Supporting Information for:

Group 4 Diaryl Metallocenes as Bespoke Aryne Precursors for Ti-Catalyzed [2 + 2 + 2] Cycloaddition of Arynes and Alkynes

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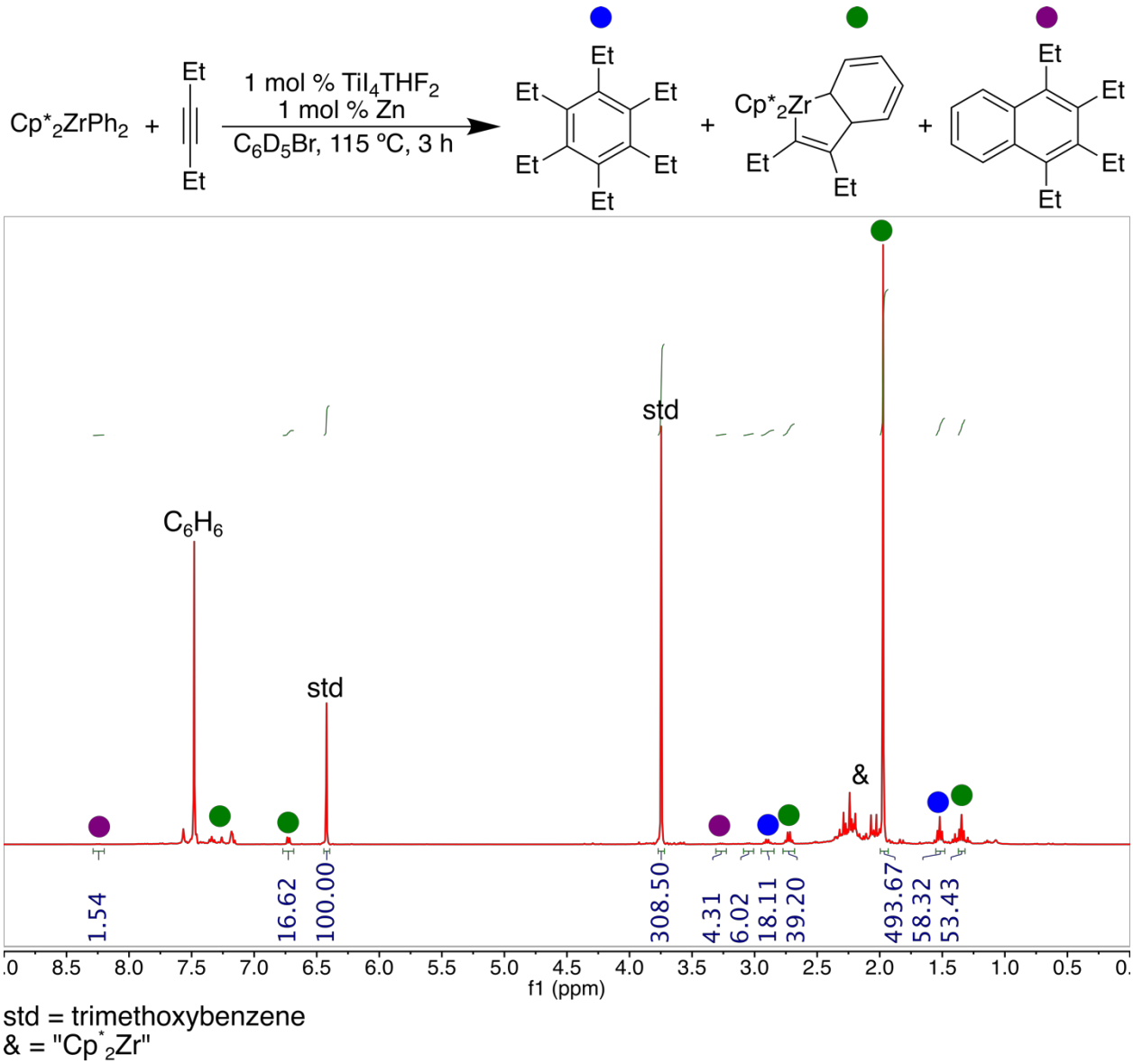
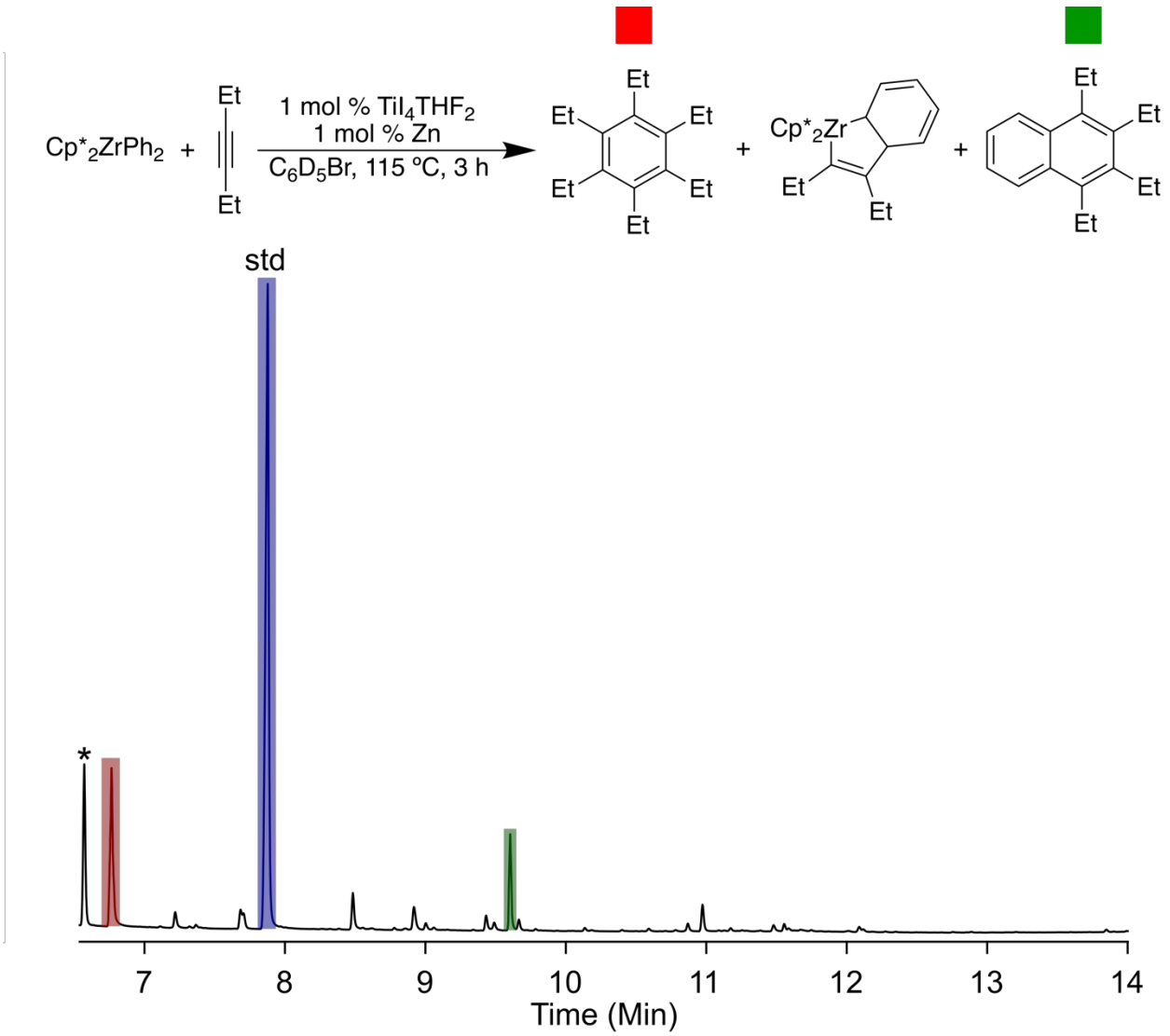


Figure S1. Table 2, entry 1a - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of 3-hexyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



* = impurity in C_6D_5Br
std = trimethoxybenzene

Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimer	6.571	128.5	18	8
trimethoxybenzene	7.869	2290.7	9	N/A
naphthalene	9.604	120.5	18	5

Figure S2. Table 2, entry 1a - Quantitative GC-FID spectrum of the attempted formal [2+2+2] cycloaddition of 3-hexyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

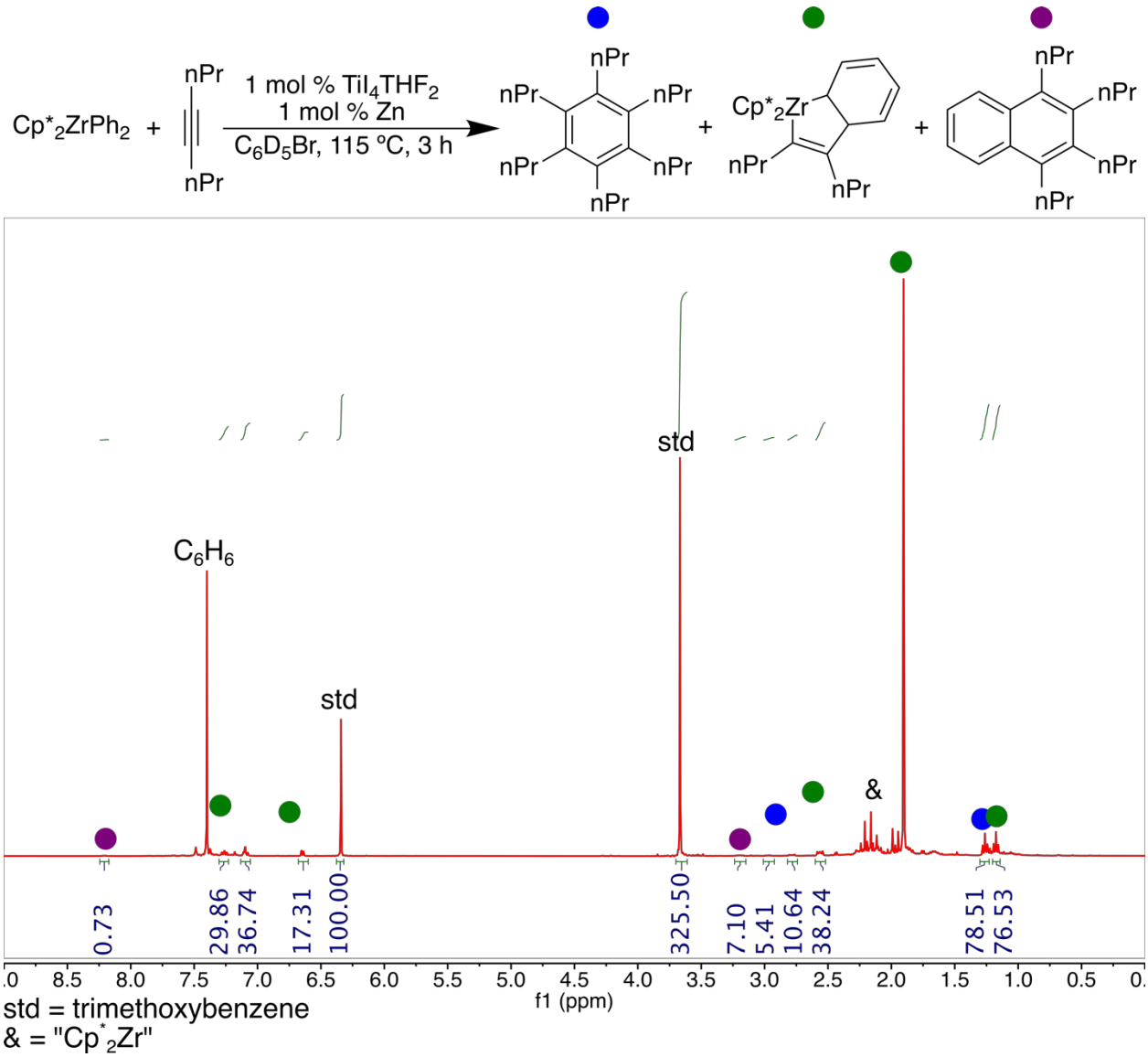
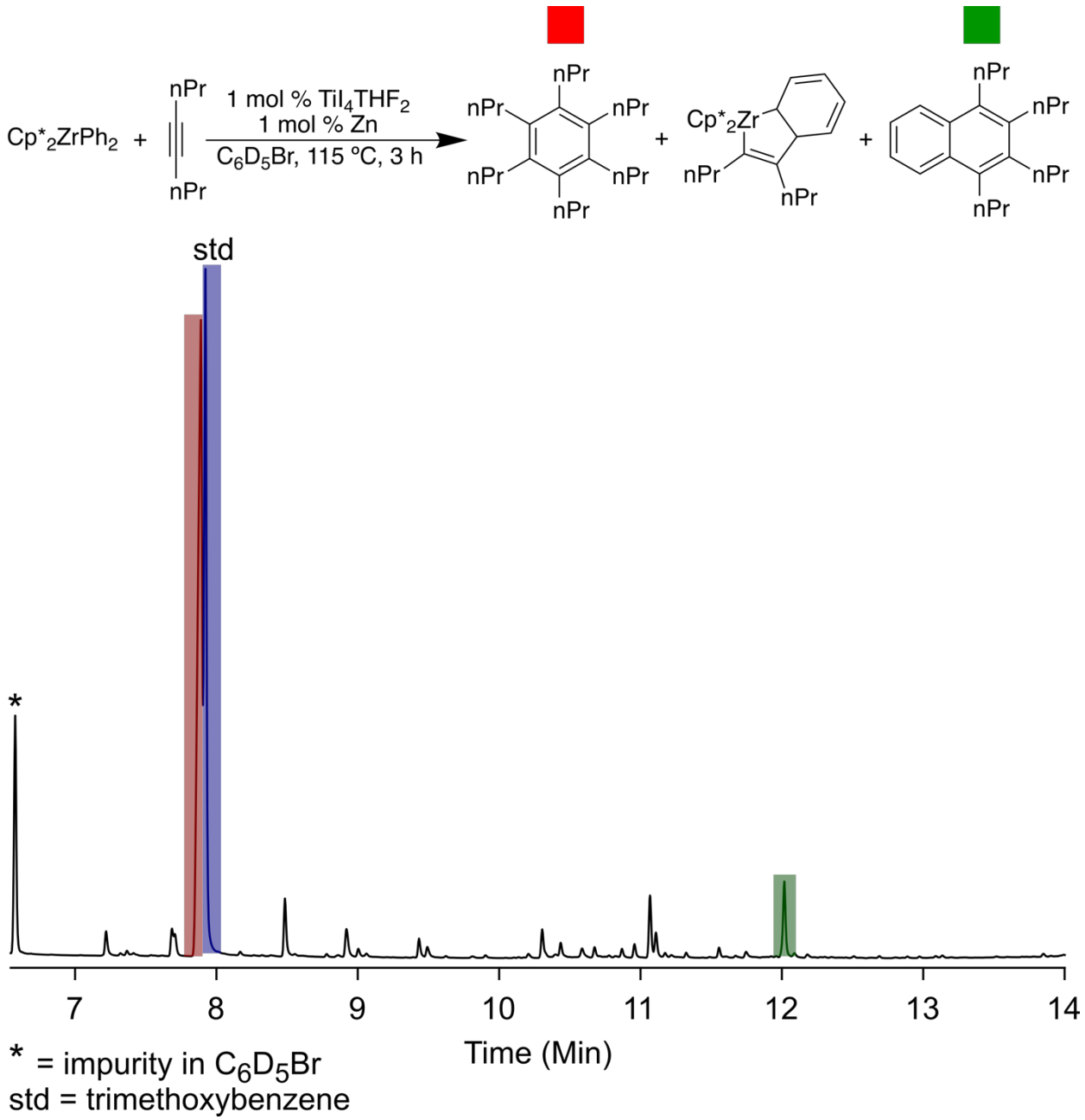


