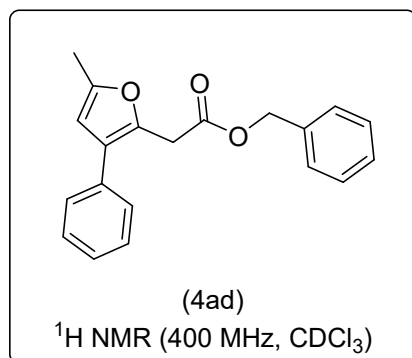


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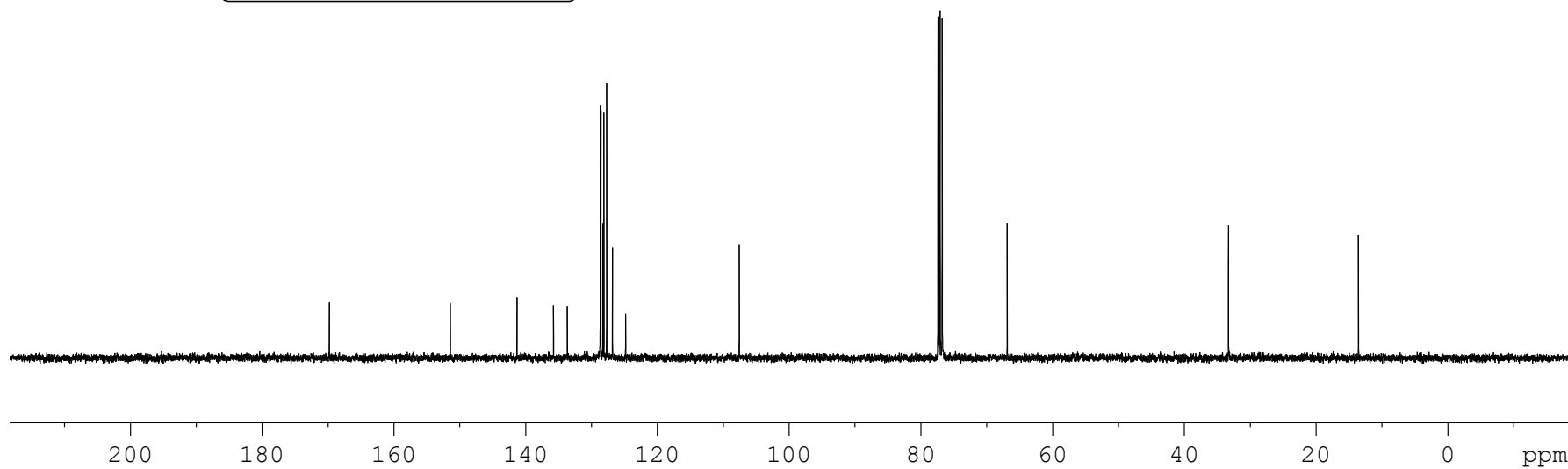
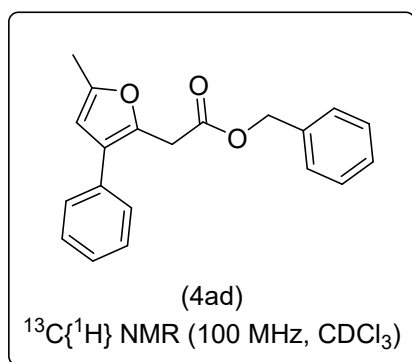


