

Electrochemical Deuteration of Allylic Esters with Divergent Site-Selectivity

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Supplementary Information

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Part I Experimental Section

1. General Information

^1H NMR and ^{13}C NMR were recorded on a Bruker 400 MHz (^1H NMR: 400MHz, ^{13}C NMR: 101 MHz). The chemical shifts (δ) and coupling constants (J) were expressed in ppm and Hz respectively. ^1H NMR spectra were referenced to the solvent residual peak (TMS, δ 0.0 ppm) and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were referenced to the solvent residual peak (CDCl_3 , δ 77.0 ppm). High resolution mass spectra and liquid phase mass spectrometry were obtained using ThermoFisher LTQ Orbitrap XL mass spectrometer with time of flight (TOF) and Ion trap analyzers, respectively. Cyclic voltammograms were recorded on electrochemical workstation CHI660E (Shanghai CH Instruments Co., Ltd.). GC analysis was conducted using CEAULIGHT GC-7920 spectrometer. All solvents were purified and dried according to the standard procedures unless otherwise noted. Commercially substrates were purchased and used directly. Allylic ester substrates **1**^[1] were prepared according to the literature procedures.

2. Optimization of reaction conditions

Table S1. Optimization of the functionalization 1,3-disubstituted allene with acrylamide^[a]

Entry	Reaction conditions	Yield of 2a/3a (%) ^[b]	D incorporation of 2a (%) ^[b]	D incorporation of 3a (%) ^[b]
1	Condition A	73/trace	97/80/97	n.d.
2	THF as solvent in Condition A	60/trace	94/70/94	n.d.
3	Cu as cathode in Condition A	54/trace	90/58/93	n.d.
4	Pb as cathode in Condition A	40/trace	93/68/78	n.d.
5	Zn as cathode in Condition A	59/trace	95/71/97	n.d.
6	MeOD as D source in Condition A	81/trace	70/45/72	n.d.
7	Remove Et ₃ N from Condition A	52/trace	94%/80%/90%	n.d.
8	Condition B	trace/95	n.d.	96
9	THF as solvent in Condition B	23/63	n.d.	88
10	C as cathode in Condition B	68/14	93/68/85	n.d.
11	Pb as cathode in Condition B	30/57	n.d.	89
12	Zn as cathode in Condition B	49/29	99/73/86	93
13	Pt as cathode in Condition B	trace/70	n.d.	91
14	D ₂ O as D source in Condition B	trace/84	n.d.	95
15	6 h in Condition B	56/3	92%/68%/81%	n.d.

[a] **Condition A:** **1a** (0.5 mmol), ^tBu₄NPF₆ (1 mmol), Et₃N (1.5 mmol), graphite rod electrodes, DMF/D₂O (9.8/0.2 mL), undivided cell, constant current electrolysis (18 mA-4.5 h, 6 F/mol). **Condition B:** **1a** (0.5 mmol), ^tBu₄NOAc (1 mmol), graphite rod anode, copper plate cathode (1.8*2.0 cm²), CH₃CN/MeOD (9.0/1.0 mL), undivided cell, constant current electrolysis (15 mA-4.0 h, 4.5 F/mol). [b] The ratio of **2a/3a** and D incorporation are determined by ¹H NMR.

¹H NMR spectra of 2a-H

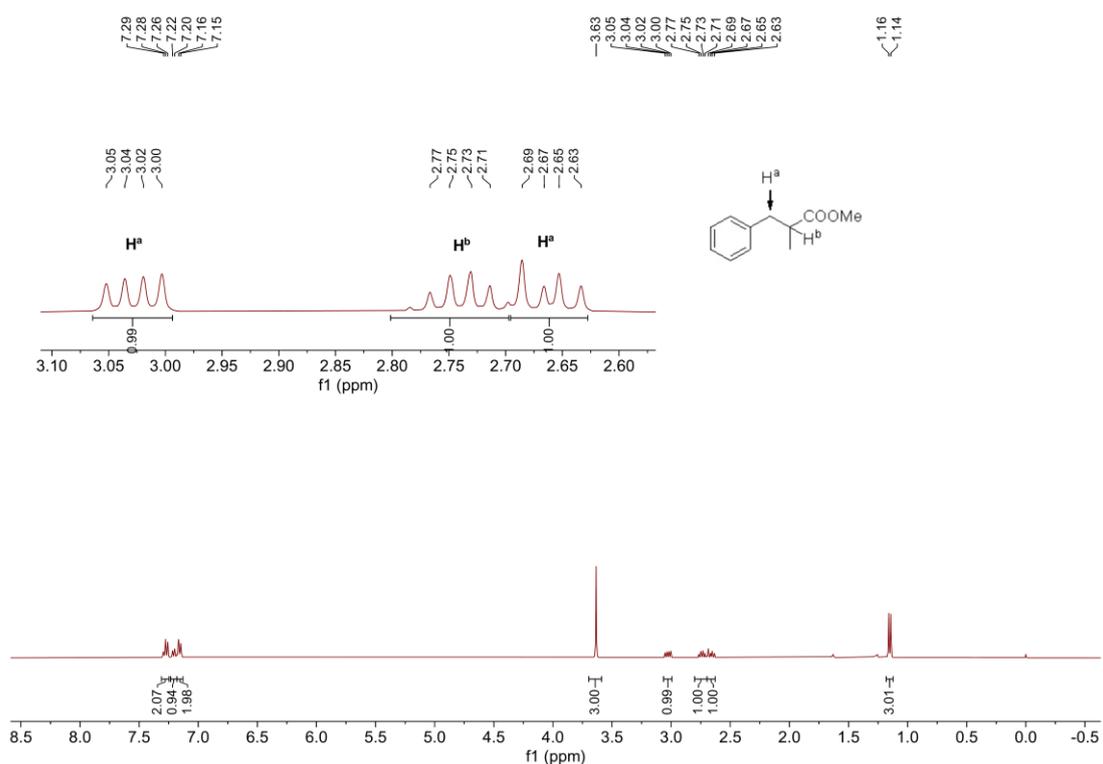


Figure S1. The ¹H NMR spectrum of the product **2a-H**.

The sextet and the doublet of doublets (dd) have been unambiguously assigned to H^b and H^a, respectively.

Entry 1

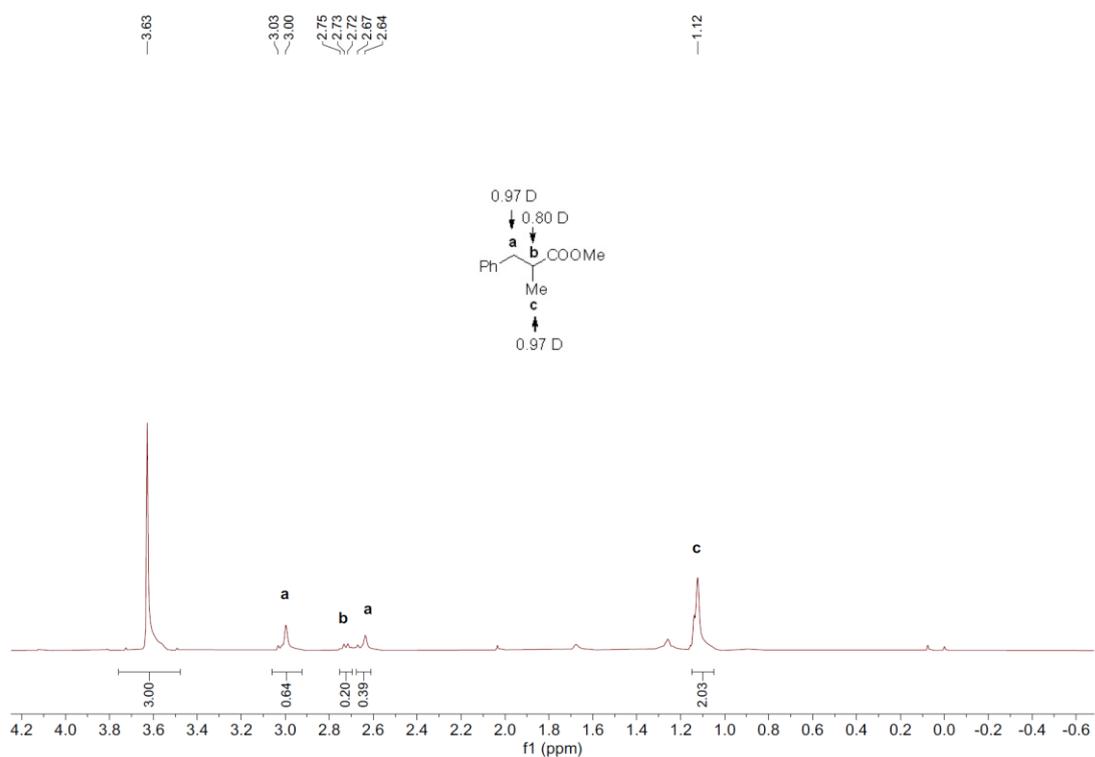


Figure S2. The ¹H NMR spectrum of the product under conditions of Entry 1.

Entry 2

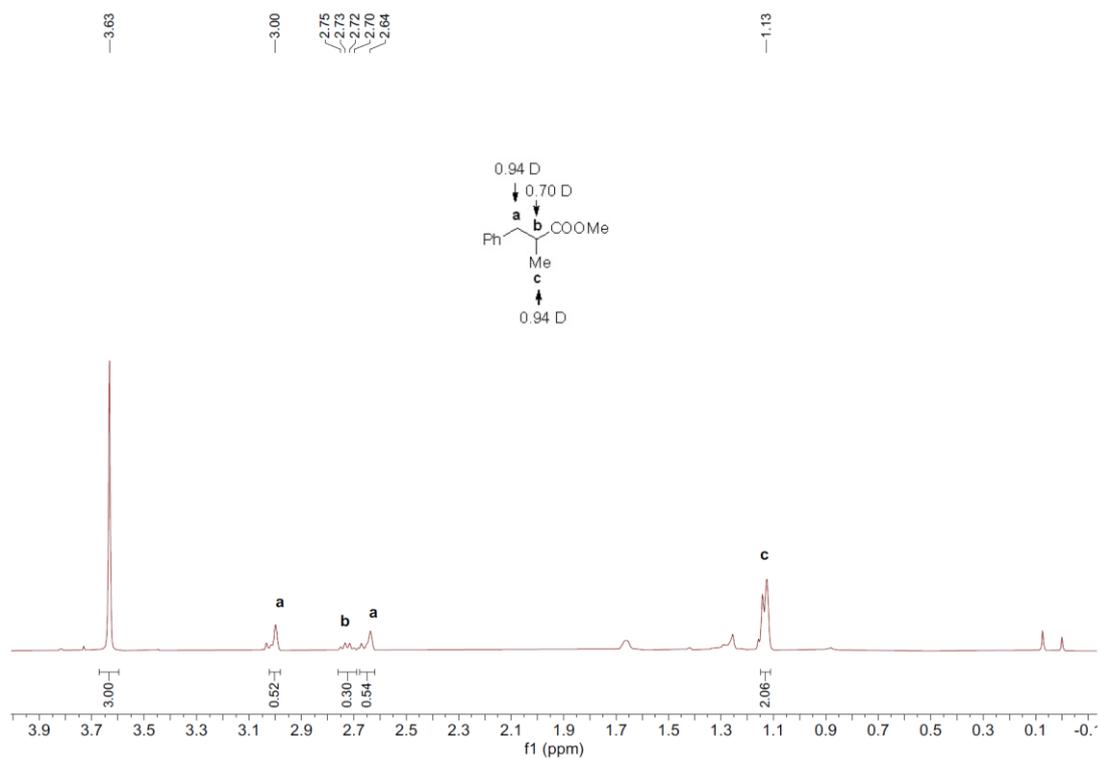


Figure S3. The ^1H NMR spectrum of the product under conditions of Entry 2.

Entry 3

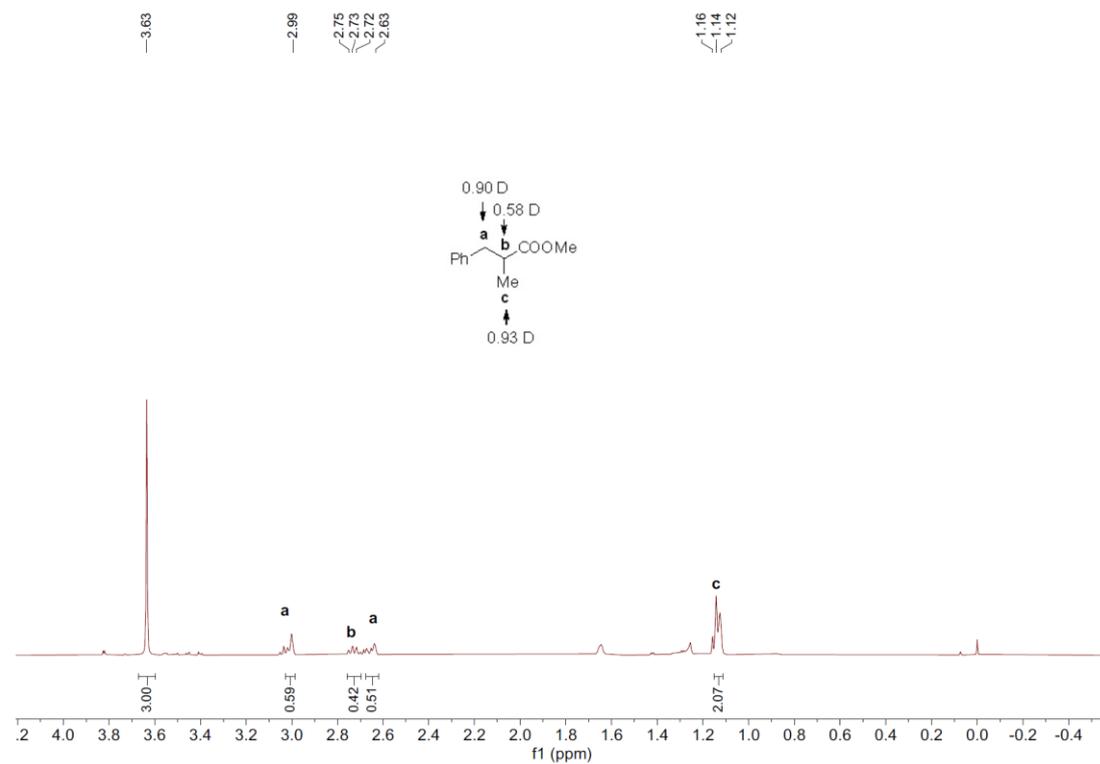


Figure S4. The ^1H NMR spectrum of the product under conditions of Entry 3.

Entry 4

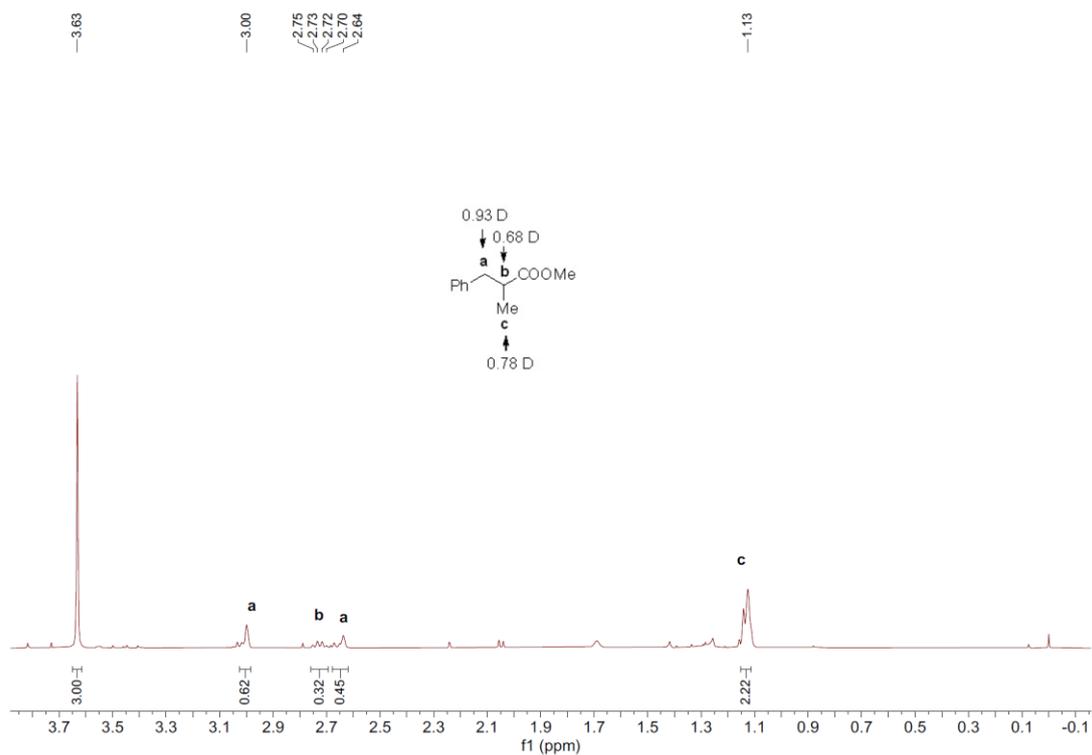


Figure S5. The ^1H NMR spectrum of the product under conditions of Entry 4.

Entry 5

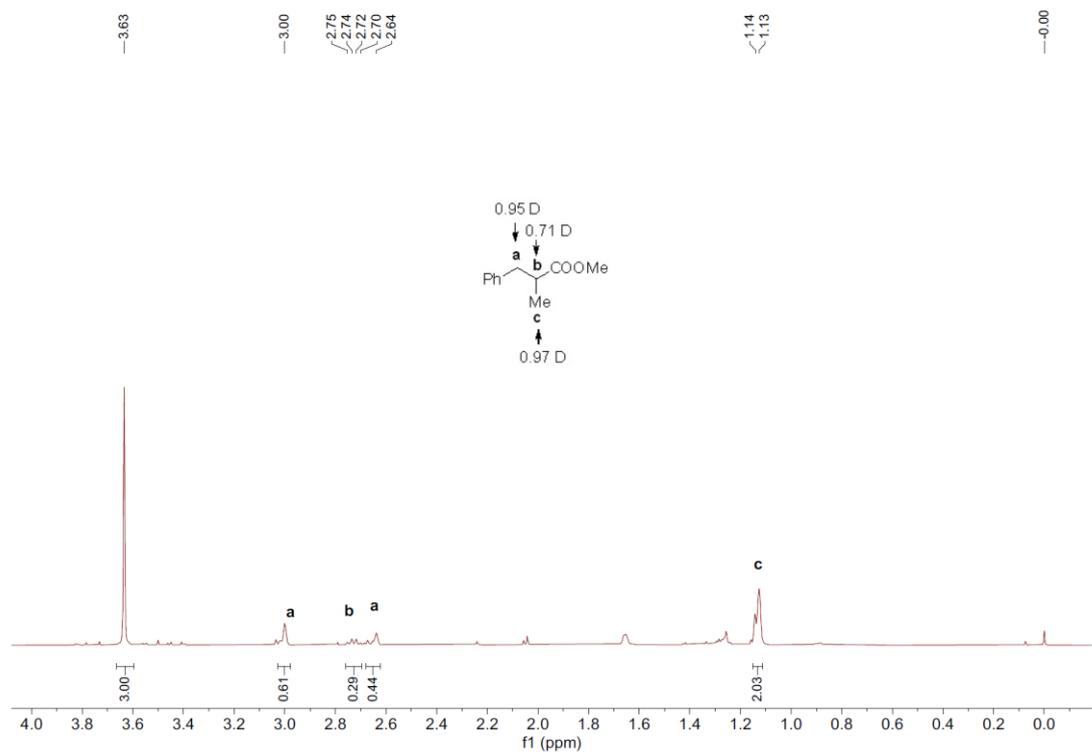


Figure S6. The ^1H NMR spectrum of the product under conditions of Entry 5.

Entry 6

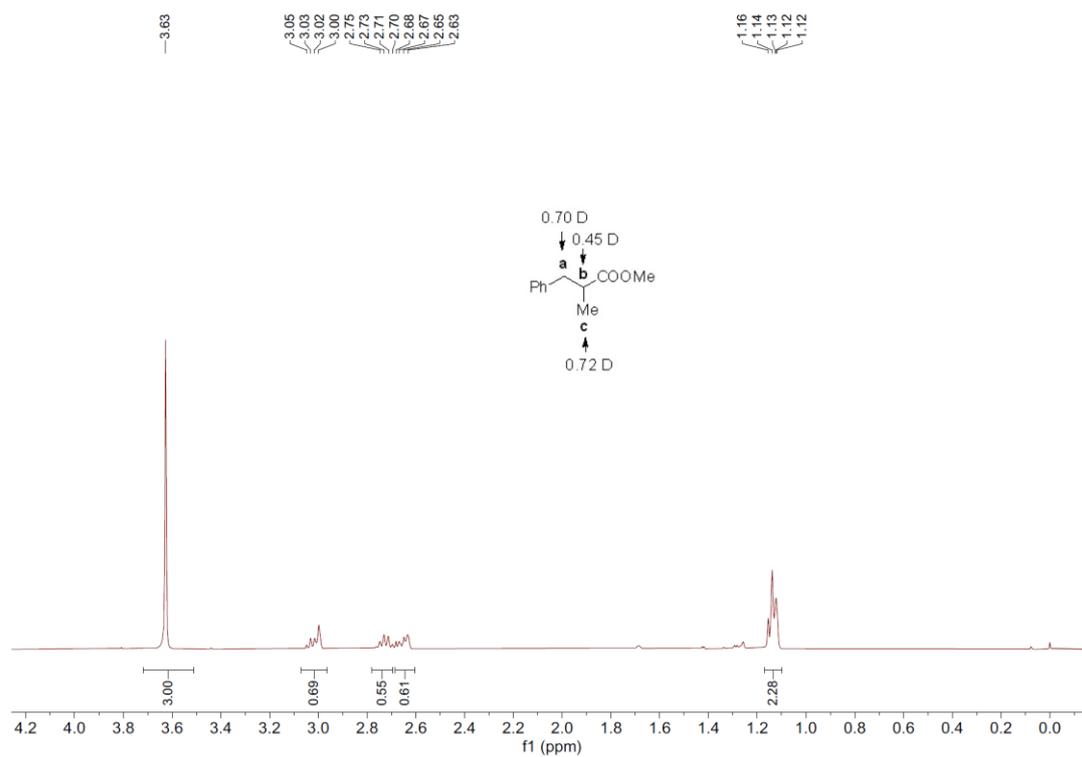


Figure S7. The ^1H NMR spectrum of the product under conditions of Entry 6.

Entry 7

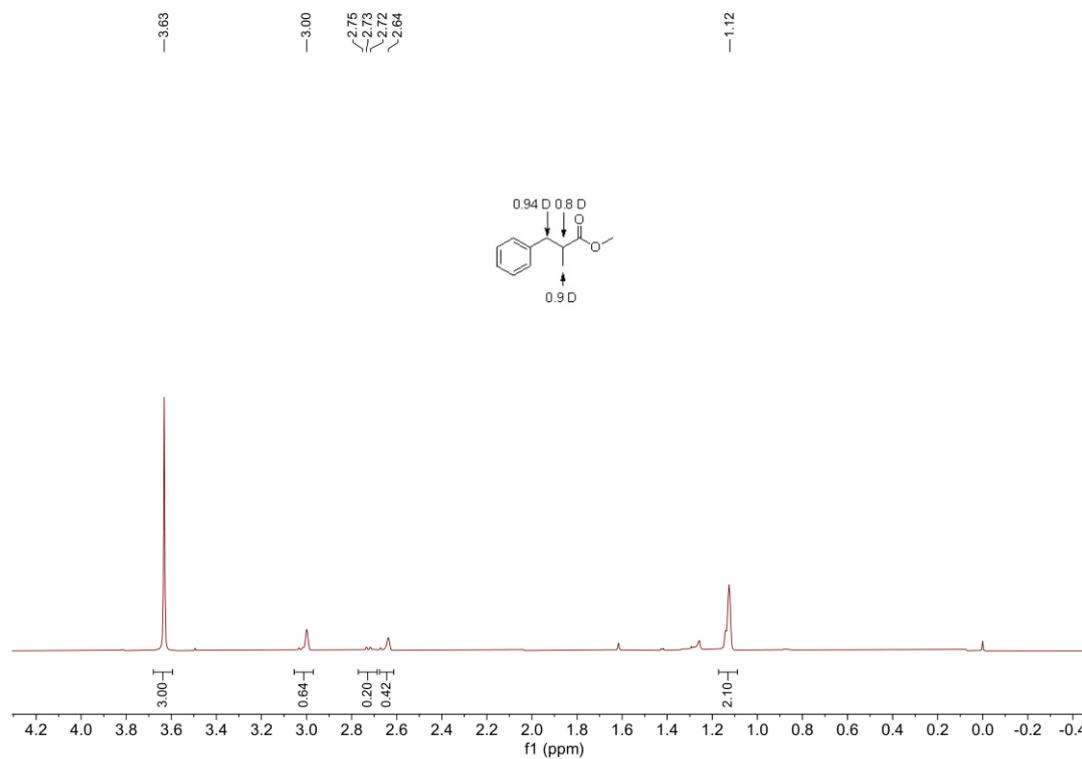


Figure S8. The ^1H NMR spectrum of the product under conditions of Entry 7.

Entry 8

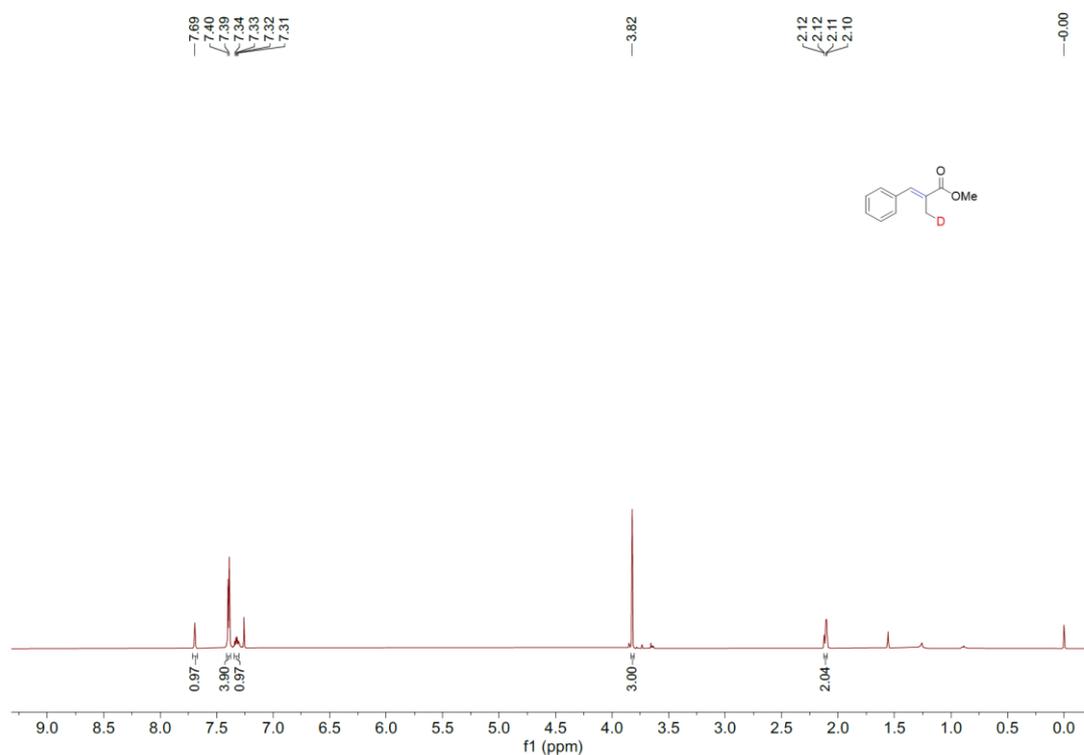


Figure S9. The ^1H NMR spectrum of the product under conditions of Entry 8.

Entry 9

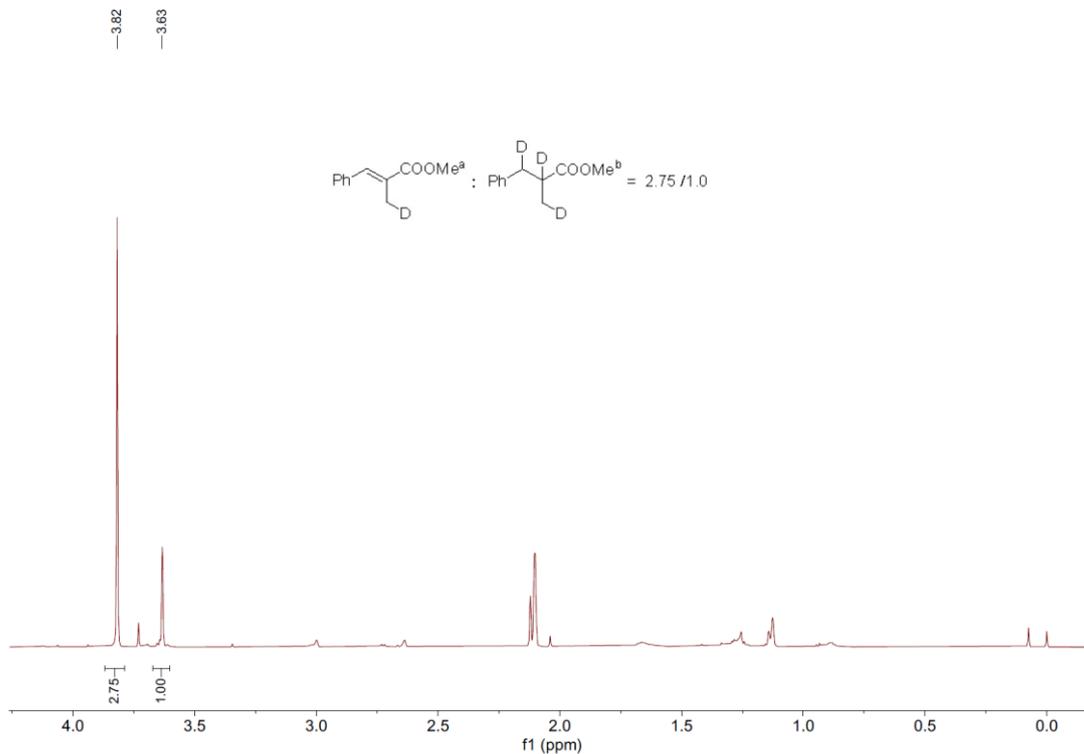


Figure S10. The ^1H NMR spectrum of the product under conditions of Entry 9.

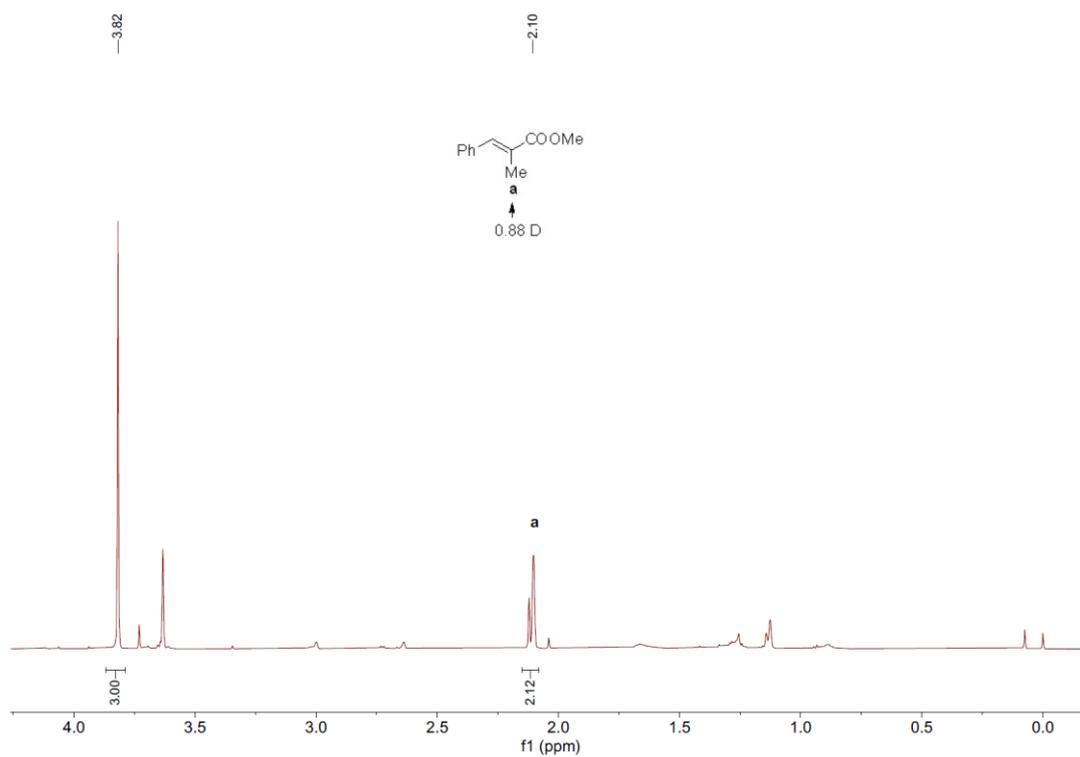


Figure S11. The ¹H NMR spectrum of the product under conditions of Entry 9.
Entry 10

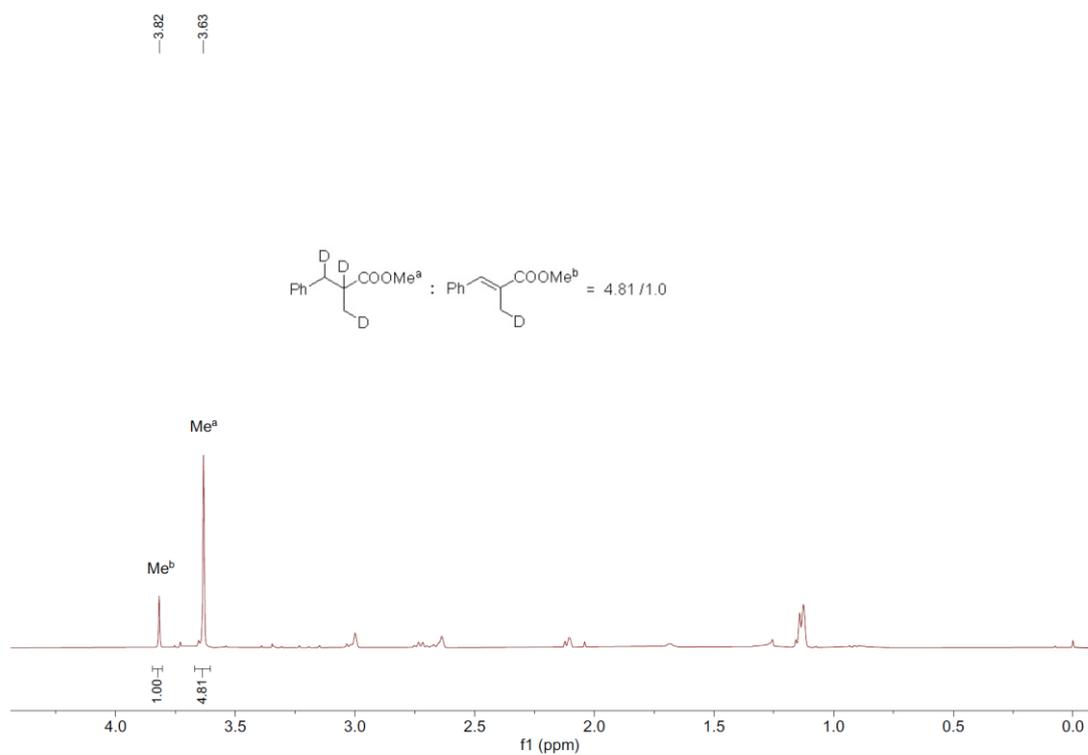


Figure S12. The ¹H NMR spectrum of the product under conditions of Entry 10.

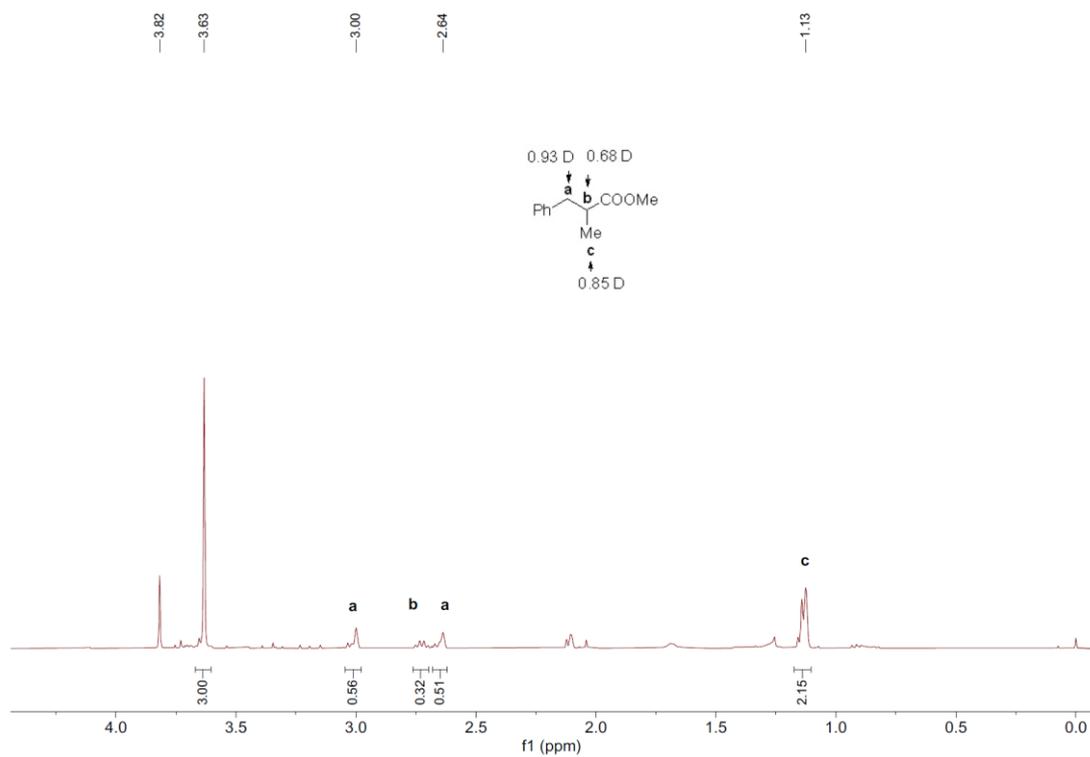


Figure S13. The ¹H NMR spectrum of the product under conditions of Entry 10.

Entry 11

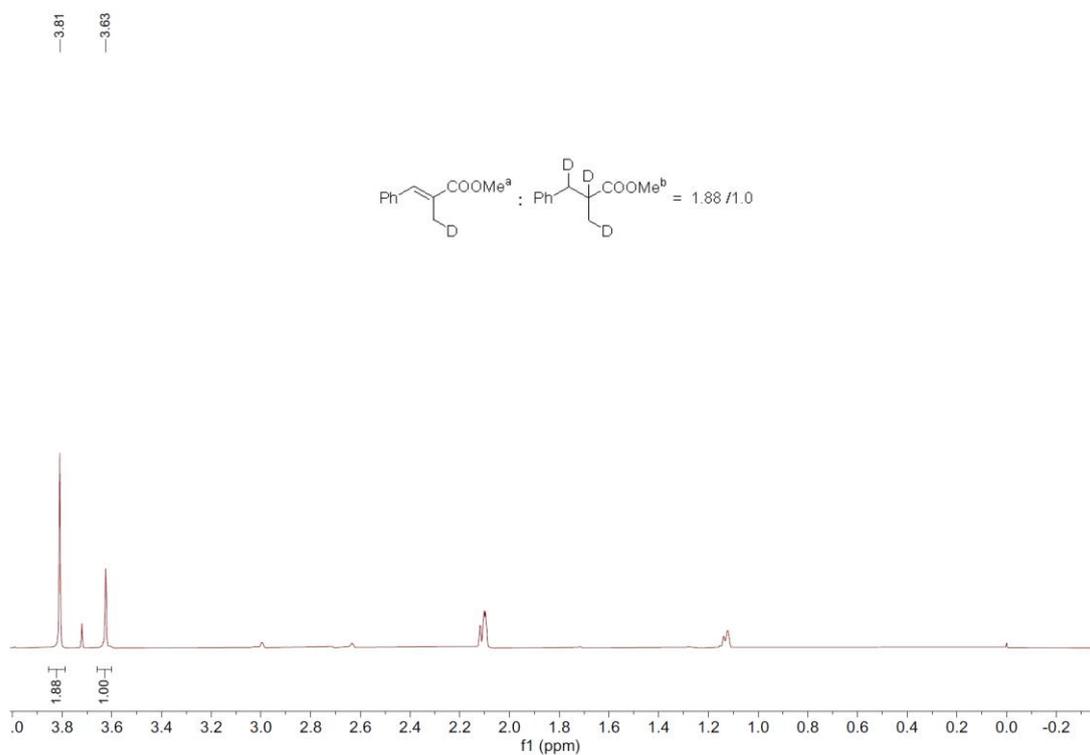


Figure S14. The ¹H NMR spectrum of the product under conditions of Entry 11.

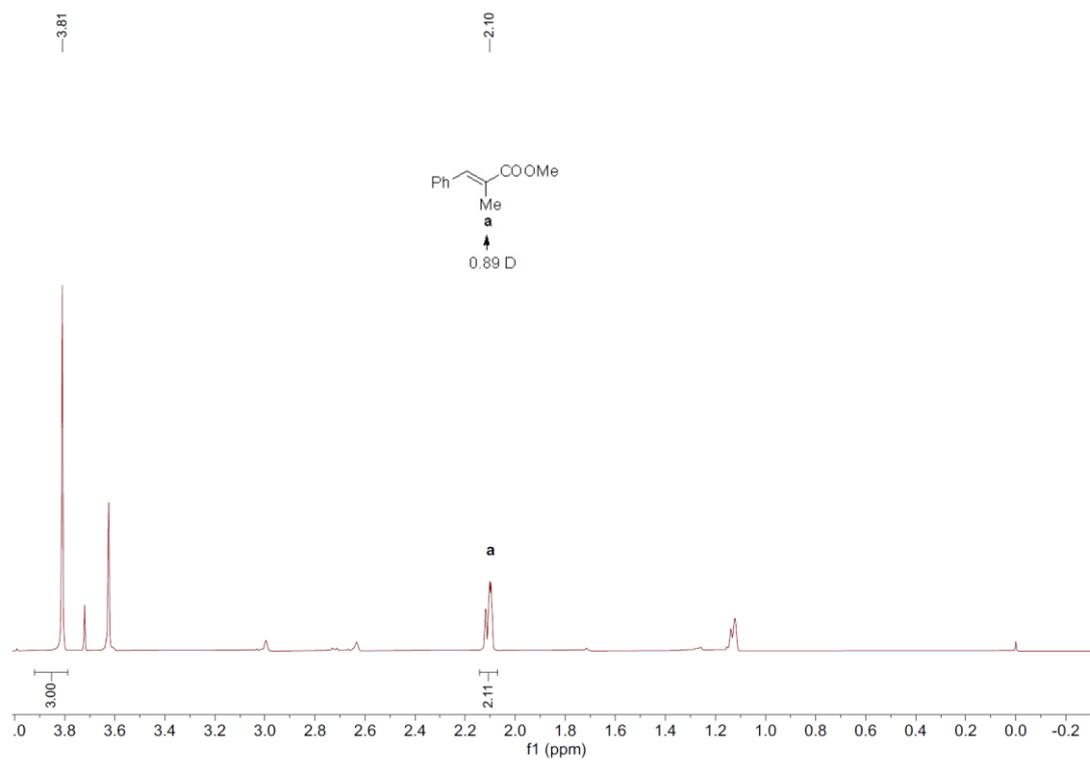


Figure S15. The ^1H NMR spectrum of the product under conditions of Entry 11.
Entry 12

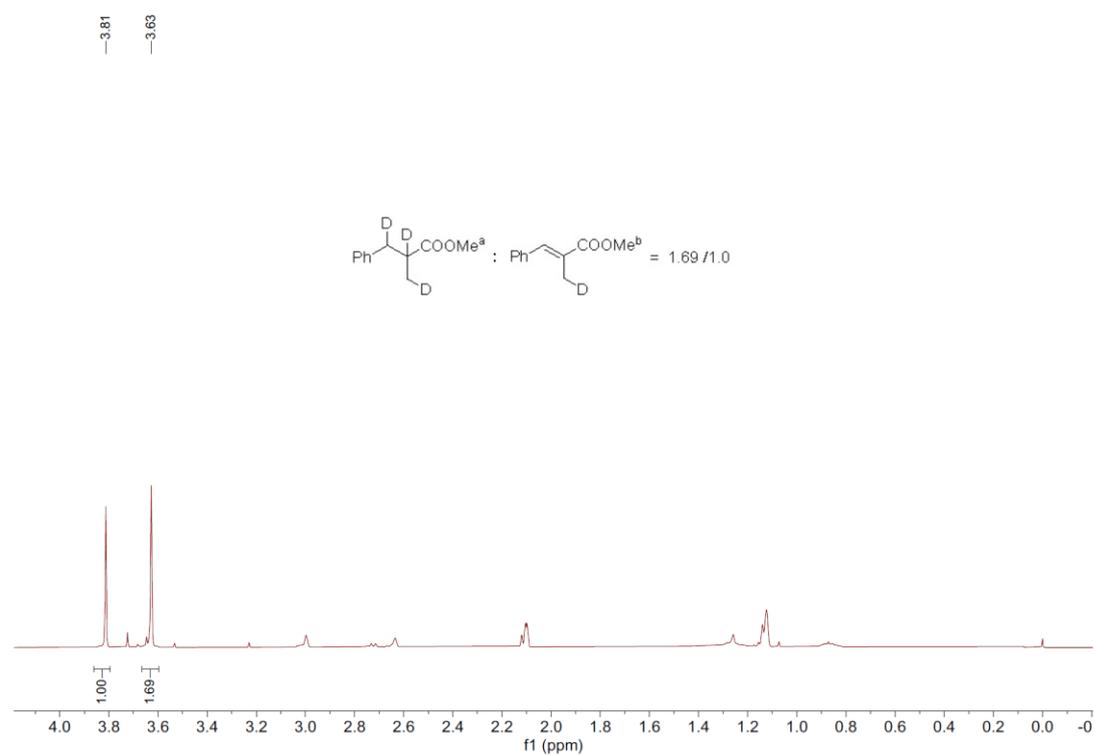


Figure S16. The ^1H NMR spectrum of the product under conditions of Entry 12.

