

Supporting Information

Merging Visible-Light Photocatalysis and Copper Catalysis in the decarboxylative difluoroalkylation of α , β -unsaturated carboxylic acids with $\text{ICF}_2\text{CO}_2\text{Et}$

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1, General Remarks

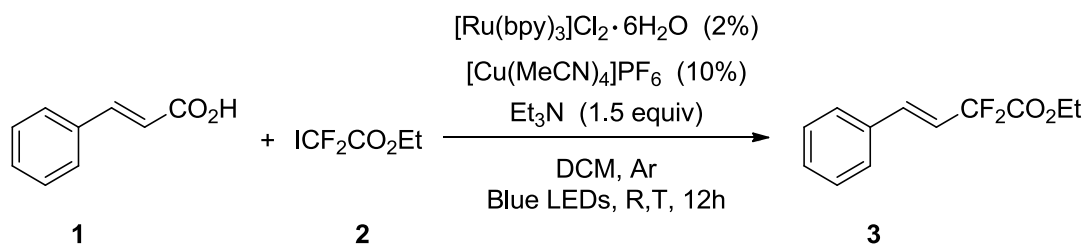
Column chromatography was carried out on silica gel. ^1H NMR spectra were recorded on 400 MHz in CDCl_3 . ^{13}C NMR spectra were recorded on 100 MHz in CDCl_3 . Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), q (quartet) or m (multiplet). All new compounds were further characterized by HRMS (high resolution mass spectra). Copies of their ^1H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Solvents were dried under standard method. Commercially available reagents were used with further purification.

2, Devices for the photocatalytic reactions



Figure 1. Devices for the photocatalytic reactions

3, General Procedure for the decarboxylative difluoroalkylation of α , β -unsaturated carboxylic acids with $\text{ICF}_2\text{CO}_2\text{Et}$



To a 10 mL of tube were added α,β -unsaturated carboxylic acid **1** (0.15 mmol), $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$ (10 mol %, 0.015 mmol, 5.5 mg) and $[\text{Ru}(\text{bpy})_3]\text{Cl}_2 \cdot 6\text{H}_2\text{O}$ (2 mol %, 2.2 mg) under air, The mixture was evacuated and backfilled with Ar (3 times). Ethyl

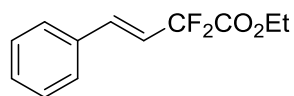
iododifluoroacetate **2** (1.5 equiv, 0.225 mmol, 56.2 mg), Et₃N (1.5 equiv, 0.225 mmol, 22.7 mg), and dichloromethane (1.5 mL) were added successively. The mixture was stirred at room temperature for 12 hours while irradiated by blue LED strip ($\lambda = 450 \pm 15$ nm, 3W electrical power). The reaction was monitored by TLC. The mixture was diluted with EtOAc, and then filtered through a pad of silica gel. The filtrate was concentrated under vacuum and purified by flash column chromatography on silica gel to give product **3**.

4, Preparation of Starting Materials

All substrates were either purchased and used from commercial suppliers directly.

5, Characterization data of 3a–3af

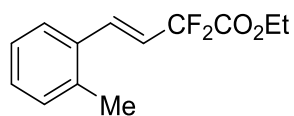
¹H NMR and ¹³C NMR spectra for compounds 3a–3af



Ethyl-2,2-difluoro-4-phenylbut-3-enoate (3a, *E/Z* = 95:5)

The procedure was operated with the general procedure. The product **3a** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (78%, 26.4 mg). This compound is known.¹

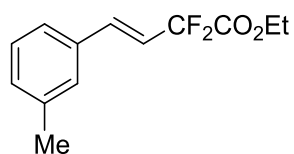
¹H NMR (400 MHz, CDCl₃): 7.45-7.43 (m, 2H), 7.38 – 7.34 (m, 3H), 7.09 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.8 (t, *J* = 34.7 Hz), 136.8 (t, *J* = 9.4 Hz), 134.0, 129.6, 128.8, 127.4, 118.8 (t, *J* = 24.8 Hz), 112.7 (t, *J* = 246.9 Hz), 63.0, 13.9. ¹⁹F NMR (476 MHz, CDCl₃): -103.1.



Ethyl-2, 2-difluoro-4-(o-tolyl)but-3-enoate (3b, *E/Z* = 98:2),

The procedure was operated with the general procedure. The product **3b** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (78%, 28.0 mg). This compound is known.¹

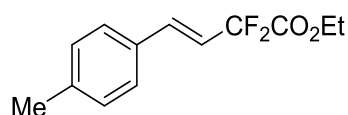
¹H NMR (400 MHz, CDCl₃): 7.45 (d, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 16.8 Hz, 1H), 7.26-7.16 (m, 3H), 6.20 (dt, *J* = 16.0, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 2.38 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.9, (t, *J* = 34.5 Hz), 136.7, 134.6 (t, *J* = 9.3 Hz), 133.1, 130.6, 129.3, 126.2, 126.0, 120.0 (t, *J* = 24.8 Hz), 112.7 (t, *J* = 246.9 Hz), 63.0, 19.5, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -102.9 (s, 2F).



Ethyl-2, 2-difluoro-4-(m-tolyl)but-3-enoate (3c, *E/Z* = 96:4),

The procedure was operated with the general procedure. The product **3c** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (85%, 30.6 mg). This compound is known.¹

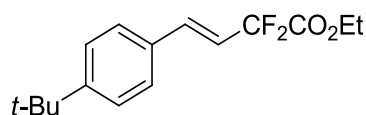
¹H NMR (400 MHz, CDCl₃) 7.24 (d, *J* = 5.6 Hz, 3H), 7.15 (d, *J* = 5.3 Hz, 1H), 7.02(dt, *J* = 16.2, 2.5 Hz, 1H), 6.28 (dt, *J* = 16.1, 11.4 Hz), 4.34 (q, *J* = 7.1 Hz, 2H), 2.35 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.9 (t, *J* = 35.0 Hz), 138.4, 136.9 (t, *J* = 9.2 Hz), 133.9, 130.4, 128.6, 128.0, 124.6, 118.5 (t, *J* = 25.0 Hz), 112.7 (t, *J* = 246.3 Hz), 63.0, 21.2, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.0.



Ethyl-2, 2-difluoro-4-(p-tolyl)but-3-enoate (3d, *E/Z* = 99:1),

The procedure was operated with the general procedure. The product **3d** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (90%, 32.4 mg). This compound is known.¹

¹H NMR (400 MHz, CDCl₃): 7.32 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.05 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.25 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 2.25 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 164.0, (t, *J* = 35.5 Hz), 139.8, 136.7 (t, *J* = 9.5 Hz), 131.3, 129.5, 127.3, 117.7 (t, *J* = 24.9 Hz), 112.8 (t, *J* = 246.6 Hz), 63.0, 21.3, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -102.8.

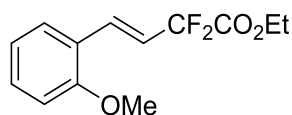


Ethyl-2, 2-difluoro-4-(4-butylphenyl)but-3-enoate (3e, *E/Z* = 98:2)

The procedure was operated with the general procedure. The product **3e** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (76%, 32.1 mg). This compound is known.²

¹H NMR (400 MHz, CDCl₃): 7.39 (s, 4H), 7.04 (dt, *J* = 16.1, 2.5 Hz, 1H), 6.27 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.32 (s, 9H). ¹³C NMR (100 MHz, CDCl₃): 163.9 (t, *J* = 34.9 Hz), 153.0, 136.5 (t, *J* = 9.4 Hz),

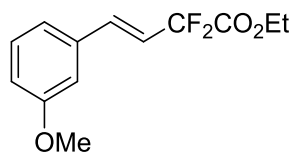
131.3, 127.2, 125.7, 117.9 (t, $J = 24.9$ Hz), 112.8 (t, $J = 246.8$ Hz), 62.9, 34.7, 31.1, 13.9. ^{19}F NMR (376 MHz, CDCl_3): -103.0.



Ethyl-2,2-difluoro-4-(2-methoxyphenyl)but-3-enoate (3f, $E/Z = 98:2$)

The procedure was operated with the general procedure. The product **3f** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless solid (82%, 31.4 mg). This compound is known.¹

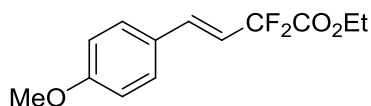
^1H NMR (400 MHz, CDCl_3): 7.42 (d, $J = 7.4$ Hz, 1H), 7.38-7.29 (m, 2H), 6.96-6.88 (m, 2H), 6.40 (dt, $J = 16.1, 11.4$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.86 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 164.1 (t, $J = 34.9$ Hz), 157.7, 132.1 (t, $J = 9.7$ Hz), 130.7, 128.3, 122.9, 120.6, 119.2 (t, $J = 24.6$ Hz), 113.0 (t, $J = 246.6$ Hz), 111.0, 62.9, 55.3, 13.9. ^{19}F NMR (376 MHz, CDCl_3): -102.8.



Ethyl-2,2-difluoro-4-(3-methoxyphenyl)but-3-enoate (3g, $E/Z = 99:1$),

The procedure was operated with the general procedure. The product **3g** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (85%, 32.6 mg). This compound is known.¹

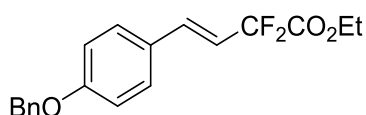
^1H NMR (400 MHz, CDCl_3): 7.28 (t, $J = 7.9$ Hz, 1H), 7.07-7.02 (m, 2H), 6.96 (s, 1H), 6.90 (dd, $J = 8.1, 2.2$ Hz, 1H), 6.29 (dt, $J = 16.2, 11.4$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.82 (s, 3H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.8, (t, $J = 34.2$ Hz), 159.9, 136.7 (t, $J = 9.3$ Hz), 135.4, 129.8, 120.0, 119.1 (t, $J = 25.0$ Hz), 115.3, 112.6 (t, $J = 246.9$ Hz), 112.5, 63.1, 55.2, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -102.8.



Ethyl-2, 2-difluoro-4-(4-methoxy)but-3-enoate (3h, *E/Z* = 99:1)

The procedure was operated with the general procedure. The product **3h** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (82%, 31.4 mg). This compound is known.¹

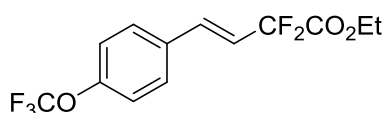
¹H NMR (400 MHz, CDCl₃): 7.37 (d, *J* = 8.7 Hz, 2H), 7.02 (dt, *J* = 16.1, 2.4 Hz, 1H), 6.89 (d, *J* = 8.7 Hz, 2H), 6.15 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 3.81 (s, 3H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 164.0 (t, *J* = 35.0 Hz), 160.7, 136.2 (t, *J* = 9.4 Hz), 128.8, 126.7, 116.3 (t, *J* = 24.8 Hz), 114.1, 112.9 (t, *J* = 246.6 Hz), 62.9, 55.2, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -102.7.



Ethyl-2, 2-difluoro-4-(4-benzyloxy)but-3-enoate (3i, *E/Z* = 99:1)

The procedure was operated with the general procedure. The product **3i** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (72%, 35.7 mg). This compound is known.¹

¹H NMR (400 MHz, CDCl₃): 7.42-7.30 (m, 7H), 7.02 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.14 (dt, *J* = 16.1, 11.4 Hz, 1H), 5.07 (s, 2H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 9.3 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 164.0 (t, *J* = 35.0 Hz), 159.9, 136.5, 136.2 (t, *J* = 9.4 Hz), 128.9, 128.6, 128.0, 127.4, 127.0, 116.5 (t, *J* = 24.9 Hz), 115.1, 112.8 (t, *J* = 246.7 Hz), 70.0, 62.9, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -102.6.

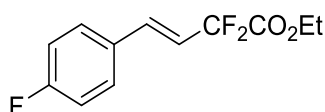


Ethyl-2,2-difluoro-4-(4-(trifluoromethoxy)phenyl)but-3-enoate (3j, *E/Z* = 85:15)

The procedure was operated with the general procedure. The product **3j** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless solid (90%, 41.8

mg). This compound is known.¹

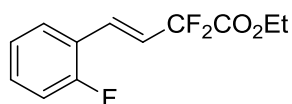
¹H NMR (400 MHz, CDCl₃): 7.46 (d, *J* = 8.8 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.05 (dt, *J* = 16.0, 2.4 Hz, 1H), 6.28 (dt, *J* = 16.0, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.7 (t, *J* = 34.5 Hz), 149.9, 135.2 (t, *J* = 9.4 Hz), 132.7, 128.8, 121.1, 120.5 (q, *J* = 113.6 Hz), 119.9 (t, *J* = 25.0 Hz), 112.4 (t, *J* = 247.3 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -57.8 (s, 3F), -103.3 (s, 2F).



Ethyl-2,2-difluoro-4-(4-fluorophenyl)but-3-enoate (3k, *E/Z* = 97:3)

The procedure was operated with the general procedure. The product **3k** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (86%, 31.4 mg). This compound is known.¹

¹H NMR (400 MHz, CDCl₃): 7.43 (dd, *J* = 8.4, 5.2 Hz, 2H), 7.08-7.02 (m, 3H), 6.22 (dt, *J* = 16.1, 11.3 Hz, 1H), 4.34 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.8 (t, *J* = 34.6 Hz), 162.2 (t, *J* = 248.5 Hz), 135.5 (t, *J* = 9.5 Hz), 130.3, 129.2 (d, *J* = 8.2 Hz), 118.5 (td, *J* = 23.8, 2.0 Hz), 115.8 (d, *J* = 21.8 Hz), 112.5 (t, *J* = 246.9 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.1 (s, 2F), -110.9 (s, F).

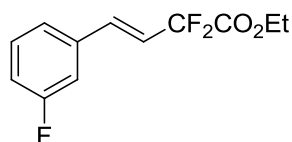


Ethyl-2,2-difluoro-4-(2-fluorophenyl)but-3-enoate (3l, *E/Z* = 84:16)

The procedure was operated with the general procedure. The product **3l** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (62%, 22.6 mg). This compound is known.¹

¹H NMR (400 MHz, CDCl₃): 7.46 (td, *J* = 7.6, 1.5 Hz, 1H), 7.35-7.29 (m, 1H), 7.22 (dt, *J* = 16.4, 2.6 Hz, 1H), 7.16-7.05 (m, 2H), 6.42 (dt, 16.1, 11.3 Hz, 1H), 4.36 (q, *J*

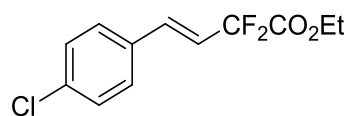
= 7.1 Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.7 (t, $J = 34.6$ Hz), 162.1 (t, $J = 251.0$ Hz), 131.1 (d, $J = 8.9$ Hz), 129.7 (td, $J = 9.7, 3.1$ Hz), 128.6 (d, $J = 2.7$ Hz), 124.3 (d, $J = 3.6$ Hz), 122.1 (d, $J = 11.6$ Hz), 121.5 (td, $J = 24.8, 6.6$ Hz), 116.1 (d, $J = 21.8$ Hz), 112.5 (t, $J = 247.2$ Hz), 63.1, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -103.6 (s, 2F), -115.7 (s, F).



Ethyl-2,2-difluoro-4-(3-fluorophenyl)but-3-enoate (3m, $E/Z = 77:23$)

The procedure was operated with the general procedure. The product **3m** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (72%, 26.3 mg). This compound is known.²

^1H NMR (400 MHz, CDCl_3): 7.36-7.28 (m, 1H), 7.21 (d, $J = 7.6$ Hz, 1H), 7.15 (d, $J = 9.8$ Hz, 1H), 7.06-7.02 (m, 2H), 6.31 (dt, 16.1, 11.3 Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.6 (t, $J = 34.4$ Hz), 161.7 (t, $J = 245.1$ Hz), 136.3 (d, $J = 7.9$ Hz), 135.7 (td, $J = 9.4, 2.4$ Hz), 130.4 (d, $J = 8.1$ Hz), 123.4 (d, $J = 2.0$ Hz), 120.2 (t, $J = 25.0$ Hz), 116.5 (d, $J = 21.2$ Hz), 113.9 (d, $J = 22.0$ Hz), 112.4 (t, $J = 247.2$ Hz), 63.1, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -103.4 (s, 2F), -112.6 (s, F).

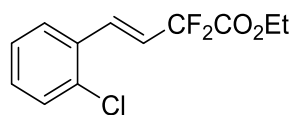


Ethyl-4-(4-chlorophenyl)-2,2-difluorobut-3-enoate (3n, $E/Z = 93:7$)

The procedure was operated with the general procedure. The product **3n** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (64%, 25.0 mg). This compound is known.¹

^1H NMR (400 MHz, CDCl_3): 7.35 (dd, $J = 16.0, 8.8$ Hz, 4H), 7.02 (dt, $J = 16.1, 2.4$ Hz, 1H), 6.28 (dt, $J = 16.2, 11.3$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.7 (t, $J = 34.5$ Hz), 135.53 (t, $J = 10.0$ Hz),

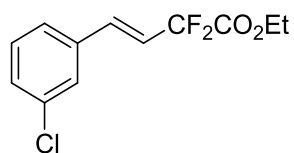
135.49, 132.5, 129.0, 128.6, 119.4 (t, $J = 25.0$ Hz), 112.5 (t, $J = 247.3$ Hz), 63.1, 13.9.
 ^{19}F NMR (376 MHz, CDCl_3): -103.3.



Ethyl-4-(2-chlorophenyl)-2,2-difluorobut-3-enoate (3o, $E/Z = 85:15$)

The procedure was operated with the general procedure. The product **3o** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (60%, 23.4 mg). This compound is known.¹

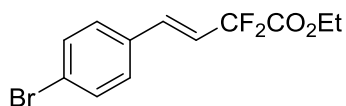
^1H NMR (400 MHz, CDCl_3): 7.56-7.53 (m, 1H), 7.51 (dt, $J = 16.2, 2.4$ Hz, 1H), 7.40-7.37 (m, 1H), 7.28-7.25 (m, 2H), 6.30 (dt, $J = 16.4, 11.3$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.37 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.6 (t, $J = 34.5$ Hz), 134.2, 133.1 (t, $J = 9.6$ Hz), 130.5, 130.0, 127.3, 127.0, 121.5 (t, $J = 25.0$ Hz), 112.4 (t, $J = 247.2$ Hz), 63.1, 13.9. ^{19}F NMR (376 MHz, CDCl_3): -103.1.



Ethyl-4-(3-chlorophenyl)-2,2-difluorobut-3-enoate (3p, $E/Z = 76:24$)

The procedure was operated with the general procedure. The product **3p** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (60%, 23.4 mg). This compound is known.¹

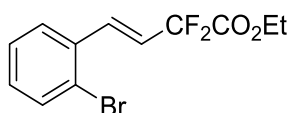
^1H NMR (400 MHz, CDCl_3): 7.43 (s, 1H), 7.33-7.27 (m, 3H), 7.00 (dt, $J = 16.0, 2.4$ Hz, 1H), 6.30 (dt, $J = 16.2, 11.3$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.6 (t, $J = 34.3$ Hz), 135.8, 135.4 (t, $J = 9.4$ Hz), 134.8, 130.0, 129.5, 127.2, 125.5, 120.3 (t, $J = 24.8$ Hz), 112.3 (t, $J = 247.6$ Hz), 63.2, 13.9. ^{19}F NMR (376 MHz, CDCl_3): -103.5.



Ethyl-4-(4-bromophenyl)-2,2-difluorobut-3-enoate (3q, *E/Z* = 88:12)

The procedure was operated with the general procedure. The product **3q** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (67%, 30.7 mg). This compound is known.¹

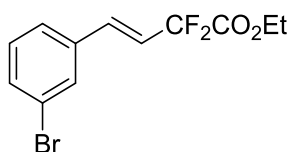
¹H NMR (400 MHz, CDCl₃): 7.48 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.8 Hz, 2H), 7.02 (dt, *J* = 16.4, 2.4 Hz, 1H), 6.29 (dt, *J* = 16.2, 11.3 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.6 (t, *J* = 34.5 Hz), 135.5 (t, *J* = 10.0 Hz), 132.9, 131.9, 128.8, 123.7, 119.5 (t, *J* = 25.0 Hz), 112.4 (t, *J* = 247.3 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.3.



Ethyl-4-(2-bromophenyl)-2,2-difluorobut-3-enoate (3r, *E/Z* = 82:18)

The procedure was operated with the general procedure. The product **3r** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (60%, 27.4 mg). This compound is known.²

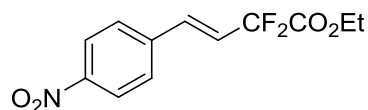
¹H NMR (400 MHz, CDCl₃): 7.58 (d, *J* = 8.0 Hz, 1H), 7.52 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.47 (dt, *J* = 16.2, 2.4 Hz, 1H), 7.33-7.29 (m, 1H), 7.22-7.18 (m, 1H), 6.28 (dt, *J* = 16.1, 11.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.5 (t, *J* = 34.2 Hz), 135.7 (t, *J* = 9.6 Hz), 133.2, 130.7, 127.7, 127.4, 124.5, 121.6 (t, *J* = 25.0 Hz), 112.3 (t, *J* = 247.1 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.0.



Ethyl-4-(3-bromophenyl)-2,2-difluorobut-3-enoate (3s, *E/Z* = 80:20)

The procedure was operated with the general procedure. The product **3s** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (65%, 29.7 mg).

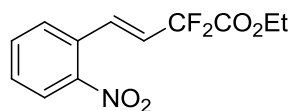
¹H NMR (400 MHz, CDCl₃): 7.59 (s, 1H), 7.46 (d, *J* = 8.9 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.27-7.21 (m, 1H), 7.02 (dt, *J* = 16.2, 2.3 Hz, 1H), 6.31 (dt, *J* = 16.2, 11.2 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.6 (t, *J* = 34.4 Hz), 136.1, 135.3 (t, *J* = 9.4 Hz), 132.4, 130.3, 130.1, 126.1, 122.9, 120.4 (t, *J* = 24.9 Hz), 112.3 (t, *J* = 247.4 Hz), 63.2, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.4. HRMS (ESI) (*m/z*): [M+NH₄]⁺ calcd. for C₁₂H₁₁BrF₂O₂: 322.0249, found: 322.0253.



Ethyl-2,2-difluoro-4-(4-nitrophenyl)but-3-enoate (3t, *E/Z* = 85:15)

The procedure was operated with the general procedure. The product **3t** was purified with flash silica gel chromatography (PE/EA = 60:1) as a yellow solid (61%, 24.7 mg). This compound is known.¹

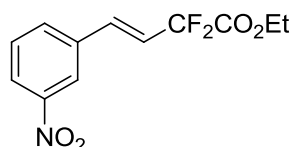
¹H NMR (400 MHz, CDCl₃): 8.23 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.14 (dt, *J* = 16.2, 2.4 Hz, 1H), 6.46 (dt, *J* = 16.2, 11.1 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.3 (t, *J* = 34.4 Hz), 148.2, 140.2, 134.5 (t, *J* = 9.2 Hz), 128.1, 124.1, 123.2 (t, *J* = 25.1 Hz), 112.0 (t, *J* = 248.0 Hz), 63.4, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.9.



Ethyl-2,2-difluoro-4-(2-nitrophenyl)but-3-enoate (3u, *E/Z* = 91:9)

The procedure was operated with the general procedure. The product **3u** was purified with flash silica gel chromatography (PE/EA = 60:1) as a yellow solid (56%, 22.7mg). This compound is known.¹

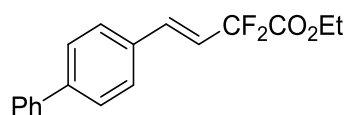
^1H NMR (400 MHz, CDCl_3): 8.04 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.68-7.51 (m, 4H), 6.26 (dt, $J = 16.0, 10.8$ Hz, 1H), 4.37 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.3 (t, $J = 34.0$ Hz), 147.9, 133.6, 133.2 (t, $J = 10.0$ Hz), 130.3, 129.9, 129.1, 124.9, 123.9 (t, $J = 25.5$ Hz), 112.0 (t, $J = 247.5$ Hz), 63.3, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -103.2.



Ethyl-2,2-difluoro-4-(3-nitrophenyl)but-3-enoate (3v, $E/Z = 58:42$)

The procedure was operated with the general procedure. The product **3v** was purified with flash silica gel chromatography (PE/EA = 60:1) as a yellow solid (42%, 17.0 mg).

^1H NMR (400 MHz, CDCl_3): 8.32 (t, $J = 1.7$ Hz, 1H), 8.24-8.17 (m, 2H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.60-7.56 (m, 1H), 7.15 (dt, $J = 16.2, 2.5$ Hz, 1H), 6.48 (dt, $J = 16.0, 10.8$ Hz, 1H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.38 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.3 (t, $J = 34.1$ Hz), 163.1 (t, $J = 33.3$ Hz), 148.6, 136.0 (t, $J = 7.5$ Hz), 135.8, 134.7 (t, $J = 3.0$ Hz), 134.4 (t, $J = 9.8$ Hz), 133.1, 129.9, 129.1, 124.9, 124.1 (t, $J = 26.2$ Hz), 124.0, 123.7 (t, $J = 3.0$ Hz), 123.2, 122.1 (t, $J = 25.0$ Hz), 121.9, 112.1 (t, $J = 247.8$ Hz), 111.9 (t, $J = 247.2$ Hz), 63.3, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -103.7. HRMS (ESI) (m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{12}\text{H}_{11}\text{F}_2\text{NO}_4$: 310.0288, found: 310.0290.

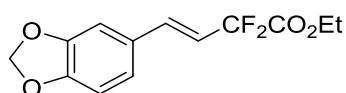


Ethyl-2,2-difluoro-4-([1,1'-biphenyl]-4-yl)but-3-enoate (3w, $E/Z = 99:1$)

The procedure was operated with the general procedure. The product **3w** was purified with flash silica gel chromatography (PE/EA = 60:1) as a white solid (66%, 29.8 mg).

This compound is known.²

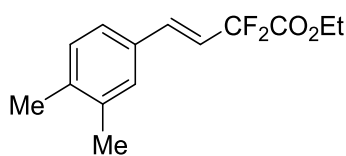
^1H NMR (400 MHz, CDCl_3): 7.55 (d, $J = 8.3$ Hz, 4H), 7.48 (d, $J = 8.2$ Hz, 2H), 7.41 (t, $J = 7.3$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.08 (d, 16.2 Hz, 1H), 6.32 (dt, 16.1, 11.3 Hz, 1H), 4.32 (q, $J = 7.1$ Hz, 2H), 1.33 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.8 (t, $J = 34.6$ Hz), 142.3, 140.0, 136.3 (t, $J = 9.4$ Hz), 132.9, 128.8, 127.8, 127.6, 127.3, 126.9, 118.6 (t, $J = 25.0$ Hz), 112.7 (t, $J = 246.9$ Hz), 63.0, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -102.9.



Ethyl-2,2-difluoro-4-(benzo[d][1,3]dioxol-5-yl)but-3-enoate (3x, $E/Z = 99:1$)

The procedure was operated with the general procedure. The product **3x** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (78%, 31.5 mg). This compound is known.¹

^1H NMR (400 MHz, CDCl_3): 6.99-6.94 (m, 2H), 6.89 (d, $J = 8.0$ Hz, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.12 (dt, $J = 16.1, 11.4$ Hz, 1H), 5.98 (s, 2H), 4.34 (q, $J = 7.1$ Hz, 2H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.9 (t, $J = 34.7$ Hz), 148.9, 148.2, 136.3 (t, $J = 9.4$ Hz), 128.4, 123.1, 116.7 (t, $J = 24.8$ Hz), 112.8 (t, $J = 246.9$ Hz), 108.3, 106.1, 101.4, 63.0, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -102.6.

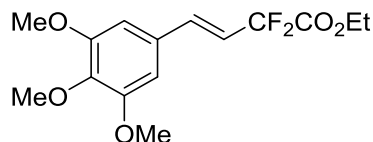


Ethyl-2,2-difluoro-4-(3,4-dimethylphenyl)but-3-enoate (3y, $E/Z = 99:1$)

The procedure was operated with the general procedure. The product **3y** was purified with flash silica gel chromatography (PE/EA = 60:1) as a yellow clear liquid (82 %, 31.2 mg). This compound is known.²

^1H NMR (400 MHz, CDCl_3): 7.21 (s, 1H), 7.16 (d, $J = 7.8$ Hz, 1H), 7.10 (d, $J = 7.7$ Hz, 1H), 7.02 (dt, $J = 16.1, 2.4$ Hz, 1H), 6.23 (dt, $J = 16.0, 11.4$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 2.25 (s, 6H), 1.35 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 164.0 (t, $J = 35.0$ Hz), 138.5, 137.0, 136.8 (t, $J = 9.3$ Hz), 131.7, 130.0, 128.5, 124.9,

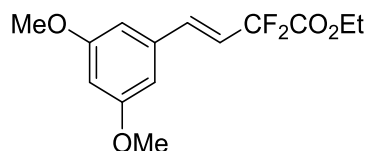
117.5 (t, $J = 24.8$ Hz), 112.8 (t, $J = 247.1$ Hz), 62.9, 19.64, 19.60, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -102.8.



Ethyl-2,2-difluoro-4-(3,4,5-trimethoxyphenyl)but-3-enoate (3z, $E/Z = 98:2$)

The procedure was operated with the general procedure. The product **3z** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (75 %, 35.5 mg). This compound is known.¹

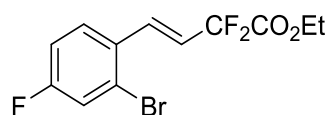
^1H NMR (400 MHz, CDCl_3): 7.02 (dt, $J = 16.1, 2.4$ Hz, 1H), 6.67 (s, 2H), 6.22 (dt, $J = 16.0, 11.4$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 3.88 (s, 6H), 3.86 (s, 3H) 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.8 (t, $J = 34.7$ Hz), 153.3, 139.4, 136.7 (t, $J = 9.4$ Hz), 129.5, 118.0 (t, $J = 24.9$ Hz), 112.6 (t, $J = 247.1$ Hz), 104.5, 63.0, 60.7, 13.8. ^{19}F NMR (376 MHz, CDCl_3): -102.9.