Figure S3. Table 2, entry 1b - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of 4-octyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimer	7.890	240.2	24	9
trimethoxybenzene	7.869	2868.3	9	N/A
naphthalene	12.017	150.8	22	4

Figure S4. Table 2, entry 1b - Quantitative GC-FID spectrum of the attempted formal [2+2+2] cycloaddition of 4-octyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

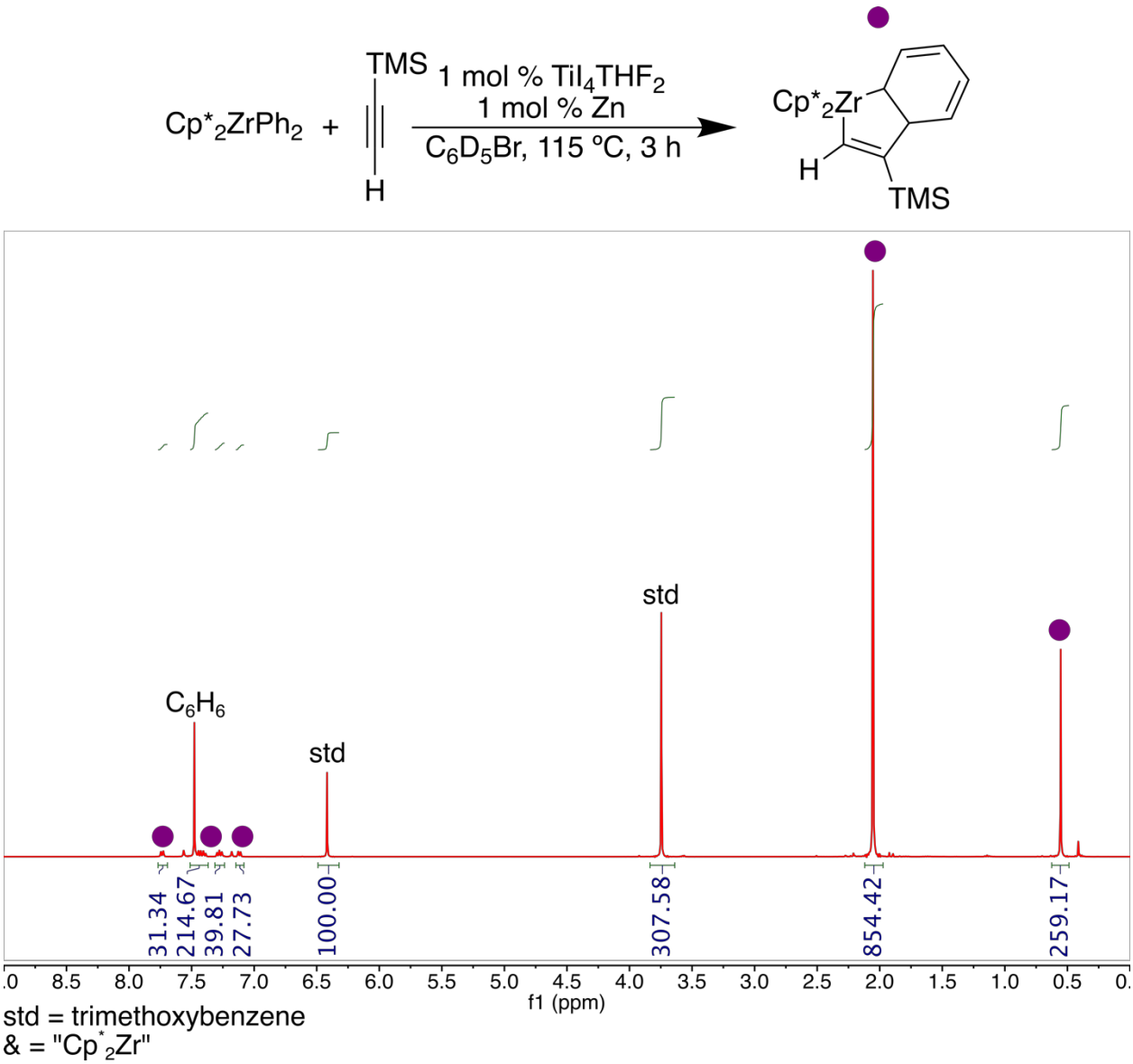


Figure S5. Table 2, entry 1c - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of trimethylsilylacetylene and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

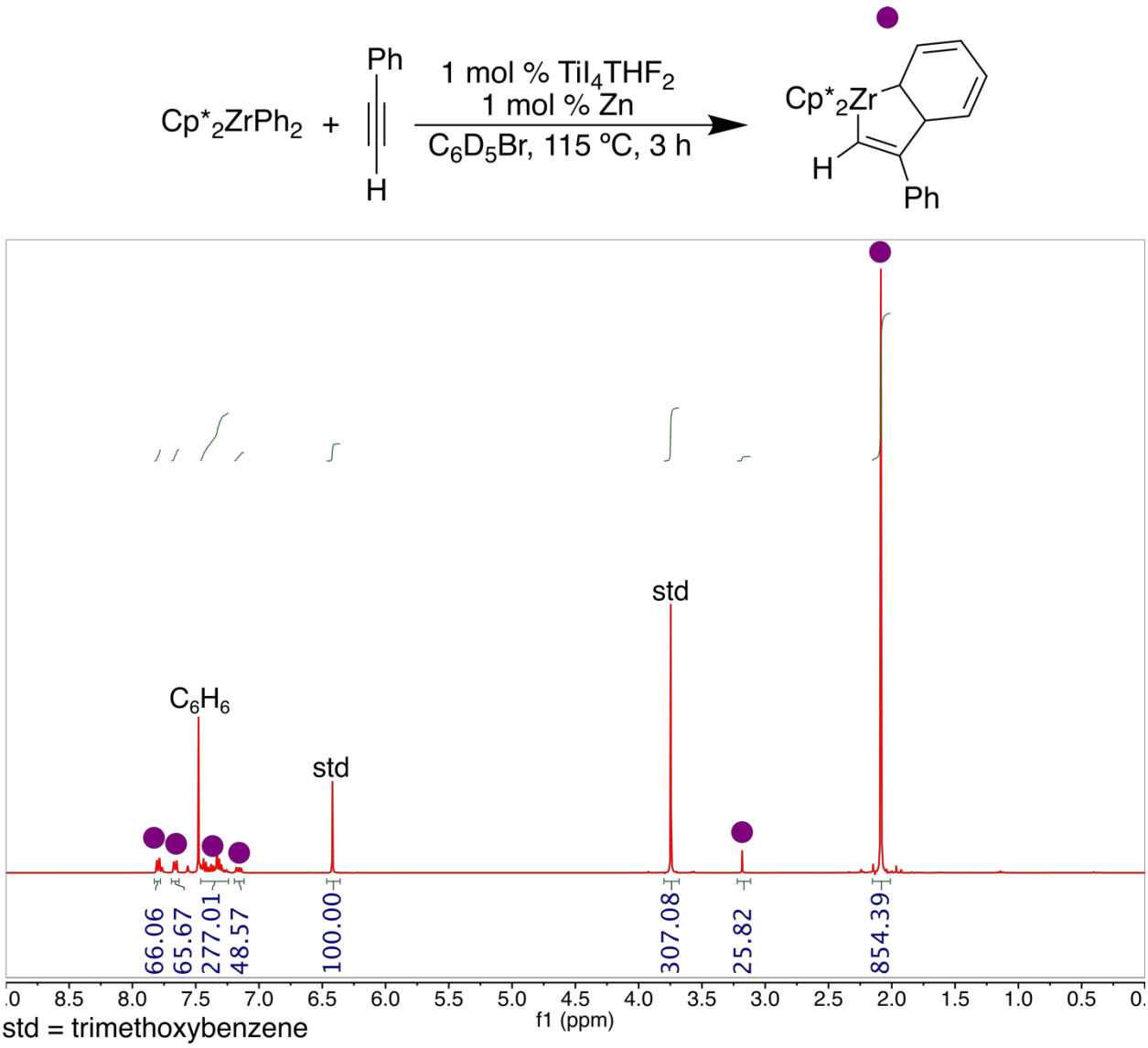


Figure S6. Table 2, entry 1d - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of phenylacetylene and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

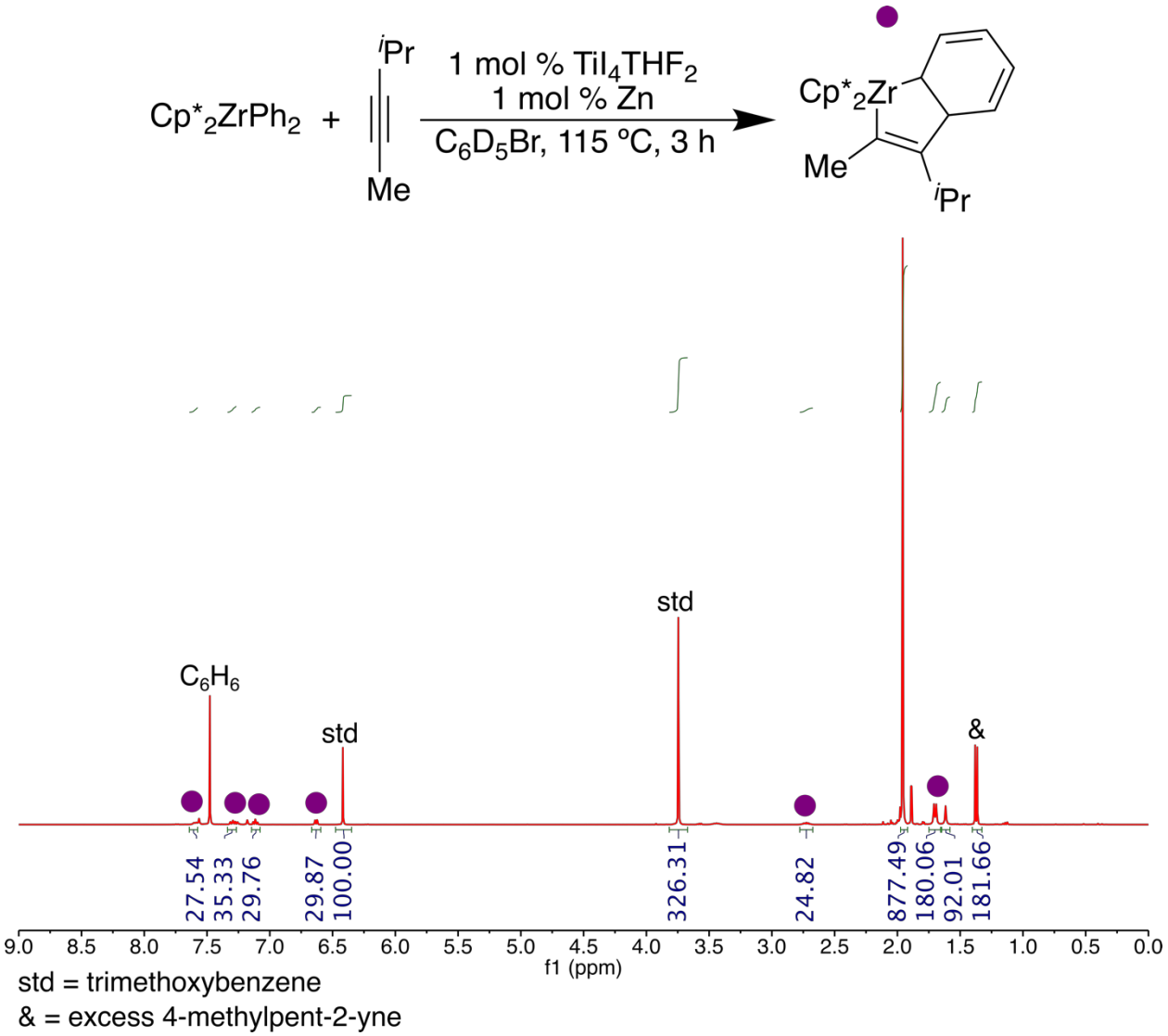


Figure S7. Table 2, entry 1e - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of 4-methylpent-2-yne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

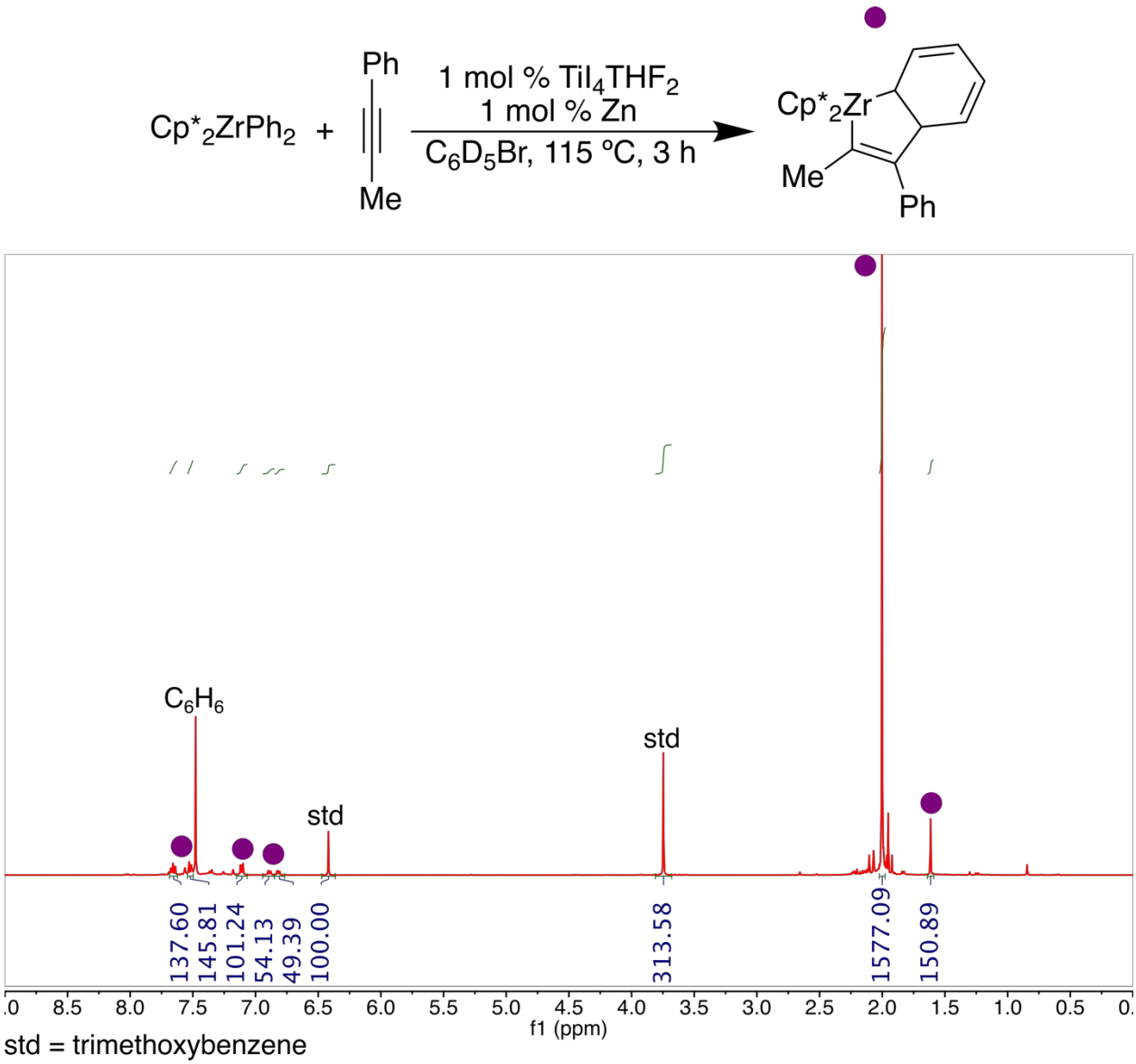


Figure S8. Table 2, entry 1f - ^{1}H NMR (C_6D_5Br) spectrum of the attempted formal [2+2+2] cycloaddition of phenyl propyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

