Electronic Supplementary Information (ESI)

Precise One-Pot Synthesis of Fully Conjugated End-Functionalized Star Polymers Containing Poly(fluorene-2,7-vinylene) (PFV) Arms

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Contents

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1. Experimental details for synthesis of starting polymer samples [poly(9,9-di-*n*-octyl-fluorene-2,7-vinylene)s (PFVs)], 2,4,6-tris(4-formylphenyl)-1,3,5-triazine (TPTA)

1-1. Polymerization Procedure (Starting polymer sample preparation): Synthesis of poly(9,9-di-*n*-octylfluorene-2,7-vinylene) (PFV) by $RuCl_2(PCy_3)(IMesH_2)(CHPh)$. The polymerization procedure employed was analogous to those reported previously.[1] Toluene (1.0 mL), 2,7-divinyl-9,9-di-*n*-octylfluorene (150 mg, 339 μmol), and $RuCl_2(PCy_3)(IMesH_2)(CHPh)$ (**Ru**, 8.5 μmol) were charged into a sealed Schlenk-type tube equipped with Kontes high-vacuum valves in the drybox. The tube was then placed into a liquid nitrogen bath and was then connected to the vacuum line for a while. The tube was then placed into an oil bath preheated at 50 ºC under a reduced pressure, and the mixture was stirred for 1-5 h. During the reaction, the mixture was placed into a liquid nitrogen bath with a certain period (every 10 min at the initial 1 h, then every 30 min for 1 h, and then every 1 h) to remove ethylene by-produced from the reaction medium by opening the valve connected to the vacuum line and then placed into the oil bath to continue the reaction. The polymerization was quenched by adding ethyl vinyl ether in excess amount. The reaction mixture was then stirred for 1 h for completion, and the resultant solution was poured into cold methanol (ca. 50 mL) and precipitated for 10 min at 5000 rpm. The yellow polymer was collected with 0.45 μm membrane filter and was then dried *in vacuo*. Yield 96 %. ^{1}H NMR ($CDCl_3$): δ 7.72 (d, 2H, J = 7.9 Hz), 7.54 (br, 4H), 7.29 (br, 2H, *trans*-CH=CH-), 6.81 (dd), 5.81 (d), 5.26(d), 2.05 (br, 4H), 1.17-1.08 (br, 20H), 0.87(t, J = 7.0 Hz, 6H), 0.68 (br, 4H). The selected data for samples prepared for the subsequent end-functionalization are shown in Table S1. The resultant PFV samples were separated into two fractions by using *n*-hexane.

References and Notes

1 (a) Yamamoto, N.; Ito, R.; Geerts, Y.; Nomura, K. *Macromolecules* **2009**, *42*, 5104. (b) Nomura, K.; Yamamoto, N.; Ito, R.; Fujiki, M.; Geerts, Y. *Macromolecules* **2008**, *41*, 4245. (c) Kuwabara, S.; Yamamoto, N.; Sharma, P. M. V.; Takamizu, K.; Fujiki, M.; Geerts, Y.; Nomura, K. *Macromolecules* **2011**, *44*, 3705.

(2) The calibration with polystyrene standards often overestimates the molecular weight averages of rigid conjugated polymers (Nomura, K.; Morimoto, H.; Imanishi, Y.; Ramhani, Z.; Geerts, Y. *J. Polym. Sci., PartA: Polym. Chem.* **2001**, *39*, 2463.). Therefore, GPC curves versus structurally similar soluble PPP [poly(*p*-phenylene)] standards were recorded, and the M_n values of rodlike polymers measured versus polymer standards are overestimated by a factor of 1.6.

(3) Nomura, K.; Haque, T.; Onuma, T.; Hajjaj, F.; Asano, M. S.; Inagaki, A. *Macromolecules* **2013**, *46*, 9563.

Table S1. Preparation of PFVs by acyclic diene metathesis (ADMET) polymerization of 9,9'-di-*n*-octyl-2,7-divinylfluorene by $RuCl_2(CHPh)(H_2IMes)(PCy_3)$.[a]

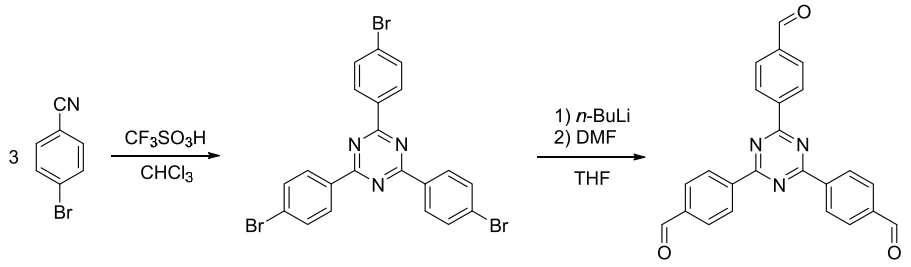
sample no.	reaction time/ h	$M_{n(GPC)}$[b]	M_w/M_n[b]	Yield[c]/ %
1	1	6380	1.99	94
2	2	8400	1.90	93
3	2	8800	1.80	96
4	3	13400	2.00	93
5	5	26800	1.60	95
6	5	30700	1.69	94

[a]Conditions: monomer/cat. = 40 (molar ratio), 180 mM in toluene at 50 °C, under reduced pressure. [b]GPC data in THF vs polystyrene standards. [c]Isolated yield.

Sample of $M_{n(GPC)}$ = 9230 [$M_{n(calcd.)}$ = 5760, $M_{n(NMR)}$ = 4900, M_w/M_n = 1.11, used for run 11 in Table 1; $M_{n(calcd)} = M_{n(GPC)}/1.6$, according reference 2) was prepared from sample 6 by extracting with *n*-hexane (*n*-hexane soluble portion, thus removing high molecular weights from the sample by filtration) according to the reported procedure.[3] Sample of $M_{n(GPC)}$ = 18000 [$M_{n(calcd.)}$ = 11000, M_w/M_n = 1.67, used for run 12, Table 1] was also prepared as the *n*-hexane soluble fraction according to the analogous procedure.