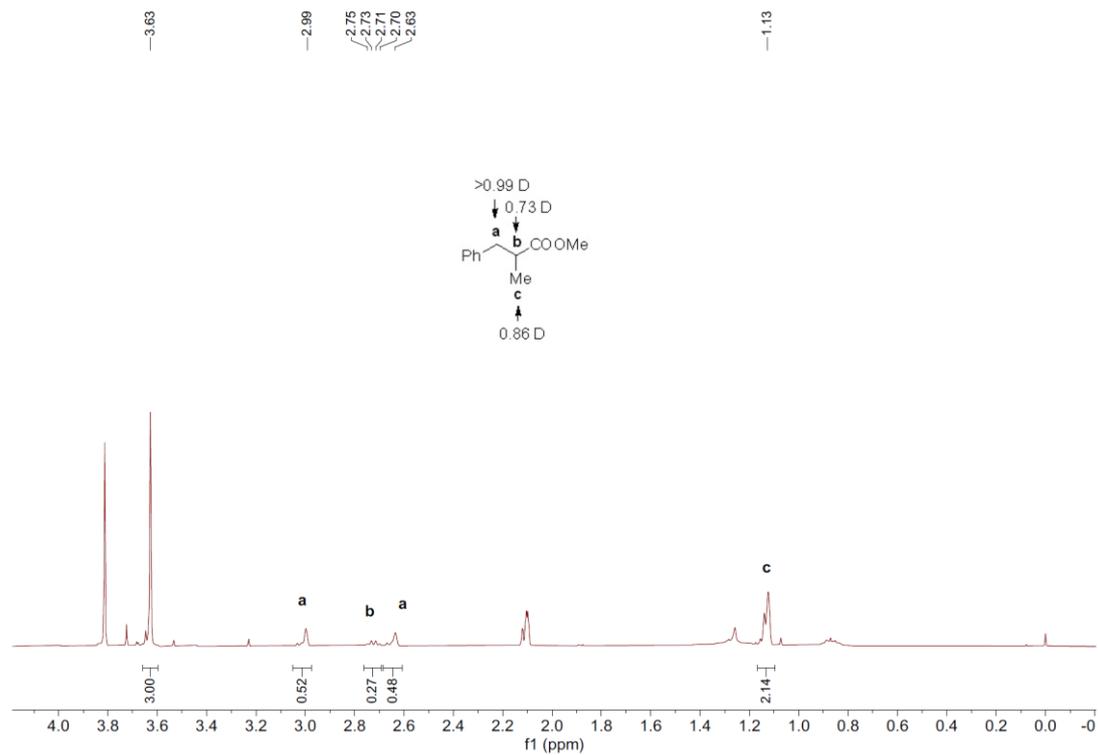


Figure S17. The ^1H NMR spectrum of the product under conditions of Entry 12.
Entry 13

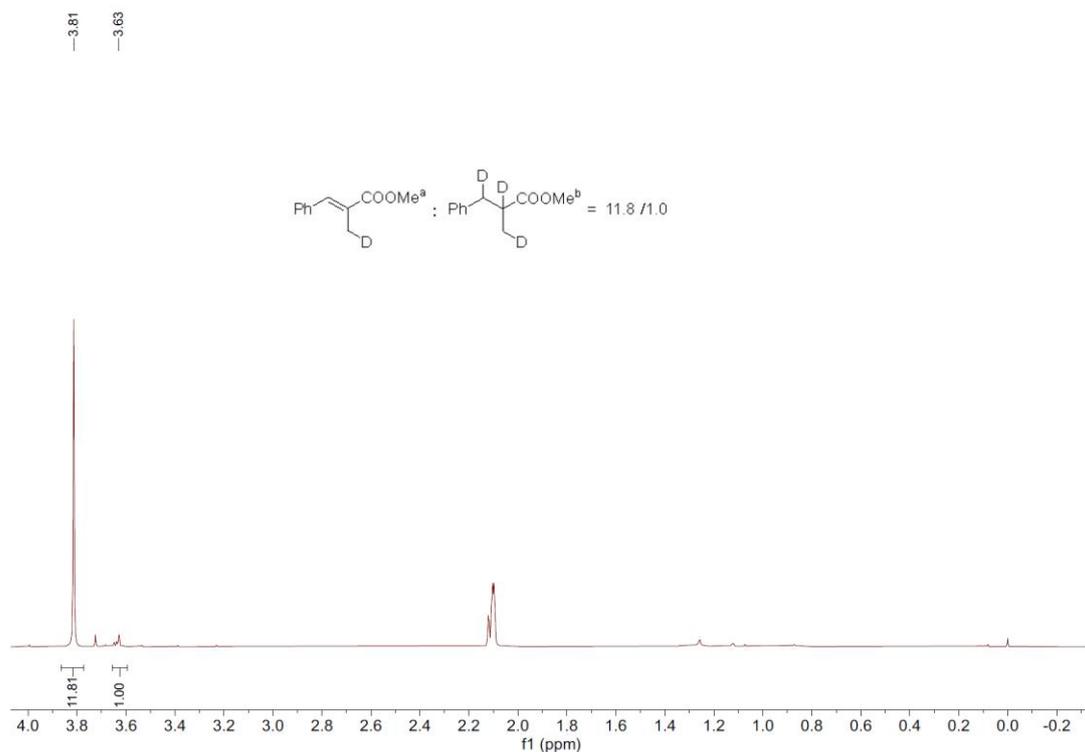


Figure S18. The ^1H NMR spectrum of the product under conditions of Entry 13.

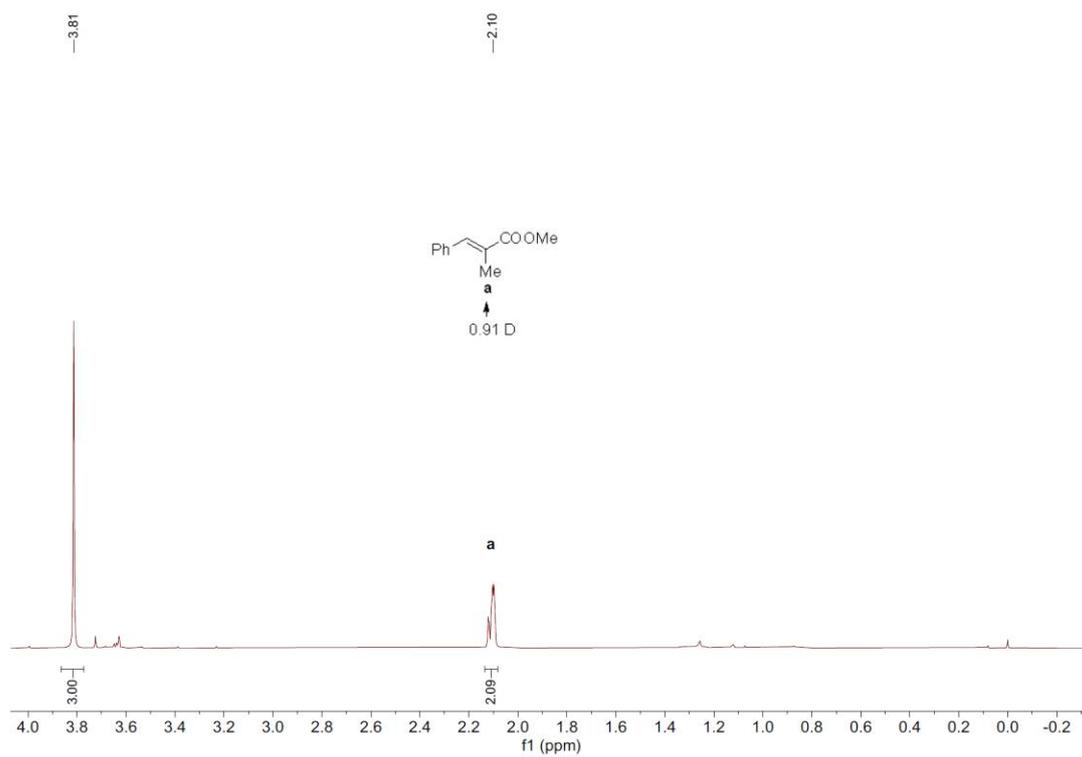


Figure S19. The ^1H NMR spectrum of the product under conditions of Entry 13.
Entry 14

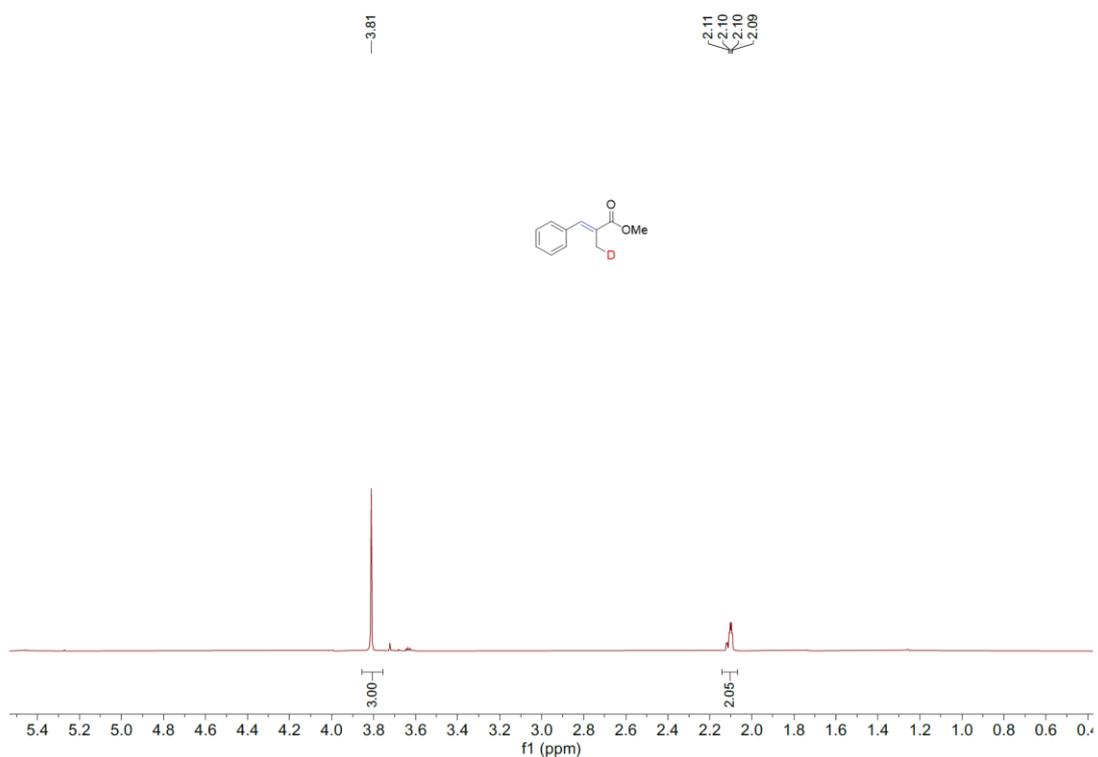


Figure S20. The ^1H NMR spectrum of the product under conditions of Entry 14.

Entry 15

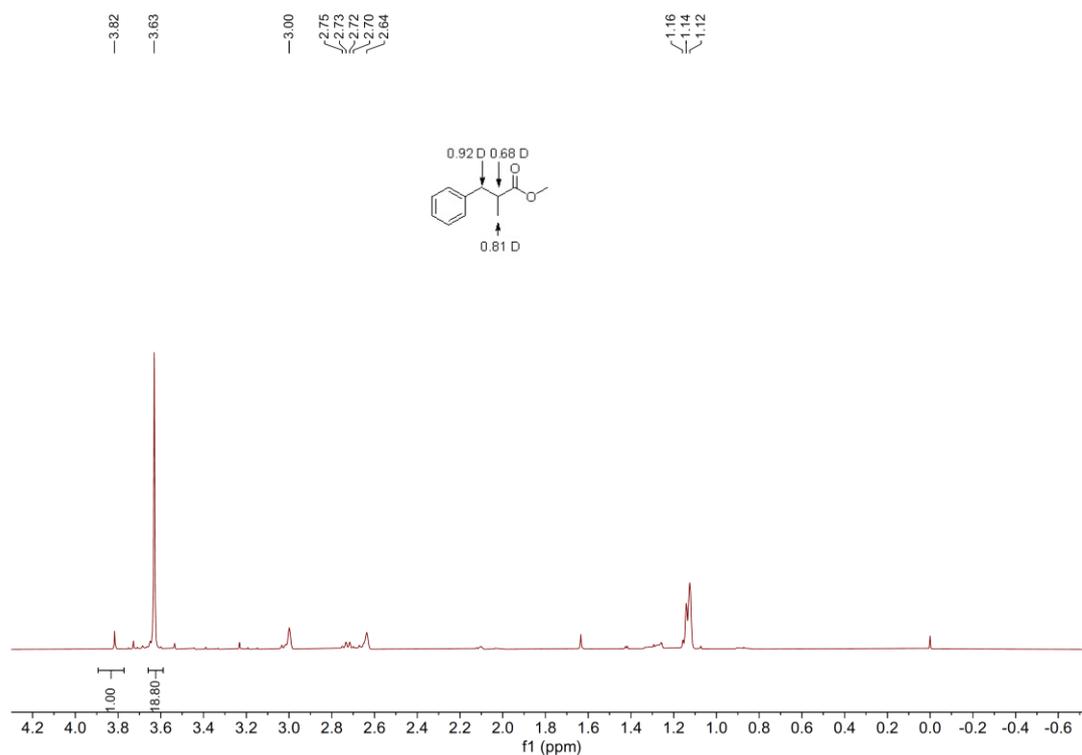


Figure S21. The ^1H NMR spectrum of the product under conditions of Entry 15.

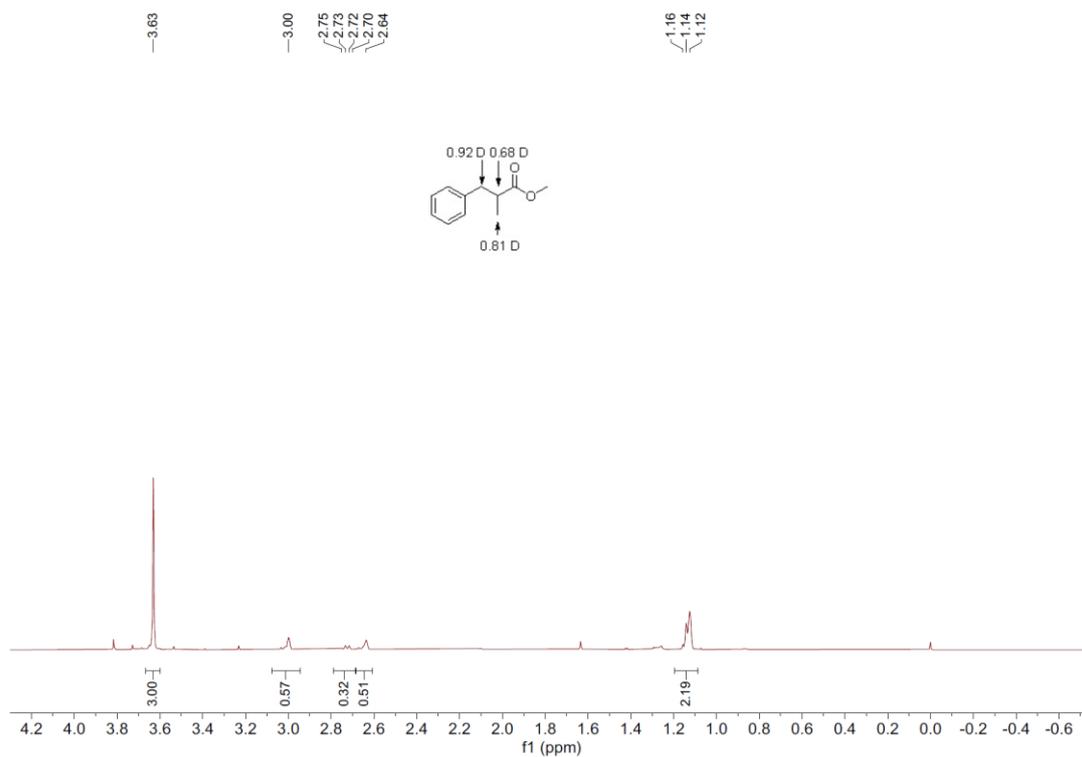


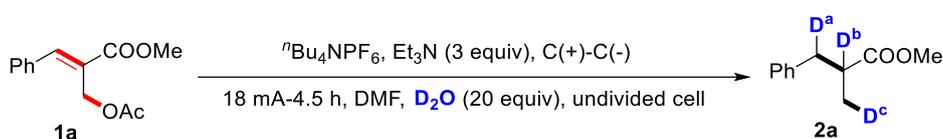
Figure S22. The ^1H NMR spectrum of the product under conditions of Entry 15.

3. General procedure for the electrochemical deuteration



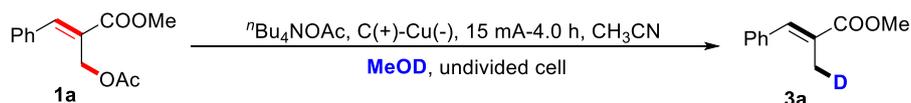
Figure S23. Electrolysis setup (graphite rod: diameter 0.6 cm; Copper plate: width 1.8 cm, immersion depth 1.5 cm)

2a as example



An undivided cell was equipped with a magnetic stirrer, graphite rods as cathode and anode (the electrolysis setup is shown in Figure S23). The substrate **1a** (117 mg, 0.5 mmol), Et₃N (210 μL, 1.5 mmol), D₂O (200 μL, 10 mmol) and ⁿBu₄NPF₆ (387 mg, 1.0 mmol) were added to the solvent DMF (9.8 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (18 mA) at room temperature for 4.5 hours. The reaction mixture was subsequently poured into water (200 mL) and extracted with ethyl acetate (40 mL*3). The combined organic phases were washed with saturated brine solution (100 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-20/1, v/v) on silica gel to afford the desired product **2a** (66 mg) in 73% yield.

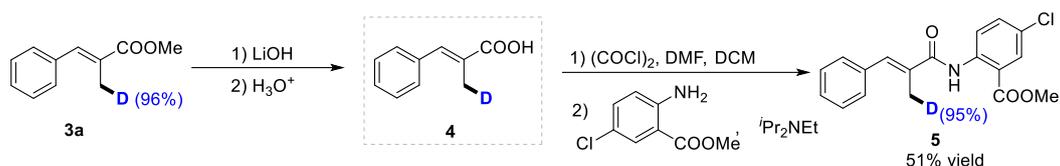
3a as example



An undivided cell was equipped with a magnetic stirrer, copper plate and graphite rod as cathode and anode, respectively (the electrolysis setup is shown in Figure S23). The substrate **1a** (117 mg, 0.5 mmol), MeOD (1 mL) and ⁿBu₄NOAc (300 mg, 1.0 mmol) were added to the solvent CH₃CN (9.0 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (15 mA) at room temperature for 4.0 hours. The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-20/1, v/v) on silica gel to afford the desired product **3a** (84 mg) in 95% yield.

4. Procedure for the derivatization of products

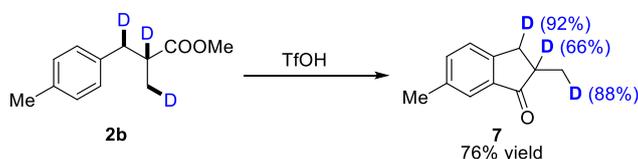
Synthesis of 5/6



A dry flask was charged with **3a** (177 mg, 1.0 mmol), LiOH (120 mg, 5.0 mmol), THF (25 mL) and H₂O (25 mL). The resulted mixture was stirred at room temperature overnight. The reaction mixture was evaporated in vacuum to remove THF, and the resulting solution was neutralized with 2M HCl (25 mL) and extracted with ethyl ether (10 mL*3). The combined organic phases were washed with saturated brine solution (30 mL). The volatile solvent was then removed with a rotary evaporator, and the intermediate (**4**) was directly used in the next step.

To the solution of **4** in DCM (10 mL), oxalyl chloride (128 μ L, 1.5 mmol) and a drop of DMF were successively added in 0 °C. After stirring at room temperature for 2 hours, additional 10 mL DCM was introduced. To the resulting solution, *i*Pr₂NEt (418 μ L, 2.4 mmol) and methyl 2-amino-5-chlorobenzoate (222 mg, 1.2 mmol) were added. The resulted mixture was stirred at room temperature overnight. The reaction mixture was diluted with DCM (50 mL), and washed with 2M HCl (20 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-10/1, v/v) on silica gel to afford the desired product **5** (168 mg) in 51 % yield.

Synthesis of 7



A vial was charged with trifluoromethanesulfonic acid (50 mmol, 4.4 mL). After cooling to 0 °C, reactant **2b** (98 mg, 0.5 mmol) was added. The reaction mixture was stirred at room temperature for four days. The reaction mixture was poured into water (25 mL) and extracted with ethyl ether (10 mL*3). The combined organic phases were washed with saturated brine solution (30 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-10/1, v/v) on silica gel to afford the desired product **6** (62 mg) in 76 % yield.

5. Electrochemical analysis for the reaction

The electrochemical analysis was demonstrated with Ag wire as a reference electrode, which is not a stable reference electrode. CVs can be calibrated using ferrocene as an external reference. (Figure S24) $E_0(\text{Fc}/\text{Fc}^+) = (0.144 - 0.014)/2 = 0.065 \text{ V}$.

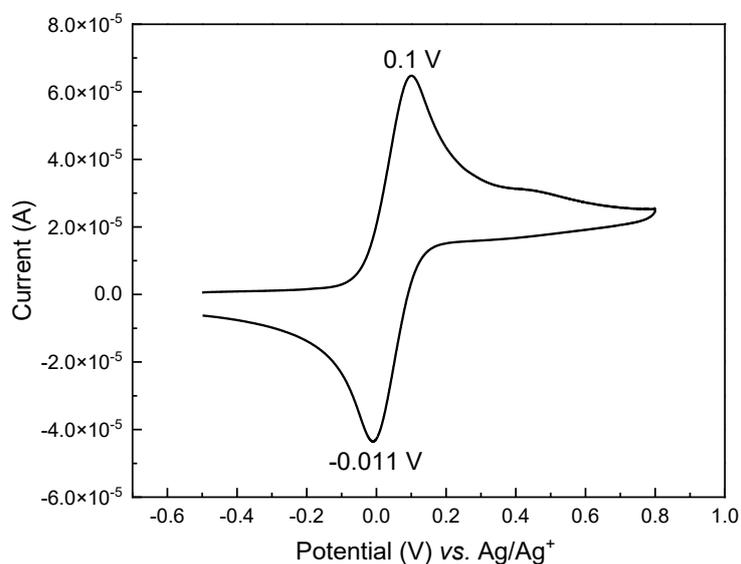


Figure S24. Cyclic voltammograms of ferrocene (0.01 mmol) in 0.1 M $n\text{Bu}_4\text{NBF}_4$ (DMF 3mL), using a glassy carbon working electrode and Pt wire, Ag/AgNO₃ (0.1 M in CH₃CN) as counter and reference electrodes at a 100 mV/s scan rate.

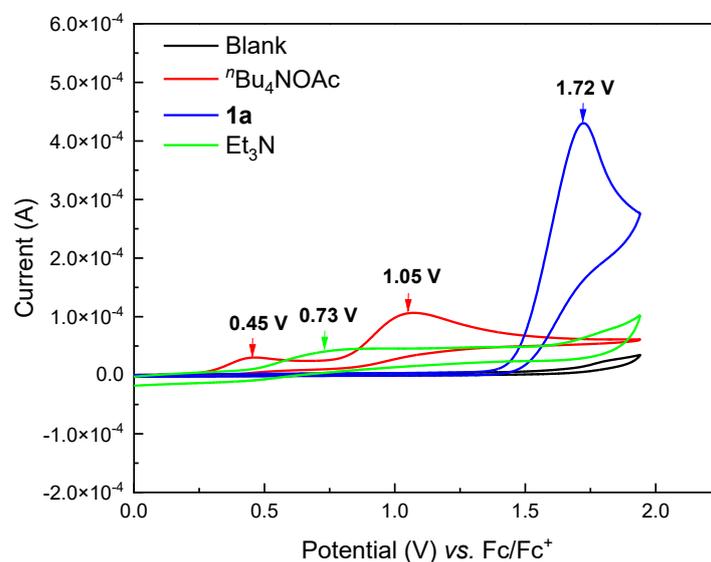


Figure S25. Cyclic voltammogram of **1a** (0.02 mmol), $n\text{Bu}_4\text{NOAc}$ (0.02 mmol) and Et₃N (0.02 mmol) in 0.1 M LiClO₄ (CH₃CN 3 mL), using a glassy carbon working electrode and Pt wire, Ag/AgNO₃ (0.1 M in CH₃CN) as counter and reference electrodes at a 100 mV/s scan rate.

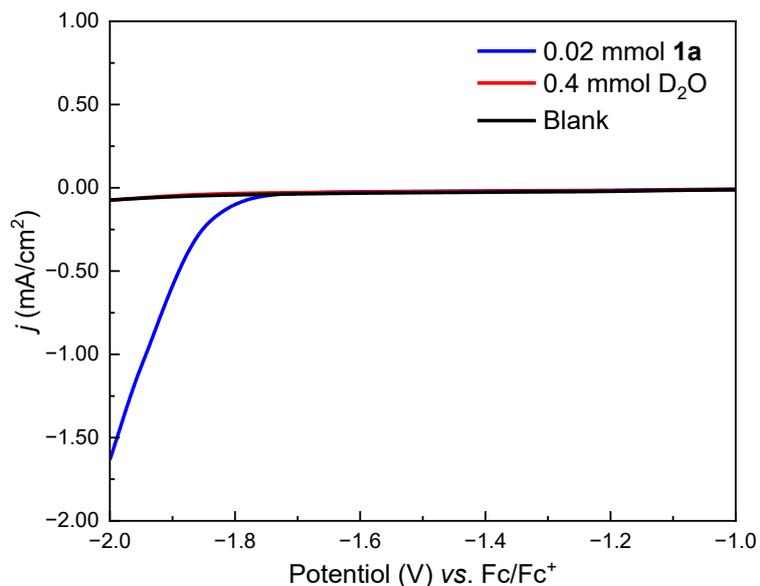


Figure S26. Linear sweep voltammograms of substrate **1a** and D₂O in DMF (0.1 M, ⁿBu₄NPF₆) using graphite, platinum wire and Ag/AgNO₃ as working, counter and referencing electrodes at a 100 mV/s scan rate.

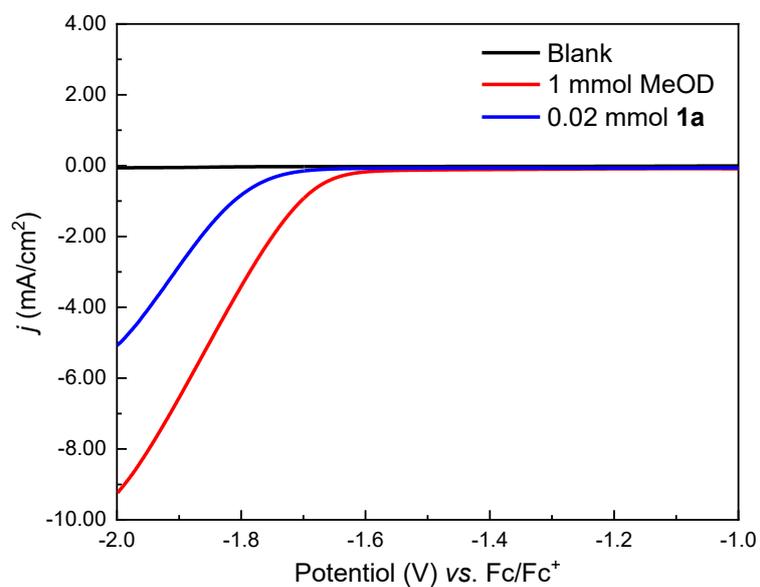
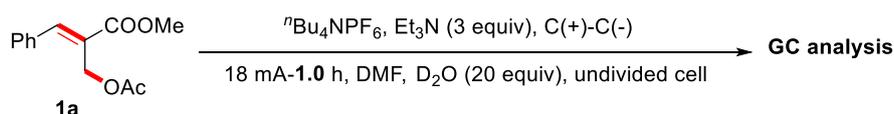


Figure S27. Linear sweep voltammograms of substrate **1a** and MeOD in CH₃CN (0.1 M, ⁿBu₄NOAc) using copper, platinum wire and Ag/AgNO₃ as working, counter and referencing electrodes at a 100 mV/s scan rate.

6. GC experiment for the reaction



To verify the hydrogen byproduct during reduction of this reaction, we also conducted a GC analysis for the reaction atmosphere. After electrolysis, the headspace atmosphere of the reaction tube was subjected to GC analysis. The GC spectra revealed the presence of a trace amount of D_2 . This assignment was made by comparing its signal to that of H_2 in a standard gas mixture, taking into account the nearly identical retention behavior of H_2 and D_2 in the GC column. The result clearly excluded the HER process and the D_2 byproduct (Figure S28).

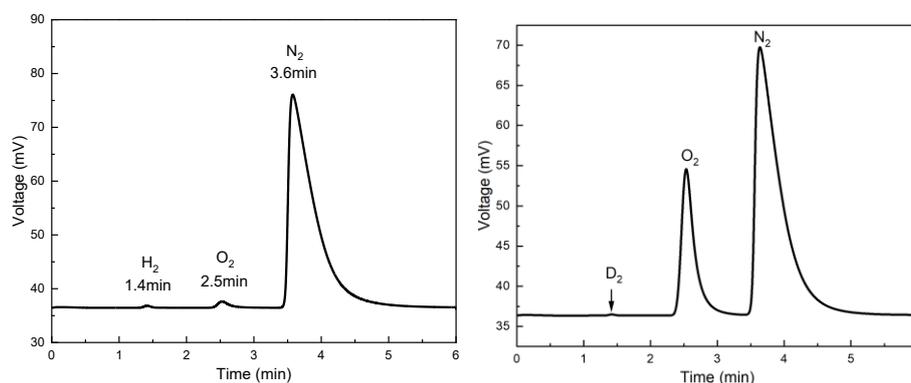
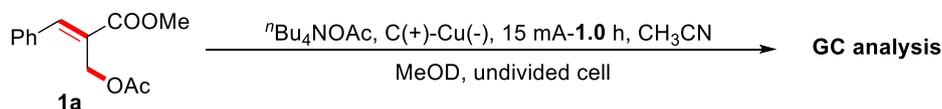


Figure S28. GC spectra of standard sample (containing H_2 , O_2 , N_2) and the reaction atmosphere (after reaction).



To verify the hydrogen byproduct during reduction of this reaction, we also conducted a GC analysis for the reaction atmosphere. After electrolysis, the headspace atmosphere of the reaction tube was subjected to GC analysis. The GC spectra revealed the presence of a substantial amount of D_2 . This assignment was made by comparing its signal to that of H_2 in a standard gas mixture, taking into account the nearly identical retention behavior of H_2 and D_2 in the GC column. The result clearly confirmed the HER process and the D_2 byproduct (Figure S29).

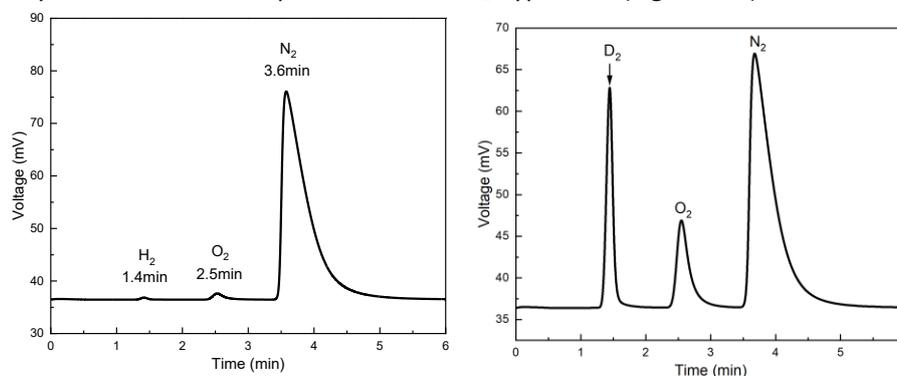
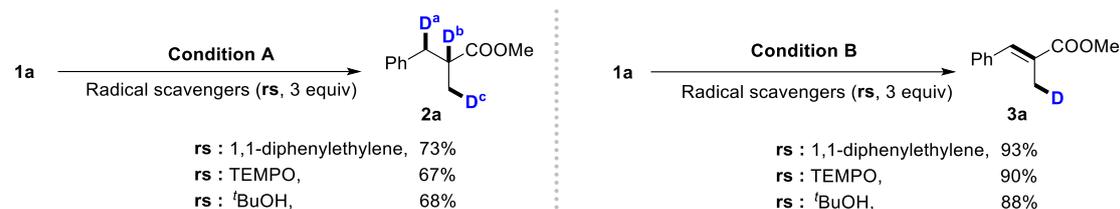


Figure S29. GC spectra of standard sample (containing H_2 , O_2 , N_2) and the reaction atmosphere (after reaction).

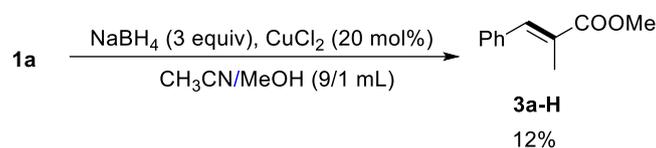
7. Procedure and details for control experiments

Radical suppression experiment



In the electrochemical reactions, some radical scavengers, including 1,1-diphenylethylene 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) and ^tBuOH, were added to the reaction mixture. The reaction results revealed that these three radical scavengers had a negligible effect on the reaction performance. Therefore, the possibility of a radical mechanism can be excluded, and the ionic pathway should be the dominant pathway in this reaction.

NaBH₄/CuCl₂ reduction



To the solution of **1a** (117 mg, 0.5 mmol) in CH₃CN and MeOH (9/1, v/v), CuCl₂ (13 mg, 0.1 mmol) and NaBH₄ (57 mg, 1.5 mmol) was successively added. The reaction mixture was stirred at room temperature for one day. The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-10/1, v/v) on silica gel to afford the desired product **3a-H** (11 mg) in 12 % yield (Figure S30).

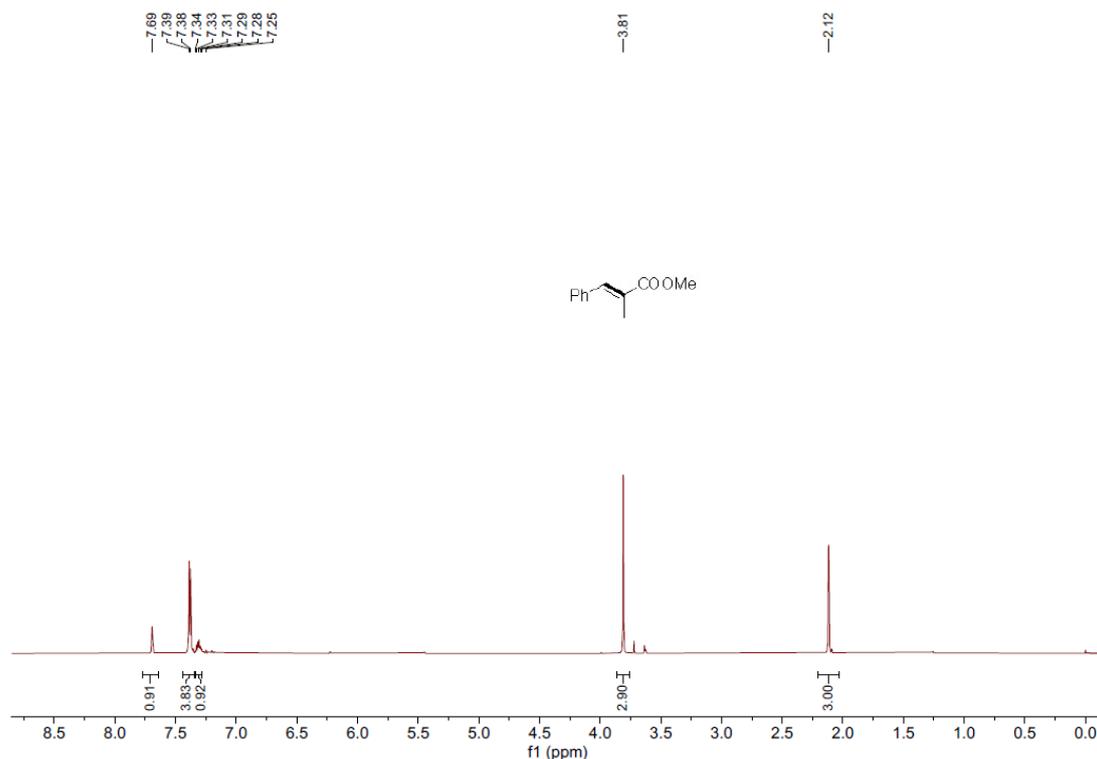
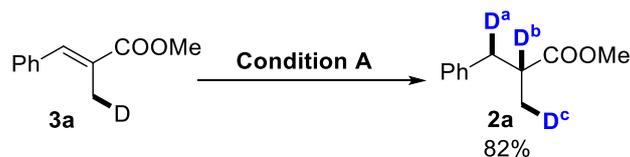


Figure S30. ¹H NMR spectrum of **3a-H**.

Intermediate testing experiment



An undivided cell was equipped with a magnetic stirrer, graphite rods as cathode and anode (the electrolysis setup is shown in Figure S31). The intermediate **3a** (88 mg, 0.5 mmol), Et₃N (210 μ L, 1.5 mmol), D₂O (200 μ L, 10 mmol) and ⁿBu₄NPF₆ (387 mg, 1.0 mmol) were added to the solvent DMF (9.8 mL). The resulting mixture was allowed to stir and electrolyze under constant current condition (18 mA) at room temperature for 4.5 hours. The reaction mixture was subsequently poured into water (200 mL) and extracted with ethyl acetate (40 mL*3). The combined organic phases were washed with saturated brine solution (100 mL). The volatile solvent was then removed with a rotary evaporator, and the residue was purified by column chromatography (PE/EA = 50/1-20/1, v/v) on silica gel to afford the desired product **2a**.

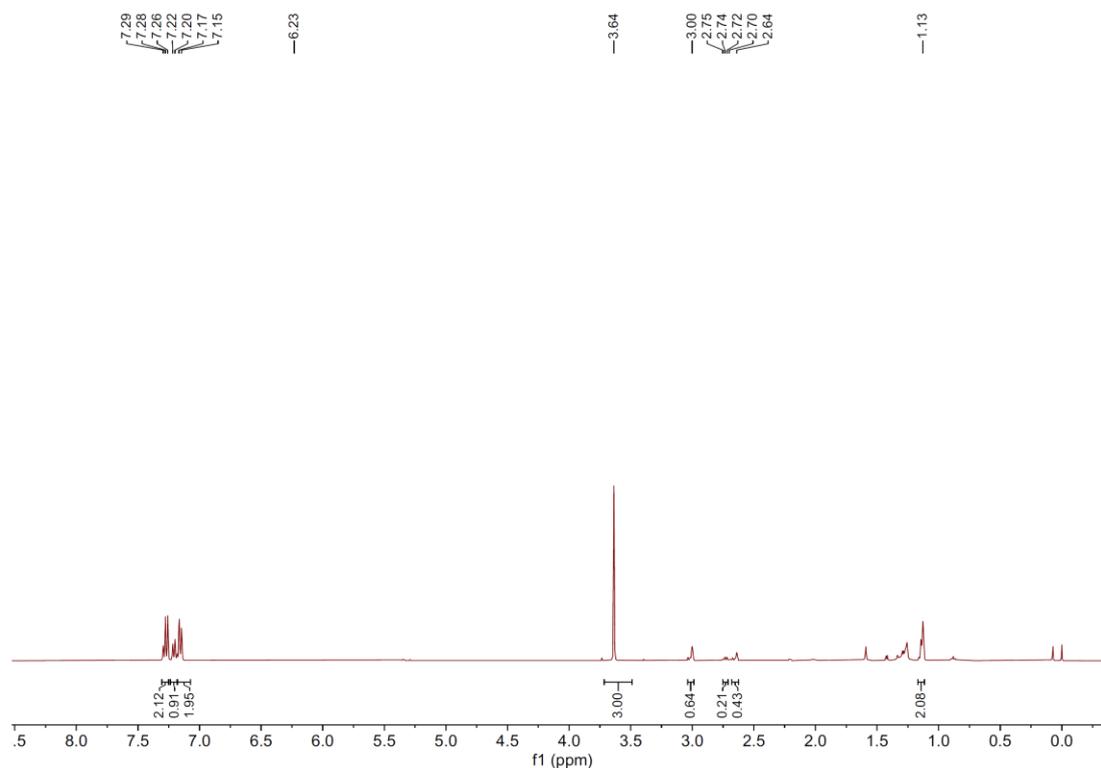
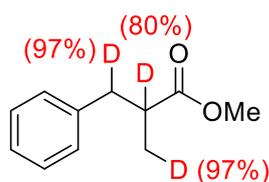
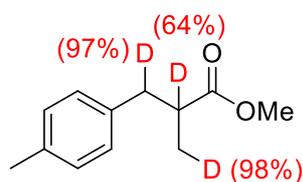


Figure S31. ¹H NMR spectrum of product **2a** starting from **3a**.

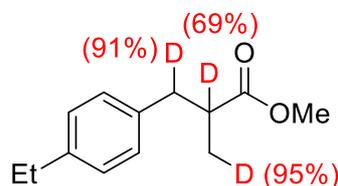
8. Experimental data



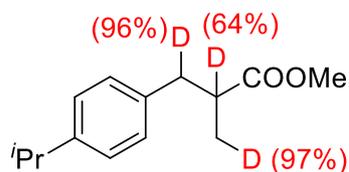
Methyl 2-(methyl-*d*)-3-phenylpropanoate-2,3-*d*₂ (**2a**): 66 mg, 73% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (t, *J* = 6.0 Hz, 2H), 7.20 (t, *J* = 6.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 3H), 3.00 (s, 0.54H), 2.73 (q, *J* = 6.7 Hz, 0.20H), 2.63 (s, 0.49H), 1.15 (m, 2.03H); ¹³C NMR (101 MHz, CDCl₃) δ 176.5, 139.3, 128.9, 128.3, 126.3, 51.5, 41.1 (m), 39.3 (m), 16.4 (m); HRMS (ESI): calcd for C₁₁H₁₁D₃O₂ (M+Na)⁺ 204.1074, found 204.1083.



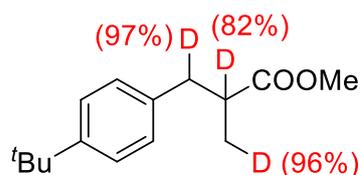
Methyl 2-(methyl-*d*)-3-(*p*-tolyl)propanoate-2,3-*d*₂ (**2b**): 72 mg, 75% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.06 (q, *J* = 8.0 Hz, 4H), 3.63 (s, 3H), 2.97 (d, *J* = 4.0 Hz), 2.70 (q, *J* = 6.7 Hz, 0.36H), 2.60 (d, *J* = 8.0 Hz, 0.39H), 2.31 (s, 3H), 1.12 (m, 2.02H); ¹³C NMR (101 MHz, CDCl₃) δ 176.6, 136.1, 135.7, 129.0, 128.7, 51.5, 41.0 (m), 38.9 (m), 21.0, 16.3 (m); HRMS (ESI): calcd for C₁₂H₁₃D₃O₂ (M+Na)⁺ 218.1231, found 218.1237.



