Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Phase-Selectively Soluble Polynorbornene as a Catalyst Support

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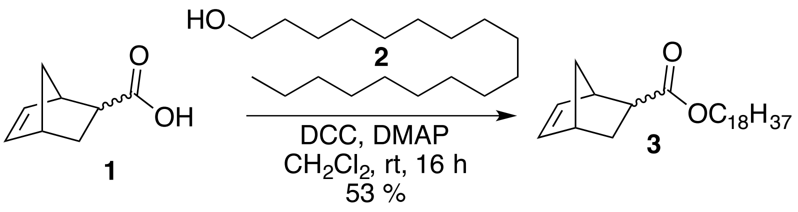
General Considerations and Materials

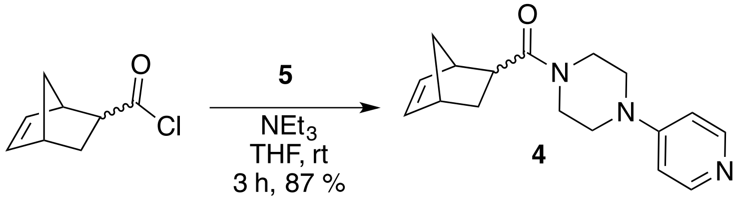
Grubbs 2^{nd} Generation Initiator **6** was donated by Materia Inc. and used as received. All other reagents were purchased from commercial sources (Sigma-Aldrich, TCI, Alfa-Aesar) and used without further purification, unless otherwise stated. Air free chemistry was carried out using standard Schlenk techniques. Size Exclusion Chromatography (SEC) measurements were obtained in THF at room temperature using a Viscotek TDA305 Triple Detection system with a T6000M general mixed column and are calculated relative to polystyrene standards. ^{1}H and ^{13}C NMR Spectroscopy were obtained on a Bruker 300 MHz (operating at 300.128 and 75.474 MHz, respectively). All peaks are reported in ppm and referenced to the $CHCl_3$ peak in $CDCl_3$. FT-IR spectroscopy measurements were performed on a Shimadzu IRPrestige. UV-vis spectrometry measurements were run on a Beckman-Coulter DU-800 spectrophotometer.

Experimental Procedures



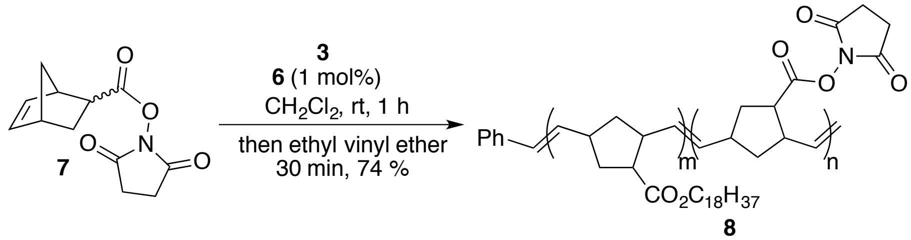
Octadecyl-Norbornene (3)

To a 50-mL, round bottomed flask, equipped with a magnetic stir bar was added 5-norbornene-2-carboxylic acid (2 g, 14.5 mmol), 1-octadecanol (4 g, 14.5 mmol), and DCM (20 mL). While stirring at room temperature, DCC (3.6 g, 17.4 mmol) was added to the reaction mixture, followed by DMAP (0.866 g, 7.25 mmol). The reaction mixture was allowed to stir overnight at room temperature under nitrogen atmosphere. The suspension was separated by vacuum filtration and the solvent was collected. The solvent was dried over Na_2SO_4 followed by filtration and evaporation of the solvent under reduced pressure to give **3** as a white, powdery solid. **3** was purified by flash column chromatography using hexane as solvent to obtain the desired product as a colourless oil (2.97 g, 53%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.25-6.1 (m, 1H), 6.0-5.9 (s, 1H), 4.12-4.0 (m, 2H), 3.28-3.17 (s, 1H), 3.07-2.9 (m, 2H), 2.0-1.86 (m, 1H), 1.7-1.5 (m, 5H), 1.48-1.3 (m, 37 H), 1.03-0.8 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.6, 137.8, 132.4, 64.4, 49.7, 46.1, 42.9, 41.5, multiple peaks 33-22, 14.0. FTIR: 3320, 2960, 1734 cm^{-1}.



