

Supplementary Information for:

**Reactivity of Organogold Compounds with $B(C_6F_5)_3$ –
A Gold-Boron Transmetalation via σ -B/ π -Au-Species**

**Max M. Hansmann,^{*,†} Frank Rominger,[†] Michael P. Boone,^{‡,‡} Douglas W. Stephan^{*,‡,‡} and
A. Stephen K. Hashmi^{*,†}**

[†] *Organisch-Chemisches Institut, Ruprecht-Karls-Universität Heidelberg, Im Neuenheimer Feld 270,
69120 Heidelberg, Germany*

[‡] *Department of Chemistry, University of Toronto, 80 St. George Street,
Toronto, Ontario, M5S 3H6, Canada*

[‡] *Chemistry Department, Faculty of Science, King Abdulaziz University (KAU), Jeddah 21589, Saudi
Arabia.*

Table of Contents

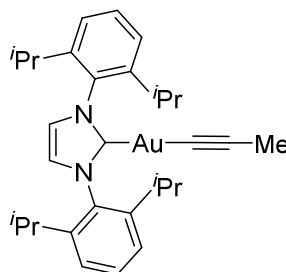
General procedures.....	S-2
Experimental Details	S-3
NMR data.....	S-21
Catalysis experiments	S-66
X-ray data.....	S-68
Computational details.....	S-69
References	S-77

General procedures

With the exception of the synthesis of starting materials, all reactions and manipulations were carried out under an atmosphere of dry, O₂-free nitrogen using standard double-manifold techniques with a rotary oil pump. An argon-filled glove box 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 120°C for 24 h prior to use. All solvents (toluene, CH₂Cl₂, THF, pentane, hexane) were dried by employing 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(C₆F₅)₃ was prepared based on a slightly modified synthesis reported in the literature.^[1] The IPr* ligand was prepared according to the literature procedure.^[2] ¹H, ¹³C ¹¹B and ¹⁹F NMR spectra were recorded on a Avance III, Avance 400, Avance-III-300, Avance DRX-300, Avance 500 or Avance 600. Chemical shifts are expressed as parts per million (ppm, δ) downfield of tetramethylsilane (TMS) and are referenced to *d*₈-toluene, *d*₆-benzene, *d*₈-THF, CDCl₃ (7.26 / 77.16 ppm) and CD₂Cl₂ (5.32 / 53.80 ppm) as internal standards. NMR spectra were referenced to CFCl₃ (¹⁹F) or 1,2-difluorobenzene (-139 ppm) and BF₃·Et₂O/CDCl₃ (¹¹B). 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). Mass spectra (MS and HRMS) were determined in the chemistry department of the University Heidelberg under the direction of Dr. J. Gross. FAB (+) spectra were obtained using a JEOL JMS-700 spectrometer. For the FAB-matrix, 3-nitrobenzyl alcohol (NBA) or *o*-nitrophenyl octyl ether (NPOE) was used. For ESI (+) spectra, a ApexQe FT-ICR-MS spectrometer was used. Infrared Spectroscopy (IR) was processed on an FT-IR (IF528), IR (283) or FT-IR Vektor 22.

Experimental Details

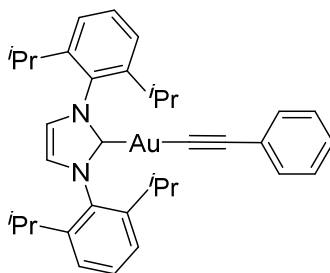
(1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(prop-1-yn-1-yl)gold (1)



(Idipp)AuCl (400 mg, 0.64 mmol) was dissolved in THF (15 mL) and cooled to -78°C . At this temperature 1-propynylmagnesium bromide (3.9 mL, 1.93 mmol, 3.0 eq., 0.5 M in THF) was added, stirred for 2 h and then warmed up to room temperature and stirred for additional 12 h. Aqueous saturated NaHCO_3 solution (10 mL) was added and the aqueous phase extracted with CH_2Cl_2 (3 x 30 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. Recrystallization from CH_2Cl_2 /pentane affords the product as white solid (382 mg, 94%). The spectral data is in accordance with literature data.^[3]

^1H NMR (500 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.55 (t, J = 7.8 Hz, 2H), 7.34 (d, J = 7.8 Hz, 4H), 7.17 (s, 2H), 2.55 (sept., J = 6.9 Hz, 4H), 1.70 (s, 3H), 1.33 (d, J = 6.9 Hz, 12H), 1.22 (d, J = 6.9 Hz, 12H); **^{13}C NMR** { ^1H } (125 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 191.7 (s), 146.3 (s), 134.9 (s), 130.9 (s), 124.6 (s), 123.7 (s), 116.1 (s), 99.1 (s), 29.3 (s), 24.9 (s), 24.2 (s), 4.9 (s).

(1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(phenylethynyl)gold (2)

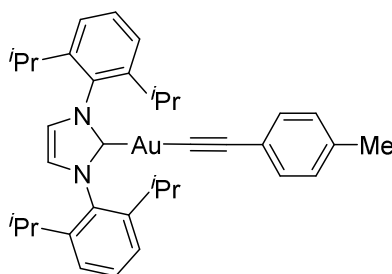


(Idipp)AuCl (100 mg, 0.0161 mmol) and phenyl acetylene (17 mg, 0.170 mmol) were placed in a Schlenk bomb along with EtOH (20 mL) and to this NaOMe (9 mg, 0.170 mmol) in EtOH (5 mL) was added. The reaction was heated to 80°C for 1 h and upon cooling to room temperature the solvent was removed *in vacuo*. The resulting residue was taken up in CH_2Cl_2 (10 mL) and filtered through Celite.

The resulting solution was then evaporated to dryness affording the colorless product (99 mg, 0.144 mmol, 85%).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): 7.50 (t, *J* = 8 Hz, 2H), 7.29 (t, *J* = 8 Hz, 4H), 7.15-7.09 (m, 4H), 7.06-6.95 (m, 3H), 2.51 (sept., *J* = 7 Hz, 4H), 1.29 (d, *J* = 7 Hz, 12H), 1.15 (d, *J* = 7 Hz, 12H).

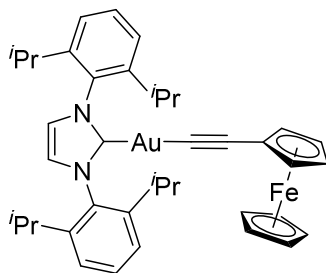
(1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)(p-tolylethynyl)gold (3)



To a solution of (Idipp)AuCl (434 mg, 0.70 mmol) in CH₂Cl₂ (4 ml) was added NEt₃ (2 ml) followed by 4-ethynyltoluene (133 μl, 1.05 mmol, 1.5 equiv.). The solution was stirred at room temperature in the dark for 3d. The solvent was removed under reduced pressure and the remaining solid purified by column chromatography (basic aluminum oxide; PE:EA 10:1 to 5:1) to afford **3** as colorless solid (442 mg, 0.63 mmol, 90%).

R_f = 0.40 (petroleum ether : ethyl acetate = 5:1); **IR** (thin film) ν_{max} = 3139 cm⁻¹, 3081, 3031, 2959, 2922, 2867, 2118, 1595, 1559, 1505, 1469, 1459, 1415, 1386, 1365, 1349, 1327, 1287, 1211, 1181, 1150, 1123, 1104, 1084, 1061, 1044, 814; **¹H NMR** (600 MHz, CDCl₃, 298 K): δ [ppm] = 7.59 (t, *J* = 7.6 Hz, 2H), 7.38 (d, *J* = 8.0 Hz, 4H), 7.21 (s, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 2.60 (sept., *J* = 7.0 Hz, 4H), 2.25 (s, 3H), 1.38 (d, *J* = 6.8 Hz, 12H), 1.24 (d, *J* = 6.8 Hz, 12H); **¹³C NMR** {¹H} (150 MHz, CDCl₃, 298 K): δ [ppm] = 191.2 (s), 146.4 (s), 136.2 (s), 134.8 (s), 132.1 (s), 131.1 (s), 129.1 (s), 124.7 (s), 124.0 (s), 123.7 (s), 103.6 (s), 29.3 (s), 24.9 (s), 24.2 (s), 21.5 (s); **EA** (elemental analysis) calcd (%) for C₃₆H₄₃AuN₂: C 61.71, H 6.19, N 4.00%; Obs. C 61.50, H 6.37, N 3.99%; **HRMS-FAB** (+) (m/z): calcd for C₃₆H₄₃AuN₂, 700.3092; found, 700.3100.

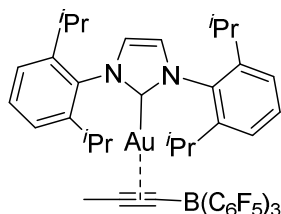
(1,3-bis(2,6-diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-yl)(ferrocenylethynyl)gold (4)



To a solution of ethynylferrocene (67.6 mg, 0.32 mmol) in Et₂O (5 ml) was added at -78°C *n*BuLi (140 µl, 0.35 mmol, 2.5 M in hexane). The solution was stirred at this temperature for 1 h and then (Idipp)AuCl (200 mg, 0.32 mmol) was added as solid. The solution turns bright yellow upon addition and was warmed up to room temperature over 12 h. A saturated solution of NaHCO₃ (5 ml) was added, the phases separated and the aqueous phase extracted with CH₂Cl₂ (2 x 5 ml). The combined organic phases were dried over MgSO₄, filtered and concentrated to afford an orange solid, which was recrystallized from CH₂Cl₂/pentane to give **4** (232 mg, 0.29 mmol, 91%).

IR (thin film) ν_{\max} = 3124 cm⁻¹, 2964, 2869, 1594, 1553, 1470, 1414, 1385, 1364, 1329, 1262, 1214, 1182, 1104, 1061, 1022, 946, 924, 864, 807, 759; **¹H NMR** (600 MHz, CD₂Cl₂, 298 K): δ [ppm] = 7.59 (t, *J* = 7.7 Hz, 2H), 7.38 (d, *J* = 7.8 Hz, 4H), 7.20 (s, 2H), 4.15 (t, *J* = 1.9 Hz, 2H), 4.06 (s, 5H), 3.99 (t, *J* = 1.8 Hz, 2H), 2.59 (sept., *J* = 6.8 Hz, 4H), 1.37 (d, *J* = 7.0 Hz, 12H), 1.23 (d, *J* = 6.9 Hz, 12H); **¹³C NMR** {¹H} (150 MHz, CD₂Cl₂, 298 K): δ [ppm] = 191.3 (s, NHC), 146.4 (s), 134.9 (s), 131.1 (s), 126.3 (s), 124.7 (s), 123.9 (s), 100.7 (s), 71.5 (s), 70.1 (s), 67.8 (s), 29.3 (s), 24.9 (s), 24.2 (s); **HRMS-FAB** (+) (*m/z*): calcd for C₃₉H₄₅AuFeN₂, 794.2598; found, 794.2586.

IPrAu-tris(perfluorophenyl)(prop-1-yn-1-yl)borate (5)

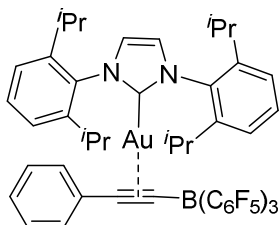


To (Idipp)Au-C≡C-Me (53.5 mg, 0.086 mmol) in CH₂Cl₂ (0.7 mL) was added B(C₆F₅)₃ (43.9 mg, 0.086 mmol) and stirred for 5 min. Slow diffusion of pentane into this solution at -20 °C afforded the product as colorless crystals. Pentane was removed via syringe and the remaining solvent evaporated under reduced pressure to give pure **5** as colorless crystals (73.4 mg, 75 %).

IR (thin film) ν_{\max} = 2966 cm⁻¹, 2875, 1644, 1514, 1456, 1421, 1387, 1367, 1353, 1330, 1275, 1185, 1087, 1062, 1013, 971, 804, 760, 745, 703; **¹H NMR** (500 MHz, CD₂Cl₂, 298 K): δ [ppm] = 7.56 (t, *J* = 7.8 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 4H), 7.26 (s, 2H), 2.49 (sept., *J* = 6.9 Hz, 4H), 1.52 (s, 3H), 1.20 (d, *J* = 6.9 Hz, 12H), 1.19 (d, *J* = 6.9 Hz, 12H); **¹³C NMR** {¹H} (150 MHz, CD₂Cl₂, 298 K): δ [ppm] = 181.5 (s, NHC), 148.4 (dm, *J*_{CF} = 241.9 Hz, C-F), 146.1 (s, NHC), 139.2 (dm, *J*_{CF} = 246.4 Hz, C-F), 137.0 (dm, *J*_{CF} = 248.8 Hz, C-F), 133.8 (s, NHC), 131.7 (s, NHC), 124.8 (s, NHC), 124.8 (s, NHC), 122.0 (brs, C-B), 101.0 (q, *J*_{C-B} = 63.3 Hz, C-B), 98.1 (s), 29.3 (s, NHC), 24.4 (s, NHC), 24.1 (s, NHC), 7.4 (s); **¹⁹F NMR** (470 MHz, CD₂Cl₂, 298 K): δ [ppm] = -132.4 (d, *J*_{FF} = 22.3 Hz, 6F, *o*-C₆F₅), -161.2 (t, *J*_{FF} = 20.6 Hz), -165.85 (m, 6F, *m*-C₆F₅); **¹¹B NMR** (95 MHz, CD₂Cl₂, 298 K): δ [ppm] = -

20.1 (s); **EA** (elemental analysis) calcd (%) for $C_{48}H_{39}AuBF_{15}N_2$: C 50.72, H 3.46, N 2.46%; Obs. C 50.38, H 3.56, N 2.25%; **HRMS-FAB** (+) (m/z): calcd for $[M-C_6F_5]$, $C_{42}H_{39}AuBF_{10}N_2$, 969.2712; found, 969.2722.

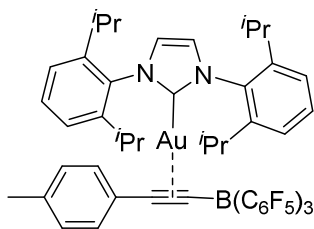
IPrAu- tris(perfluorophenyl)(phenylethynyl)borate (6)



$B(C_6F_5)_3$ (21 mg, 0.041 mmol) in CH_2Cl_2 (2 mL) was added to (Idipp)Au-C \equiv C-Ph (28 mg, 0.041 mmol) in CH_2Cl_2 (2 mL) and stirred overnight yielding a yellow solution. The reaction was then pumped dried in vacuo and the resulting residue dissolved in toluene (8 mL). To this was added hexanes (10 mL) and upon cooling to $-35^\circ C$, x-ray quality yellow crystals were obtained (42 mg, 0.035 mmol, 85% yield).

1H NMR (400 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.54 (t, 2H, Ar, $J_{HH} = 7.7$ Hz), 7.30 (t, 1H, Ar, $J_{HH} = 7.7$ Hz), 7.26-7.19 (m, 6H, Ar), 7.13 (t, 2H, Ar, $J_{HH} = 7.4$ Hz), 6.65 (d, 2H, *o*-Ph acetylene, $J_{HH} = 7.4$ Hz), 2.45 (septet, 4H, CH-*iPr*, $^3J_{HH} = 6.8$ Hz), 1.14 (d, 12H, -CH₃, $^3J_{HH} = 6.8$ Hz), 1.04 (d, 12H, -CH₃, $^3J_{HH} = 6.8$ Hz). **^{11}B NMR** (128 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -19.51 (s). **^{19}F NMR** (376 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -131.75 (d, 2F, *o*-C₆F₅, $^3J_{FF} = 23.3$ Hz), -161.25 (t, 1F, *p*-C₆F₅, $^3J_{FF} = 20.6$ Hz), -165.75 (dt, 2F, *m*-C₆F₅, $t\text{-}^3J_{FF} = 22.9$ Hz, $d\text{-}^3J_{FF} = 6.6$ Hz). **$^{13}C\{^1H\}$ NMR** (101 MHz, CD_2Cl_2 , 298 K, partial): δ [ppm] = 180.09 (s, carbene), 147.77 (br, C₆F₅), 145.35 (s, Ar), 138.90 (br, C₆F₅), 137.19 (br, C₆F₅), 136.31 (br, C₆F₅), 133.22 (s, Ar), 131.50 (s, Ar), 131.06 (s, Ar), 129.63 (s, Ar), 128.70 (s, Ar), 124.33 (s, Ar), 124.26 (s, Ar), 121.56 (s, Ar), 99.70 (alkyne C, found via HMBC), 28.72 (s, *iPr*), 23.79 (s, *iPr*), 23.31 (s, *iPr*). The B-C and some C-F carbons were not observed. **EA** Anal. Calcd. for $C_{53}H_{41}AuBF_{15}N_2$: C, 53.11; H, 3.45; N, 2.34 %. Found: C, 53.50; H, 3.98; N, 2.08 %.

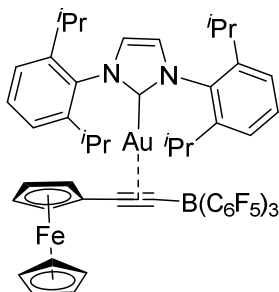
IPrAu-tris(perfluorophenyl)(p-tolylethynyl)borate (7)



$\text{B}(\text{C}_6\text{F}_5)_3$ (37.0 mg, 0.072 mmol) in CH_2Cl_2 (1.0 mL) was added to (Idipp)Au-C \equiv C-tol (50.0 mg, 0.071 mmol) in CH_2Cl_2 (1.0 mL) and stirred for 30 min. Slow diffusion of pentane into this solution at -20°C afforded the product **7** as colorless crystals (63.0 mg, 72 %).

IR (thin film) $\nu_{\text{max}} = 3208.9\text{ cm}^{-1}$, 2968, 1739, 1643, 1603, 1514, 1459, 1387, 1367, 1331, 1278, 1216, 1083, 1062, 977, 932, 888, 820, 805, 758, 703; **^1H NMR** (500 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.53 (t, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 7.7$ Hz, 4H), 7.20 (s, 2H), 6.94 (d, $J = 8.1$ Hz, 2H), 6.58 (d, $J = 8.0$ Hz, 2H), 2.44 (sept., $J = 6.8$ Hz, 4H), 2.36 (s, 3H), 1.14 (d, $J = 6.8$ Hz, 12H), 1.04 (d, $J = 6.8$ Hz, 12H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -131.8 (d, $J_{\text{FF}} = 22.8$ Hz, 6F, *o*- C_6F_5), -161.3 (t, $J_{\text{FF}} = 20.9$ Hz, 3F, *p*- C_6F_5), -165.8 (m, 6F, *m*- C_6F_5); **^{11}B NMR** (95 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -19.5 (s); **^{13}C NMR** { ^1H } (125 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 180.6 (s, NHC), 148.5 (dm, $J_{\text{CF}} = 242.2$ Hz, C-F), 145.9 (s, NHC), 140.9 (s), 139.4 (dm, $J_{\text{CF}} = 246.1$ Hz, C-F), 137.0 (dm, $J_{\text{CF}} = 250.6$ Hz, C-F), 133.8 (s, NHC), 132.1 (s), 131.6 (s, NHC), 130.0 (s), 124.9 (s, NHC), 124.8 (s, NHC), 118.9 (s), 29.3 (s, NHC), 24.4 (s, NHC), 23.9 (s, NHC), 21.8 (s); **EA** (elemental analysis) calcd (%) for $\text{C}_{54}\text{H}_{43}\text{AuBF}_{15}\text{N}_2$: C 53.48, H 3.57, N 2.31%; Obs. C 53.52, H 3.67, N 2.19%; **HRMS-FAB** (+) (m/z): calcd for $[\text{M}-\text{C}_6\text{F}_5]$ $\text{C}_{48}\text{H}_{43}\text{AuBF}_{10}\text{N}_2$, 1045.3025; found, 1045.3019.

IPrAu-tris(perfluorophenyl)(ferrocenylethynyl)borate (8)

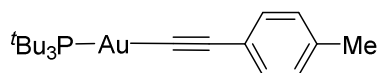


To (Idipp)Au-C \equiv C-ferrocene (31.2 mg, 0.039 mmol) in CH_2Cl_2 (1.5 mL) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (20.1 mg, 0.039 mmol) and stirred for 5 min. Pentane (3 mL) was added and the product precipitated as orange crystals. The solution was stored at -20°C for 1 h followed by removal of the solvent via

syringe and evaporation of the remaining solvent under vacuum afforded the product as orange crystals (43.2 mg, 84%).

IR (thin film) ν_{\max} = 3132.4 cm^{-1} , 2969, 2058, 1643, 1599, 1512, 1460, 1386, 1331, 1278, 1216, 1086, 1063, 1041, 1025, 978, 950, 887, 826, 805, 770, 759, 740; **^1H NMR** (500 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.50 (t, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 4H), 7.19 (s, 2H), 4.08 (t, J = 1.5 Hz, 2H), 3.92 (s, 5H), 3.71 (t, J = 1.5 Hz, 2H), 2.43 (sept., J = 6.8 Hz, 4H), 1.13 (d, J = 6.8 Hz, 12H), 1.07 (d, J = 6.8 Hz, 12H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -131.2 (d, J_{FF} = 21.8 Hz, 6F, *o*- C_6F_5), -161.7 (t, J_{FF} = 20.8 Hz, 3F, *p*- C_6F_5), -165.7 (m, 6F, *m*- C_6F_5); **^{11}B NMR** (95 MHz, CD_2Cl_2 , 298 K): -19.5 (s); **^{13}C NMR** $\{^1\text{H}\}$ (100 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 180.5 (s, NHC), 148.4 (dm, J_{CF} = 243.0 Hz, C-F), 145.8 (s, NHC), 139.3 (dm, J_{CF} = 248.0 Hz, C-F), 137.1 (dm, J_{CF} = 248.0 Hz, C-F), 134.0 (s, NHC), 131.5 (s, NHC), 124.8 (s, NHC), 124.8 (s, NHC), 122.3 (brs., C-B), 102.4 (s), 72.0 (s), 70.2 (s), 70.0 (s), 64.3 (s), 29.3 (s), 24.4 (s), 24.1 (s). One of the C-B could not be observed; **HRMS-FAB** (+) (m/z): calcd for $\text{C}_{57}\text{H}_{46}\text{AuBF}_{15}\text{FeN}_2$, 1307.2529; found, 1307.2557.

Tris-*tert*-butylphosphine (*p*-tolylethynyl)gold (9)

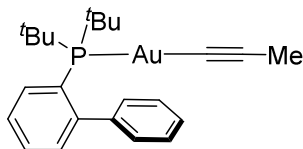


To a solution of 1-ethynyl-4-methylbenzene (105 μL , 0.83 mmol, 1.2 equiv.) in THF (5 mL) was added at -78°C *n*BuLi (330 μL , 0.83 mmol, 2.5 M in hexanes; 1.2 equiv.). The solution was stirred at this temperature for 1 h and then transferred *via* cannula to a solution of $t\text{Bu}_3\text{PAuCl}$ (300.0 mg, 0.69 mmol) dissolved in THF (8 mL) at -78°C . The solution was warmed up and then further stirred for 2 h at room temperature. A saturated solution of NaHCO_3 (5 mL) was added, the phases separated and the aqueous phases extracted with CH_2Cl_2 (2x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The crude material was recrystallized from CH_2Cl_2 /pentane to afford a slightly greenish solid (185 mg, 0.360 mmol, 52%).

IR (thin film) ν_{\max} = 2991.1 cm^{-1} , 2953, 2911, 2870, 2115, 1505, 1481, 1472, 1442, 1392, 1368, 1215, 1202, 1171, 1105, 1024, 932, 811; **^1H NMR** (600 MHz, CDCl_3 , 298 K): δ [ppm] = 7.39 (d, J = 7.7 Hz, 2H), 7.02 (d, J = 7.5 Hz, 2H), 2.29 (s, 3H), 1.52 (d, J_{HP} = 13.3 Hz, 27H); **^{31}P NMR** (243 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 91.4 (s); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CDCl_3 , 298 K): δ [ppm] = 136.4 (s), 134.5 (d, J_{CF} = 127.5 Hz), 132.4 (s), 128.7 (s), 122.2 (s), 103.5 (d, J_{CF} = 23.7 Hz), 39.2 (d, J_{CF} = 17.9 Hz), 32.54 (d, J_{CF} = 3.6 Hz), 21.5 (s); **EA** (elemental analysis) calcd (%) for $\text{C}_{21}\text{H}_{34}\text{AuP}$: C 49.03, H

6.66 %; Obs. C 48.66, H 6.33 %. **HRMS-FAB** (+) (m/z): calcd for $[M+H]^+$ $C_{21}H_{35}AuP$, 515.2142; found, 515.2151.

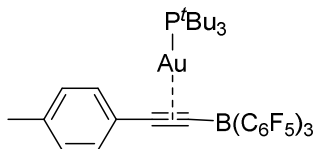
^tBu-JohnPhos (prop-1-yn-1-yl)gold (10)



^tBu-JohnPhosAuCl (600 mg, 1.13 mmol) was dissolved in THF (10 mL) and cooled to -78 °C. 1-Propynylmagnesium bromide (2.71 mL, 1.36 mmol, 0.5 M in THF) was added and the resulting mixture stirred at room temperature for 5 h. The reaction was quenched with aqueous saturated NaHCO₃ solution, extracted three times with CH₂Cl₂ and dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was washed several times with Et₂O to yield the desired complex **10** (490 mg, 917 μmol, 81%).

IR (ATR): ν_{\max} = 3060 cm⁻¹, 2987, 2960, 2910, 2857, 1746, 1573, 1467, 1440, 1430, 1387, 1364, 1238, 1175, 1130, 1083, 1070, 1027, 1008, 989, 961, 939, 906, 840, 812, 774, 754, 697, 617; **¹H NMR** (400 MHz, CD₂Cl₂, 298 K): δ [ppm] = 7.85-7.91 (m, 1 H), 7.38-7.52 (m, 5 H), 7.21-7.26 (m, 1 H), 7.12-7.18 (m, 2 H), 1.77 (d, J = 1.9 Hz, 3 H), 1.39 (s, 9 H), 1.36 (s, 9 H); **¹³C NMR** (100 MHz, CD₂Cl₂): δ [ppm] = 150.67 (d, J_{CP} = 15.3 Hz), 143.02 (d, J_{CP} = 6.1 Hz), 135.11 (d, J_{CP} = 1.1 Hz), 133.36 (d, J_{CP} = 7.4 Hz), 130.52 (d, J_{CP} = 2.2 Hz), 129.68 (s), 129.08 (s), 128.04 (s), 127.92 (d, J_{CP} = 38.6 Hz), 127.02 (d, J_{CP} = 5.9 Hz), 121.88 (d, J_{CP} = 133.0 Hz), 97.03 (d, J_{CP} = 24.0 Hz), 37.78 (d, J_{CP} = 22.2 Hz), 31.22 (s), 31.15 (s), 4.72 (d, J_{CP} = 2.5 Hz); **³¹P NMR** (162 MHz, CD₂Cl₂): δ = 64.47 ppm; **MS** (FAB (+)): m/z = 535 $[M+H]^+$ (48), 534 $[M]^+$ (45), 495 (100); **HRMS-FAB** (+): m/z : calcd. for $[C_{23}H_{30}AuP]^+$, 534.1751; found, 534.1768.

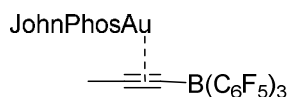
Tris-tertbutylphosphinegold-tris(perfluorophenyl)(p-tolylethynyl)borate (11)



B(C₆F₅)₃ (22.1 mg, 0.043 mmol) was added to ^tBu₃PAu-C≡C-tol (22.2 mg, 0.043 mmol) dissolved in CH₂Cl₂ (0.6 mL) and stirred for 30 min. Slow diffusion of pentane into this solution at -20 °C afforded the product as colorless crystals (35.2 mg, 79 %).

IR (thin film) ν_{\max} = 2953.9 cm^{-1} , 2059, 1642, 1513, 1459, 1396, 1374, 1280, 1170, 1088, 1023, 978, 940, 921, 903, 821, 798, 771, 762, 742; **^1H NMR** (600 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.42 (d, J = 7.6 Hz, 2H), 7.21 (d, J = 7.6 Hz, 2H), 2.377 (s, 3H), 1.32 (d, J_{PH} = 14.3 Hz, 27H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -131.6 (d, J_{FF} = 21.7 Hz, 6F, *o*- C_6F_5), -161.2 (t, J_{FF} = 20.4 Hz, 3F, *p*- C_6F_5), -165.9 (m, 6F, *m*- C_6F_5); **^{31}P NMR** (243 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 96.5 (s); **^{11}B NMR** (96 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -19.5 (s); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 148.7 (dm, J_{CF} = 239.8 Hz), 142.0 (s), 139.7 (dm, J_{CF} = 248.7 Hz), 137.4 (dm, J_{CF} = 248.7 Hz), 132.5 (s), 130.2 (s), 122.1 (brs, C-B), 118.8 (s), 111.4 (q, J_{CB} = 56 Hz, C-B), 104.5 (brs), 40.1 (d, J_{CP} = 18.9 Hz), 32.2 (s), 21.9 (s); **EA** (elemental analysis) calcd (%) for $\text{C}_{39}\text{H}_{34}\text{AuBF}_{15}\text{P}$: C 45.64, H 3.34 %; Obs. C 45.25, H 3.61 %; **HRMS-ESI** (-) (m/z): calcd for $[\text{C}_{27}\text{H}_7\text{BF}_{15}]^-$, 627.0401; found, 627.0401.

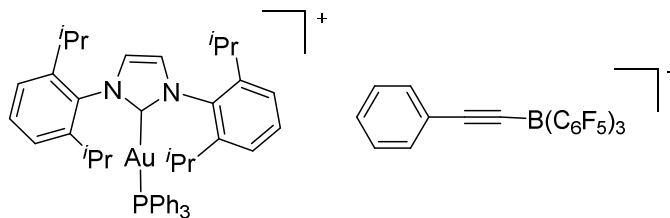
^tBu -JohnPhos gold-tris(perfluorophenyl)(prop-1-yn-1-yl)borate (12)



$\text{B}(\text{C}_6\text{F}_5)_3$ (35.2 mg, 0.069 mmol) was added to ^tBu -JohnPhosAu-C \equiv C-Me (36.7 mg, 0.069 mmol) dissolved in CH_2Cl_2 (0.6 mL) and stirred for 30 min. Slow diffusion of pentane into this solution at -20 $^\circ\text{C}$ afforded the product as colorless crystals (63.0 mg, 88%).

IR (thin film) ν_{\max} = 2970.6 cm^{-1} , 1643, 1514, 1456, 1392, 1370, 1278, 1174, 1087, 1010, 973, 868, 794, 767, 746, 702, 679; **^1H NMR** (600 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.86 (t, J = 7.4 Hz, 1H), 7.57-7.50 (m, 2H), 7.40-7.36 (m, 1H), 7.33-7.29 (m, 2H), 7.22-7.18 (m, 1H), 7.05 (d, J = 7.4 Hz, 2H), 2.02 (s, 3H), 1.28 (d, J = 16.1 Hz, 18H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -131.4 (d, J_{FF} = 22.0 Hz, 6F, *o*- C_6F_5), -161.5 (t, J_{FF} = 20.0 Hz, 3F, *p*- C_6F_5), -166.2 (m, 6F, *p*- C_6F_5); **^{31}P NMR** (243 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 63.9 (s); **^{11}B NMR** (96 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -19.8 (s); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 149.8 (d, J_{CP} = 12.9 Hz), 148.6 (dm, J_{CF} = 240.5 Hz), 142.8 (d, J_{CP} = 6.3 Hz), 139.5 (dm, J_{CF} = 247.4 Hz), 137.3 (dm, J_{CF} = 245.5 Hz), 134.5 (d, J_{CP} = 3.0 Hz), 134.2 (d, J_{CP} = 7.8 Hz), 131.7 (d, J_{CP} = 2.1 Hz), 130.0 (s), 129.3 (s), 128.4 (s), 127.9 (d, J_{CP} = 7.0 Hz), 124.5 (d, J_{CP} = 45.4 Hz), 122.0 (brs, C-B), 106.1 (q, J = 60.9 Hz, C-B), 101.3 (brs), 38.7 (d, J_{CP} = 23.9 Hz), 31.0 (d, J_{CP} = 6.6 Hz), 9.33 (s); **EA** (elemental analysis) calcd (%) for $\text{C}_{41}\text{H}_{30}\text{AuBF}_{15}\text{P}$: C 47.06, H 2.89 %; Obs. C 46.76, H 2.99 %; **HRMS-ESI** (-) (m/z): calcd for $[\text{C}_{21}\text{H}_3\text{BF}_{15}]^-$, 551.0088; found, 551.0086.

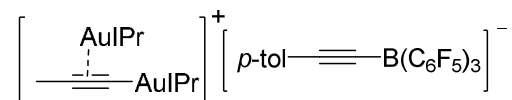
Compound [IPrAuPPh₃][Ph-C≡C-B(C₆F₅)₃] (13)



(Idipp)Au-[Ph-C≡C-B(C₆F₅)₃] (25 mg, 0.021 mmol) in CH₂Cl₂ (2 mL) was added to PPh₃ (5.5 mg, 0.021 mmol) in CH₂Cl₂ (2 mL) and stirred overnight going from yellow to colorless. To the resulting solution was then added hexanes (10 mL) and upon cooling to -35°C, x-ray quality white crystals were obtained (28 mg, 0.019 mmol, 90% yield).

¹H NMR (400 MHz, CD₂Cl₂, 298 K): δ [ppm] = 7.66-7.58 (m, 2H, Ar), 7.53-7.46 (m, 2H, Ar), 7.43-7.28 (m, 13H, Ar), 7.20-7.09 (m, 2H, Ar), 7.05-6.96 (m, 4H, Ar), 2.56 (sept., 4H, CH-*i*Pr, ³J_{HH} = 6.6 Hz), 1.26 (d, 12H, -CH₃, ³J_{HH} = 6.6 Hz), 1.19 (d, 12H, -CH₃, ³J_{HH} = 6.6 Hz). **¹³C NMR** (128 MHz, CD₂Cl₂, 298 K): δ [ppm] = -20.87 (s). **¹⁹F NMR** (376 MHz, CD₂Cl₂, 298 K): δ [ppm] = -132.67 (d, 2F, *o*-C₆F₅, ³J_{FF} = 23.9 Hz), -163.92 (t, 1F, *p*-C₆F₅, ³J_{FF} = 20.3 Hz), -167.38 (t, 2F, *m*-C₆F₅, ³J_{FF} = 21.7 Hz). **³¹P{¹H} NMR** (162 MHz, CD₂Cl₂, 298 K): δ [ppm] = 39.91 (s, PPh₃). **¹³C{¹H} NMR** (101 MHz, CD₂Cl₂, 298 K, partial): δ [ppm] = 189.32 (s, carbene), 146.25 (s, Ar), 134.05 (d, Ar, J_{PC} = 13.8 Hz), 133.50 (s, Ar), 132.62 (d, Ar, J_{PC} = 2.6 Hz), 131.66 (s, Ar), 131.50 (s, Ar), 129.80 (d, Ar, J_{PC} = 11.7 Hz), 128.17 (s, Ar), 128.12 (s, Ar), 127.58 (s, Ar), 126.02 (s, Ar), 125.00 (s, Ar), 124.98 (d, Ar, J_{PC} = 3.4 Hz), 68.14 (s, alkyne), 29.30 (s, *i*Pr), 24.86 (s, *i*Pr), 24.04 (s, *i*Pr). Anal. Calcd. for C₇₁H₅₆AuBF₁₅N₂P: C, 58.37; H, 3.86; N, 1.92 %. Found: C, 58.44; H, 4.02; N, 2.08 %.

Compound (14)

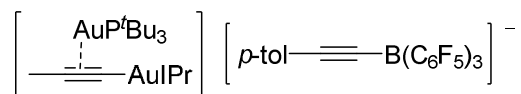


To a solution of (Idipp)Au-C≡C-*p*tol (34.3 mg, 0.047 mmol) in C₆D₆ (1 mL) was added B(C₆F₅)₃ (24.2 mg, 0.047 mmol). The solution was stirred for 10 min at room temperature and then (Idipp)Au-C≡C-Me (30.5 mg, 0.047 mmol) added. The solution was layered with pentane to afford the desired product as colorless solid (63.2 mg, 72%).

IR (thin film) ν_{max} = 2965.3 cm⁻¹, 2929, 2872, 1642, 1595, 1555, 1510, 1459, 1419, 1386, 1366, 1329, 1273, 1215, 1182, 1087, 975, 951, 803; **¹H NMR** (500 MHz, C₆D₆, 298 K): δ [ppm] = 7.57 (d, *J* = 8.0

Hz, 2H), 7.24 (t, $J = 7.8$ Hz, 4H), 7.01 (d, $J = 7.5$ Hz, 8H), 6.77 (d, $J = 7.8$ Hz, 2H), 6.46 (s, 4H), 2.36 (sept., $J = 6.9$ Hz, 8H), 2.05 (s, 3H), 1.08 (d, $J = 6.9$ Hz, 24H), 1.06 (d, $J = 6.9$ Hz, 24H); **^{19}F NMR** (470 MHz, C_6D_6 , 298 K): δ [ppm] = -131.1 (d, $J_{\text{FF}} = 21.7$ Hz, 6F, *o*- C_6F_5), -163.8 (t, $J_{\text{FF}} = 20.9$ Hz, 3F, *p*- C_6F_5), -166.9 (m, 6F, *m*- C_6F_5); **^{11}B NMR** (160 MHz, C_6D_6 , 298 K): δ [ppm] = -19.9 (s); **^{13}C NMR** $\{^1\text{H}\}$ (100 MHz, C_6D_6 , 298 K): δ [ppm] = 183.0 (s), 149.4 (dm, $J_{\text{CF}} = 239$ Hz), 145.6 (s), 138.9 (dm, $J_{\text{CF}} = 250$ Hz), 137.3 (dm, $J_{\text{CF}} = 245$ Hz), 133.9 (s), 132.0 (s), 131.2 (s), 128.8 (s), 128.4 (s), 128.0 (s), 124.5 (s), 123.9 (s), 115.1 (s), 110.8 (s), 28.9 (s), 24.7 (s), 23.6 (s), 21.3 (s), 6.2 (s). Carbons attached to boron could not be observed; **EA** (elemental analysis) calcd (%) for $\text{C}_{84}\text{H}_{82}\text{Au}_2\text{BF}_{15}\text{N}_4$: C 54.91, H 4.50 %, N 3.05 Obs. C 54.43, H 4.64, N 2.84 %; **HRMS-ESI** (+) (m/z): calcd for $[\text{C}_{57}\text{H}_{75}\text{Au}_2\text{N}_4]^+$, 1209.5323; found, 1209.5333; **HRMS-ESI** (-) (m/z): calcd for $[\text{C}_{27}\text{H}_7\text{BF}_{15}]^-$, 627.0401; found, 627.0399.

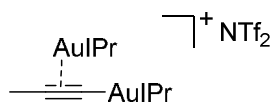
Compound (15)



To a solution of $t\text{Bu}_3\text{PAu-C}\equiv\text{C-ptol}$ (19.2 mg, 0.037 mmol) in CD_2Cl_2 (0.6 mL) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (19.1 mg, 0.037 mmol). The solution was stirred for 10 min at room temperature and then (Idipp)Au-C \equiv C-Me (24.0 mg, 0.037 mmol) added. The solution was concentrated under reduced pressure and layered with pentane to afford the desired product as colorless solid (45.6 mg, 73%).

IR (thin film) $\nu_{\text{max}} = 2965.0\text{ cm}^{-1}$, 2928, 2873, 1643, 1510, 1460, 1366, 1329, 1273, 1173, 1087, 1075, 804 759, 744; **^1H NMR** (500 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 7.54 (t, $J = 7.7$ Hz, 2H), 7.33 (d, $J = 7.7$ Hz, 4H), 7.25 (s, 2H), 7.19 (d, $J = 7.7$ Hz, 2H), 7.00 (d, $J = 7.7$ Hz, 2H), 2.54 (sept., $J = 6.9$ Hz, 4H), 2.28 (s, 3H), 2.14 (s, 3H), 1.36 (d, $J_{\text{PH}} = 14.3$ Hz, 27H), 1.30 (d, $J = 6.8$ Hz, 12H), 1.23 (d, $J = 6.8$ Hz, 12H); **^{19}F NMR** (282 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -132.6 (d, $J_{\text{FF}} = 24.0$ Hz, 6F, *o*- C_6F_5), -164.0 (t, $J_{\text{FF}} = 20.1$ Hz, 3F, *p*- C_6F_5), -167.4 (m, 6F, *m*- C_6F_5); **^{11}B NMR** (96 MHz, CD_2Cl_2 , 298 K): δ [ppm] = -20.8 (s); **^{31}P NMR** (121 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 93.6 (s); **^{13}C NMR** $\{^1\text{H}\}$ (100 MHz, CD_2Cl_2 , 298 K): δ [ppm] = 183.7 (d, $J = 109$ Hz), 148.9 (dm, $J_{\text{CF}} = 241$ Hz), 146.3 (s), 138.8 (dm, $J = 240$ Hz), 137.1 (dm, $J = 225$ Hz), 136.0 (s), 134.3 (s), 131.5 (s), 131.4 (s), 129.1 (s), 124.9 (s), 124.8 (s), 124.7 (s), 40.0 (d, $J_{\text{CP}} = 19$ Hz), 32.6 (d, $J_{\text{CP}} = 4$ Hz), 29.4 (s), 25.2 (s), 24.1 (s), 21.6 (s), 7.4 (s). Carbons attached to boron could not be observed; **HRMS-ESI** (+) (m/z): calcd for $[\text{C}_{42}\text{H}_{66}\text{Au}_2\text{N}_2\text{P}]^+$, 1023.4295; found, 1023.4283; **HRMS-ESI** (-) (m/z): calcd for $[\text{C}_{27}\text{H}_7\text{BF}_{15}]^-$, 627.0401; found, 627.0400.

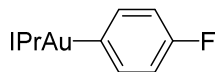
Compound (16)



According to the literature procedure,^[3] (Idipp)AuCl (249 mg, 0.400 mmol) was dissolved in CH₂Cl₂ (10 mL) and AgNTf₂ (155 mg, 0.400 mmol) added. The solution was stirred for 30 min in the dark and then (Idipp)Au-C≡C-Me (250 mg, 0.400 mmol) added. The solution was stirred for an additional 1 h, then filtered through Celite with CH₂Cl₂, the solvent removed under reduced pressure and the remaining solid recrystallized from CH₂Cl₂/pentane to give a colorless solid (260.6mg, 54%). The spectral data is in accordance with the literature reports.^[3]

¹H NMR (400 MHz, CDCl₃, 298 K): δ [ppm] = 7.50 (t, *J* = 7.7 Hz, 4H), 7.24 (d, *J* = 7.8 Hz, 8H), 7.22 (s, 4H), 2.43 (sept., *J* = 6.8 Hz, 8H), 1.62 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 24H), 1.09 (d, *J* = 6.9 Hz, 24H); **¹⁹F NMR** (283 MHz, CDCl₃, 298 K): δ [ppm] = -78.7 (s); **¹³C NMR** {¹H} (100 MHz, CDCl₃, 298 K): δ [ppm] = 183.0 (s), 145.6 (s), 133.8 (s), 130.9 (s), 124.4 (s), 124.2 (s), 121.8 (s), 118.6 (s), 115.1 (s), 110.3 (s), 28.8 (s), 24.7 (s), 24.0 (s), 6.9 (s).

(1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)(4-fluorophenyl)gold (17)

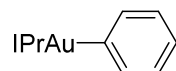


According to the literature procedure,⁴ (Idipp)AuCl (200 mg, 0.322 mmol), 4-fluorophenyl boronic acid (45.1 mg, 0.322 mmol), powdered KOH (36.1 mg, 0.644 mmol, 2.0 equiv.) were dispensed in toluene (3.2 mL). The dark solution was stirred at room temperature for 6 h. The solution was filtered through Celite with toluene and the solvent evaporated. The remaining solid was recrystallized from CH₂Cl₂/pentane to give the desired compound **17** as colorless solid (145 mg, 97%).