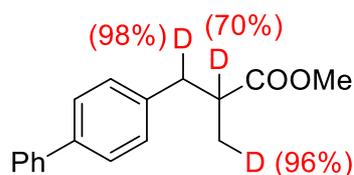
Methyl 3-(4-ethylphenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2c**): 88 mg, 84% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 3H), 2.97 (s, 0.65H), 2.71 (q, *J* = 6.7 Hz, 0.31H), 2.61 (q, *J* = 8.0 Hz, 2.44H), 1.21 (t, *J* = 6.0 Hz, 3H), 1.12 (m, 2.05H); ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 142.1, 136.4, 128.8, 127.8, 51.5, 42.0 (m), 38.9 (m), 28.4, 16.3 (m), 15.5; HRMS (ESI): calcd for C₁₃H₁₅D₃O₂ (M+Na)⁺ 232.1387, found 232.1388.



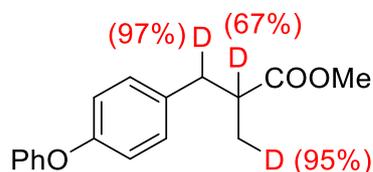
Methyl 3-(4-isopropylphenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2d**): 93 mg, 83% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.13 (d, *J* = 8.0 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 2.98 (d, *J* = 8.0 Hz, 0.64H), 2.87 (m, 1H), 2.71 (q, *J* = 8.0 Hz, 0.36H), 2.61 (d, *J* = 4.0 Hz, 0.40H), 1.23 (d, *J* = 8.0 Hz, 6H), 1.12 (s, 2.03H); ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 146.8, 136.6, 128.8, 126.4, 51.5, 41.0 (m), 38.9 (m), 33.7, 24.0, 16.3 (m); HRMS (ESI): calcd for C₁₄H₁₇D₃O₂ (M+Na)⁺ 246.1544, found 246.1545.



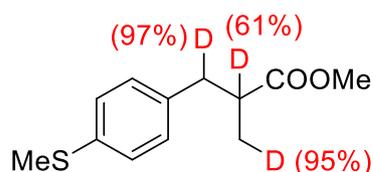
Methyl 3-(4-(tert-butyl)phenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2e**): 113 mg, 95% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 2.98 (m, 0.54H), 2.71 (q, *J* = 8.0 Hz, 0.18H), 2.60 (m, 0.49 H), 1.30 (s, 9H), 1.16 (m, 2.04H); ¹³C NMR (101 MHz, CDCl₃) δ 176.7, 149.0, 136.2, 128.6, 125.2, 51.5, 40.9 (m), 38.7 (m), 34.3, 31.6, 16.3 (m); HRMS (ESI): calcd for C₁₅H₁₉D₃O₂ (M+Na)⁺ 260.1700, found 260.1699.



Methyl 3-([1,1'-biphenyl]-4-yl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2f**): 91 mg, 71% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.42 (t, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.65 (s, 3H), 3.05 (d, *J* = 8.0 Hz, 0.58H), 2.77 (q, *J* = 6.7 Hz, 0.30H), 2.69 (d, *J* = 4.0 Hz, 0.45H), 1.16 (m, 2.04H); ¹³C NMR (101 MHz, CDCl₃) δ 176.5, 140.9, 139.2, 138.4, 129.3, 128.7, 127.1, 127.0, 126.9, 51.6 41.0 (m), 39.0 (m), 16.4 (m); HRMS (ESI): calcd for C₁₇H₁₅D₃O₂ (M+Na)⁺ 280.1387, found 280.1391.

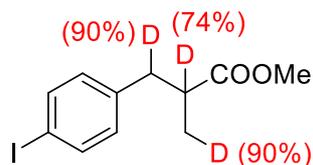


Methyl 2-(methyl-*d*)-3-(4-phenoxyphenyl)propanoate-2,3-*d*₂ (**2g**): 120 mg, 88% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 2H), 7.10 (t, *J* = 8.0 Hz, 3H), 6.98 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 2.98 (d, *J* = 8.0 Hz, 0.63H), 2.71 (q, *J* = 6.7 Hz, 0.33H), 2.64 (d, *J* = 4.0 Hz, 0.40H), 1.14 (m, 2.05H); ¹³C NMR (101 MHz, CDCl₃) δ 176.5, 157.4, 155.6, 134.2, 130.1, 129.7, 123.0, 118.8, 118.6, 51.5, 41.1(m), 38.6(m), 16.3(m); HRMS (ESI): calcd for C₁₇H₁₅D₃O₃ (M+Na)⁺ 296.1336, found 296.1399.

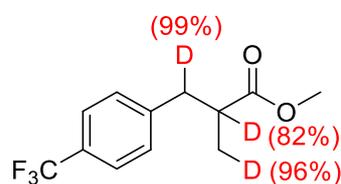


Methyl 2-(methyl-*d*)-3-(4-(methylthio)phenyl)propanoate-2,3-*d*₂ (**2h**): 92 mg, 81% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 3.63 (s, 3H), 2.96 (d, *J* = 8.0 Hz, 0.58H), 2.69 (t, *J* = 8.0 Hz, 0.39H), 2.61 (d, *J* = 8.0 Hz, 0.45H), 2.48 (s, 3H), 1.13 (m, 2.05H); ¹³C NMR (101 MHz, CDCl₃) δ 176.4, 136.2, 136.0, 129.4, 126.8, 51.5, 41.3 (m), 38.7 (m), 16.5 (m),

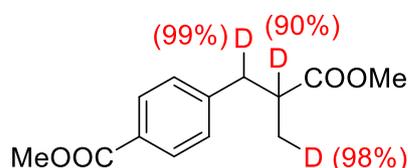
16.0; HRMS (ESI): calcd for $C_{12}H_{13}D_3O_2S$ (M+Na)⁺ 250.0952, found 250.0951.



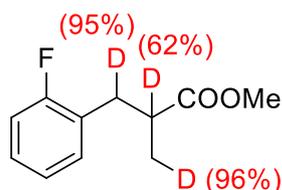
Methyl 3-(4-iodophenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2i**): 57 mg, 37% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.27 (m, 2H), 7.16 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 3.30 (m, 0.54H), 2.73 (q, *J* = 6.7 Hz, 0.26H), 2.63 (m, 0.56H), 1.13 (m, 2.10H); ¹³C NMR (101 MHz, CDCl₃) δ 176.6, 139.3, 129.0, 128.4, 128.3, 126.3, 51.6, 41.3 (m), 39.4 (m), 16.4 (m); HRMS (ESI): calcd for $C_{11}H_{10}D_3IO_2$ (M+H)⁺ 308.0221, found 308.0229.



Methyl 2-(methyl-*d*)-3-(4-(trifluoromethyl)phenyl)propanoate-2,3-*d*₂ (**2j**): 70 mg, 56% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.54 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 3.64 (s, 3H), 3.05 (s, 0.53H), 2.77 (t, *J* = 6.0 Hz, 0.18H), 2.71 (s, 0.48H), 1.15 (m, 2.04H); ¹³C NMR (101 MHz, CDCl₃) δ 176.1, 143.4, 129.2, 128.8 (q, *J*_{F-C} = 25.0 Hz), 125.3 (q, *J*_{F-C} = 3.7 Hz), 124.2 (t, *J*_{F-C} = 273.2 Hz), 51.7, 40.7 (m), 40.0 (m), 16.5 (m); HRMS (ESI): calcd for $C_{12}H_{10}D_3F_3O_2$ (M+H)⁺ 250.1129, found 250.1127.

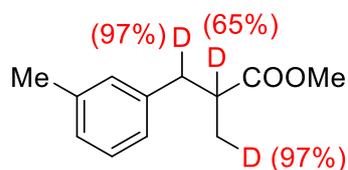


Methyl 4-(3-methoxy-2-(methyl-*d*)-3-oxopropyl-1,2-*d*₂)benzoate (**2k**): 65 mg, 54% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 3.63 (s, 3H), 3.06 (d, *J* = 12.0 Hz, 0.46H), 2.76 (m, 0.10H), 2.69 (d, *J* = 20.0 Hz, 0.55H), 1.14 (m, 2.02H); ¹³C NMR (101 MHz, CDCl₃) δ 176.1, 167.0, 144.7, 129.7, 128.9, 128.3, 52.0, 51.6, 40.7 (m), 39.11 (m), 16.4 (m); HRMS (ESI): calcd for $C_{13}H_{13}D_3O_4$ (M+H)⁺ 240.1310, found 240.1306.

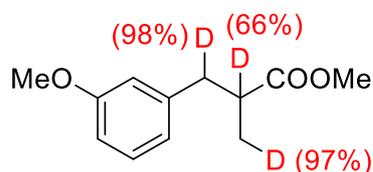


Methyl 3-(2-fluorophenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2l**): 70 mg, 70% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (m, 2H), 7.04 (m, 2H), 3.64 (s, 3H), 2.99 (d, *J* = 8.0 Hz, 0.63H), 2.79 (t, *J* = 8.0 Hz, 0.38H), 2.75 (d, *J* = 8.0 Hz, 0.42H), 1.14 (m, 2.04H); ¹³C NMR (101 MHz, CDCl₃) δ 176.3, 161.3 (d, *J*_{F-C} = 246.4 Hz), 131.3 (d, *J*_{F-C} = 5.1 Hz), 128.1 (d, *J*_{F-C} = 9.1 Hz), 123.9 (d, *J*_{F-C} = 4.0 Hz), 115.4

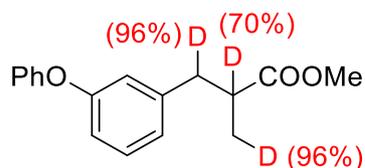
(d, $J_{F-C} = 22.2$ Hz), 51.6, 39.6 (m), 32.6 (m), 16.4 (m); HRMS (ESI): calcd for $C_{11}H_{10}D_3FO_2$ (M+H)⁺ 200.1161, found 200.1165.



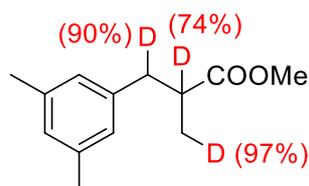
Methyl 2-(methyl-*d*)-3-(*m*-tolyl)propanoate-2,3-*d*₂ (**2m**): 75 mg, 77% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.16 (t, $J = 8.0$ Hz, 1H), 6.99 (m, 3H), 3.64 (s, 3H), 2.98 (d, $J = 8.0$ Hz, 0.65H), 2.71 (q, $J = 8.0$ Hz, 0.35H), 2.60 (d, $J = 4.0$ Hz, 0.38H), 2.32 (s, 3H), 1.12 (m, 2.03H); ¹³C NMR (101 MHz, CDCl₃) δ 176.6, 139.3, 137.9, 129.7, 128.2, 127.0, 125.9, 51.5, 41.1 (m), 39.3 (m), 21.4, 16.4 (m); HRMS (ESI): calcd for $C_{12}H_{13}D_3O_2$ (M+Na)⁺ 218.1231, found 218.1235.



Methyl 3-(3-methoxyphenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2n**): 89 mg, 84% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.18 (t, $J = 8.0$ Hz, 1H), 6.73 (t, $J = 8.0$ Hz, 3H), 3.77 (s, 3H), 3.64 (s, 3H), 2.99 (d, $J = 8.0$ Hz, 0.62H), 2.72 (q, $J = 8.0$ Hz, 0.34H), 2.61 (d, $J = 8.0$ Hz, 0.40H), 1.12 (m, 2.03H); ¹³C NMR (101 MHz, CDCl₃) δ 176.4, 159.5, 140.8, 129.2, 121.2, 114.6, 111.6, 55.0, 51.5, 40.9 (m), 39.4 (m), 16.3 (m); HRMS (ESI): calcd for $C_{12}H_{13}D_3O_3$ (M+Na)⁺ 234.1180, found 234.1174.

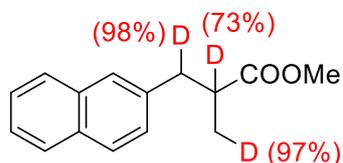


Methyl 2-(methyl-*d*)-3-(3-phenoxyphenyl)propanoate-2,3-*d*₂ (**2o**): 119 mg, 87% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.32 (t, $J = 8.0$ Hz, 2H), 7.23 (t, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 6.99 (d, $J = 8.0$ Hz, 2H), 6.86 (m, 3H), 3.62 (s, 3H), 2.97 (s, 0.61H), 2.71 (q, $J = 6.7$ Hz, 0.30H), 2.63 (d, $J = 4.0$ Hz, 0.43H), 1.12 (m, 2.04H); ¹³C NMR (101 MHz, CDCl₃) δ 176.3, 157.2, 157.2, 129.7, 129.6, 123.9, 123.1, 119.4, 118.7, 116.8, 51.6, 40.9 (m), 39.2 (m), 16.3 (m); HRMS (ESI): calcd for $C_{17}H_{15}D_3O_3$ (M+Na)⁺ 296.1136, found 296.1333.

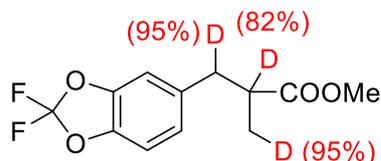


Methyl 3-(3,5-dimethylphenyl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2p**): 95 mg, 91% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 6.83 (s, 1H), 6.77 (s, 2H), 3.64 (s, 3H), 2.96 (s, 0.65H), 2.69 (q, $J = 8.0$

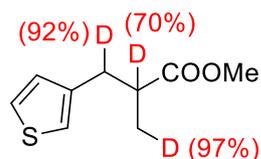
Hz, 0.26H), 2.53 (s, 0.45H), 2.27 (s, 6H), 1.11 (m, 2.03H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.7, 139.2, 137.7, 127.9, 126.7, 51.4, 40.9 (m), 39.1 (m), 21.2, 16.3 (m); HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{15}\text{D}_3\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 232.1387, found 232.1388.



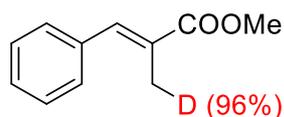
Methyl 2-(methyl-*d*)-3-(naphthalen-2-yl)propanoate-2,3-*d*₂ (**2q**): 77 mg, 67% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (m, 3H), 7.60 (s, 1H), 7.44 (m, 2H), 7.30 (d, $J = 12.0$ Hz, 1H), 3.63 (s, 3H), 3.18 (d, $J = 8.0$ Hz, 0.59H), 2.83 (t, $J = 4.0$ Hz, 0.27H), 2.81 (d, $J = 4.0$ Hz, 0.43H), 1.16 (m, 2.03H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.6, 136.8, 133.5, 132.2, 128.0, 127.6, 127.5, 127.4, 125.9, 125.4, 51.6, 41.0 (m), 39.5 (m), 16.4 (m); HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{D}_3\text{O}_2$ ($\text{M}+\text{Na}$) $^+$ 254.1231, found 254.1234.



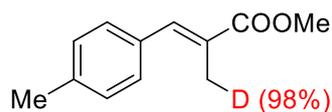
Methyl 3-(2,2-difluorobenzo[d][1,3]dioxol-5-yl)-2-(methyl-*d*)propanoate-2,3-*d*₂ (**2r**): 93 mg, 71% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.95 (d, $J = 8.0$ Hz, 1H), 6.86 (t, $J = 8.0$ Hz, 2H), 3.64 (s, 3H), 2.97 (s, 0.66H), 2.70 (t, $J = 8.0$ Hz, 0.18H), 2.66 (d, $J = 4.0$ Hz, 0.39H), 1.14 (m, 2.05H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.1, 143.8, 142.3, 135.4, 131.6 (t, $J_{\text{F-C}} = 255.5$ Hz), 123.9, 110.0, 109.1, 51.7, 41.1 (m), 39.0 (m), 16.5 (m); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_9\text{D}_3\text{F}_2\text{O}_4$ ($\text{M}+\text{Na}$) $^+$ 284.0784, found 284.0791.



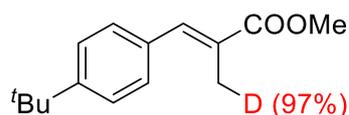
Methyl 2-(methyl-*d*)-3-(thiophen-3-yl)propanoate-2,3-*d*₂ (**2s**): 70 mg, 75% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.24 (m, 1H), 6.97 (d, $J = 4.0$ Hz, 1H), 6.91 (d, $J = 4.0$ Hz, 1H), 3.65 (s, 3H), 3.01 (d, $J = 4.0$ Hz, 0.54H), 2.74 (t, $J = 4.0$ Hz, 0.30H), 2.72 (d, $J = 4.0$ Hz, 0.54H), 1.14 (m, 2.03H); ^{13}C NMR (101 MHz, CDCl_3) δ 176.5, 139.5, 128.3, 125.4, 121.5, 51.6, 40.5 (m), 33.6 (m), 16.5 (m); HRMS (ESI): calcd for $\text{C}_9\text{H}_9\text{D}_3\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 188.0819, found 188.0814.



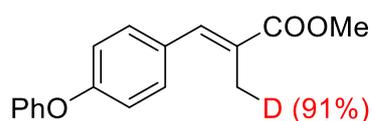
Methyl (E)-2-(methyl-*d*)-3-phenylacrylate (**3a**): 84 mg, 95% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 4.0$ Hz, 4H), 7.33 (q, $J = 4.0$ Hz, 1H), 3.82 (s, 3H), 2.11 (m, 2.04H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 139.0, 135.9, 129.6, 128.4, 128.3, 52.1, 13.8 (t, $J_{\text{D-C}} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{11}\text{DO}_2$ ($\text{M}+\text{H}$) $^+$ 178.0973, found 178.0967.



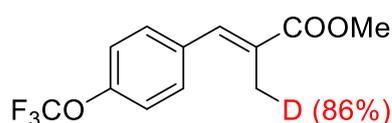
Methyl (*E*)-2-(methyl-*d*)-3-(*p*-tolyl)acrylate (**3b**): 89 mg, 93% yield; brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.31 (d, $J = 8.0$ Hz, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 3.81 (s, 3H), 2.37 (s, 3H), 2.11 (m, 2.02H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.3, 139.0, 138.5, 133.0, 129.7, 129.1, 127.3, 52.0, 21.3, 13.8 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{13}\text{DO}_2$ ($\text{M}+\text{Na}$) $^+$ 214.0949, found 214.0954.



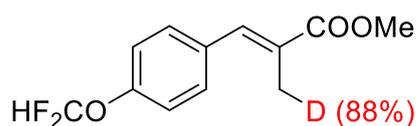
Methyl (*E*)-3-(4-(tert-butyl)phenyl)-2-(methyl-*d*)acrylate (**3c**): 105 mg, 90% yield; white solid, m.p. 39-42°C; ^1H NMR (400 MHz, CDCl_3) δ 7.67 (s, 1H), 7.41 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 3.80 (s, 3H), 2.13 (m, 2.03H), 1.33 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 151.6, 138.8, 133.0, 129.6, 127.4, 125.3, 51.9, 34.7, 31.2, 13.8 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{19}\text{DO}_2$ ($\text{M}+\text{Na}$) $^+$ 256.1418, found 256.1426.



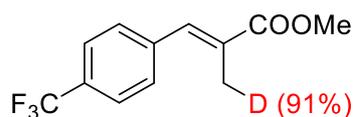
Methyl (*E*)-2-(methyl-*d*)-3-(4-phenoxyphenyl)acrylate (**3d**): 78 mg, 58% yield; white oil; ^1H NMR (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.37 (m, 4H), 7.14 (t, $J = 8.0$ Hz, 1H), 7.03 (m, 4H), 3.81 (s, 3H), 2.12 (m, 2.09H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 157.7, 156.4, 138.3, 131.4, 130.6, 129.9, 127.1, 123.8, 119.5, 118.1, 52.0, 13.8 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{17}\text{H}_{15}\text{DO}_3$ ($\text{M}+\text{H}$) $^+$ 292.1054, found 292.1061.



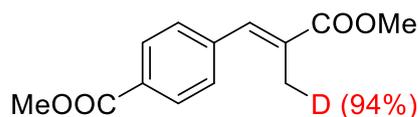
Methyl (*E*)-2-(methyl-*d*)-3-(4-(trifluoromethoxy)phenyl)acrylate (**3e**): 120 mg, 92% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 6.06 (s, 1H), 5.83 (d, $J = 12.0$ Hz, 2H), 5.65 (d, $J = 8.0$ Hz, 2H), 2.24 (s, 3H), 0.50 (m, 2.14H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.8, 148.9, 137.3, 134.5, 131.0, 130.2, 129.2, 120.7, 119.1 (q, $J_{F-C} = 258.6$ Hz), 52.2, 13.7 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{10}\text{DF}_3\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 262.0796, found 262.0804.



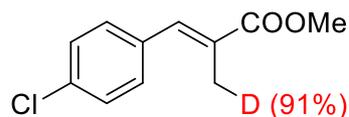
Methyl (*E*)-3-(4-(difluoromethoxy)phenyl)-2-(methyl-*d*)acrylate (**3f**): 117 mg, 96% yield; white solid, m.p. 35-38°C; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.55 (t, $J_{F-H} = 76.0$ Hz, 1H), 3.82 (s, 3H), 2.09 (m, 2.08H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 150.9 (t, $J_{F-C} = 2.5$ Hz), 137.6, 133.0, 131.2, 128.5, 119.2, 115.7 (t, $J_{F-C} = 261.6$ Hz), 52.0, 13.7 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{11}\text{DF}_2\text{O}_3$ ($\text{M}+\text{H}$) $^+$ 244.0890, found 244.0898.



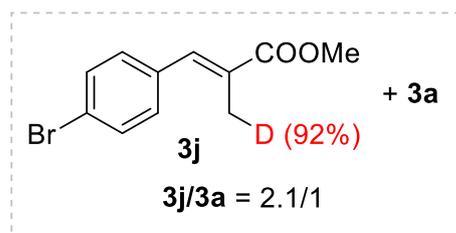
Methyl (*E*)-2-(methyl-*d*)-3-(4-(trifluoromethyl)phenyl)acrylate (**3g**): 86 mg, 70% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1H), 7.65 (d, $J = 8.0$ Hz, 2H), 7.48 (d, $J = 8.0$ Hz, 2H), 3.84 (s, 3H), 2.09 (m, 2.09H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.6, 139.4, 137.2 (q, $J_{\text{F-C}} = 3.0$ Hz), 130.1 (q, $J_{\text{F-C}} = 30.0$ Hz), 129.2, 126.6 (q, $J_{\text{F-C}} = 4.0$ Hz), 124.5 (q, $J_{\text{F-C}} = 262.0$ Hz), 52.2, 13.8 (t, $J_{\text{D-C}} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{10}\text{DF}_3\text{O}_2$ ($\text{M}+\text{H}$) $^+$ 246.0847, found 246.0851.



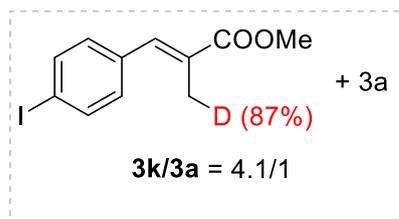
Methyl (*E*)-4-(3-methoxy-2-(methyl-*d*)-3-oxoprop-1-en-1-yl)benzoate (**3h**): 96 mg, 82% yield; white oil; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (s, 1H), 7.38 (d, $J = 8.0$ Hz, 2H), 6.92 (d, $J = 8.0$ Hz, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 2.12 (m, 2.06H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.4, 159.7, 138.6, 131.4, 128.4, 126.0, 113.8, 55.2, 51.9, 13.8 (t, $J_{\text{D-C}} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{13}\text{H}_{13}\text{DO}_4$ ($\text{M}+\text{Na}$) $^+$ 258.0847, found 258.0850.



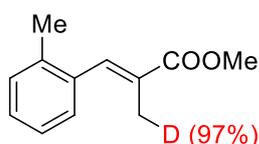
Methyl (*E*)-3-(4-chlorophenyl)-2-(methyl-*d*)acrylate (**3i**): 87 mg, 82% yield; brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.63 (s, 1H), 7.37 (d, $J = 12.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 3.82 (s, 3H), 2.10 (m, 2.09H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 137.6, 134.3, 134.2, 130.9, 128.9, 128.6, 52.1, 13.8 (t, $J_{\text{D-C}} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{10}\text{DClO}_2$ ($\text{M}+\text{H}$) $^+$ 212.0583, found 212.0589.



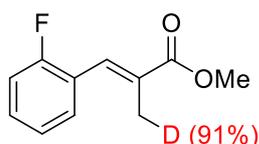
Methyl (*E*)-3-(4-bromophenyl)-2-(methyl-*d*)acrylate (**3j**): 100 mg, 78% yield; white oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 0.30H), 7.60 (s, 0.65H), 7.52 (d, $J = 8.0$ Hz, 1.33H), 7.39 (m, 1H), 7.25 (d, $J = 8.0$ Hz, 2H), 3.82 (s, 3H), 2.10 (m, 2.08H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 137.7, 134.3, 134.2, 130.9, 128.9, 128.6, 52.1, 13.8 (t, $J_{\text{D-C}} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{10}\text{DBrO}_2$ ($\text{M}+\text{H}$) $^+$ 256.0078, found 256.0077.



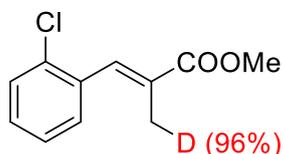
Methyl (*E*)-3-(4-iodophenyl)-2-(methyl-*d*)acrylate (**3k**): 85 mg, 56% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (s, 1.82H), 7.39 (m, 7.25H), 3.82 (s, 5.56H), 2.11 (m, 4.16H), 2.07 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 169.2, 139.0, 137.6, 135.8, 131.2, 129.6, 128.4, 52.1, 13.8 (t, $J_{D-C} = 19.7$); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{10}\text{DIO}_2$ ($\text{M}+\text{Na}$) $^+$ 325.9759, found 325.9763.



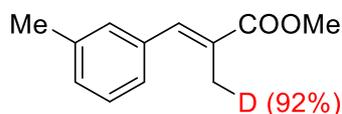
Methyl (*E*)-2-(methyl-*d*)-3-(*o*-tolyl)acrylate (**3l**): 71 mg, 74% yield; brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.75 (s, 1H), 7.20 (m, 4H), 3.82 (s, 3H), 2.28 (s, 3H), 1.95 (m, 2.03H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.9, 138.4, 136.8, 135.1, 130.0, 128.9, 128.8, 128.1, 125.5, 51.9, 19.8, 13.6 (t, $J_{D-C} = 19.7$); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_{13}\text{DO}_2$ ($\text{M}+\text{Na}$) $^+$ 214.0949, found 214.0957.



Methyl (*E*)-3-(2-fluorophenyl)-2-(methyl-*d*)acrylate (**3m**): 91 mg, 93% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.71 (s, 1H), 7.32 (m, 2H), 7.15 (t, $J = 8.0$ Hz, 1H), 7.09 (t, $J = 8.0$ Hz, 1H), 3.82 (s, 3H), 2.04 (m, 2.09H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 160.3 (d, $J_{F-C} = 251.5$ Hz), 131.7 (d, $J_{F-C} = 3.0$ Hz), 130.6, 130.4 (d, $J_{F-C} = 3.0$ Hz), 130.1 (d, $J_{F-C} = 8.1$ Hz), 123.7 (d, $J_{F-C} = 3.0$ Hz), 123.6, 115.6 (d, $J_{F-C} = 22.2$ Hz), 52.0, 14.0 (t, $J_{D-C} = 18.7$ Hz); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{10}\text{DFO}_2$ ($\text{M}+\text{H}$) $^+$ 196.0879, found 196.0887.

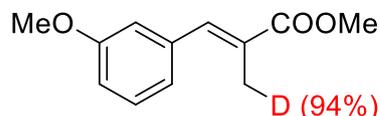


Methyl (*E*)-3-(2-chlorophenyl)-2-(methyl-*d*)acrylate (**3n**): 93 mg, 88% yield; brown oil; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (s, 1H), 7.42 (m, 1H), 7.29 (m, 3H), 3.83 (s, 3H), 1.99 (m, 2.04H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.5, 136.0, 134.3, 134.1, 130.4, 130.2, 129.5, 129.4, 126.3, 52.1, 13.8 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_{10}\text{DClO}_2$ ($\text{M}+\text{H}$) $^+$ 212.0583, found 212.0589.

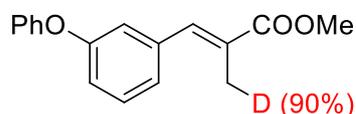


Methyl (*E*)-2-(methyl-*d*)-3-(*m*-tolyl)acrylate (**3o**): 75 mg, 78% yield; white oil; ^1H NMR (400 MHz,

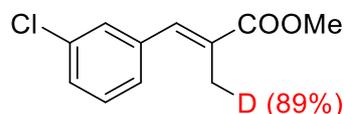
CDCl₃) δ 7.66 (s, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 4.0 Hz, 2H), 7.14 (d, *J* = 4.0 Hz, 1H), 3.82 (s, 3H), 2.37 (s, 3H), 2.11 (m, 2.08H); ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 139.1, 138.0, 135.8, 130.3, 129.1, 128.2, 128.0, 126.7, 52.0, 21.4, 13.8 (t, *J*_{D-C} = 19.7 Hz); HRMS (ESI): calcd for C₁₂H₁₃DO₂ (M+Na)⁺214.0949, found 214.0956.



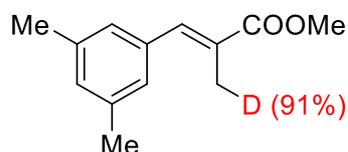
Methyl (*E*)-3-(3-methoxyphenyl)-2-(methyl-*d*)acrylate (**3p**): 99 mg, 96% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.66 (s, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.88 (m, 2H), 3.82 (s, 3H), 3.82 (s, 3H), 2.11 (m, 2.06H); ¹³C NMR (101 MHz, CDCl₃) δ 169.1, 159.5, 138.8, 137.2, 129.4, 128.5, 122.1, 115.1, 113.9, 55.2, 52.1, 13.9 (t, *J*_{D-C} = 19.7 Hz); HRMS (ESI): calcd for C₁₂H₁₃DO₃ (M+Na)⁺230.0898, found 230.0905.



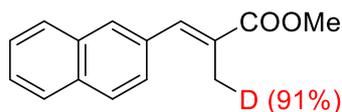
Methyl (*E*)-2-(methyl-*d*)-3-(3-phenoxyphenyl)acrylate (**3q**): 118 mg, 88% yield; white oil; ¹H NMR (400 MHz, CDCl₃) δ 7.62 (s, 1H), 7.35 (t, *J* = 8.0 Hz, 3H), 7.12 (t, *J* = 6.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 3H), 6.97 (m, 1H), 3.80 (s, 3H), 2.07 (m, 2.10H); ¹³C NMR (101 MHz, CDCl₃) δ 169.0, 157.4, 156.8, 138.3, 137.6, 129.8, 129.7, 128.9, 124.4, 123.6, 119.6, 119.1, 118.6, 52.1, 13.8 (t, *J*_{D-C} = 20.2 Hz); HRMS (ESI): calcd for C₁₇H₁₅DO₃ (M+Na)⁺292.1054, found 292.1063.



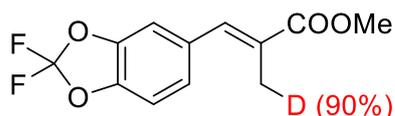
Methyl (*E*)-3-(3-chlorophenyl)-2-(methyl-*d*)acrylate (**3r**): 95 mg, 90% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.61 (s, 1H), 7.36 (s, 1H), 7.30 (m, 3H), 3.82 (s, 3H), 2.09 (m, 2.11H); ¹³C NMR (101 MHz, CDCl₃) δ 168.8, 137.6, 137.4, 134.3, 129.6, 129.4, 128.3, 127.7, 52.2, 13.8 (t, *J*_{D-C} = 19.7 Hz); HRMS (ESI): calcd for C₁₁H₁₀DClO₂ (M+H)⁺ 212.0583, found 212.0590.



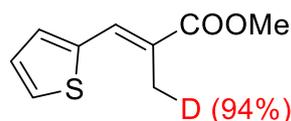
Methyl (*E*)-3-(3,5-dimethylphenyl)-2-(methyl-*d*)acrylate (**3s**): 71 mg, 69% yield; yellow oil; ¹H NMR (400 MHz, CDCl₃) δ 7.63 (s, 1H), 7.01 (s, 2H), 6.95 (s, 1H), 3.80 (s, 3H), 2.33 (s, 6H), 2.10 (m, 2.09H); ¹³C NMR (101 MHz, CDCl₃) δ 169.2, 139.3, 137.8, 135.8, 130.0, 127.8, 127.4, 51.9, 21.2, 13.8 (t, *J*_{D-C} = 20.2 Hz); HRMS (ESI): calcd for C₁₃H₁₅DO₂ (M+H)⁺ 228.1105, found 228.1113.



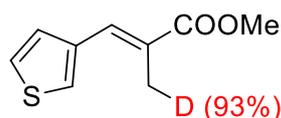
Methyl (*E*)-2-(methyl-*d*)-3-(naphthalen-2-yl)acrylate (**3t**): 105 mg, 92% yield; yellow solid, m.p. 55-58°C; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.83 (m, 5H), 7.49 (m, 3H), 3.84 (s, 3H), 2.19 (m, 2.09H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.8, 137.5, 133.5, 133.1, 131.5, 130.5, 128.6, 128.5, 126.6, 126.3, 126.1, 125.1, 124.7, 52.1, 14.0 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{15}\text{H}_{13}\text{DO}_2$ ($\text{M}+\text{Na}$) $^+$ 250.0949, found 250.0956.



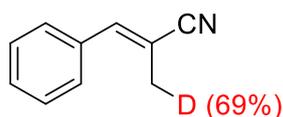
Methyl (*E*)-3-(2,2-difluorobenzo[*d*][1,3]dioxol-5-yl)-2-(methyl-*d*)acrylate (**3u**): 116 mg, 90% yield; yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.62 (s, 1H), 7.09 (m, 3H), 3.82 (s, 3H), 2.09 (m, 2.10H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 168.7, 143.8, 143.4, 137.4, 132.0, 131.6 (t, $J_{F-C} = 257.0$ Hz), 128.8, 125.7, 123.9, 110.3, 109.3, 52.1, 13.7 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{12}\text{H}_9\text{DF}_2\text{O}_4$ ($\text{M}+\text{H}$) $^+$ 258.0683, found 258.0689.



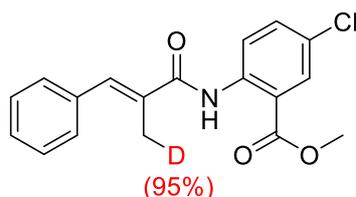
Methyl (*E*)-2-(methyl-*d*)-3-(thiophen-2-yl)acrylate (**3v**): 53 mg, 58% yield; brown oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.86 (s, 1H), 7.49 (d, $J = 4.0$ Hz, 1H), 7.28 (d, $J = 4.0$ Hz, 1H), 7.11 (m, 1H), 3.81 (s, 3H), 2.20 (m, 2.06H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.0, 139.2, 131.72, 131.68, 129.1, 127.3, 124.6, 52.1, 14.0 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_9\text{H}_9\text{DO}_2\text{S}$ ($\text{M}+\text{Na}$) $^+$ 206.0356, found 206.0361.



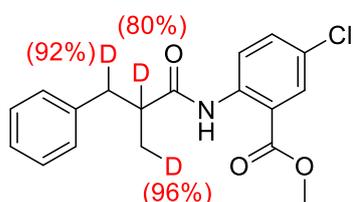
Methyl (*E*)-2-(methyl-*d*)-3-(thiophen-3-yl)acrylate (**3w**): 71 mg, 77% yield; brown oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (s, 1H), 7.45 (d, $J = 4.0$ Hz, 1H), 7.34 (m, 1H), 7.25 (t, $J = 4.0$ Hz, 1H), 3.80 (s, 3H), 2.15 (m, 2.07H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 169.2, 137.4, 132.7, 128.8, 127.1, 126.5, 125.6, 52.0, 14.0 (t, $J_{D-C} = 20.2$ Hz); HRMS (ESI): calcd for $\text{C}_9\text{H}_9\text{DO}_2\text{S}$ ($\text{M}+\text{H}$) $^+$ 184.0537, found 184.0544.



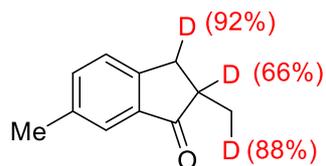
(*E*)-2-(methyl-*d*)-3-phenylacrylonitrile (**3x**): 61 mg, 84% yield; yellow oil; $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.69 (d, $J = 8.0$ Hz, 2H), 7.40 (m, 3H), 6.93 (s, 1H), 2.14 (m, 2.31H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.0, 133.8, 129.8, 128.7, 128.4, 119.2, 106.0, 21.9 (t, $J_{D-C} = 20.2$ Hz); HRMS (ESI): calcd for $\text{C}_{10}\text{H}_8\text{DN}$ ($\text{M}+\text{H}$) $^+$ 145.0871, found 145.0876.



Methyl (*E*)-5-chloro-2-(2-(methyl-*d*)-3-phenylacrylamido)benzoate (**5**): 168 mg, 51% yield; White solid, m.p. 115-118 °C; ^1H NMR (400 MHz, CDCl_3) δ 11.58 (s, 1H), 8.87 (d, $J = 8.0$ Hz, 1H), 8.03 (m, 1H), 7.62 (s, 1H), 7.53 (m, 1H), 7.42 (d, $J = 4.0$ Hz, 4H), 7.33 (m, 1H), 3.95 (s, 3H), 2.26 (m, 2.05H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 167.8, 140.5, 136.0, 136.0, 134.5, 132.3, 130.4, 129.5, 128.4, 128.1, 127.5, 121.9, 116.3, 52.7, 13.8 (t, $J_{D-C} = 19.7$ Hz); HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{DClNO}_3$ ($\text{M}+\text{Na}$) $^+$ 353.0744, found 353.0748.



Methyl 5-chloro-2-(2-(methyl-*d*)-3-phenylpropanamido-2,3- d_2)benzoate (**6**): 157 mg, 47% yield; white solid, m.p. 64-67 °C; ^1H NMR (400 MHz, CDCl_3) δ 10.90 (s, 1H), 8.71 (d, $J = 12.0$ Hz, 2H), 7.95 (m, 1H), 7.47 (q, $J = 4.0$ Hz, 1H), 7.22 (m, 5H), 3.90 (s, 3H), 3.09 (d, $J = 8.0$ Hz, 0.53H), 2.77 (d, $J = 8.0$ Hz, 0.20H), 2.73 (d, $J = 4.0$ Hz, 0.55H), 1.26 (m, 2.04H); ^{13}C NMR (101 MHz, CDCl_3) δ 174.8, 167.5, 140.0, 139.3, 134.4, 130.3, 129.0, 128.4, 127.3, 126.3, 121.8, 116.1, 52.5, 45.2 (m), 40.2 (m), 16.9 (m); HRMS (ESI): calcd for $\text{C}_{18}\text{H}_{15}\text{D}_3\text{ClNO}_3$ ($\text{M}+\text{Na}$) $^+$ 357.1056, found 357.1059.



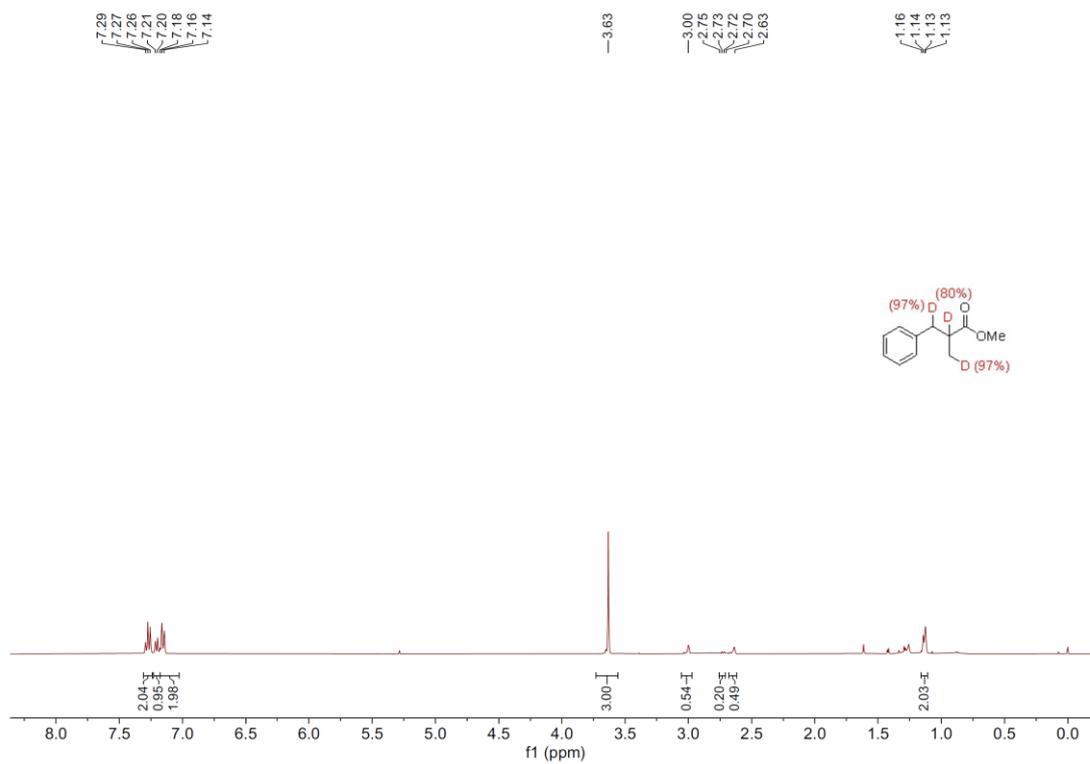
6-methyl-2-(methyl-*d*)-2,3-dihydro-1H-inden-1-one-2,3- d_2 (**7**): 62 mg, 76% yield; yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.54 (s, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 8.0$ Hz, 1H), 3.31 (s, 0.47H), 2.70 (t, $J = 6.0$ Hz, 1H), 2.64 (s, 0.61H), 2.39 (s, 3H), 1.29 (m, 2.12H); ^{13}C NMR (101 MHz, CDCl_3) δ 209.6, 150.7, 137.4, 136.5, 135.8, 126.2, 123.8, 41.9 (m), 34.2 (m), 21.0, 16.0 (m); HRMS (ESI): calcd for $\text{C}_{11}\text{H}_9\text{D}_3\text{O}$ ($\text{M}+\text{H}$) $^+$ 164.1149, found 164.1156.

9. References

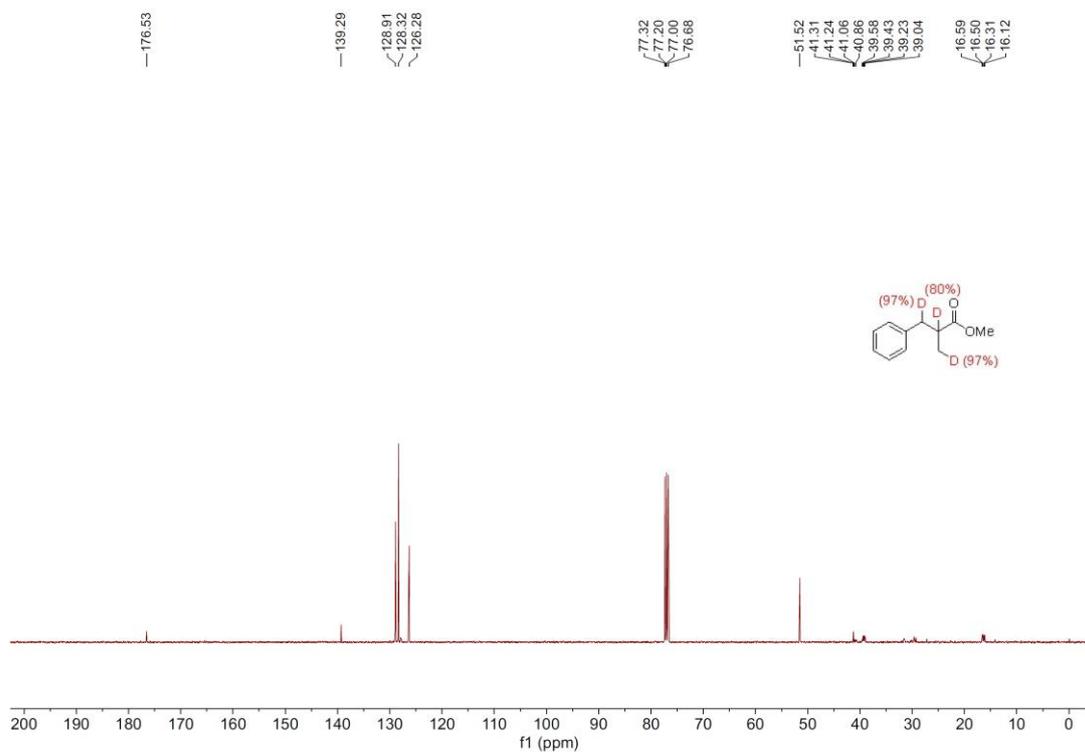
1. X. Wang, K. Liu, X. Jin, X. Li, M. Shen, S. Zhang, M.-B. Li, Oxygen Atom Migration of Allylic Esters via an Organocatalyzed Claisen-type Rearrangement. *Eur. J. Org. Chem.* **2025**, *28*, e202401401.

