

Supporting Information

for

High-Spin Iron (II) Alkynyl Complexes with *N*-Heterocyclic Carbene Ligation: Synthesis, Characterization, and Reactivity Study

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Table S1. Crystal data and summary of data collection and refinement for **1**, and **3-5**.^{a,b}

	1	3	4	5
Temperature, K	143(2)	140(2)	140(2)	140(2)
formula	C ₃₄ H ₅₈ FeN ₄	C ₃₆ H ₆₁ FeN ₅ Si	C ₂₄ H ₅₄ FeP ₄	C ₄₃ H ₇₄ FeN ₆
fw	578.69	647.83	522.40	730.93
crystal system	Hexagonal	Orthorhombic	Monoclinic	Monoclinic
space group	<i>R</i> 3	<i>Pbca</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> , Å	27.826(3)	18.8526(14)	15.0186(14)	22.574(2)
<i>b</i> , Å	27.826(3)	19.5760(15)	10.5172(10)	9.7981(9)
<i>c</i> , Å	13.4682(14)	20.9753(16)	20.224(19)	20.4582(18)
α , deg	90	90	90	90
β , deg	90	90	105.155(2)	96.290(2)
γ , deg	120	90	90	90
<i>V</i> , Å ³	9030.9(17)	7741.1(10)	3083.5(5)	4497.8(7)
<i>Z</i>	9	8	4	4
<i>d</i> _{calcd} , g/cm ³	0.958	1.112	1.125	1.079
2 θ range, deg	3.46 to 61.02	3.57-61.09	2.80-61.16	1.81-61.06
GOF (<i>F</i> ²)	1.023	1.017	1.032	1.024
<i>R</i> 1 ^b	0.0563, ^d 0.0799 ^e	0.0520, ^d 0.0974 ^e	0.0360, ^d 0.0543 ^e	0.0428, ^d 0.0684 ^e
<i>wR</i> 2 ^c	0.1294, ^d 0.1386 ^e	0.1322, ^d 0.1618 ^e	0.0951, ^d 0.1073 ^e	0.1098, ^d 0.1240 ^e

^a Collected using Mo K α radiation ($\lambda = 0.71073$ Å). ^b $R1 = \Sigma[(F_o - F_c)] / \Sigma(F_o)$. ^c $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. ^d $I > 2\sigma(I)$. ^e All data.

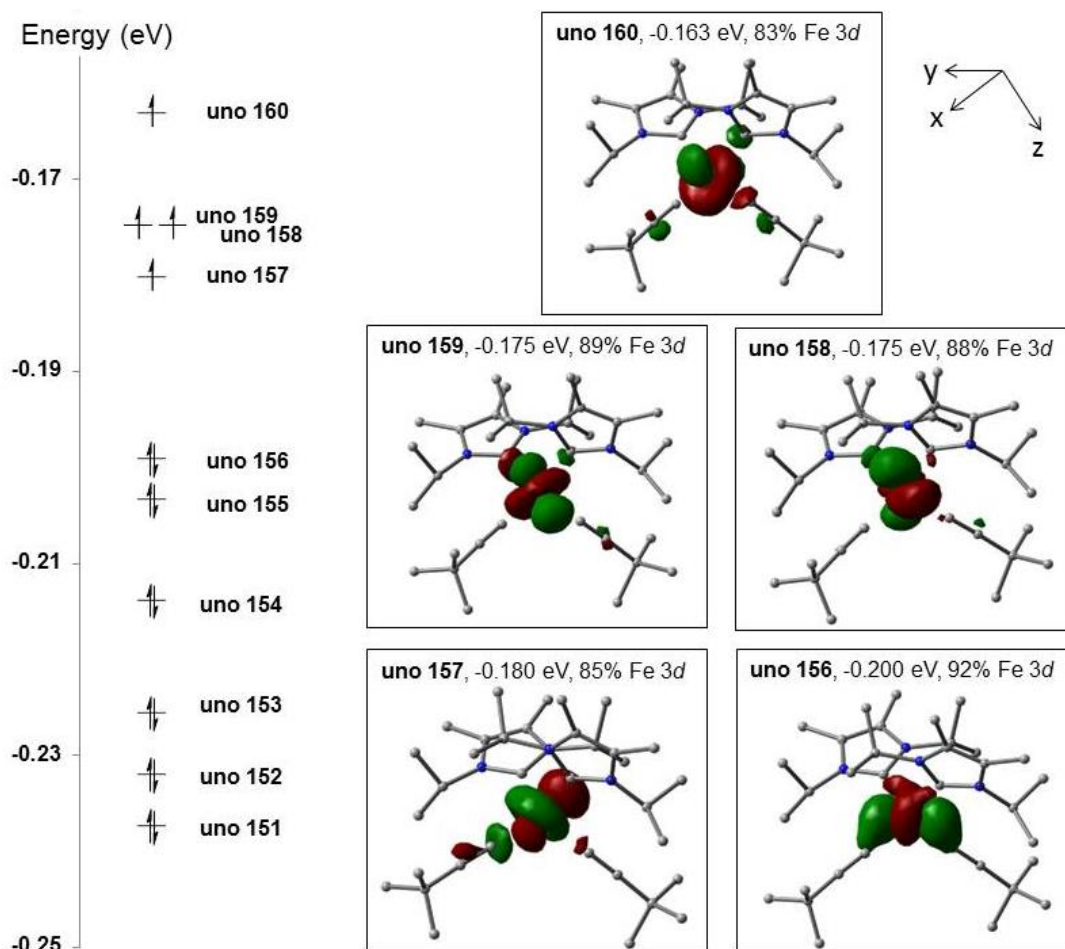
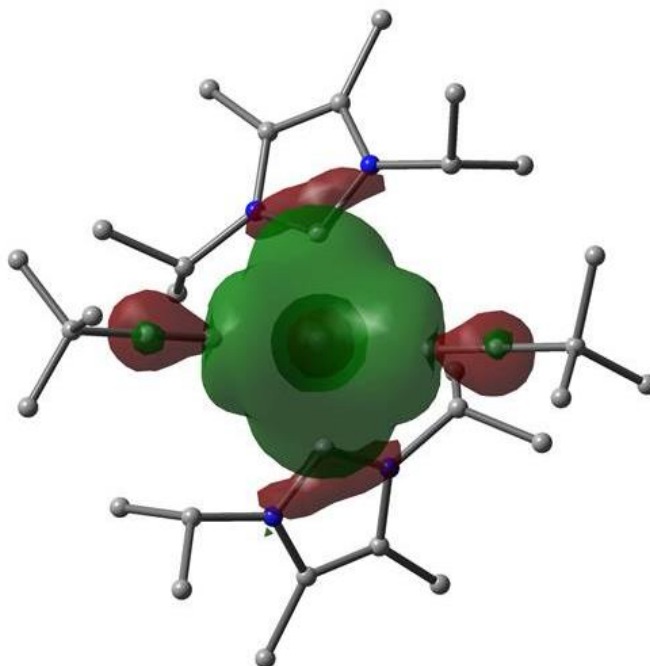


Figure S1. Frontier UNO energy level diagram for (IPr₂Me₂)₂Fe(C≡CBu')₂ (*S* = 2) and selected UNO plots.

uno 151 (-0.237 eV)



Fe center: 26% Fe 4s

Alkynyl A: 4% C 2p + 10% C 2p

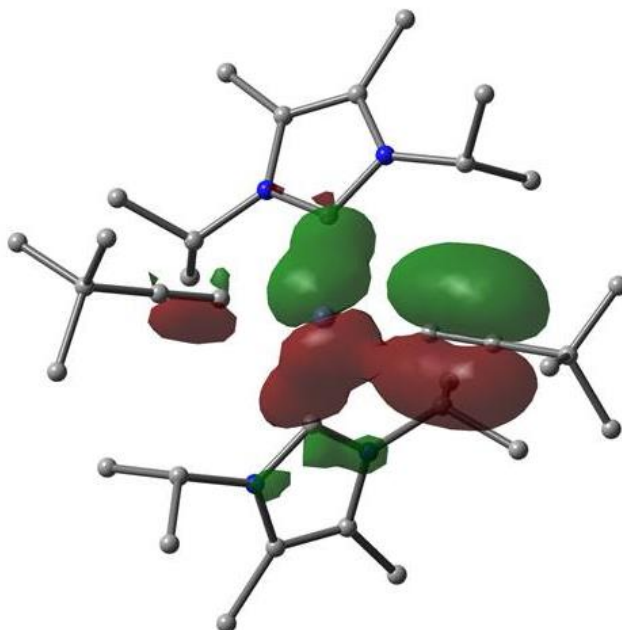
Carbene A: 4% C 2s + 11% C 2p

Alkynyl B: 5% C 2p + 12% C 2p

Carbene B: 4% C 2p + 11% C 2p

Figure S2. The UHF natural orbital 151 of $(\text{IPr}_2\text{Me}_2)_2\text{Fe}(\text{C}\equiv\text{CBu}^t)_2$ ($S = 2$), depicted using isodensity at 0.03 au.

uno 146 (-0.306 eV)



Fe center: 54% Fe 4p

Alkynyl A: 15% C 2p + 15% C 2p

Alkynyl B: 1% C 2p + 1% C 2p

Figure S3. The UHF natural orbital 146 of $(\text{IPr}_2\text{Me}_2)_2\text{Fe}(\text{C}\equiv\text{CBu}^t)_2$ ($S = 2$), depicted using isodensity at 0.03 au.

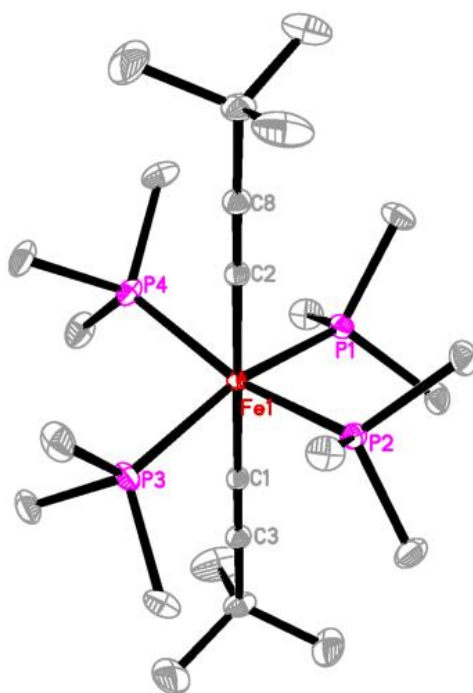


Figure S4. Molecular structure of **4**, showing 30% probability ellipsoilds and the partial atom numbering scheme. Selected bond distances (Å) and angles (deg): Fe(1)-C(1) 1.9495(16), Fe(1)-C(2) 1.9420(16), Fe(1)-P(1) 2.2197(5), Fe(1)-P(2) 2.2274(5), Fe(1)-P(3) 2.2320(5), Fe(1)-P(4) 2.2262(5). C(1)-C(3) 1.222(2), C(2)-C(8) 1.223(2).

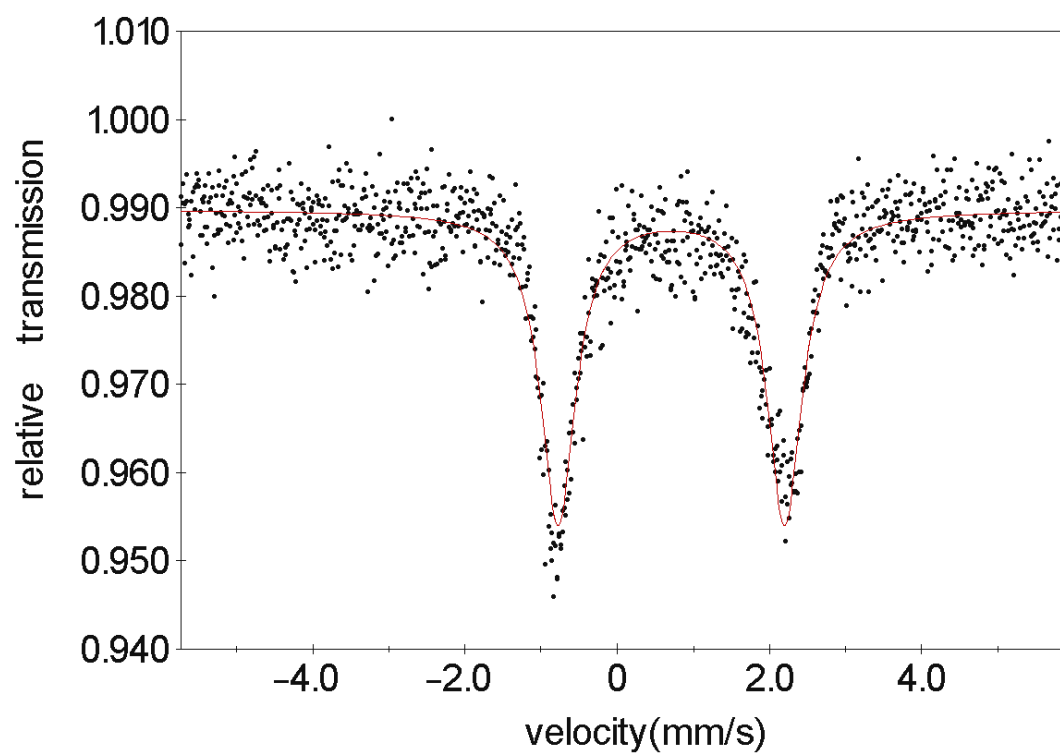


Figure S5. The zero-field ^{57}Fe Mössbauer spectrum of $(\text{IPr}_2\text{Me}_2)_2\text{FeI}_2$ recorded at 80 K.