IR (thin film) ν_{max} = 3126.1 cm⁻¹, 2968, 2963, 2927, 2868, 1571, 1477, 1414, 1385, 1365, 1349, 1328, 1257, 1207, 1180, 1156, 1104, 1075, 1060, 1019, 973, 939, 804, 760; **¹H NMR** (600 MHz, CDCl₃, 298 K): 7.47 (t, *J* = 7.8 Hz, 2H), 7.28 (d, *J* = 7.7 Hz, 4H), 7.15 (s, 2H), 7.01 (m, 2H), 6.73 (m, 2H), 2.66 (sept., *J* = 6.9 Hz, 4H), 1.39 (d, *J* = 6.9 Hz, 12H), 1.24 (d, *J* = 6.9 Hz, 12H); **¹⁹F NMR** (243 MHz, CD₂Cl₂, 298 K): -119.1 (s); **¹³C NMR** {¹H} (150 MHz, CDCl₃, 298 K): 196.6 (s), 164.3 (s), 161.0 (d, *J*_{CF} = 241 Hz), 145.9 (s), 140.9 (s), 134.7 (s), 130.3 (s), 124.1 (s), 122.9 (s), 113.5 (d, *J*_{CF} = 17.1 Hz), 28.9 (s), 24.7 (s), 24.1 (s); **EA** (elemental analysis) calcd (%) for C₃₃H₄₀AuFN₂: C 58.23, H5.92, N

4.12 %; Obs. C 58.12, H 5.99, N 3.98 %; **HRMS-ESI** (+) (m/z): calcd for $[M+H]^+$ $C_{33}H_{41}AuFN_2$, 681.2919; found, 681.2926.

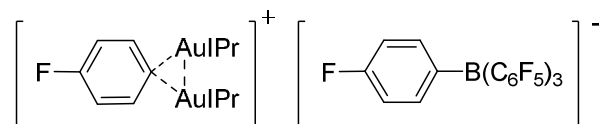
(1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)phenylgold (18)



To a solution of (Idipp)AuCl (502 mg, 0.808 mmol) in THF (15 mL) was added at -78°C phenyl lithium (493 μL , 0.887 mmol, 1.8M in Bu_2O). The solution was stirred at this temperature for 2 h, then stirred an additional 1 h at room temperature. A saturated aqueous solution of NaHCO_3 (5 mL) was added, the phases separated and the aqueous phase extracted with CH_2Cl_2 (10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The remaining solid was dissolved in CH_2Cl_2 and filtered through a pad of basic aluminium oxide. Recrystallization from CH_2Cl_2 /pentane afforded the desired compound as white solid (453 mg, 85%).

IR (thin film) $\nu_{\text{max}} = 3154.5\text{ cm}^{-1}$, 3126, 3051, 2963, 2927, 2868, 1594, 1572, 1554, 1471, 1412, 1384, 1364, 1347, 1330, 1273, 1256, 1214, 1181, 1119, 1106, 1083, 1060, 1025, 947; **^1H NMR** (400 MHz, CDCl_3 , 298 K): 7.46 (t, $J = 7.8\text{ Hz}$, 2H), 7.28 (d, $J = 7.8\text{ Hz}$, 4H), 7.14 (s, 2H), 7.09-7.05 (m, 2H), 7.02-6.97 (m, 2H), 6.85-6.80 (m, 1H), 2.68 (sept., $J = 6.9\text{ Hz}$, 4H), 1.41 (d, $J = 7.0\text{ Hz}$, 12H), 1.24 (d, $J = 7.0\text{ Hz}$, 12H); **^{13}C NMR** $\{^1\text{H}\}$ (100 MHz, CDCl_3 , 298 K): 197.3 (s), 169.9 (s), 145.9 (s), 140.7 (s), 134.8 (s), 130.3 (s), 126.8 (s), 124.3 (s), 124.1 (s), 122.9 (s), 28.9 (s), 24.6 (s), 24.1 (s); **HRMS-FAB** (+) (m/z): calcd for $[M+H]^+$ $C_{33}H_{42}N_2Au$, 663.3014; found, 663.3026.

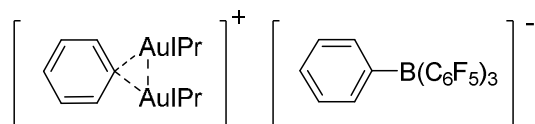
Compound (19)



To a solution of (Idipp)(4-fluorophenyl)gold (**17**) (34.3 mg, 0.050 mmol) in CH_2Cl_2 (0.7 mL) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (12.9 mg, 0.025 mmol) and stirred for 7 h at room temperature. The solvent was removed under reduced pressure, pentane (1 mL) added and the pentane removed under reduced vacuum to afford the desired compound **19** as colorless solid (44.9 mg, 95%).

IR (thin film) ν_{\max} = 2966.2 cm^{-1} , 2873, 1642, 1590, 1573, 1511, 1458, 1419, 1386, 1365, 1329, 1272, 1220, 1183, 1160, 1082, 1018, 976, 880, 804, 756; **^1H NMR** (600 MHz, CD_2Cl_2 , 298 K): 7.49 (t, J = 7.7 Hz, 4H), 7.24 (m, 2H), 7.20 (d, J = 7.8 Hz, 8H), 7.16 (s, 4H), 6.72 (m, 2H), 6.56 (m, 2H), 6.41 (m, 2H), 2.31 (sept., J = 6.8 Hz, 8H), 1.10 (d, J = 6.8 Hz, 24H), 0.85 (d, J = 6.8 Hz, 24H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): -104.8 (s, 1F), -122.4 (s, 1F), -130.5 (d, J = 21.1 Hz, *o*- C_6F_5 , 6F), -164.6 (t, J = 20.2 Hz, *p*- C_6F_5 , 4F), -167.4 (m, *m*- C_6F_5 , 6F); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298 K): 184.6 (s), 167.3 (d, J_{CF} = 255 Hz), 160.9 (d, J_{CF} = 239 Hz), 149.3 (d, J_{CF} = 8.2 Hz), 148.4 (dm, J = 242 Hz), 146.0 (s), 138.6 (dm, J_{CF} = 230 Hz), 137.1 (dm, J_{CF} = 242 Hz), 134.5 (d, J_{CF} = 6.2 Hz), 134.2 (s), 131.1 (s), 124.7 (s), 124.3 (s), 115.3 (d, J_{CF} = 19.9 Hz), 112.6 (d, J_{CF} = 19.0 Hz), 29.1 (s), 24.4 (s), 24.2 (s); C-atoms attached to boron and the *gem*-diaurated fragment could not be observed; **HRMS-ESI (+)** (m/z): calcd for $[\text{C}_{60}\text{H}_{76}\text{Au}_2\text{FN}_4]^+$, 1265.5385; found, 1265.5367; **HRMS-ESI (-)** (m/z): calcd for $[\text{C}_{24}\text{H}_4\text{BF}_{16}]^-$, 607.0151; found, 607.0145.

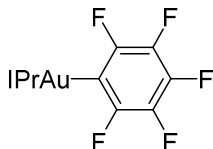
Compound (20)



To a solution of (Idipp)AuPh (39.6 mg, 0.060 mmol) in CD_2Cl_2 (0.7 mL) was added $\text{B}(\text{C}_6\text{F}_5)_3$ (15.3 mg, 0.030 mmol). The solution was stirred for 4 h, the solvent removed under reduced pressure, pentane (1 mL) added and the pentane removed under reduced vacuum to afford the desired compound **20** as colorless solid (34.8 mg, 63%).

IR (thin film) ν_{\max} = 2965.6 cm^{-1} , 2872, 1643, 1511, 1456, 1420, 1386, 1365, 1329, 1272, 1215, 1181, 1085, 975, 802, 757; **^1H NMR** (500 MHz, CD_2Cl_2 , 298 K): 7.49 (t, J = 7.7 Hz, 4H), 7.35-7.29 (m, 2H), 7.20 (d, J = 7.9 Hz, 8H), 7.15 (s, 4H), 7.03-6.99 (m, 3H), 6.94-6.90 (m, 1H), 6.81 (t, J = 7.5 Hz, 2H), 6.41 (d, J = 7.8 Hz, 2H), 2.33 (sept., J = 6.9 Hz, 8H), 1.10 (d, J = 6.8 Hz, 24H), 0.85 (d, J = 6.8 Hz, 24H); **^{19}F NMR** (283 MHz, CD_2Cl_2 , 298 K): -130.2 (d, J_{FF} = 21 Hz, 6F, *o*- C_6F_5), -164.7 (t, J_{FF} = 20.6 Hz, 3F, *p*- C_6F_5), 167.4 (m, 6F, *m*- C_6F_5); **^{11}B NMR** (96 MHz, CD_2Cl_2 , 298 K): -12.8 (s); **^{13}C NMR** $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298 K): 185.2 (s), 148.5 (dm, J_{CF} = 234 Hz), 147.4 (s), 146.0 (s), 138.4 (dm, J_{CF} = 240 Hz), 136.9 (dm, J_{CF} = 249 Hz), 136.3 (s), 134.3 (s), 133.9 (s), 133.4 (s), 131.1 (s), 127.6 (s), 126.2 (s), 124.7 (s), 124.2 (s), 123.7 (s), 29.1 (s), 24.4 (s), 24.2 (s). Some carbons attached to boron could not be observed; **HRMS-ESI (+)** (m/z): calcd for $[\text{C}_{60}\text{H}_{77}\text{Au}_2\text{N}_4]^+$, 1247.5479; found, 1247.5463; **HRMS-ESI (-)** (m/z): calcd for $[\text{C}_{24}\text{H}_5\text{BF}_{15}]^-$, 589.0245; found, 589.0242.

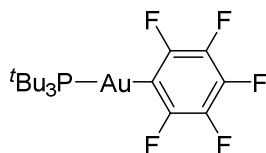
(1,3-bis(2,6-diisopropylphenyl)-1,3-dihydro-2H-imidazol-2-ylidene)(pentafluorophenyl)gold (21)



To a suspension of Mg turnings (150 mg, 6.17 mmol) in THF (10 mL) was added bromopentafluorobenzene (770 μ L, 6.17 mmol). Upon completion of the exothermic reaction the slightly greyish solution was stirred for an additional 1 h at room temperature. In a separate flask (Idipp)AuCl (250 mg, 0.40 mmol) was dissolved in THF (5 mL) and cooled to -78°C . To this was added 780 μ L of the freshly prepared Grignard solution. The solution was warmed up to room temperature and stirred for 2 h at room temperature. A saturated aqueous solution of NaHCO_3 (5 mL) was added, the phases separated and the organic phase extracted with CH_2Cl_2 (2x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The desired compound was recrystallized from CH_2Cl_2 /pentane to give a light sensitive/temperature sensitive greyish solid (145 mg, 0.19 mmol, 48%).

IR (thin film) $\nu_{\text{max}} = 3156.2\text{ cm}^{-1}$, 3129, 2962, 2931, 2873, 1555, 1500, 1469, 1451, 1436, 1419, 1386, 1366, 1354, 1331, 1256, 1216, 1182, 1102, 1061, 1051, 952, 807. **^1H NMR** (500 MHz, CDCl_3 , 298 K): 7.49 (t, $J = 7.6$ Hz, 2H), 7.29 (d, $J = 7.6$ Hz, 4H), 7.20 (s, 2H), 2.62 (sept., $J = 6.8$ Hz, 4H), 1.36 (d, $J = 6.7$ Hz, 12H), 1.24 (d, $J = 6.7$ Hz, 12H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): -116.2 (m, 2F, *o*- C_6F_5), -161.2 (t, $J_{\text{FF}} = 20.1$ Hz, 1F, *p*- C_6F_5), -163.9 (m, 2F, *m*- C_6F_5); **^{13}C NMR** $\{^1\text{H}\}$ (125 MHz, CDCl_3 , 298 K): 192.1 (s), 145.9 (s), 134.2 (s), 130.6 (s), 124.1 (s), 123.1 (s), 29.0 (s), 24.5 (s), 24.2 (s). Some carbon attached to fluorine could not be observed; **HRMS-FAB** (+) (m/z): calcd for $\text{C}_{33}\text{H}_{36}\text{AuF}_5\text{N}_2$, 752.2464; found, 752.2439.

(tris-terbutylphosphine)(pentafluorophenyl)gold (22)

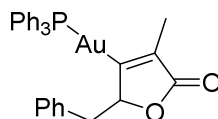


To a suspension of Mg turnings (150 mg, 6.17 mmol) in THF (10 mL) was added bromopentafluorobenzene (770 μ L, 6.17 mmol). Upon completion of the exothermic reaction the slightly greyish

solution was stirred for an additional 1 h at room temperature. In a separate flask $t\text{Bu}_3\text{PAuCl}$ (100 mg, 0.23 mmol) was dissolved in THF (5 mL) and cooled to $-78\text{ }^\circ\text{C}$. To this was added 445 μL of the freshly prepared Grignard solution. The solution was warmed up to room temperature and stirred for 2 h at room temperature. A saturated aqueous solution of NaHCO_3 (5 mL) was added, the phases separated and the organic phase extracted with CH_2Cl_2 (2x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. The desired compound was recrystallized from CH_2Cl_2 /pentane to give a colorless solid (112 mg, 0.20 mmol, 88%).

IR (thin film) $\nu_{\text{max}} = 3002.8\text{ cm}^{-1}$, 2952, 1636, 1501, 1483, 1452, 1435, 1394, 1370, 1352, 1257, 1172, 1072, 1061, 1052, 1024, 950; **^1H NMR** (600 MHz, CDCl_3 , 298 K): 1.56 (d, $J_{\text{HP}} = 13.3\text{ Hz}$, 27H); **^{19}F NMR** (470 MHz, CD_2Cl_2 , 298 K): -116.7 (m, 2F), -159.4 (t, $J_{\text{FF}} = 20.0\text{ Hz}$, 1F), -162.6 (m, 2F); **^{31}P NMR** (243 MHz, CD_2Cl_2 , 298 K): 92.0 (m); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298 K): 148.6 (ddm, $J_{\text{CF}} = 225.9\text{ Hz}$, $J_{\text{CP}} = 23.6\text{ Hz}$), 139.7 (m), 139.1 (m), 137.3 (dm, $J_{\text{CF}} = 245.0$), 39.5 (d, $J_{\text{CP}} = 17.0\text{ Hz}$), 32.6 ($J_{\text{CP}} = 4.1\text{ Hz}$); **EA** (elemental analysis) calcd (%) for $\text{C}_{18}\text{H}_{27}\text{AuF}_5\text{P}$: C 38.17, H 4.81 %; Obs. C 38.56, H 4.78 %; **HRMS-ESI** (+) (m/z): calcd for $[\text{M}-\text{C}_6\text{F}_5+\text{P}(t\text{Bu})_3]^+ \text{C}_{24}\text{H}_{54}\text{AuP}_2$ 601.3366; found, 601.3365.

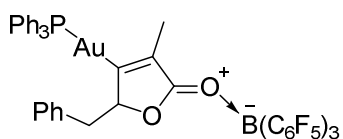
Compound (24)



The compound was prepared according to the literature procedure.^[5] The spectral data is in accordance with the reported data.^[5]

^1H NMR (500 MHz, CD_2Cl_2 , 298 K): 7.57-7.52 (m, 3H), 7.52-7.43 (m, 12H), 7.29 (d, $J = 7.1\text{ Hz}$, 2H), 7.10-7.06 (m, 2H), 7.02-6.98 (m, 1H), 5.16 (t, $J = 6.8\text{ Hz}$, 1H), 3.06 (dd, $J = 13.8\text{ Hz}$, 6.9 Hz, 1H), 3.00 (dd, $J = 13.8\text{ Hz}$, 6.9 Hz, 1H), 1.94 (s, 3H); **^{13}C NMR** $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298 K): 200.0 (d, $J = 113\text{ Hz}$), 176.4 (d, $J = 10\text{ Hz}$), 138.7 (s), 134.8 (d, $J = 14\text{ Hz}$), 132.6 (d, $J = 2\text{ Hz}$), 132.1 (d, $J = 2\text{ Hz}$), 130.7 (d, $J = 52\text{ Hz}$), 129.7 (d, $J = 11\text{ Hz}$), 129.4 (d, $J = 235\text{ Hz}$), 126.8 (s), 91.2 (d, $J = 8\text{ Hz}$), 41.7 (s), 14.7 (s); **^{31}P NMR** $\{^1\text{H}\}$ (202 MHz, CD_2Cl_2 , 298 K): 43.7 (s).

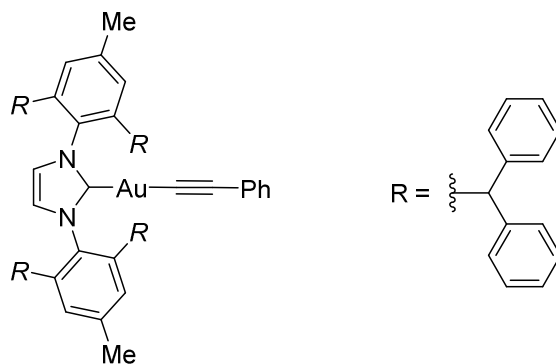
Compound (25)



To a solution of vinyl gold compound **24** (15.7 mg, 0.024 mmol) in CD₂Cl₂ (0.6 mL) was added B(C₆F₅)₃ (12.4 mg, 0.024 mmol) and stirred for 15 min. The solvent was removed under reduced pressure, pentane (0.5 mL) added and the pentane removed under reduced vacuum to afford the desired compound **25** as colorless solid (26.3 mg, 94%). Crystals suitable for X-ray diffraction were obtained by slow diffusion of pentane into a saturated solution of **25** in CH₂Cl₂ at -20°C.

IR (thin film) ν_{\max} = 1648 cm⁻¹, 1608, 1518, 1466, 1439, 1381, 1286, 1179, 1101, 977, 956, 863, 798, 774, 747, 712, 692; **¹H NMR** (500 MHz, CD₂Cl₂, 298 K): 7.60-7.55 (m, 3H), 7.53-7.48 (m, 6H), 7.45-7.39 (m, 6H), 7.06-7.00 (m, 5H), 5.66 (t, *J* = 7.06 Hz, 1H), 2.95 (d, *J* = 7.4 Hz, 2H), 2.12 (s, 3H); **¹⁹F NMR** (470 MHz, CD₂Cl₂, 298 K): -135.2 (d, *J*_{CF} = 21.4 Hz, 6F, *o*-C₆F₅), -159.5 (t, *J*_{CF} = 20.2 Hz, 3F, *p*-C₆F₅), -165.6 (m, 6F, *m*-C₆F₅); **³¹P NMR** (202 MHz, CD₂Cl₂, 298 K): 42.53 (s); **¹¹B NMR** (160 MHz, CD₂Cl₂, 298 K): -0.53 (brs.); **¹³C NMR** {¹H} (100 MHz, CD₂Cl₂, 298 K): 216.3 (d, *J* = 111 Hz), 183.8 (d, *J* = 10 Hz), 148.5 (dm, *J*_{CF} = 243 Hz), 140.1 (dm, *J*_{CF} = 247 Hz), 137.3 (dm, *J*_{CF} = 249 Hz), 136.2 (s), 134.8 (d, *J* = 14 Hz), 132.6 (d, *J* = 2 Hz), 132.4 (d, *J* = 2 Hz), 129.9 (d, *J* = 12 Hz), 129.8 (d, *J* = 54 Hz), 129.2 (d, *J* = 58 Hz), 127.6 (s), 119.0 (brs, C-B), 102.4 (s), 39.3 (s), 13.4 (s); **HRMS-FAB** (+) (*m/z*): calcd for [M-C₆F₅]⁺ C₄₂H₂₆AuBF₁₀O₂P, 991.1269; found, 991.1292.

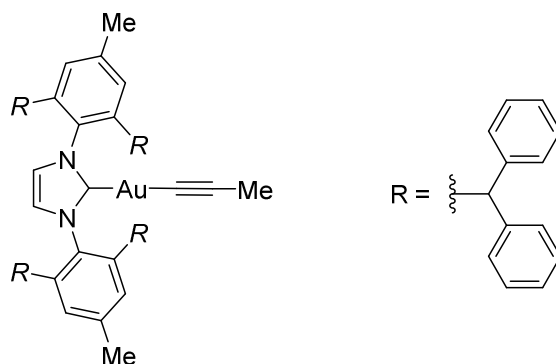
IPr*Au-CCPh (**26**)



To a solution of phenylacetylene (43.1 μ L, 0.392 mmol, 1.5 eq.) in THF (5 mL) was added at -78°C *n*BuLi (160 μ L, 0.400 mmol, 2.5 M in hexane, 1.5 eq.) and stirred for 1 h. To this solution was added at once IPr*AuCl (300 mg, 0.262 mmol, 1 eq.) as solid at -78 °C and the solution was warmed up to room temperature over 2 h. The solution was further stirred for 12 h and then aqueous sat. NaHCO₃ (3 mL) added. The aqueous phase was extracted with THF (2 x 15 mL), the combined organic phases dried over MgSO₄, filtered and the solvent removed under reduced pressure. The crude material was recrystallized from CH₂Cl₂/pentane to give the desired compound as white solid (254 mg, 80%).

IR (thin film) ν_{\max} = 3059.2 cm^{-1} , 3026, 2960, 2117, 1598, 1493, 1471, 1446, 1413, 1369, 1340, 1262, 1217, 1155, 1077, 1030, 945, 916, 884, 856, 806, 759; **^1H NMR** (500 MHz, CDCl_3 , 298 K): 7.48 (d, J = 7.8 Hz, 2H), 7.32-7.21 (m, 18H), 7.21-7.14 (m, 17H), 6.96 (s, 4H), 6.90-6.87 (m, 8H), 5.79 (s, 2H), 5.38 (s, 4H), 2.28 (s, 6H); **^{13}C NMR** $\{^1\text{H}\}$ (125 MHz, CDCl_3 , 298 K): 190.9 (s), 143.3 (s), 143.3 (s), 141.6 (s), 140.8 (s), 134.5 (s), 132.5 (s), 130.7 (s), 130.5 (s), 130.4 (s), 129.8 (s), 129.0 (s), 128.9 (s), 128.5 (s), 127.5 (s), 127.2 (s), 127.1 (s), 126.3 (s), 123.9 (s), 104.2 (s), 51.8 (s), 22.1 (s); **HRMS-FAB** (+) (m/z): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{77}\text{H}_{62}\text{AuN}_2$, 1211.4579; found, 1211.4576.

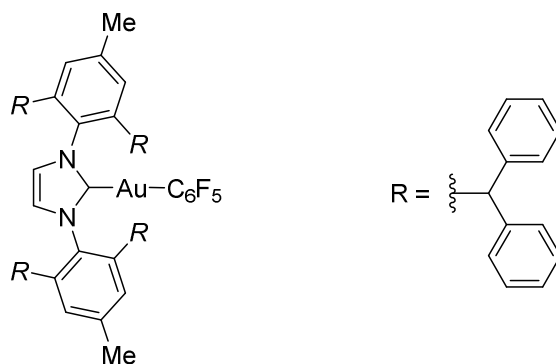
IPr*Au-C \equiv C-Me (27)



To a solution of IPr*AuCl (350 mg, 0.306 mmol) in THF (5 mL) was added at $-78\text{ }^{\circ}\text{C}$ 1-propynyl-magnesium bromide (1.24 mL, 0.620 mmol, 2.0 eq., 0.5 M in THF), stirred for 2 h and then warmed up to room temperature and stirred for additional 12 h. Aqueous saturated NaHCO_3 solution (5 mL) was added and the aqueous phase extracted with CH_2Cl_2 (3 x 10 mL). The combined organic phases were dried over MgSO_4 , filtered and the solvent removed under reduced pressure. Recrystallization from CH_2Cl_2 /pentane affords the product as white solid (318 mg, 90%).

IR (thin film) ν_{\max} = 3060 cm^{-1} , 3026, 2906, 1600, 1493, 1471, 1447, 1414, 1372, 1341, 1288, 1261, 1220, 1183, 1154, 1078, 1031, 1003, 953, 916, 884, 854, 832, 786; **^1H NMR** (400 MHz, CDCl_3 , 298 K): 7.29-7.13 (m, 34H), 6.93 (s, 4H), 6.89-6.84 (m, 8H), 5.72 (m, 2H), 5.37 (m, 4H), 2.27 (m, 6H), 2.01 (m, 3H); **^{13}C NMR** $\{^1\text{H}\}$ (100 MHz, CDCl_3 , 298 K): 191.8 (s), 143.5 (s), 143.3 (s), 141.7 (s), 140.7 (s), 134.7 (s), 130.7 (s), 130.5 (s), 129.9 (s), 129.0 (s), 129.0 (s), 128.9 (s), 127.2 (s), 127.1 (s), 123.7 (s), 116.2 (s), 99.5 (s), 51.8 (s), 22.1 (s), 5.2 (s); **HRMS-FAB** (+) (m/z): calcd for $[\text{M}+\text{H}]^+$ $\text{C}_{72}\text{H}_{60}\text{AuN}_2$, 1149.4422; found, 1149.4415.

IPr*Au-C₆F₅ (28)

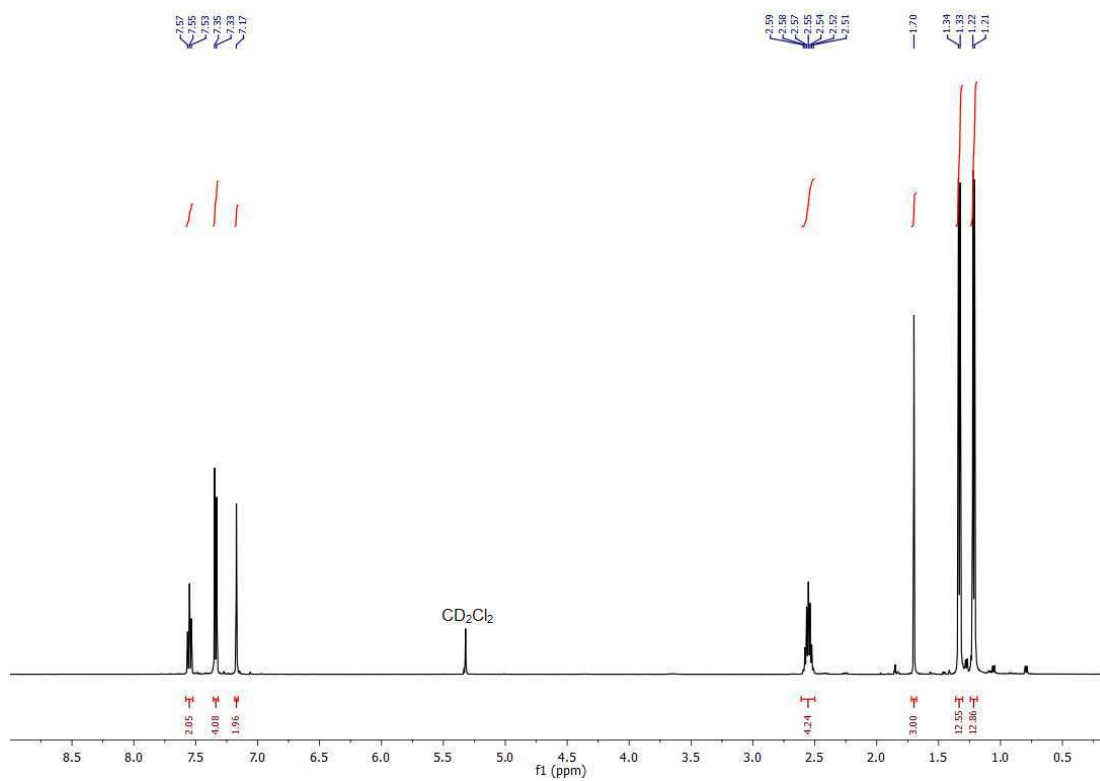


To a solution of IPr*Au-C≡C-Me (50.0 mg, 0.044 mmol) in CD₂Cl₂ (0.7 mL) was added B(C₆F₅)₃ (22.3 mg, 0.044 mmol) and stirred for 4h. Slow diffusion of pentane into this solution at -20°C afforded single crystals (22.3 mg, 40%).

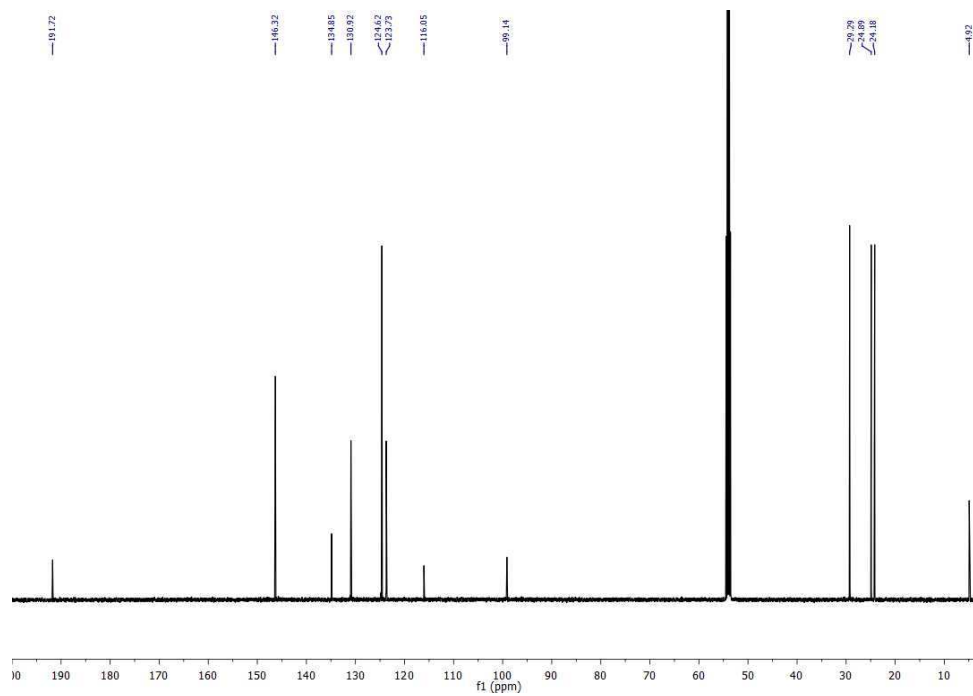
IR (thin film) ν_{max} = 3061.2 cm⁻¹, 3027, 1601, 1495, 1472, 1452, 1416, 1311, 1238, 1030, 982, 953, 790, 764; **¹H NMR** (600 MHz, CD₂Cl₂, 298 K): 7.25-7.22 (m, 8H), 7.19-7.14 (m, 24 H), 6.91 (s, 4H), 6.89-6.86 (m, 8H), 5.75 (s, 2H), 5.42 (s, 4H), 2.24 (s, 6H); **¹³C NMR** {¹H} (150 MHz, CD₂Cl₂, 298 K): 191.1(s), 143.5 (s), 143.1 (s), 141.5 (s), 140.7 (s), 134.3 (s), 130.6 (s), 130.3 (s), 129.8 (s), 128.9 (s), 128.9 (s), 127.2 (s), 127.2 (s), 124.0 (s), 51.9 (s), 22.1 (s); **¹⁹F NMR** (470 MHz, CD₂Cl₂, 298 K): -115.7 (m, 6F, *o*-C₆F₅), -161.6 (t, J_{FF} = 20.9 Hz, 3F, *p*-C₆F₅), -164.2 (m, 6F, *m*-C₆F₅); **HRMS-EI** (+) (m/z): calcd for [M-C₆F₅]⁺ C₆₉H₅₆AuN₂, 1109.4109; found, 1109.4124.

NMR data

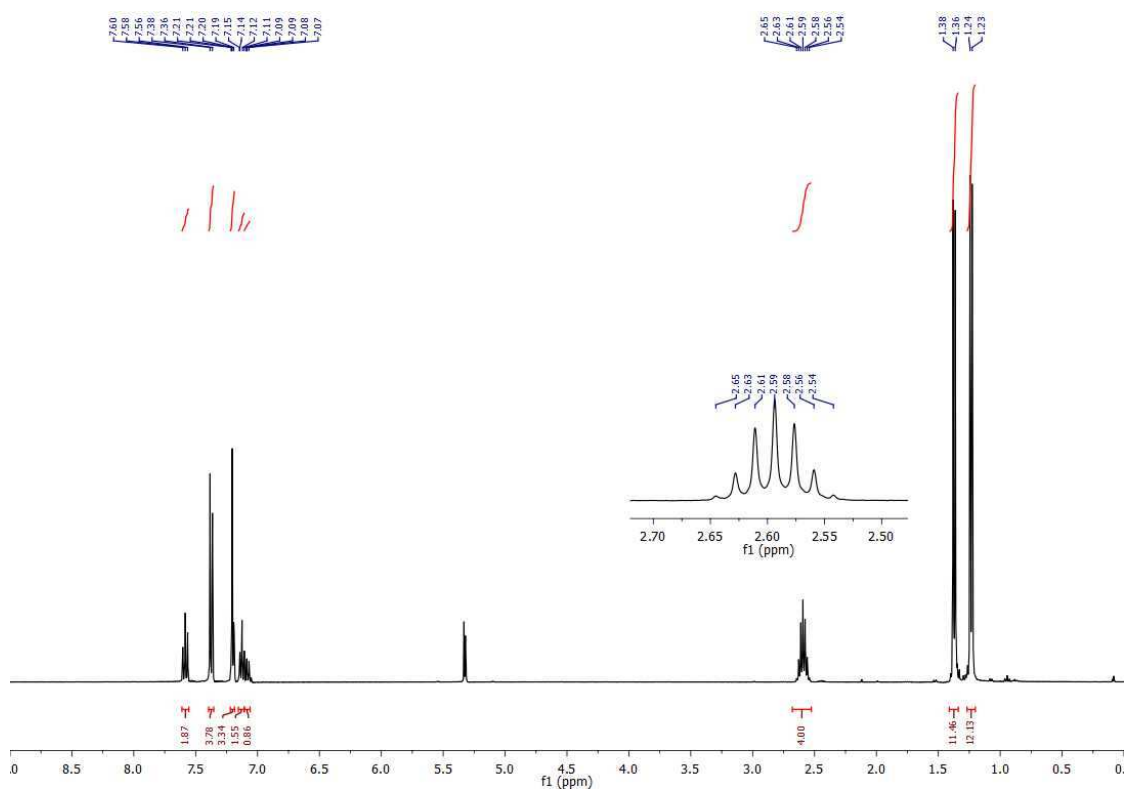
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPrAu-C}\equiv\text{C-Me}$ (**1**)



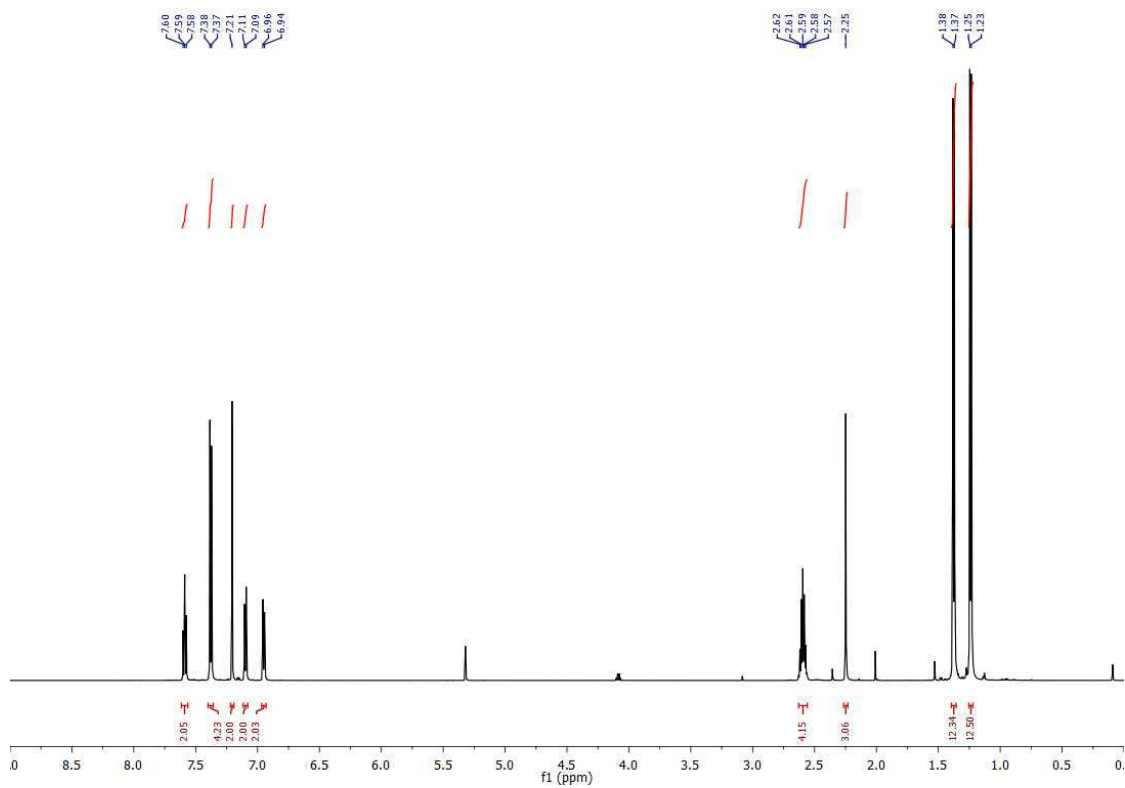
^{13}C NMR (125 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPrAu-C}\equiv\text{C-Me}$ (**1**)



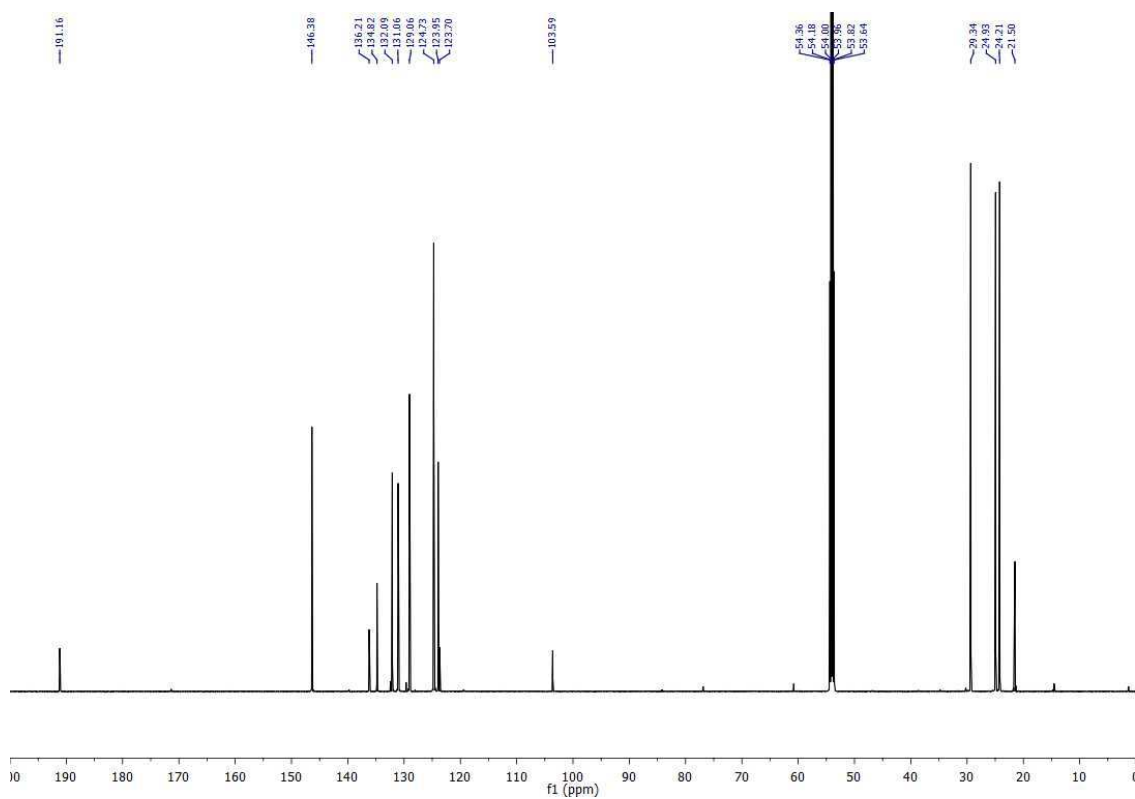
^1H NMR (400 MHz, CD_2Cl_2 , 298K) spectrum of (2)



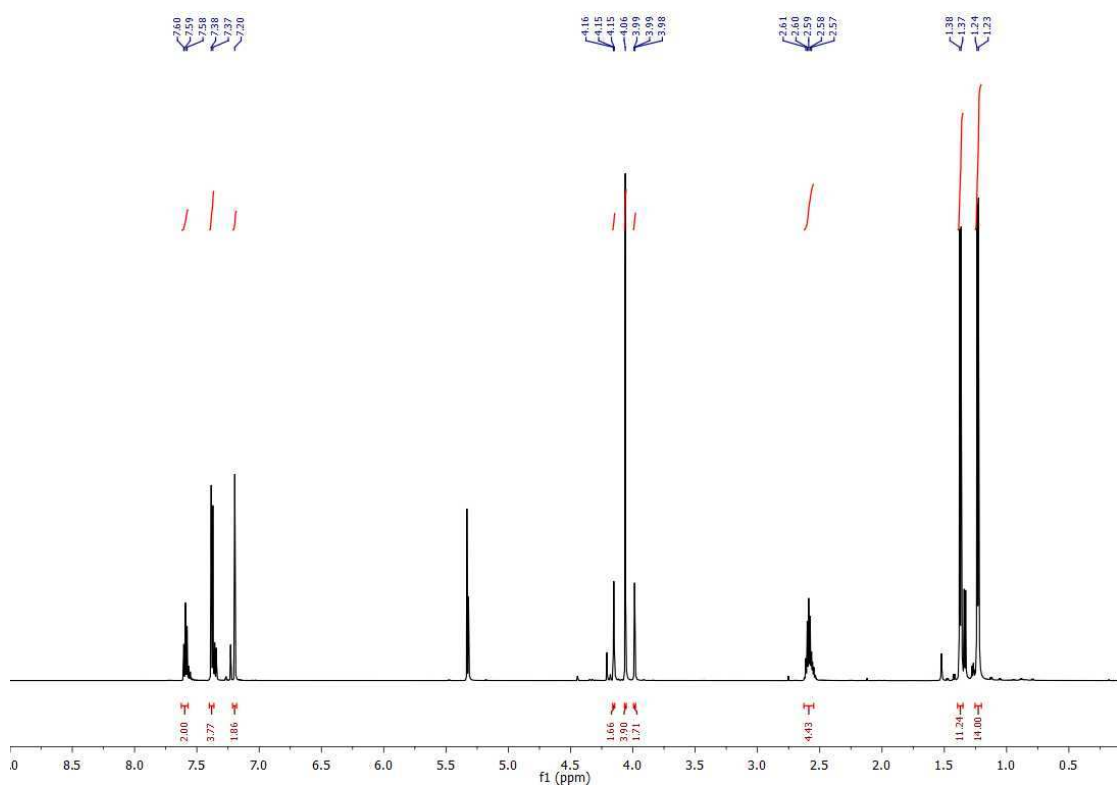
^1H NMR (600 MHz, CD_2Cl_2 , 298K) spectrum of (3)



