

Supporting Information

Fast Living Polymerization of Challenging Aryl Isocyanides Using an Air-Stable Bisphosphine-Chelated Nickel (II) Initiator

Jaeho Lee,[†] Suyong Shin,[†] and Tae-Lim Choi^{*,†}

[†]Department of Chemistry, Seoul National University, Seoul 08826, Republic of Korea.

*E-mail: tlc@snu.ac.kr

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1. Materials

Unless otherwise noted, all reagents were purchased from commercial sources and used without further purification. Tetrahydrofuran (THF) was distilled over sodium and benzophenone, and degassed by argon bubbling for 10 minutes before using on polymerization. The aryl nickel initiators **B**,¹ **C**, and **D**,² were prepared by the previously reported methods.

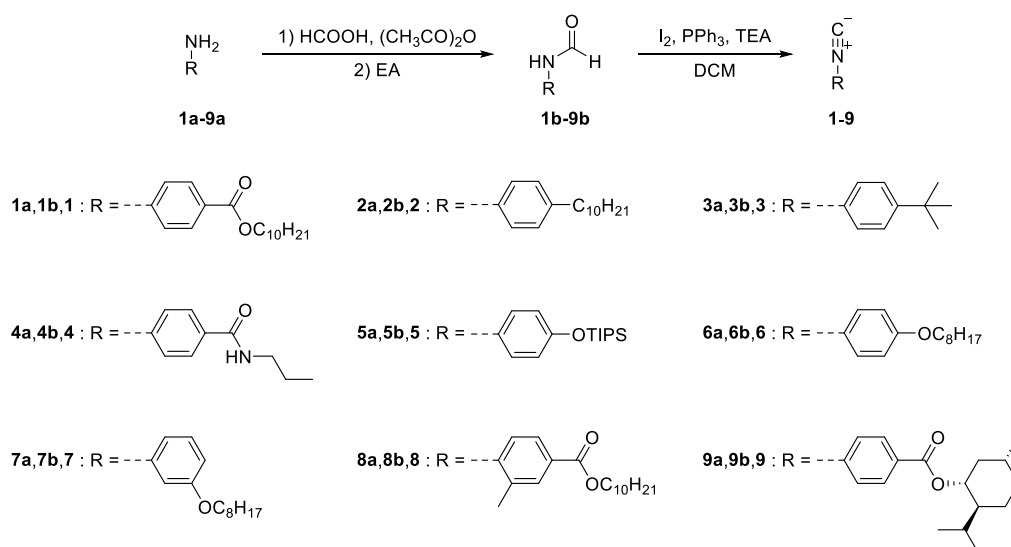
2. General analytical information

NMR spectra were recorded by Varian/Oxford As-500 (500 MHz for ¹H NMR, and 125MHz for ¹³C NMR), Agilent 400-MR DD2 Magnetic Resonance System (162 MHz for ³¹P NMR) spectrometers. ¹³C NMR spectra of polymers were recorded by Bruker AVNACE III HD (213 MHz for ¹³C NMR) spectrometer in National Center for Inter-University Research Facilities (NCIRF). THF size exclusion chromatography (SEC) for polymer molecular weight analysis was carried out with Waters system (1515 pump, 2414 refractive index detector and 2489 UV detector) and Shodex SEC LF-804 column eluted with THF (SEC grade, Honeywell Burdick & Jackson). Flow rate was 1.0 mL/min and temperature of the column was maintained at 35 °C. Samples were diluted in 0.001-0.005 wt% by THF and filtered through a 0.20 μm PTFE filter before injection into the SEC. IR spectra were measured by Shimadzu Inc. IRTTracer-100 spectrometer. High-resolution mass spectroscopy (HRMS) analyses were performed by ultra-high resolution ESI Q-TOF mass spectrometer (Bruker, Germany) in Sogang Center for Research Facilities. UV-vis spectra were obtained by Jasco Inc. UV-vis Spectrometer V-650. Circular dichroism (CD) measurements were carried out by AppliedPhotophysics Inc. circular dichroism detector Chirascan plus in National Instrumentation Center for Environmental Management (NICEM).

3. Preparation and characterization of monomers and polymers

(a) General procedure for formylation and dehydration to afford monomers 1-9

Compounds **1a**,³ **4a**,⁴ **6a**,⁵ **7a**,⁶ and **9a**,⁷ were prepared by the previously reported synthetic methods.



To a dried and argon-purged round-bottom flask containing a magnetic stir bar, formic acid (25 mmol) and acetic anhydride (12.5 mmol) were added. The mixture was stirred at rt for 1 h for *in-situ* preparation of acetic formic anhydride. A solution of compound **1a** (5 mmol) in degassed EA (25 ml) was prepared in another flask, and the preformed acetic formic anhydride solution was injected to the **1a** solution at 0 °C. After stirring overnight at rt, the removal of volatiles under reduced pressure gave compound **1b** as white solid, and it was used for the next step without further purification.

Dehydration step was implemented according to the procedure from the previous literature.⁸ A round-bottom flask was charged with **1b**, I₂ (7.5 mmol), and PPh₃ (7.5 mmol), and purged with argon. The reagents were dissolved in DCM (15 ml), followed by the dropwise addition of trimethylamine (15 mmol) at rt. After the consumption of **1b**, the crude reaction mixture was diluted with DCM, and washed with ice-cold sat. aq Na₂S₂O₃ solution. The organic layer was dried over anhydrous MgSO₄, concentrated under reduced pressure, and purified by flash column chromatography on silica gel to afford aryl isocyanide **1** as white solid.

1 (white solid, two-step: 83%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.³

2 (white solid, two-step: 83%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.⁹

3 (yellow liquid, two-step: 78%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.¹⁰

4 (white solid, two-step: 76%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.⁴

5 (yellow liquid, two-step :72%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.24 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.2 Hz, 2H), 1.32-1.18 (m, 3H), 1.09 (d, *J* = 7.4 Hz, 18H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) = 163.0, 157.1, 128.0, 120.8, 120.0, 18.1, 12.9. IR (neat): 2122 cm⁻¹. HRMS (ESI): *m/z* for C₁₆H₂₅NNaOSi [M+Na]⁺, calcd. 298.1598, found: 298.1601.

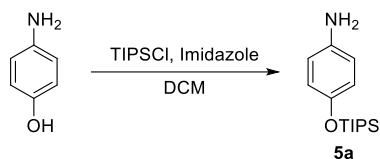
6 (yellow liquid, two-step: 83%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.⁵

7 (yellow liquid, two-step: 74%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.26 (t, *J* = 8.5 Hz, 1H), 6.99-6.90 (m, 2H), 6.88 (s, 1H), 3.94 (t, *J* = 6.5 Hz, 2H) 1.84-1.72 (m, 2H), 1.51-1.40 (m, 2H), 1.40-1.19 (m, 8H), 0.89 (t, *J* = 6.7 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) = 164.2, 159.9, 130.4, 127.6, 118.7, 116.4, 112.7, 68.7, 32.1, 29.6, 29.5, 29.3, 26.2, 22.9, 14.3. IR (neat): 2123 cm⁻¹. HRMS (ESI): *m/z* for C₁₅H₂₁NNaO [M+Na]⁺, calcd. 254.1515, found: 254.1514.

8 (yellow liquid, two-step: 82%): ¹H NMR (500 MHz, CDCl₃) δ (ppm) = 7.96 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 4.31 (t, *J* = 6.6 Hz, 2H), 2.48 (s, 3H), 1.75 (dd, *J* = 14.2, 7.2 Hz, 2H), 1.51-1.17 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H). ¹³C NMR (125 MHz, CDCl₃) δ (ppm) = 169.0, 165.6, 135.5, 132.0, 131.4, 130.3, 128.3, 126.8, 66.0, 32.2, 29.8 (d, *J* = 1.9 Hz), 29.6 (d, *J* = 4.1 Hz), 29.0, 26.3, 23.0, 18.9, 14.4. IR (neat): 2117, 1723 cm⁻¹. HRMS (ESI): *m/z* for C₁₉H₂₇NNaO₂ [M+Na]⁺, calcd. 324.1934, found: 324.1933.

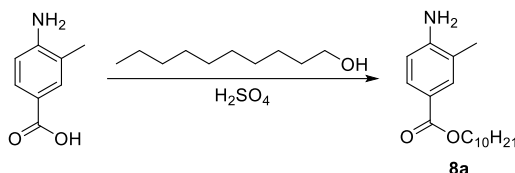
9 (yellow liquid, two-step: 84%): The structure was confirmed by matching its spectroscopic data with corresponding reported data.⁷

(b) Preparation of compound 5a



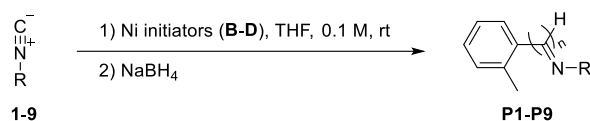
A round-bottom flask was charged with 4-aminophenol (5 mmol), imidazole (7.5 mmol), and purged with argon. The reagents were dissolved in DCM (50 ml), followed by the dropwise addition of triisopropylsilyl chloride (7.5 mmol). After stirring for 17 h at rt, the crude reaction mixture was diluted with DCM, and washed with brine. The organic layer was dried over anhydrous MgSO_4 , concentrated under reduced pressure, and purified by flash column chromatography on silica gel to afford **5a** as yellow liquid (4.25 mmol, 85%). ^1H NMR (500 MHz, CDCl_3) δ (ppm) = 6.77-6.66 (m, 2H), 6.62-6.53 (m, 2H), 3.33 (s, 2H), 1.35-1.16 (m, 3H), 1.10 (d, J = 7.3 Hz, 18H). ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) = 149.0, 140.2, 120.7, 116.6, 18.2, 12.9. HRMS (ESI): m/z for $\text{C}_{15}\text{H}_{28}\text{NOSi}$ $[\text{M}+\text{H}]^+$, calcd. 266.1935, found: 266.1939.

(c) Preparation of compound 8a



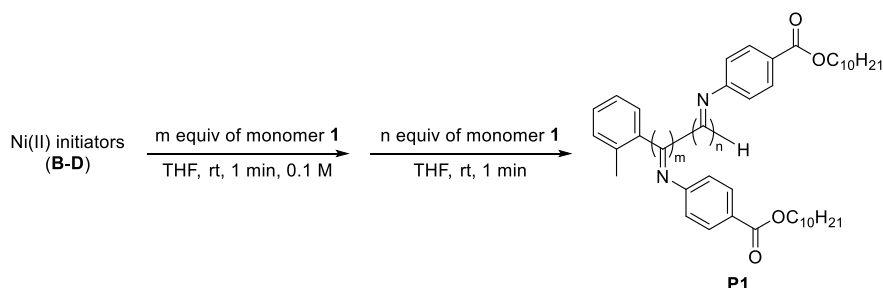
A round-bottom flask was charged with 4-amino-3-methylbenzoic acid (10 mmol), and a magnetic stir bar. The flask was purged with argon, and 1-decanol (15 ml) and H_2SO_4 (1 ml) was added. After stirring overnight at 80 °C, the crude reaction mixture was diluted with EA, and washed with sat. aq NaHCO_3 solution. The organic layer was dried over anhydrous MgSO_4 , concentrated under reduced pressure, and purified by flash column chromatography on silica gel afford **8a** as white solid (7.78 mmol, 78%). ^1H NMR (500 MHz, CDCl_3) δ (ppm) = 7.79-7.71 (m, 2H), 6.64 (d, J = 8.1 Hz, 1H), 4.26 (t, J = 6.8 Hz 2H), 4.09 (br, 1H), 2.18 (s, 3H), 1.81-1.68 (m, 2H), 1.50-1.17 (m, 14H), 0.88 (t, J = 6.9 Hz, 3H). ^{13}C NMR (125 MHz, CDCl_3) δ (ppm) = 167.3, 149.2, 132.5, 129.6, 121.4, 120.5, 114.1, 64.8, 32.2, 29.9, 29.6, 29.2, 26.4, 23.0, 17.5, 14.4. HRMS (ESI): m/z for $\text{C}_{18}\text{H}_{29}\text{NNaO}_2$ $[\text{M}+\text{Na}]^+$, calcd. 314.2090, found: 314.2094.

(d) General procedure for polymerization



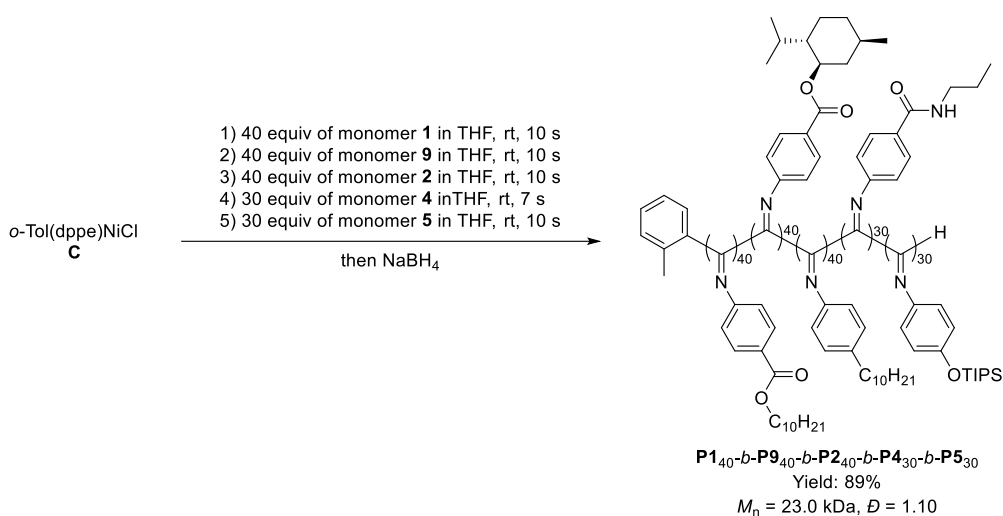
A 4-ml sized screw-cap vial with septum was flame dried, and charged with monomer (0.1 mmol) and a magnetic stir bar. The vial was purged with argon three times, and degassed anhydrous THF (0.9 ml) was added. After the argon-purged initiator (0.002 mmol) in another 4-ml vial was dissolved in THF (0.1 ml), the solution was rapidly injected to the monomer solution at rt under vigorous stirring. The reaction was quenched by excess amount of NaBH₄ after the desired reaction time. The crude reaction mixture was diluted with CHCl₃, and washed with brine. The organic layer was dried over anhydrous MgSO₄, and concentrated under reduced pressure. The polymer was purified by precipitation in methanol. The precipitate was collected by filtration, washed with methanol, and dried under vacuum.

(e) General procedure for chain extension experiment with monomer 1



A 4-ml sized screw-cap vial with septum was flame dried, and charged with **1** (0.1 mmol) and a magnetic stir bar. The vial was purged with argon three times, and degassed anhydrous THF (0.9 ml) was added. After the argon-purged initiator (0.002 mmol) in another 4-ml vial was dissolved in THF (0.1 ml), the solution was rapidly injected to the monomer solution at rt under vigorous stirring. The polymerization was left to stir for 1 min. Subsequently, a solution of **1** (0.1 mmol) in THF (0.1 ml) was added to the reaction mixture, and the further polymerization underwent for 1 min. Then, the reaction was quenched by excess amount of NaBH₄. The crude reaction mixture was diluted with CHCl₃, and washed with brine. The organic layer was dried over anhydrous MgSO₄, and concentrated under reduced pressure. The polymer was purified by precipitation in methanol. The precipitate was collected by filtration, washed with methanol, and dried under vacuum.

(f) Synthesis of pentablock copolymer



A 4-ml sized screw-cap vial with septum was flame dried and charged with **1** (0.055 mmol) and a magnetic stir bar. The vial was purged with argon three times, and degassed anhydrous THF (0.5 ml) was added. After the argon-purged initiator **C** (0.00138 mmol) in another 4-ml vial was dissolved in THF (0.05 ml), the solution was rapidly injected to the monomer solution at rt under vigorous stirring. After stirring for 10 s, a solution of **9** (0.055 mmol) in THF (0.05 ml) was added, and the reaction underwent for 10 s. To the reaction pot, a solution of **2** (0.055 mmol) in THF (0.05 ml) was added, and the polymerization was left to stir for 10 s. Further addition of a solution of **4** (0.041 mmol) in THF (0.05 ml) was implemented, and the polymerization was left to stir for 7 s. Subsequently, a solution of **5** (0.041 mmol) in THF (0.05 ml) was added to the reaction mixture, and the further polymerization underwent for 10 s. Then, the reaction was quenched by excess amount of NaBH₄. The crude reaction mixture was diluted with CHCl₃, and washed with brine. The organic layer was dried over anhydrous MgSO₄, and concentrated under reduced pressure. The polymer was purified by precipitation in methanol. The precipitate was collected by filtration, washed with methanol, and dried under vacuum.

4. Procedure for *in-situ* ³¹P NMR experiments

A NMR tube with septum was flame dried and charged with initiator (0.01 mmol, 1 equiv.), and purged with argon. Trimethyl phosphate (internal standard) and THF-*d*₈ (0.4 ml) were added to the tube. The initial phosphine was measured by an integral ratio of initiator to trimethyl phosphate in ³¹P NMR spectrum. After the argon-purged **1** (0.1 mmol, 10 equiv.) in a 4-ml sized vial was dissolved in THF-*d*₈ (0.1 ml), the solution was rapidly injected to the NMR tube, and ³¹P NMR measurement was recorded. Then, an integral ratio between dissociated phosphine from the Ni center and the internal standard was calculated.

