Avoiding Olefin Isomerization During Decyanation of Alkylcyano α,ω-Dienes: A Deuterium Labeling and Structural Study of Mechanism

*Giovanni Rojas, Kenneth B. Wagener**

Center for Macromolecular Science and Engineering, George and Josephine Butler Polymer Research Laboratory, Department of Chemistry, University of Florida , Gainesville, Florida 32611-7200
wagener@chem.ufl.edu

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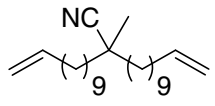
General Information

All ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded in $CDCl_3$. Chemical shifts were referenced to residual signals from $CDCl_3$ (7.27 ppm for ^{1}H, 77.23 ppm for ^{13}C) with 0.03% v/v TMS as an internal reference. The NMR splitting patterns are designated as follows: s, singlet; d, doublet; t, triplet; m, multiplet; and br, broad signal. Analysis of samples by gas chromatography (GC) was performed on a gas chromatograph, equipped with a flame ionization detector, using a capillary column coated with 5% diphenyl - 95% dimethylpolysiloxane. High-resolution mass spectrometry (HRMS) was performed using a mass spectrometer in the electron ionization (EI) mode. The mass resolution was ~6000 for EI measured at Full-Width-Half-Maximum (FWHM) in the high resolution detection mode. Thin layer chromatography (TLC) was used to monitor all reactions and was performed on aluminum plates coated with silica gel (250 μm thickness). TLC plates were developed to produce a visible

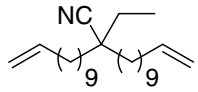
signature by any of the following: ultraviolet light, iodine, vanillin, $KMnO_4$, or phosphomolybdic acid. Flash column chromatography was performed using ultra pure silica gel (40-63 μm, 60 Å pore size). All reactions were performed in flame-dried glassware under argon unless otherwise stated.

Experimental section

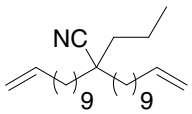
General methodology of alkylation of nitriles: All following alkylcyano α,ω-dienes were synthesized according to the literature procedure.[1, 2]



2-Methyl-2-(undec-10-enyl)tridec-12-enenitrile (1a): After purification, 6.41 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm), 1.20-1.64 (m, 35H), 2.04 (q, 4H), 4.96 (m, 4H), 5.81 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 24.8, 28.9, 29.1, 29.4, 29.5, 29.7, 33.8, 36.7, 39.4, 114.1, 124.7, 139.1; EI/HRMS: $[M]^+$ calculated for $C_{25}H_{45}N$: 359.3552, found: 359.3697. Elemental analysis calculated for $C_{25}H_{45}N$: 83.49 C, 12.61 H, 3.89 N; found 83.23 C, 12.59 H, 4.18 N.

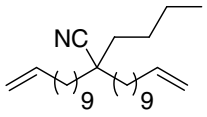


2-Ethyl-2-(undec-10-enyl)tridec-12-enenitrile (1b): After purification, 6.46 g (96% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.99 (t, 3H), 1.01-1.56 (m, 34H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 8.9, 14.3, 22.9, 24.5, 29.1, 29.3, 29.6, 29.7, 29.7, 30.0, 31.8, 34.0, 35.8, 41.3, 114.3, 124.5, 139.4; EI/HRMS: $[M]^+$ calculated for $C_{26}H_{47}N$: 373.3709, found: 373.3710. Elemental analysis calculated for $C_{26}H_{47}N$: 83.57 C, 12.68 H, 3.75 N; found 83.59 C, 12.67 H, 3.74 N.

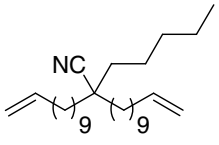


2-propyl-2-(undec-10-enyl)tridec-12-enenitrile (1c): After purification, 5.28 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR

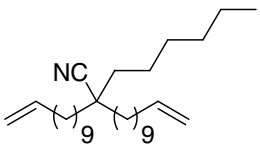
($CDCl_3$): δ(ppm) 0.94 (t, 3H), 1.23-1.56 (m, 36H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.4, 17.9, 24.5, 29.1, 29.3, 29.6, 29.6, 30.0, 34.0, 36.3, 38.6, 40.8, 114.3, 124.6, 139.4; EI/HRMS: $[M]^+$ calculated for $C_{27}H_{49}N$: 387.3865, found: 387.3871. Elemental analysis calculated for $C_{27}H_{49}N$: 83.65 C, 12.74 H, 3.61 N; found 83.61 C, 12.79 H, 3.60 N.



2-butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d): After purification, 7.16 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.94 (t, 3H), 1.23-1.56 (m, 38H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.0, 23.0, 24.4, 26.6, 29.0, 29.2, 29.6, 29.6, 29.9, 33.9, 36.0, 36.7, 40.7, 114.2, 124.4, 139.1; EI/HRMS: $[M]^+$ calculated for $C_{28}H_{51}N$: 401.4022, found: 401.4031. Elemental analysis calculated for $C_{28}H_{51}N$: 83.72 C, 12.80 H, 3.49 N; found 83.71 C, 12.81 H, 3.48 N.

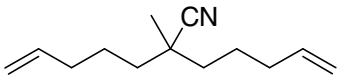


2-pentyl-2-(undec-10-enyl)tridec-12-enenitrile (1e): After purification, 6.53 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.90 (t, 3H), 1.29-1.56 (m, 40H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.3, 22.7, 24.2, 24.5, 27.1, 27.4, 29.1, 29.3, 29.7, 30.0, 32.2, 33.5, 34.0, 36.3, 40.8, 114.4, 122.6, 139.4; EI/HRMS: $[M]^+$ calculated for $C_{29}H_{53}N$: 415.4178, found: 415.4173. Elemental analysis calculated for $C_{29}H_{53}N$: 83.78 C, 12.85 H, 3.37 N; found 83.79 C, 12.83 H, 3.40 N.

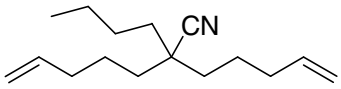


2-Hexyl-2-(undec-10-enyl)tridec-12-enenitrile (1f): After purification, 7.66 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.90 (t, 3H), 1.29-1.56 (m, 42H), 2.04 (q, 4H), 4.97 (m, 4H), 5.82 (m, 2H); ^{13}C-

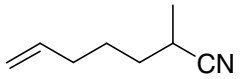
NMR ($CDCl_3$): δ(ppm) 14.2, 22.8, 24.5, 24.5, 29.2, 29.3, 29.6, 29.7, 30.0, 31.8, 34.0, 36.4, 40.9, 114.3, 124.7, 139.4; EI/HRMS: $[M]^+$ calculated for $C_{30}H_{55}N$: 429.4335, found: 429.4346. Elemental analysis calculated for $C_{30}H_{55}N$: 83.84 C, 12.90 H, 3.26 N; found 83.41 C, 13.37 H, 3.49 N.



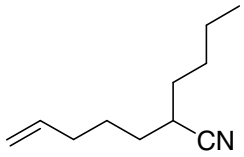
2-methyl-2-(pent-4-enyl)hept-6-enenitrile (4a): After purification, 1.32 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 1.33 (m, 4H), 1.51 (s, 3H), 1.58 (t, 4H), 1.95 (q, 4H), 5.01 (m, 4H), 5.71 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 23.21, 24.17, 32.37, 41.26, 115.34, 124.47, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{13}H_{21}N$: 191.1674, found: 191.1678. Elemental analysis calculated for $C_{13}H_{21}N$: 81.61 C, 11.06 H, 7.32 N; found 81.62 C, 11.07 H, 7.33 N.



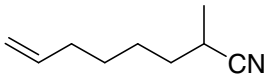
2-butyl-2-(pent-4-enyl)hept-6-enenitrile (4b): After purification, 1.05 g (98% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.96 (t, 3H), 1.33-1.58 (m, 14H), 1.95 (q, 4H), 4.98 (m, 4H), 5.71 (m, 2H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.10, 23.04, 23.72, 26.59, 33.84, 35.68, 36.00, 40.66, 115.47, 124.40, 138.06; EI/HRMS: $[M]^+$ calculated for $C_{16}H_{27}N$: 233.2143, found: 233.2137. Elemental analysis calculated for $C_{16}H_{27}N$: 82.34 C, 11.66 H, 6.00 N; found 82.27 C, 11.71 H, 5.99 N.



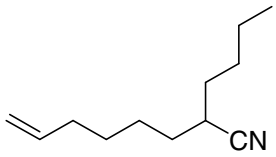
2-methylhept-6-enenitrile (13a): After purification, 1.08 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 1.33 (m, 2H), 1.40 (d, 3H), 1.63 (q, 2H), 1.97 (q, 2H), 2.67 (m, 1H), 4.98 (m, 2H), 5.71 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 17.03, 25.65, 25.79, 29.90, 31.73, 115.34, 123.22, 139.00; EI/HRMS: $[M]^+$ calculated for $C_8H_{13}N$: 123.1048, found: 123.1055. Elemental analysis calculated for $C_8H_{13}N$: 77.99 C, 10.64 H, 11.37 N; found 80.01 C, 10.61 H, 11.33 N.



