Design, Synthesis, and Self-Assembly of Polymers with Tailored Graft Distributions

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SUPPORTING INFORMATION

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Materials and Methods

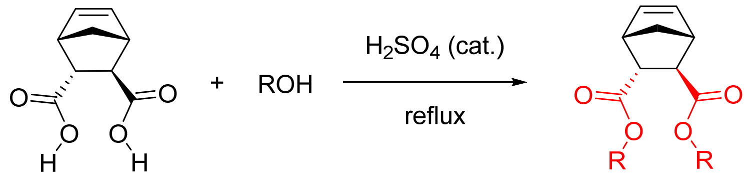
General. Norbornene macromonomers **PLA**,[1] **PDMS**,[2] and **PS**[3] were prepared according to reported precedures. Norbornene diluents were prepared according to reported procedures, summarized in Schemes S1–S6. The second-generation ruthenium metathesis catalyst [$(H_2IMes)(PCy_3)(Cl)_2Ru$=CHPh] was generously provided by Materia, and **G3** was prepared according to the reported precedure.[4] CH_2Cl_2 was dried by passing through an activated alumina column. Deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and used as received.

NMR, SEC, and SAXS characterization. Ambient temperature NMR spectra were recorded on a Varian 400 MHz NMR spectrometer. Chemical shifts (δ) were given in ppm and referenced against residual solvent signals (^{1}H, ^{13}C). SEC data were collected using two Agilent PLgel MIXED-B 300 × 7.5 mm columns with 10 µm beads, connected to an Agilent 1260 Series pump, a Wyatt 18-angle DAWN HELEOS light scattering detector, and Optilab rEX differential refractive index detector. Online determination of d*n*/d*c* assumed 100% mass elution under the peak of interest. The mobile phase was THF. SAXS data were collected at beamline 12-ID at Argonne National Laboratory's Advanced Photon Source. The samples were probed using 12 keV (1.033 Å) X-rays, and the sample-to-detector distance was calibrated from a silver behenate standard. The beam was collimated using two sets of slits and a pinhole was used to remove parasitic scattering. The beamwidth was approximately 200 – 300 µm horizontally and 50 µm vertically.

Standard procedure for the determination of homopolymerization rate constants. A 4 mL vial was charged with a flea stir bar and the norbornene monomer (0.025 mmol) in CH_2Cl_2 at 298 K. While stirring vigorously, the polymerization was initiated by adding a CH_2Cl_2 solution of **G3** (0.0125 M, 20 µL, 0.25 µmol) to achieve initial conditions of $[\text{norbornene}]_0$ (0.05 M) and $[\textbf{G3}]_0$ (0.5 mM). Over the course of the reaction, aliquots (~20 µL) were extracted at different time points and immediately quenched in a seperate vial containing a large excess of ethyl vinyl ether (~0.2 mL) and silica-bound metal scavenger (SiliaMetS, dimercaptotriazine (DMT)) in THF. The quenched reaction mixtures were subsequentially subjected to SEC and ^{1}H NMR analysis, allowing the determination of $[\text{norbornene}]_t$. For each homopolymerization experiment, the self-propagation rate constant k_{homo} was determined according to Eq. 1.

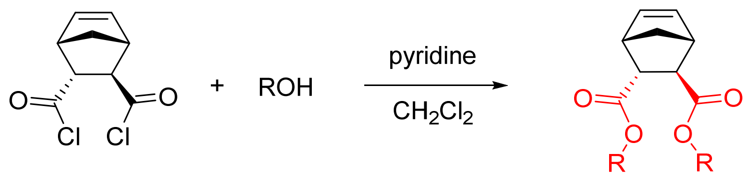
Standard procedure for the determination of copolymerization reactivity ratios. A 4 mL vial was charged with a flea stir bar and a CH_2Cl_2 solution of two norbornene monomers (M_1, M_2, each 0.025 mmol) at 298 K. While stirring vigorously, the copolymerization was initiated by adding a CH_2Cl_2 solution of **G3** (0.0125 M, 20 µL, 0.25 µmol) to achieve initial conditions of $[M_1]_0$ (0.05 M), $[M_2]_0$ (0.05 M), and $[\textbf{G3}]_0$ (0.5 mM). Over the course of the reaction, aliquots (~20 µL) were extracted at different time points and immediately quenched in a seperate vial containing a large excess of ethyl vinyl ether (~0.2 mL) and silica-bound metal scavenger (SiliaMetS, dimercaptotriazine (DMT)) in THF. The quenched reaction mixtures were subsequentially subjected to SEC and ^{1}H NMR analysis, allowing the determination of $[M_1]_t$ and $[M_2]_t$. Values of k_{12} and k_{21} were obtained by fitting the experimentally determined kinetic data with the best numerical solutions using MATLAB non-linear least-square solver (*lsqcurvefit*) in conjunction with non-stiff differential equation solver (*ode45*).[2]

Density functional theory. All calculations were carried out using version 4.0 of the ORCA package.[5] For all complexes, the singlet potential energy surface was searched for minima in the gas phase using the BP86 exchange-correlation functional, along with the 6-31G(d) basis set on all main group elements and the LANL2DZ basis set and associated effective core potential for Ru. For each structure, frequency calculations were carried out at the same level of theory to ensure true minima (no imaginary frequencies). To account for solvation effects, single point calculations were carried out on the optimized geometries using the SMD implicit solvation model (CH_2Cl_2) with the M06 functional in combination with the def2-TZVP basis set on Ru with the SDD pseudopotential, the 6-311+G(d,p) basis set on all heteroatoms and carbons in the primary coordination sphere of Ru, and the 6-31G(d) basis set on all other C and H atoms. Free energies at 298.15 K were thus calculated as $G = H^{BP86} - T \times S^{BP86} + (E^{M06} - E^{BP86})$, where H^{BP86}, S^{BP86}, E^{BP86} are the total enthalpy, entropy, and electronic energy calculated at the BP86 level, and E^{M06} is the electronic energy calculated at the M06 level. All calculations were carried out on a fine integration grid (ORCA Grid5, FinalGrid6).



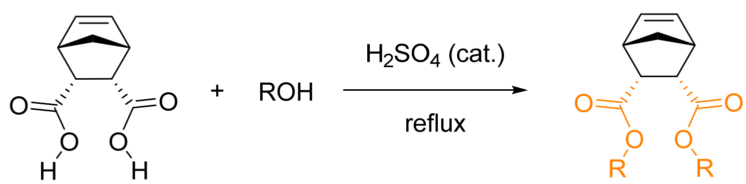
R = Me (**1a**), Et (**1b**), ^{n}Pr (**1c**), ^{n}Bu (**1d**)

Scheme S1. Synthesis of 1a–1d. *Cis*-5-norbornene-*endo,exo*-2,3-dicarboxylic acid (5 g, 27.5 mmol) was added to 50 mL of the corresponding anhydrous alcohol. To this mixture was added ~50 mg of conc. H_2SO_4. After stirring at 50 °C for 12 h, an excess of solid $KHCO_3$ was added to quench the reaction. The alcohol was removed under reduced pressure, and 30 mL CH_2Cl_2 was added. The organic solution was washed with brine (20 mL × 3), dried with $MgSO_4$, and filtered to afford a colorless oil. The product was purified by either vacuum distillation or recrystallization from cold *n*-pentane.



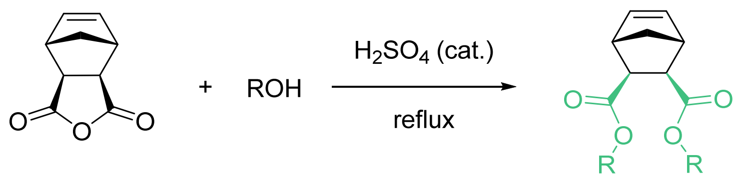
R = ^{i}Pr (**1e**), ^{t}Bu (**1f**), CH_2CF_3 (**1g**), Ph (**1h**), *p*-CF_3Ph (**1i**), *p*-MeOPh (**1j**)

Scheme S2. Synthesis of 1e–1j. *Cis*-5-norbornene-*endo,exo*-2,3-diacyl chloride (3 mL, 18.5 mmol) was dissolved in CH_2Cl_2 (25 mL) and pyridine (4.91 mL, 61.0 mmol). A CH_2Cl_2 solution (5 mL) of the corresponding anhydrous alcohol (42.5 mmol) was slowly added at –78 °C. The mixture was allowed to slowly warm to room temperature over 1 hour and was allowed to stir for 12 h. The pyridinium salt was removed by filtration. The organic solution was washed with brine (20 mL × 3), dried with $MgSO_4$, and filtered to afford a colorless oil. The product was purified by either vacuum distillation or recrystallization from cold *n*-pentane.



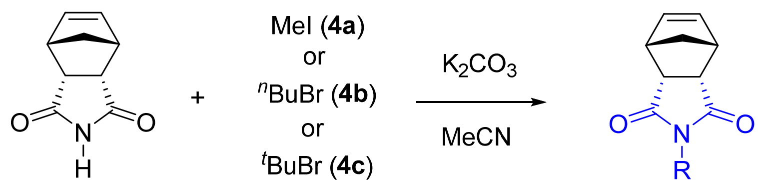
R = Me (**2a**), Et (**2b**), ^{n}Pr (**2c**), ^{n}Bu (**2d**)

Scheme S3. Synthesis of 2a–2d. A suspension of *cis*-5-norbornene-*endo,endo*-2,3-dicarboxylic acid (2.0 g, 11 mmol), 4 drops of concentrated sulfuric acid, and 20 mL of the corresponding anhydrous alcohol was stirred under air at 75 °C. After 36 hours, the solution was cooled to room temperature and was concentrated under reduced pressure. The resulting oil was redissolved in 50 mL CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (1 × 30 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford an oil. The oil was filtered through a plug of basic alumina, precipitated from cold (–78 °C) hexanes, and dried *in vacuo* to obtain the product as a white crystalline solid (**2a**), pink oil (**2b–2c**) or colorless oil (**2d**).



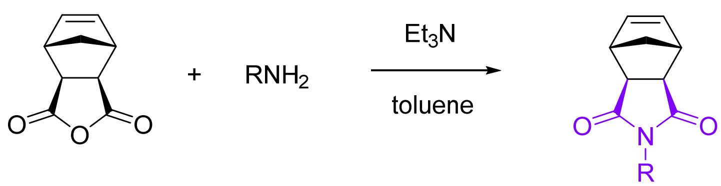
R = Me (**3a**), Et (**3b**),
^{n}Pr (**3c**), ^{n}Bu (**3d**)

Scheme S4. Synthesis of 3a–3d. A suspension of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (2.00 g, 12.2 mmol), 4 drops of concentrated sulfuric acid, and 20 mL of the corresponding anhydrous alcohol was stirred under air at 75 °C. After 20 hours, the colorless solution was cooled to room temperature and was concentrated under reduced pressure. The resulting pale yellow oil was redissolved in 50 mL CH_2Cl_2 and washed with saturated aqueous $NaHCO_3$ (2 × 30 mL) and brine (1 × 30 mL). The organic solution was dried over $MgSO_4$, filtered, and concentrated *in vacuo* to afford a colorless oil. Precipitation from cold (–78 °C) hexanes produced the product as a white crystalline solid (**3a**) or colorless oil (**3b**–**3d**) that was dried *in vacuo.*



R = Me (**4a**), ^{n}Bu (**4b**),
^{t}Bu (**4c**)

Scheme S5. Synthesis of 4a–4c. To a 10 mL MeCN solution of *cis*-5-norbornene-*endo*-2,3-diimide (1 g, 6.13 mmol) was added the corresponding alkyl halide (12.3 mmol) and K_2CO_3 (1.69 g, 12.3 mmol). The resulting mixture was allowed to stir at room temperature for 24 h (**4a**) or at 65 °C for 54 h (**4b** and **4c**). The product was purified using column chromatography.



R = Me (**5a**), ^{n}Bu (**5b**),
Ph (**5c**)

Scheme S6. Synthesis of 5a–5c. To a 20 mL toluene solution of *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride (1 g, 6.09 mmol) was added the corresponding alkyl amine (6.70 mmol) and Et_3N (0.85 mL, 0.609 mmol). The resulting mixture was allowed to stir at 110 °C for 15 h. The product was purified using column chromatography.

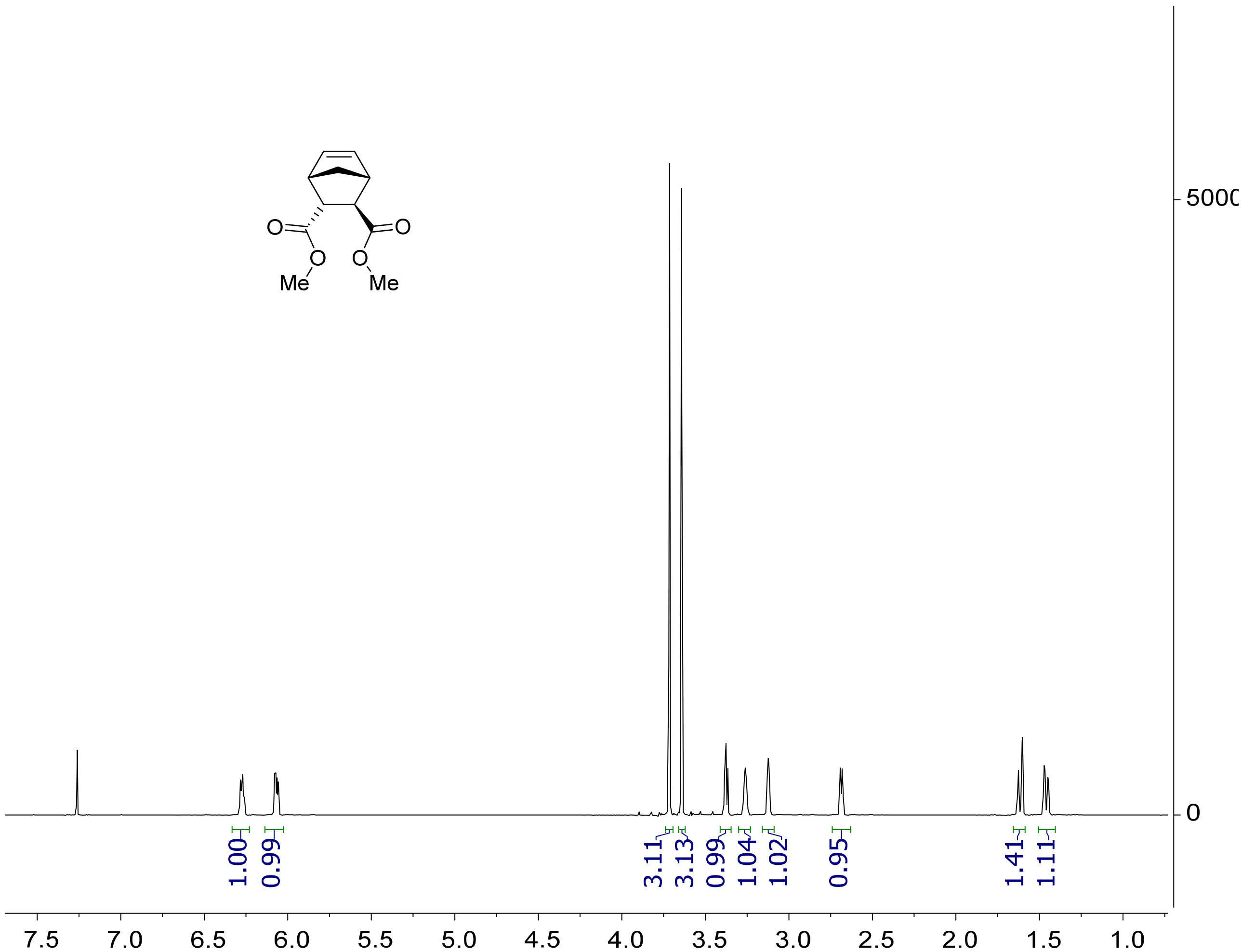


Figure S1A. ^{1}H NMR spectrum of **1a** in $CDCl_3$.

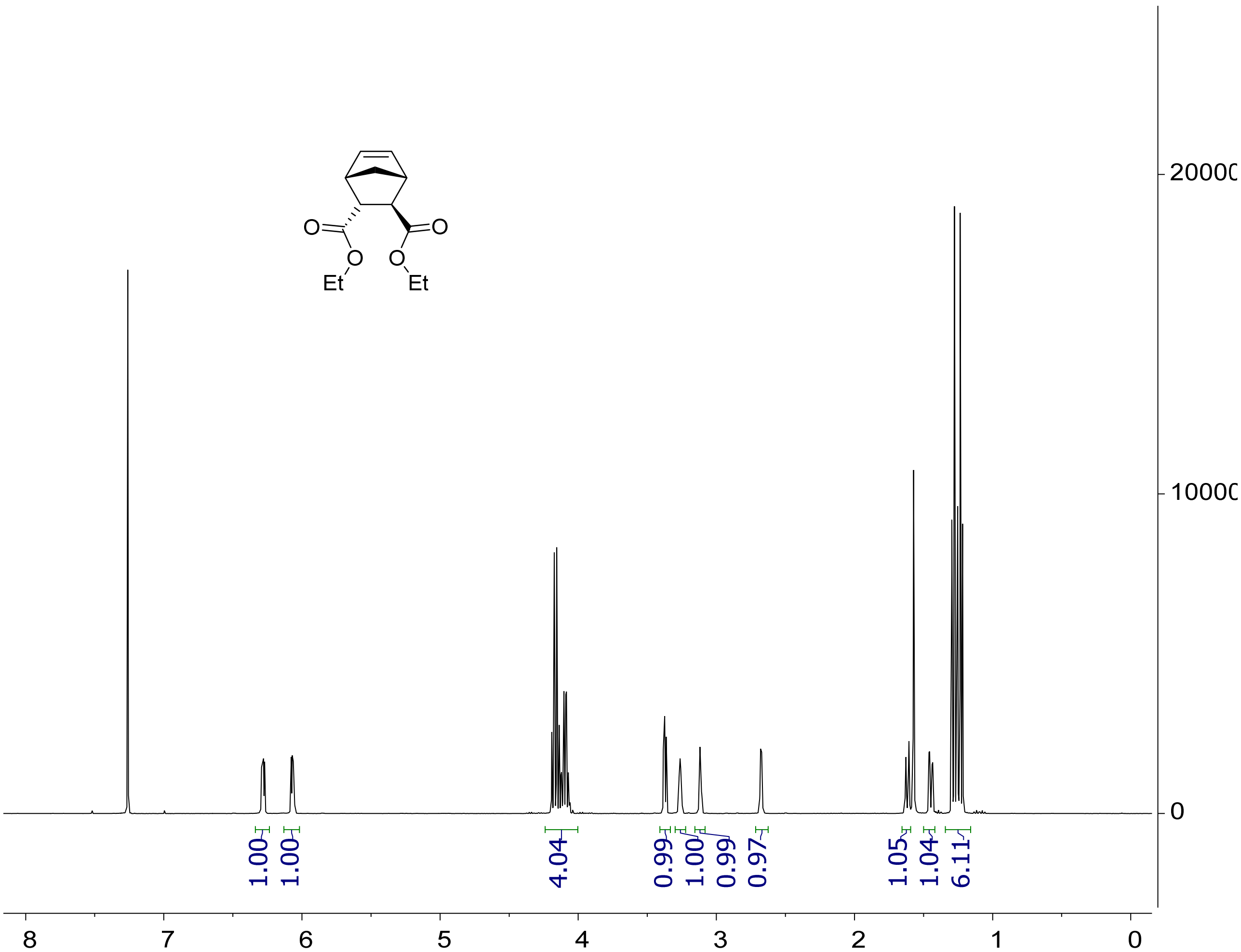


Figure S1B. [1]H NMR spectrum of **1b** in $CDCl_3$.

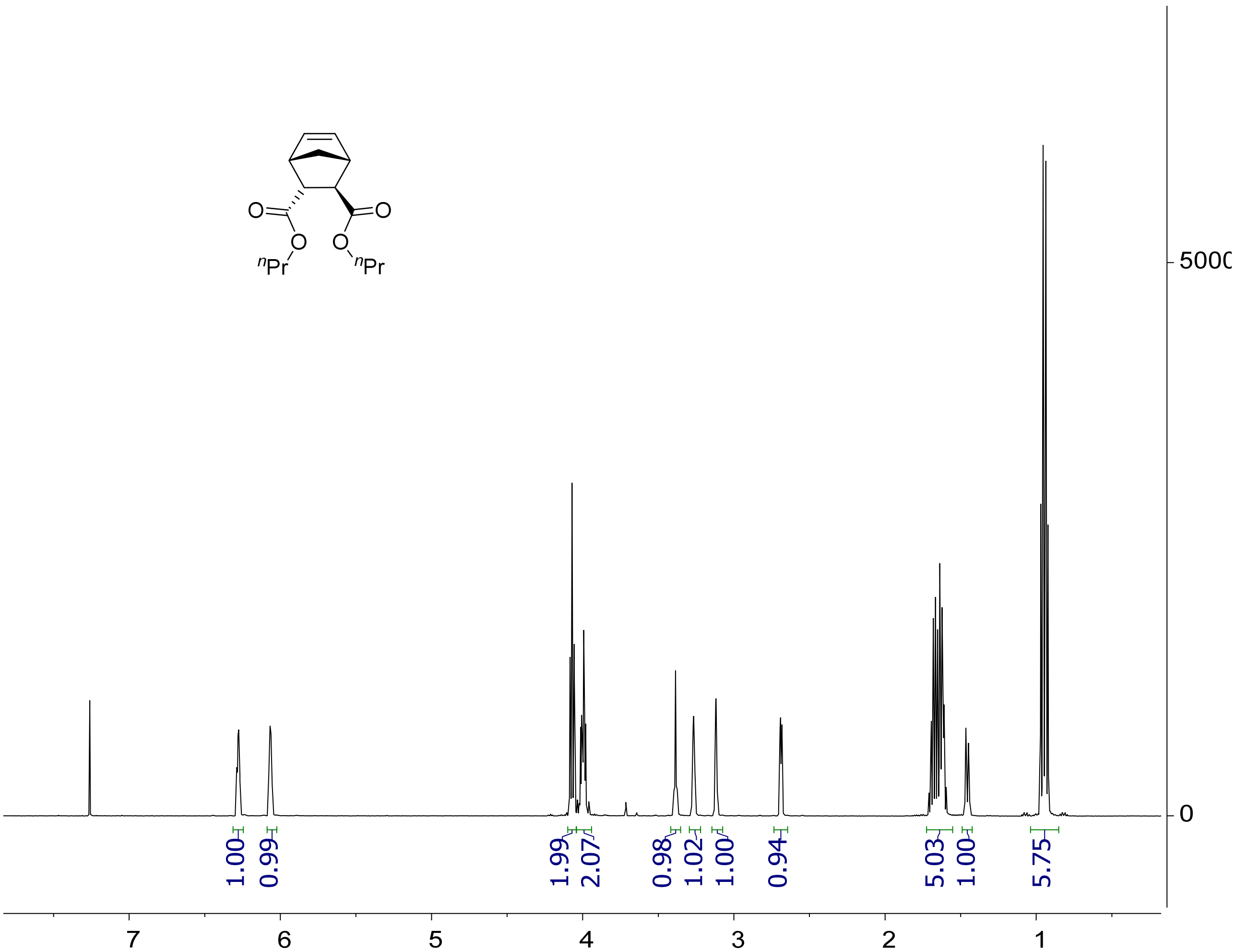


Figure S1C. ^{1}H NMR spectrum of **1c** in $CDCl_3$.

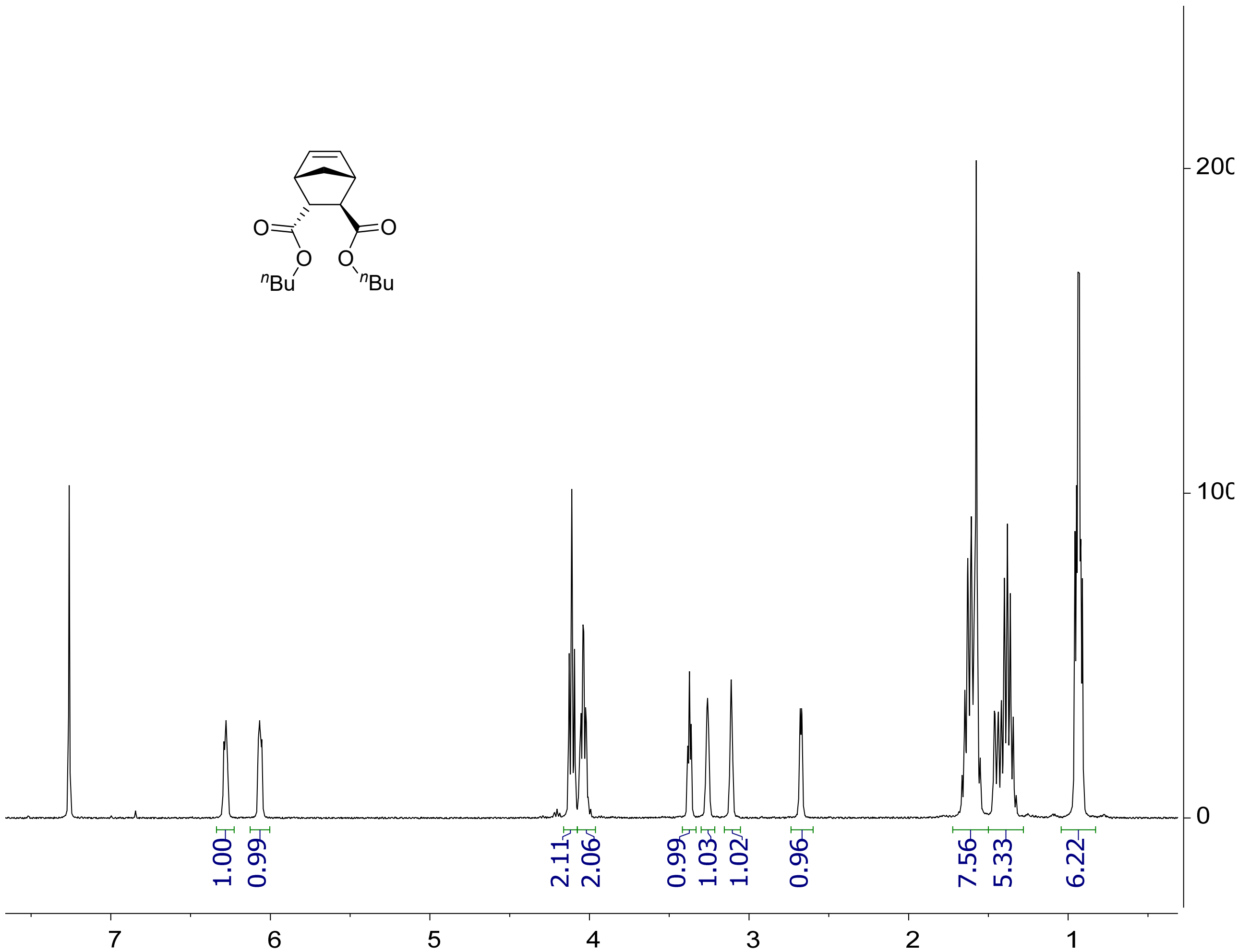


Figure S1D. ^{1}H NMR spectrum of **1d** in $CDCl_3$.