Sample of $M_{n(GPC)}$ = 13400 [$M_{n(calcd.)}$ = 8370, $M_{n(NMR)}$ = 8300, M_w/M_n = 2.00, used for run 8] was used from sample 4. Sample of $M_{n(GPC)}$ = 19900 [$M_{n(calcd.)}$ = 12400, $M_{n(NMR)}$ = 11000, M_w/M_n = 1.80, used for runs 9 and 13] was used as the mixture of samples 3 and 5. Sample of $M_{n(GPC)}$ = 8400 [$M_{n(calcd.)}$ = 5250, $M_{n(NMR)}$ = 4700, M_w/M_n = 1.90, used for run 10] was used from sample 2. Sample of $M_{n(GPC)}$ = 6380 [$M_{n(calcd.)}$ = 3990, $M_{n(NMR)}$ = 3500, M_w/M_n = 1.99, used for runs 14-17, Table 2] was used from sample 1. The other samples [$M_{n(GPC)}$ = 9400 (M_w/M_n = 1.83, used for run 1), $M_{n(GPC)}$ = 10400 (M_w/M_n = 1.75, used for run 2), $M_{n(GPC)}$ = 8000 (M_w/M_n = 1.79, used for run 3), $M_{n(GPC)}$ = 10700 (M_w/M_n = 2.12, used for run 4), $M_{n(GPC)}$ = 8100 (M_w/M_n = 1.94, used for run 5), and $M_{n(GPC)}$ = 11300 (M_w/M_n = 1.95, used run 6)] were prepared by the independent experimental runs.

1-2. Synthesis of 2,4,6-Tris(4-formylphenyl)-1,3,5-triazine (TPTA). 2,4,6-Tris(4-formyl-phenyl)-1,3,5-triazine (TPTA) was prepared from 4-bromobenzonitrile according to the following equation.



(i) Synthesis of 2,4,6-tris(4-bromolphenyl)-1,3,5-triazine. The compound was prepared according to the published method (Ranganathan, A.; Heisen, B. C.; Dix, I.; Meter, F. *Chem. Commun.* **2007**, *35*, 3637.). Into a Schlenk tube containing CF_3SO_3H (3.39 g, 22.6 mmol) mixed in $CHCl_3$ (5 mL) at 0 ºC, a $CHCl_3$ solution (30 mL) containing 4-bromo-benzonitrile (2.0 g, 11.1 mmol) was added slowly at 0 ºC. The solution was stirred for 2 h, and the mixture was then taken out from the drybox, and the solution was continued stirring overnight under nitrogen atmosphere. The reaction was then quenched by addition of $NaHCO_3$ aqueous solution, and the mixture was then extracted with $CHCl_3$ (30 mL×3). The resultant $CHCl_3$ solution was dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The desired product was obtained as white solids by recrystallization with $CHCl_3$. Yield 574 mg (27.4 %). ^{1}H NMR ($CDCl_3$) δ: 8.61 (d, 6H, J = 8.4Hz), 7.71 (d, 6H, J = 8.3Hz).

(ii) Synthesis of 2,4,6-Tris(4-formylphenyl)-1,3,5-triazine [TPTA(CHO)$_3$]. Into a Schlenk tube containing 2,4,6-tris(4-bromophenyl)-1,3,5-triazine (300 mg, 0.546 mmol), TMEDA (tetramethyl-ethylenediamine, 0.4 g, 3.44 mmol), and THF (15 mL), *n*-BuLi (1.3 mL, 2.08 mmol) was added slowly at -78 ºC. The solution was stirred for 2 h at -78 ºC, and was added DMF (dimethylformamide, 1.5 mL, 19.4 mmol). The resultant reaction mixture was stirred for 12 h at -78 ºC. The reaction was quenched by addition of water, and the mixture was extracted with Et_2O (30 mL×3). The resultant Et_2O solution was dried over $MgSO_4$, and the volatiles were removed *in vacuo*. The desired product was purified by column chromatography (*n*-hexane: CH_3CO_2Et = 2:1), and was obtained as the white solid. Yield 96 mg (44.6 %). ^{1}H NMR ($CDCl_3$) δ: 10.1 (s, 3H), 8.00 (d, 6H, J = 8.4Hz), 7.85 (d, 6H, J = 8.1Hz). ^{13}C NMR ($CDCl_3$) δ: 190.95, 190.89, 139.07, 137.57, 135.47, 133.71, 133.23, 130.24, 118.03, 117.93. EI-MS: Calcd for MH^+, $C_{24}H_{15}N_3O_3$: 394.11. Found: 394.44. Anal. Calcd for $C_{24}H_{15}N_3O_3 \cdot 1/6\ CHCl_3$: C, 70.23; H, 3.70; N, 10.17. Found: C, 70.28; H, 3.75; N, 10.21.

2. Selected ^{1}H NMR spectra (in $CDCl_3$ at 25 ºC) for the end-functionalized star conjugated polymers.

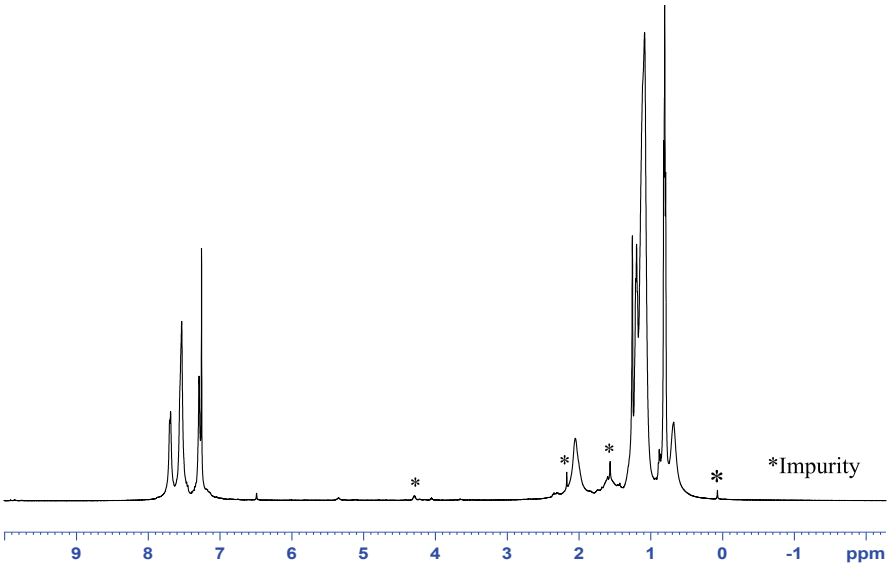


Figure 2-1. ^{1}H NMR spectrum of **TPA[PFV-C_6F_5]$_3$** (run 1).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (br, Ar-H), 7.55 (br, Ar-H), 7.31 (br, *trans* -CH=CH–), 2.06 (br), 1.24–1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.21 (d, olefinic protons adjacent to TPA), and 7.16 (br, aromatic protons in TPA) ppm were observed.