5. THF SEC traces of polymers

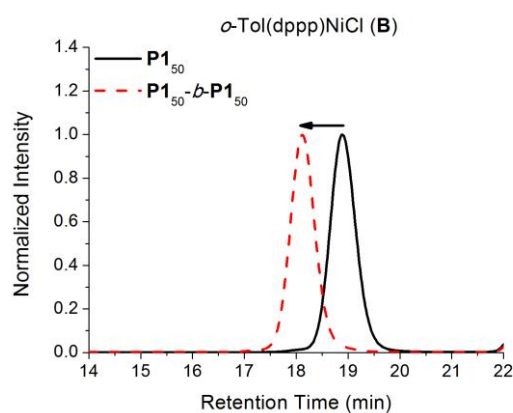
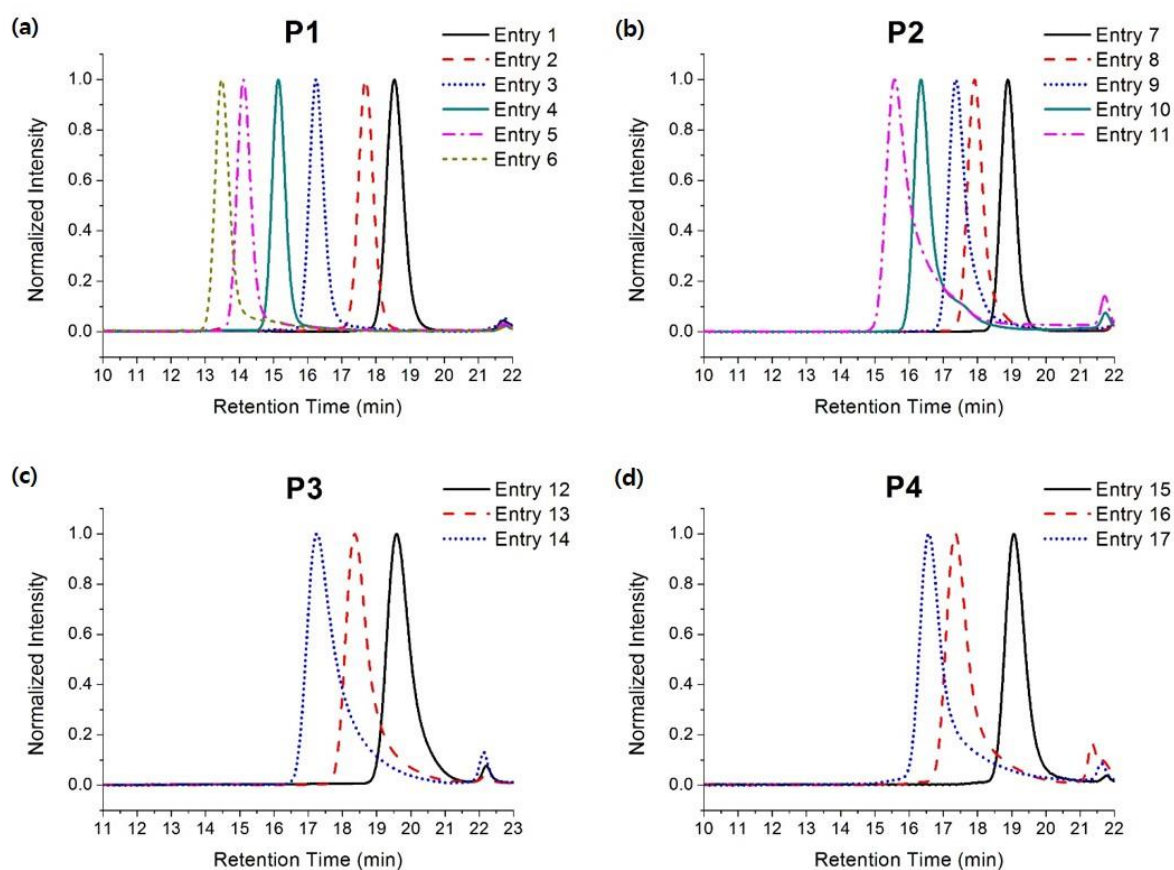


Figure S1. THF SEC traces of a homopolymer and a chain-extended polymer initiated by *o*-Tol(dppp)NiCl (B) (Table 1; entries 2 and 5).



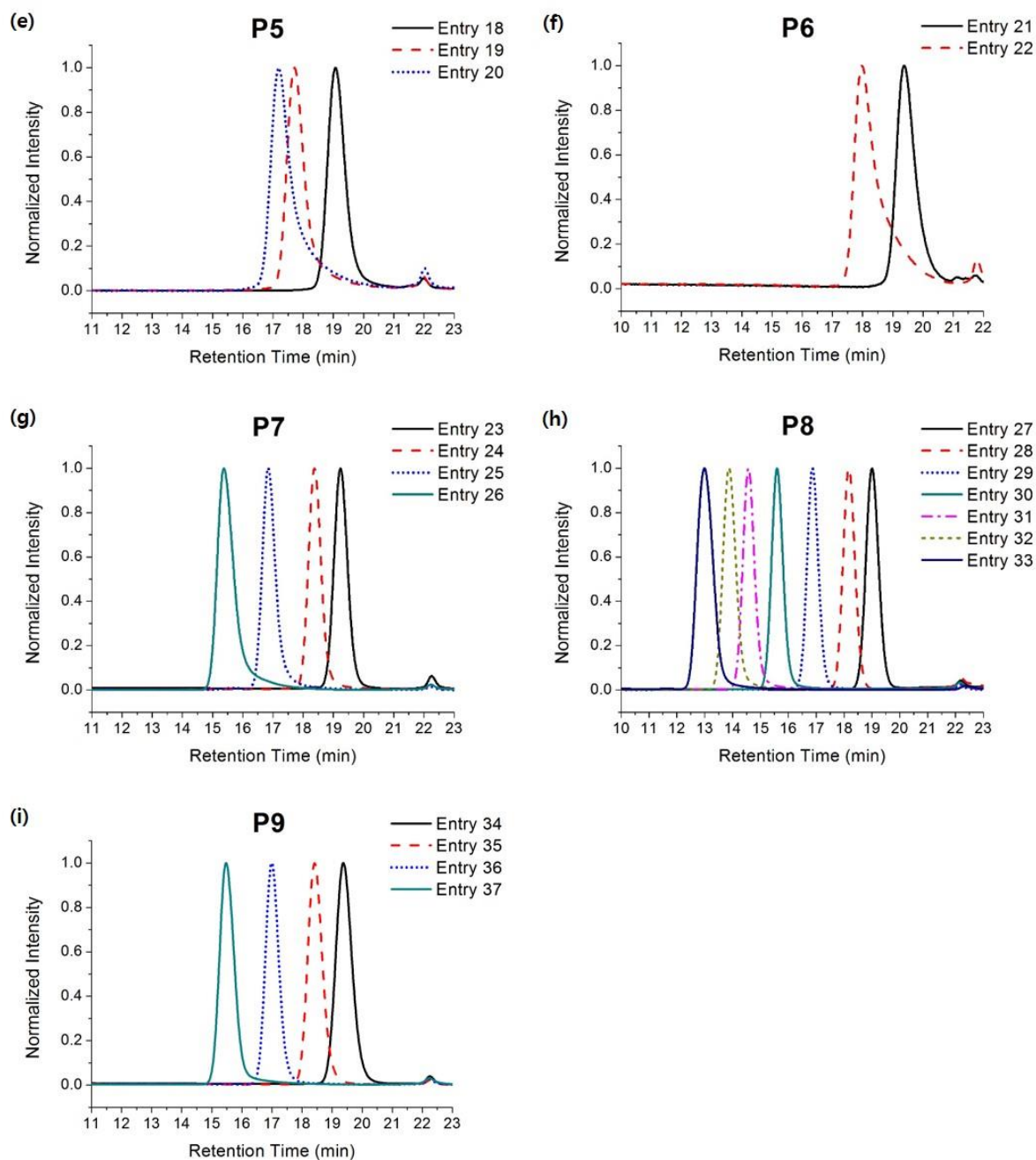


Figure S2. THF SEC traces of polymers in Table 2 (a) **P1** (entries 1-6), (b) **P2** (entries 7-11), (c) **P3** (entries 12-14), (d) **P4** (entries 15-17), (e) **P5** (entries 18-20), (f) **P6** (entries 21 and 22), (g) **P7** (entries 23-26), (h) **P8** (entries 27-33), and (i) **P9** (entries 34-37).

6. Plots of M_n vs. M/I ratios and their corresponding \bar{D} values

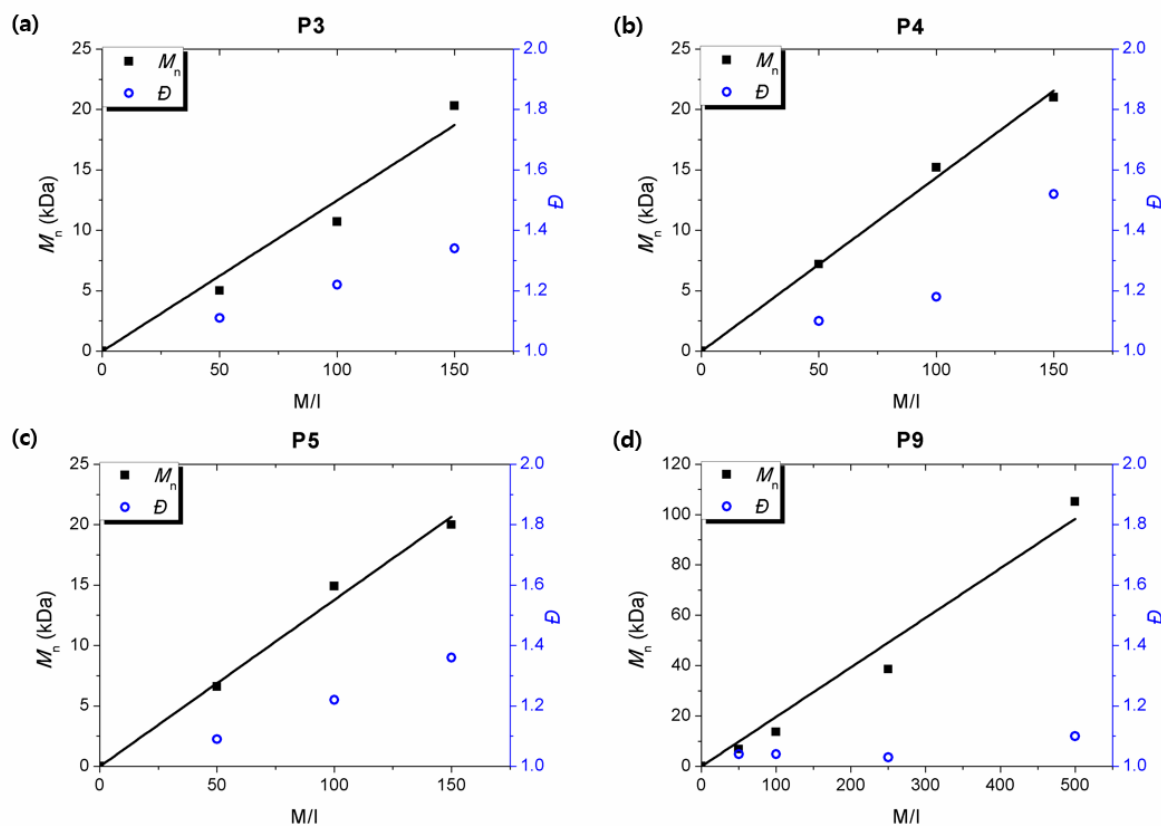


Figure S3. Plots of M_n vs. M/I ratios and their corresponding \bar{D} values for (a) **P3**, (b) **P4**, (c) **P5**, and (d) **P9**. The actual M/I values were calculated from the initial feeding ratios and the final conversions.

7. Imino carbon peaks of P1 and P8 in ^{13}C NMR spectra

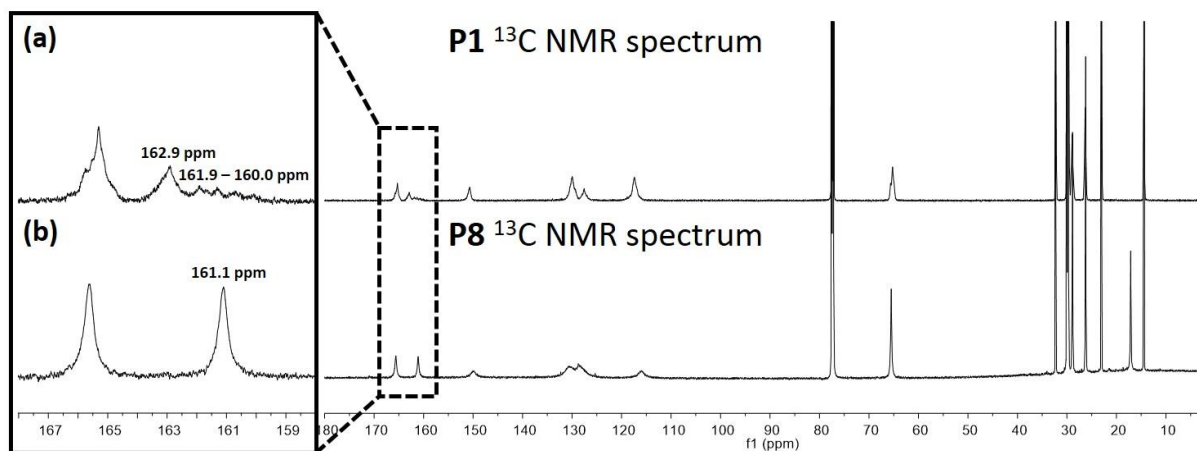


Figure S4. ^{13}C NMR spectra of (a) **P1** and (b) **P8**. Peaks in the range of 160-164 ppm correspond to the imino carbon of the polymer backbone.