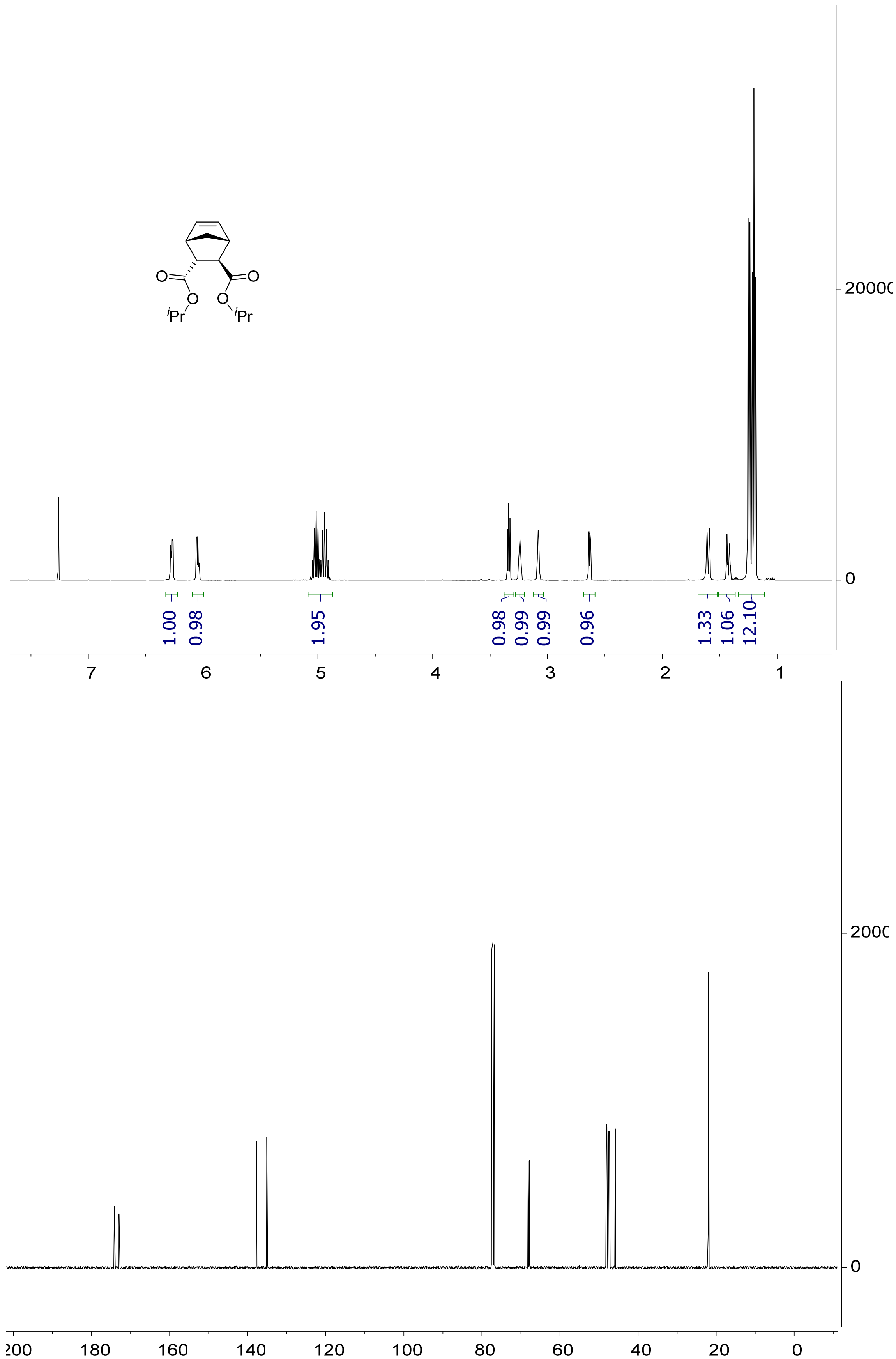


Figure S1E. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1e** in $CDCl_3$.

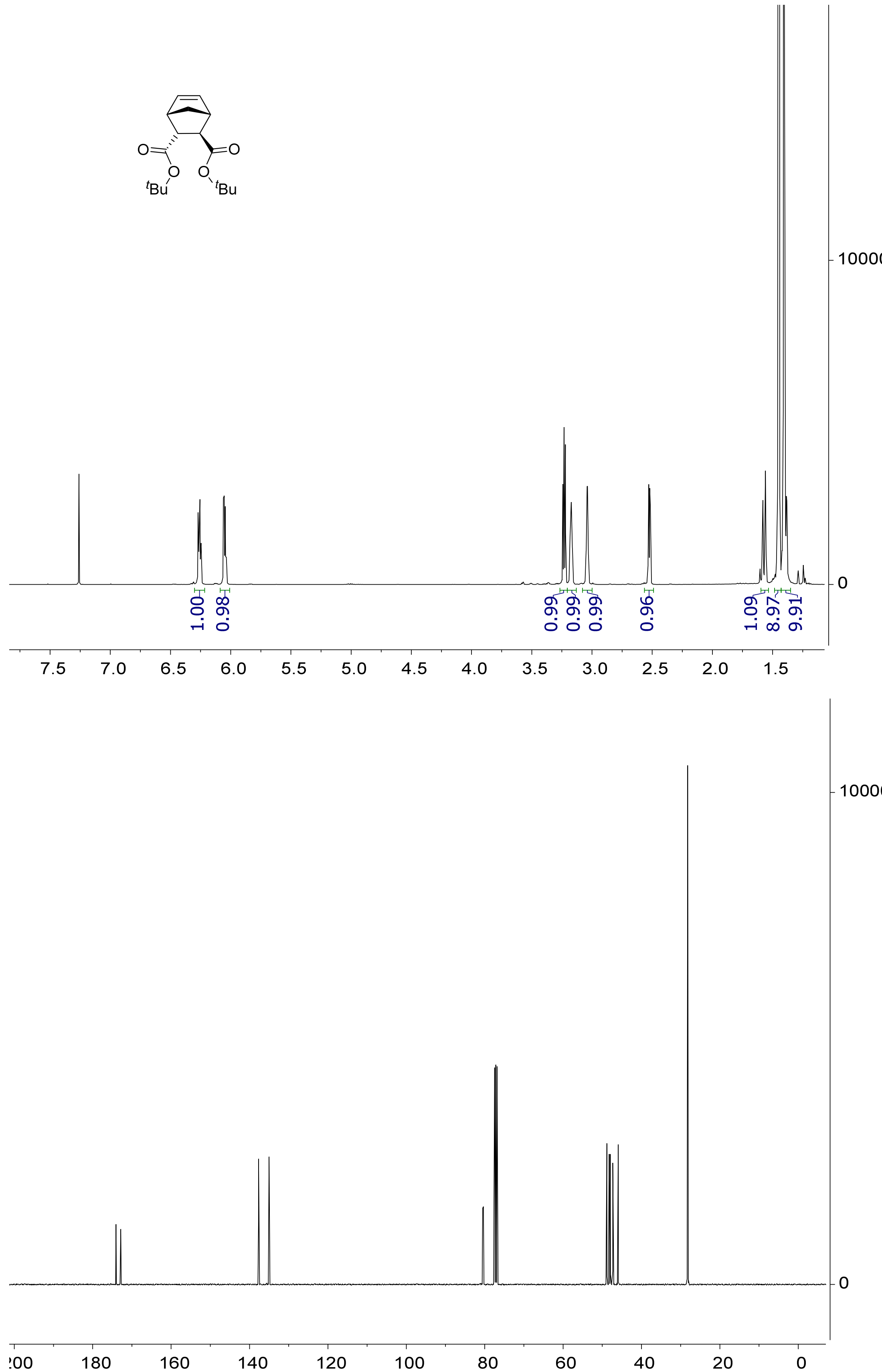


Figure S1F. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1f** in $CDCl_3$.

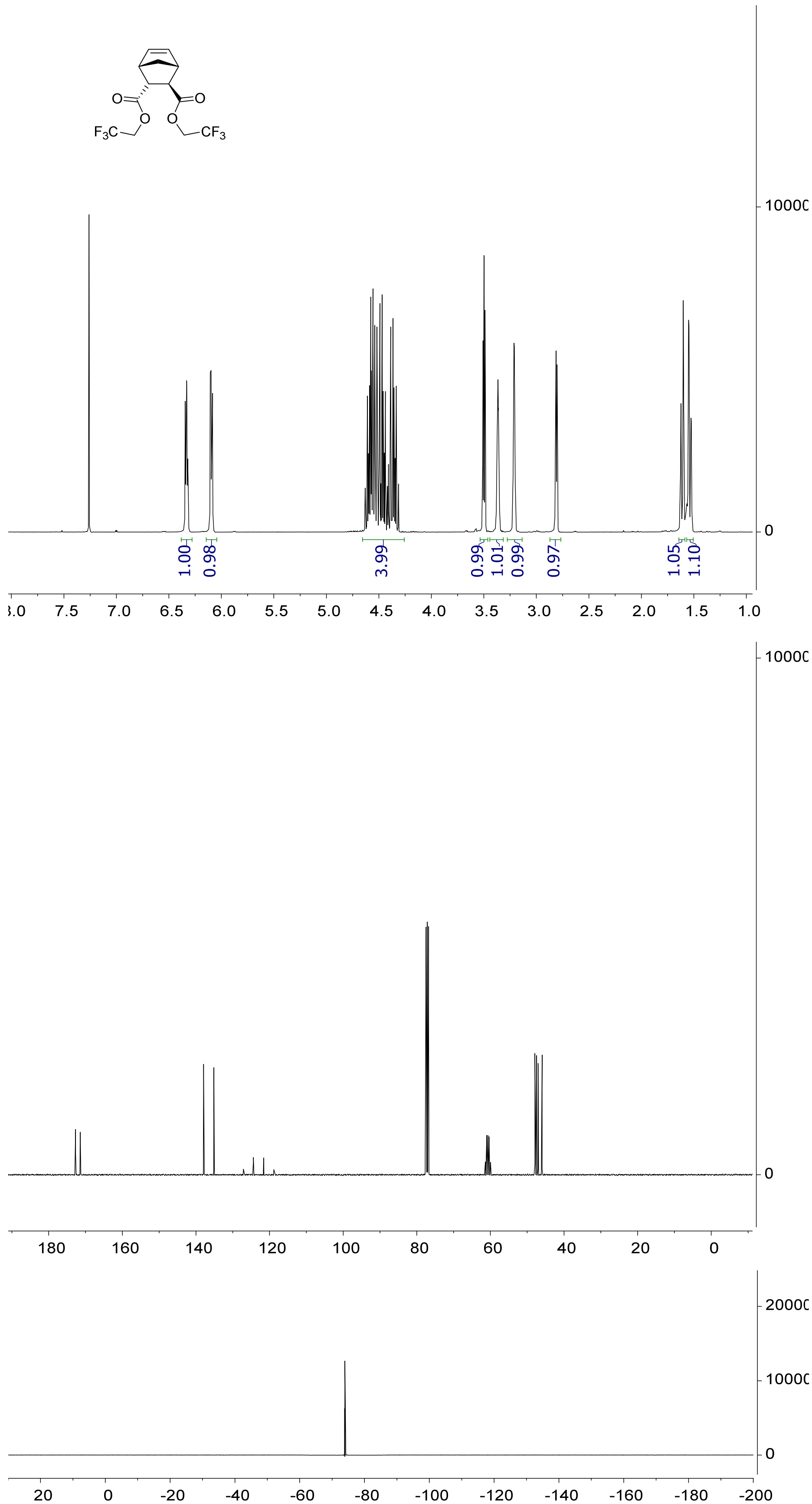


Figure S1G. ^{1}H (top), ^{13}C (middle), and ^{19}F (bottom) NMR spectra of **1g** in $CDCl_3$.

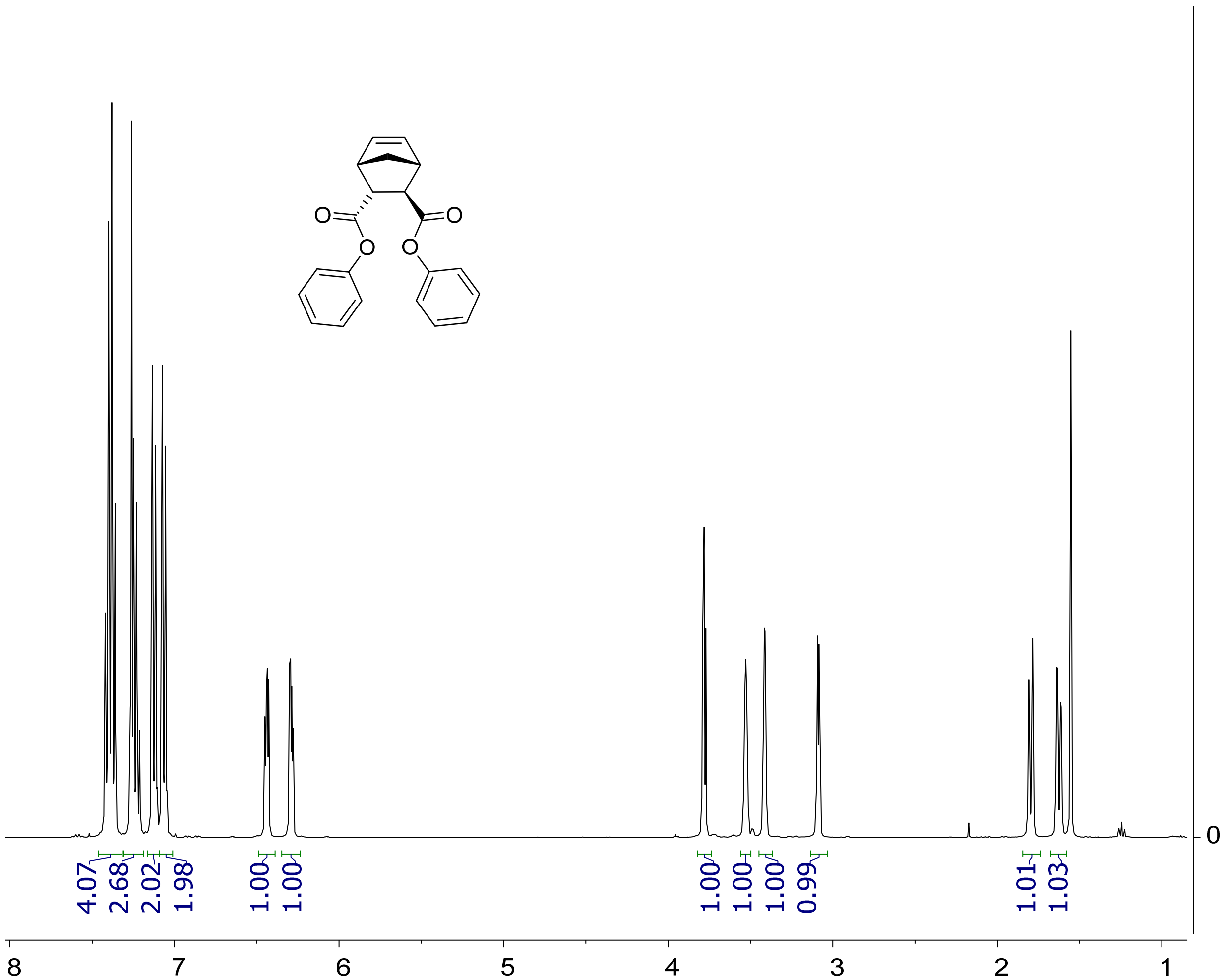


Figure S1H. ^{1}H NMR spectrum of **1h** in $CDCl_3$.

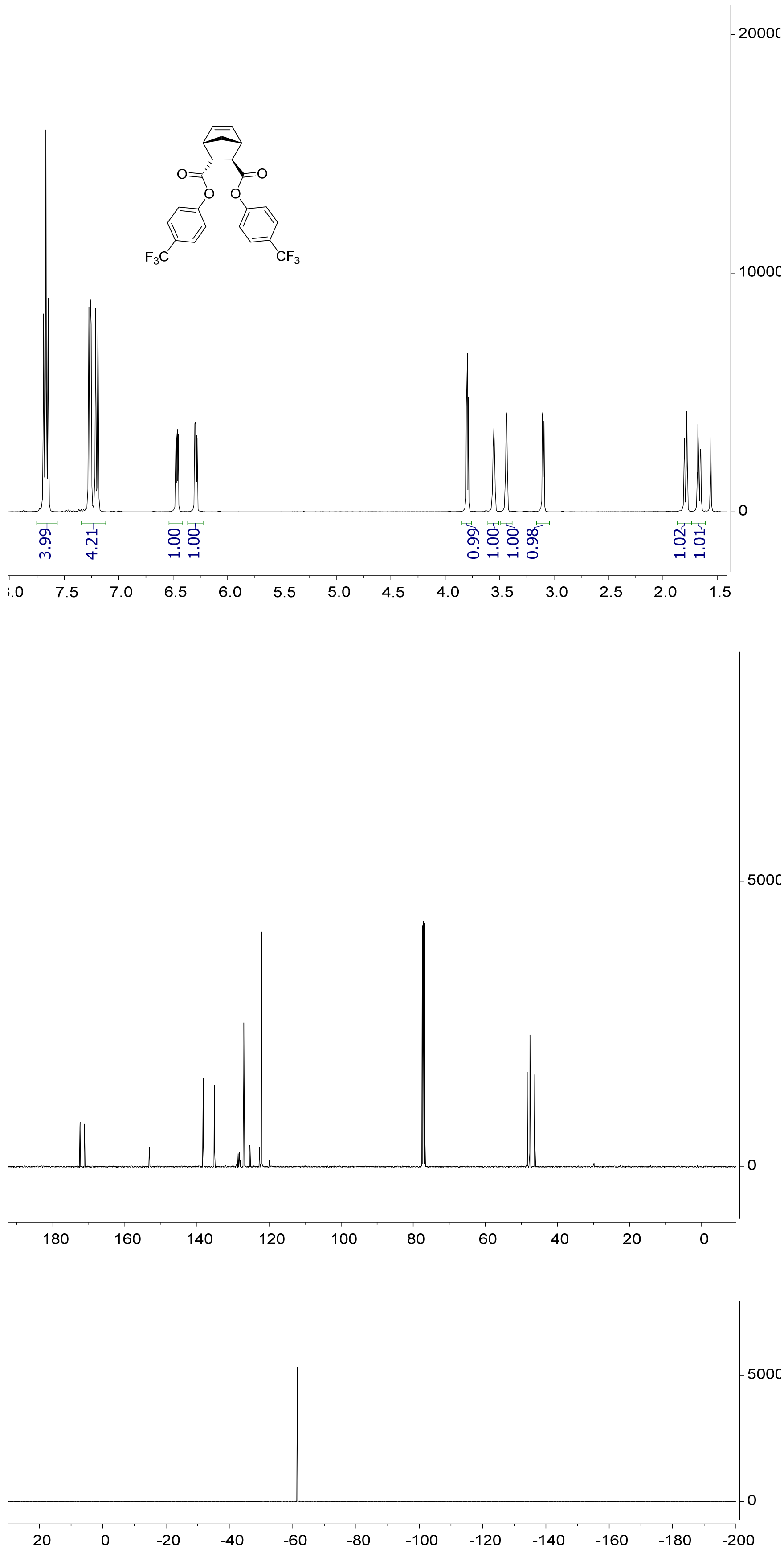


Figure S1I. ^{1}H (top), ^{13}C (middle), and ^{19}F (bottom) NMR spectra of **1i** in $CDCl_3$.

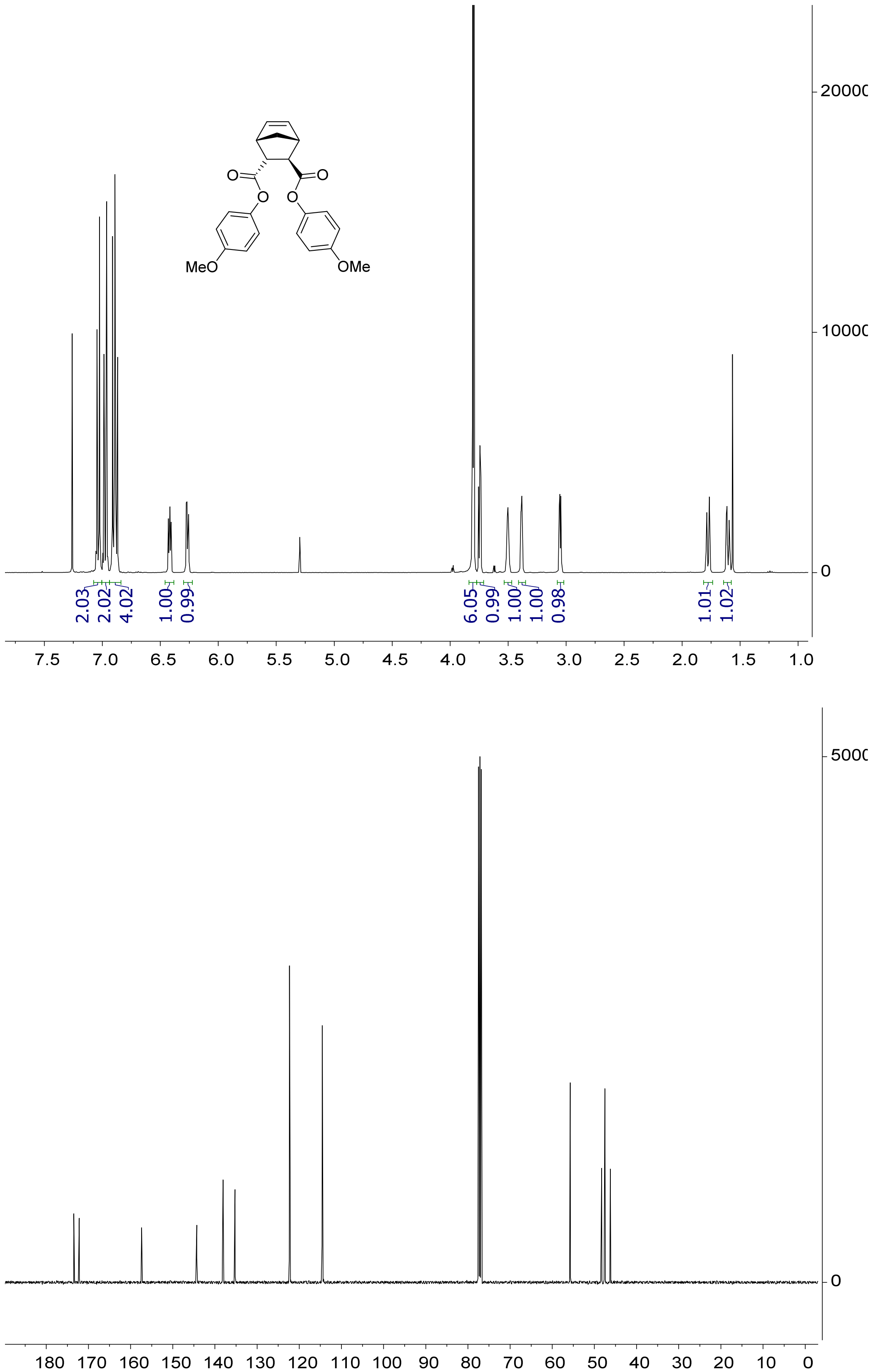


Figure S1J. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **1j** in $CDCl_3$.

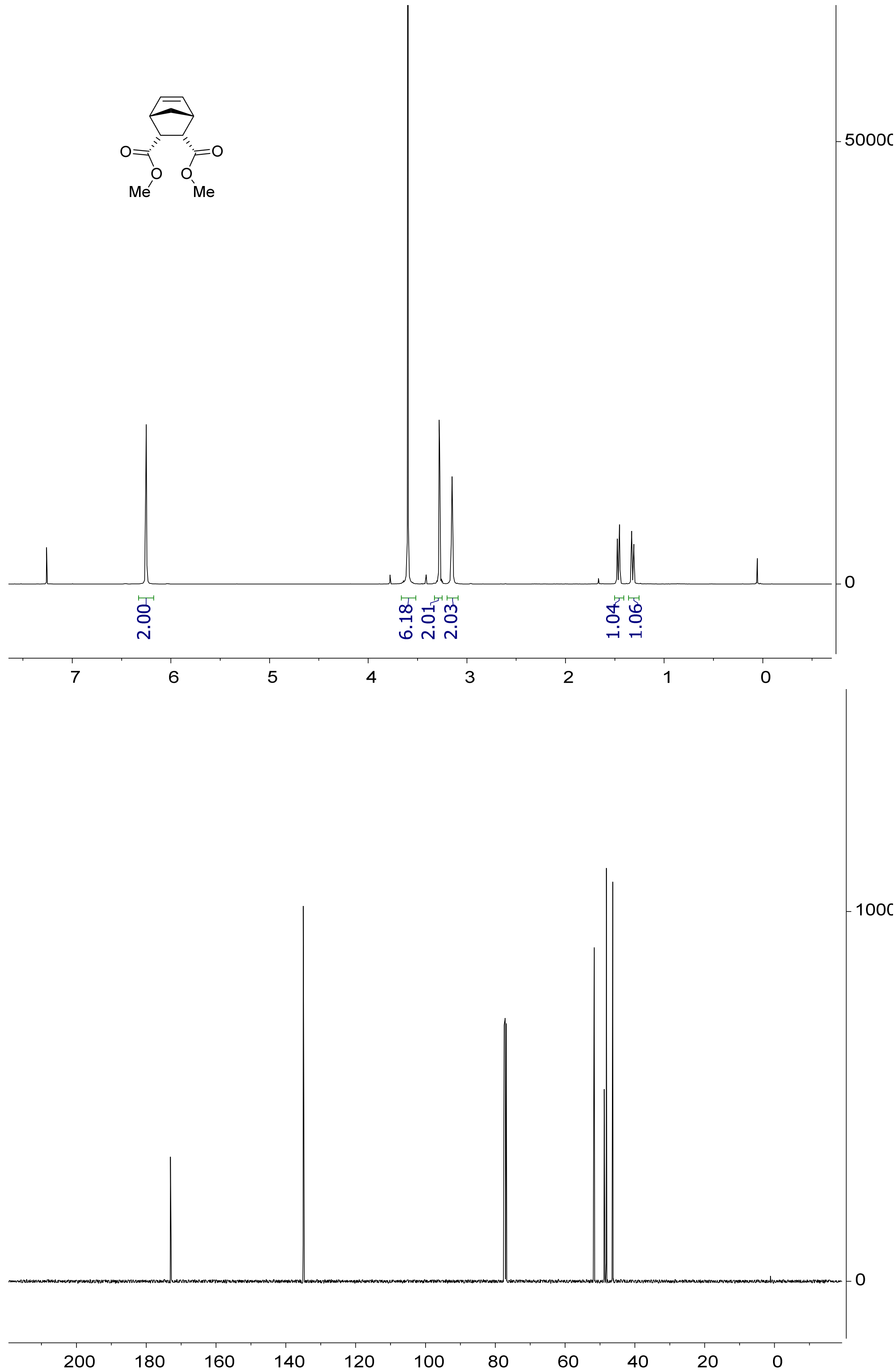


Figure S2A. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2a** in $CDCl_3$.

