

Spatiotemporal Control of Pre-Existing Alkene Geometry: A Bio-Inspired Route to 4-Trifluoromethyl- 2H-Chromenes

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[‡] Both authors contributed equally to this work.

1. General Information

All chemicals were purchased as reagent grade and used without further purification. Solvents for purification (extraction and chromatography) were purchased as technical grade and distilled on the rotary evaporator prior to use. For column chromatography SiO₂-40-63 µm for flash chromatography, VWR Chemicals) was used as stationary phase. Analytical thin layer chromatography (TLC) was performed on aluminium foil pre-coated with SiO₂-60 F₂₅₄ (*Merck*) and visualized with a UV-lamp (254 nm) or CAM stain solution. Concentration *in vacuo* was performed at ~10 mbar and 40 °C, drying at ~10⁻² mbar and rt. NMR spectra were measured by the NMR service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster on a *Bruker AV300* or an *Agilent DD2 600* spectrometer at rt. The resonance multiplicity is abbreviated as: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet) and b (broad). Assignments of unknown compounds are based on DEPT, COSY (HH and FF), HMBC, HSQC and NOESY spectra. Melting points were measured on a *Büchi B-545* melting-point apparatus in open capillaries and are uncorrected. IR spectra were recorded on a *Perkin-Elmer 100 FT-IR* spectrometer, selected adsorption bands are reported in wavenumbers (cm⁻¹) and intensities are reported as: w (weak), m (medium), s (strong) and br (broad). High-resolution mass spectra (HR ESI) were measured by the MS service of the Organisch-Chemisches Institut, Westfälische Wilhelms-Universität Münster. Isomerization reactions were performed utilising a UVA LED (emission spectrum see Figure 1). Further isomerization reactions were performed with a *Winger WEPRB3-S1 Power LED Star royalblue (450 nm) 3 W* (emission spectrum see Figure 2). The forward current per chip was set to 700 mA, the resulting forward voltage was 3.4 V while the resulting radiant flux was 3000 mW. The distance between the reaction vessels and the UV-lamp was set at approximately 1 cm.

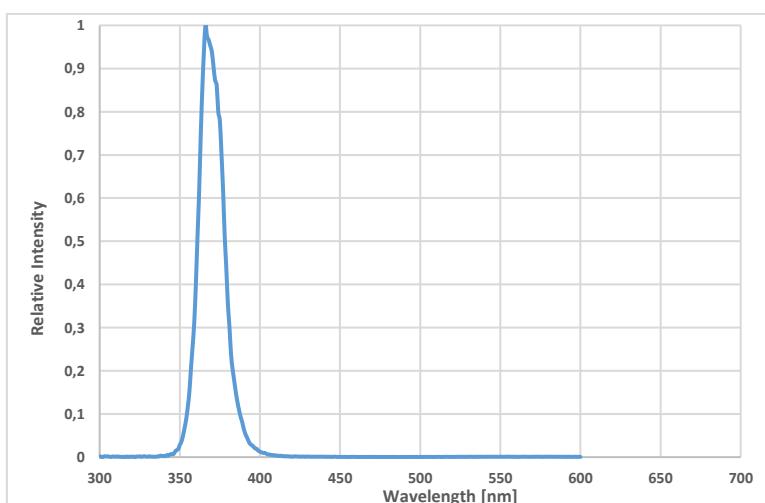


Figure 1: Emission spectrum of the utilized UVA-LED (365 nm).

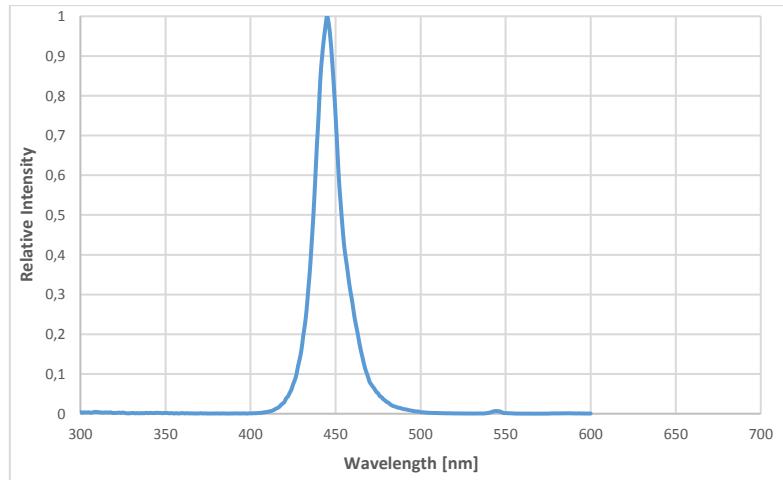


Figure 2: Emission spectrum of the utilized UV-lamp *Winger WEPRB3-S1 Power LED Star royalblue (450 nm) 3W – 35lm by Winger.*

2. Experimental Section

2.1. Preparation of α,β -unsaturated esters

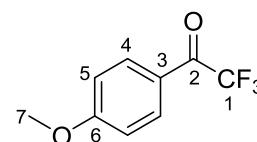
General Procedure A for the preparation of 2,2,2-trifluoromethyl acetophenones^[1]

The specified benzaldehyde (1.0 eq.), potassium carbonate (0.01 eq.) and TMS-CF₃ (1.2 eq.) were stirred in dry DMF for 15 min at RT before HCl (1M) was added. The mixture was stirred for 1 h at RT, the organic phase was separated and the aqueous phase was extracted with Et₂O (3x). The combined organic phases were washed with brine, dried over MgSO₄ and concentrated *in vacuo*. The residue was dissolved in DCM, Dess-Martin periodinane (2.4 eq.) and NaHCO₃ (4.0 eq.) were added and the resulting mixture was stirred at RT overnight before Na₂S₂O₃⁻, NaHCO₃-solution (aq., sat.) and Et₂O were added. The mixture was filtered over celite, the organic phase was separated, the aqueous phase was extracted with Et₂O (3x) and the combined organic phases were dried over MgSO₄. The crude product was concentrated *in vacuo* and purified by column chromatography (SiO₂, 4% Et₂O/*n*-pentane).

General Procedure B for the preparation of α,β -unsaturated esters^[2]

NaH (60% in mineral oil, 1.1 eq.) was dissolved in dry THF, the mixture was cooled to 0°C, triethylphosphonoacetate (1.05 eq.) was added dropwise before the resulting solution was stirred for 1 hour at 0°C. The specified aromatic ketone (1.0 eq.) was added to the reaction mixture, before the mixture was stirred for 1 hour at 0°C and subsequently being gradually warmed to RT. The resulting mixture was stirred for 24 h before water and Et₂O were added. The organic phase was separated, the aqueous phase was extracted with Et₂O (3x), the combined organic phases were dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO₂, specified combination of Et₂O/*n*-pentane).

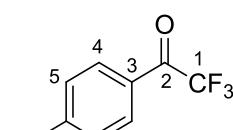
2,2,2-Trifluoro-1-(4-methoxyphenyl)ethan-1-one (5e)

 Prepared according to General Procedure A, *p*-anisaldehyde (5.0 mmol) was converted to **5e** yielding a colorless oil (674 mg, 66%).

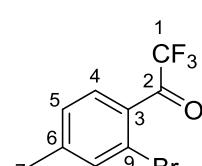
R_f = 0.29 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS:** *m/z*: 227.0293 ([M+Na]⁺, calcd. for C₉H₇O₂F₃Na⁺: 227.0296); **1H NMR** (500 MHz, CDCl₃) δ = 8.09 – 8.03 (m, 2H, H-C4), 7.03 – 6.97 (m, 2H, H-C5), 3.92 (d, *J* = 0.6 Hz, 3H, H-C7) ppm; **13C NMR** (126 MHz, CDCl₃) δ = 179.1 (q, *J*_{CF} = 34.4 Hz, C2), 165.6 (C6), 132.9 (q, *J*_{CF} = 2.2 Hz, 2C, C4), 123.0 (C3), 117.1 (q, *J*_{CF} = 291.4 Hz, C1), 114.6 (2C, C5), 55.9 (C7) ppm; **19F NMR** (470 MHz, CDCl₃) δ = -71.05

(d, $J = 1.2$ Hz, 3F, F-C1) ppm; **IR (ATR)**: $\tilde{\nu} = 3018(\text{w})$, $2942(\text{w})$, $2847(\text{w})$, $1703(\text{m})$, $1598(\text{s})$, $1572(\text{m})$, $1514(\text{m})$, $1462(\text{w})$, $1429(\text{w})$, $1344(\text{w})$, $1317(\text{w})$, $1270(\text{m})$, $1196(\text{m})$, $1160(\text{s})$, $1134(\text{s})$, $1025(\text{m})$, $937(\text{s})$, $843(\text{s})$, $801(\text{w})$, $767(\text{s})$, $737(\text{m})$, $702(\text{w})$ cm^{-1} ; analytical data in agreement with the literature.^[3]

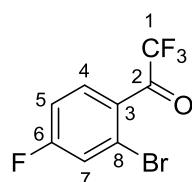
2,2,2-Trifluoro-1-(*p*-tolyl)ethan-1-one (5g)

 Prepared according to General Procedure **A**, *p*-tolualdehyde (4.5 mmol) was converted to **5g** yielding a colorless oil (547 mg, 65%). $R_f = 0.83$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:4); **HR-ESI-MS**: m/z : 243.0617 ([$M+\text{Na}+\text{MeOH}$] $^+$, calcd. for $\text{C}_{11}\text{H}_{11}\text{F}_3\text{O}_2\text{Na}^+$: 243.0603); **$^1\text{H NMR}$** (500 MHz, CDCl_3) $\delta = 7.97$ (dq, $J = 8.0, 1.1$ Hz, 2H, H-C4), 7.34 (dq, $J = 7.9, 0.6$ Hz, 2H, H-C5), 2.46 (q, $J = 0.5$ Hz, 3H, H-C7) ppm; **$^{13}\text{C NMR}$** (126 MHz, CDCl_3) $\delta = 180.3$ (q, $J_{\text{CF}} = 34.8$ Hz, C2), 147.2 (C6), 130.4 (q, $J_{\text{CF}} = 2.1$ Hz, 2C, C4), 130.0 (2C, C5), 127.6 (C3), 116.9 (q, $J_{\text{CF}} = 291.4$ Hz, C1), 22.1 (C7) ppm; **$^{19}\text{F NMR}$** (470 MHz, CDCl_3) $\delta = -71.37$ (d, $J = 1.2$ Hz) ppm; **IR (ATR)**: $\tilde{\nu} = 2928(\text{w})$, 1713(s), 1607(m), 1569(w), 1450(w), 1413(w), 1381(w), 1339(w), 1319(w), 1293(w), 1202(m), 1194(m), 1171(w), 1137(s), 1039(w), 993(w), 935(s), 832(w), 750(s), 736(s), 694(w) cm^{-1} ; analytical data in agreement with the literature.^[4]

1-(2-Bromo-4-methylphenyl)-2,2,2-trifluoroethan-1-one (5o)

 Prepared according to General Procedure **A**, 2-bromo-4-methylbenzaldehyde (4.0 mmol) was converted to **5o** yielding a colorless oil (389 mg, 34%). $R_f = 0.77$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:5); **HR-ESI-MS**: m/z : 320.9704 ([$M+\text{Na}+\text{MeOH}$] $^+$, calcd. for $\text{C}_{10}\text{H}_{10}\text{BrF}_3\text{O}_2\text{Na}^+$: 320.9708); **$^1\text{H NMR}$** (600 MHz, CDCl_3) $\delta = 7.65$ (dq, $J = 8.0, 1.6$ Hz, 1H; H-C4), 7.59 (dd, $J = 1.6, 0.8$ Hz, 1H, H-C8), 7.27 – 7.23 (m, 1H, H-C5), 2.42 (d, $J = 0.7$ Hz, 3H, H-C7) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) $\delta = 181.4$ (q, $J_{\text{CF}} = 35.9$ Hz, C2), 146.01 (C6), 136.1 (C8), 130.6 (q, $J_{\text{CF}} = 3.7, 3.1$ Hz, C4), 128.9 (C3), 128.2 (C5), 122.5 (C9), 116.0 (d, $J_{\text{CF}} = 292.3$ Hz, C1), 21.5 (C7) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) $\delta = -72.43$ ppm; **IR (ATR)**: $\tilde{\nu} = 1724(\text{m})$, 1599 (m), 1553(w), 1487(w), 1449(w), 1383(w), 1320(w), 1278(w), 1183(s), 1139(s), 1051(m), 939(s), 880(w), 845(m), 822(m), 765(m), 738(s), 695(w), 671(w) cm^{-1} .

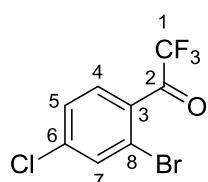
1-(2-Bromo-4-fluorophenyl)-2,2,2-trifluoroethan-1-one (5p)



Prepared according to General Procedure **A**, 2-Bromo-4-fluorobenzaldehyde (4.8 mmol) was converted to **5p** yielding a colorless oil (666 mg, 51%).

R_f = 0.74 (Et₂O/n-pentane 1:5); **HR-ESI-MS:** *m/z* 324.9449 ([M+Na+MeOH]⁺, calcd. for C₉H₇BrF₄NaO₂⁺: 324.9458); **¹H NMR** (600 MHz, CDCl₃) δ = 7.79 (ddd, *J* = 8.8, 5.6, 1.4 Hz, 1H, H-C4), 7.52 (dd, *J* = 8.1, 2.5 Hz, 1H, H-C7), 7.19 (ddd, *J* = 8.8, 7.5, 2.5 Hz, 1H, H-C5) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 180.5 (d, *J_{CF}* = 36.3 Hz, C2), 164.6 (d, *J_{CF}* = 261.2 Hz, C6), 132.3 (dq, *J_{CF}* = 9.9, 3.3 Hz, C4), 128.0 (d, *J_{CF}* = 3.5 Hz, C3), 124.0 (d, *J_{CF}* = 10.0 Hz, C8), 123.1 (d, *J_{CF}* = 24.7 Hz, C7), 115.3 (d, *J_{CF}* = 291.1 Hz, C1), 114.9 (d, *J_{CF}* = 21.8 Hz, C5); **¹⁹F NMR** (564 MHz, CDCl₃) δ = -72.56 (d, *J* = 1.5 Hz, 3F, F-C1), -101.54 (td, *J* = 7.9, 5.6 Hz, F-C6) ppm; **IR (ATR):** ν = 3088(w), 1731(m), 1595(s), 1576(m), 1488(w), 1385(w), 1322(w), 1290(w), 1202(s), 1178(s), 1140(s), 1041(m), 942(s), 867(s), 824(m), 767(m), 740(m), 692(w), 671(w) cm⁻¹; analytical data in agreement with the literature.^[5]

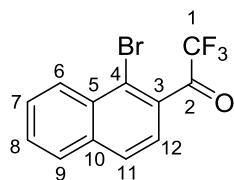
1-(2-Bromo-4-chlorophenyl)-2,2,2-trifluoroethan-1-one (5q)



Prepared according to General Procedure **A**, 2-bromo-4-chlorobenzaldehyde (4 mmol) was converted to **5q** yielding a colorless oil (681 mg, 64%).

R_f = 0.81 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z* 340.9149 ([M+Na+MeOH]⁺, calcd. for C₉H₇BrClF₃NaO₂⁺: 340.9162); **¹H NMR** (600 MHz, CDCl₃) δ = 7.78 (d, *J* = 2.0 Hz, 1H, H-C7), 7.66 (dq, *J* = 8.4, 1.4 Hz, 1H, H-C4), 7.46 (dd, *J* = 8.4, 2.0 Hz, 1H, H-C5) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 181.2 (q, *J_{CF}* = 36.7 Hz, C2), 140.4 (C6), 135.2 (C7), 131.1 (q, *J_{CF}* = 3.0 Hz, C4), 130.4 (C3), 127.9 (C5), 123.1 (C8), 115.7 (q, *J_{CF}* = 291.8 Hz, C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -72.87 (d, *J* = 1.5 Hz) ppm; **IR (ATR):** ν = 1734(m), 1699(w), 1578(s), 1548(w), 1470(w), 1371(w), 1317(w), 1279(w), 1263(w), 1203(s), 1182(s), 1142(s), 1102(m), 1049(m), 934(s), 874(m), 826(m), 789(m), 765(m), 729(m), 691(w), 660(w) cm⁻¹; analytical data in agreement with the literature.^[6]

1-(3-Bromonaphthalen-2-yl)-2,2,2-trifluoroethan-1-one (5r)

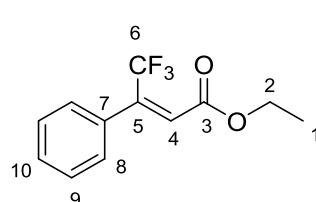


Prepared according to General Procedure **A**, 1-(2-bromo-4-methylphenyl)-2,2,2-trifluoroethan-1-one (4.0 mmol) was converted to **5r** yielding a colorless oil (561 mg, 46 %).

R_f = 0.68 (Et₂O/n-pentane 1:9); **HR-ESI-MS:** *m/z* 356.9707 ([M+Na+MeOH]⁺, calcd. for C₁₃H₁₀BrF₃O₂Na⁺: 356.9708); **¹H NMR** (600 MHz, CDCl₃) δ = 8.44 (ddt, *J* = 8.6, 1.4, 0.8 Hz, 1H, H-C6), 7.93 (dt, *J* = 8.5, 0.6 Hz, 1H, H-C11), 7.90 (ddt, *J* = 8.0,

1.3, 0.6 Hz, 1H, H-C8), 7.73 – 7.66 (m, 2H, H-C7, H-C9), 7.54 (dq, J = 8.5, 1.2 Hz, 1H, H-C12) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 184.6 (q, J_{CF} = 36.9 Hz, C2), 135.7 (C10), 132.3 (C5), 131.8 (C3), 129.3 (C7), 129.0 (C9), 128.6 (C6), 128.5 (C8), 128.4 (C11), 123.5 (q, J_{CF} = 2.1 Hz, C12), 123.0 (C4), 115.7 (q, J_{CF} = 292.1 Hz, C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -73.82 ppm; **IR (ATR)**: $\tilde{\nu}$ = 1732(m), 1620(w), 1593(w), 1553(w), 1500(w), 1463(w), 1373(w), 1323(w), 1304(w), 1256(m), 1204(s), 1191(s), 1143(s), 1033(s), 1014(s), 944(s), 865(w), 843(w), 808(s), 759(s), 746(m), 731(s), 676(m), 653(m) cm⁻¹.

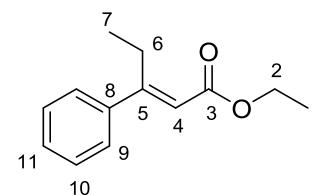
Ethyl (Z)-4,4,4-trifluoro-3-phenylbut-2-enoate (4c)



Prepared according to General Procedure **B**, 2,2,2-trifluoroacetophenone (10.0 mmol) was converted to **4c** in 30 min yielding a colourless oil (270 mg, 11%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

¹H NMR (400 MHz, CDCl₃) δ = 7.51 – 7.35 (m, 5H, H-C8, H-C9, H-C10), 6.34 (s, 1H, H-C4), 4.31 (q, J = 7.1 Hz, 2H, H-C2), 1.35 (t, J = 7.1 Hz, 3H, H-C1) ppm; analytical data in agreement with the literature.^[2]

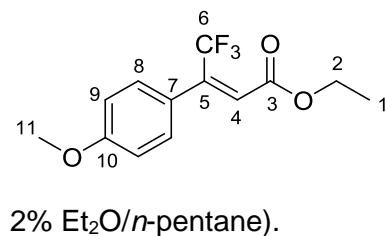
Ethyl (E)-3-phenylpent-2-enoate (4d)



Prepared according to General Procedure **B**, propiophenone (30 mmol) was converted to **4d** in 24 hours yielding a colourless oil (2627 mg, 43%) after purification by column chromatography (SiO₂, 2% Et₂O/ n-pentane).

¹H NMR (300 MHz, CDCl₃) δ = 7.49 – 7.33 (m, 5H, H-C8, H-C9, H-C10), 6.01 (s, 1H, H-C4), 4.21 (q, J = 7.1 Hz, 2H, H-C2), 3.11 (q, J = 7.5 Hz, 2H, H-C6), 1.32 (t, J = 7.1 Hz, 3H, H-C1), 1.08 (t, J = 7.5 Hz, 3H, H-C7) ppm; analytical data in agreement with the literature.^[2]

Ethyl (Z)-4,4,4-trifluoro-3-(4-methoxyphenyl)but-2-enoate (4e)

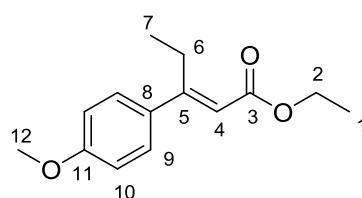


Prepared according to General Procedure **B**, 2,2,2-trifluoro-1-(4-methoxyphenyl)ethan-1-one **5e** (2.5 mmol) was converted to **4e** in 1 h yielding a colorless liquid (75 mg, 11%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

R_f = 0.36 (Et₂O/n-pentane 1:6); **HR-ESI-MS**: *m/z* 297.0721 ([M+Na]⁺, calcd. for C₁₃H₁₃F₃O₃Na⁺: 297.0714); **¹H NMR** (600 MHz, CDCl₃) δ = 7.37 – 7.33 (m, 2H, H-C8), 6.95 –

6.88 (m, 2H, H-C9), 6.29 (s, 1H, H-C4), 4.30 (q, $J = 7.2$ Hz, 2H, H-C2), 3.83 (s, 3H, H-C11), 1.34 (t, $J = 7.2$ Hz, 3H, H-C1) ppm; **^{13}C NMR** (151 MHz, CDCl_3) $\delta = 165.0$ (C3), 160.8 (C10), 137.6 (q, $J_{\text{CF}} = 31.8$ Hz, C5), 129.3 (d, $J_{\text{CF}} = 1.2$ Hz, 2C, C8), 126.4 (q, $J_{\text{CF}} = 3.4$ Hz, C4), 126.0 (q, $J_{\text{CF}} = 1.4$ Hz, C7), 122.5 (d, $J_{\text{CF}} = 275.8$ Hz, C6), 114.2 (2C, C9), 61.8 (C2), 55.5 (C11), 14.1 (C1) ppm; **^{19}F NMR** (564 MHz, CDCl_3) $\delta = -60.14$ ppm; **IR (ATR)**: $\tilde{\nu} = 2983(\text{w}), 2907(\text{w}), 2842(\text{w}), 1732(\text{m}), 1655(\text{w}), 1609(\text{m}), 1576(\text{w}), 1514(\text{m}), 1465(\text{w}), 1444(\text{w}), 1376(\text{w}), 1278(\text{m}), 1249(\text{s}), 1203(\text{m}), 1167(\text{s}), 1126(\text{s}), 1028(\text{s}), 986(\text{m}), 943(\text{w}), 923(\text{w}), 895(\text{w}), 832(\text{s}), 804(\text{w}), 736(\text{w}), 692(\text{w}), 657(\text{m}) \text{ cm}^{-1}$; analytical data in agreement with the literature.^[7]

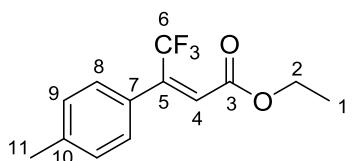
Ethyl (*E*)-3-(4-methoxyphenyl)pent-2-enoate (4f)



Prepared according to General Procedure **B**, 4'-methoxypropiophenone (5.0 mmol) was converted to **4f** in 24 hours yielding a colorless oil (178 mg, 15%) after purification by column chromatography (SiO_2 , 5% $\text{Et}_2\text{O}/n\text{-pentane}$).

^1H NMR (300 MHz, CDCl_3) $\delta = 7.51 - 7.33$ (m, 2H, H-C9), 7.01 – 6.71 (m, 2H, H-C10), 6.00 (s, 1H, H-C4), 4.20 (q, $J = 7.1$ Hz, 2H, H-C2), 3.83 (s, 3H, H-C12), 3.09 (q, $J = 7.5$ Hz, 2H, H-C6), 1.31 (t, $J = 7.1$ Hz, 3H, H-C1), 1.08 (t, $J = 7.5$ Hz, 3H, H-C7) ppm; analytical data in agreement with the literature.^[2]

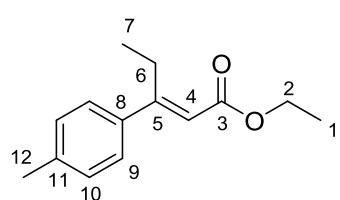
Ethyl (*Z*)-4,4,4-trifluoro-3-(*p*-tolyl)but-2-enoate (4g)



Prepared according to General Procedure **B**, 4'-methyl-2,2,2-trifluoroacetophenone **5g** (3.1 mmol) was converted to **4g** in 2 h yielding a colorless liquid (97 mg, 12%) after purification by column chromatography (SiO_2 , 1% $\text{Et}_2\text{O}/n\text{-pentane}$).

$R_f = 0.65$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:6); **HR-ESI-MS**: m/z 281.0771 ([$M+\text{Na}$] $^+$, calcd. for $\text{C}_{13}\text{H}_{13}\text{O}_2\text{F}_3\text{Na}^+$: 281.0760); **^1H NMR** (600 MHz, CDCl_3) $\delta = 7.30$ (d, $J = 7.9$ Hz, 2H, H-C8), 7.23 – 7.19 (m, 2H, H-C9), 6.31 (s, 1H, H-C4), 4.30 (q, $J = 7.1$ Hz, 2H, H-C2), 2.38 (s, 3H, H-C11), 1.35 (t, $J = 7.1$ Hz, 3H, H-C1) ppm; **^{13}C NMR** (151 MHz, CDCl_3) $\delta = 165.0$ (C3), 139.9 (C10), 137.9 (d, $J_{\text{CF}} = 31.9$ Hz, C5), 130.8 (C7), 129.48 (C9), 127.8 (C8), 127.0 (q, $J_{\text{CF}} = 3.5$ Hz, C4) 122.4 (d, $J_{\text{CF}} = 275.8$ Hz, C6), 61.8 (C2), 21.4 (C11), 14.1 (C1) ppm; **^{19}F NMR** (564 MHz, CDCl_3) $\delta = -60.12$ ppm; **IR (ATR)**: $\tilde{\nu} = 2986(\text{w}), 1735(\text{m}), 1656(\text{w}), 1613(\text{w}), 1515(\text{w}), 1447(\text{w}), 1378(\text{w}), 1362(\text{w}), 1282(\text{s}), 1253(\text{s}), 1201(\text{s}), 1175(\text{s}), 1165(\text{s}), 1128(\text{s}), 1030(\text{m}), 1023(\text{m}), 987(\text{w}), 929(\text{w}), 897(\text{w}), 821(\text{m}), 723(\text{w}), 692(\text{w}), 657(\text{m}) \text{ cm}^{-1}$.

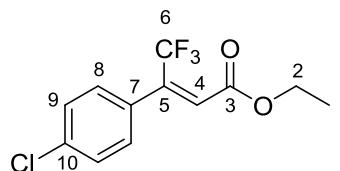
Ethyl (E)-3-(*p*-tolyl)pent-2-enoate (4h)



Prepared according to General Procedure **B**, 4'-methylpropiophenone (15.0 mmol) was converted to **4h** in 24 h yielding a colorless oil (955 mg, 29%) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

$R_f = 0.78$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:6); **HR-ESI-MS:** m/z : 241.1199 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_2\text{Na}^+$: 241.1199); **¹H NMR** (600 MHz, Chloroform- d) δ = 7.44 – 7.32 (m, 2H, H-C9), 7.21 – 7.13 (m, 2H, H-C10), 6.01 (s, 1H, H-C4), 4.21 (q, $J = 7.1$ Hz, 2H, H-C2), 3.10 (q, $J = 7.5$ Hz, 2H, H-C6), 2.37 (s, 3H, H-C12), 1.31 (t, $J = 7.1$ Hz, 3H, H-C1), 1.08 (t, $J = 7.5$ Hz, 3H, H-C7) ppm; **¹³C-NMR** (151 MHz, CDCl_3) δ = 166.7 (C3), 162.1 (C5), 139.1 (C11), 138.2 (C8), 129.4 (C10), 126.7 (C9), 116.1 (C4), 59.9 (C2), 24.3 (C6), 21.3 (C12), 14.5 (C1), 13.8 (C7) ppm; **IR (ATR):** $\tilde{\nu}$ = 2976(w), 2935(w), 2875(w), 1710(s), 1621(m), 1609(m), 1568(w), 1511(w), 1463(w), 1446(w), 1409(w), 1366(w), 1346(w), 1312(w), 1290(m), 1257(w), 1239(w), 1215(w), 1153(s), 1101(m), 1067(w), 1042(m), 1016(m), 972(w), 910(w), 875(m), 818(s), 719(w) cm^{-1} .

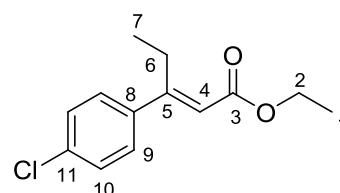
Ethyl (Z)-3-(4-chlorophenyl)-4,4,4-trifluorobut-2-enoate (4i)



Prepared according to General Procedure **B**, 4'-chloro-2,2,2-trifluoroacetophenone (5.0 mmol) was converted to **4i** in 4 h yielding a colorless liquid (140 mg, 10%) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

$R_f = 0.68$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:6); **HR-ESI-MS:** m/z : 301.0206 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{ClF}_3\text{Na}^+$: 301.0214); **¹H NMR** (600 MHz, CDCl_3) δ = 7.41 – 7.37 (m, 2H, H-C9), 7.37 – 7.33 (m, 2H, H-C8), 6.33 (s, 1H, H-C4), 4.31 (q, $J = 7.2$ Hz, 2H, H-C2), 1.35 (t, $J = 7.1$ Hz, 3H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl_3) δ = 164.5 (C3), 136.8 (d, $J_{\text{CF}} = 32.4$ Hz, C5), 136.1 (C10), 132.0 (C7), 129.3 (2C, C8), 129.1 (2C, C9), 128.1 (q, $J_{\text{CF}} = 3.5$ Hz, C4) 122.2 (d, $J_{\text{CF}} = 275.8$ Hz, C6), 62.0 (C2), 14.1 (C1) ppm; **¹⁹F NMR** (564 MHz, CDCl_3) δ = -60.29 ppm; **IR (ATR):** $\tilde{\nu}$ = 2985(w), 1733(m), 1595(w), 1494(m), 1378(w), 1283(s), 1256(s), 1205(m), 1179(s), 1133(s), 1092(m), 1029(m), 1018(m), 988(w), 902(w), 828(m), 723(w), 660(m) cm^{-1} ; analytical data in agreement with the literature.^[7]

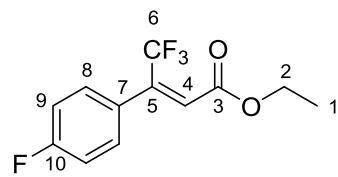
Ethyl (E)-3-(4-chlorophenyl)pent-2-enoate (4j)



Prepared according to General Procedure **B**, 4'-chloropropiophenone (15 mmol) was converted to **4j** in 24 hours yielding a colorless oil (950 mg, 27%) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

R_f = 0.78 (Et₂O/n-pentane 1:7); **HR-ESI-MS:** *m/z*: 261.0658 ([M+Na]⁺, calcd. for C₁₃H₁₅O₂ClNa⁺: 261.0653); **¹H NMR** (600 MHz, CDCl₃) δ = 7.39 – 7.36 (m, 2H, H-C9), 7.35 – 7.32 (m, 2H, H-C10), 5.99 (s, 1H, H-C4), 4.21 (q, *J* = 7.1 Hz, 2H, H-C2), 3.11 – 3.03 (m, 2H, H-C6), 1.31 (t, *J* = 7.1 Hz, 3H, H-C1), 1.06 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 166.4 (C3), 160.7 (C5), 139.7 (C8), 135.0 (C11), 128.9 (2C; C10), 128.2 (2C; C9), 117.3 (C4), 60.1 (C2), 24.4 (C6), 14.5 (C1), 13.6 (C7) ppm; **IR (ATR):** $\tilde{\nu}$ = 2977(w), 2937(w), 2875(w), 1711(s), 1623(m), 1591(w), 1566(w), 1491(m), 1463(w), 1403(w), 1367(w), 1347(w), 1288(m), 1239(w), 1158(s), 1091(s), 1042(m), 1011(m), 973(w), 910(w), 878(w), 828(s), 755(w), 718(w) cm⁻¹; analytical data in agreement with the literature.^[8]

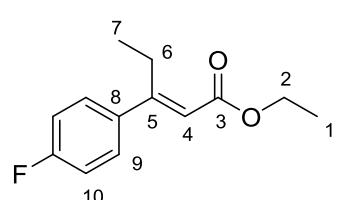
Ethyl (*Z*)-4,4,4-trifluoro-3-(4-fluorophenyl)but-2-enoate (4k)



Prepared according to General Procedure **B**, 4'-fluoro-2,2,2-trifluoroacetophenone (2.5 mmol) was converted to **4k** in 1 h yielding a colorless liquid (74 mg, 11%) after purification by column chromatography (SiO₂, 2% Et₂O/ *n*-pentane).

R_f = 0.79 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z*: 285.0504 ([M+Na]⁺, calcd. for C₁₂H₁₀F₄O₂Na⁺: 285.0509); **¹H NMR** (600 MHz, CDCl₃) δ = 7.41 – 7.37 (m, 2H, H-C8), 7.13 – 7.07 (m, 2H, H-C9), 6.31 (s, 1H, H-C4), 4.31 (q, *J* = 7.1 Hz, 2H, H-C2), 1.35 (t, *J* = 7.2 Hz, 3H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 164.4 (C3), 163.4 (d, *J*_{CF} = 250.2 Hz, C10), 136.7 (d, *J*_{CF} = 32.1 Hz, C5), 129.8 (d, *J*_{CF} = 8.2 Hz, 2C, C8), 129.5 (C7), 127.7 (q, *J*_{CF} = 3.7 Hz, C4), 122.0 (d, *J*_{CF} = 275.7 Hz, C6), 115.8 (d, *J*_{CF} = 21.8 Hz, 2C, C9), 61.8 (C2), 13.9 (C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -60.42 (3F, F-C6), -111.22 (tt, *J* = 8.5, 5.1 Hz, F-C10).ppm; **IR (ATR):** $\tilde{\nu}$ = 2987(w), 1732(m), 1654(w), 1606(w), 1511(s), 1447(w), 1377(w), 1363(w), 1283(m), 1255(m), 1203(m), 1178(s), 1169(s), 1158(s), 1128(s), 1098(m), 1028(m), 988(m), 946(w), 926(w), 901(m), 838(m), 817(w), 727(w), 693(w), 655(m) cm⁻¹.

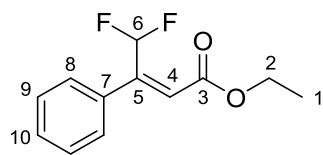
Ethyl (*E*)-3-(4-fluorophenyl)pent-2-enoate (4l)



Prepared according to General Procedure **B**, 4'-fluoropropiophenone (15.0 mmol) was converted to **4l** in 24 hours yielding a colourless oil (700 mg, 21%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

¹H NMR (400 MHz, CDCl₃) δ = 7.48 – 7.33 (m, 2H, H-C9), 7.13 – 6.99 (m, 2H, H-C10), 5.97 (s, 1H, H-C4), 4.21 (q, *J* = 7.1 Hz, 2H, H-C2), 3.08 (q, *J* = 7.5 Hz, 2H, H-C6), 1.31 (t, *J* = 7.1 Hz, 3H, H-C1), 1.06 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; analytical data in agreement with the literature.^[2]

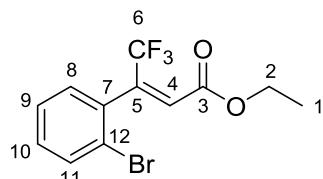
Ethyl (Z)-4,4-difluoro-3-phenylbut-2-enoate (4m)



Prepared according to General Procedure **B**, difluoroacetophenone (5.0 mmol) was converted to **4m** in 1 h yielding a colorless oil (628 mg, 56%) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

R_f = 0.71 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:7); **HR-ESI-MS:** m/z : 249.0699 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{F}_2\text{Na}^+$: 249.0698); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.43 – 7.38 (m, 3H, H-C9, H-C10), 7.32 – 7.27 (m, 2H, H-C8), 6.37 (t, J = 2.1, 1H, H-C4), 6.25 (t, J = 55.1, 1H, H-C6), 4.06 (qd, J = 7.1, 0.9 Hz, 2H, H-C2), 1.08 (td, J = 7.1, 0.7 Hz, 3H, H-C1) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 164.8 (C3), 146.9 (t, J_{CF} = 20.2 Hz, C5), 132.7 (d, J_{CF} = 1.3 Hz, C7), 129.0 (C10), 128.5 (2C, C8), 128.25 (2C, C9), 123.1 (t, J_{CF} = 8.9 Hz, C4), 114.4 (t, J_{CF} = 242.7 Hz, C6), 60.9 (C2), 13.9 (C1) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -116.30 (dq, J = 55.1, 2.0 Hz) ppm; **IR (ATR):** $\tilde{\nu}$ = 3081(w), 2981(w), 2904(w), 1706(s), 1615(m), 1598(m), 1489(w), 1442(w), 1383(w), 1279(s), 1155(s), 1122(m), 1095(w), 1036(m), 994(w), 932(w), 911(w), 861(m), 816(w), 769(m), 736(m), 700(s), 667(w) cm^{-1} .

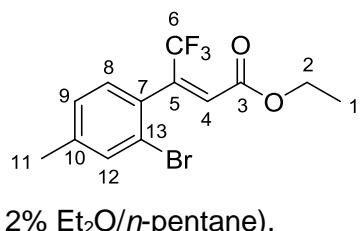
Ethyl (Z)-3-(2-bromophenyl)-4,4,4-trifluorobut-2-enoate (4n)



Prepared according to General Procedure **B**, 2'-Bromo-2,2,2-trifluoroacetophenone (2.0 mmol) was converted to **4n** in 2 h yielding a colorless liquid (215 mg, 33%) after purification by column chromatography (SiO_2 , 1% $\text{Et}_2\text{O}/n\text{-pentane}$).

R_f = 0.40 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:6); **HR-ESI-MS:** m/z : 344.9708 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{12}\text{H}_{10}\text{O}_2\text{BrF}_3\text{Na}^+$: 344.9706); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.66 – 7.64 (m, 1H, H-C11), 7.37 – 7.33 (m, 1H, H-C9), 7.31 – 7.26 (m, 2H, H-C8, H-C10), 6.23 (s, 1H, H-C4), 4.33 (q, J = 7.1 Hz, 2H, H-C2), 1.36 (t, J = 7.2 Hz, 3H, H-C1) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 163.8 (C3), 138.0 (d, J_{CF} = 33.8 Hz, C5), 134.9 (C7), 133.3 (C11), 130.9 (C8/C10), 130.8 (C8/C10), 130.7 (q, J_{CF} = 3.2 Hz, C4), 127.4 (C9), 123.4 (C12), 121.5 (d, J_{CF} = 275.6 Hz, C6), 62.0 (C2), 14.1 (C1) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -60.70 ppm; **IR (ATR):** $\tilde{\nu}$ = 2986(w), 1735(m), 1666(w), 1471(w), 1435(w), 1369(w), 1355(m), 1289(m), 1255(m), 1169(s), 1134(s), 1096(m), 1054(w), 1024(m), 984(w), 925(w), 889(w), 844(w), 760(m), 750(m), 729(m), 659(w) cm^{-1} .

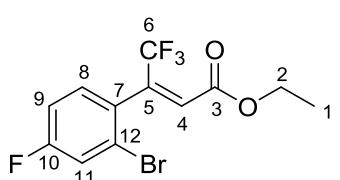
Ethyl (Z)-3-(2-bromo-4-methylphenyl)-4,4,4-trifluorobut-2-enoate (4o)



Prepared according to General Procedure **B**, 1-(2-bromo-4-methylphenyl)-2,2,2-trifluoroethan-1-one **5o** (2.0 mmol) was converted to **4o** in 1 h yielding a colorless liquid (224 mg, 33%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

R_f = 0.59 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z* 358.9879 ([M+Na]⁺, calcd. for C₁₃H₁₂BrF₃O₂Na⁺: 358.9870); **¹H NMR** (600 MHz, CDCl₃) δ = 7.51 – 7.44 (m, 1H, H-C12), 7.17 (d, *J* = 7.8 Hz, 1H, H-C8), 7.15 (dd, *J* = 1.6, 0.8 Hz, 1H, H-C9), 6.21 (s, 1H, H-C4), 4.32 (q, *J* = 7.2 Hz, 2H, H-C2), 2.36 (s, 3H, H-C11), 1.35 (t, *J* = 7.2 Hz, 3H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 163.9 (C3), 141.4 (C10), 137.9 (q, *J*_{CF} = 33.9 Hz, C5), 133.8 (C12), 131.9 (d, *J*_{CF} = 1.7 Hz, C7), 130.6 (q, *J*_{CF} = 3.2 Hz, C4), 130.5 (C8), 128.2 (C9), 123.1 (C13), 121.6 (d, *J*_{CF} = 275.7 Hz, C6), 61.9 (C2), 21.0 (C11), 14.1 (C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -60.79 ppm; **IR (ATR):** ν = 2987(w), 2928(w), 1737(m), 1659(w), 1604(w), 1490(w), 1369(m), 1357(m), 1285(m), 1260(m), 1168(s), 1133(s), 1096(m), 1051(m), 1025(m), 984(m), 928(w), 887(w), 841(m), 821(m), 735(w), 722(w), 668(w), 658(w) cm⁻¹.

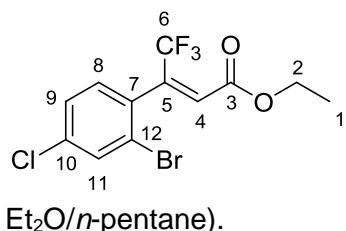
Ethyl (Z)-3-(2-bromo-4-fluorophenyl)-4,4,4-trifluorobut-2-enoate (4p)



Prepared according to General Procedure **B**, 2'-Bromo-4'-fluoro-2,2,2-trifluoroacetophenone **5p** (2.1 mmol) was converted to **4p** in 2 h yielding a colorless liquid (252 mg, 34%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

R_f = 0.61 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z* 362.9622 ([M+Na]⁺, calcd. for C₁₂H₁₀O₂BrF₄Na⁺: 362.9614); **¹H NMR** (600 MHz, CDCl₃) δ = 7.40 (dd, *J* = 8.1, 2.6 Hz, 1H, H-C11), 7.29 (dd, *J* = 8.6, 5.8 Hz, 1H, H-C8, H-C8), 7.08 (ddd, *J* = 8.6, 7.9, 2.6 Hz, 1H, H-C9), 6.23 (s, 1H, H-C4), 4.33 (q, *J* = 7.1 Hz, 2H, H-C2), 1.36 (t, *J* = 7.1 Hz, 3H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 163.6 (C3), 162.8 (d, *J*_{CF} = 254.1 Hz, C10), 136.8 (d, *J*_{CF} = 34.1 Hz, C5), 131.9 (d, *J*_{CF} = 8.8 Hz, C8), 131.3 (q, *J*_{CF} = 2.9 Hz, C4), 130.9 (dq, *J*_{CF} = 3.2, 1.4 Hz, C7), 124.1 (d, *J*_{CF} = 9.6 Hz, C12), 121.4 (d, *J*_{CF} = 276.3 Hz, C6), 120.8 (d, *J*_{CF} = 24.6 Hz, C11), 114.9 (d, *J*_{CF} = 21.5 Hz, C9), 62.0 (C2), 14.1 (C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -60.99 (3F, F-C6), -109.35 (q, *J* = 7.7 Hz F-C10) ppm; **IR (ATR):** ν = 3079(w), 2986(w), 1732(m), 1598(m), 1578(w), 1490(m), 1375(w), 1282(s), 1253(s), 1212(s), 1181(s), 1160(s), 1132(s), 1027(m), 988(m), 933(w), 904(m), 878(m), 859(m), 818(m), 703(w), 666(w), 658(m) cm⁻¹.

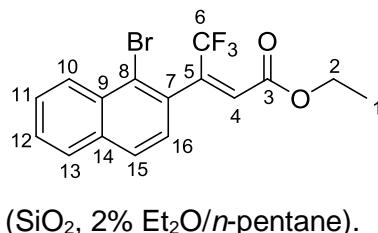
Ethyl (Z)-3-(2-bromo-4-chlorophenyl)-4,4,4-trifluorobut-2-enoate (4q)



Prepared according to General Procedure **B**, 1-(2-bromo-4-chlorophenyl)-2,2,2-trifluoroethan-1-one **5q** (1.3 mmol) was converted to **4q** in 1 h yielding a colorless oil (150 mg, 33 %) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

R_f = 0.74 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:10); **HR-ESI-MS:** m/z : 378.9319 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{12}\text{H}_9\text{BrClF}_3\text{O}_2\text{Na}^+$: 378.9319); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.68 (d, J = 2.1 Hz, 1H, H-C11), 7.35 (dd, J = 8.3, 2.1 Hz, 1H, H-C9), 7.24 (d, J = 8.3 Hz, 1H, H-C8), 6.23 (s, 1H, H-C4), 4.33 (q, J = 7.2 Hz, 1H, H-C2), 1.36 (t, J = 7.1 Hz, 1H, H-C1) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 163.6 (C3), 136.8 (d, J_{CF} = 34.3 Hz, C5), 136.3 (C10), 133.27 (d, J_{CF} = 1.7 Hz, C7), 133.1 (C11), 131.5 (C8), 131.2 (q, J_{CF} = 3.1 Hz, C4), 127.84 (C9), 124.0 (C12), 121.3 (d, J_{CF} = 275.7 Hz, C6), 62.1 (C2), 14.1 (C1) ppm; **$^{19}\text{F NMR}$** (282 MHz, CDCl_3) δ = -60.79 ppm; **IR (ATR):** $\tilde{\nu}$ = 2985(w), 2930(w), 1737(m), 1663(w), 1582(w), 1548(w), 1471(m), 1369(m), 1356(m), 1281(m), 1251(m), 1171(s), 1135(s), 1096(m), 1049(m), 1025(m), 982(w), 924(m), 869(w), 824(m), 786(m), 732(w), 698(w), 654(m) cm^{-1} .

Ethyl (Z)-3-(1-bromonaphthalen-2-yl)-4,4,4-trifluorobut-2-enoate (4r)



Prepared according to General Procedure **B**, 1-(3-bromonaphthalen-2-yl)-2,2,2-trifluoroethan-1-one **5r** (1.8 mmol) was converted to **4r** in 1 h yielding a colorless liquid (96 mg, 14%) after purification by column chromatography (SiO_2 , 2% $\text{Et}_2\text{O}/n\text{-pentane}$).

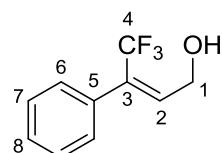
R_f = 0.46 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:9); **HR-ESI-MS:** m/z : 394.9892 ($[M+\text{Na}]^+$, calcd. for $\text{C}_{16}\text{H}_{12}\text{BrF}_3\text{O}_2\text{Na}^+$: 394.9865); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 8.40 – 8.35 (m, 1H, H-C10), 7.88 – 7.86 (m, 1H, H-C13), 7.86 – 7.83 (m, 1H, H-C15), 7.66 (ddd, J = 8.4, 6.8, 1.3 Hz, 1H, H-C11), 7.60 (ddd, J = 8.1, 6.9, 1.2 Hz, 1H, H-C12), 7.36 (d, J = 8.4 Hz, 1H, H-C16), 6.31 (s, 1H, H-C4), 4.36 (q, J = 7.1 Hz, 2H, H-C2), 1.38 (t, J = 7.2 Hz, 3H, H-C1) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 163.9 (C3), 138.9 (d, J_{CF} = 33.9 Hz, C5), 134.4 (C14), 132.9 (C7), 132.3 (C9), 130.7 (d, J_{CF} = 3.1 Hz, C4), 128.4 (C13), 128.3 (C11), 128.2 (C10), 128.0 (C15), 127.8 (C12), 126.7 (C16), 124.3 (C8), 121.6 (d, J_{CF} = 276.0 Hz, C6), 62.0 (C2), 14.1 (C1) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -60.29 (d, J = 1.0 Hz) ppm; **IR (ATR):** $\tilde{\nu}$ = 3060(s), 2985(w), 1735(s), 1660(w), 1555(w), 1499(w), 1465(w), 1446(w), 1368(w), 1344(w), 1322(w), 1300(w), 1273(m), 1253(s), 1214(m), 1170(s), 1137(s), 1096(m), 1025(m), 1014(m), 962(w), 941(w), 889(w), 864(w), 815(s), 774(w), 748(s), 718(m), 694(m), 670(w) cm^{-1} .

2.2. Preparation of allylic alcohols

General Procedure C for the preparation of allylic alcohols

The specified α,β -unsaturated ester was dissolved in dry THF. The alkylmagnesium bromide (2.2 eq.) was added dropwise over 5 min before the mixture was stirred overnight at RT. The reaction was quenched by the addition of a saturated solution of NH₄Cl. The organic phase was separated, the aqueous phase was extracted with Et₂O (3x), the combined organic phase were dried over MgSO₄, and concentrated *in vacuo*. The crude product was purified by column chromatography (SiO₂, specified combination of Et₂O/*n*-pentane).

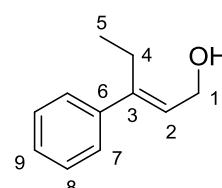
(Z)-4,4,4-Trifluoro-3-phenylbut-2-en-1-ol (1a)



Ethyl (*Z*)-4,4,4-trifluoro-3-phenylbut-2-enoate **4c** (120 mg, 0.5 mmol, 1.0 eq.) was dissolved in dry THF (10 mL) under argon before being cooled to -78 °C. DIBAL-H (1.0 M in toluene, 1.1 mL, 1.3 mmol, 2.2 eq.) was added dropwise over 5 minutes and the resulting mixture was stirred at -78 °C for 4 h before being gradually warmed to RT and being stirred overnight. The reaction was quenched by the addition of NH₄Cl-sol. (aq.), the organic phase was separated and the aqueous phase was extracted with Et₂O (3x 5 mL). The combined organic phases were dried over MgSO₄ and concentrated *in vacuo*. Purification by column chromatography (SiO₂, 10% Et₂O/*n*-pentane) yielded **1a** as a colorless oil (73 mg, 74%).

*R*_f = 0.16 (Et₂O/*n*-pentane 1:4); **HR-ESI-MS:** *m/z*: 225.0518 ([M+Na]⁺, calcd. for C₁₀H₉F₃ONa⁺: 225.0498); **¹H NMR** (600 MHz, CDCl₃) δ = 7.38 – 7.31 (m, 5H, H-C6, H-C7, H-C8), 6.21 (td, *J* = 5.7, 0.7 Hz, 1H, H-C2), 4.60 (dq, *J* = 5.7, 2.8 Hz, 2H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 140.7 (q, *J*_{CF} = 2.8 Hz, C2), 135.4 (q, *J*_{CF} = 1.8 Hz, C5), 131.4 (q, *J*_{CF} = 30.9 Hz, C3), 128.7 (2C, C6/ C7), 128.6 (2C, C6/ C7), 128.1 (C8), 123.8 (q, *J*_{CF} = 275.6 Hz, C4), 59.7 (q, *J*_{CF} = 3.7 Hz, C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -58.17 (t, *J* = 2.9 Hz) ppm; **IR (ATR):** ̄ = 3342(b), 1495(w), 1447(w), 1365(m), 1279(w), 1198(s), 1158(s), 1113(s), 1039(m), 1028(m), 1002(m), 907(m), 758(m), 696(s) cm⁻¹; analytical data in agreement with the literature.^[9]

(E)-3-Phenylpent-2-en-1-ol (1b)^[2]

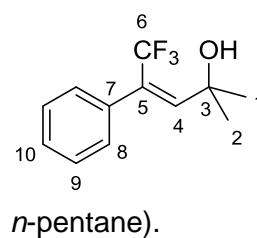


Ethyl (*E*)-3-phenylpent-2-enoate **4d** (125 mg, 0.6 mmol, 1.0 eq.) was dissolved in dry THF (10 mL) under Argon before being cooled to -78 °C. DIBAL-H (1.2 M in toluene, 1.1 mL, 1.3 mmol, 2.2 eq.) was added dropwise over 5 minutes and the resulting mixture was stirred at -78 °C for 4 h before being gradually warmed to RT and being stirred overnight. The reaction

was quenched by the addition of NH₄Cl-sol. (aq.), the organic phase was separated and the aqueous phase was extracted with Et₂O (3x 5 mL). The combined organic phases were dried over MgSO₄, and concentrated *in vacuo*. Purification by column chromatography (SiO₂, 30% Et₂O/*n*-pentane) yielded **1b** as a colorless oil (73 mg, 74%).

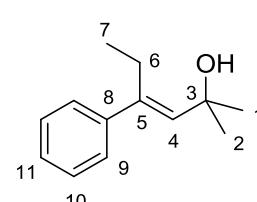
¹H NMR (400 MHz, CDCl₃) δ = 7.42 – 7.20 (m, 5H, H-C7, H-C8, H-C9), 5.82 (t, *J* = 6.8 Hz, 1H, H-C2), 4.34 (d, *J* = 6.8 Hz, 2H, H-C1), 2.53 (q, *J* = 7.6 Hz, 2H, H-C4), 0.97 (t, *J* = 7.6 Hz, 3H, H-C5) ppm; analytical data in agreement with the literature.^[2]

(Z)-5,5,5-Trifluoro-2-methyl-4-phenylpent-3-en-2-ol (**1c**)

 Prepared according to General Procedure **C**, ethyl (*Z*)-4,4,4-trifluoro-3-phenylbut-2-enoate **4c** (0.5 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1c** yielding a colorless oil (115 mg, 99%) after purification by column chromatography (SiO₂, 10% Et₂O/*n*-pentane).

*R*_f = 0.15 (Et₂O/*n*-pentane 1:6); **HR-ESI-MS**: *m/z* 253.0822 ([M+Na]⁺, calcd. for C₁₂H₁₂F₃ONa⁺: 253.0811); **¹H NMR** (600 MHz, CDCl₃) δ = 7.37 – 7.33 (m, 3H, H-C9, H-C10), 7.30 – 7.27 (m, 2H, H-C8), 6.15 (d, *J* = 0.6 Hz, 1H, H-C4), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 149.0 (q, *J* = 3.2 Hz, C4), 137.2 (d, *J*_{CF} = 2.5 Hz, C7), 130.4 (q, *J*_{CF} = 32.6 Hz, C5), 128.2 (C9), 128.2 (C10), 128.1 (C8), 123.3 (d, *J*_{CF} = 274.6 Hz, C6), 70.88 (C3), 30.6 (q, *J*_{CF} = 2.3 Hz, 2C, C1, C2) ppm; **¹⁹F NMR** (282 MHz, CDCl₃) δ = -53.98 ppm; **IR (ATR)**: $\tilde{\nu}$ = 3412(b), 2977(w), 1494(w), 1446(w), 1369(m), 1331(w), 1277(w), 1195(s), 1153(s), 1116(s), 1078(m), 1034(w), 994(w), 970(m), 928(w), 912(w), 899(w), 796(w), 749(m), 697(s) cm⁻¹.

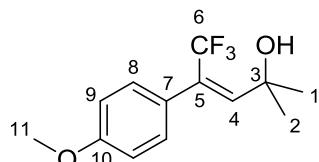
(E)-2-Methyl-4-phenylhex-3-en-2-ol (**1d**)

 Prepared according to General Procedure **C**, ethyl (*E*)-3-phenylpent-2-enoate **4d** (5.1 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1d** yielding a colorless oil (709 mg, 73%) after purification by column chromatography (SiO₂, 15% Et₂O/*n*-pentane).

*R*_f = 0.48 (Et₂O/*n*-pentane 1:3); **HR-ESI-MS**: *m/z* 213.1248 ([M+Na]⁺, calcd. for C₁₃H₁₈ONa⁺: 213.1358); **¹H NMR** (400 MHz, CDCl₃) δ = 7.35 – 7.16 (m, 4H, H-C9, H-C10), 5.67 (s, 1H, H-C4), 2.81 (q, *J* = 7.5 Hz, 2H, H-C6), 1.46 (s, 6H, H-C1, H-C2), 0.91 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ = 143.4 (C5), 141.9 (C8), 135.8 (C4), 132.7 (C11), 128.4 (C9/C10), 128.2 (C9/C10), 71.5 (C3), 31.7 (2C, C1, C2), 23.0 (C6), 13.6 (C7) ppm; **IR (ATR)**: $\tilde{\nu}$ = 3370 (w), 2967(m), 2931(w), 2873(w), 1635(w), 1598(w), 1492(m), 1464(m), 1443(m),

1361(m), 1279(w), 1219(m), 1164(m), 1139(m), 1094(m), 1078(m), 1032(w), 957(m), 896(m), 852(m), 786(m), 756(s), 740(s), 707(s) cm⁻¹.

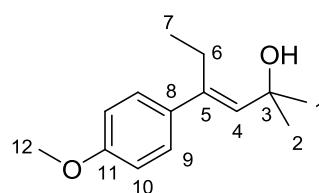
(Z)-5,5,5-Trifluoro-4-(4-methoxyphenyl)-2-methylpent-3-en-2-ol (1e)



Prepared according to General Procedure C, ethyl (Z)-4,4,4-trifluoro-3-(4-methoxyphenyl)but-2-enoate **4e** (0.3 mmol) and methylmagnesium bromide (0.6 mmol, 2.2 eq.) were converted to **1e** yielding a light yellow oil (35 mg, 67%) after purification by column chromatography (SiO₂, 20% Et₂O/n-pentane).

R_f = 0.13 (Et₂O/n-pentane 1:5); **HR-ESI-MS:** *m/z*: 283.0908 ([M+Na]⁺, calcd. for C₁₃H₁₅O₂F₃Na⁺: 283.0916); **¹H NMR** (600 MHz, CDCl₃) δ = 7.24 – 7.16 (m, 2H, H-C8), 6.89 – 6.83 (m, 2H, H-C9), 6.11 (s, 1H, H-C4), 3.82 (s, 3H, H-C11), 1.51 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 159.7 (C10), 148.4 (d, J_{CF} = 3.0 Hz, C4), 131.5 (C7), 130.1 (d, J_{CF} = 32.3 Hz, C5), 129.7 (2C, C8), 123.6 (d, J_{CF} = 274.7 Hz, C6), 113.8 (2C, C9), 71.0 (C3), 55.5 (C11), 30.8 (d, J_{CF} = 2.3 Hz, 2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.34 ppm; **IR (ATR):** ν = 3476(b), 2987 (w), 2917(w), 2844(w), 1609(m), 1573(w), 1511(m), 1464(w), 1455(w), 1441(w), 1397(w), 1367(m), 1294(m), 1278(m), 1252(m), 1226(m), 1193(s), 1175(m), 1145(s), 1130(s), 1113(s), 1030(s), 979(s), 911(w), 829(s), 806(m), 777(w), 762(w), 728(w) cm⁻¹.

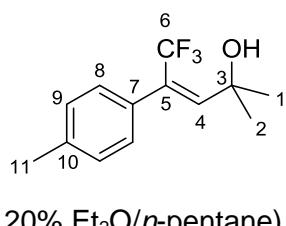
(E)-4-(4-Methoxyphenyl)hex-3-en-2-ol (1f)



Prepared according to General Procedure C, ethyl (Z)-4,4,4-trifluoro-3-(4-methoxyphenyl)but-2-enoate **4f** (1.5 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1f** yielding a white solid (261 mg, 79%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

R_f = 0.24 (Et₂O/n-pentane 1:3); **M.p.:** 63.1 – 64.6 °C; **HR-ESI-MS:** *m/z*: 243.1363 ([M+Na]⁺, calcd. for C₁₄H₂₀O₂Na⁺: 243.1356); **¹H NMR** (500 MHz, CD₃OD) δ = 7.28 – 7.19 (m, 2H, H-C9), 6.89 – 6.80 (m, 2H, H-C10), 5.63 (s, 1H, H-C4), 3.79 (s, 3H, H-C12), 2.81 (qd, *J* = 7.5, 0.7 Hz, 2H, H-C6), 1.44 (s, 6H, H-C1, H-C2), 0.91 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (126 MHz, CD₃OD) δ = 160.14 (C11), 144.45 (C5), 137.16 (C8), 135.29 (C4), 128.73 (2C, C10), 114.51 (2C, C9), 71.68 (C3), 55.65 (C12), 31.60 (2C, C1, C2), 23.79 (C6), 13.72 (C7) ppm; **IR (ATR):** ν = 3486(w), 2970(w), 2935(w), 1629(w), 1604 (m), 1512(s), 1463(m), 1440(m), 1361(m), 1352(m), 1285(m), 1256(s), 1218(m), 1181(s), 1164(m), 1138(s), 1037(s), 954(s), 898(w), 853(m), 815(s), 780(m), 705(m) cm⁻¹.

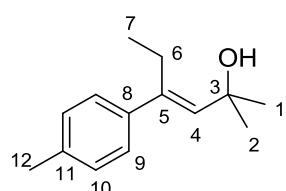
(Z)-5,5,5-Trifluoro-2-methyl-4-(*p*-tolyl)pent-3-en-2-ol (1g)



Prepared according to General Procedure **C**, ethyl (*Z*)-4,4,4-trifluoro-3-(*p*-tolyl)but-2-enoate **4g** (0.3 mmol) and methylmagnesium bromide (0.59 mmol, 2.2 eq.) were converted to **1g** yielding a colorless oil (60 mg, 91%) after purification by column chromatography (SiO₂, 20% Et₂O/*n*-pentane).

*R*_f = 0.19 (Et₂O/*n*-pentane 1:4); **HR-ESI-MS:** *m/z* 267.0967([*M*+Na]⁺, calcd. for C₁₃H₁₅OF₃Na⁺: 267.0967); **¹H NMR** (600 MHz, CDCl₃) δ = 7.17 (d, *J* = 3.8 Hz, 4H, H-C8, H-C9), 6.13 (s, 1H, H-C4), 2.36 (s, 3H, H-C11), 1.51 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 148.6 (q, *J*_{CF} = 3.1 Hz, C4), 138.2 (C10), 134.5 (q, *J*_{CF} = 2.2 Hz, C7), 130.4 (d, *J*_{CF} = 32.3 Hz, C5), 129.1 (2C, C8/ C9), 128.3 (2C, C8/ C9), 123.6 (d, *J*_{CF} = 274.6 Hz, C6), 71.0 (C3), 30.8 (d, *J*_{CF} = 2.3 Hz, 2C, C1, C2), 21.3 (C11) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.17 ppm; **IR (ATR):** ν = 3482(b), 2984(w), 2922(w), 1513(w), 1462(w), 1453(w), 1395(w), 1368(m), 1275(w), 1227(m), 1217(m), 1194(s), 1182(s), 1129(s), 1110(s), 1026(w), 975(m), 965(m), 937(w), 929(w), 914(w), 883(w), 843(w), 819(m), 801(m), 773(m), 763(w), 722(m) cm⁻¹.

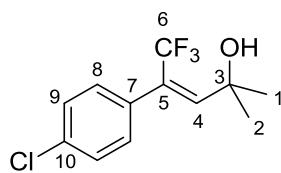
(E)-2-Methyl-4-(*p*-tolyl)hex-3-en-2-ol (1h)



Prepared according to General Procedure **C**, ethyl (*E*)-3-(*p*-tolyl)pent-2-enoate **4h** (2.8 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1h** yielding a colorless oil (461 mg, 81%) after purification by column chromatography (SiO₂, 20% Et₂O/*n*-pentane).

*R*_f = 0.43 (Et₂O/*n*-pentane 1:2); **HR-ESI-MS:** *m/z* 227.1440 ([*M*+Na]⁺, calcd. for C₁₄H₂₀ONa⁺: 227.1406); **¹H NMR** (600 MHz, CDCl₃) δ = 7.24 – 7.20 (m, 2H, H-C9), 7.14 – 7.10 (m, 2H, H-C10), 5.69 (s, 1H, H-C4), 2.83 (q, *J* = 7.5, 2H, H-C6), 2.35 (s, 3H, H-C12), 1.47 (s, 6H, H-C1, H-C2), 0.94 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 144.2 (C5), 140.3 (C8), 136.5 (C11), 134.6 (C4), 128.8 (C10), 126.6 (C9), 71.3 (C3), 31.6 (2C, C1, C2), 22.9 (C6), 21.2 (C12), 13.6 (C7) ppm; **IR (ATR):** ν = 3347(m), 2973(m), 2924(w), 2866(w), 1630(w), 1511(m), 1457(w), 1370(m), 1358(m), 1214(m), 1164(m), 1140(s), 1094(w), 956(s), 898(w), 859(w), 803(s), 779(m), 718(m), 667(m) cm⁻¹.

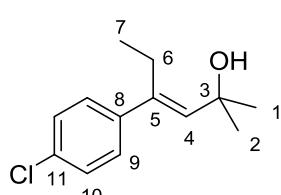
(Z)-4-(4-Chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1i)



Prepared according to General Procedure **C**, ethyl (*Z*)-3-(4-chlorophenyl)-4,4,4-trifluorobut-2-enoate **4i** (0.4 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1i** yielding a white solid (66 mg, 62%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

*R*_f = 0.16 (Et₂O/n-pentane 1:7); **M.p.**: 54.5 – 57.0 °C; **HR-ESI-MS**: *m/z*: 287.0418 ([M+Na]⁺, calcd. for C₁₂H₁₂OCIF₃Na⁺: 287.0421); **¹H NMR** (500 MHz, CDCl₃) δ = 7.35 – 7.29 (m, 2H, H-C9), 7.23 – 7.17 (m, 2H, H-C8), 6.14 (s, 1H, H-C4), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 149.6 (q, *J*_{CF} = 3.1 Hz, C4), 135.8 (q, *J*_{CF} = 2.3 Hz, C7), 134.5 (C10), 129.79 (2C, C8), 129.6 (d, *J*_{CF} = 32.8 Hz, C5), 128.6 (2C, C9), 123.3 (q, *J*_{CF} = 274.6 Hz, C6), 71.1 (d, *J*_{CF} = 1.2 Hz, C3), 30.7 (q, *J*_{CF} = 2.3 Hz, 2C, C1, C2) ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ = -54.15 ppm; **IR (ATR)**: ν = 3486(b), 2987(w), 2933(w), 1651(w), 1596(w), 1491(m), 1456(w), 1393(w), 1365(s), 1278(w), 1266(w), 1226(m), 1196(s), 1152(s), 1140(s), 1125(s), 1087(s), 1016(m), 973(s), 938(w), 911(w), 881(w), 834(s), 826(s), 791(m), 724(m), 708(w) cm⁻¹.

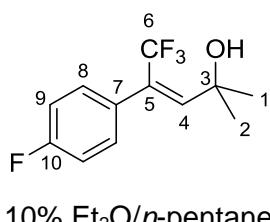
(E)-4-(4-Chlorophenyl)-2-methylhex-3-en-2-ol (1j)



Prepared according to General Procedure **B**, ethyl (*E*)-3-(4-chlorophenyl)pent-2-enoate **4j** (2.8 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1j** yielding a white solid (136 mg, 22%) after purification by column chromatography (SiO₂, 2% Et₂O/n-pentane).

*R*_f = 0.16 (Et₂O/n-pentane 1:5); **M.p.**: 59.8 – 61.0 °C; **HR-ESI-MS**: *m/z*: 247.0862 ([M+Na]⁺, calcd. for C₁₃H₁₇ClONa⁺: 247.1263); **¹H NMR** (400 MHz, CDCl₃) δ = 7.30 – 7.19 (m, 4H, H-C9, H-C10), 5.67 (s, 1H, H-C4), 2.81 (q, *J* = 7.5 Hz, 2H, H-C6), 1.46 (s, 6H, H-C1, H-C2), 0.91 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ = 143.4 (C5), 141.9 (C8), 135.8 (C4), 132.7 (C11), 128.4 (C9/C10), 128.2 (C9/C10), 71.5 (C3), 31.7 (C1, C2), 23.0 (C6), 13.6 (C7) ppm; **IR (ATR)**: ν = 3479(w), 2983(w), 2969(m), 2936(w), 2876(w), 1629(w), 1489(m), 1458(m), 1352(m), 1219(m), 1164(m), 1141(m), 1095(m), 1008(m), 959(s), 898(w), 864(w), 802(s), 784(m), 718(w), 671(m) cm⁻¹.

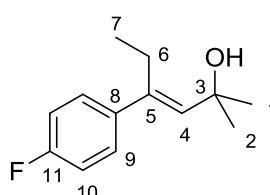
(Z)-5,5,5-Trifluoro-4-(4-fluorophenyl)-2-methylpent-3-en-2-ol (1k)



Prepared according to General Procedure **C**, ethyl (*Z*)-4,4,4-trifluoro-3-(4-fluorophenyl)but-2-enoate **4k** (0.2 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1k** yielding a colorless oil (33 mg, 66%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

*R*_f = 0.19 (Et₂O/n-pentane 1:7); **HR-ESI-MS:** *m/z*: 271.0753 ([M+Na]⁺, calcd. for C₁₂H₁₂F₄ONa⁺: 271.0716); **¹H NMR** (600 MHz, CDCl₃) δ = 7.26 – 7.23 (m, 2H, H-C8), 7.06 – 7.01 (m, 2H, H-C9), 6.13 (s, 1H, H-C4), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 162.8 (d, *J*_{CF} = 247.7 Hz, C10), 149.4 (d, *J*_{CF} = 3.2 Hz, C4), 133.4 (C7), 130.3 (d, *J*_{CF} = 8.2 Hz, 2C, C8), 129.6 (d, *J*_{CF} = 32.7 Hz, C5), 123.3 (d, *J*_{CF} = 274.4 Hz, C6), 115.4 (d, *J*_{CF} = 21.7 Hz, 2C, C9), 71.1 (C3), 30.7 (d, *J*_{CF} = 2.3 Hz, 2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.32 (3F, F-C6), -113.73 (tt, *J* = 8.6, 5.2 Hz, F-C10) ppm; **IR (ATR):** ν = 3427(b), 2978(w), 2933(w), 1719(w), 1669(w), 1605(w), 1510(m), 1461(w), 1366(w), 1286(m), 1226(m), 1167(s), 1115(s), 989(m), 975(m), 894(w), 837(m), 817(m), 785(m), 759(w), 739(m), 707(m), 675(m) cm⁻¹.

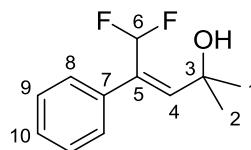
(E)-4-(4-fluorophenyl)-2-methylhex-3-en-2-ol (1l)



Prepared according to General Procedure **C**, ethyl (*E*)-3-(4-fluorophenyl)pent-2-enoate **4l** (3.2 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1l** yielding a yellow solid (542 mg, 81%) after purification by column chromatography (SiO₂, 20% Et₂O/n-pentane).

*R*_f = 0.33 (Et₂O/n-pentane 1:5); **M.p.:** 63.4 – 65.0 °C; **HR-ESI-MS:** *m/z*: 231.1163 ([M+Na]⁺, calcd. for C₁₃H₁₇FONa⁺: 231.1156); **¹H NMR** (400 MHz, CDCl₃) δ = 7.31 – 7.23 (m, 2H, H-C10), 7.03 – 6.95 (m, 2H, H-C9), 5.65 (s, 1H, H-C4), 2.81 (q, *J* = 7.4, 0.7 Hz, 2H, H-C6), 1.46 (s, 7H, H-C1, H-C2), 0.91 (t, *J* = 7.5 Hz, 3H, H-C7) ppm; **¹³C NMR** (101 MHz, CDCl₃) δ = 162.1 (d, *J*_{CF} = 245.3 Hz, C11), 143.6 (C5), 139.4 (d, *J*_{CF} = 3.3 Hz, C8), 135.4 (C4), 128.4 (d, *J*_{CF} = 7.8 Hz, 2C, C10), 115.1 (d, *J*_{CF} = 21.2 Hz, 2C, C9), 71.5 (C3), 31.8 (C1, C2), 23.3 (C6), 13.6 (C7) ppm; **¹⁹F NMR** (282 MHz, CDCl₃) δ = -116.25 (tt, *J* = 8.7, 5.4 Hz) ppm; **IR (ATR):** ν = 3476(w), 2983(w), 2970(w), 2936(w), 1629(w), 1598(w), 1507(m), 1458(m), 1371(m), 1356(m), 1219(m), 1162(s), 1142(m), 1108 (m), 1089(w), 1011(w), 959(s), 898(w), 868(w), 831(s), 816(s), 800(m), 781(m), 708(m) cm⁻¹.

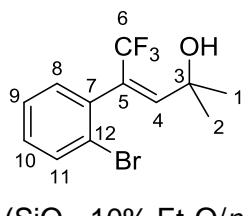
(Z)-5,5-Difluoro-2-methyl-4-phenylpent-3-en-2-ol (1m)



Prepared according to General Procedure **C**, ethyl (Z)-4,4-difluoro-3-phenylbut-2-enoate **4m** (0.5 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1m** yielding a white solid (115 mg, 99%) after purification by column chromatography (SiO_2 , 10% $\text{Et}_2\text{O}/n\text{-pentane}$).

$R_f = 0.15$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:6); **HR-ESI-MS:** m/z : 235.0903 ([$M+\text{Na}$] $^+$, calcd. for $\text{C}_{12}\text{H}_{14}\text{F}_2\text{ONa}^+$: 235.0910); **M.p.:** 37.5 – 39.6 °C; **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.63 (td, J = 55.5, 0.6 Hz, 1H, H-C6), 7.43 – 7.39 (m, 2H, H-C8), 7.37 – 7.31 (m, 3H, H-C9, H-C10), 6.00 (q, J = 0.9 Hz, 1H, H-C4), 1.50 (s, 6H, H-C1, H-C2) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 144.3 (t, J_{CF} = 9.1 Hz, C4), 136.8 (C7), 135.2 (t, J_{CF} = 22.4 Hz, C5), 128.4 (2C, C8), 128.3 (2C, C9), 128.0 (C10), 112.2 (t, J_{CF} = 233.7 Hz, C6), 72.2 (C3), 32.0 (t, J_{CF} = 1.6 Hz, 2C, C1, C2) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -113.83 (d, J = 55.4 Hz) ppm; **IR (ATR):** $\tilde{\nu}$ = 3321(b), 2980(w), 1494(w), 1447(w), 1396(w), 1380(m), 1366(m), 1332(w), 1274(w), 1223(m), 1170(m), 1137(s), 1090(s), 1055(m), 1012(s), 962(m), 934(m), 925(m), 913(m), 886(w), 880(w), 844(w), 802(w), 758(s), 696(s), 664(m) cm^{-1} .

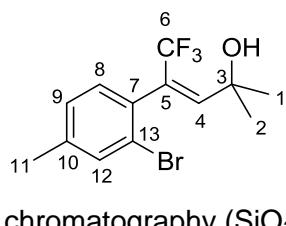
(Z)-4-(2-Bromophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1n)



Prepared according to General Procedure **C**, ethyl (Z)-3-(2-bromophenyl)-4,4,4-trifluorobut-2-enoate **4n** (0.4 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1n** yielding a colorless oil (103 mg, 83%) after purification by column chromatography (SiO_2 , 10% $\text{Et}_2\text{O}/n\text{-pentane}$).

$R_f = 0.19$ ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:7); **HR-ESI-MS:** m/z : 330.9916 ([$M+\text{Na}$] $^+$, calcd. for $\text{C}_{12}\text{H}_{12}\text{OBrF}_3\text{Na}^+$: 330.9906); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.66 – 7.63 (m, 1H, H-C11), 7.34 (td, J = 7.5, 1.2 Hz, 1H, H-C9), 7.29 – 7.22 (m, 2H, H-C8, H-C10), 6.52 (q, J = 1.5 Hz, 1H, H-C4), 1.35 (s, 3H, H-C1/H-C2), 1.28 (s, 3H, H-C1/H-C2) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 143.2 (q, J_{CF} = 4.7 Hz, C4), 133.7 (C7), 133.0 (C11), 131.9 (C8), 130.3 (C10), 127.3 (q, J_{CF} = 30.2 Hz, C5), 127.3 (C9), 124.7 (C12), 123.2 (q, J_{CF} = 274.4 Hz, C6), 71.5 (C3), 29.8 (C1/C2), 29.6 (C1/C2) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -66.23 (d, J = 1.5 Hz) ppm; **IR (ATR):** $\tilde{\nu}$ = 3404(b), 2978(w), 1470(w), 1435(w), 1368(m), 1331(w), 1287(w), 1255(w), 1228(w), 1195(s), 1156(s), 1120(s), 1052(m), 1025(m), 991(w), 973(m), 926(w), 904(w), 798(w), 750(s), 724(m), 682(m) cm^{-1} .

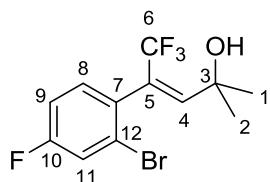
(Z)-4-(2-Bromo-4-methylphenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1o)



Prepared according to General Procedure **C**, ethyl (*Z*)-3-(2-bromo-4-methylphenyl)-4,4,4-trifluorobut-2-enoate **4o** (0.6 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1o** yielding a colorless liquid (140 mg, 72%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

R_f = 0.18 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z* 345.0075 ([M+Na]⁺, calcd. for C₁₃H₁₄BrF₃Na⁺: 345.0072); **¹H NMR** (600 MHz, CDCl₃) δ = 7.46 – 7.42 (m, 1H, H-C9), 7.15 – 7.08 (m, 2H, H-C8, H-C12), 5.99 (s, 1H, H-C4), 2.34 (s, 3H, H-C11), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 150.5 (q, *J*_{CF} = 3.1 Hz, C4), 140.3 (C10), 135.1 (d, *J*_{CF} = 2.5 Hz, C7), 133.4 (C9), 130.9 (C12), 128.8 (d, *J*_{CF} = 34.0 Hz, C5), 128.1 (C8), 124.0 (C13), 122.8 (d, *J*_{CF} = 274.4 Hz, C6), 71.2 (d, *J*_{CF} = 1.1 Hz, C3), 30.3 (2C, C1, C2), 21.0 (C11) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.15 (3F, F-C6) ppm; **IR (ATR):** ν = 3429(b), 2976(w), 2929(w), 1604(w), 1489(w), 1463(w), 1367(m), 1287(w), 1260(w), 1229(w), 1196(m), 1159(s), 1120(s), 1048(m), 991(w), 972(m), 875(w), 842(w), 821(m), 782(m), 760(w), 667(w) cm⁻¹.

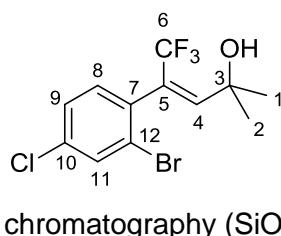
(Z)-4-(2-Bromo-4-fluorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1p)



Prepared according to General Procedure **C**, ethyl (*Z*)-3-(2-bromo-4-fluorophenyl)-4,4,4-trifluorobut-2-enoate **4p** (0.6 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1p** yielding a colorless oil (144 mg, 74%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

R_f = 0.12 (Et₂O/n-pentane 1:6); **HR-ESI-MS:** *m/z* 348.9835 ([M+Na]⁺, calcd. for C₁₂H₁₁OBrF₄Na⁺: 348.9822); **¹H NMR** (600 MHz, CDCl₃) δ = 7.36 (dd, *J* = 8.2, 2.6 Hz, 1H, H-C11), 7.22 (dd, *J* = 8.5, 5.9 Hz, 1H, H-C8), 7.03 (td, *J* = 8.2, 2.6 Hz, 1H, H-C9), 6.01 (s, 1H, H-C4), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 162.2 (d, *J*_{CF} = 252.2 Hz, C10), 151.2 (q, *J*_{CF} = 3.0 Hz, C4), 134.20 (t, *J*_{CF} = 3.1 Hz, C7), 132.1 (d, *J*_{CF} = 8.6 Hz, C8), 128.1 (q, *J*_{CF} = 34.4 Hz, C5), 124.7 (d, *J*_{CF} = 9.6 Hz, C12), 122.6 (q, *J*_{CF} = 274.4 Hz, C6), 120.3 (d, *J*_{CF} = 24.6 Hz, C9), 114.6 (d, *J* = 21.2 Hz, C11), 71.3 (d, *J*_{CF} = 1.2 Hz, C3), 30.3 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.20 (3F, F-C6), -111.18 (td, *J* = 8.1, 5.8 Hz, F-C10) ppm; **IR (ATR):** ν = 3422(b), 2980(w), 2933(w), 1597(m), 1576(w), 1486(m), 1370(m), 1330(w), 1260(w), 1207(s), 1189(s), 1159(s), 1122(s), 1038(m), 973(m), 929(w), 859(s), 822(m), 785(w), 760(w), 666(w) cm⁻¹.

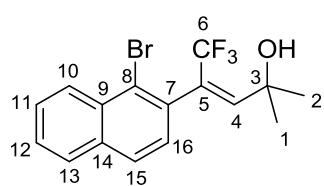
(Z)-4-(2-Bromo-4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1q)



Prepared according to General Procedure **C**, ethyl (*Z*)-3-(2-bromo-4-chlorophenyl)-4,4,4-trifluorobut-2-enoate **4q** (0.31 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1q** yielding a light yellow solid (35 mg, 33%) after purification by column chromatography (SiO₂, 5% Et₂O/n-pentane).

*R*_f = 0.29 (Et₂O/n-pentane 1:5); **M.p.**: 64.0 - 67.9 °C; **HR-ESI-MS**: *m/z* 364.9518 ([M+Na]⁺, calcd. for C₁₂H₁₁BrClF₃Na⁺: 364.9526); **¹H NMR** (600 MHz, CDCl₃) δ = 7.63 (d, *J* = 2.1 Hz, 1H, H-C11), 7.29 (dd, *J* = 8.2, 2.2 Hz, 1H, H-C9), 7.17 (d, *J* = 8.2 Hz, 1H, H-C8), 6.00 (s, 1H, H-C4), 1.52 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 151.2 (q, *J*_{CF} = 3.0 Hz, C4), 136.6 (q, *J*_{CF} = 2.4 Hz, C7), 135.1 (C10), 132.7 (C11), 131.9 (C8), 128.0 (q, *J*_{CF} = 34.6 Hz, C5), 127.7 (C9), 124.8 (C12), 122.5 (q, *J*_{CF} = 274.3 Hz, C6), 71.3 (d, *J*_{CF} = 1.1 Hz, C3), 30.3 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -54.05 ppm; **IR (ATR)**: ν = 3343(b), 2986(w), 1583(w), 1550(w), 1467(m), 1402(w), 1371(m), 1365(m), 1284(m), 1248(w), 1226(m), 1197(s), 1169(s), 1157(s), 1134(s), 1110(s), 1098(s), 1046(m), 970(s), 870(m), 862(m), 823(s), 802(s), 772(m), 749(m), 657(m) cm⁻¹.

