Half Sandwich Ruthenium(II) Hydrides for the Hydrogenation of Terminal, Internal, Cyclic Olefins and Olefins with Functional Groups

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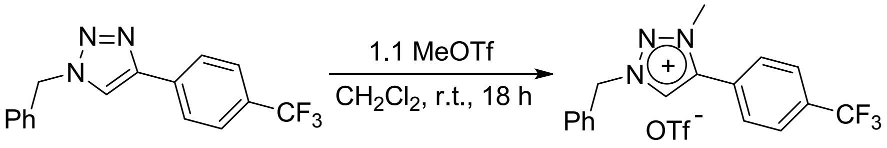
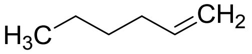
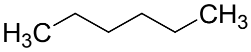
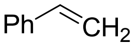
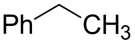
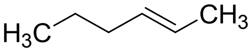
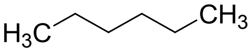
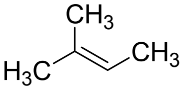
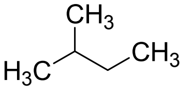
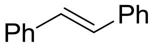
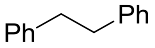
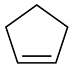
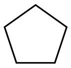
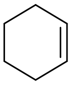
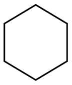
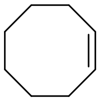
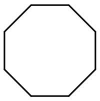
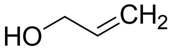
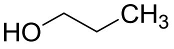
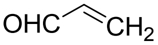
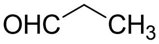
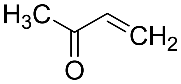
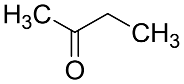
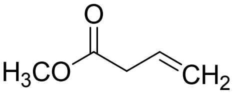
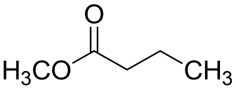
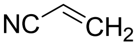
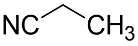
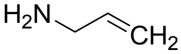
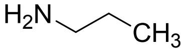
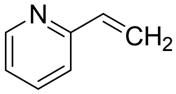
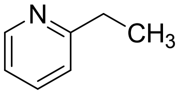
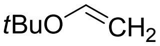
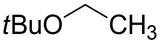
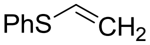
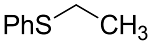
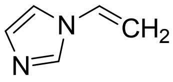
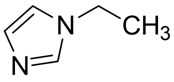
Synthesis of [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$][OTf]. MeOTf (1.805 g, 11.00 mmol) was added dropwise to a solution of 1,2,3-triazole [$PhCH_2N_3C_2H(C_6H_4CF_3)$] (3.035 g, 10.00 mmol) in CH_2Cl_2 (20 mL) at r.t. The reaction mixture was stirred for 18 h resulting in a colorless solution. All volatiles were removed under high vacuum yielding a colorless oil which solidified on standing. The solid was washed with hexane (3 x 15 mL) and dried under vacuum to give [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$][OTf] (4.239 g, 91%) as pure product. ^{1}H NMR (CD_2Cl_2): δ 4.25 (s, 3H, N-CH_3), 5.81 (s, 2H, CH_2), 7.37-7.49 (m, 3H, C_6H_5), 7.52-7.63 (m, 2H, C_6H_5), 7.75-7.88 (m, 4H, C_6H_4), 8.78 (s, 1H, triazolium-H). ^{13}C NMR (CD_2Cl_2): δ 39.27 (N-CH_3), 58.14 (CH_2), 126.00, 126.94, 129.45, 129.80, 130.03, 130.39, 130.60, 131.48, 133.65, 142.57 (Ar-C and triazolium-C). ^{19}F NMR (CD_2Cl_2): δ -63.54, -78.96. Anal. Calcd for $C_{18}H_{15}F_6N_3O_3S$ (467.39): C, 46.26; H, 3.23; N, 8.99. Found: C, 46.21; H, 3.25; N, 9.02.



Hydrogenation of olefins at 80 °C by 5d. In a glove box, a sample of the ruthenium-hydride complex **5d** (6.5 mg, 10 μmol), C_6D_5Br (0.5 mL) and substrate (0.2 mmol) were combined in a vial. The mixture was transferred to a J. Young tube and the J. Young tube was sealed. On a Schlenk line, the reaction mixture was degassed four times using the freeze-pump-thaw method. The sample was then frozen once more in liquid nitrogen and 4 atm of H_2 was added. The J. Young tube was sealed again and warmed to room temperature and then placed in an oil bath pre-heated to 80 °C. ^{1}H NMR spectra were measured at appropriate intervals and relative integration of substrate and product peaks were used to determine the composition of the mixture. The results are summarized in Table S1.

Note: Catalyst **5d** slowly decomposed at 80 °C over time (Figure S30). In C_6D_5Br the hydride resonance of **5d** was observed at -5.91 ppm. Heating a solution of **5d** in C_6D_5Br for an hour, another hydride resonance at -6.31 ppm was observed. The intensity of the second hydride resonance (-6.31 ppm) increased with time whereas the intensity of the first hydride resonance (-5.91 ppm) decreased. In 5 hours, both of the hydride resonances disappeared completely and species **5d** completely decomposed to unidentified products. As compared to the hydrogenation of olefins catalyzed by **5d** at 50 °C, the hydrogenation of 1-hexene, 2-hexene, allyl alcohol and acrylaldehyde at 80 °C was faster. Similar activity of **5d** was observed for the reduction of 3-buten-2-one both at 50 and 80 °C. At 80 °C much reduced activity was observed for rest of the substrates as compared to activity at 50 °C.

Table S1. Hydrogenation catalysis with **5d**[a]

entry	substrate	product	cat	time/yield (h/%)[b]
1			**2a**	2/100
2			**2a**	3/19 5/37 24/41
3			**2a**	2/100
4			**2a**	3/36 5/50 24/55
5			**2a**	3/15 5/22 24/28
6			**2a**	3/34 5/51 24/61
7			**2a**	3/29 5/44 24/55
8			**2a**	3/24 5/40 24/51
9			**2a**	2/100
10			**2a**	1/100
11			**2a**	4/100
12			**2a**	8/100
13			**2a**	4/100
14			**2a**	3/29 5/48 24/53
15			**2a**	3/18 5/31 24/36
16			**2a**	3/17 5/21 24/31
17			**2a**	3/15 5/20 24/25
18			**2a**	3/21 5/29 24/32

[a] Conditions: 0.10 mmol of substrate and 5 mol % of catalyst in C_6D_5Br at 80 °C under 4 atm of H_2.
[b] Yields were determined by ^1H NMR spectroscopy.

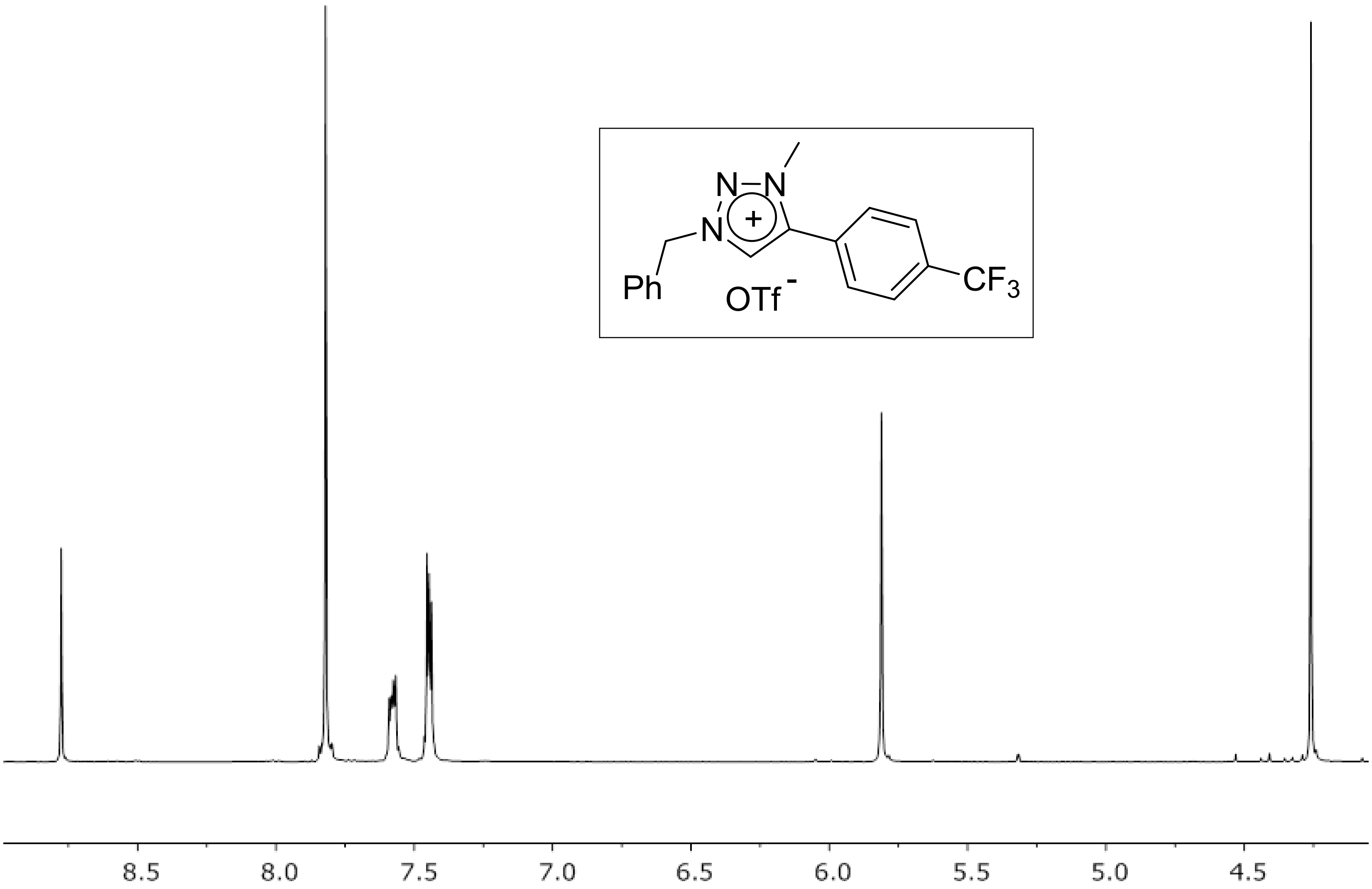


Figure S1. ^{1}H NMR spectrum of [$PhCH_2N_2(NMe)C_2(C_6H_4CF_3)$][OTf] in CD_2Cl_2 at r.t.

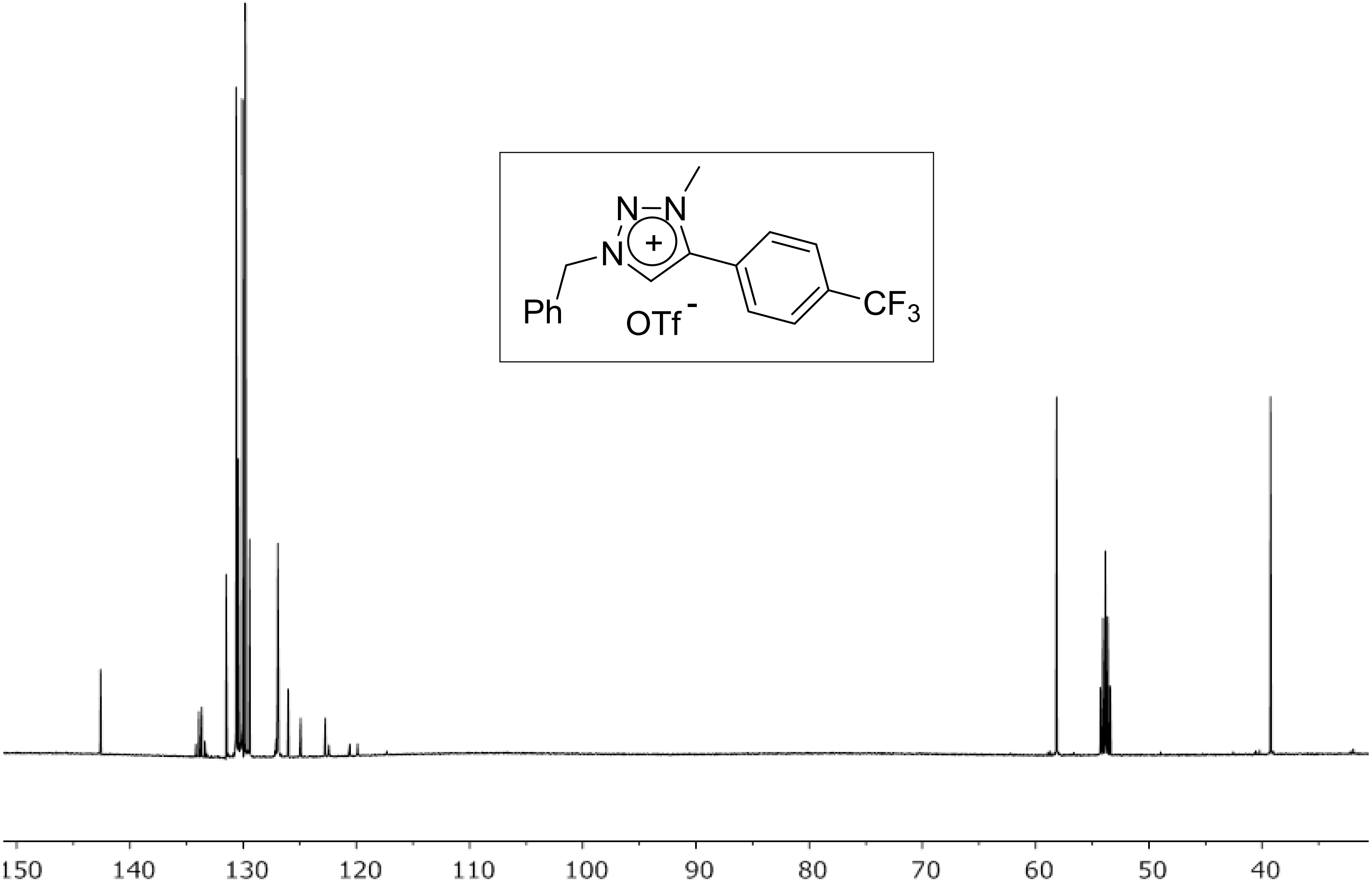


Figure S2. ^{13}C NMR spectrum of $[PhCH_2N_2(NMe)C_2(C_6H_4CF_3)][OTf]$ in CD_2Cl_2 at r.t.