Ethyl-2,2-difluoro-4-(3,5-dimethoxyphenyl)but-3-enoate (3aa, $E/Z = 98:2$)

The procedure was operated with the general procedure. The product **3aa** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (55 %, 23.5 mg).

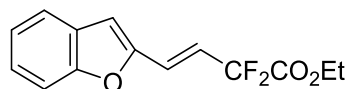
^1H NMR (400 MHz, CDCl_3): 7.01 (dt, $J = 16.1, 2.4$ Hz, 1H), 6.58 (d, $J = 2.0$ Hz, 2H), 6.46 (t, $J = 2.0$ Hz, 1H), 6.26 (dt, $J = 16.1, 11.4$ Hz, 1H), 4.34 (q, $J = 7.1$ Hz, 2H), 3.80 (s, 6H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.8 (t, $J = 34.5$ Hz), 161.0, 136.8 (t, $J = 9.3$ Hz), 135.9, 119.3 (t, $J = 24.8$ Hz), 112.6 (t, $J = 247.1$ Hz), 105.4, 101.7, 63.1, 55.3, 13.9. ^{19}F NMR (376 MHz, CDCl_3): -103.2. HRMS (ESI) (m/z): $[\text{M}+\text{K}]^+$ calcd. for $\text{C}_{14}\text{H}_{16}\text{F}_2\text{O}_4$: 325.0648, found: 325.0653.



Ethyl-2,2-difluoro-4-(2-bromo-4-fluorophenyl)but-3-enoate (3ab, *E/Z* = 80:20)

The procedure was operated with the general procedure. The product **3ab** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (62 %, 30.0 mg). This compound is known.¹

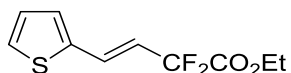
¹H NMR (400 MHz, CDCl₃): 7.53 (dd, *J* = 8.7, 5.8 Hz, 1H), 7.37 (dt, *J* = 16.0, 2.5 Hz, 1H), 7.33 (dd, *J* = 8.2, 2.6 Hz, 1H), 7.05 (td, *J* = 8.3, 2.5 Hz, 1H), 6.21 (dt, *J* = 16.1, 11.4 Hz, 1H), 4.36 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.5 (t, *J* = 34.5 Hz), 161.4 (d, *J* = 242.3 Hz), 134.5 (t, *J* = 9.6 Hz), 130.5 (d, *J* = 3.8 Hz), 128.5 (d, *J* = 8.7 Hz), 124.6 (d, *J* = 9.5 Hz), 124.6 (d, *J* = 9.5 Hz), 121.5 (t, *J* = 25.4 Hz), 120.5 (d, *J* = 24.4 Hz), 115.0 (t, *J* = 21.5 Hz), 112.2 (t, *J* = 248.3 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.0 (s, 2F), -109.0 (s, 1F).



Ethyl-2,2-difluoro-4-(benzofuran-2-yl)but-3-enoate (3ac, *E/Z* = 99:1)

The procedure was operated with the general procedure. The product **3ac** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (58%, 23.1 mg).

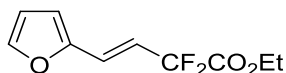
¹H NMR (400 MHz, CDCl₃): 7.55 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 7.35-7.31 (m, 1H), 7.22 (t, *J* = 8.2 Hz, 1H), 6.98 (dt, *J* = 15.8, 2.4 Hz, 1H), 6.81 (s, 1H), 6.51 (dt, *J* = 15.7, 12.0 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.6 (t, *J* = 34.6 Hz), 155.2, 151.6, 128.2, 126.0, 124.5 (t, *J* = 9.8 Hz), 123.2, 121.6, 119.8 (t, *J* = 25.0 Hz), 112.4 (t, *J* = 256.2 Hz), 111.2, 109.3, 63.2, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -103.7. HRMS (ESI) (*m/z*): [M+K]⁺ calcd. for C₁₄H₁₂F₂O₃: 305.0386, found: 305.0390.



Ethyl-2,2-difluoro-4-(thiophen-2-yl)but-3-enoate (3ad, *E/Z* = 99:1)

The procedure was operated with the general procedure. The product **3ad** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (70%, 24.3 mg). This compound is known.¹

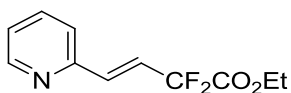
¹H NMR (400 MHz, CDCl₃): 7.31 (d, *J* = 4.9 Hz, 1H), 7.20-7.14 (m, 2H), 7.01 (dd, *J* = 4.8, 3.6 Hz, 1H), 6.12 (dt, *J* = 15.8, 11.5 Hz, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.7 (t, *J* = 34.7 Hz), 138.8, 129.7 (t, *J* = 10.0 Hz), 129.3, 127.7, 127.2, 117.5 (t, *J* = 25.1 Hz), 112.4 (t, *J* = 247.1 Hz), 63.1, 13.9. ¹⁹F NMR (376 MHz, CDCl₃): -102.8.



Ethyl-2,2-difluoro-4-(furan-2-yl)but-3-enoate (3ae, *E/Z* = 99:1)

The procedure was operated with the general procedure. The product **3ae** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (52%, 16.5 mg). This compound is known.¹

¹H NMR (400 MHz, CDCl₃): 7.43 (s, 1H), 6.87 (dt, *J* = 15.9, 2.5 Hz, 1H), 6.48 (d, *J* = 3.2 Hz, 1H), 6.42 (dd, *J* = 3.3, 1.8 Hz, 1H), 6.22 (dt, *J* = 15.8, 12.0 Hz, 1H), 4.32 (q, *J* = 7.1 Hz, 2H), 1.35 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃): 163.7 (t, *J* = 34.6 Hz), 150.1, 143.9, 124.1 (t, *J* = 10.1 Hz), 116.6 (t, *J* = 25.0 Hz), 112.7, 112.6 (t, *J* = 246.9 Hz), 111.8, 63.0, 13.8. ¹⁹F NMR (376 MHz, CDCl₃): -103.4.



Ethyl-2,2-difluoro-4-(pyridin-2-yl)but-3-enoate (3af, *E/Z* = 95:5)

The procedure was operated with the general procedure. The product **3af** was purified with flash silica gel chromatography (PE/EA = 60:1) as a colorless clear liquid (15%, 5.1 mg). This compound is known.²

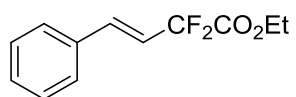
¹H NMR (400 MHz, CDCl₃): 8.62 (d, *J* = 4.2 Hz, 1H), 7.70 (td, *J* = 7.6, 1.7 Hz, 1H),

7.32 (d, $J = 7.7$ Hz, 1H), 7.26-7.23 (m, 1H), 7.14 (dt, $J = 15.8, 2.3$ Hz, 1H), 6.22 (dt, $J = 15.8, 11.8$ Hz, 1H), 4.35 (q, $J = 7.1$ Hz, 2H), 1.36 (t, $J = 7.1$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3): 163.5 (t, $J = 34.3$ Hz), 152.2, 149.8, 136.7, 135.8 (t, $J = 9.2$ Hz), 123.8, 123.5, 122.9 ($J = 24.8$ Hz), 112.6 (t, $J = 246.8$ Hz), 63.0, 13.7. ^{19}F NMR (376 MHz, CDCl_3): -103.8.

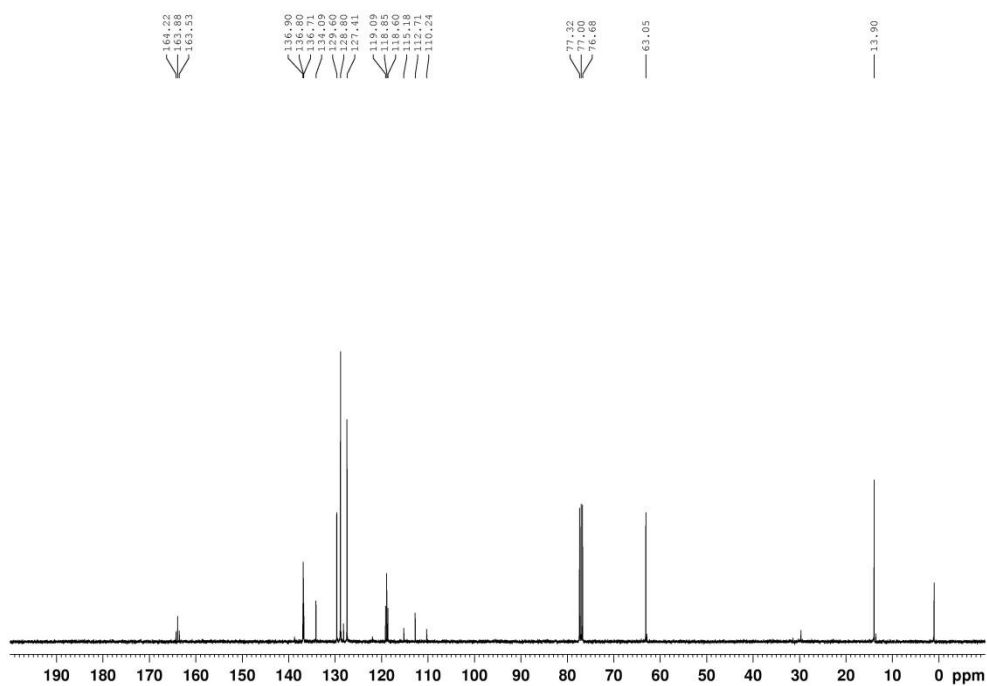
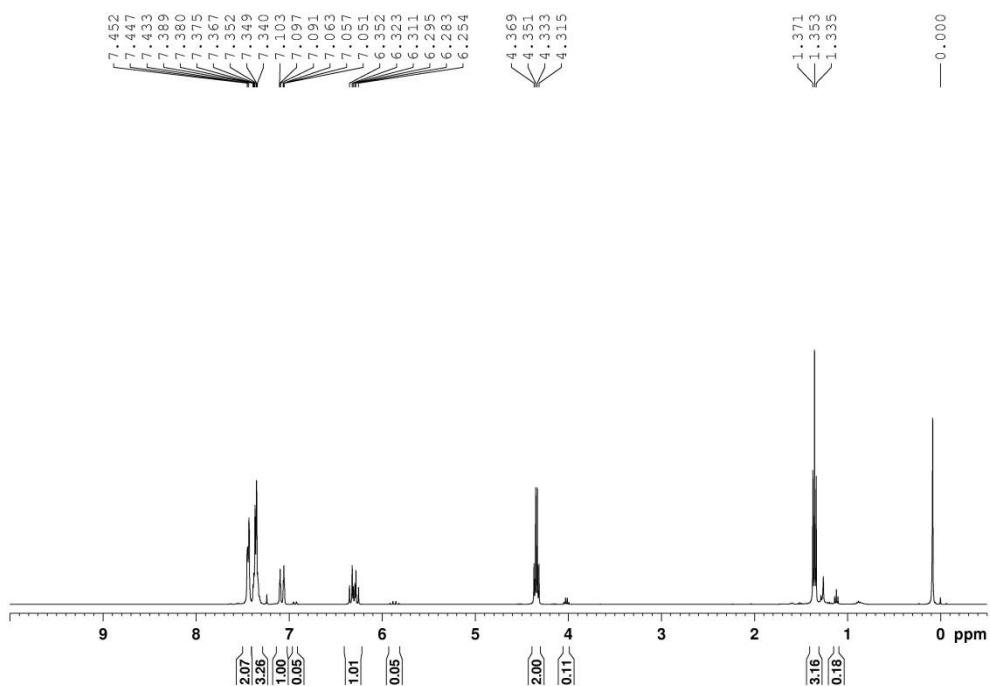
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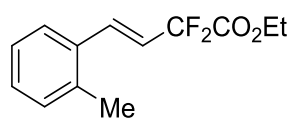
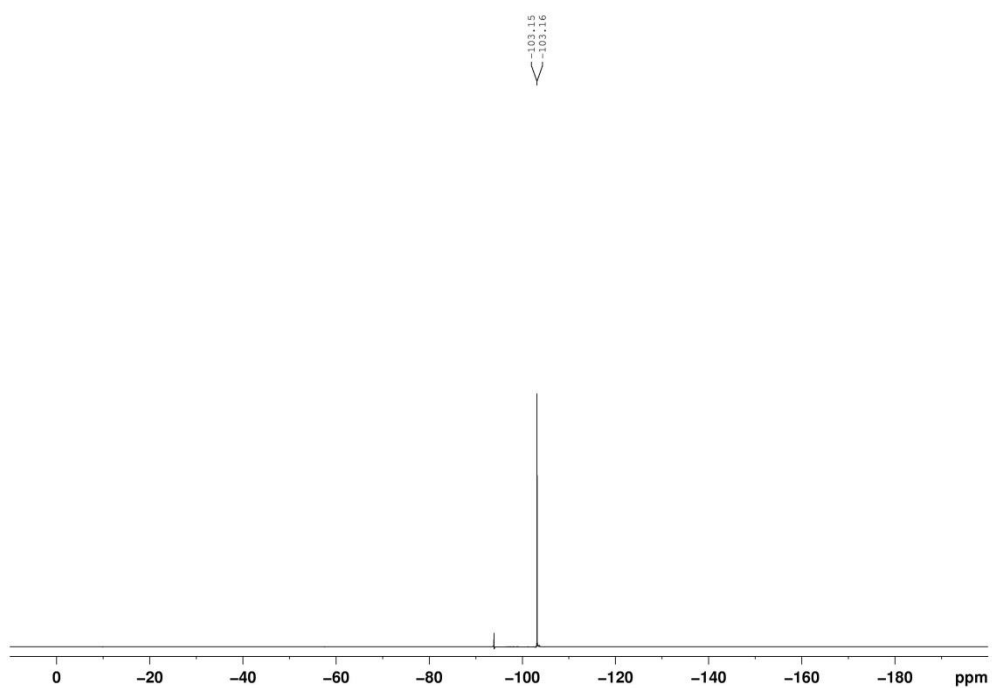
- 1) Li, G.; Wang, T.; Fei, F.; Su, Y. M.; Li, Y.; Lan, Q.; Wang, X. S. *Angew. Chem., Int. Ed.* **2016**, *55*, 3491-3495.
- 2) Ke, M.; Feng, Q.; Yang, K.; Song, Q. *Org. Chem. Front.* **2016**, *3*, 150-155.

¹H NMR and ¹³C NMR Spectra of the Products

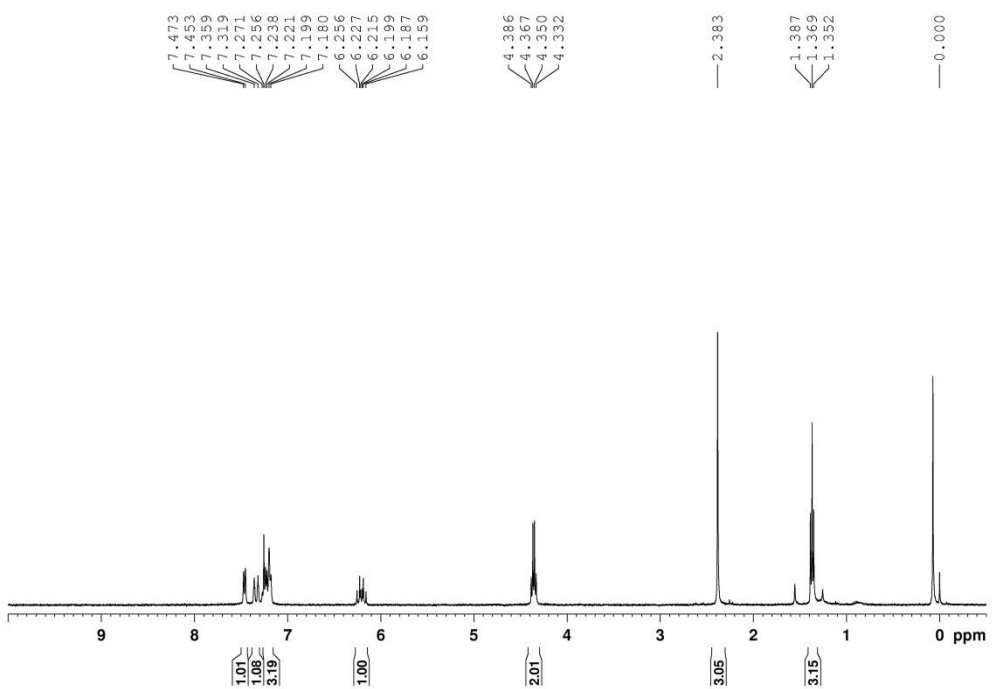


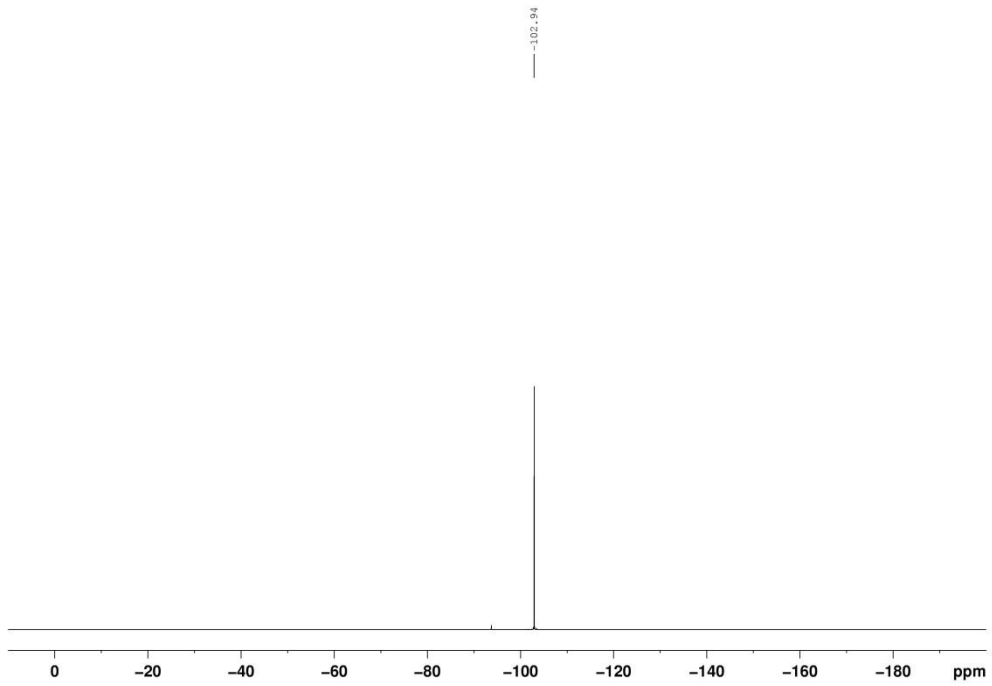
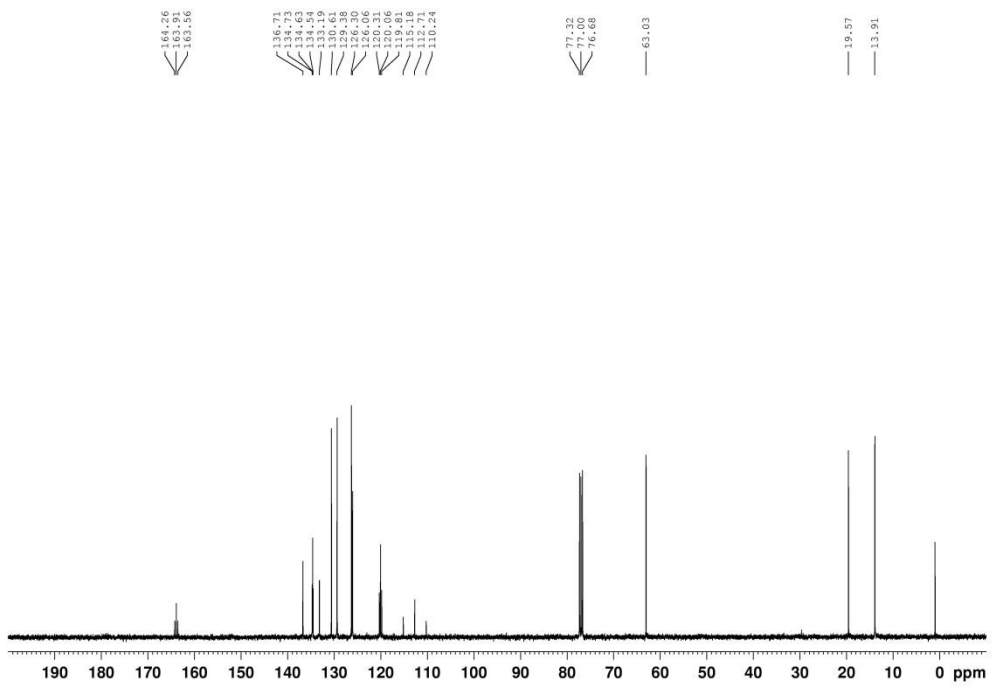
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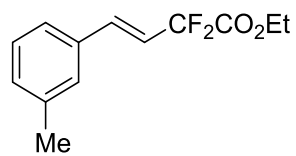




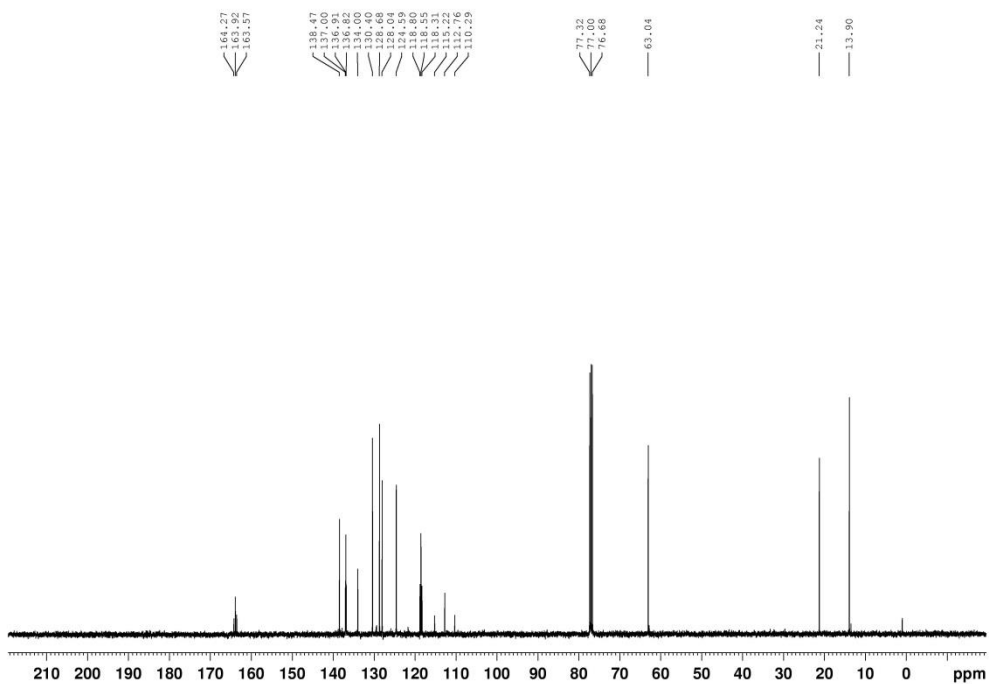
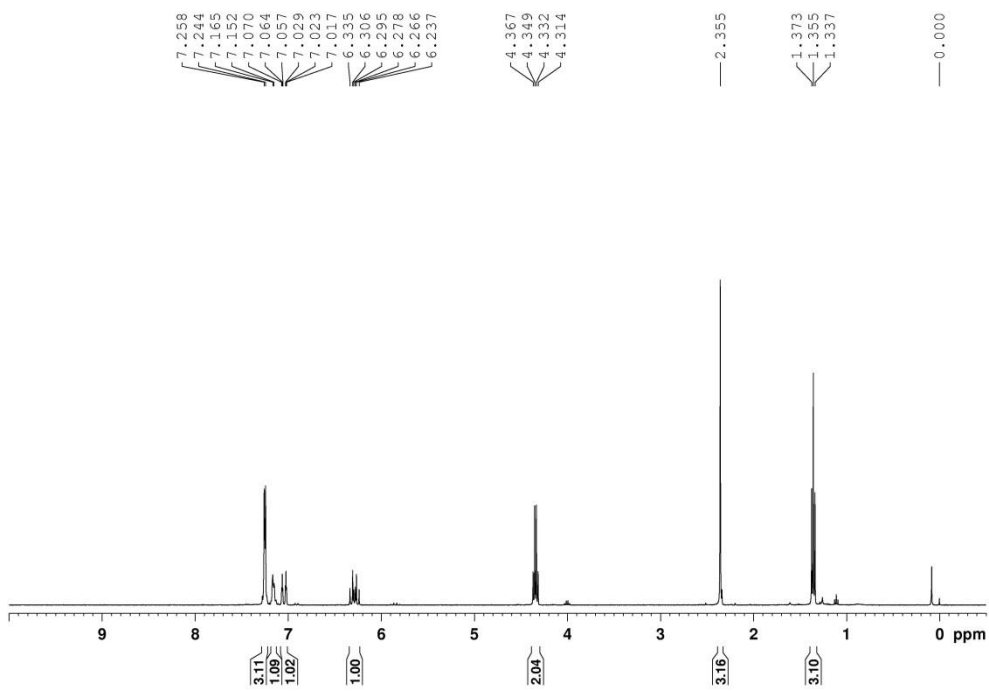
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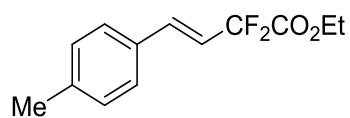
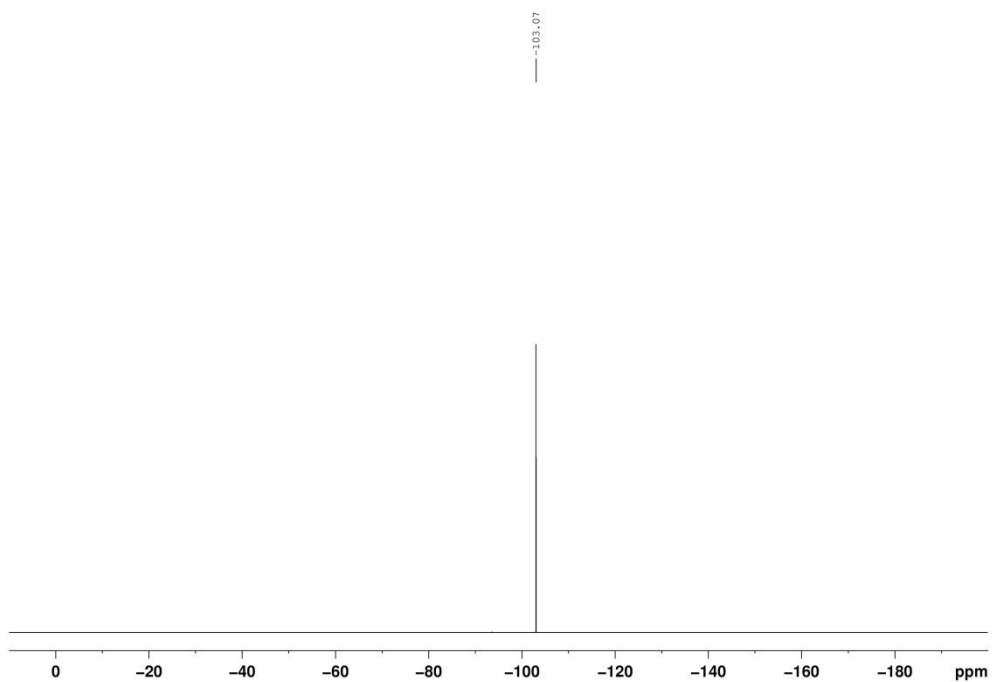