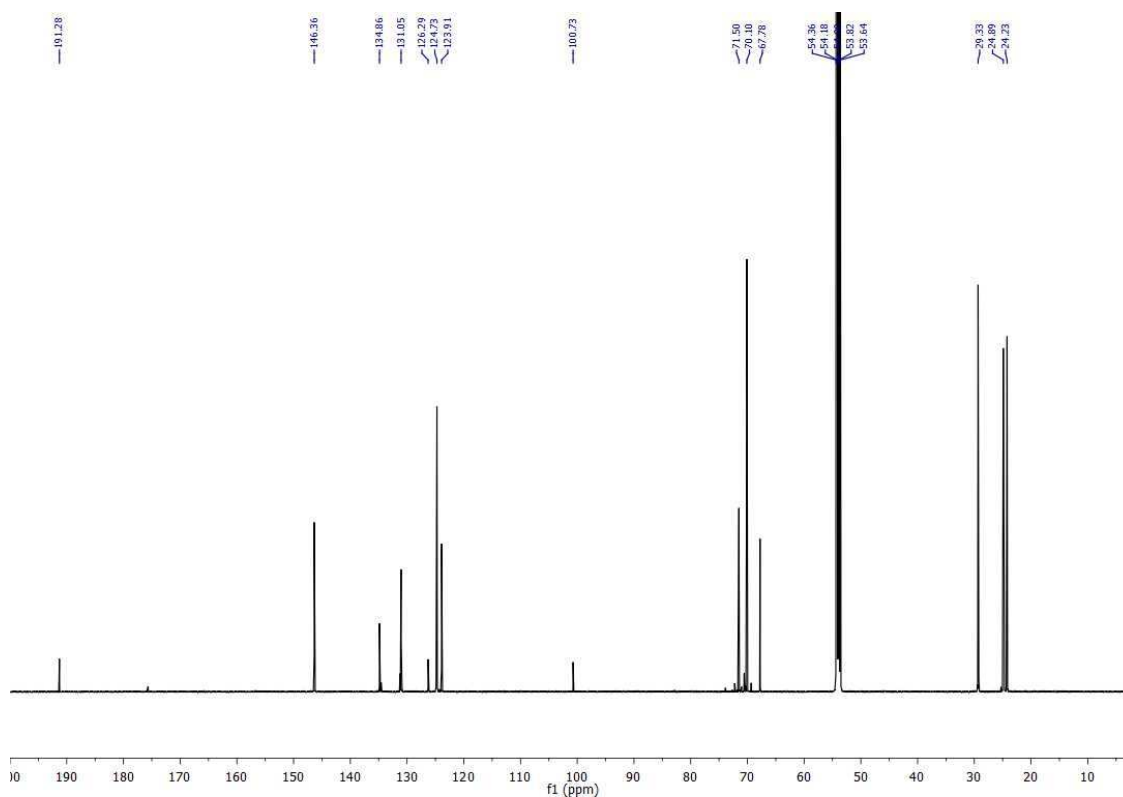
^{13}C NMR (150 MHz, CD_2Cl_2 , 298K) spectrum of (3)



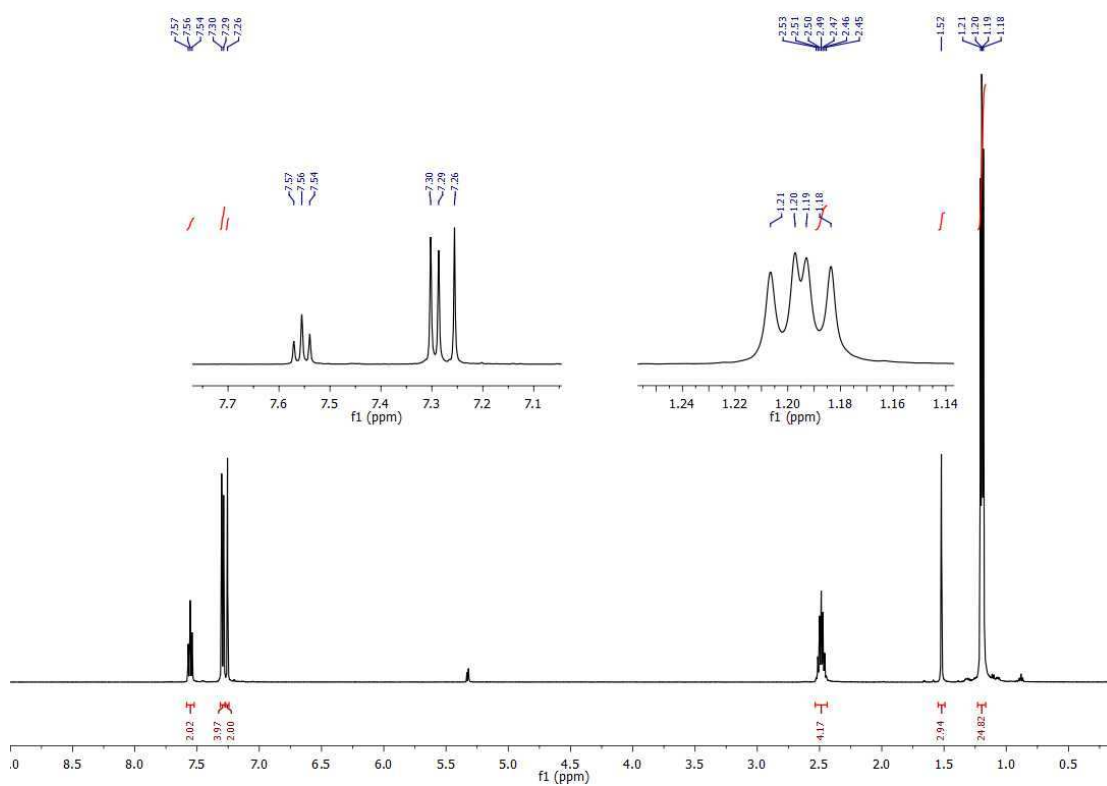
^1H NMR (600 MHz, CD_2Cl_2 , 298K) spectrum of (4)



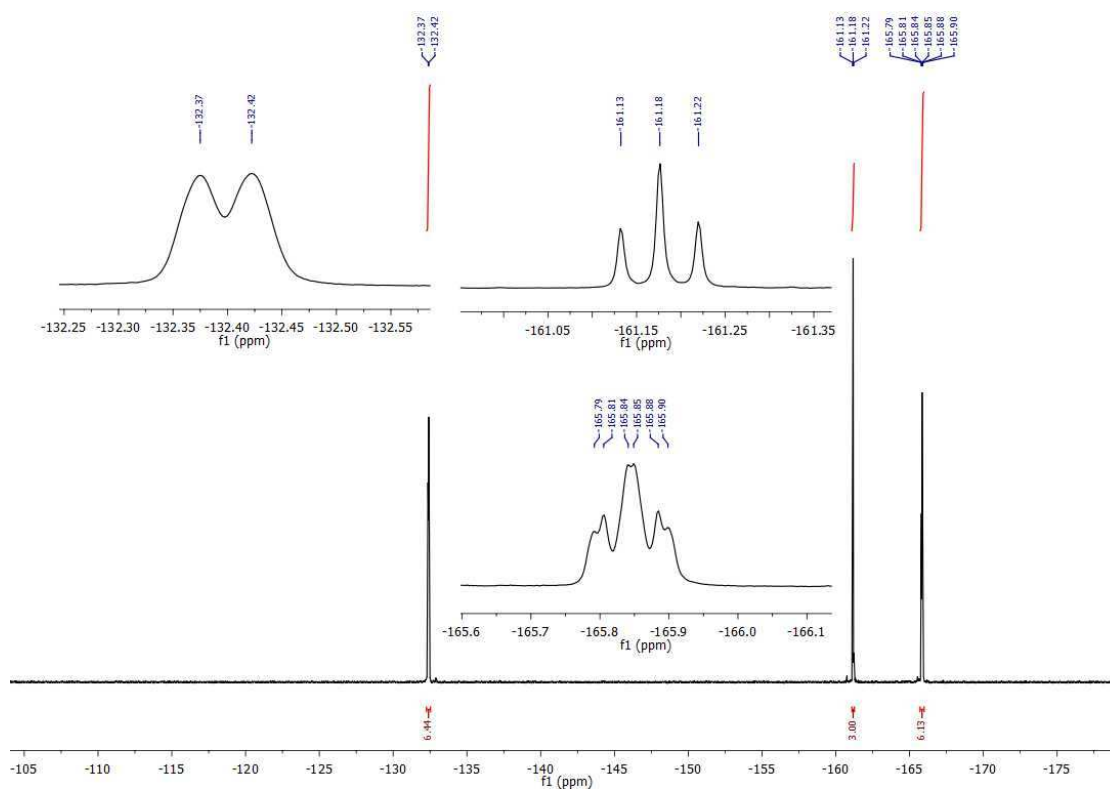
^{13}C NMR (150 MHz, CD_2Cl_2 , 298K) spectrum of (4)



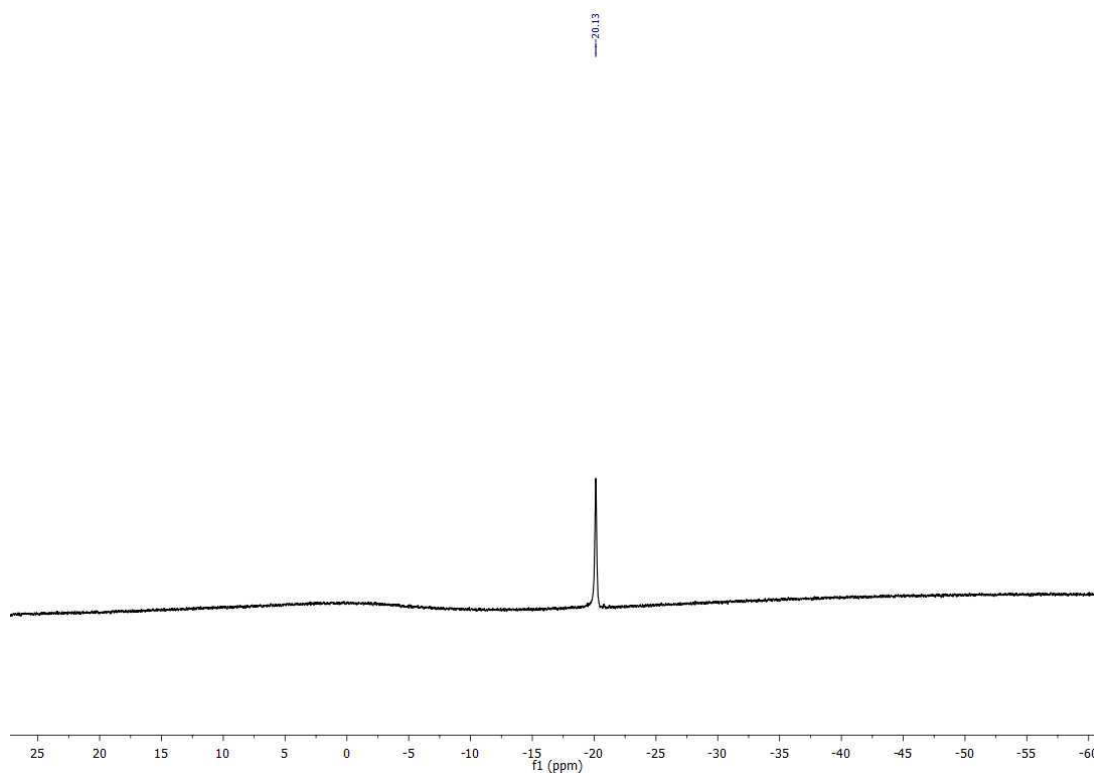
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (5)



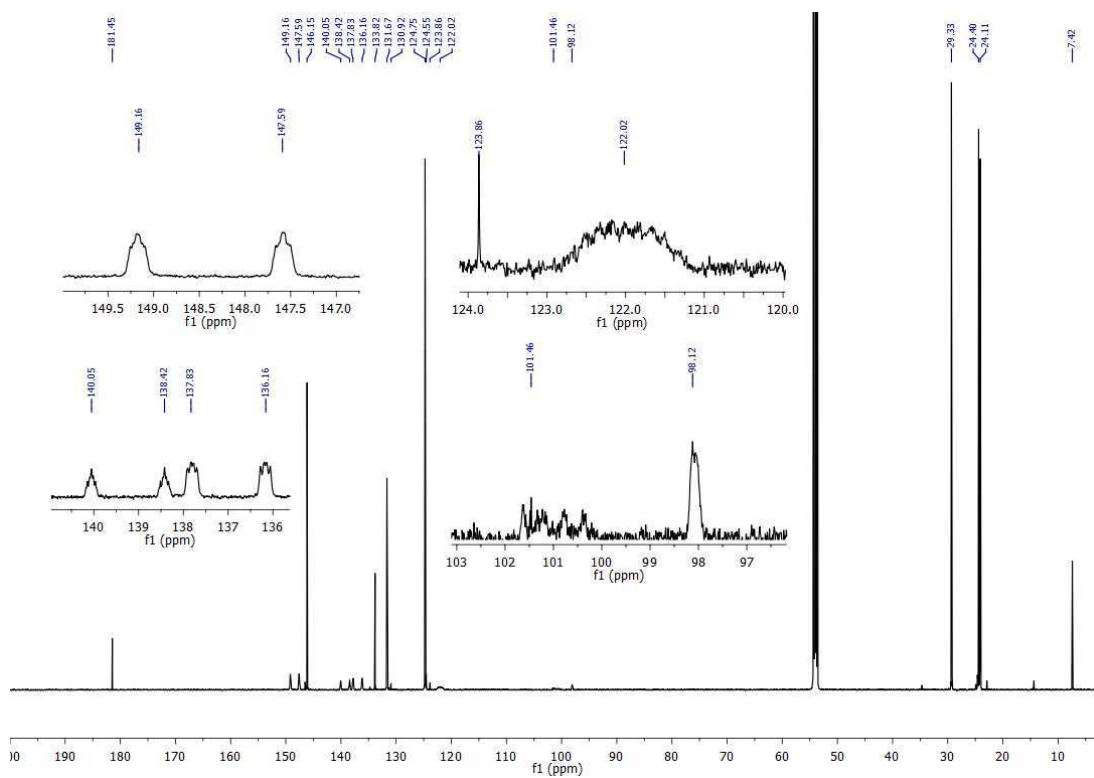
^{19}F NMR (470 MHz, CD_2Cl_2 , 298K) spectrum of (5)



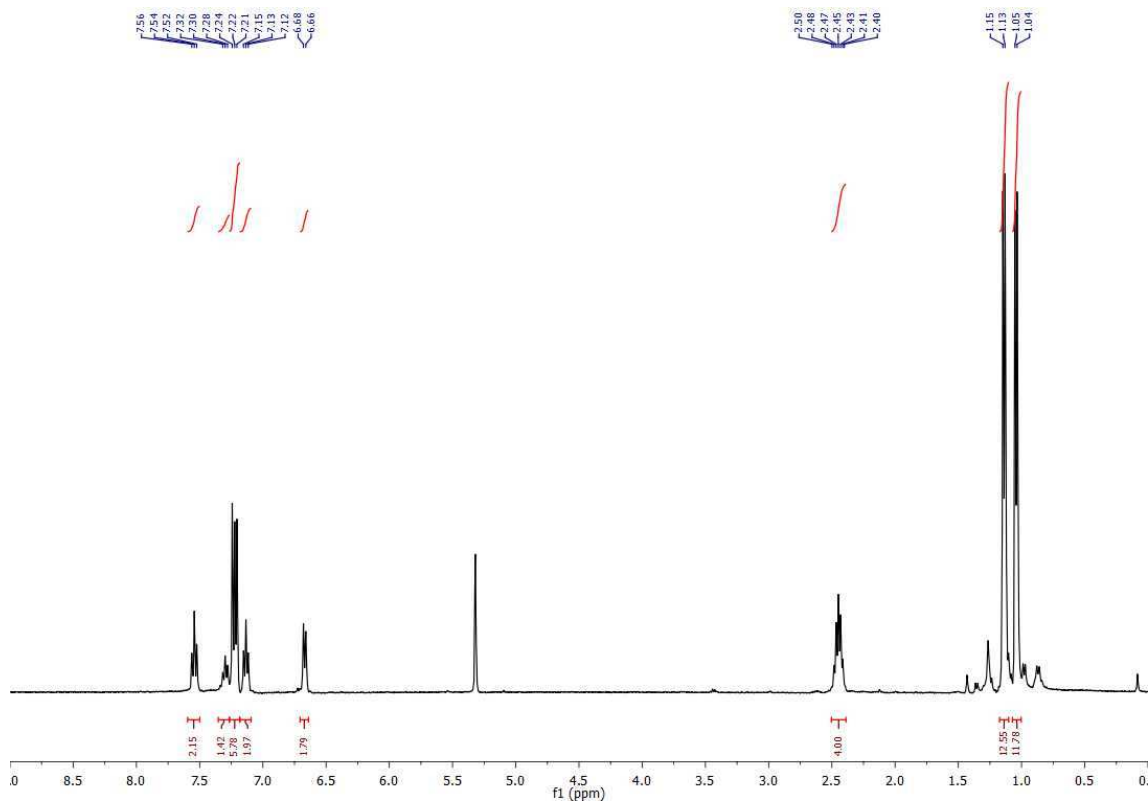
^{11}B NMR (95 MHz, CD_2Cl_2 , 298K) spectrum of (5)



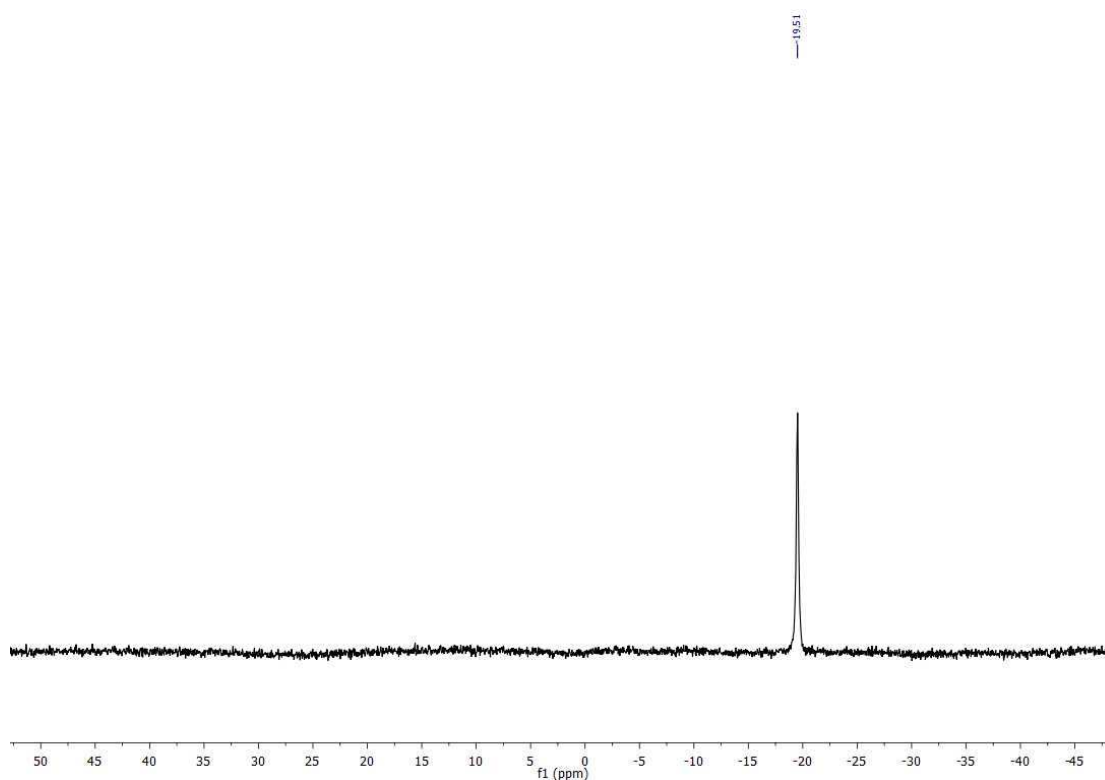
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298K) spectrum of (5)



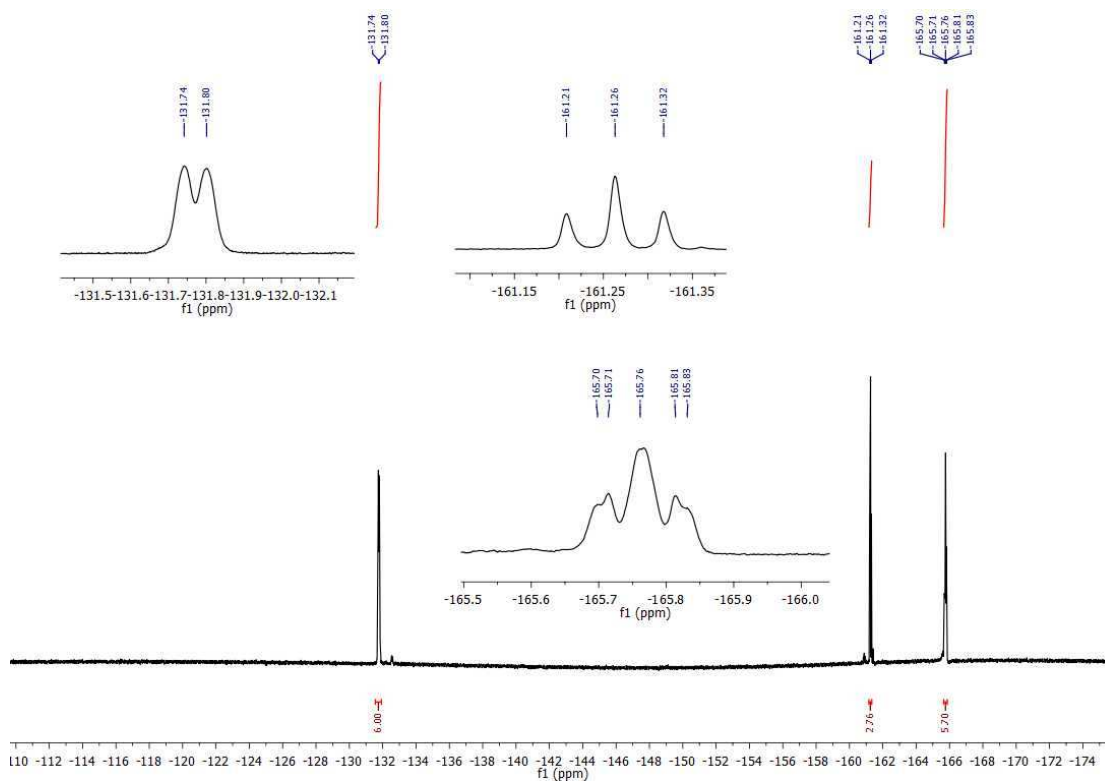
^1H NMR (400 MHz, CD_2Cl_2 , 298K) spectrum of (6)



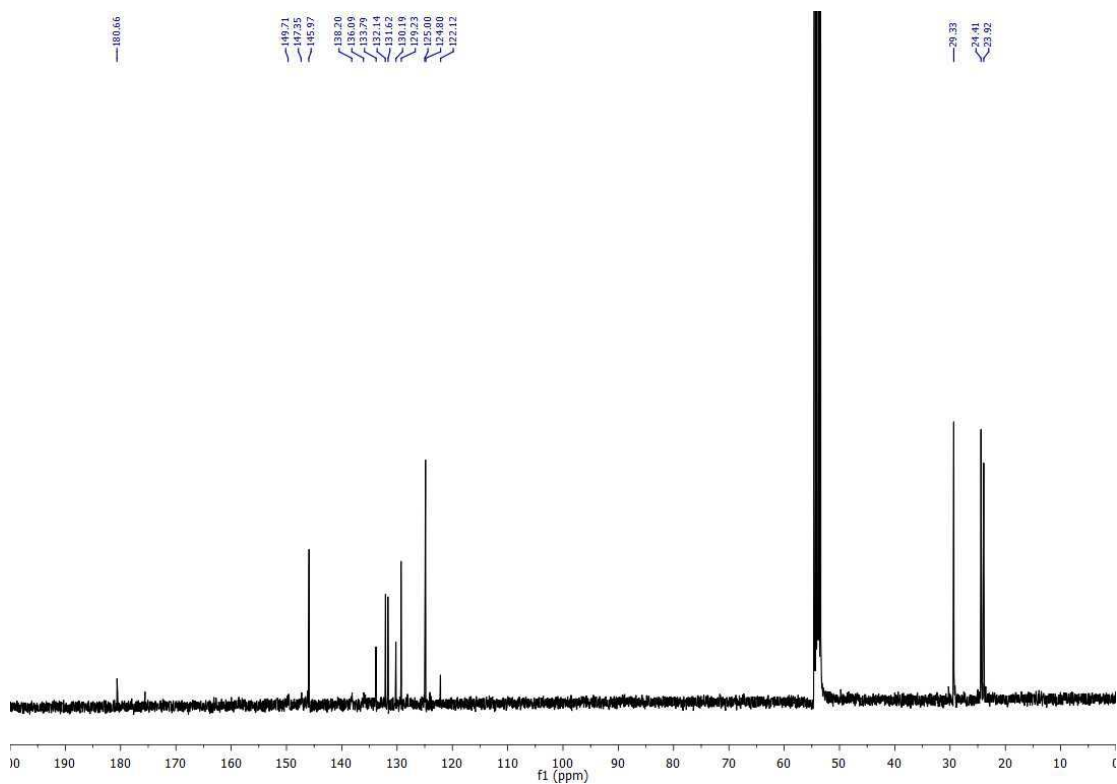
^{11}B NMR (128 MHz, CD_2Cl_2 , 298K) spectrum of (6)



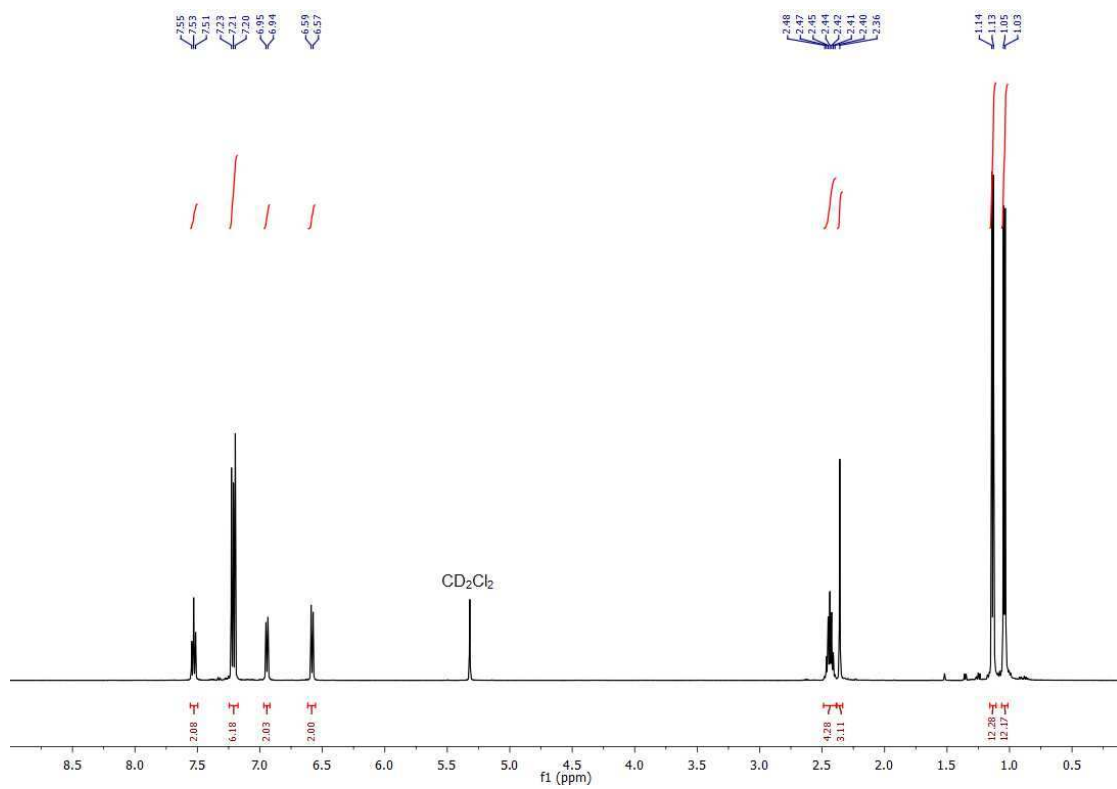
^{19}F NMR (376 MHz, CD_2Cl_2 , 298K) spectrum of (6)



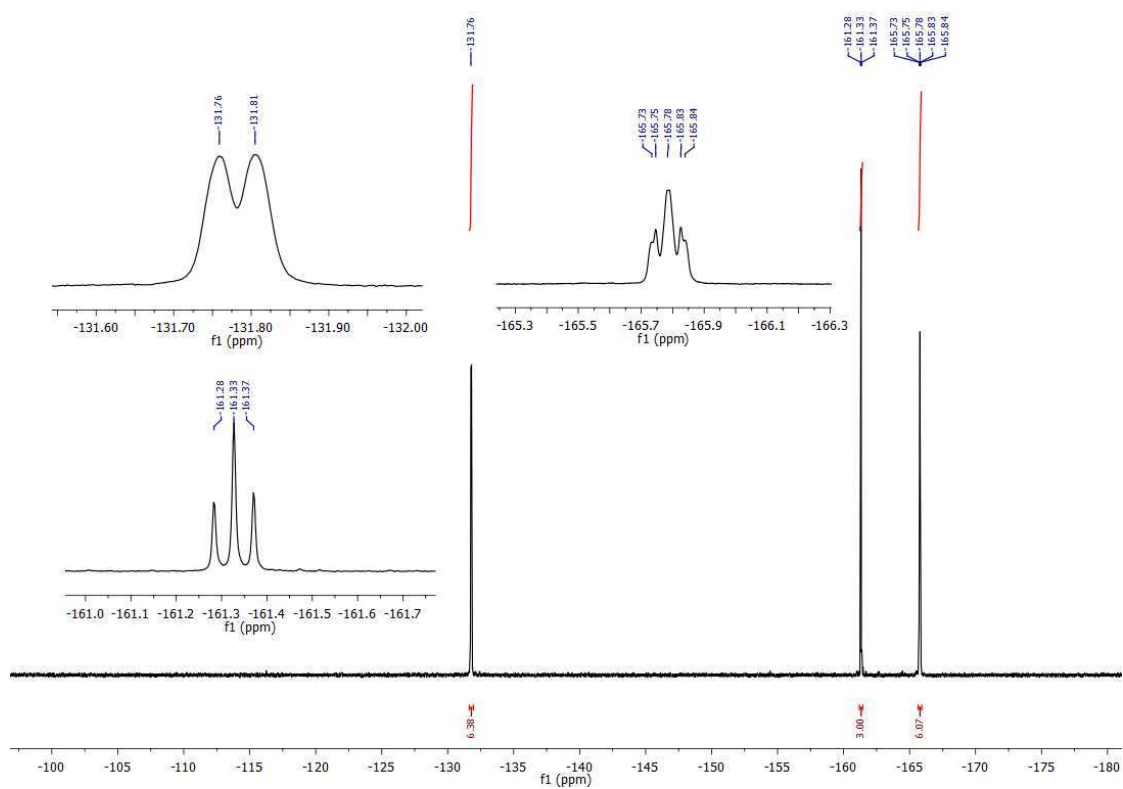
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CD_2Cl_2 , 298K) spectrum of (6)



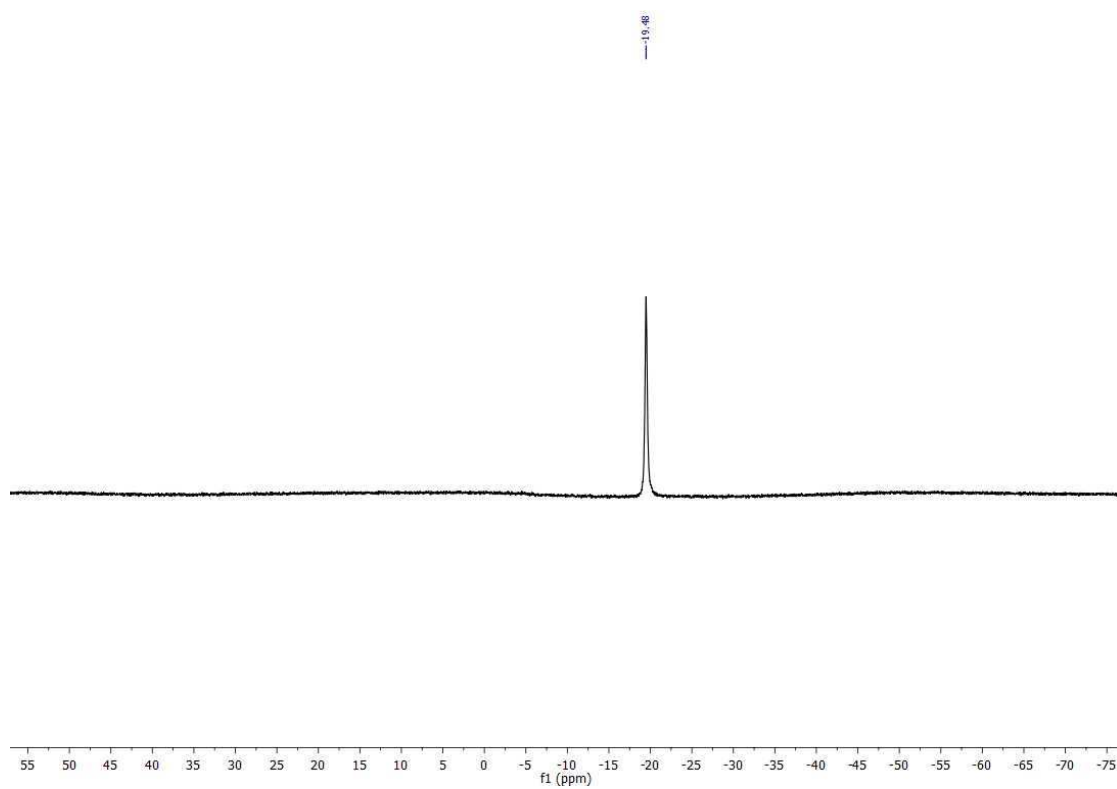
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (7)



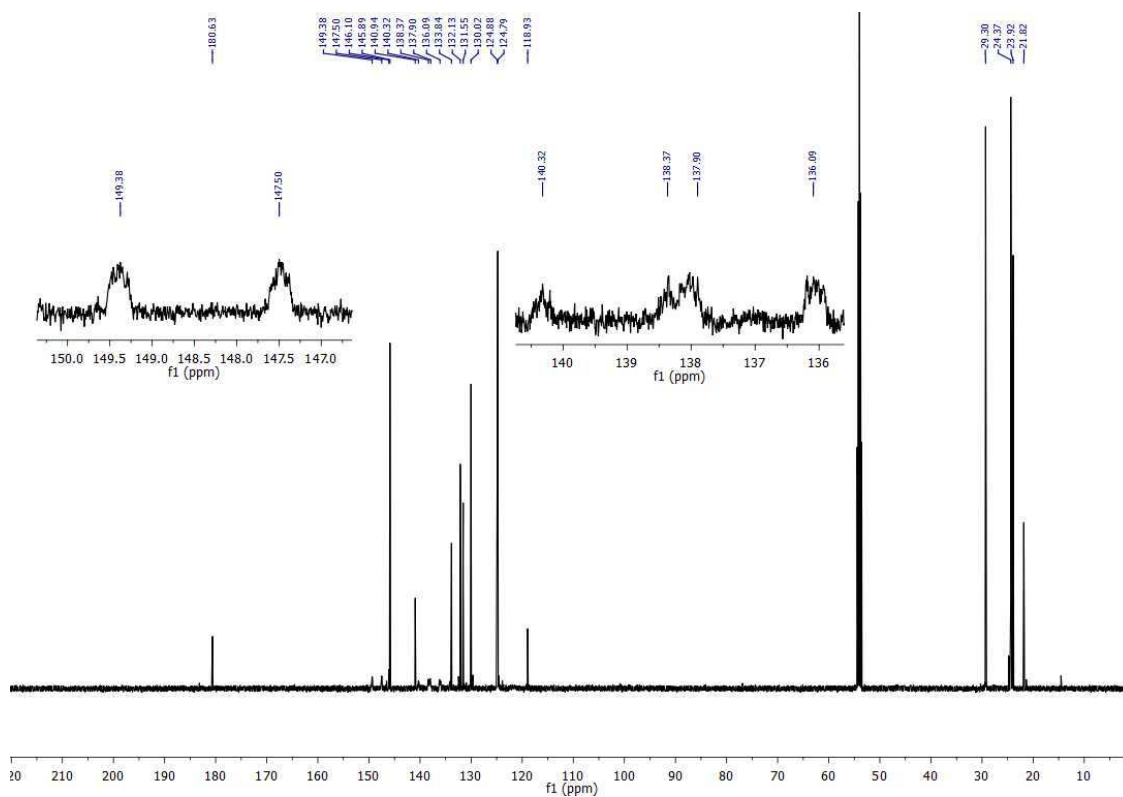
^{19}F NMR (470 MHz, CD_2Cl_2 , 298K) spectrum of (7)



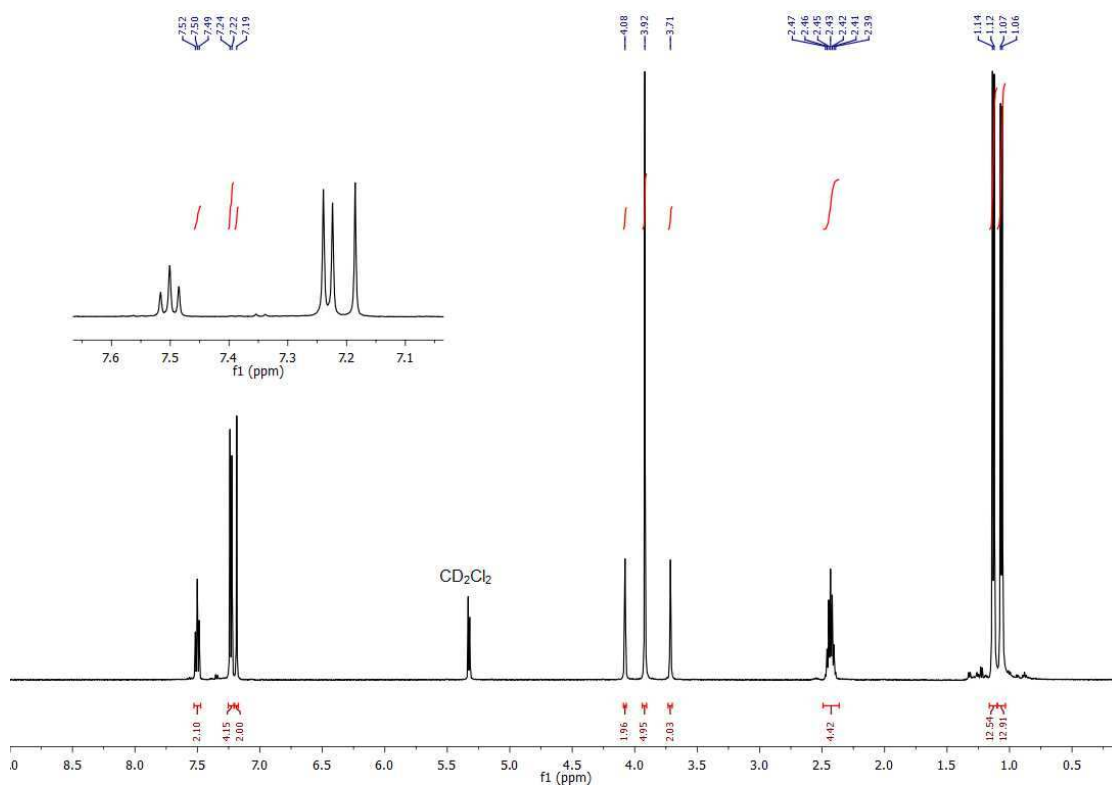
^{11}B NMR (95 MHz, CD_2Cl_2 , 298K) spectrum of (7)



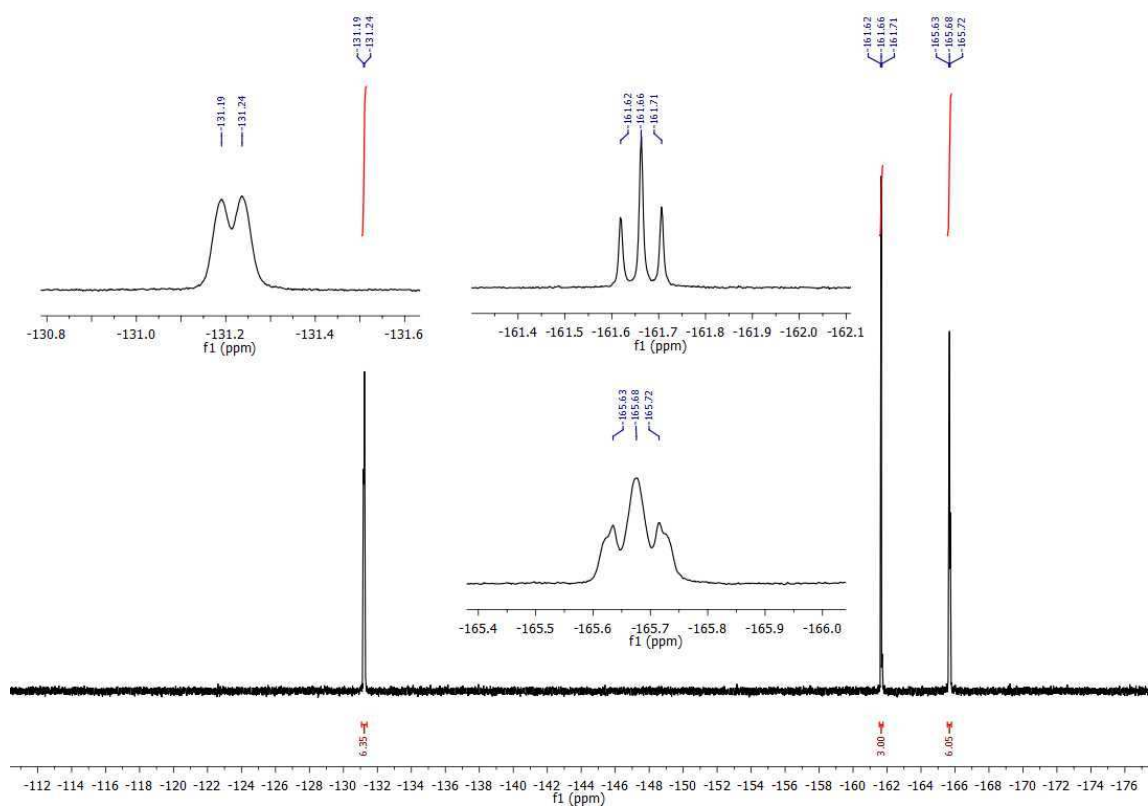
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298K) spectrum of (7)



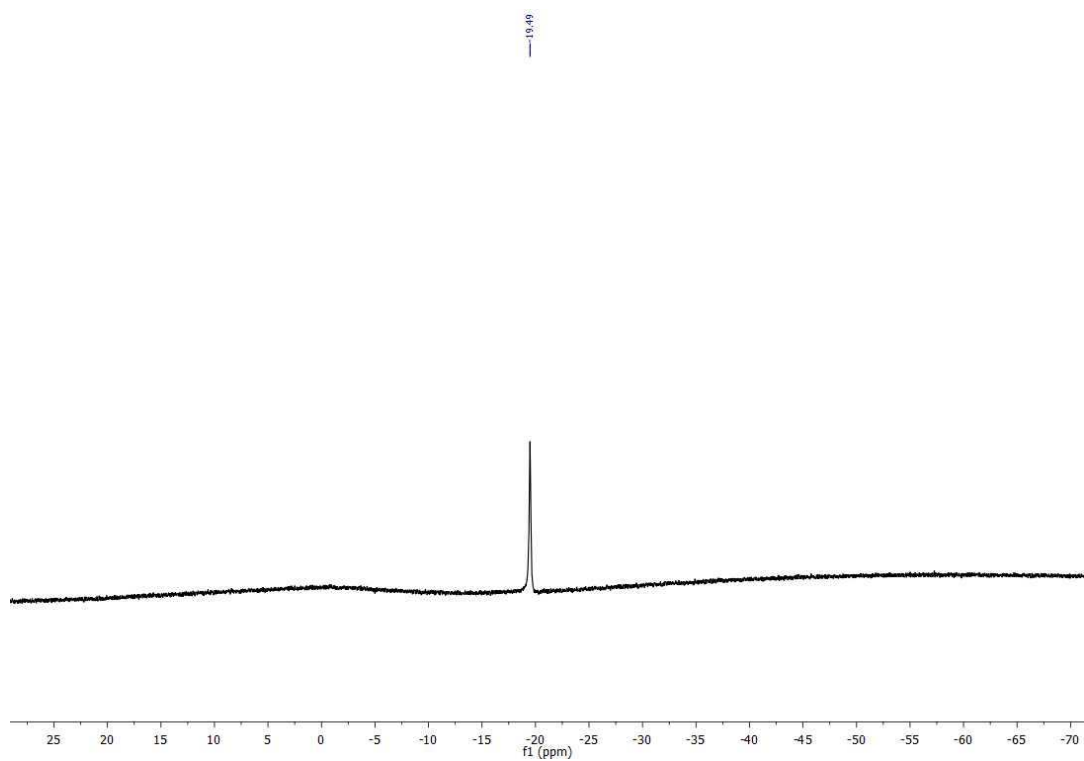
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (8)



