

Supporting Information

Gradient Helical Copolymers: Synthesis, Chiroptical Property, Thermotropic Liquid Crystallinity, and Self-Assembly in Selective Organic Solvents

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1. Experimental Section

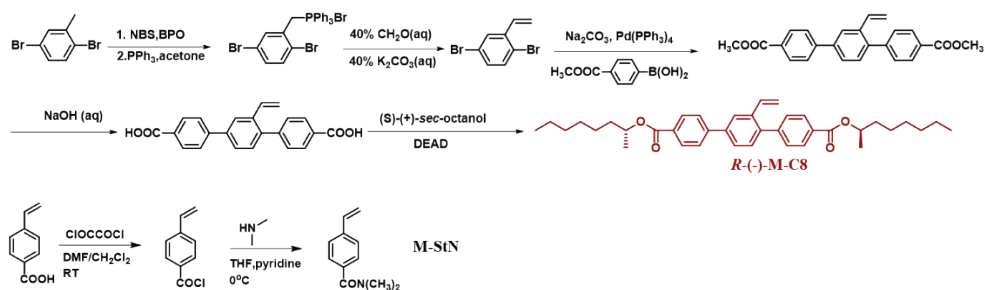
Materials Tris(2-dimethylaminoethyl)amine (Me6Tren, 99%, TCI) , Methyl 2-chloropropionate (McP, 99%, J&K) and Dimethylamine (2.0 M in THF, J&K) were used as purchased. CuCl (98%, Aldrich) was purified by stirring overnight in acetic acid. After filtration, it was washed with ethanol and ether and then dried under vacuum. Tetrahydrofuran (THF, Fisher Chemical Co., HPLC grade) was refluxed with sodium and distilled out just before using in the gel permeation chromatography (GPC), circular dichroism (CD) and optical rotation measurements. Anisole (Beijing Chemical Co., A.R.) was distilled out over CaH₂ just before use. The monomer *R*-(-)-M-C8¹ and *p*-vinylbenzoic acid² was synthesized almost following the procedure reported previously. Other reagents and solvents were purchased from Beijing Chemical Reagents Co. and used as received unless otherwise specified.

Instruments Room and high temperature ¹H/¹³C NMR spectra were obtained with a Bruker ARX 400/500 MHz NMR spectrometer with chloroform-*d* (CDCl₃) or dimethyl sulfoxide-*d* (DMSO-*d*⁶) as the solvent and tetramethylsilane as the internal reference. Elementary analyses were run on an Elemental Vario EL instrument. Mass spectra were obtained on a Finnigan-MAT ZAB-HS

spectrometer. The number-average molecular mass (M_n), weight-average molecular mass (M_w), and molecular mass polydispersity (M_w/M_n) of the polymer were estimated with a gel permeation chromatography (GPC) apparatus equipped with a Waters 2410 refractive index detector and a Waters 515 pump. THF was employed as the eluent at a flow rate of 1.0 mL/min at 35 °C. All GPC curves were calibrated against a series of monodispersed polystyrene standards. Thermogravimetric analyses (TGA) were performed under nitrogen atmosphere on a TA Instrument Q600 analyzer. Differential scanning calorimetry (DSC) spectra measured on a TA DSC Q100 instrument at a heating rate of 20 °C/min under a nitrogen atmosphere. The samples were first annealed at 270 °C for 5 min and then cooled to room temperature at a cooling rate of 2 °C/min. Optical rotations were measured on a Jasco P-1030 polarimeter in a 5 cm cell at 20 °C with THF as solvent. Circular dichroism (CD) spectra were obtained on a Jasco J-810 spectropolarimeter in a 1 cm cell using THF as solvent at 20 °C and analyzed by the associated J800 software. The sample concentration was 10⁻⁵ mol/L. UV-vis absorption measurements were carried out on a Varian Cary 1E UV-vis spectrometer. One dimensional wide-angle X-ray diffraction (1D-WAXD) was run on a Philips X'Pert (Cu K α , λ = 0.154 nm) diffractometer equipped with an Anton Parr TTK 450 heating stage and an Anton Parr TCU-100 thermal controller. The sample stage was set horizontally. The reflection peak positions were calibrated with silicon powder ($2\theta > 15^\circ$) and silver behenate ($2\theta < 10^\circ$). Background scattering was recorded and subtracted from the sample patterns. The heating and cooling rates in the WAXD experiments were 5 °C/min. TEM images were obtained on a JEM 2100 instrument operating at an acceleration voltage of 200 kV. Dynamic light scatter (DLS) and static light scatter (SLS) were carried out on a commercialized spectrometer from Brookhaven Instrument Corporation (BI-200SM Goniometer, Holtsville, NY) with a vertically polarized, 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operated at 633 nm and a BITurboCo digital correlator (Brookhaven Instruments Corp.).