Part II NMR spectra

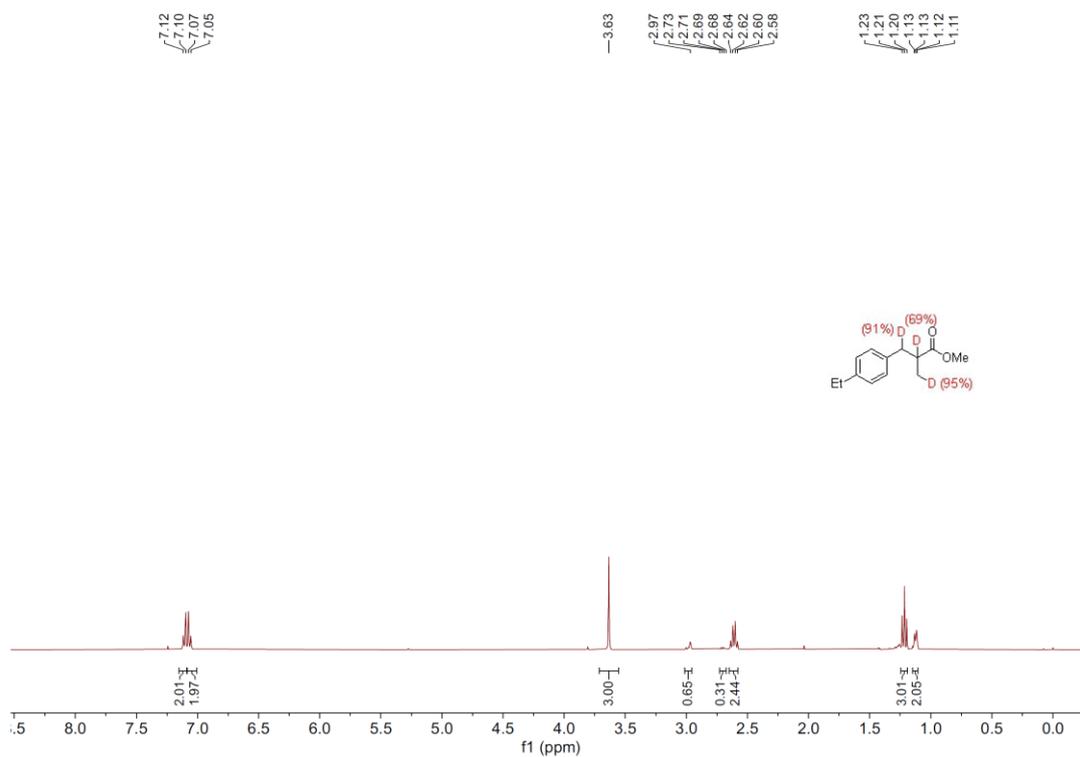
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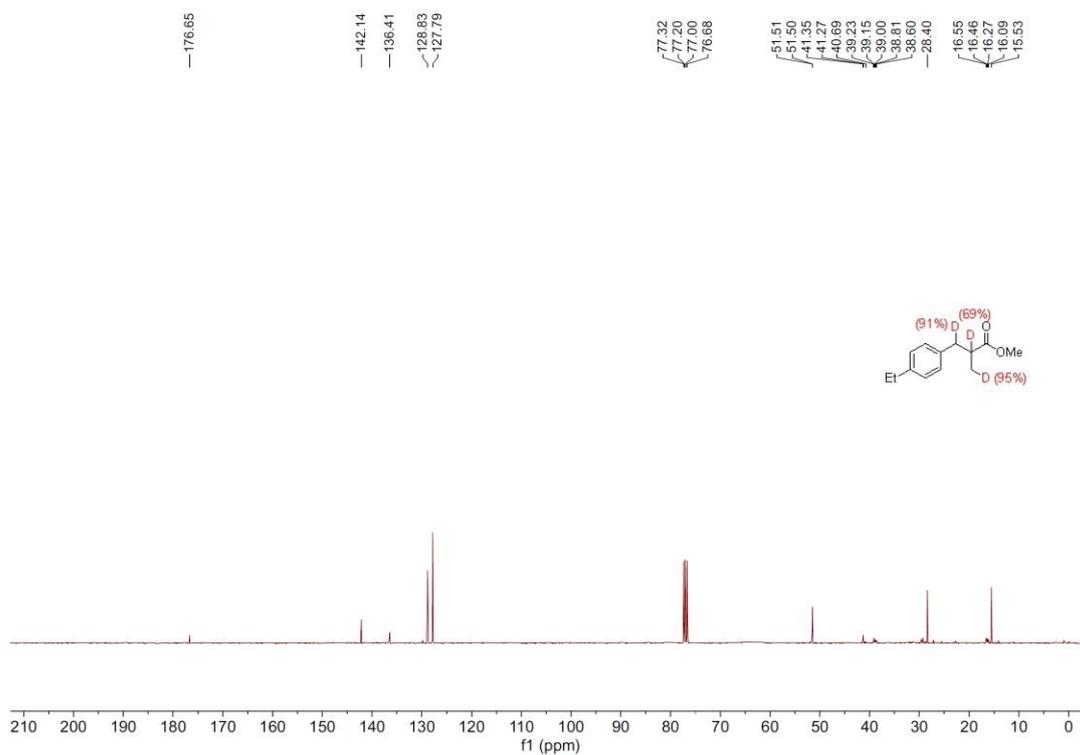
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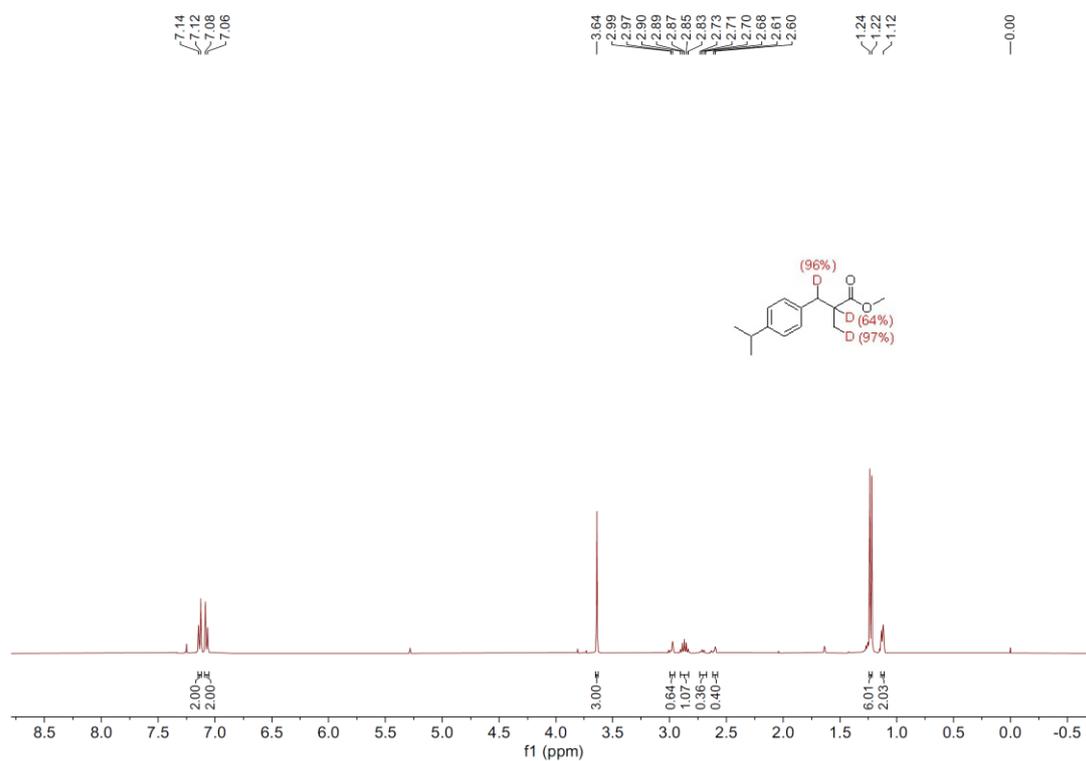
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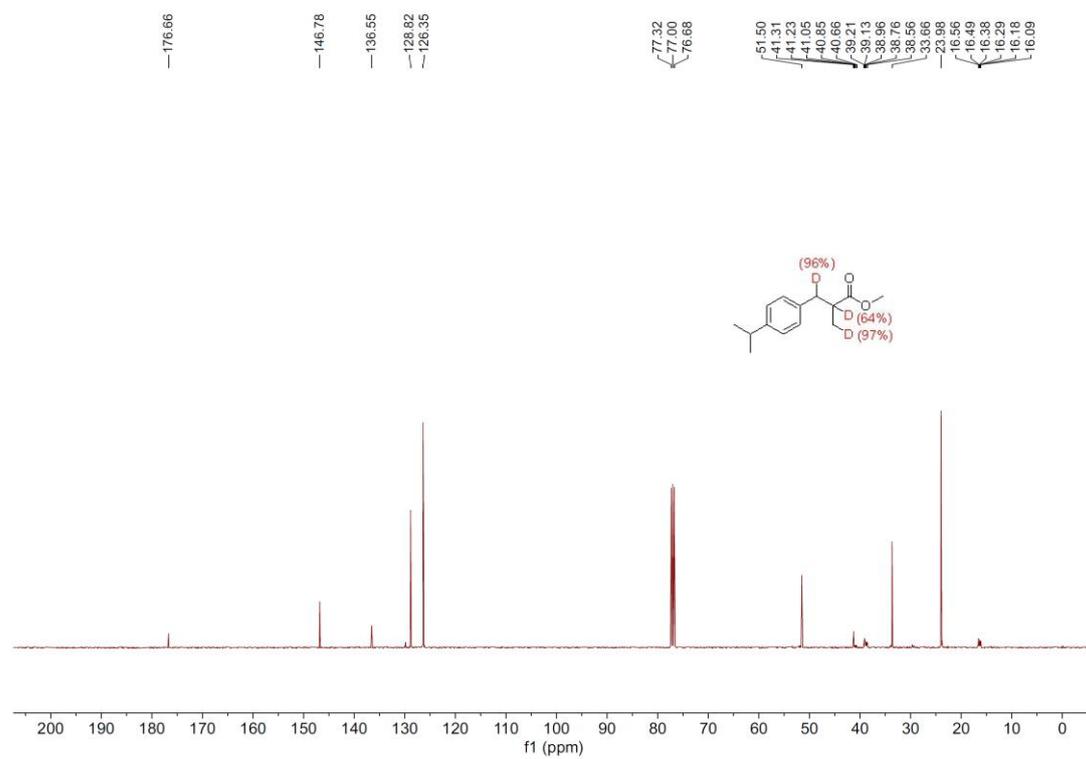
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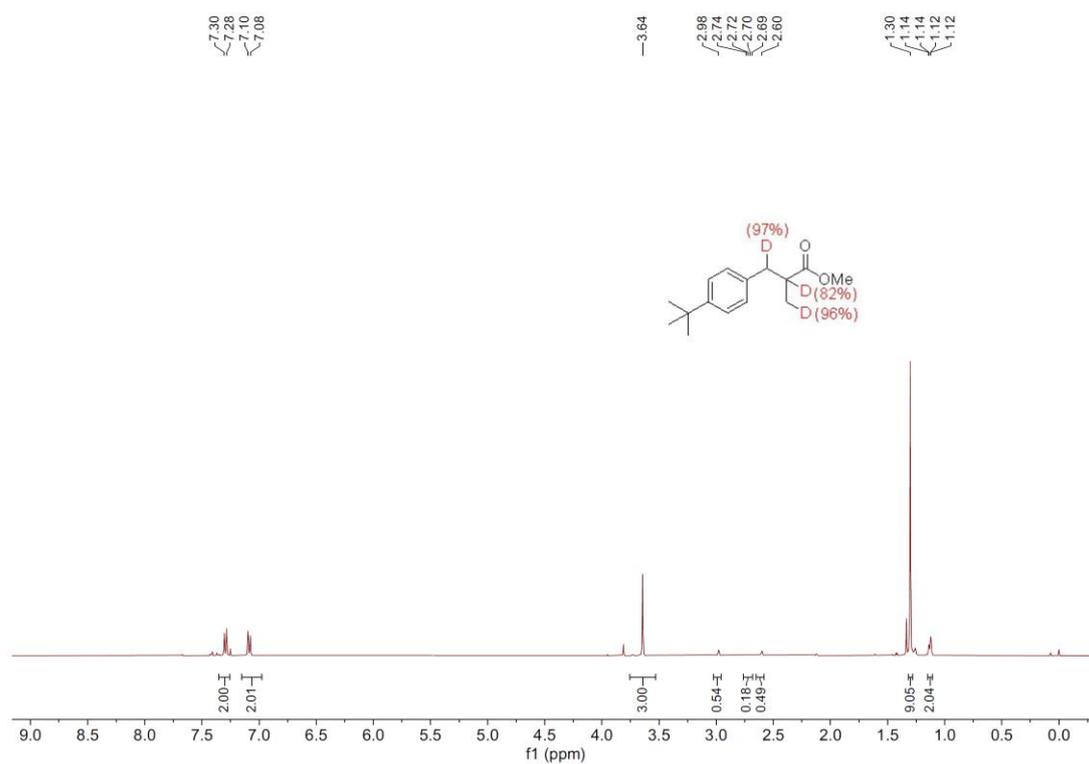
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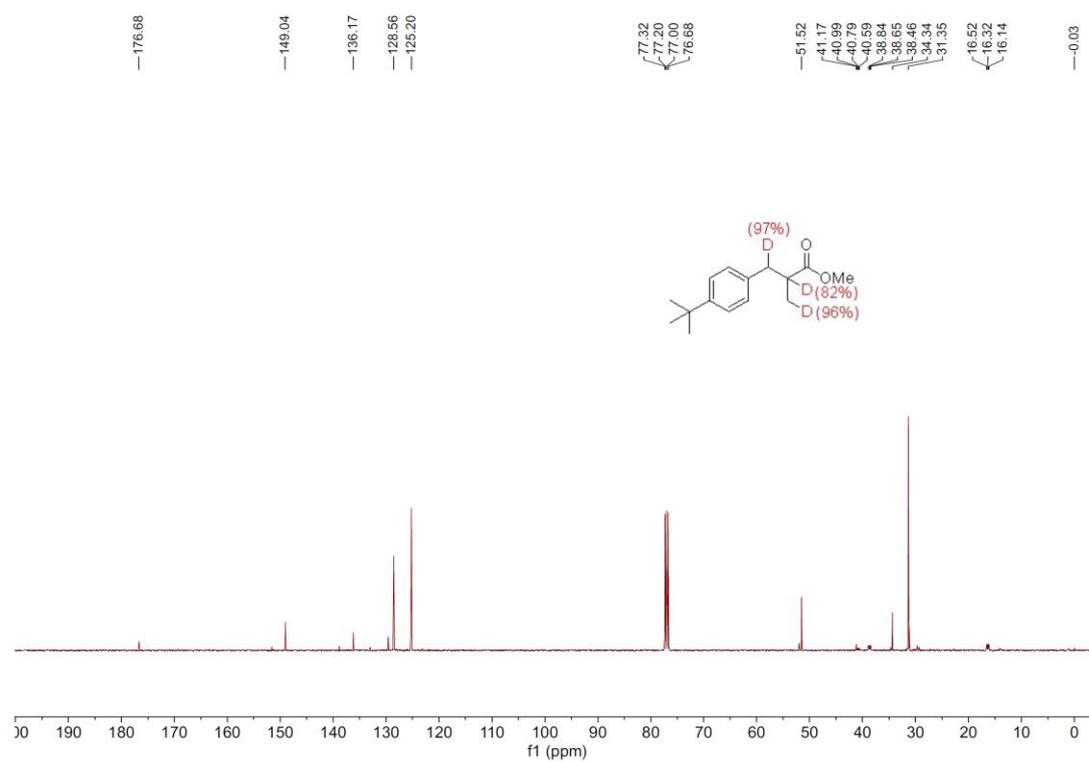
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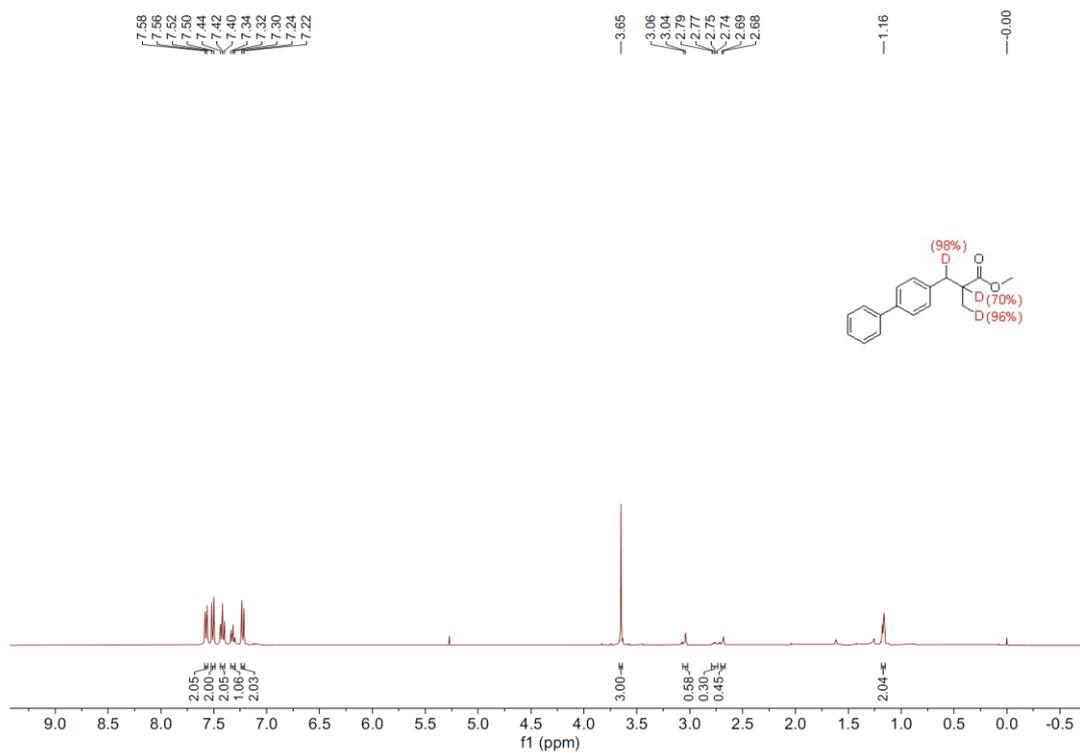
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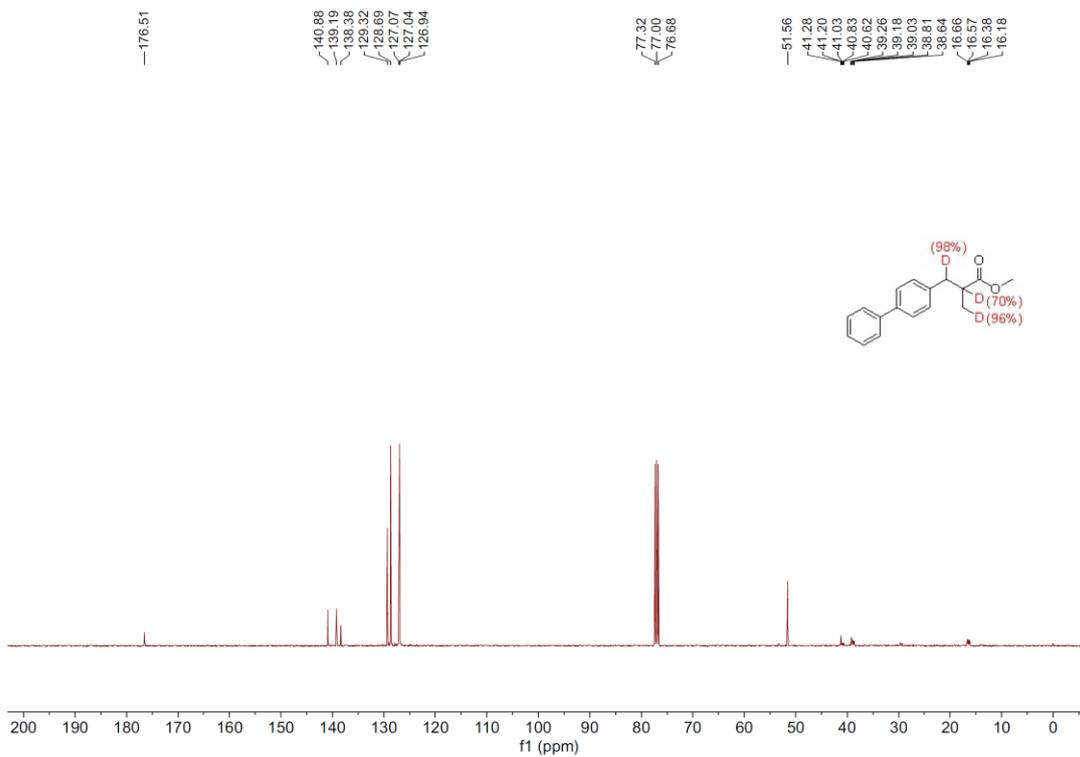
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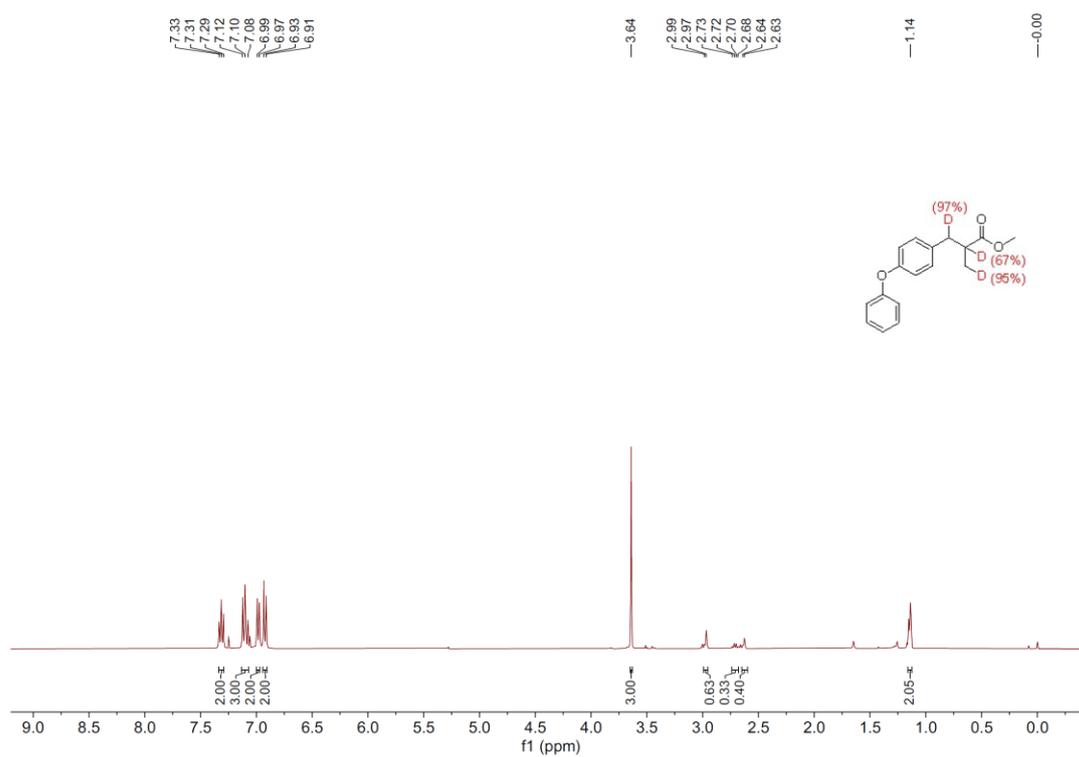
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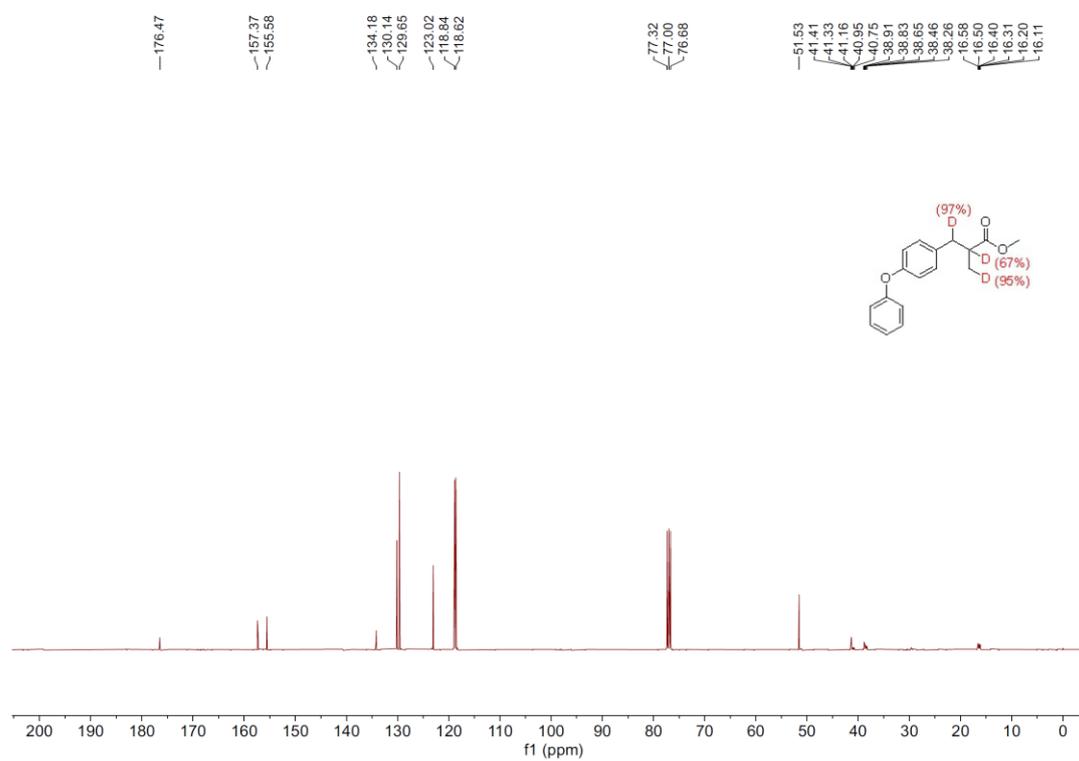
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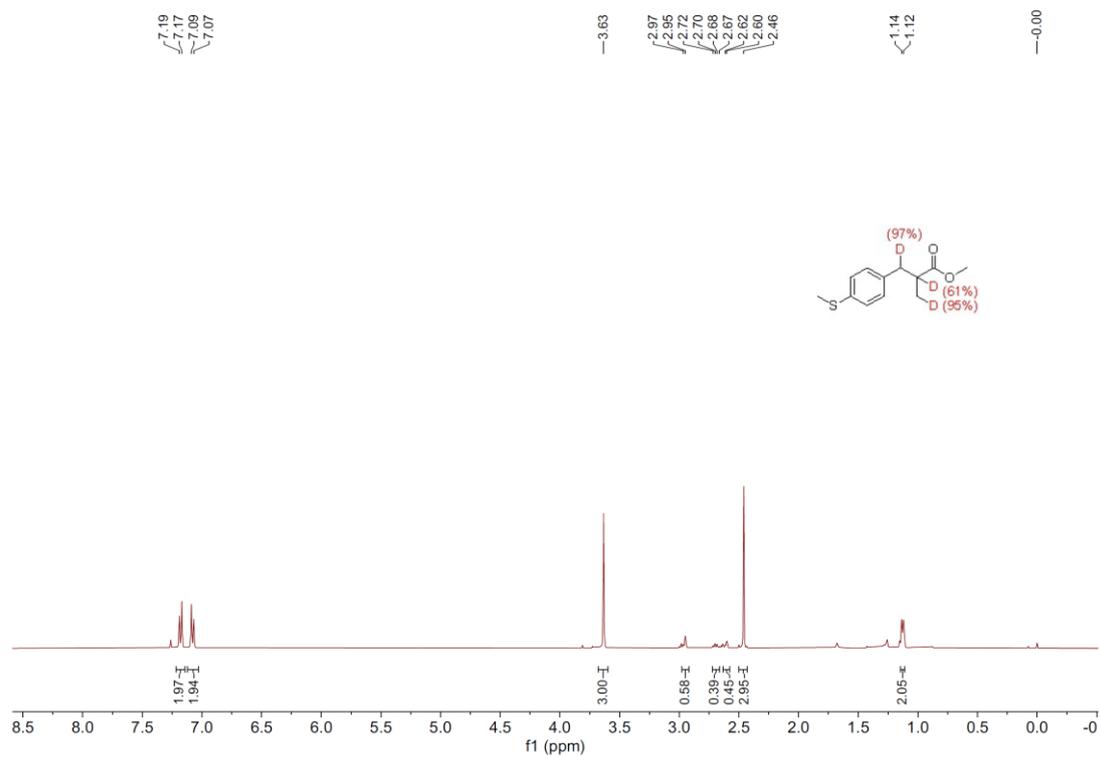
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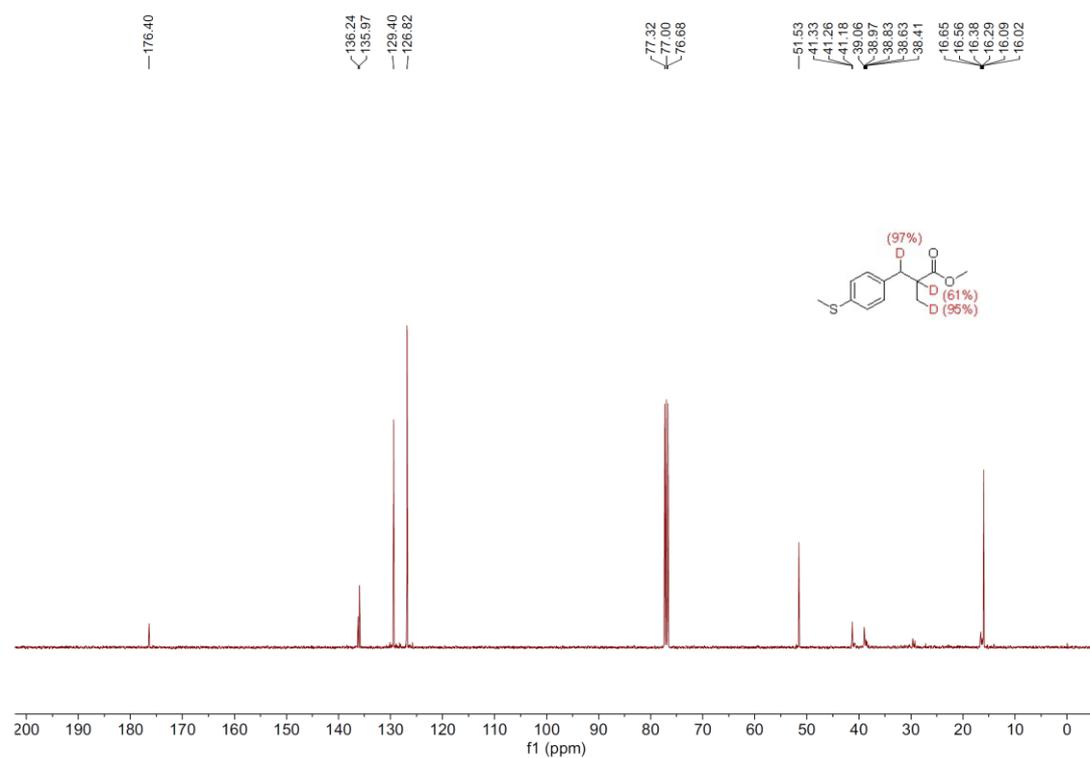
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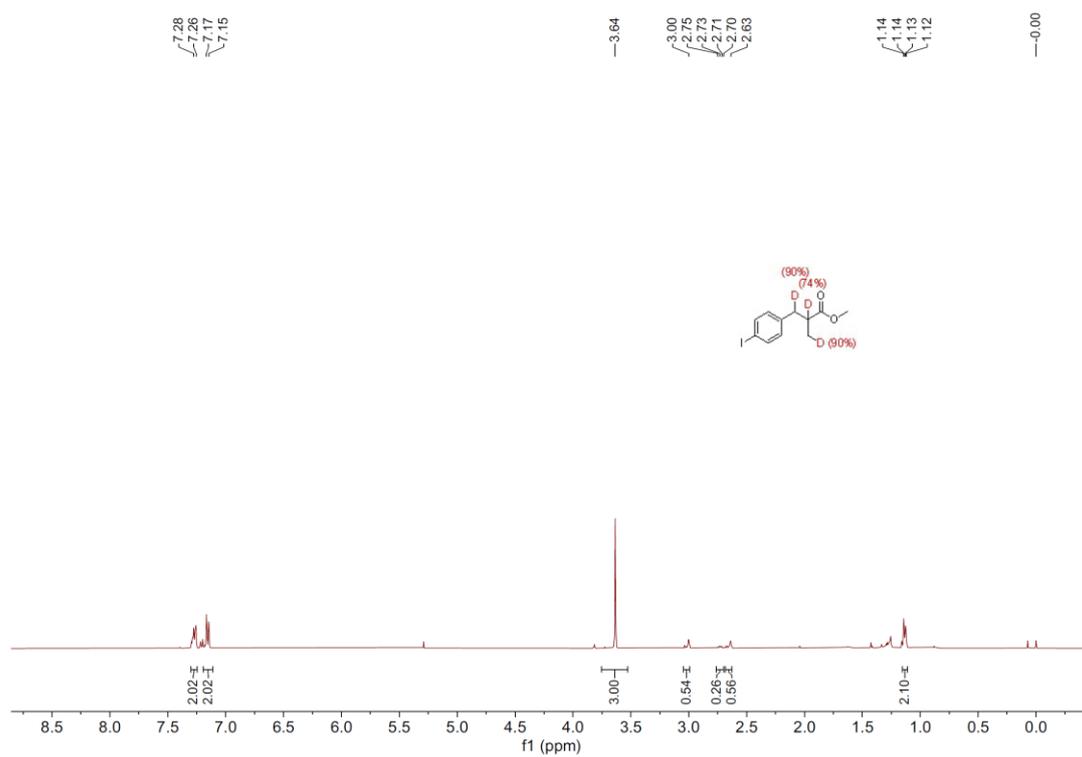
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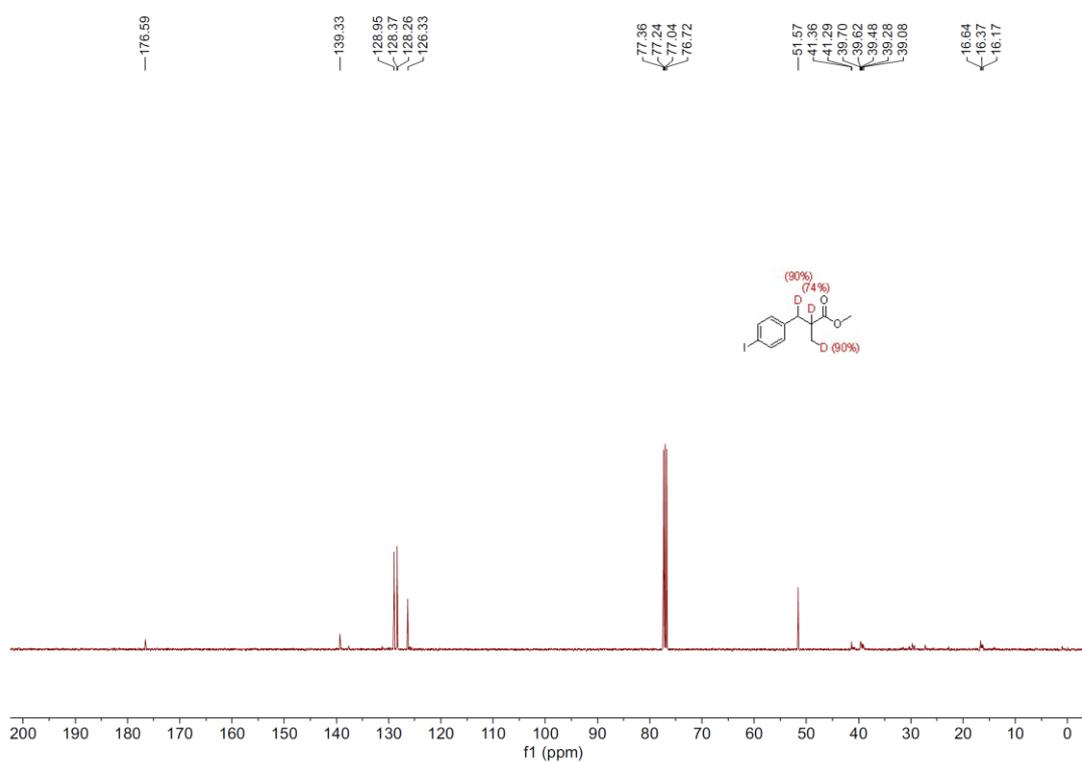
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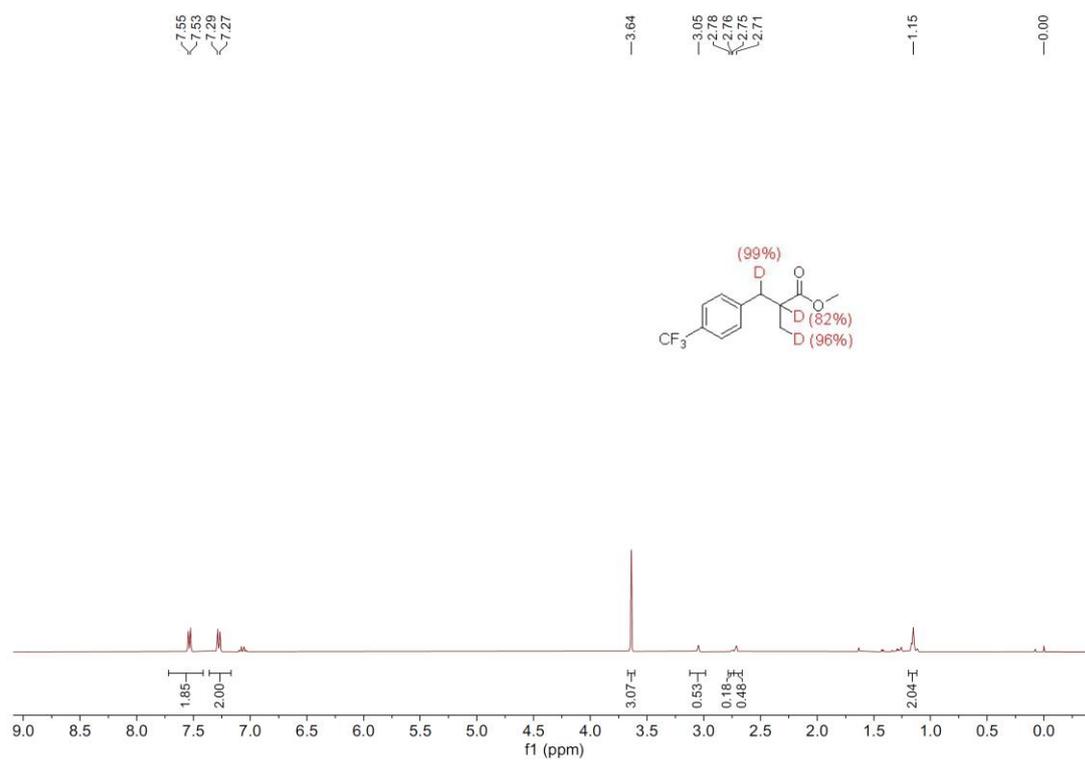
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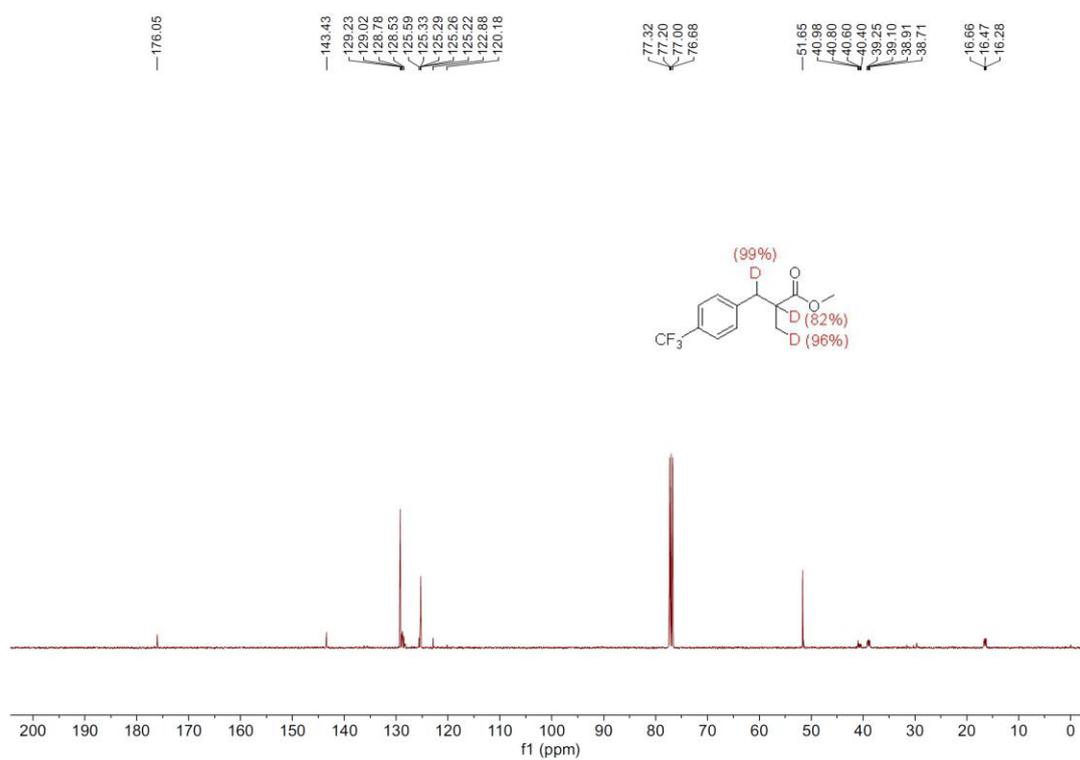
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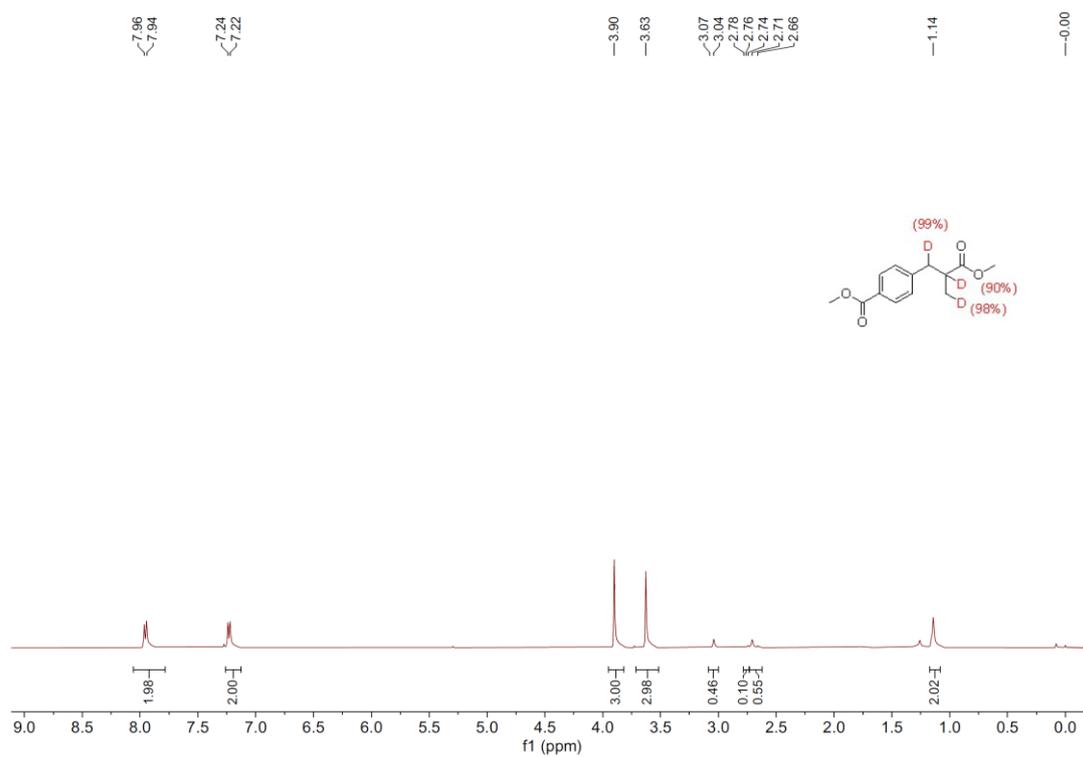