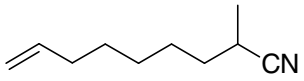
2-butylhept-6-enenitrile (13b): After purification, 1.15 g (97% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.96 (t, 3H), 1.33 (m, 6H), 1.63 (q, 4H), 1.97 (q, 2H), 2.48 (m, 1H), 5.01 (m, 2H), 5.71 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.01, 23.40, 25.90, 28.83, 28.94, 30.24, 31.20, 31.73, 115.34, 122.56, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{11}H_{19}N$: 165.1517, found: 167.1508. Elemental analysis calculated for $C_{11}H_{19}N$: 79.94 C, 11.59 H, 8.47 N; found 79.90 C, 11.61 H, 8.45 N.



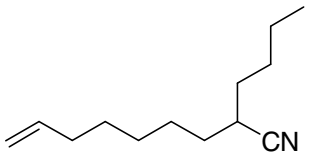
2-methyloct-7-enenitrile (13c): After purification, 1.52 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 1.32 (m, 4H), 1.42 (d, 3H), 1.61 (q, 2H), 1.95 (q, 2H), 2.67 (m, 1H), 5.01 (m, 2H), 5.69 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 17.03, 25.65, 27.25, 29.34, 31.18, 31.30, 115.34, 123.22, 139.00; EI/HRMS: $[M]^+$ calculated for $C_9H_{15}N$: 137.1204, found: 137.1208. Elemental analysis calculated for $C_9H_{15}N$: 78.77 C, 11.02 H, 10.21 N; found 78.80 C, 11.00 H, 10.24 N.



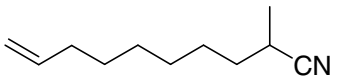
2-butyloct-7-enenitrile (13d): After purification, 1.02 g (98% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.96 (t, 3H), 1.29 (m, 8H), 1.61 (q, 4H), 1.95 (q, 2H), 2.48 (m, 1H), 5.01 (m, 2H), 5.69 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.01, 23.40, 27.14, 28.94, 29.34, 29.67, 30.24, 31.20, 31.30, 115.34, 122.56, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{12}H_{21}N$: 179.1674, found: 179.1670. Elemental analysis calculated for $C_{12}H_{21}N$: 80.38 C, 11.81 H, 7.81 N; found 80.33 C, 11.79 H, 7.85 N.



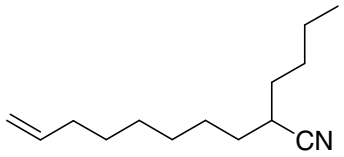
2-methylnon-8-enenitrile (13e): After purification, 1.34 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 1.29 (m, 6H), 1.42 (d, 3H), 1.61 (q, 2H), 1.95 (q, 2H), 2.65 (m, 1H), 5.01 (m, 2H), 5.71 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 17.03, 25.65, 27.68, 28.52, 29.13, 31.18, 31.30, 115.34, 123.22, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{10}H_{17}N$: 151.1361, found: 151.1368. Elemental analysis calculated for $C_{10}H_{17}N$: 79.41 C, 11.33 H, 9.26 N; found 79.44 C, 11.36 H, 9.21 N.



2-butylnon-8-enenitrile (13f): After purification, 1.12 g (98% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.96 (t, 3H), 1.29 (m, 10H), 1.61 (q, 4H), 1.95 (q, 2H), 2.48 (m, 1H), 4.98 (m, 2H), 5.71 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.01, 23.40, 27.79, 28.52, 28.94, 29.13, 29.67, 30.24, 31.20, 31.30, 115.34, 122.56, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{13}H_{23}N$: 193.1830, found: 193.1835. Elemental analysis calculated for $C_{13}H_{23}N$: 80.76 C, 11.99 H, 7.25 N; found 80.73 C, 11.95 H, 7.28 N.



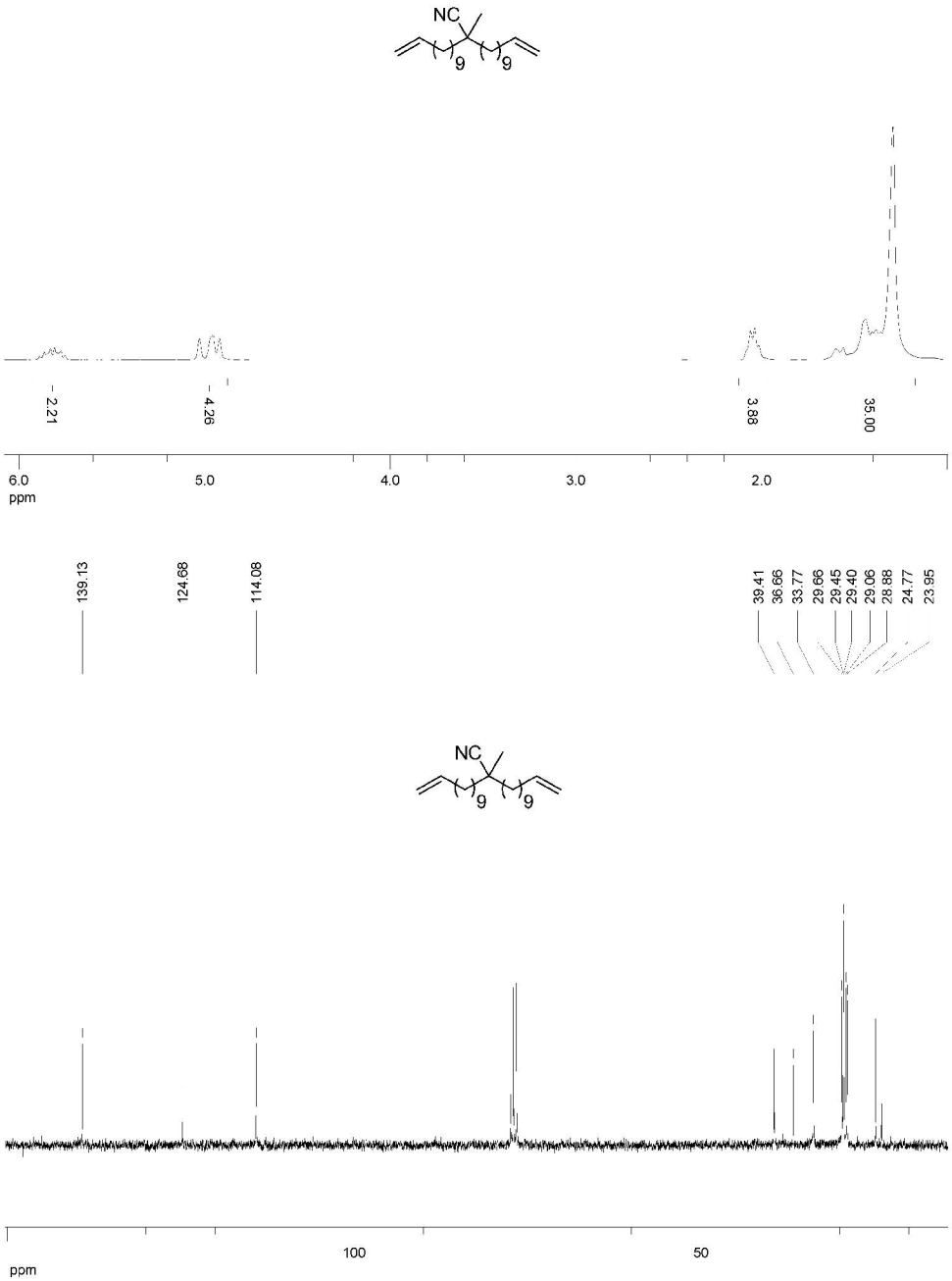
2-methyldec-9-enenitrile (13g): After purification, 1.63 g (99% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 1.29 (m, 8H), 1.40 (d, 3H), 1.61 (q, 2H), 1.95 (q, 2H), 2.67 (m, 1H), 5.01 (m, 2H), 5.69 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 17.03, 25.65, 27.68, 28.72, 29.13, 29.19, 31.18, 31.30, 115.34, 123.22, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{11}H_{19}N$: 165.1517, found: 165.1523. Elemental analysis calculated for $C_{11}H_{19}N$: 79.94 C, 11.59 H, 8.47 N; found 79.96 C, 11.61 H, 8.45 N.



