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Supplemental Information

The Introduction of the Radical Cascade Reaction into Polymer Chemistry: A One-Step Strategy for Synchronized Polymerization and Modification

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Supplemental Figures

NMR Spectra of raw materials

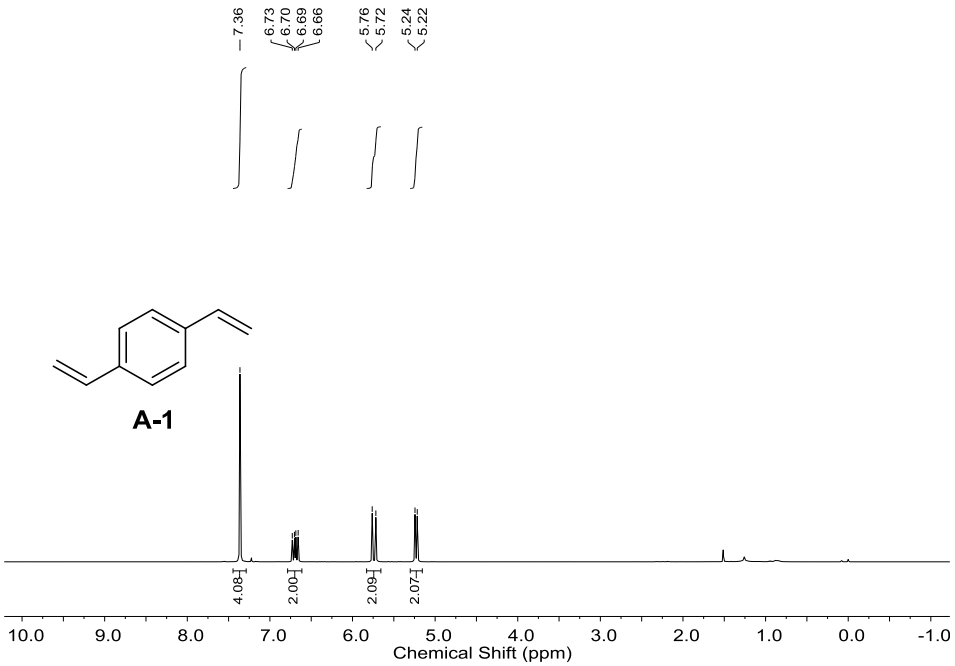


Figure S1: ^{1}H NMR spectrum of compound **A-1,** related to **Table 1.**

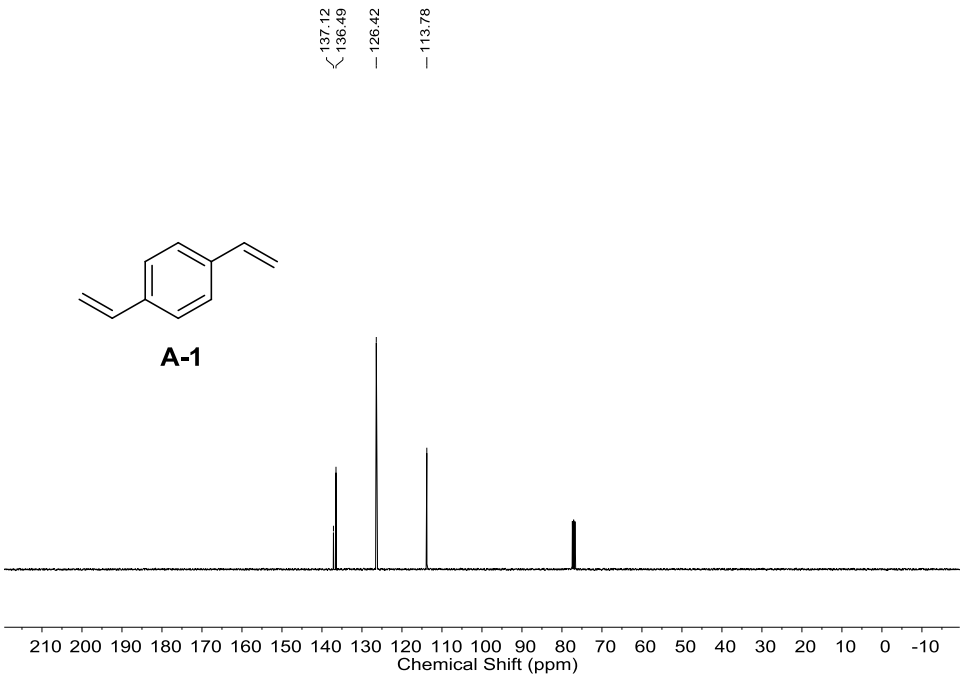


Figure S2: ^{13}C NMR spectrum of compound **A-1,** related to **Table 1.**

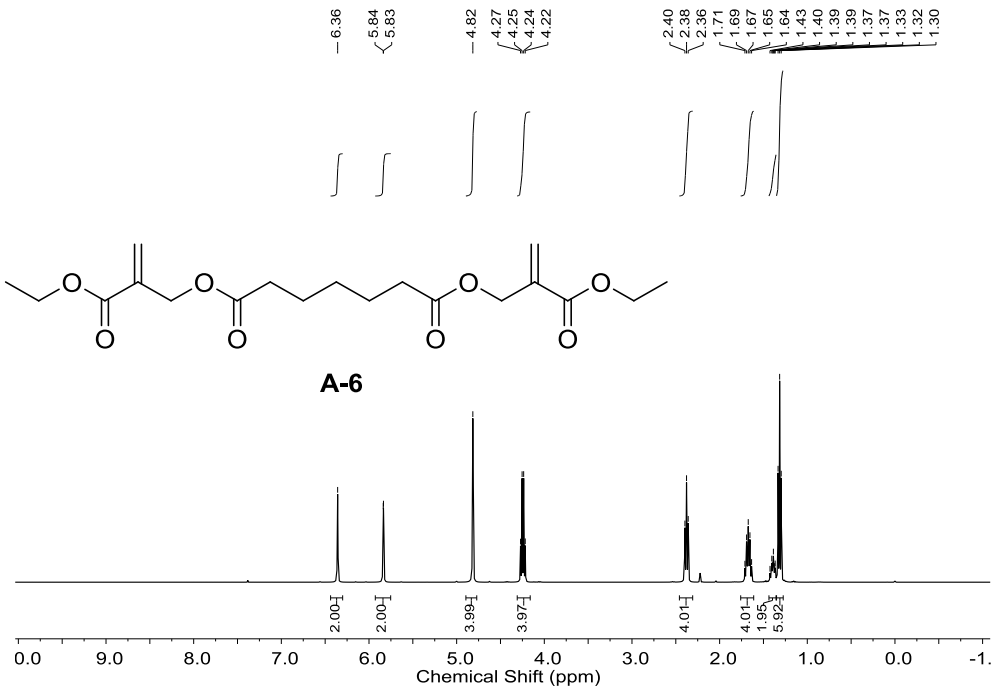


Figure S3: ^{1}H NMR spectrum of compound **A-6,** related to **Table 1.**

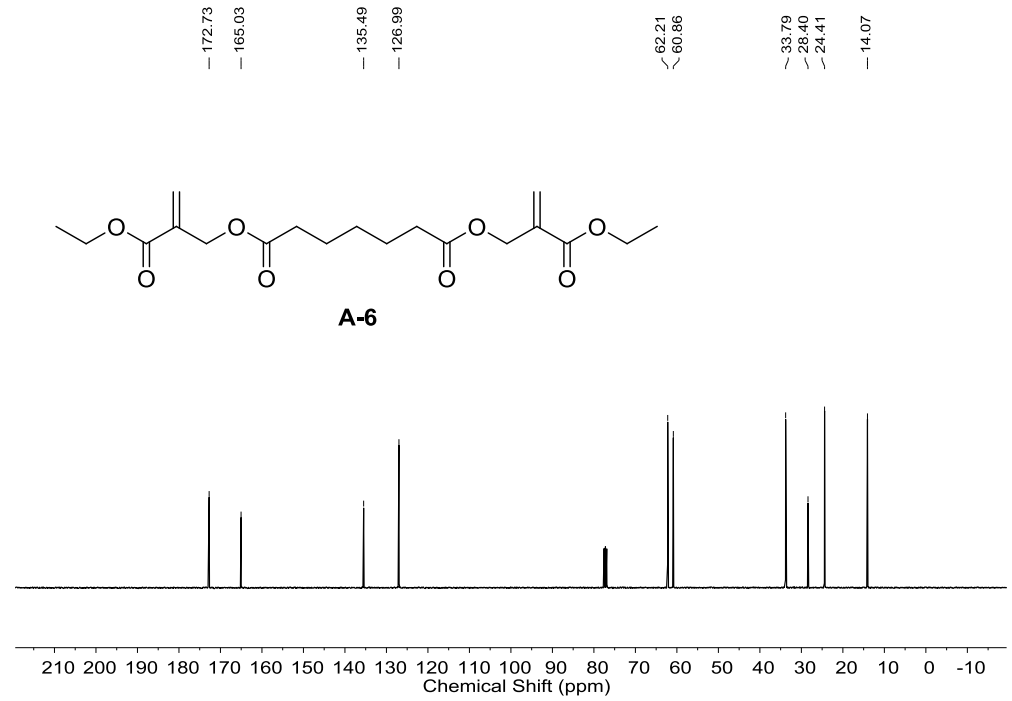


Figure S4: ^{13}C NMR spectrum of compound **A-6,** related to **Table 1.**

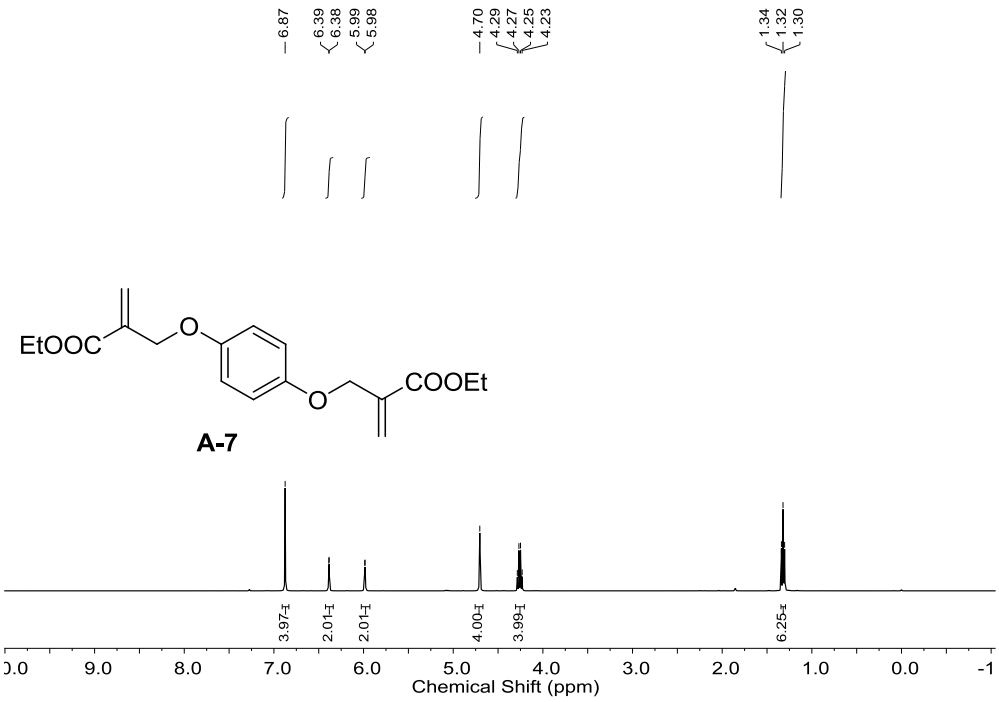


Figure S5: ^{1}H NMR spectrum of compound **A-7,** related to **Table 1.**

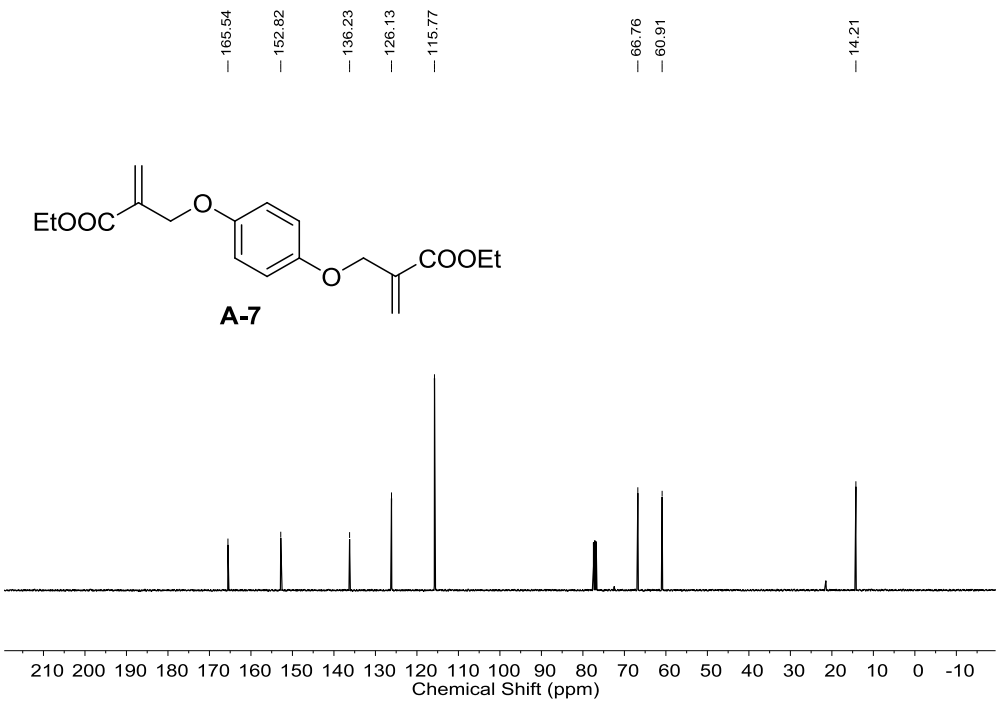


Figure S6: ^{13}C NMR spectrum of compound **A-7,** related to **Table 1.**

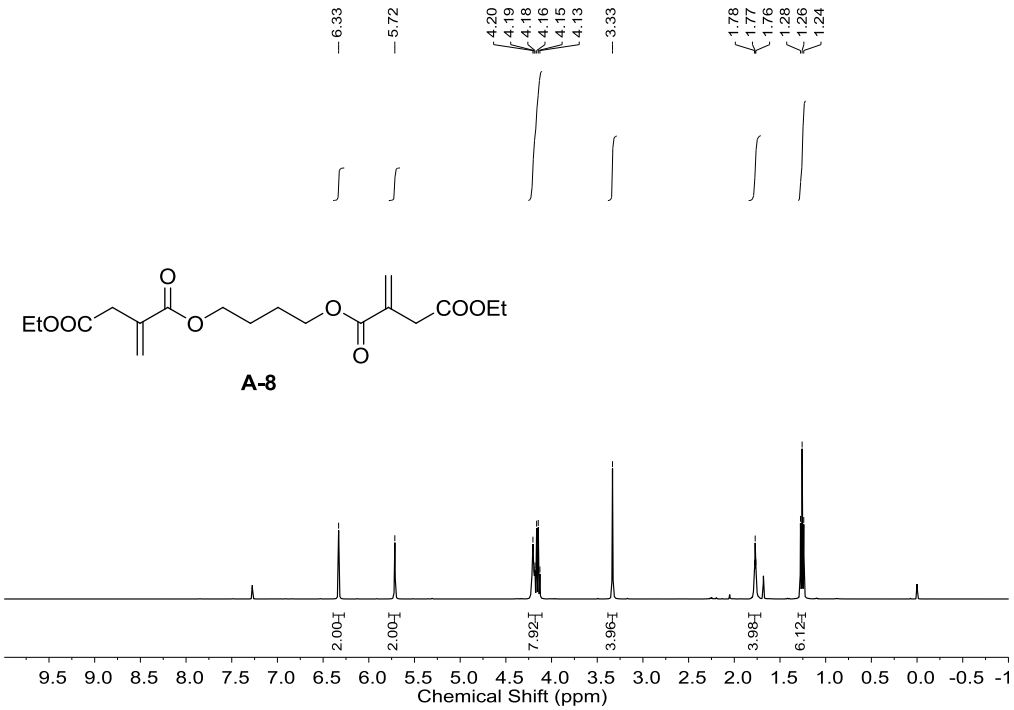