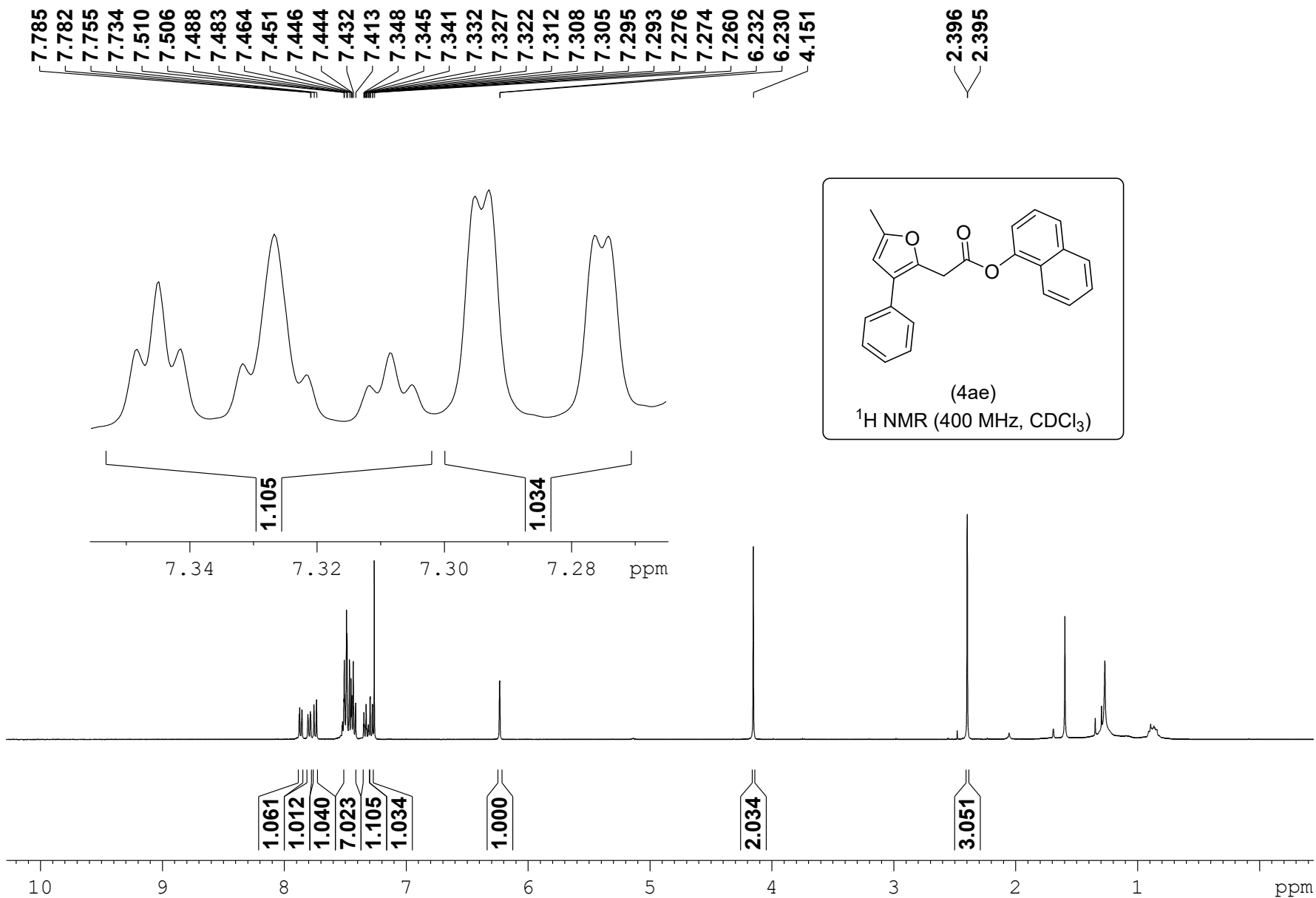
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33.274

13.552



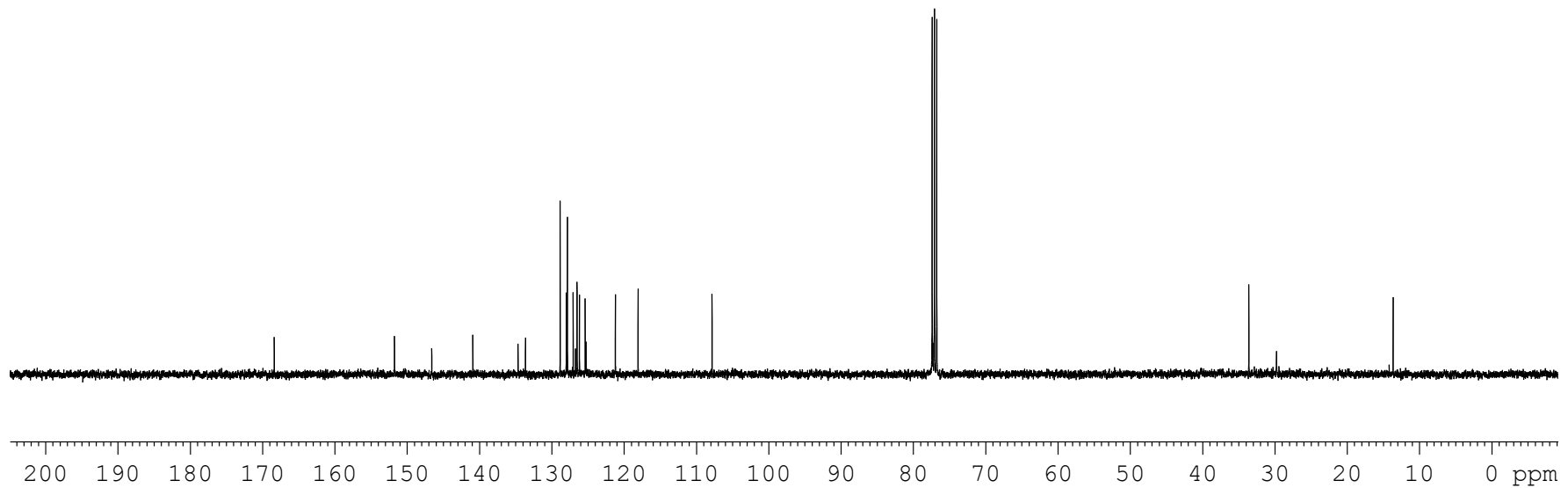
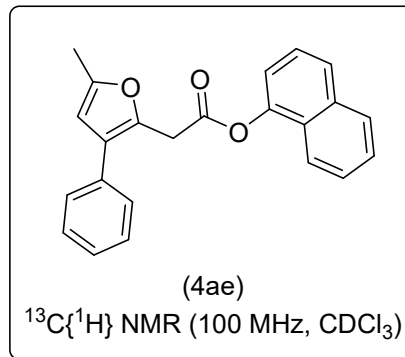


