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Supplementary Information for:

Lewis acid-base mediated 1,2-addition reactions: Synthesis of pyrylium borates from en-ynoate precursors.

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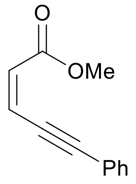
1. Experimental

1.1 General Experimental

With the exception of the starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O_2-free nitrogen using standard double-manifold techniques with a rotary oil pump. An argon- or nitrogen-filled glove box (MBraun) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. All solvents (toluene, CH_2Cl_2, hexane) were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800 and stored under a nitrogen atmosphere. Deuterated solvents were distilled and/or dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. ^{1}H, ^{13}C, ^{11}B and ^{19}F NMR spectra were recorded on a Bruker Avance II 400, Bruker Avance 500, Bruker Avance III 600 or JEOL Eclipse 300 spectrometers. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to $CDCl_3$ (7.26/77.16 ppm) as internal standards. NMR spectra were referenced to $CFCl_3$ (^{19}F) and $BF_3 \cdot Et_2O/CDCl_3$ (^{11}B). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, sep = septet, m = multiplet and br. = broad. All coupling constants are absolute values and are expressed in Hertz (Hz). ^{13}C NMR was measured as ^{1}H decoupled. Yields are given as isolated yields. All spectra were analysed assuming a first order approximation. IR-Spectra were measured on a Shimadzu IRAffinity-1 photospectrometer. Mass spectra were measured on a Waters LCT Premier/XE or a Waters GCT Premier spectrometer.

1.2 Synthesis of starting materials.

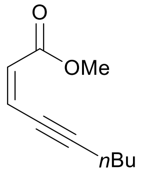
*Synthesis of methyl (Z)-5-phenylpent-2-en-4-ynoate (**1a**).*



Compound **1a** was synthesised using similar methods to that reported in the literature. The ^{1}H and ^{13}C NMR data agree with the literature reported values confirming the isolation of the product.[1]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 7.55-7.53 (m, 2H, Ph-H), 7.35 (m, 3H, Ph-H), 6.37 (d, $^3J_{HH}$ = 11.4 Hz, 1H, =CH), 6.15 (d, $^3J_{HH}$ = 11.4 Hz, 1H, =CH), 3.80 (s, 3H, OCH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): 165.3 (s), 132.2 (s), 129.3 (s), 128.5 (s), 127.9 (s), 123.3 (s), 122.8 (s), 101.5 (s), 86.5 (s), 51.6 (s).

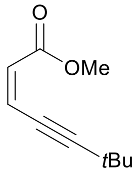
*Synthesis of methyl (Z)-non-2-en-4-ynoate (**1b**).*



Compound **1b** was synthesised using similar methods to that reported in the literature. The ^{1}H and ^{13}C NMR data agree with the literature reported values confirming the isolation of the product.[1]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 6.16-6.13 (dt, $^3J_{HH}$ = 11.4 Hz, $^4J_{HH}$ = 2.4 Hz, 1H, =CH), 6.02 (d, $^3J_{HH}$ = 11.4 Hz, 1H, =CH), 3.74 (s, 3H, OCH_3), 2.45 (td, $^3J_{HH}$ = 7.0 Hz, $^4J_{HH}$ = 2.4 Hz, 2H, CH_2), 1.60-1.54 (m, 2H, CH_2), 1.49-1.43 (m, 2H, CH_2), 0.92 (t, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3). **^{13}C NMR** (126 MHz, $CDCl_3$, 298 K): 165.5 (s, 1C), 127.1 (s, 1C), 124.3 (s, 1C), 104.5 (s, 1C), 77.8 (s, 1C), 51.4 (s, 1C), 30.6 (s, 1C), 22.1 (s, 1C), 19.9 (s, 1C), 13.7 (s, 1C).

*Synthesis of methyl (Z)-6,6-dimethylhept-2-en-4-ynoate (**1c**).*

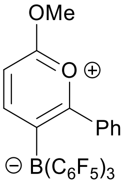


Compound **1c** was synthesised using similar methods to that reported in the literature. The ^{1}H data agrees with the literature reported values confirming the isolation of the product.[1]

^{1}H NMR (500 MHz, $CDCl_3$, 298 K): 6.14 (d, $^3J_{HH}$ = 11.5 Hz, 1H, =CH), 6.01 (d, $^3J_{HH}$ = 11.5 Hz, 1H, =CH), 3.75 (s, 3H, OCH_3), 1.30 (s, 9H, *t*Bu).

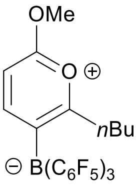
1.3 Synthesis of products.

*Synthesis of (6-methoxy-2-phenylpyrylium-3-yl)tris(pentafluorophenyl)borate (**2a**).*



(*Z*)-methyl 5-phenylpent-2-en-4-ynoate (**1a**) (37 mg, 0.2 mmol) was dissolved in toluene (*ca.* 2 ml) and was added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give a yellow solution. The reaction was left at room temperature without stirring for 12 h. Slow evaporation of the solvent yielded colourless crystals of the product which could be characterised by single crystal X-ray diffraction. The remaining solvent was decanted off and the product was washed with petroleum ether (3 × 3 ml) and dried *in vacuo* to give pure **2a**. Yield: 91 mg, 0.13 mmol, 65%. m.p. = 194–198 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.65 (br. s, 1H, pyrylium CH), 7.44-7.40 (m, 1H, Ph-H), 7.27-7.25 (m, 2H, Ph-H), 7.23-7.20 (m, 2H, Ph-H), 7.06 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, pyrylium CH), 4.34 (s, 3H, CH_3). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K): 168.8 (s, 1C), 167.9 (s,1C), 167.1 (s, 1C), 131.4 (s, 1C), 130.9 (s, 1C), 128.7 (s, 1C), 127.8 (s, 1C), 106.4 (s, 1C), 58.3 (s, 1C). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K): -14.4. **^{19}F NMR** (565 MHz, $CDCl_3$, 298 K): -128.6 (d, $^{3}J_{FF}$ = 20.6 Hz, 1F, *o*-F), -130.3 (br. s, 4F, *o*-F), -131.1 (d, $^{3}J_{FF}$ = 20.6 Hz, 1F, *o*-F), -159.2 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-F), -160.0 (t, $^{3}J_{FF}$ = 20.3 Hz, 2F, *p*-F), -163.5 (br. t, 1F, $^{3}J_{FF}$ = 18.8 Hz, *m*-F), -164.7 (br. t, $^{3}J_{FF}$ = 18.8 Hz, 1F, *m*-F), -165.4 (t, $^{3}J_{FF}$ = 18.8 Hz, 4F, *m*-F). **IR** ν_{max} (cm^{-1}): 1643, 1616, 1599, 1550, 1515, 1492, 1436, 1385, 1346, 1273, 1242, 1192, 1081, 965, 841, 833, 792, 771, 761, 703, 694, 679, 664, 640, 629. **Elemental analysis** (%) for $C_{30}H_{10}BF_{15}O_2$: calculated: C: 51.61, H: 1.44; found: C: 51.64 H: 1.44.

*Synthesis of (2-butyl-6-methoxy-pyrylium-3-yl)tris(pentafluorophenyl)borate (**2b**).*



