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Photochemical Synthesis of a Zirconium Cyclobutadienyl Complex

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Supporting Information

Contents

1. General Considerations

1.1 Materials

Air- and moisture-sensitive procedures were performed under inert atmosphere of a high vacuum line, using Schlenk and cannula techniques, or in a N_2-filled MBraun glovebox. Light-sensitive reactions were conducted in glassware covered with aluminum foil under minimal lighting. All solvents for these manipulations were dried and deoxygenated using a Glass Contour Solvent Purification System and stored over 4 Å molecular sieves,

Diphenylacetylene, 4-methylbenzyl bromide, 1,3,5-trimethoxybenzene, and potassium graphite came from commercial sources and were used without further purification. Syntheses of tetrabenzylzirconium[1,2] and 3,5-dimethyl-2-(2-pyridyl)pyrrole ($H^{Me}PMP^{Me}$)[3] followed reported literature procedures. For glovebox use, all solids were dried under high vacuum overnight. Low boiling liquid substrates were stirred for at least two days over CaH_2 and vacuum transferred into oven-dried glassware prior to bringing into the glovebox; high boiling liquids were dried over CaH_2, degassed, and filtered through Celite in the glovebox. Deuterated solvents for NMR Spectroscopy were vacuum transferred from sodium metal (C_6D_6) or CaH_2 ($CDCl_3$ and CD_2Cl_2).

1.2 Physical Measurements

One- and two-dimensional NMR spectra were collected on an Agilent 400 MHz and Varian $INOVA^{Unity}$ 600 MHz spectrometer at 25 °C. The FIDs (free induction decays) of the 1D and 2D NMR spectra were processed using the NMR software package MestReNova, Product Version 11.0.4-18998. ^1H NMR chemical shifts are reported relative to the residual solvent proton peak at 7.16 ppm (C_6D_6), whereas $^{13}C\{^1H\}$ NMR chemical shifts in C_6D_6 are reported relative to the central peak of the solvent at 128.0 ppm. Mass spectra of organic products were obtained using a Thermo Single Quadrupole mass spectrometer equipped with TraceGOLD GC Columns. Electronic absorption spectra were recorded using a Shimadzu UV-1800 spectrophotometer in gastight quartz cuvettes with a 10 mm path length fitted with J-Young valves. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Ledgewood, NJ.

1.3 Remarks on Elemental Analysis Results

Despite repeated attempts for each compound, the obtained elemental analysis results provided carbon values that were consistently low by 1-2% while the values for hydrogen and nitrogen were generally accurate. This is a well-known problem in early transition metal chemistry and likely

due to the formation of metal carbides even in the presence of combustion aid. For full transparency, we report the most accurate elemental analysis data for each compound in the following experimental section. We also note that we did not observe any indication of impurities in any of the other experimental techniques employed in this study.

1.4 Experimental Setup for Photoreactions

Photoreactions for both NMR- and large-scale were performed using commercially available LED light strips with an emission maximum at 462 nm (Figure S2). A water bath in a jacketed glass beaker or a fan setup helped to support constant room temperature for NMR- and large-scale reactions, respectively (Figure S1).

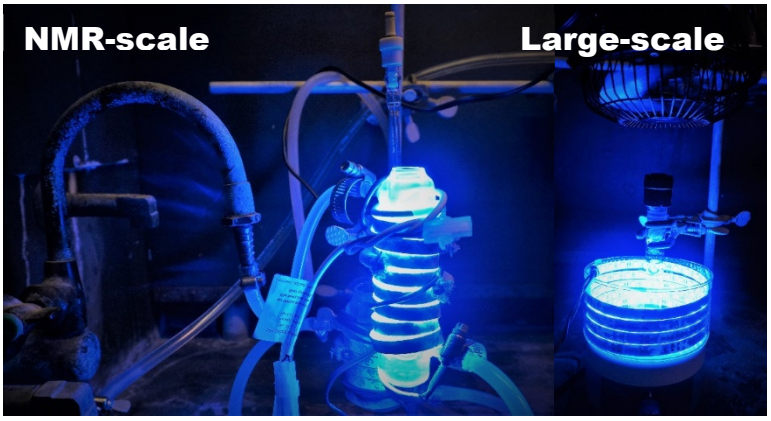


Figure S1. Apparatus for blue light irradiation of NMR tubes and thick-walled glass vessels with Teflon screw caps.

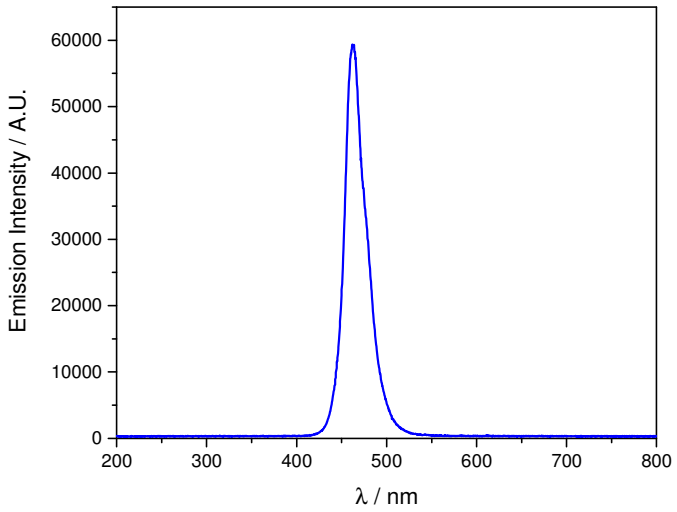


Figure S2. Emission profile of LED light strips in the above setup (λ_{max} = 462 nm).

2. Synthetic Procedures

Preparation of (^{Me}PMP^{Me})$_2$ZrBn$_2$. In the glovebox, a 50 mL round-bottom flask was charged with a solution of $ZrBn_4$ (1.672 g, 3.67 mmol, 1.00 equiv) in 18 mL of toluene. Slow addition of H^{Me}PMP^{Me} (1.264 g, 7.34 mmol, 2.00 equiv) in 10 mL toluene to the above flask resulted in an immediate color change of the reaction mixture to shimmering orange. After stirring overnight, toluene was removed *in vacuo*. The resulting bright orange powder was washed three times with pentane and yielded 1.724 g (76%, 2.80 mmol) of analytically pure product. Layering a saturated toluene solution of this solid with excess *n*-pentane at -33 ºC gave vivid orange crystals suitable for X-ray analysis. ^{1}H NMR (599.67 MHz, C_6D_6; δ, ppm): 7.95 (d, *J* = 5.9 Hz, 2H, *o*-pyH), 7.08 (d, *J* = 8.3 Hz, 2H, *m*-pyH), 6.88 (m, 4H, *o*-PhH), 6.87 (m, 4H, *m*-PhH), 6.83 (m, 2H, *p*-pyH), 6.55 (m, 2H, *p*-PhH), 6.11 (m, 2H, *m*-pyH), 5.74 (s, 2H, pyrrole-H), 2.86 (br.s, 2H, $PhCH_2$), 2.63 (br.s, 2H, $PhCH_2$), 2.22 (s, 6H, pyrrole-CH_3), 1.91 (s, 6H, pyrrole-CH_3). ^{13}C (150.80 MHz, C_6D_6; δ, ppm): 14.50, 15.67, 77.55, 115.70, 116.12, 118.07, 123.36, 124.51, 128.81, 130.68, 134.47, 137.98, 140.82, 142.72, 148.47, 156.82. Anal. Calcd for (^{Me}PMP^{Me})$_2$ZrBn$_2$, $C_{36}H_{36}N_4Zr$: C, 70.19; H, 5.90; N, 9.10. Found: C, 68.33; H, 5.89; N, 9.06.

Preparation of (^{Me}PMP^{Me})$_2$ZrBr$_2$. Under minimal lighting in a glovebox, (^{Me}PMP^{Me})$_2$ZrBn$_2$ (58 mg, 1.00 equiv) and 4-methylbenzylbromide (35 mg, 2.00 equiv) were combined in a thick-walled glass vessel containing 10 mL benzene. The reaction vessel was sealed with a PTFE screw cap and covered with aluminum foil before removal from the glovebox. After irradiating with blue LED light (λ_{max} = 462 nm) for three hours, solvent was removed *in vacuo* inside the N_2 filled glovebox. The orange red powder was washed three times with pentane. After drying under vacuum, 46 mg (82% yield) of product were collected. Layering a saturated toluene solution of this solid with excess *n*-pentane at -33 ºC gave intense red crystals suitable for X-ray analysis. ^{1}H NMR (399.78 MHz, C_6D_6; δ, ppm): 7.27 (d, *J* = 6.3 Hz, 2H, *o*-pyH), 6.73 (d, *J* = 9.2 Hz, 2H, *m*-pyH), 6.47 (m, 2H, *p*-pyH), 5.90 (s, 2H, pyrrole-H), 5.86 (m, 2H, *m*-pyH), 2.96 (s, 6H, pyrrole-CH_3), 2.02 (s, 6H, pyrrole-CH_3). ^{13}C (100.53 MHz, C_6D_6; δ, ppm): 14.26, 18.86, 116.35, 117.20, 118.01, 127.13, 133.83, 139.07, 141.46, 147.95, 155.25. Anal. Calcd for (^{Me}PMP^{Me})$_2$ZrBr$_2$ · 0.5 C_6H_6, $C_{25}H_{25}N_4Br_2Zr$: C, 47.47; H, 3.98; N, 8.86. Found: C, 45.29; H, 3.94; N, 8.64.

Preparation of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$). Under minimal lighting in a glovebox, (^{Me}PMP^{Me})$_2$ZrBn$_2$ (103 mg, 1.00 equiv) and diphenylacetylene (66 mg, 2.20 equiv) were combined

in a thick-walled glass vessel containing 10 mL benzene. The reaction vessel was sealed with a PTFE screw cap and covered with aluminum foil before leaving the glovebox. After irradiating with blue LED light (λ_{max} = 462 nm) for four hours, solvent was removed *in vacuo* inside the N_2 filled box. Attempts to remove bibenzyl by washing with pentane lead to minor decomposition of $(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$ to the corresponding *cis*-1,2,3,4-tetraphenylcyclobutene and *cis,trans*-1,2,3,4-tetraphenylbutadiene.[4] Recrystallization of the crude reaction mixture from toluene and pentane at -33 °C provided 69 mg of dark brown crystals (52% yield). ^{1}H NMR (399.78 MHz, C_6D_6; δ, ppm): 8.07 (br.s, 2H, *o*-pyH), 7.81 (d, *J* = 7.8 Hz, 8H, *o*-PhH), 7.04 (m, 8H, *m*-PhH), 6.90 (d, *J* = 8.7 Hz, 2H, *m*-pyH), 6.87 (m, 4H, *p*-PhH), 6.65 (m, 2H, *m*-pyH), 5.96 (m, 2H, *p*-pyH), 5.71 (s, 2H, pyrrole-H), 1.96 (s, 6H, pyrrole-CH_3), 1.73 (br.s, 6H, CH_3 adjacent to pyrrole-N). ^{13}C (150.80 MHz, C_6D_6; δ, ppm): 15.08, 17.34, 114.83, 114.84, 117.54, 117.72, 124.86, 128.29, 128.00 (2 overlapped peaks), 129.01, 129.39, 138.63, 138.87, 149.09, 154.51. Anal. Calcd for $(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$, $C_{50}H_{42}N_4Zr$: C, 76.00; H, 5.37; N, 7.09. Found: C, 74.25; H, 5.49; N, 6.72.

Preparation of $(^{Me}PMP^{Me})_2Zr(C_4Ph_4)$. In the glovebox, $(^{Me}PMP^{Me})_2ZrBr_2$ (126 mg, 1.00 equiv.) and diphenylacetylene (76 mg, 2.00 equiv.) were dissolved in 10 mL toluene before cooling to -33 °C. This cold solution was then added to a scintillation vial containing solid KC_8 (88 mg, 3.07 equiv.) also at -33 °C. The orange suspension was stirred at ambient temperature with no significant color change for 6.5 hours. After 20 hours, the resulting brown suspension was filtered through Celite followed by removal of all volatiles *in vacuo*. Recrystallization of the crude material from toluene and pentane at -33 °C gave a small amount of orange crystals suitable for X-ray analysis. ^{1}H NMR (from crude reaction mixture, 599.67 MHz, C_6D_6; δ, ppm): 8.05 (d, *J* = 5.8 Hz, 2H, *o*-pyH), 7.10 (d, *J* = 7.5 Hz, 4H, *o*-PhH), 6.96 (d, *J* = 8.4 Hz, 2H, *m*-pyH), 6.82 (m, 8H, *o*-PhH and *m*-PhH), 6.83 (m, 4H, *m*-PhH), 6.70 (m, 2H, *p*-PhH), 6.68 (m, 2H, *m*-pyH), 6.62 (m, 2H, *p*-PhH), 5.97 (m, 2H, *p*-pyH), 5.88 (s, 2H, pyrrole-H), 2.71 (s, 6H, CH_3 adjacent to pyrrole-N), 2.15 (s, 6H, pyrrole-CH_3).

3. X-Ray Crystallography

Single crystals suitable for X-ray diffraction were coated with polyisobutylene oil (Sigma-Aldrich) in a drybox, transferred to a nylon loop, and then quickly transferred to the goniometer head of a Bruker AXS D8 Venture fixed-chi X-ray diffractometer equipped with a Triumph monochromator, a Mo Kα radiation source (λ = 0.71073 Å), and a PHOTON 100 CMOS detector. The samples were cooled to 100 K with an Oxford Cryostream 700 system and optically aligned using a video camera. The APEX3 software program (version 2016.9-0)[5] was used for diffractometer control, preliminary frame scans, indexing, orientation matrix calculations, least-squares refinement of cell parameters, collection strategy optimization, and data collection. Three sets of 12 frames each were collected using the omega scan method with a 10 s exposure time and indexed to produce a crystal orientation matrix for the crystal lattice that was then used to determine an optimal strategy for data collection. The data were integrated using the SAINT+ program and corrected for absorption using SADABS. The structures were solved using direct methods (SHELXS) or intrinsic phasing (SHELXT) completed by subsequent Fourier synthesis and refined by full-matrix least-squares procedures using the programs provided by SHELXL-2014.[6]

Table S1. Crystallographic Data Collection and Refinement Details for $(^{Me}PMP^{Me})_2ZrBn_2$, $(^{Me}PMP^{Me})_2Zr(\eta_4\text{-}C_4Ph_4) \cdot 2\ C_7H_8$, $(^{Me}PMP^{Me})_2ZrBr_2$, and $(^{Me}PMP^{Me})_2Zr(C_4Ph_4) \cdot 2\ C_7H_8$.

	$(^{Me}PMP^{Me})_2ZrBn_2$	$(^{Me}PMP^{Me})_2Zr(\eta_4\text{-}C_4Ph_4) \cdot 2\ C_7H_8$	$(^{Me}PMP^{Me})_2ZrBr_2$	$(^{Me}MP^{Me})_2Zr(C_4Ph_4) \cdot 1.5\ C_7H_8$
Chem. Formula	$C_{36}H_{36}N_4Zr$	$C_{64}H_{58}N_4Zr$	$C_{22}H_{22}Br_2N_4Zr$	$C_{60.5}H_{54}N_4Zr$
Cryst. Size, mm^3	0.064 x 0.418 x 0.443	0.050 x 0.278 x 0.518	0.116 x 0.298 x 0.572	0.350 × 0.309 × 0.132
Fw, g/mol	615.91	974.36	593.47	928.29
Space Group	C2/c	Aba2	$P2_1/c$	$P2_1/n$
a, Å	32.4207(13)	19.5532(9)	8.8984(5)	15.9626(8)
b, Å	11.5918(5)	25.1205(11)	15.1436(9)	19.6034(9)
c, Å	16.0701(6)	20.2947(9)	16.4410(10)	16.6714(8)
α, deg	90°	90°	90°	90°
β, deg	104.6983(11)°	90°	95.628(2)°	114.863(2)
γ, deg	90°	90°	90°	90°
V, Å	5841.7(4)	9968.5(8)	2204.8(2)	4733.3(4)
Z	8	8	4	4
T, K	100(2)	100(2)	100(2)	100(2)
ρ calcd, g cm^{-3}	1.401	1.298	1.788	1.303
Reflns Collected/$2\Theta_{max}$	34862/65.24	45692/55.14	41553/60.00	94628/55.23
Unique Reflns/I>2σ(*I*)	10660/8655	11009/9687	6431/5370	10870/8198
No. of Params/restraints	374/0	616/1	266/0	824/799
λ, Å	0.71073	0.71073	0.71073	0.71073
R1[a]/goodness of fit[b]	0.0414/1.085	0.0431/1.086	0.0553/1.085	0.0509/1.057
wR2[c] (*I*>2σ(*I*))	0.0915	0.0790	0.1079	0.0995
Residual density, e$Å^{-3}$	1.106 and -0.772	0.549 and -0.414	1.582 and -1.542	0.66 and -0.70
Flack parameter	-	0.028(12)	-	-

[a]Observation criterion: $I > 2\sigma(I)$, $R_1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$. [b]GoF = $[\Sigma[w(F_o^2 - F_c^2)^2] / (n\text{-}p)]^{1/2}$. [c]$wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

4. NMR Spectroscopic Characterization

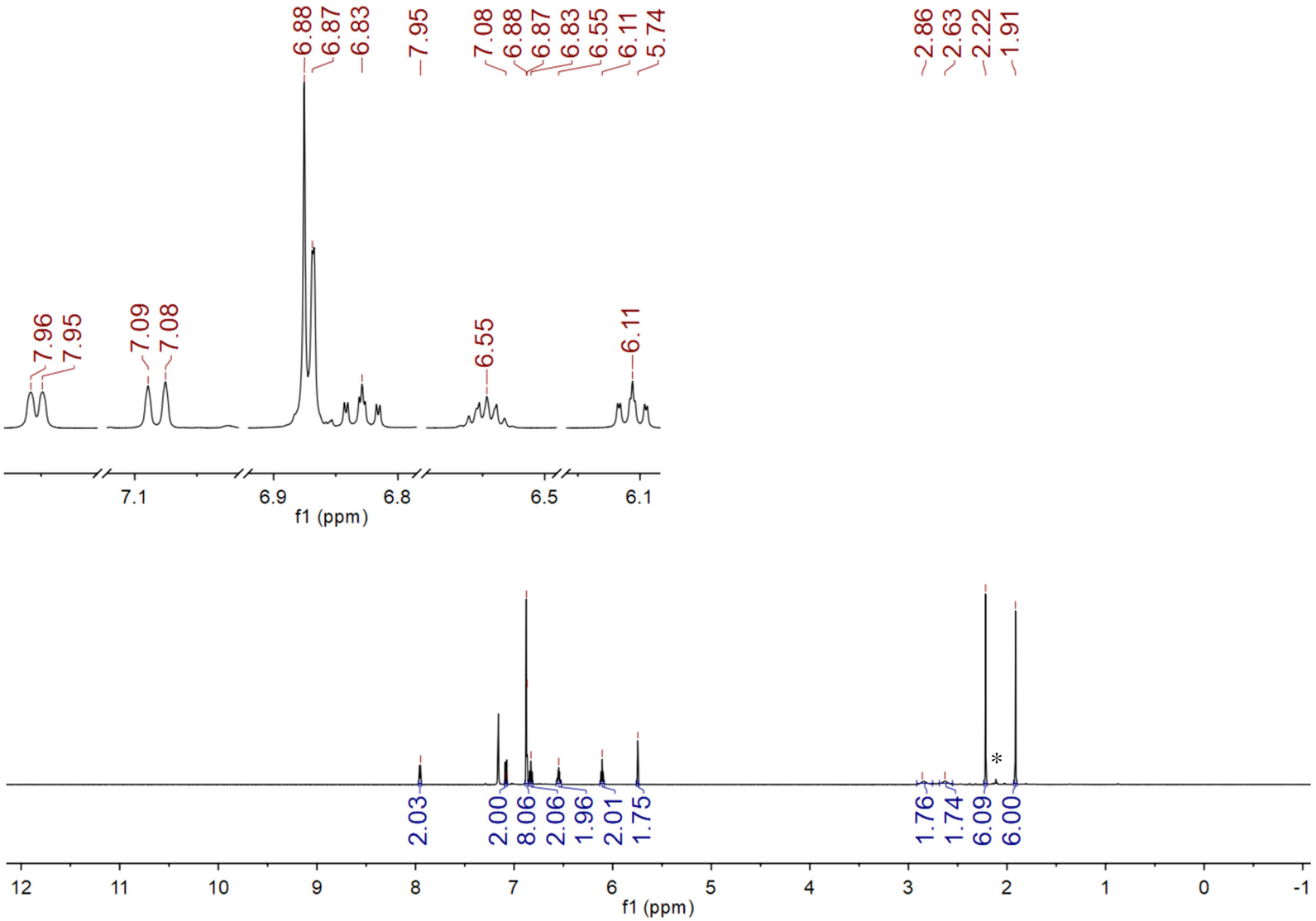


Figure S3. ^{1}H NMR spectrum of (^{Me}PMP^{Me})$_2$ZrBn$_2$ in C_6D_6 at room temperature. *Toluene solvent peak.

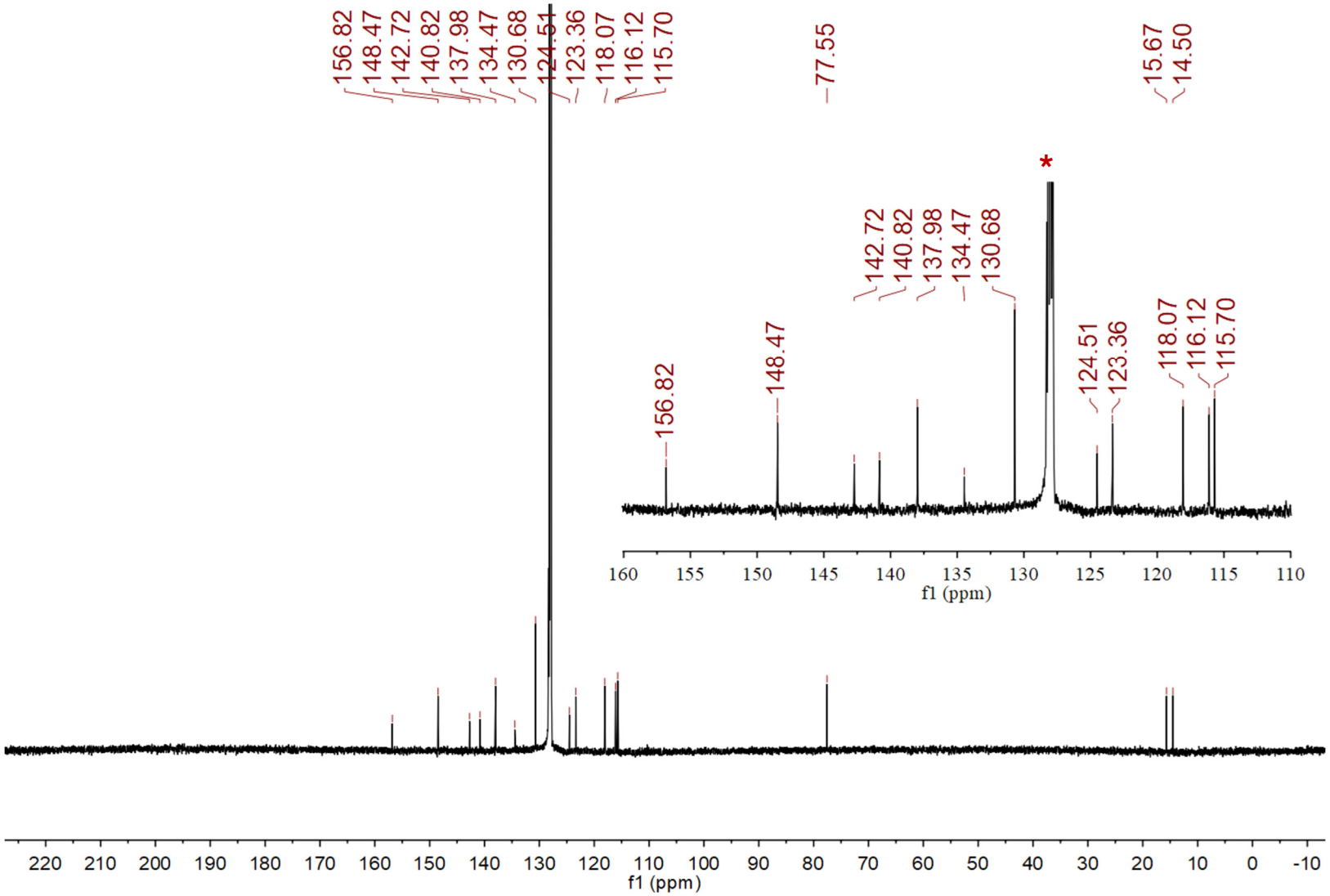


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of $(^{Me}PMP^{Me})_2ZrBn_2$ in C_6D_6. *One ^{13}C resonance is hidden under the solvent residual signal (see HSQC, Figure S5).