5-Norbornene-2-pyridinyl-piperazine (4)

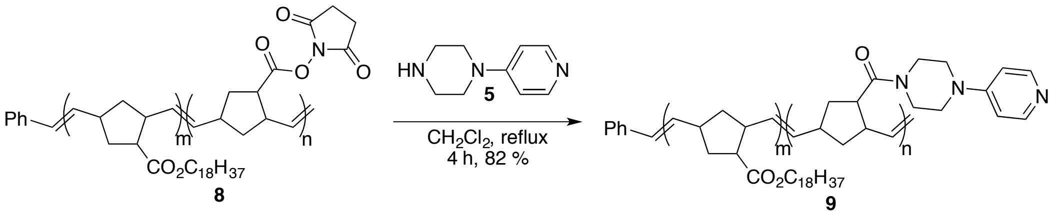
To a 25 mL, round-bottomed flask, equipped with a magnetic stir bar was added 1-(4-pyridinyl)piperazine **5** (0.52 g, 3.2 mmol), triethylamine (0.5 mL, 4 mmol), and THF (16 mL). To this stirring solution was added 5-norbornene-2-carbonyl chloride (0.5 g, 3.2 mmol). The reaction mixture was allowed to stir for 3 hours. At this point, the solvent was removed under reduced pressure and the crude mixture was extracted with DCM. The organic phase was washed with 3 50 mL portions of water and the organic phase was dried with Na_2SO_4, filtered, and the solvent was removed under reduced pressure to yield **4** as a yellow oil (0.78 g, 87 %). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, 2H, J = 5.6 Hz), 6.68 (d, 2H, J = 5.3 Hz), 6.23-6.03 (m, 2H), 3.83-3.60 (bs, 4H), 3.46-3.27 (bs, 4H), 3.16-3.05 (bs, 1H), 2.98-2.91 (bs, 1H), 2.05-1.86 (m, 2H), 1.52-1.41 (m, 2H), 1.37-1.29 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.9, 154.7, 150.2, 136.7, 132.8, 108.5, 49.6, 45.7, 44.5, 42.6, 41.9, 41.09, 30.9.



Polymer (8)

To a 25-mL, round bottomed flask, equipped with a magnetic stir bar and a rubber septum was added **3** (1 g, 2.56 mmol), **7** (0.06 g, 0.256 mmol), and DCM (10 mL). A bath of liquid nitrogen was used to freeze the reaction mixture. At this time, Grubb's second generation initiator **6** (0.024 g, 0.0284 mmol) was added to the reaction mixture. At this time the reaction was degassed by three freeze-pump-thaw cycles. The reaction mixture was then allowed to stir for 1 hour. (At this point, it was possible to visually observe the phase selectivity of **8** by removing the reaction solvent under reduced pressure, followed by the addition of either heptane (or hexane) and acetonitrile to form a biphasic mixture. At this time, ethyl vinyl ether (6 mL) was added to the reaction mixture and allowed to stir for 1 hour. Upon completion, the reaction mixture was precipitated into methanol (20 mL). the suspension was separated by vacuum filtration in which 0.783 g of **8** was isolated as an off white, sticky solid in 74%. ^{1}H NMR (300

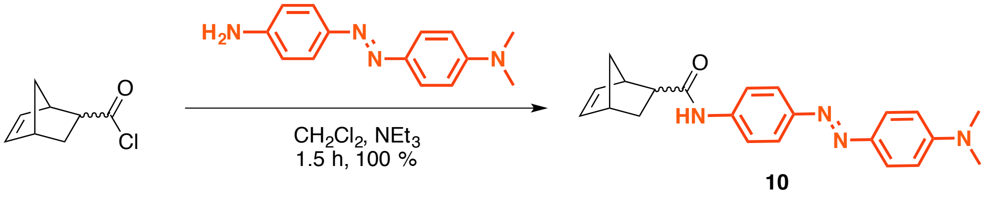
MHz, $CDCl_3$) δ 5.53-5.15 (m, 2H), 4.16-3.9 (s, 2H), 3.55-3.47 (s, 1H), 3.3-3.1 (s, 1H), 3.0-2.7 (m, 2H), 2.6-2.36 (s, 1H), 2.2-2.17 (s, 2H), 2.14-1.7 (m, 3H), 1.68-1.43 (m, 5H), 1.4-1.0 (s, 26 H), 0.95-0.8 (m, 3H). GPC analysis showed M_n = 113,000 Da and $Đ$ = 1.77.