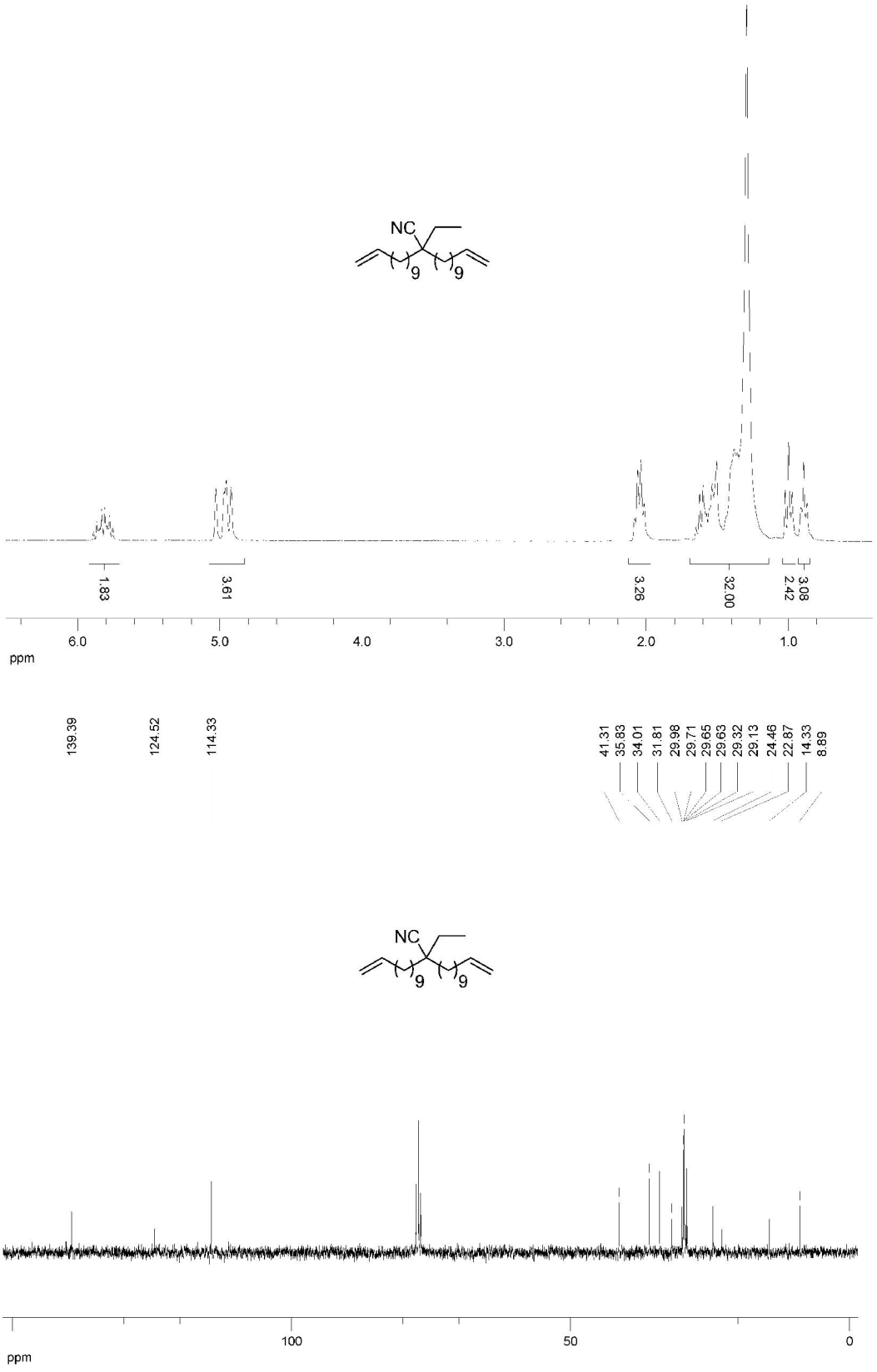
2-butyldec-9-enenitrile (13h): After purification, 1.17 g (97% yield) of a pale yellow liquid was collected. The following spectral properties were observed: ^{1}H-NMR ($CDCl_3$): δ(ppm) 0.96 (t, 3H), 1.29 (m, 12H), 1.61 (q, 4H), 1.95 (q, 2H), 2.48 (m, 1H), 5.01 (m, 2H), 5.71 (m, 1H); ^{13}C-NMR ($CDCl_3$): δ(ppm) 14.01, 23.40, 27.79, 28.72, 28.94, 29.13, 29.19, 29.67, 30.24, 31.20, 31.30, 115.34, 122.56, 139.00; EI/HRMS: $[M]^+$ calculated for $C_{14}H_{25}N$: 207.1987, found: 207.1983. Elemental analysis calculated for $C_{14}H_{25}N$: 81.09 C, 12.15 H, 6.75 N; found 81.08 C, 12.11 H, 6.78 N.

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

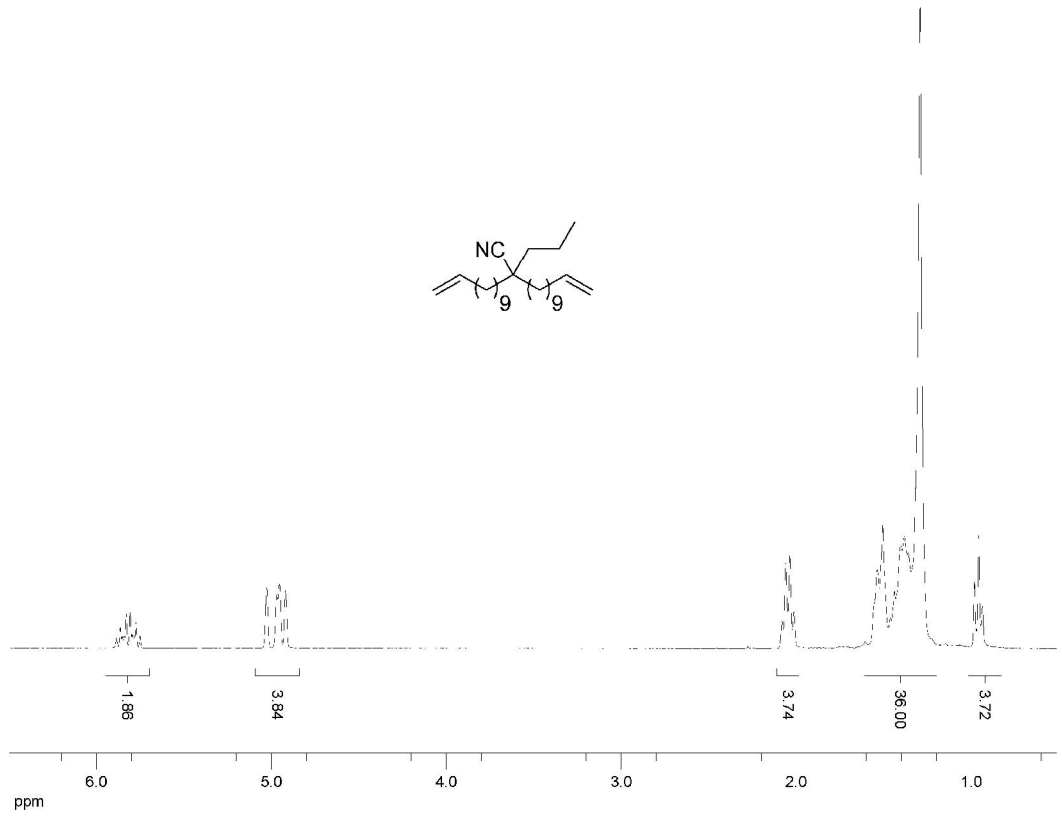
2-Methyl-2-(undec-10-enyl)tridec-12-enenitrile (1a)

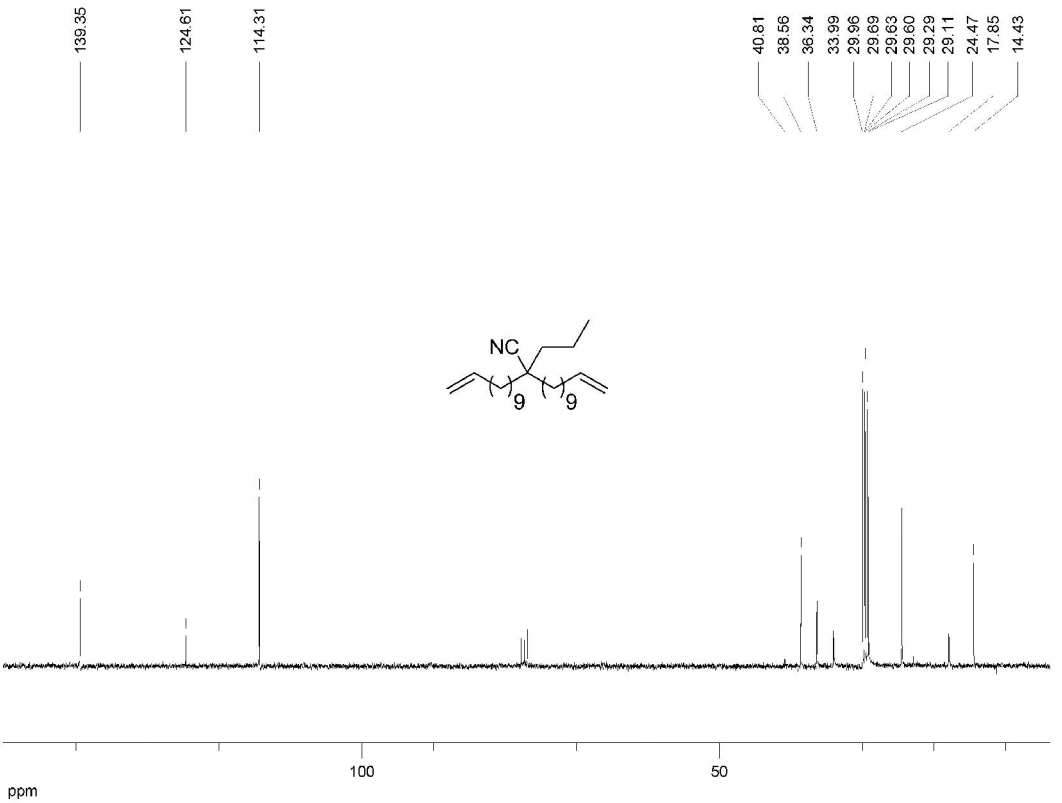


2-Ethyl-2-(undec-10-enyl)tridec-12-enenitrile (1b)