(Z)-4-(1-Bromonaphthalen-2-yl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (1r)



Prepared according to General Procedure **C**, **4r** (0.26 mmol) and methylmagnesium bromide (2.2 eq.) were converted to **1r** yielding a colorless oil (64 mg, 69%) after purification by column chromatography (SiO₂, 10% Et₂O/n-pentane).

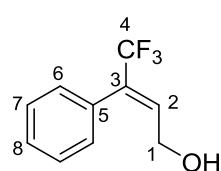
*R*_f = 0.12 (Et₂O/n-pentane 1:9); **HR-ESI-MS**: *m/z* 381.0069 ([M+Na]⁺, calcd. for C₁₆H₁₄OBrF₃Na⁺: 381.0072); **¹H NMR** (500 MHz, CDCl₃) δ = 8.36 (dd, *J* = 8.5, 1.1 Hz, 1H, H-C10), 7.86 – 7.83 (m, 1H, H-C13), 7.80 (dt, *J* = 8.4, 0.6 Hz, 1H, H-C15), 7.63 (ddd, *J* = 8.4, 6.9, 1.3 Hz, 1H, H-C11), 7.56 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H-C12), 7.33 (d, *J* = 8.4 Hz, 1H, H-C16), 6.09 (d, *J* = 0.6 Hz, 1H, H-C4), 1.60 (s, 3H, H-C1/H-C2), 1.53 (s, 3H, H-C1/H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 150.6 (q, *J*_{CF} = 3.0 Hz, C4), 136.1 (d, *J*_{CF} = 2.6 Hz, C7), 134.1 (C14), 132.4 (C9), 129.7 (q, *J*_{CF} = 34.1 Hz, C5), 128.3 (C13), 128.1 (C10/ C11), 128.0 (C10/C11), 127.7 (C15), 127.6 (C16), 127.2 (C12), 124.7 (C8), 122.8 (q, *J*_{CF} = 274.5 Hz, C6), 71.4 (d, *J* = 1.2 Hz, C3), 30.7 (C1/C2), 30.0 (C1/C2) ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ = 53.58 ppm; **IR (ATR)**: ν = 3423(b), 3057(w), 2978(w), 2934(w), 1554(w), 1498(w), 1464(w), 1367(m), 1322(w), 1272(w), 1250(m), 1197(m), 1154(s), 1120(s), 1033(m), 1008(m), 964(m), 942(m), 909(w), 864(w), 837(w), 813(s), 779(w), 759(m), 744(s), 713(w), 672(m), 654(m) cm⁻¹.

2.3. Isomerization of allylic alcohols

General Procedure D for the isomerization of allylic alcohols

A round-bottom flask was charged with the specified allylic alcohol (1 eq.) and anthracene (0.05 eq.) dissolved in MeCN. The reaction vessel was placed above the UV-lamp with a distance of approximately 1 cm and the mixture stirred at RT for 24 h under UV-light irradiation (UVA LED, 365 nm). The crude product was concentrated *in vacuo* and purified as specified. The *E*-/*Z*-isomer ratio was determined by integration of the ¹H NMR spectra.

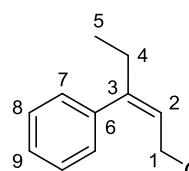
(*E*)-4,4,4-Trifluoro-3-phenylbut-2-en-1-ol (2a)



Prepared according to General Procedure D, (*Z*)-4,4,4-trifluoro-3-phenylbut-2-en-1-ol **1a** (0.1 mmol) in MeCN (1.5 mL) was converted to **2a**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (quant., **2a**:**1a** >95:5).

*R*_f = 0.14 (Et₂O/*n*-pentane 1:4); **HR-ESI-MS:** *m/z* 225.0515 ([*M*+Na]⁺, calcd. for C₁₀H₉F₃ONa⁺: 225.0498); **¹H NMR** (600 MHz, CDCl₃) δ = 7.42 – 7.39 (m, 3H, H-C7, H-C8), 7.24 (dd, *J* = 6.7, 3.0 Hz, 2H, H-C6), 6.56 (ddt, *J* = 6.3, 4.8, 1.6 Hz, 1H, H-C2), 4.15 (dq, *J* = 6.4, 2.2 Hz, 2H, H-C1) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 134.8 (q, *J* = 5.4 Hz, C2), 132.6 (q, *J* = 30.2 Hz, C3), 131.5 (C5), 129.5 (2C, C6), 129.1 (C7), 128.7 (2C, C6), 123.2 (q, *J* = 273.3 Hz, C4), 59.4 (C1) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -66.23 (d, *J* = 2.8 Hz) ppm; **IR (ATR):** ν = 3335(b), 1497(w), 1445(w), 1346(w), 1290(m), 1219(w), 1168(s), 1114(s), 1026(m), 980(m), 931(m), 906(m), 846(w), 771(m), 700(s), 668(m) cm⁻¹.

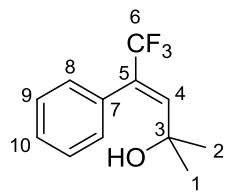
(*Z*)-3-Phenylpent-2-en-1-ol (2b)



Prepared according to General Procedure D, (*E*)-3-phenylpent-2-en-1-ol **1b** (0.2 mmol) in MeCN (3 mL) was converted to **2b** yielding a colorless oil (16 mg, 48%, **2b**:**1b** = 78:22) after purification by column chromatography (SiO₂, 4% EtOAc/ CH₃Cl).

¹H NMR (600 MHz, CDCl₃) δ = 7.35 – 7.31 (m, 2H, H-C8), 7.29 – 7.25 (m, 1H, H-C9), 7.14 – 7.12 (m, 2H, H-C7), 5.68 (tt, *J* = 7.0, 1.4 Hz, 1H, H-C2), 4.04 (dt, *J* = 6.9, 0.9 Hz, 2H, H-C1), 2.40 (qq, *J* = 7.4, 1.0 Hz, 2H, H-C4), 1.00 (t, *J* = 7.4 Hz, 3H, H-C5) ppm; analytical data in agreement with the literature.^[10]

(E)-5,5,5-Trifluoro-2-methyl-4-phenylpent-3-en-2-ol (2c)



Prepared according to General Procedure **D**, (*Z*)-5,5,5-trifluoro-2-methyl-4-phenylpent-3-en-2-ol **1c** (0.1 mmol) in MeCN (1.5 mL) was converted to **2c**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL).

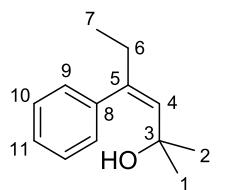
Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a light yellow oil (quant., **2c:1c** >95:5).

*R*_f = 0.08 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS**: *m/z*: 253.0822 ([M+Na]⁺, calcd. for C₁₂H₁₃F₃ONa⁺: 253.0811); **¹H NMR** (600 MHz, CD₂Cl₂) δ = 7.44 – 7.37 (m, 3H, H-C9, H-C10), 7.31 – 7.23 (m, 2H, H-C8), 6.53 (q, *J* = 1.6 Hz, 1H, H-C4), 1.25 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CD₂Cl₂) δ = 143.2 (q, *J*_{CF} = 5.1 Hz, C4), 132.5 (C7), 130.7 (2C, C8), 129.3 (C10), 129.2 (d, *J*_{CF} = 29.3 Hz, C5), 128.8 (2C, C9), 124.1 (d, *J*_{CF} = 273.4 Hz, C6), 71.7 (C3), 30.9 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CD₂Cl₂) δ = -67.33 (d, *J* = 1.6 Hz) ppm; **IR (ATR)**: ν = 3390(b), 2977(w), 1496(w), 1463(w), 1445(w), 1365(w), 1327(w), 1284(m), 1236(m), 1165(s), 1113(s), 1073(w), 1032(w), 989(w), 973(w), 937(w), 891(m), 793(w), 771(m), 703(s), 684(m) cm⁻¹.

As a representative example, this reaction was repeated on a 1 mmol scale:

A 10 mL round-bottomed flask was charged with (*Z*)-5,5,5-trifluoro-2-methyl-4-phenylpent-3-en-2-ol **1c** (230 mg, 1.0 mmol), anthracene (9.0 mg, 0.05 mmol, 0.05 eq.), and MeCN (7.5 mL). The reaction vessel was sealed with a septum and irradiated at 365 nm for 24 h at ambient temperature. After this time, the reaction mixture was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug followed by elution with *n*-pentane (5 mL). Subsequent elution of the product with Et₂O (10 mL) and removal of the solvents under reduced pressure furnished a light yellow oil (223 mg, 97%, **2c:1c** = 81:19).

(Z)-2-Methyl-4-phenylhex-3-en-2-ol (2d)

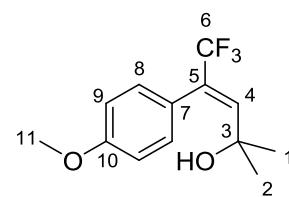


Prepared according to General Procedure **D**, (*E*)-2-methyl-4-phenylhex-3-en-2-ol **1h** (0.2 mmol) in MeCN (3 mL) was converted to **2h** yielding a colorless oil (19 mg, 50%, **2d:1d** >95:5) after purification by column chromatography (SiO₂, 4% Et₂O/*n*-pentane).

*R*_f = 0.13 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS**: *m/z*: 213.1248 ([M+Na]⁺, calcd. for C₁₃H₁₈ONa⁺: 213.1358); **¹H NMR** (600 MHz, CDCl₃) δ = 7.35 – 7.30 (m, 2H, H-C10), 7.28 – 7.24 (m, 1H, H-C11), 7.17 – 7.13 (m, 2H, H-C9), 5.58 (t, *J* = 1.4 Hz, 1H, H-C4), 2.24 (qd, *J* = 7.4, 1.4 Hz, 2H, H-C6), 1.16 (s, 6H, H-C1, H-C2), 0.95 (t, *J* = 7.4 Hz, 3H, H-C7) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 142.2 (C8), 141.7 (C5), 133.7 (C4), 129.1 (2C, C9), 128.6 (2C, C10), 127.2 (C11), 71.7 (C3), 35.0 (C6), 31.9 (2C, C1, C2), 13.1 (C7) ppm; **IR (ATR)**: ν = 3378(b), 2967(m),

2930(w), 1599(w), 1493(w), 1460(w), 1441(w), 1360(w), 1315(w), 1238(w), 1206(w), 1141(m), 1094(w), 1046(w), 1027(w), 982(w), 962(w), 907(m), 858(w), 804(w), 775(m), 761(m), 729(m), 701(s) cm⁻¹; analytical data in agreement with the literature.^[11]

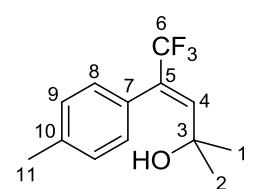
(E)-5,5,5-Trifluoro-4-(4-methoxyphenyl)-2-methylpent-3-en-2-ol (2e)



Prepared according to General Procedure D, (Z)-5,5,5-trifluoro-4-(4-methoxyphenyl)-2-methylpent-3-en-2-ol **1e** (0.1 mmol) in MeCN (1.5 mL) was converted to **2e**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a light yellow oil (23 mg, 90%, **2e:1e** >95:5).

R_f = 0.14 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS:** *m/z* 283.0908 ([M+Na]⁺, calcd. for C₁₃H₁₅O₂F₃Na⁺: 283.0916); **¹H NMR** (500 MHz, CDCl₃) δ = 7.24 – 7.18 (m, 2H, H-C9), 7.17 (d, *J* = 8.1 Hz, 2H, H-C8), 6.48 (d, *J* = 1.7 Hz, 1H, H-C4), 2.37 (d, *J* = 0.7 Hz, 3H, H-C11), 1.28 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 142.1 (q, *J_{CF}* = 4.9 Hz, C4), 139.0 (C10), 130.1 (2C, C9), 129.3 (2C, C8), 129.1 (d, *J_{CF}* = 29.4 Hz, C5), 128.7 (C7), 123.5 (d, *J_{CF}* = 273.7 Hz, C6), 71.5 (C3), 30.8 (2C, C1, C2), 21.4 (C11) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -67.24 (d, *J* = 1.5 Hz) ppm; **IR (ATR):** ν = 3387(b), 2923(w), 2853(w), 1716(w), 1514(w), 1461(w), 1366(w), 1285(m), 1238(m), 1163(s), 1113(s), 990(m), 973(m), 925(w), 891(m), 820(m), 800(m), 783(m), 734(m), 706(m), 678(m) cm⁻¹.

(E)-5,5,5-Trifluoro-2-methyl-4-(*p*-tolyl)pent-3-en-2-ol (2g)

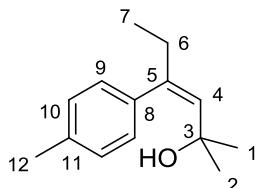


Prepared according to General Procedure D, (Z)-5,5,5-trifluoro-4-(4-methoxyphenyl)-2-methylpent-3-en-2-ol **1g** (0.1 mol) in MeCN (1.5 mL) was converted to **2g**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a white solid (19 mg, 95%, **2g:1g** >95:5).

R_f = 0.14 (Et₂O/*n*-pentane 1:5); **M.p.:** 60.0 - 61.8 °C **HR-ESI-MS:** *m/z* 267.0967 ([M+Na]⁺, calcd. for C₁₃H₁₅OF₃Na⁺: 267.0967); **¹H NMR** (600 MHz, CDCl₃) δ = 7.23 – 7.19 (m, 2H, H-C9), 7.17 (d, *J* = 7.9 Hz, 2H, H-C8), 6.49 (q, *J* = 1.6 Hz, 1H, H-C4), 2.37 (s, 3H, H-C11), 1.28 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 142.1 (d, *J_{CF}* = 5.0 Hz, C4), 139.0 (C7), 130.1 (2C, C8), 129.3 (2C, C9), 129.1 (d, *J_{CF}* = 29.5 Hz, C5), 128.7 (C10), 123.5 (q, *J_{CF}* = 273.6 Hz, C6), 71.4 (C3), 30.8 (2C, C1, C2), 21.4 (C11) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -67.22 (d, *J* = 1.6 Hz) ppm; **IR (ATR):** ν = 3264(b), 2979(w), 2931(w), 1666(w), 1514(w),

1454(w), 1374(w), 1361(w), 1279(s), 1239(m), 1167(s), 1148(s), 1134(s), 1113(s), 1011(w), 995(m), 953(w), 929(m), 908(m), 879(m), 825(m), 813(w), 800(m), 785(m), 734(s), 706(m), 693(m), 678(s) cm⁻¹.

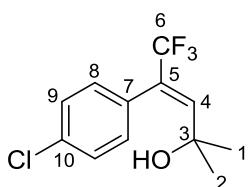
(Z)-2-Methyl-4-(*p*-tolyl)hex-3-en-2-ol (**2h**)



Prepared according to General Procedure **D**, (*E*)-2-methyl-4-(*p*-tolyl)hex-3-en-2-ol **1h** (0.2 mmol) in MeCN (3 mL) was converted to **2h** yielding a colorless oil (20 mg, 50%, **2h**:**1h** = 91:9) after purification by column chromatography (SiO₂, 4% Et₂O/*n*-pentane).

R_f = 0.28 (Et₂O/*n*-pentane 1:6); **HR-ESI-MS**: *m/z*: 227.1406 ([M+Na]⁺, calcd. for C₁₄H₂₀ONa⁺: 227.1406); **¹H NMR** (600 MHz, CD₂Cl₂) δ = 7.17 – 7.12 (m, 2H, H-C10), 7.05 – 7.01 (m, 2H, H-C9), 5.57 (t, *J* = 1.4 Hz, 1H, H-C4), 2.36 – 2.32 (m, 3H, H-C12), 2.22 (qd, *J* = 7.4, 1.4 Hz, 2H, H-C6), 1.17 (s, 6H, H-C1, H-C2), 0.94 (t, *J* = 7.4 Hz, 3H, H-C7) ppm; **¹³C NMR** (151 MHz, CD₂Cl₂) δ = 141.1 (C5), 138.3 (C8), 136.4 (C11), 133.0 (C4), 128.7 (2C, C10), 128.3 (2C, C9), 71.1 (C3), 34.4 (C6), 31.3 (2C, C1, C2), 20.8 (C12), 12.5 (C7) ppm; **IR (ATR)**: ν = 3293(m), 2971(m), 2929(m), 2876(w), 2839(w), 1645(w), 1567(w), 1508(m), 1450(m), 1435(w), 1399(w), 1372(m), 1360(m), 1313(w), 1241(w), 1214(w), 1202(m), 1181(w), 1142(s), 1109(m), 1046(w), 988(m), 928(m), 904(m), 847(m), 824(s), 805(s), 794(s), 729(m), 676(m), 656(m) cm⁻¹.

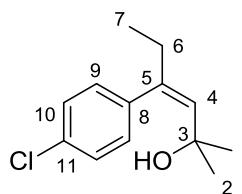
(E)-4-(4-Chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (**2i**)



Prepared according to General Procedure **D**, (*Z*)-4-(4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1i** (0.1 mmol) in MeCN (1.5 mL) was converted to **2i**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (quant., **2i**:**1i** >95:5).

R_f = 0.23 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS**: *m/z*: 287.0419 ([M+Na]⁺, calcd. for C₁₂H₁₂OCF₃Na⁺: 287.0421); **¹H NMR** (600 MHz, CDCl₃) δ = 7.39 – 7.35 (m, 2H, H-C9), 7.23 – 7.20 (m, 2H, H-C8), 6.51 (q, *J* = 1.6 Hz, 1H, H-C4), 1.29 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 142.8 (q, *J*_{CF} = 4.9 Hz, C4), 135.2 (C10), 131.6 (2C, C8), 130.5 (C7), 128.7 (2C, C9), 128.2 (d, *J*_{CF} = 29.8 Hz, C5), 123.2 (d, *J*_{CF} = 273.7 Hz, C6), 71.4 (C3), 30.8 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -67.10 ppm; **IR (ATR)**: ν = 3389(b), 2989(w), 2940(w), 1722(w), 1671(w), 1595(w), 1492(m), 1467(w), 1371(w), 1360(w), 1277(s), 1235(m), 1172(m), 1155(s), 1117(s), 1088(s), 1017(m), 992(m), 975(m), 924(w), 901(m), 876(m), 825(m), 792(w), 763(m), 733(m), 681(m) cm⁻¹.

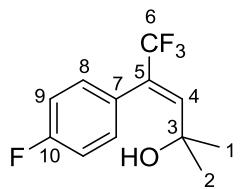
(Z)-4-(4-Chlorophenyl)-2-methylhex-3-en-2-ol (2j)



Prepared according to General Procedure D, (Z)-4-(4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1j** (0.2 mmol) in MeCN (3 mL) was converted to **2j** yielding a colorless oil (31 mg, 69%, **2j:1j** = 95:5) after purification by column chromatography (SiO_2 , 4% $\text{Et}_2\text{O}/n\text{-pentane}$).

R_f = 0.14 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:5); **HR-ESI-MS:** m/z : 247.0855 ([$M+\text{Na}^+$], calcd. for $\text{C}_{13}\text{H}_{17}\text{ClONa}^+$: 247.0860); **$^1\text{H NMR}$** (600 MHz, CD_2Cl_2) δ = 7.32 – 7.29 (m, 2H, H-C10), 7.12 – 7.07 (m, 2H, H-C9), 5.60 (t, J = 1.4 Hz, 1H, H-C4), 2.22 (qd, J = 7.4, 1.4 Hz, 2H, H-C6), 1.16 (s, 6H, H-C1, H-C2), 0.94 (t, J = 7.4 Hz, 4H, H-C7) ppm; **$^{13}\text{C NMR}$** (151 MHz, CD_2Cl_2) δ = 140.8 (C8), 140.7 (C5), 134.4 (C4), 132.9 (C11), 130.6 (2C, C9), 128.6 (2C, C10), 71.7 (C3), 34.9 (C6), 31.8 (2C, C1, C2), 13.1 (C7) ppm; **IR (ATR):** $\tilde{\nu}$ = 3473(b), 2986(w), 2944(w), 1649(w), 1593(w), 1490(m), 1459(w), 1393(w), 1367(m), 1281(w), 1267(w), 1225(m), 1194(s), 1104(s), 1089(s), 1018(m), 974(m), 965(m), 955(m), 931(w), 888(w), 836(s), 819(m), 791(m), 722(m), 710(w) cm^{-1} .

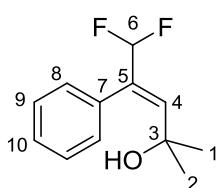
(E)-5,5,5-Trifluoro-4-(4-fluorophenyl)-2-methylpent-3-en-2-ol (2k)



Prepared according to General Procedure D, (Z)-4-(4-fluorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1k** (0.1 mmol) in MeCN (1.5 mL) was converted to **2k**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO_2 -plug with *n*-pentane (2 mL). Subsequent elution of the product with Et_2O (5 mL) and concentration *in vacuo* yielded a colorless oil (24 mg, 96%, **2k:1k** >95:5).

R_f = 0.14 ($\text{Et}_2\text{O}/n\text{-pentane}$ 1:5); **HR-ESI-MS:** m/z : 271.0757 ([$M+\text{Na}^+$], calcd. for $\text{C}_{12}\text{H}_{12}\text{F}_4\text{ONa}^+$: 271.0716); **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ = 7.27 – 7.21 (m, 2H, H-C8), 7.09 (t, J = 8.7 Hz, 2H, H-C9), 6.51 (q, J = 1.6 Hz, 1H, H-C4), 1.28 (s, 6H, H-C1, H-C2) ppm; **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 163.1 (d, J_{CF} = 248.7 Hz, C10), 142.8 (q, J = 5.0 Hz, C4), 132.1 (d, J_{CF} = 8.2 Hz, 2C, C8), 128.3 (d, J_{CF} = 29.7 Hz, C5), 127.8 (d, J_{CF} = 3.6 Hz, C7), 123.3 (d, J_{CF} = 274.4 Hz, C6), 115.6 (d, J_{CF} = 21.7 Hz, 2C, C9), 71.4 (C3), 30.7 (2C, C1, C2) ppm; **$^{19}\text{F NMR}$** (564 MHz, CDCl_3) δ = -67.27 (3F, F-C6), -112.54 (dd, J = 8.9, 4.3 Hz, F-C10) ppm; **IR (ATR):** $\tilde{\nu}$ = 3413(b), 2978(w), 2936(w), 1718(w), 1668(w), 1605(w), 1510(m), 1462(w), 1366(w), 1286(m), 1226(m), 1167(s), 1115(s), 989(w), 975(m), 894(w), 838(m), 817(m), 785(w), 739(m), 708(w), 675(m) cm^{-1} .

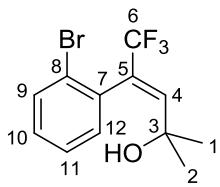
(E)-5,5-Difluoro-2-methyl-4-phenylpent-3-en-2-ol (2m)



Prepared according to General Procedure **D**, (*Z*)-5,5-difluoro-2-methyl-4-phenylpent-3-en-2-ol **1m** (0.1 mmol) in MeCN (1.5 mL) was converted to **2m**. The crude product was purified by column chromatography (SiO₂, 5% Et₂O/*n* pentane) yielding a colorless oil (19 mg, 89%, **2m**:**1m** >95:5).

R_f = 0.10 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS**: *m/z*: 235.0903 ([M+Na]⁺, calcd. for C₁₂H₁₄F₂ONa⁺: 235.0910); **¹H NMR** (600 MHz, CDCl₃) δ = 7.30 – 7.23 (m, 3H, H-C9, H-C10), 7.17 – 7.10 (m, 2H, H-C8), 6.03 (t, J = 2.3 Hz, 1H, H-C4), 5.96 (t, J = 56.1 Hz, 1H, H-C6), 1.16 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 142.4 (t, J_{CF} = 8.9 Hz, C4), 133.2 (t, J_{CF} = 21.1 Hz, C5), 132.9 (C7), 130.0 (2C, C8), 128.6 (C10), 128.5 (2C, C9), 116.6 (t, J_{CF} = 239.7 Hz, C6), 71.6 (C3), 30.8 (d, J = 1.6 Hz, 2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -112.36 (dd, J = 56.1, 2.3 Hz) ppm; **IR (ATR)**: ν = 3302(b), 3001(w), 2978(w), 2933(w), 1662(w), 1602(w), 1577(w), 1496(w), 1458(w), 1444(w), 1377(m), 1357(m), 1207(m), 1152(m), 1121(s), 1067(m), 1009(s), 977(s), 911(m), 866(m), 782(m), 707(s), 678(m) cm⁻¹.

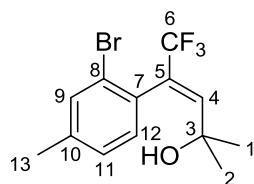
(E)-4-(2-Bromophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (2n)



Prepared according to General Procedure **D**, (*Z*)-4-(2-bromophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1n** (0.1 mmol) in MeCN (1.5 mL) was converted to **2n**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a white solid (28 mg, 91%, **2n**:**1n** >95:5).

R_f = 0.14 (Et₂O/*n*-pentane 1:5); **M.p.**: 37.1 – 38.8 °C; **HR-ESI-MS**: *m/z*: 330.9916 ([M+Na]⁺, calcd. for C₁₂H₁₂OBrF₃Na⁺: 330.9906); **¹H NMR** (600 MHz, CDCl₃) δ = 7.64 – 7.60 (m, 1H, H-C11), 7.36 – 7.31 (m, 1H, H-C9), 7.24 (ddd, J = 8.0, 7.3, 1.8 Hz, 2H, H-C10, H-C12), 6.51 (d, J = 1.5 Hz, 1H, H-C4), 1.35 (s, 3H, H-C1/ H-C2), 1.28 (s, 3H, H-C1/ H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 143.2 (q, J_{CF} = 4.7 Hz, C4), 133.7 (C7), 133.0 (C11), 131.9 (C10/ C12), 130.3 (C10/ C12), 127.4 (d, J_{CF} = 31.4 Hz, C5), 127.3 (C9), 124.8 (C8), 123.2 (d, J_{CF} = 274.5 Hz, C6), 71.6 (C3), 29.8 (C1/C2), 29.7 (C1/ C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -66.27 (d, J = 1.4 Hz) ppm; **IR (ATR)**: ν = 3326(b), 2985(w), 1669(w), 1588(w), 1561(w), 1470(m), 1426(m), 1381(w), 1367(w), 1279(s), 1215(w), 1172(s), 1145(s), 1115(s), 1052(m), 1032(m), 1011(m), 986(m), 929(m), 917(m), 888(m), 795(m), 769(m), 749(s), 734(s), 680(s), 658(m) cm⁻¹.

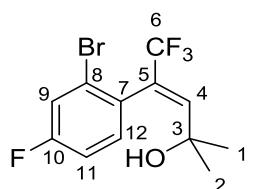
(E)-4-(2-bromo-4-methylphenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (2o)



Prepared according to General Procedure D, (*Z*)-4-(2-bromo-4-methylphenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1o** (0.1 mmol) in MeCN (1.5 mL) was converted to **2o**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (quant., **2o:1o** = 72:28).

R_f = 0.17 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS:** *m/z*: 345.0065 ([M+Na]⁺, calcd. for C₁₃H₁₄OBrF₃Na⁺: 345.0072); **¹H NMR** (500 MHz, CDCl₃) δ = 7.45 (dt, *J* = 1.4, 0.8 Hz, 1H, H-C9), 7.13 (d, *J* = 1.0 Hz, 2H, H-C11, H-C12), 6.49 (q, *J* = 1.5 Hz, 1H, H-C4), 2.44 – 2.23 (m, 3H, H-C13), 1.34 (d, *J* = 0.5 Hz, 3H, H-C1/H-C2), 1.27 (d, *J* = 0.5 Hz, 3H, H-C1/H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 143.2 (q, *J_{CF}* = 4.7 Hz, C4), 140.8 (C10), 133.5 (C9), 131.5 (C12), 130.5 (C7), 128.2 (C11), 127.3 (d, *J_{CF}* = 30.3 Hz, C5), 124.4 (C8), 123.2 (d, *J_{CF}* = 274.4 Hz, C6), 71.6 (C3), 29.8 (C1/C2), 29.7 (C1/C2), 21.0 (C13) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -66.41 (d, *J* = 1.5 Hz) ppm; **IR (ATR):** ν = 3402(b), 2978(w), 2930(w), 1703(w), 1603(w), 1490(w), 1458(w), 1367(w), 1286(m), 1267(w), 1233(m), 1197(m), 1162(s), 1118(s), 1047(m), 974(m), 930(w), 897(m), 821(w), 784(m), 742(w), 710(w), 674(m), 667(m) cm⁻¹.

(E)-4-(2-Bromo-4-fluorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (2p)



Prepared according to General Procedure D, (*Z*)-4-(2-bromo-4-fluorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1p** (0.1 mmol) in MeCN (1.5 mL) was converted to **2p**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (29 mg, 89%, **2p:1p** >95:5).

R_f = 0.17 (Et₂O/*n*-pentane 1:5); **HR-ESI-MS:** *m/z*: 348.9799 ([M+Na]⁺, calcd. for C₁₂H₁₁F₄BrONa⁺: 348.9822); **¹H NMR** (500 MHz, CDCl₃) δ = 7.38 (dd, *J* = 8.2, 2.6 Hz, 1H, H-C9), 7.25 – 7.18 (m, 1H, H-C12), 7.09 – 7.02 (m, 1H, H-C11), 6.52 (q, *J* = 1.5 Hz, 1H, H-C4), 1.34 (s, 3H, H-C1/H-C2), 1.28 (s, 3H, H-C1/H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 162.5 (d, *J_{CF}* = 252.8 Hz, C10), 143.9 (q, *J_{CF}* = 4.7 Hz, C4), 132.8 (d, *J_{CF}* = 8.6 Hz, C12), 129.8 (d, *J_{CF}* = 3.9 Hz, C7), 126.6 (q, *J_{CF}* = 30.4 Hz, C5), 125.1 (d, *J_{CF}* = 9.7 Hz, C8), 123.0 (qd, *J_{CF}* = 274.4, 1.4 Hz, C6), 120.4 (d, *J_{CF}* = 24.5 Hz, C11), 114.7 (d, *J_{CF}* = 21.3 Hz, C9), 71.6 (C3), 29.9 (d, *J* = 1.0 Hz, C1/C2), 29.7 (d, *J_{CF}* = 0.9 Hz, C1/C2) ppm; **¹⁹F NMR** (470 MHz, CDCl₃) δ = -66.45 (d, *J* = 1.5 Hz, 3F, H-C6), -110.70 (td, *J* = 8.1, 5.9 Hz, F-C10) ppm; **IR (ATR):** ν = 3404(b), 2980(w), 1598(m), 1580(w), 1489(m), 1463(w), 1383(w), 1365(w), 1288(m),

1263(m), 1236(m), 1213(s), 1170(s), 1116(s), 1038(m), 975(m), 934(w), 897(w), 871(s), 862(s), 821(m), 787(m), 740(m), 711(w), 670(m) cm^{-1} .

(E)-4-(2-Bromo-4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (2q)

Prepared according to General Procedure D, (*Z*)-4-(2-bromo-4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1q** (0.1 mmol) in MeCN (1.5 mL) was converted to **2q**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (quant., **2q:1q** >95:5).

R_f = 0.24 (Et₂O/*n*-pentane 1:5); **HR-APCI-MS:** *m/z* 376.9329 ([M+Cl]⁺, calcd. for C₁₂H₁₁OB₂Cl₂F₃Cl⁺: 376.9317); **¹H NMR** (600 MHz, CDCl₃) δ = 7.64 (d, *J* = 2.1 Hz, 1H, H-C9), 7.32 (dd, *J* = 8.2, 2.1 Hz, 1H, H-C11), 7.20 – 7.15 (m, 1H, H-C12), 6.51 (q, *J* = 1.5 Hz, 1H, H-C4), 1.36 (s, 3H, H-C1/H-C2), 1.29 (s, 3H, H-C1/H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 143.8 (q, *J*_{CF} = 4.7 Hz, C4), 135.5 (C10), 132.7 (C9), 132.5 (C7), 132.4 (C12), 127.6 (C11), 126.5 (d, *J*_{CF} = 30.4 Hz, C5), 125.2 (C8), 123.0 (d, *J*_{CF} = 274.4 Hz, C6), 71.6 (C3), 30.0 (C1/C2), 29.7 (C1/C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -66.31 (d, *J* = 1.3 Hz) ppm; **IR (ATR):** $\tilde{\nu}$ = 3437(b), 2978(w), 2930(w), 1583(w), 1549(w), 1472(m), 1365(w), 1287(m), 1253(m), 1235(m), 1166(s), 1118(s), 1045(m), 975(m), 931(w), 897(w), 869(w), 825(m), 796(s), 739(m), 689(m), 669(m) cm^{-1} .

(E)-4-(1-Bromonaphthalen-2-yl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol (2r)

Prepared according to General Procedure D, (*Z*)-4-(1-bromo-naphthalen-2-yl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **1r** (0.1 mmol) in MeCN (1.5 mL) was converted to **2r**. The crude product was concentrated *in vacuo*, the residual catalyst was removed by filtration through a SiO₂-plug with *n*-pentane (2 mL). Subsequent elution of the product with Et₂O (5 mL) and concentration *in vacuo* yielded a colorless oil (quant., **2r:1r** = 85:15).

R_f = 0.12 (Et₂O/*n*-pentane 1:9); **HR-ESI-MS:** *m/z* 381.0070 ([M+Na]⁺, calcd. for C₁₆H₁₄OB₂F₃Na⁺: 381.0072); **¹H NMR** (500 MHz, CDCl₃) δ = 8.41 – 8.28 (m, 1H, H-C10), 7.87 – 7.84 (m, 1H, H-C13), 7.83 (dt, *J* = 8.3, 0.7 Hz, 1H, H-C15), 7.63 (ddd, *J* = 8.4, 6.9, 1.4 Hz, 1H, H-C11), 7.57 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H, H-C12), 7.34 (dd, *J* = 8.3, 0.8 Hz, 1H, H-C16), 6.58 (q, *J* = 1.5 Hz, 1H, H-C4), 1.35 (s, 3H, H-C1/H-C2), 1.29 (s, 3H, H-C1/H-C2) ppm; **¹³C NMR** (126 MHz, CDCl₃) δ = 142.90 (q, *J*_{CF} = 4.7 Hz, m, C4), 134.3 (C14), 132.3 (C9), 131.9 (C7), 128.4 (C13), 128.3 (C16), 128.2 (d, *J*_{CF} = 30.1 Hz, C5), 128.1 (C11), 128.0 (C10), 127.8

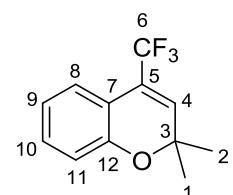
(C15), 127.5 (C12), 125.1 (C8), 123.3 (d, $J_{\text{CF}} = 274.8$ Hz, C6), 71.6 (C3), 29.8 (C1/C2), 29.6 (C1/C2) ppm; **^{19}F NMR** (470 MHz, CDCl_3) $\delta = -65.56$ (d, $J = 1.5$ Hz) ppm; **IR (ATR)**: $\tilde{\nu} = 3391(\text{b})$, 3059(w), 2977(w), 2934(w), 1553(w), 1499(w), 1465(w), 1364(w), 1320(w), 1282(m), 1255(m), 1164(s), 1114(s), 1027(w), 1015(w), 1001(m), 967(m), 939(m), 916(w), 897(m), 858(w), 814(s), 784(m), 748(s), 712(m), 703(m) cm^{-1} .

2.4. Preparation of 2H-Chromenes

General Procedure F for the preparation of 2H-Chromenes^[12]

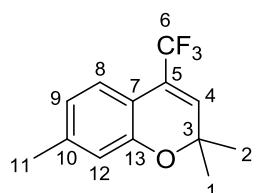
A flame dried flask was charged with the (*Z*-allylic alcohol (0.15 mmol, 1.0 eq.), $\text{Pd}(\text{OAc})_2$ (0.05 eq.), dppf (0.05 eq.) and NaO^+Bu (2.0 eq.). Dry toluene (degased) was added and the mixture was stirred at 110°C overnight. The reaction was quenched by the addition of NH_4Cl -solution (aq., sat.), the organic phase was separated, the aqueous phase was extracted with Et_2O (3x), the combined organic phases were dried over MgSO_4 and concentrated *in vacuo*. The crude product purified by column chromatography (SiO_2 , specified combination of $\text{Et}_2\text{O}/n$ -pentane).

2,2-Dimethyl-4-(trifluoromethyl)-2H-chromene (3n)^[12]

 Prepared according to the General Procedure F, (*E*)-4-(2-bromophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **2n** (0.15 mmol) was converted to **3n** yielding a light yellow oil (22 mg, 69%) after purification by column chromatography (SiO_2 , 4% $\text{Et}_2\text{O}/n$ -pentane).

$R_f = 0.76$ ($\text{Et}_2\text{O}/n$ -pentane 1:5); **HR-APCI-MS**: m/z : 229.0841 ([$M+\text{H}$] $^+$, calcd. for $\text{C}_{12}\text{H}_{11}\text{OF}_3\text{H}^+$: 229.0835); **^1H NMR** (600 MHz, CD_2Cl_2) $\delta = 7.31$ (dt, $J = 7.9, 1.9$ Hz, 1H, H-C8), 7.24 – 7.20 (m, 1H, H-C10), 6.93 (td, $J = 7.6, 1.2$ Hz, 1H, H-C9), 6.86 (dd, $J = 8.2, 1.2$ Hz, 1H, H-C11), 6.21 (q, $J = 1.5$ Hz, 1H, H-C4), 1.46 (s, 6H, H-C1, H-C2) ppm; **^{13}C NMR** (151 MHz, CD_2Cl_2) $\delta = 153.5$ (C12), 133.1 (C4), 131.1 (C10), 124.7 (C8), 124.4 (C5), 123.5 (C6), 121.7 (C9), 117.8 (C11), 116.4 (C7), 75.8 (C3), 27.2 (2C, C1, C2); **^{19}F NMR** (564 MHz, CD_2Cl_2) $\delta = -65.36$ (t, $J = 1.7$ Hz) ppm; **IR (ATR)**: $\tilde{\nu} = 2980(\text{w})$, 1469(w), 1435(w), 1384(w), 1368(w), 1287(m), 1269(m), 1168(s), 1114(s), 1050(w), 1030(m), 974(w), 918(m), 825(w), 797(w), 763(m), 736(s), 701(m), 689(m), 656(m) cm^{-1} .

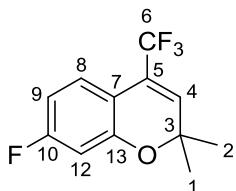
2,2,7-Trimethyl-4-(trifluoromethyl)-2*H*-chromene (**3o**)^[12]



Prepared according to the General Procedure **F**, (*E*)-4-(2-bromo-4-methylphenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **2o** (0.15 mmol) was converted to **3o** yielding a light yellow oil (35 mg, 96%) after purification by column chromatography (SiO₂, 4% Et₂O/n-pentane).

R_f = 0.86 (Et₂O/n-pentane 1:4); **HR-APCI-MS**: *m/z*: 243.0987 ([M+H]⁺, calcd. for C₁₃H₁₃F₃OH⁺: 243.0991); **¹H NMR** (600 MHz, CDCl₃) δ = 7.20 (dd, *J* = 8.0, 2.0 Hz, 1H, H-C8), 6.74 (dtd, *J* = 7.9, 1.1, 0.5 Hz, 1H, H-C9), 6.69 (dd, *J* = 1.7, 0.8 Hz, 1H, H-C12), 6.09 (d, *J* = 1.5 Hz, 1H, H-C4), 2.30 (s, 3H, H-C11), 1.46 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 152.9 (C13), 141.2 (C10), 131.1 (q, *J*_{CF} = 5.9 Hz, C4), 124.3 (d, *J*_{CF} = 31.4 Hz, C5), 124.2 (q, *J*_{CF} = 2.0 Hz, C8), 122.7 (d, *J*_{CF} = 273.2 Hz, C6) 122.2 (C9), 117.9 (C12), 113.3 (C7), 75.3 (C3), 27.1 (2C, C1, C2), 21.5 (C11) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -65.08 ppm; **IR (ATR)**: ν = 2980(w), 2929(w), 1619(w), 1564(w), 1505(w), 1459(w), 1389(w), 1364(w), 1307(s), 1276(m), 1236(w), 1203(m), 1180(m), 1146(s), 1118(s), 1011(w), 986(m), 950(w), 938(w), 899(w), 851(m), 807(m), 764(w), 722(m), 693(w) cm⁻¹.

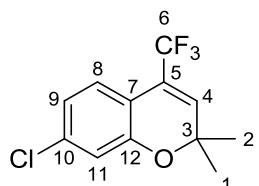
7-Fluoro-2,2-dimethyl-4-(trifluoromethyl)-2*H*-chromene (**3p**)^[12]



Prepared according to the General Procedure **F**, (*E*)-4-(2-bromo-4-fluorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **2p** (0.15 mmol) was converted to **3p** yielding a light yellow oil (27 mg, 74%) after purification by column chromatography (SiO₂, 4% Et₂O/n-pentane).

R_f = 0.77 (Et₂O/n-pentane 1:5); **HR-APCI-MS**: *m/z*: 247.0737 ([M+H]⁺, calcd. for C₁₂H₁₀F₄OH⁺: 247.0741); **¹H NMR** (600 MHz, CDCl₃) δ = 7.30 – 7.25 (m, 1H, H-C8), 6.64 (td, *J* = 8.5, 2.6 Hz, 1H, H-C9), 6.59 (dd, *J* = 9.8, 2.6 Hz, 1H, H-C12), 6.11 (q, *J* = 1.5 Hz, 1H, H-C4), 1.47 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 164.0 (d, *J*_{CF} = 249.1 Hz, C10), 154.7 (d, *J*_{CF} = 12.5 Hz, C13), 130.82 (qd, *J*_{CF} = 5.9, 2.4 Hz, C4), 125.7 (dd, *J*_{CF} = 10.1, 2.2 Hz, C8), 125.5 (d, *J*_{CF} = 28.1 Hz, C5), 122.8 (d, *J*_{CF} = 272.9 Hz, C6), 112.3 (d, *J*_{CF} = 3.2 Hz, C7), 108.4 (d, *J*_{CF} = 22.0 Hz, C9), 105.1 (d, *J*_{CF} = 24.7 Hz, C12), 76.1 (C3), 27.2 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -65.18 (t, *J* = 1.6 Hz, 3F, F-C6), -109.41 (ddd, *J* = 9.8, 8.4, 6.2 Hz, F-C10) ppm; **IR (ATR)**: ν = 2984(w), 2932(w), 1614(m), 1585(w), 1504(m), 1428(w), 1390(w), 1366(w), 1306(s), 1279(m), 1239(w), 1204(m), 1173(s), 1110(s), 997(s), 957(w), 903(w), 851(s), 810(m), 764(w), 724(w), 696(m) cm⁻¹.

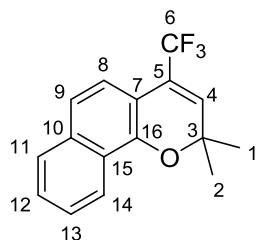
7-Chloro-2,2-dimethyl-4-(trifluoromethyl)-2*H*-chromene (3q)^[12]



Prepared according to the General Procedure F; (*E*)-4-(2-bromo-4-chlorophenyl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **2q** (0.15 mmol) was converted to **3q** yielding a light yellow oil (30 mg, 76%) after purification by column chromatography (SiO₂, 4% Et₂O/ *n*-pentane).

*R*_f = 0.86 (Et₂O/*n*-pentane 1:9); **HR-APCI-MS:** *m/z*: 263.0448 ([M+H]⁺, calcd. for C₁₂H₁₀OCIF₃H⁺: 263.0445); **¹H NMR** (600 MHz, CDCl₃) δ = 7.23 (dq, *J* = 8.4, 1.8 Hz, 1H, H-C11), 6.91 (dd, *J* = 8.4, 2.1 Hz, 1H, H-C9), 6.88 (d, *J* = 2.1 Hz, 1H, H-C8), 6.15 (q, *J* = 1.4 Hz, 1H, H-C4), 1.47 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 153.7 (C12), 135.7 (C10), 132.0 (q, *J* = 5.8 Hz, C4), 125.1 (q, *J*_{CF} = 2.2 Hz, C11), 123.6 (d, *J*_{CF} = 31.6 Hz, C5), 122.5 (d, *J*_{CF} = 272.9 Hz, C6), 121.4 (C9), 117.6 (C8), 114.3 (C7), 75.9 (C3), 27.0 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -65.17 (t, *J* = 1.7 Hz) ppm; **IR (ATR):** ν = 2982(w), 2928(w), 2855(w), 1601(m), 1560(w), 1489(m), 1412(w), 1389(w), 1365(w), 1305(s), 1272(w), 1228(w), 1203(m), 1176(m), 1164(m), 1147(s), 1120(s), 1080(s), 979(s), 949(w), 937(m), 880(w), 856(m), 809(m), 755(w), 739(w), 711(m) cm⁻¹.

2,2-Dimethyl-4-(trifluoromethyl)-2*H*-benzo[*h*]chromene (3r)^[12]



Prepared according to the General Procedure F, (*E*)-4-(1-bromonaphthalen-2-yl)-5,5,5-trifluoro-2-methylpent-3-en-2-ol **2r** (0.15 mmol) was converted to **3r** yielding a light yellow oil (23 mg, 81%) after purification by column chromatography (SiO₂, 4% Et₂O/*n*-pentane).

*R*_f = 0.83 (Et₂O/*n*-pentane 1:9); **HR-ESI-MS:** *m/z*: 333.1459 ([M+Na+MeOH]⁺, calcd. for C₁₇H₁₇F₃NaO₂⁺: 333.1073); **¹H NMR** (600 MHz, CDCl₃) δ = 8.24 – 8.19 (m, 1H, H-C14), 7.77 (dd, *J* = 7.8, 1.6 Hz, 1H, H-C11), 7.51 – 7.47 (m, 2H, H-C12, H-C13), 7.46 (dd, *J* = 8.6, 1.7 Hz, 1H, H-C8), 7.42 (dd, *J* = 8.5, 0.7 Hz, 1H, H-C9), 6.19 (q, *J* = 1.6 Hz, 1H, H-C4), 1.57 (s, 6H, H-C1, H-C2) ppm; **¹³C NMR** (151 MHz, CDCl₃) δ = 149.1 (C16), 134.8 (C10), 130.5 (q, *J*_{CF} = 5.9 Hz, C4), 127.7 (C11), 127.3 (C12/C13), 125.9 (C12/C13), 125.2 (C15), 125.0 (d, *J*_{CF} = 31.2 Hz, C5), 123.1 (d, *J*_{CF} = 272.8 Hz, C6), 122.5 (C14), 121.4 (q, *J*_{CF} = 2.2 Hz, C8), 120.6 (C9), 110.3 (C7), 76.1 (C3), 27.1 (2C, C1, C2) ppm; **¹⁹F NMR** (564 MHz, CDCl₃) δ = -64.68 (t, *J* = 1.7 Hz) ppm; **IR (ATR):** ν = 3070(w), 2979(w), 2928(w), 1703(w), 1624(w), 1566(w), 1508(w), 1460(w), 1384(m), 1364(w), 1299(s), 1266w, 1231(w), 1201(m), 1187(m), 1143(s), 1116(s), 1096(s), 1033(m), 957(w), 932(m), 848(m), 810(m), 802(m), 747(s), 707(m) cm⁻¹.

3. Reaction Progress Monitoring

The isomerization of **Z-1** was performed according to General Procedure **D**. The conversion was monitored by ^{19}F NMR spectroscopy (*Agilent DD2 600* spectrometer, 500 MHz, CDCl_3) of 0.1 mL samples taken from the same reaction solution after the specified time with δ_{F} (**Z-1**) = -54.27 ppm and product δ_{F} (**E-1**)= -67.23 ppm.

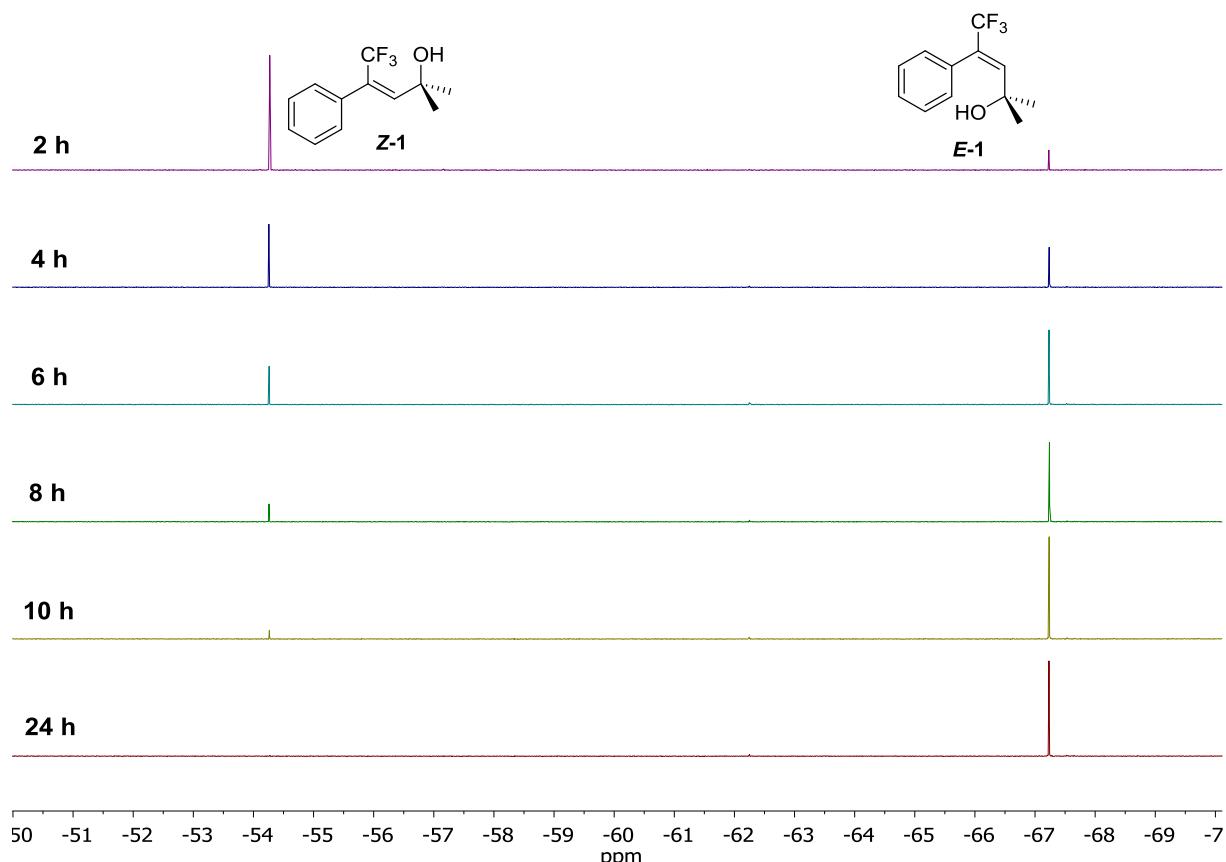


Figure 3: Reaction progress monitoring of the isomerization of compound **Z-1** by ^{19}F NMR spectroscopy.

The isomerization was also monitored by HPLC analysis (CHIRACEL OJ H column, *n*-hexane/*i*-PrOH 90:10, 0.5 mL/min) of 0.1 mL samples taken from the same reaction solution after the specified time with the *Z*-isomer **Z-1** eluting at 10.2 min and the *E*-isomer **E-1** at 22.1 min.

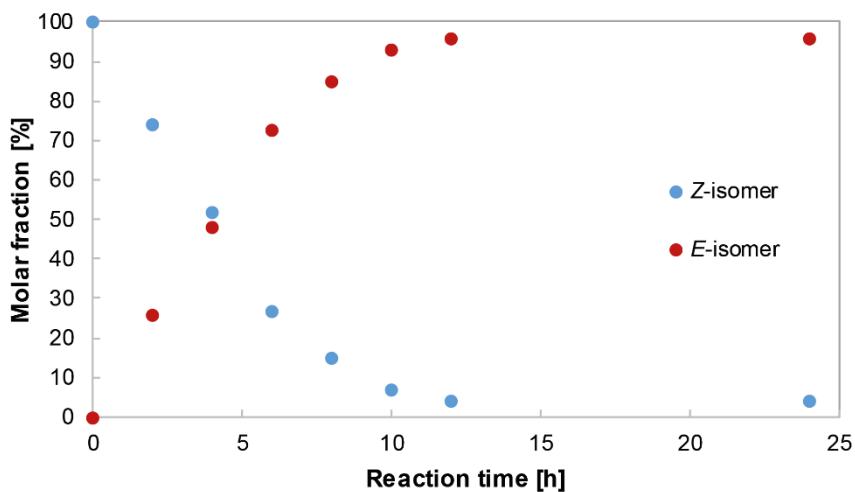
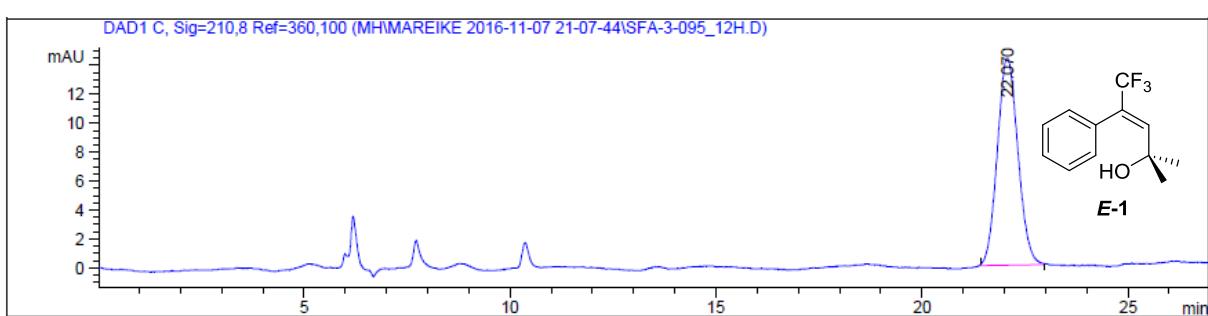
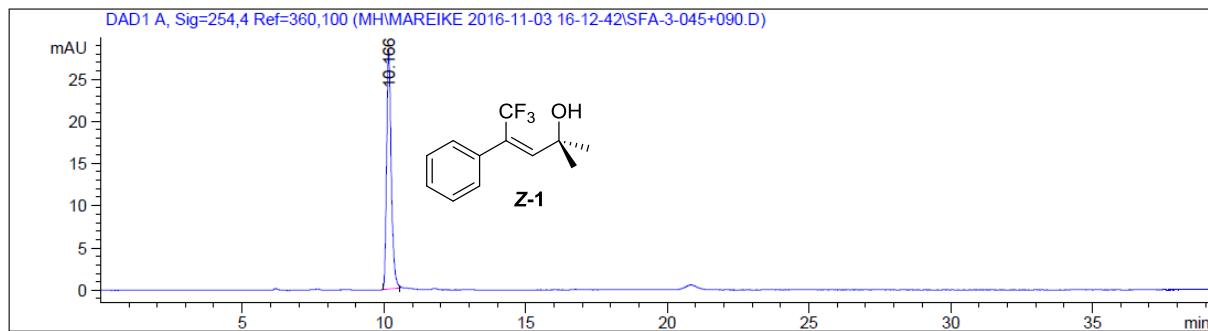
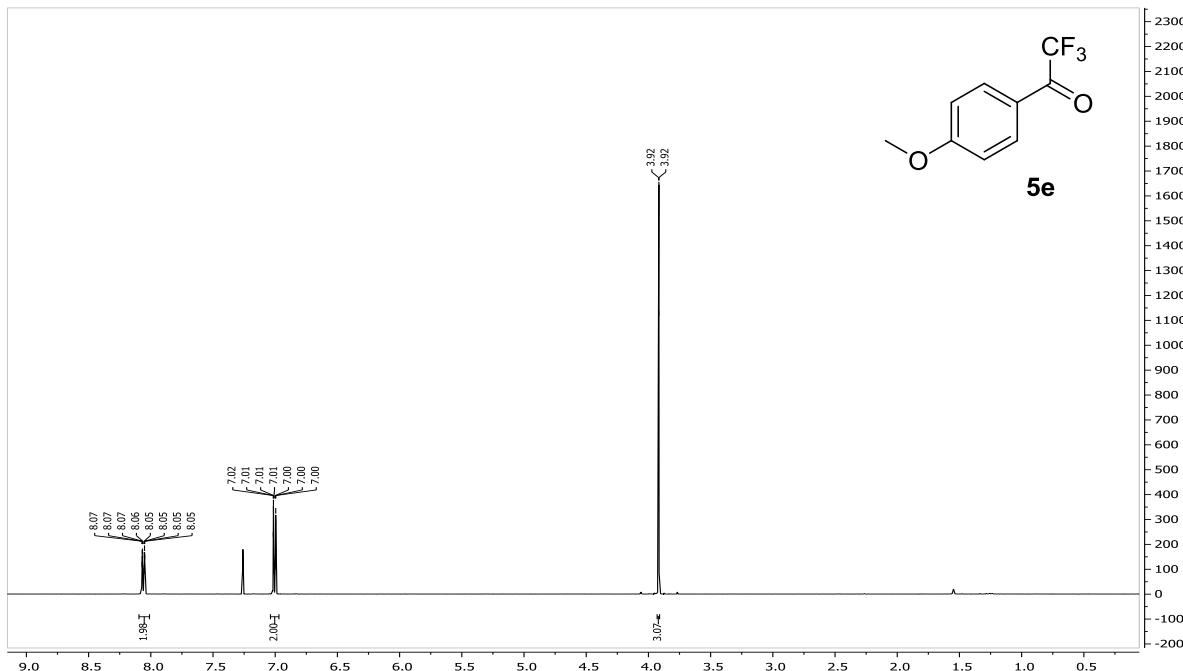


Figure 4: Reaction progress monitoring of the isomerization of compound Z-1 by HPLC analysis.

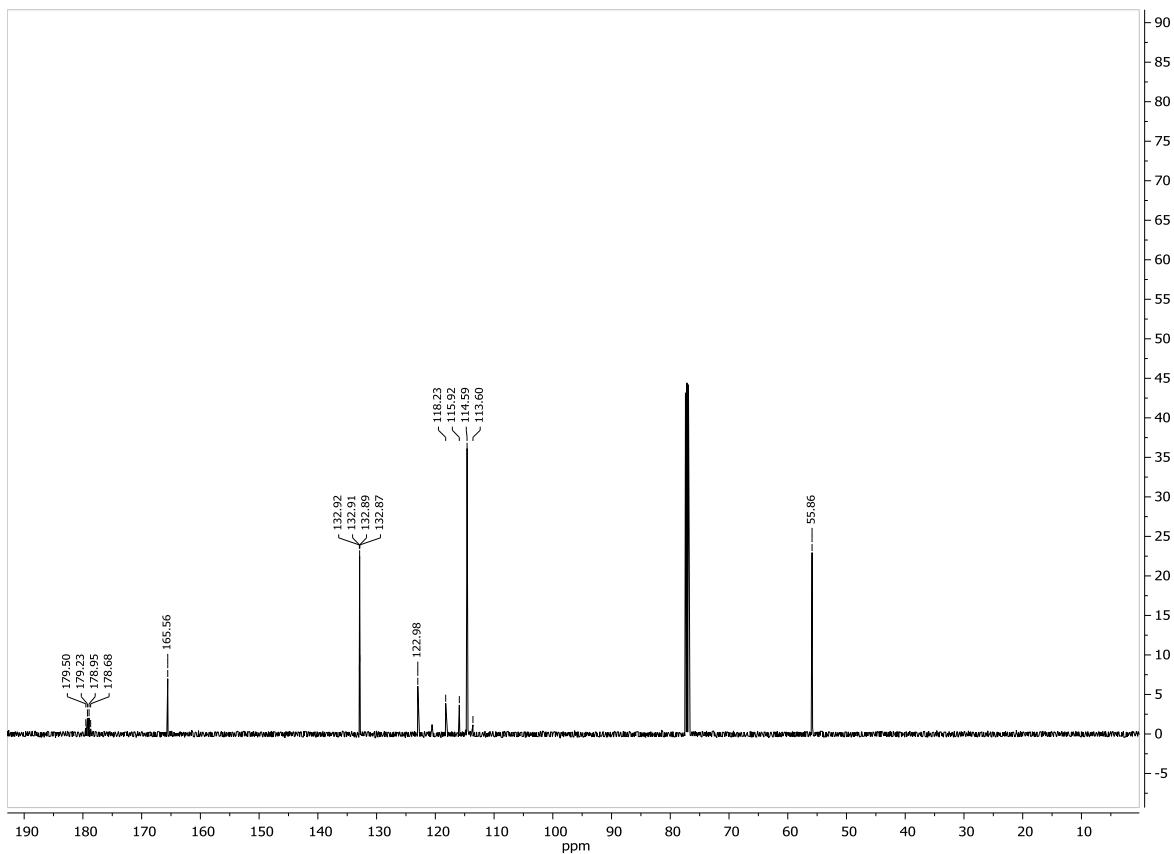


4. NMR Spectra of Key Compounds

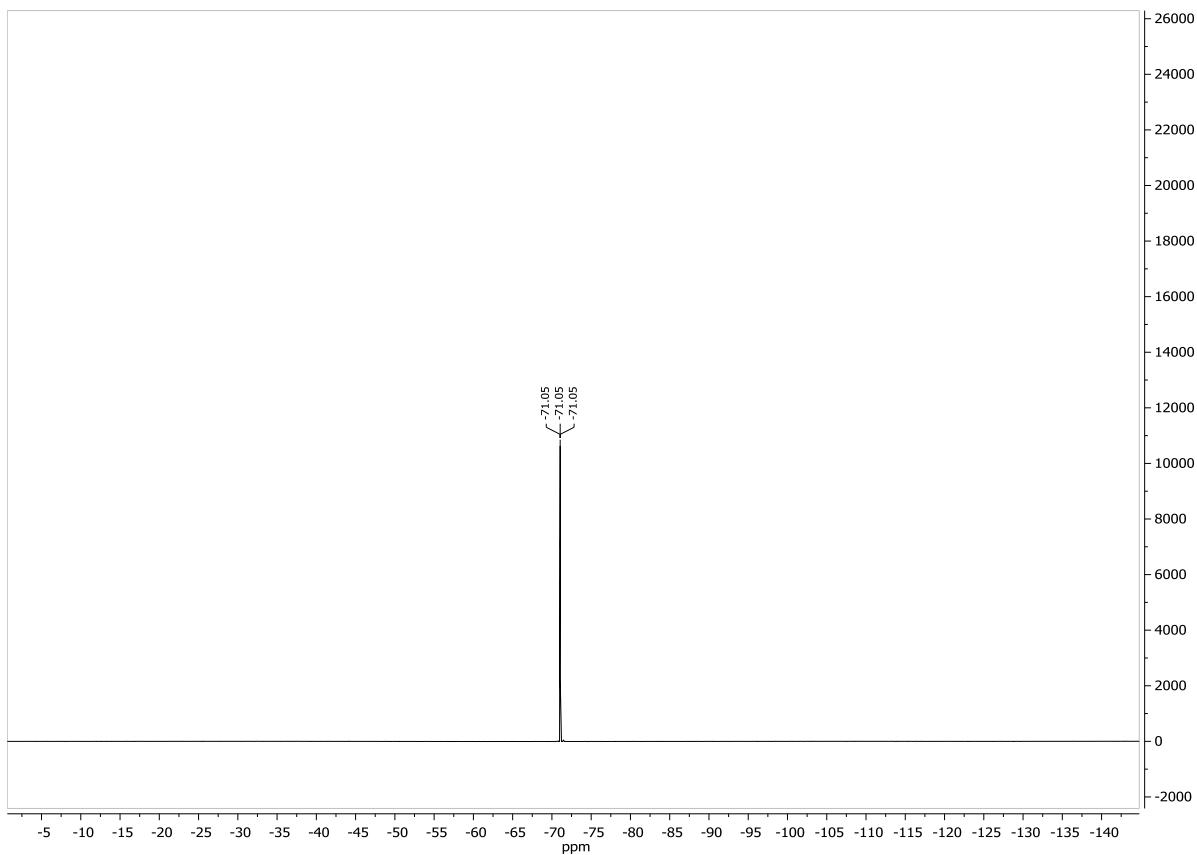
¹H NMR (CDCl₃, 500 MHz)



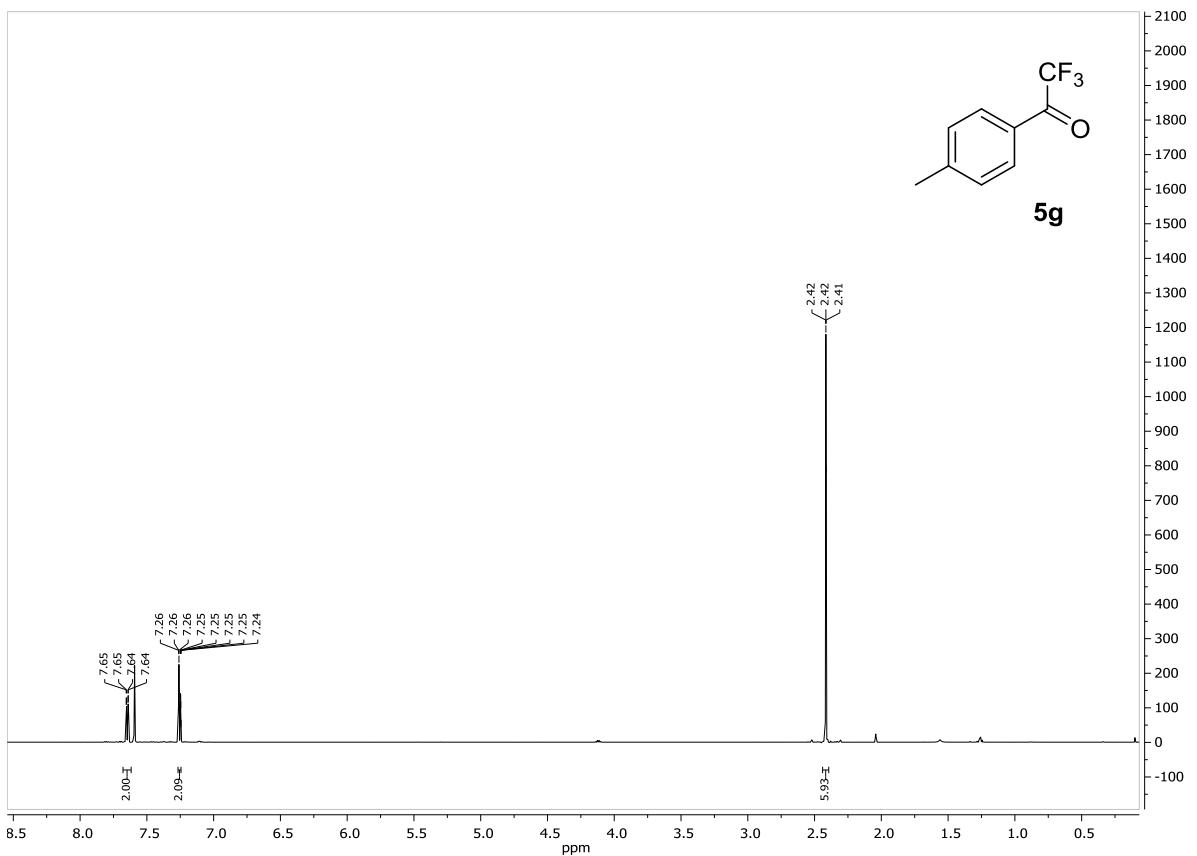
¹³C NMR (CDCl₃, 126 MHz)



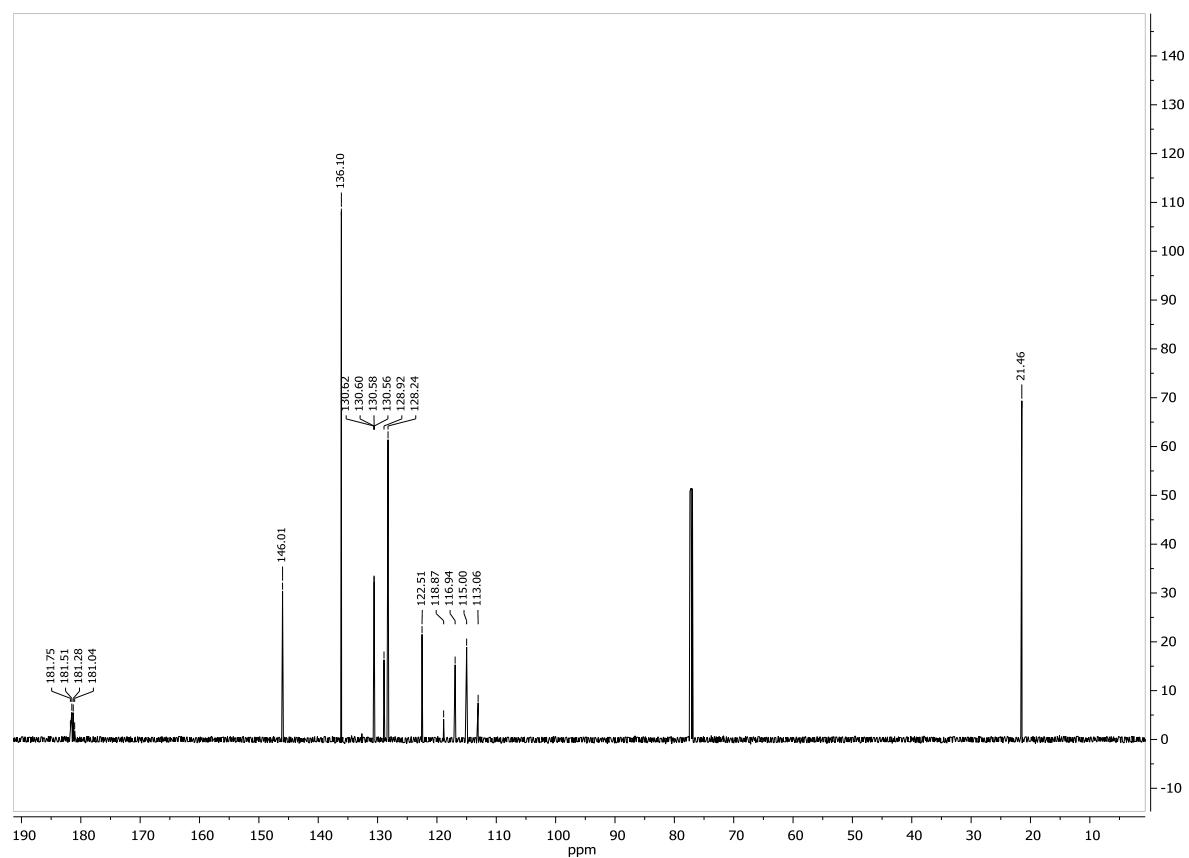
¹⁹F NMR (CDCl₃, 470 MHz)



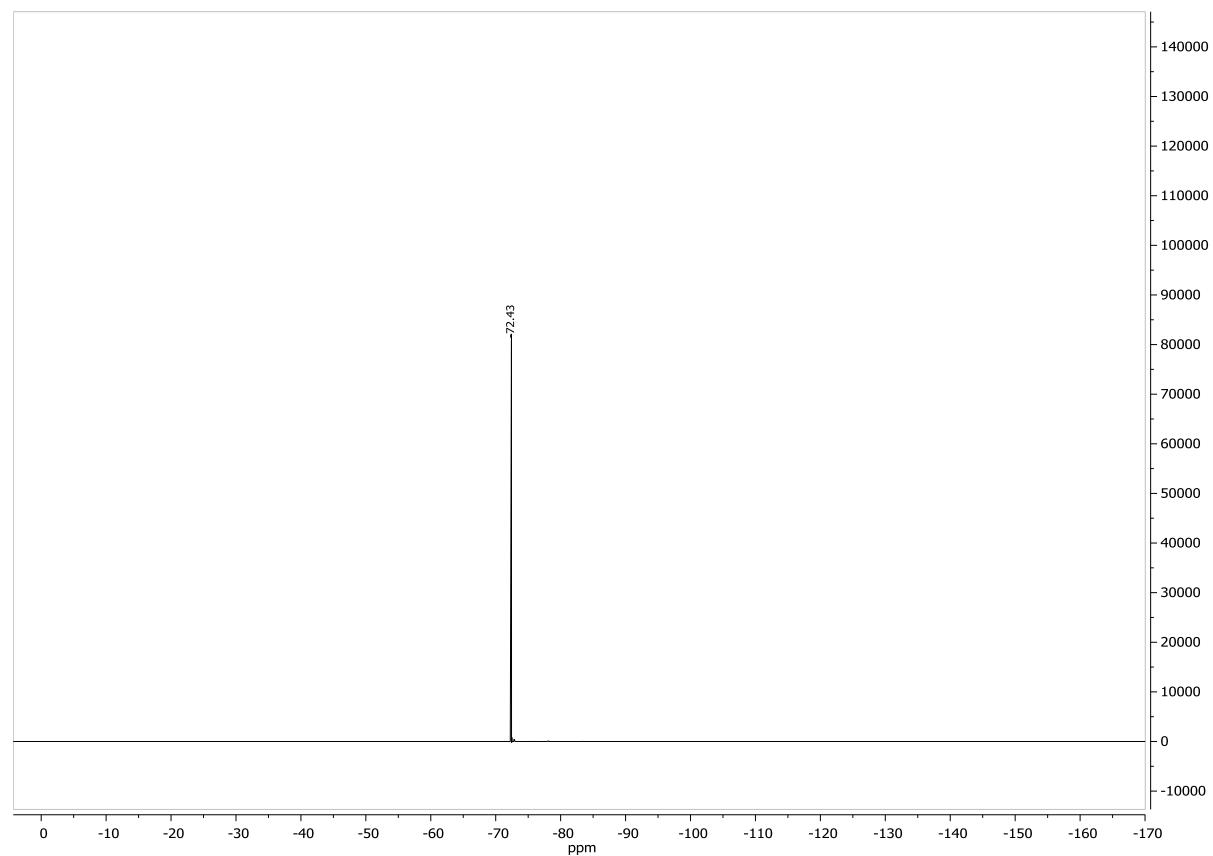
¹H NMR (CDCl₃, 500 MHz)



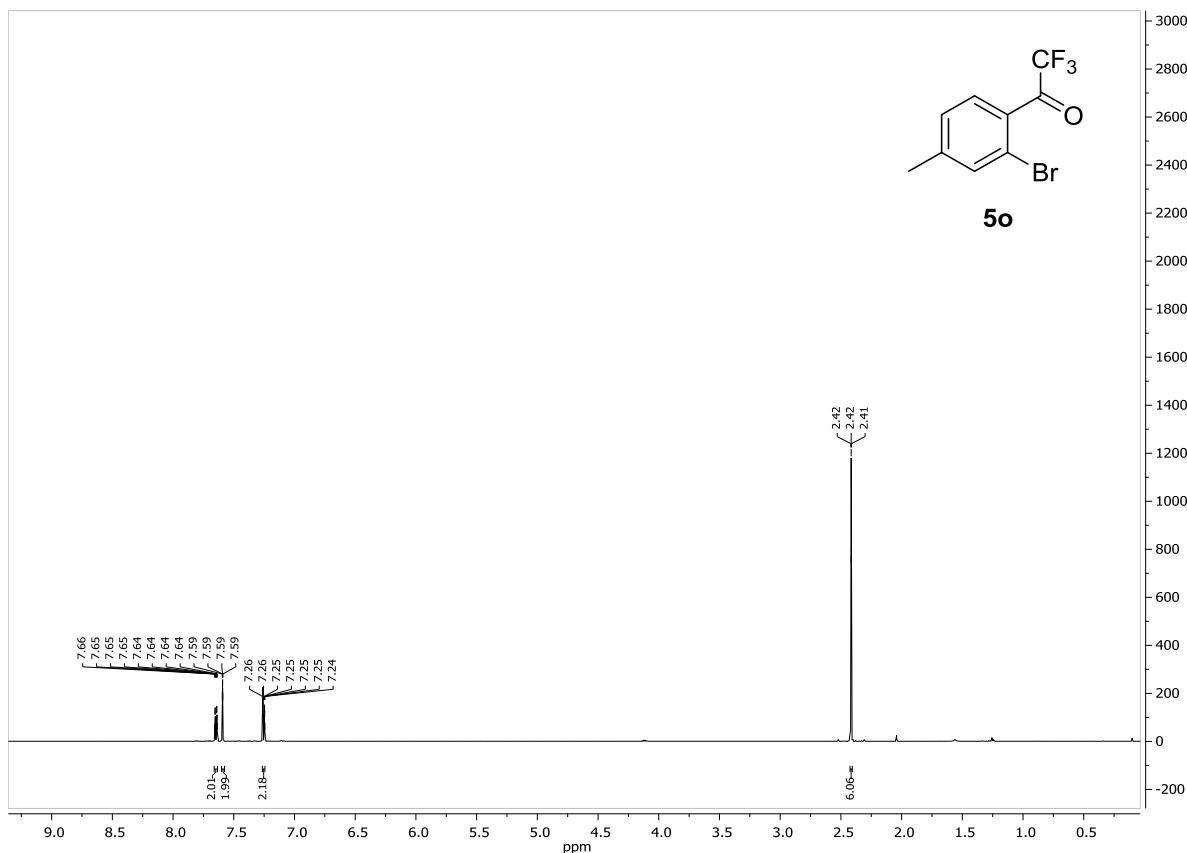
¹³C NMR (CDCl₃, 126 MHz)



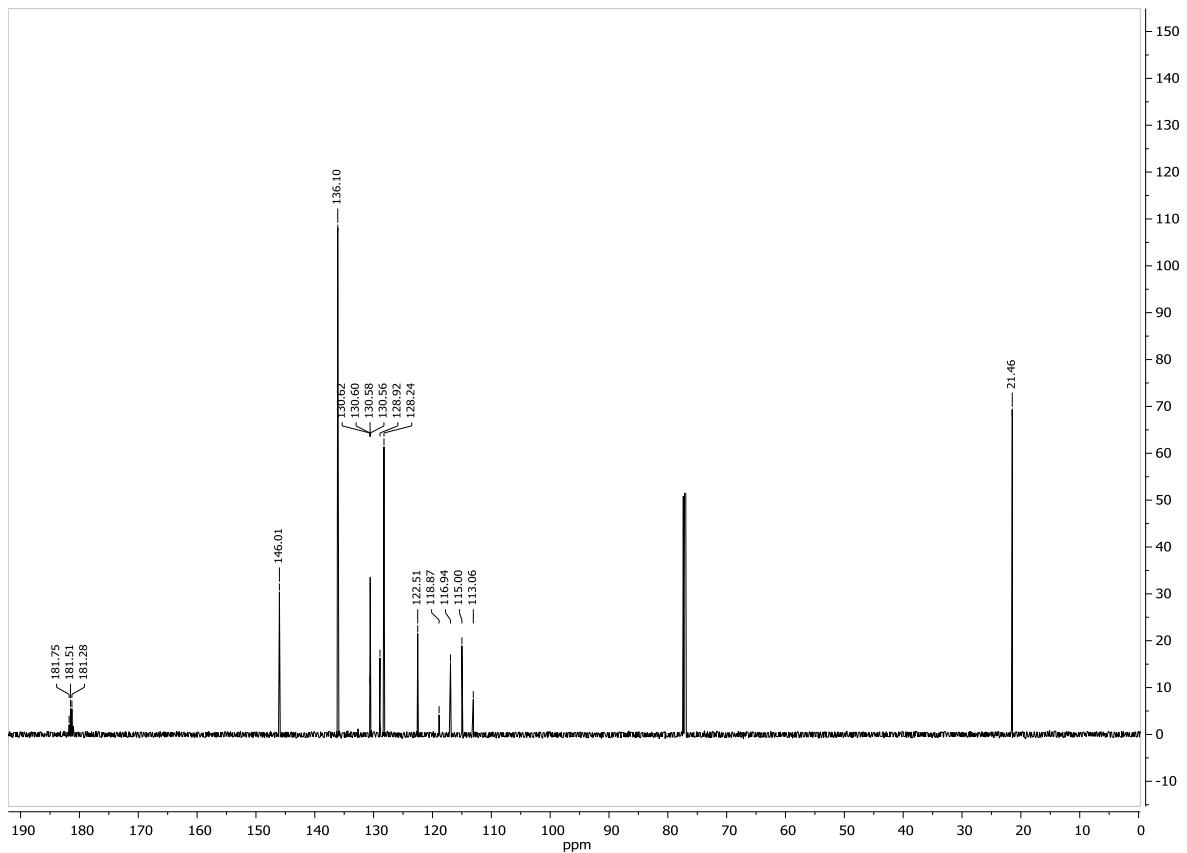
¹⁹F NMR (CDCl₃, 470 MHz)



