**Supplementary Information for:**

# $B(C_6F_5)_3$ Promoted Cyclisation of Internal Propargyl Esters: Structural Characterisation of 1,3-Dioxolium Compounds

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## General procedures

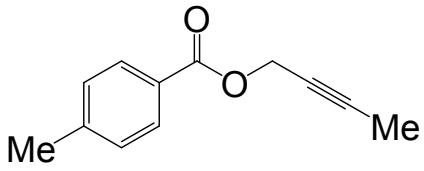
With the exception of the synthesis of starting materials, all reactions and manipulations were carried out under an atmosphere of dry, $O_2$-free nitrogen using standard double-manifold techniques with a rotary oil pump. An argon-filled glove box (MBRAUN) was used to manipulate solids including the storage of starting materials, room temperature reactions, product recovery and sample preparation for analysis. Molecular sieves (4 Å) were dried at 120ºC for 24 h prior to use. All solvents (toluene, $CH_2Cl_2$, pentane) were dried by employing a Grubbs-type column system (Innovative Technology) or a solvent purification system MB SPS-800, degassed and stored over molecular sieves under a nitrogen atmosphere. Deuterated solvents were dried over molecular sieves before use. Chemicals were purchased from commercial suppliers and used as received. $B(C_6F_5)_3$ was prepared based on a slightly modified synthesis reported in the literature.[1] $^1H$, $^{13}C$, $^{11}B$ and $^{19}F$ NMR spectra were recorded on a Bruker Avance III, Bruker Avance 400, Varian Unity 500, Bruker Avance-III-300, Bruker Avance DRX-300, Bruker Avance 500 or Bruker Avance 600. 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) and $CD_2Cl_2$ (5.32 / 53.80 ppm) as internal standards. NMR spectra were referenced to $CFCl_3$ ($^{19}F$) or 1,2-difluorobenzene (-139 ppm) and $BF_3{\cdot}Et_2O/CDCl_3$ ($^{11}B$). The description of signals include: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and br. = broad. All coupling constants are absolute values and *J* values are expressed in Hertz (Hz). All spectra were analyzed assuming a first order approximation. A Perkin-Elmer Analyzer was used for carbon, hydrogen and nitrogen elemental analyzes. High resolution mass spectrometry was performed in house employing DART or electrospray ionization techniques in positive ion mode. Mass spectral data were recorded on an AB/Sciex QStarXL mass spectrometer (ESI), a JEOL AccuTOF model JMS-T1000LC mass spectrometer and an ICR Apex-Qe (DART). Mass spectral data collected in the chemistry department of the University Heidelberg (MS and HRMS) were collected using a Bruker ApexQe FT-ICR-MS spectrometer under the direction of Dr. J. Gross.

## 1. Experimental Details

**General procedure A:**

Triethylamine (1.0 equiv.) and DMAP (5 mol%) were added to a solution of the propargyl alcohol (1.0 equiv.) in $CH_2Cl_2$ and was stirred for 15 min. The solution was then cooled to 0°C and the acyl chloride was added dropwise. The resulting mixture was stirred at this temperature for 30 min and was allowed to warm to room temperature and further stirred. After quenching the reaction with water the aqueous layer was extracted with $CH_2Cl_2$ (x2). The collective organic phases were washed with brine, dried with $MgSO_4$, filtered, and the solvent was removed under vacuum and the product purified by column chromatography on $SiO_2$.

**But-2-yn-1-yl 4-methylbenzoate (1)**




According to general procedure A, 2-butyne-1-ol (374 µl, 5.0 mmol), DMAP (12.2 mg), $NEt_3$ (693 µl, 8.0 mmol) and *p*-toluoyl chloride (661 µl, 5.0 mmol) were reacted in 15 ml $CH_2Cl_2$. Column chromatography on $SiO_2$ (hexane/EtOAc, 19:1) afforded the product as a colourless liquid (788 mg, 4.19 mmol, 84%).

**$R_f$** = 0.32 (petrolether/EtOAc, 19:1).

**IR** (thin film) $\nu_{max}$ = 3036 $cm^{-1}$, 2945, 2921, 2320, 2241, 1732, 1613, 1578, 1509, 1438, 1409, 1374, 1310, 1281, 1255, 1209, 1178, 1154, 1110, 952, 841.

**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K): 7.96 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 7.24 (d, $^3J_{HH}$ = 8.2 Hz, 2H), 4.87 (q, $^5J_{HH}$ = 2.4 Hz, 2H, -$CH_2$), 2.41 (s, 3H, -$CH_3$), 1.88 (t, $^4J_{HH}$ = 2.4 Hz, 3H, -C≡C-Me).

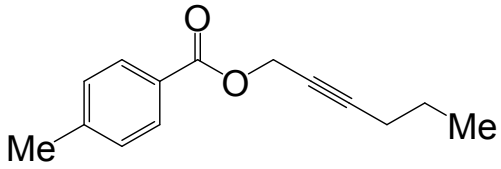
**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$, 298 K): 166.2 (s), 144.0 (s), 130.0 (s), 129.2 (s), 127.2 (s), 83.3 (s), 73.5 (s), 53.3 (s), 21.8 (s), 3.9 (s).

**EA** (elemental analysis) calcd (%) for $C_{12}H_{12}O_2$: C 76.57, H 6.41%; Obs. C 75.53, H 6.70%.

**EI** (+) (m/z): 188.1 $[M]^+$ (74), 143.1 (8), 129.1 (15), 120.1 (15), 119.0 (100) 91.1 (22).

**HRMS-EI** (+) (m/z): calcd for $C_{12}H_{12}O_2$,188.0837; found, 188.0834.

**Hex-2-yn-1-yl 4-methylbenzoate (2)**




According to general procedure A, 2-hexyne-1-ol (2.2 ml, 20.4 mmol), DMAP (45.0 mg), $NEt_3$ (2.82 ml, 20.4 mmol) and *p*-toluoyl chloride (2.69 ml, 20.4 mmol) were reacted in 40 ml $CH_2Cl_2$. Column chromatography on $SiO_2$ (petroleum ether /EtOAc, 20:1) afforded the product as a colourless liquid (3.06 g, 14.1 mmol, 69%).

**$R_f$** = 0.26 (petroleum ether /EtOAc, 50:1).

**IR** (thin film) $\nu_{max}$ = 3036 $cm^{-1}$, 2964, 2873, 2307, 2239, 1730, 1613, 1577, 1509, 1454, 1436, 1409, 1372, 1339, 1310, 1276, 1209, 1178, 1150, 1104, 1021, 952, 894.

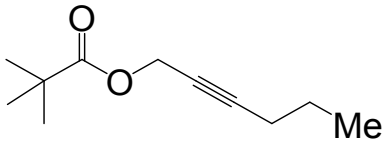
**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K): 8.00 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 7.23 (d, $^3J_{HH}$ = 8.3 Hz, 2H), 4.90 (t, $^5J_{HH}$ = 2.2 Hz, 2H), 2.41 (s, 3H), 2.22 (tt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 2.2 Hz, 2H), 1.55 (tq, $^3J_{HH}$ = 7.3 Hz, 7.1 Hz, 2H), 0.99 (t, $^3J_{HH}$ = 7.3 Hz, 3H).

**$^{13}$C{$^1$H} NMR** (100 MHz, $CDCl_3$, 298 K): 166.2 (s), 143.9 (s), 130.0 (s), 129.2 (s), 127.3 (s), 87.6 (s), 74.5 (s), 53.3 (s), 22.0 (s), 21.8 (s), 20.9 (s), 13.6 (s).

**EI** (+) (m/z): 216.1 $[M]^+$ (11), 188.1 (24), 187.1 (24), 162.0 (7), 137.1 (8), 120.0 (43), 119.0 (100), 91.1 (54), 79.1 (28).

**HRMS-EI** (+) (m/z): calcd for $C_{14}H_{16}O_2$, 216.1150; found, 216.1139.

**Hex-2-yn-1-yl pivalate (3)**




According to general procedure A, 2-hexyne-1-ol (2.0 ml, 18.2 mmol), DMAP (110 mg), $NEt_3$ (2.52 ml, 18.2 mmol) and pivaloyl chloride (2.24 ml, 18.2 mmol) were reacted in 50 ml $CH_2Cl_2$. Column chromatography on $SiO_2$ (petroleum ether /EtOAc, 25:1) afforded the product as a colourless liquid (2.79 g, 15.3 mmol, 84%).

**$R_f$** = 0.40 ( petroleum ether /EtOAc, 25:1)

**IR** (thin film) $\nu_{max}$ = 2967 $cm^{-1}$, 2937, 2909, 2874, 2306, 2239, 1739, 1537, 1480, 1460, 1397, 1366, 1339, 1280, 1229, 1156, 1033, 964, 941, 914.

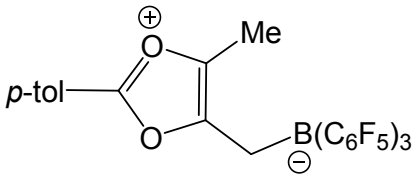
**$^1$H NMR** (400 MHz, $CDCl_3$, 298 K): 4.64 (t, $^5J_{HH}$ = 2.3 Hz, 2H), 2.18 (tt, $^3J_{HH}$ = 7.1 Hz, $^5J_{HH}$ = 2.2 Hz, 2H), 1.53 (tq, $^3J_{HH}$ = 7.4 Hz, 7.1 Hz, 2H), 1.21 (s, 9H), 0.97 (t, $^3J_{HH}$ = 7.4 Hz, 3H).

**$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$, 298 K): 178.0 (s), 87.2 (s), 74.6 (s), 52.9 (s), 38.9 (s), 27.2 (s, 3C), 22.0 (s), 20.9 (s), 13.5 (s).

**EI** (+) (m/z): 182.1 $[M]^+$ (4), 154.1 (12), 153.1 (19), 126.1 (21), 98.1 (7), 85.1 (24), 81.1 (11), 79.1 (29), 70.0 (10).

**HRMS-EI** (+) (m/z): calcd for $C_{11}H_{18}O_2$, 182.1307; found, 182.1300.

**Synthesis of (4)**




$B(C_6F_5)_3$ (205 mg, 0.4 mmol) was dissolved in toluene (3 ml) and was added to but-2-yn-1-yl 4-methylbenzoate (75 mg, 0.4 mmol). The reaction was left to stand at room temperature for 4 days affording a purple solution and colourless crystals of the product. The remaining solution was decanted off and the remaining solid washed with pentane (3 x 2 ml) and dried *in vacuo* to give the pure product (114 mg, 41%, 0.16 mmol).

**$^1H$ NMR** (500 MHz, $CD_2Cl_2$, 298K): 7.86 (d, $^3J_{HH}$ = 8.67 Hz, 2H, Ar-H), 7.52 (m, 2H, Ar-H), 2.95 (m, br., 2H, $-CH_2$), 2.55 (s, 3H, $-CH_3$), 2.20 (s, 3H, $CH_3$).

**$^{11}B$ NMR** (128 MHz, $CD_2Cl_2$, 298 K): -14.3 (s).

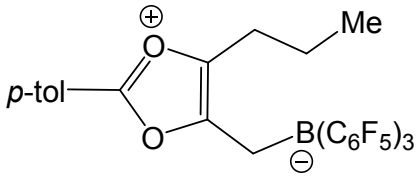
**$^{19}F$ NMR** (377 MHz, $CD_2Cl_2$, 298 K): -132.8 (d, 2F, $J_{FF}$ = 22.6 Hz, *o*-F), -161.9 (t, 1F, $J_{FF}$ = 20.4 Hz, *p*-F), -166.2 (m, 2F, *m*-F).

**$^{13}C\{^1H\}$ NMR** (125 MHz, $CD_2Cl_2$, 298K): 173.0 (s, dioxolium), 157.1 (s, dioxolium), 153.8 (s), 148.7 (m, $^1J_{CF}$ = 242 Hz), 143.5 (s, dioxolium), 139.0 (m, $^1J_{CF}$ *ca*. 234 Hz), 137.2 (m, $^1J_{CF}$ *ca.* 246 Hz), 132.42 (s), 131.0 (s), 113.7 (s), 23.1 (s), 18.9 (m), 9.0 (s), the signals due to the carbon atoms bonded to boron in the $C_6F_5$ rings could not be observed.

**EA** (elemental analysis) calcd (%) for $C_{30}H_{12}O_2BF_{15}$: C 51.46; H 1.73; Found: C 51.33, H 1.94.

**EI+ MS, m/z**: 700.1 (calcd for [M]+: 700.1), 533.0 (calcd for $[(M-C_6F_5)]$+: 533.0), 119.0 (calcd for [*p*-tol-≡O]+: 119.0).

**Synthesis of (5)**




Hex-2-yn-1-yl 4-methylbenzoate (169 mg, 0.78 mmol) was added to a solution of $B(C_6F_5)_3$ (400 mg, 0.78 mmol) dissolved in $CH_2Cl_2$ (4 ml). The solution was stirred at room temperature for 2 days. Slow vapour diffusion of pentane into the solution at -20°C afforded yellow crystals of the product. The remaining solution was decanted off and the remaining solid washed with pentane (3 x 2 ml) and dried *in vacuo* to give the pure product (480 mg, 85%, 0.66 mmol).

**IR** (thin film) $\nu_{max}$ = 1691 $cm^{-1}$, 1640, 1602, 1540, 1511, 1441, 1382, 1361, 1304, 1274, 1255, 1213, 1189, 1129, 1078, 970, 958, 909, 829, 803, 768, 742, 703, 658.

**$^1$H NMR** (500 MHz, $CD_2Cl_2$, 298K): 7.85 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 7.52 (d, $^3J_{HH}$ = 8.4 Hz, 2H, Ar-H), 2.97 (m, br., 2H, -$CH_2$-$BR_3$), 2.54 (s, 3H), 2.50 (t, $^3J_{HH}$ = 7.4 Hz, 2H), 1.58 (tq, $^3J_{HH}$ = 7.4 Hz, 7.4 Hz, 2H), 0.95 (t, $^3J_{HH}$ = 7.4 Hz, 3H).

**$^{11}$B NMR** (160 MHz, $CD_2Cl_2$, 298 K): -14.4 (s).

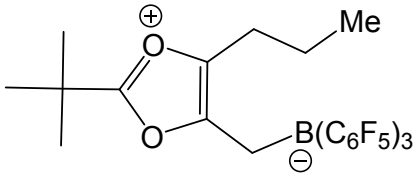
**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$, 298 K): -132.8 (d, 2F, $J_{FF}$ = 22.4 Hz, *o*-F), -162.0 (t, 1F, $J_{FF}$ = 20.4 Hz, *p*-F), -166.2 (m, 2F, *m*-F).