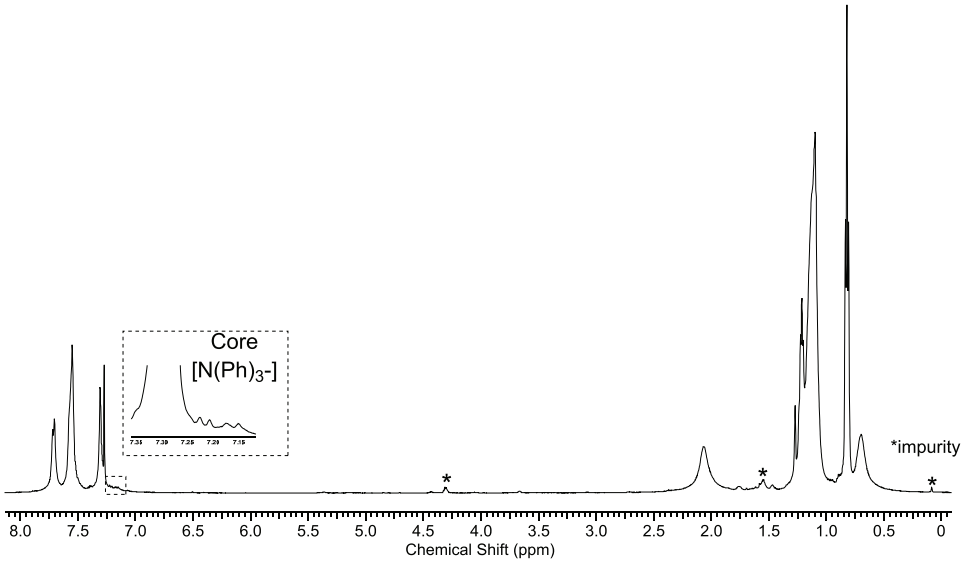


Figure 2-2. ^{1}H NMR spectrum of **TPA[PFV-C_6F_5]$_3$** (run 8).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (br, Ar-H), 7.55 (br, Ar-H), 7.31 (br, *trans* -CH=CH–), 2.06 (br), 1.24–1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.21 (d, olefinic protons adjacent to TPA), and 7.16 (br, aromatic protons in TPA) ppm were observed.

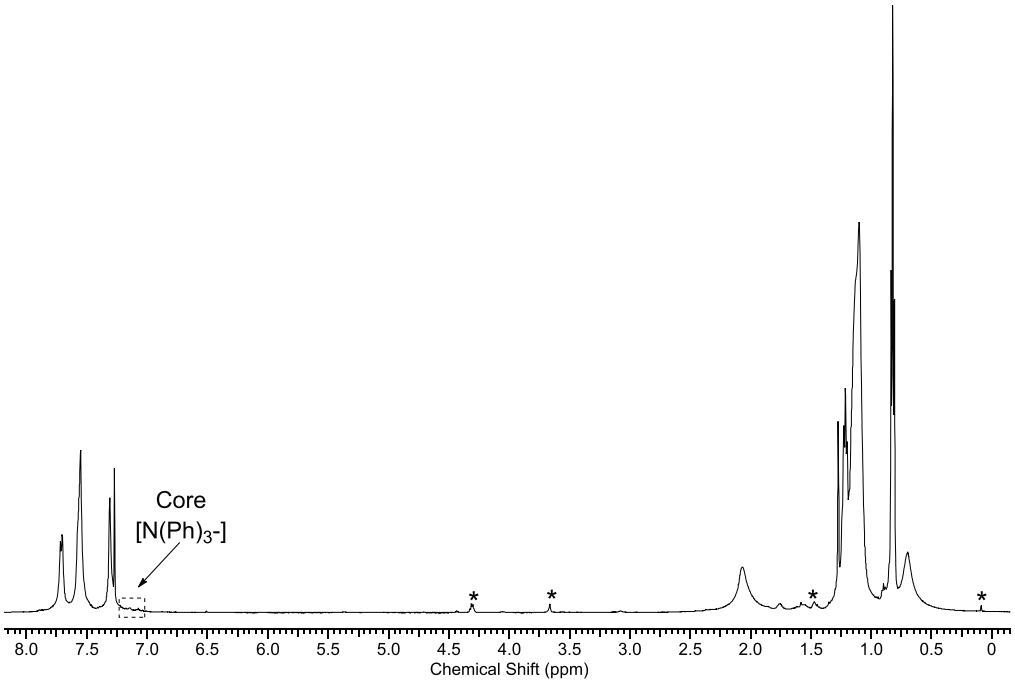


Figure 2-3. ^{1}H NMR spectrum of **TPA[PFV-C_6F_5]$_3$** (run 9).

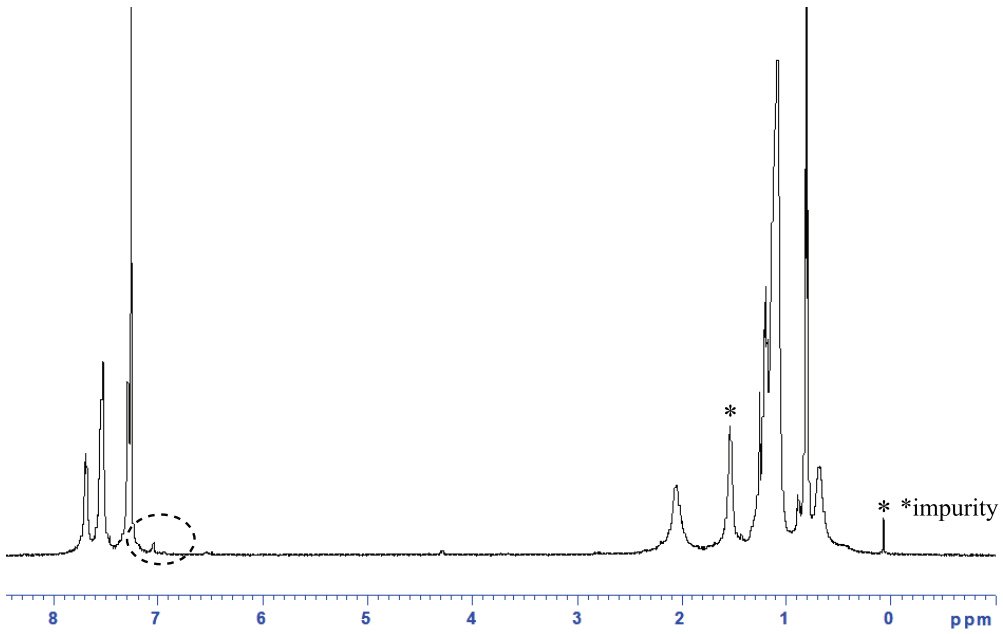


Figure 2-4. ^{1}H NMR spectrum of **TPA[PFV-DH4T]$_3$** (run 4).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.70 (br 2H), 7.53 (br, 4H), 7.32 (br, 2H), 2.08 (br, 4H), 1.11 (br, 20H), 0.83 (m, 6H), 0.71 (br, 4H) ppm. In addition, small resonances at δ 7.00-8.00 (olefinic protons adjacent to TPA, aromatic protons in TPA), and 7.20-6.80 (m, quarterthiophene) ppm were observed.