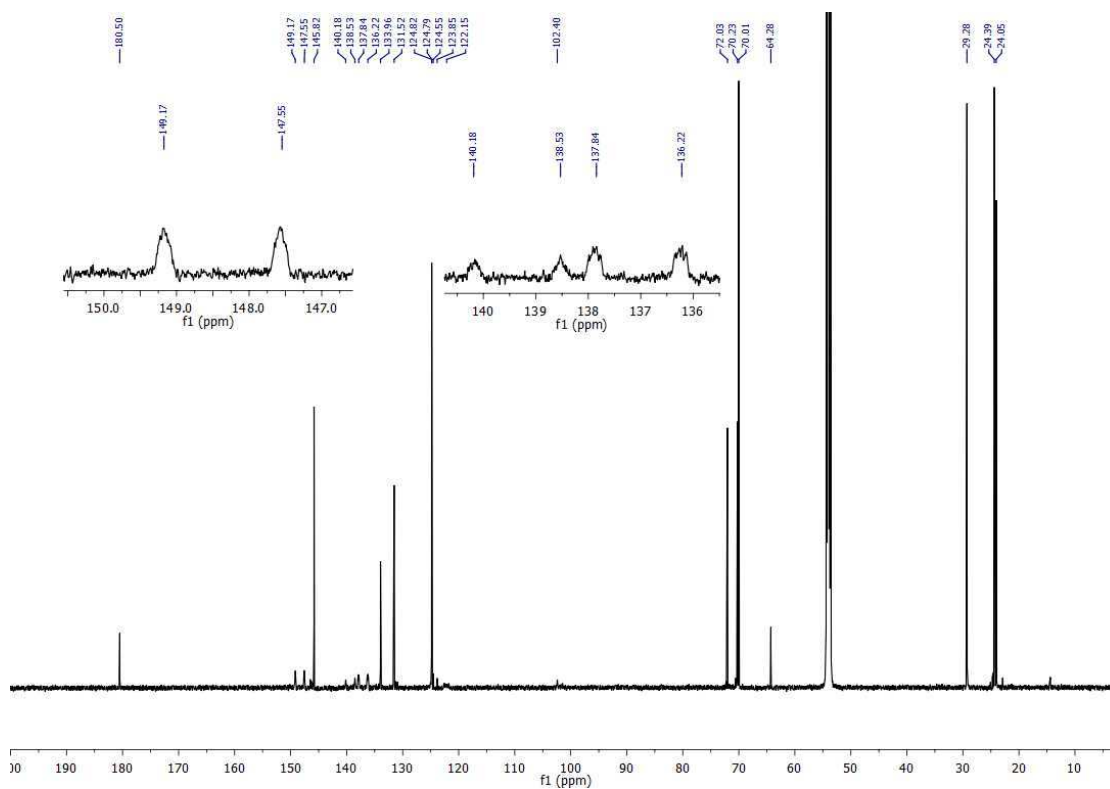
^{19}F NMR (470 MHz, CD_2Cl_2 , 298K) spectrum of (8)



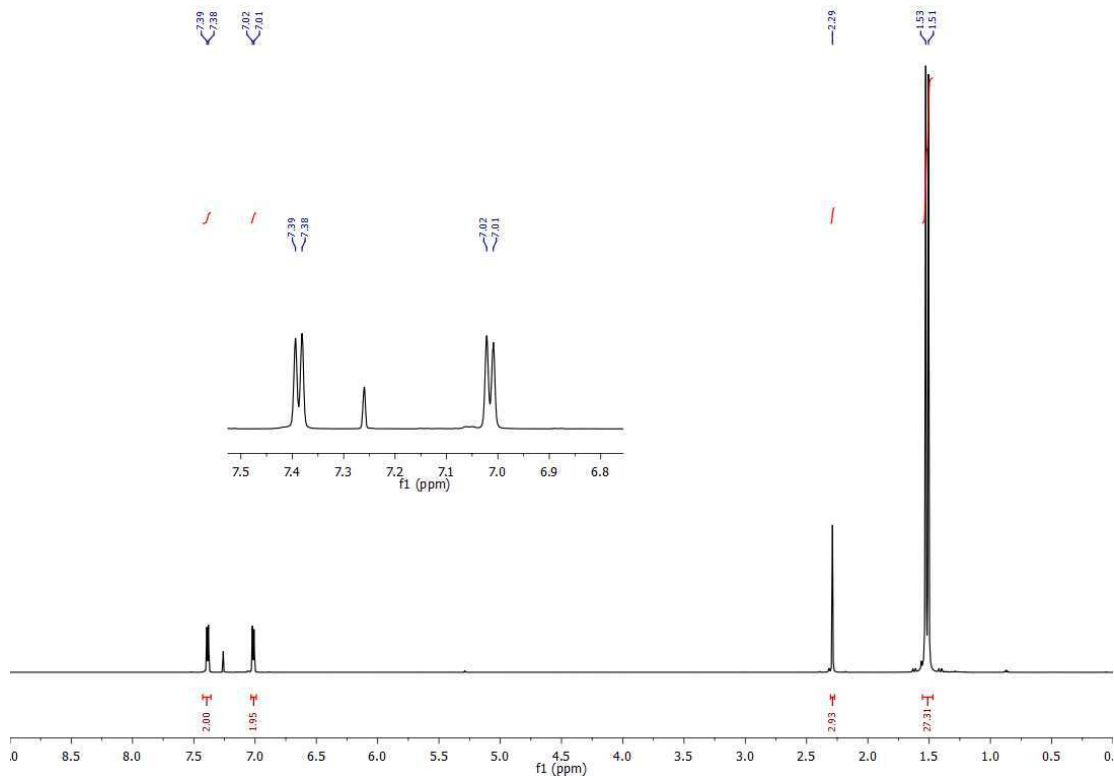
^{11}B NMR (95 MHz, CD_2Cl_2 , 298K) spectrum of (8)



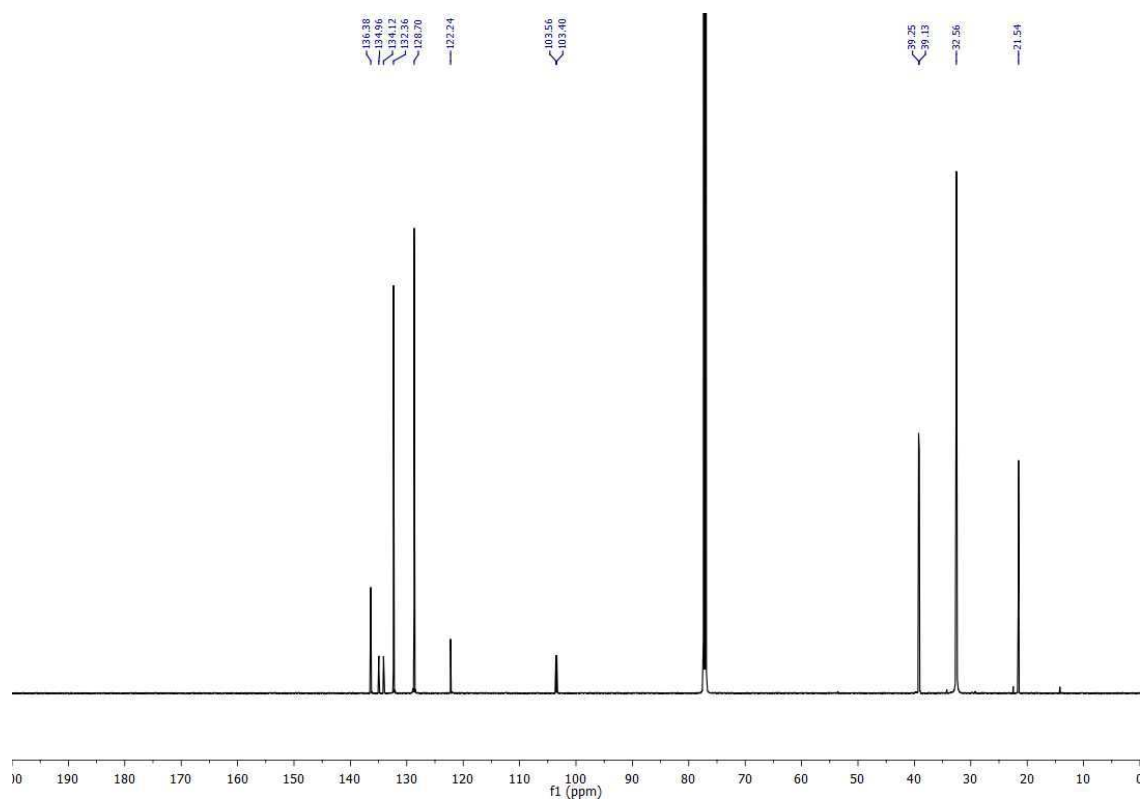
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298K) spectrum of (**8**)



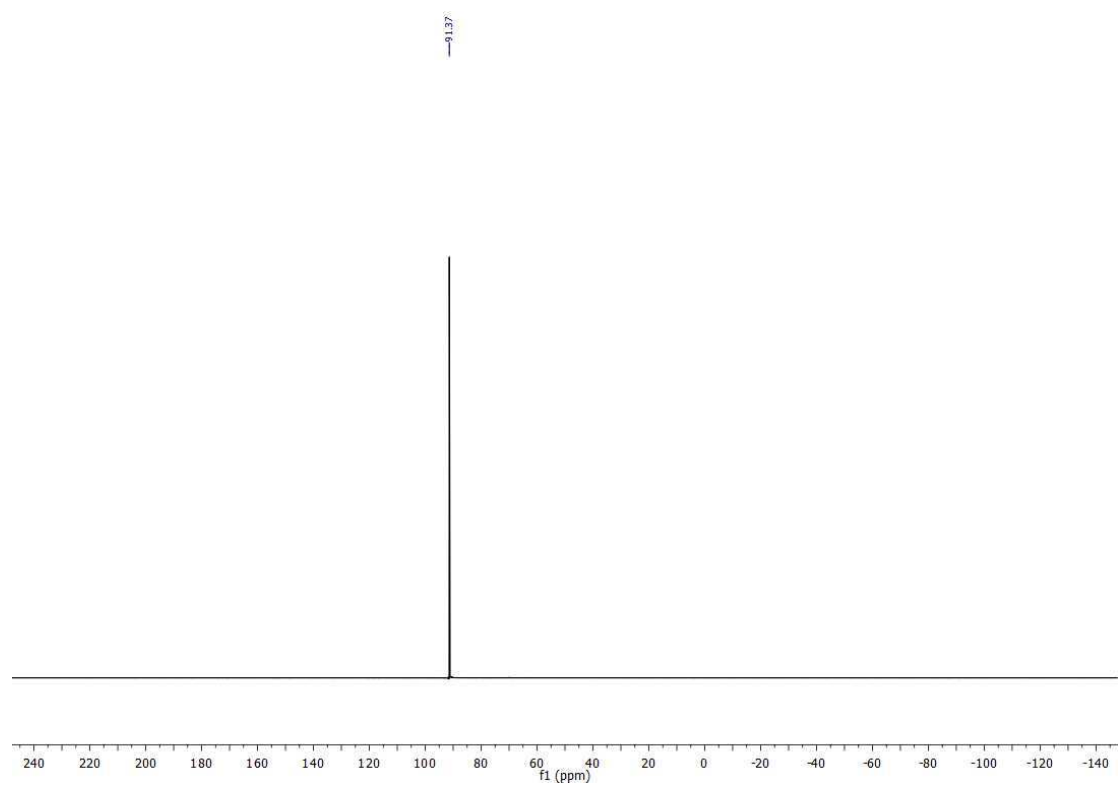
^1H NMR (600 MHz, CDCl_3 , 298K) spectrum of (**9**)



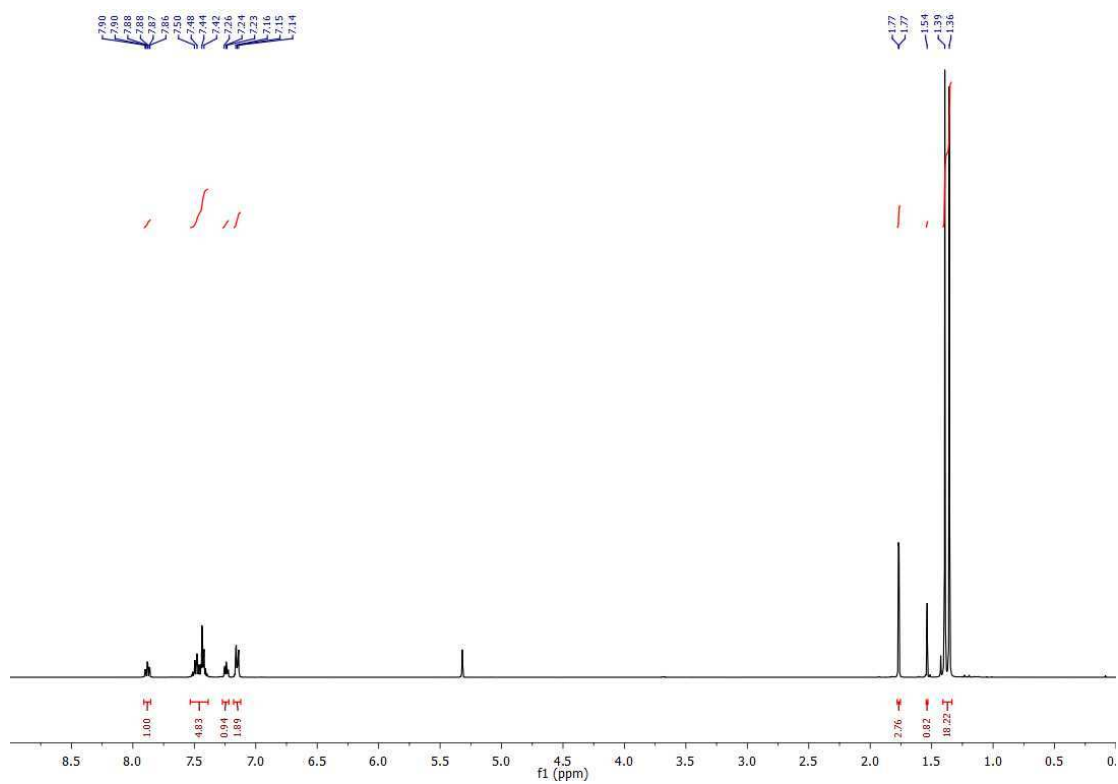
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CDCl_3 , 298K) spectrum of (9)



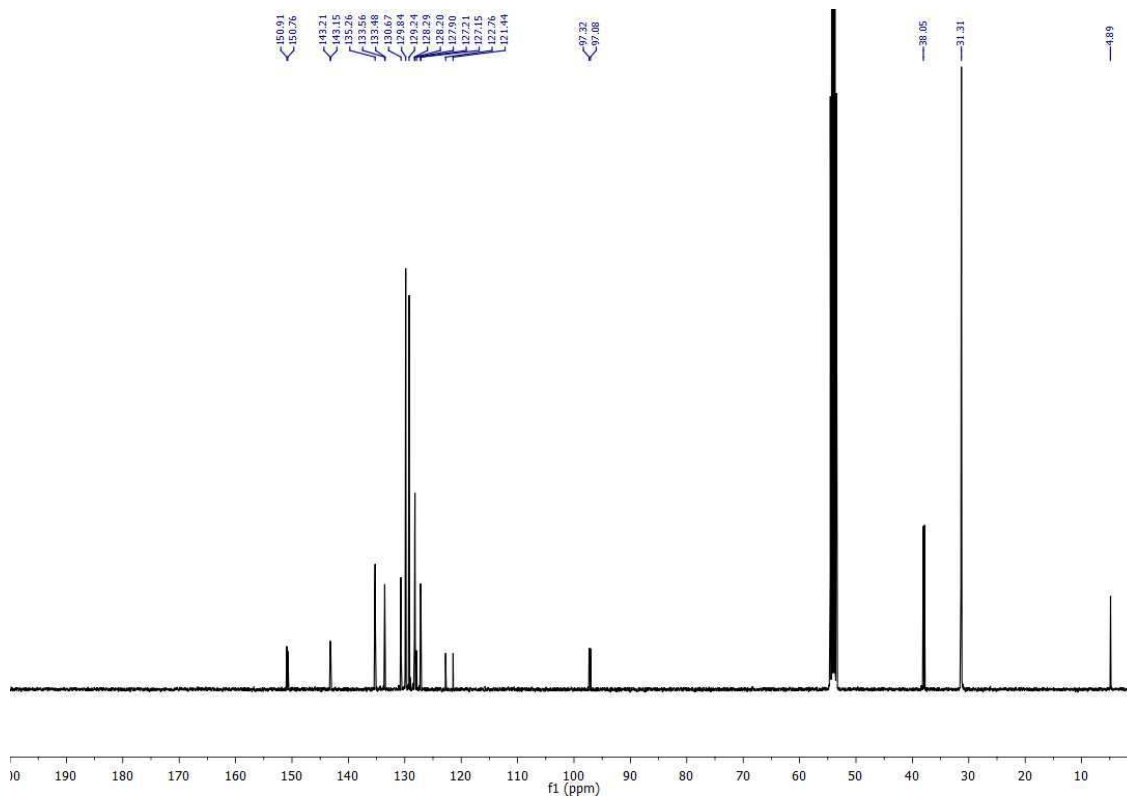
^{31}P NMR $\{^1\text{H}\}$ (243 MHz, CDCl_3 , 298K) spectrum of (9)



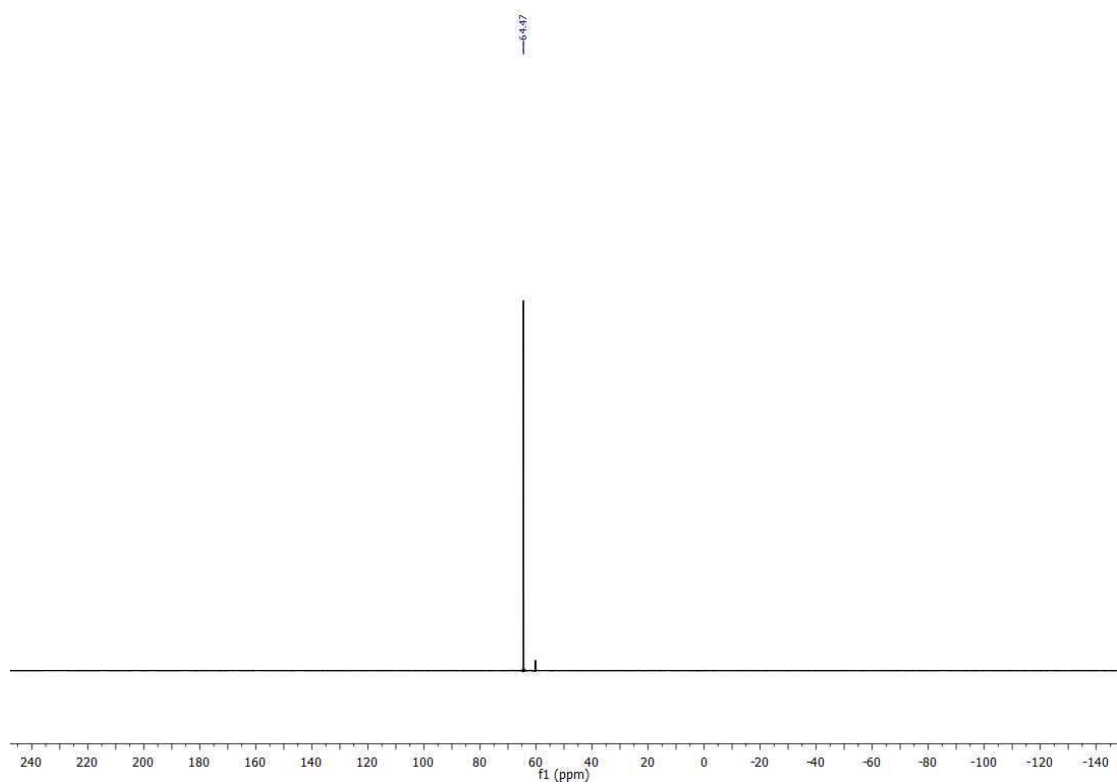
^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of (**10**)



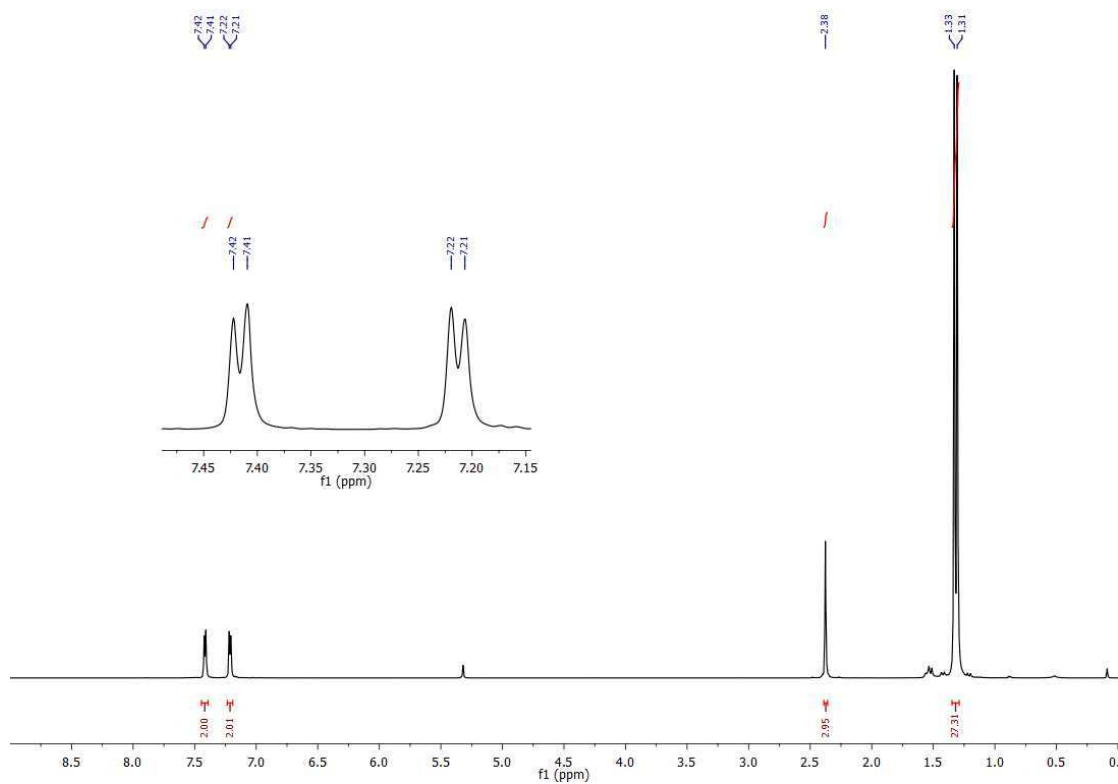
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CDCl_3 , 298K) spectrum of (**10**)



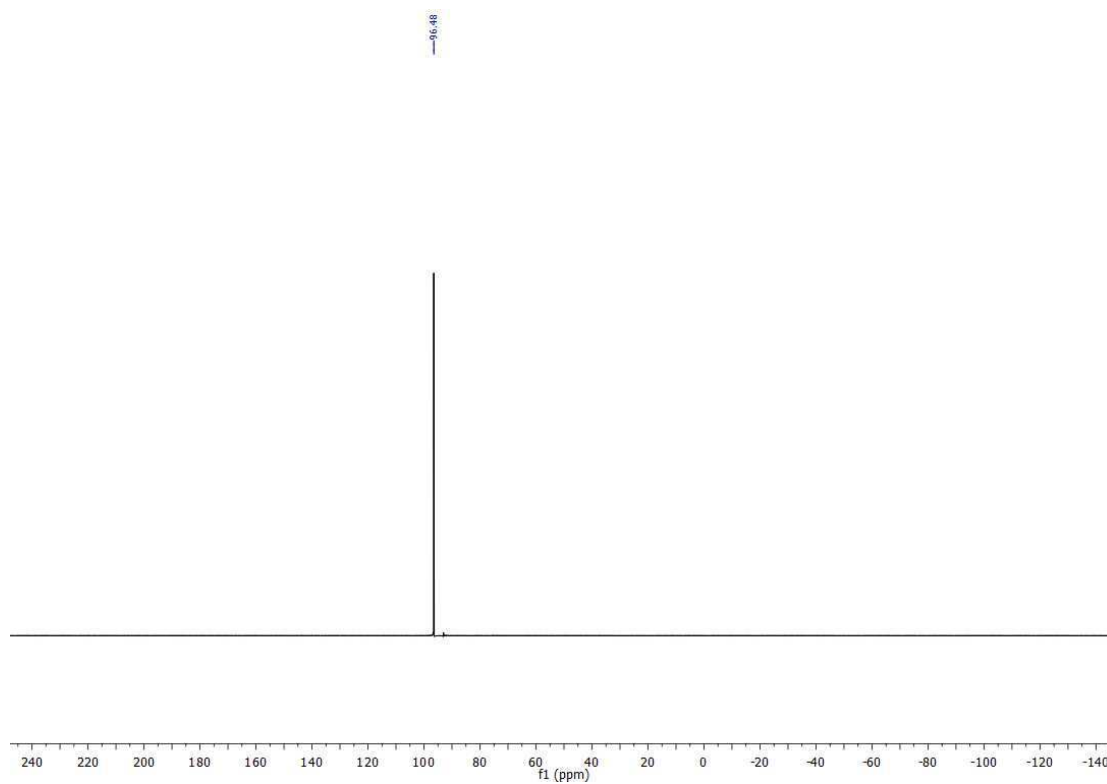
^{31}P NMR $\{^1\text{H}\}$ (162 MHz, CDCl_3 , 298K) spectrum of (10)



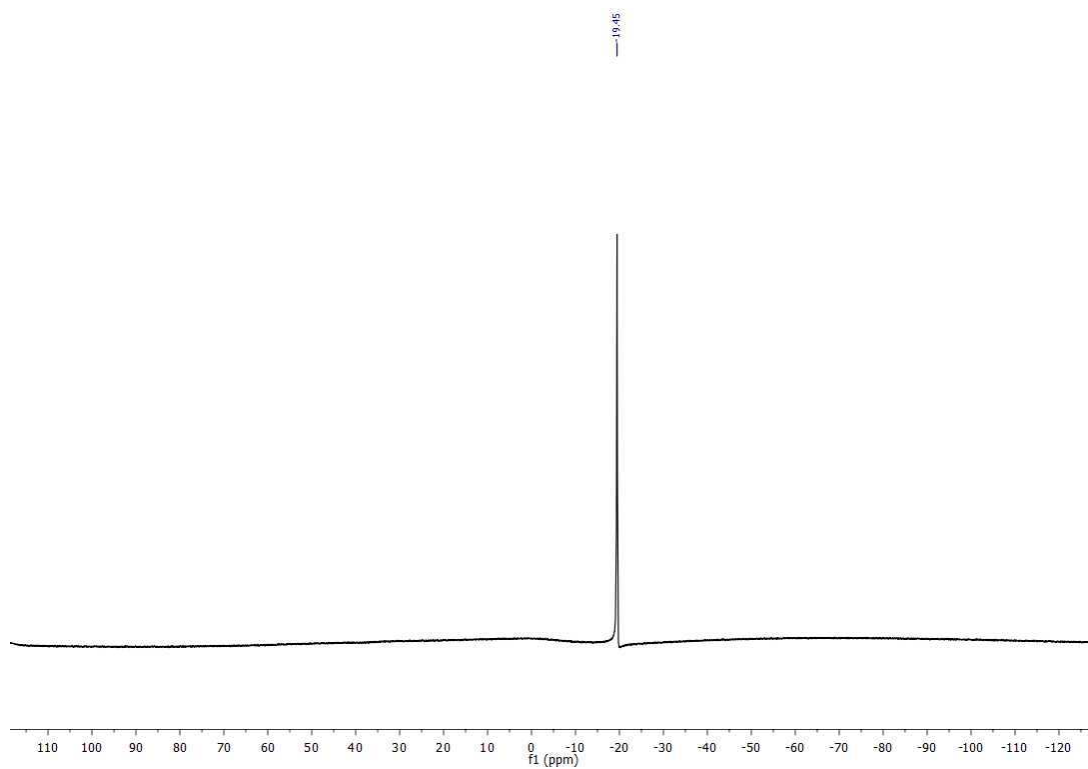
^1H NMR (600 MHz, CD_2Cl_2 , 298K) spectrum of (11)



^{31}P NMR (243 MHz, CD_2Cl_2 , 298K) spectrum of **(11)**



^{11}B NMR (96 MHz, CD_2Cl_2 , 298K) spectrum of **(11)**



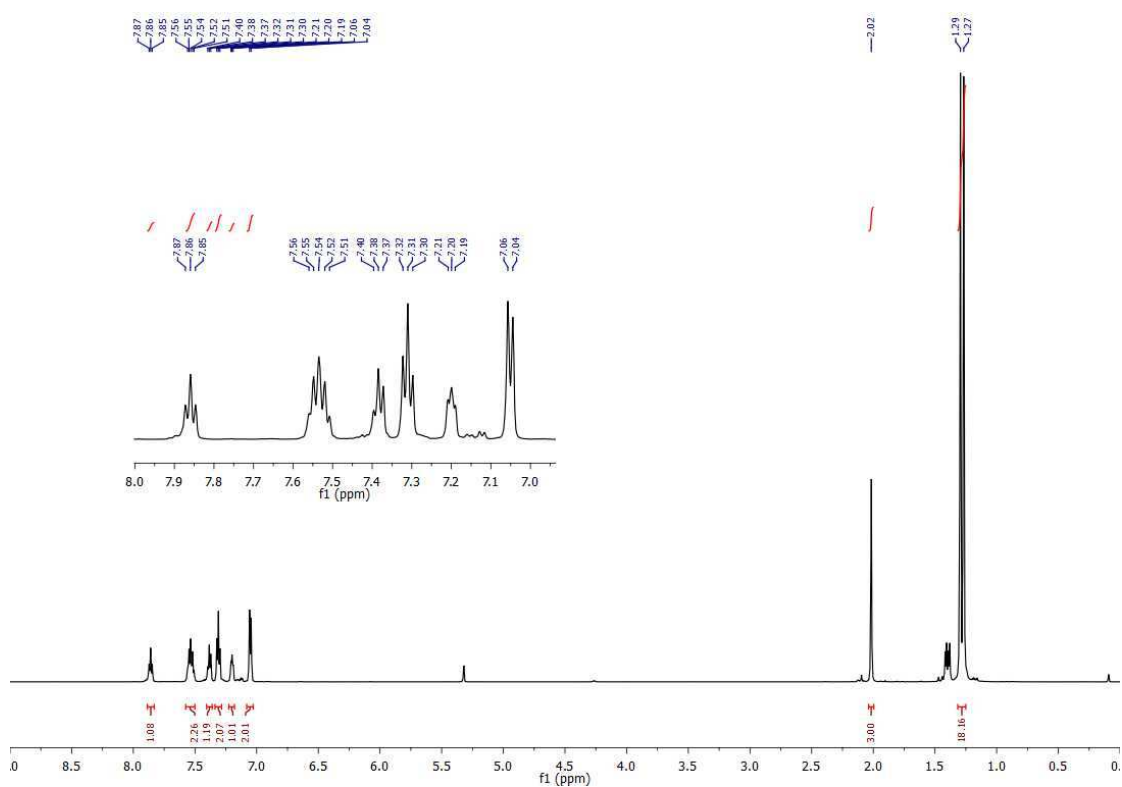
13C NMR spectrum (CDCl₃) of compound 10. The spectrum shows several peaks, with three regions expanded for clarity:

- Region 1 (Top Left):** Expansion of the peak at approximately -131.5 ppm. Peaks are labeled at 131.56 and 131.60 ppm.
- Region 2 (Top Middle):** Expansion of the peak at approximately -161.2 ppm. Peaks are labeled at 161.15, 161.19, and 161.24 ppm.
- Region 3 (Bottom Left):** Expansion of the peak at approximately -165.9 ppm. Peaks are labeled at 165.85, 165.90, 165.94, and 165.95 ppm.

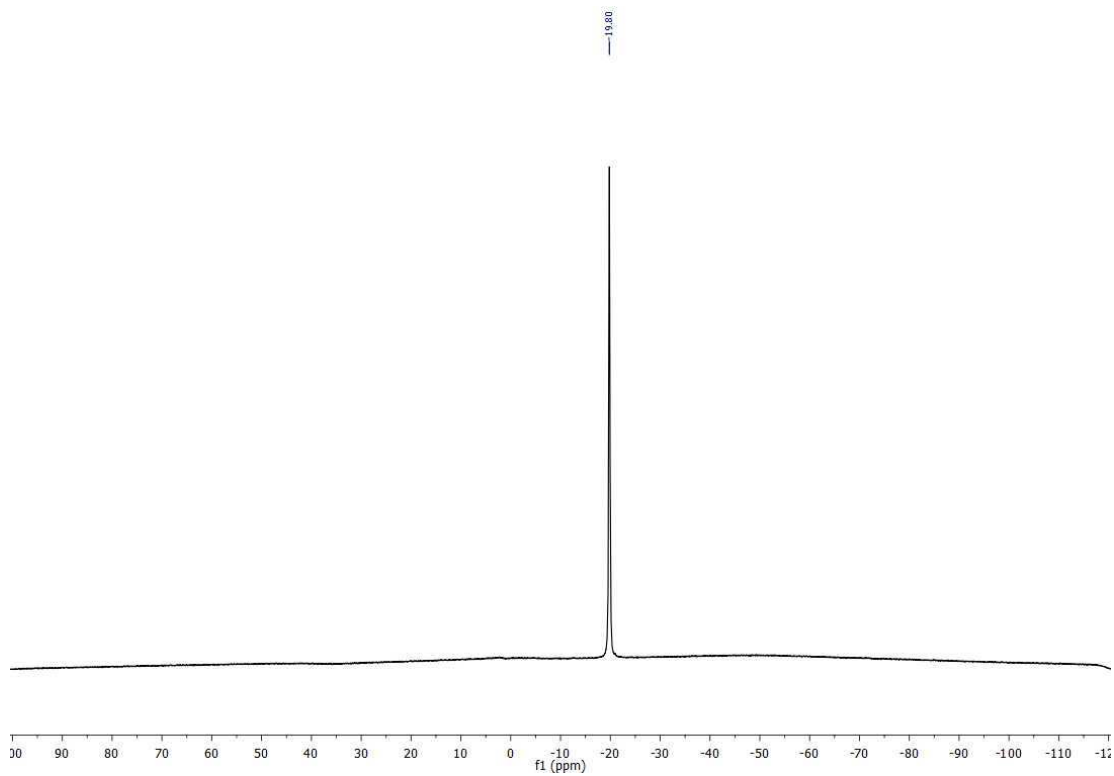
The main spectrum shows peaks at approximately -131.5 ppm (9.00 integration), -161.2 ppm (2.81 integration), and -165.9 ppm (5.61 integration).

[illegible]

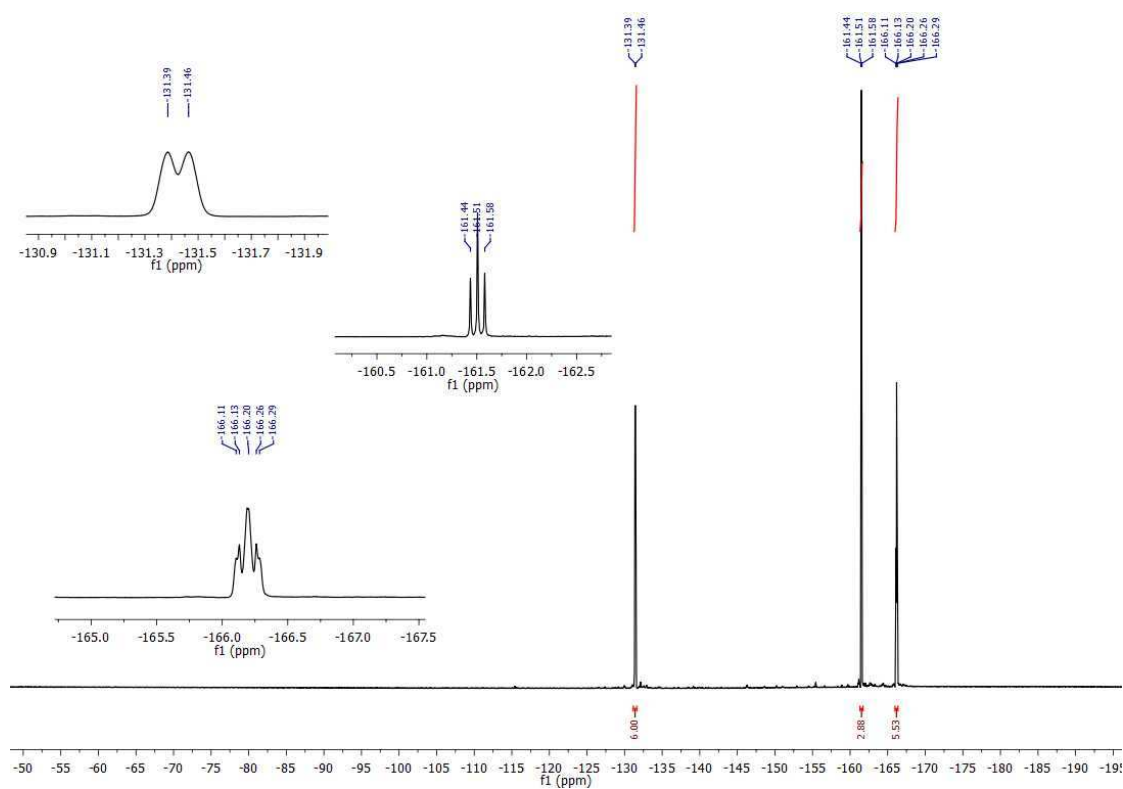
^1H NMR (600 MHz, CD_2Cl_2 , 298K) spectrum of (12)



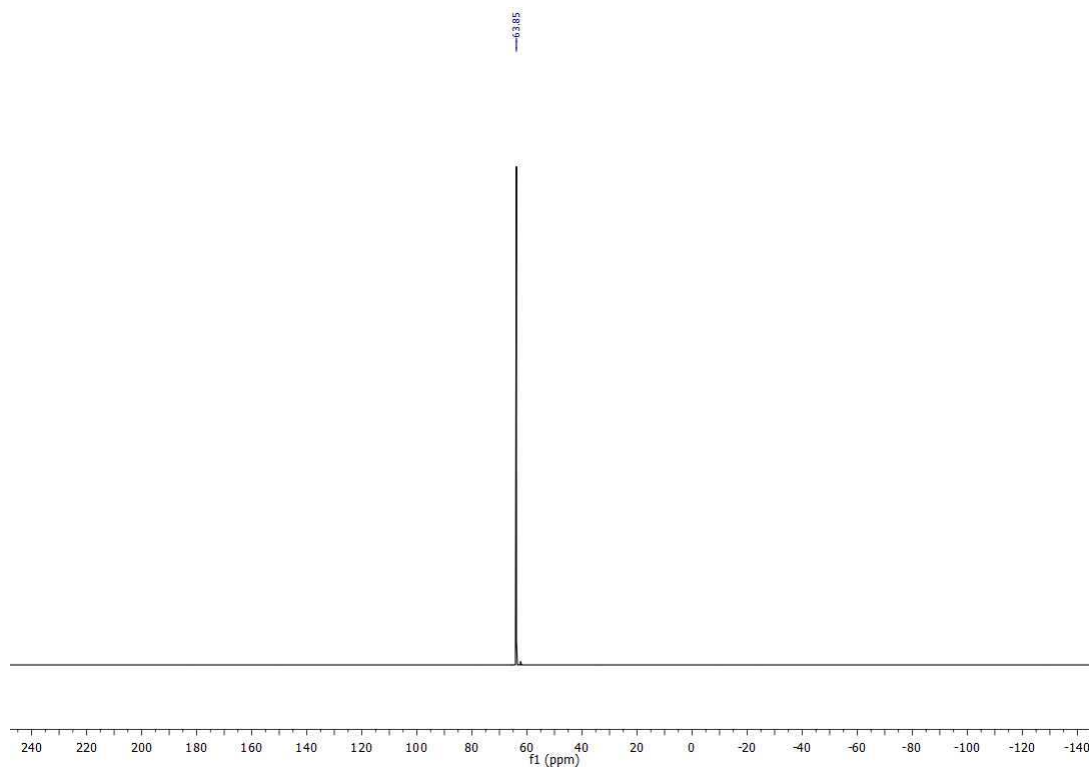
^{11}B NMR (96 MHz, CD_2Cl_2 , 298K) spectrum of (12)



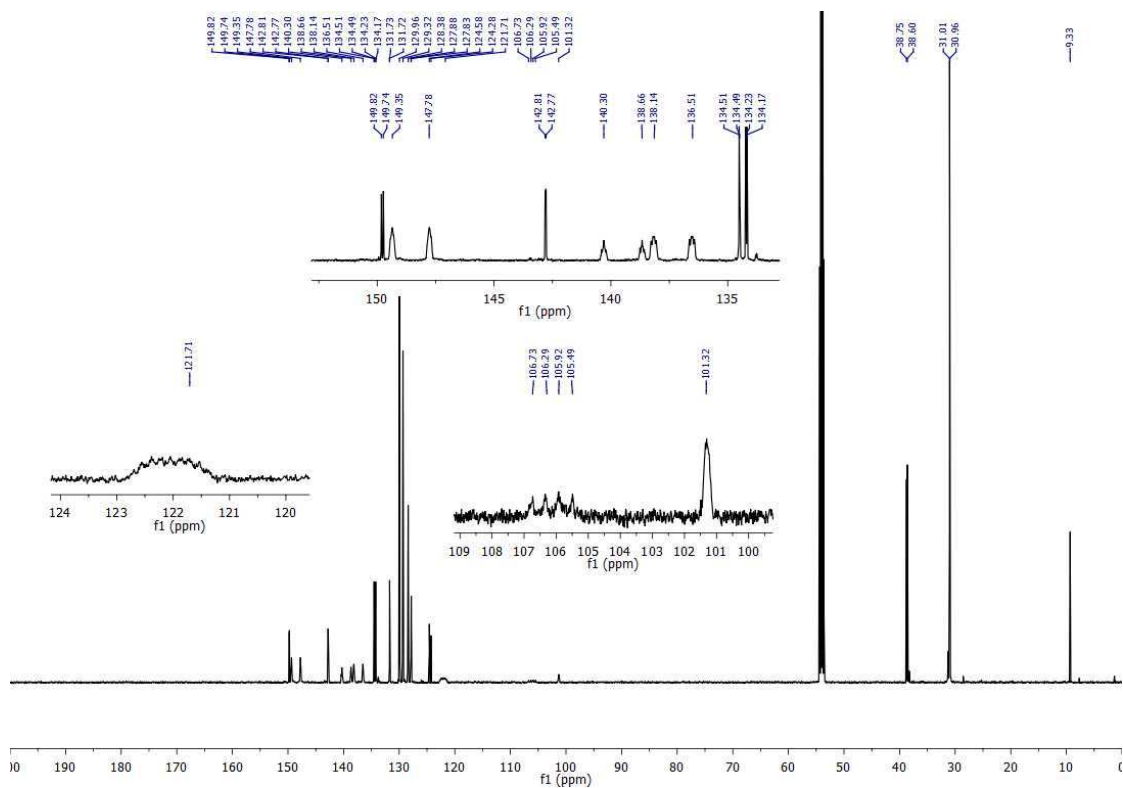
^{19}F NMR (470 MHz, CD_2Cl_2 , 298K) spectrum of (12)