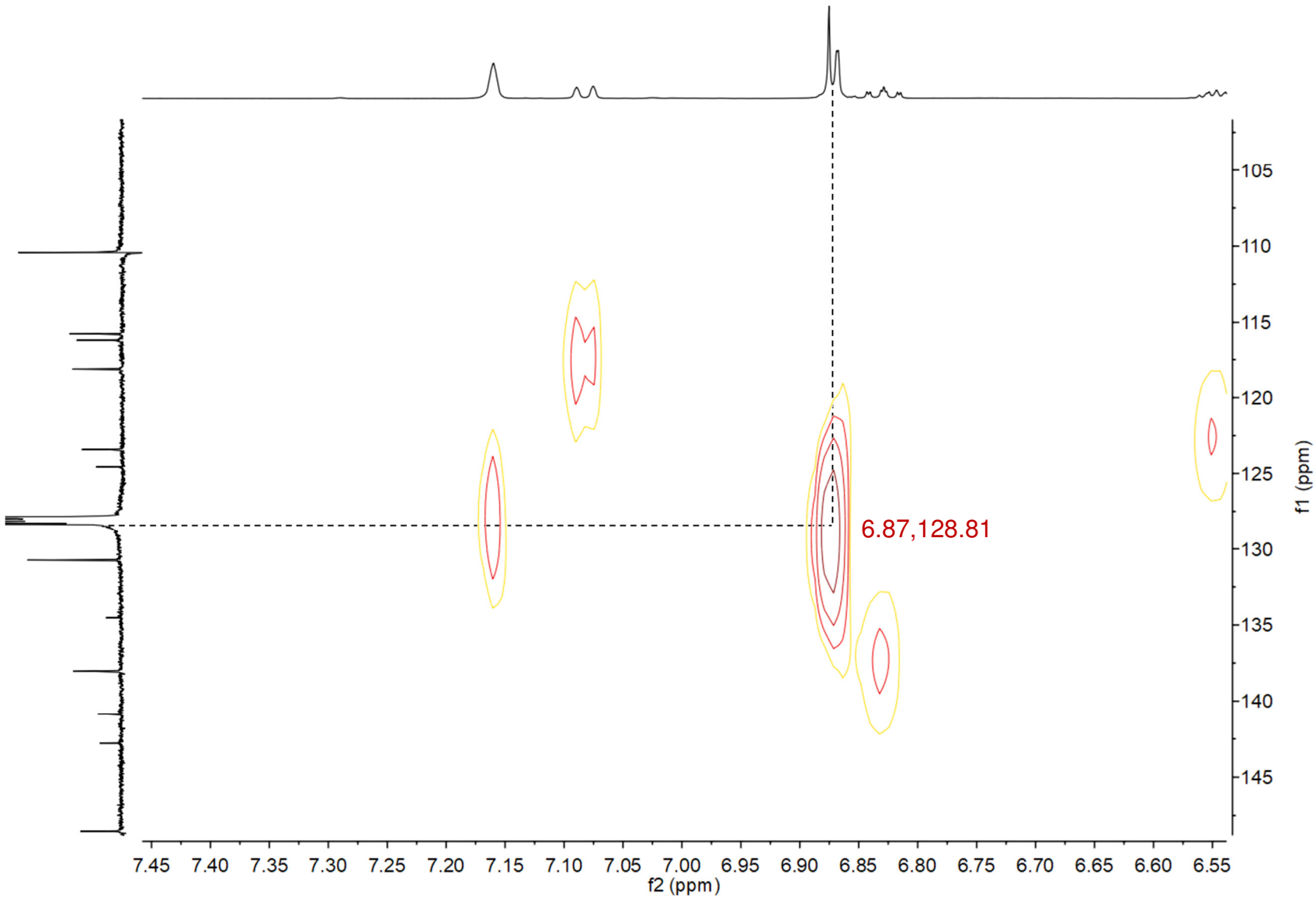


Figure S5. The expanded region of gHSQCAD of (^{Me}PMP^{Me})$_2$ZrBn$_2$ showing the overlap between the solvent residual signal and one of the phenyl resonances at ca. 128 ppm.

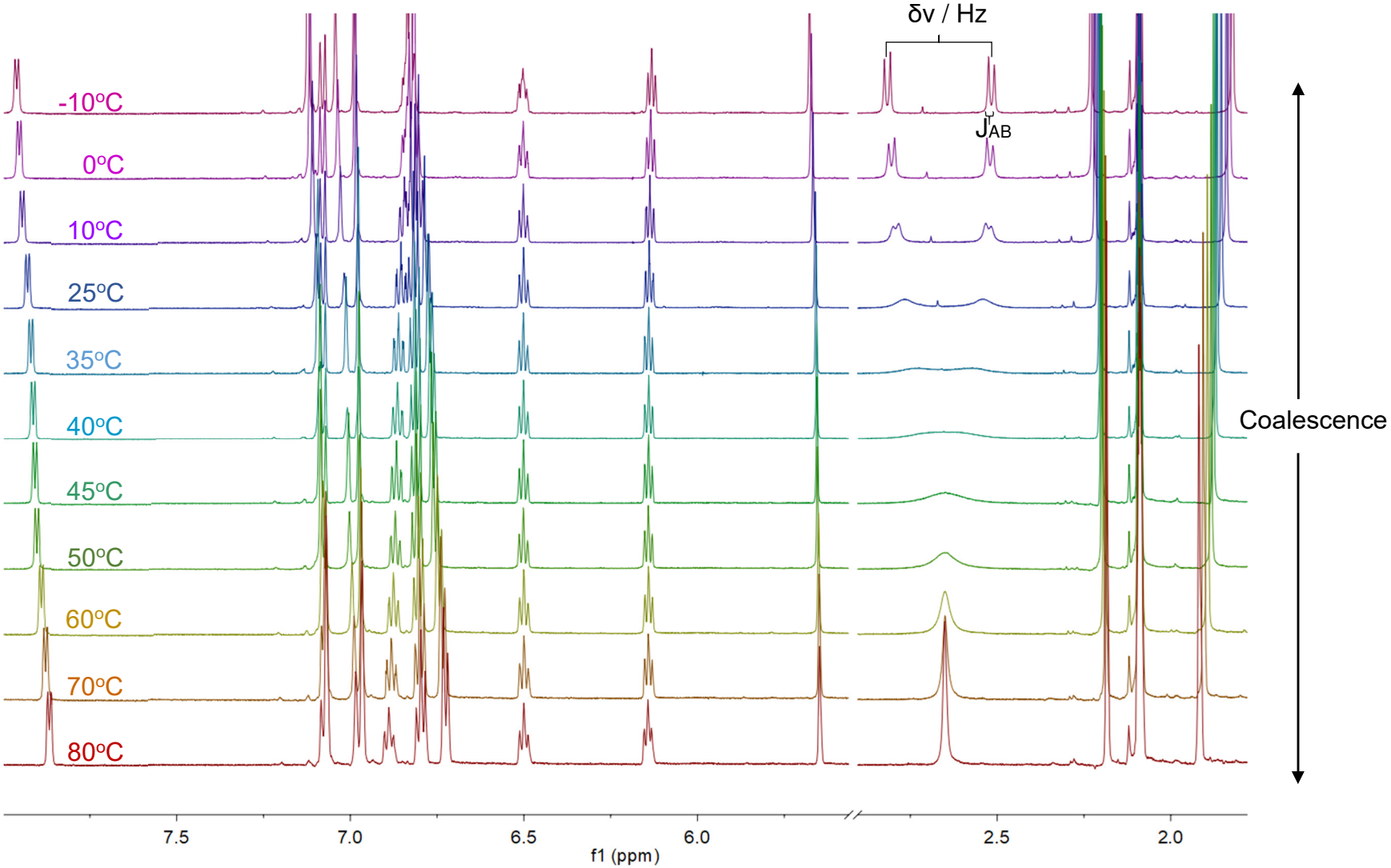


Figure S6. Variable-temperature ^{1}H NMR spectra (599.67 MHz) of (^{Me}PMP^{Me})$_2$ZrBn$_2$ in toluene-*d*$_8$ from -10 °C to 80 °C highlighting the dynamic behavior associated with the benzyl groups. Only parts of the aliphatic and aromatic regions are shown for clarity.

4.1 Variable Temperature NMR Analysis of the Dynamic Process in $(^{Me}PMP^{Me})_2ZrBn_2$

- Energy barrier for the dynamic process at 2.86 and 2.63 ppm

From Figure S6

$\delta\nu$ = 179.71 Hz
J_{AB} = 10.17 Hz

$$\Delta G^{\ddagger} = RT_C\left[22.96 + \ln\left(\frac{T_C}{\delta\nu}\right)\right]\left(\frac{J}{mol}\right)$$

$= (8.314\ J\ K^{-1}\ mol^{-1})(313.15\ K)[22.96 + \ln(\frac{313.15}{179.71})] = 61{,}223\ J\ mol^{-1} = 14.6\ kcal\ mol^{-1}$

- Rate constant at coalescent temperature of 313.15 K (40°C)

$$k_{coal} = \frac{\pi\sqrt{(\nu_A - \nu_B)^2 + 6J_{AB}^2}}{\sqrt{2}} = \frac{\pi\sqrt{(179.71\ Hz)^2 + [6*(10.17\ Hz)^2]}}{\sqrt{2}} = 403\ s^{-1}$$

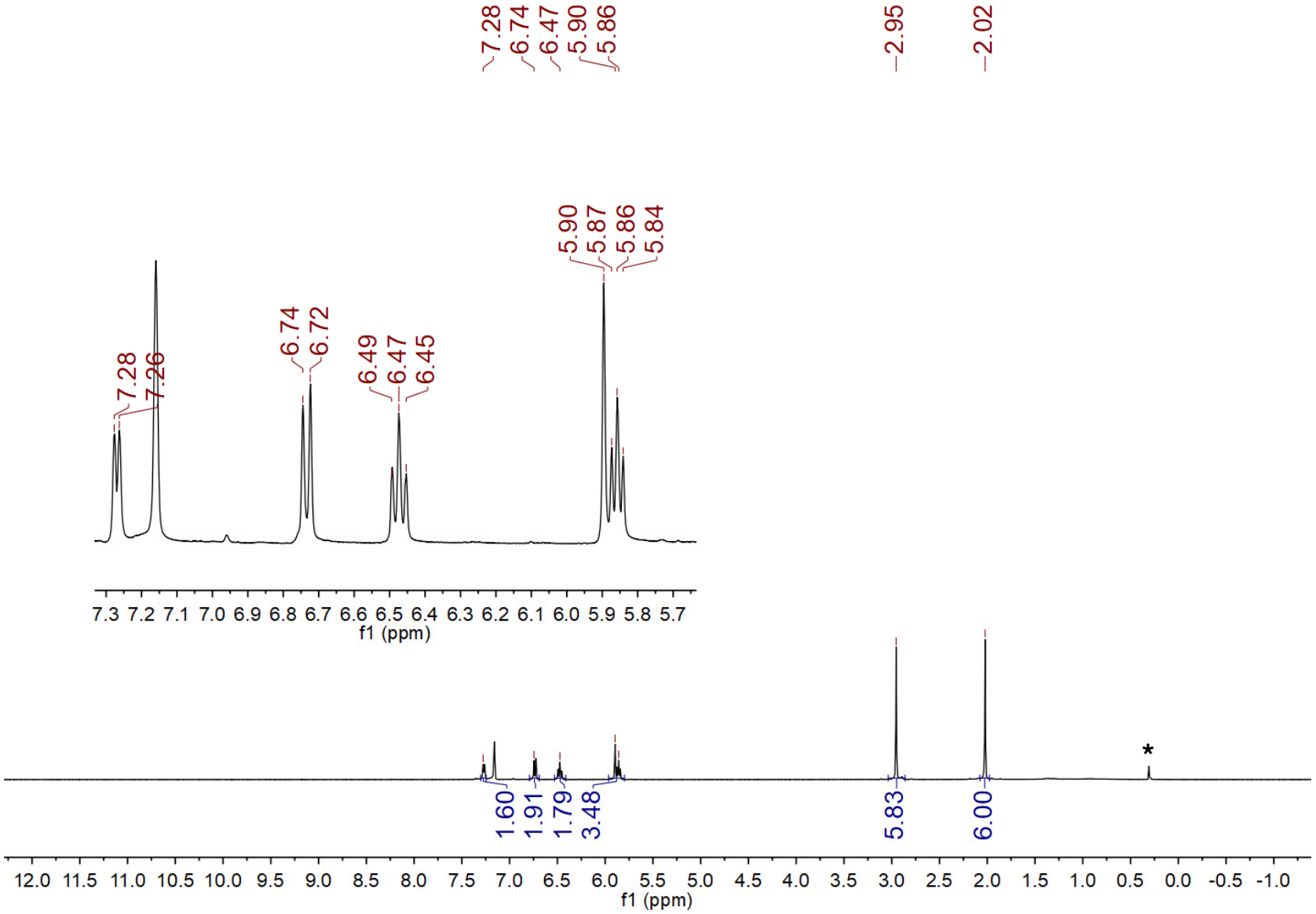


Figure S7. ^{1}H NMR spectrum of $(^{Me}PMP^{Me})_2ZrBr_2$ in C_6D_6 (399.78 MHz). *Silicone grease.

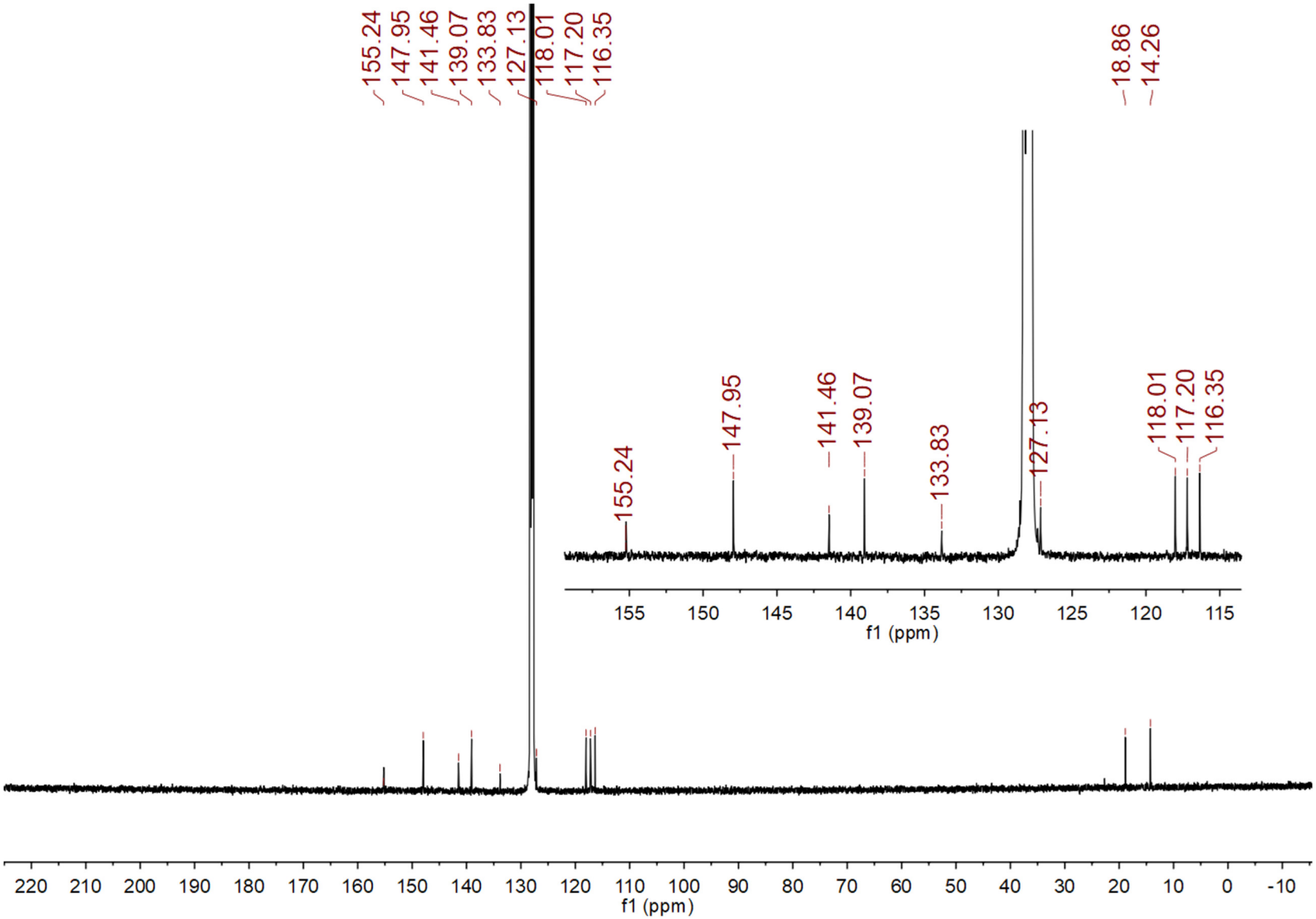


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of $(^{Me}PMP^{Me})_2ZrBr_2$ in C_6D_6 (100.53 MHz).

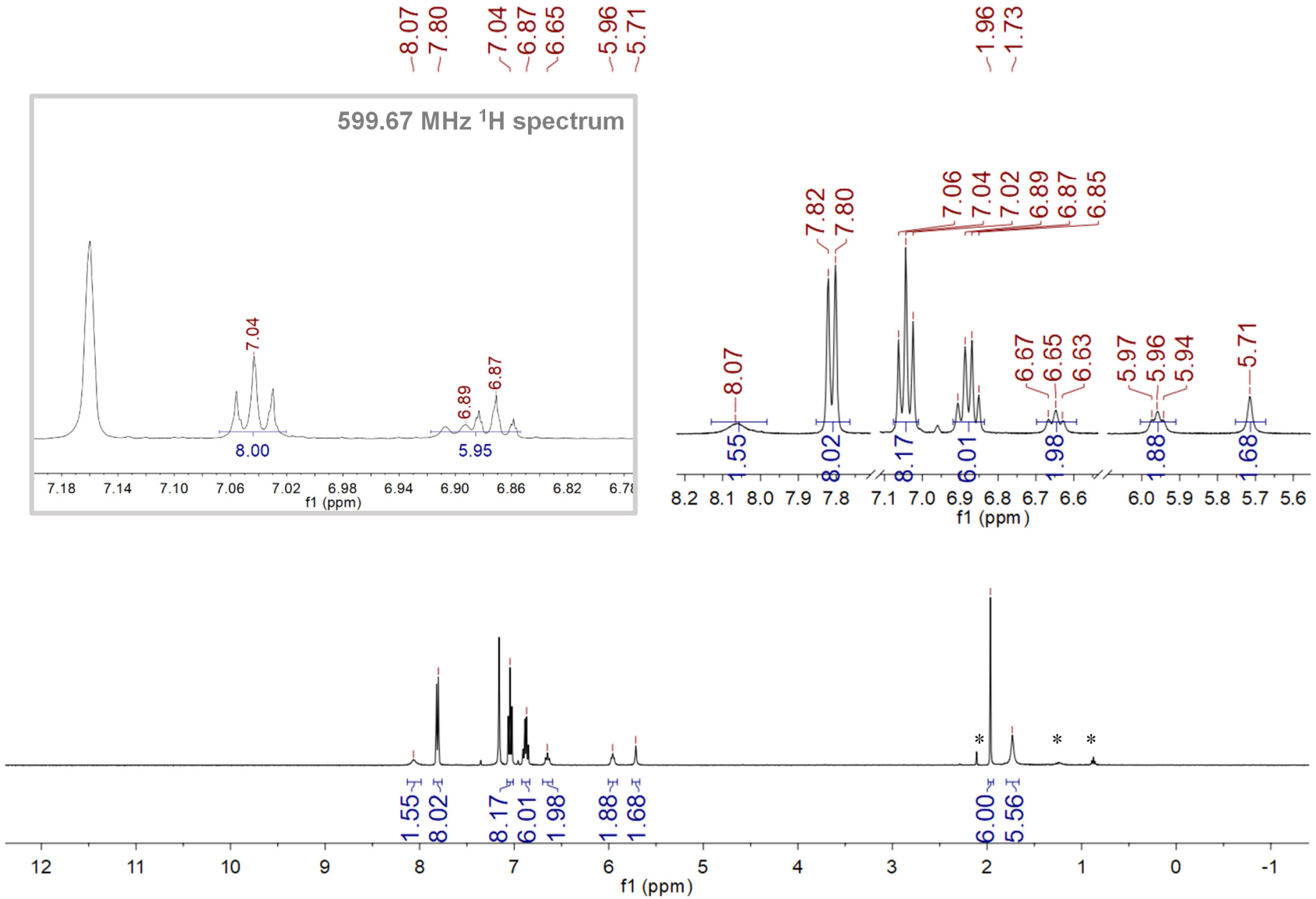


Figure S9. ^{1}H NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) in C$_6$D$_6$ (399.78 MHz). The inserted spectrum (599.67 MHz) shows partially resolved overlap between *p*-PhH (4H) and *m*-pyH (2H). *Pentane (0.87 and 1.25 ppm) and toluene (2.11 ppm) solvent peaks.

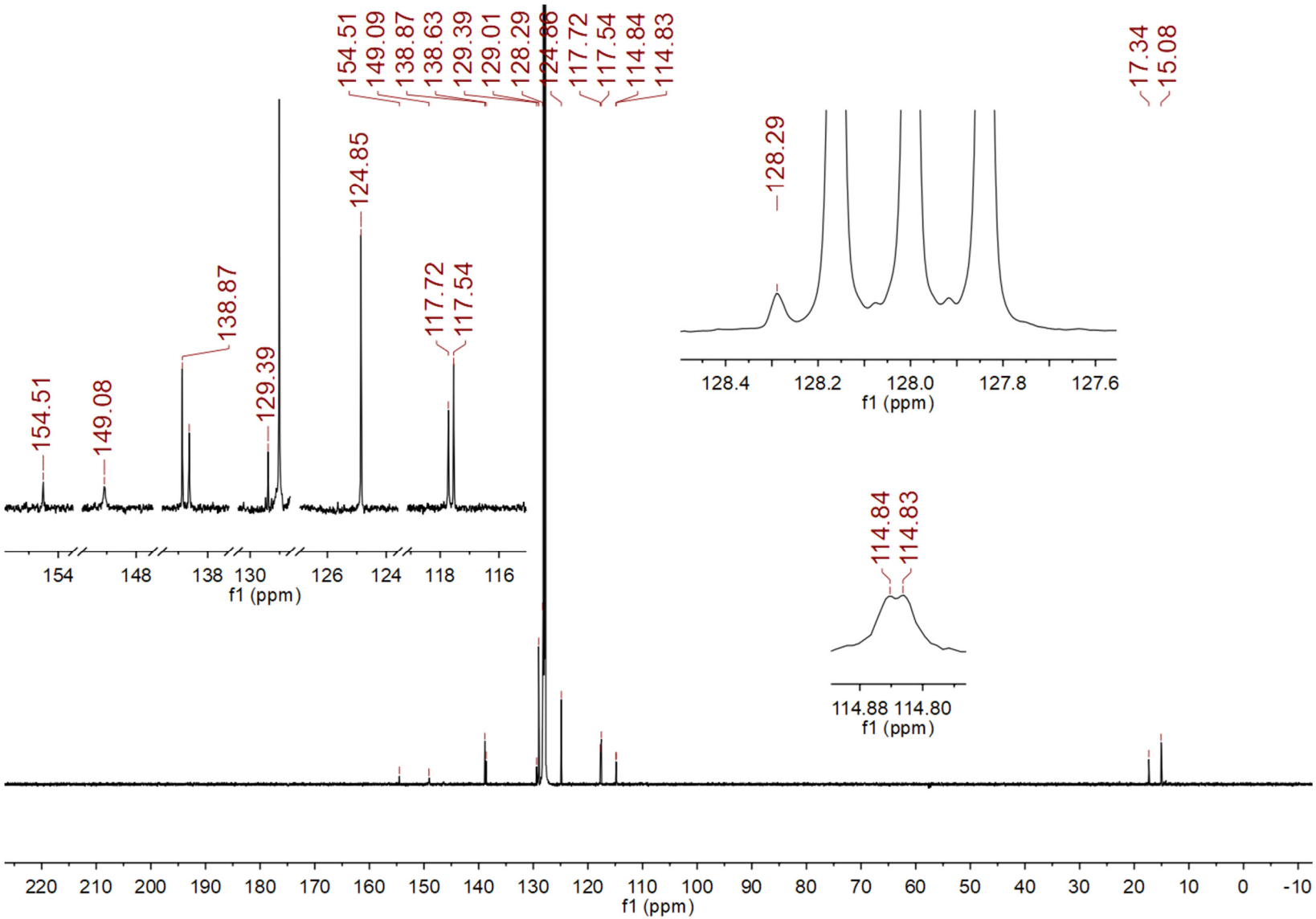


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of $(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$ in C_6D_6. Validity of the 128.29 ppm peak is confirmed by gHSQCAD spectrum in Figure S11.