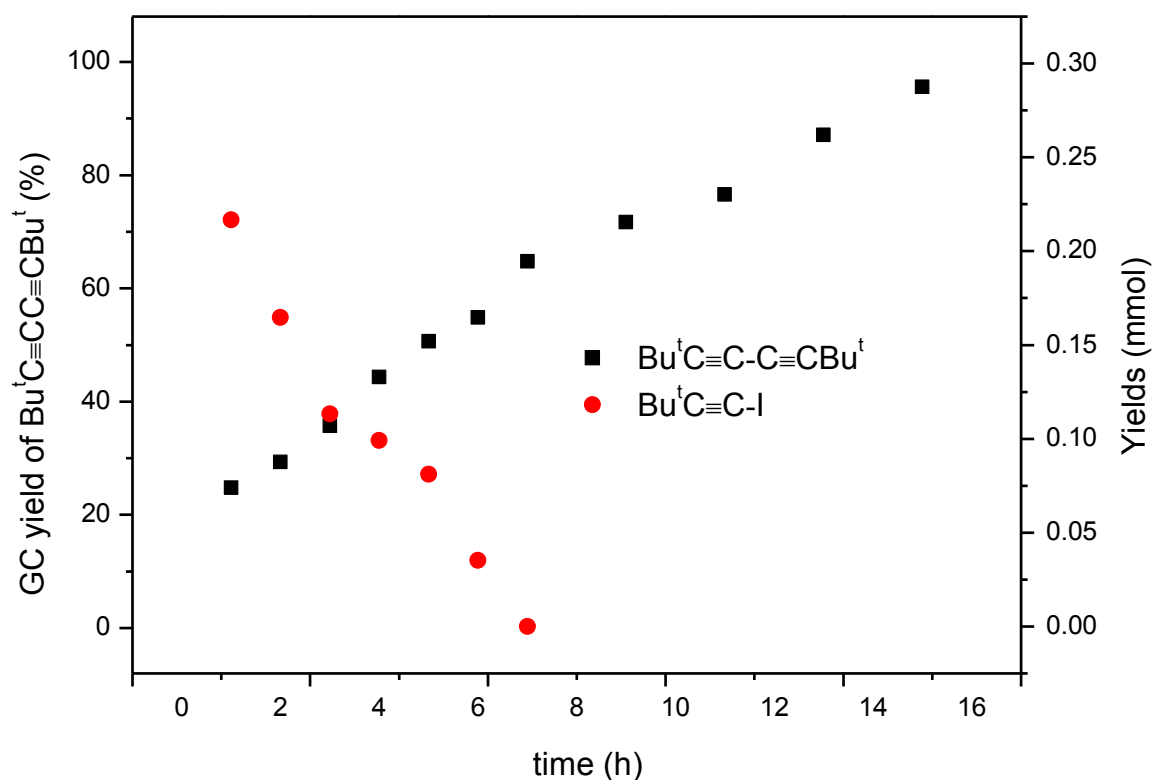


Figure S6. GC-Yields of organic products versus time for the reaction of **1** (0.30 mmol) with I_2 (0.30 mmol) in THF (2 mL).

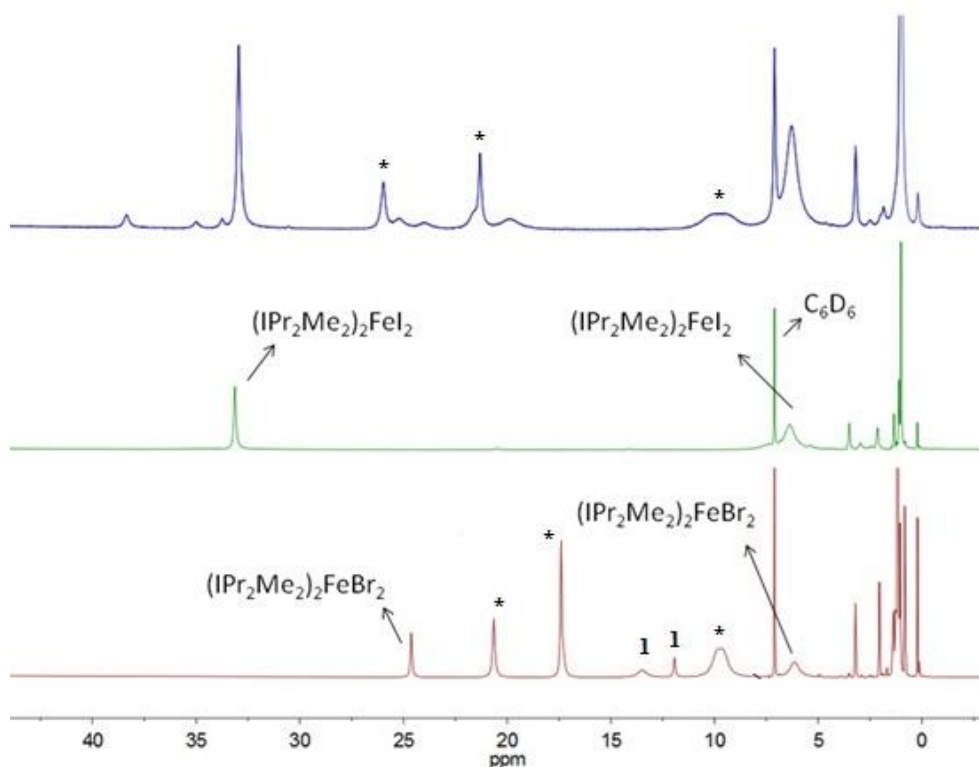


Figure S7. ^1H NMR spectra of the reaction of **1** (0.04 mmol) with I_2 (1 equiv.) in C_6D_6 (0.4 mL) after 10 min (upper), after 6 h (middle), and the reaction of **1** (0.04 mmol) with $n\text{-C}_8\text{H}_{17}\text{Br}$ (1 equiv.) in C_6D_6 (0.4 mL) after 43 h (bottom). Peaks labeled with stars are signals of the intermediates, presumably $(\text{IPr}_2\text{Me}_2)_2\text{Fe}(\text{C}\equiv\text{CBu}^t)\text{X}$ ($\text{X} = \text{I}$ or Br).

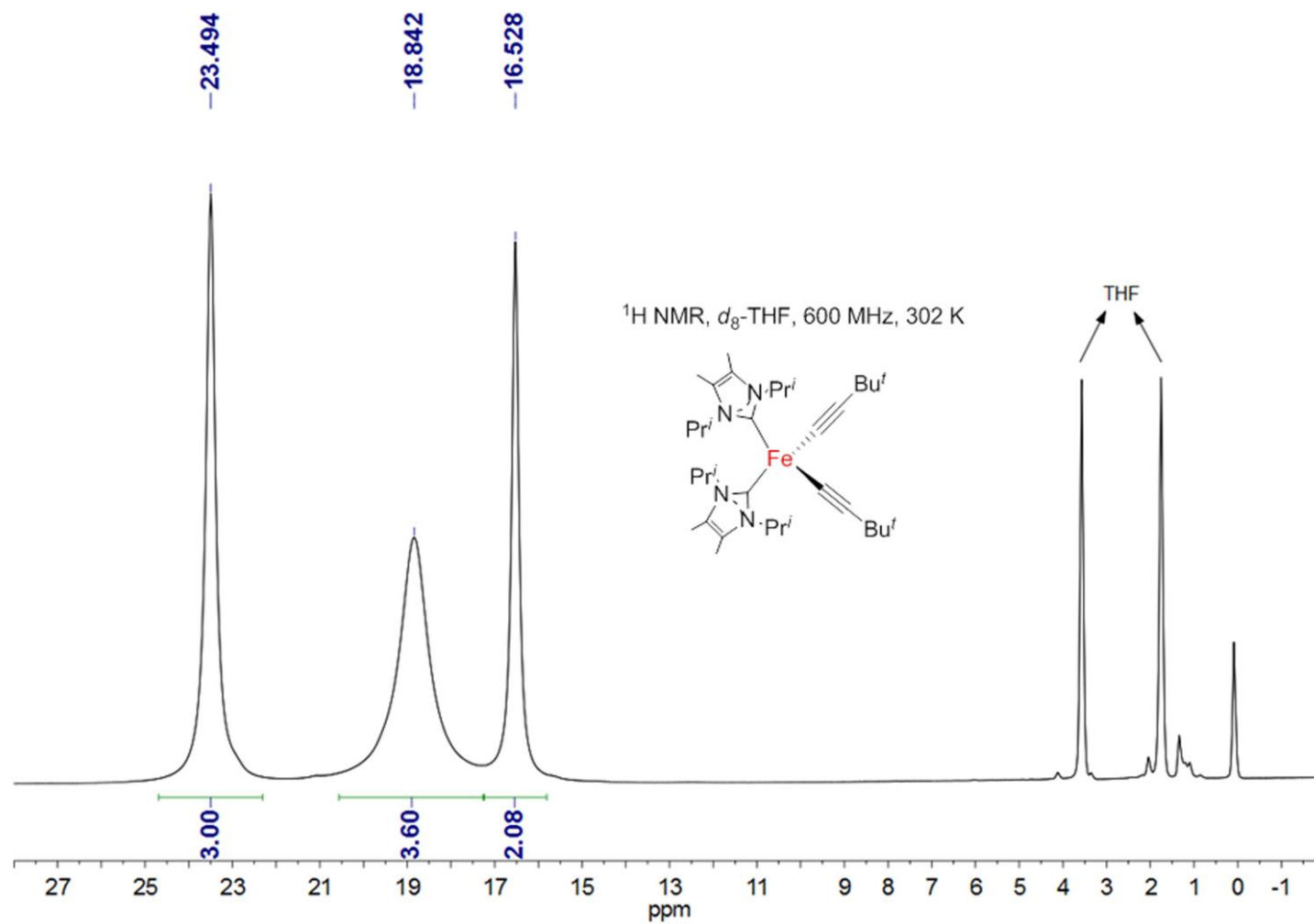


Figure S8. ¹H NMR spectrum of [(IPr₂Me₂)₂Fe(C≡CBu^t)₂] (**1**) in THF-*d*₈.

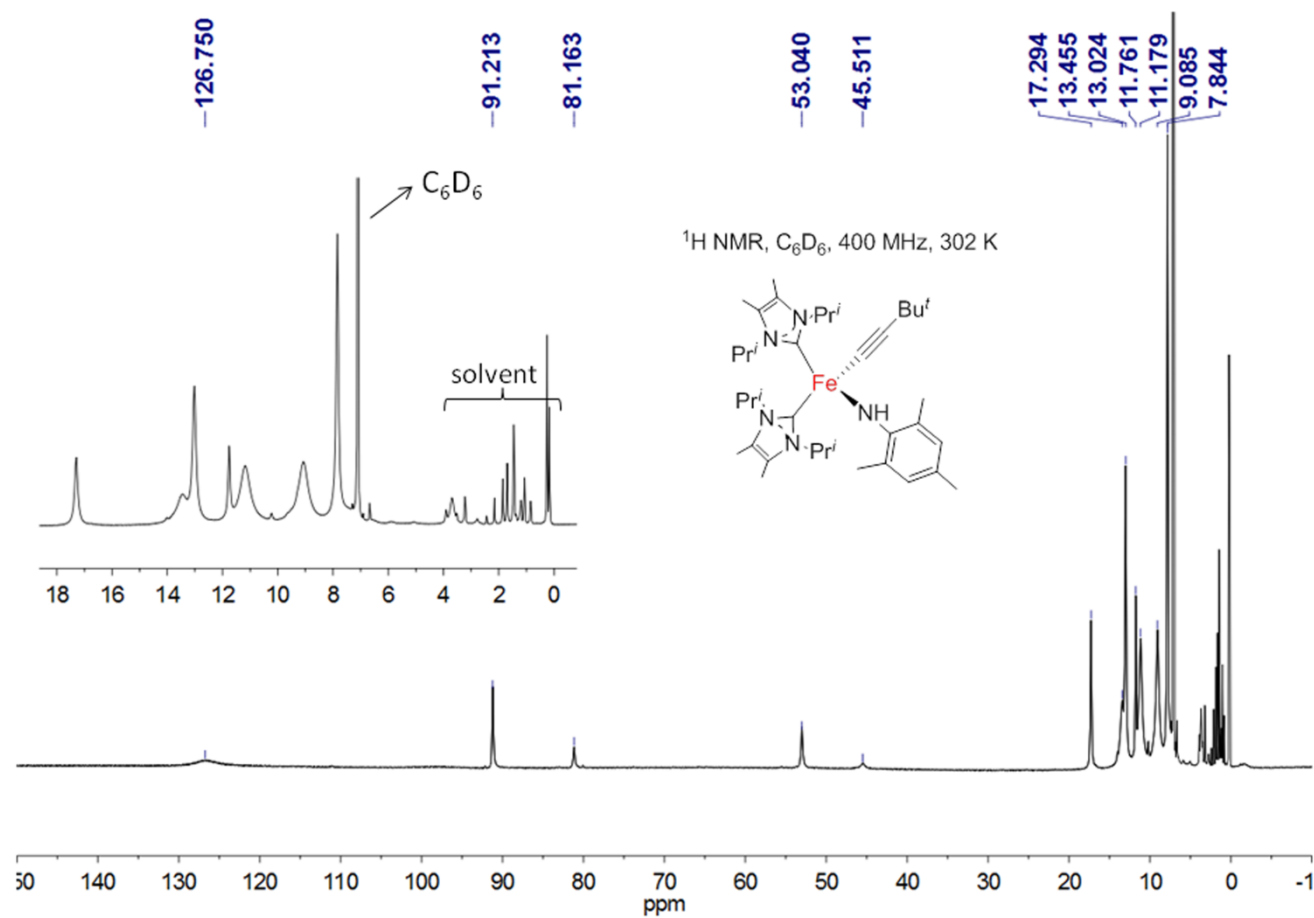


Figure S9. ¹H NMR spectrum of [(IPr₂Me₂)₂Fe(C≡CBu^t)(NHMe_s)] (2) in C₆D₆.