8. UV-vis and CD spectra of P9₁₀₀

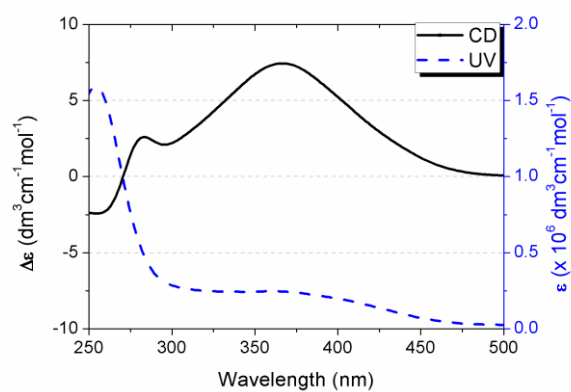
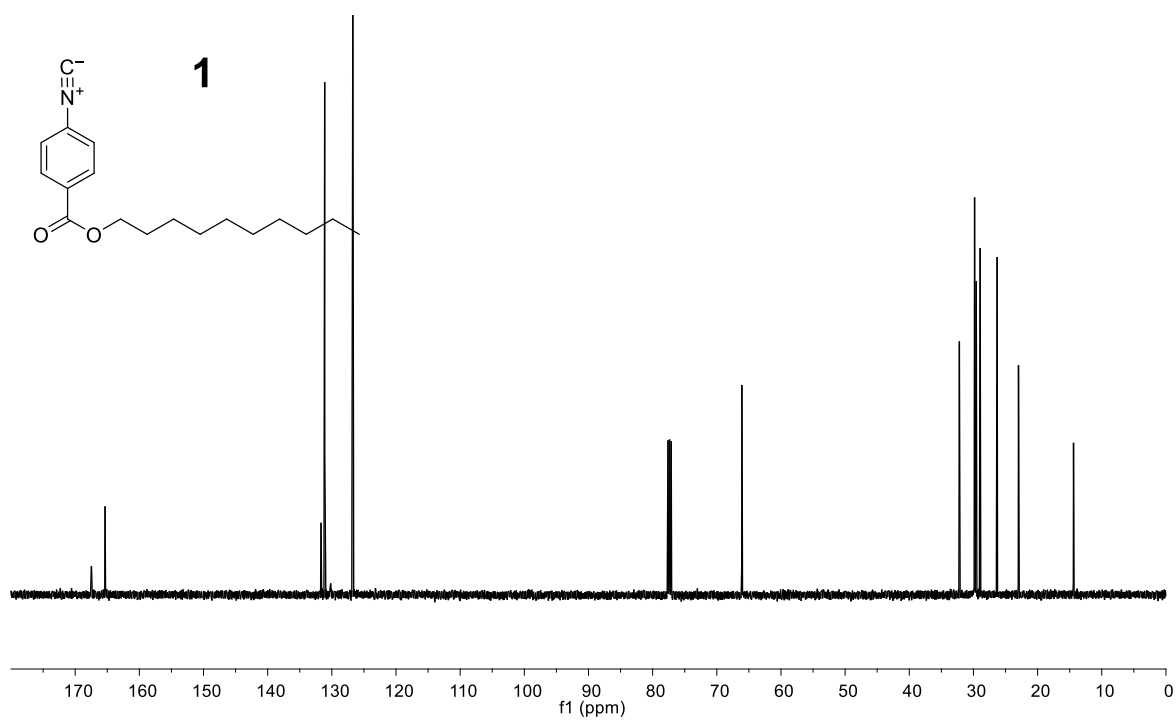
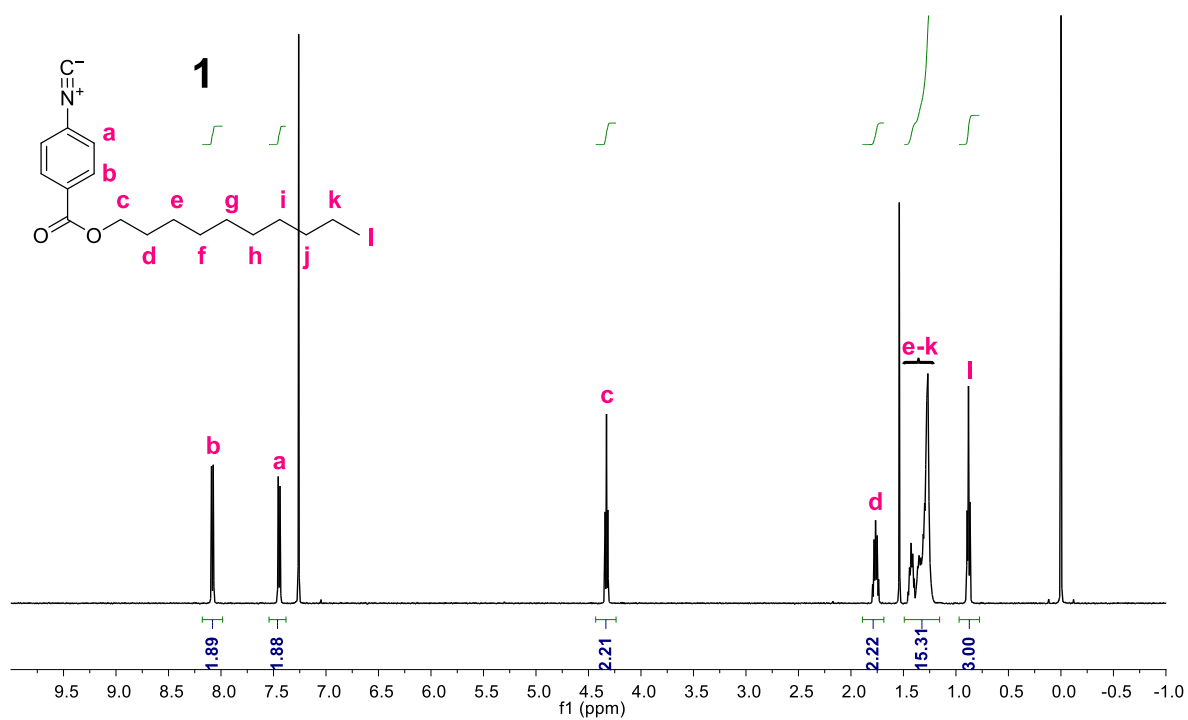
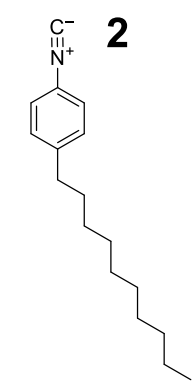
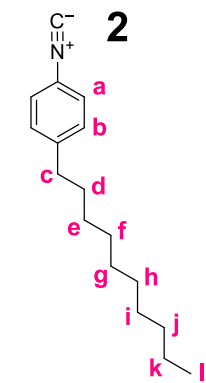
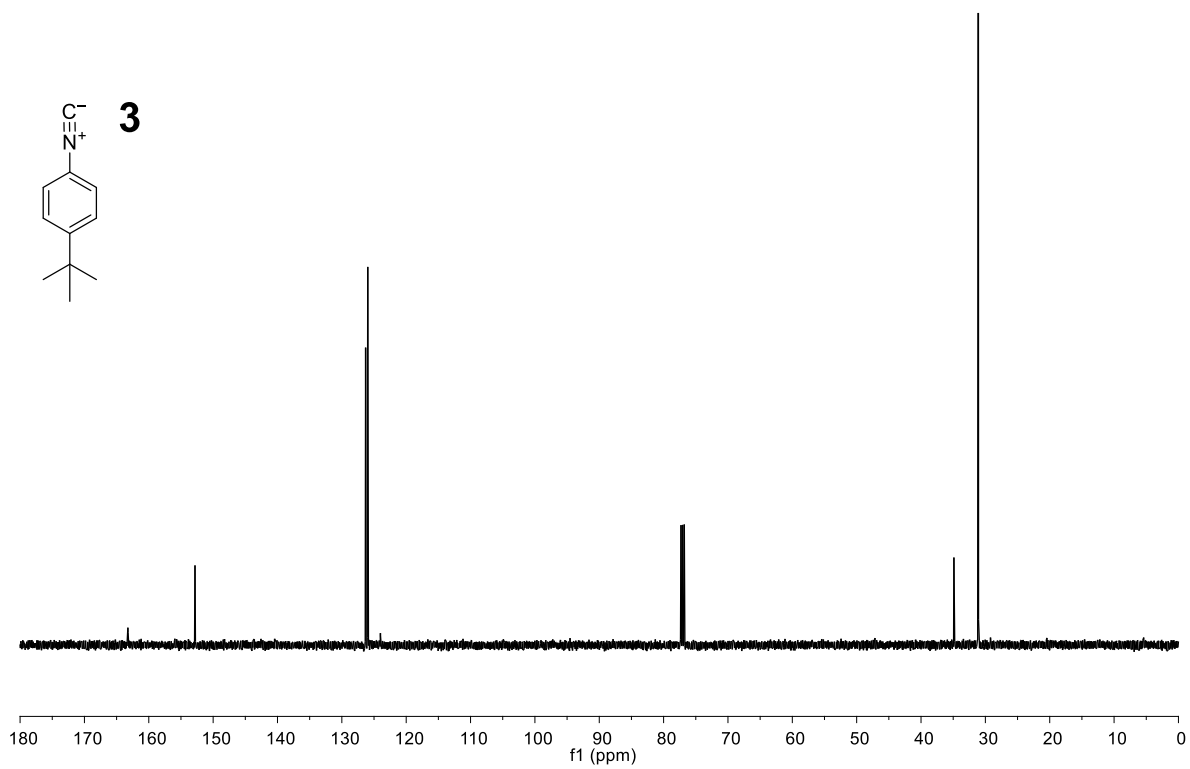
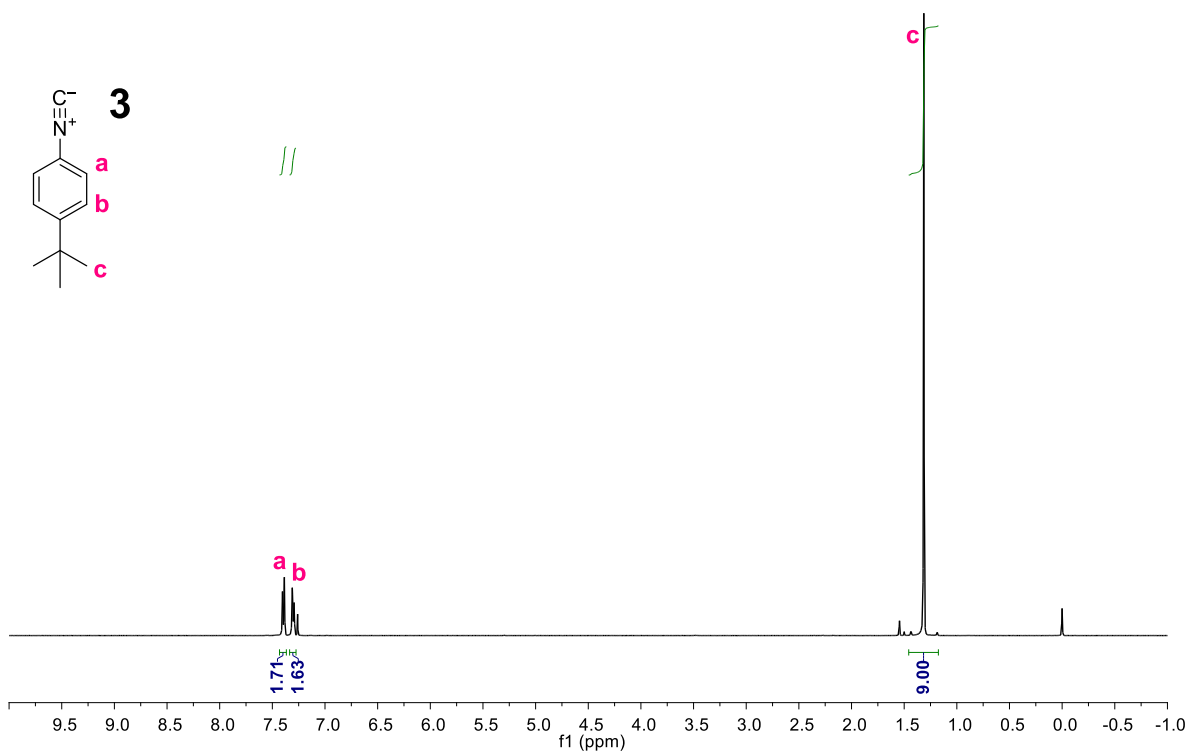


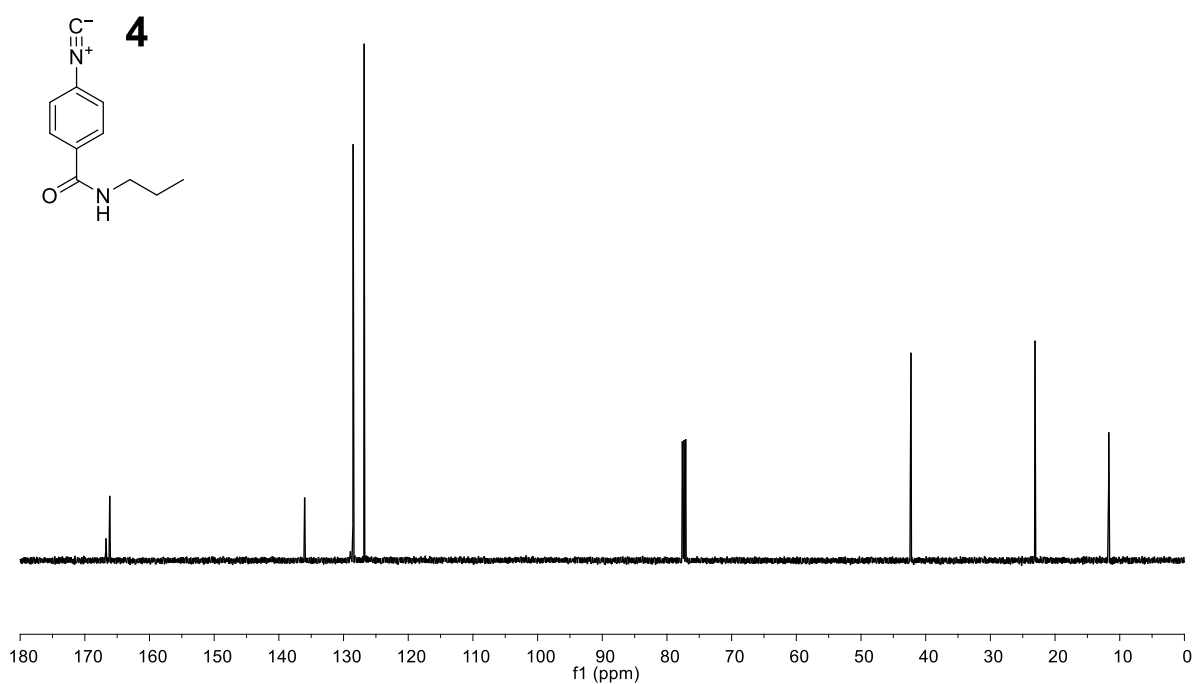
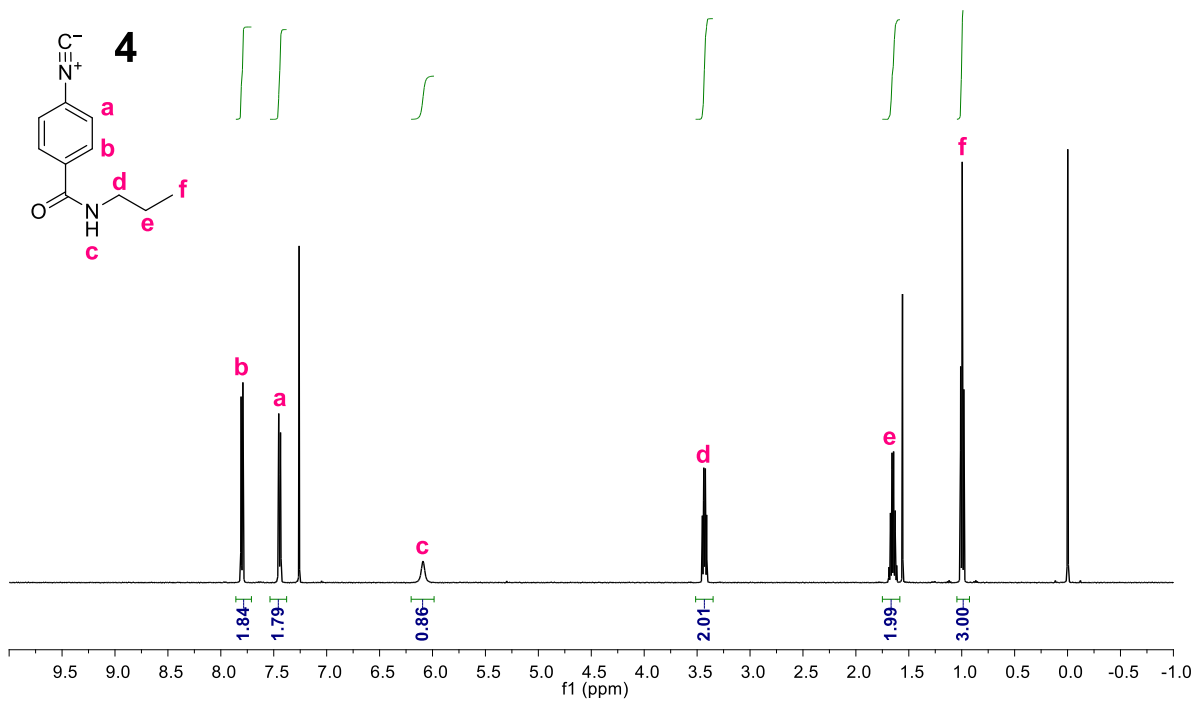
Figure S5. CD spectrum of P9₁₀₀ measured in CHCl₃ (5 mg/ml), and UV-vis spectrum of P9₁₀₀ measured in CHCl₃ (0.01 mg/ml) at rt. Molar ellipticity ($[\theta]$) was converted to $\Delta\epsilon$ by the following equation: $[\theta] = 3298.2\Delta\epsilon$.