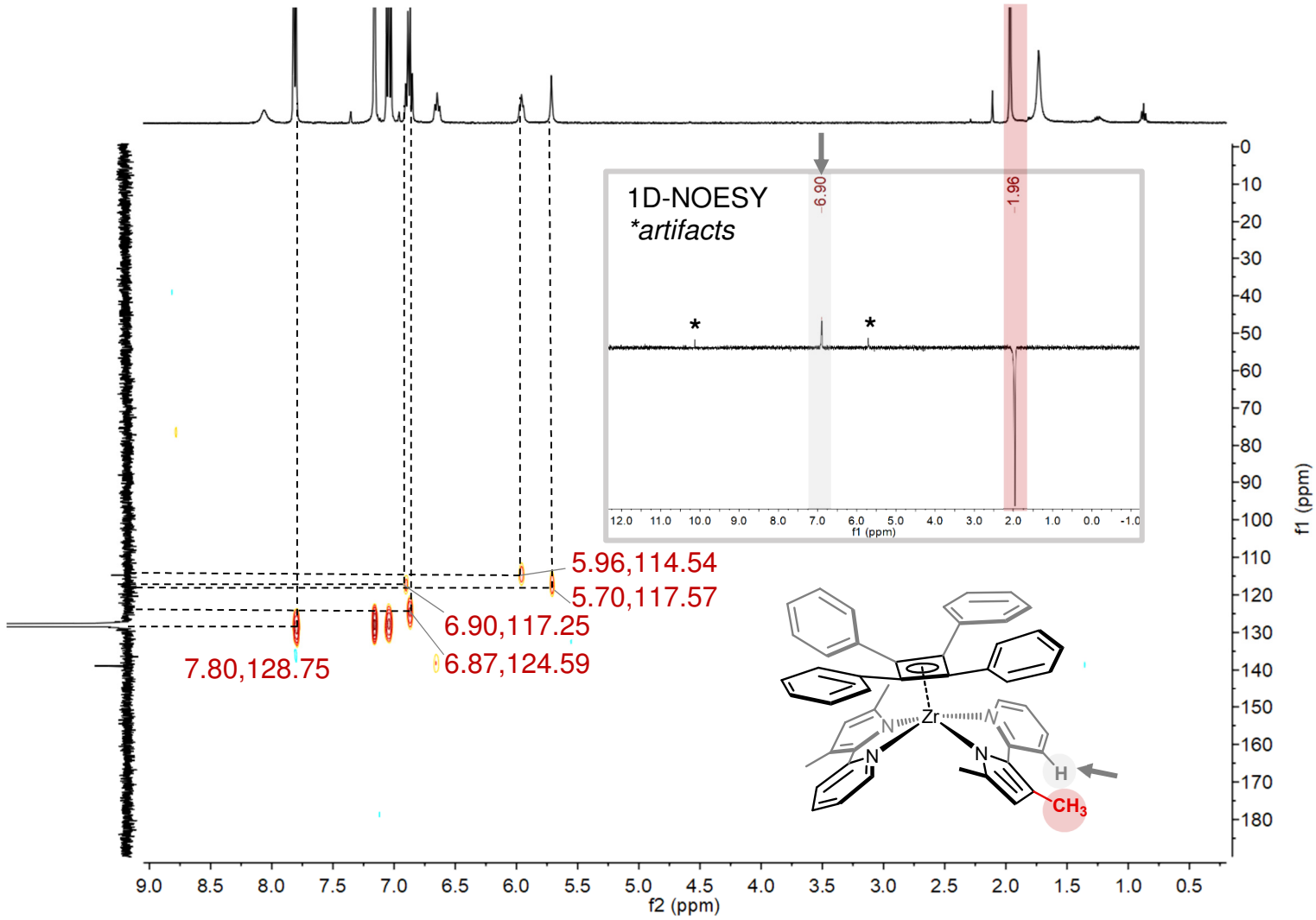


Figure S11. gHSQCAD NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) in C_6D_6 (599.67 MHz). Inserted 1D-NOESY (599.67 MHz) spectrum shows that methyl's ^{1}H at 1.97 ppm is not adjacent to pyrrole-N. Overlapping of *p*-PhH (6.87 ppm) and *m*-pyH (6.90 ppm) in 399.78 MHz ^{1}H NMR is confirmed by two distinct cross peaks with ^{13}C shifts at 124.59 and 117.25 ppm respectively. One of the two overlapping ^{13}C peaks at 114 ppm belongs to *p*-pyH. Partially obscured by C_6D_6 in ^{13}C NMR is *o*-PhH (see Figure S10), shown here at (7.80 ppm, 128.75 ppm) crosspeak.

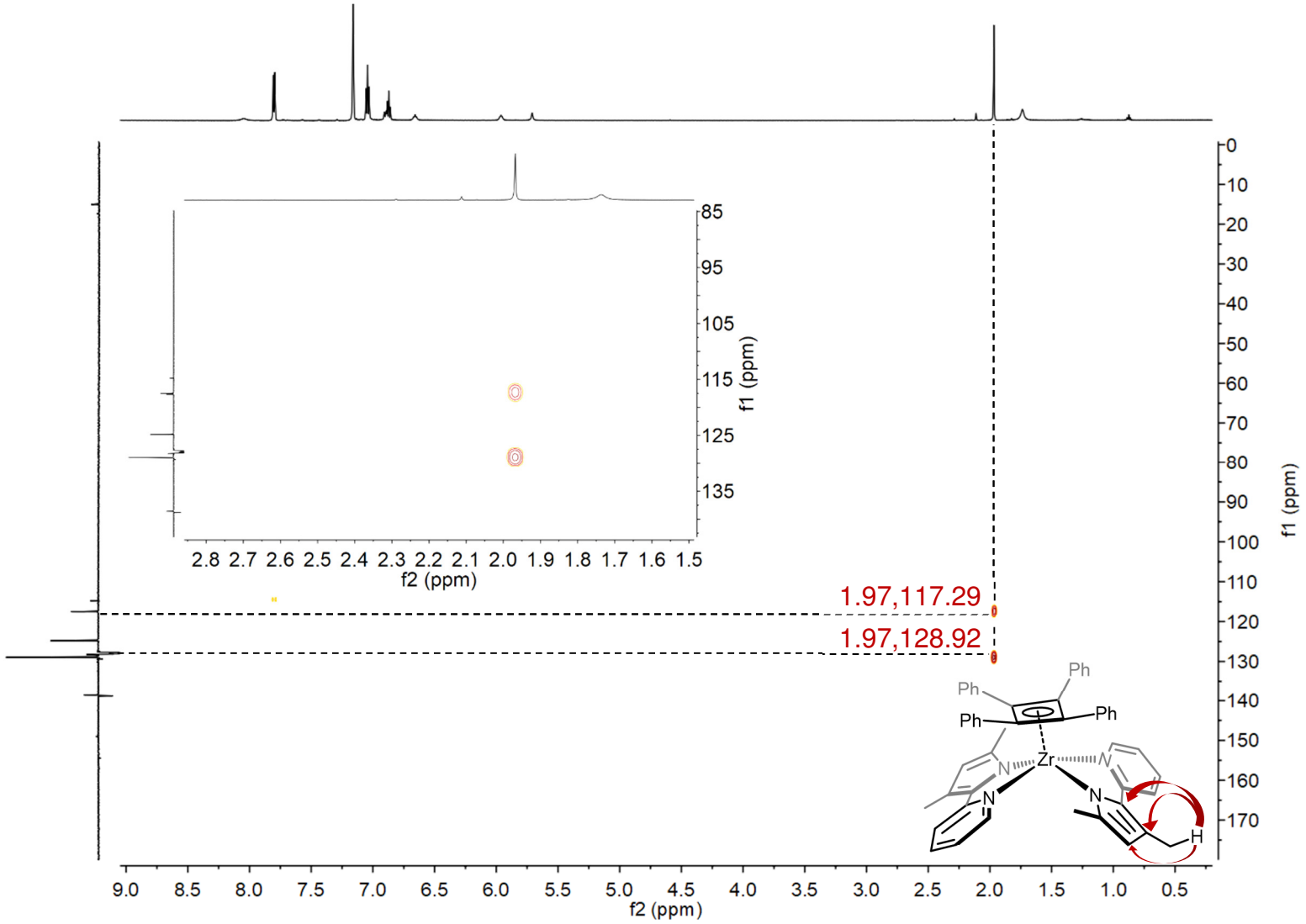


Figure S12. gHMBCAD NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) in C$_6$D$_6$. Between the two three-bond crosspeaks, correlation at 128.92 ppm is slightly more intense (see zoomed in insert) due to overlapping of the three-bond with a two-bond crosspeak. This suggests two quaternary peaks of similar chemical shifts under C$_6$D$_6$ in the ^{13}C{^{1}H} NMR spectrum (Figure S10).

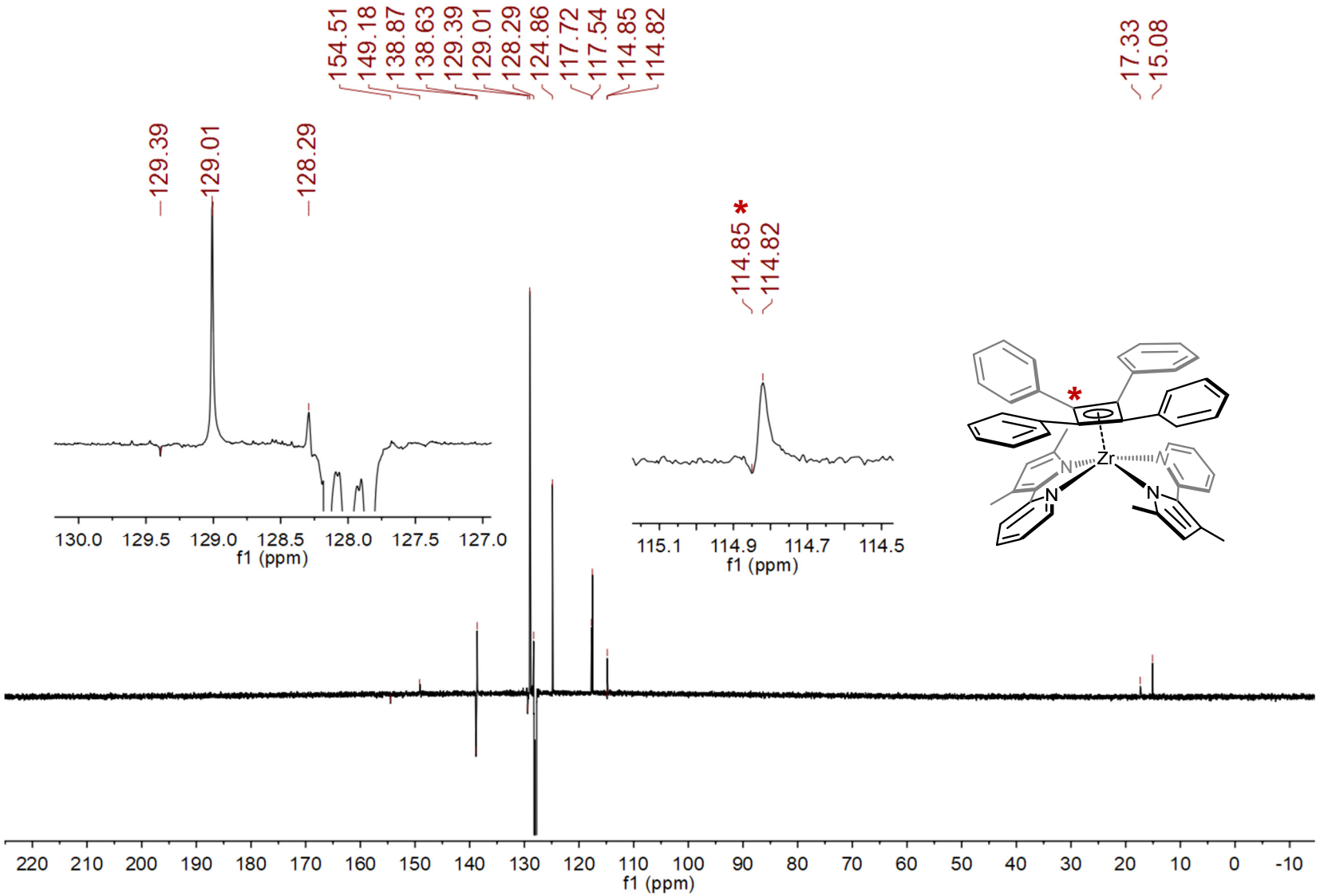


Figure S13. DEPT-135 NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) in C$_6$D$_6$ (150.80 MHz). The resonance for the quaternary carbon of the cyclobutadienyl ring is located at 114.85 ppm, which overlaps with pyrrole's tertiary carbon at 114.82 ppm. Only one positive peak at 128.29 ppm confirms the quaternary nature of the peaks underneath C$_6$D$_6$ in the ^{13}C{^{1}H} spectrum (Figure S10 and Figure S12).

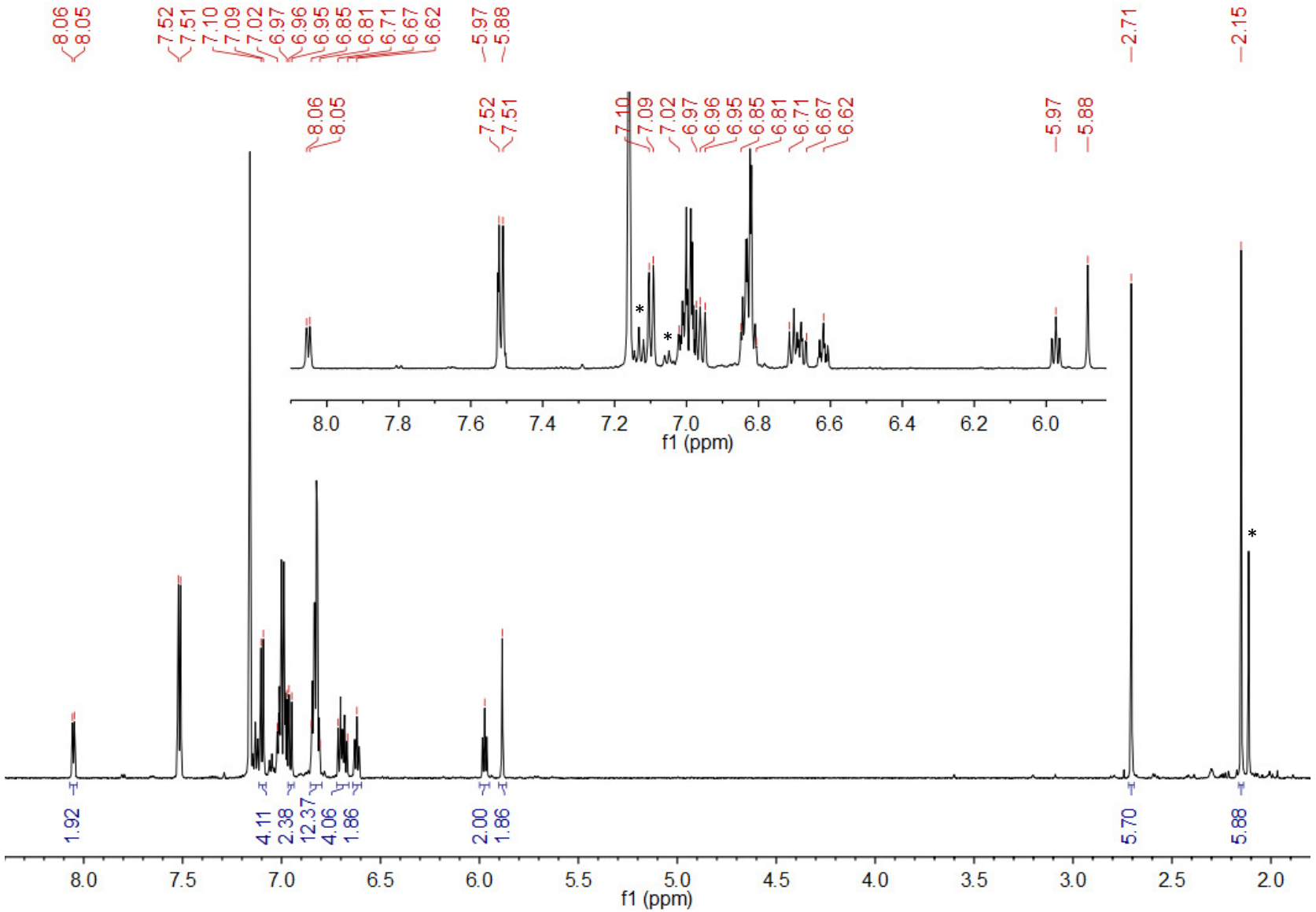


Figure S14. ^{1}H NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(C_4Ph_4) in C_6D_6 (599.67 MHz). *Toluene (7.13, 7.02, and 2.11 ppm) solvent peaks.

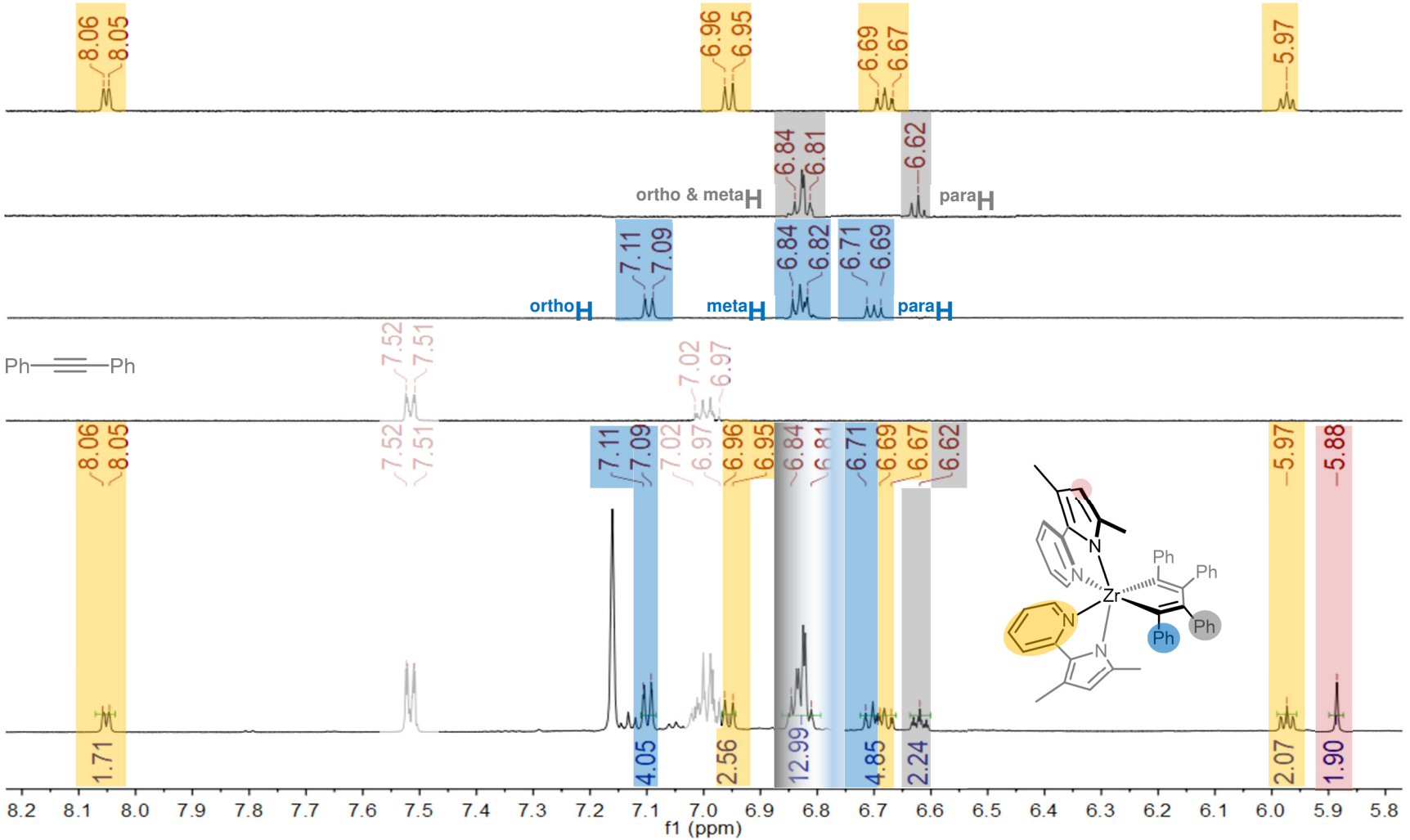


Figure S15. Assignment of resonances in the aromatic region of the ^{1}H NMR spectrum of (^{Me}PMP^{Me})$_2$Zr(C$_4$Ph$_4$) (bottom) by zTOCSY1D from crude reaction mixture in C$_6$D$_6$ (599.67 MHz).

5. Reaction Quantum Yield Determination

5.1 Irradiation Setup

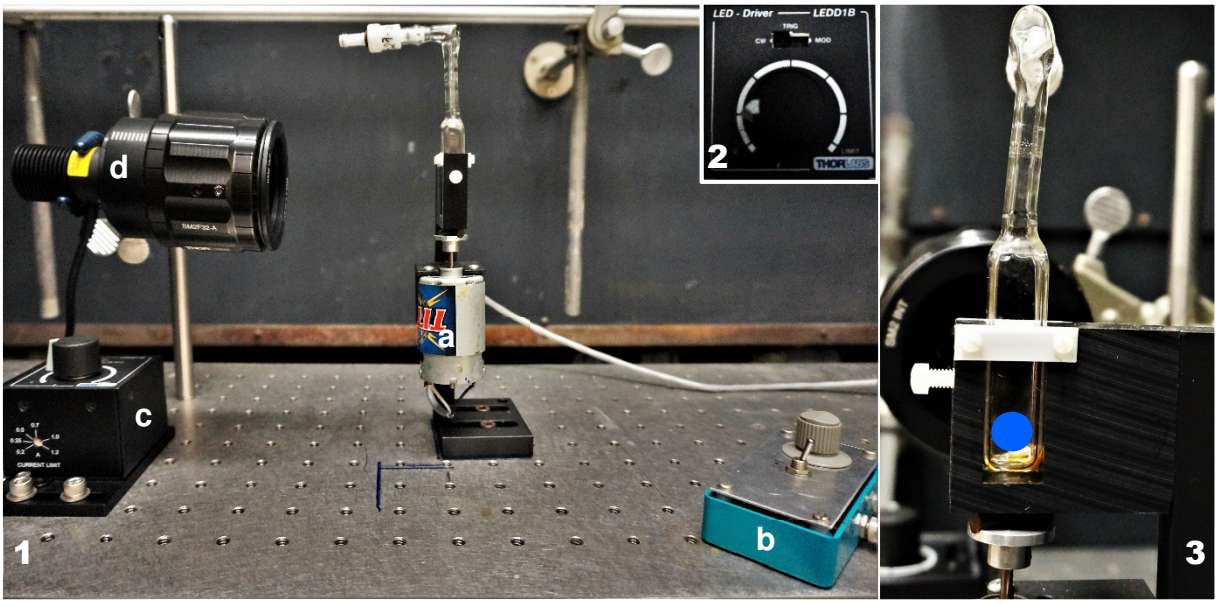


Figure S16. 1) Photoreaction setup for photon flux and reaction quantum yield measurements. a: magnetic stirrer, b: stir rate controller, c: 455-nm LED power control, d: Blue LED (900 mW) with focusing lense. 2) Power setting for all experiments. 3) Focus area of the LED (blue circle).