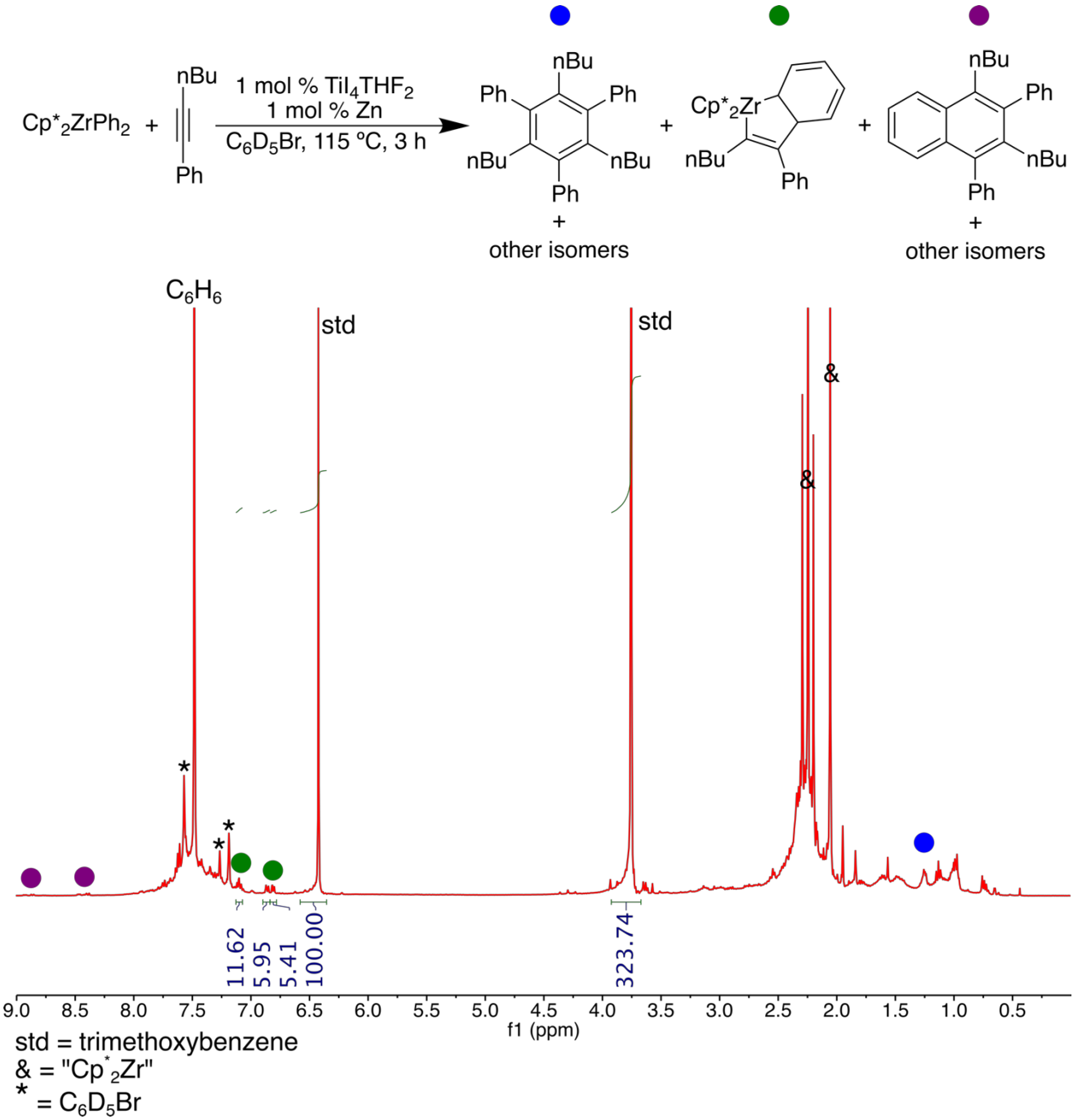
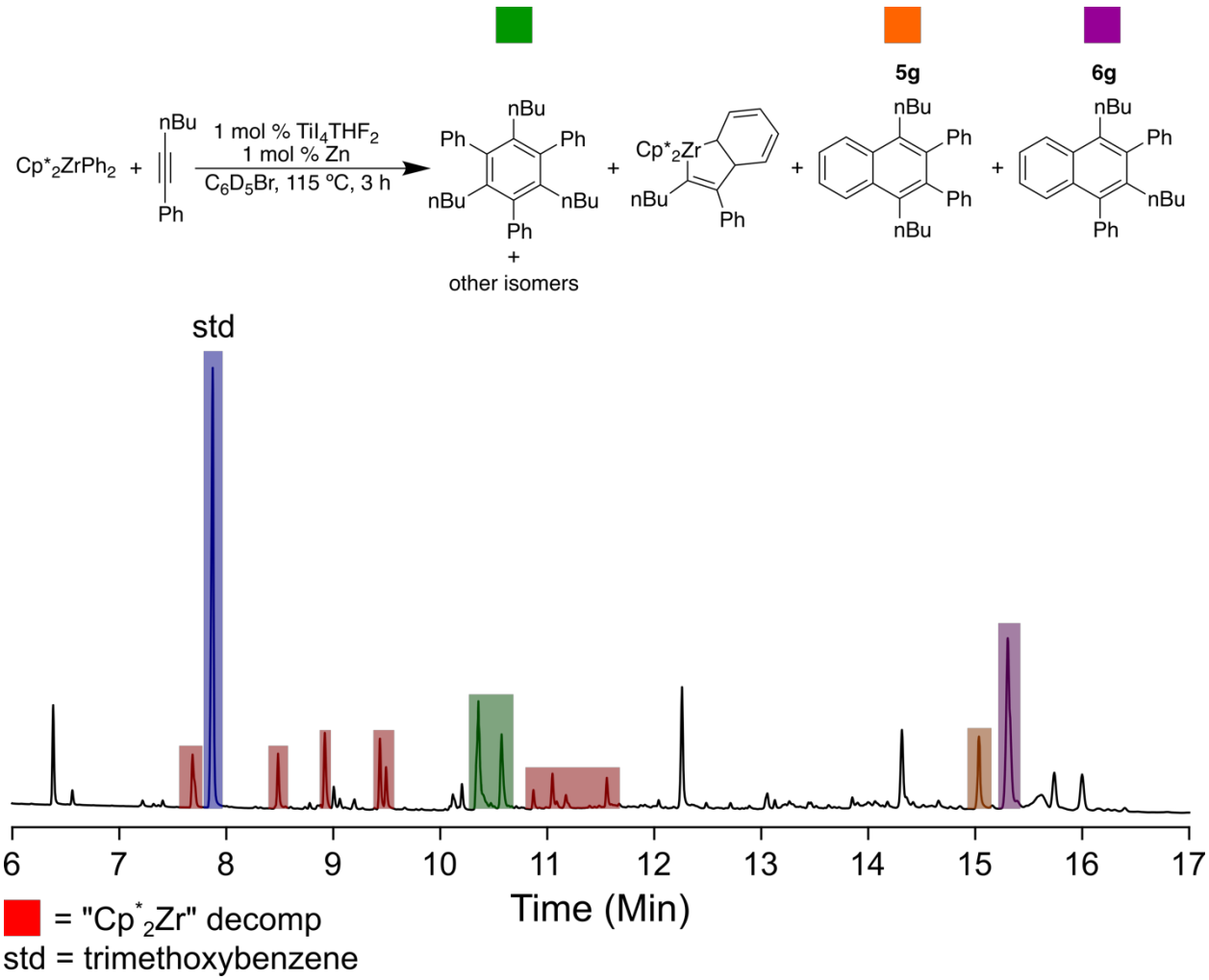
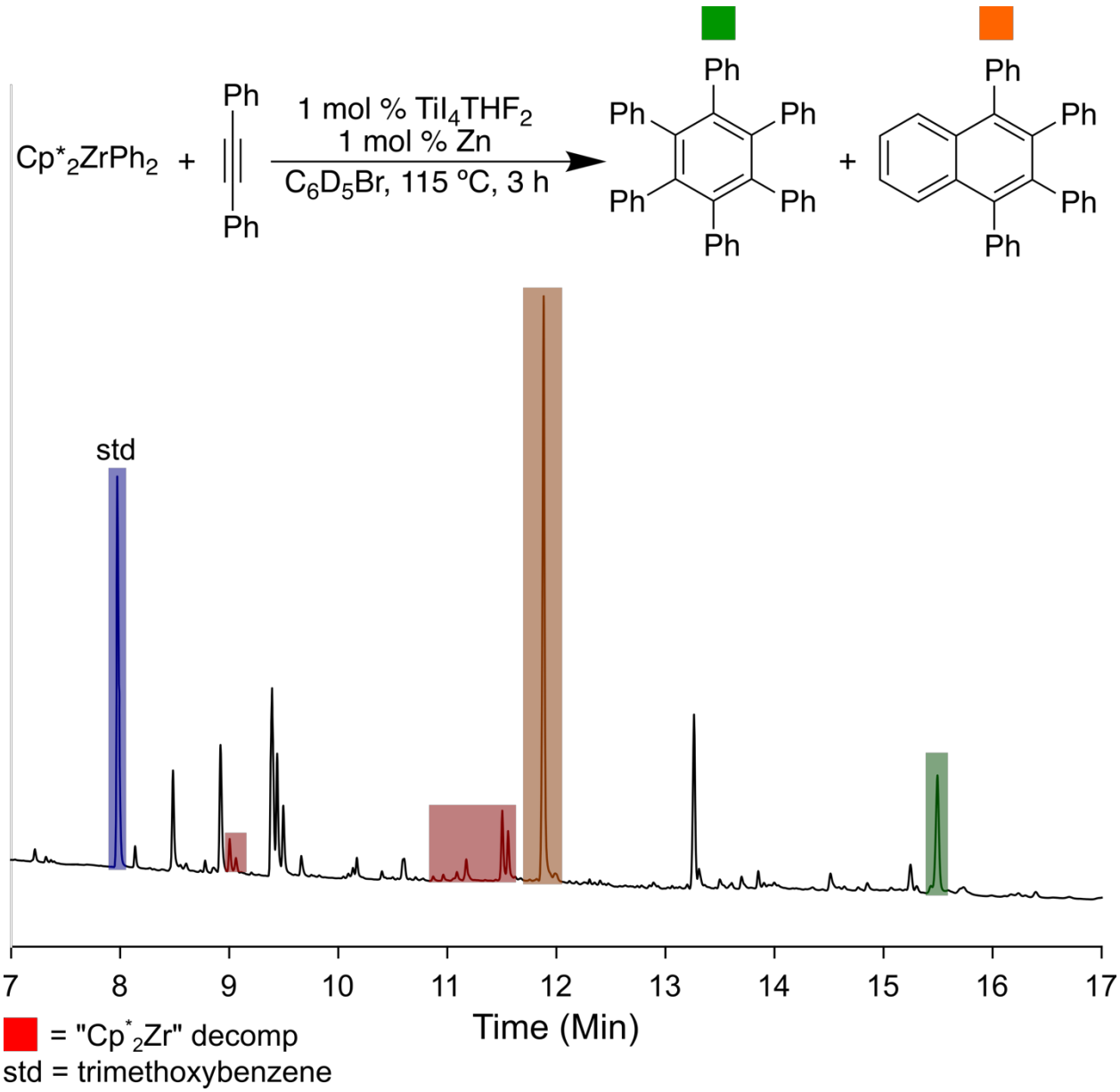


Figure S9. Table 2, entry 1g - ^{1}H NMR (C_6D_5Br) spectrum of the cyclotrimerization of phenyl hexyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



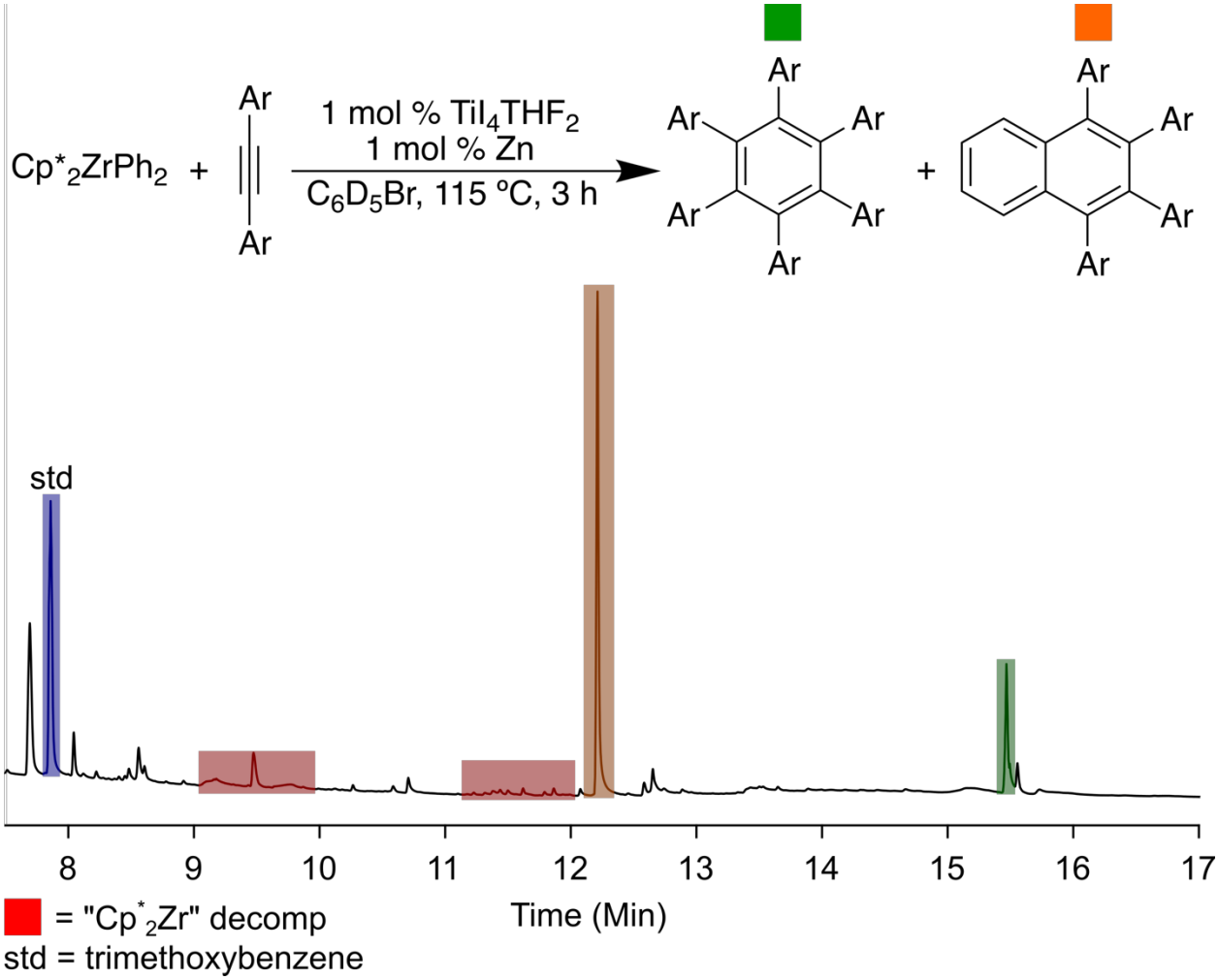
Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2632.5	9	N/A
trimer 1	10.350	353.4	36	10
trimer 2	10.588	207.3	36	6
naphthalene **5**	15.020	179.2	30	4
naphthalene **6**	15.320	435.6	30	10