Polymer (9)

To a 15-mL, round bottomed flask, equipped with a magnetic stir bar, a water-jacketed reflux condenser, and a rubber septum was added **8** (0.369 g, 0.0098 mmol) and DCM (9 mL). Once **8** was dissolved, 1-(4-pyridyl)piperazine (0.048 g, 0.295 mmol) was added to the reaction mixture. This mixture was placed on an oil bath regulated at 50°C and was allowed to stir for 4 hours. At this time, the mixture was allowed to cool to room temperature and was then precipitated into methanol (15 mL). the suspension was separated by vacuum filtration in which 0.284 g of **10** was isolated as an off-white, rubbery solid in 82 % yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43-8.31 (s, 0.2H), 6.73-6.6 (s, 0.2H), 5.58-5.13 (m, 2H), 4.17-3.88 (s, 2H), 3.6-3.5 (m, 2H), 3.39-3.26 (s, 1H), 3.24-3.06 (s, 1H), 3.0-2.63 (m, 2H), 2.6-2.35 (s, 1H), 2.2-1.0 (m, 34H), 0.97-0.8 (m, 3H), 0.15-0.04 (s, 1H).

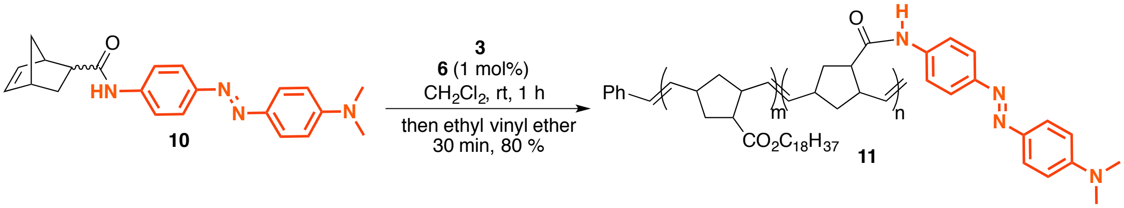
Dye-labelled norbornene (10)



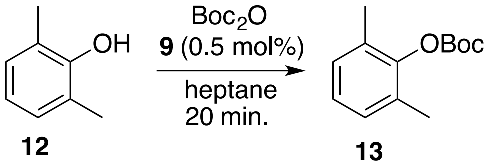
To a 10-mL, round bottomed flask, equipped with a magnetic stir bar and a rubber septum was added *N,N*-dimethyl-4,4'-azodianiline (0.153 g, 0.64 mmol), triethylamine (0.15 mL, 1.09 mmol) and DCM (2 mL). Norbornene acid chloride (0.1g, 0.64 mmol), in DCM (1 mL) was then added to the reaction mixture. This mixture was allowed to stir at room temperature for 1.5 h. At this time, DCM (25 mL) was added to the reaction mixture which was then washed with 3 15-mL portions of H_2O, followed by saturated NaCl. The organic layer was then dried over Na_2SO_4, filtered and the solvent was removed under reduced pressure to provide 0.23 g of **10** as a red/orange solid, 100 % yield. This material was used with no further purification. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9-7.8 (m, 4H), 7.62 (d, 2H, J = 9 Hz), 6.77 (d, 2H, J = 9 Hz), 6.23-6.03 (m, 2H), 3.26 (bs, 1H), 3.10-3.02

(m, 8H), 2.15-1.98 (m, 1H), 1.6-1.1 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.6, 152.3, 149.5, 143.6, 139.0, 138.3, 132.2, 124.8, 123.3, 119.7, 111.7, 50.3, 46.6, 42.9, 40.3, 30.1.

Polymer (11)