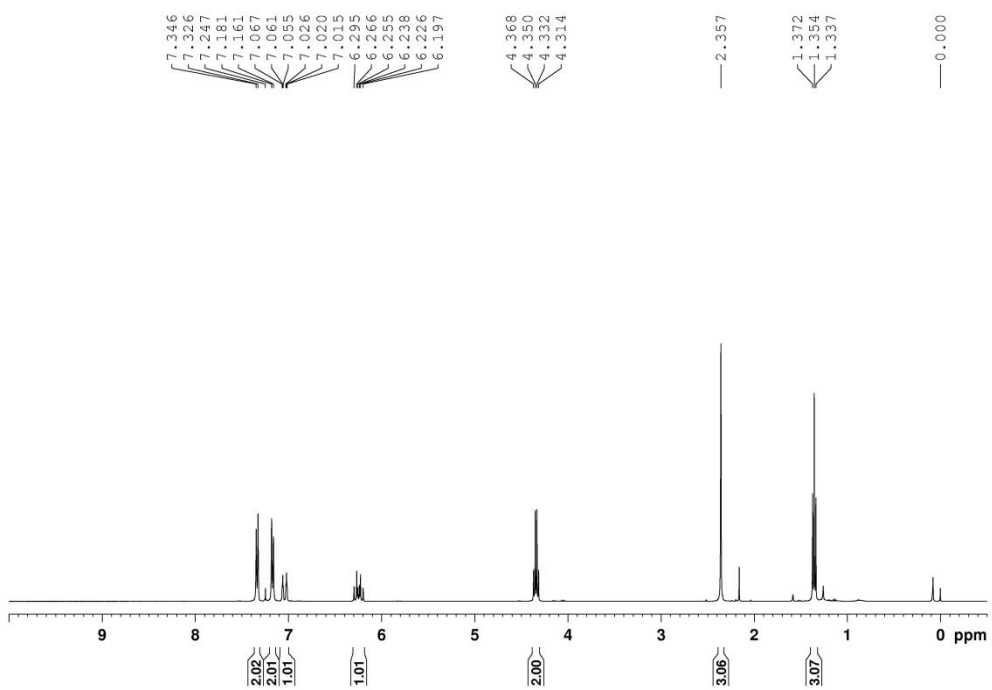


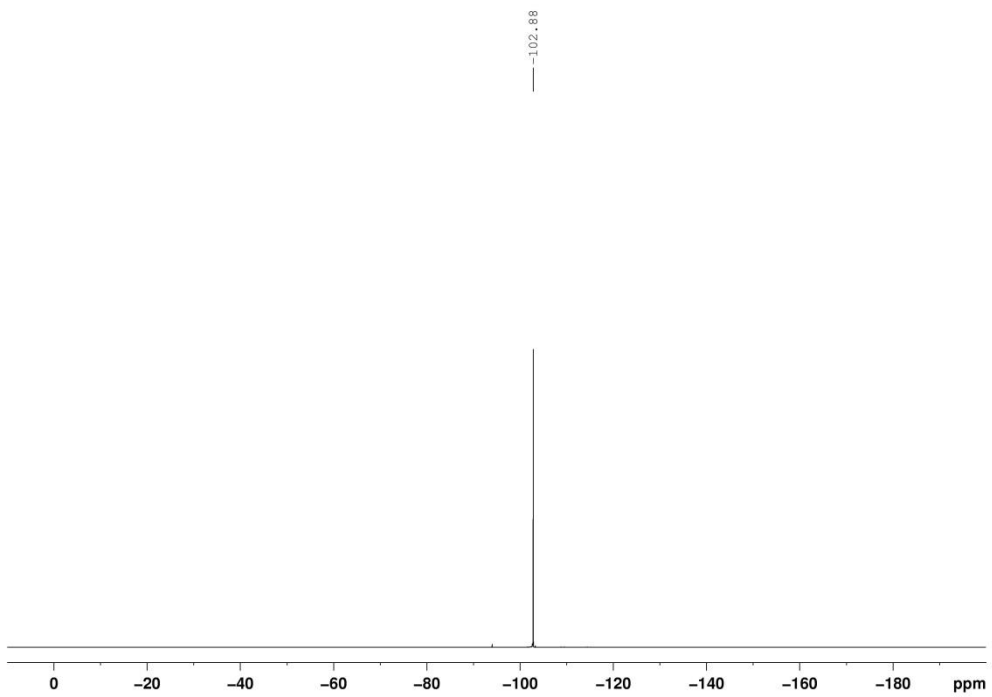
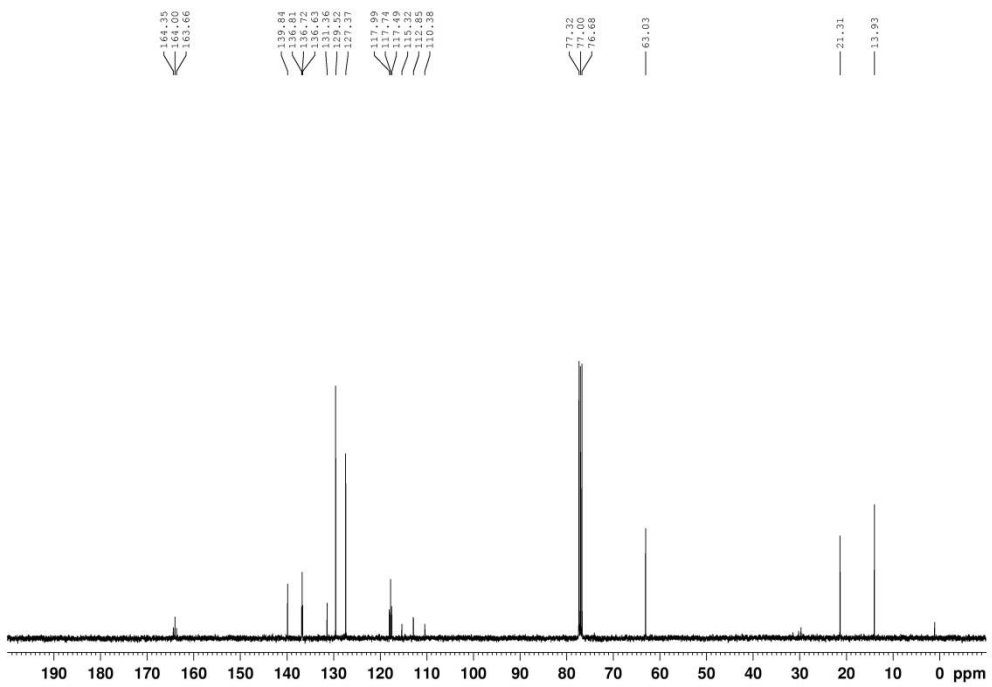
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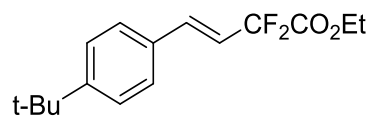




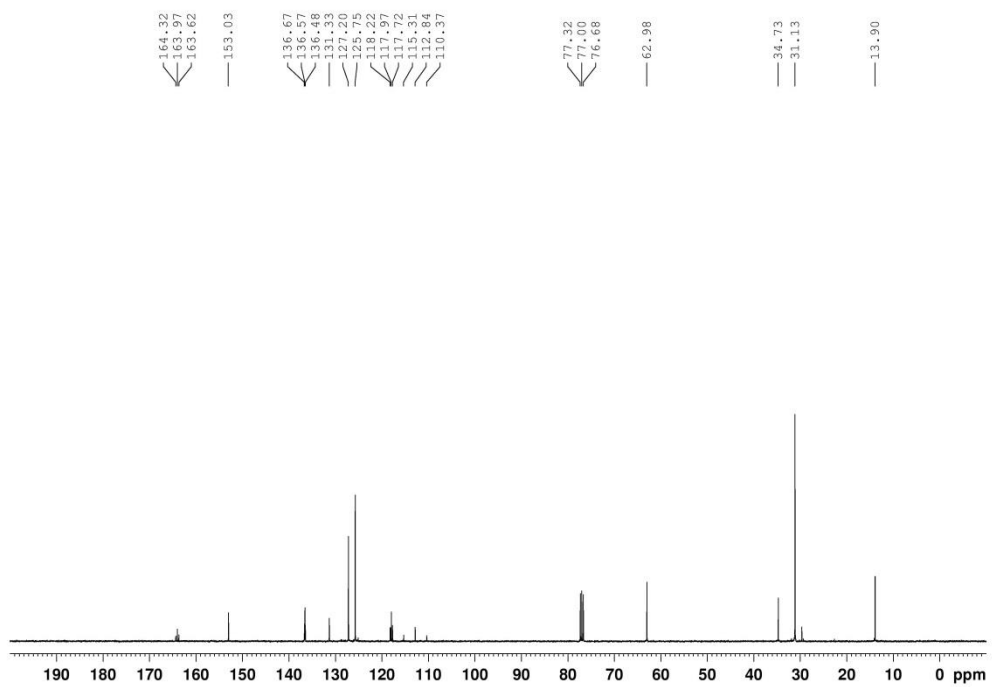
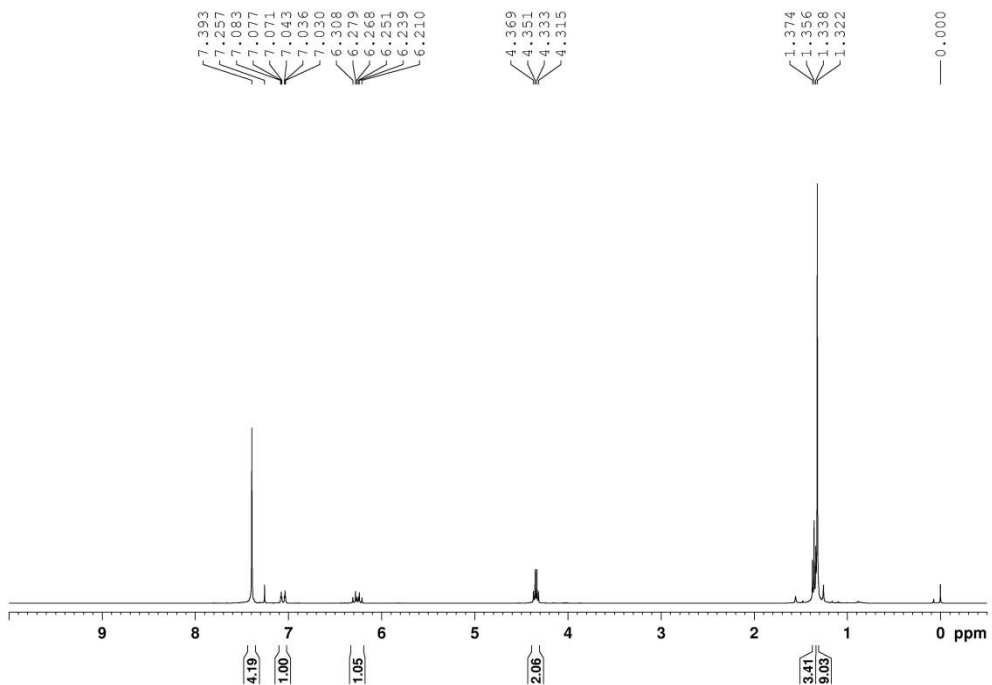
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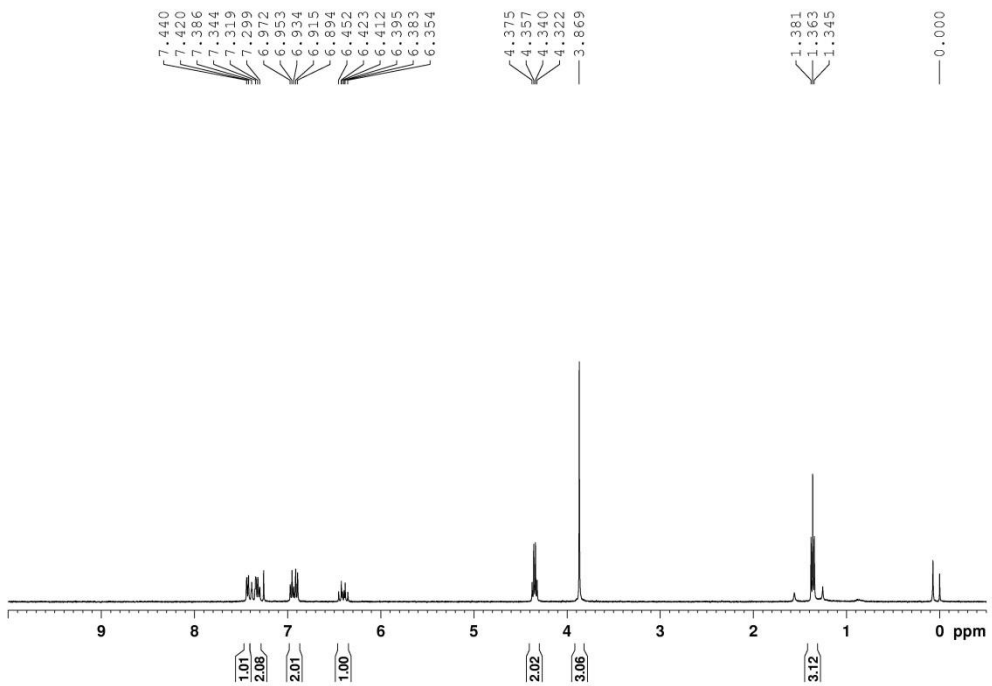
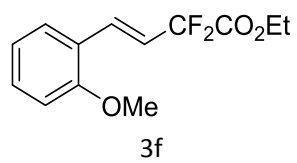
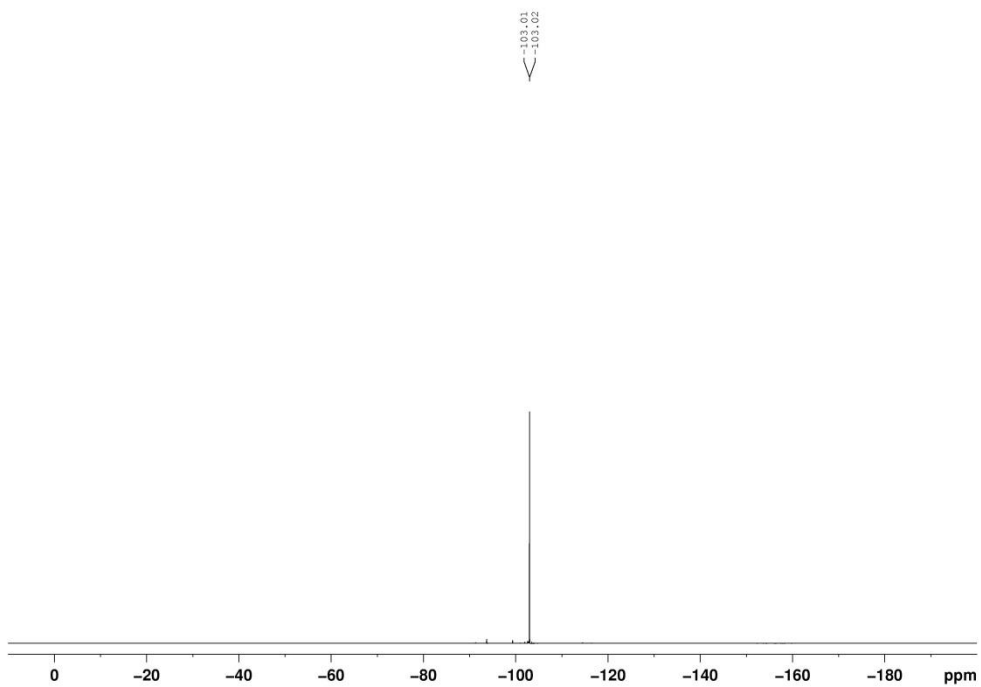


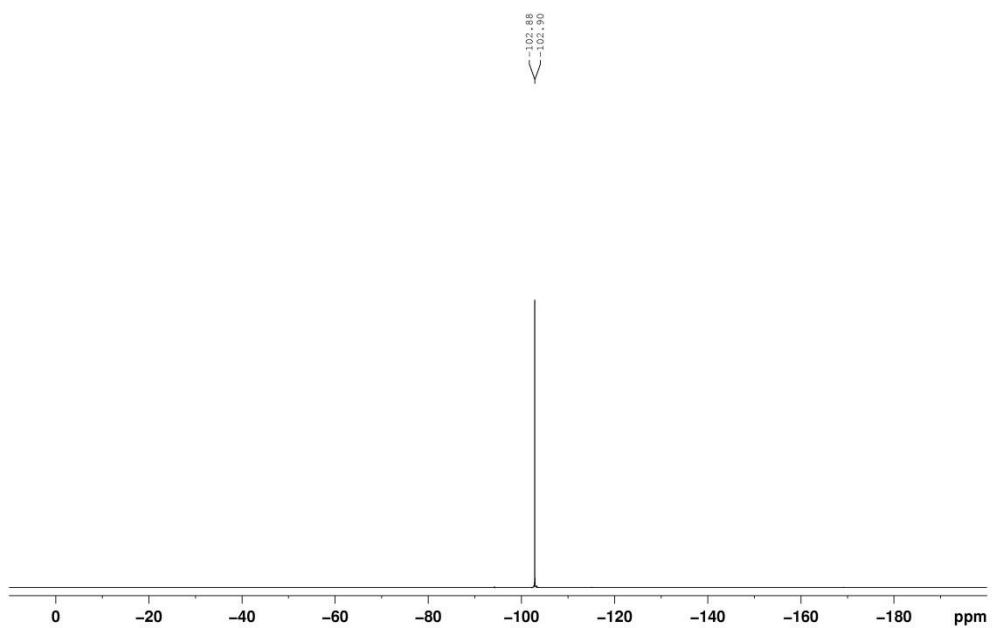
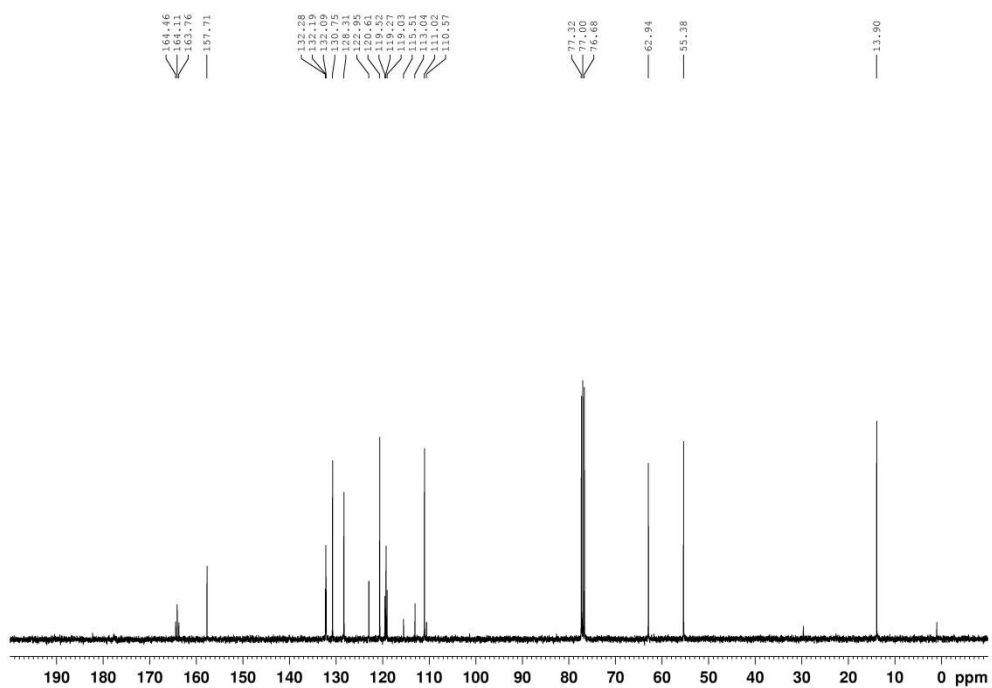


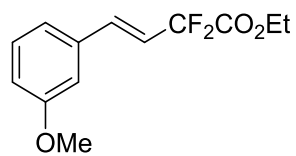


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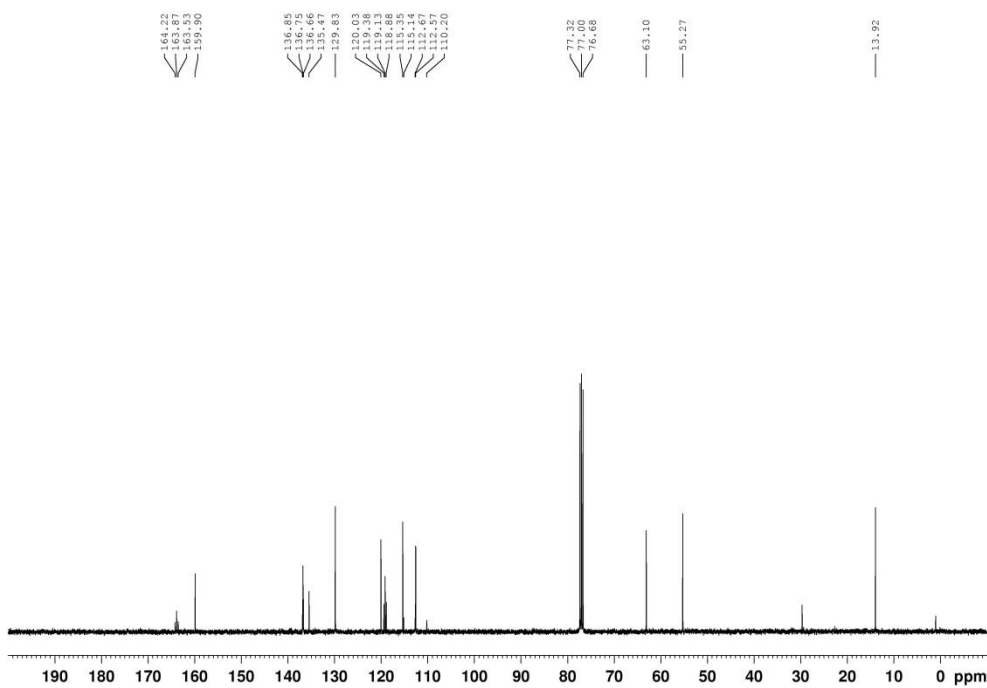
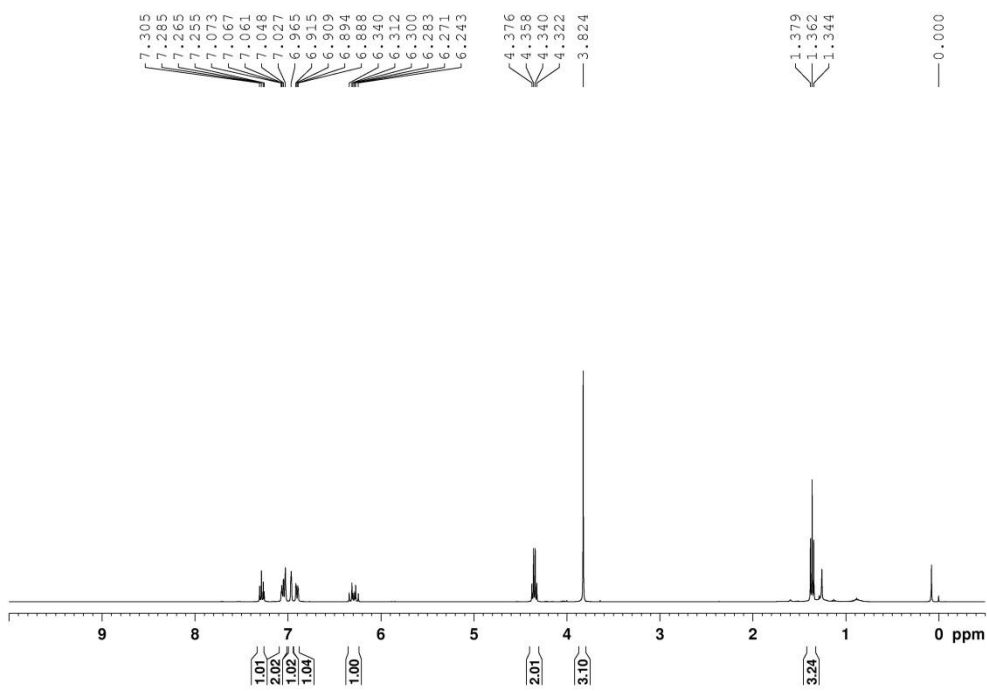


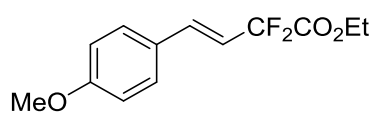
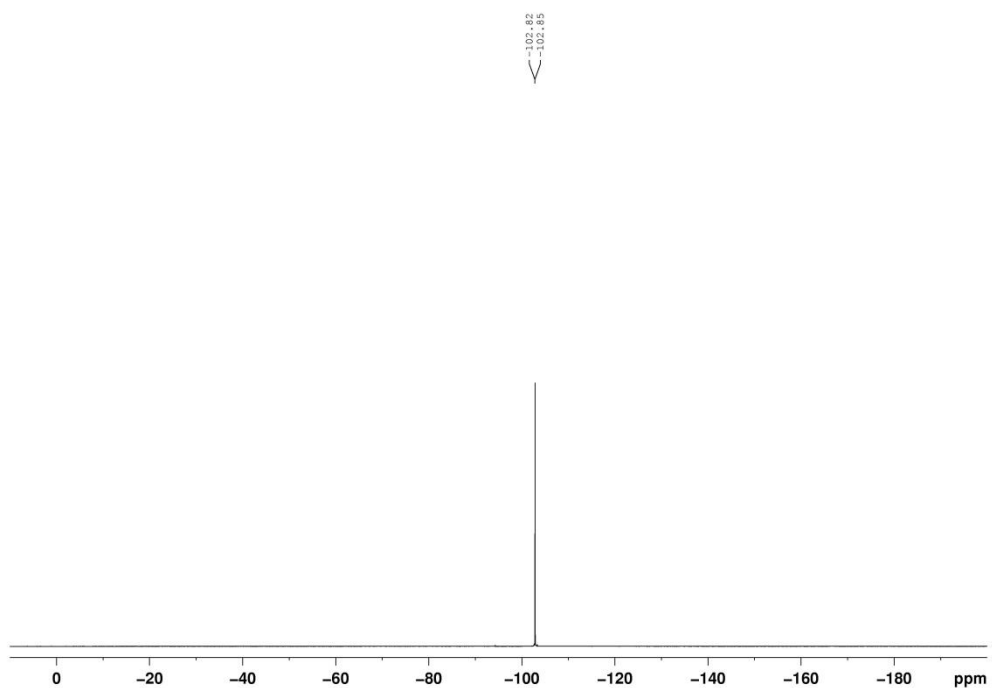




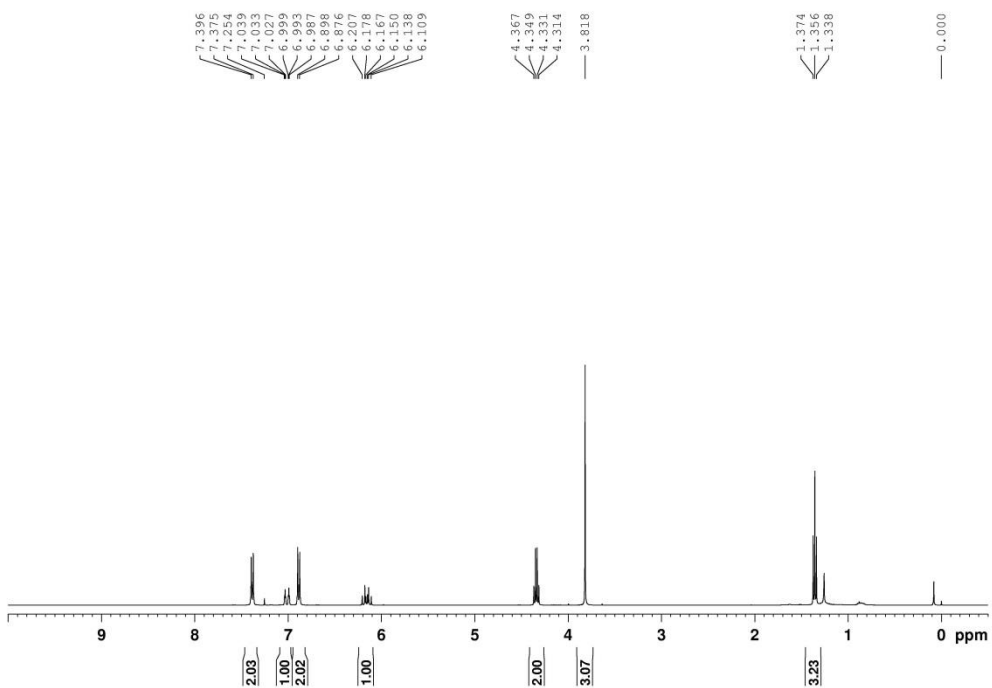


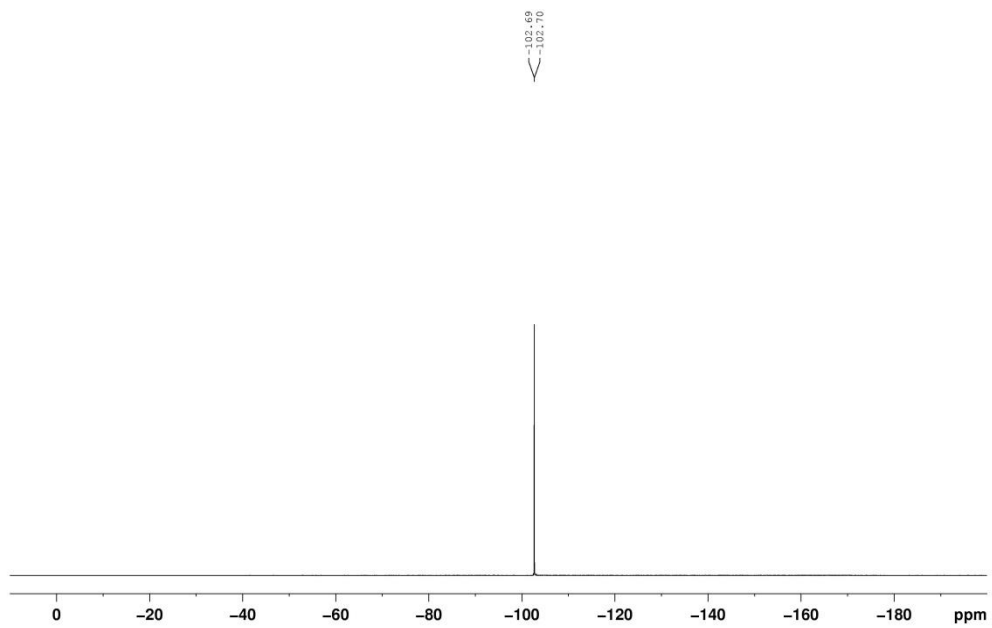
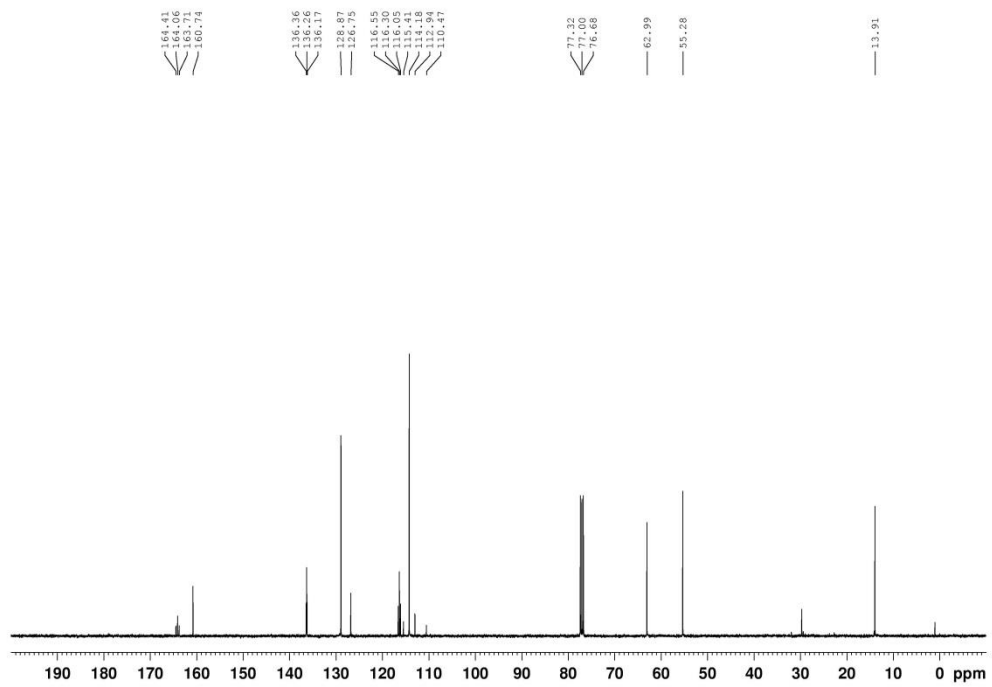
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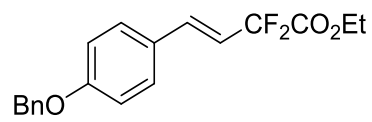