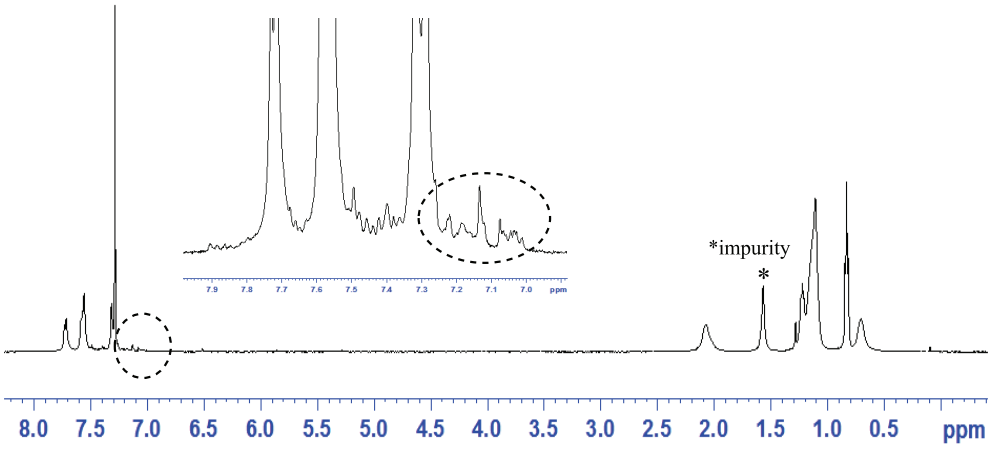


Figure 2-5. ^{1}H NMR spectrum of **TPA[PFV-3T]$_3$** (run 5).

^{1}H NMR ($CDCl_3$) δ: 7.69 (br 2H), 7.54 (br, 4H), 7.30 (br, 4 H), 2.04 (br, 4H), 1.08 (m, 20H), 0.81 (m, 6H), 0.69 (br, 4H) ppm. In addition, small resonances at δ 7.00-8.00 (olefinic protons adjacent to TPA, aromatic protons in TPA), and 6.20-7.20 (m, terthiophene) ppm were observed.

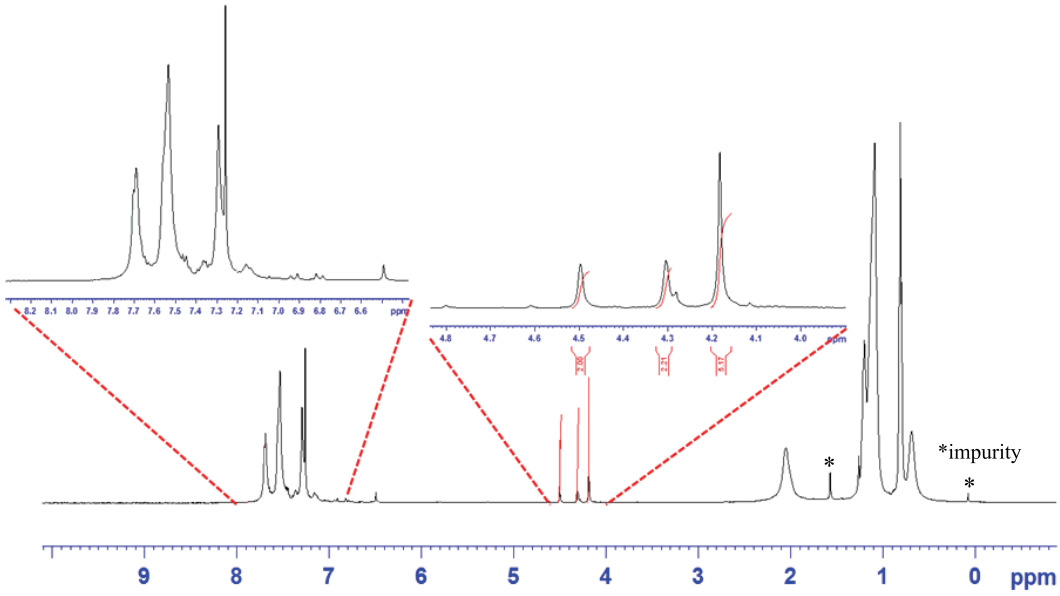


Figure 2-6. ^{1}H NMR spectrum of **TPA[PFV-Fc]$_3$** (run 7).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (br, Ar-H), 7.55 (br, Ar-H), 7.31 (br, *trans* -CH=CH–), 4.77-4.35 (ferrocenyl-H), 2.07 (br), 1.23–1.10 (m), 0.82 (t), 0.71 (br) ppm. In addition, small resonances at δ 7.21 (d, olefinic protons adjacent to TPA), 7.16 (br, aromatic protons in TPA), 6.87 and 6.60 (br, olefinic protons adjacent to ferrocene) were observed.

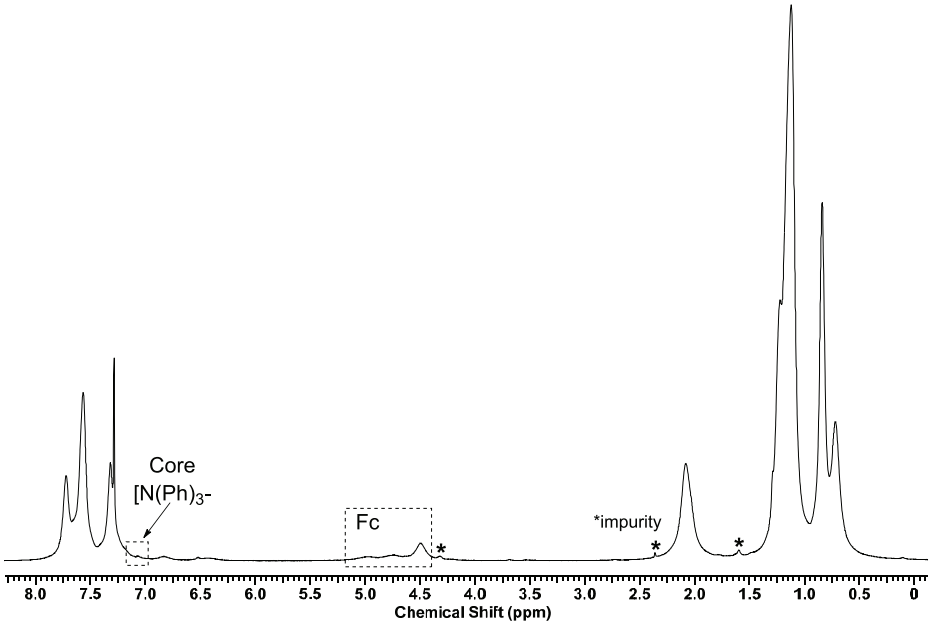


Figure 2-7. ^{1}H NMR spectrum of **TPA[PFV-Fc]$_3$** (run 10).