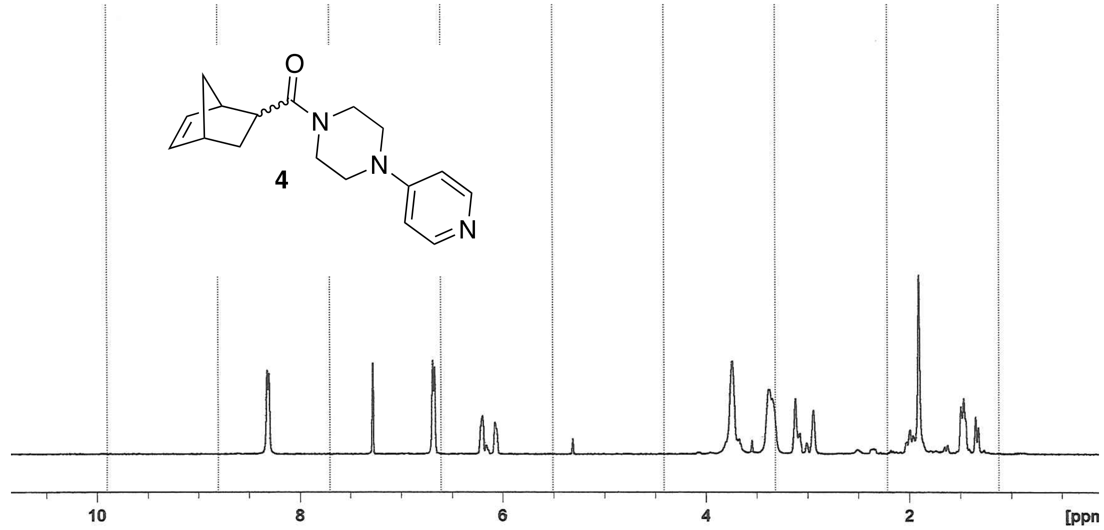
To a 25-mL, round bottomed flask, equipped with a magnetic stir bar and a rubber septum was added **3** (0.5 g, 1.28 mmol), **10** (0.046 g, 0.128 mmol), and DCM (5 mL). A bath of liquid nitrogen was used to freeze the reaction mixture. At this time, Grubbs' second generation initiator **6** (0.012 g, 0.0142 mmol) was added to the reaction mixture. At this time the reaction was degassed by three freeze-pump-thaw cycles. At this time, ethyl vinyl ether (6 mL) was added to the reaction mixture and allowed to stir for 1 hour. Upon completion, the reaction mixture was precipitated into methanol (20 mL). the suspension was separated by vacuum filtration in which 0.44 g of **11** was isolated as an orange, sticky solid in 80%. The phase selectivity of this material was determined according to literature procedures using UV-vis spectrometry.[1] ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.9-7.8 (s, 0.2H), 6.8-6.7 (s, 0.2H), 5.53-5.12 (m, 2H), 4.13-3.90 (s, 2H), 3.6-3.5 (bs, 2H), 2.38-2.26 (m, 0.3H), 2.15-1.10 (m 34H), 0.97-0.8 (m, 3H).