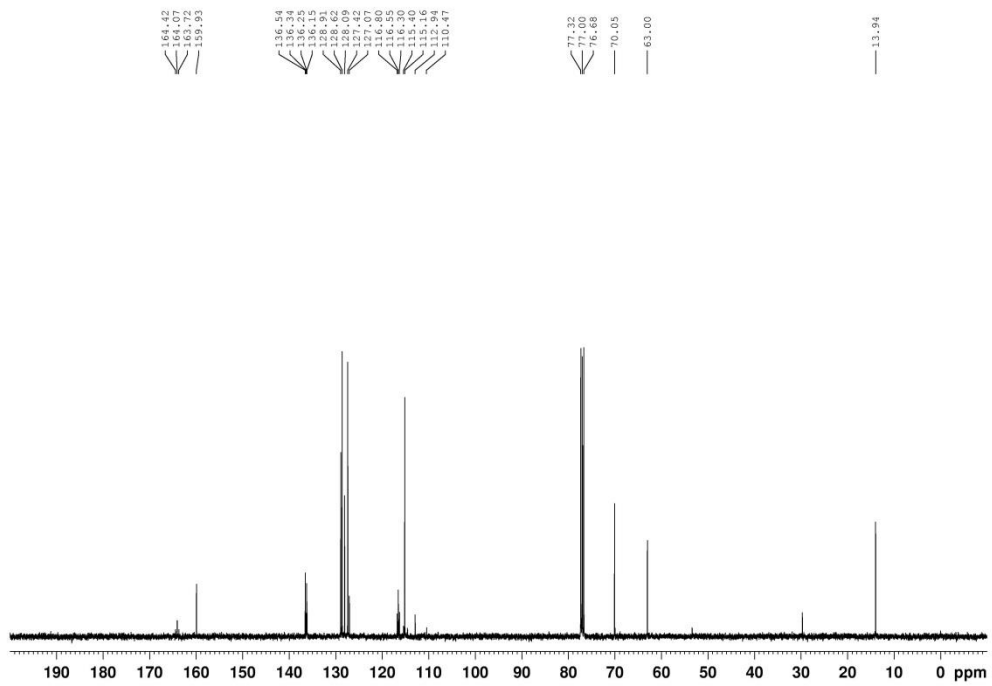
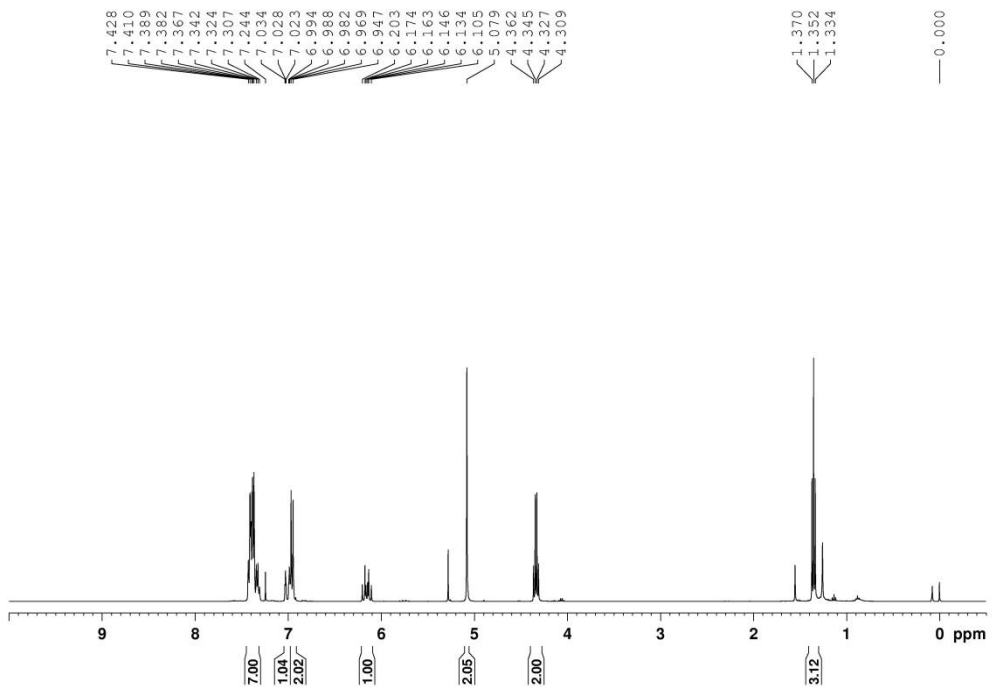
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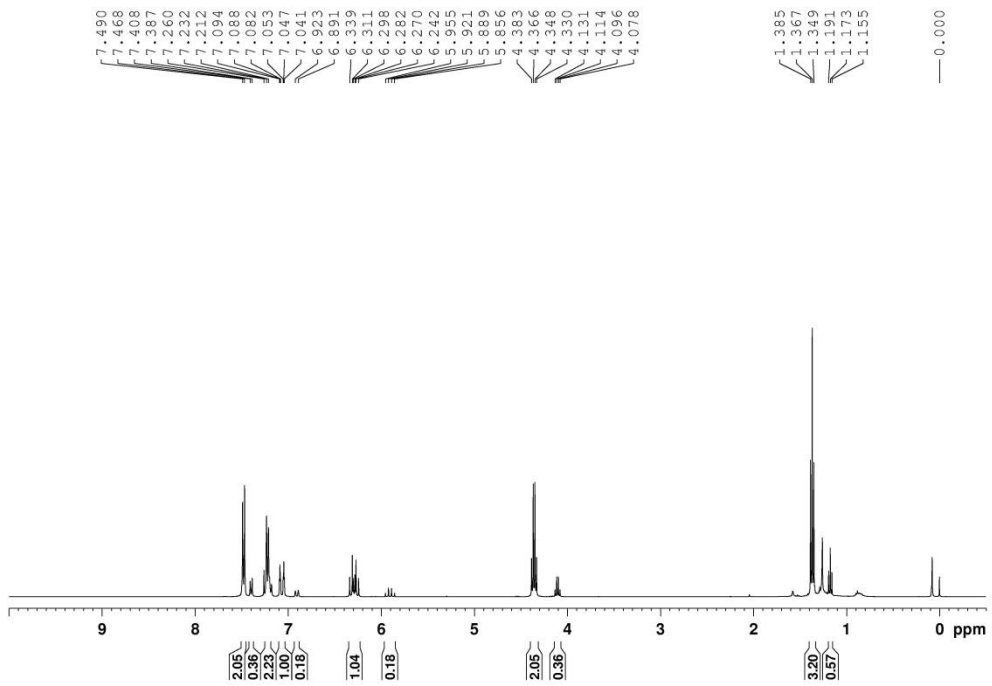
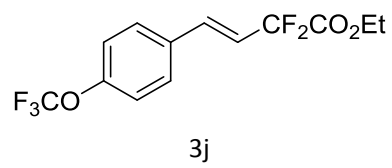
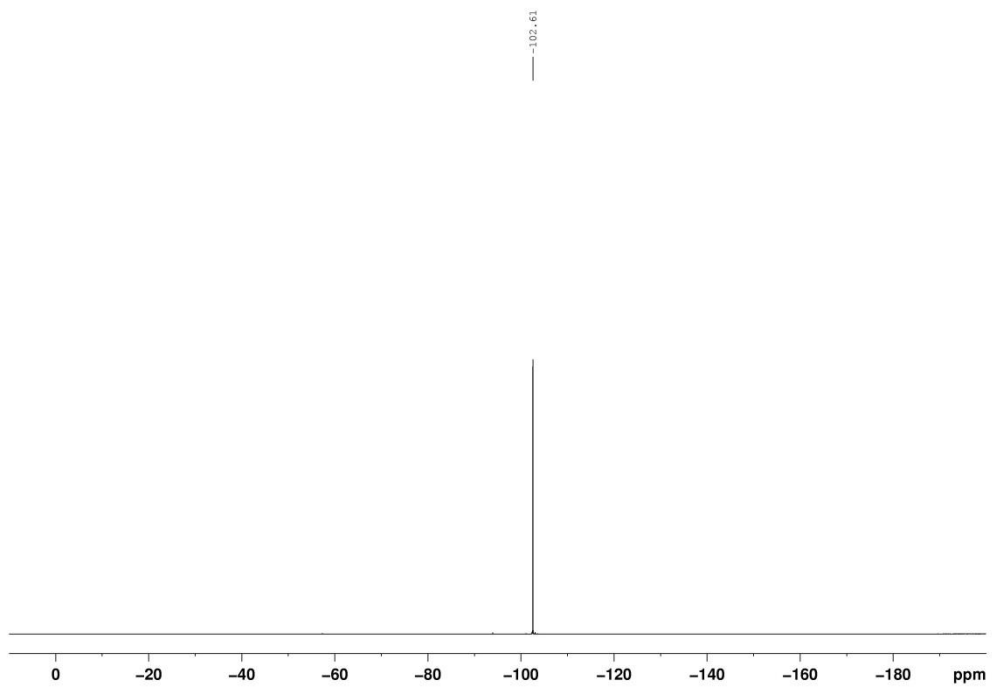


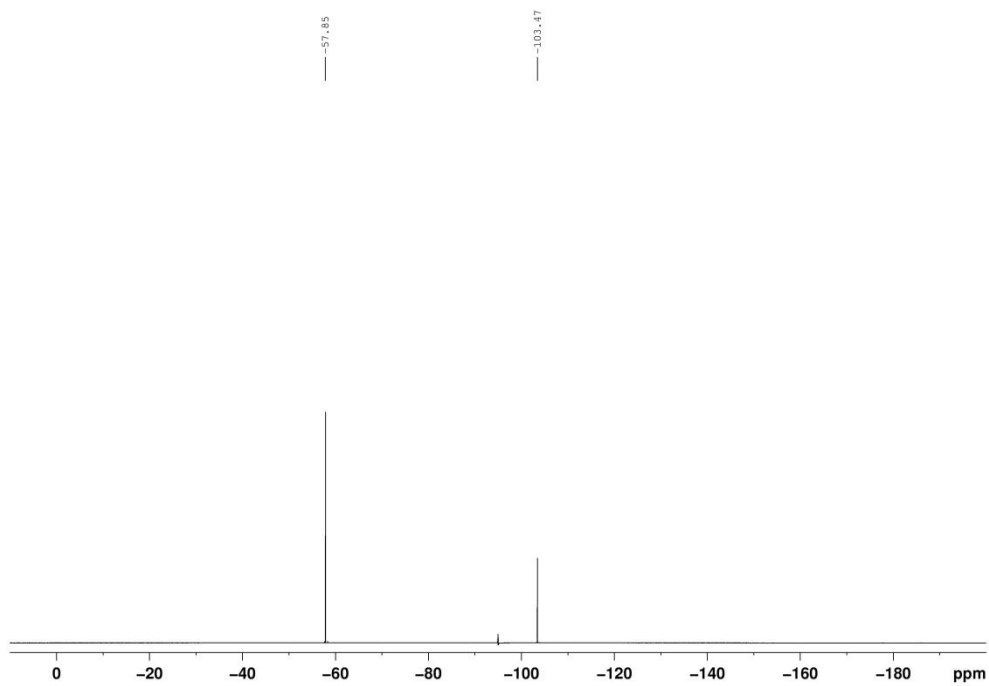
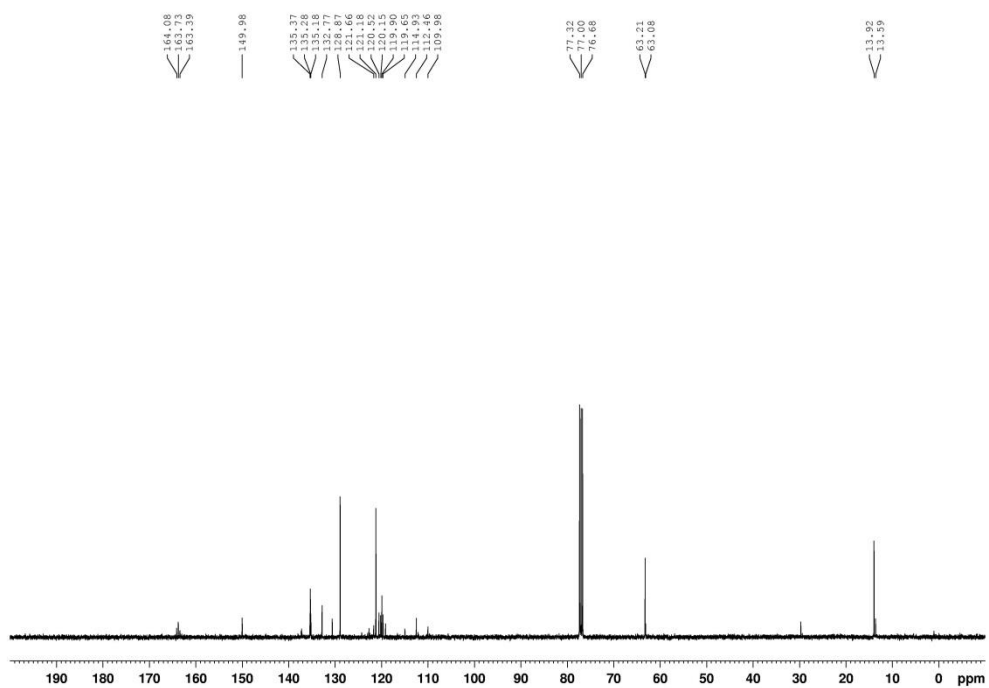


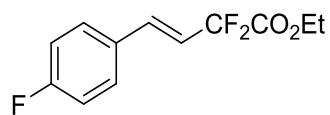


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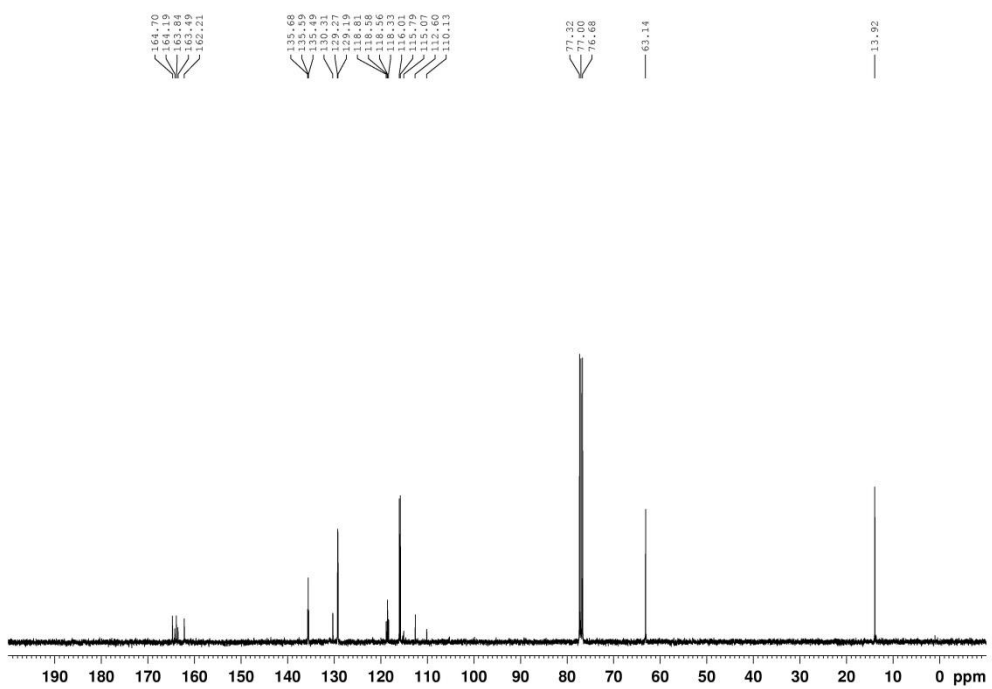
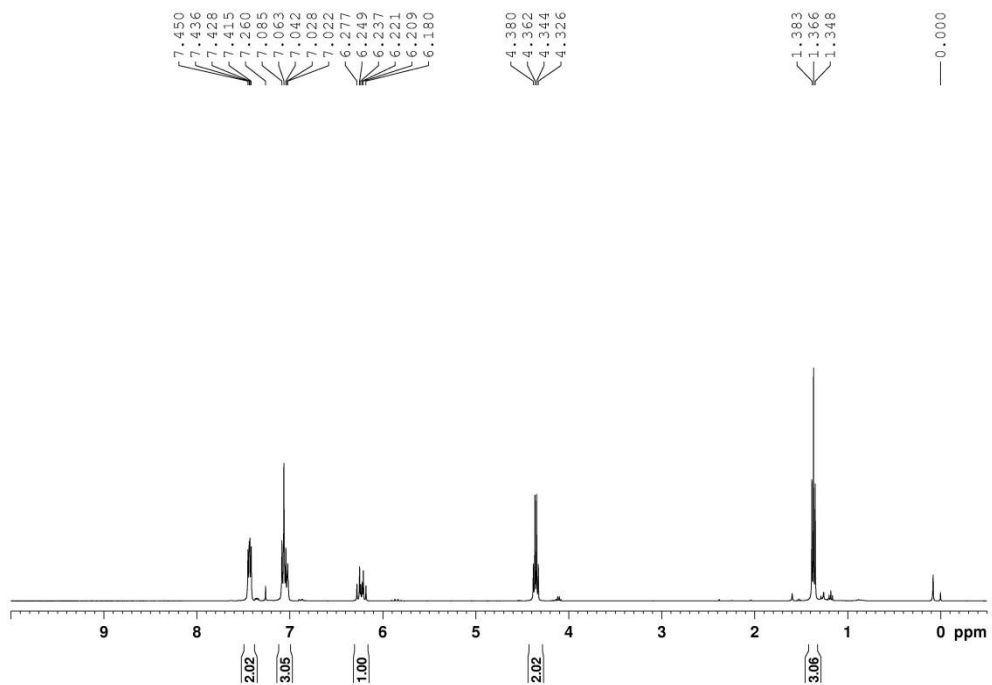


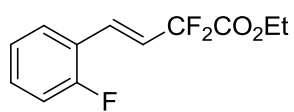
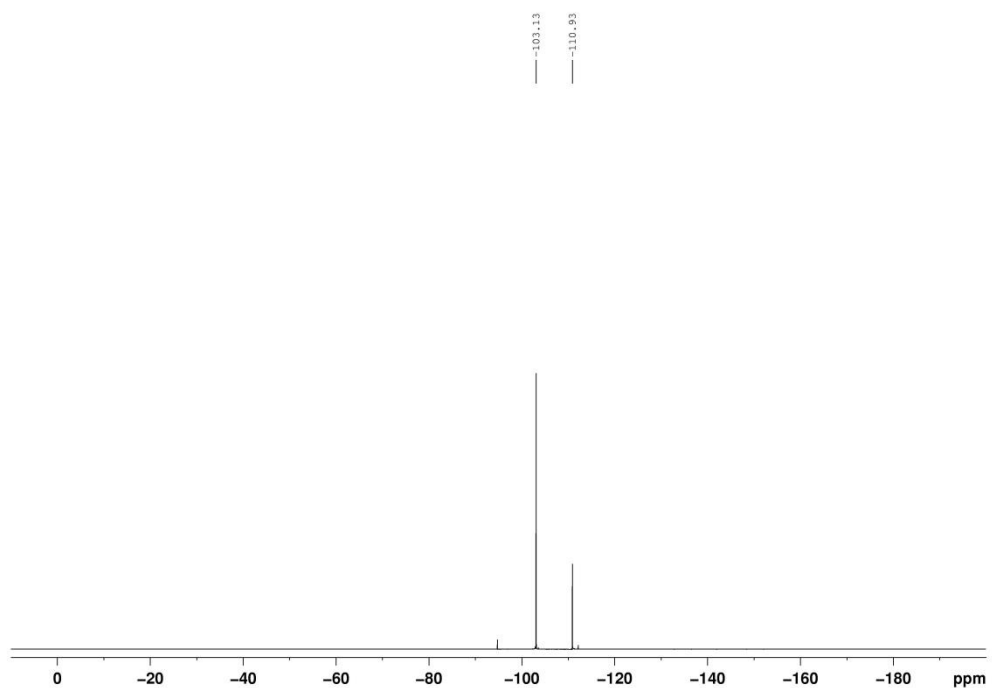




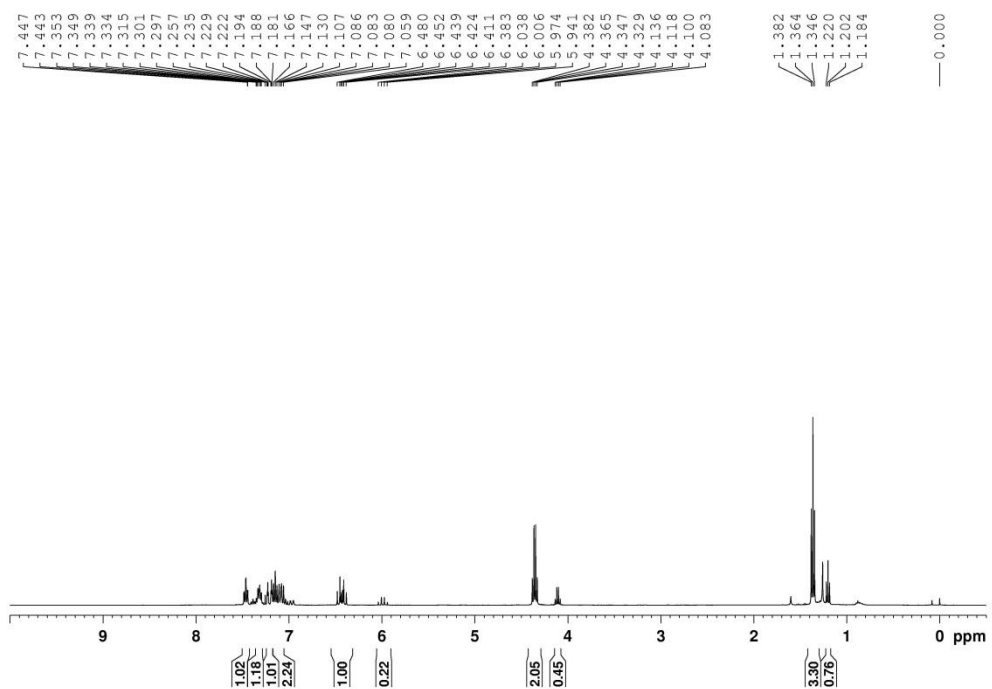


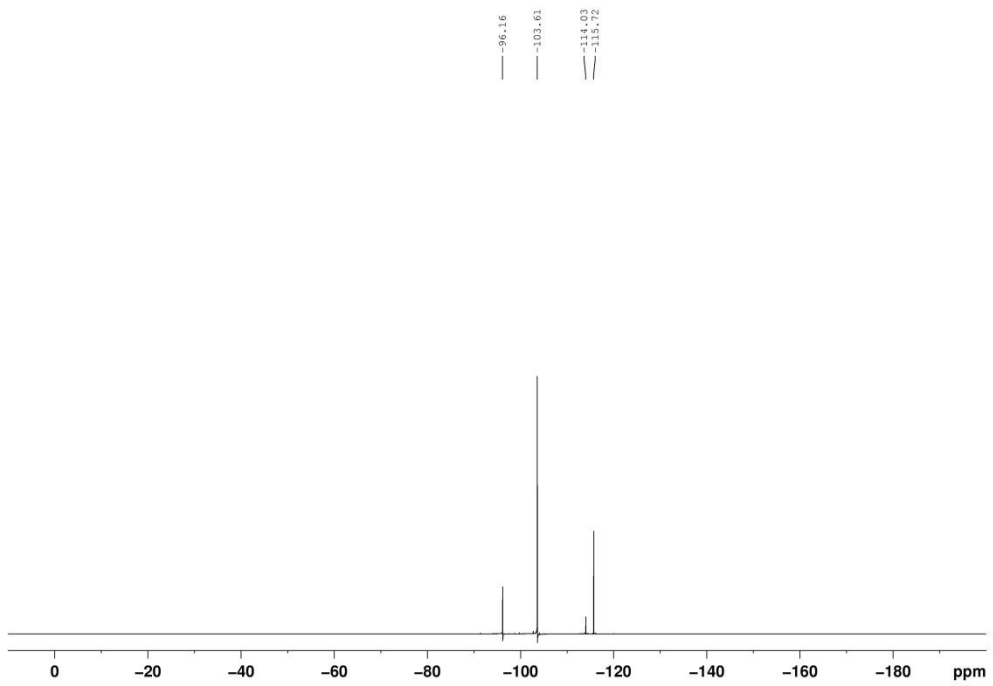
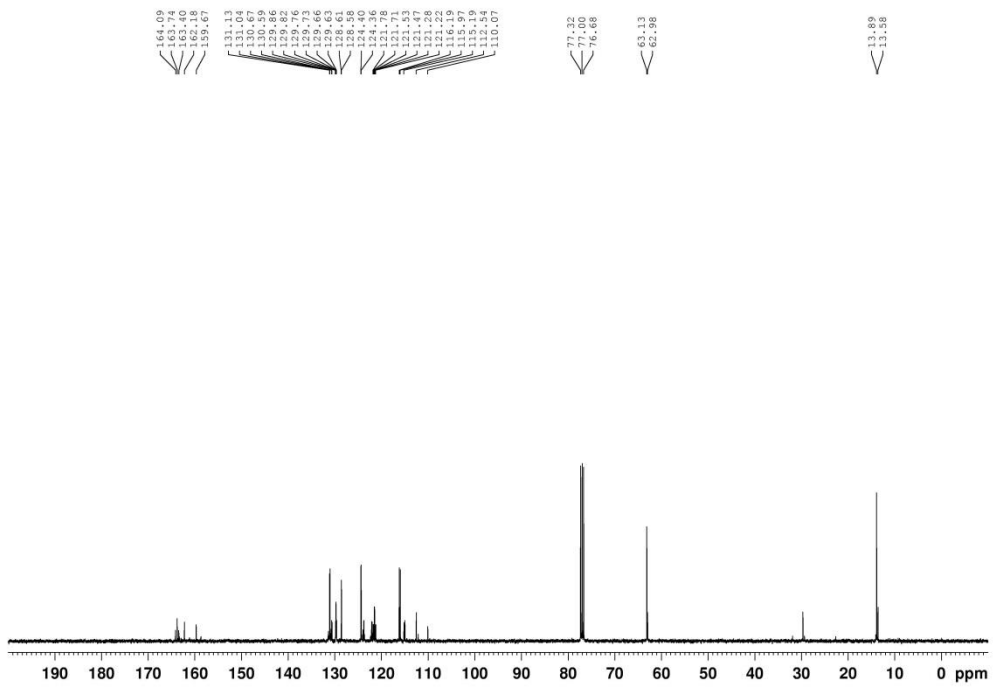
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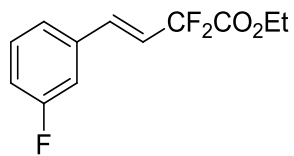




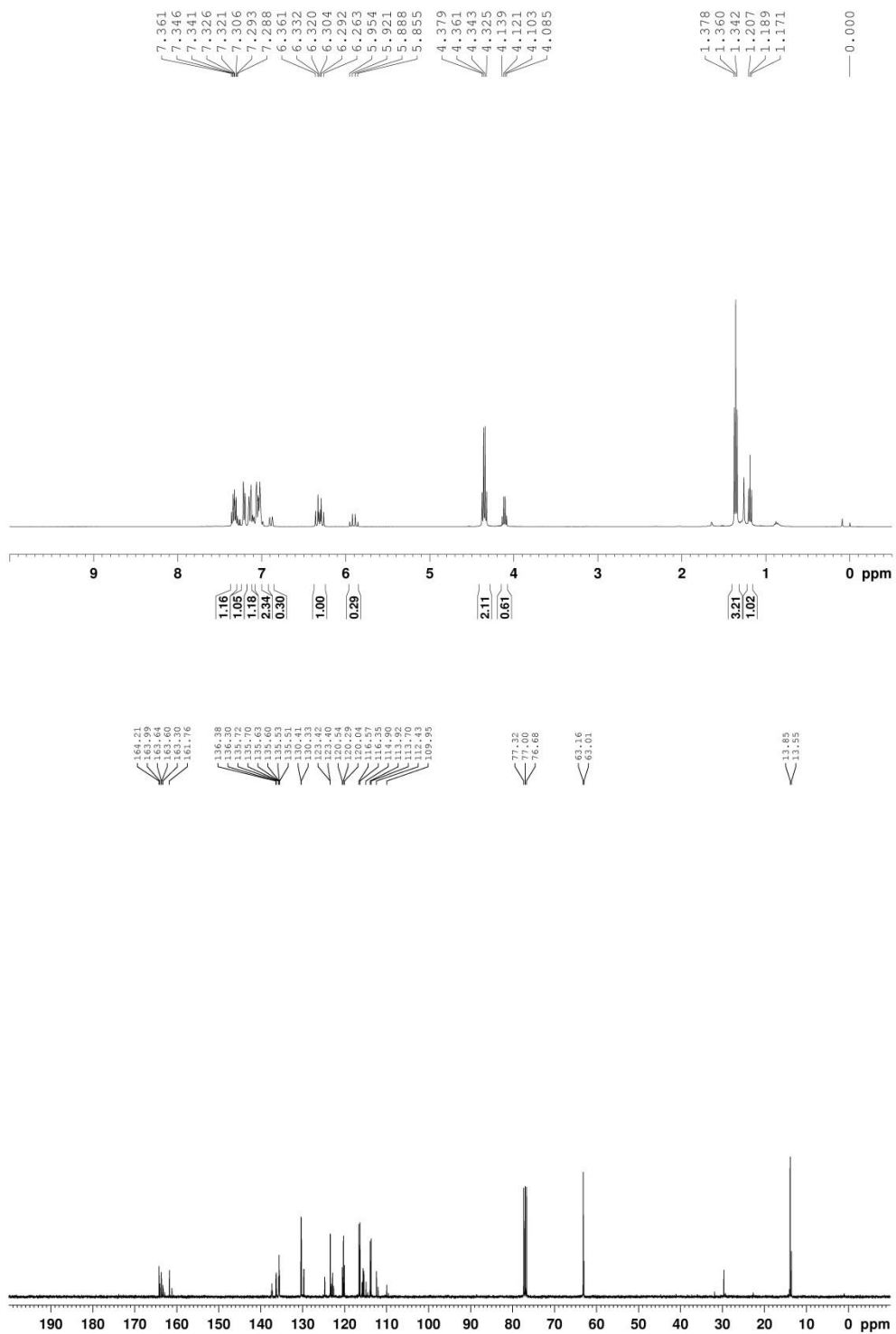
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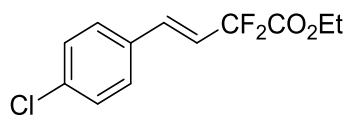
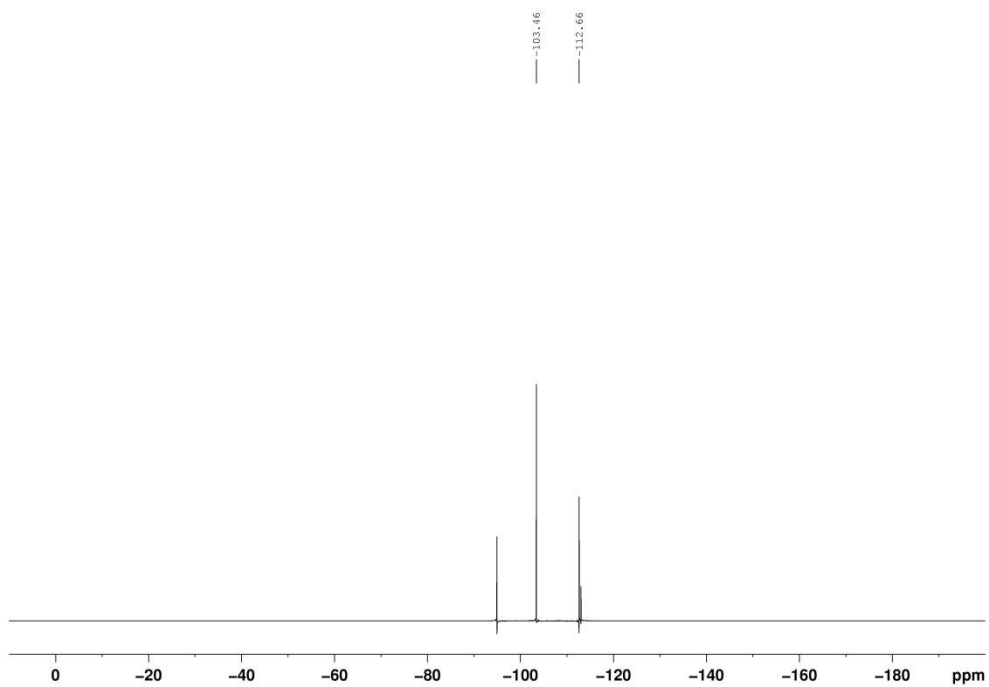




