

Support Information for:

Stereoselective Synthesis of Conjugated Trienes via 1,4-Palladium Migration/Heck Sequence

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1. General Information:

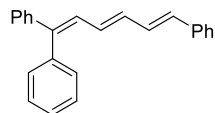
All reactions were carried out with standard Schlenk techniques under an argon atmosphere. All the solvents were dried using standard procedure and distilled before use. All commercially available chemical resources were used as received. Reactions were monitored by thin layer chromatography (TLC) supplied by Yantai Jiangyou Silicon Material Company (China). Visualization was accomplished with UV light or basic aqueous potassium permanganate (KMnO₄). Chromatography was achieved using forced flow (flash chromatography) of the indicated solvent system on 300-400 mesh silica gel (Silicycle flash F60). Nuclear Magnetic Resonance (NMR) spectra were acquired on Agilent 400 or Bruker 400 instrument operating at 400, 100 and 376 MHz for ¹H, ¹³C and ¹⁹F, respectively. Chemical shifts are reported in δ ppm referenced to an internal SiMe₄ standard (TMS: δ 0.000 ppm) for ¹H NMR, CDCl₃ (δ 77.16) for ¹³C NMR. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, quintet = quint, heptet = hept, m = multiplet, br = broad resonance. High-resolution mass spectra (HRMS) and Low resolution mass spectrometry (LRMS) were acquired through the National Center for Organic Mass Spectrometry in Shanghai, Shanghai Institute of Organic Chemistry (CAS) and determined on a Waters Micromass GCT Premie spectrometer.

The *ortho*-vinyl bromobenzenes (**1a-r**) were prepared according to the literatures.¹ Spectral data are in accordance with the literature references. The diene (**2a-g**) were prepared Wittig olefination of the commercially available α,β-unsaturated aldehydes with methyltriphenylphosphonium bromide and potassium *tert*-butoxide in tetrahydrofuran.² Spectral data are in accordance with the literature references.

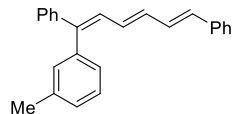
2. General Procedure for 1,4-Palladium Migration/Heck Sequence:

In a 10 mL sealed tube, a mixture of *ortho*-vinyl bromobenzene **1a** (0.2 mmol, 1.0 equiv), diene **2a** (0.40 mmol, 2.0 equiv), Pd(OAc)₂ (2.2 mg, 0.010 mmol, 5.0 mol %), (2-MeOPh)₃P (7.0 mg, 0.020 mmol, 10 mol %) and CsOPiv (94 mg, 2.0 equiv) in 1,4-dioxane (2.0 mL) was stirred at 70 °C under Ar in dark for 7 h. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by flash chromatography (elute: hexane / DCM = 100:1) in dark to afford product **3a**.

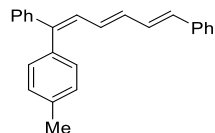
3. Characterization of the Obtained Products 3



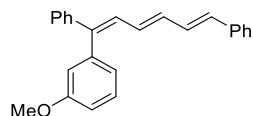
((3E,5E)-hexa-1,3,5-triene-1,1,6-triyl)tribenzene (3a): Yellow solid. 60.3 mg, 98% yield. **R_f** = 0.5 (PE). **Melting point:** 151-153 °C. **IR** (neat, cm⁻¹): 3025, 2960, 2925, 1597, 1493, 1446, 1261, 1078, 1028, 991, 765, 749, 700. **¹H NMR** (400 MHz, CDCl₃) δ 7.45 - 7.35 (m, 5H), 7.30 - 7.25 (m, 9H), 7.21 - 7.17 (m, 1H), 6.85 - 6.72 (m, 2H), 6.62 - 6.56 (m, 2H), 6.44 (dd, *J* = 15.0, 11.3 Hz, 1H) ppm. **¹³C NMR** (100 MHz, CDCl₃) δ 143.07, 142.26, 139.90, 137.50, 134.78, 132.74, 131.71, 130.71, 129.55, 128.74, 128.39, 128.36, 128.29, 127.65, 127.61, 127.58, 126.48 ppm. **HRMS** (EI) *m/z* Calcd for C₂₄H₂₀ [M]⁺ 308.1560, found 308.1556.



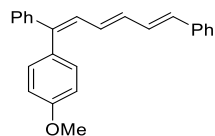
((1Z,3E,5E)-1-(*m*-tolyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3b) (It contains about 10% inseparable geometrical isomer **3h**, which was generated during the purification process.): Yellow oil. 54.7 mg, 85% yield. $R_f = 0.5$ (PE). **IR** (neat, cm^{-1}): 3411, 3028, 2924, 1721, 1657, 1600, 1493, 1448, 1279, 1071, 765, 700. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.36 - 7.31 (m, 3H), 7.30 - 7.21 (m, 7H), 7.19 - 7.14 (m, 2H), 7.07 - 7.02 (m, 2H), 6.86 - 6.69 (m, 2H), 6.64 - 6.49 (m, 2H), 6.44 (dd, $J = 14.9, 11.0$ Hz, 1H), 2.36 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.26, 142.31, 139.82, 137.98, 137.52, 134.58, 132.63, 131.85, 131.18, 129.60, 128.73, 128.33, 128.25, 128.15, 127.82, 127.62, 127.58, 127.52, 126.47, 21.60 ppm. **HRMS** (DART) m/z Calcd for $\text{C}_{25}\text{H}_{22}$ $[\text{M}]^+$ 322.1716, found 322.1713.



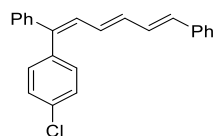
((1Z,3E,5E)-1-(*p*-tolyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3c): Yellow solid. 60.5 mg, 94% yield. $R_f = 0.5$ (PE). **Melting point**: 104-107 °C. **IR** (neat, cm^{-1}): 3024, 2922, 1595, 1510, 1492, 1447, 1182, 1079, 990, 825, 765, 748, 692, 645. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.36 (d, $J = 7.6$ Hz, 2H), 7.31 - 7.17 (m, 10H), 7.14 (d, $J = 7.7$ Hz, 2H), 6.85 - 6.70 (m, 2H), 6.66 - 6.36 (m, 3H), 2.42 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.19, 142.52, 137.57, 137.34, 136.91, 134.51, 132.53, 131.96, 130.63, 129.65, 129.09, 128.75, 128.33, 128.12, 127.73, 127.58, 127.55, 126.47, 21.46 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}$ $[\text{M}]^+$ 322.1722, found 322.1723.