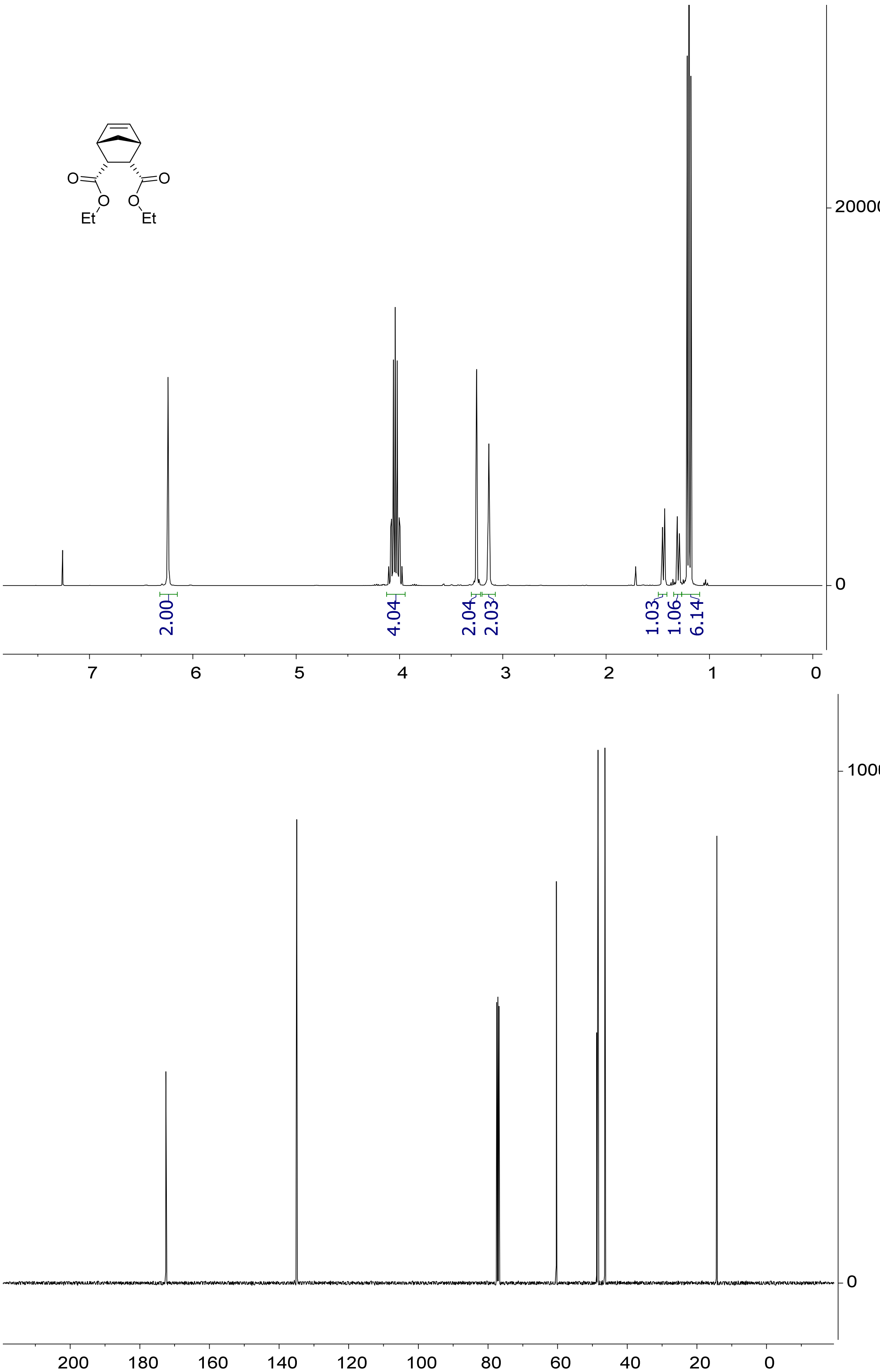


Figure S2B. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2b** in $CDCl_3$.

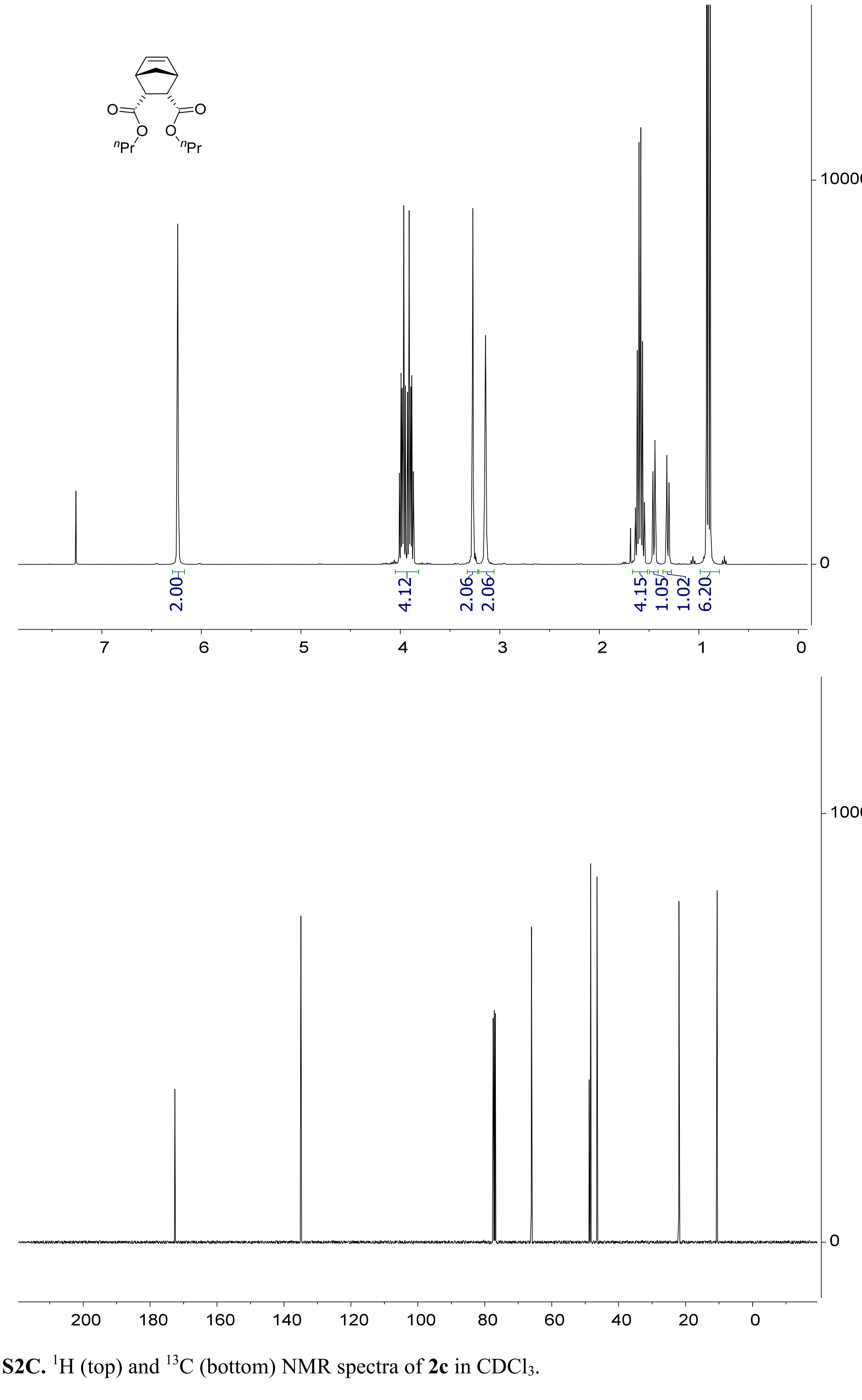


Figure S2C. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2c** in $CDCl_3$.

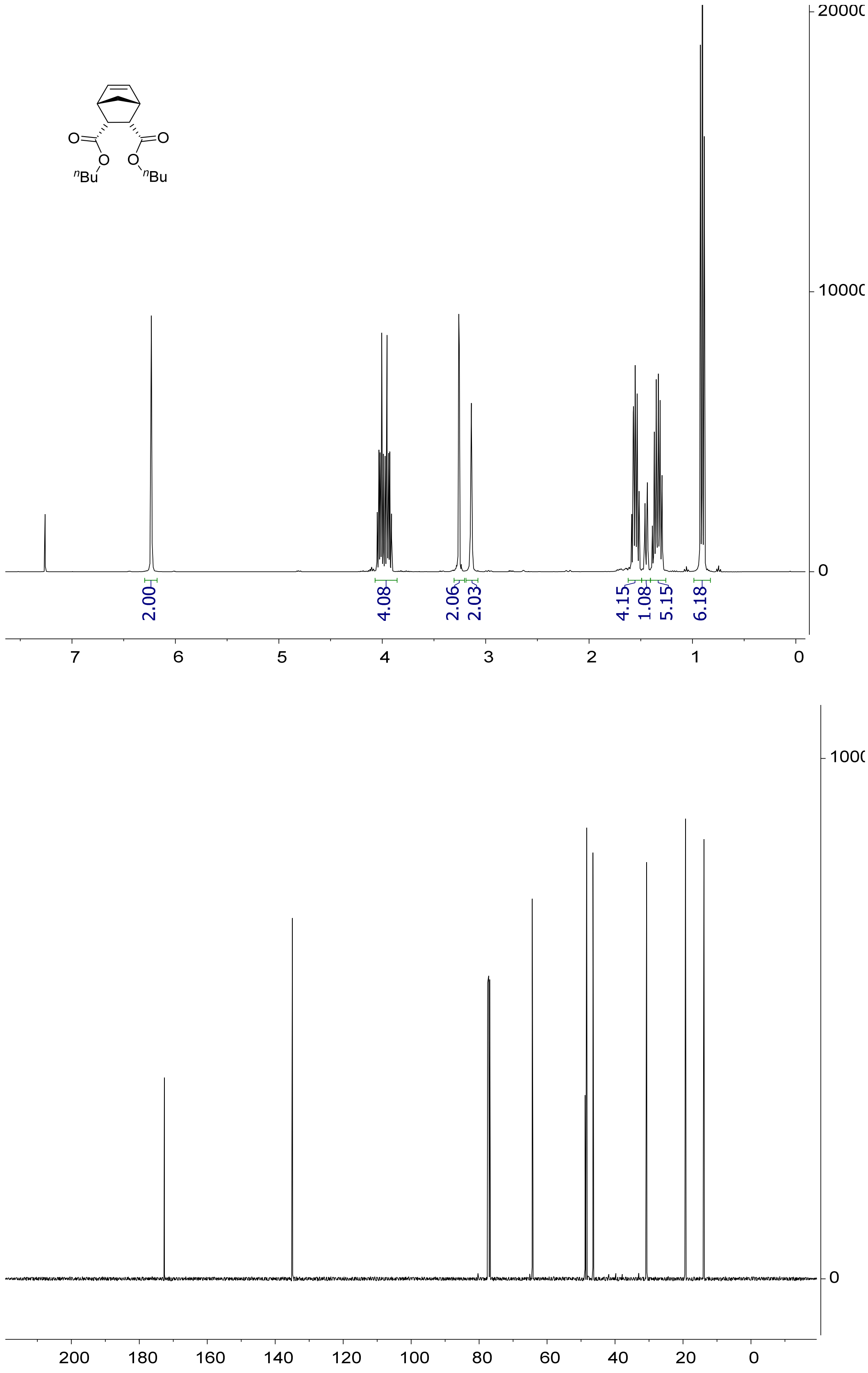


Figure S2D. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **2d** in $CDCl_3$.

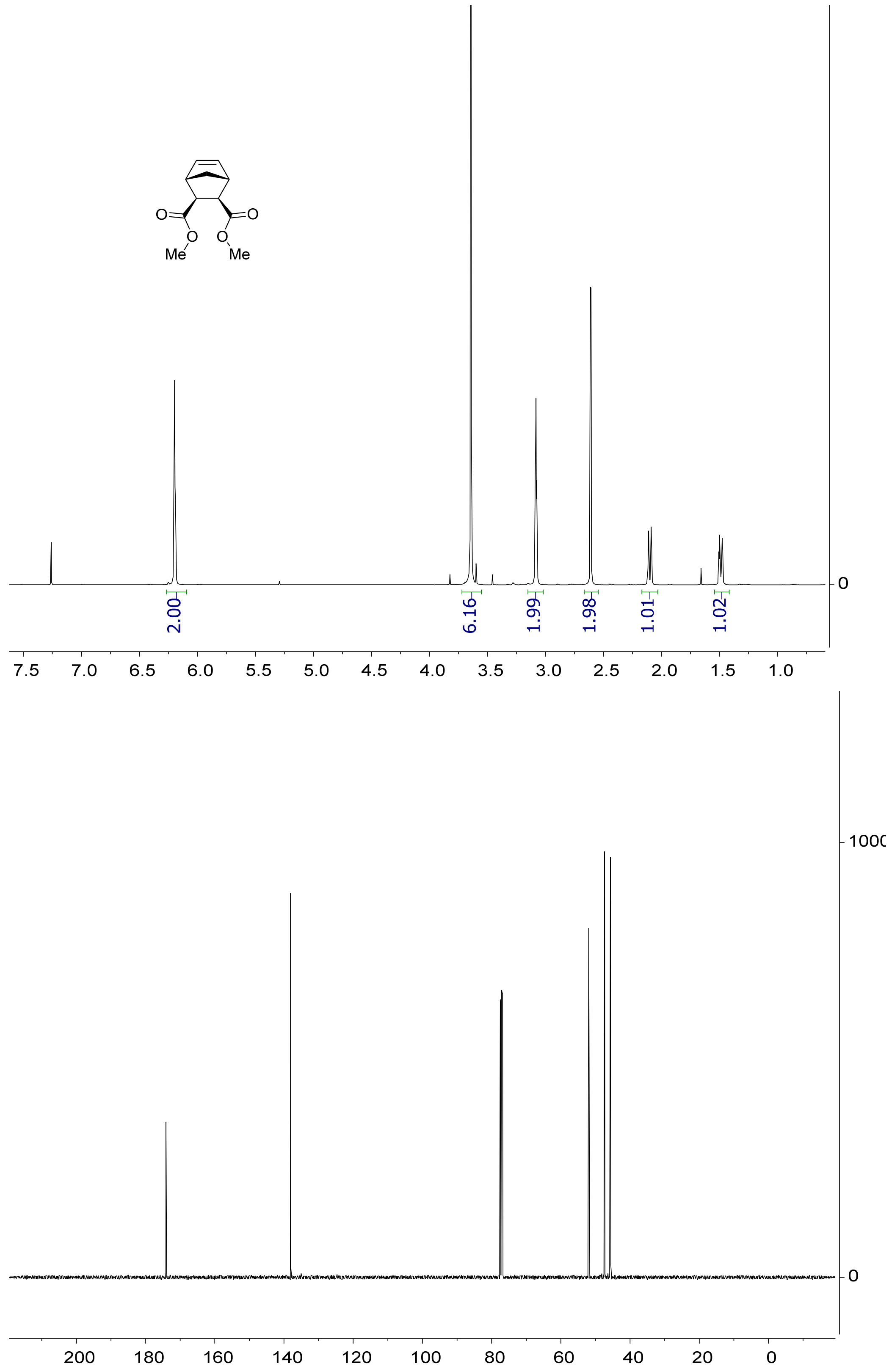


Figure S3A. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3a** in $CDCl_3$.

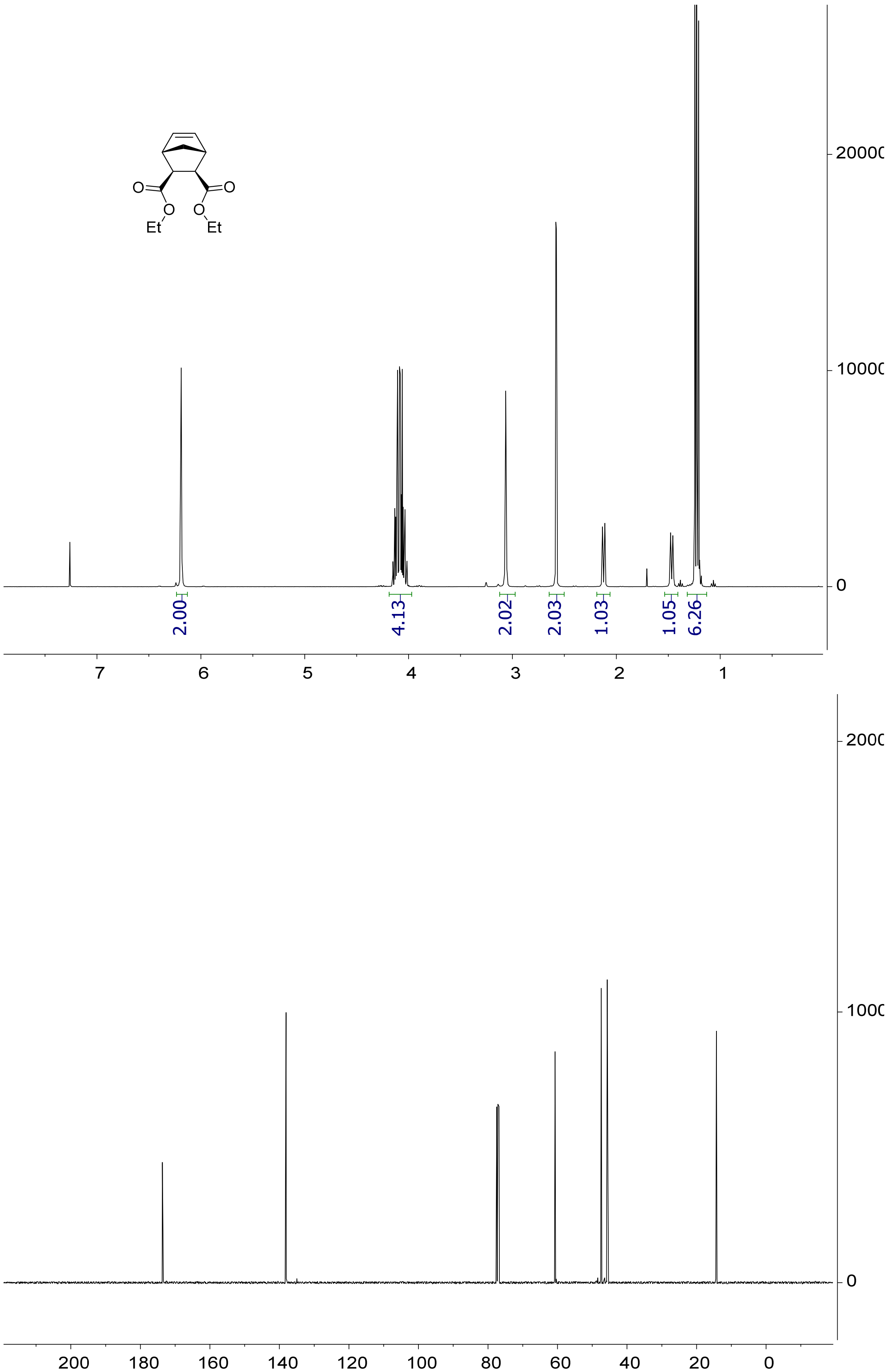


Figure S3B. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3b** in $CDCl_3$.

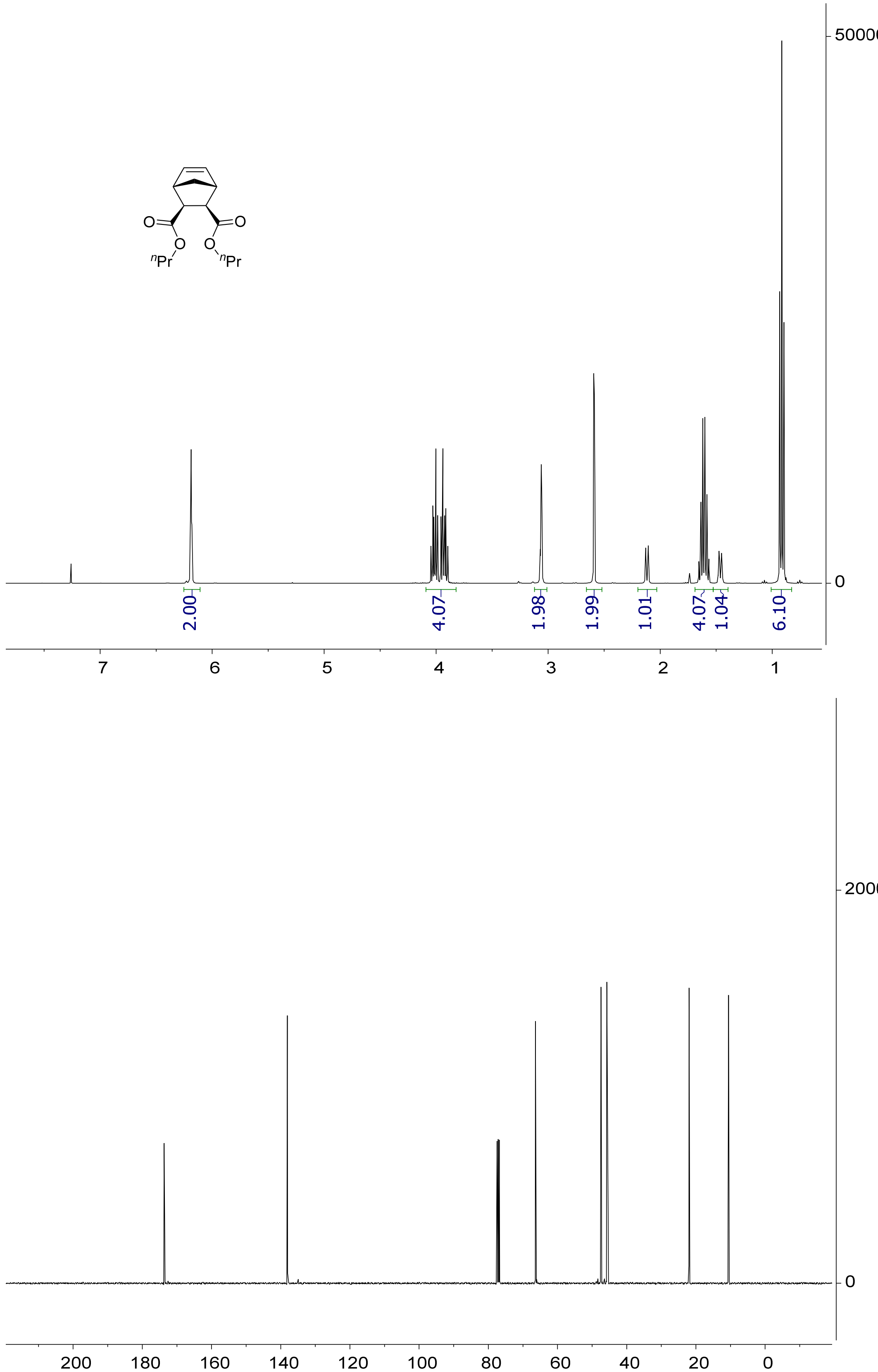


Figure S3C. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3c** in $CDCl_3$.

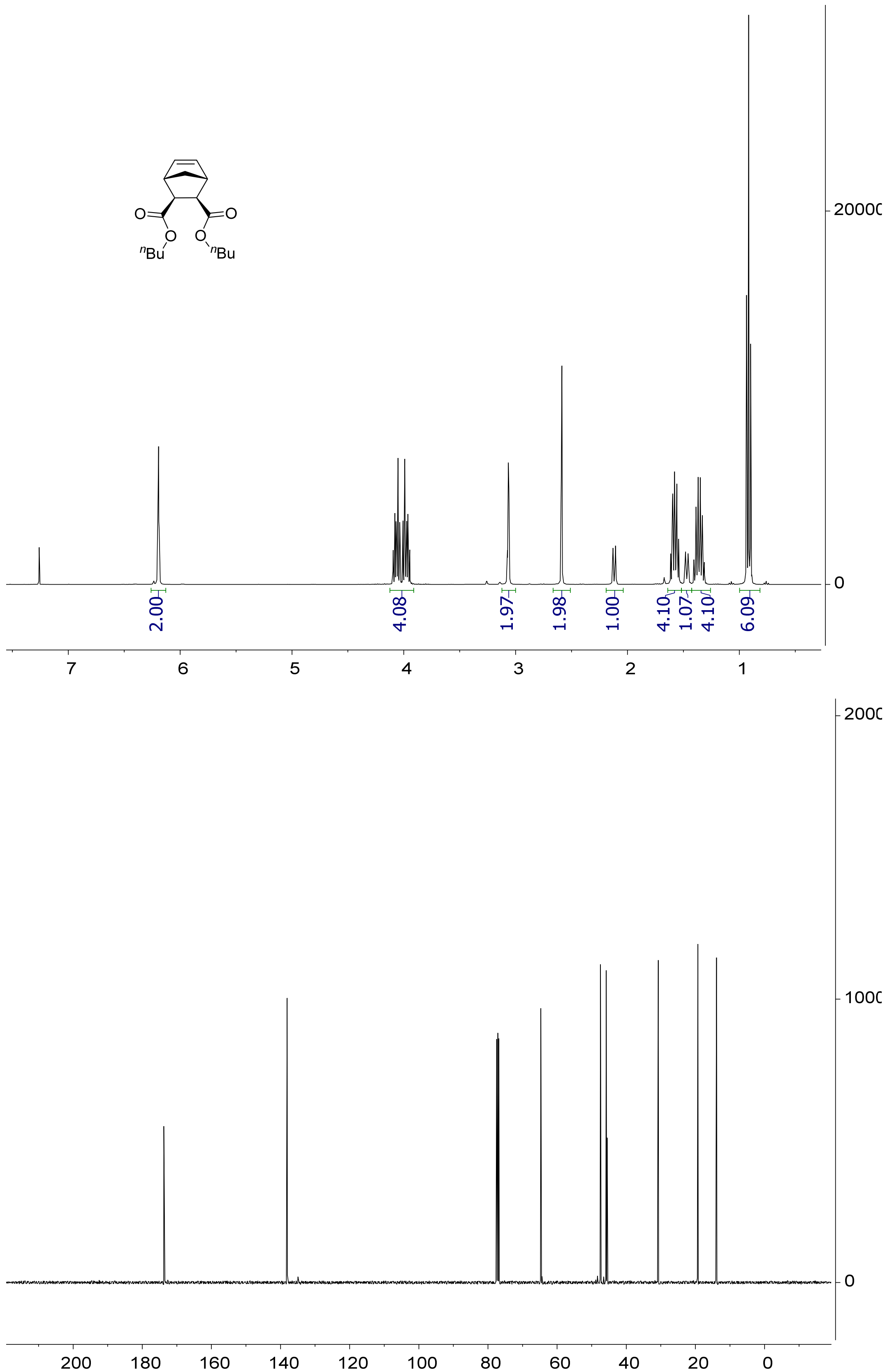


Figure S3D. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **3d** in $CDCl_3$.

