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Supporting Information

Syntheses, characterisation and catalytic role of (η^5-C_5Me_5)Rh(III) guanidinato complexes in transfer hydrogenation (TH) and TH-etherification

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1. General considerations

Sym N,N′,N″-triarylguanidines, $(ArNH)_2C{=}NAr$ (*Sym* = *Symmetrical*; Ar = C_6H_5 (**L1**); 2-MeC_6H_4 (**L2**); 4-MeC_6H_4 (**L3**); 2-ClC_6H_4 (**L4**); 4-ClC_6H_4 (**L5**); 2-FC_6H_4 (**L6**)),[1,2] [(η^5-C_5Me_5)MCl(μ-Cl)]$_2$ (M = Rh and Ir),[3] **9**,[4] **10**,[5] **11**,[5] **13**[6] and (*E*)-chalcone[7] were prepared following the literature procedures. $MCl_3{\cdot}xH_2O$ (M = Rh and Ir), NaOAc, activated basic alumina, silica and substrates used for TH were purchased from commercial vendors and used as received. The IR spectral data were obtained using Nujol or KBr pellet on a Shimadzu IR435 spectrometer in the frequency range 400–4000 cm^{-1}. Time of flight mass (TOF–MS) spectra were recorded on a Agilent Technologies 6530, Accurate-Mass Q-TOF LC/MS instrument using electrospray positive ion mode. ^1H, $^{13}C\{^1H\}$, ^{19}F and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL ECX 400 NMR spectrometer operating at 400, 100.5, 376.5 (with CF_3COOH as an external standard), 161.8 MHz (with 85% H_3PO_4 as an external standard), respectively. The ^1H NMR chemical shifts are reported in ppm relative to tetramethylsilane or residual solvent signal. Variable temperature (VT) ^{19}F NMR for measurements for **3** and VT ^1H NMR measurements for **4** were carried out in $CDCl_3$ and CD_2Cl_2 respectively, on a Bruker AMX 400 MHz NMR spectrometer. Melting points were recorded on a Buchi melting point apparatus (Model: M–560) and the reported values are uncorrected.

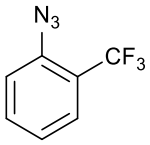
Caution: Sodium azide is shock sensitive and explosive, only a small amount of material should be used with care.

2. Syntheses and characterization of aryl azides

General Procedure Aryl azides were prepared following the literature procedure[8] with a slight modification as described below. Trifluoroacetic acid (17 mL) and aniline (1 mL) were added to a 100 mL RB flask containing a stir bar. The RB flask was externally cooled to −10 °C with salt-

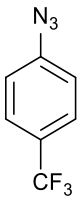
ice bath, and sodium nitrite (2 equiv) was added in small portion over 15 min. The reaction mixture was stirred for 30 min and to it NaN_3 (2 equiv) was added in portion over 5 min and stirred for additional 2 h. Subsequently, distilled water (20 mL) was added carefully and the solution was warmed to RT. The reaction mixture was extracted with ethyl acetate (3 × 20 mL) and the extract was washed with water (20 mL), saturated aqueous sodium bicarbonate solution (20 mL), and a brine solution (20 mL) in sequence. The organic layer was dried over sodium sulfate, filtered and the filtrate concentrated under vacuum to afford yellow oil.

2-(Trifluoromethyl)phenyl azide



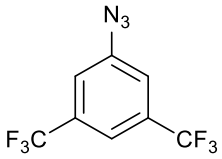
Yield: 95% (1.42 g, 7.56 mmol). IR (Nujol, cm^{-1}): 2131 (vs, N_3), 1605 (m), 1589 (m), 1494 (s), 1458 (s), 1322 (vs), 1297 (vs), 1273 (sh, m), 1178 (s), 1134 (vs), 1117 (sh, s), 1041 (m), 950 (w), 822 (w), 758 (s), 742 (sh, m), 685 (m), 642 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.23 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*), 7.30 (d, J_{HH} = 7.6 Hz, 1H, Ar*H*), 7.58 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*), 7.64 (d, J_{HH} = 8.0 Hz, 1H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 119.6, 121.3 (q, J_{CF} = 31.4 Hz), 123.1 (q, J_{CF} = 272.5 Hz), 124.6, 127.6 (q, J_{CF} = 5.1 Hz), 133.2, 138.7. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –61.77. NMR (^{1}H, ^{13}C, and ^{19}F) and IR spectral data of the title compound presented herein favorably matched with those known in the literature.[9]

4-(Trifluoromethyl)phenyl azide



Yield: 99% (1.48 g, 7.88 mmol). IR (Nujol, cm^{-1}): 2134 (s, N_3), 2111 (sh, w), 1739 (w), 1544 (w), 1463 (w), 1327 (s), 1169 (s), 1133 (s), 1071 (w), 1018 (w), 759 (w), 637 (w). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.12, 7.61 (each d, J_{HH} = 9.2 Hz, 2 × 2H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm): δ 119.3, 124.0 (q, J_{CF} = 271.6 Hz), 127.2 (two q, J_{CF} = 32.8 and 3.5 Hz), 143.9. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –63.30. The ^1H NMR spectral data of the title compound presented herein favorably matched with that known in literature.[10]

3,5-Bis(trifluoromethyl)phenyl azide

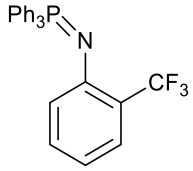


Yield: 98% (1.60 g, 6.27 mmol; lit. yield = 96%[8]). IR (Nujol, cm^{-1}): 2118 (vs, N_3), 1618 (w, br), 1466 (m), 1371 (s), 1280 (vs), 1185 (s), 1143 (s), 908 (w), 882 (w), 848 (w), 699 (w), 683 (w). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.44 (s, 2H, Ar*H*), 7.64 (s, 1H, Ar*H*). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –63.21. ^1H data reported herein favorably matched with those reported in the literature.[8]

3. Syntheses and characterization of aryl iminophosporanes

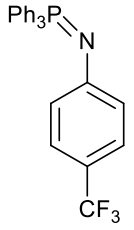
General Procedure All aryl iminophosphoranes were prepared from the corresponding aryl azides and PPh_3 through Staudinger reaction following the literature procedure[8] with a slight modification as described below. Aryl azide (500 mg) was dissolved in dry diethyl ether (10 mL) and triphenylphosphine (1 equiv) in 20 mL diethyl ether was added drop wise under nitrogen atmosphere and the evolution of N_2 gas was observed. The reaction mixture was stirred for 24 h at RT and stored at RT for one day to afford crystals of aryl iminophoshphoranes.

2-(Trifluoromethyl)phenyl iminophoshphorane



Yield: 90% (1.01 g, 2.40 mmol). Mp: 129 °C. IR (KBr, cm^{-1}): 3062 (w), 3035 (sh, w), 2725 (w), 2370 (w), 2346 (w), 1602 (m), 1482 (s), 1457 (s), 1438 (m), 1355 (vs), 1313 (vs), 1300 (s), 1247 (m), 1183 (w), 1159 (m), 1106 (vs), 1062 (m), 1033 (m), 1020 (sh, m), 999 (sh, m), 742 (sh, w), 734 (sh, m), 716 (m), 691 (m), 643 (w), 598 (w), 573 (w), 525 (s), 504 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.48 (d, J_{HH} = 8.4 Hz, 1H, Ar*H*), 6.63 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*), 6.98 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*), 7.43–7.55 (m, 10H, Ar*H*), 7.76–7.81 (m, 6H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 116.0, 122.2 (d, J_{CP} = 10.5 Hz), 123.5 (qd, J_{CF} = 26.6 Hz, J_{CP} = 23.3 Hz), 125.7 (q, J_{CF} = 272.5 Hz), 126.9 (q, J_{CF} = 6.4 Hz), 128.7 (d, J_{CP} = 12.5 Hz), 130.4, 131.4, 131.7, 131.86, 131.89, 132.7 (d, J_{CP} = 10.5 Hz), 150.4. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –62.10. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz, ppm): δ 2.48. MS (ESI^+) *m/z* [ion]: 422.1277 $[M + H]^+$. Calcd for $C_{25}H_{20}F_3NP$: 422.1285 $[M + H]^+$.

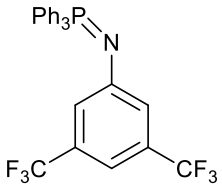
4-(Trifluoromethyl)phenyl iminophoshphorane



Yield: 93% (1.05 g, 2.48 mmol). Mp: 113 °C. IR (KBr, cm^{-1}): 3056 (w), 2925 (w), 1897 (w), 1736 (w), 1605 (s), 1511 (s), 1482 (w), 1458 (w), 1436 (m), 1353 (s), 1319 (vs), 1274 (sh, m), 1180 (m), 1152 (m), 1104 (vs), 1065 (s), 1014 (s), 998 (m), 834 (m), 788 (w), 752 (sh, m), 716

(s), 694 (s), 638 (w), 594 (m), 542 (m), 529 (s), 500 (m), 448 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.79 (d, J_{HH} = 8.4 Hz, 2H, Ar*H*), 7.23(d, J_{HH} = 8.8 Hz, 2H, Ar*H*), 7.44–7.49 (m, 6H, Ar*H*), 7.54–7.56 (m, 3H, Ar*H*), 7.72–7.77 (m, 6H, Ar*H*). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –60.50. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz, ppm): δ 5.86. ^{31}P{^{1}H} NMR data of the title compound favorably matched with that reported in literature.[11] MS (ESI$^+$) *m/z* [ion]: 422.1283 [M + H]$^+$. Calcd for $C_{25}H_{20}F_3NP$: 422.1285 [M + H]$^+$.

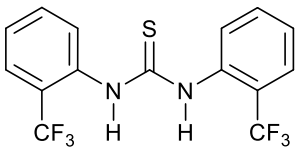
3,5-Bis(trifluoromethyl)phenyl iminophoshphorane



Yield: 95% (0.910 g, 1.86 mmol). Mp: 132 °C. IR (KBr, cm^{-1}): 3058 (w), 1598 (m), 1470 (m), 1441 (m), 1398 (vs), 1298 (s), 1279 (s), 1168 (s), 1120 (s), 1110 (vs), 1053 (s), 1029 (sh, w), 998 (sh, w), 902 (w), 861 (m), 744 (sh, m), 724 (m), 692 (m), 680 (sh, m), 566 (w), 526 (s), 503 (sh, m). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.06 (s, 1H, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.47–7.52 (m, 6H, Ar*H*), 7.56–7.60 (m, 3H, Ar*H*), 7.71–7.76 (m, 6H, Ar*H*). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –62.97. ^{31}P{^{1}H} NMR ($CDCl_3$, 161.8 MHz, ppm): δ 7.11. MS (ESI$^+$) *m/z* [ion]: 490.1153 [M + H]$^+$. Calcd for $C_{26}H_{19}F_6NP$: 490.1159 [M + H]$^+$.

4. Syntheses and characterization of *sym N,N′*-diarylthiourea

***N,N′*-bis(2-trifluoromethyl)phenyl thiourea**



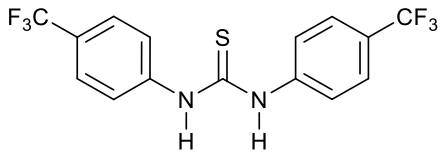
The title thiourea was prepared from $ArNH_2$ and ArNCS (Ar = 2–$(CF_3)C_6H_4$) following the literature procedure[12] with a slight modification as described below. 2-Trifluoromethyl aniline (1 mL, 7.96 mmol) and 2-(trifluoromethyl)phenyl isothiocyanate (1.2 mL, 7.96 mmol) were stirred in anhydrous pyridine (20 mL) at 100 °C for 2 h. Then, the reaction mixture was cooled and pyridine was removed under vacuum to afford yellowish solid which was washed with cold CH_2Cl_2 to afford thiourea as a white solid.

Yield: 50% (1.45 g, 3.98 mmol; Lit. yield: 42%[12]). Mp: 154–155 °C (Lit. Mp: 163–165 °C[11]). IR (KBr, cm^{-1}): 3382 (m, NH), 3137 (m), 2951 (m), 1604 (m), 1591 (m), 1560 (sh, w), 1534 (vs), 1509 (sh, m), 1458 (m), 1362 (sh, s), 1320 (s), 1278 (s), 1227 (m), 1205 (m), 1171 (s), 1138 (s), 1124 (s), 1110 (s), 1058 (s), 1035 (m), 776 (m), 766 (m), 722 (w), 658 (m), 634 (w), 532 (w), 471 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.44 (t, J_{HH} = 7.6 Hz, 2H, Ar*H*), 7.60–7.75 (m, 4H (Ar*H*), 2H (N*H*)), 7.77 (d, J_{HH} = 8.4 Hz, 2H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 123.3 (q, J_{CF} = 273.4 Hz), 126.3 (q, J_{CF} = 30.0 Hz), 127 (br, m), 128.1, 130.2, 133.1, 134.7, 181.5 (N_2C=S). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –62.57. MS (ESI^+) *m/z* [ion]: 365.0545 $[M + H]^+$. Calcd for $C_{15}H_{11}F_6N_2S$: 365.0547 $[M + H]^+$.

General procedure for syntheses of *N*,*N*′-bis(3,5-bis(trifluoromethyl)phenyl) thiourea and *N*,*N*′-bis(4-trifluoromethyl)phenyl thiourea

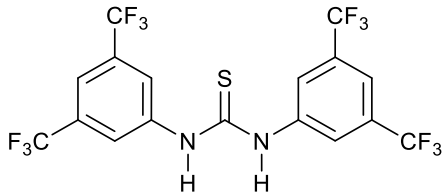
The procedure given below is a slight modification of the literature procedure[13] published for *N*,*N*′-bis(3,5-bis(trifluoromethyl)phenyl) thiourea. To a solution of aniline (0.5 mL) in 10 mL dry THF in a 50 mL RB flask was added aryl isothiocyanate (1 equiv), and the resulting mixture was heated at 50 °C for 80 h with constant stirring and cooled. The reaction mixture was concentrated under vacuum to afford a yellowish solid which was washed with cold CH_2Cl_2 to afford a white solid.

***N,N′*-Bis(4-trifluoromethyl)phenyl thiourea**



Yield: 60% (0.870 g, 2.38 mmol). Mp: 167–168 °C (Lit. Mp: 164–165 °C[12]; 161–163 °C[14]). IR (KBr, cm^{-1}): 3194 (m, NH), 3143 (m, NH), 3089 (m), 3027 (m), 1617 (m), 1600 (m), 1539 (s), 1411 (m), 1321 (s), 1255 (m), 1238 (m), 1192 (s), 1175 (s), 1121 (s), 1066 (s), 1016 (m), 839 (s), 816 (sh, s), 740 (m), 699 (m), 660 (w), 631 (w), 589 (w), 569 (w), 504 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.54, 7.69 (each d, J_{HH} = 8.4 Hz, 2 × 4H, Ar*H*), 7.93 (s, 2H, N*H*). ^{13}C{^{1}H} NMR (DMSO–d_6, 100.5 MHz, ppm): δ 123.2, 124.4 (q, J_{CF} = 271.5 Hz), 124.5 (q, J_{CF} = 31.9 Hz), 125.8, 143.2, 179.8 (N_2C=S). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –63.61. MS (ESI^+) *m/z* [ion]: 365.0541 $[M + H]^+$. Calcd for $C_{15}H_{11}F_6N_2S$: 365.0547 $[M + H]^+$. Anal. Calcd for $C_{15}H_{10}F_6N_2S$ (M_w: 364.31): C, 49.45; H, 2.77; N, 7.69; S, 8.80. Found: C, 49.47; H, 2.60; N, 7.68; S, 9.17. ^{1}H and ^{13}C{^{1}H} NMR data reported herein favorably matched with those reported in the literature.[14]

***N,N′*-Bis(3,5-bis(trifluoromethyl)phenyl) thiourea**

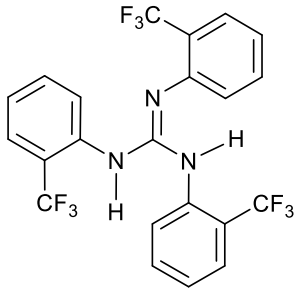


Yield: 86% (1.38 g, 2.75 mmol). Mp: 165 °C (Lit. Mp: 172–173 °C[13]). IR (KBr, cm^{-1}): 3210 (m, NH), 3052 (m), 2988 (w), 1559 (m), 1467 (m), 1376 (s), 1326 (sh, w), 1289 (s), 1181 (s), 1134 (s), 1006 (w), 930 (m), 891 (m), 713 (m), 702 (m), 685 (m), 620 (w), 593 (w). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 7.77 (s, 2H, Ar*H*), 7.90 (s, 4H, Ar*H*), 7.99 (s, 2H, N*H*). ^{13}C{^{1}H} NMR

(DMSO–d_6, 100.5 MHz, ppm): δ 117.7, 123.2 (q, J_{CF} = 272.5 Hz), 124.1, 130.5 (q, J_{CF} = 33.2 Hz), 141.3, 180.7 (N_2C=S). ^{19}F NMR (DMSO–d_6, 376.5 MHz, ppm): δ –61.63. MS (ESI$^+$) *m/z* [ion]: 501.0275 $[M + H]^+$. Calcd for $C_{17}H_8F_{12}N_2S$: 501.0295 $[M + H]^+$. ^{1}H and ^{13}C{^{1}H} NMR data reported herein favorably matched with those reported in the literature.[13]

5. Syntheses and characterisation of *sym N,N′,N″*-triarylguanidines

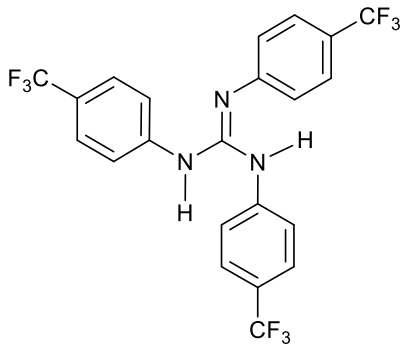
Guanidine, **L7**



Guanidine **L7** was prepared following a literature procedure published earlier for guanidine **L5**[15] with a slight modification as outlined below. *sym N,N′*-bis(2-(trifluoromethyl)phenyl)thiourea (1.025 g, 2.814 mmol) and Ph_3P=NAr (Ar = 2-(CF_3)C_6H_4; 1.186 g, 2.814 mmol) were dispersed in toluene (50 mL) in a 100 mL RB flask attached to a water condenser capped with $CaCl_2$ guard tube. The heterogeneous mixture in the flask was simultaneously stirred and heated at 100 °C for 24 h and cooled. The volatiles from the reaction mixture were removed under vacuum to afford a solid. The solid was subjected to column chromatography over activated basic alumina using *n*-hexane as eluent. The volatiles from the first fraction were evaporated under vacuum to afford **L7** as light yellow solid. Yield: 60% (0.8295 g, 1.688 mol). Mp: 86–87 °C. Anal. Calcd for $C_{22}H_{14}F_9N_3$ (M_w: 491.35): C, 53.78; H, 2.87; N, 8.55. Found: C, 53.43; H, 2.92; N, 8.31. IR (KBr, cm^{-1}): ν (NH) 3437 (m), 3411 (m); ν (C=N) 1649 (s); ν (CF_3, str, asym) 1319 (s); ν (CF_3, str, sym) 1121 (m); ν (CF_3, def, asym) 761 (s). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.10 (br,

2H, N*H*), 7.20 (br, 3H, Ar*H*), 7.55 (t, J_{HH} = 8.0 Hz, 6H, Ar*H*), 7.65 (d, J_{HH} = 8.0 Hz, 3H, Ar*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm): δ 122.9 (br), 124.2 (br), 125.6 (br), 126.8, 133.1, 144.3. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –61.53. MS (ESI^+) *m/z* [ion]: 492.1117 $[M + H]^+$. Calcd for $C_{22}H_{15}F_9N_3$: 492.1122 $[M + H]^+$.

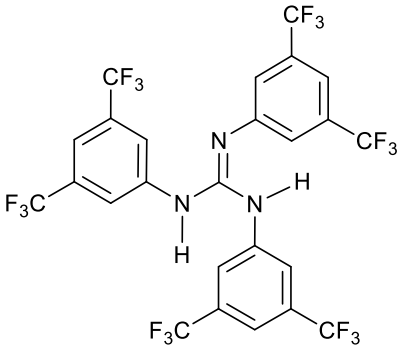
Guanidine, **L8**



Guanidine, **L8** was prepared from *sym N,N′*-bis(4-(trifluoromethyl)phenyl)thiourea (1.0128 g, 2.7801 mmol) and Ph_3P=NAr (Ar = 4-$(CF_3)C_6H_4$; 1.172 g, 2.780 mmol) by following the procedure analogous to that described previously for the guanidine **L7**. Guanidine, **L8** was eluted in the second fraction during the column chromatography work up on alumina using ethylacetate/*n*-hexane (2/98, v/v) mixture as eluent. Guanidine **L8** was obtained as a white solid after evaporation of the eluent under vacuum. Yield: 85% (1.161 g, 2.363 mmol). Mp: 138 °C. Anal. Calcd for $C_{22}H_{14}F_9N_3$ (M_w: 491.35): C, 53.78; H, 2.87; N, 8.55. Found: C, 53.75; H, 2.62; N, 8.36. IR (KBr, cm^{-1}): ν (NH) 3430 (br); ν (C=N) 1593 (s); ν (CF_3, str, asym) 1315 (s); ν (CF_3, str, sym) 1243 (m); ν (CF_3, def, asym) 1107 (s); ν (CF_3, def, sym) 835 (m). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 5.98 (br, 2H, N*H*), 7.22 (d, J_{HH} = 8.4 Hz, 6H, Ar*H*), 7.54 (d, J_{HH} = 8.0 Hz, 6H, Ar*H*). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm): δ 121.0 (Ar*C*H), 124.3 (q, J_{CF} = 271.2 Hz, *C*F_3), 125.7 (q, J_{CF} = 32.5 Hz, *C*CF_3), 126.9 (Ar*C*H), 144.0 (Ar*C*), 145.1 (br, *C*N_3). The δ values for Ar*C*H and Ar*C* carbons were confirmed by HETCOR NMR. ^{19}F NMR ($CDCl_3$,

376.5 MHz, ppm): δ –61.92. MS (ESI$^+$) *m/z* [ion]: 492.1109 [M + H]$^+$. Calcd for $C_{22}H_{15}F_9N_3$: 492.1122 [M + H]$^+$.

Guanidine, **L9**



Guanidine, **L9** was prepared from *sym N,N′*-bis(3,5-bis(trifluoromethyl)phenyl)thiourea (1.008 g, 2.016 mmol) and Ph_3P=NAr (Ar = 3,5-$(CF_3)_2C_6H_3$; 0.9865 g, 2.016 mmol) by following a procedure analogous to that described previously for **L7**. Guanidine, **L9** was eluted in the second fraction during the column chromatography work up on alumina using ethyl acetate/*n*-hexane (40/60, v/v) mixture as eluent. Guanidine, **L9** was obtained as a white solid after evaporation of the eluent under vacuum. Yield: 72% (1.009 g, 1.451 mmol). Mp: 141 °C. Anal. Calcd for $C_{25}H_{11}F_{18}N_3$ (M_w: 695.35): C, 43.18; H, 1.59; N, 6.04. Found: C, 43.18; H, 1.42; N, 6.18. IR (KBr, cm^{-1}): ν (NH) 3420 (m); ν (C=N) 1671 (s); ν (CF_3, str, asym) 1376 (s); ν (CF_3, str, sym) 1280 (s); ν (CF_3, def, asym) 1132 (s); ν (CF_3, def, sym) 888 (m). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 6.35 (br, 2H, N*H*), 7.54 (br, 9H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 117.6 (Ar*C*H), 121.4 (Ar*C*H), 123.0 (q, J_{CF} = 273.1 Hz, *C*F_3), 133.1 (q, J_{CF} = 33.6 Hz *C*CF_3), 144.1 (Ar*C* and *C*N_3). The δ values for Ar*C*H and Ar*C* carbons were confirmed by HETCOR NMR. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –64.69. MS (ESI$^+$) *m/z* [ion]: 696.0722 [M + H]$^+$. Calcd for $C_{25}H_{12}F_{18}N_3$: 696.0744 [M + H]$^+$.

6. Syntheses of complexes 1–8

Complex 1 To a solution of [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50.00 mg, 0.0809 mmol) in methanol (10 mL) was added two equiv of **L7** (79.50 mg, 0.1618 mmol) and two equiv. of NaOAc (13.27 mg, 0.1618 mmol) in a 25 mL RB flask capped with a $CaCl_2$ guard tube and the resulting orange colored solution was stirred at RT for 24 h. The volatiles were removed under vacuum to afford an orange solid and subsequently the solid was dispersed in CH_2Cl_2 and the insoluble NaCl was filtered off. The filtrate was layered with toluene and stored at ambient temperature over a period of four days to afford **1** as orange needle crystals. Yield: 89% (110.7 mg, 0.1449 mmol). Mp: 225 °C. Anal. Calcd for $C_{32}H_{28}N_3F_9ClRh$ (M_w: 763.93): C, 50.31; H, 3.69; N, 5.50. Found: C, 50.47; H, 3.74; N, 5.51. IR (KBr, cm^{-1}): ν (NH) 3344 (br, m); ν (C=N) 1539 (m); ν (CF_3, str, asym) 1485 (s); ν (CF_3, str, sym) 1084 (m); ν (CF_3, def, asym) 828 (m). The ^{1}H NMR spectrum of **1** revealed the presence of three isomers hereafter indicated as isomers 1, 2, and 3 in about 0.34:1.00:0.12 ratio respectively, as estimated from the integrals of CH_3 protons. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.40 (s, 15H, C*H*$_3$, isomer 1), 1.54 (s, 15H, C*H*$_3$, isomer 2), 1.57 (s, 15H, C*H*$_3$, isomer 3), 5.84 (s, 3 × 1H, N*H*, isomers 1–3), 6.65, 6.76, 6.81 (each t, J_{HH} = 7.8 Hz, 3 × 1H, Ar*H*, isomers 2, 1, and 3, respectively), 6.97 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*, isomer 2), 7.04 (t, J_{HH} = 7.6 Hz, 2H, Ar*H*, isomer 2), 7.09 (d, J_{HH} = 8.8 Hz, 1H, Ar*H*, isomer 2), 7.11–7.14 (m, 4H, Ar*H*, isomer 1), 7.20 (t, J_{HH} = 7.8 Hz, 1H, Ar*H*, isomer 1), 7.23 (d, J_{HH} = 8.0 Hz, 2H, Ar*H*, isomer 3), 7.27 (br, 1H, Ar*H*, isomer 3), 7.34 (dt, J_{HH} = 7.8 Hz, 1.2 Hz, 3 × 2H, Ar*H*, isomers 1–3), 7.44 (dd, J_{HH} = 8.0 Hz, 1.2 Hz, 2H, Ar*H*, isomer 2), 7.49–7.57 (m, 5H, Ar*H*; isomer 2 (1H), isomer 3 (4H)), 7.64 (d, J_{HH} = 8.0 Hz, 2H, Ar*H*, isomer 3), 7.92 (d, J_{HH} = 8.0 Hz, 2 × 2H, Ar*H*, isomers 1 and 2), 8.46 (d, J_{HH} = 8.0 Hz, 2H, Ar*H*, isomer 1). The ^{19}F NMR spectrum of **1** also revealed the presence of three isomers in about 0.33:1.00:0.13 ratio respectively, as

estimated from the integrals of CF_3 fluorine signals. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ −62.02 (s, 2 × 3F, C*F*$_3$, isomers 1 and 3), −61.44 (s, 3F, C*F*$_3$, isomer 2), −59.09 (s, 2 × 3F, C*F*$_3$, isomer 2), −58.83 (s, 2 × 3F, C*F*$_3$, isomer 3), −57.94 (s, 2 × 3F, C*F*$_3$, isomer 1). MS (ESI^+) *m/z* [ion]: 728.1188 $[M - Cl]^+$. Calcd for $C_{32}H_{28}N_3F_9ClRh$: 728.1195 $[M - Cl]^+$.