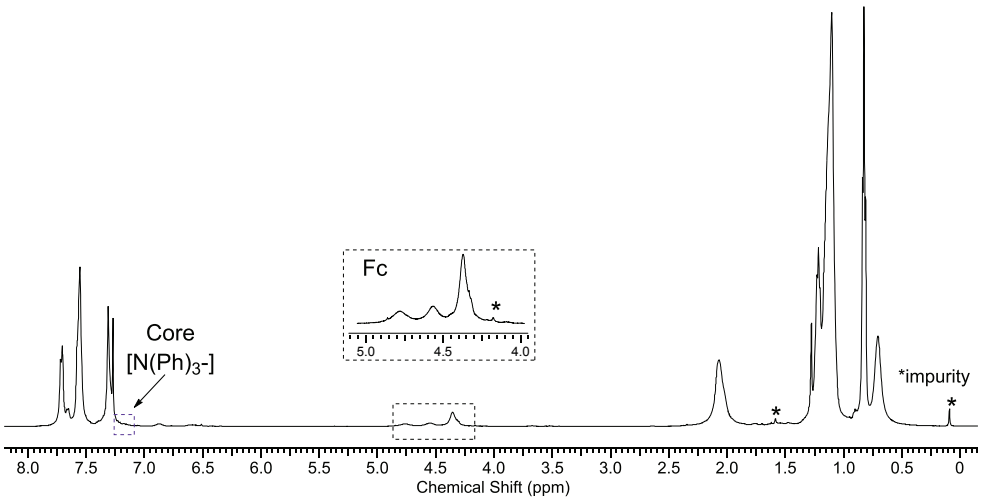


Figure 2-8. ^{1}H NMR spectrum of **TPA[PFV-Fc]$_3$** (run 11).

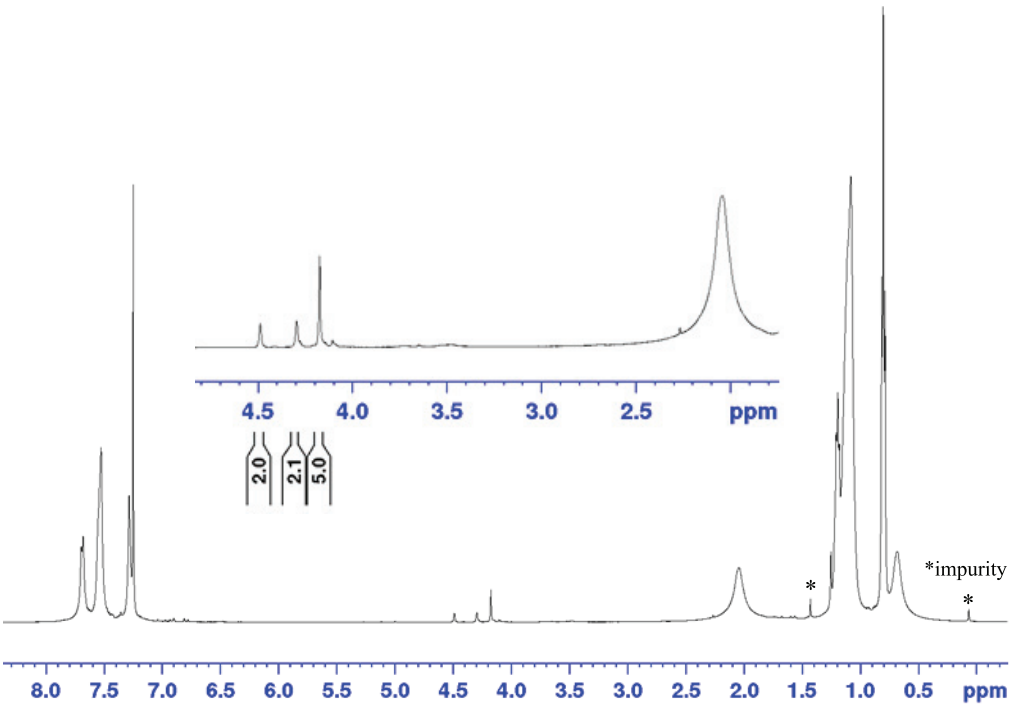


Figure 2-9. ^{1}H NMR spectrum of **TPA[PFV-Fc]$_3$** (run 12).