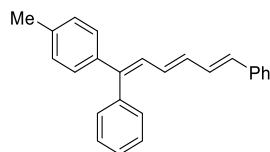
((1Z,3E,5E)-1-(3-methoxyphenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3d) (It contains about 10% inseparable geometrical isomer **3m**, which was generated during the purification process.): Yellow oil. 48.0 mg, 71% yield. $R_f = 0.4$ (PE/EA = 100/1). **IR** (neat, cm^{-1}): 3025, 2926, 1595, 1575, 1486, 1448, 1285, 1232, 1048, 991, 765, 748, 692. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.37 - 7.22 (m, 10H), 7.20 - 7.14 (m, 1H), 6.91 (ddd, $J = 8.4, 2.6, 1.0$ Hz, 1H), 6.87 - 6.72 (m, 4H), 6.60 - 6.51 (m, 2H), 6.45 (dd, $J = 15.0, 10.9$ Hz, 1H), 3.78 (s, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 159.64, 142.83, 141.96, 141.27, 137.49, 134.78, 132.77, 131.69, 129.55, 129.38, 128.73, 128.36, 128.24, 127.61, 127.58, 127.52, 126.48, 123.19, 116.01, 113.20, 55.37 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 338.1671, found 338.1674.



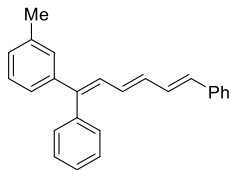
((1Z,3E,5E)-1-(4-methoxyphenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3e): Yellow oil. 56.7 mg, 84% yield. $R_f = 0.4$ (PE/EA = 100/1). **IR** (neat, cm^{-1}): 3028, 2928, 2837, 1724, 1655, 1601, 1509, 1447, 1250, 1177, 1030, 833, 766, 700. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.38 - 7.33 (m, 3H), 7.31 - 7.22 (m, 6H), 7.21 - 7.15 (m, 3H), 6.98 - 6.92 (m, 2H), 6.85 - 6.71 (m, 2H), 6.61 - 6.49 (m, 3H), 3.86 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 159.10, 142.85, 142.66, 137.54, 134.40, 132.45, 132.14, 131.98, 131.94, 129.63, 128.74, 128.35, 128.32, 128.01, 127.79, 127.56, 126.44, 113.73, 55.41 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 338.1671, found 338.1676.



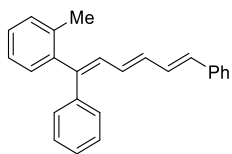
((1Z,3E,5E)-1-(4-chlorophenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3f): Yellow solid. 49.4 mg, 72% yield. $R_f = 0.4$ (PE). **Melting point:** 96-99 °C. **IR** (neat, cm^{-1}): 3025, 2924, 1594, 1488, 1447, 1088, 1015, 990, 832, 758, 747, 691, 507, 404. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.42 - 7.35 (m, 4H), 7.33 - 7.24 (m, 7H), 7.23 - 7.17 (m, 3H), 6.86 - 6.70 (m, 2H), 6.67 - 6.52 (m, 2H), 6.40 (dd, $J = 15.0, 11.3$ Hz, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 141.86, 141.67, 138.33, 137.39, 135.32, 133.51, 133.17, 132.08, 131.16, 129.35, 128.78, 128.72, 128.68, 128.47, 127.78, 127.76, 127.61, 126.53 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{24}\text{H}_{19}\text{Cl}$ $[\text{M}]^+$ 342.1175, found 342.1181.



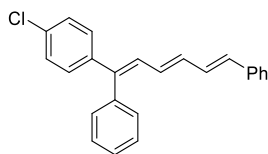
((1E,3E,5E)-1-(p-tolyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3g): Yellow solid. 52.7 mg, 82% yield. $R_f = 0.5$ (PE). **Melting point:** 102-103 °C. **IR** (neat, cm^{-1}): 3055, 3023, 2920, 1508, 1491, 1447, 1072, 990, 817, 777, 748, 701, 691. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.43 - 7.30 (m, 5H), 7.30 - 7.21 (m, 4H), 7.21 - 7.13 (m, 3H), 7.08 (d, $J = 8.0$ Hz, 2H), 6.82 - 6.70 (m, 2H), 6.60 - 6.49 (m, 2H), 6.42 (dd, $J = 14.9, 11.1$ Hz, 1H), 2.32 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.07, 140.05, 139.46, 137.57, 137.49, 134.33, 132.46, 131.86, 130.69, 129.63, 129.10, 128.73, 128.34, 127.55, 127.51, 126.45, 21.29 ppm. (Two carbon signals overlapped) **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}$ $[\text{M}]^+$ 322.1716, found 322.1714.



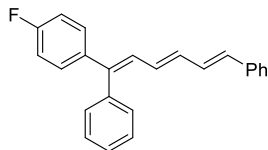
((1E,3E,5E)-1-(*m*-tolyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3h): Yellow oil. 51.5 mg, 80% yield. R_f = 0.5 (PE). **IR** (neat, cm^{-1}): 3439, 3058, 3028, 2921, 1725, 1660, 1599, 1493, 1448, 1278, 1175, 1071, 1027, 758, 700. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 7.44 - 7.41 (m, 2H), 7.39 - 7.34 (m, 2H), 7.32 - 7.23 (m, 6H), 7.22 - 7.16 (m, 2H), 7.13 - 7.03 (m, 2H), 6.83 - 6.75 (m, 2H), 6.62 - 6.53 (m, 2H), 6.44 (dd, J = 14.8, 11.2 Hz, 1H), 2.32 (s, 3H) ppm. **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 143.26, 142.30, 140.00, 137.91, 137.55, 134.61, 132.62, 131.80, 130.71, 129.61, 128.75, 128.43, 128.35, 128.29, 128.25, 128.20, 127.60, 127.54, 126.48, 124.95, 21.62 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}$ $[\text{M}]^+$ 322.1722, found 322.1730.



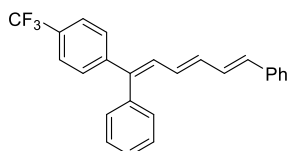
((1E,3E,5E)-1-(*o*-tolyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3i): Yellow solid. 58.6 mg, 91% yield. R_f = 0.5 (PE). **Melting point:** 105-107 °C. **IR** (neat, cm^{-1}): 3446, 3059, 3027, 2928, 1667, 1598, 1493, 1448, 1267, 1192, 1097, 977, 763, 734, 699. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.41 - 7.15 (m, 13H), 7.15 - 7.09 (m, 1H), 6.90 - 6.70 (m, 2H), 6.61 - 6.47 (m, 2H), 6.40 (d, J = 11.4 Hz, 1H), 2.02 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.58, 143.53, 140.43, 137.54, 136.63, 135.04, 132.75, 131.04, 130.68, 130.58, 130.35, 130.00, 129.51, 128.76, 128.24, 127.62, 127.34, 126.50, 125.75, 20.79 ppm. **HRMS** (ESI) m/z Calcd for $\text{C}_{25}\text{H}_{23}$ $[\text{M}+\text{H}]^+$ 323.1794, found 323.1793.