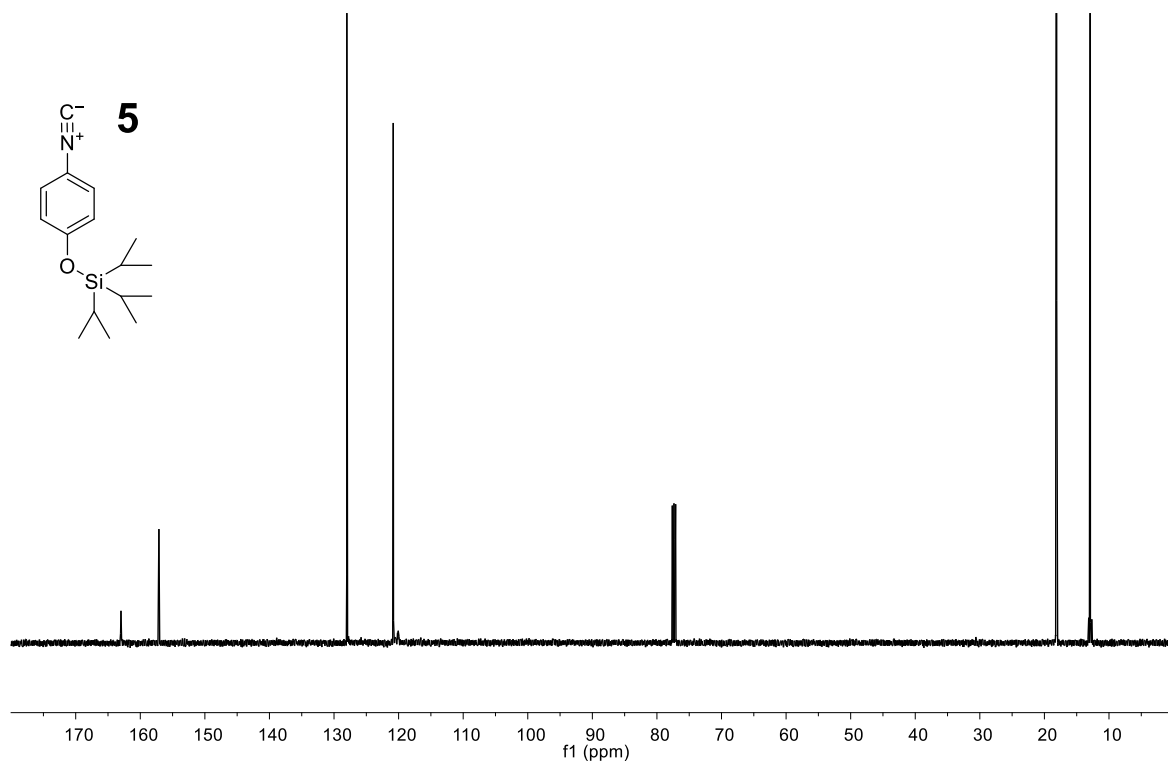
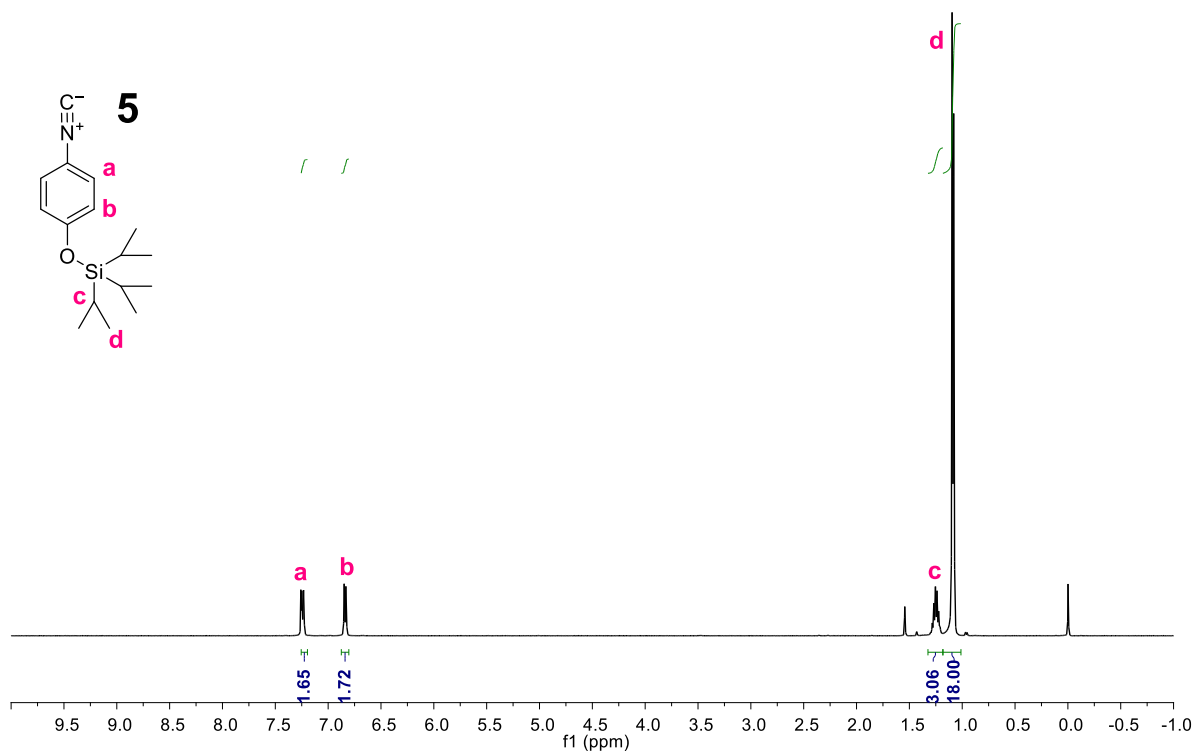
9. ^1H and ^{13}C NMR spectra of monomers and polymers

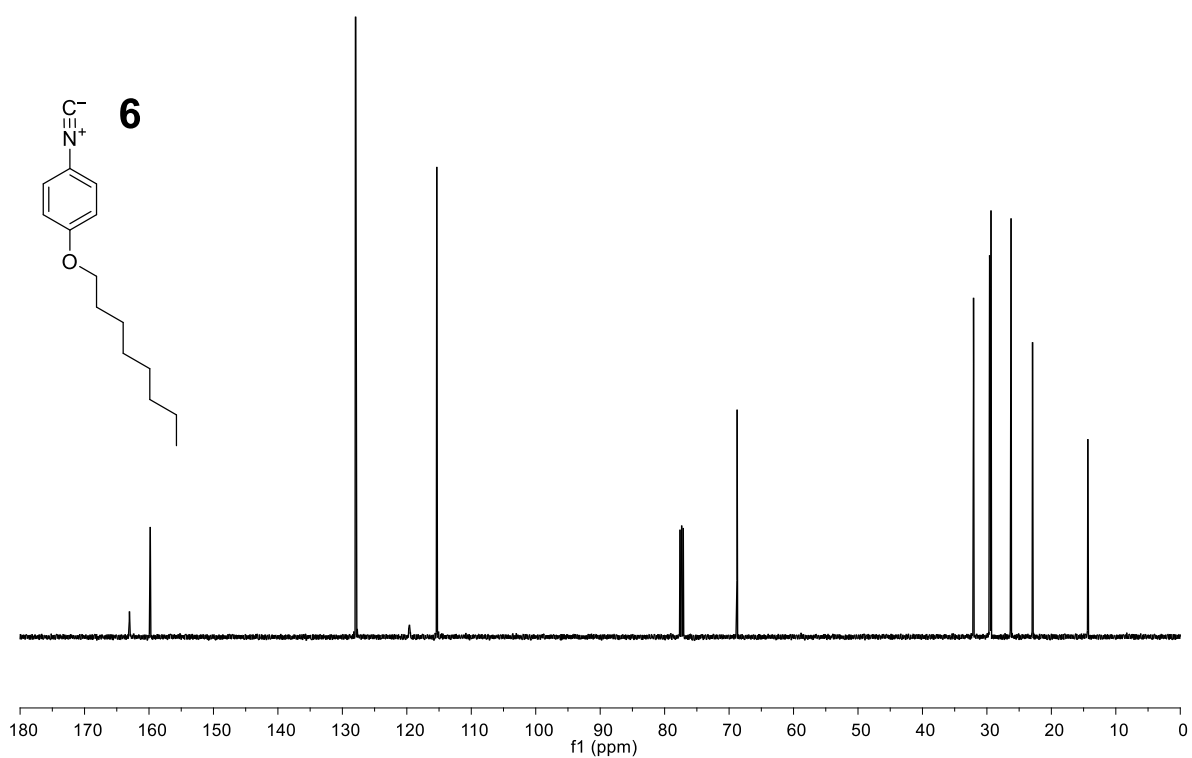
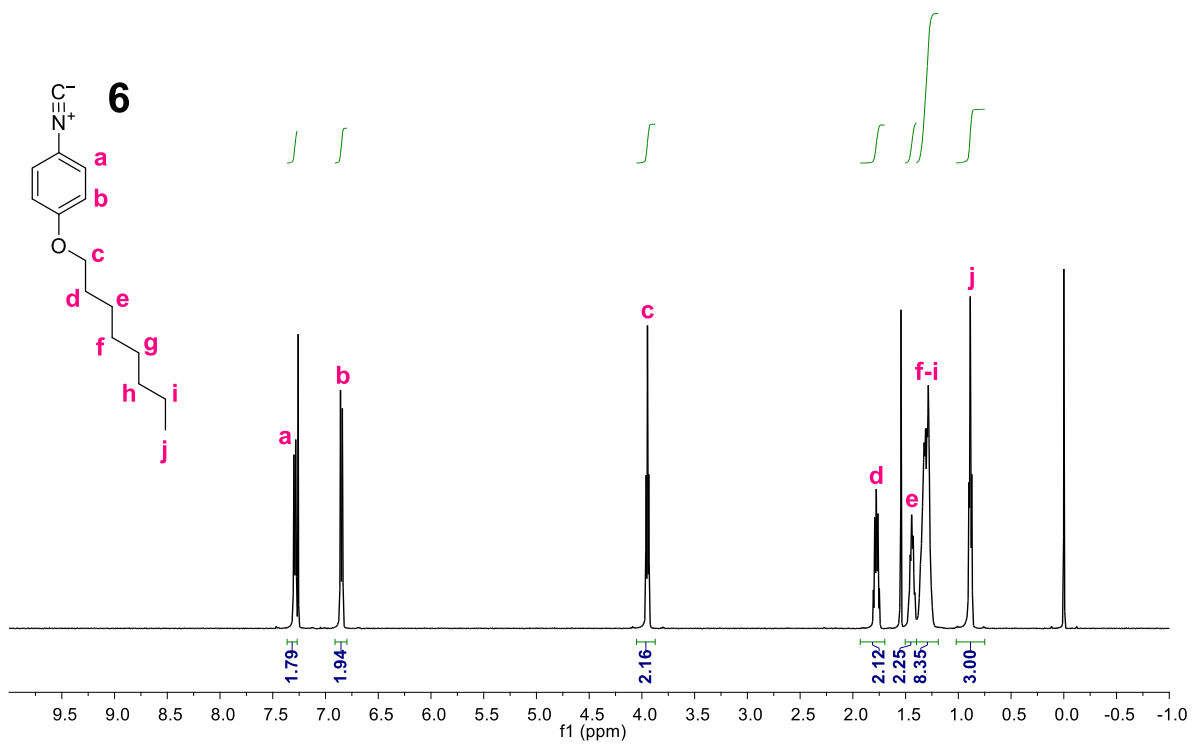


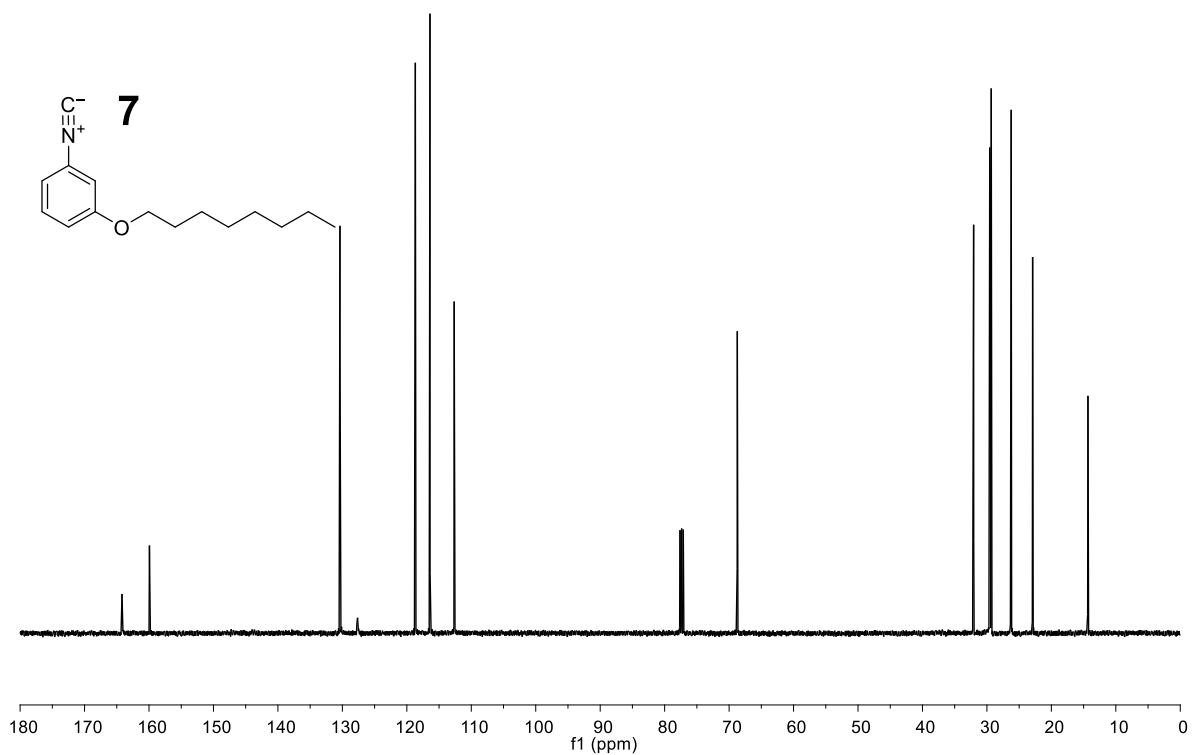
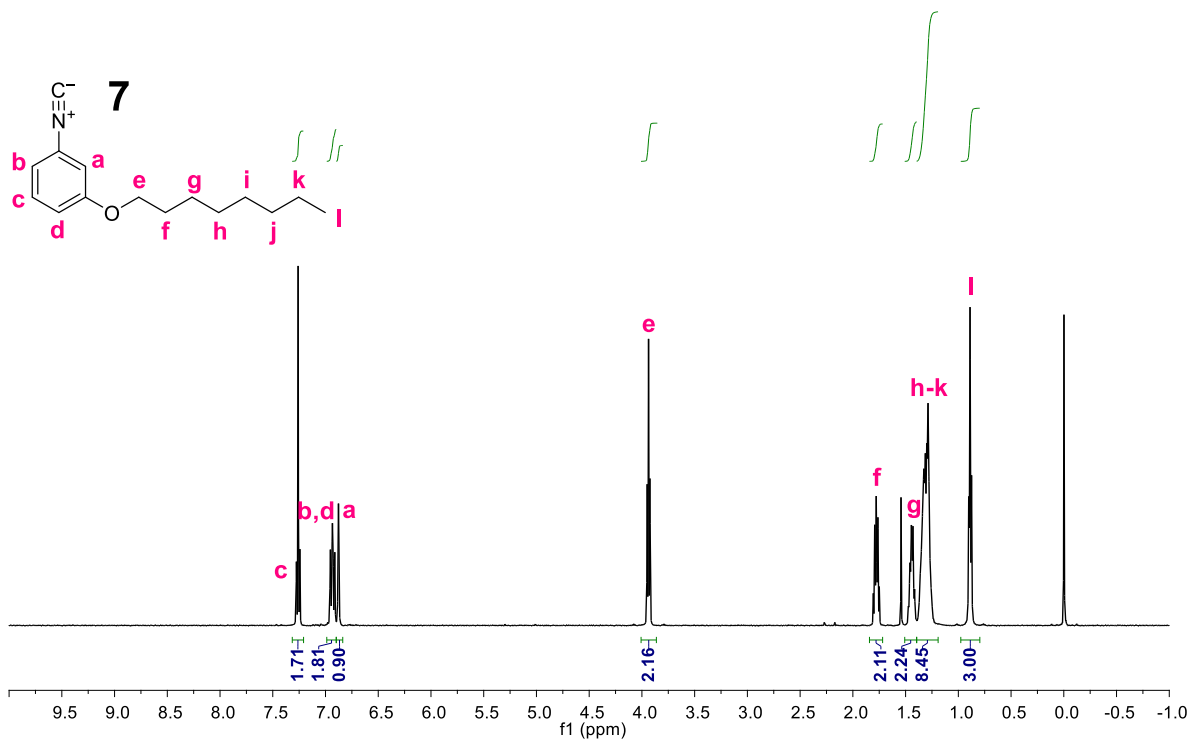


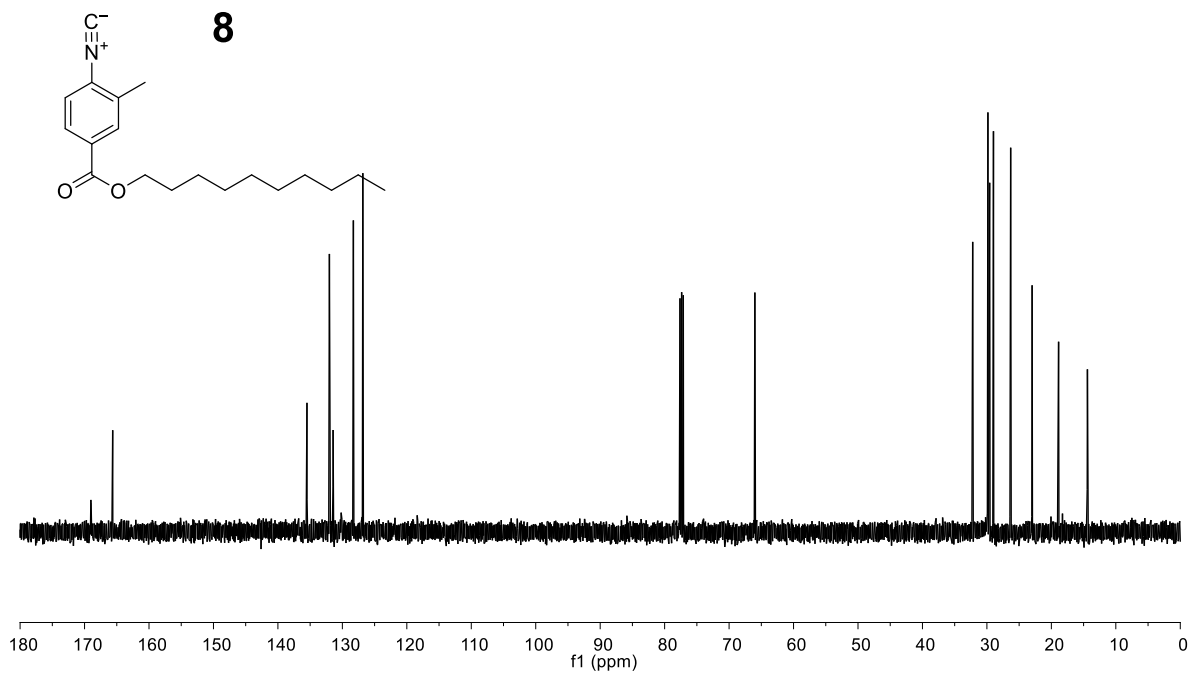
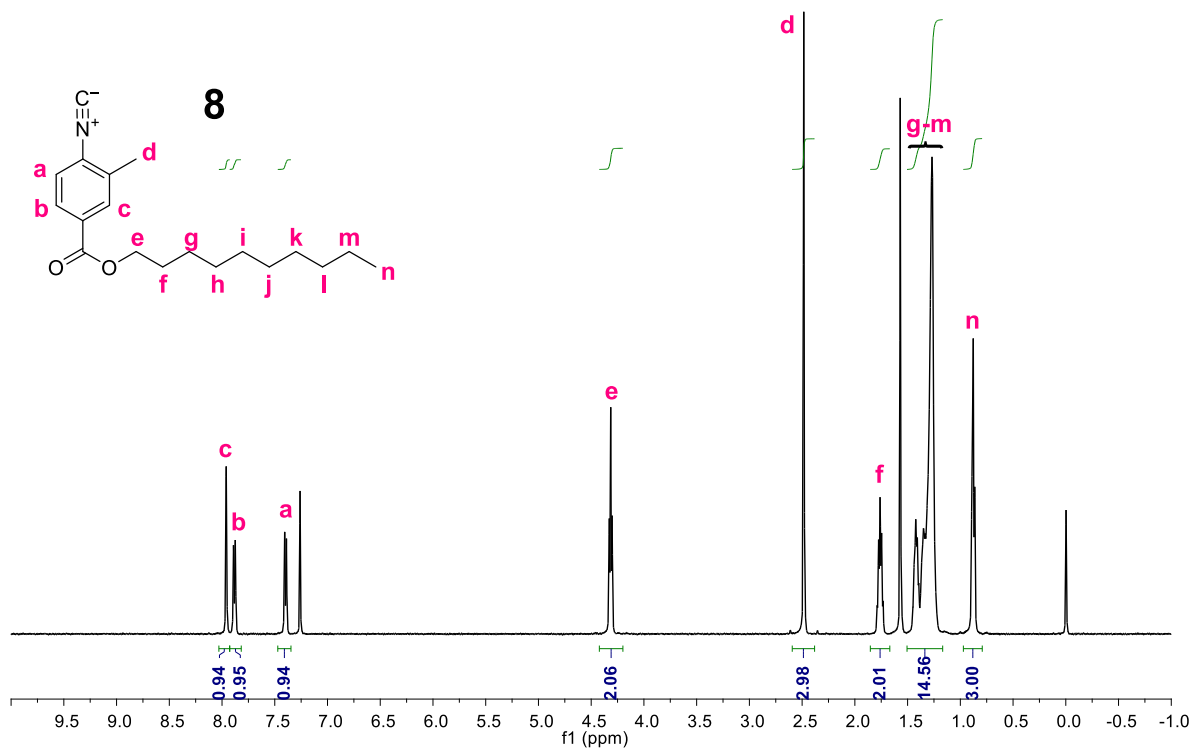