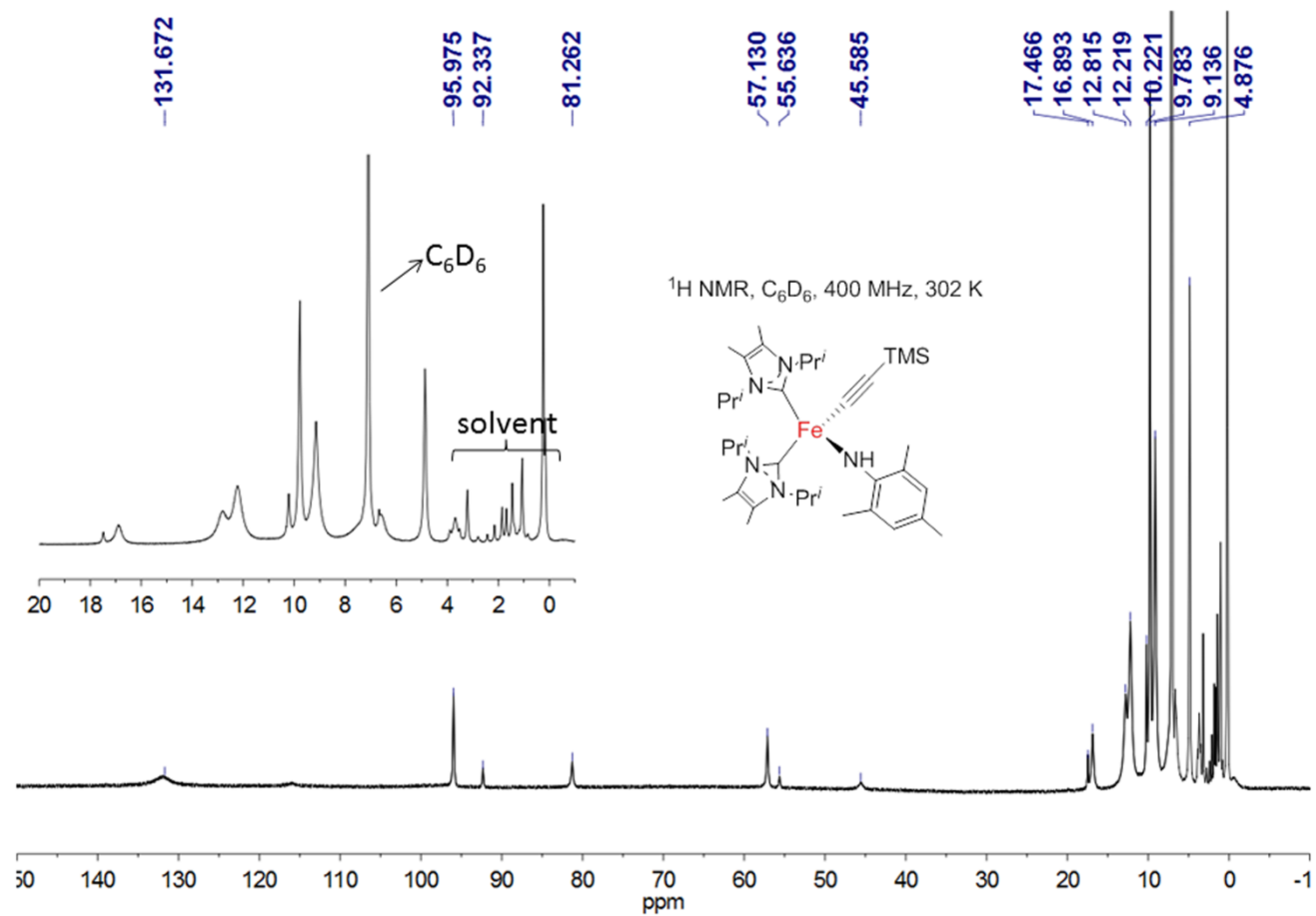


Figure S10. ¹H NMR spectrum of [(IPr₂Me₂)₂Fe(C≡CTMS)(NHMe)] (3) in C₆D₆.

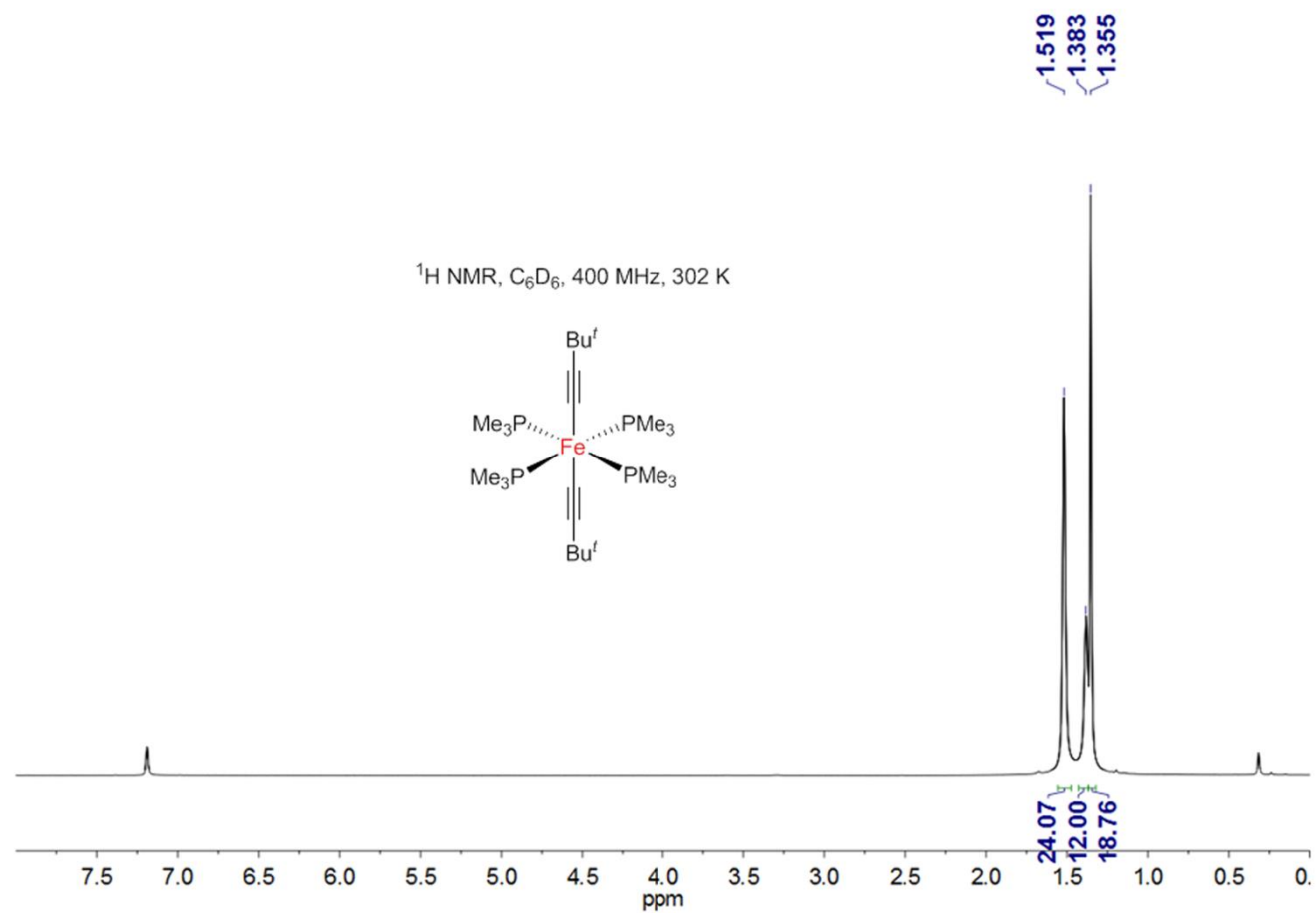


Figure S11. ^1H NMR spectrum of $[(\text{PMe}_3)_4\text{Fe}(\text{C}\equiv\text{CBu}^t)_2]$ (**4**) in C_6D_6 .

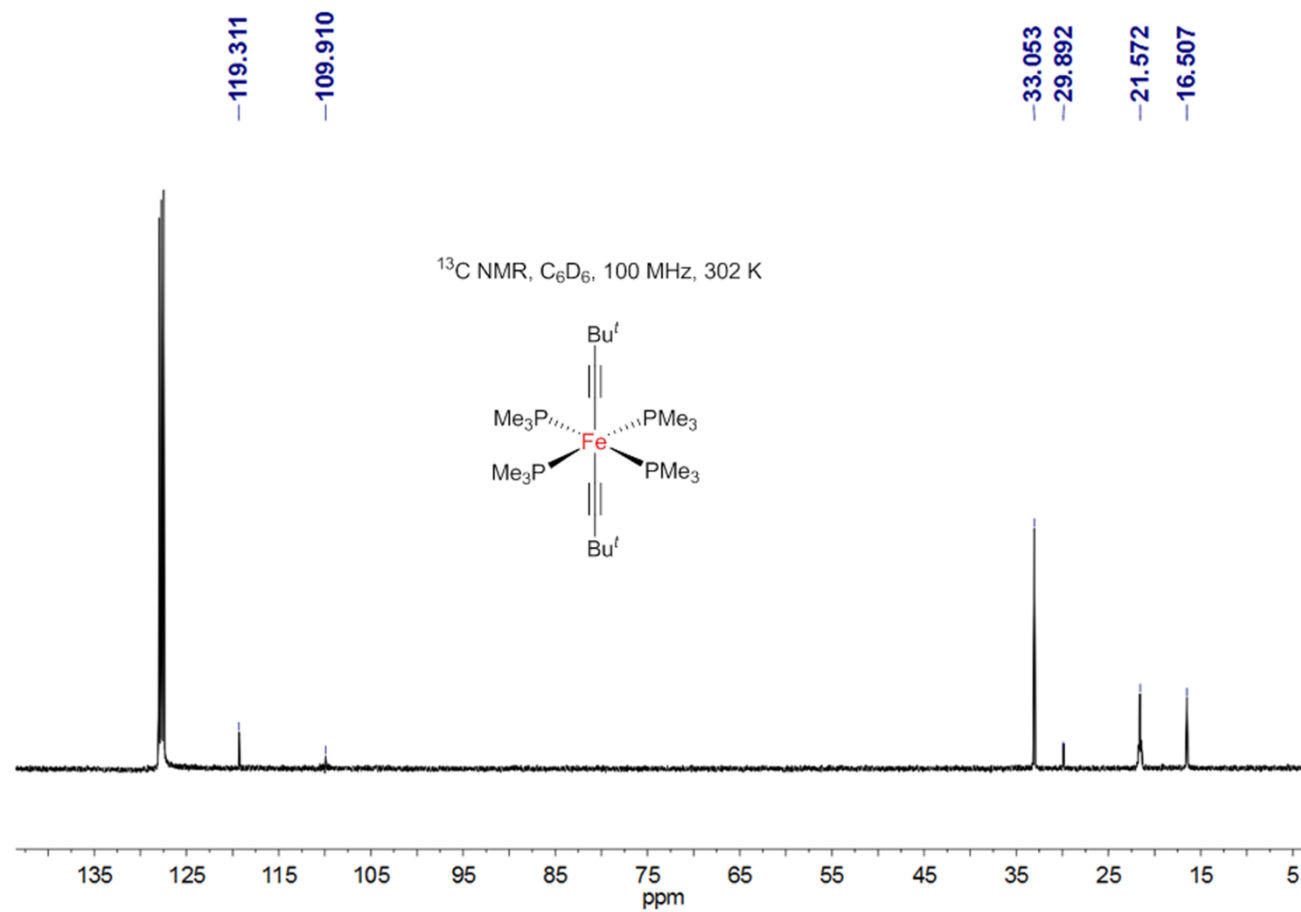


Figure S12. ^{13}C NMR spectrum of $[(\text{PMe}_3)_4\text{Fe}(\text{C}\equiv\text{CBu}^t)_2]$ (4) in C_6D_6 .

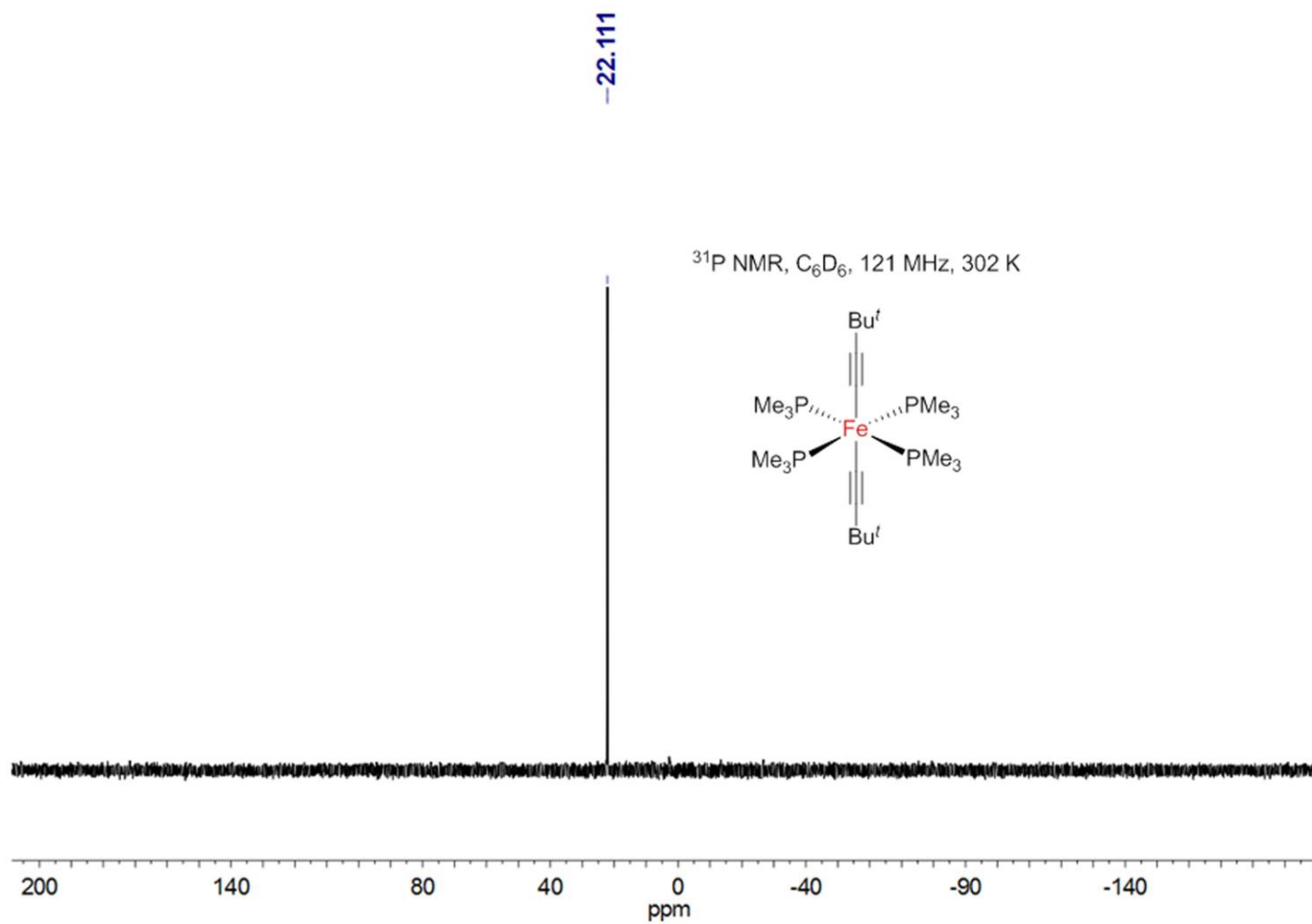


Figure S13. ³¹P NMR spectrum of [(PMe₃)₄Fe(C≡CBu^t)₂] (**4**) in C₆D₆.