Figure S7: ^{1}H NMR spectrum of compound **A-8,** related to **Table 1.**

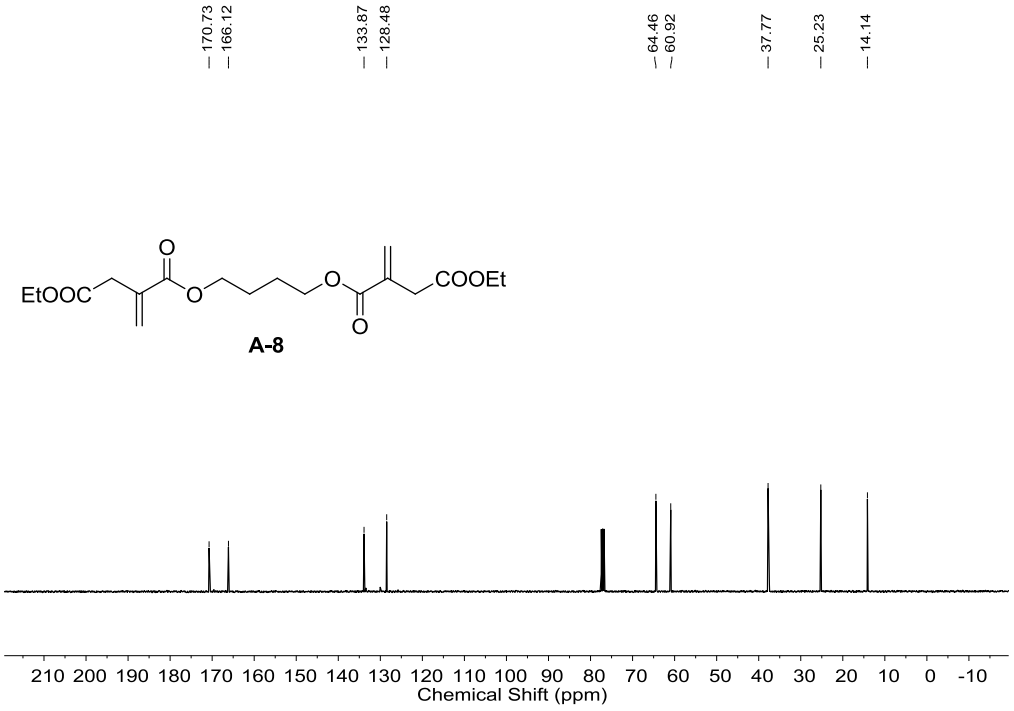


Figure S8: ^{13}C NMR spectrum of compound **A-8,** related to **Table 1.**

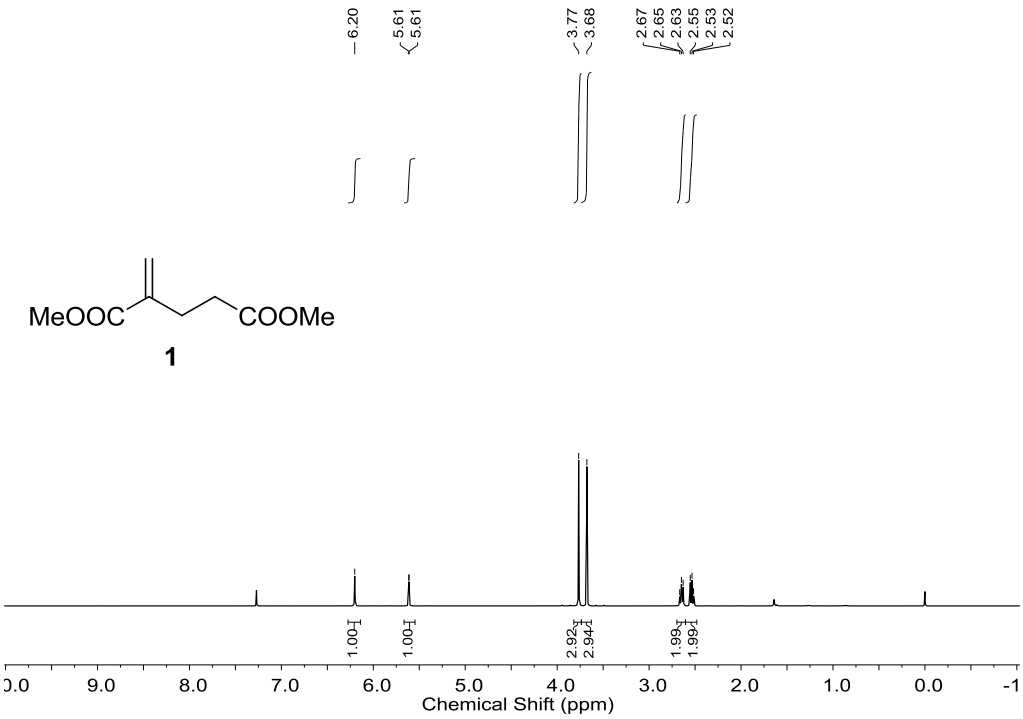


Figure S9: ^{1}H NMR spectrum of compound **1,** related to **Table 1.**

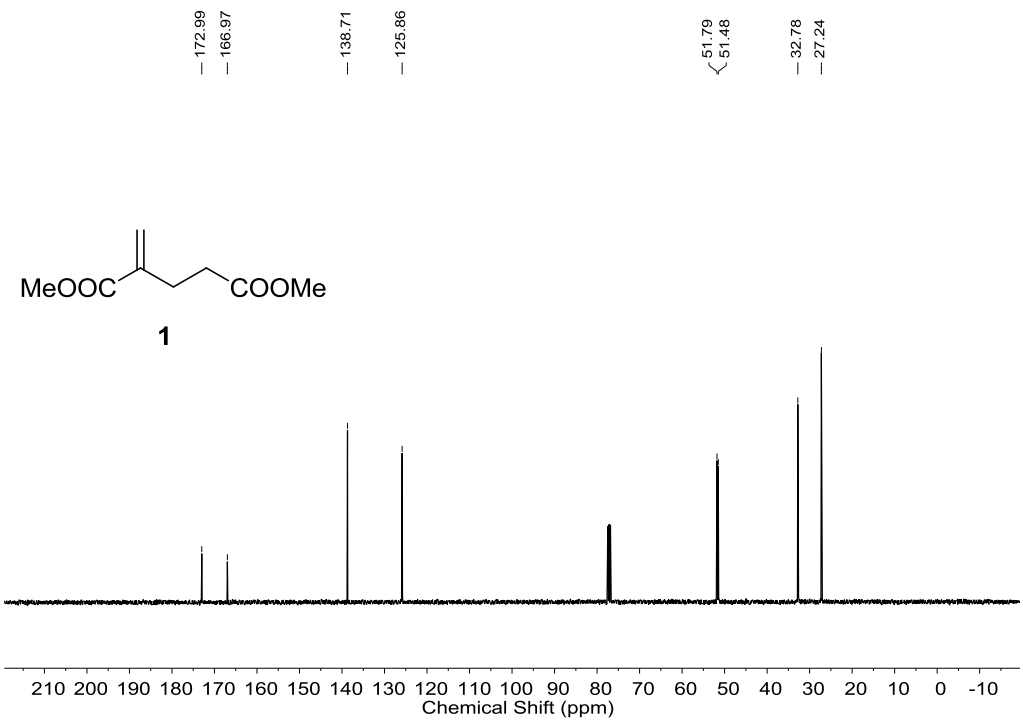


Figure S10: ^{13}C NMR spectrum of compound **1,** related to **Table 1.**

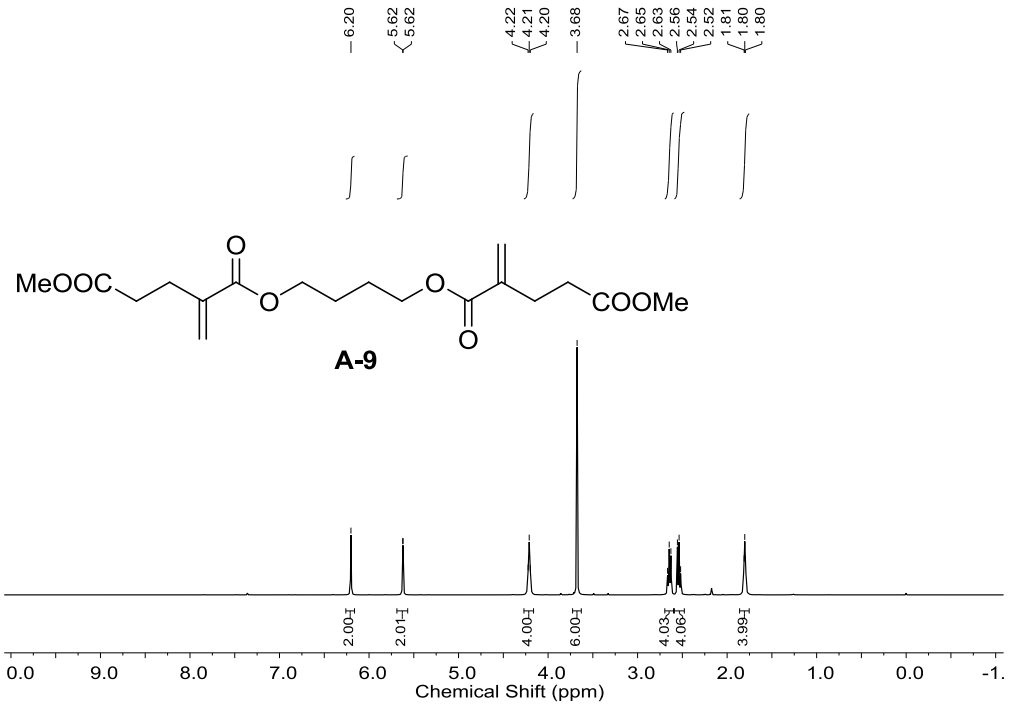


Figure S11: ^{1}H NMR spectrum of compound **A-9,** related to **Table 1.**

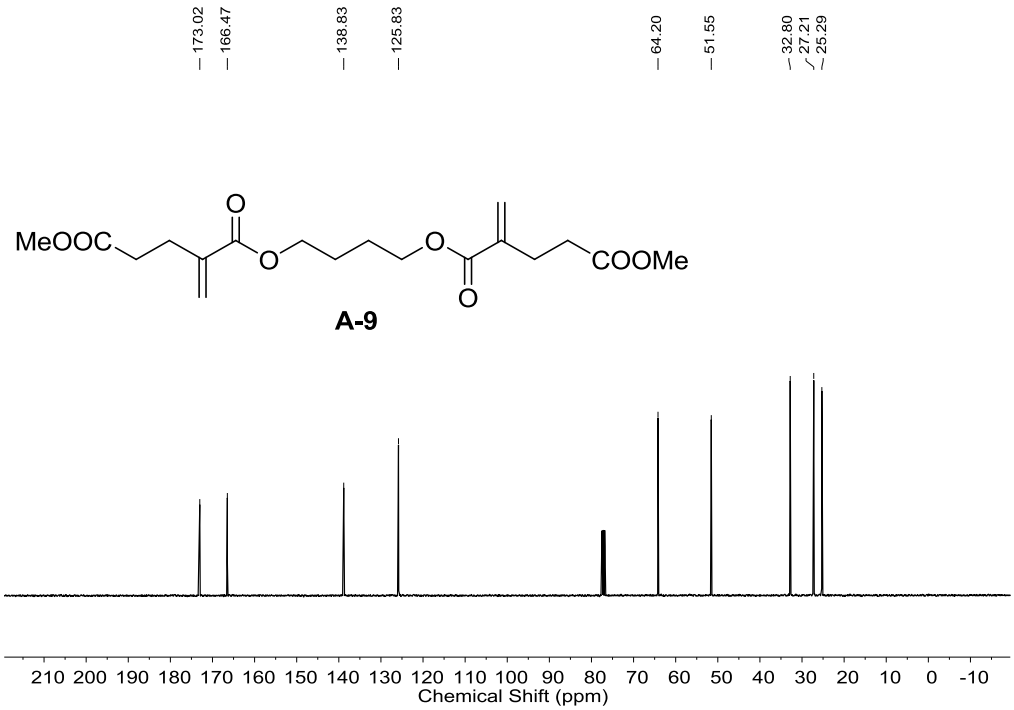


Figure S12: ^{13}C NMR spectrum of compound **A-9,** related to **Table 1.**

Characterization of polymers

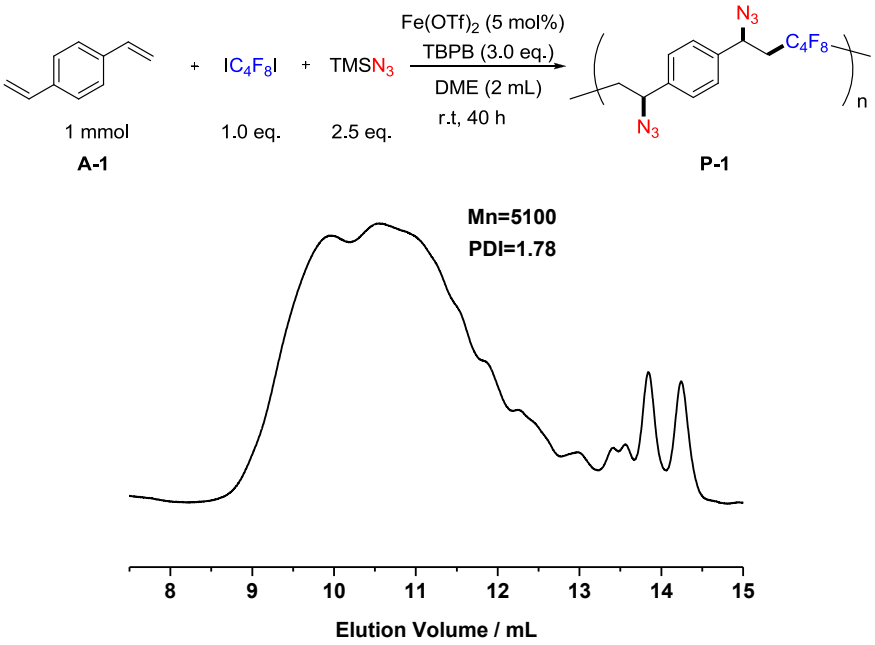


Figure S13: GPC curve of **P-1**, related to **Table 1.**

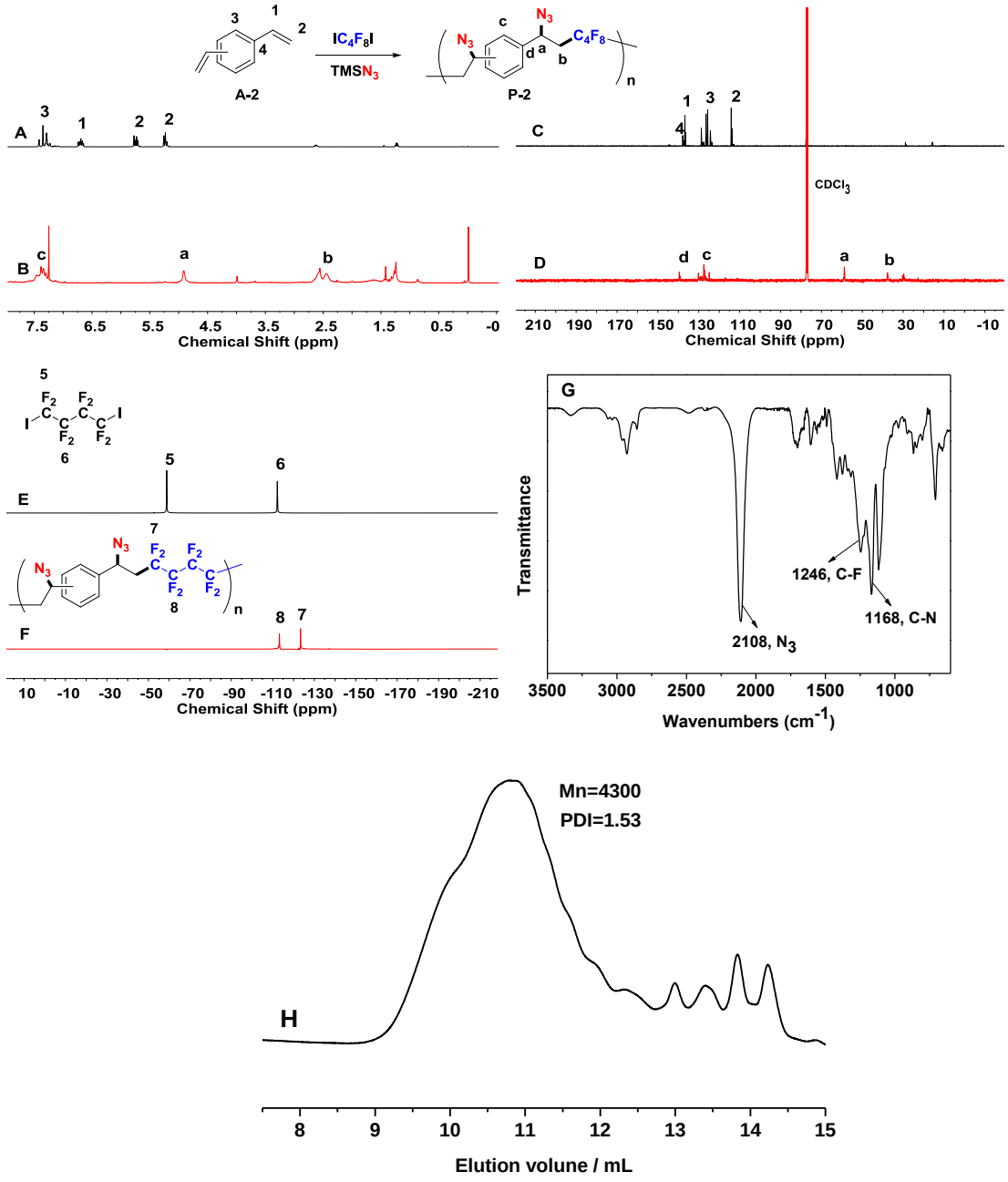


Figure S14: ^{1}H NMR spectra (A: **A-2**; B: **P-2**); ^{13}C NMR spectra (C: **A-2**; D: **P-2**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-2**); FT-IR spectrum of **P-2** (G). GPC curve of **P-2** (H), related to **Table 1.**