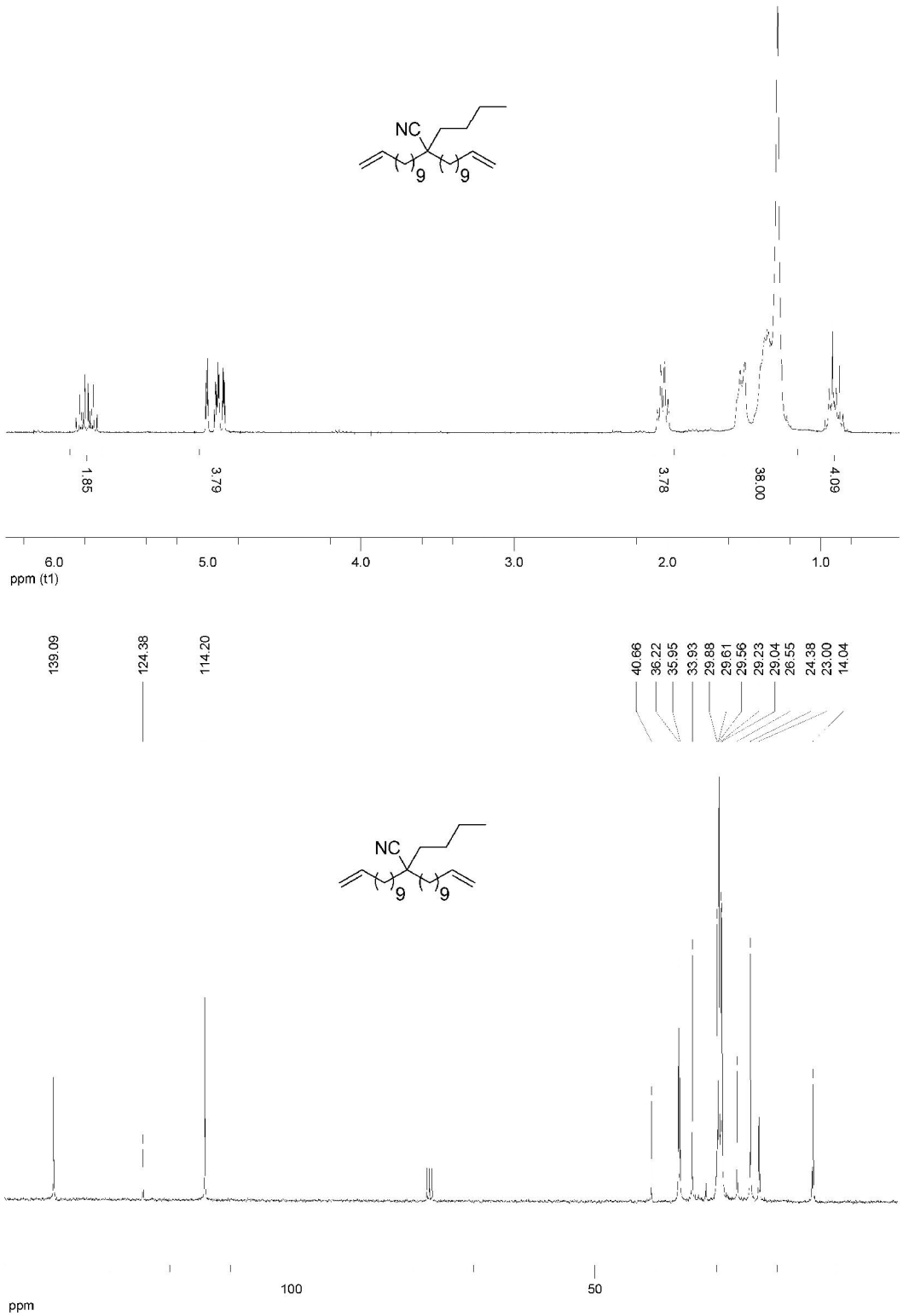


2-propyl-2-(undec-10-enyl)tridec-12-enenitrile (1c)

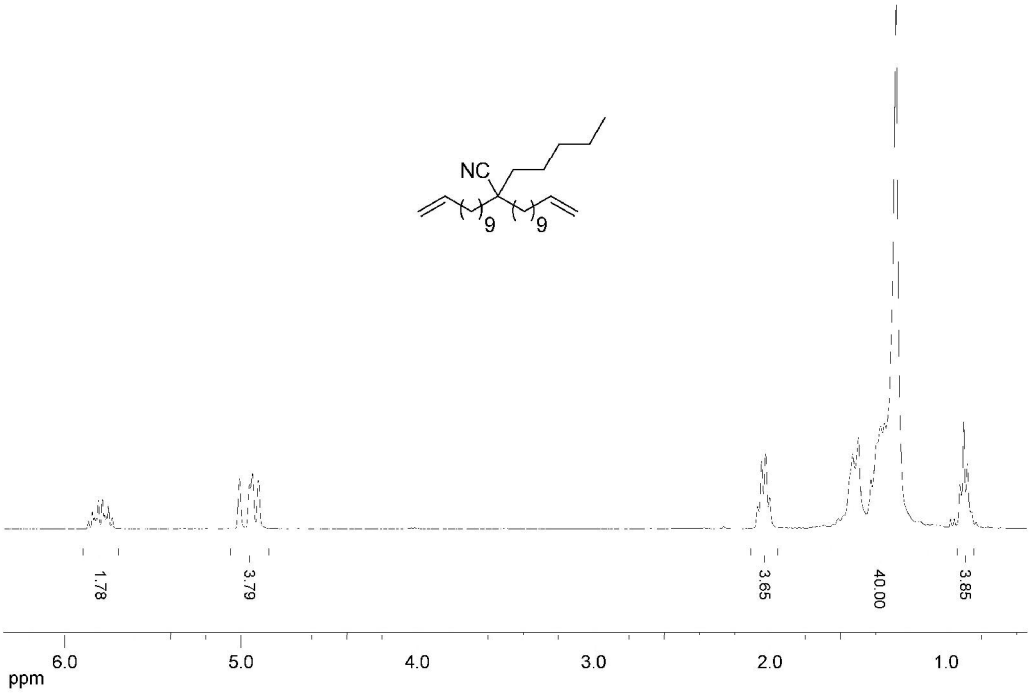


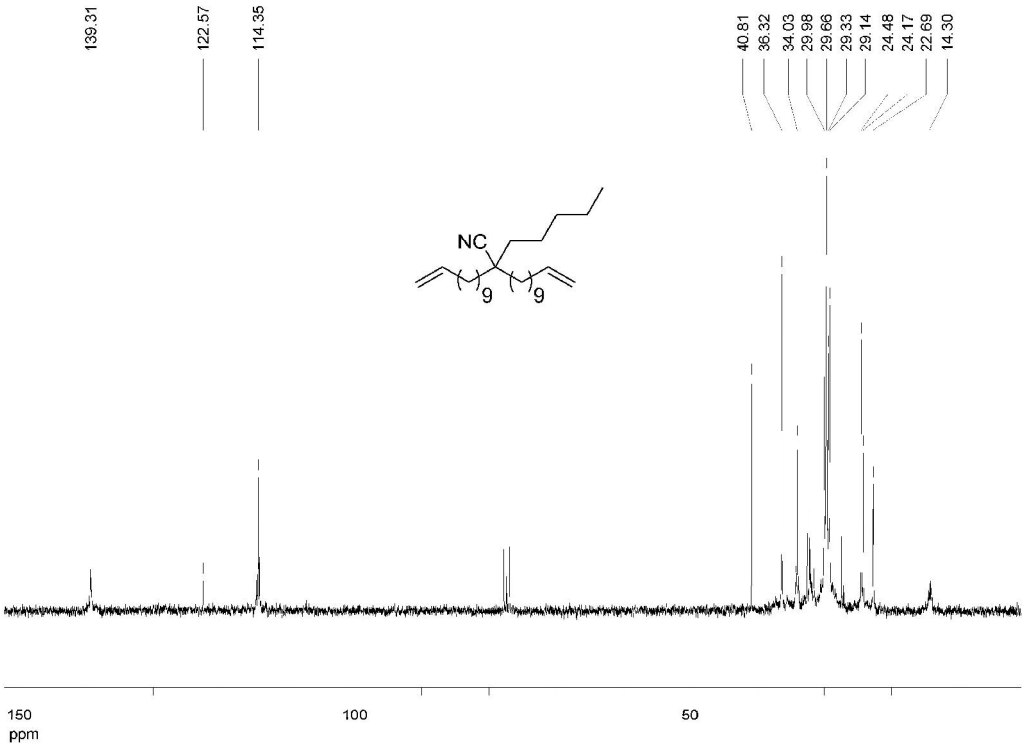


2-butyl-2-(undec-10-enyl)tridec-12-enenitrile (1d)