5.2 Light intensity calculation

Standard ferrioxalate actinometry was used to determine the photon flux of the 455 nm LED light source.[7–9]

1) Fraction of light (f) absorbed at 455 nm for the ferrioxalate solution:

Dissolving 2.21 g of potassium ferrioxalate trihydrate in 30 mL of 0.05 M H_2SO_4 produced a 0.15 M solution of ferrioxalate, which was promptly stored in the dark (solution 1). The absorbance (A) of the 0.15 M ferrioxalate solution at λ =455 nm was 1.370 (Figure S17). Calculated fraction of light absorbed by this solution:

$$f = 1 - 10^{-A} = 1 - 10^{-1.370} = 0.957$$

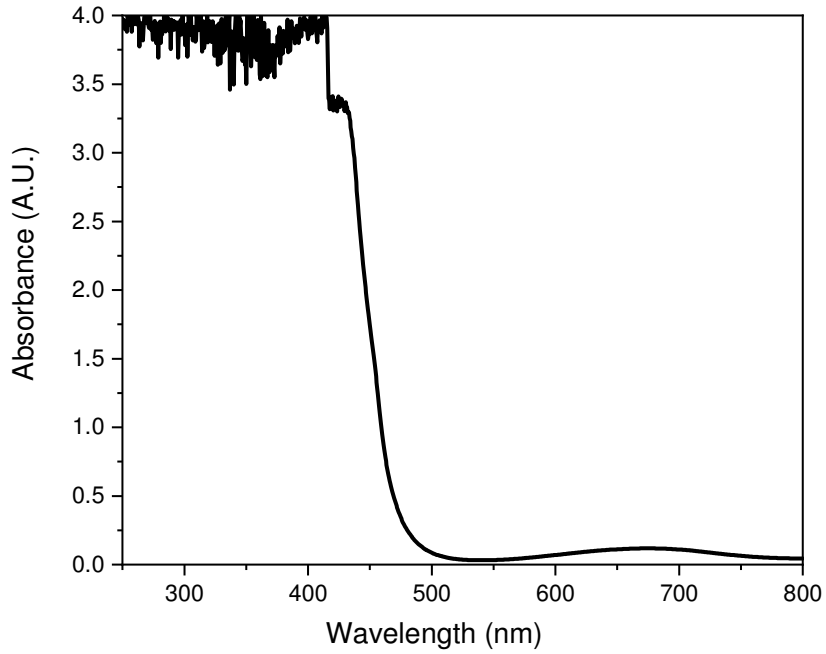


Figure S17. Absorbance of the 0.15 M ferrioxalate actinometer solution

2) Ferrous ions generated after irradiation:

A buffered solution was prepared by dissolving 50 mg of phenanthroline and 18.66 g of sodium acetate trihydrate in 50 mL 0.5 M H_2SO_4 (solution 2). This solution was also stored in the dark. A cuvette containing 2.0 mL of solution 1 was irradiated by a 455-nm LED for an average of 101 seconds (three trials) while stirring (Table S2). After irradiation, 0.35 mL of solution 2 was added to the cuvette before resting the samples in the dark for one hour. This process enabled complete coordination between the ferrous ion and phenanthroline. Meanwhile, three non-irradiated samples of the same composition (2.0 mL of solution 1 and 0.35 mL of solution 2) were made, which were also kept in the dark for an hour. The absorbance was then measured at 510 nm for all six cuvettes, three irradiated and three non-irradiated samples.

Table S2. Photon flux calculation of 455 nm LED using ferrioxalate actinometer.

Trial (**irradiation time / s**)	Absorbance at 510 nm		$\Delta A = A_i - A_{ni}$	$\text{mol } Fe^{2+} = \frac{V \,.\, \Delta A}{l \,.\, \varepsilon}$	Photon flux = $\frac{\text{mol } Fe^{2+}}{\Phi \,.\, t \,.\, f}$ / einstein s^{-1}
	Irradiated sample (A_i)	Non-irradiated sample (A_{ni})			
1 (**111**)	2.606	0.097	2.509	5.312×10^{-7}	5.38×10^{-9}
2 (**95**)	2.606	0.095	2.511	5.316×10^{-7}	6.28×10^{-9}
3 (**97**)	2.806	0.092	2.713	5.744×10^{-7}	6.65×10^{-9}
Average	2.672	0.095	2.578	5.457×10^{-7}	**6.07×10^{-9}**

V is the total volume of the sample including phenanthroline (2.35 mL), l is the cuvette's path length (1.00 cm), ε is molar absorptivity at 510 cm (11,100 mol^{-1} cm^{-1}), Φ is the quantum yield of the ferrioxalate actinometer (0.93 for a 0.15M solution at λ = 468 nm), t is the irradiation time in seconds, and f is the fraction of light absorbed (0.957).

5.3 Quantum Yield of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) synthesis using 455 nm LED

In an N_2-filled box with minimal lighting, (^{Me}PMP^{Me})$_2$ZrBn$_2$ (10 mg, 0.016 mmol, 1.00 equiv.) and diphenylacetylene (18 mg, 0.101 mmol, 6.23 equiv.) were weighed out in a vial wrapped in black electrical tape before adding 10 mL of benzene. An aliquot of 3 mL was delivered to a quartz cuvette and the sample was irradiated with the 455 nm LED using the same power as the photon flux experiment (*vide supra*) for 1800 s. This process was repeated twice, each time with a freshly prepared solution due to slow decomposition (^{Me}PMP^{Me})$_2$ZrBn$_2$ in solution over time. After removing benzene, the yield of product formation was determined by ^{1}H NMR (JEOL 399.78 MHz) based on an 8.32 mM 1,3,5-trimethoxybenzene solution in C_6D_6 (0.8 mL per NMR sample). Three collected spectra had the same ^{1}H NMR parameters of 10 seconds relaxation delay, zero pre-scan and 64 acquisition scans (Figure S18). The quantum yield was calculated based on the equation in Table S3.

The absorption spectrum of the reaction mixture prior to irradiation showed that all the incident light was absorbed by (^{Me}PMP^{Me})$_2$ZrBn$_2$, f > 0.999 (Abs > 3 at 455 nm).

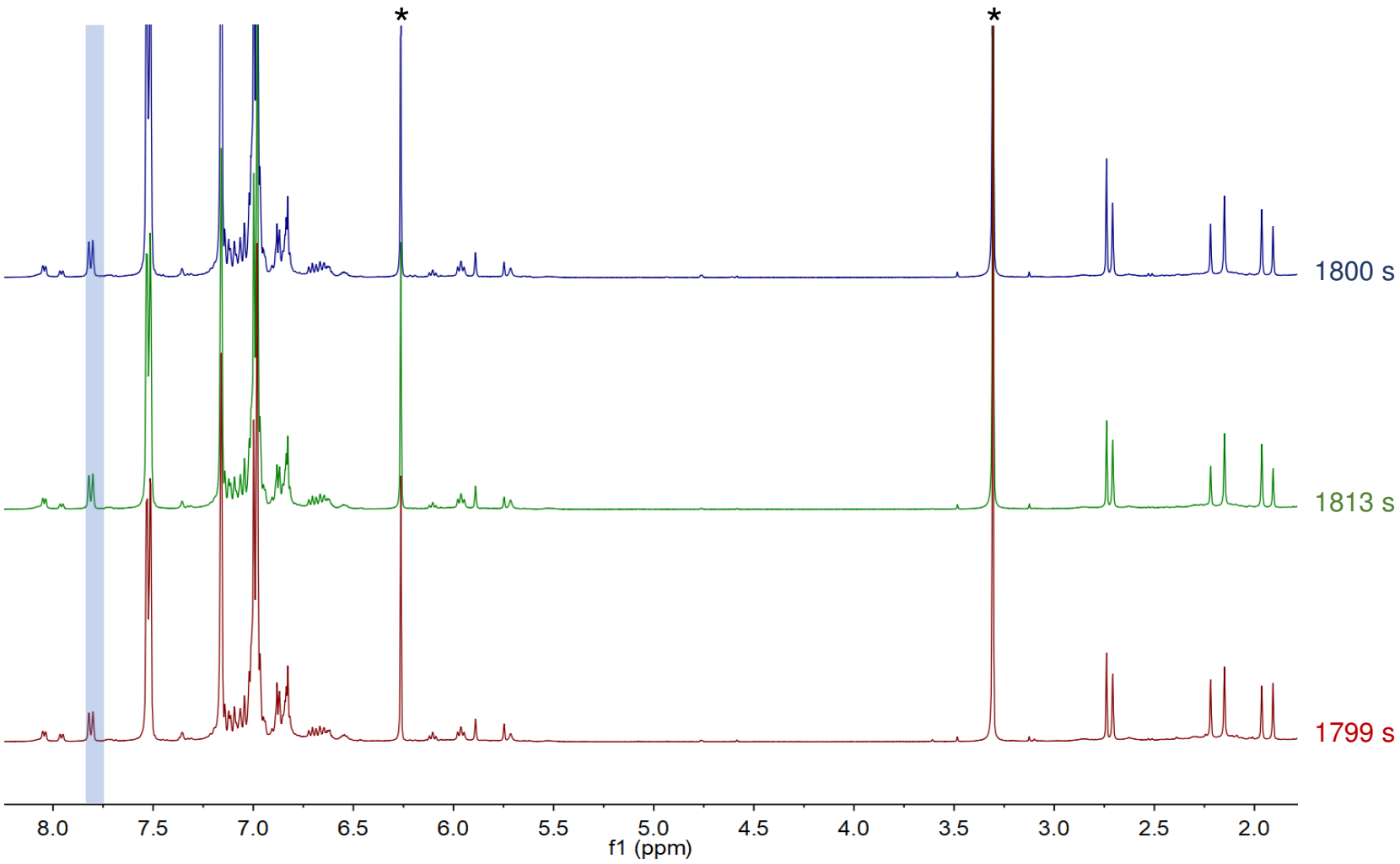


Figure S18. ^{1}H NMR spectrum (399.78 MHz) in C_6D_6 with *1,3,5-trimethoxybenzene as the internal standard. Irradiation time is shown on the right according to the spectrum's color. Highlighted in blue is the peak used to calculate the number of moles of $(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$ for reaction the quantum yield determination.

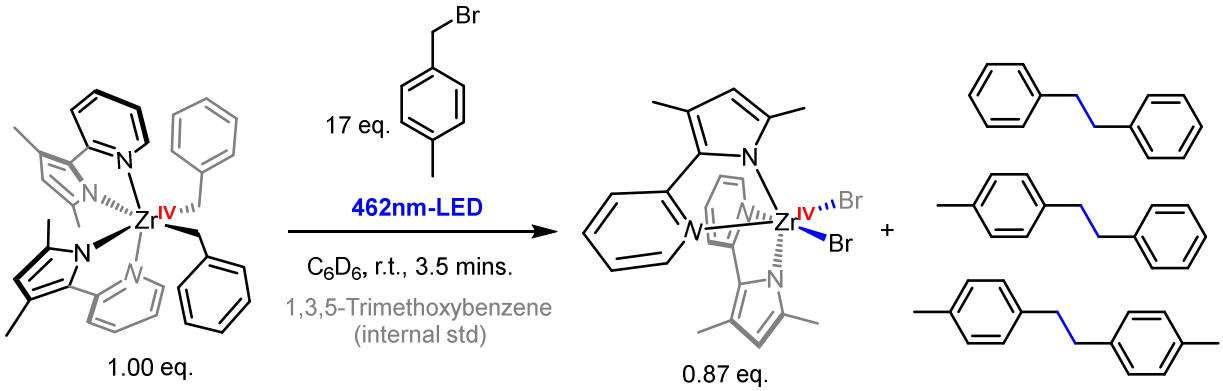
Table S3. Reaction Quantum Yield of $(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$ formation

Irradiation Time (**s**)	Integration of Internal Standard at 6.24 ppm [a]	$(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$		$\Phi = \frac{\text{mol of product}}{\text{Photon flux} \cdot t \cdot f}$
		Equivalence [b] (*Integration*)	mol	
1 799	2.66	0.096 (*0.77*)	6.41×10^{-7}	0.059
1 813	2.64	0.137 (*1.10*)	9.16×10^{-7}	0.083
1 800	2.62	0.136 (*1.09*)	9.07×10^{-7}	0.083
			Average	**0.075**

[a]The integral for the internal standard resonance at 3.31 ppm was set to 9.00 ^{1}H for all spectra.
[b]Equivalence = Integration / (# chemically equivalent ^{1}H per molecule)

6. Intermittent Irradiation Experiments

6.1 Crossover Photoreaction with 4-Methylbenzyl bromide (^{Me}BnBr)



In a J. Young NMR tube, (^{Me}PMP^{Me})$_2$ZrBn$_2$ (5 mg, 1.00 equiv) was added along with 1,3,5-trimethoxybenzene as an internal standard. With the NMR tube sealed and completely covered in aluminum foil, an initial ^{1}H NMR spectrum was taken in approximately 0.9 mL C_6D_6. The sample was then brought into the glovebox where 4-methylbenzyl bromide (26 mg, 17 equiv) was added under minimal lighting. The sample was sonicated for five minutes before a second ^{1}H NMR spectrum was acquired. After three hours in the dark in the glovebox, a third spectrum was taken before a series of intermittent blue light irradiation (see Figure S19). A total of 13 spectra were collected using the same ^{1}H NMR parameters of 10 seconds relaxation delay, zero pre-scan and 64 acquisition scans. Except for the initial three hours in the dark, the tube was left inside the JEOL 400 MHz NMR Spectrometer for all other dark experiments after irradiation. Average equivalence came from integrations of five and three well separated peaks that belonged to (^{Me}PMP^{Me})$_2$ZrBn$_2$ and (^{Me}PMP^{Me})$_2$ZrBr$_2$, respectively (see Figure S19 and Table S4).

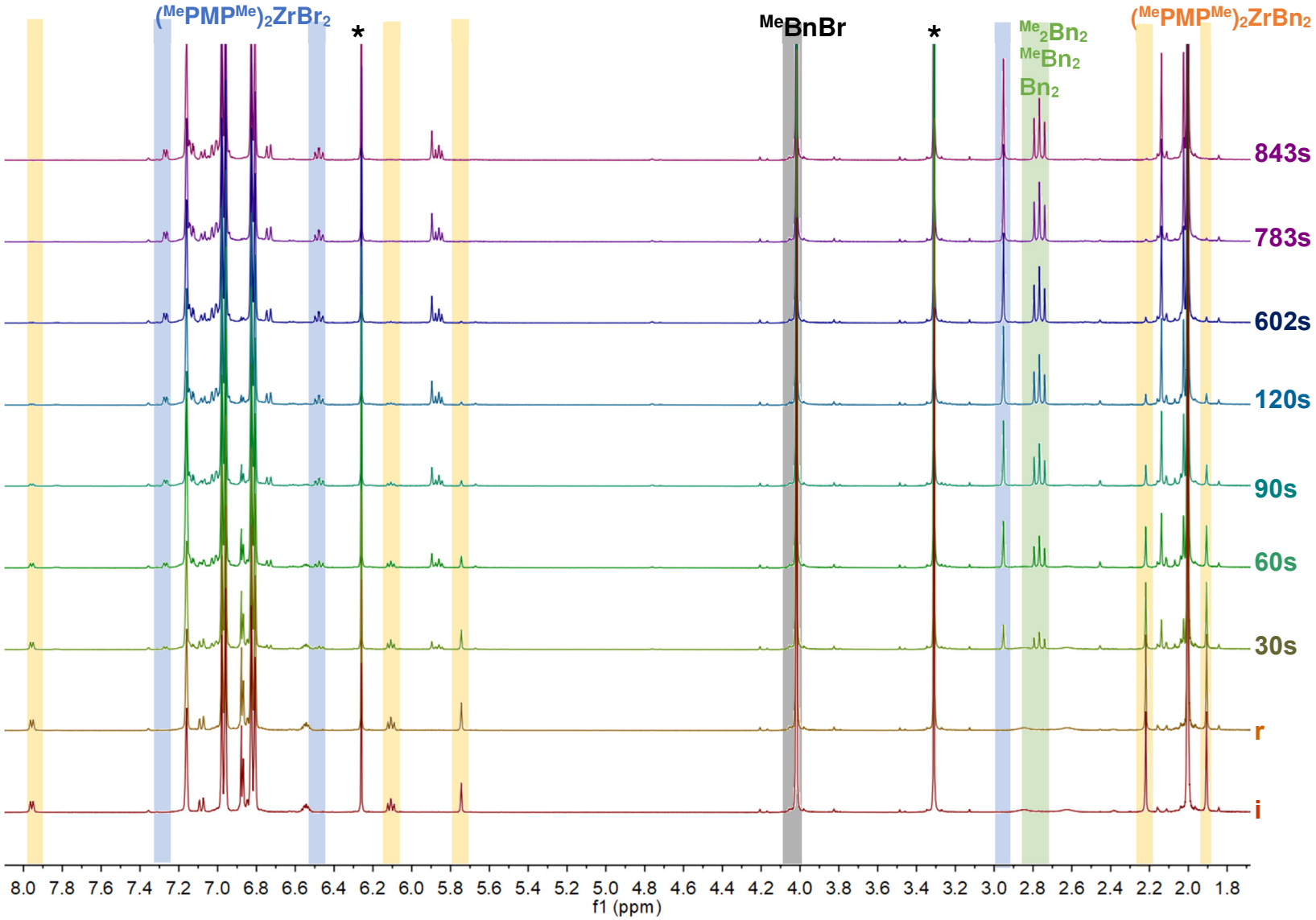


Figure S19. ^{1}H NMR time course in C_6D_6 with *1,3,5-trimethoxybenzene as the internal standard. Integrated peaks for average equivalence are highlighted according to the colors of the species written above. (i: initial spectrum; r: in the dark for 3 hrs.)

Table S4. Integration results for ^{1}H NMR spectra of $(^{Me}PMP^{Me})_2ZrBr_2$ synthesis using blue light.

Irradiation Time / s (mins under dark)	Equivalence [a] (*Integration*)									
	Internal Standard at 6.24 ppm [b]	^{Me}BnBr at 4.02 ppm	$(^{Me}PMP^{Me})_2ZrBn_2$					$(^{Me}PMP^{Me})_2ZrBr_2$			Bn_2 derivatives mixture at 2.79, 2.77 and 2.74 ppm [c]
			1.91	2..22	5.75	6.11	7.95	2.95	6.48	7.26	
0	2.17 (*6.51*)	16.71 (*33.42*)	1.00 (*6.00*)	0.94 (*5.67*)	0.92 (*1.84*)	1.01 (*2.02*)	0.89 (*1.79*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)
			Average equivalence (A.e.) = 0.95					0.00			
0 (180)	2.16 (*6.49*)	16.69 (*33.38*)	0.97 (*5.83*)	0.92 (*5.55*)	0.88 (*1.76*)	0.96 (*1.93*)	0.85 (*1.71*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)
			A.e. = 0.92					0.00			
30	2.18 (*6.53*)	16.04 (*32.09*)	0.65 (*3.93*)	0.63 (*3.80*)	0.57 (*1.14*)	0.66 (*1.32*)	0.50 (*1.00*)	0.23 (*1.41*)	0.26 (*0.52*)	0.16 (*0.33*)	0.60 (*2.39*)
			A.e. = 0.60					0.22			
60	2.19 (*6.56*)	15.63 (*31.26*)	0.42 (*2.55*)	0.38 (*2.29*)	0.34 (*0.68*)	0.43 (*0.86*)	0.25 (*0.51*)	0.44 (*2.64*)	0.49 (*0.99*)	0.34 (*0.68*)	1.02 (*4.07*)
			A.e. = 0.36					0.42			
60 (10)	2.18 (*6.55*)	15.60 (*31.21*)	0.43 (*2.56*)	0.37 (*2.25*)	0.33 (*0.66*)	0.42 (*0.85*)	0.26 (*0.52*)	0.43 (*2.59*)	0.48 (*0.97*)	0.33 (*0.67*)	1.00 (*4.01*)
			A.e. = 0.36					0.42			
90	2.25 (*6.74*)	15.58 (*31.17*)	0.25 (*1.50*)	0.21 (*1.24*)	0.16 (*0.33*)	0.24 (*0.49*)	0.1 (*0.20*)	0.62 (*3.74*)	0.68 (*1.37*)	0.50 (*1.01*)	1.38 (*5.52*)
			A.e. = 0.19					0.60			
90 (20)	2.17 (*6.50*)	15.17 (*30.34*)	0.22 (*1.31*)	0.20 (*1.19*)	0.14 (*0.29*)	0.22 (*0.45*)	0.09 (*0.19*)	0.60 (*3.61*)	0.64 (*1.29*)	0.53 (*1.06*)	1.34 (*5.38*)
			A.e. = 0.18					0.59			
120	2.18 (*6.54*)	15.03 (*30.07*)	0.12 (*0.72*)	0.10 (*0.59*)	0.06 (*0.12*)	0.12 (*0.24*)	-	0.74 (*4.46*)	0.78 (*1.57*)	0.61 (*1.23*)	1.57 (*6.30*)
			A.e. = 0.10					0.71			
150	2.19	14.86	0.06	0.06	0.00	0.04	-	0.82	0.83	0.74	1.70

	(*6.57*)	(*29.72*)	(*0.34*)	(*0.34*)	(*0.01*)	(*0.08*)		(*4.93*)	(*1.67*)	(*1.48*)	(*6.79*)
			A.e. = 0.04					0.80			
180	2.17 (*6.52*)	14.71 (*29.42*)	0.03 (*0.20*)	0.03 (*0.17*)	0.00 (*0.00*)	0.01 (*0.03*)	-	0.87 (*5.21*)	0.89 (*1.78*)	0.75 (*1.50*)	1.78 (*7.12*)
			A.e. = 0.02					0.84			
210	2.18 (*6.55*)	14.84 (*29.69*)	0.01 (*0.08*)	0.02 (*0.14*)	-	-	-	0.90 (*5.38*)	0.89 (*1.78*)	0.86 (*1.50*)	1.83 (*7.33*)
			A.e. = 0.01					0.88			
210 (60)	2.19 (*6.58*)	14.79 (*29.59*)	0.01 (*0.09*)	0.01 (*0.09*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.89 (*5.35*)	0.91 (*1.82*)	0.80 (*1.60*)	1.86 (*7.45*)
			A.e. = 0.01					0.87			

[a] Equivalence = Integration / (# chemically equivalent H per molecule). [b] Integration of internal standard at 3.31 ppm were set to 22.58H for all spectra. [c] Equivalence = Integration / 4H since all three Bn_2 derivatives have four benzylic ^1H

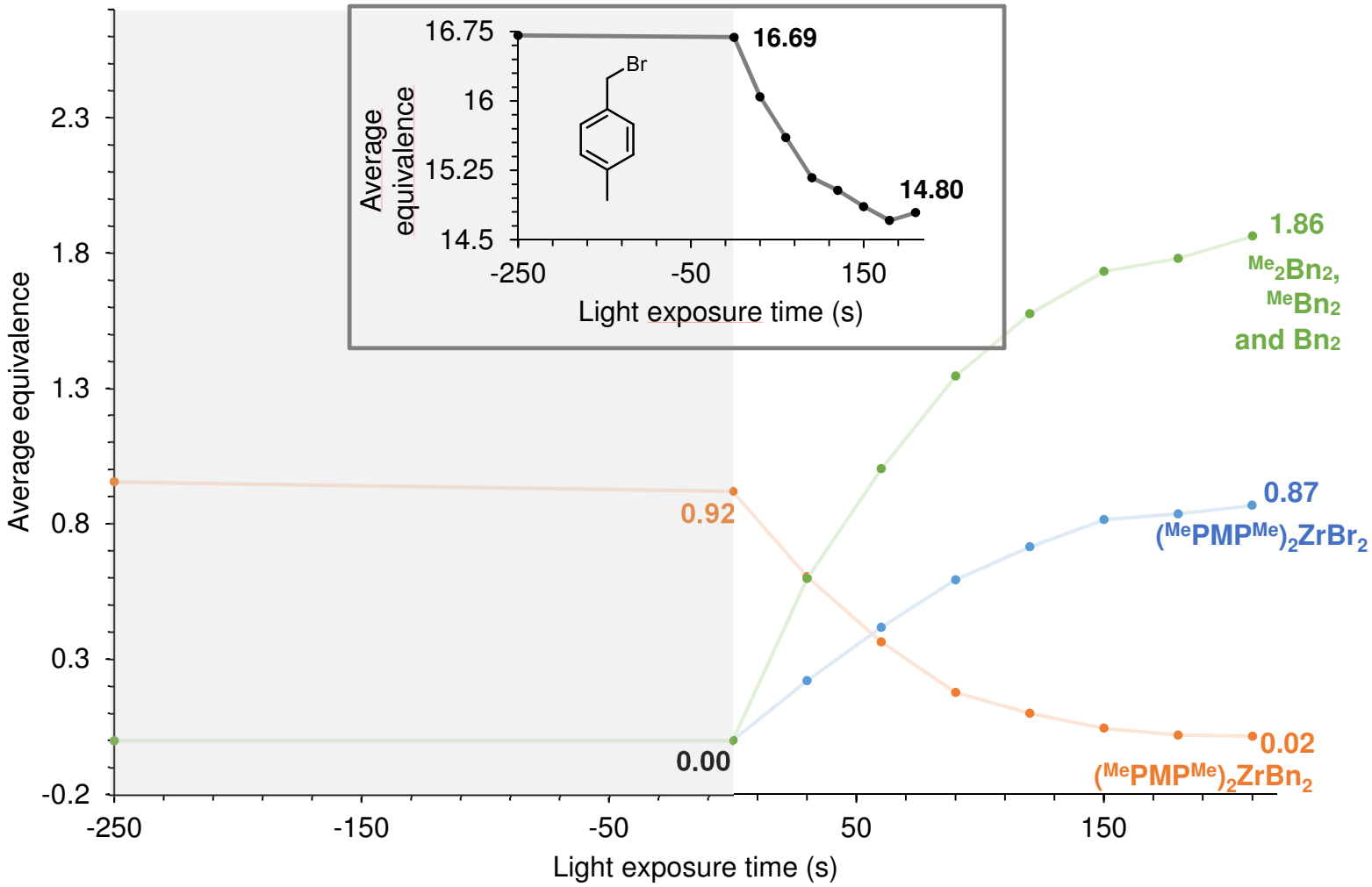


Figure S20. Reaction time course before and after blue light exposure. Shaded area represents the reaction in the dark. Due to rapid reaction progress under blue light, the full 10 800 s in the dark is omitted for clarity. Consumption of 4-methylbenzyl bromide over time is in a separate chart insert for visual acuity.