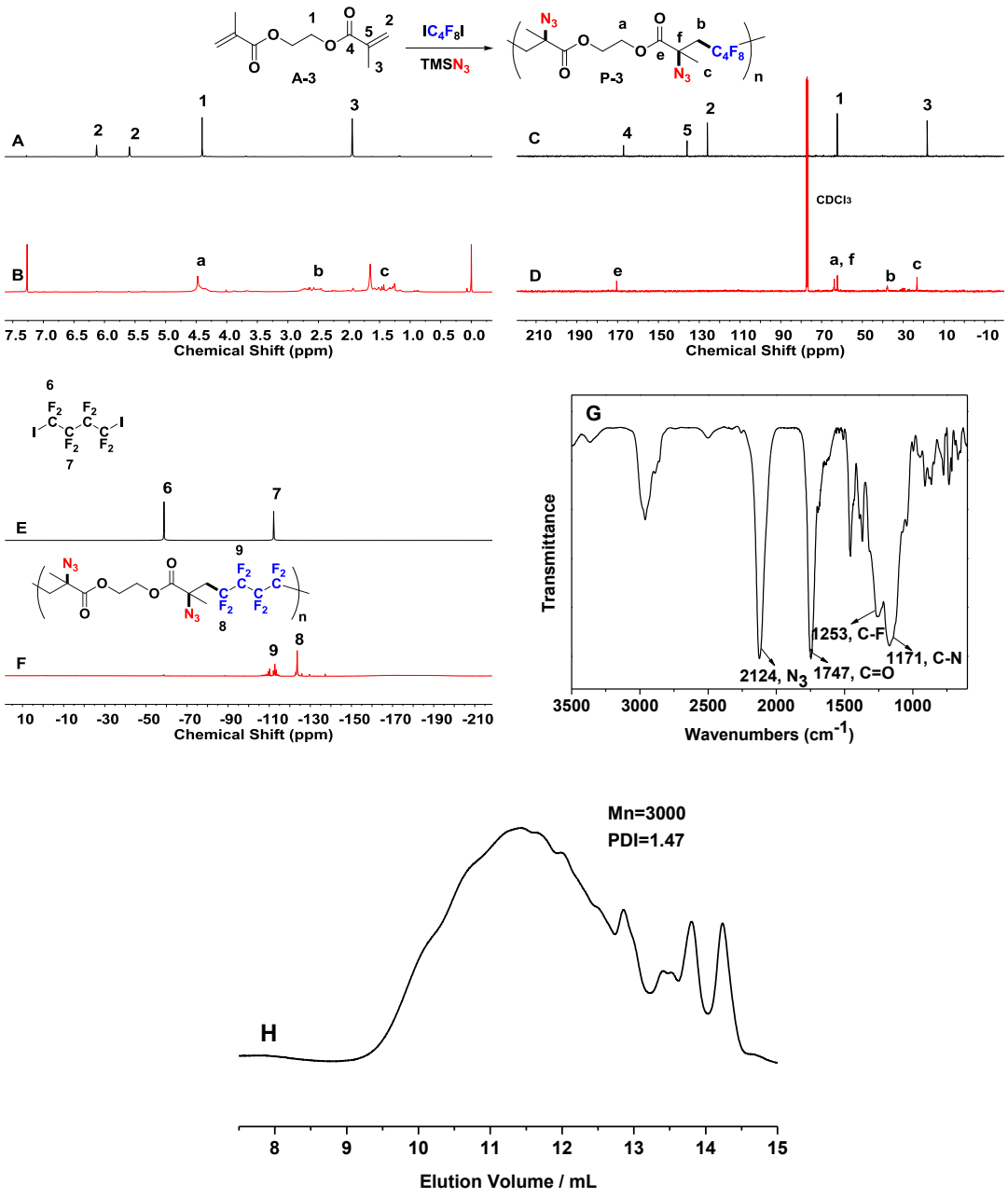


Figure S15: ^{1}H NMR spectra (A: **A-3**; B: **P-3**); ^{13}C NMR spectra (C: **A-3**; D: **P-3**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-3**); FT-IR spectrum of **P-3** (G). GPC curve of **P-3** (H), related to **Table 1.**

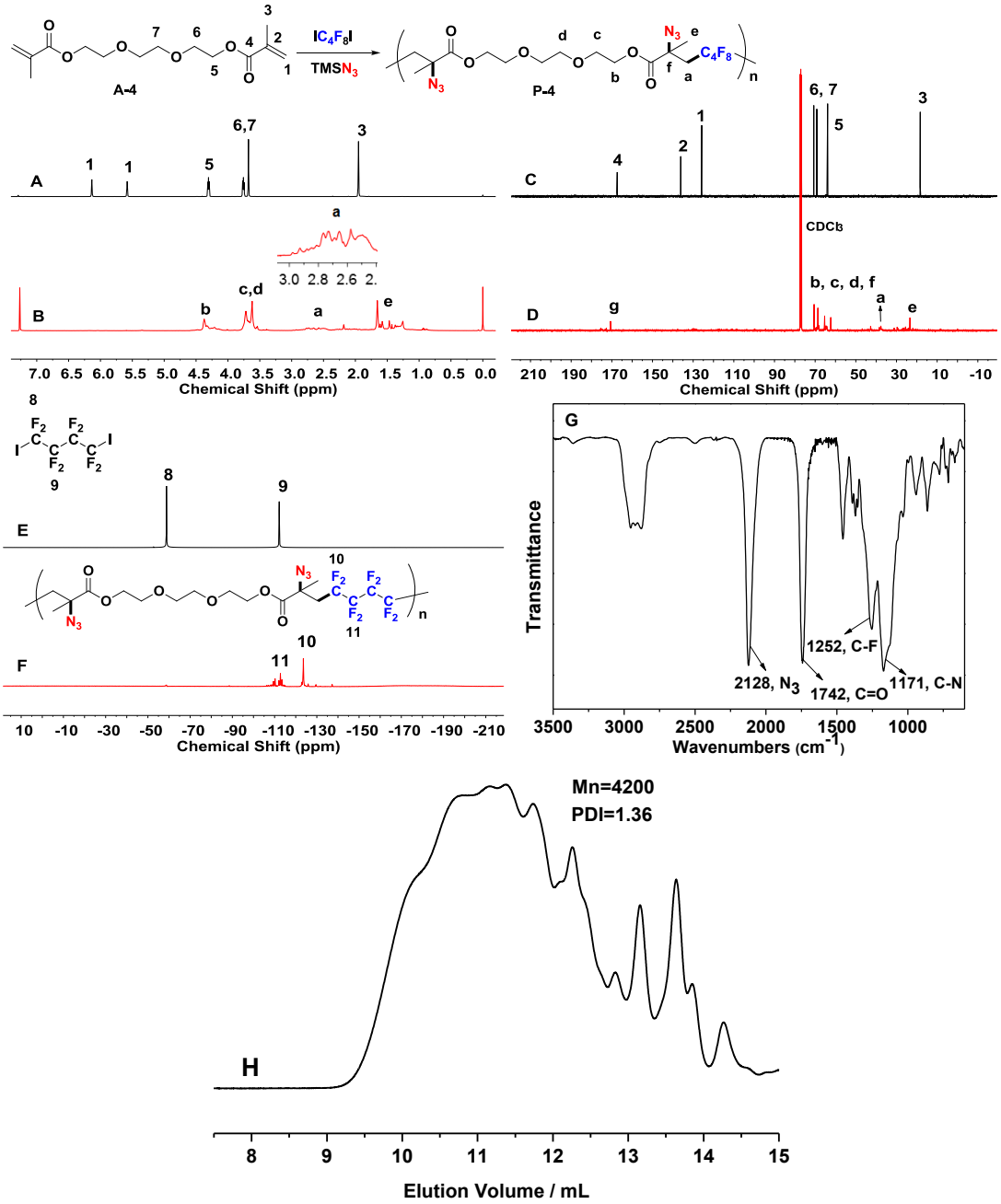


Figure S16: ^{1}H NMR spectra (A: **A-4**; B: **P-4**); ^{13}C NMR spectra (C: **A-4**; D: **P-4**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-4**); FT-IR spectrum of **P-4** (G). GPC curve of **P-4** (H), related to **Table 1.**

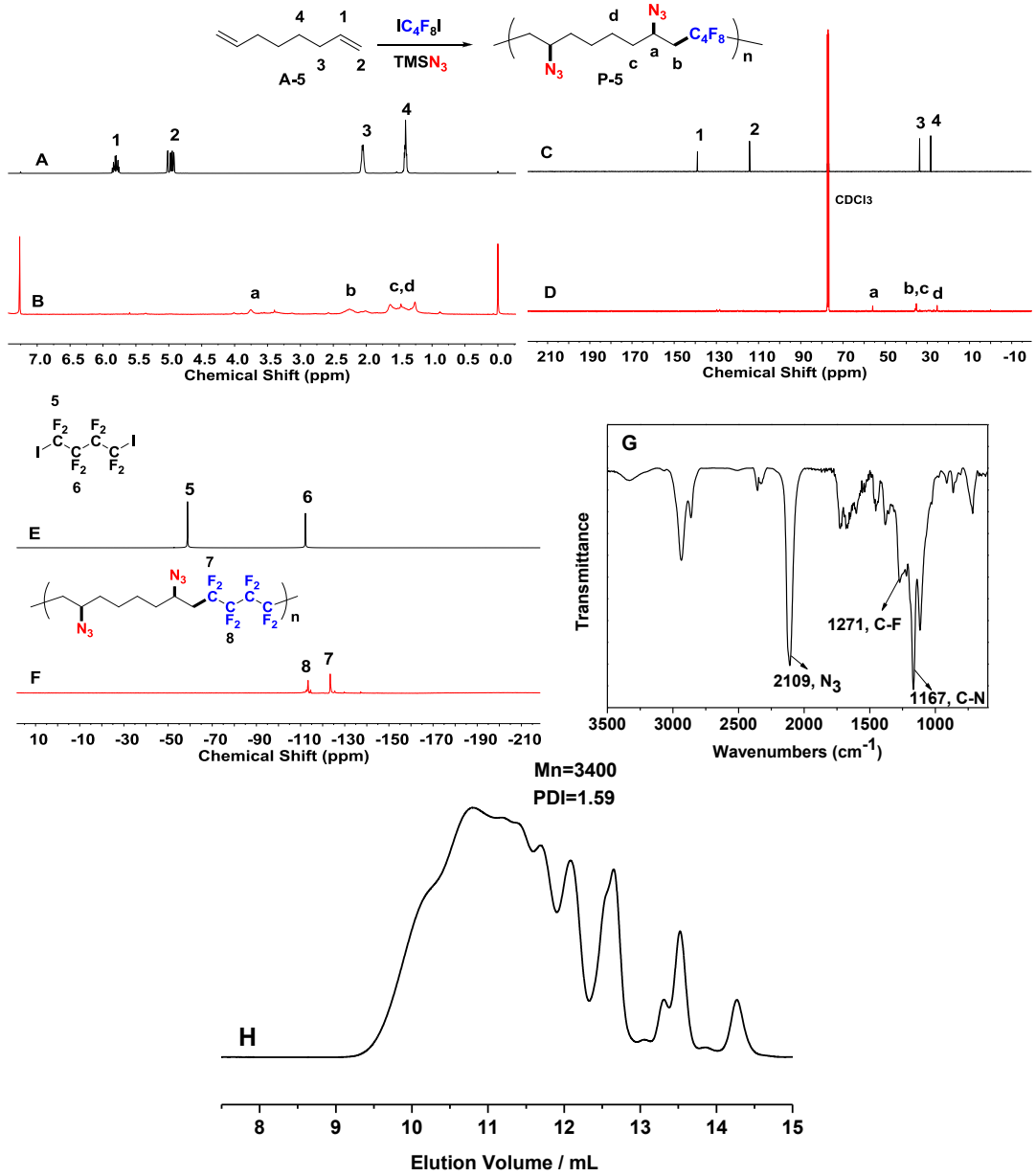


Figure S17: ^{1}H NMR spectra (A: **A-5**; B: **P-5**); ^{13}C NMR spectra (C: **A-5**; D: **P-5**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-5**); FT-IR spectrum of **P-5** (G), GPC curve of **P-5** (H), related to **Table 1.**

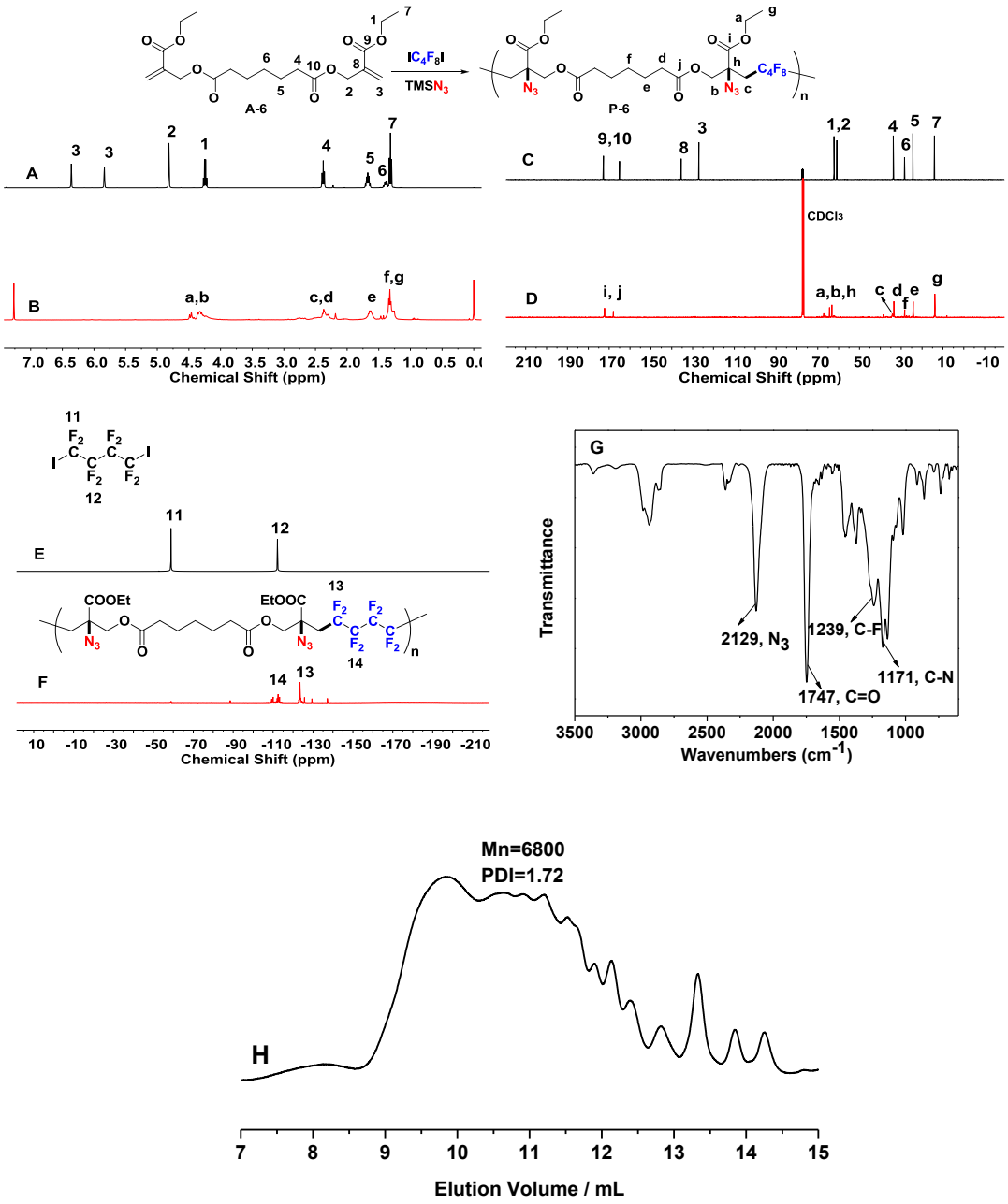


Figure S18: ^{1}H NMR spectra (A: **A-6**; B: **P-6**); ^{13}C NMR spectra (C: **A-6**; D: **P-6**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-6**); FT-IR spectrum of **P-6** (G), GPC curve of **P-6** (H). related to **Table 1.**