Synthesis

Scheme S1. Synthetic route of monomers



*(-)-2,5-bis{4'-[(*R*)-sec-octyloxycarbonyl]phenyl}styrene (*R*-(-)-*M-C8*). The chiral monomer *R*-(-)-*M-C8* were synthesized almost according to the procedure reported previously¹ (Scheme S1). Yield: 72%. ¹H NMR (CDCl₃, δ, ppm): 0.86-0.92 (t, 6H, CH₂CH₃), 1.22-1.45 (m, 22H, CH(CH₃)CH₂(CH₂)₄), 1.58-1.82 (M, 4H, CHCH₂), 5.14-5.25 (q, 2H, OCH), 5.27-5.32 (d, 1H, =CH₂), 5.77-5.83 (d, 1H, =CH₂), 6.68-6.77 (q, 1H, ArCH=), 7.37-8.17 (m, 11H, ArH). ¹³C NMR (CDCl₃, δ, ppm): 166.05, 144.84, 139.94, 139.56, 136.44, 135.48, 130.54, 130.14, 130.01, 129.83, 129.74, 129.39, 127.01, 126.65, 124.96, 115.98, 71.85, 36.13, 31.76, 29.20, 25.346, 22.62, 20.13, 14.08. Analysis calc. for C₃₈H₄₈O₄: C, 80.24%; H, 8.51%; Found: C, 79.99%; H, 8.41%. MS: *m/z* = 568 (calcd. 568.36).*

N,N-dimethyl-4-ethenylbenzamide (*M-StN*). The achiral monomer *M-StN* were synthesized via esterification (Scheme S1). *P*-vinylbenzoic acid which was synthesized following the procedure reported previously² (1.06 g, 6.8 mmol) and 3 mL of oxalyl chloride were stirred in 100 mL dried dichloromethane. 3 drops of *N,N*-dimethylformamide (DMF) were added to the mixed solution. The solution was stirred at room temperature for 3 h. After evaporation of excess oxalyl chloride, the crude acid chloride was obtained and employed directly for the next step reaction. The acid chloride was dissolved in 20 mL of dried dichloromethane. Then the acid chloride solution was added into a mixture of dimethylamine (5 mL, 10.2 mmol) and dried pyridine (16 mL, 20.4 mmol) at 0°C. The solution was stirred at room temperature overnight and then washed by 0.5 M dilute hydrochloric acid and 0.5 M sodium bicarbonate solution successively. The organic phase was combined and washed with brine and dried over with anhydrous MgSO₄. The resultant crude product, after evaporation of the solvent, was purified by silica gel column chromatography with the mixture of ethyl acetate/petroleum ether (5/1, v/v) as an eluent. Then 0.91 g pure product was obtained. Yield: 75%. ¹H NMR (DMSO-*d*₆, δ, ppm): 3.05 (s, 6H, NCH₃), 5.28-5.34 (d, 1H, CH₂), 5.76-5.84 (d, 1H, CH₂), 6.67-6.77 (q, H, OCH), 5.28-5.30 (t, 1H, CH), 7.36-7.47 (m, 4H, ArH). ¹³C NMR (DMSO-*d*₆, δ, ppm): 40.0, 116.0, 126.4, 127.8, 136.2, 136.5, 138.5, 170.3. Analysis calc. for C₁₁H₁₃NO: C, 75.40%; H, 7.40%; Found: C, 76.01%; H, 7.48%. MS: *m/z* = 175 (calcd. 175.10).