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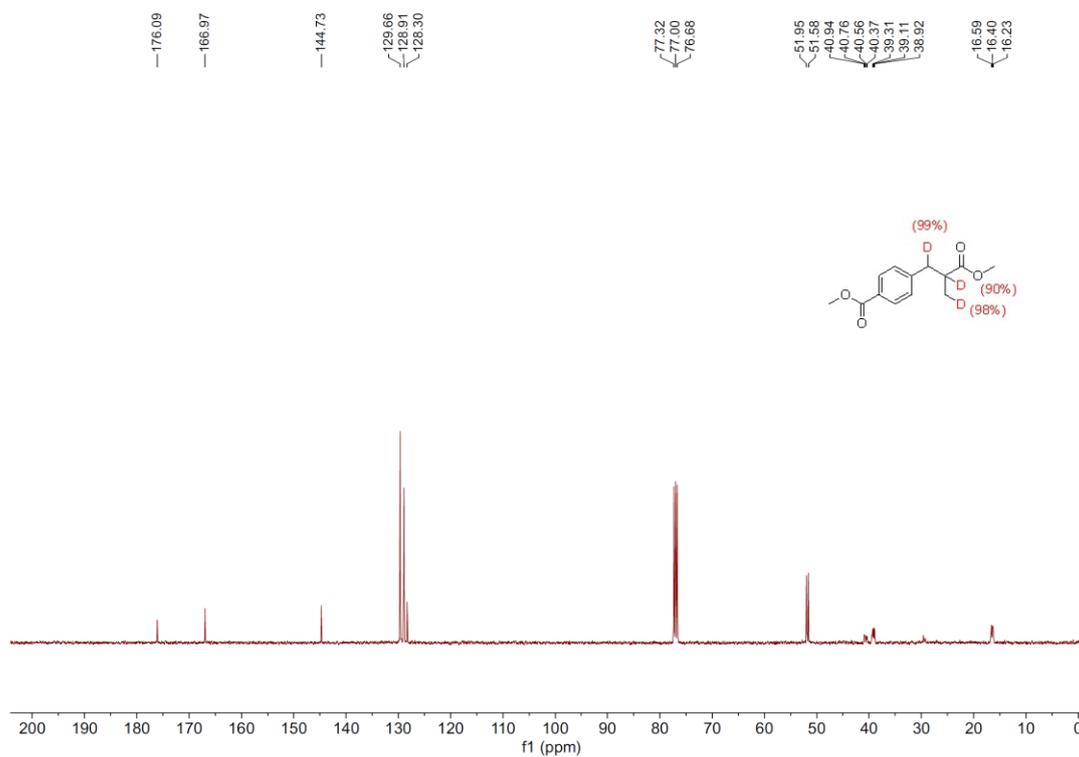
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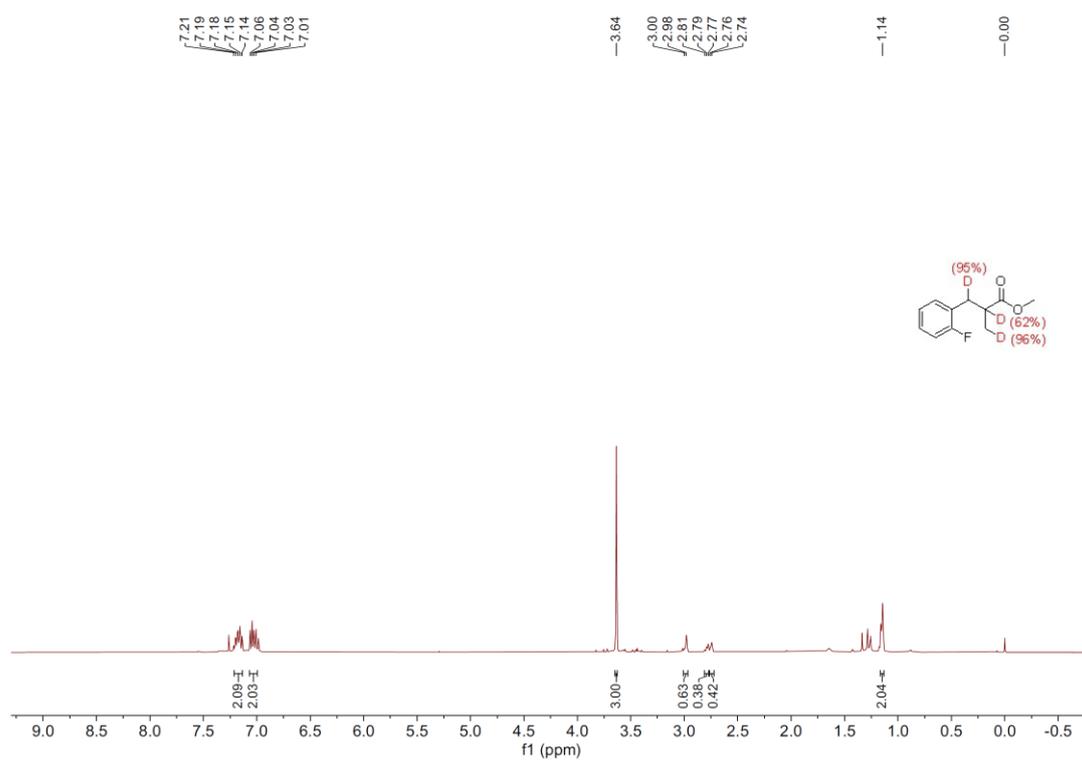
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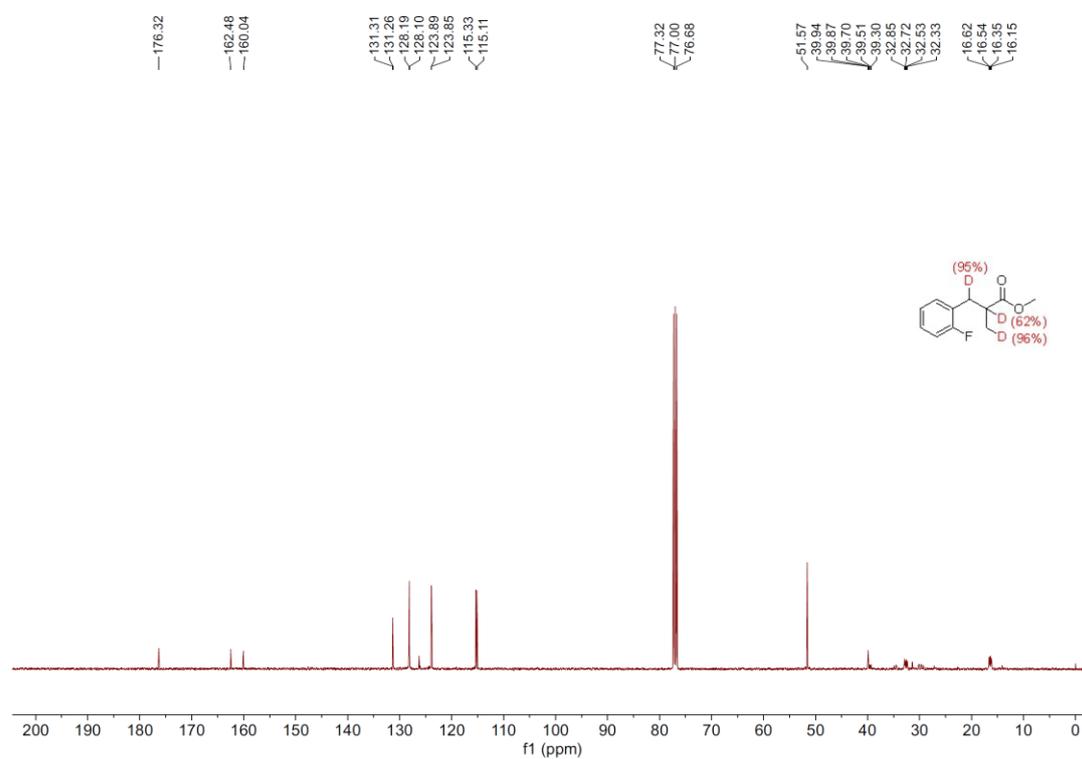
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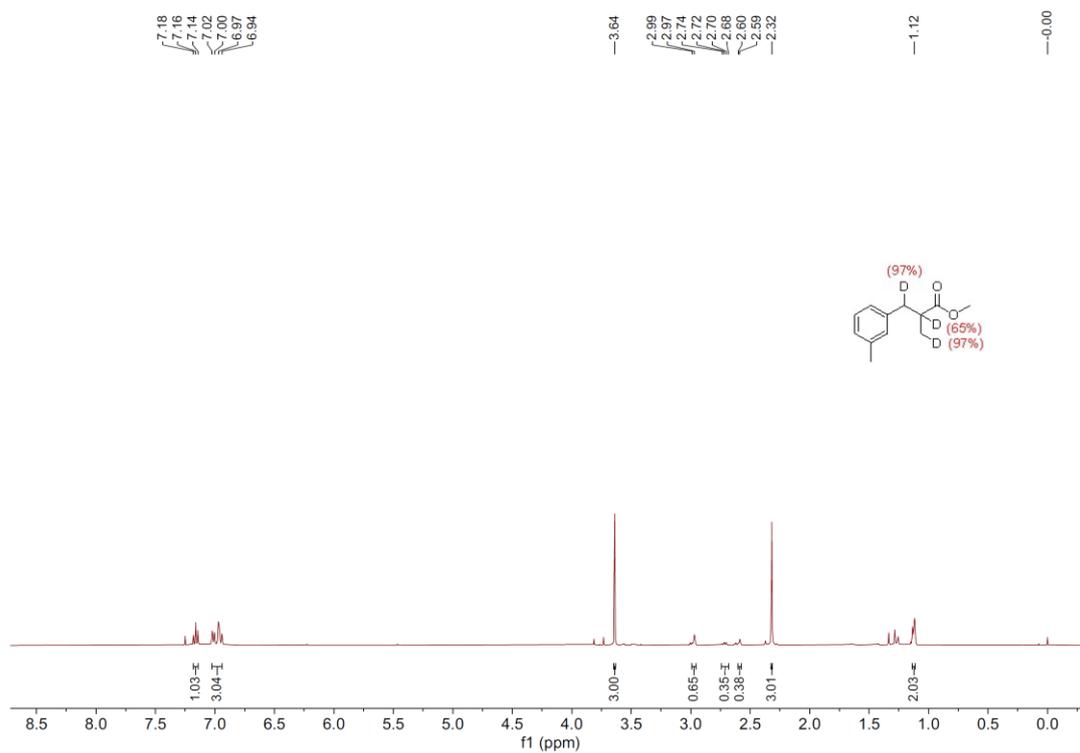
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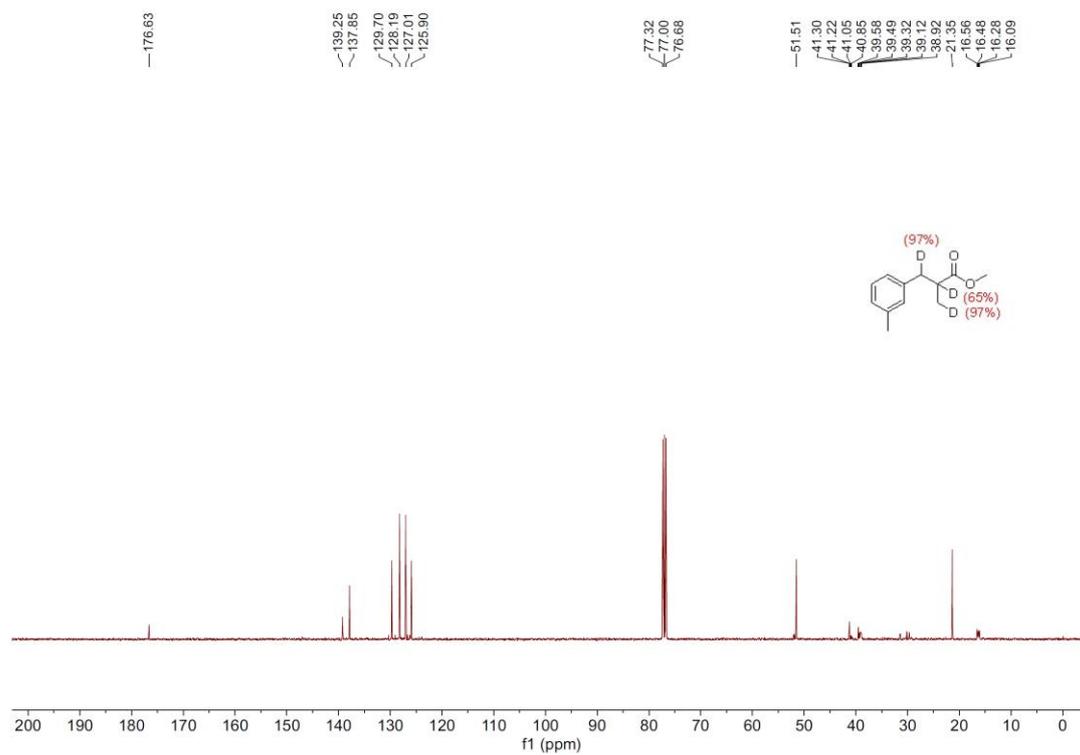
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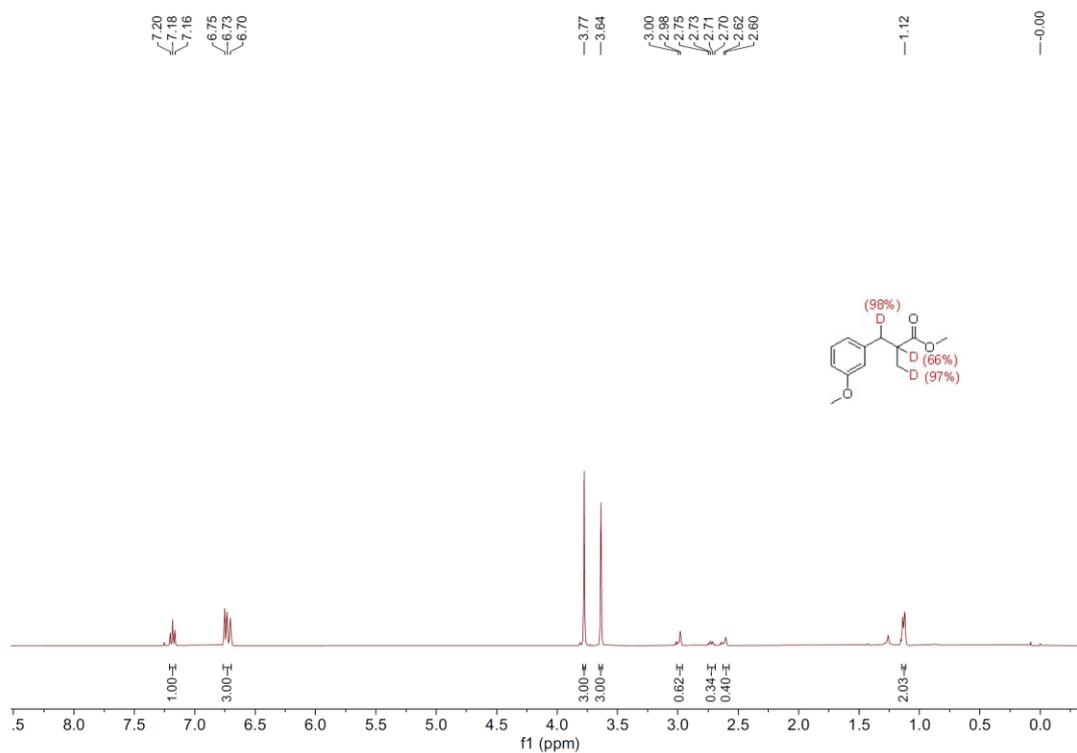
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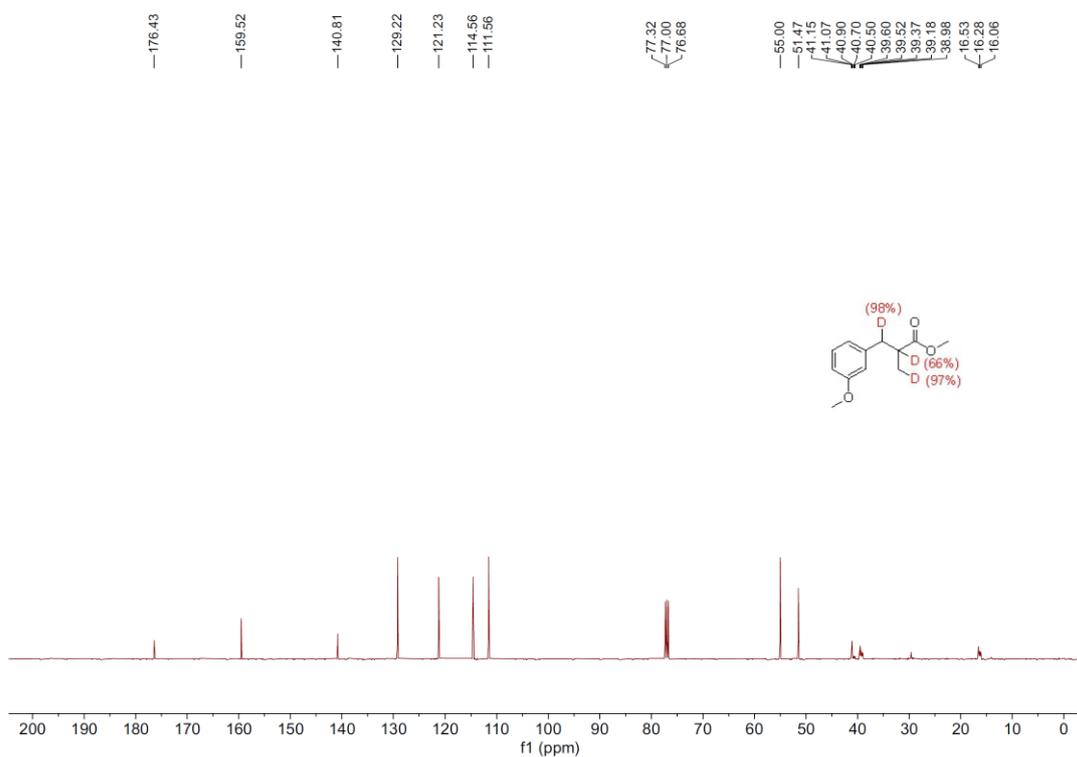
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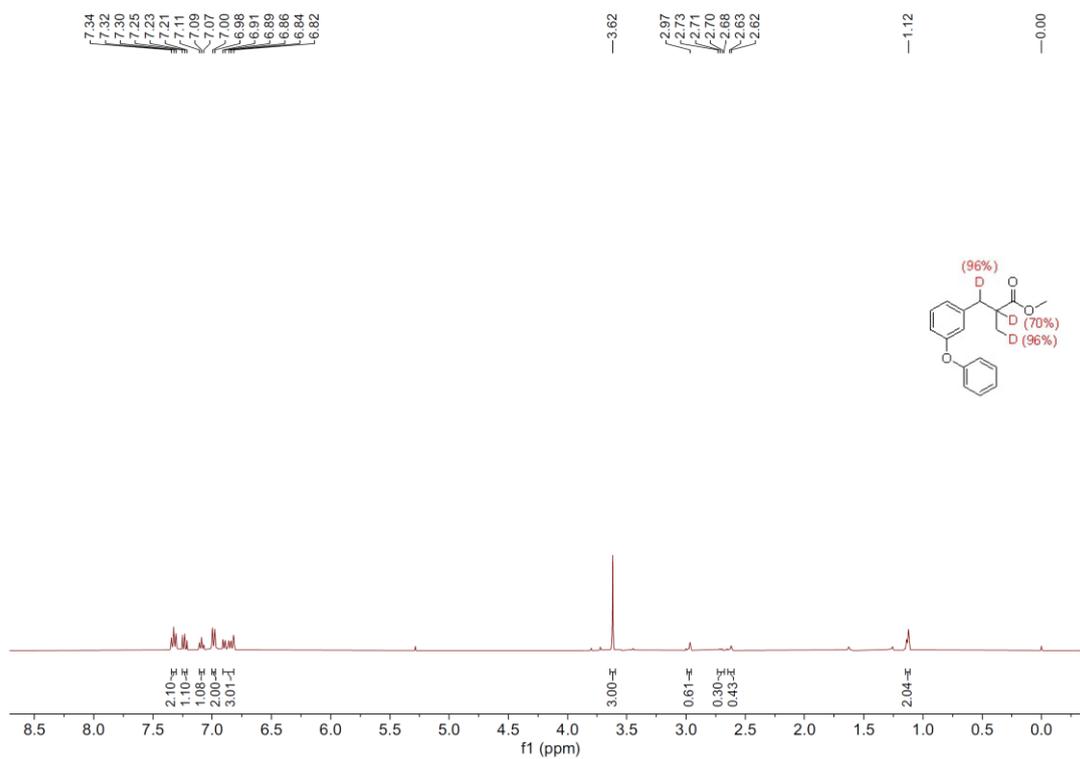
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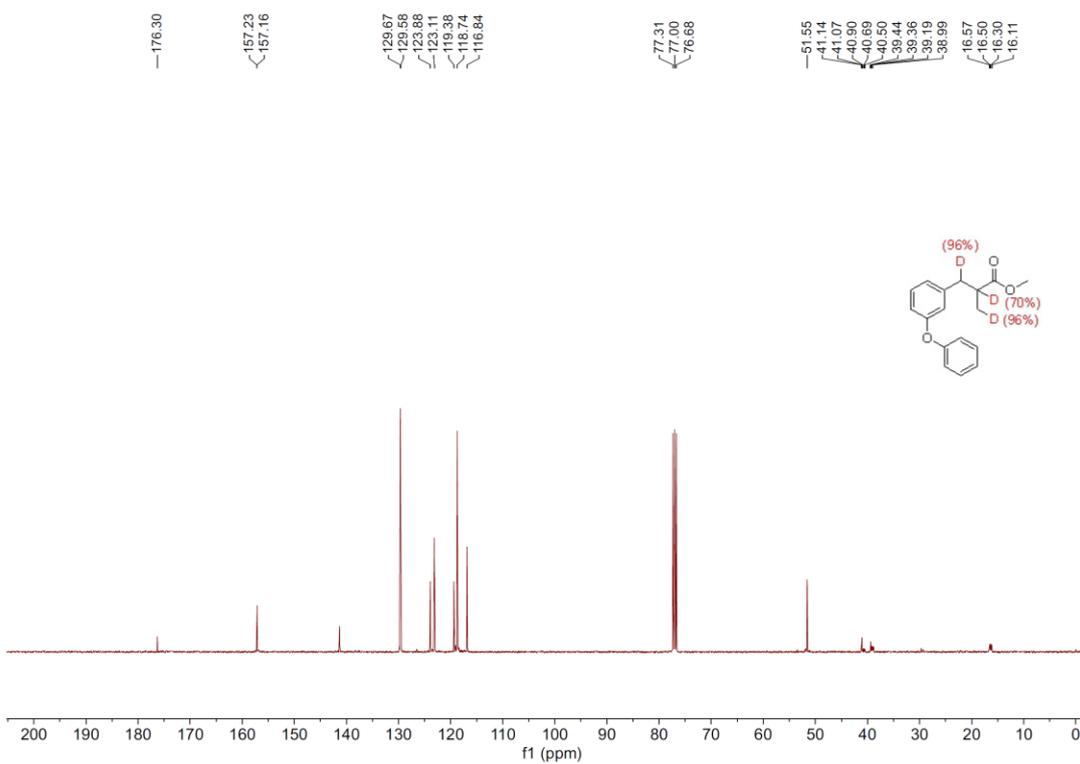
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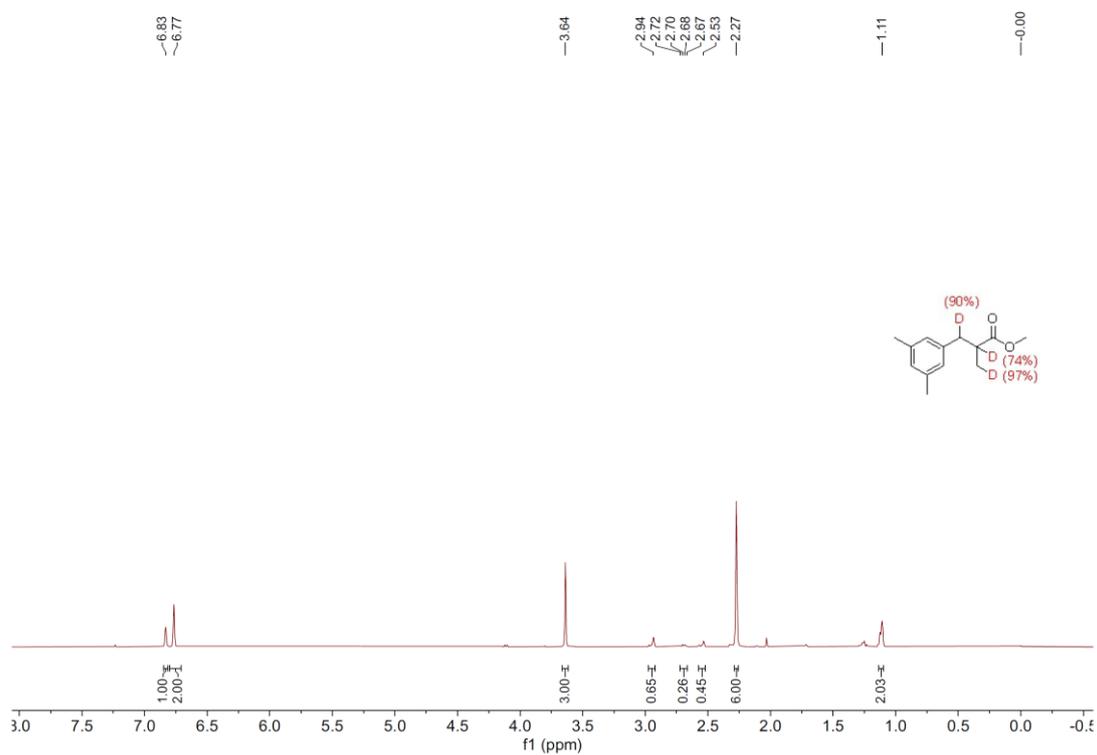
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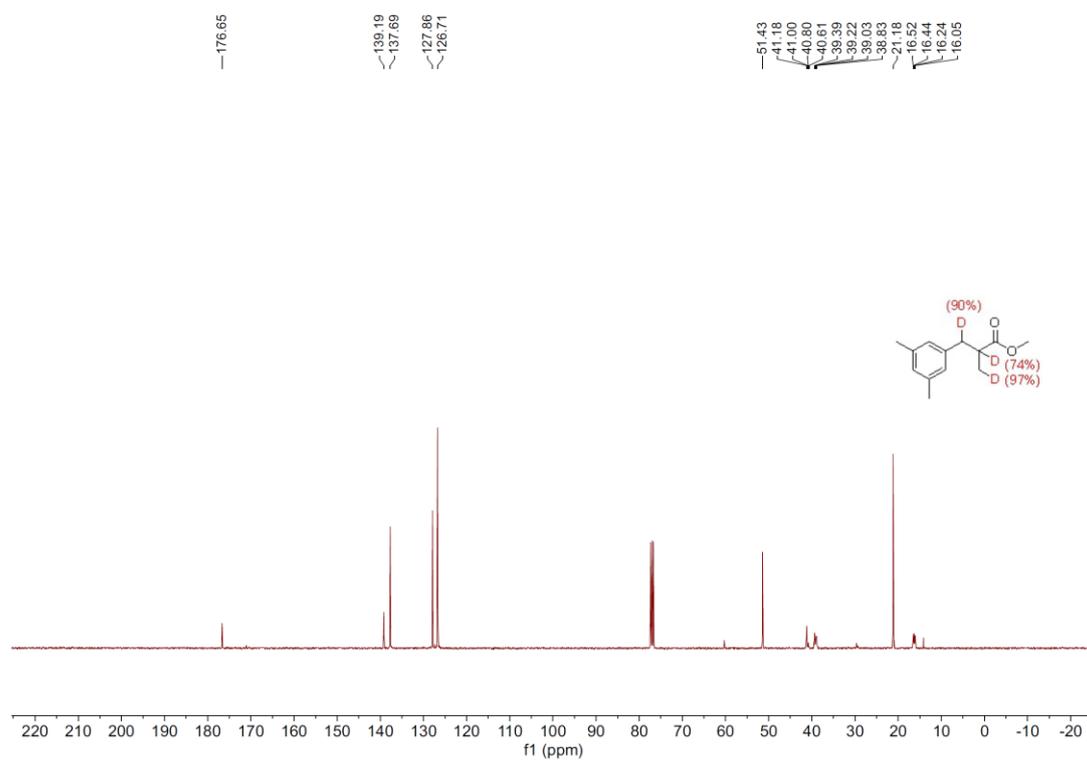
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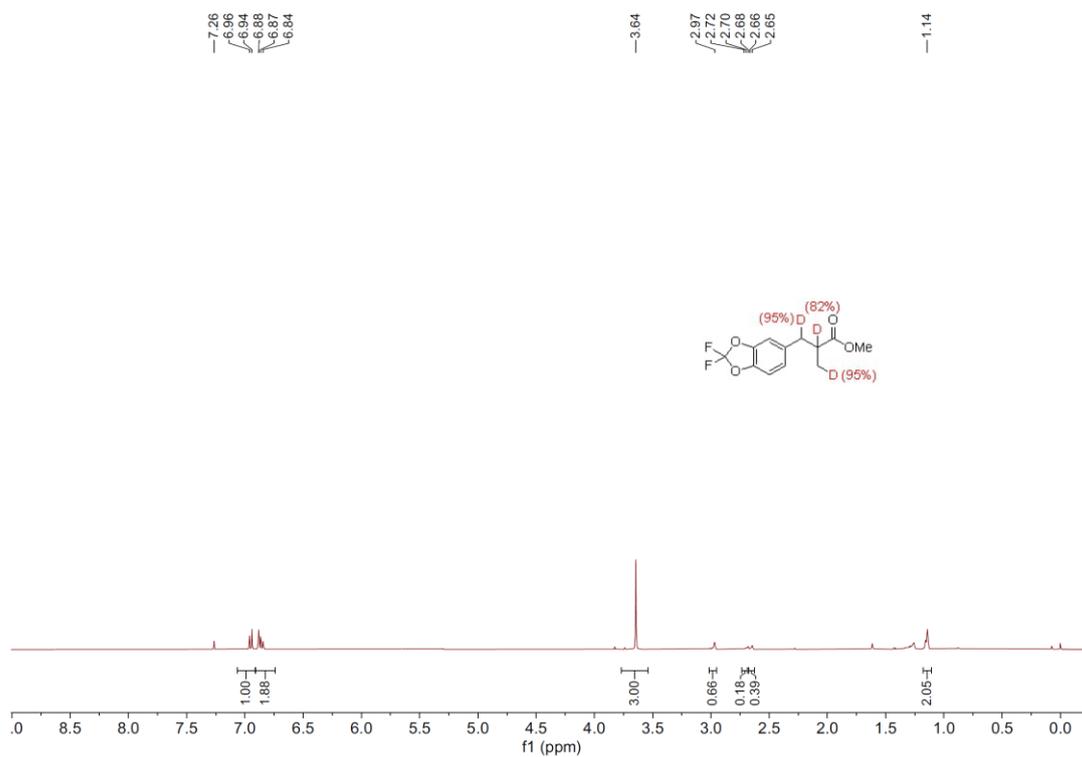
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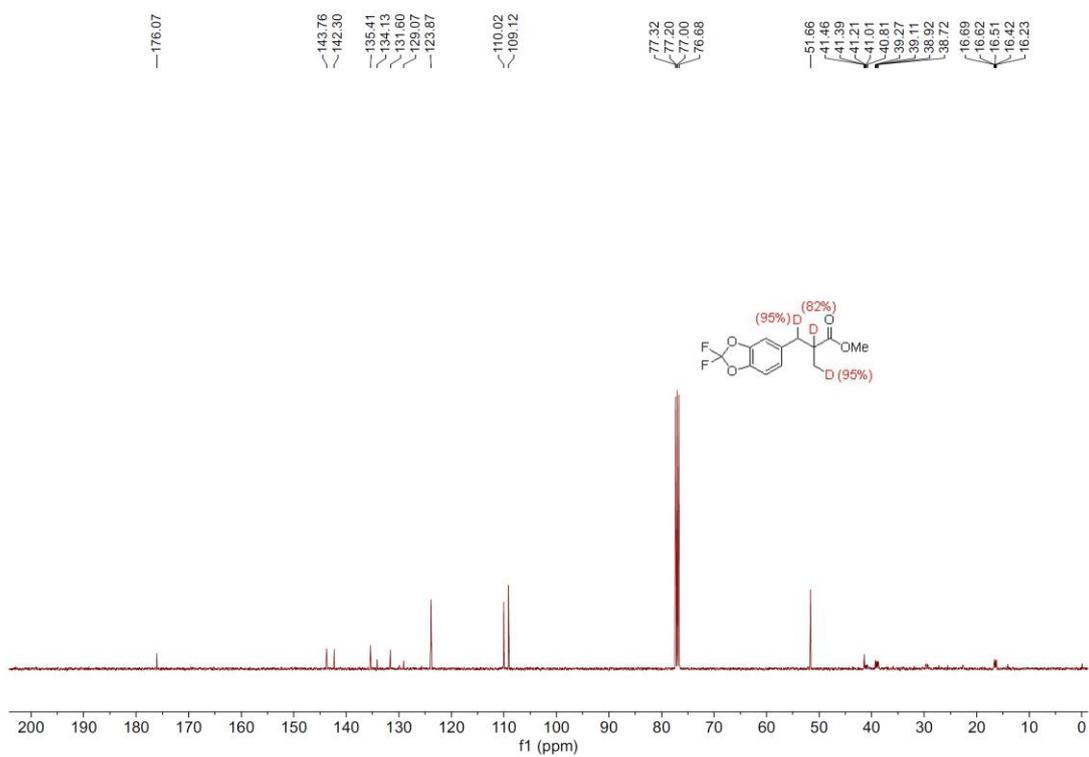
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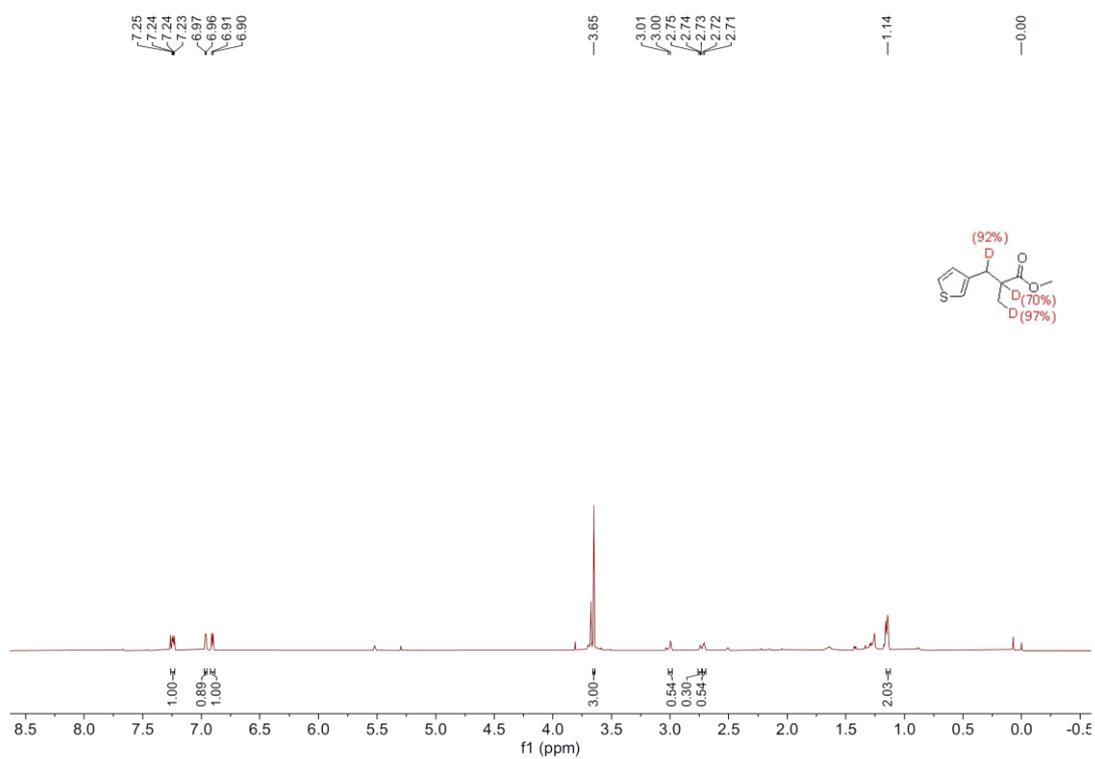
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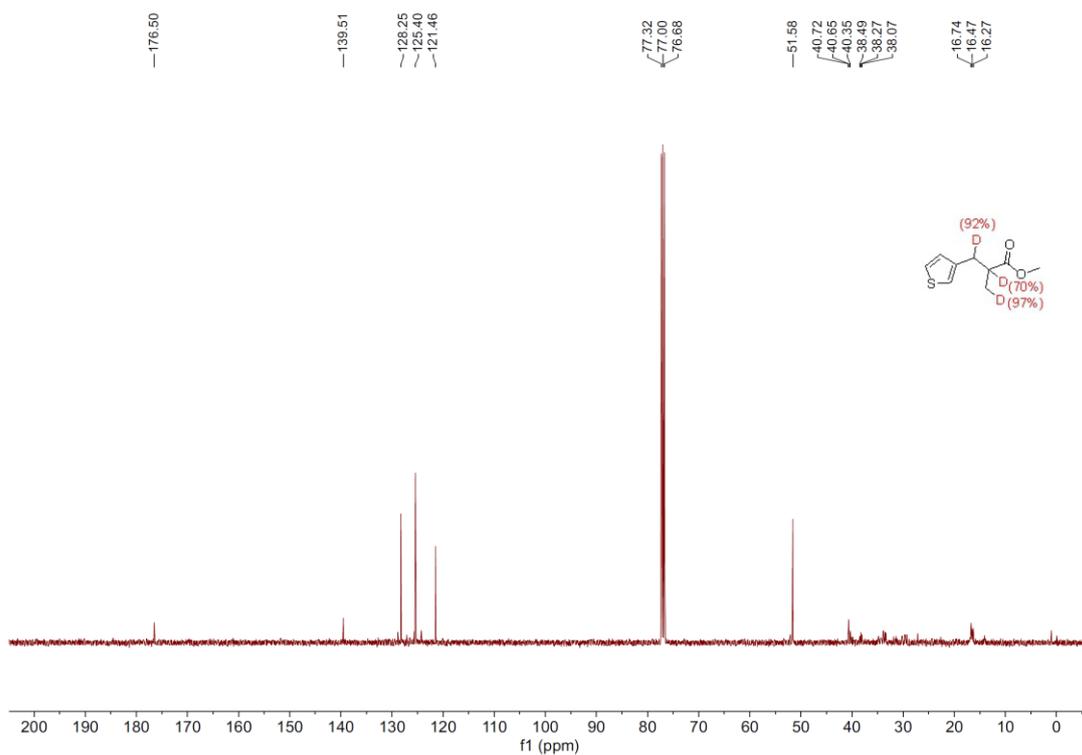
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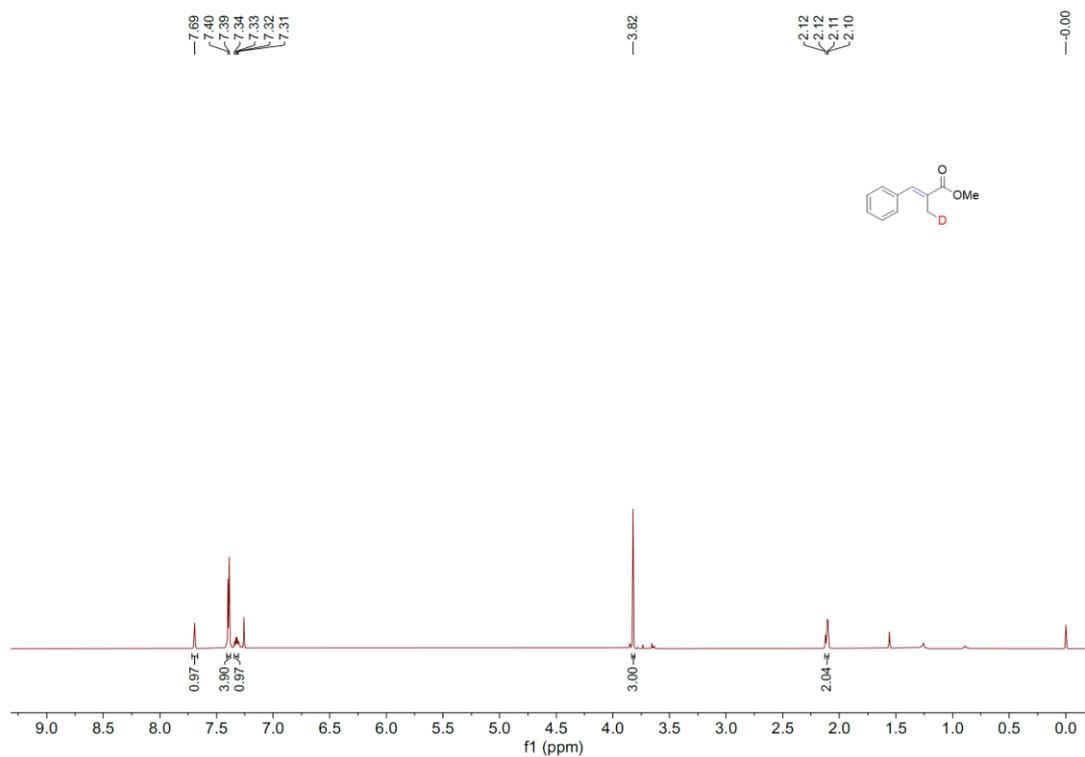
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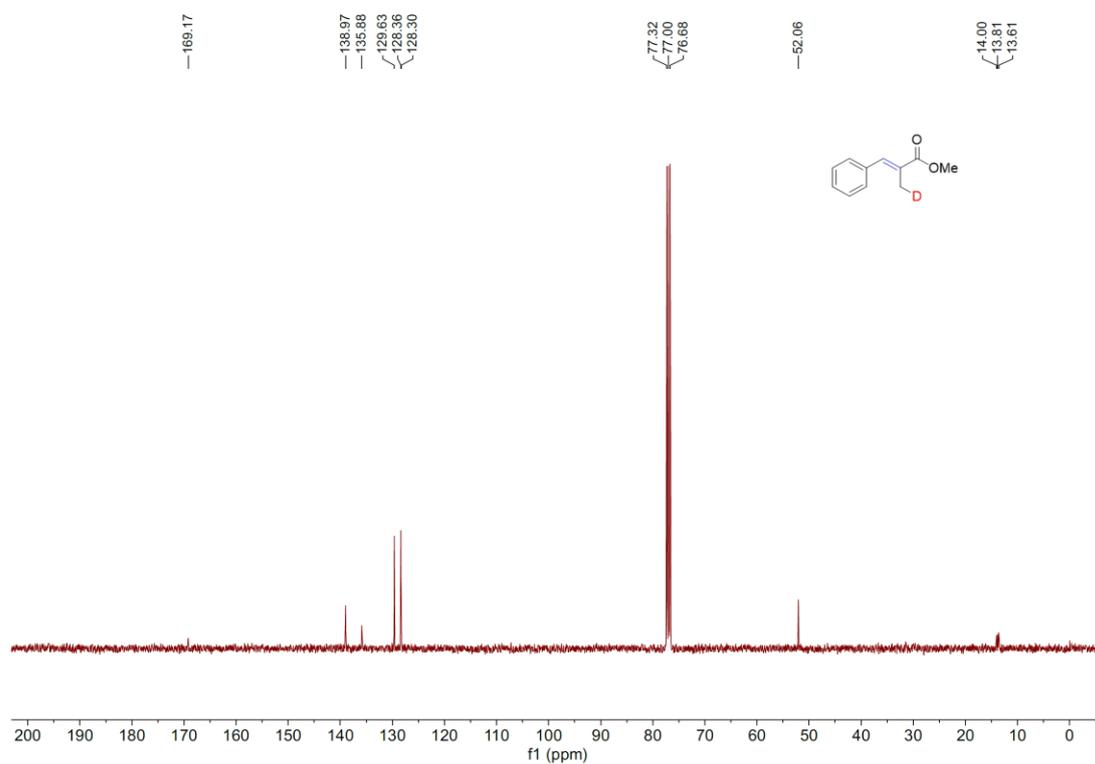