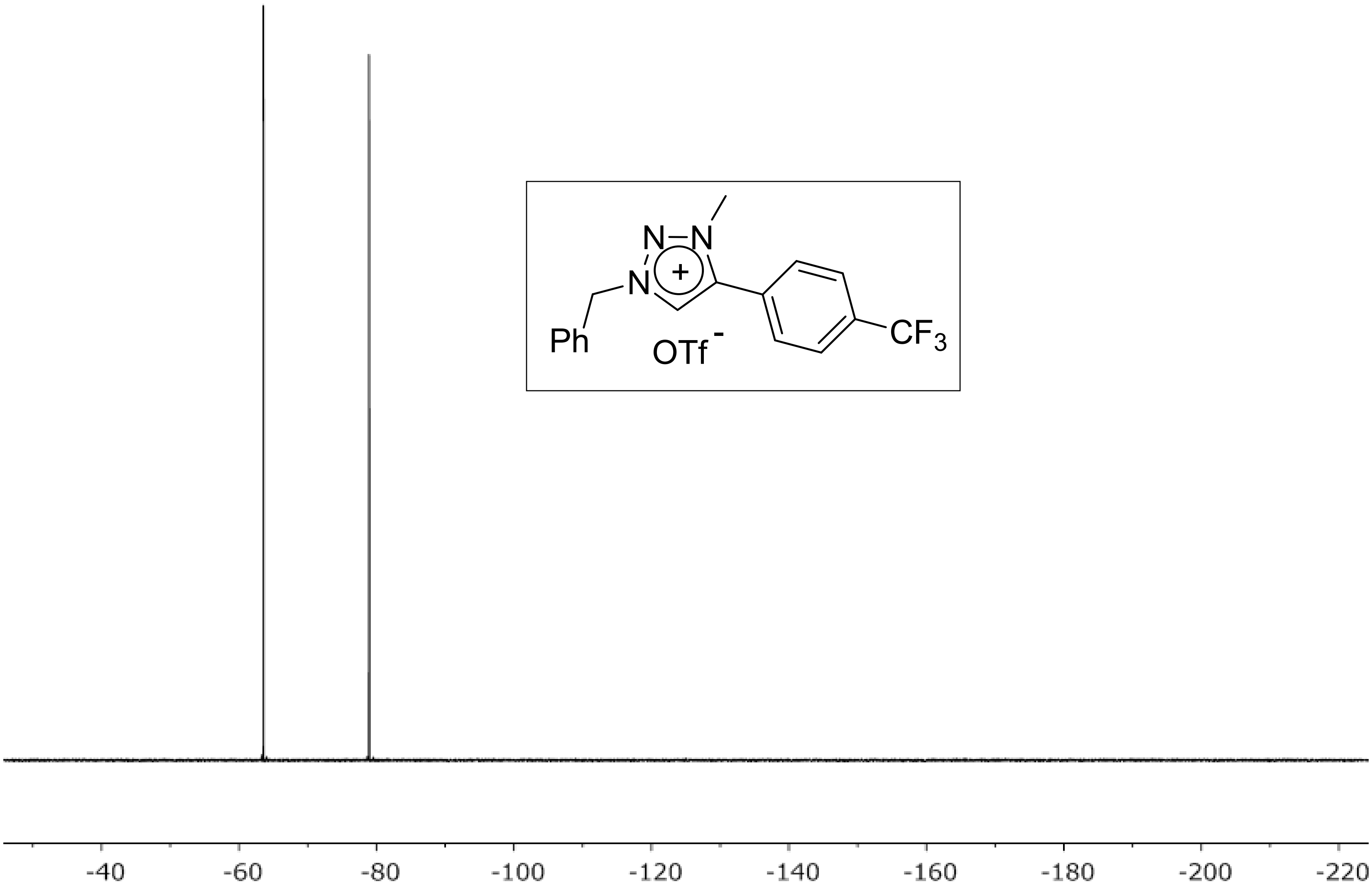


Figure S3. ^{19}F NMR spectrum of [PhCH$_2$N$_2$(NMe)C$_2$(C$_6$H$_4$CF$_3$)][OTf] in CD$_2$Cl$_2$ at r.t.

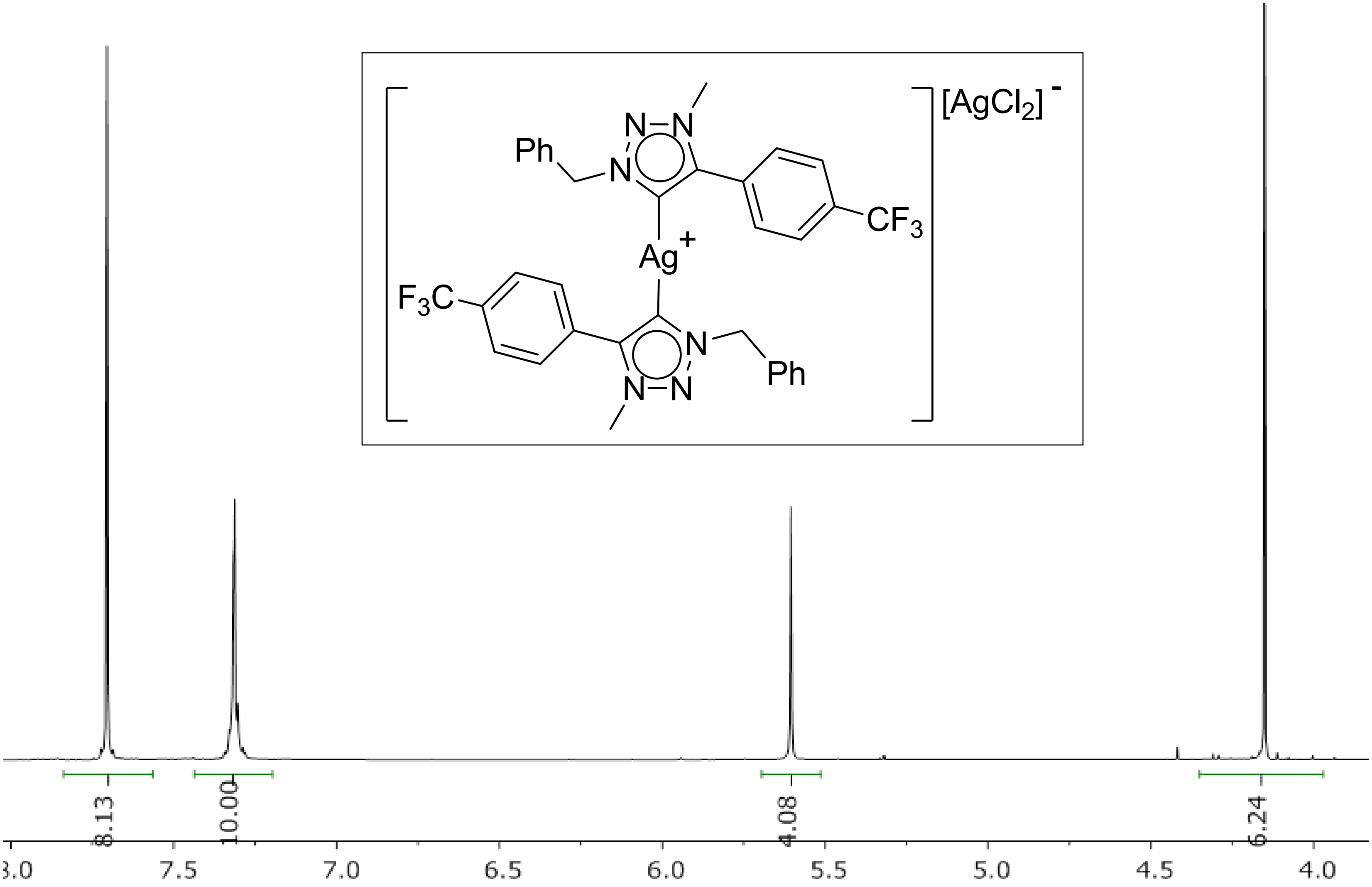


Figure S4. ^{1}H NMR spectrum of **1a** in CD_2Cl_2 at r.t.

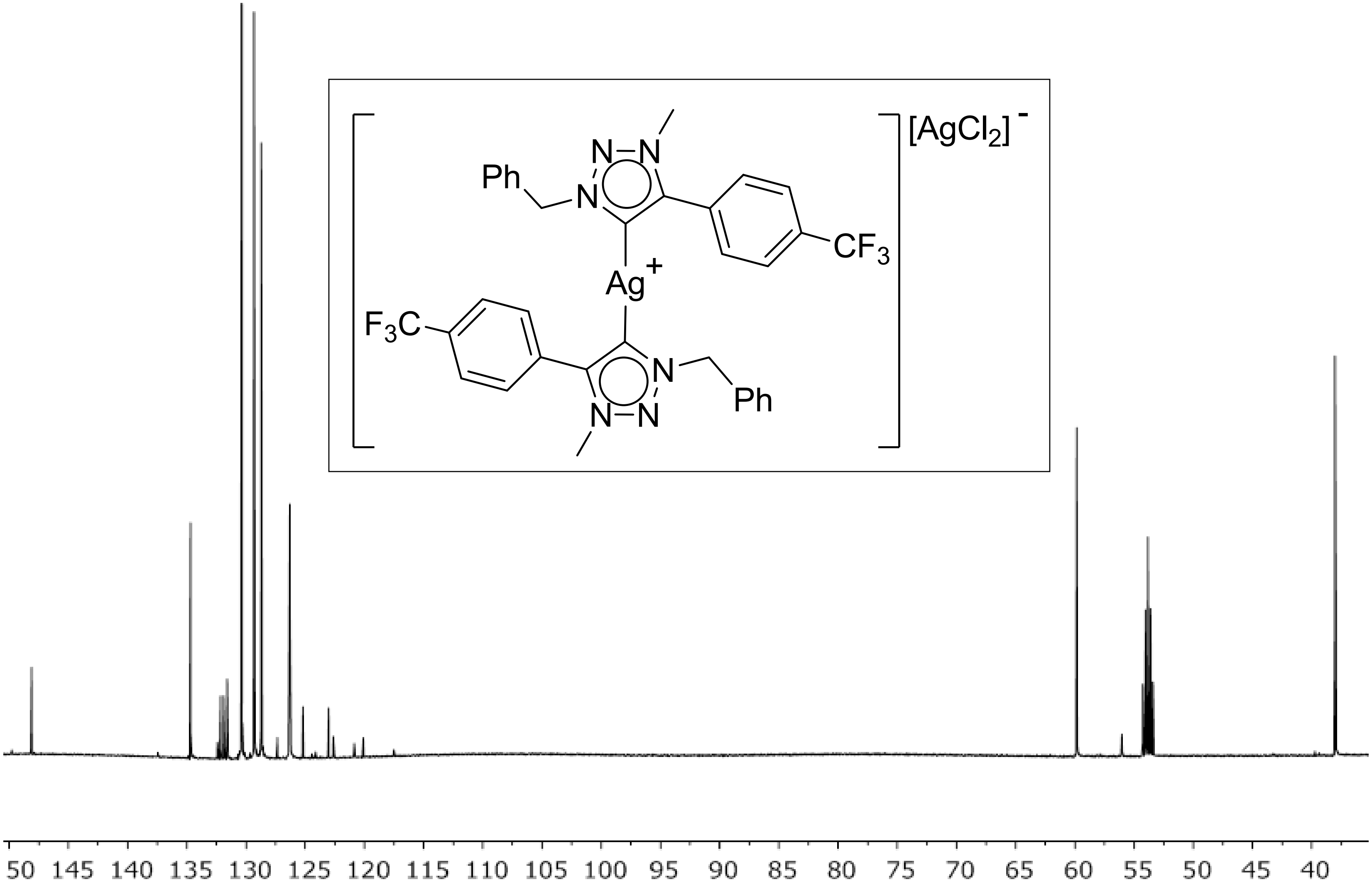


Figure S5. ^{13}C NMR spectrum of **1a** in CD_2Cl_2 at r.t.

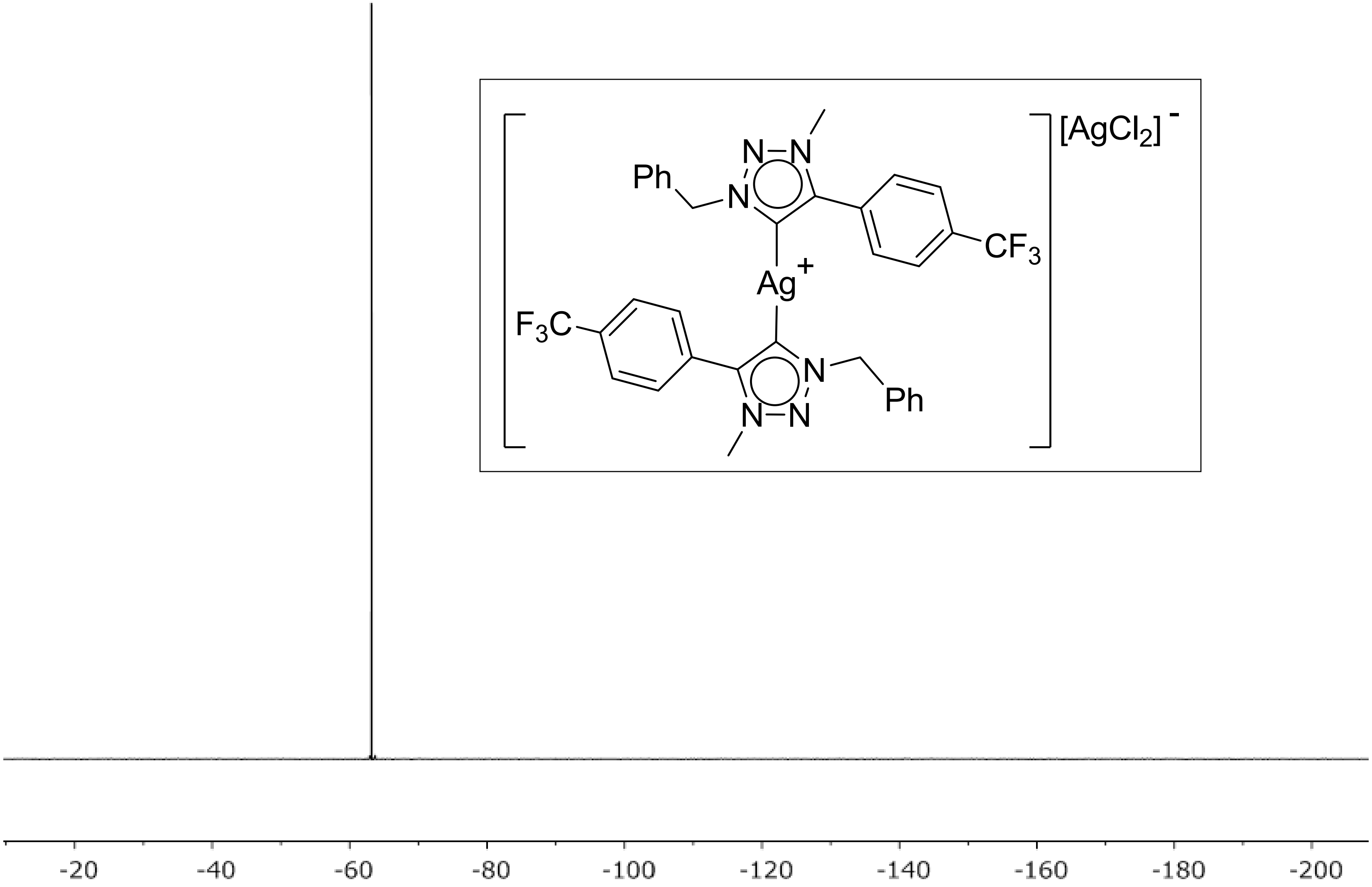


Figure S6. ^{19}F NMR spectrum of **1a** in CD_2Cl_2 at r.t.