**$^{13}$C{$^1$H} NMR/ $^{13}$C{$^1$H,$^{19}$F} NMR** (125 MHz, $CD_2Cl_2$, 298K): 173.1 (s, dioxolium), 156.9 (s, dioxolium), 153.7 (s), 148.8 (m, $^1J_{CF}$ = 239 Hz), 147.2 (s, dioxolium), 139.0 (m, $^1J_{CF}$ *ca.* 234 Hz), 137.2 (m, $^1J_{CF}$ *ca.* 246 Hz), 132.2 (s), 131.0 (s), 124.4 (q, $^1J_{CB}$ = 48.5 Hz), 113.2 (s), 25.3 (s), 23.1 (s), 21.0 (s), 18.9 (q, $^1J_{CB}$ = 39.0 Hz), 13.6 (s).

**EA** (elemental analysis) calcd (%) for [$C_{32}H_{16}BF_{15}O_2$*0,5$CH_2Cl_2$]: C 50.65; H 2.22; Found: C 50.47, H 2.49.

**HRFAB** (+) (m/z): calcd for $C_{32}H_{16}O_2BF_{15}$, 728.1004; found, 728.1041.

**Synthesis of (6)**




Hex-2-yn-1-yl pivalate (107 mg, 0.59 mmol) was added to a solution of $B(C_6F_5)_3$ (300 mg, 0.59 mmol) dissolved in toluene (2 ml). The solution was stirred at room temperature for 2 days. Slow vapour diffusion of pentane into the solution at -20°C afforded colorless crystals of the product. The remaining solution was decanted off and the remaining solid washed with pentane (3 x 2 ml) and dried *in vacuo* to give the pure product (320 mg, 78%, 0.46 mmol).

**IR** (thin film) $\nu_{max}$ = 1687 $cm^{-1}$, 1643, 1559, 1514, 1498, 1457, 1378, 1273, 1247, 1220, 1203, 1086, 978, 963, 920, 903, 812, 802, 779, 767, 736, 698, 669, 648.

**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$, 298K): 2.90 (m, br., 2H, -$CH_2$-$BR_3$), 2.38 (t, $^{3}J_{HH}$ = 7.7 Hz, 2H), 1.48 (tq, $^{3}J_{HH}$ = 7.7 Hz, 7.5 Hz, 2H), 1.40 (s, 9H), 0.90 (t, $^{3}J_{HH}$ = 7.5 Hz, 3H).

**$^{11}$B NMR** (160 MHz, $CD_2Cl_2$, 298 K): -14.4 (s).

**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$, 298 K): -132.8 (d, 2F, $J_{FF}$ = 21.5 Hz, *o*-F), -161.8 (t, 1F, $J_{FF}$ = 20.8 Hz, *p*-F), -166.1 (m, 2F, *m*-F).

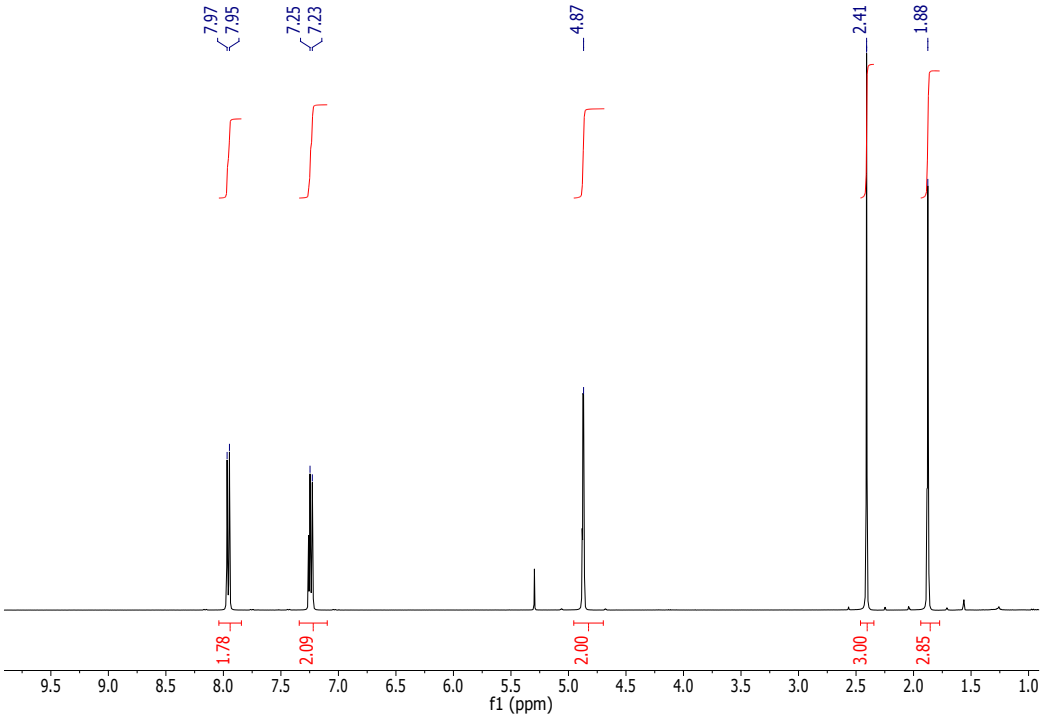
**$^{13}$C{$^{1}$H}/ $^{13}$C{$^{1}$H,$^{19}$F} NMR** (125 MHz, $CD_2Cl_2$, 298K): 186.8 (s, dioxolium),158.0 (s, dioxolium), 148.7 (m, $^{1}J_{CF}$ = 240 Hz), 148.2 (s, dioxolium), 139.0 (m, $^{1}J_{CF}$ *ca*. 234 Hz), 137.2 (m, $^{1}J_{CF}$ *ca*. 246 Hz), 124.1 (q, $^{1}J_{CB}$ = 50.0 Hz), 37.2 (s), 26.6 (s, 3C), 25.0 (s), 20.8 (s), 19.0 (q, $^{1}J_{CB}$ = 40.0 Hz), 13.6 (s).

**EA** (elemental analysis) calcd (%) for [$C_{29}H_{18}O_2BF_{15}$*0,5$C_7H_8$]: C 52.73; H 3.00; Found: C 52.60, H 3.09.

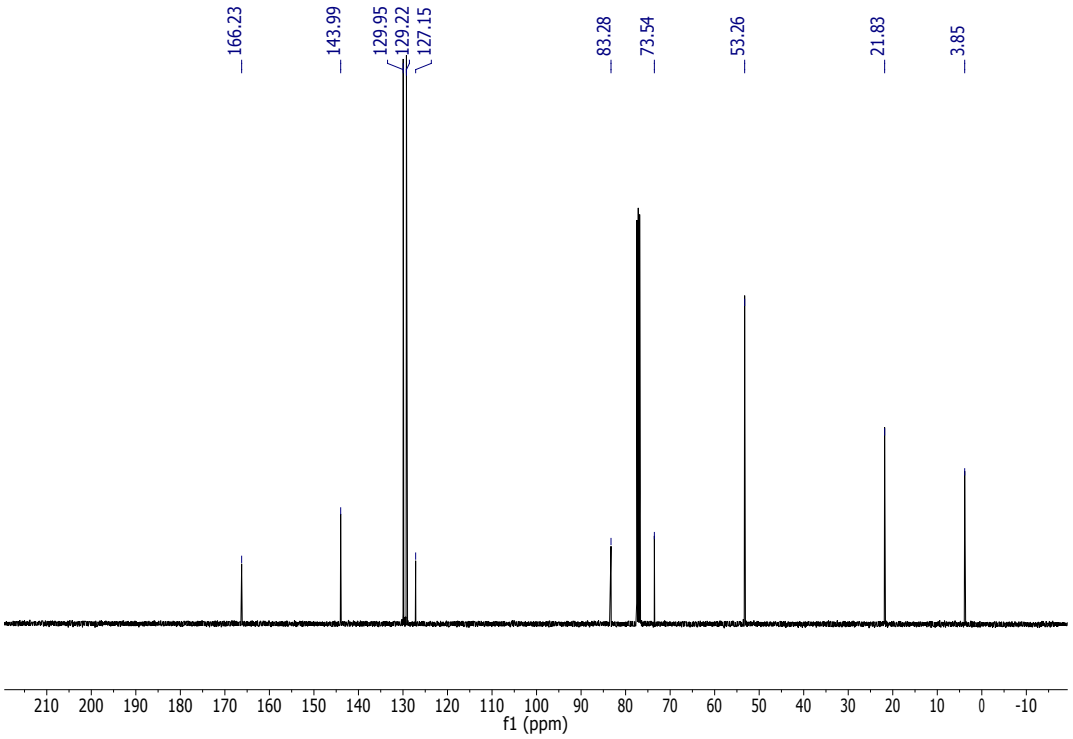
**HRMS-DART** (+) (m/z): calcd for [$C_{29}H_{18}O_2BF_{15}$+$NH_4$]$^{+}$, 712.1504; found, 712.14919.

2. **NMR Spectra**

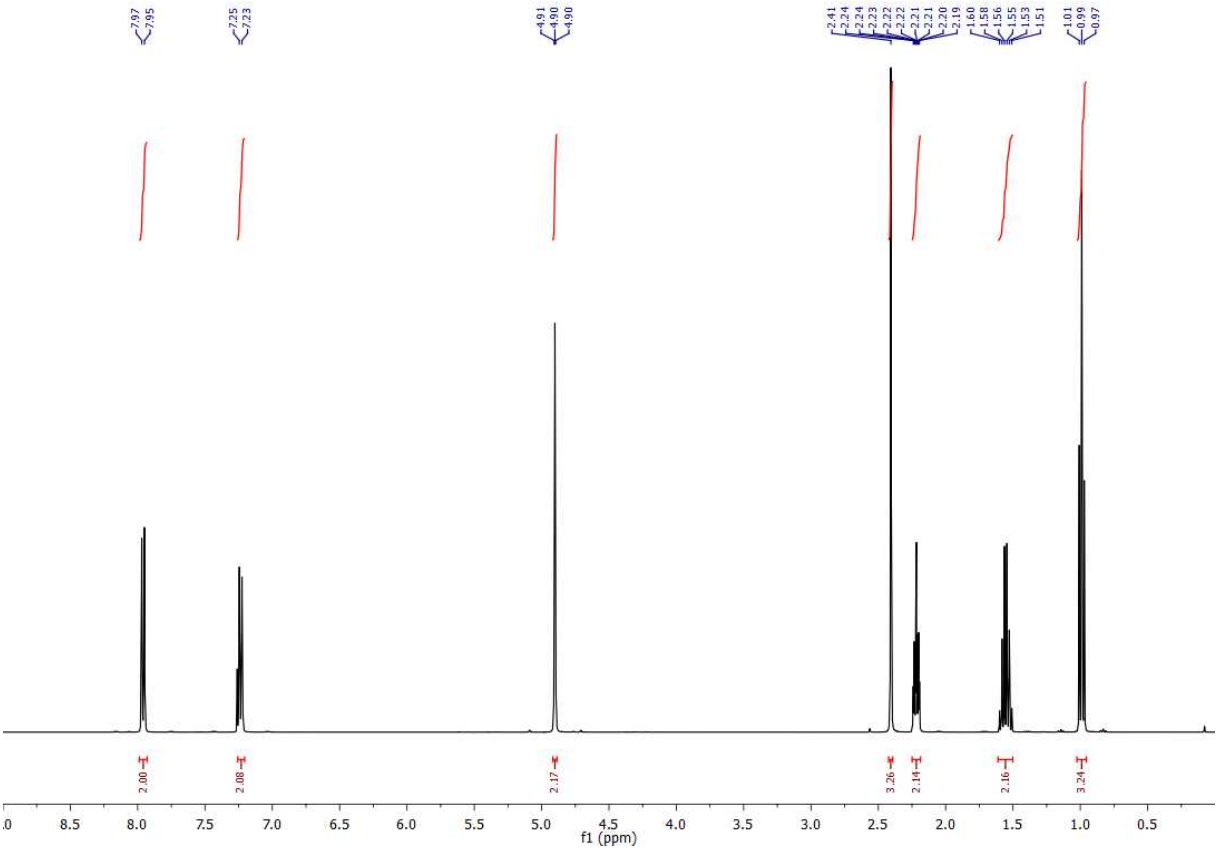
**$^{1}$H NMR** (400 MHz, $CDCl_3$, 298K) spectrum of but-2-yn-1-yl 4-methylbenzoate (**1**)