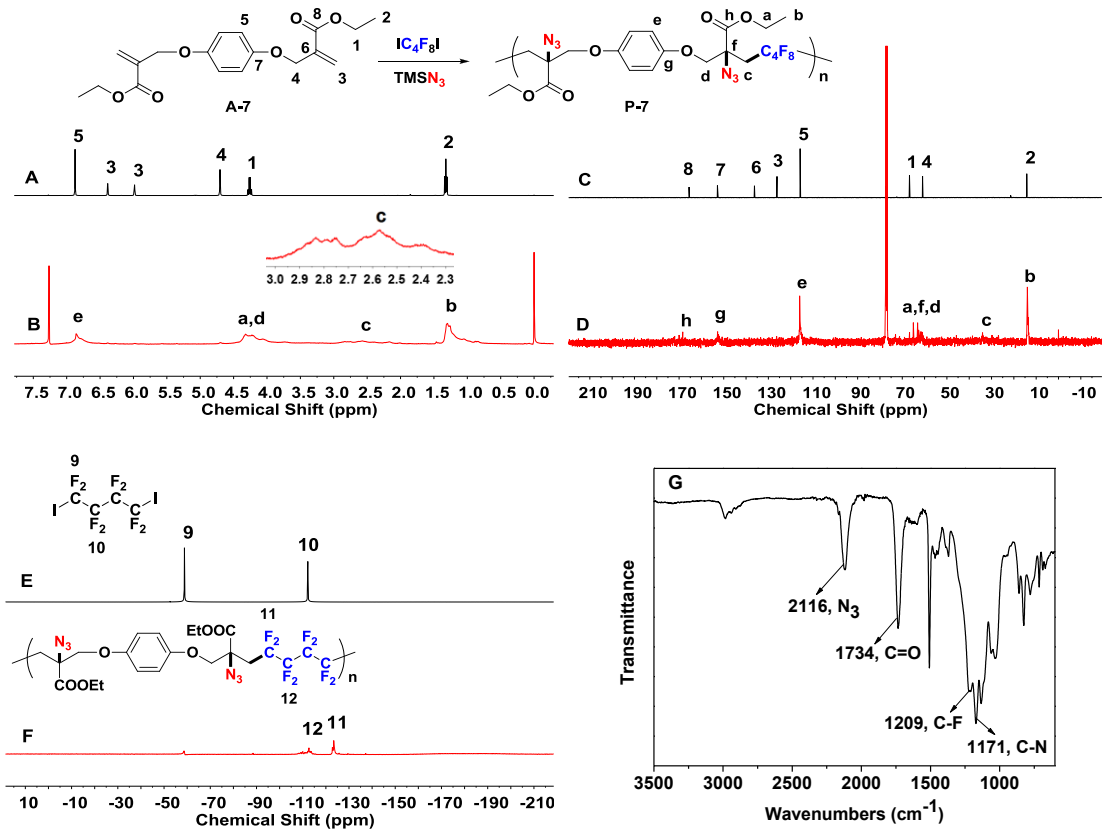


Figure S19: ^{1}H NMR spectra (A: **A-7**; B: **P-7**); ^{13}C NMR spectra (C: **A-7**; D: **P-7**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-7**); FT-IR spectrum of **P-7** (G), related to **Table 1.**

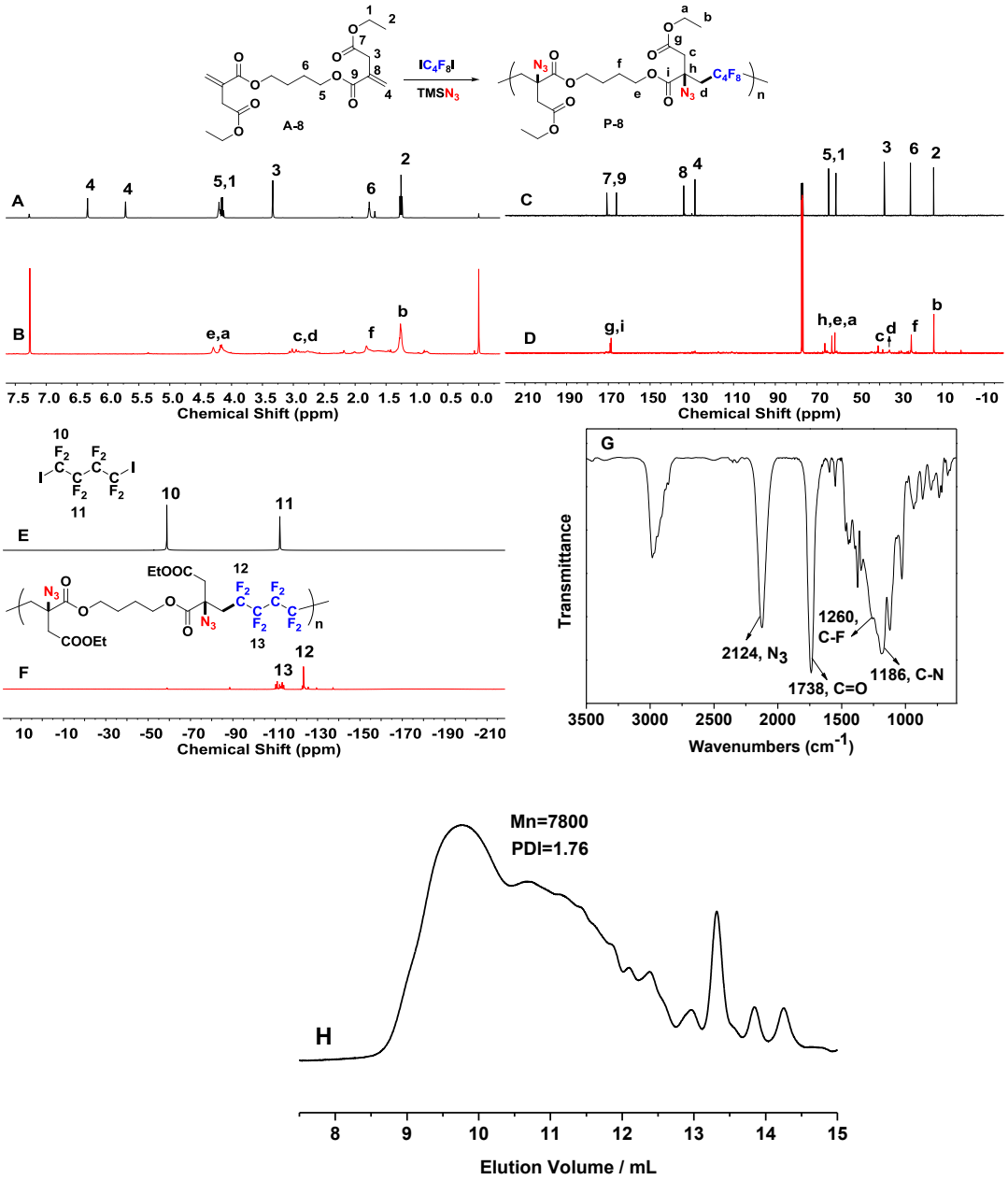


Figure S20: ^{1}H NMR spectra (A: **A-8**; B: **P-8**); ^{13}C NMR spectra (C: **A-8**; D: **P-8**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-8**); FT-IR spectrum of **P-8** (G). GPC curve of **P-8** (H), related to **Table 1.**

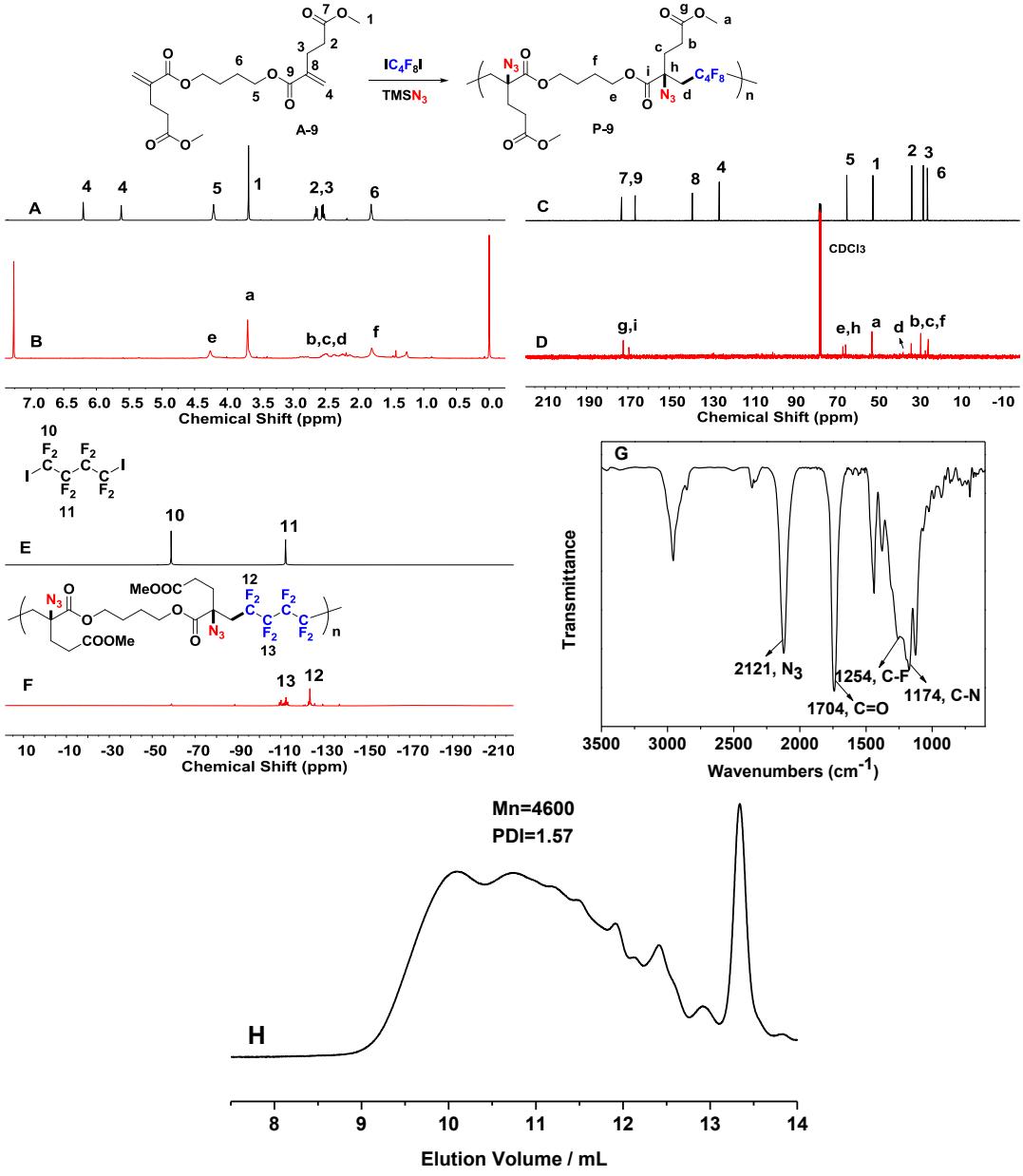


Figure S21: ^{1}H NMR spectra (A: **A-9**; B: **P-9**); ^{13}C NMR spectra (C: **A-9**; D: **P-9**); ^{19}F NMR spectra (E: 1,4-diiodoperfluorobutane; F: **P-9**); FT-IR spectrum of **P-9** (G). GPC curve of **P-9** (H), related to **Table 1.**

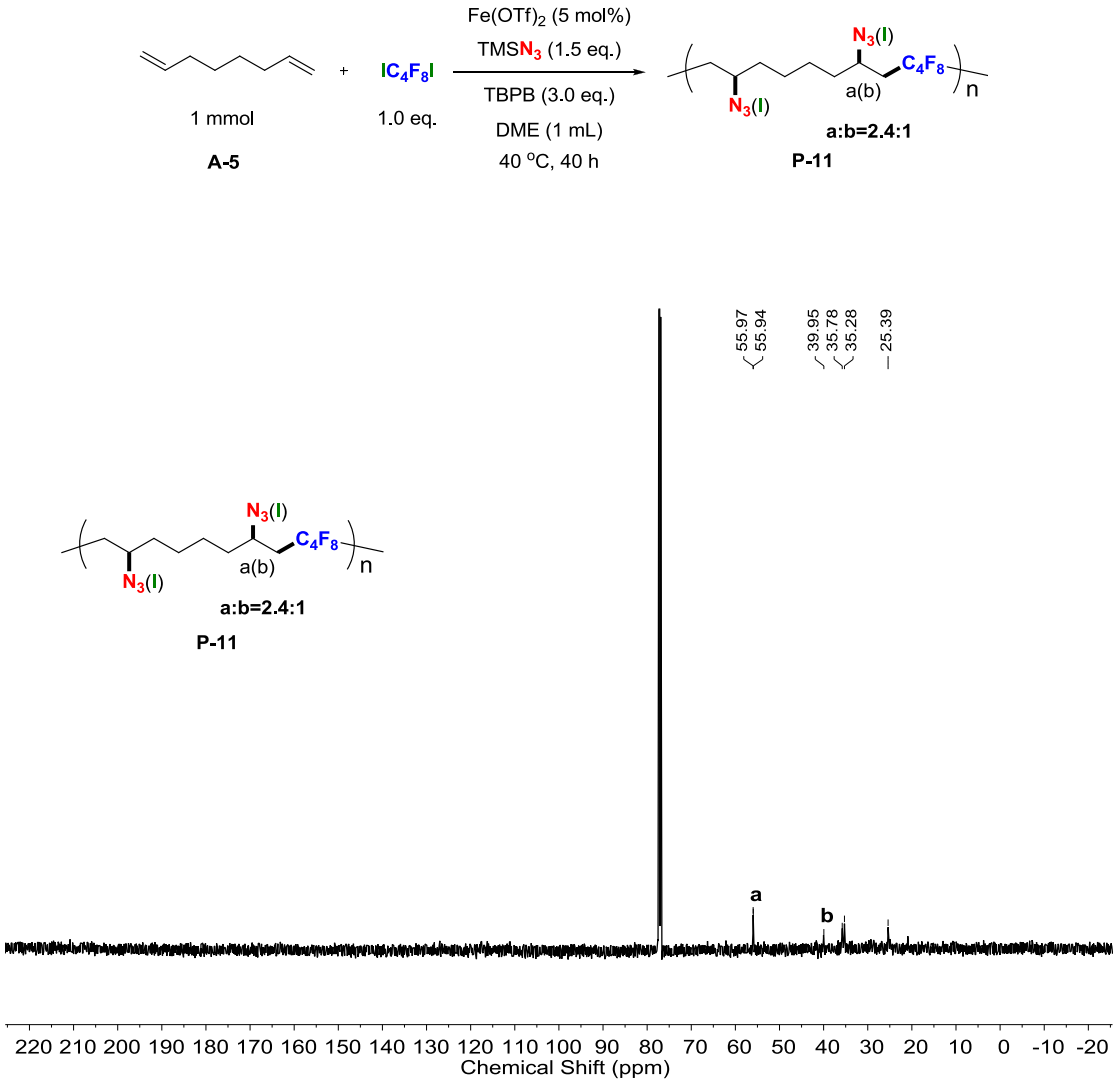


Figure S22: ^{13}C NMR spectrum of **P-11**, related to **Figure 2.**

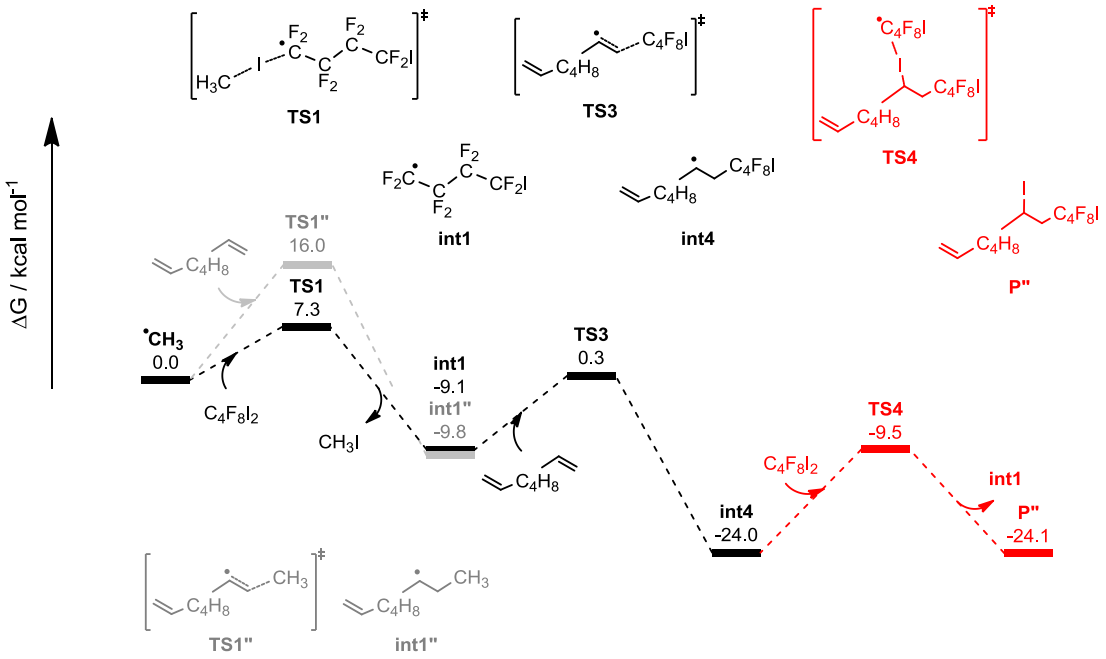


Figure S23: The free energy profile of radical cascade reactions (RCR) involving octa-1,7-diene, related to **Figure 4**.