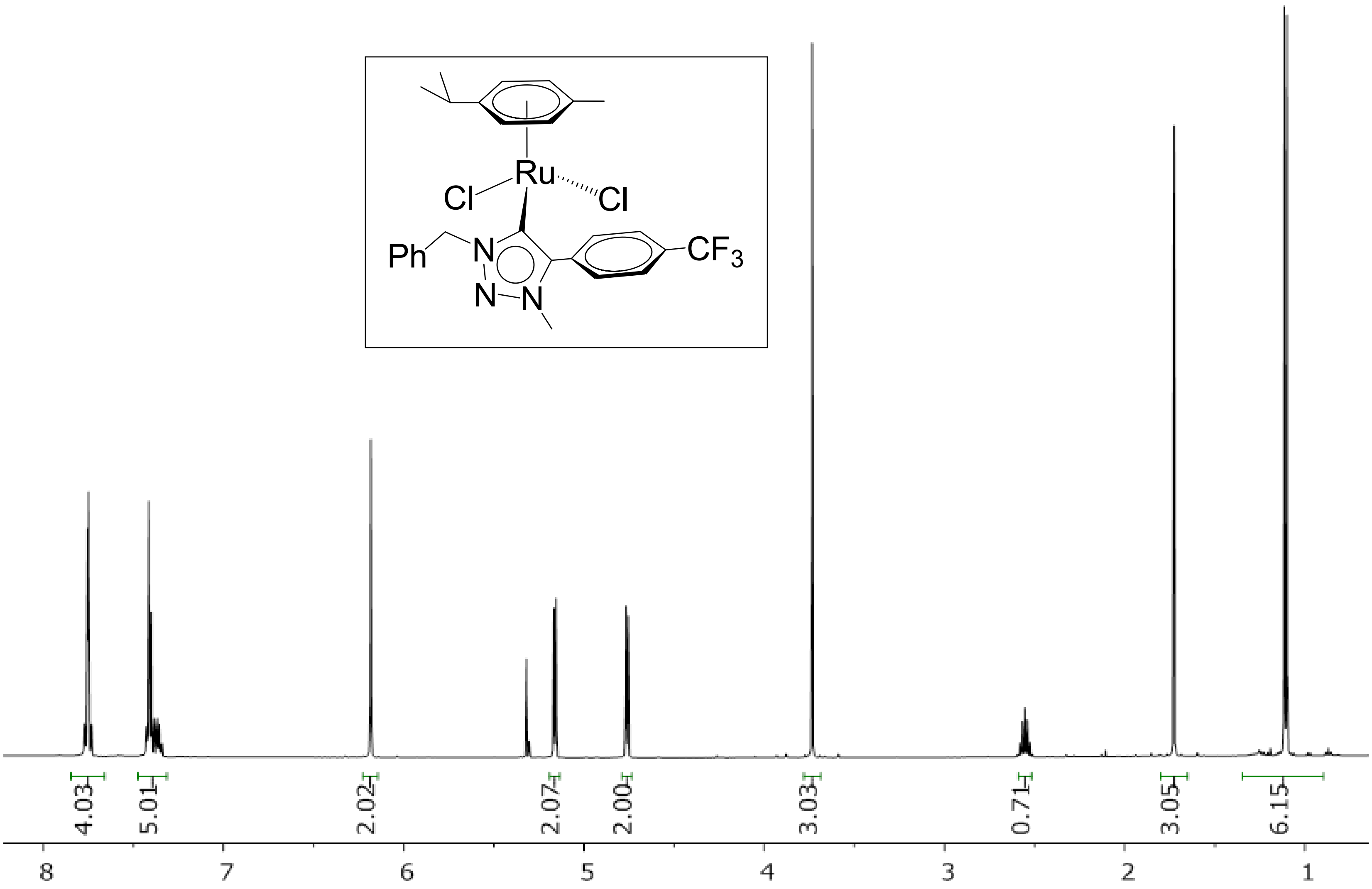


Figure S7. ^{1}H NMR spectrum of **2a** in CD_2Cl_2 at r.t.

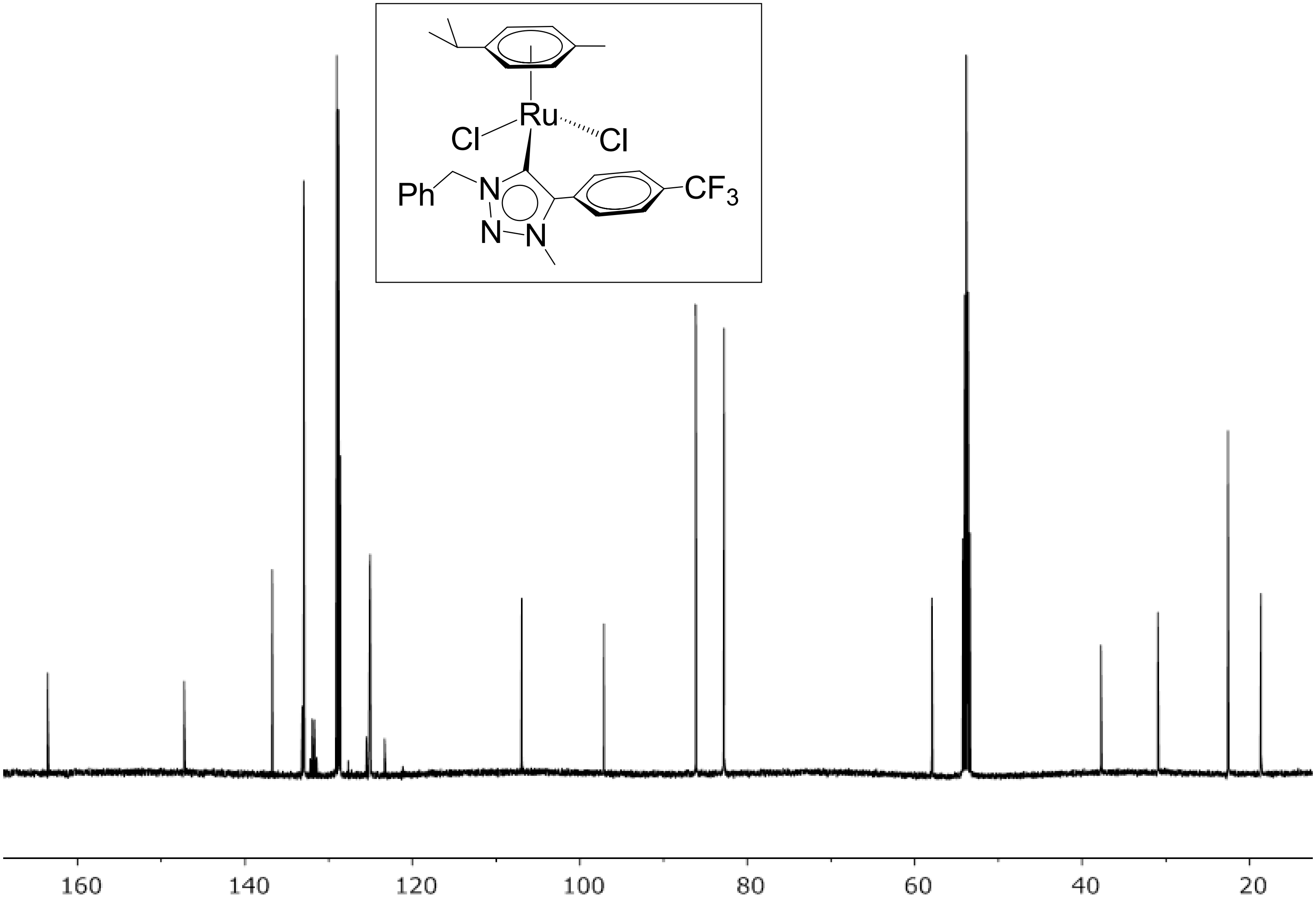


Figure S8. ^{13}C NMR spectrum of **2a** in CD_2Cl_2 at r.t.

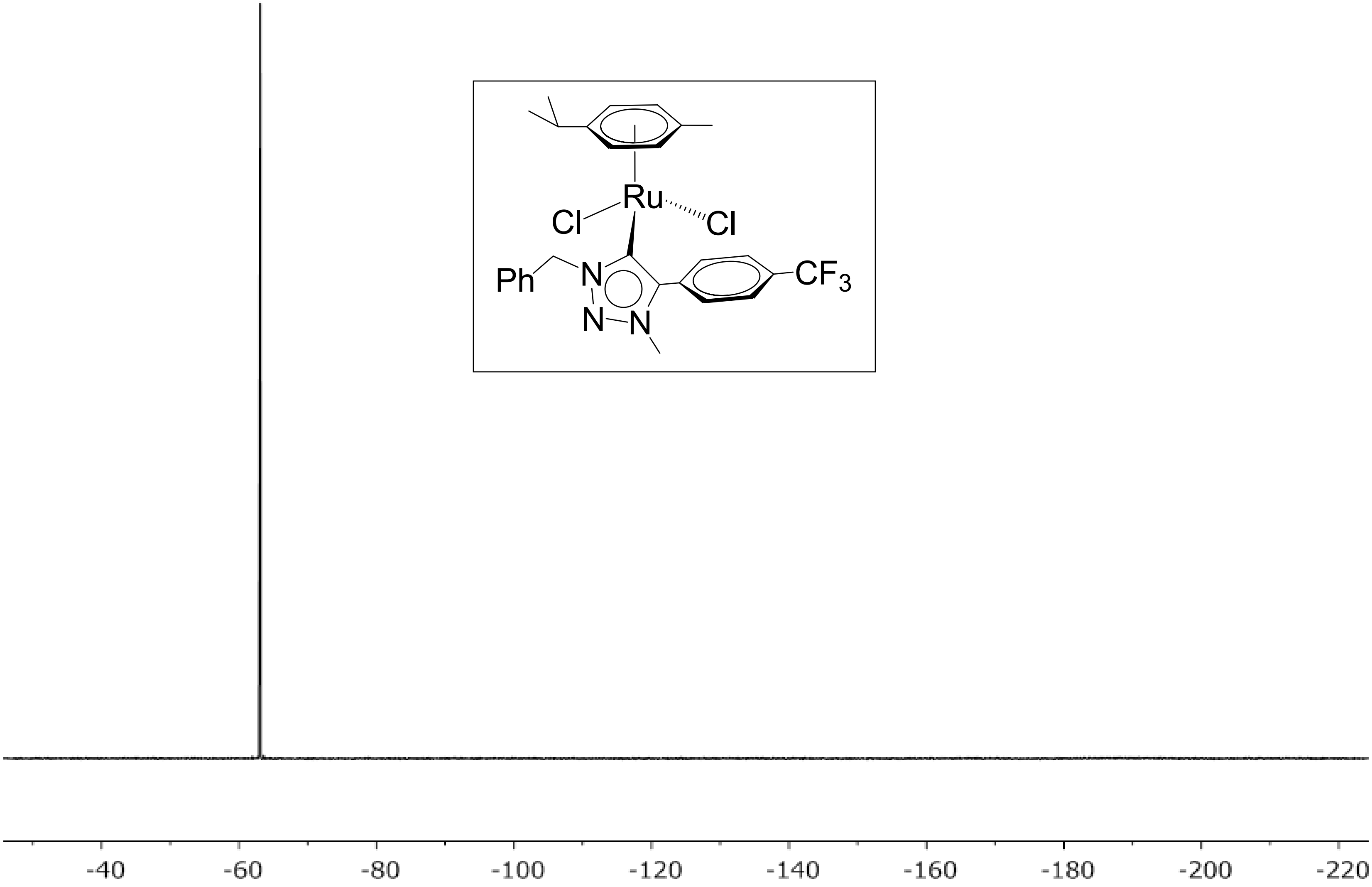


Figure S9. ^{19}F NMR spectrum of **2a** in CD_2Cl_2 at r.t.

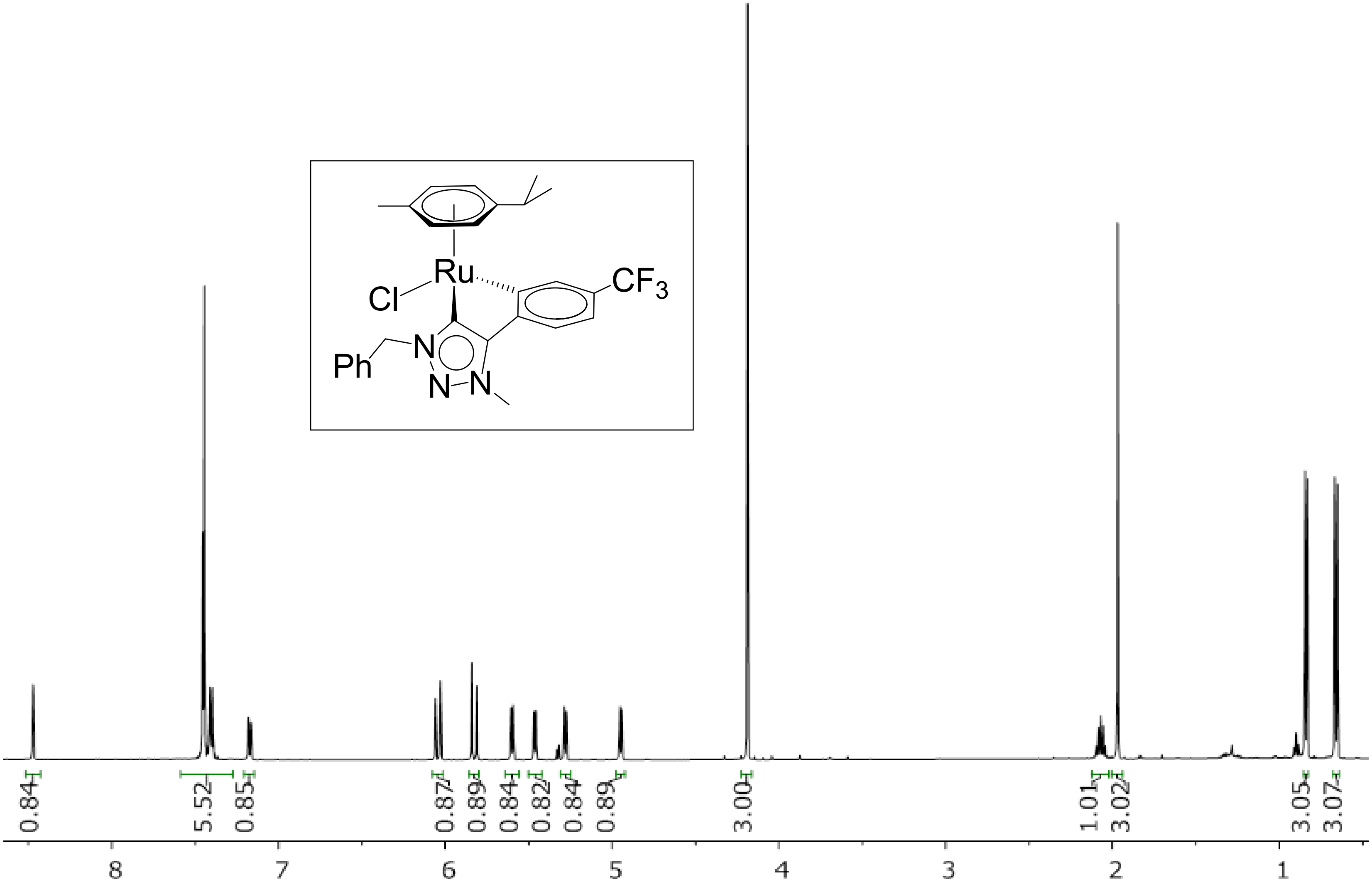


Figure S10. ^{1}H NMR spectrum of **2a’** in CD_2Cl_2 at r.t.