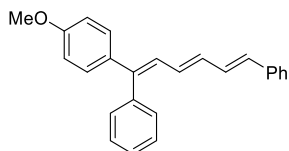
((1E,3E,5E)-1-(4-chlorophenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3j): Yellow solid. 55.6 mg, 81% yield. R_f = 0.4 (PE). **Melting point:** 131-133 °C. **IR** (neat, cm^{-1}): 3056, 3025, 2924, 1600, 1487, 1446, 1404, 1092, 1011, 990, 830, 747, 705, 691, 509. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.44 - 7.32 (m, 5H), 7.31 - 7.16 (m, 9H), 6.84 - 6.71 (m, 2H), 6.63 - 6.52 (m, 2H), 6.41 (dd, J = 14.9, 11.2 Hz, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 141.75, 140.76, 139.43, 137.40, 135.27, 133.35, 133.11, 132.08, 131.40, 130.63, 129.40, 128.85, 128.77, 128.61, 128.52, 127.79, 127.72, 126.52 ppm. **HRMS** (DART) m/z Calcd for $\text{C}_{24}\text{H}_{19}\text{Cl}$ $[\text{M}]^+$ 342.1170, found 342.1170.



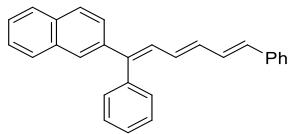
((1E,3E,5E)-1-(4-fluorophenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3k): Yellow solid. 42.3 mg, 65% yield. $R_f = 0.4$ (PE). **Melting point:** 112-115 °C. **IR** (neat, cm^{-1}): 3435, 3061, 3031, 1726, 1660, 1599, 1507, 1448, 1277, 1228, 1158, 837, 763, 738, 700, 600. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.45 - 7.32 (m, 5H), 7.31 - 7.15 (m, 7H), 7.02 - 6.91 (m, 2H), 6.82 - 6.70 (m, 2H), 6.61 - 6.52 (m, 2H), 6.42 (dd, $J = 14.9, 11.2$ Hz, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 162.46 (d, $J = 247.5$ Hz), 141.96, 139.72, 138.48 (d, $J = 3.4$ Hz), 137.46, 134.83, 132.84, 131.53, 130.63, 129.47, 129.25 (d, $J = 8.0$ Hz), 128.76, 128.48, 128.10 (d, $J = 1.7$ Hz), 127.73, 127.66, 126.49, 115.26 (d, $J = 21.4$ Hz) ppm. **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -119.46 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{24}\text{H}_{19}\text{F}$ $[\text{M}]^+$ 326.1471, found 326.1476.



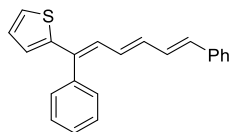
((1E,3E,5E)-1-(4-(trifluoromethyl)phenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3l): Yellow solid. 68.4 mg, 91% yield. $R_f = 0.4$ (PE). **Melting point:** 87-89 °C. **IR** (neat, cm^{-1}): 3434, 3061, 2927, 1726, 1666, 1616, 1494, 1449, 1409, 1325, 1167, 1125, 1067, 1017, 843, 752, 700. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.53 (d, $J = 8.2$ Hz, 2H), 7.47 - 7.35 (m, 7H), 7.32 - 7.18 (m, 7H), 6.86 (d, $J = 11.2$ Hz, 1H), 6.79 (dd, $J = 15.6, 10.5$ Hz, 1H), 6.67 - 6.57 (m, 2H), 6.44 (dd, $J = 14.6, 11.2$ Hz, 1H) ppm. **$^{13}\text{C NMR}$** (150 MHz, CDCl_3) δ 145.76, 141.50, 139.17, 137.32, 136.16, 133.69, 131.11, 130.62, 130.08, 129.27, 129.23 (q, $J = 32.4$ Hz), 128.80, 128.63, 127.94, 127.87, 127.76, 126.60, 125.30 (q, $J = 3.7$ Hz), 124.39 (q, $J = 269.9$ Hz), 77.37, 77.16, 76.95 ppm. **$^{19}\text{F NMR}$** (376 MHz, CDCl_3) δ -67.17 (d, $J = 14.3$ Hz) ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{19}\text{F}_3$ $[\text{M}]^+$ 376.1439, found 376.1429.



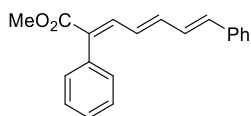
((1E,3E,5E)-1-(4-methoxyphenyl)hexa-1,3,5-triene-1,6-diyl)dibenzene (3m): Yellow solid. 54.8 mg, 81% yield. $R_f = 0.4$ (PE/EA = 100/1). **Melting point:** 135-136 °C. **IR** (neat, cm^{-1}): 3438, 3058, 3029, 2931, 1724, 1651, 1601, 1510, 1447, 1251, 1177, 1031, 833, 740, 700. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.44 - 7.31 (m, 5H), 7.31 - 7.19 (m, 6H), 7.19 - 7.14 (m, 1H), 6.85 - 6.79 (m, 2H), 6.78 - 6.70 (m, 2H), 6.59 - 6.54 (m, 1H), 6.54 - 6.49 (m, 1H), 6.41 (dd, $J = 14.8, 11.1$ Hz, 1H), 3.79 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 159.35, 142.74, 140.09, 137.60, 134.92, 133.89, 132.21, 131.97, 130.68, 129.69, 128.84, 128.73, 128.35, 127.53, 127.49, 126.68, 126.42, 113.79, 55.43 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}\text{O}$ $[\text{M}]^+$ 338.1671, found 338.1677.