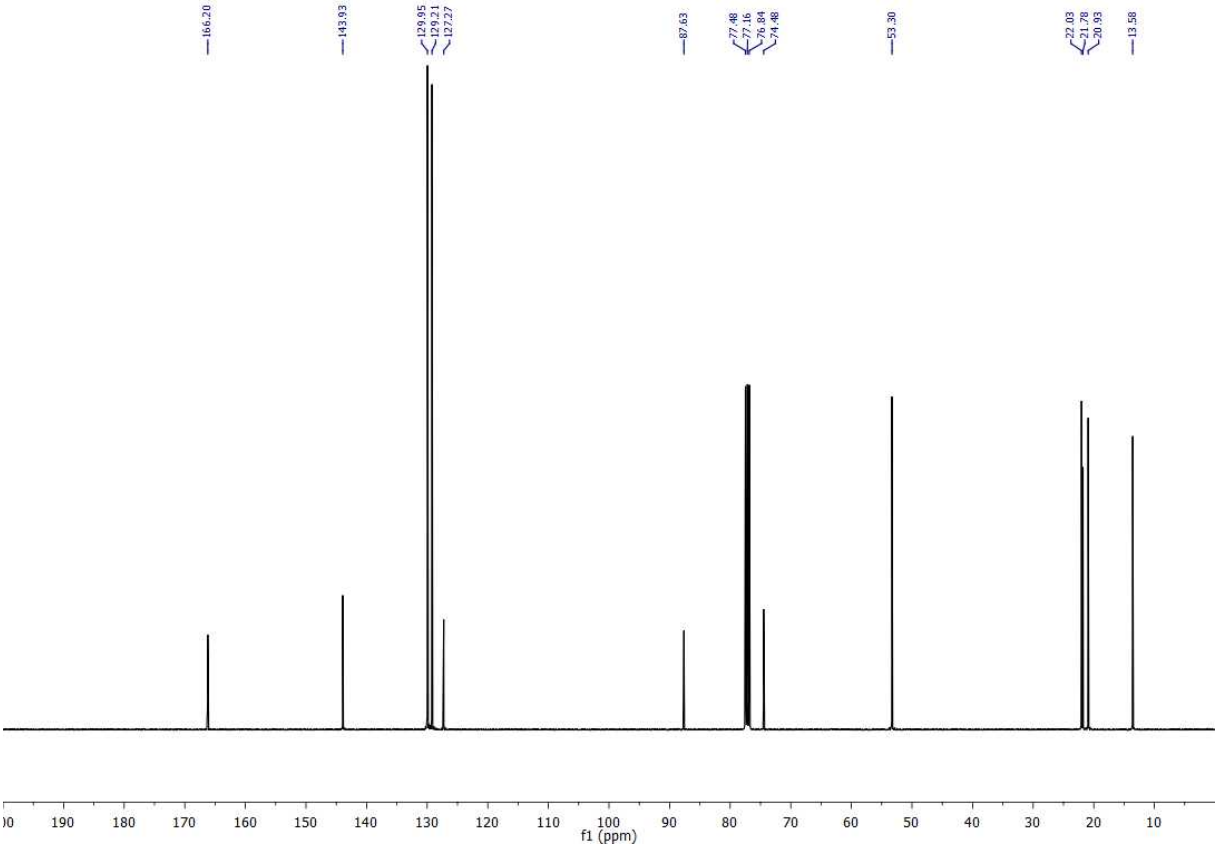

**$^{13}$C NMR** (100 MHz, $CDCl_3$, 298K) spectrum of but-2-yn-1-yl 4-methylbenzoate (**1**)



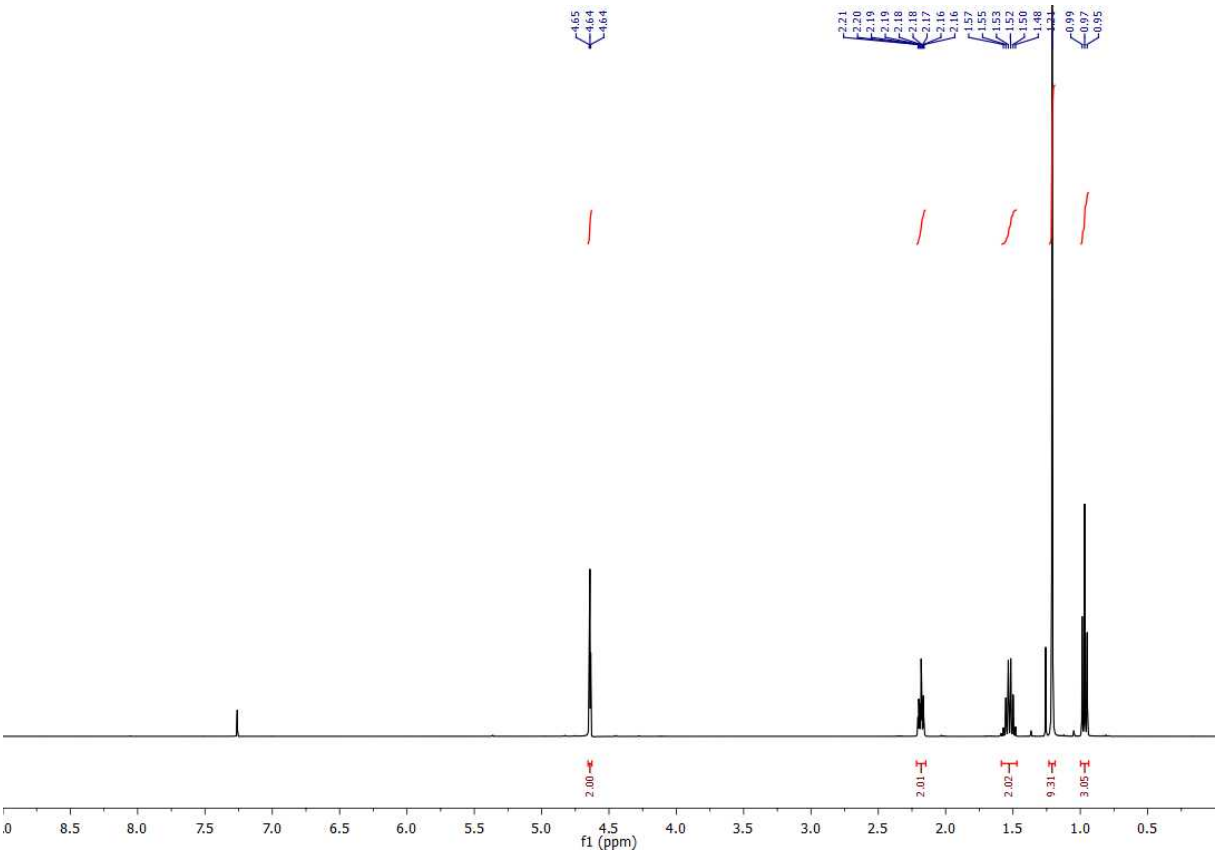
**$^{1}$H NMR** (400 MHz, $CDCl_3$, 298K) spectrum of hex-2-yn-1-yl 4-methylbenzoate (**2**)



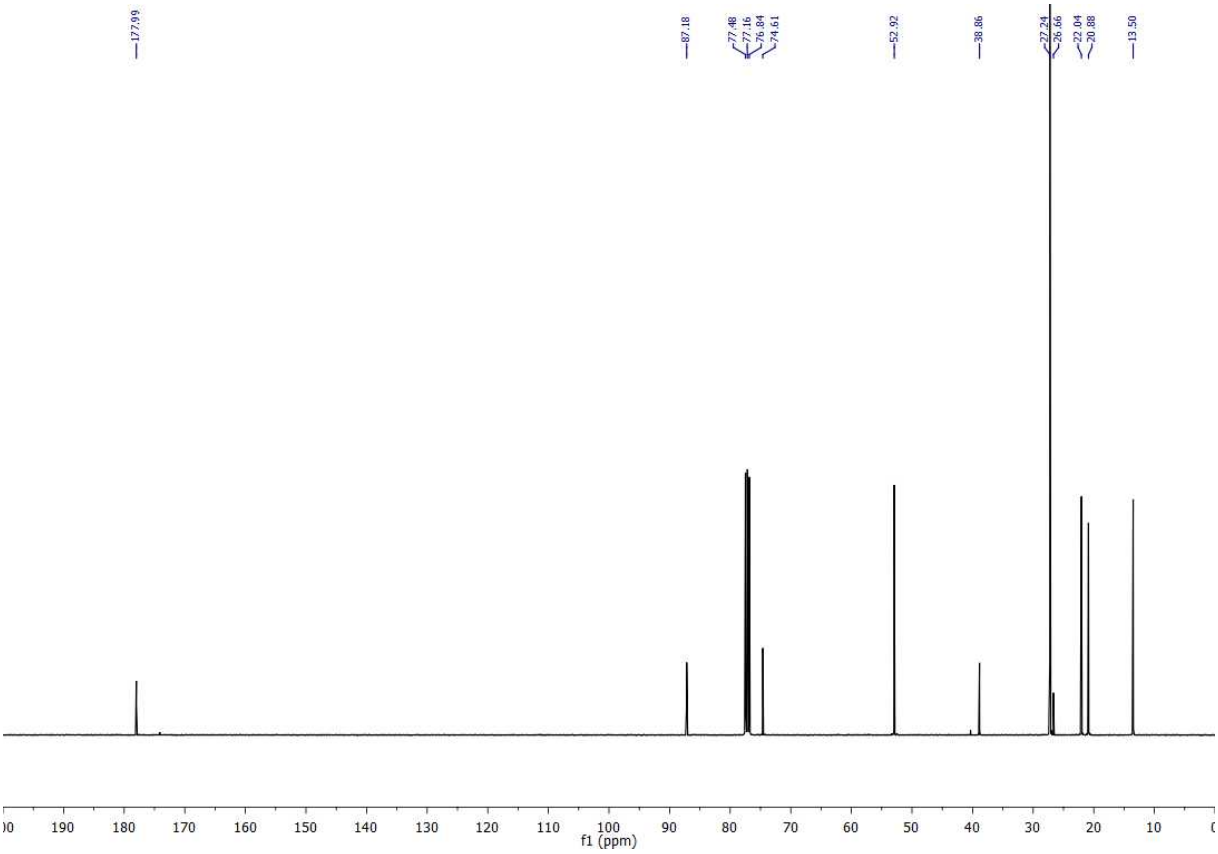

**$^{13}$C NMR** (100 MHz, $CDCl_3$, 298K) spectrum of hex-2-yn-1-yl 4-methylbenzoate (**2**)



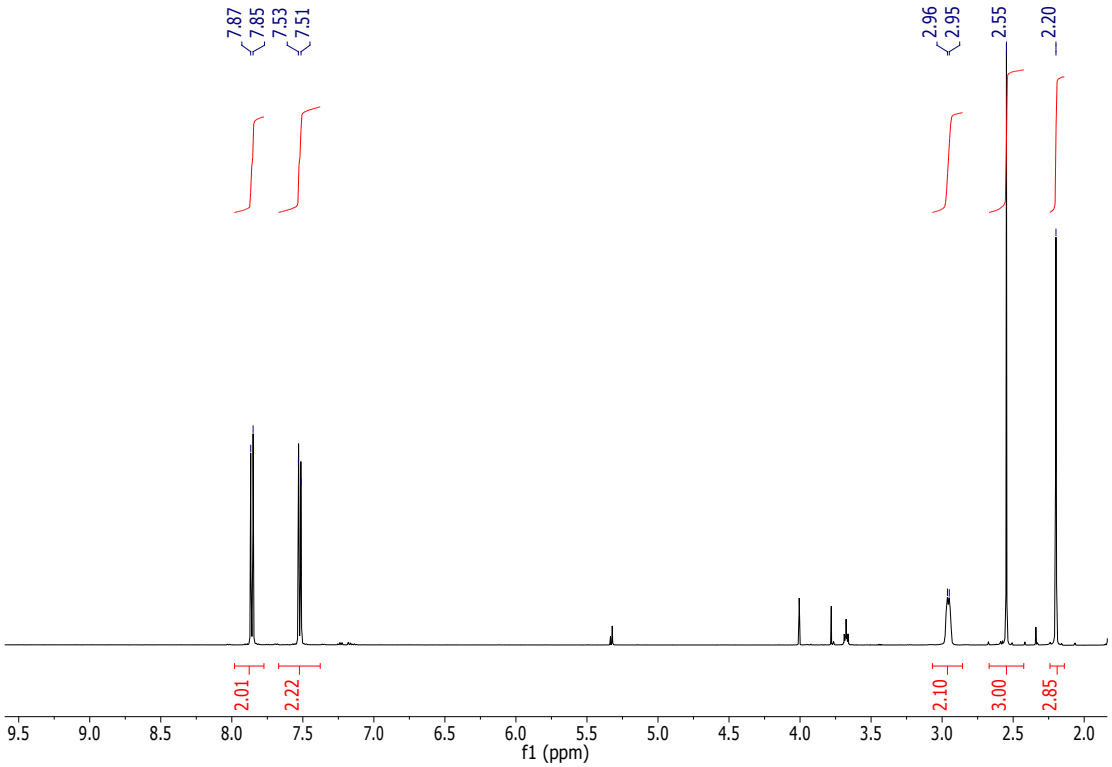
**$^{1}$H NMR** (400 MHz, $CDCl_3$, 298K) spectrum of hex-2-yn-1-yl pivalate (**3**)