Supplemental Tables

Table S1: chemicals and reagents, related to **Table 1.**

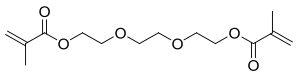
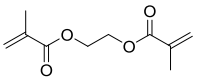
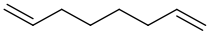
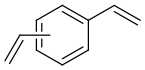
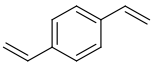
Alkenes	Company	Alkenes	Company
	Energy		Energy
	TCI		Energy
	Ref[(Gauler and Risch, 1998)]		

Table S2: Electronic potential energies and correction to zero point energies, thermal energies, enthalpies, free energies (in Hartree) and imaginary frequencies (cm^{-1}) of optimized structures calculated at the B3LYP-D3/Def2-TZVP/(SMD-DME)//B3LYP-D3/Def2-SVP, related to **Figure 4.**

Entry	Structure	$E_{0,sol}$	$E_{0,gas}$	$cZPE_{298,gas}$	$cU_{298,gas}$	$cH_{298,gas}$	$cG_{298,gas}$	Imaginary Frequency
1	CH_3	-39.860112	-39.809533	0.029384	0.032479	0.033423	0.009546	
2	$C_4F_8I_2$	-1547.166601	-1545.992430	0.048245	0.062374	0.063318	0.003196	
3	**TS1**	-1587.029020	-1585.806085	0.080794	0.098316	0.099260	0.026628	-194.1464
4	**int1**	-1249.304365	-1248.142518	0.046553	0.059175	0.060119	0.003641	
5	CH_3I	-337.738235	-337.675604	0.036197	0.039386	0.040331	0.010417	
6	1,4-divinylbenzene	-387.213853	-386.786608	0.166125	0.175249	0.176194	0.131222	
7	**TS1'**	-427.071701	-426.596410	0.198351	0.210336	0.211280	0.158575	-277.7003
8	**int1'**	-427.130784	-426.661644	0.204433	0.215252	0.216196	0.166881	
9	**int2**	-1636.580988	-1635.001002	0.216344	0.238356	0.239300	0.160461	
10	$\mathbf{Fe^{III}N_3}$	-4490.549692	-4487.360850	0.435082	0.480612	0.481556	0.350644	
11	**int3**	-6127.143891	-6122.393287	0.653113	0.722376	0.723320	0.537355	
12	^{7}**MECP**	-6127.143600	-6122.392388					
13	^{5}**MECP**	-6127.143659	-6122.392555					
14	**P**	-1800.876122	-1799.105518	0.233181	0.258064	0.259008	0.172626	
15	**TS2**	-3183.735859	-3180.983660	0.265616	0.303733	0.304677	0.179546	-94.0418
16	**P'**	-1934.429575	-1932.837980	0.219390	0.243225	0.244169	0.159437	
17	octa-1,7-diene	-313.381642	-313.029914	0.198267	0.208225	0.209169	0.162294	
18	**TS1"**	-353.234366	-352.835316	0.230847	0.243511	0.244456	0.189876	-389.5851
19	**int1"**	-353.280079	-352.887510	0.235373	0.247541	0.248486	0.194576	
20	**TS3**	-1562.688345	-1561.179150	0.245236	0.269011	0.269955	0.183373	-164.5514
21	**int4**	-1562.732438	-1561.228537	0.247619	0.270836	0.271780	0.188702	
22	**TS4**	-3109.900185	-3107.229354	0.298190	0.336511	0.337455	0.216133	-150.6131
23	**P"**	-1860.597726	-1859.082790	0.252179	0.276606	0.277550	0.191216	

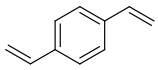
Transparent Methods

Materials and methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker-BioSpin AVANCE III HD or ECZ600S. Data for ^{1}H NMR spectra are reported relative to chloroform (7.26 ppm) as an internal standard and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform (77.23 ppm) as an internal standard and are reported in terms of chemical shift (ppm). Fourier transform infrared (FT-IR) spectra were measured on a Bruker Vertex 70 FT-IR spectrometer (KBr disk). Gel permeation chromatography (GPC) for polymer molecular weight analysis was carried out with TOSOH HLC-8320 system equipped with an refractive index (RI) detector, using polystyrenes as standards and THF was used as the eluent in a flow rate of 1.0 mL/min.

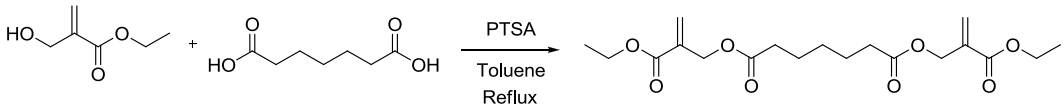
Raw Materials

The chemicals and reagents were purchased from following companies (**Table S1**) or synthesized following corresponding supplemental references:



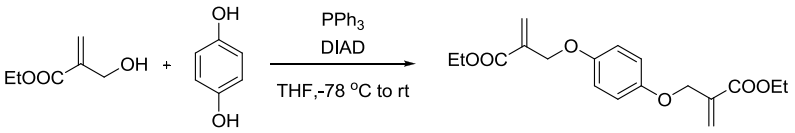
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.36 (s, 4H), 6.69 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.74 (d, *J* = 17.6 Hz, 2H), 5.23 (d, *J* = 10.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.12, 136.49, 126.42, 113.78.

Other materials were synthesized following corresponding procedure:

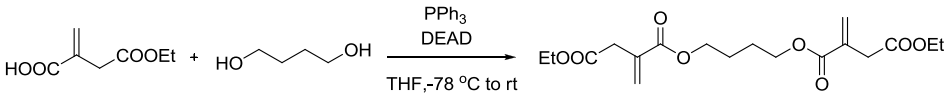


A mixture of ethyl 2-(hydroxymethyl)acrylate (2600 mg, 20 mmol, 2.5 eq.), pimelic acid (1280 mg, 4.0 mmol, 1.0 eq.), *p*-toluenesulfonic acid (0.2 mmol, 38 mg, 0.05 eq.) and toluene (50 mL) was refluxed with a Dean-Stark trap until the completion of water released. The organic layer concentrated by rotary evaporator under reduced pressure and the residue was purified by column chromatography on silica gel (PE:EA=10:1-3:1) to yield product as clean oil (2800 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.36 (s, 2H), 5.84 (d, *J* = 0.9 Hz, 2H), 4.82 (s, 4H), 4.24 (q, *J* = 7.1 Hz, 4H), 2.38 (t, *J* = 7.5 Hz,

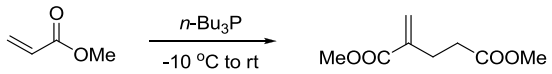
4H), 1.78 – 1.59 (m, 4H), 1.44 – 1.36 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 172.73, 165.03, 135.49, 126.99, 62.21, 60.86, 33.79, 28.40, 24.41, 14.07.



Ethyl 2-(hydroxymethyl)acrylate (2.73 g, 21 mmol, 2.1 eq.), 1,4-dihydroxybenzene (1.1 g, 10 mmol, 1.0 eq.) and triphenylphosphine (6.25 g, 24 mmol, 2.4 eq.) and THF (100 mL) were added to the single necked flask with a stirring bar under nitrogen protection. The solution was stirred at 0 °C and diisopropylazodicarboxylate (DIAD, 4.65 g, 24 mmol, 2.4 eq.) was added dropwise to the mixture. The solution was stirred at room temperature overnight. Then, the solution was concentrated by rotary evaporator under reduced and the residue was purified by column chromatography on silica gel (PE:EA=8:1-2:1) to yield product as white solid (601 mg, 36% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.87 (s, 4H), 6.39 (d, *J* = 1.1 Hz, 2H), 5.98 (d, *J* = 1.4 Hz, 2H), 4.70 (s, 4H), 4.26 (q, *J* = 7.1 Hz, 4H), 1.32 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) 165.54, 152.82, 136.23, 126.13, 115.77, 66.76, 60.91, 14.21.

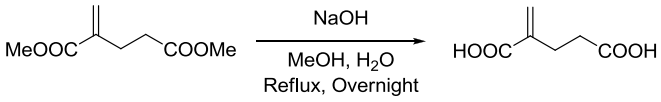


Monoethyl itaconate (1595 mg, 10.1 mmol, 2.02 eq.), 1,4-Butanediol (450 mg, 5 mmol, 1.0 eq.), triphenylphosphine (2882 mg, 11 mmol, 2.2 eq.) and THF (40 mL) were added to the single necked flask with a stirring bar under nitrogen protection. The solution was stirred at -78 °C and diethyl azodicarboxylate (DEAD, 1914 mg, 11 mmol, 2.2 eq.) was added dropwise to the mixture. The solution was stirred at -78 °C for 30 min and room temperature for 1 hour. Then, the solution was concentrated by rotary evaporator under reduced and the residue was purified by column chromatography on silica gel (PE:EA=8:1-2:1) to yield product as white solid (1221 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.33 (s, 2H), 5.72 (s, 2H), 4.28 – 4.09 (m, 8H), 3.33 (s, 4H), 1.77 (t, *J* = 2.8 Hz, 4H), 1.26 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) δ 170.73, 166.12, 133.87, 128.48, 64.46, 60.92, 37.77, 25.23, 14.14.

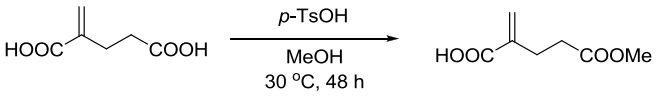


The synthesis method was following the supplemental reference.[(Tello-Aburto et al., 2014)] Methyl acrylate (4.5 mL, 50 mmol, 1.0 eq.) were added to the single necked flask with a stirring bar under nitrogen protection and cooed to -10 °C. Tributylphosphine (n-Bu_3P, 1.24 mL, 5.0 mmol, 0.1 eq.) was added to the flask slowly and stirred for 30 min. Then, the reaction mixture was then stirred at room temperature

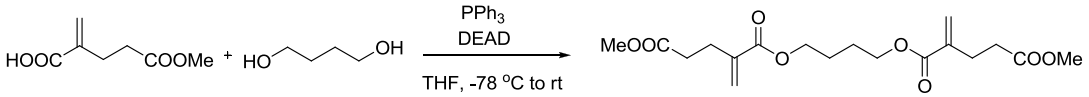
for 4 hours before excess acrylate was removed in rotary evaporator under reduced. The residue was purified by column chromatography on silica gel (PE:EA=40:1-5:1) to yield product as clean oil (2.4 g, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.20 (s, 1H), 5.61 (d, *J* = 1.0 Hz, 1H), 3.77 (s, 3H), 3.68 (s, 3H), 2.65 (t, *J* = 7.4 Hz, 1H), 2.53 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm) δ 172.99, 166.97, 138.71, 125.86, 51.79, 51.48, 32.78, 27.24.



The synthesis method was following the supplemental reference.[(Tello-Aburto et al., 2014)] Dimethyl ester (1 g, 5.8 mmol), methanol (6 mL), water (3 mL) and NaOH (697 mg, 17.4 mmol) were added to the single necked flask with a stirring bar. The flask was adapted to a condenser, and the solution refluxed overnight. The solution was then cooled to room temperature and acidified with 6N HCl solution. The solution was extracted with ethyl acetate. The organic layer was dried over $MgSO_4$, filtered and concentrated to give 818 mg of a white solid in 98% yield.



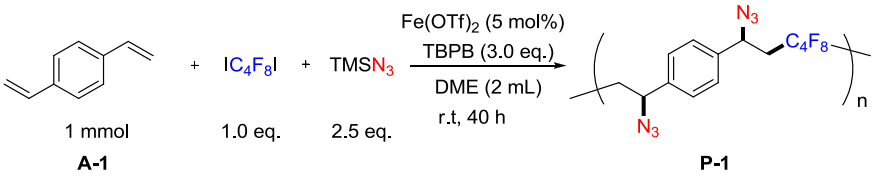
The synthesis method was following the supplemental reference.[(Tello-Aburto et al., 2014)] 2-methylenepentanedioic acid (1 g, 6.9 mmol), methanol (20 mL), and *p*-Toluenesulfonamide (*p*-TsOH, 60 mg, 0.34 mmol) were added to the single necked flask with a stirring bar. The solution was stirred at room temperature for 48 hours before concentrating in rotary evaporator under reduced. The residue was purified by column chromatography on silica gel (PE:EA=5:1-1:1) to yield product as clean oil (905 mg, 83% yield).



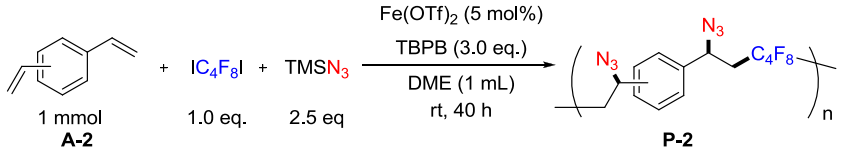
5-methoxy-2-methylene-5-oxopentanoic acid (1595 mg, 10.1 mmol, 2.02 eq.), 1,4-Butanediol (450 mg, 5 mmol, 1.0 eq.) and triphenylphosphine (2882 mg, 11 mmol, 2.2 eq.) and THF (20 mL) were added to the single necked flask with a stirring bar under nitrogen protection. The solution was stirred at -78 °C and diethyl azodicarboxylate (DEAD, 1914 mg, 11 mmol, 2.2 eq.) was added dropwise to the mixture. The solution was stirred at -78 °C for 1 hour and room temperature for 3 hours. Then, the solution was concentrated by rotary evaporator under reduced and the residue was purified by column chromatography on silica gel (PE:EA=10:1-5:1) to yield product as clean oil (1202 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.20 (s, 2H), 5.62 (d, *J* = 0.9 Hz, 2H), 4.21 (t, *J* = 4.9 Hz, 4H), 3.68 (s, 6H), 2.65 (t, *J* = 7.4 Hz, 4H), 2.54 (t, *J* = 7.1 Hz, 4H), 1.86-1.75 (m, 4H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ (ppm) 173.02, 166.47, 138.83, 125.83, 64.20, 51.55, 32.80, 27.21, 25.29.

Polymerization

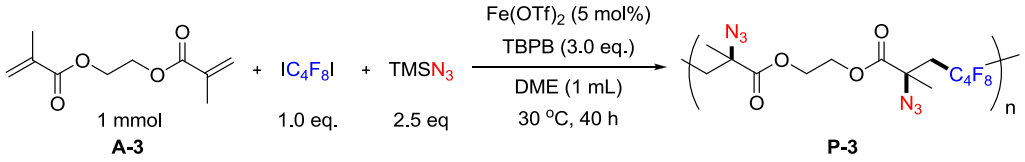


$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-1**) (130 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at r.t. The reaction mixture was stirred for 40 hours and then workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 157 mg polymer (**P-1**) was obtained as a viscous brown solid with a yield of 38%. *M*n: 5100, *M*w: 9100, *Đ*: 1.78. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.47-7.32 (broad, 4H), 5.06-4.72 (broad, 2H), 2.63-2.36 (broad, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 139.22, 127.52, 126.92, 58.62, 37.59 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -113.27 (s, 2F), -123.34 (s, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2927, 2855, 2109, 1427, 1378, 1246, 1168, 1106, 844, 734.