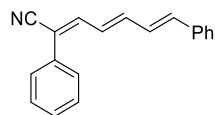
2-((1E,3E,5E)-1,6-diphenylhexa-1,3,5-trien-1-yl)naphthalene (3n): Yellow solid. 69.5 mg, 97% yield. $R_f = 0.5$ (PE). **Melting point:** 160-162 °C. **IR** (neat, cm^{-1}): 3055, 3024, 2960, 1596, 1492, 1447, 1189, 1081, 990, 857, 816, 747, 700, 476. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.83 - 7.65 (m, 3H), 7.61 (s, 1H), 7.51 (d, $J = 8.7$ Hz, 1H), 7.47 - 7.23 (m, 11H), 7.23 - 7.13 (m, 1H), 6.95 (d, $J = 11.1$ Hz, 1H), 6.79 (dd, $J = 15.6, 10.4$ Hz, 1H), 6.66 - 6.53 (m, 2H), 6.53 - 6.42 (m, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.02, 139.87, 139.60, 137.50, 134.96, 133.47, 132.91, 132.85, 131.76, 130.80, 129.57, 128.83, 128.75, 128.47, 128.39, 127.89, 127.68, 127.65, 127.06, 126.50, 126.32, 126.11, 125.42 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{28}\text{H}_{22}$ $[\text{M}]^+$ 358.1722, found 358.1726.



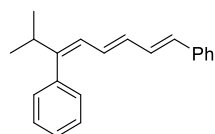
2-((1E,3E,5E)-1,6-diphenylhexa-1,3,5-trien-1-yl)thiophene (3o): Yellow solid. 57.7 mg, 92% yield. $R_f = 0.3$ (PE/EA = 100/1). **Melting point:** 103-105 °C. **IR** (neat, cm^{-1}): 3057, 3025, 2924, 1676, 1598, 1492, 1447, 1263, 1072, 1027, 990, 828, 748, 698. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.46 - 7.39 (m, 3H), 7.34 (td, $J = 7.6, 1.7$ Hz, 4H), 7.31 - 7.23 (m, 3H), 7.21 - 7.14 (m, 2H), 6.92 (dd, $J = 5.1, 3.6$ Hz, 1H), 6.84 (d, $J = 11.3$ Hz, 1H), 6.79 - 6.68 (m, 2H), 6.60 - 6.50 (m, 2H), 6.29 (dd, $J = 14.9, 11.3$ Hz, 1H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 147.14, 138.90, 137.53, 136.97, 134.49, 132.78, 131.01, 130.29, 129.54, 128.75, 128.44, 127.96, 127.75, 127.63, 127.03, 126.50, 126.25, 124.95 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{22}\text{H}_{18}\text{S}$ $[\text{M}]^+$ 314.1129, found 314.1136.



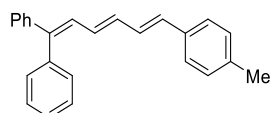
methyl (2E,4E,6E)-2,7-diphenylhepta-2,4,6-trienoate (3p): Yellow solid. 55.1 mg, 95% yield. $R_f = 0.2$ (PE/EA = 100/1). **Melting point:** 115-117 °C. **IR** (neat, cm^{-1}): 3027, 2948, 1706, 1601, 1588, 1494, 1433, 1299, 1240, 1134, 1039, 1023, 994, 750, 712, 691. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.56 (d, $J = 11.7$ Hz, 1H), 7.44 - 7.32 (m, 5H), 7.33 - 7.18 (m, 5H), 6.81 - 6.65 (m, 3H), 6.41 - 6.29 (m, 1H), 3.76 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 167.99, 141.19, 140.70, 136.78, 136.54, 135.35, 132.05, 130.40, 129.04, 128.82, 128.55, 128.43, 128.14, 127.81, 126.88, 52.24 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$ 290.1301, found 290.1301.



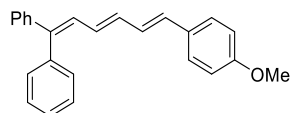
((2E,4E,6E)-2,7-diphenylhepta-2,4,6-trienitrile (3q): Yellow oil. 19.1 mg, 37% yield. $R_f = 0.3$ (PE/EA = 100/1). **IR** (neat, cm^{-1}): 2926, 2853, 1731, 1583, 1472, 1444, 1242, 1211, 1187, 1046, 1029, 985, 802, 749, 698. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.49 - 7.37 (m, 6H), 7.36 - 7.22 (m, 4H), 7.05 (d, $J = 11.1$ Hz, 1H), 6.87 - 6.63 (m, 4H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.61, 142.37, 138.22, 136.55, 133.12, 129.15, 128.99, 128.95, 128.89, 127.95, 127.17, 127.11, 125.73, 120.61, 112.47 ppm. **HRMS** (ESI) m/z Calcd for $\text{C}_{19}\text{H}_{16}\text{N}$ $[\text{M}+\text{H}]^+$ 258.1277, found 258.1276.



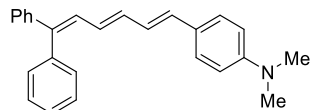
((1E,3E,5Z)-7-methylocta-1,3,5-triene-1,6-diyl)dibenzene (3r): White solid. 23.5 mg, 43% yield. $R_f = 0.6$ (PE). **Melting point:** 46-48 °C. **IR** (neat, cm^{-1}): 3435, 2963, 2928, 1722, 1688, 1599, 1493, 1449, 1286, 1177, 1071, 1026, 978, 759, 701. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.41 - 7.30 (m, 5H), 7.30 - 7.22 (m, 2H), 7.20 - 7.13 (m, 3H), 6.70 (dd, $J = 15.5, 10.6$ Hz, 1H), 6.49 (d, $J = 15.6$ Hz, 1H), 6.45 - 6.33 (m, 1H), 6.26 - 6.16 (m, 2H), 2.69 (hept, $J = 6.9$ Hz, 1H), 1.08 (d, $J = 6.8$ Hz, 6H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 151.19, 141.10, 137.71, 132.18, 131.61, 131.52, 129.76, 129.19, 128.68, 128.12, 127.33, 126.92, 126.33, 124.68, 36.19, 21.96 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{21}\text{H}_{22}$ $[\text{M}]^+$ 274.1722, found 274.1727.



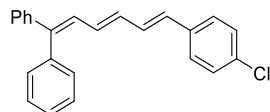
((3E,5E)-6-(p-tolyl)hexa-1,3,5-triene-1,1-diyl)dibenzene (3s): Yellow solid. 63.1 mg, 98% yield. $R_f = 0.5$ (PE). **Melting point:** 100-104 °C. **IR** (neat, cm^{-1}): 2957, 2924, 1725, 1662, 1606, 1494, 1446, 1276, 1182, 1079, 989, 970, 765, 701. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.44 - 7.33 (m, 3H), 7.31 - 7.19 (m, 9H), 7.08 (d, $J = 7.9$ Hz, 2H), 6.81 (d, $J = 11.2$ Hz, 1H), 6.73 (dd, $J = 15.6, 10.4$ Hz, 1H), 6.62 - 6.49 (m, 2H), 6.41 (dd, $J = 14.6, 11.2$ Hz, 1H), 2.31 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 142.71, 142.31, 139.94, 137.58, 134.99, 134.74, 132.78, 131.17, 130.72, 129.48, 128.62, 128.38, 128.35, 127.62, 127.52, 126.42, 21.39 ppm. **HRMS** (EI) m/z Calcd for $\text{C}_{25}\text{H}_{22}$ $[\text{M}]^+$ 322.1722, found 322.1728.