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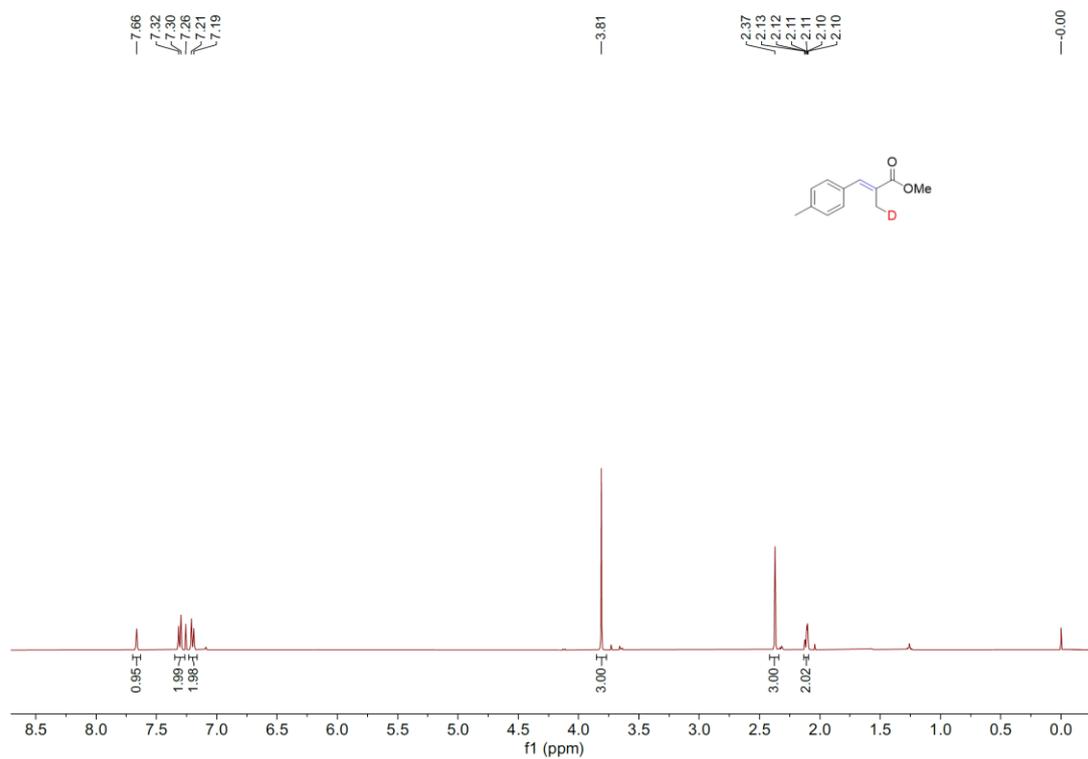
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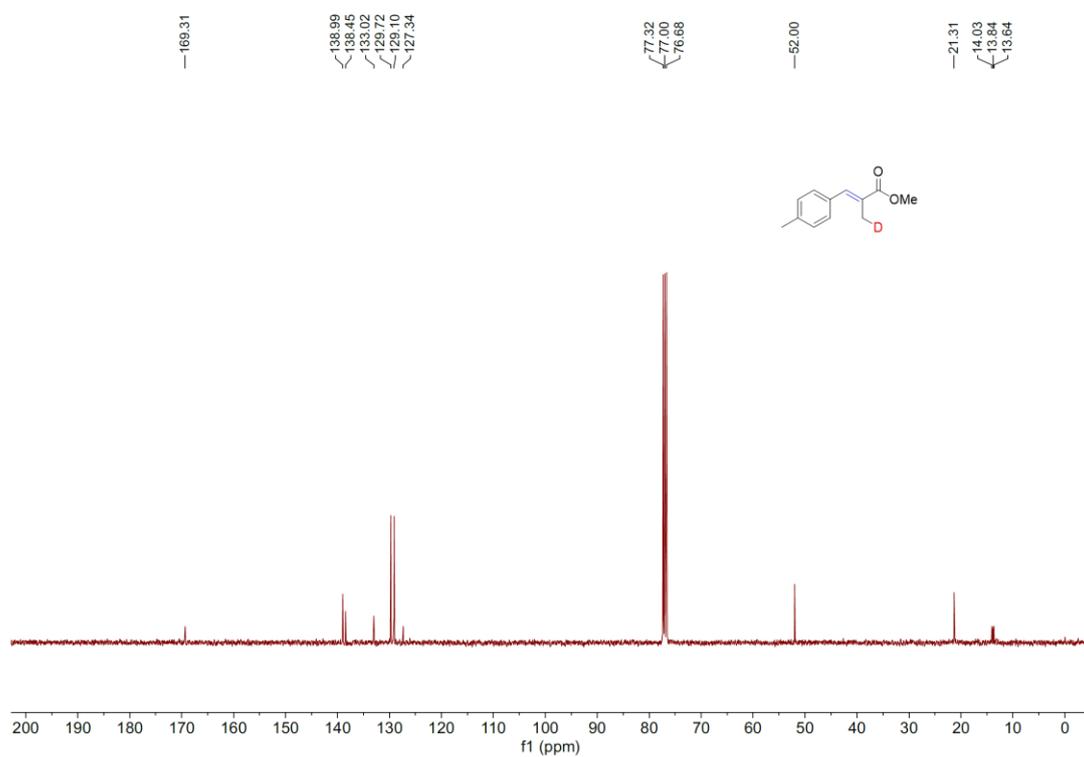
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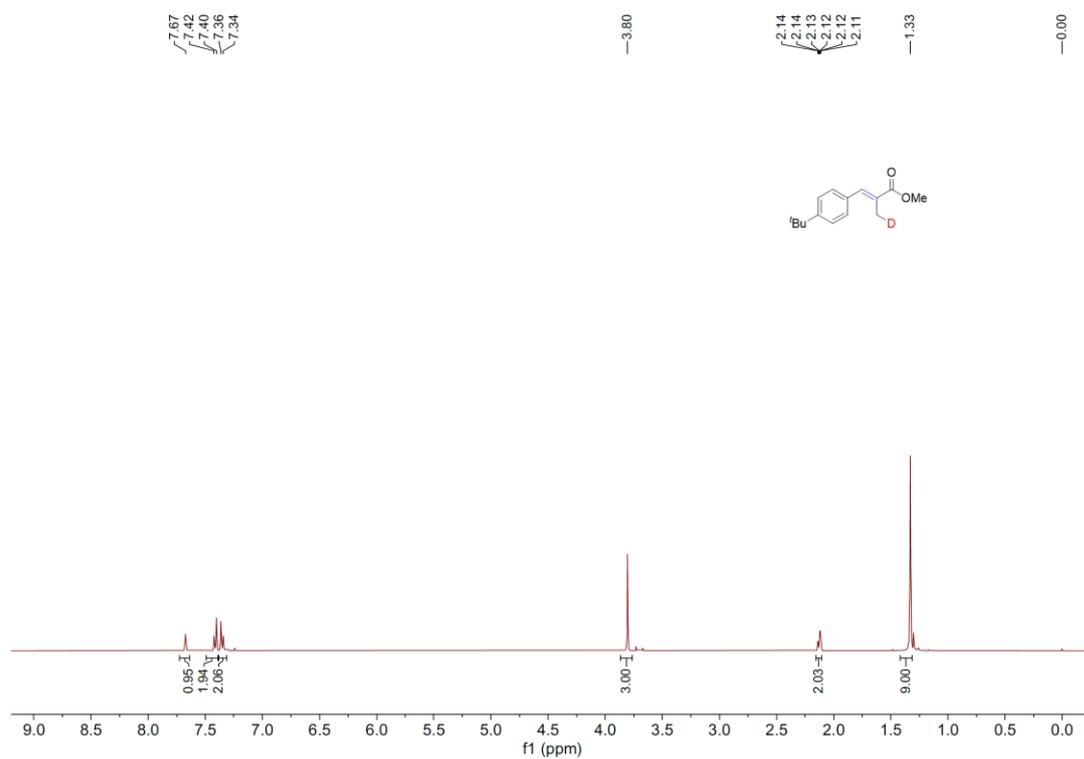
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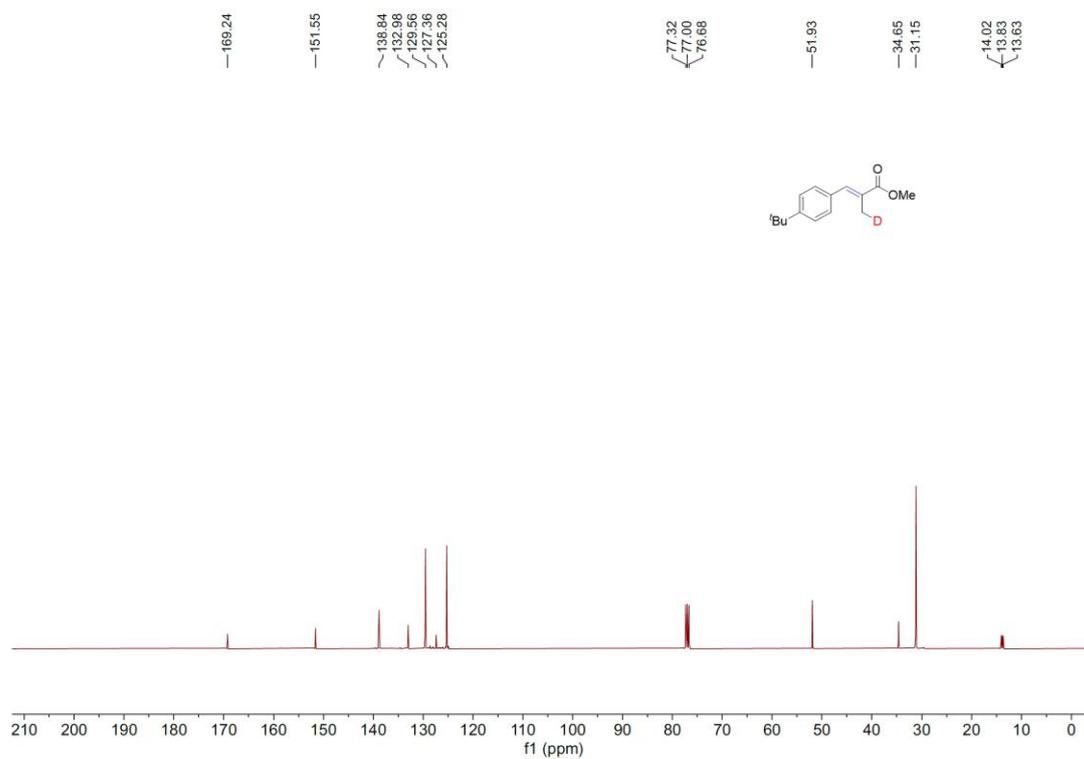
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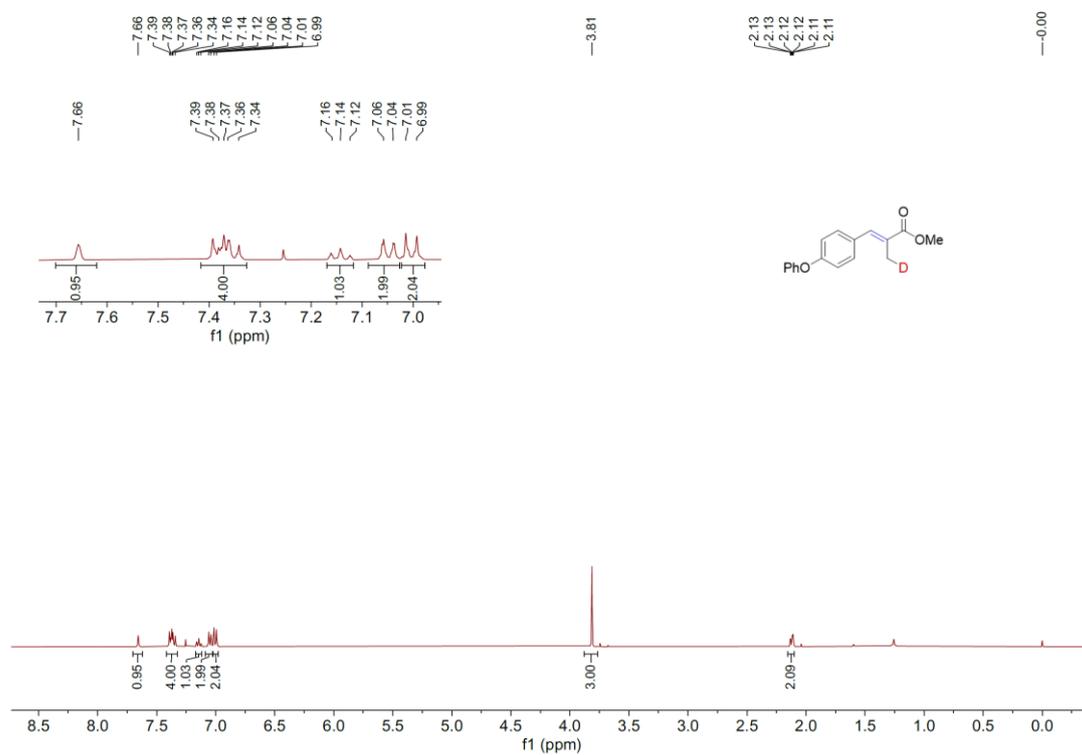
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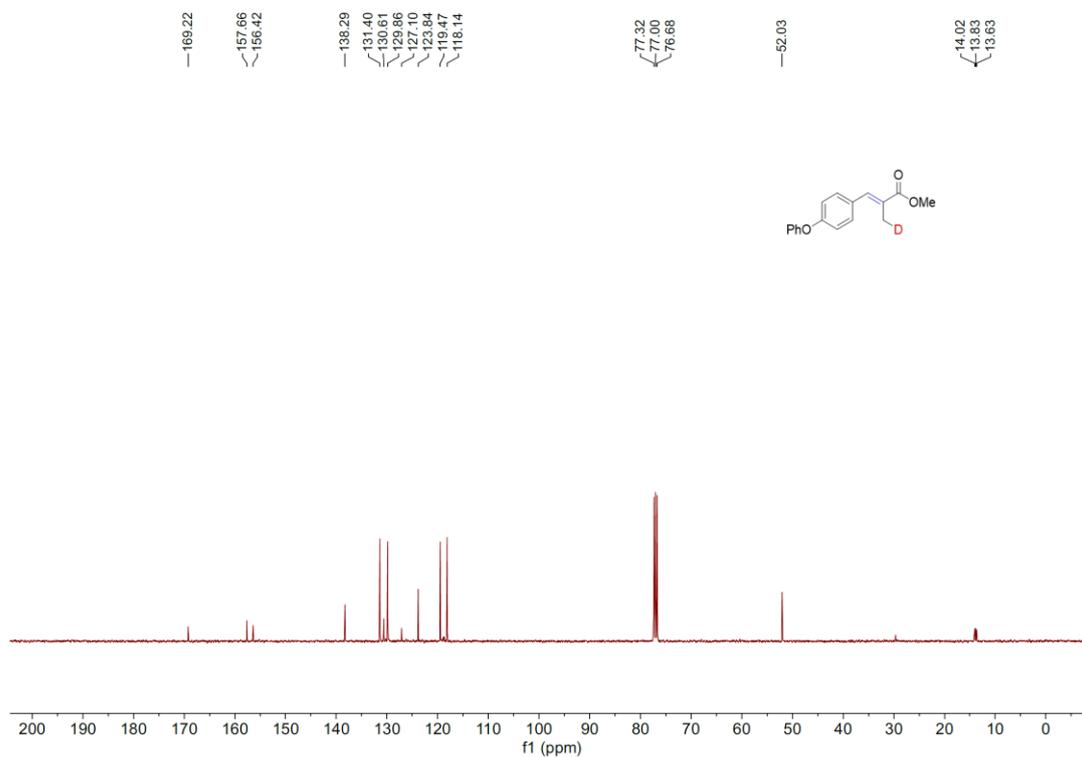
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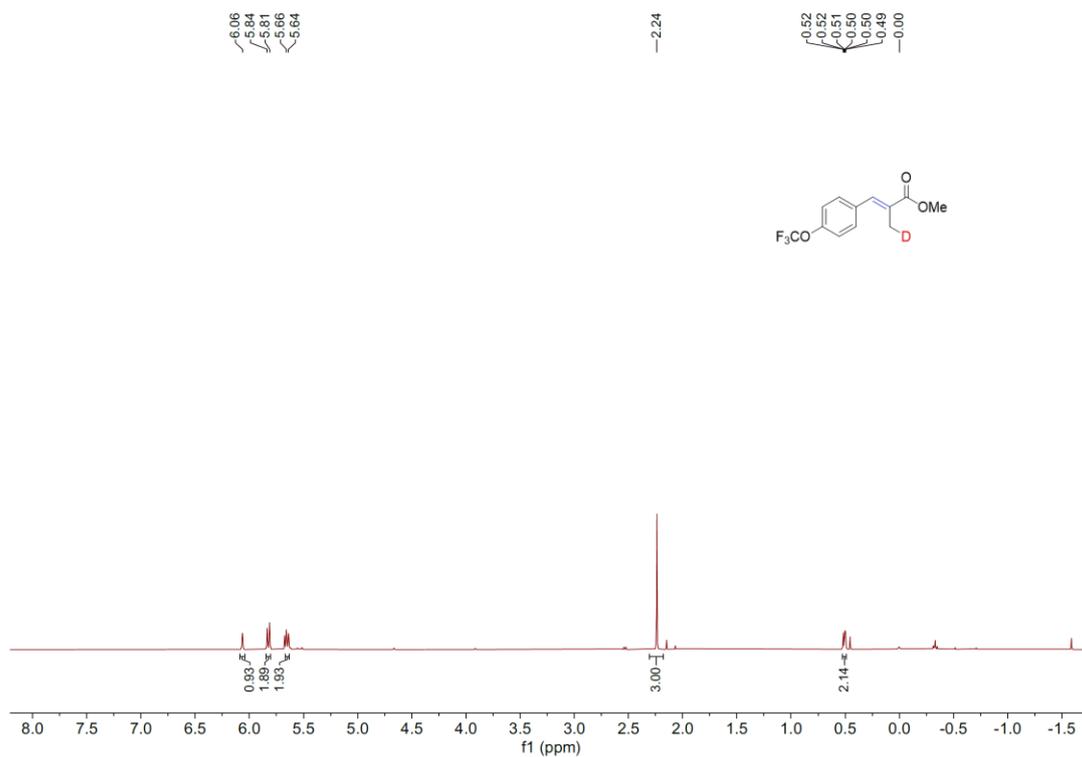
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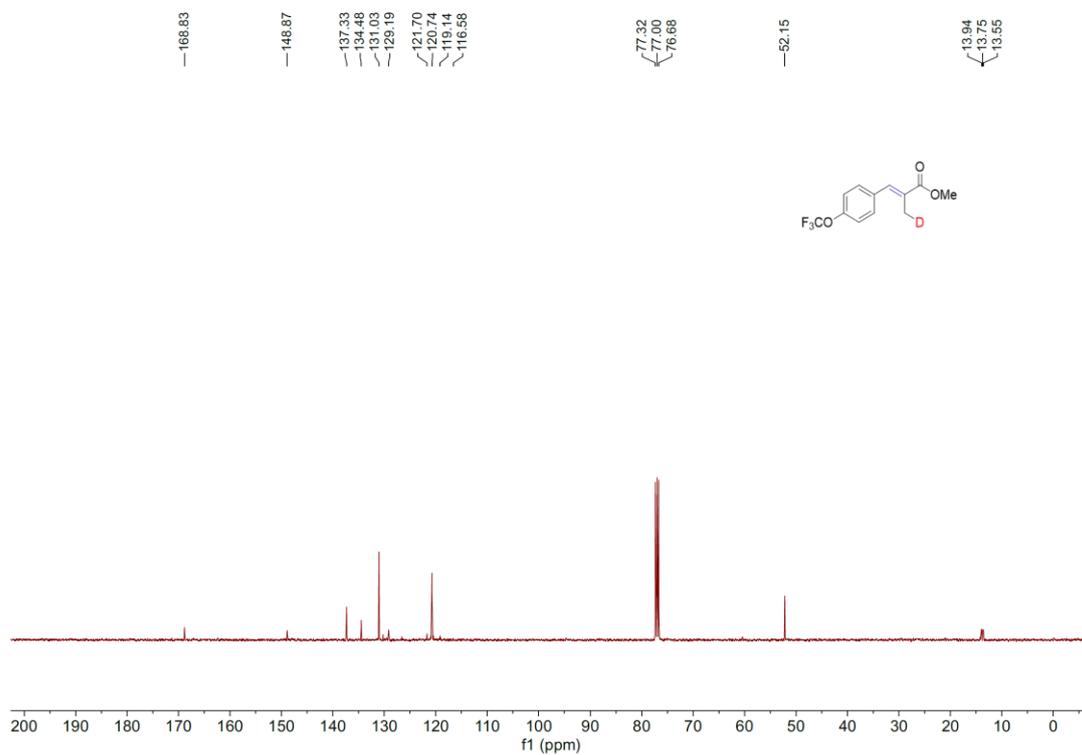
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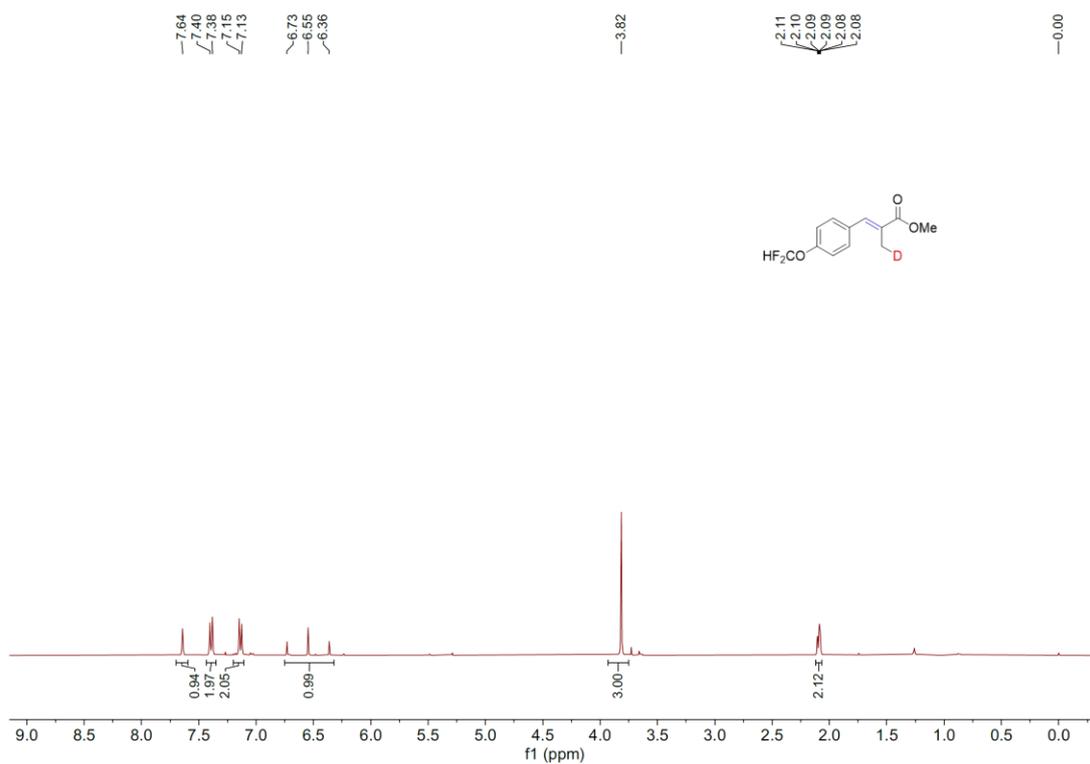
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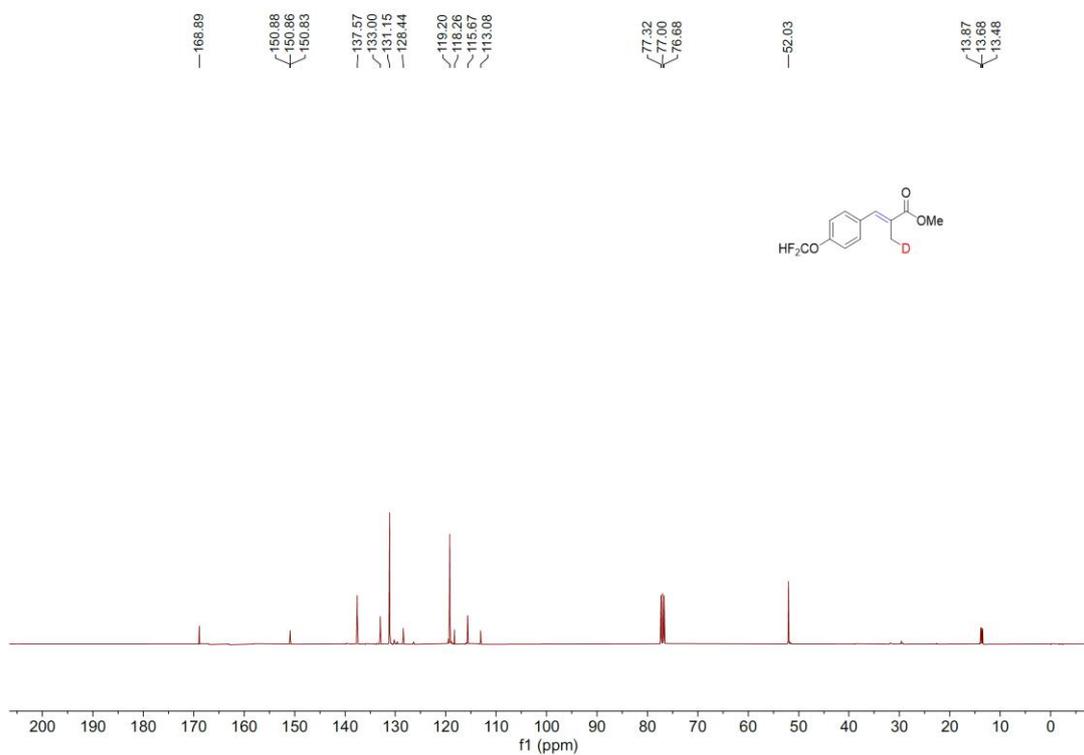
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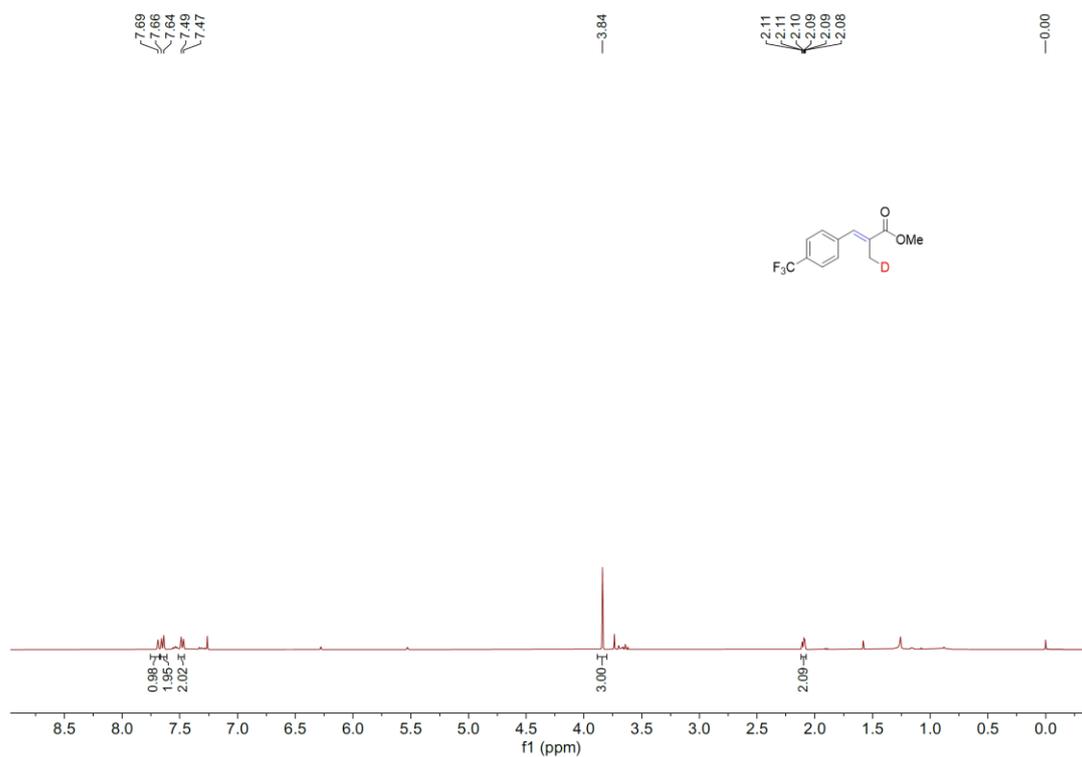
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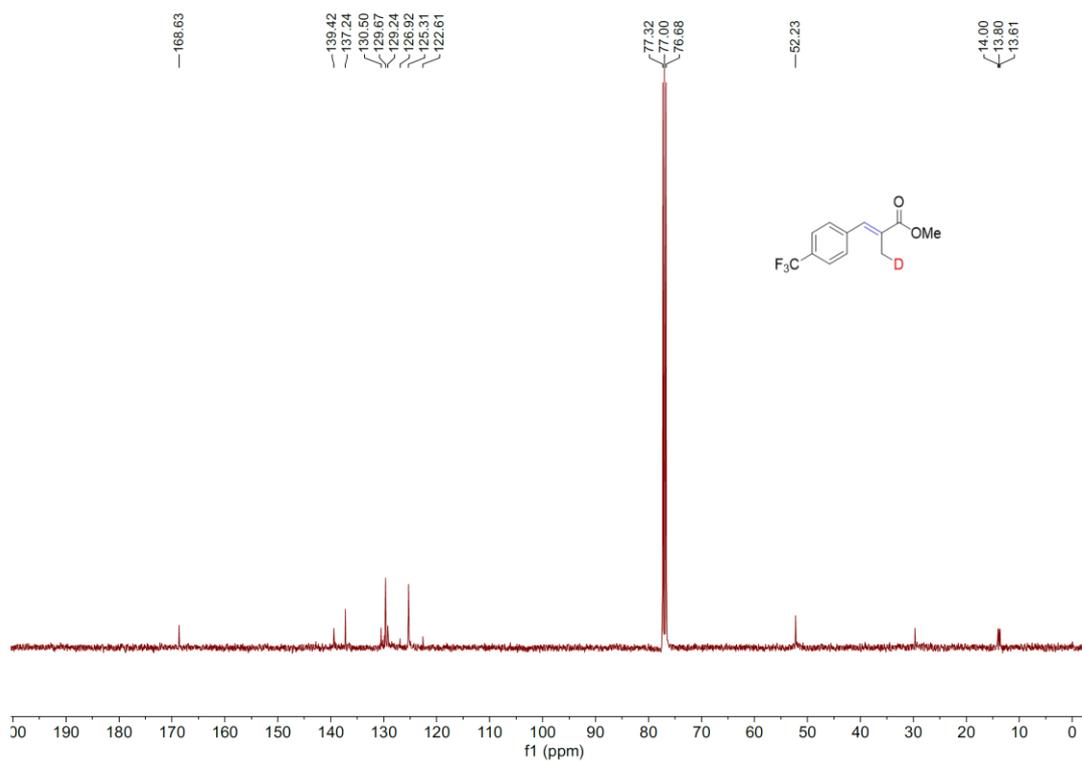
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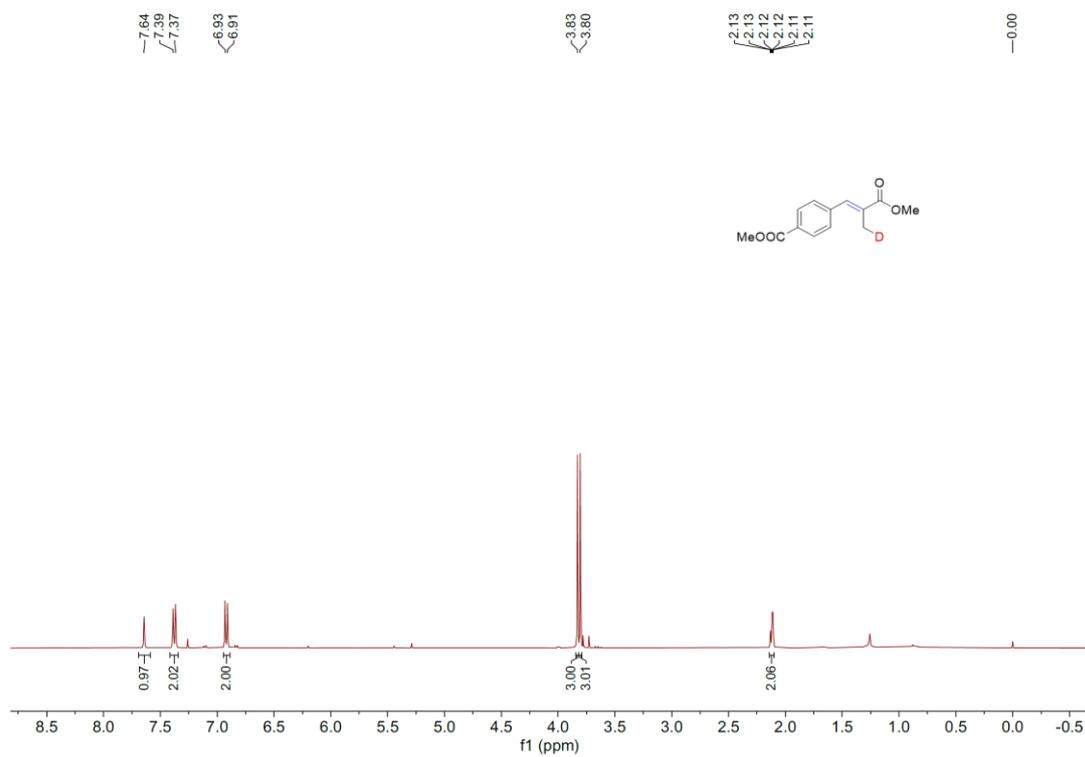
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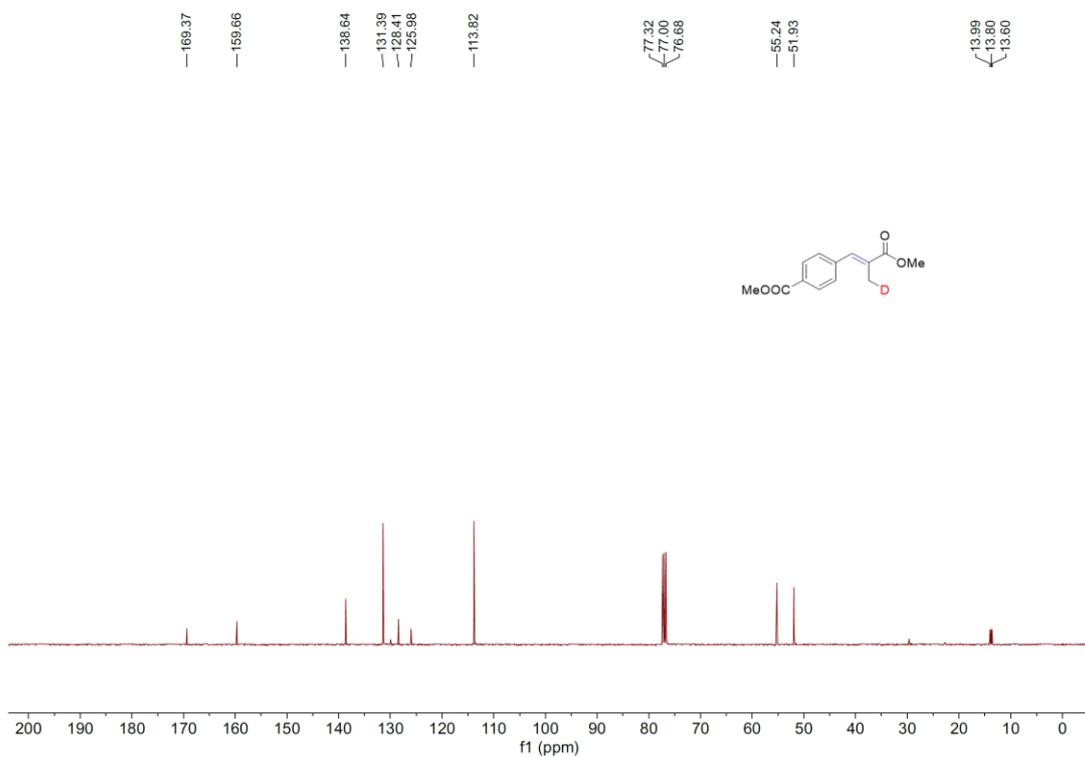
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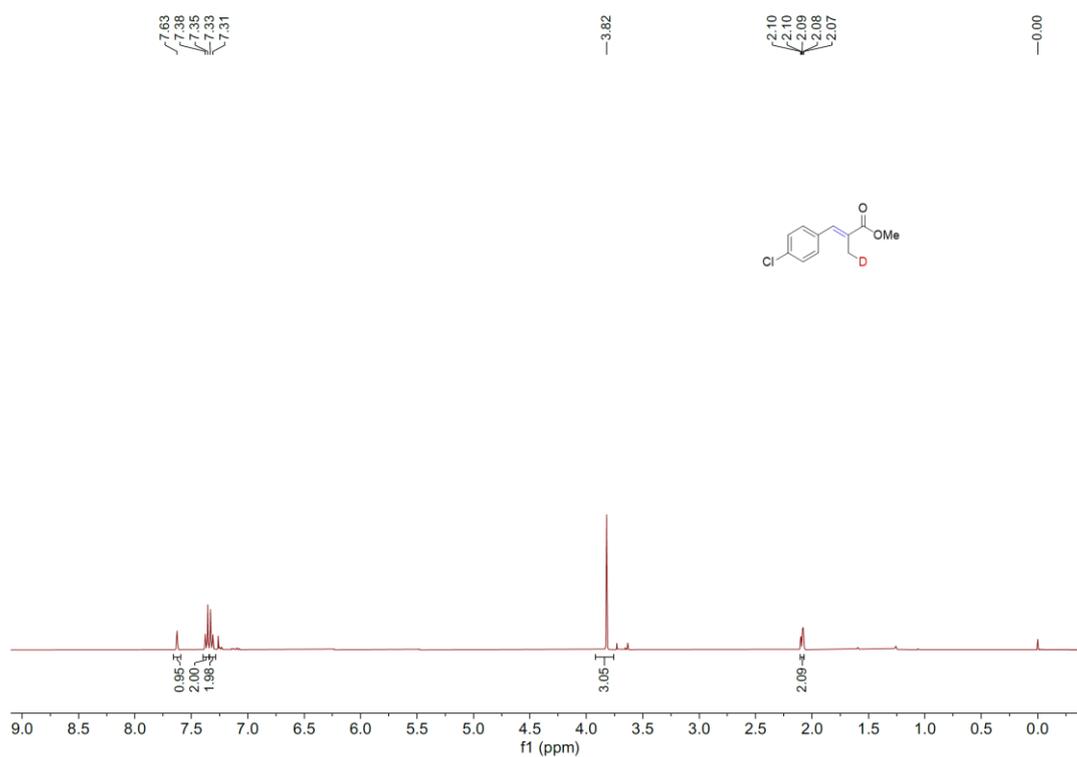
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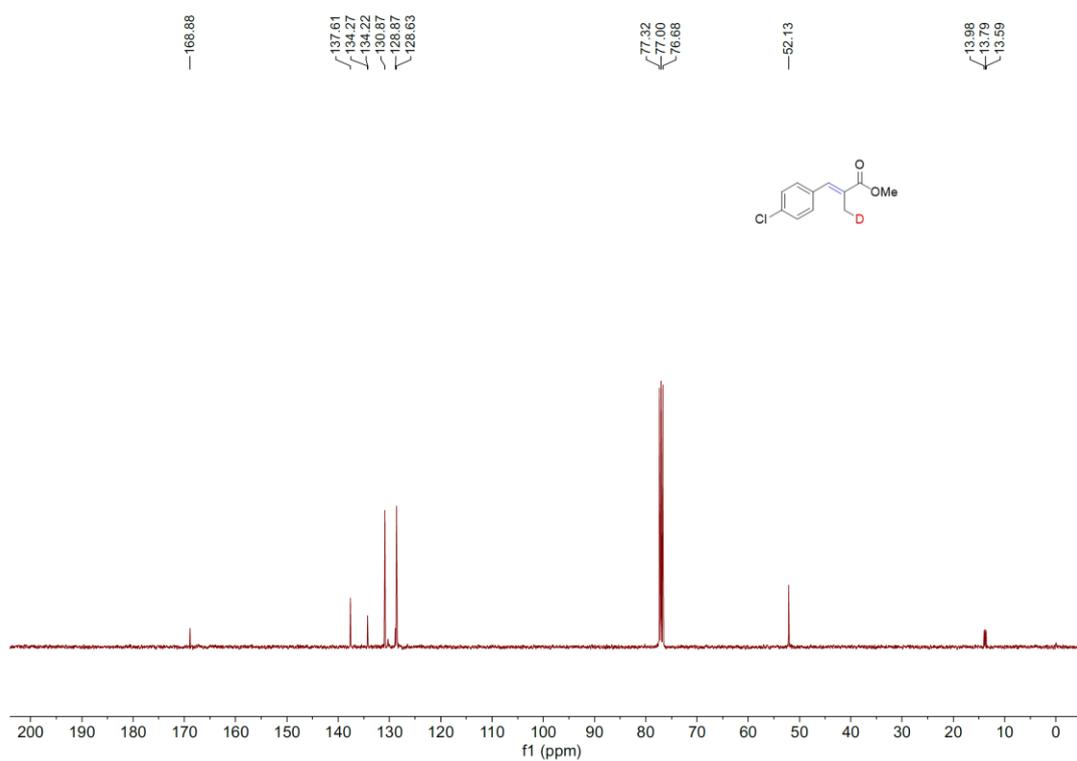
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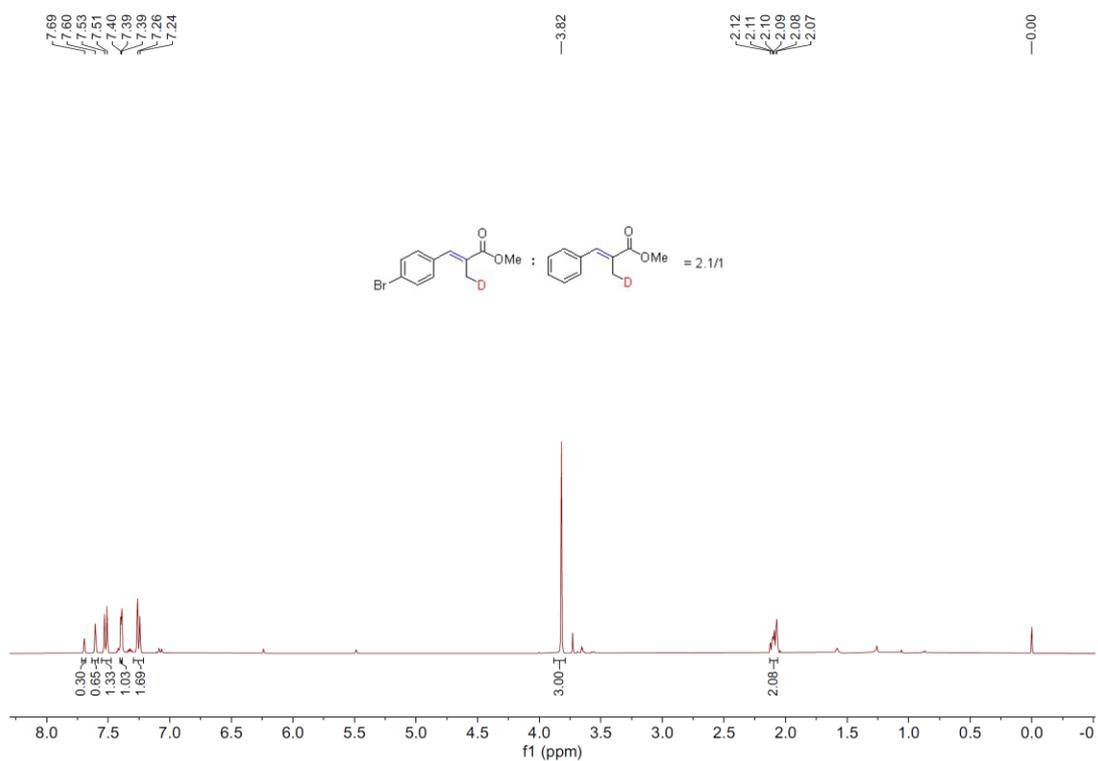