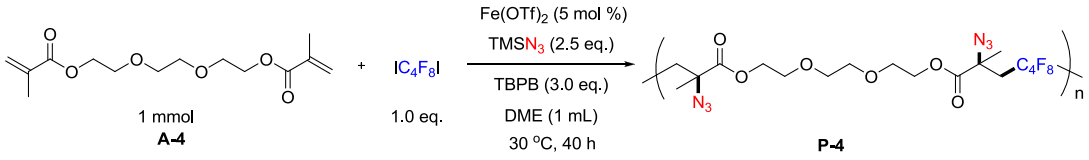


$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-2)** (130 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at r.t. The reaction mixture was stirred for 40 hours and then workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 203 mg polymer (**P-2**) was obtained as a viscous brown solid with a yield of 48%. *M*n: 4300, *M*w: 6600, *Đ*: 1.53. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.48-7.28 (broad, 4H), 5.09-4.72 (broad, 2H), 2.64-2.39 (broad, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 139.52, 139.21,

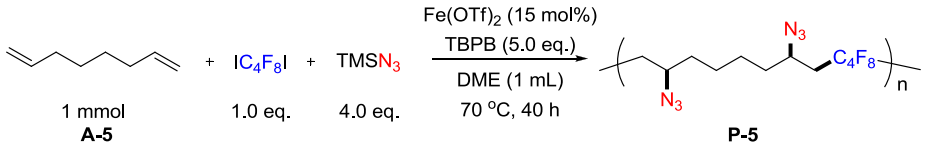
130.20, 127.51, 127.25, 124.89, 58.81, 37.65 (m). ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -113.17 (s, 2F), -123.35 (s, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2927, 2108, 1417, 1246, 1168, 1117, 708.



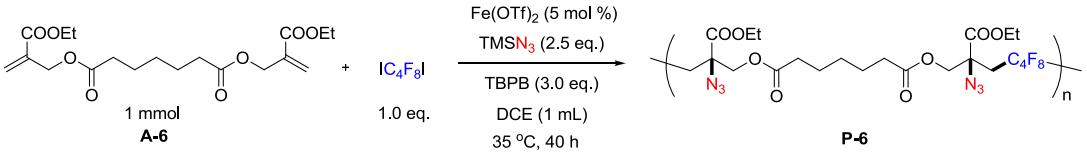
$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-3)** (198 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at r.t. The reaction mixture was stirred for 40 hours and then workup with dichloromethane/water. The organic solution was dried with anhydrous MgSO4 and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 242 mg polymer (**P-3)** was obtained as a viscous brown solid with a yield of 50%. *M*n: 3000, *M*w: 4400, *Đ*: 1.47. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.57-4.29 (broad, 4H), 2.89-2.41 (broad, 4H), 1.65-1.08 (broad, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.50, 63.75, 62.25, 37.98 (m), 23.23. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -112.73 (m, 2F), -123.69 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2961, 2124, 1747, 1456, 1369, 1253, 1171.



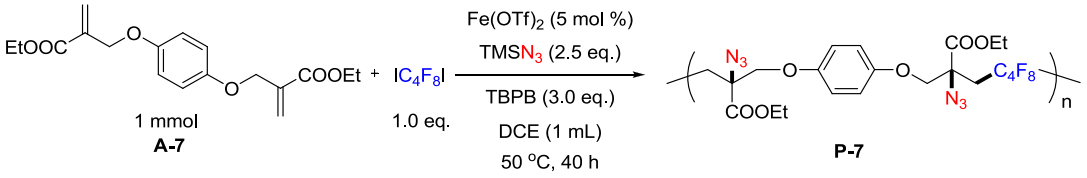
$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-4)** (286 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at r.t. The reaction mixture was stirred for 40 hours and then workup with dichloromethane/water. The organic solution was dried with anhydrous MgSO4 and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 340 mg polymer (**P-4)** was obtained as a viscous brown solid with a yield of 60%. *M*n: 4200, *M*w: 5700, *Đ*: 1.36. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.42-4.14(broad, 4H), 3.74-3.55 (broad, 8H), 2.98-2.34 (broad, 4H), 1.62-1.24 (broad, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 170.64, 70.52, 68.67, 65.33, 62.33, 37.72, 23.38. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -112.75 (m, 2F), -123.61 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2878, 2173, 1457, 1253, 1171, 941, 862.



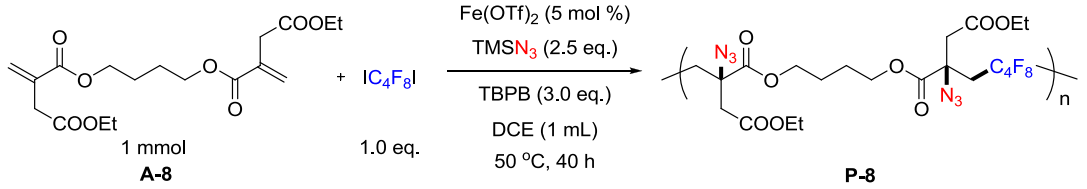
$Fe(OTf)_2$ (53.1 mg, 15 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-5)** (110 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (460 mg, 4.0 eq.), TBPB (970 mg, 5.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at 70 °C. The reaction mixture was stirred for 40 hours. Then, the reaction mixture was cooled to ambient temperature and workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 230 mg polymer (**P-5)** was obtained as a viscous brown solid with a yield of 58%. *M*n: 3400, *M*w: 5400, *Đ*: 1.59. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 3.85-3.48(broad, 2H), 2.36-1.98 (broad, 4H), 1.67-1.35 (broad, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 55.89, 35.71, 35.22, 25.36. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -113.42 (m, 2F), -123.42 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2936, 2862, 2109, 1271, 1167, 1116, 715.



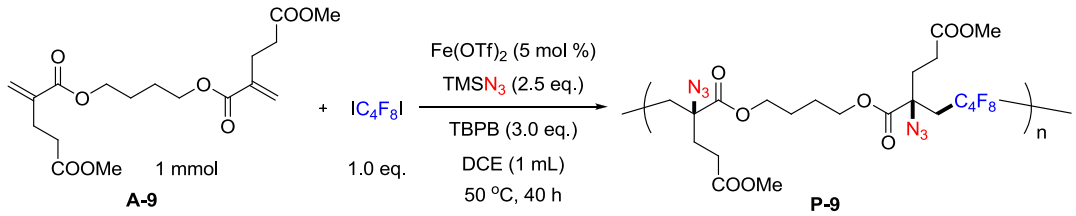
$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-6)** (384 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at r.t. The reaction mixture was stirred for 40 hours and then workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 434 mg polymer (**P-6)** was obtained as a viscous brown solid with a yield of 65%. *M*n: 6800, *M*w: 11700, *Đ*: 1.72. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.54-4.06 (broad, 8H), 2.86-2.24 (broad, 8H), 1.74-1.57 (broad, 4H), 1.38-1.21 (broad, 8H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.19, 167.97, 67.09, 64.36, 63.21, 34.28, 34.08, 33.52, 28.29, 24.22, 13.89. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -112.53 (s, 2F), -123.48 (s, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2937, 2129, 1747, 1456, 1372, 1239, 1171, 1136, 1018.



$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-7)** (334 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at 50 °C. The reaction mixture was stirred for 40 hours. Then, the reaction mixture was cooled to ambient temperature and workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 464 mg polymer (**P-7)** was obtained as a brown solid with a yield of 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.11-6.56 (broad, 4H), 4.57-3.76 (broad, 8H), 2.97-2.24 (broad, 4H), 1.37-1.11 (broad, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.37, 152.73, 115.98, 66.74, 65.03, 63.13, 34.02, 13.94. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -113.33 (m, 2F), -123.40 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2983, 2116, 1734, 1507, 1209, 1171, 1134, 1032, 825, 713.

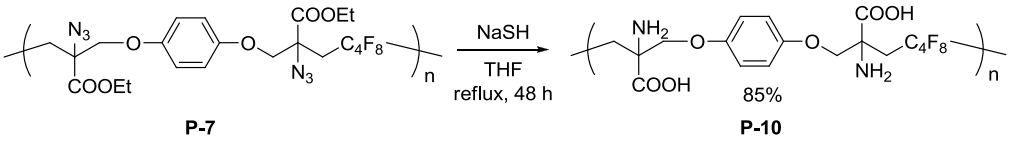


$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-8)** (370 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at 50 °C. The reaction mixture was stirred for 40 hours. Then, the reaction mixture was cooled to ambient temperature and workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 510 mg polymer (**P-8)** was obtained as a viscous brown solid with a yield of 78%. *M*n: 7800, *M*w: 13700, *Đ*: 1.76. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.39-4.03 (broad, 8H), 3.09-2.54 (broad, 8H), 1.87-1.74 (broad, 4H), 1.29-1.25 (broad, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 169.11, 168.68, 66.24, 62.88, 61.43, 40.71, 35.35, 24.82, 13.99. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -112.71 (m, 2F), -123.35 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2982, 2124, 1738, 1446, 1374, 1260, 1186, 1121, 1027, 935.



$Fe(OTf)_2$ (17.7 mg, 5 mol%) and 0.5 mL DME were added into a flame dried schlenk tube with a stirring bar under nitrogen protection. The mixture of alkene (**A-9)** (370 mg, 1 mmol, 1.0 equiv), IC_4F_8I (453 mg, 1.0 eq.), $TMSN_3$ (287.5 mg, 2.5 eq.), TBPB (582 mg, 3.0 eq.) and DME (0.5 mL) was added to the schlenk tube drop by drop at 50 °C. The reaction mixture was stirred for 40 hours. Then, the reaction mixture was cooled to ambient temperature and workup with dichloromethane/water. The organic solution was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The mixture was diluted with 1.5 mL THF, and then precipitated in 60 mL of petroleum ether. The precipitates were filtered and washed with petroleum ether and dried under vacuum to a constant weight. 476 mg polymer (**P-9)** was obtained as a viscous brown solid with a yield of 73%. *M*n: 4600, *M*w: 7200, *Đ*: 1.57. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 4.35-4.09 (broad, 4H), 3.73-3.63 (broad, 6H), 2.93-2.16 (broad, 12H), 1.83-1.73 (broad, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 172.25, 169.53, 66.09, 64.82, 52.01, 37.00, 33.06, 28.46, 24.81. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm): -112.36 (m, 2F), -123.51 (m, 2F). FT-IR (KBr disk), *v* (cm^{-1}): 2957, 2121, 1740, 1439, 1378, 1254, 1174, 1125.

Reduction and deprotection of poly(anmino acids) precursor



Polymer **P-7** (0.5 mmol, 309 mg, 1.0 equiv), NaSH (20 mmol, 1120 mg, 40 eq.) and THF (20 mL) were added into a round-bottomed flask with a stirring bar. The reaction mixture was heated to reflux for 48 hours. Then, the reaction mixture was cooled to ambient temperature and workup with dichloromethane/water. The pH of the water solution was adjusted to neutral. After stand still for 24 hours, a brown solid was precipitated. The precipitates were filtered and dried under vacuum to a constant weight. 434 mg polymer **P-10** was obtained as a viscous brown solid with a yield of 85%. FT-IR (KBr disk), *v* (cm^{-1}): 3385, 2960, 2921, 1626, 1507, 1259, 1097, 998, 797, 622.

Computational method and details

In this study, the hybrid density functional theory B3LYP[(Becke, 1993, Lee et al., 1988)] with Grimme's dispersion correction (DFT-D3)(Grimme et al., 2010, Grimme et al., 2011) was employed for all of geometrical optimizations, thermal energy calculations and frequency analyses. Basis sets Def2-SVP were employed here for all atoms.[(Weigend and Ahlrichs, 2005, Weigend, 2006)] Transition state structures were searched by simply performing a crude relaxed potential energy surface (RPES) scan connecting reactants and products, and then optimized by the rational function optimization (RFO) method of TS.[(Besalú and Bofill, 1998)] Furthermore, imaginary frequencies for all of transition states were verified to be the only one in theirs vibrations and were confirmed the correctness by viewing the normal mode vector. The intrinsic reaction coordinate (IRC) path calculations were also performed to confirm the connection from transition states to intermediates or products.[(Fukui, 1981)] All optimized stationary points were characterized by frequency calculation for identification of minimum points and saddle points. Then, single point solvated energies were calculated at the B3LYP-D3/Def2-TZVP[(Weigend and Ahlrichs, 2005, Weigend, 2006)] level of theory with SMD solvation model calculation in DME solution based upon the optimized structures,[(Marenich et al., 2009)] and the reported Gibbs free energy is obtained by adding the solution-phase electronic energy with the gas-phase Gibbs free energy correction for saving the computational time consumption. On the other hand, for benzyl and alkyl radical coupling with the sextet $Fe^{III}N_3$ species to grab the azide, the minimum energy crossing point (MECP) crossing the septet and quintet state was also located by using the hybrid approach method of Harvey.[(Harvey et al., 1998)] All calculations were performed by the Gaussian 09 package.[(Frisch et al., 2013)]

Coordinate of optimized structures

Structure S1. CH_3

E(B3LYP)sol = -39.8601119636 E(B3LYP)gas = -39.8095333169

6	0.000000	-0.000026	0.000255
1	-0.938485	-0.556488	-0.000510
1	0.951282	-0.534327	-0.000510
1	-0.012796	1.090973	-0.000510

Structure S2. $C_4F_8I_2$

E(B3LYP)sol = -1547.16660136 E(B3LYP)gas = -1545.99243017

6	0.716069	0.320103	0.009859
9	0.812442	1.203107	1.017921
9	0.876382	0.958595	-1.159511
6	1.850443	-0.737428	0.181183
9	1.794943	-1.250750	1.410548
9	1.679811	-1.719230	-0.707777
53	3.834461	0.180302	-0.116841
6	-0.716018	-0.319887	0.009569
6	-1.850445	0.737527	0.181429
53	-3.834450	-0.180447	-0.116822
9	-0.812527	-1.203543	1.017272
9	-0.876250	-0.957712	-1.160105
9	-1.679978	1.719585	-0.707636
9	-1.794918	1.250589	1.410610

Structure S3. TS1

E(B3LYP)sol = -1587.02901951 E(B3LYP)gas = -1585.80608450

6	-0.433094	-0.197180	0.060917
9	-0.564681	-0.962420	1.158835
9	-0.640821	-0.945697	-1.034739
6	-1.498433	0.926030	0.121127
9	-1.422110	1.582497	1.275846
9	-1.335403	1.778638	-0.889598
53	-3.658429	-0.005296	-0.028925
6	1.033311	0.353154	-0.011007
6	2.113427	-0.746353	0.225449
53	4.140491	0.047600	-0.148633
9	1.194406	1.305365	0.924398
9	1.207574	0.891049	-1.228601
9	1.887506	-1.776940	-0.593020
9	2.046664	-1.171963	1.486958
6	-5.963675	-1.145303	-0.311979
1	-6.221267	-1.315176	0.736679

1	-6.503691	-0.349726	-0.831987
1	-5.691783	-2.024069	-0.901868

Frequencies -- -194.1464

Red. masses -- 10.4902

Frc consts -- 0.2330

IR Inten -- 3.5630

Structure S4. int1

E(B3LYP)sol = -1249.30436511 E(B3LYP)gas = -1248.14251772

6	-2.026832	0.544073	0.119804
9	-2.114062	1.465041	-0.858973
9	-2.097865	1.148986	1.320718
6	-3.209915	-0.401118	-0.012704
9	-3.422651	-0.876466	-1.221336
9	-3.290903	-1.332009	0.915923
6	-0.643559	-0.180728	0.016016
6	0.579469	0.778857	-0.035845
53	2.475244	-0.354709	-0.009943
9	-0.653063	-0.926755	-1.105199
9	-0.533467	-0.988123	1.084681
9	0.543225	1.598685	1.017227
9	0.526239	1.505425	-1.152667

Structure S5. CH_3I

E(B3LYP)sol = -337.738234904 E(B3LYP)gas = -337.675603497

6	-1.841716	0.000003	-0.000066
1	-2.176791	-0.888710	-0.546994
1	-2.175209	-0.029724	1.043532
1	-2.176797	0.918400	-0.495537
53	0.331681	0.000000	-0.000011

Structure S6. 1,4-divinylbenzene

E(B3LYP)sol = -387.213853145 E(B3LYP)gas = -386.786607924

6	0.889447	-1.073353	0.000001
6	-0.483200	-1.299695	-0.000002
6	-1.409004	-0.236016	-0.000004
6	-0.889460	1.073306	-0.000004
6	0.483011	1.299552	-0.000001
6	1.409005	0.235760	0.000002
1	1.567346	-1.929564	0.000003
1	-0.855737	-2.328137	-0.000002
1	-1.567501	1.929378	-0.000006