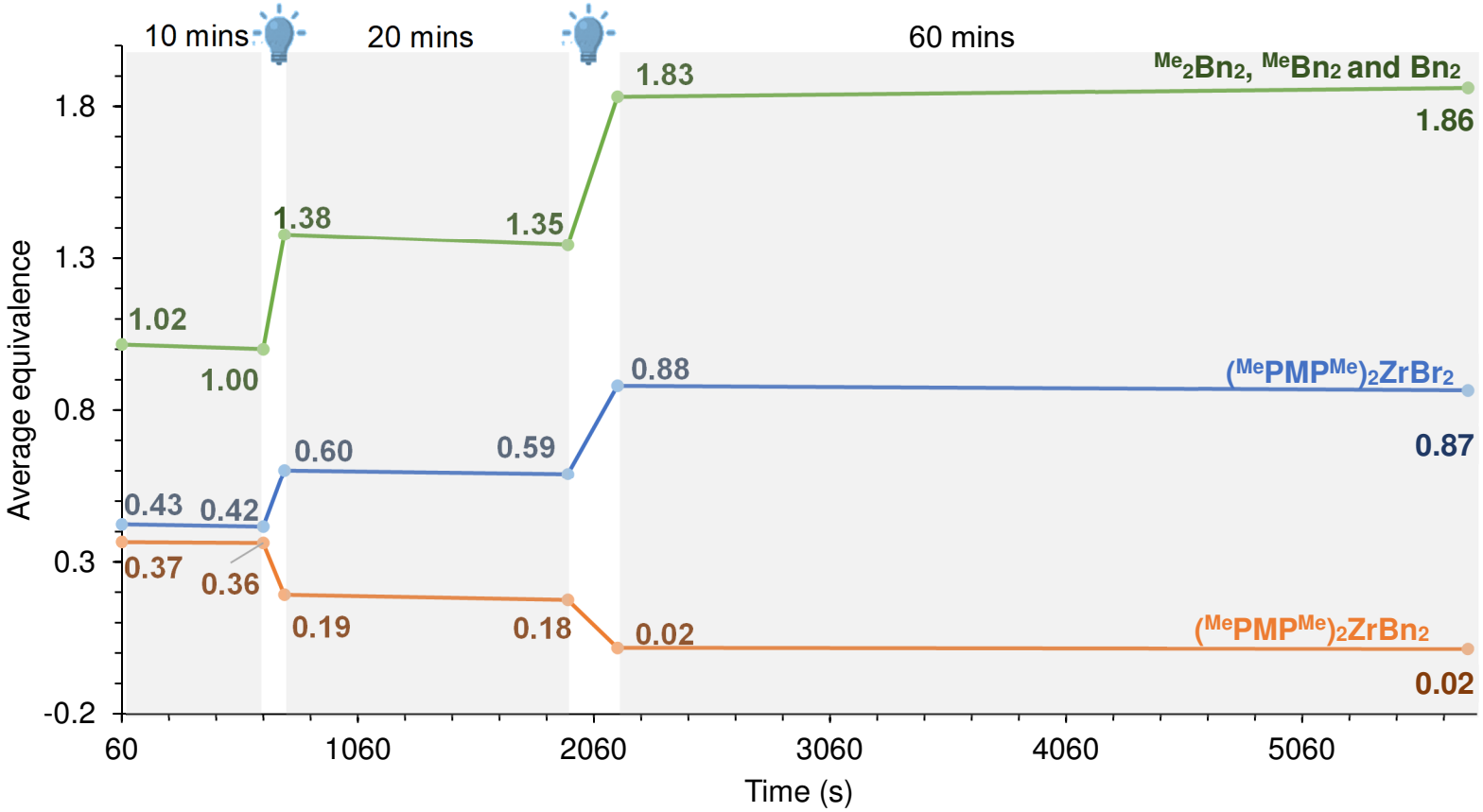
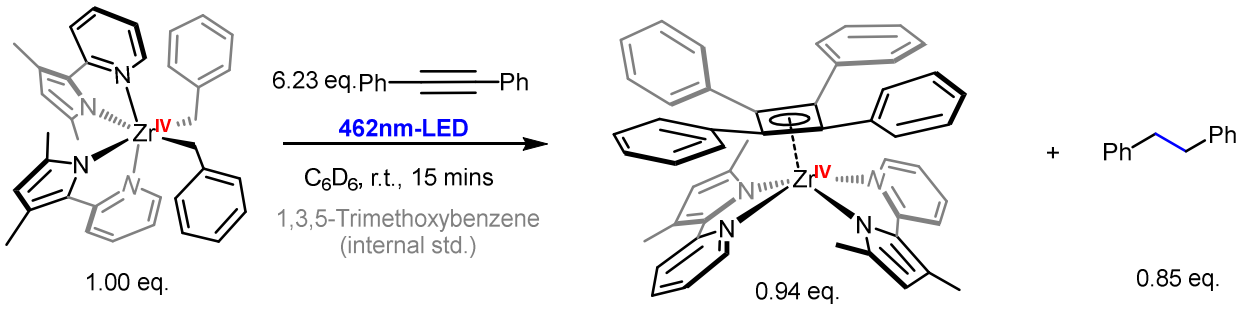


Figure S21. Intermittent light/dark experiments show lack of productive chemistry without light exposure. Shaded areas are the time that the reaction was kept in the dark.

6.2 Photoreaction with Diphenylacetylene



In a J. Young NMR tube, (^{Me}PMP^{Me})$_2$ZrBn$_2$ (5 mg, 1.00 equiv) was added along with 1,3,5-trimethoxybenzene as an internal standard. With the NMR tube sealed and completely covered in aluminum foil, an initial ^{1}H NMR spectrum was taken in approximately 0.8 mL C_6D_6. Then, the sample was brought into the glovebox where diphenylacetylene (9 mg, 6.23 equiv) was added under minimal lighting. The sample was sonicated for five minutes before a second ^{1}H NMR spectrum was acquired. After an hour in the dark in the glovebox, a third spectrum was taken before a series of intermittent blue light irradiation (see Figure S22). A total of 36 spectra were collected using the same ^{1}H NMR parameters of 10 seconds relaxation delay, zero pre-scan and 64 acquisition scans. Except for the initial one hour in the dark, the tube was left inside the JEOL 400 MHz NMR Spectrometer for all other dark experiments after irradiation. Average equivalence came from integrations of five and four well separated peaks belonged to (^{Me}PMP^{Me})$_2$ZrBn$_2$ and (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$), respectively (see Figure S22 and Table S5)

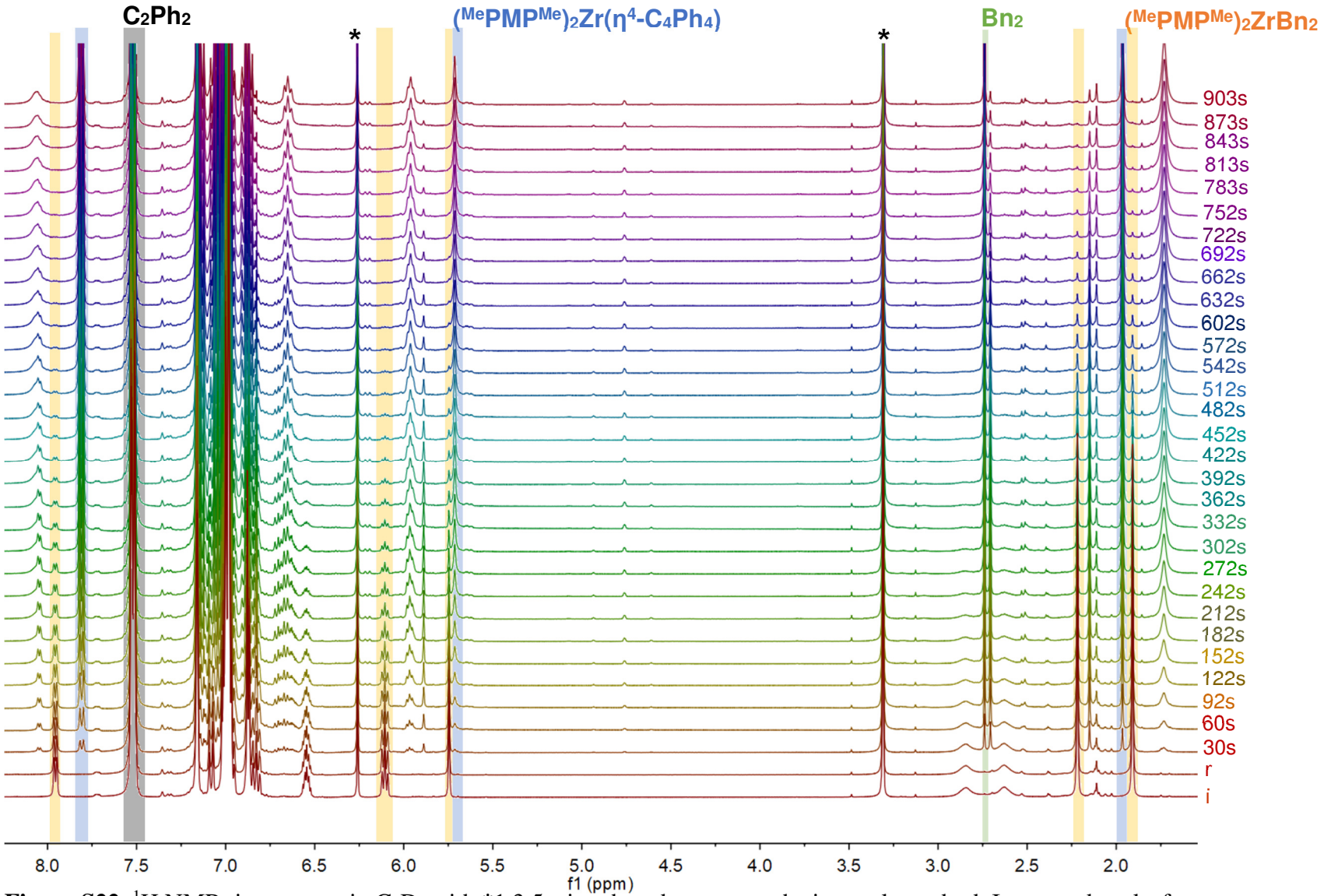


Figure S22. ^{1}H NMR time course in C_6D_6 with *1,3,5-trimethoxybenzene as the internal standard. Integrated peaks for average equivalence are highlighted according to the colors of the species written above. (i: initial spectrum; r: in the dark for 1 h).

Table S5. Integration results for ^{1}H NMR spectra of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) synthesis using blue LED.

Irradiation Time / s (mins under dark)	Equivalence [a] (*Integration*)										
	Internal Standard at 6.24 ppm [b]	C_2Ph_2 at 7.52 ppm	(^{Me}PMP^{Me})$_2$ZrBn$_2$ / ppm					(^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) / ppm				Bn_2 at 1.74 ppm
			1.91	2.22	5.75	6.11	7.95	1.97	5.71	5.96	7.82	
0	0.61 (*1.84*)	6.23 (*24.91*)	1.00 (*6.00*)	1.01 (*6.09*)	0.94 (*1.89*)	1.00 (*2.01*)	1.02 (*2.04*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)
			Average equivalence (A. e.) = 1.00					0.00				
0 (60)	0.62 (*1.86*)	6.21 (*24.84*)	1.00 (*6.00*)	1.01 (*6.09*)	0.94 (*1.89*)	1.00 (*2.01*)	1.02 (*2.04*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)	0.00 (*0.00*)
			A. e. = 1.00					0.00				
30	0.62 (*1.85*)	5.93 (*23.73*)	0.84 (*5.02*)	0.85 (*5.12*)	0.79 (*1.58*)	0.83 (*1.66*)	0.86 (*1.73*)	0.07 (*0.44*)	0.03 (*0.07*)	0.10 (*0.21*)	0.07 (*0.55*)	0.15 (*0.62*)
			A. e. = 0.83					0.16				
60	0.62 (*1.86*)	5.68 (*22.72*)	0.71 (*4.26*)	0.73 (*4.35*)	0.67 (*1.35*)	0.71 (*1.42*)	0.71 (*1.42*)	0.13 (*0.81*)	0.09 (*0.18*)	0.24 (*0.49*)	0.13 (*1.03*)	0.25 (*1.02*)
			A. e. = 0.71					0.15				
60 (10)	0.63 (*1.90*)	5.66 (*22.65*)	0.72 (*4.30*)	0.73 (*4.36*)	0.69 (*1.38*)	0.74 (*1.49*)	0.67 (*1.33*)	0.13 (*0.80*)	0.10 (*0.21*)	0.27 (*0.55*)	0.12 (*0.93*)	0.25 (*1.02*)
			A. e. = 0.71					0.16				
92	0.63 (*1.88*)	5.43 (*21.06*)	0.59 (*3.57*)	0.60 (*3.63*)	0.57 (*1.14*)	0.62 (*1.24*)	0.54 (*1.08*)	0.21 (*1.65*)	0.16 (*0.41*)	0.38 (*0.92*)	0.19 (*2.18*)	0.35 (*1.70*)
			A. e. = 0.59					0.24				
122	0.63 (*1.88*)	5.26 (*21.06*)	0.49 (*2.96*)	0.51 (*3.04*)	0.47 (*0.95*)	0.49 (*0.99*)	0.46 (*0.93*)	0.27 (*1.65*)	0.20 (*0.41*)	0.46 (*0.92*)	0.27 (*2.18*)	0.42 (*1.70*)
			A. e. = 0.48					0.30				
122 (20)	0.63 (*1.89*)	5.28 (*21.12*)	0.49 (*2.93*)	0.50 (*3.03*)	0.46 (*0.93*)	0.47 (*0.95*)	0.49 (*0.99*)	0.27 (*1.65*)	0.19 (*0.39*)	0.44 (*0.88*)	0.28 (*2.23*)	0.43 (*1.71*)

			A. e. = 0.48					0.29				
152	0.63 (*1.90*)	5.13 (*20.51*)	0.41 (*2.49*)	0.43 (*2.59*)	0.40 (*0.80*)	0.40 (*0.80*)	0.41 (*0.82*)	0.33 (*1.99*)	0.24 (*0.48*)	0.51 (*1.03*)	0.34 (*2.69*)	0.49 (*1.95*)
			A. e. = 0.41					0.36				
182	0.64 (*1.91*)	4.99 (*19.95*)	0.34 (*2.07*)	0.36 (*2.16*)	0.33 (*0.67*)	0.32 (*0.65*)	0.34 (*0.69*)	0.39 (*2.37*)	0.29 (*0.58*)	0.58 (*1.16*)	0.40 (*3.22*)	0.54 (*2.18*)
			A. e. = 0.34					0.41				
182 (23)	0.64 (*1.92*)	4.99 (*19.96*)	0.34 (*2.06*)	0.36 (*2.16*)	0.33 (*0.67*)	0.32 (*0.64*)	0.34 (*0.69*)	0.39 (*2.37*)	0.29 (*0.58*)	0.57 (*1.15*)	0.40 (*3.22*)	0.54 (*2.18*)
			A. e. = 0.34					0.42				
212	0.67 (*2.01*)	4.88 (*19.51*)	0.29 (*1.73*)	0.30 (*1.82*)	0.28 (*0.57*)	0.26 (*0.53*)	0.29 (*0.58*)	0.45 (*2.69*)	0.33 (*0.66*)	0.62 (*1.25*)	0.47 (*3.73*)	0.56 (*2.26*)
			A. e. = 0.28					0.47				
212 (58)	0.67 (*2.01*)	4.87 (*19.50*)	0.29 (*1.72*)	0.30 (*1.81*)	0.28 (*0.56*)	0.26 (*0.52*)	0.29 (*0.58*)	0.45 (*2.70*)	0.33 (*0.66*)	0.62 (*1.25*)	0.47 (*3.74*)	0.56 (*2.26*)
			A. e. = 0.28					0.47				
242	0.67 (*2.02*)	4.79 (*19.16*)	0.24 (*1.45*)	0.25 (*1.53*)	0.24 (*0.48*)	0.21 (*0.43*)	0.24 (*0.49*)	0.50 (*3.01*)	0.37 (*0.74*)	0.67 (*1.34*)	0.52 (*4.15*)	0.60 (*2.42*)
			A. e. = 0.24					0.52				
272	0.67 (*2.01*)	4.72 (*18.87*)	0.20 (*1.23*)	0.22 (*1.30*)	0.20 (*0.41*)	0.17 (*0.35*)	0.21 (*0.42*)	0.54 (*3.26*)	0.40 (*0.81*)	0.70 (*1.40*)	0.56 (*4.51*)	0.63 (*2.53*)
			A. e. = 0.20					0.55				
302	0.67 (*2.01*)	4.66 (*18.65*)	0.17 (*1.03*)	0.18 (*1.10*)	0.18 (*0.36*)	0.14 (*0.28*)	0.18 (*0.36*)	0.58 (*3.50*)	0.43 (*0.86*)	0.73 (*1.46*)	0.61 (*4.85*)	0.65 (*2.62*)
			A. e. = 0.17					0.59				
332	0.68 (*2.04*)	4.57 (*18.28*)	0.15 (*0.92*)	0.16 (*0.94*)	0.16 (*0.32*)	0.17 (*0.34*)	0.05 (*0.10*)	0.65 (*3.89*)	0.47 (*0.94*)	0.81 (*1.62*)	0.62 (*4.98*)	0.68 (*2.72*)
			A. e. = 0.14					0.64				
362	0.68 (*2.04*)	4.54 (*18.17*)	0.13 (*0.81*)	0.13 (*0.79*)	0.14 (*0.29*)	0.12 (*0.25*)	0.06 (*0.13*)	0.69 (*4.12*)	0.54 (*1.08*)	0.80 (*1.61*)	0.67 (*5.35*)	0.69 (*2.77*)
			A. e. = 0.12					0.67				
392	0.67 (*2.02*)	4.52 (*18.08*)	0.11 (*0.65*)	0.11 (*0.67*)	0.12 (*0.24*)	0.08 (*0.16*)	0.09 (*0.19*)	0.73 (*4.36*)	0.57 (*1.14*)	0.83 (*1.66*)	0.71 (*5.69*)	0.71 (*2.84*)

			A. e. = 0.10					0.71				
422	0.67 (*2.00*)	4.50 (*17.99*)	0.09 (*0.54*)	0.10 (*0.59*)	0.10 (*0.21*)	0.05 (*0.10*)	0.11 (*0.22*)	0.75 (*4.51*)	0.58 (*1.17*)	0.82 (*1.65*)	0.74 (*5.94*)	0.72 (*2.89*)
			A. e. = 0.09					0.73				
452	0.67 (*2.01*)	4.46 (*17.84*)	0.06 (*0.39*)	0.08 (*0.50*)	0.08 (*0.16*)	0.04 (*0.08*)	0.07 (*0.14*)	0.79 (*4.73*)	0.61 (*1.23*)	0.84 (*1.69*)	0.77 (*6.15*)	0.73 (*2.94*)
			A. e. = 0.07					0.75				
482	0.68 (*2.04*)	4.43 (*17.72*)	0.05 (*0.33*)	0.07 (*0.43*)	0.07 (*0.14*)	0.04 (*0.09*)	0.03 (*0.07*)	0.81 (*4.89*)	0.64 (*1.29*)	0.87 (*1.75*)	0.79 (*6.30*)	0.75 (*3.00*)
			A. e. = 0.06					0.78				
512	0.67 (*2.00*)	4.43 (*17.72*)	0.04 (*0.26*)	0.05 (*0.29*)	0.06 (*0.12*)	0.02 (*0.04*)	0.05 (*0.10*)	0.83 (*4.99*)	0.67 (*1.35*)	0.86 (*1.73*)	0.81 (*6.50*)	0.77 (*3.10*)
			A. e. = 0.04					0.80				
542	0.66 (*1.99*)	4.42 (*17.68*)	0.04 (*0.23*)	0.04 (*0.25*)	0.05 (*0.10*)	0.005 (*0.01*)	0.06 (*0.12*)	0.85 (*5.09*)	0.72 (*1.44*)	0.85 (*1.71*)	0.84 (*6.69*)	0.79 (*3.15*)
			A. e. = 0.04					0.81				
572	0.67 (*2.02*)	4.40 (*17.59*)	0.03 (*0.21*)	0.03 (*0.21*)	0.04 (*0.09*)	0.02 (*0.04*)	0.03 (*0.06*)	0.86 (*5.18*)	0.75 (*1.51*)	0.88 (*1.77*)	0.84 (*6.75*)	0.79 (*3.17*)
			A. e. = 0.03					0.84				
602	0.66 (*1.99*)	4.39 (*17.57*)	0.02 (*0.15*)	0.03 (*0.18*)	0.04 (*0.08*)	-	0.05 (*0.11*)	0.88 (*5.28*)	0.74 (*1.48*)	0.86 (*1.72*)	0.87 (*6.93*)	0.79 (*3.18*)
			A. e. = 0.04					0.84				
632	0.68 (*2.03*)	4.37 (*17.48*)	0.02 (*0.15*)	0.02 (*0.15*)	0.03 (*0.07*)	0.01 (*0.02*)	0.02 (*0.04*)	0.89 (*5.34*)	0.78 (*1.56*)	0.89 (*1.79*)	0.87 (*7.00*)	0.80 (*3.21*)
			A. e. = 0.02					0.86				
662	0.67 (*2.01*)	4.37 (*17.48*)	0.02 (*0.12*)	0.02 (*0.13*)	0.03 (*0.06*)	-	0.02 (*0.05*)	0.91 (*5.45*)	0.78 (*1.57*)	0.88 (*1.77*)	0.89 (*7.10*)	0.80 (*3.21*)
			A. e. = 0.02					0.87				
692	0.67 (*2.00*)	4.37 (*17.48*)	0.02 (*0.10*)	0.02 (*0.11*)	0.03 (*0.06*)	-	0.02 (*0.05*)	0.92 (*5.53*)	0.78 (*1.57*)	0.88 (*1.77*)	0.90 (*7.20*)	0.80 (*3.21*)
			A. e. = 0.02					0.87				
722	0.66 (*1.99*)	4.37 (*17.48*)	0.01 (*0.08*)	0.02 (*0.10*)	0.02 (*0.05*)	-	0.03 (*0.06*)	0.92 (*5.53*)	0.79 (*1.59*)	0.87 (*1.75*)	0.91 (*7.29*)	0.80 (*3.22*)

							A. e. = 0.02	0.88				
752	0.67 (*2.00*)	4.36 (*17.44*)	0.01 (*0.07*)	0.01 (*0.08*)	0.02 (*0.04*)	-	0.03 (*0.06*)	0.94 (*5.62*)	0.80 (*1.60*)	0.88 (*1.76*)	0.92 (*7.34*)	0.81 (*3.23*)
							A. e. = 0.02	0.88				
783	0.68 (*2.03*)	4.35 (*17.39*)	0.01 (*0.07*)	0.01 (*0.07*)	0.02 (*0.04*)	-	-	0.95 (*5.69*)	0.82 (*1.65*)	0.91 (*1.83*)	0.92 (*7.36*)	0.81 (*3.25*)
							A. e. = 0.01	0.90				
813	0.68 (*2.03*)	4.34 (*17.36*)	0.01 (*0.06*)	0.01 (*0.06*)	0.02 (*0.04*)	-	-	0.95 (*5.72*)	0.83 (*1.66*)	0.92 (*1.84*)	0.93 (*7.42*)	0.82 (*3.27*)
							A. e. = 0.01	0.91				
843	0.67 (*2.00*)	4.34 (*17.39*)	0.01 (*0.04*)	0.01 (*0.05*)	-	-	-	0.96 (*5.81*)	0.84 (*1.67*)	0.89 (*1.87*)	0.94 (*7.55*)	0.82 (*3.34*)
							A. e. = 0.01	0.91				
873	0.68 (*2.04*)	4.33 (*17.31*)	0.01 (*0.04*)	0.01 (*0.05*)	-	-	-	0.97 (*5.81*)	0.83 (*1.67*)	0.93 (*1.87*)	0.94 (*7.55*)	0.83 (*3.34*)
							A. e. = 0.01	0.92				
903	0.68 (*2.04*)	4.33 (*17.32*)	0.01 (*0.04*)	0.01 (*0.04*)	-	-	-	0.98 (*5.87*)	0.88 (*1.77*)	0.94 (*1.88*)	0.96 (*7.67*)	0.85 (*3.40*)
							A. e. = 0.01	0.94				