Complex 2 Complex **2** was prepared from $[(\eta^5\text{-Cp*})Rh(\mu\text{-Cl})Cl]_2$ (50.00 mg, 0.0809 mmol), **L8** (79.50 mg, 0.1618 mmol) and NaOAc (13.27 mg, 0.1618 mmol) following the procedure previously discussed for complex **1**. Needle shaped crystals suitable for SCXRD were grown from a mixture of CH_2Cl_2 and MeOH over a period of several days at ambient temperature. Yield: 88% (109.5 mg, 0.1433 mmol). Mp: 252 °C (decompn). Anal. Calcd for $C_{32}H_{28}N_3F_9ClRh{\cdot}H_2O$ (M_w: 763.93 + 18.01): C, 49.15; H, 3.87; N, 5.37. Found: C, 49.52; H, 3.82; N, 5.45. IR (KBr, cm^{-1}): ν (NH) 3328 (m); ν (C=N) 1538 (m); ν (CF_3, str, asym) 1322 (s); ν (CF_3, str, sym) 1112 (m); ν (CF_3, def, asym) 843 (s). The number of solution species of **2** is concentration dependent. ^1H NMR ($CDCl_3$, 400 MHz, ppm, 1.309 × 10^{-2} M): δ 1.64 (s, 15H, C*H*$_3$), 6.14 (s, 1H, N*H*), 6.85 (d, J_{HH} = 8.0 Hz, 2H, Ar*H*), 7.15 (m, 6H, Ar*H*), 7.38 (d, J_{HH} = 8.0 Hz, 4H, Ar*H*). The ^1H NMR spectrum of **2** revealed the presence of two isomers in about 1:0.7 ratio at 13.09 × 10^{-2} M concentration as determined from integrals of CH_3 protons of the Cp* ring. ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.59, 1.63 (each s, 15H, C*H*$_3$, isomers 1 and 2 respectively), 6.18 (s, 2 × 1H, N*H*, isomers 1 and 2), 6.85 (d, J_{HH} = 8.4 Hz, 2H, Ar*H*, isomer 1), 7.08–7.16 (m, 8H, Ar*H*, isomer 1 (2H) and isomer 2 (6H)), 7.22–7.26 (br, 2H, Ar*H*, isomer 2), 7.37 (d, J_{HH} = 8.4 Hz, 4H, Ar*H*, isomer 1), 7.48 (d, J_{HH} = 8.4 Hz, 2 × 4H, Ar*H*, isomers 1 and 2). The $^{13}C\{^1H\}$ NMR spectrum also revealed the presence of two isomers namely, isomer 1 (major) and isomer 2 (minor) and assignments to these isomers are made wherever possible. $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm, 13.09 × 10^{-2} M): δ 9.39, 9.49 (*C*H$_3$, isomers 1 and 2,

respectively), 92.29, 94.33 (each d, J_{RhC} = 8.6 Hz, C_5Me_5, isomers 1 and 2, respectively), 120.28 (isomer 1), 120.76 (br), 122.46 (isomer 2), 122.59, 122.94, 123.94 (isomer 1), 124.02 (q, J_{CF} = 271.2 Hz, CF_3, isomer 1), 124.49 (q, J_{CF} = 271.5 Hz, CF_3, isomer 2), 124.56 (q, J_{CF} = 33.9 Hz, CCF_3, isomer 1), 124.70 (q, J_{CF} = 32.6 Hz, CCF_3, isomer 2), 125.03, 125.62, 125.79, 125.82, 126.07, 126.11, 126.47 (br), 126.54 (br), 126.58 (br), 126.62 (br), 128.33, 129.14, 140.98, 147.85, 153.68 (d, J_{RhC} = 3.9 Hz, CN_3, isomers 1 and 2). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm, 1.309×10^{-2} M): δ –62.22 (s, 3F, CF_3), –61.80 (s, 2 × 3F, CF_3). The ^{19}F NMR spectrum measured at 13.09×10^{-2} M concentration revealed the presence of two isomers in about 1:0.7 ratio as determined from the integrals of CF_3 fluorines. ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –62.31 (s, 3F, CF_3, isomer 2), –62.17 (s, 3F, CF_3, isomer 1), –61.89 (s, 2 × 3F, CF_3, isomer 1), –61.75 (s, 2 × 3F, CF_3, isomer 2). MS (ESI$^+$) *m/z* [ion]: 728.1191 [M – Cl]$^+$, 580.9520 [{(η^5-Cp*)Rh(μ-Cl)Cl}$_2$ – Cl]$^+$, 492.1121 [**L8**H]$^+$. Calcd for $C_{32}H_{28}N_3F_9ClRh$: 728.1195 [M – Cl]$^+$, 580.9523 [{(η^5-Cp*)Rh(μ-Cl)Cl}$_2$ – Cl]$^+$, 492.1122 [**L8**H]$^+$.

Complex 3 Complex **3** was prepared from [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50.00 mg, 0.0809 mmol), **L9** (112.30 mg, 0.1618 mmol) and NaOAc (13.30 mg, 0.1618 mmol) following the procedure previously described for complex **1**. Needle shaped crystals suitable for SCXRD were obtained from MeOH over a period of several days at ambient temperature. Yield: 84% (132.3 mg, 0.1367 mmol). Mp: 234 °C. Anal. Calcd for $C_{35}H_{25}N_3F_{18}ClRh$ (M_w: 967.92): C, 43.43; H, 2.60; N, 4.34. Found: C, 43.70; H, 2.98; N, 4.31. IR (KBr, cm^{-1}): ν(NH) 3327 (br, w); ν(C=N) 1539 (m); ν(CF_3, str, asym) 1373 (s); ν(CF_3, str, sym) 1280 (s); ν(CF_3, def, asym) 1129 (s); ν(CF_3, str, sym) 883 (m). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.66 (s, 15H, CH_3), 6.37 (s, 1H, N*H*), 7.25 (s, 1H, Ar*H*), 7.33 (s, 2H, Ar*H*), 7.39 (s, 2H, Ar*H*), 7.49 (s, 4H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 9.40 (CH_3), 92.84 (d, J_{RhC} = 8.6 Hz, C_5Me_5), 116.38 (br), 117.54

(br), 121.46, 122.65 (q, J_{CF} = 273.0 Hz, *C*F_3), 123.18 (q, J_{CF} = 273.0 Hz, 2 × *C*F_3), 123.61, 132.49 (q, J_{CF} = 33.2 Hz, 2 × *C*CF_3), 132.44 (q, J_{CF} = 33.2 Hz, *C*CF_3), 138.49, 145.66, 152.95 (d, J_{RhC} = 2.9 Hz, *C*N_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –63.39 (s, 12F, C*F*$_3$, isomers 1 and 2), –63.18 (s, 12F, C*F*$_3$, isomer 2), –63.97 (s, 12F, C*F*$_3$, isomer 1). MS (ESI$^+$) *m/z* [ion]: 932.0825 [M – Cl]$^+$, 696.0748 [**L9**H]$^+$. Calcd for $C_{35}H_{25}N_3F_{18}ClRh$: 932.0816 [M – Cl]$^+$, 696.0744 [**L9**H]$^+$.

Complex 4 Complex **4** was prepared from [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50.00 mg, 0.0809 mmol), **L4** (63.20 mg, 0.1618 mmol) and NaOAc (13.30 mg, 0.1618 mmol) following the procedure previously described for complex **1**. Needle shaped crystals suitable for SCXRD were obtained from a mixture of CH_2Cl_2 and *n*-hexane over a period of several days at ambient temperature. Yield: 82% (88.00 mg, 0.1327 mmol). Mp: 246 °C (decompn). Anal. Calcd for $C_{29}H_{28}Cl_4N_3Rh$ (M_w: 663.27): C, 52.51; H, 4.26; N, 6.34. Found: C, 52.31; H, 4.24; N, 6.25. IR (KBr, cm^{-1}): 3380 (m, NH), 1532 (vs, C=N), 743 (s, C–Cl). The ^{1}H NMR spectrum of **4** revealed the presence of two isomers in about 1.00:0.07 ratio as estimated from the integrals of CH_3 protons. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.533 (br, 15H, C*H*$_3$, isomer 1), 1.598 (s, 15H, C*H*$_3$, isomer 2), 6.222 (s, 2 × 1H, N*H*, isomers 1 and 2), 6.537 (t, J_{HH} = 7.2 Hz, 2 × 2H, Ar*H*, isomers 1 and 2), 6.682 (br, 2 × 1H, Ar*H*, isomers 1 and 2), 6.850 (br, 2 × 1H, Ar*H*, isomers 1 and 2), 6.956 (dd, J_{HH} = 8.4 Hz, 1.6 Hz, 2 × 2H, Ar*H*, isomers 1 and 2), 7.075 (br, 2 × 3H, Ar*H*, isomers 1 and 2), 7.201 (br, 2 × 1H, Ar*H*, isomers 1 and 2), 7.256 (s, 2 × 1H, Ar*H*, isomers 1 and 2), 7.535 (br, 2 × 1H, Ar*H*, isomers 1 and 2). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 8.91 (*C*H_3), 91.97 (br, *C*$_5$Me$_5$), 122.31, 122.54, 124.25 (br), 126.56 (br), 127.52 (br), 127.81, 128.09, 129.22 (br), 130.30 (br), 134.69, 141.97 (Ar*C* and Ar*C*H), 152.88 (br, *C*N_3). MS (ESI$^+$) *m/z*

[ion]: 626.0406 [M – Cl]$^+$, 390.0332 [**L4**H]$^+$. Calcd for $C_{29}H_{28}Cl_4N_3Rh$: 626.0404 [M – Cl]$^+$, 390.0332 [**L4**H]$^+$.

Complex 5 Complex **5** was prepared from [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50.00 mg, 0.0809 mmol), **L5** (63.20 mg, 0.1618 mmol) and NaOAc (13.30 mg, 0.1618 mmol) following the procedure previously described for complex **1**. Plate like crystals suitable for SCXRD were obtained from a mixture of CH_2Cl_2 and *n*-hexane over a period of several days at ambient temperature. Yield: 85% (91.20 mg, 0.1375 mmol). Mp: 274 °C (decompn). Anal. Calcd for $C_{29}H_{28}Cl_4N_3Rh$ (M_w: 663.27): C, 52.51; H, 4.26; N, 6.34. Found: C, 52.37; H, 4.39; N, 6.57. IR (KBr, cm^{-1}): 3334 (w, NH), 1485 (vs, C=N), 828 (m, C–Cl). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.60 (s, 15H, C*H*$_3$), 5.83 (s, 1H, N*H*), 6.74 (d, J_{HH} = 8.4 Hz, 2H, Ar*H*), 6.88 (d, J_{HH} = 8.8 Hz, 2H, Ar*H*), 7.02 (d, J_{HH} = 8.4 Hz, 4H, Ar*H*), 7.08 (d, J_{HH} = 6.8 Hz, 4H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 9.32 (*C*H$_3$), 91.86 (d, J_{RhC} = 8.5 Hz, *C*$_5$Me$_5$), 122.05, 125.36, 127.87, 128.26, 128.59, 128.87, 129.53, 136.77, 143.40 (Ar*C* and Ar*C*H), 154.49 (*C*N$_3$). MS (ESI$^+$) *m/z* [ion]: 626.0399 [M – Cl]$^+$, 390.0328 [**L5**H]$^+$. Calcd for $C_{29}H_{28}Cl_4N_3Rh$: 626.0404 [M – Cl]$^+$, 390.0332 [**L5**H]$^+$.

Complex 6 Complex **6** was prepared from [(η^5-Cp*)Rh(μ-Cl)Cl]$_2$ (50.00 mg, 0.0809 mmol), **L6** (55.20 mg, 0.1618 mmol) and NaOAc (13.30 mg, 0.1618 mmol) following the procedure previously described for complex **1**. Needle shaped crystals suitable for SCXRD were obtained from a mixture of CH_2Cl_2 and *n*-hexane over a period of several days at ambient temperature. Yield: 80% (79.40 mg, 0.1294 mmol). Mp: 233 °C. Anal. Calcd for $C_{29}H_{28}F_3ClN_3Rh$ (M_w: 613.91): C, 56.74; H, 4.60; N, 6.84. Found: C, 56.57; H, 4.28; N, 6.76. IR (KBr, cm^{-1}): 3394 (m, NH), 1500 (vs, C=N), 748 (s, C–F). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.58 (s, 15H, C*H*$_3$), 6.02 (s, 1H, N*H*), 6.58 (m, 2H, Ar*H*), 6.73 (m, 1H, Ar*H*), 6.81–6.97 (m, 6H,

Ar*H*), 7.01 (m, 1H, Ar*H*), 7.33 (t, J_{HH} = 8.4 Hz, 2H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm): δ 8.88 (*C*H_3), 91.96 (d, J_{RhC} = 8.5 Hz, *C*$_5$Me$_5$), 114.27 (d, J_{CF} = 19.2 Hz, Ar*C*), 115.28 (d, J_{CF} = 21.1 Hz, Ar*C*), 122.71, 122.95, 123.50, 123.73 (d, J_{CF} = 7.6 Hz, Ar*C*), 124.38, 124.73, 126.06 (d, J_{CF} = 11.5 Hz, Ar*C*), 126.50, 132.40 (d, J_{CF} = 11.5 Hz, Ar*C*), 154.50, 155.68 (Ar*C* and Ar*C*H), 158.10 (*C*N_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –67.09 (s, 1F, ArC*F*), –60.26 (s, 2F, ArC*F*). MS (ESI^+) *m/z* [ion]: 578.1294 [M – Cl]$^+$, 342.1216 [**L6**H]$^+$. Calcd for $C_{29}H_{28}F_3ClN_3Rh$: 578.1290 [M – Cl]$^+$, 342.1218 [**L6**H]$^+$.

Complex 7 Complex **7** was prepared from [(η^5-Cp*)Ir(μ-Cl)Cl]$_2$ (50.00 mg, 0.0627 mmol), **L9** (87.07 mg, 0.1254 mmol) and NaOAc (10.30 mg, 0.1254 mmol) following the procedure previously described for complex **1**. Rectangular crystals suitable for SCXRD were obtained from a mixture of CH_2Cl_2 and *n*-hexane over a period of two days at ambient temperature. Yield: 74% (98.20 mg, 0.0929 mmol). Mp: 221 °C. Anal. Calcd for $C_{35}H_{25}N_3F_{18}ClIr$ (M_w: 1057.23): C, 39.76; H, 2.38; N, 3.97. Found: C, 39.64; H, 2.33; N, 3.96. IR (KBr, cm^{-1}): 3429 (w, NH), 1537 (m, C=N), 1375 (m, CF_3, str, asym), 1286 (m, CF_3, str, sym), 1133 (s, CF_3, def, asym), 906 (m, CF_3, def, sym). ^1H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.64 (s, 15H, C*H*$_3$), 6.60 (s, 1H, N*H*), 7.27 (s, 1H, Ar*H*), 7.39 (s, 2H, Ar*H*), 7.48 (s, 6H, Ar*H*). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100.5 MHz, ppm): δ 9.54 (*C*H_3), 84.60 (s, *C*$_5$Me$_5$), 116.62 (br), 118.00 (br), 122.14, 122.64 (q, J_{CF} = 272.8 Hz, *C*F_3), 123.11 (q, J_{CF} = 273.1 Hz, 2 × *C*F_3), 123.19, 132.49 (q, J_{CF} = 33.2 Hz, *C*CF_3), 137.84, 144.35, 155.26 (*C*N_3). ^{19}F NMR ($CDCl_3$, 376.5 MHz, ppm): δ –63.44 (s, 6F, C*F*$_3$), –63.04 (s, 12F, C*F*$_3$). MS (ESI^+) *m/z* [ion]: 1022.1405 [M – Cl]$^+$, 696.0747 [**L9**H]$^+$. Calcd for $C_{35}H_{25}N_3F_{18}ClIr$: 1022.1390 [M – Cl]$^+$, 696.0744 [**L9**H]$^+$.

Complex 8 Complex **4** (50.00 mg, 0.0753 mmol) and $AgSbF_6$ (28.50 mg, 0.0829 mmol) were dispersed in MeCN in a 25 mL RB capped with $CaCl_2$ guard tube and the resulting

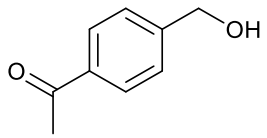
heterogeneous mixture was stirred at RT for 6 h in dark. The volatiles from the reaction mixture were removed under vacuum to afford a blackish orange solid and the solid was extracted with CH_2Cl_2 and the insoluble AgCl was filtered off. The extract was layered with *n*-hexane and stored at ambient condition for several days to afford orange needle crystals suitable for SCXRD. Yield: 90% (61.20 mg, 0.0677 mmol). Mp: 198 °C. Anal. Calcd for $C_{31}H_{31}Cl_3F_6N_4RhSb{\cdot}H_2O$ (M_w: 904.61 + 18.01): C, 40.36; H, 3.60; N, 6.07. Found: C, 40.38; H, 3.37; N, 5.83. IR (KBr, cm^{-1}): 3387 (w, NH), 1546 (m, C=N), 755 (w, C–Cl), 658 (m, Sb–F). The ^{1}H NMR spectrum of **8** revealed the presence of two isomers in about 1.00:0.13 ratio as estimated from the integrals of CH_3 and NH protons. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.49 (s, 15H, C*H*$_3$, isomer 1), 1.60 (br, 15H, C*H*$_3$, isomer 2), 2.36 (br, 2 × 3H, C*H*$_3$CN, isomers 1 and 2), 6.25, 6.40 (each s, 2 × 1H, N*H*, isomers 2 and 1, respectively), 6.69 (m, 2 × 2H, Ar*H*, isomers 1 and 2), 6.79 (m, 2 × 1H, Ar*H*, isomers 1 and 2), 6.98–7.15 (m, 2 × 5H, Ar*H*, isomers 1 and 2), 7.19–7.25 (m, 2 × 1H, Ar*H*, isomers 1 and 2), 7.28–7.45 (m, 2 × 2H, Ar*H*, isomers 1 and 2), 7.50–7.62 (m, 2 × 1H, Ar*H*, isomers 1 and 2). The ^{13}C{^{1}H} NMR spectrum of **8** revealed the presence of two isomers as identified from the signals of *C*H_3 and *C*$_5$Me$_5$ carbons. ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 3.08 (*C*H_3CN, isomers 1 and 2), 8.55, 9.34 (*C*H_3, isomers 1 and 2, respectively), 95.06 (d, J_{RhC} = 8.6 Hz, *C*$_5$Me$_5$, isomer 1), 97.80 (J_{RhC} = 5.7 Hz, *C*$_5$Me$_5$, isomer 2), 120.75, 121.72, 123.79, 124.31, 124.92, 125.56 (br), 126.20, 126.85, 127.51, 127.81, 128.35 (br), 128.42, 128.49, 128.74, 128.97, 129.07, 129.57, 129.92, 130.20, 130.52, 130.76, 130.86, 132.24, 133.64, 133.92, 137.04 (Ar*C* and Ar*C*H, isomers 1 and 2), 139.73 (CH$_3$*C*N, isomer 1), 144.21 (CH$_3$*C*N, isomer 2), 152.62 (*C*N$_3$, isomer 2), 155.92 (*C*N$_3$, isomer 1). Λ_m (Ω^{-1} cm^2 mol^{-1}, 300 K, MeCN) = 64.0 (10^{-3} M). MS (ESI$^+$) *m/z* [ion]: 580.9514 [{(η^5-Cp*)Rh(μ-Cl)Cl}$_2$ – Cl]$^+$, 390.0326 [**L4**H]$^+$. Calcd for 580.9520 [{(η^5-Cp*)Rh(μ-Cl)Cl}$_2$ – Cl]$^+$, 390.0332 [**L4**H]$^+$.

7. General procedure for transfer hydrogenation and etherification catalysis

The catalyst (0.01 mmol) was dissolved in a solution containing the substrate (1.0 mmol), and 2-propanol (4.0 mL) in a 10 mL RB flask which was fitted to a water condenser capped with $CaCl_2$ guard tube. The solution was simultaneously stirred and heated at 82 °C for 4 h and cooled. The volatiles were removed under vacuum. The percentage conversions in TH of substrates studied were estimated by ^{1}H NMR spectroscopy through comparisons of the integrals of signature proton(s) of the substrates and the respective reduction products. Note: KOH (1.0 mmol) was added wherever TH was carried out in the presence of a base.

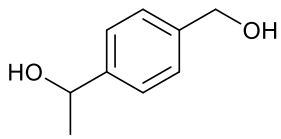
8. Syntheses and characterization data of 17 and 18

Complex **3** (6.5 mg, 1.0 mol %) was dissolved in a solution containing 4-acetylbenzaldehyde (100.0 mg, 0.670 mmol), and 2-propanol (4.0 mL) in a 10 RB flask which was fitted to a water condenser capped with $CaCl_2$ guard tube. The solution was simultaneously stirred and heated at 82 °C for 10 min (for **17**) and 500 min (for **18**) and cooled. The volatiles from the reaction mixture were removed under vacuum and the product in each case was purified by a short column on silica gel using ethylacetate/*n*-hexane (10/90, v/v) mixture as eluent.



17

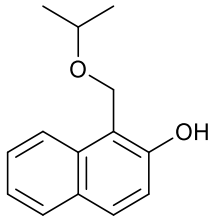
Isolated yield: 91% (91.6 mg, 0.610 mmol). Mp: 53 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 2.58 (s, 3H, C*H*$_3$), 4.76 (s, 2H, C*H*$_2$), 7.43, 7.92 (each d, J_{HH} = 8.4 Hz, 2 × 2H, Ar*H*).



18

Isolated yield: 98% (101 mg, 0.660 mmol). Mp: 65 °C. ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.45 (d, J_{HH} = 6.8 Hz, 3H, C*H*$_3$), 2.53 (br, 1H, O*H*), 4.60 (s, 2H, C*H*$_2$), 4.84 (q, J_{HH} = 6.0 Hz, 1H, MeC*H*(OH)), 7.27, 7.30 (each d, J_{HH} = 8.4 Hz, 2 × 2H, Ar*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 25.2, 65.0, 70.2, 125.7, 127.3, 140.1, 145.3.

9. Characterisation data for 1-(isopropoxymethyl)naphthalen-2-ol



Isolated yield: 82% (103 mg, 0.480 mmol). ^{1}H NMR ($CDCl_3$, 400 MHz, ppm): δ 1.34 (d, J_{HH} = 6.4 Hz, 6H, OCH(C*H*$_3$)$_2$), 3.89 (m, 1H, OC*H*(CH$_3$)$_2$), 5.26 (s, 2H, C*H*$_2$), 7.12 (d, J_{HH} = 8.4 Hz, 1H, Ar*H*), 7.32 (t, J_{HH} = 7.6 Hz, 1H, Ar*H*), 7.46 (t, J_{HH} = 7.4 Hz, 1H, Ar*H*), 7.69 (d, J_{HH} = 8.4 Hz, 1H, Ar*H*), 7.70 (d, J_{HH} = 9.2 Hz, 1H, Ar*H*), 7.78 (d, J_{HH} = 7.6 Hz, 1H, Ar*H*), 9.12 (s, 1H, O*H*). ^{13}C{^{1}H} NMR ($CDCl_3$, 100.5 MHz, ppm): δ 22.0, 67.0, 73.0, 112.1, 119.5, 120.9, 123.0, 126.6, 128.7, 128.9, 129.5, 131.6, 154.8. This compound is an oil and our attempts to obtain satisfactory HR-MS data were not successful.

X-ray crystallography

Single crystals of guanidines **L5** and **L6** were grown from CH_2Cl_2/*n*-hexane mixture and ethanol, respectively. Single crystals of **L9** were grown from $CHCl_3$/*n*-hexane mixture at RT by slow evaporation method (see Figs. S8 and S9). Suitable crystals for X-ray diffraction were carefully selected after examination under an optical microscope and mounted on the goniometer head. The unit cell parameters and intensity data were collected on Oxford Xcalibur S diffractometer (4-circle kappa goniometer, Sapphire–3 CCD detector, omega scans, graphite monochrometer, and a single wavelength Enhance X-ray source with MoKα radiation).[16] Pre-experiment, data

collection, data reduction, and absorption corrections were performed with the CrysAlisPro software suite.[17] The structures were solved by direct methods using SIR 92,[18] which revealed the atomic positions, and refined using the SHELX-97 program package[19] and SHELXL97 (within the WinGX program package).[20] Non-hydrogen atoms were refined anisotropically. C−H/N−H hydrogen atoms were placed in geometrically calculated positions by using a riding model. The molecular structures were created with Olex2 program.[21]

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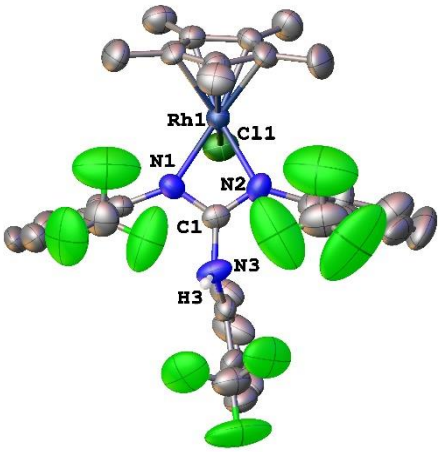

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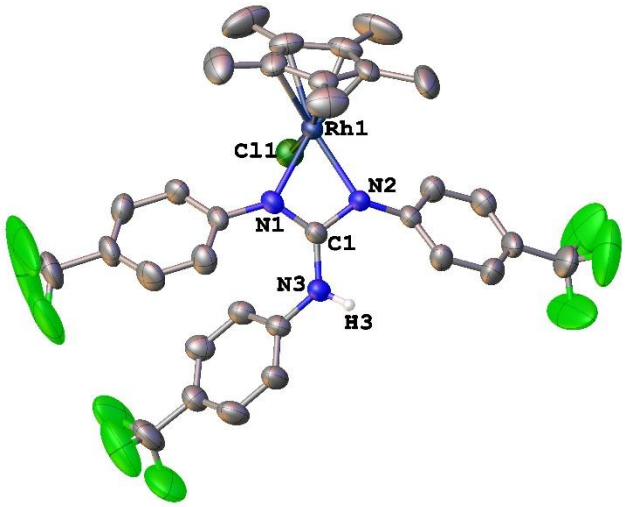

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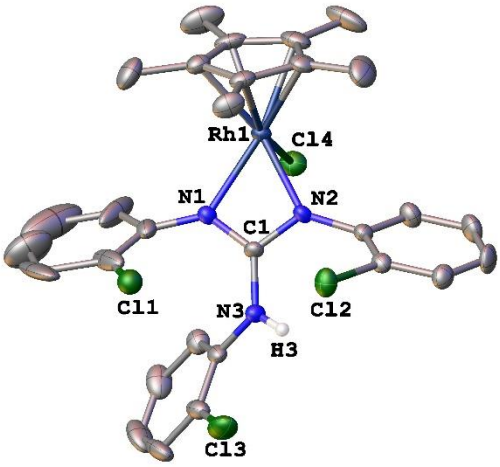


4

Fig. S1 Molecular structures of **1**, **2** and **4** at the 30% probability level.