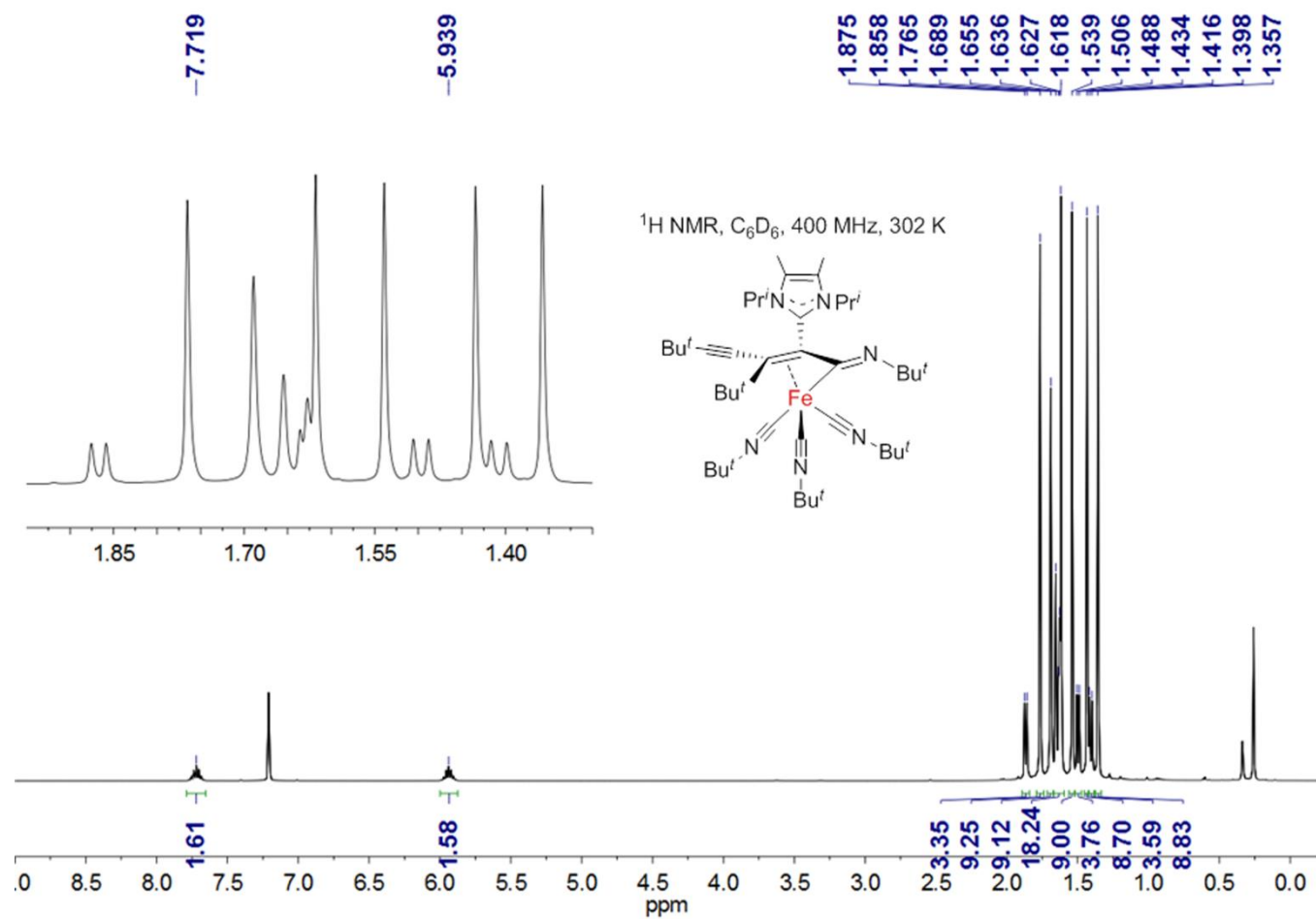


Figure S14. ¹H NMR spectrum of **5** in C₆D₆.

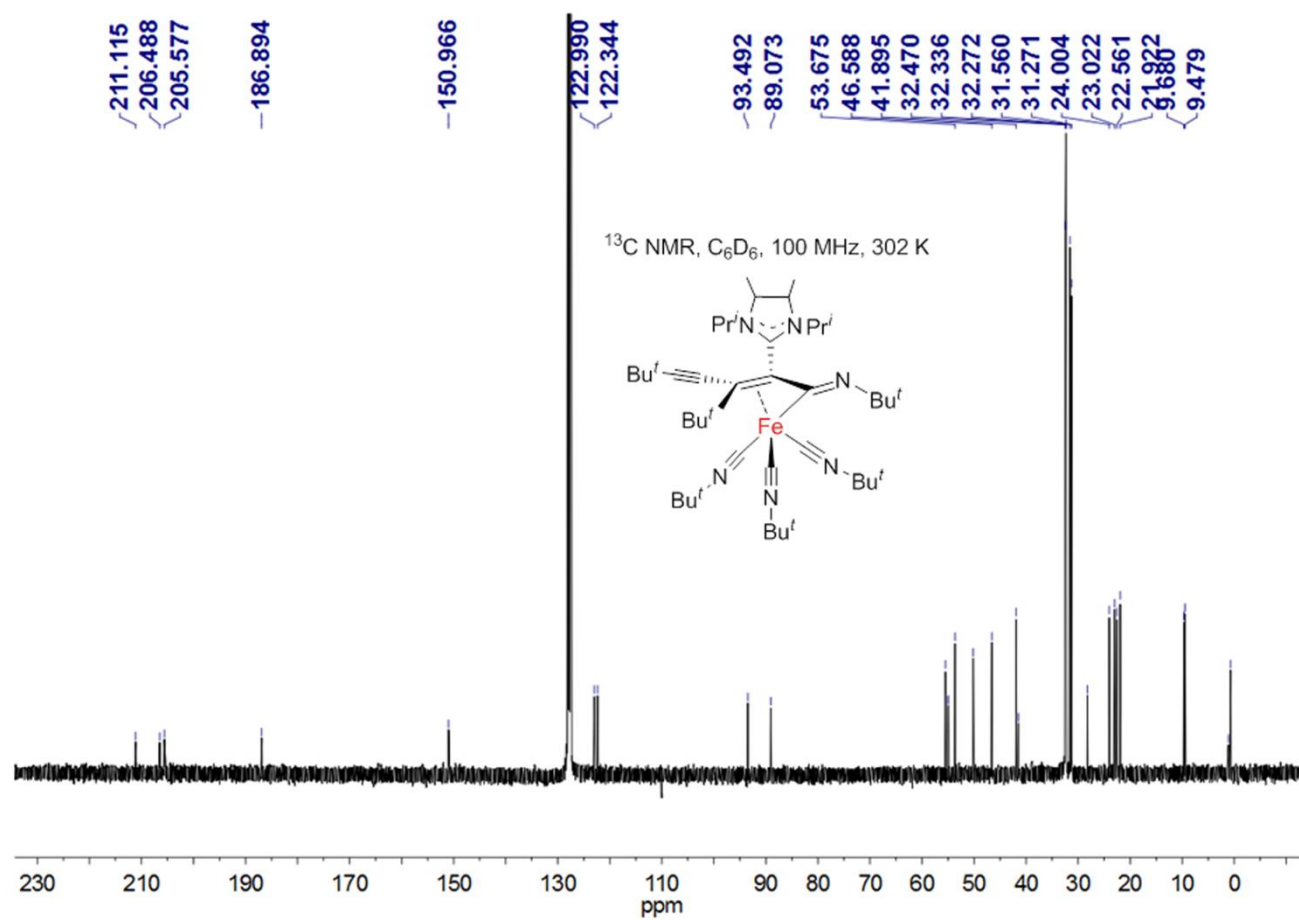


Figure S15. ^{13}C NMR spectrum of 5 in C_6D_6 .

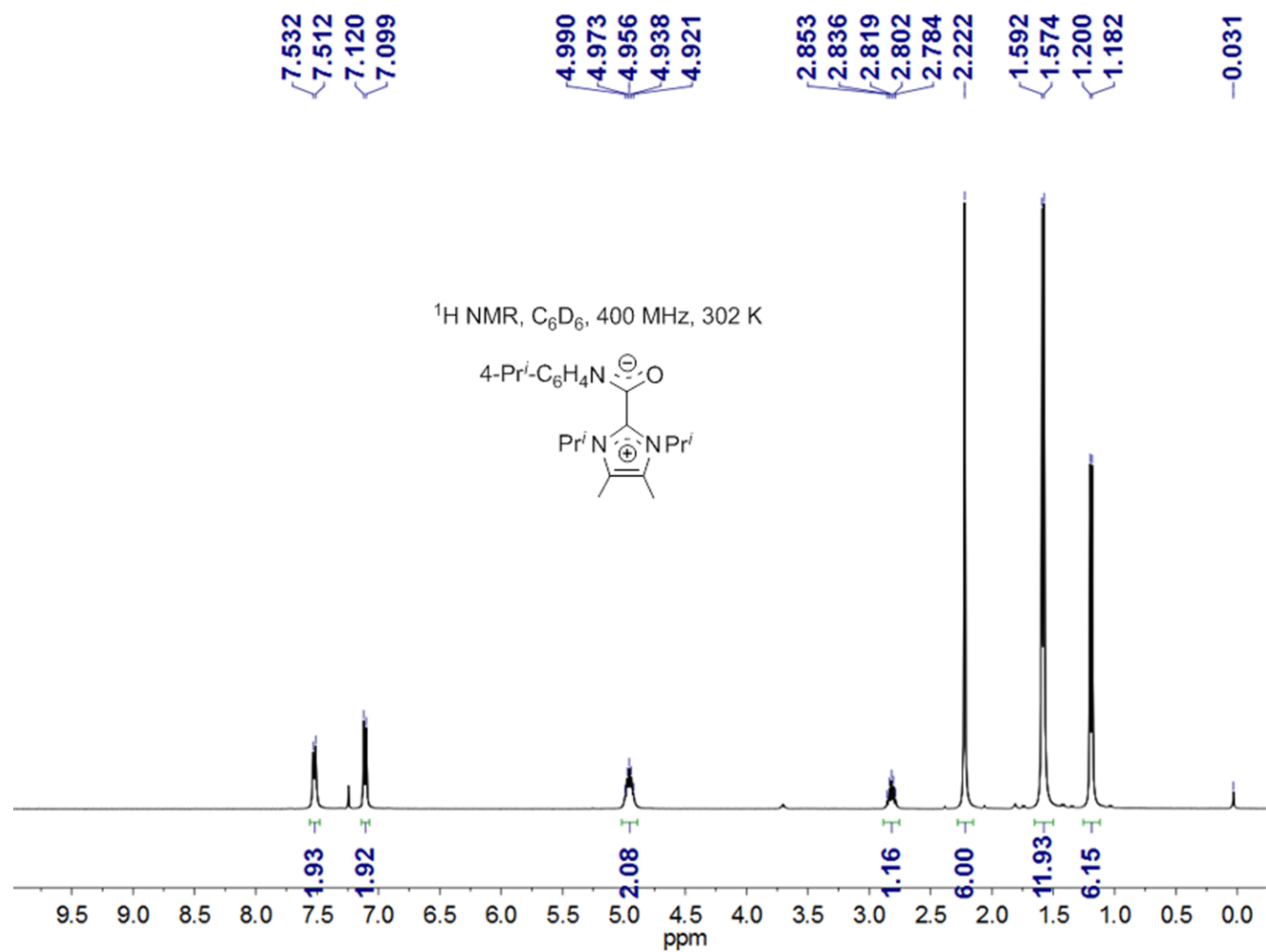


Figure S16. ^1H NMR spectrum of **6** in C_6D_6 .

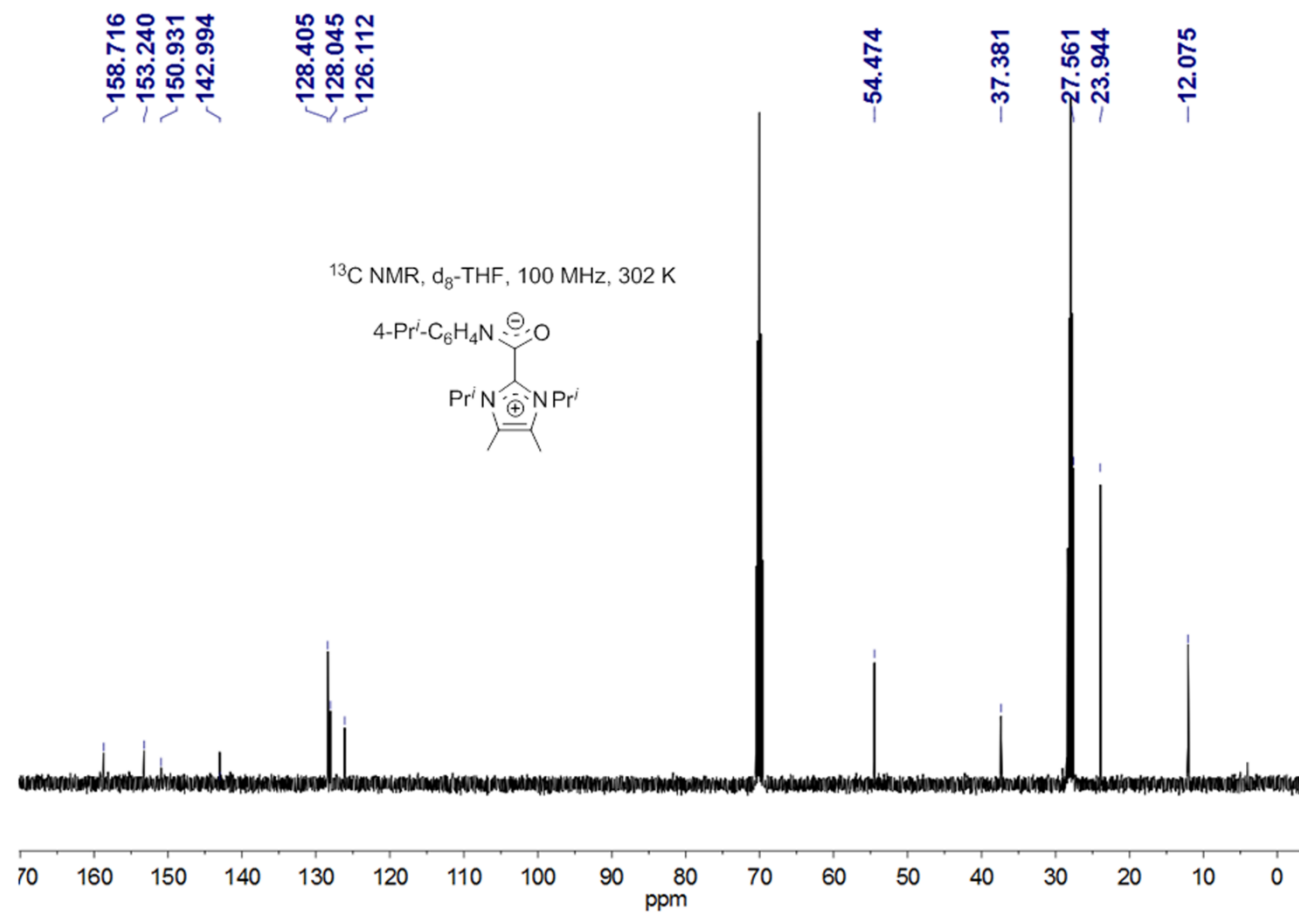


Figure S17. ^{13}C NMR spectrum of **6** in $\text{d}_8\text{-THF}$.