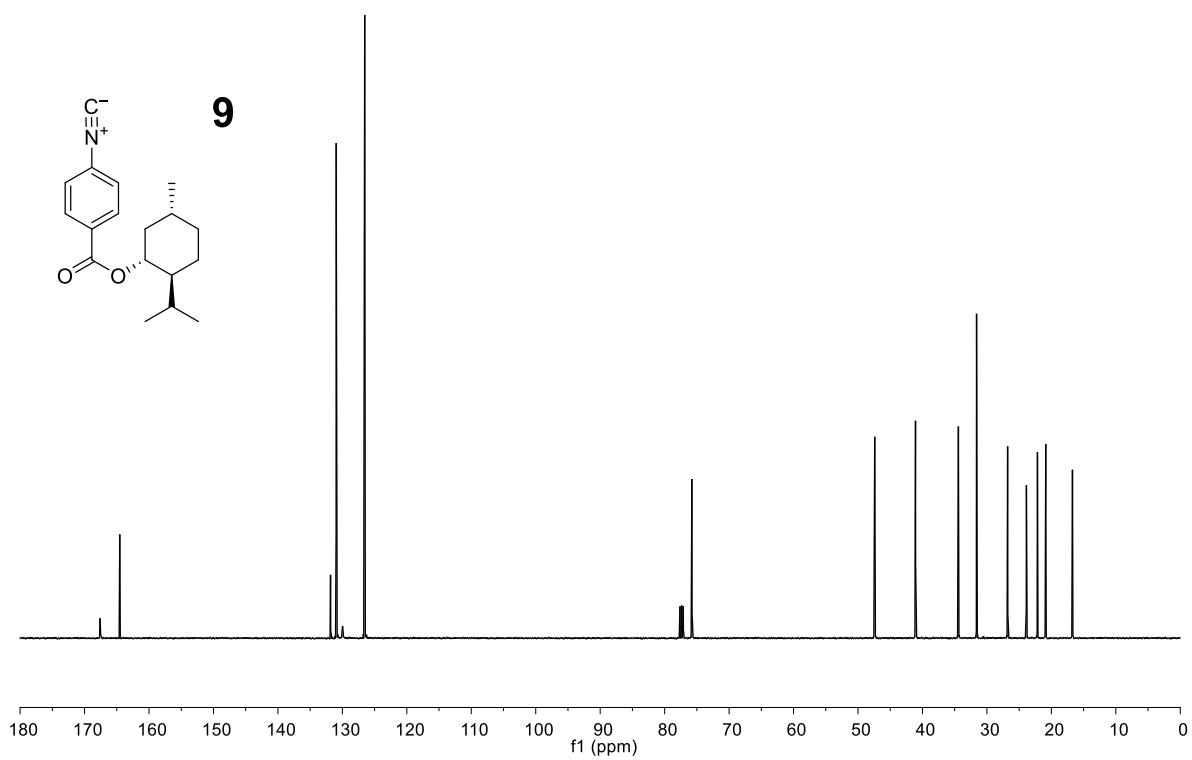
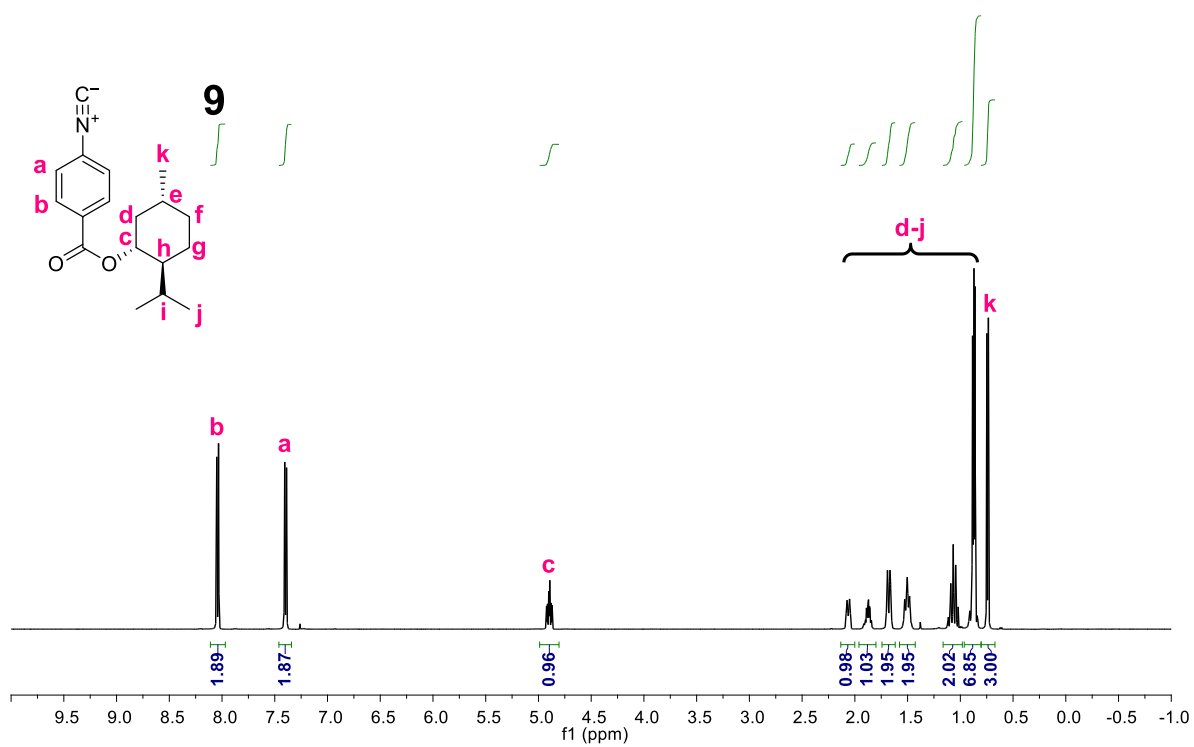


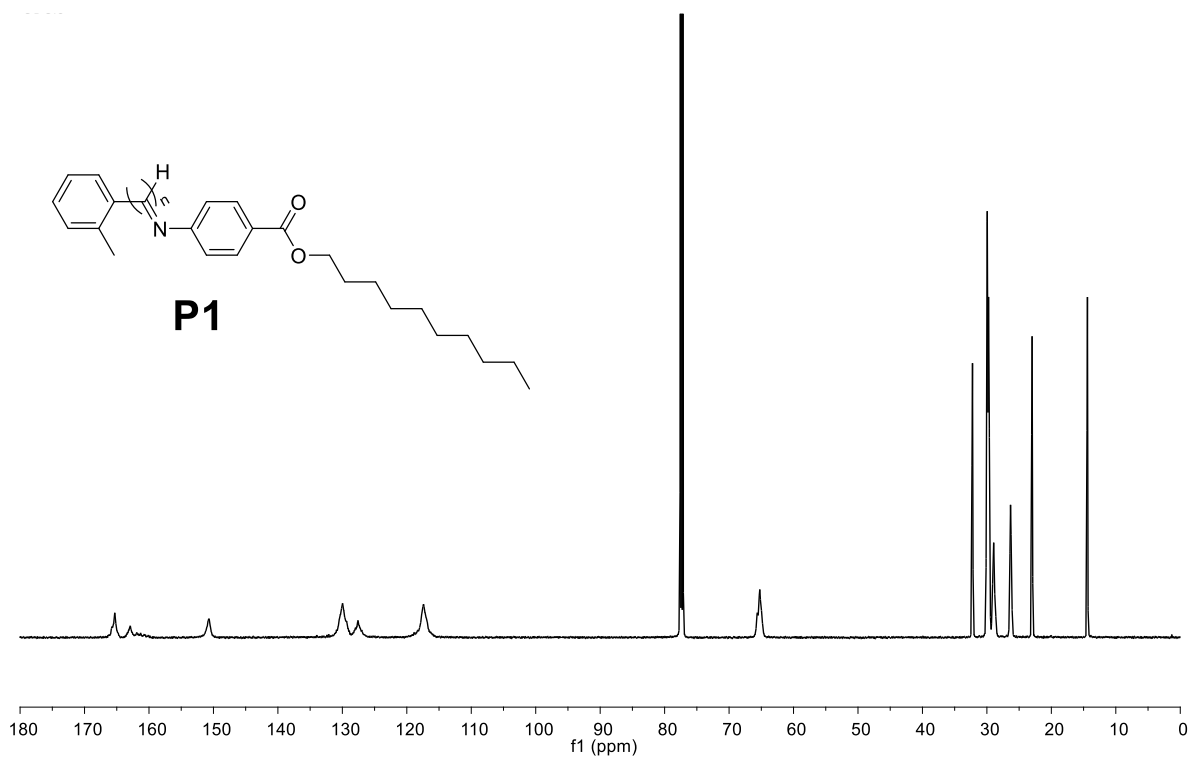
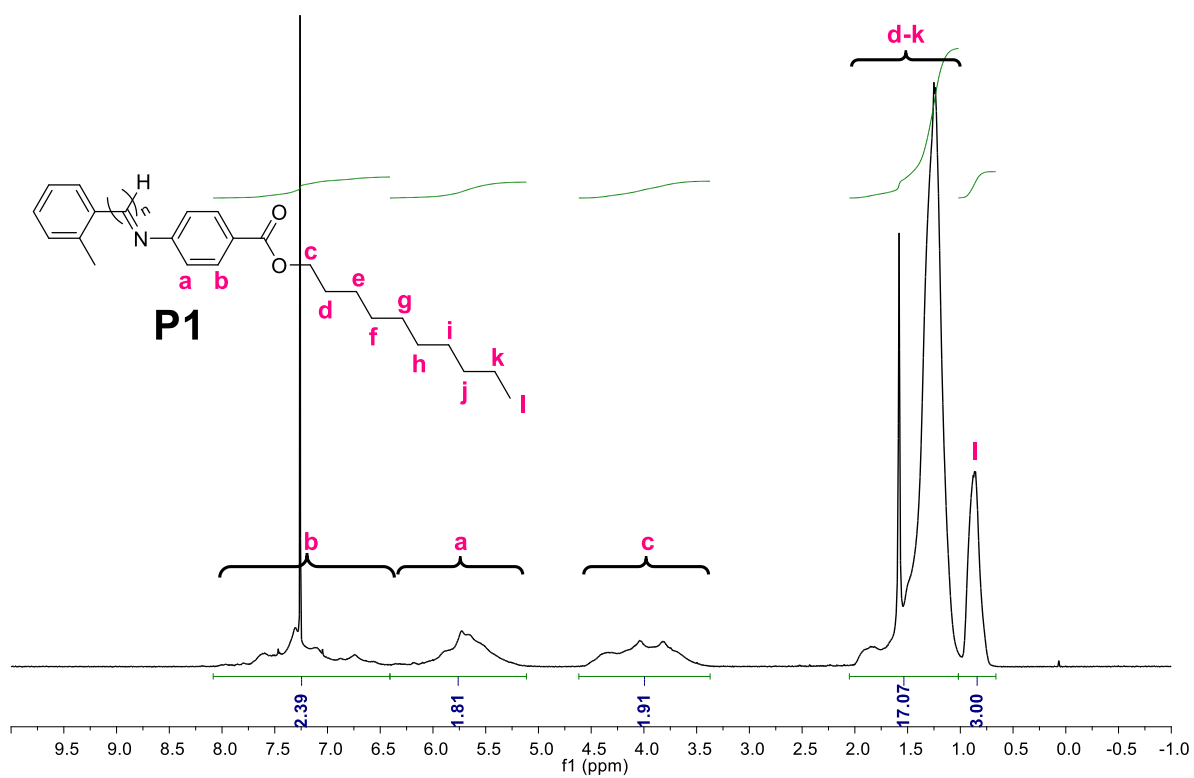


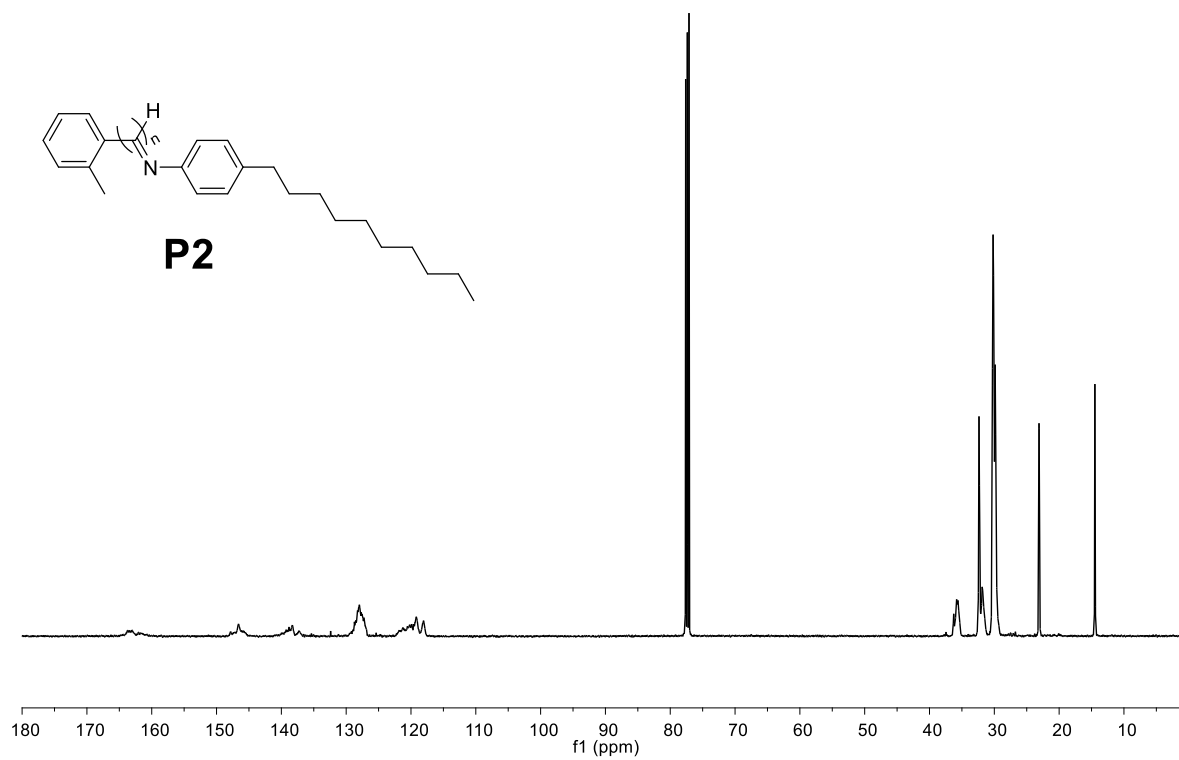
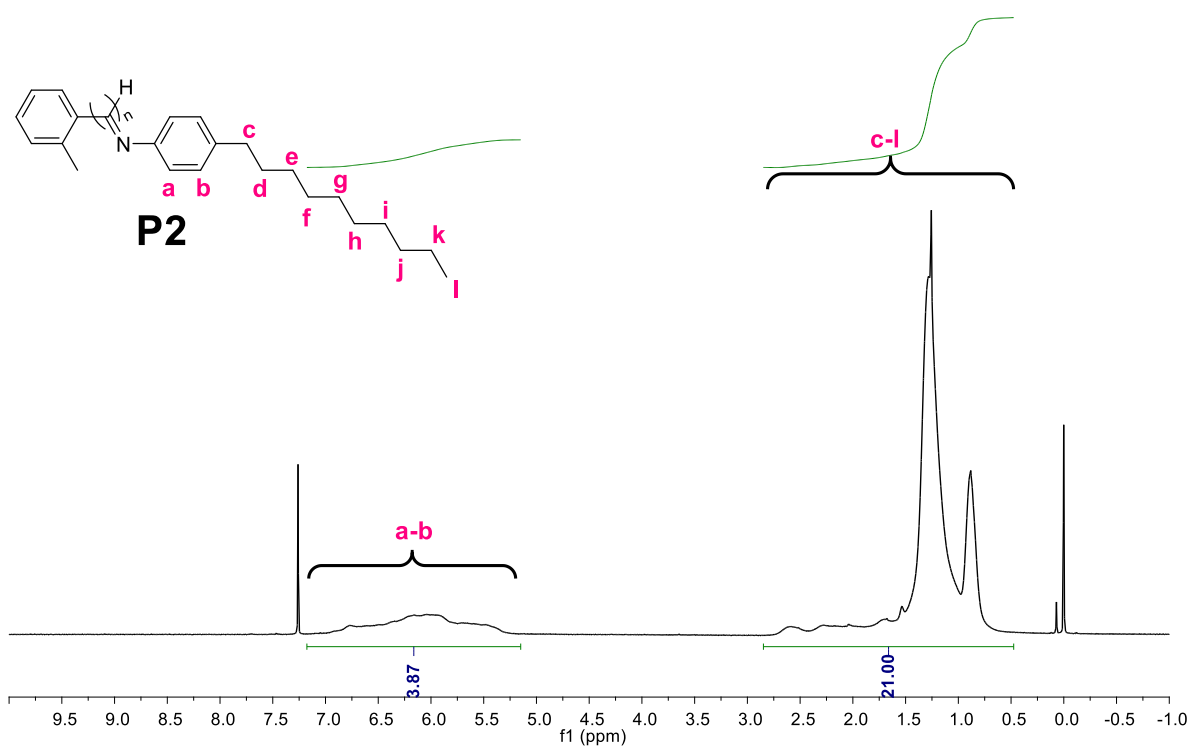