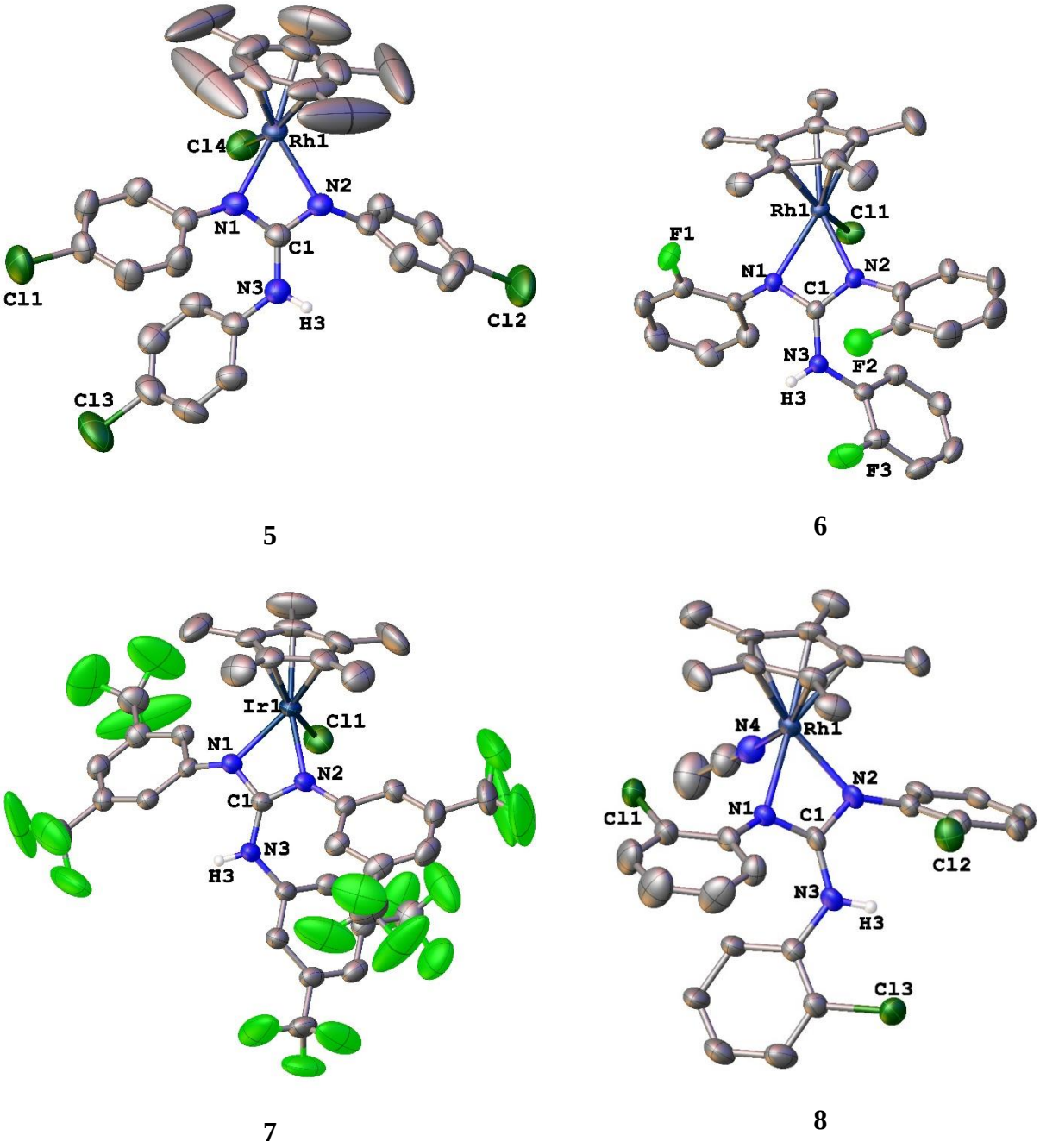


Fig. S2 Molecular structures of **5**–**8** at the 30% probability level.

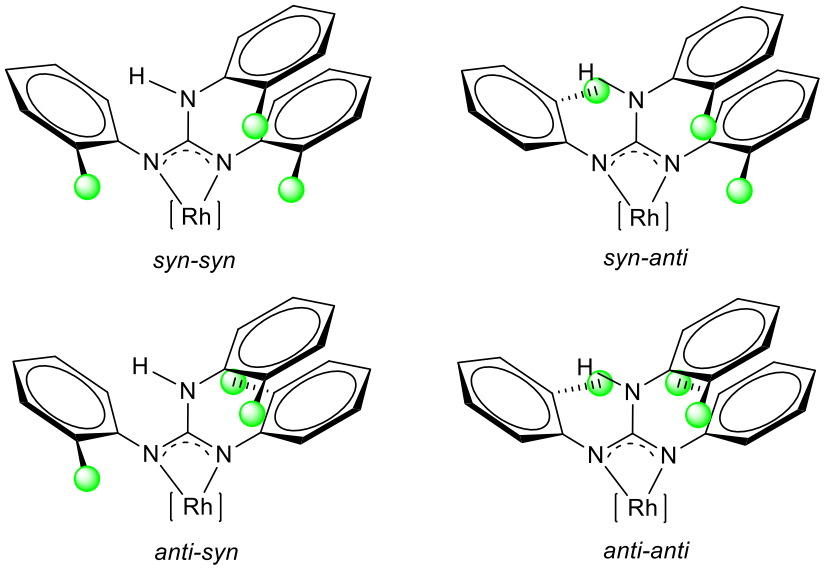


Fig. S3 Four conformers of the guanidinato ligands in **1**, **4** and **6**. ● = CF_3, Cl, F; [Rh] = [(η^5-Cp*)RhCl].

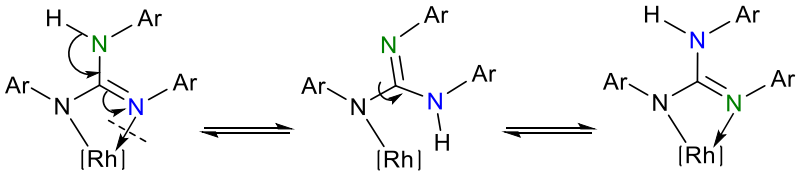


Fig. S4 Plausible guanidine centered rearrangements of [(η^5-Cp*)RhCl(*NN*)]; *NN* = *N*,*N*′,*N*″-Triarylguanidinato ligands with Ar being *o*-substituted aryl ring.

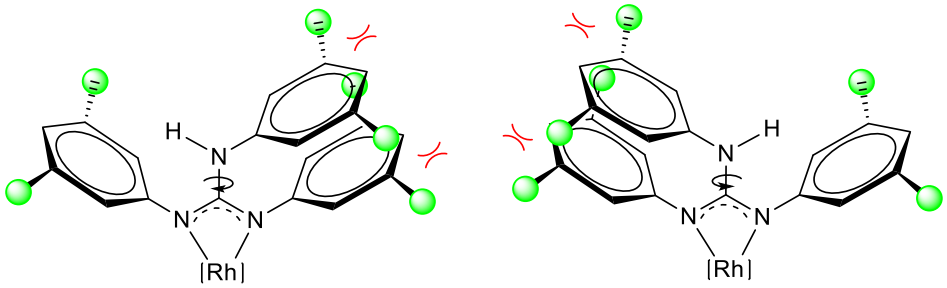


Fig. S5 Two rotamers of **3** in solution as revealed by ^{19}F NMR spectroscopy. ● = CF_3; [Rh] = [(η^5-Cp*)RhCl].

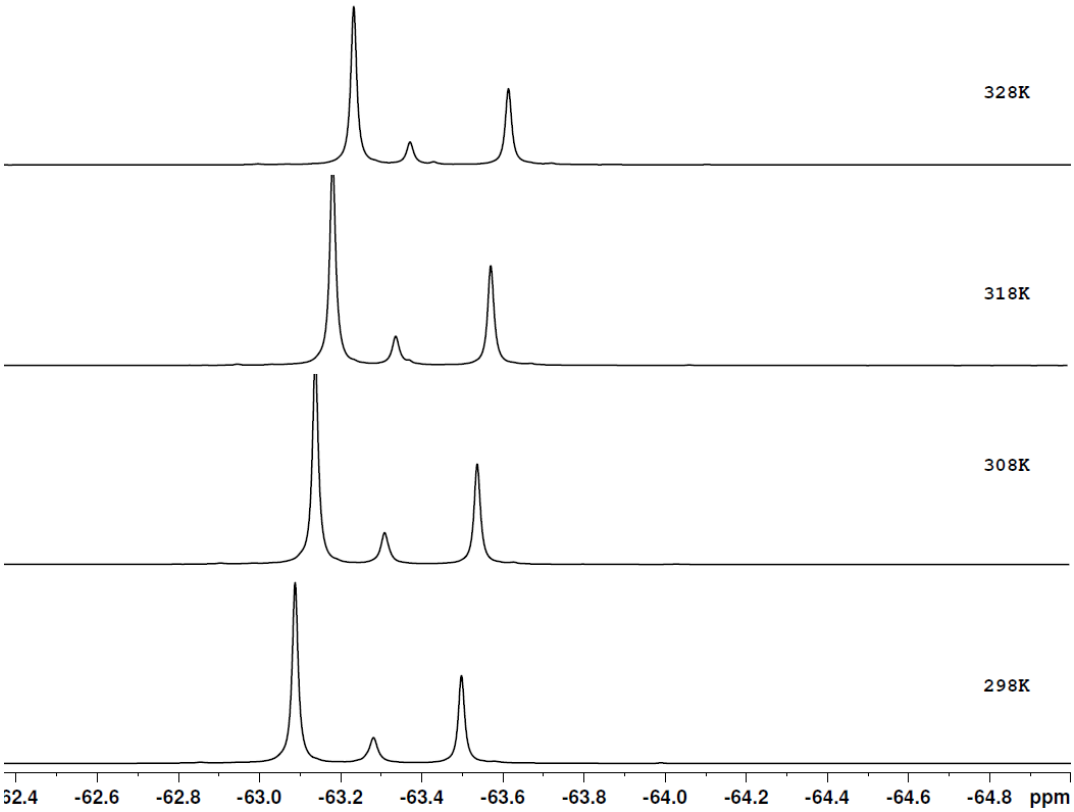


Fig. S6 VT ^{19}F NMR (376.5 MHz, $CDCl_3$) spectra of **3** illustrated for CF_3 fluorine of the guanidinato ligand

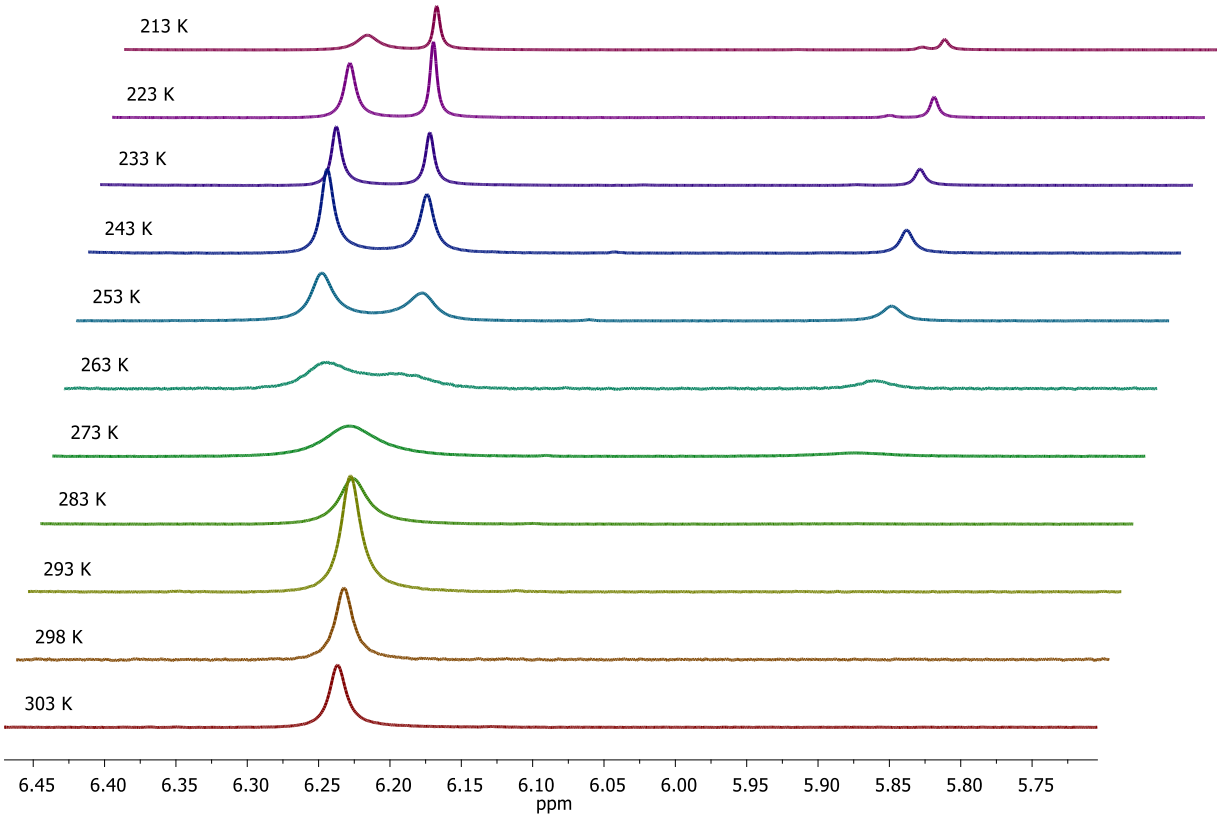
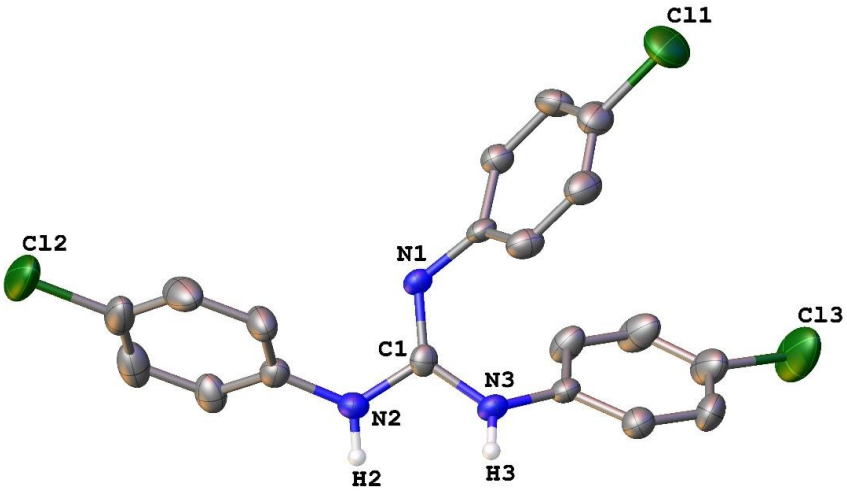
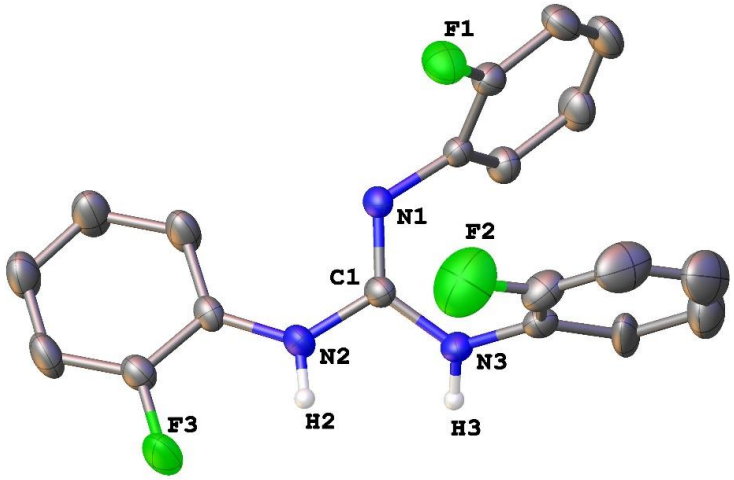


Fig. S7 VT ^{1}H NMR (400 MHz, CD_2Cl_2) spectra of **4** illustrated for NH proton of the guanidinate ligand.

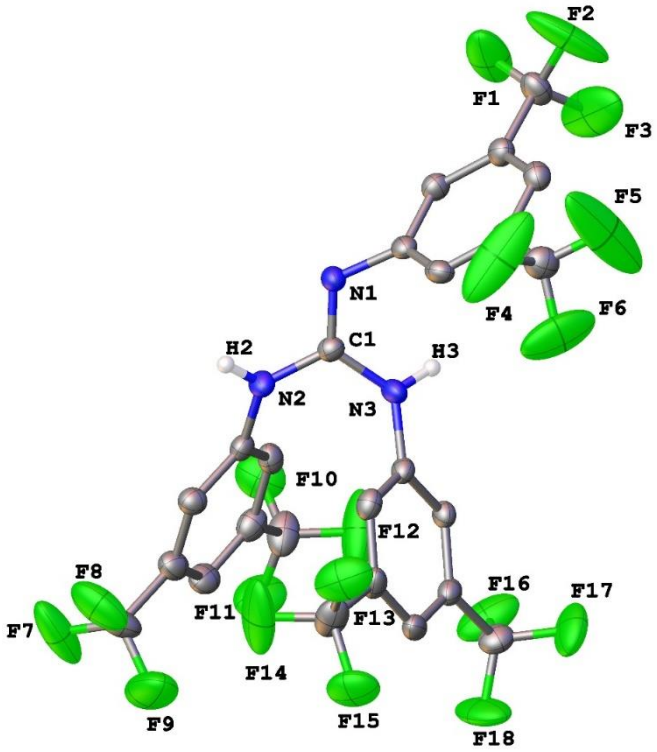


L5



L6

Fig. S8 Molecular structures of **L5** and **L6** at the 30% probability level.



L9

Fig. S9 Molecular structure of **L9** at the 30% probability level. There are two molecules per asymmetric unit of **L9** but only molecule one is shown here.