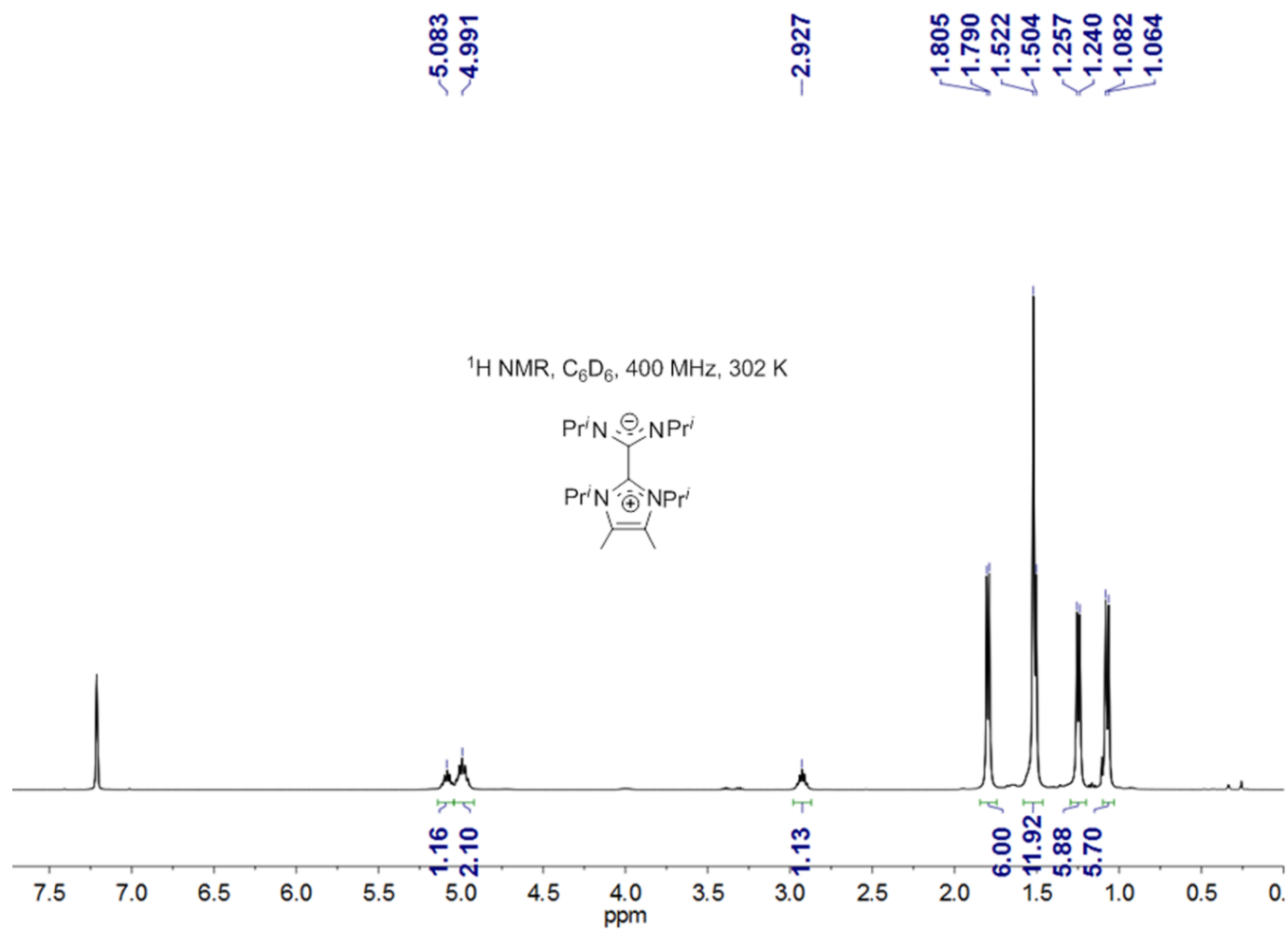


Figure S18. ^1H NMR spectrum of **7** in C_6D_6 .

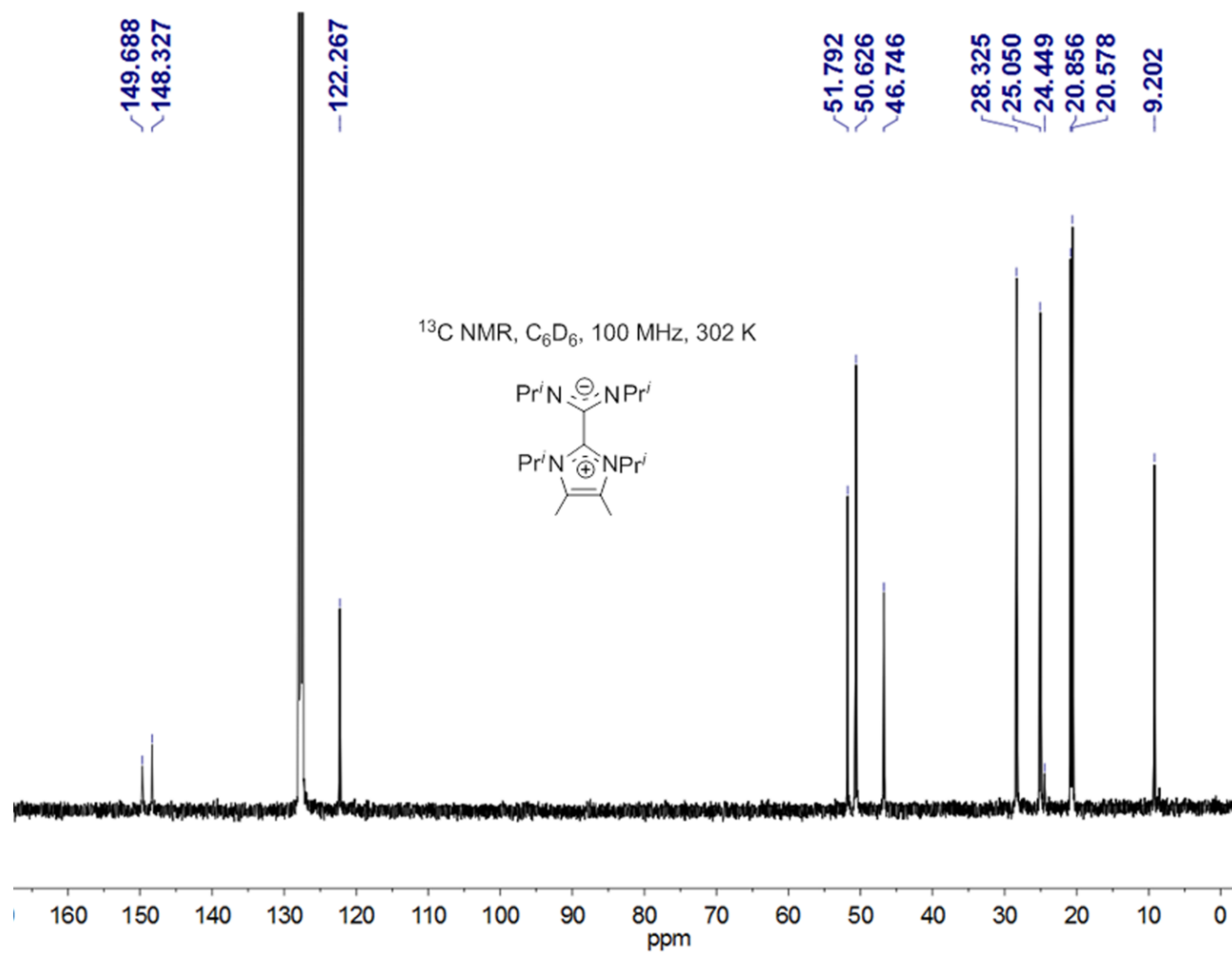


Figure S19. ^{13}C NMR spectrum of 7 in C_6D_6 .

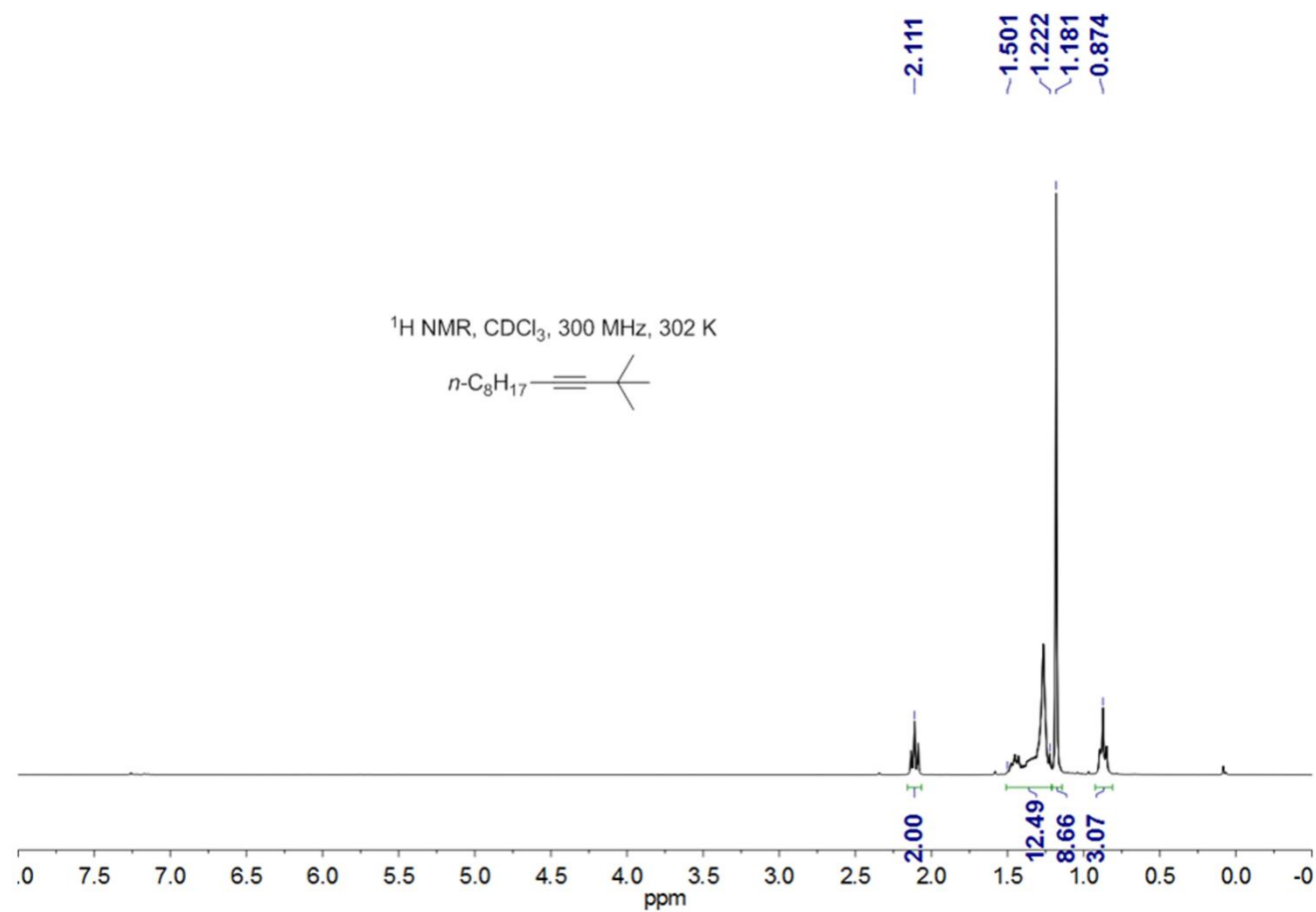


Figure S20. ¹H NMR spectrum of $n\text{-C}_8\text{H}_{17}\text{-C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$ in CDCl₃.

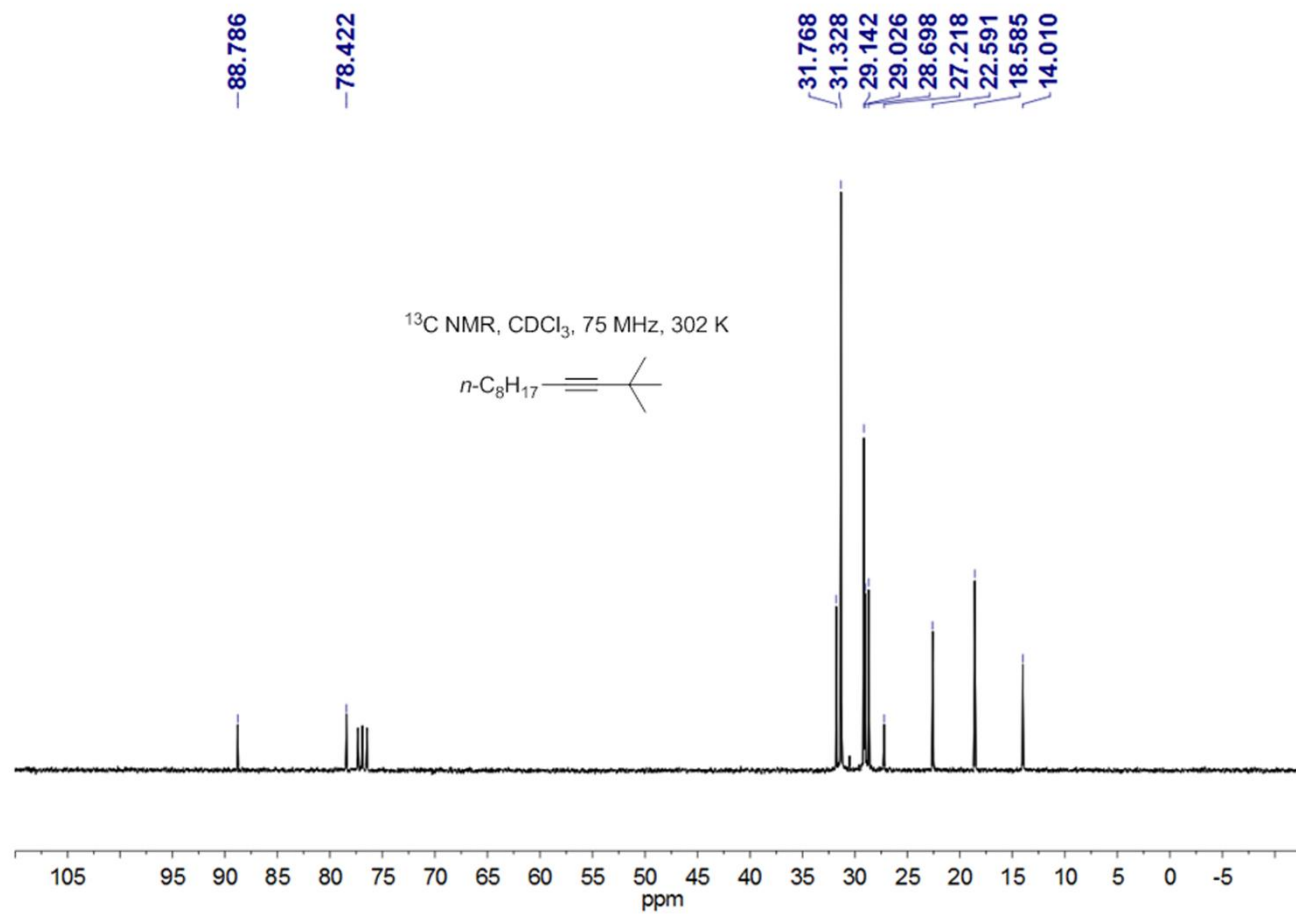


Figure S21. ^{13}C NMR spectrum of $n\text{-C}_8\text{H}_{17}\text{-C}\equiv\text{C}-\text{C}(\text{CH}_3)_3$ in CDCl_3 .