Figure S10. Table 2, entry 1g - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of phenyl hexyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



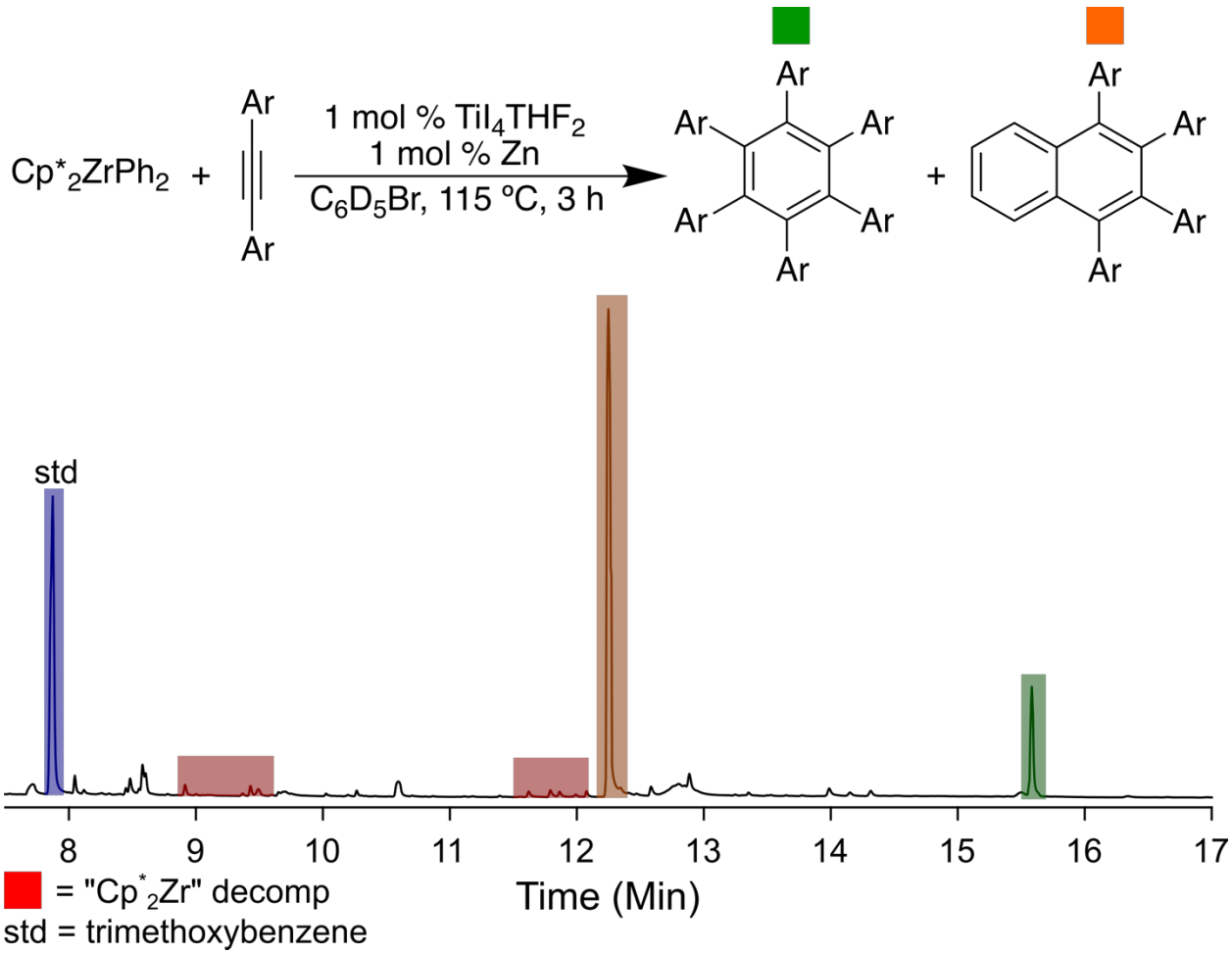
Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2200.1	9	N/A
naphthalene	11.899	2965.1	34	71
trimer	15.260	818.5	42	24

Figure S11. Table 2, entry 1h - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of diphenylacetylene and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



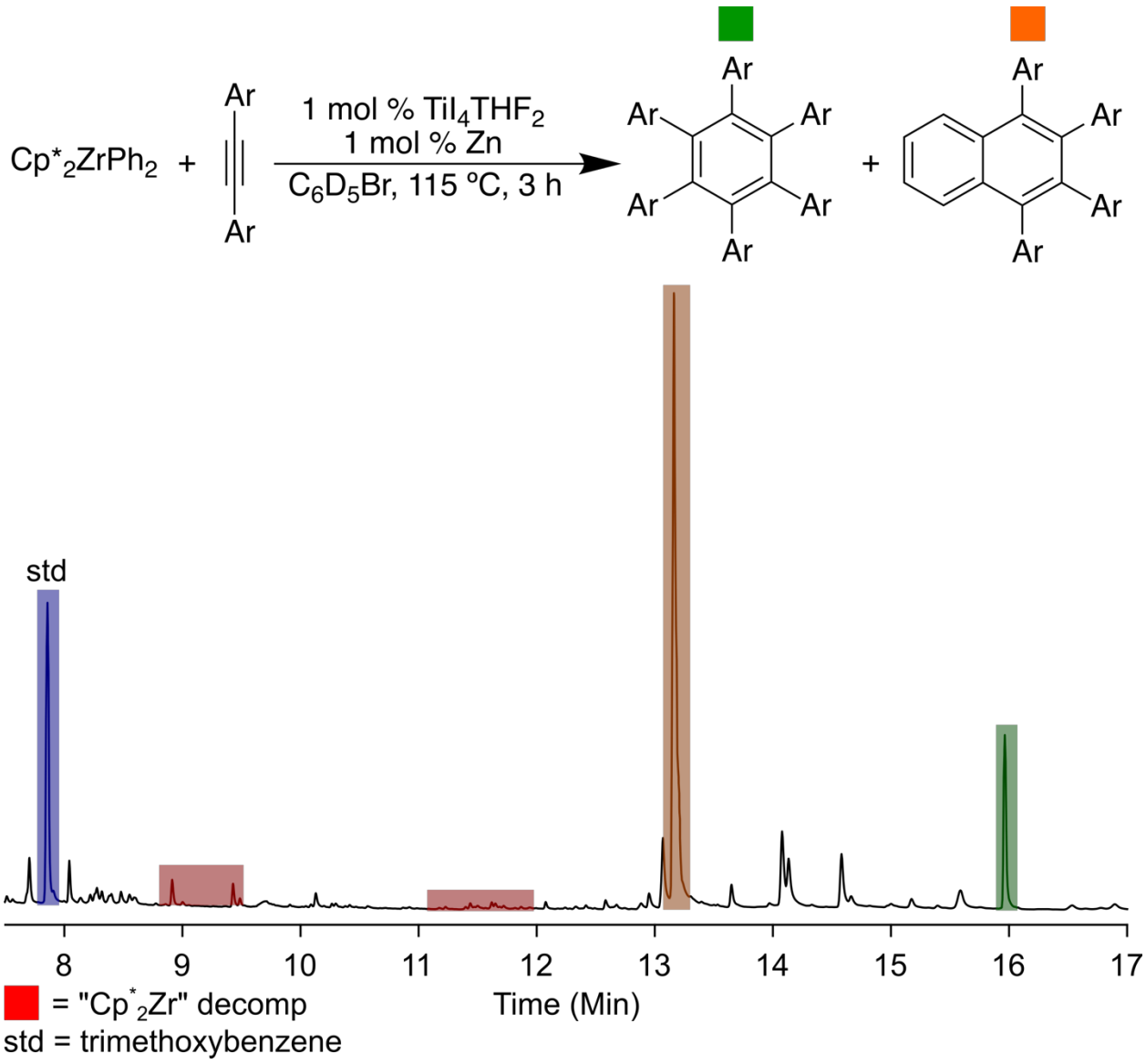
Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2317.7	9	N/A
naphthalene	12.299	3111.0	38	64
trimer	15.571	795.4	48	19

Figure S12. Table 2, entry 1i - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of bis(4-trifluoromethylphenyl)ethyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



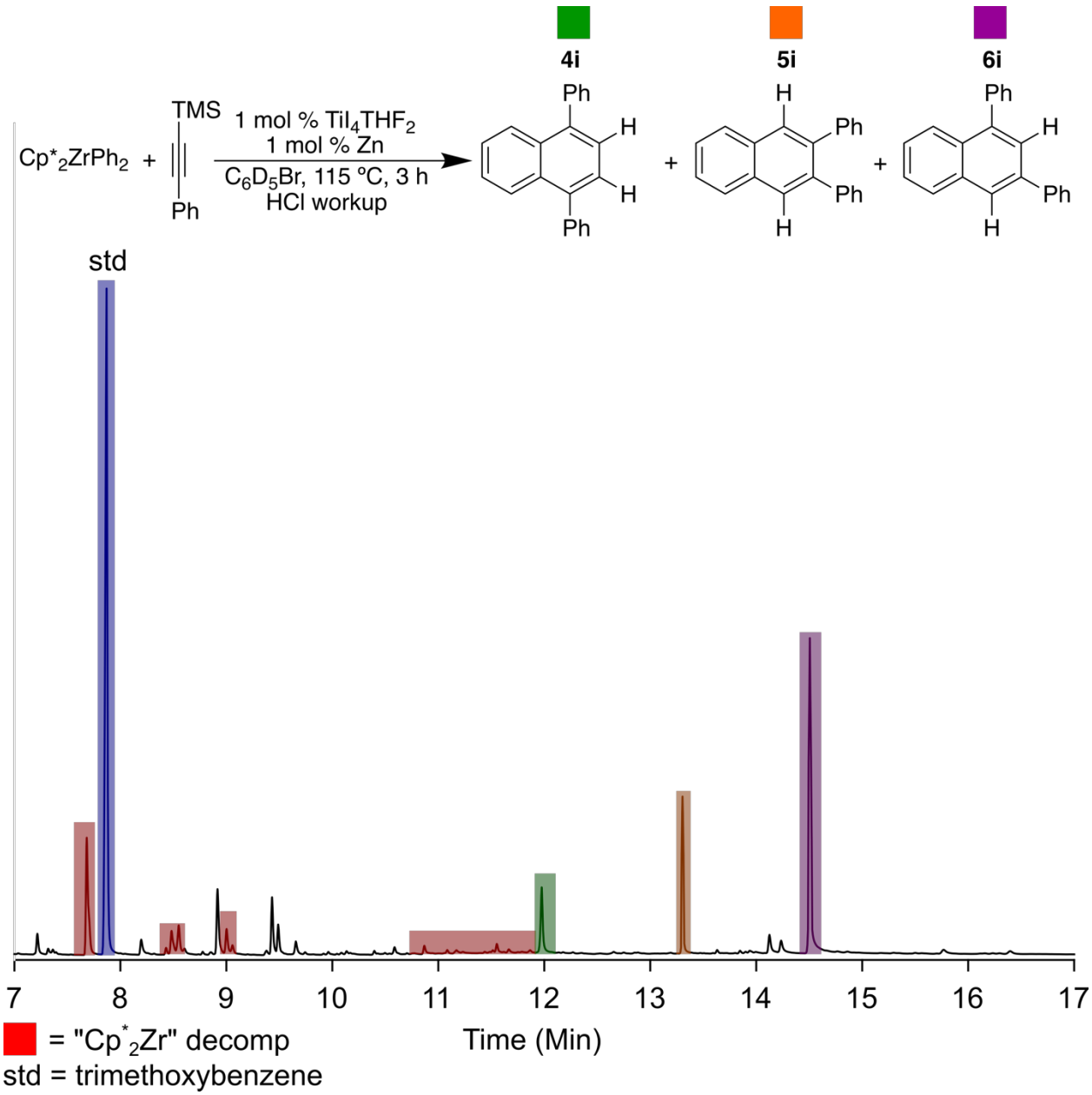
Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2261.1	9	N/A
naphthalene	12.289	3750.4	38	78
trimer	15.560	600.4	48	15

Figure S13. Table 2, entry 1j - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of bis(4-methoxyphenyl)ethyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



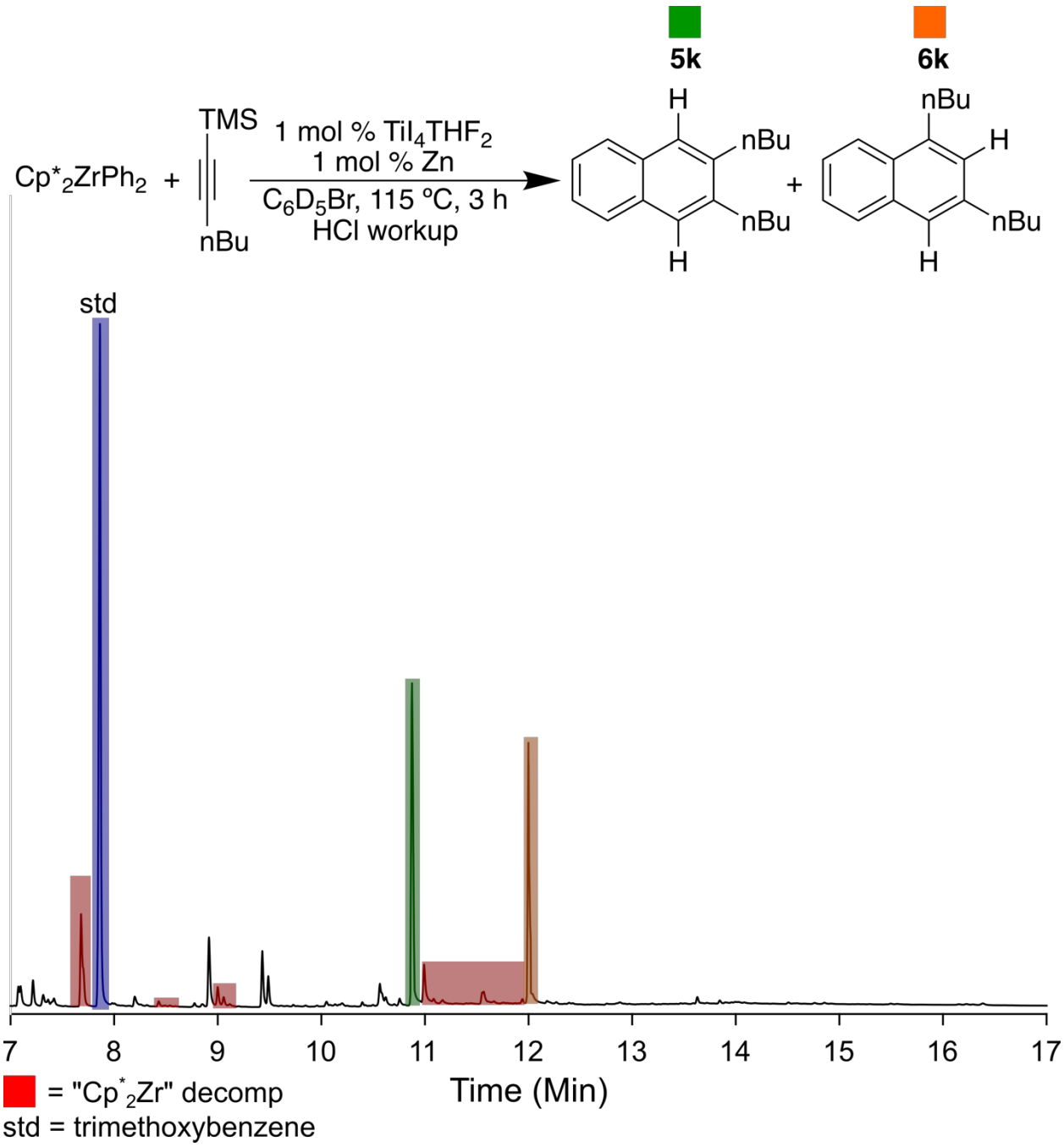
Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2495.0	9	N/A
naphthalene	13.255	5261.2	50	78
trimer	16.040	1360.0	66	15

Figure S14. Table 2, entry 1k - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of bis(4-(*tert*-butyl)phenyl)ethyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	1901.5	9	N/A
naphthalene **4**	11.981	122.5	28	8
naphthalene **5**	13.320	412.8	28	14
naphthalene **6**	14.555	765.6	28	26

Figure S15. Table 2, entry 11 - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of trimethyl(phenylethynyl)silane and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.



Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2239.0	9	N/A
naphthalene **5**	10.888	1002.7	24	34
naphthalene **6**	12.055	897.8	24	31

Figure S16. Table 2, entry 1m - Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of trimethyl(*n*-butylethynyl)silane and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %), and 1,3,5-trimethoxybenzene internal standard.

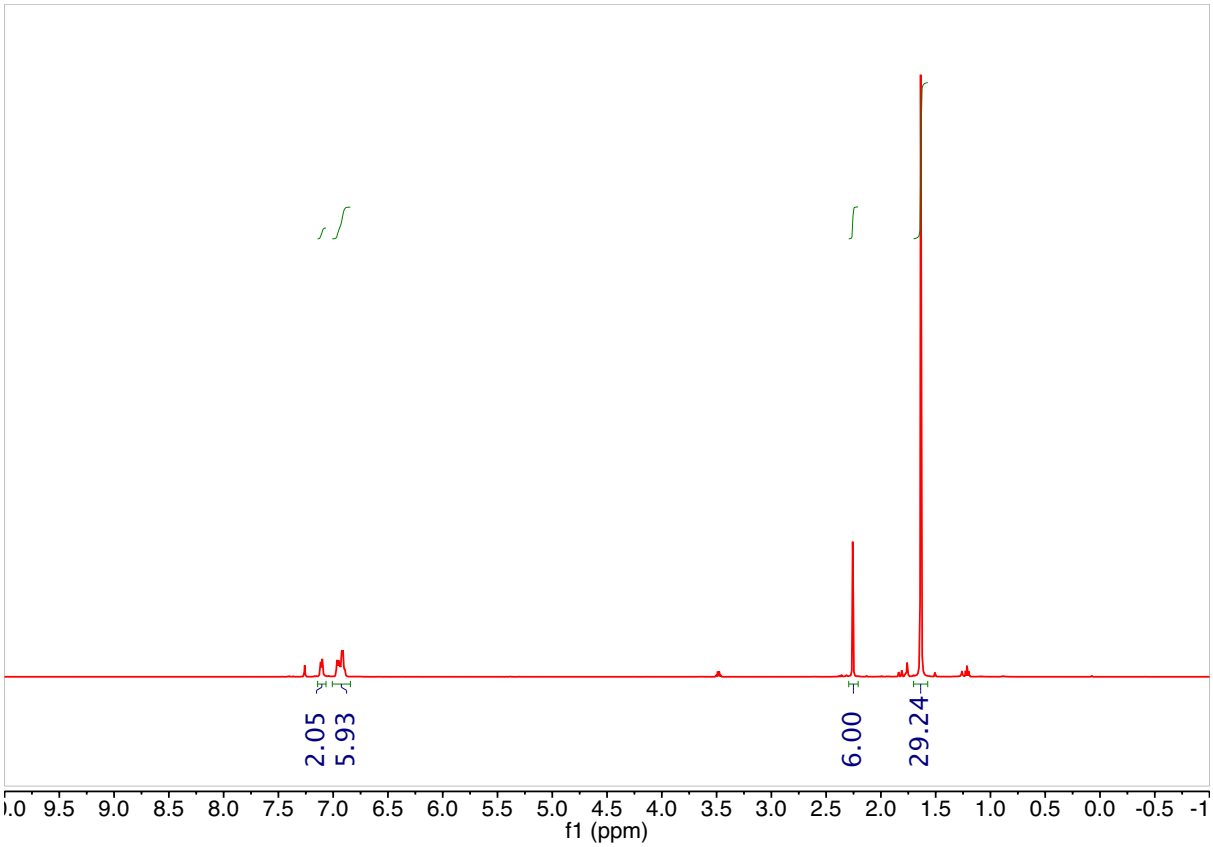


Figure S17. ^{1}H NMR spectrum ($CDCl_3$) of **8**.

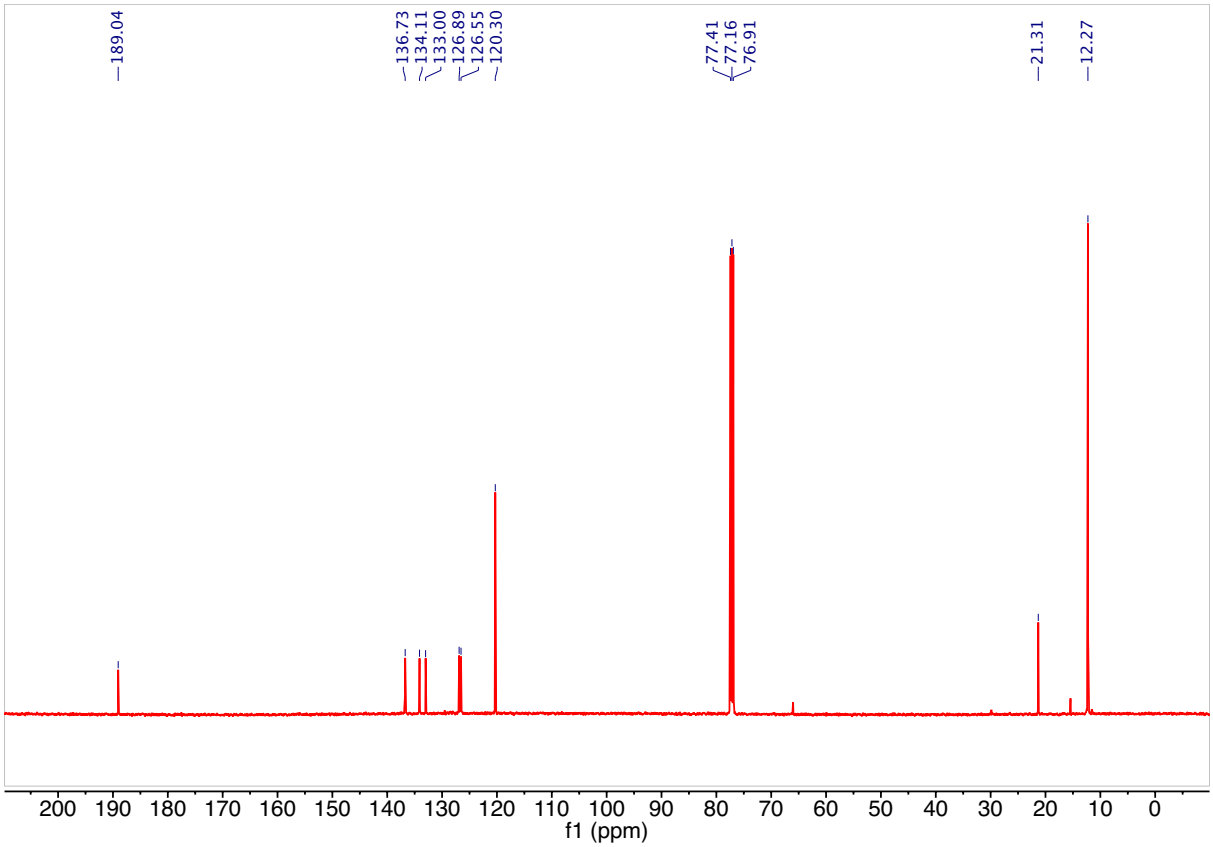
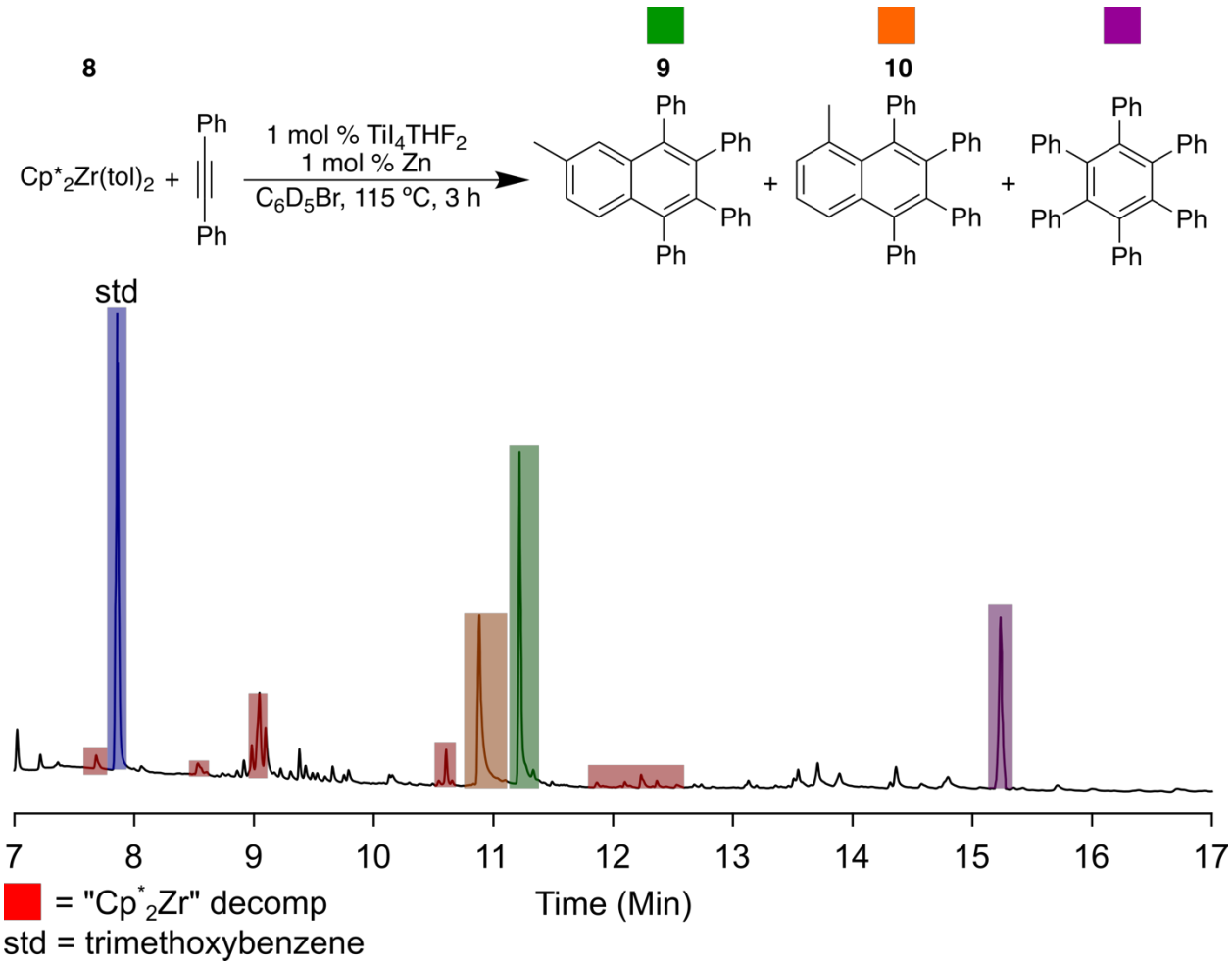


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **8**.



Product	Retention time (min)	Peak area (a.u.)	Carbon #	Yield (%)
trimethoxybenzene	7.869	2611.1	9	N/A
naphthalene **10**	10.899	861.5	28	21
naphthalene **9**	11.220	1731.1	28	43
trimer	15.490	665.0	36	19

Figure S19. Quantitative GC-FID spectrum of the formal [2+2+2] cycloaddition of diphenylacetylene and **8** with $TiI_4(THF)_2$ (1 mol %), Zn^0 (1 mol %) and 1,3,5-trimethoxybenzene internal standard.

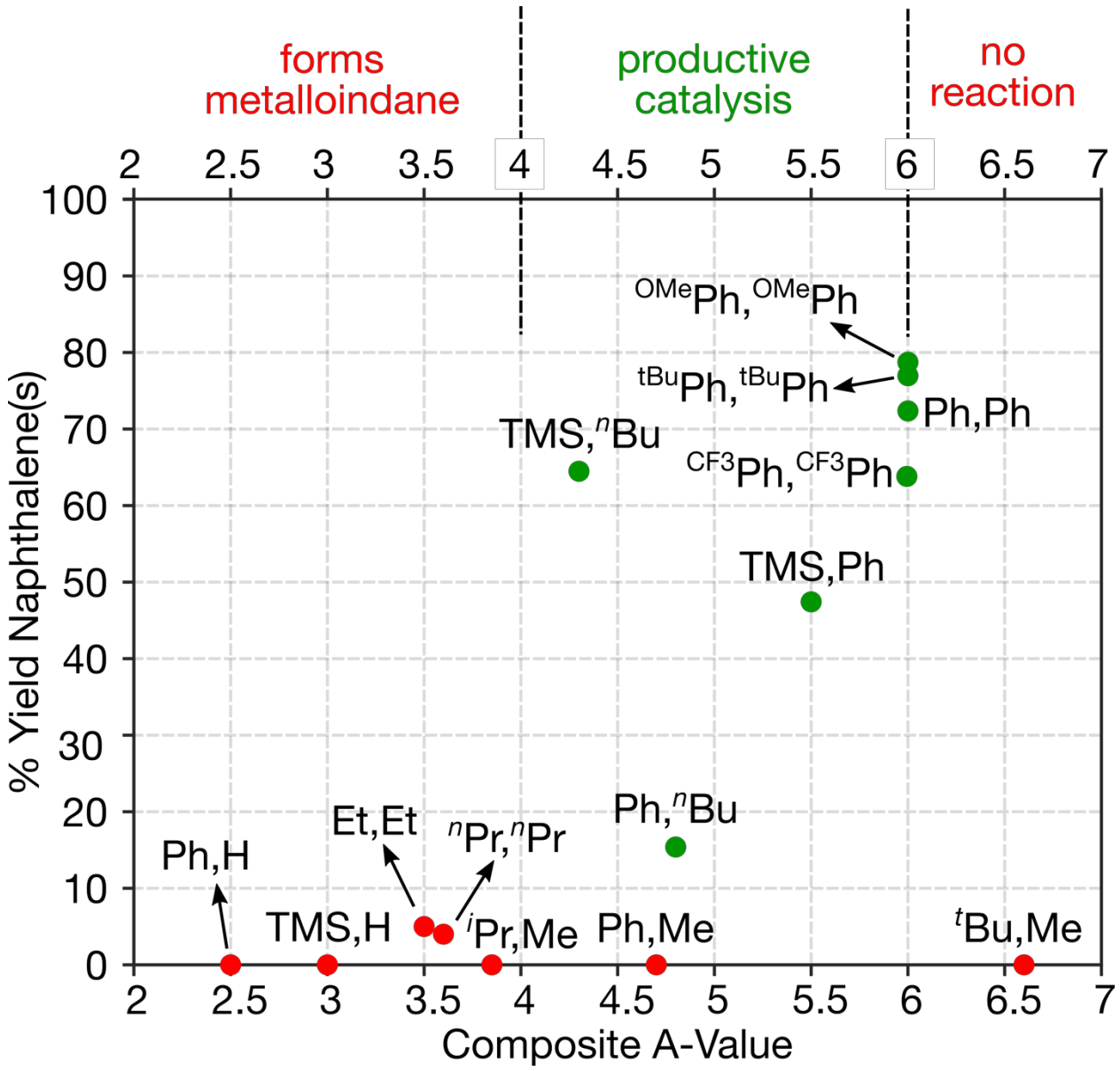


Figure S20. Alkyne "composite A-values" vs total yield of naphthalene products formed during the formal [2+2+2] cycloaddition of an alkyne and $Cp^*_2ZrPh_2$ with $TiI_4(THF)_2$ (1 mol %) and Zn^0 (1 mol %). Composite A-value was calculated by summing the A-value of both substituents of the alkyne coupling partner. Red dots correspond to reactions where naphthalene products were delivered in < 10% yield while green dots correspond to reactions where higher yields of naphthalene products were observed. Each dot is labeled according to the substituents of the alkyne coupling partner. The dotted lines above the plot designate regions where the size of the alkyne is appropriate for productive catalysis.