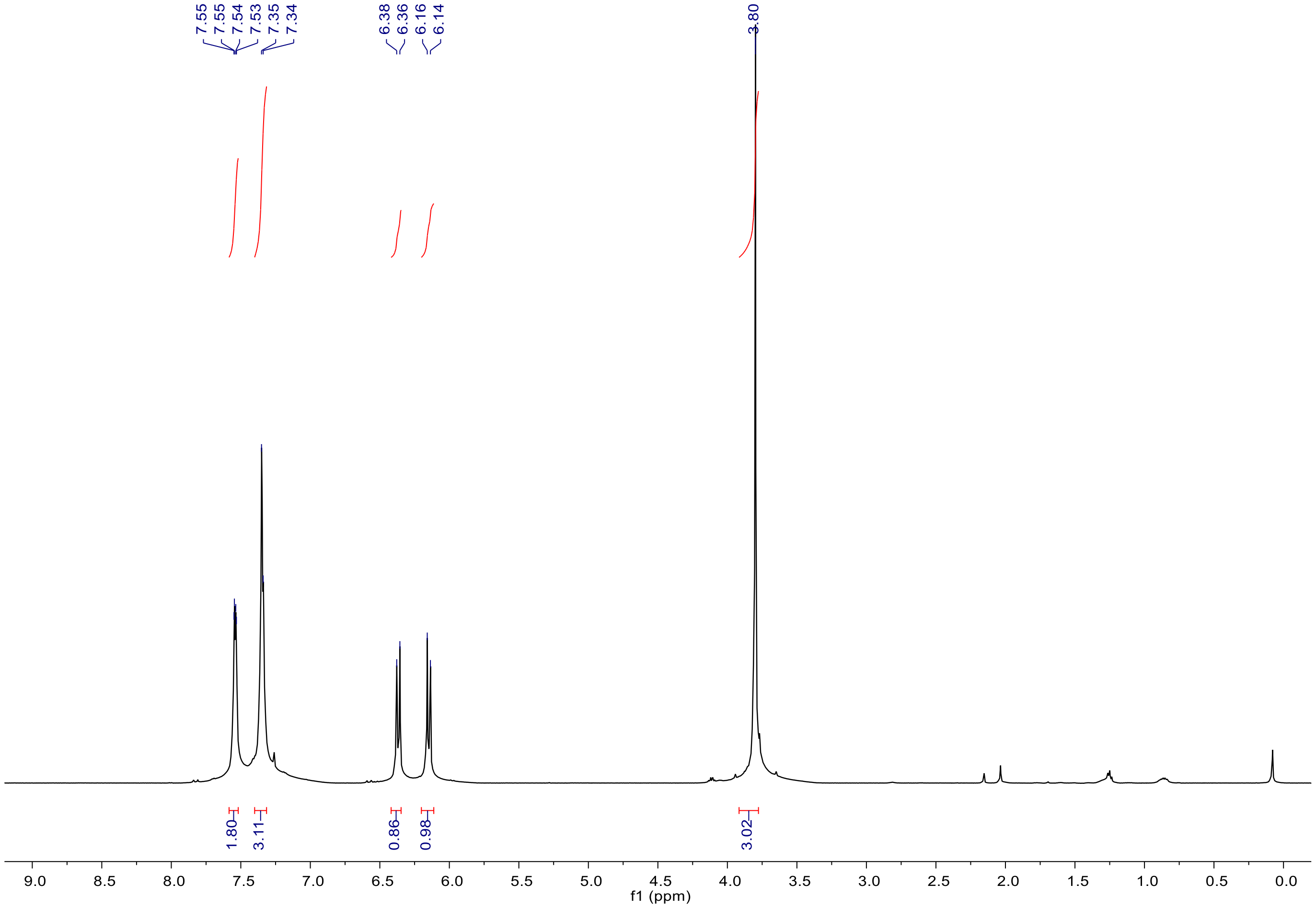
(*Z*)-methyl non-2-en-4-ynoate (**1b**) (33 mg, 0.2 mmol) was dissolved in toluene (2 ml) and added to $B(C_6F_5)_3$ (102 mg, 0.2 mmol) to give an orange solution. The reaction mixture was left at room temperature for 30 min before being cooled to -40 °C for 18 h. The product could be recrystallised from the slow evaporation of a toluene/petroleum ether solution to give small colourless crystals of the product suitable for X-ray diffraction. The remaining solvent was removed and the crystals were washed with petroleum ether 40-60 (3 x 3ml) to give the product **2b** as a pale green solid. Yield: 87 mg, 64%, 0.13 mmol. m.p.: 191–194 °C. **^{1}H NMR** (400 MHz, $CDCl_3$, 298 K): 8.47 (s, 1H, =CH), 6.90 (d, $^{3}J_{HH}$ = 8.8 Hz, 1H, =CH), 4.36 (s, 3H, O-CH_3), 2.92-2.80 (m, 2H, CH_2), 1.43 (br. s, 1H, CH), 1.31-1.19 (m, 2H, CH_2), 0.80 (t, $^{3}J_{HH}$ = 7.3 Hz, 3H, CH_3) 0.64 (br. s, 1H, CH) (two α-protons of *n*-butyl are diastereotopic). **^{13}C NMR** *partial* (126 MHz, $CDCl_3$, 298 K): 175.8 (s, 1C), 168.5 (s, 1C), 165.0 (s, 1C), 104.4 (s, 1C), 58.2 (s, 1C), 33.4 (s, 1C), 29.2 (s, 1C), 22.5 (s, 1C), 13.4 (s, 1C). **^{11}B NMR** (160 MHz, $CDCl_3$, 298 K): -14.5. **^{19}F NMR** (565 MHz, $CDCl_3$, 298 K): -128.2 (br. s, 1F, *o*-F), -128.6 (br. s, 1F, *o*-F), -130.8 (br. d, $^{3}J_{FF}$ = 19.3 Hz, 1F, *o*-F), -132.3 (br. s, 1F, *o*-F), -134.4 (br. d, $^{3}J_{FF}$ = 19.3 Hz, 1F, *o*-F), -135.0 (br. s, 1F, *o*-F), -159.0 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-F), -159.6 (t, $^{3}J_{FF}$ = 20.3 Hz, 1F, *p*-F), -159.8 (t, J_{FF} = 20.3 Hz, 1F, *p*-F), -162.9 (br. t, $^{3}J_{FF}$ = 22.9 Hz, 1F, *m*-F), -164.2 (br. dt, $^{3}J_{FF}$ = 23.1 Hz, $^{4}J_{FF}$ = 8.3 Hz, 1F, *m*-F), -164.39 (br. t, $^{3}J_{FF}$ = 19.6 Hz, 1F, *m*-F), -164.6 (m, 1F, *m*-F), -164.8 (m, 1F, *m*-F), -165.3 (br. t, $^{3}J_{FF}$ = 19.6 Hz, 1F, *m*-F). **IR** ν_{max} (cm^{-1}): 2957, 2936, 2877, 2863, 1643, 1606, 1551, 1515, 1498, 1453, 1346, 1276, 1081, 1002, 966, 864, 824, 794, 771, 760, 749, 679, 632, 557. **HRMS** (ES^{-}) $[M-H]^{-}$ $[C_{28}H_{13}BF_{15}O_2]^{-}$: calculated 676.0805, found: 676.0806. Elemental analysis (%) for $C_{28}H_{14}BF_{15}O_2$: calculated: C: 49.59, H: 2.08; found: C: 49.64, H: 1.97.

Note: Partial ^{13}C NMR spectra recorded for **2a**,**b** due to broad resonances observed for fluorine coupled carbon nuclei of C_6F_5-rings.