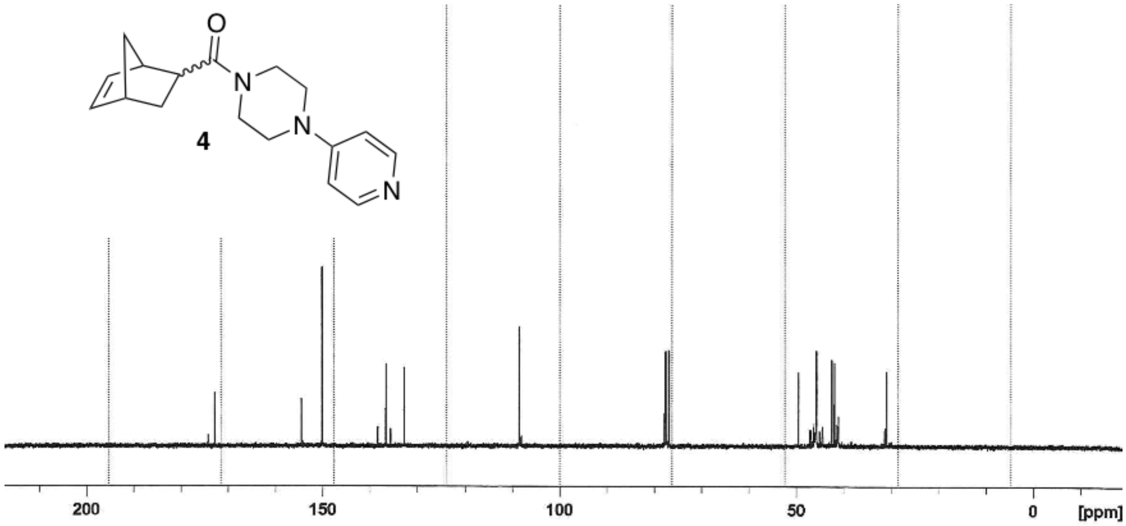


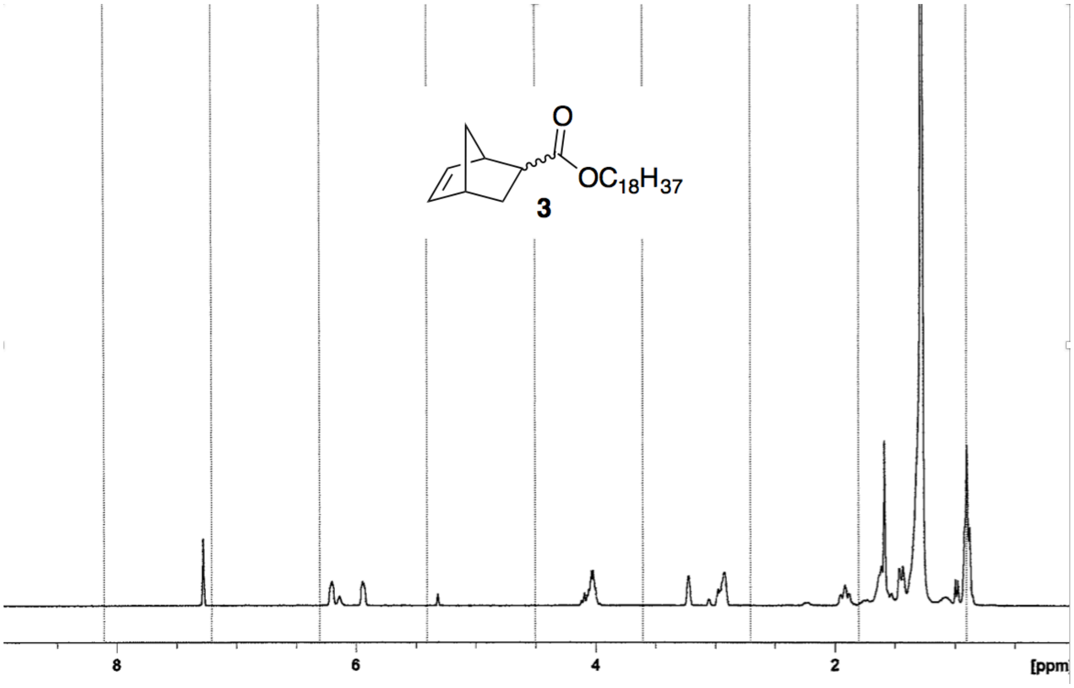
Boc-Protection of 2,6-Dimethylphenol Catalyzed by 10 using a Liquid/Liquid Separation for Catalyst Recovery

To a 5-mL, round bottomed flask, equipped with a stir bar and a rubber septum was added **10** (0.15 g, 0.004 mmol), 2,6-dimethylphenol **11** (0.10 g, 0.8 mmol), Boc_2O (0.175 g, 0.8 mmol), and hexane (2 mL). This mixture was allowed to stir for 20 minutes followed by the addition of 95:5 acetonitrile (2 mL) which resulted in a biphasic mixture. Pure product was isolated by removal of the polar solvent layer, followed by solvent removal under reduced pressure while **10** was reused 5 times with an average product yield of 87%. Product spectral data (^{1}H, ^{13}C NMR, and FT-IR) matched literature examples.[2]

^{1}H and ^{13}C NMR Spectra







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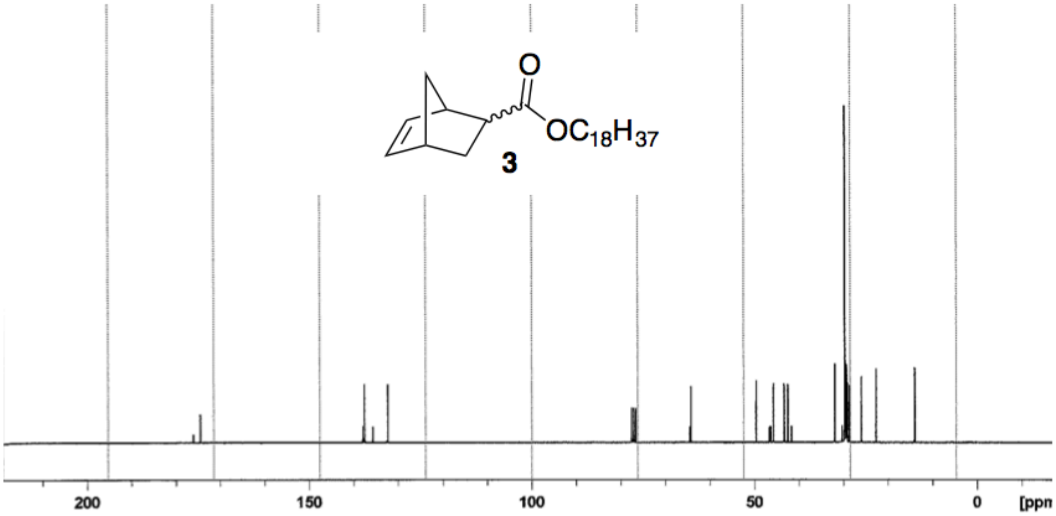