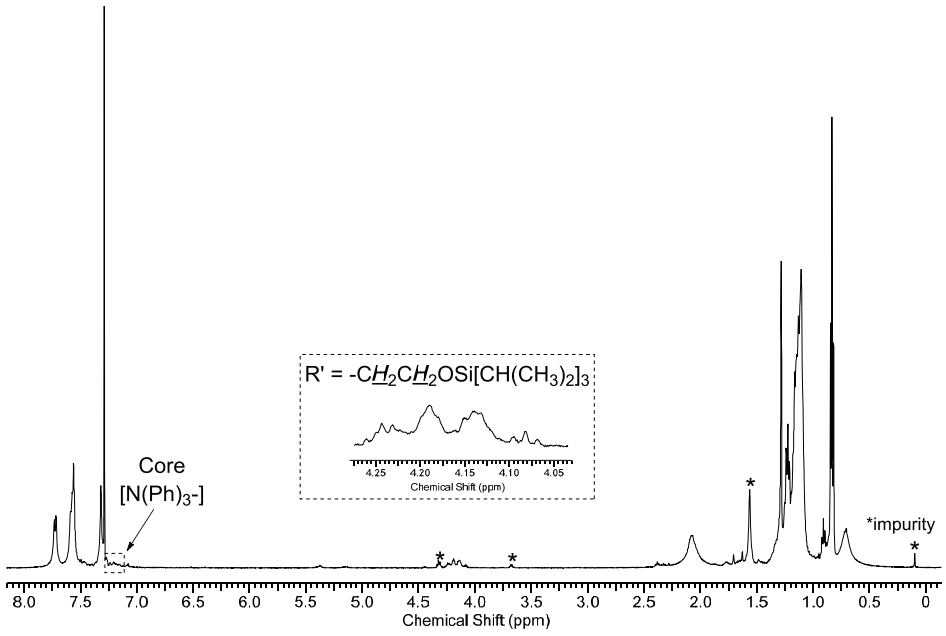


Figure 2-10. ^{1}H NMR spectrum of **TPA[{(PFV)$_2$-3PV}-C$_6$F$_5$]$_3$** (run 14).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (br, Ar-H), 7.57–7.54 (m, Ar-H), 7.30 (br, *trans* -CH=CH–), 4.24–4.10 (-OC$\underline{H}_2$C$\underline{H}_2$OSi[CH(CH$_3$)$_2$]$_3$ of 3PV), 2.06 (br), 1.24–1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.22 (d, olefinic protons adjacent to TPA), 7.18 (br, aromatic protons in TPA) were observed.

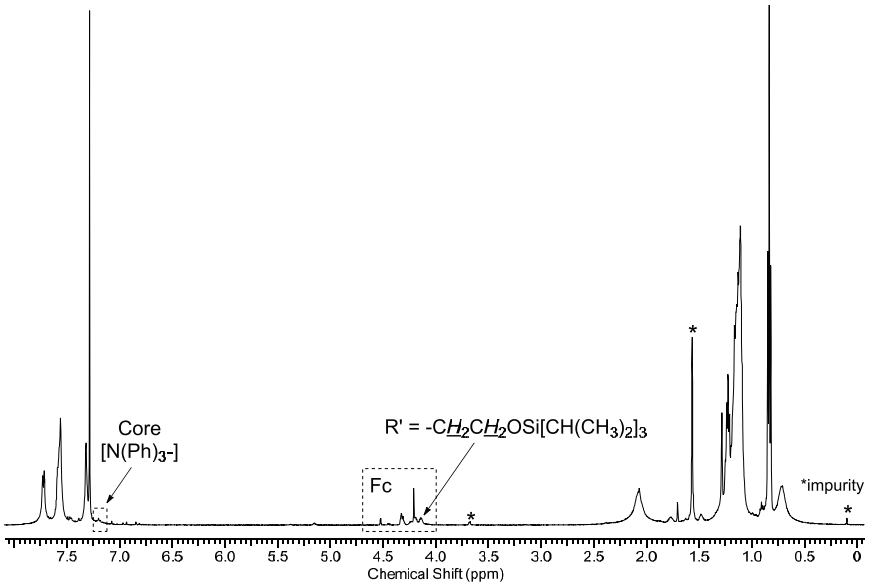


Figure 2-11. ^{1}H NMR spectrum of **TPA[{(PFV)$_2$-3PV}-Fc]$_3$** (run 15).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (d, Ar-H), 7.57–7.54 (m, Ar-H), 7.30 (br, *trans* -CH=CH–), 4.51-4.19 (ferrocenyl-H), 4.24-4.10 [-OC$\underline{H}_2$C$\underline{H}_2$OSi{$CH(CH_3)_2$}$_3$ of 3PV], 2.06 (br), 1.24-1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.18 (br, aromatic protons in TPA), 6.87 and 6.60 (br, olefinic protons adjacent to ferrocene) were observed.

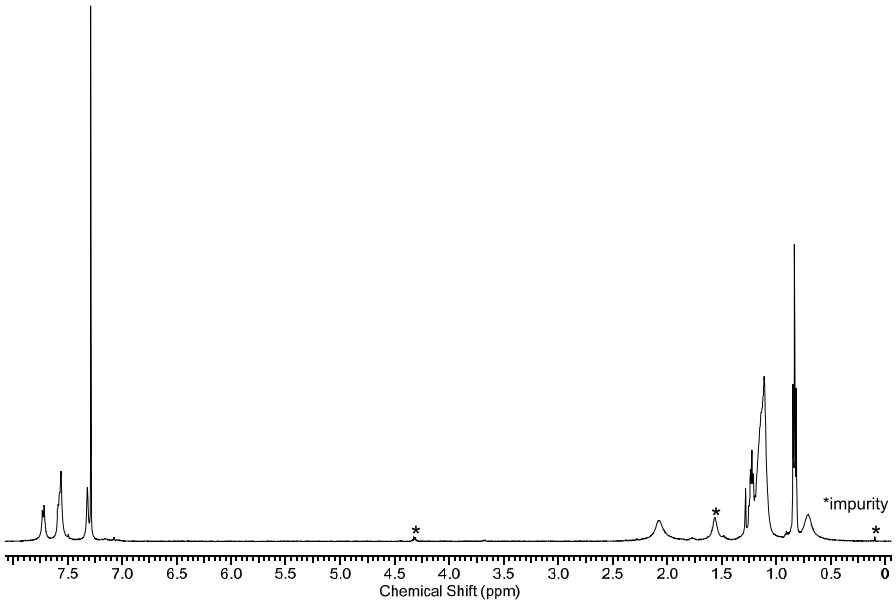


Figure 2-12. ^{1}H NMR spectrum of **TPA[{(PFV)$_2$-3T}-C$_6$F$_5$]$_3$** (run 16).

^{1}H NMR ($CDCl_3$ at 25 °C): δ 7.71 (d, Ar-H), 7.57-7.54 (m, Ar-H), 7.30 (br, *trans* -CH=CH–), 2.06 (br), 1.24–1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, very small resonances probably ascribed to olefinic protons adjacent to TPA, aromatic protons in TPA), and 6.20-7.20 (m, terthiophene) ppm were observed.