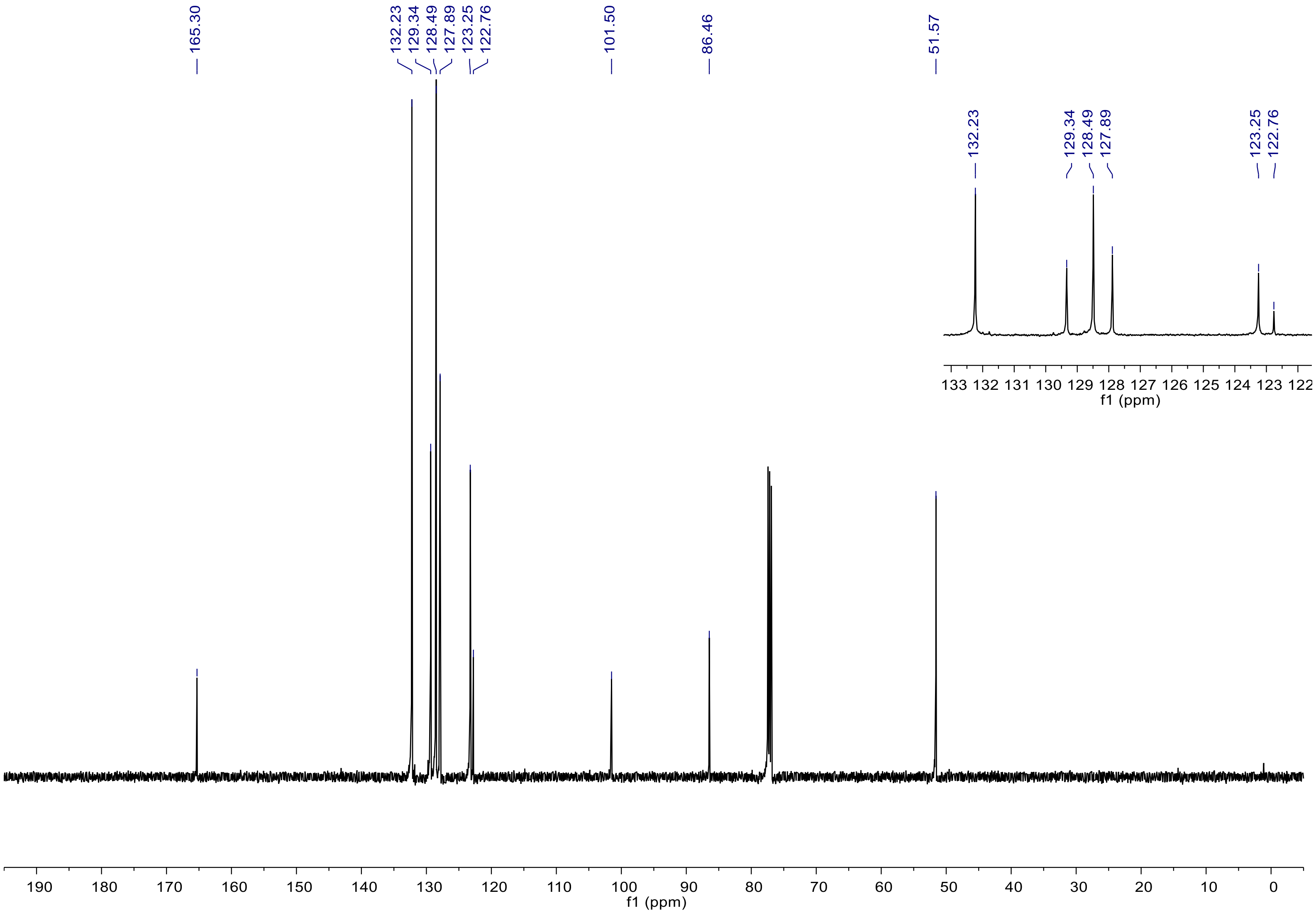
2. Experimental: NMR spectra

2.1 NMR spectra of starting materials.

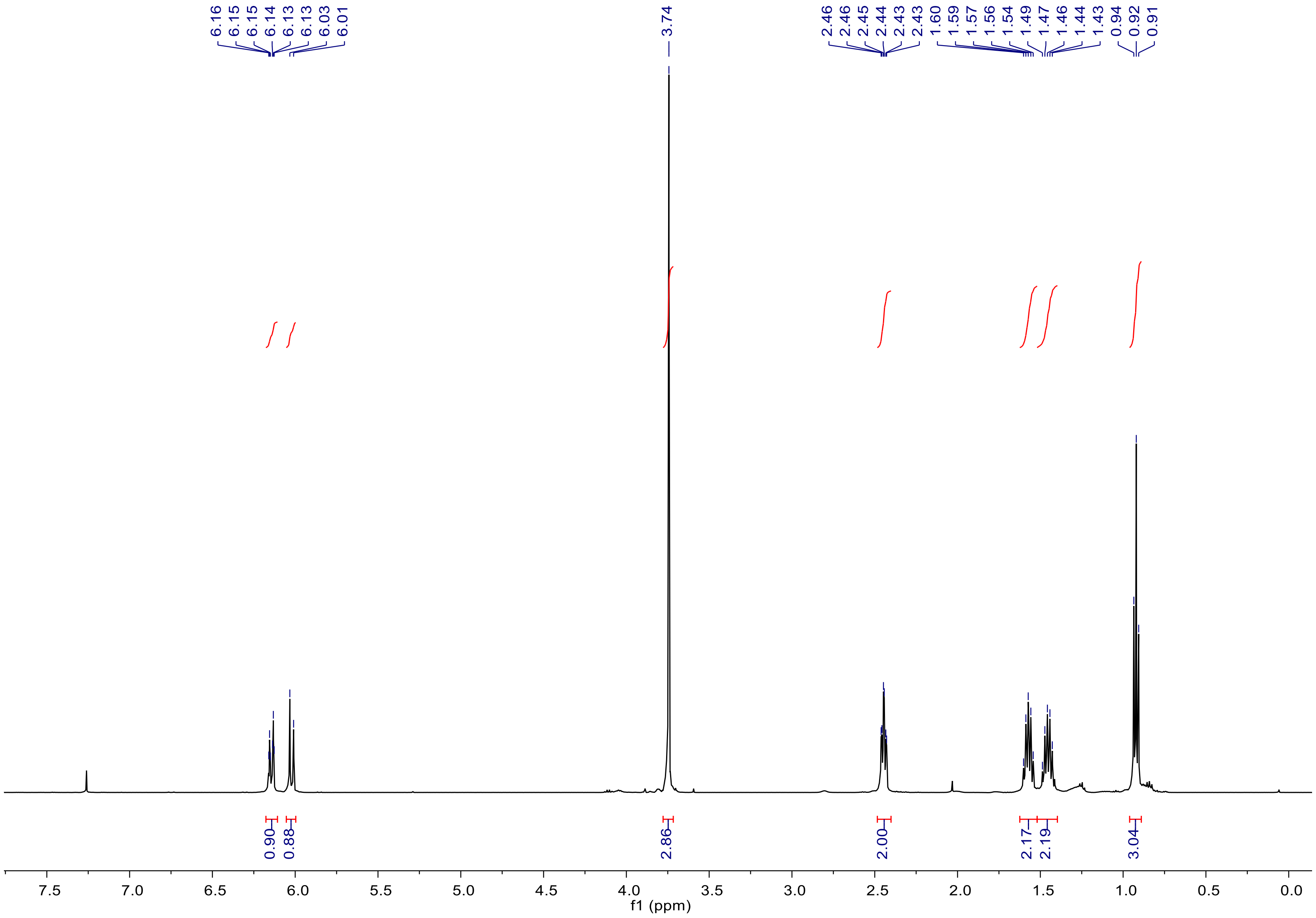
S1 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of methyl (Z)-5-phenylpent-2-en-4-ynoate (**1a**).



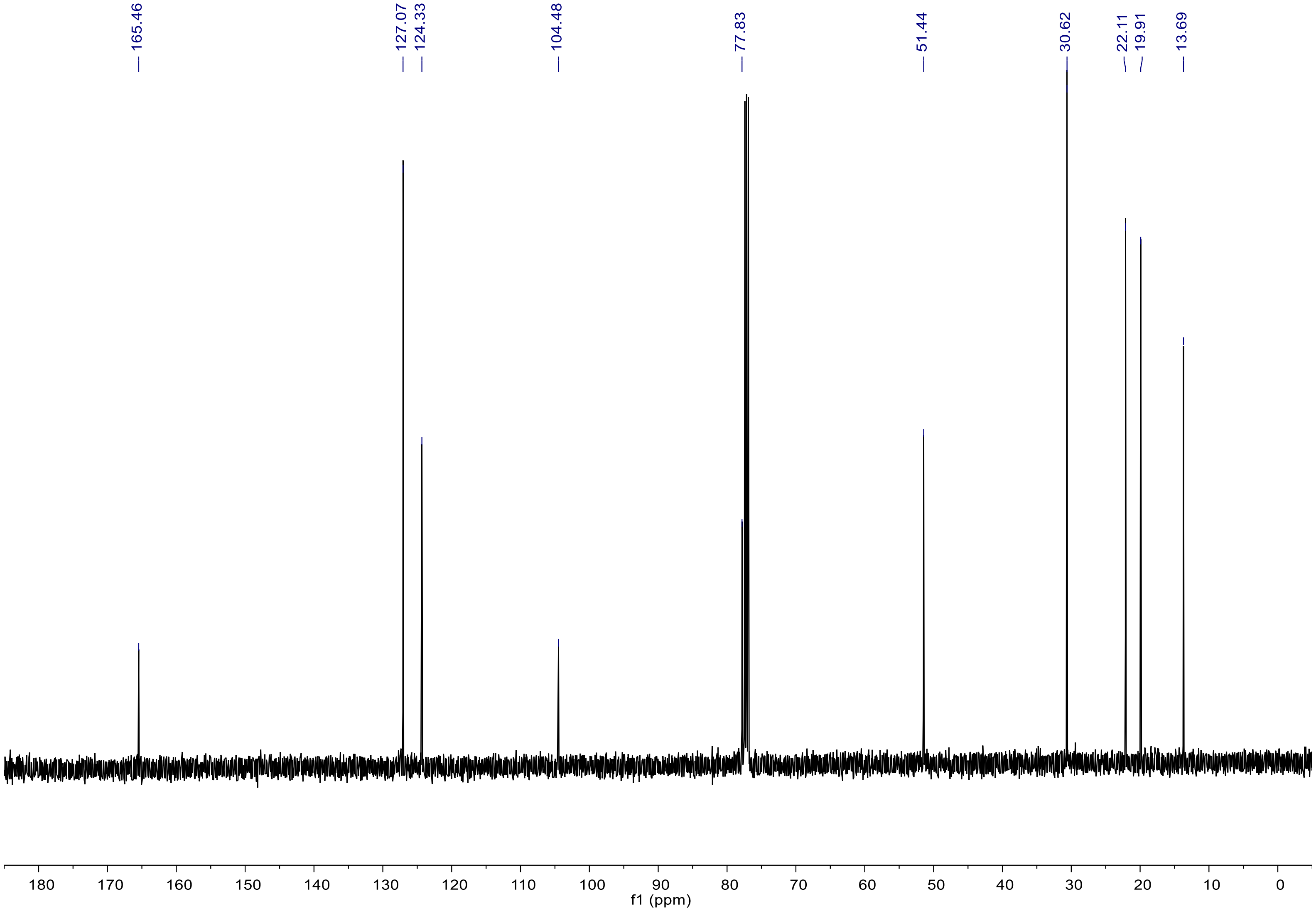
S2 ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) spectrum of methyl (Z)-5-phenylpent-2-en-4-ynoate (**1a**).