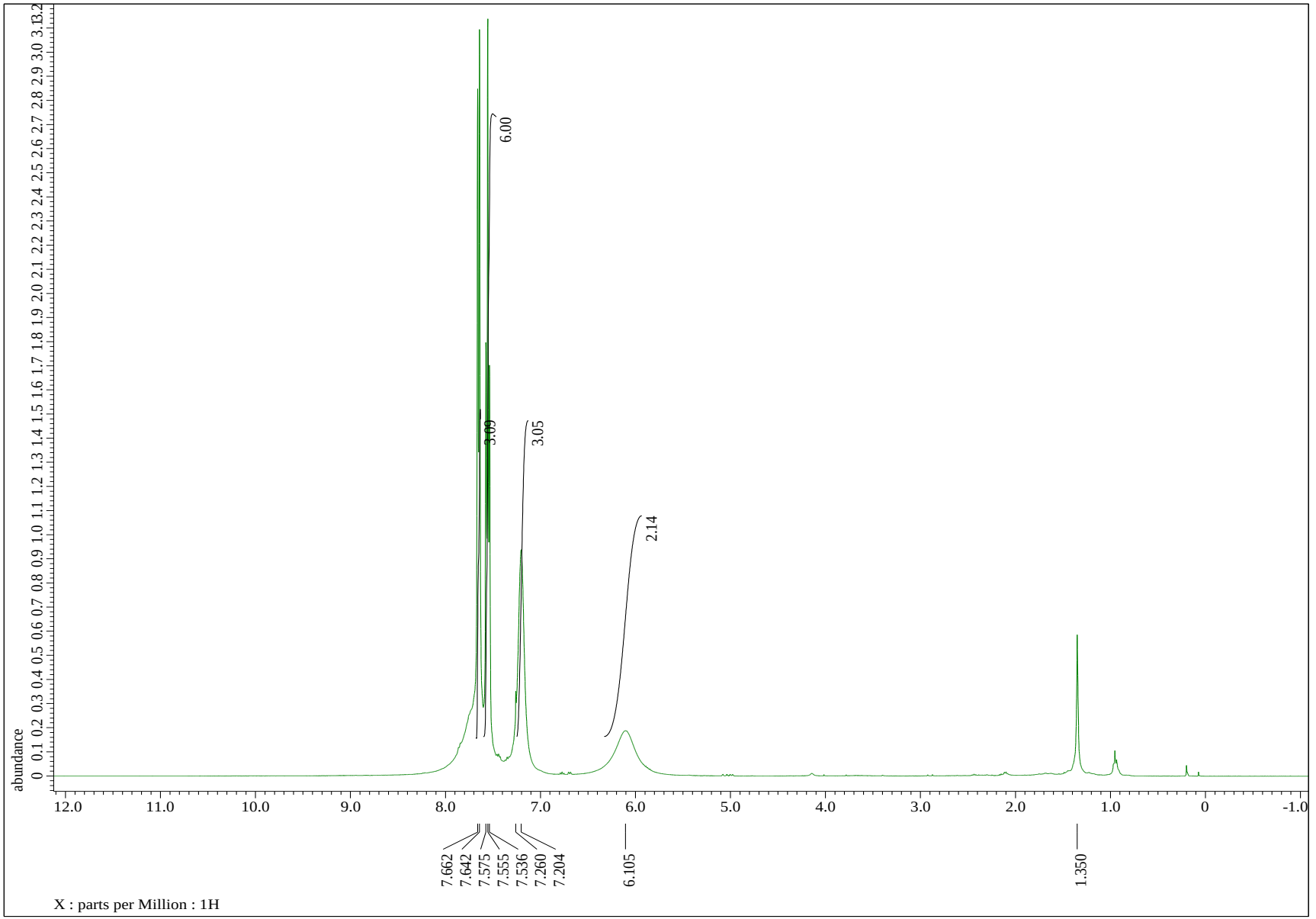


Fig. S10 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L7**

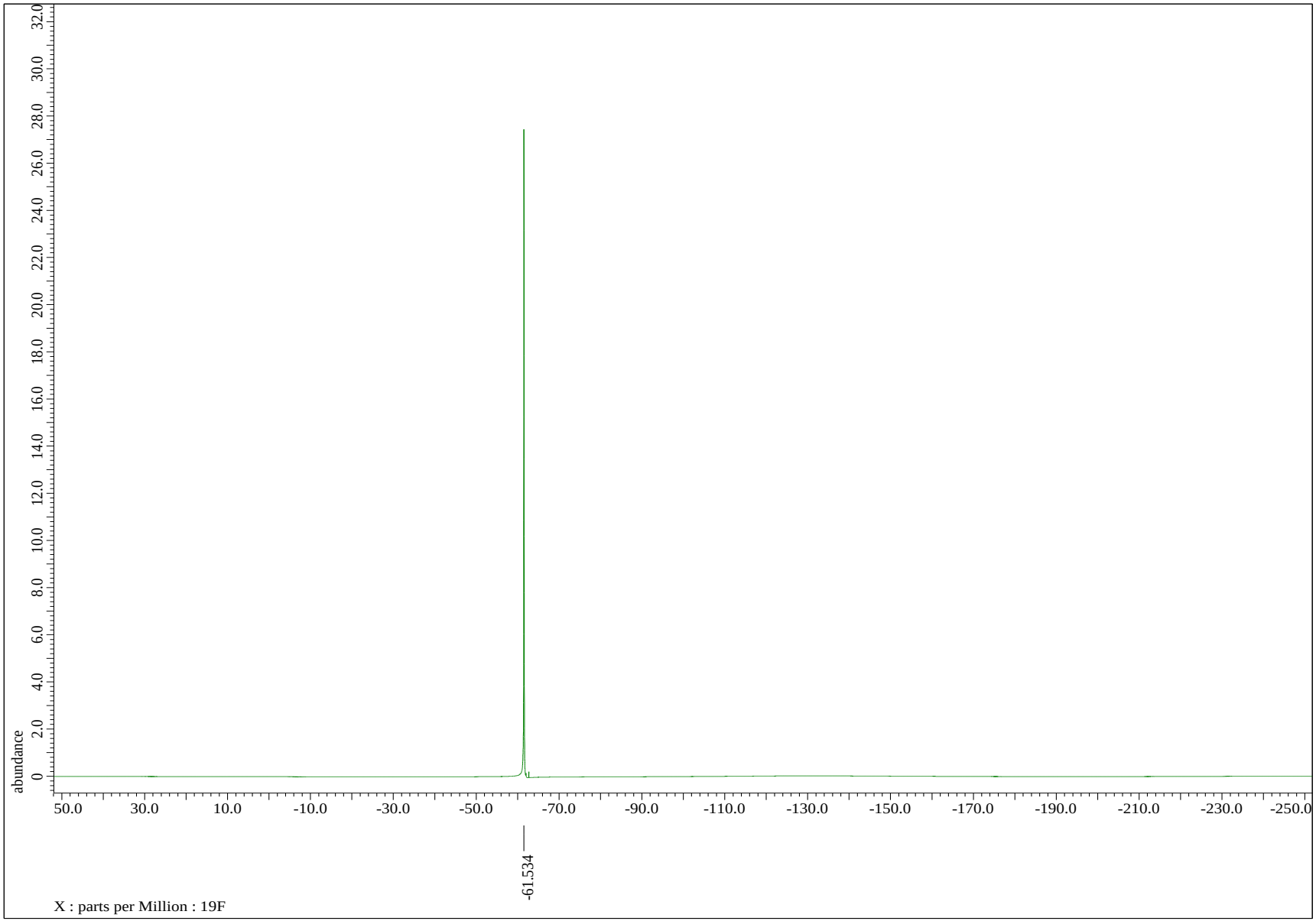


Fig. S11 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **L7**

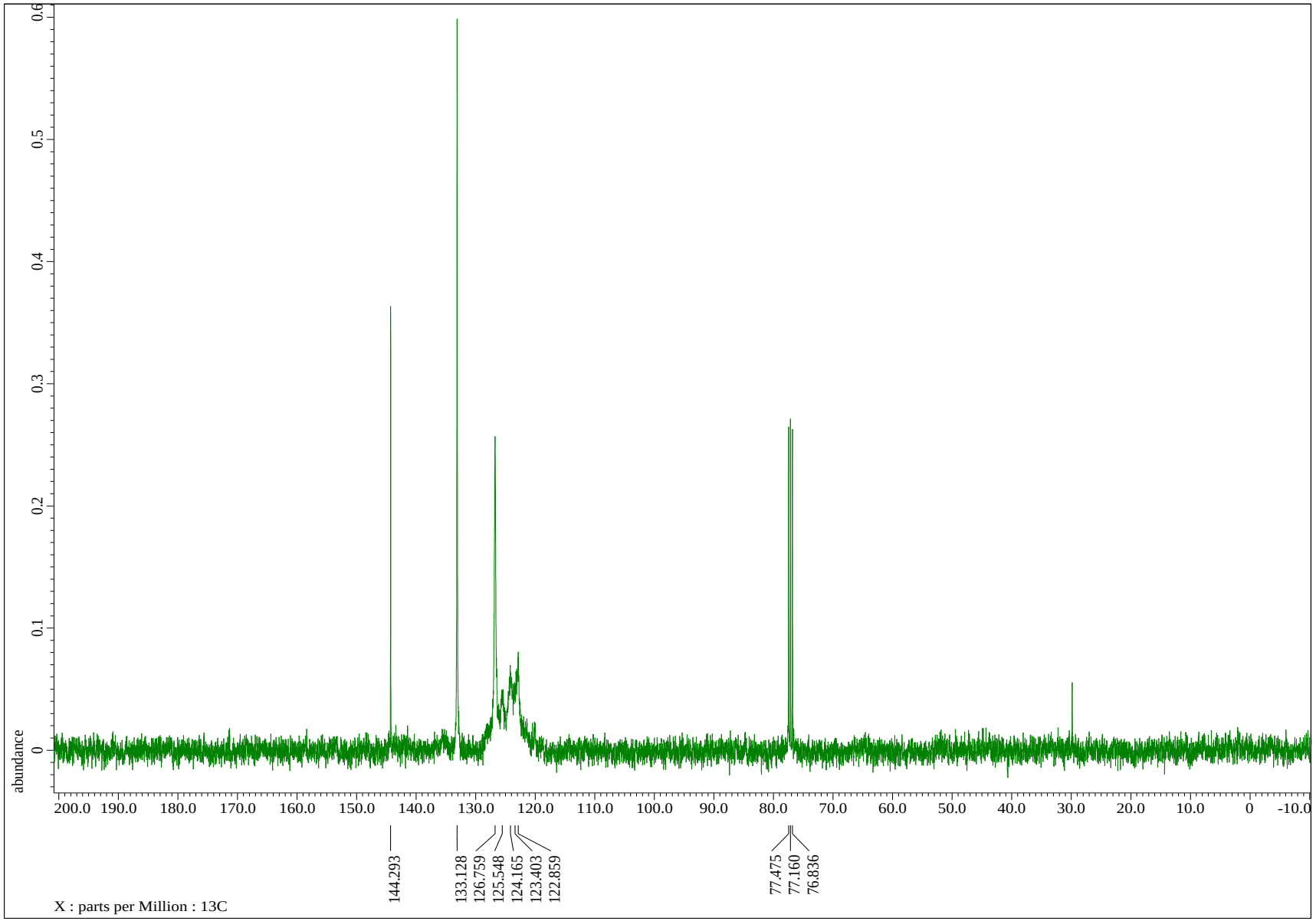


Fig. S12 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **L7**

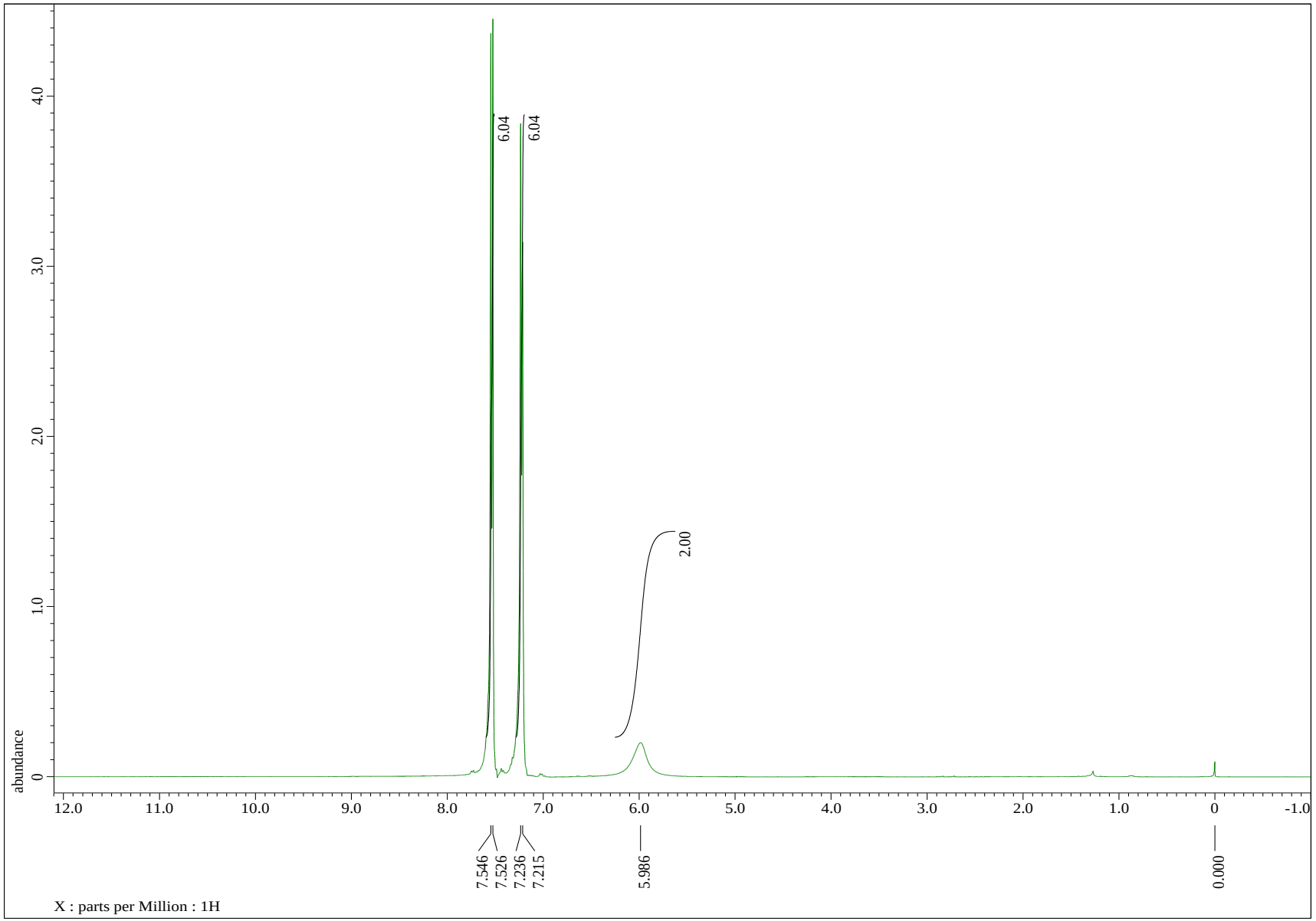


Fig. S13 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L8**

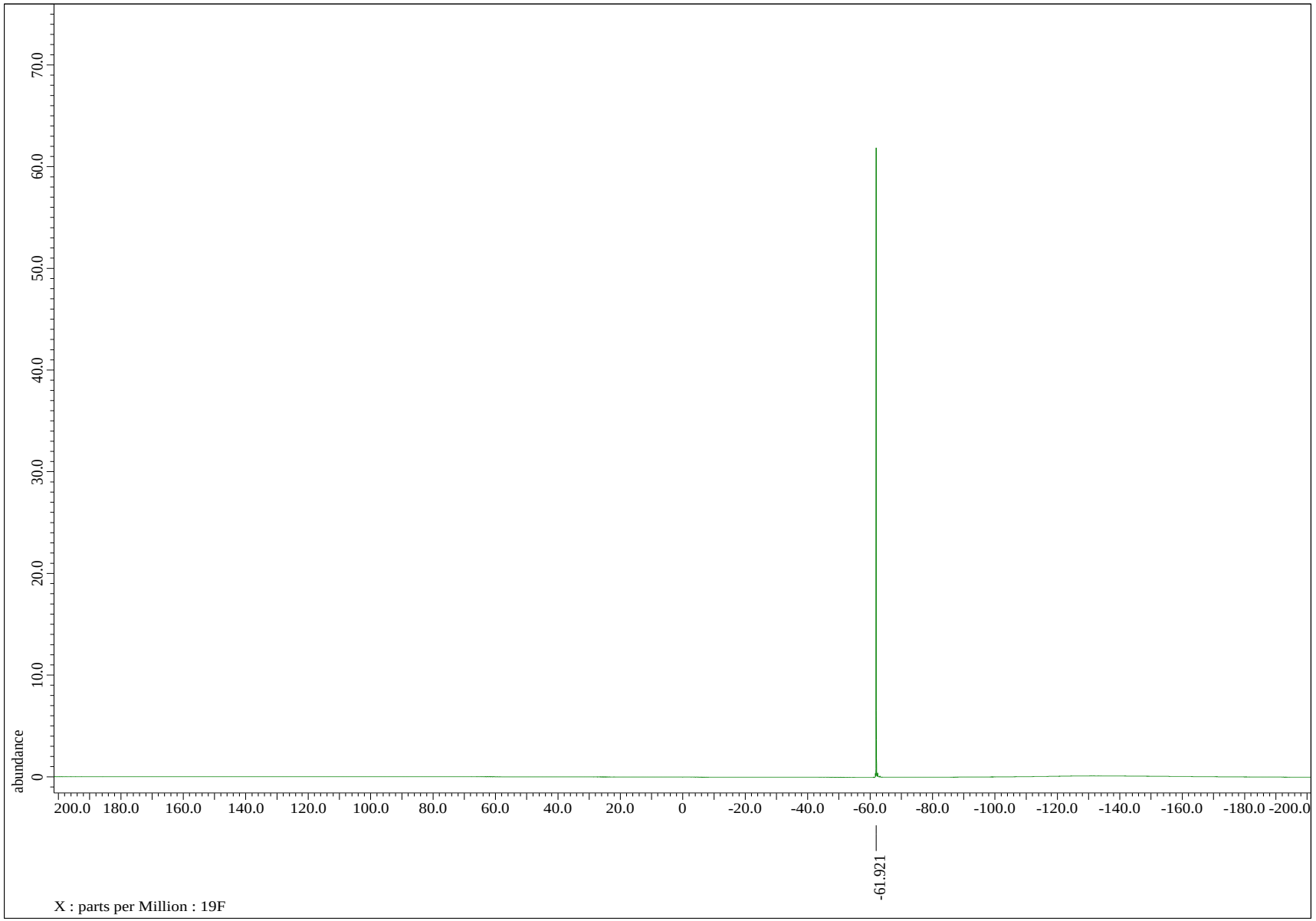


Fig. S14 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **L8**

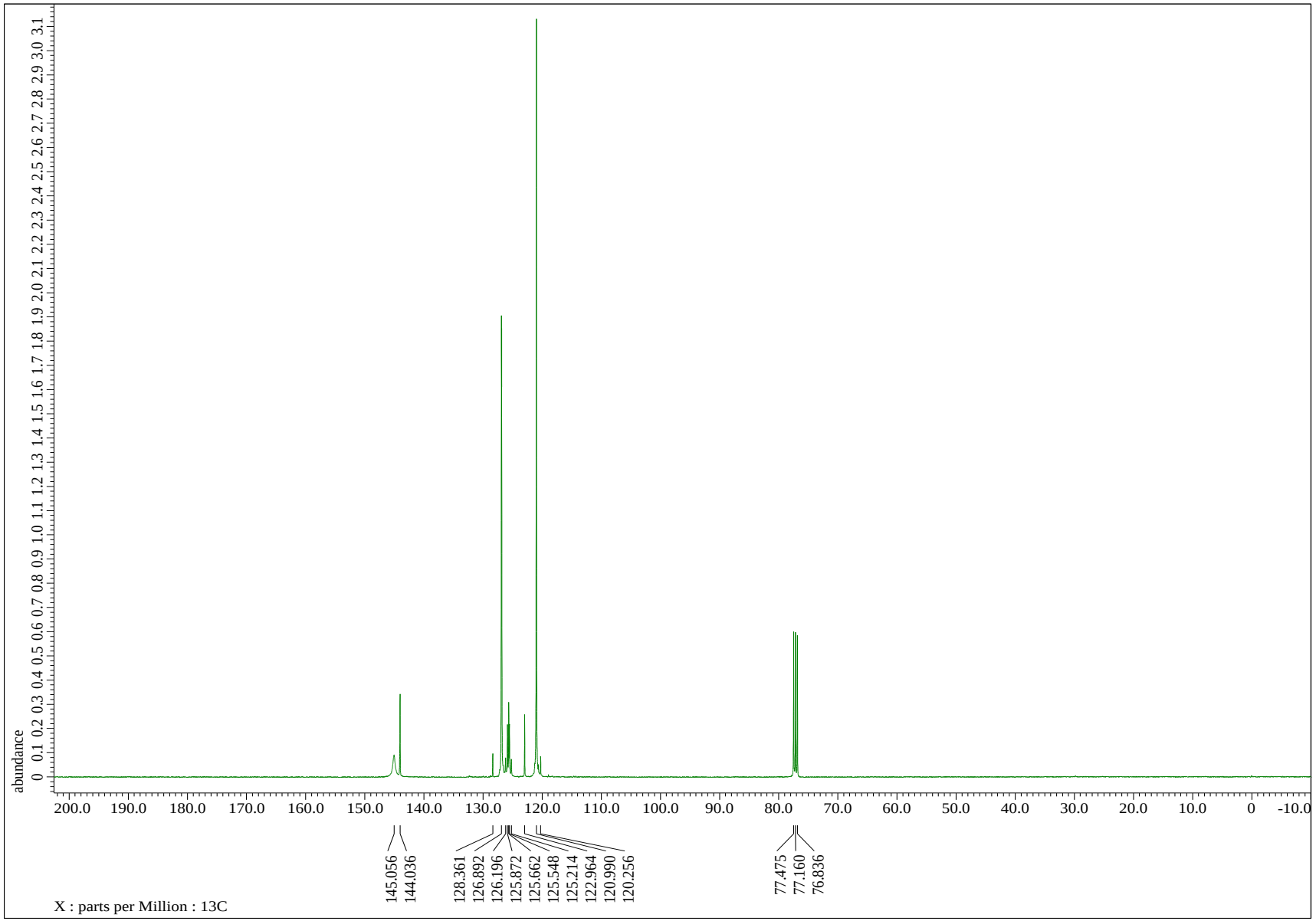


Fig. S15 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **L8**

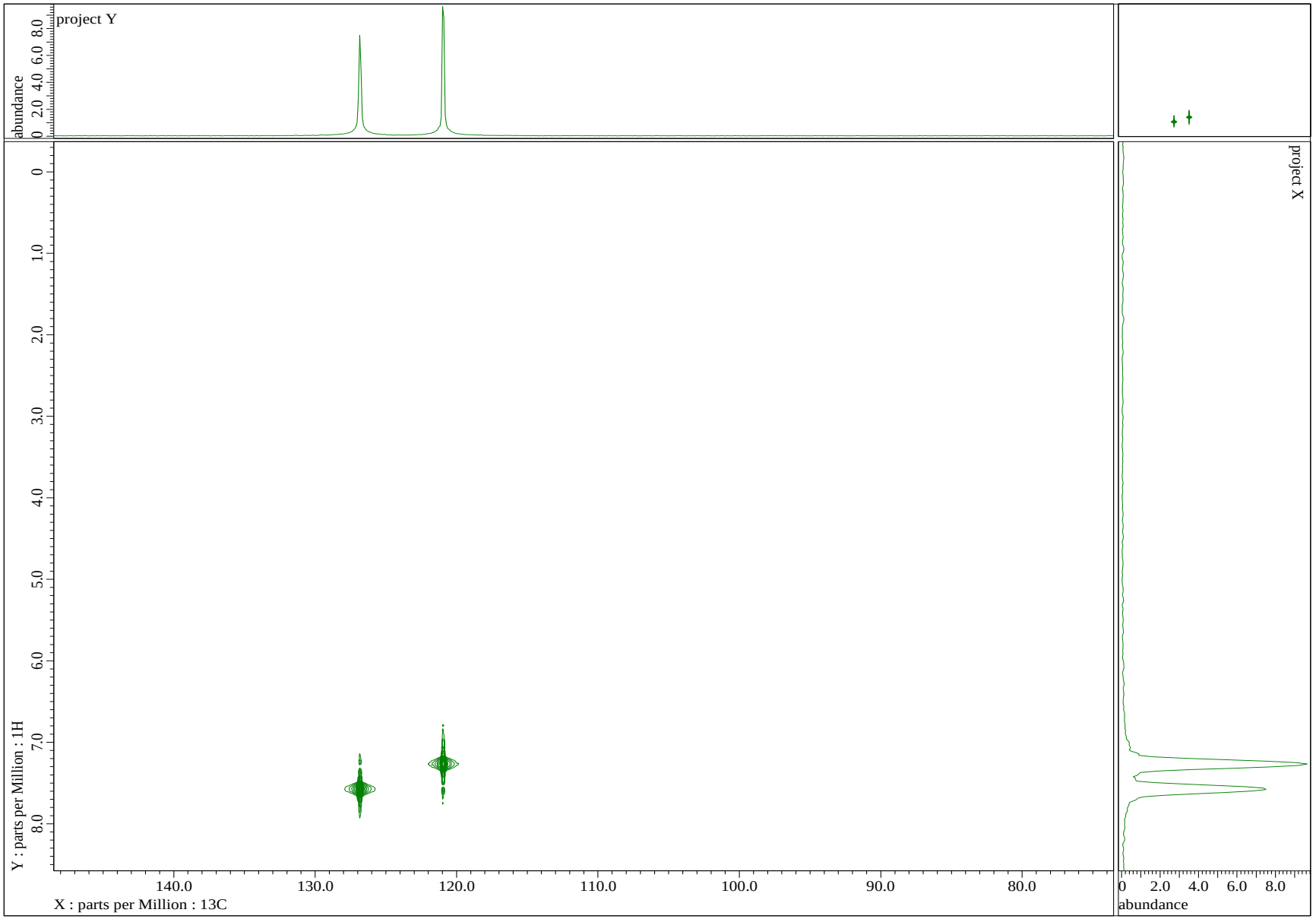


Fig. S16 HETCOR spectrum for **L8**

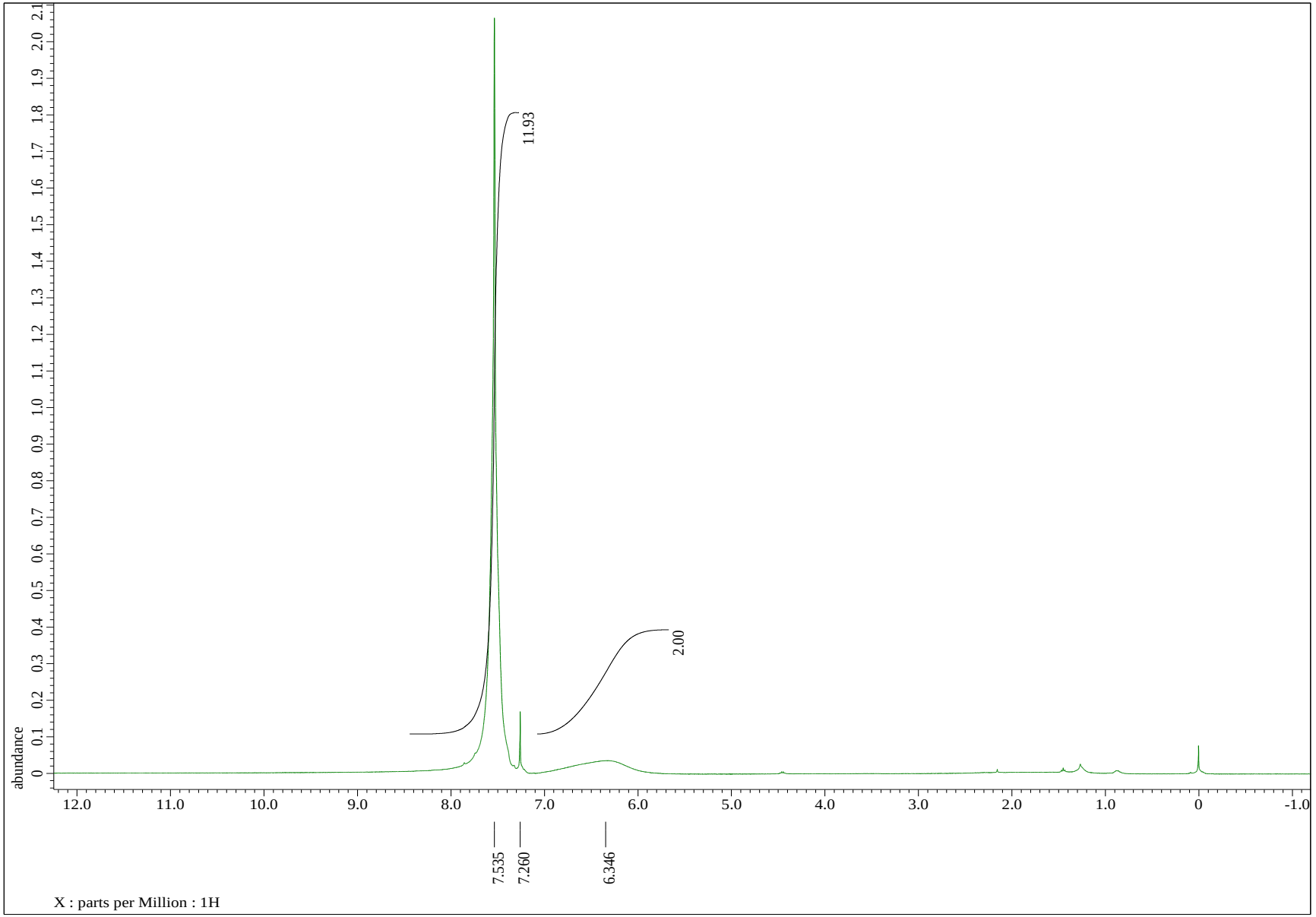


Fig. S17 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **L9**

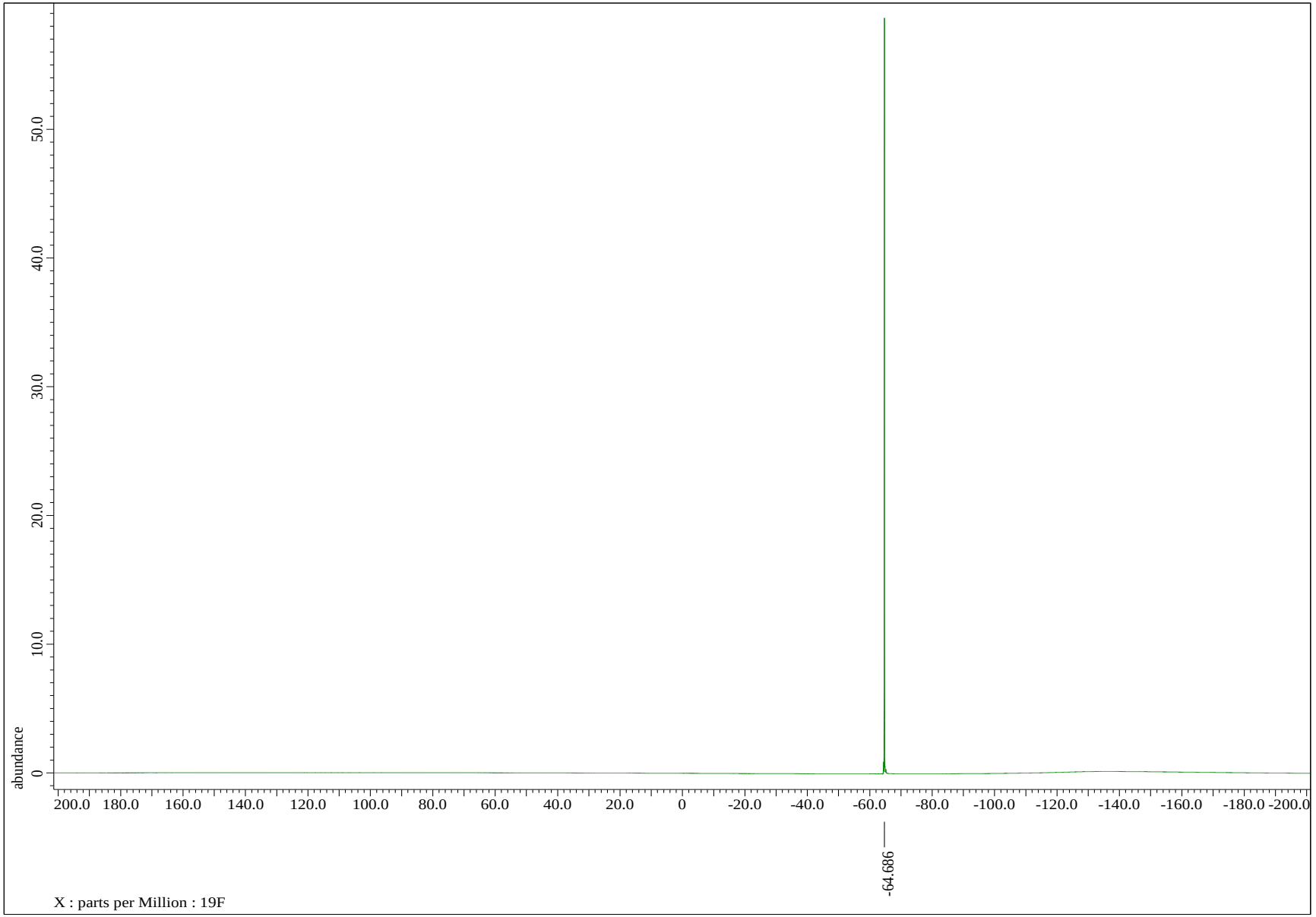


Fig. S18 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **L9**

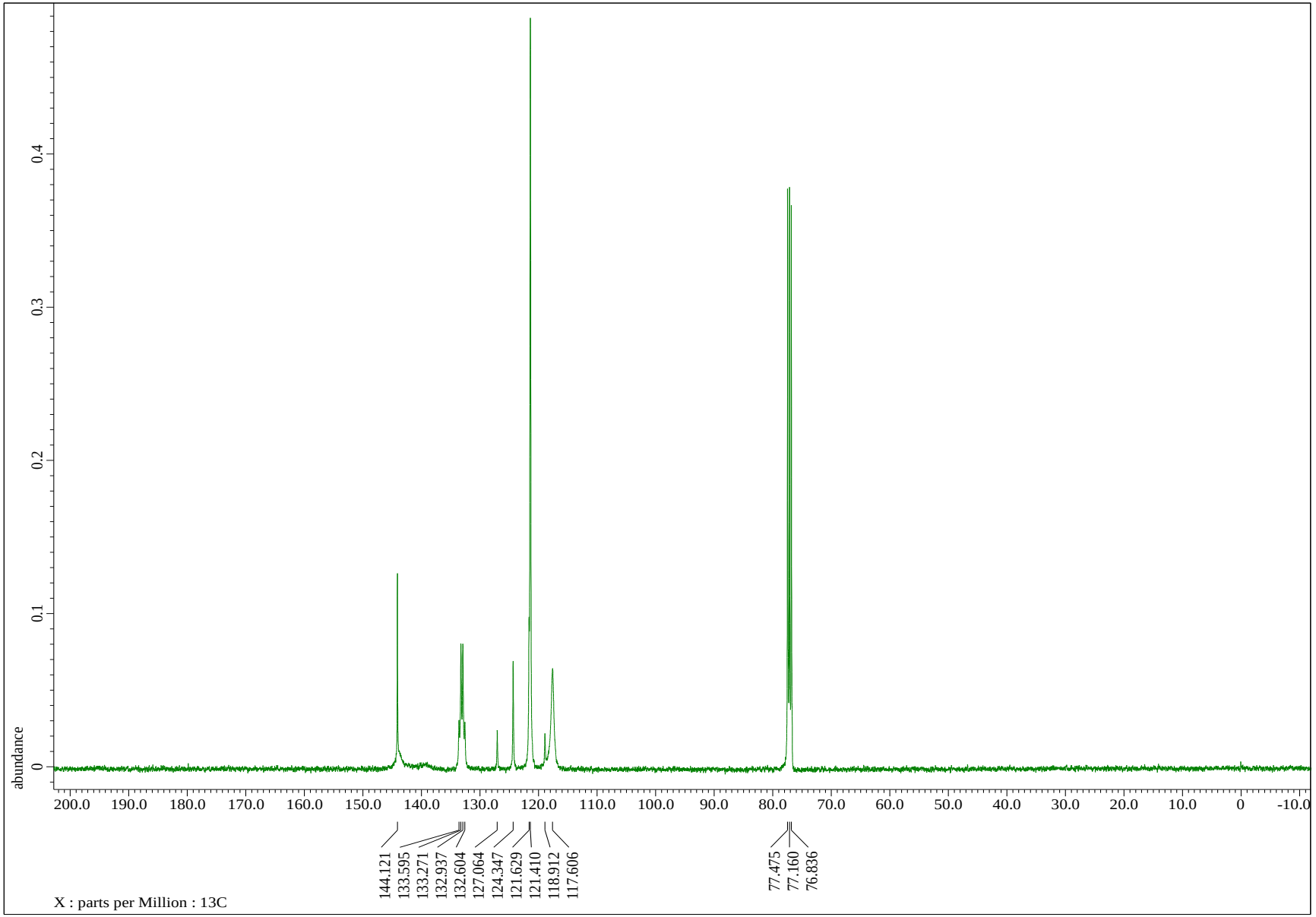