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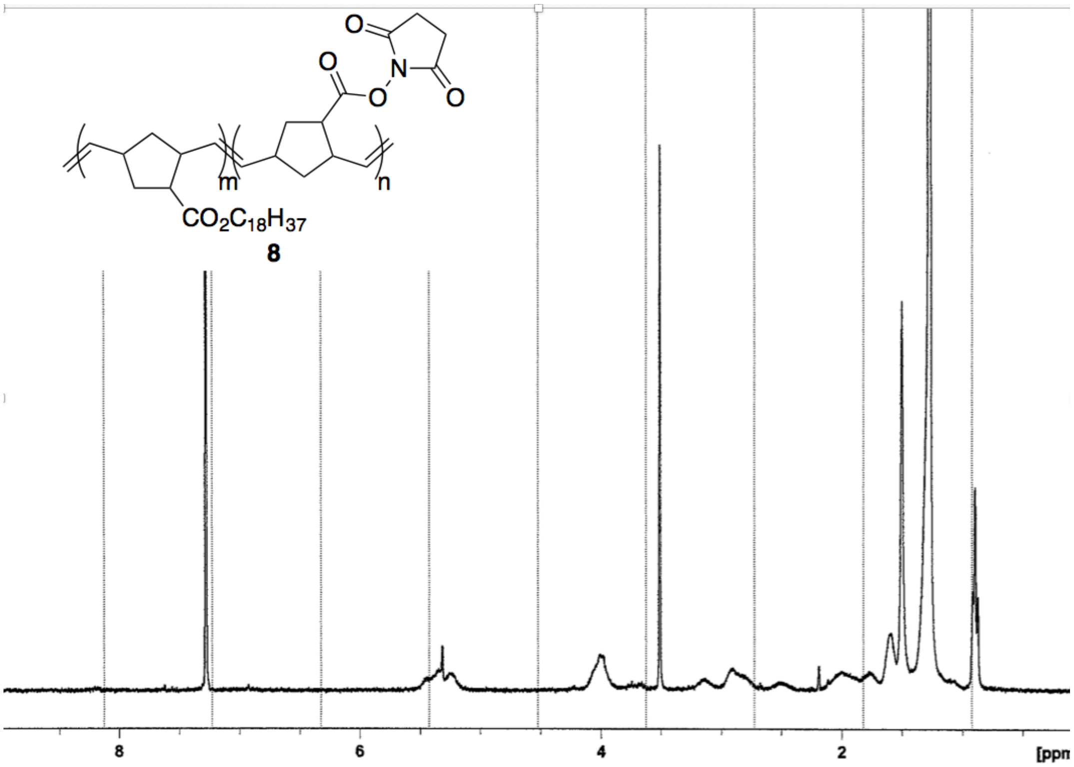