[a] Equivalence = Integration / (# chemically equivalent ^{1}H per molecule). [b] Integration for internal standard at 3.31 ppm were set to 6.83 ^{1}H for all spectra

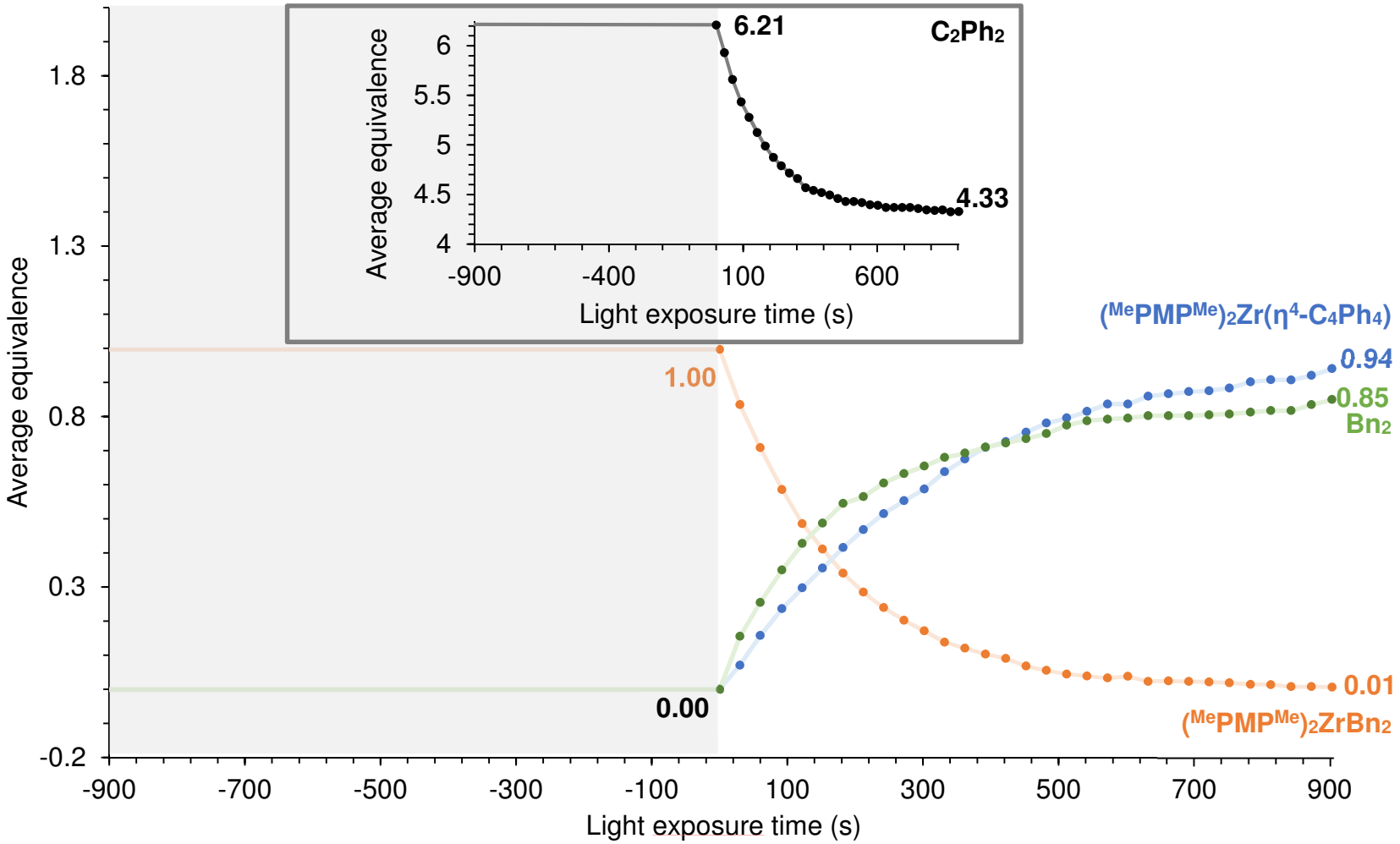


Figure S23. Reaction time course before and after blue light exposure. Shaded area represents the reaction mixture in the dark. Due to fast reactivity under blue light, the full 3 600 s in the dark is not included for clarity. Consumption of diphenylacetylene over time is in a separate chart insert for visual acuity.

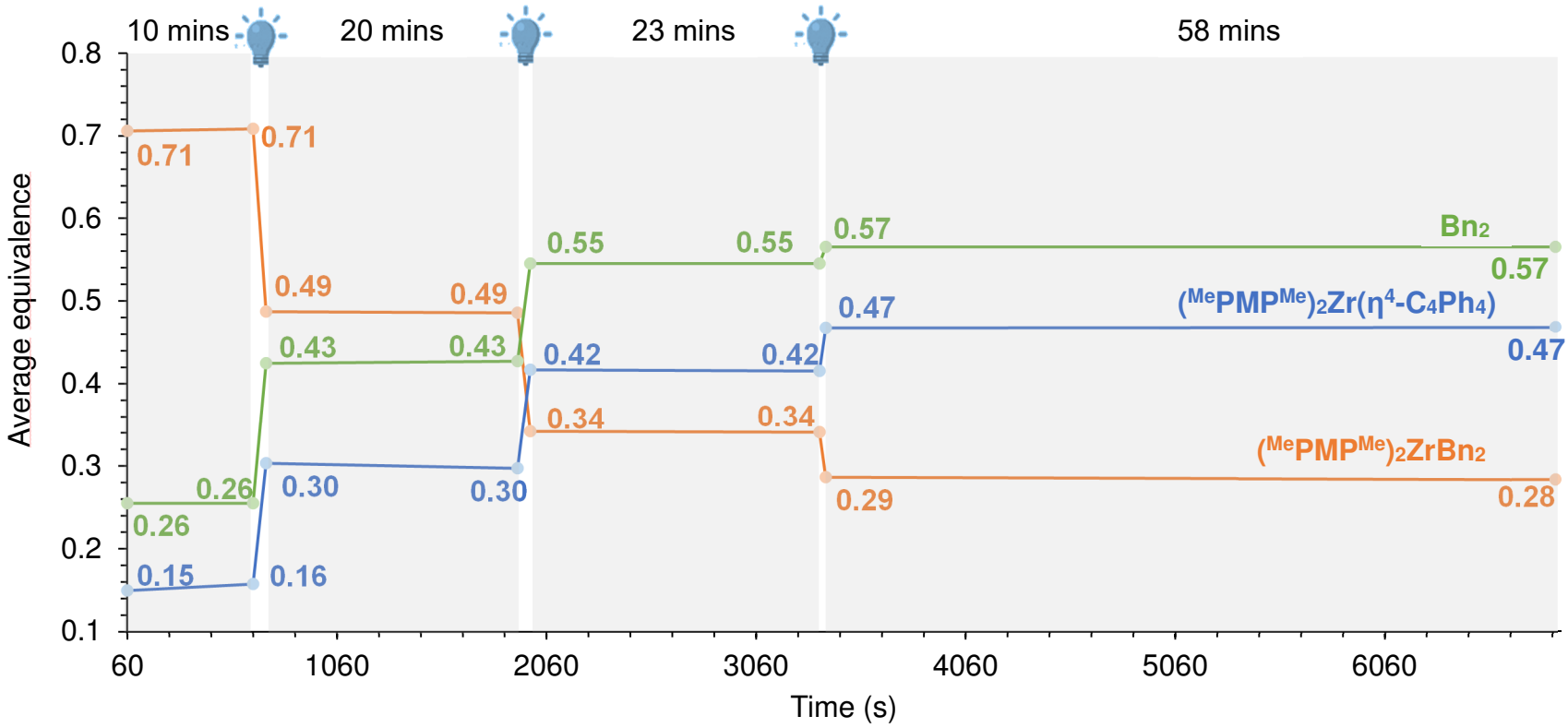


Figure S24. Intermittent light/dark experiments show lack of productive chemistry without light exposure. Shaded areas represent the time that the reaction mixture was kept in the dark.

7. Characterization of the Bibenzyl Products from Crossover Experiments

7.1 Isolation procedure of the bibenzyl mixture.

The purification of $(^{Me}PMP^{Me})_2ZrBr_2$ generated a pale orange pentane filtrate containing three bibenzyl derivatives. Running the filtrate through a glass pipette packed with glass filters and celite gave a pale-yellow solution. Drying under vacuum resulted 5 mg of organic products that was used for NMR sample in C_6D_6 followed by GC-MS in hexane.

7.2 NMR Spectroscopy.

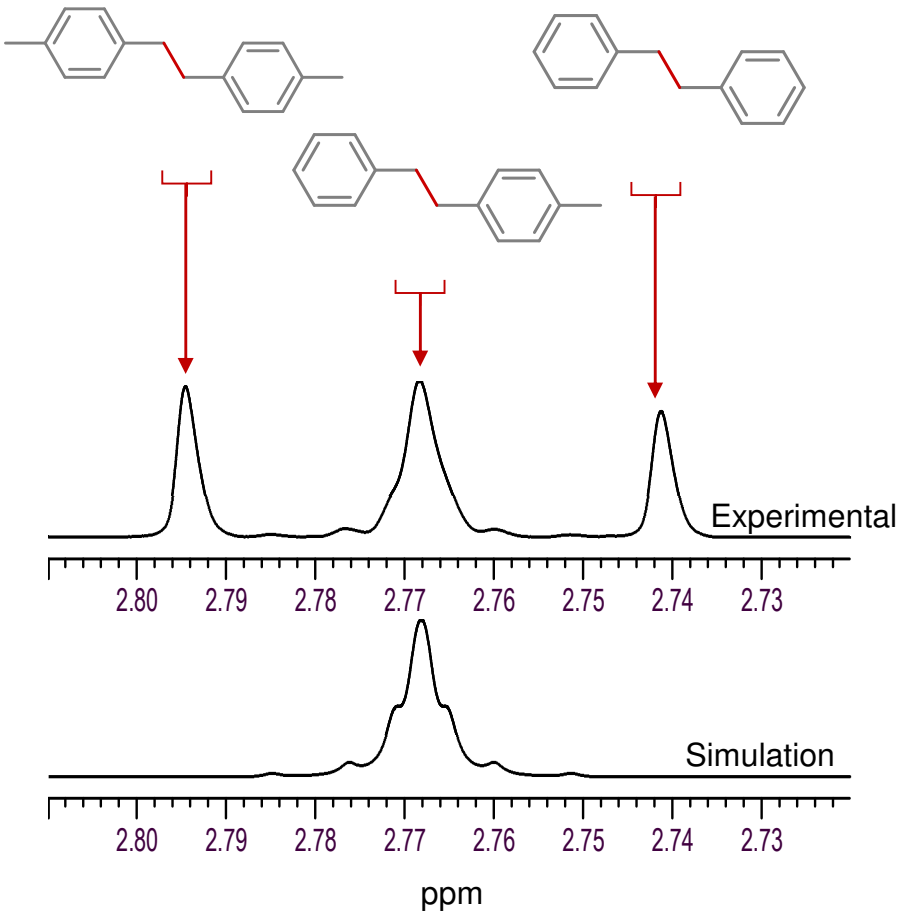


Figure S25. gNMR (Version 5.0.2.0) simulated spectrum that confirms the chemical shift (2.77 ppm) in C_6D_6 and splitting pattern, or lack thereof, for the asymmetric 4-methylbibenzyl ($^{Me}Bn_2$).

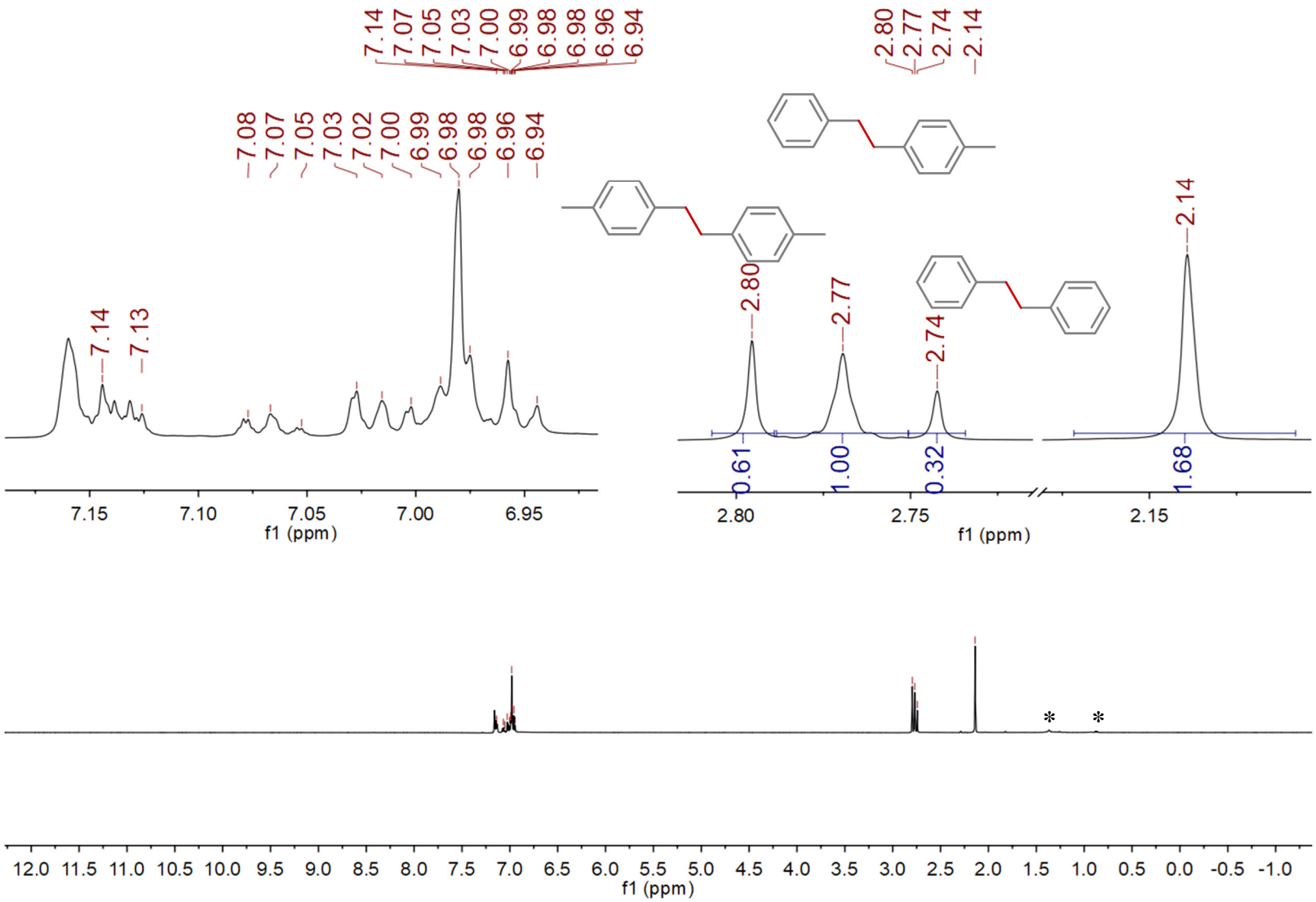


Figure S26. ^{1}H NMR spectrum of $^{Me}{}_2Bn_2$, $^{Me}Bn_2$ and Bn_2 in C_6D_6 (599.67 MHz). Overlap of $^{Me}{}_2Bn_2$ and $^{Me}Bn_2$'s methyl ^{1}H at 2.14 ppm can be deduced from COSY spectrum (see Figure S29). *Pentane solvent peaks.

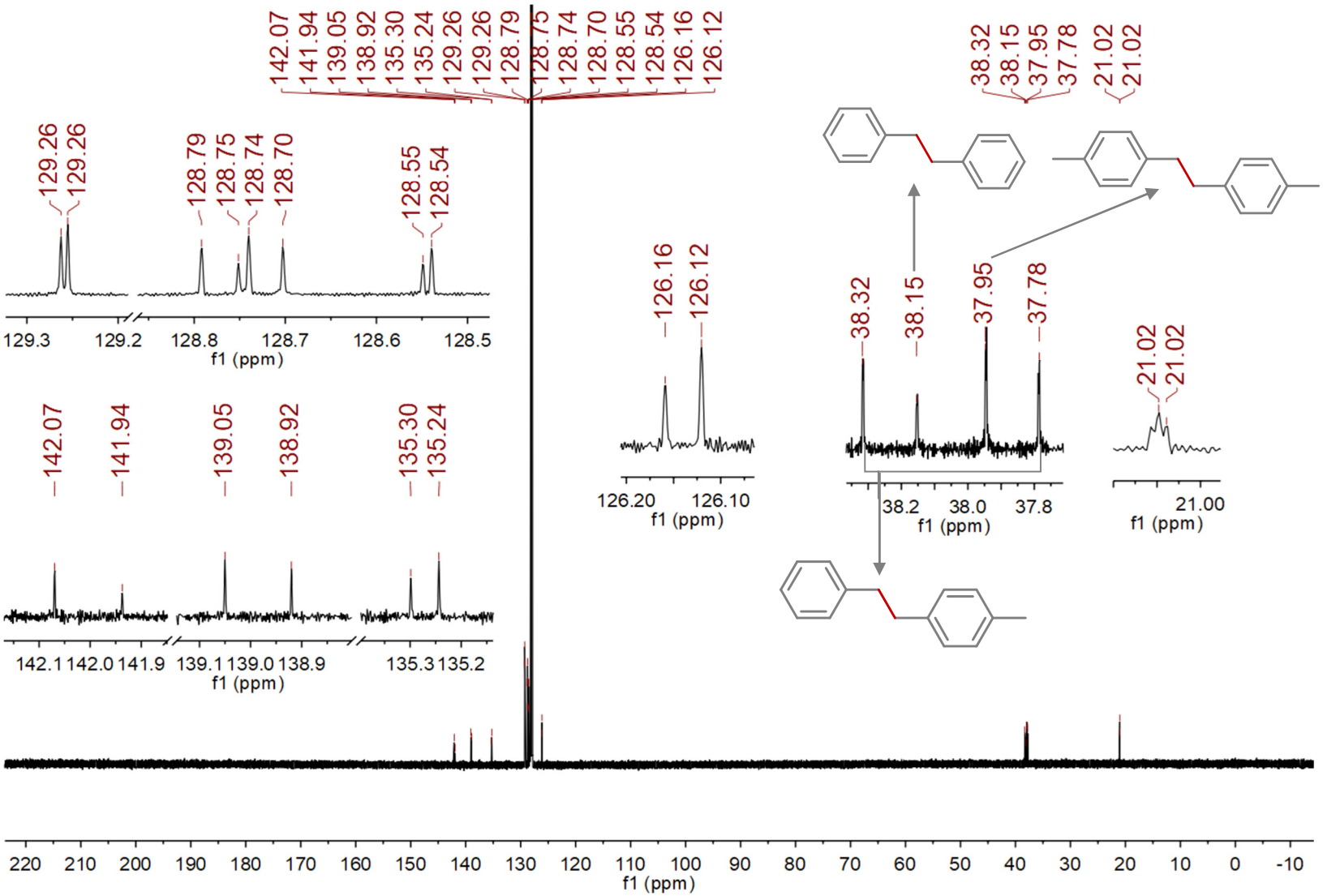


Figure S27. ^{13}C NMR spectrum of $^{Me}{}_2Bn_2$, $^{Me}Bn_2$ and Bn_2 mixture in C_6D_6. All 22 ^{13}C peaks are present. Overlap of two methyl peaks are confirmed by COSY crosspeaks to two different benzylic ^{1}H (2.77 and 2.80 ppm).

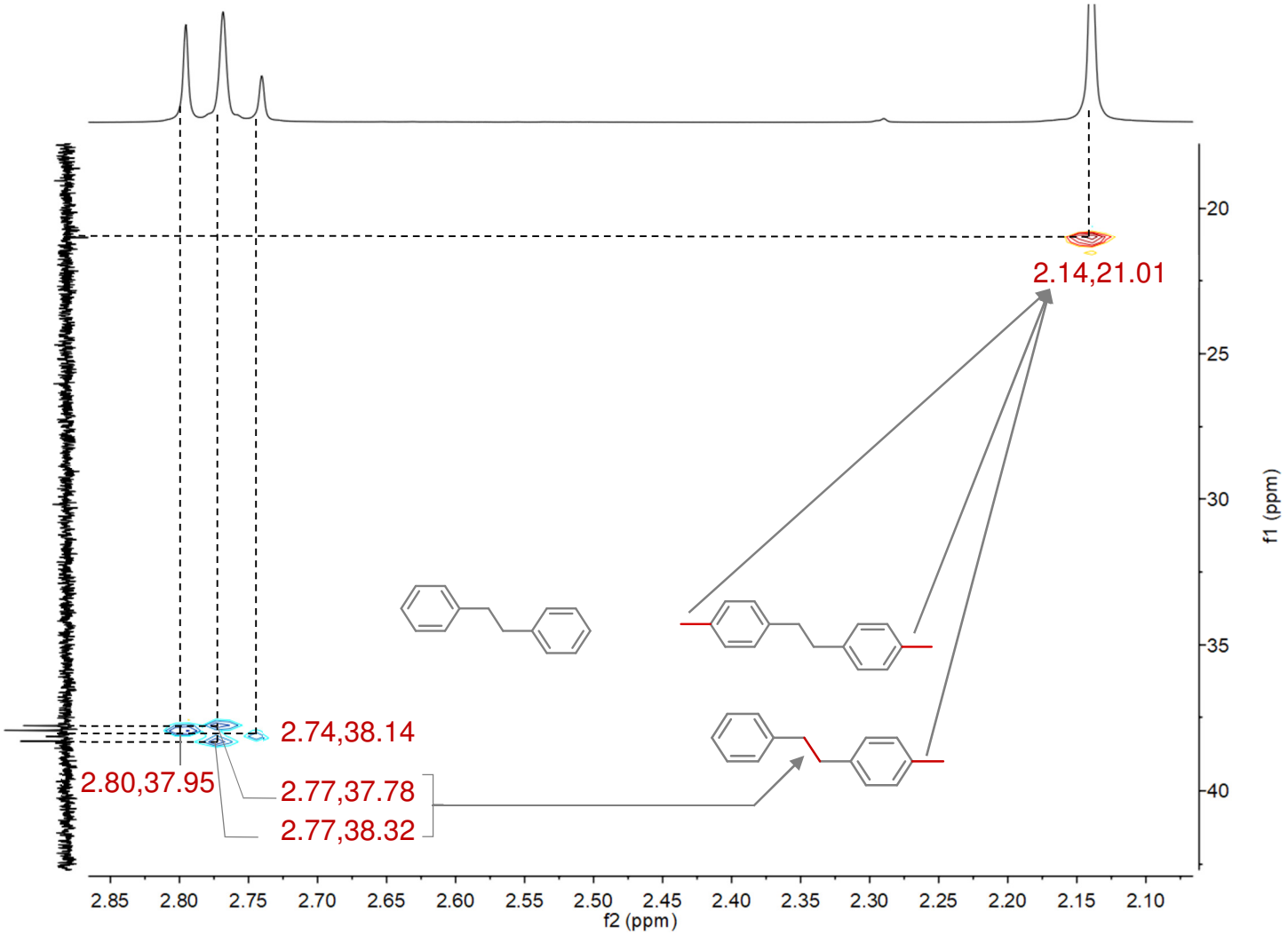


Figure S28. gHSQCAD NMR spectrum shows only aliphatic region of $^{Me}{}_2Bn_2$, $^{Me}Bn_2$ and Bn_2 mixture in C_6D_6 (599.67 MHz). Cross peaks with two different ^{13}C confirms benzylic ^{1}H at 2.77 ppm to be of the only asymmetric derivative, $^{Me}Bn_2$. Intense correlation at (2.14 ppm, 21.01 ppm) suggests two methyl peaks of similar chemical shifts in both ^{13}C (Figure S27) and ^{1}H (Figure S26) NMR spectra.