Fig. S19 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **L9**

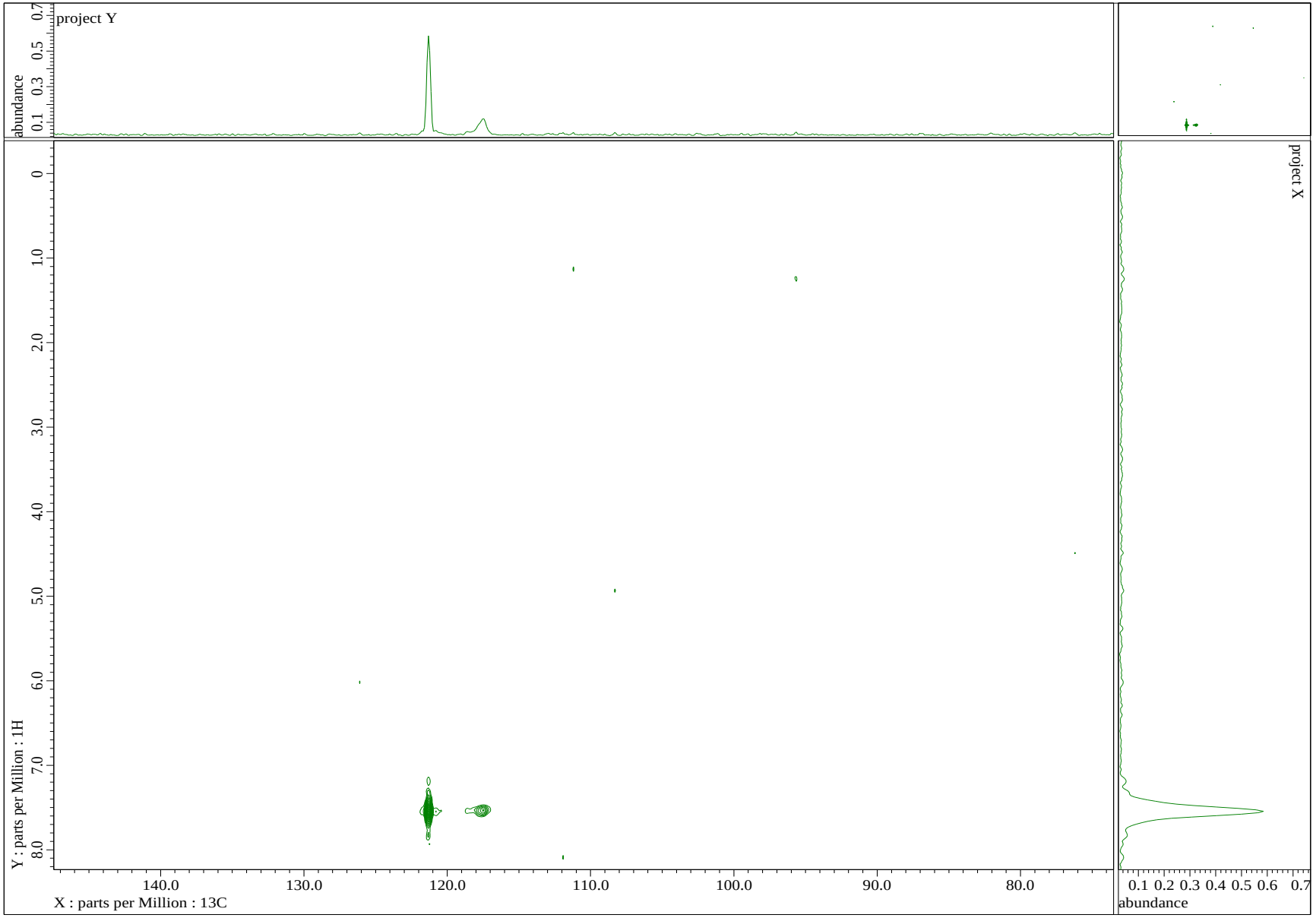


Fig. S20 HETCOR spectrum for **L9**

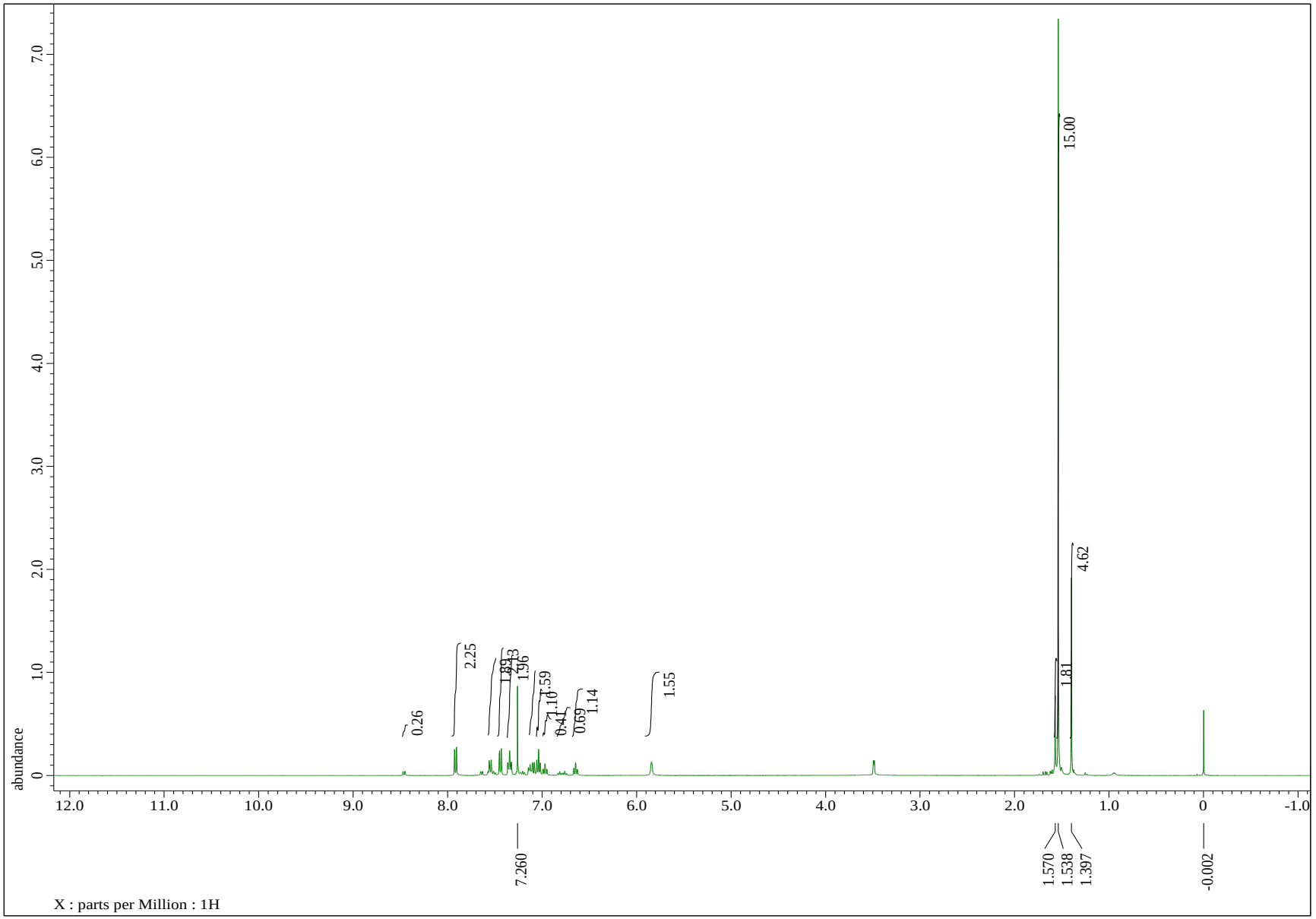


Fig. S21 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **1**

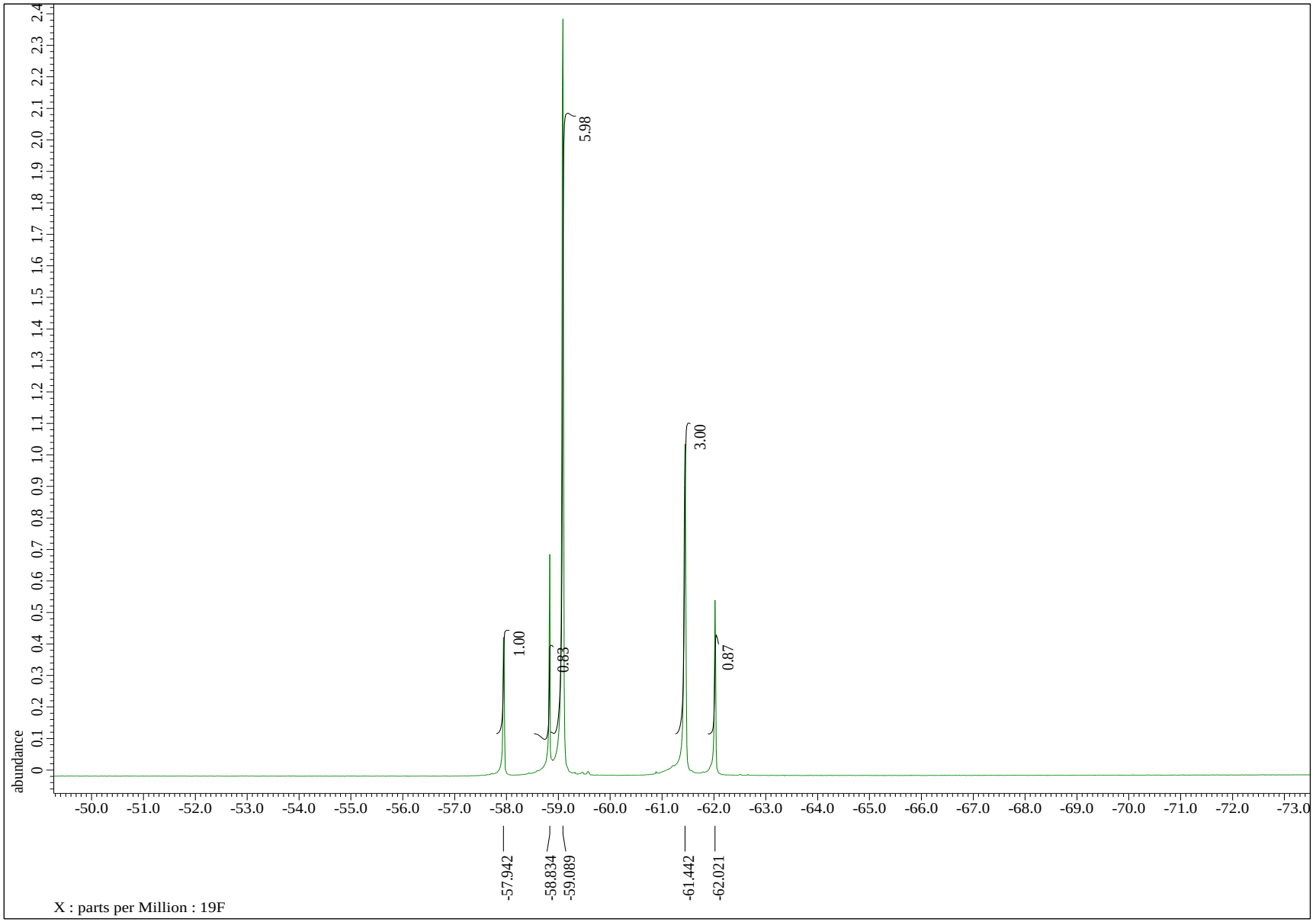


Figure S22 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **1**

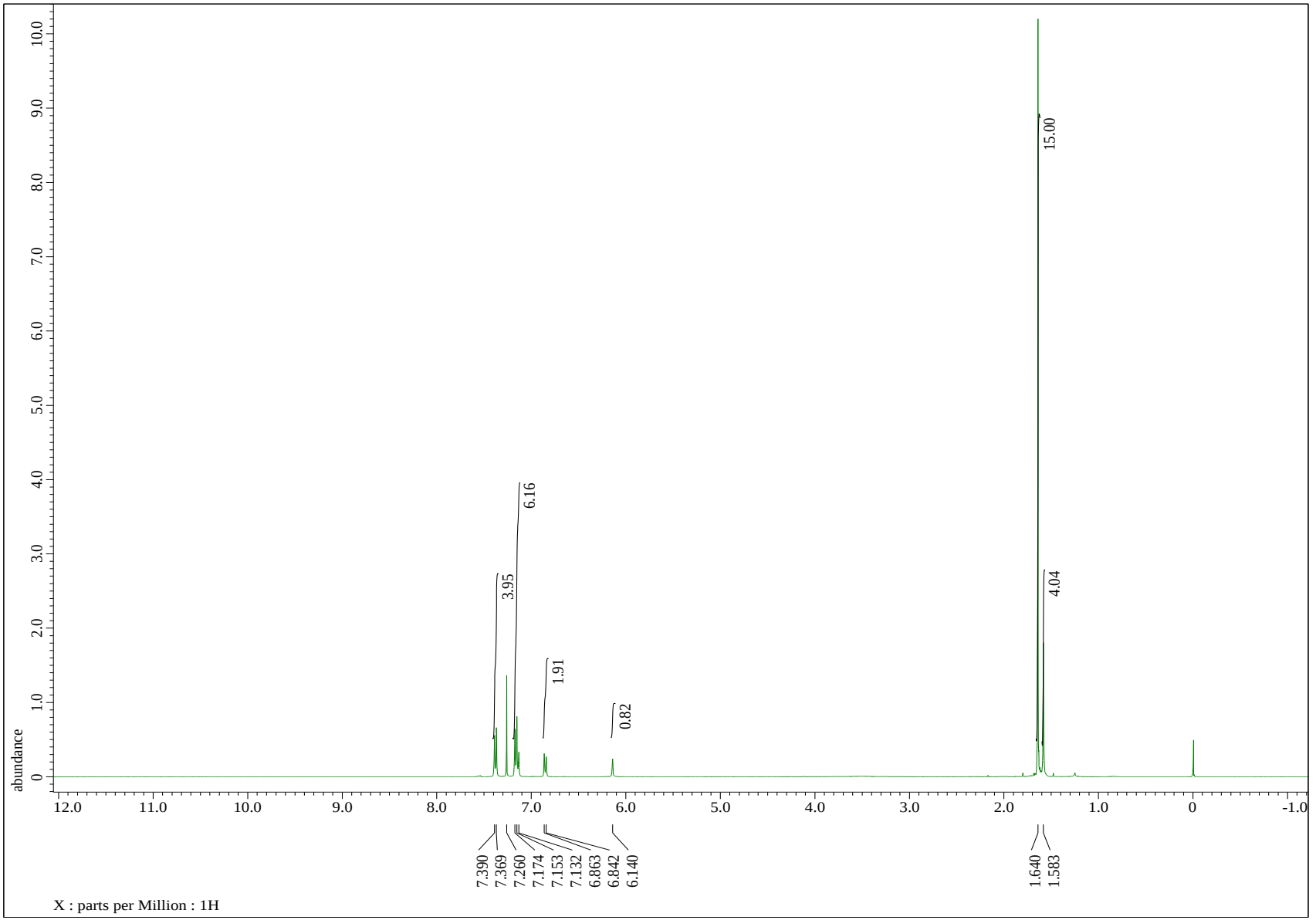


Fig. S23 ^{1}H NMR (400 MHz, $CDCl_3$, at 1.3090×10^{-2} M) spectrum of **2**

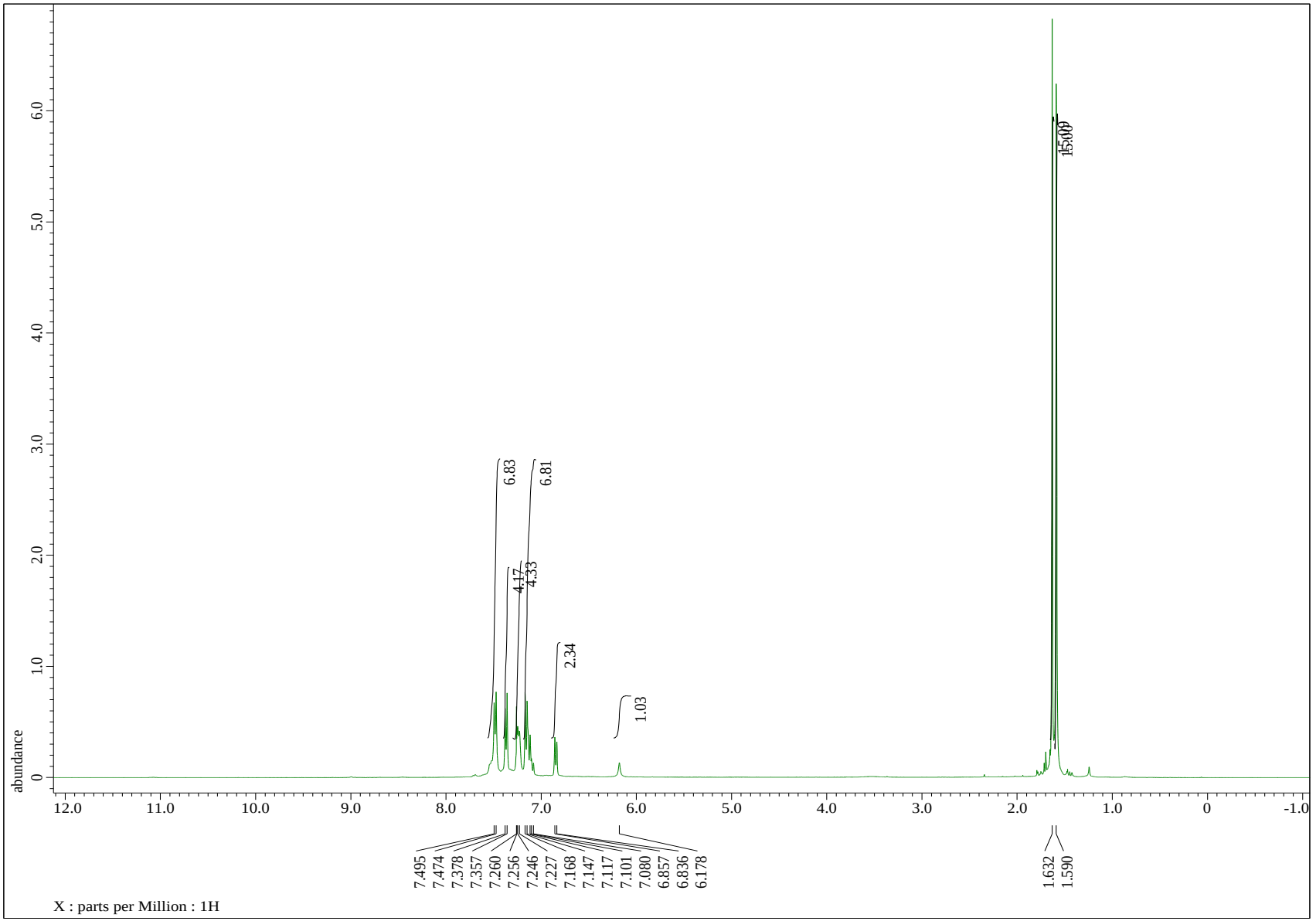


Fig. S24 ^{1}H NMR (400 MHz, $CDCl_3$, at 13.090 × 10^{-2} M) spectrum of **2**

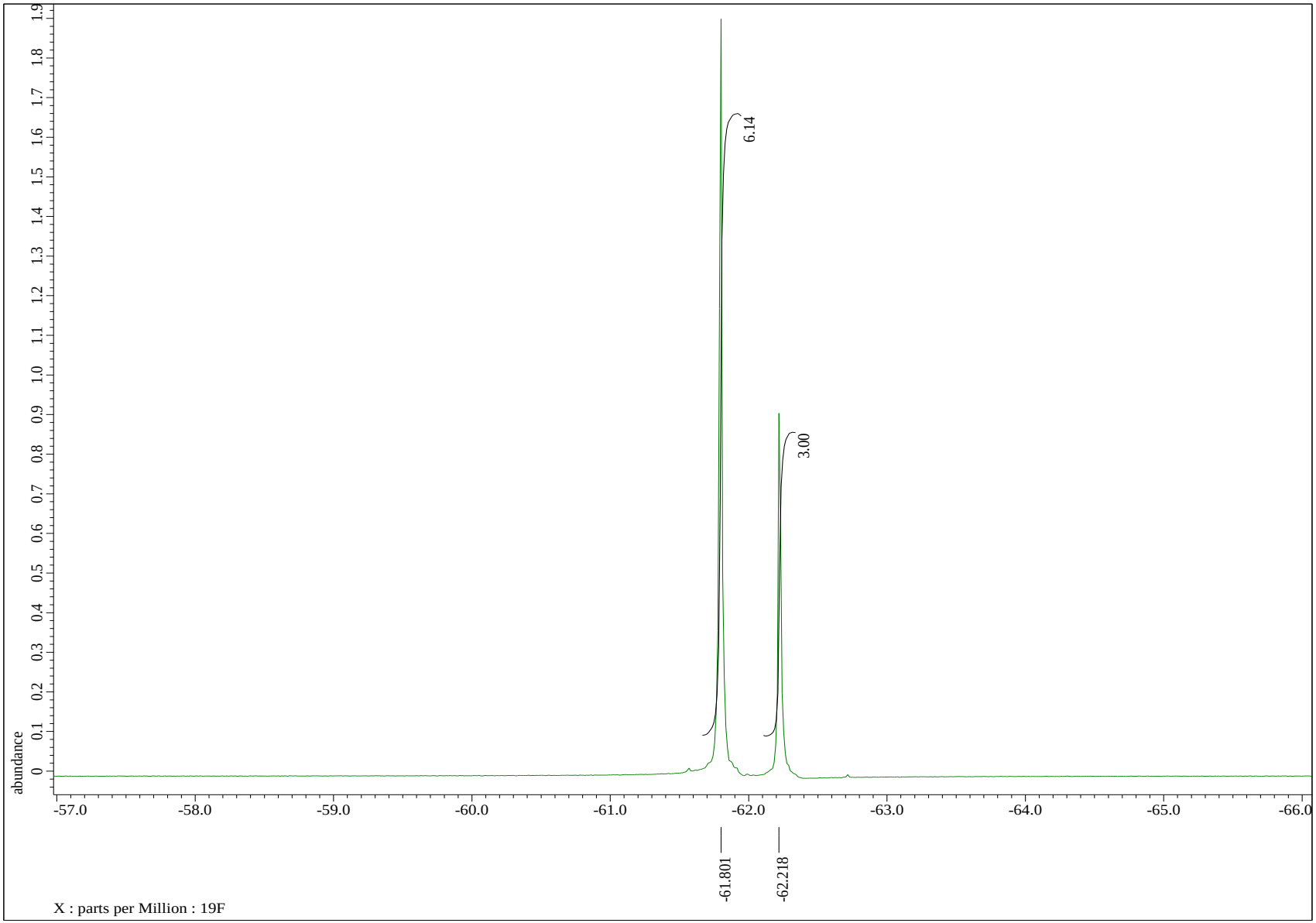


Fig. S25 ^{19}F NMR (376.5 MHz, $CDCl_3$, at 1.3090×10^{-2} M) spectrum of **2**

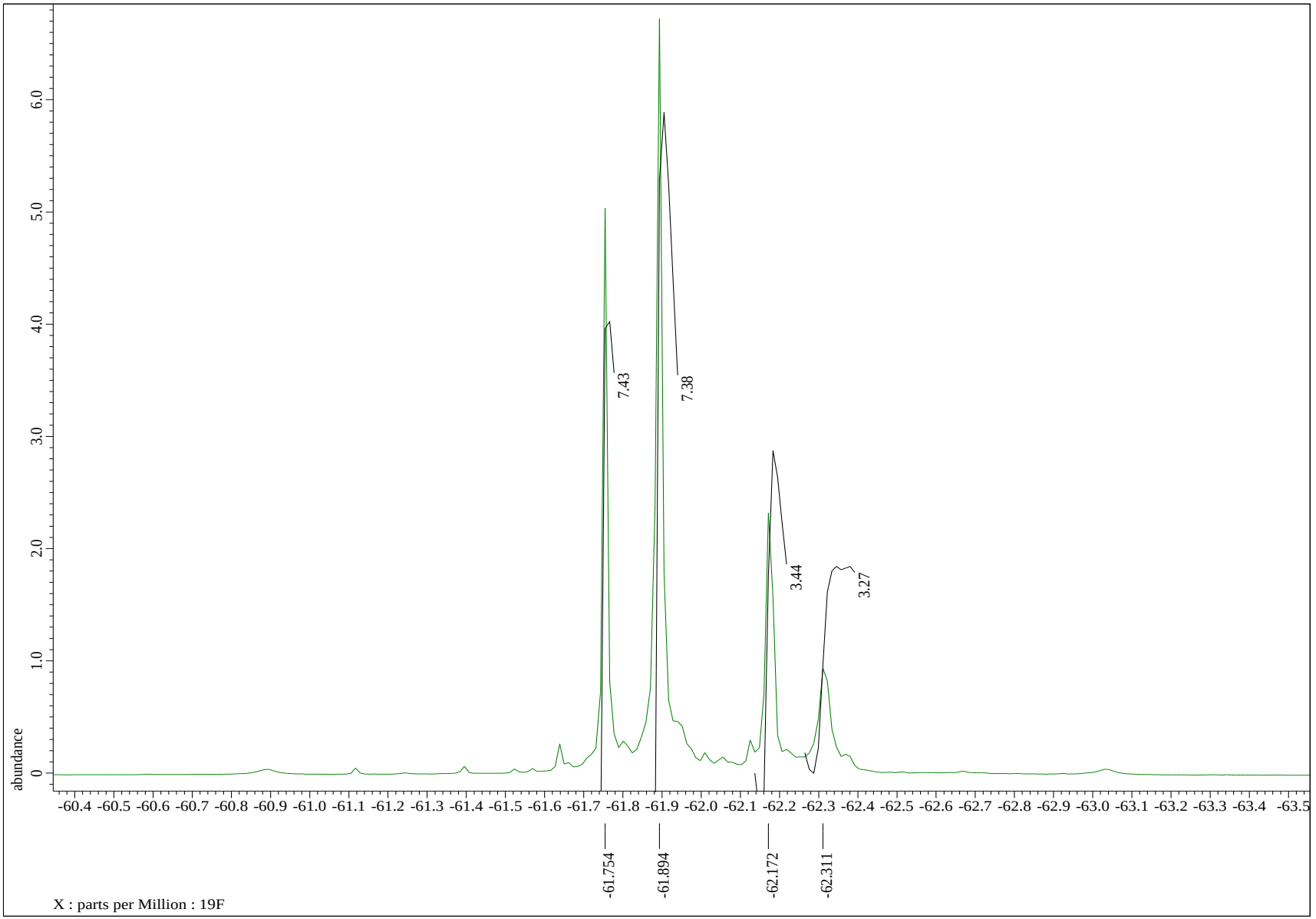


Fig. S26 ^{19}F NMR (376.5 MHz, $CDCl_3$, at 13.090×10^{-2} M) spectrum of **2**

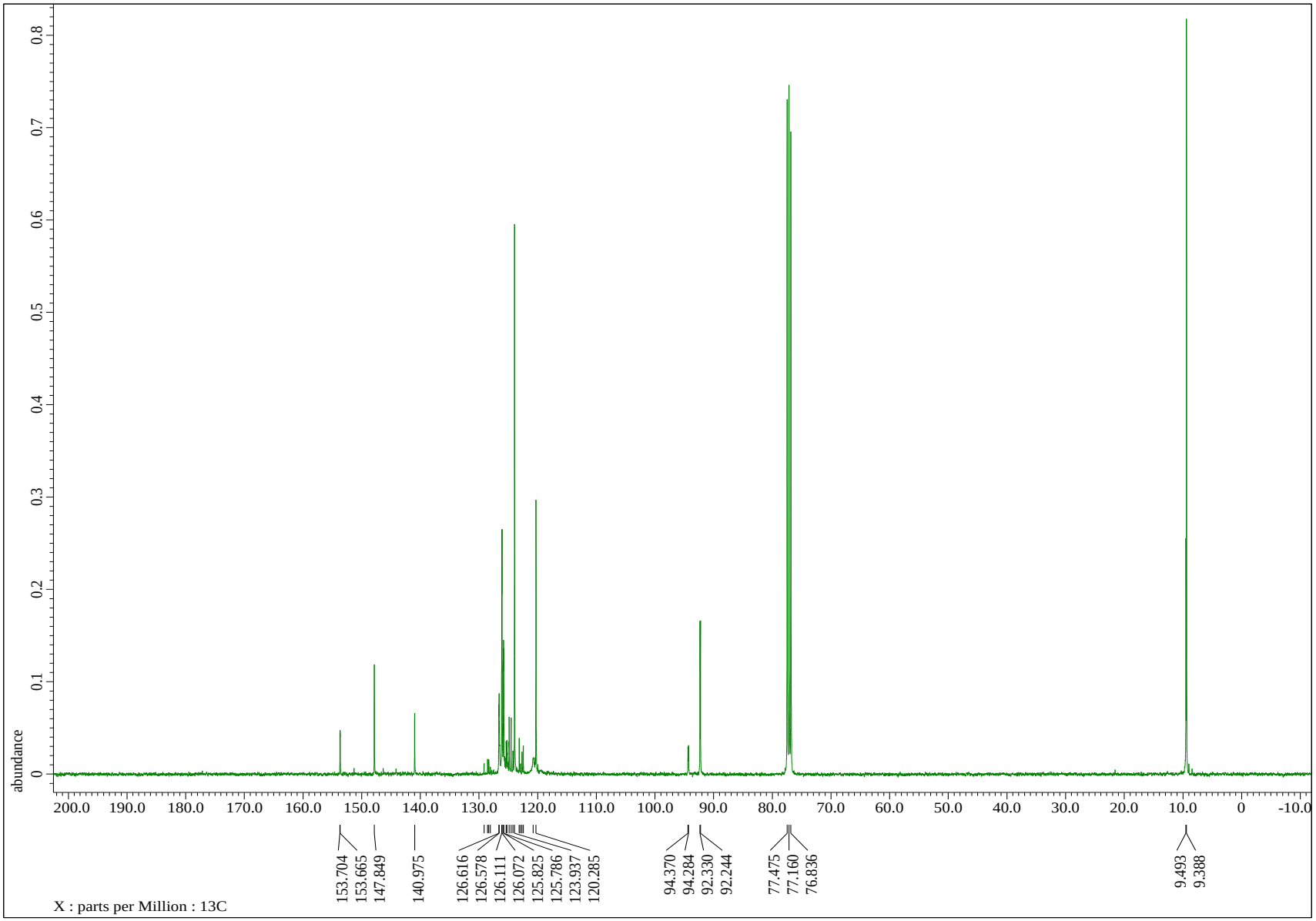


Fig. S27 ^{13}C NMR (100.5 MHz, $CDCl_3$, at 13.090 × 10^{-2} M) spectrum of **2**