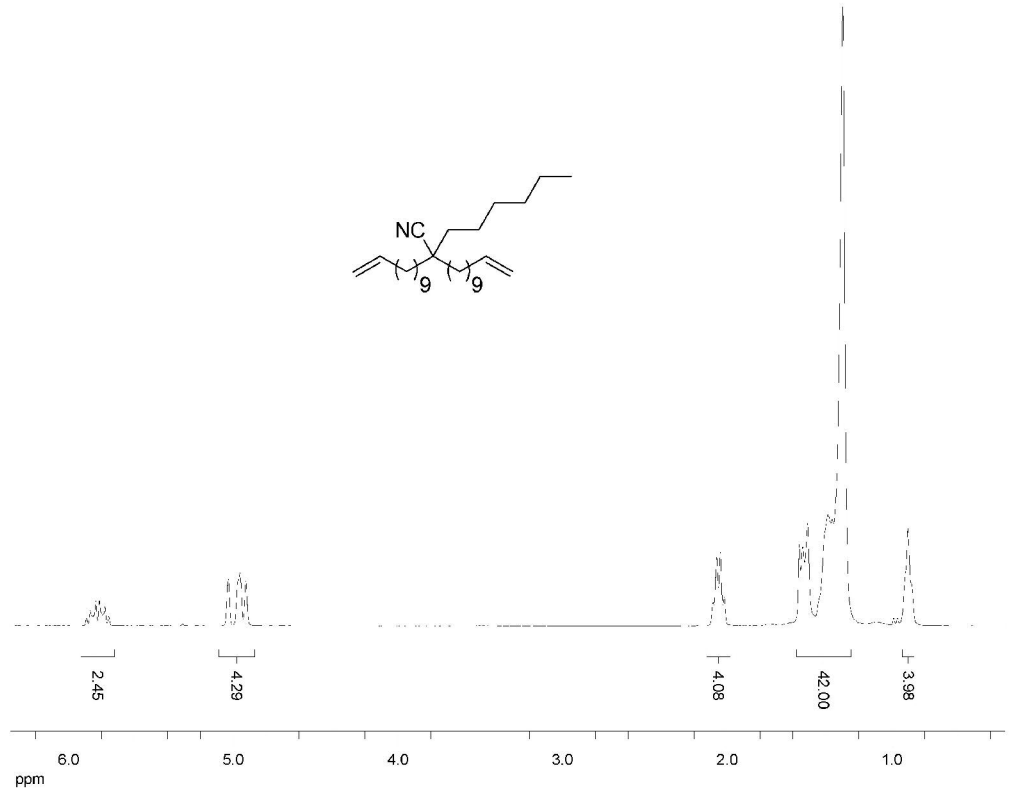


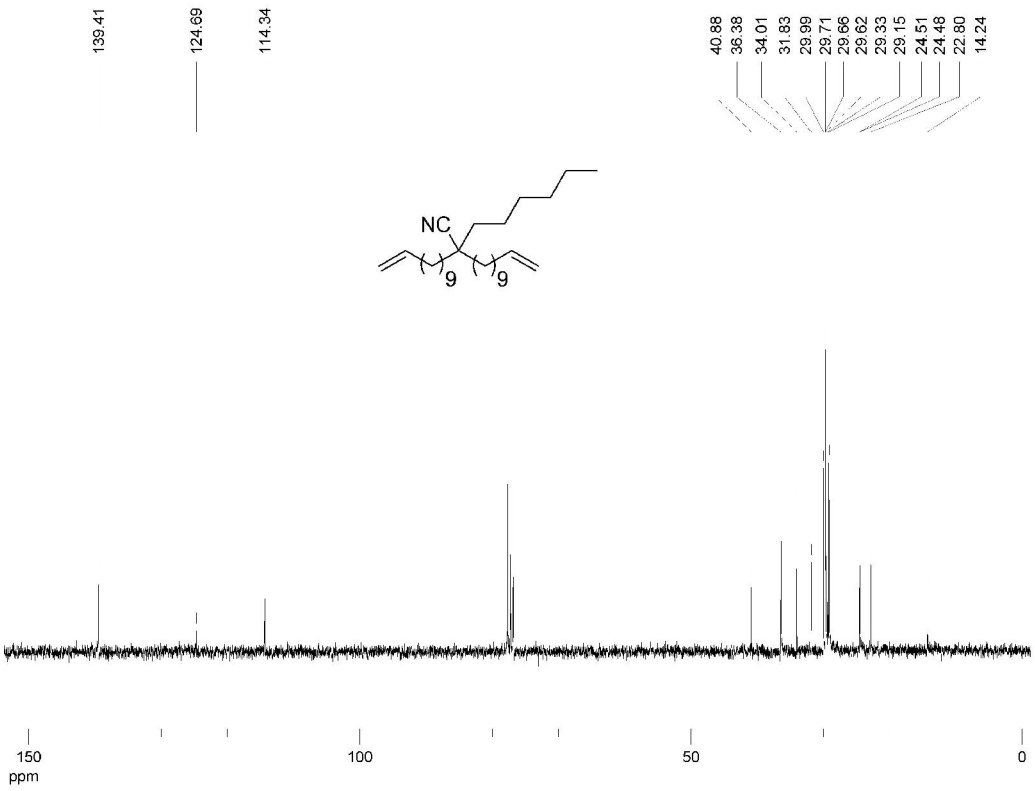
2-pentyl-2-(undec-10-enyl)tridec-12-enenitrile (1e)