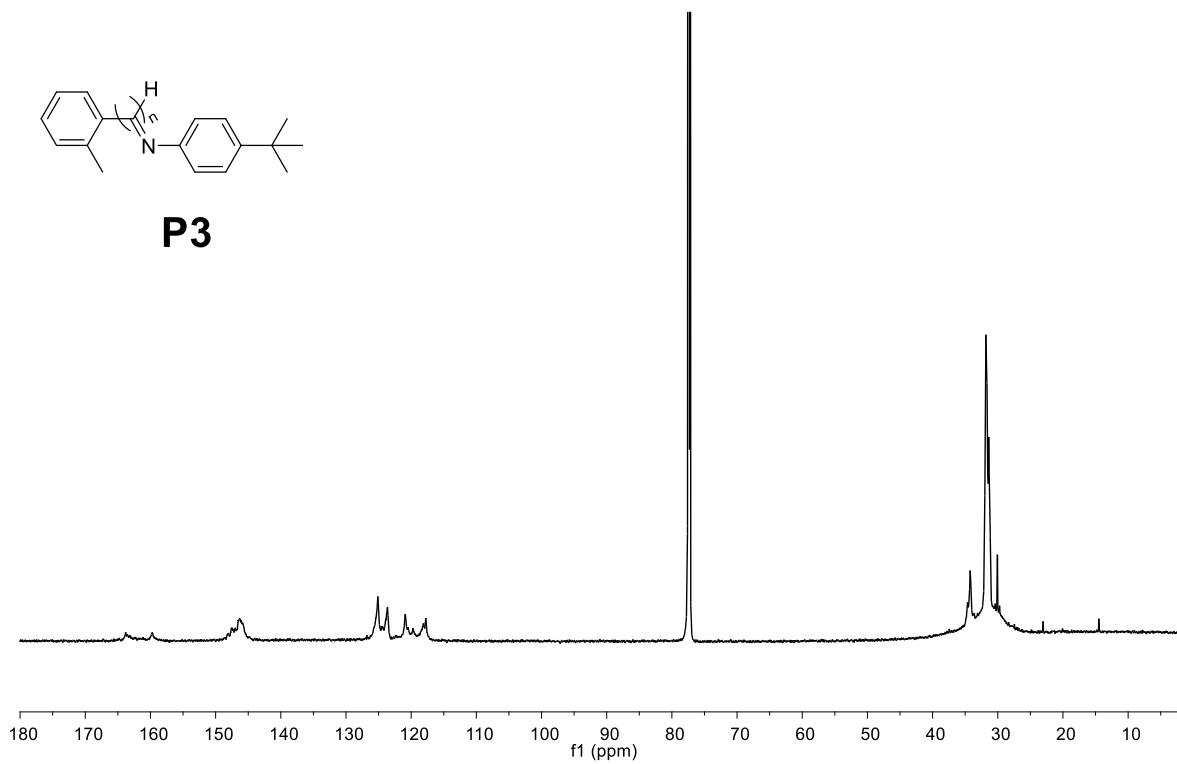
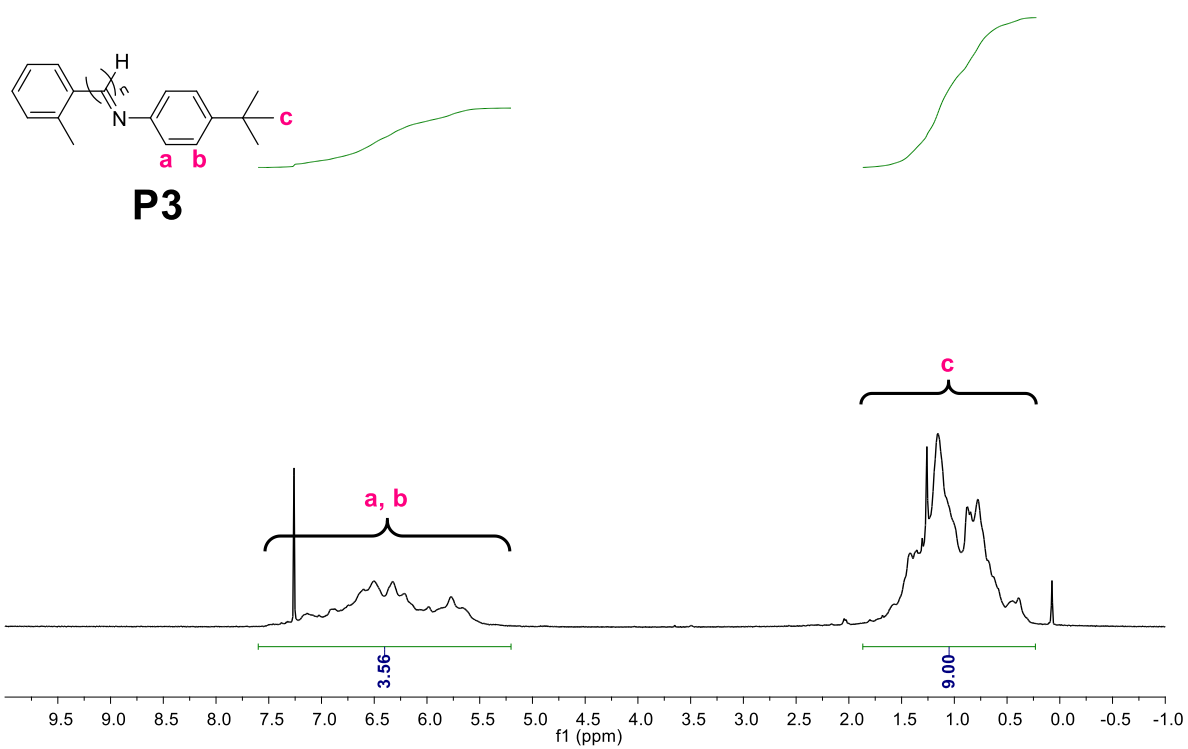


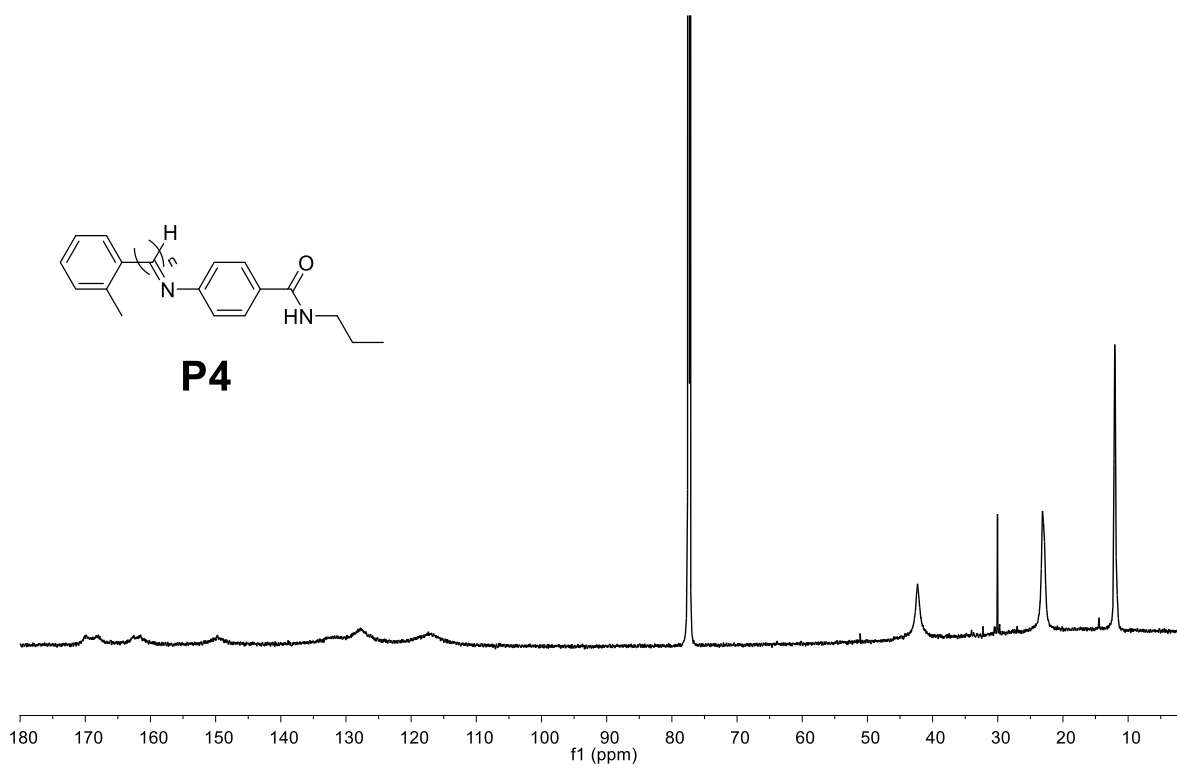
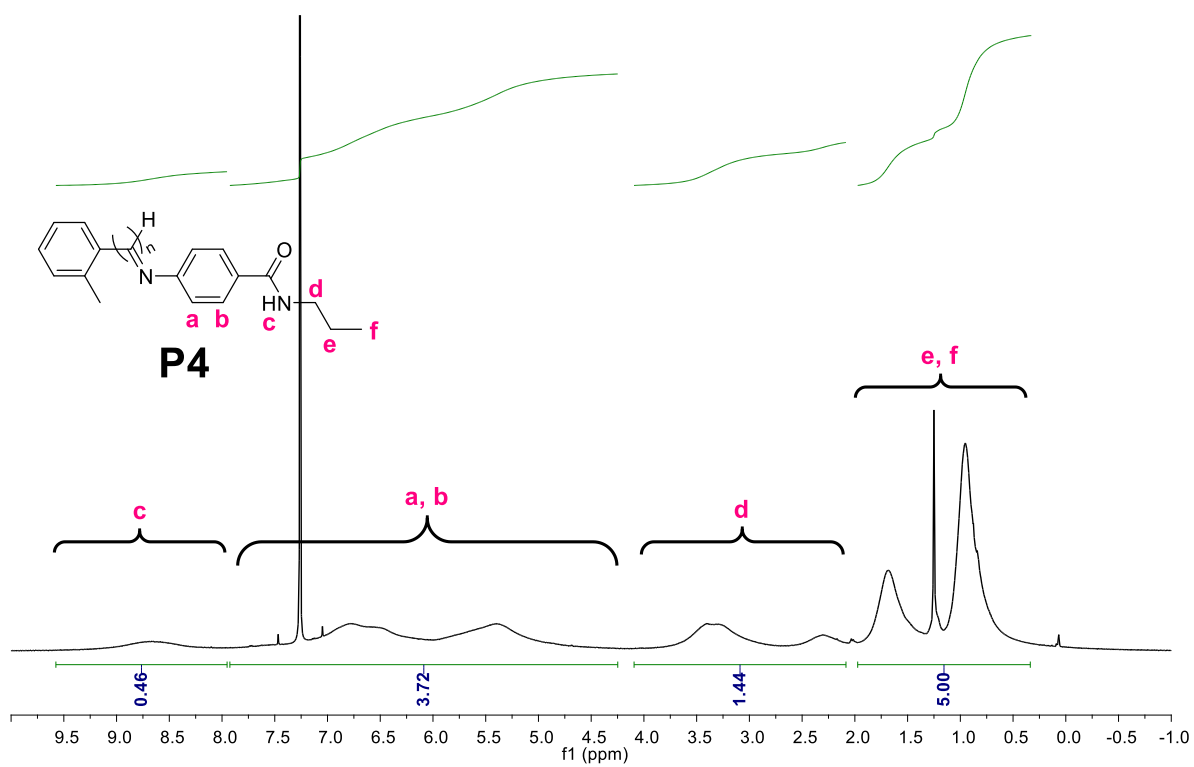


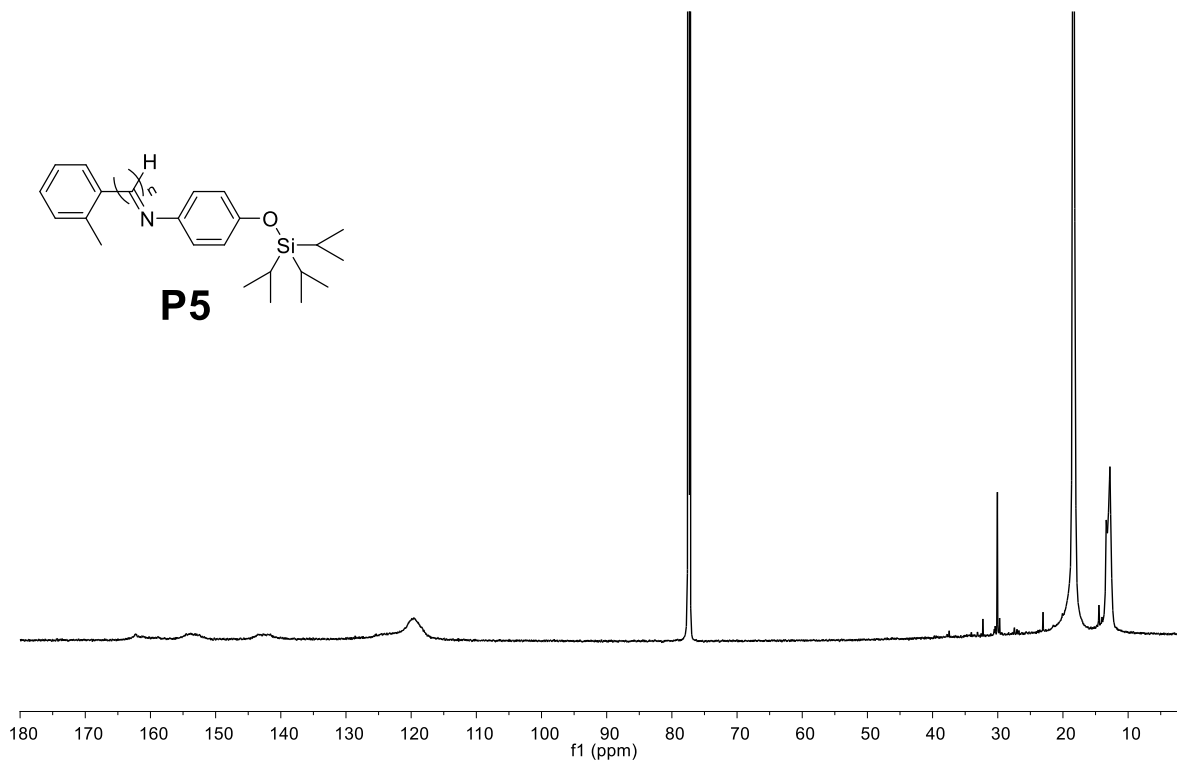
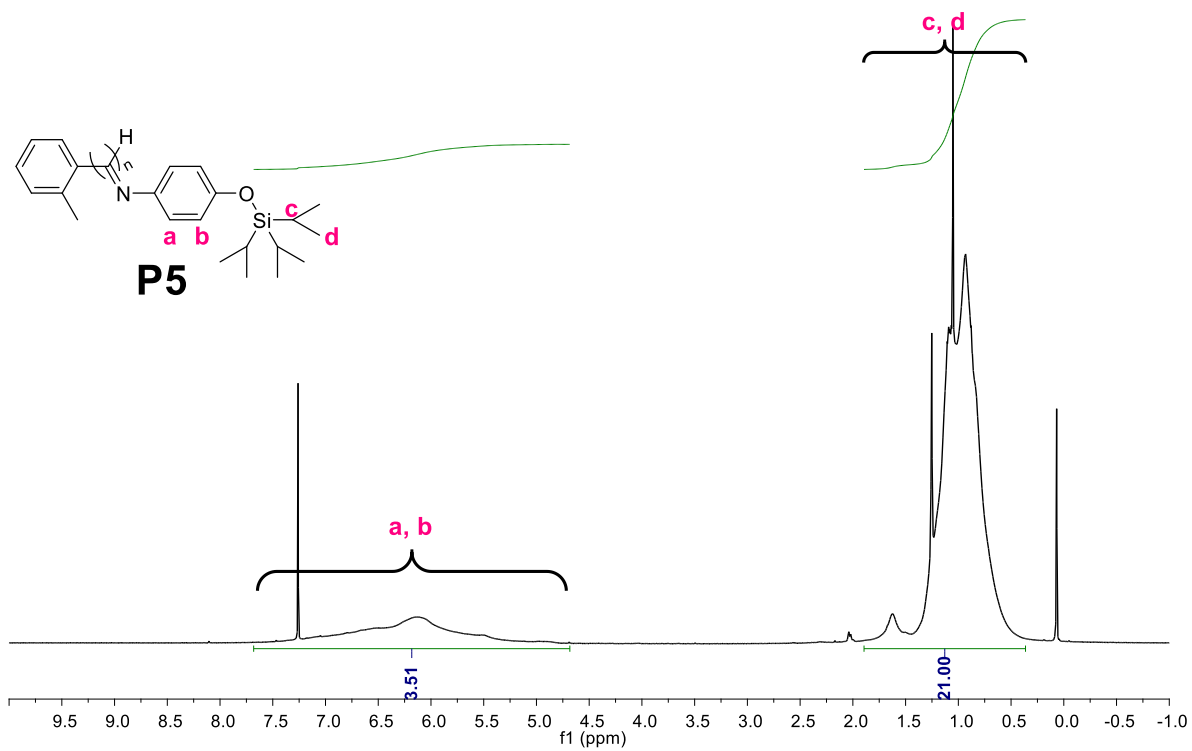