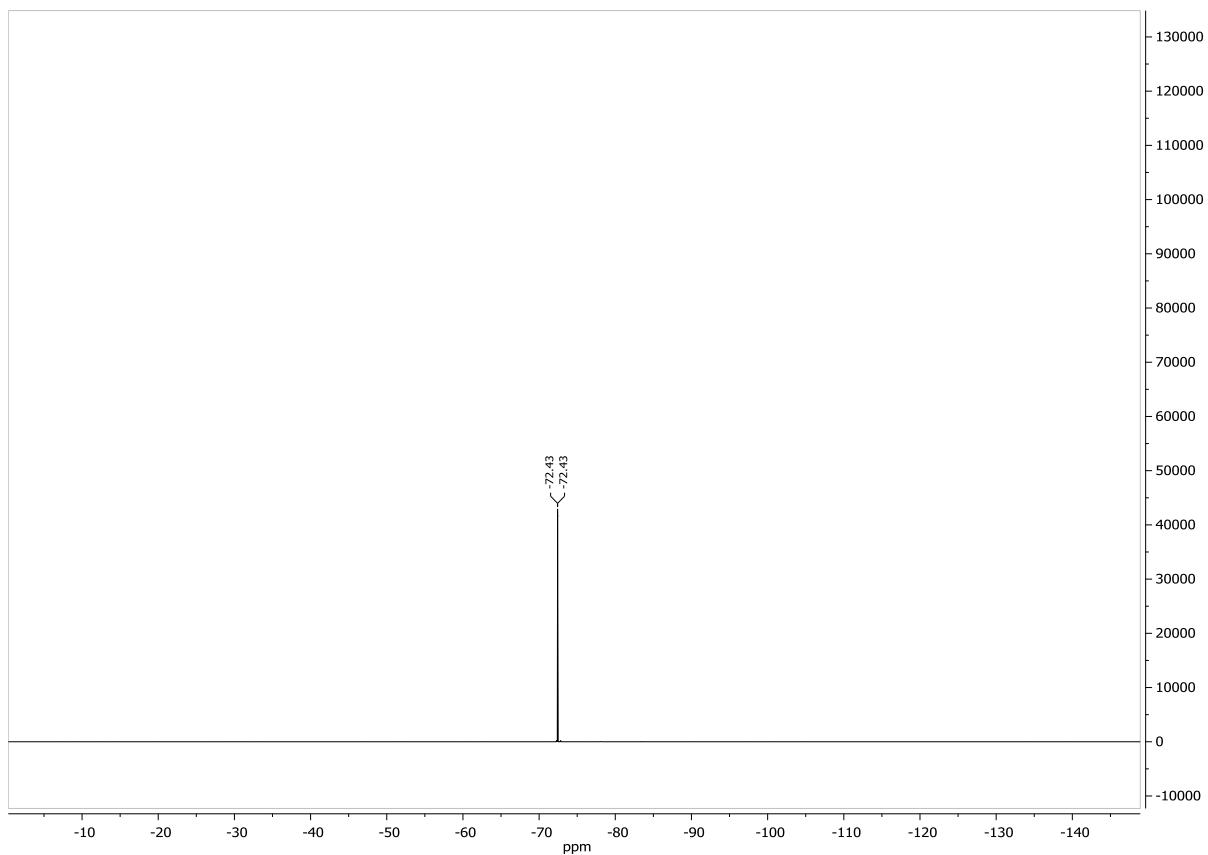
¹H NMR (CDCl₃, 600 MHz)



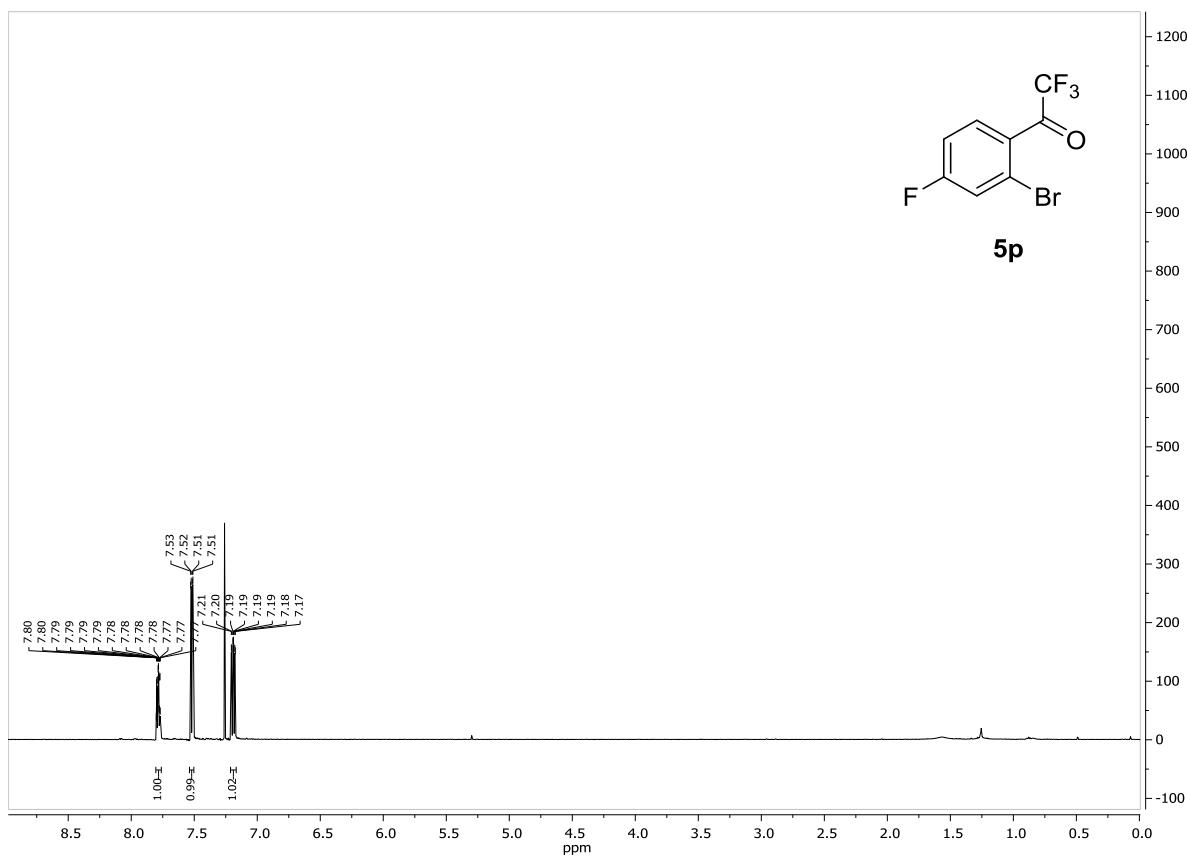
¹³C NMR (CDCl₃, 151 MHz)



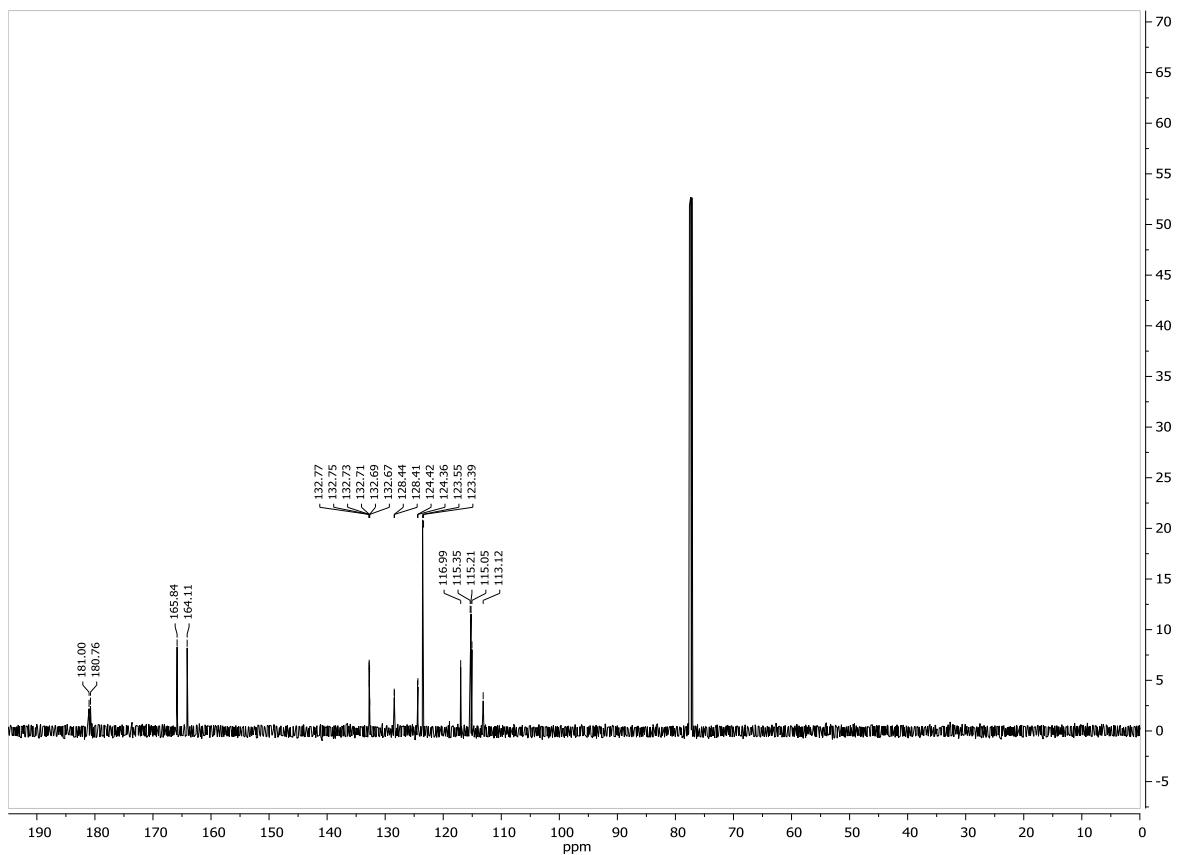
¹⁹F NMR (CDCl₃, 564 MHz)



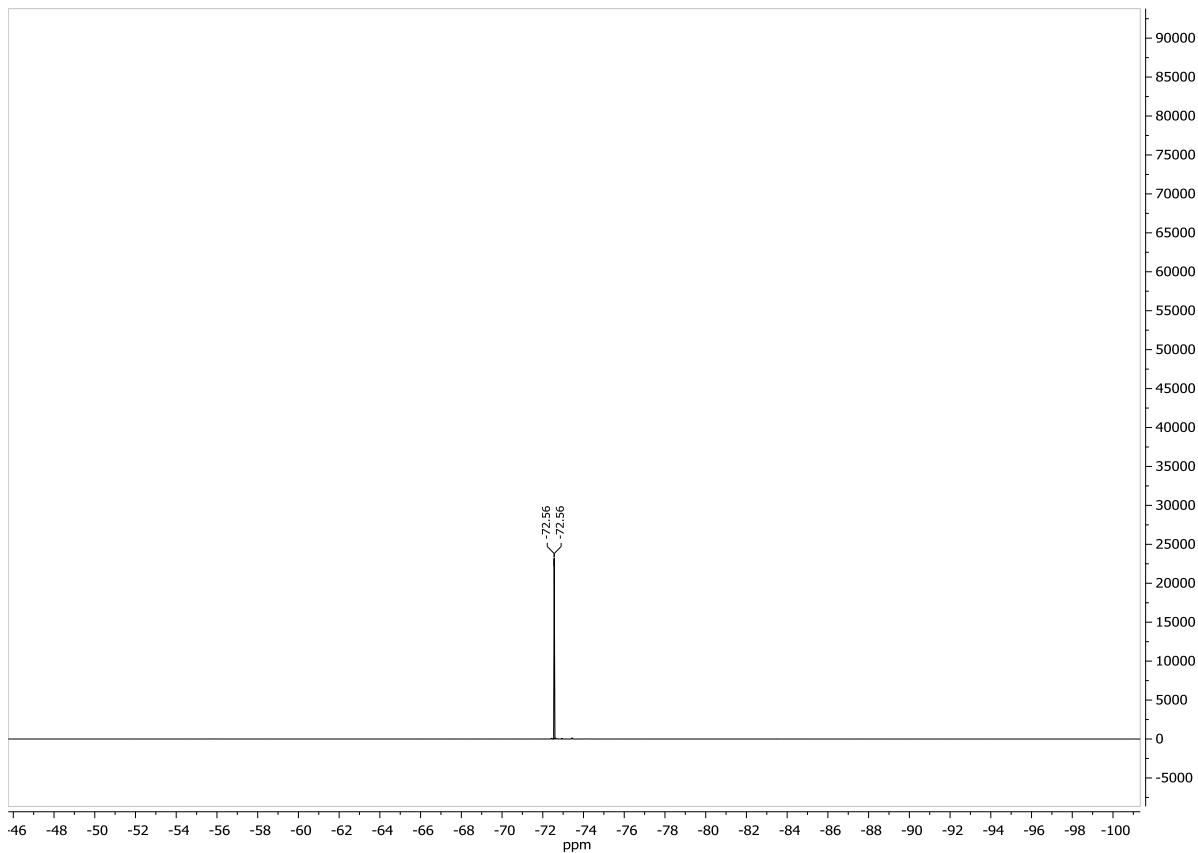
¹H NMR (CDCl₃, 600 MHz)



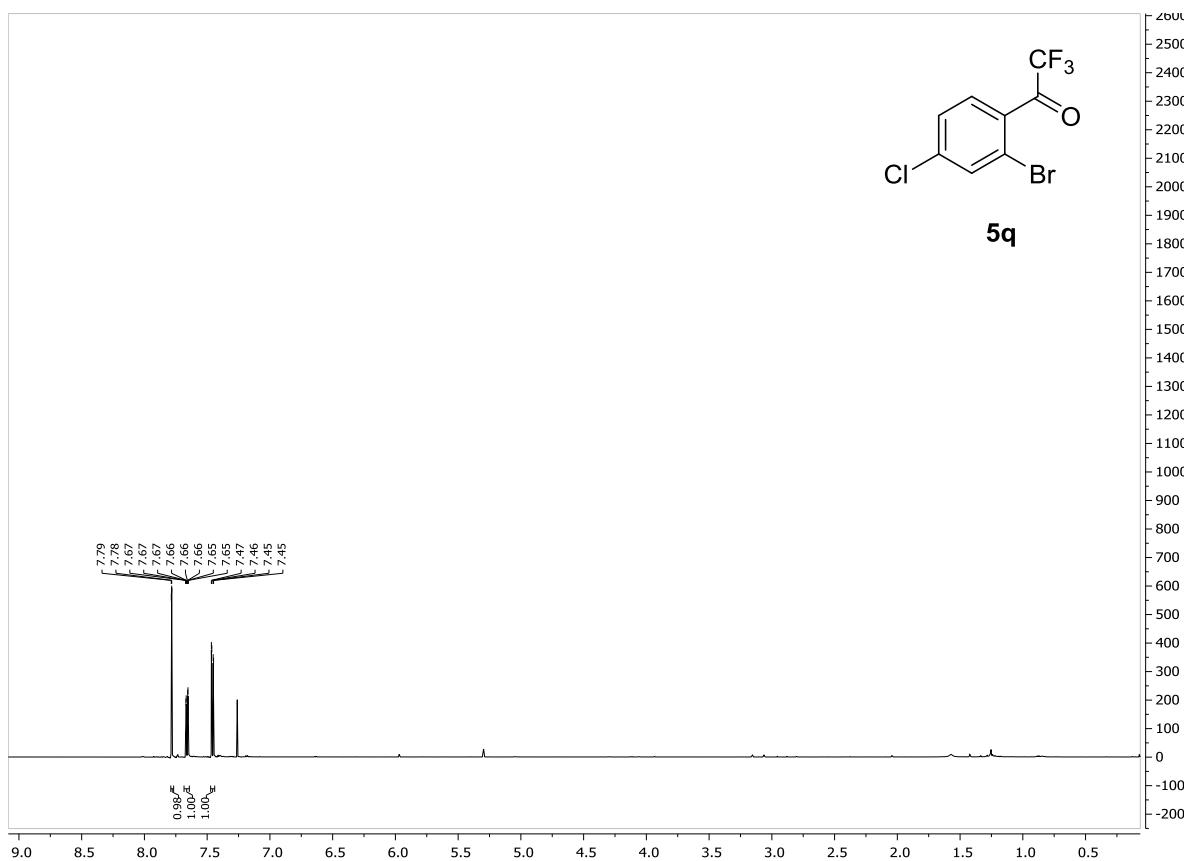
¹³C NMR (CDCl_3 , 151 MHz)



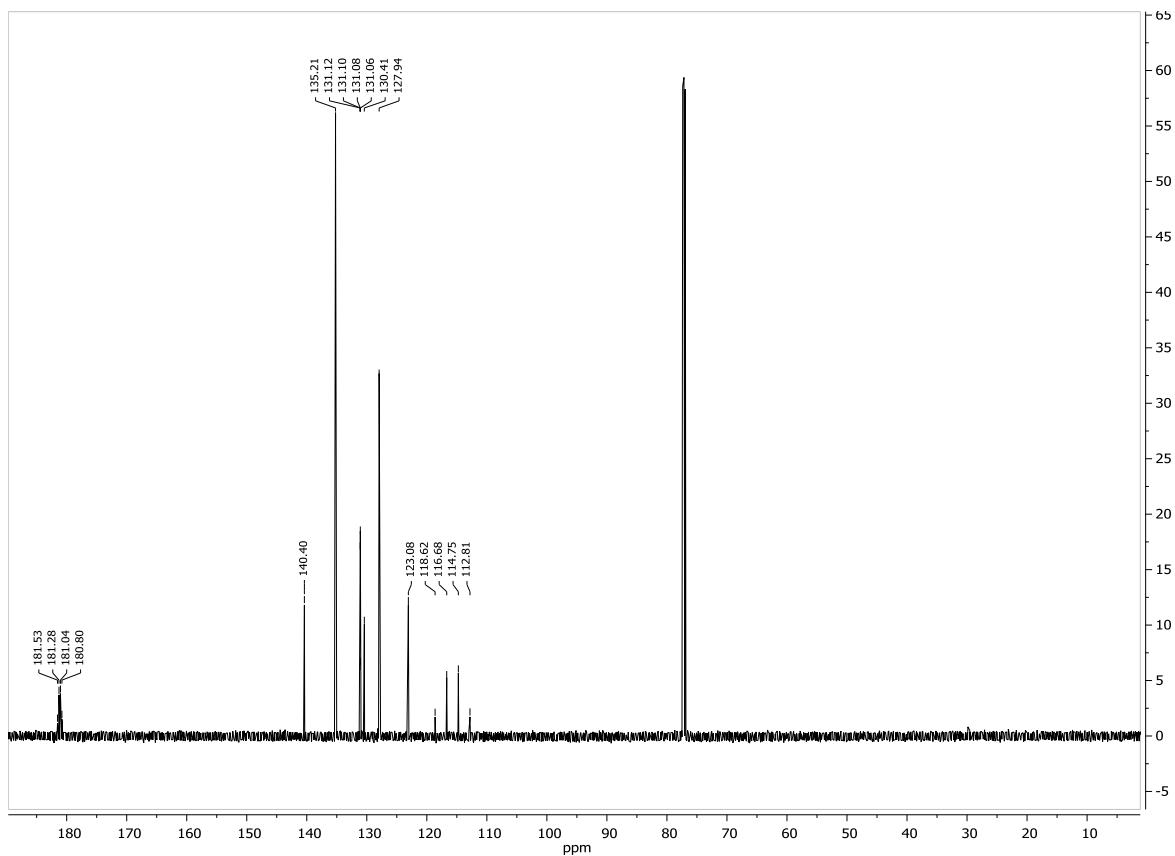
¹⁹F NMR (CDCl_3 , 564 MHz)



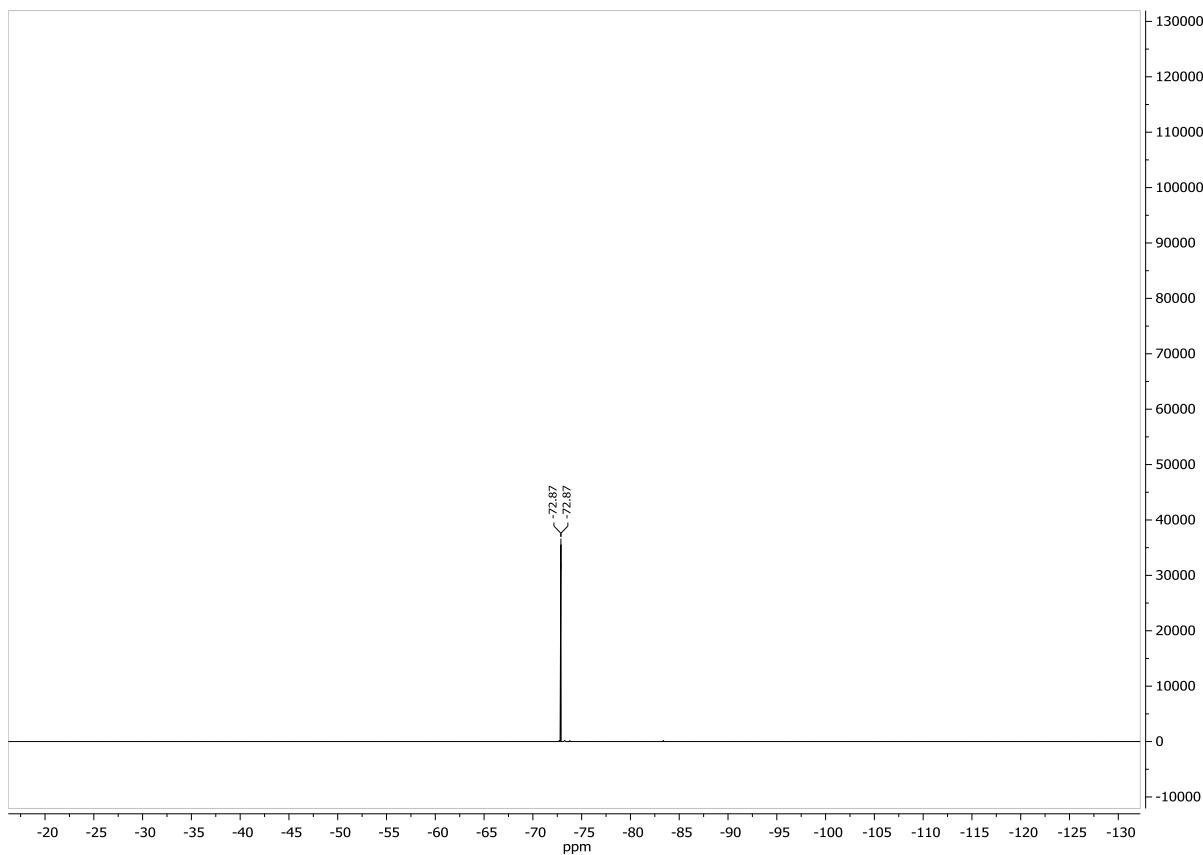
¹H NMR (CDCl₃, 600 MHz)



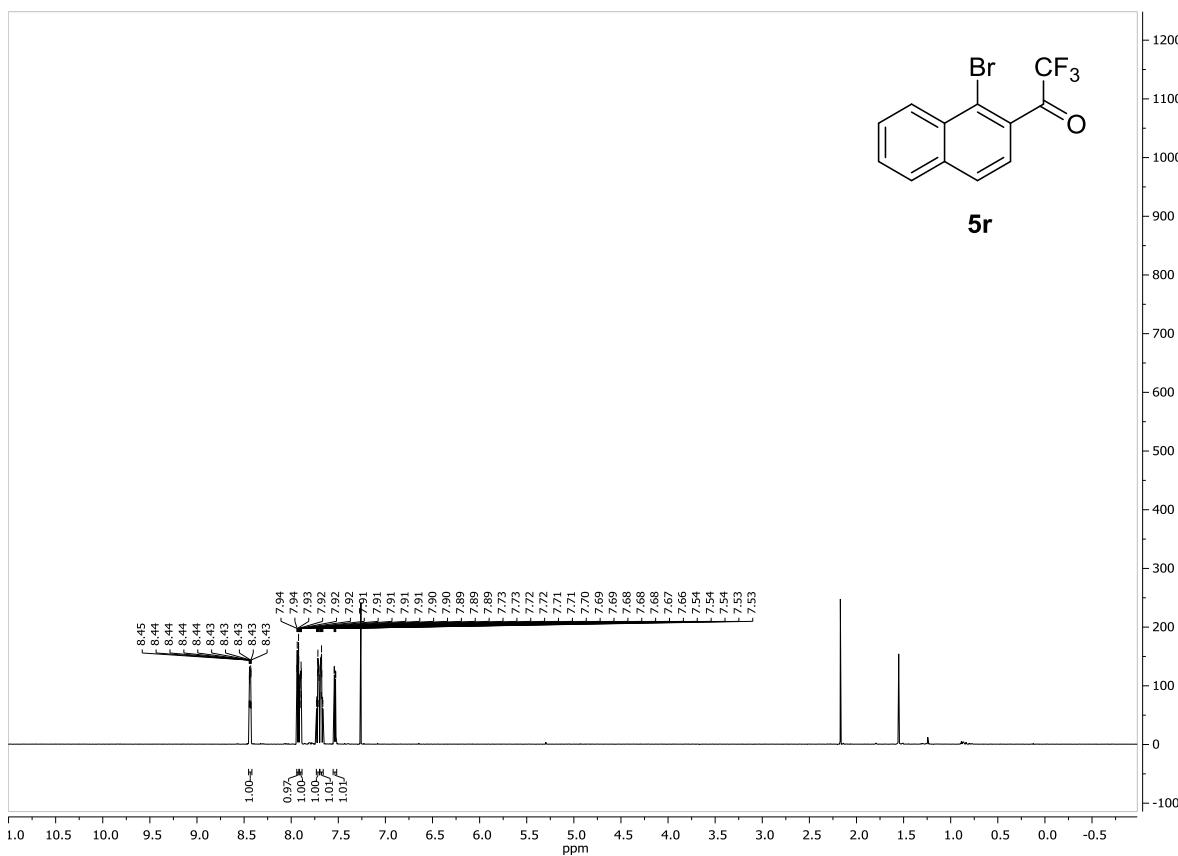
¹³C NMR (CDCl₃, 151 MHz)



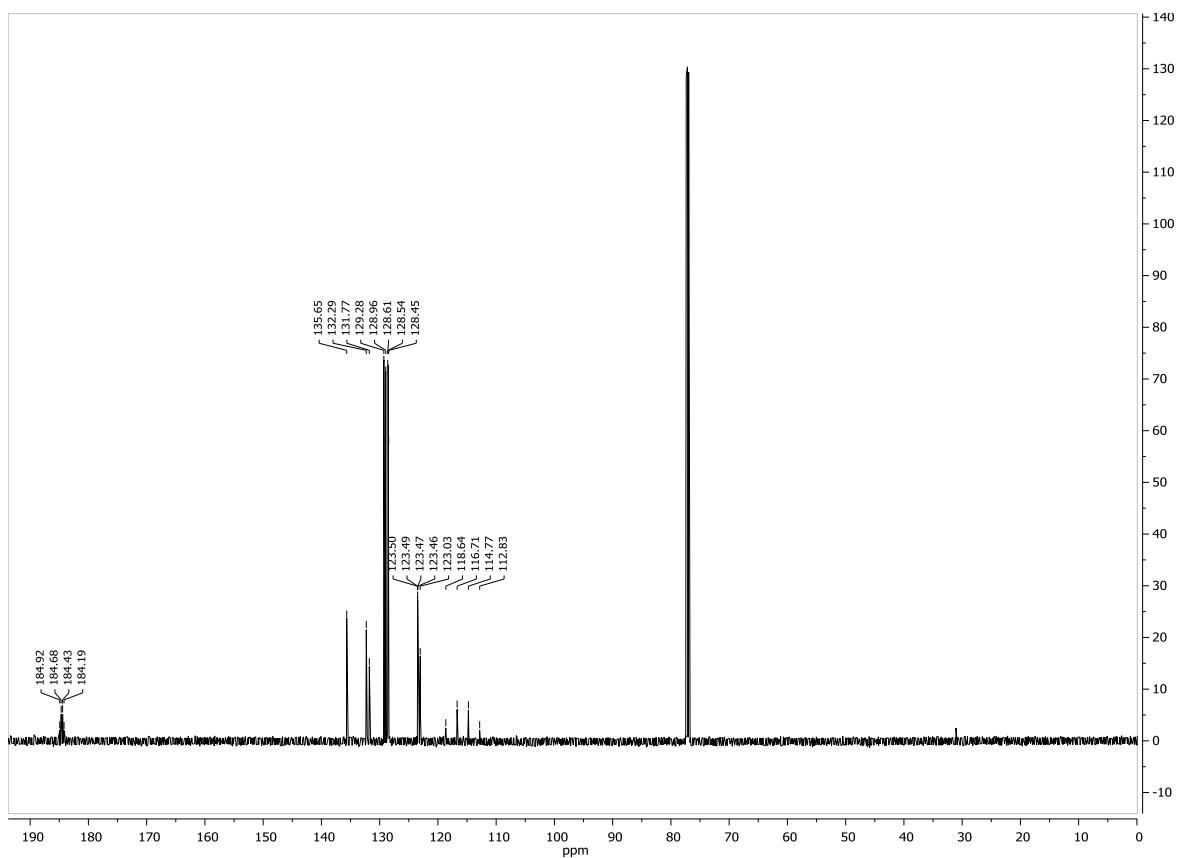
¹⁹F NMR (CDCl₃, 564 MHz)



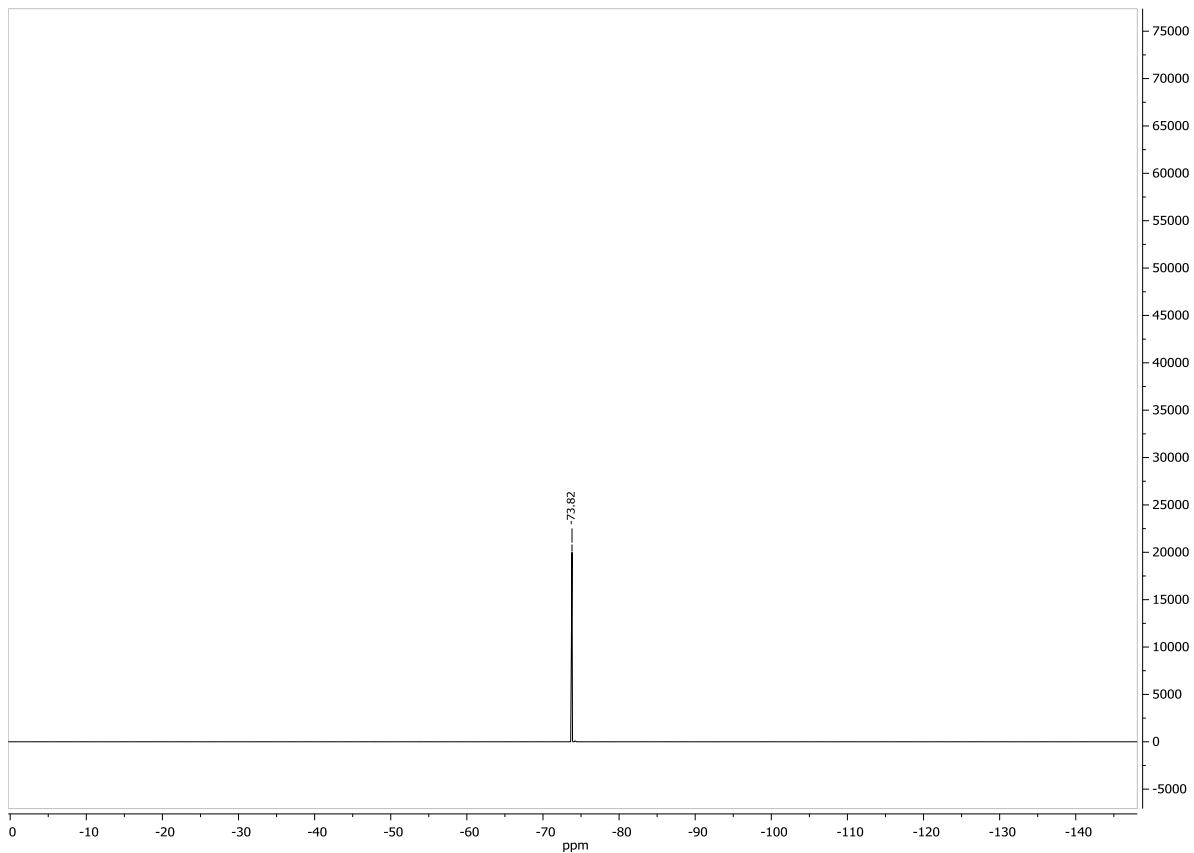
¹H NMR (CDCl₃, 600 MHz)



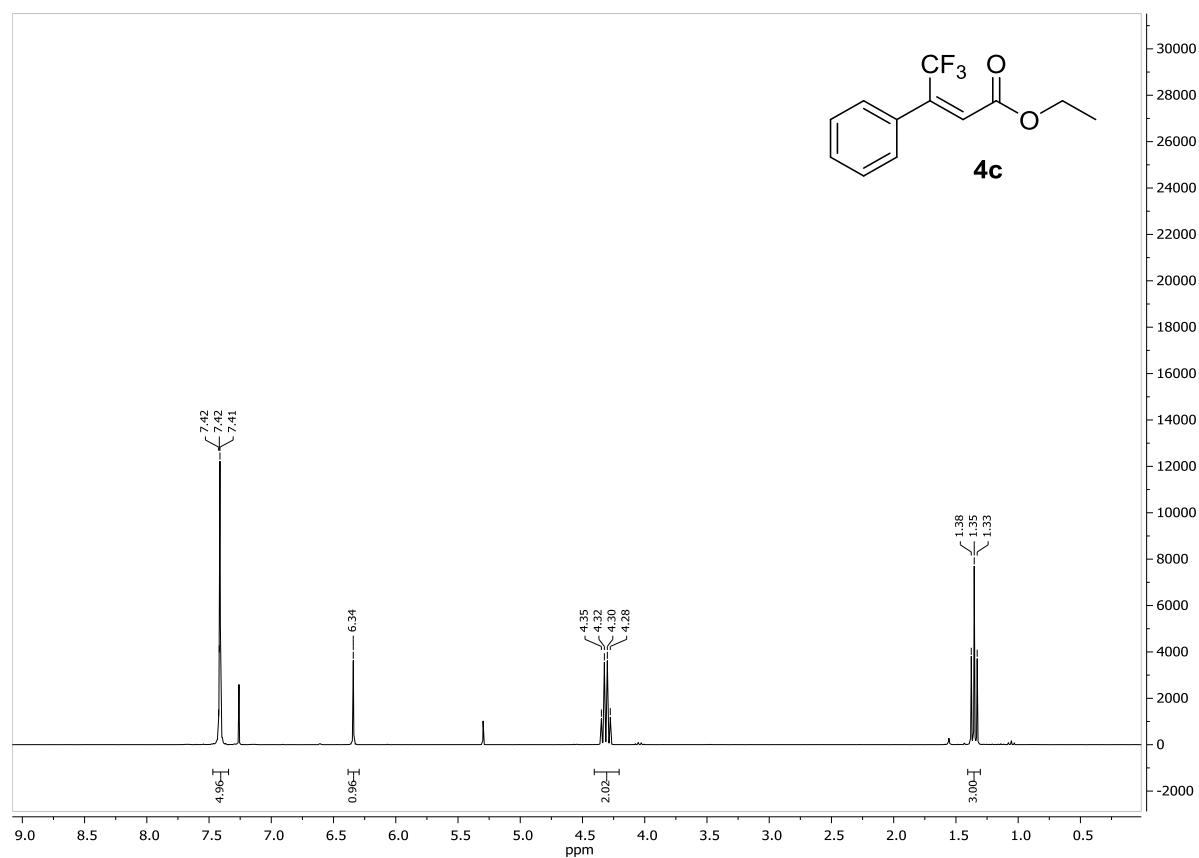
¹³C NMR (CDCl₃, 151 MHz)



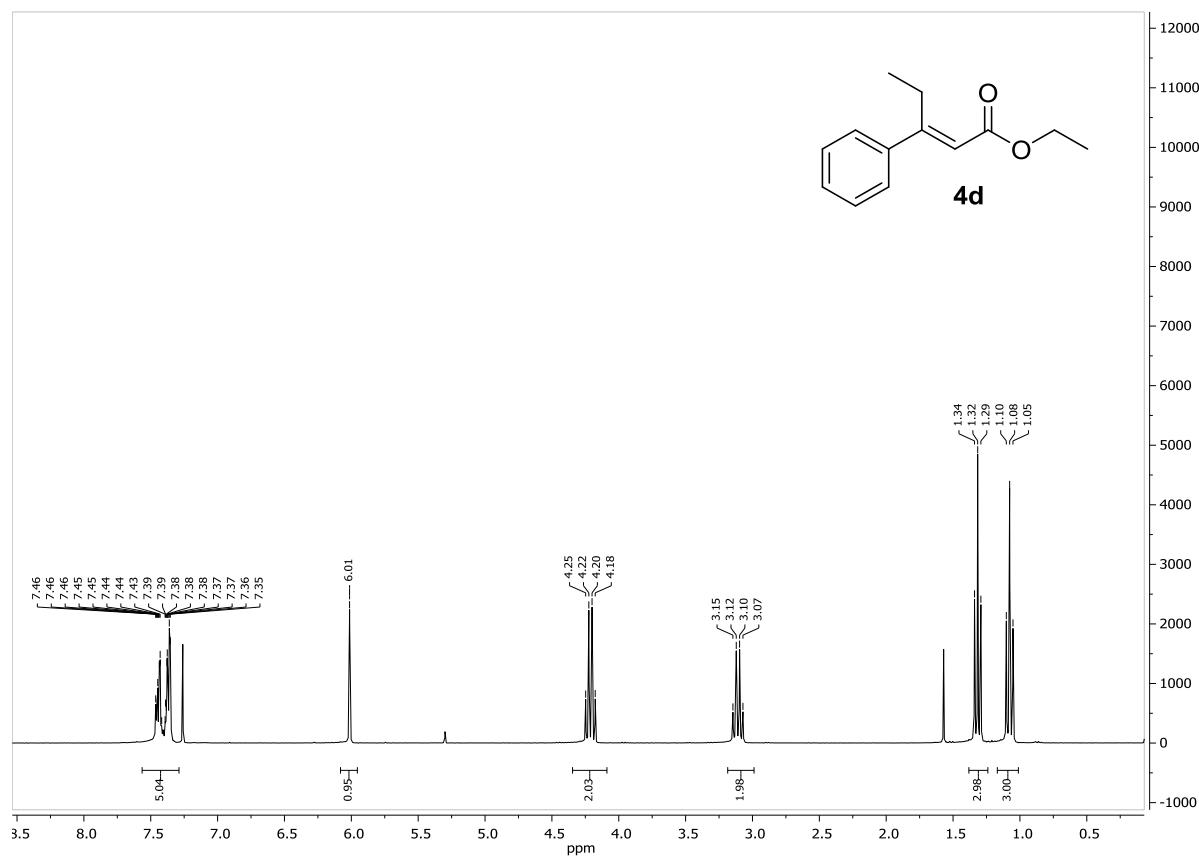
¹⁹F NMR (CDCl₃, 564 MHz)



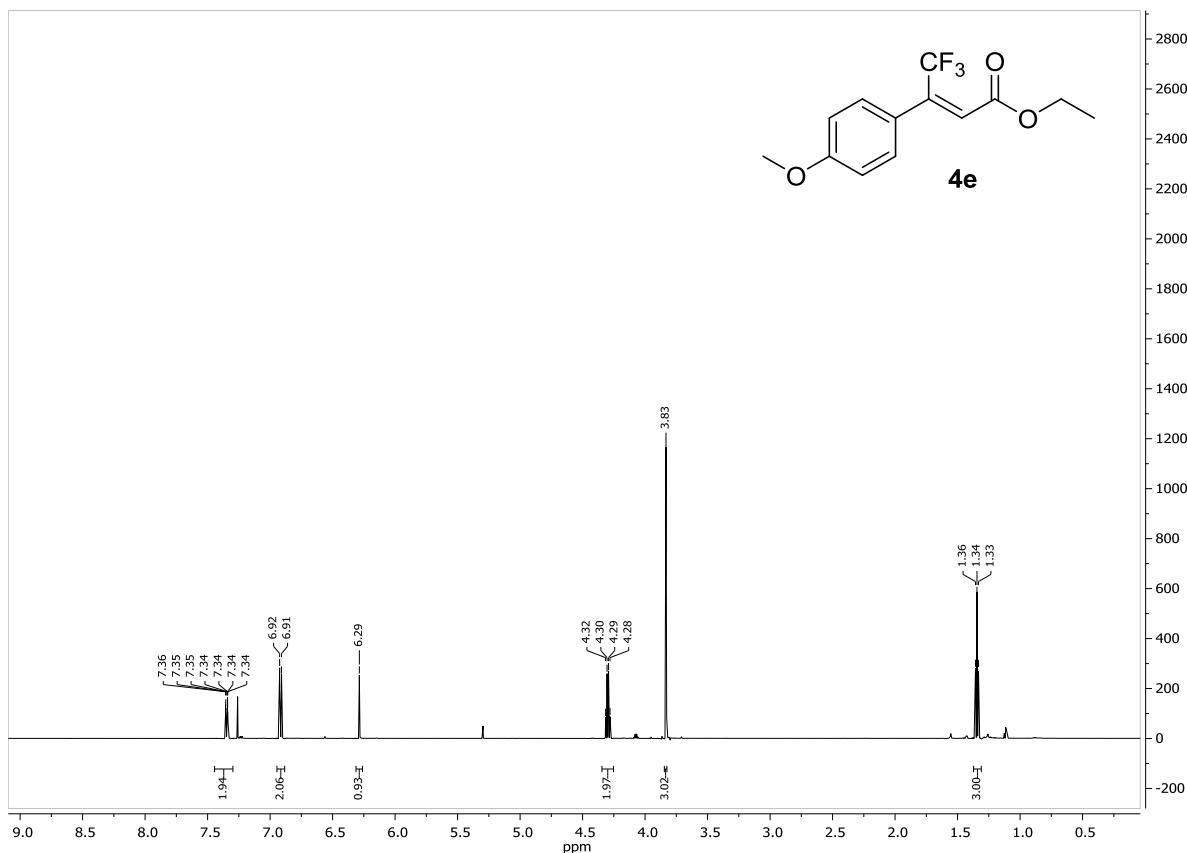
¹H NMR (CDCl₃, 300 MHz)



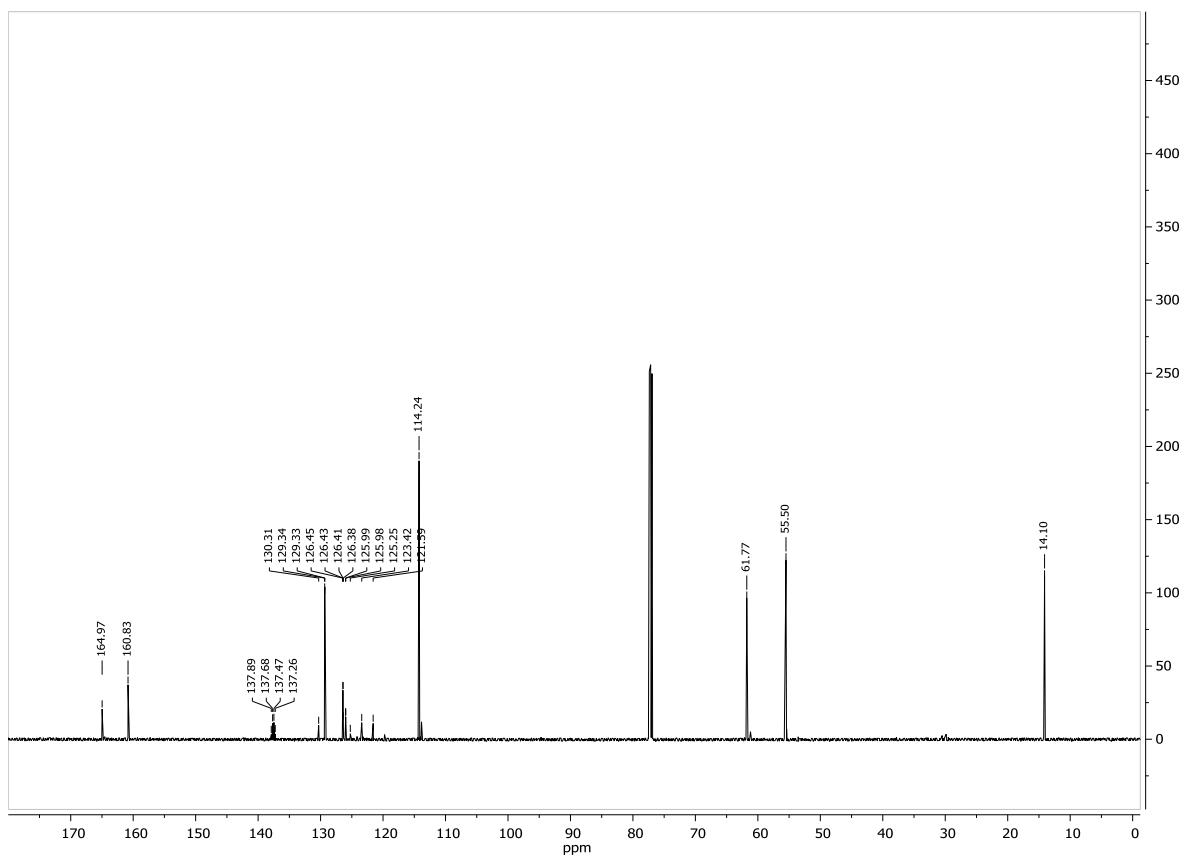
¹H NMR (CDCl₃, 300 MHz)



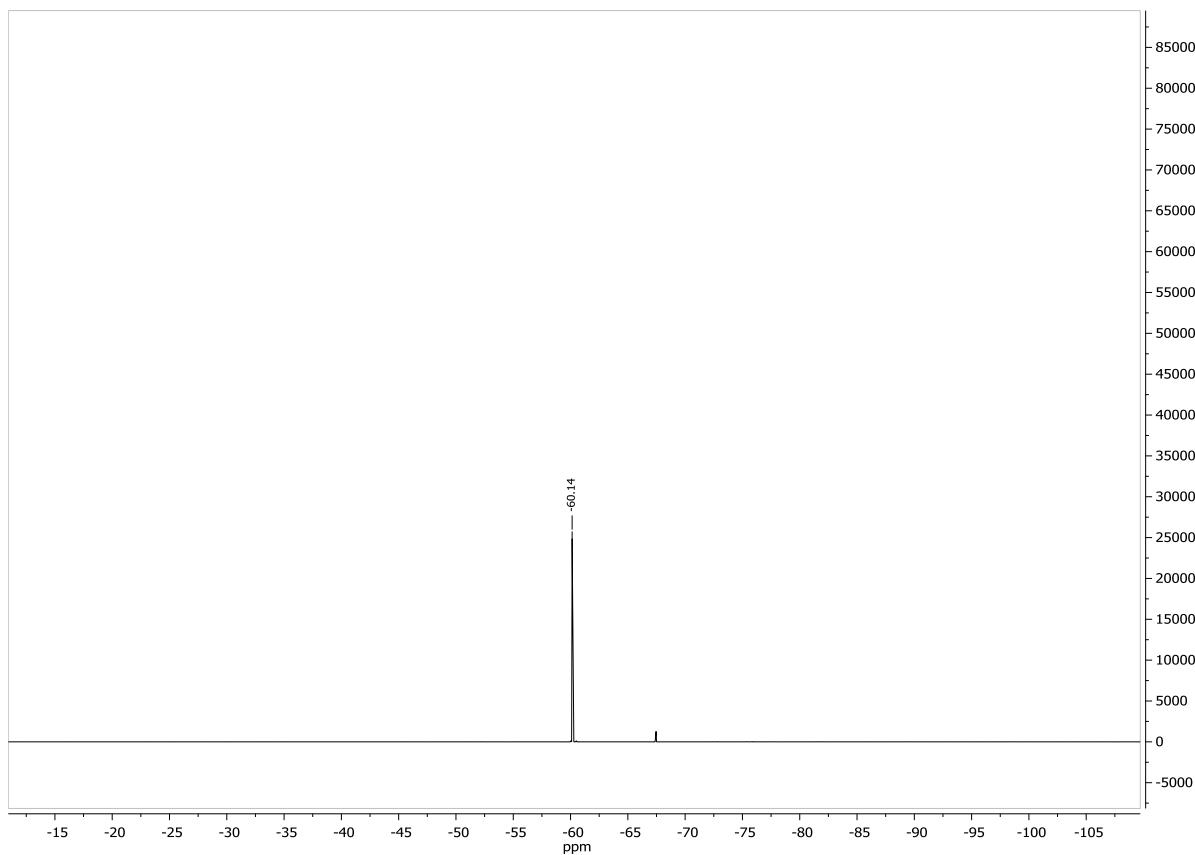
¹H NMR (CDCl₃, 600 MHz)



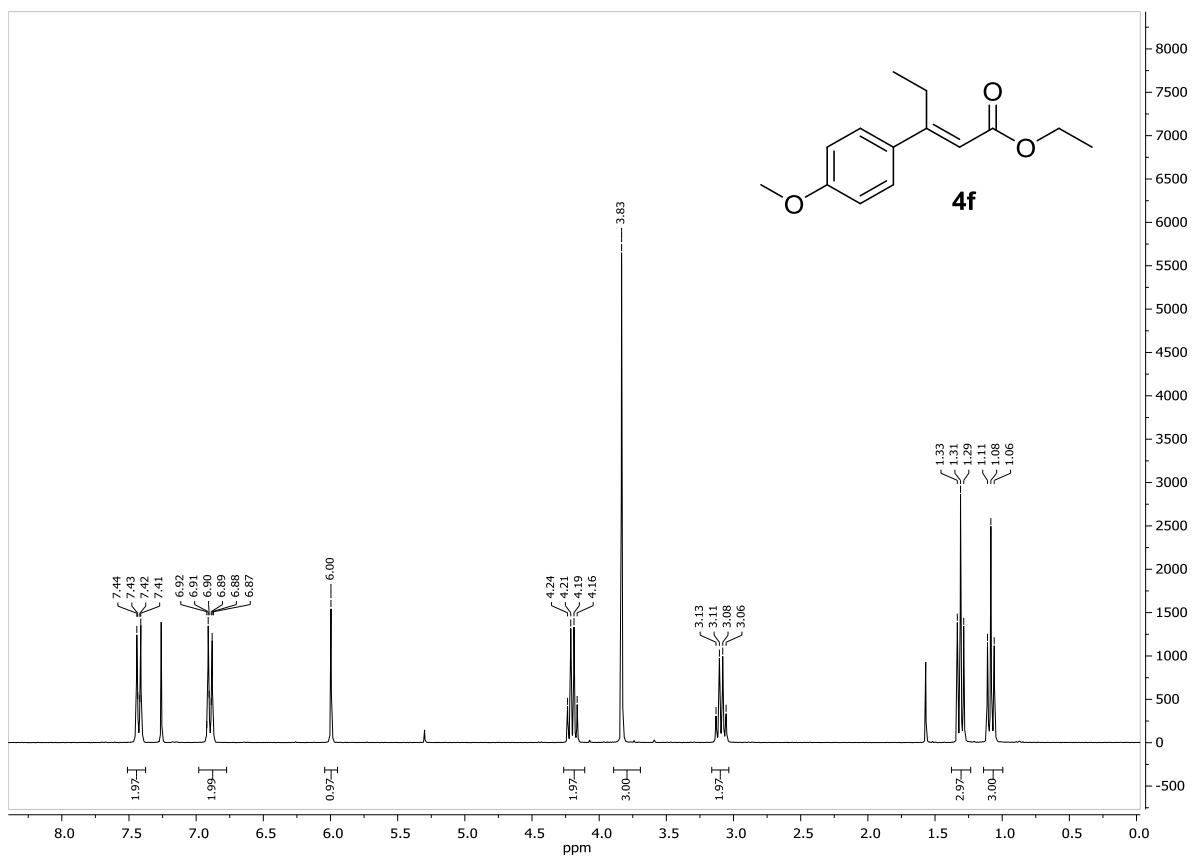
¹³C NMR (CDCl₃, 151 MHz)



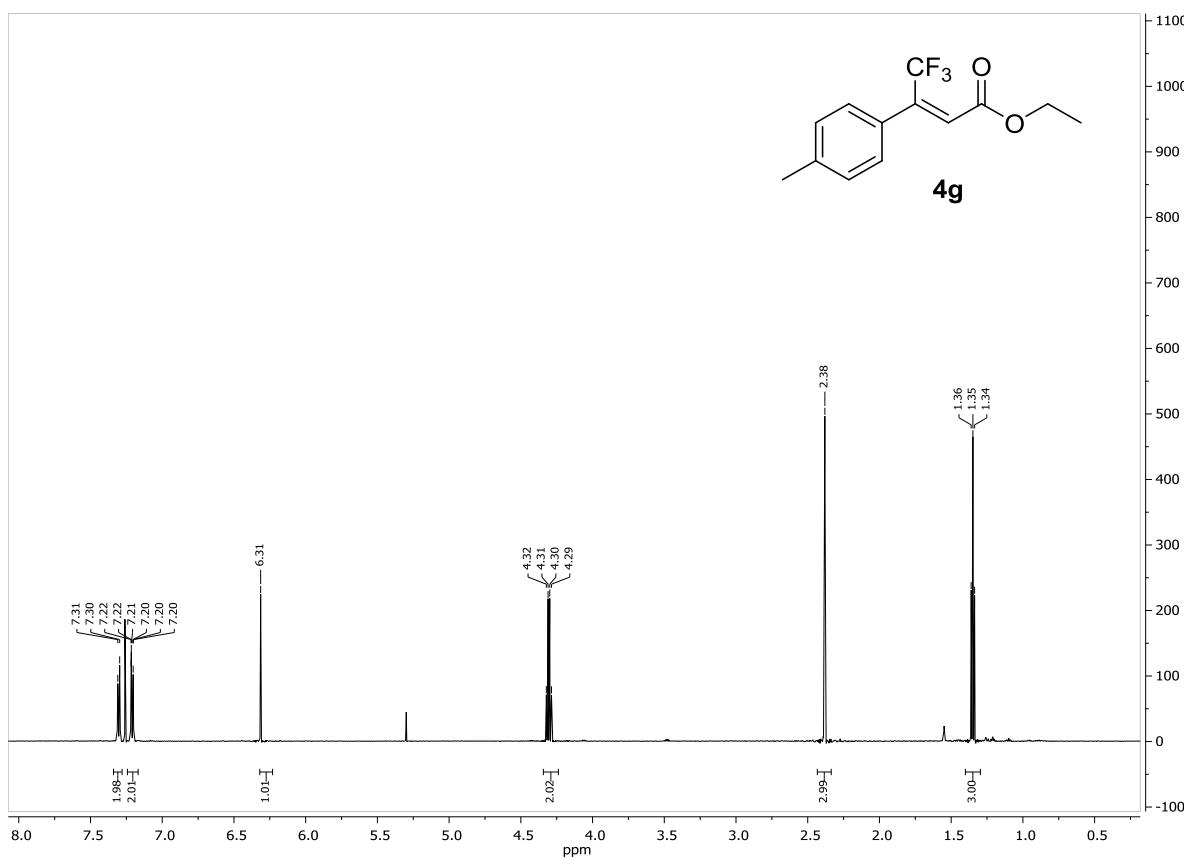
¹⁹F NMR (CDCl₃, 564 MHz)



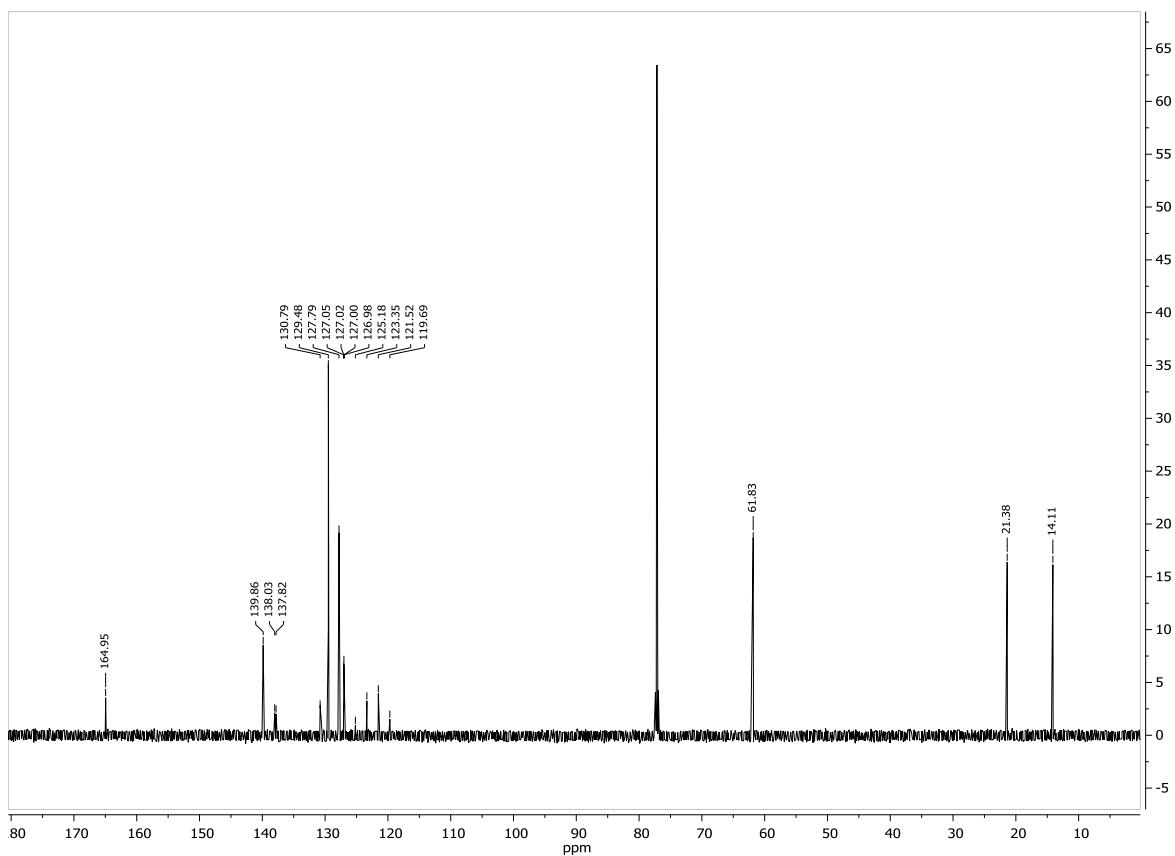
¹H NMR (CDCl₃, 300 MHz)



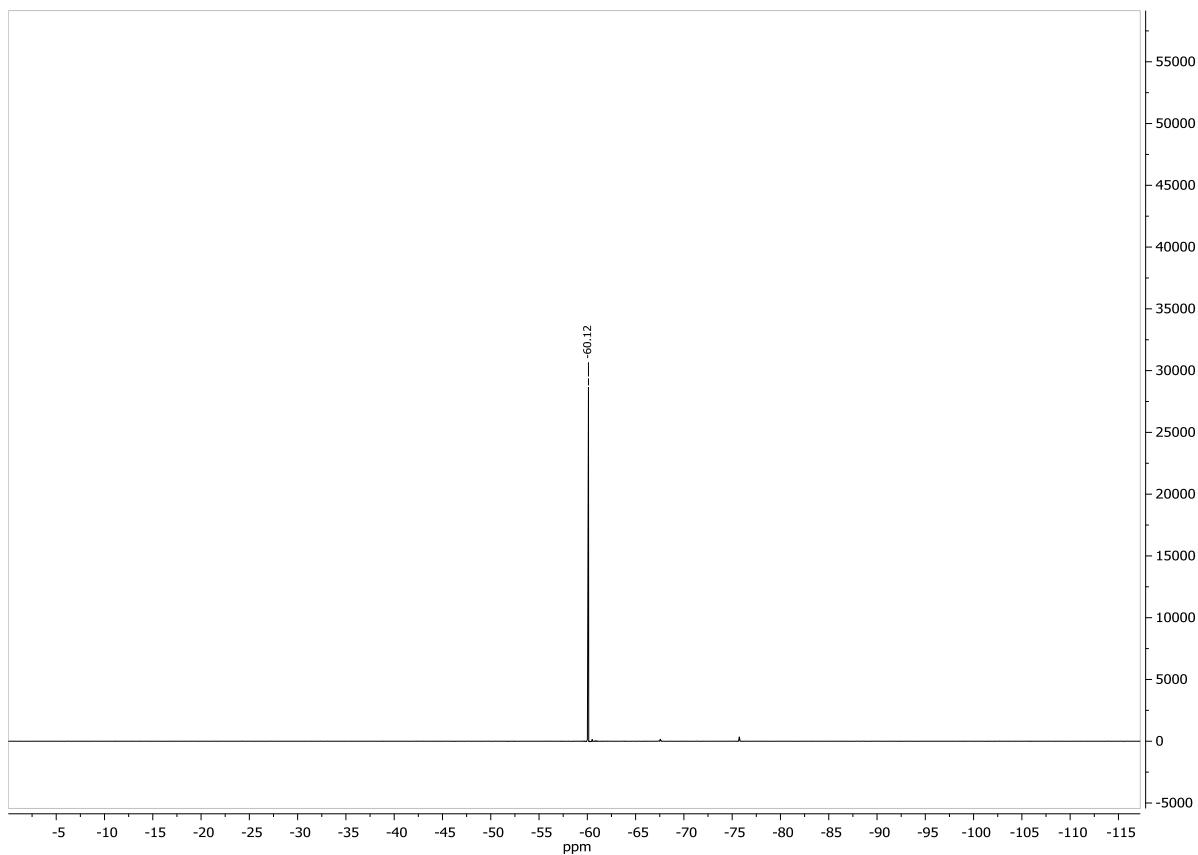
¹H NMR (CDCl₃, 600 MHz)



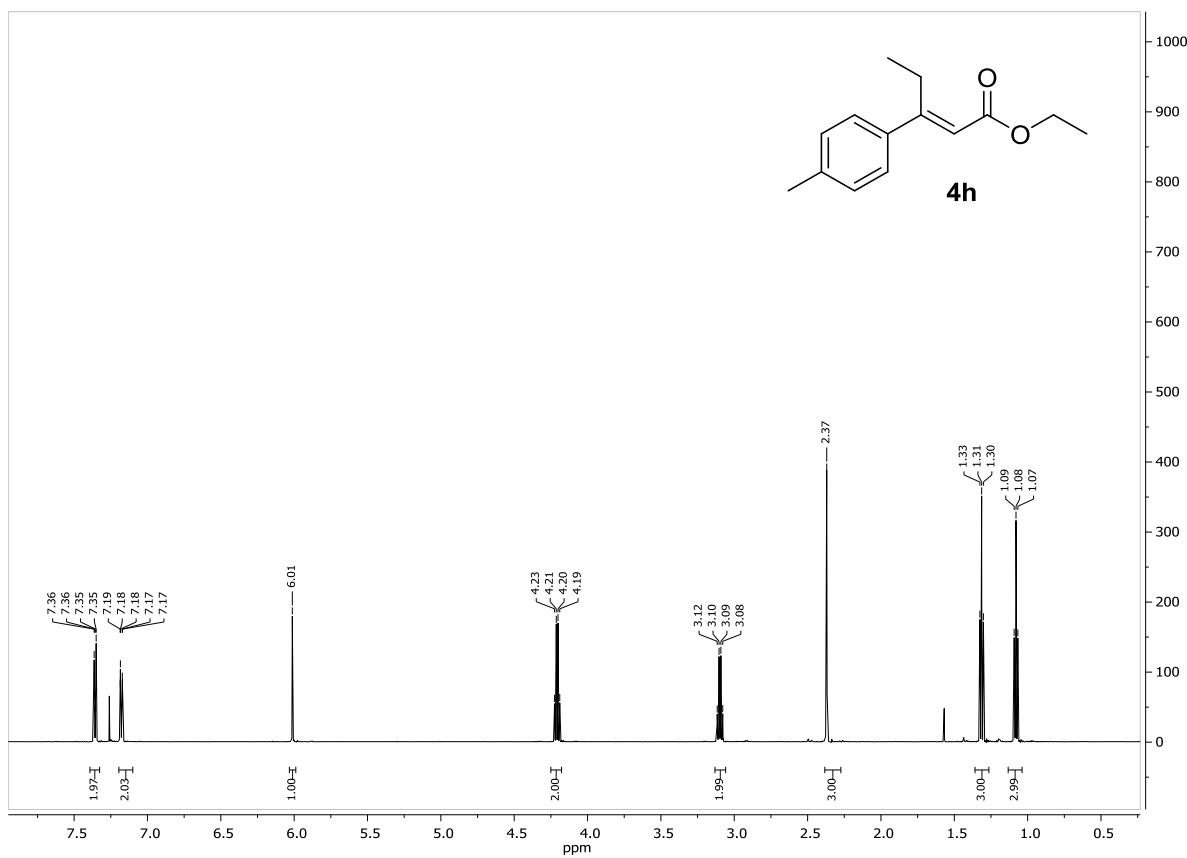
¹³C NMR (CDCl₃, 151 MHz)



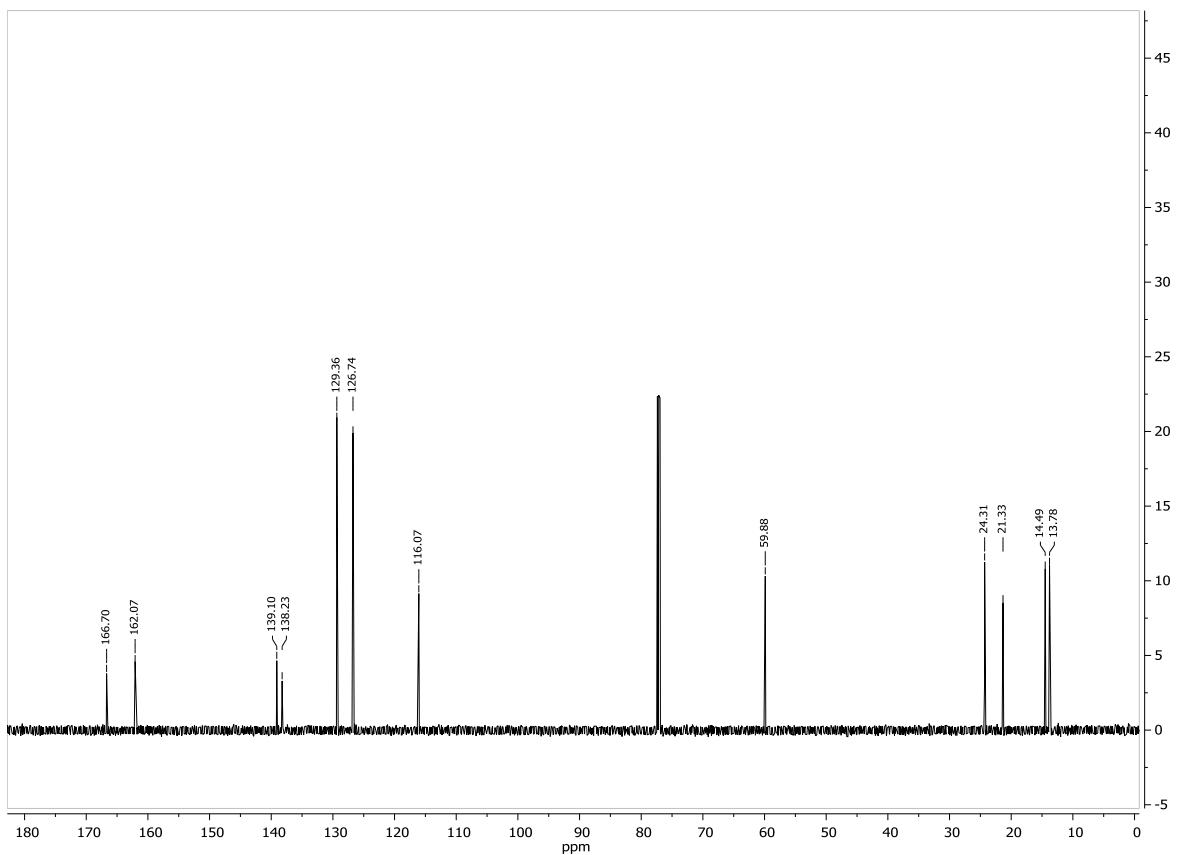
¹⁹F NMR (CDCl₃, 564 MHz)



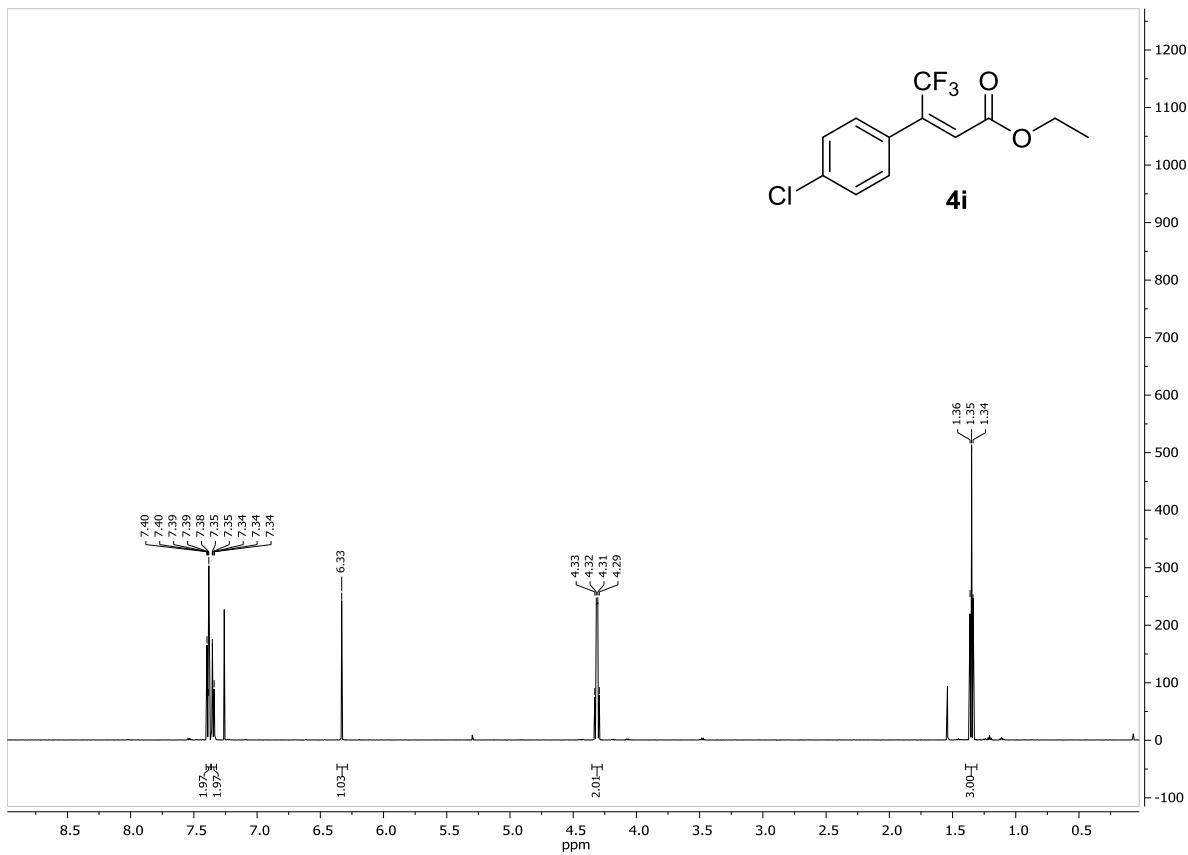
¹H NMR (CDCl₃, 600 MHz)



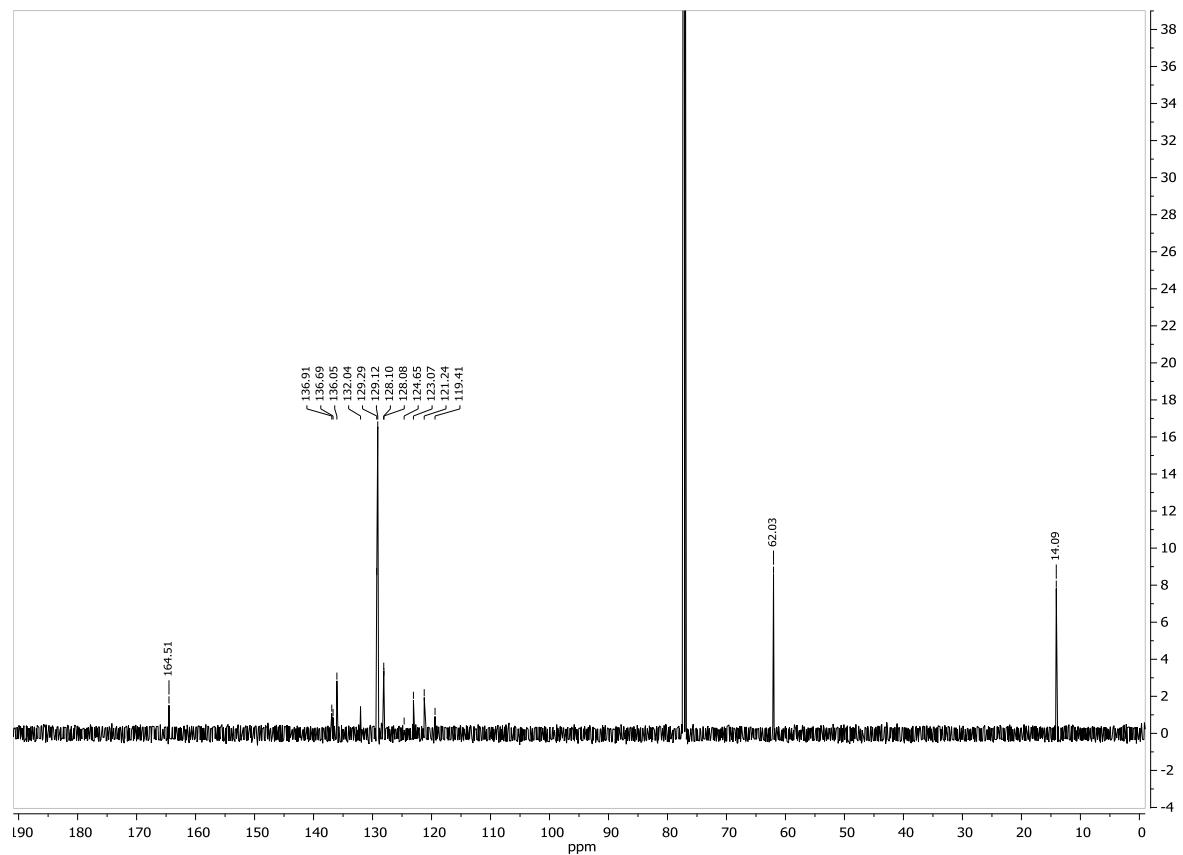
¹³C NMR (CDCl_3 , 151 MHz)



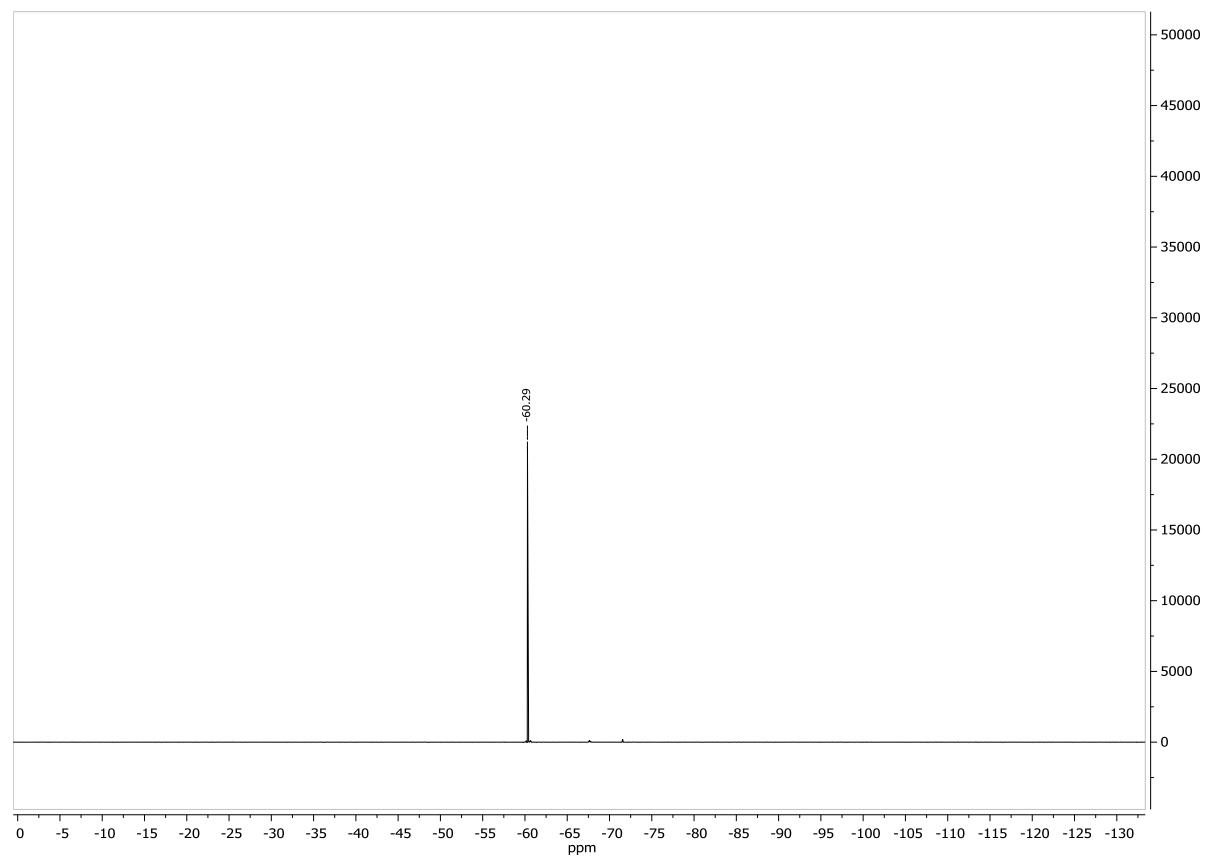
¹H NMR (CDCl₃, 600 MHz)



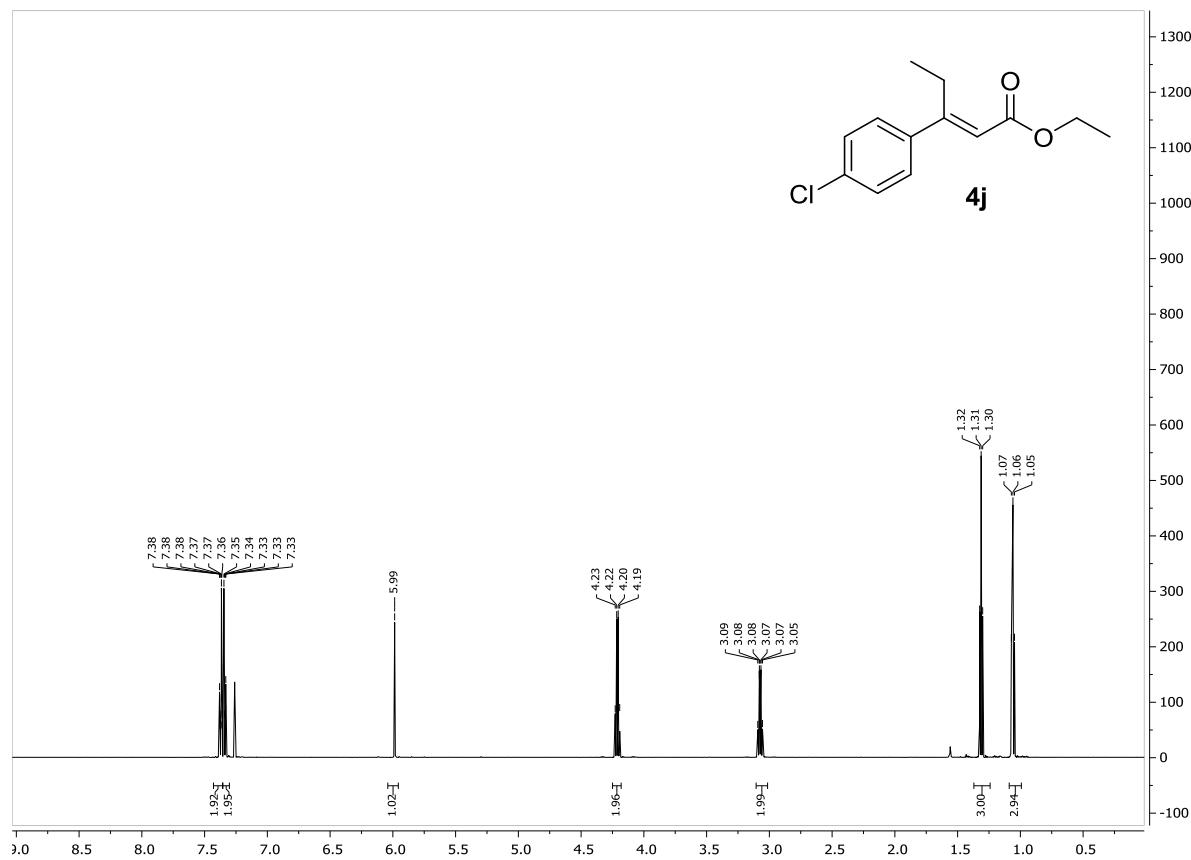
¹³C NMR (CDCl₃, 151 MHz)



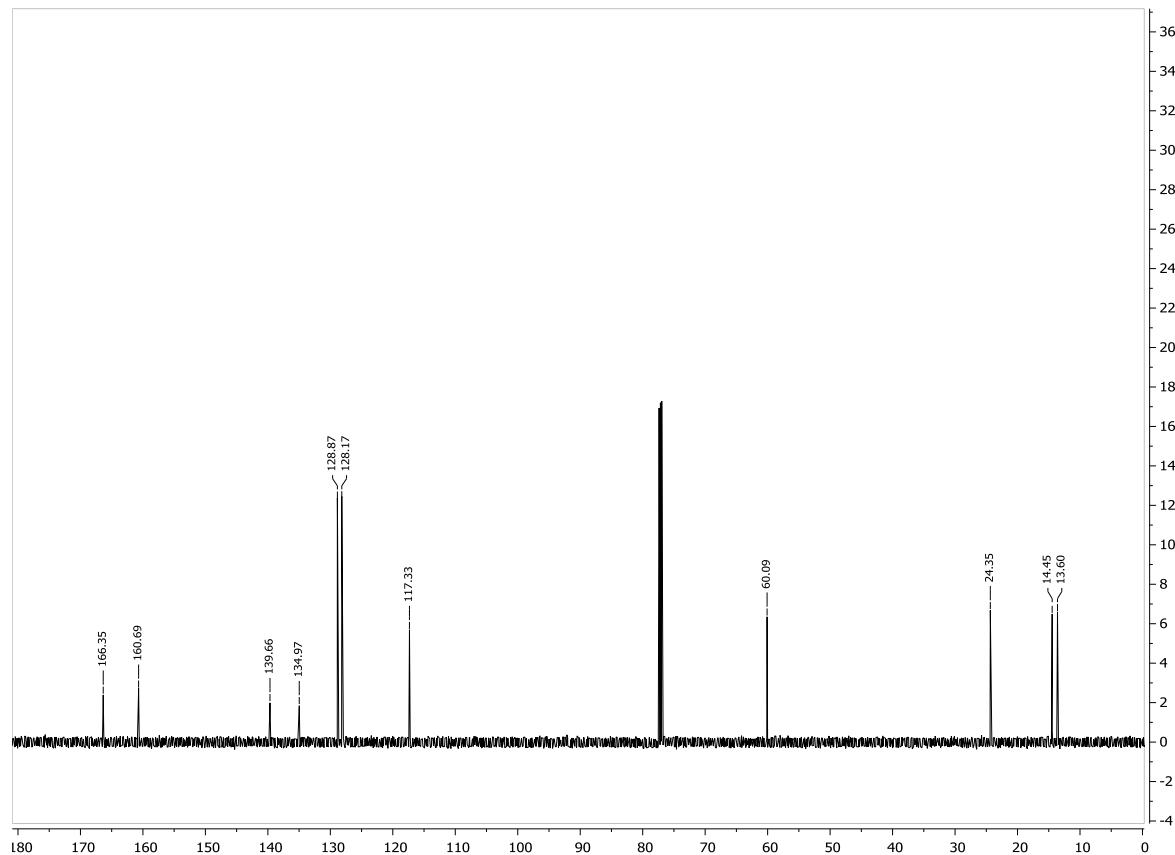
¹⁹F NMR (CDCl₃, 564 MHz)