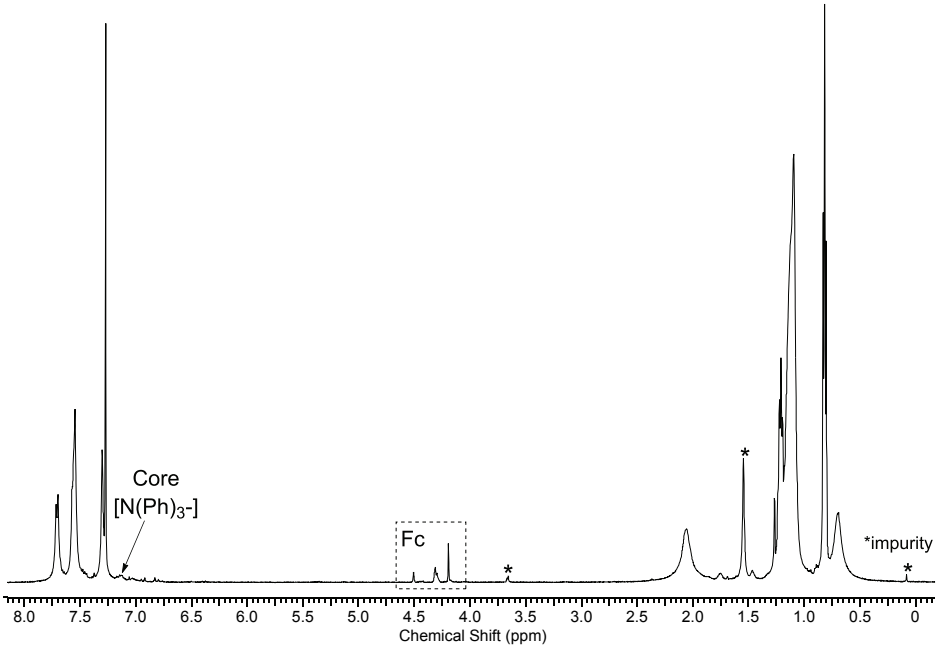


Figure 2-13. ^{1}H NMR spectrum of **TPA[{(PFV)$_2$-3T}-Fc]$_3$** (run 17).

^{1}H NMR ($CDCl_3$ at 25 °C): 7.71 (br, Ar-H), 7.57–7.54 (br, Ar-H), 7.30 (br, *trans* -CH=CH–), 4.51–4.19 (ferrocenyl-H), 2.06 (br), 1.24–1.09 (m), 0.82 (t), 0.69 (br) ppm. In addition, small resonances at δ 7.21 (br, olefinic protons adjacent to TPA), 7.16 (br, aromatic protons in TPA), 7.05–7.00 (m, terthiophene), 6.93 and 6.81 (br, olefinic protons adjacent to ferrocene) were observed.

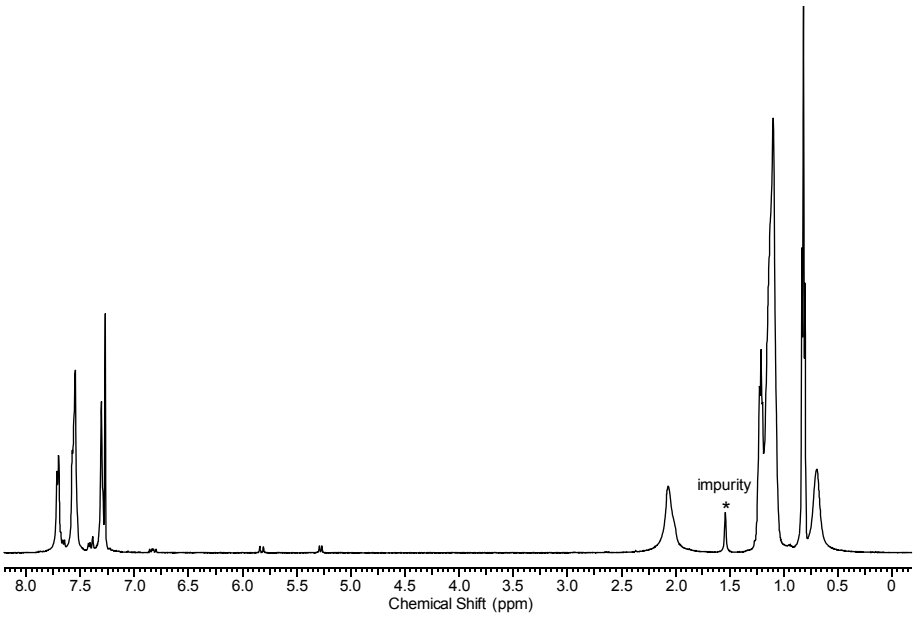


Figure 2-14. ^{1}H NMR spectrum ($CDCl_3$) of **PFV** (starting sample).