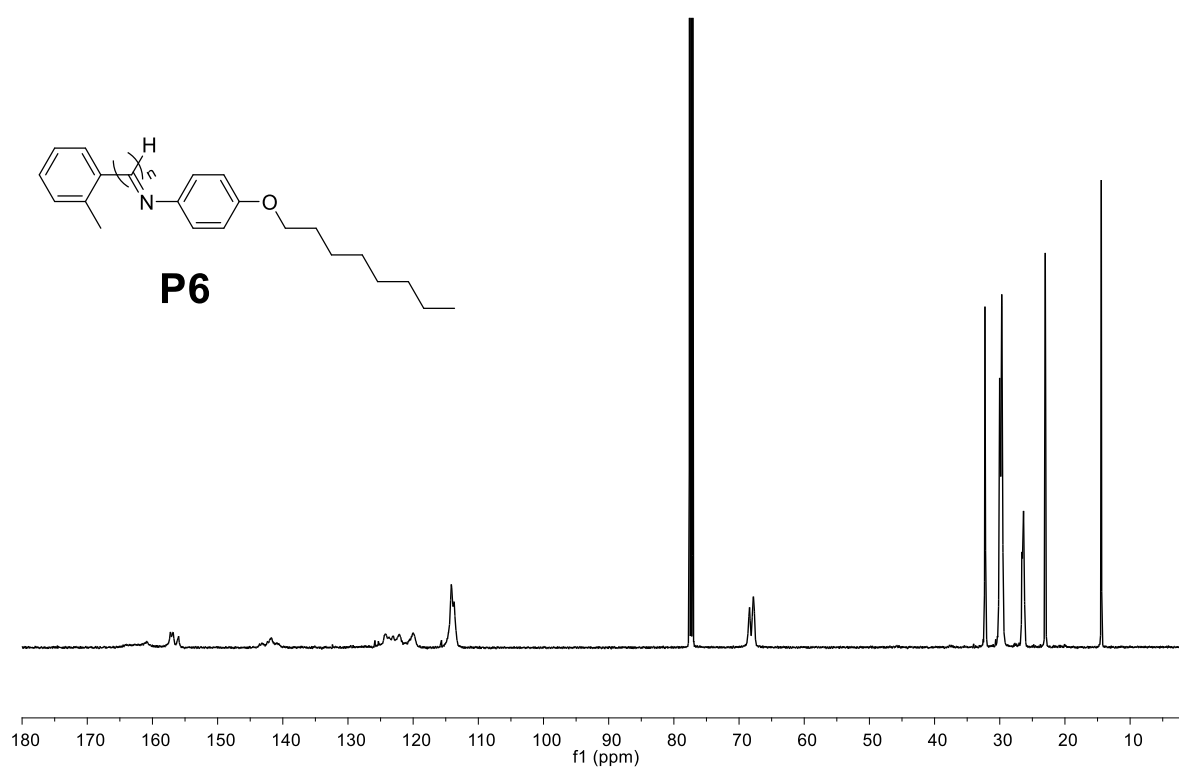
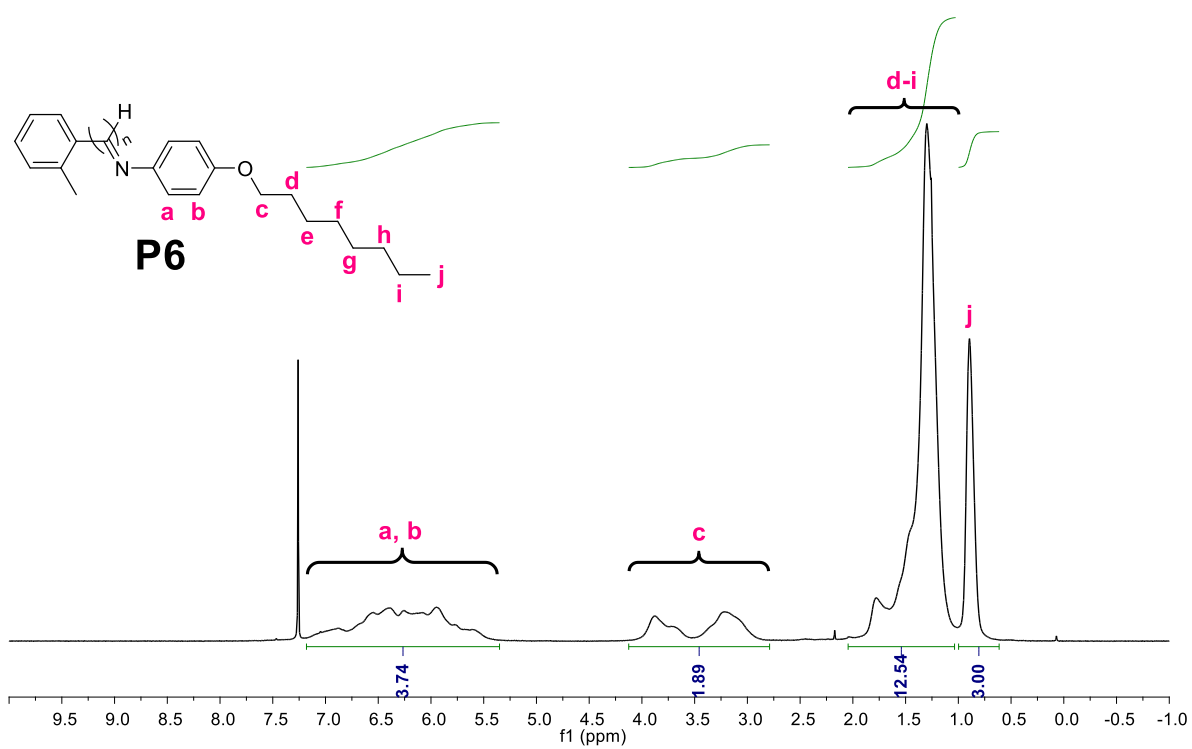


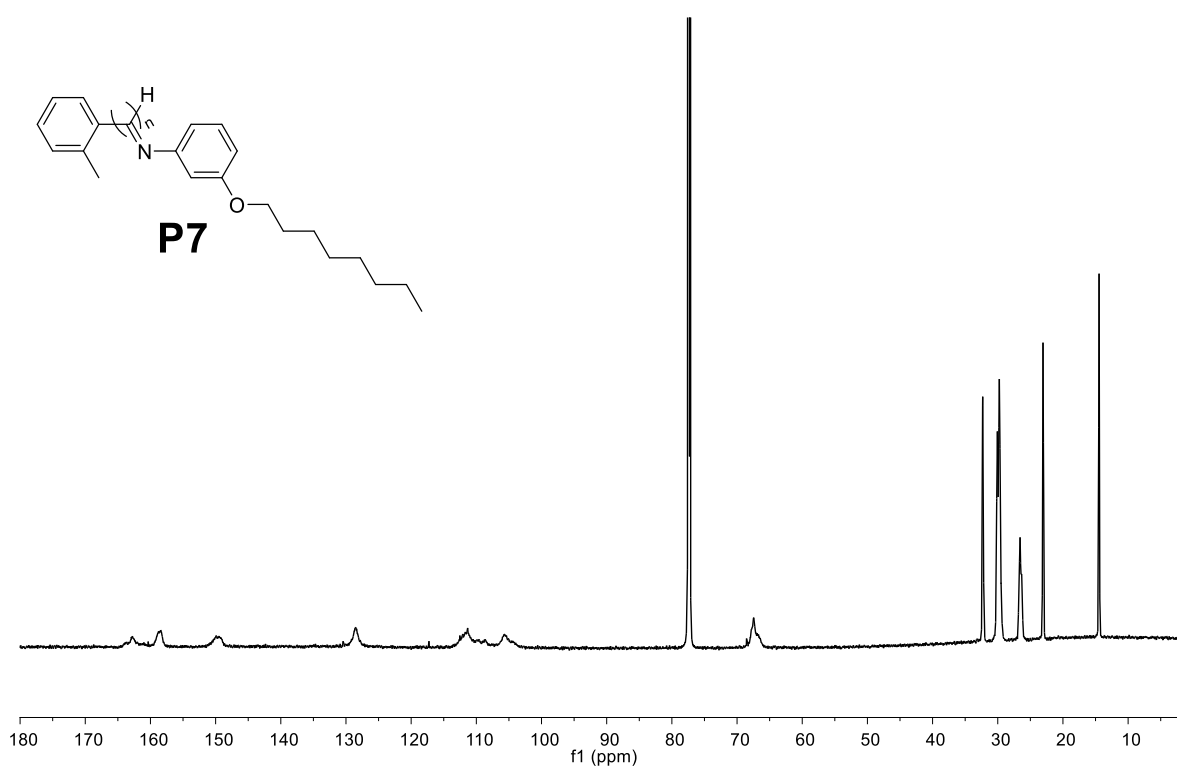
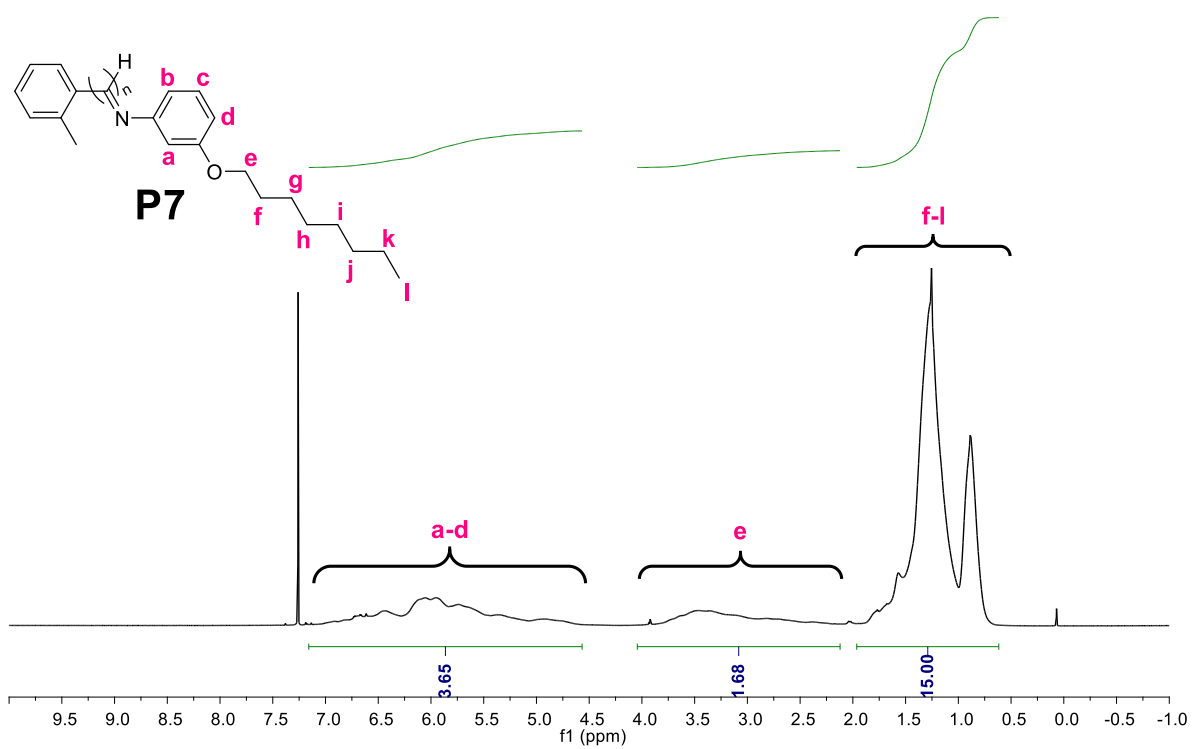