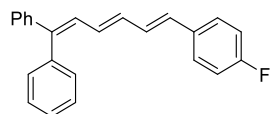
((3E,5E)-6-(4-methoxyphenyl)hexa-1,3,5-triene-1,1-diyl)dibenzene (3t): Yellow solid. 60.8 mg, 90% yield. $R_f = 0.4$ (PE/EA = 100/1). **Melting point:** 127-129 °C. **IR** (neat, cm^{-1}): 3025, 2930, 1608, 1584, 1509, 1443, 1298, 1251, 1174, 1031, 989, 839, 766, 701. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.44 - 7.35 (m, 3H), 7.32 - 7.22 (m, 9H), 6.87 - 6.77 (m, 3H), 6.71 - 6.61 (m, 1H), 6.60 - 6.49 (m, 2H), 6.39 (dd, $J = 14.4$, 11.2 Hz, 1H), 3.79 (s, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 159.35, 142.38, 142.35, 139.99, 135.14, 132.42, 130.73, 130.62, 130.36, 128.47, 128.37, 128.35, 127.74, 127.60, 127.56, 127.50, 127.46, 114.23, 55.41 ppm. **HRMS** (ESI) m/z Calcd for $\text{C}_{25}\text{H}_{23}\text{O}$ $[\text{M}+\text{H}]^+$ 339.1743, found 339.1745.



4-((1E,3E)-6,6-diphenylhexa-1,3,5-trien-1-yl)-N,N-dimethylaniline (3u): Yellow solid. 30.2 mg, 43% yield. $R_f = 0.3$ (PE/EA = 20/1). **Melting point:** 214-216 °C. **IR** (neat, cm^{-1}): 3019, 2920, 1608, 1578, 1522, 1442, 1357, 1189, 1149, 988, 766, 701, 689. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.44 - 7.32 (m, 3H), 7.30 - 7.22 (m, 10H), 6.81 (d, $J = 11.3$ Hz, 1H), 6.68 - 6.47 (m, 4H), 6.35 (dd, $J = 13.9$, 11.3 Hz, 1H), 2.95 (s, 6H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 150.14, 142.51, 141.47, 140.16, 135.81, 133.34, 130.78, 129.30, 128.78, 128.35, 128.32, 127.68, 127.53, 127.38, 127.27, 125.47, 112.49, 40.54 ppm. **HRMS** (ESI) m/z Calcd for $\text{C}_{26}\text{H}_{26}\text{N}$ $[\text{M}+\text{H}]^+$ 352.2060, found 352.2061.

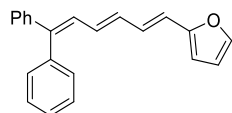


((3E,5E)-6-(4-chlorophenyl)hexa-1,3,5-triene-1,1-diyl)dibenzene (3v): Yellow solid. 46.6 mg, 68% yield. $R_f = 0.4$ (PE). **Melting point:** 130-132 °C. **IR** (neat, cm^{-1}): 3055, 3026, 1600, 1489, 1443, 1404, 1090, 1011, 989, 840, 803, 765, 701, 636, 511. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.45 - 7.36 (m, 3H), 7.32 - 7.21 (m, 11H), 6.85 - 6.79 (m, 1H), 6.79 - 6.70 (m, 1H), 6.61 - 6.39 (m, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 143.51, 142.17, 139.80, 136.03, 134.32, 133.07, 132.28, 131.21, 130.68, 130.14, 128.91, 128.38, 128.12, 127.67, 127.64, 127.57 ppm. (Two carbon signal overlapped) **HRMS** (EI) m/z Calcd for $\text{C}_{24}\text{H}_{19}\text{Cl}$ $[\text{M}]^+$ 342.1175, found 342.1177.

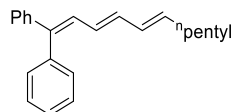


((3E,5E)-6-(4-fluorophenyl)hexa-1,3,5-triene-1,1-diyl)dibenzene (3w): Yellow solid. 49.6 mg, 76% yield. $R_f = 0.4$ (PE). **Melting point:** 120-122 °C. **IR** (neat, cm^{-1}): 3435, 3058, 2925, 1726, 1659, 1600, 1509, 1447, 1277, 1227, 1157, 836, 765, 701. **$^1\text{H NMR}$** (400 MHz, CDCl_3) δ 7.45 - 7.33 (m, 3H), 7.33 - 7.20 (m, 9H), 7.00 - 6.91 (m, 2H), 6.80 (d, $J = 11.0$ Hz, 1H), 6.67 (dd, $J = 15.5$, 10.3 Hz, 1H), 6.60 - 6.38 (m, 3H) ppm. **$^{13}\text{C NMR}$** (100 MHz, CDCl_3) δ 162.36 (d, $J = 247.5$ Hz), 143.20, 142.25, 139.90, 134.51,

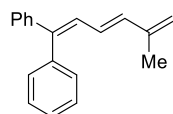
133.76 (d, $J = 3.4$ Hz), 131.75, 131.39, 130.70, 129.35 (d, $J = 2.7$ Hz), 128.39 (d, $J = 2.3$ Hz), 128.21, 127.97, 127.89, 127.66, 127.61, 115.72 (d, $J = 21.6$ Hz) ppm. ^{19}F NMR (376 MHz, CDCl_3) δ -114.11 ppm. HRMS (EI) m/z Calcd for $\text{C}_{24}\text{H}_{19}\text{F}$ $[\text{M}]^+$ 326.1471, found 326.1470.



2-((1E,3E)-6,6-diphenylhexa-1,3,5-trien-1-yl)furan (3x): Yellow oil. 13.1 mg, 22% yield. $R_f = 0.4$ (PE). IR (neat, cm^{-1}): 3055, 3026, 2923, 2851, 1590, 1493, 1444, 1259, 1151, 1074, 1013, 988, 926, 883, 765, 733, 700, 592. ^1H NMR (400 MHz, CDCl_3) δ 7.42 - 7.33 (m, 3H), 7.32 - 7.18 (m, 8H), 6.79 (d, $J = 10.3$ Hz, 1H), 6.67 (dd, $J = 15.4, 10.1$ Hz, 1H), 6.54 - 6.30 (m, 4H), 6.23 (d, $J = 3.3$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 153.55, 143.03, 142.34, 142.28, 139.85, 134.27, 131.85, 130.69, 128.35, 128.27, 128.23, 127.65, 127.57, 127.55, 119.99, 111.89, 108.65 ppm. HRMS (ESI) m/z Calcd for $\text{C}_{22}\text{H}_{19}\text{O}$ $[\text{M}+\text{H}]^+$ 299.1430, found 299.1431.