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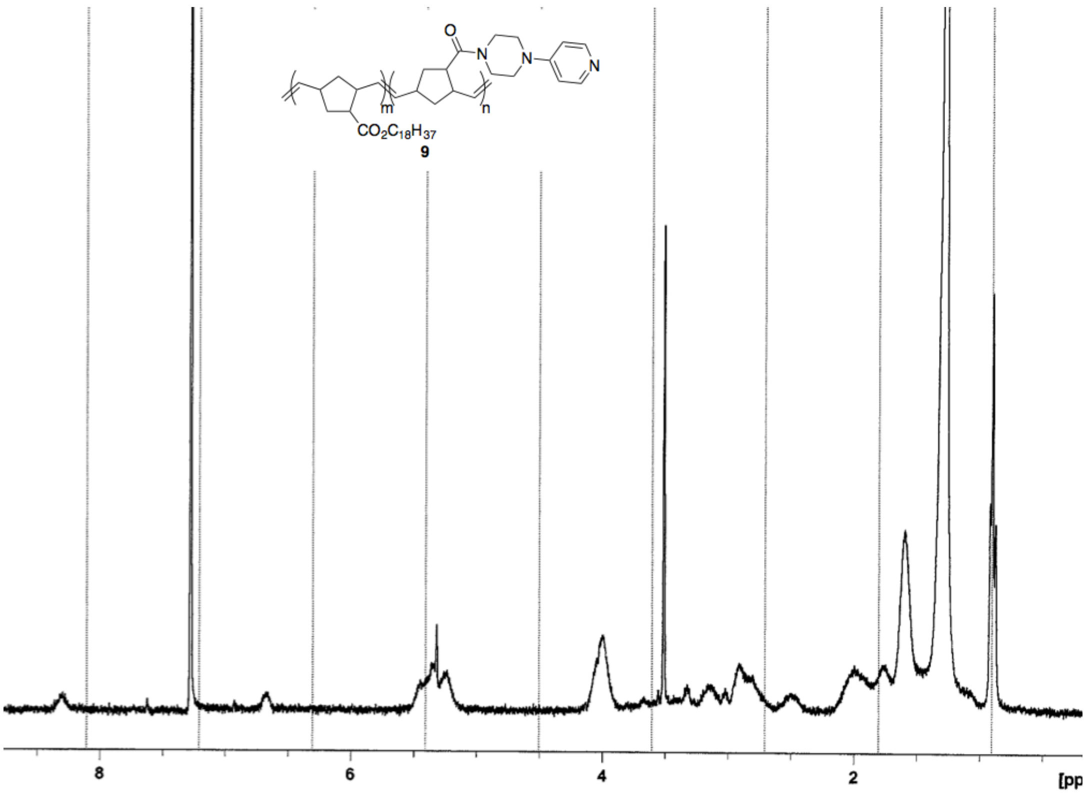