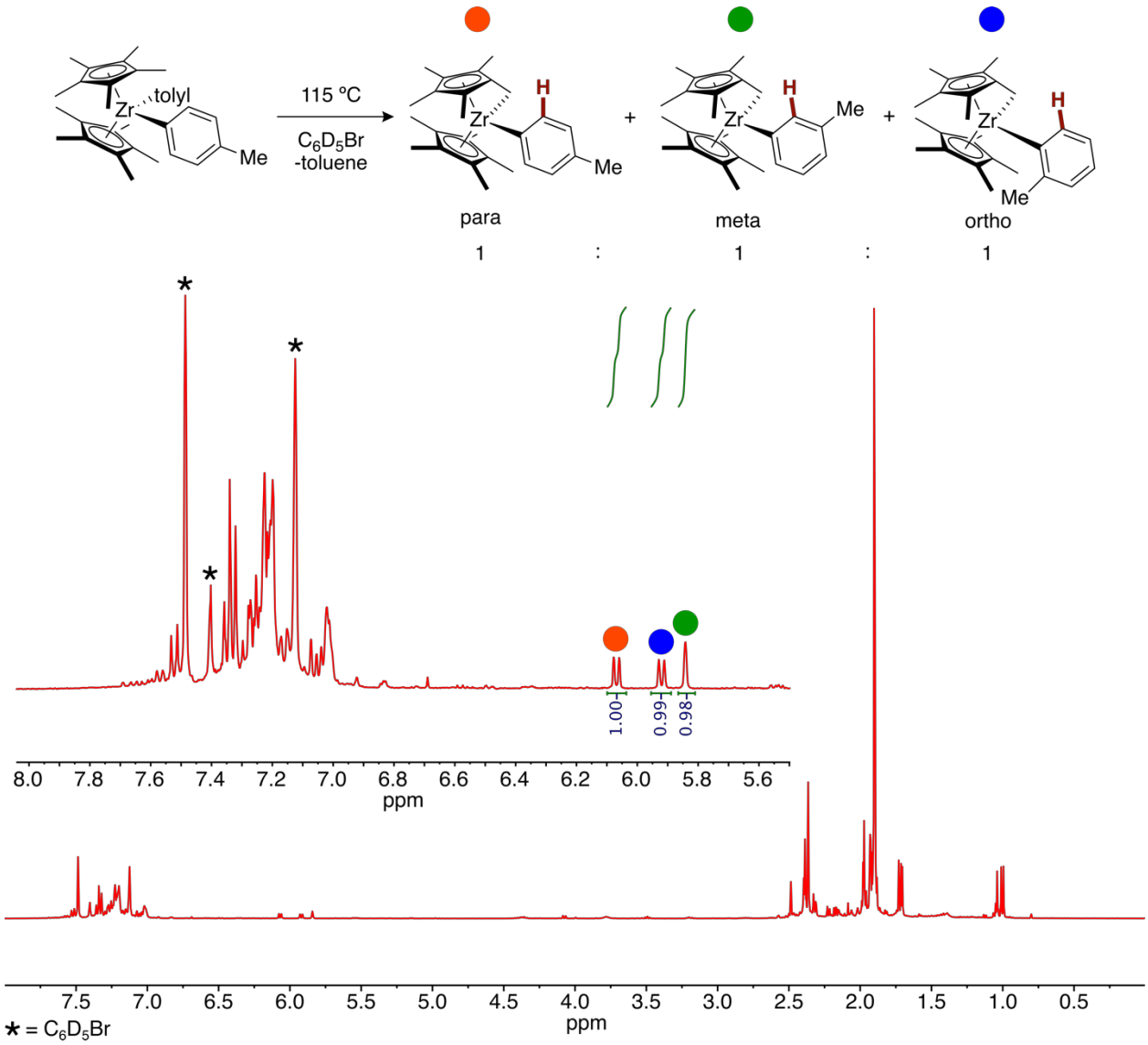


Figure S21. ^{1}H NMR spectrum (C_6D_5Br) of the thermolysis of **8** after 1 h.

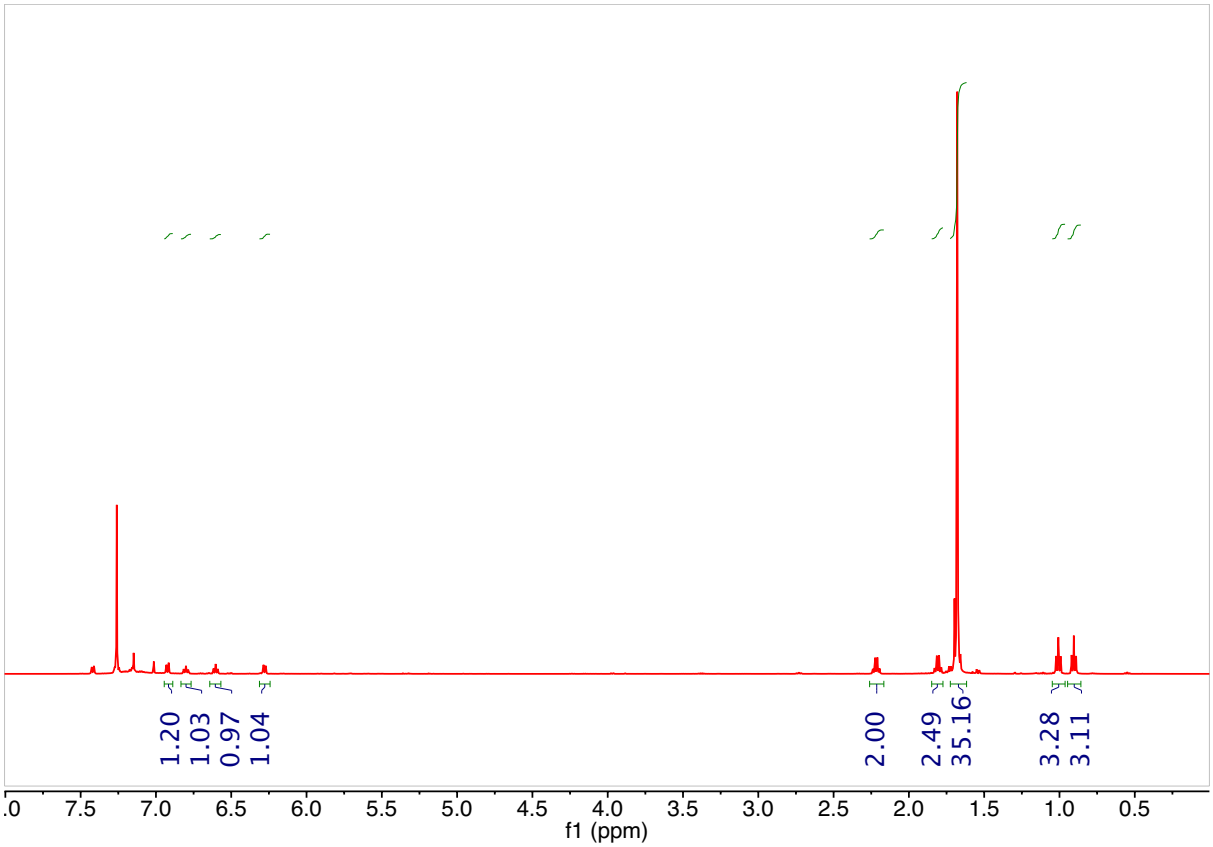


Figure S22. ^{1}H NMR spectrum ($CDCl_3$) of **7a**.

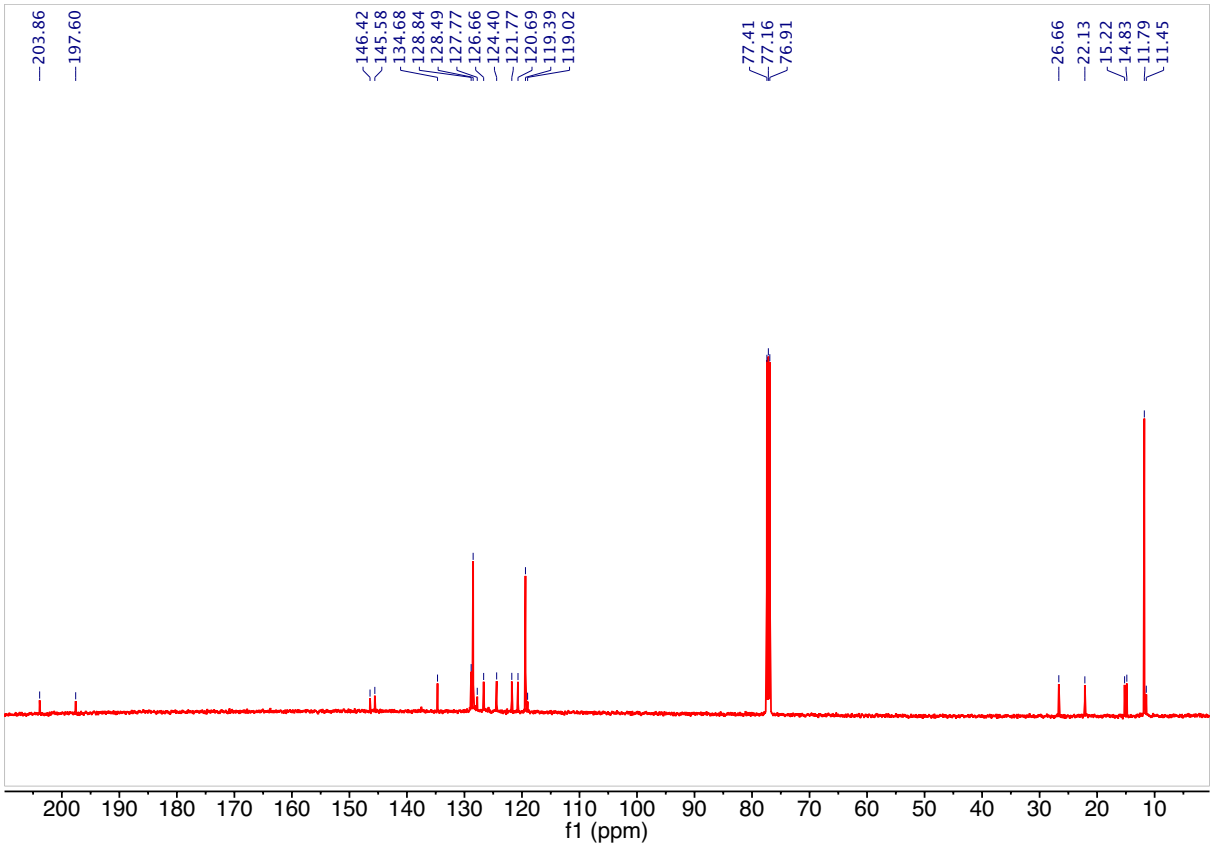


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7a**.

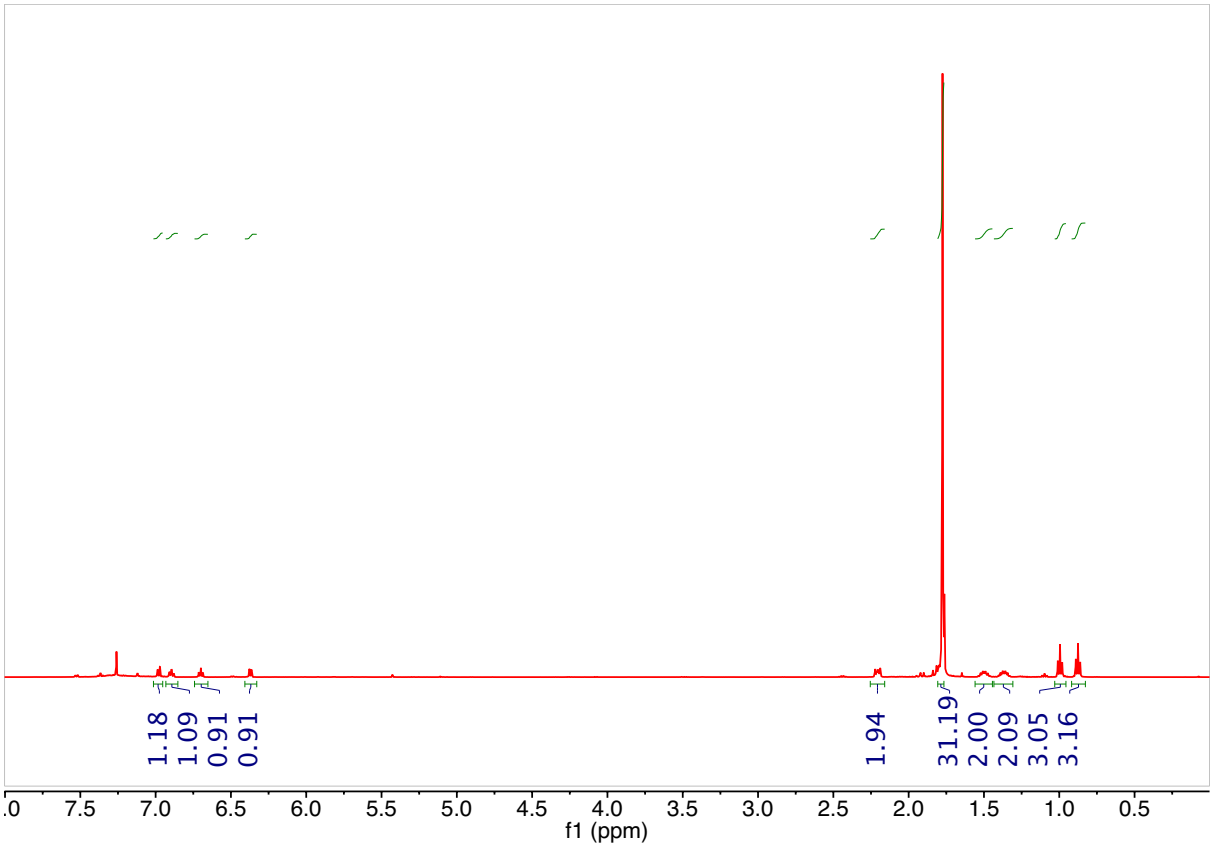


Figure S24. ^{1}H NMR spectrum ($CDCl_3$) of **7b**.