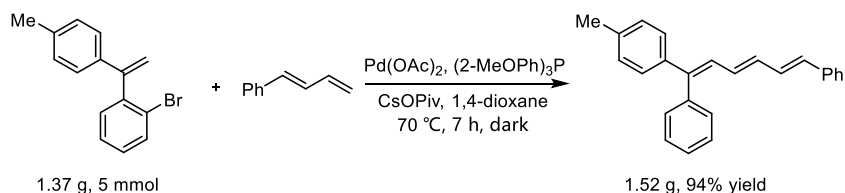


((3E,5E)-undeca-1,3,5-triene-1,1-diyl)dibenzene (3y): Colorless oil. 25.4 mg, 55% yield. $R_f = 0.6$ (PE). IR (neat, cm^{-1}): 3432, 3057, 2928, 2858, 1724, 1663, 1598, 1493, 1447, 1277, 1028, 764, 700. ^1H NMR (400 MHz, Chloroform- d) δ 7.42 - 7.32 (m, 3H), 7.31 - 7.19 (m, 7H), 6.73 (d, $J = 11.2$ Hz, 1H), 6.39 (dd, $J = 14.9, 10.5$ Hz, 1H), 6.21 (dd, $J = 14.9, 11.1$ Hz, 1H), 6.07 - 5.95 (m, 1H), 5.83 - 5.67 (m, 1H), 2.07 (dt, $J = 7.1$ Hz, 7.1 Hz, 2H), 1.46 - 1.20 (m, 6H), 0.94 - 0.80 (m, 3H) ppm. ^{13}C NMR (100 MHz, cdCl_3) δ 142.47, 141.83, 140.06, 136.28, 135.08, 130.87, 130.79, 130.68, 128.80, 128.48, 128.30, 127.53, 127.37, 127.31, 32.98, 31.54, 29.07, 22.66, 14.17 ppm. HRMS (EI) m/z Calcd for $\text{C}_{23}\text{H}_{26}$ $[\text{M}]^+$ 302.2029, found 302.2026.



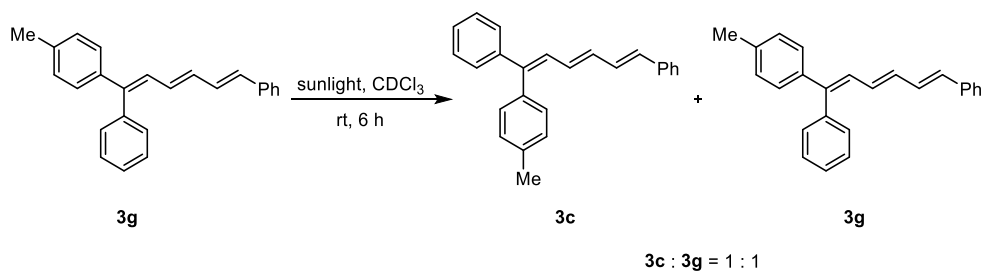
(E)-(5-methylhexa-1,3,5-triene-1,1-diyl)dibenzene (3z): Colorless oil. 15.3 mg, 31% yield. $R_f = 0.6$ (PE). IR (neat, cm^{-1}): 3432, 3058, 2926, 2854, 1720, 1661, 1598, 1493, 1447, 1277, 1177, 1074, 1031, 764, 701. ^1H NMR (400 MHz, CDCl_3) δ 7.42 - 7.31 (m, 3H), 7.29 - 7.23 (m, 7H), 6.76 (d, $J = 10.9$ Hz, 1H), 6.51 (d, $J = 15.3$ Hz, 1H), 6.34 (dd, $J = 15.3, 11.0$ Hz, 1H), 5.02 (s, 1H), 4.98 (s, 1H), 1.74 (s, 3H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 143.06, 142.60, 142.54, 139.96, 137.19, 130.65, 128.44, 128.34, 128.31, 127.72, 127.55, 127.51, 127.49, 117.20, 18.64 ppm. HRMS (EI) m/z Calcd for $\text{C}_{19}\text{H}_{18}$ $[\text{M}]^+$ 246.1409, found 246.1405.

4. The Gram-Scale Reaction

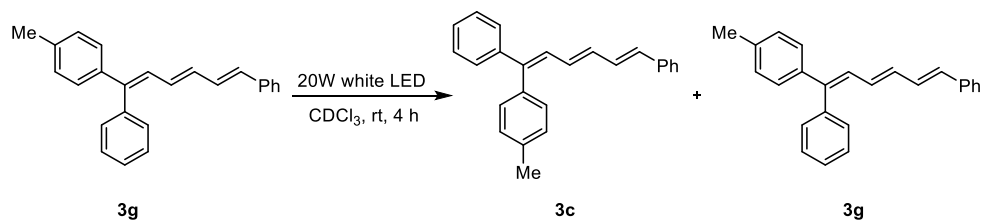


In a 200 mL sealed tube, a mixture of *ortho*-vinyl bromobenzene **1g** (5.0 mmol, 1.0 equiv), diene **2a** (10 mmol, 2.0 equiv), Pd(OAc)₂ (56 mg, 0.25 mmol, 5.0 mol %), (2-MeOPh)₃P (18 mg, 0.50 mmol, 10 mol %) and CsOPiv (2.3 g, 2.0 equiv) in 1,4-dioxane (50 mL) was stirred at 70 °C under Ar in dark for 7 hours. After cooling to room temperature, the mixture was filtered through a celite pad and concentrated under vacuum. The residue was purified by flash chromatography on silica gel (elute: hexane / DCM = 100:1) to afford product **3g** 1.52 g (94% yield).