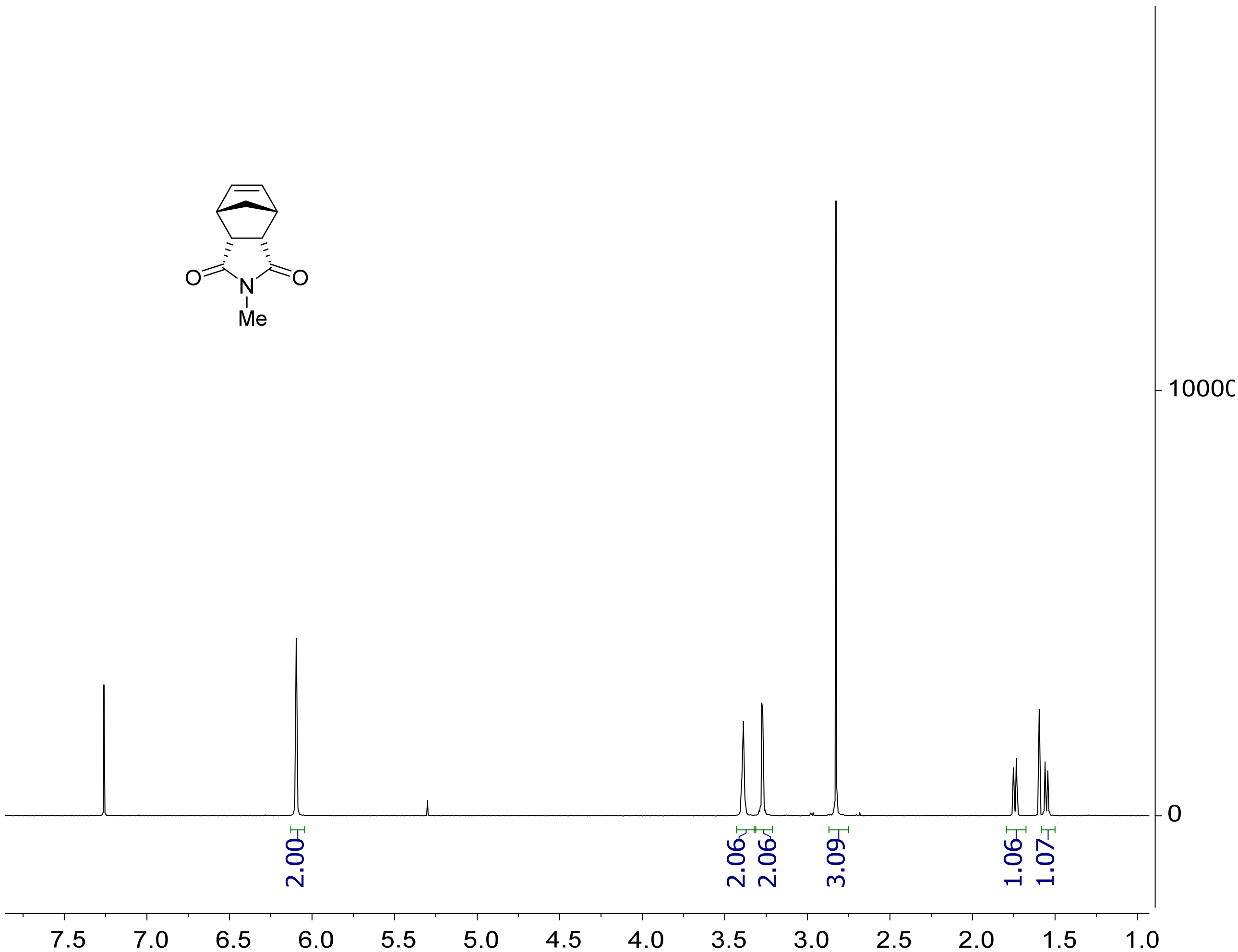


Figure S4A. ^{1}H NMR spectrum of **4a** in $CDCl_3$.

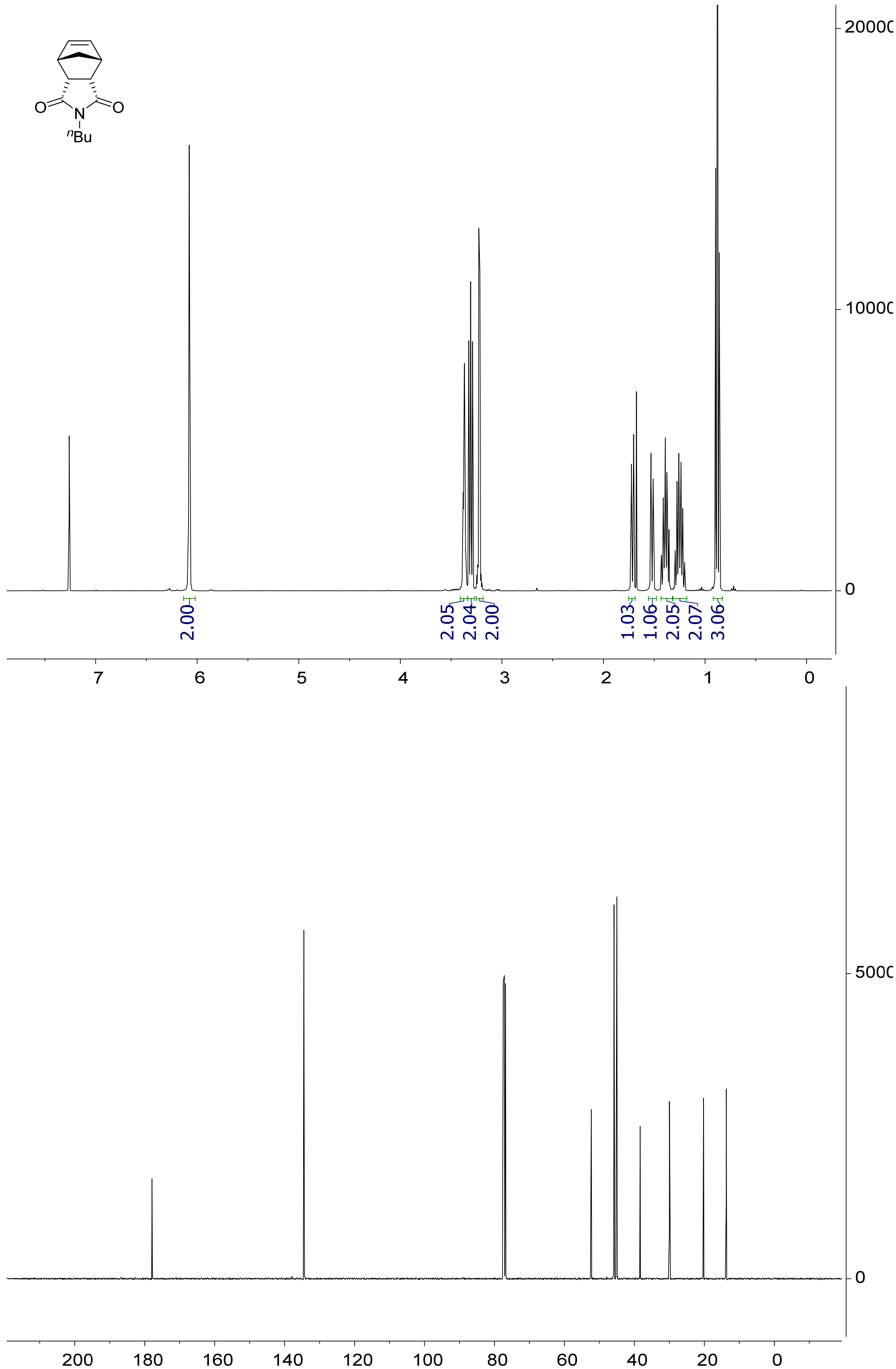


Figure S4B. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4b** in $CDCl_3$.

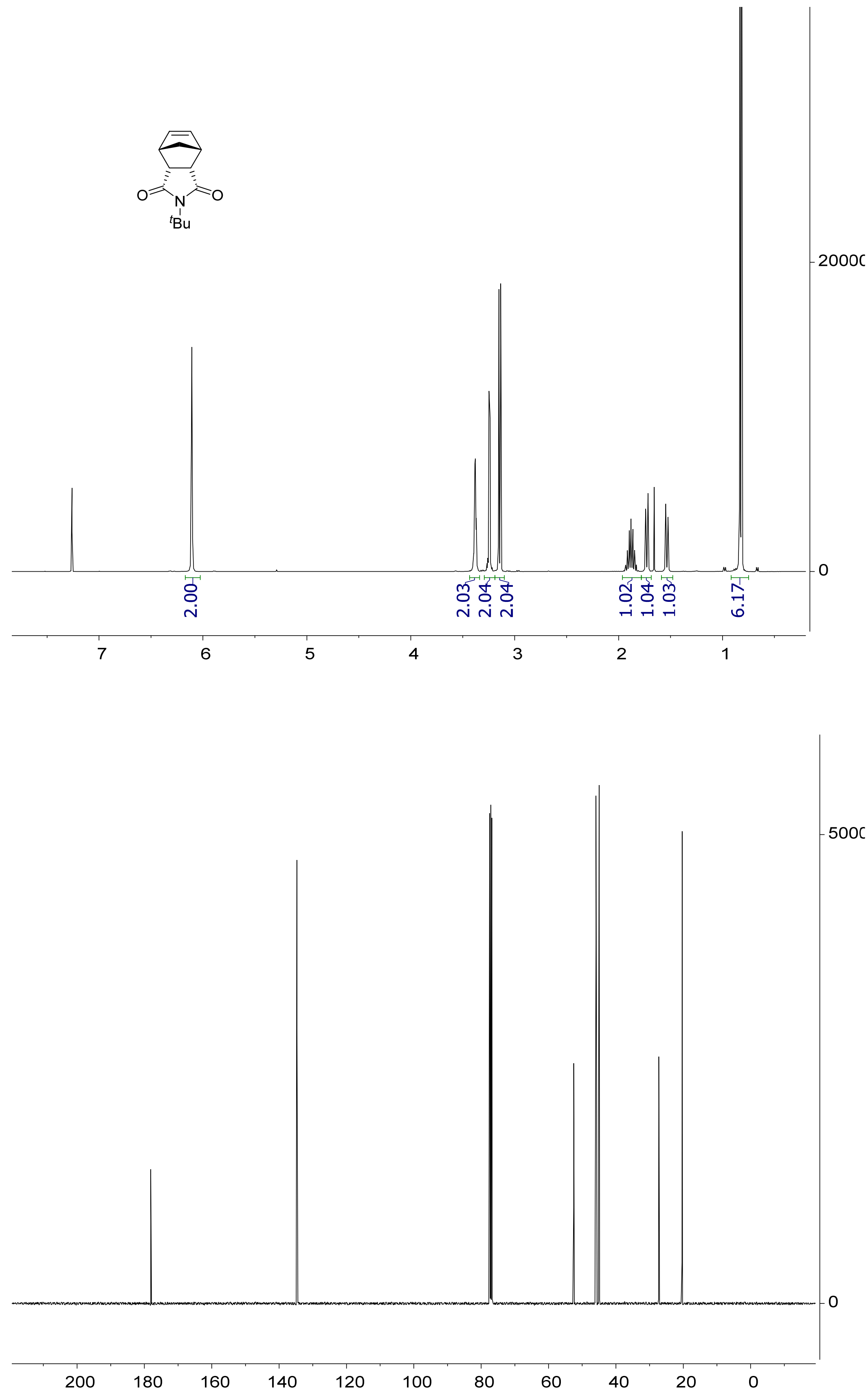


Figure S4C. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **4c** in $CDCl_3$.

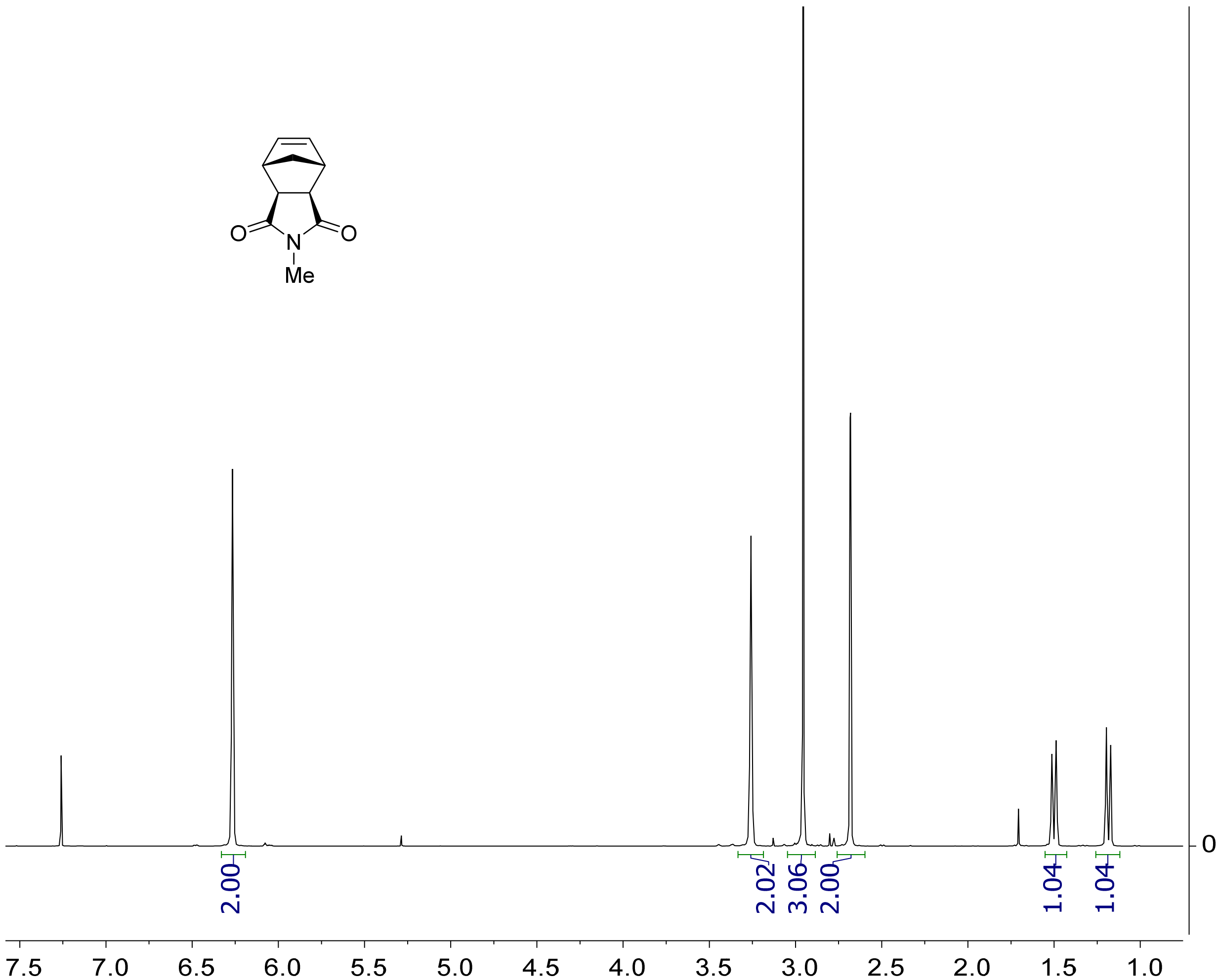


Figure S5A. ^{1}H NMR spectrum of **5a** in $CDCl_3$.

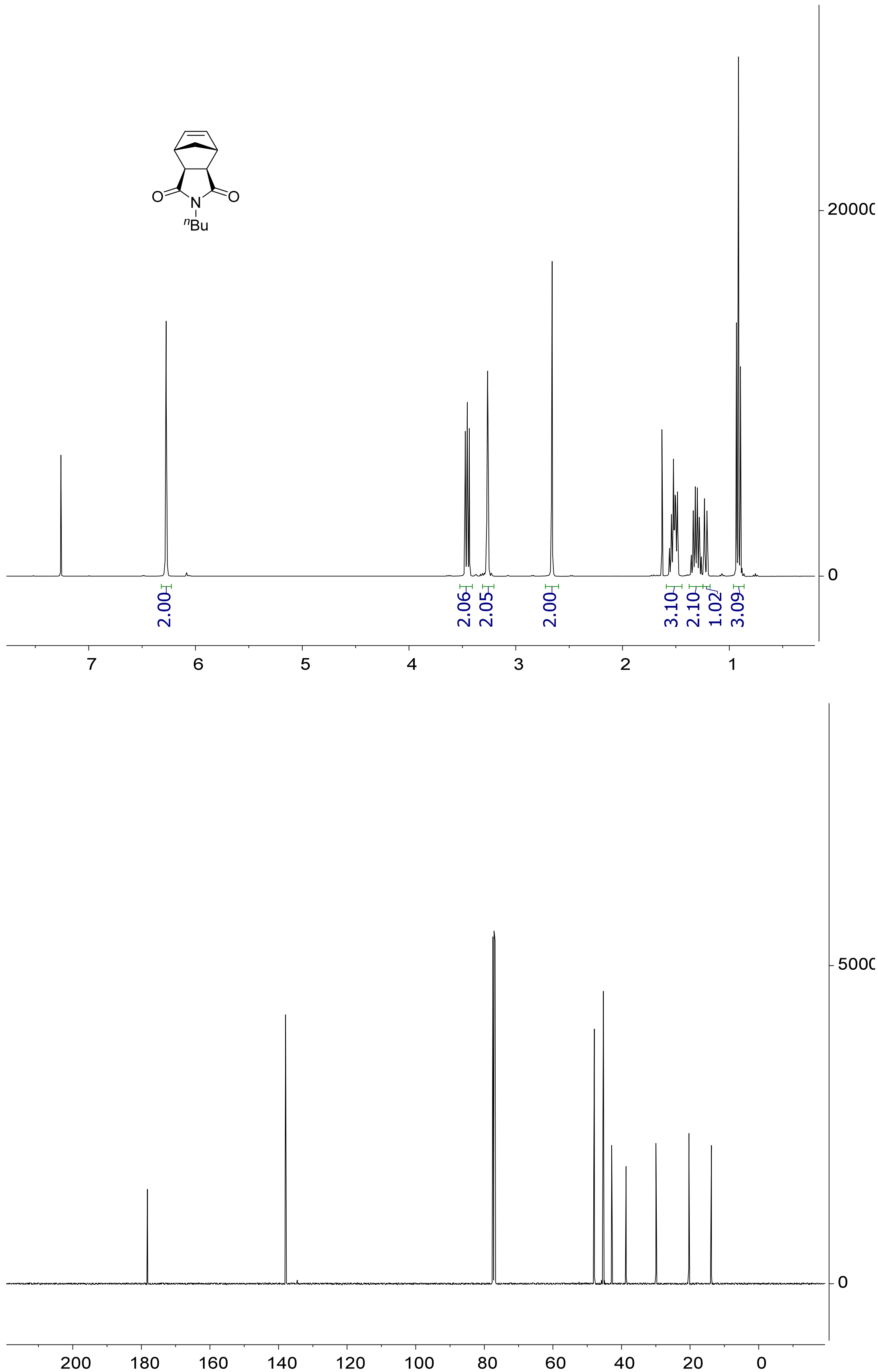


Figure S5B. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **5b** in $CDCl_3$.

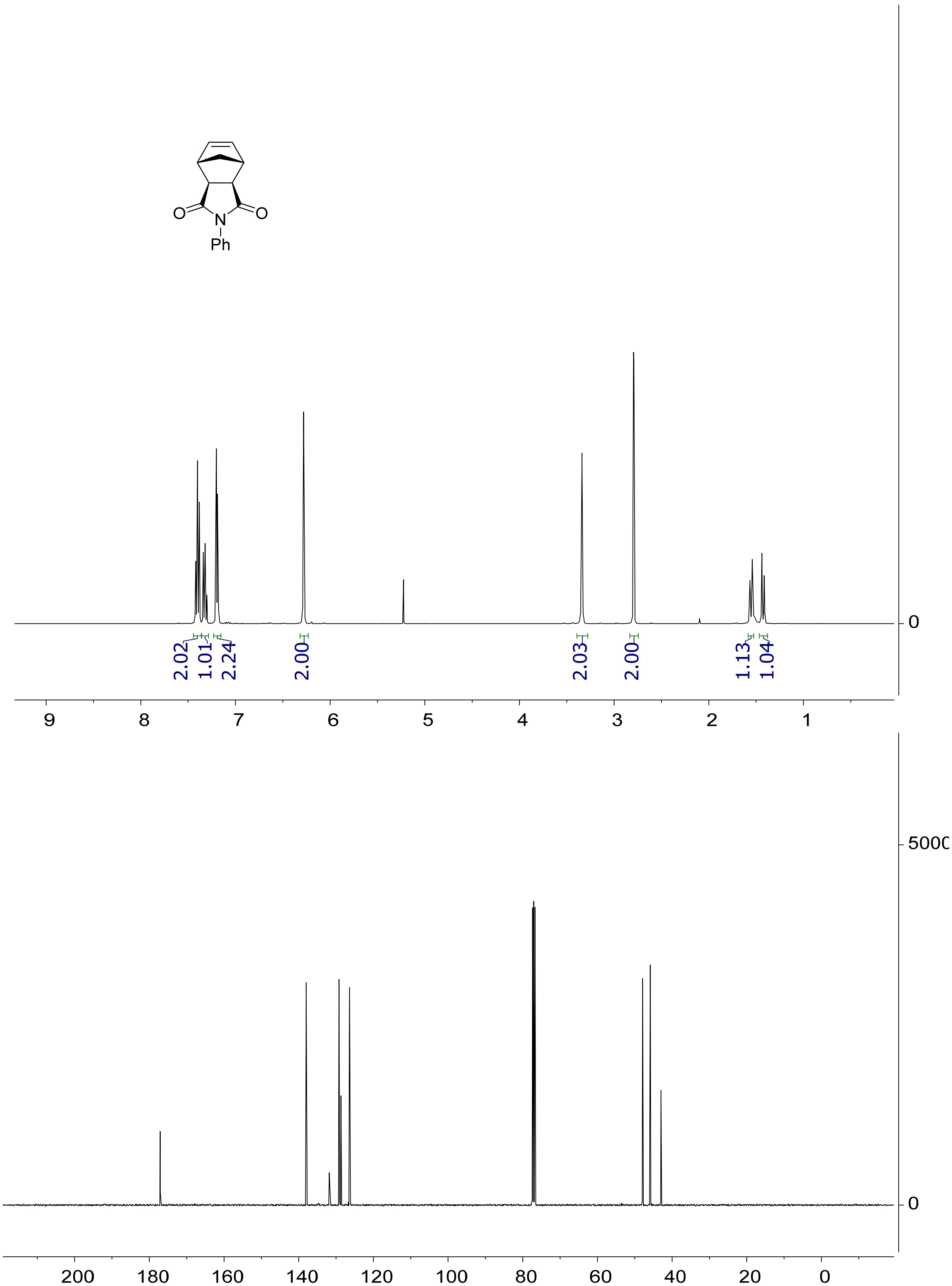
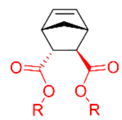
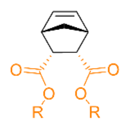
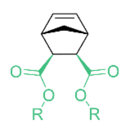
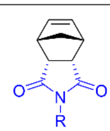
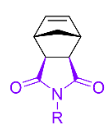


Figure S5C. ^{1}H (top) and ^{13}C (bottom) NMR spectra of **5c** in $CDCl_3$.

Table S1. Structures and homopolymerization rate constants (k_{homo}) for all monomers synthesized and studied in this report.