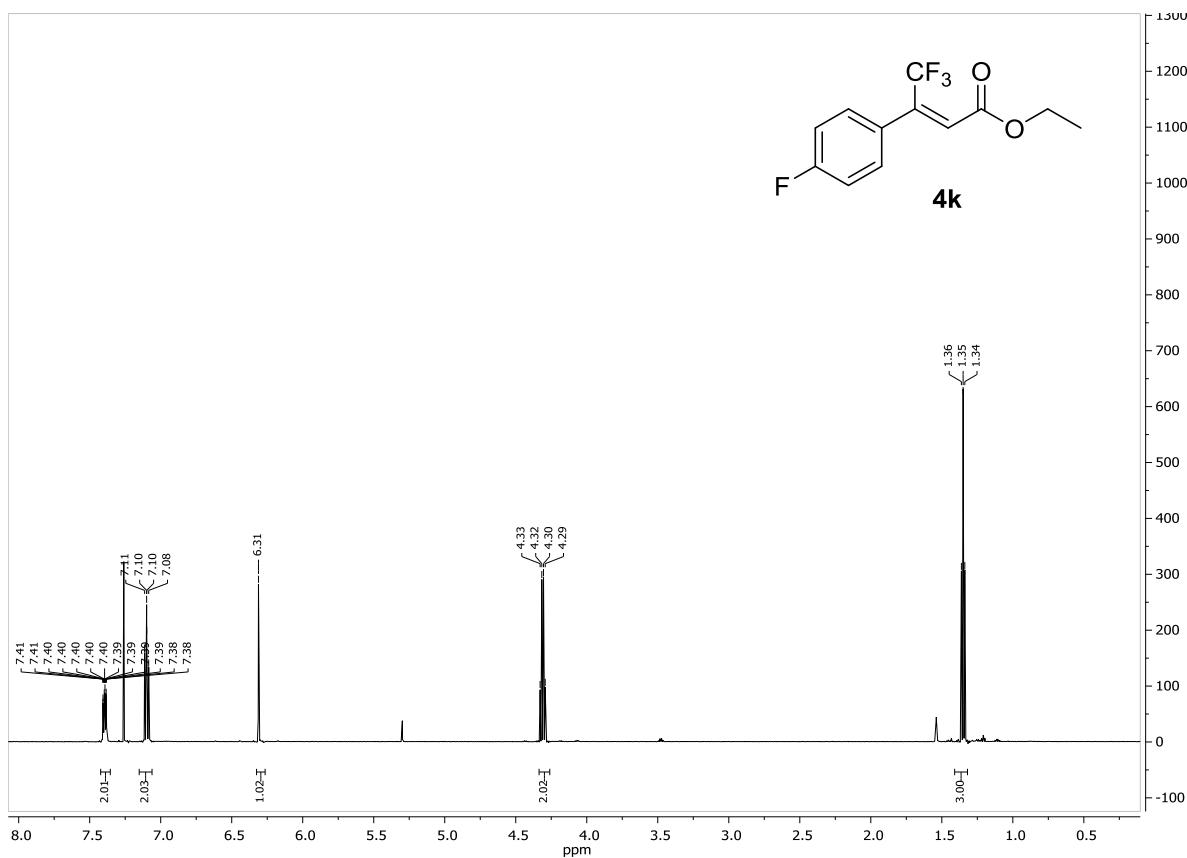
¹H NMR (CDCl₃, 151 MHz)



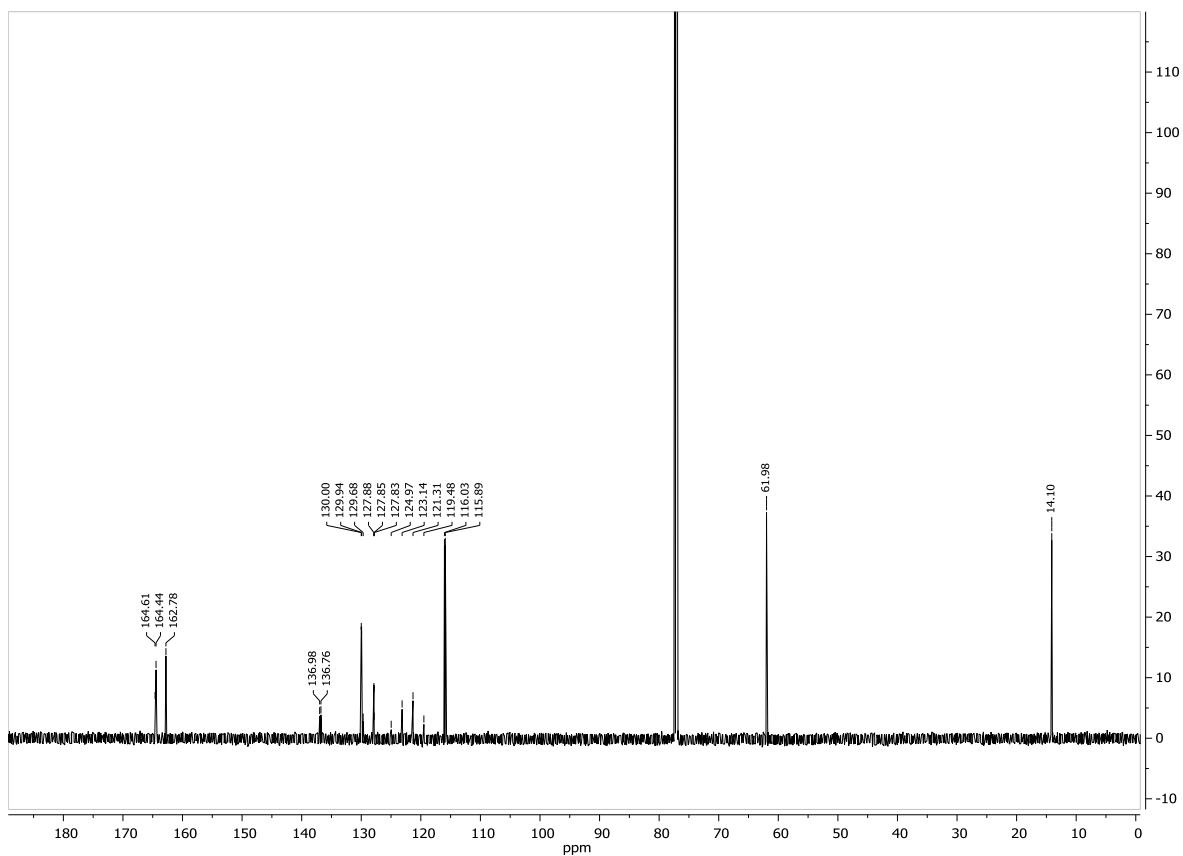
¹³C NMR (CDCl₃, 151 MHz)



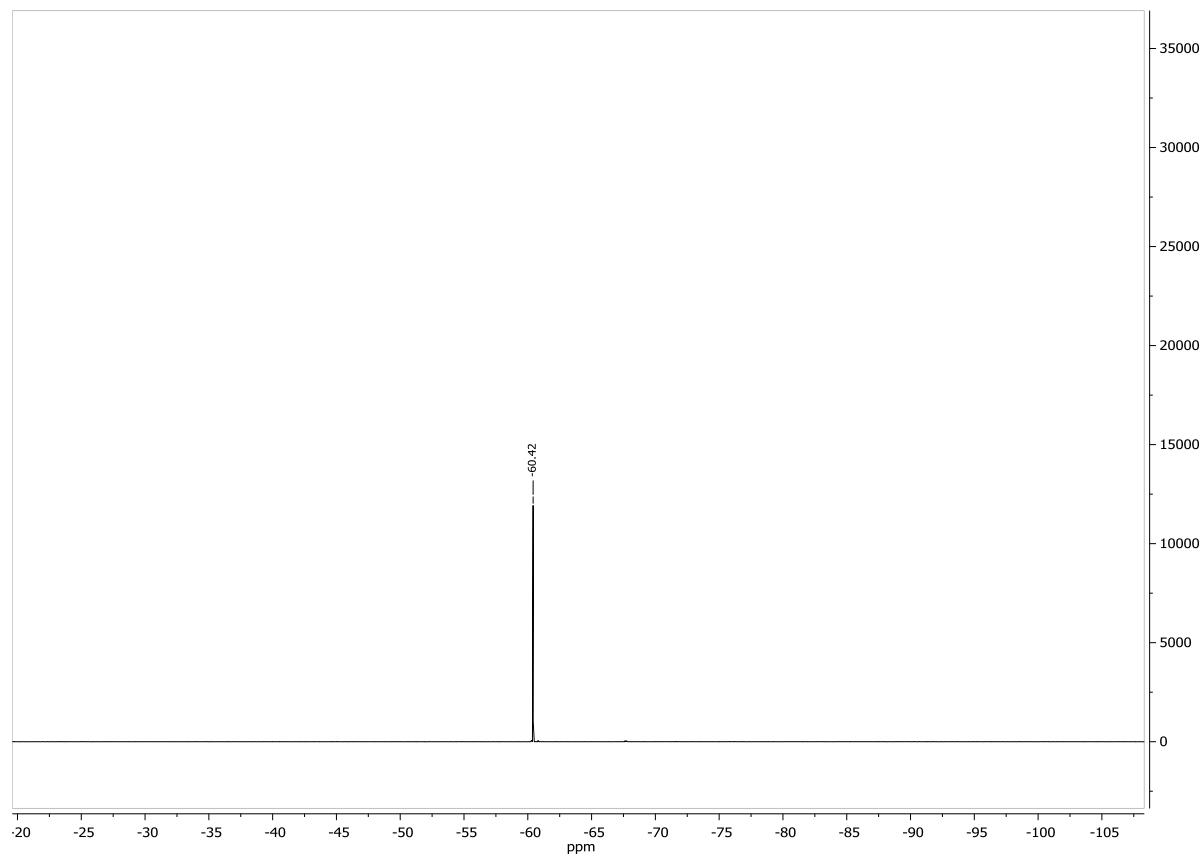
¹H NMR (CDCl₃, 600 MHz)



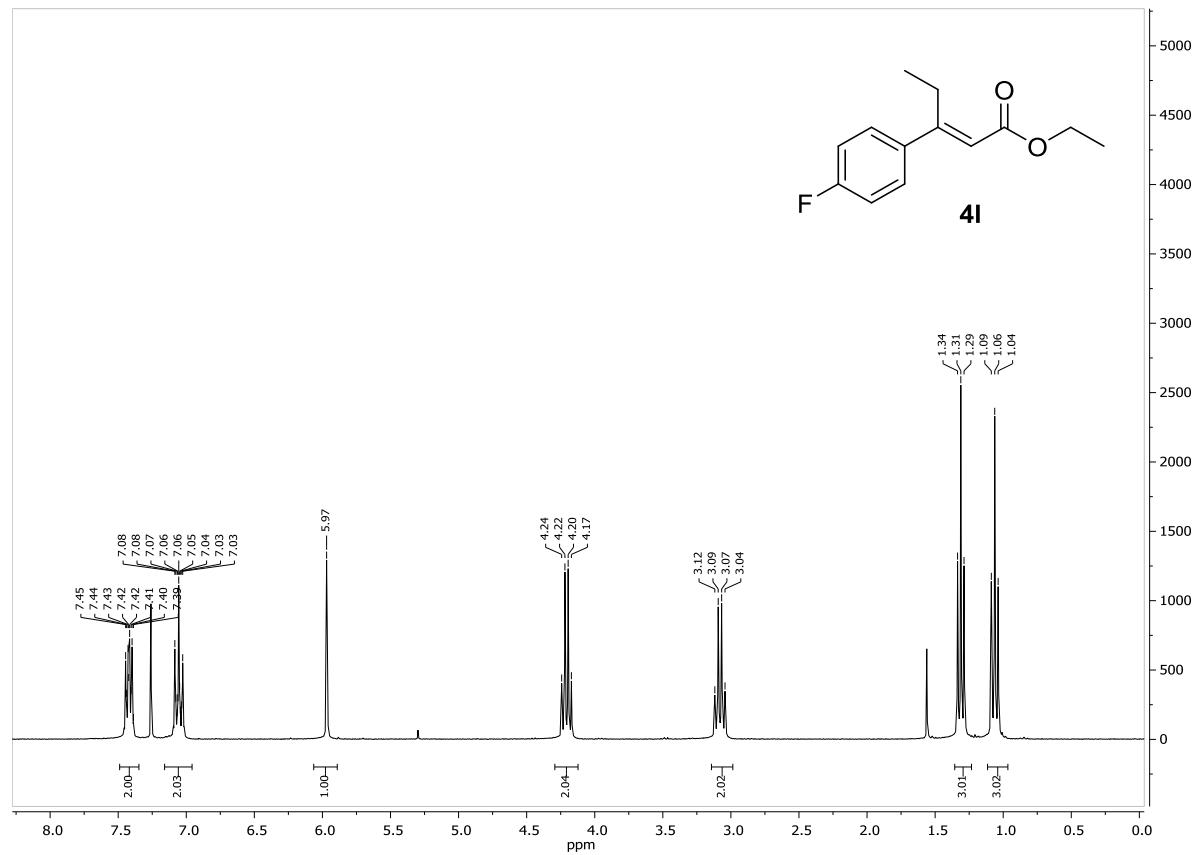
¹³C NMR (CDCl₃, 151 MHz)



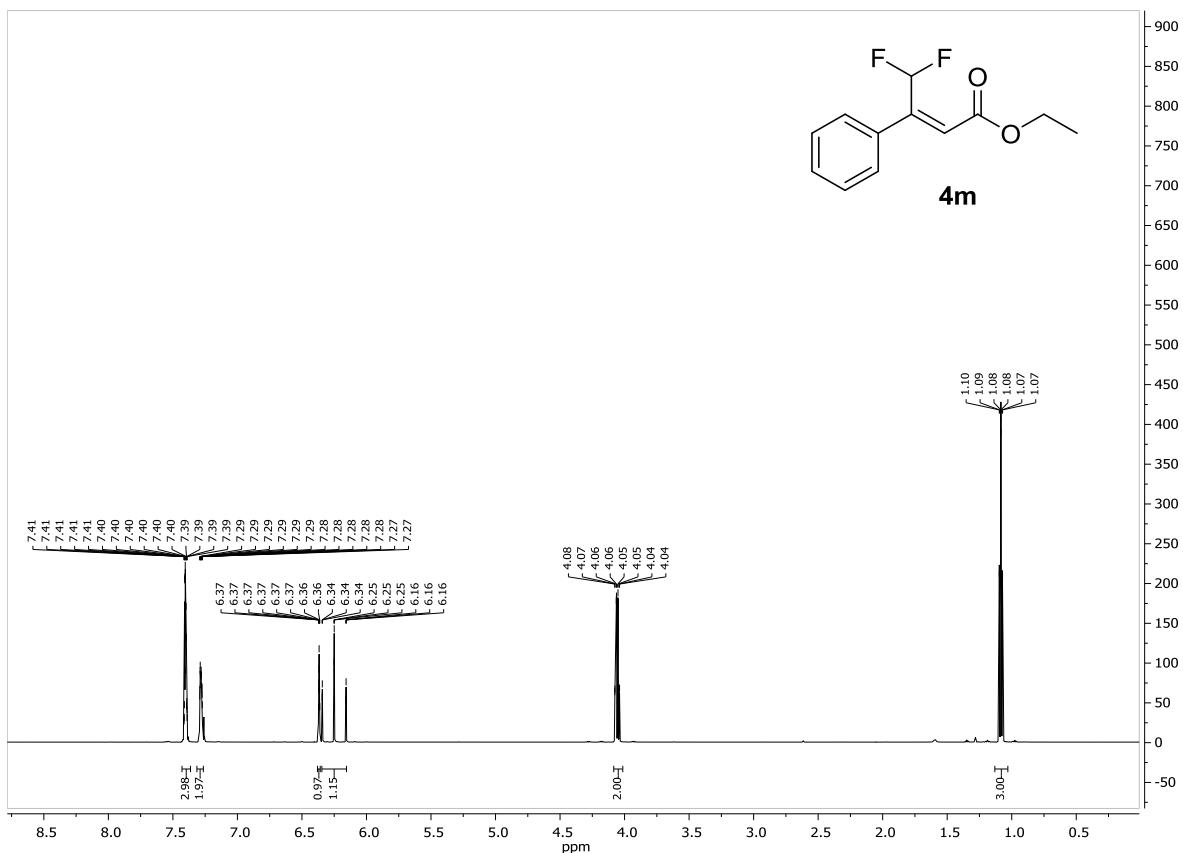
¹⁹F NMR (CDCl₃, 564 MHz)



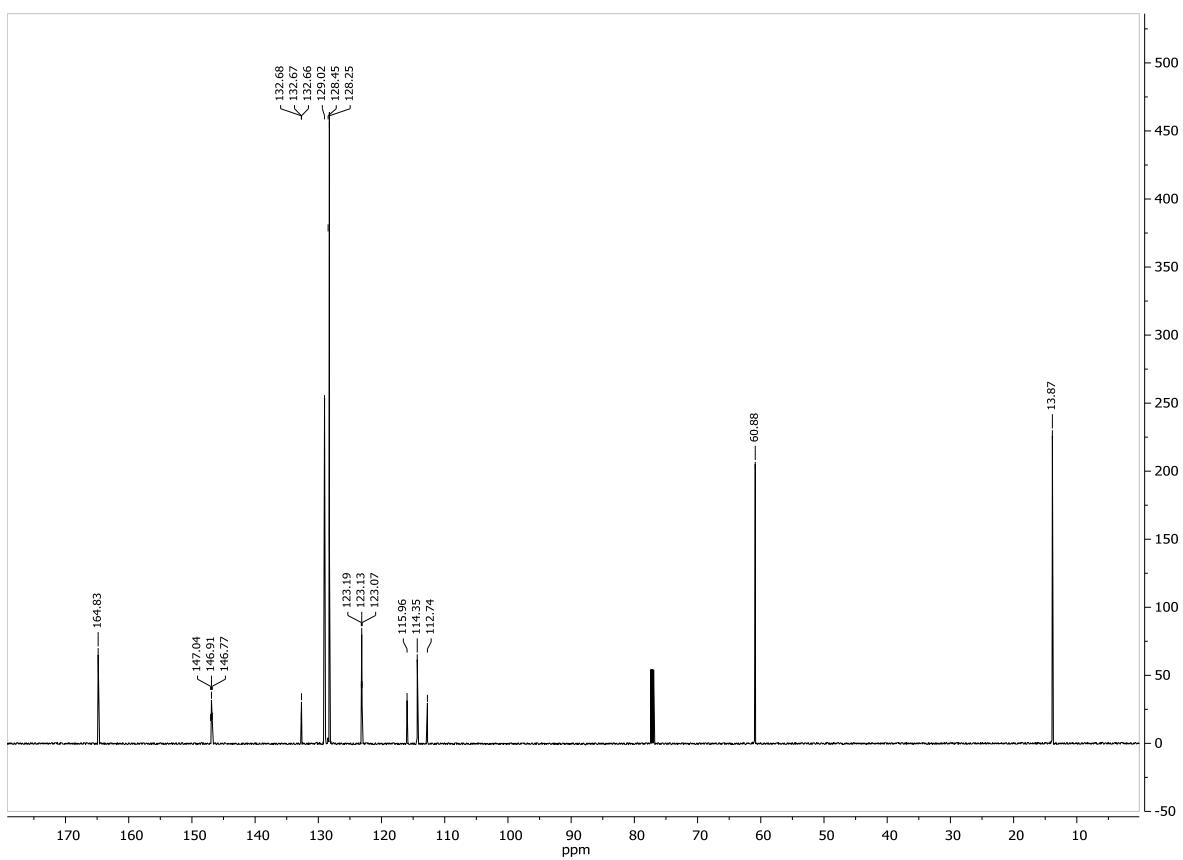
¹H NMR (CDCl₃, 400 MHz)



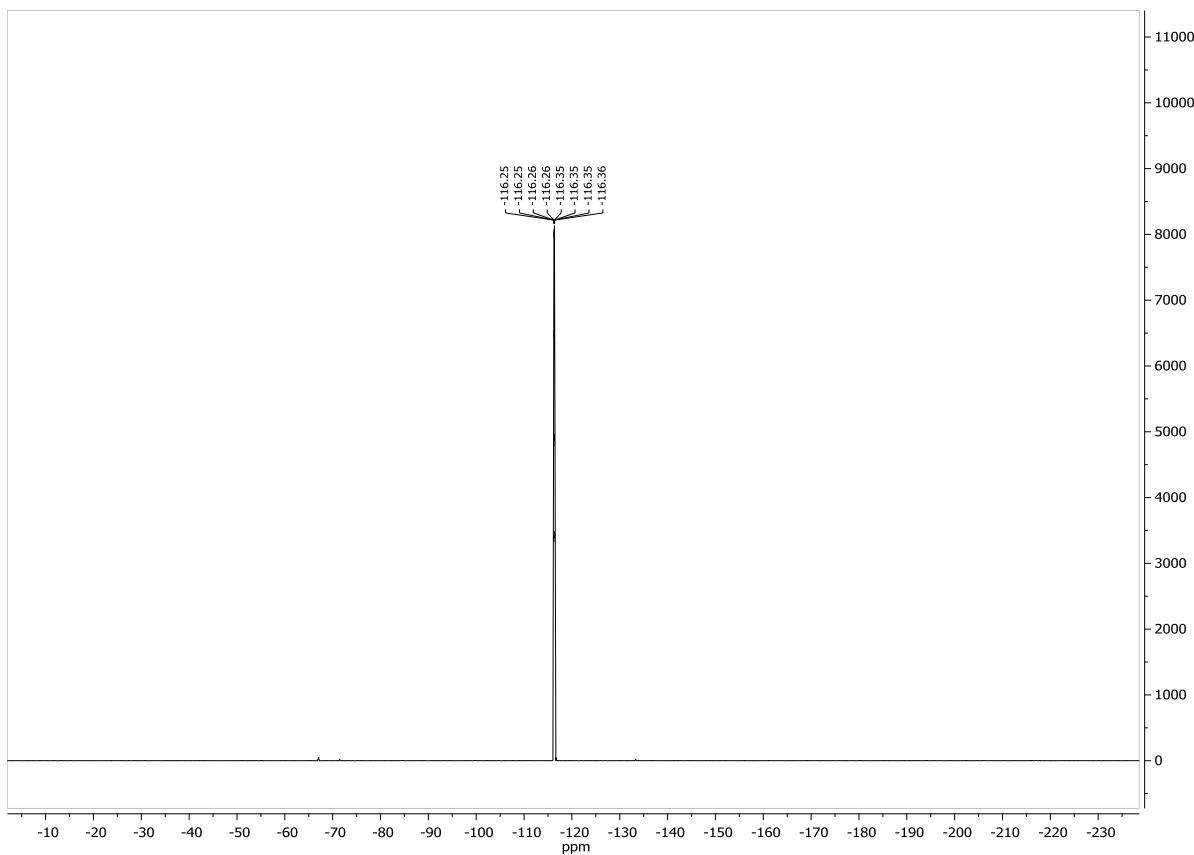
¹H NMR (CDCl₃, 600 MHz)



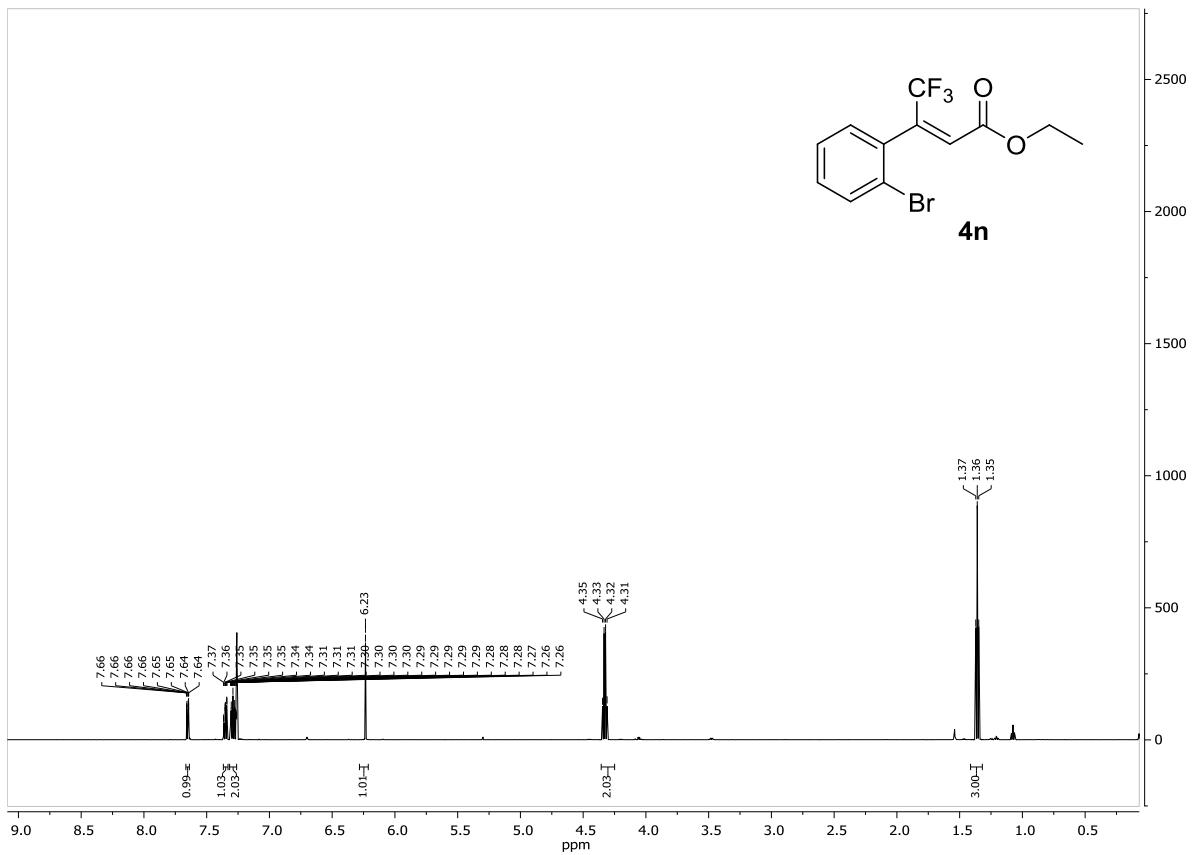
¹³C NMR (CDCl₃, 151 MHz)



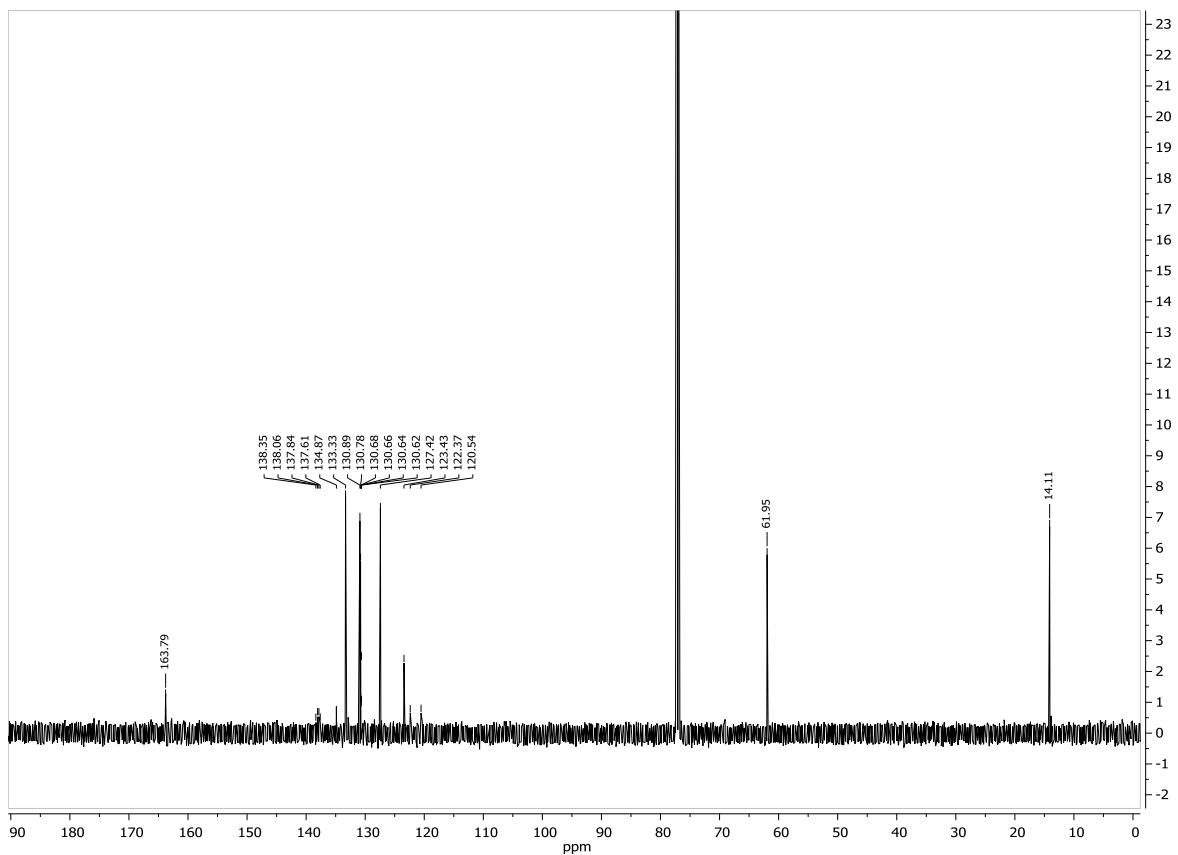
¹⁹F NMR (CDCl₃, 564 MHz)



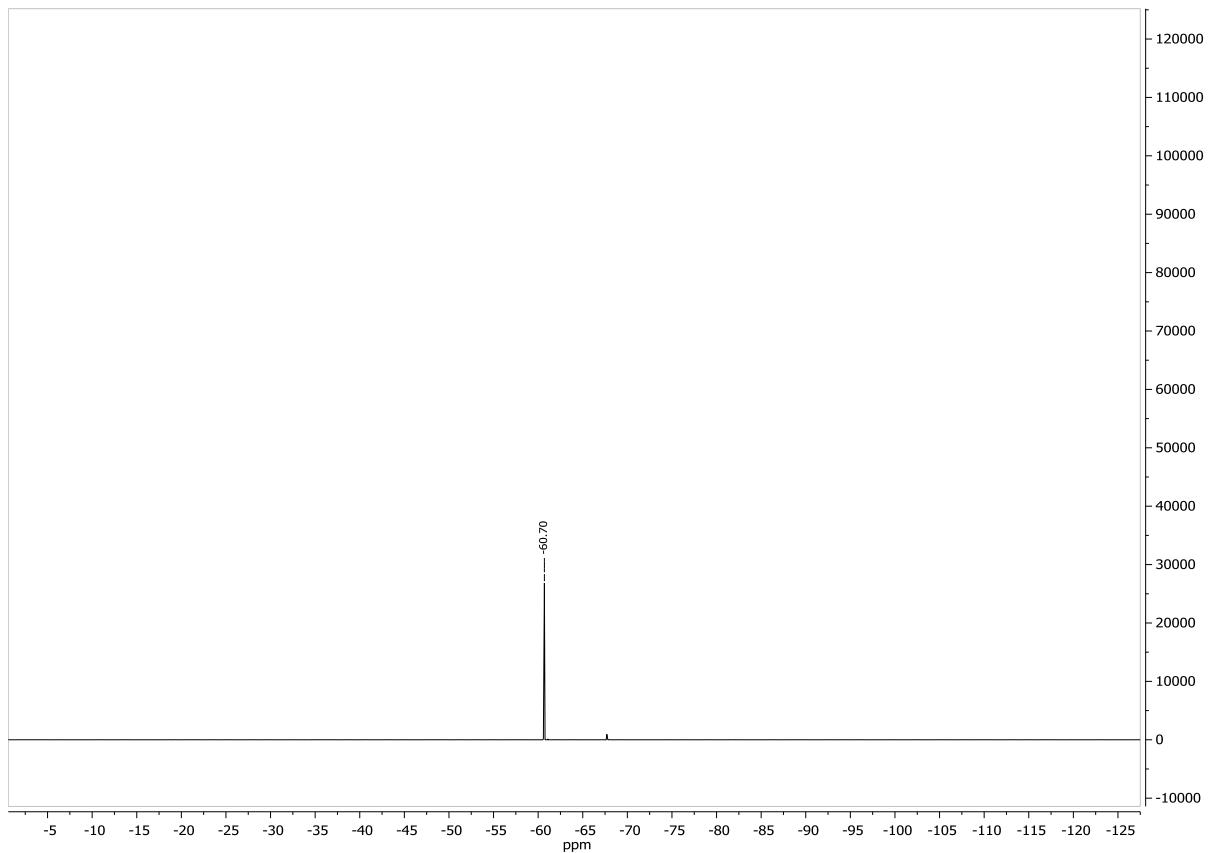
¹H NMR (CDCl₃, 600 MHz)



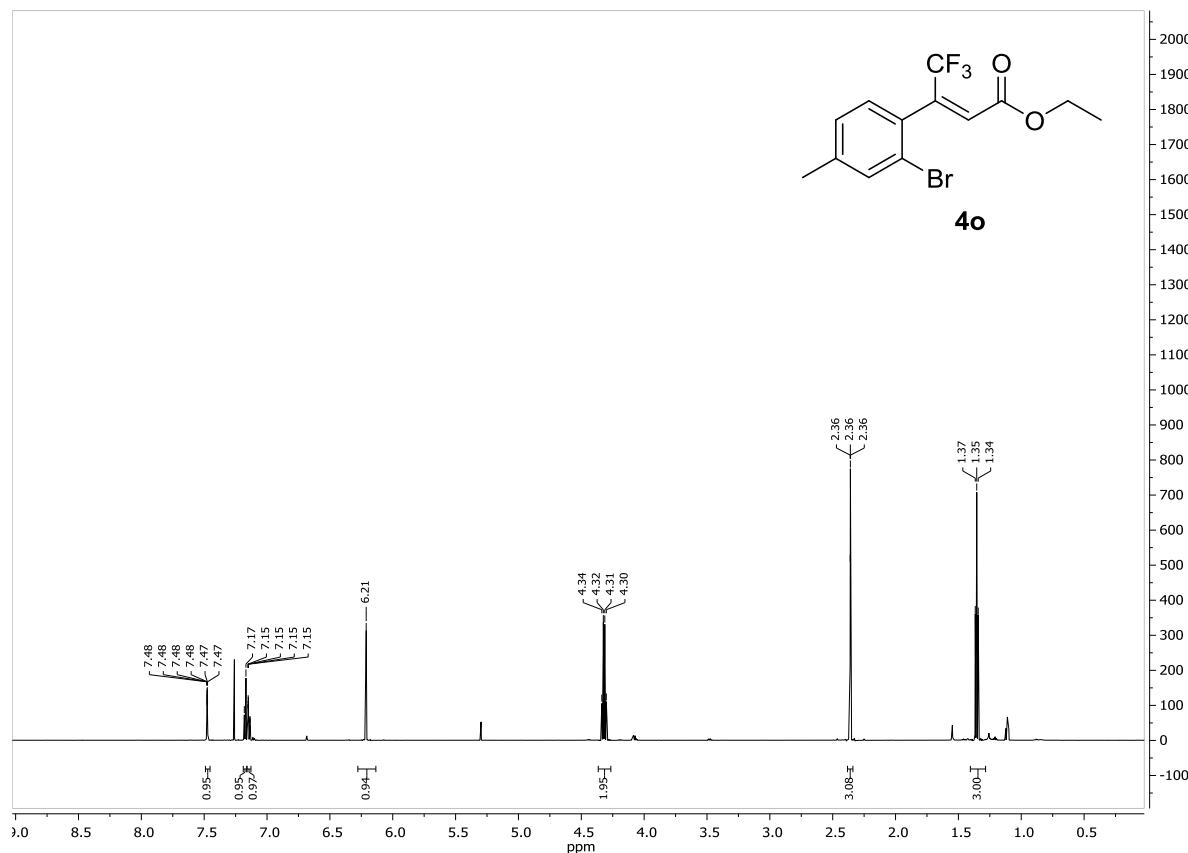
^{13}C NMR (CDCl_3 , 151 MHz)



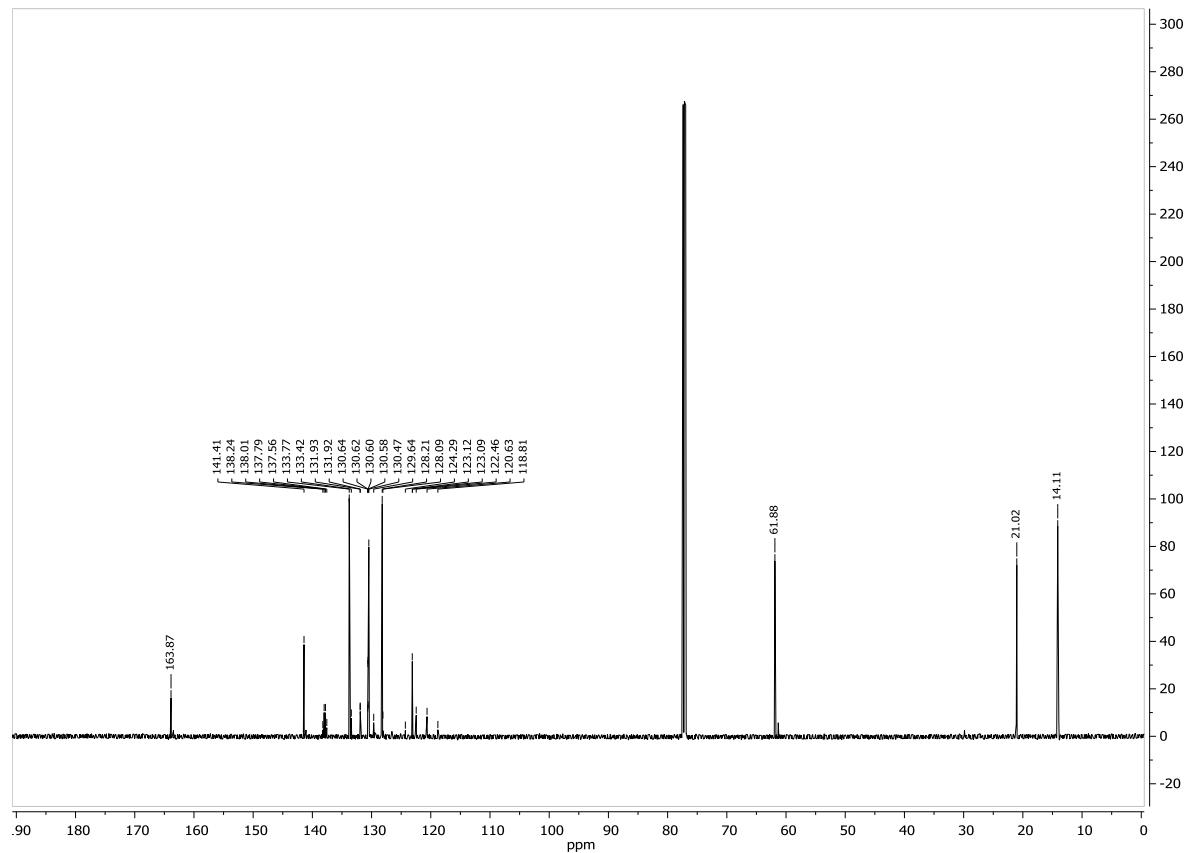
^{19}F NMR (CDCl_3 , 564 MHz)



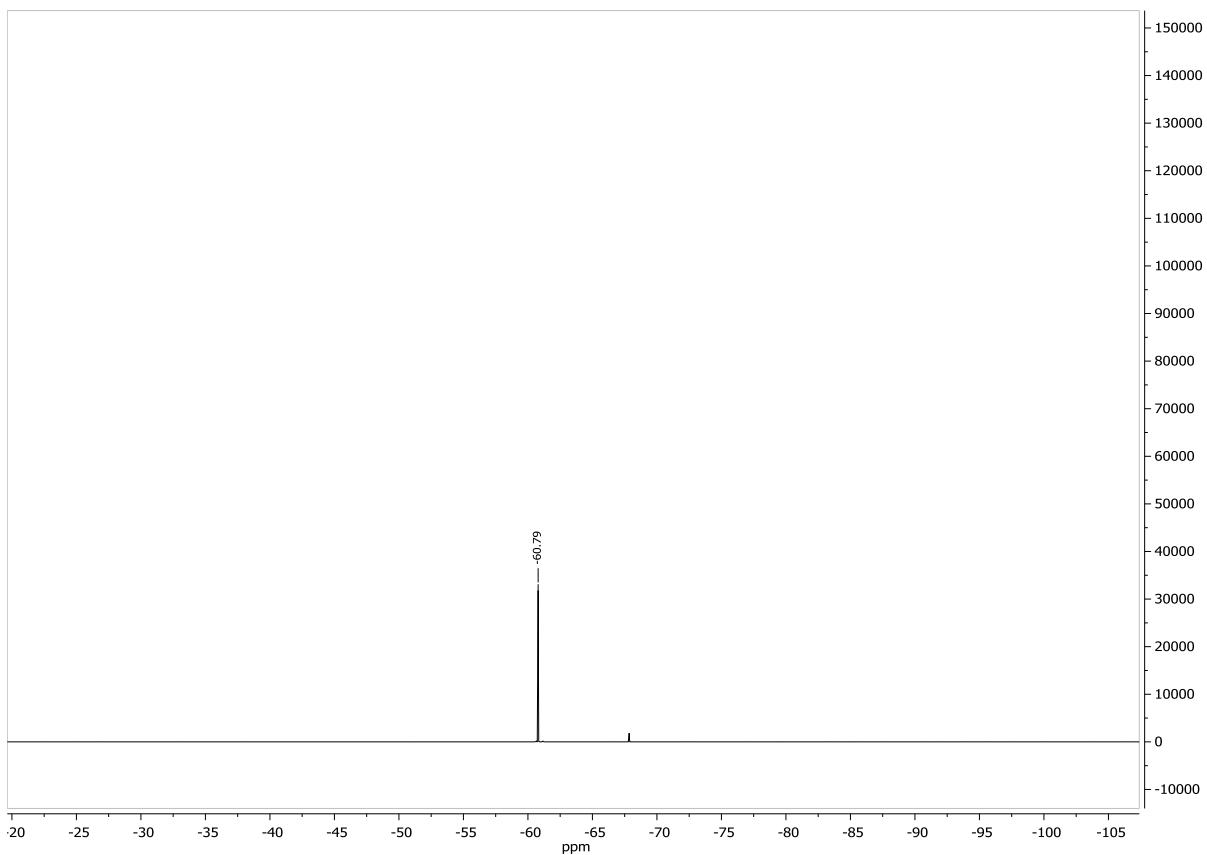
¹H NMR (CDCl₃, 600 MHz)



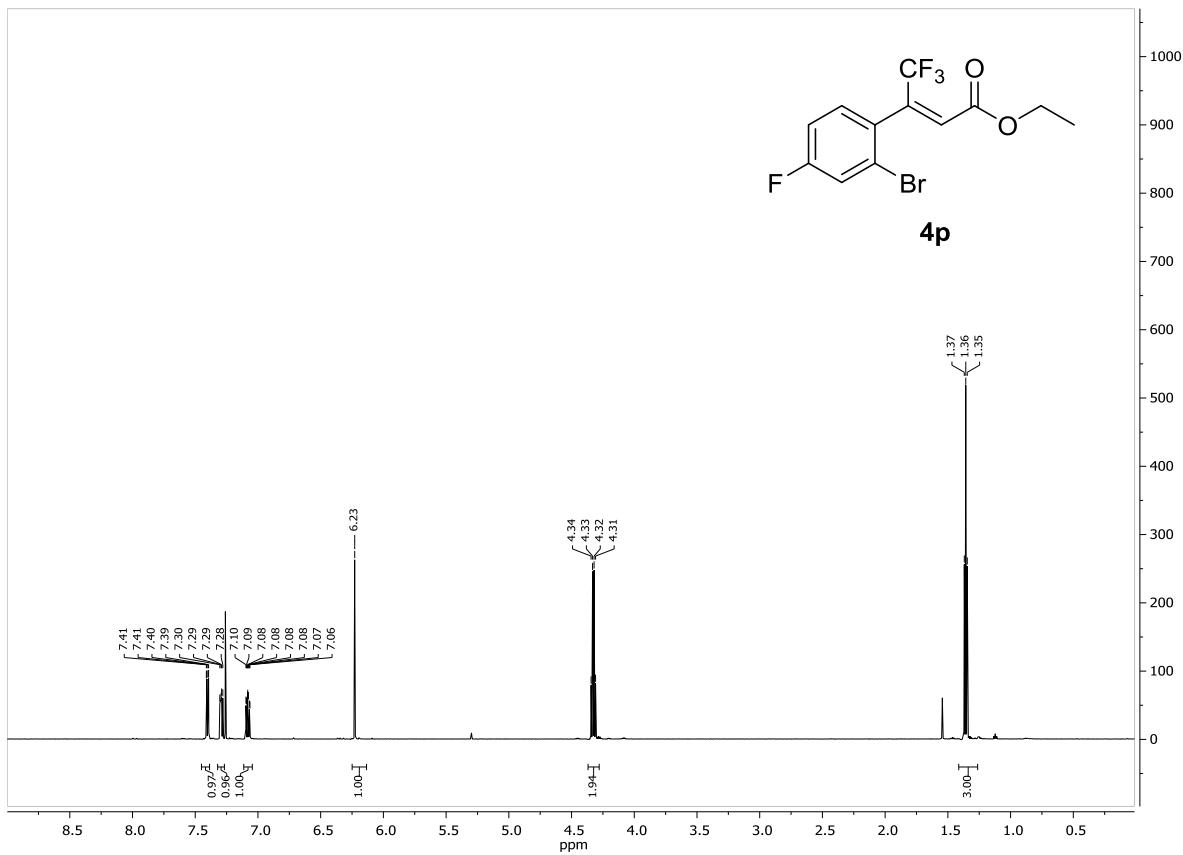
¹³C NMR (CDCl₃, 151 MHz)



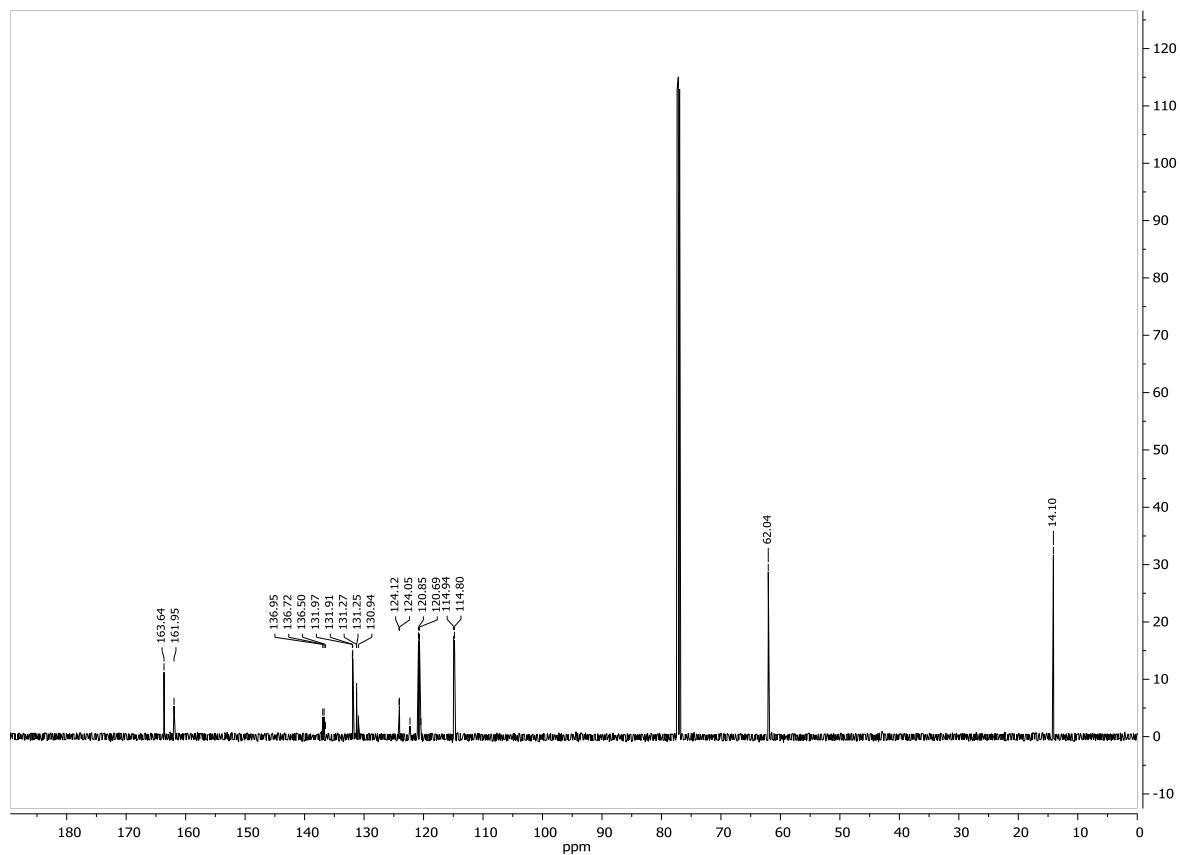
¹⁹F NMR (CDCl₃, 564 MHz)



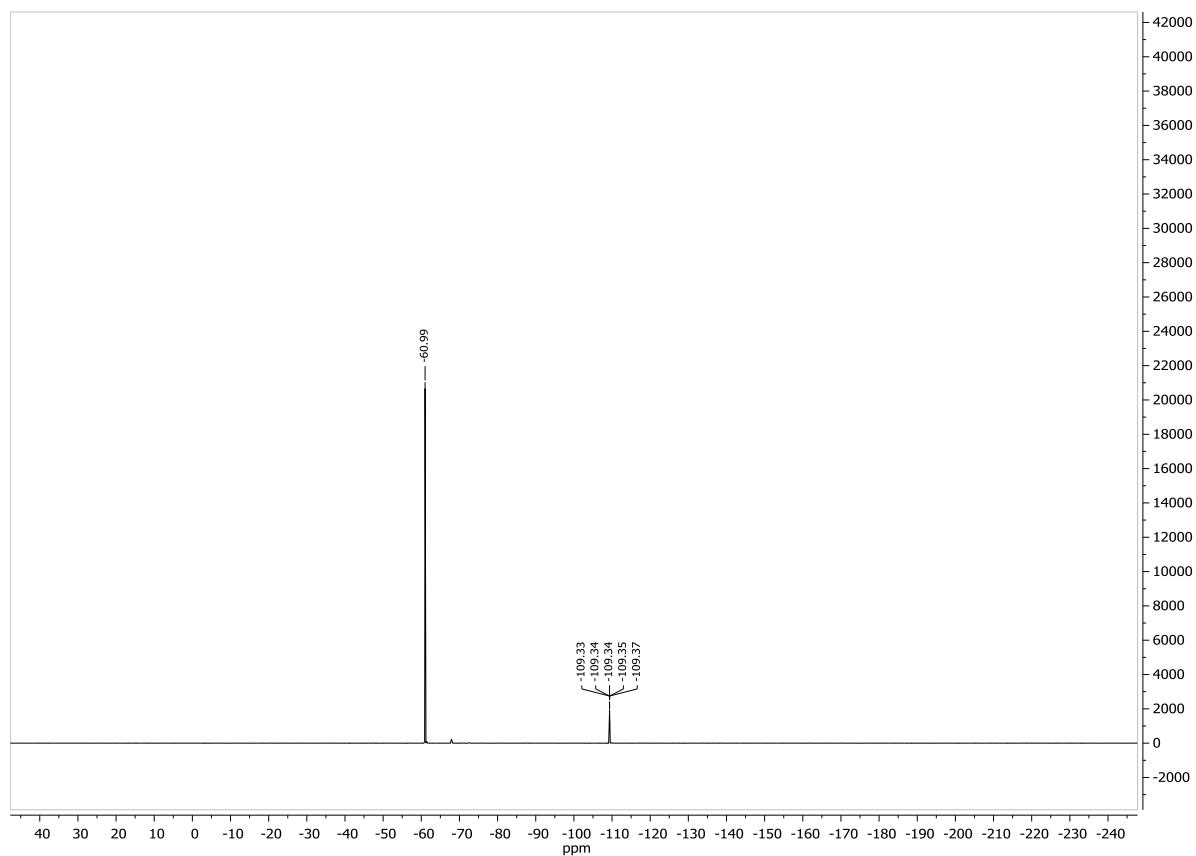
¹H NMR (CDCl₃, 600 MHz)



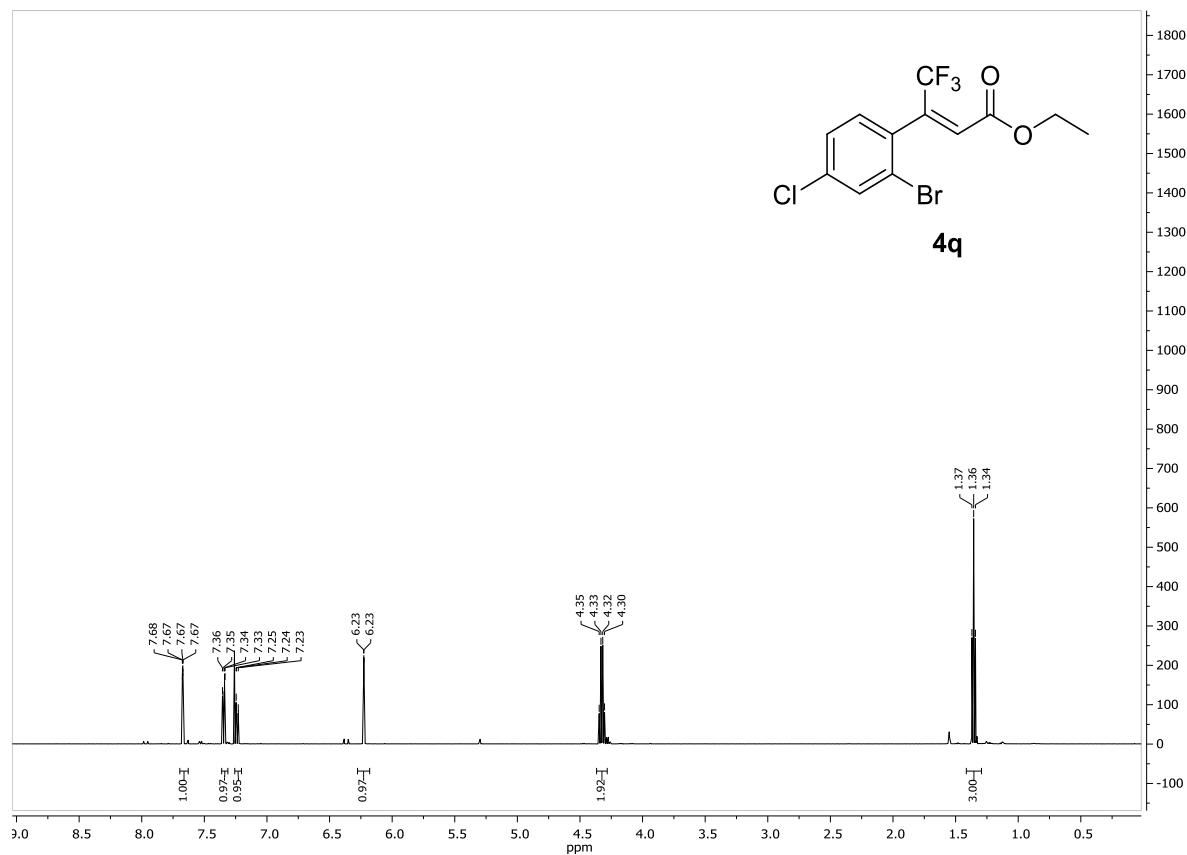
¹³C NMR (CDCl_3 , 151 MHz)



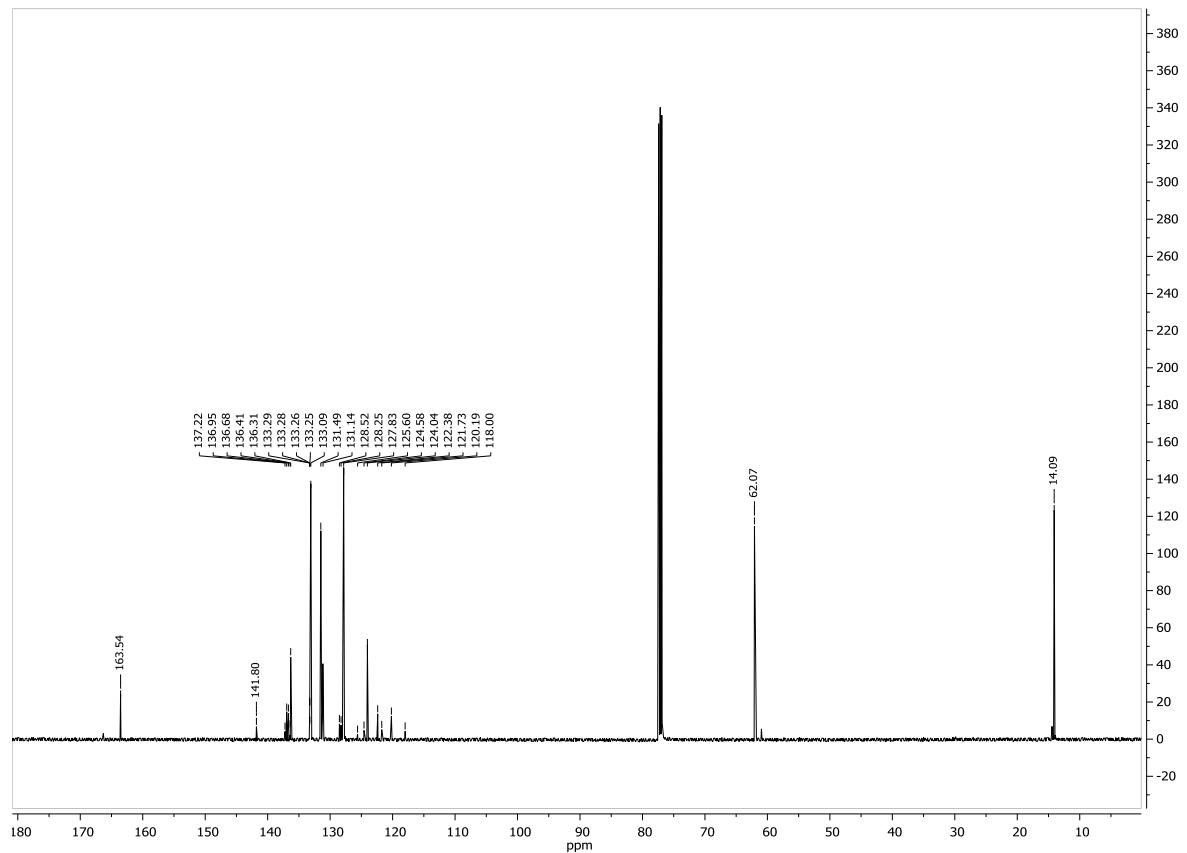
¹⁹F NMR (CDCl_3 , 564 MHz)



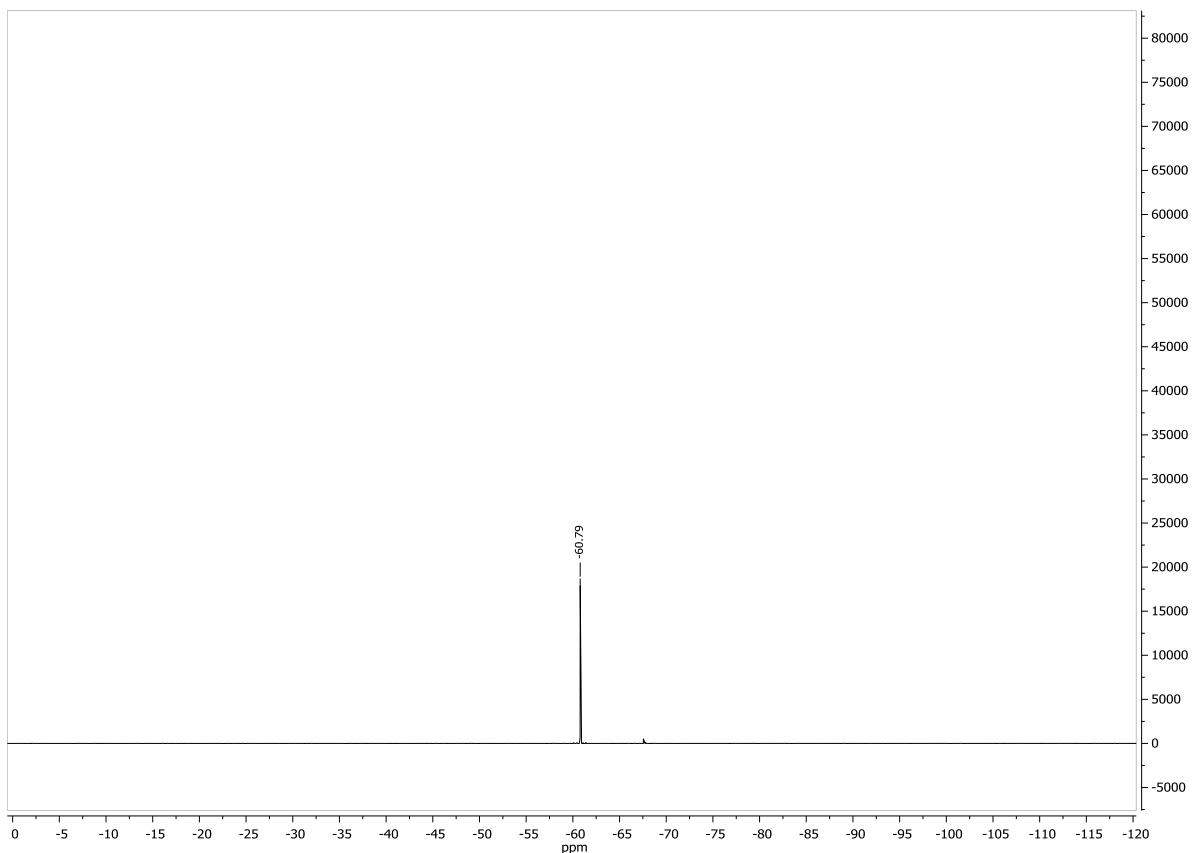
¹H NMR (CDCl₃, 600 MHz)



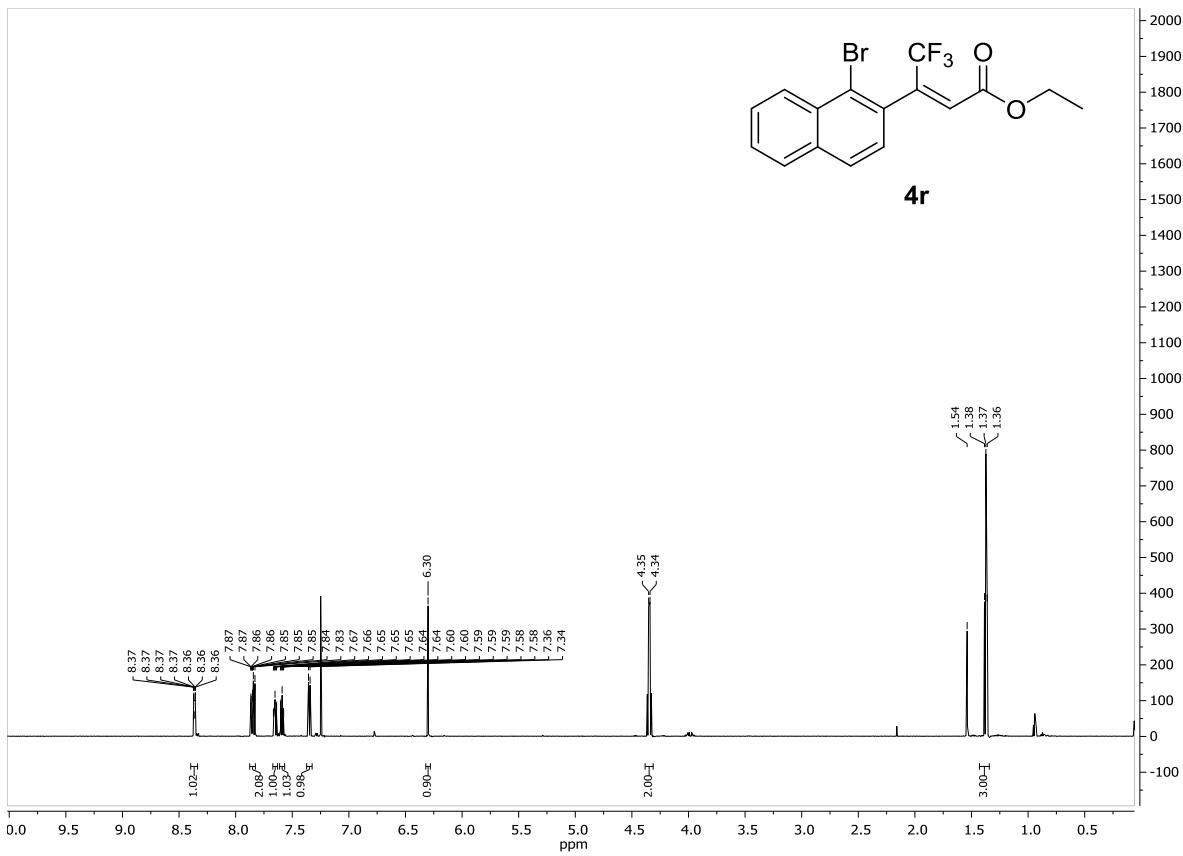
¹³C NMR (CDCl₃, 151 MHz)



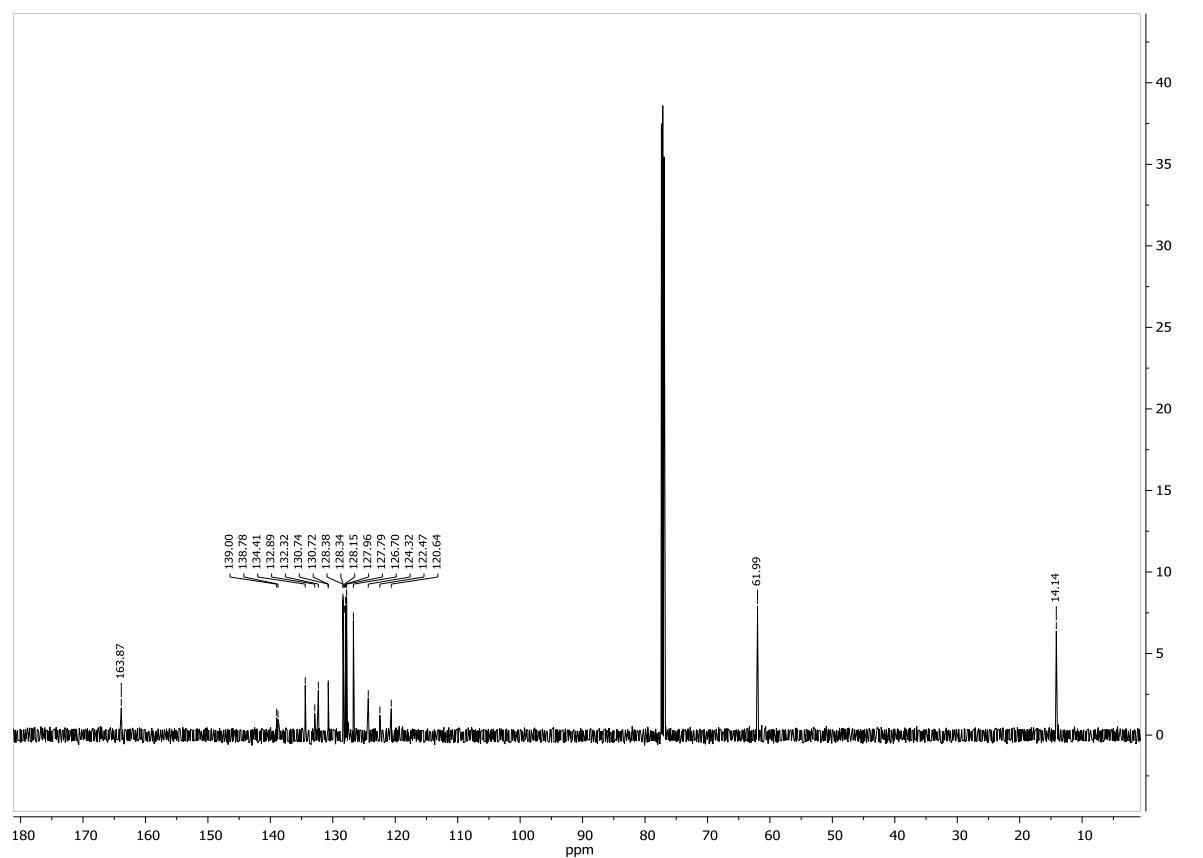
¹⁹F NMR (CDCl₃, 564 MHz)



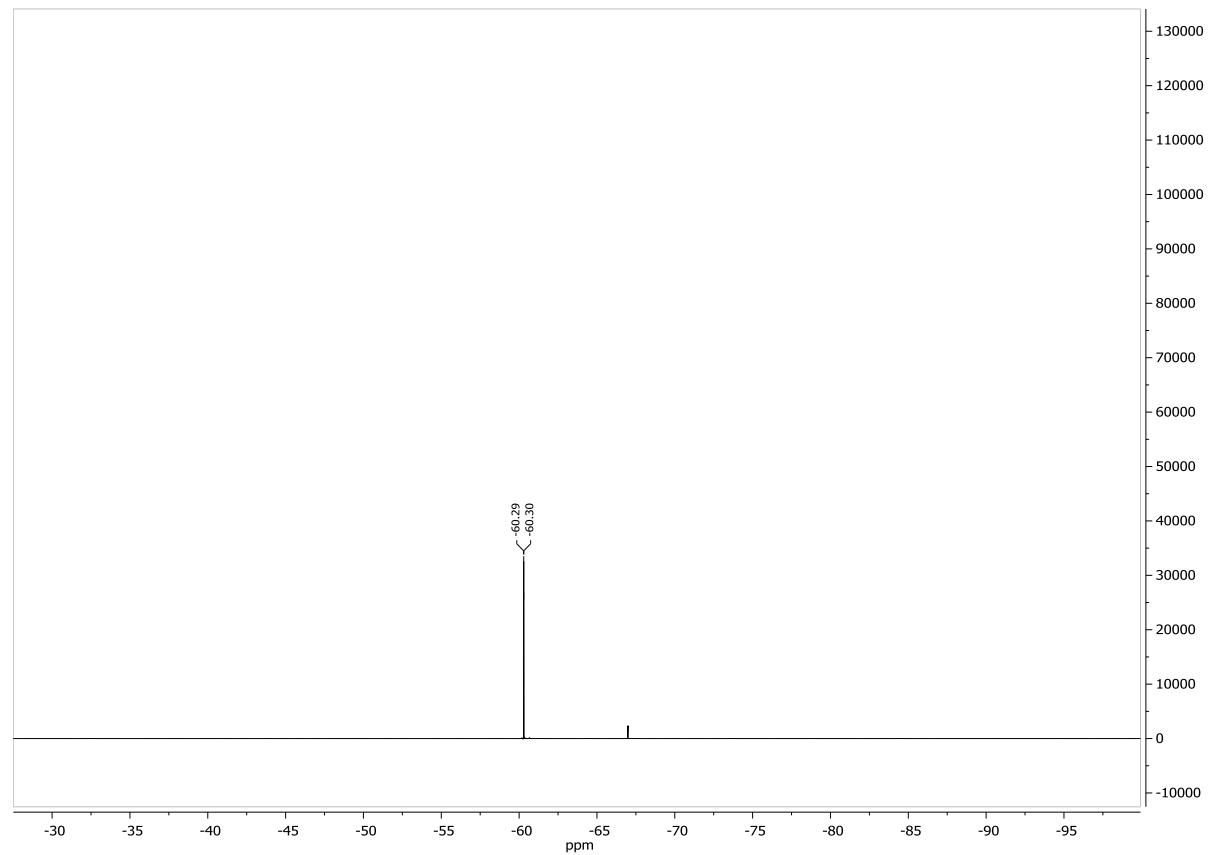
¹H NMR (CDCl₃, 600 MHz)



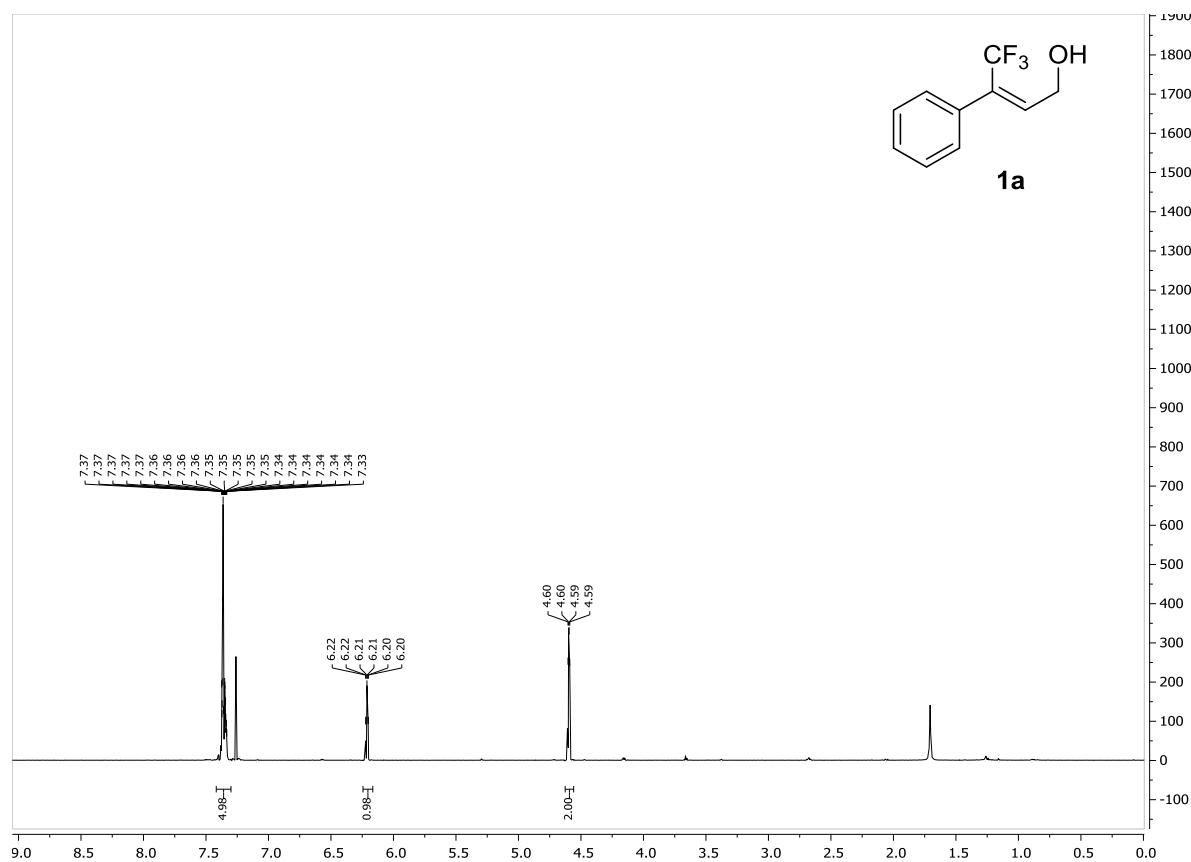
¹³C NMR (CDCl_3 , 151 MHz)



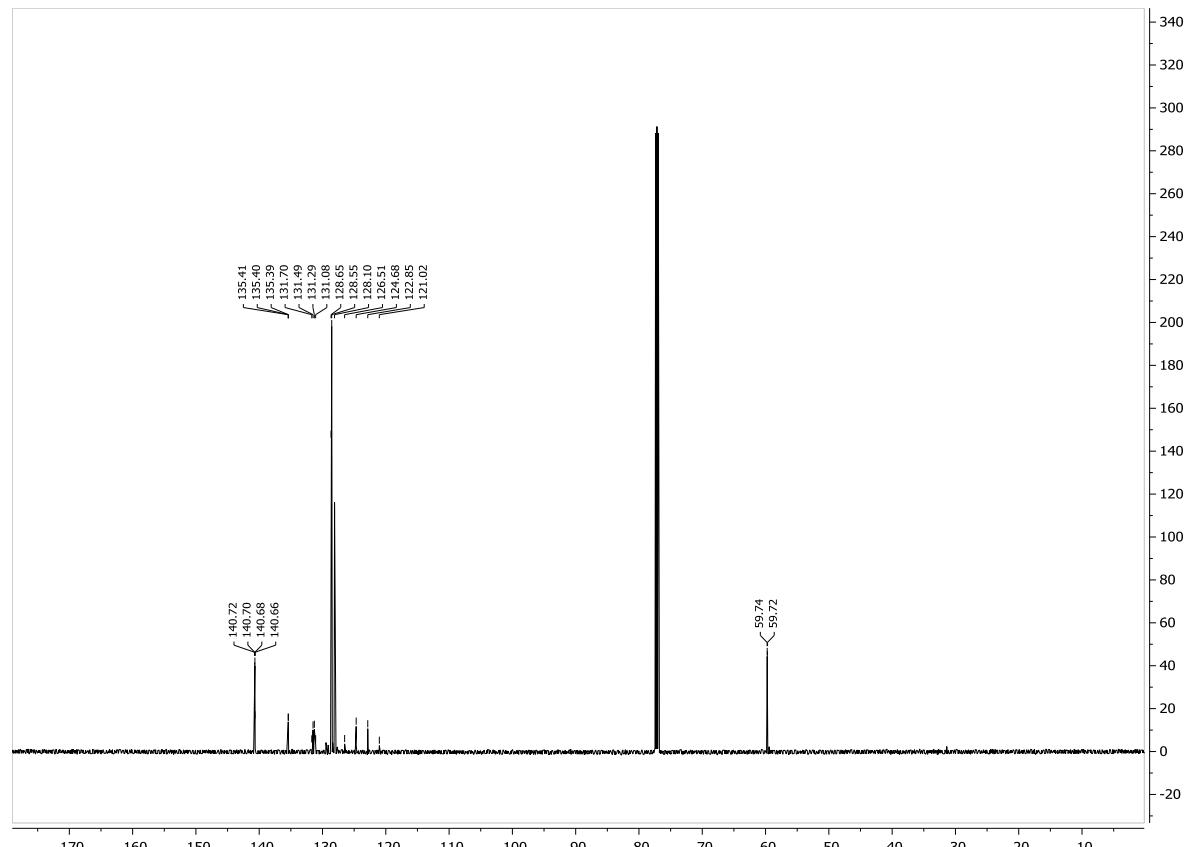
¹⁹F NMR (CDCl_3 , 564 MHz)



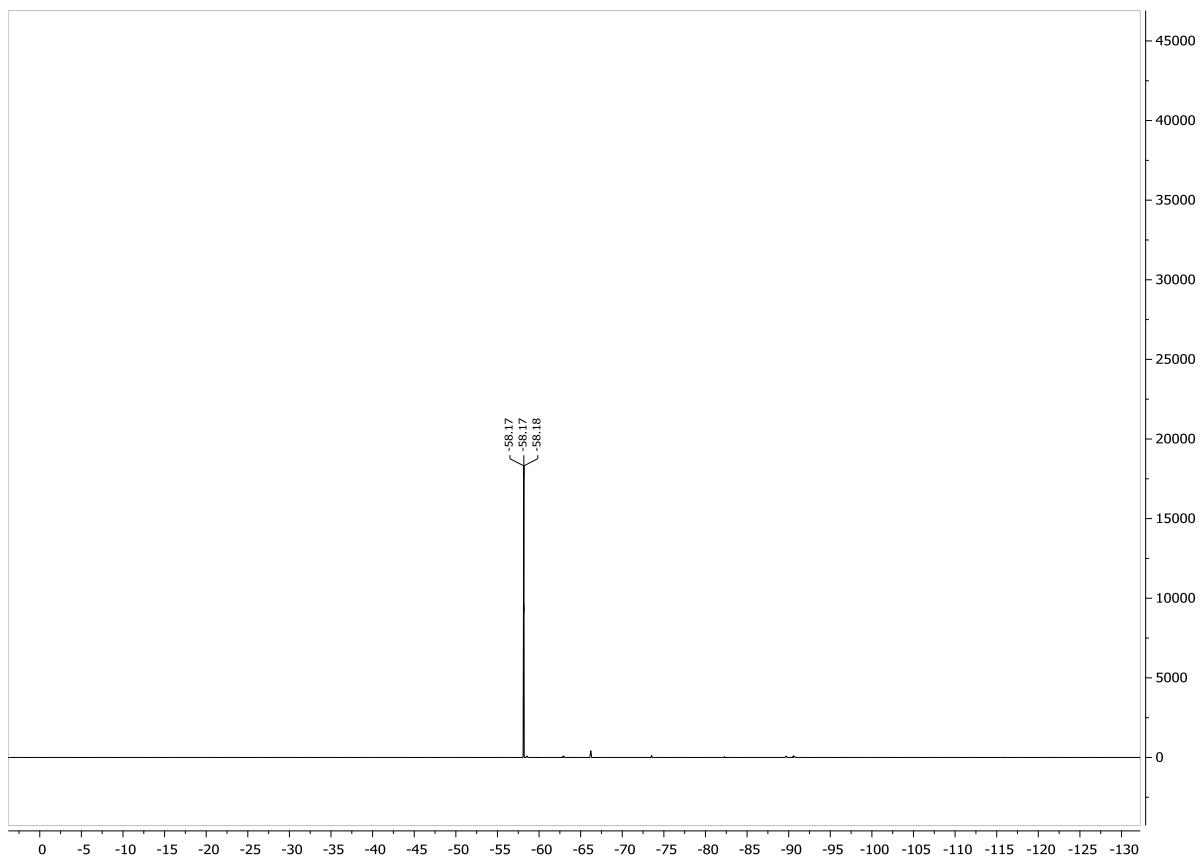
¹H NMR (CDCl_3 , 600 MHz)