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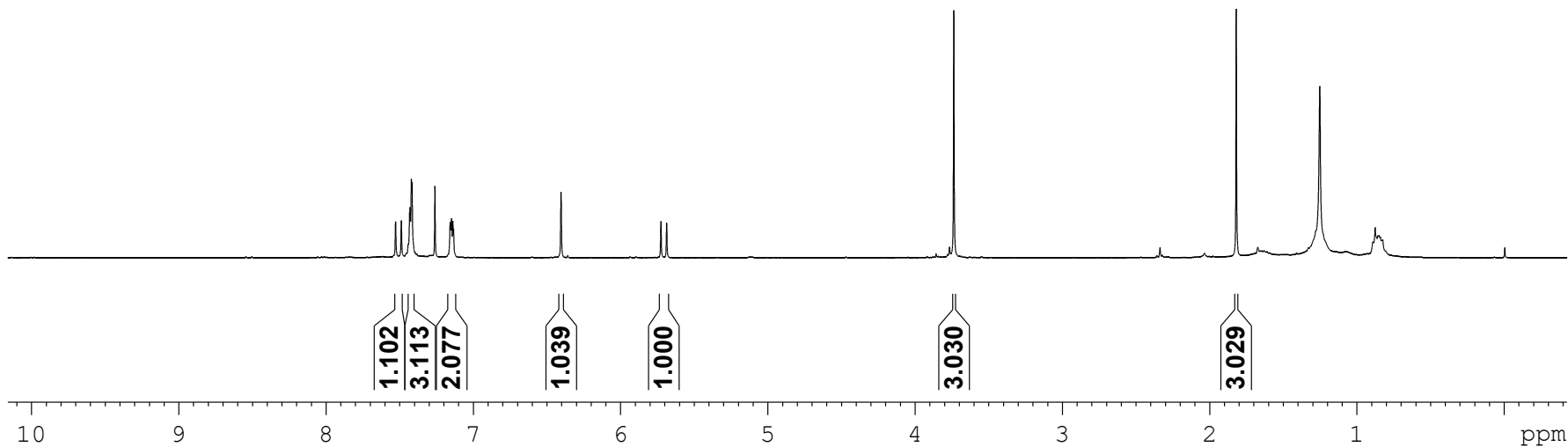
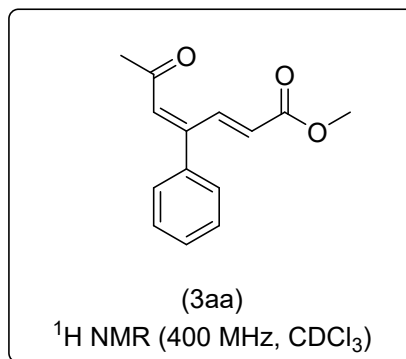
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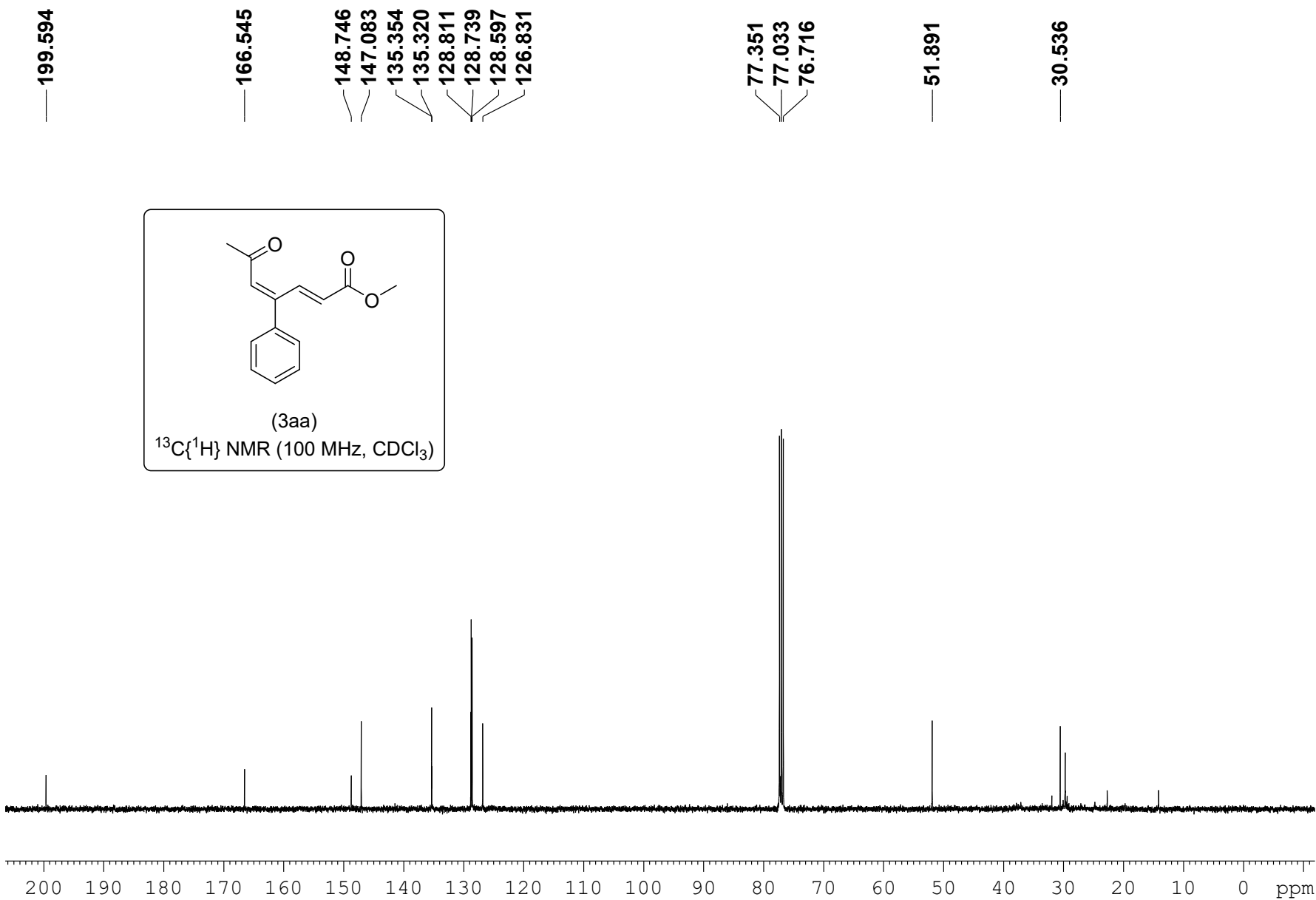