Anchor Group		ID	R	k_{homo} (M^{-1} s^{-1})
endo,exo-diester (*dx*-DE)		**1a**	Me	18.7
		1b	Et	14.6
		1c	^{n}Pr	10.4
		1d	^{n}Bu	6.90
		1e	^{i}Pr	6.14
		1f	^{t}Bu	5.32
		1g	CH_2CF_3	10.5
		1h	Ph	8.36
		1i	*p*-CF_3Ph	5.14
		1j	*p*-MeOPh	7.76
endo,endo-diester (*dd*-DE)		**2a**	Me	2.24
		2b	Et	0.934
		2c	^{n}Pr	0.518
		2d	^{n}Bu	0.362
exo,exo-diester (*xx*-DE)		**3a**	Me	30.8
		3b	Et	16.4
		3c	^{n}Pr	11.2
		3d	^{n}Bu	10.4
endo-imide (*d*-I)		**4a**	Me	0.814
		4b	^{n}Bu	0.930
		4c	^{t}Bu	0.782
exo-imide (*x*-I)		**5a**	Me	82.4
		5b	^{n}Bu	63.2
		5c	Ph	34.8
		PDMS	PDMS (1k)	21.6
		PLA	PLA (3k)	17.2
		PS	PS (4k)	4.18

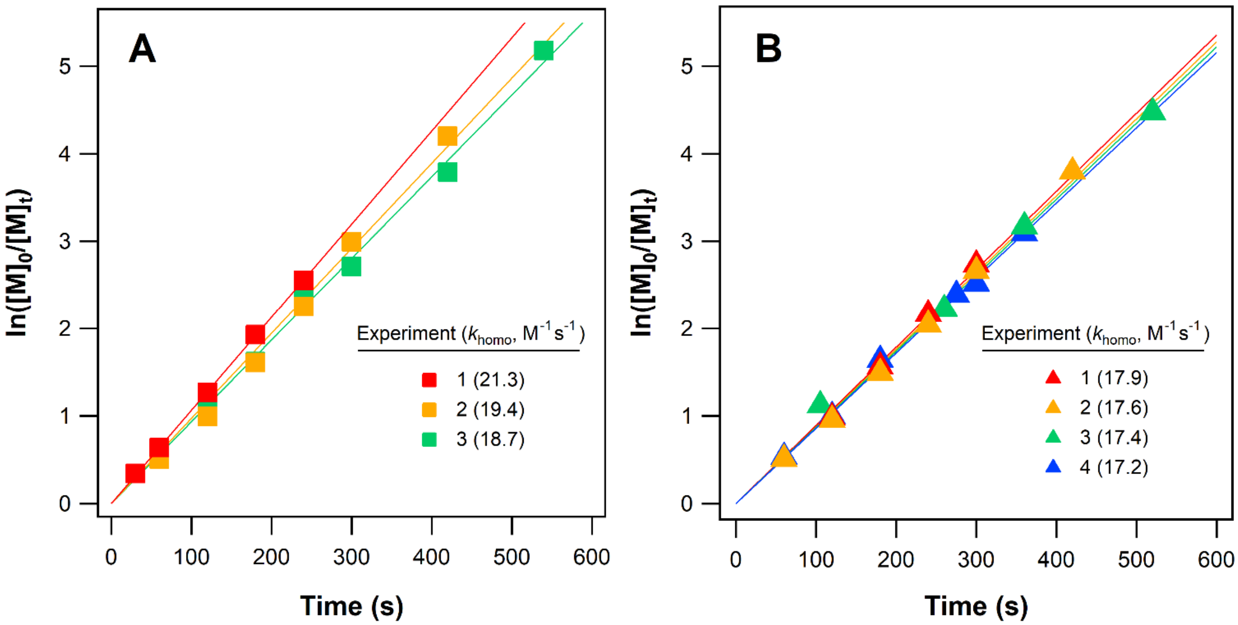


Figure S6. Representative repeated runs to determine rate constants (k_{homo}) for (A) **1a**, *endo,exo*-norbornenyl dimethylester; and (B) **PLA**, poly(D,L-lactide) macromonomer. k_{homo} is calculated from Eq. 1.

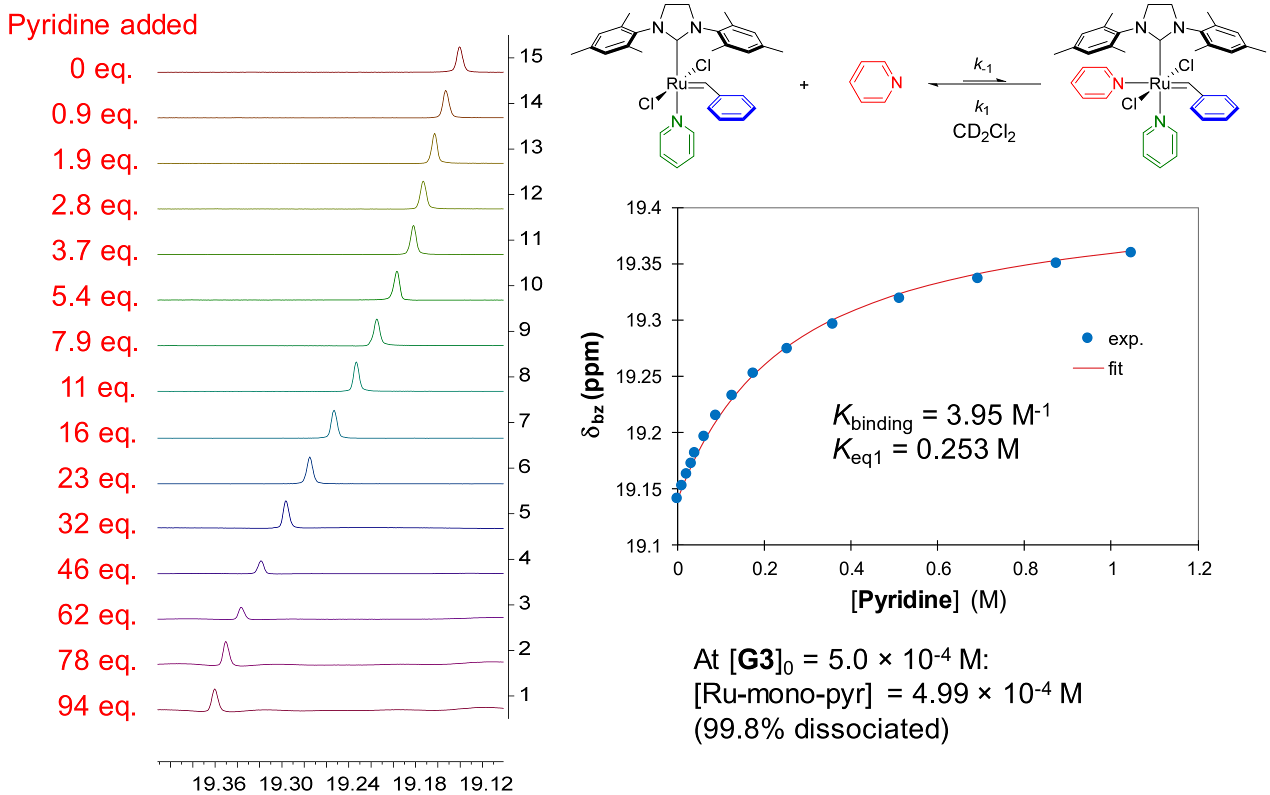
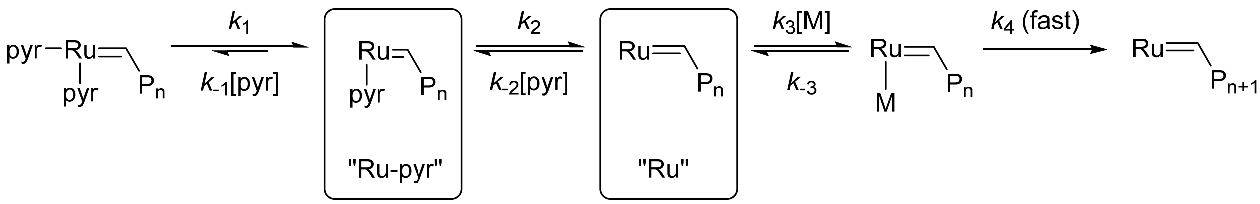


Figure S7. Stacked ^{1}H NMR spectra obtained during the pyridine titration experiments. To an NMR tube containing a CD_2Cl_2 solution of the monopyridine complex (11.2 mM) was titrated with a CD_2Cl_2 solution containing both pyridine (1.47 M) and the monopyridine complex (11.2 mM). The concentration of the monopyridine complex remained constant during the titrations. The chemical shifts of the benzylidene ^{1}H resonance was monitored at 298 K and could be employed to fit the pyridine binding constant ($K_{binding} = 1/K_{eq,1}$).

Derivation of Rate Expression (Eq. 2)

We derived a simplified rate expression corresponding to the proposed dissociative ROMP mechanism in which olefin coordination is the rate-limiting step:



The large value estimated for $K_{eq,1} = k_1/k_{-1}$ indicates that >99.8% of the precatalyst **G3** exists as the monopyridine adduct in solution under the conditions employed in our homo- and copolymerization studies. The initial concentration of **G3** equals the sum of the concentrations of the monopyridine adduct ("Ru-pyr") and the 14-electron vacant species ("Ru"):

$$[\mathbf{G3}]_0 = [\text{Ru}-\text{pyr}] + [\text{Ru}] \tag{S1}$$

A steady-state approximation can be made for the 14-electron vacant species:

$$-\frac{\text{d[Ru]}}{\text{dt}} = k_2[\text{Ru}-\text{pyr}] - k_{-2}[\text{Ru}][\text{pyr}] - k_3[\text{Ru}][\text{M}] = 0 \tag{S2}$$

Substituting S1 in S2 obtains the following:

$$-\frac{\text{d[Ru]}}{\text{dt}} = k_2[\mathbf{G3}]_0 - k_2[\text{Ru}] - k_{-2}[\text{Ru}][\text{pyr}] - k_3[\text{Ru}][\text{M}] = 0 \tag{S3}$$

$$[\text{Ru}] = \frac{k_2[\mathbf{G3}]_0}{k_2 + k_{-2}[\text{pyr}] + k_3[\text{M}]} \tag{S4}$$

$$[\text{Ru}] \times \frac{1/k_{-2}}{1/k_{-2}} = \frac{K_{eq,2}[\mathbf{G3}]_0}{K_{eq,2} + [\text{pyr}] + \frac{k_3}{k_{-2}}[\text{M}]} \approx \frac{K_{eq,2}[\mathbf{G3}]_0}{K_{eq,2} + [\text{pyr}]} \tag{S5}$$

In Eq. S5, since $k_3 << k_{-2}$, the third term in the denominator is close to 0. The time-dependent consumption of the monomer ("M") is provided by Eq. S6 (Eq. 2 in the main text):

$$-\frac{\text{d[M]}}{\text{dt}} = k_3[\text{Ru}][\text{M}] = \frac{K_{eq,2}k_3}{K_{eq,2} + [\text{pyr}]}[\mathbf{G3}]_0[\text{M}] \tag{S6}$$

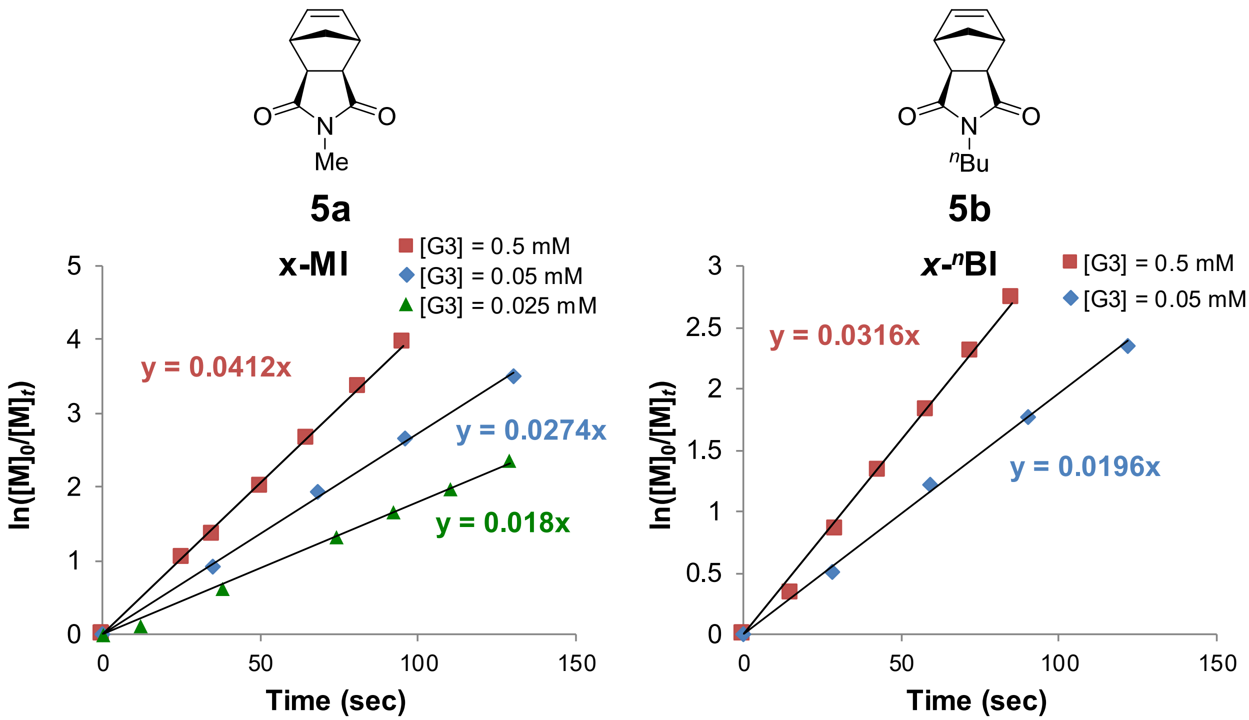


Figure S8. ROMP of **5a** (left) and **5b** (right) in CH_2Cl_2 at 298 K showing the rate dependence on $[\mathbf{G3}]_0$ (maroon: $[\mathbf{G3}]_0$ = 0.5 mM, blue: $[\mathbf{G3}]_0$ = 0.05 mM, green: $[\mathbf{G3}]_0$ = 0.025 mM). The slope corresponds to the k_{obs} (s^{-1}). These polymerization reactions have the same $[\mathbf{5a}]_0/[\mathbf{G3}]_0$ and $[\mathbf{5b}]_0/[\mathbf{G3}]_0$ ratio of 100. Time-lapse kinetic traces were obtained using our standard homopolymerization procedure.

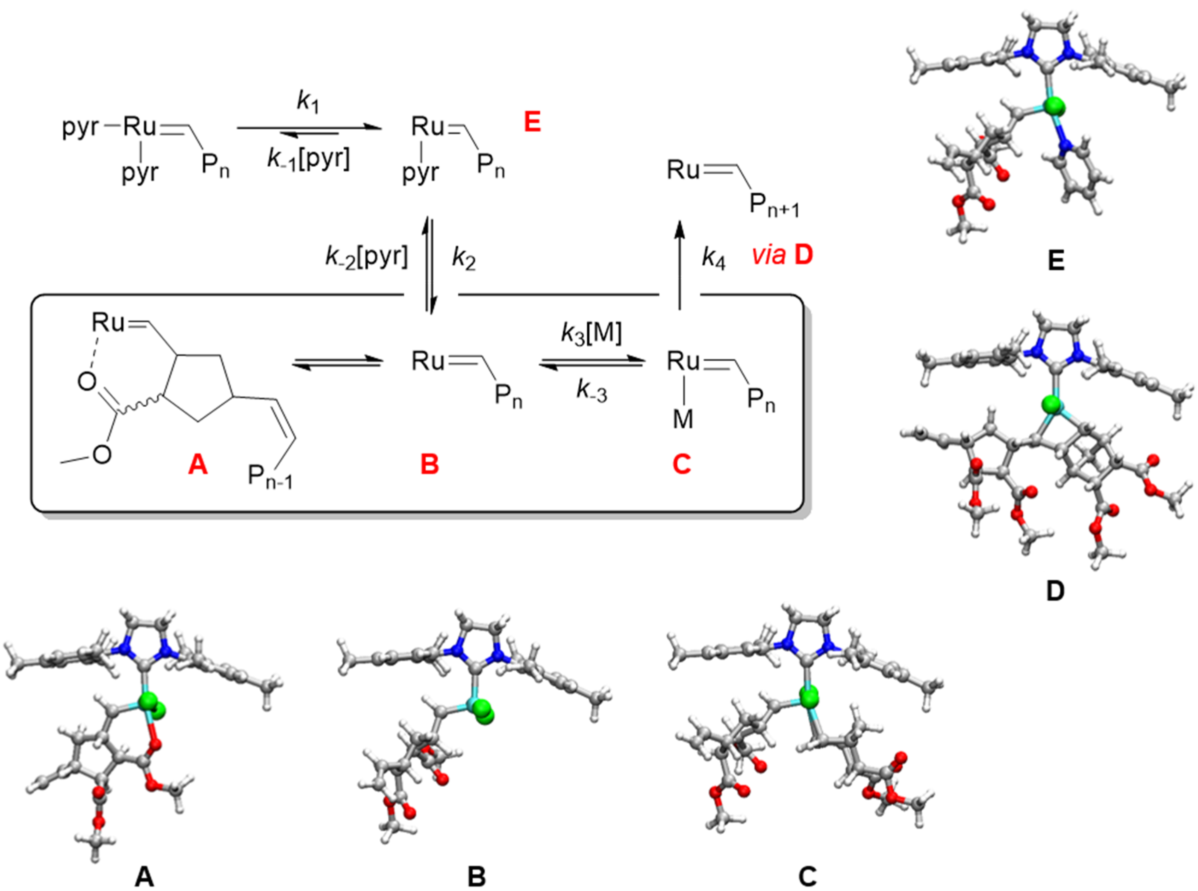


Figure S9. DFT-optimized structures of catalytically relevant ruthenium species, corresponding to the proposed dissociative ROMP pathway (Figure 5A): (A) Six-membered Ru–O chelate, (B) 14-electron vacant species, (C) olefin adduct, (D) metallacyclobutane intermediate, and (E) monopyridine adduct.

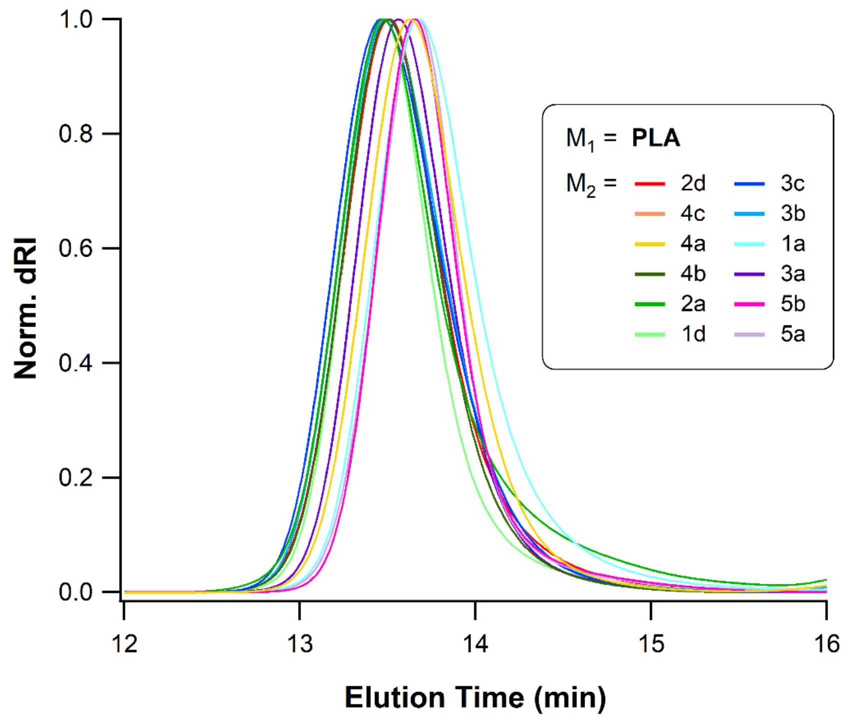


Figure S10. SEC traces for **PLA** + diluent copolymerizations at full conversion.

Table S2. Compiled SEC data for **PLA** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)[a]	$Đ$
2d	*dd*-D^{n}BuE	95.4	1.07
4c	*d*-^{t}BuI	89.9	1.10
4a	*d*-MeI	90.5	1.04
4b	*d*-^{n}BuI	103	1.04
2a	*dd*-DMeE	94.5	1.05
1d	*dx*-D^{n}BuE	101	1.04
3d	*xx*-D^{n}BuE	—[b]	—[b]
3c	*xx*-D^{n}PrE	101	1.08
3b	*xx*-DEtE	99.5	1.06
1a	*dx*-DMeE	108	1.05
3a	*xx*-DMeE	95.4	1.04
5b	*x*-^{n}BuI	95.9	1.02
5a	*x*-MeI	86.4	1.02

[a] The number-average molecular weight (M_n) is reported relative to polystyrene in THF (d*n*/d*c* = 0.185 mL g^{-1}).
[b] Data is not available for **PLA** + **3d**.

Table S3. Kinetic data for the copolymerization of **PLA** (M_1, M_n = 3230 g mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
2d	*dd*-D^{n}BuE	0.362	17.2	8.03	0.860	2.14	0.421	0.902	5.09
4c	*d*-^{t}BuI	0.782	17.2	11.0	1.72	1.56	0.455	0.708	3.43
4a	*d*-MeI	0.814	17.2	4.55	1.24	3.78	0.656	2.48	5.76
4b	*d*-^{n}BuI	0.930	17.2	8.14	1.08	2.11	0.861	1.82	2.45
2a	*dd*-DMeE	2.24	17.2	8.05	2.71	2.14	0.827	1.77	2.58
1d	*dx*-D^{n}BuE	6.90	17.2	16.4	7.35	1.05	0.939	0.983	1.12
3d	*xx*-D^{n}BuE	10.4	17.2	46.0	8.94	0.374	1.17	0.436	0.320
3c	*xx*-D^{n}PrE	11.2	17.2	47.2	9.38	0.364	1.20	0.436	0.304
3b	*xx*-DEtE	16.4	17.2	48.6	10.1	0.354	1.63	0.577	0.217
1a	*dx*-DMeE	18.7	17.2	18.0	15.7	0.953	1.19	1.13	0.801
3a	*xx*-DMeE	30.8	17.2	49.2	18.3	0.350	1.68	0.588	0.208
5b	*x*-^{n}BuI	63.2	17.2	27.2	21.4	0.633	2.95	1.87	0.214
5a	*x*-MeI	82.4	17.2	28.4	27.1	0.606	3.05	1.85	0.199

Table S4. Kinetic data for the copolymerization of **PDMS** (M_1, M_n = 1280 mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
4a	*d*-MeI	0.814	21.6	3.34	2.44	6.47	0.334	2.16	19.4
4b	*d*-^{n}BuI	0.930	21.6	6.85	2.00	3.15	0.465	1.47	6.78
1d	*dx*-D^{n}BuE	6.90	21.6	19.5	15.9	1.11	0.434	0.481	2.55
3d	*xx*-D^{n}BuE	10.4	21.6	48.2	10.3	0.448	1.02	0.455	0.441
1a	*dx*-DMeE	18.7	21.6	19.9	19.9	1.09	0.940	1.02	1.16
3a	*xx*-DMeE	30.8	21.6	50.4	26.3	0.429	1.17	0.502	0.367

Table S5. Kinetic data for the copolymerization of **PS** (M_1, M_n = 3990 mol^{-1}) with selected diluents (M_2). The self-propagation rate constants k_{22} and k_{11} were determined from homopolymerization experiments, and the cross-propagation rate constants k_{12} and k_{21} were determined by fitting copolymerization data using non-linear least squares regression. The reactivity ratios $r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$ are also provided.

ID	Diluent	k_{22} (M^{-1} s^{-1})	k_{11} (M^{-1} s^{-1})	k_{12} (M^{-1} s^{-1})	k_{21} (M^{-1} s^{-1})	r_1	r_2	r_1r_2	r_1/r_2
1d	*dx*-D^{n}BuE	6.90	4.18	5.23	5.66	0.799	1.22	0.974	0.656
3d	*xx*-D^{n}BuE	10.4	4.18	29.9	7.58	0.140	1.38	0.193	0.102
1b	*dx*-DEtE	14.6	4.18	7.77	8.75	0.538	1.67	0.897	0.322
1a	*dx*-DMeE	18.7	4.18	7.74	13.2	0.540	1.42	0.765	0.381
3a	*xx*-DMeE	30.8	4.18	30.8	23.3	0.136	1.32	0.180	0.103
5b	*x*-^{n}BuI	63.2	4.18	30.8	38.9	0.136	1.63	0.221	0.0836
5a	*x*-MeI	82.4	4.18	31.9	63.2	0.131	1.30	0.171	0.100

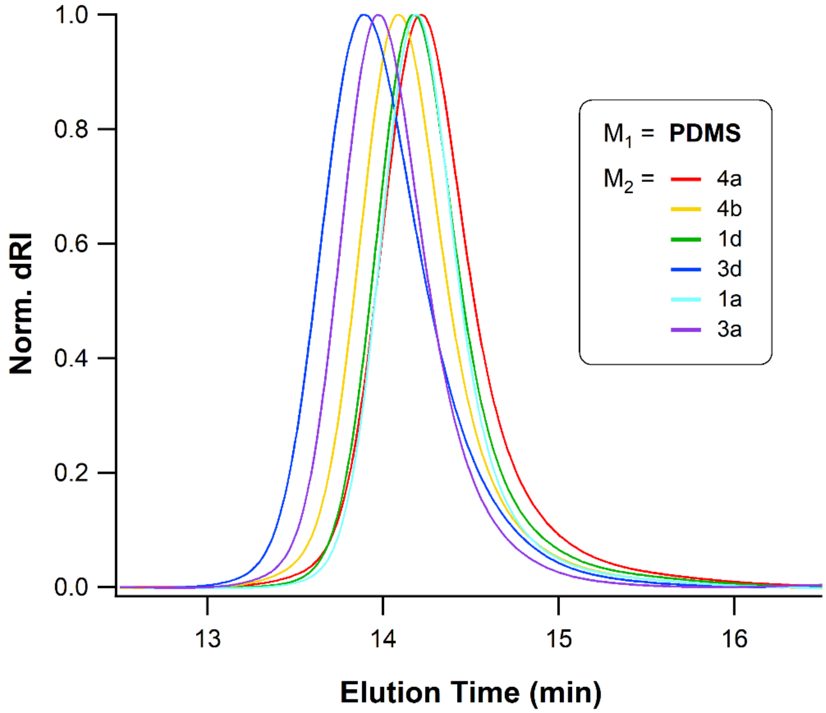


Figure S11. SEC traces for **PDMS** + diluent copolymerizations at full conversion.

Table S6. Compiled SEC data for **PDMS** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)[a]	*Đ*
4a	*d*-MeI	39.3	1.04
4b	*d*-^{n}BuI	42.7	1.05
1d	*dx*-D^{n}BuE	32.5	1.06
3d	*xx*-D^{n}BuE	39.9	1.09
1a	*dx*-DMeE	32.2	1.04
3a	*xx*-DMeE	37.9	1.03

[a] The number-average molecular weight (M_n) is reported relative to polystyrene in THF (d*n*/d*c* = 0.185 mL g^{-1}).