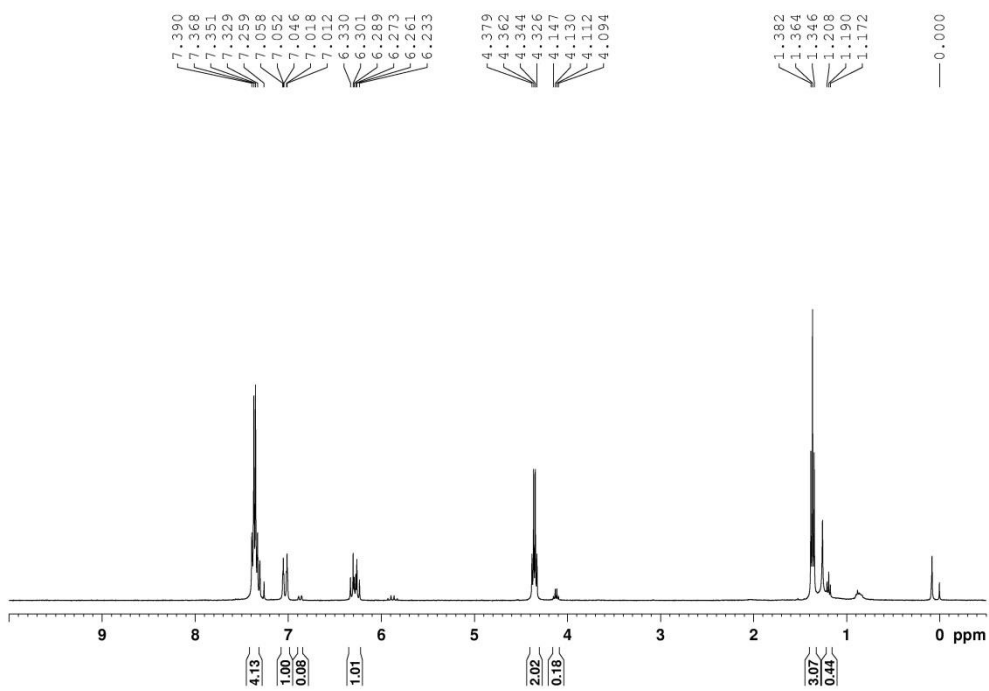


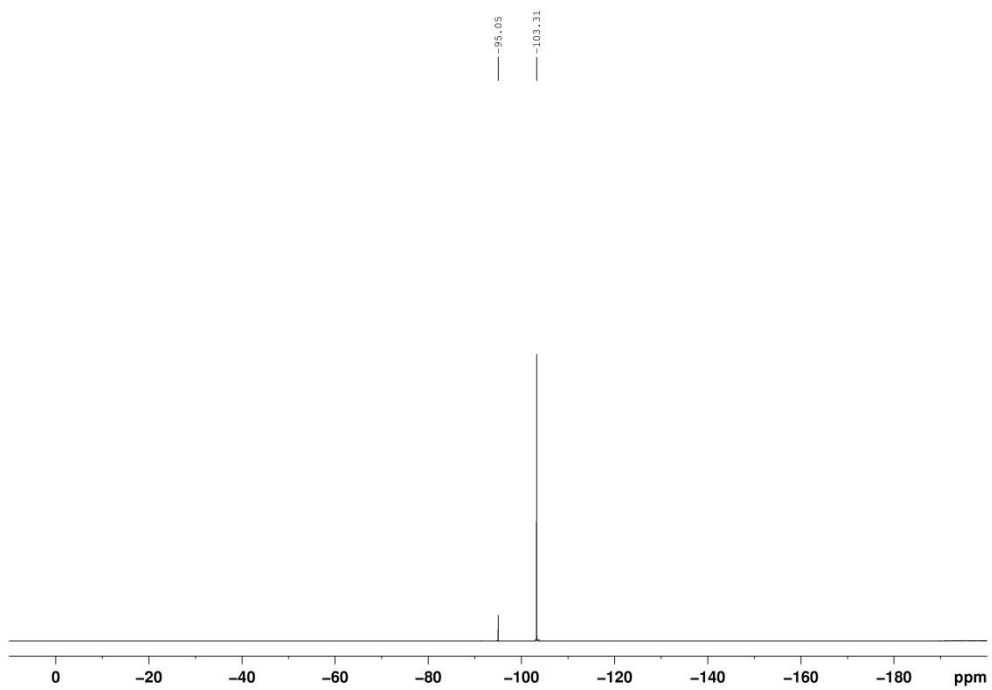
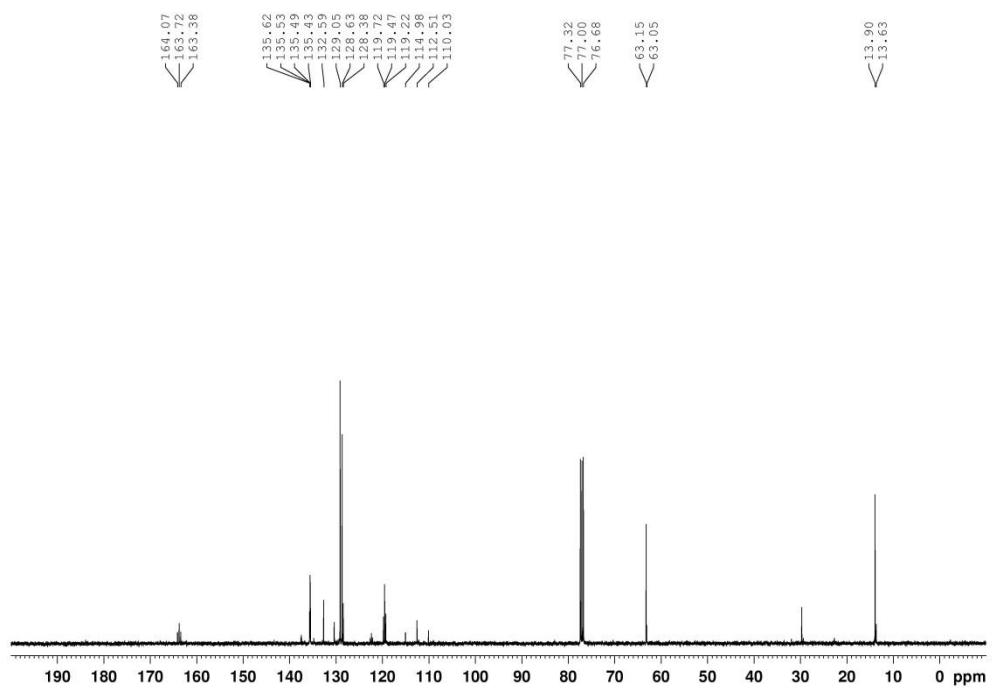
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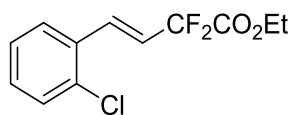




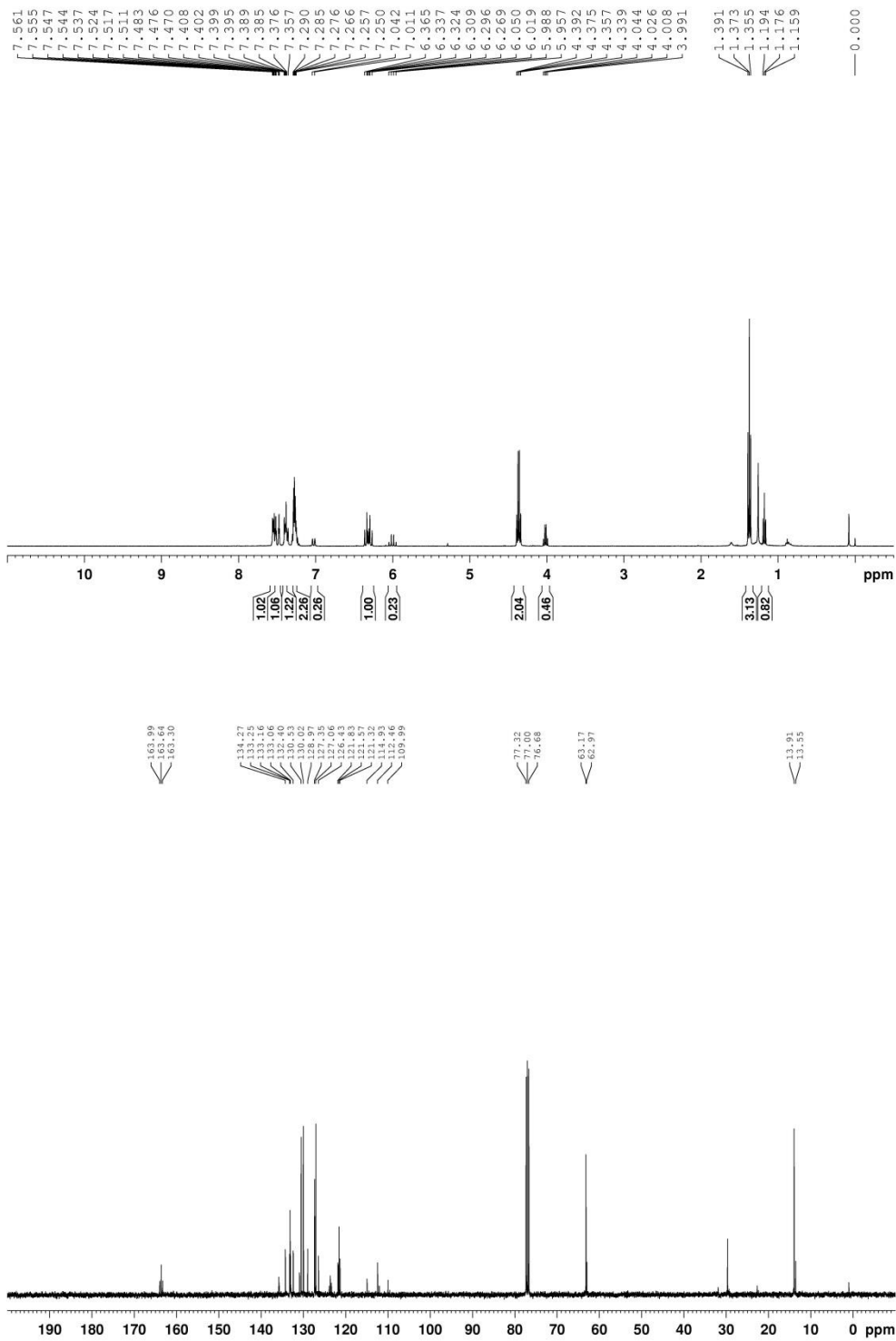
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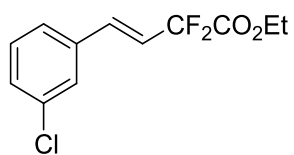
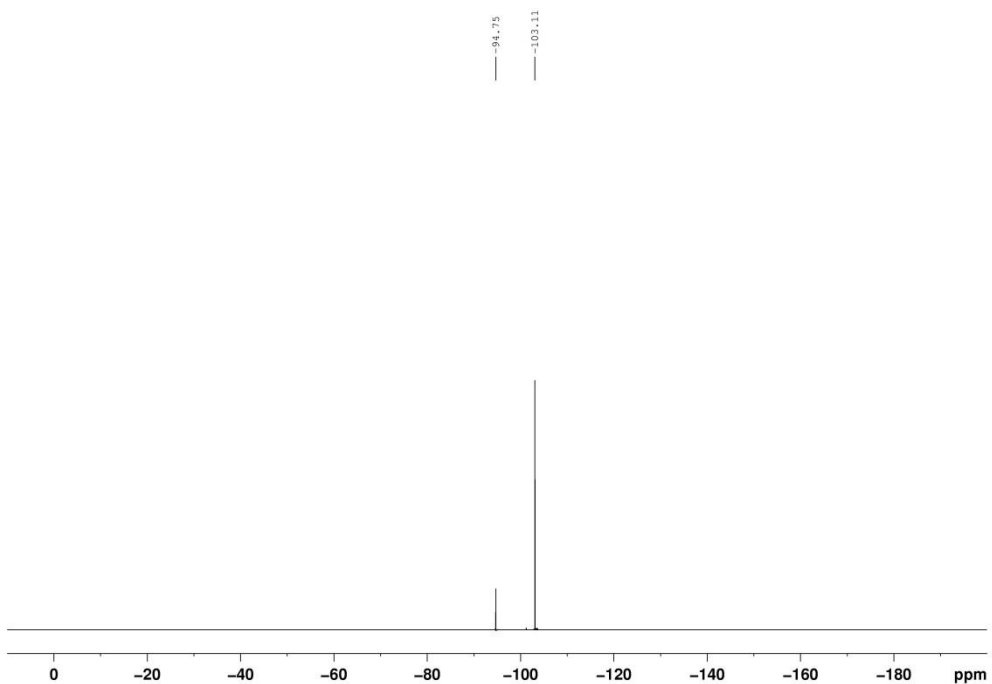




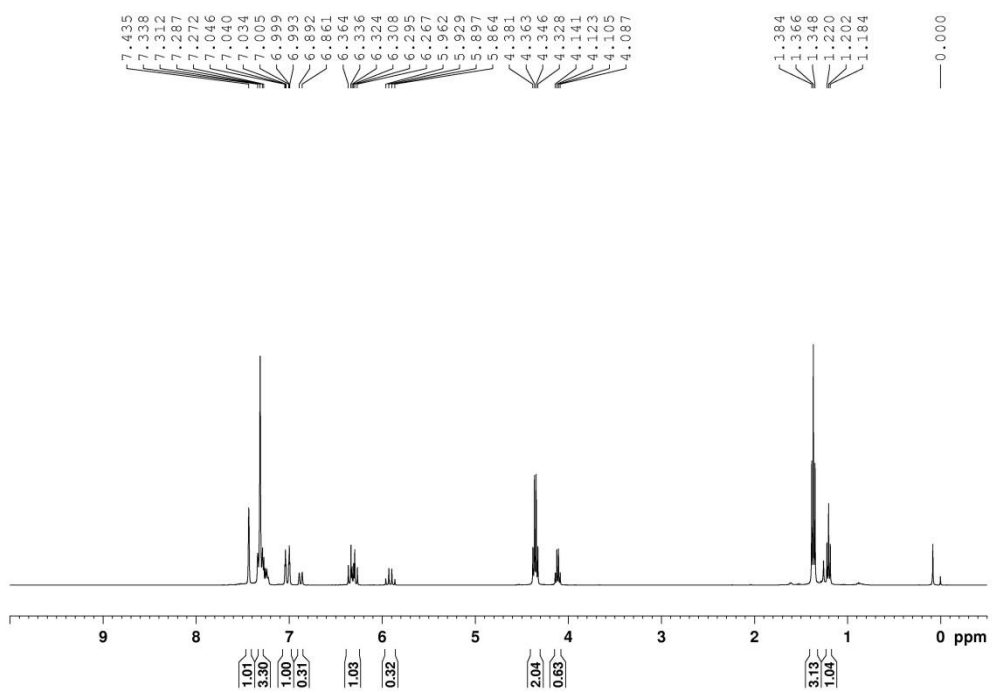


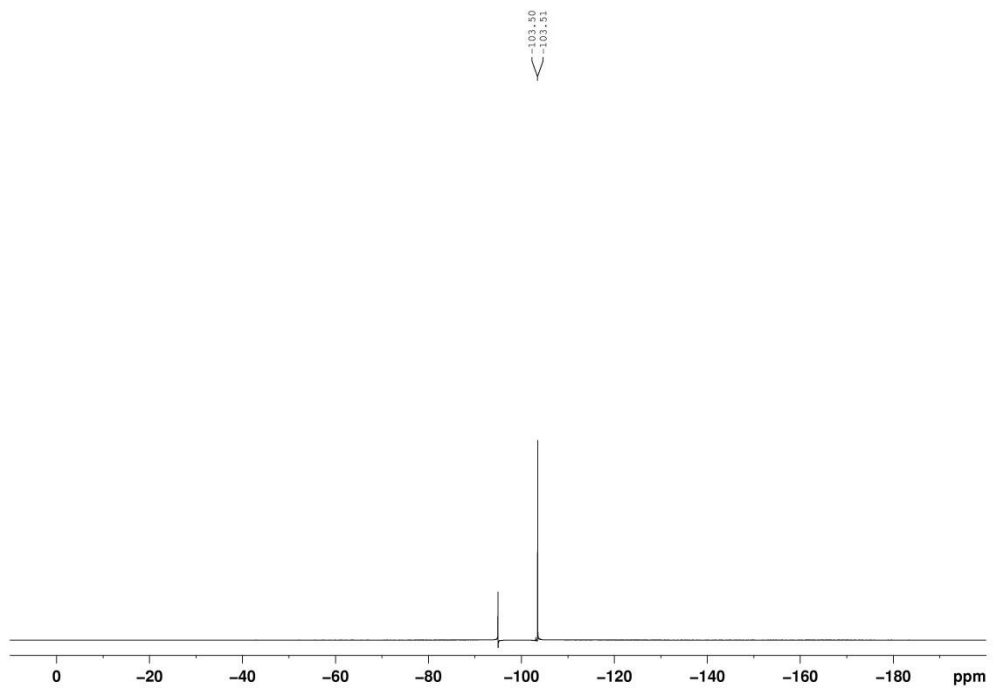
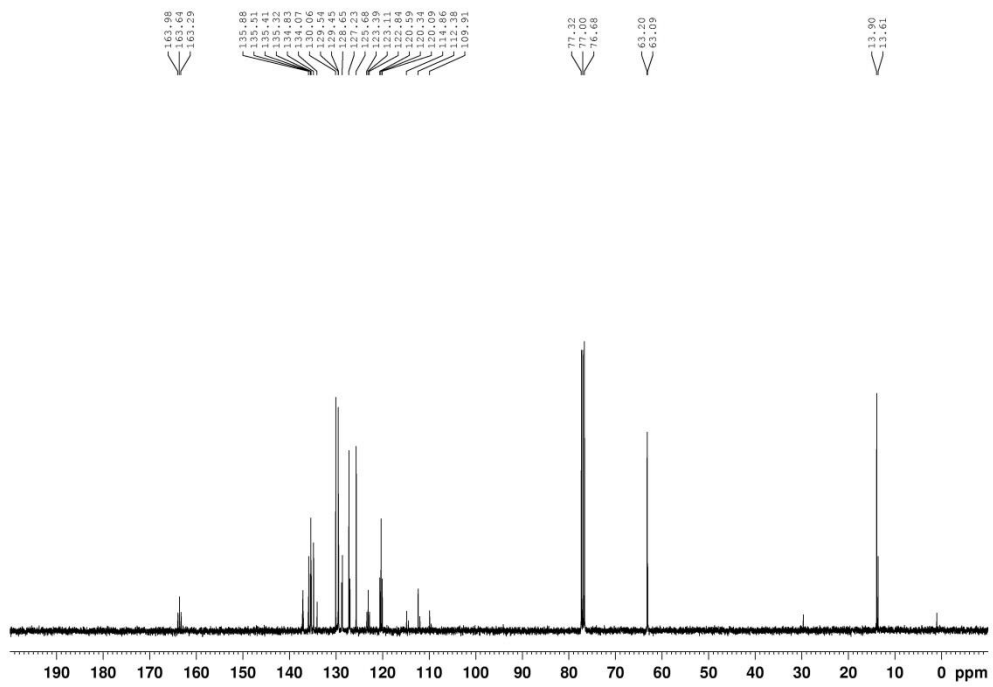
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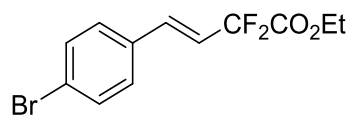




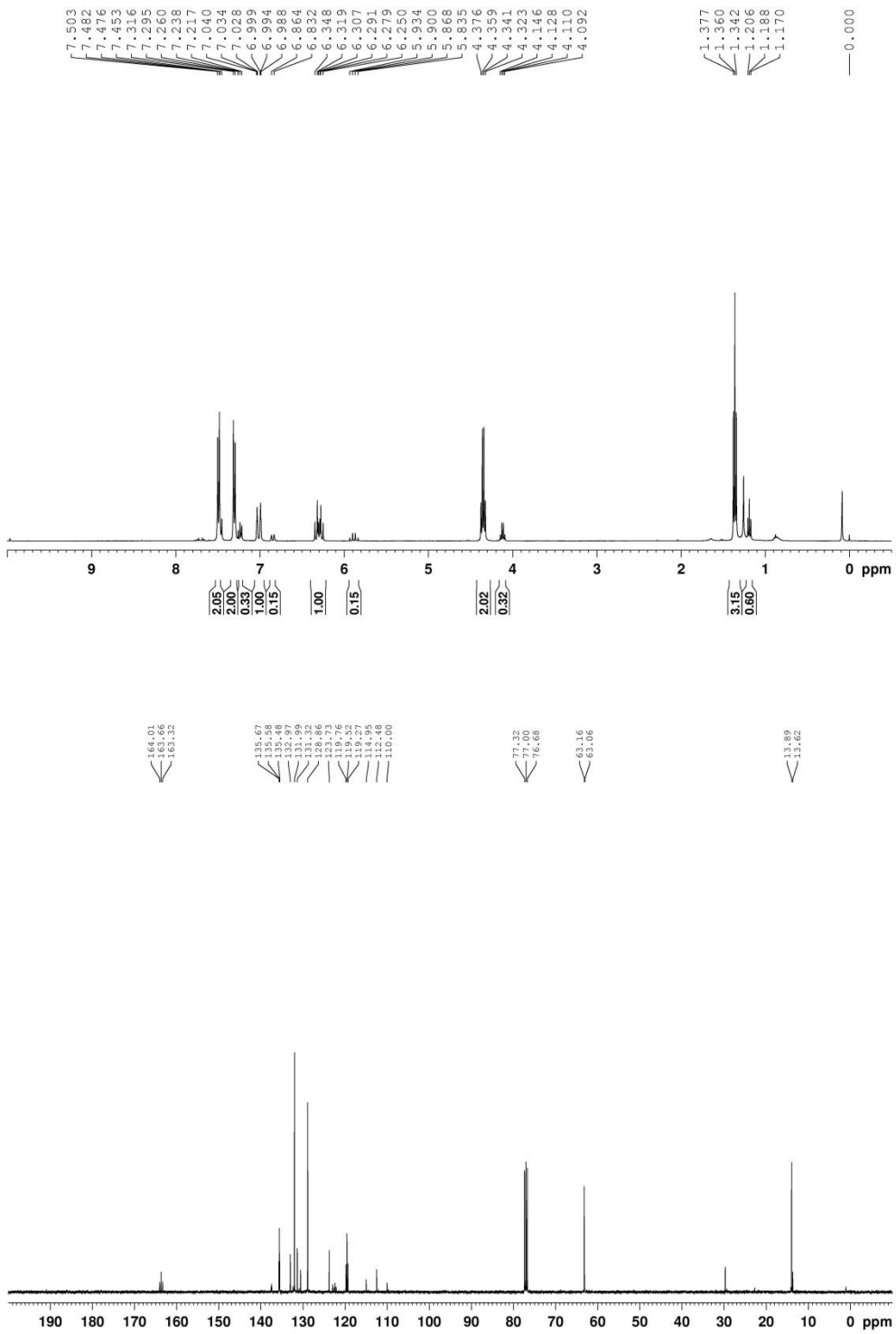
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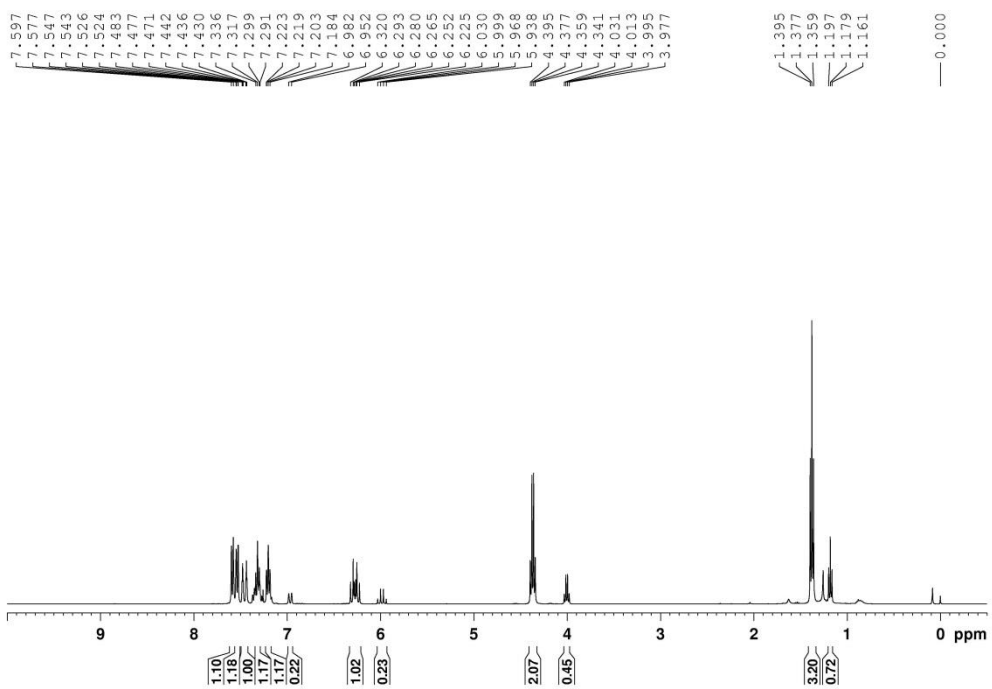
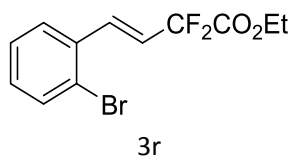
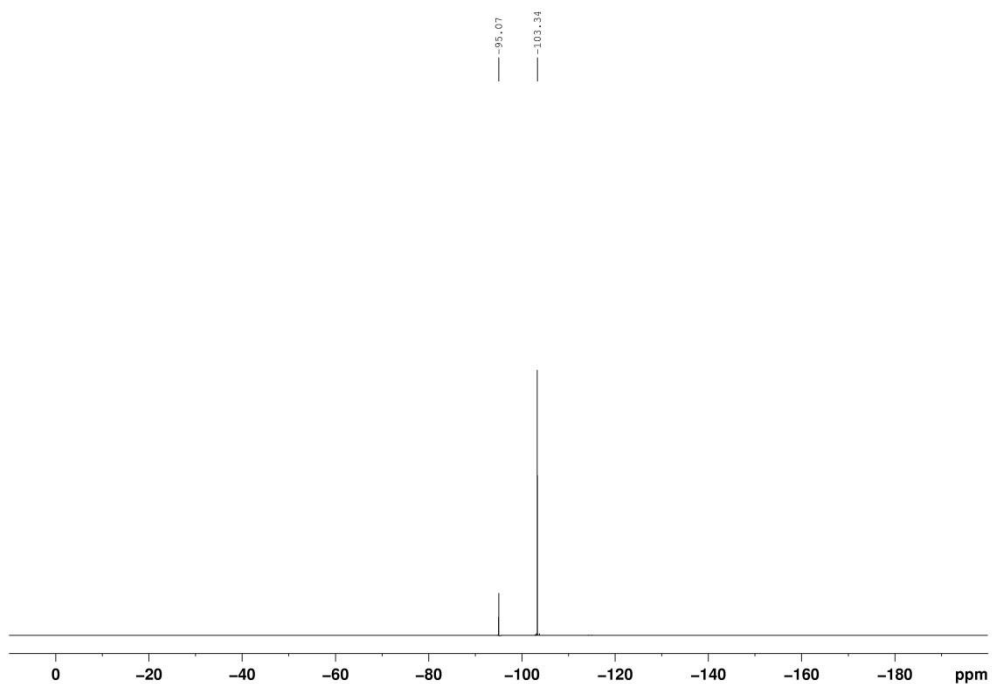