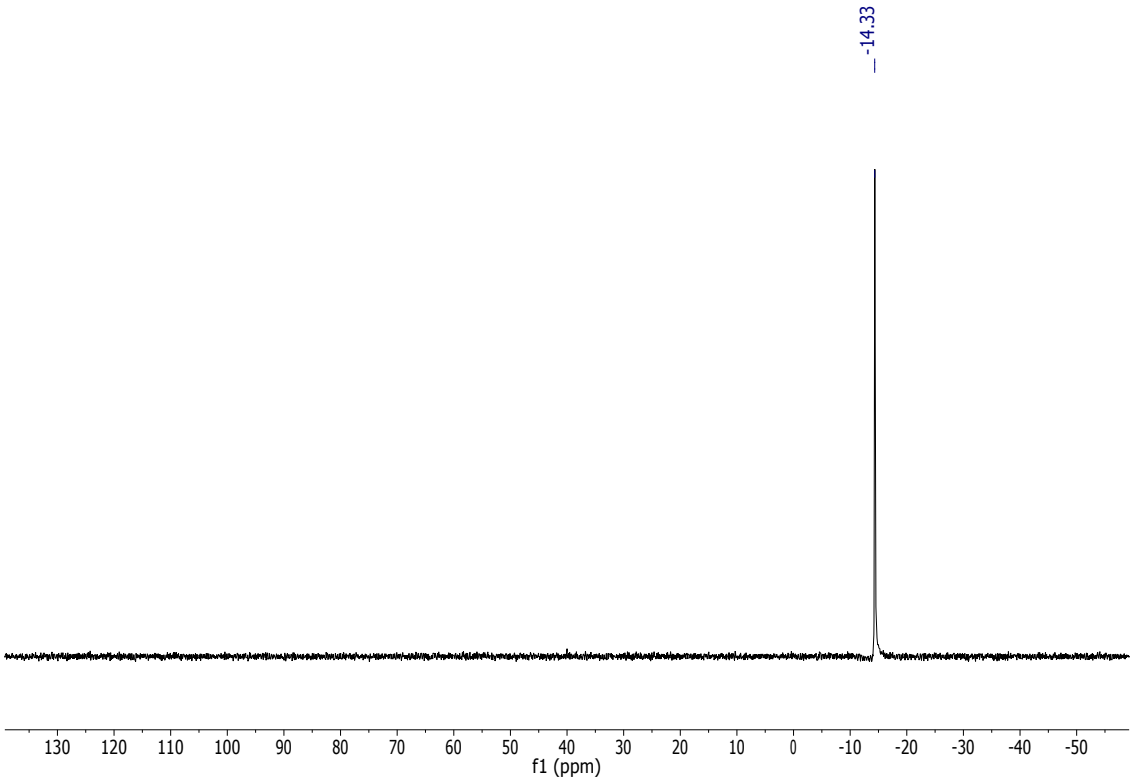

**$^{13}$C NMR** (100 MHz, $CDCl_3$, 298K) spectrum of hex-2-yn-1-yl pivalate (**3**)



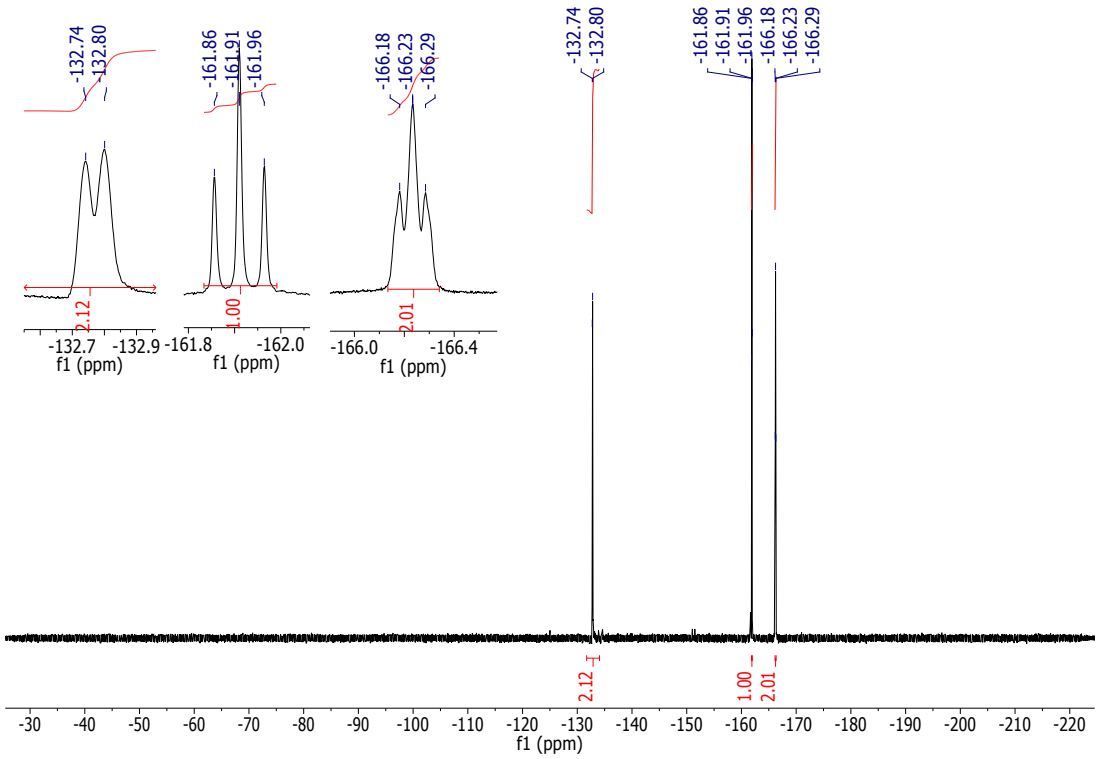
**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$, 298K) spectrum of (**4**)



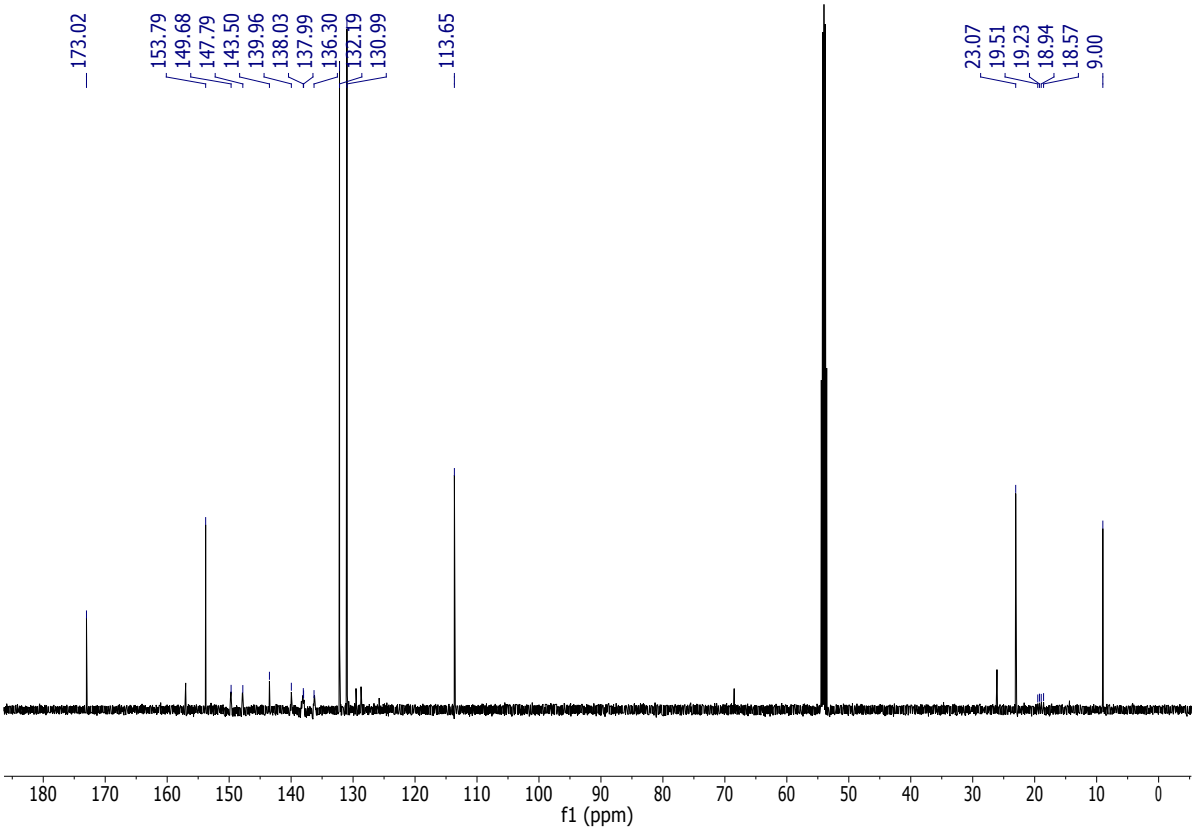

**$^{11}$B NMR** (128 MHz, $CD_2Cl_2$, 298 K) spectrum of (**4**)



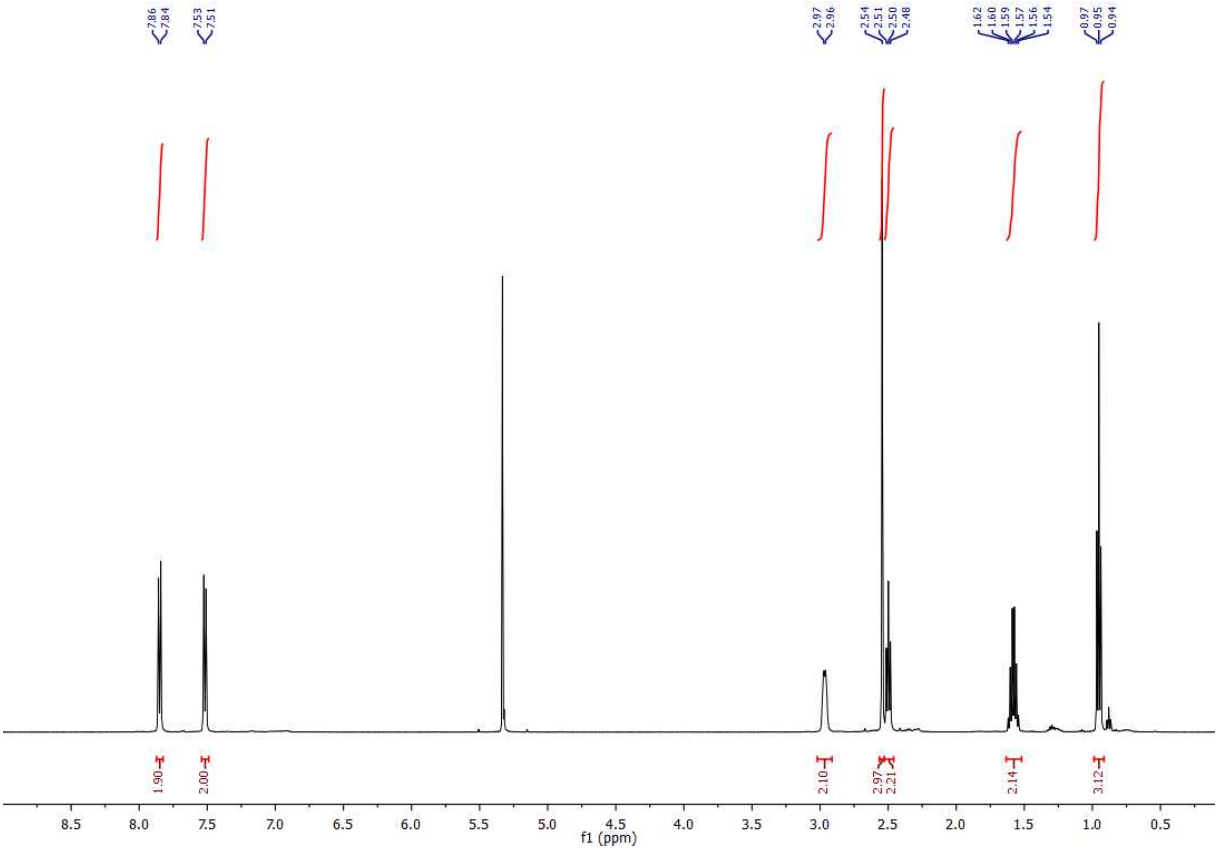
**$^{19}$F NMR** (377 MHz, $CD_2Cl_2$, 298 K) spectrum of (**4**)



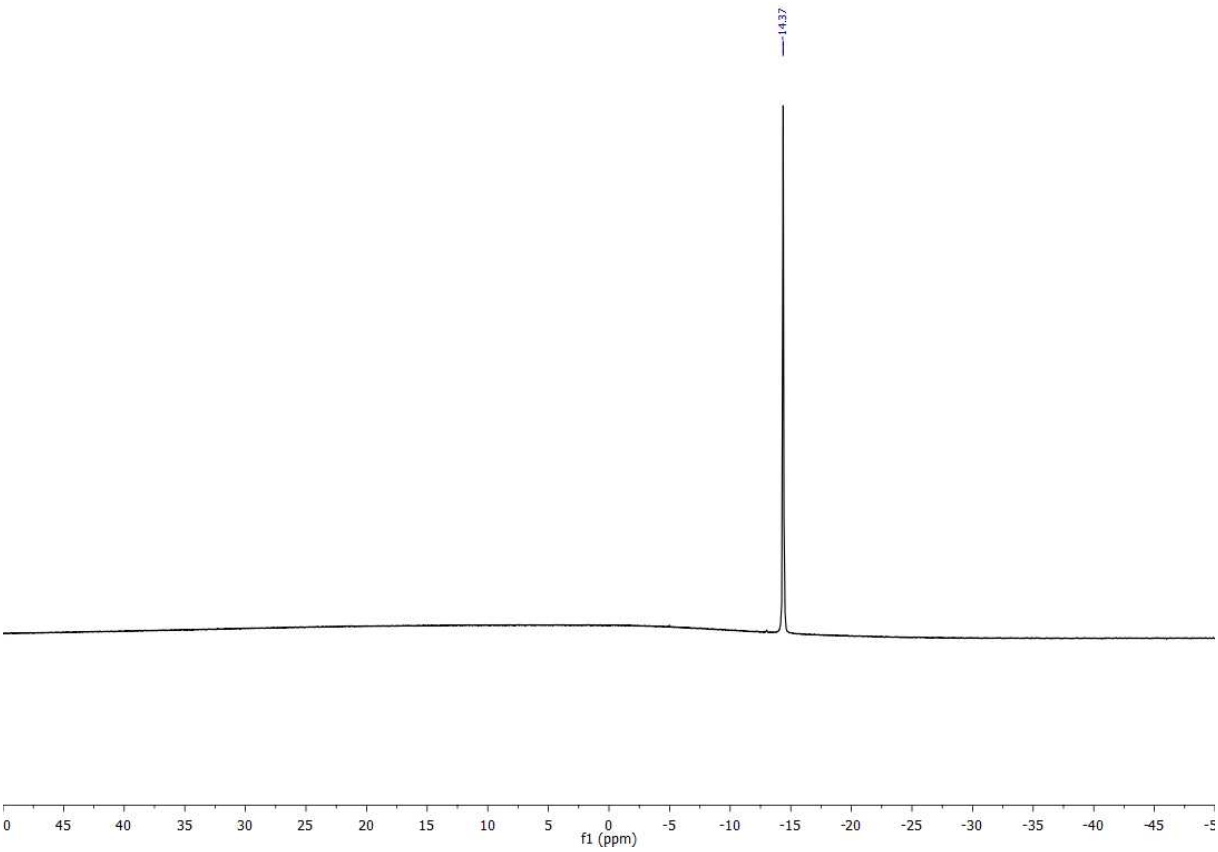

**$^{13}$C NMR** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**4**)



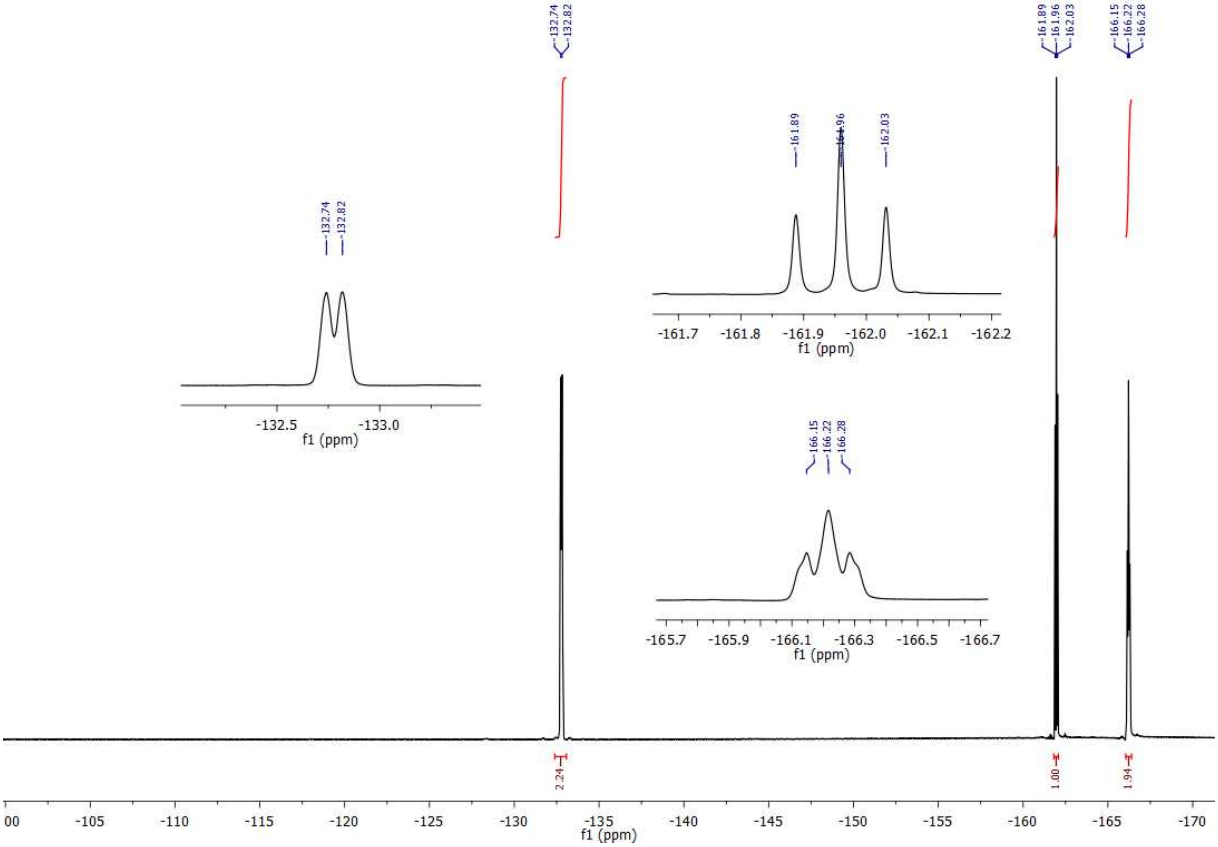
**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$, 298K) spectrum of (**5**)