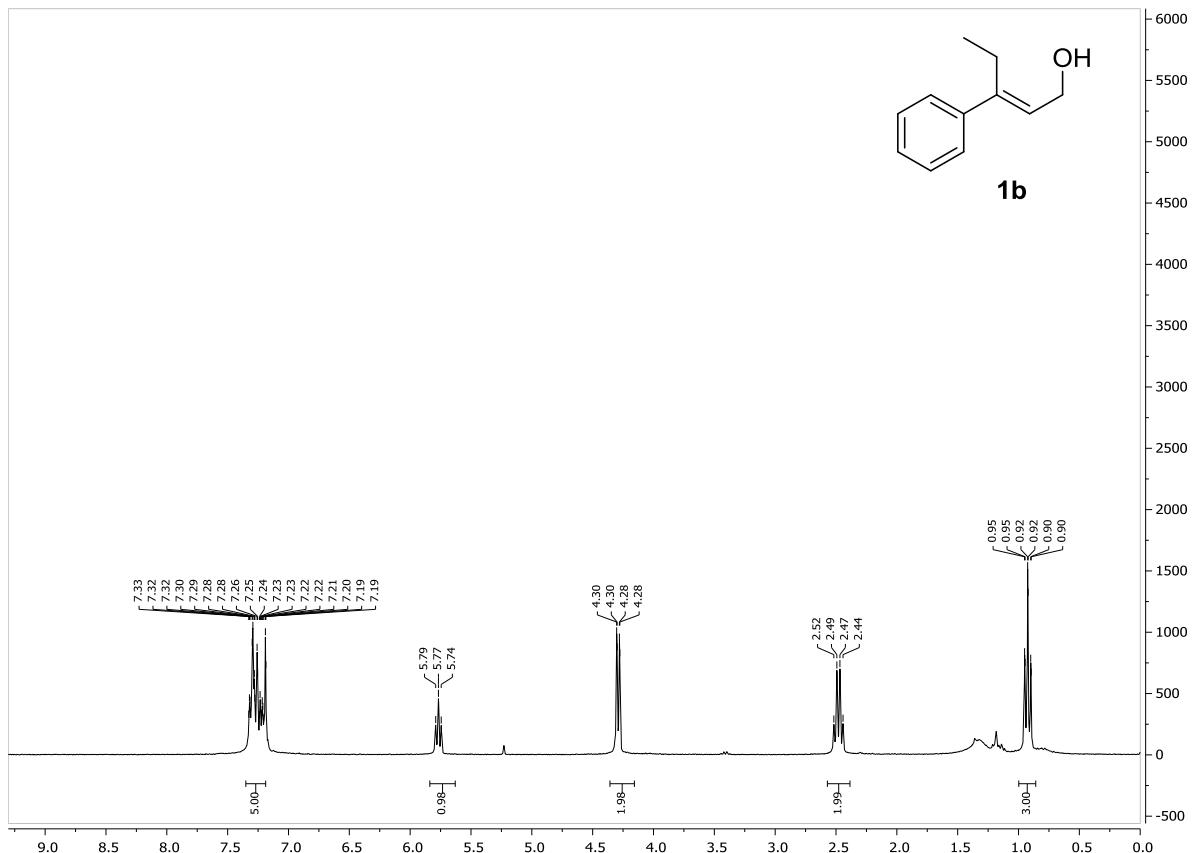
¹³C NMR (CDCl_3 , 151 MHz)



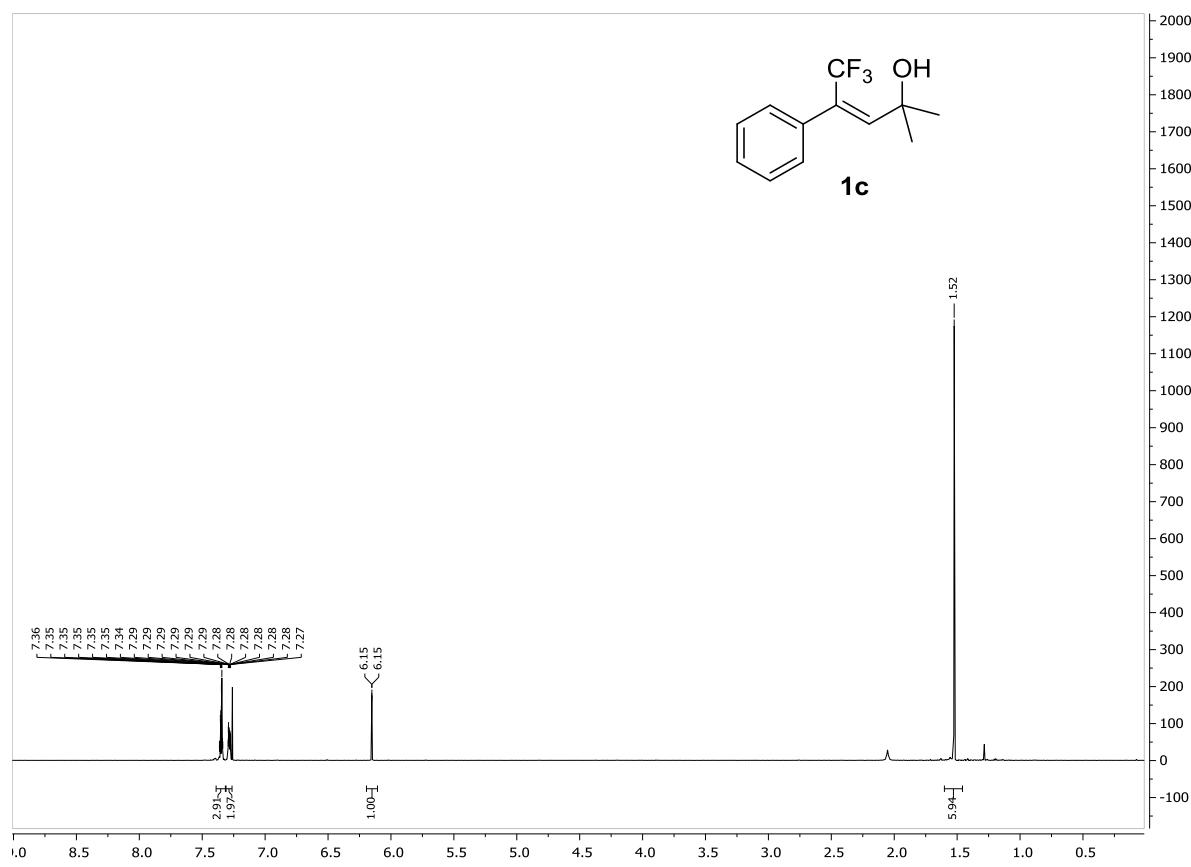
¹⁹F NMR (CDCl_3 , 564 MHz)



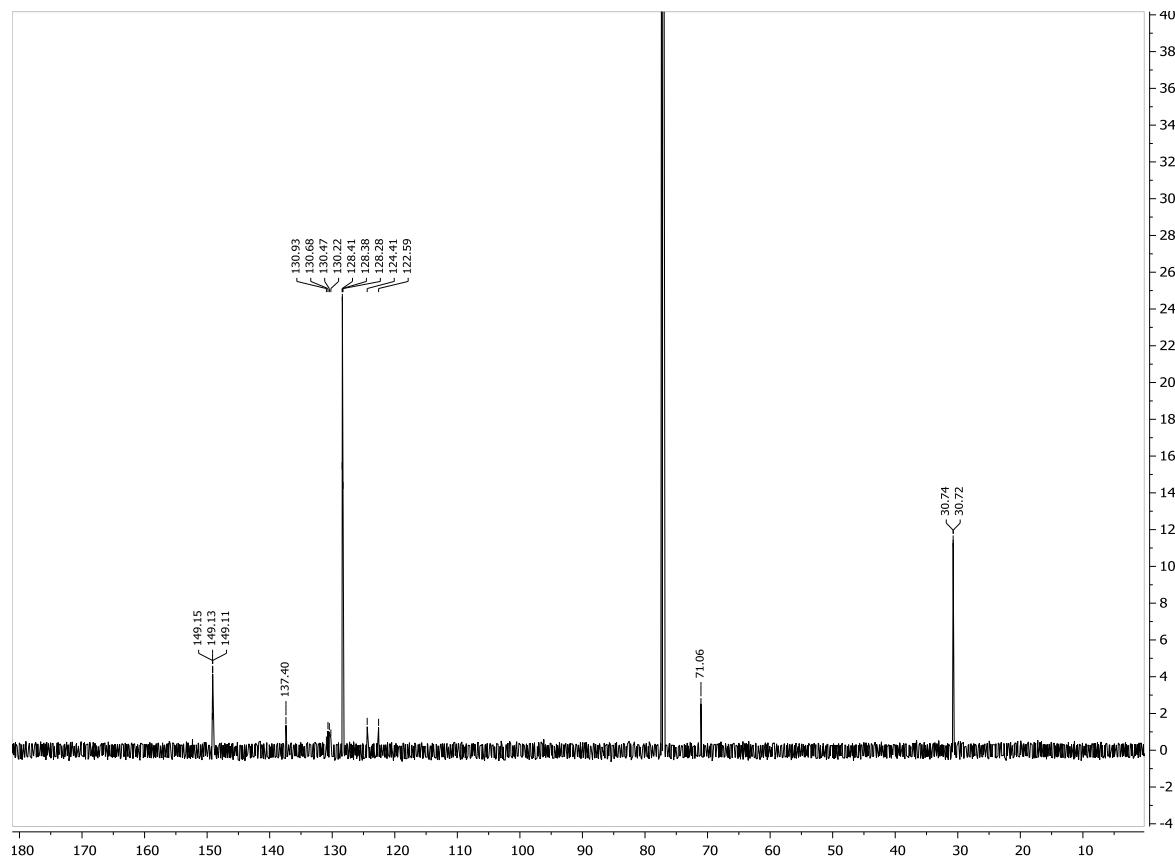
¹H NMR (CDCl_3 , 400 MHz)



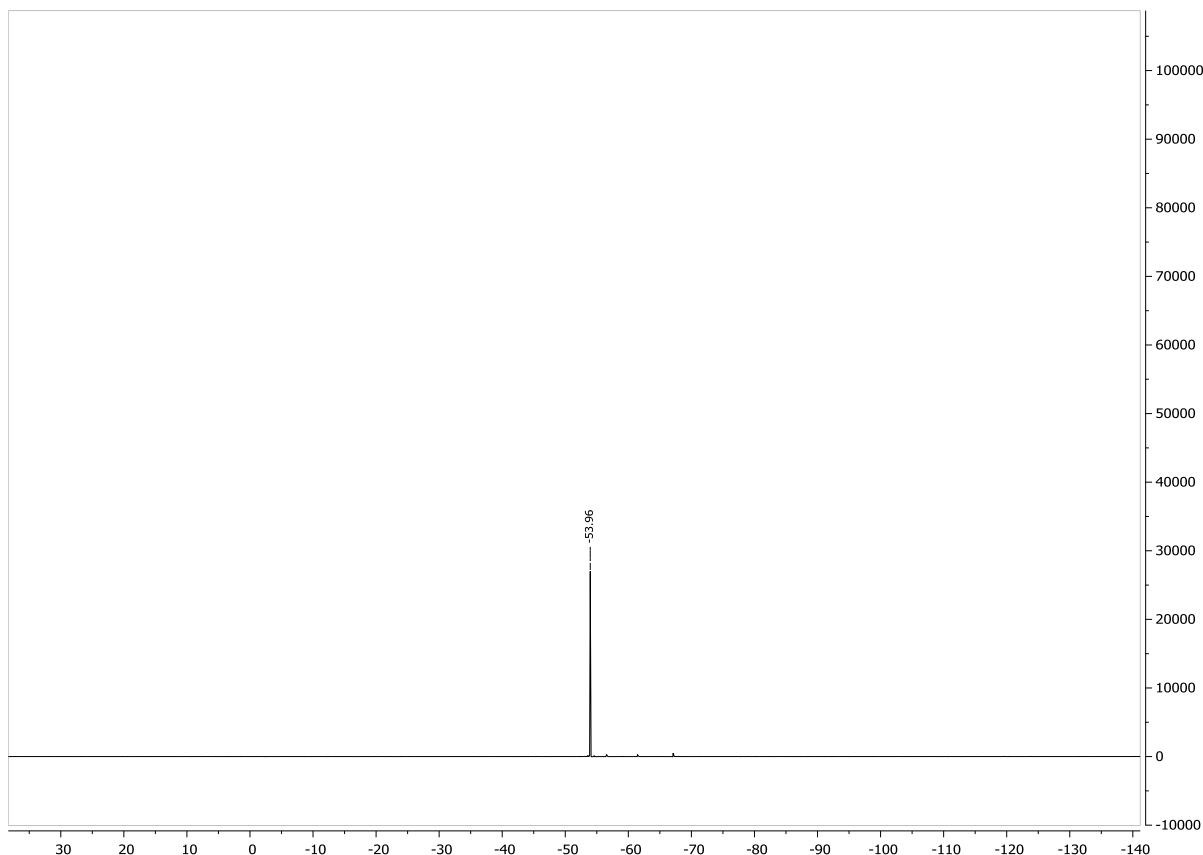
¹H NMR (CDCl_3 , 600 MHz)



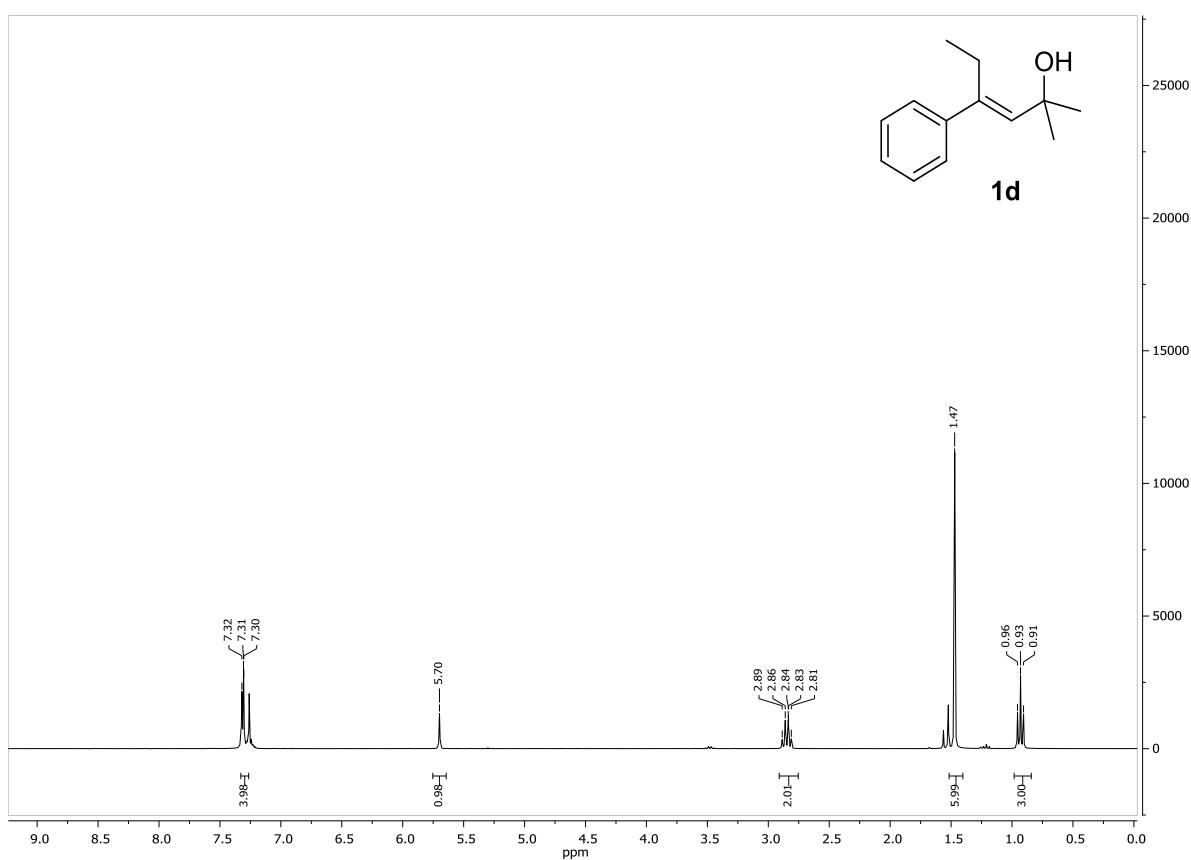
¹³C NMR (CDCl_3 , 151 MHz)



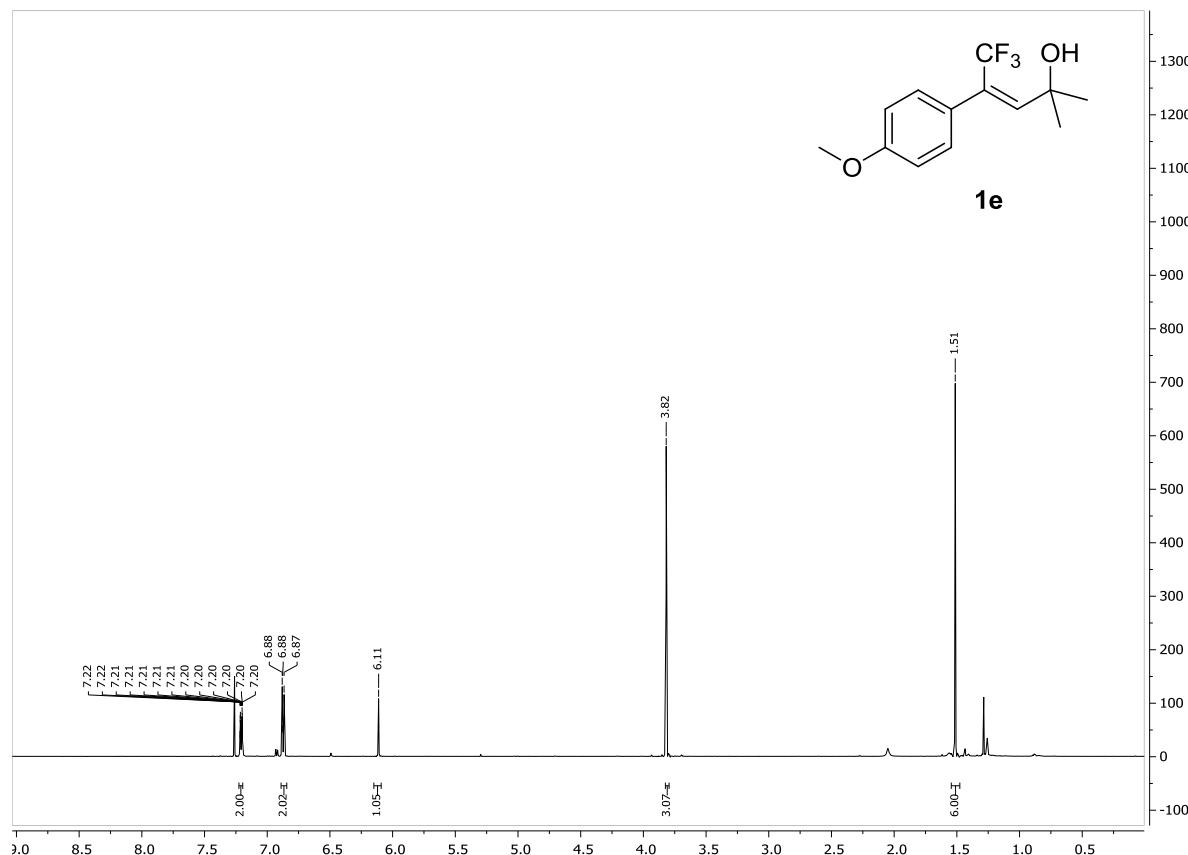
¹⁹F NMR (CDCl₃, 282 MHz)



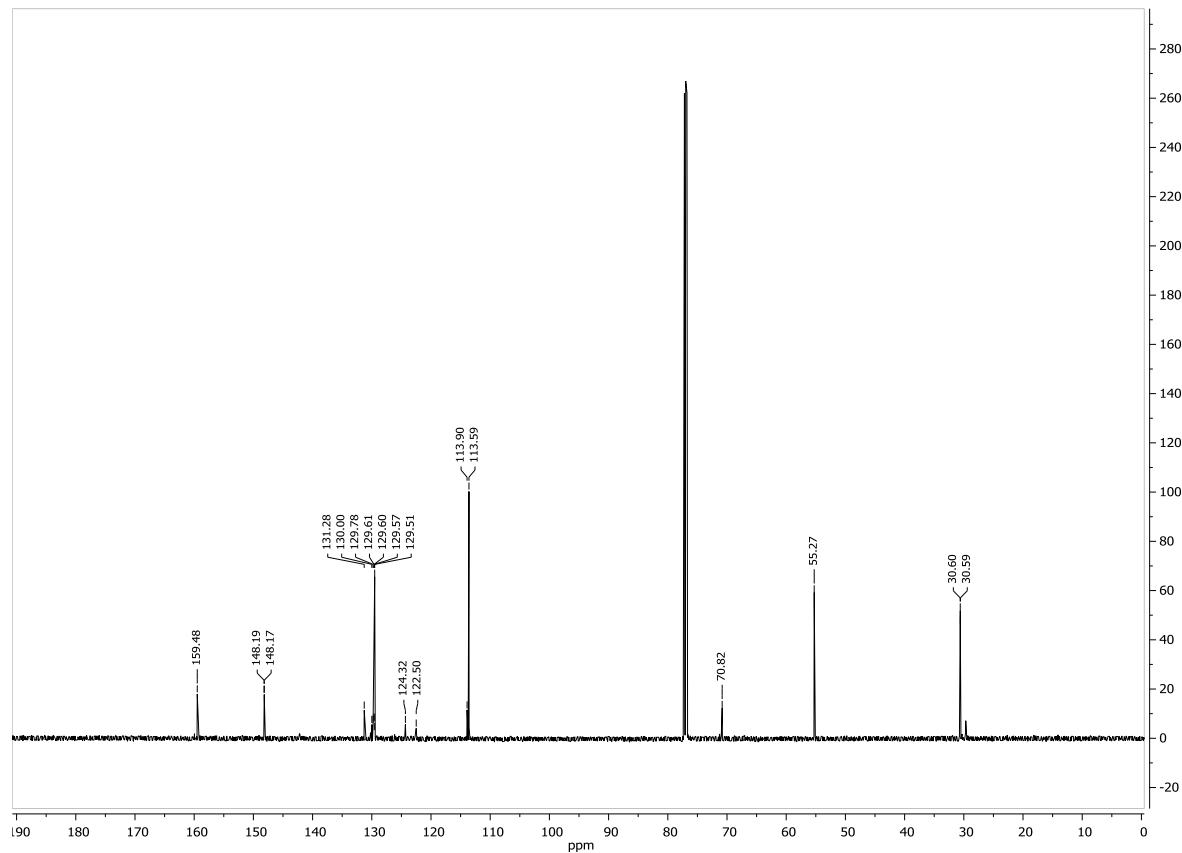
¹H NMR (CDCl₃, 400 MHz)



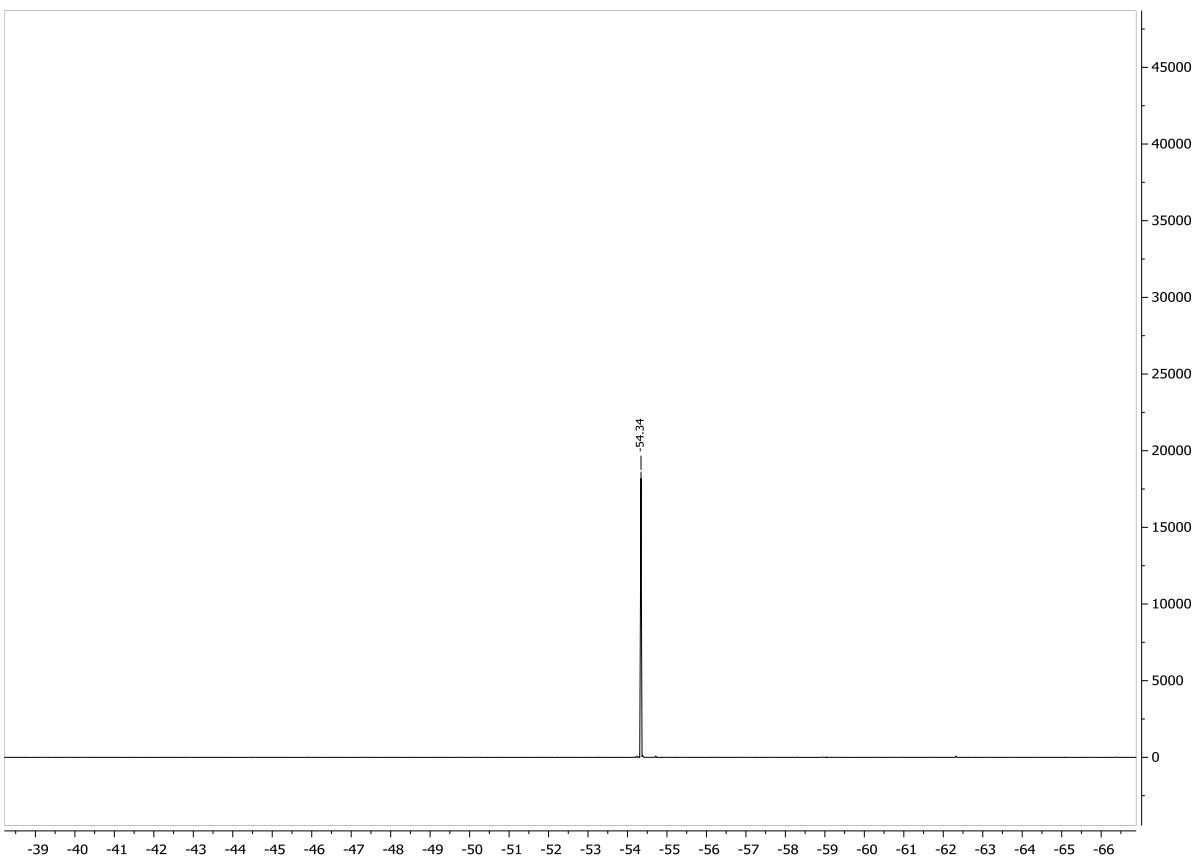
¹H NMR (CDCl₃, 600 MHz)



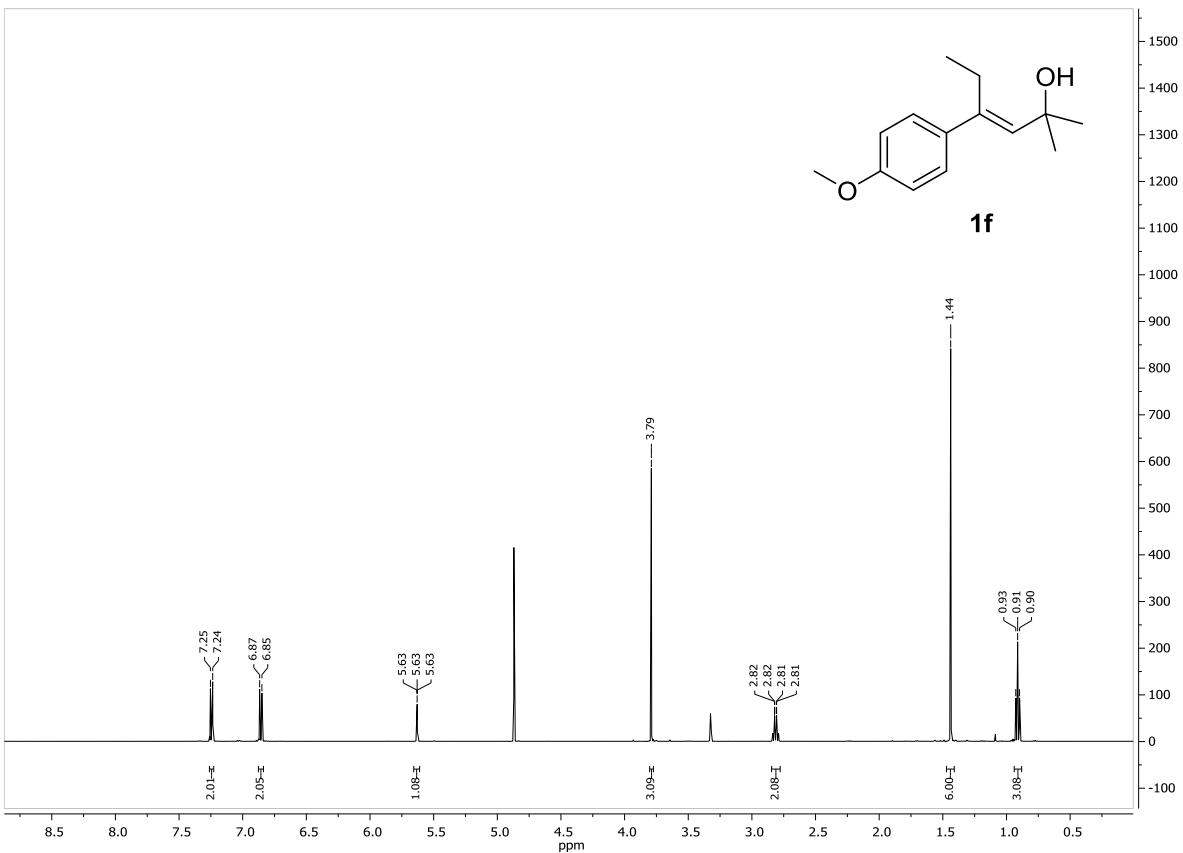
¹³C NMR (CDCl₃, 151 MHz)



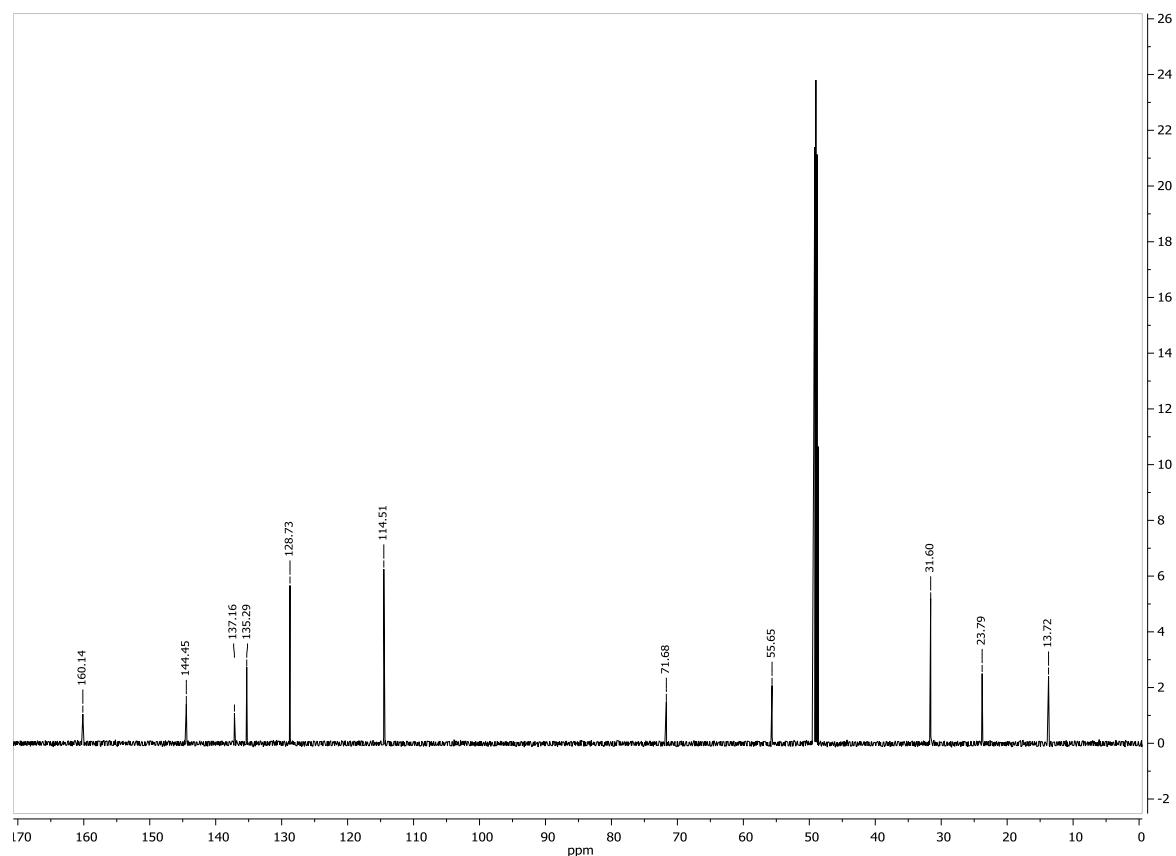
¹⁹F NMR (CDCl₃, 564 MHz)



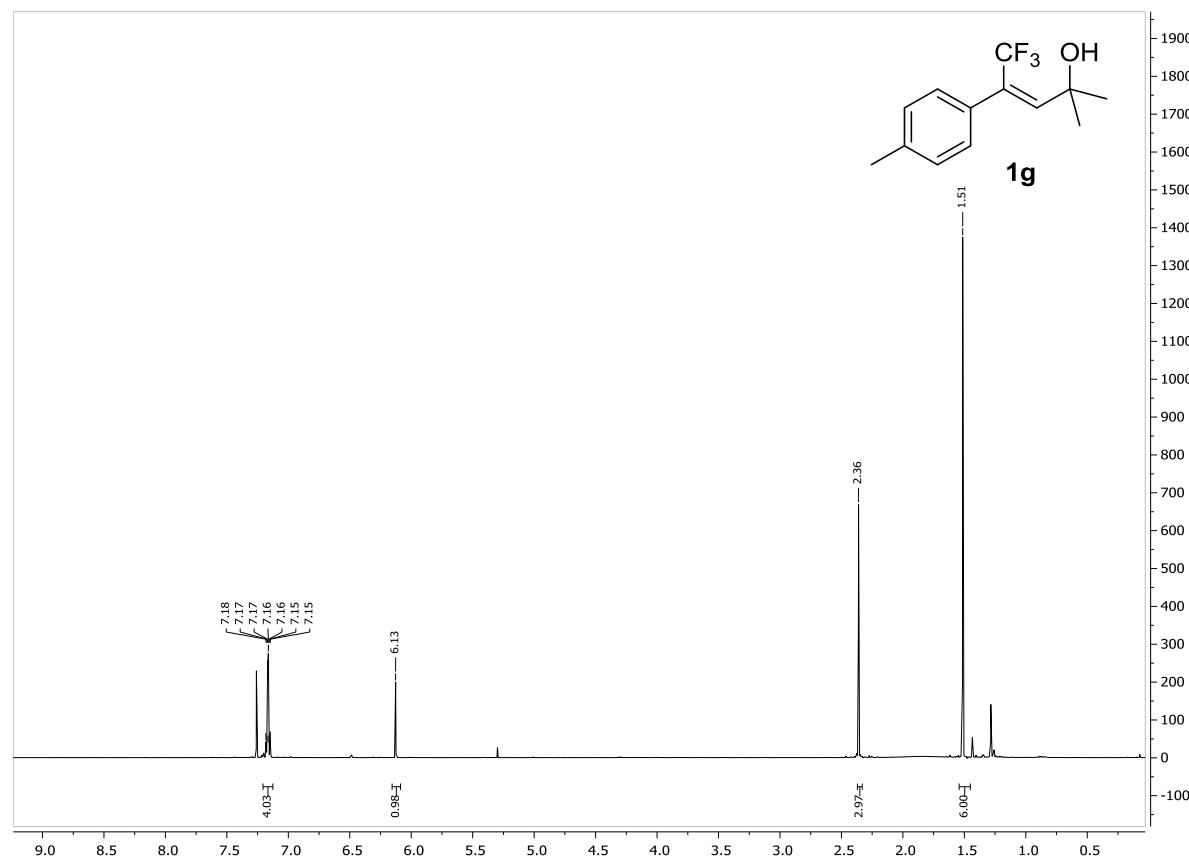
¹H NMR (CDOD₃, 500 MHz)



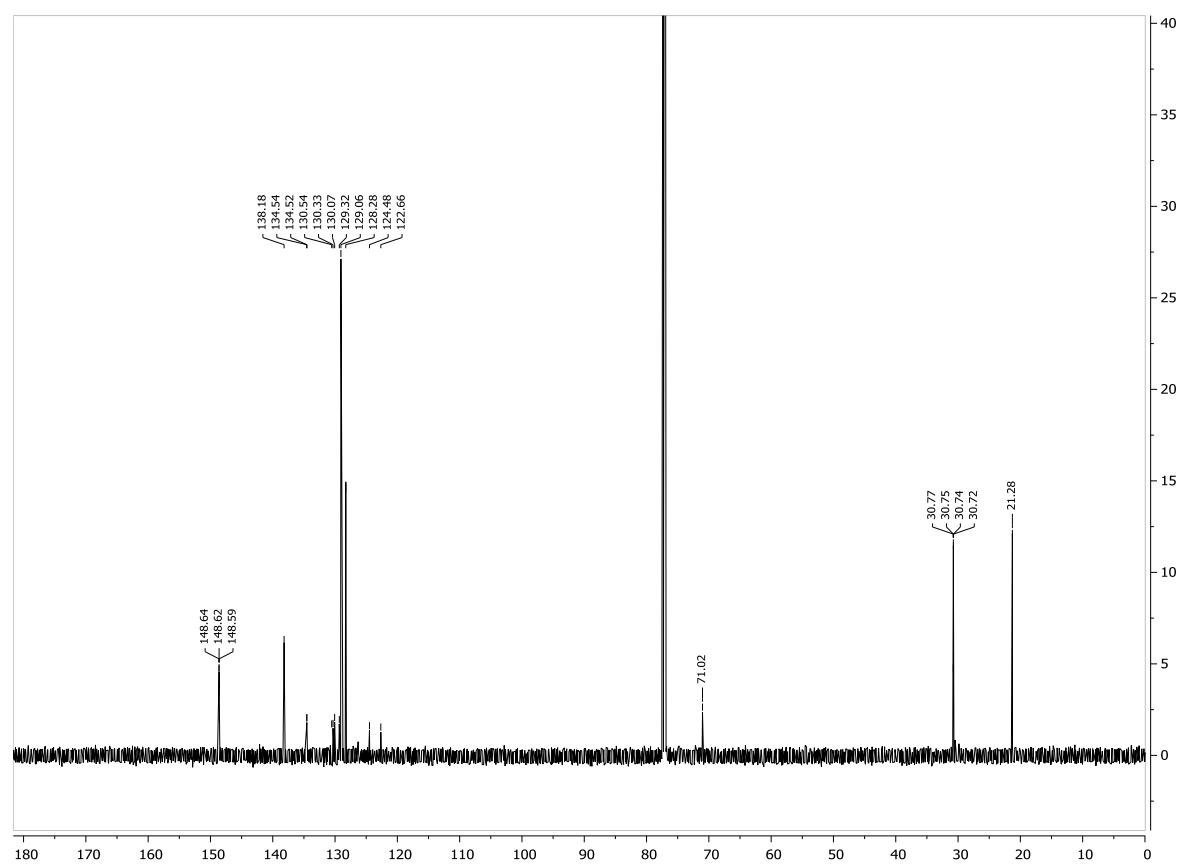
¹³C NMR (CDOD₃, 126 MHz)



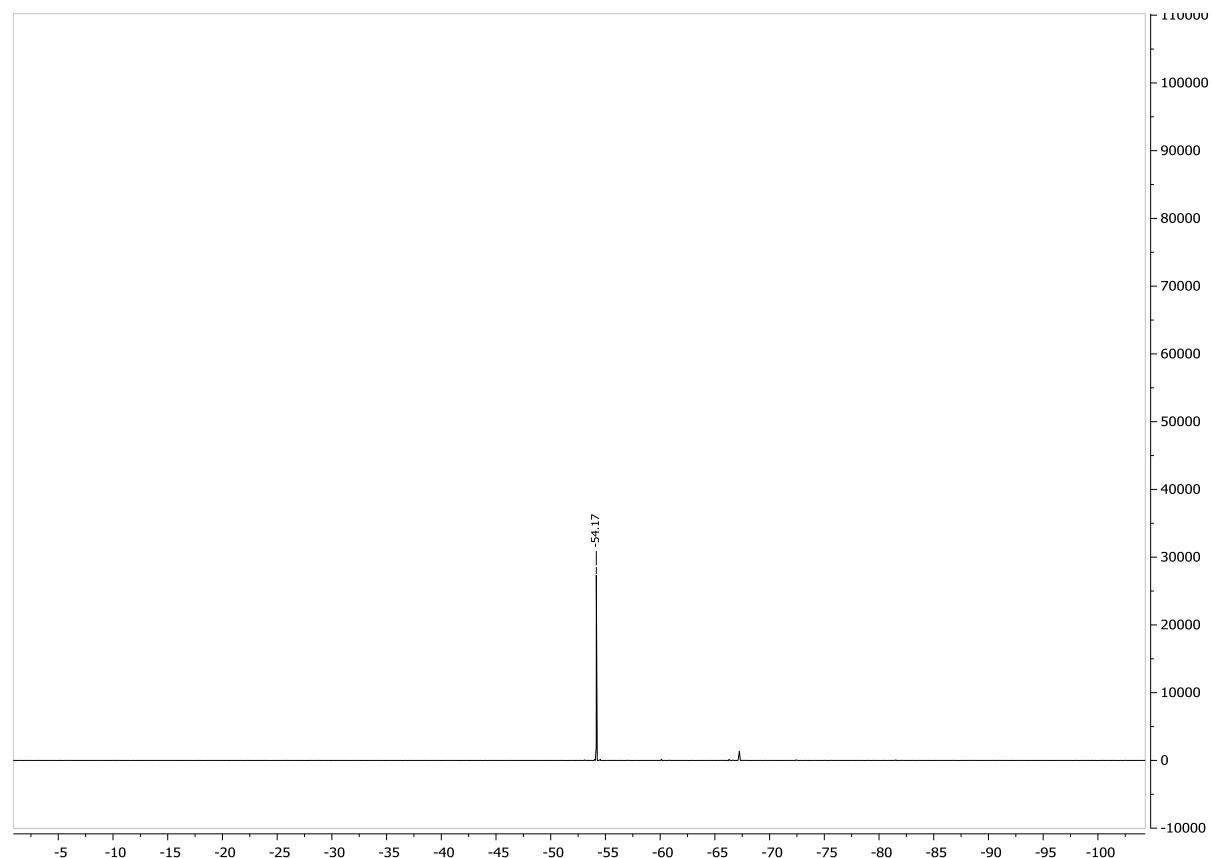
¹H NMR (CDCl₃, 600 MHz)



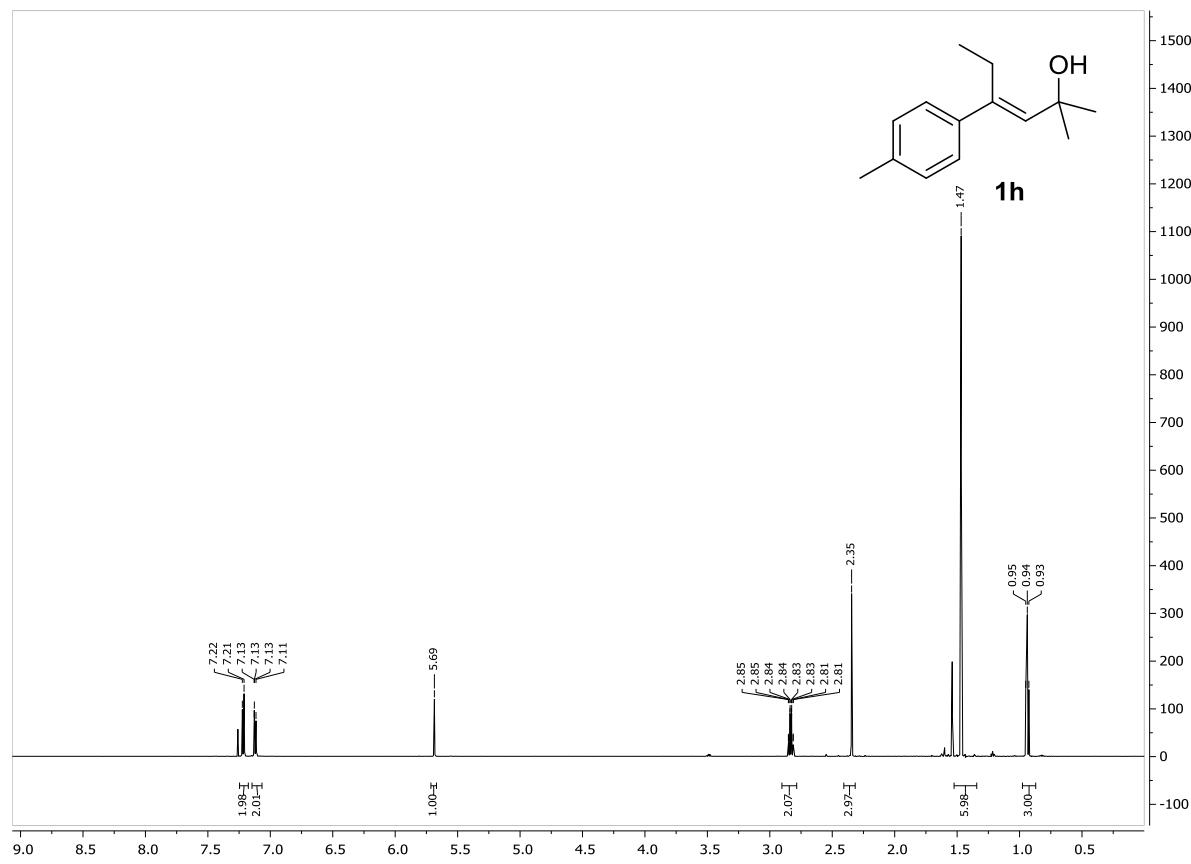
¹³C NMR (CDCl_3 , 151 MHz)



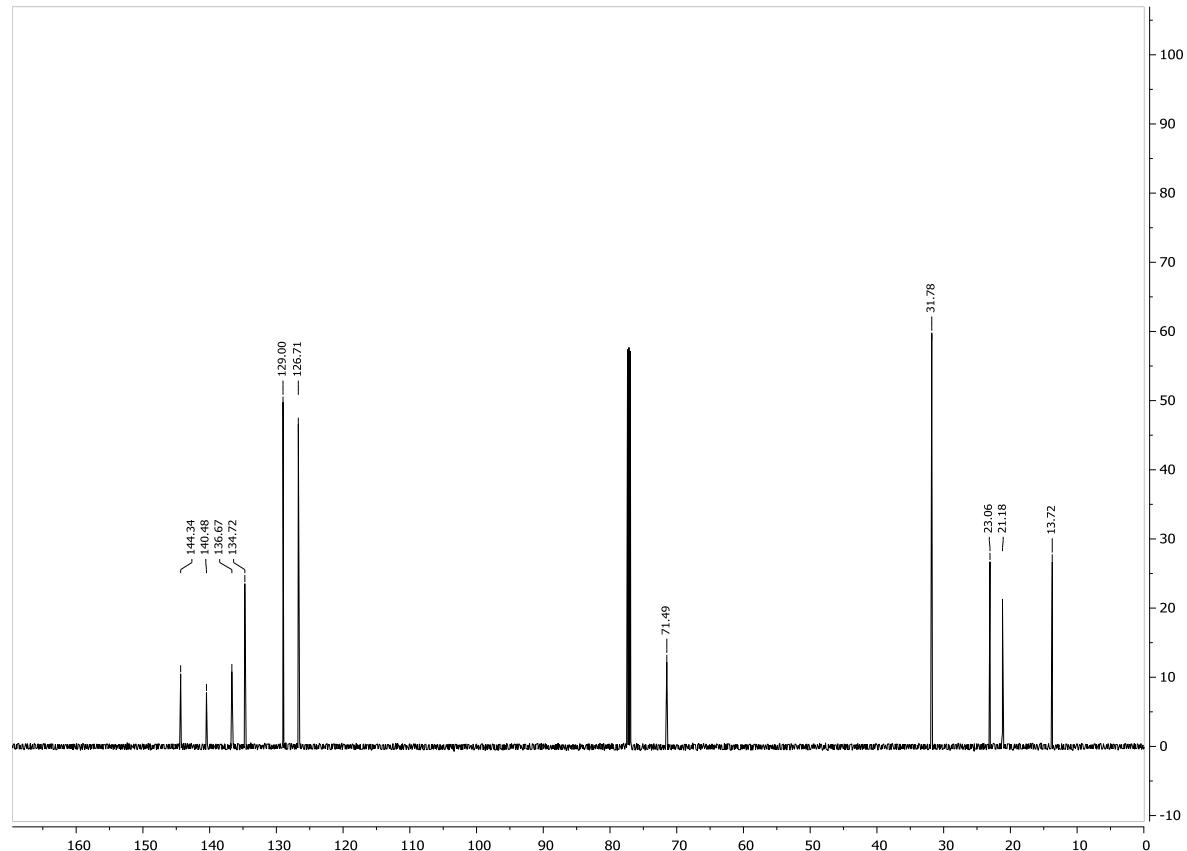
¹⁹F NMR (CDCl_3 , 564 MHz)



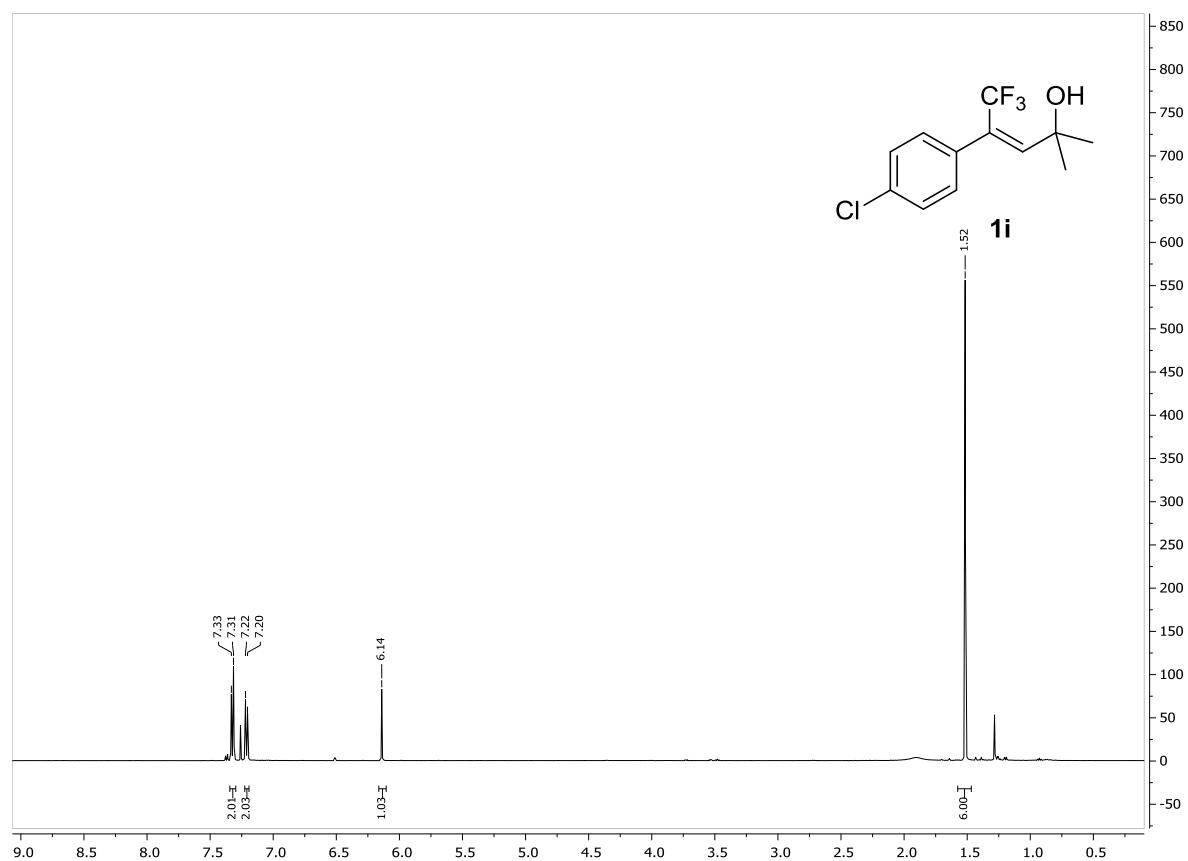
¹H NMR (CDCl₃, 600 MHz)



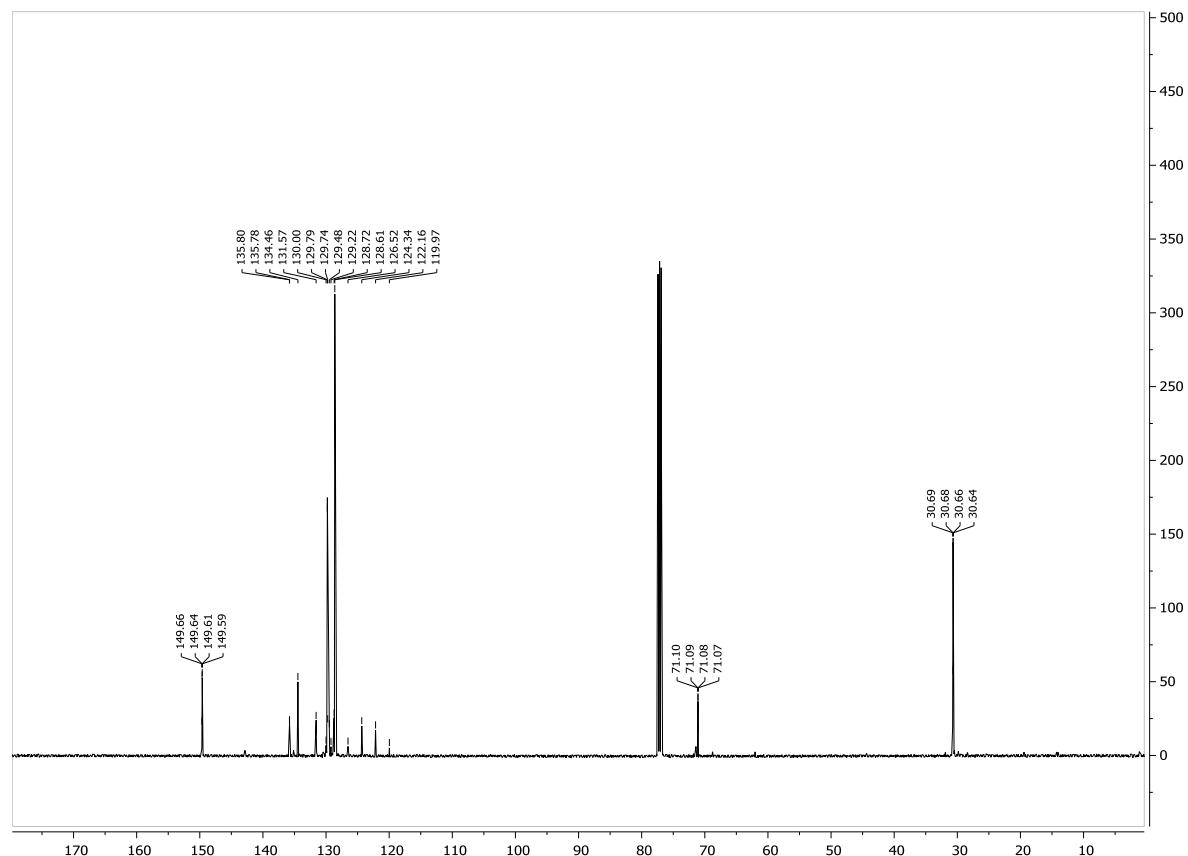
¹³C NMR (CDCl₃, 151 MHz)



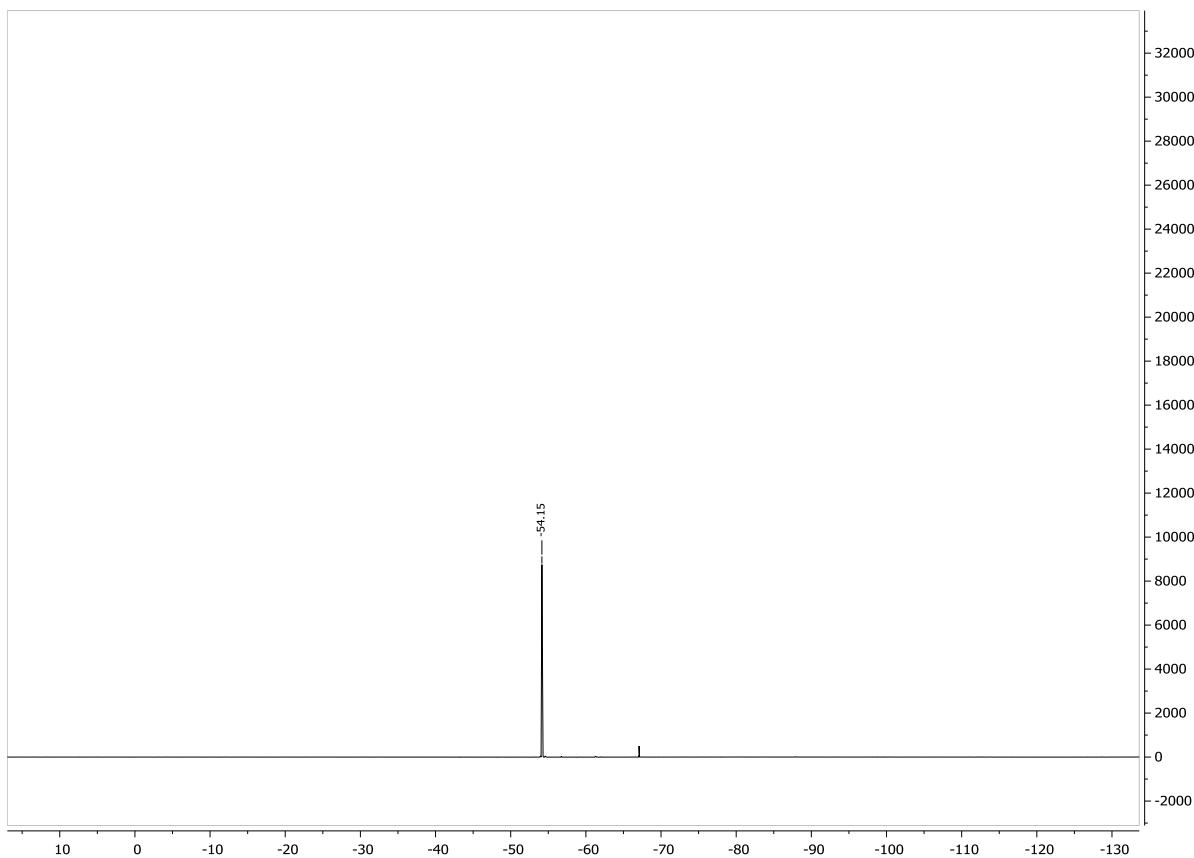
¹H NMR (CDCl₃, 500 MHz)



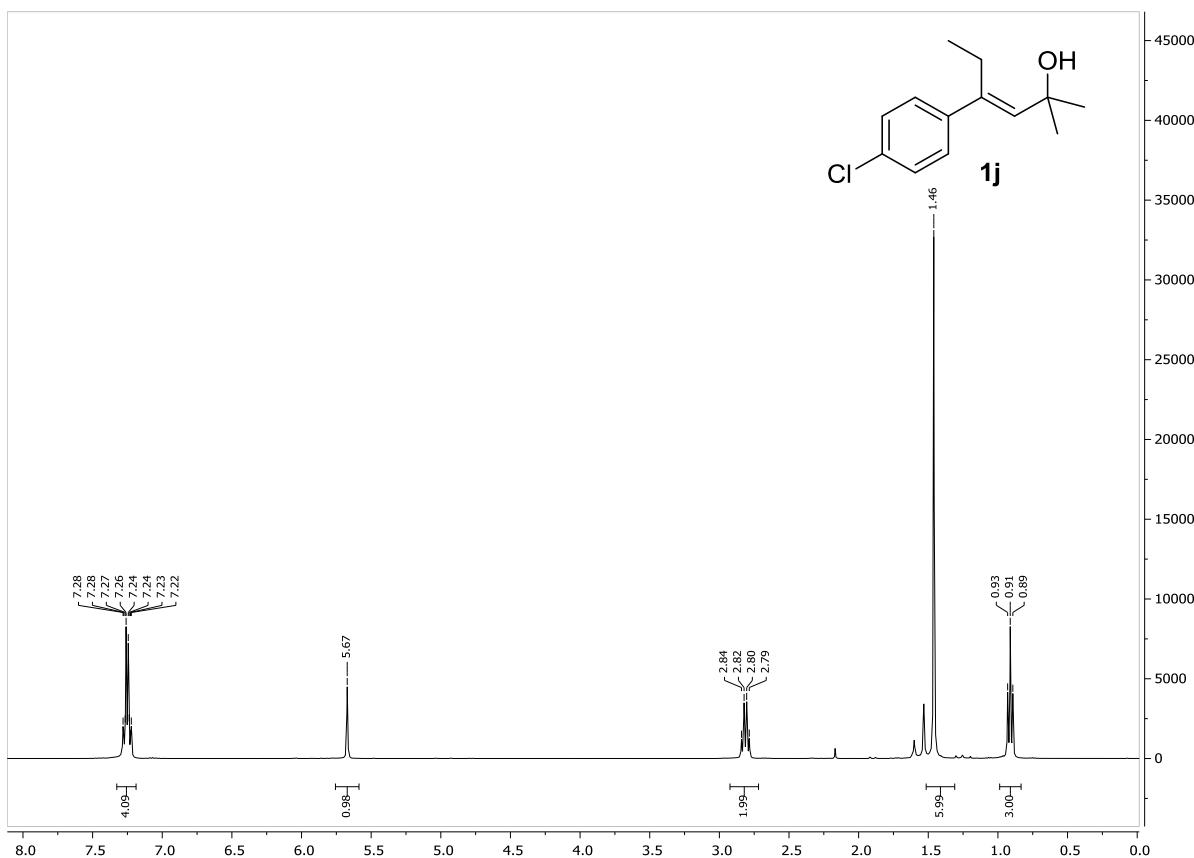
¹³C NMR (CDCl₃, 126 MHz)



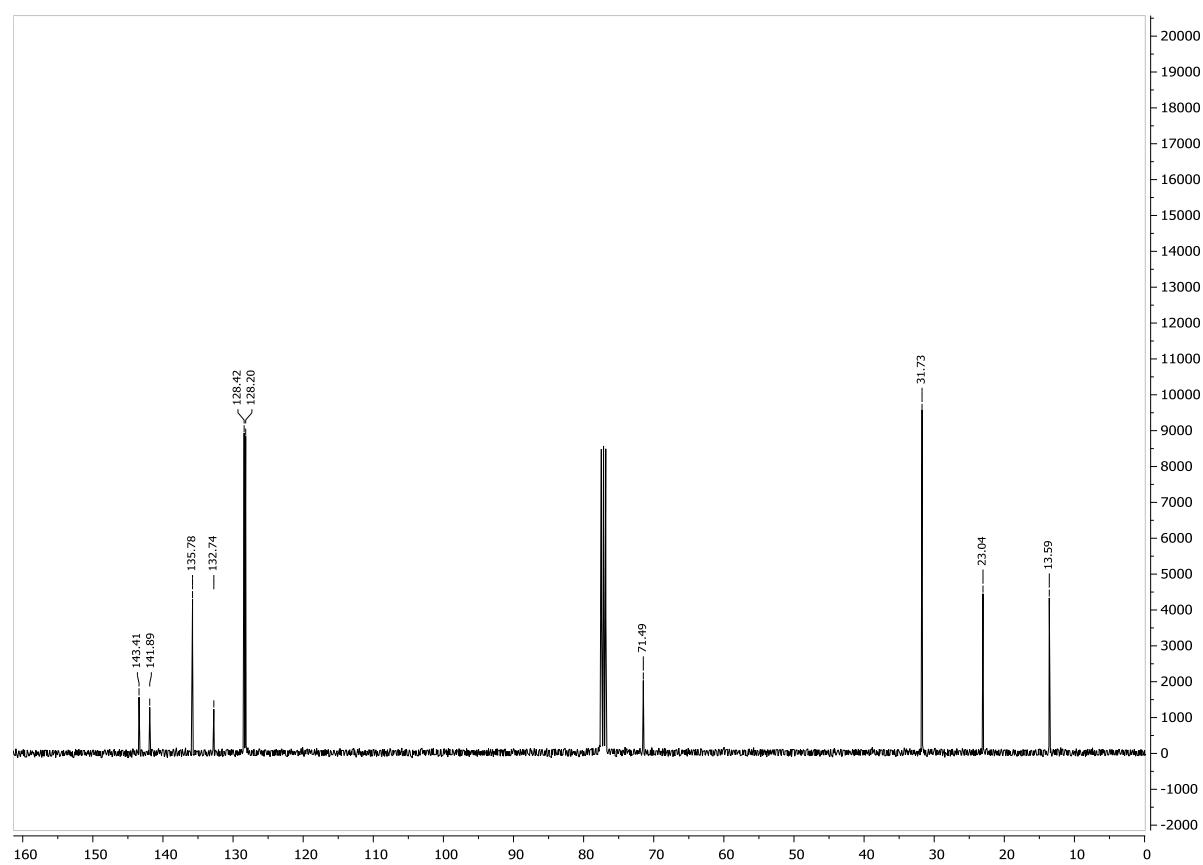
¹⁹F NMR (CDCl₃, 470 MHz)



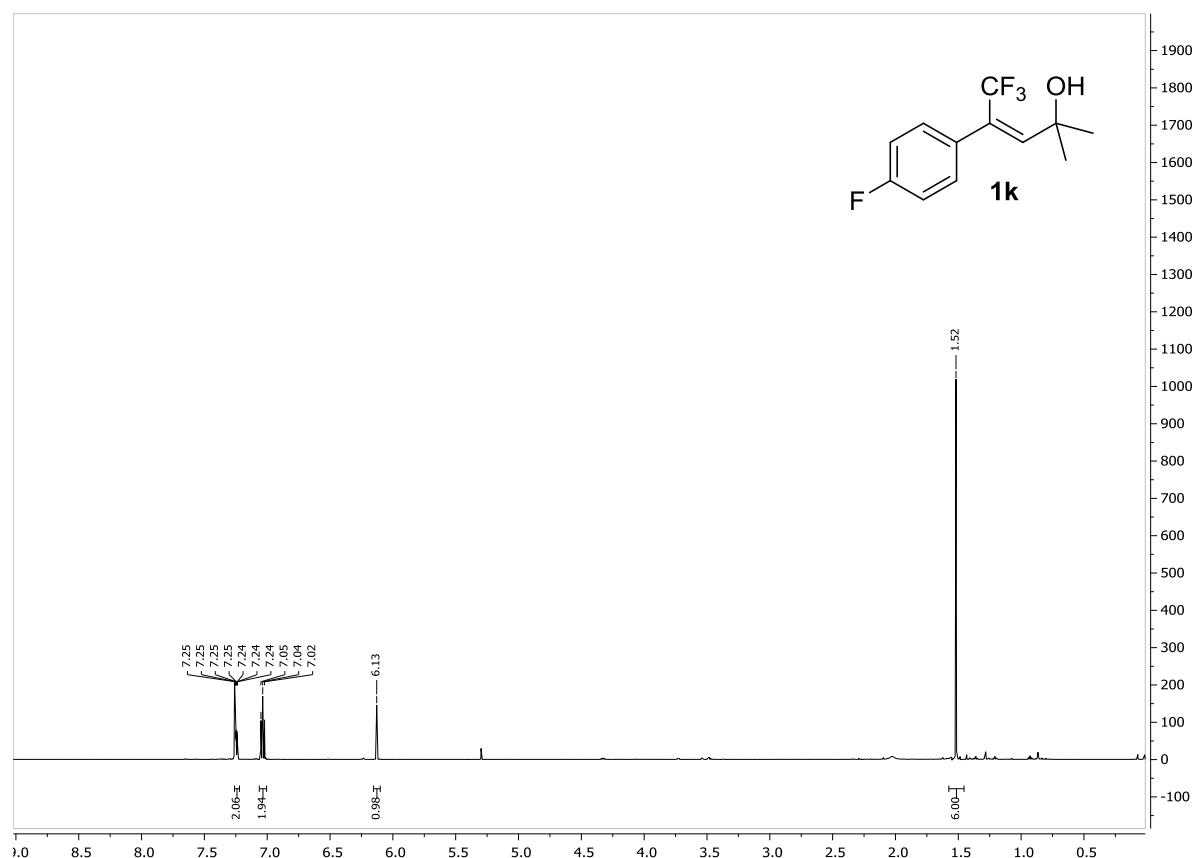
¹H NMR (CDCl₃, 400 MHz)



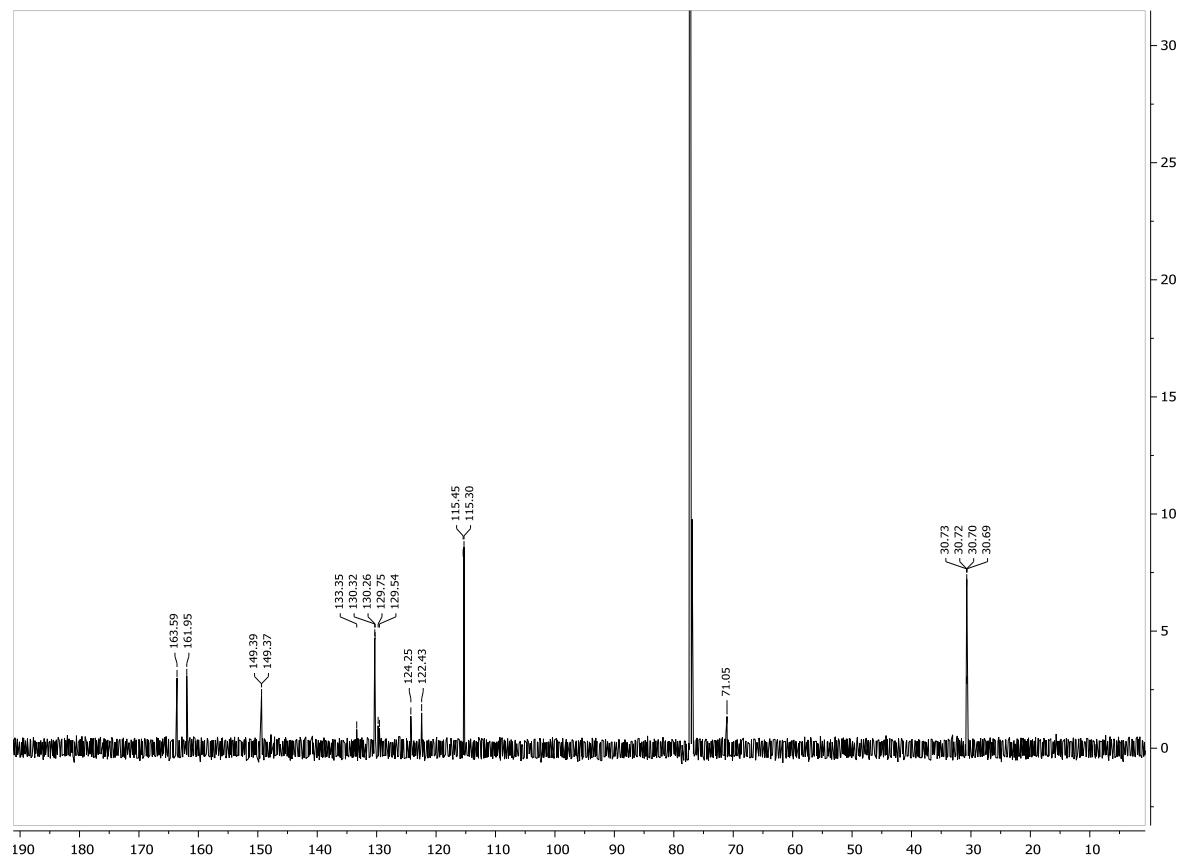
¹³C NMR (CDCl_3 , 101 MHz)



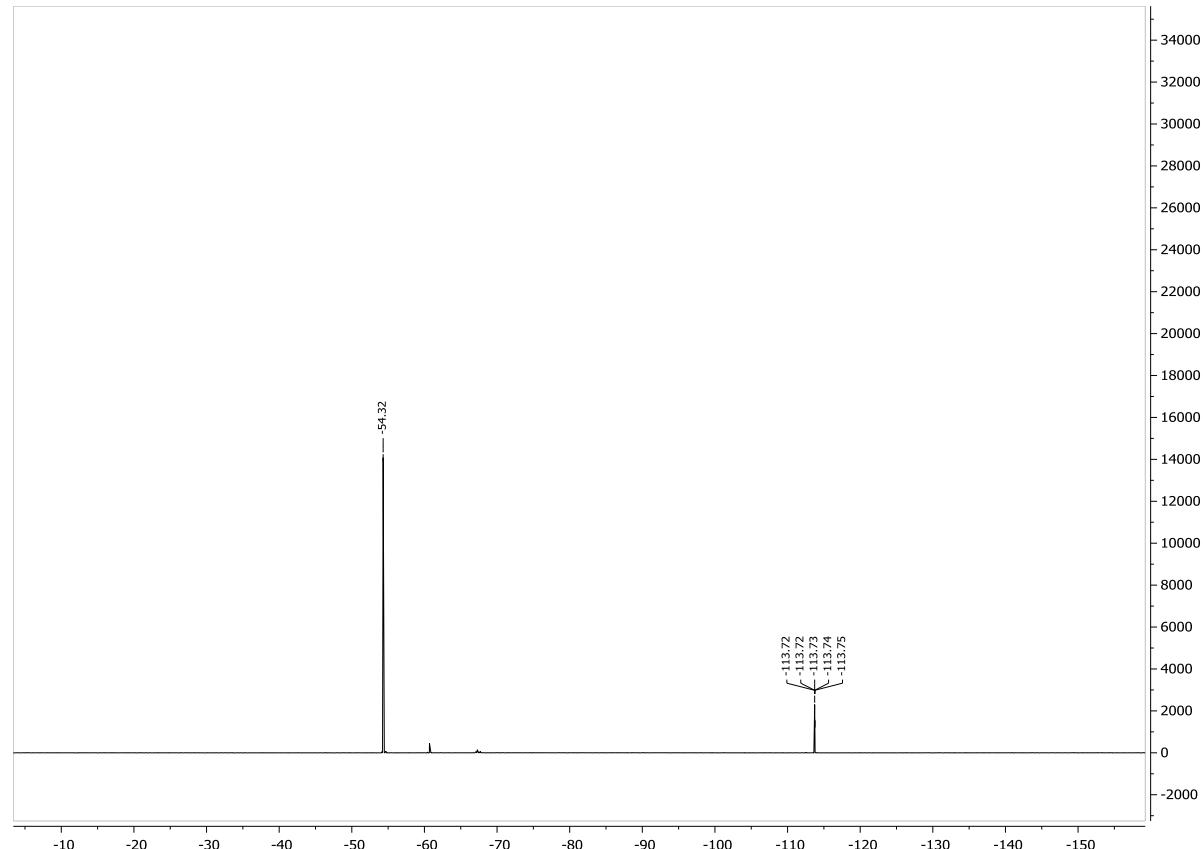
¹H NMR (CDCl_3 , 600 MHz)



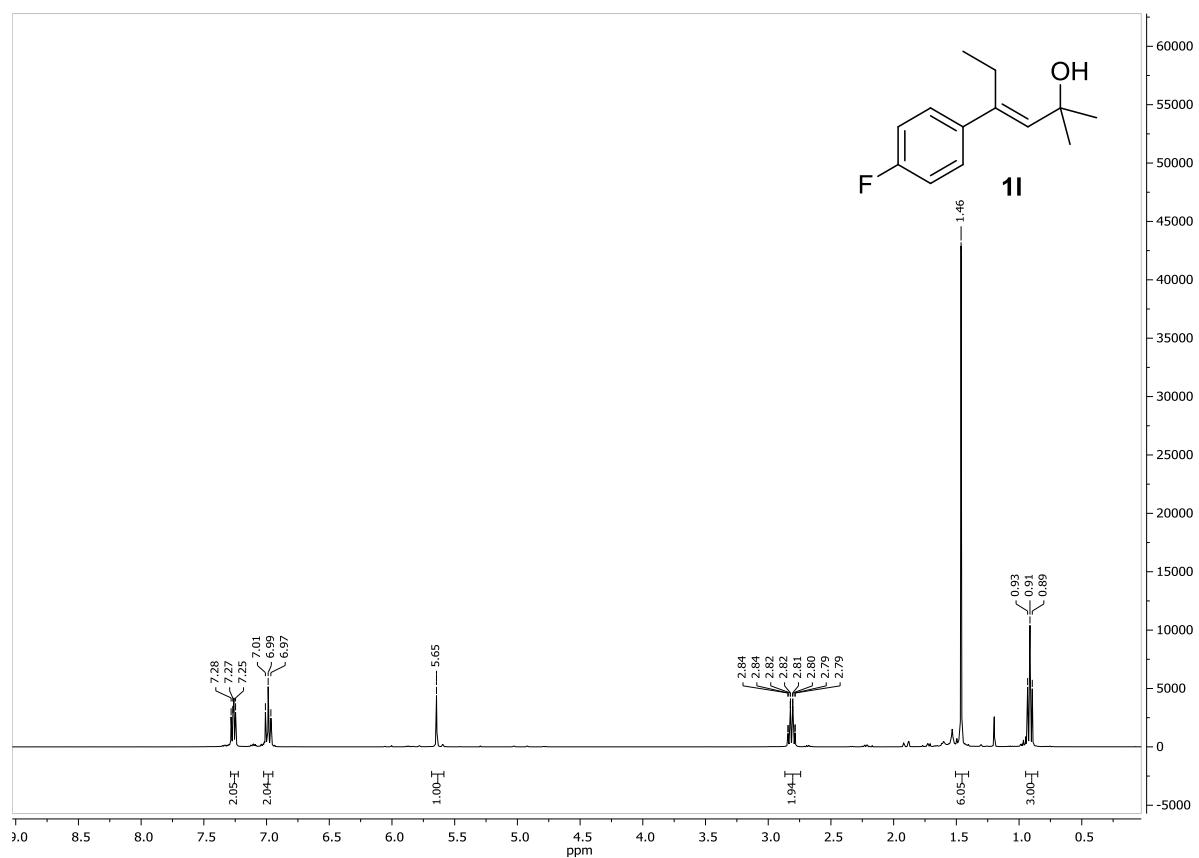
^{13}C NMR (CDCl_3 , 151 MHz)



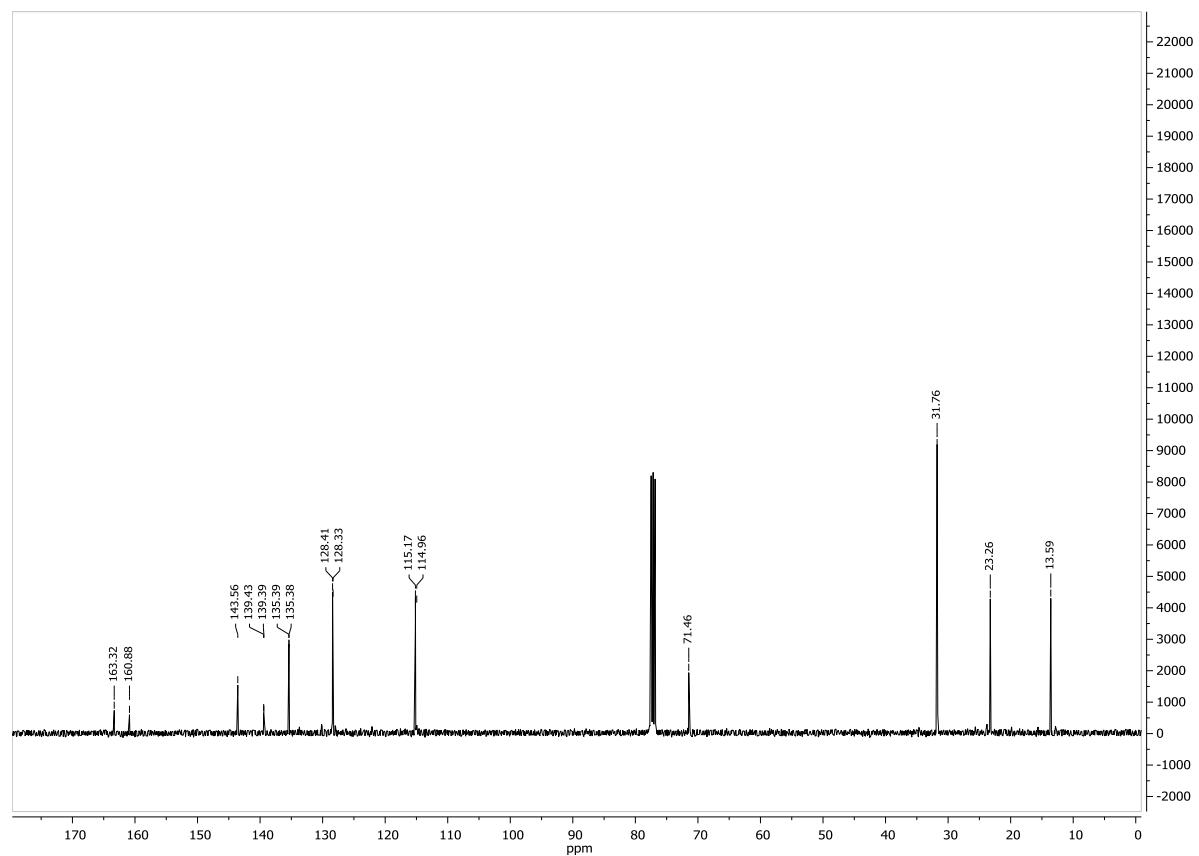
^{19}F NMR (CDCl_3 , 564 MHz)