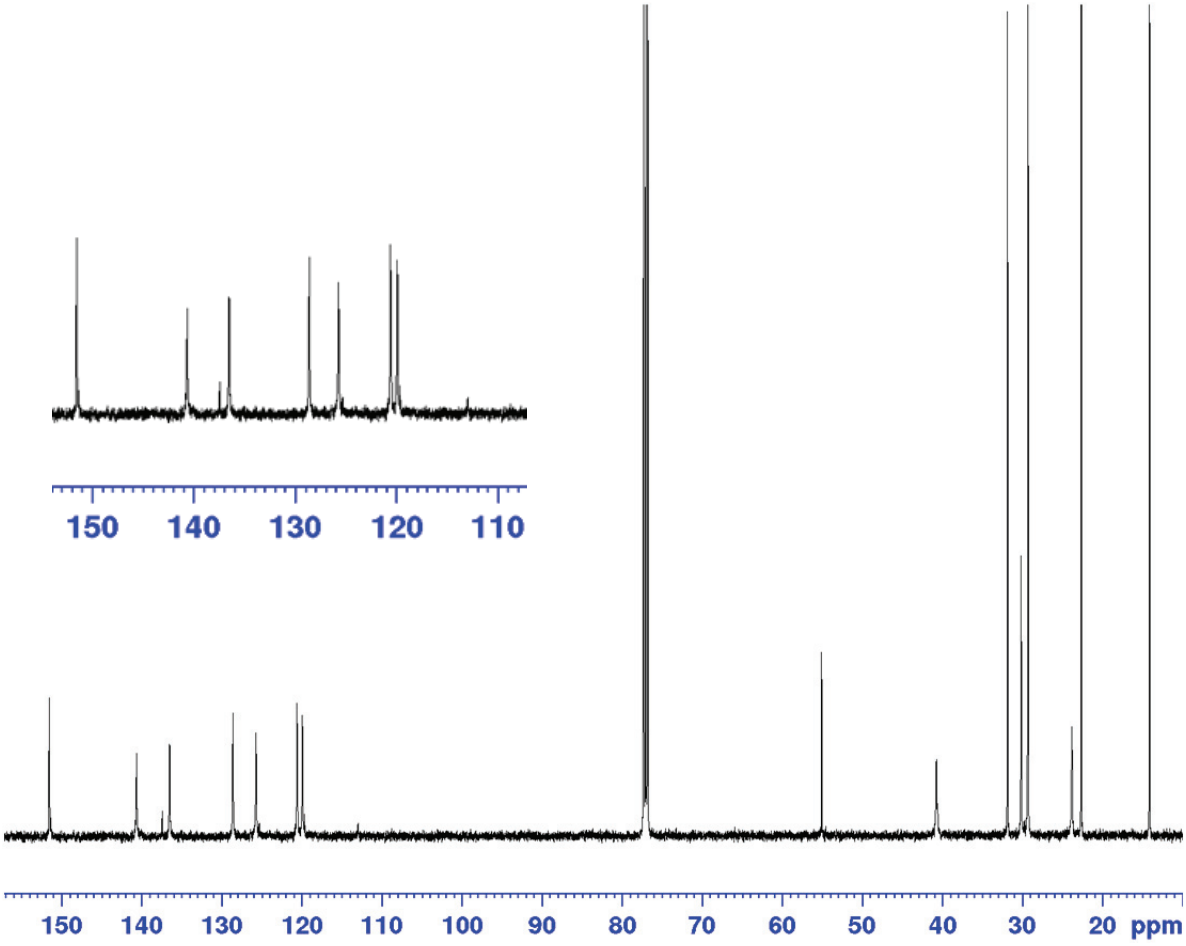


Figure 2-15. ^{13}C NMR spectrum of **PFV** (starting sample).

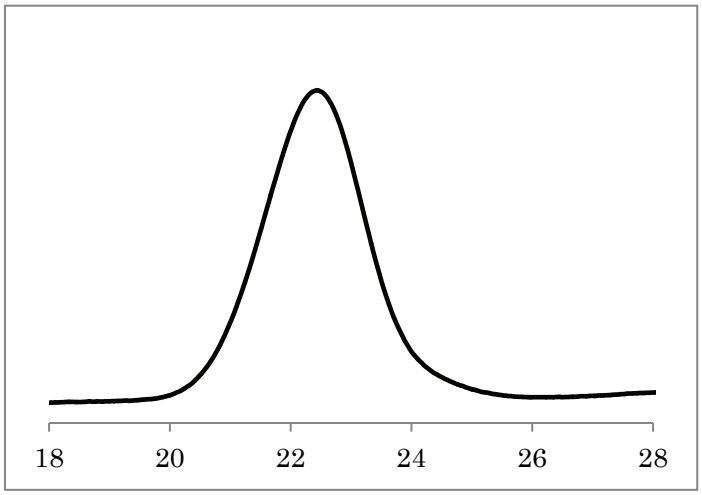


Figure 3-1. GPC trace for **TPA[{(PFV)$_2$-3PV}-C_6F_5]$_3$** (run 14).

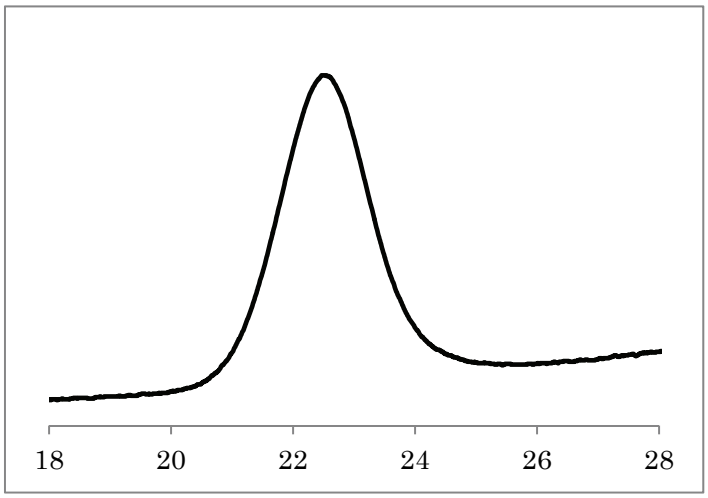


Figure 3-2. GPC trace for **TPA[{(PFV)$_2$-3PV}-Fc]$_3$** (run 15).

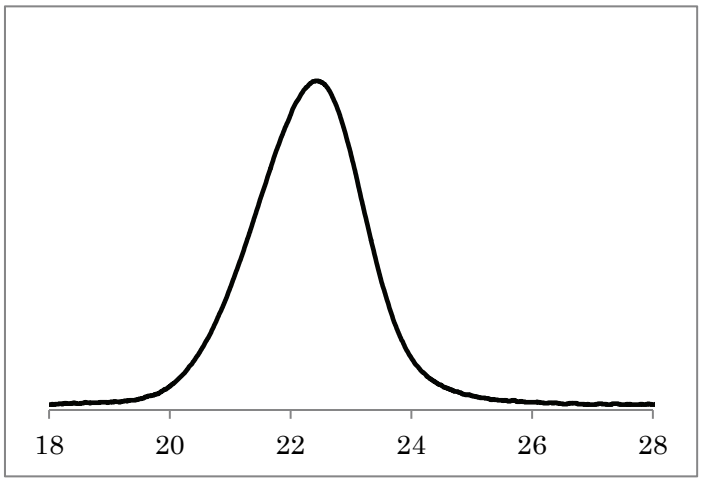


Figure 3-3. GPC trace for **TPA[{(PFV)$_2$-3T}-C_6F_5]$_3$** (run 16).

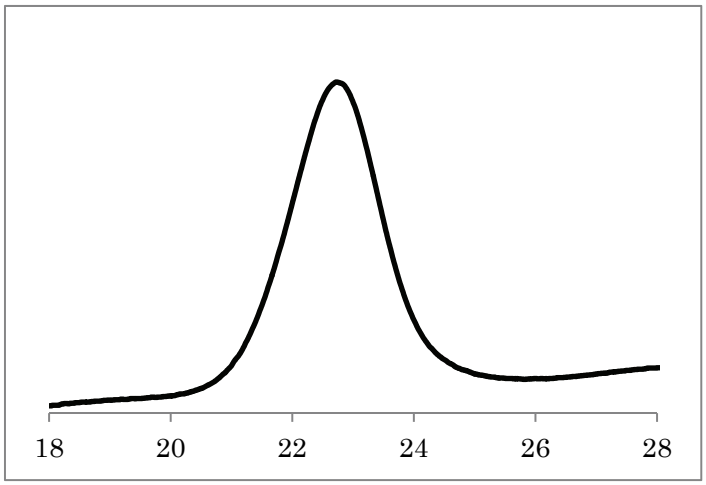


Figure 3-4. GPC trace for **TPA[{(PFV)$_2$-3T}-Fc]$_3$** (run 17).