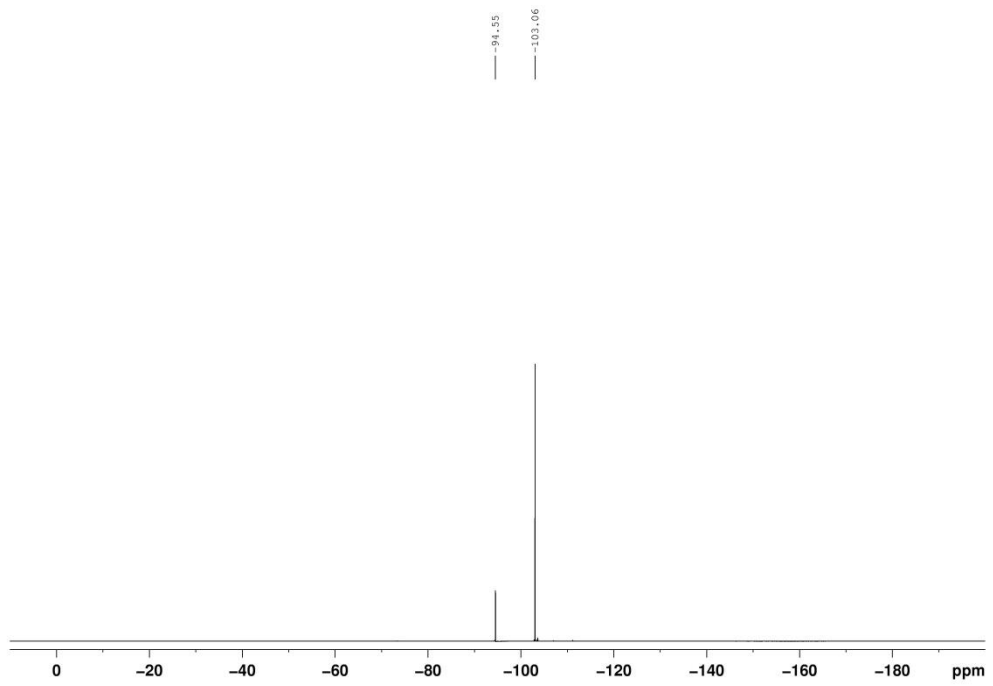
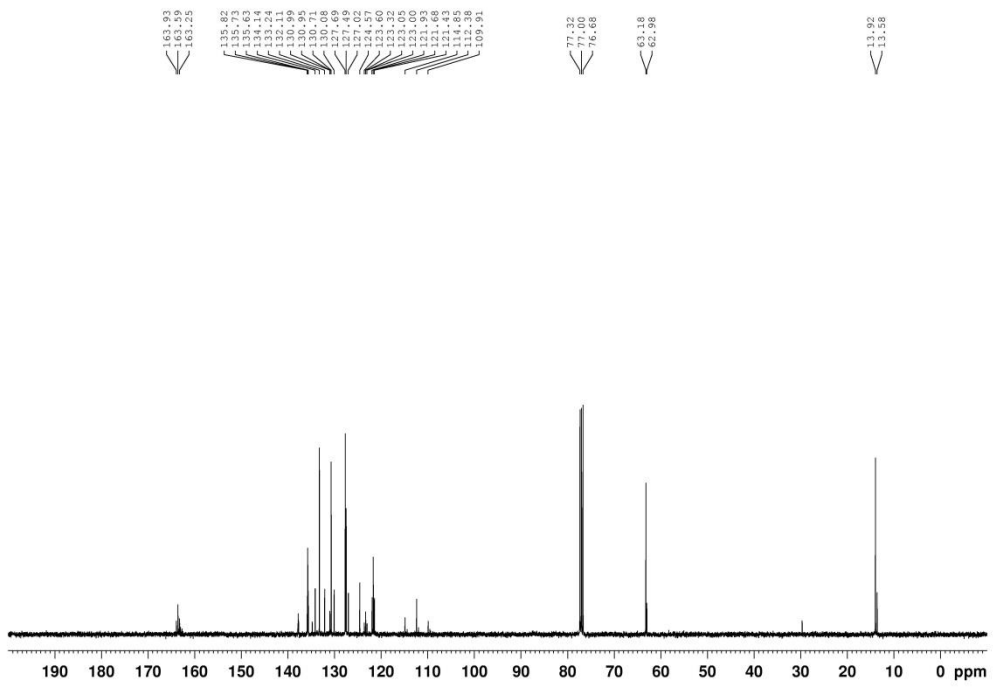


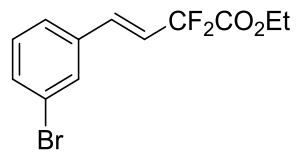


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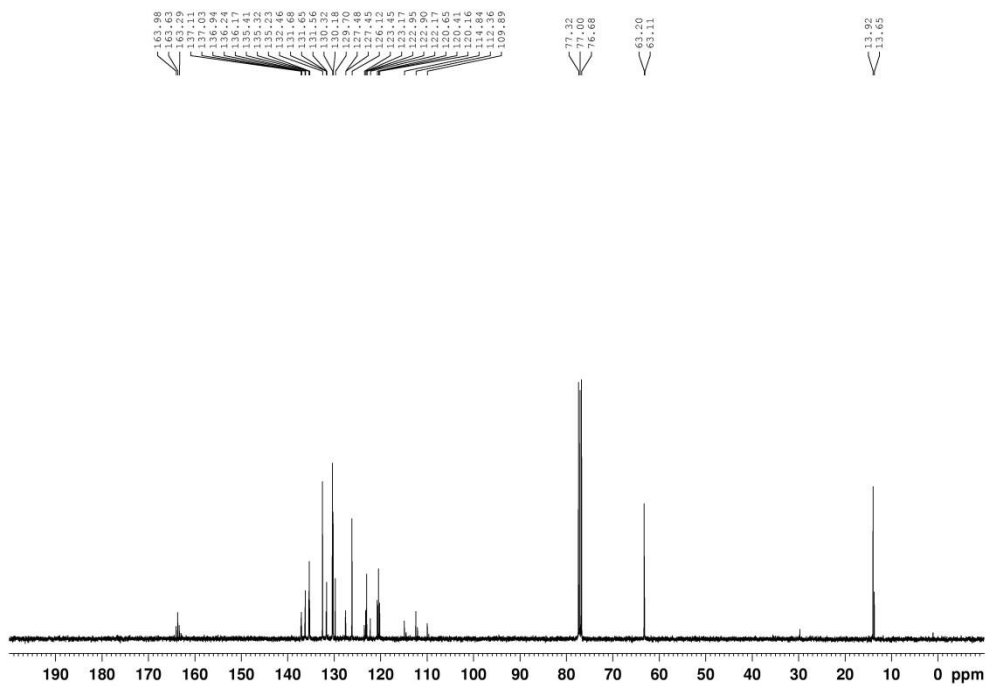
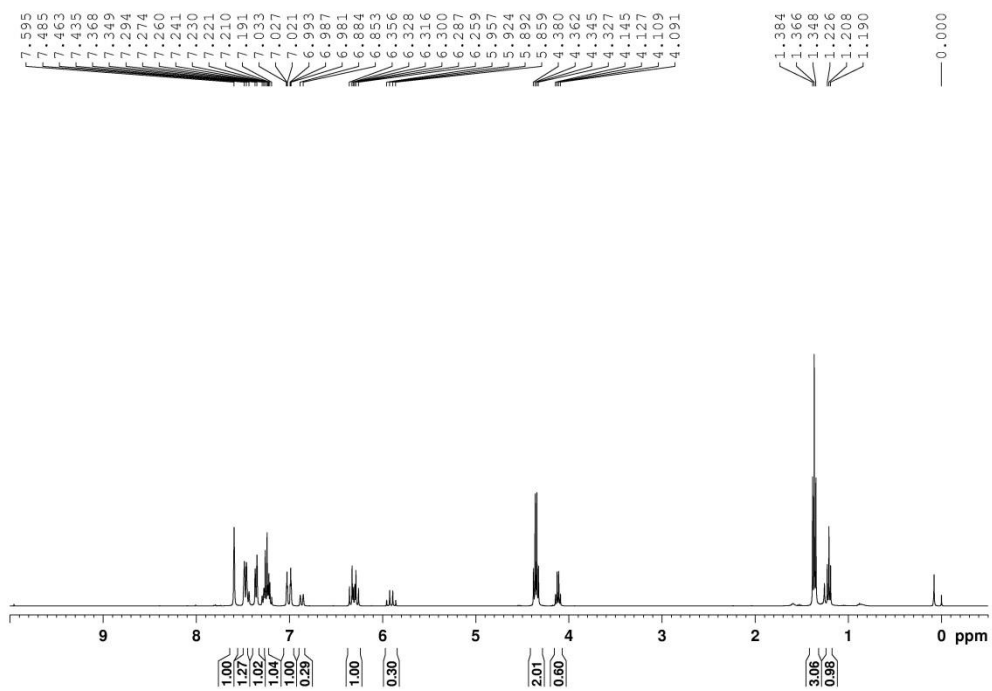


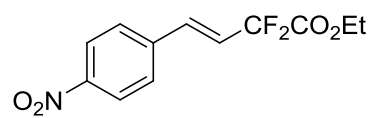
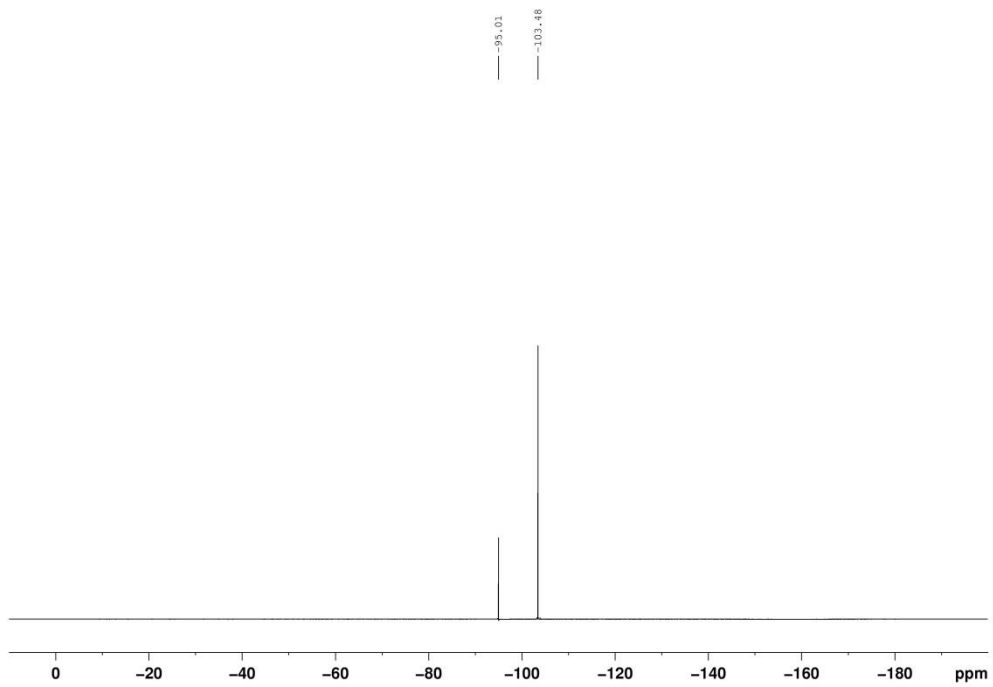




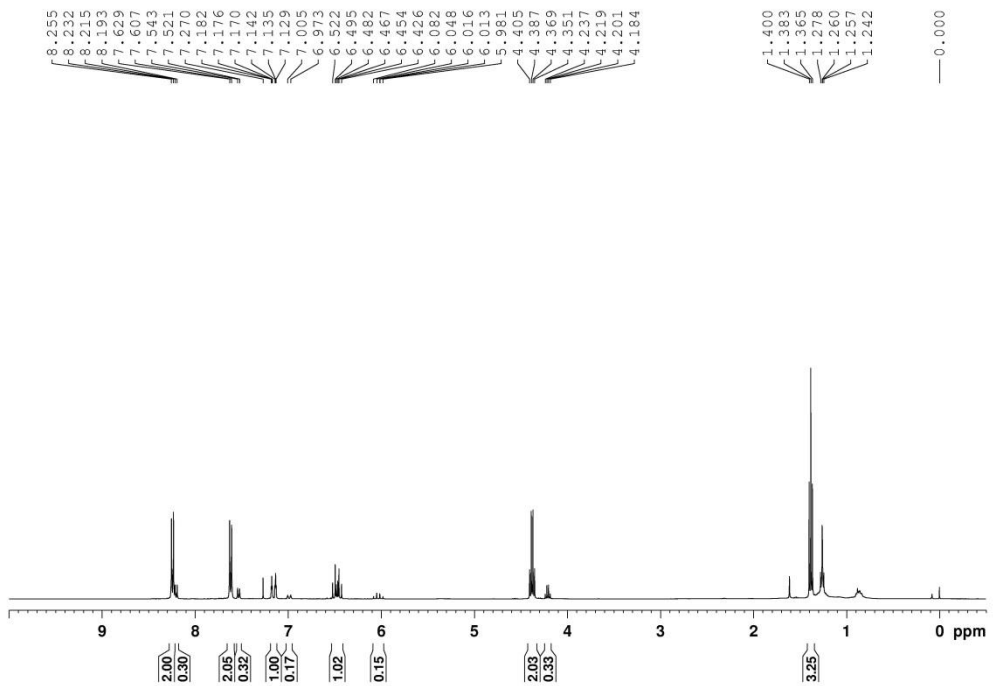


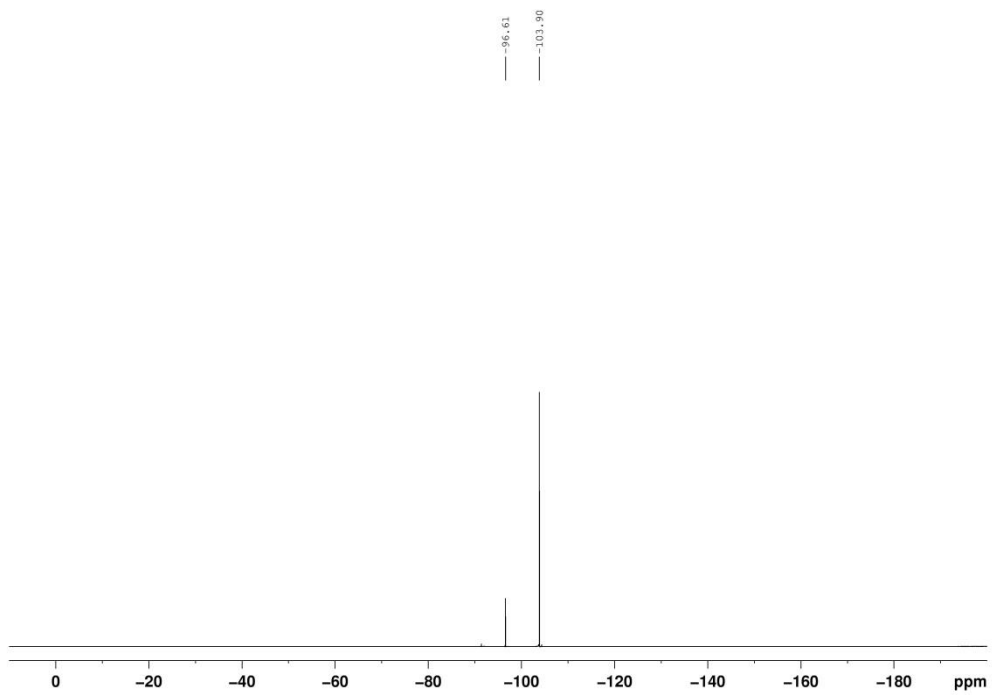
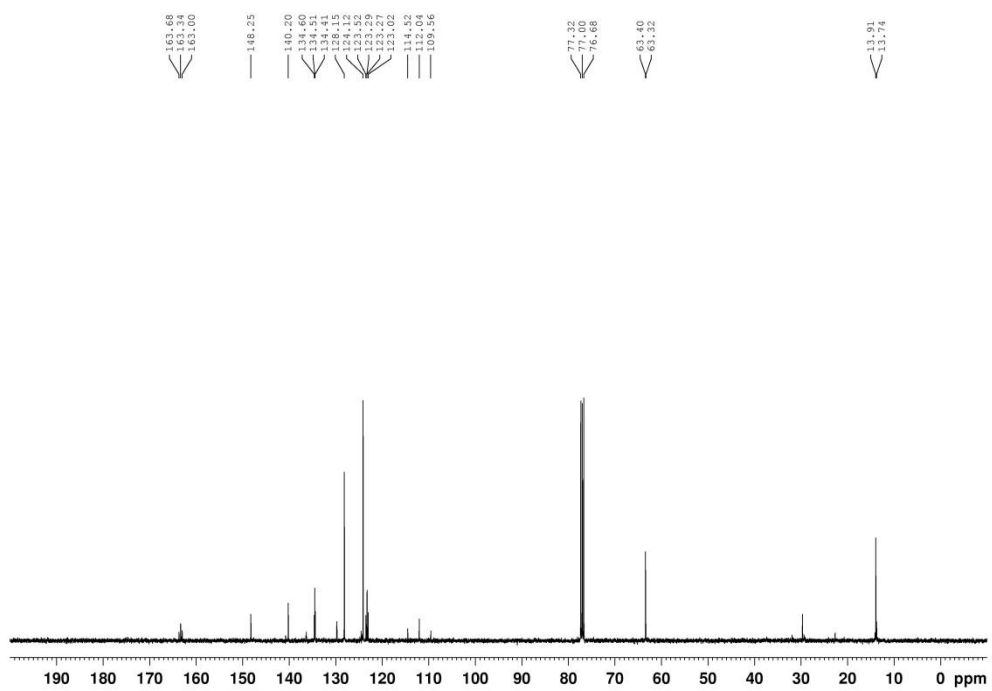
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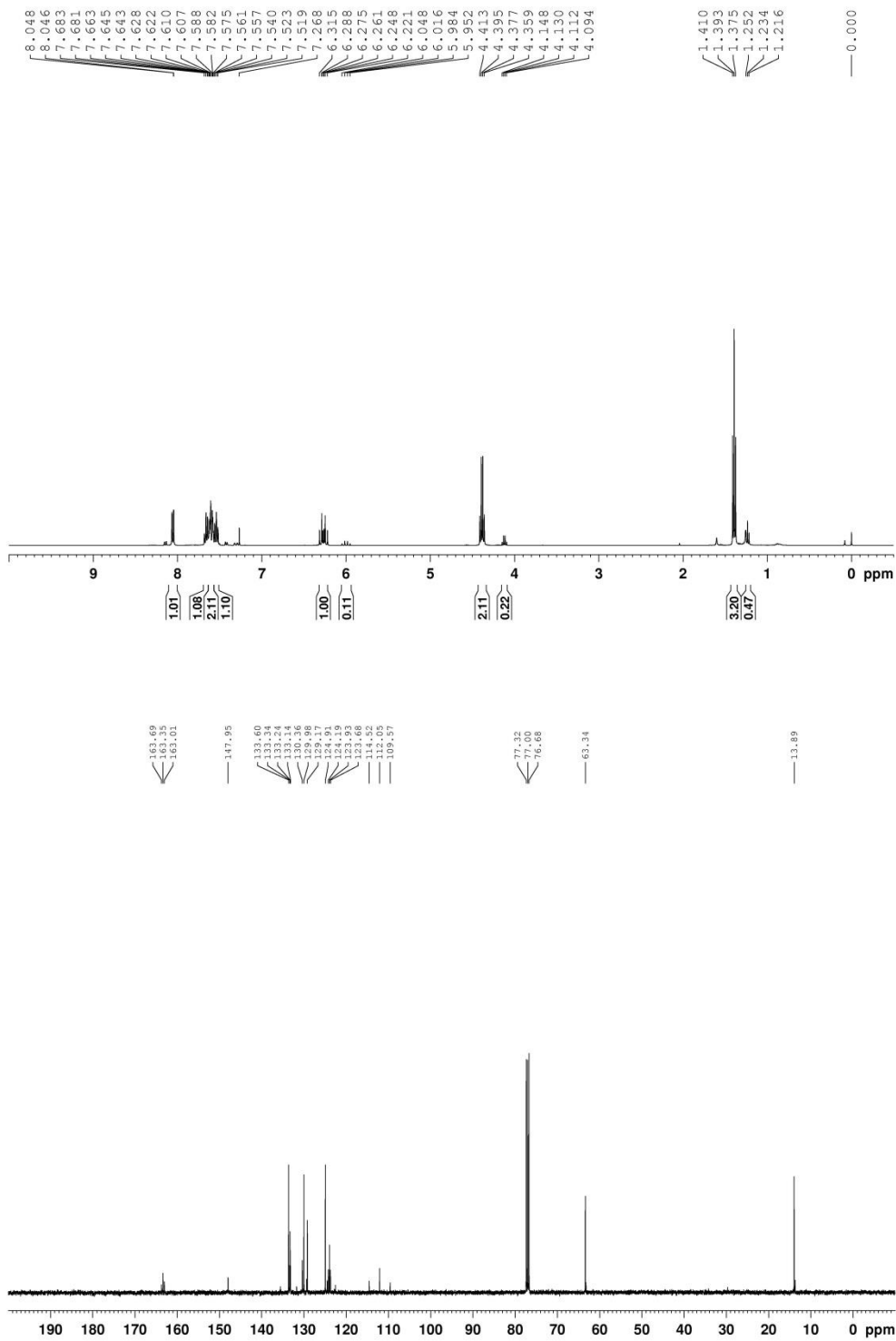
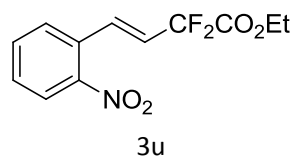


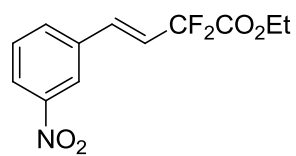
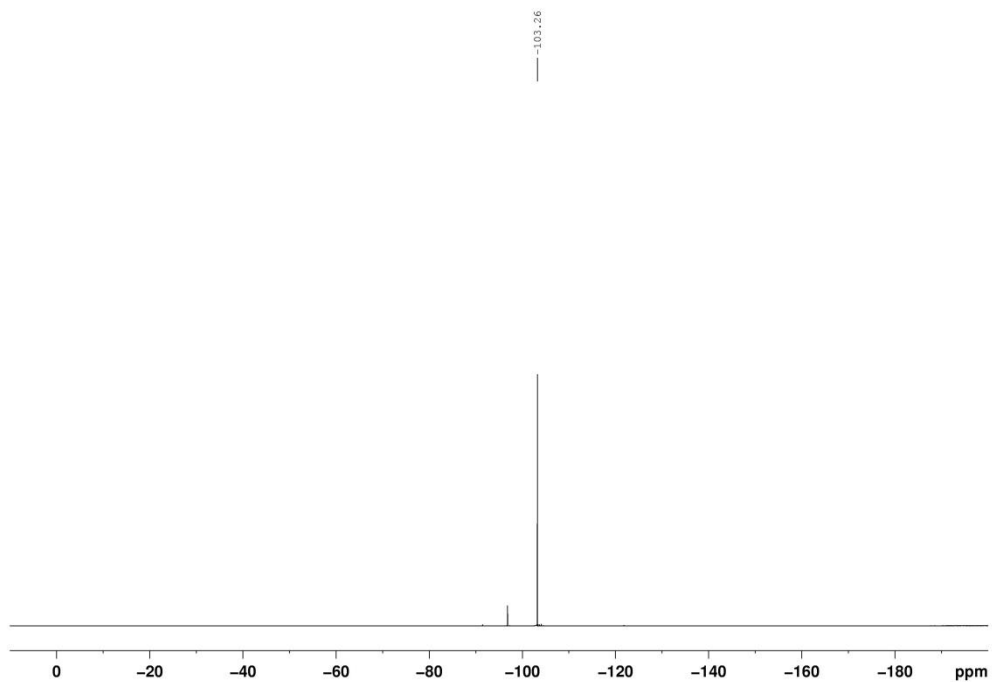


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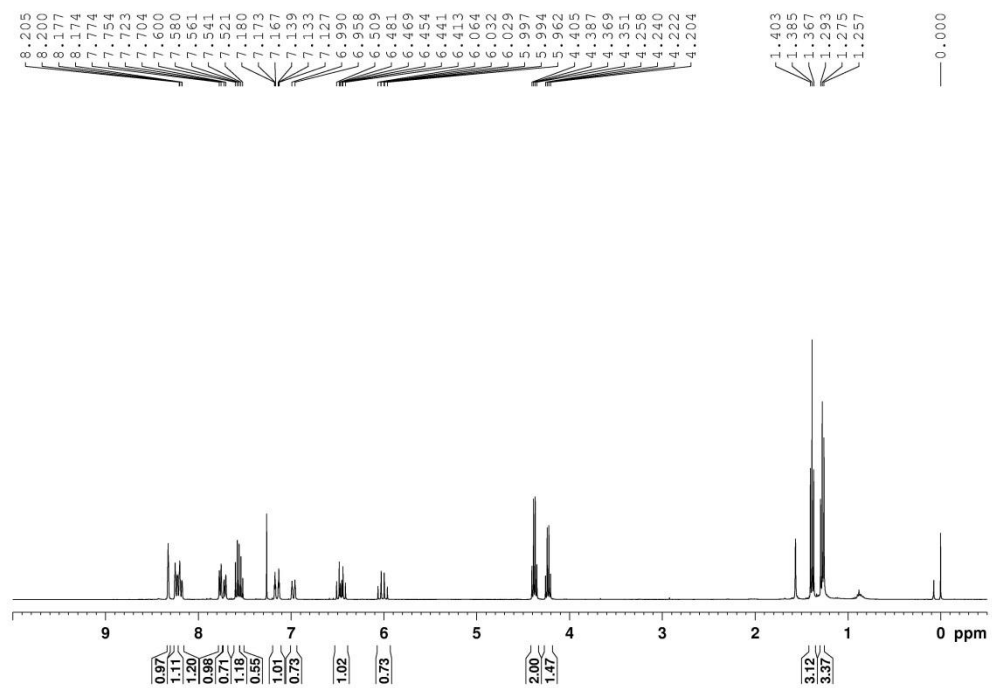


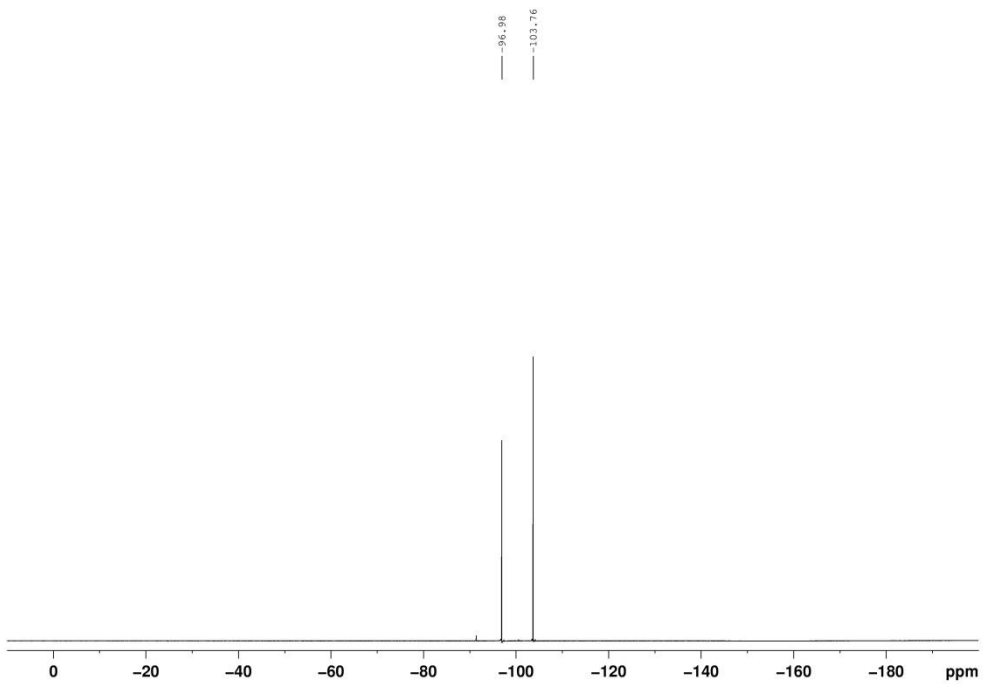
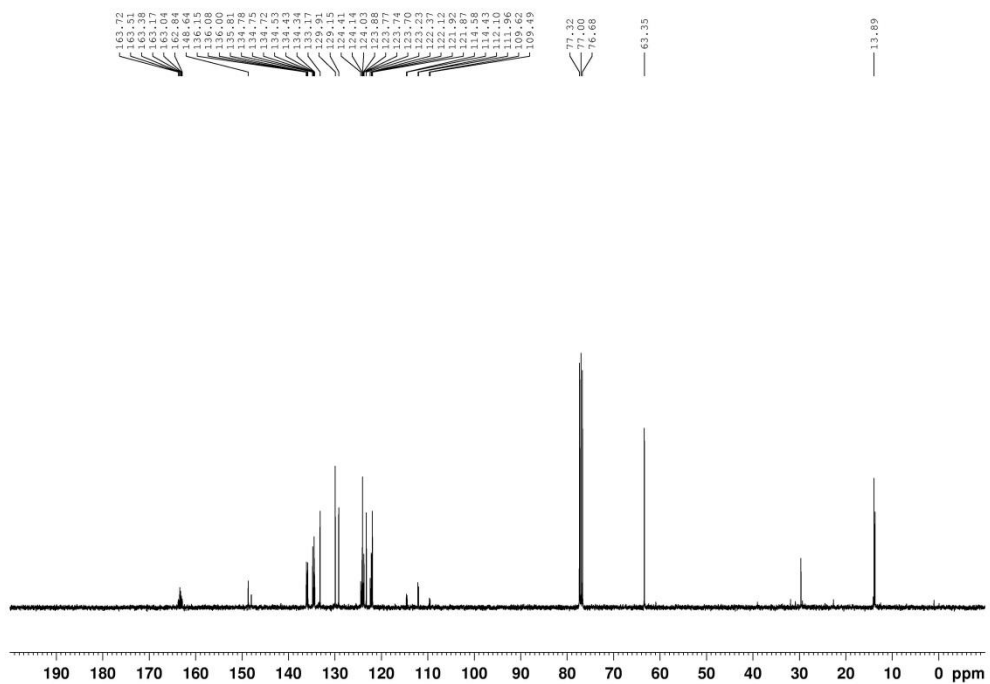