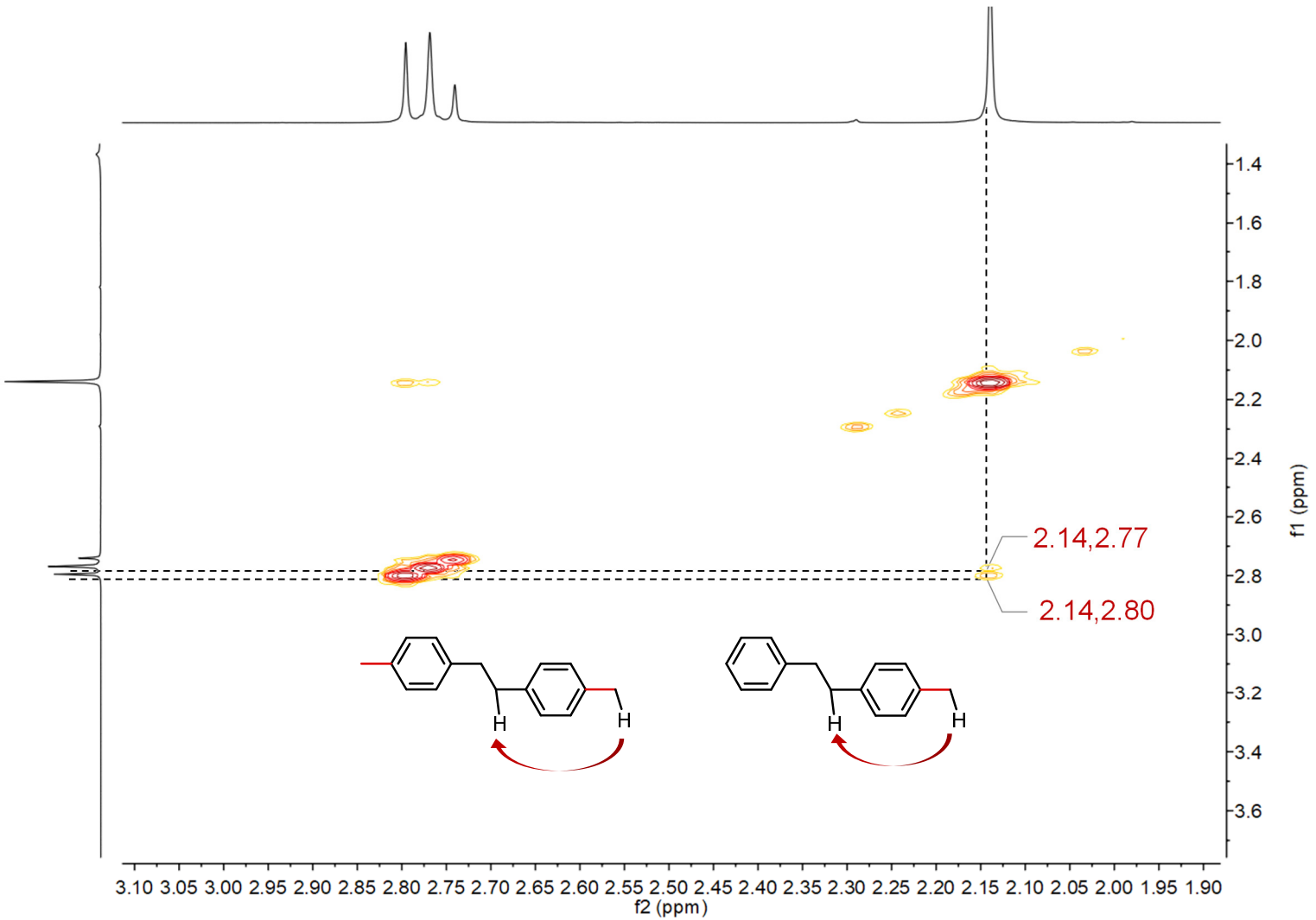


Figure S29. gCOSY NMR spectrum shows only aliphatic region of $^{Me}{}_2Bn_2$, $^{Me}Bn_2$ and Bn_2 mixture in C_6D_6 (599.67 MHz). Long-range coupling correlation between methyl at 2.14 ppm and two different benzylic ^1H (2.77 and 2.80 ppm) confirms two bibenzyl derivatives with similar methyl's chemical shift in ^1H (Figure S26) and hence ^{13}C (Figure S27) NMR spectra.

7.3 GC-MS

Using hexane as the carrier solvent, a 3 ppm solution of the bibenzyl mixture was prepared. Integration of the isolated organic mixture in ^{1}H NMR showed 4-methylbibenzyl at the highest concentration. Hence, the concentration calculation was based on the molecular weight of this derivative to avoid obstructing the analytical column. Carrier gas, pure helium gas (99.99%), flowed at a rate of 1.00 mL/min. Injection volume into the GC-MS was 1.5 µL using splitless mode. The initial temperature of 50 °C was ramped to 150 °C at the rate of 10 °C/min. After holding for 1.25 min, the temperature was increased to 200 °C at the same rate followed by a hold time of 2.00 min. At 40 °C/min, the temperature rose to 250 °C before another 2.0 minutes of holing time. Using the initial rate of 10 °C/min for the rest of the experiment, the last two target temperatures of 285 °C and 300 °C were achieved and separated from each other by another 2.00 minutes of holding at 300 °C, the final hold time was 10 minutes.

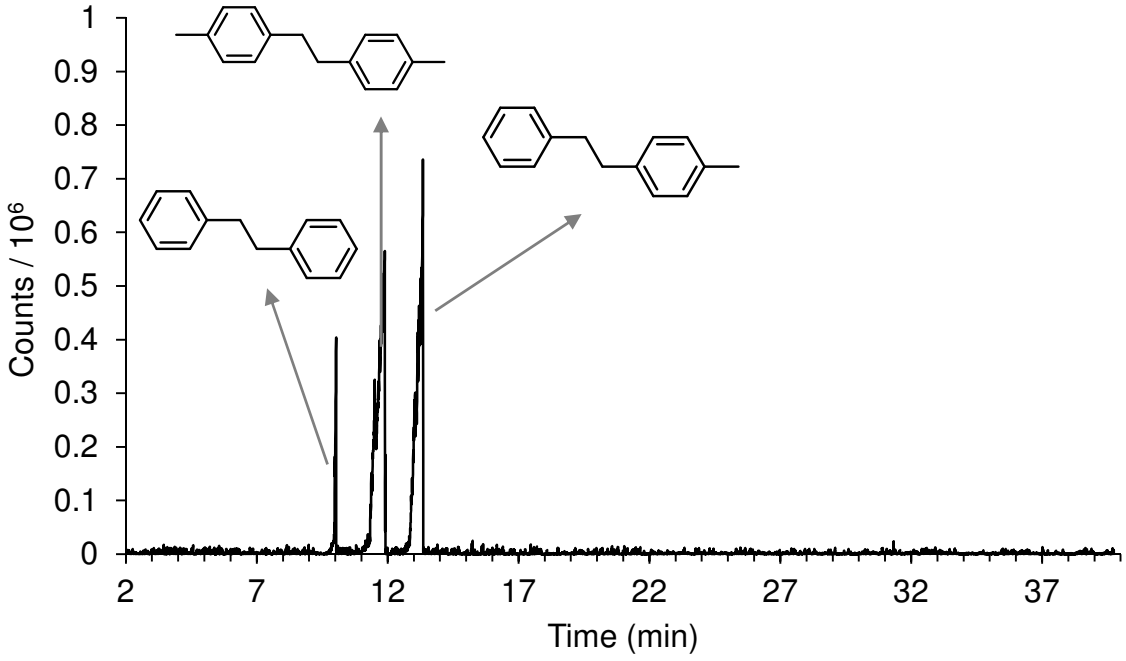


Figure S30. Gas chromatogram of $^{Me}{}_2Bn_2$, $^{Me}Bn_2$ and Bn_2 mixture in hexane. Hexane solvent peak is excluded for clarity.

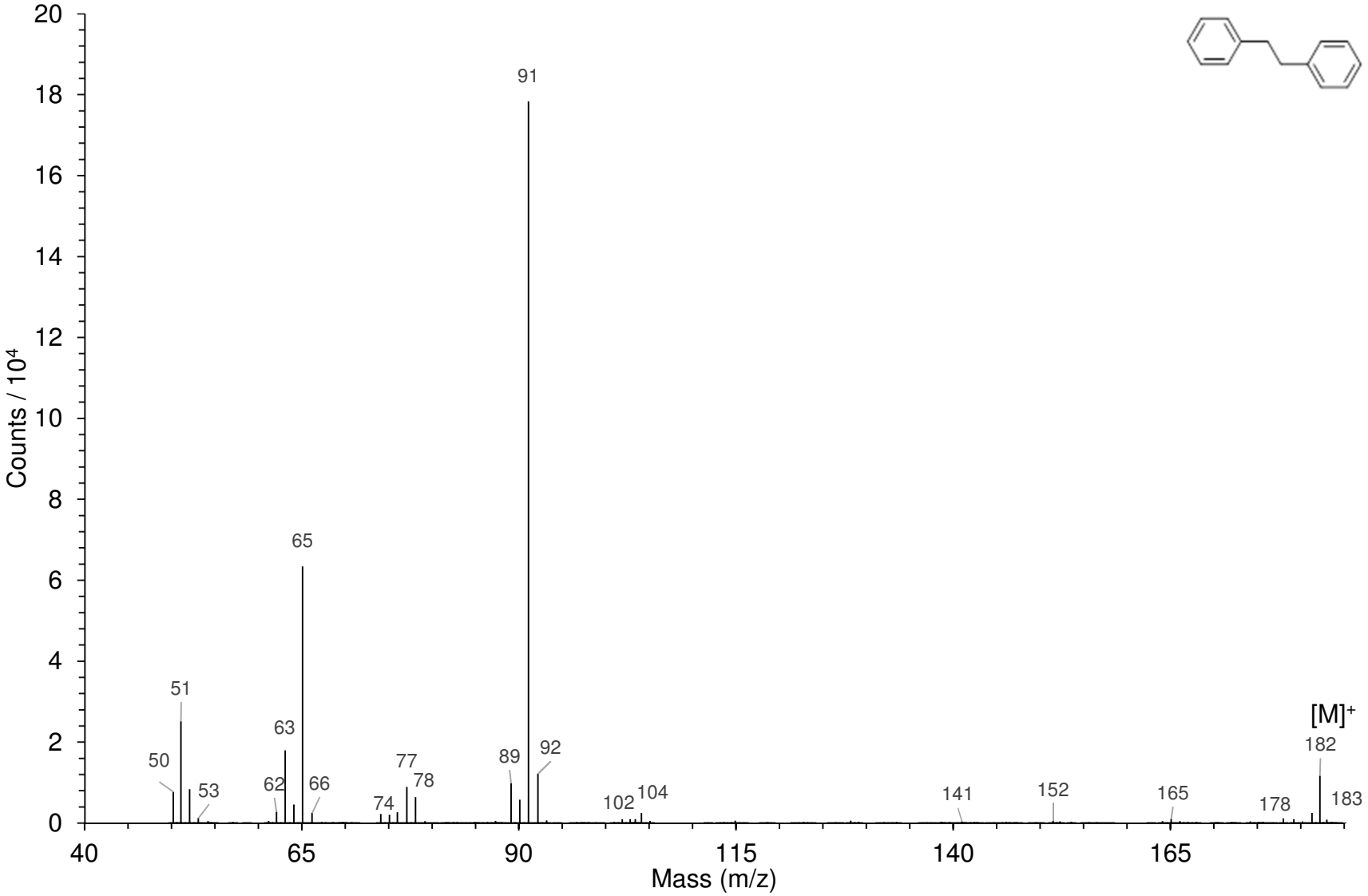


Figure S31. Mass spectrum of Bn_2 at 10.0 minutes retention time and matches with that reported in NIST Chemistry WebBook, SRD 69. [11]

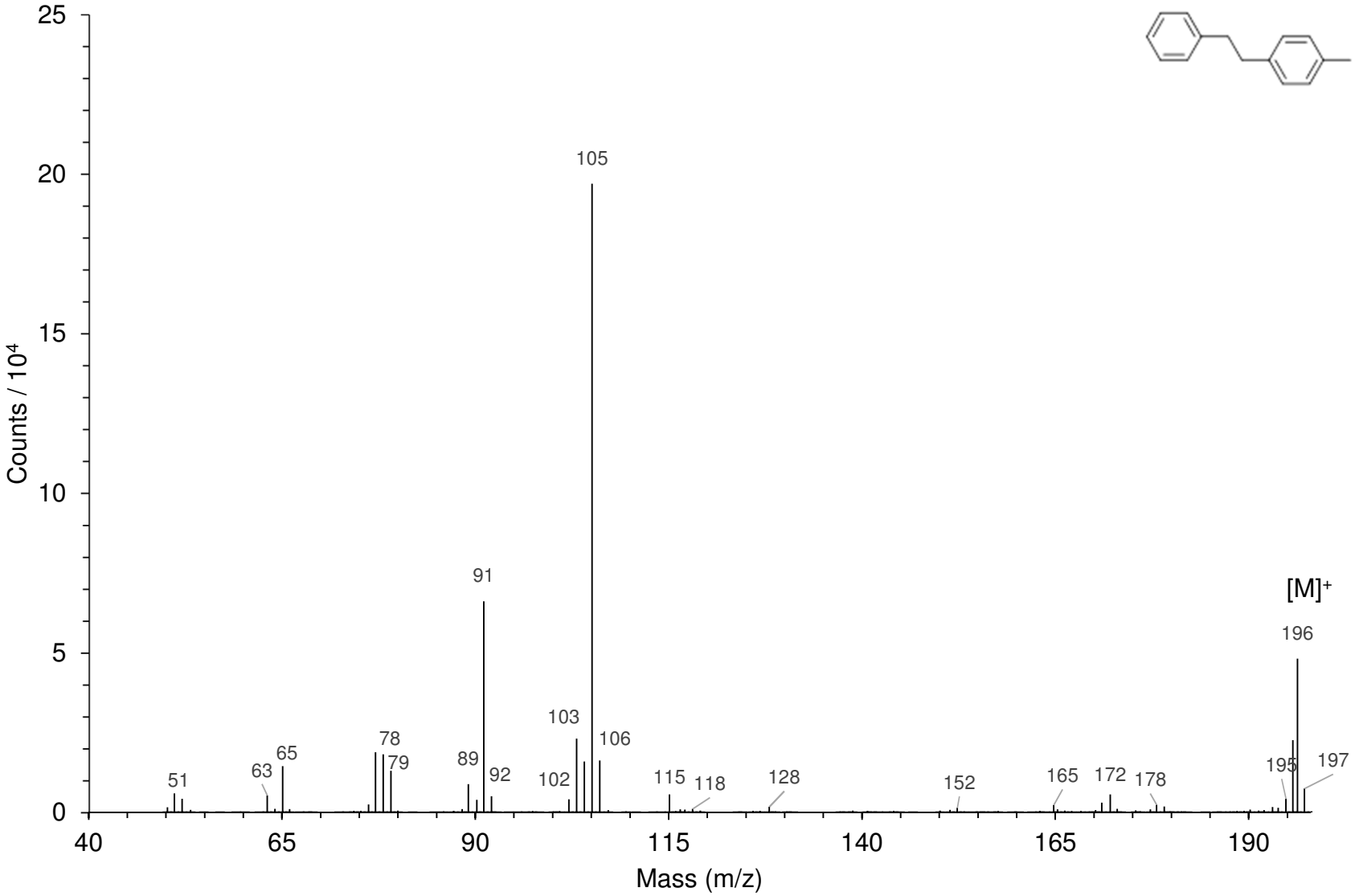


Figure S32. Mass spectrum of $^{Me}Bn_2$ at 11.9 minutes retention time and matches with that of the structural isomer reported in NIST Chemistry WebBook, SRD 69. [12]

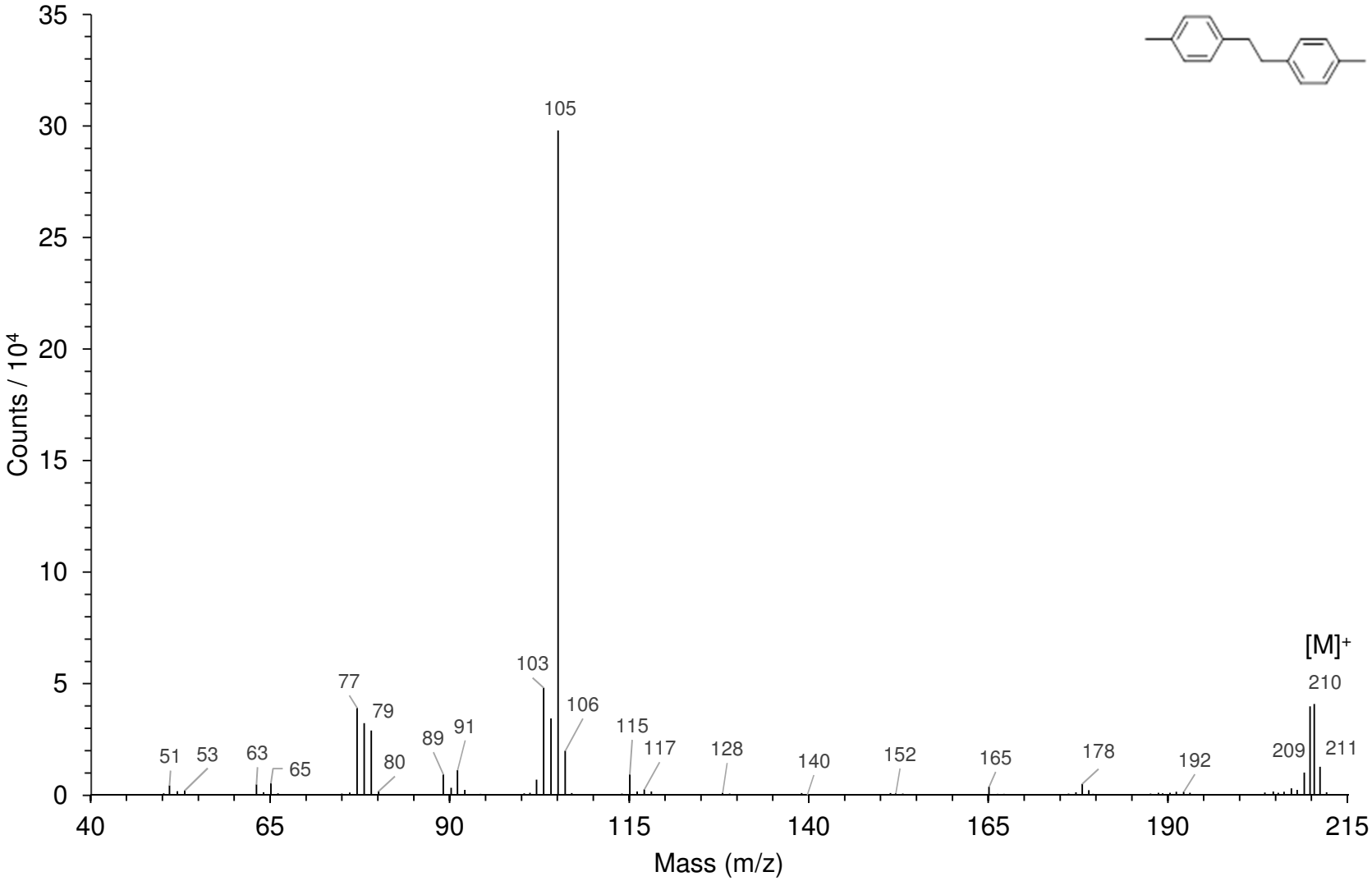


Figure S33. Mass spectrum of $^{Me}_2Bn_2$ at 13.3 minutes retention time and matches with that reported in NIST Chemistry WebBook, SRD 69. [13]

8. DFT Calculations

All DFT calculations were performed with the ORCA program package (version 3.0.2).[10] Geometry optimizations of the complexes and single-point calculations on the optimized geometries were carried out at the B3LYP level of DFT.[11–13] The all-electron Gaussian basis sets were those developed by the Ahlrichs group.[14–16] Triple-ζ quality basis sets def2-TZVP with one set of polarization functions were used for all atoms. Auxiliary basis sets to expand the electron density in the resolution-of-the-identity (RIJCOSX)[17–19] approach were chosen to match the orbital basis.[20–22] Time-dependent DFT calculations were performed at the B3LYP level of theory. To reduce computational cost, numerical frequencies were calculated at the BP86 level of theory[11,23] to derive thermochemical data under standard conditions (298 K, 1 atm). All molecular orbital plots were generated using the program Gabedit.[24] The WVU High Performance Computing facilities are funded by the National Science Foundation EPSCoR Research Infrastructure Improvement Cooperative Agreement #1003907, the state of West Virginia (WVEPSCoR via the Higher Education Policy Commission), the WVU Research Corporation, and faculty investments.

8.1 Input File Example

Geometry Optimizations

```
! RKS B3LYP RIJCOSX SlowConv TightSCF def2-TZVP(-f) def2-TZVP/J Normalprint Opt

%scf MaxIter 500
       TolE 1E-7
       TolErr 1E-6
     end

*xyz 0 1
xyz coordinates from X-ray structure
*
```

TD-DFT Calculations

```
! RKS B3LYP RIJCOSX SlowConv TightSCF def2-TZVP(-f) def2-TZVP/J

%scf MaxIter 500
       TolE 1E-7
       TolErr 1E-6
```

```
      end

%tddft nroots 50
         MaxDim 500
         triplets false
        end

*xyz 0 1
xyz coordinates from geometry optimization
*
```

Numerical Frequency Analysis

```
! RKS BP86 RI SlowConv TightSCF def2-TZVP(-f) def2-TZVP/J Normalprint Opt Grid4
NoFinalGrid NumFreq

%scf MaxIter 500
       TolE 1E-7
       TolErr 1E-6
      end

%freq CentralDiff true
        Increment 0.01
       end

*xyz 0 1
xyz coordinates from X-ray structure
*
```

8.2 Selected Molecular Orbitals

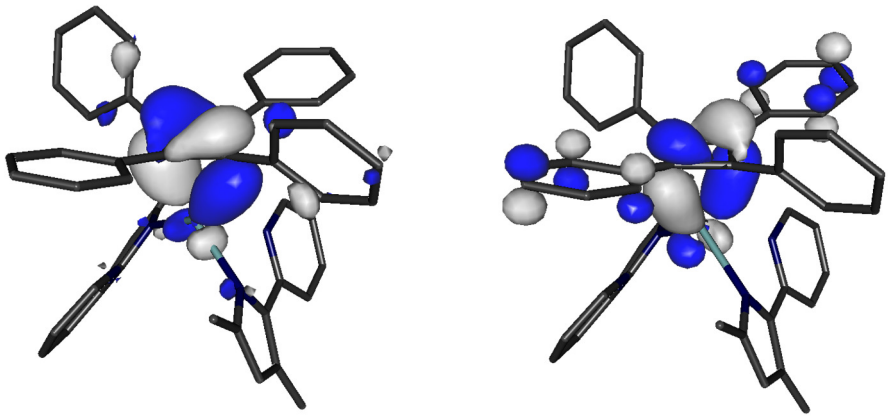


Figure S34. HOMO-1 (left) and HOMO (right) of (^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$).