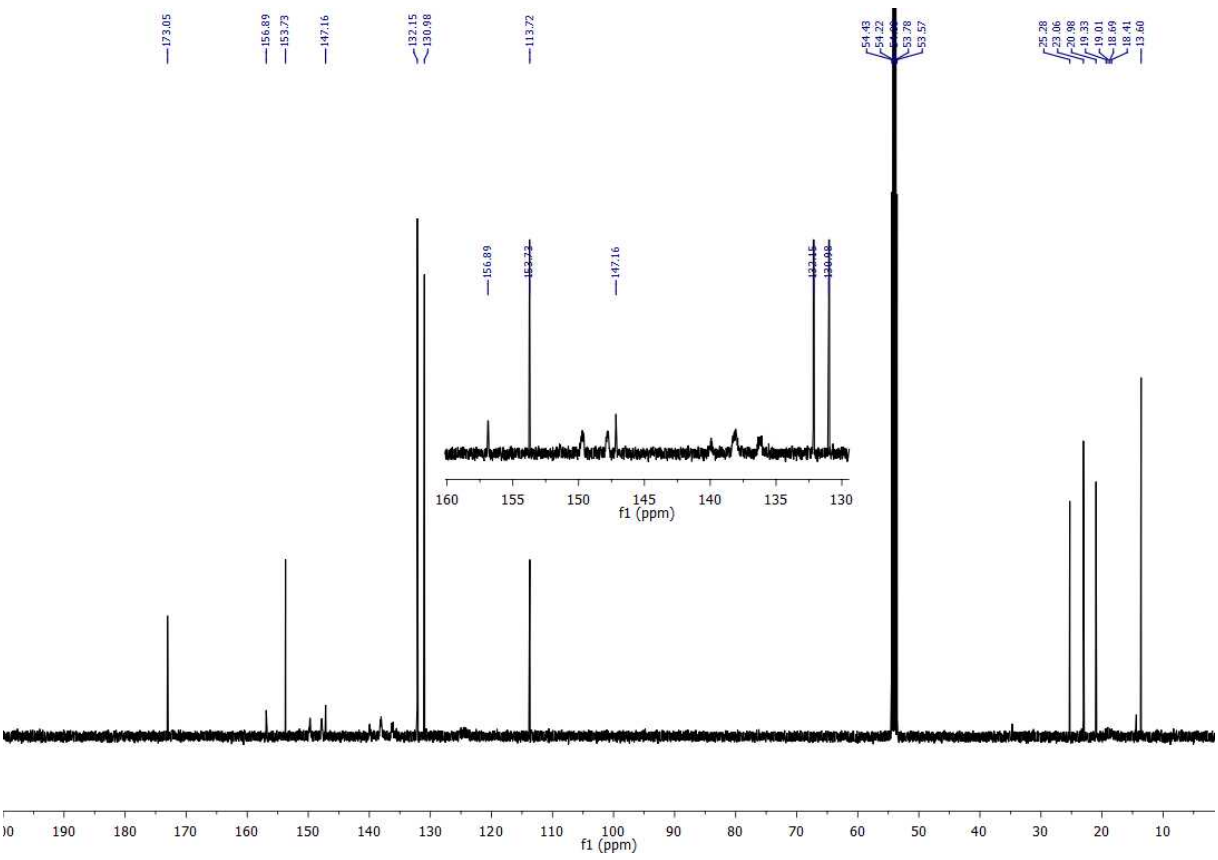

**$^{11}$B NMR** (160 MHz, $CD_2Cl_2$, 298 K) spectrum of (**5**)



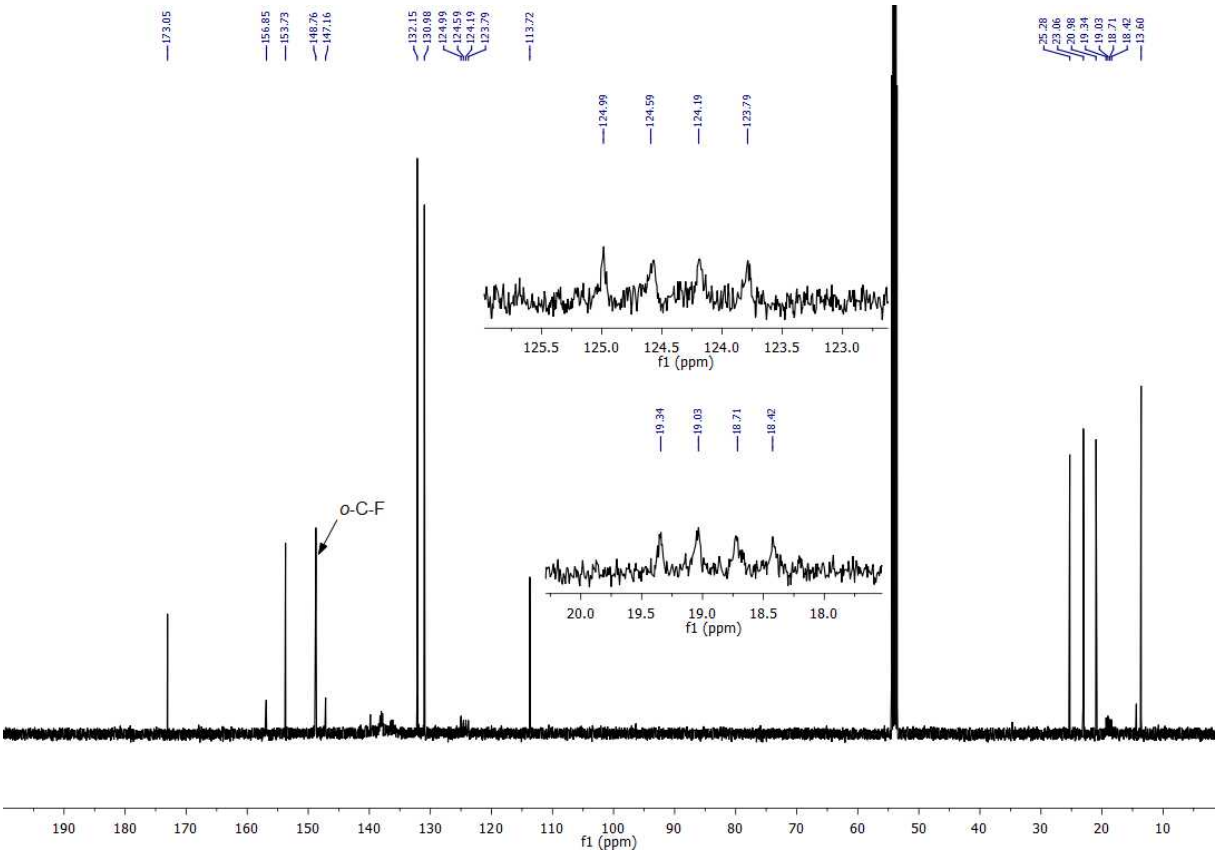
**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$, 298 K) spectrum of (**5**)



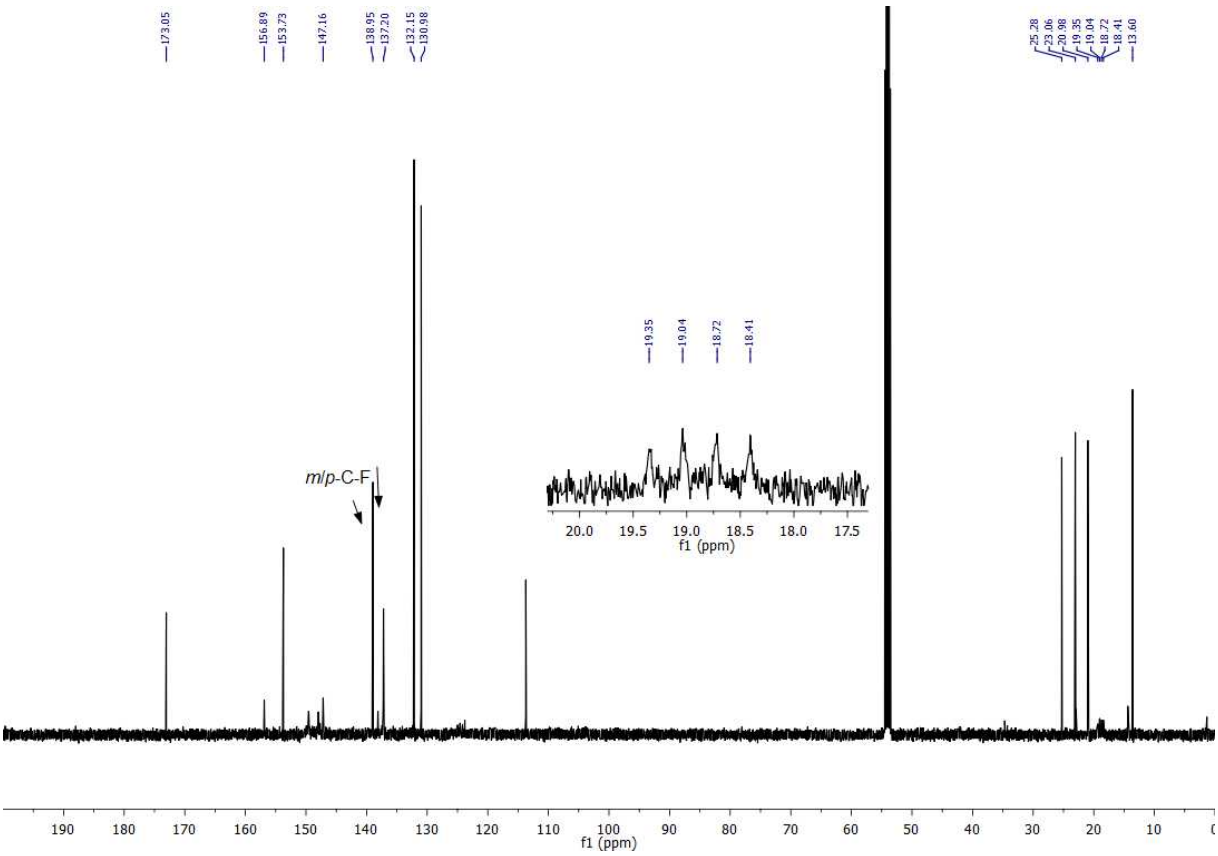

**$^{13}$C NMR {$^{1}$H}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**5**)



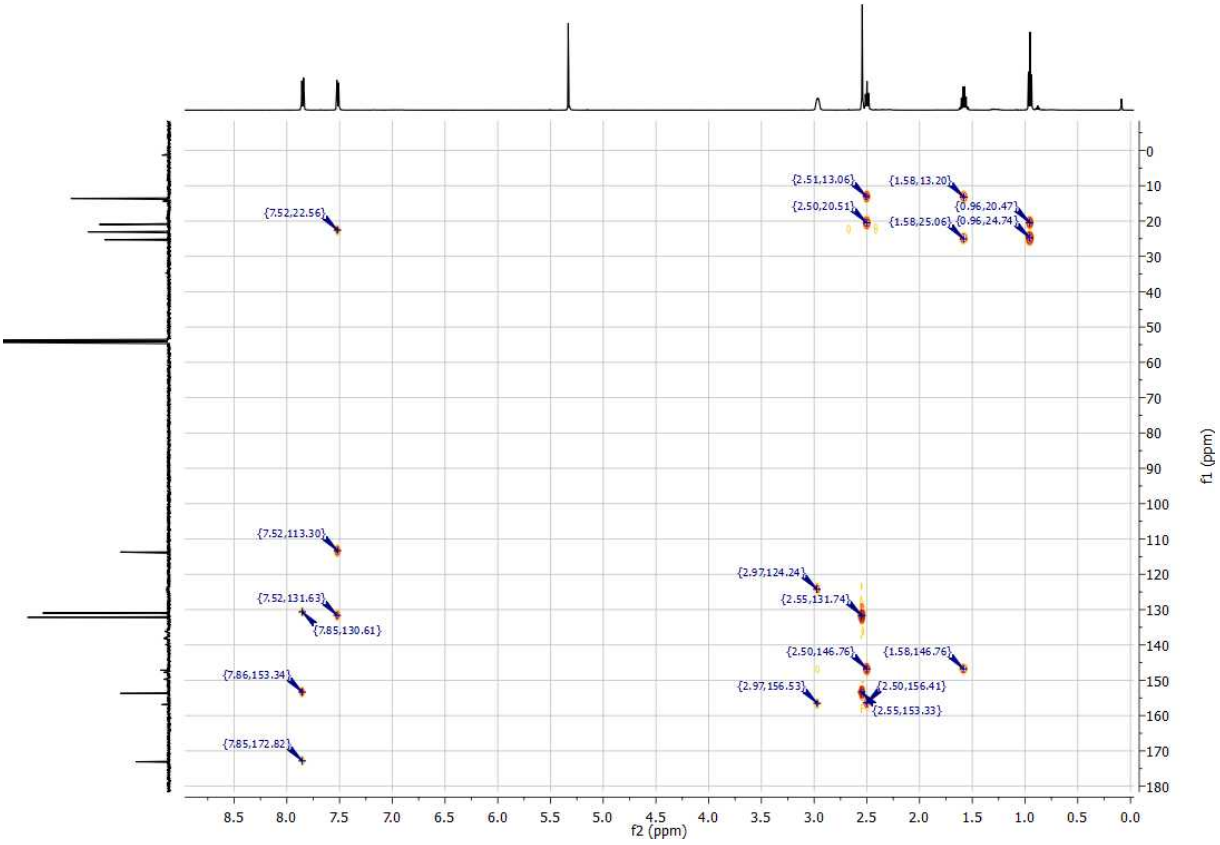
**$^{13}$C NMR {$^{1}$H; $^{19}$F at -132 ppm}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**5**)