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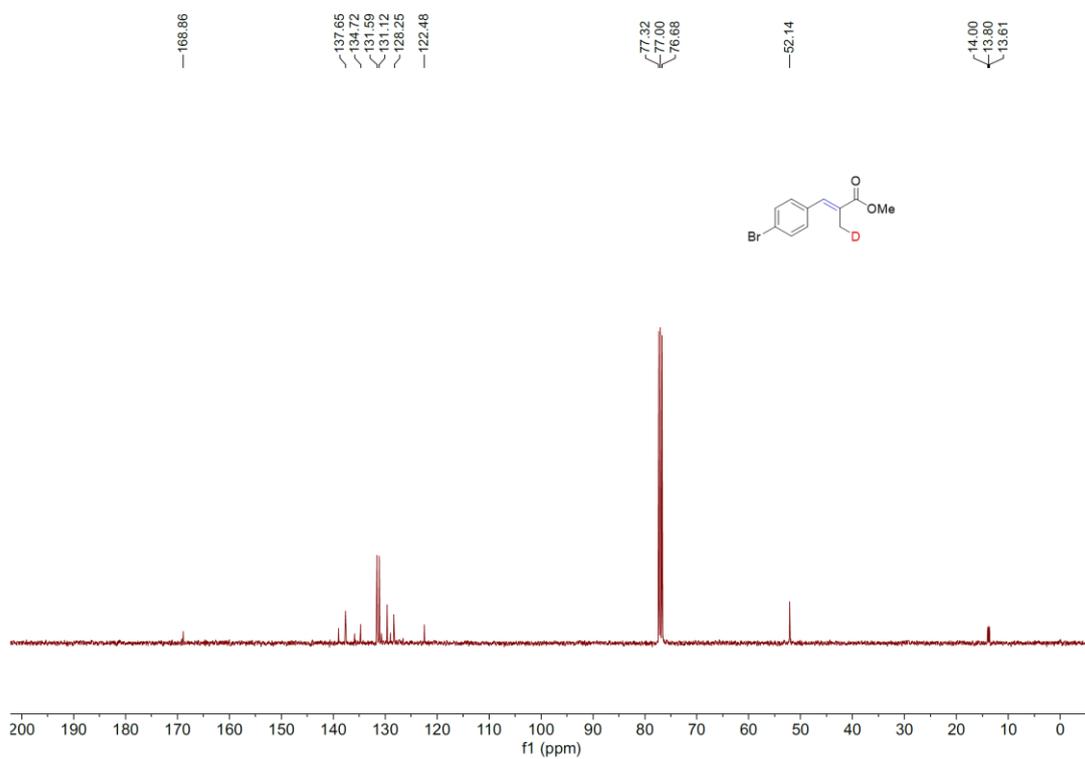
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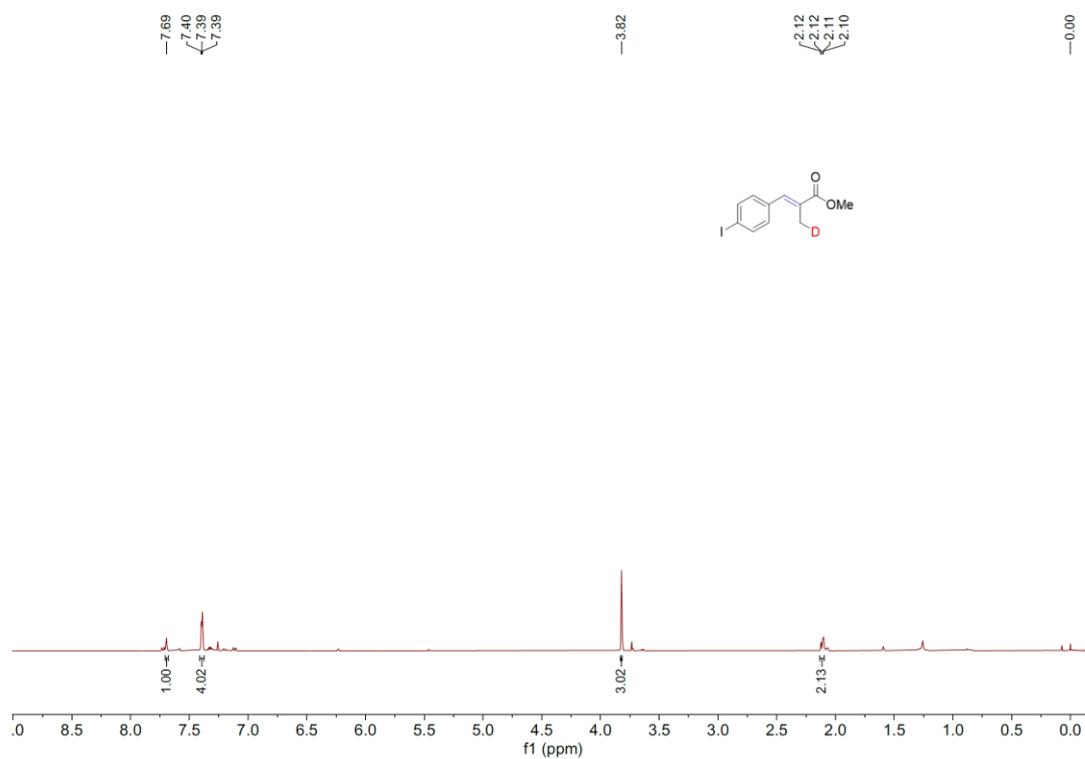
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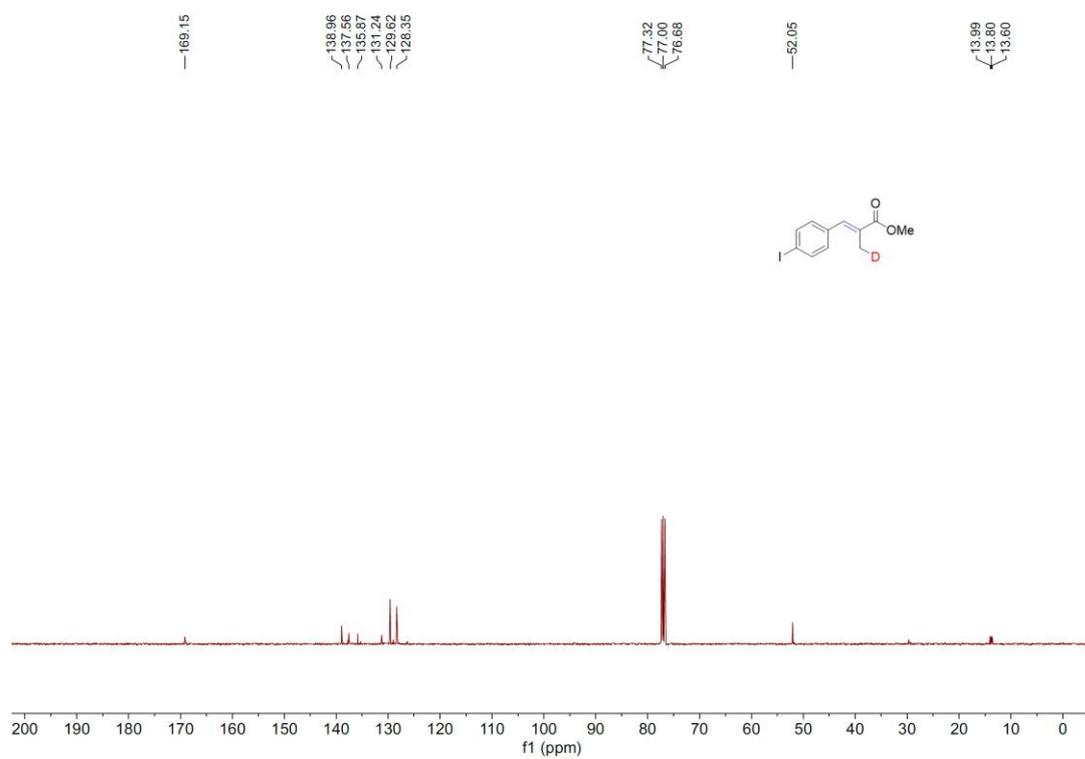
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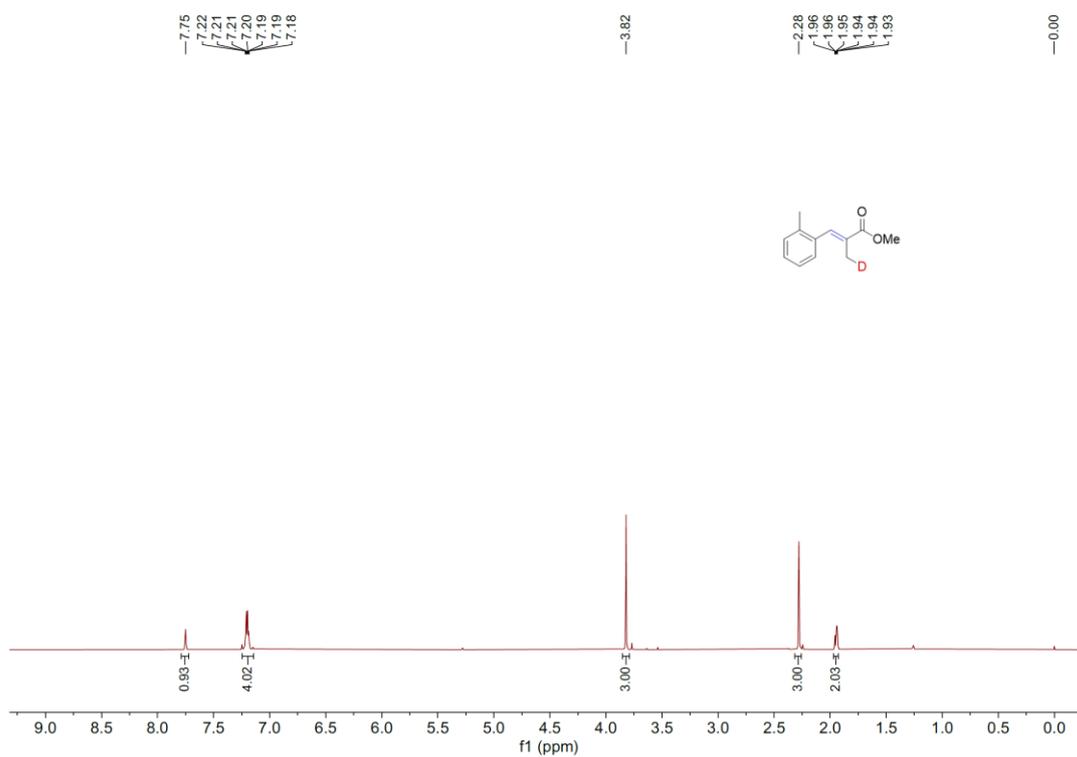
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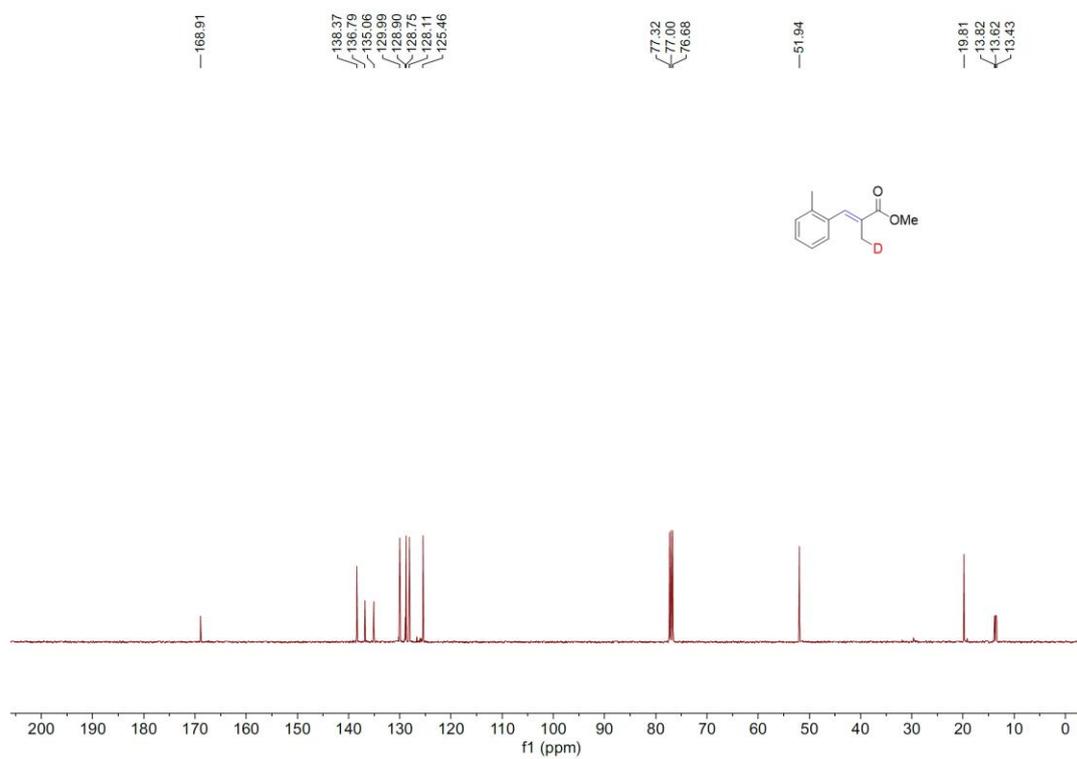
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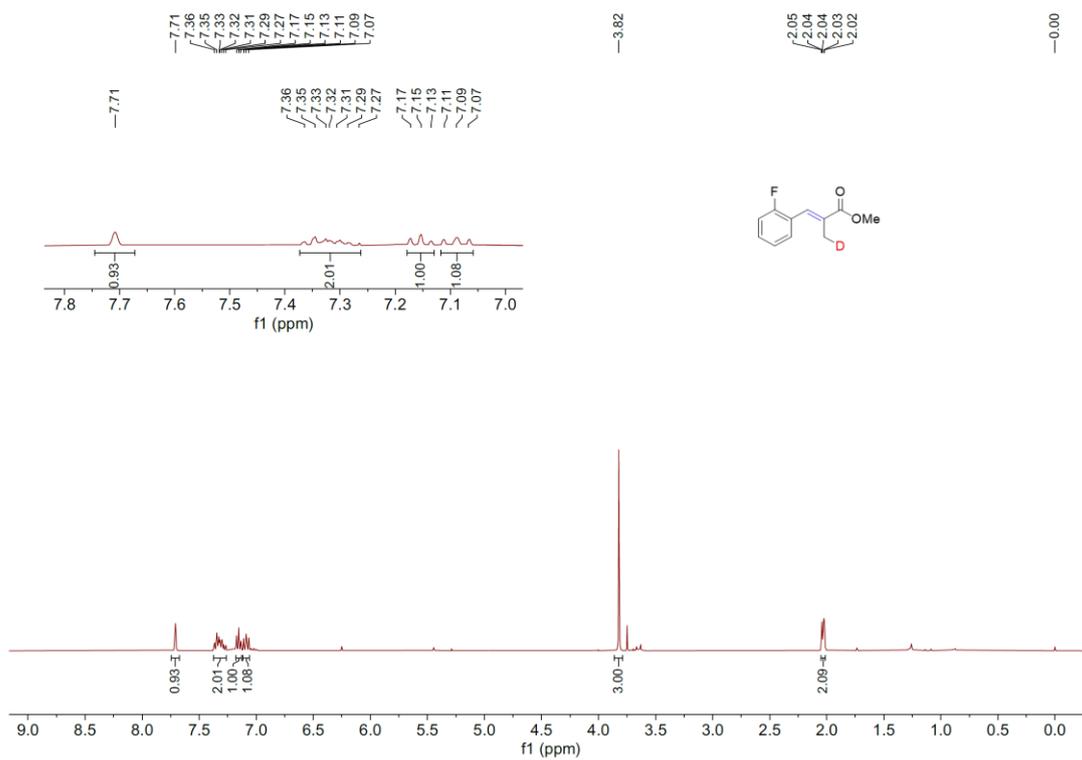
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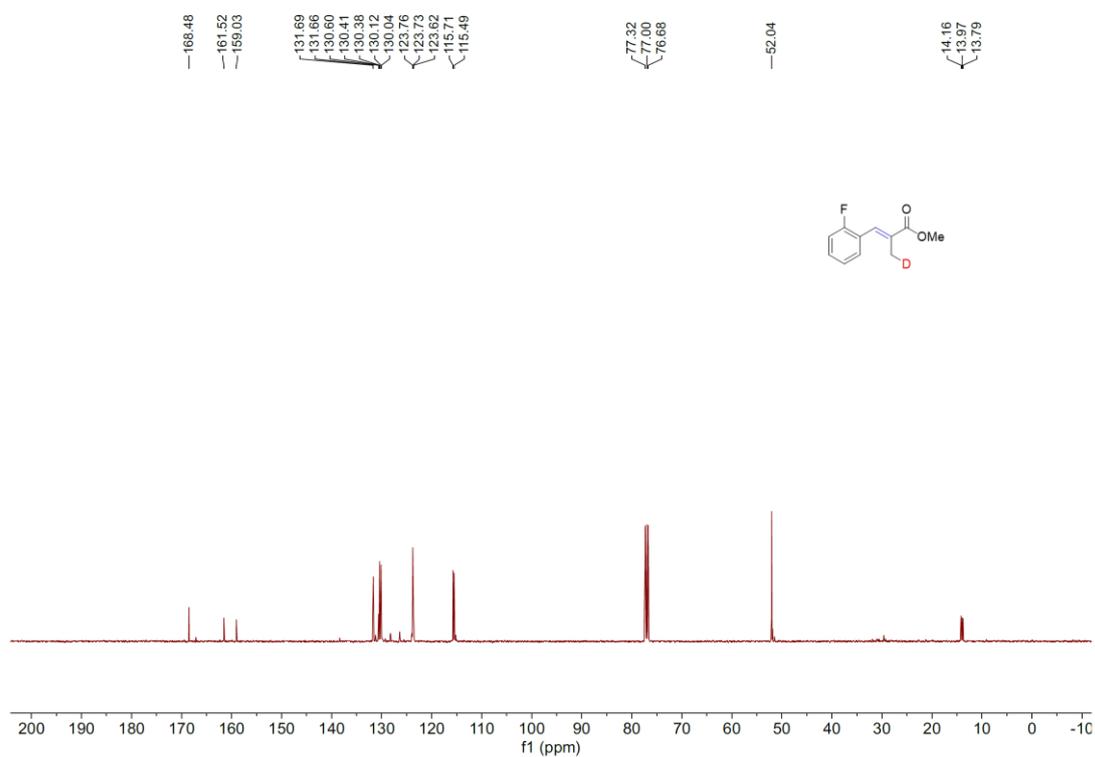
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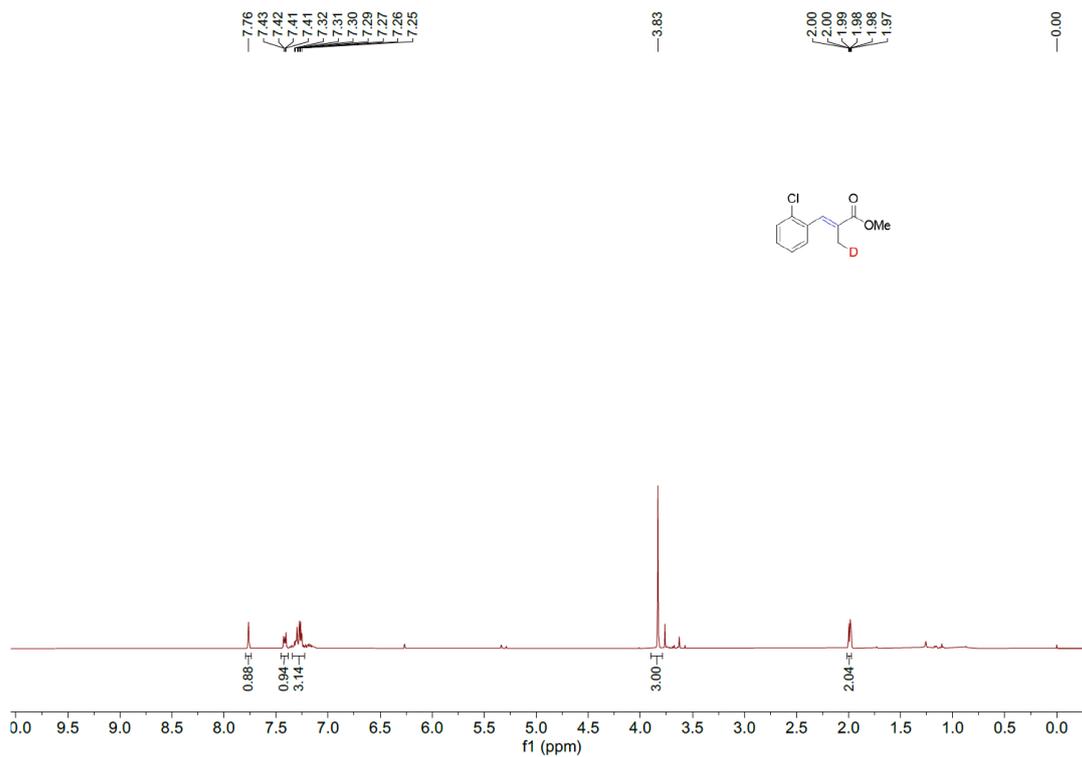
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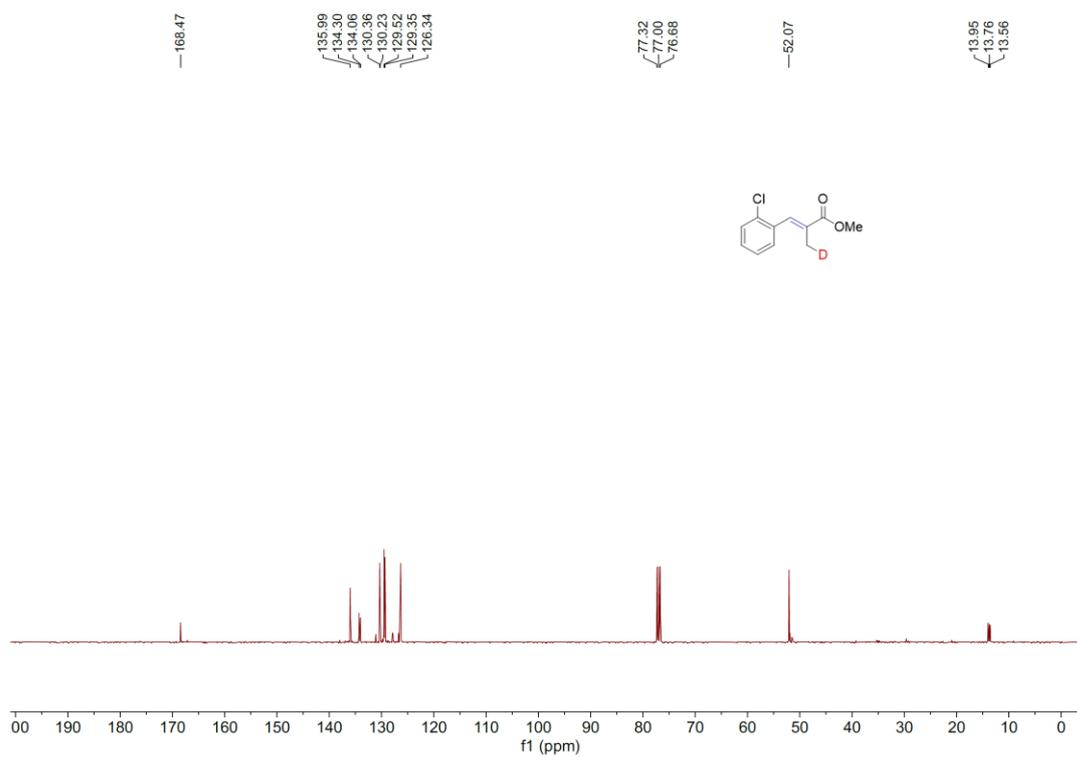
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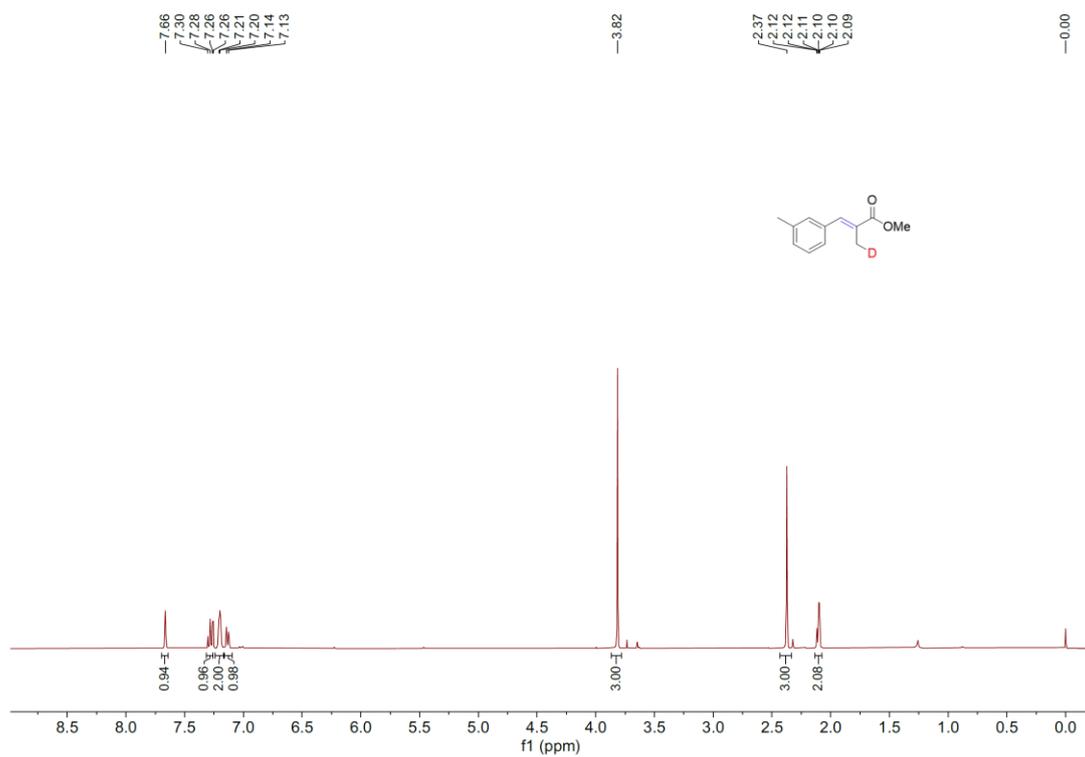
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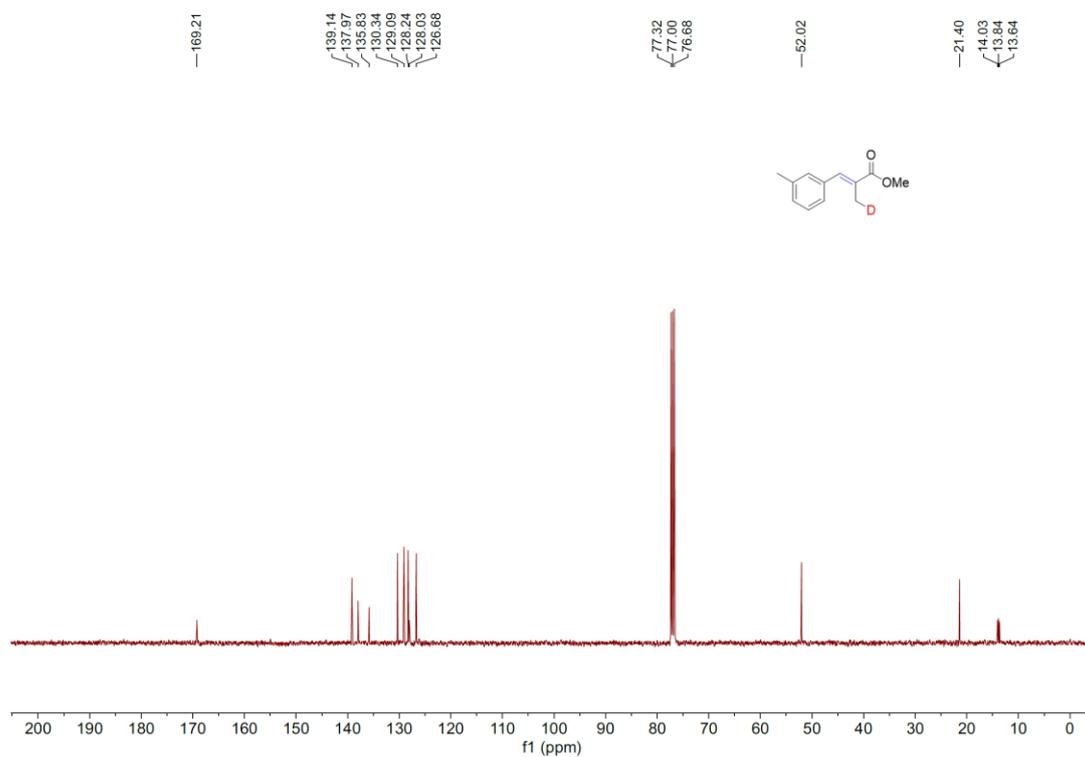
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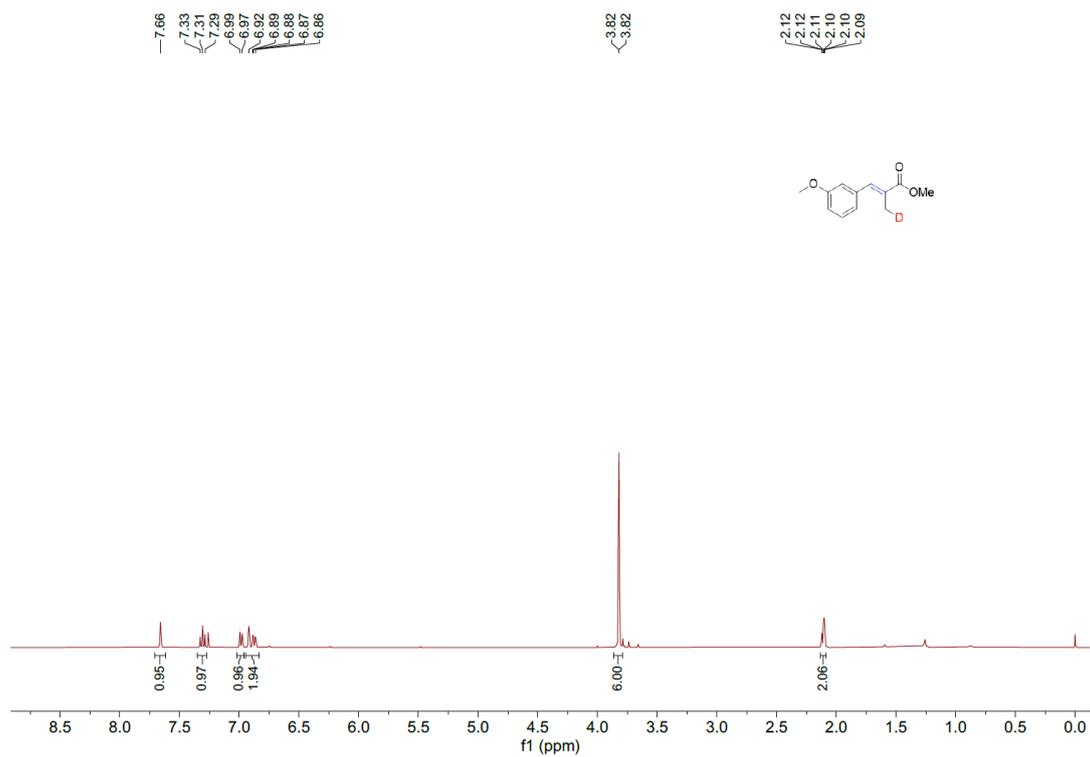
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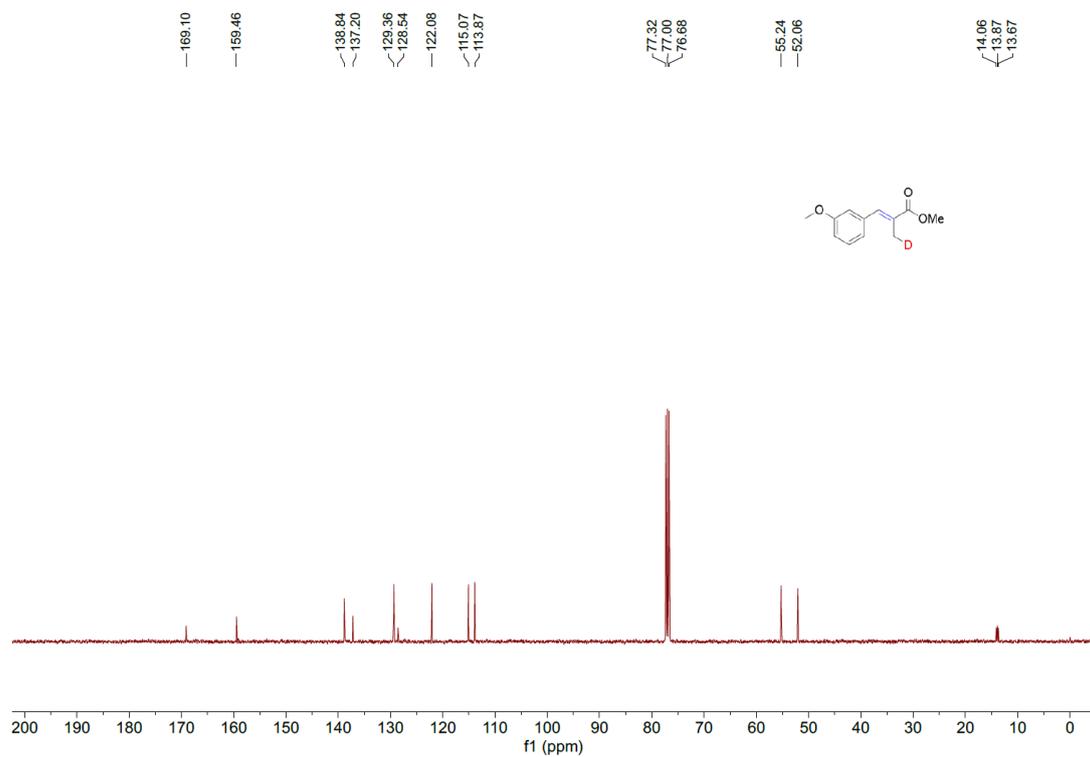
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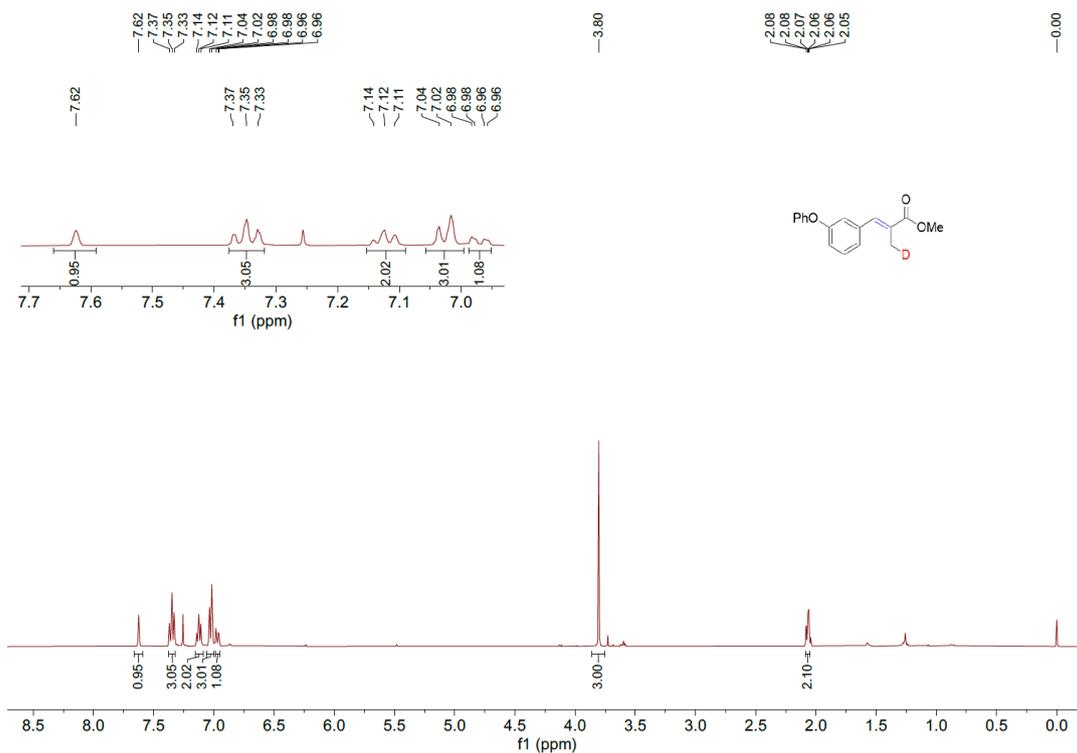
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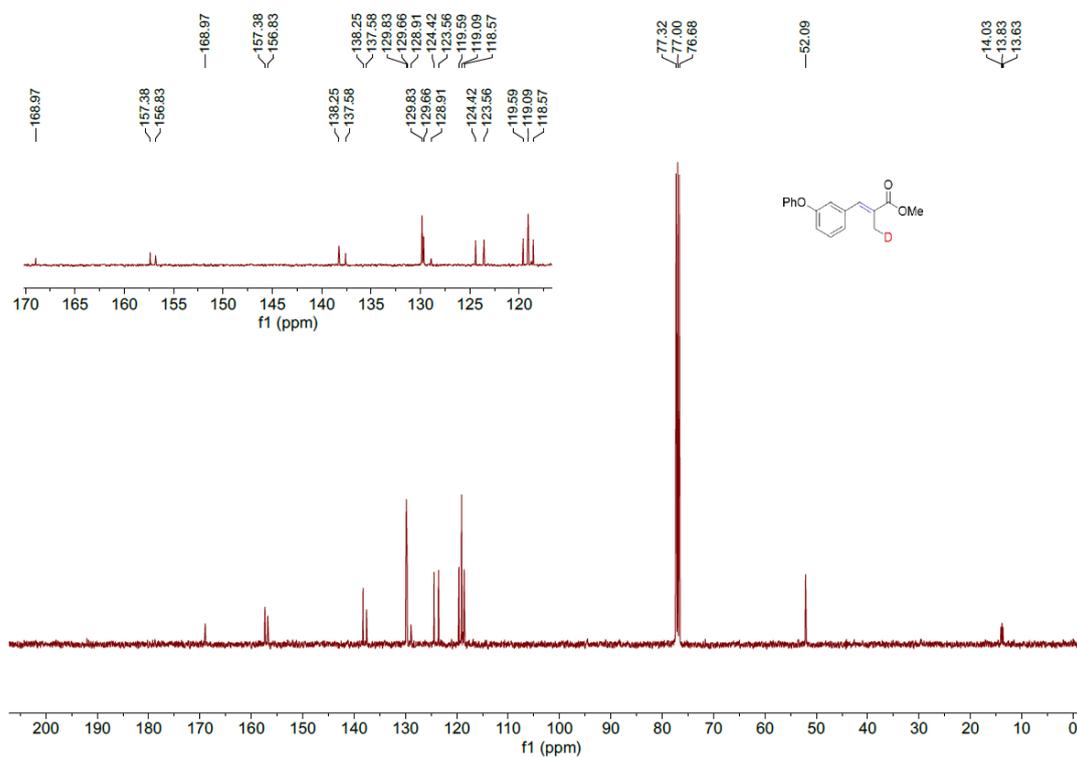
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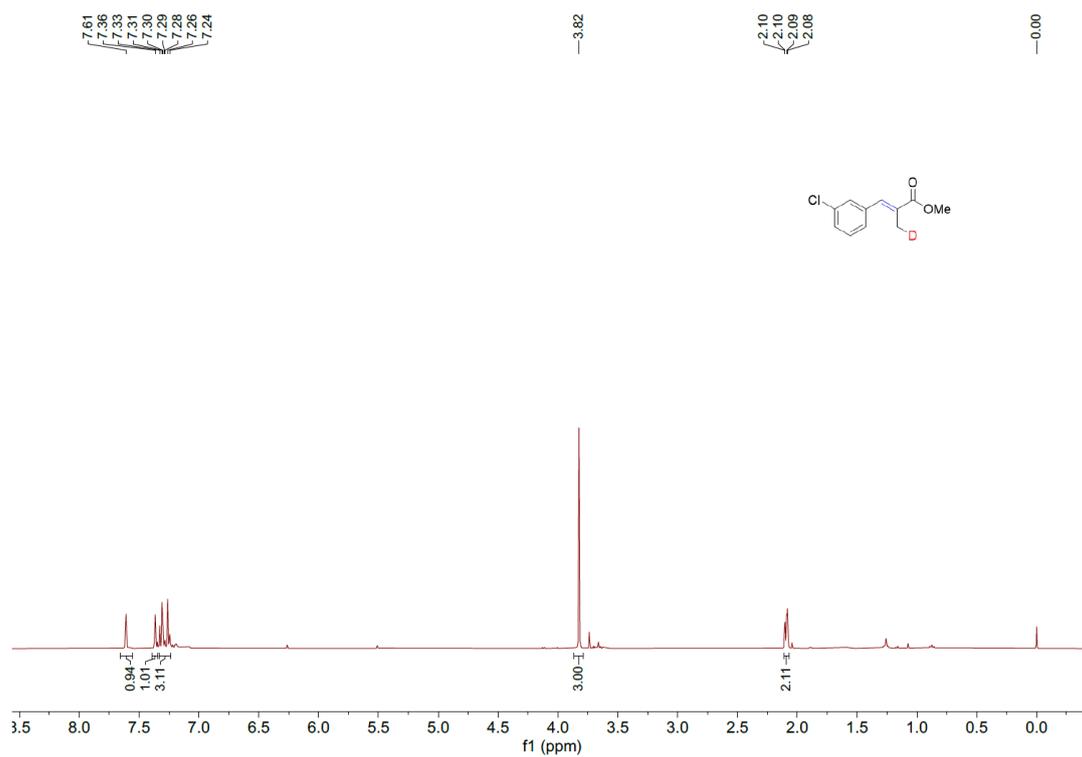
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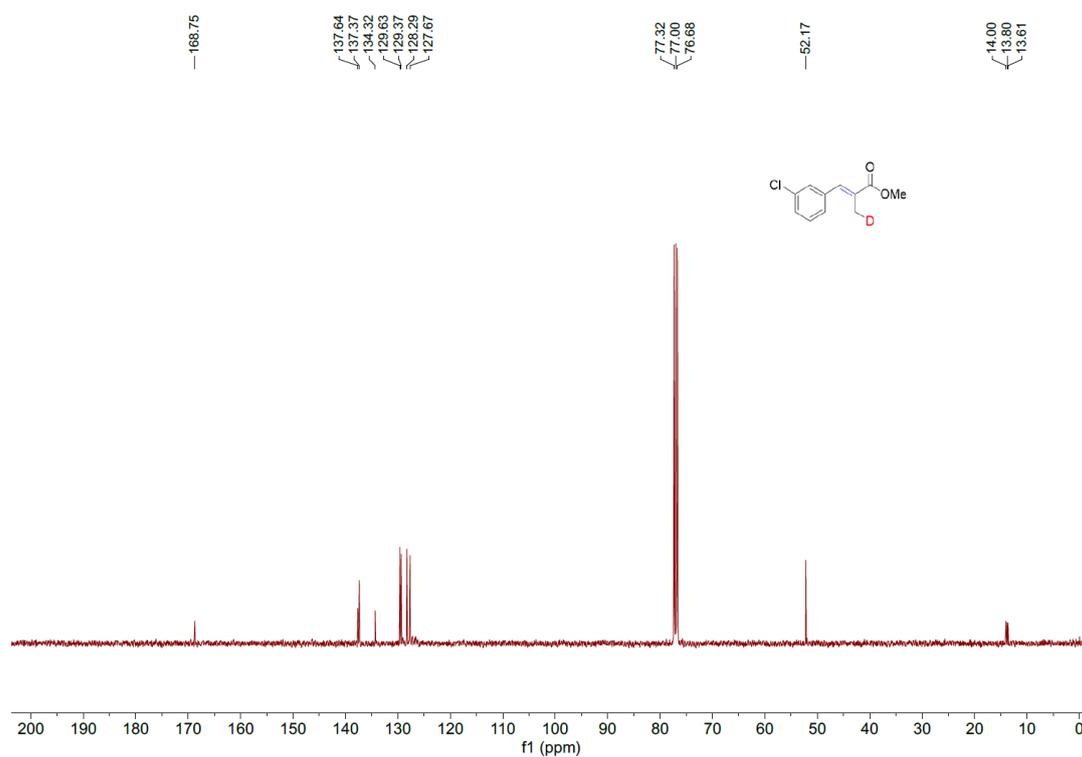
3q ¹³C NMR