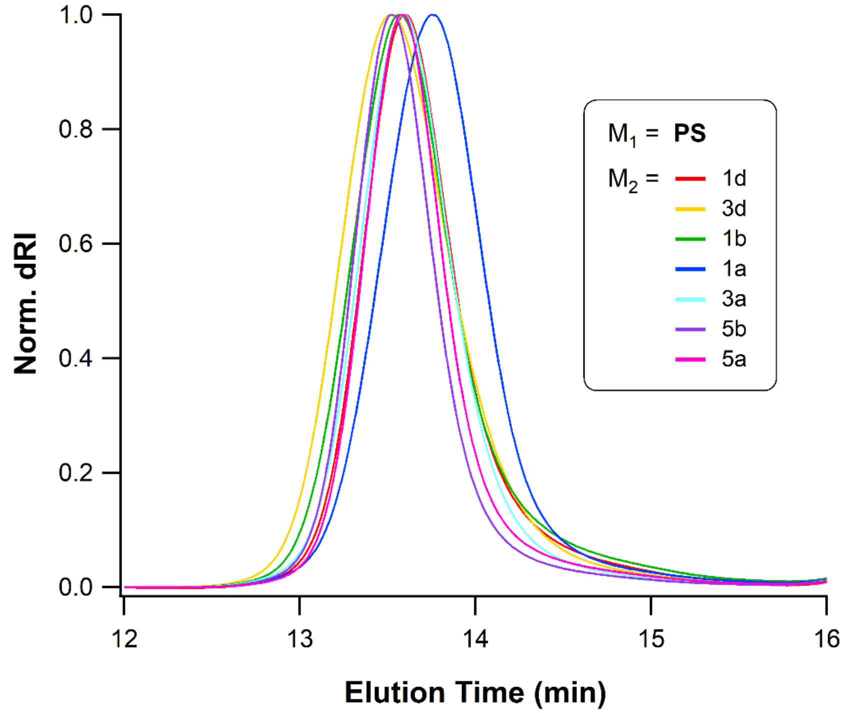


Figure S12. SEC traces for **PS** + diluent copolymerizations at full conversion.

Table S7. Compiled SEC data for **PS** + diluent copolymerizations at full conversion.

ID	Diluent	M_n (kDa)	*Đ*
1d	*dx*-D^{n}BuE	362	1.09
3d	*xx*-D^{n}BuE	379	1.09
1b	*dx*-DEtE	398	1.10
1a	*dx*-DMeE	375	1.04
3a	*xx*-DMeE	376	1.05
5b	*x*-^{n}BuI	386	1.04
5a	*x*-MeI	364	1.06

[a] The number-average molecular weight (M_n) is reported relative to polystyrene in THF (d*n*/d*c* = 0.185 mL g^{-1}).

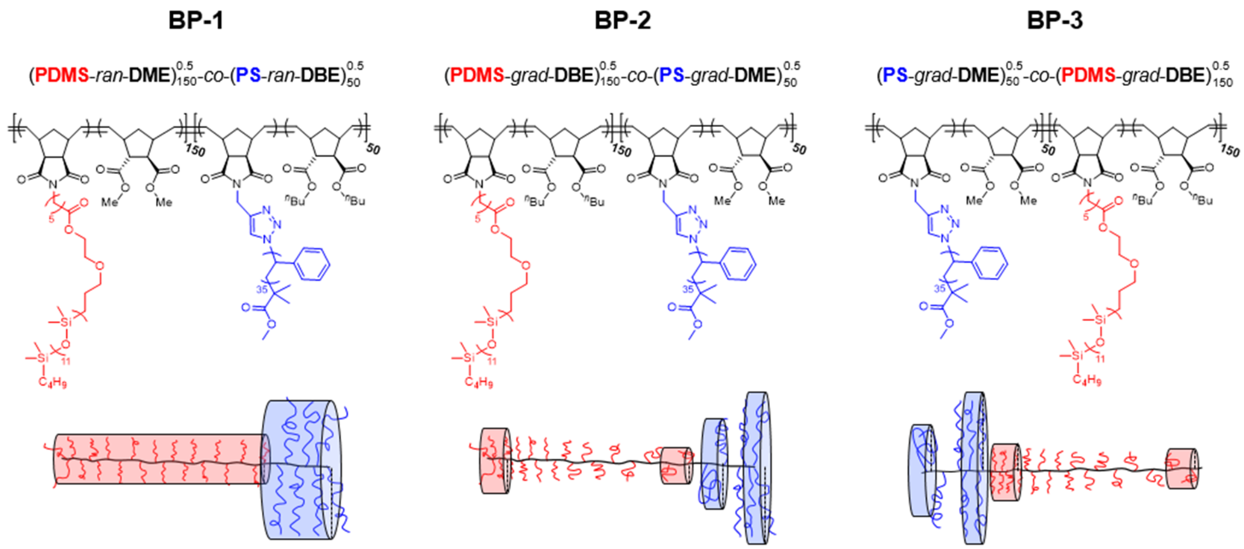


Figure S13. (Top) Chemical structures of graft block polymers **BP-1**, **BP-2**, and **BP-3**. (Bottom) Schematic illustrations of the anticipated molecular "shapes," drawn in the limit of fully extended backbones for ease of visualization.

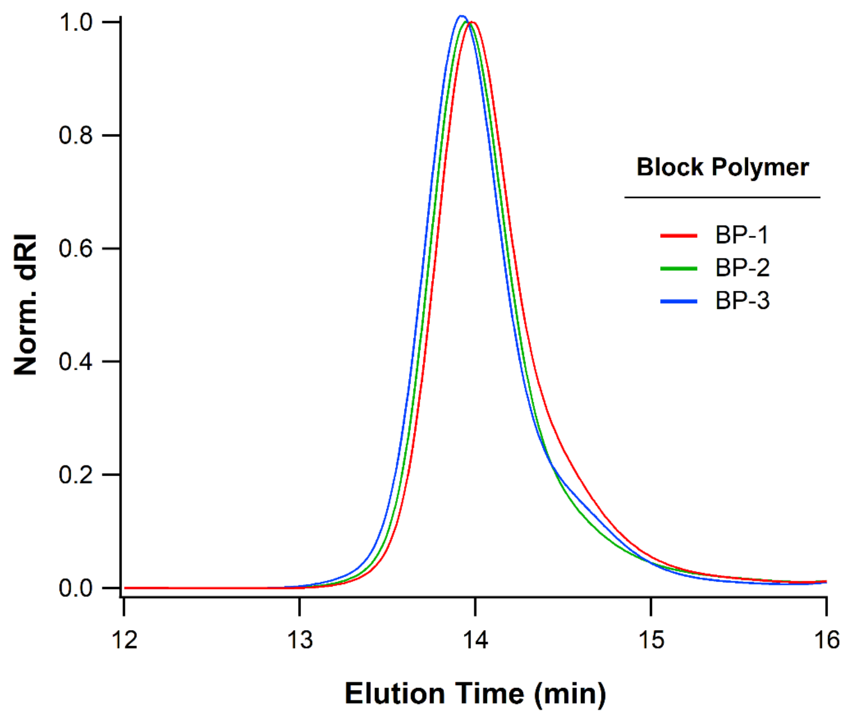


Figure S14. SEC traces for graft block polymers **BP-1**, **BP-2**, and **BP-3**, indicating essentially identical molecular weights and dispersities.

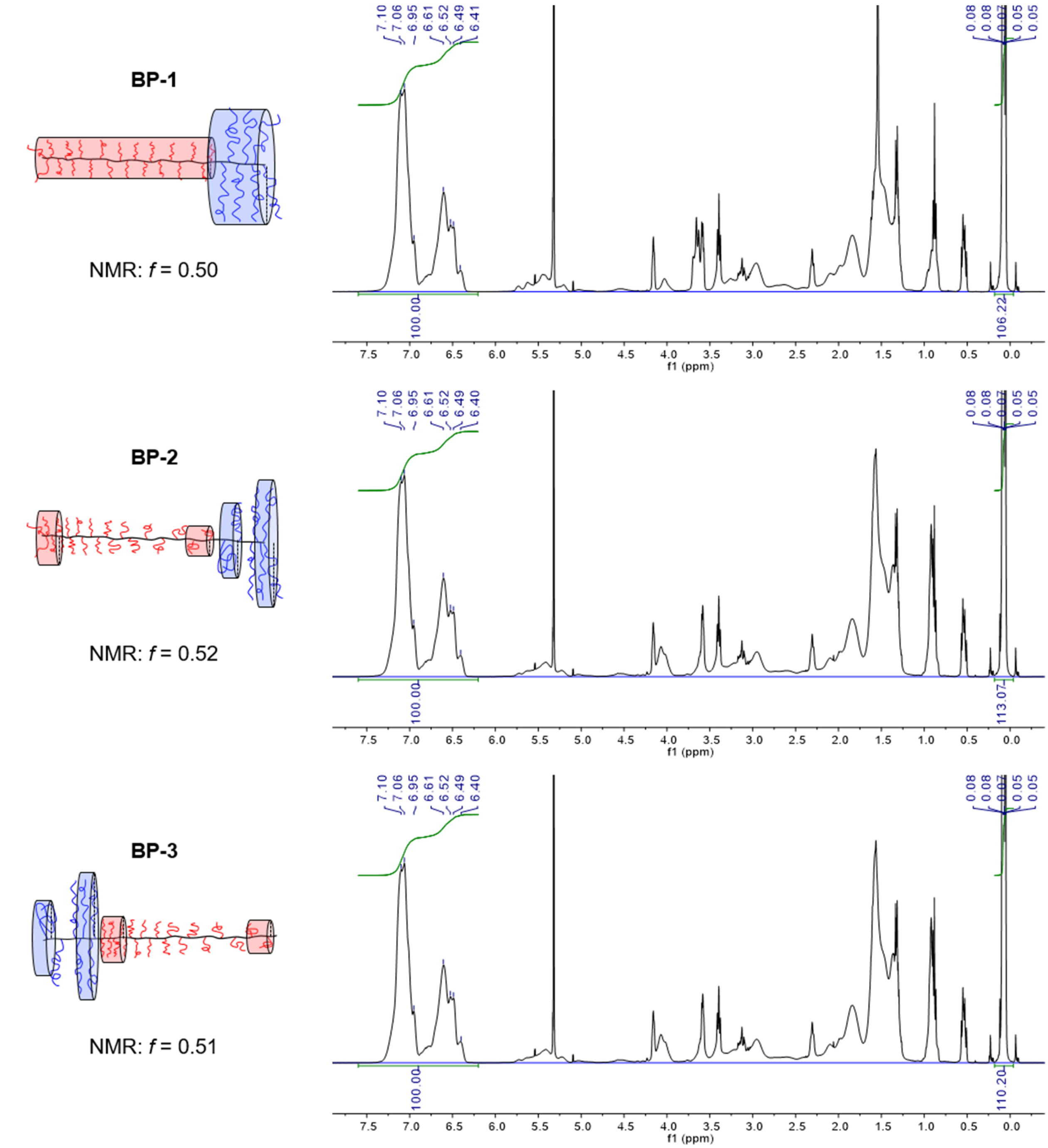


Figure S15. ^{1}H NMR data for graft block polymers **BP-1**, **BP-2**, and **BP-3**, indicating essentially identical chemical compositions ($f \approx 0.5$).

Table S8. xyz coordinates (in Angstroms) for structures in Figures S10: *endo* isomer (**2a**).

olefin *endo* (2a)

C	1.37924E+00	3.92831E-01	-3.22856E-01
C	1.16270E+00	-9.39169E-01	-2.65412E-01
O	-9.72876E-02	2.15024E+00	-2.19202E+00
O	-2.27946E+00	1.48833E+00	-2.26447E+00
O	-2.43997E+00	-2.31171E+00	-1.62638E+00
O	-7.30496E-01	-1.10449E+00	-2.52547E+00
C	2.79507E-01	1.06702E+00	4.86745E-01
C	-8.10609E-02	-1.16530E+00	5.81677E-01
C	-1.34579E+00	-6.49205E-01	-2.42913E-01
C	-1.06624E+00	9.05880E-01	-3.14351E-01
H	-1.88335E+00	1.40366E+00	2.40453E-01
H	-2.24511E+00	-8.32600E-01	3.65716E-01
C	5.39175E-02	3.47364E-03	1.59193E+00
H	-8.54421E-01	1.72316E-01	2.19954E+00
H	9.29488E-01	-1.12527E-01	2.25139E+00
H	-2.30996E-01	-2.17697E+00	9.87862E-01
H	1.69050E+00	-1.71993E+00	-8.18140E-01
H	2.11273E+00	9.23746E-01	-9.31238E-01
H	4.70643E-01	2.10252E+00	8.04631E-01
C	-1.04361E+00	1.56452E+00	-1.68620E+00
C	-1.59258E+00	-1.43417E+00	-1.52086E+00
C	-2.37037E+00	2.10899E+00	-3.56562E+00
H	-3.40808E+00	1.95389E+00	-3.89040E+00
H	-1.66592E+00	1.63678E+00	-4.26851E+00
H	-2.13915E+00	3.18414E+00	-3.49946E+00
C	-9.05792E-01	-1.87012E+00	-3.73855E+00
H	-1.53347E-01	-1.48092E+00	-4.43738E+00
H	-1.92285E+00	-1.73248E+00	-4.13837E+00
H	-7.43190E-01	-2.94249E+00	-3.54617E+00

chelate *endo* (Fig. S10A)

Ru	2.51298E+00	-2.83991E+00	1.99790E+00
C	1.82535E+00	-1.48956E+00	9.77774E-01
C	4.28400E+00	-3.09559E+00	1.11161E+00
N	5.17130E+00	-4.03946E+00	1.57214E+00
N	4.89236E+00	-2.45658E+00	6.42919E-02
O	6.65926E-01	-2.84820E+00	3.19021E+00
O	-1.22902E+00	-1.98641E+00	4.03640E+00
O	-3.33328E+00	-9.09042E-01	1.02780E+00
O	-1.34432E+00	-2.01365E+00	8.26982E-01
Cl	3.35846E+00	-1.34486E+00	3.70978E+00
Cl	1.46186E+00	-4.58682E+00	6.51703E-01
C	-8.27318E-01	1.20405E+00	1.15747E+00
C	1.10551E+00	-2.91703E-01	1.54542E+00
C	-1.33078E+00	2.74034E-02	2.06495E+00
C	4.88660E-03	-5.18496E-01	2.65677E+00
C	6.49035E+00	-3.97113E+00	9.08613E-01
C	6.21706E+00	-3.02710E+00	-2.74732E-01
H	6.16629E+00	-3.56374E+00	-1.24047E+00
C	4.36805E+00	-1.40755E+00	-7.63900E-01
C	4.06401E-01	5.80081E-01	4.62618E-01
C	4.98068E+00	-4.91335E+00	2.70433E+00
H	7.24820E+00	-3.56608E+00	1.60497E+00
C	-1.84115E+00	1.80210E+00	2.20939E-01
C	-2.16952E+00	3.10431E+00	1.92397E-01
H	1.08210E+00	1.34434E+00	4.65121E-02
H	7.63865E-02	-5.74638E-02	-3.78048E-01
C	-2.13755E+00	-9.97183E-01	1.26637E+00
H	-4.79652E-01	1.99676E+00	1.84913E+00
H	1.91235E+00	2.89956E-01	2.03916E+00
H	-1.72188E+00	3.82750E+00	8.85133E-01
H	-2.31842E+00	1.11183E+00	-4.87369E-01
C	3.68129E+00	-1.73937E+00	-1.95803E+00
C	3.23637E+00	-6.86731E-01	-2.77795E+00
C	3.46294E+00	6.63162E-01	-2.45071E+00
C	4.15083E+00	9.51903E-01	-1.25857E+00
C	4.48041E+00	-6.22311E+00	2.47903E+00

C	4.31315E+00	-7.06877E+00	3.58927E+00
C	4.65216E+00	-6.66730E+00	4.89346E+00
C	5.22464E+00	-5.39627E+00	5.06633E+00
C	5.42086E+00	-4.50989E+00	3.99150E+00
C	4.17339E+00	-6.72798E+00	1.08927E+00
C	6.16339E+00	-3.21319E+00	4.22168E+00
C	4.41365E+00	-7.58229E+00	6.07529E+00
C	3.38799E+00	-3.17708E+00	-2.32345E+00
C	3.00658E+00	1.77196E+00	-3.37533E+00
H	3.94729E+00	-7.80665E+00	1.11444E+00
H	5.02776E+00	-6.57808E+00	4.04097E-01
H	7.24393E+00	-3.34406E+00	4.01488E+00
H	5.77851E+00	-2.39554E+00	3.59550E+00
H	5.12597E+00	-7.38190E+00	6.89345E+00
H	4.50600E+00	-8.64426E+00	5.79043E+00
H	2.81445E+00	-3.22809E+00	-3.26333E+00
H	4.31332E+00	-3.76410E+00	-2.46948E+00
C	4.61915E+00	-6.23716E-02	-4.02344E-01
C	5.35853E+00	2.81360E-01	8.70892E-01
H	5.48020E+00	1.37280E+00	9.66800E-01
H	4.82436E+00	-9.09074E-02	1.76445E+00
H	2.06051E+00	1.51394E+00	-3.88083E+00
H	2.85646E+00	2.71858E+00	-2.82975E+00
H	6.96712E+00	-2.22401E+00	-3.68618E-01
H	6.81553E+00	-4.97614E+00	5.91689E-01
H	6.06886E+00	-2.89276E+00	5.27154E+00
H	3.30519E+00	-6.19909E+00	6.58265E-01
H	3.39607E+00	-7.44241E+00	6.48566E+00
H	2.80459E+00	-3.68471E+00	-1.53222E+00
H	3.75553E+00	1.96491E+00	-4.16631E+00
H	6.36774E+00	-1.69857E-01	8.90609E-01
H	5.54415E+00	-5.08207E+00	6.06744E+00
H	3.91613E+00	-8.07764E+00	3.42344E+00
H	4.33820E+00	1.99804E+00	-9.86679E-01
H	2.69471E+00	-9.31865E-01	-3.69981E+00
H	1.88651E+00	-1.51676E+00	-1.26084E-01
C	-1.21050E-01	-1.89760E+00	3.27451E+00
C	-1.99960E+00	-3.05629E+00	6.19953E-02
H	-2.34427E+00	-2.65356E+00	-9.03869E-01
H	-1.22663E+00	-3.82375E+00	-7.39152E-02
H	-2.86600E+00	-3.44543E+00	6.18671E-01
C	-1.42371E+00	-3.25544E+00	4.71500E+00
H	-5.99728E-01	-3.43623E+00	5.42191E+00
H	-1.46447E+00	-4.07564E+00	3.98287E+00
H	-2.37950E+00	-3.14886E+00	5.24370E+00
H	-2.90057E+00	3.49776E+00	-5.21047E-01
H	-2.00732E+00	4.03936E-01	2.84711E+00
H	2.57913E-01	1.35145E-01	3.51335E+00

vacant *endo* (Fig. S10B)

Ru	2.95468E+00	-2.53803E+00	2.28144E+00
C	1.60566E+00	-1.74763E+00	1.33824E+00
C	4.25479E+00	-3.10926E+00	9.54312E-01
O	-1.47766E+00	-3.12470E+00	-1.78657E-02
O	-1.38177E+00	-8.53069E-01	-1.60651E-01
O	-3.80276E+00	-1.29270E+00	1.44332E+00
O	-4.00359E+00	-5.02317E-01	3.57129E+00
N	4.41627E+00	-2.73169E+00	-3.55362E-01
N	5.31358E+00	-3.92952E+00	1.27572E+00
Cl	4.17252E+00	-6.35523E-01	2.99402E+00
Cl	1.88733E+00	-4.56009E+00	2.85127E+00
C	-1.15394E+00	5.61245E-01	2.71186E+00
C	5.02974E-01	-1.21251E+00	2.20505E+00
C	-1.80078E+00	-8.91894E-01	2.81262E+00
C	-9.11992E-01	-1.85880E+00	1.98350E+00
C	6.32000E+00	-4.00325E+00	1.96801E-01
C	5.56275E+00	-3.41225E+00	-1.00153E+00
H	5.19893E+00	-4.18985E+00	-1.70002E+00
C	3.53251E+00	-1.97819E+00	-1.20169E+00
C	2.50457E-01	3.14172E-01	2.07030E+00
C	5.55112E+00	-4.61622E+00	2.52205E+00

H	7.21204E+00	-3.40662E+00	4.65074E-01
C	-1.96203E+00	1.57297E+00	1.93985E+00
C	-2.40276E+00	2.73731E+00	2.44461E+00
H	1.04373E+00	8.99830E-01	2.56055E+00
H	2.31510E-01	5.89616E-01	1.00329E+00
C	-3.28843E+00	-9.36306E-01	2.49572E+00
H	-1.02968E+00	9.37301E-01	3.74209E+00
H	7.50605E-01	-1.41727E+00	3.27034E+00
H	-2.20977E+00	3.02414E+00	3.48549E+00
H	-2.16978E+00	1.31323E+00	8.94143E-01
C	2.48456E+00	-2.64422E+00	-1.88085E+00
C	1.72157E+00	-1.90381E+00	-2.80386E+00
C	1.96993E+00	-5.43129E-01	-3.05726E+00
C	3.01363E+00	8.53800E-02	-2.35303E+00
C	5.06969E+00	-5.94251E+00	2.65841E+00
C	5.32820E+00	-6.62153E+00	3.86077E+00
C	6.05872E+00	-6.03408E+00	4.90796E+00
C	6.58109E+00	-4.74460E+00	4.70815E+00
C	6.36246E+00	-4.02146E+00	3.52167E+00
C	4.32435E+00	-6.63275E+00	1.53902E+00
C	7.04596E+00	-2.68784E+00	3.31908E+00
C	6.28216E+00	-6.76818E+00	6.21230E+00
C	2.16693E+00	-4.09847E+00	-1.61050E+00
C	1.13445E+00	2.32851E-01	-4.05336E+00
H	4.09469E+00	-7.67461E+00	1.81498E+00
H	4.91727E+00	-6.65664E+00	6.05811E-01
H	7.91535E+00	-2.78875E+00	2.64073E+00
H	6.36840E+00	-1.92866E+00	2.89799E+00
H	5.61421E+00	-6.38045E+00	7.00355E+00
H	7.31792E+00	-6.64661E+00	6.57454E+00
H	1.29919E+00	-4.42430E+00	-2.20529E+00
H	3.01431E+00	-4.76256E+00	-1.86081E+00
C	3.81193E+00	-6.08298E-01	-1.42719E+00
C	4.93276E+00	9.29668E-02	-6.94324E-01
H	4.79705E+00	3.10315E-02	4.00004E-01
H	5.91708E+00	-3.56224E-01	-9.22937E-01
H	4.49712E-01	9.34478E-01	-3.54223E+00
H	1.76791E+00	8.36326E-01	-4.72674E+00
H	6.16135E+00	-2.68648E+00	-1.57567E+00
H	6.63664E+00	-5.04683E+00	3.67537E-02
H	7.42750E+00	-2.30093E+00	4.27787E+00
H	3.37207E+00	-6.12160E+00	1.32306E+00
H	6.07913E+00	-7.84699E+00	6.10889E+00
H	1.92755E+00	-4.26532E+00	-5.45493E-01
H	5.20093E-01	-4.38764E-01	-4.67540E+00
H	4.97806E+00	1.15622E+00	-9.80752E-01
H	7.19303E+00	-4.28486E+00	5.49388E+00
H	4.94472E+00	-7.64174E+00	3.98046E+00
H	3.22223E+00	1.14671E+00	-2.53519E+00
H	9.16749E-01	-2.41390E+00	-3.34692E+00
H	1.51773E+00	-1.64027E+00	2.44568E-01
C	-1.30062E+00	-2.04026E+00	5.14509E-01
C	-5.43205E+00	-4.37513E-01	3.35661E+00
H	-5.66679E+00	2.72112E-01	2.54765E+00
H	-5.82817E+00	-1.43007E+00	3.09048E+00
H	-5.85265E+00	-9.20309E-02	4.31036E+00
C	-1.88096E+00	-9.79092E-01	-1.51052E+00
H	-2.89432E+00	-1.40903E+00	-1.49279E+00
H	-1.21812E+00	-1.62188E+00	-2.10945E+00
H	-1.89848E+00	4.37867E-02	-1.91075E+00
H	-2.96947E+00	3.45072E+00	1.83703E+00
H	-1.70276E+00	-1.19840E+00	3.86845E+00
H	-9.28168E-01	-2.87539E+00	2.40434E+00

olefin adduct *endo* (Fig. S10C)

Ru	2.78629E+00	-2.64299E+00	2.55817E+00
C	1.40559E+00	-1.91739E+00	1.58761E+00
C	4.19891E+00	-3.06497E+00	1.05222E+00
C	2.07251E+00	-1.85353E+00	4.62129E+00
C	1.34854E+00	-3.02166E+00	4.35842E+00
N	5.35550E+00	-3.73648E+00	1.33089E+00

N	4.19961E+00	-2.78281E+00	-2.78811E-01
O	-3.11283E+00	2.08198E+00	2.74260E+00
O	-3.58219E+00	-1.02816E-01	2.29459E+00
O	-1.85751E+00	-2.78398E+00	2.90201E+00
O	-1.78179E+00	-1.94838E+00	7.88705E-01
O	-7.46843E-01	-2.21975E+00	6.62167E+00
O	-8.90751E-01	-4.49262E+00	6.59710E+00
O	1.46586E+00	1.12303E-02	6.90170E+00
O	9.81721E-01	-1.22240E+00	8.76094E+00
Cl	3.97967E+00	-4.87109E-01	2.80845E+00
Cl	1.86702E+00	-4.88353E+00	2.05216E+00
C	-7.63334E-01	1.14821E+00	7.97353E-01
C	7.36835E-01	-5.85949E-01	1.78544E+00
C	-1.26244E+00	6.99678E-01	2.23644E+00
C	-6.54225E-01	-6.99878E-01	2.52766E+00
C	6.25818E+00	-3.84925E+00	1.58549E-01
C	5.36745E+00	-3.36541E+00	-9.92028E-01
H	5.02861E+00	-4.18808E+00	-1.64747E+00
C	3.24746E+00	-2.06619E+00	-1.08981E+00
C	3.90226E-01	1.48053E-01	4.64568E-01
C	5.81371E+00	-4.27055E+00	2.59319E+00
H	7.14739E+00	-3.21049E+00	3.08187E-01
C	-1.82454E+00	1.15814E+00	-2.74283E-01
C	-2.15163E+00	2.23372E+00	-1.01164E+00
H	1.27109E+00	6.59852E-01	4.93272E-02
H	4.90200E-02	-5.81194E-01	-2.88432E-01
C	-2.76816E+00	8.03028E-01	2.42439E+00
H	-3.61279E-01	2.17187E+00	8.90788E-01
H	1.37384E+00	6.35766E-02	2.40940E+00
H	-1.66527E+00	3.20525E+00	-8.60680E-01
H	-2.33176E+00	2.00303E-01	-4.45755E-01
C	2.21194E+00	-2.77794E+00	-1.74424E+00
C	1.38549E+00	-2.06842E+00	-2.63627E+00
C	1.57934E+00	-7.04538E-01	-2.91522E+00
C	2.65009E+00	-4.59131E-02	-2.28439E+00
C	5.58442E+00	-5.64439E+00	2.87541E+00
C	6.07086E+00	-6.16071E+00	4.08890E+00
C	6.80886E+00	-5.37764E+00	4.99455E+00
C	7.08935E+00	-4.04786E+00	4.64077E+00
C	6.63050E+00	-3.47544E+00	3.43876E+00
C	4.88643E+00	-6.55632E+00	1.89459E+00
C	7.06311E+00	-2.07744E+00	3.06386E+00
C	7.33719E+00	-5.97276E+00	6.28263E+00
C	2.00389E+00	-4.25926E+00	-1.52944E+00
C	6.48412E-01	4.42692E-02	-3.84378E+00
H	4.79510E+00	-7.57197E+00	2.31265E+00
H	5.45478E+00	-6.63947E+00	9.48736E-01
H	7.72907E+00	-2.09126E+00	2.18014E+00
H	6.20436E+00	-1.42568E+00	2.82960E+00
H	7.62389E+00	-5.18851E+00	7.00260E+00
H	8.23291E+00	-6.59466E+00	6.09726E+00
H	1.10660E+00	-4.60483E+00	-2.06839E+00
H	2.86014E+00	-4.84751E+00	-1.91041E+00
C	3.49755E+00	-6.99148E-01	-1.37227E+00
C	4.64514E+00	4.41322E-02	-7.28988E-01
H	4.57008E+00	1.84599E-02	3.73206E-01
H	5.62380E+00	-3.95567E-01	-9.99253E-01
H	-1.36006E-01	5.71389E-01	-3.26842E+00
H	1.18891E+00	8.06109E-01	-4.43136E+00
H	5.84813E+00	-2.59896E+00	-1.62082E+00
H	6.59668E+00	-4.89081E+00	3.71591E-02
H	7.62871E+00	-1.61644E+00	3.88988E+00
H	3.87557E+00	-6.18705E+00	1.65166E+00
H	6.58730E+00	-6.62357E+00	6.76441E+00
H	1.89100E+00	-4.51489E+00	-4.60103E-01
H	1.42005E-01	-6.37672E-01	-4.54735E+00
H	4.65590E+00	1.09648E+00	-1.05666E+00
H	7.70244E+00	-3.43214E+00	5.30988E+00
H	5.87795E+00	-7.21492E+00	4.32200E+00
H	2.83528E+00	1.01228E+00	-2.50625E+00
H	5.74435E-01	-2.60868E+00	-3.13957E+00