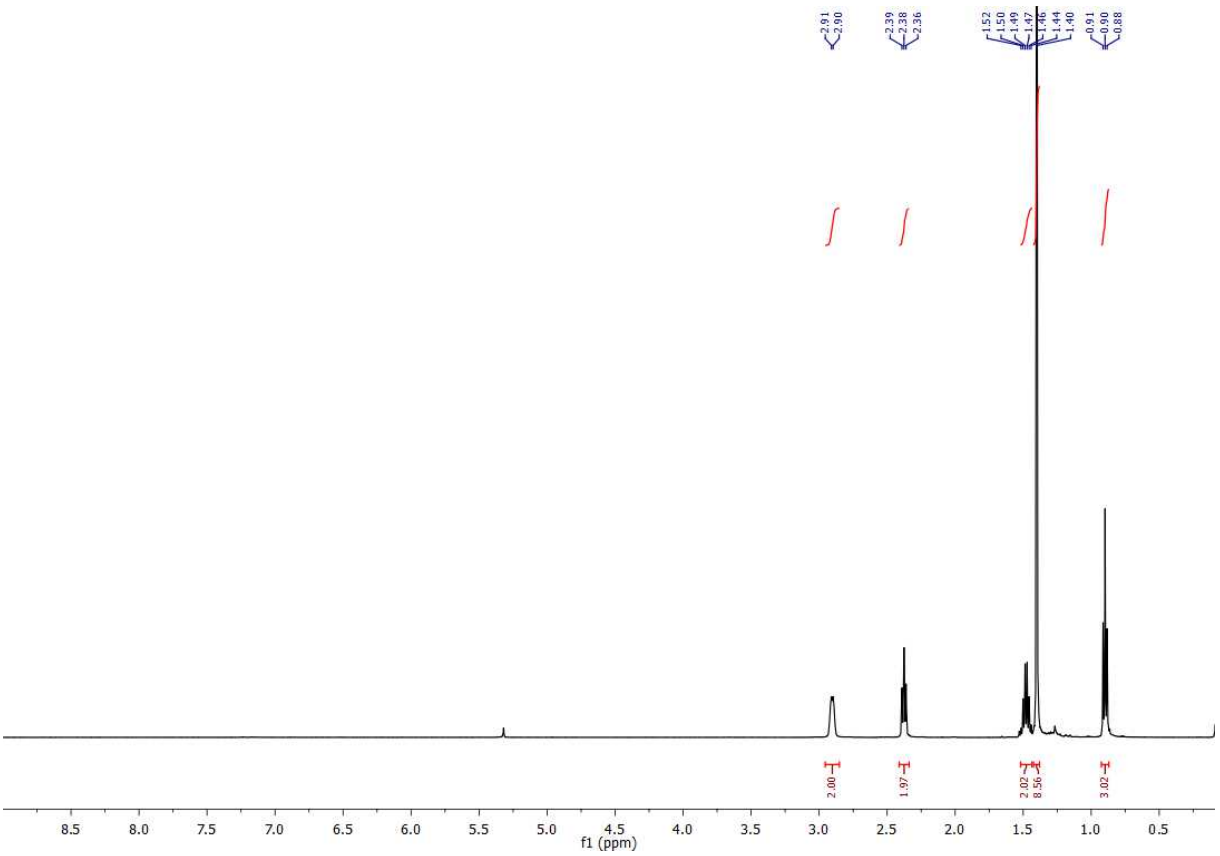

**$^{13}$C NMR {$^{1}$H; $^{19}$F at -162 ppm}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**5**)



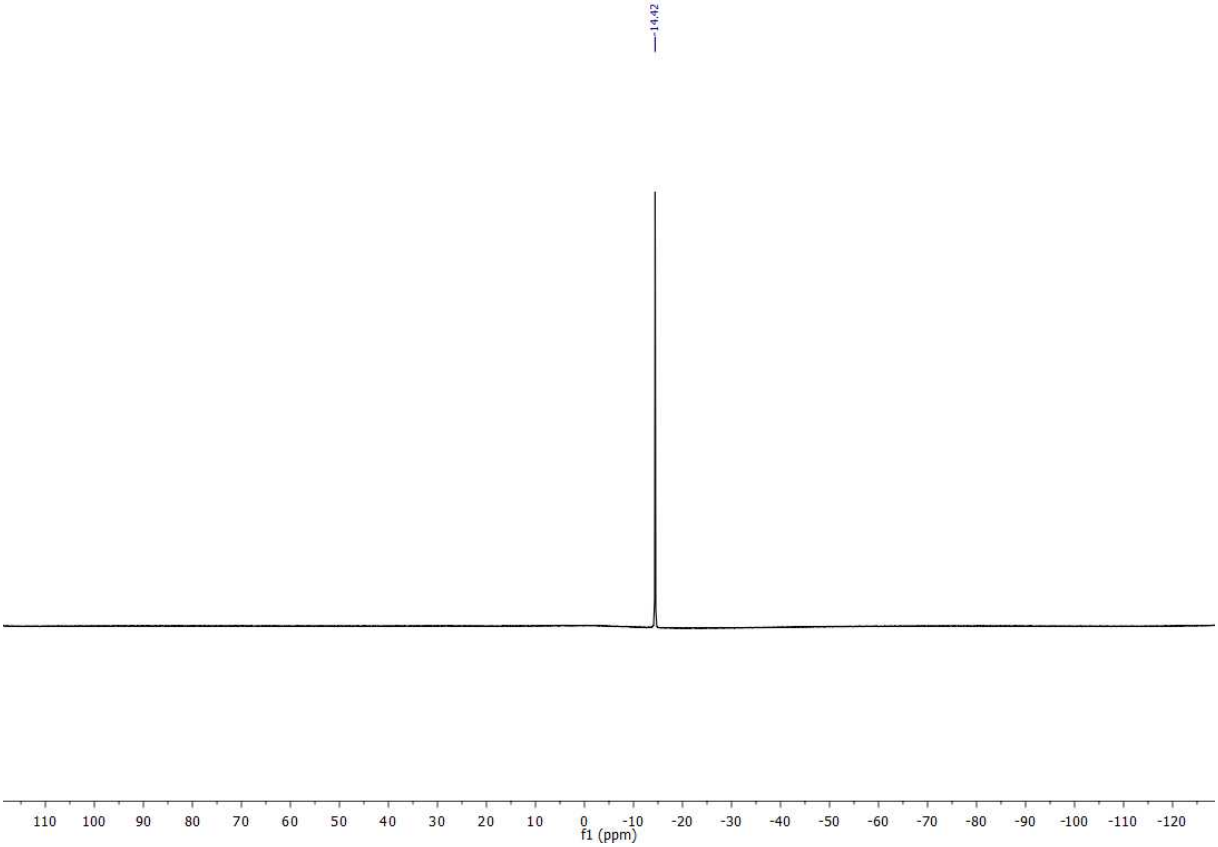
**$^{1}$H/$^{13}$C-HMBC** (500/125 MHz, $CD_2Cl_2$, 298K) spectrum of (**5**)



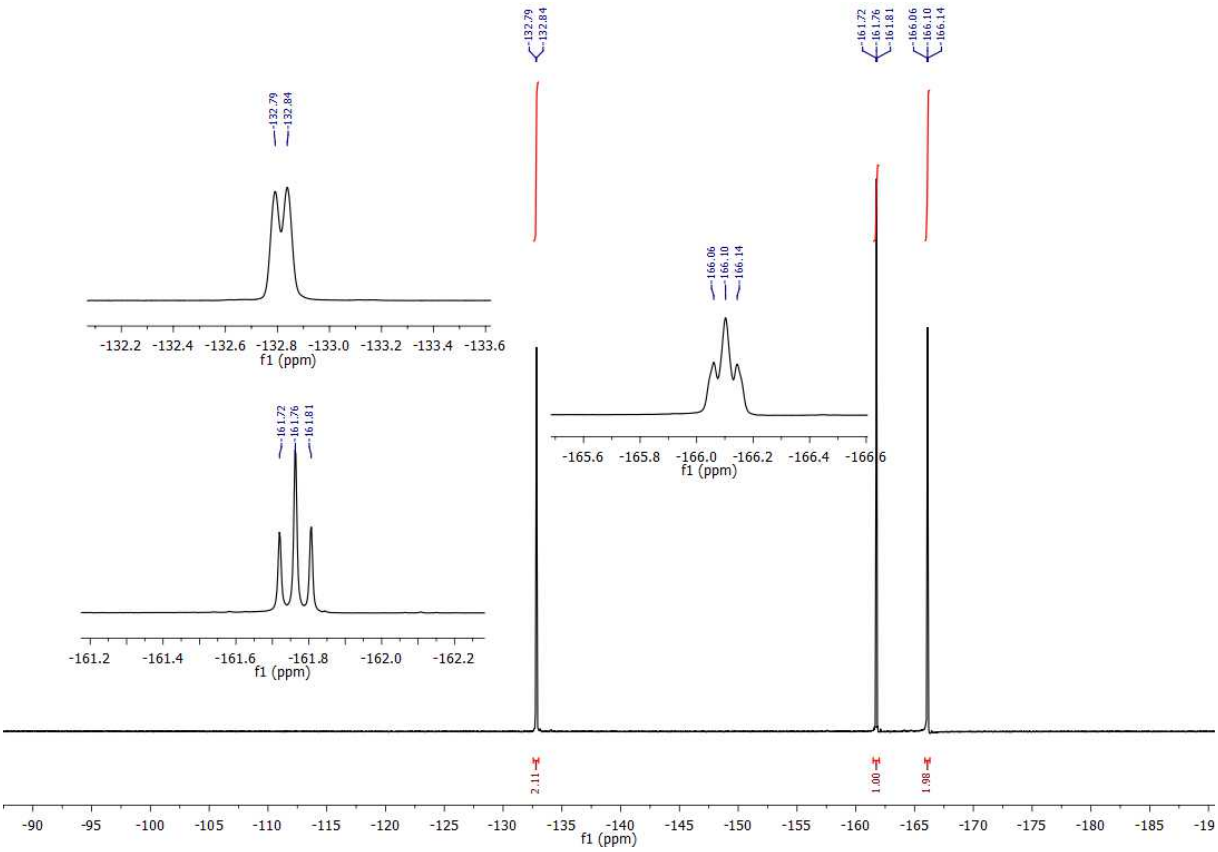

**$^{1}$H NMR** (500 MHz, $CD_2Cl_2$, 298K) spectrum of (**6**)



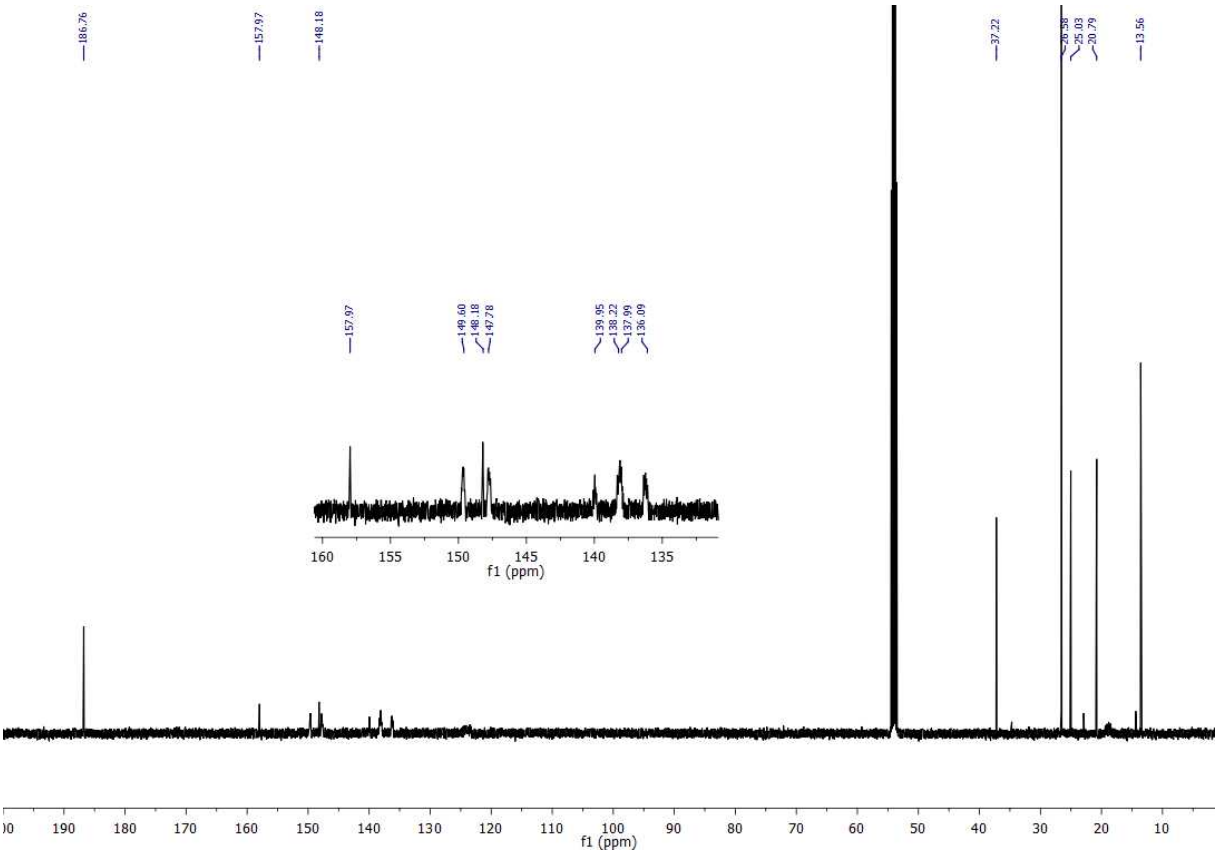
**$^{11}$B NMR** (160 MHz, $CD_2Cl_2$, 298 K) spectrum of (**6**)