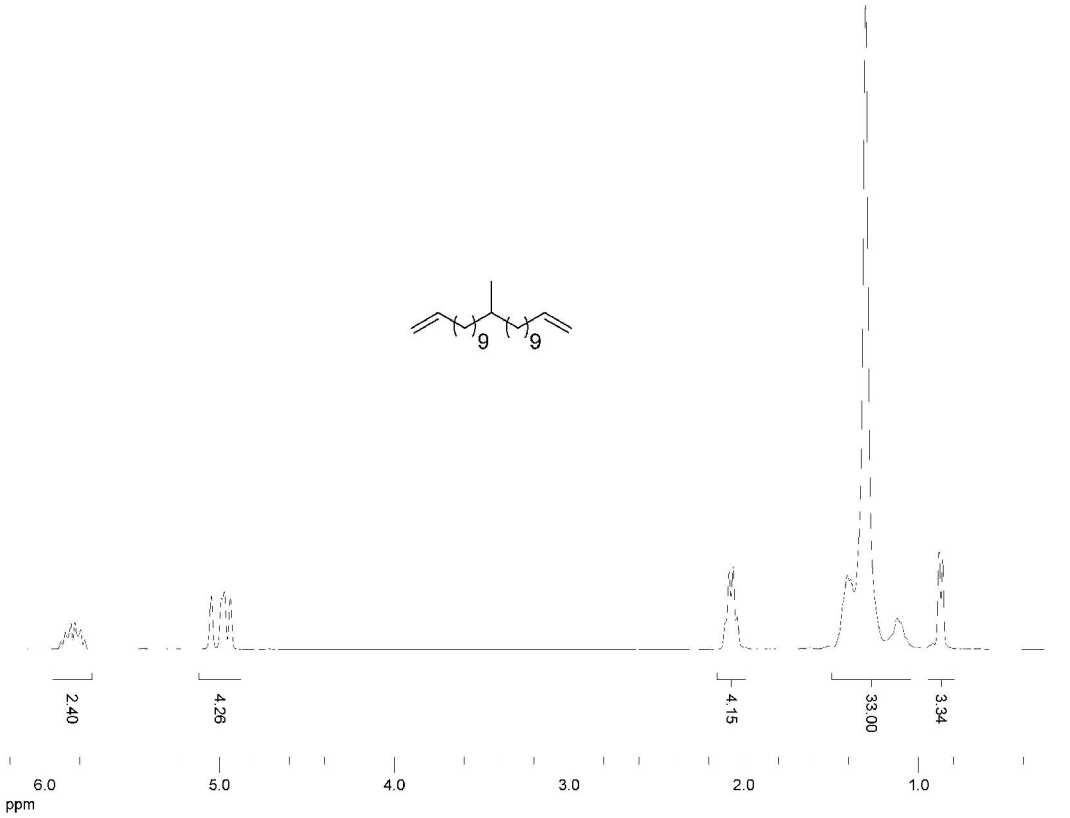


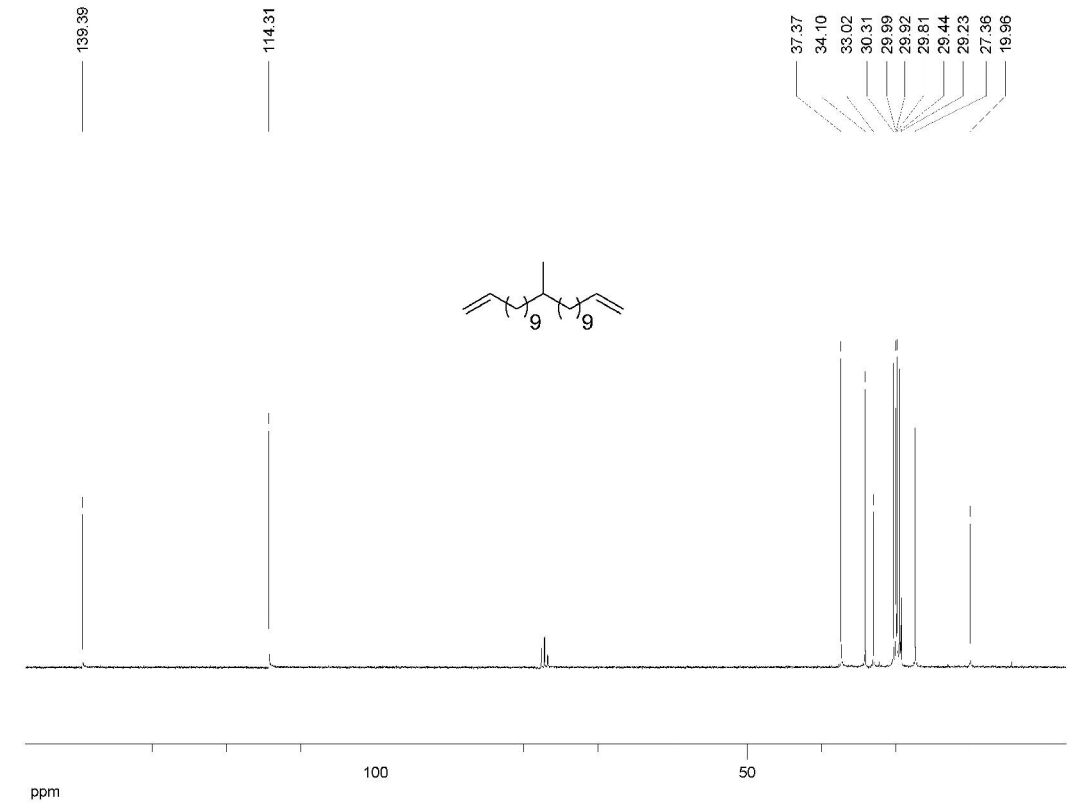
2-Hexyl-2-(undec-10-enyl)tridec-12-enenitrile (1f)



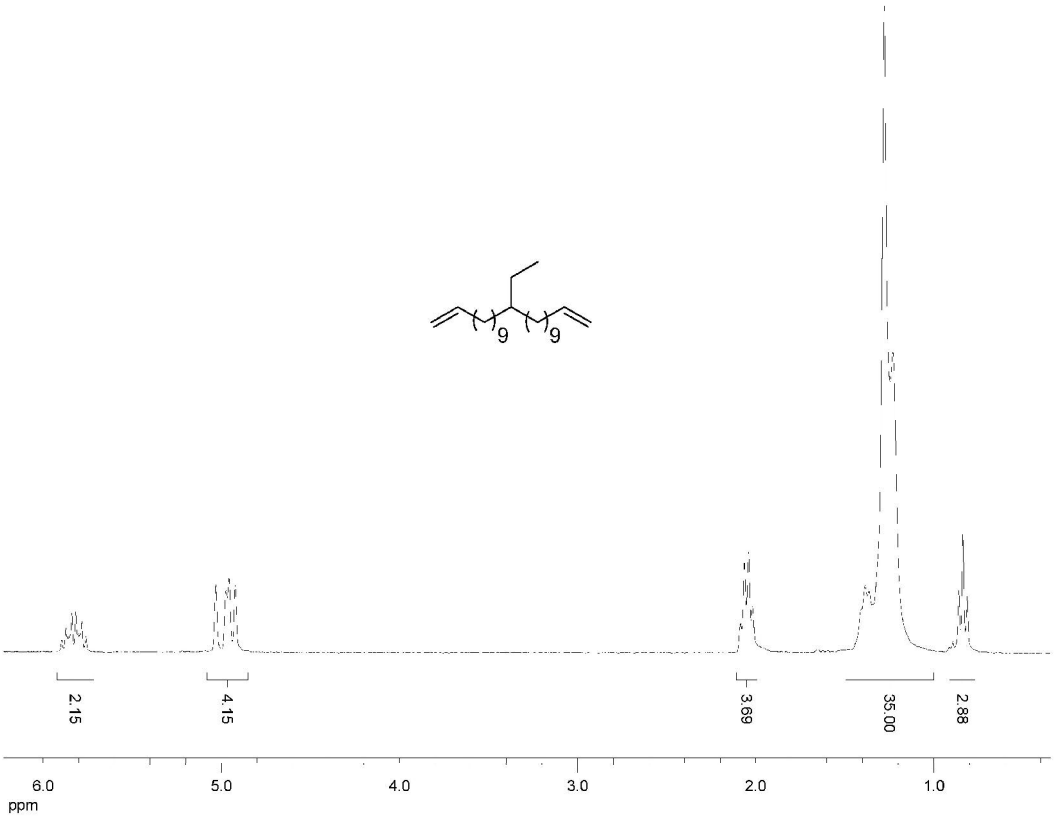


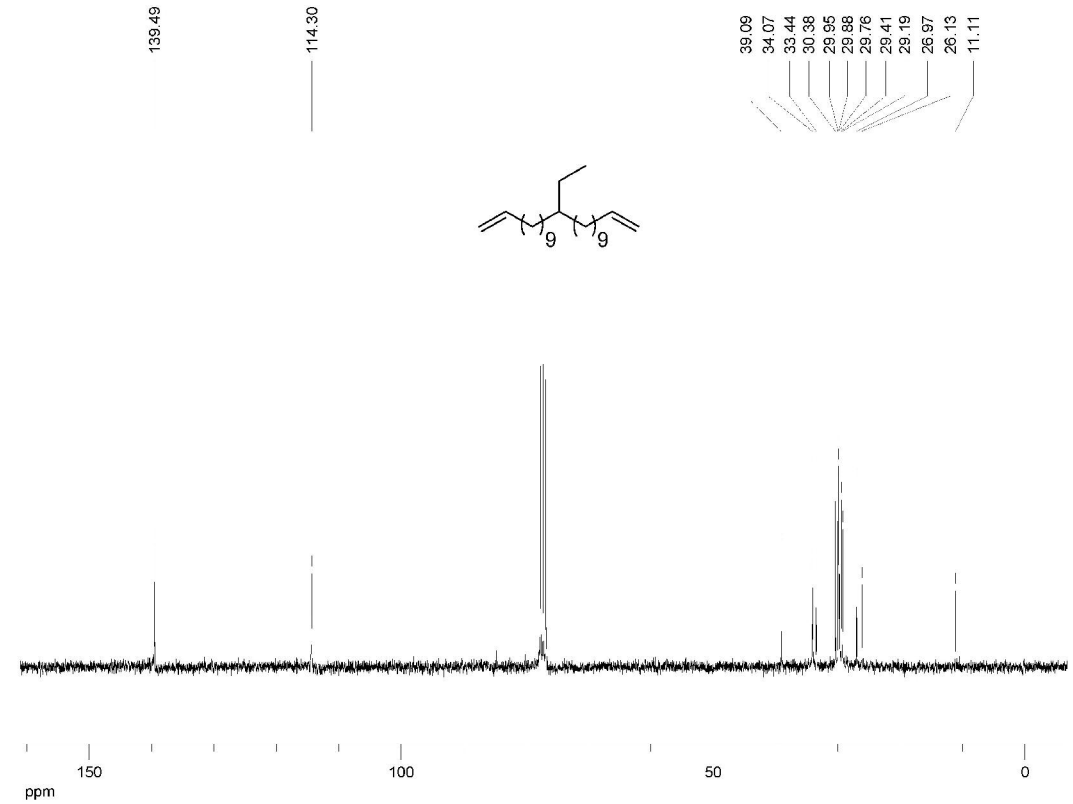
12-Methyltricosa-1,22-diene (2a)