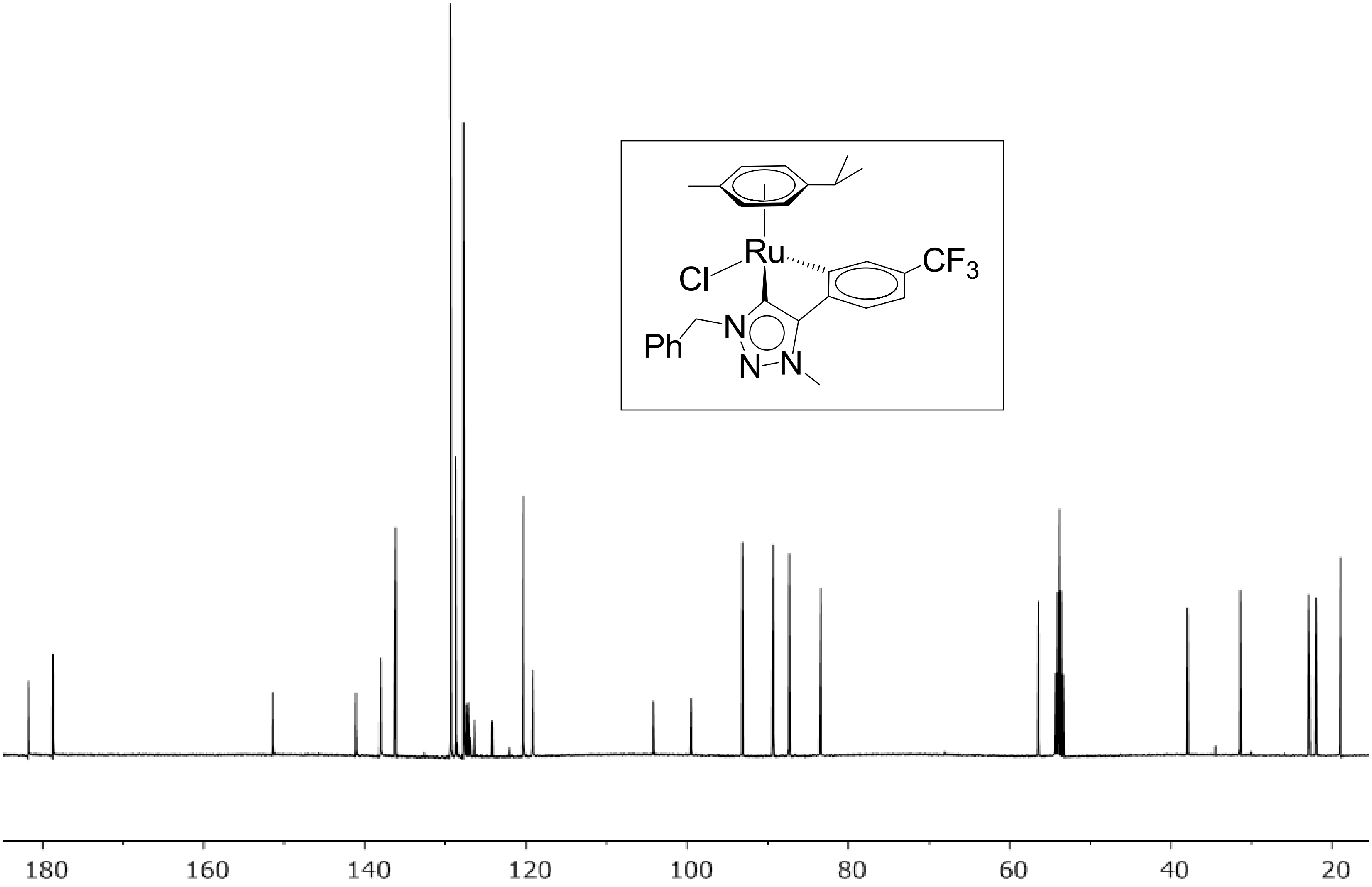


Figure S11. ^{13}C NMR spectrum of **2a’** in CD_2Cl_2 at r.t.

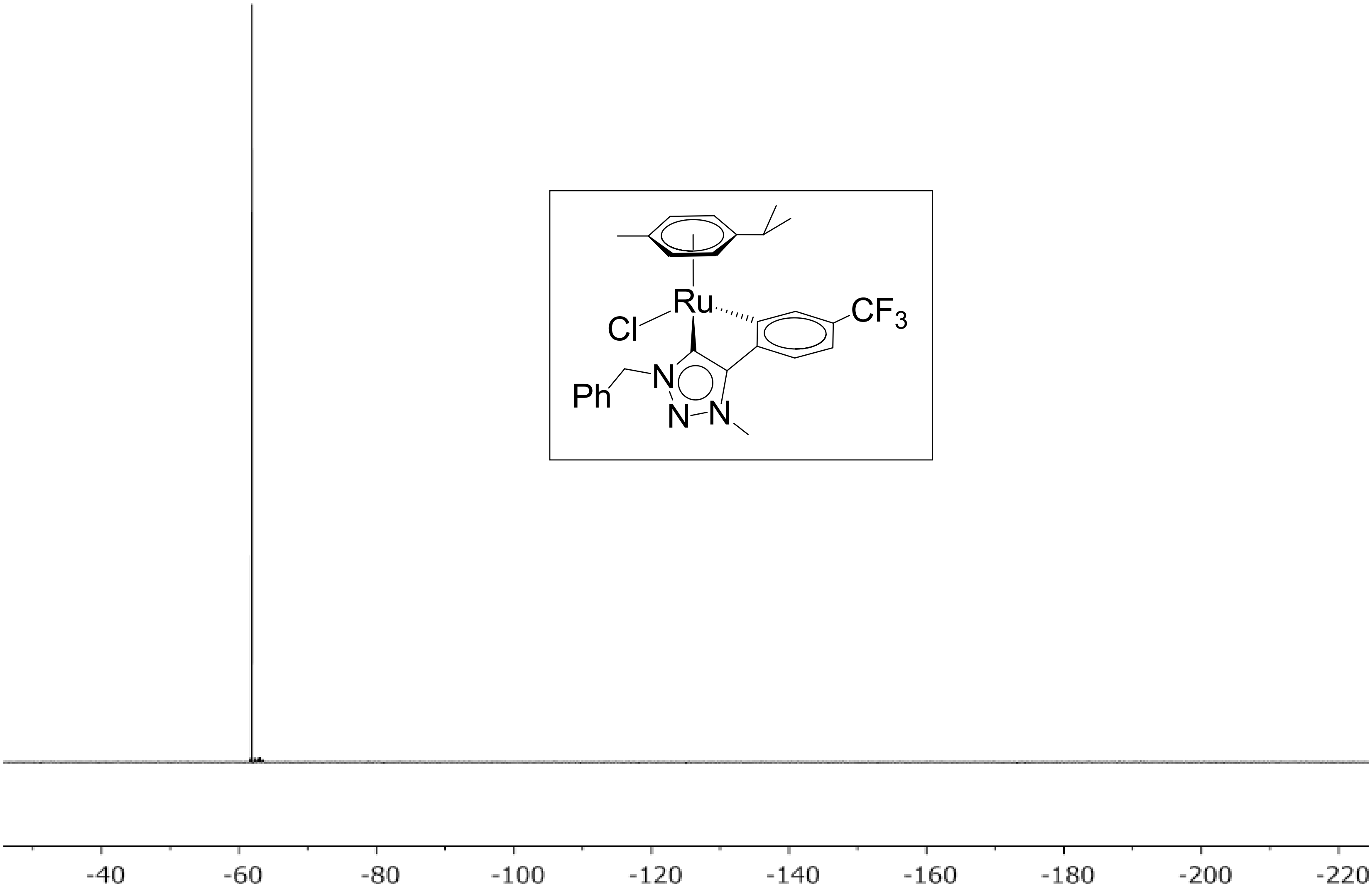


Figure S12. ^{19}F NMR spectrum of **2a’** in CD_2Cl_2 at r.t.

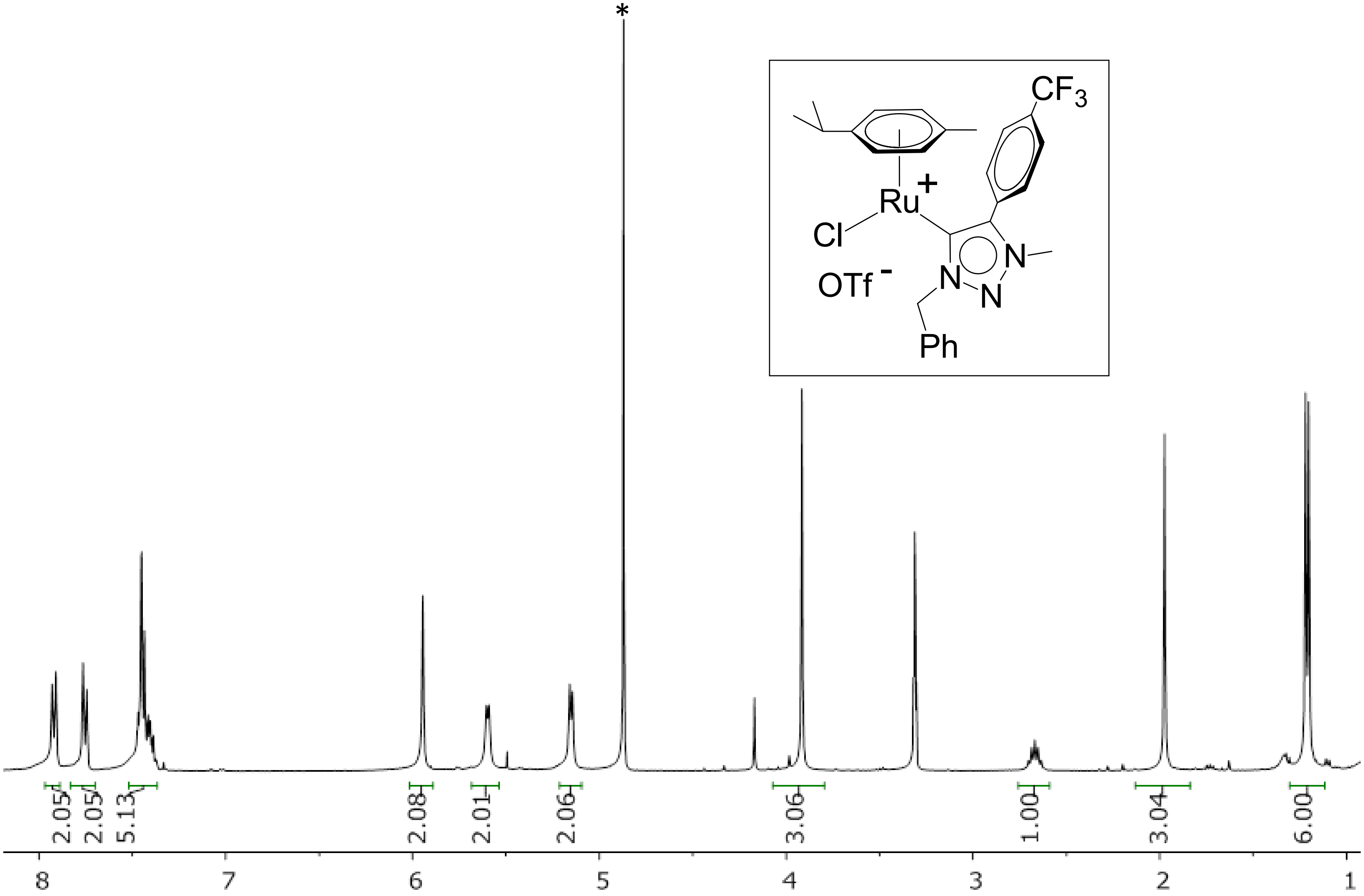


Figure S13. ^{1}H NMR spectrum of **3a** in CD_3OD at r.t. (* indicates water).

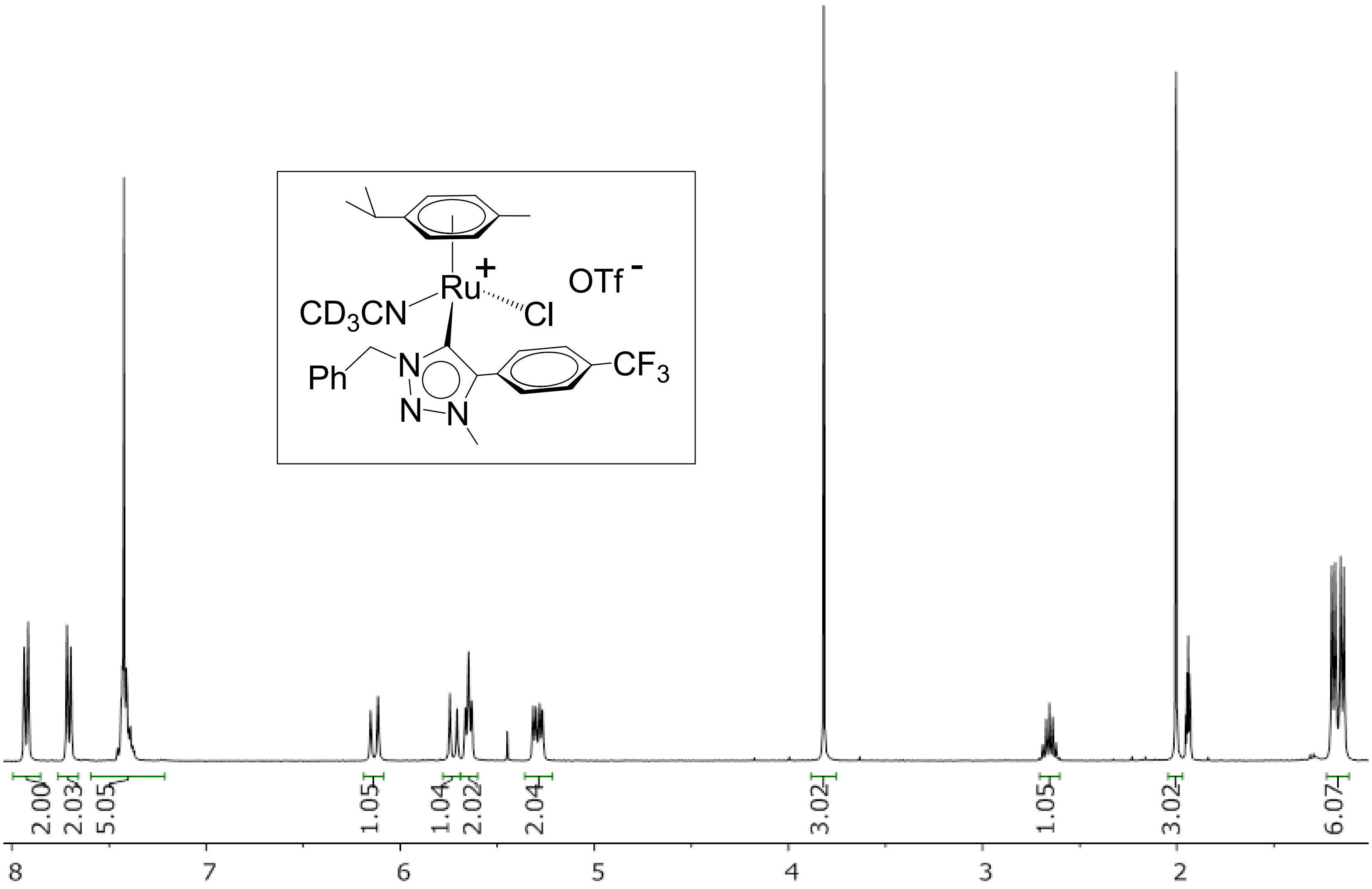


Figure S14. ^{1}H NMR spectrum of **4a** in CD_3CN at r.t.