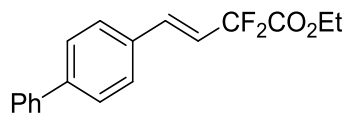




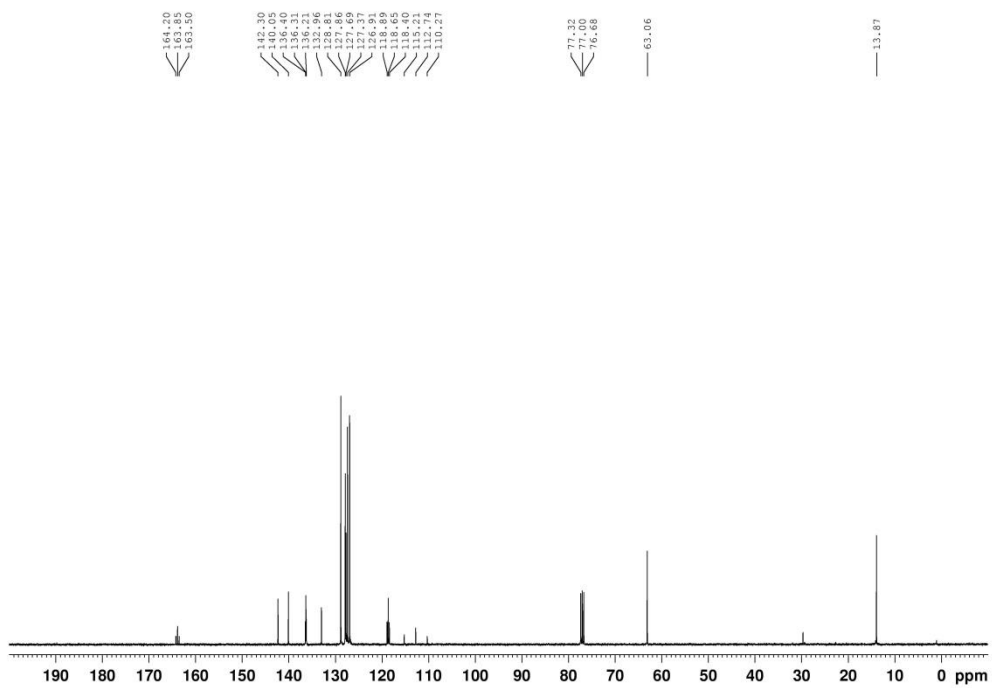
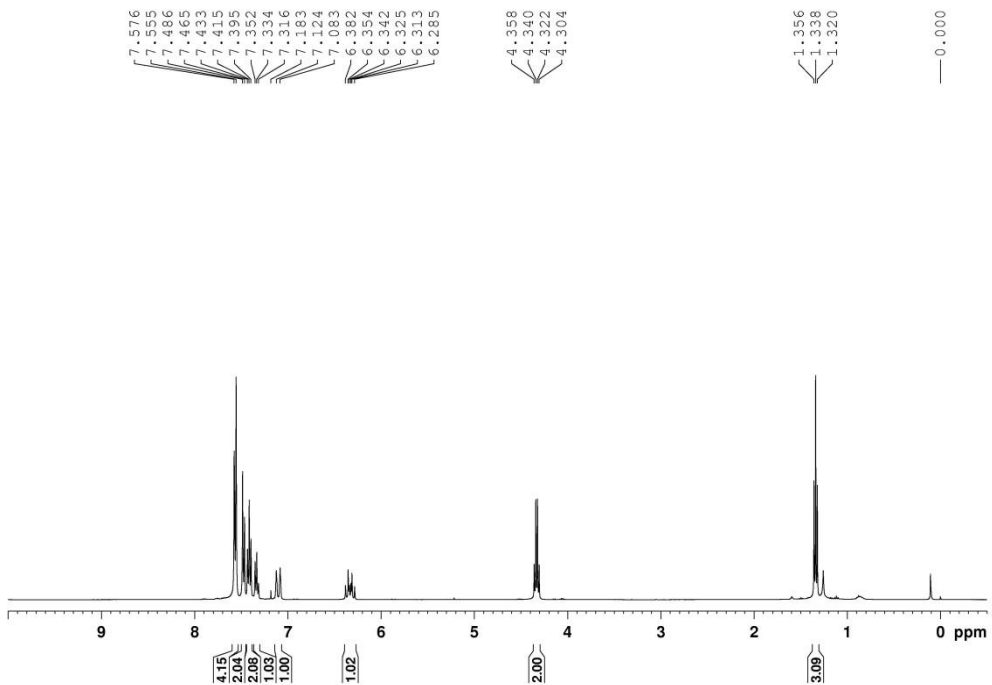
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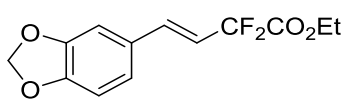
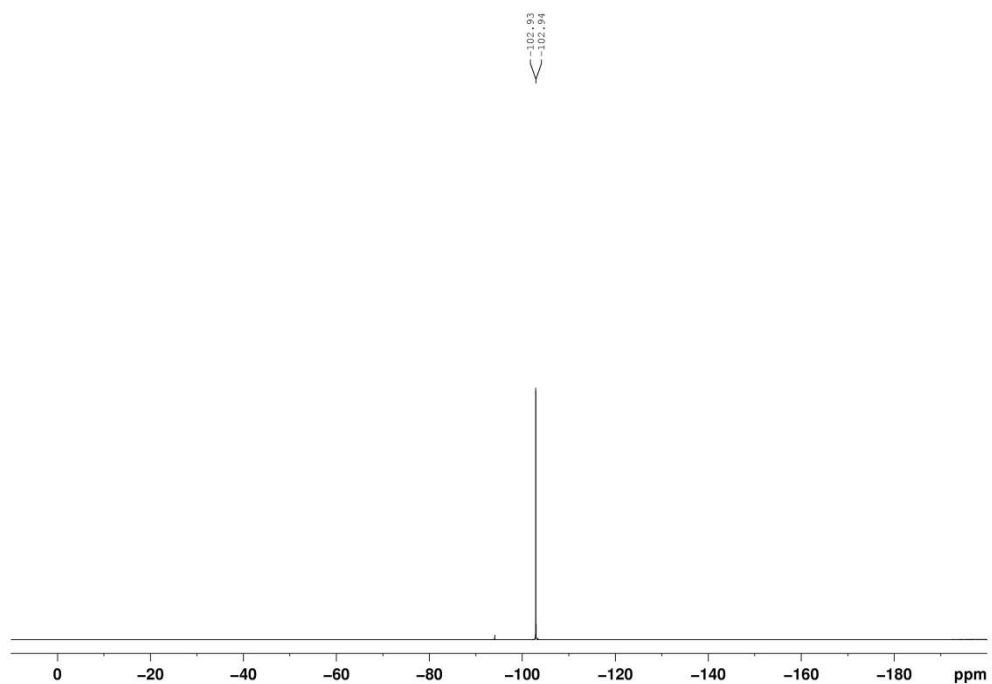




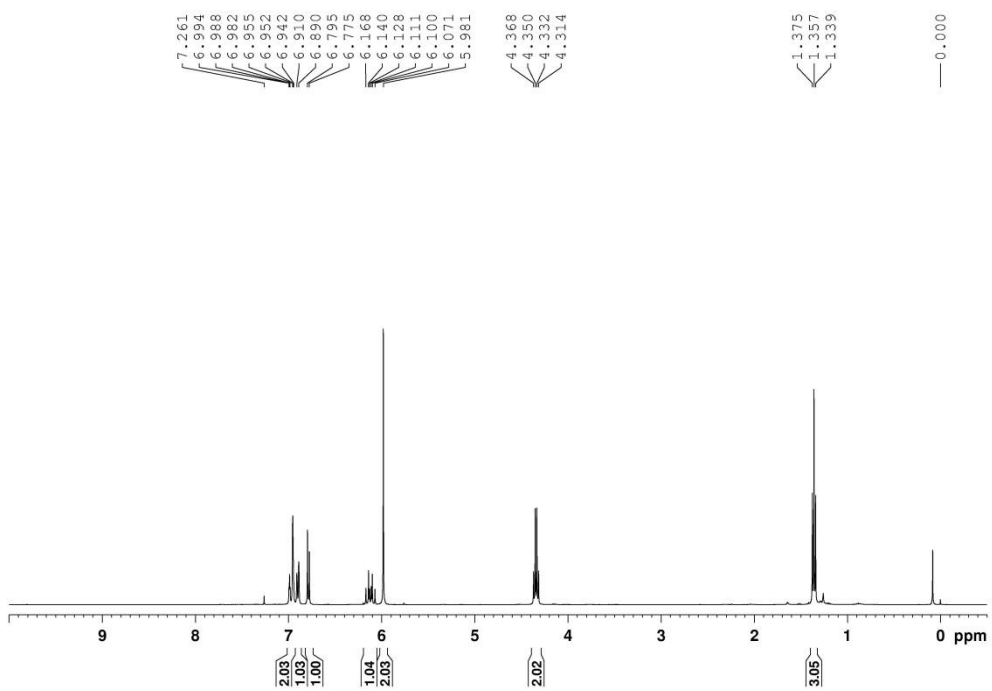


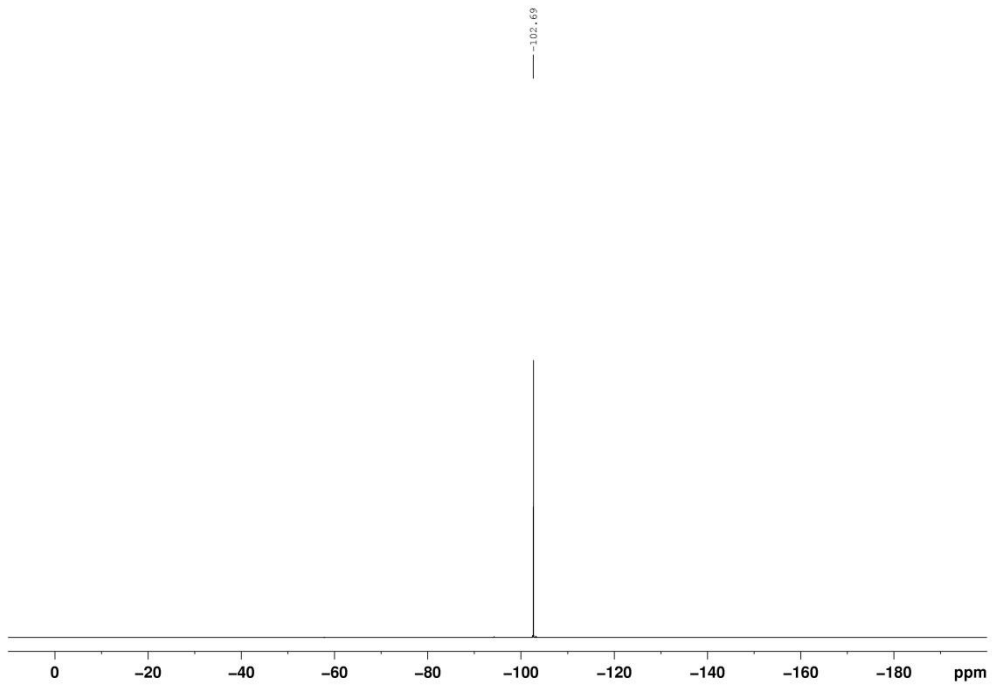
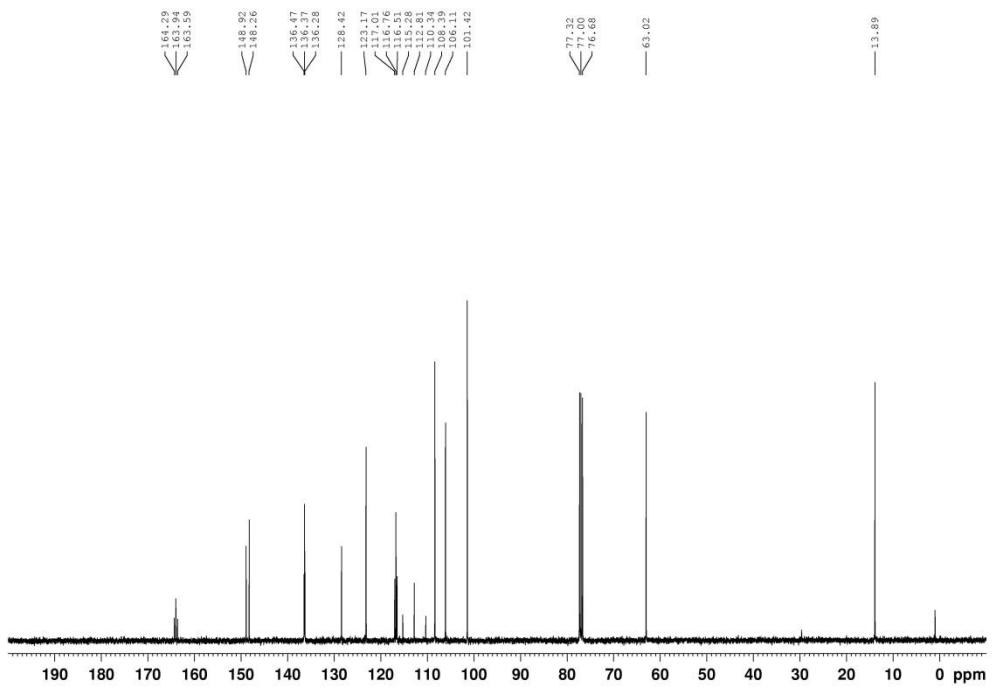
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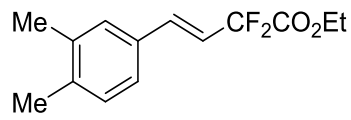




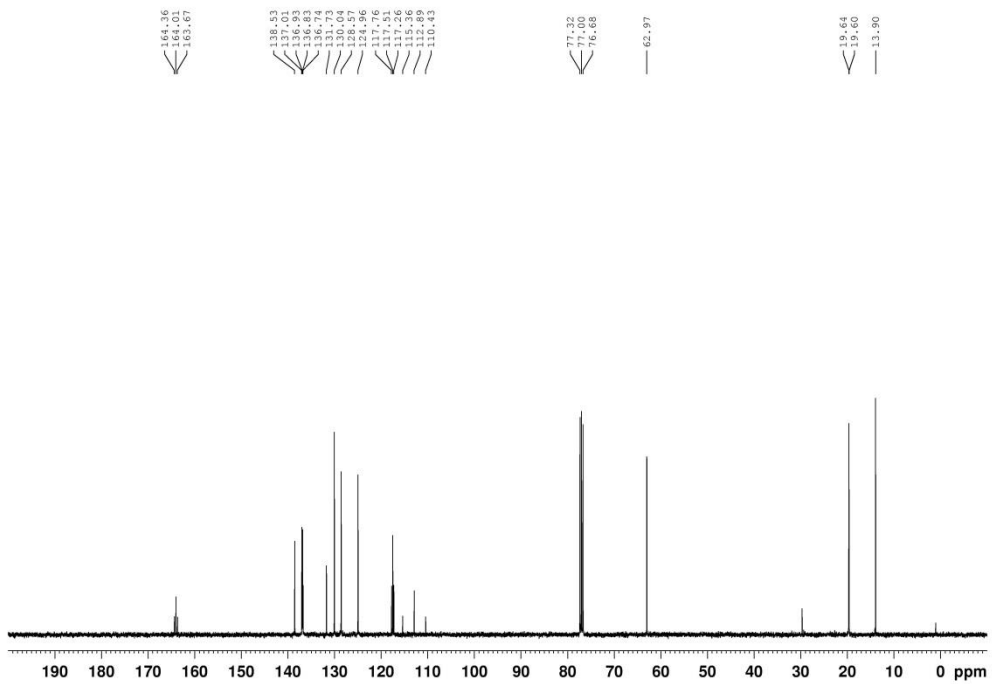
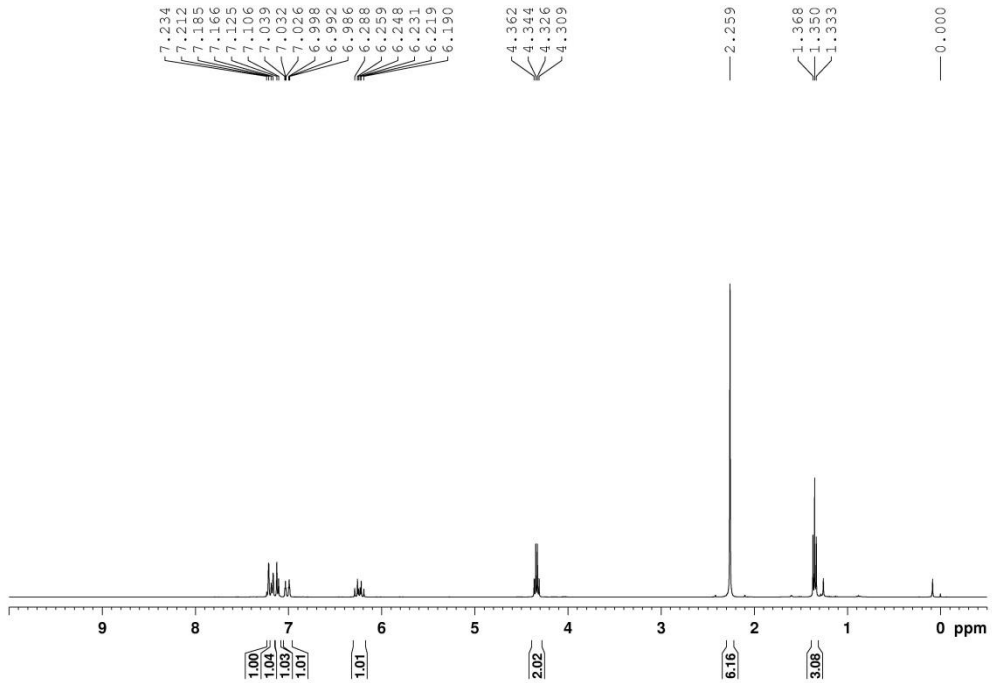
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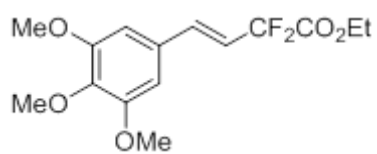
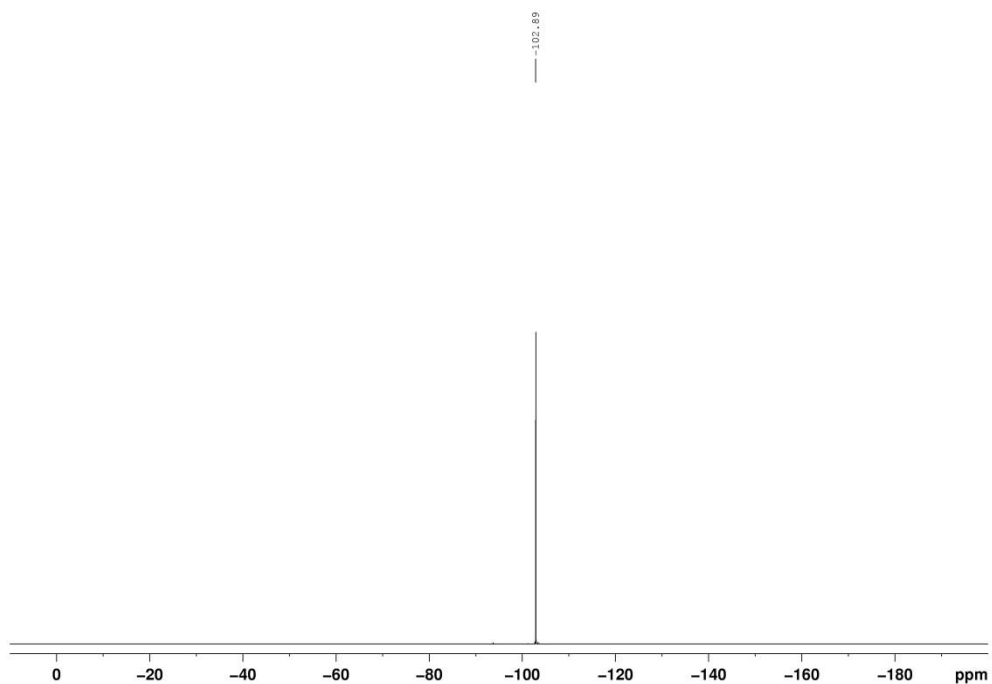




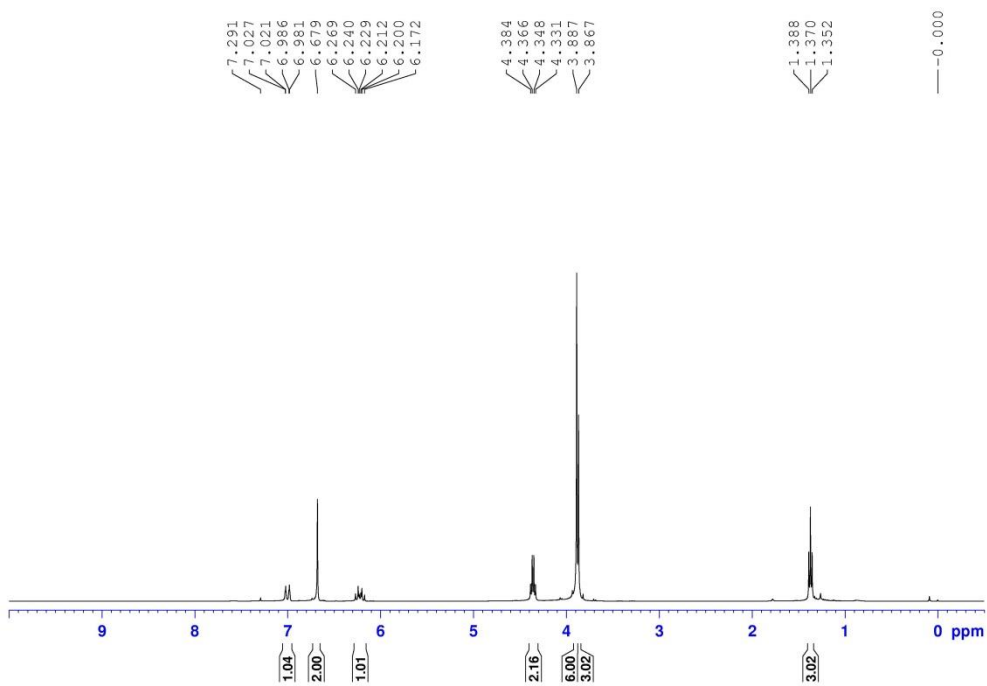


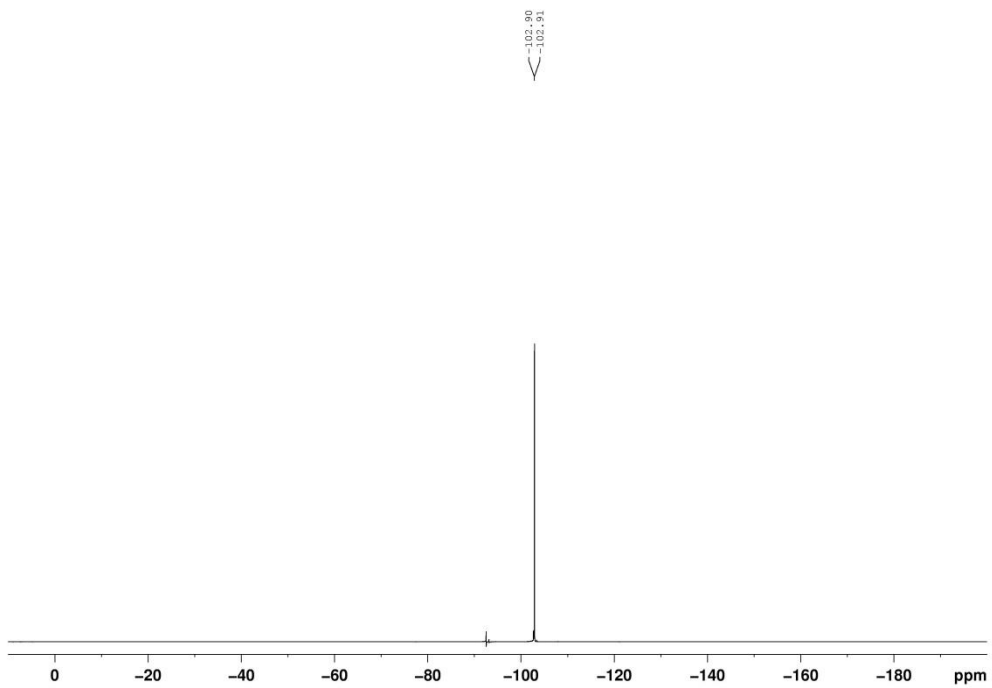
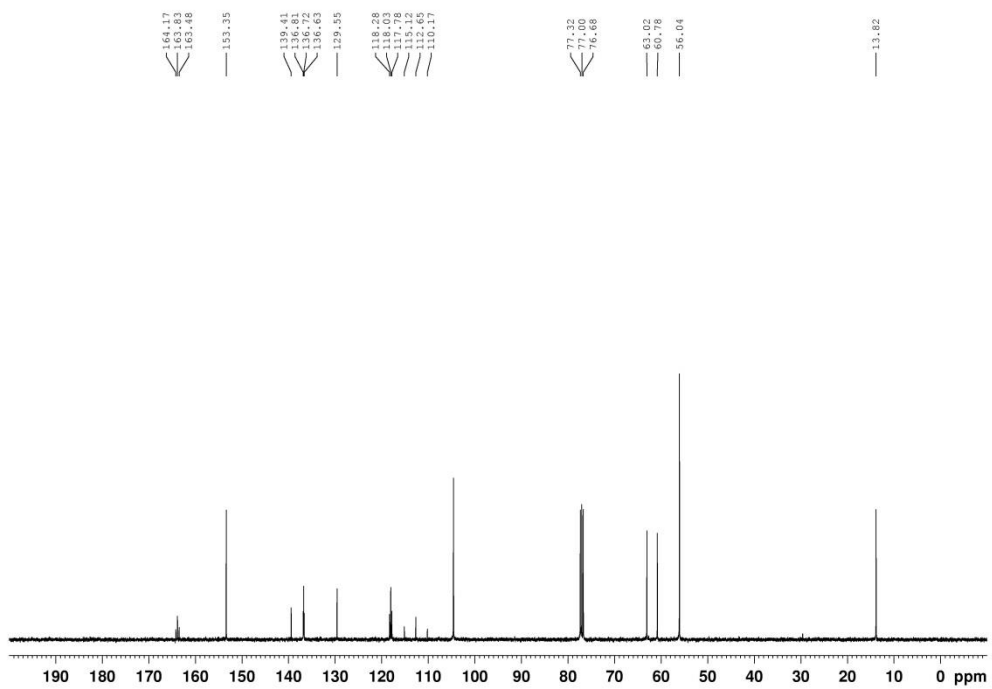
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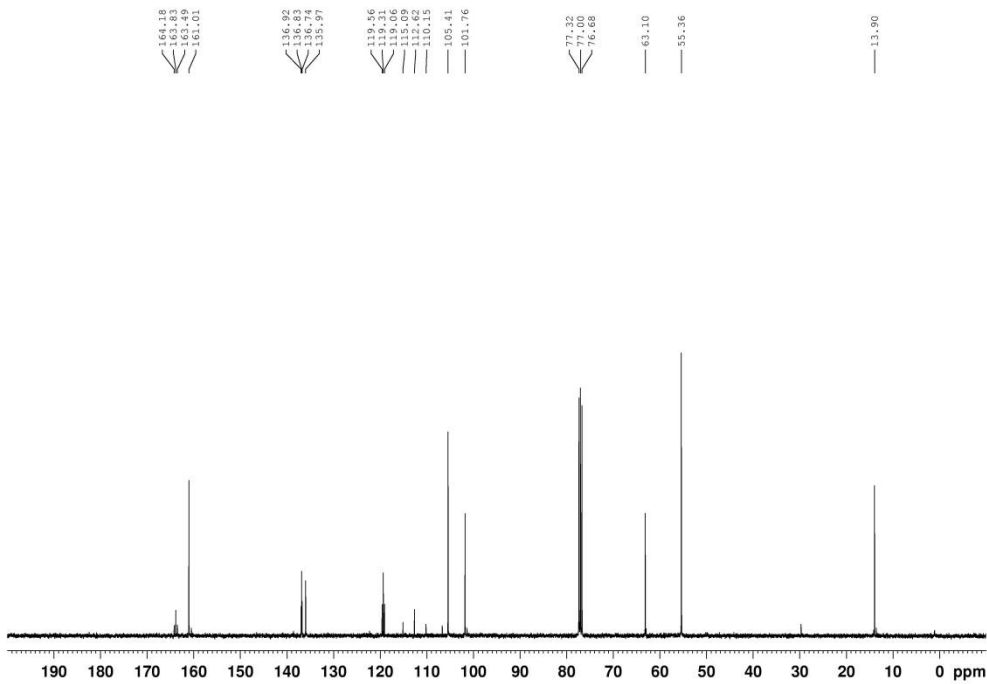
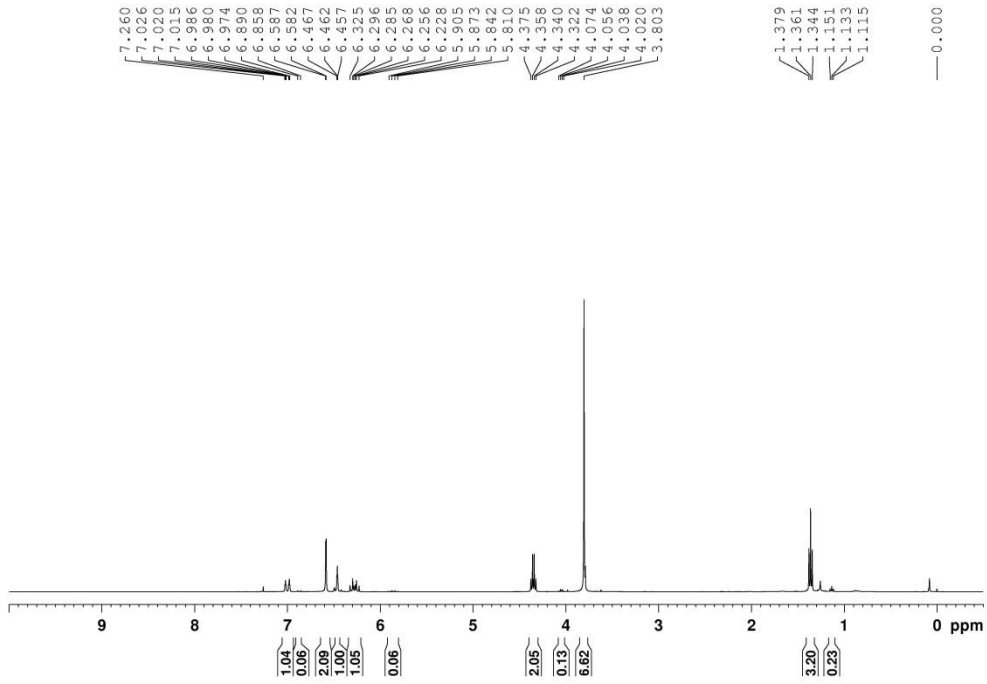
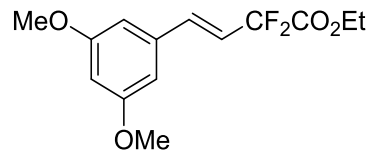