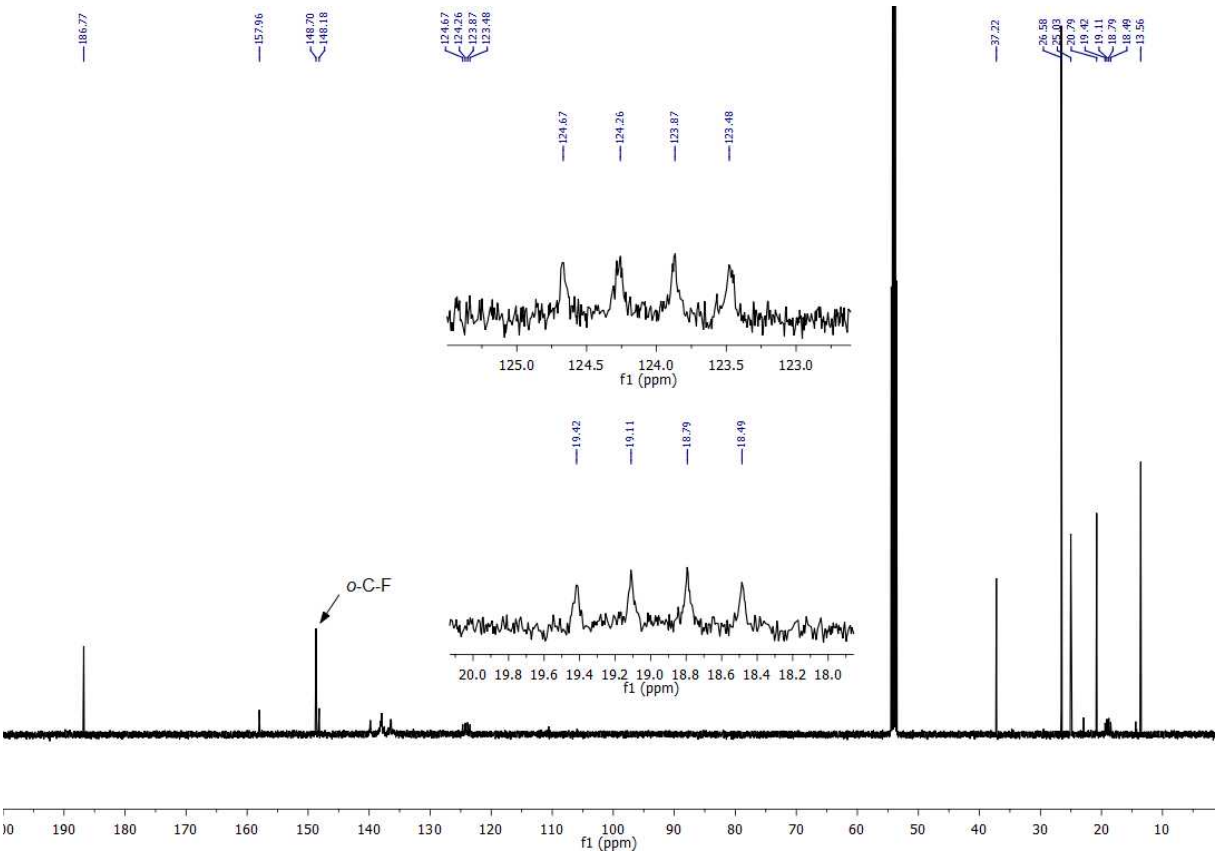

**$^{19}$F NMR** (283 MHz, $CD_2Cl_2$, 298 K) spectrum of (**6**)



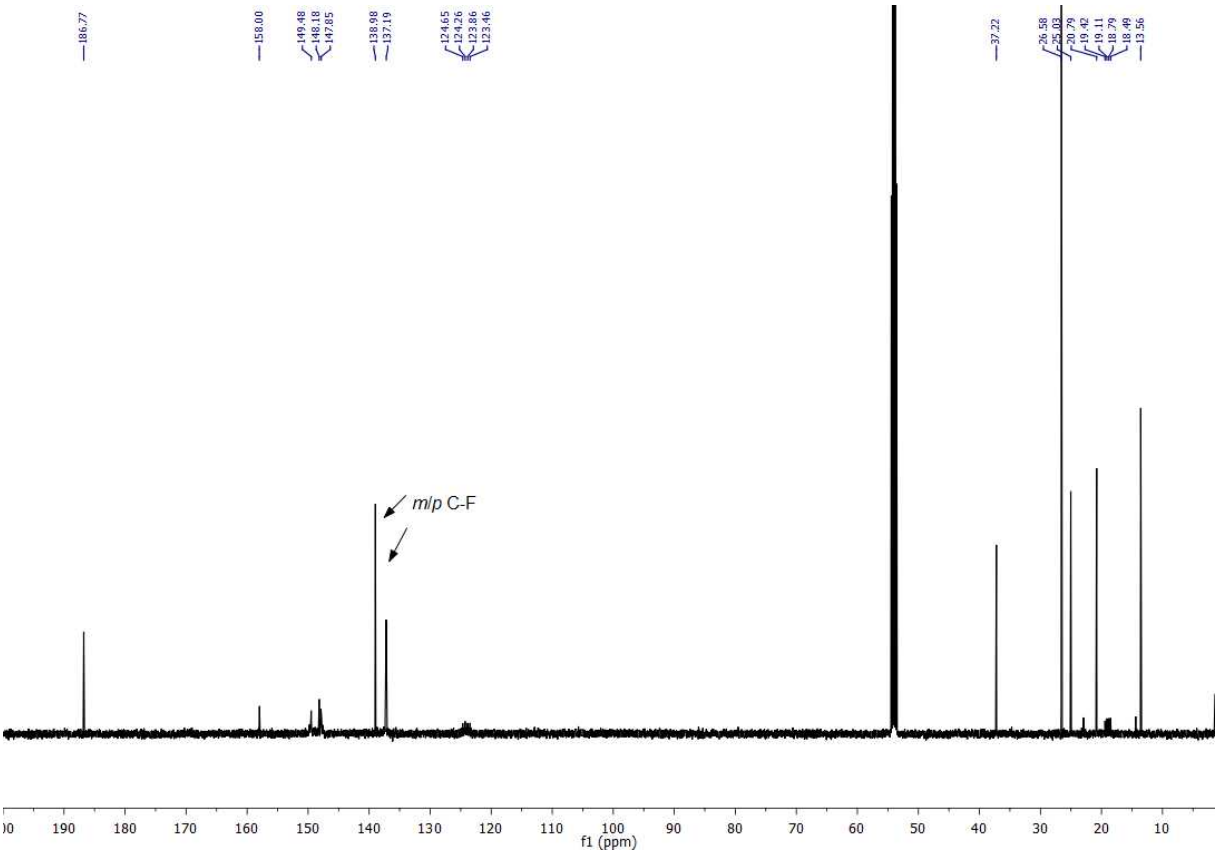
**$^{13}$C NMR {$^{1}$H}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**6**)



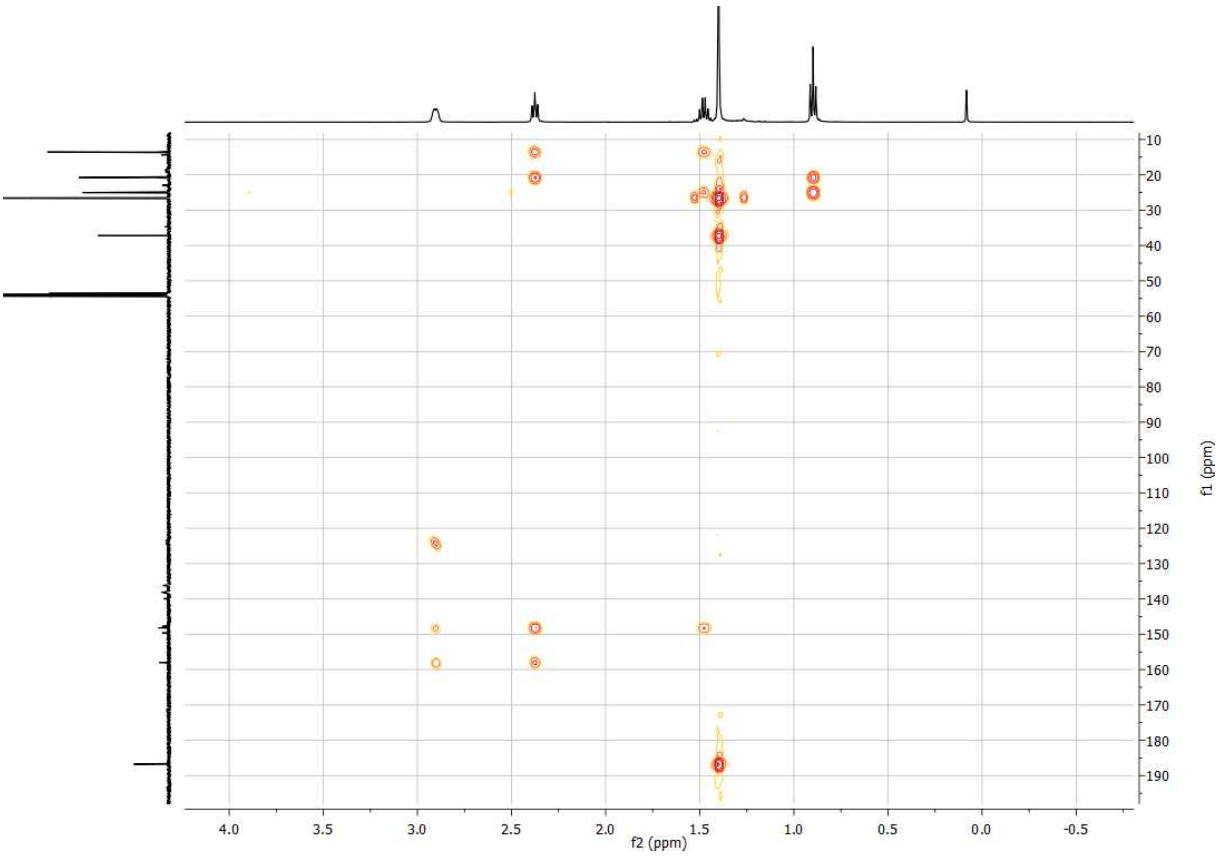

**$^{13}$C NMR {$^{1}$H; $^{19}$F at -132 ppm}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**6**)



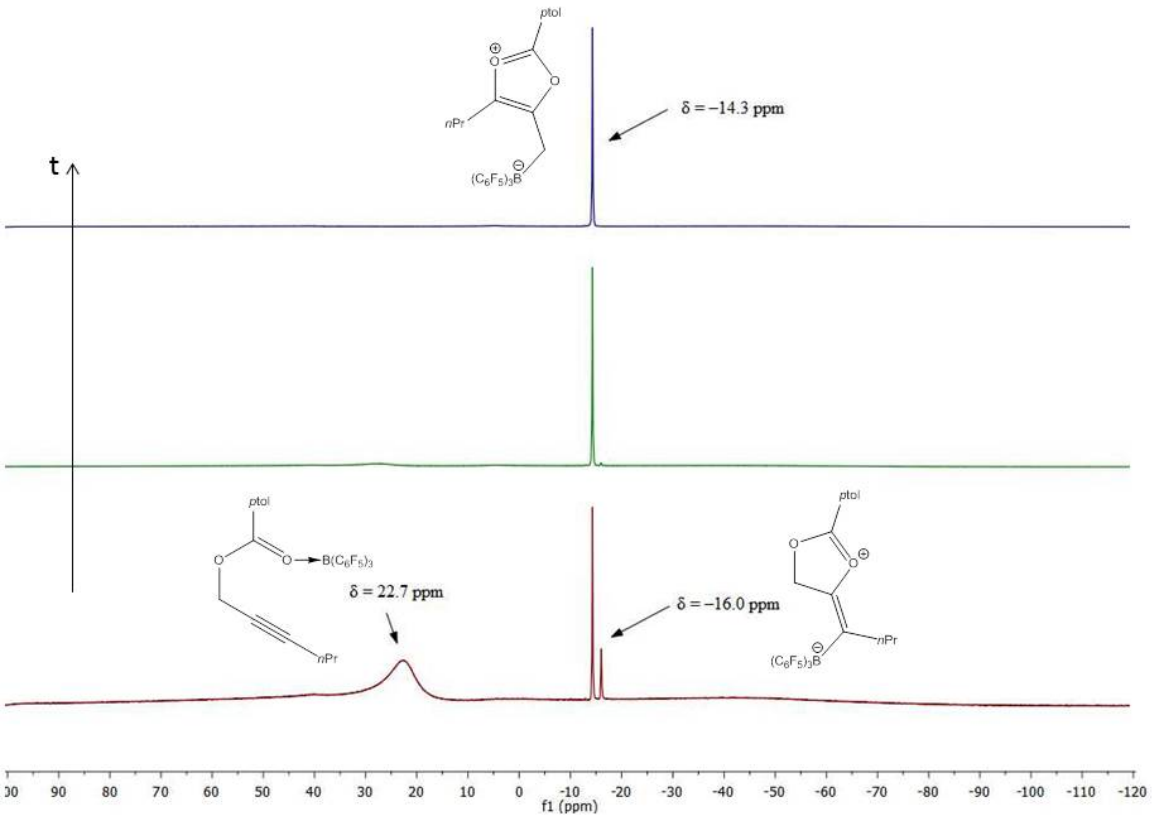
**$^{13}$C NMR {$^{1}$H; $^{19}$F at -162 ppm}** (125 MHz, $CD_2Cl_2$, 298K) spectrum of (**6**)