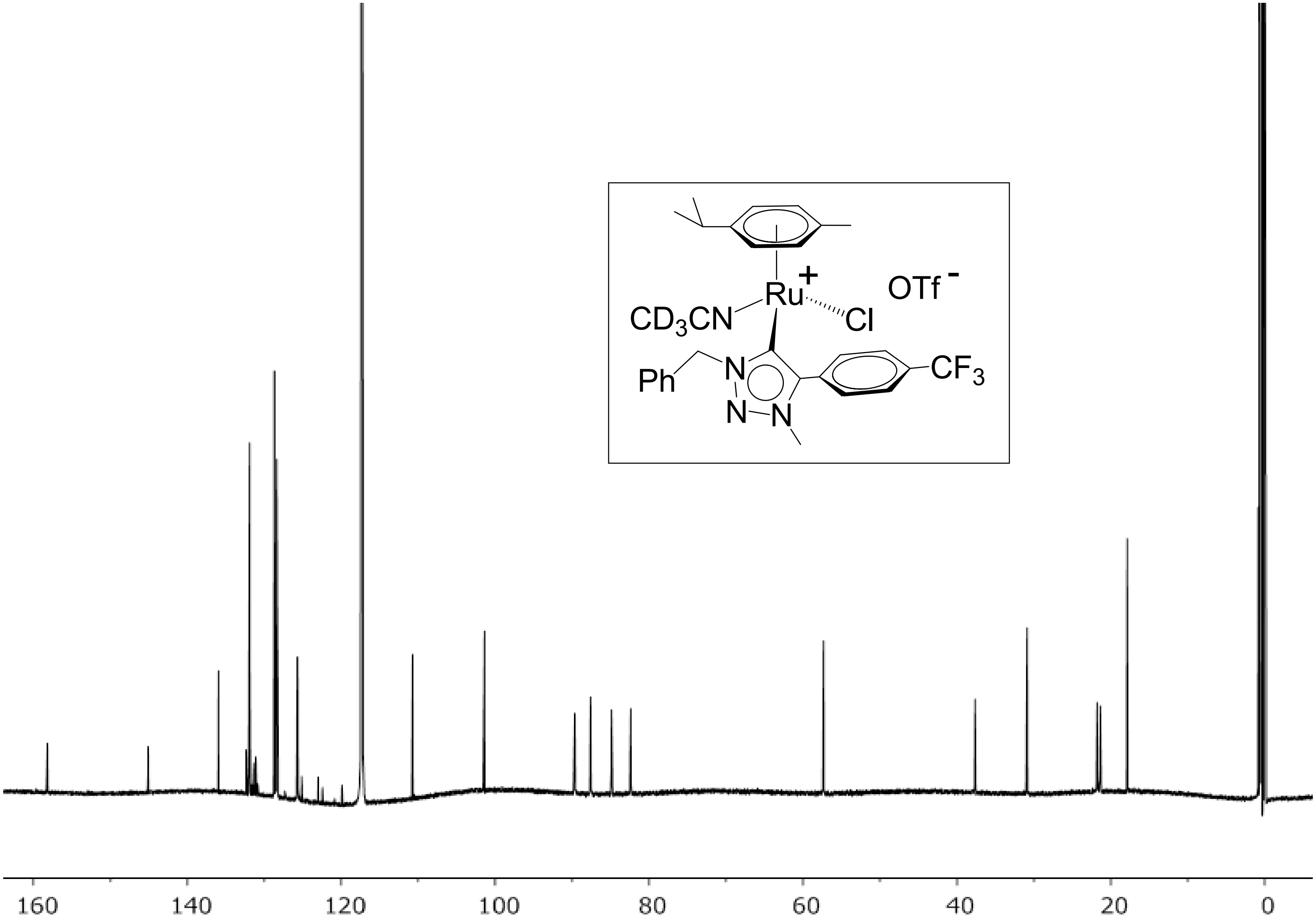


Figure S15. ^{13}C NMR spectrum of **4a** in CD$_3$CN at r.t.

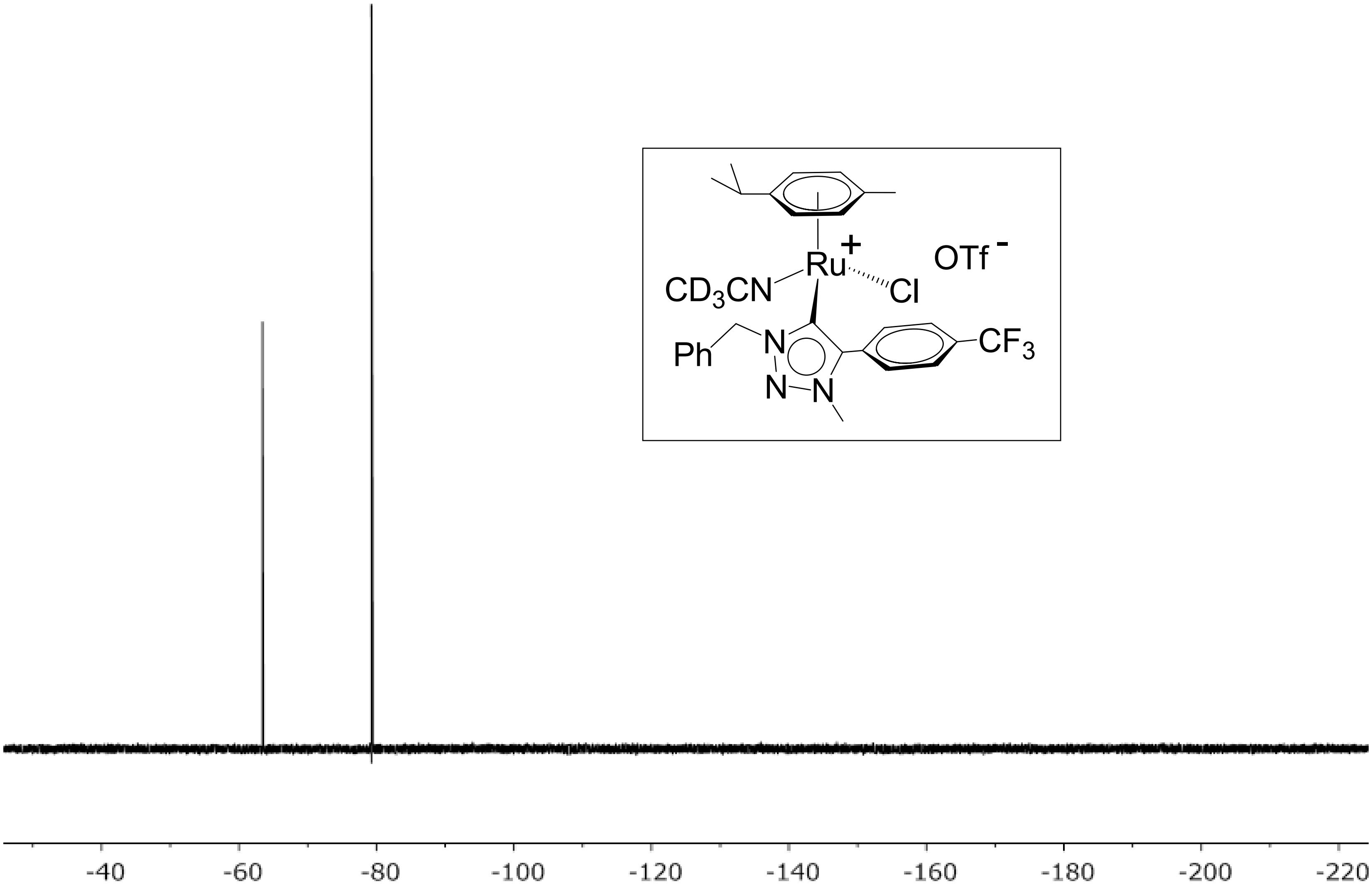


Figure S16. ^{19}F NMR spectrum of **4a** in CD$_3$CN at r.t.

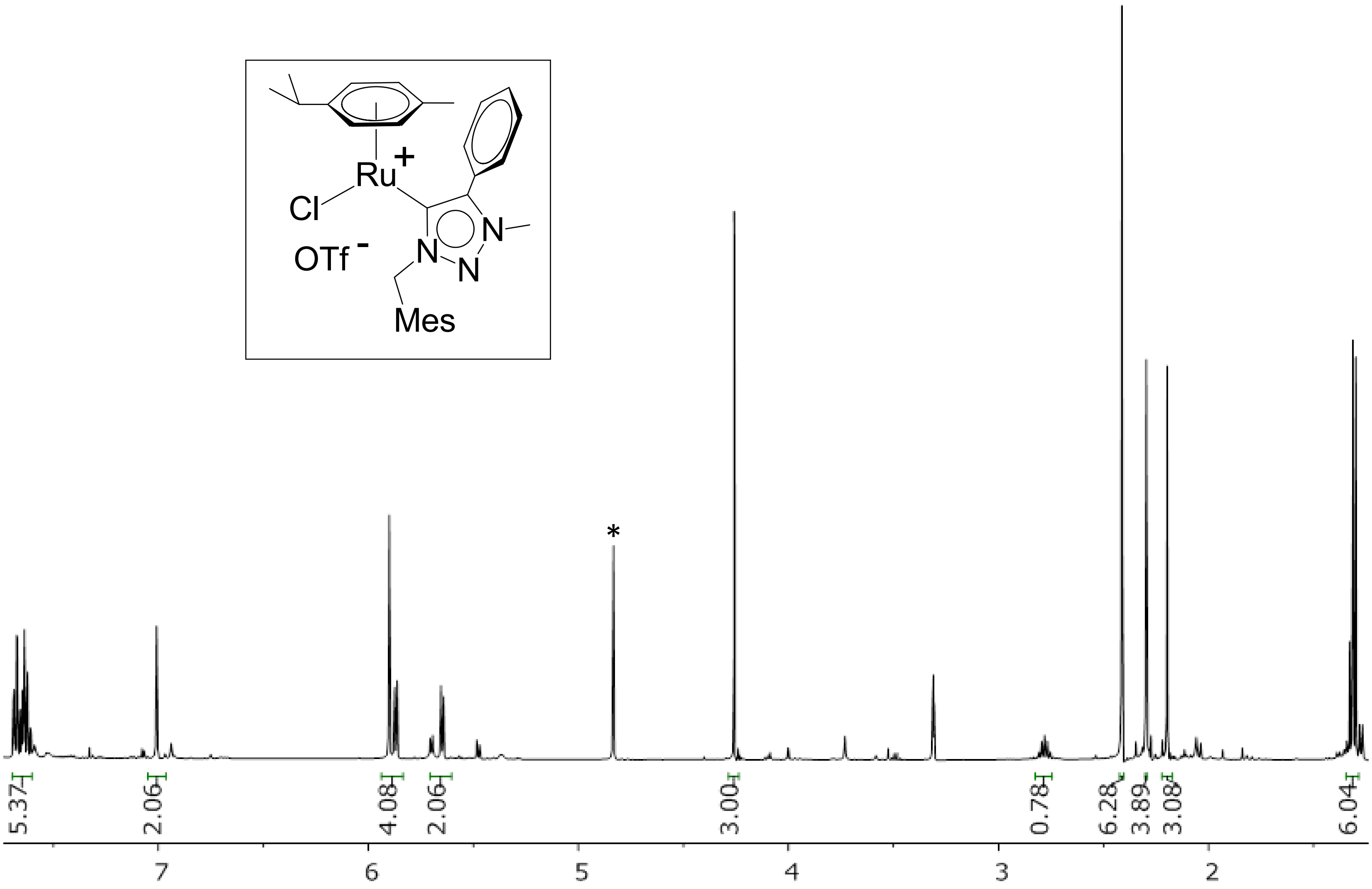


Figure S17. ^{1}H NMR spectrum of **3b** in CD_3OD at r.t. (* indicates water).

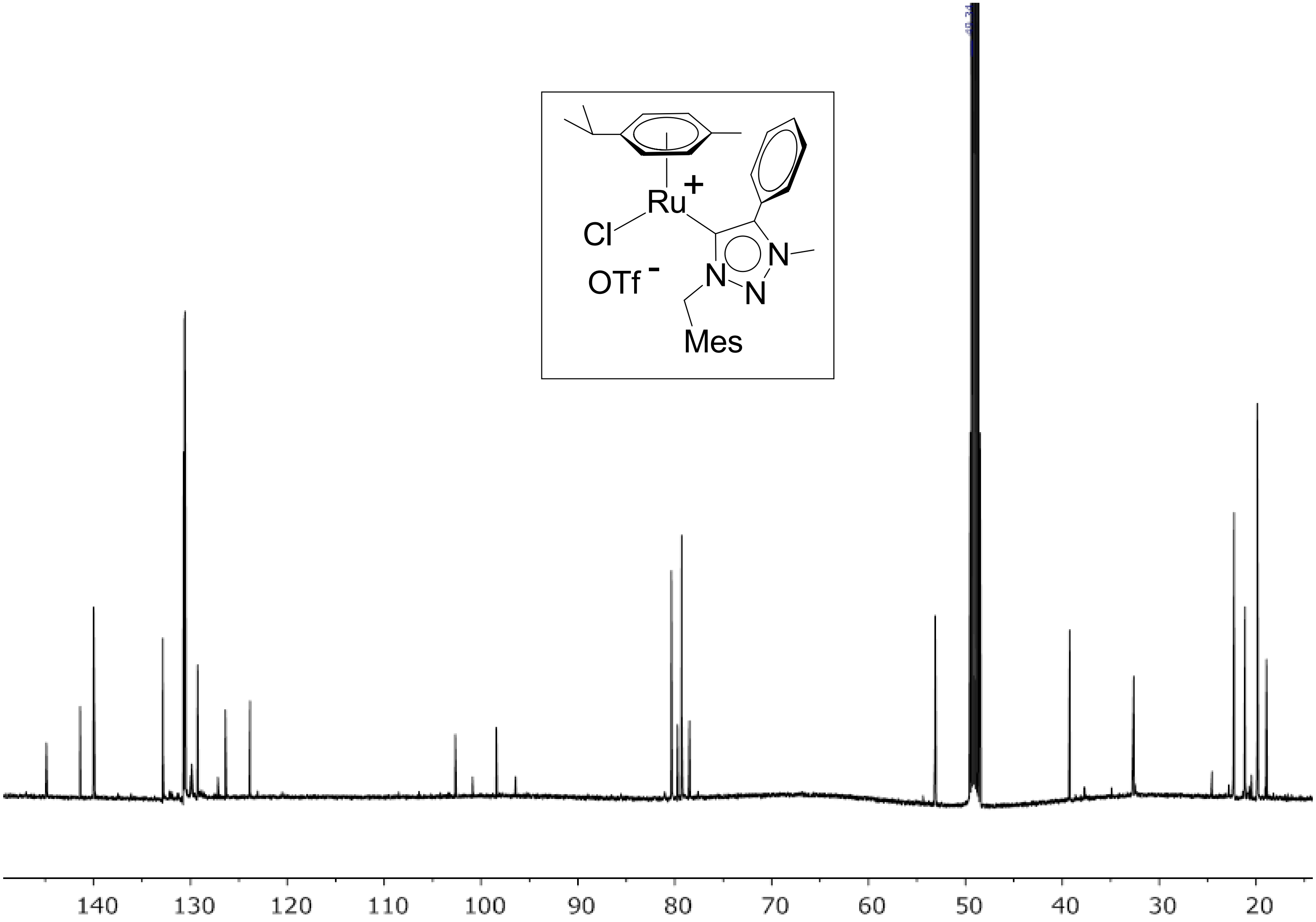


Figure S18. ^{13}C NMR spectrum of **3b** in CD_3OD at r.t.