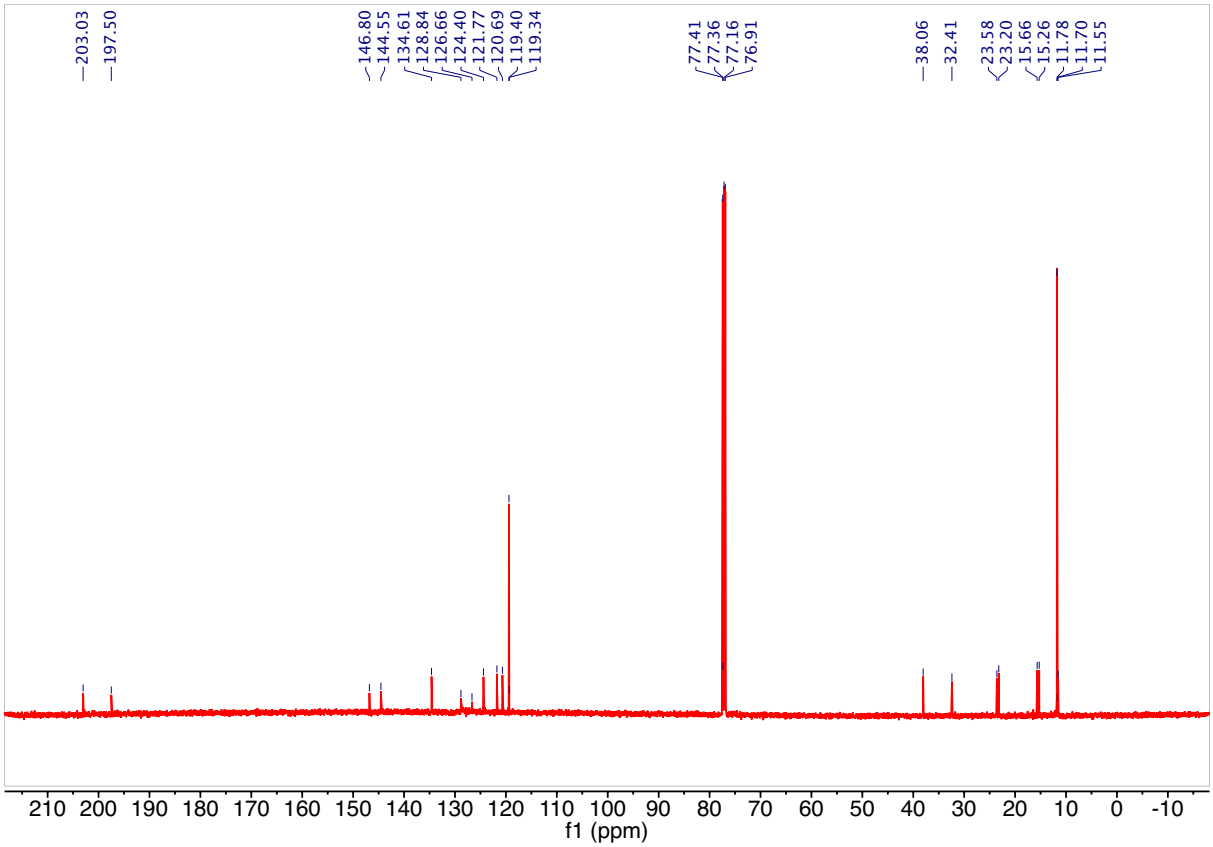


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7b**.

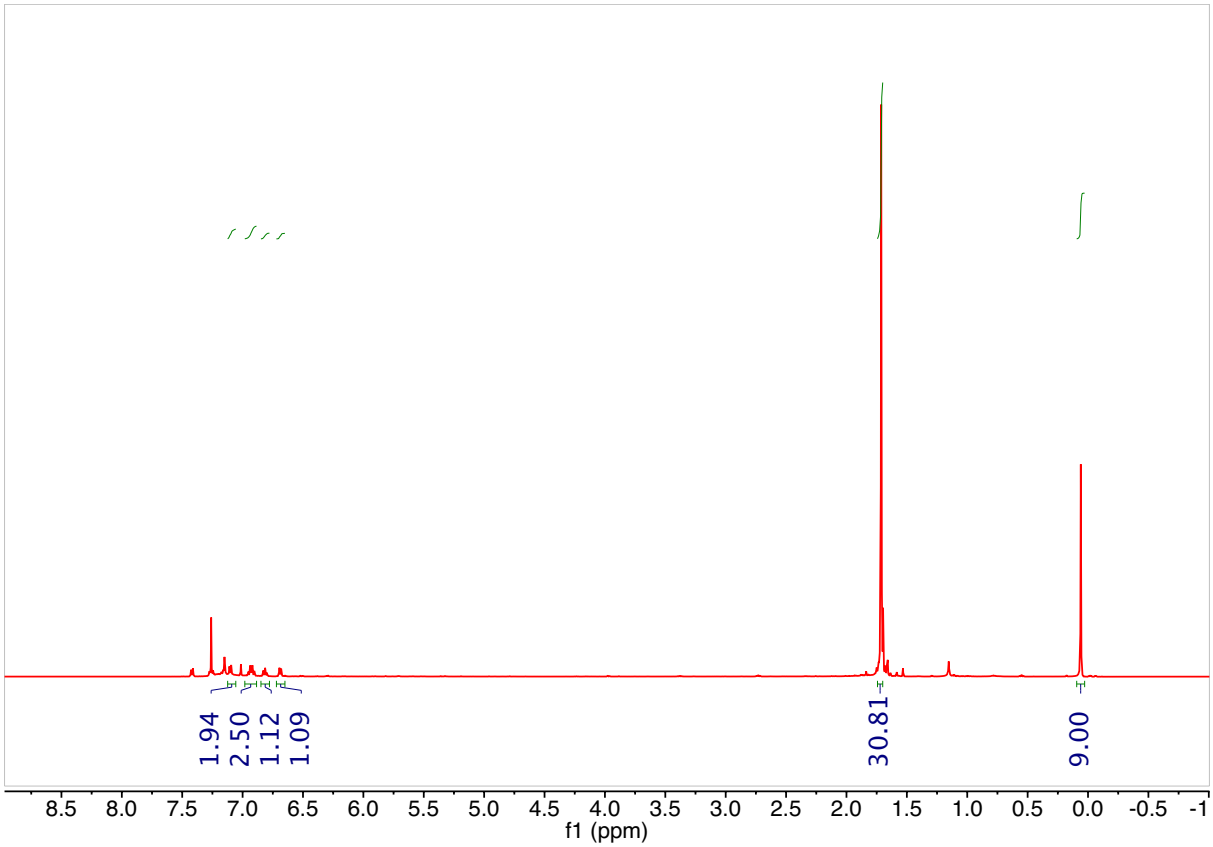


Figure S26. ^{1}H NMR spectrum ($CDCl_3$) of **7c**.

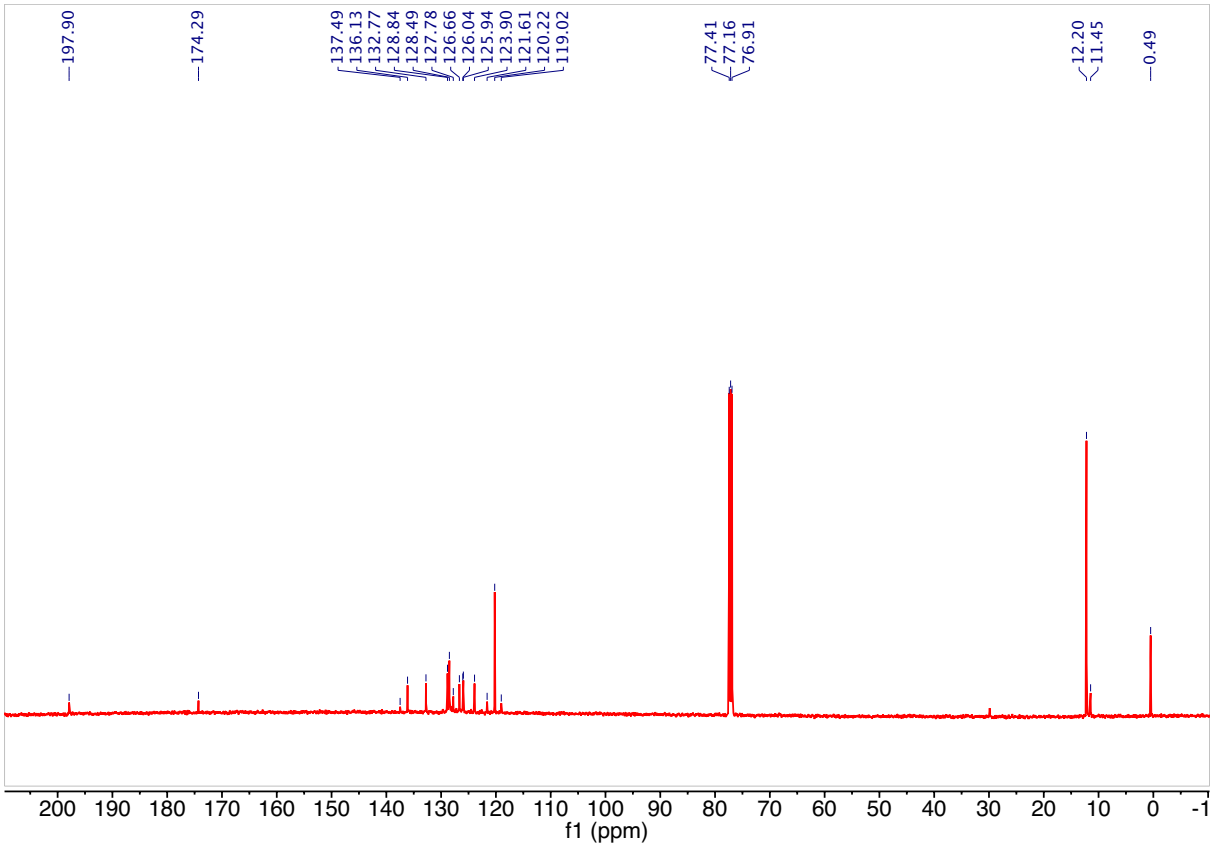


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7c**.

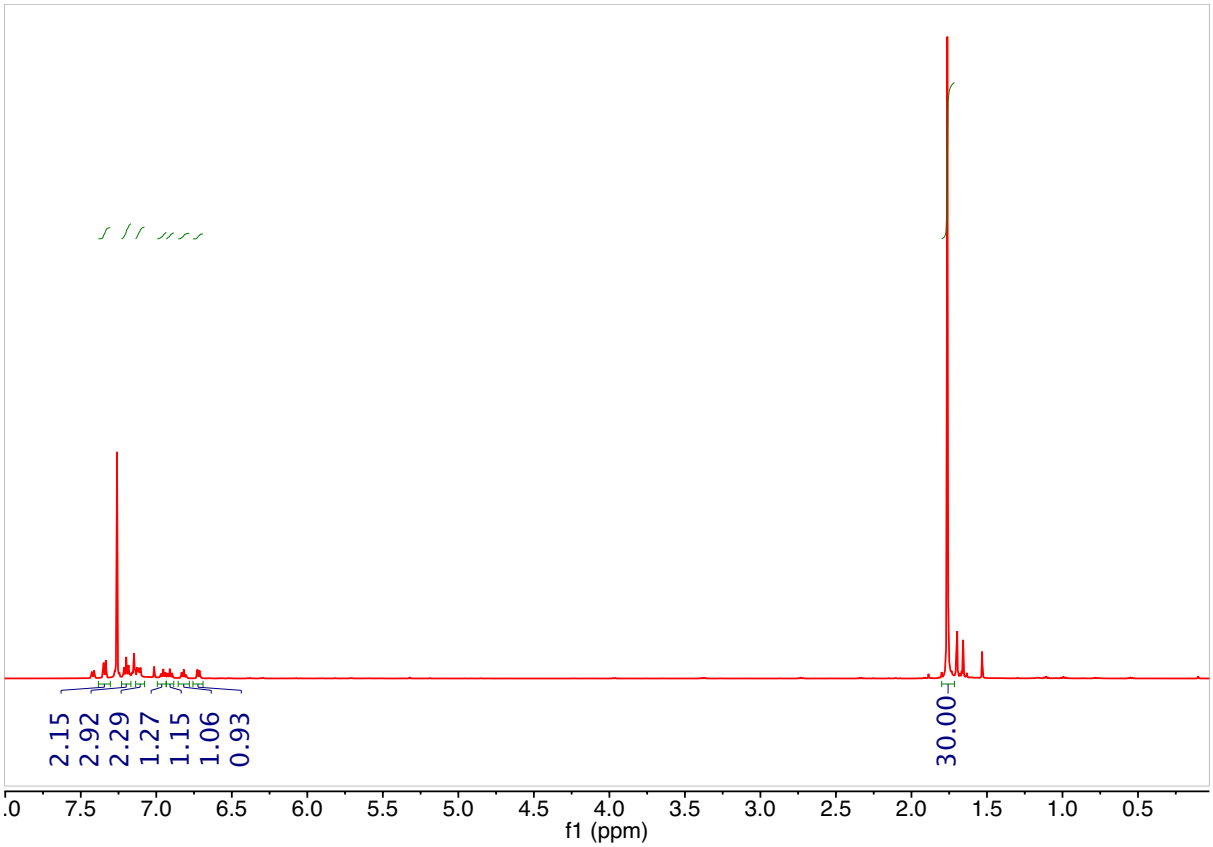


Figure S28. ^{1}H NMR spectrum ($CDCl_3$) of **7d**.