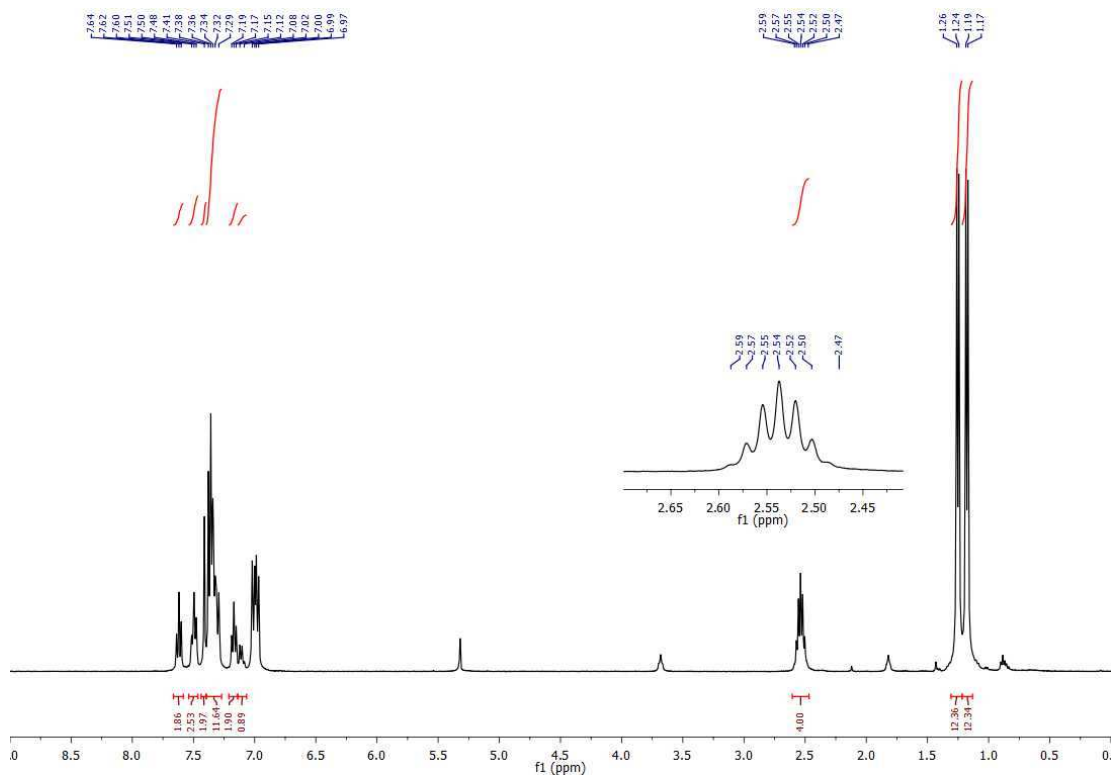
^{31}P NMR (243 MHz, CD_2Cl_2 , 298K) spectrum of (12)



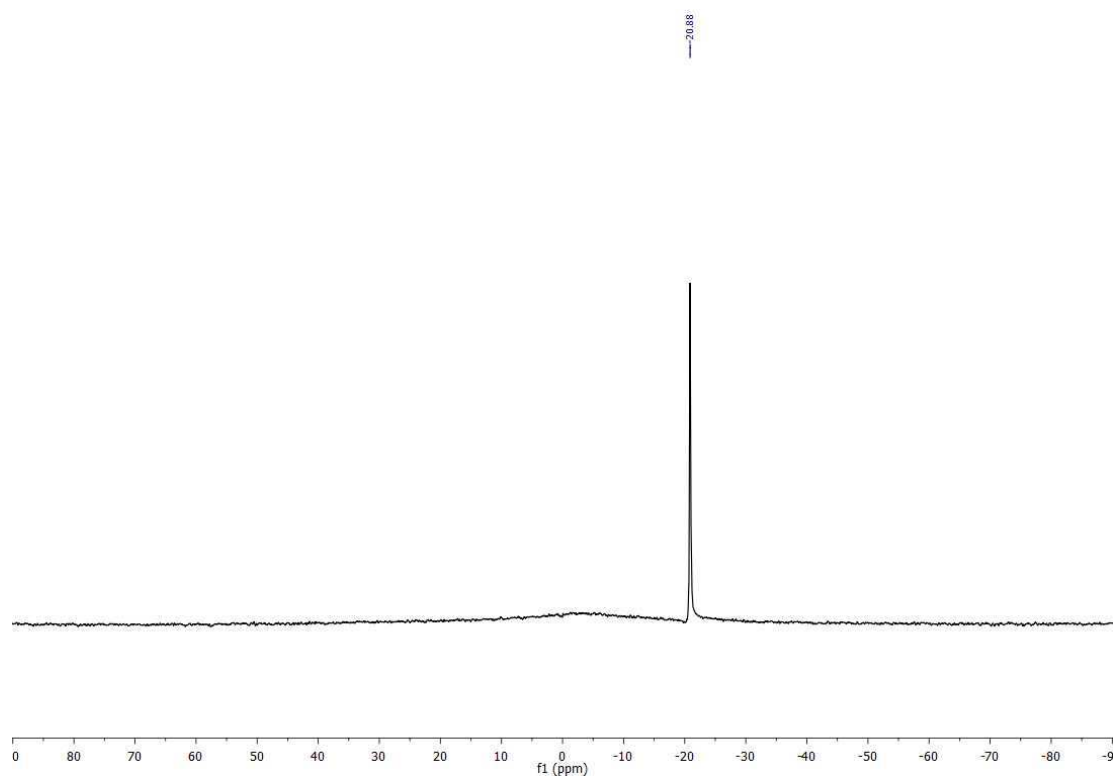
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298K) spectrum of (12)



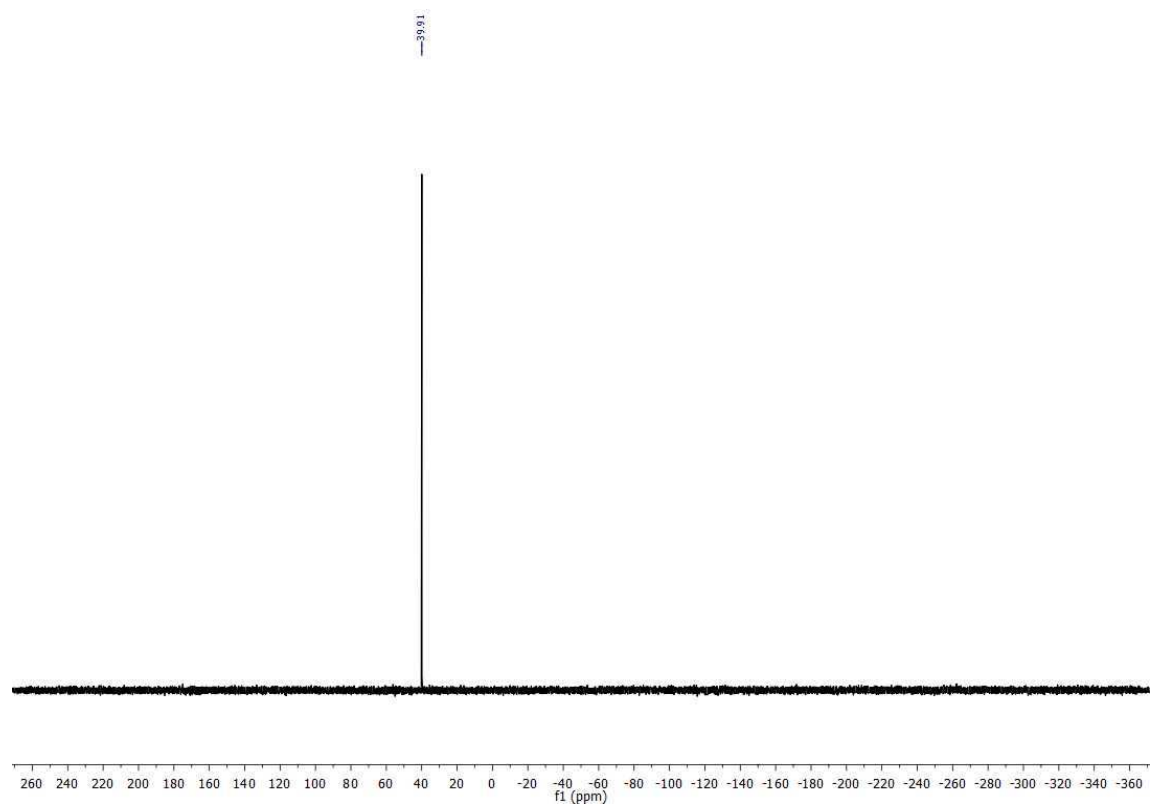
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (13)



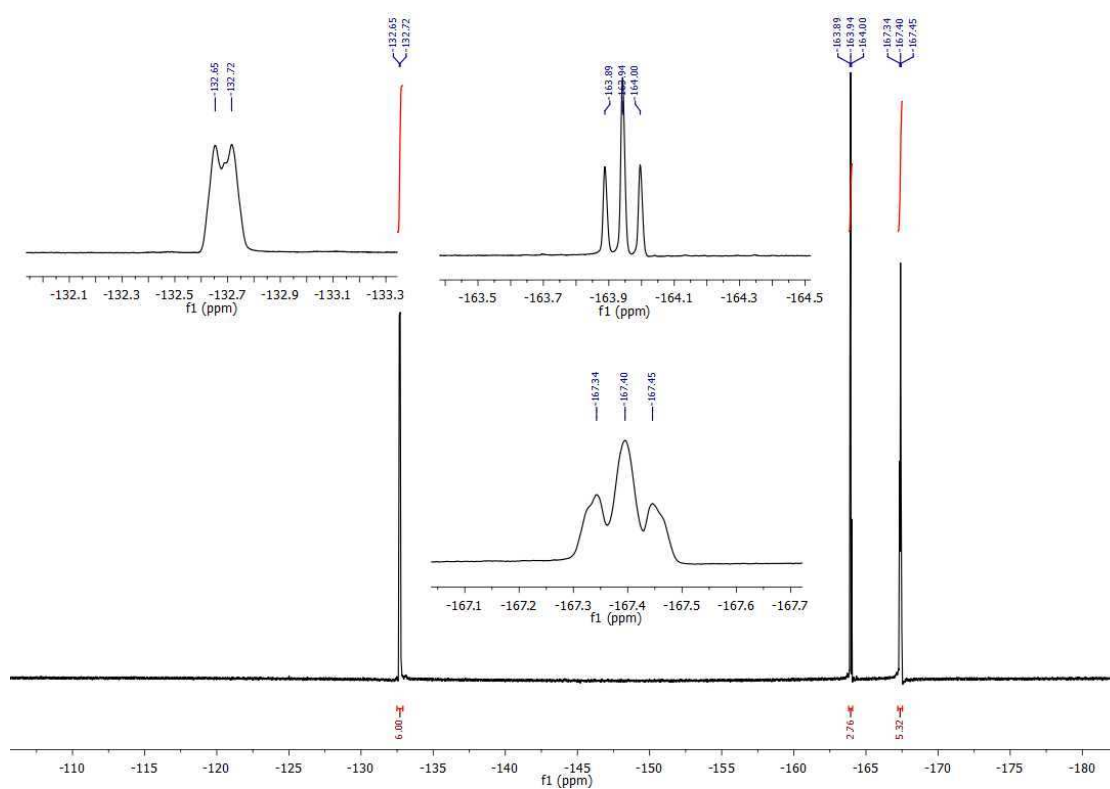
^{11}B NMR (128 MHz, CD_2Cl_2 , 298K) spectrum of (13)



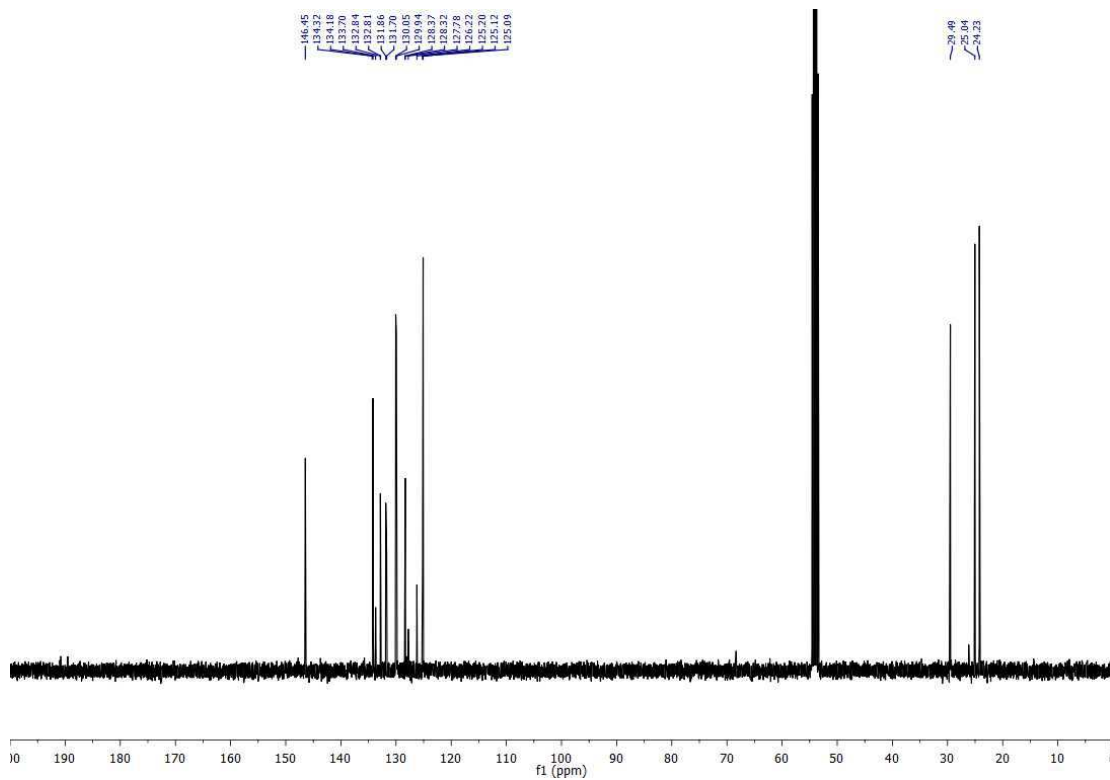
^{31}P NMR (162 MHz, CD_2Cl_2 , 298K) spectrum of (13)



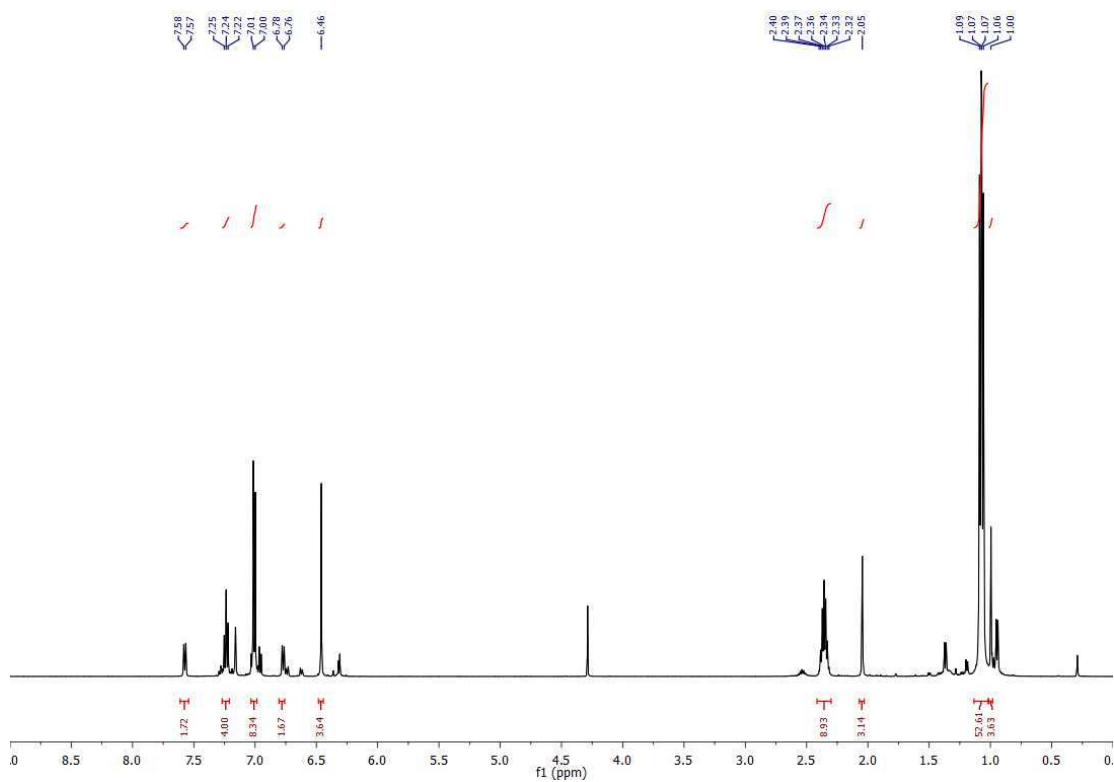
^{19}F NMR (377 MHz, CD_2Cl_2 , 298K) spectrum of (13)



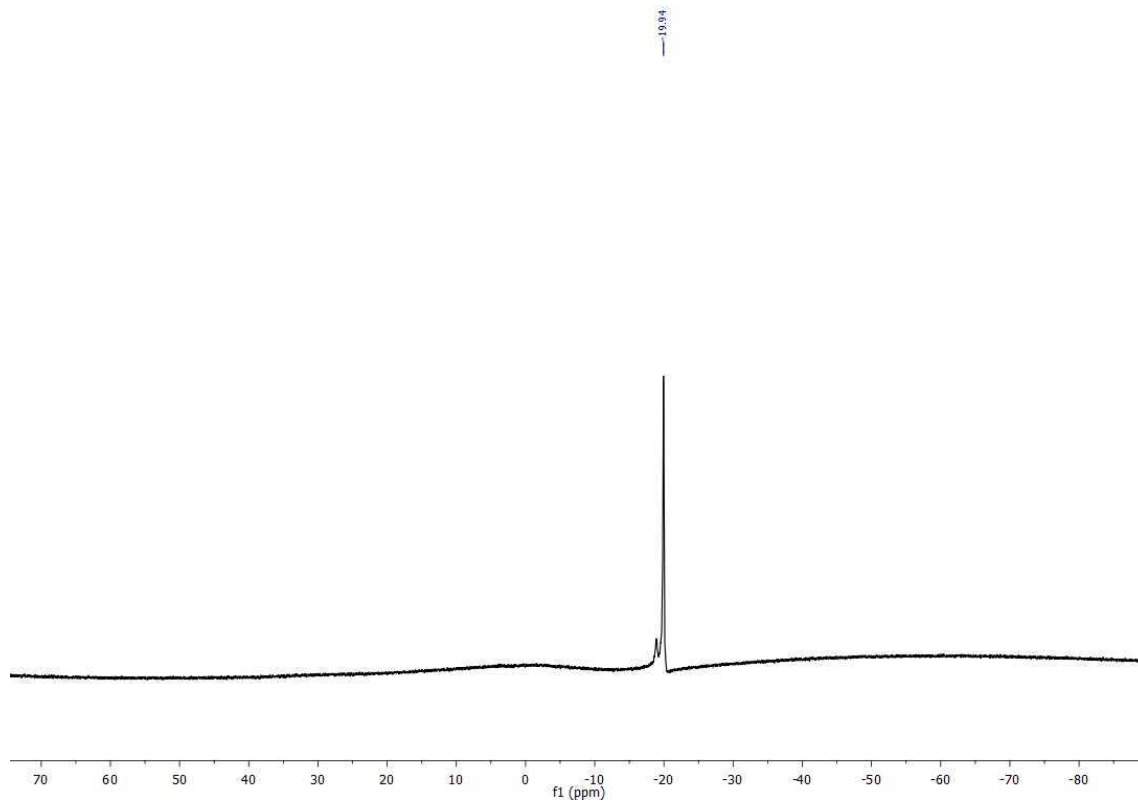
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CD_2Cl_2 , 298K) spectrum of (13)



^1H NMR (500 MHz, C_6D_6 , 298K) spectrum of (14)



^{11}B NMR (160 MHz, C_6D_6 , 298K) spectrum of (14)



13C NMR spectrum of compound 10a in CDCl₃.

Chemical structure of 10a: CC1=CC=C(C=C1)C(=O)N(C)C2=CC=CC=C2

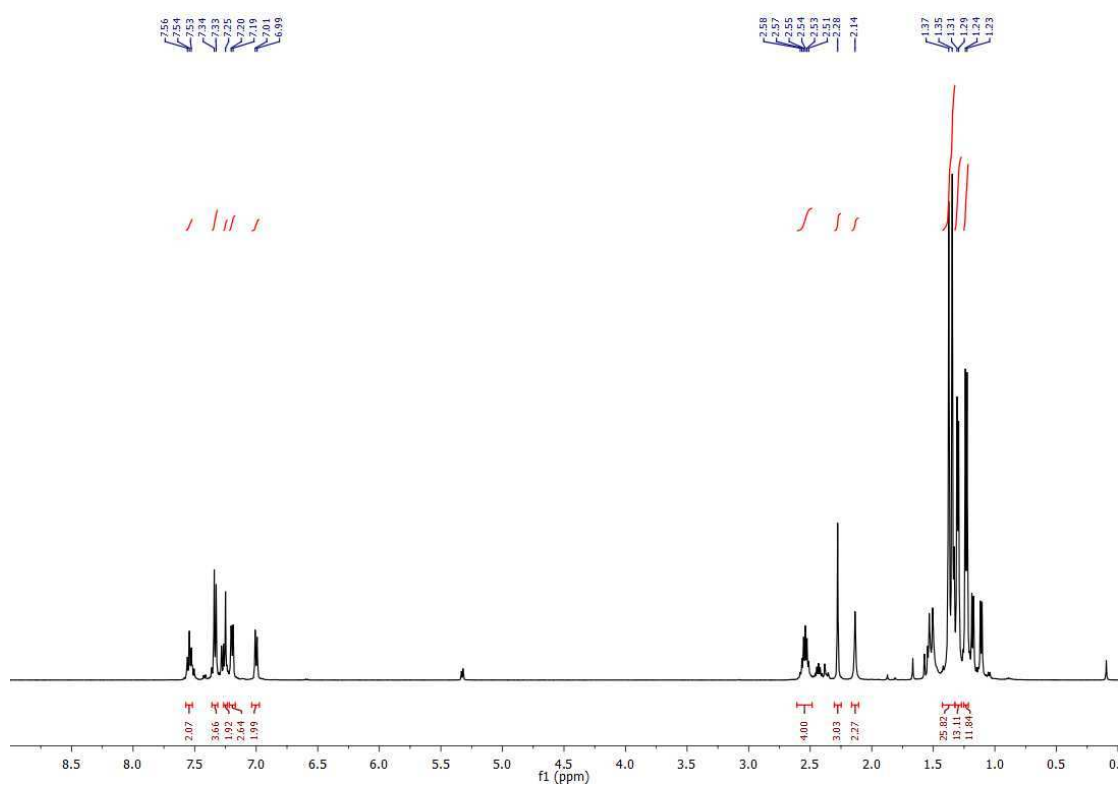
Peak list (ppm):

- 149.86, 147.77, 146.30, 139.80, 137.76, 137.70, 136.28, 136.02, 134.52, 131.52, 131.42, 129.06, 128.46, 128.81, 124.66
- 40.09, 39.94, 32.66, 29.37, 25.18, 24.06, 21.57
- 7.40

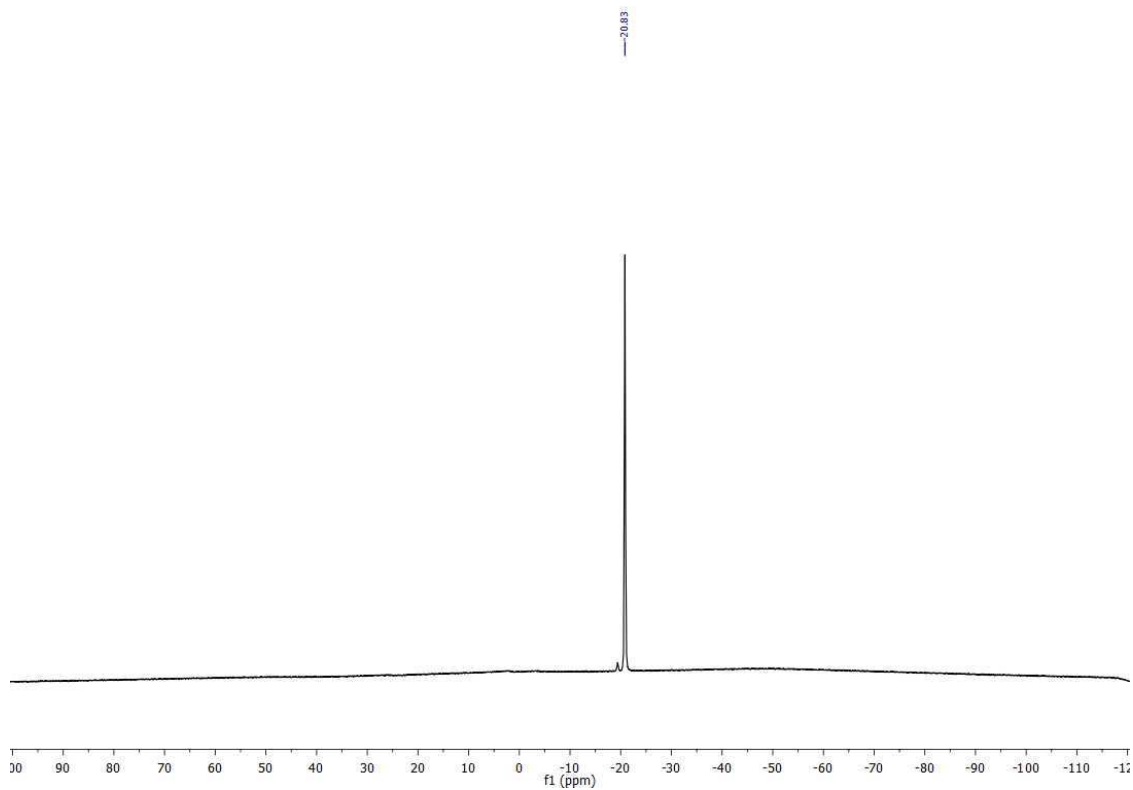
Inset peak list (ppm):

- 149.86, 147.77, 146.30, 139.80, 137.70, 136.28, 136.02, 134.52, 131.42, 128.46, 124.66

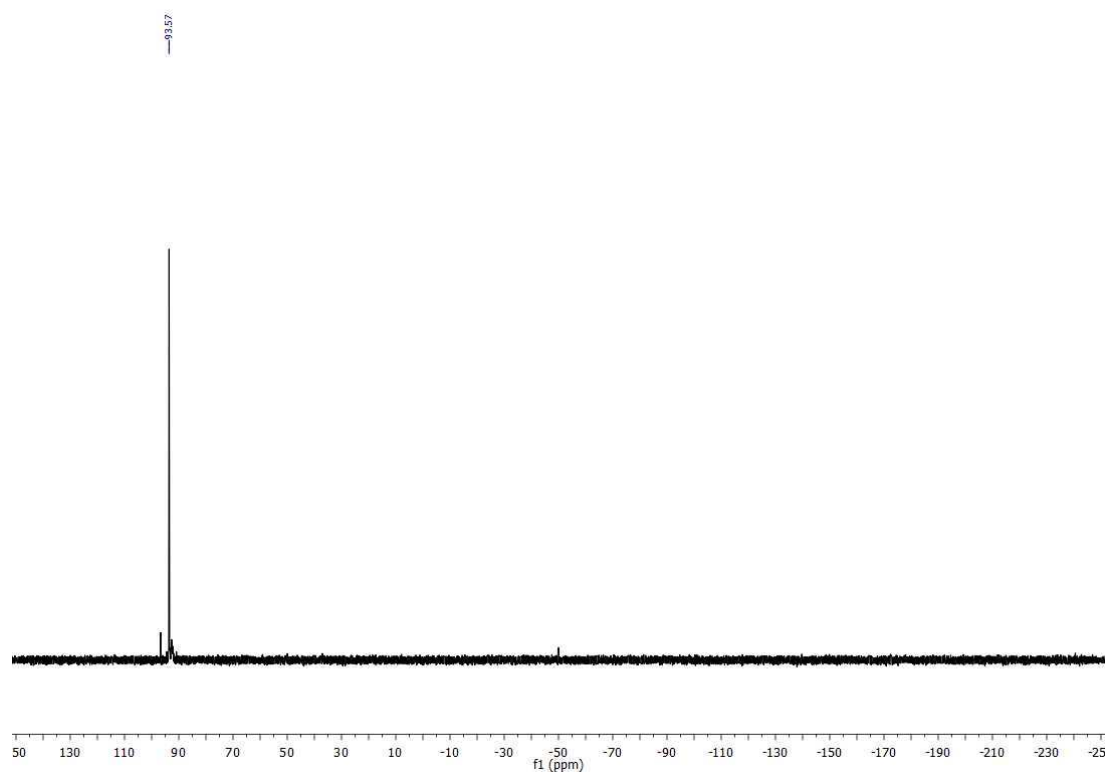
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (15)



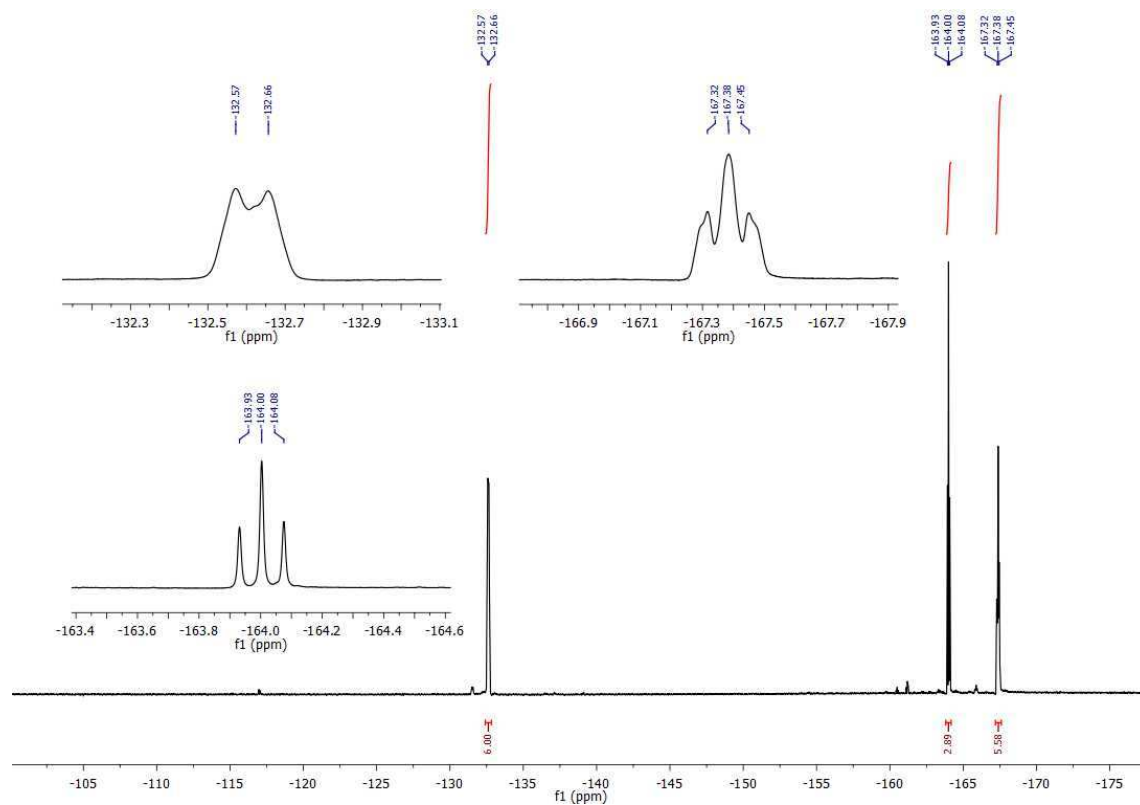
^{11}B NMR (96 MHz, CD_2Cl_2 , 298K) spectrum of (15)



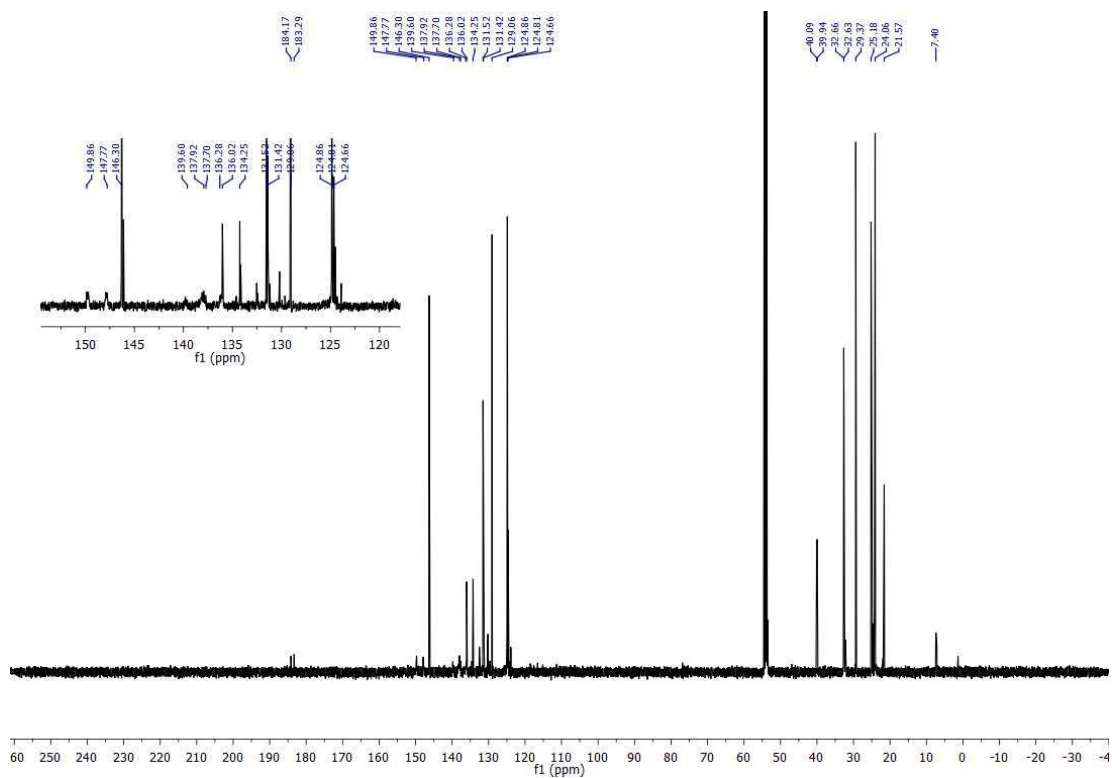
^{31}P NMR (121 MHz, CD_2Cl_2 , 298K) spectrum of (15)



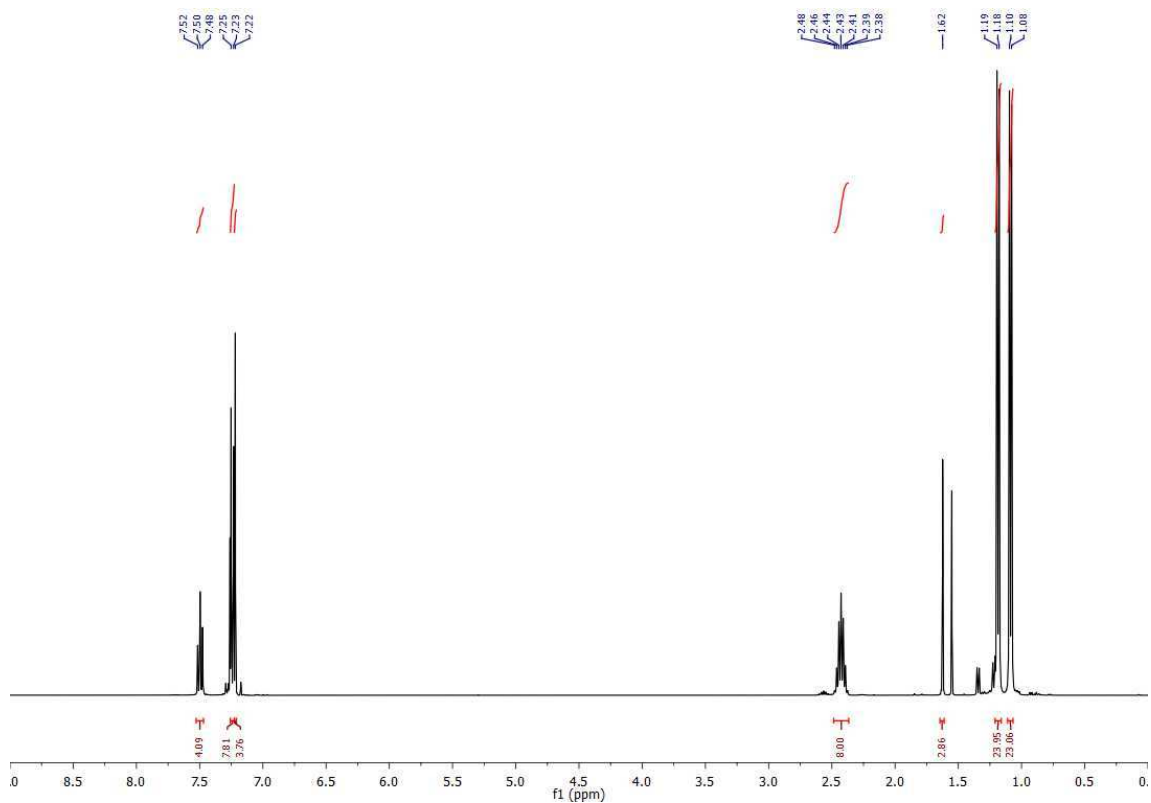
^{19}F NMR (282 MHz, CD_2Cl_2 , 298K) spectrum of (15)



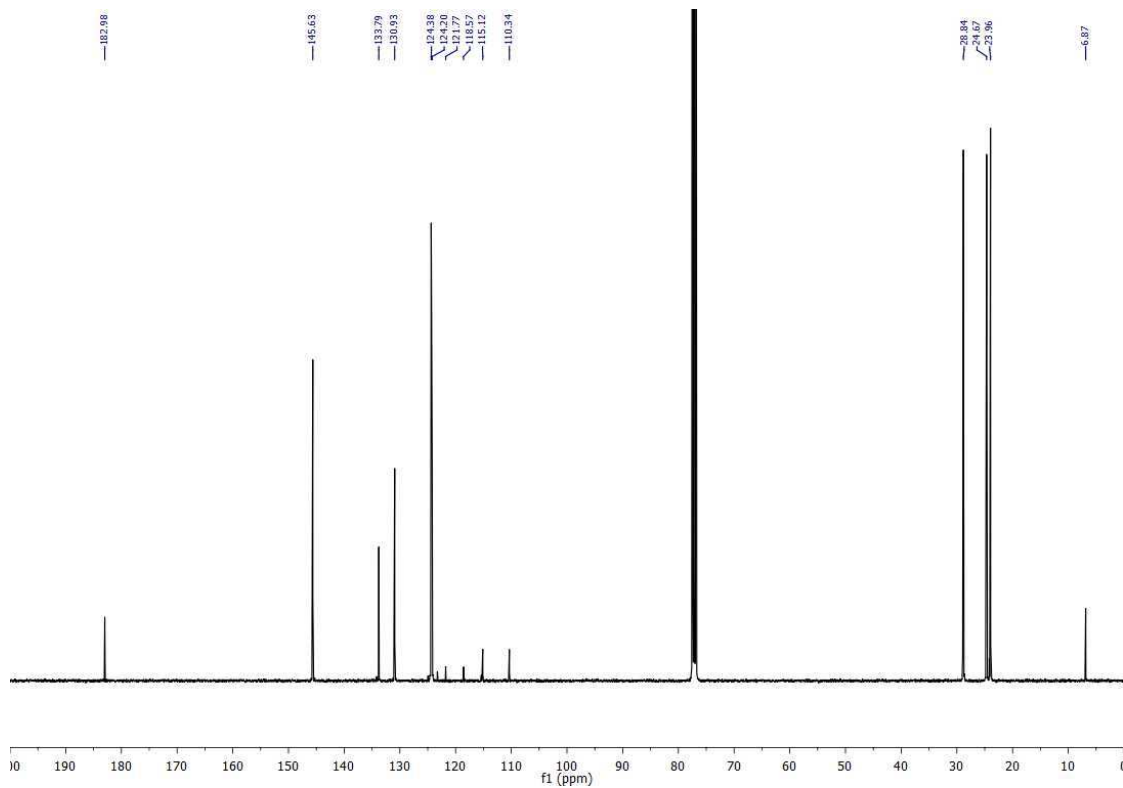
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298K) spectrum of (15)



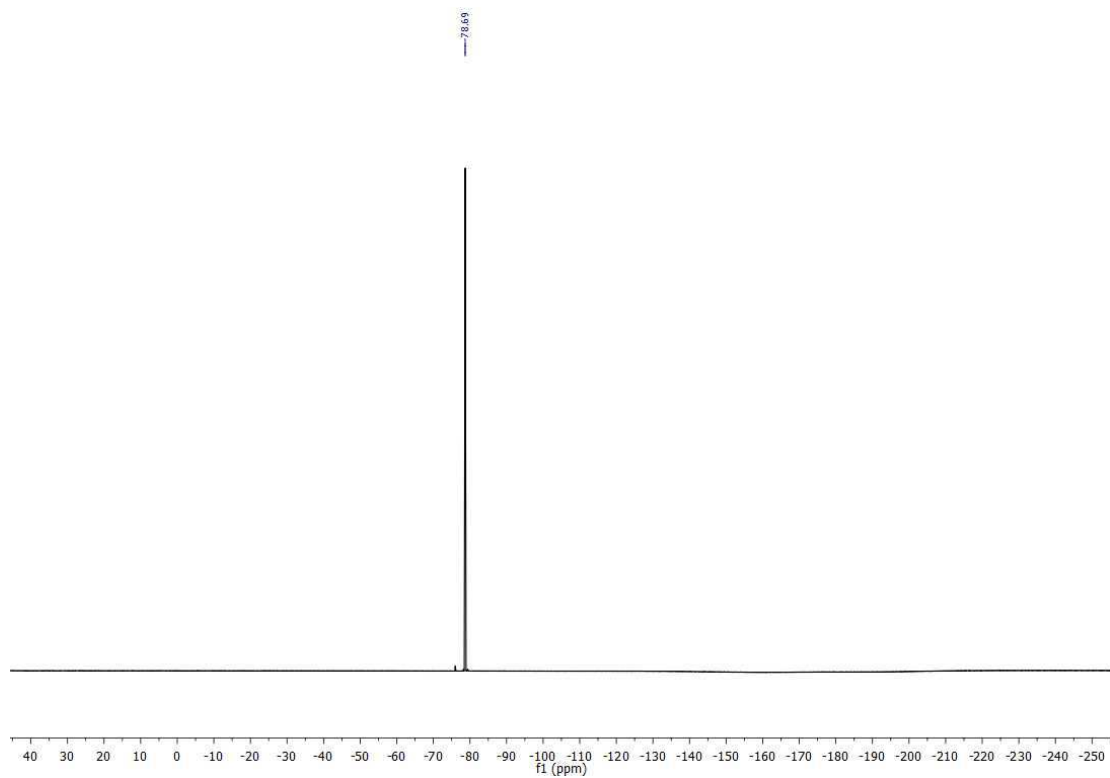
^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of (16)