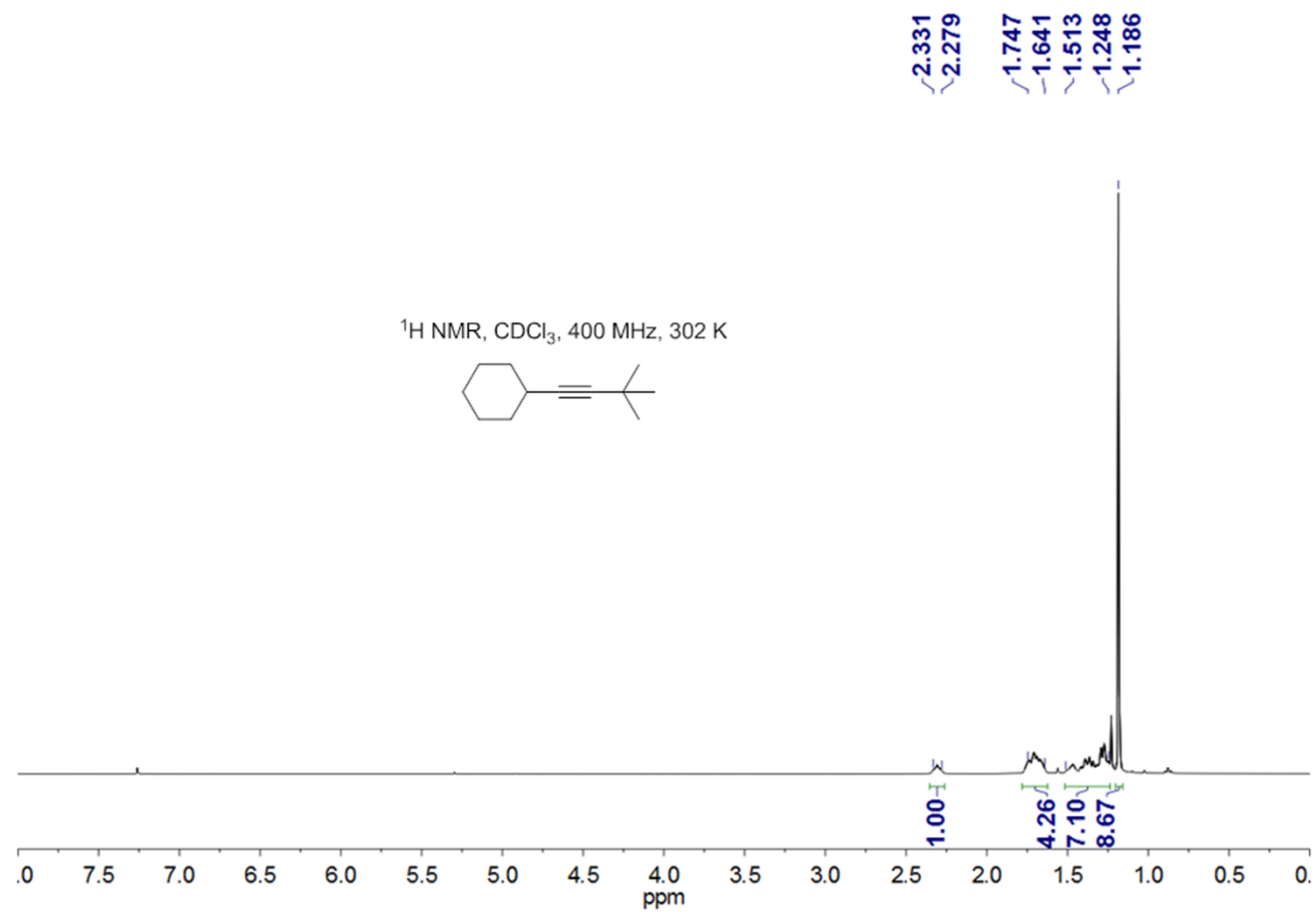


Figure S22. ¹H NMR spectrum of *c*-C₆H₁₁-C≡C*Bu*^{*t*} in CDCl₃.

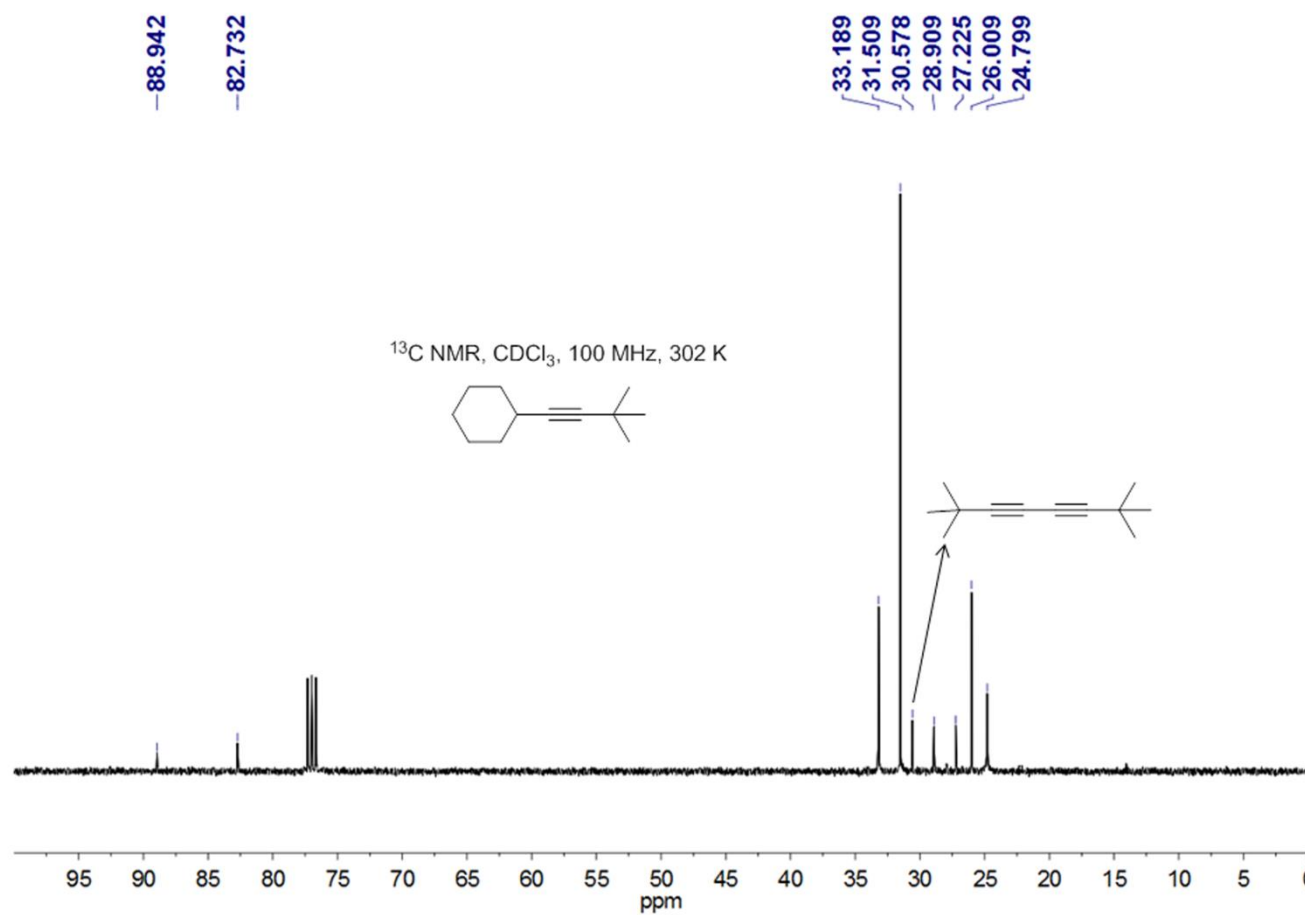


Figure S23. ¹³C NMR spectrum of *c*-C₆H₁₁-C≡C*Bu*^{*t*} in CDCl₃.

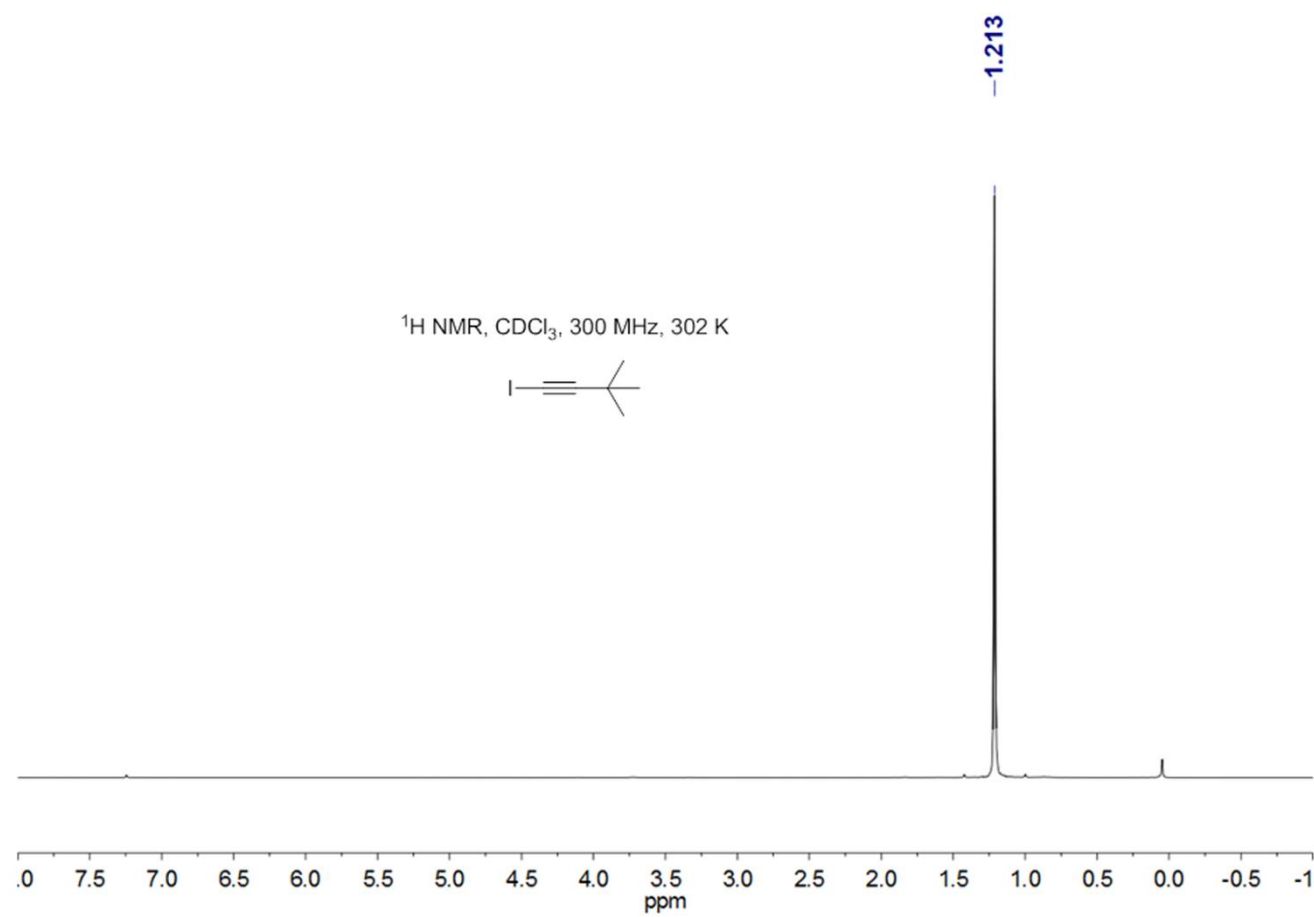


Figure S24. ^1H NMR spectrum of $\text{Bu}^t\text{C}\equiv\text{C-I}$ in CDCl_3 .