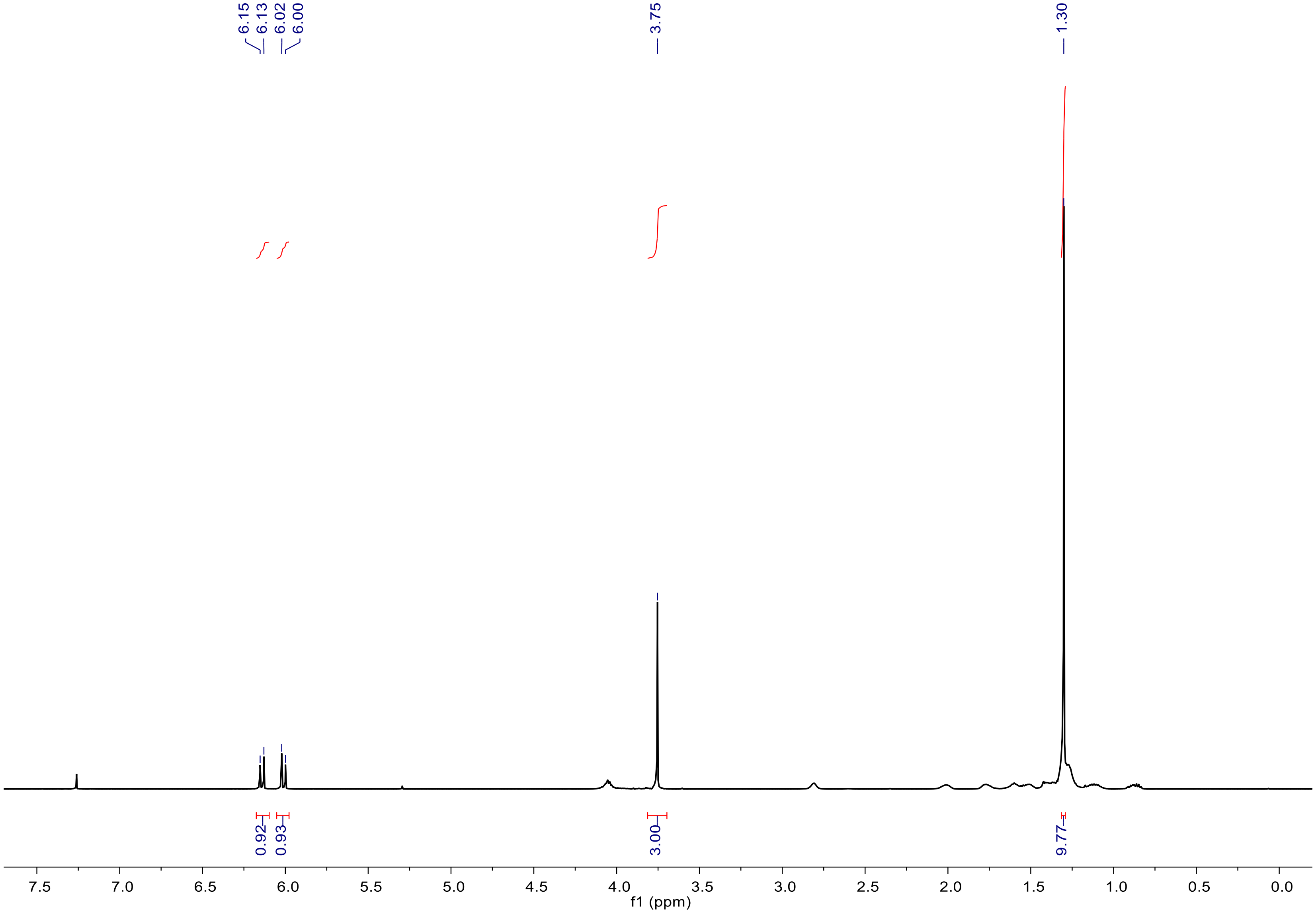
S3 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of methyl (Z)-non-2-en-4-ynoate (**1b**).



S4 ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of methyl (Z)-non-2-en-4-ynoate (**1b**).

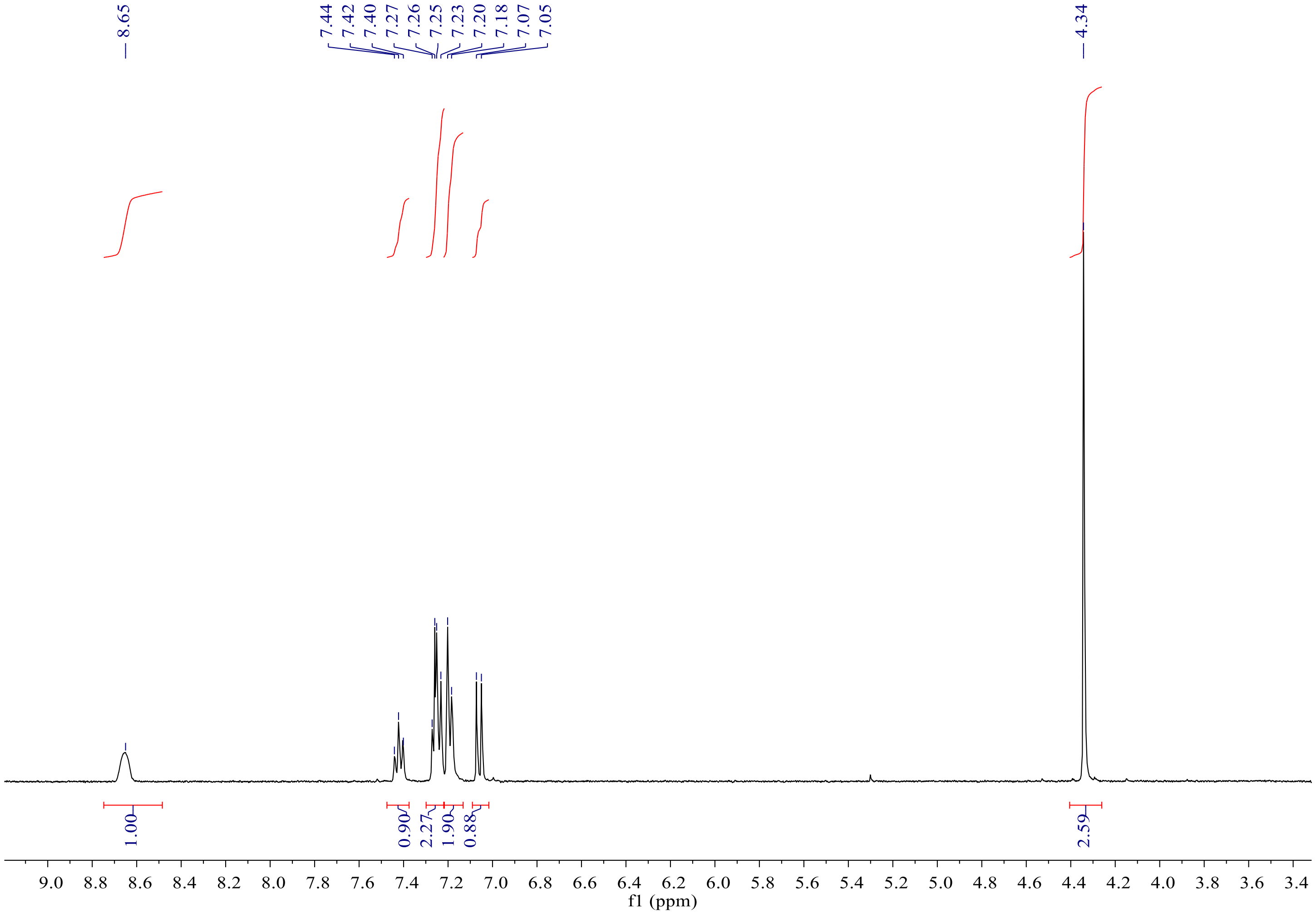


S5 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of methyl (Z)-6,6-dimethylhept-2-en-4-ynoate (**1c**).