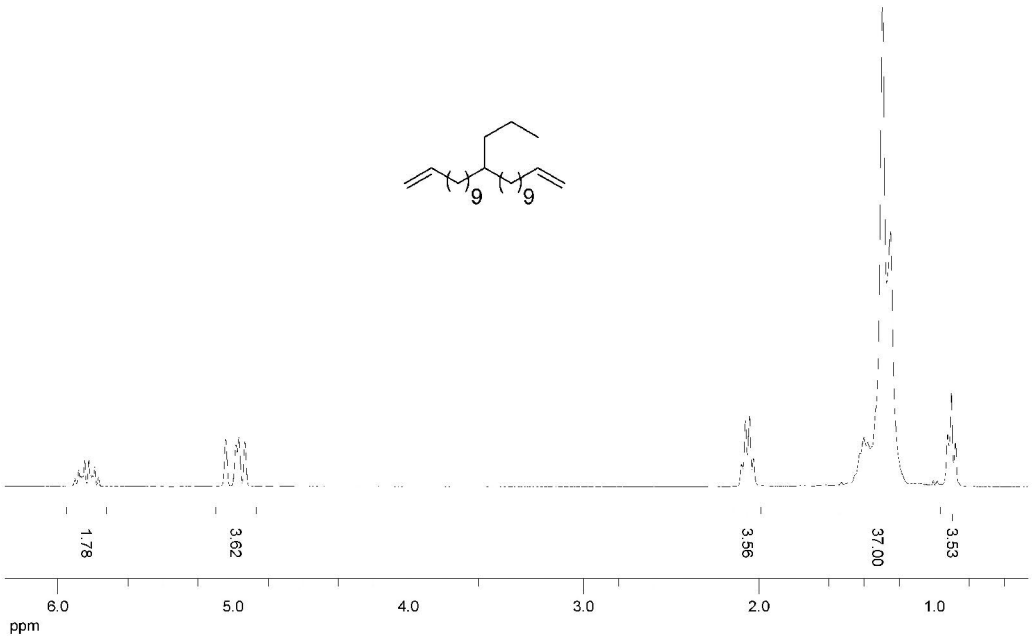


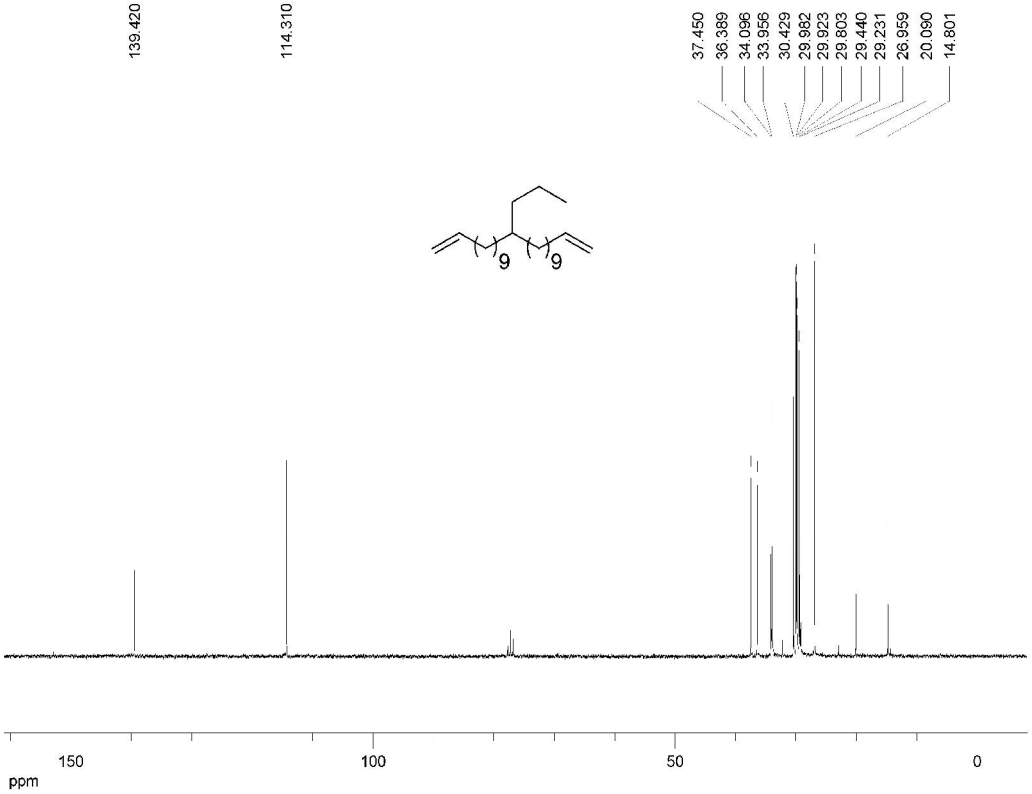
12-Ethyltricosa-1,22-diene (2b)



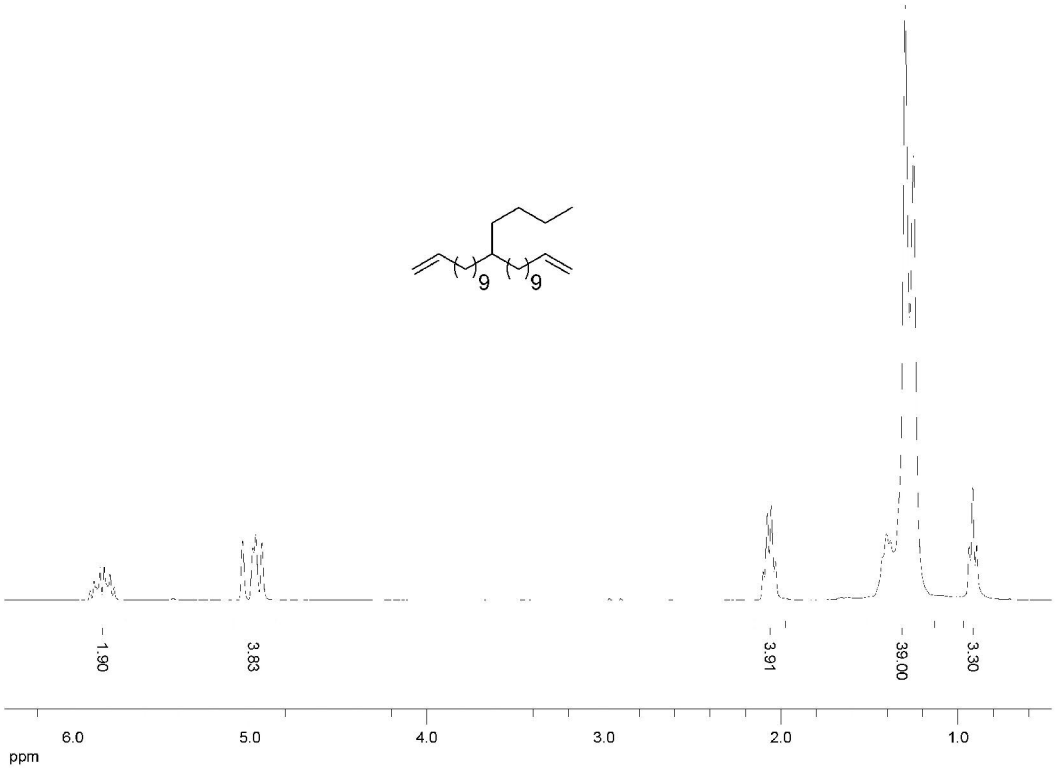


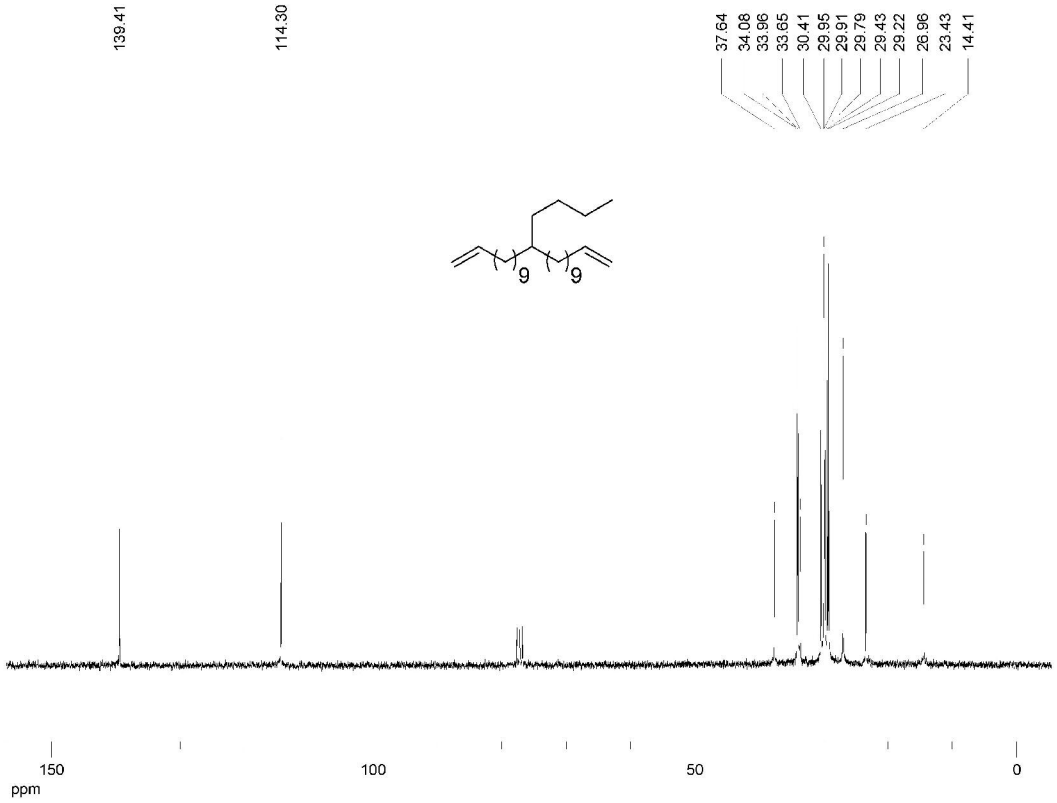
2-Propyltricosa-1,22-diene (2c)