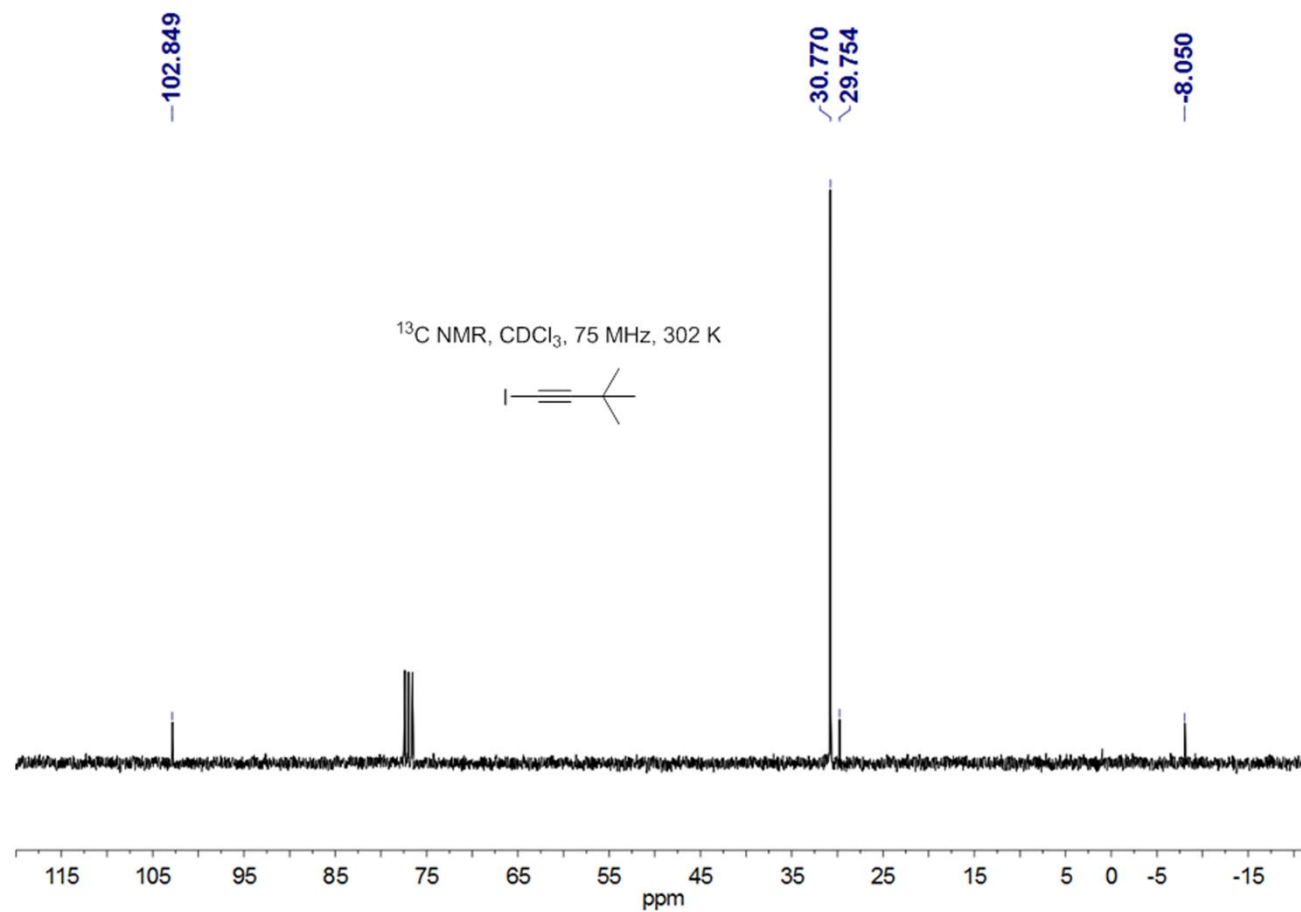


Figure S25. ^{13}C NMR spectrum of $\text{Bu}^t\text{C}\equiv\text{C-I}$ in CDCl_3 .

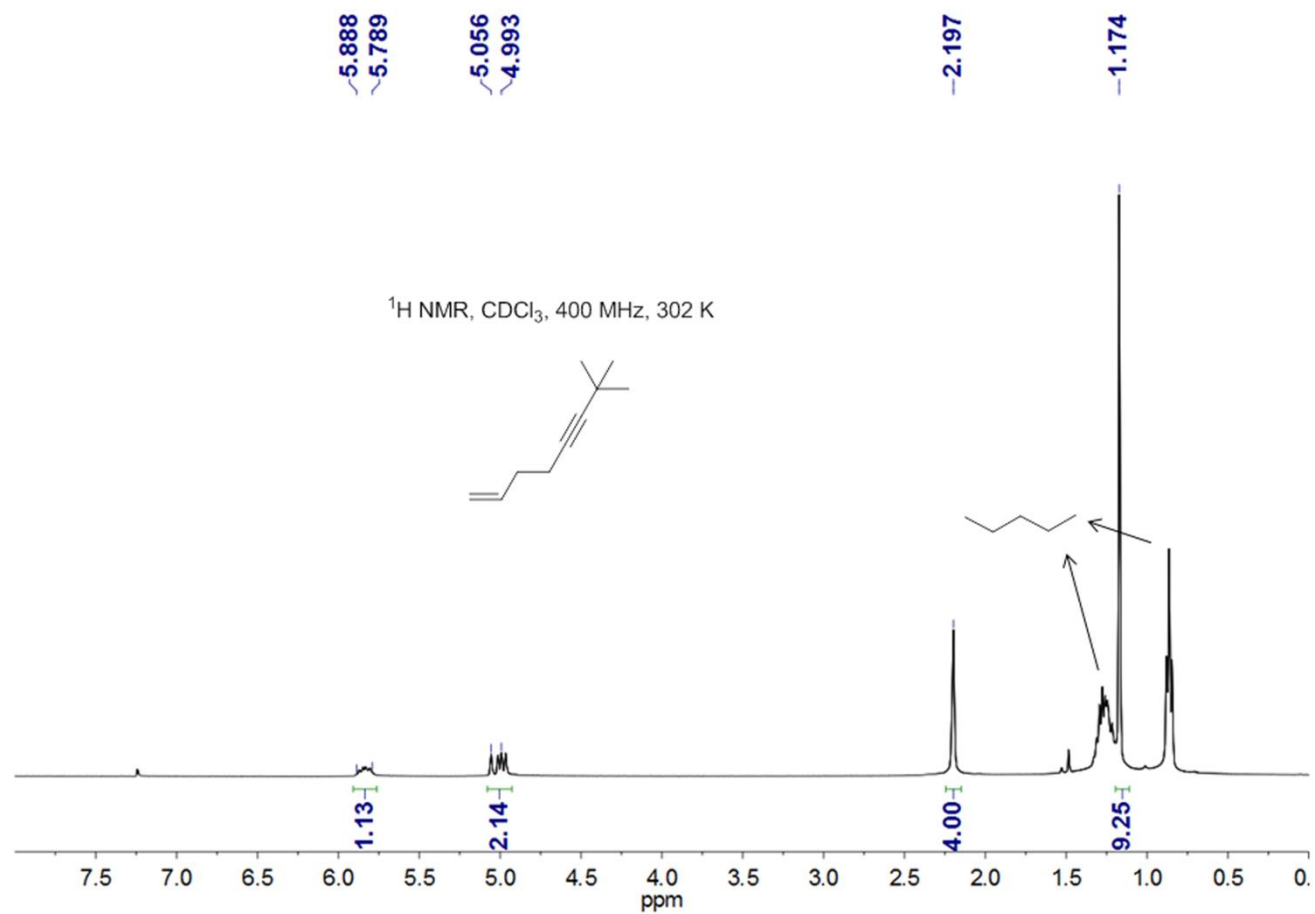


Figure S26. ¹H NMR spectrum of CH₂=CH(CH₂)₂C≡CBu^t in CDCl₃.

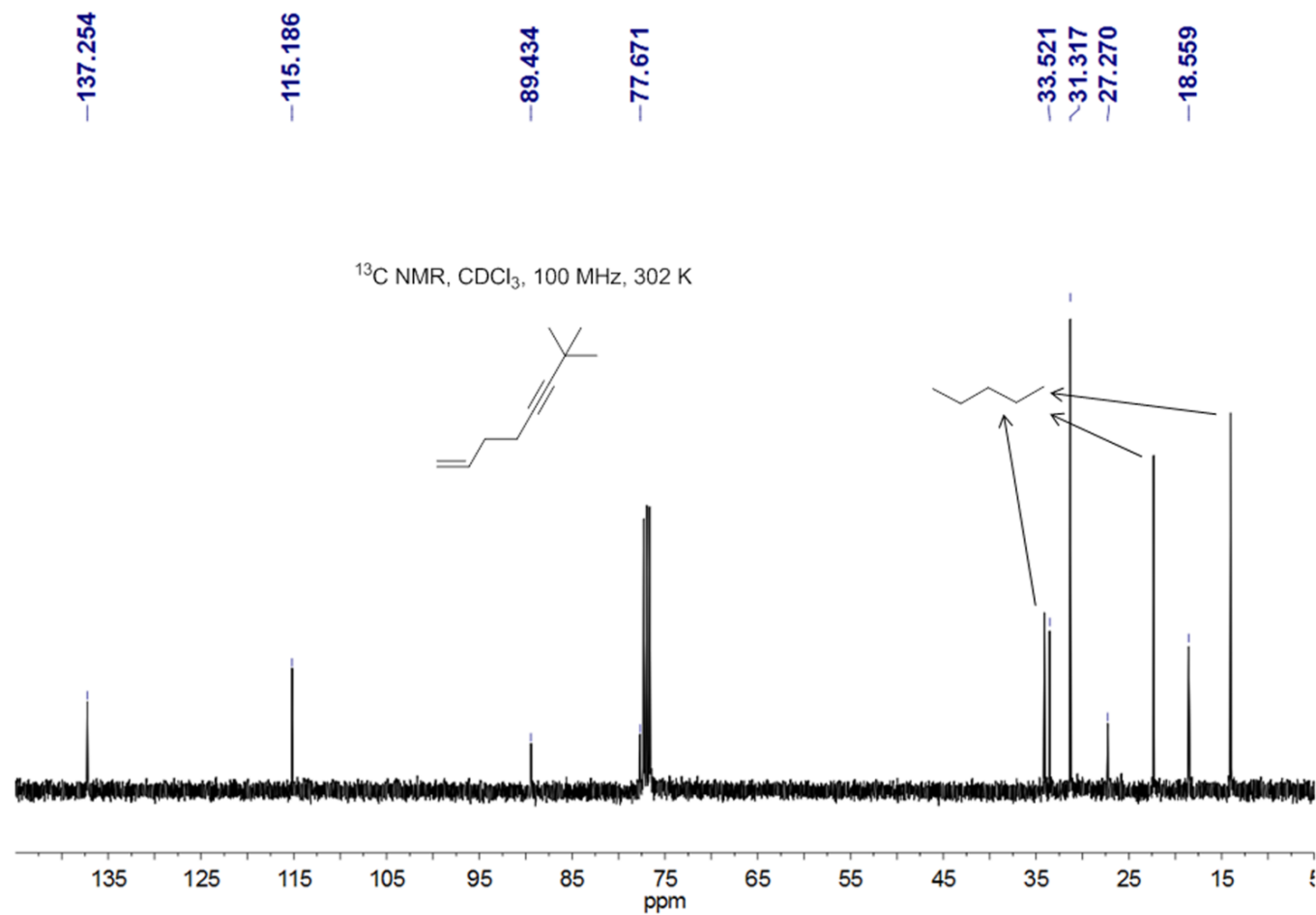


Figure S27. ¹³C NMR spectrum of CH₂=CH(CH₂)₂C≡CBu^t in CDCl₃.

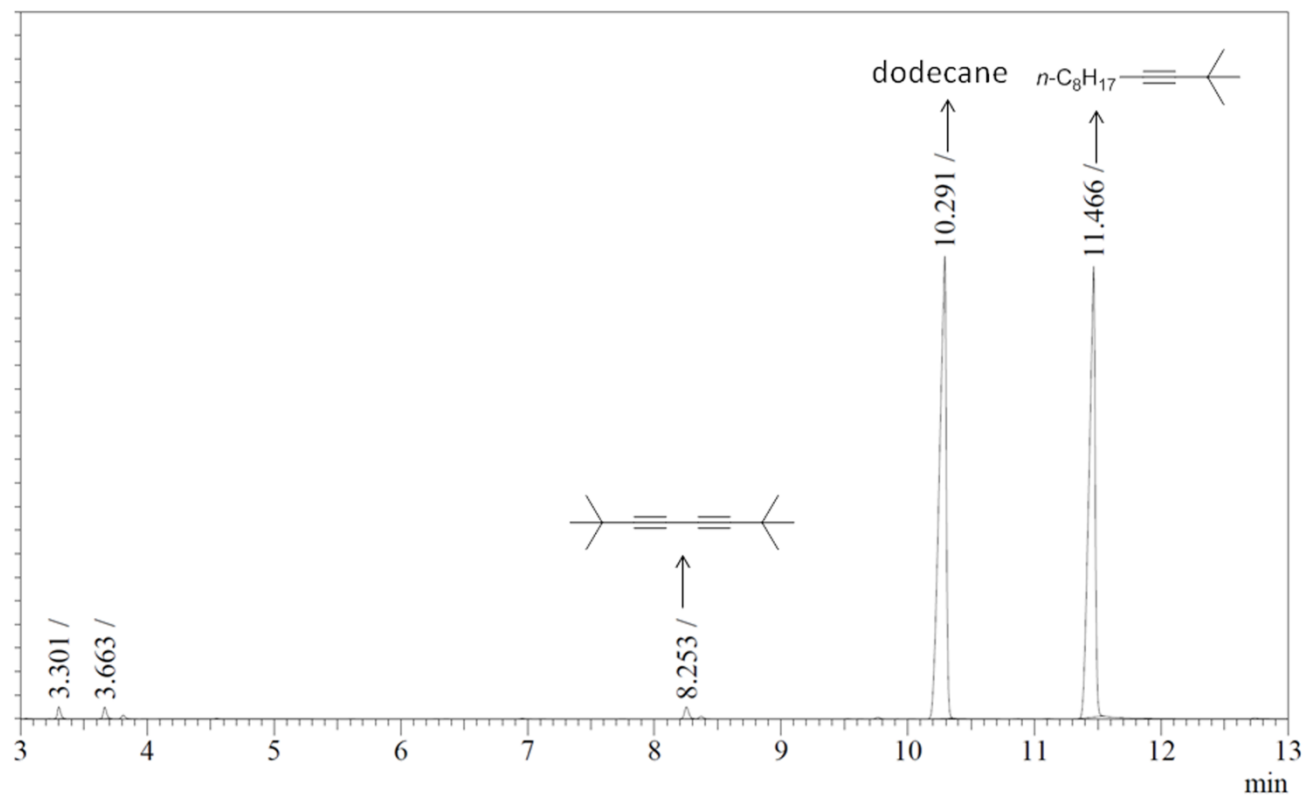
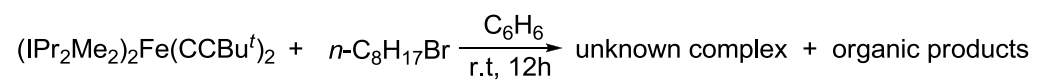


Figure S28. The GC graph for the quenched reaction mixture of **1** with $n\text{-C}_8\text{H}_{17}\text{Br}$.