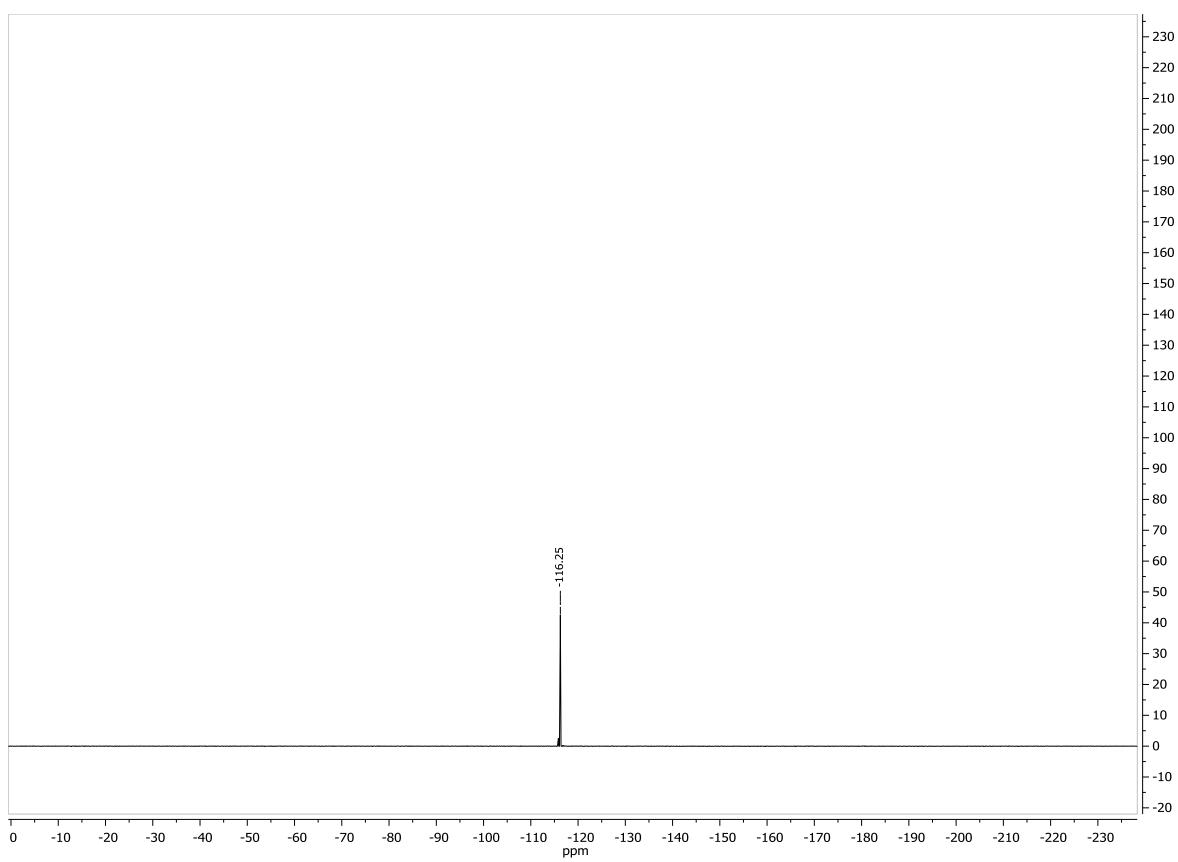
¹H NMR (CDCl₃, 400 MHz)



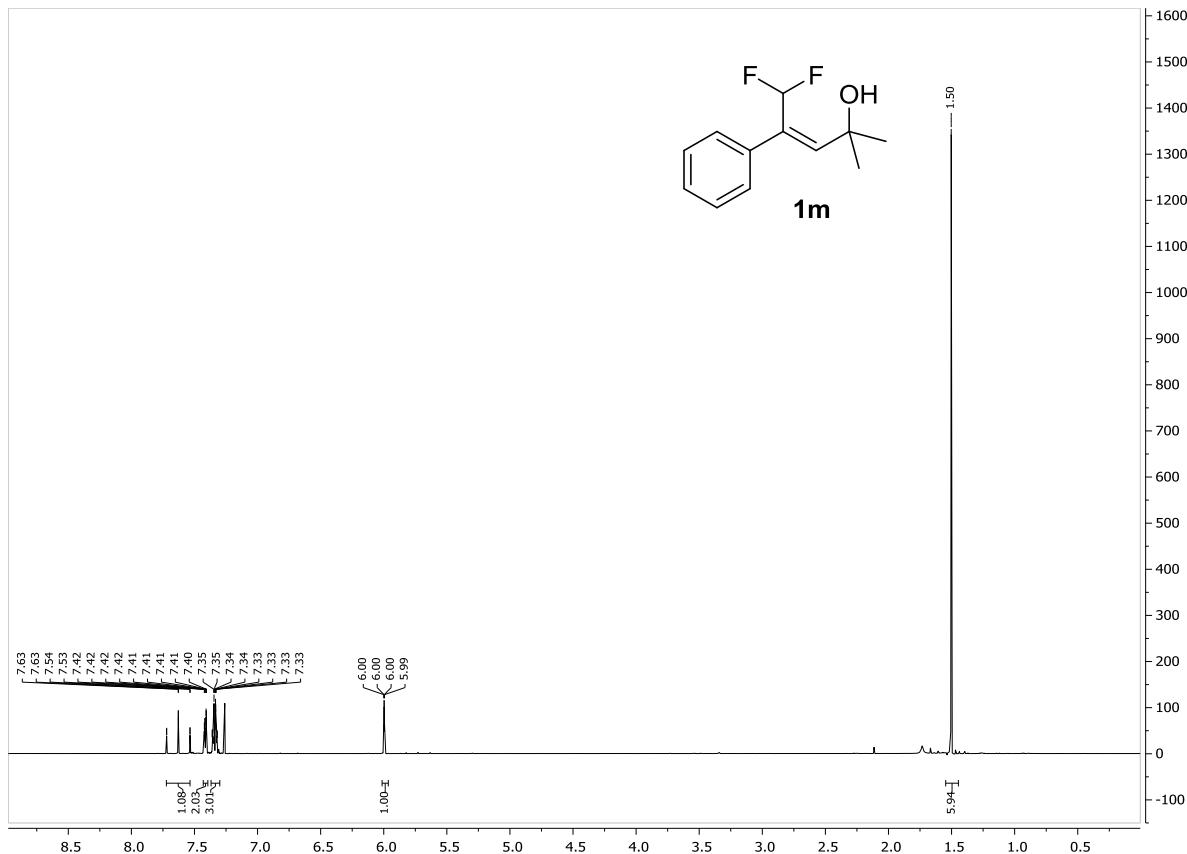
¹³C NMR (CDCl₃, 101 MHz)



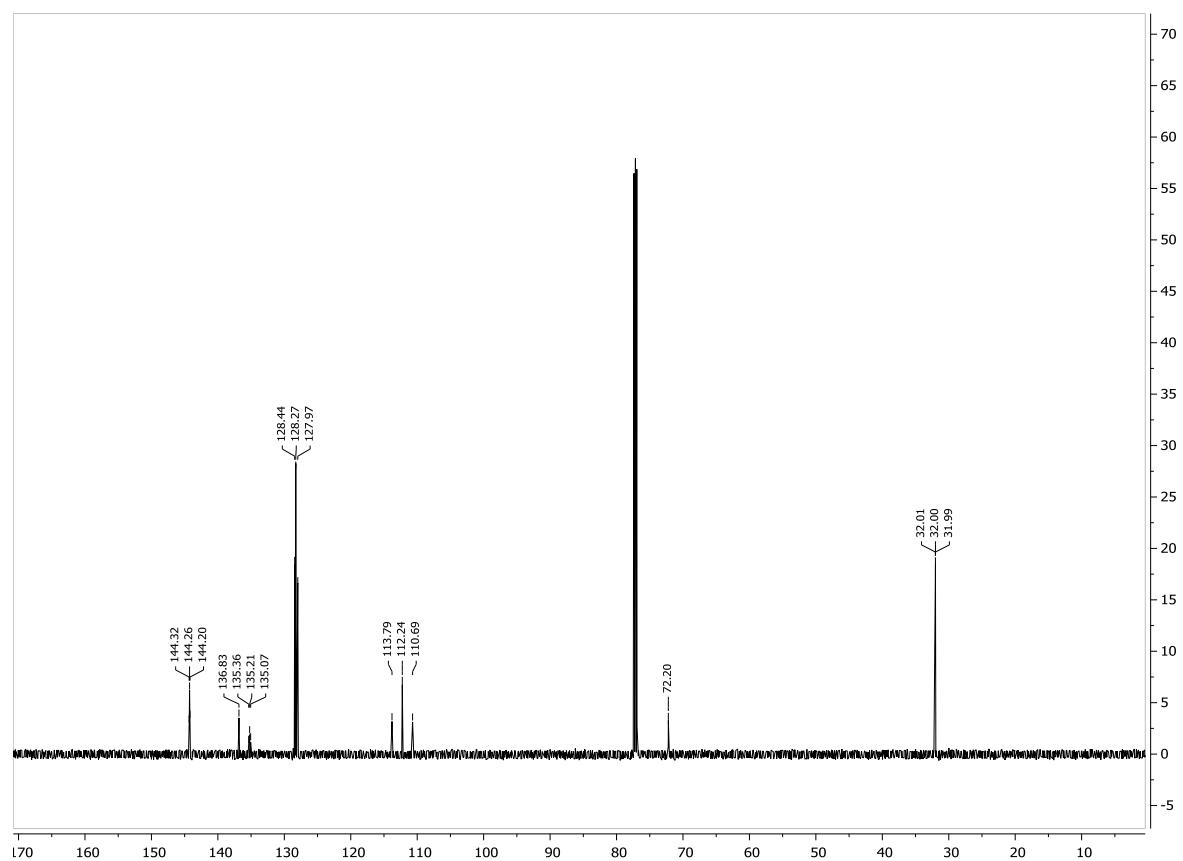
¹⁹F NMR (CDCl_3 , 282 MHz)



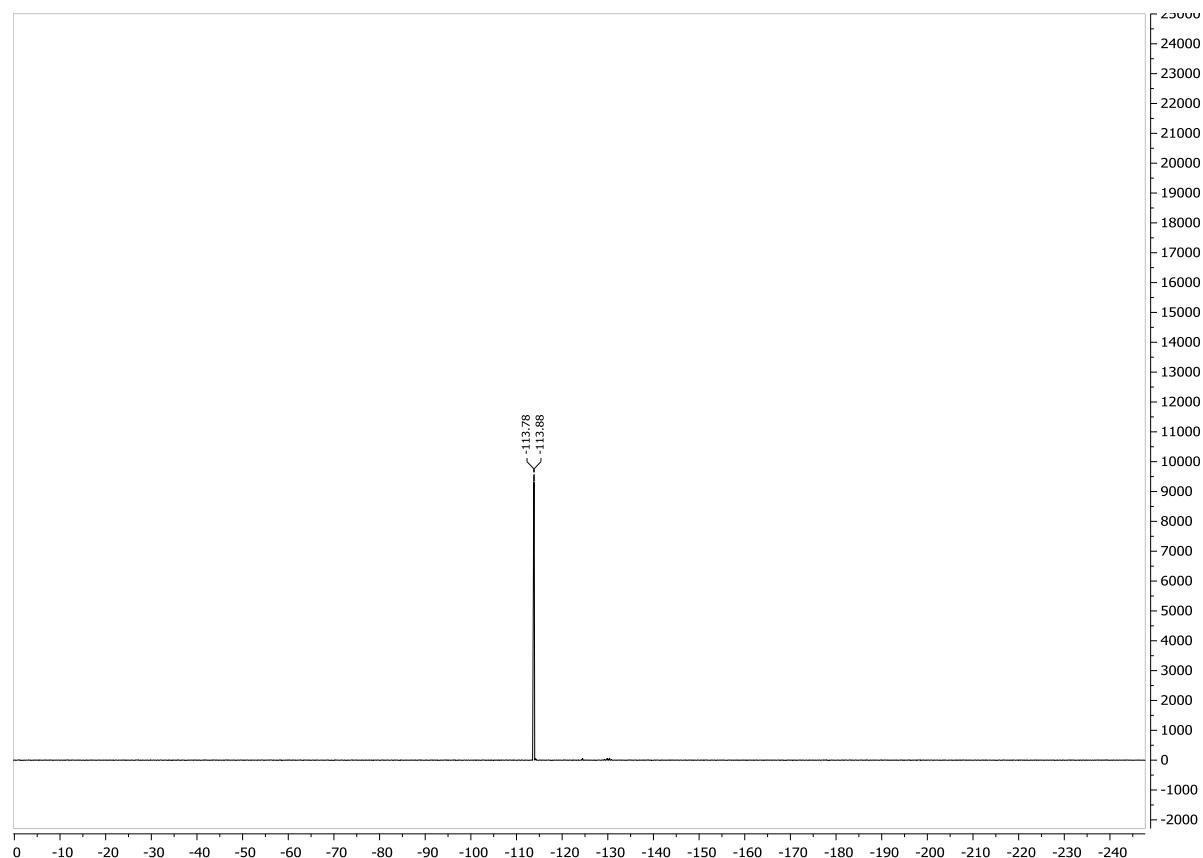
¹H NMR (CDCl_3 , 600 MHz)



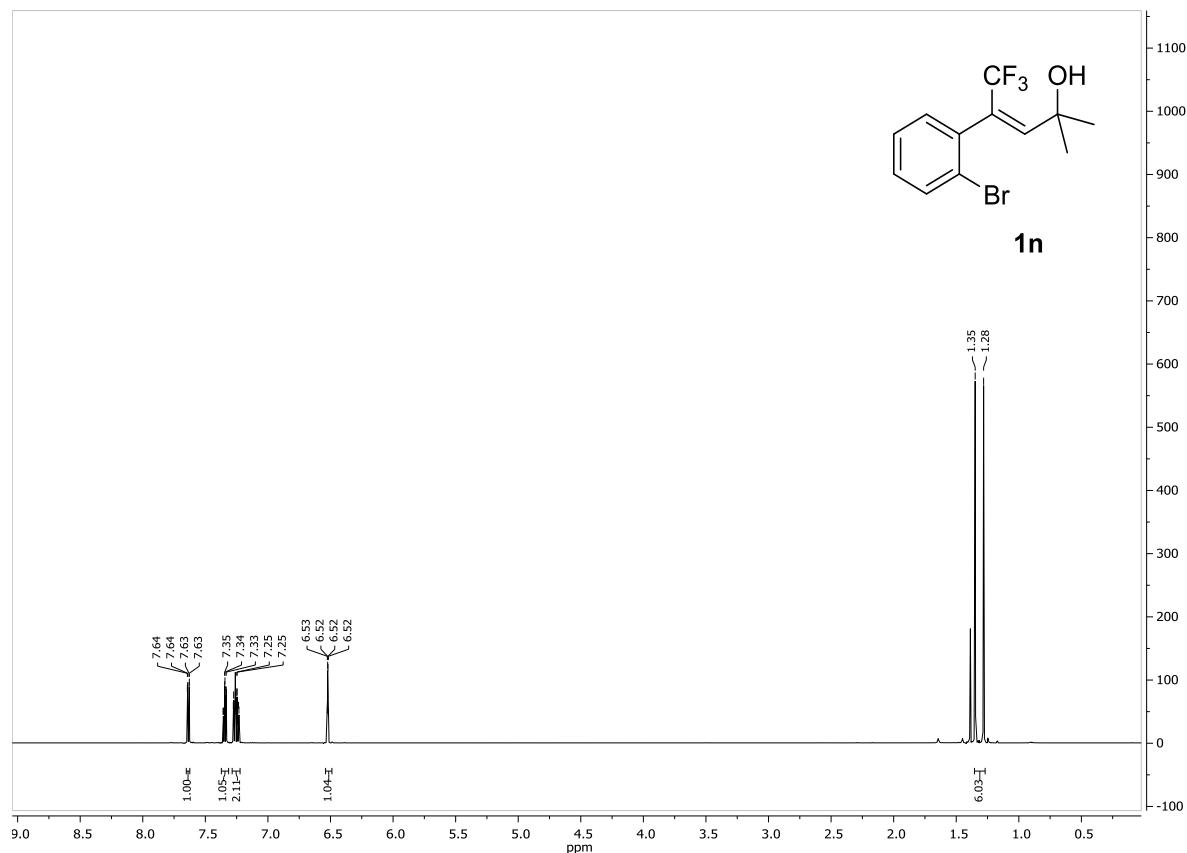
¹³C NMR (CDCl_3 , 151 MHz)



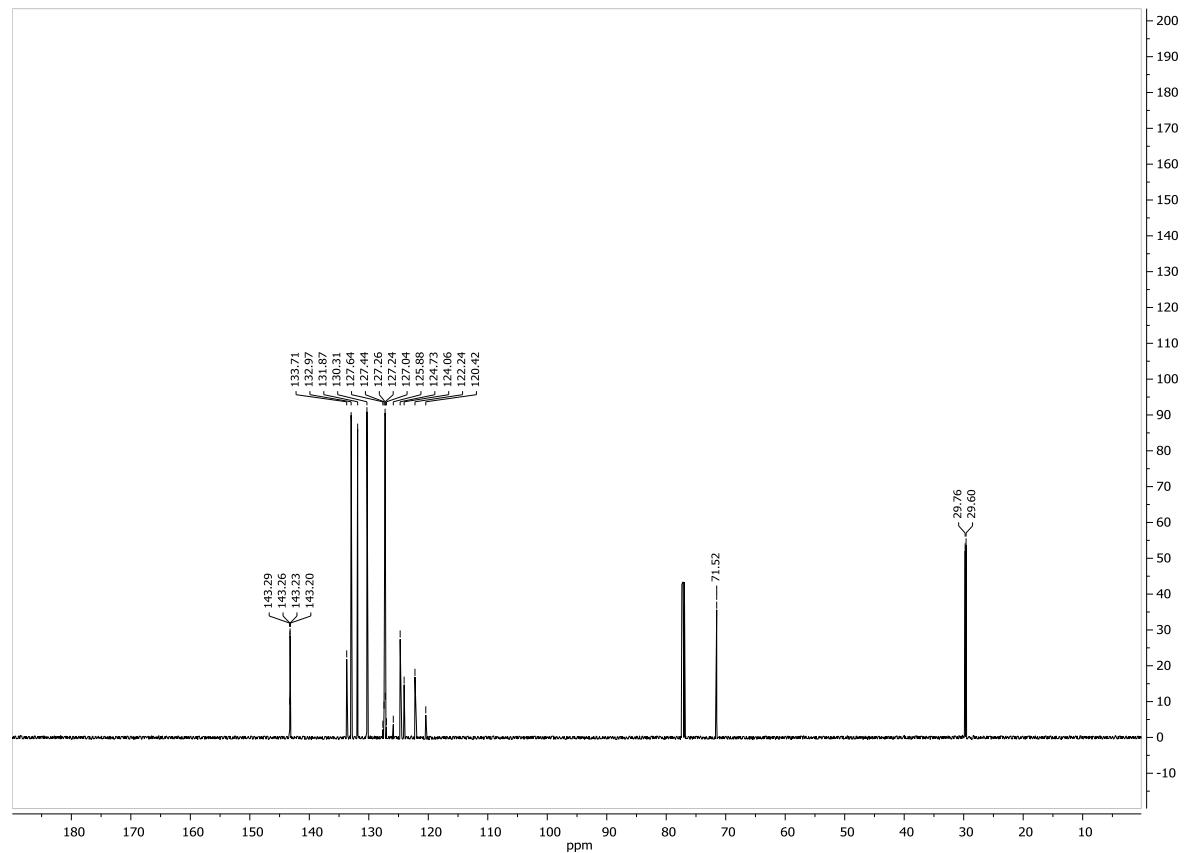
¹⁹F NMR (CDCl_3 , 564 MHz)



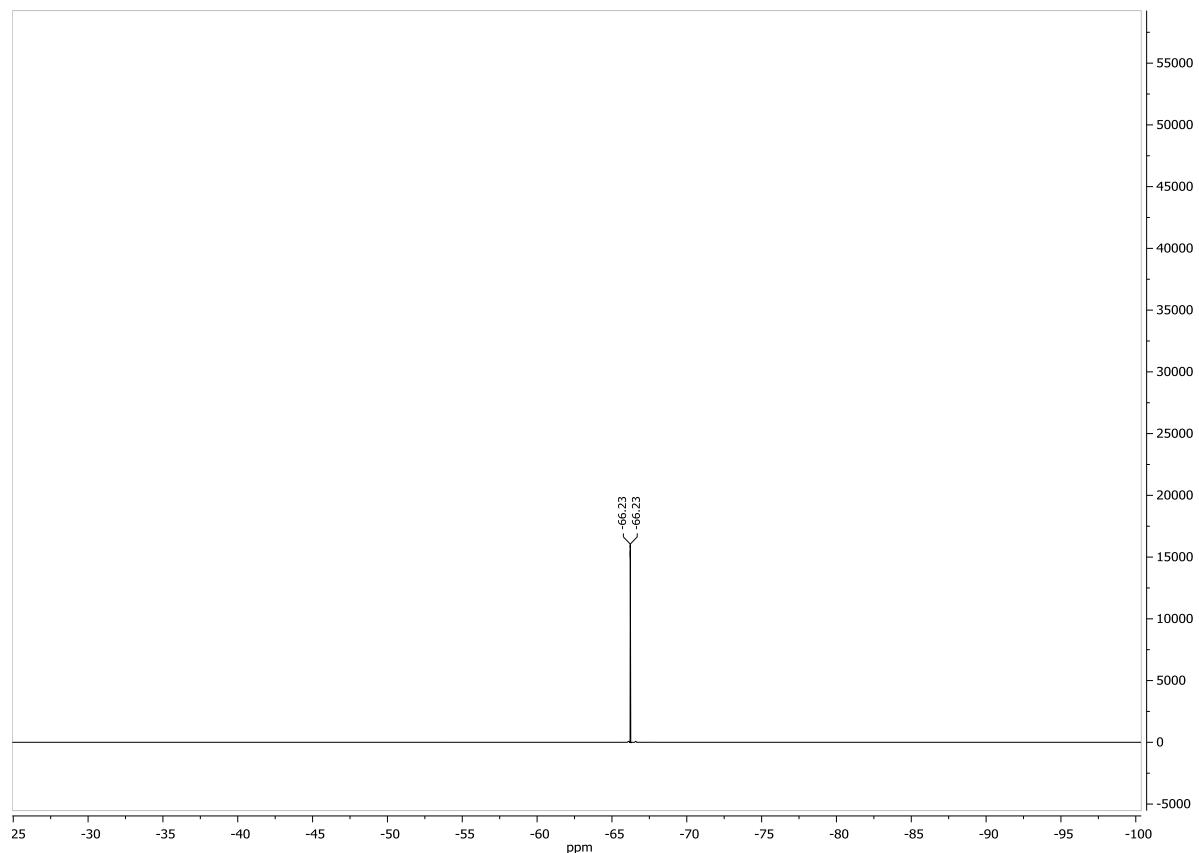
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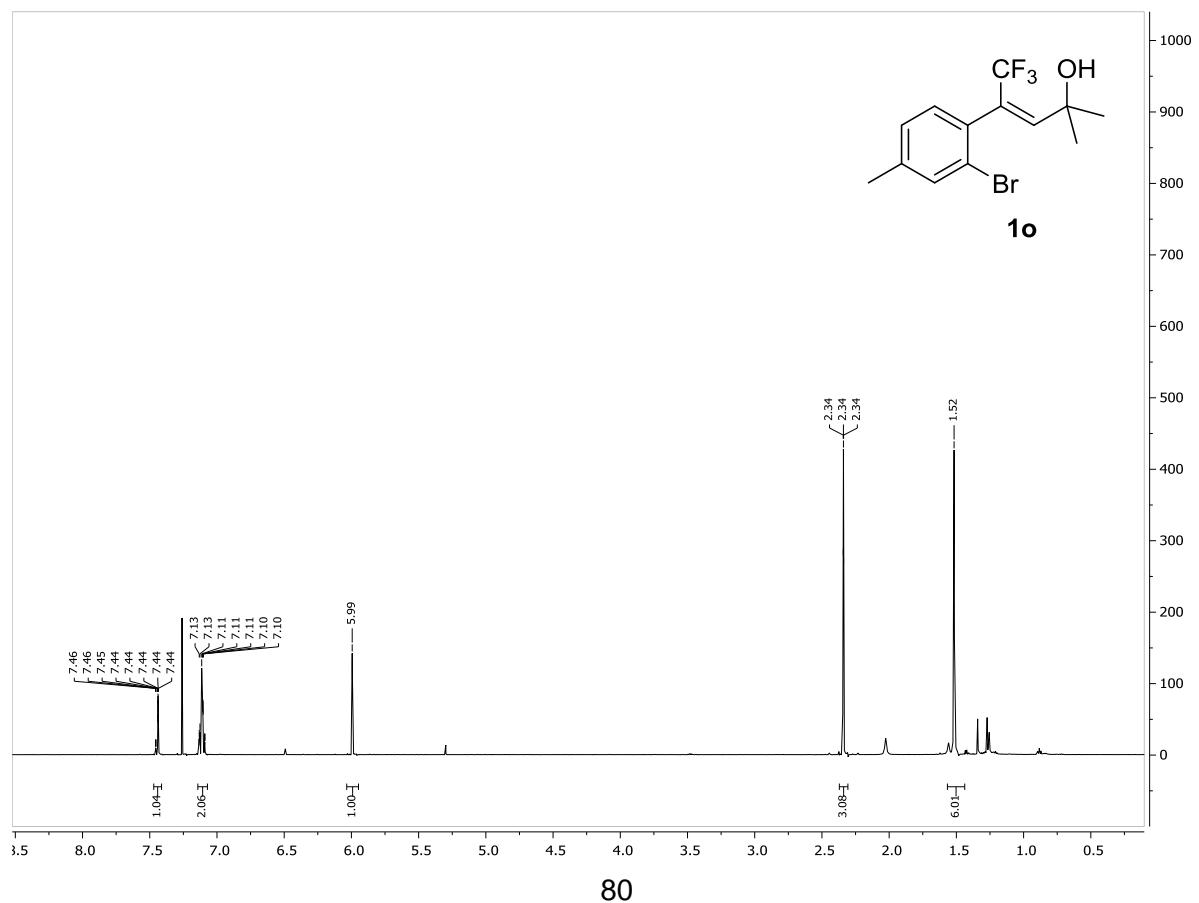
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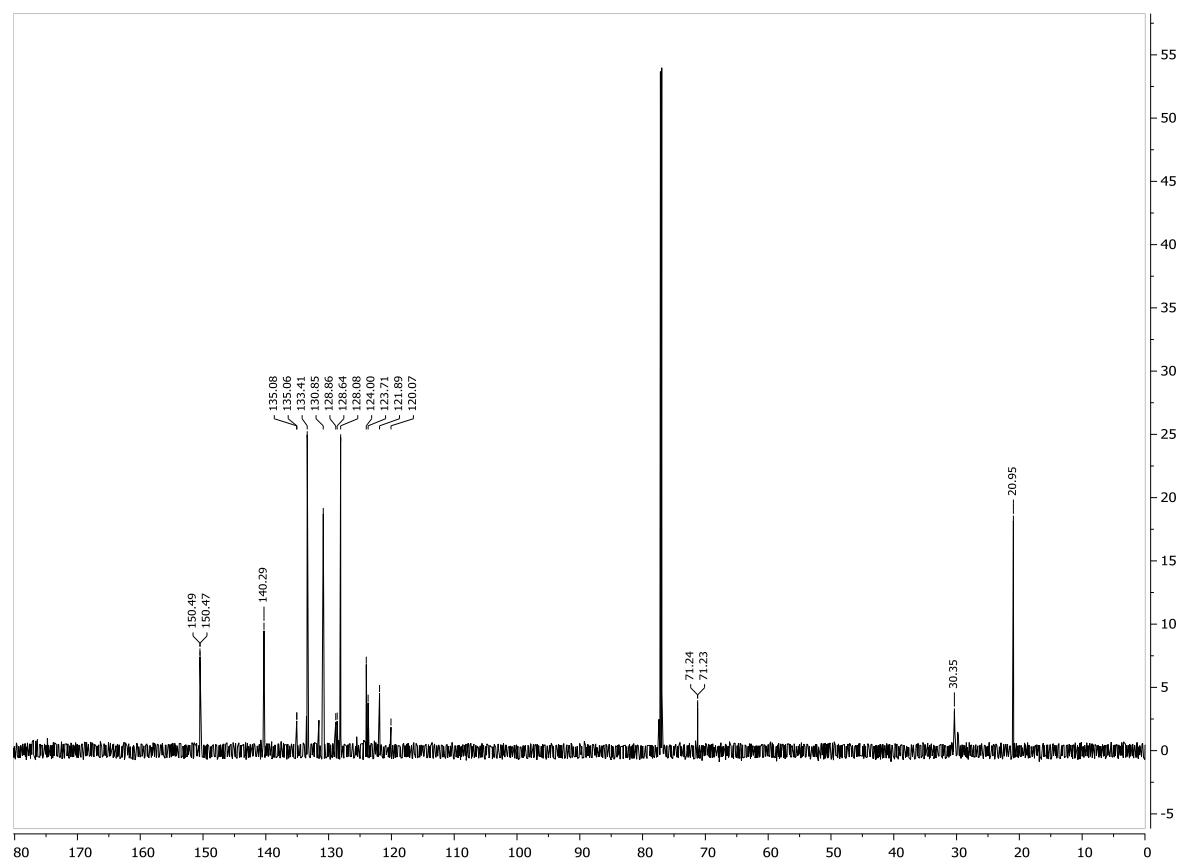
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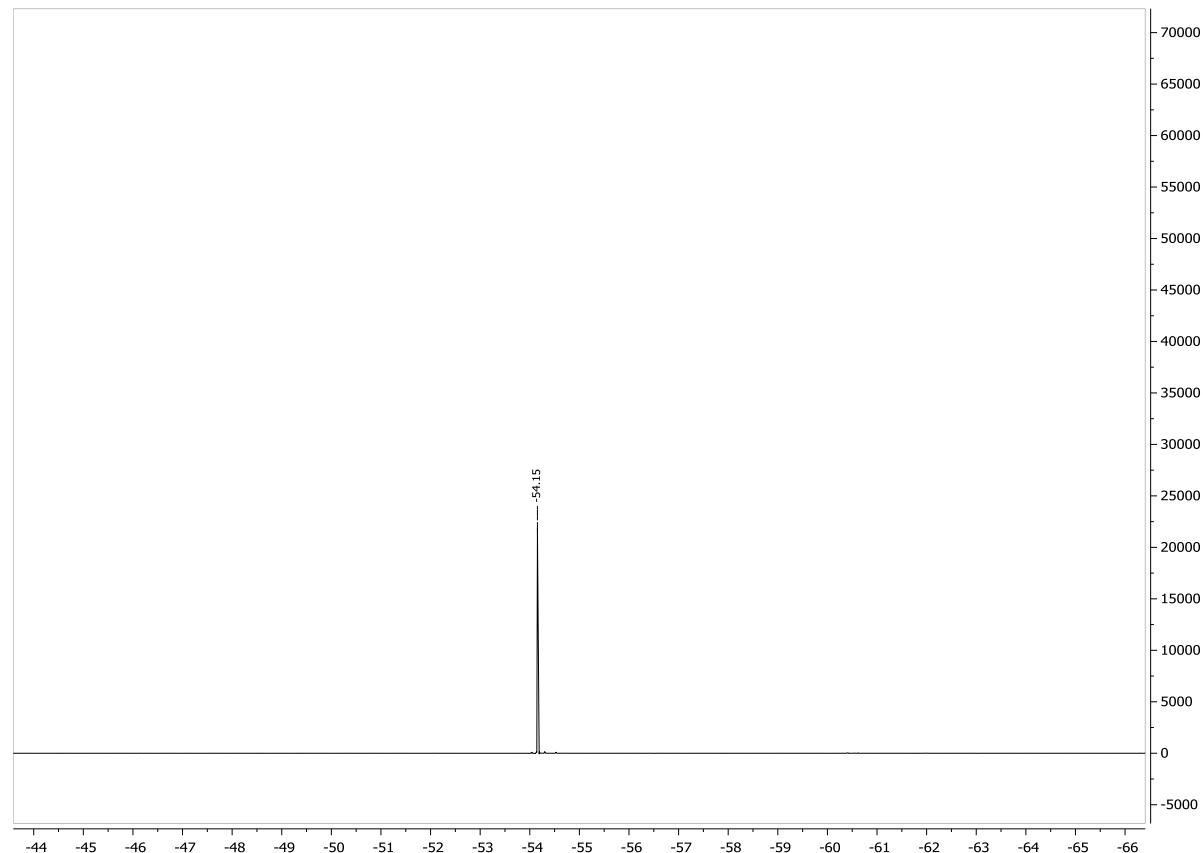
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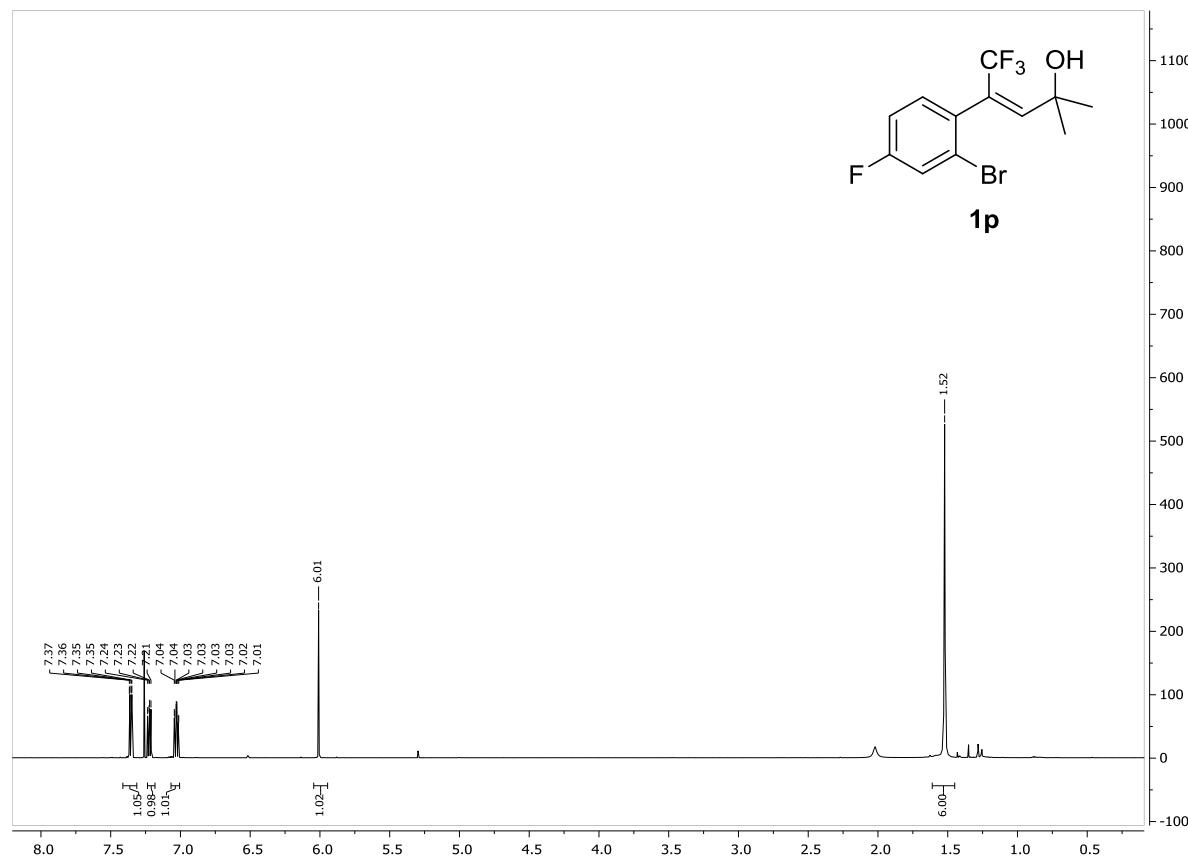
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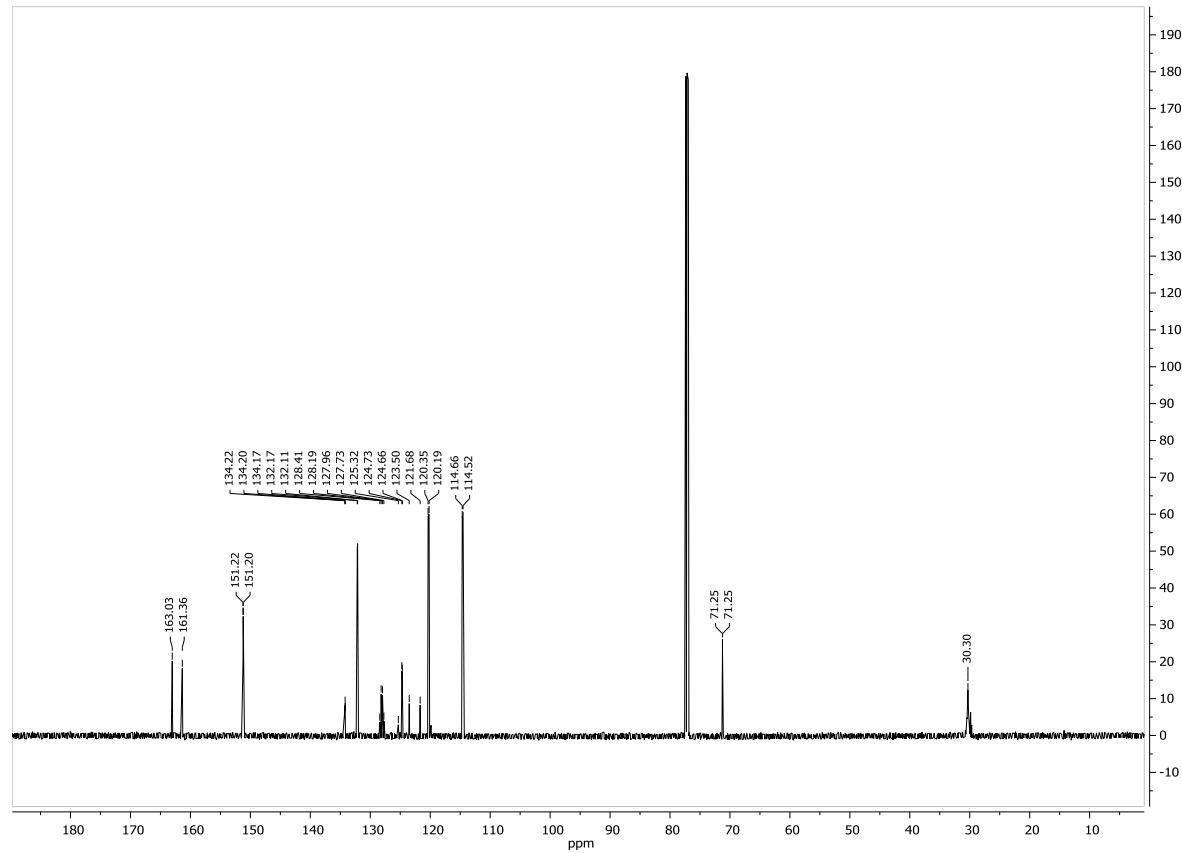
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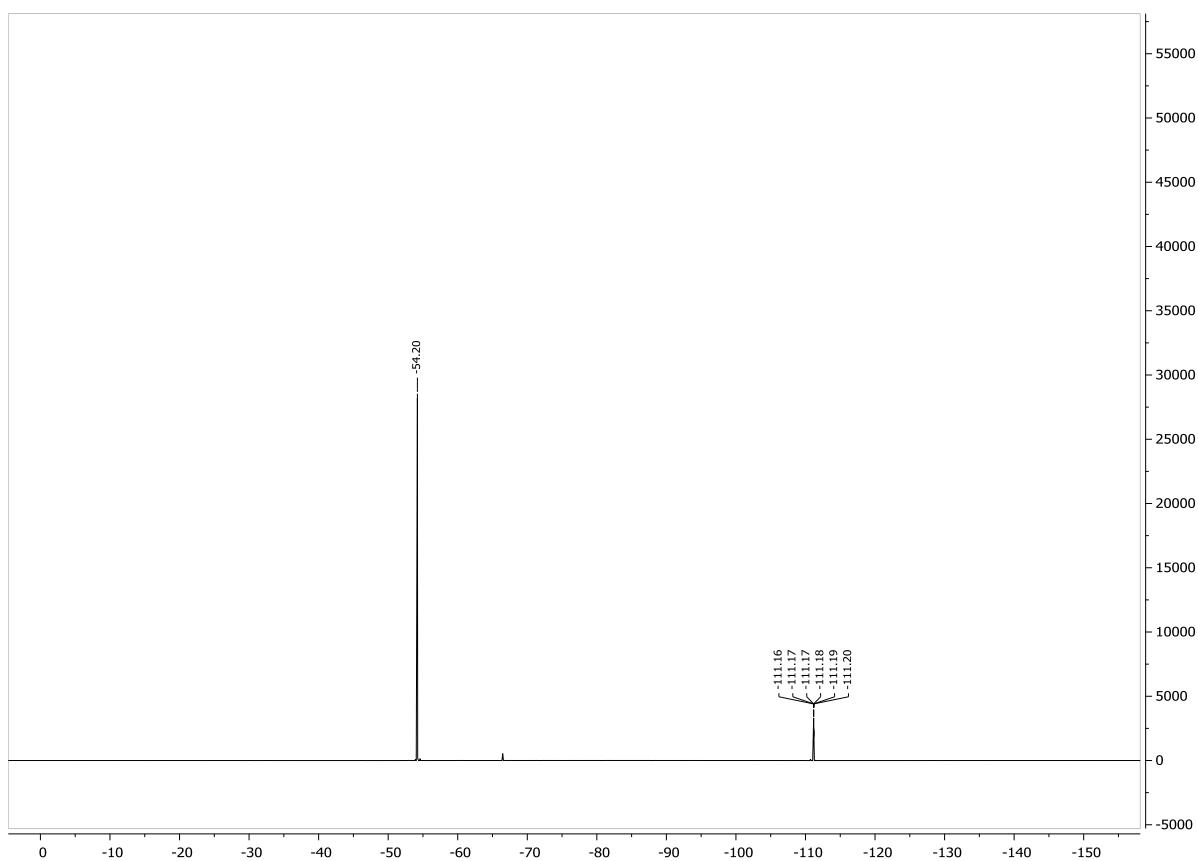
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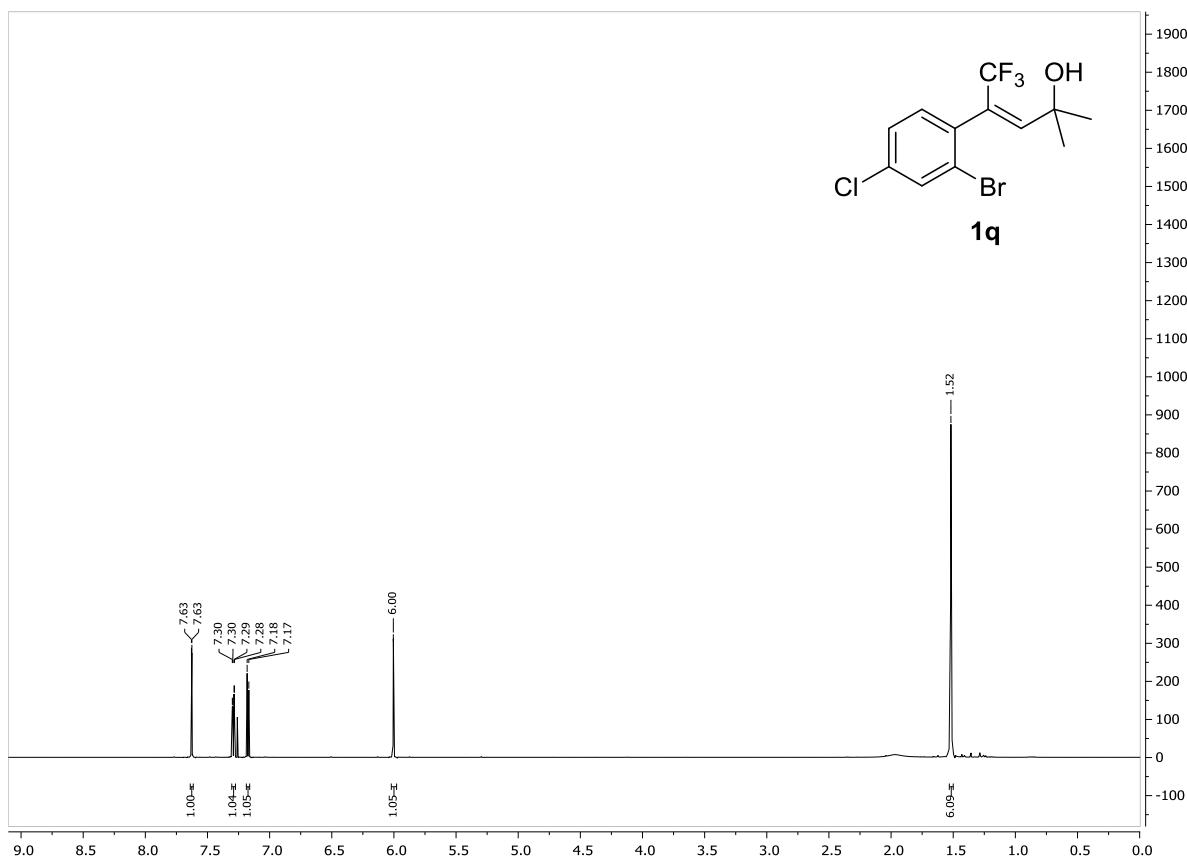
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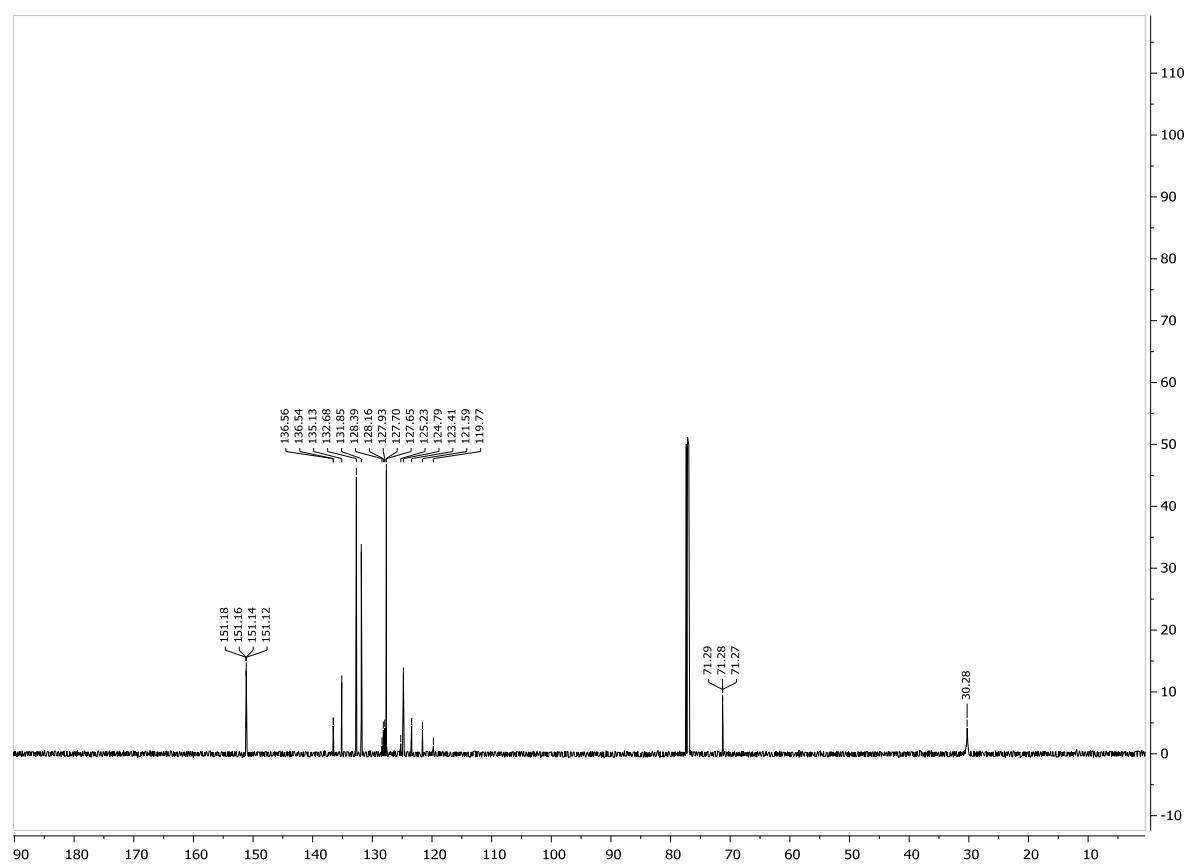
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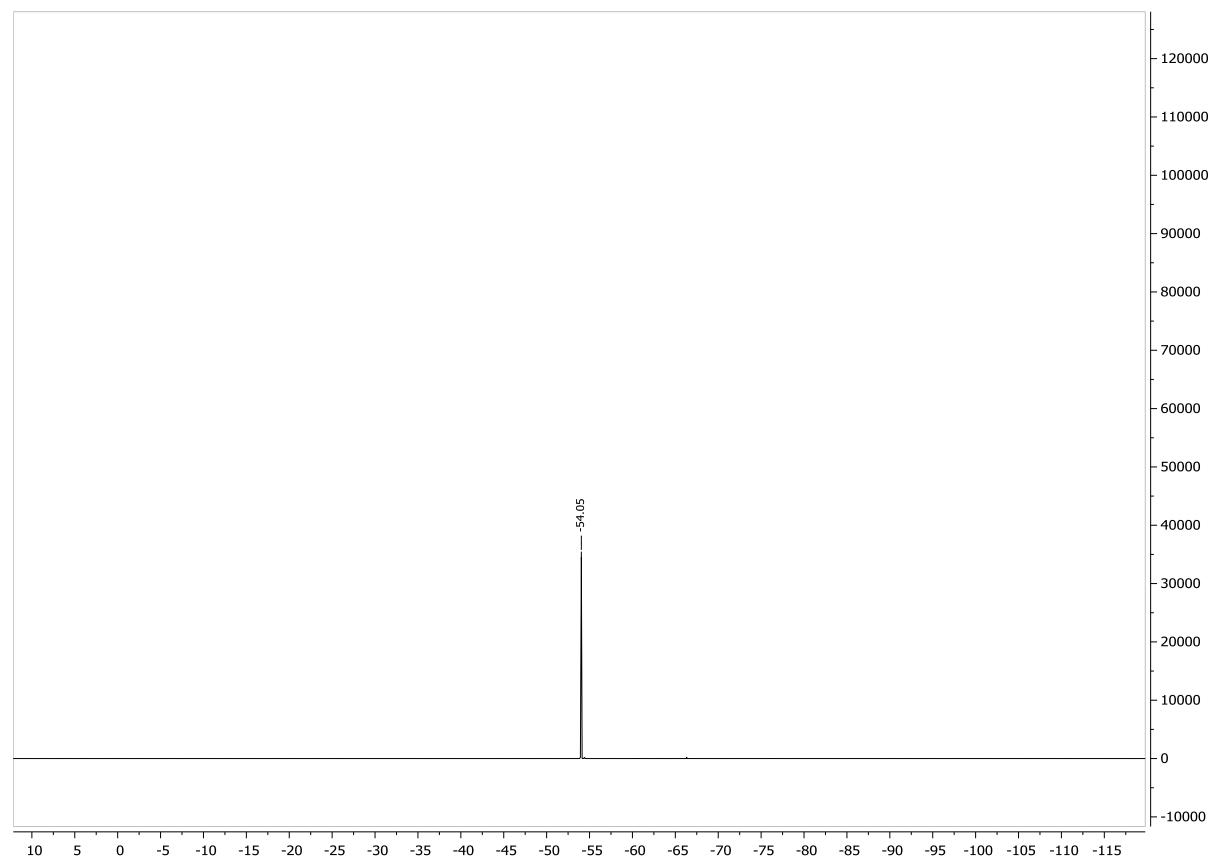
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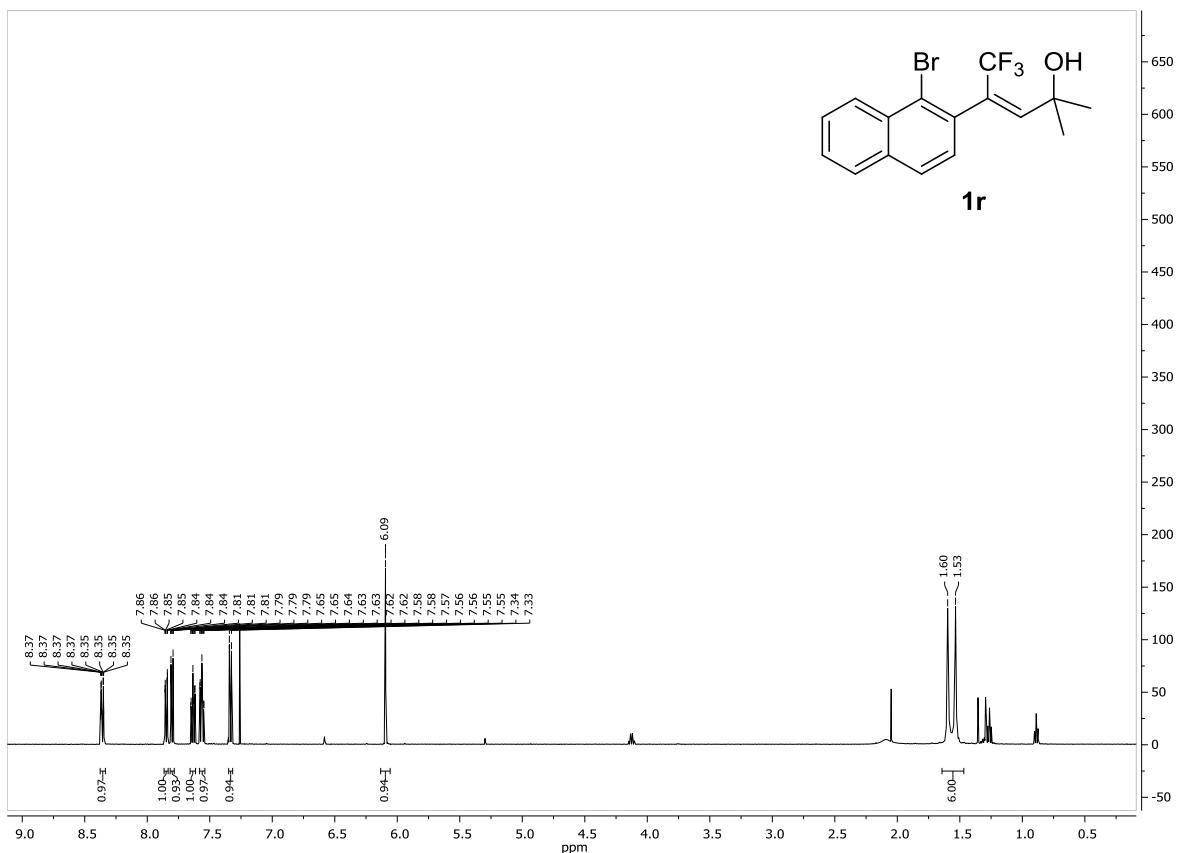
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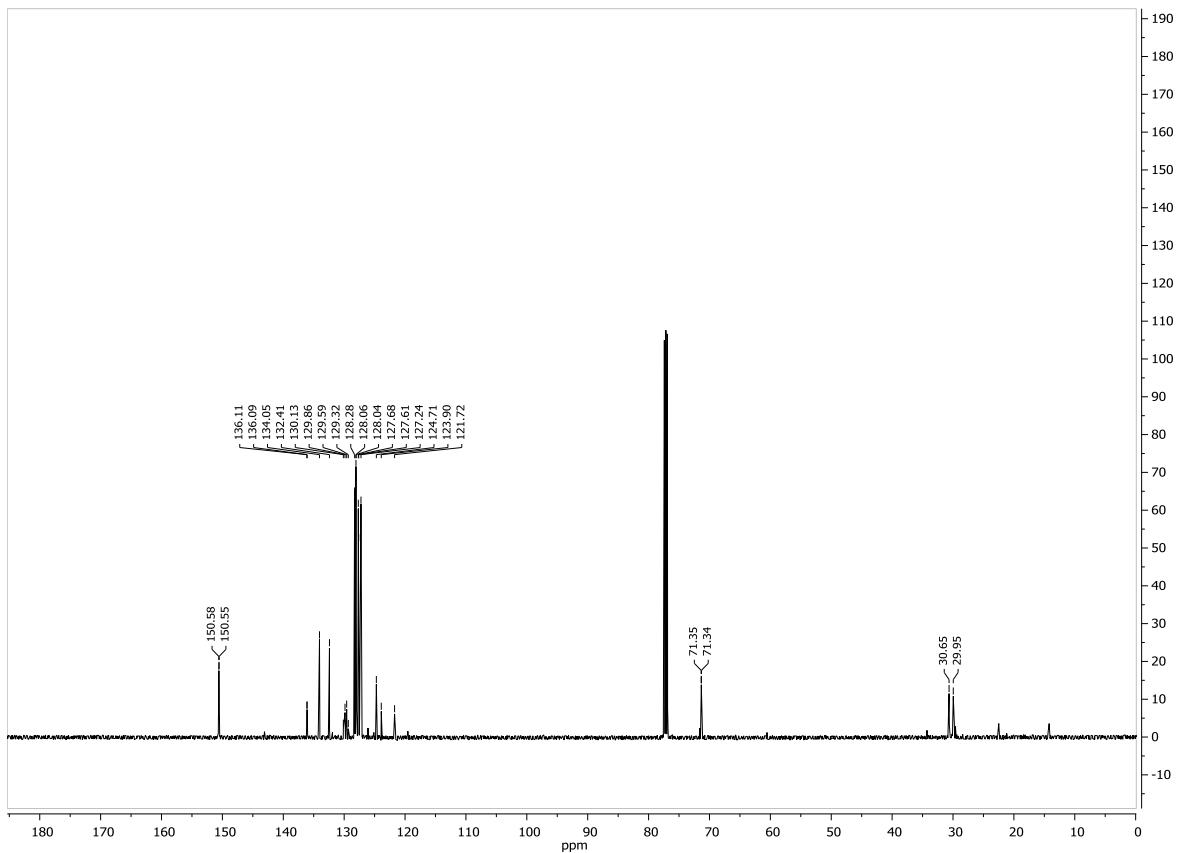
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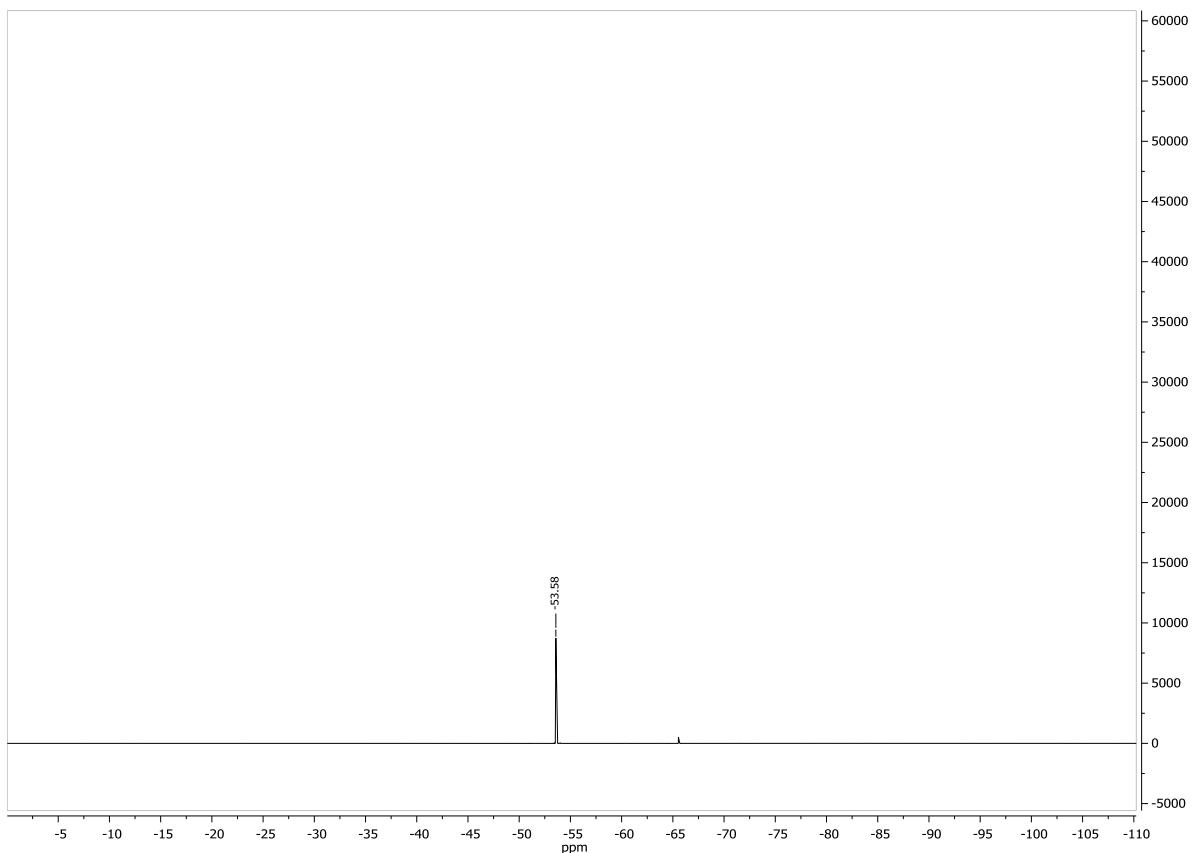
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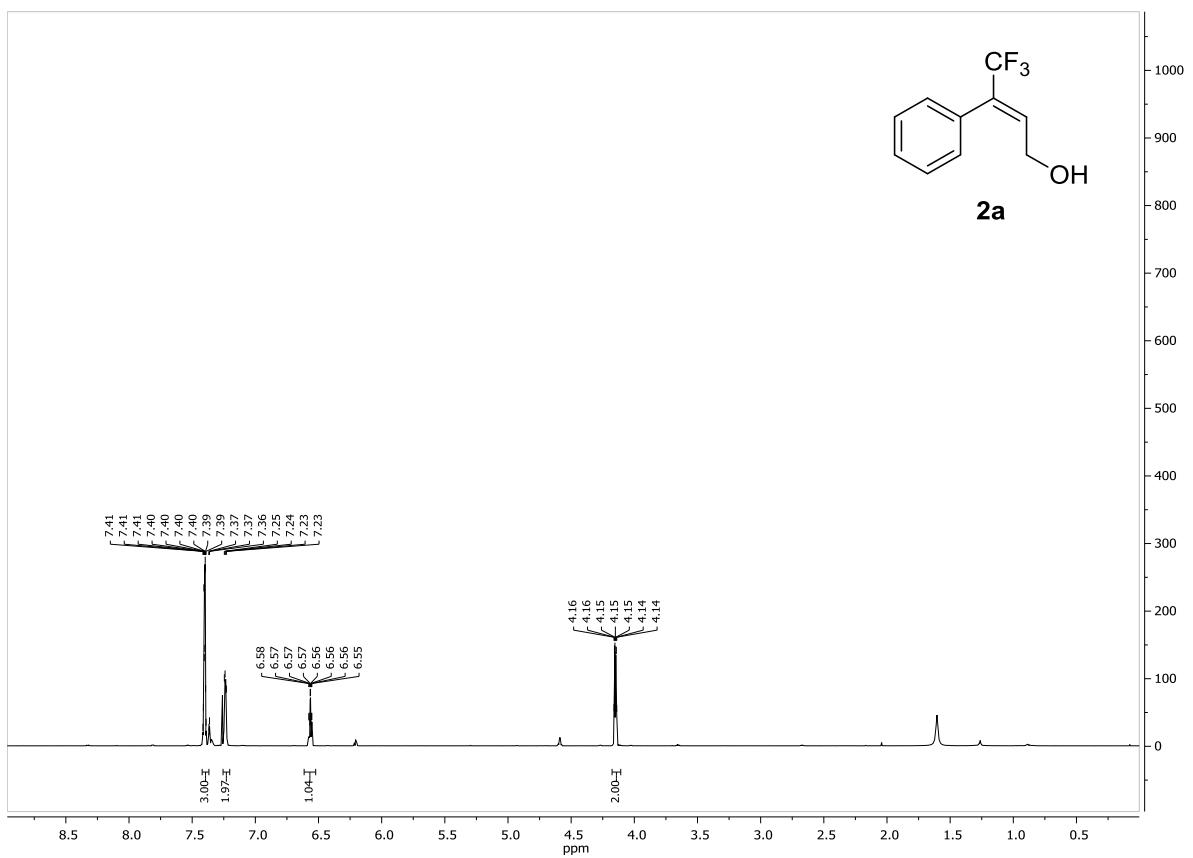
¹³C NMR (CDCl_3 , 126 MHz)



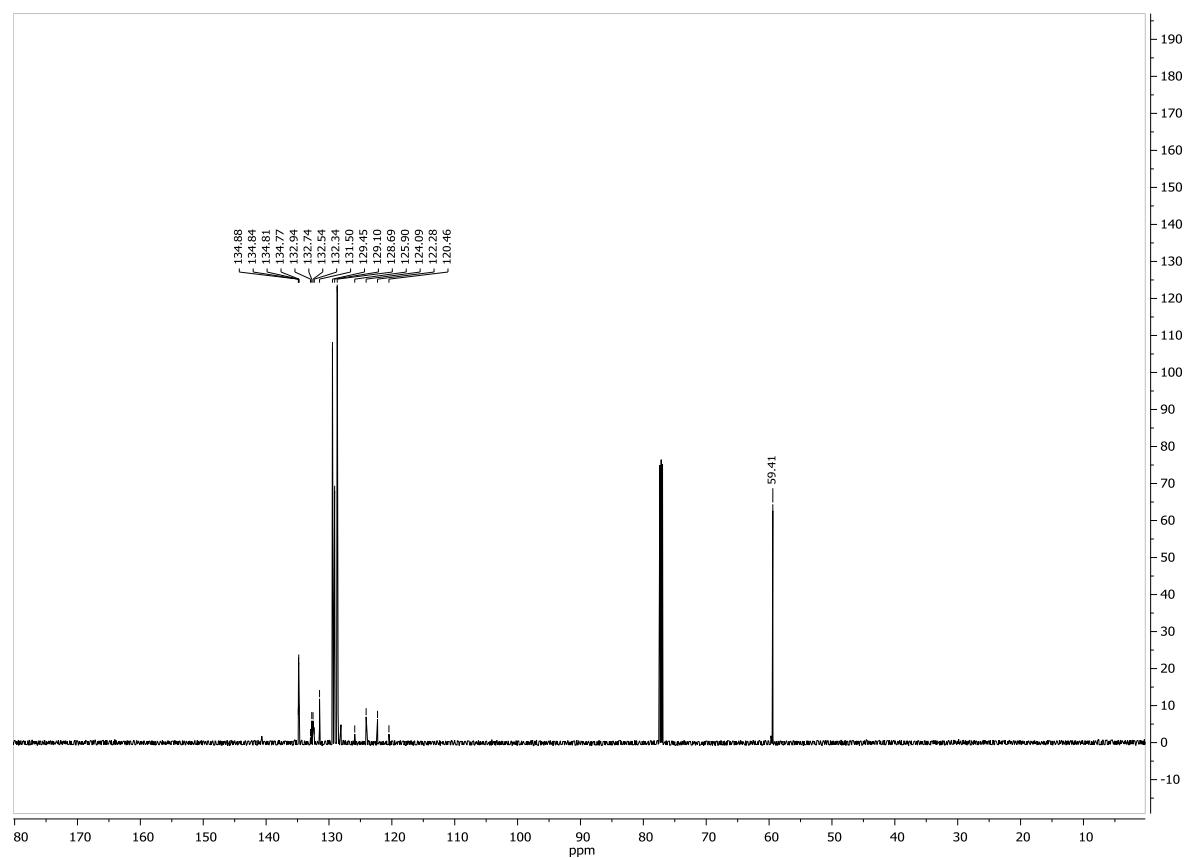
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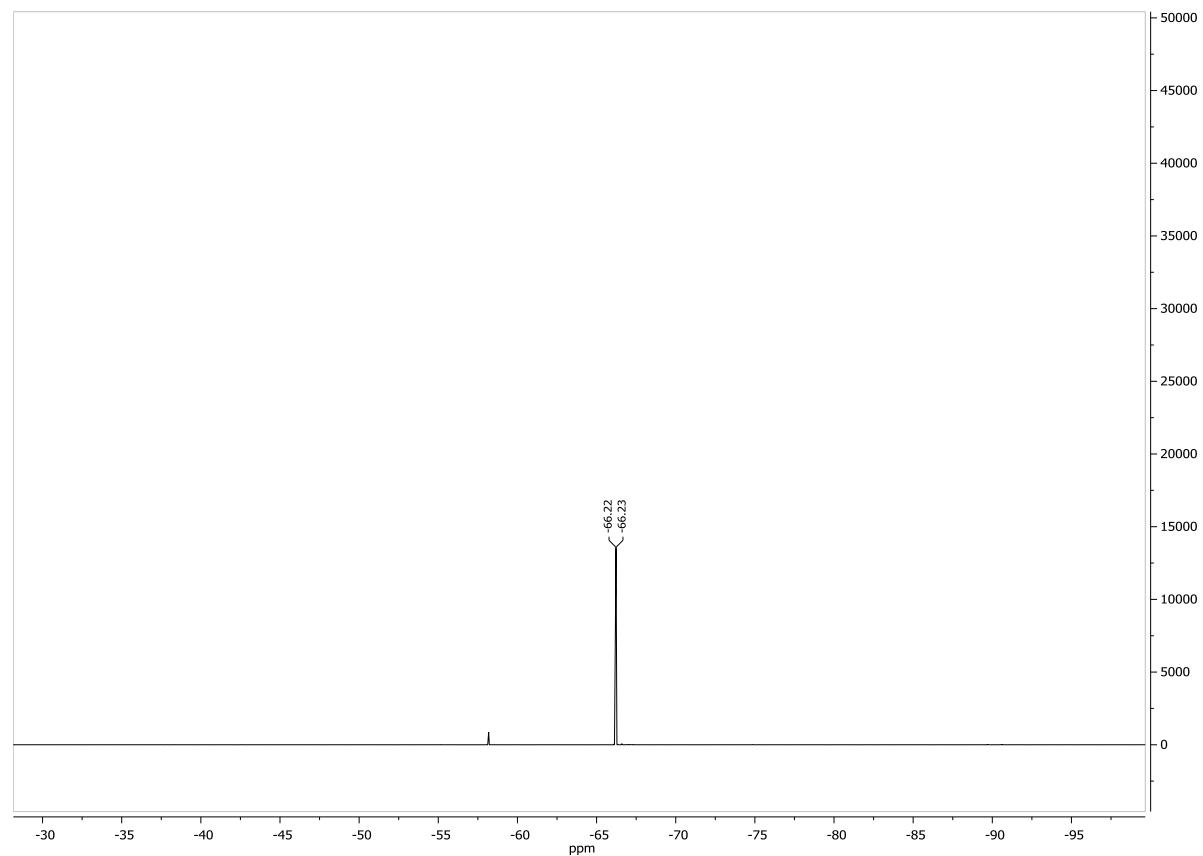
¹H NMR (CDCl₃, 600 MHz)



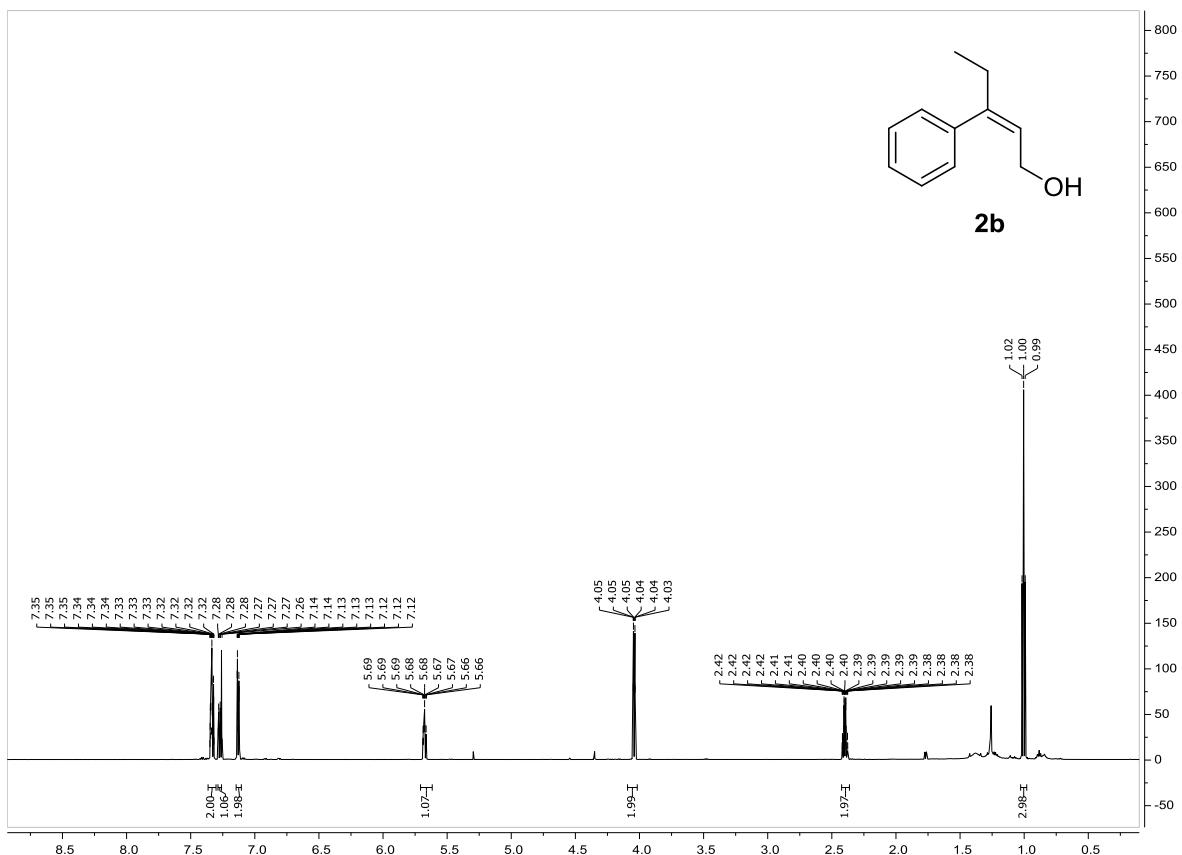
¹³C NMR (CDCl_3 , 151 MHz)



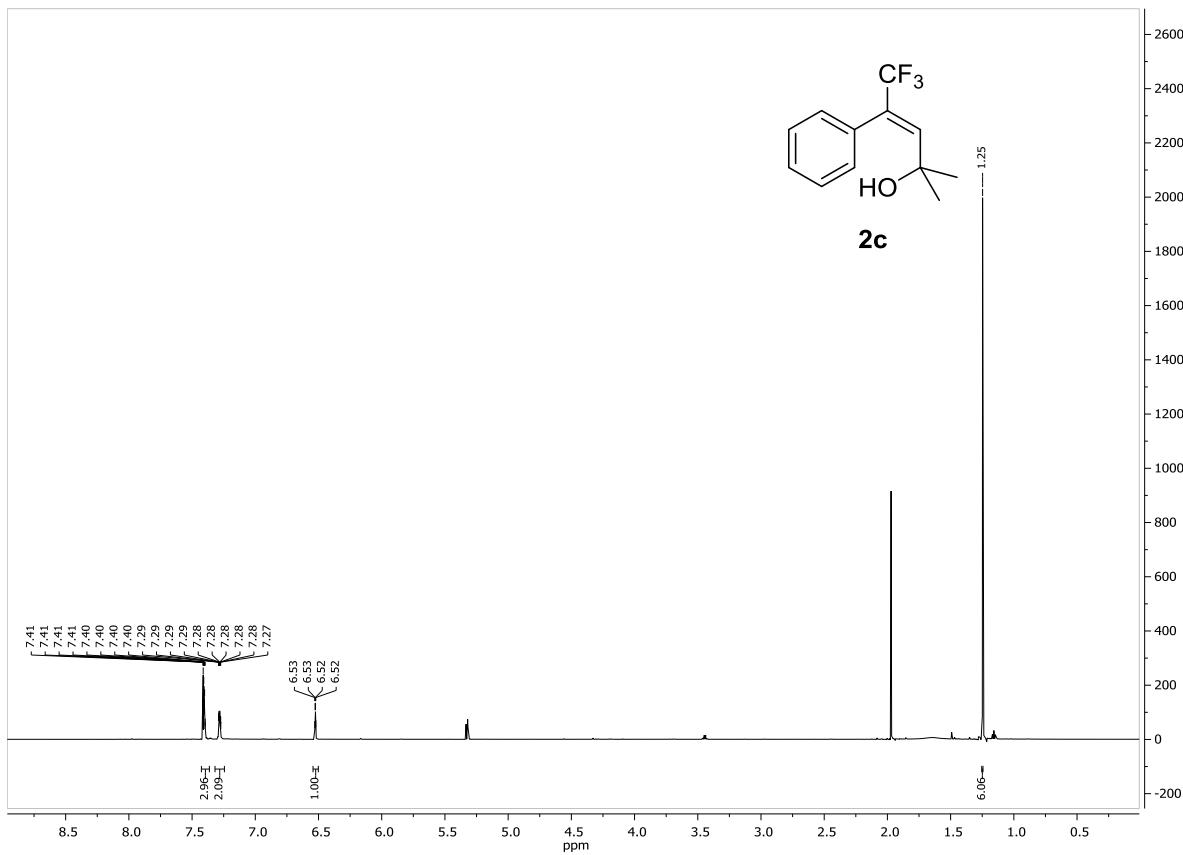
¹⁹F NMR (CDCl_3 , 564 MHz)