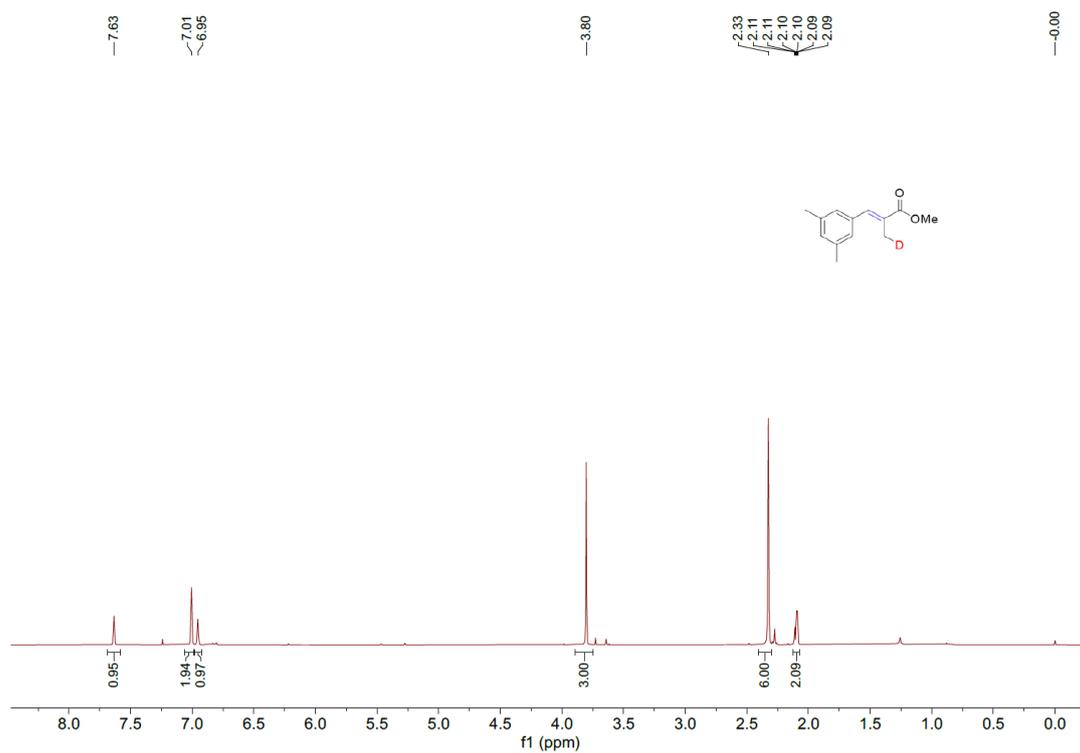
3r ¹H NMR



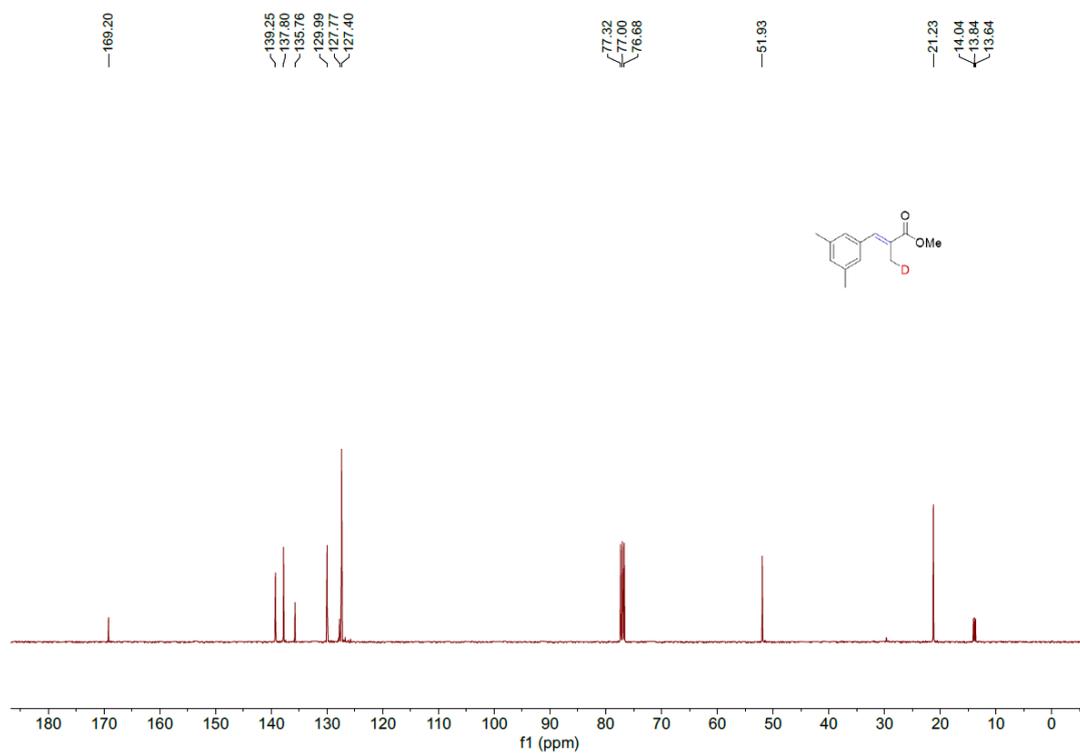
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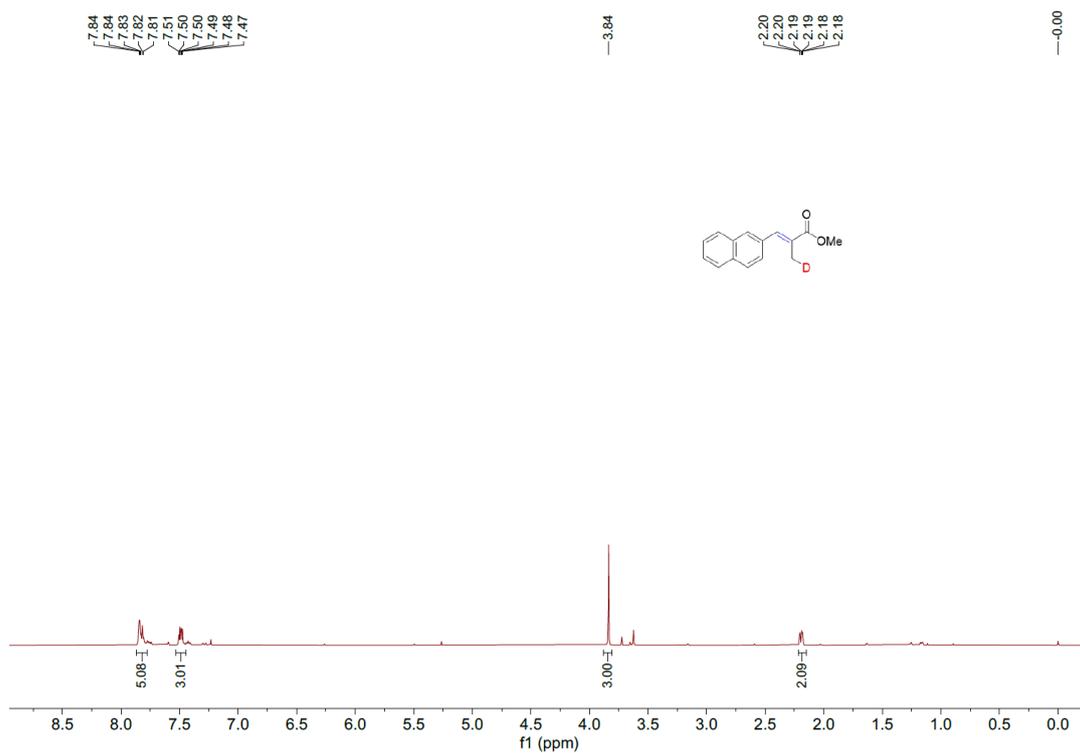
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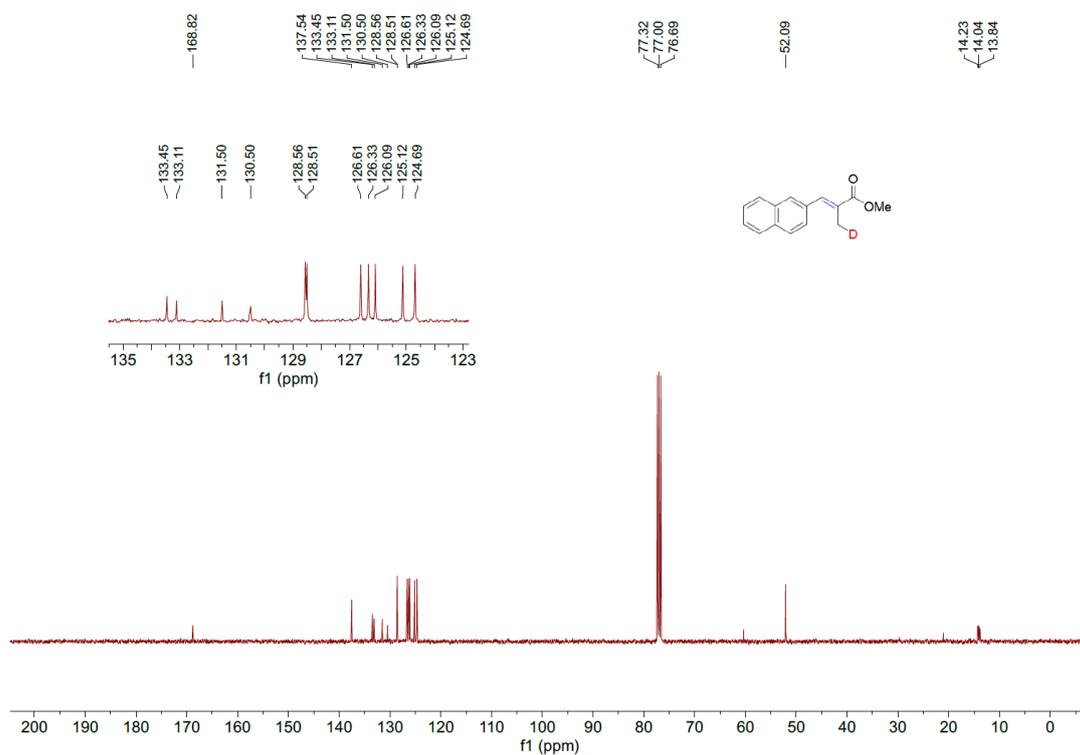
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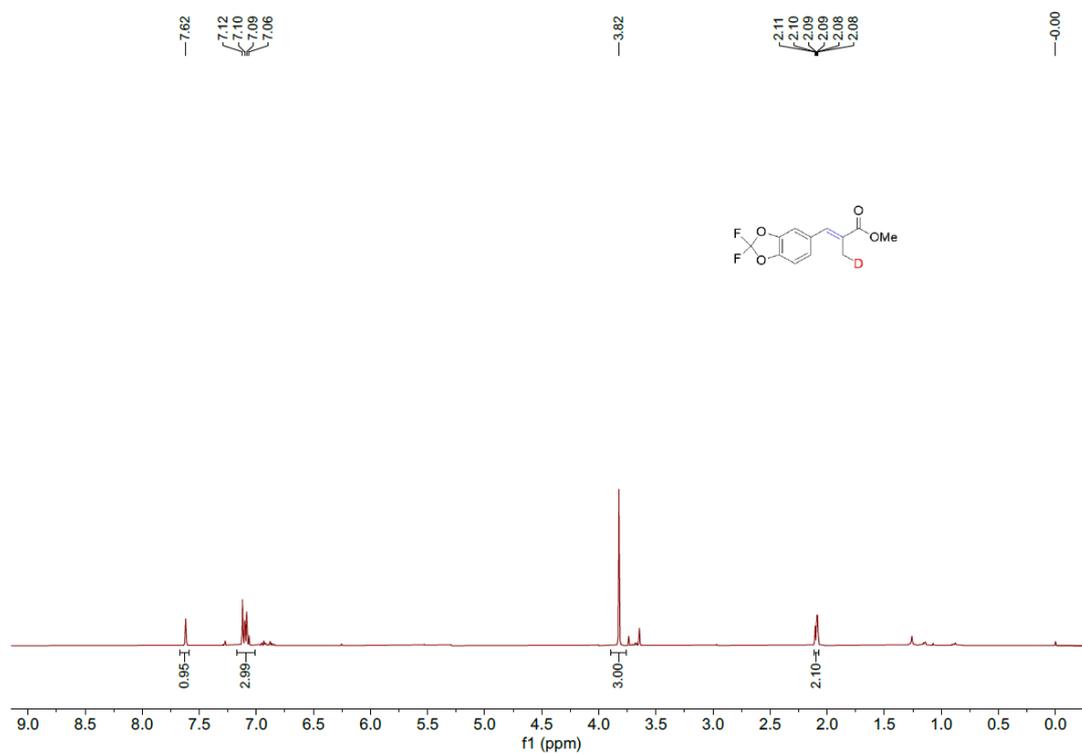
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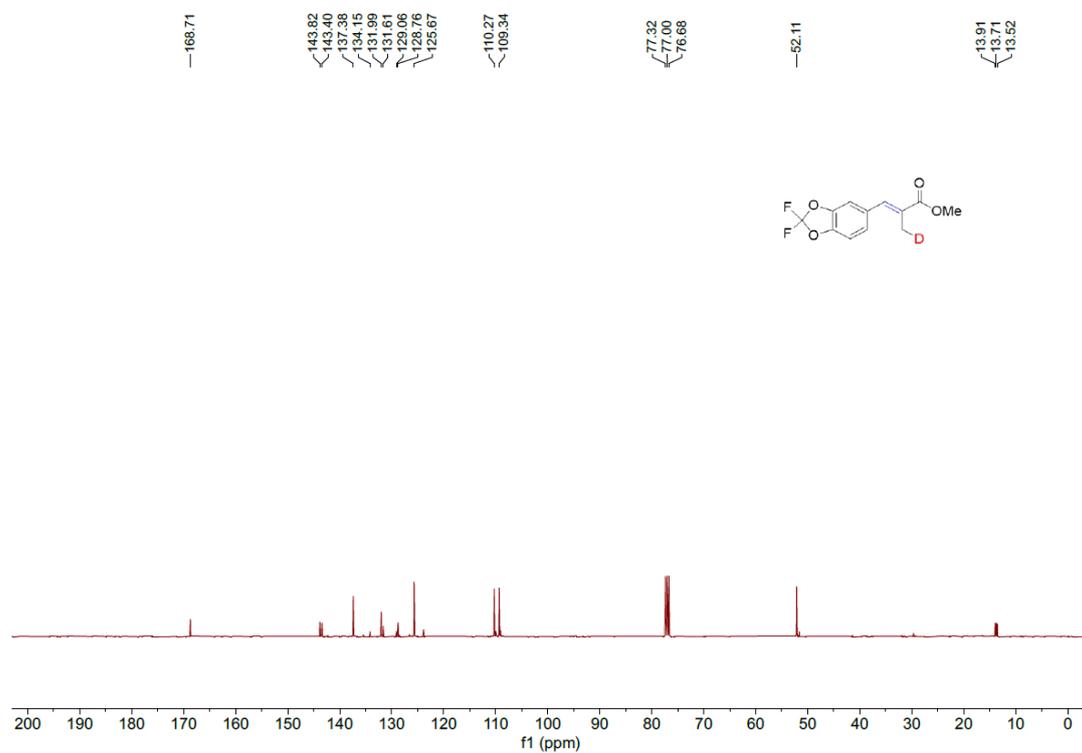
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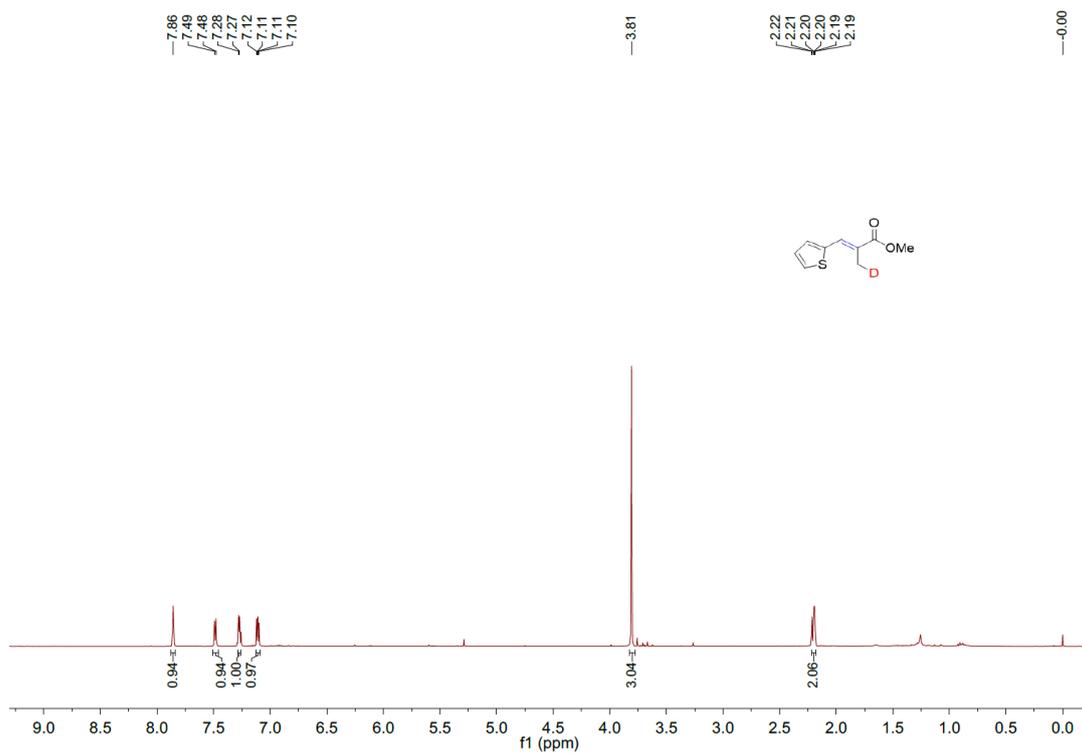
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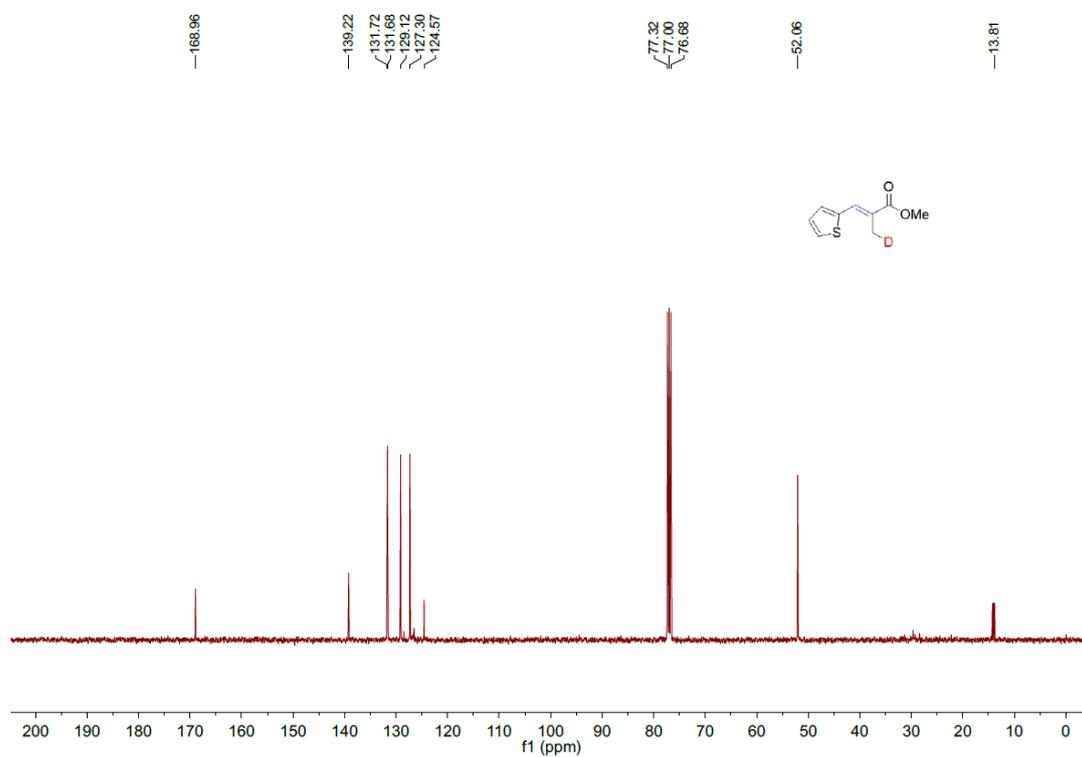
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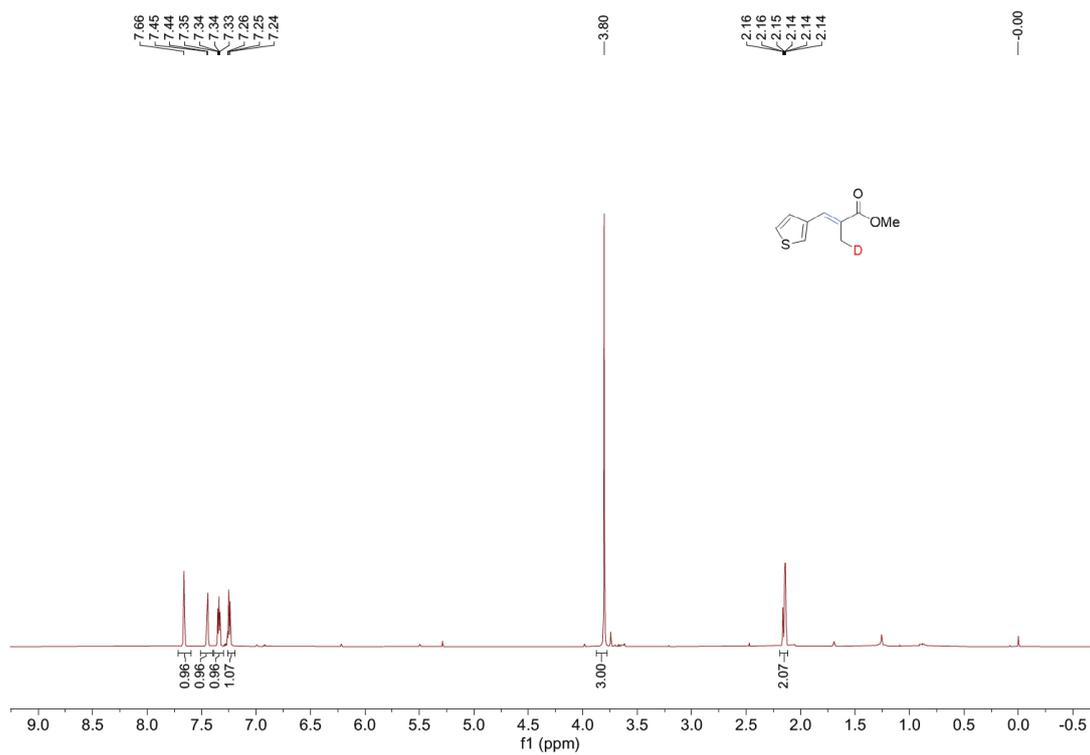
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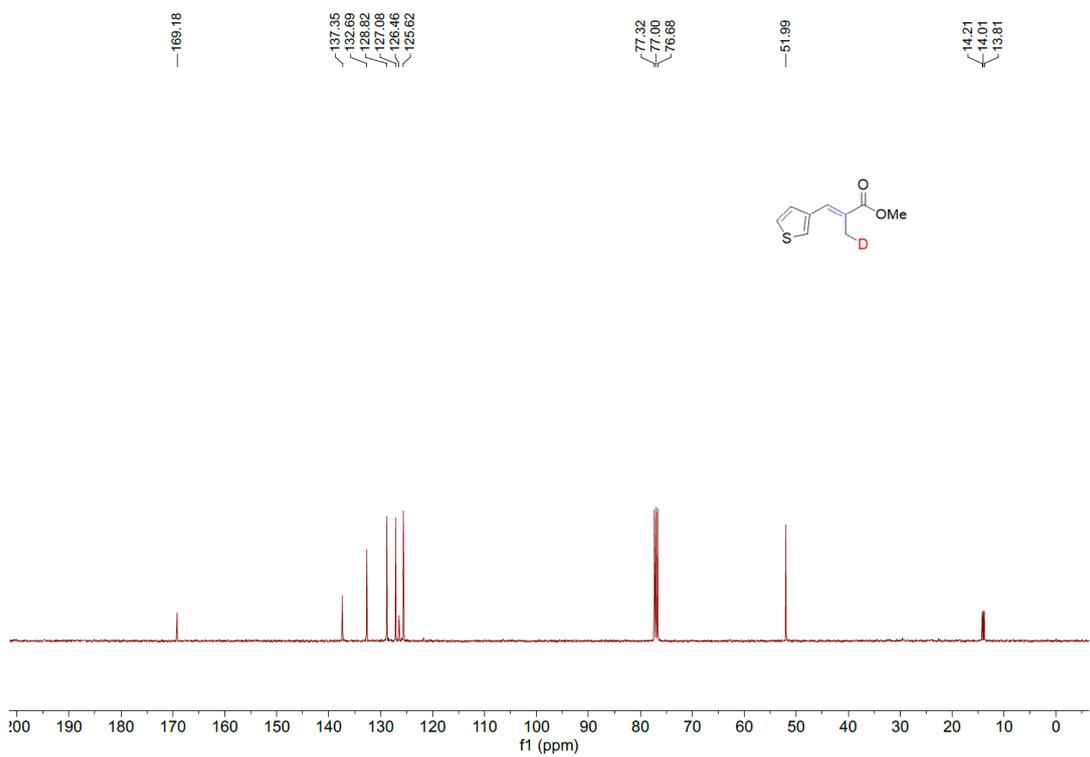
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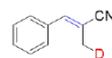
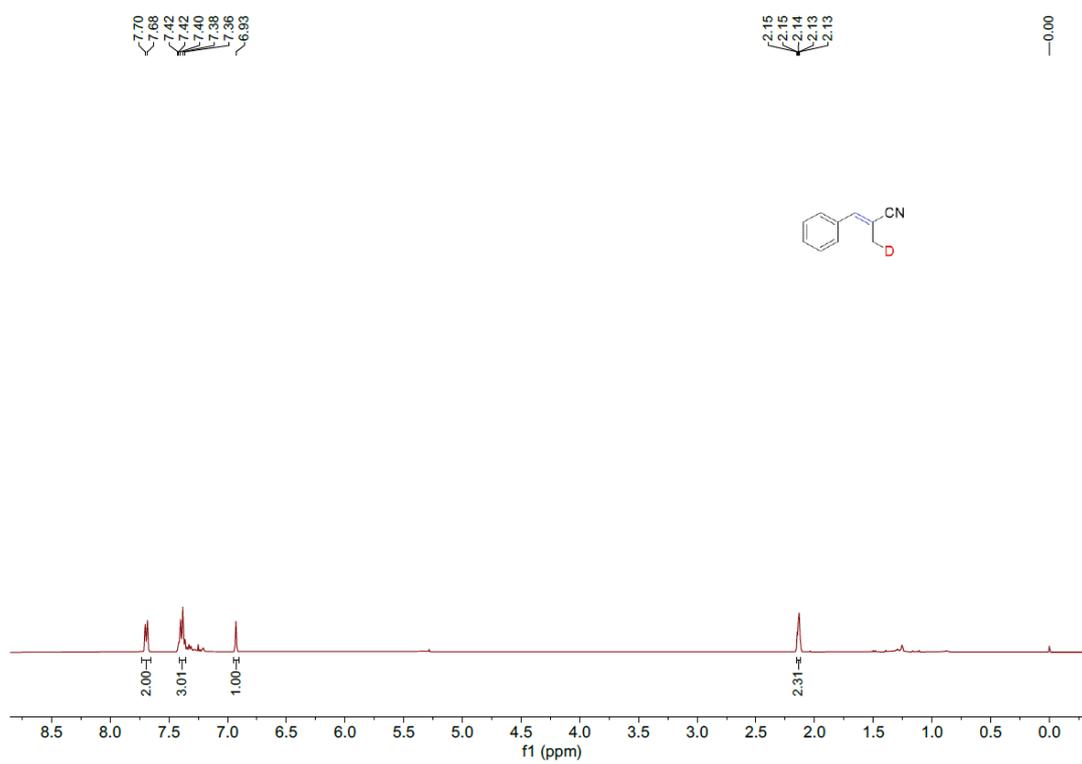
3w ¹H NMR



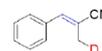
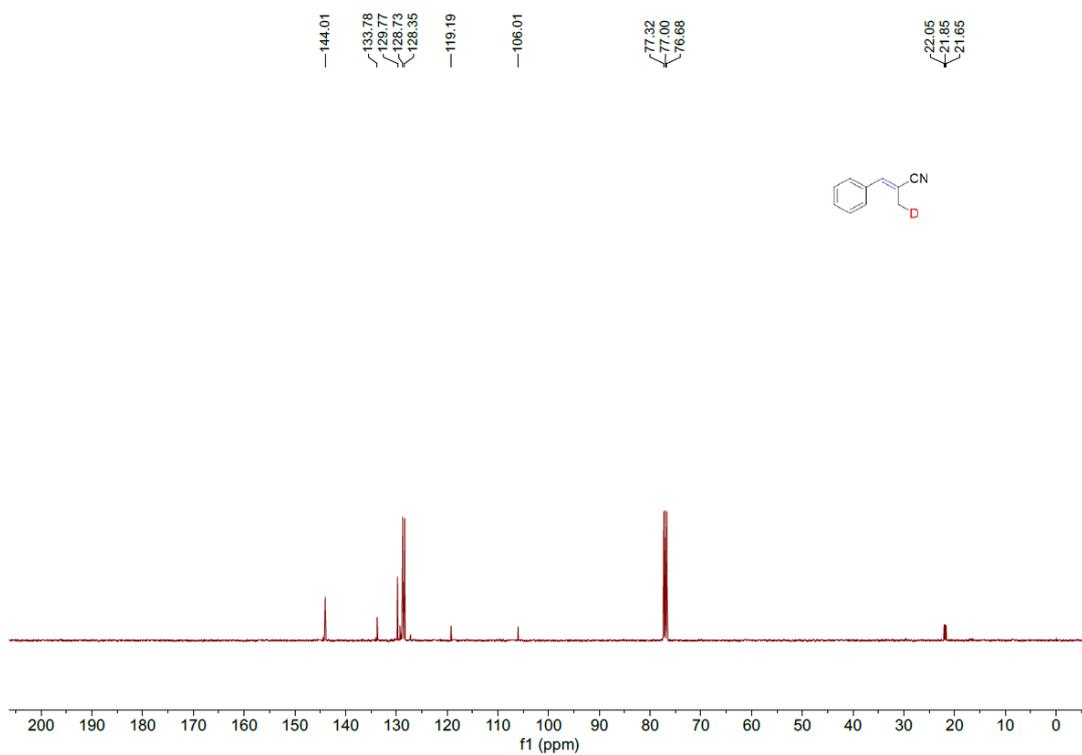
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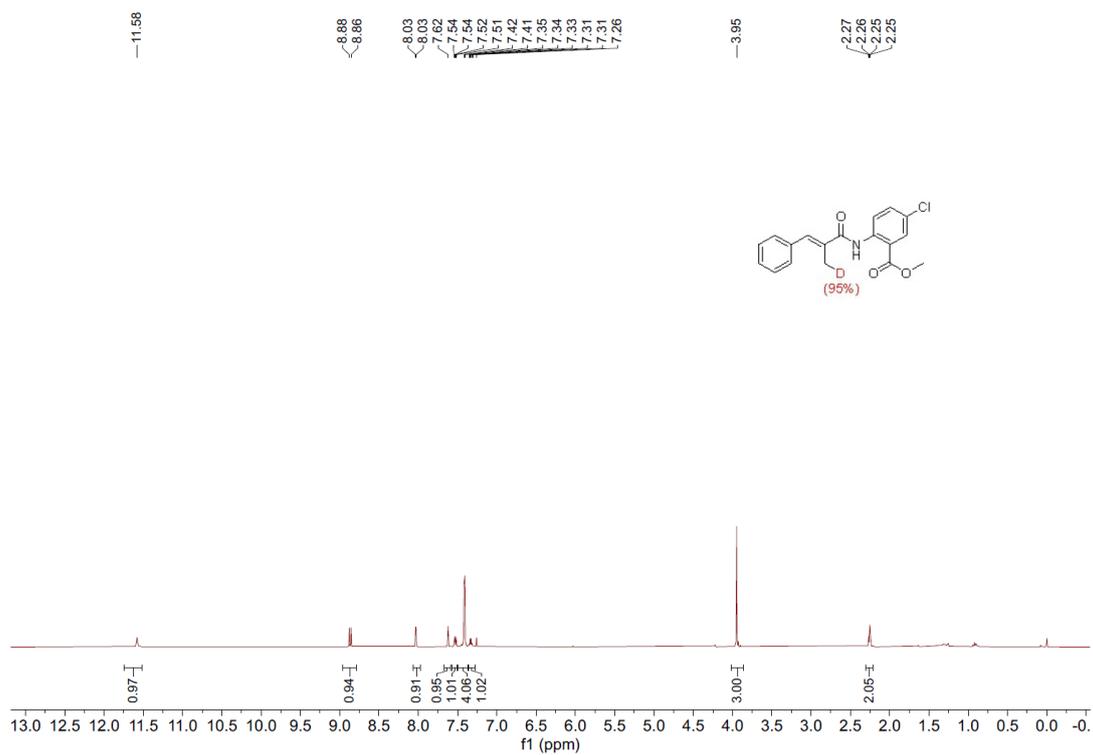
3x ¹H NMR



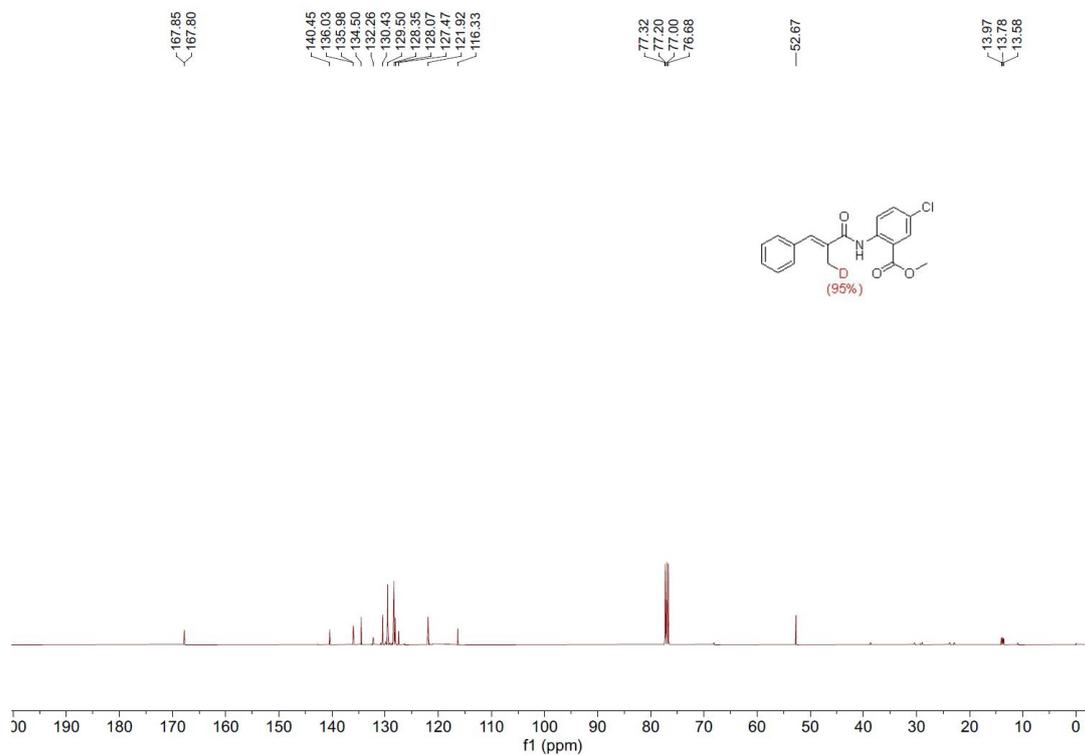
3x ¹³C NMR



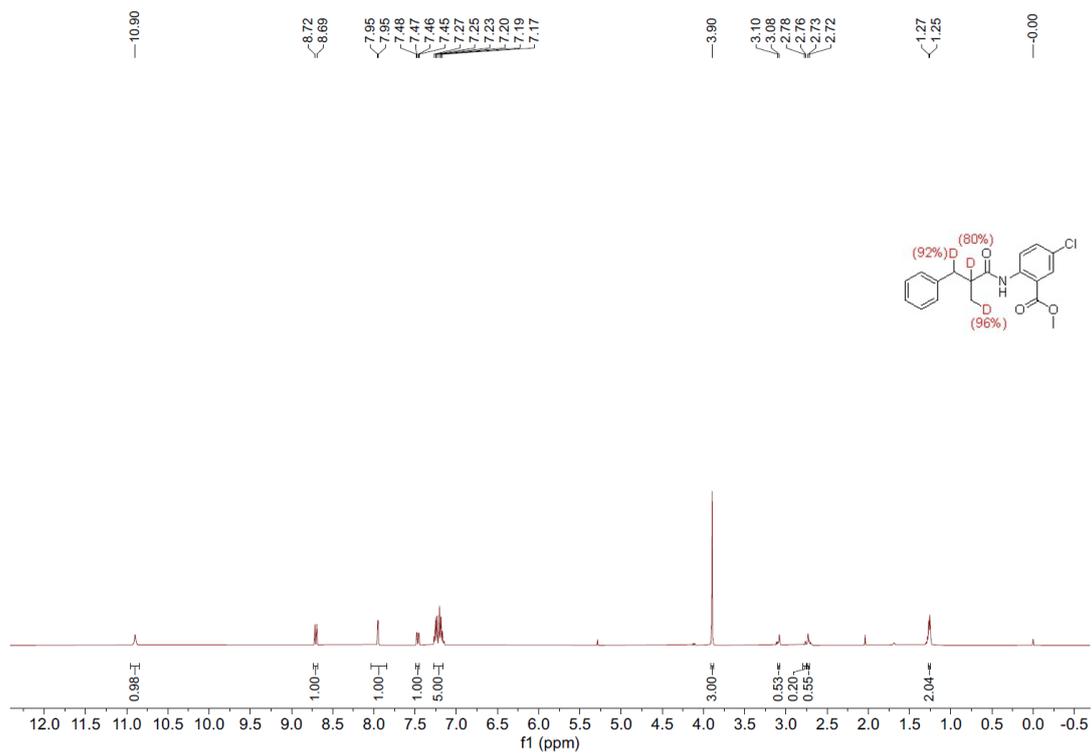
5 ¹H NMR



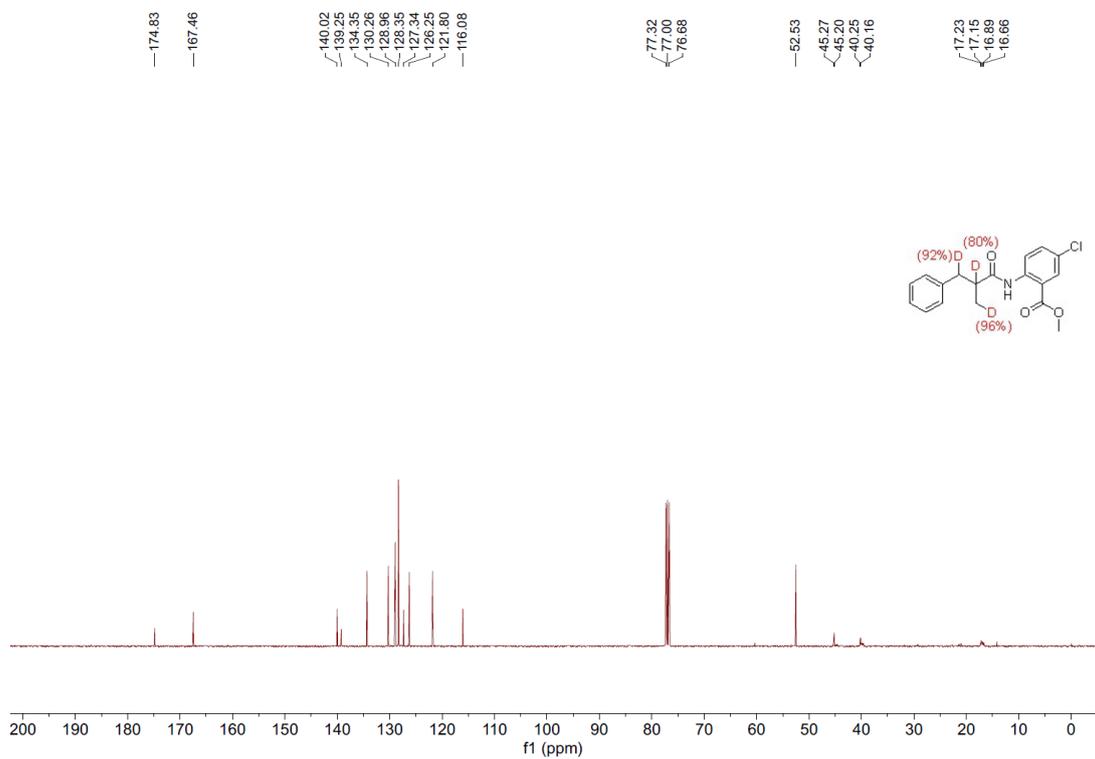
5 ¹³C NMR



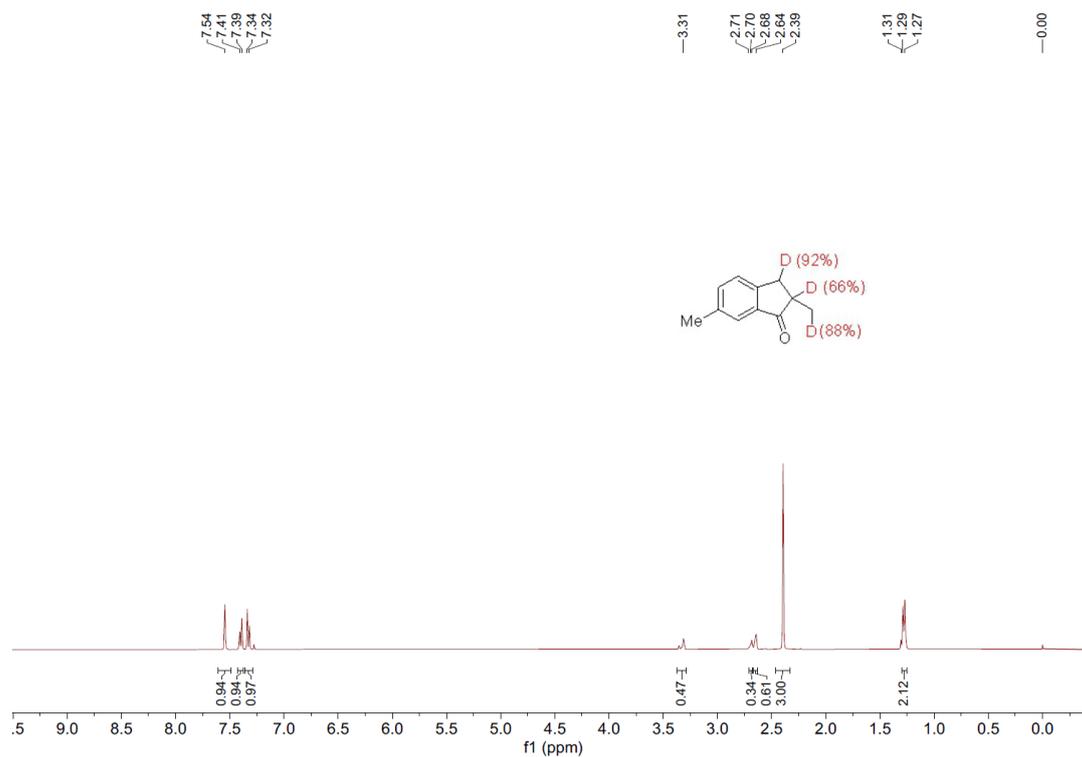
6 ¹H NMR



6 ¹³C NMR



7 ¹H NMR



7 ¹³C NMR