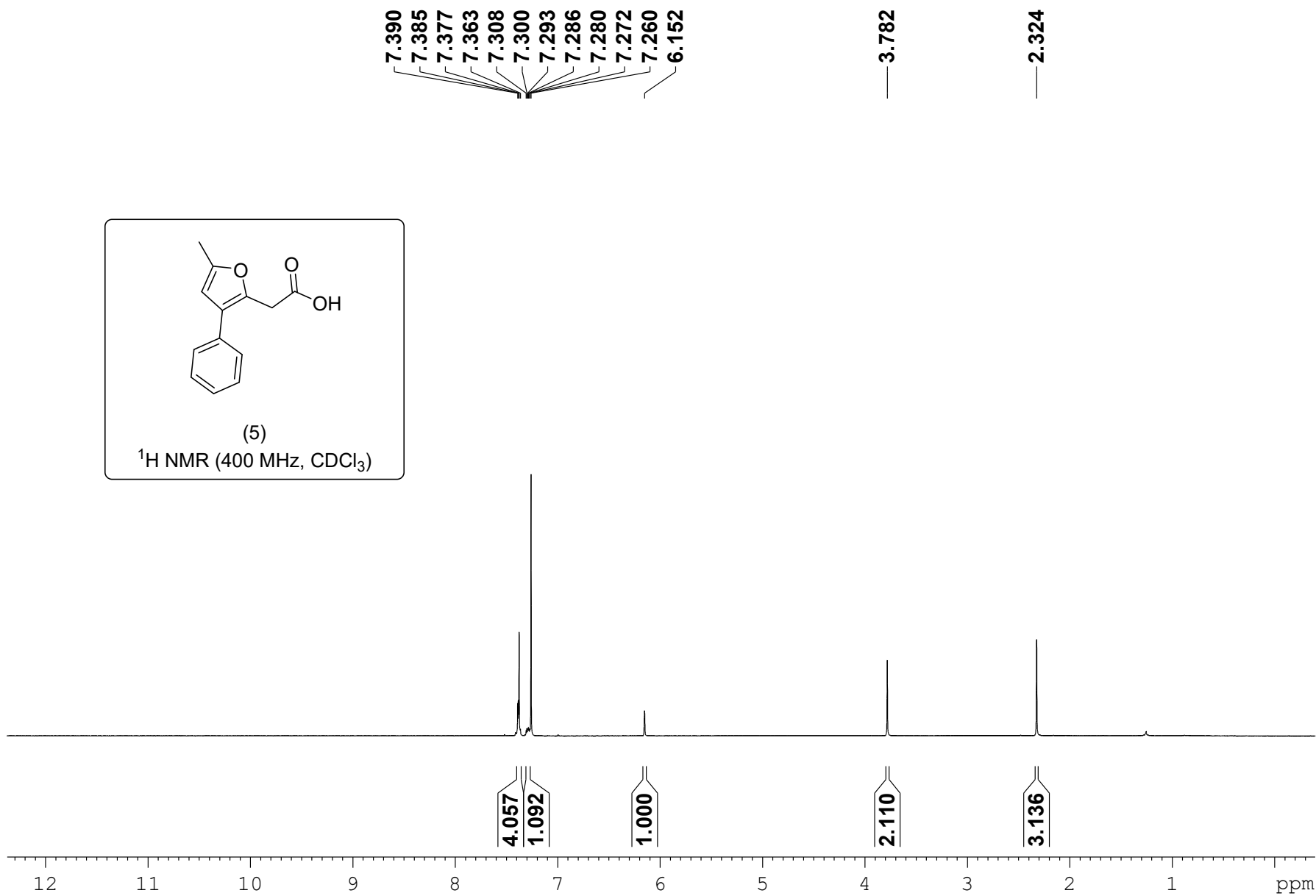
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3.736