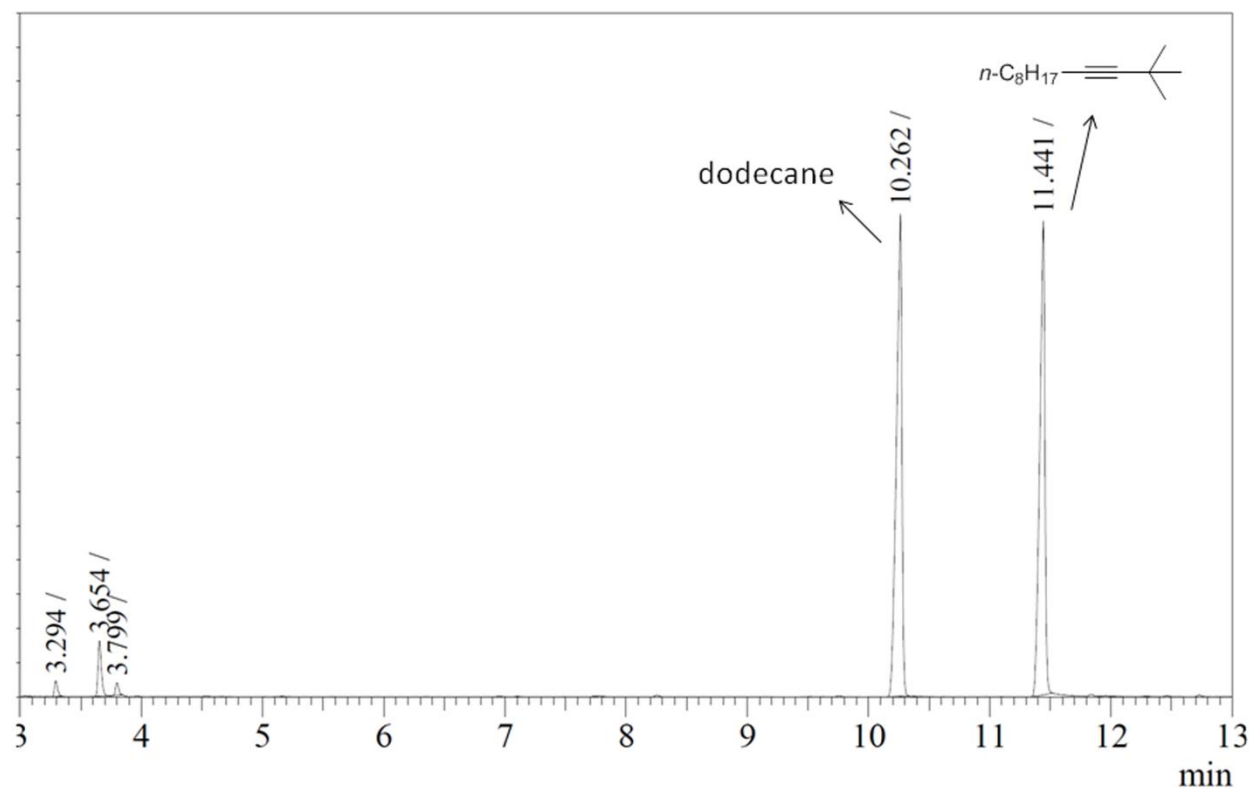
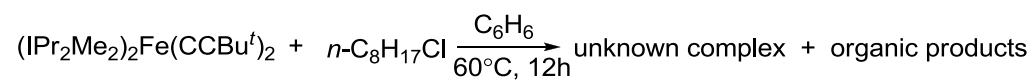


Figure S29. The GC graph for the quenched reaction mixture of **1** with $n\text{-C}_8\text{H}_{17}\text{Cl}$.

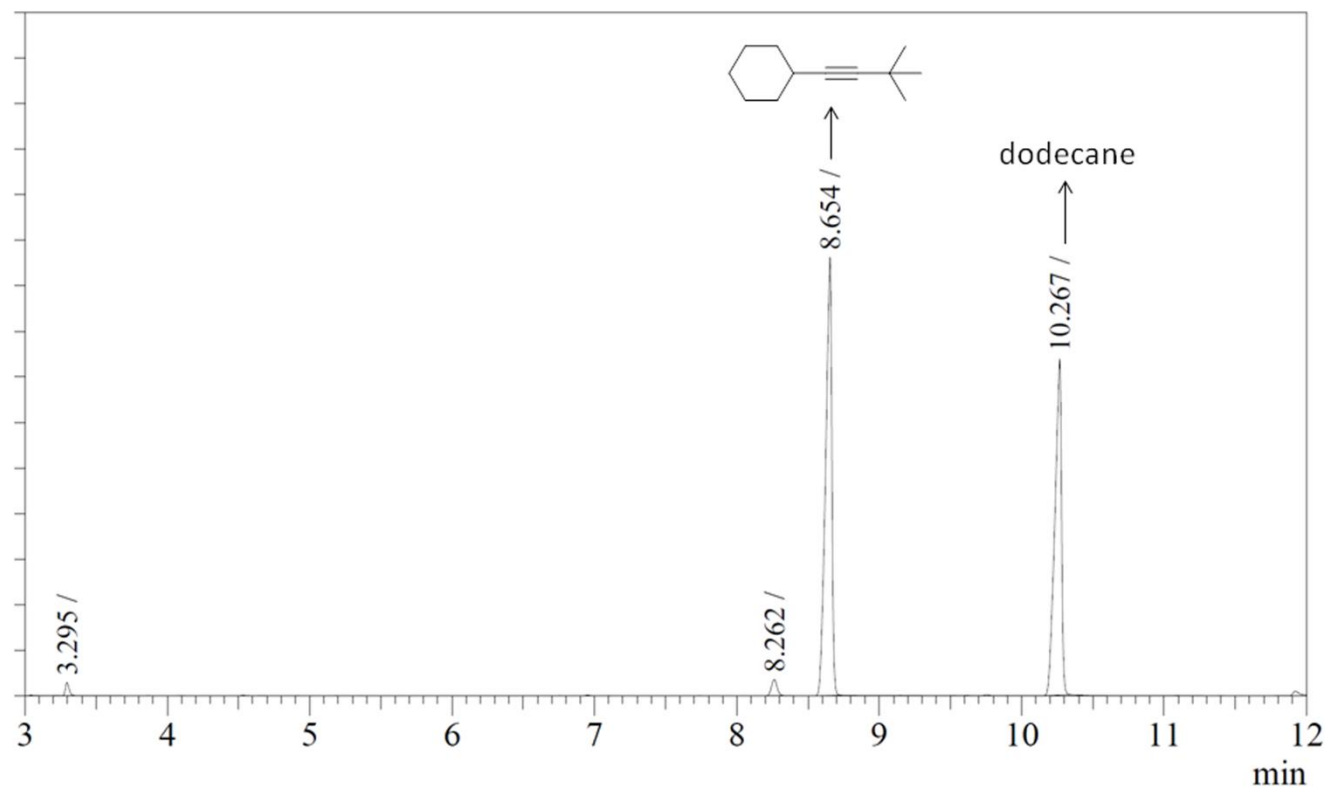
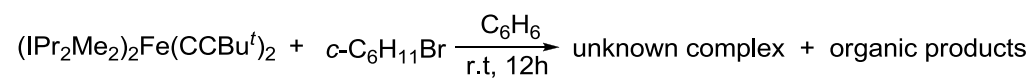


Figure S30. The GC graph for the quenched reaction mixture of **1** with $c\text{-C}_6\text{H}_{11}\text{Br}$.

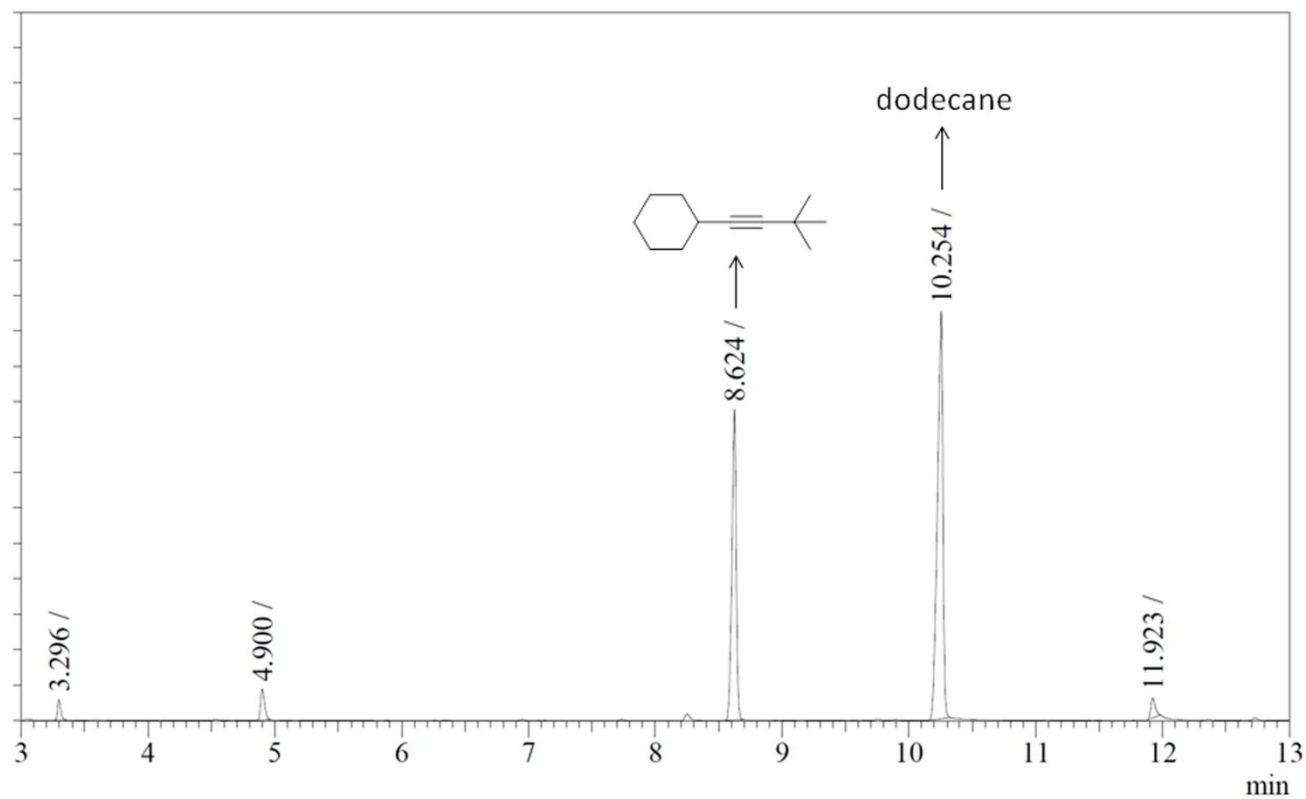
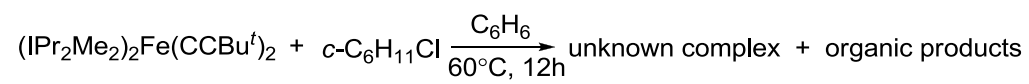


Figure S31. The GC graph for the quenched reaction mixture of **1** with $c\text{-C}_6\text{H}_{11}\text{Cl}$.

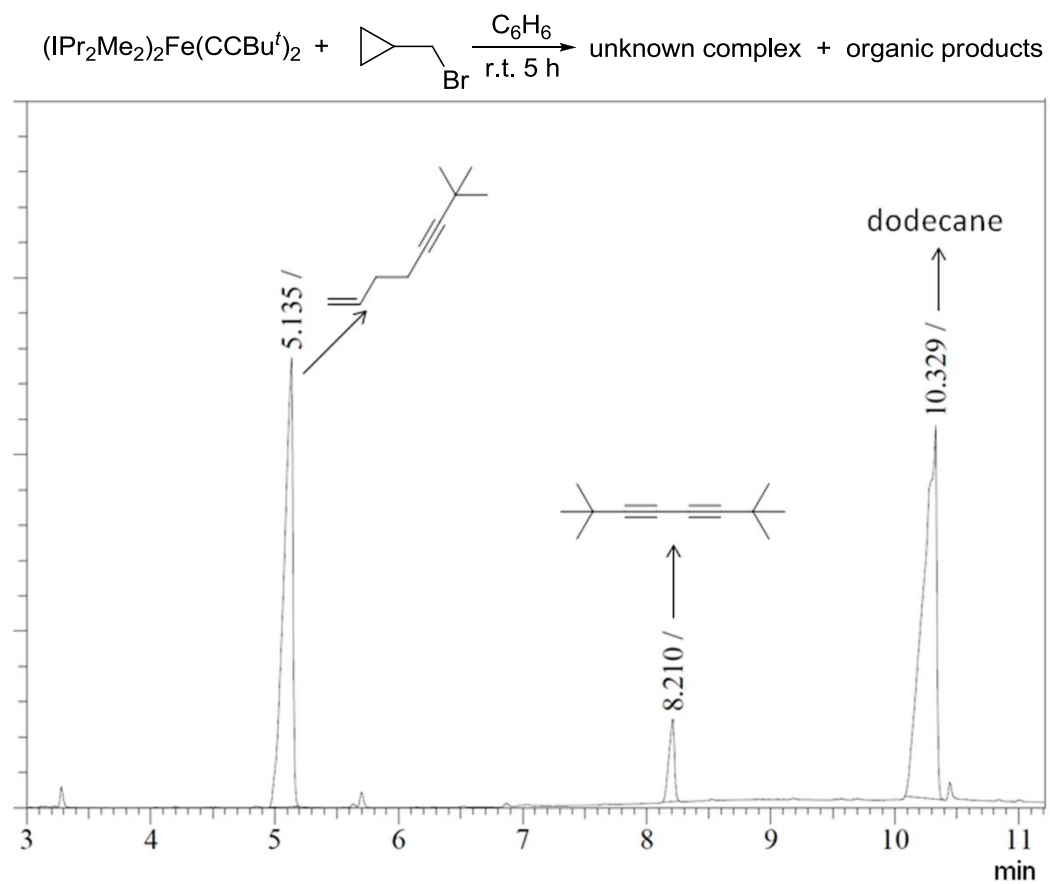
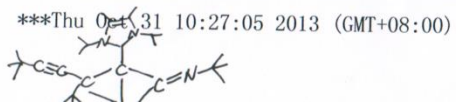


Figure S32. The GC graph for the quenched reaction mixture of **1** with $c\text{-C}_3\text{H}_5\text{CH}_2\text{Br}$.



Number of sample scans: 32
Number of background scans: 32
Resolution: 4.000