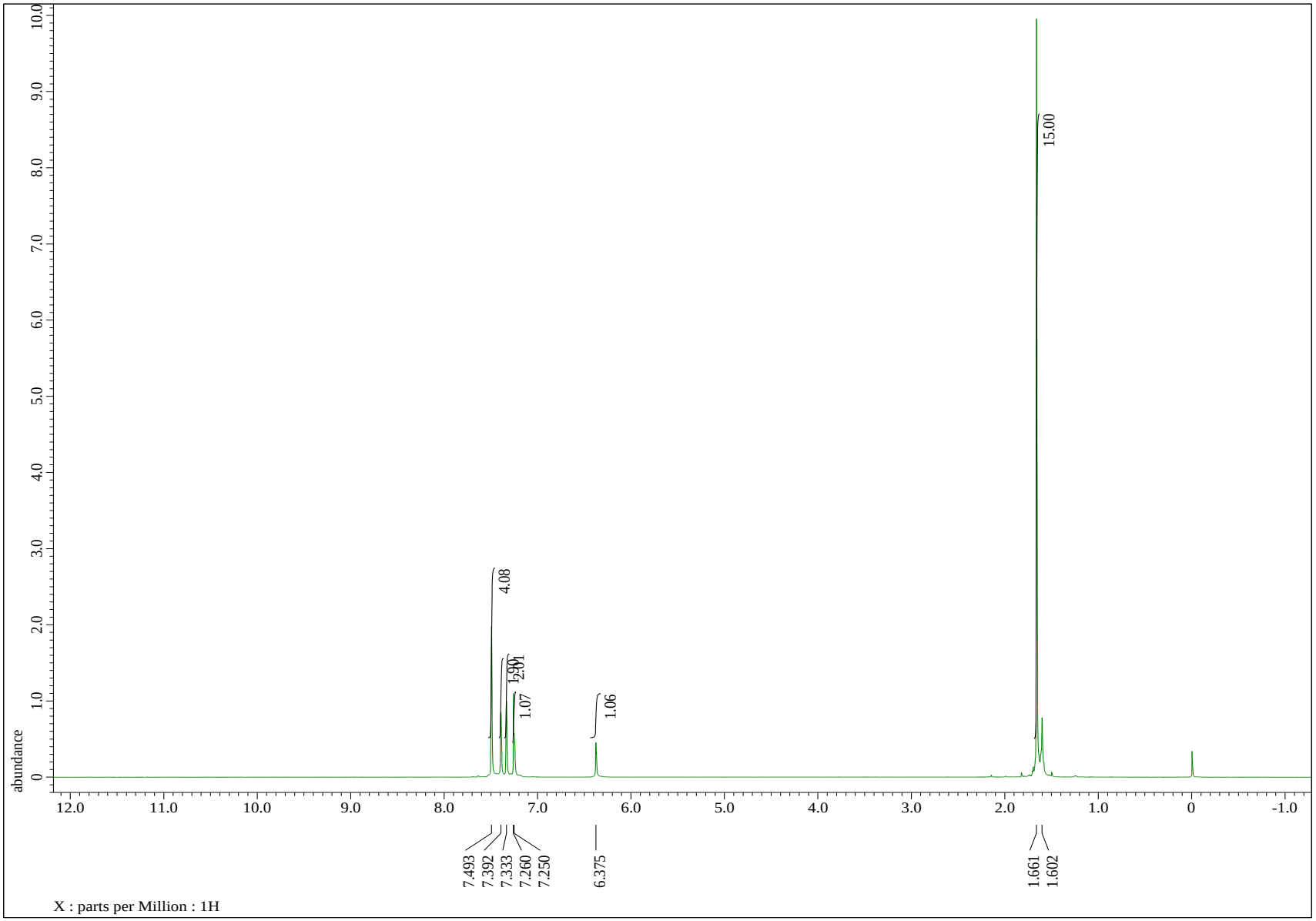


Fig. S28 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **3**

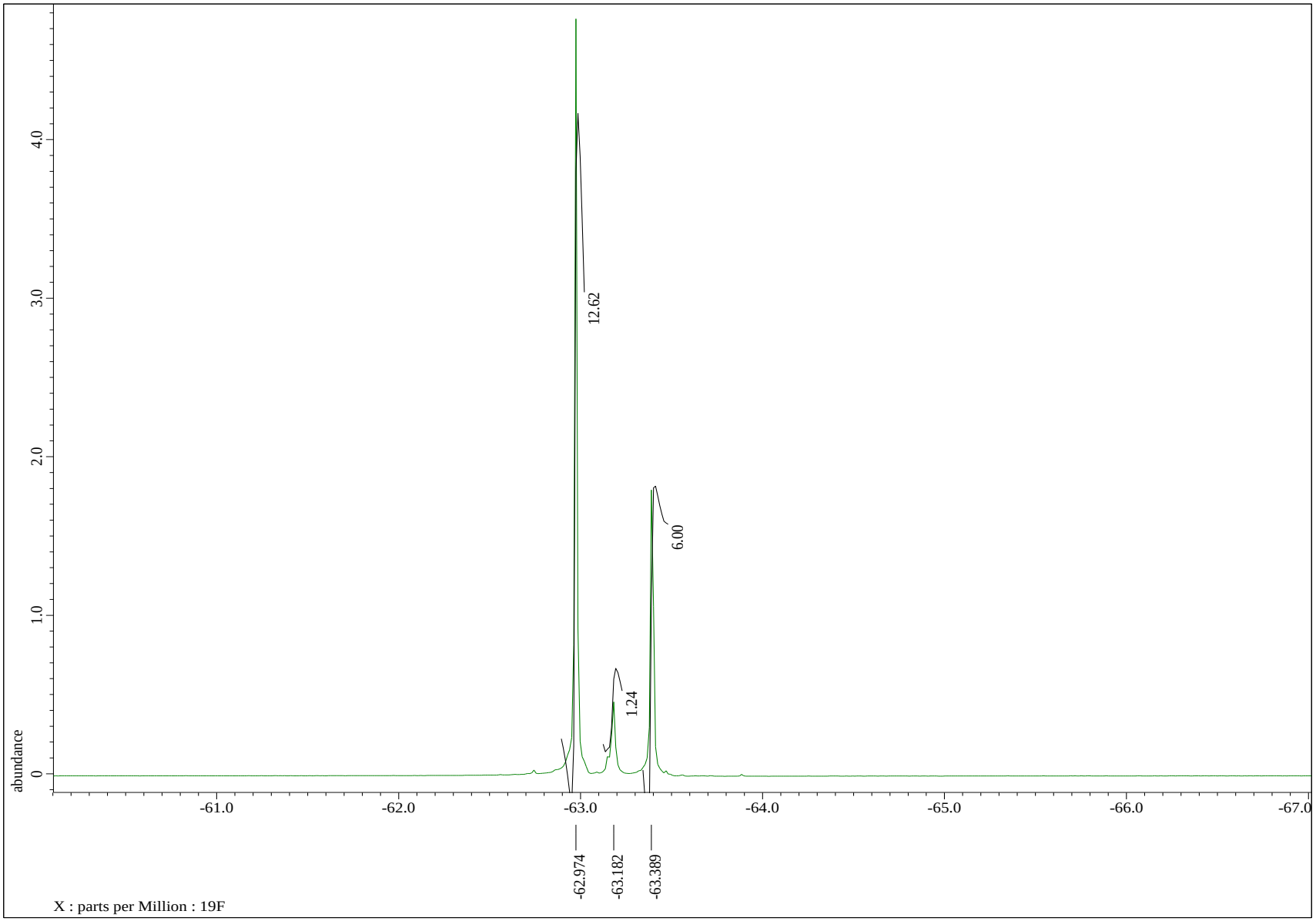


Fig. S29 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **3**

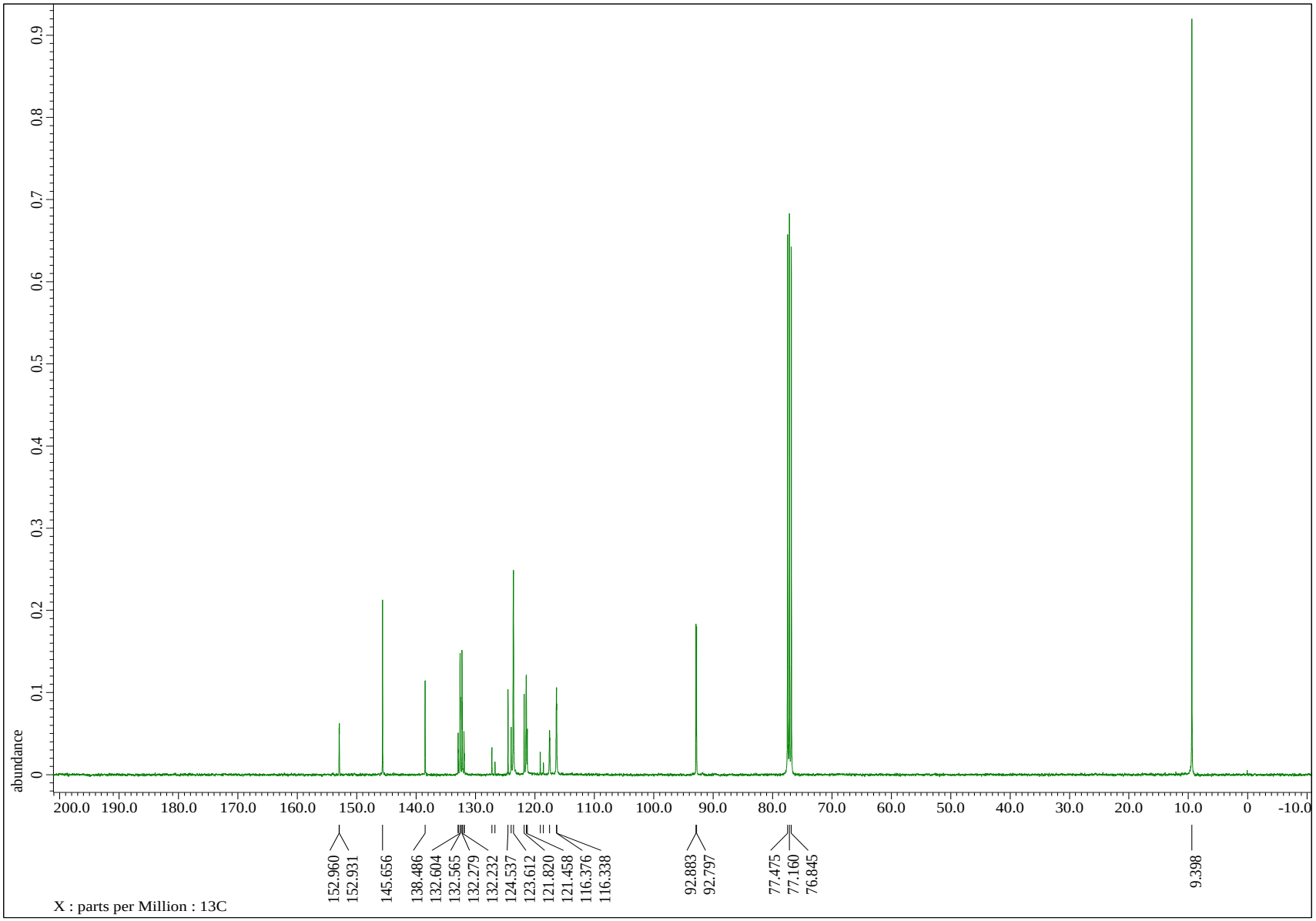


Fig. S30 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **3**

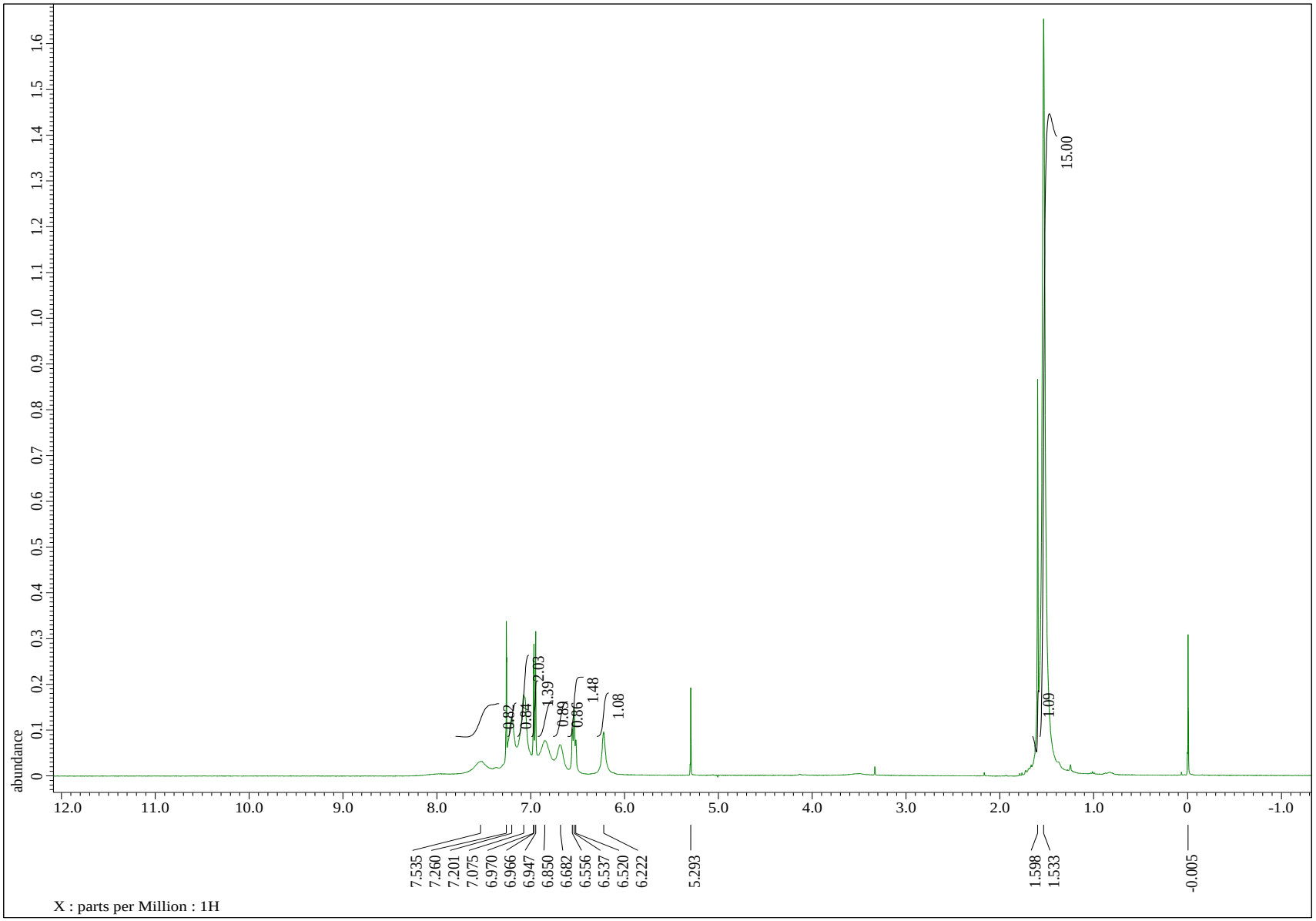


Fig. S31 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **4**

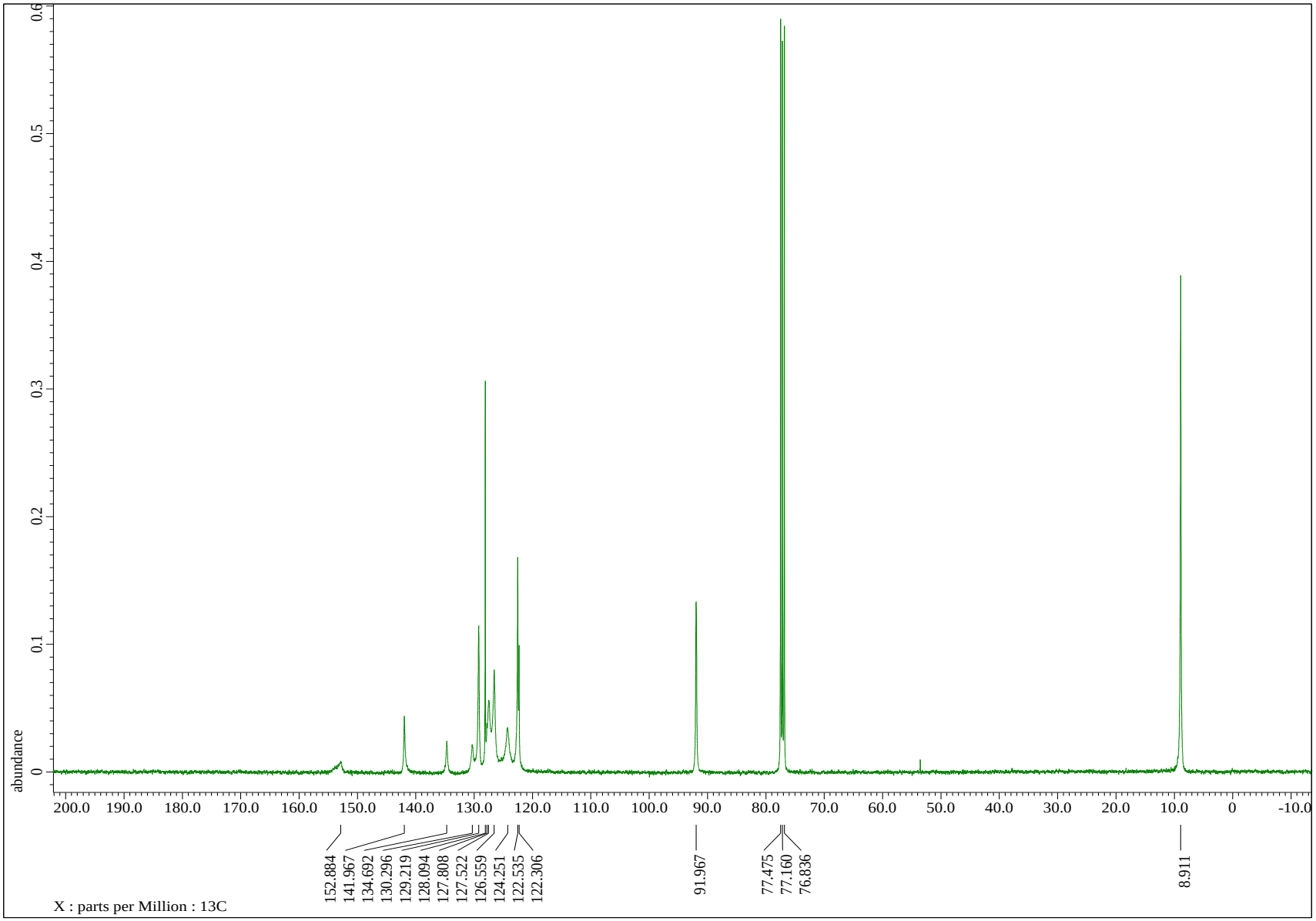


Fig. S32 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **4**

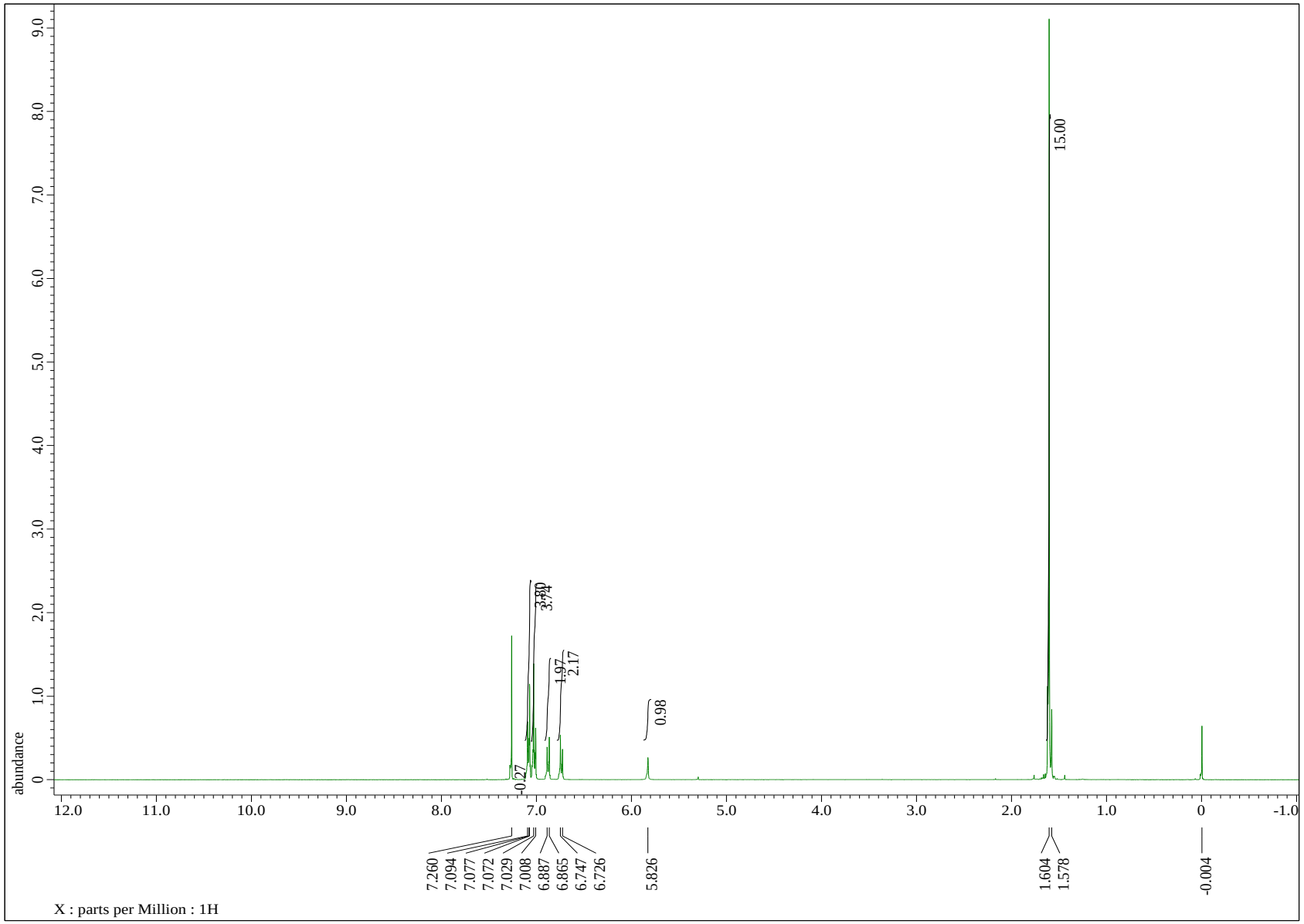


Fig. S33 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **5**

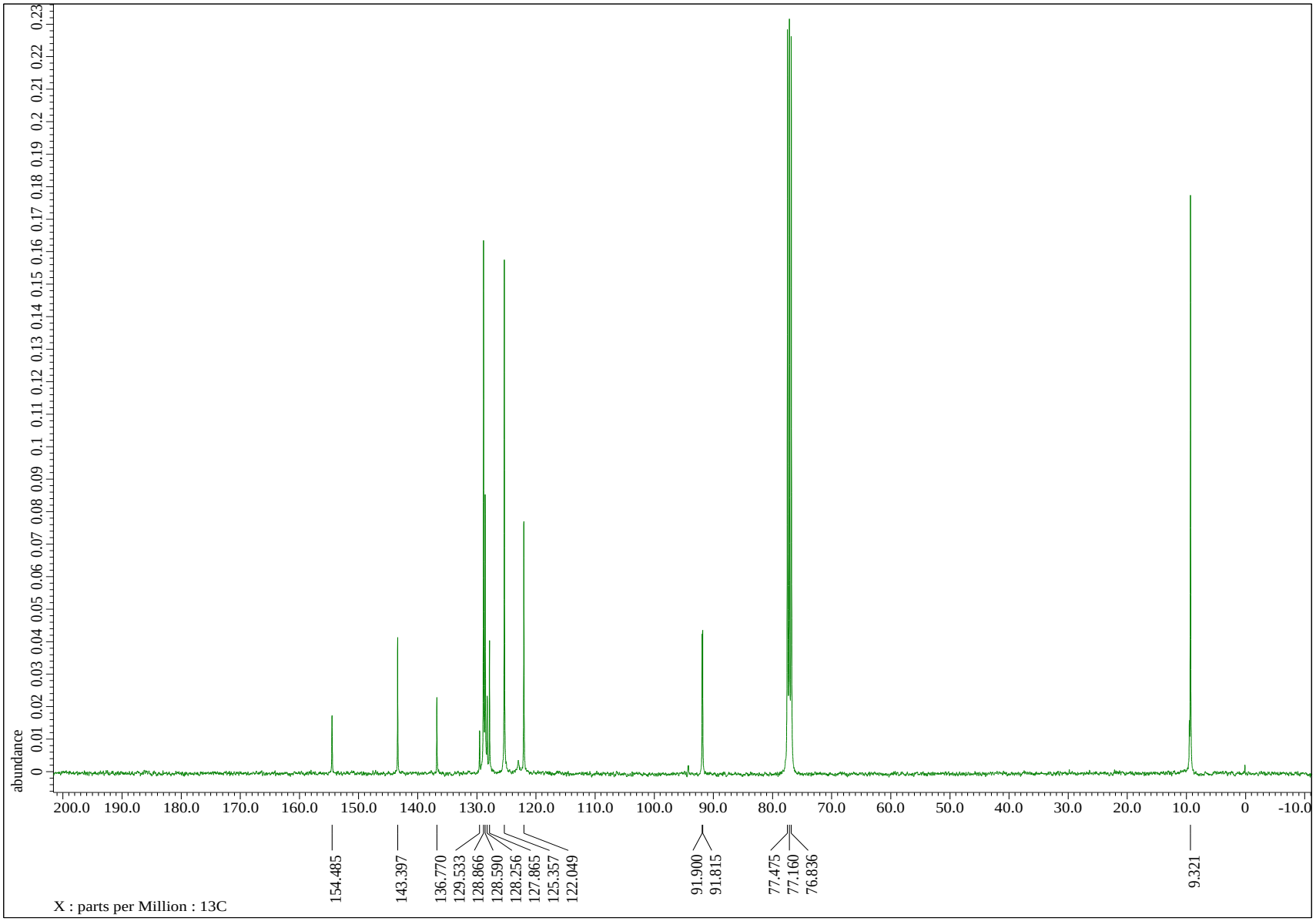


Fig. S34 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **5**

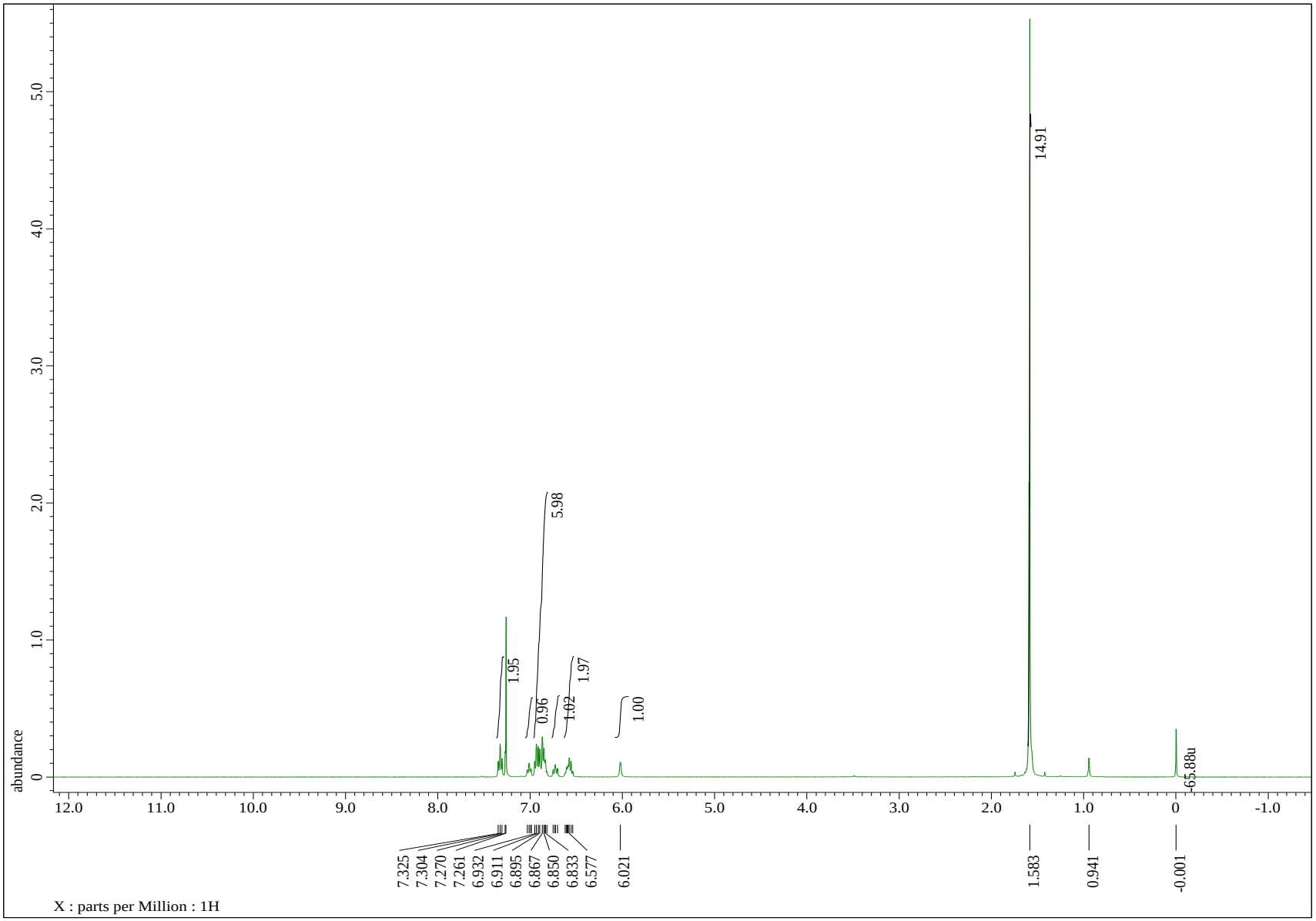


Fig. S35 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**

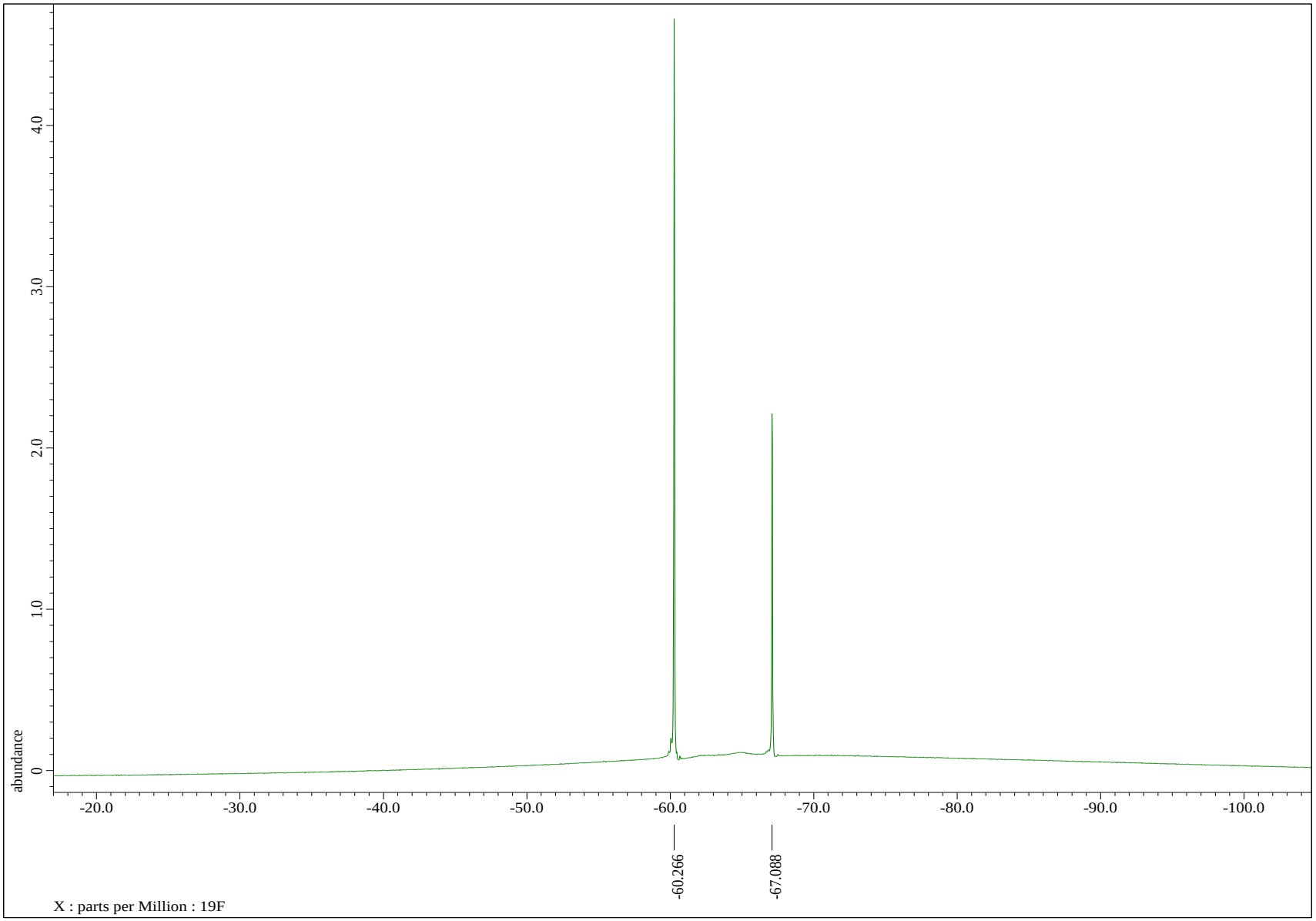