1	0.855689	2.327959	0.000000
6	-2.849711	-0.535666	-0.000007
1	-3.092915	-1.604998	-0.000013
6	-3.867310	0.339515	-0.000003
1	-3.713648	1.422288	0.000004
1	-4.903891	-0.006174	-0.000005
6	2.849688	0.535625	0.000006
1	3.092451	1.605117	0.000005
6	3.867583	-0.339174	0.000009
1	3.713919	-1.421950	0.000010
1	4.903982	0.006955	0.000011

Structure S7. TS1'

E(B3LYP)sol = -427.071700529 E(B3LYP)gas = -426.596410056

6	1.494909	1.053155	0.267042
6	0.163915	1.441233	0.177414
6	-0.844965	0.545115	-0.244024
6	-0.445095	-0.771044	-0.561543
6	0.887389	-1.157987	-0.469434
6	1.893849	-0.260388	-0.055812
1	2.238246	1.782675	0.595739
1	-0.113815	2.466968	0.436696
1	-1.189191	-1.504606	-0.878936
1	1.164190	-2.185989	-0.720976
6	-2.230062	1.001537	-0.320099
1	-2.409805	2.013339	0.061131
6	-3.299642	0.288201	-0.760468
1	-3.187397	-0.678247	-1.255413
1	-4.285937	0.750899	-0.823271
6	-4.094550	-1.065499	1.198728
1	-3.131453	-1.543472	1.382835
1	-4.391269	-0.235727	1.841323
1	-4.872824	-1.631599	0.683366
6	3.286212	-0.725641	0.022533
1	3.431868	-1.776631	-0.254974
6	4.367499	-0.017803	0.387135
1	4.312223	1.035026	0.677805
1	5.358418	-0.477909	0.405846

Frequencies -- -277.7003

Red. masses -- 9.5754

Frc consts -- 0.4351

IR Inten -- 7.1976

Structure S8. int1'

E(B3LYP)sol = -427.130783744 E(B3LYP)gas = -426.661643721

6	1.474726	1.090887	0.109045
6	0.145798	1.449735	0.027839
6	-0.889076	0.482224	-0.198611
6	-0.465287	-0.878421	-0.334120
6	0.871872	-1.225447	-0.249531
6	1.885664	-0.262053	-0.026954
1	2.223110	1.867284	0.282494
1	-0.137840	2.500380	0.137594
1	-1.207833	-1.660371	-0.504312
1	1.158698	-2.275854	-0.356613
6	-2.236715	0.882560	-0.275729
1	-2.450136	1.946325	-0.123727
6	-3.406831	-0.034798	-0.464565
1	-3.153462	-0.841867	-1.174176
1	-4.237456	0.526461	-0.924937
6	-3.900173	-0.665545	0.853864
1	-3.103917	-1.265151	1.322652
1	-4.200007	0.110248	1.576369
1	-4.768057	-1.322131	0.678354
6	3.280439	-0.689615	0.052322
1	3.435903	-1.768574	-0.069142
6	4.367658	0.080388	0.252992
1	4.306005	1.164277	0.383407
1	5.366544	-0.360515	0.292718

Structure S9. int2

E(B3LYP)sol = -1636.58098801 E(B3LYP)gas = -1635.00100231

6	-6.369876	0.138328	-0.670105
6	-5.339925	1.047173	-0.787222
6	-4.106418	0.888776	-0.072292
6	-3.996190	-0.269403	0.760770
6	-5.037639	-1.173352	0.868632
6	-6.255586	-1.004043	0.165866
1	-7.289523	0.305003	-1.234861
1	-5.457815	1.917394	-1.438786
1	-3.068354	-0.461418	1.300835
1	-4.917725	-2.050404	1.511141
6	-3.088388	1.850020	-0.207932
1	-3.251074	2.670970	-0.911122
6	-1.773821	1.821139	0.507830
1	-1.854897	1.382892	1.512845
1	-1.373764	2.839808	0.624116
6	-7.319364	-1.993258	0.323057
1	-7.077369	-2.823683	0.997095
6	-8.534589	-1.990812	-0.258122
1	-8.859262	-1.202357	-0.942559

1	-9.250602	-2.792248	-0.061396
6	-0.709461	1.023965	-0.247912
6	0.675766	1.081384	0.456312
9	-0.560821	1.512762	-1.502350
9	-1.071118	-0.281921	-0.349753
9	1.130500	2.350522	0.367612
9	0.504349	0.782687	1.763299
6	1.746039	0.097143	-0.119562
6	3.195202	0.434541	0.348212
9	1.721342	0.140689	-1.461674
9	1.427463	-1.140216	0.294093
53	4.609907	-1.153046	-0.245852
9	3.213295	0.564972	1.678325
9	3.586191	1.583382	-0.204256

Structure S10. $Fe^{III}N_3$

E(B3LYP)sol = -4490.54969239 E(B3LYP)gas = -4487.36084973

26	-0.584317	-0.974223	0.312620
8	-2.817943	1.550377	1.251964
16	-3.108980	0.958953	-0.051873
8	-3.019012	1.800449	-1.252969
8	-2.422125	-0.407121	-0.255153
6	-4.881270	0.364037	0.005119
9	-5.694623	1.403852	0.159318
9	-5.185824	-0.263540	-1.131526
9	-5.046833	-0.477474	1.021918
8	2.405107	-3.571557	-0.603987
16	2.593557	-2.167558	-0.220195
8	1.319733	-1.548351	0.340222
8	3.763893	-1.798839	0.576402
6	2.833114	-1.257198	-1.858017
9	2.125111	-1.831963	-2.831084
9	4.118233	-1.293868	-2.187219
9	2.454862	0.023689	-1.755381
8	-1.046575	-3.025591	-0.172610
8	-0.399934	-1.079119	-1.930477
6	-0.794217	-3.371340	-1.541160
1	0.274918	-3.607968	-1.662726
1	-1.403912	-4.249411	-1.816278
6	-1.178631	-2.181790	-2.385501
1	-0.952135	-2.391670	-3.445596
1	-2.250439	-1.941020	-2.274875
6	-0.637257	-4.036353	0.761081
1	-1.211533	-4.958607	0.575171
1	0.441759	-4.226140	0.660054
1	-0.859764	-3.648861	1.761463
6	-0.563418	0.104446	-2.717280

1	-1.588149	0.493677	-2.625804
1	0.141868	0.845047	-2.330608
1	-0.315317	-0.120422	-3.767670
8	0.044671	0.956202	0.219651
6	1.078963	1.645048	0.252776
8	2.142186	1.305358	0.909939
6	1.140178	2.909371	-0.515051
6	-0.034748	3.415157	-1.101655
6	2.357533	3.598824	-0.657507
6	0.017407	4.606266	-1.825484
1	-0.979319	2.882503	-0.980703
6	2.401137	4.783519	-1.390701
1	3.260153	3.187885	-0.202877
6	1.231159	5.287959	-1.972834
1	-0.895869	5.003648	-2.274099
1	3.347262	5.316482	-1.510624
1	1.266906	6.219436	-2.543902
7	-1.073956	-1.134784	2.144453
7	-2.082483	-0.954066	2.787247
14	2.697026	0.988534	2.538912
7	-3.018922	-0.800159	3.425642
6	2.104952	-0.633012	3.230435
6	4.547009	1.034866	2.310408
6	1.987947	2.446455	3.484066
1	2.382101	-0.668909	4.298485
1	1.015271	-0.749557	3.146427
1	2.589744	-1.467924	2.708754
1	4.830820	0.235582	1.607638
1	4.887997	2.004461	1.914123
1	5.063145	0.850740	3.266953
1	2.302604	3.405183	3.041661
1	0.885553	2.409888	3.477340
1	2.317016	2.428764	4.536228

Structure S11. int3

E(B3LYP)sol = -6122.39328728 E(B3LYP)gas = -6122.39328728

6	0.686471	6.302697	0.136802
6	0.434338	5.156544	0.857970
6	-0.893916	4.640726	1.013946
6	-1.946407	5.379530	0.389169
6	-1.679278	6.532075	-0.328046
6	-0.363056	7.032947	-0.480233
1	1.719775	6.638380	0.031466
1	1.257289	4.602019	1.307633
1	-2.974076	5.017378	0.446957
1	-2.505628	7.070001	-0.802080
6	-1.089584	3.453797	1.742630

1	-0.202729	2.920732	2.089910	8	4.360049	1.861076	1.257698
6	-2.415601	2.802440	1.983275	8	3.120697	1.182718	-0.802361
1	-3.241528	3.525541	2.044427	6	3.546318	3.713304	-0.476648
1	-2.403537	2.235090	2.927175	9	3.626399	4.709335	0.409269
6	-0.143304	8.251074	-1.255989	9	4.709432	3.612769	-1.118487
1	-1.051490	8.694167	-1.682609	9	2.586918	3.987222	-1.352320
6	1.028813	8.870855	-1.495527	8	2.359068	-3.952537	-3.222997
1	1.980280	8.497855	-1.106896	16	1.883908	-3.883599	-1.835844
1	1.068350	9.782869	-2.096001	8	1.625074	-2.452471	-1.381228
6	-2.777708	1.806267	0.884510	8	0.811368	-4.781310	-1.409318
6	-4.073150	1.007911	1.196286	6	3.376276	-4.396266	-0.796132
9	-1.771364	0.898946	0.723535	9	4.515821	-4.034940	-1.387585
9	-2.963409	2.434336	-0.303108	9	3.370037	-5.715807	-0.652784
9	-3.812160	0.181698	2.235092	9	3.329801	-3.833996	0.418099
9	-5.036396	1.868795	1.584686	8	2.723667	-0.509310	-3.157105
6	-4.632605	0.184882	-0.018645	8	4.246608	-1.277886	-1.070543
6	-5.494515	-1.035288	0.426740	6	4.000270	-1.110323	-3.411401
9	-3.618903	-0.280133	-0.768591	1	3.871620	-2.199283	-3.514632
9	-5.382639	1.012431	-0.761735	1	4.423620	-0.693962	-4.342049
53	-6.525244	-1.959446	-1.285672	6	4.895496	-0.786940	-2.240584
9	-6.393769	-0.633534	1.328949	1	5.869346	-1.290630	-2.370937
9	-4.700091	-1.957846	0.988674	1	5.050213	0.301352	-2.140483
26	2.115284	-0.552712	-1.086379	6	1.734386	-0.811520	-4.152115
8	1.880999	2.265427	1.075744	1	2.058530	-0.406022	-5.124517
16	3.180497	2.108260	0.418310	1	1.586666	-1.899760	-4.217013

1	0.806485	-0.324859	-3.831468
6	5.042090	-1.173739	0.113632
1	5.240232	-0.119438	0.357239
1	4.470515	-1.632887	0.924934
1	5.982180	-1.731498	-0.029865
8	2.067609	-0.846679	0.919601
6	1.754715	-1.686212	1.782428
8	0.893390	-2.628413	1.581310
6	2.420894	-1.650123	3.105854
6	3.271377	-0.574242	3.420549
6	2.205398	-2.678144	4.040779
6	3.897695	-0.534084	4.666041
1	3.430252	0.226081	2.697331
6	2.840814	-2.633015	5.280795
1	1.550419	-3.510135	3.778236
6	3.685485	-1.560517	5.593949
1	4.552892	0.304651	4.911990
1	2.679923	-3.434384	6.005705
1	4.180514	-1.525472	6.567983
7	0.469282	0.344369	-1.391099
7	0.139139	1.506777	-1.443860
14	-0.807022	-2.943037	1.297268
7	-0.200374	2.596899	-1.512773
6	-1.369753	-2.381265	-0.379633
6	-0.884919	-4.793698	1.512524
6	-1.620762	-1.971999	2.677143
1	-2.464412	-2.497571	-0.423391
1	-1.134294	-1.323777	-0.561244
1	-0.908689	-2.994792	-1.163203
1	-0.255060	-5.269348	0.744844
1	-0.541449	-5.106027	2.511565
1	-1.919113	-5.150783	1.375936
1	-1.230182	-2.264498	3.664608
1	-1.447328	-0.894894	2.530293
1	-2.710587	-2.127798	2.667472

Structure S12. **^{7,5}MECP**

E(B3LYP)sol = -6127.14360046

6	0.602632	6.422682	0.144579
6	0.356641	5.205118	0.742116
6	-0.976336	4.709130	0.928576
6	-2.037707	5.539061	0.449522
6	-1.776922	6.765638	-0.137416
6	-0.456928	7.251807	-0.308677
1	1.639131	6.744807	0.021493
1	1.185190	4.587542	1.085466
1	-3.072588	5.202353	0.535869
1	-2.614089	7.379605	-0.484241

6	-1.163382	3.470067	1.570961	16	3.164569	2.141849	0.346013
1	-0.272041	2.892984	1.822264	8	4.344230	1.930942	1.194145
6	-2.483856	2.813965	1.823524	8	3.132934	1.188199	-0.857100
1	-3.317267	3.528159	1.872212	6	3.500666	3.736437	-0.577090
1	-2.465681	2.263675	2.778578	9	3.569778	4.745033	0.293866
6	-0.244518	8.557017	-0.930054	9	4.660313	3.642961	-1.225005
1	-1.161779	9.073577	-1.238384	9	2.530196	3.978582	-1.449466
6	0.928554	9.179450	-1.159182	8	2.429013	-4.024617	-3.132564
1	1.891439	8.740268	-0.885048	16	1.959584	-3.915847	-1.746213
1	0.956613	10.163936	-1.633240	8	1.684962	-2.471874	-1.340745
6	-2.840292	1.791347	0.747044	8	0.900263	-4.810651	-1.282941
6	-4.118351	0.980841	1.099849	6	3.462856	-4.375009	-0.697867
9	-1.821897	0.894172	0.593420	9	4.594650	-4.008547	-1.300669
9	-3.045159	2.386910	-0.453485	9	3.479629	-5.690233	-0.522506
9	-3.827998	0.198788	2.165873	9	3.408665	-3.783476	0.502359
9	-5.093160	1.837613	1.468754	8	2.772638	-0.571611	-3.150861
6	-4.683950	0.095182	-0.065829	8	4.283089	-1.260699	-1.033331
6	-5.528995	-1.108597	0.455220	6	4.056278	-1.170272	-3.378584
9	-3.676534	-0.400617	-0.805080	1	3.937160	-2.262859	-3.448304
9	-5.450827	0.877315	-0.839806	1	4.481226	-0.779815	-4.319589
53	-6.598282	-2.117171	-1.184893	6	4.939321	-0.801781	-2.212588
9	-6.409394	-0.671039	1.359105	1	5.918609	-1.300928	-2.318092
9	-4.716624	-2.001532	1.039322	1	5.083629	0.290232	-2.145119
26	2.140813	-0.558007	-1.087460	6	1.793490	-0.911398	-4.144457
8	1.856720	2.282084	0.989506	1	2.128089	-0.541943	-5.127290

1	1.646702	-2.001160	-4.170599
1	0.862238	-0.413681	-3.852659
6	5.068116	-1.110860	0.153380
1	5.252253	-0.047744	0.365766
1	4.497212	-1.552407	0.974431
1	6.016049	-1.660697	0.035033
8	2.061812	-0.814705	0.909491
6	1.789629	-1.657668	1.785940
8	0.929287	-2.605574	1.621405
6	2.505467	-1.611438	3.081438
6	3.329707	-0.509448	3.374940
6	2.366596	-2.658899	4.009664
6	4.008635	-0.462866	4.592167
1	3.428896	0.304281	2.656547
6	3.056607	-2.608430	5.220108
1	1.729727	-3.509201	3.762668
6	3.876075	-1.510212	5.511611
1	4.642444	0.396608	4.821544
1	2.958201	-3.425074	5.938925
1	4.413630	-1.470702	6.462546
7	0.501539	0.314063	-1.440950
7	0.154029	1.458883	-1.625764
14	-0.773057	-2.915557	1.314964
7	-0.202816	2.525497	-1.830414
6	-1.314310	-2.399738	-0.383577
6	-0.868993	-4.758403	1.582979
6	-1.594759	-1.896957	2.653426
1	-2.409591	-2.510375	-0.428717
1	-1.073725	-1.348930	-0.594517
1	-0.854636	-3.039607	-1.146528
1	-0.230518	-5.262237	0.840907
1	-0.546231	-5.043909	2.596777
1	-1.904004	-5.110362	1.438879
1	-1.216792	-2.160304	3.653862
1	-1.415950	-0.825633	2.473529
1	-2.684785	-2.049427	2.635428

Structure S13. **P**

E(B3LYP)sol = -1800.87612248 E(B3LYP)gas = -1799.10551758

6	-5.792091	-1.267751	0.868655
6	-4.593953	-0.578307	1.025854
6	-4.201845	0.409839	0.107307
6	-5.045301	0.693416	-0.971550
6	-6.247293	0.000039	-1.127456
6	-6.648799	-0.994748	-0.217519
1	-6.068164	-2.024559	1.605672
1	-3.951833	-0.808101	1.881949