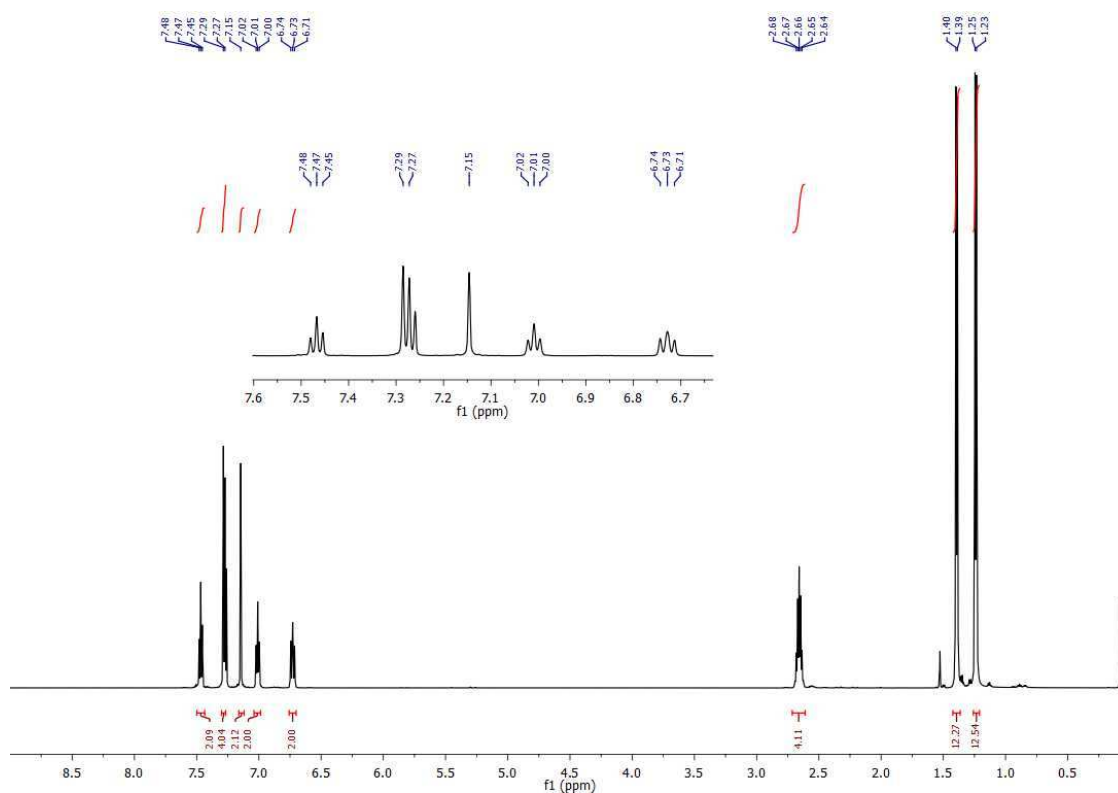
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CDCl_3 , 298K) spectrum of **(16)**



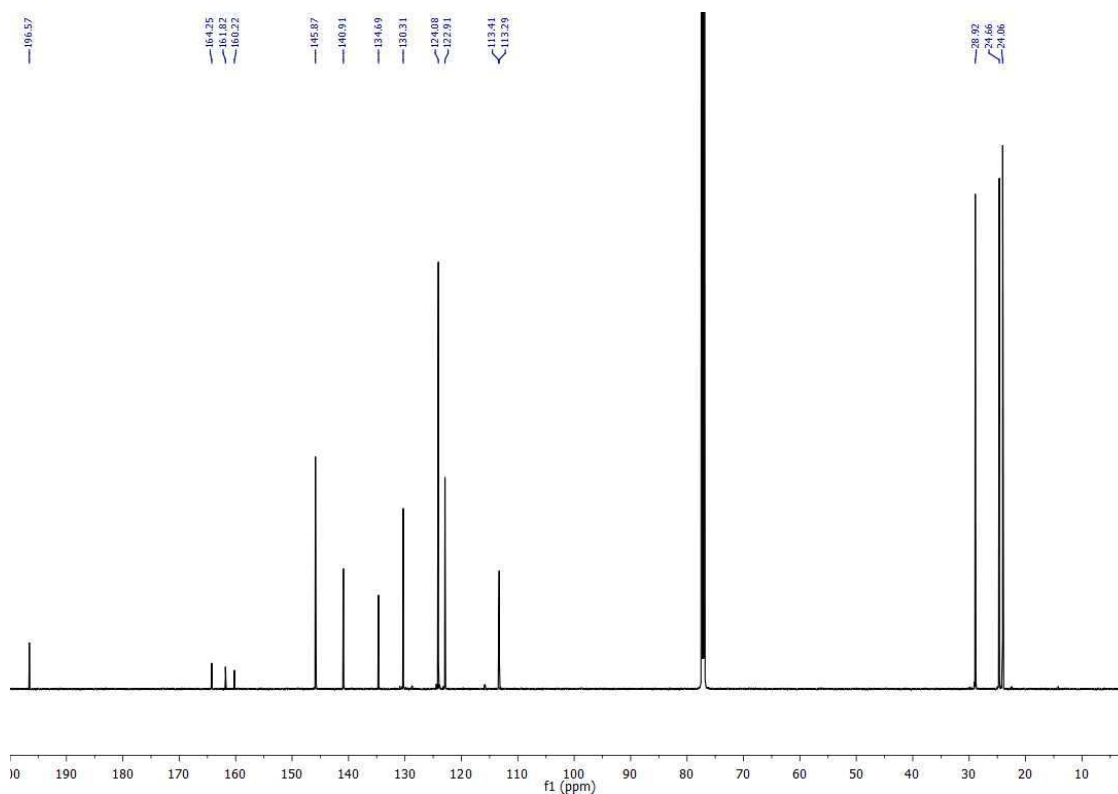
^{19}F NMR $\{^1\text{H}\}$ (283 MHz, CDCl_3 , 298K) spectrum of **(16)**



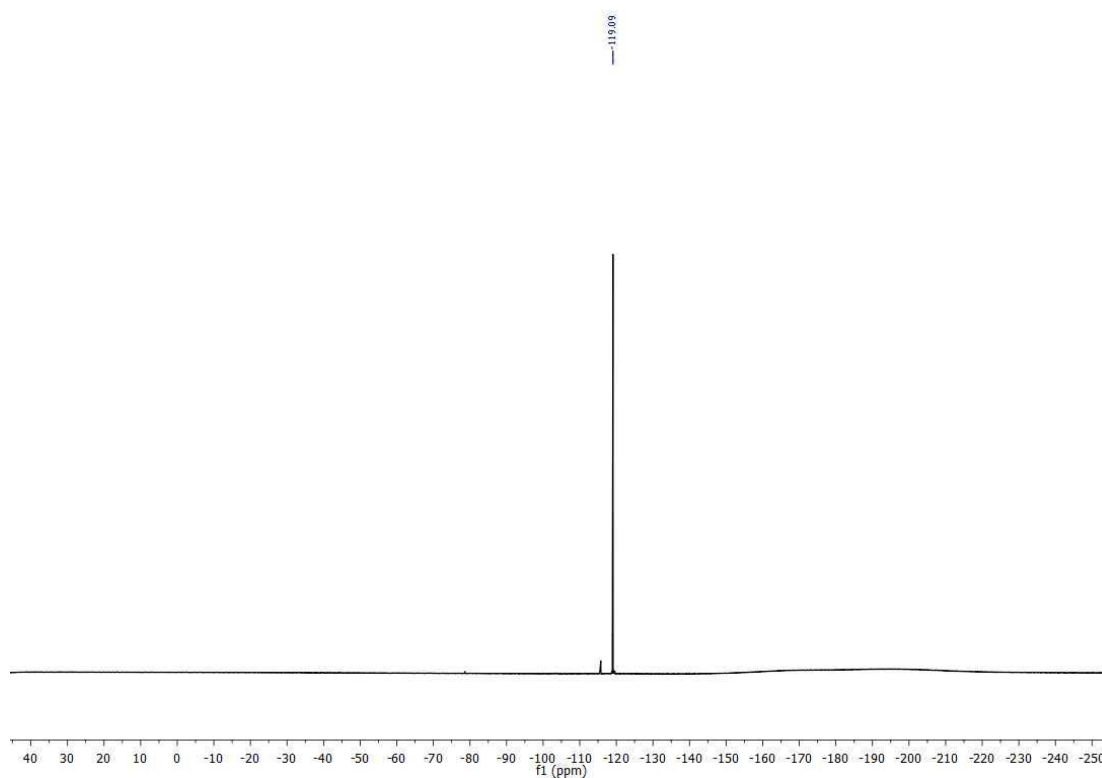
^1H NMR (300 MHz, CDCl_3 , 298K) spectrum of (17)



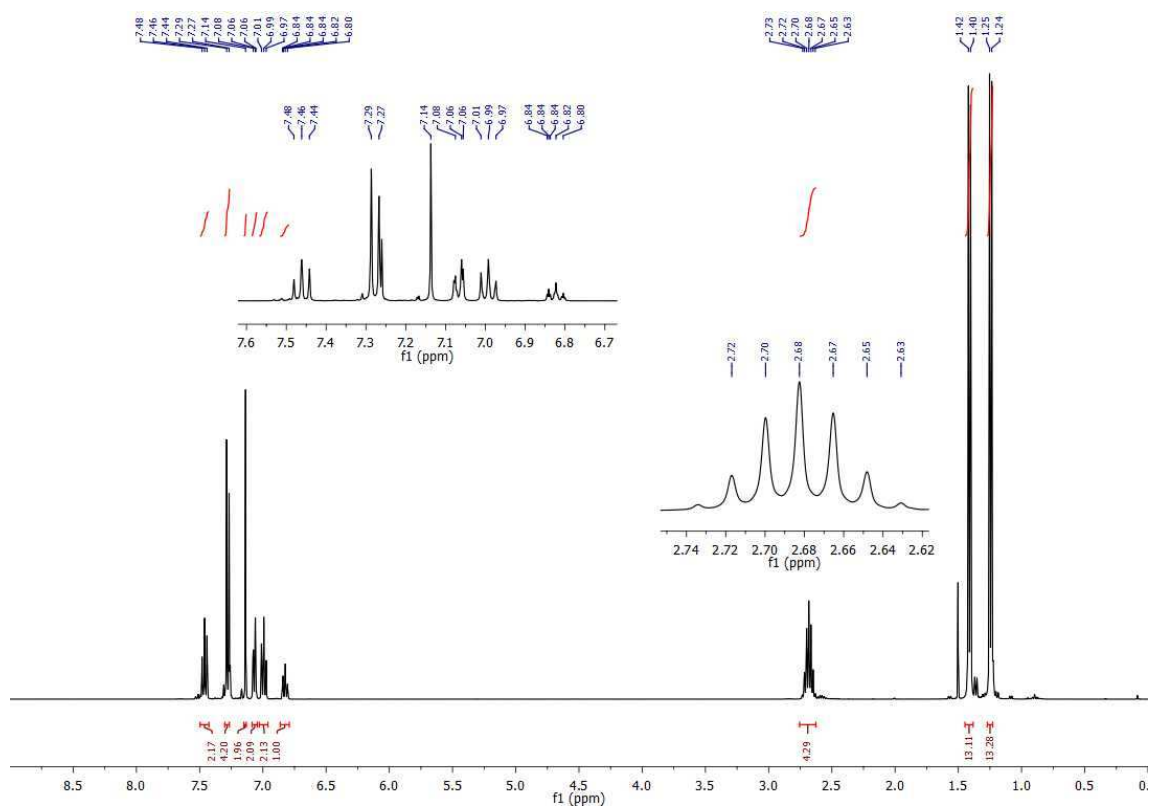
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CDCl_3 , 298K) spectrum of (17)



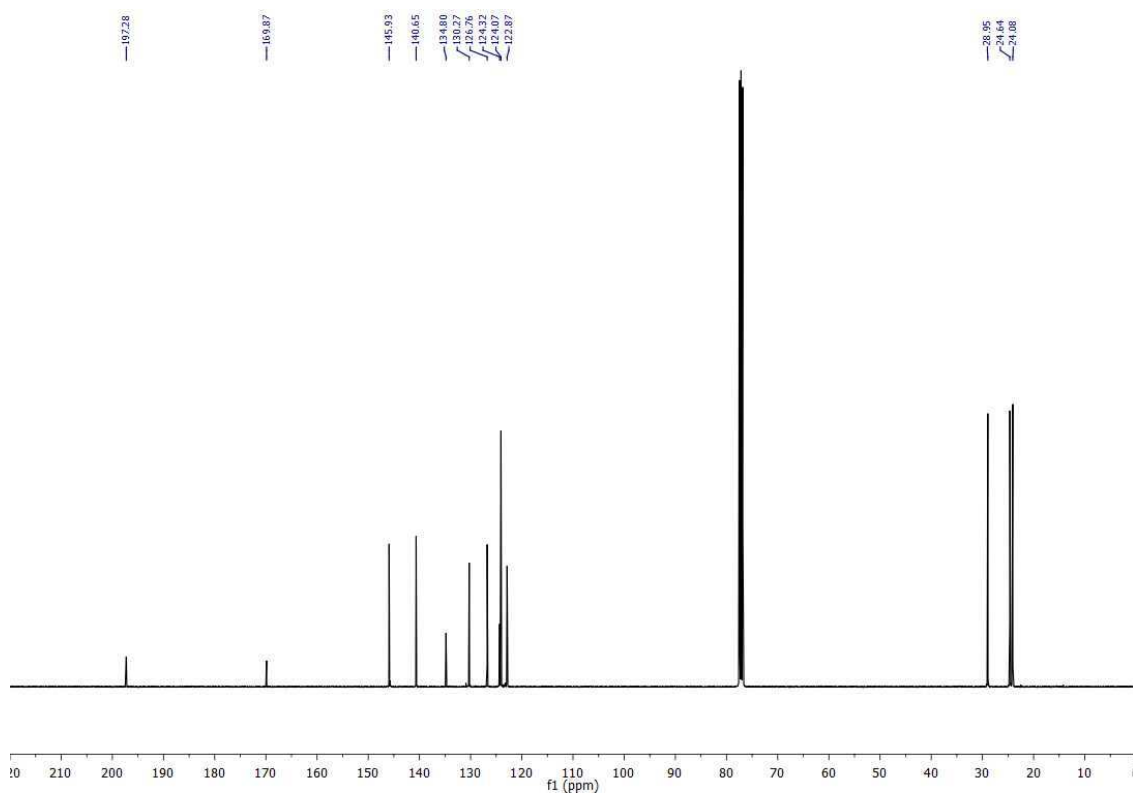
^{19}F NMR $\{^1\text{H}\}$ (283 MHz, CDCl_3 , 298K) spectrum of (17)



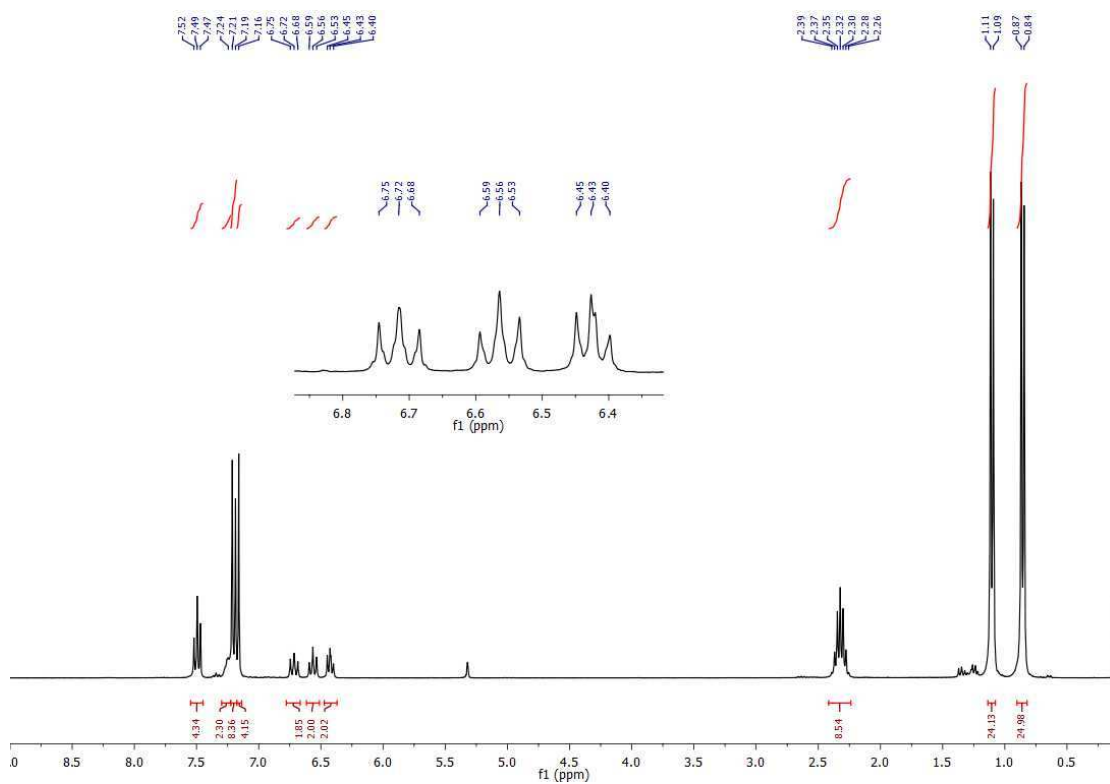
^1H NMR (400 MHz, CDCl_3 , 298K) spectrum of (18)



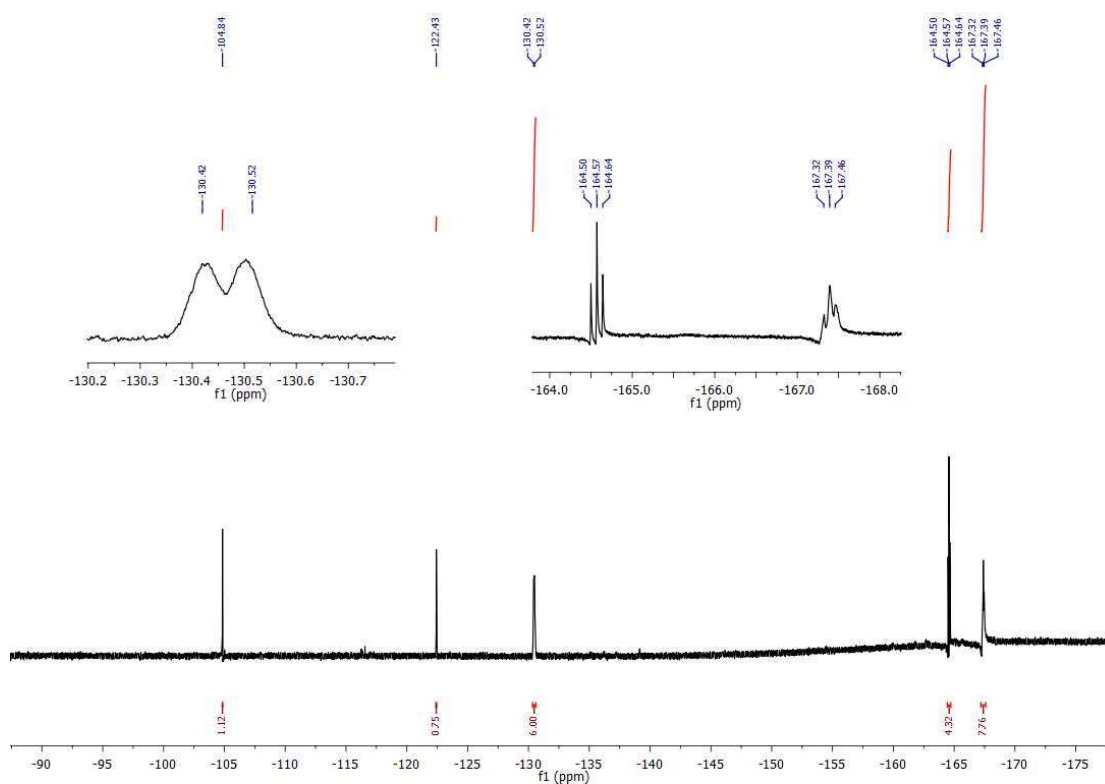
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CDCl_3 , 298K) spectrum of (**18**)



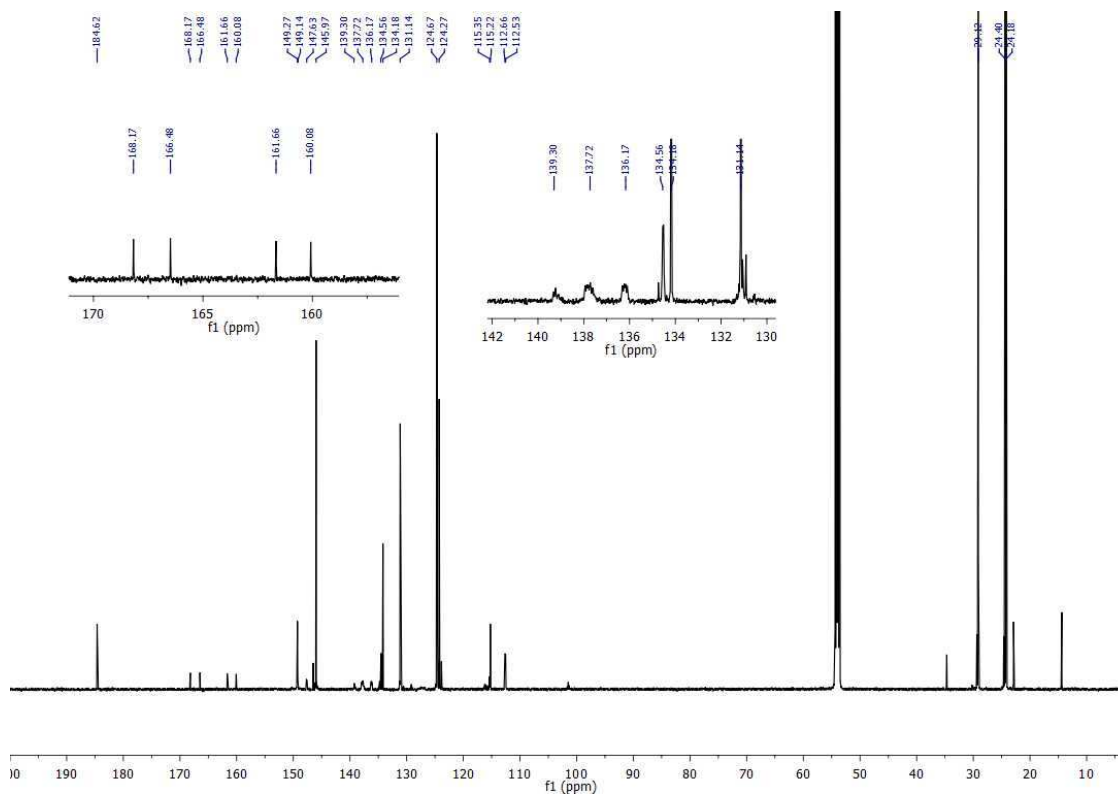
^1H NMR (300 MHz, CD_2Cl_2 , 298K) spectrum of (**19**)



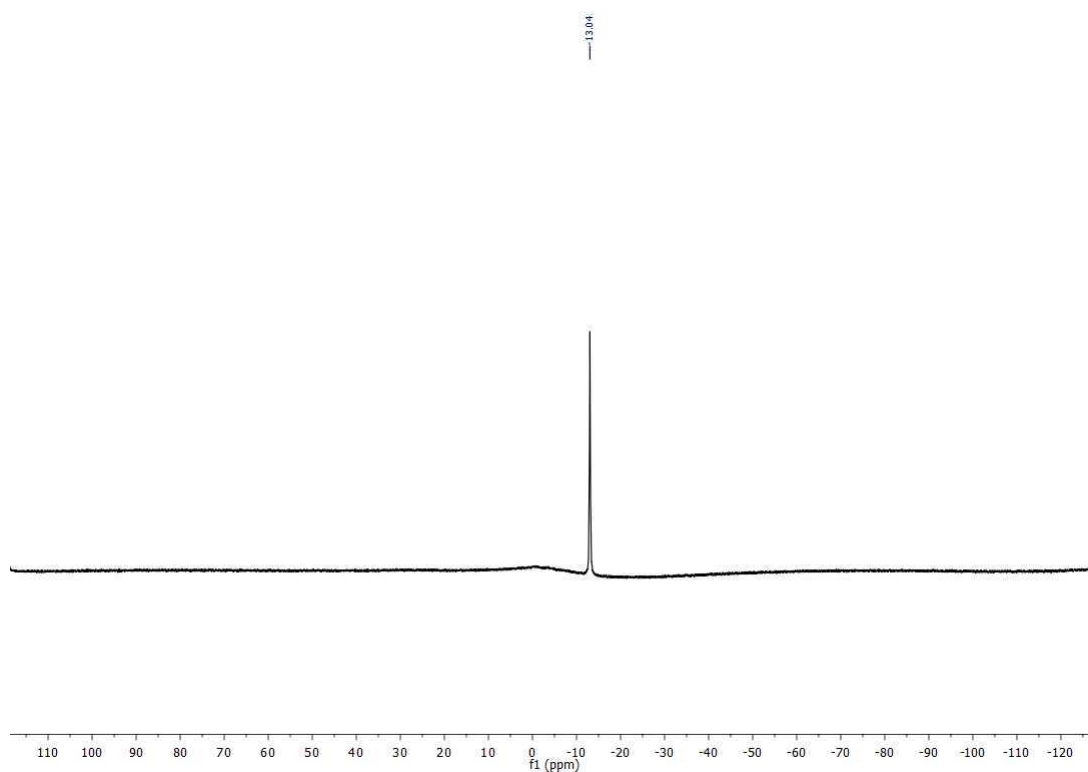
^{19}F NMR $\{^1\text{H}\}$ (283 MHz, CD_2Cl_2 , 298K) spectrum of (19)



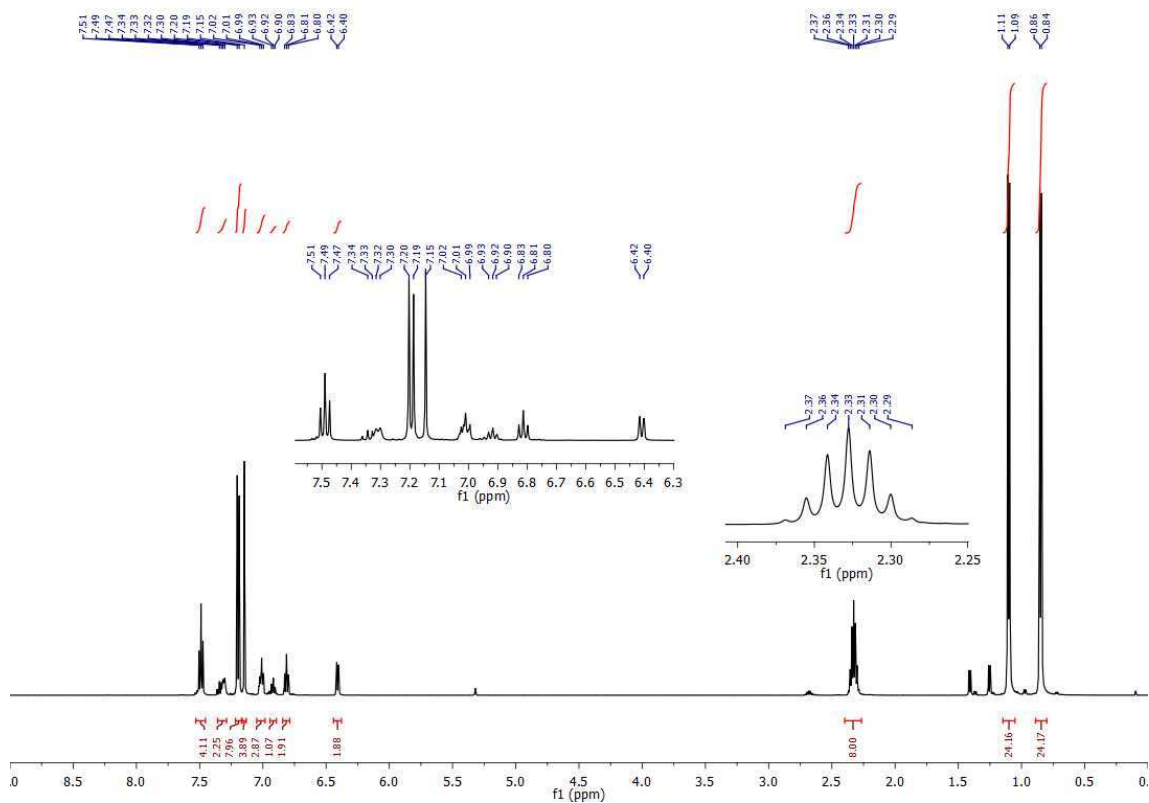
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298K) spectrum of (19)



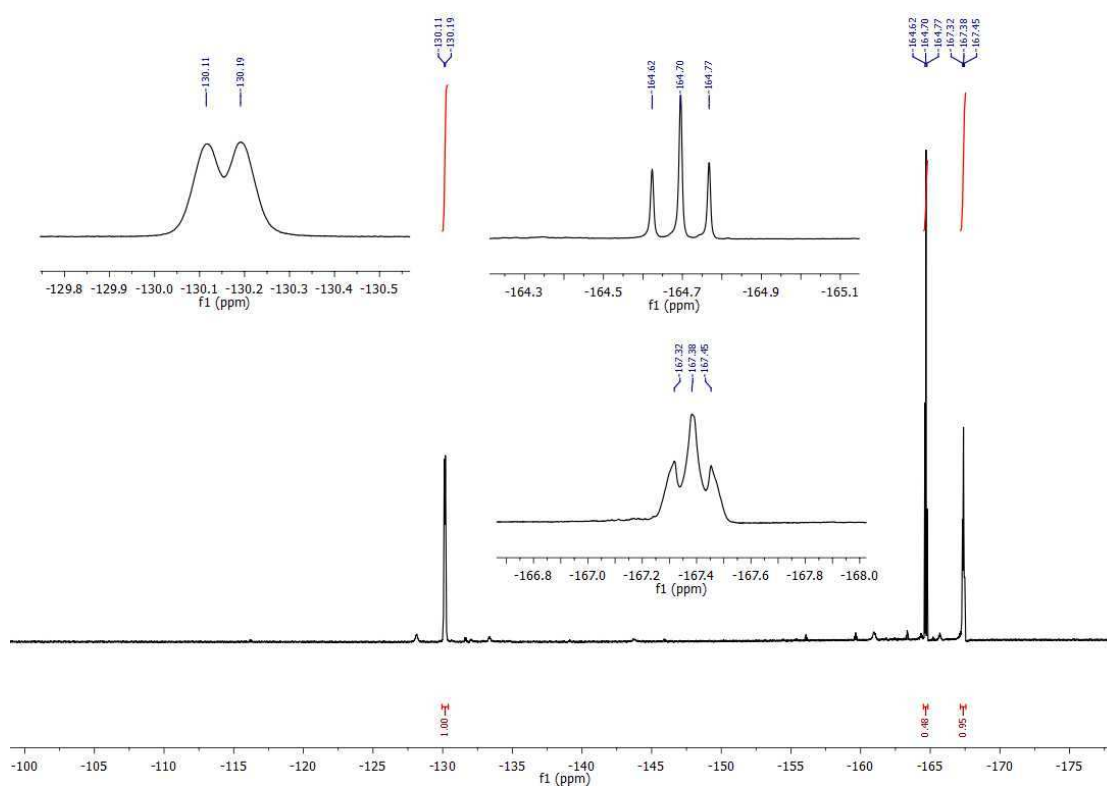
^{11}B NMR $\{^1\text{H}\}$ (96 MHz, CD_2Cl_2 , 298K) spectrum of (**19**)



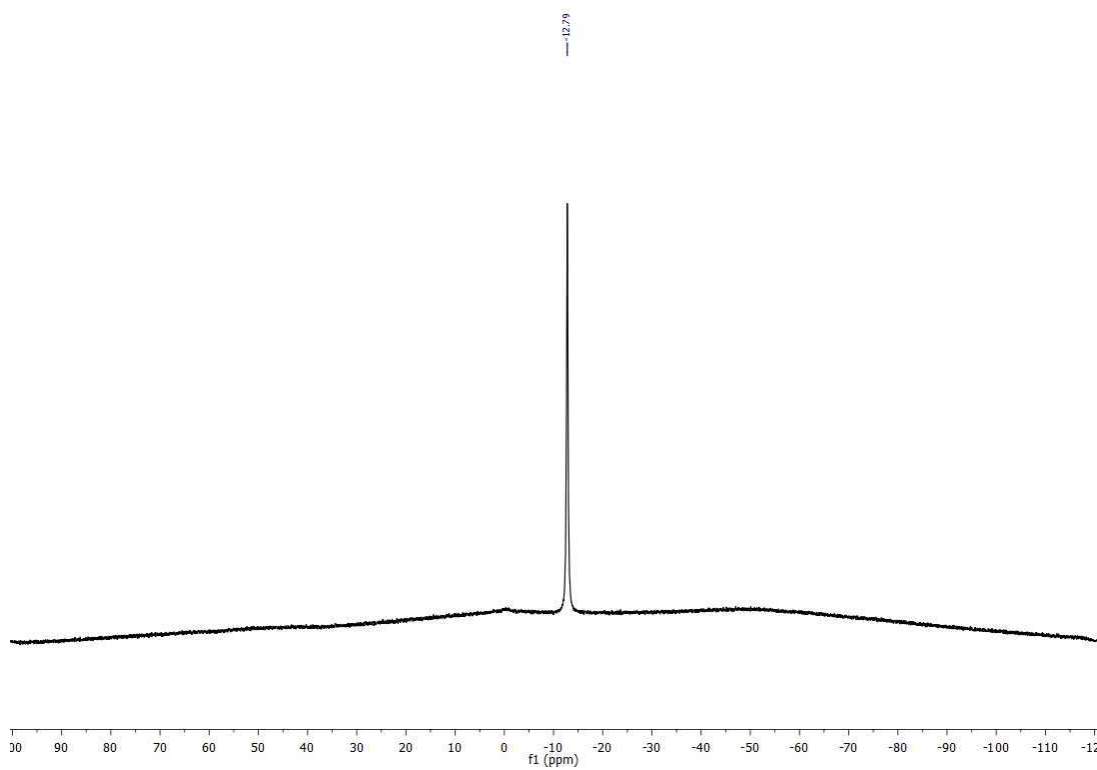
^1H NMR (600 MHz, CDCl_3 , 298K) spectrum of (**20**)



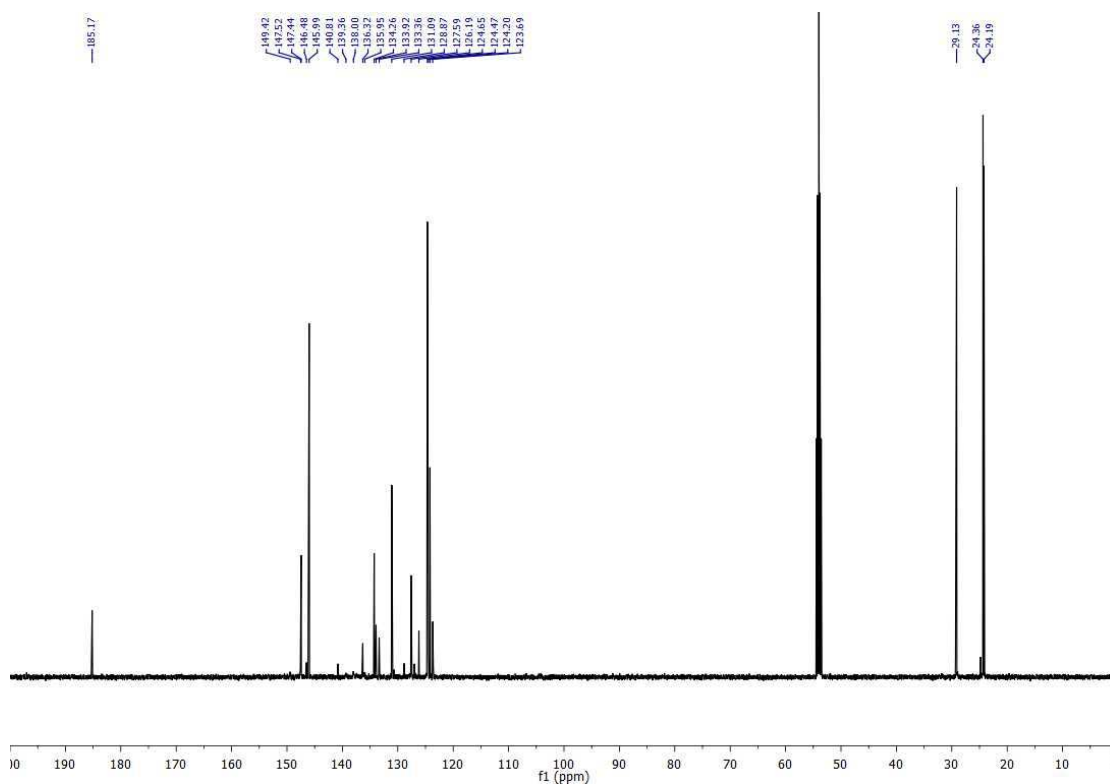
^{19}F NMR $\{^1\text{H}\}$ (283 MHz, CD_2Cl_2 , 298K) spectrum of (**20**)



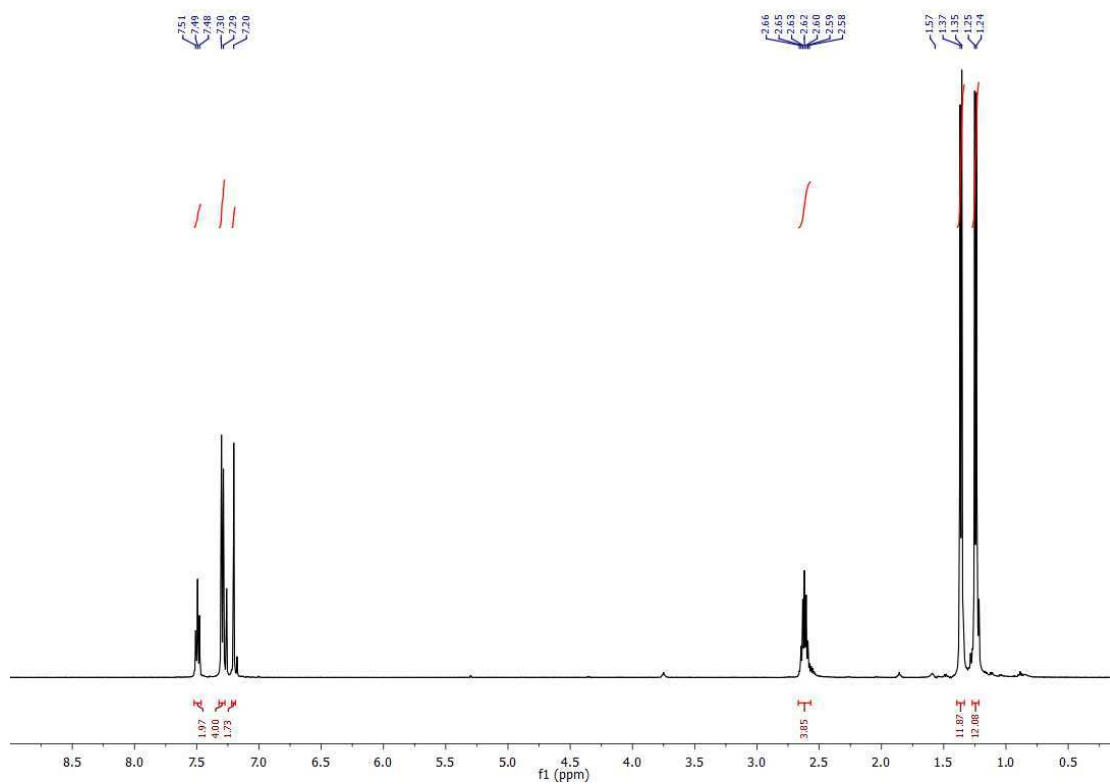
^{11}B NMR $\{^1\text{H}\}$ (96 MHz, CD_2Cl_2 , 298K) spectrum of (**20**)



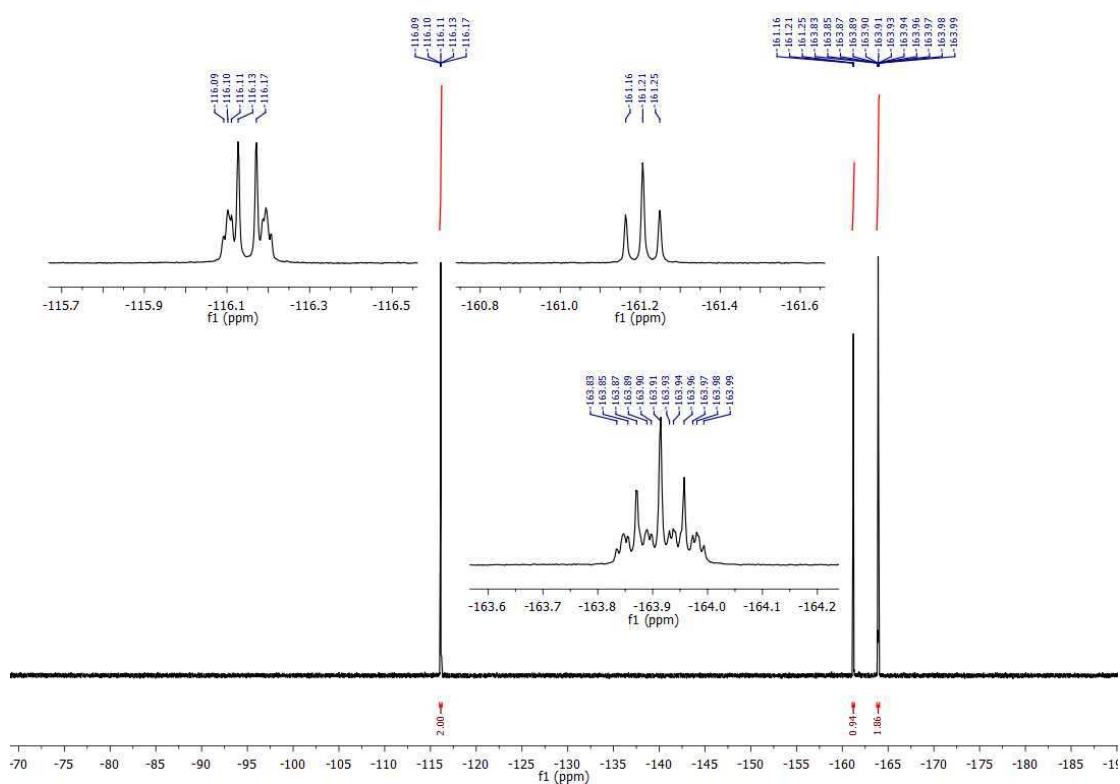
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298K) spectrum of (20)