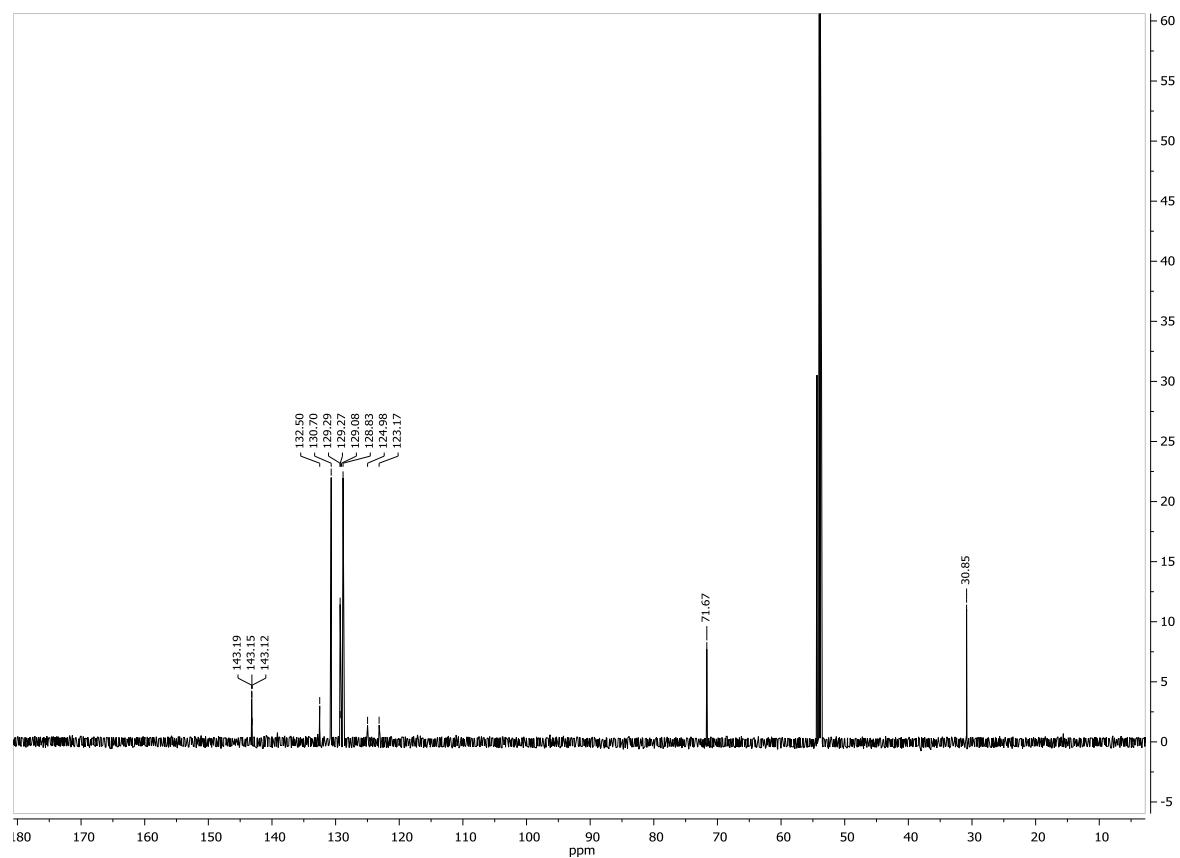
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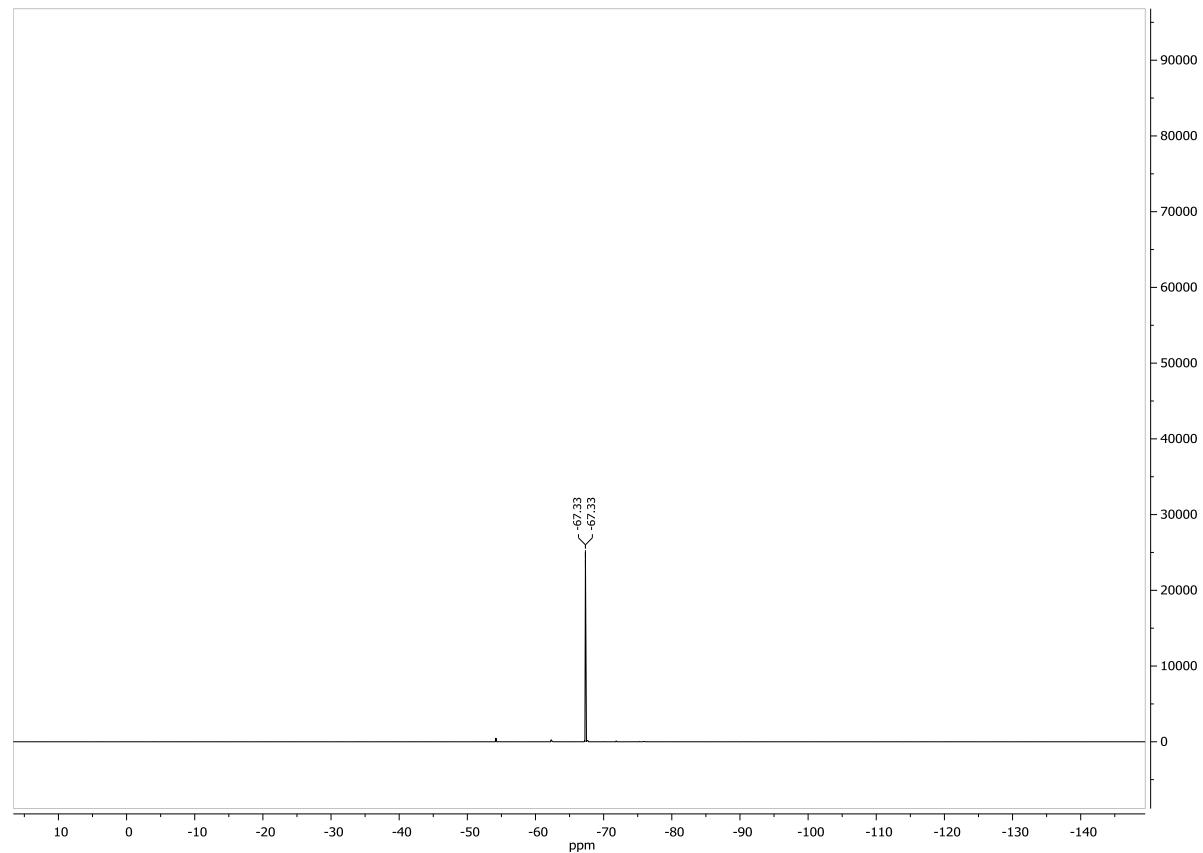
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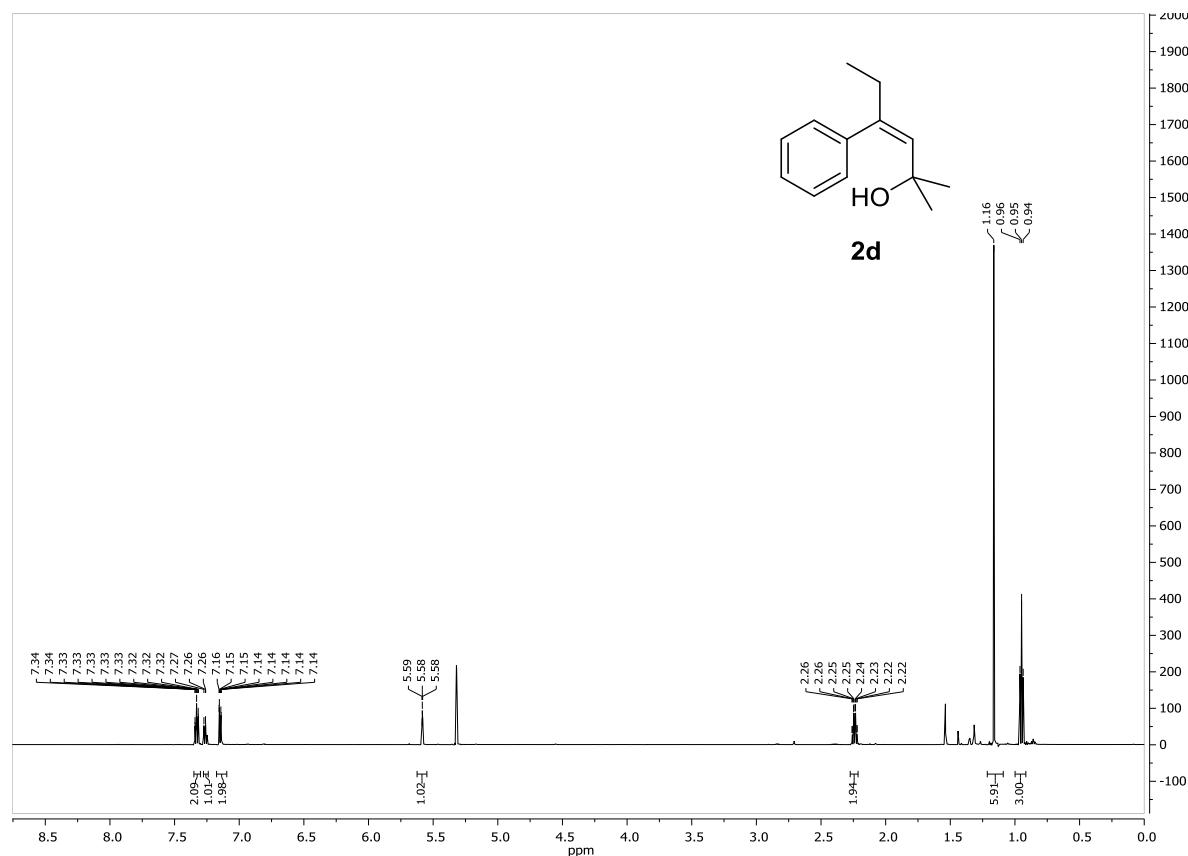
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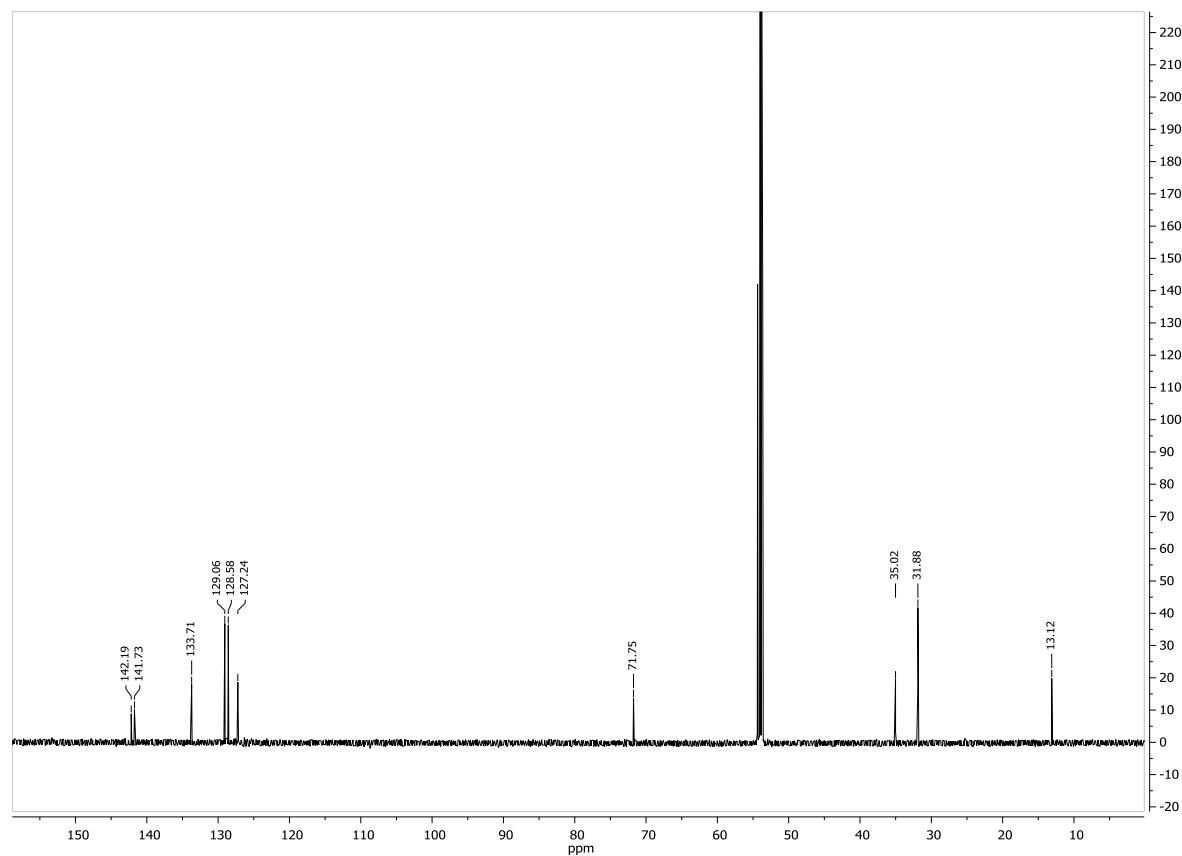
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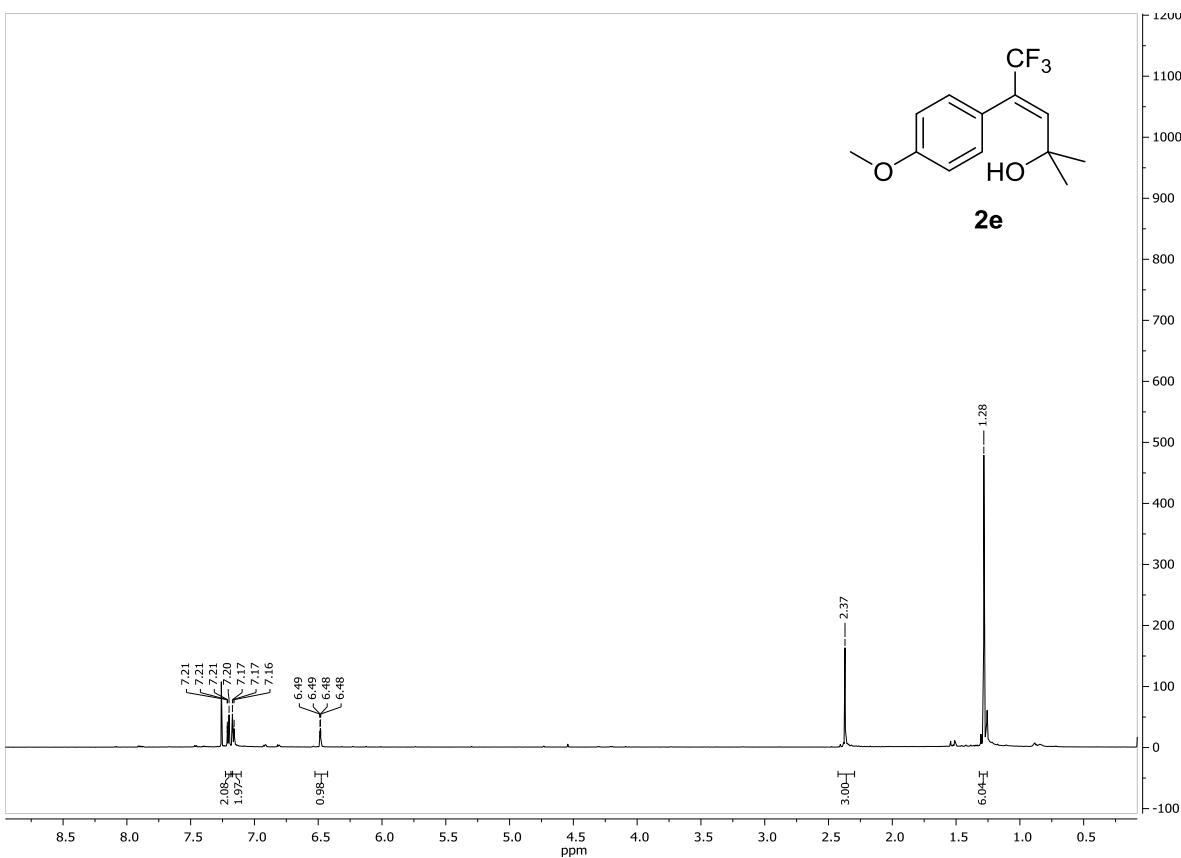
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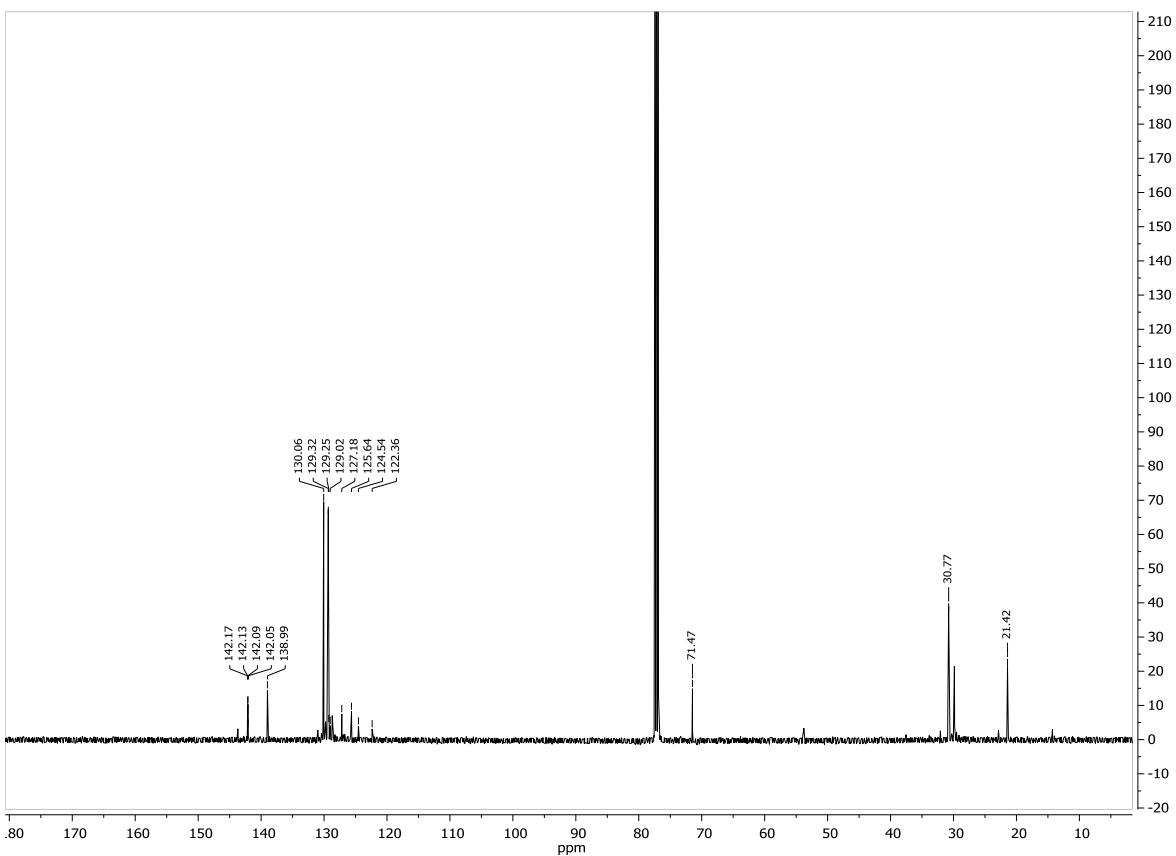
¹³C NMR (CD₂Cl₂, 151 MHz)