1.818









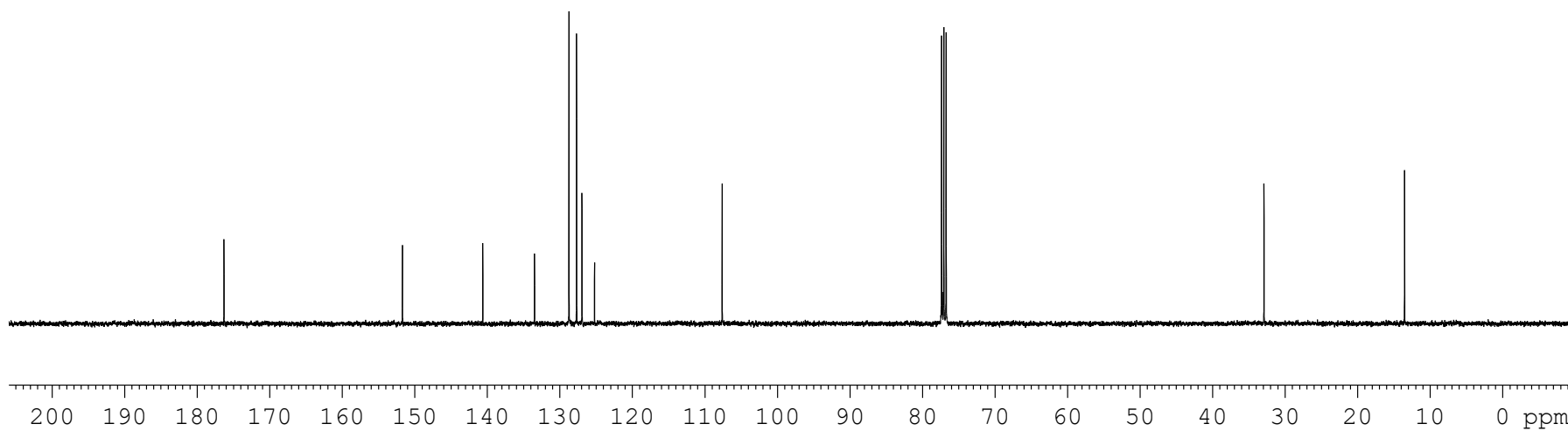
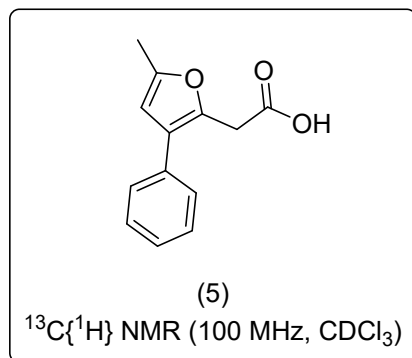
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— 107.609