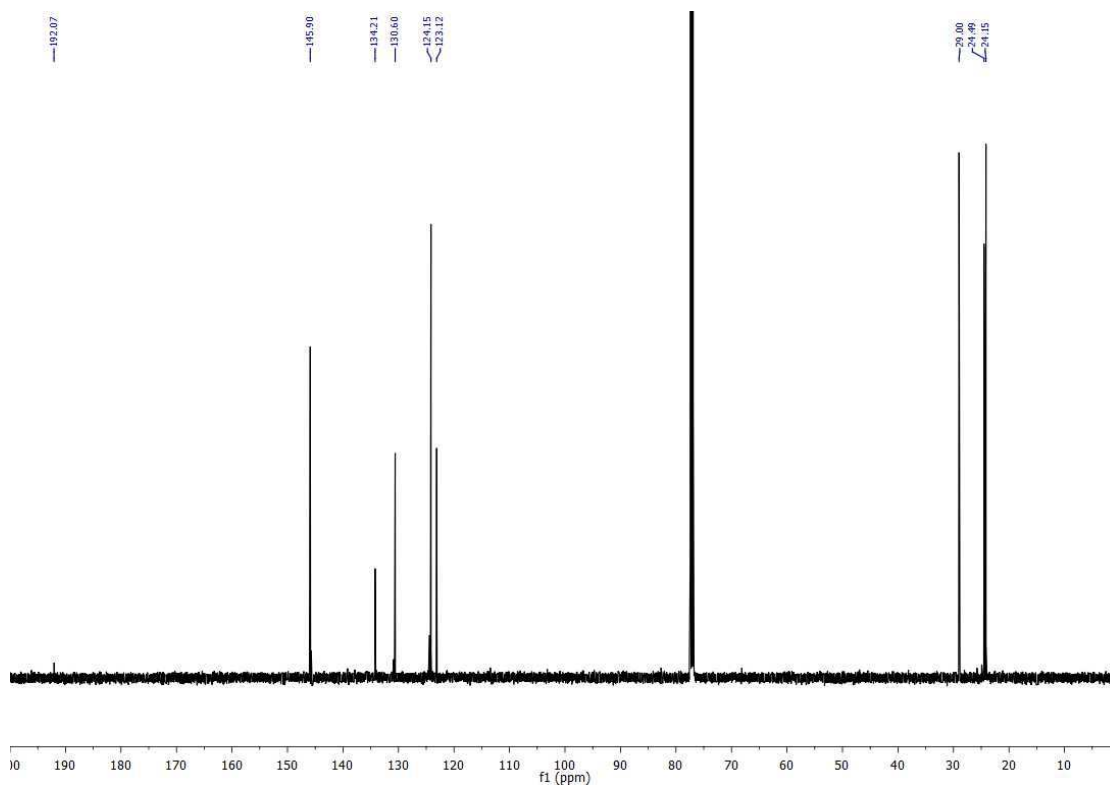
^1H NMR (500 MHz, CDCl_3 , 298K) spectrum of (21)



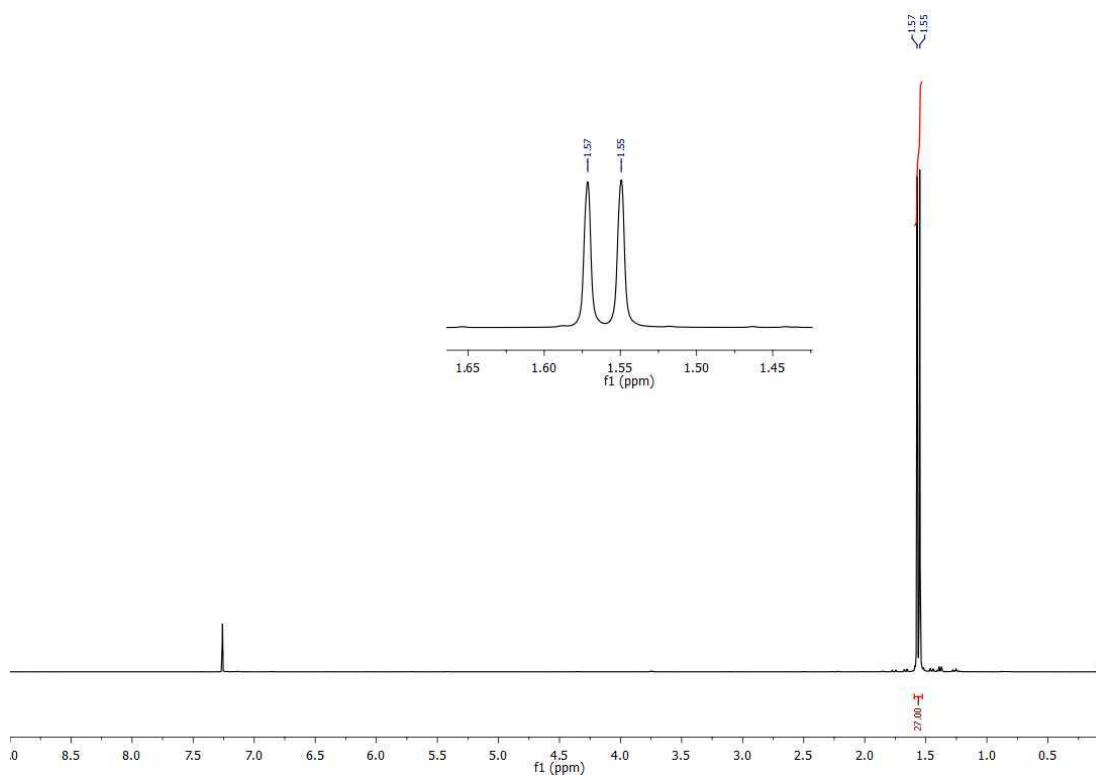
^{19}F NMR $\{^1\text{H}\}$ (470 MHz, CDCl_3 , 298K) spectrum of (**21**)



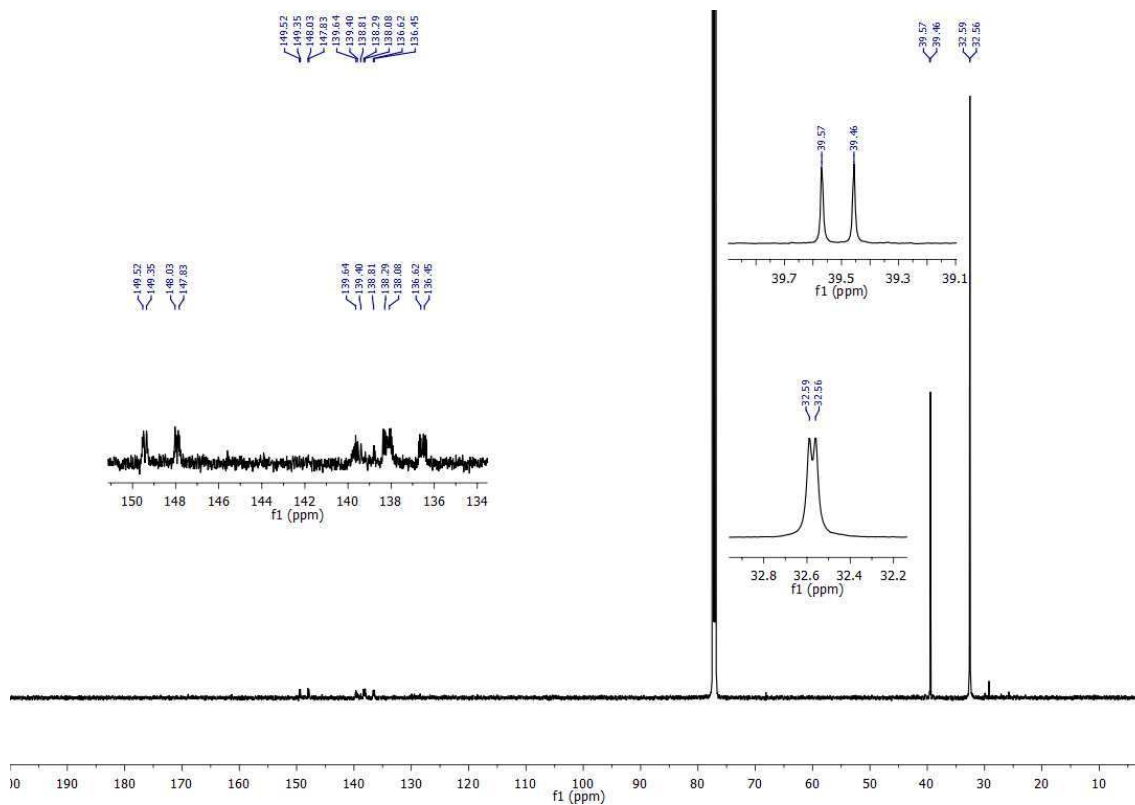
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CDCl_3 , 298K) spectrum of (**21**)



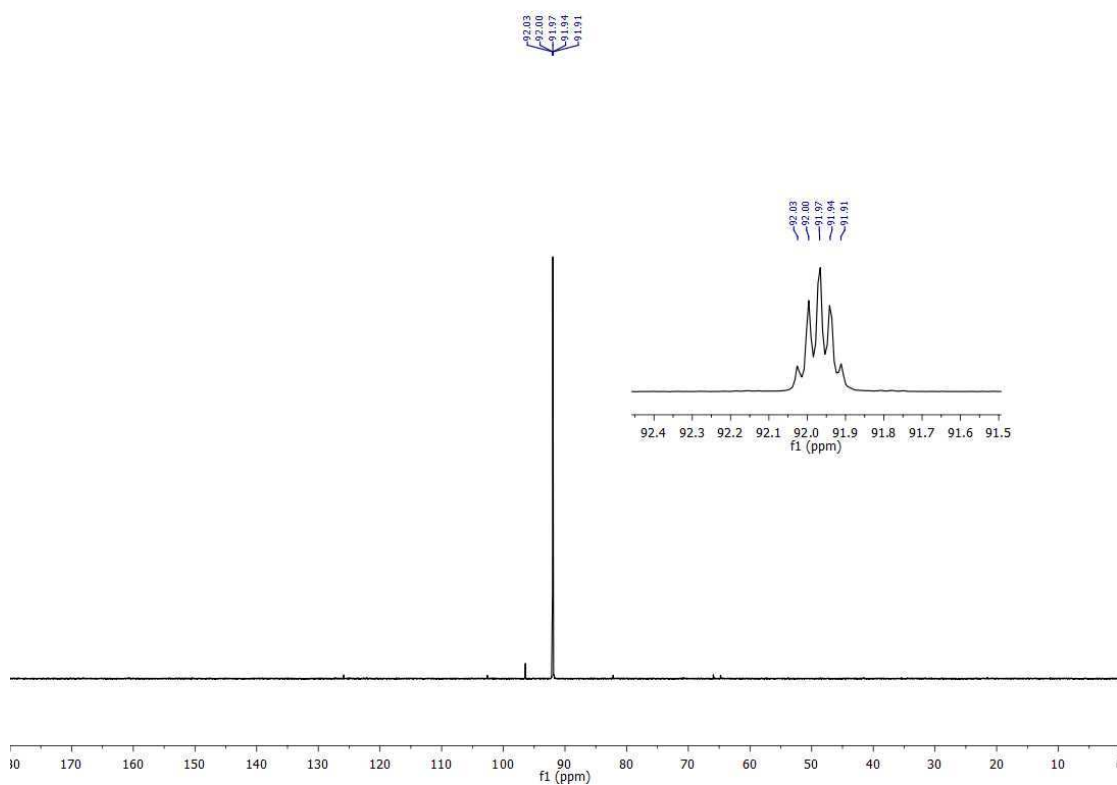
^1H NMR (600 MHz, CDCl_3 , 298K) spectrum of (22)



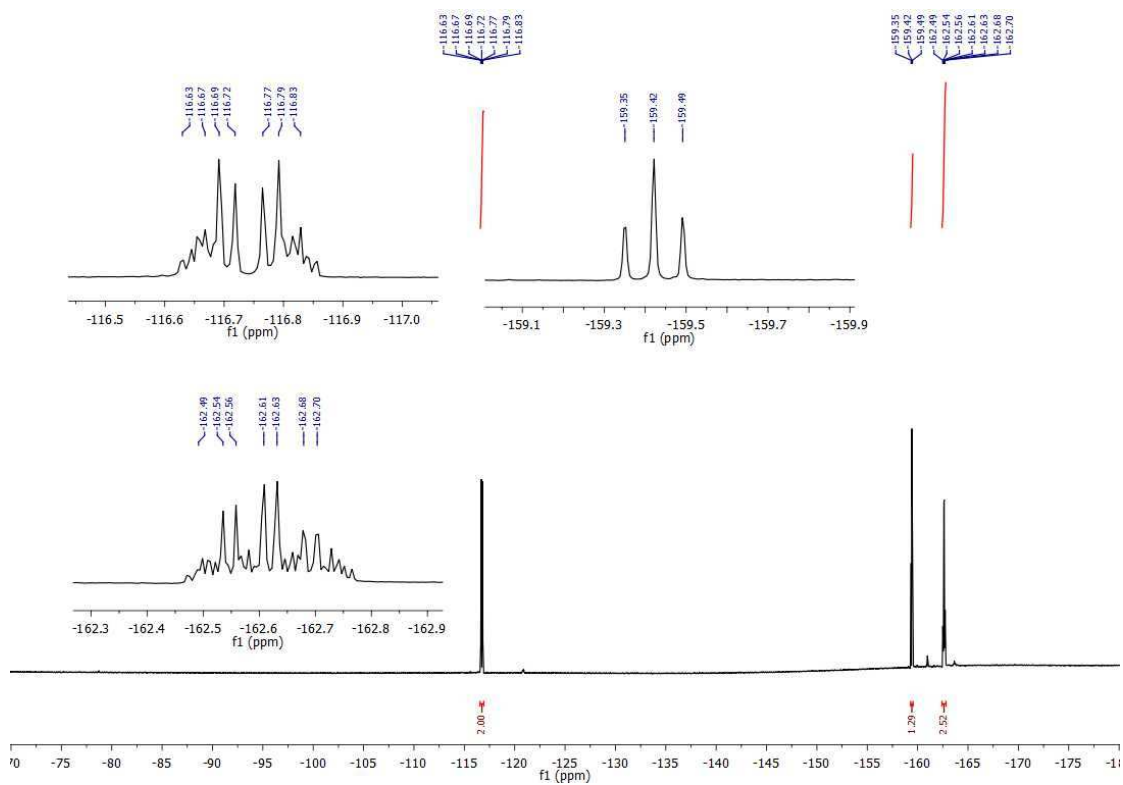
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CDCl_3 , 298K) spectrum of (22)



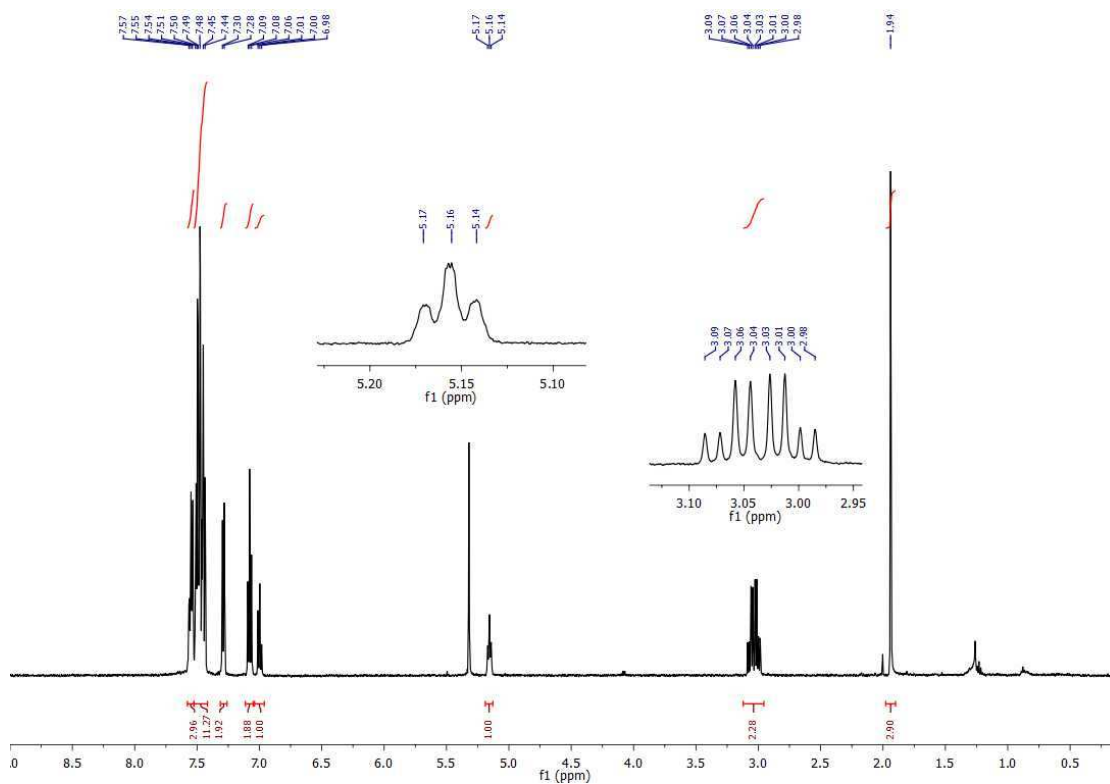
^{31}P NMR (243 MHz, CDCl_3 , 298 K) spectrum of (22)



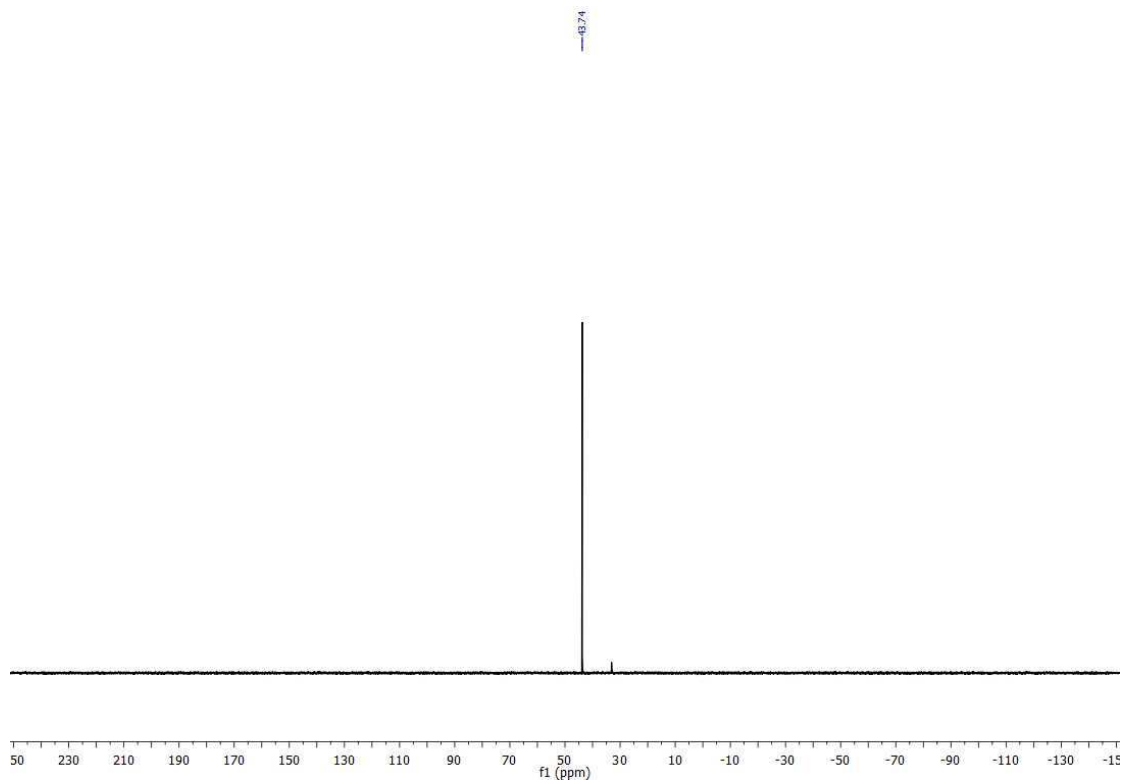
^{19}F NMR (243 MHz, CDCl_3 , 298 K) spectrum of (22)



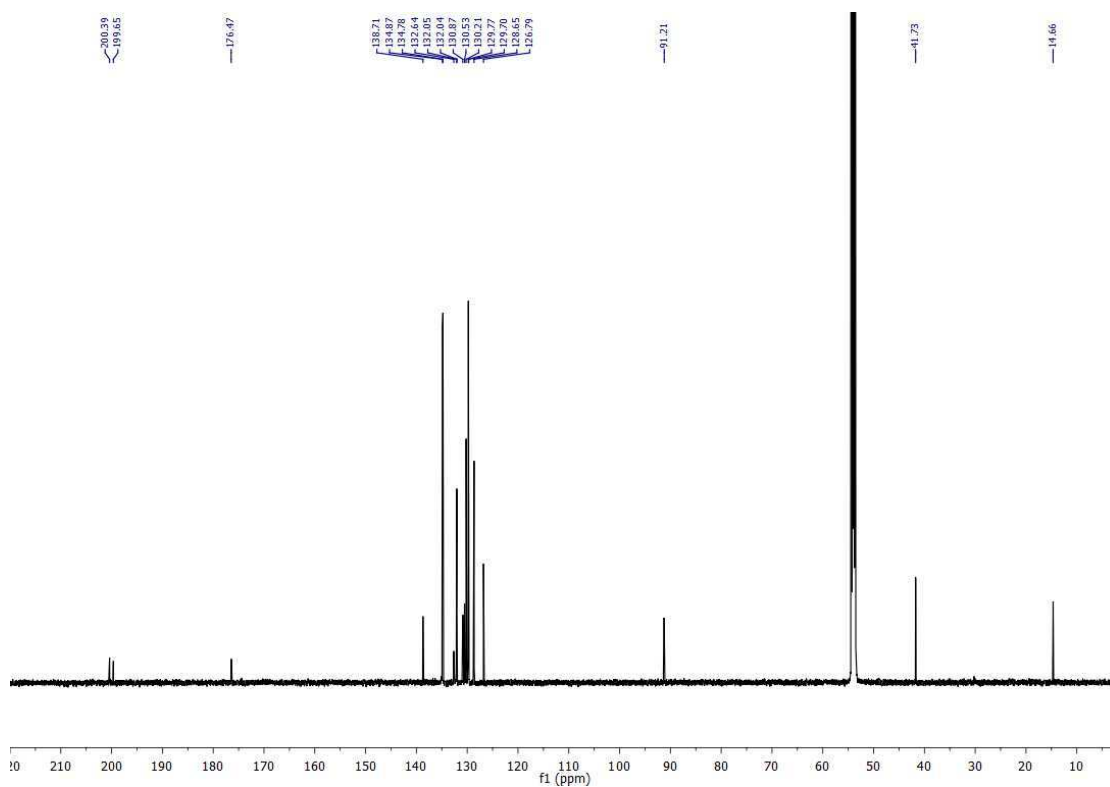
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (24)



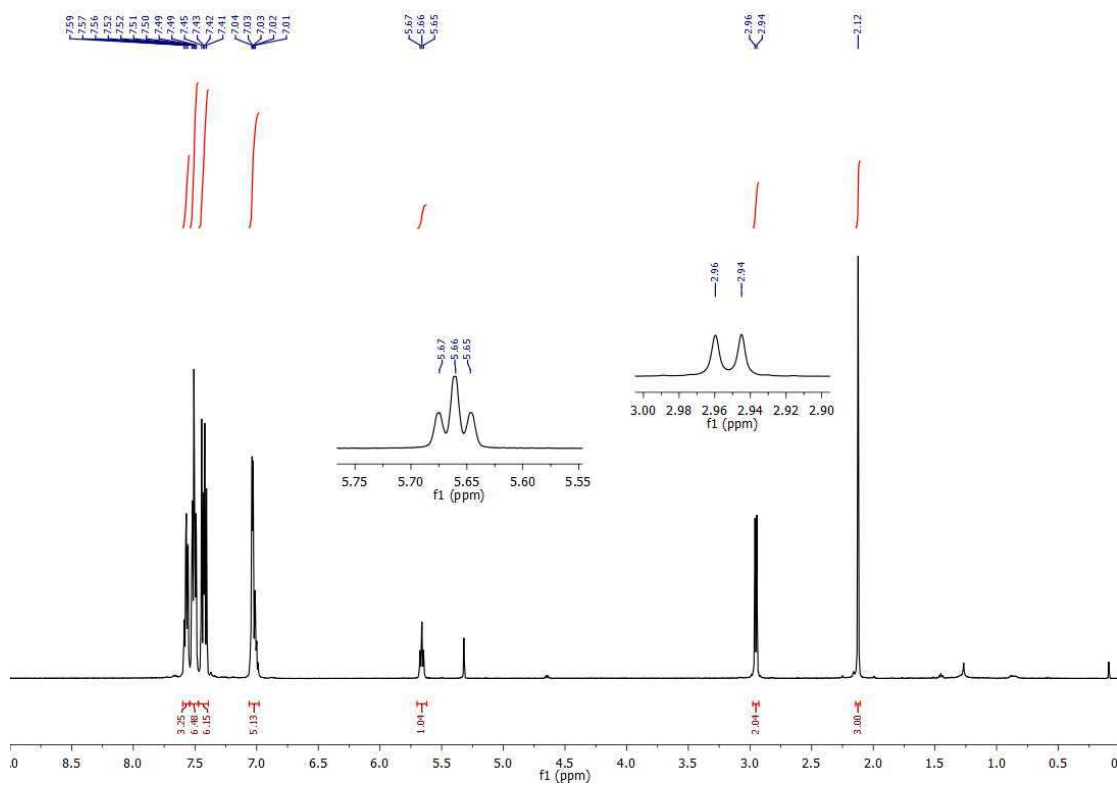
^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K) spectrum of (24)



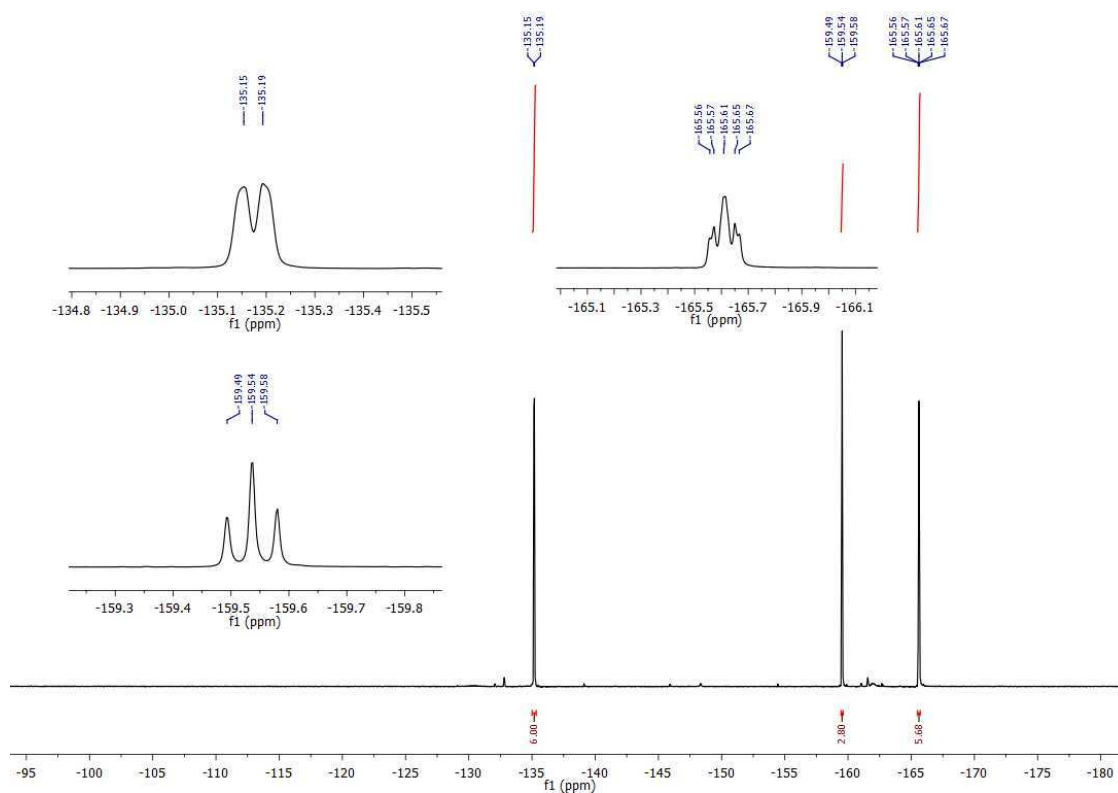
^{13}C NMR $\{^1\text{H}\}$ (150 MHz, CD_2Cl_2 , 298K) spectrum of (**24**)



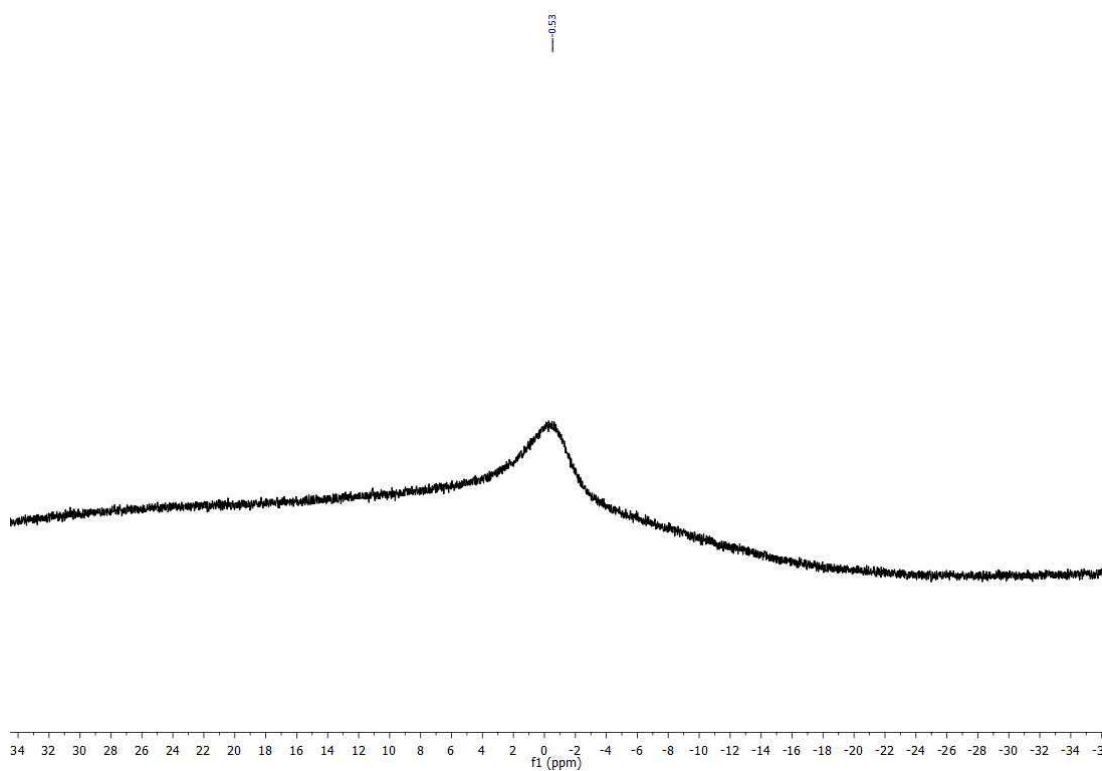
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of (**25**)



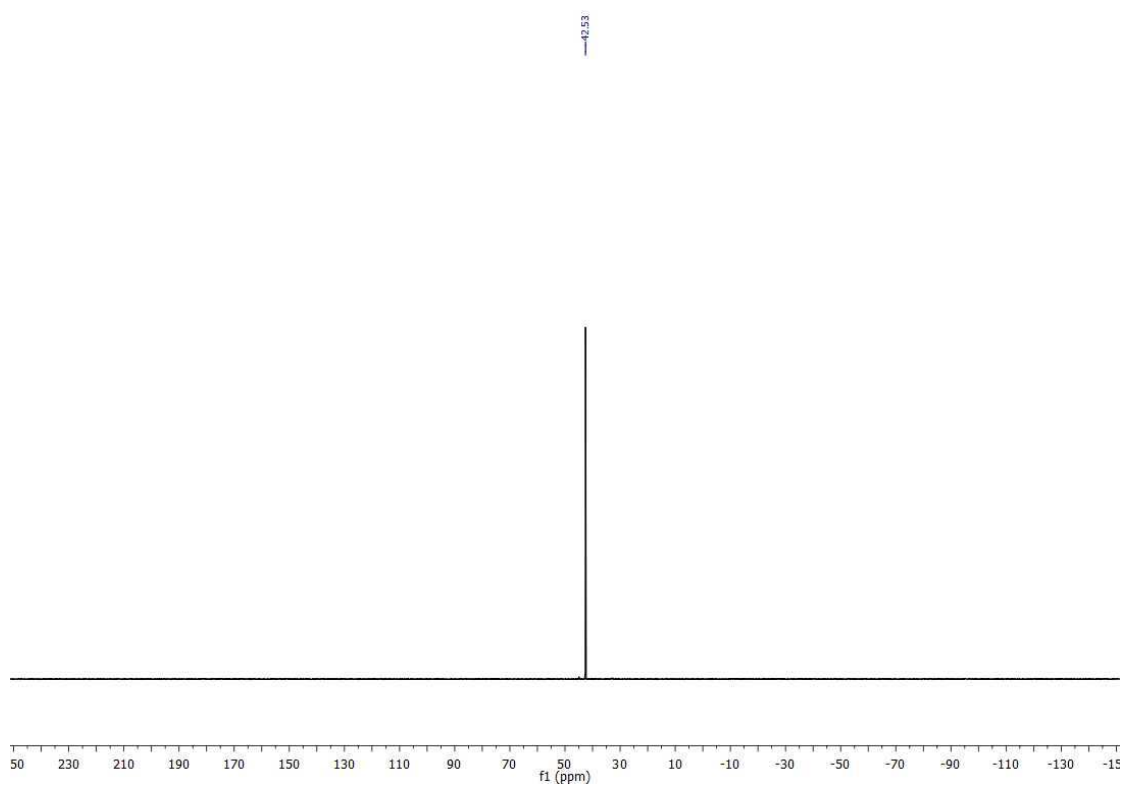
^{19}F NMR (471 MHz, CD_2Cl_2 , 298 K) spectrum of (25)



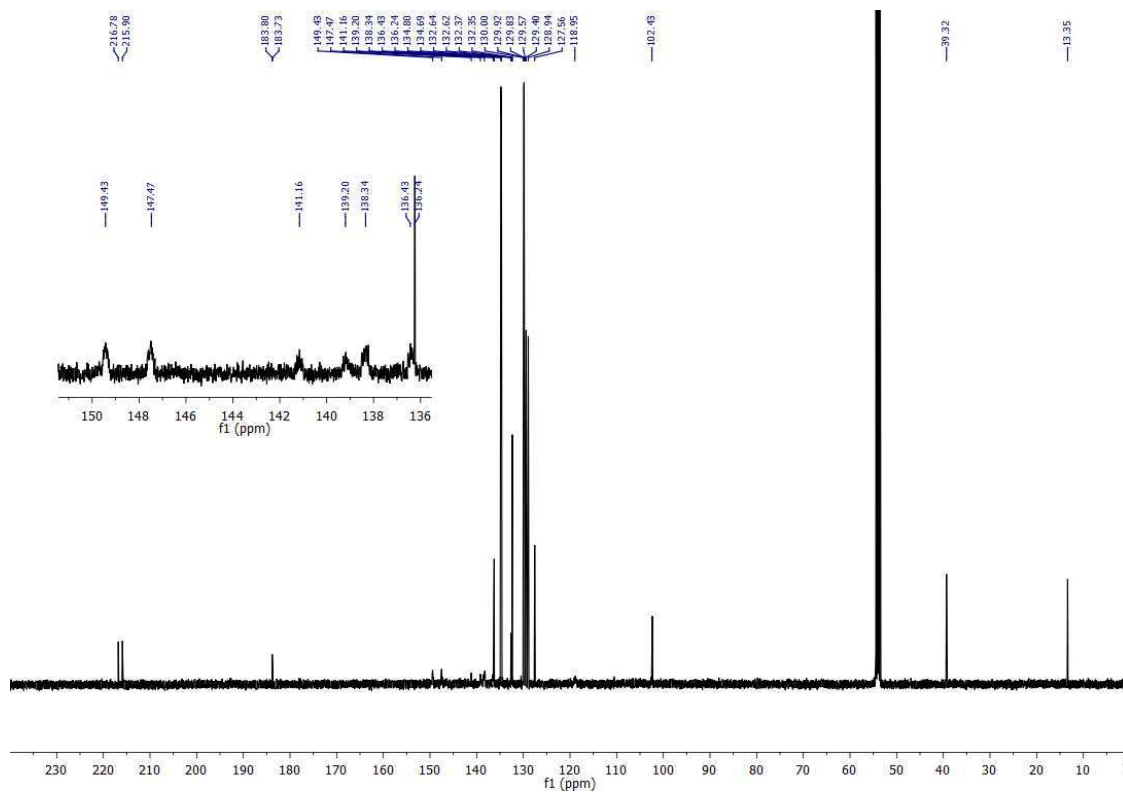
^{11}B NMR (160 MHz, CD_2Cl_2 , 298 K) spectrum of (25)



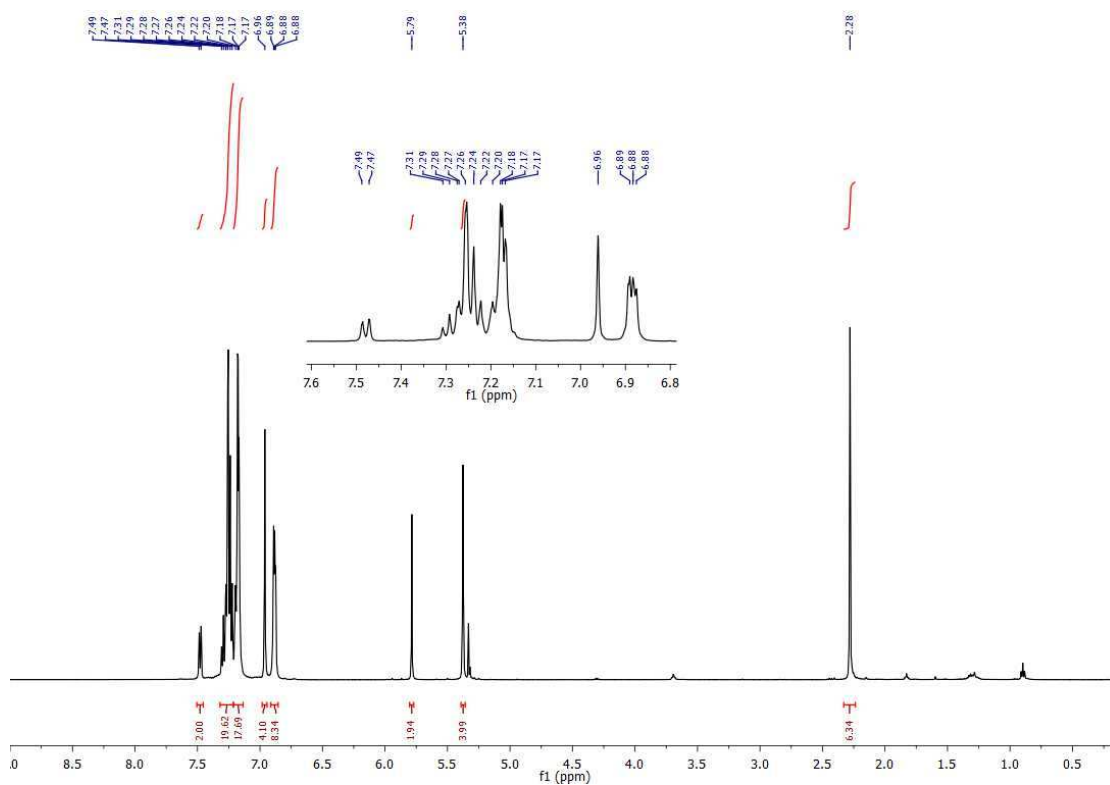
^{31}P NMR (202 MHz, CD_2Cl_2 , 298 K) spectrum of (**25**)



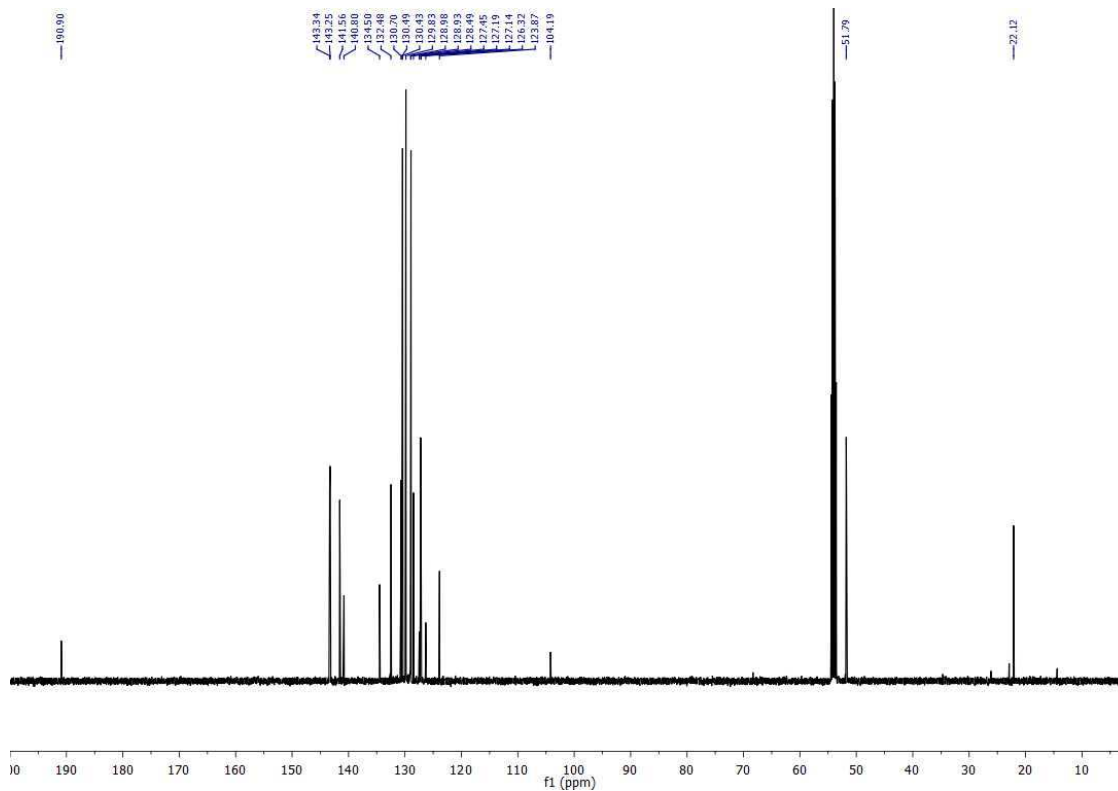
^{13}C NMR $\{^1\text{H}\}$ (100 MHz, CD_2Cl_2 , 298K) spectrum of (**25**)



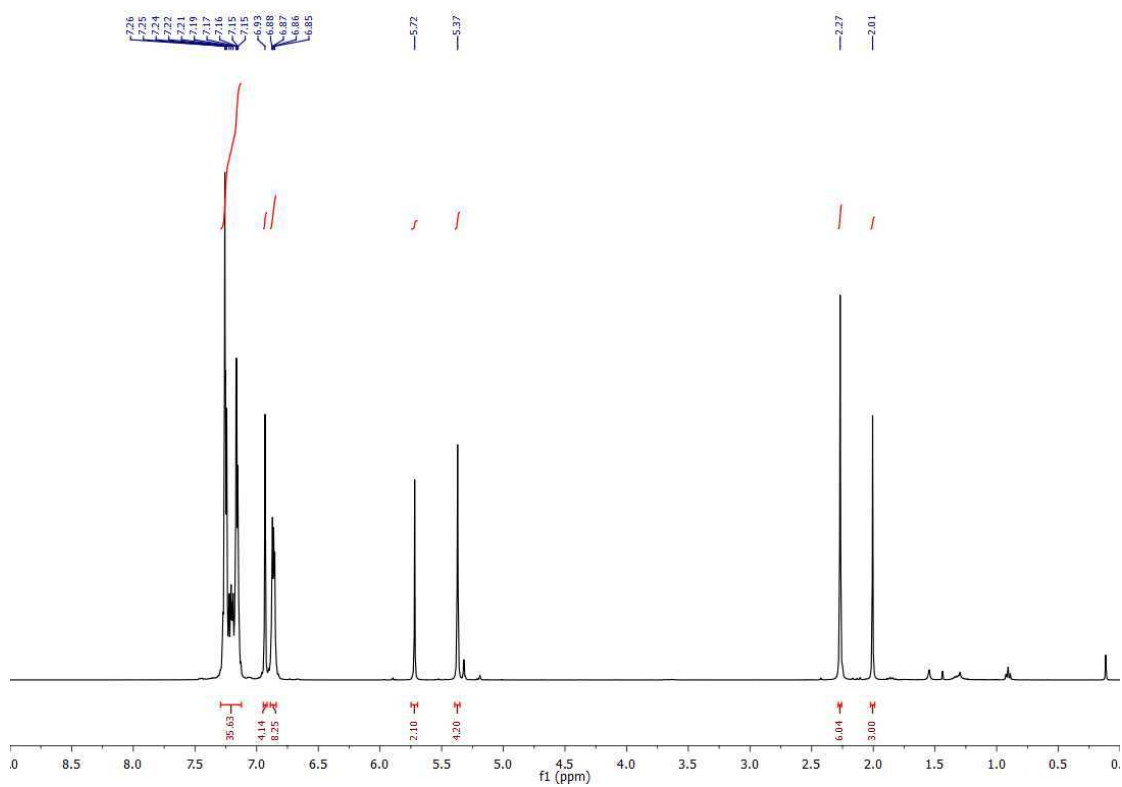
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{Au-C}\equiv\text{C-Ph}$ (**26**)