Atom Transfer Radical Polymerization (ATRP) *R*-(-)-*P*-C8. Homopolymers of *R*-(-)-*M*-C8 with different molar masses were prepared via ATRP at 90°C in anisole. The initiating system was McP/CuCl/Me6Tren (1:1.2:1.5, molar ratio). The molar ratio of monomer to initiator was 300:1. The molar mass was adjusted by changing the polymerization time and fractionation. In a typical run, *R*-(-)-*M*-C8 (0.56 g, 1 mmol), McP (0.37 mg, 0.0033 mmol), Me6Tren (1.2 µL, 0.005 mmol), and anisole (1.00 g) were introduced into a glass reaction tube. After three freeze-pump-thaw cycles, CuCl (0.36 mg, 0.0039 mmol) was added to the tube. After another three freeze-pump, the tube was sealed under vacuum and put into an oil bath thermostated at 90 °C. The reaction was terminated after 60 h by breaking the tube. The reaction mixture was diluted with 20mL of THF and allowed to pass through a short Al₂O₃ column. The crude product was obtained by adding the filtrate into 300 mL of methanol under rapid stirring and collection of precipitate by filtration. The operations of dissolution in THF and precipitation in methanol were repeated three times to remove unreacted monomer. After being dried at 50 °C under vacuum, 0.41 g of *R*-(-)-*P*-C8 was obtained. The monomer conversion in weight was 74%. The 5% weight loss temperature (T_d) under an inert atmosphere was 312 °C, the glass transition temperature (T_g) was 102 °C.

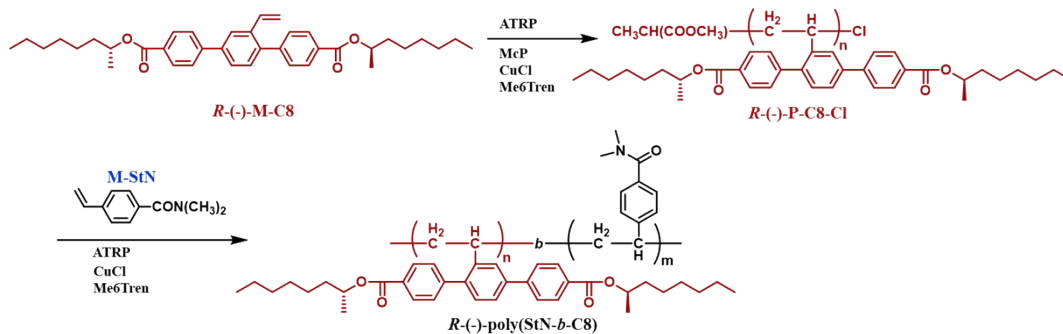
***P*-StN** Homopolymer of *M*-StN were also prepared by the same method with *R*-(-)-*P*-C8. The molar ratio of monomer to initiator was 100:1. The crude product was obtained by adding the filtrate into 300 mL of hexane under rapid stirring and collection of precipitate by filtration. The operations of dissolution in THF and precipitation in hexane were repeated three times to remove unreacted monomer. After being dried at 50 °C under vacuum, 0.15 g of *P*-StN was obtained. The monomer conversion in weight was 89%. The 5% weight loss temperature (T_d) under an inert atmosphere was 369 °C, the glass transition temperature (T_g) was 149 °C.

***R*-(-)-*poly*(StN-*grad*-C8).** Copolymers of *M*-StN and *R*-(-)-*M*-C8 with different compositions and molar masses were prepared via ATRP at 90°C in anisole. The initiating system was McP/CuCl/Me6Tren (1:1.2:1.5, molar ratio). The molar mass was adjusted by changing the polymerization time or molar ratio of monomer to initiator. In a typical run, *R*-(-)-*M*-C8 (0.45 g, 0.8 mmol), *M*-StN(0.035 g, 0.2 mmol), McP (0.61 mg, 0.005 mmol), Me6Tren (2.0 µL, 0.0075 mmol), and anisole (1.00 g) were introduced into a glass reaction tube. After three freeze-pump-thaw cycles, CuCl (0.59 mg, 0.006 mmol) was added to the tube. After another three freeze-pump, the tube was sealed under vacuum and put into an oil bath thermostated at 90 °C. The reaction was terminated after 96 h by breaking the tube. The reaction mixture was diluted with 20mL of THF and allowed to pass through a short Al₂O₃ column. The crude product was obtained by adding the filtrate into 300 mL of methanol under rapid stirring and collection of precipitate by filtration. The operations of dissolution in THF and

precipitation in methanol were repeated three times to remove unreacted monomer. After being dried at 50 °C under vacuum, 0.43 g of *R*-(-)-poly(StN-*grad*-C8) was obtained. The monomer conversion in weight was 89%. The 5% weight loss temperature (T_d) under an inert atmosphere was 319 °C, the glass transition temperature (T_g) was 126 °C.