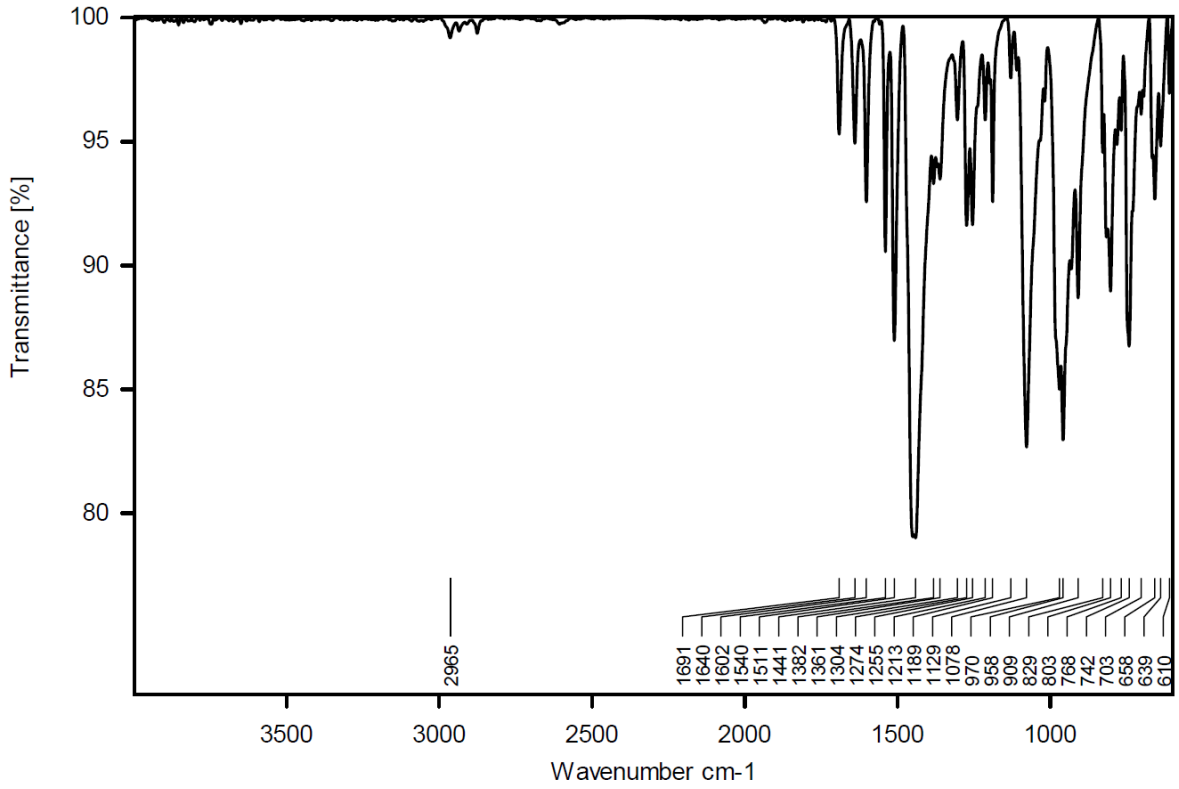

**$^{1}$H/$^{13}$C-HMBC** (500/125 MHz, $CD_2Cl_2$, 298K) spectrum of (**4**)



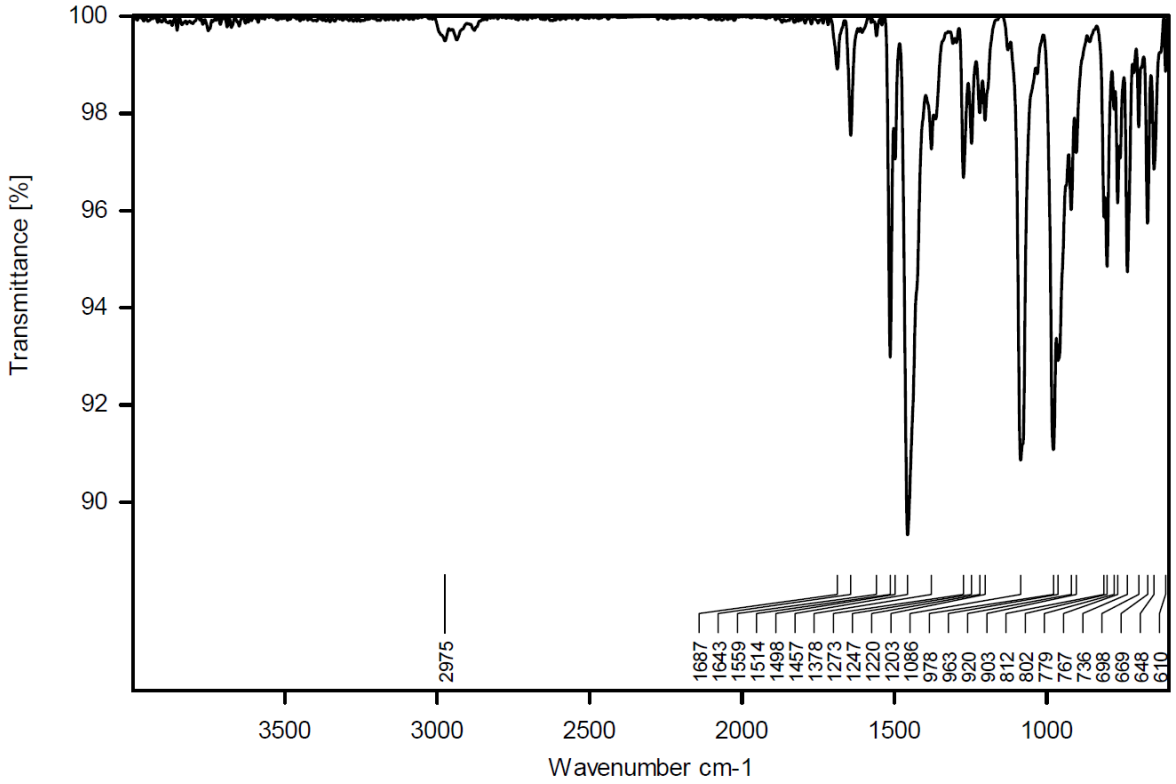
***In situ* $^{11}$B NMR** ($96$ MHz, $CD_2Cl_2$, $298$K) spectrum at various time intervals.




**IR spectrum** (ATR) of (**5**)



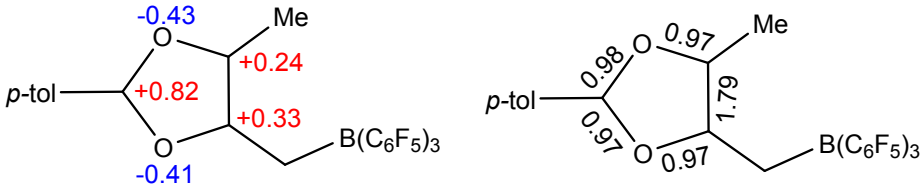
**IR spectrum** (ATR) of (**6**)



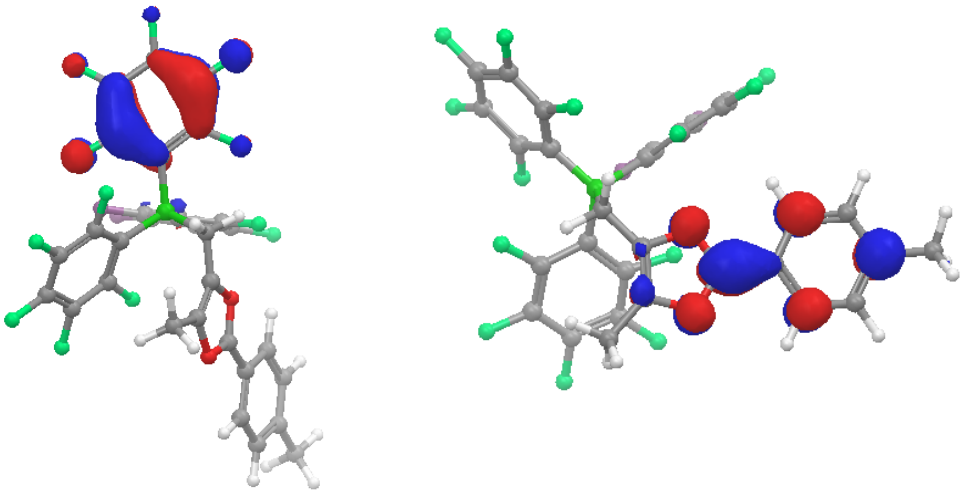
## 3. DFT Studies

Computational Details

Gas phase geometry-optimised structures for **4** were determined using the B3LYP functional and 6-31G* basis set within Jaguar.[2] Additional DFT calculations were performed on the B3LYP/cc-pVDZ level of theory with Gaussian09[3]. Frequency calculations were performed on all structures and minima on the potential energy surface and minima were uniquely characterized by zero imaginary frequencies. NBO analyses[4] were undertaken to probe the dominant Lewis structure for **4**. NBO partial charges (left) and bond orders (right) for **4** based on the DFT-optimised (B3LYP/6-31G*) geometry are shown below:




The frontier orbitals of **4** are shown in Figure below.



HOMO LUMO

## 4. Crystallographic Details

X-ray diffraction studies to determine the solid-state structure of crystalline materials were undertaken on single crystals grown under an inert atmosphere and protected from atmospheric air and moisture using an inert per-fluorinated polyether oil. A single crystal was then mounted in a cryoloop. For compound **4**: Crystals were examined on a Bruker APEX-II diffractometer using monochromatic Mo-Kα radiation (0.71073 Å) and a CCD area detector. Data were collected at 150(2) K with temperatures maintained using an Oxford Cryostream cooler for both initial indexing and full data collection. Data were processed using SAINT and an absorption correction applied using multi-scan within the APEX-2 program.[5] The structures were solved by direct methods within the SHELXTL package. All structures were refined against $F^2$ using the SHELXTL package.[6] Crystal data for **4**: $C_{30}H_{12}BF_{15}O_2$, $M$ = 700.21, triclinic *P-1*, $a$ = 10.6886(5), $b$ = 11.3024(5), $c$ = 12.7940(6) Å, α = 67.050(2), β = 74.863(2), γ = 83.714(2)°, $V$ = 1373.83(11) Å$^3$ , λ(Mo-Kα) = 0.71, $T$ = 150(2) K, $Z$ = 2, $D_c$ = 1.693 Mg m$^{-3}$, $F$(000) = 696, independent reflections 7118 ($R_{int}$ = 0.0887), $R_1$ ($I > 2\sigma(I)$) = 0.0441, $wR_2$ (all data) = 0.1000, $S$ = 1.007 (all data). For compound **5**: Crystals were examined on a Bruker APEX-II diffractometer using monochromatic Mo-Kα radiation (0.71073 Å) and a CCD area detector. Data were collected at 200(2) K with temperatures maintained for full data collection. Crystal data for **5**: $C_{32}H_{16}BF_{15}O_2$,colourless crystal (plate), dimensions 0.280 x 0.200 x 0.080 mm$^3$, crystal system monoclinic, space group $P2_1/c$, a = 11.732(2) Å, b = 20.805(4) Å, c = 13.426(2) Å, α = 90°, β = 107.896(4)°, γ = 90°, $V$ = 3118.5(9) Å$^3$, T = 200(2) K, Z = 4, $D_c$ = 1.642 Mg m$^{-3}$, $Theta_{max}$= 24.108°, λ(Mo-Kα) = 0.71073 Å, 0.5° omega-scans with CCD area detector, covering the asymmetric unit in reciprocal space with a mean redundancy of 3.05 and a completeness of 100.0% to a resolution of 0.83Å, 16881 reflections measured, 4974 unique (R(int)=0.0397), 3703 observed ($I > 2\sigma(I)$), intensities were corrected for Lorentz and polarization effects, an empirical absorption correction was applied using SADABS[7] based on the Laue symmetry of the reciprocal space, mu=0.25mm$^{-1}$, $T_{min}$=0.90, $T_{max}$=0.96, structure refined against $F^2$ with a Full-matrix least-squares algorithm using the SHELXL (Version 2013-4) software[6], 479 parameters refined, hydrogen atoms were treated using appropriate riding models, goodness of fit 1.03 for observed reflections, final residual values $R_1(F)$=0.040, $wR(F^2)$=0.101 for observed reflections, residual electron density -0.53 to 0.57 eÅ$^{-3}$.

Unit cell parameters and refinement statistics are presented in Table 1. For additional data see: CCDC 987406 and CCDC 987407.

**Table 1:** Selected Crystallographic Data for **4** and **5**.

| Compound **4** | | | |
|---|---|---|---|
| Empirical Formula | $C_{30}H_{12}BF_{15}O_2$ | $T$/K | 150(2) |
| Crystal System | Triclinic | $D_c$/g.cm$^{-3}$ | 1.693 |
| Space Group | *P-1* | Crystal size/mm | 0.10 × 0.10 × 0.10 |
| $a$/Å | 10.6886(5) | Total data | 7118 |
| $b$/Å | 11.3024(5) | Unique data | 4464 |
| $c$/Å | 12.7940(6) | $R_{int}$ | 0.0887 |
| α/° | 67.050(2) | $R_1[F^2>2\ \sigma(F^2)]$ | 0.0441 |
| β/° | 74.863(2) | $wR_2$ (all data) | 0.1000 |
| γ/° | 83.714(2) | GoF | 1.007 |
| V/Å$^3$ | 1373.83(11) | $\rho_{min}/\rho_{max}$/eÅ$^{-3}$ | -0.282/+0.337 |
| $Z$ | 2 | | |

| Compound **5** | | | |
|---|---|---|---|
| Empirical Formula | $C_{32.50}H_{17}BClF_{15}O_2$ | $T$/K | 200(2) |
| Crystal System | monoklin | $D_c$/g.cm$^{-3}$ | 1.64 |
| Space Group | $P2_1/c$ | Crystal size/mm | 0.28x0.20x0.08 |
| $a$/Å | 11.732(2) | Total data | 16881 |
| $b$/Å | 20.805(4) | Unique data | 4974 |
| $c$/Å | 13.426(2) | $R_{int}$ | 0.0397 |
| α/° | 90.0 | $R_1[F^2>2\ \sigma(F^2)]$ | 0.040 |
| β/° | 107.896(4) | $wR_2$ (all data) | 0.101 |
| γ/° | 90.0 | GoF | 1.03 |
| V/Å$^3$ | 3118.5(9) | $\rho_{min}/\rho_{max}$/eÅ$^{-3}$ | -0.53/0.57 |
| $Z$ | 4 | | |

## 5. References: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6. SHELXTL, Bruker AXS, Madison, WI, USA. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
7. Program SADABS 2012/1 for absorption correction; G.M. Sheldrick, Bruker Analytical X-ray-Divisioin, Madison, Wisconsin, 2012.