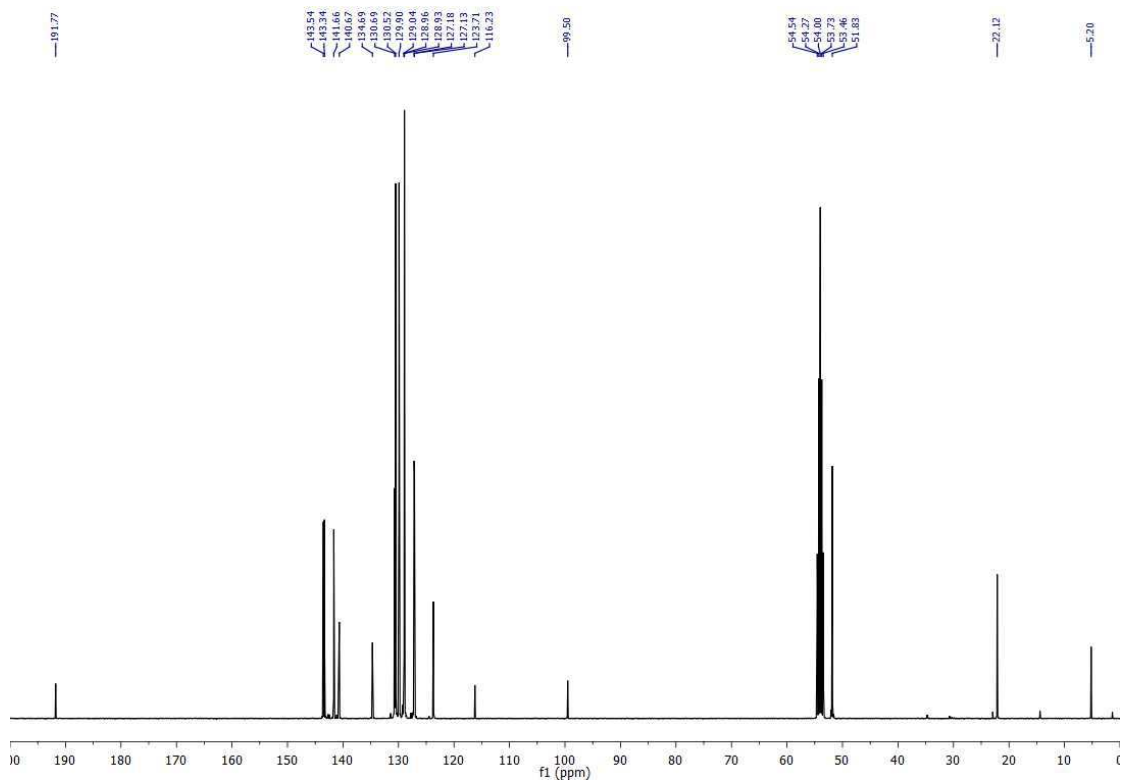
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{Au-C}\equiv\text{C-Ph}$ (**26**)



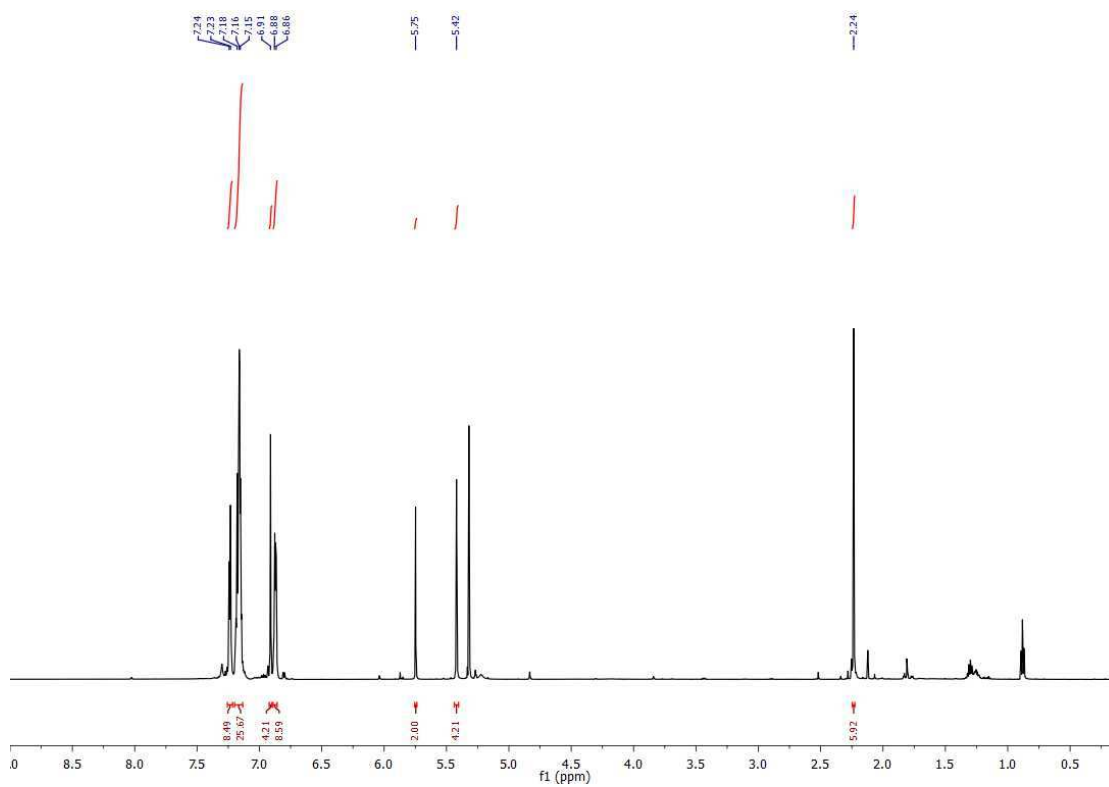
^1H NMR (400 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{Au-C}\equiv\text{C-Me}$ (**27**)



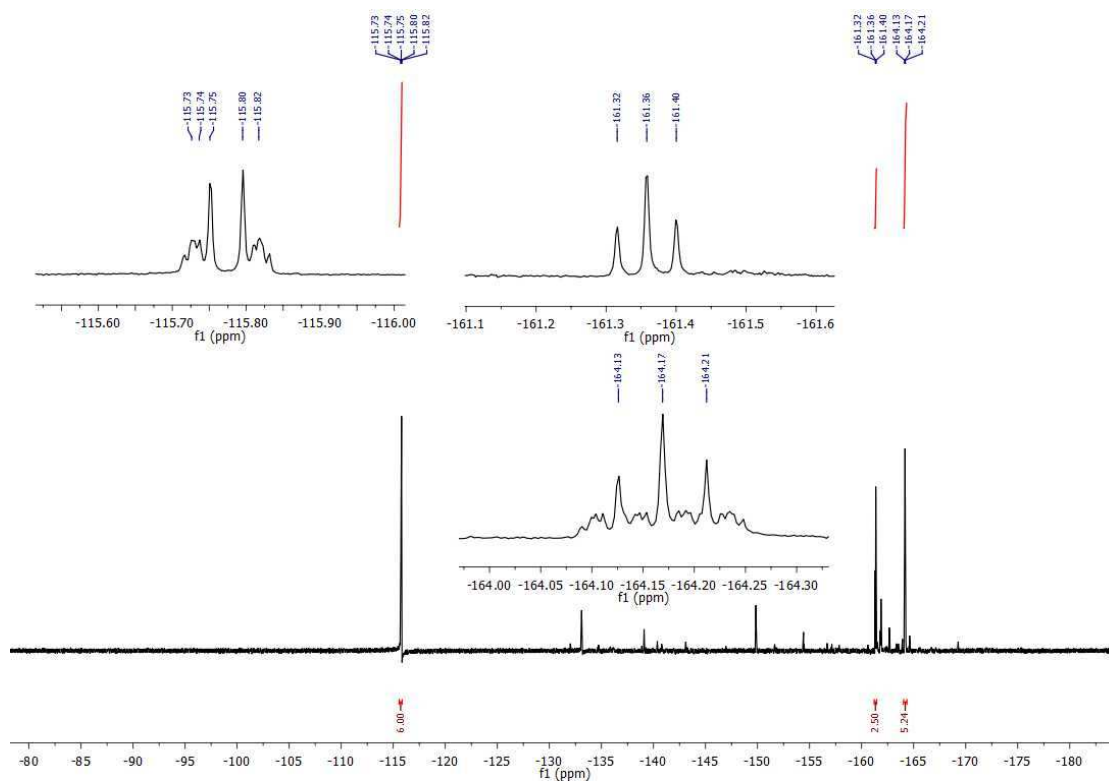
^{13}C NMR (100 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{Au-C}\equiv\text{C-Me}$ (**27**)



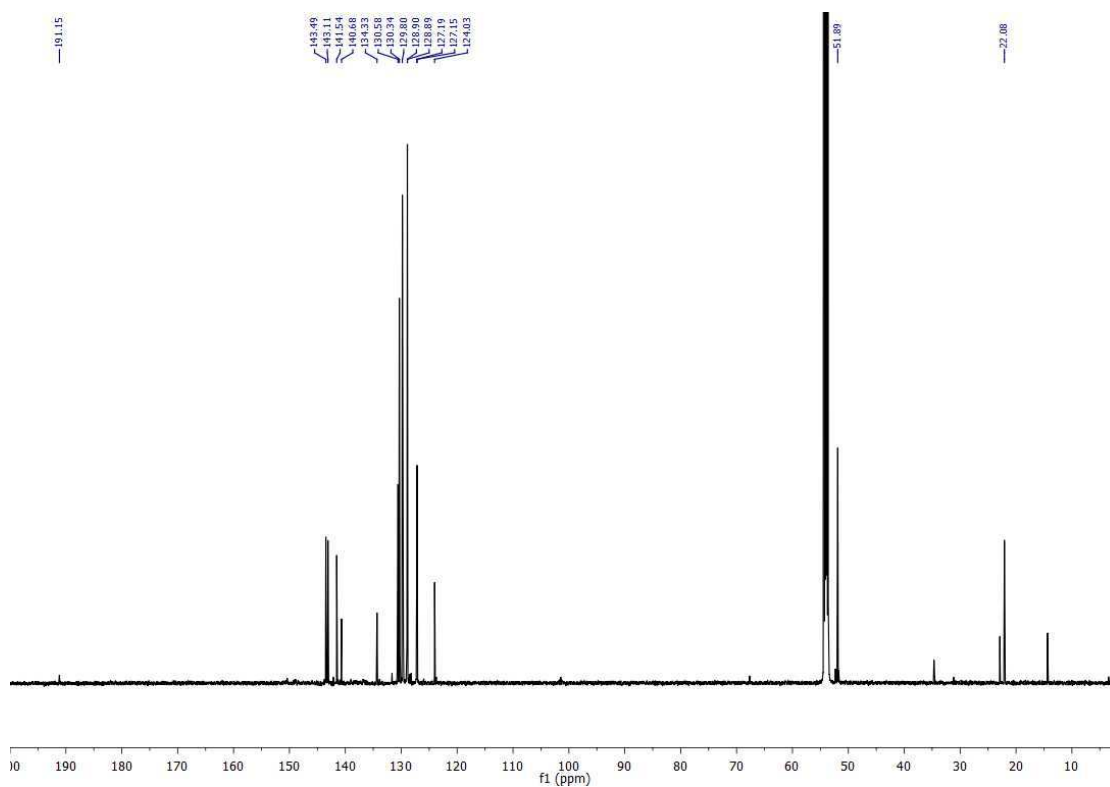
^1H NMR (500 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{AuC}_6\text{F}_5$ (**28**)



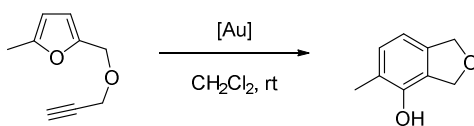
^{19}F NMR (470 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{AuC}_6\text{F}_5$ (**28**)



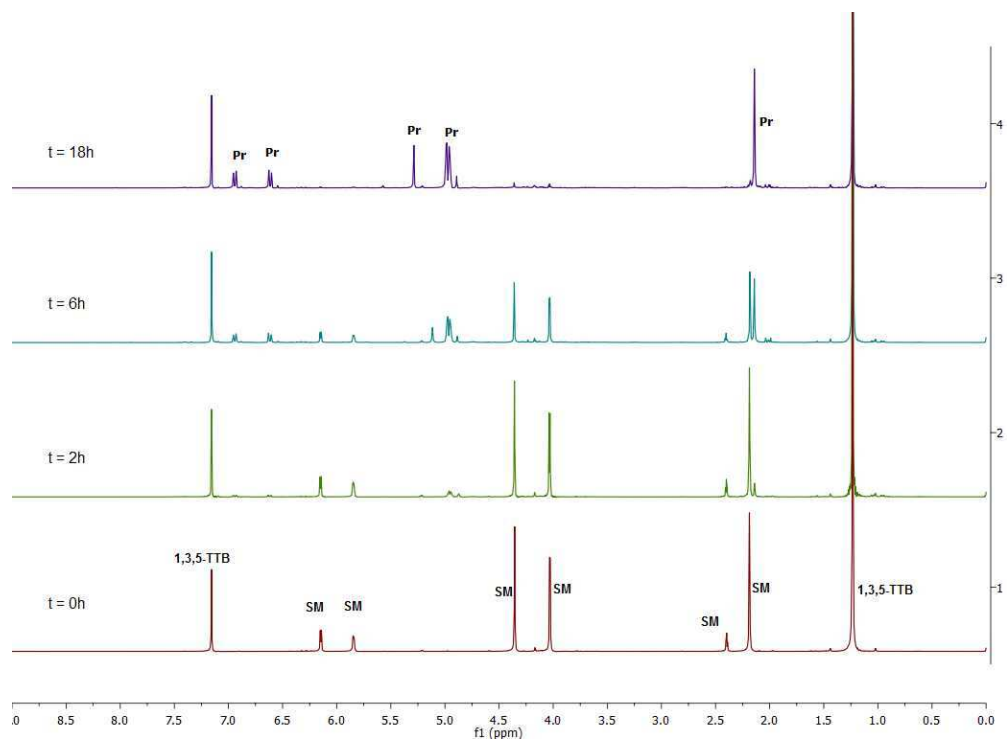
^{13}C NMR $\{^1\text{H}\}$ (125 MHz, CD_2Cl_2 , 298K) spectrum of $\text{IPr}^*\text{AuC}_6\text{F}_5$ (**28**)



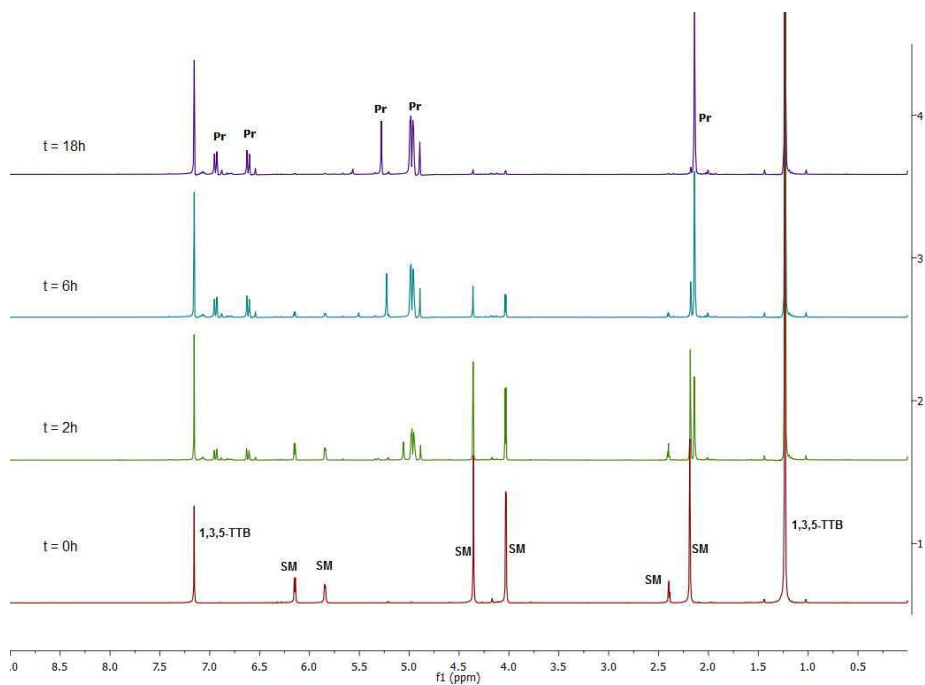
Catalysis experiments



$\text{IPrAu-C}\equiv\text{C-tol}$ (7.0 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (1.0 mL) and $\text{B}(\text{C}_6\text{F}_5)_3$ (5.1 mg, 0.01 mmol) added. The solution was stirred for 5 min and then 100 μL of this solution (0.5 mol%) was added to a substrate solution of 2-methyl-5-((prop-2-yn-1-yloxy)methyl)furan (0.2 mmol) in CH_2Cl_2 (0.5 mL) containing 1,3,5-trisertbutylbenzene (16.4 mg, 0.067 mmol) as internal standard. ^1H NMR spectra were measured as indicated (see below).



$\text{IPr}^*\text{Au-C}\equiv\text{C-Ph}$ (12.1 mg, 0.01 mmol) was dissolved in CD_2Cl_2 (1.0 mL) and $\text{B}(\text{C}_6\text{F}_5)_3$ (5.1 mg, 0.01 mmol) added. The solution was stirred for 5 min and then 100 μL of this solution (0.5 mol%) was added to a substrate solution of 2-methyl-5-((prop-2-yn-1-yloxy)methyl)furan (0.2 mmol) in CH_2Cl_2 (0.5 mL) containing 1,3,5-trisertbutylbenzene (16.4 mg, 0.067 mmol) as internal standard. ^1H NMR spectra were measured as indicated (see below).



X-ray data

X-ray data (cif) can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

X-ray crystal structure analyses were measured on a Bruker Smart CCD or Bruker Smart APEX instrument using Mo-K α radiation. Diffraction intensities were corrected for Lorentz and polarization effects. An empirical absorption correction was applied using SADABS^[6] based on the Laue symmetry of reciprocal space. Heavy atom diffractions were solved by direct methods and refined against F^2 with the full matrix least square algorithm using the SHELXL (Version 2014-3) software.^[7] Hydrogen atoms were either isotropically refined or calculated. The structures were solved and refined using the SHELXTL software package.

University of Toronto X-Ray Data

X-Ray Data Collection and Reduction

Crystals were coated in Paratone-N oil in the glovebox, mounted on a MiTegen Micromount and placed under an N₂ stream, thus maintaining a dry, O₂-free environment for each crystal. The data were collected on a Kappa Bruker Apex II diffractometer. Data collection strategies were determined using Bruker Apex 2 software and optimized to provide >99.5% complete data to a 2θ value of at least 55°. The data were collected at 150(\pm 2) K for all. The data integration and absorption correction were performed with the Bruker Apex 2 software package.^[8]

X-Ray Data Solution and Refinement

Non-hydrogen atomic scattering factors were taken from the literature tabulations.^[9] The heavy atom positions were determined using direct methods employing the SHELX-2013 direct methods routine. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. The refinements were carried out by using full-matrix least squares techniques on F , minimizing the function $\omega (F_o - F_c)^2$ where the weight ω is defined as $4F_o^2/2\sigma(F_o^2)$ and F_o and F_c are the observed and calculated structure factor amplitudes, respectively. In the final cycles of each refinement, all non-hydrogen atoms were assigned anisotropic temperature factors in the absence of disorder or insufficient data. In the latter cases atoms were treated isotropically. C-H atom positions were calculated and allowed to ride on the carbon to which they are bonded assuming a C-H bond length of 0.95 Å. H-atom temperature factors were fixed at 1.20 times the isotropic temperature factor of the C-atom to which they are bonded. The H-atom contributions were calculated, but not refined. The locations of the largest peaks in the final difference Fourier map calculation as well as the magnitude of the residual electron densities in each case were of no chemical significance.

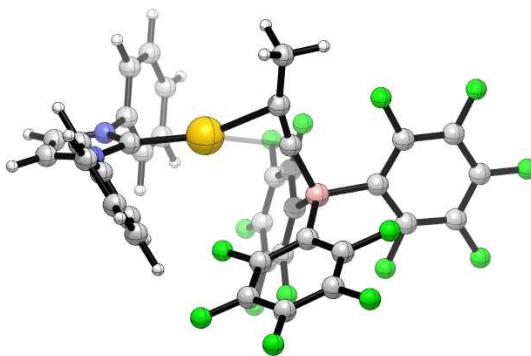
Computational details

Computational methods

All calculations were performed by employing the Gaussian09 program package.^[10] The theoretical approach is based on density functional theory (DFT),^[11,12] in combination with the hybrid B3LYP functional,^[6] together with a relativistic pseudopotential for Au.^[13] The pseudopotential basis set and the all-electron basis sets for the other light elements (H, C, B, F) were of cc-pVDZ quality for all systems. Geometries were fully optimized without symmetry restrictions. All intermediates were uniquely characterized by occurrence of none imaginary frequency. Gibbs free energies are calculated for standard temperature and pressure (298.15 K, 1 atm) and are corrected in respect to zero point energies which are calculated based on gas phase frequency calculations. 3D structures were generated with the program package CYLview, 1.0b; Legault, C. Y., Université de Sherbrooke, 2009 (<http://www.cylview.org>).

Preliminary theoretical studies of the σ -B/ π -Au alkynyl borate species at the B3LYP/cc-pVDZ level of theory indicate that the thermodynamics of a C₆F₅-group transfer from boron to gold *versus* boron to carbon are very close in energy ($\Delta G_{B-Au} = -12.3$ kcal/mol vs. $\Delta G_{B-C} = -12.0$ kcal/mol) suggesting that a kinetic barrier precludes concerted 1,2-C₆F₅ boron to carbon shift.

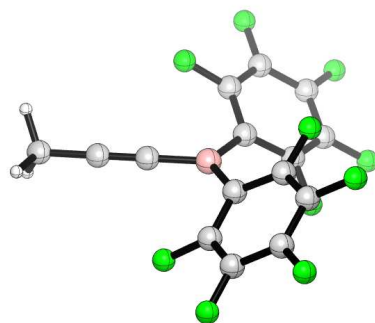
x,y,z-coordinates for optimized structures:



70

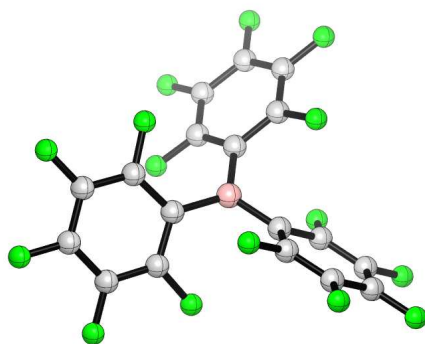
C	2.181786	2.883591	0.296546
C	1.393794	1.758447	0.569822
C	0.279293	2.032409	1.368689
C	-0.024358	3.286228	1.887671
C	0.798665	4.369303	1.596697

C	1.915053	4.162168	0.794880
B	1.639558	0.264985	-0.113809
C	3.193710	0.060919	-0.664084
C	4.232705	0.084322	0.275817
C	5.573143	-0.129402	-0.032068
C	5.934130	-0.386906	-1.352711
C	4.944043	-0.419103	-2.327938
C	3.611310	-0.197459	-1.971703
F	3.950050	0.345236	1.571701
F	6.515334	-0.087036	0.922958
F	7.217289	-0.597177	-1.677423
F	5.274333	-0.662329	-3.607522
F	2.731452	-0.241416	-3.000918
F	-0.613923	1.048224	1.660121
F	-1.137070	3.474334	2.631403
F	0.501643	5.590415	2.064049
F	2.715923	5.193946	0.488716
F	3.260943	2.798831	-0.508108
C	0.594711	0.235478	-1.354761
C	-0.000703	0.333839	-2.445431
C	-0.253198	0.472437	-3.889799
C	1.376035	-1.032470	0.888253
C	1.378714	-1.020004	2.287956
C	1.194483	-2.163220	3.069941
C	1.032404	-3.398920	2.451893
C	1.070886	-3.473879	1.063555
C	1.236811	-2.306672	0.322408
F	1.560087	0.124539	2.974618
F	1.173450	-2.080010	4.410030
F	0.818566	-4.509127	3.180731
F	0.924737	-4.665891	0.455511
F	1.266212	-2.458133	-1.020915
Au	-1.650891	-0.084804	-1.035338
C	-3.524293	-0.422119	-0.294541
N	-4.091900	-1.619944	0.023748
C	-5.403576	-1.453075	0.448527
C	-5.664172	-0.119908	0.396359
N	-4.504484	0.497370	-0.056559
C	-3.442771	-2.906477	-0.058042
C	-2.717436	-3.378137	1.038702
C	-2.117343	-4.637446	0.967574
C	-2.242568	-5.408930	-0.191537
C	-2.974145	-4.928000	-1.281252
C	-3.580379	-3.670449	-1.219175
C	-4.387030	1.923132	-0.231961
C	-3.496973	2.648441	0.563599
C	-3.417146	4.034496	0.402182
C	-4.223419	4.682488	-0.538059
C	-5.114304	3.945434	-1.324764
C	-5.199431	2.558953	-1.175778
H	-2.618909	-2.758693	1.931441
H	-4.149399	-3.277193	-2.063240
H	-2.876051	2.139880	1.300707
H	-5.881073	1.970731	-1.793241
H	-6.017571	-2.292821	0.755086
H	-6.550691	0.447664	0.657176
H	-0.747361	-0.421132	-4.300496
H	0.718760	0.593794	-4.393783
H	-0.881527	1.347942	-4.113605
H	-1.530279	-5.004705	1.810406
H	-1.757569	-6.384994	-0.247360
H	-3.068071	-5.528442	-2.188093
H	-2.724301	4.599947	1.026782
H	-4.158132	5.765816	-0.657837
H	-5.742333	4.448118	-2.062903



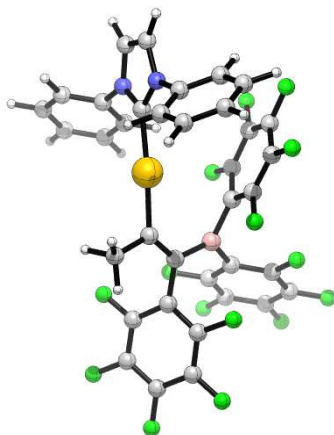
29

B	-0.022200	-0.029204	0.372899
C	-0.029211	-0.129794	1.878175
C	1.355496	-0.015266	-0.392033
C	-1.394764	0.059624	-0.396888
C	2.470845	-0.741854	0.058023
C	3.703592	-0.708975	-0.590352
C	3.860348	0.089378	-1.722552
C	2.784102	0.836334	-2.201936
C	1.561454	0.764982	-1.541530
F	2.374963	-1.539855	1.130760
F	4.734919	-1.432818	-0.139474
F	5.037067	0.138218	-2.347319
F	2.938503	1.608629	-3.283452
F	0.560032	1.513333	-2.036981
C	-1.596637	-0.572145	-1.634625
C	-2.815284	-0.555018	-2.305987
C	-3.890987	0.133482	-1.744799
C	-3.737705	0.786034	-0.522292
C	-2.509055	0.731958	0.132427
F	-0.594888	-1.258944	-2.212016
F	-2.966339	-1.187700	-3.475198
F	-5.063888	0.168469	-2.377850
F	-4.768299	1.455305	0.007849
F	-2.415307	1.392392	1.295350
C	-0.035931	-0.210242	3.099845
C	-0.050326	-0.304389	4.551639
H	0.968169	-0.340596	4.969906
H	-0.576091	0.560570	4.989192
H	-0.588010	-1.211906	4.873360



34

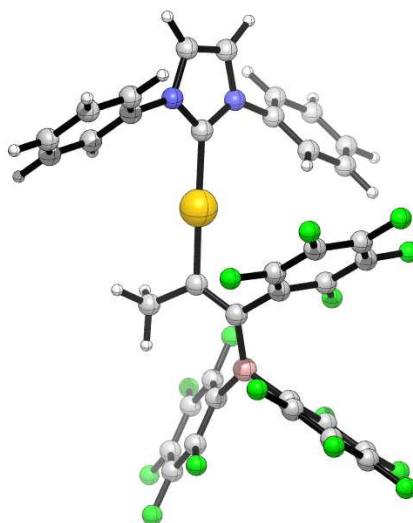
B	0.000332	0.000193	0.379602
C	0.021670	0.155715	1.942486
C	1.348003	-0.144185	-0.414133
C	-1.368969	-0.011172	-0.389907
C	-0.873265	0.997840	2.622856
C	-0.861800	1.156392	4.005148
C	0.059523	0.435429	4.765346
C	0.962264	-0.422958	4.137194
C	0.936794	-0.538574	2.750822
F	-1.773245	1.721449	1.935382
F	-1.719350	1.985219	4.609036
F	0.077327	0.566659	6.090396
F	1.837754	-1.119407	4.868994
F	1.820502	-1.385071	2.195221
C	1.474486	-0.995152	-1.524366
C	2.663037	-1.144909	-2.232211
C	3.781858	-0.405164	-1.848170
C	3.703579	0.462841	-0.758705
C	2.504929	0.569247	-0.060230
F	0.428839	-1.736568	-1.928358
F	2.743532	-1.982880	-3.270654
F	4.924365	-0.527565	-2.521260
F	4.774616	1.177060	-0.398384
F	2.478514	1.425501	0.975344
C	-1.528048	0.604175	-1.642392
C	-2.736078	0.615262	-2.332759
C	-3.842198	-0.030233	-1.779346
C	-3.731719	-0.666613	-0.542691
C	-2.513942	-0.637102	0.129664
F	-0.495286	1.247218	-2.213668
F	-2.847081	1.231640	-3.513761
F	-5.003247	-0.039304	-2.431501
F	-4.790709	-1.292417	-0.019311
F	-2.456939	-1.272567	1.312591



70

C	-0.541324	-2.402405	-0.166125
C	0.039542	-1.415304	0.634884
C	-0.562270	-1.199357	1.874429
C	-1.705869	-1.871604	2.294839
C	-2.257078	-2.844246	1.463216
C	-1.664878	-3.124359	0.233166
B	1.342065	-0.613911	0.196649
C	2.631808	-0.882995	1.088198
C	3.371196	0.159180	1.658874

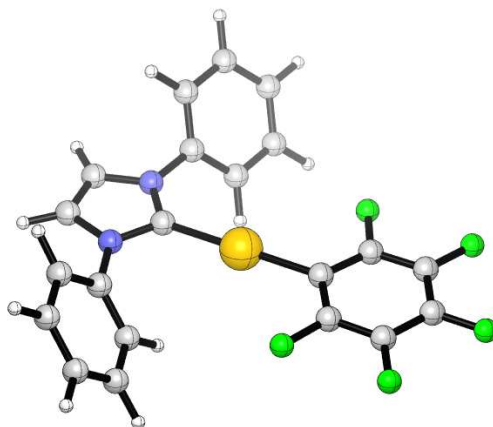
C	4.483098	-0.058082	2.470075
C	4.895548	-1.365946	2.723308
C	4.191486	-2.436227	2.172340
C	3.075677	-2.178031	1.378958
F	2.997760	1.436708	1.454765
F	5.154101	0.968660	3.009169
F	5.963508	-1.593157	3.493713
F	4.592461	-3.691665	2.411248
F	2.427173	-3.238577	0.861498
F	-0.068048	-0.241604	2.694901
F	-2.292797	-1.568583	3.463937
F	-3.374825	-3.490969	1.832591
F	-2.199210	-4.064331	-0.560189
F	-0.016994	-2.684461	-1.369109
C	1.381265	0.327366	-1.011934
C	0.250569	0.884897	-1.588283
C	2.746670	0.640869	-1.563310
Au	-1.650552	0.853193	-0.795920
C	3.587330	-0.373852	-2.036459
C	4.867849	-0.124659	-2.526525
C	5.348514	1.183546	-2.548763
C	4.545399	2.221531	-2.078864
C	3.269893	1.939470	-1.592689
F	3.162548	-1.651885	-2.015451
F	5.638121	-1.126595	-2.973688
F	6.575489	1.441509	-3.017098
F	5.006979	3.480284	-2.095584
F	2.532378	2.970116	-1.145397
C	0.363004	1.734807	-2.833504
H	0.232268	2.798486	-2.564979
H	1.321473	1.636340	-3.368908
H	-0.454641	1.494991	-3.531896
C	-3.561527	0.953647	-0.001537
N	-4.648580	0.184837	-0.309561
C	-5.755449	0.544335	0.454636
C	-5.358510	1.565108	1.256914
N	-4.017127	1.801338	0.968956
C	-3.236460	2.821052	1.619559
H	-5.893234	2.132400	2.010774
H	-6.714532	0.050122	0.345501
C	-4.676068	-0.857011	-1.301139
C	-3.617090	4.158838	1.476055
C	-2.878023	5.154766	2.119155
C	-1.763695	4.813196	2.891235
C	-1.392393	3.472316	3.026434
C	-2.130640	2.467071	2.396966
H	-4.475564	4.415239	0.852276
H	-3.168926	6.200957	2.005508
H	-1.182257	5.593608	3.386326
H	-0.523082	3.199054	3.627217
H	-1.849577	1.421538	2.512501
C	-4.959958	-2.167122	-0.905287
C	-5.006128	-3.177740	-1.868968
C	-4.768412	-2.878782	-3.213130
C	-4.479943	-1.565410	-3.596857
C	-4.435872	-0.546402	-2.642716
H	-5.107796	-2.398841	0.150721
H	-5.208734	-4.204745	-1.560837
H	-4.798754	-3.672363	-3.962387
H	-4.288855	-1.329099	-4.645414
H	-4.215912	0.482583	-2.928399



70

C	4.666609	-2.326704	-2.024356
C	5.184901	-1.054917	-1.762992
C	5.712480	-0.270117	-2.792898
C	5.721815	-0.766860	-4.098685
C	5.200188	-2.034448	-4.371735
C	4.672144	-2.809752	-3.334882
N	5.200379	-0.546619	-0.418579
C	4.104208	-0.399897	0.384696
N	4.608248	0.112438	1.547617
C	5.988145	0.278581	1.469115
C	6.360911	-0.132861	0.230383
Au	2.120725	-0.817579	-0.058747
C	0.137486	-1.238235	-0.425279
C	-0.165868	-2.684425	-0.722185
C	3.835292	0.457626	2.710712
C	4.180392	-0.095124	3.947848
C	3.443661	0.253521	5.082885
C	2.366277	1.138052	4.978169
C	2.027006	1.683289	3.736270
C	2.766514	1.351127	2.598733
C	-0.849735	-0.267881	-0.375323
B	-2.374188	-0.463233	-0.326070
C	-3.343838	0.784827	-0.534187
C	-3.315499	1.569553	-1.691567
C	-4.175019	2.646523	-1.896973
C	-5.100998	2.975967	-0.907377
C	-5.161778	2.224518	0.265557
C	-4.294870	1.145284	0.426231
F	-2.443075	1.277551	-2.674766
F	-4.123544	3.364309	-3.027187
F	-5.928287	4.011174	-1.082797
F	-6.046660	2.546391	1.218677
F	-4.381740	0.448106	1.575748
C	-3.124236	-1.818985	0.027068
C	-2.867455	-2.550972	1.191682
C	-3.583733	-3.695473	1.534686
C	-4.593331	-4.150980	0.686820
C	-4.880315	-3.455689	-0.487071
C	-4.152537	-2.306043	-0.786920
F	-1.898995	-2.155327	2.036881
F	-4.450086	-1.664992	-1.935267
F	-5.844498	-3.896128	-1.306372
F	-5.281819	-5.253908	0.997905

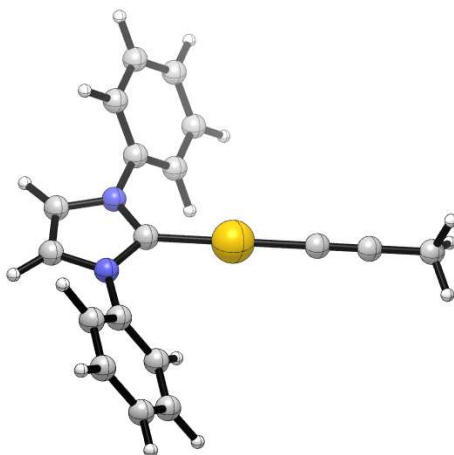
F	-3.312541	-4.364316	2.663954
H	0.076779	-3.304583	0.159394
H	-1.199228	-2.891727	-1.031570
H	0.507225	-3.032249	-1.524179
H	6.566383	0.687120	2.290477
H	7.335362	-0.184816	-0.242596
H	5.005950	-0.806211	4.016533
H	3.706858	-0.180203	6.049655
H	1.786916	1.400974	5.865403
H	1.184817	2.370865	3.644837
H	2.518441	1.778605	1.627643
H	6.093158	0.729376	-2.574499
H	6.126887	-0.153230	-4.905638
H	5.202456	-2.417619	-5.394109
H	4.265549	-3.801217	-3.543454
H	4.267723	-2.927005	-1.206511
C	-0.374653	1.157264	-0.263161
C	0.291333	1.806592	-1.310877
C	0.745593	3.121444	-1.205055
C	0.534541	3.833992	-0.025431
C	-0.135356	3.221989	1.032611
C	-0.581331	1.909249	0.897842
F	0.524763	1.164055	-2.464097
F	1.388955	3.704653	-2.227280
F	0.971893	5.094558	0.090749
F	-0.318379	3.889426	2.187229
F	-1.212169	1.353989	1.950021



41

C	-3.414419	0.859078	2.889051
C	-2.484200	-0.069921	2.410271
C	-2.869838	-1.067948	1.510292
C	-4.197169	-1.124310	1.080043
C	-5.135489	-0.204674	1.556918
C	-4.742749	0.783717	2.463916
N	-1.124986	0.006126	2.868849
C	-0.014723	0.020935	2.068576
N	1.029675	0.129110	2.946549
C	0.576223	0.193611	4.261527
C	-0.777374	0.116341	4.212718
C	2.418106	0.210027	2.586993
C	2.978332	-0.734065	1.721219
C	4.330889	-0.637346	1.387539

C	5.121846	0.381164	1.926616
C	4.555168	1.314838	2.798933
C	3.199829	1.236905	3.127359
Au	0.064078	-0.063967	0.017018
C	0.143554	-0.157490	-2.037756
C	-1.003853	-0.260956	-2.824705
C	-0.975806	-0.325230	-4.217551
C	0.253518	-0.287215	-4.873792
C	1.428720	-0.187415	-4.130630
C	1.348900	-0.126120	-2.739668
F	-2.226723	-0.305735	-2.239442
F	-2.110056	-0.424117	-4.934747
F	0.305447	-0.347961	-6.213891
F	2.615498	-0.153266	-4.763935
F	2.523662	-0.033451	-2.067680
H	1.256581	0.252443	5.103661
H	-1.518688	0.094020	5.003599
H	-2.135744	-1.787806	1.149209
H	-4.495319	-1.894705	0.366797
H	-6.172058	-0.255018	1.217677
H	-5.468055	1.511664	2.832837
H	-3.094675	1.648801	3.571562
H	2.744168	1.982379	3.781852
H	5.164618	2.119091	3.215858
H	6.179065	0.450430	1.662822
H	4.765153	-1.365972	0.700778
H	2.358695	-1.531319	1.311454



36

C	1.136536	-0.517085	1.914690
C	0.071955	0.230129	1.399184
C	0.185137	0.874755	0.163373
C	1.379148	0.772564	-0.553604
C	2.446369	0.023143	-0.049959
C	2.321887	-0.622731	1.183241
N	-1.150903	0.308132	2.146987
C	-1.817823	1.461707	2.468336
N	-2.900141	1.026752	3.188240
C	-2.894569	-0.359673	3.322308
C	-1.795769	-0.811089	2.668196
C	-3.909729	1.865741	3.769184
C	-4.243086	1.693010	5.116940
C	-5.243127	2.484927	5.686174
C	-5.897888	3.450518	4.916529
C	-5.553226	3.619749	3.572349

C	-4.563649	2.825117	2.989721
Au	-1.286342	3.392420	2.029054
C	-0.767268	5.261942	1.610196
C	-0.447491	6.418224	1.348117
C	-0.063114	7.795350	1.041388
H	-1.433621	-1.818179	2.494640
H	-3.686885	-0.892499	3.835957
H	-4.294294	2.947475	1.940984
H	-6.058397	4.374143	2.966275
H	-6.673735	4.074110	5.365406
H	-5.499374	2.353954	6.739445
H	-3.706899	0.958227	5.720536
H	1.043945	-0.993859	2.892363
H	3.154694	-1.201230	1.588172
H	3.376627	-0.053974	-0.616501
H	1.470679	1.282140	-1.514639
H	-0.652868	1.452185	-0.226105
H	0.611108	7.846073	0.168458
H	-0.942334	8.423061	0.813053
H	0.463925	8.267670	1.888932

References

1. Frohn, H. -J. in "Efficient Preparations of Fluorine Compounds" (chapt. 10), 1. Ed., H. W. Roesky (Ed.), Wiley-VCH, Weinheim, **2013**.
2. Berthon-Gelloz, G.; Siegler, M. A.; Spek, A. L.; Tinant, B.; Reek, J. N. H.; Markó, I. E. *Dalton Trans.*, **2010**, 39, 1444-1446.
3. Hashmi, A. S. K.; Lauterbach, T.; Nösel, P.; Vilhelmsen, M. H.; Rudolph, M.; Rominger, F. *Chem. Eur. J.*, **2013**, 19, 1058-1065.
4. Dupuy, S.; Crawford, L.; Bühl, M.; Slawin, A. M. Z.; Nolan, S. P. *Adv. Synth. Catal.*, **2012**, 354, 2380-2386.
5. Liu, L.-P.; Xu, B.; Mashuta, M. S.; Hammond, G. B. *J. Am. Chem. Soc.*, **2008**, 130, 17642-17643.
6. Program SADABS 2012/1 for absorption correction; Sheldrick, G. M. Bruker Analytical X-ray-Division, Madison, Wisconsin 2012
7. Program SHELXL 2014-3 for structure refinement; Sheldrick, G.M. *Acta Cryst.* **2008**, A64, 112-122.
8. Apex 2 Software Package; Bruker AXS Inc. **2013**.
9. D. T. Cromer, J. T. W., *Int. Tables X-Ray Crystallography*. 1974; Vol. 4.
10. Gaussian 09, Revision B.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2010.
11. Hohenberg, P.; Kohn, W. *Phys. Rev.*, **1964**, 136, B864.
12. Kohn, W.; Sham, L. J. *Phys. Rev.*, **1965**, 140, A1133.
13. Figgen, D.; Rauhut, G.; Dolg, M.; Stoll, H. *Chem. Phys.*, **2005**, 311, 227.