R-(-)-poly(StN-*b*-C8). Homopolymers of *R*-(-)-M-C8 were synthesized by the same method mentioned above at the first step. Then the obtained polymers *R*-(-)-M-C8-Cl was used as macroinitiator to initiate the polymerization of M-StN (Scheme S2). The initiating system was *R*-(-)-M-C8-Cl /CuCl/Me6Tren (1:1.2:1.5, molar ratio). The block copolymer with different compositions were prepared via ATRP at 90°C in anisole. The molar masses of the block copolymers were adjusted by changing the molar ratio of monomer to initiator. In a typical run, M-StN(0.070 g, 0.4 mmol), *R*-(-)-P-C8-Cl ($M_n = 1.8 \times 10^4$ g/mol, 0.072 g, 0.004 mmol), Me6Tren (1.5 μ L, 0.006 mmol), and anisole (1.00 g) were introduced into a glass reaction tube. After three freeze-pump-thaw cycles, CuCl (0.48 mg, 0.0048 mmol) was added to the tube. After another three freeze-pump, the tube was sealed under vacuum and put into an oil bath thermostated at 90 °C. The reaction was terminated after 48 h by breaking the tube. The reaction mixture was diluted with 20mL of THF and allowed to pass through a short Al₂O₃ column. The crude product was obtained by adding the filtrate into 300 mL of hexane under rapid stirring and collection of precipitate by filtration. The operations of dissolution in THF and precipitation in hexane were repeated three times to remove unreacted monomer. After being dried at 50 °C under vacuum, 0.13 g of *R*-(-)-poly(StN-*b*-C8) was obtained. The monomer conversion in weight was 90%. The 5% weight loss temperature (T_d) under an inert atmosphere was 320 °C, the glass transition temperature (T_g) was 140 °C.

Scheme S2. Synthetic route of block copolymer *R*-(-)-poly(StN-*b*-C8)



Reactivity Ratios Copolymer composition values calculated from the data of low conversion copolymerization have large errors. The calculation may be biased by prior initiation of one monomer by the initiating radical³. Therefore, we used extended conversion kinetic data (20% - 80%) to estimate monomer reactivity ratios by a nonlinear regression technique, “sum-of-squares space” (SS-space) approach, which was constructed by Visual Basic for Applications (VBA) code according to the published literature⁴.

Preparation of Assemblies

Dissolving *R*-(-)-poly(StN-*grad*-C8)-1, *R*-(-)-poly(StN-*b*-C8)-1, *R*-(-)-poly(StN-*grad*-C8)-2, *R*-(-)-poly(StN-*b*-C8)-2 (Table S4) in THF to obtain the solutions with polymer concentration of 0.2 mg/mL. Then hexane was dropwise added in to the solution of *R*-(-)-poly(StN-*grad*-C8)-1 and *R*-(-)-poly(StN-*b*-C8)-1, while methanol was dropwise added in to the solution of *R*-(-)-poly(StN-*grad*-C8)-2 and *R*-(-)-poly(StN-*b*-C8)-2 until the solution became turbid. The TEM specimen was prepared by drop-casting the sample solution onto a carbon-coated copper grid for a few minutes. Excess solution was draw away with a strip of filter paper, and the sample grid was dried in air.

2. Results of Polymerizations and Copolymerizations

Table S1. Summary of ATRP results of *R*-(-)-M-C8 and characterization of the resultant polymers^a

Sample	$M_n^* \cdot 10^{-4b}$	PDI	$[\alpha]_{20}^{365c}$	liquid crystallinity
<i>R</i> -(-)-M-C8	-	-	-256°	no
<i>R</i> -(-)-P-C8-1	0.49	1.10	-12°	no
<i>R</i> -(-)-P-C8-2	0.92	1.29	+480°	no
<i>R</i> -(-)-P-C8-3	1.0	1.21	+514°	no
<i>R</i> -(-)-P-C8-4	1.9	1.37	+802°	yes
<i>R</i> -(-)-P-C8-5	2.6	1.28	+797°	yes
<i>R</i> -(-)-P-C8-6	3.2	1.18	+936°	yes
<i>R</i> -(-)-P-C8-7	4.3	1.16	+850°	yes
<i>R</i> -(-)-P-C8-8	6.0	1.29	+798°	yes

<i>R</i> -(-)-P-C8-9	14	1.22	+1030°	yes
<i>R</i> -(-)-P-C8-10	18	1.34	+986°	yes

^a Polymerization condition: global monomer concentration in anisole (20 wt %); temperature, 90°C; initiating system, McP/CuCl/Me6Tren (1:1.2:1.5, molar ratio); ^b Number-averaged molecular weight (M_n), and polydispersity distribution index (PDI) were obtained by gel permeation chromatography, calibrated against a series of monodispersed polystyrene standards. ^c Specific optical rotations were measured in THF at 20 °C THF. Concentration: $c = 2.0$ g/ L. Solvent: THF.