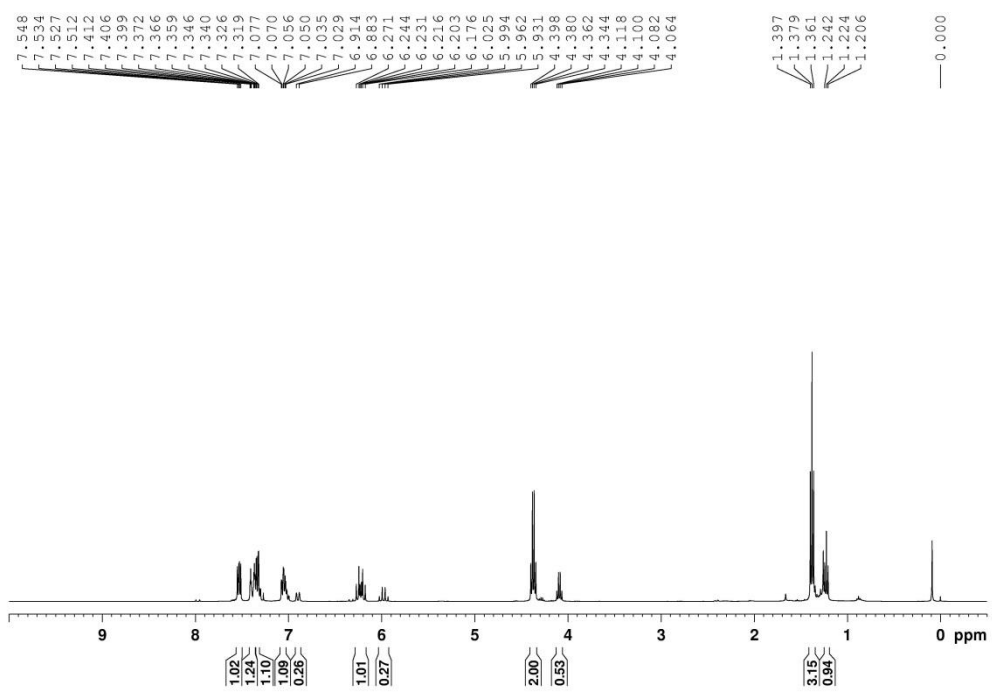
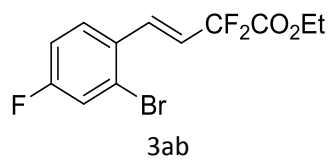
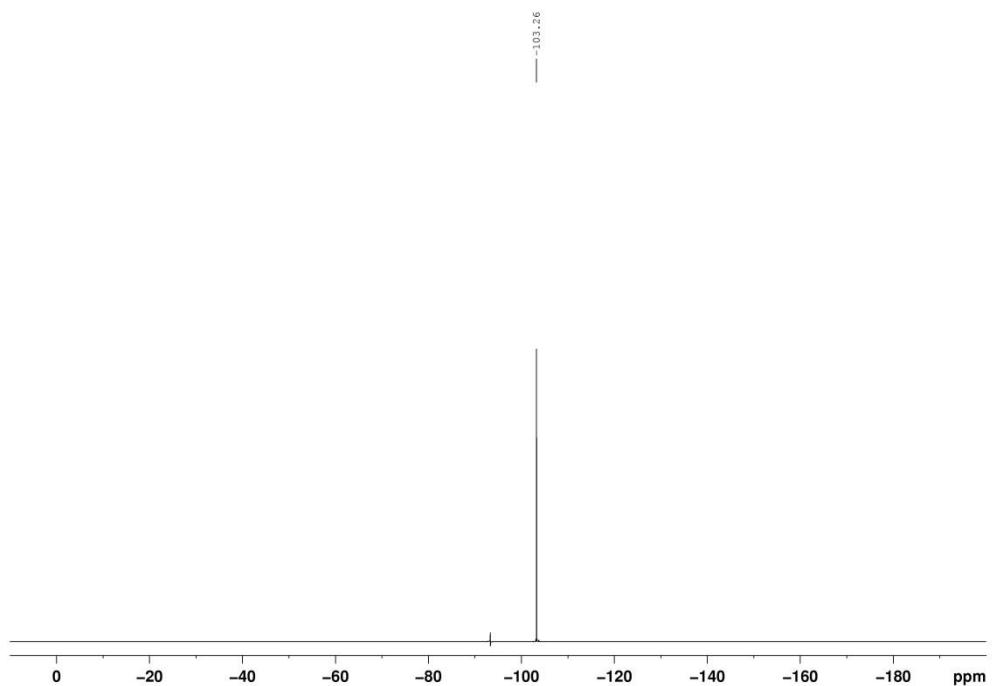


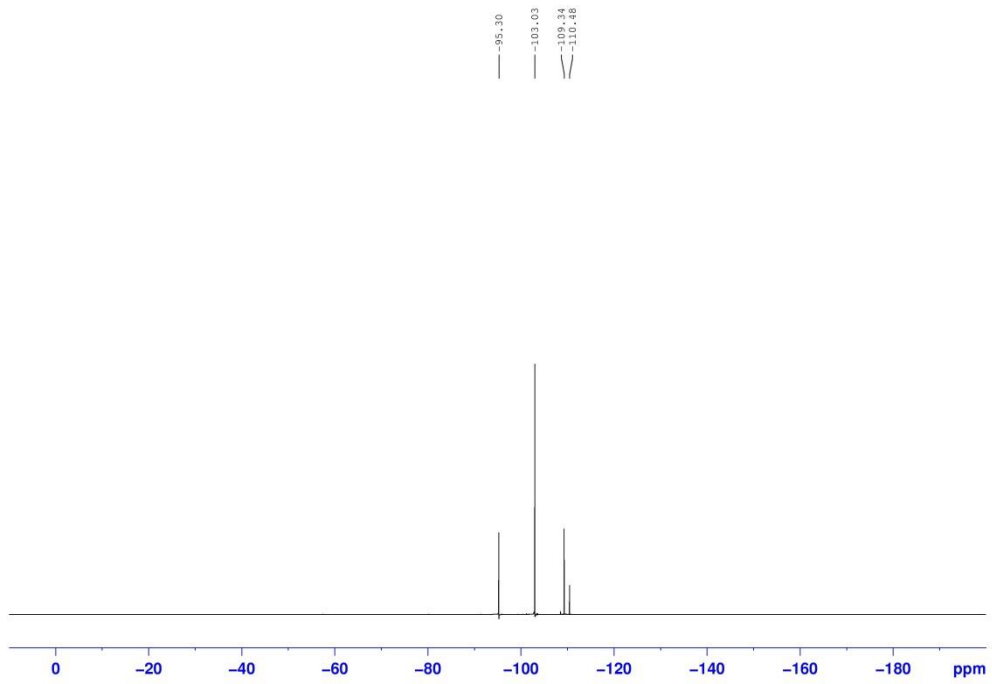
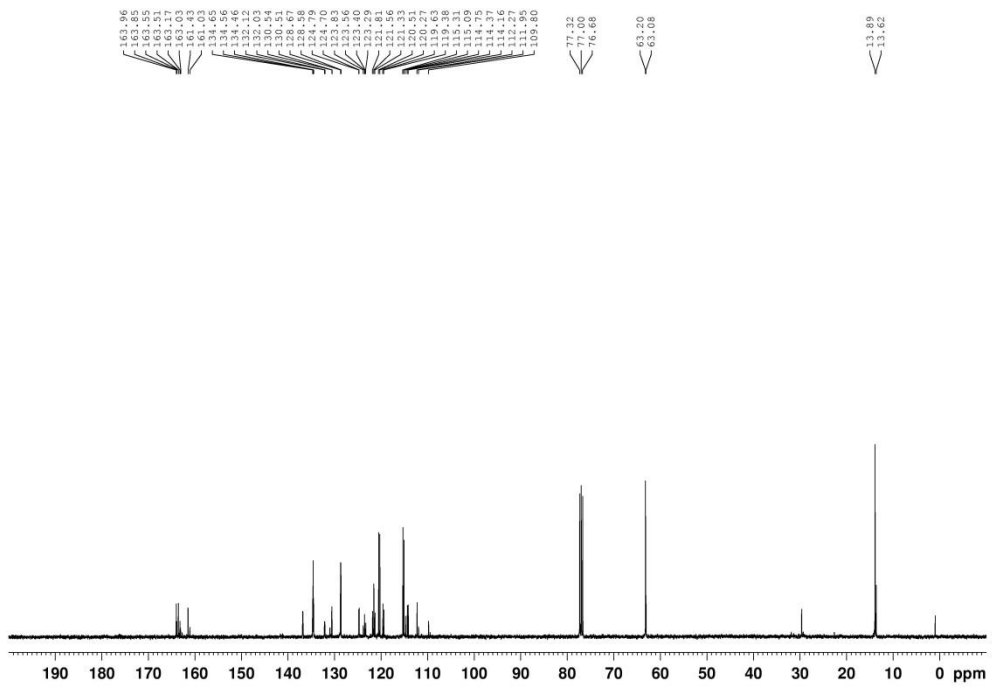
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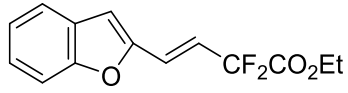




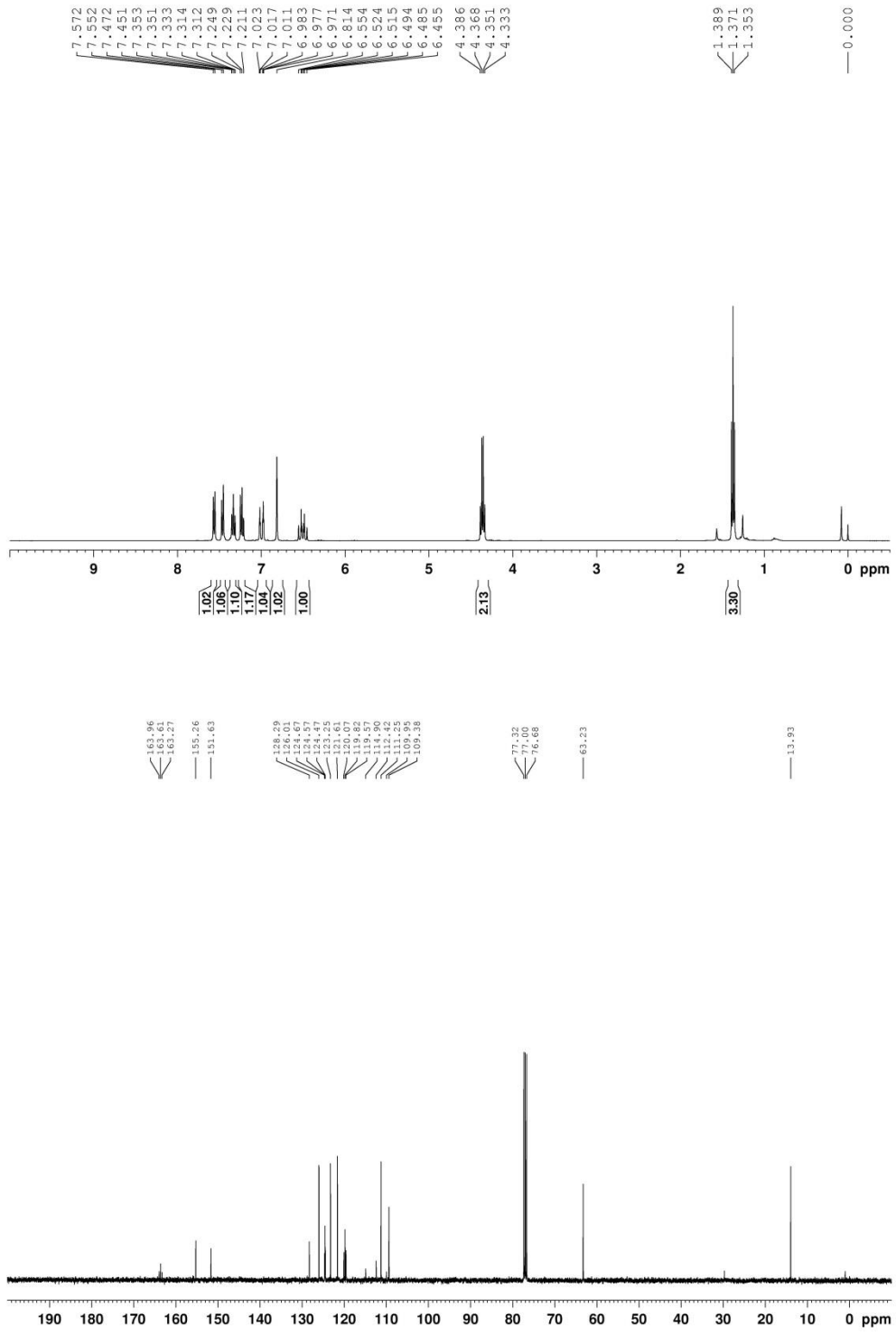


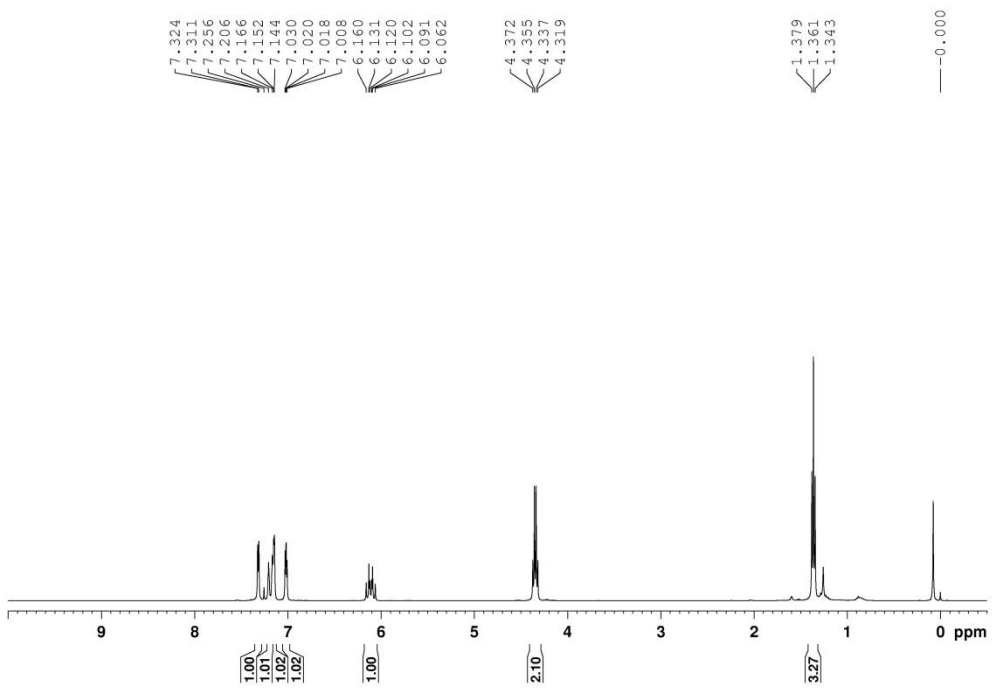
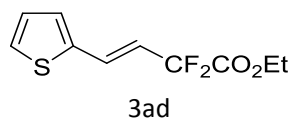
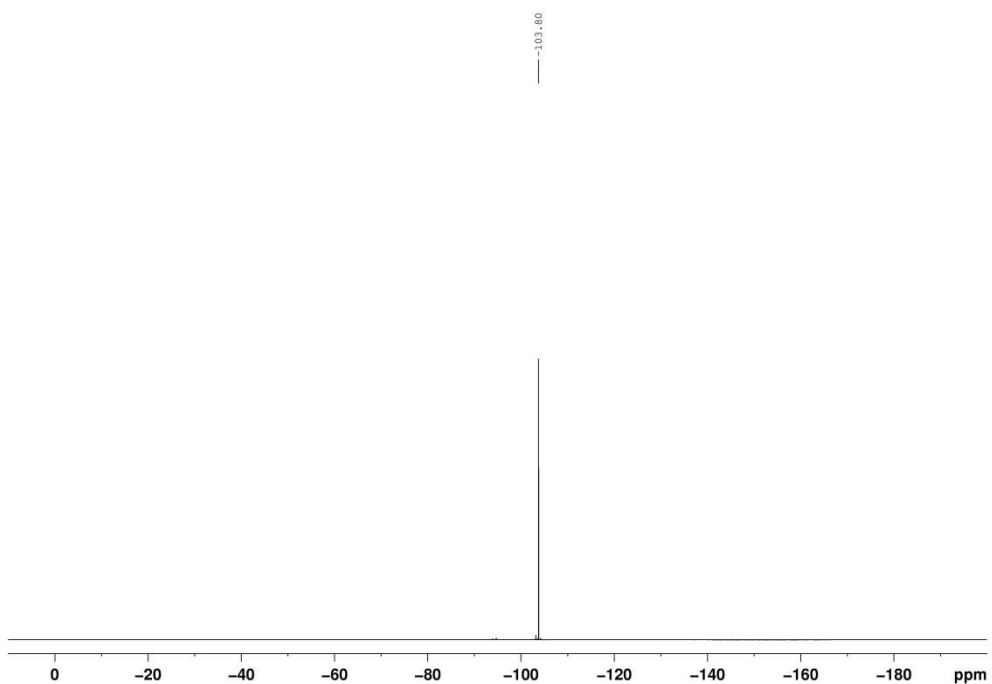


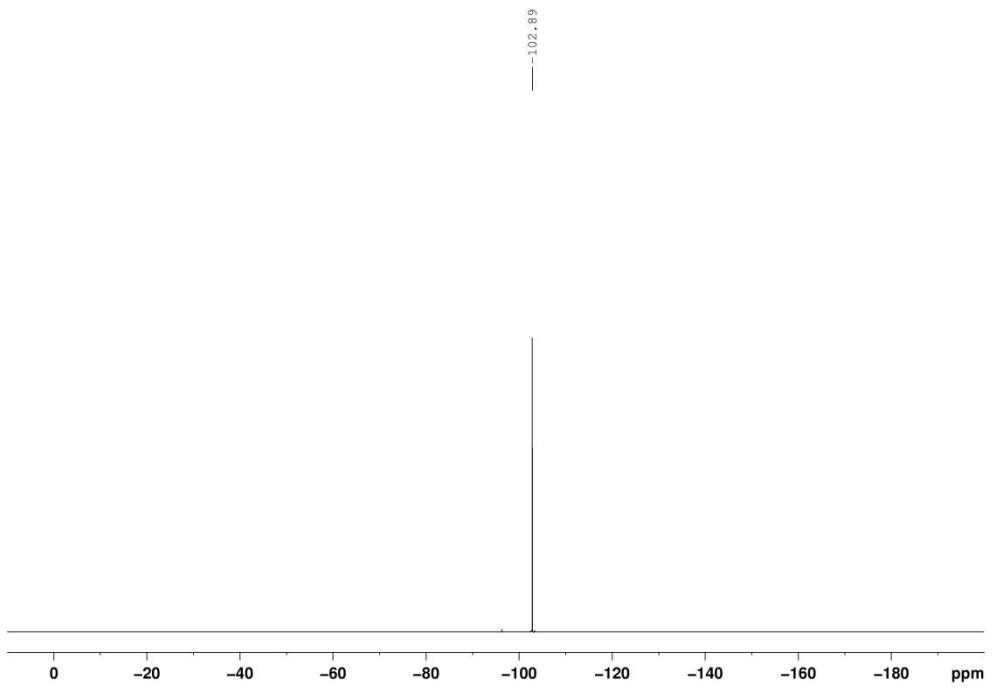
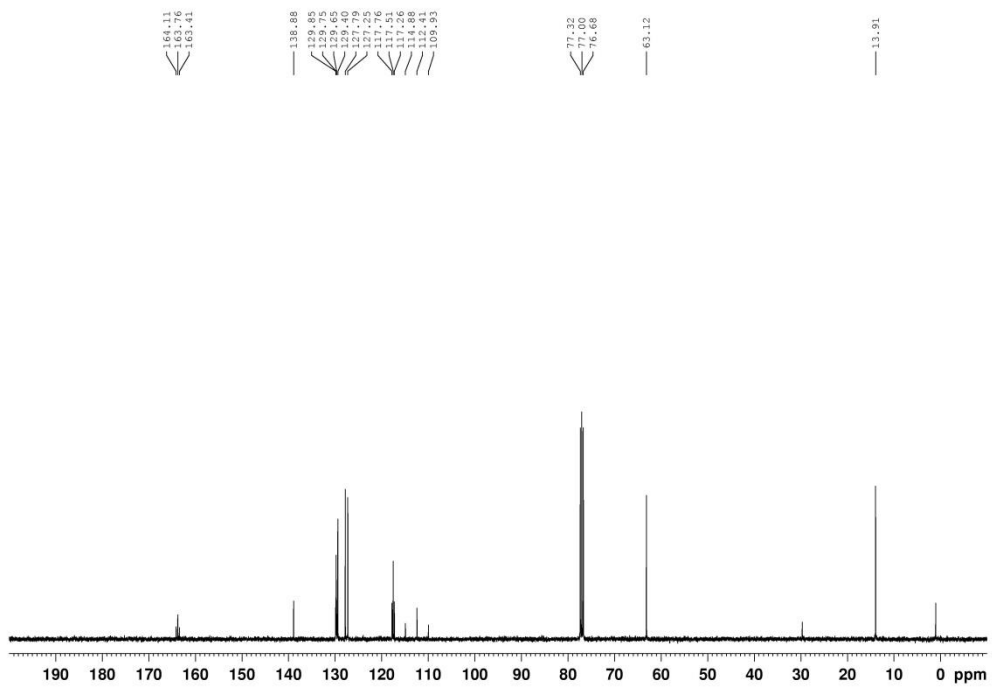


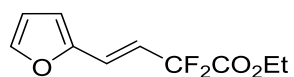


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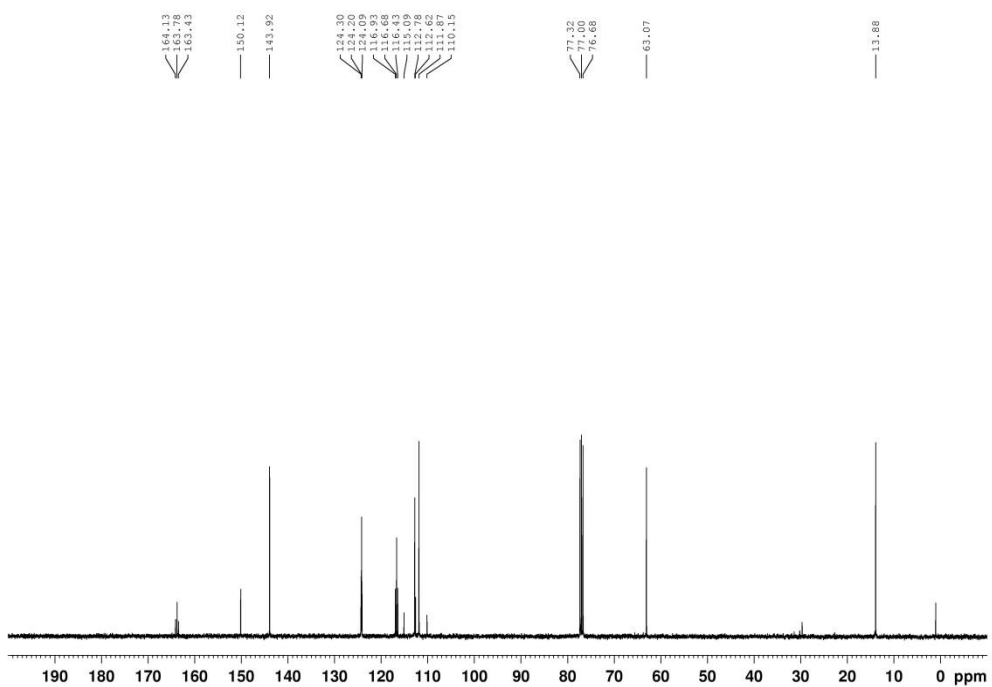
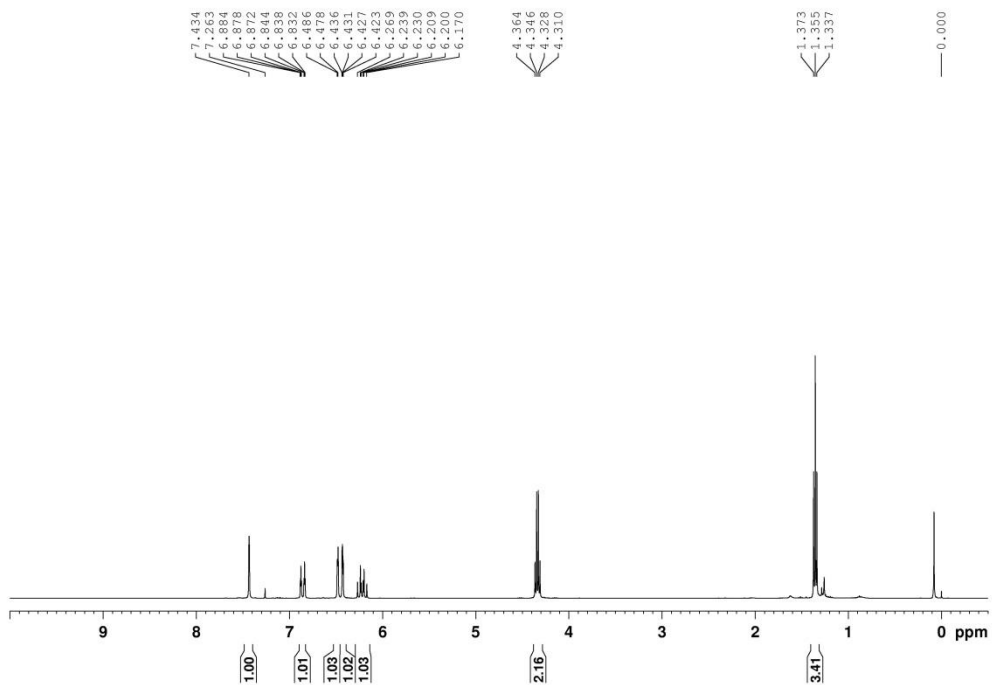


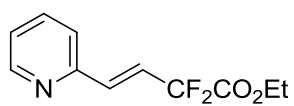
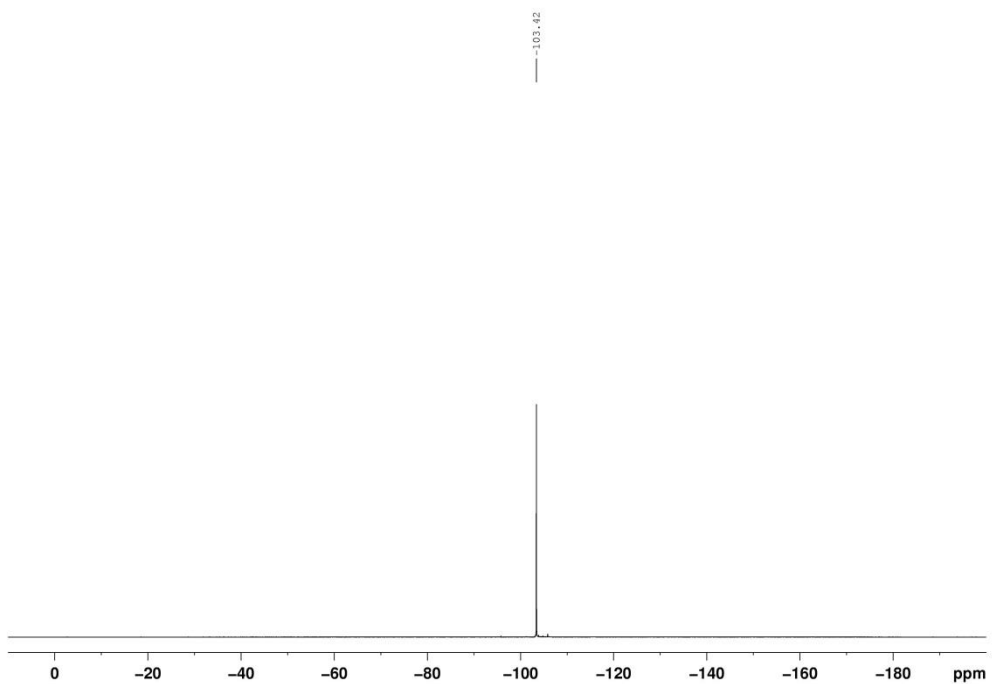






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