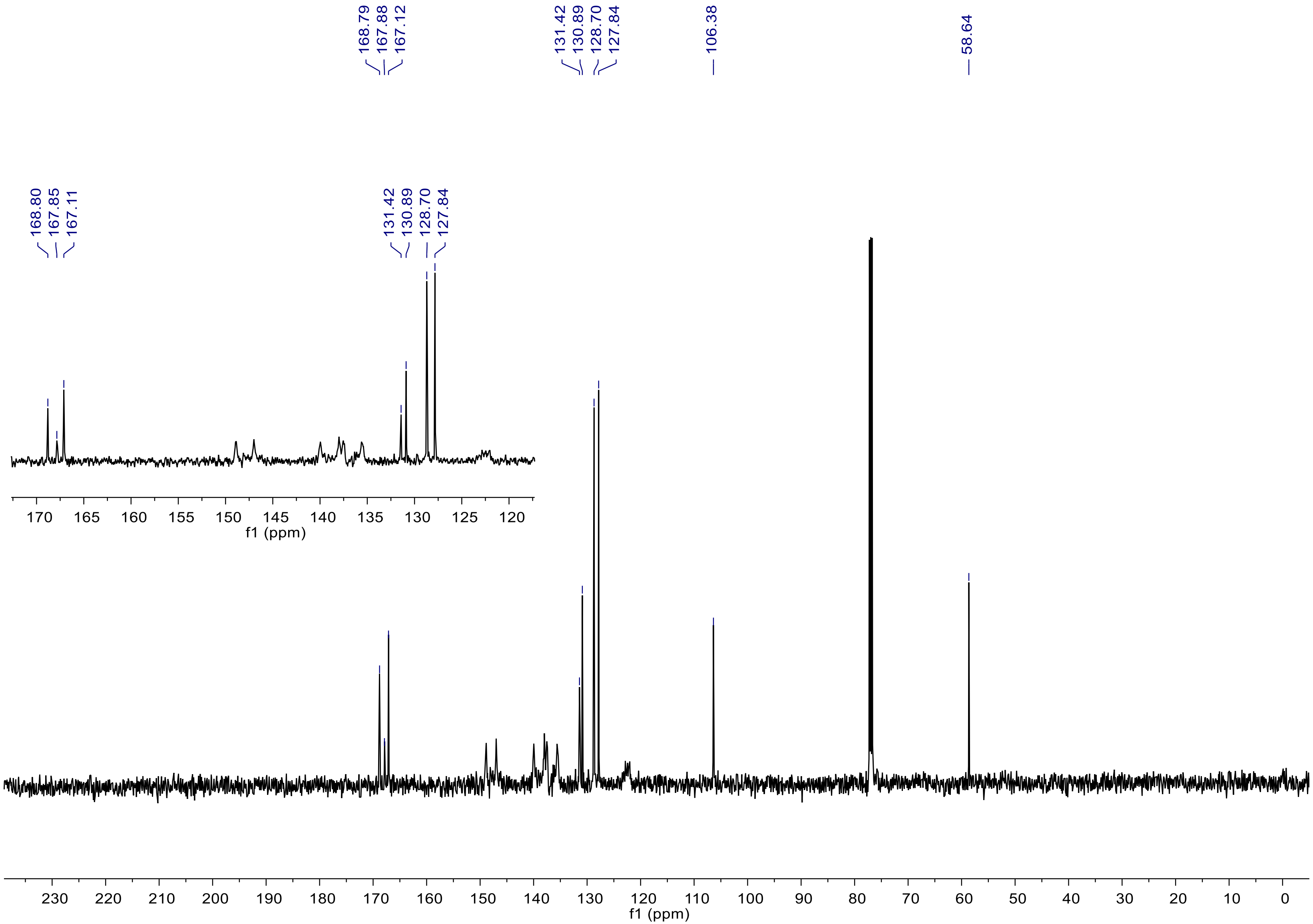


2.2 NMR spectra of products.

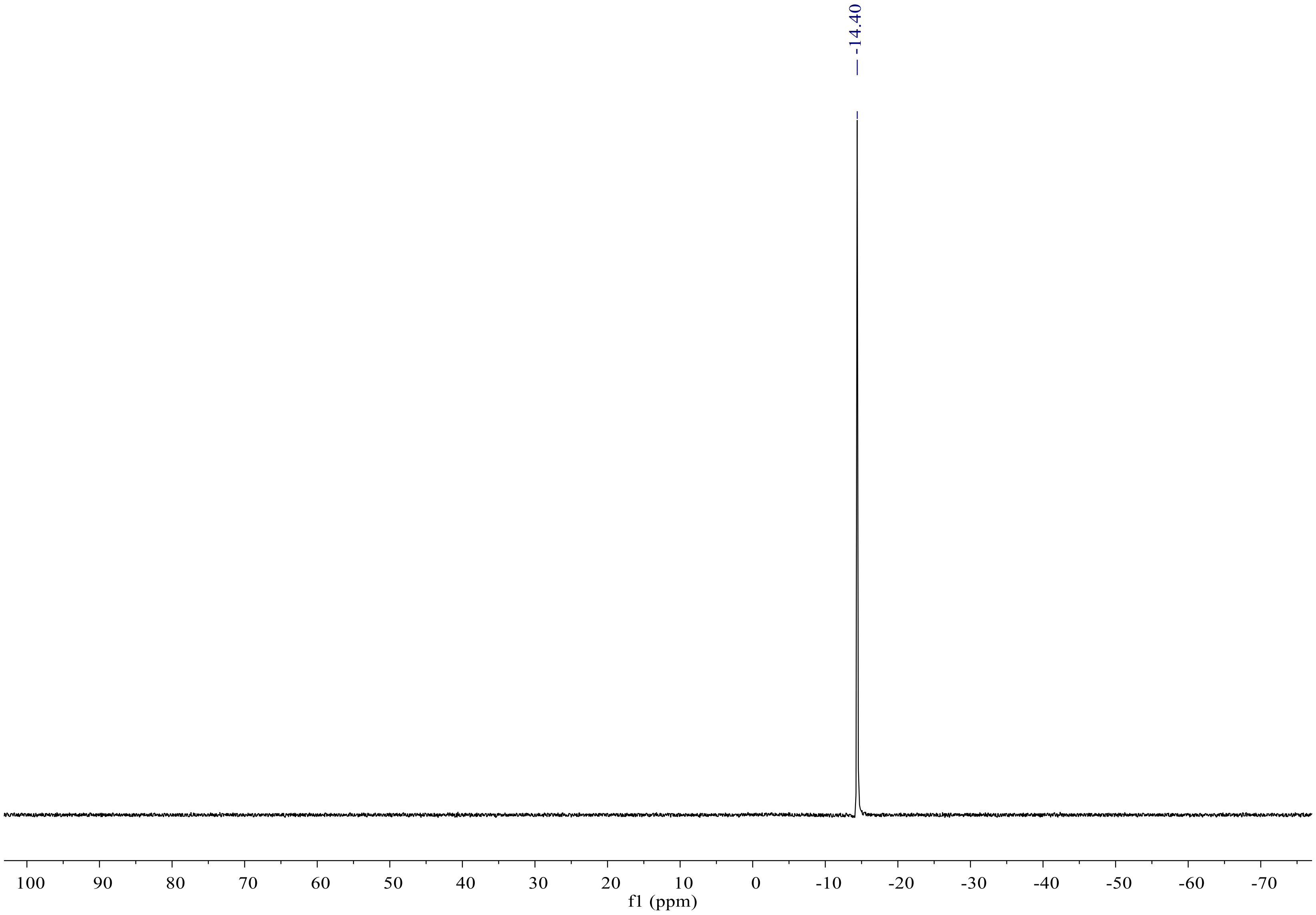
S6 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of (6-methoxy-2-phenylpyrylium-3-yl)tris(pentafluorophenyl)borate (**2a**).