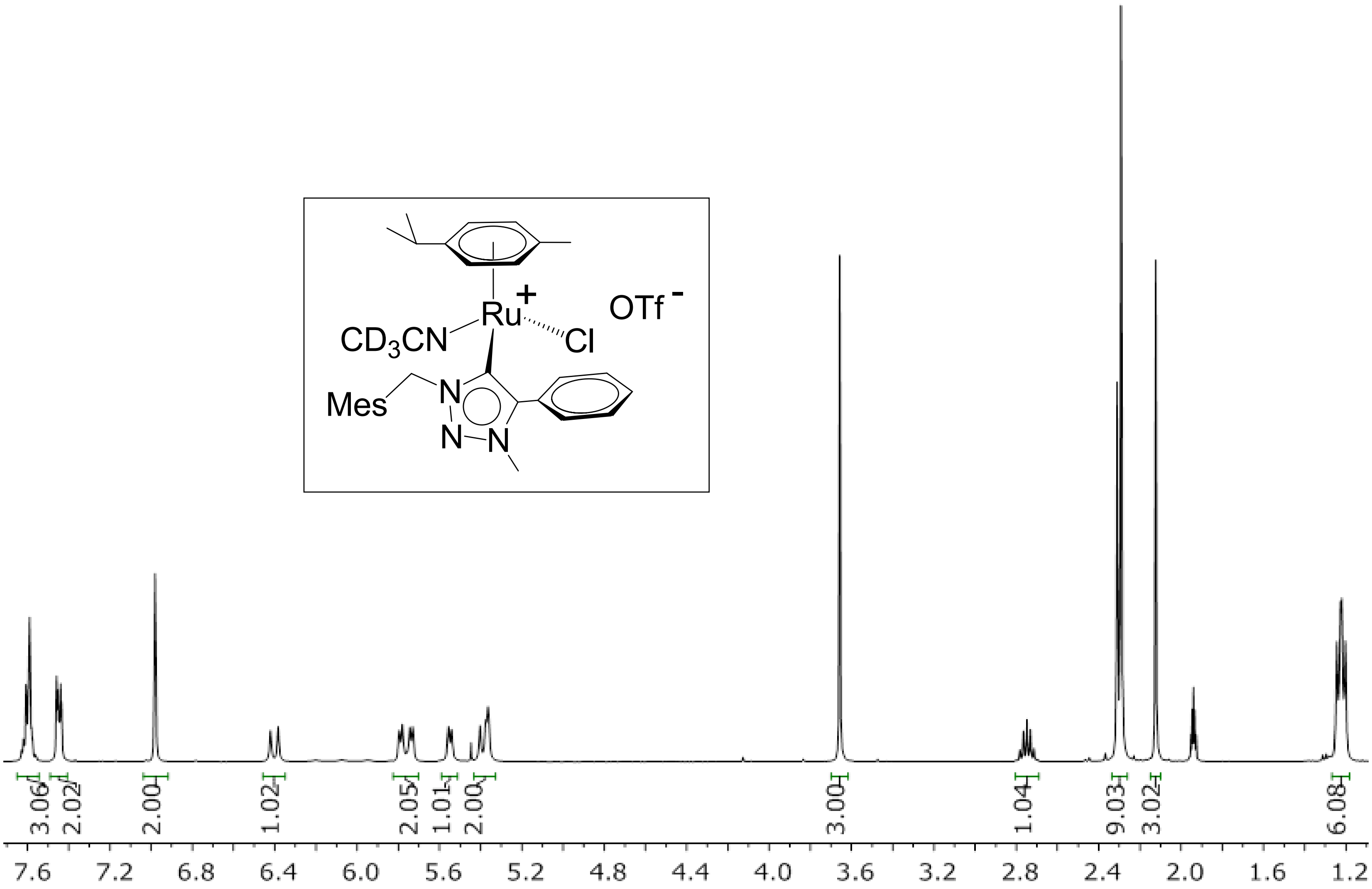


Figure S19. ^{1}H NMR spectrum of **4b** in CD_3CN at r.t.

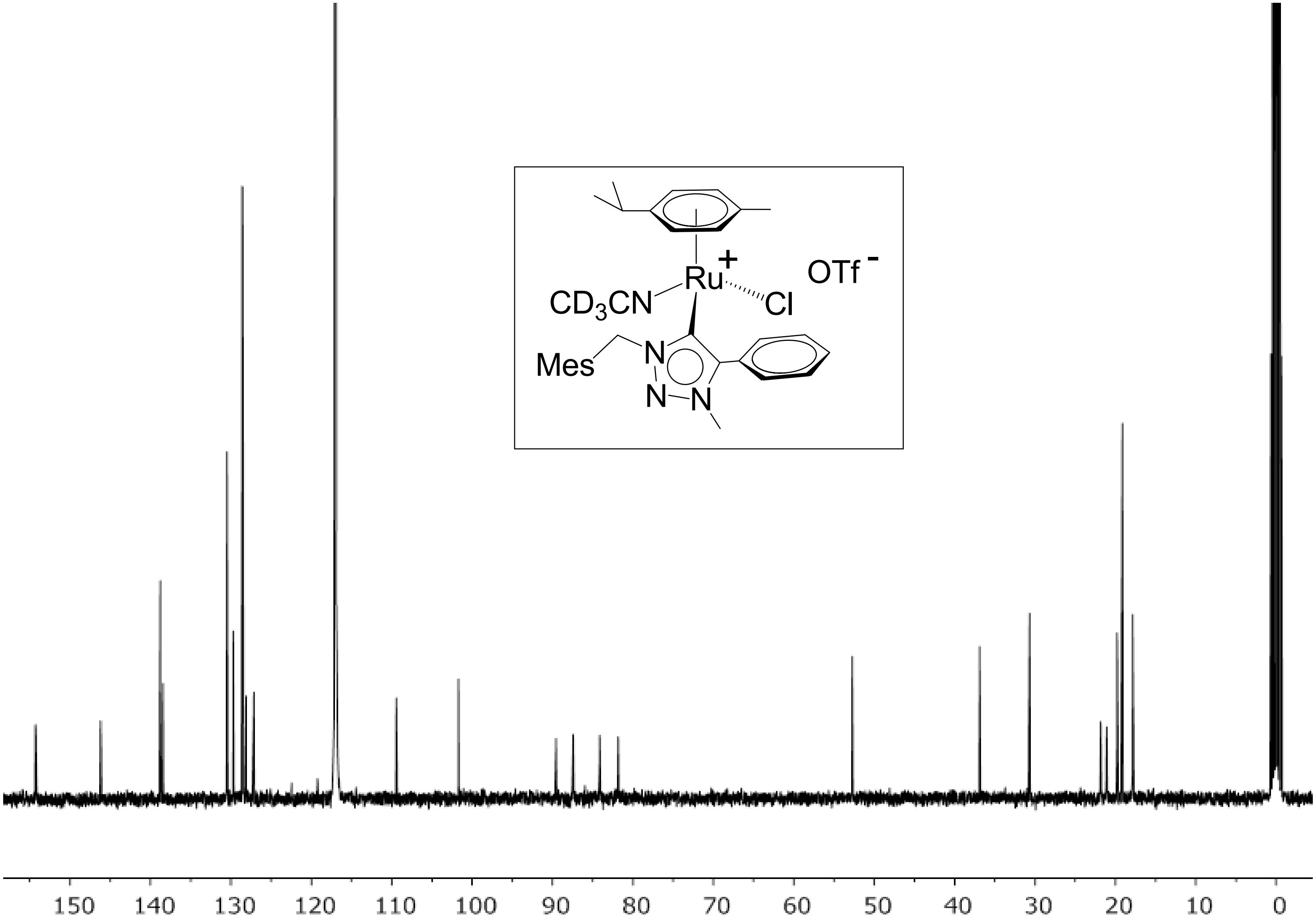


Figure S20. ^{13}C NMR spectrum of **4b** in CD$_3$CN at r.t.

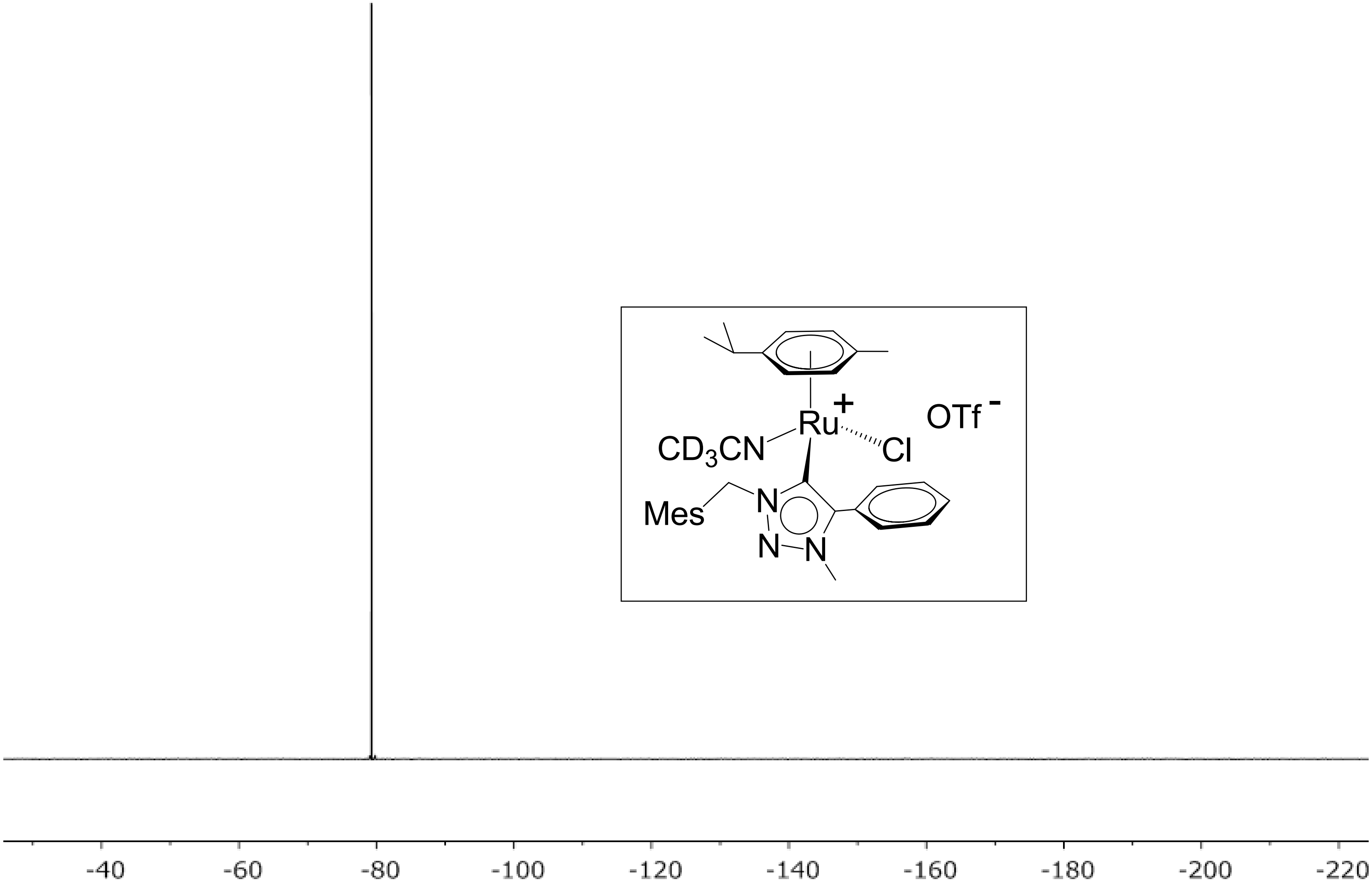


Figure S21. ^{19}F NMR spectrum of **4b** in CD_3CN at r.t.

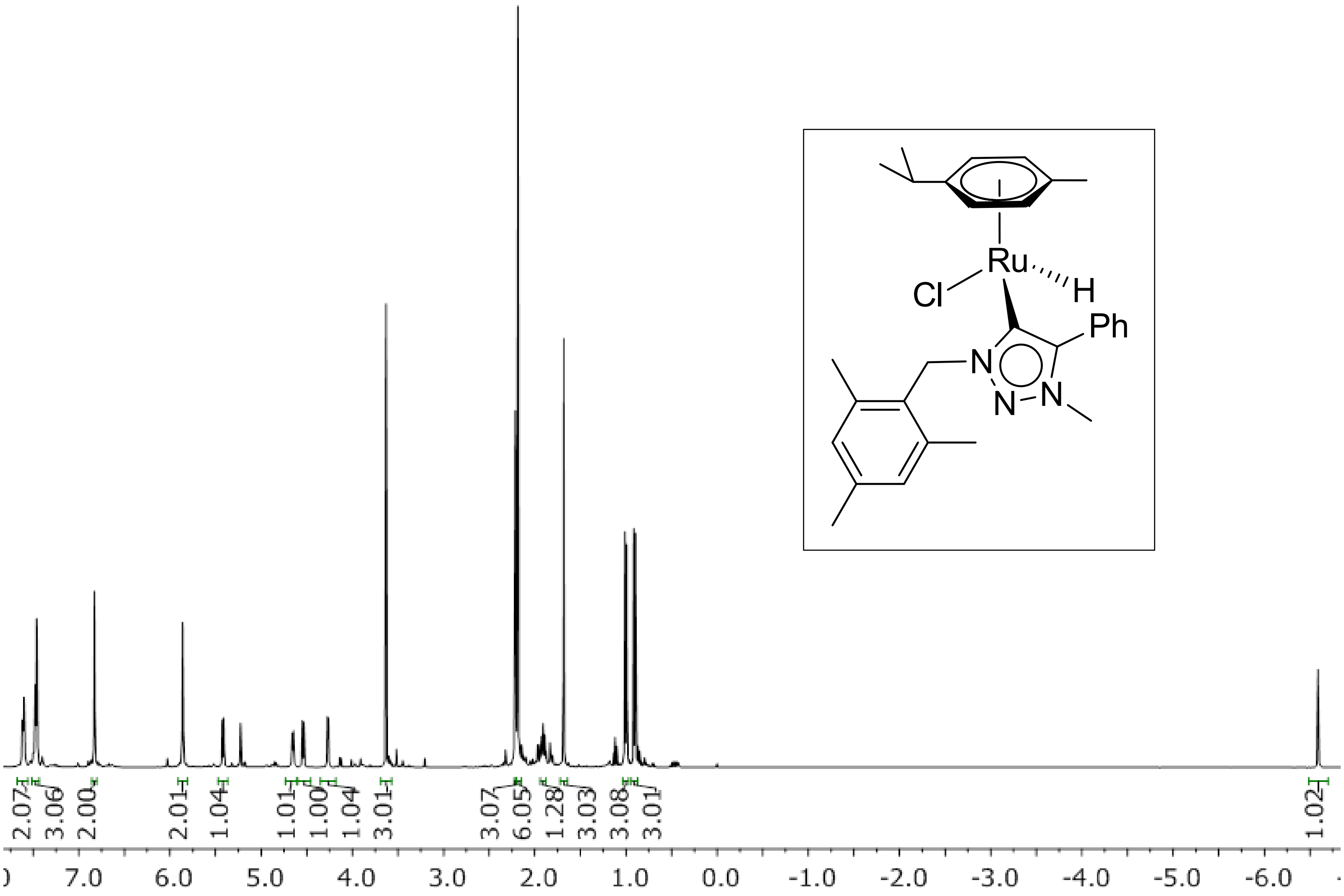


Figure S22. ^{1}H NMR spectrum of **5b** in CD_2Cl_2 at r.t.