Fig. S36 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **6**

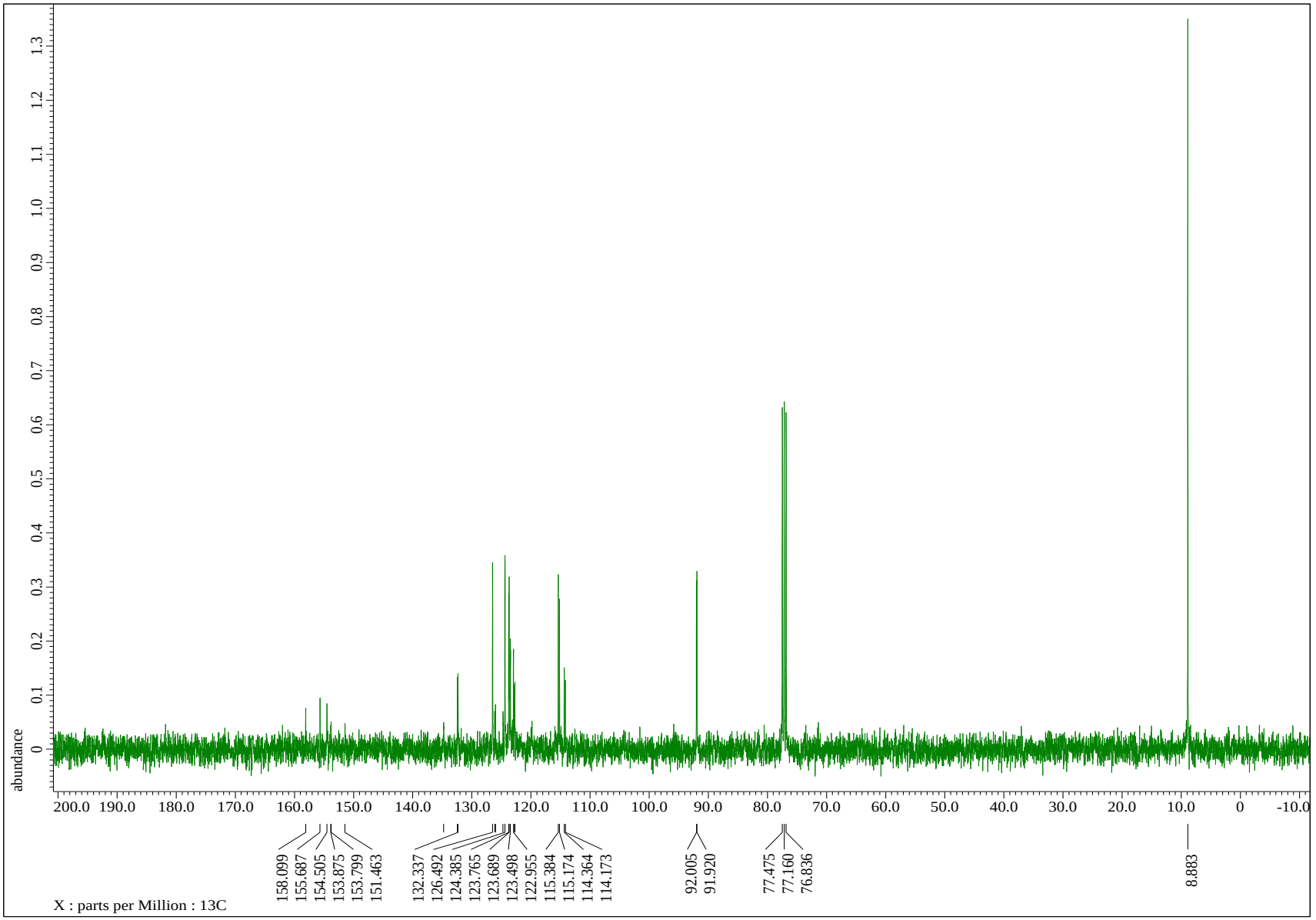


Fig. S37 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **6**

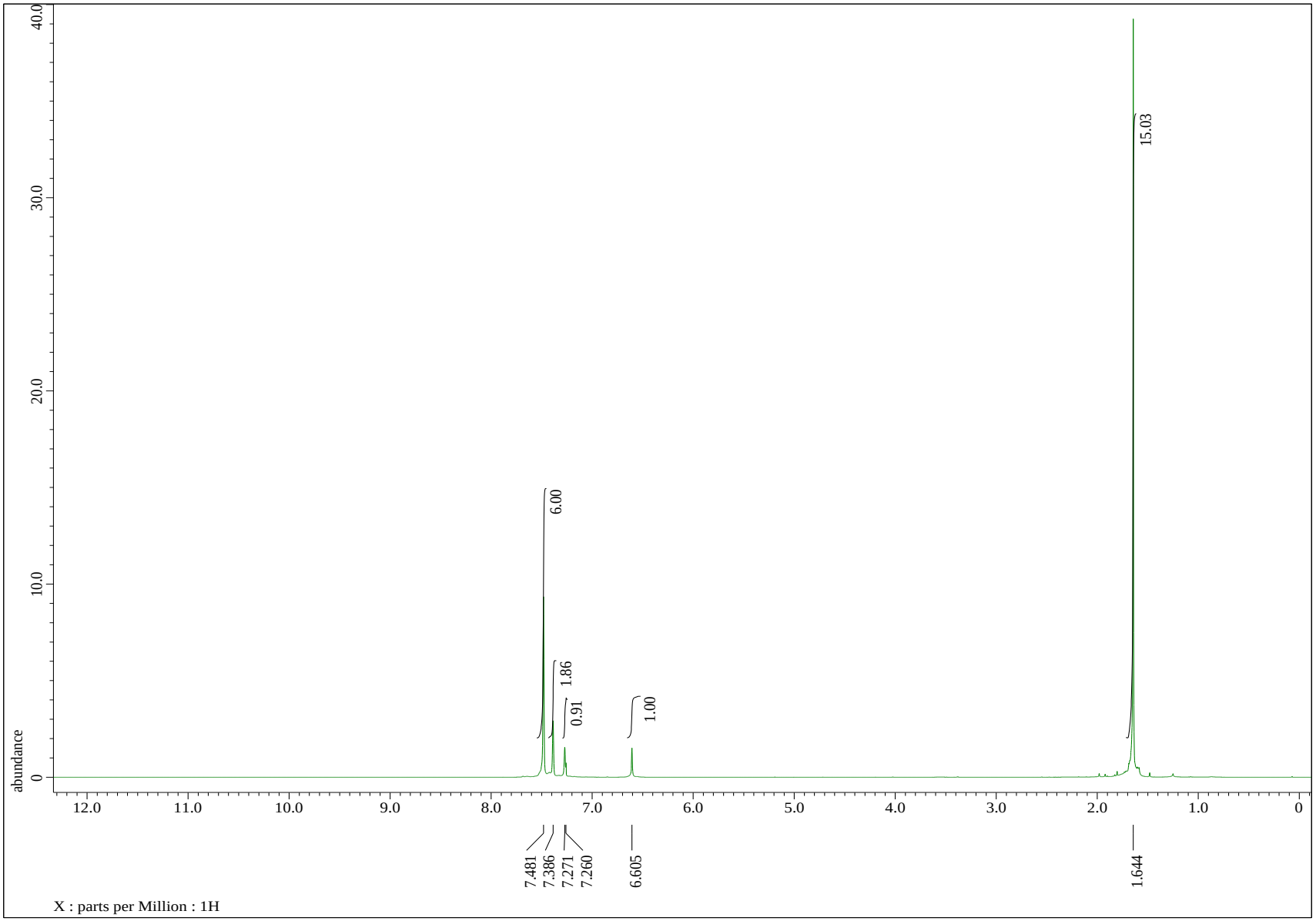


Fig. S38 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

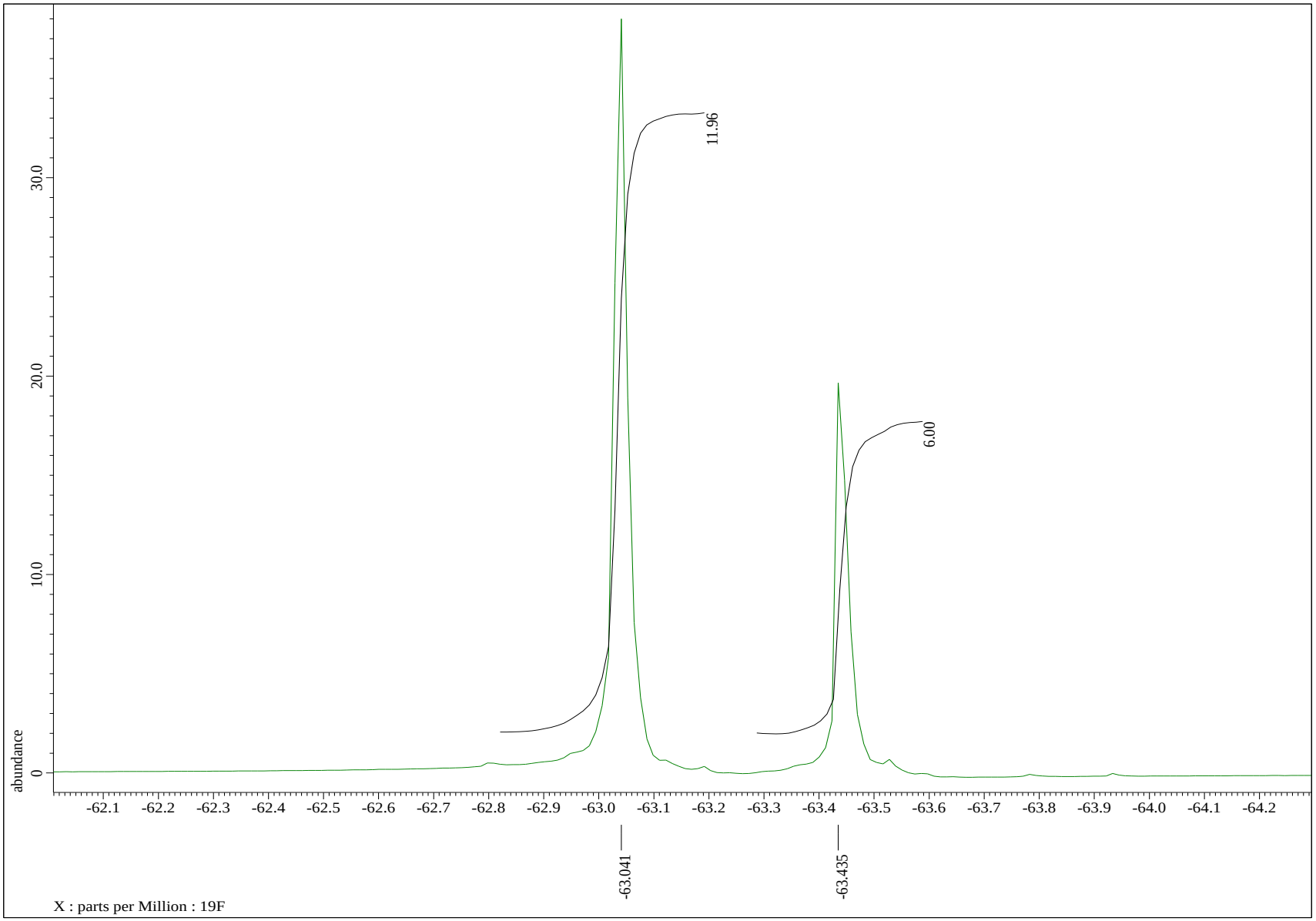


Fig. S39 ^{19}F NMR (376.5 MHz, $CDCl_3$) spectrum of **7**

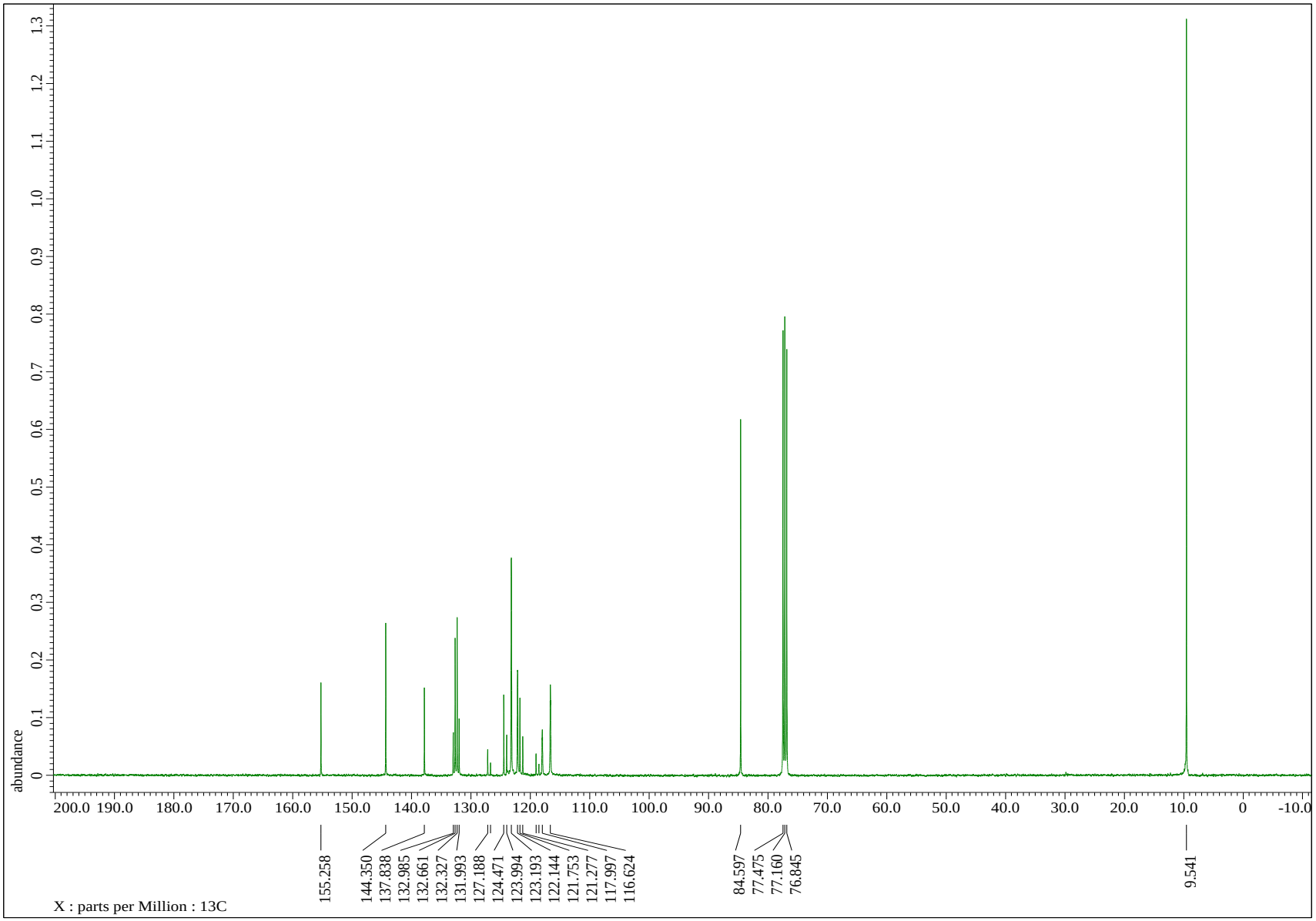


Fig. S40 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **7**

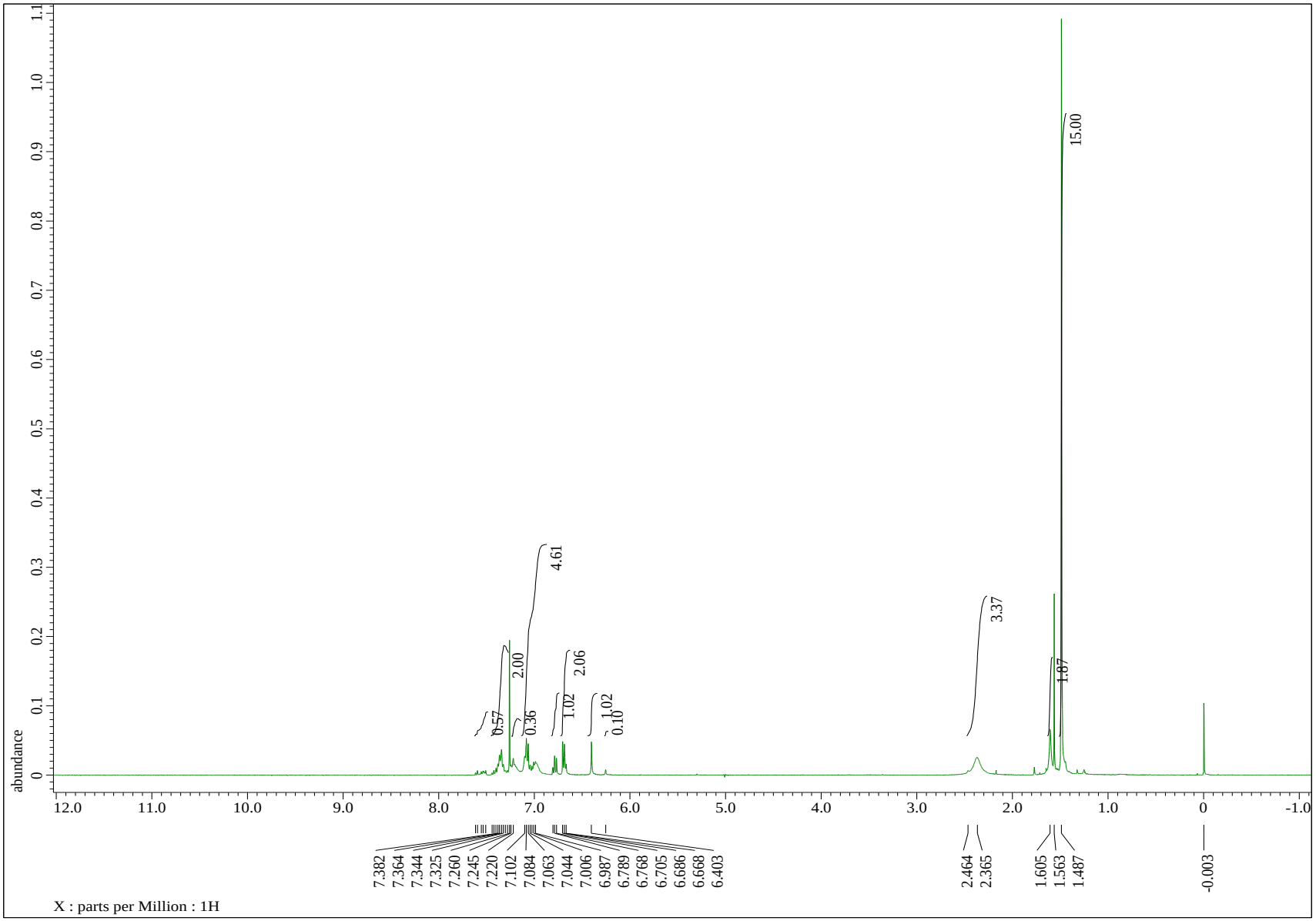


Fig. S41 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**

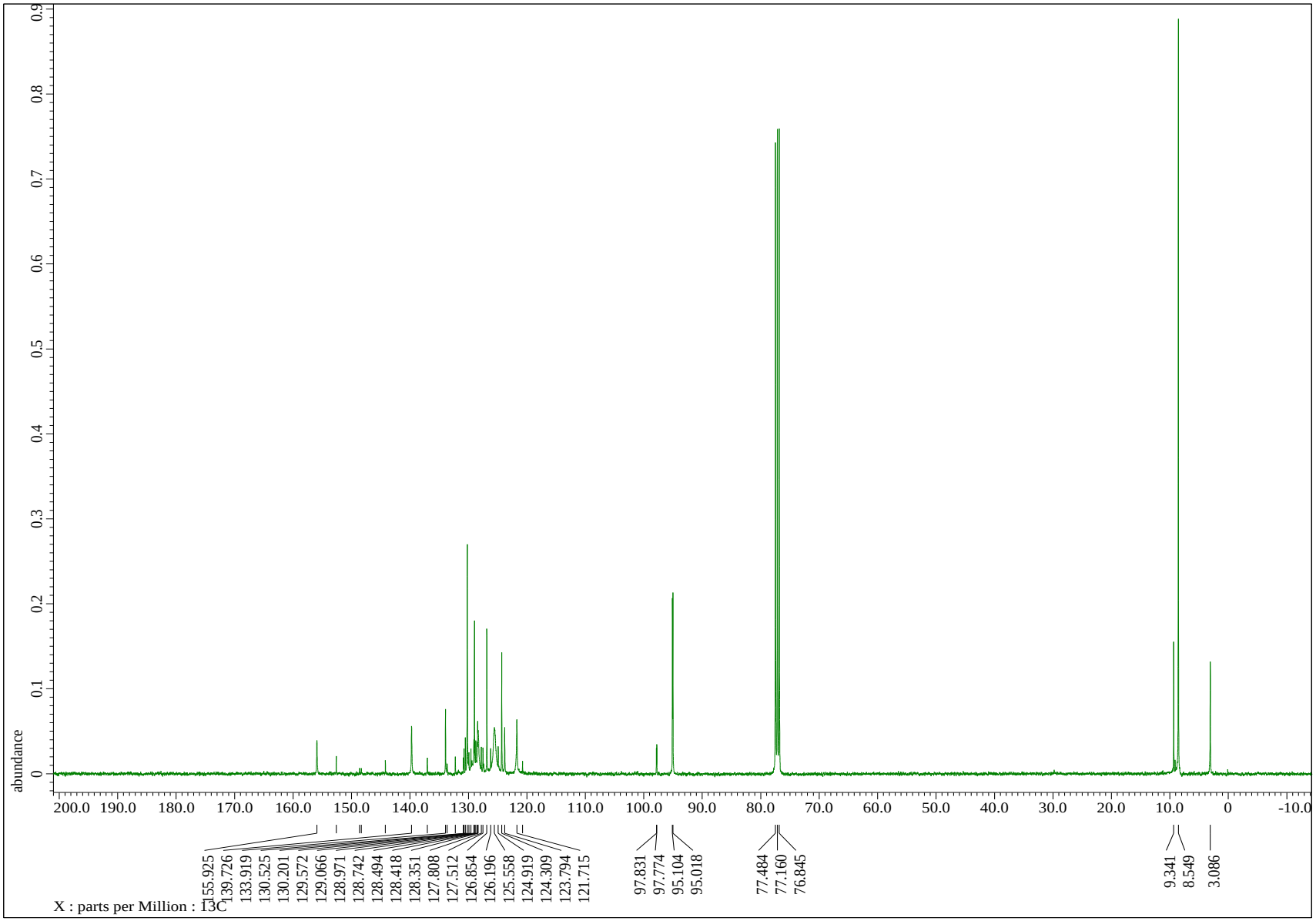


Fig. S42 ^{13}C NMR (100.5 MHz, $CDCl_3$) spectrum of **8**

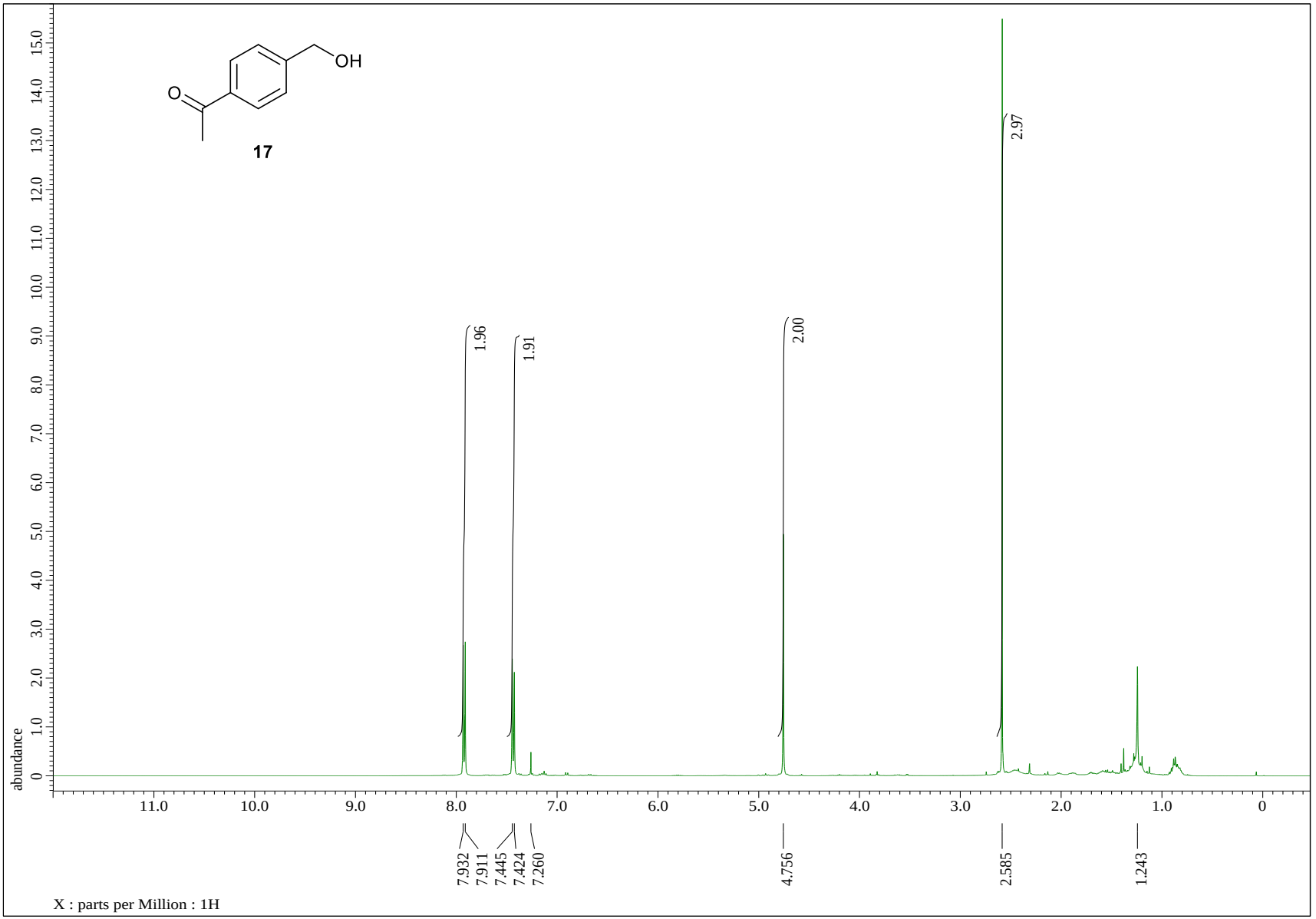


Fig. S43 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **17**

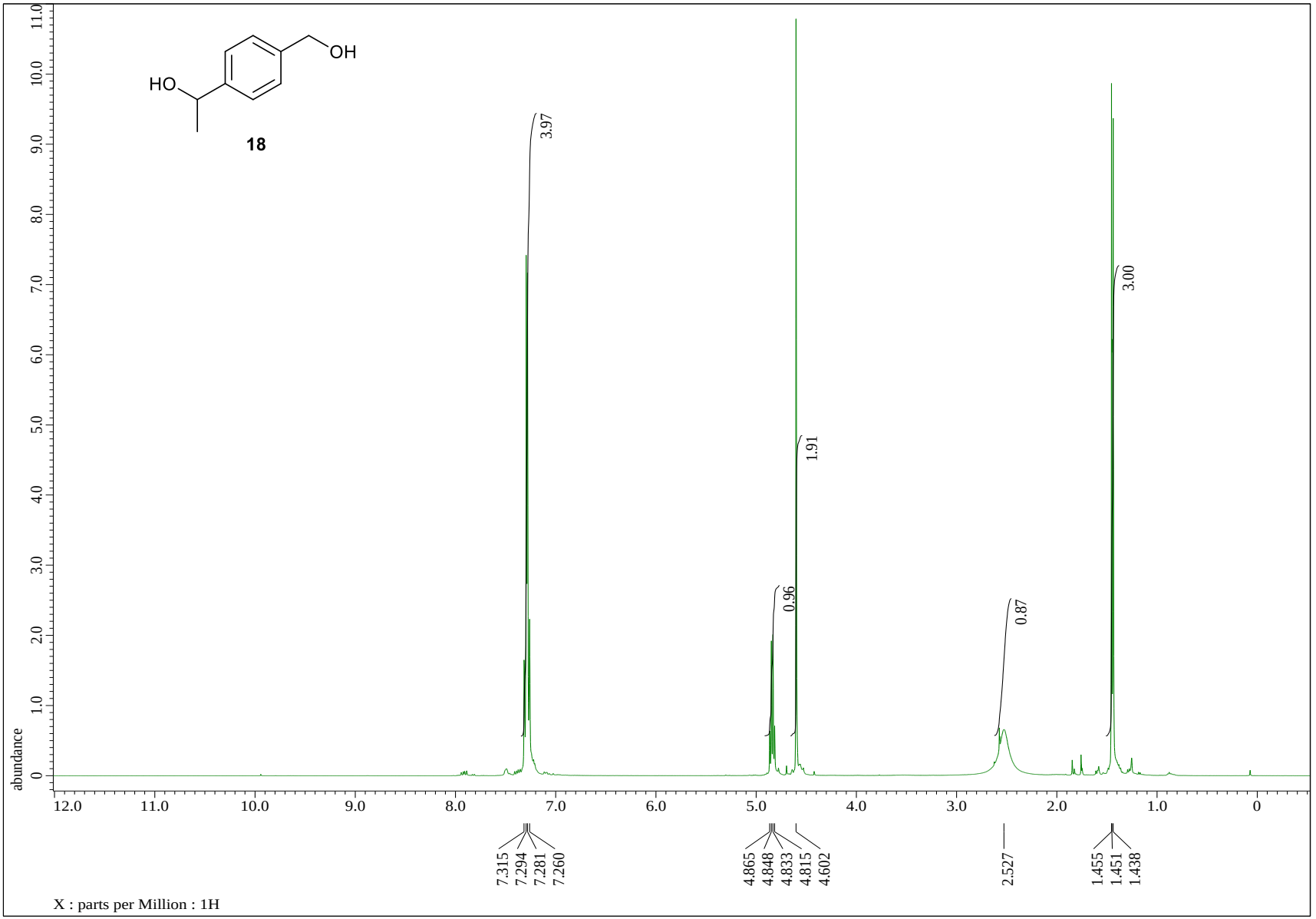


Fig. S44 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **18**