Table S2. Summary of atom transfer radical copolymerization results of M-StN and *R*-(-)-M-C8^a

Sample	Conv.	$M_n * 10^{-4b}$	PDI	$[\alpha]_{20}^{365c}$
S2-P-1	10%	0.9	1.12	-100°
S2-P-2	17%	1.4	1.18	-79°
S2-P-3	44%	2.7	1.09	-59°
S2-P-4	49%	2.8	1.12	-51°
S2-P-5	61%	3.7	1.09	+2°
S2-P-6	65%	3.6	1.10	+3°
S2-P-7	76%	4.0	1.10	+68°
S2-P-8	89%	4.3	1.10	+184°

^a Polymerization condition: anisole solution (50 wt %); temperature, 90°C; initiating system, McP/CuCl/ Me6Tren (1:1.2:1.5, molar ratio); initial monomer feed ratio $[M_{StN}]_0 / [M_{C8}]_0$ (20:80, molar ratio); monomer/initiator (200:1, molar ratio). ^b Number-averaged molecular weight (M_n), and polydispersity distribution index (PDI) were obtained by gel permeation chromatography, calibrated against a series of monodispersed polystyrene standards. ^c Specific optical rotations were measured in THF at 20 °C THF. Concentration: $c = 2.0$ g/ L. Solvent: THF.

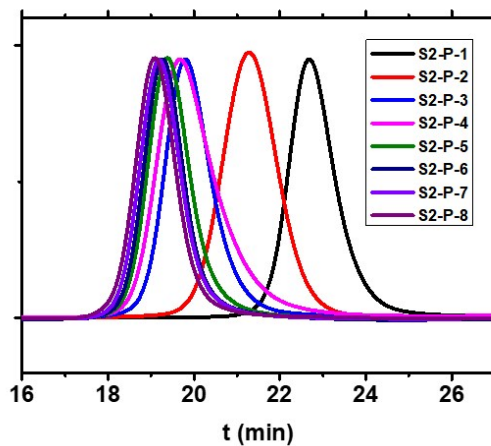


Figure S1. GPC trace of gradient copolymers shown in Table S2 using THF as eluent.

Table S3. Summary of atom transfer radical copolymerization results of M-StN and R(-)-M-C8^a

Sample	Conv.	$M_n \cdot 10^{-4b}$	PDI	$[\alpha]_{20}^{365c}$
S3-P-1	13%	1.4	1.19	-100°
S3-P-2	16%	1.0	1.17	-69°
S3-P-3	22%	1.5	1.17	-59°
S3-P-4	24%	1.6	1.20	-81°
S3-P-5	29%	1.6	1.12	-72°
S3-P-6	31%	1.7	1.18	-57°
S3-P-7	33%	1.6	1.22	-56°
S3-P-8	49%	2.5	1.25	-46°
S3-P-9	50%	2.6	1.13	-57°
S3-P-10	51%	2.8	1.17	-35°
S3-P-11	63%	2.5	1.31	-8°
S3-P-12	75%	3.2	1.12	+90°
S3-P-13	87%	4.5	1.19	+211°

^a Polymerization condition: anisole solution (50 wt %); temperature, 90°C; initiating system, McP/CuCl/ Me6Tren (1:1.2:1.5, molar ratio); initial monomer feed ratio $[M_{\text{StN}}]_0 / [M_{\text{C8}}]_0$ (20:80, molar ratio); monomer/initiator (300:1, molar ratio). ^b Number-averaged molecular weight (M_n), and polydispersity distribution index (PDI) were obtained by gel permeation chromatography, calibrated against a series of monodispersed polystyrene standards. ^c Specific optical rotations were measured in THF at 20 °C THF. Concentration: $c = 2.0 \text{ g/L}$. Solvent: THF.