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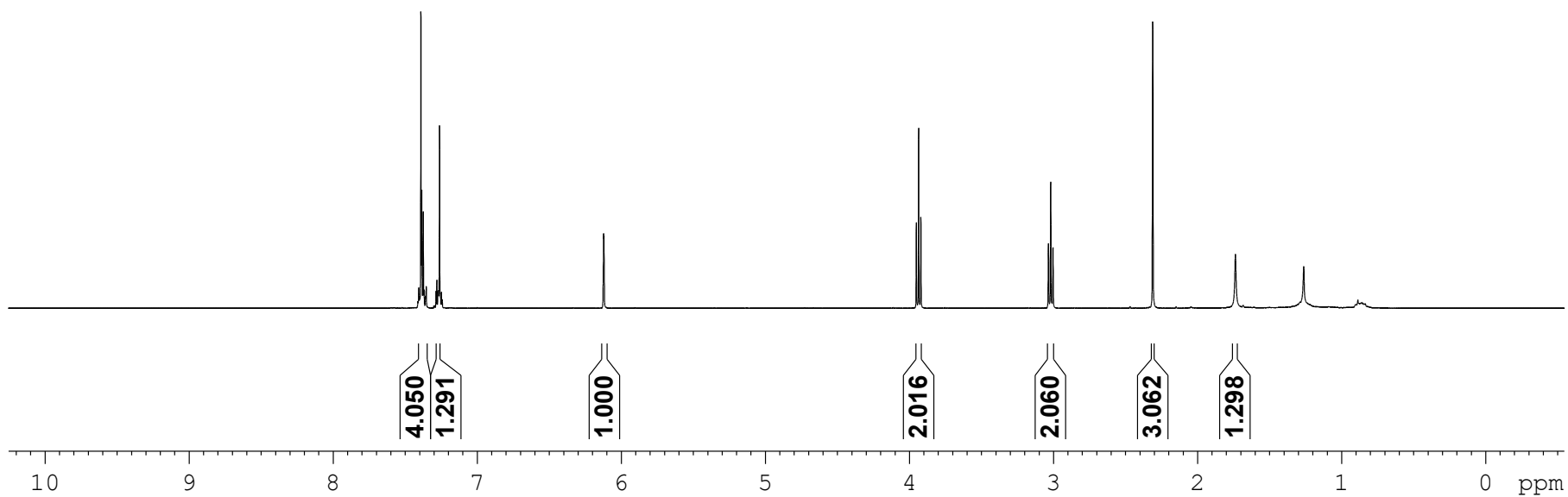
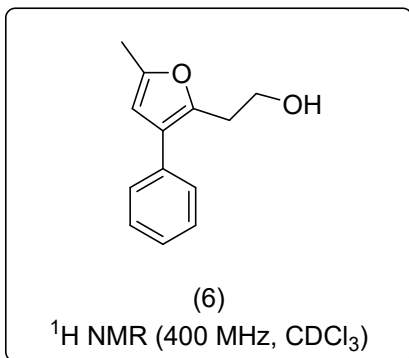
— 32.933

— 13.551



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