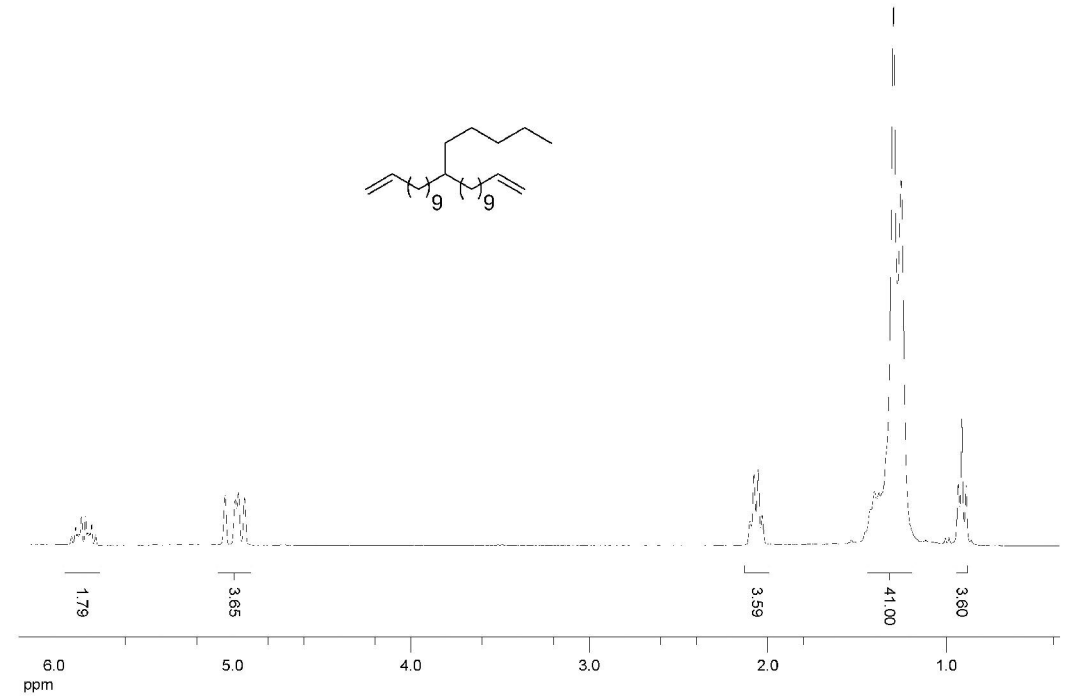


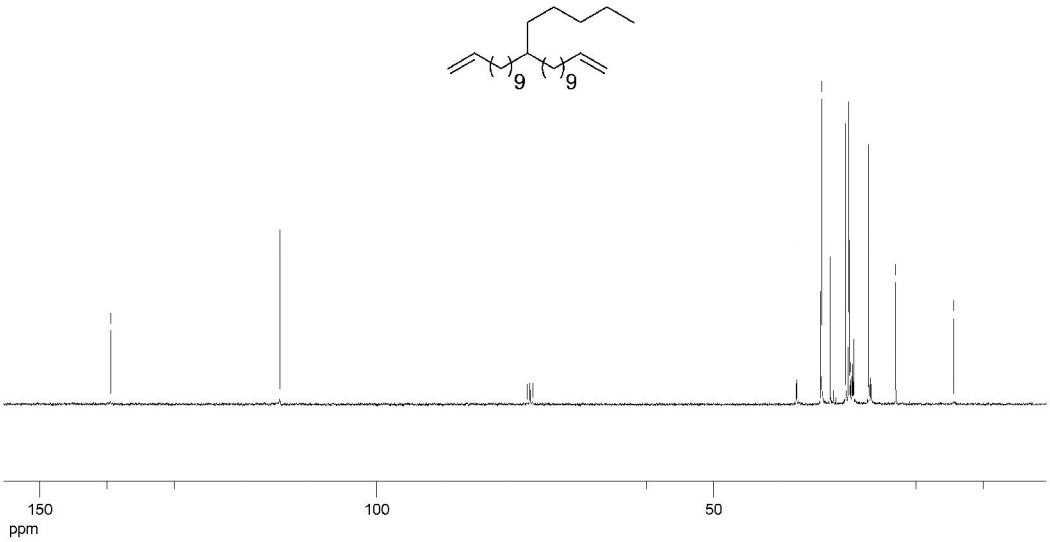
12-Butyltricosa-1,22-diene (2d)



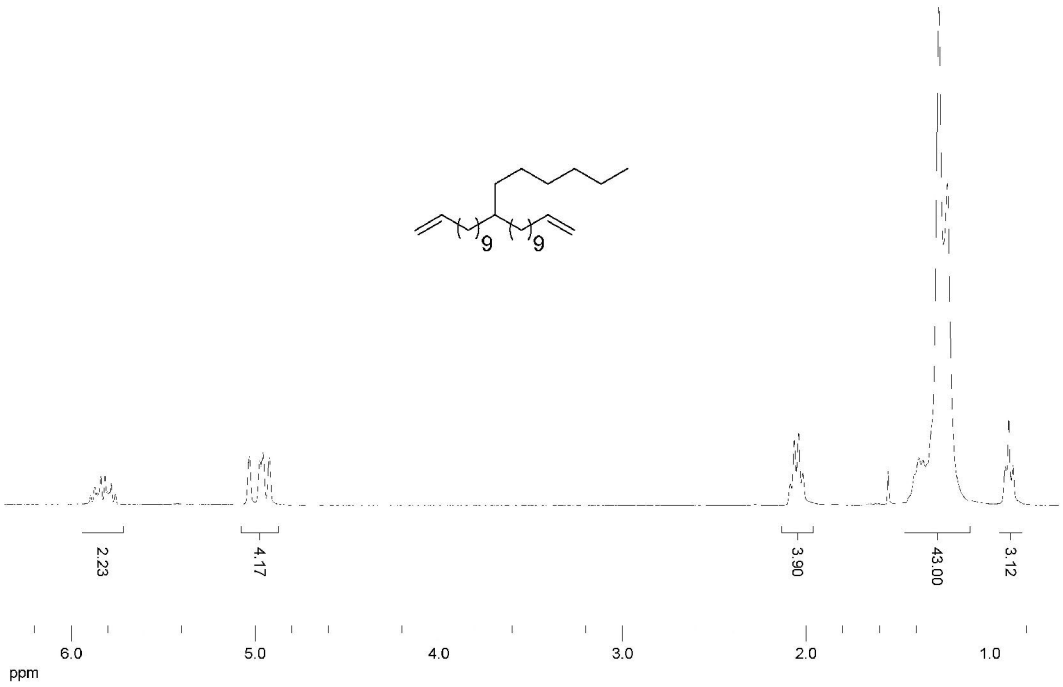


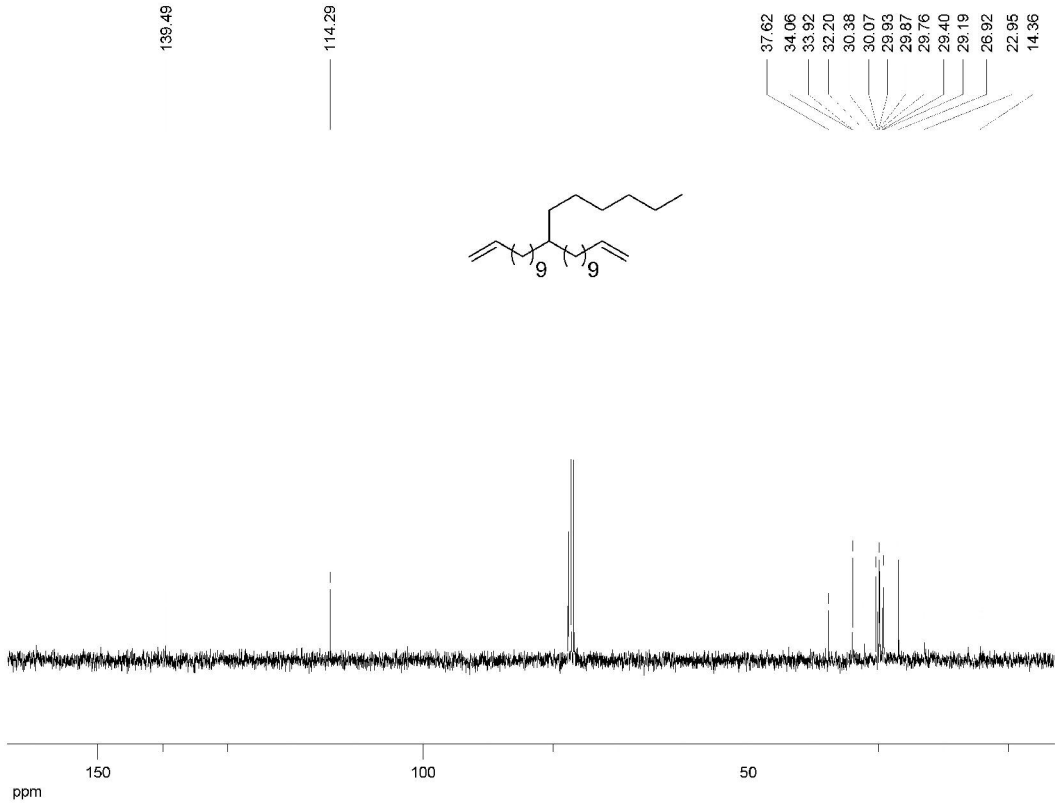
12-Pentyltricosa-1,22-diene (2e)





12-Hexyltricosa-1,22-diene (2f)





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(2) Baughman, T. W.; Sworen, J. C.; Wagener, K. B. *Tetrahedron* **2004**, *60*, 10943-10948.