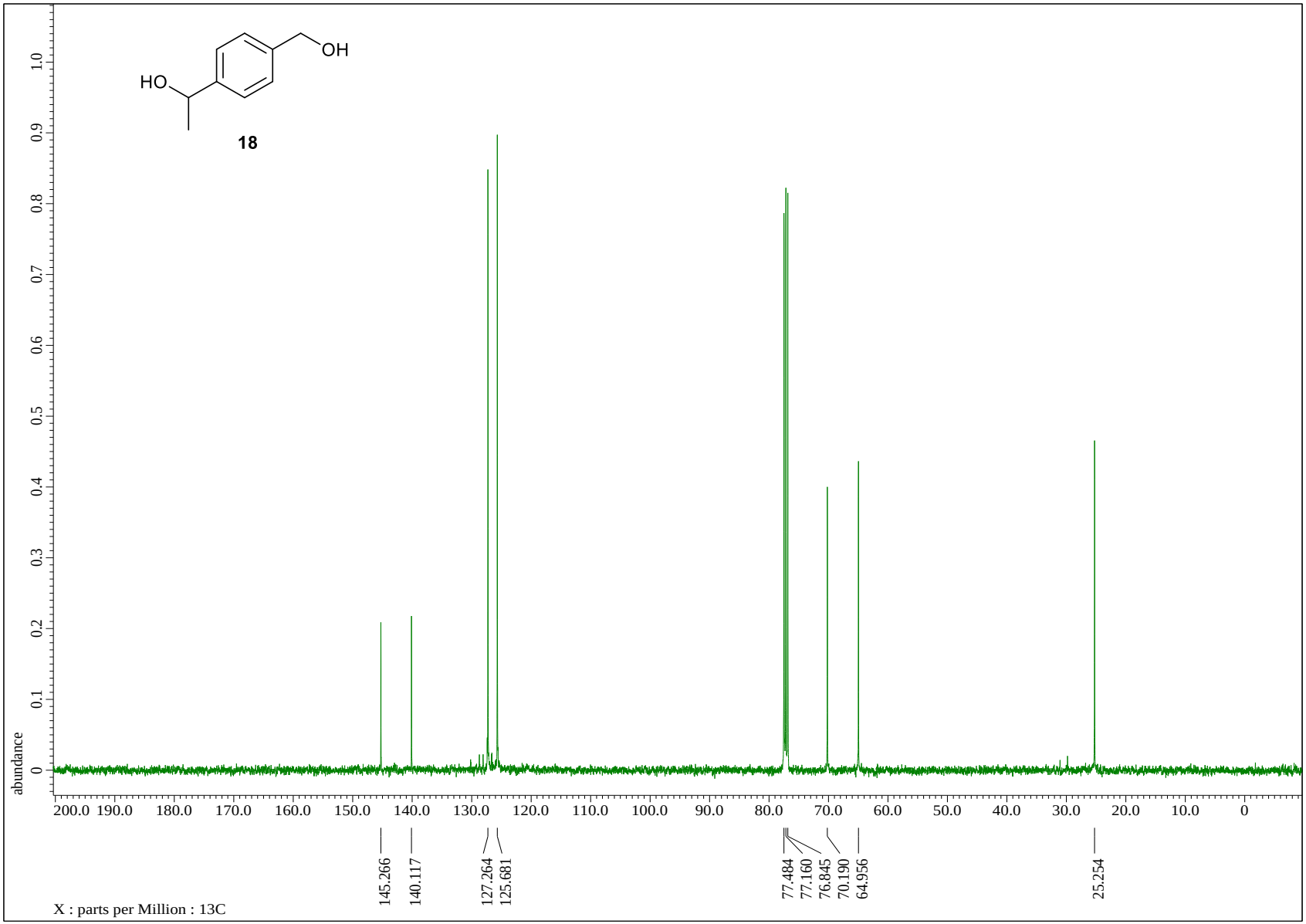


Fig. S45 ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of **18**

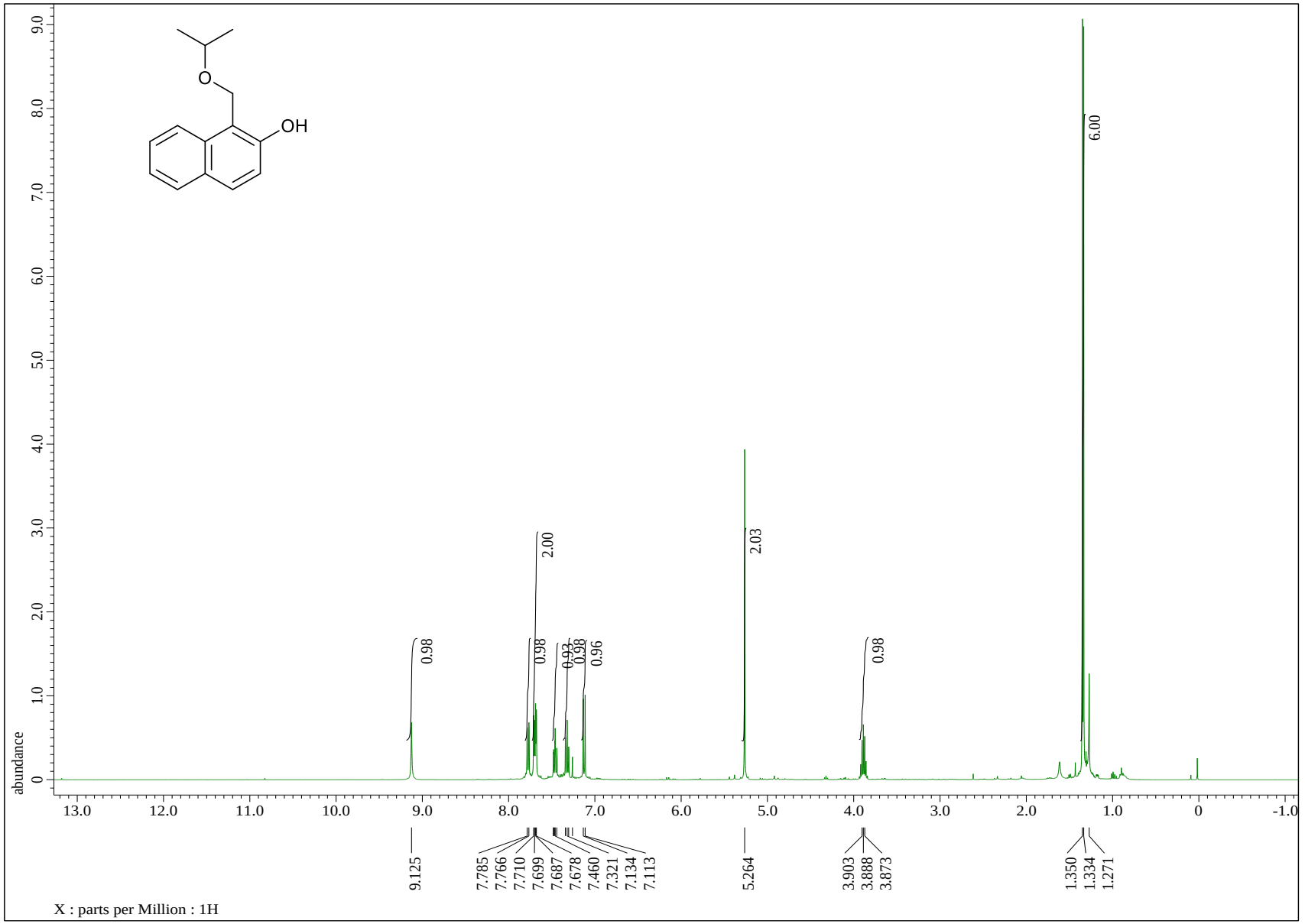


Fig. S46 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum of 1-(Isopropoxymethyl)naphthalen-2-ol

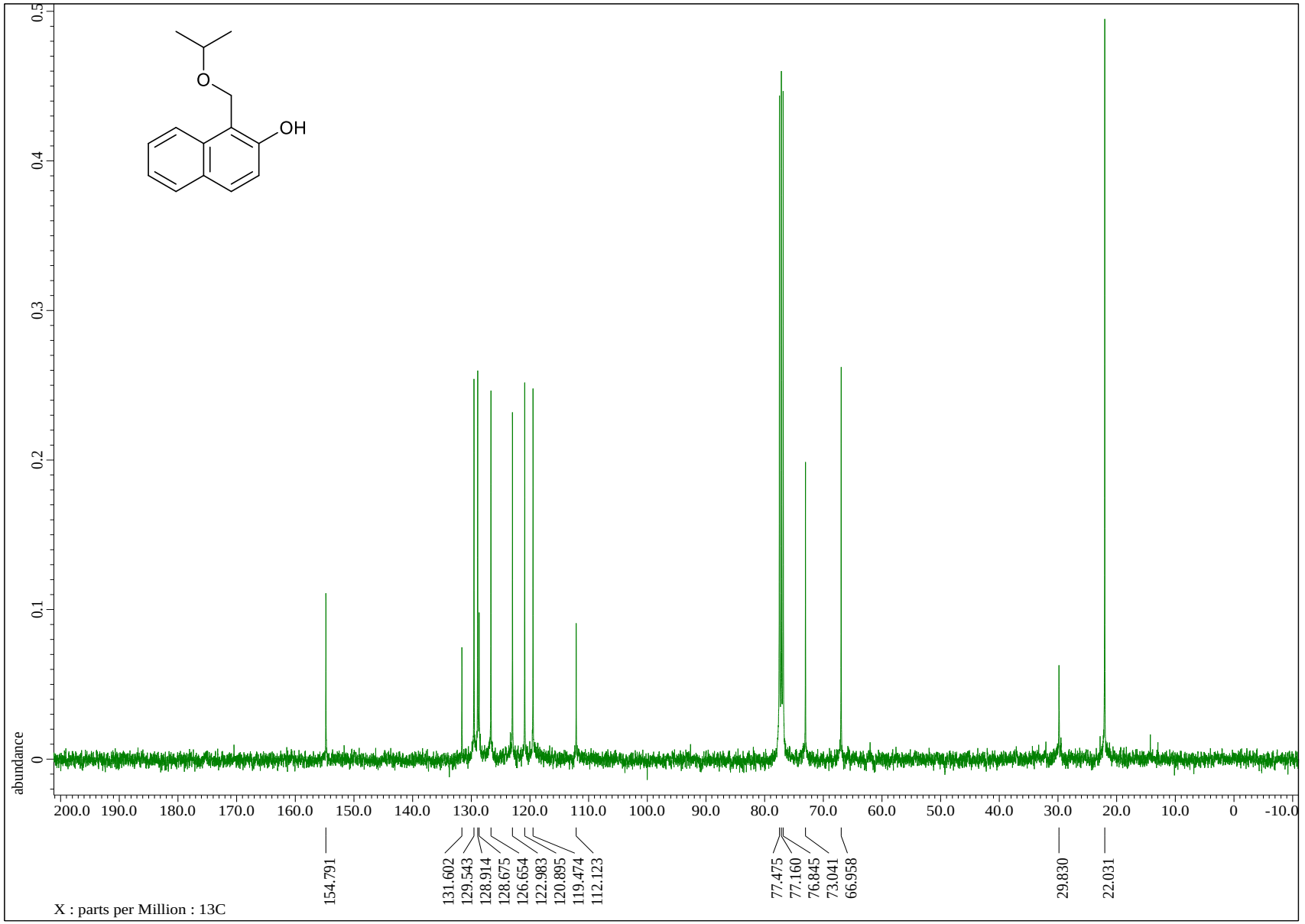
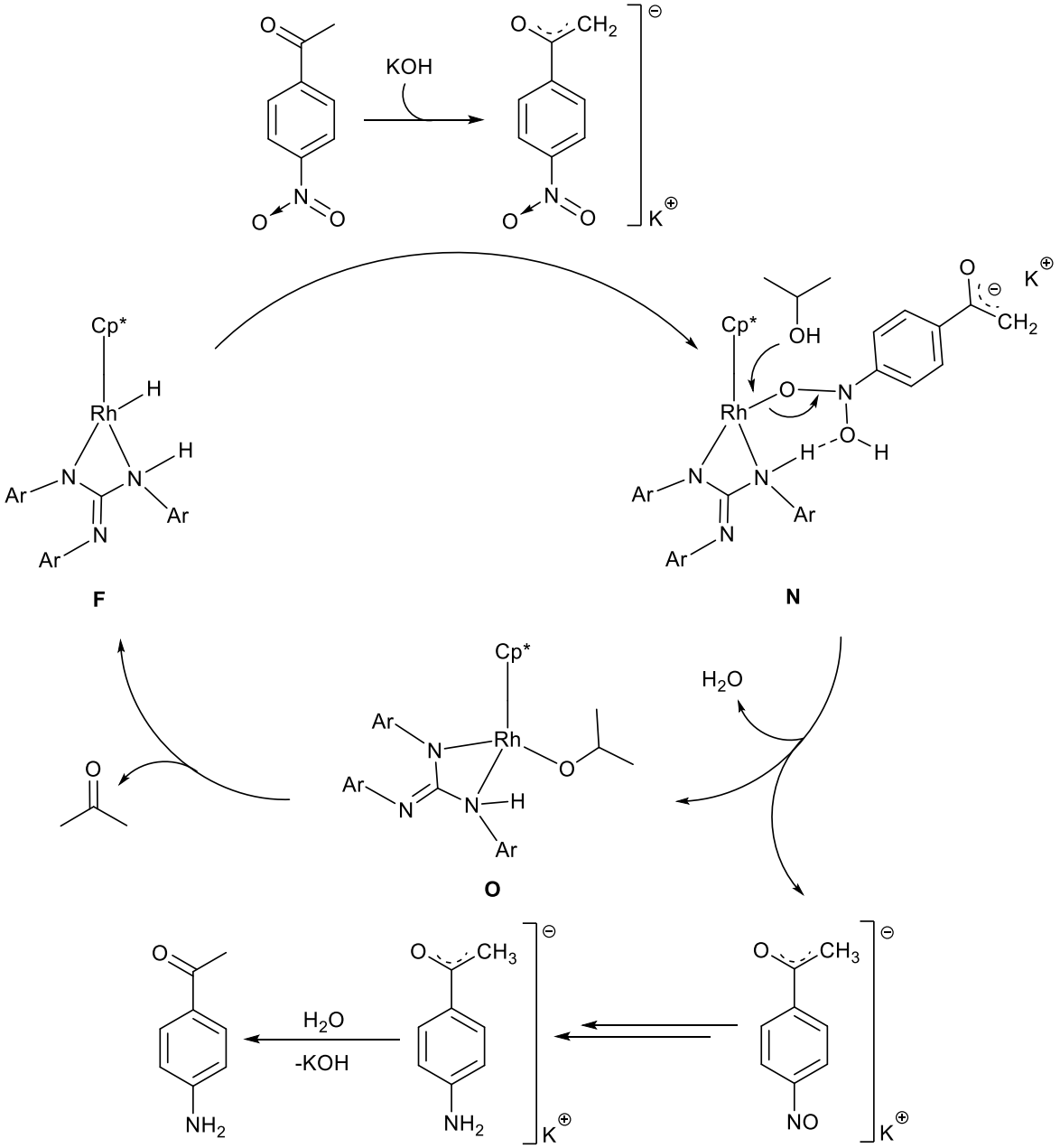
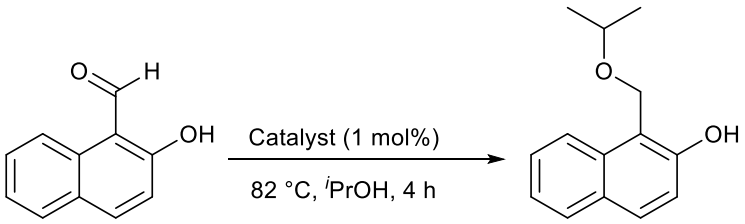


Fig. S47 ^{13}C NMR (400 MHz, $CDCl_3$) spectrum of 1-(Isopropoxymethyl)naphthalen-2-ol



Scheme S1 Plausible mechanism of TH of 4-nitroacetophenone in the presence of **3** under basic condition

Table S1 Screening of (η^5-Cp*)Rh(III) guanidinato complexes as catalysts in TH-etherification of 2-hydroxy-1-naphthaldehyde.



Entry	Catalyst	Conversion (%)	TON
1	**1**	95	95
2	**2**	97	97
3	**4**	97	97
4	**6**	98	98
5	**9**	99	99
6	**10**	98	98
7	**3**	2	2[a]

[a]Reaction was carried out at RT for 12 h