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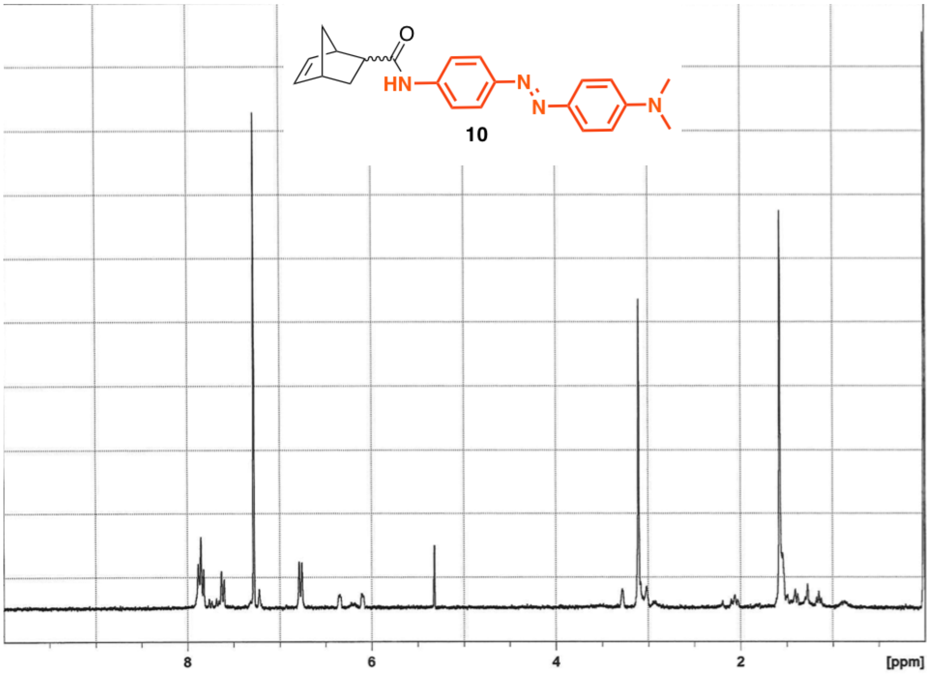
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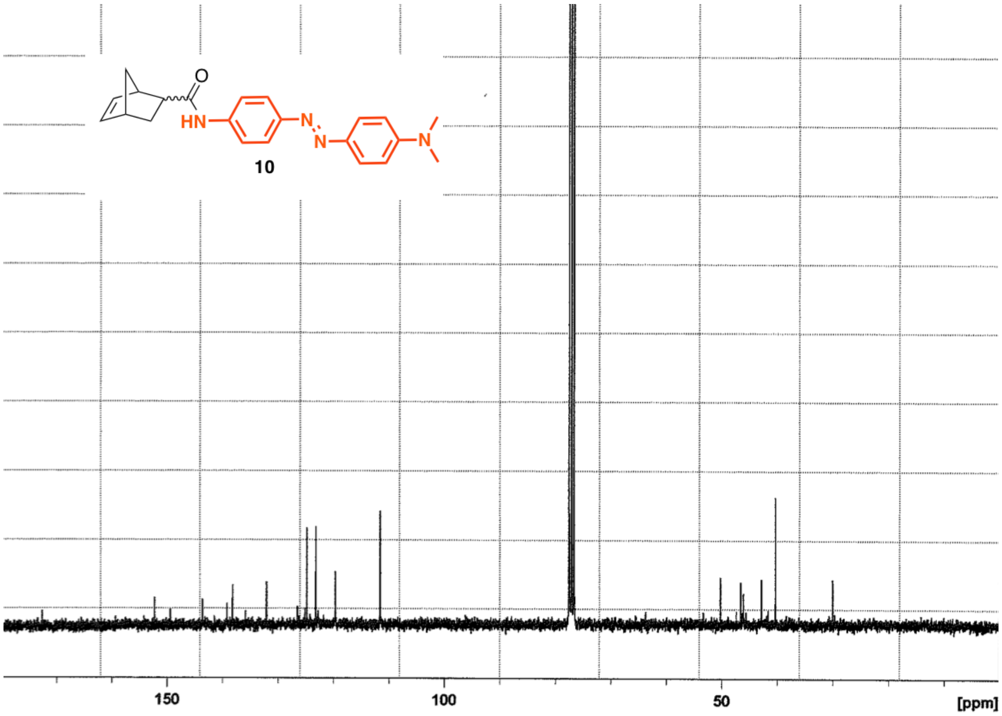
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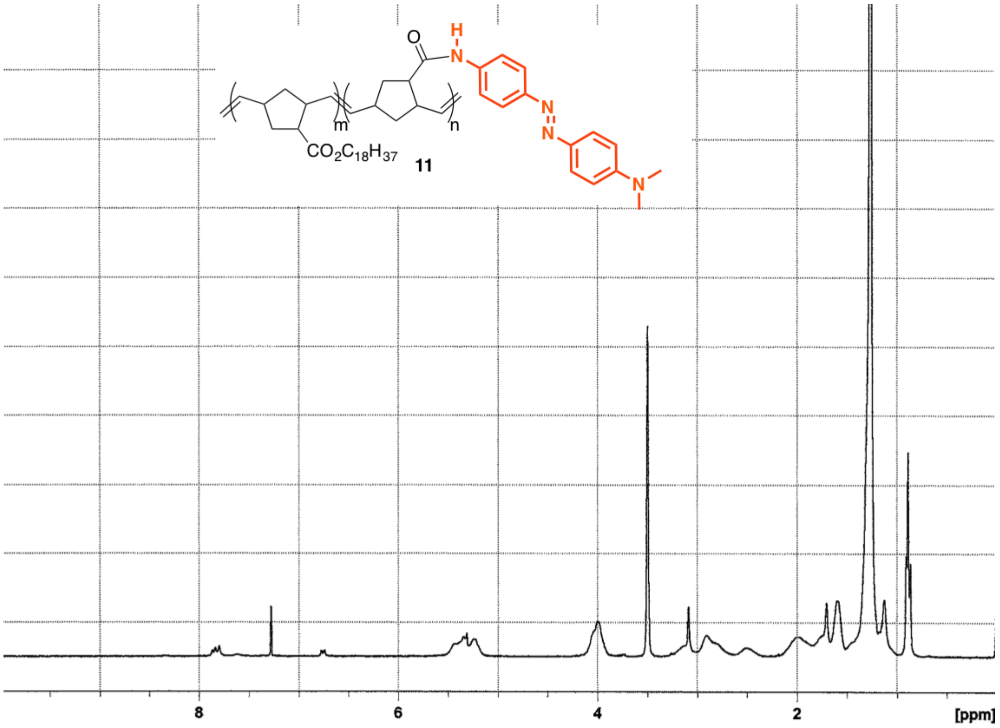

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References:

1. Bergbreiter, D. E.; Sung, S. D.; Li, J.; Ortiz, D.; Hamilton, P. N. *Org. Process Res. Dev.* **2004**, *8*, 461.
2. Khamatnurova, T. V.; Bergbreiter, D. E.; *Polym. Chem*. **2013**, *4*, 1617.