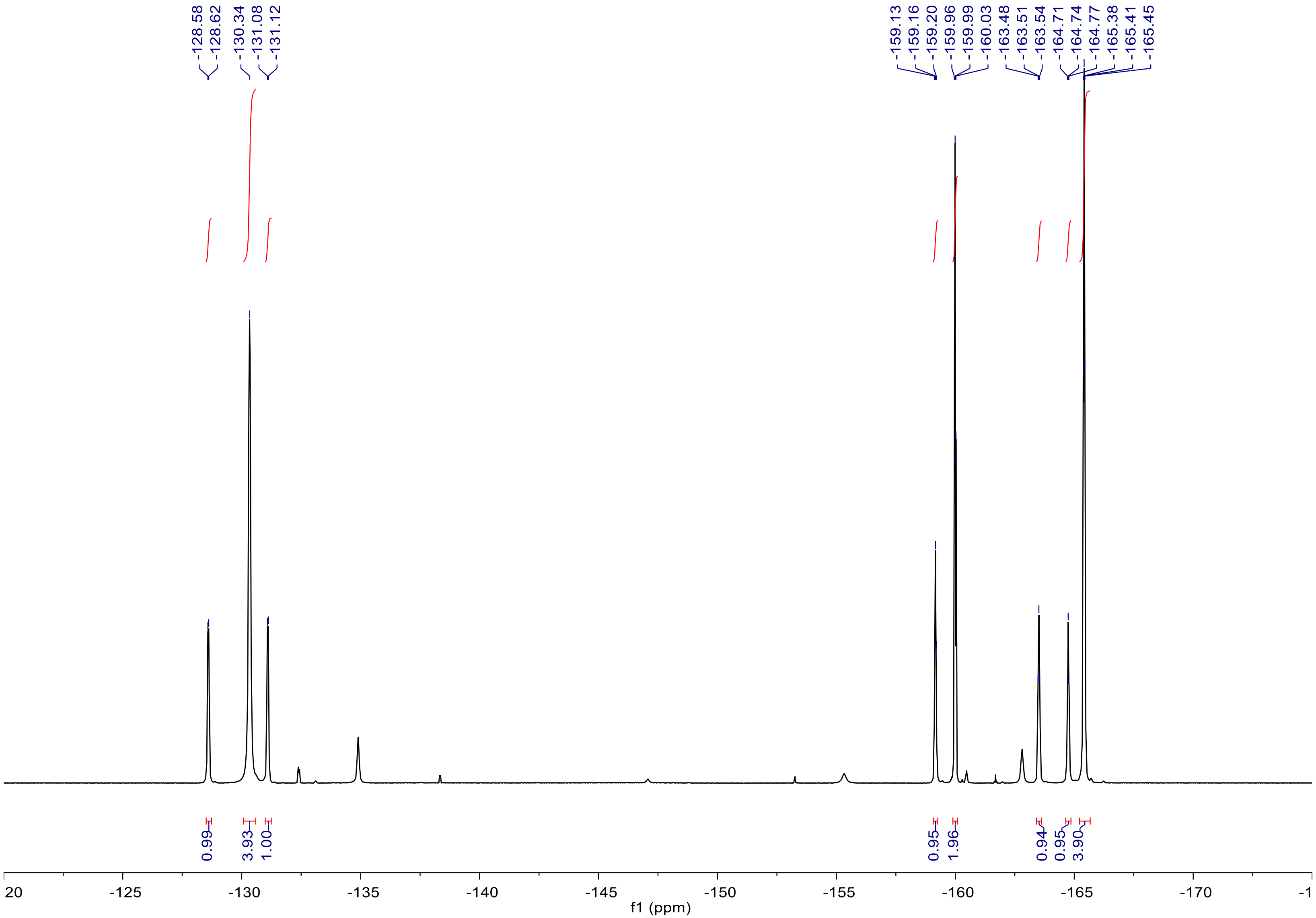
S7 ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of (6-methoxy-2-phenylpyrylium-3-yl)tris(pentafluorophenyl)borate (**2a**).



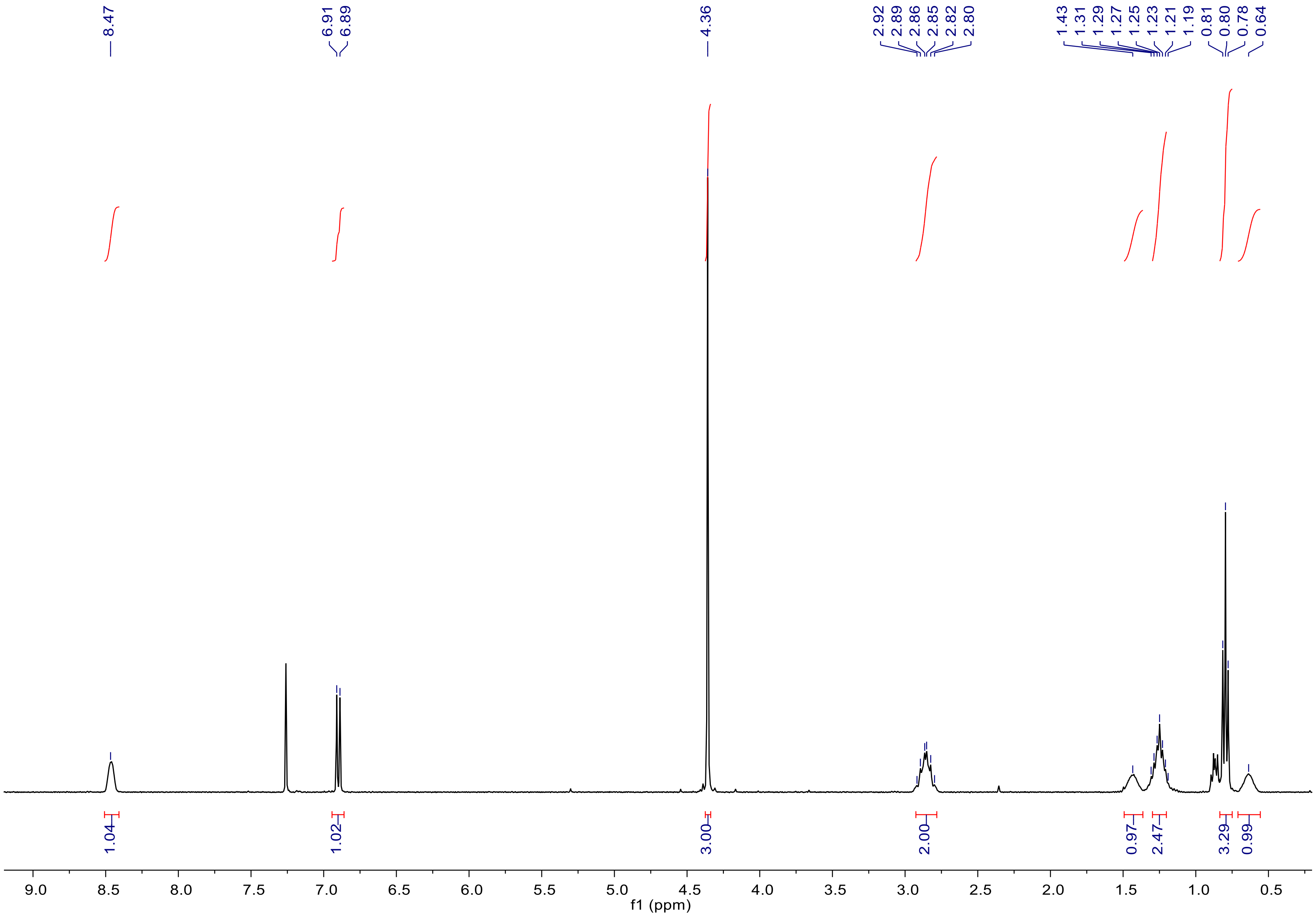
S8 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of (6-methoxy-2-phenylpyrylium-3-yl)tris(pentafluorophenyl)borate (**2a**).