H	8.98947E-01	-2.57615E+00	8.53466E-01
C	-1.50687E+00	-1.90663E+00	2.12306E+00
C	-4.53536E+00	2.30573E+00	2.87305E+00
H	-5.04697E+00	2.09101E+00	1.92155E+00
H	-4.95651E+00	1.66170E+00	3.66096E+00
H	-4.63830E+00	3.36611E+00	3.13943E+00
C	-2.62098E+00	-3.05949E+00	3.92081E-01
H	-3.59913E+00	-2.98325E+00	8.91269E-01
H	-2.14436E+00	-4.01510E+00	6.58485E-01
H	-2.72987E+00	-2.96480E+00	-6.96700E-01
H	-2.91983E+00	2.18609E+00	-1.79081E+00
H	-8.04128E-01	1.39782E+00	2.95718E+00
H	-5.02469E-01	-8.27154E-01	3.61031E+00
C	3.04840E+00	-2.18330E+00	5.74754E+00
C	1.84765E+00	-4.07133E+00	5.34263E+00
C	1.28835E+00	-3.58683E+00	6.75395E+00
C	2.19235E+00	-2.32987E+00	7.05505E+00
H	2.86947E+00	-2.60819E+00	7.88386E+00
H	1.45811E+00	-4.38611E+00	7.49508E+00
C	3.33446E+00	-3.68003E+00	5.47683E+00
H	3.85627E+00	-4.18635E+00	6.30725E+00
H	3.90853E+00	-3.86685E+00	4.54876E+00
H	1.60501E+00	-5.11423E+00	5.10228E+00
H	3.45960E-01	-3.07675E+00	3.92794E+00
H	1.74552E+00	-8.30441E-01	4.44418E+00
H	3.90692E+00	-1.50520E+00	5.84463E+00
C	1.49289E+00	-1.05165E+00	7.50529E+00
C	-2.07807E-01	-3.31873E+00	6.67485E+00
C	2.33090E-01	-9.06581E-02	9.25278E+00
H	-8.32188E-02	-3.68259E-01	1.02678E+01
H	-6.41548E-01	8.91697E-02	8.60790E+00
H	8.60721E-01	8.14495E-01	9.27324E+00
C	-2.30831E+00	-4.34057E+00	6.32983E+00
H	-2.70080E+00	-5.36493E+00	6.27772E+00
H	-2.45521E+00	-3.81210E+00	5.37522E+00
H	-2.79452E+00	-3.77682E+00	7.14170E+00

metallacyclobutane *endo* (Fig. S10D)

Ru	2.48432E+00	-2.45240E+00	2.26077E+00
C	5.04808E-01	-1.94731E+00	2.29378E+00
C	4.08056E+00	-2.81180E+00	1.03692E+00
C	2.27404E+00	-2.66601E+00	4.22552E+00
C	8.41763E-01	-2.00079E+00	3.82367E+00
N	5.18936E+00	-3.44965E+00	1.49947E+00
N	4.25495E+00	-2.52706E+00	-2.79432E-01
O	-3.43500E+00	2.57195E+00	8.30333E-01
O	-4.23411E+00	4.92799E-01	1.31388E+00
O	-2.98984E+00	-2.03839E+00	3.06256E+00
O	-2.60902E+00	-1.94667E+00	8.22609E-01
O	9.64500E-01	-4.28823E-01	6.51783E+00
O	-1.20064E+00	-9.14663E-01	7.03891E+00
O	3.67828E+00	-2.50757E+00	7.00893E+00
O	1.96990E+00	-2.38579E+00	8.51498E+00
Cl	3.18321E+00	-1.55039E-01	2.69746E+00
Cl	1.74965E+00	-4.65973E+00	1.43527E+00
C	-1.04194E+00	7.09439E-01	-5.49562E-02
C	-2.40763E-02	-6.19749E-01	1.78173E+00
C	-1.81627E+00	9.20249E-01	1.32258E+00
C	-1.50472E+00	-3.07422E-01	2.21411E+00
C	6.25751E+00	-3.53213E+00	4.73361E-01
C	5.52558E+00	-3.09303E+00	-8.04775E-01
H	5.30438E+00	-3.93884E+00	-1.47999E+00
C	3.40892E+00	-1.78757E+00	-1.18678E+00
C	-4.96489E-02	-4.59556E-01	2.44997E-01
C	5.45708E+00	-3.89372E+00	2.84900E+00
H	7.09131E+00	-2.85800E+00	7.42305E-01
C	-1.93924E+00	4.40666E-01	-1.23693E+00
C	-2.12963E+00	1.29309E+00	-2.25975E+00
H	9.56394E-01	-2.53374E-01	-1.52722E-01
H	-4.09857E-01	-1.38946E+00	-2.25452E-01
C	-3.28989E+00	1.25903E+00	1.16944E+00

H	-4.82666E-01	1.63899E+00	-2.57848E-01
H	5.97251E-01	1.87812E-01	2.20782E+00
H	-1.62792E+00	2.26779E+00	-2.29788E+00
H	-2.46975E+00	-5.19504E-01	-1.22011E+00
C	2.51612E+00	-2.48319E+00	-2.04105E+00
C	1.79007E+00	-1.73457E+00	-2.98465E+00
C	1.94783E+00	-3.44815E-01	-3.12470E+00
C	2.88098E+00	3.00733E-01	-2.29517E+00
C	5.27303E+00	-5.26178E+00	3.16869E+00
C	5.56333E+00	-5.67523E+00	4.48268E+00
C	6.04784E+00	-4.78610E+00	5.45637E+00
C	6.29287E+00	-3.45555E+00	5.07598E+00
C	6.02452E+00	-2.98555E+00	3.78009E+00
C	4.80771E+00	-6.26923E+00	2.14341E+00
C	6.35728E+00	-1.55770E+00	3.41489E+00
C	6.29943E+00	-5.23408E+00	6.87895E+00
C	2.36665E+00	-3.98589E+00	-1.99751E+00
C	1.13354E+00	4.29095E-01	-4.13711E+00
H	4.70478E+00	-7.26578E+00	2.60325E+00
H	5.52878E+00	-6.36619E+00	1.30958E+00
H	6.99858E+00	-1.50061E+00	2.51619E+00
H	5.44825E+00	-9.64590E-01	3.20867E+00
H	5.58862E+00	-4.73923E+00	7.56489E+00
H	7.31617E+00	-4.96397E+00	7.21586E+00
H	1.51920E+00	-4.30619E+00	-2.62545E+00
H	3.27006E+00	-4.49107E+00	-2.39013E+00
C	3.63278E+00	-3.94452E-01	-1.33013E+00
C	4.66476E+00	3.36499E-01	-5.03722E-01
H	4.38736E+00	3.42137E-01	5.65553E-01
H	5.66259E+00	-1.33399E-01	-5.81377E-01
H	1.31114E-01	6.62407E-01	-3.73108E+00
H	1.61802E+00	1.38395E+00	-4.40195E+00
H	6.07087E+00	-2.32451E+00	-1.37585E+00
H	6.64784E+00	-4.56074E+00	4.15842E-01
H	6.90037E+00	-1.07066E+00	4.24087E+00
H	3.83396E+00	-5.98096E+00	1.71146E+00
H	6.18153E+00	-6.32483E+00	6.98972E+00
H	2.19795E+00	-4.35346E+00	-9.70925E-01
H	9.84965E-01	-1.50609E-01	-5.06448E+00
H	4.76074E+00	1.38042E+00	-8.44105E-01
H	6.69864E+00	-2.75298E+00	5.81238E+00
H	5.40965E+00	-6.72905E+00	4.74557E+00
H	3.04668E+00	1.37871E+00	-2.41054E+00
H	1.09101E+00	-2.26393E+00	-3.64341E+00
H	-8.72236E-02	-2.81318E+00	1.95135E+00
C	-2.46196E+00	-1.49481E+00	2.09950E+00
C	-4.79937E+00	2.97952E+00	5.81839E-01
H	-5.22145E+00	2.41128E+00	-2.61978E-01
H	-5.42268E+00	2.81254E+00	1.47448E+00
H	-4.74307E+00	4.04938E+00	3.40043E-01
C	-3.54164E+00	-3.04393E+00	6.81876E-01
H	-4.54880E+00	-2.71742E+00	9.83468E-01
H	-3.23113E+00	-3.89786E+00	1.30304E+00
H	-3.51873E+00	-3.30831E+00	-3.83770E-01
H	-2.80054E+00	1.05386E+00	-3.09193E+00
H	-1.34375E+00	1.79252E+00	1.80666E+00
H	-1.54495E+00	-3.00760E-02	3.27976E+00
C	1.90753E+00	-3.91633E+00	5.03193E+00
C	-1.10395E-01	-2.93941E+00	4.63922E+00
C	1.00901E-01	-2.69830E+00	6.18324E+00
C	1.47141E+00	-3.43883E+00	6.45741E+00
H	1.22574E+00	-4.34393E+00	7.04542E+00
H	-7.21075E-01	-3.21592E+00	6.70250E+00
C	5.27060E-01	-4.33453E+00	4.48227E+00
H	2.61521E-02	-5.09491E+00	5.10859E+00
H	5.65576E-01	-4.68628E+00	3.44304E+00
H	-1.16362E+00	-2.82792E+00	4.34178E+00
H	8.95414E-01	-9.59943E-01	4.17690E+00
H	2.92543E+00	-1.95106E+00	4.74672E+00
H	2.70157E+00	-4.67707E+00	5.05316E+00
C	2.50763E+00	-2.70850E+00	7.30055E+00

C	4.69337E-02	-1.23876E+00	6.59711E+00
C	2.85856E+00	-1.65135E+00	9.38578E+00
H	2.29281E+00	-1.49582E+00	1.03145E+01
H	3.12675E+00	-6.87427E-01	8.92581E+00
H	3.77693E+00	-2.22745E+00	9.58079E+00
C	-1.37000E+00	4.74700E-01	7.40082E+00
H	-2.41999E+00	5.67678E-01	7.70822E+00
H	-1.15484E+00	1.12916E+00	6.54151E+00
H	-6.94240E-01	7.41666E-01	8.22879E+00

pyridine adduct *endo*(Fig. S10E)

Ru	3.05288E+00	-2.28463E+00	2.52684E+00
C	1.67715E+00	-1.41400E+00	1.67128E+00
C	4.09879E+00	-3.07536E+00	9.87837E-01
N	5.05130E+00	-4.02595E+00	1.28793E+00
N	4.24184E+00	-2.78066E+00	-3.38327E-01
N	2.53498E+00	-1.59335E+00	4.60362E+00
O	-4.43645E+00	-1.81721E+00	2.35141E+00
O	-3.67745E+00	-7.65497E-01	4.78694E-01
O	-8.48756E-01	6.27190E-02	-1.42354E-01
O	-1.21369E+00	-2.00026E+00	-1.03967E+00
Cl	4.56546E+00	-3.60281E-01	2.39956E+00
Cl	1.70118E+00	-4.29090E+00	2.90579E+00
C	-1.66970E+00	-2.46136E-02	2.98809E+00
C	2.90238E-01	-1.34350E+00	2.25314E+00
C	-2.10985E+00	-1.37379E+00	2.26731E+00
C	-9.12386E-01	-1.81754E+00	1.36481E+00
C	5.99433E+00	-4.26048E+00	1.73780E-01
C	5.22789E+00	-3.66666E+00	-1.01000E+00
H	4.69321E+00	-4.43638E+00	-1.59898E+00
C	3.41417E+00	-1.99595E+00	-1.21599E+00
C	-1.32736E-01	7.79299E-02	2.71811E+00
C	5.29872E+00	-4.64233E+00	2.56878E+00
H	6.94856E+00	-3.73322E+00	3.64511E-01
C	-2.40708E+00	1.21760E+00	2.55806E+00
C	-3.10065E+00	2.01093E+00	3.39179E+00
H	4.12862E-01	3.90367E-01	3.62200E+00
H	6.82121E-02	8.15827E-01	1.92544E+00
C	-3.45784E+00	-1.27659E+00	1.57010E+00
H	-1.84434E+00	-1.65896E-01	4.06935E+00
H	2.61035E-01	-2.01104E+00	3.13142E+00
H	-3.19119E+00	1.78468E+00	4.46150E+00
H	-2.33714E+00	1.46911E+00	1.49314E+00
C	2.20334E+00	-2.53885E+00	-1.70688E+00
C	1.53129E+00	-1.83820E+00	-2.72807E+00
C	2.03501E+00	-6.43801E-01	-3.27006E+00
C	3.22761E+00	-1.20825E-01	-2.73643E+00
C	4.74257E+00	-5.92819E+00	2.80876E+00
C	5.00007E+00	-6.54473E+00	4.04211E+00
C	5.80324E+00	-5.93902E+00	5.02726E+00
C	6.39648E+00	-4.70366E+00	4.72750E+00
C	6.18825E+00	-4.04592E+00	3.49761E+00
C	3.91833E+00	-6.63802E+00	1.76018E+00
C	6.98336E+00	-2.79958E+00	3.17833E+00
C	6.04189E+00	-6.62294E+00	6.35669E+00
C	1.64797E+00	-3.85003E+00	-1.19368E+00
C	1.33497E+00	5.29615E-02	-4.41914E+00
H	3.64498E+00	-7.64883E+00	2.10430E+00
H	4.47094E+00	-6.74493E+00	8.08683E-01
H	7.84115E+00	-3.04632E+00	2.52286E+00
H	6.38367E+00	-2.02233E+00	2.67814E+00
H	6.71950E+00	-6.03473E+00	6.99723E+00
H	6.48918E+00	-7.62432E+00	6.22064E+00
H	5.85002E-01	-3.94340E+00	-1.46469E+00
H	2.18673E+00	-4.71356E+00	-1.62977E+00
C	3.93930E+00	-7.77578E-01	-1.71901E+00
C	5.23592E+00	-2.01323E-01	-1.19808E+00
H	5.22122E+00	-1.19252E-01	-9.72136E-02
H	6.10521E+00	-8.31437E-01	-1.46670E+00
H	1.21447E+00	1.13436E+00	-4.22887E+00
H	1.91595E+00	-4.39110E-02	-5.35518E+00

H	5.86432E+00	-3.08480E+00	-1.69483E+00
H	6.20511E+00	-5.33642E+00	6.26108E-02
H	7.39860E+00	-2.36017E+00	4.10022E+00
H	2.98978E+00	-6.08091E+00	1.55361E+00
H	5.09564E+00	-6.76700E+00	6.90904E+00
H	1.72762E+00	-3.93491E+00	-9.69470E-02
H	3.36497E-01	-3.76201E-01	-4.60527E+00
H	5.41281E+00	7.98900E-01	-1.62663E+00
H	7.06728E+00	-4.23845E+00	5.46018E+00
H	4.55996E+00	-7.53014E+00	4.23792E+00
H	3.62949E+00	8.19424E-01	-3.13418E+00
H	5.86305E-01	-2.24477E+00	-3.10313E+00
H	1.86094E+00	-8.26384E-01	7.49739E-01
C	-1.00356E+00	-1.28950E+00	-6.61100E-02
C	-5.76832E+00	-1.71557E+00	1.79697E+00
H	-6.04342E+00	-6.59560E-01	1.64781E+00
H	-5.82423E+00	-2.24011E+00	8.30105E-01
H	-6.42701E+00	-2.18979E+00	2.53675E+00
C	-1.12243E+00	6.23853E-01	-1.44684E+00
H	-2.15896E+00	3.91882E-01	-1.73587E+00
H	-4.23823E-01	2.16704E-01	-2.19151E+00
H	-9.79883E-01	1.70694E+00	-1.33055E+00
H	-3.60282E+00	2.91796E+00	3.03925E+00
H	-2.20823E+00	-2.13990E+00	3.05318E+00
H	-8.93141E-01	-2.91350E+00	1.26780E+00
C	2.08537E+00	-2.16708E+00	6.91106E+00
C	2.26348E+00	-2.51222E+00	5.56598E+00
C	2.63981E+00	-2.91624E-01	4.97878E+00
C	2.46333E+00	1.30664E-01	6.30110E+00
C	2.18153E+00	-8.21535E-01	7.29080E+00
H	1.87235E+00	-2.95228E+00	7.64210E+00
H	2.17463E+00	-3.54340E+00	5.21114E+00
H	2.90893E+00	4.04669E-01	4.18085E+00
H	2.55442E+00	1.19367E+00	6.54189E+00
H	2.04440E+00	-5.21451E-01	8.33474E+00

Table S9. xyz coordinates (in Angstroms) for structures in Figures S10: *exo* isomer (**3a**).

olefin *exo* (3a)

C	1.51577E+00	7.97488E-01	-8.82461E-01
C	1.65083E+00	-5.40666E-01	-1.00826E+00
O	-3.09073E+00	-1.55260E+00	-1.59129E+00
O	-1.94766E+00	-2.49705E+00	1.39336E-01
O	-2.78016E+00	7.48375E-01	5.42960E-01
O	-2.87026E+00	2.06177E+00	-1.31714E+00
C	2.36582E-01	1.04923E+00	-9.27080E-02
C	4.61180E-01	-1.18911E+00	-3.06953E-01
C	-7.84719E-01	-8.86527E-01	-1.22450E+00
C	-9.50477E-01	6.84973E-01	-1.08638E+00
C	2.23659E-01	-1.82496E-01	8.46485E-01
H	-7.38888E-01	-3.23640E-01	1.36189E+00
H	1.05525E+00	-1.64510E-01	1.57030E+00
H	5.61971E-01	-2.24993E+00	-4.06910E-02
H	2.39764E+00	-1.07960E+00	-1.59866E+00
H	2.12578E+00	1.57672E+00	-1.34817E+00
H	1.28653E-01	2.04266E+00	3.68740E-01
H	-8.12345E-01	1.18112E+00	-2.05760E+00
H	-5.62775E-01	-1.11765E+00	-2.28038E+00
C	-2.07040E+00	-1.65545E+00	-9.22527E-01
C	-2.28889E+00	1.12718E+00	-5.15068E-01
C	-4.14787E+00	2.54558E+00	-8.42355E-01
H	-4.47615E+00	3.27879E+00	-1.59109E+00
H	-4.04053E+00	3.01760E+00	1.47209E-01
H	-4.86590E+00	1.71414E+00	-7.67602E-01
C	-3.15752E+00	-3.21777E+00	4.68403E-01
H	-2.89484E+00	-3.84675E+00	1.32951E+00
H	-3.48447E+00	-3.83494E+00	-3.83243E-01
H	-3.95913E+00	-2.50991E+00	7.29858E-01

chelate *exo* (Fig. S10A)

Ru	2.56860E+00	-2.69210E+00	2.06412E+00
C	1.71712E+00	-1.38818E+00	1.09789E+00
C	4.16879E+00	-3.00884E+00	9.24580E-01
N	5.07949E+00	-3.99113E+00	1.25101E+00
N	4.69444E+00	-2.33431E+00	-1.50400E-01
O	-3.70287E+00	-3.32121E-01	3.34125E+00
O	-1.60105E+00	5.45584E-01	3.45414E+00
O	-1.18034E+00	-2.46084E+00	4.32821E+00
O	9.85226E-01	-2.52826E+00	3.68811E+00
Cl	3.82745E+00	-1.18276E+00	3.45556E+00
Cl	1.30221E+00	-4.61624E+00	1.31385E+00
C	-1.97426E+00	-4.71675E-01	4.92621E-01
C	3.02548E-01	-9.36260E-01	1.32734E+00
C	-2.07117E+00	-1.25883E+00	1.87653E+00
C	-6.71240E-01	-1.89936E+00	2.04719E+00
C	6.33588E+00	-3.89832E+00	4.78774E-01
C	5.95486E+00	-2.93131E+00	-6.50263E-01
H	5.77275E+00	-3.44883E+00	-1.61196E+00
C	4.07301E+00	-1.33828E+00	-9.77281E-01
C	-4.92769E-01	-6.35767E-01	3.15992E-02
C	4.94760E+00	-5.00970E+00	2.26456E+00
H	7.14652E+00	-3.49973E+00	1.11705E+00
C	-2.96713E+00	-9.61022E-01	-5.26510E-01
C	-3.90014E+00	-2.00817E-01	-1.12289E+00
H	-1.25848E-01	2.55785E-01	-5.01239E-01
H	-4.00949E-01	-1.49641E+00	-6.56774E-01
C	-2.39291E+00	-2.62425E-01	2.98050E+00
H	-2.16227E+00	5.99507E-01	6.85204E-01
H	3.62498E-01	7.05167E-04	1.92489E+00
H	-4.00881E+00	8.64916E-01	-8.88531E-01
H	-2.88950E+00	-2.02682E+00	-7.90472E-01
C	3.16347E+00	-1.73579E+00	-1.98741E+00
C	2.62384E+00	-7.38138E-01	-2.81927E+00
C	2.96850E+00	6.18830E-01	-2.67883E+00
C	3.87572E+00	9.73713E-01	-1.66389E+00
C	4.40309E+00	-6.26521E+00	1.88488E+00

C	4.29265E+00	-7.26631E+00	2.86321E+00
C	4.72808E+00	-7.06852E+00	4.18583E+00
C	5.34494E+00	-5.84750E+00	4.50199E+00
C	5.49266E+00	-4.81221E+00	3.55882E+00
C	3.99592E+00	-6.55196E+00	4.57943E-01
C	6.29227E+00	-3.58188E+00	3.92096E+00
C	4.54489E+00	-8.14583E+00	5.23285E+00
C	2.74485E+00	-3.18057E+00	-2.14536E+00
C	2.40073E+00	1.66599E+00	-3.61365E+00
H	3.68616E+00	-7.60448E+00	3.51661E-01
H	4.82964E+00	-6.37537E+00	-2.46861E-01
H	7.31028E+00	-3.63755E+00	3.48816E+00
H	5.81451E+00	-2.65412E+00	3.56860E+00
H	5.28079E+00	-8.04802E+00	6.04875E+00
H	4.64525E+00	-9.15515E+00	4.79792E+00
H	2.07500E+00	-3.29767E+00	-3.01298E+00
H	3.61172E+00	-3.84817E+00	-2.30078E+00
C	4.44606E+00	1.66230E-02	-8.05005E-01
C	5.39399E+00	4.30452E-01	2.97860E-01
H	5.51094E+00	1.52623E+00	3.18359E-01
H	5.02872E+00	9.69952E-02	1.28648E+00
H	1.40656E+00	1.37473E+00	-3.99249E+00
H	2.30472E+00	2.64480E+00	-3.11397E+00
H	6.71047E+00	-2.14718E+00	-8.21568E-01
H	6.64018E+00	-4.89316E+00	1.13555E-01
H	6.40928E+00	-3.50548E+00	5.01431E+00
H	3.15042E+00	-5.91413E+00	1.52697E-01
H	3.53893E+00	-8.08752E+00	5.68904E+00
H	2.21697E+00	-3.54906E+00	-1.24674E+00
H	3.05536E+00	1.81230E+00	-4.49341E+00
H	6.39990E+00	-8.63422E-03	1.62058E-01
H	5.74549E+00	-5.69359E+00	5.51144E+00
H	3.85853E+00	-8.23235E+00	2.57844E+00
H	4.14791E+00	2.02799E+00	-1.53134E+00
H	1.91294E+00	-1.03306E+00	-3.60097E+00
H	2.25684E+00	-7.67166E-01	3.62992E-01
C	-2.02797E-01	-2.29985E+00	3.42112E+00
C	-4.10171E+00	6.34315E-01	4.34106E+00
H	-3.92595E+00	1.66007E+00	3.98017E+00
H	-5.17280E+00	4.56231E-01	4.50500E+00
H	-3.53278E+00	4.82413E-01	5.27172E+00
C	-7.44689E-01	-2.91000E+00	5.63989E+00
H	-6.85304E-02	-2.16603E+00	6.08703E+00
H	-2.24450E-01	-3.87556E+00	5.55376E+00
H	-1.66706E+00	-3.00859E+00	6.22635E+00
H	-6.48244E-01	-2.85222E+00	1.47808E+00
H	-2.86833E+00	-2.01686E+00	1.84040E+00
H	-4.58976E+00	-6.12433E-01	-1.86683E+00

vacant *exo* (Fig. S10B)