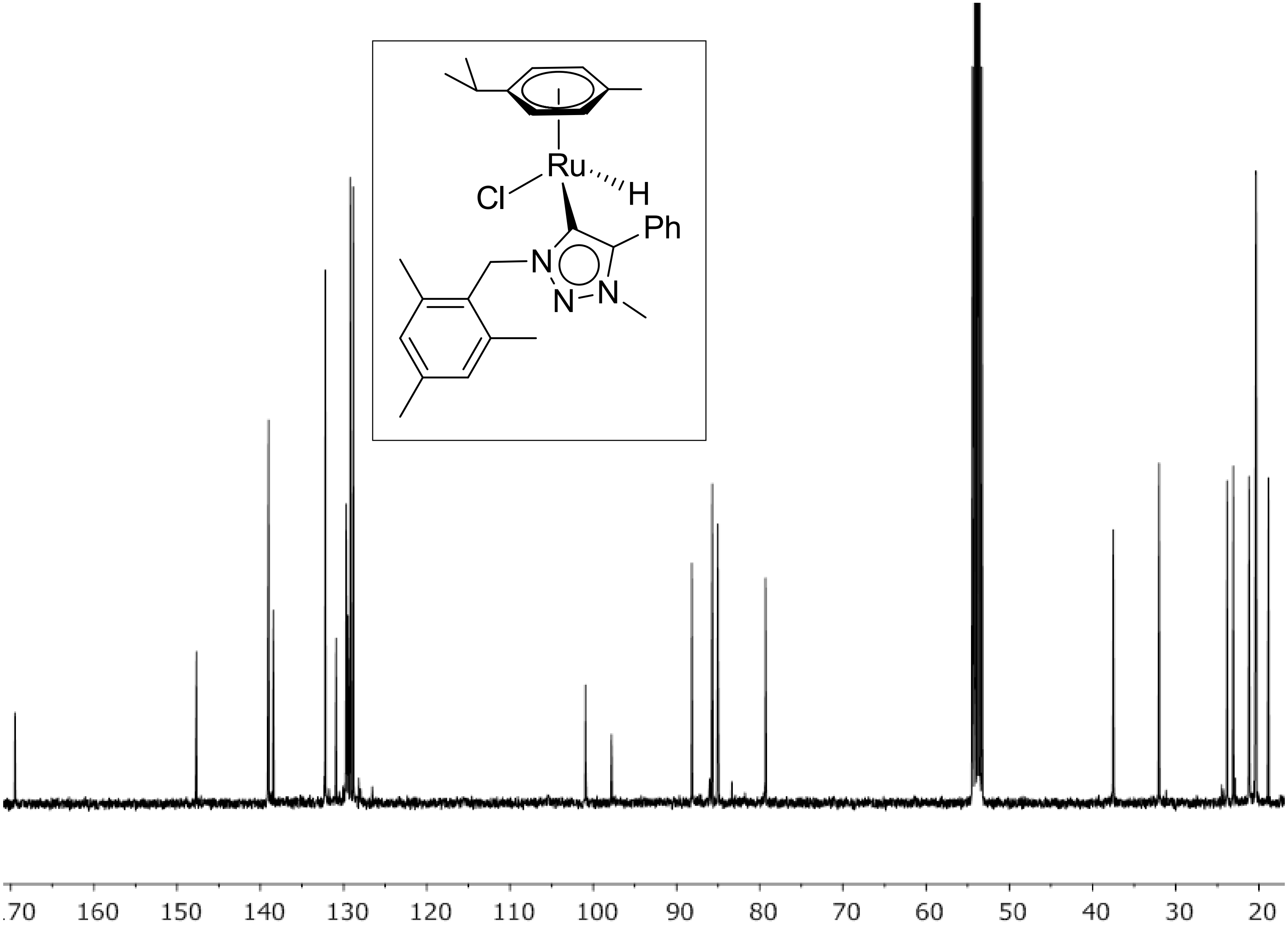


Figure S23. ^{13}C NMR spectrum of **5b** in CD_2Cl_2 at r.t.

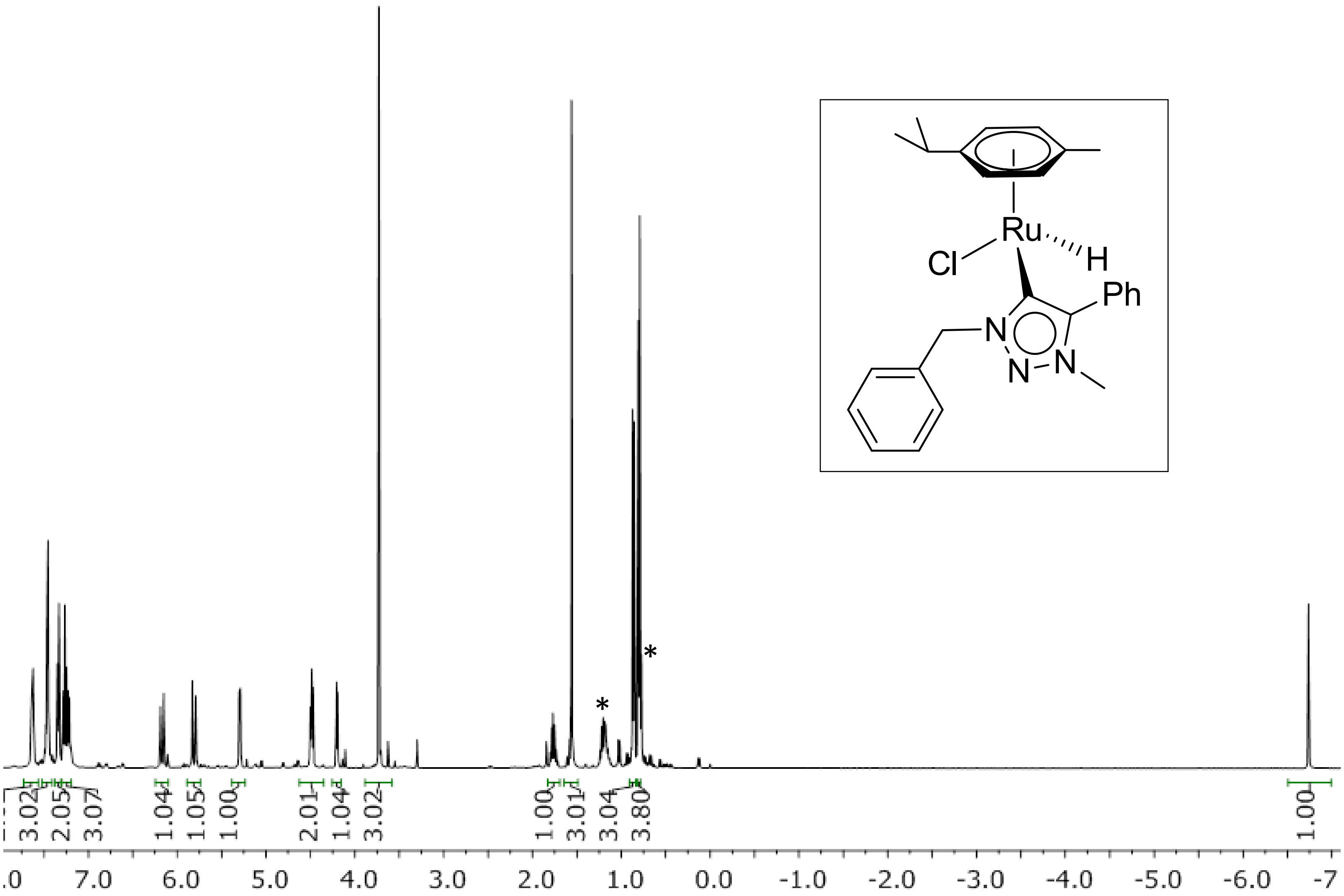


Figure S24. ^{1}H NMR spectrum of **5c** in CD_2Cl_2 at r.t. (* indicated pentane).

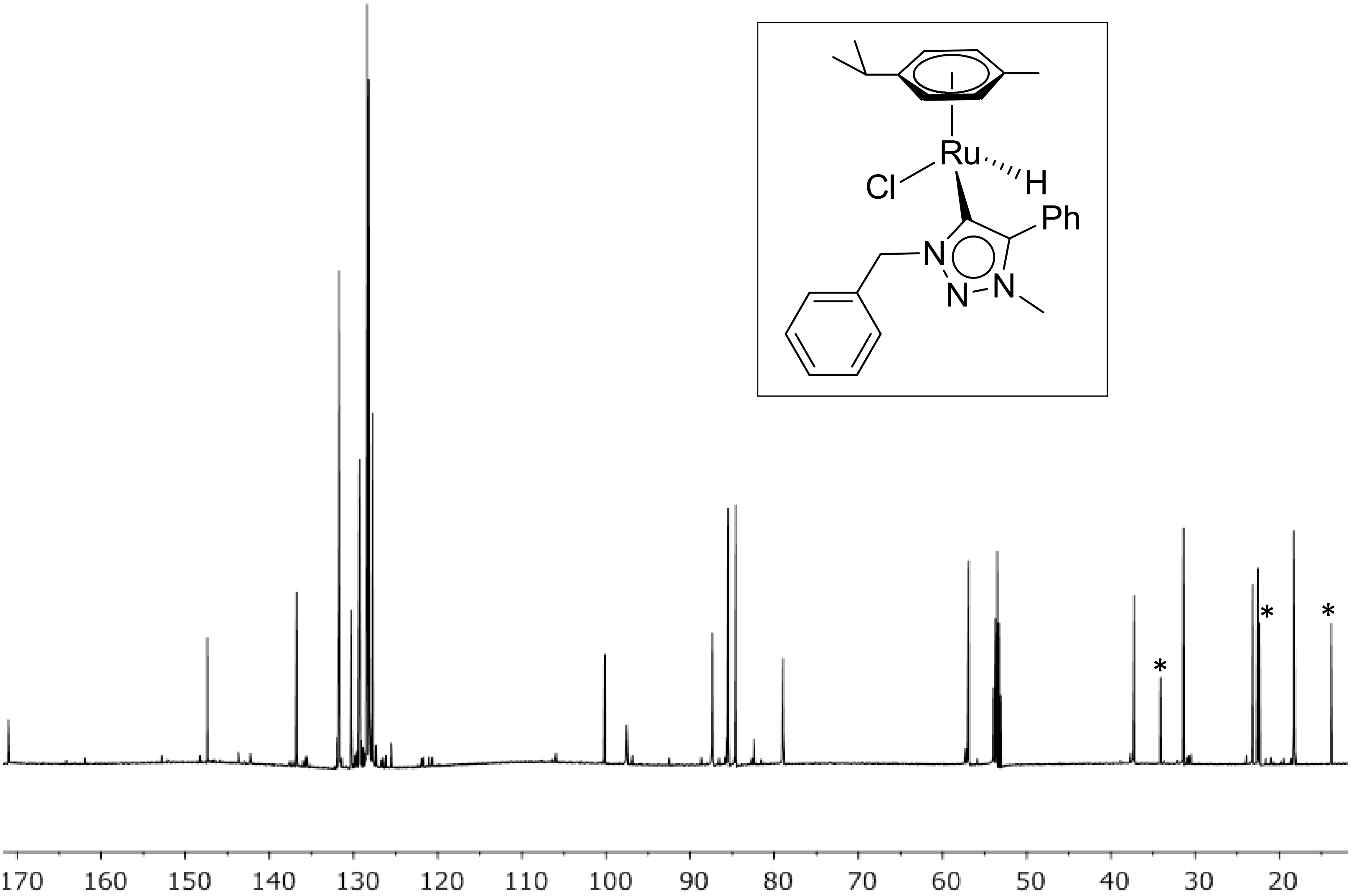


Figure S25. ^{13}C NMR spectrum of **5c** in CD_2Cl_2 at r.t. (* indicated pentane).

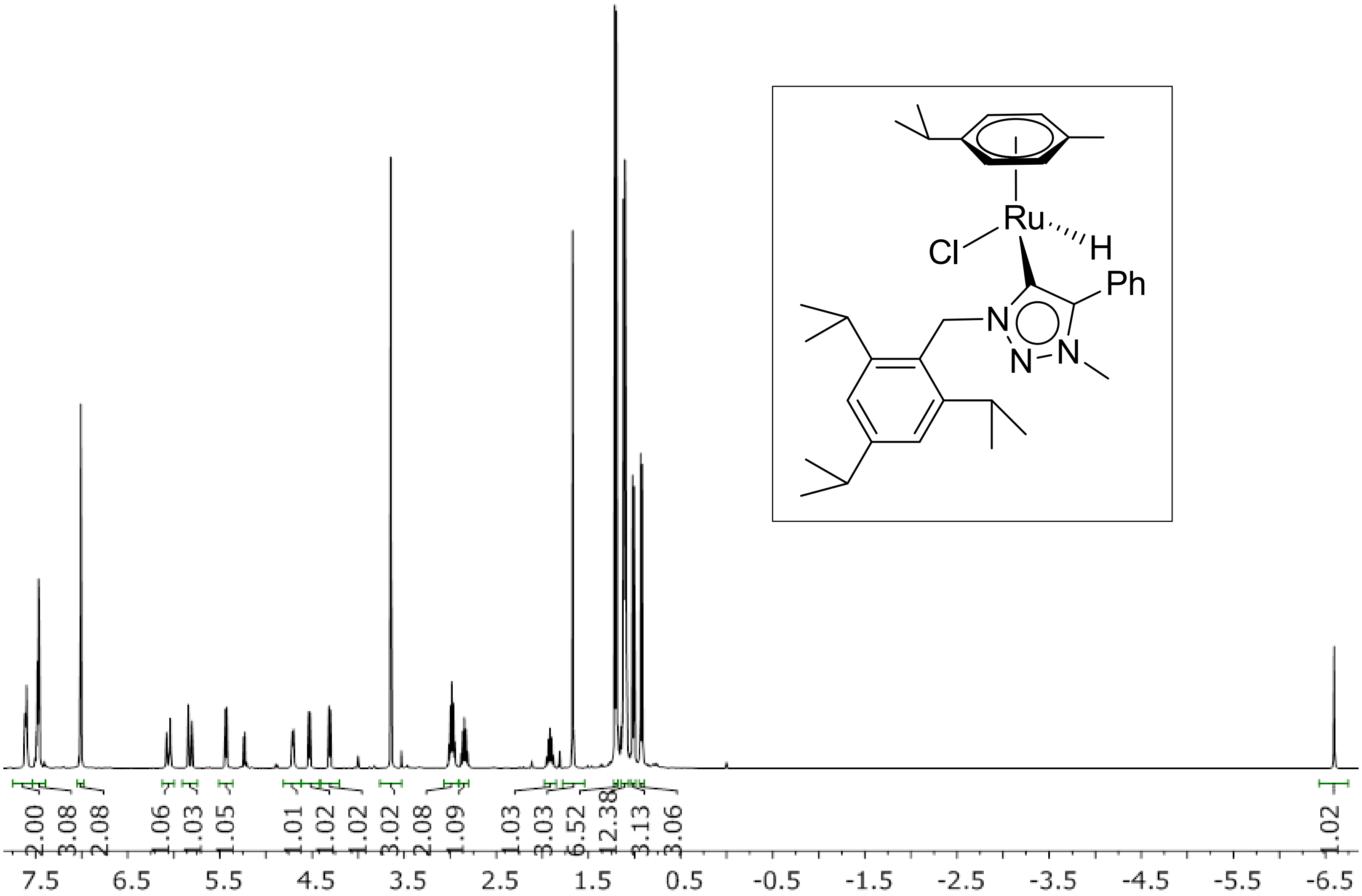


Figure S26. ^{1}H NMR spectrum of **5d** in CD_2Cl_2 at r.t.