Table S4. Summary of copolymers with different structure^a

Sample	$M_n * 10^{-4b}$	PDI	$DP_{\text{StN}}/DP_{\text{C8}}^c$
<i>R</i> -(-)-poly(StN- <i>grad</i> -C8)-1	3.6	1.12	80/39
<i>R</i> -(-)-poly(StN- <i>b</i> -C8)-1	3.1	1.14	75/31
<i>R</i> -(-)-poly(StN- <i>grad</i> -C8)-2	4.5	1.19	22/72
<i>R</i> -(-)-poly(StN- <i>b</i> -C8)-2	4.3	1.32	32/65

^a Polymerization condition: anisole solution (50 wt %); temperature, 90°C; initiating system, McP/CuCl/ Me6Tren (1:1.2:1.5, molar ratio); ^b Number-averaged molecular weight (M_n), and polydispersity distribution index (PDI) were obtained by gel permeation chromatography, calibrated against a series of monodispersed polystyrene standards. ^c Degree of polymerization was measured by elemental analysis.

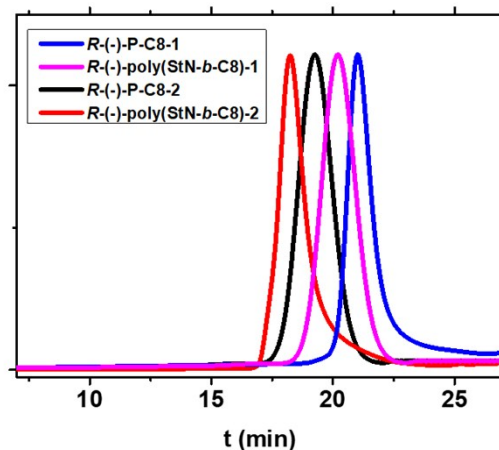


Figure S2. GPC trace of macroinitiators and block copolymers shown in parent manuscript and Table S4 using THF as eluent.

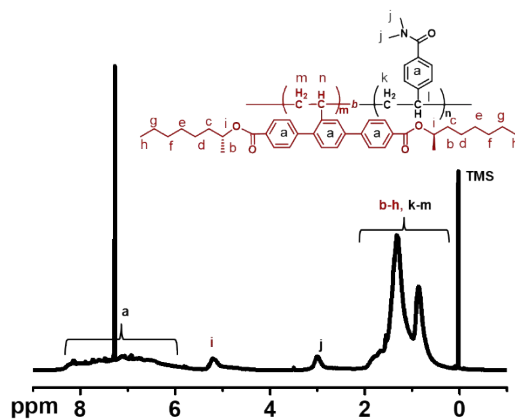


Figure S3. ^1H NMR spectra of the block copolymer $R(-)\text{-poly}(\text{StN-}b\text{-C8})\text{-2}$ recorded in CDCl_3 .

3. Monomer Reactivity Ratio Calculations

We used the “sum-of-squares space” (SS-space) method to estimate monomer reactivity ratios from kinetic data. A non-linear least squares fit was used to integrate form of the terminal model composition equation⁴ (eq1):

$$1 - \frac{[M]}{[M]_0} = 1 - \left(\frac{f_1}{(f_1)_0} \right)^\alpha \left(\frac{1-f_1}{1-(f_1)_0} \right)^\beta \left(\frac{(f_1)_0 - \delta}{f_1 - \delta} \right)^\gamma \quad \text{eq1}$$

where $1-[M]/[M_0]$ is the total conversion of copolymerization, f_{StN} is the feed composition of M-StN at that value of conversion, $(f_{StN})_0$ is the initial feed composition of M-StN, $\alpha = r_{C8}/(1-r_{C8})$, $\beta = r_{StN}/(1-r_{StN})$, $\delta = (1-r_{C8})/(2-r_{StN}-r_{C8})$, $\gamma = (1-r_{StN}r_{C8})/(1-r_{StN})(1-r_{C8})$, r_{StN} was the reactivity ratio of M-StN and r_{C8} was the reactivity ratio of R(-)-M-C8. To determine r_{StN} and r_{C8} by eq1, a non-linear squares analysis was used. The sum of squares of residuals between measured and predicted conversion (eq2) are minimized by changing r_{StN} and r_{C8} :

$$SS_{(r_1, r_2)} = \sum_{i=1}^n \frac{1}{w} \{y_i - f(r_1, r_2)_i\}^2 \quad \text{eq2}$$

where y_i is the measured value of conversion at the i th experimental data point, $f(r_{StN}, r_{C8})_i$ is the value of the right side of eq1 at the i th experimental data point calculated from measured f_{StN} and $(f_{StN})_0$, and w is a weighting factor. Table S5-S13 displayed the initial M-StN feeds (f_{StN}), measured conversions, calculated parameters of eq1 and the conversion residuals (defined in eq2). The value of r_{StN} and r_{C8} were calculated at the point estimates from the data listed in Table 1 of the parent manuscript, shown at the end of each table title. Full details of the complete VBA code as well as the calculations used to construct the SS-space surface were published in the Supporting Information to ref 4.