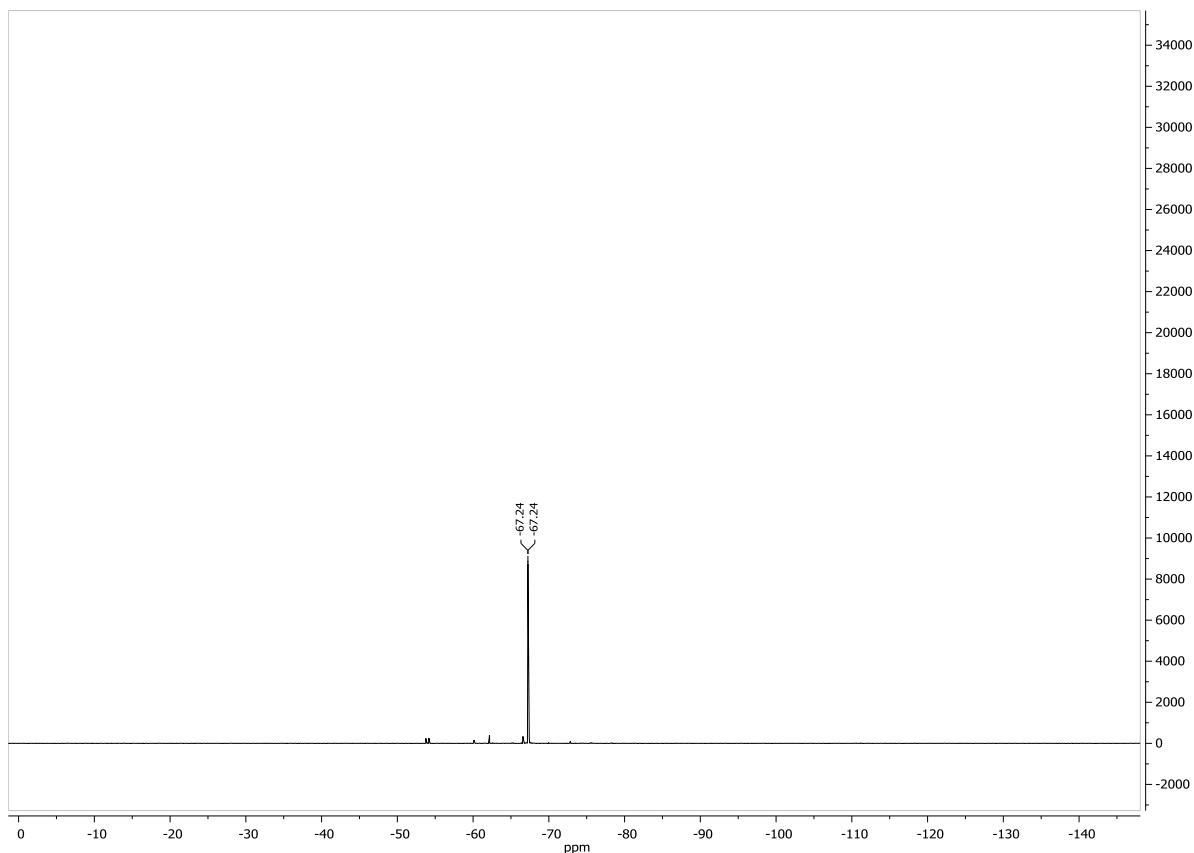
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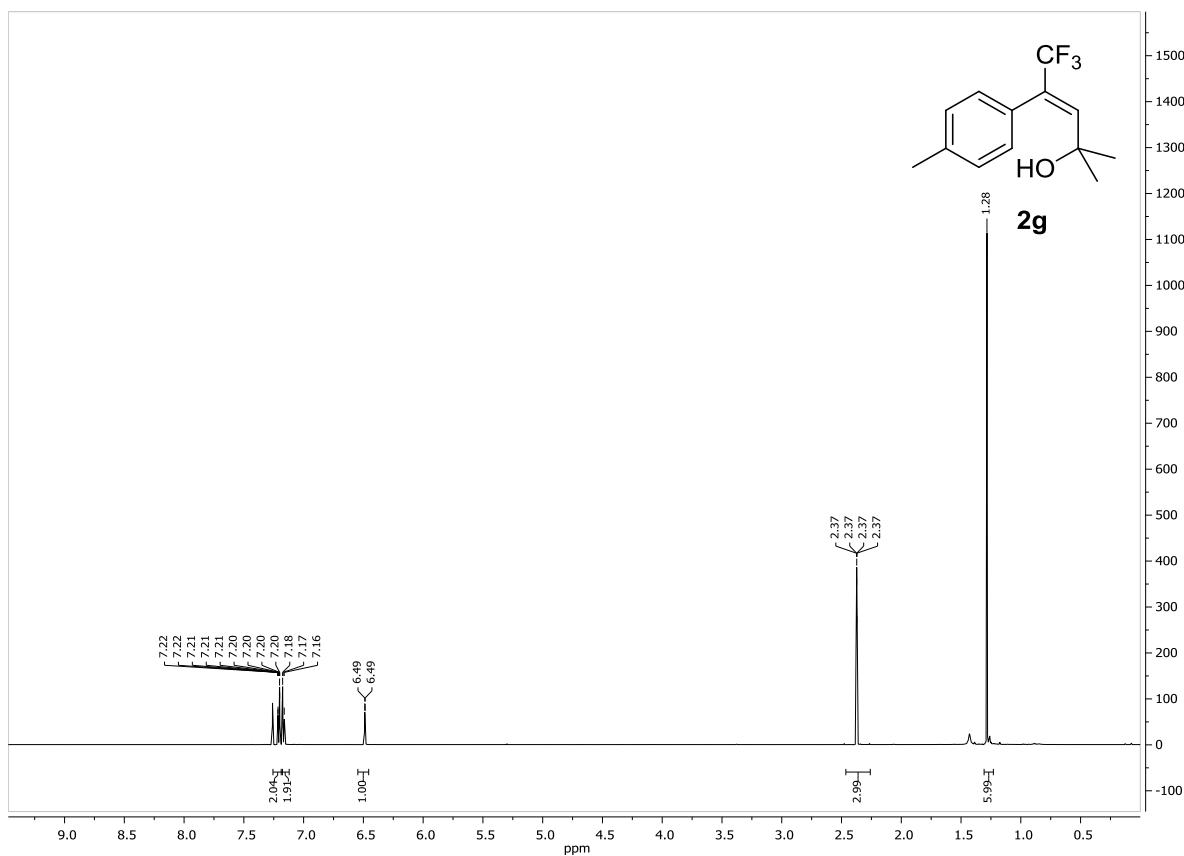
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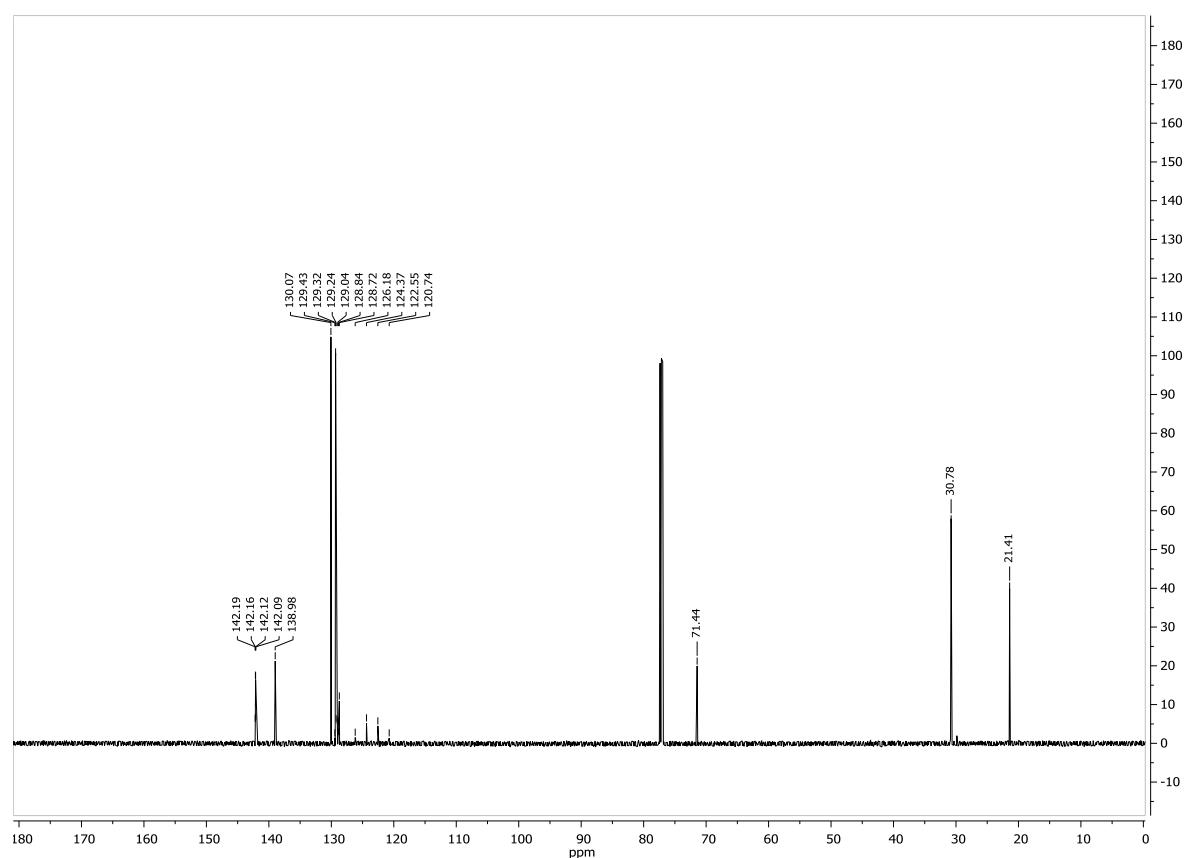
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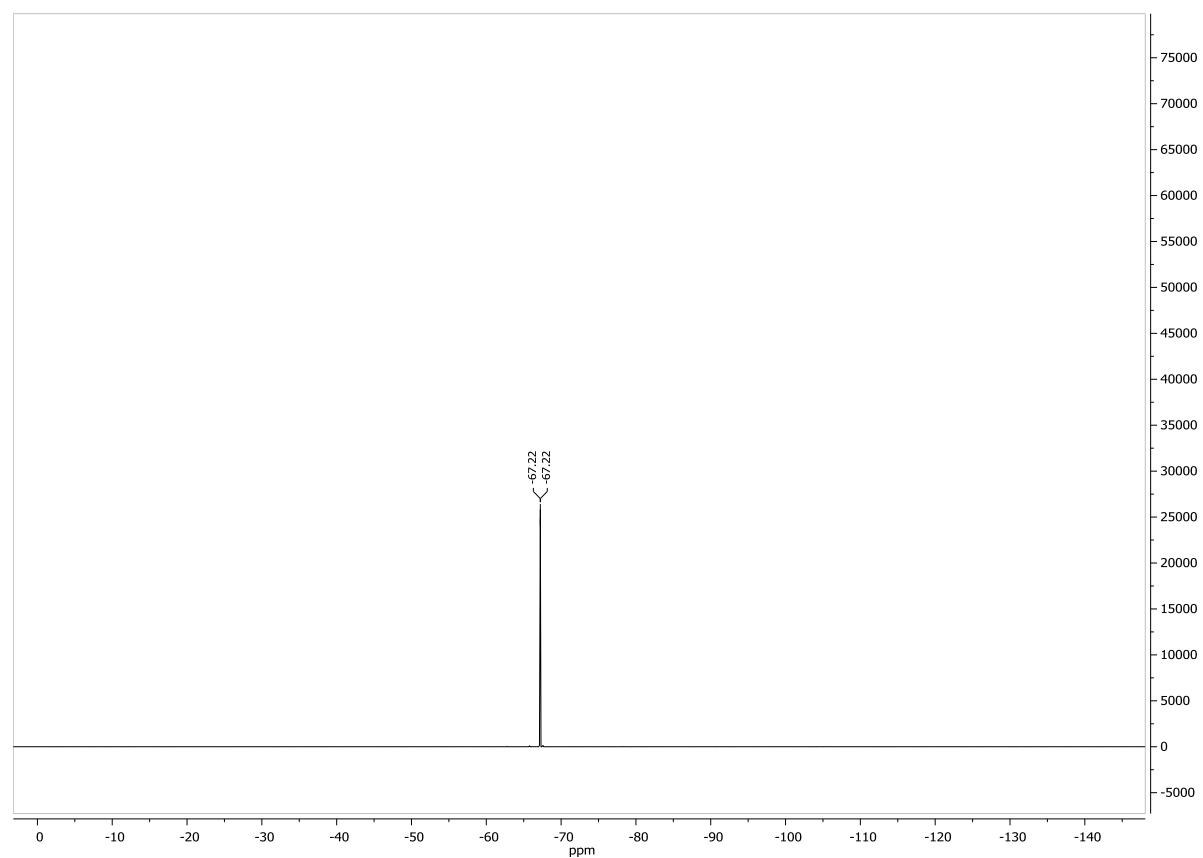
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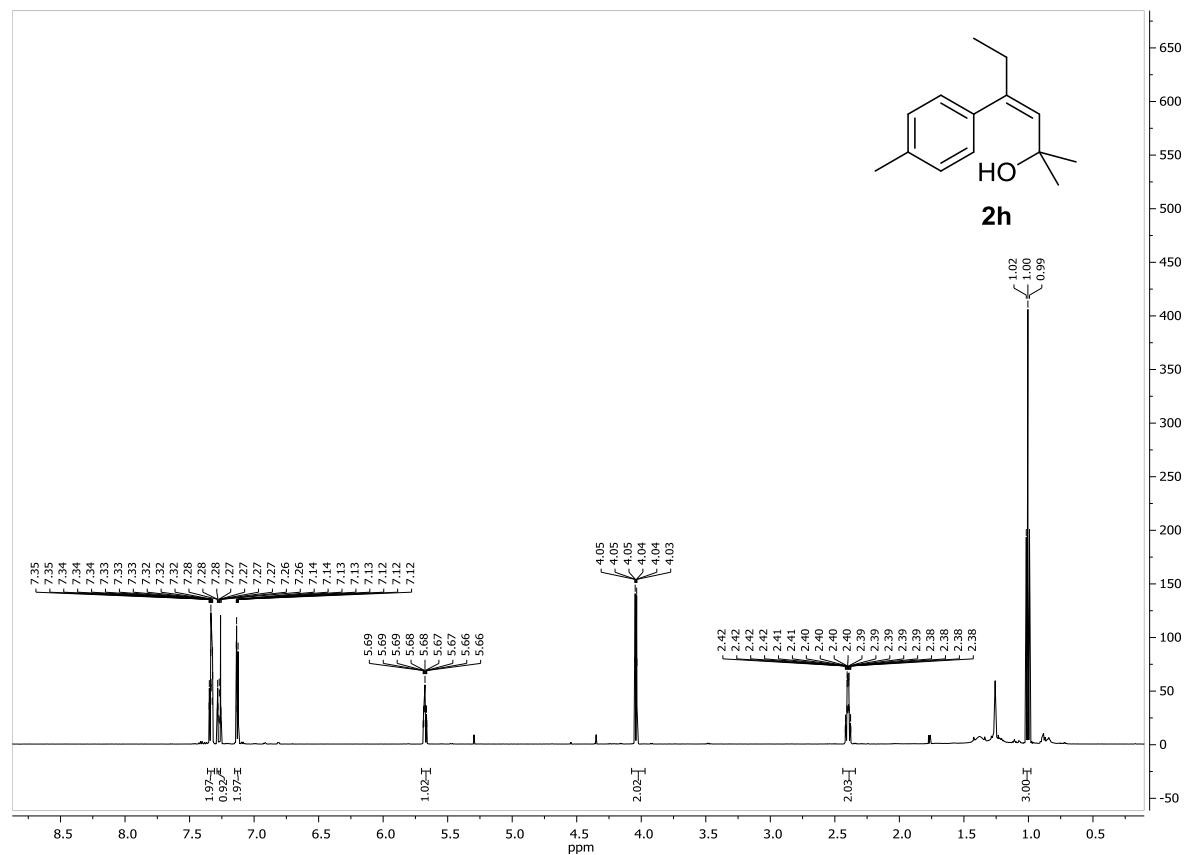
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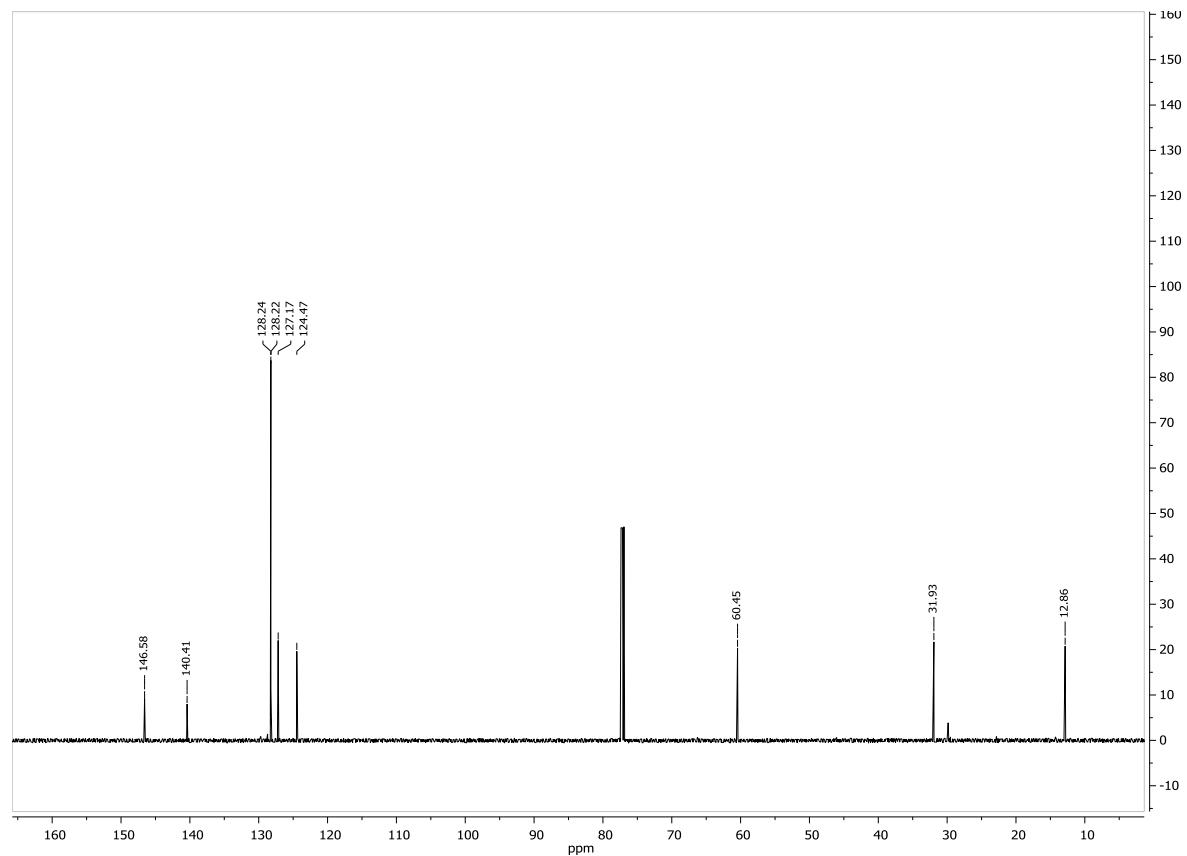
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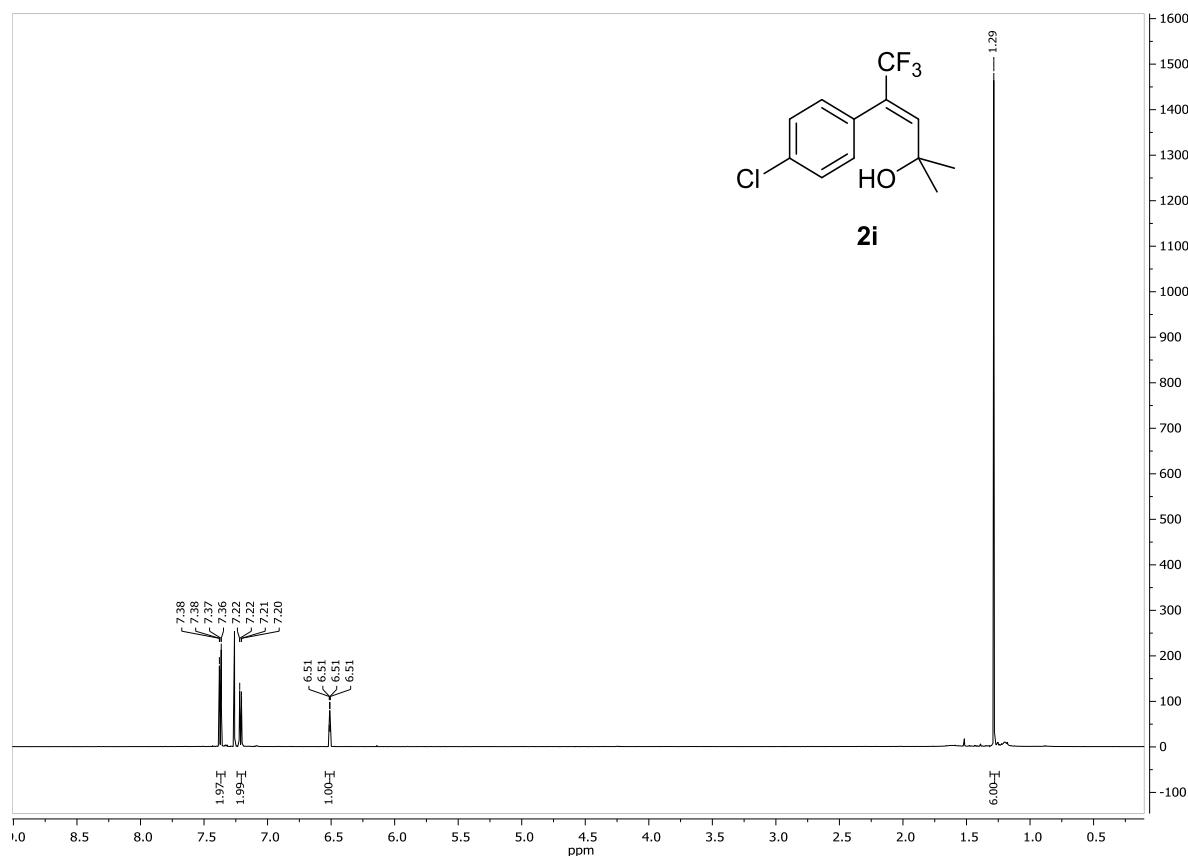
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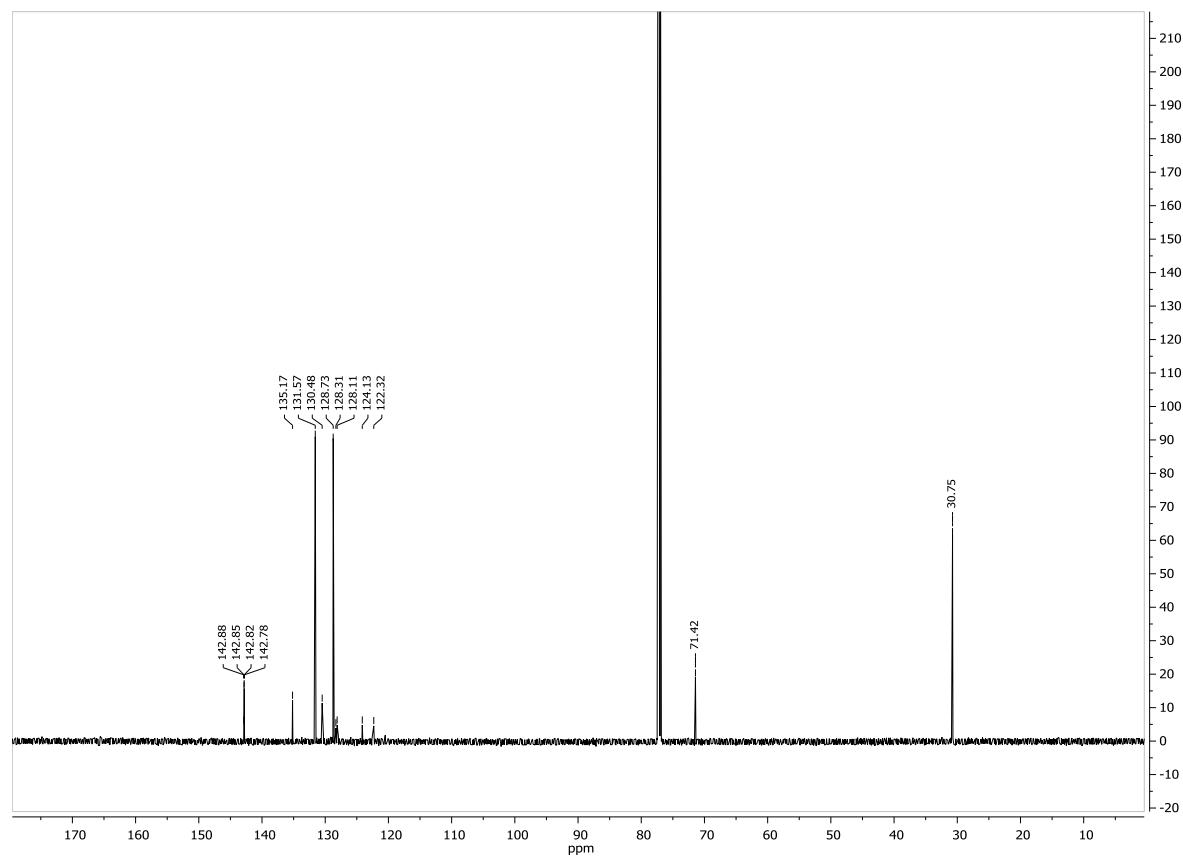
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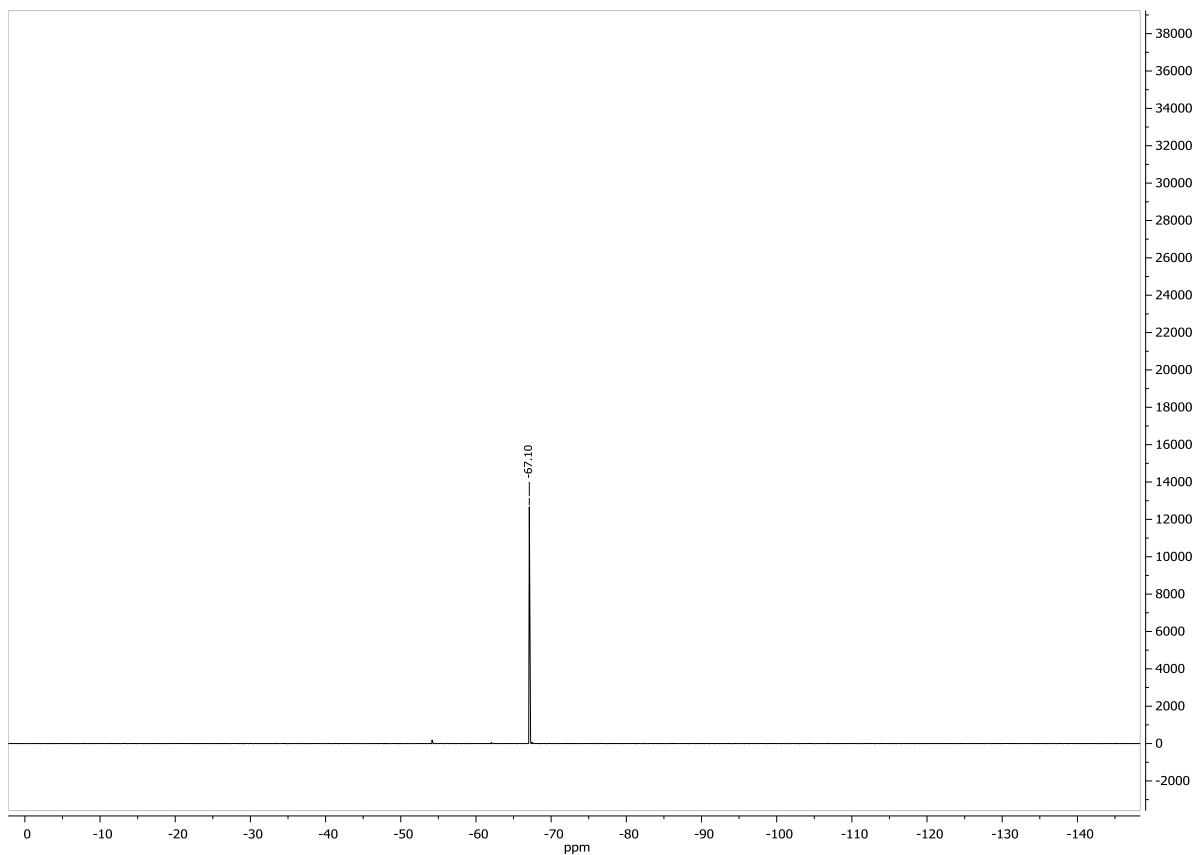
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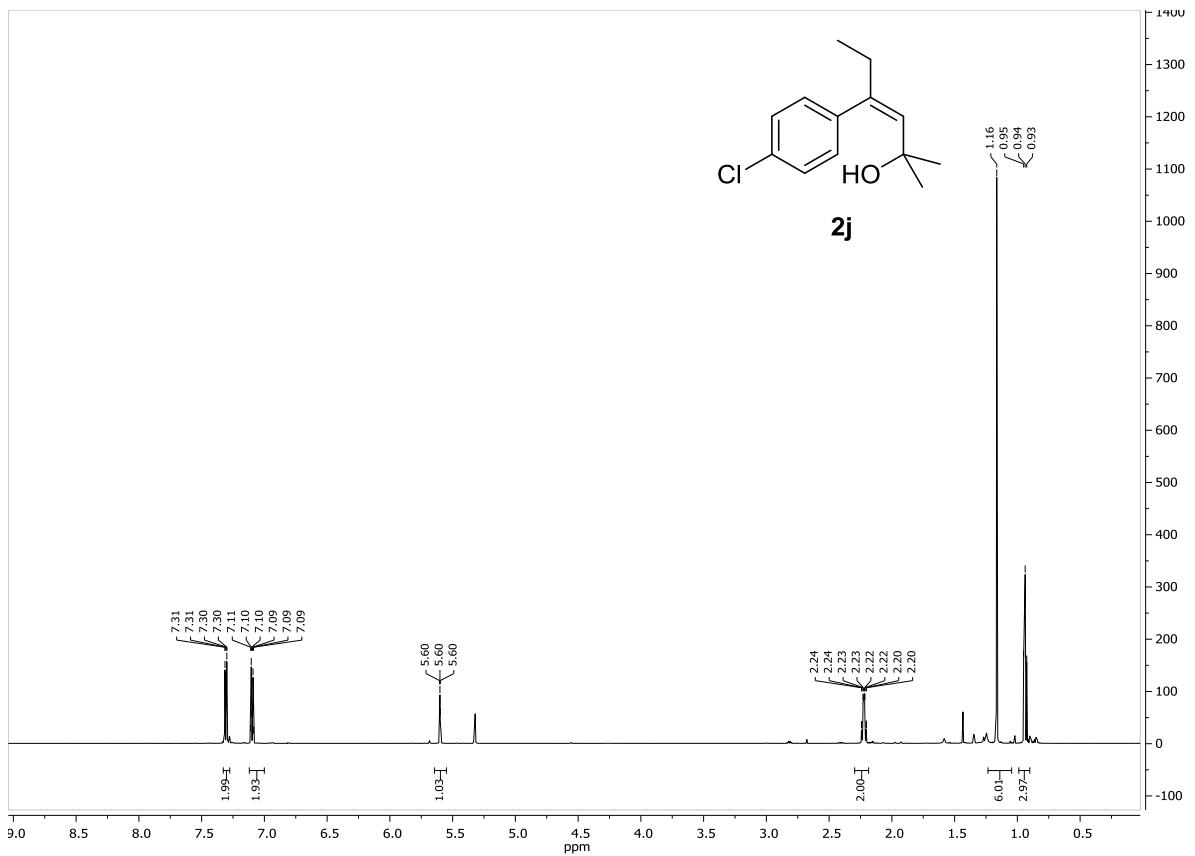
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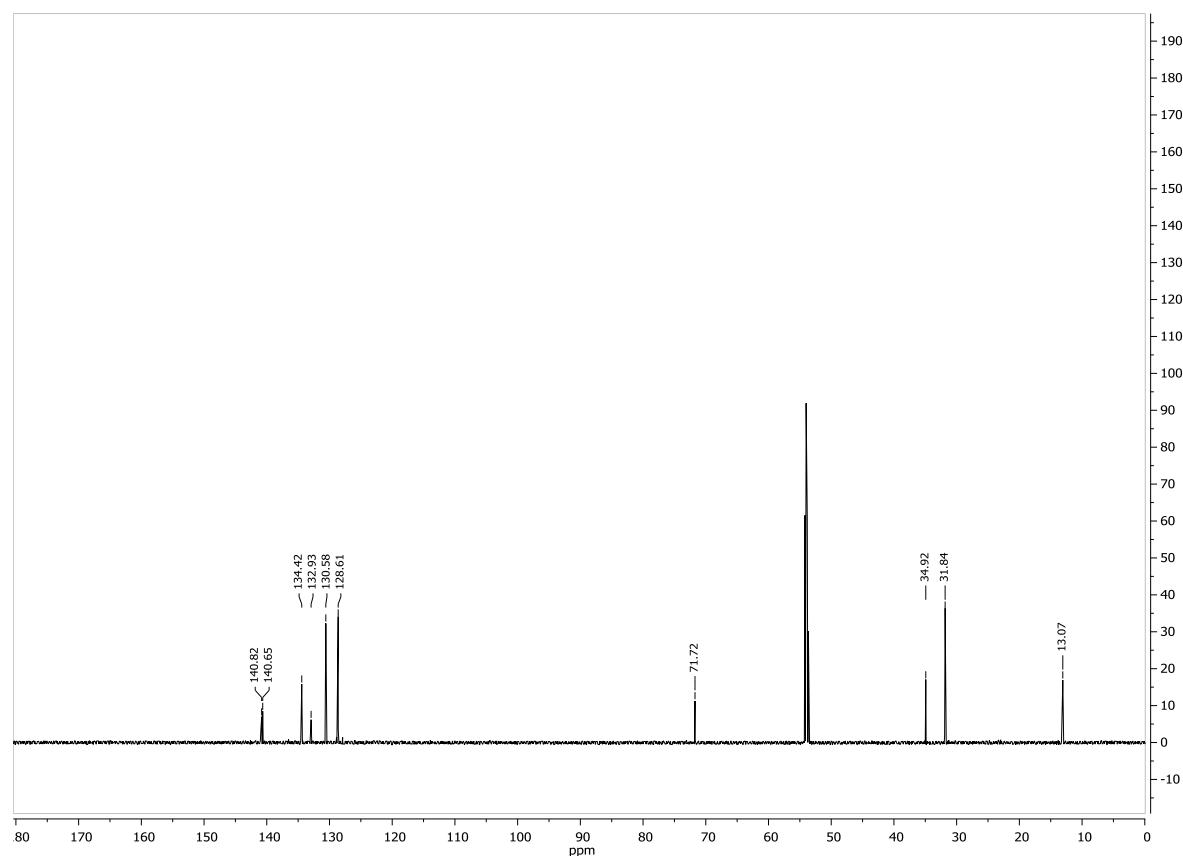
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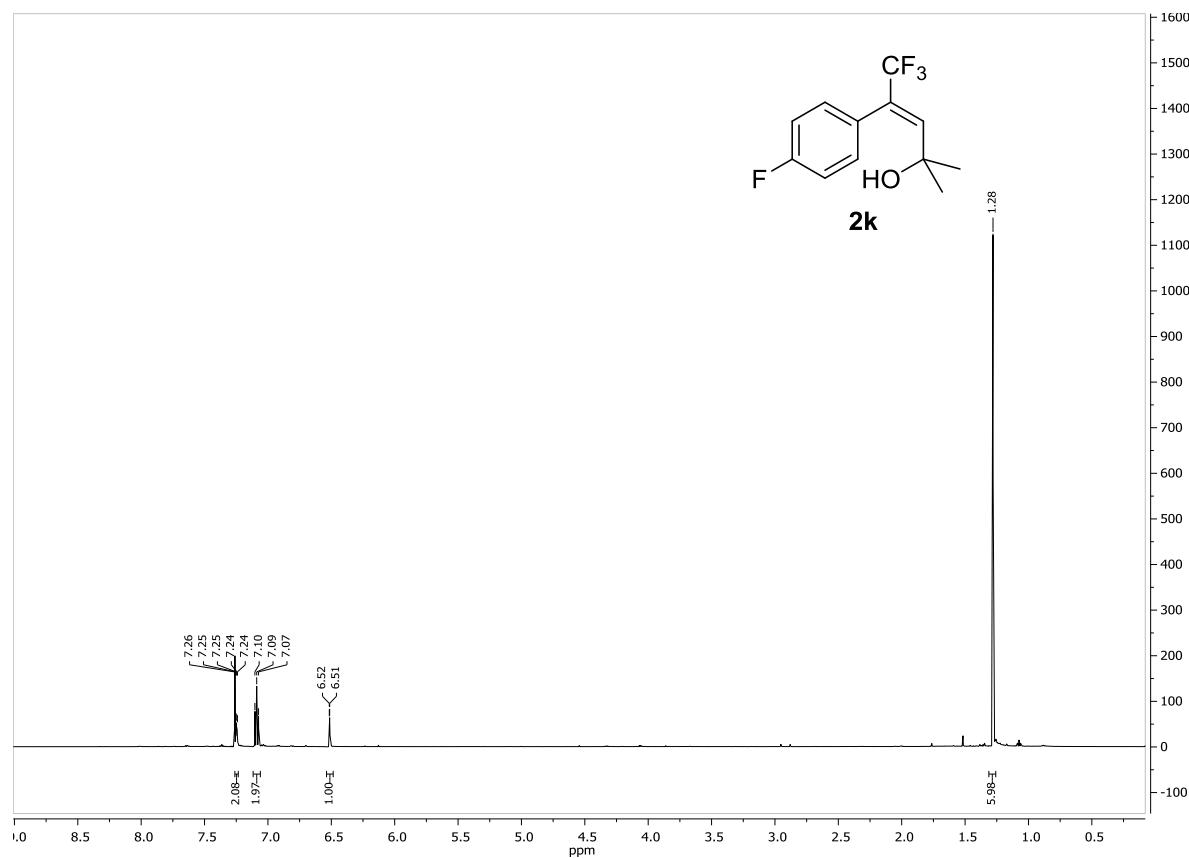
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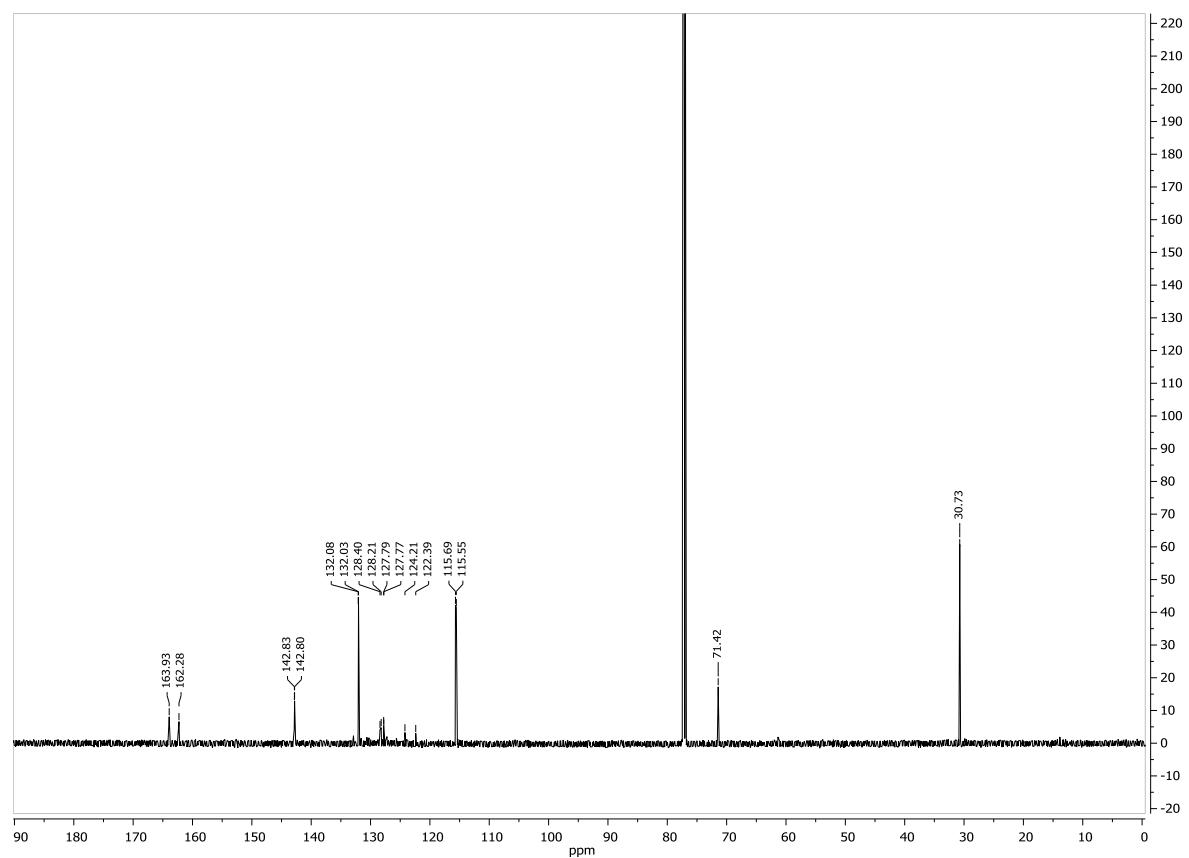
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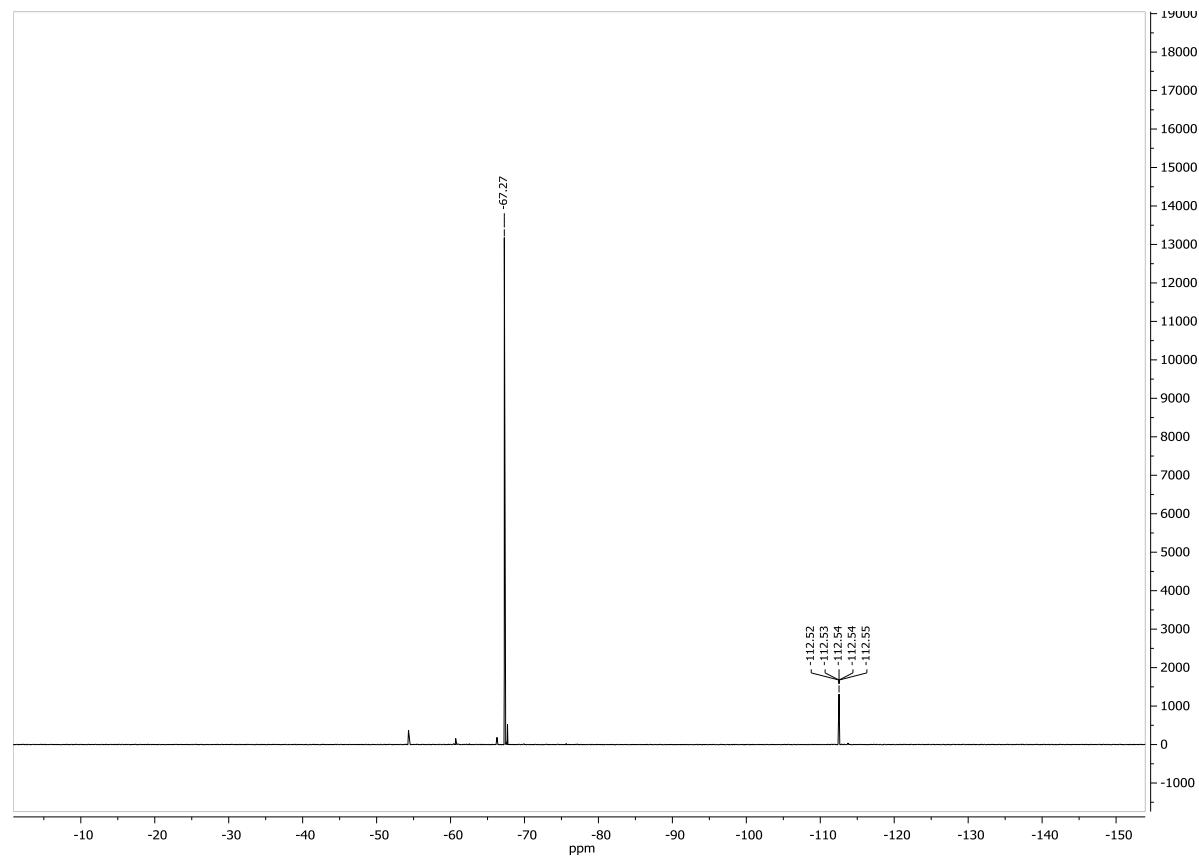
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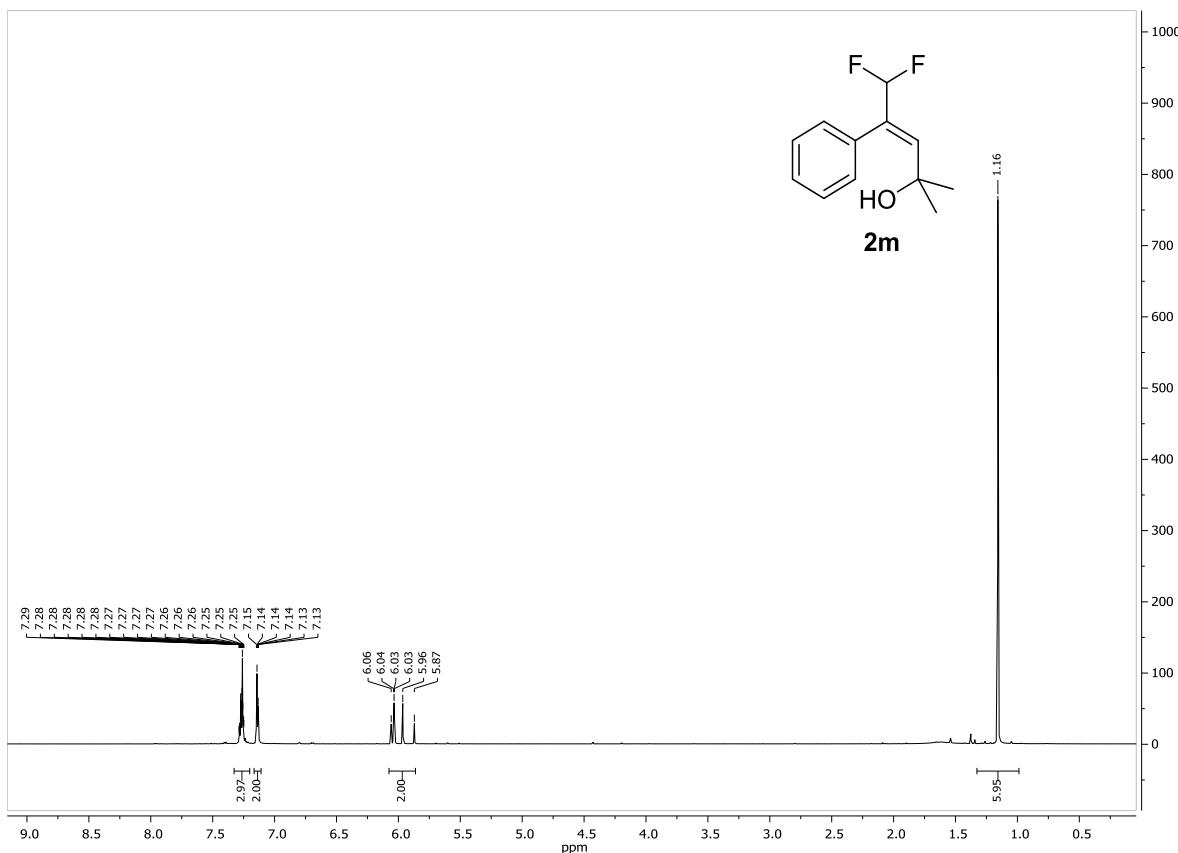
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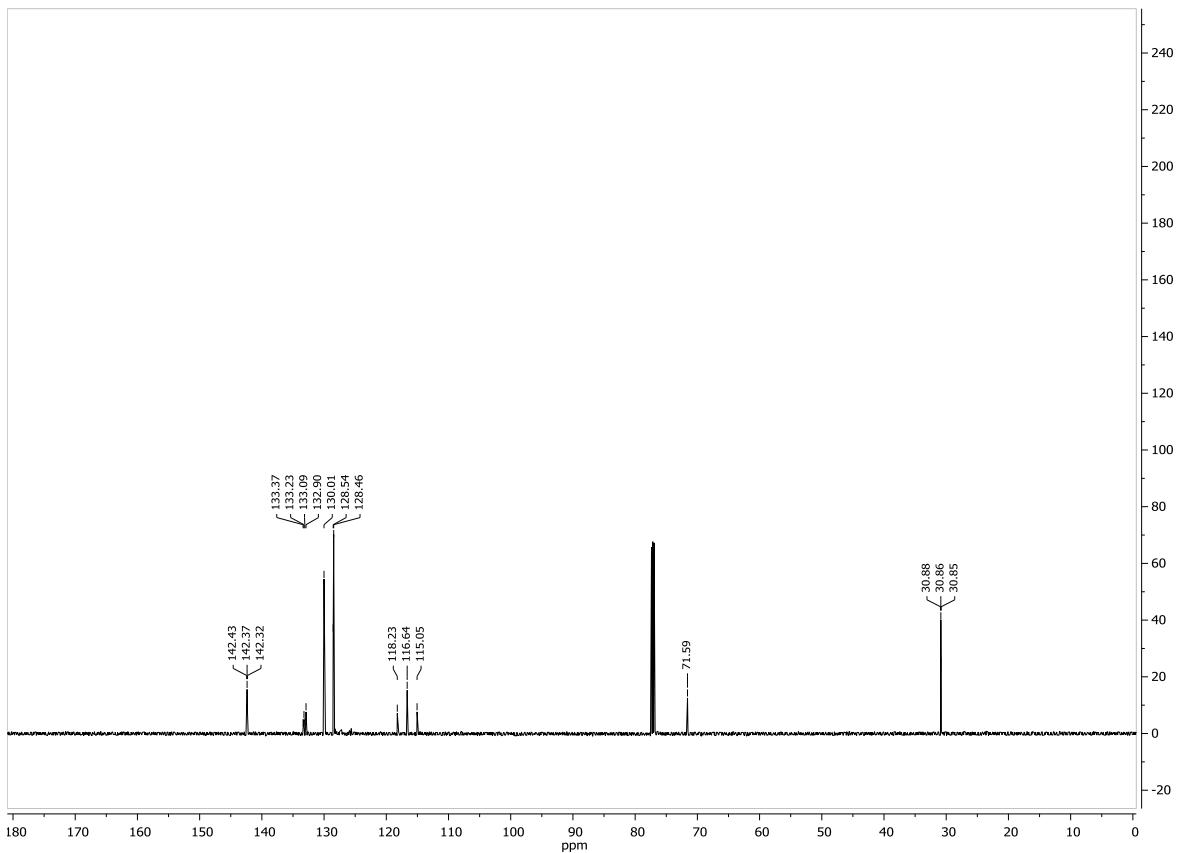
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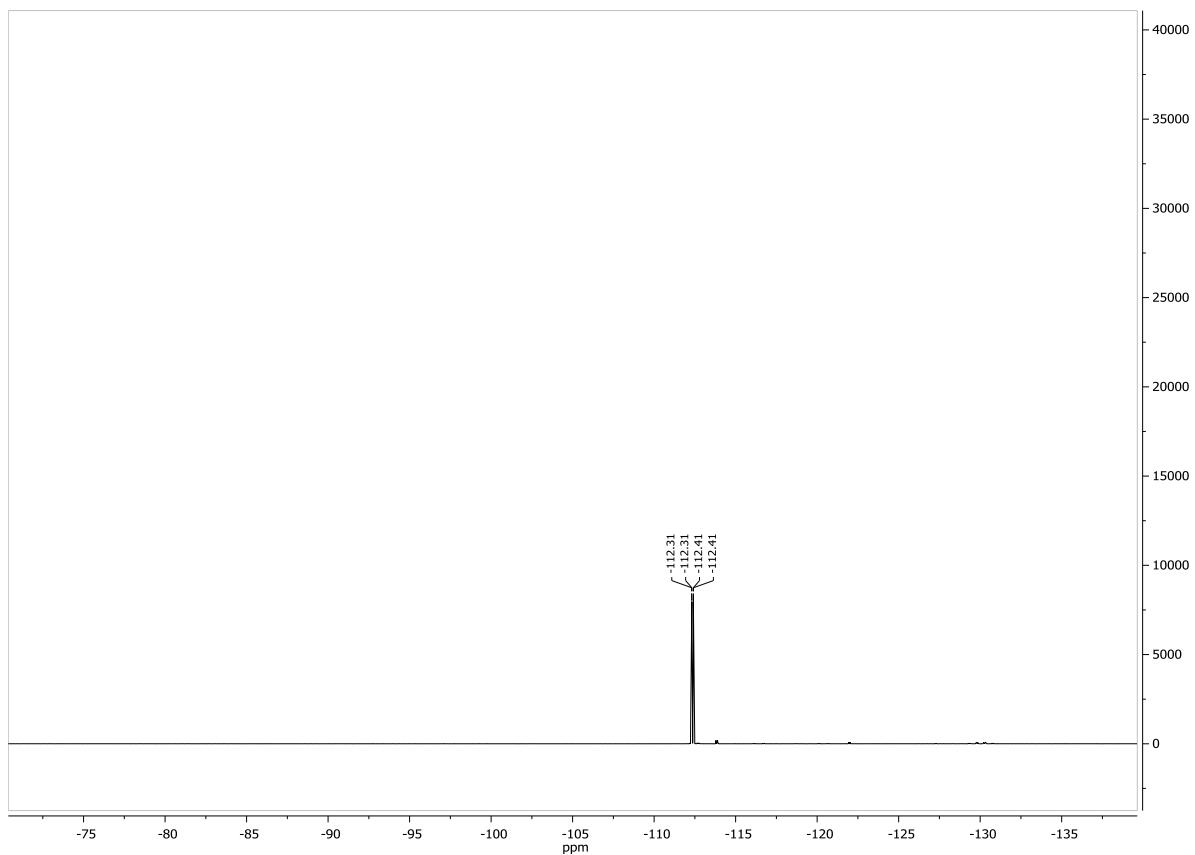
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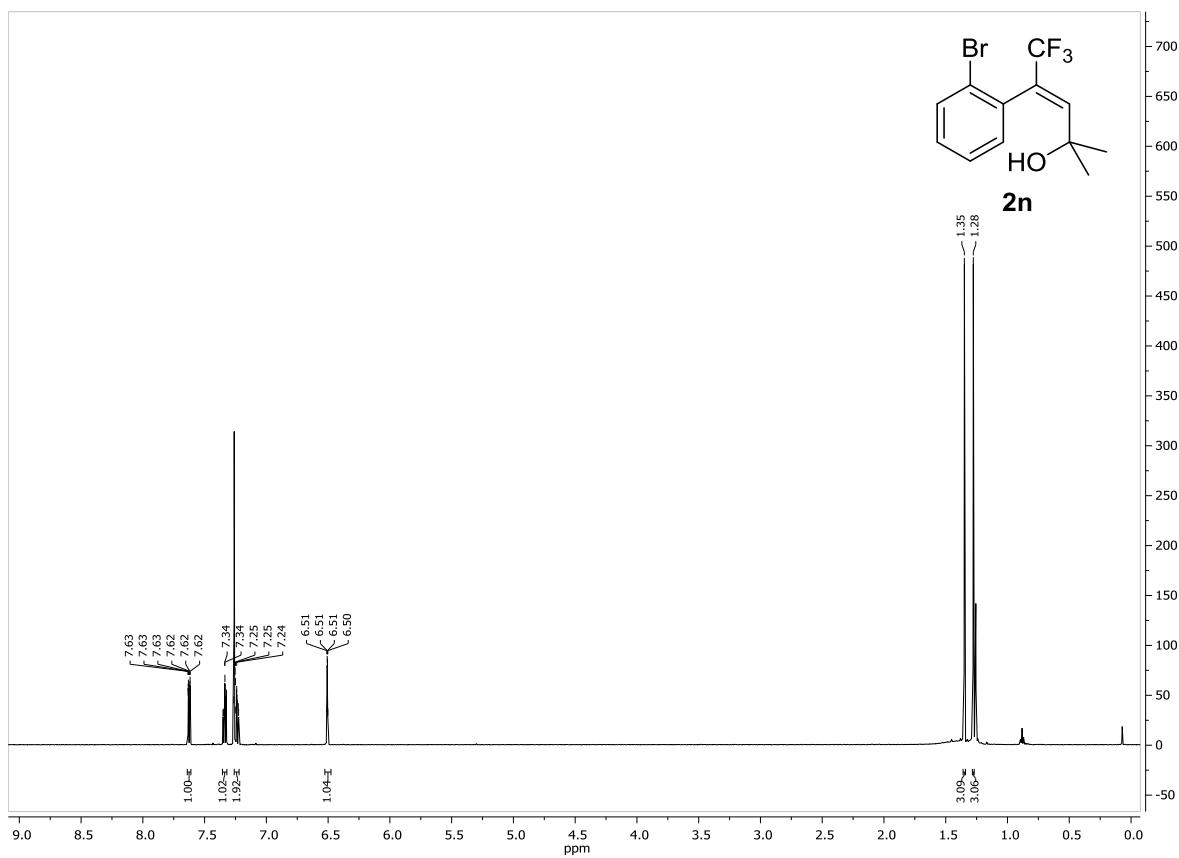
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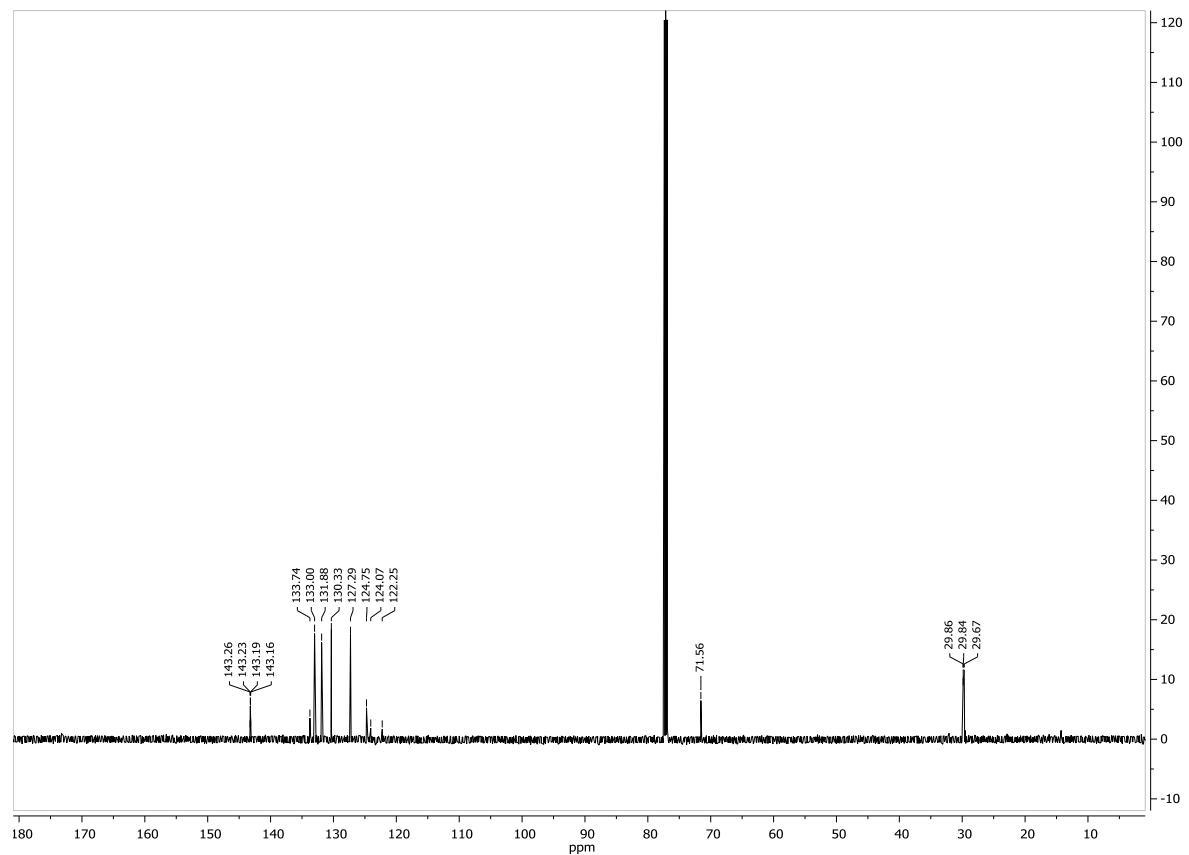
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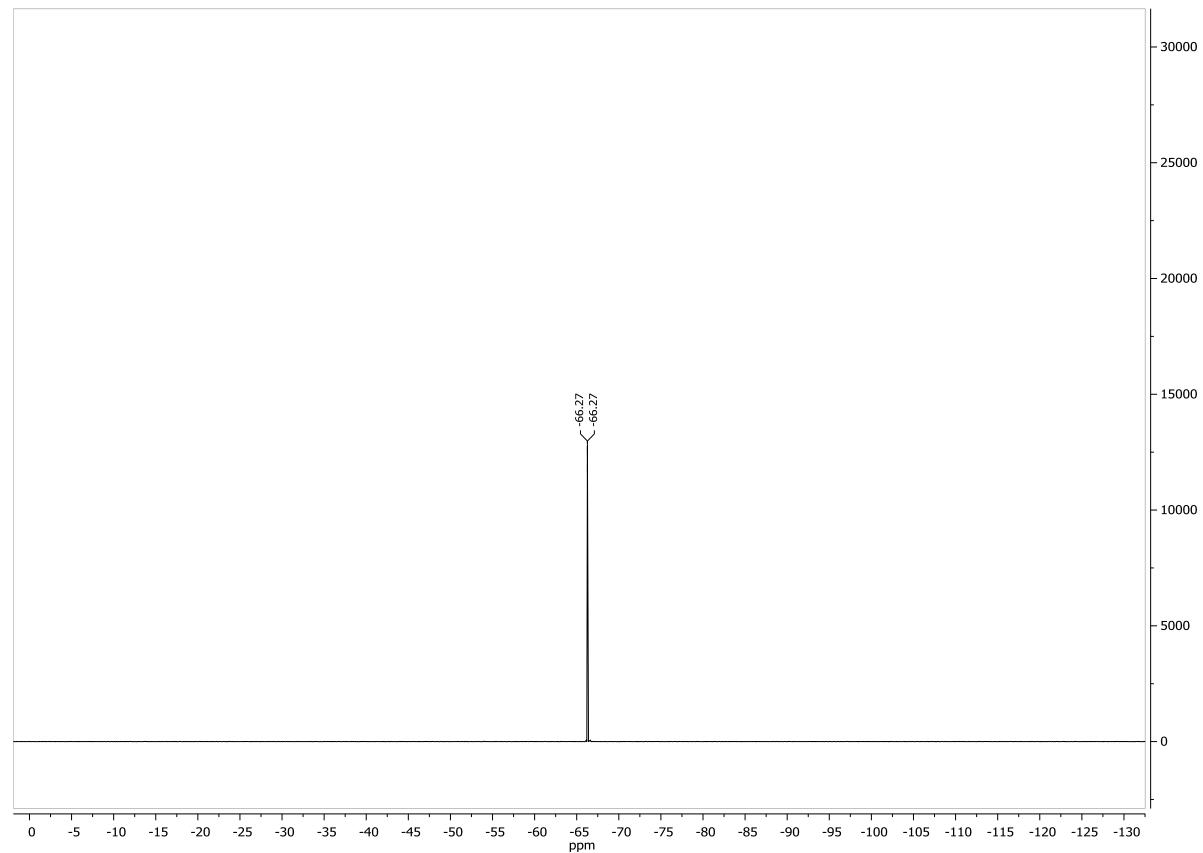
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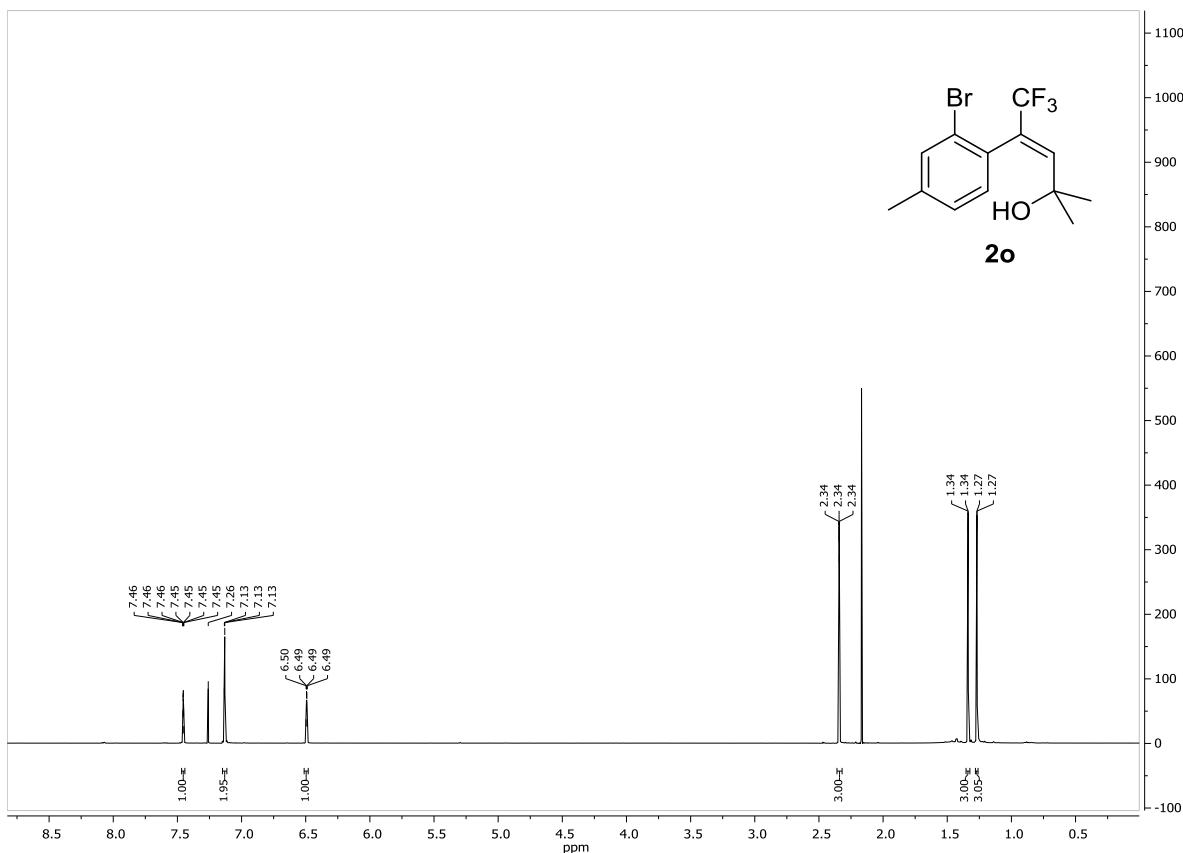
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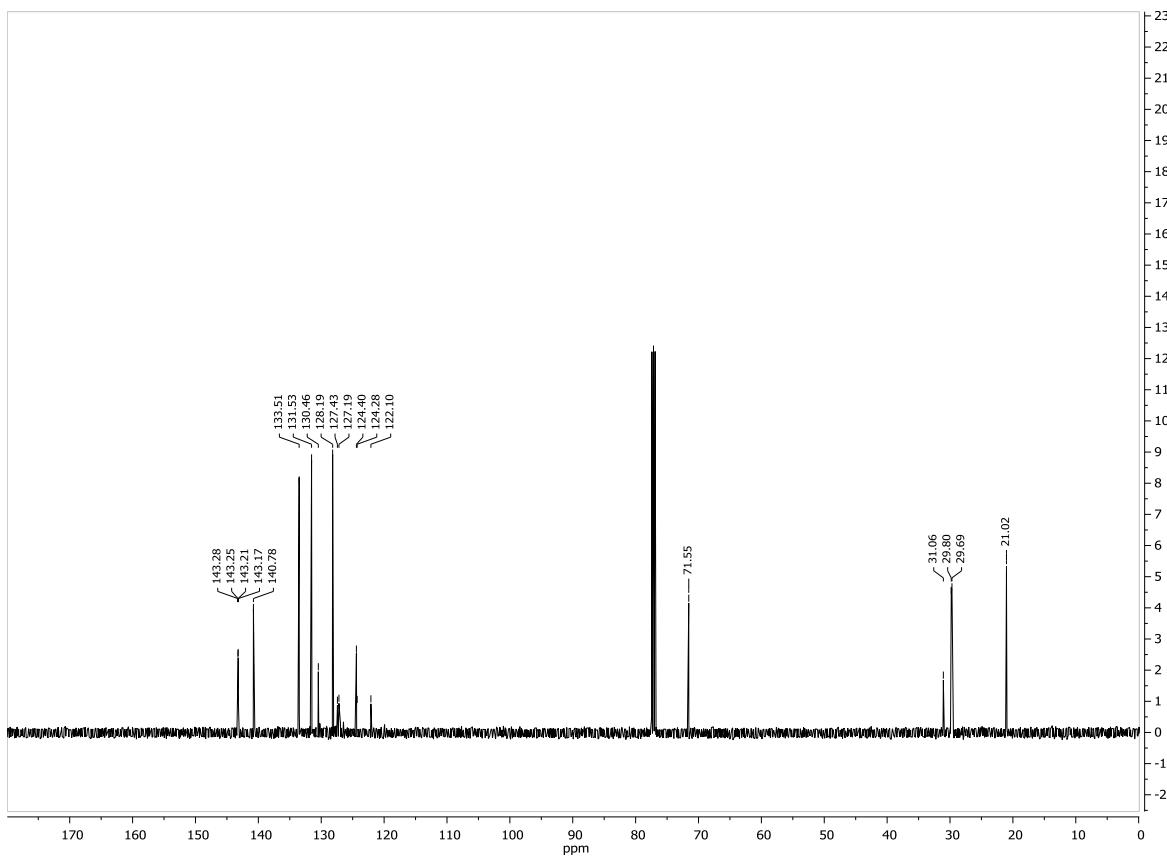
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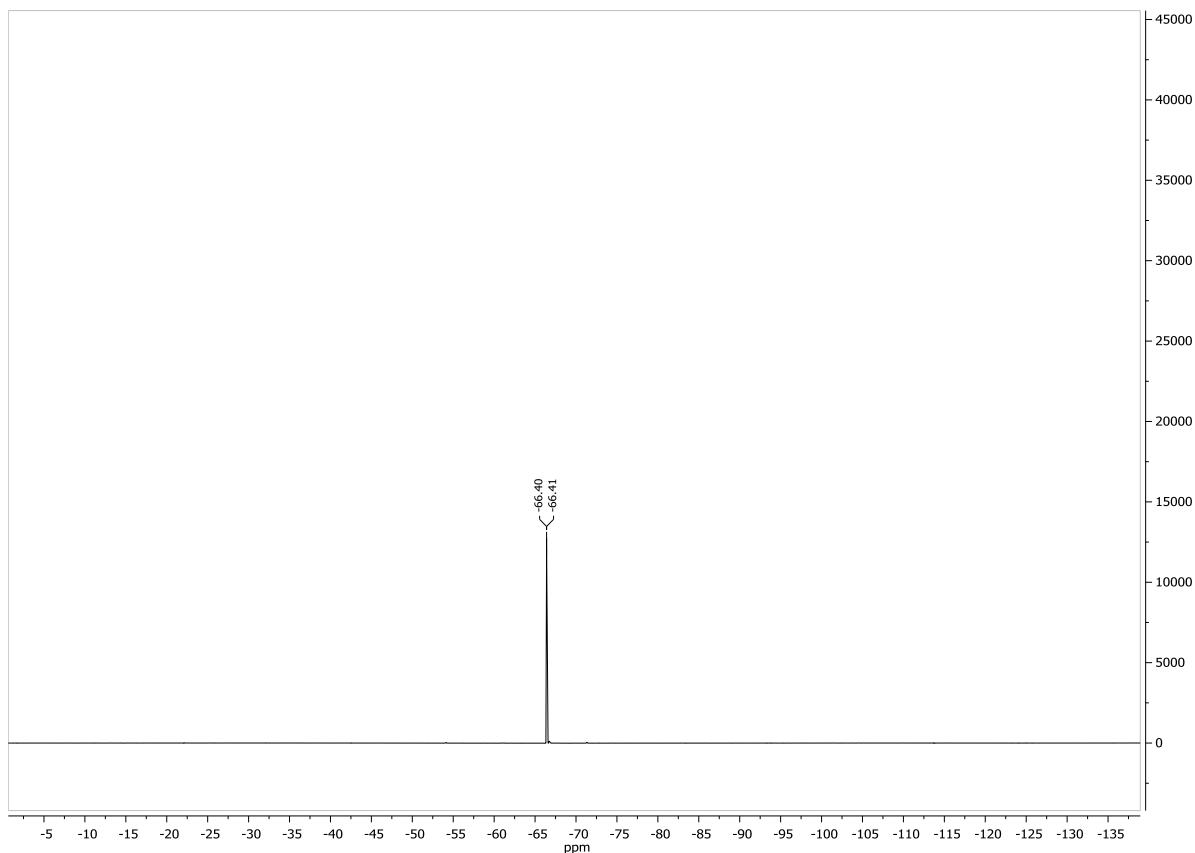
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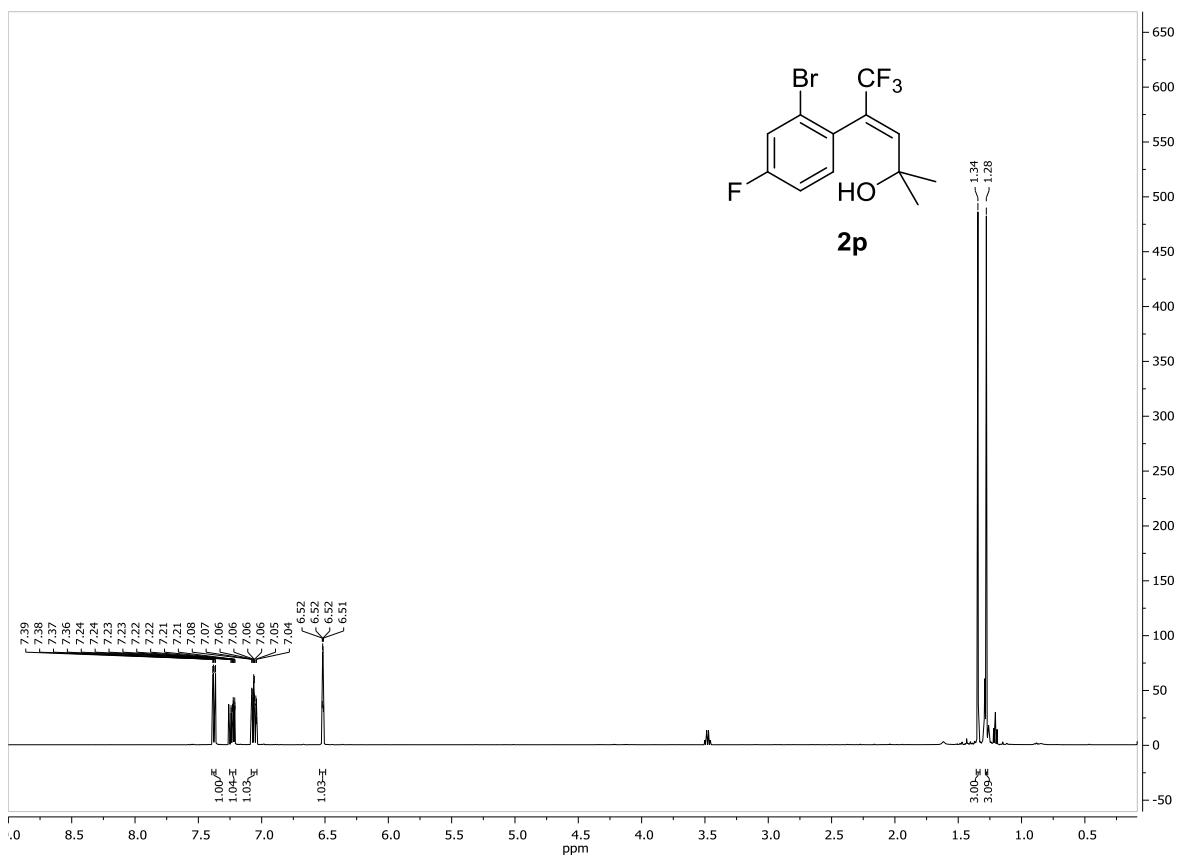
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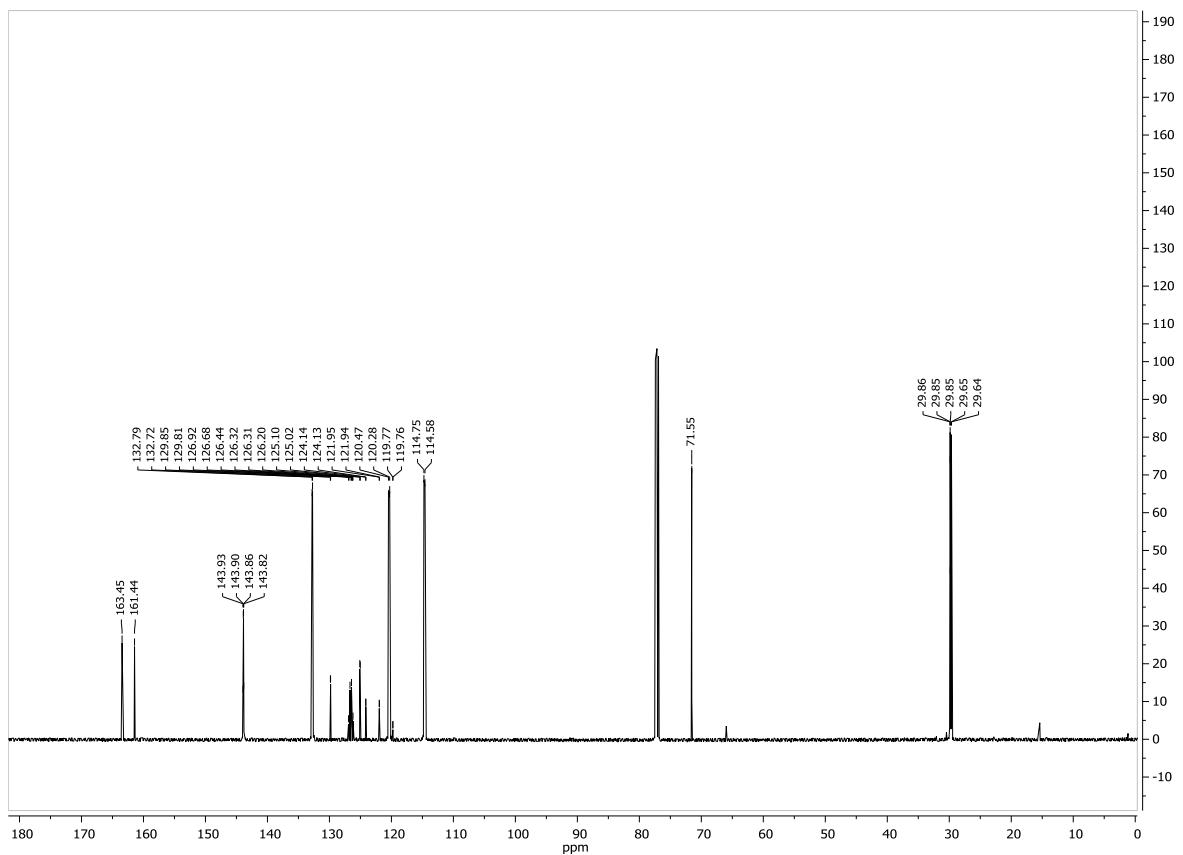
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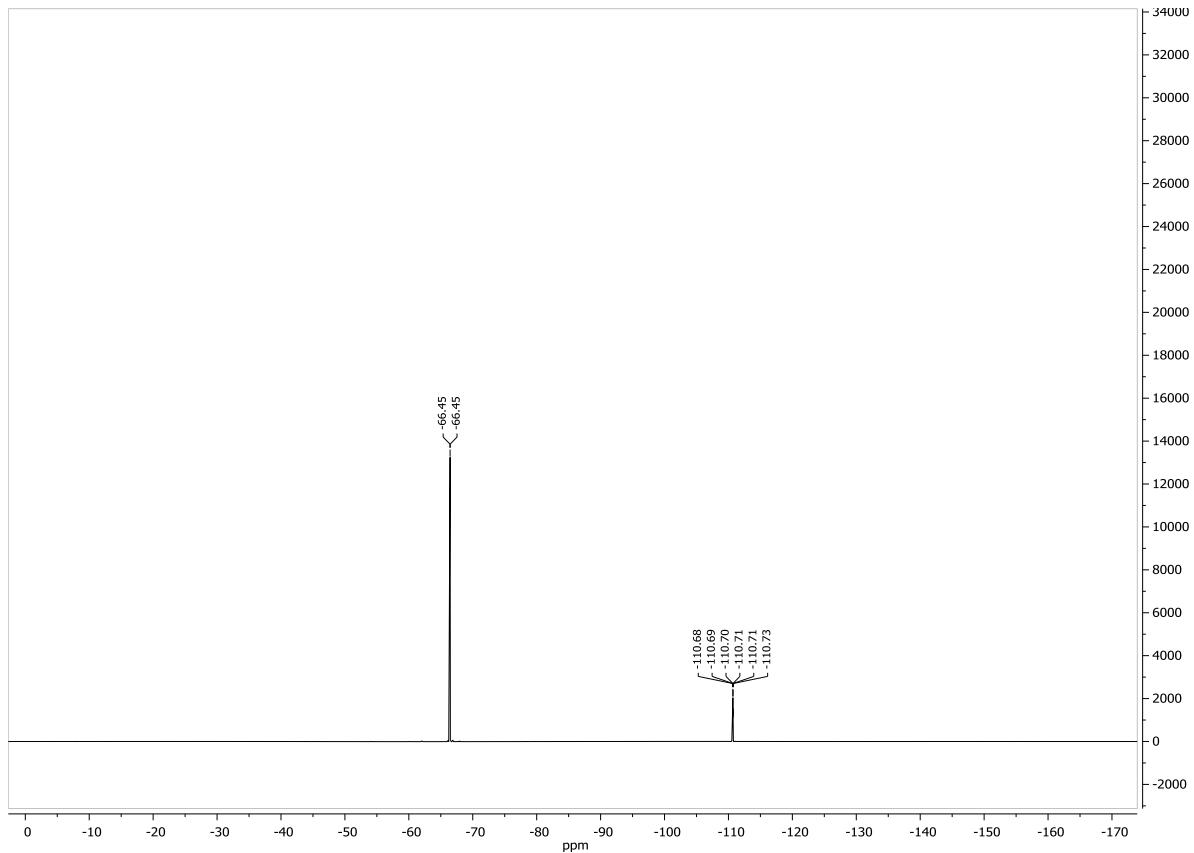
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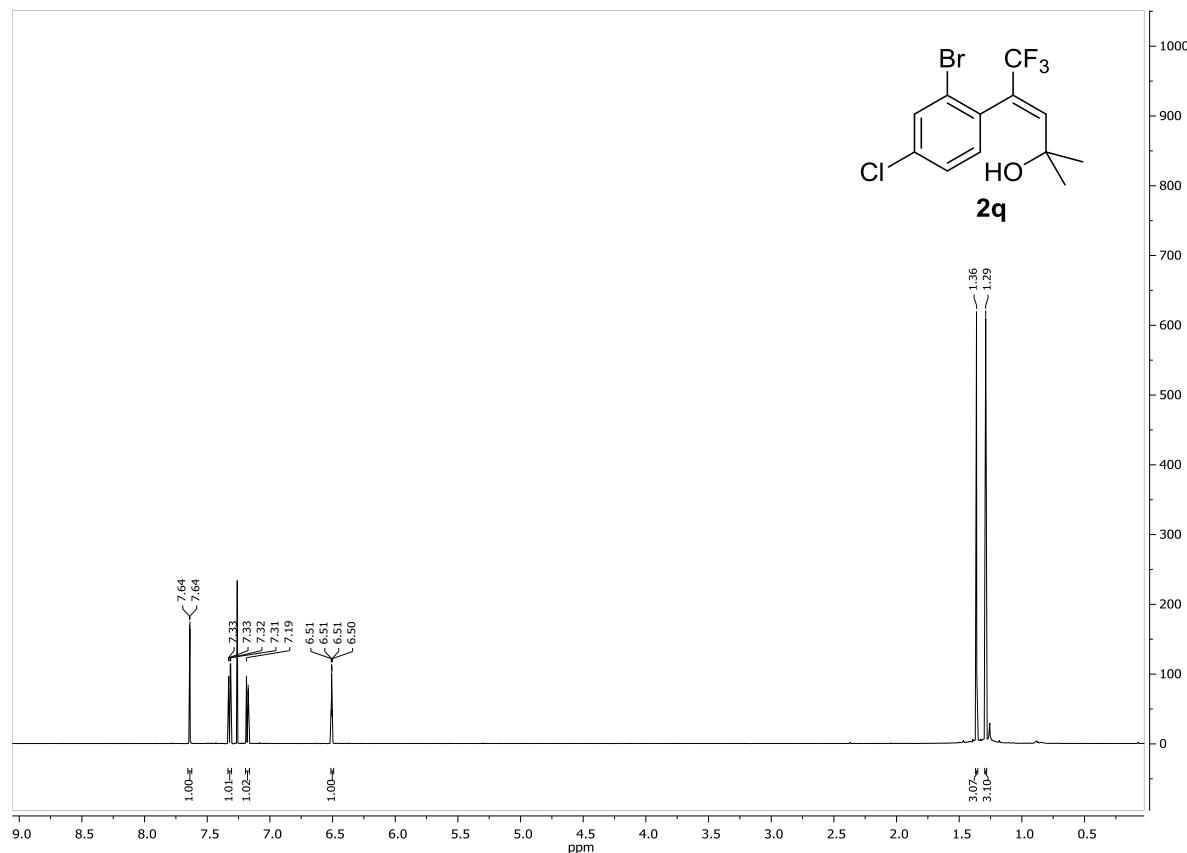
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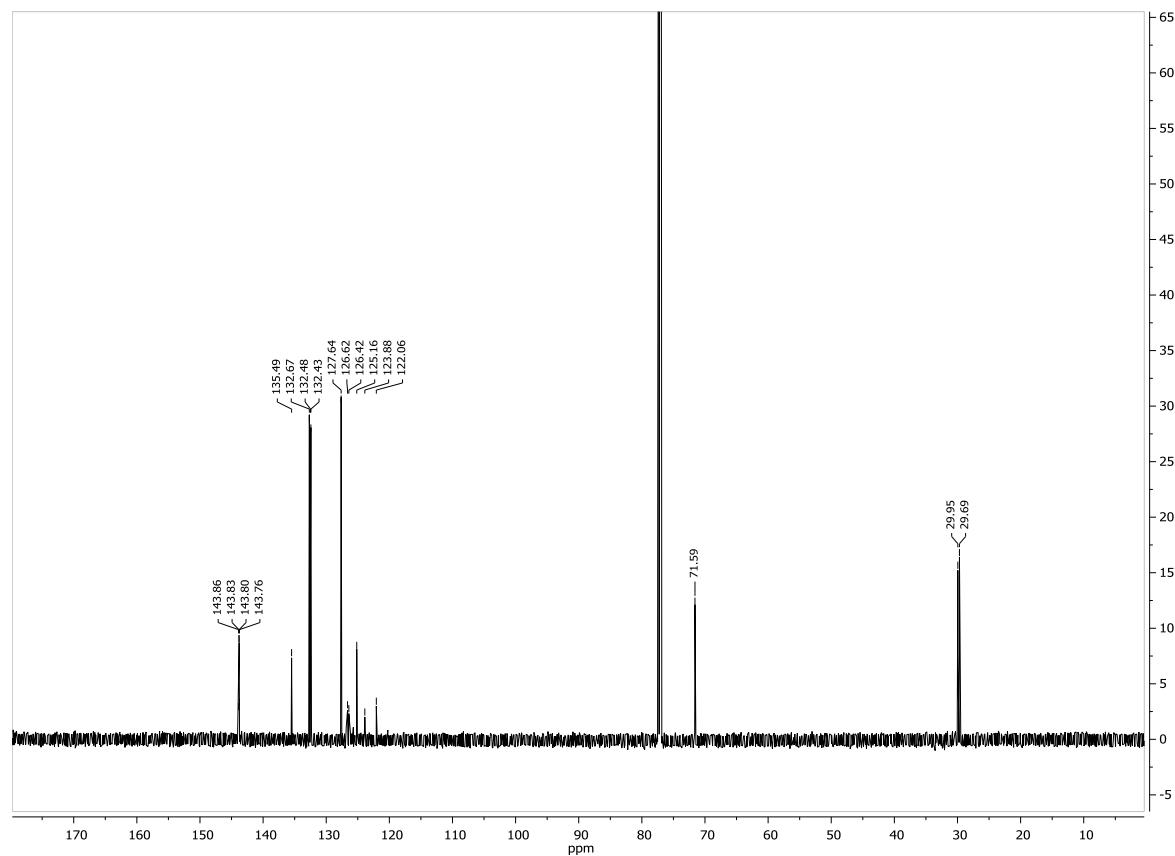
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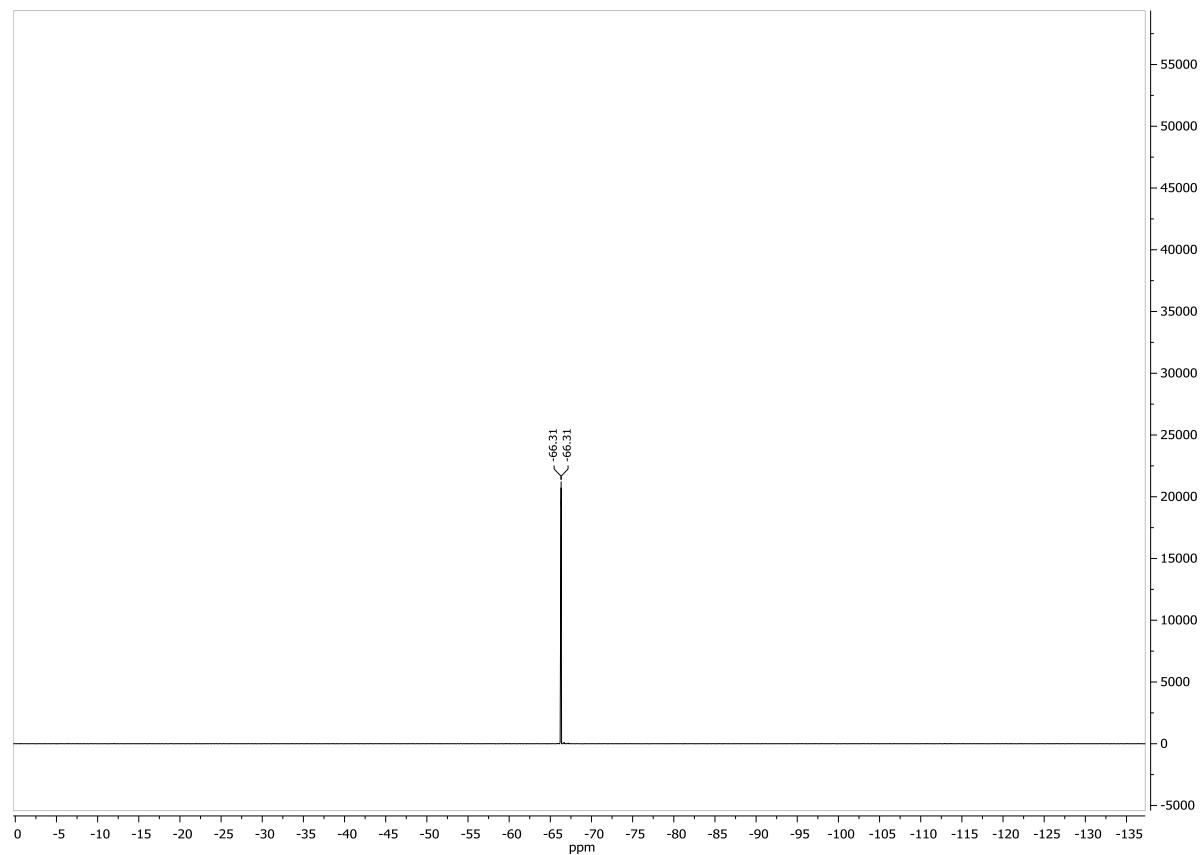
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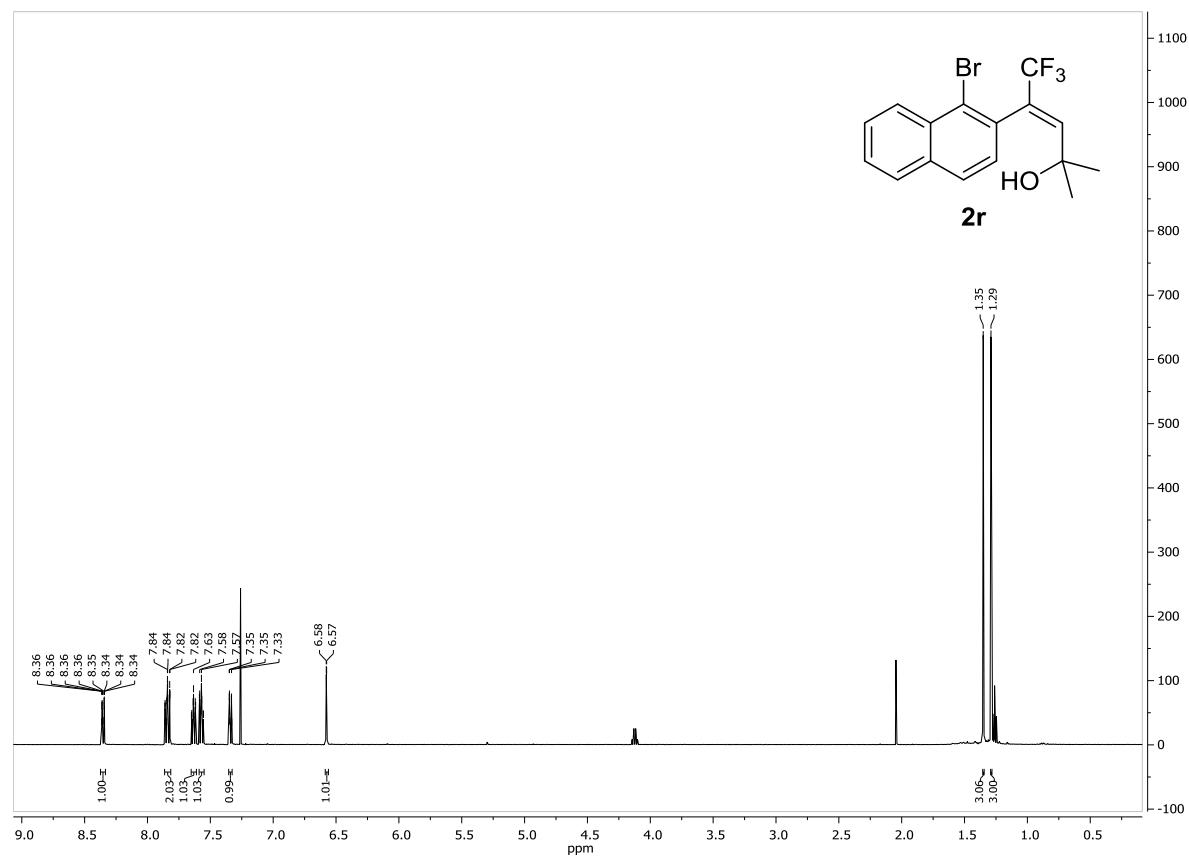
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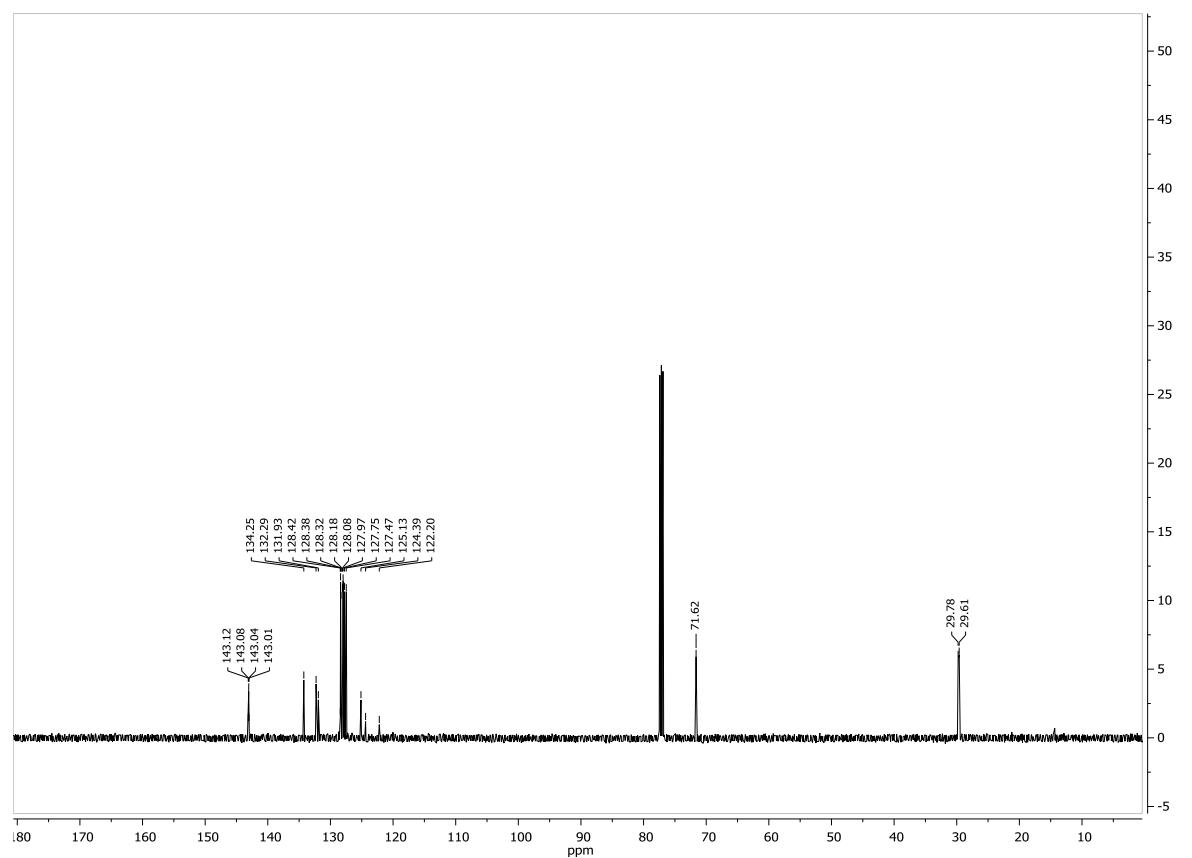
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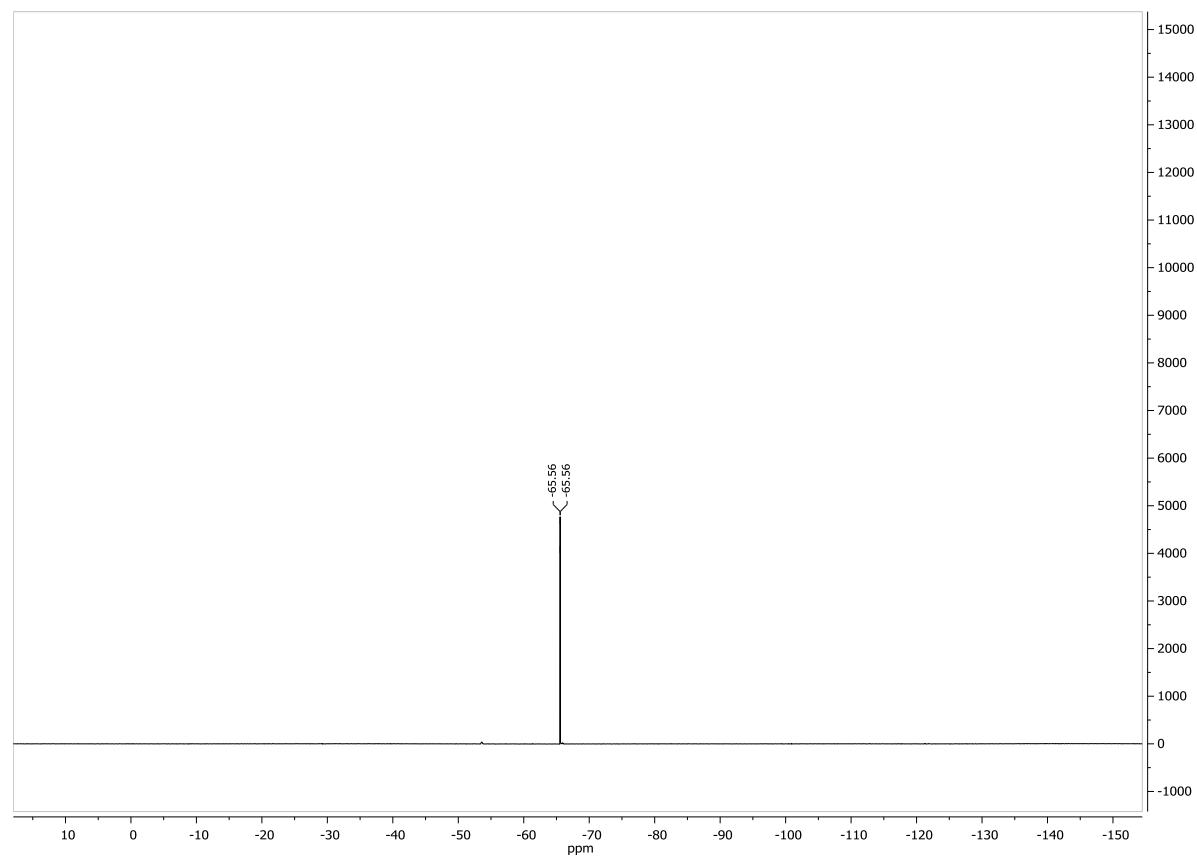
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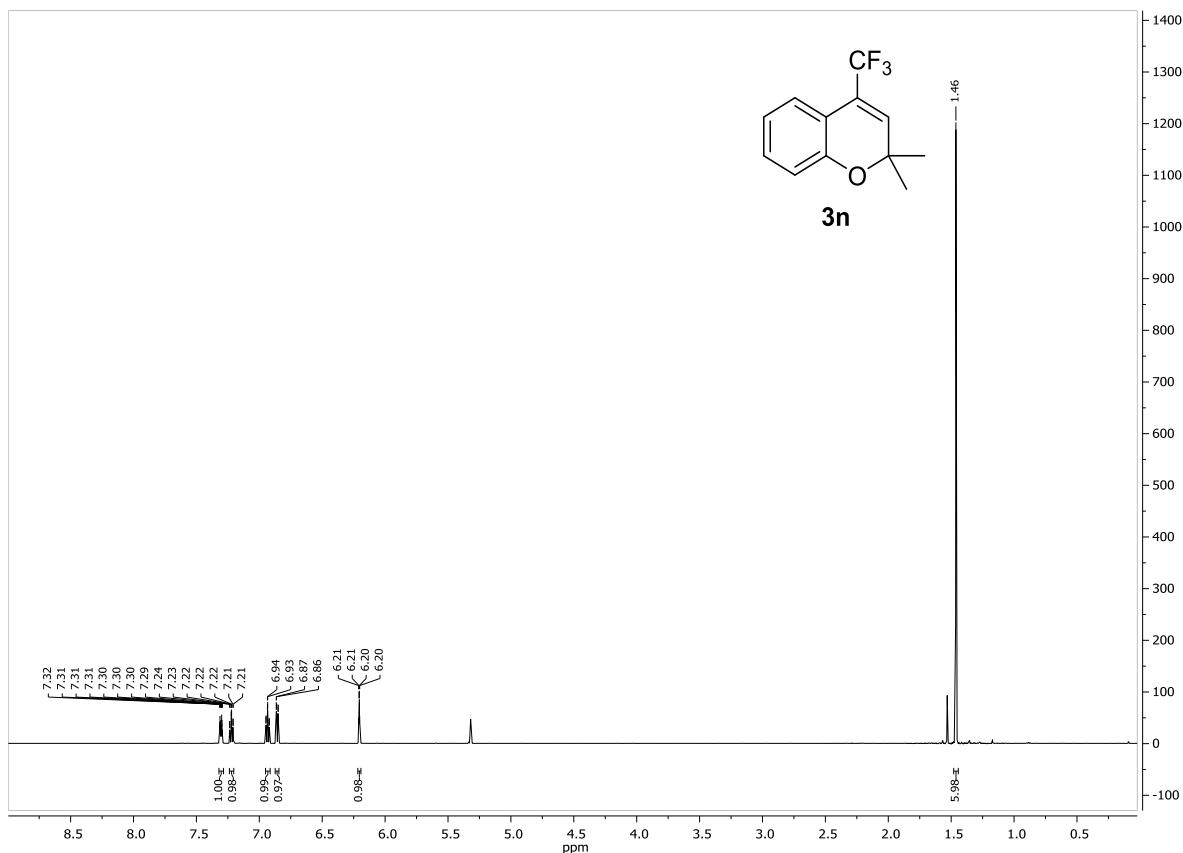
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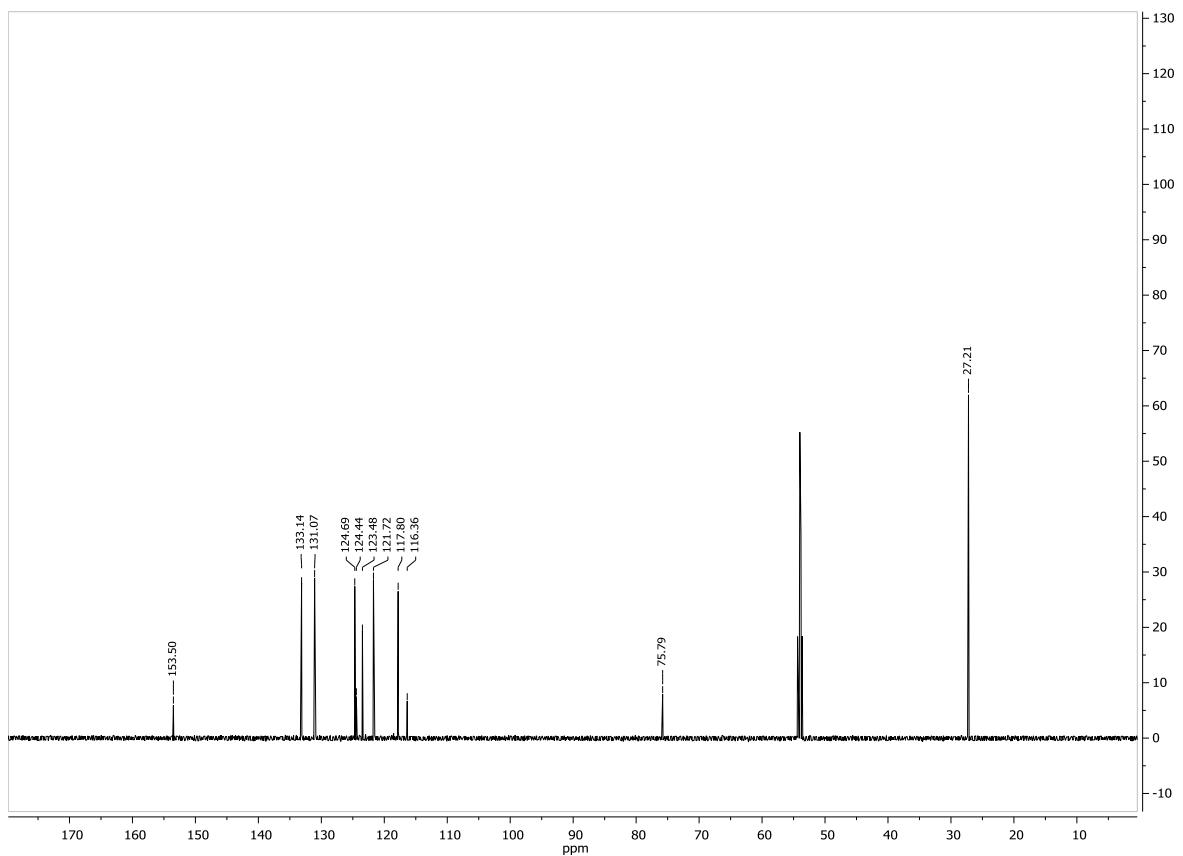
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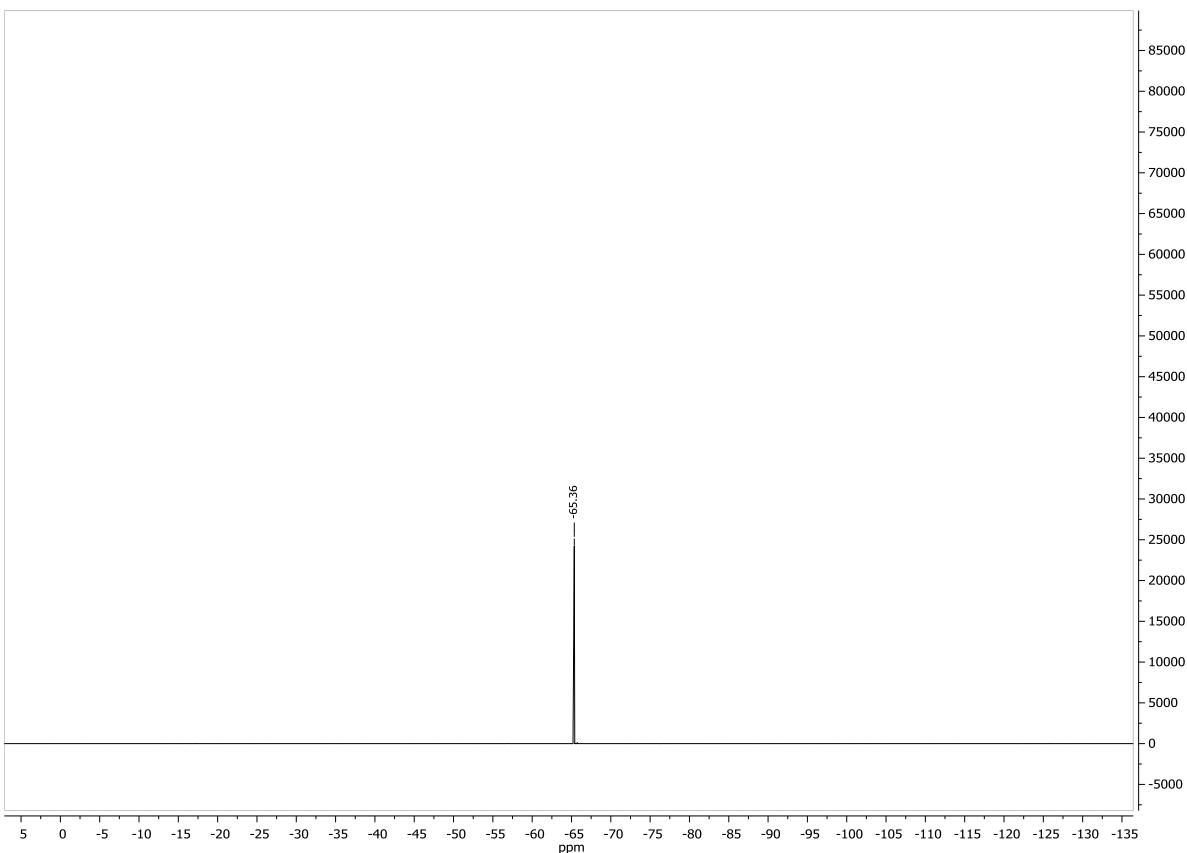
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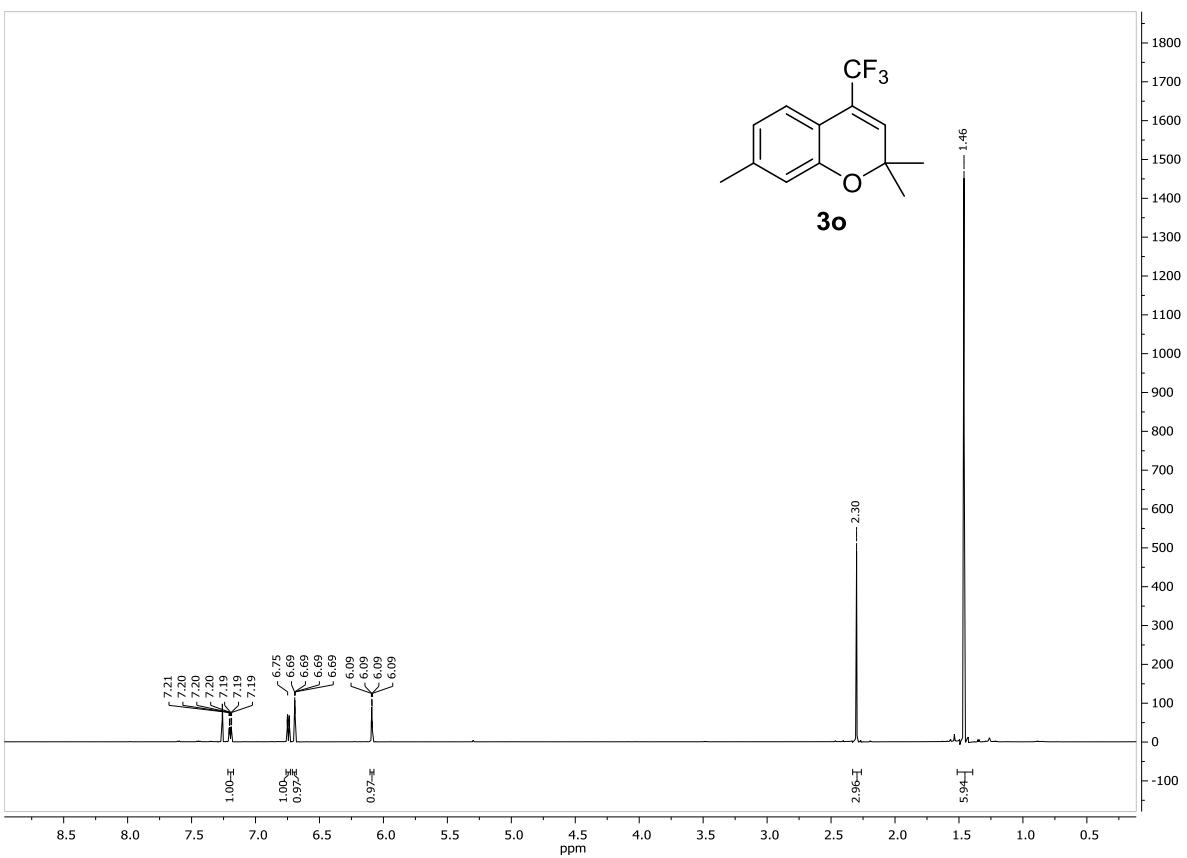
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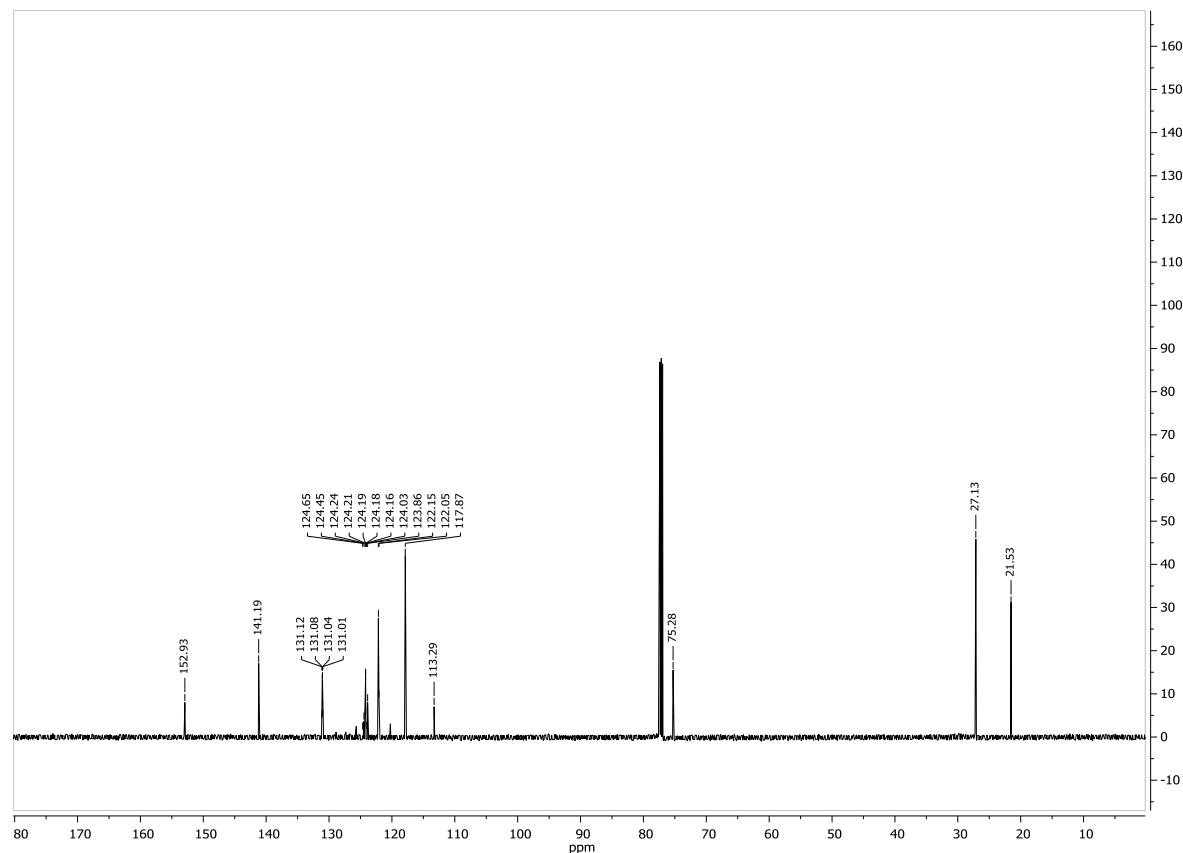
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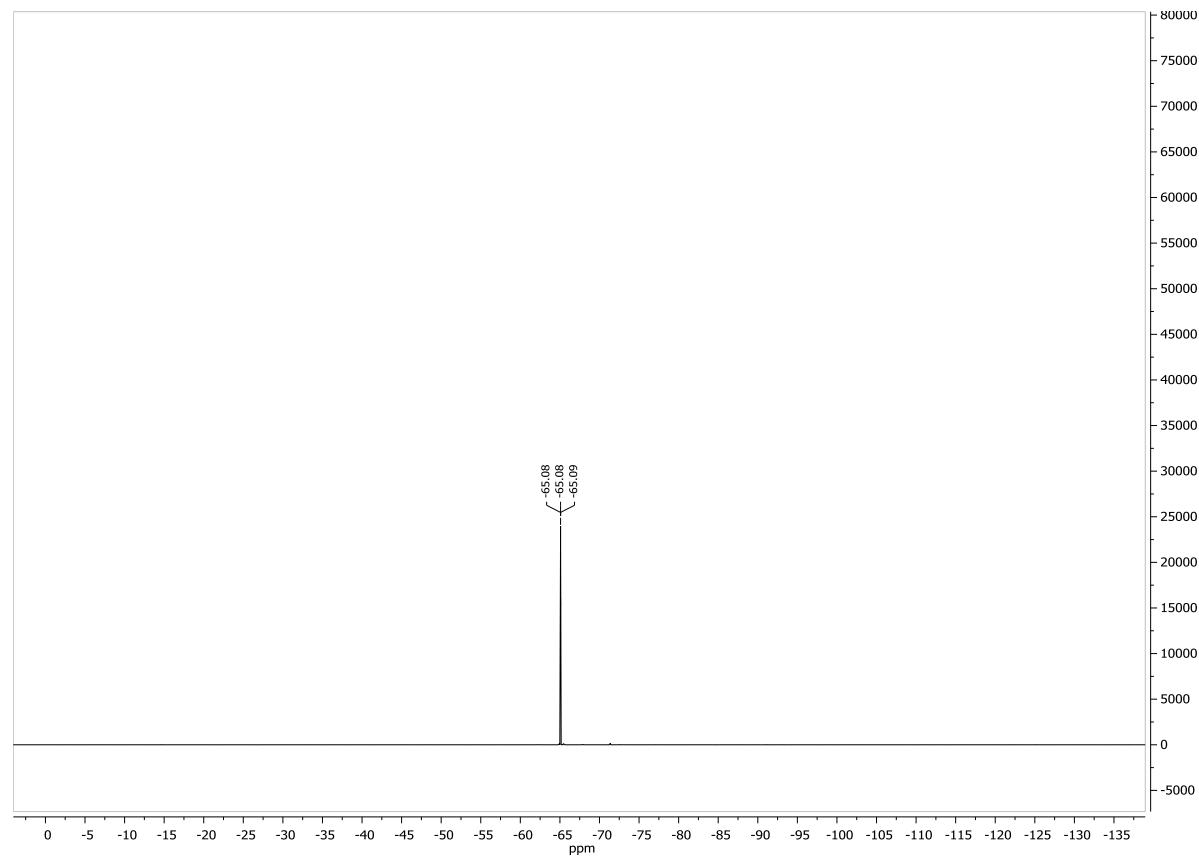
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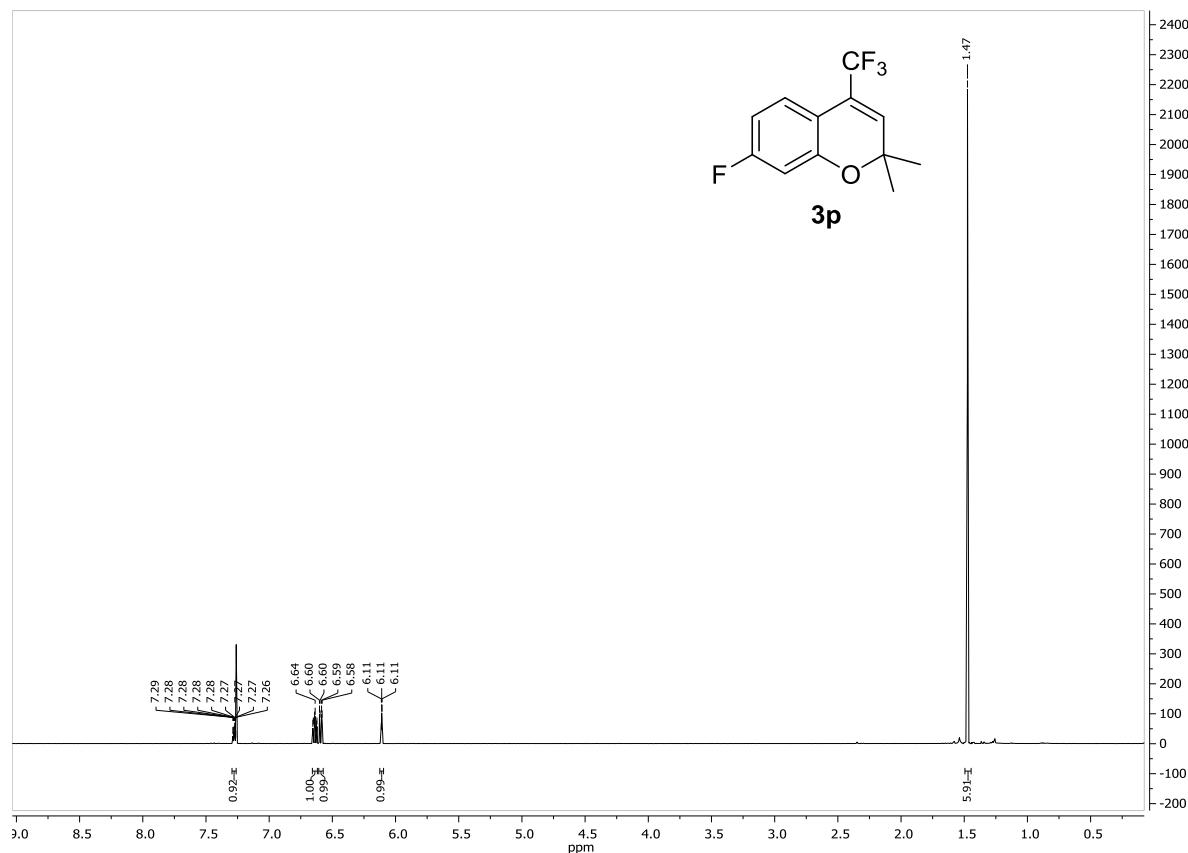
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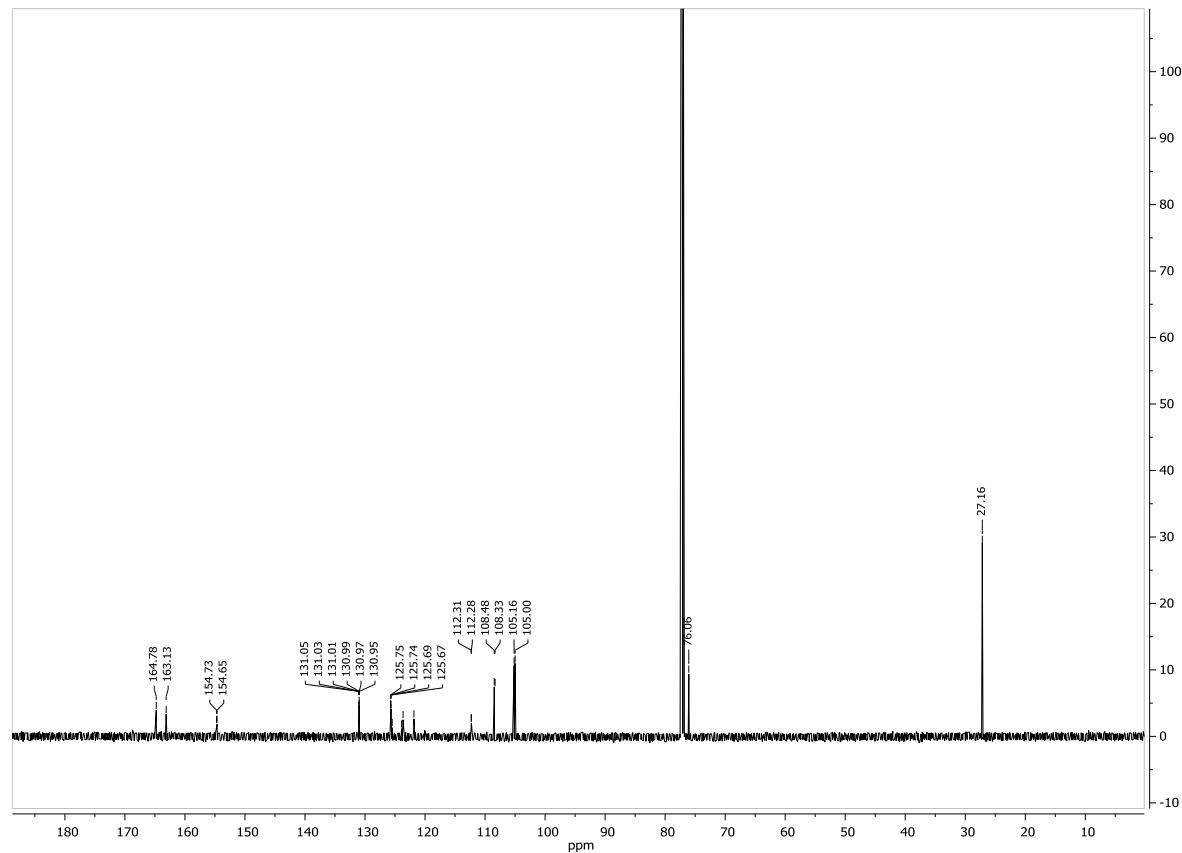
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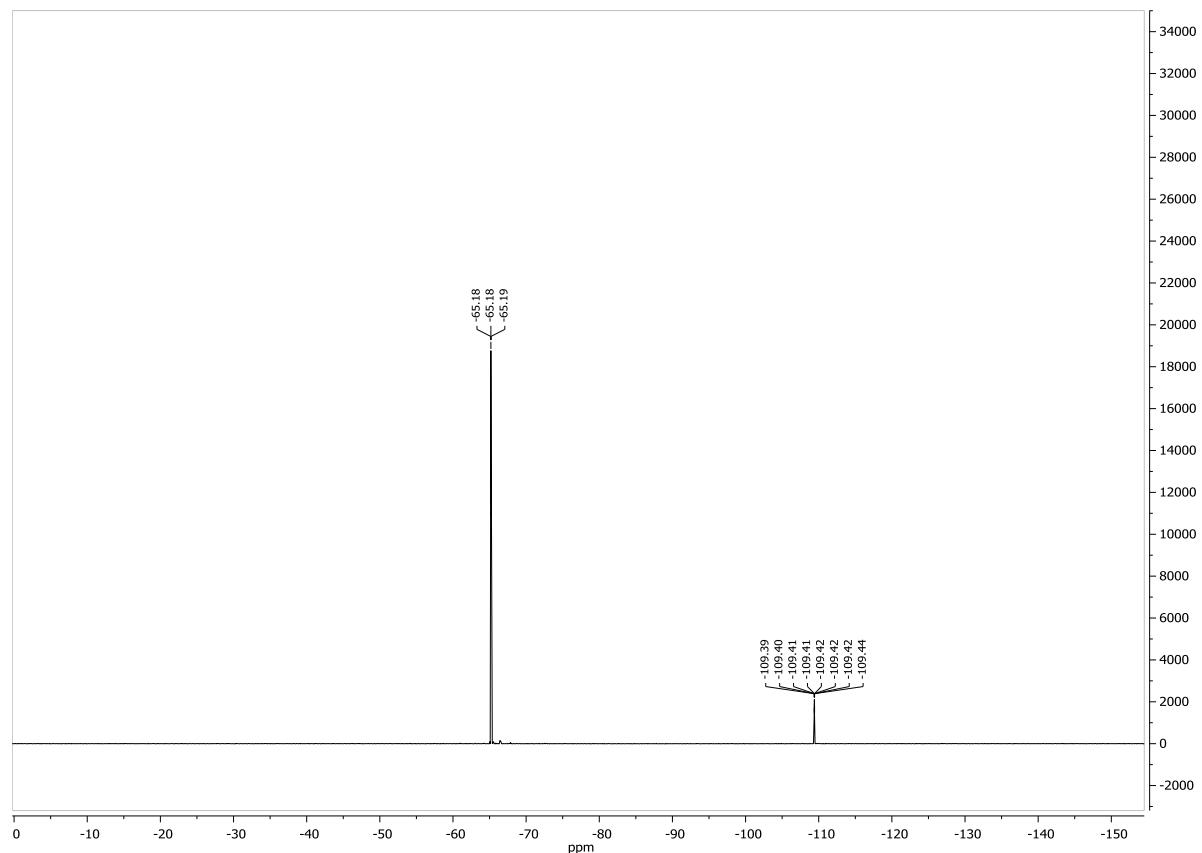
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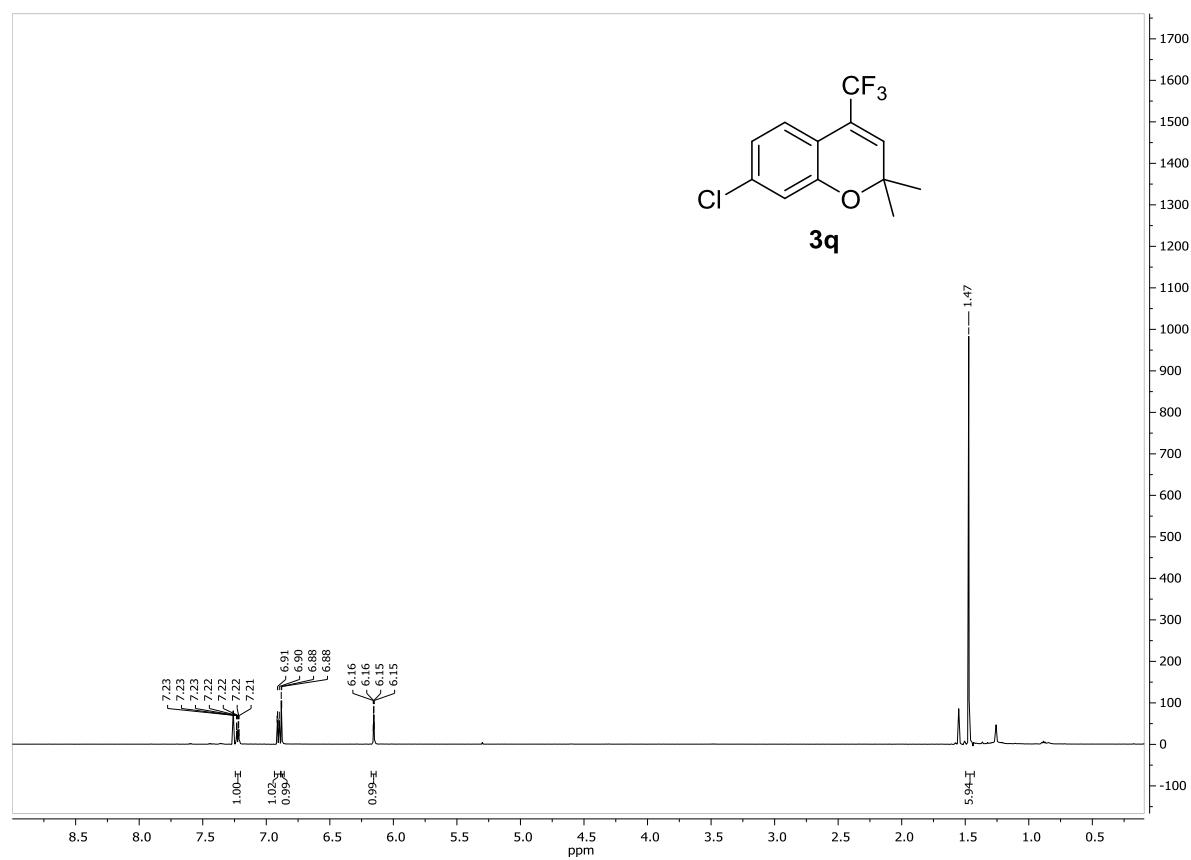
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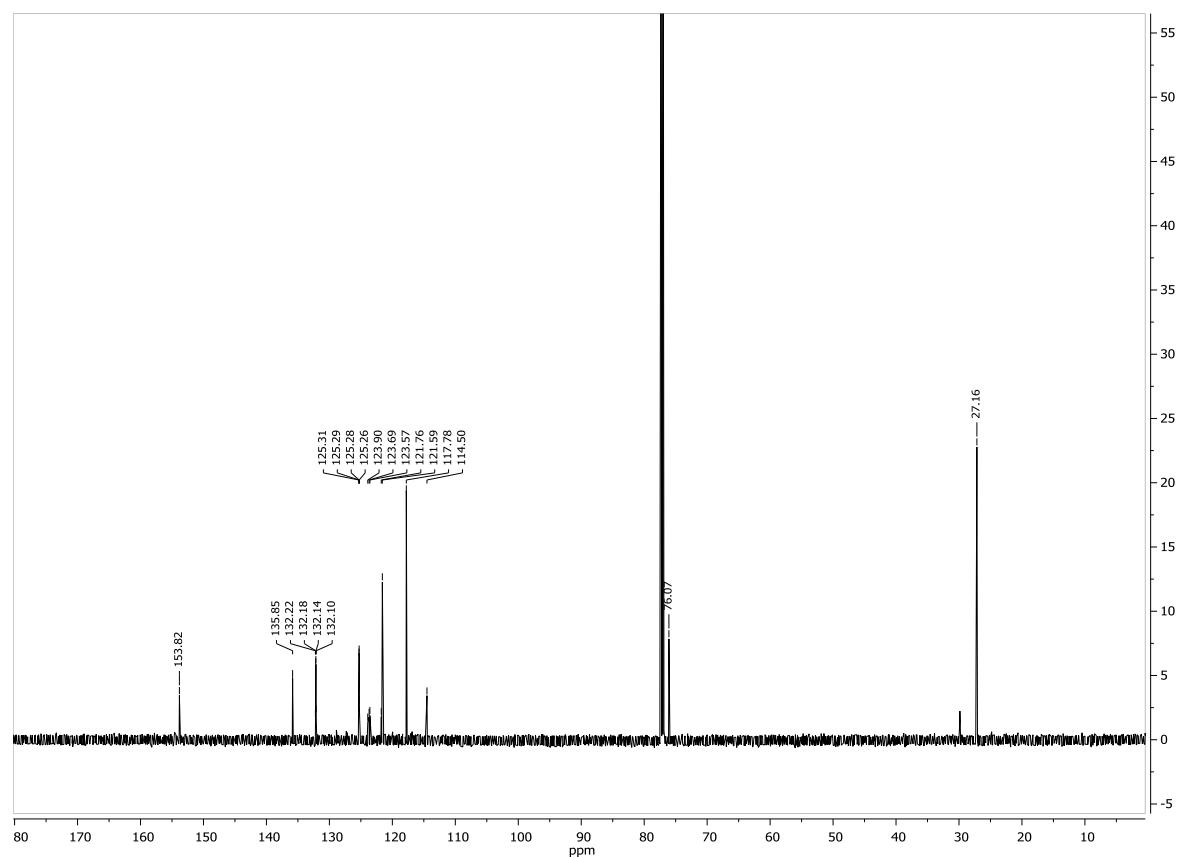
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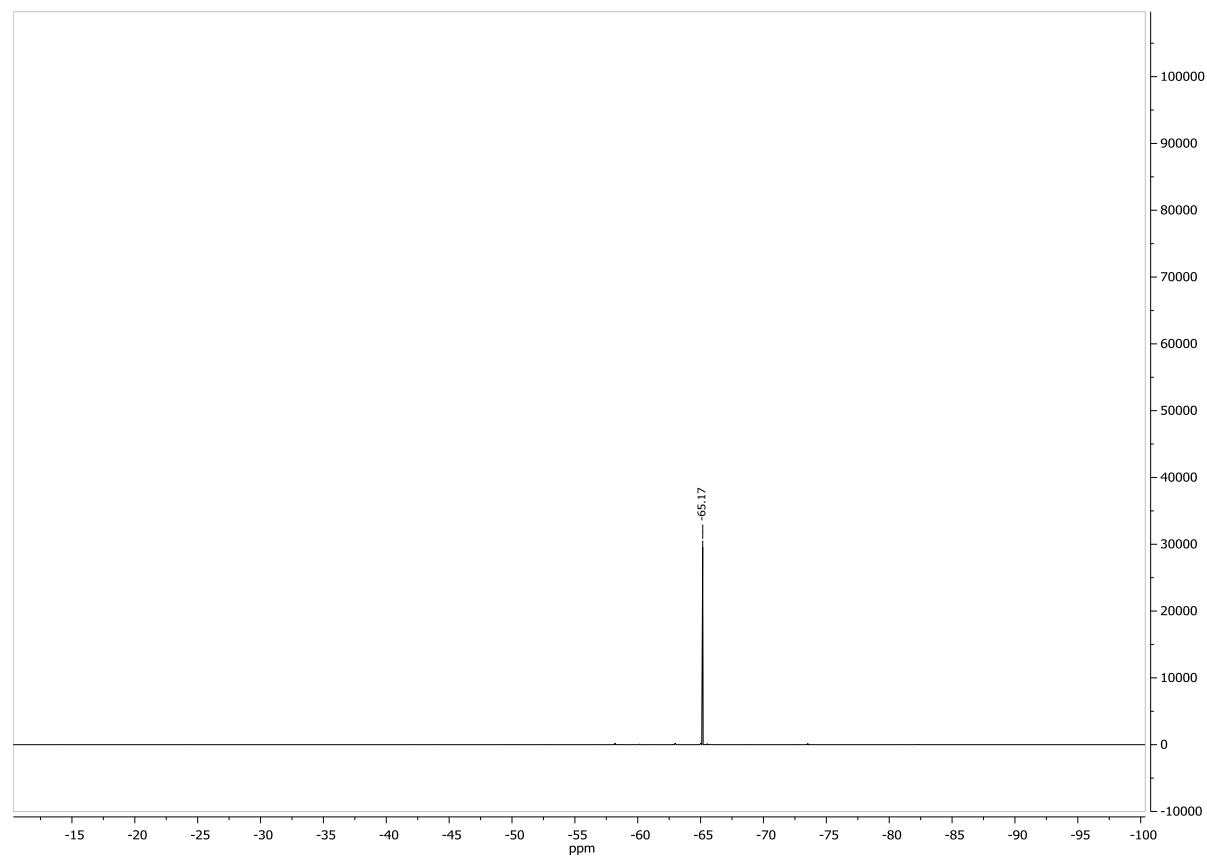
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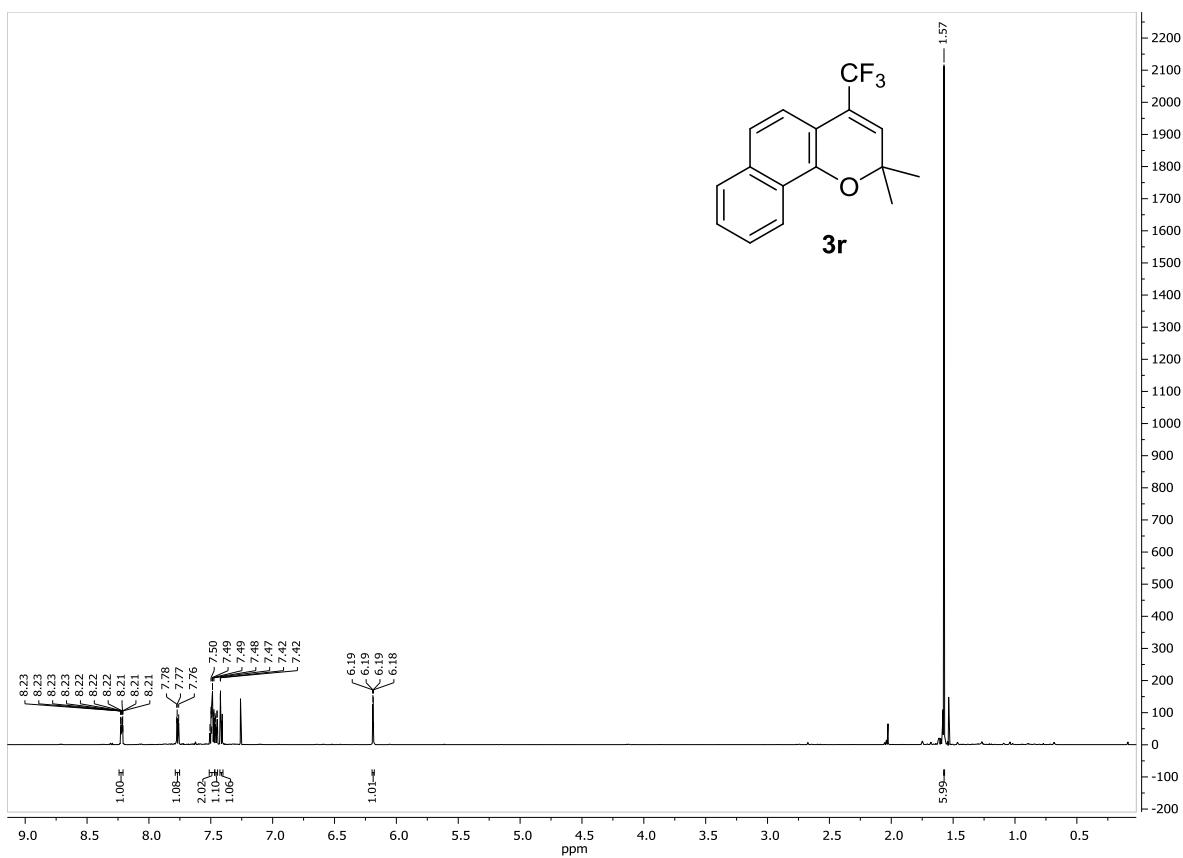
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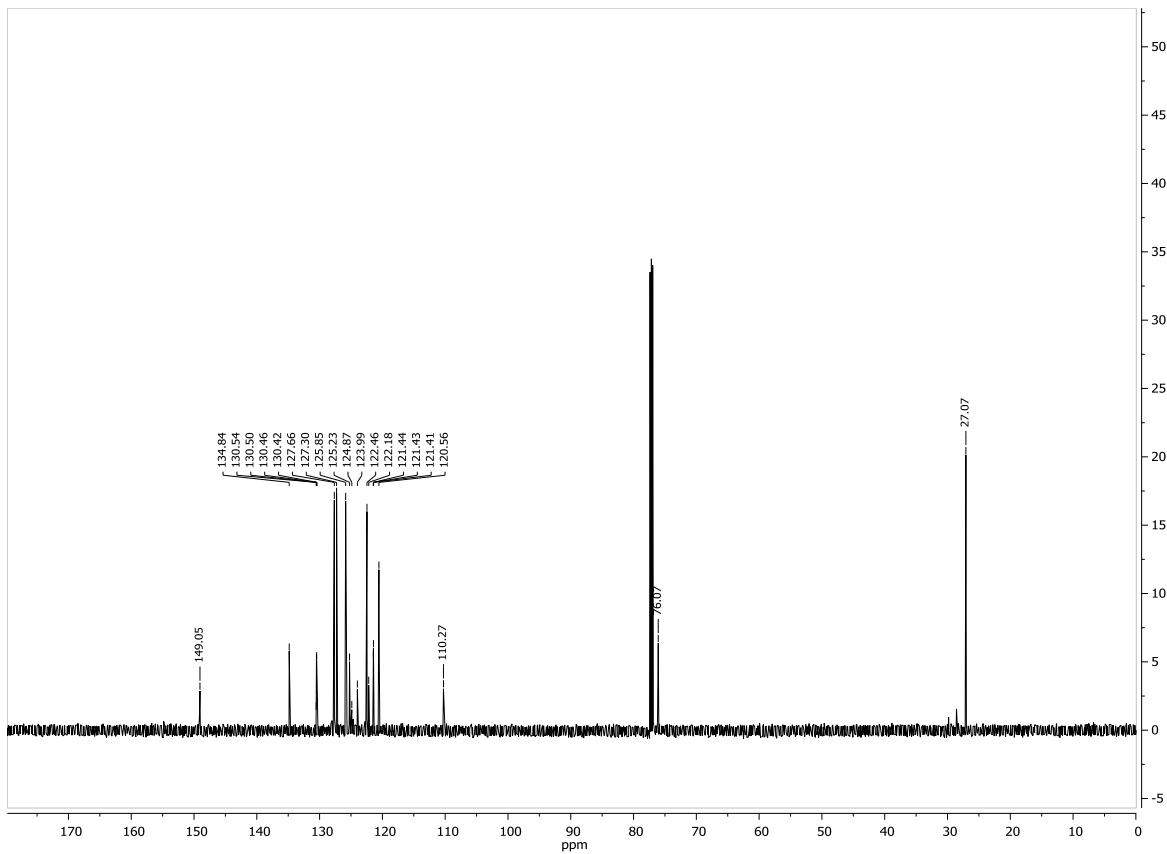
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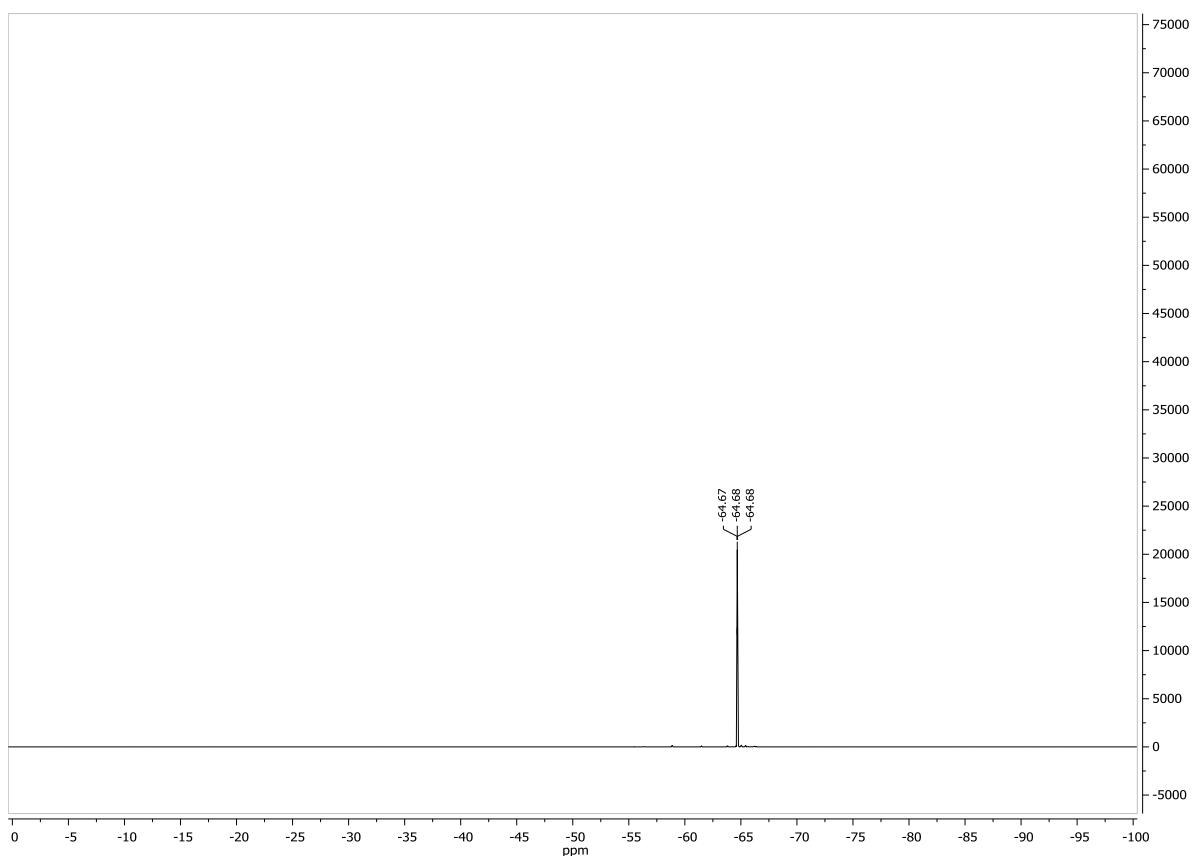
¹H NMR (CDCl₃, 600 MHz)



¹³C NMR (CDCl_3 , 151 MHz)



¹⁹F NMR (CDCl₃, 564 MHz)



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