Ru	3.03309E+00	-2.71505E+00	2.35199E+00
C	1.93637E+00	-1.62589E+00	1.37604E+00
C	4.41760E+00	-3.23564E+00	1.08998E+00
N	5.39056E+00	-4.15238E+00	1.42484E+00
N	4.72092E+00	-2.76673E+00	-1.65666E-01
O	-3.46966E+00	-2.22773E-01	2.16922E+00
O	-2.45060E+00	8.20582E-01	3.92443E+00
O	-1.45276E+00	-3.08562E+00	1.11275E+00
O	-1.51262E+00	-2.30280E+00	3.25823E+00
Cl	4.30804E+00	-1.05355E+00	3.45488E+00
Cl	1.73531E+00	-4.68862E+00	2.42202E+00
C	-1.07301E-01	1.39463E+00	2.38191E+00
C	9.13192E-01	-7.96028E-01	2.09389E+00
C	-1.22217E+00	4.56240E-01	1.82628E+00
C	-5.33121E-01	-9.28432E-01	1.50215E+00
C	6.49466E+00	-4.18581E+00	4.44094E-01
C	5.87612E+00	-3.47246E+00	-7.66579E-01
H	5.52847E+00	-4.18102E+00	-1.54276E+00
C	3.95573E+00	-1.88821E+00	-1.00516E+00
C	1.21616E+00	7.20711E-01	1.95138E+00
C	5.48991E+00	-4.91410E+00	2.64611E+00

H	7.37483E+00	-3.64731E+00	8.43822E-01
C	-2.40998E-01	2.81945E+00	1.91316E+00
C	-4.73695E-01	3.87548E+00	2.70962E+00
H	2.07804E+00	1.02538E+00	2.56473E+00
H	1.44929E+00	9.54390E-01	8.93980E-01
C	-2.41163E+00	3.78804E-01	2.78701E+00
H	-1.85073E-01	1.36937E+00	3.48341E+00
H	8.64946E-01	-1.04363E+00	3.17265E+00
H	-5.91189E-01	3.75914E+00	3.79275E+00
H	-1.37561E-01	2.97450E+00	8.27318E-01
C	2.92233E+00	-2.42028E+00	-1.81367E+00
C	2.23033E+00	-1.53948E+00	-2.66507E+00
C	2.54246E+00	-1.69173E-01	-2.73390E+00
C	3.57455E+00	3.21095E-01	-1.91237E+00
C	4.93884E+00	-6.22258E+00	2.66582E+00
C	5.05047E+00	-6.97102E+00	3.84749E+00
C	5.70412E+00	-6.47119E+00	4.98936E+00
C	6.30728E+00	-5.20657E+00	4.90544E+00
C	6.23832E+00	-4.41686E+00	3.74149E+00
C	4.28068E+00	-6.82167E+00	1.44421E+00
C	7.03248E+00	-3.13208E+00	3.66845E+00
C	5.75761E+00	-7.27948E+00	6.26737E+00
C	2.52582E+00	-3.87783E+00	-1.72554E+00
C	1.80605E+00	7.49250E-01	-3.68577E+00
H	4.03971E+00	-7.88280E+00	1.61943E+00
H	4.93851E+00	-6.76767E+00	5.57392E-01
H	8.05165E+00	-3.33241E+00	3.28353E+00
H	6.55645E+00	-2.37734E+00	3.02663E+00
H	6.58664E+00	-6.95452E+00	6.91785E+00
H	5.88307E+00	-8.35640E+00	6.06089E+00
H	1.69750E+00	-4.09718E+00	-2.41828E+00
H	3.36188E+00	-4.55321E+00	-1.98248E+00
C	4.29926E+00	-5.16210E-01	-1.04512E+00
C	5.39173E+00	4.06975E-02	-1.60749E-01
H	5.50983E+00	1.12419E+00	-3.23588E-01
H	5.16844E+00	-1.29390E-01	9.07746E-01
H	8.00557E-01	3.63957E-01	-3.92376E+00
H	1.69530E+00	1.76330E+00	-3.26566E+00
H	6.56050E+00	-2.75017E+00	-1.24045E+00
H	6.79010E+00	-5.22592E+00	2.30832E-01
H	7.14456E+00	-2.68534E+00	4.66941E+00
H	3.34385E+00	-6.29328E+00	1.20202E+00
H	4.82128E+00	-7.16640E+00	6.84467E+00
H	2.19850E+00	-4.14337E+00	-7.04106E-01
H	2.35258E+00	8.51984E-01	-4.64196E+00
H	6.36754E+00	-4.36796E-01	-3.65791E-01
H	6.86491E+00	-4.81933E+00	5.76680E+00
H	4.61488E+00	-7.97704E+00	3.87491E+00
H	3.82679E+00	1.38796E+00	-1.94614E+00
H	1.42113E+00	-1.93785E+00	-3.28911E+00
H	1.96508E+00	-1.50795E+00	2.79770E-01
C	-1.22859E+00	-2.15548E+00	2.07629E+00
C	-4.61758E+00	-4.27499E-01	3.02465E+00
H	-4.97515E+00	5.32467E-01	3.42881E+00
H	-5.38004E+00	-8.89125E-01	2.38258E+00
H	-4.35014E+00	-1.09551E+00	3.85814E+00
C	-1.98853E+00	-4.33891E+00	1.60374E+00
H	-2.90513E+00	-4.16322E+00	2.18771E+00
H	-1.23542E+00	-4.83834E+00	2.23257E+00
H	-2.20174E+00	-4.93321E+00	7.05178E-01
H	-4.60149E-01	-1.04603E+00	4.08351E-01
H	-1.62214E+00	8.50851E-01	8.74967E-01
H	-5.62342E-01	4.89060E+00	2.30853E+00

olefin adduct *exo* (Fig. S10C)

Ru	2.73883E+00	-2.97367E+00	2.66814E+00
C	1.61472E+00	-1.96591E+00	1.62172E+00
C	4.25302E+00	-3.32244E+00	1.26000E+00
C	1.86029E+00	-2.47878E+00	4.79128E+00
C	9.76582E-01	-3.39680E+00	4.22805E+00
N	5.33434E+00	-4.09009E+00	1.58971E+00

N	4.39625E+00	-2.96305E+00	-4.76807E-02
O	-3.23978E+00	6.18223E-01	2.42301E+00
O	-1.60718E+00	1.08758E+00	3.94606E+00
O	-2.00026E+00	-2.39358E+00	5.21051E-01
O	-1.83272E+00	-2.08593E+00	2.77436E+00
O	1.30955E+00	-6.44831E+00	7.60410E+00
O	-9.11108E-01	-6.12536E+00	7.20828E+00
O	3.46159E+00	-4.13098E+00	8.47917E+00
O	1.35729E+00	-3.95197E+00	9.34124E+00
Cl	4.09274E+00	-1.07523E+00	3.46091E+00
Cl	1.70669E+00	-5.02188E+00	1.71572E+00
C	2.86755E-01	1.62149E+00	1.81873E+00
C	8.10929E-01	-7.61679E-01	2.01750E+00
C	-1.03071E+00	8.01222E-01	1.57362E+00
C	-5.47821E-01	-6.63244E-01	1.26142E+00
C	6.33657E+00	-4.18752E+00	5.02673E-01
C	5.58857E+00	-3.57752E+00	-6.90392E-01
H	5.26594E+00	-4.33712E+00	-1.42493E+00
C	3.59308E+00	-2.09098E+00	-8.64089E-01
C	1.45136E+00	6.04079E-01	1.64659E+00
C	5.64870E+00	-4.66347E+00	2.87729E+00
H	7.24214E+00	-3.61682E+00	7.79026E-01
C	4.12054E-01	2.82049E+00	9.16802E-01
C	5.20347E-01	4.09288E+00	1.33370E+00
H	2.31969E+00	8.31733E-01	2.28184E+00
H	1.79292E+00	5.76042E-01	5.95665E-01
C	-1.95105E+00	8.59082E-01	2.79486E+00
H	2.66036E-01	1.95503E+00	2.87066E+00
H	6.07136E-01	-7.63842E-01	3.10270E+00
H	5.18357E-01	4.34855E+00	2.39973E+00
H	4.21450E-01	2.60617E+00	-1.63492E-01
C	2.61886E+00	-2.64347E+00	-1.73243E+00
C	1.91558E+00	-1.76549E+00	-2.57857E+00
C	2.17639E+00	-3.84197E-01	-2.60906E+00
C	3.17503E+00	1.21133E-01	-1.75673E+00
C	5.30672E+00	-6.01867E+00	3.12800E+00
C	5.60182E+00	-6.55026E+00	4.39602E+00
C	6.23423E+00	-5.79220E+00	5.39770E+00
C	6.66267E+00	-4.49477E+00	5.06921E+00
C	6.41410E+00	-3.91800E+00	3.81117E+00
C	4.66021E+00	-6.88713E+00	2.07429E+00
C	7.04861E+00	-2.58897E+00	3.46852E+00
C	6.43404E+00	-6.34242E+00	6.79194E+00
C	2.32941E+00	-4.12680E+00	-1.76411E+00
C	1.43599E+00	5.26935E-01	-3.56533E+00
H	4.52504E+00	-7.91304E+00	2.45394E+00
H	5.28166E+00	-6.95048E+00	1.16133E+00
H	8.07932E+00	-2.74976E+00	3.09505E+00
H	6.47814E+00	-2.03154E+00	2.71349E+00
H	7.40846E+00	-6.03913E+00	7.21248E+00
H	6.37732E+00	-7.44363E+00	6.80720E+00
H	1.43951E+00	-4.33266E+00	-2.38103E+00
H	3.17045E+00	-4.69366E+00	-2.20673E+00
C	3.90218E+00	-7.08393E-01	-8.82940E-01
C	4.98774E+00	-1.31888E-01	-3.75449E-03
H	5.07951E+00	9.54702E-01	-1.63722E-01
H	4.78520E+00	-3.11501E-01	1.06781E+00
H	4.40104E-01	1.25740E-01	-3.81741E+00
H	1.30295E+00	1.53716E+00	-3.14230E+00
H	6.17068E+00	-2.80715E+00	-1.22176E+00
H	6.62474E+00	-5.23901E+00	3.42121E-01
H	7.11881E+00	-1.94658E+00	4.36051E+00
H	3.67347E+00	-6.49154E+00	1.77599E+00
H	5.65053E+00	-5.95503E+00	7.46932E+00
H	2.15365E+00	-4.53335E+00	-7.51676E-01
H	1.99160E+00	6.43898E-01	-4.51472E+00
H	5.97235E+00	-5.84443E-01	-2.26611E-01
H	7.21572E+00	-3.90823E+00	5.81272E+00
H	5.31404E+00	-7.58672E+00	4.60889E+00
H	3.40596E+00	1.19328E+00	-1.77512E+00
H	1.14752E+00	-2.18147E+00	-3.24189E+00

H	1.42329E+00	-2.31784E+00	5.88487E-01
C	-1.52392E+00	-1.76895E+00	1.62970E+00
C	-4.17057E+00	5.22539E-01	3.52678E+00
H	-4.15285E+00	1.44454E+00	4.12830E+00
H	-5.15583E+00	3.76548E-01	3.06373E+00
H	-3.90611E+00	-3.35005E-01	4.16458E+00
C	-2.88820E+00	-3.50609E+00	7.89319E-01
H	-3.74108E+00	-3.17883E+00	1.40374E+00
H	-2.34348E+00	-4.30503E+00	1.31578E+00
H	-3.22435E+00	-3.85093E+00	-1.97375E-01
H	-3.46816E-01	-7.28513E-01	1.77862E-01
H	-1.60489E+00	1.17903E+00	7.11146E-01
H	6.16685E-01	4.92503E+00	6.28438E-01
C	2.63264E+00	-3.21522E+00	5.88243E+00
C	1.18587E+00	-4.70973E+00	4.97483E+00
C	5.55538E-01	-4.44164E+00	6.41242E+00
C	1.59579E+00	-3.42282E+00	7.04088E+00
C	2.69009E+00	-4.64770E+00	5.30699E+00
H	3.00944E+00	-5.39827E+00	6.04518E+00
H	3.32943E+00	-4.74328E+00	4.40966E+00
H	8.09292E-01	-5.61240E+00	4.47515E+00
H	4.74024E-02	-3.15724E+00	3.70600E+00
H	1.75670E+00	-1.39198E+00	4.79061E+00
H	3.57823E+00	-2.76138E+00	6.20410E+00
H	1.06448E+00	-2.48743E+00	7.29034E+00
H	-4.40090E-01	-3.98327E+00	6.31815E+00
C	4.01746E-01	-5.75617E+00	7.15568E+00
C	2.27198E+00	-3.89301E+00	8.32812E+00
C	1.88686E+00	-4.44525E+00	1.05918E+01
H	1.04690E+00	-4.40741E+00	1.12989E+01
H	2.71801E+00	-3.81148E+00	1.09391E+01
H	2.24730E+00	-5.47856E+00	1.04673E+01
C	-1.14700E+00	-7.40971E+00	7.82686E+00
H	-2.23494E+00	-7.55512E+00	7.78793E+00
H	-7.90457E-01	-7.40804E+00	8.86915E+00
H	-6.26427E-01	-8.20807E+00	7.27428E+00

metallacyclobutane *exo* (Fig. S10D)

Ru	2.79827E+00	-3.19662E+00	2.28691E+00
C	7.94338E-01	-2.74882E+00	2.25230E+00
C	4.56579E+00	-3.20713E+00	1.26221E+00
C	2.44357E+00	-3.88923E+00	4.09447E+00
C	9.85875E-01	-3.22192E+00	3.72425E+00
N	5.62308E+00	-3.92811E+00	1.72811E+00
N	4.93922E+00	-2.56671E+00	1.25610E-01
O	-2.85137E+00	1.31721E+00	3.18429E+00
O	-7.53097E-01	2.08650E+00	2.73441E+00
O	-3.00529E+00	-2.00376E+00	3.61803E+00
O	-1.23591E+00	-9.65080E-01	4.61854E+00
O	-1.19478E+00	-6.52338E+00	6.07945E+00
O	-1.99015E+00	-4.54913E+00	6.88658E+00
O	2.08302E+00	-7.41534E+00	6.53701E+00
O	1.00681E+00	-6.12041E+00	8.07575E+00
Cl	3.35953E+00	-1.09507E+00	3.39277E+00
Cl	2.21207E+00	-5.07201E+00	8.04586E-01
C	-5.20535E-01	3.63870E-01	4.32099E-01
C	2.70152E-01	-1.34253E+00	2.02538E+00
C	-1.63292E+00	1.36808E-01	1.51790E+00
C	-1.27410E+00	-1.24445E+00	2.18677E+00
C	6.85464E+00	-3.68676E+00	9.36583E-01
C	6.31550E+00	-2.94175E+00	-2.94349E-01
H	6.26869E+00	-3.58292E+00	-1.19293E+00
C	4.19609E+00	-1.64310E+00	-7.00103E-01
C	4.49528E-01	-8.42903E-01	5.75134E-01
C	5.67312E+00	-4.78111E+00	2.89417E+00
H	7.56817E+00	-3.08023E+00	1.52406E+00
C	-1.10752E+00	5.27347E-01	-9.45682E-01
C	-1.14272E+00	1.67784E+00	-1.64108E+00
H	1.49275E+00	-5.65418E-01	3.57265E-01
H	1.69531E-01	-1.64979E+00	-1.30419E-01
C	-1.65513E+00	1.28853E+00	2.52661E+00

H	1.31338E-02	1.28753E+00	7.13910E-01
H	7.50801E-01	-6.40301E-01	2.72726E+00
H	-7.11503E-01	2.60298E+00	-1.24048E+00
H	-1.55982E+00	-3.76347E-01	-1.38362E+00
C	3.49249E+00	-2.12524E+00	-1.83244E+00
C	2.86903E+00	-1.18218E+00	-2.66963E+00
C	2.95162E+00	2.01287E-01	-2.43645E+00
C	3.70300E+00	6.41847E-01	-1.33278E+00
C	5.49344E+00	-6.17816E+00	2.72310E+00
C	5.56699E+00	-6.99733E+00	3.86283E+00
C	5.83330E+00	-6.47840E+00	5.14333E+00
C	6.08358E+00	-5.10046E+00	5.25744E+00
C	6.02875E+00	-4.23141E+00	4.15081E+00
C	5.24578E+00	-6.79135E+00	1.36509E+00
C	6.36655E+00	-2.76853E+00	4.32275E+00
C	5.83142E+00	-7.38141E+00	6.35694E+00
C	3.43772E+00	-3.59411E+00	-2.18210E+00
C	2.25207E+00	1.18605E+00	-3.34590E+00
H	5.16210E+00	-7.88703E+00	1.44828E+00
H	6.07006E+00	-6.57466E+00	6.59921E-01
H	7.21277E+00	-2.46683E+00	3.67808E+00
H	5.51254E+00	-2.11396E+00	4.07083E+00
H	6.33524E+00	-6.90727E+00	7.21587E+00
H	6.33575E+00	-8.34106E+00	6.14869E+00
H	2.77777E+00	-3.75762E+00	-3.04963E+00
H	4.43712E+00	-3.98290E+00	-2.45542E+00
C	4.34618E+00	-2.53345E-01	-4.59216E-01
C	5.19618E+00	2.72528E-01	6.73687E-01
H	5.24636E+00	1.37282E+00	6.37511E-01
H	4.78458E+00	-2.49697E-02	1.65430E+00
H	2.18273E+00	8.03918E-01	-4.37865E+00
H	1.22079E+00	1.37302E+00	-2.99159E+00
H	6.89248E+00	-2.03664E+00	-5.41717E-01
H	7.33688E+00	-4.64498E+00	6.85940E-01
H	6.65992E+00	-2.56332E+00	5.36526E+00
H	4.31400E+00	-6.40268E+00	9.18719E-01
H	4.79371E+00	-7.61648E+00	6.65745E+00
H	3.06446E+00	-4.20313E+00	-1.34073E+00
H	2.77587E+00	2.15664E+00	-3.37122E+00
H	6.23241E+00	-1.10520E-01	6.21454E-01
H	6.34260E+00	-4.68172E+00	6.23755E+00
H	5.40893E+00	-8.07576E+00	3.74306E+00
H	3.81041E+00	1.71795E+00	-1.15110E+00
H	2.31785E+00	-1.54630E+00	-3.54509E+00
H	2.80635E-01	-3.50073E+00	1.62705E+00
C	-1.79563E+00	-1.37633E+00	3.60823E+00
C	-2.92777E+00	2.31063E+00	4.23424E+00
H	-2.72449E+00	3.31467E+00	3.83088E+00
H	-3.95376E+00	2.24551E+00	4.62113E+00
H	-2.19532E+00	2.08101E+00	5.02363E+00
C	-3.63661E+00	-2.07423E+00	4.91905E+00
H	-3.76565E+00	-1.06203E+00	5.33287E+00
H	-3.02799E+00	-2.67665E+00	5.61102E+00
H	-4.61129E+00	-2.54786E+00	4.73915E+00
H	-1.75149E+00	-2.03143E+00	1.57482E+00
H	-2.64254E+00	6.86539E-02	1.07959E+00
H	-1.61306E+00	1.74061E+00	-2.62819E+00
C	2.09935E+00	-5.30193E+00	4.56814E+00
C	5.78226E-02	-4.41214E+00	4.15301E+00
C	9.03988E-02	-4.46427E+00	5.72771E+00
C	1.52390E+00	-5.08325E+00	6.00416E+00
C	8.34819E-01	-5.68806E+00	3.78189E+00
H	3.50147E-01	-6.59308E+00	4.18045E+00
H	1.01465E+00	-5.79817E+00	2.70433E+00
H	-9.62254E-01	-4.31604E+00	3.74727E+00
H	9.02787E-01	-2.32122E+00	4.35407E+00
H	2.98000E+00	-3.27472E+00	4.83754E+00
H	2.94145E+00	-6.00773E+00	4.54610E+00
H	2.11512E+00	-4.33788E+00	6.56850E+00
H	-7.26832E-03	-3.45739E+00	6.16120E+00
C	-1.06121E+00	-5.31609E+00	6.23895E+00

C	1.56347E+00	-6.35423E+00	6.85087E+00
C	9.70560E-01	-7.27462E+00	8.94564E+00
H	5.30666E-01	-6.91618E+00	9.88616E+00
H	1.98629E+00	-7.66542E+00	9.11409E+00
H	3.48469E-01	-8.06564E+00	8.49839E+00
C	-3.12938E+00	-5.28962E+00	7.38469E+00
H	-3.76176E+00	-4.54552E+00	7.88702E+00
H	-2.80014E+00	-6.06460E+00	8.09405E+00
H	-3.67214E+00	-5.77235E+00	6.55673E+00

pyridine adduct *exo* (Fig. S10E)

Ru	2.96707E+00	-2.90511E+00	2.66262E+00
C	1.79328E+00	-1.91159E+00	1.66108E+00
C	4.36426E+00	-3.23431E+00	1.22604E+00
N	5.45116E+00	-4.02733E+00	1.51631E+00
N	4.57620E+00	-2.73406E+00	-3.19151E-02
N	1.79169E+00	-2.84941E+00	4.56149E+00
O	-3.34125E+00	3.12413E-01	2.28019E+00
O	-1.92025E+00	7.83741E-01	4.00223E+00
O	-1.49726E+00	-2.73309E+00	4.90717E-01
O	-1.84248E+00	-2.27069E+00	2.69812E+00
Cl	4.26023E+00	-1.01863E+00	3.49765E+00
Cl	1.82025E+00	-5.01210E+00	2.21354E+00
C	1.70198E-01	1.51007E+00	2.12939E+00
C	8.70924E-01	-8.27772E-01	2.13879E+00
C	-1.06439E+00	6.40004E-01	1.70092E+00
C	-4.71366E-01	-7.70140E-01	1.33947E+00
C	6.51559E+00	-3.96025E+00	4.91840E-01
C	5.79815E+00	-3.27227E+00	-6.77551E-01
H	5.52149E+00	-3.97872E+00	-1.48331E+00
C	3.69519E+00	-1.94734E+00	-8.49702E-01
C	1.41300E+00	6.08271E-01	1.89525E+00
C	5.67700E+00	-4.78498E+00	2.72371E+00
H	7.36952E+00	-3.36720E+00	8.69502E-01
C	2.44984E-01	2.82932E+00	1.40822E+00
C	2.23687E-01	4.03566E+00	1.99890E+00
H	2.25193E+00	8.47442E-01	2.56517E+00
H	1.77084E+00	6.95379E-01	8.51583E-01
C	-2.11606E+00	5.88468E-01	2.81135E+00
H	6.99553E-02	1.69191E+00	3.21393E+00
H	6.49318E-01	-9.35827E-01	3.21432E+00
H	1.41845E-01	4.13872E+00	3.08715E+00
H	3.30640E-01	2.76963E+00	3.11692E-01
C	2.70365E+00	-2.59404E+00	-1.62767E+00
C	1.90639E+00	-1.80129E+00	-2.47384E+00
C	2.07928E+00	-4.08869E-01	-2.57410E+00
C	3.08014E+00	1.95429E-01	-1.79099E+00
C	5.26968E+00	-6.14634E+00	2.75301E+00
C	5.49888E+00	-6.88361E+00	3.92580E+00
C	6.14437E+00	-6.32719E+00	5.04531E+00
C	6.62278E+00	-5.01146E+00	4.94372E+00
C	6.42958E+00	-4.22798E+00	3.78916E+00
C	4.65502E+00	-6.81518E+00	1.54608E+00
C	7.11137E+00	-2.88254E+00	3.68471E+00
C	6.32973E+00	-7.13274E+00	6.31303E+00
C	2.46886E+00	-4.08475E+00	-1.52436E+00
C	1.23552E+00	4.13647E-01	-3.52506E+00
H	4.51220E+00	-7.89161E+00	1.73569E+00
H	5.30032E+00	-6.71426E+00	6.53857E-01
H	8.09785E+00	-2.99079E+00	3.19242E+00
H	6.51318E+00	-2.15018E+00	3.12349E+00
H	7.13505E+00	-6.71849E+00	6.94246E+00
H	6.57408E+00	-8.18616E+00	6.09141E+00
H	1.68560E+00	-4.40230E+00	-2.23176E+00
H	3.38126E+00	-4.66415E+00	-1.75441E+00
C	3.90359E+00	-5.49707E-01	-9.26810E-01
C	4.96768E+00	1.28853E-01	-9.43302E-02
H	4.93627E+00	1.22106E+00	-2.38631E-01
H	4.83669E+00	-8.78506E-02	9.80874E-01
H	2.71509E-01	-7.74136E-02	-3.73900E+00
H	1.02656E+00	1.41730E+00	-3.11699E+00

H	6.38673E+00	-2.45541E+00	-1.12646E+00
H	6.87922E+00	-4.97114E+00	2.43860E-01
H	7.29485E+00	-2.45943E+00	4.68587E+00
H	3.67346E+00	-6.37251E+00	1.30808E+00
H	5.40470E+00	-7.13599E+00	6.91909E+00
H	2.15400E+00	-4.37954E+00	-5.05425E-01
H	1.75175E+00	5.58623E-01	-4.49266E+00
H	5.98248E+00	-2.13219E-01	-3.71322E-01
H	7.18576E+00	-4.57843E+00	5.77976E+00
H	5.17074E+00	-7.92956E+00	3.95921E+00
H	3.23062E+00	1.28018E+00	-1.85453E+00
H	1.12792E+00	-2.29019E+00	-3.07199E+00
H	1.68977E+00	-2.13521E+00	5.82809E-01
C	-1.35635E+00	-1.97423E+00	1.61120E+00
C	-4.38504E+00	1.21720E-01	3.26164E+00
H	-4.48802E+00	1.01531E+00	3.89701E+00
H	-5.30162E+00	-5.26799E-02	2.68171E+00
H	-4.14958E+00	-7.49285E-01	3.89267E+00
C	-2.20544E+00	-3.98128E+00	6.85446E-01
H	-3.15753E+00	-3.80833E+00	1.20985E+00
H	-1.58017E+00	-4.67513E+00	1.26970E+00
H	-2.37699E+00	-4.37764E+00	-3.24206E-01
H	-2.20666E-01	-7.68307E-01	2.64477E-01
H	-1.56324E+00	1.04777E+00	8.05348E-01
H	2.88753E-01	4.96290E+00	1.41989E+00
C	5.11646E-01	-3.29350E+00	4.64466E+00
C	-1.73730E-01	-3.40599E+00	5.85905E+00
C	4.84532E-01	-3.07008E+00	7.04886E+00
C	1.81069E+00	-2.62208E+00	6.97139E+00
C	2.42341E+00	-2.51976E+00	5.71815E+00
H	3.66767E-02	-3.56422E+00	3.70197E+00
H	-1.21188E+00	-3.74828E+00	5.85494E+00
H	-2.48725E-02	-3.15091E+00	8.01454E+00
H	2.37261E+00	-2.34353E+00	7.86754E+00
H	3.44382E+00	-2.14491E+00	5.60322E+00

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