1	-4.761919	1.469665	-1.684178
1	-6.894227	0.237925	-1.976529
6	-2.858955	1.099773	0.285421
1	-2.693428	1.271287	1.363094
6	-1.727067	0.181774	-0.227701
1	-1.756166	0.130810	-1.324244
1	-1.879819	-0.833694	0.164719
6	-7.928234	-1.693289	-0.431178
1	-8.486483	-1.361389	-1.314569
6	-8.462807	-2.665935	0.322179
1	-7.972112	-3.055701	1.218478
1	-9.425808	-3.111388	0.061195
6	-0.343228	0.623684	0.213678
6	0.751963	-0.406027	-0.187836
9	-0.312485	0.759849	1.566670
9	-0.009946	1.826025	-0.323377
9	0.547472	-1.525086	0.540978
9	0.590731	-0.712662	-1.492251
6	2.220349	0.093899	0.010801
6	3.266389	-1.062228	-0.035340
9	2.327193	0.705989	1.201853
9	2.488455	0.970846	-0.969449
53	5.324510	-0.268067	-0.052765
9	3.066368	-1.796067	-1.134603
9	3.116734	-1.840595	1.037289
7	-1.838301	4.299250	0.498924
7	-2.307653	3.343663	0.101284
7	-2.850411	2.384684	-0.436628

Structure S14. **TS2**

E(B3LYP)sol = -3183.73585909 E(B3LYP)gas = -3180.98365996

6	2.250876	5.632161	0.407124
6	1.808086	4.438733	0.958797
6	1.605713	3.291460	0.160397
6	1.850036	3.401038	-1.222641
6	2.291570	4.598012	-1.773124
6	2.505167	5.742841	-0.977022
1	2.402624	6.493326	1.060614
1	1.613486	4.380749	2.033118
1	1.691161	2.542938	-1.877850
1	2.478014	4.655744	-2.848848
6	1.126699	2.048193	0.788703
1	1.221361	2.071105	1.879296
6	1.565047	0.706734	0.226618
1	1.396027	0.629691	-0.854505
1	0.999620	-0.104916	0.704337
6	2.973928	6.981412	-1.614058

1	3.119269	6.912101	-2.698388
6	3.234486	8.155467	-1.016786
1	3.116785	8.309366	0.059382
1	3.580238	9.014099	-1.597285
6	3.042053	0.433729	0.499871
6	3.439197	-1.013992	0.088506
9	3.304457	0.579950	1.823413
9	3.840786	1.296367	-0.177520
9	2.814010	-1.866633	0.927734
9	2.986056	-1.239843	-1.163746
6	4.977858	-1.293857	0.099015
6	5.317890	-2.815378	0.053566
9	5.519061	-0.777878	1.214941
9	5.509328	-0.690916	-0.976614
53	7.482427	-3.134756	-0.233518
9	4.649794	-3.387733	-0.952657
9	4.948956	-3.388202	1.199618
6	-4.103450	0.089943	0.091349
9	-3.686180	0.112033	-1.187936
9	-3.347857	-0.767553	0.799503
6	-3.938770	1.495380	0.676226
9	-4.492281	2.440335	-0.065315
9	-4.331537	1.584824	1.935936
53	-1.244763	2.050578	0.633814
6	-5.582921	-0.423536	0.133836
6	-5.810757	-1.753215	-0.643657
53	-7.874579	-2.491235	-0.356758
9	-6.376379	0.522212	-0.402048
9	-5.912786	-0.601393	1.423982
9	-4.951135	-2.677176	-0.208386
9	-5.605216	-1.549291	-1.945093

Frequencies -- -94.0418

Red. masses -- 29.1981

Frc consts -- 0.1521

IR Inten -- 42.5544

Structure S15. P'

E(B3LYP)sol = -1934.42957549 E(B3LYP)gas = -1932.83797974

6	-4.133666	2.597773	1.017974
6	-3.634576	1.319829	1.249908
6	-3.161015	0.522096	0.194182
6	-3.217228	1.043696	-1.107791
6	-3.718358	2.320538	-1.339666
6	-4.186380	3.130439	-0.284920
1	-4.486600	3.189260	1.865041
1	-3.604334	0.931239	2.271508
1	-2.877301	0.441270	-1.953215

1	-3.751555	2.705730	-2.362443
6	-2.612039	-0.838162	0.484232
1	-2.527444	-0.995070	1.564996
6	-1.291540	-1.206884	-0.190725
1	-1.337149	-1.090604	-1.280818
1	-1.040883	-2.255712	0.019328
6	-4.703401	4.475158	-0.587857
1	-4.687135	4.741679	-1.651225
6	-5.177633	5.380994	0.280933
1	-5.227493	5.196378	1.357658
1	-5.536656	6.353553	-0.064196
6	-0.132008	-0.362093	0.328588
6	1.235426	-0.896320	-0.189503
9	-0.103822	-0.392684	1.686300
9	-0.246844	0.933945	-0.052834
9	1.456837	-2.095146	0.390957
9	1.142630	-1.080782	-1.524272
6	2.448189	0.053526	0.080118
6	3.825594	-0.655648	-0.100736
9	2.380696	0.519736	1.338149
9	2.363814	1.078562	-0.782807
53	5.483241	0.798042	-0.006164
9	3.850835	-1.277624	-1.283576
9	3.992253	-1.558132	0.866534
53	-4.119076	-2.414613	-0.079140

Structure S16. octa-1,7-diene

E(B3LYP)sol = -313.381642219 E(B3LYP)gas = -313.029913534

6	-0.667017	-0.345934	0.143405
1	-0.836640	-0.388393	1.234311
1	-0.614639	-1.397334	-0.195000
6	-1.866856	0.344739	-0.524646
1	-1.681925	0.390013	-1.615041
1	-1.934326	1.390617	-0.177208
6	-3.168677	-0.363054	-0.273977
1	-3.221080	-1.400070	-0.633690
6	-4.227740	0.155502	0.354094
1	-4.219735	1.183309	0.733753
1	-5.143140	-0.422423	0.510469
6	0.666923	0.346215	-0.143529
1	0.614590	1.397613	0.194898
1	0.836493	0.388676	-1.234444
6	1.866740	-0.344479	0.524472
1	1.934071	-1.390446	0.177257
1	1.681953	-0.389521	1.614902
6	3.168614	0.363105	0.273550
1	3.220786	1.400518	0.632160

6	4.228003	-0.156091	-0.353433
1	5.143439	0.421726	-0.509995
1	4.220215	-1.184304	-0.731994

Structure S17. **TS1"**

E(B3LYP)sol = -353.234366225 E(B3LYP)gas = -352.835315731

6	1.354058	0.247460	-0.160427
1	1.410198	1.070433	0.574594
1	1.255138	0.732455	-1.149268
6	2.664165	-0.555377	-0.116142
1	2.593291	-1.381410	-0.849564
1	2.776549	-1.028778	0.875019
6	3.876330	0.277011	-0.426419
1	3.884027	0.751619	-1.417510
6	4.904798	0.491817	0.398889
1	4.938441	0.043406	1.398084
1	5.752896	1.118991	0.109395
6	0.112414	-0.603405	0.113660
1	0.210877	-1.088348	1.102457
1	0.056224	-1.426463	-0.621276
6	-1.198183	0.199300	0.071102
1	-1.309962	0.674421	-0.919743
1	-1.120343	1.029734	0.801523
6	-2.412790	-0.623767	0.381613
1	-2.418274	-1.128597	1.356654
6	-3.514089	-0.715983	-0.411456
1	-4.317442	-1.416330	-0.171907
1	-3.491393	-0.335677	-1.437025
6	-4.955898	1.073684	0.124685
1	-5.151201	0.855390	1.176519
1	-4.294272	1.914600	-0.093491
1	-5.759581	0.870112	-0.587484

Frequencies -- -389.5851

Red. masses -- 10.6222

Frc consts -- 0.9499

IR Inten -- 0.7675

Structure S18. **int1"**

E(B3LYP)sol = -353.280079319 E(B3LYP)gas = -352.887509549

6	1.322518	-0.082610	0.313818
1	1.312032	-1.144771	0.009620
1	1.300798	-0.085586	1.419470
6	2.631622	0.563615	-0.167233
1	2.627530	1.628591	0.134679

1	2.667217	0.553846	-1.270774
6	3.857980	-0.102194	0.390507
1	3.941922	-0.098782	1.486205
6	4.814525	-0.698210	-0.327024
1	4.770938	-0.730591	-1.421400
1	5.677981	-1.172942	0.147866
6	0.069932	0.617037	-0.216284
1	0.093260	0.622650	-1.321681
1	0.080822	1.678572	0.090501
6	-1.238488	-0.028603	0.253889
1	-1.266907	-0.052957	1.361790
1	-1.228173	-1.102534	-0.043363
6	-2.472499	0.635161	-0.262608
1	-2.413278	1.152906	-1.228033
6	-3.823951	0.322996	0.296204
1	-4.525493	1.144226	0.066026
1	-3.764097	0.261787	1.399461
6	-4.420987	-0.999682	-0.234118
1	-4.533614	-0.971303	-1.330128
1	-3.771066	-1.855154	0.011953
1	-5.413781	-1.193029	0.204907

Structure S19. **TS3**

E(B3LYP)sol = -1562.68834528 E(B3LYP)gas = -1561.17915042

6	6.510653	-0.577759	0.154268
1	6.344013	-1.180874	-0.756167
1	6.143748	-1.193746	0.995912
6	8.017848	-0.328639	0.323867
1	8.171472	0.283701	1.233075
1	8.392706	0.272621	-0.522928
6	8.814159	-1.597708	0.442975
1	8.551164	-2.244323	1.291586
6	9.776048	-1.993389	-0.395482
1	10.068818	-1.383692	-1.257524
1	10.310239	-2.937118	-0.252870
6	5.690208	0.711039	0.073822
1	6.055738	1.327427	-0.768065
1	5.855643	1.314198	0.984508
6	4.183891	0.458728	-0.097632
1	3.804266	-0.146784	0.743406
1	4.029194	-0.153093	-1.007859
6	3.379100	1.715719	-0.225547
1	3.663513	2.393134	-1.041344
6	2.305011	2.026846	0.535537
1	1.775217	2.975107	0.417291
1	2.038667	1.420662	1.406655

6	0.545227	0.834208	-0.652696
6	-0.628458	0.804452	0.307053
9	1.085689	-0.351973	-0.894617
9	0.316782	1.500320	-1.774671
9	-0.246816	0.124566	1.410962
9	-0.925545	2.076642	0.648848
6	-1.921569	0.141428	-0.270401
6	-3.067628	-0.043618	0.764168
9	-1.584390	-1.068783	-0.755178
9	-2.355711	0.918668	-1.277877
53	-4.889884	-0.841142	-0.204149
9	-3.352425	1.132454	1.328397
9	-2.678416	-0.895731	1.713538

Frequencies -- -164.5514

Red. masses -- 7.0940

Frc consts -- 0.1132

IR Inten -- 21.4162

Structure S20. int4

E(B3LYP)sol = -1562.73243844 E(B3LYP)gas = -1561.22853677

6	6.466003	-0.336229	0.337542
1	6.105857	-1.372550	0.208279
1	6.430704	-0.138050	1.424852
6	7.920834	-0.245065	-0.149671
1	8.267510	0.798690	-0.024152
1	7.964091	-0.458849	-1.232025
6	8.848980	-1.165829	0.591613
1	8.917011	-0.998276	1.675485
6	9.560247	-2.156651	0.046473
1	9.520404	-2.363855	-1.028711
1	10.211043	-2.796179	0.649636
6	5.523983	0.628260	-0.384868
1	5.560374	0.431473	-1.472069
1	5.882020	1.665204	-0.253103
6	4.071075	0.529118	0.093734
1	4.016677	0.718183	1.183528
1	3.724538	-0.521312	-0.020197
6	3.131221	1.439707	-0.620761
1	3.324286	1.675251	-1.672422
6	1.785775	1.778298	-0.068047
1	1.392692	2.709637	-0.502106
1	1.817956	1.899150	1.027663
6	0.747993	0.688163	-0.350510
6	-0.648444	1.026176	0.244027
9	1.151294	-0.491699	0.189175
9	0.603760	0.502928	-1.687502
9	-0.538568	0.999546	1.590589

9	-0.982344	2.280797	-0.129674
6	-1.803332	0.073332	-0.208167
6	-3.083785	0.210092	0.671773
9	-1.387445	-1.202252	-0.140600
9	-2.109383	0.377162	-1.479966
53	-4.764611	-0.932950	-0.191805
9	-3.427547	1.498535	0.759774
9	-2.835777	-0.255947	1.896226

Structure S21. **TS4**

E(B3LYP)sol = -3109.90018507 E(B3LYP)gas = -3107.22935428

6	1.674736	2.808919	-0.193794
1	1.379101	3.533220	-0.973832
1	1.888784	1.863174	-0.718450
6	2.957112	3.298449	0.496716
1	3.247082	2.548326	1.255167
1	2.757927	4.239131	1.039684
6	4.102468	3.486688	-0.458310
1	4.403153	2.593235	-1.017731
6	4.753059	4.633385	-0.674272
1	4.487660	5.552658	-0.140274
1	5.579953	4.696316	-1.387588
6	0.507674	2.600648	0.777689
1	0.248177	3.568187	1.238945
1	0.841782	1.954593	1.607575
6	-0.746129	1.986571	0.111942
1	-0.624322	1.940266	-0.984404
1	-1.618542	2.648793	0.272058
6	-1.166377	0.633805	0.618542
1	-1.203762	0.548223	1.711952
6	-2.303926	-0.079764	-0.075528
1	-2.340203	-1.137579	0.219025
1	-2.199089	-0.036037	-1.169794
6	-3.668486	0.513254	0.278701
6	-4.835831	-0.295882	-0.359610
9	-3.767474	1.793968	-0.161832
9	-3.844423	0.525852	1.624680
9	-4.756341	-0.135420	-1.697734
9	-4.658452	-1.603466	-0.075191
6	-6.261643	0.110163	0.140426
6	-7.403386	-0.451594	-0.761936
9	-6.367072	1.449096	0.160832
9	-6.406420	-0.368711	1.386386
53	-9.380345	-0.097388	0.151084
9	-7.225801	-1.764701	-0.935423
9	-7.365953	0.150967	-1.951055
6	4.016279	-0.600807	0.029909

9	3.730367	0.167085	-1.041705
9	3.808649	0.107739	1.155550
6	3.059593	-1.812462	0.018973
9	3.118602	-2.463856	-1.138326
9	3.323558	-2.644680	1.023037
53	0.788524	-0.934766	0.299986
6	5.531971	-0.985772	-0.018874
6	6.479796	0.242027	-0.189876
53	8.595320	-0.374649	-0.068013
9	5.729866	-1.822369	-1.052054
9	5.830721	-1.613849	1.129847
9	6.227585	1.139274	0.765142
9	6.265412	0.807771	-1.380882

Frequencies -- -150.6131

Red. masses -- 21.7262

Frc consts -- 0.2904

IR Inten -- 1.3803

Structure S22. P"

E(B3LYP)sol = -1860.59772634 E(B3LYP)gas = -1859.08278956

6	-5.461531	1.512684	0.247725
1	-5.286342	2.203618	1.091784
1	-5.604275	0.513521	0.693489
6	-6.742911	1.930214	-0.489206
1	-6.904273	1.228384	-1.329856
1	-6.608533	2.930034	-0.938559
6	-7.956603	1.924711	0.396901
1	-8.205356	0.956077	0.851978
6	-8.719176	2.985074	0.677884
1	-8.506262	3.971249	0.250396
1	-9.585910	2.910066	1.340839
6	-4.227558	1.495290	-0.659703
1	-4.072268	2.510001	-1.063515
1	-4.430980	0.855498	-1.536493
6	-2.936074	1.022201	0.042660
1	-3.073200	0.995449	1.137160
1	-2.133645	1.755733	-0.136024
6	-2.378823	-0.317525	-0.423515
1	-2.248573	-0.323152	-1.513805
6	-1.080282	-0.765723	0.252193
1	-0.823565	-1.781541	-0.074090
1	-1.183871	-0.783927	1.346863
6	0.114285	0.123982	-0.078455
6	1.459691	-0.523882	0.366208
9	0.018096	1.326580	0.547485
9	0.182983	0.361379	-1.415190
9	1.447651	-0.598243	1.714238

9	1.521598	-1.777615	-0.130322
6	2.742108	0.234932	-0.111870
6	4.033106	-0.230259	0.630715
9	2.594756	1.553150	0.098567
9	2.882456	0.005824	-1.427579
53	5.833899	0.658418	-0.284379
9	4.122697	-1.562260	0.576353
9	3.970645	0.147408	1.908164
53	-3.854244	-1.967800	-0.132128

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