Table S5. Reactivity ratio calculations for experiment 1 and experiment 4 ($r_{StN} = 2.18$, $r_{C8} = 0.40$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversion	Residual
0.7444	0.393	0.953112689	0.635607132	0.994451237	0.392669527	0.000330473
0.1363	0.326	0.225578788	0.86801987	0.990467508	0.326879414	-0.000879414

Table S6. Reactivity ratio calculations for experiment 1 and experiment 5 ($r_{StN} = 1.68$, $r_{C8} = 0.35$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversion	Residual
0.6895	0.686	0.923079762	0.337318029	0.995414664	0.687073112	-0.001073112
0.1363	0.326	0.186555793	0.827553889	0.997284344	0.32648497	-0.00048497

Table S7. Reactivity ratio calculations for experiment 1 and experiment 6 ($r_{StN} = 1.59$, $r_{C8} = 0.33$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversion	Residual
						n

0.6756	0.757	0.92012661	0.271600622	1.019778653	0.756453292	0.000546708
0.1363	0.326	0.172104118	0.813452628	1.00937636	0.327848408	-0.001848408

Table S8. Reactivity ratio calculations for experiment 2 and experiment 4 ($r_{StN} = 2.25$, $r_{CB} = 0.44$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversio n	Residual
0.7444	0.393	0.944974329	0.643049586	0.999498566	0.392200097	0.000799903
0.1051	0.5055	0.396815748	0.817274337	0.998593721	0.506893086	-0.001393086

Table S9. Reactivity ratio calculations for experiment 2 and experiment 5 ($r_{StN} = 1.69$, $r_{CB} = 0.40$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversio n	Residual
0.6895	0.686	0.905655139	0.340495195	0.988399347	0.687750565	-0.001750565
0.1051	0.5055	0.348798868	0.759903075	0.989167704	0.503676303	0.001823697

Table S10. Reactivity ratio calculations for experiment 2 and experiment 6 ($r_{StN} = 1.59$, $r_{CB} = 0.38$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversion	Residual
0.6756	0.757	0.901597484	0.271600622	1.00677702	0.757279091	-0.000279091
0.1051	0.5055	0.325878592	0.739263632	1.005018034	0.502401467	0.003098533

Table S11. Reactivity ratio calculations for experiment 3 and experiment 4 ($r_{StN} = 2.09$, $r_{CB} = 0.32$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$ α	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$ γ	Predicted conversio n	Residual
0.7444	0.393	0.966670121	0.624790501	0.989830653	0.393137976	-0.000137976
0.0226	0.753	0.641581964	0.68111012	0.956162913	0.751733309	0.001266691

Table S12. Reactivity ratio calculations for experiment 3 and experiment 5 ($r_{StN} = 1.67$, $r_{CB} = 0.29$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN})_0)$	$((1-f_{StN})/(1-(f_{StN})_0))^\beta$	$((f_{StN})_0-\delta)/((f_{StN}-\delta))$	Predicted	Residual
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		α	$(f_{StN}^0)^\beta$	γ	conversion	
					n	
0.6895	0.686	0.941092196	0.334077008	1.007069283	0.688030098	-0.002030098
0.0226	0.753	0.589579332	0.607006376	1.010962874	0.752231751	0.000768249

Table S13. Reactivity ratio calculations for experiment 3 and experiment 6 ($r_{StN} = 1.59$, $r_{CB} = 0.28$)

f_{StN}	Conversion	$(f_{StN}/(f_{StN}^0))^\alpha$	$((1-f_{StN})/(1-(f_{StN}^0)))^\beta$	$((f_{StN}^0-\delta)/(f_{StN}-\delta))^\gamma$	Predicted conversion	Residual
0.6756	0.757	0.936387098	0.271600622	1.034424341	0.756835808	0.000164192
0.0226	0.753	0.571695411	0.582894482	1.043618975	0.756152703	-0.003152703

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