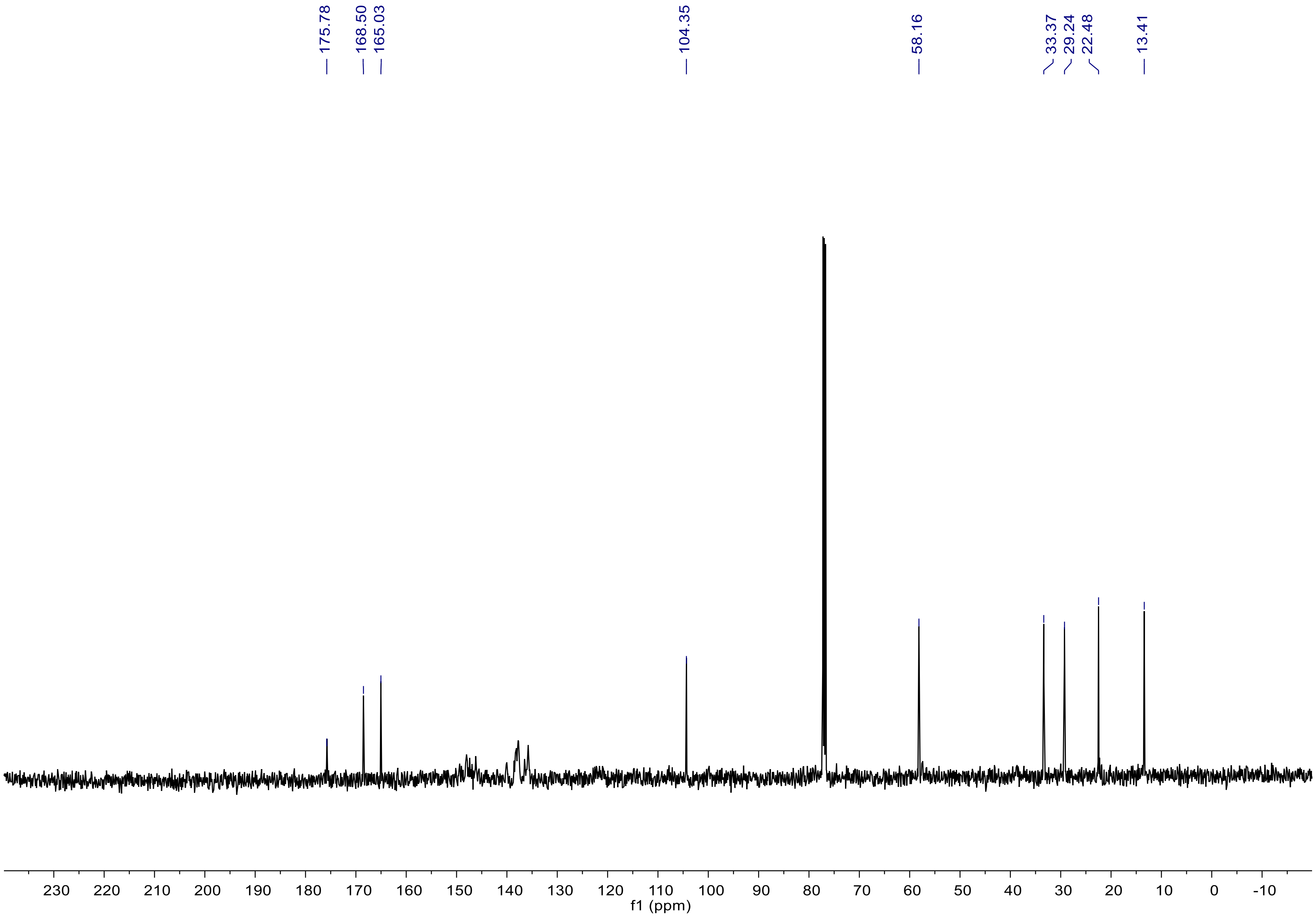
S9 ^{19}F NMR (565 MHz, CDCl$_3$, 298 K) spectrum of (6-methoxy-2-phenylpyrylium-3-yl)tris(pentafluorophenyl)borate (**2a**).



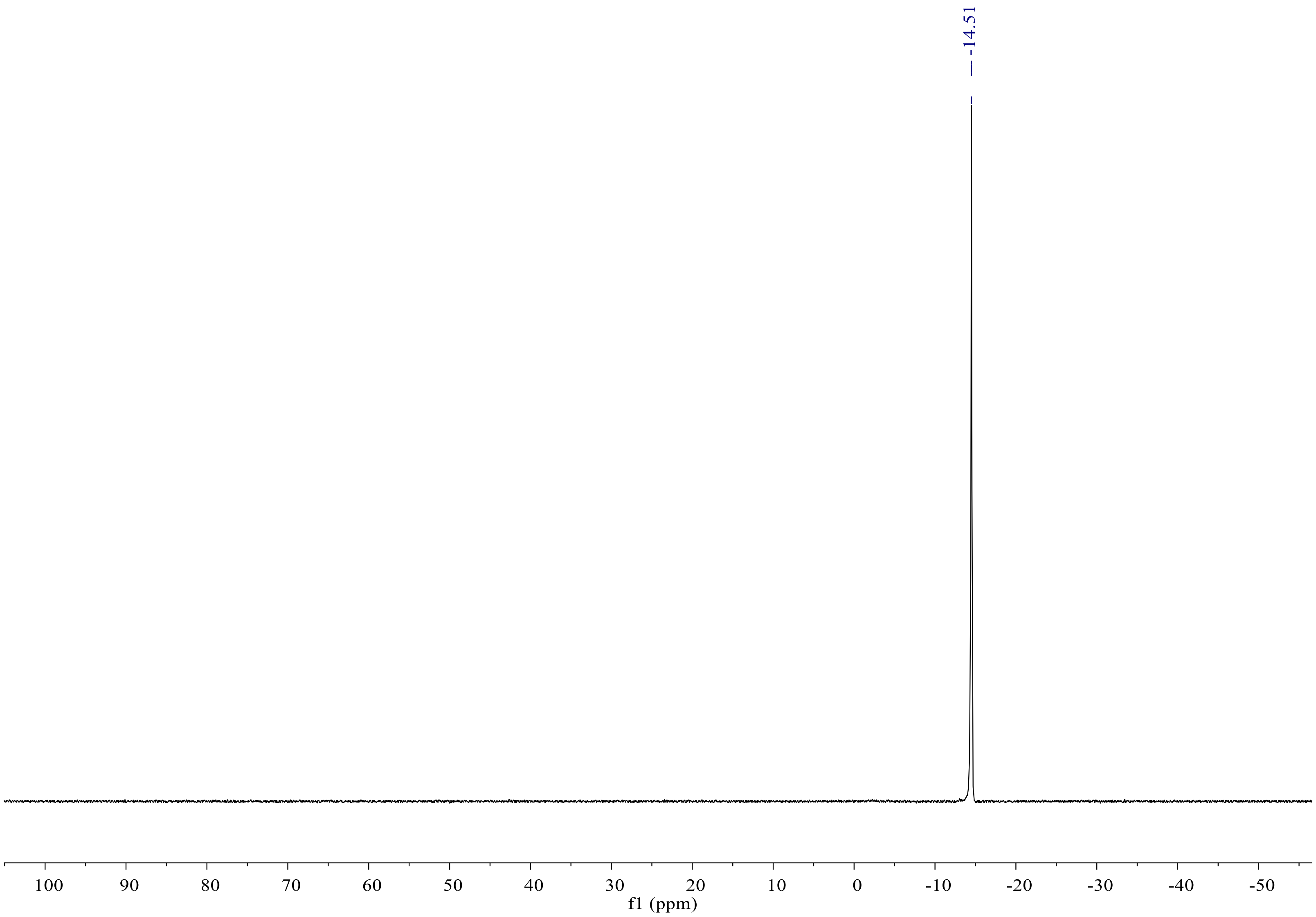
S10 ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of (2-butyl-6-methoxy-pyrylium-3-yl)tris(pentafluorophenyl)borate (**2b**).