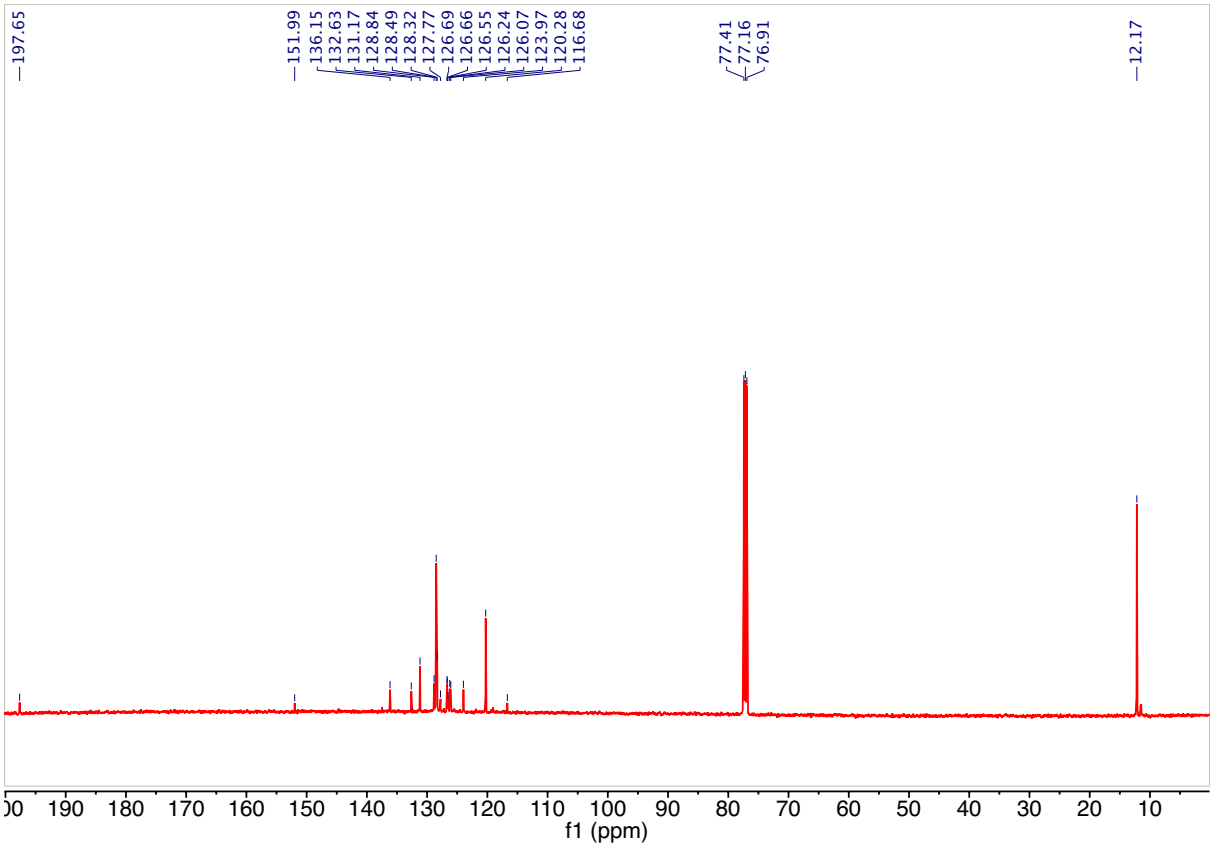


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7d**.

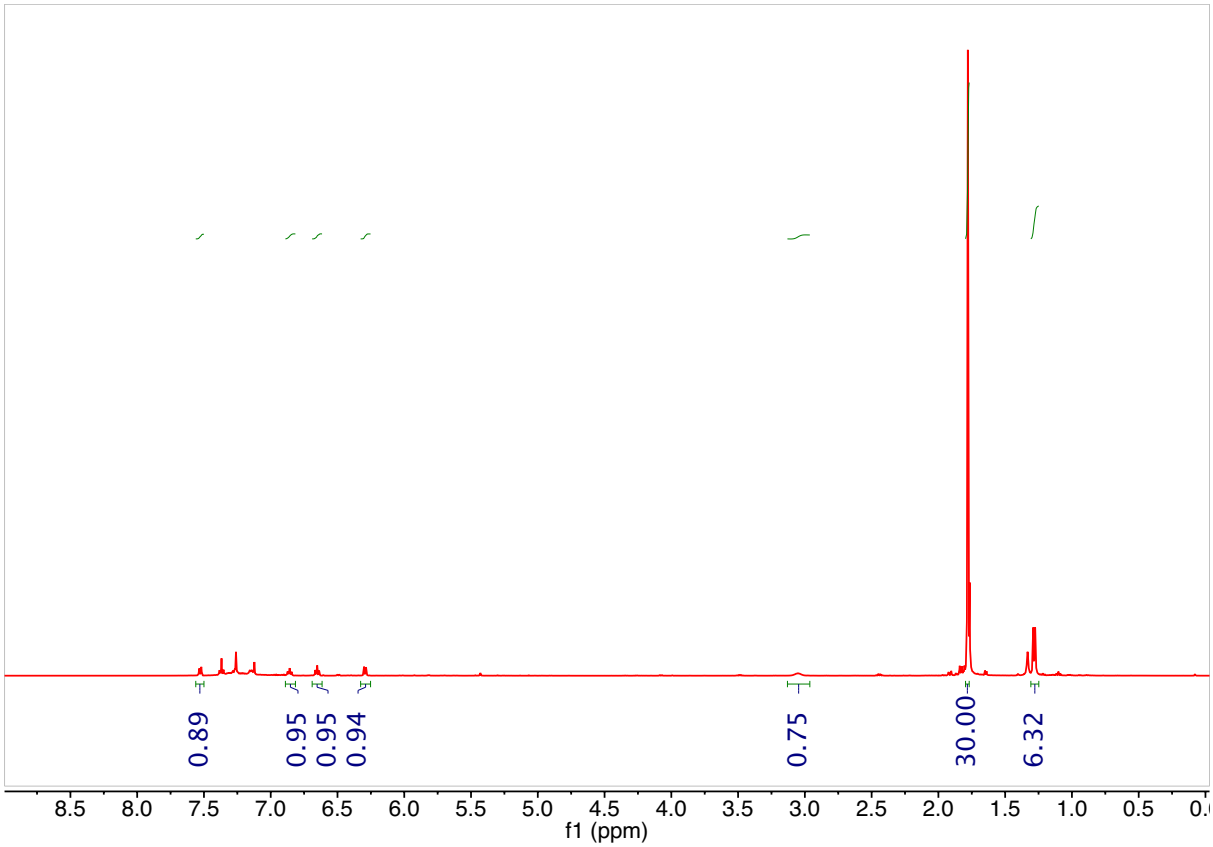


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) of **7e**.

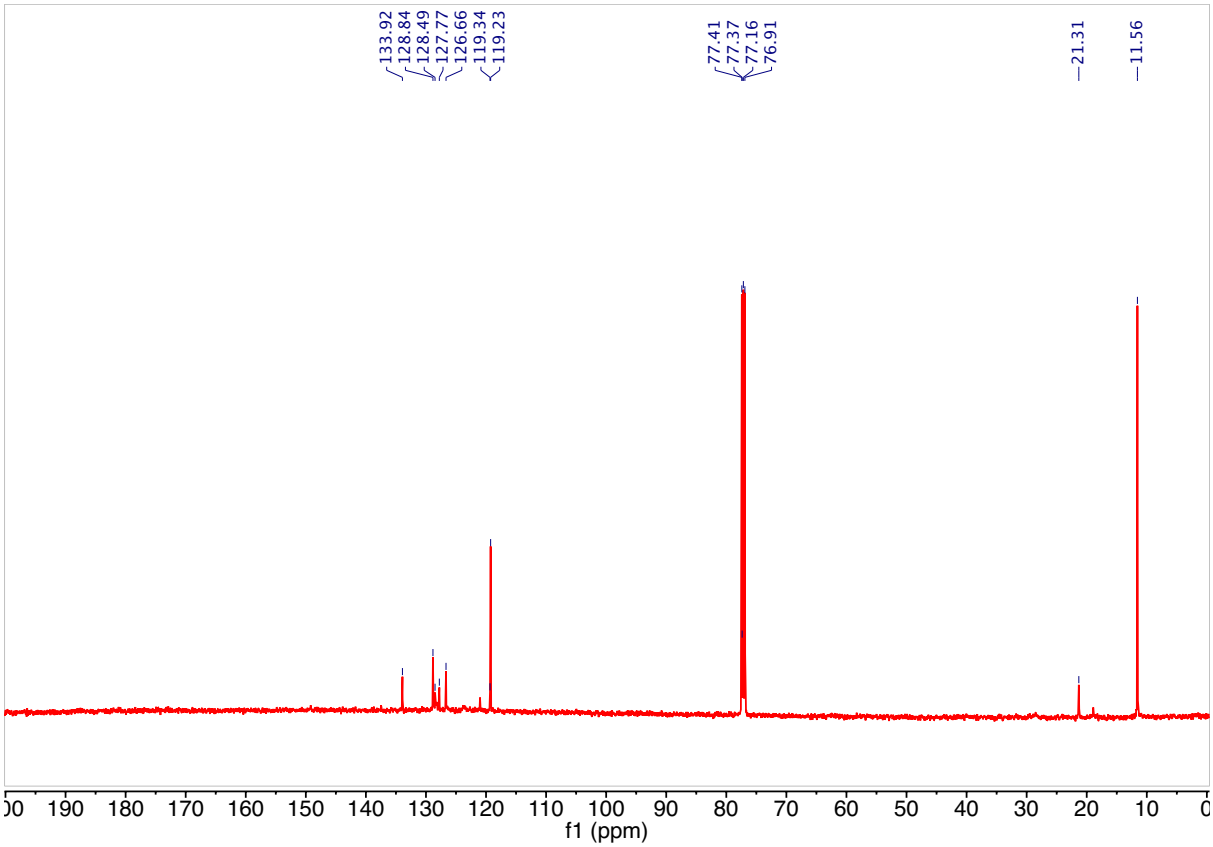


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7e**.

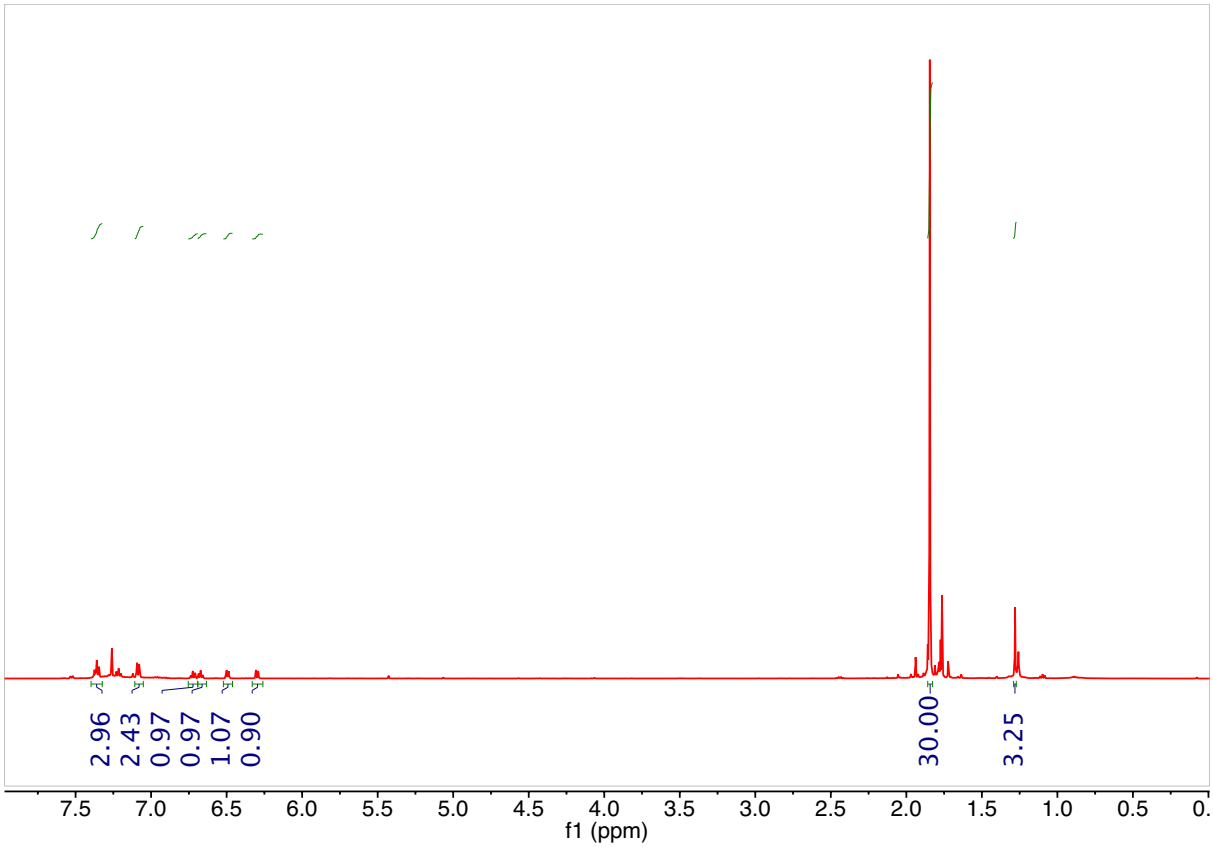


Figure S32. ^{1}H NMR spectrum ($CDCl_3$) of **7f**.

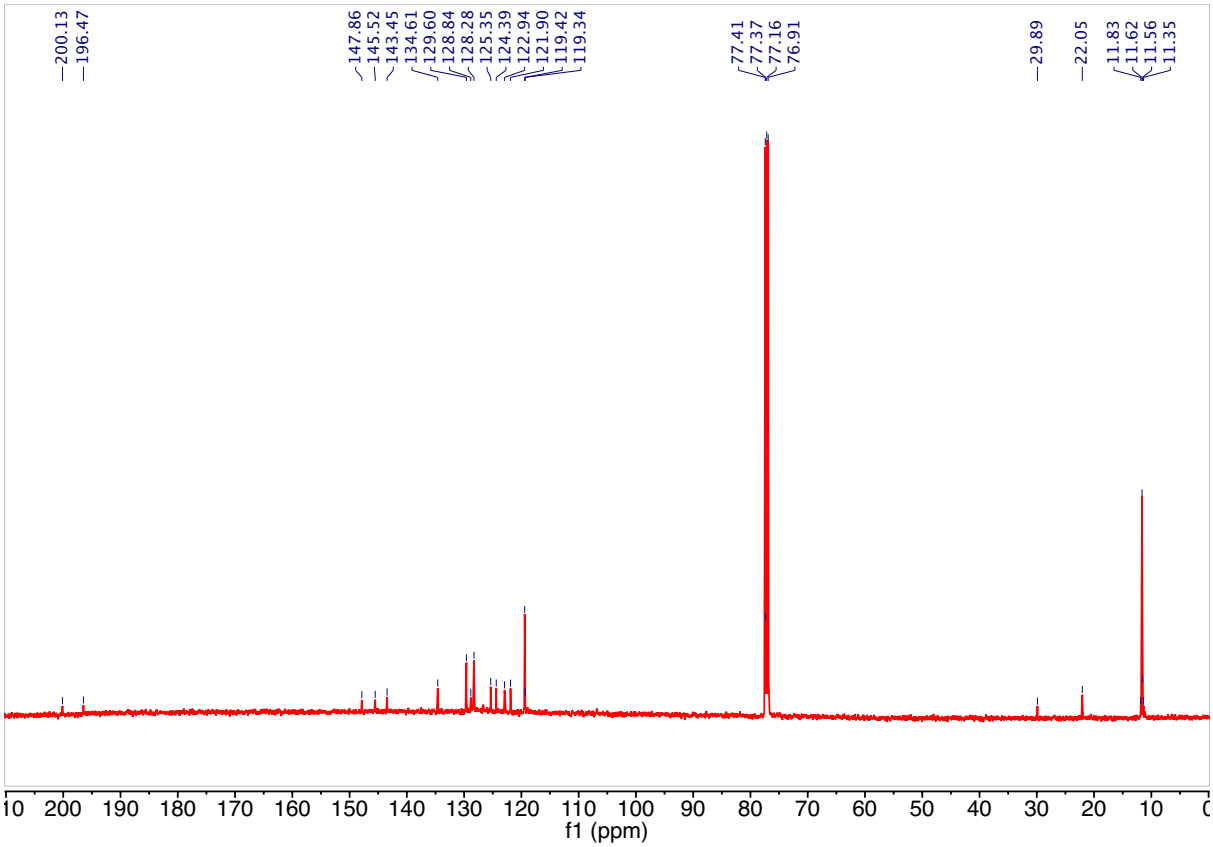


Figure S33. $^{13}C\{^{1}H\}$ NMR spectrum ($CDCl_3$) of **7f**.