8.3 Optimized Geometries

(^{Me}PMP^{Me})$_2$ZrBn$_2$ (B3LYP)

Zr	-0.261120	-0.290577	0.026696
N	-0.780262	-2.353868	-0.585169
N	-0.575797	-0.454866	-2.441071
N	-2.167094	-0.066544	1.119643
N	0.093069	-0.245454	2.508358
C	-0.916840	-3.481025	0.184938
C	-1.051098	-4.593633	-0.645382
C	-1.012537	-4.151087	-1.988392
C	-0.852846	-2.755116	-1.913997
C	-0.786708	-1.725456	-2.909122
C	-0.957023	-1.961004	-4.294376
C	-0.922896	-0.904182	-5.186468
C	-0.711827	0.392564	-4.697424
C	-0.541015	0.554274	-3.330031
C	-1.114902	-5.042658	-3.192217
C	-0.944140	-3.459422	1.681208
C	-3.422581	0.125708	0.603216
C	-4.312072	0.393779	1.643839
C	-3.589863	0.360095	2.861608
C	-2.262437	0.067541	2.497595
C	-1.046869	-0.069992	3.248672
C	-0.987649	-0.040081	4.661965
C	0.230207	-0.164045	5.308778
C	1.392722	-0.317303	4.542996
C	1.264171	-0.354289	3.161239
C	-4.171383	0.614769	4.222599
C	-3.733008	0.016569	-0.857597
C	2.022011	-0.663701	0.195956
C	2.608698	-0.902534	-1.151484
C	3.074128	0.161542	-1.956067
C	3.637354	-0.066778	-3.212947
C	3.762923	-1.369899	-3.706122
C	3.310237	-2.439437	-2.925816
C	2.734712	-2.209755	-1.674835
C	-0.241522	1.949287	-0.587935
C	-0.088109	2.772589	0.643463
C	-1.206562	3.152646	1.421406
C	-1.061227	3.930537	2.570940
C	0.206002	4.349459	2.991968
C	1.327488	3.981349	2.241418
C	1.181695	3.206850	1.088014
H	-1.179642	-5.623859	-0.311727

H	-1.137068	-2.973346	-4.647722
H	-1.069472	-1.084914	-6.255064
H	-0.680353	1.261880	-5.355421
H	-0.370146	1.548727	-2.923820
H	-0.275154	-4.900263	-3.893571
H	-2.044969	-4.874859	-3.764641
H	-1.110623	-6.099158	-2.882971
H	0.036283	-3.205898	2.120547
H	-1.232719	-4.449248	2.064590
H	-1.670088	-2.725520	2.064434
H	-5.377704	0.597658	1.533586
H	-1.905382	0.082101	5.232192
H	0.279981	-0.141882	6.401029
H	2.377685	-0.414961	5.002434
H	2.150957	-0.481915	2.545088
H	-4.157692	-0.286088	4.861942
H	-5.219731	0.939712	4.139796
H	-3.627843	1.405434	4.766513
H	-3.103216	0.677652	-1.474228
H	-4.780971	0.294702	-1.042986
H	-3.581612	-1.010928	-1.231449
H	2.463930	0.227169	0.670694
H	2.180403	-1.537493	0.847372
H	3.011098	1.184969	-1.573008
H	3.997135	0.778794	-3.805476
H	4.217448	-1.552559	-4.683209
H	3.417901	-3.464144	-3.294635
H	2.386550	-3.057021	-1.077091
H	0.604791	2.105584	-1.275857
H	-1.180702	2.185086	-1.113164
H	-2.204448	2.830616	1.112245
H	-1.947824	4.214921	3.144768
H	0.319737	4.958176	3.892911
H	2.322506	4.312833	2.553349
H	2.066871	2.948795	0.498936

$(^{Me}PMP^{Me})_2Zr(\eta^4\text{-}C_4Ph_4)$ (B3LYP)

Zr	0.003455	0.180616	0.031588
N	-0.448372	2.196348	-0.980380
N	2.034639	1.050737	-0.813255
N	0.800474	0.113070	2.168199
N	-1.839765	0.408856	1.493395
C	-1.520423	2.978114	-1.318260
C	-1.085737	4.192818	-1.830040

C	0.312391	4.202733	-1.820057
C	0.691914	2.959974	-1.285354
C	1.987084	2.371614	-1.164856
C	3.188654	3.056130	-1.450079
C	4.382080	2.375054	-1.486328
C	4.397587	1.001841	-1.234650
C	3.207197	0.397714	-0.894836
C	1.139354	5.335169	-2.348453
C	-2.955289	2.608000	-1.158594
C	1.983070	-0.090654	2.825664
C	1.813537	0.125847	4.186500
C	0.479671	0.475625	4.417724
C	-0.133556	0.475705	3.154184
C	-1.501256	0.672656	2.792165
C	-2.504963	1.068222	3.703106
C	-3.824458	1.086221	3.314552
C	-4.162268	0.712418	2.012861
C	-3.138391	0.401985	1.146263
C	-0.095061	0.701754	5.783990
C	3.276554	-0.480869	2.192278
C	-0.975548	-2.084104	-0.249498
C	-1.167058	-1.332929	-1.491112
C	0.275041	-1.404179	-1.757772
C	0.444070	-2.199738	-0.530139
C	-1.876606	-2.882303	0.613324
C	-1.912238	-2.778295	2.009334
C	-2.740322	-3.592306	2.774419
C	-3.551280	-4.541549	2.163376
C	-3.522670	-4.668859	0.779138
C	-2.697231	-3.851892	0.015864
C	-2.313769	-0.933129	-2.296441
C	-3.632605	-1.267778	-1.928073
C	-4.720594	-0.900881	-2.709803
C	-4.537955	-0.190604	-3.890810
C	-3.242616	0.147038	-4.274884
C	-2.153521	-0.213934	-3.498107
C	1.022479	-1.375973	-3.036986
C	1.390764	-2.593182	-3.630227
C	2.071838	-2.633625	-4.840000
C	2.390452	-1.454766	-5.505305
C	2.016886	-0.240085	-4.944471
C	1.343651	-0.201623	-3.728791
C	1.520913	-2.993584	0.052018
C	2.746418	-3.189988	-0.616046
C	3.763413	-3.956568	-0.060698
C	3.599133	-4.559912	1.180325

C	2.389057	-4.394712	1.848979
C	1.370937	-3.633505	1.299097
H	-1.726229	4.983359	-2.192009
H	3.162774	4.111045	-1.661698
H	5.297947	2.901795	-1.724679
H	5.305790	0.419107	-1.289368
H	3.180423	-0.658637	-0.675772
H	0.487628	6.094968	-2.782446
H	1.830490	5.014259	-3.132794
H	1.733967	5.821591	-1.569219
H	-3.172443	1.606458	-1.525854
H	-3.568126	3.302970	-1.732228
H	-3.278751	2.672357	-0.117321
H	2.581492	0.014132	4.937929
H	-2.231896	1.353453	4.704644
H	-4.592528	1.381420	4.018872
H	-5.186873	0.682096	1.670461
H	-3.354750	0.134643	0.123929
H	0.648875	0.445273	6.539292
H	-0.973905	0.079955	5.970794
H	-0.387764	1.742071	5.956390
H	3.164447	-1.305337	1.488675
H	3.968252	-0.809557	2.968294
H	3.742332	0.356835	1.668265
H	-1.285158	-2.050615	2.505469
H	-2.755346	-3.476677	3.851810
H	-4.196889	-5.175663	2.758051
H	-4.140542	-5.411049	0.288399
H	-2.676612	-3.973978	-1.059808
H	-3.808895	-1.828592	-1.022862
H	-5.717017	-1.183256	-2.390237
H	-5.386050	0.097591	-4.498665
H	-3.077951	0.704647	-5.189056
H	-1.164944	0.073463	-3.820476
H	1.131009	-3.518463	-3.132624
H	2.345725	-3.589900	-5.269189
H	2.920139	-1.483331	-6.449173
H	2.256193	0.687486	-5.450510
H	1.070872	0.756210	-3.309326
H	2.902512	-2.751537	-1.590204
H	4.687807	-4.088458	-0.610699
H	4.393628	-5.151808	1.616847
H	2.236154	-4.861729	2.814179
H	0.450462	-3.521831	1.849828

(^{Me}PMP^{Me})$_2$Zr(η^4-C$_4$Ph$_4$) (BP86)

Zr	-0.055394	0.042686	0.119581
N	0.168104	-1.980346	-0.871253
N	2.062565	-0.034478	-0.846050
N	-0.424439	1.964936	-1.005044
N	-2.270921	0.002716	-0.676654
C	-0.560163	-3.121940	-1.065967
C	-0.245670	-3.679935	-2.314675
C	0.732407	-2.878184	-2.923164
C	0.991478	-1.829405	-2.003905
C	2.031076	-0.842925	-1.966430
C	3.036929	-0.698701	-2.953243
C	4.086208	0.181342	-2.753186
C	4.148068	0.931730	-1.569426
C	3.109572	0.799430	-0.660463
C	1.359040	-3.157910	-4.256284
C	-1.482971	-3.698148	-0.043418
C	0.275153	3.100830	-1.322499
C	-0.263083	3.680217	-2.478535
C	-1.349425	2.895001	-2.902643
C	-1.441391	1.836621	-1.965810
C	-2.432362	0.819296	-1.777977
C	-3.560426	0.648174	-2.616450
C	-4.526438	-0.291270	-2.302297
C	-4.379154	-1.071975	-1.146811
C	-3.237905	-0.892812	-0.379938
C	-2.206591	3.199719	-4.095834
C	1.403026	3.630328	-0.500058
C	-0.304089	1.002963	2.275743
C	-0.962363	-0.323170	2.407625
C	0.329624	-0.992615	2.368243
C	1.000438	0.312644	2.314340
C	-0.734306	2.332678	2.773665
C	-1.496400	3.235464	2.009260
C	-1.925143	4.453083	2.545151
C	-1.594461	4.803722	3.856328
C	-0.833110	3.922014	4.629623
C	-0.412249	2.702746	4.096766
C	-2.321507	-0.712216	2.752896
C	-3.358059	0.249107	2.828298
C	-4.654107	-0.110960	3.190215
C	-4.970848	-1.441353	3.486872
C	-3.961443	-2.406525	3.421450
C	-2.660359	-2.051642	3.064177
C	0.823048	-2.340506	2.721763

C	0.496414	-2.873809	3.986604
C	0.992244	-4.111408	4.400437
C	1.837843	-4.846981	3.565480
C	2.181570	-4.328986	2.313727
C	1.678941	-3.094846	1.895851
C	2.362061	0.760535	2.561977
C	3.435583	-0.152235	2.699411
C	4.729383	0.289306	2.967936
C	5.006685	1.654237	3.106406
C	3.959312	2.572160	2.982080
C	2.660413	2.136623	2.718800
H	-0.668339	-4.594774	-2.725585
H	2.990887	-1.298681	-3.857651
H	4.866102	0.277341	-3.510518
H	4.973530	1.609104	-1.357897
H	3.100298	1.374535	0.265039
H	0.852037	-4.003883	-4.739681
H	2.425308	-3.425107	-4.170106
H	1.290645	-2.297764	-4.940466
H	-1.461133	-3.121236	0.887254
H	-1.185694	-4.729822	0.199500
H	-2.522478	-3.735968	-0.402964
H	0.084783	4.596821	-2.950757
H	-3.665120	1.270622	-3.500301
H	-5.398920	-0.412691	-2.946607
H	-5.126774	-1.803117	-0.844304
H	-3.083448	-1.479078	0.524021
H	-1.826025	4.091156	-4.612293
H	-3.253887	3.404158	-3.819780
H	-2.215267	2.375159	-4.826427
H	1.457895	3.131281	0.474647
H	1.271591	4.706868	-0.316320
H	2.374659	3.502103	-1.002157
H	-1.741897	2.978512	0.978397
H	-2.514898	5.134315	1.928874
H	-1.926214	5.756158	4.273041
H	-0.570922	4.181018	5.657213
H	0.173029	2.015881	4.710330
H	-3.135456	1.291575	2.605607
H	-5.426698	0.658507	3.242516
H	-5.986550	-1.719882	3.771142
H	-4.184868	-3.448648	3.658421
H	-1.889849	-2.820922	3.039416
H	-0.139932	-2.294967	4.657683
H	0.725200	-4.496371	5.386379
H	2.227762	-5.813491	3.888624

H	2.839768	-4.893130	1.650343
H	1.934397	-2.711387	0.908228
H	3.244945	-1.219754	2.599848
H	5.532279	-0.443185	3.071309
H	6.021225	1.995519	3.316687
H	4.150637	3.640431	3.101051
H	1.856462	2.868791	2.655992

(^{Me}PMP^{Me})$_2$Zr(C_4Ph_4), *trans*-pyridine (BP86)

Zr	-0.091595	-0.098128	-0.061298
N	-1.644000	-1.515633	-0.761021
N	-0.137478	-0.218450	-2.503699
N	-1.624452	1.108651	0.993108
N	0.426476	0.090366	2.314505
C	-2.539056	-2.268126	-0.035509
C	-3.342605	-2.999444	-0.912499
C	-2.945567	-2.698438	-2.236349
C	-1.888644	-1.773822	-2.109486
C	-1.063241	-1.084643	-3.050063
C	-1.144326	-1.250308	-4.453683
C	-0.284766	-0.556452	-5.286225
C	0.666404	0.307065	-4.723017
C	0.694957	0.437638	-3.341876
C	-3.560246	-3.280592	-3.473794
C	-2.582391	-2.252899	1.458450
C	-2.770338	1.699026	0.510326
C	-3.459375	2.298380	1.566831
C	-2.726325	2.081287	2.756924
C	-1.591918	1.339918	2.368278
C	-0.470110	0.809740	3.077479
C	-0.240560	0.993660	4.462321
C	0.895535	0.470772	5.053492
C	1.815144	-0.237210	4.265515
C	1.533292	-0.397732	2.916548
C	-3.128106	2.569650	4.116515
C	-3.142788	1.680407	-0.937145
C	1.723624	-1.465266	-0.002034
C	1.581192	1.371412	-0.522283
C	2.830304	-0.770878	-0.430236
C	2.795363	0.731081	-0.449658
C	1.361156	2.820325	-0.380020
C	1.858119	3.542370	0.729559

C	0.556305	3.524701	-1.303425
C	1.575345	4.897138	0.894719
C	0.293008	4.886407	-1.147884
C	0.798699	5.581590	-0.046183
C	4.096207	1.461099	-0.333584
C	5.034806	1.102074	0.651230
C	4.412834	2.533296	-1.186509
C	5.621184	3.219696	-1.061882
C	6.237588	1.796268	0.787767
C	6.538254	2.857149	-0.071104
C	4.067131	-1.448035	-0.931679
C	4.626165	-1.083534	-2.169959
C	4.690444	-2.475730	-0.202111
C	5.831401	-3.113796	-0.690146
C	5.757942	-1.730815	-2.667443
C	6.368388	-2.747567	-1.927671
C	1.561855	-2.928942	-0.043011
C	1.139258	-3.638659	1.102915
C	1.733351	-3.666134	-1.236577
C	0.933724	-5.018735	1.067613
C	1.505597	-5.040771	-1.275062
C	1.112788	-5.728926	-0.122461
H	-4.135145	-3.686776	-0.623147
H	-1.882815	-1.932722	-4.867196
H	-0.347071	-0.685862	-6.368180
H	1.367909	0.869828	-5.337189
H	1.417730	1.090168	-2.852576
H	-2.833214	-3.858195	-4.067312
H	-3.982017	-2.506607	-4.134938
H	-4.378032	-3.962986	-3.206144
H	-1.619005	-2.560891	1.896286
H	-3.348727	-2.950025	1.820726
H	-2.820044	-1.250544	1.848994
H	-4.396465	2.845350	1.483143
H	-0.959104	1.557994	5.051491
H	1.072948	0.615091	6.120714
H	2.727138	-0.659441	4.685028
H	2.212993	-0.938608	2.257817
H	-3.231954	1.747766	4.842818
H	-4.097185	3.083728	4.063852
H	-2.401409	3.285706	4.533329
H	-2.414821	2.236712	-1.550061
H	-4.123687	2.151412	-1.080488

H	-3.196471	0.654535	-1.334128
H	2.467624	3.021360	1.468750
H	0.145191	2.993802	-2.164758
H	1.967835	5.425509	1.765931
H	-0.319946	5.405220	-1.887574
H	0.582527	6.643109	0.083359
H	4.814102	0.269468	1.320921
H	3.699915	2.828941	-1.957239
H	5.847290	4.043171	-1.741724
H	6.946377	1.503627	1.564608
H	7.482242	3.395443	0.028461
H	4.161213	-0.285640	-2.751379
H	4.272572	-2.774642	0.760246
H	6.302257	-3.903275	-0.101558
H	6.168959	-1.435829	-3.634704
H	7.258548	-3.248747	-2.311354
H	0.984552	-3.096932	2.038418
H	2.044573	-3.142704	-2.141327
H	0.622747	-5.541038	1.974584
H	1.640212	-5.581799	-2.213880
H	0.939994	-6.805736	-0.153967

$(^{Me}PMP^{Me})_2Zr(C_4Ph_4)$, *trans*-pyrrole (BP86)

Zr	0.160620	-0.173331	-0.059632
N	-0.596815	-0.240761	2.021199
N	-2.076794	0.619081	-0.080864
N	-0.196784	-0.771551	-2.174501
N	-1.030168	-2.307930	-0.144118
C	-0.071328	-0.622278	3.234265
C	-1.080483	-0.614315	4.197977
C	-2.287588	-0.213702	3.577573
C	-1.963940	0.010662	2.224669
C	-2.750426	0.456671	1.103675
C	-4.135934	0.732544	1.159821
C	-4.800124	1.179231	0.028479
C	-4.093621	1.348824	-1.169217
C	-2.737915	1.051923	-1.170937
C	1.377584	-0.934388	3.428118
C	-3.600611	-0.060846	4.286905
C	0.164981	-0.191569	-3.371649
C	-0.386685	-0.923496	-4.425377

C	-1.114974	-2.006729	-3.883180
C	-0.979428	-1.892037	-2.484444
C	-1.415015	-2.720373	-1.397684
C	-2.178486	-3.902872	-1.545453
C	-2.516566	-4.652543	-0.431015
C	-2.105018	-4.227728	0.840218
C	-1.376325	-3.049067	0.928340
C	1.037735	1.016964	-3.457113
C	-1.840936	-3.041535	-4.690482
C	2.392017	0.011662	-0.103000
C	2.941098	1.265345	-0.004182
C	1.989082	2.415736	-0.037771
C	0.638281	2.143567	-0.103281
C	3.058992	-1.289068	0.031046
C	2.701756	-2.345989	-0.843088
C	3.238188	-3.628172	-0.694699
C	4.140013	-3.899571	0.335036
C	4.504846	-2.871411	1.215383
C	3.975210	-1.592852	1.070584
C	4.408742	1.490074	0.139941
C	5.307146	0.910012	-0.774183
C	6.684992	1.079672	-0.633924
C	7.196887	1.819909	0.435537
C	6.317126	2.396215	1.356460
C	4.938227	2.243353	1.204311
C	2.537998	3.809206	-0.036718
C	3.408720	4.240005	-1.053937
C	3.896193	5.547813	-1.077395
C	3.537686	6.450208	-0.072130
C	2.681930	6.033888	0.951247
C	2.184099	4.729693	0.965004
C	-0.337333	3.252065	-0.179039
C	-0.444954	4.071192	-1.322639
C	-1.389667	5.097068	-1.397146
C	-2.248255	5.347362	-0.323885
C	-2.152928	4.551051	0.822055
C	-1.222284	3.513604	0.888240
H	-0.952862	-0.850428	5.252648
H	-4.674854	0.595472	2.093522
H	-5.868561	1.396806	0.075516
H	-4.577128	1.703097	-2.078057
H	-2.139986	1.156437	-2.077081
H	1.724026	-1.764735	2.793473

H	1.564461	-1.215772	4.472581
H	2.010957	-0.064586	3.193053
H	-3.991455	0.967704	4.227258
H	-3.485297	-0.304805	5.351574
H	-4.376979	-0.729026	3.880579
H	-0.260470	-0.703607	-5.483705
H	-2.494397	-4.218300	-2.536555
H	-3.102273	-5.566298	-0.546636
H	-2.348865	-4.788176	1.741465
H	-1.053547	-2.661415	1.896274
H	0.531681	1.918746	-3.079328
H	1.325451	1.201644	-4.500224
H	1.951584	0.892729	-2.856510
H	-1.434206	-4.053967	-4.534524
H	-1.752834	-2.816133	-5.761757
H	-2.915642	-3.080713	-4.450521
H	2.018899	-2.138645	-1.670480
H	2.949265	-4.415947	-1.392880
H	4.558581	-4.900167	0.453608
H	5.212388	-3.072301	2.022508
H	4.267830	-0.803913	1.763896
H	4.912622	0.322716	-1.604782
H	7.362171	0.629086	-1.361798
H	8.274427	1.949677	0.549117
H	6.706225	2.975870	2.195517
H	4.262054	2.708066	1.922971
H	3.702945	3.541348	-1.838965
H	4.563289	5.861677	-1.882488
H	3.923523	7.470951	-0.085980
H	2.396525	6.729573	1.742561
H	1.508828	4.414009	1.760985
H	0.237791	3.909114	-2.158723
H	-1.445178	5.713061	-2.297164
H	-2.980981	6.154139	-0.377636
H	-2.811104	4.738286	1.673135
H	-1.162479	2.894528	1.785742

$Cp_2Zr(\eta^4\text{-}C_4Ph_4)$ (BP86)

Zr	7.076209	2.450970	4.427875
C	7.789762	4.860137	3.910634
C	7.248131	4.896326	5.225100

C	8.202424	4.299461	6.102640
C	9.294060	3.857565	5.331304
C	9.027093	4.174941	3.969552
C	8.373261	0.387025	5.415490
C	8.291758	1.255439	6.530037
C	6.925212	1.414565	6.863420
C	6.162524	0.577488	5.997625
C	7.052302	-0.058686	5.106004
C	5.939347	2.635065	2.297457
C	5.319495	1.572511	3.148746
C	4.621903	2.651830	3.899416
C	5.156007	3.648225	2.989576
C	7.246373	2.563810	1.687273
C	8.080026	1.464158	2.067818
C	9.404850	1.357266	1.607128
C	9.936062	2.326049	0.768202
C	9.128003	3.415019	0.379352
C	7.825435	3.542617	0.830363
C	4.854537	0.241032	2.781554
C	5.252556	-0.363366	1.564536
C	4.814646	-1.638946	1.208924
C	3.952351	-2.355991	2.043876
C	3.526933	-1.766438	3.238640
C	3.966671	-0.494295	3.602482
C	3.372421	2.673484	4.695714
C	2.134374	2.600464	4.027194
C	0.933320	2.638575	4.736667
C	0.940208	2.751051	6.130360
C	2.159233	2.827642	6.807934
C	3.361402	2.789835	6.096151
C	4.819213	5.048372	2.797962
C	4.224929	5.808382	3.832004
C	3.845440	7.131891	3.623487
C	4.040825	7.740888	2.378436
C	4.601444	6.997464	1.336015
C	4.978048	5.670313	1.539468
H	7.345188	5.300795	3.026085
H	6.330469	5.397574	5.520546
H	8.087214	4.189037	7.177583
H	10.171847	3.330957	5.694964
H	9.681556	3.968095	3.125991
H	9.289446	0.064253	4.926068
H	9.127002	1.747480	7.014589

H	6.531593	2.011610	7.682380
H	5.086349	0.444858	6.027437
H	6.772082	-0.770127	4.334693
H	7.632352	0.614696	2.592098
H	10.001689	0.490465	1.896037
H	10.958573	2.241707	0.399108
H	9.535995	4.173960	-0.290949
H	7.230765	4.397226	0.512603
H	5.894821	0.189727	0.878443
H	5.139671	-2.070095	0.259765
H	3.605509	-3.350838	1.761597
H	2.837231	-2.300478	3.895337
H	3.599822	-0.050326	4.527681
H	2.122233	2.512582	2.939749
H	-0.013774	2.580938	4.197265
H	0.000458	2.780993	6.683999
H	2.176311	2.919328	7.895449
H	4.054840	5.345351	4.804188
H	3.392397	7.695886	4.440821
H	3.745609	8.778869	2.219578
H	4.734168	7.449437	0.351425
H	5.355629	5.084459	0.701149
H	4.313398	2.855500	6.625917

$Cp_2Zr(C_4Ph_4)$ (BP86)

Zr	7.181497	2.485572	5.132525
C	7.447692	2.433272	2.859959
C	6.232471	2.407880	2.212724
C	4.972608	2.318207	3.005507
C	5.023345	2.394700	4.379388
C	7.643745	4.930047	4.502954
C	6.597232	4.942972	5.465910
C	7.133891	4.474067	6.699108
C	8.514413	4.188963	6.495920
C	8.828041	4.470760	5.141562
C	8.685219	0.618318	5.943686
C	7.858845	0.944462	7.056990
C	6.526270	0.577708	6.739057
C	6.523587	0.023638	5.429697
C	7.858487	0.037737	4.939298
C	8.742959	2.698151	2.209734

C	9.879877	1.917270	2.519198
C	11.135389	2.197755	1.975954
C	11.306444	3.290040	1.122146
C	10.200151	4.088708	0.812025
C	8.943061	3.795869	1.338881
C	6.139606	2.521586	0.721789
C	5.398443	3.552460	0.115885
C	5.346674	3.680081	-1.272940
C	6.023524	2.769168	-2.089529
C	6.757080	1.734595	-1.502750
C	6.817525	1.616645	-0.112883
C	3.677670	2.096294	2.285012
C	2.588846	2.962520	2.485132
C	1.367236	2.744492	1.845605
C	1.204569	1.646725	0.996412
C	2.277533	0.774988	0.787495
C	3.501387	1.001874	1.418910
C	3.884201	2.142146	5.278767
C	3.614091	3.003427	6.366523
C	2.588684	2.738757	7.276845
C	1.811246	1.585255	7.148311
C	2.068292	0.707866	6.088989
C	3.078725	0.983322	5.168944
H	7.560361	5.233574	3.464806
H	5.578660	5.272942	5.288864
H	6.591216	4.361022	7.634988
H	9.207052	3.823774	7.249829
H	9.793916	4.332083	4.661971
H	9.759980	0.773770	5.881875
H	8.192901	1.393890	7.988568
H	5.651440	0.719028	7.368799
H	5.653042	-0.353294	4.903269
H	8.183916	-0.343121	3.976562
H	9.766487	1.061064	3.185179
H	11.985443	1.560837	2.227163
H	12.287926	3.517667	0.703604
H	10.316596	4.947339	0.147581
H	8.092213	4.423622	1.071612
H	4.861077	4.265048	0.743771
H	4.771256	4.492748	-1.720315
H	5.976654	2.863629	-3.175689
H	7.287470	1.015649	-2.130044
H	7.397711	0.810660	0.339316

H	2.709032	3.816883	3.152957
H	0.538024	3.434363	2.012981
H	0.249636	1.472901	0.497596
H	2.162244	-0.085652	0.125929
H	4.333715	0.318738	1.241870
H	4.211705	3.908072	6.485847
H	2.399851	3.437360	8.094602
H	1.016011	1.370557	7.863723
H	1.471425	-0.199380	5.975077
H	3.255149	0.294016	4.342269

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