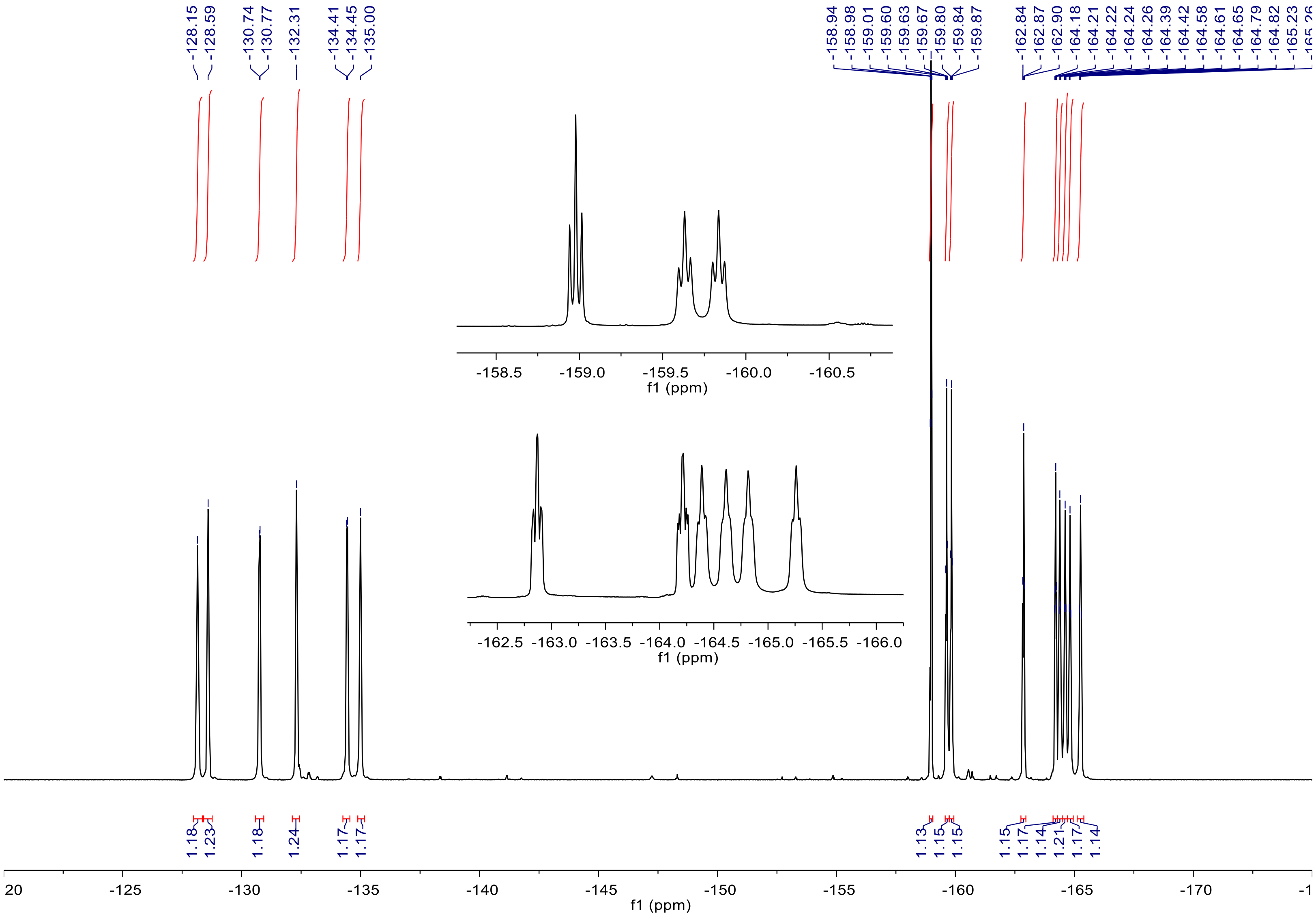
S11 ^{13}C NMR (126 MHz, CDCl$_3$, 298 K) spectrum of (2-butyl-6-methoxy-pyrylium-3-yl)tris(pentafluorophenyl)borate (**2b**).



S12 ^{11}B NMR (160 MHz, $CDCl_3$, 298 K) spectrum of (2-butyl-6-methoxy-pyrylium-3-yl)tris(pentafluorophenyl)borate (**2b**).



S13 ^{19}F NMR (565 MHz, CDCl$_3$, 298 K) spectrum of (2-butyl-6-methoxy-pyrylium-3-yl)tris(pentafluorophenyl)borate (**2b**).



3. Crystallographic studies.

Single crystals of **2a** and **2b** were grown under an inert atmosphere. Crystallographic studies were undertaken of a single crystal mounted in paratone and studied on an Agilent SuperNova Dual three-circle diffractometer using Cu-Kα radiation and a CCD detector. Measurements were carried out at 150(1) K with temperatures maintained using an Oxford cryostream unless otherwise stated. Data were collected and integrated and data corrected for absorption using a numerical absorption correction based on gaussian integration over a multifaceted crystal model within CrysAlisPro.[2] The structures were solved by direct methods and refined against F^2 within SHELXL-2013.[3] A summary of crystallographic data are available as ESI and the structures deposited with the Cambridge Structural Database (CCDC deposition numbers 1417004–1417005). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

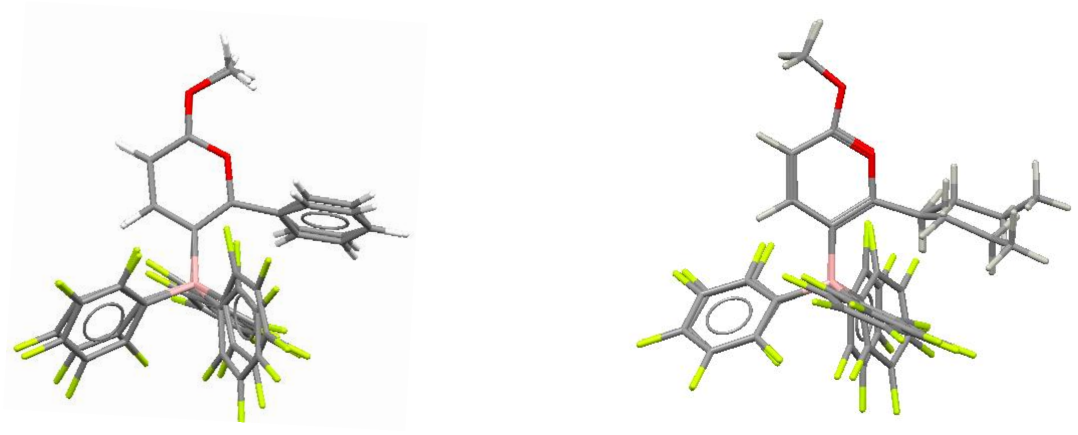
Table S1. Crystallographic data for **2a** and **2b**.

Compound	**2a**	**2b**
Empirical Formula	$C_{30}H_{10}BF_{15}O_2$	$C_{28}H_{14}BF_{15}O_2$
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a/Å	10.53693(10)	10.9906(3)
b/Å	13.77283(16)	10.9906(3)
c/Å	36.3610(4)	14.4145(3)
α/°	90	90
β/°	95.1711(10)	91.562(2)
γ/°	90	90
V/Å^3	5255.36(10)	2539.55(10)
Z	8	4
T /K	150(2)	150(2)
D_c/g.cm^{-3}	1.765	1.774
Crystal size/mm	0.370 x 0.130 x 0.090	0.170 x 0.060 x 0.040
Total data	21738	10428
Unique data	10388	5024
R_{int}	0.0188	0.0415
$R_1[F^2>2\sigma(F^2)]$	0.0343	0.0389
wR2 (all data)	0.0915	0.1235
GoF	1.041	1.140
ρ_{min}/ρ_{max}/eÅ^{-3}	-0.250/0.288	-0.224/0.423
CCDC code	1417004	1417005

4. Computational studies.

All geometry optimisations were undertaken using the B3LYP functional[4] and 6-31G* basis set[5] within Jaguar.[6] Subsequent single point calculations were undertaken using the B3LYP functional and larger 6-311G* basis set. In addition, partial charges were determined using an NBO analysis.[7] Further to this nucleus independent chemical shift, NICS(0), calculations were undertaken at the B3LYP/6-311G* level.[8]

Figure S13. Overlay of geometry optimised structure and experimental solid-state crystal structures **2a**,**b** (one of two crystallographically independent molecules shown for **2a**).



2a **2b**

Figure S14. Wiberg bond indices for **2a**.

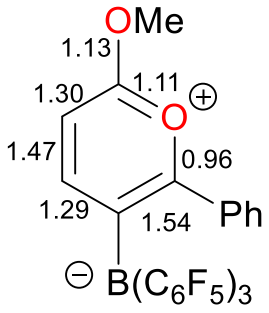
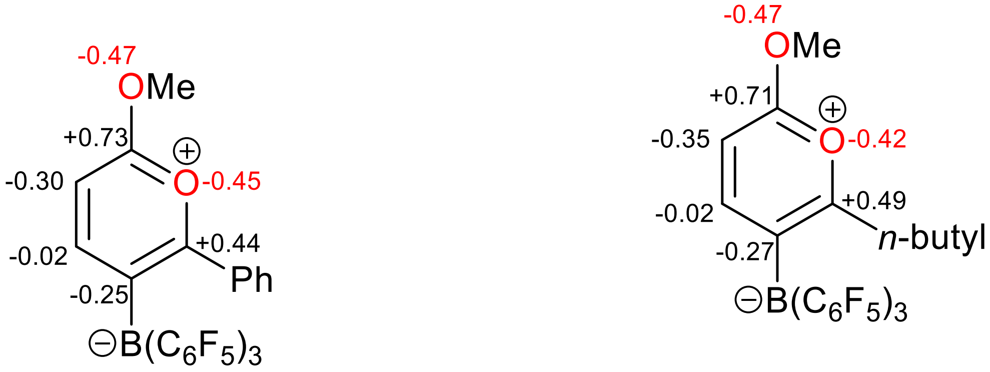


Figure S15. Key NBO charge distributions and NICS(0) values for **2a** and **2b.**



2a **2b**

NICS(0) = -3.93 ppm **-4.86 ppm**

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