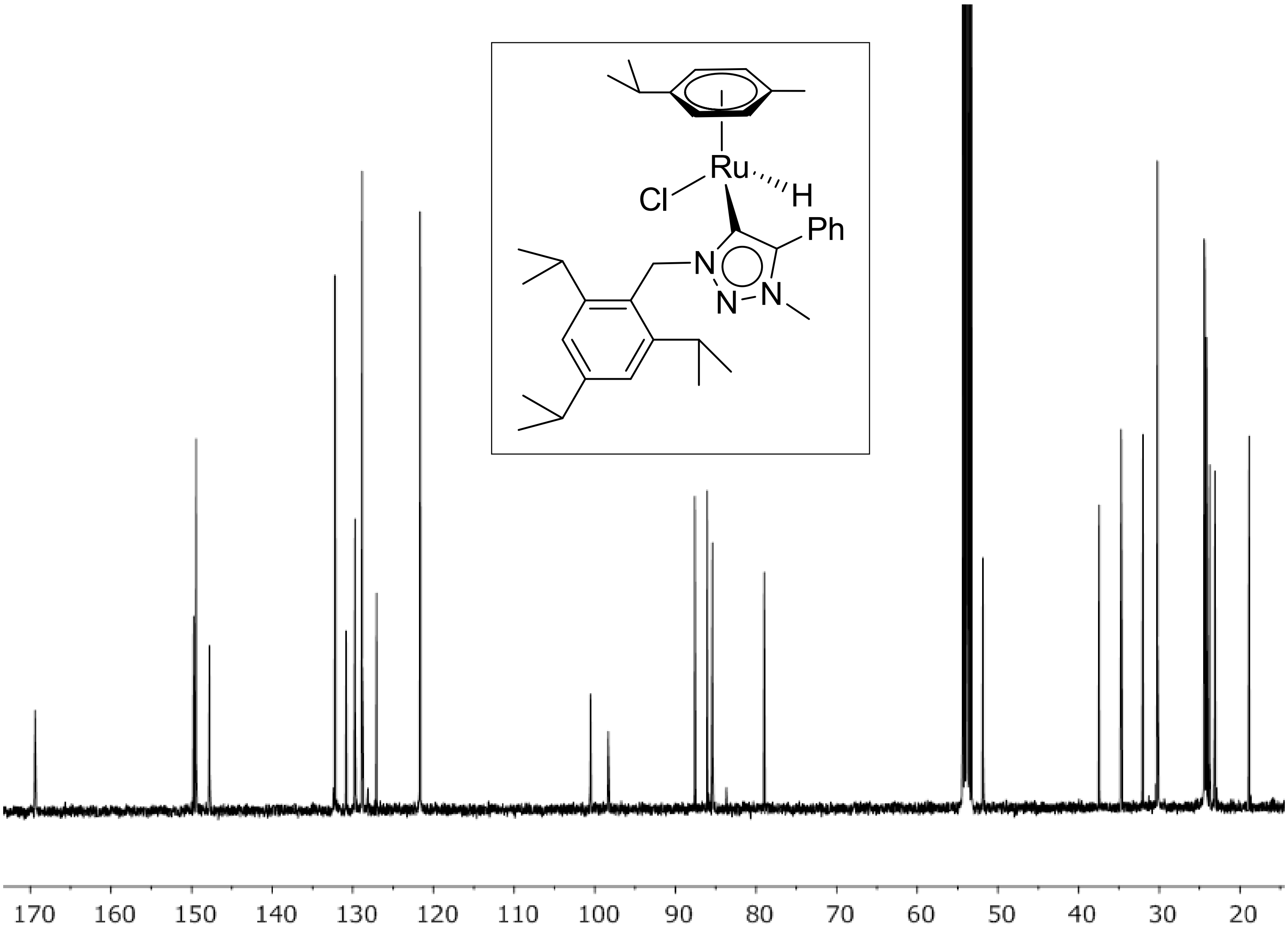


Figure S27. ^{13}C NMR spectrum of **5d** in CD_2Cl_2 at r.t.

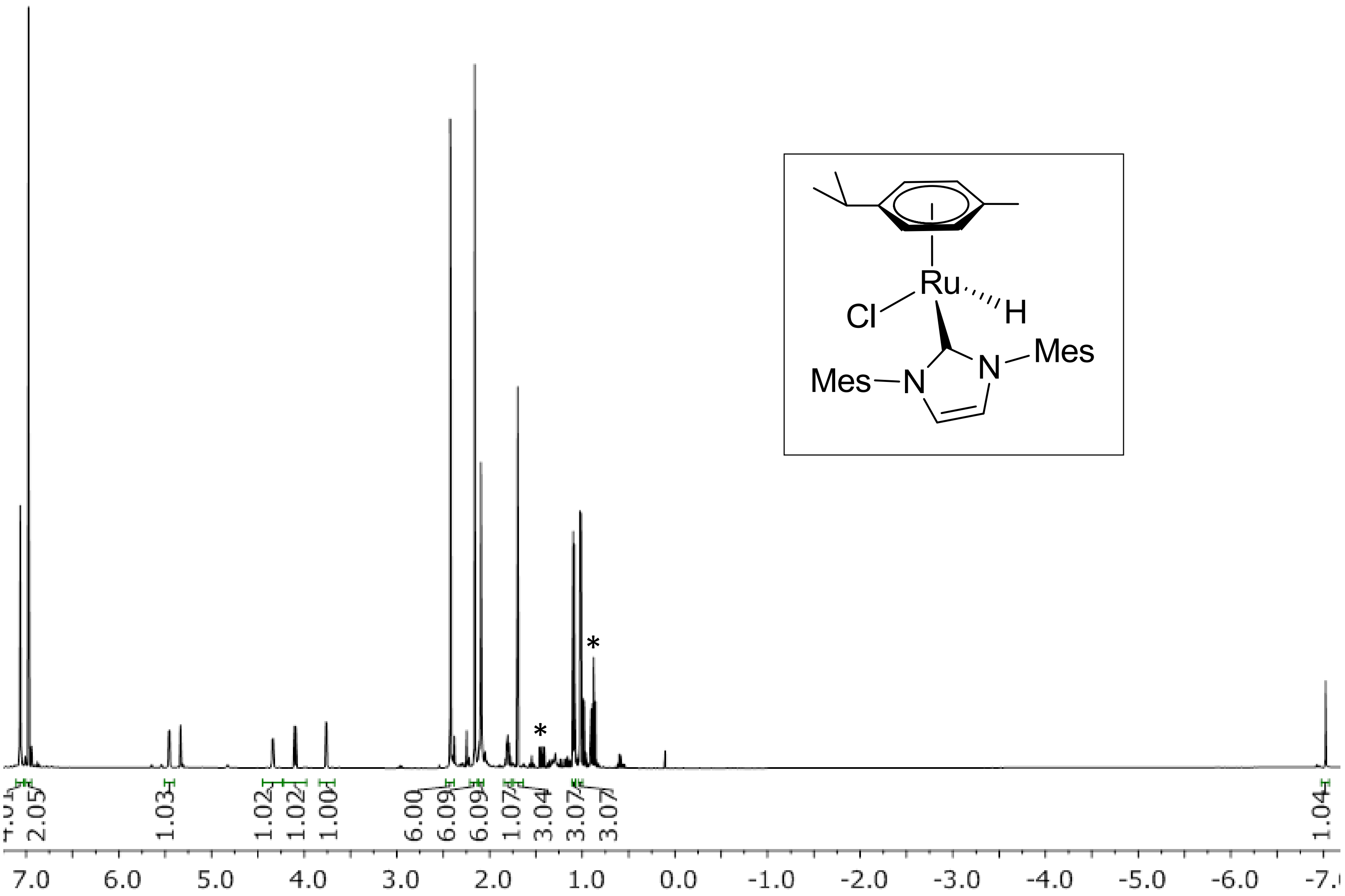


Figure S28. ^{1}H NMR spectrum of **5e** in CD_2Cl_2 at r.t. (* indicates pentane).

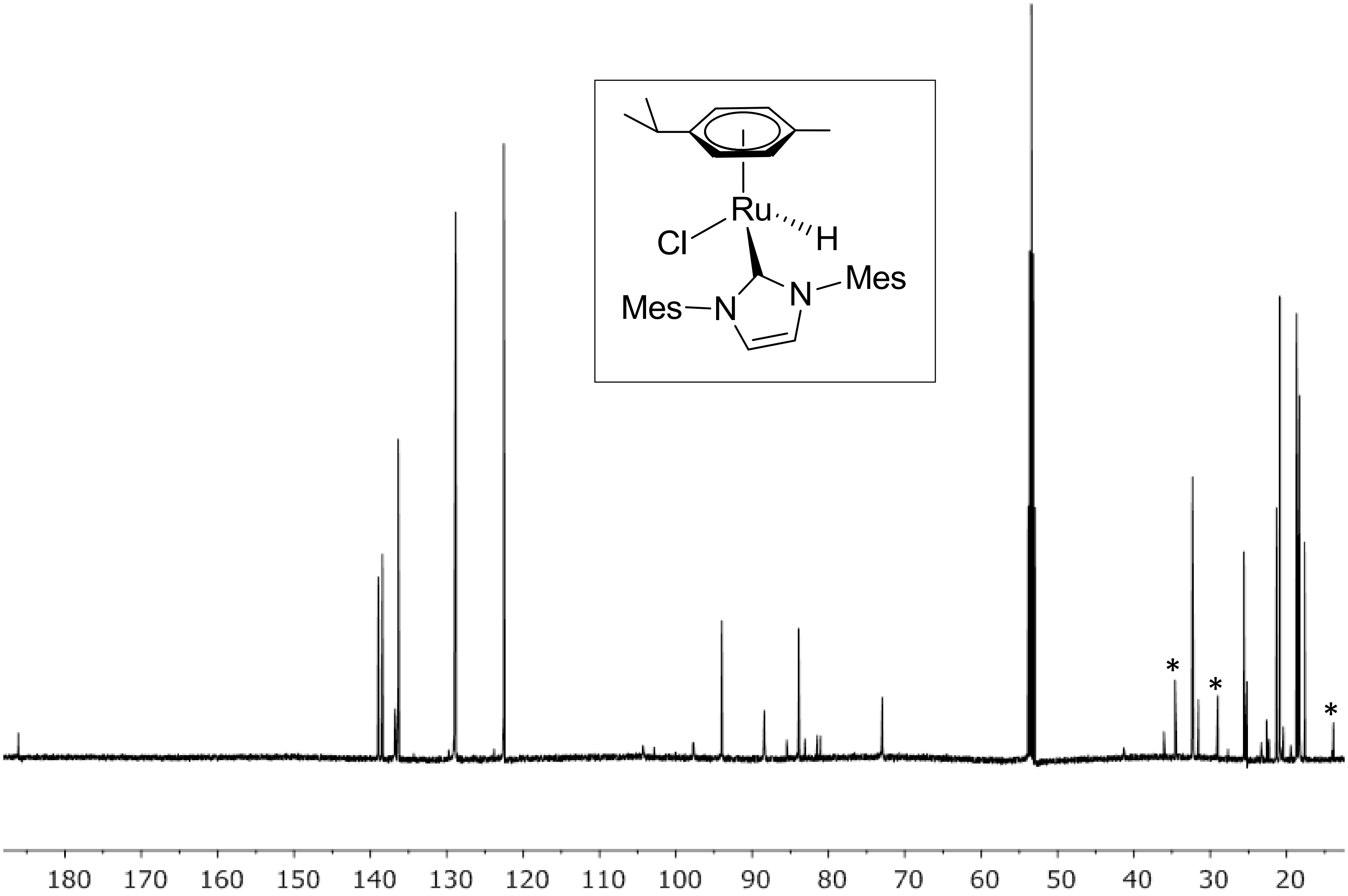


Figure S29. ^{13}C NMR spectrum of **5e** in CD_2Cl_2 at r.t. (* indicates pentane).

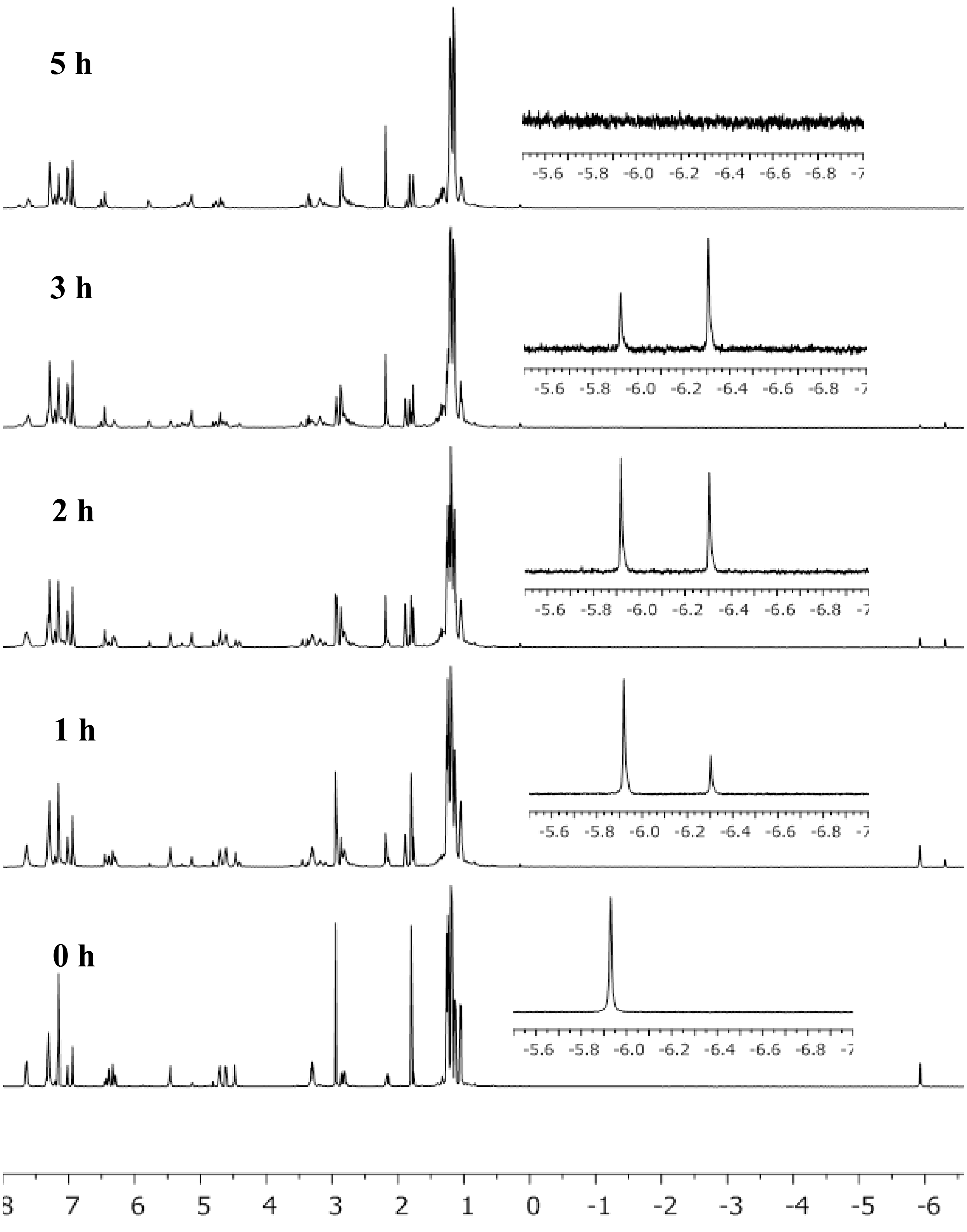


Figure S30. Decomposition of **5d** in C_6D_5Br at 80 °C over time.