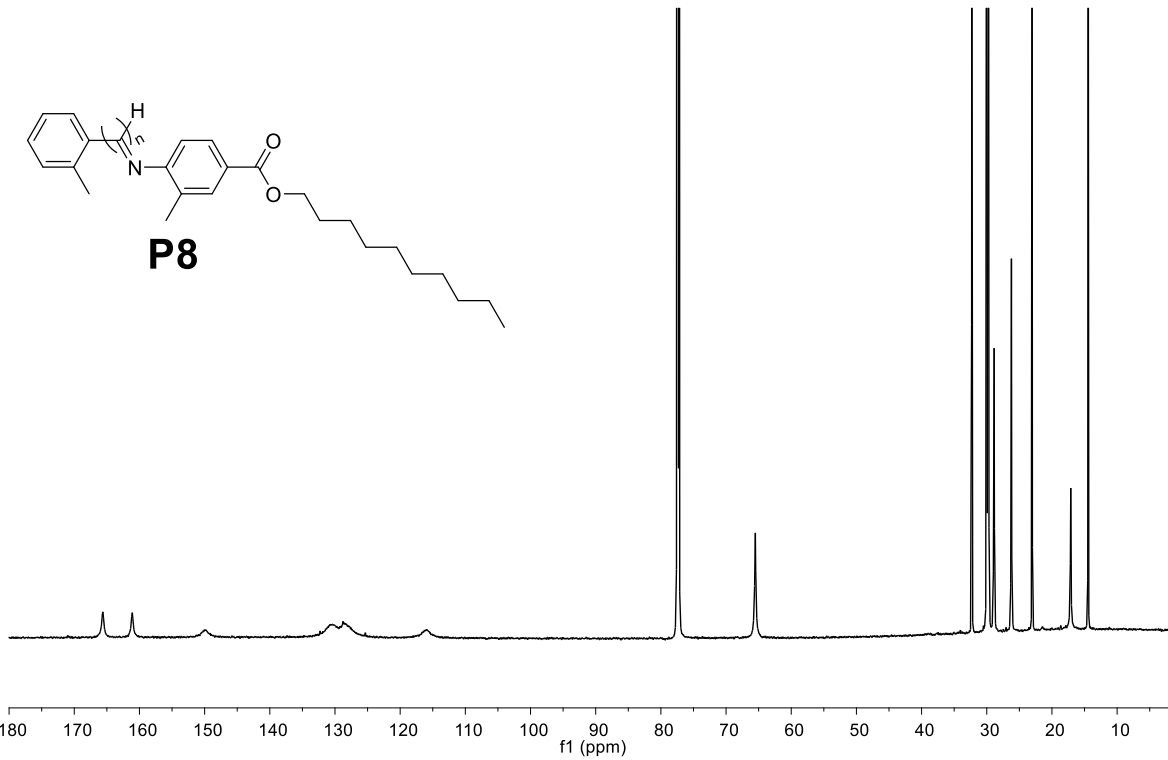


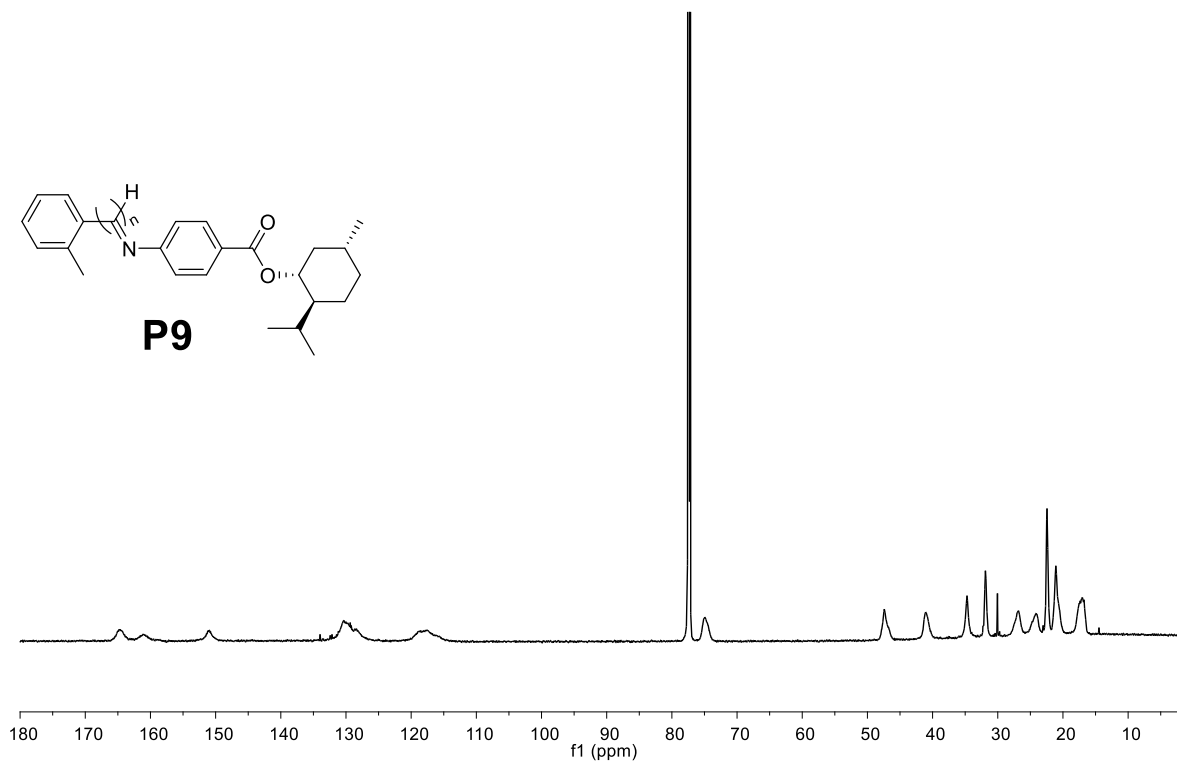
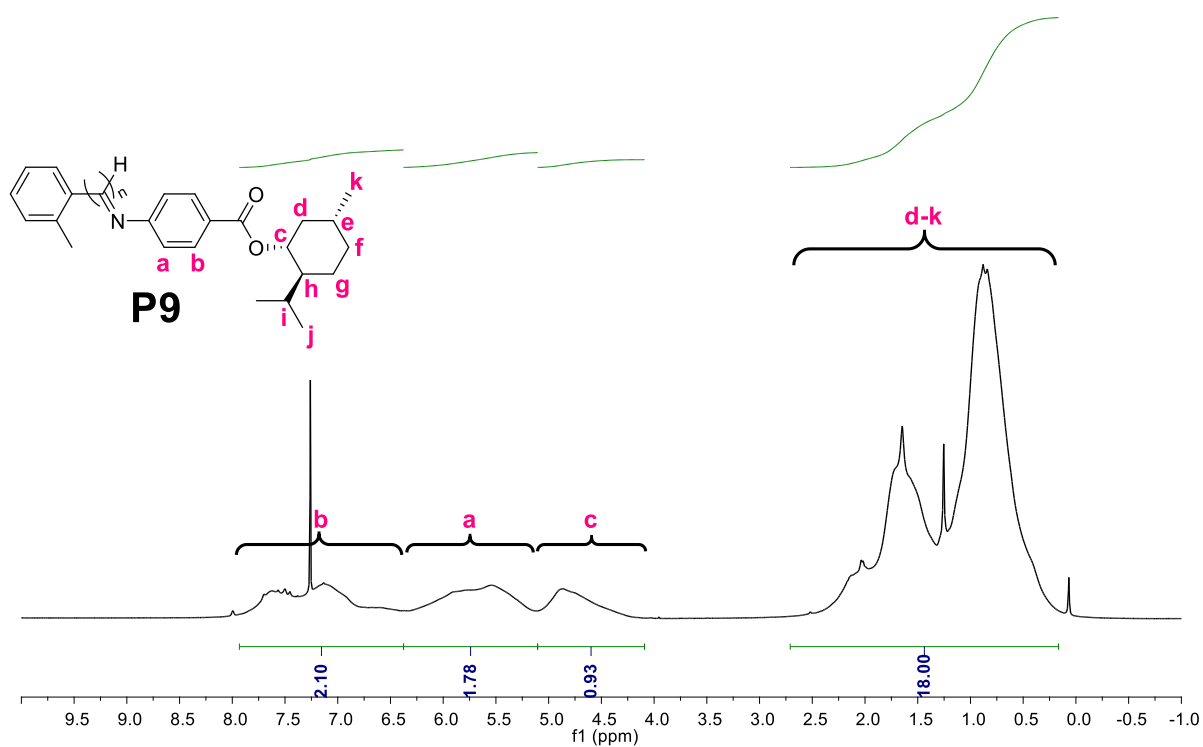


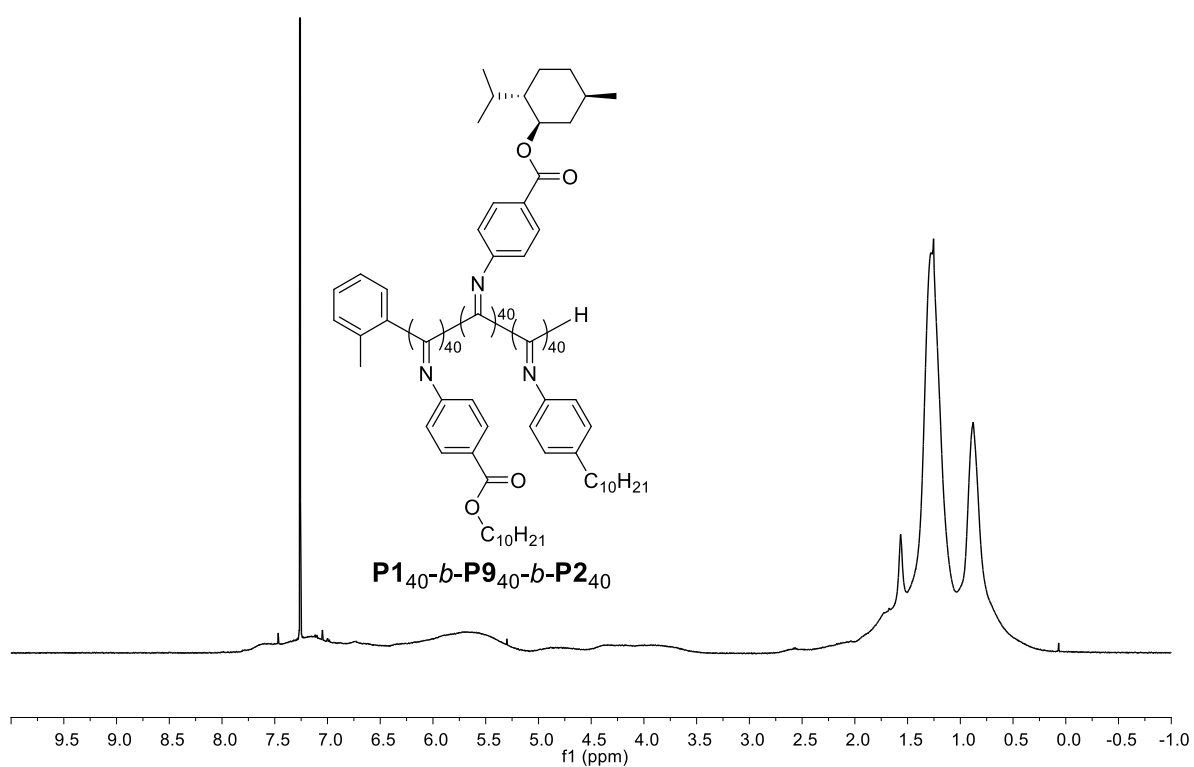
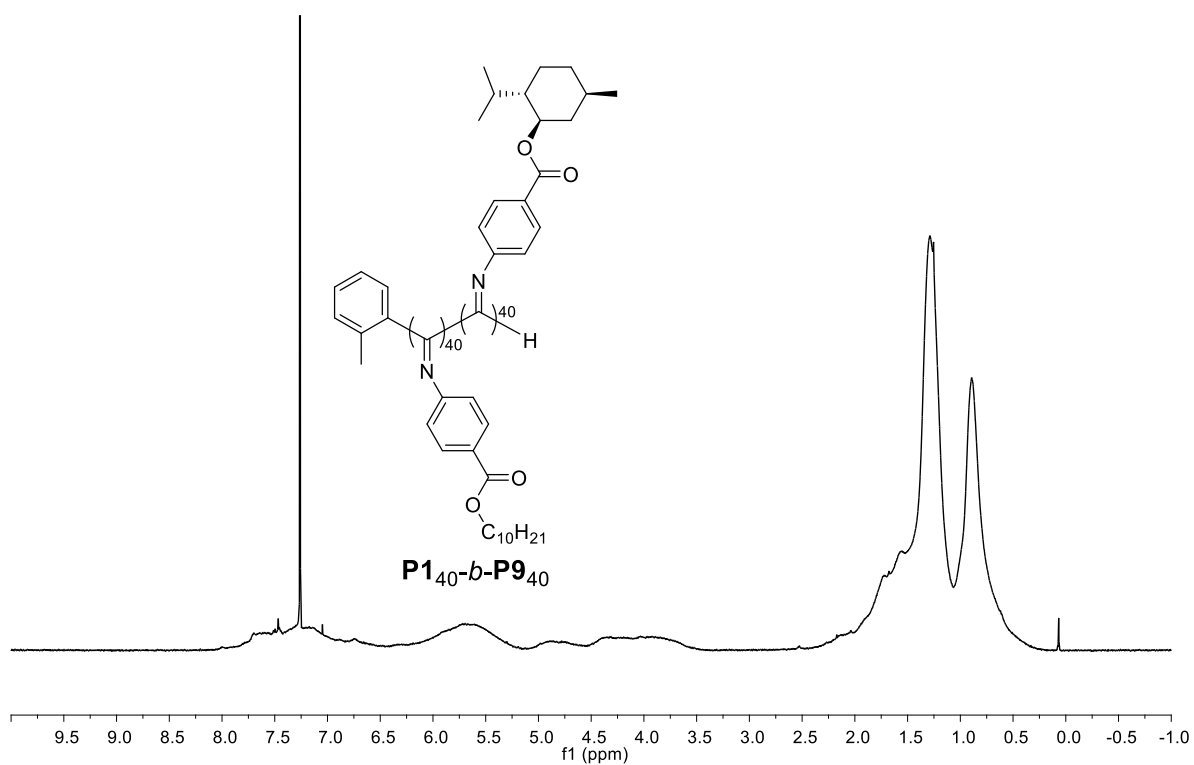


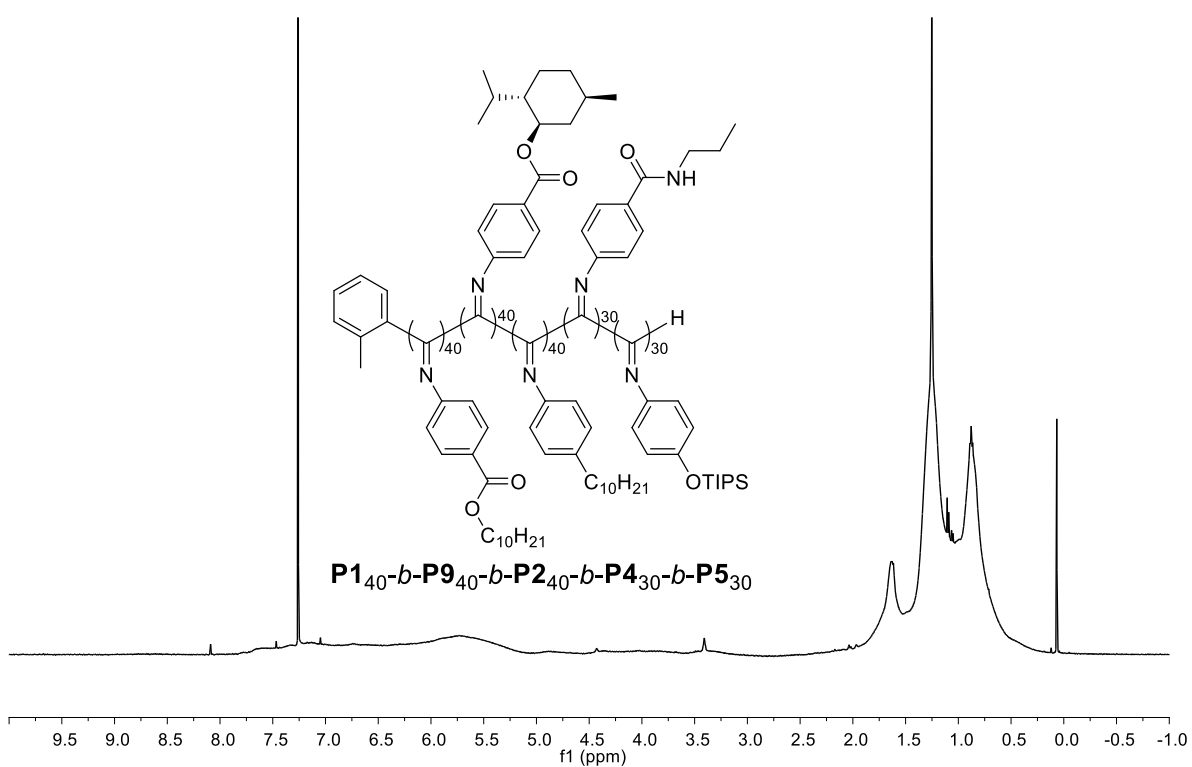
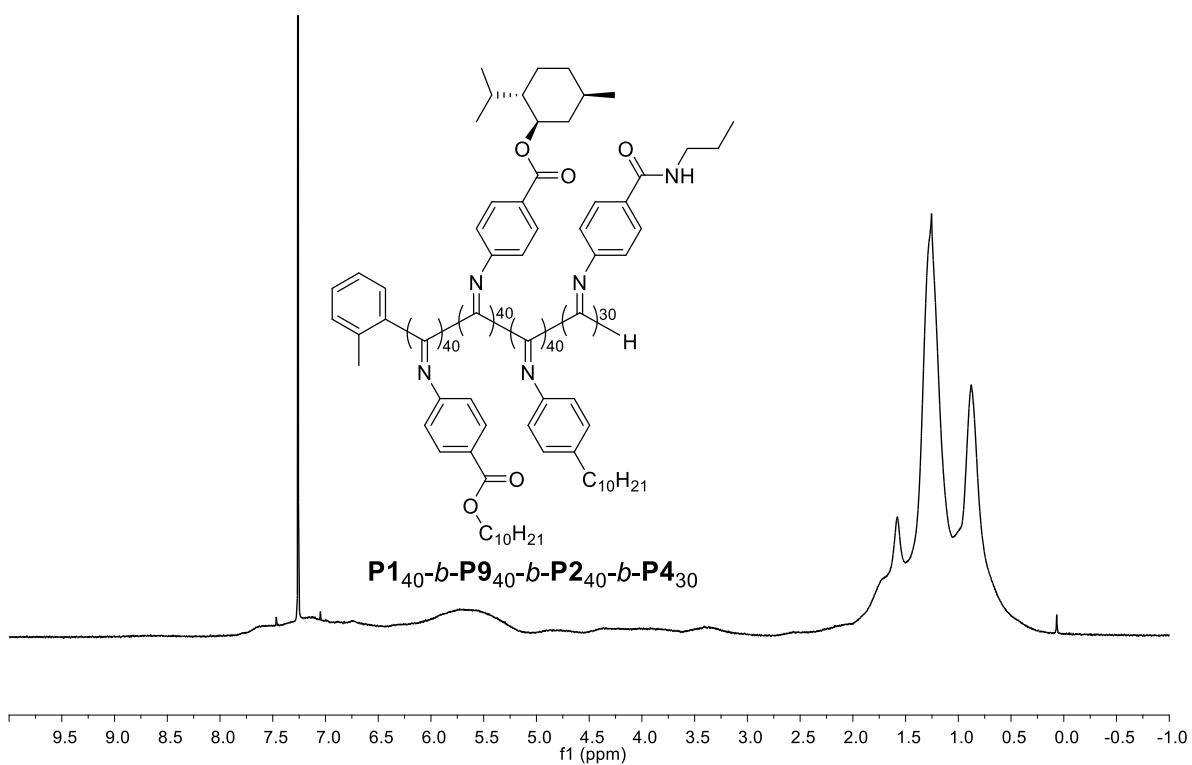












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