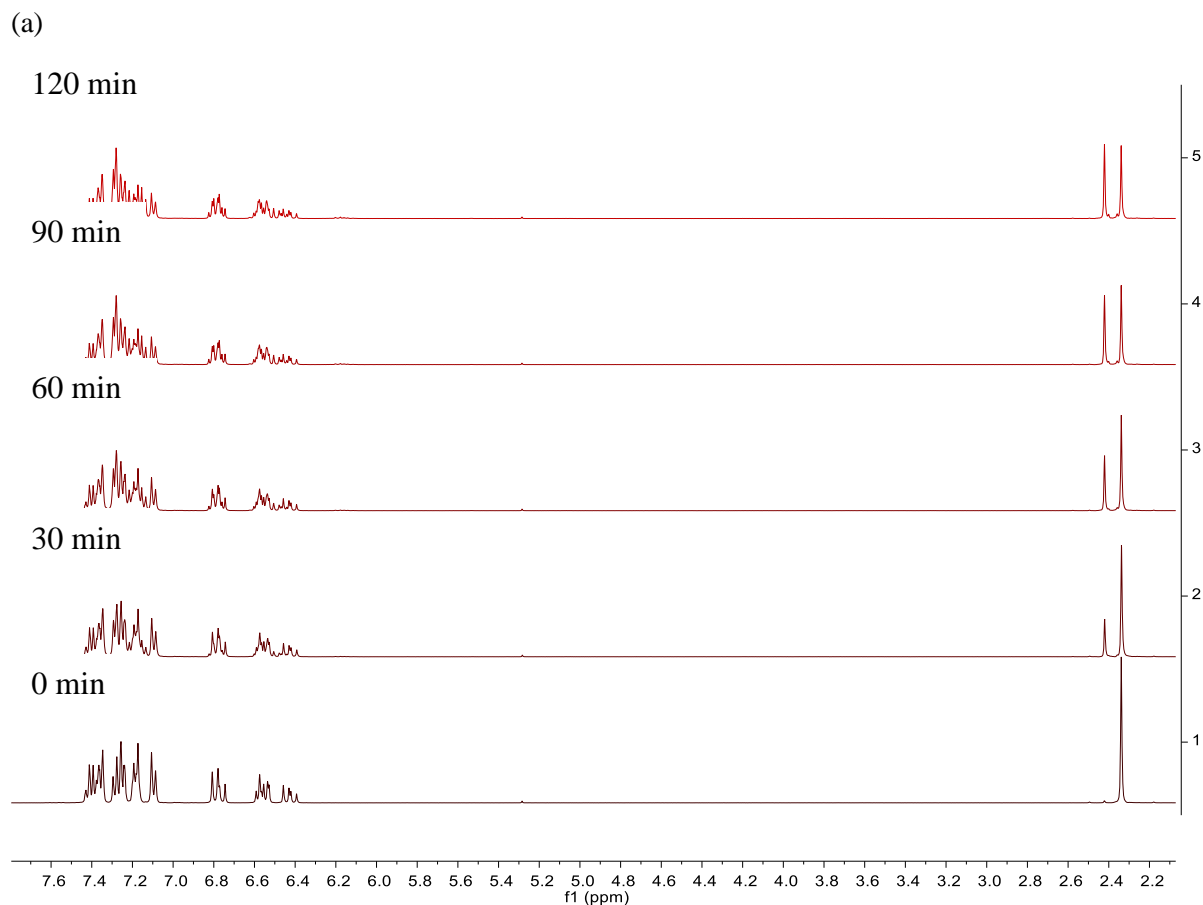
5. Light-Induced *E/Z* Isomerization of **3g**



3g (10 mg, 0.031 mmol) in CDCl₃ (0.5 mL) was exposed to sunlight under Ar for 6 h. The transformation was detected by ¹H NMR.

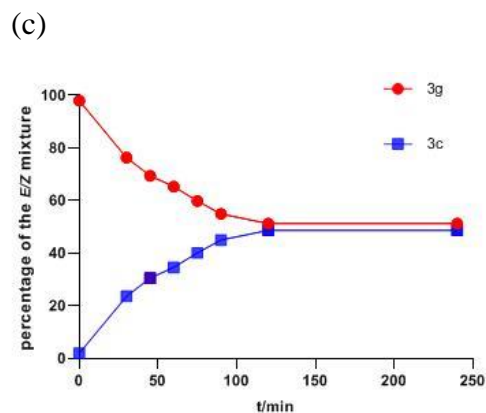


3g (10 mg, 0.031 mmol) in CDCl₃ (0.5 mL) was exposed to 20 W white LED under Ar for 4 h. The ratio of **3c** and **3g** was detected by ¹H NMR at a regular time.



(b)

entry	time/min	3g : 3c
1	0	1:0.02
2	30	1:0.31
3	45	1:0.44
4	60	1:0.53
5	75	1:0.67
6	90	1:0.82
7	120	1:0.95
8	240	1:0.95



(a) detection of the isomerization by ^1H NMR; (b) the ratio of **3g** and **3c** at regular time; (c) kinetic curve of the isomerization.

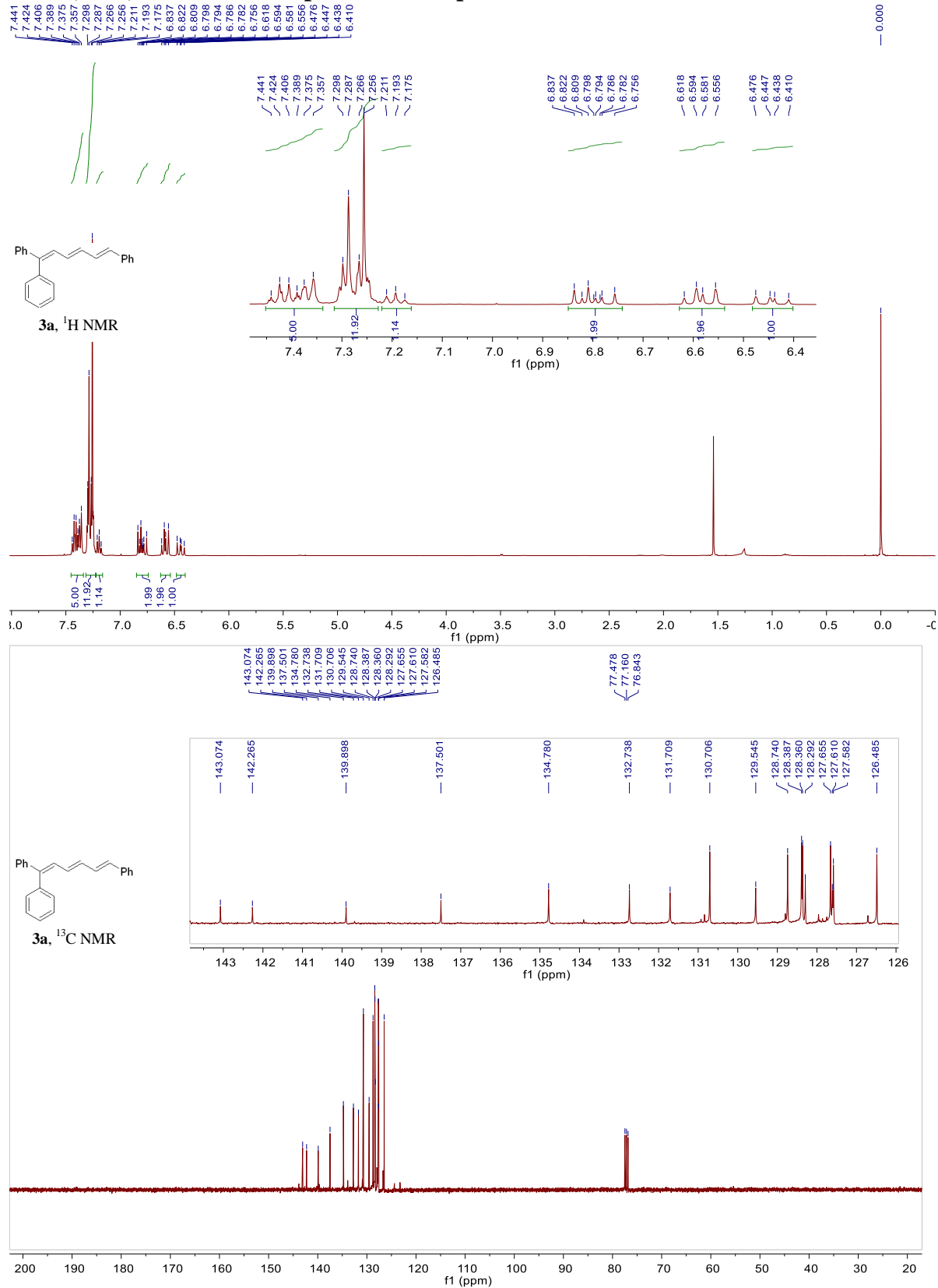
6. References:

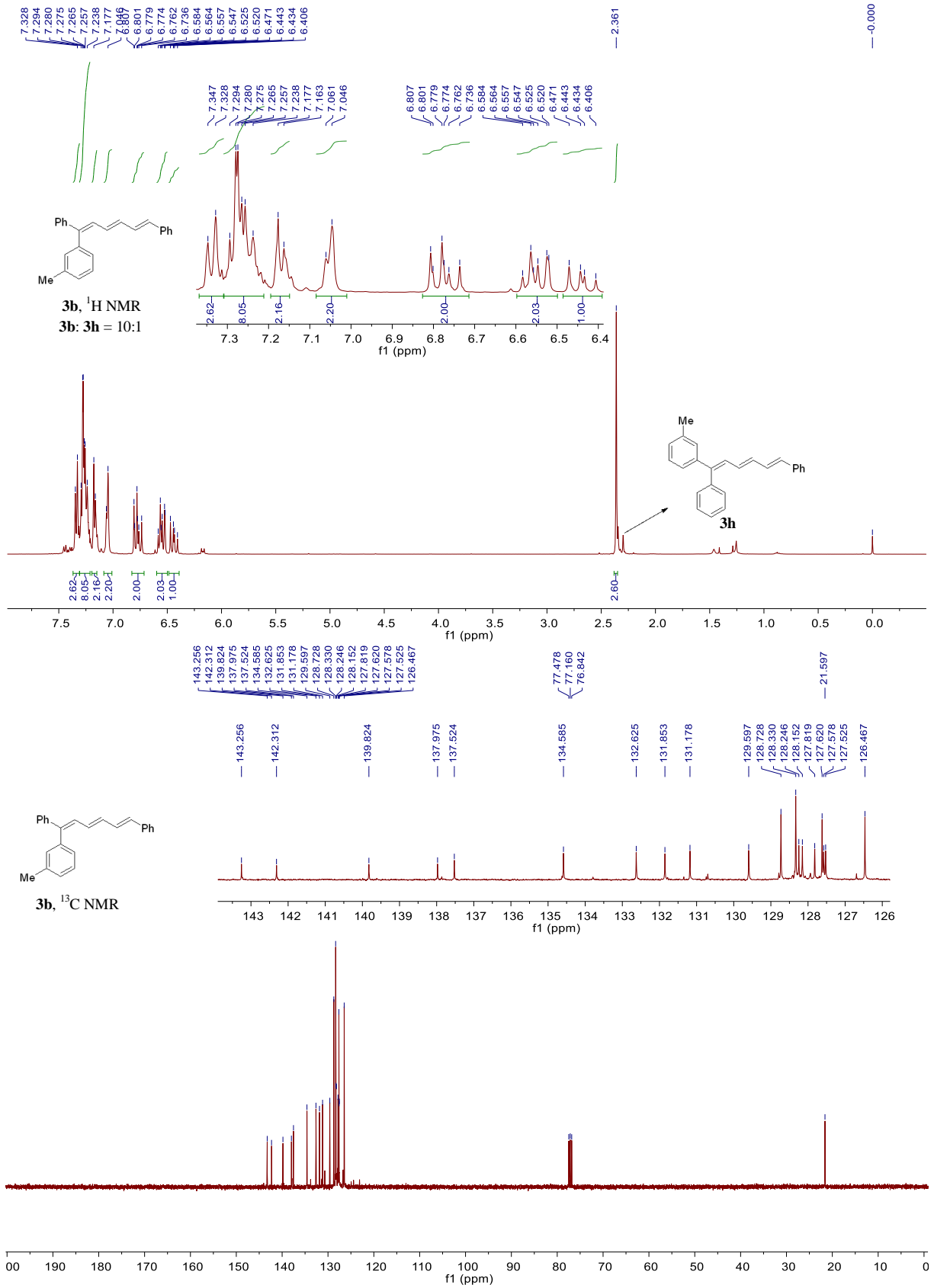
- (1) (a) D. Wei, M.-Y. Li, B.-B. Zhu, X.-D. Yang, F. Zhang, C.-G. Feng and G.-Q. Lin, *Angew. Chem. Int. Ed.*, 2019, **58**, 16543. (b) D. Wei, T.-J. Hu, C.-G. Feng and G.-Q. Lin, *Chin. J. Chem.*, 2018, **36**, 743. (c) R. Hayashi, A. Shimizu, J. A. Davies, Y. Ishizaki, C. Willis and J.-i. Yoshida, *Angew. Chem. Int. Ed.*, 2018, **57**, 12891. (d) T.-J. Hu, M.-Y. Li, Q. Zhao, C.-G. Feng and G.-Q. Lin, *Angew. Chem. Int. Ed.*, 2018, **57**, 5871. (e) X. Shen, P. Liu, Y. Liu and B. Dai, *Tetrahedron*, 2017, **73**, 6558. (f) R. Rossi, A.

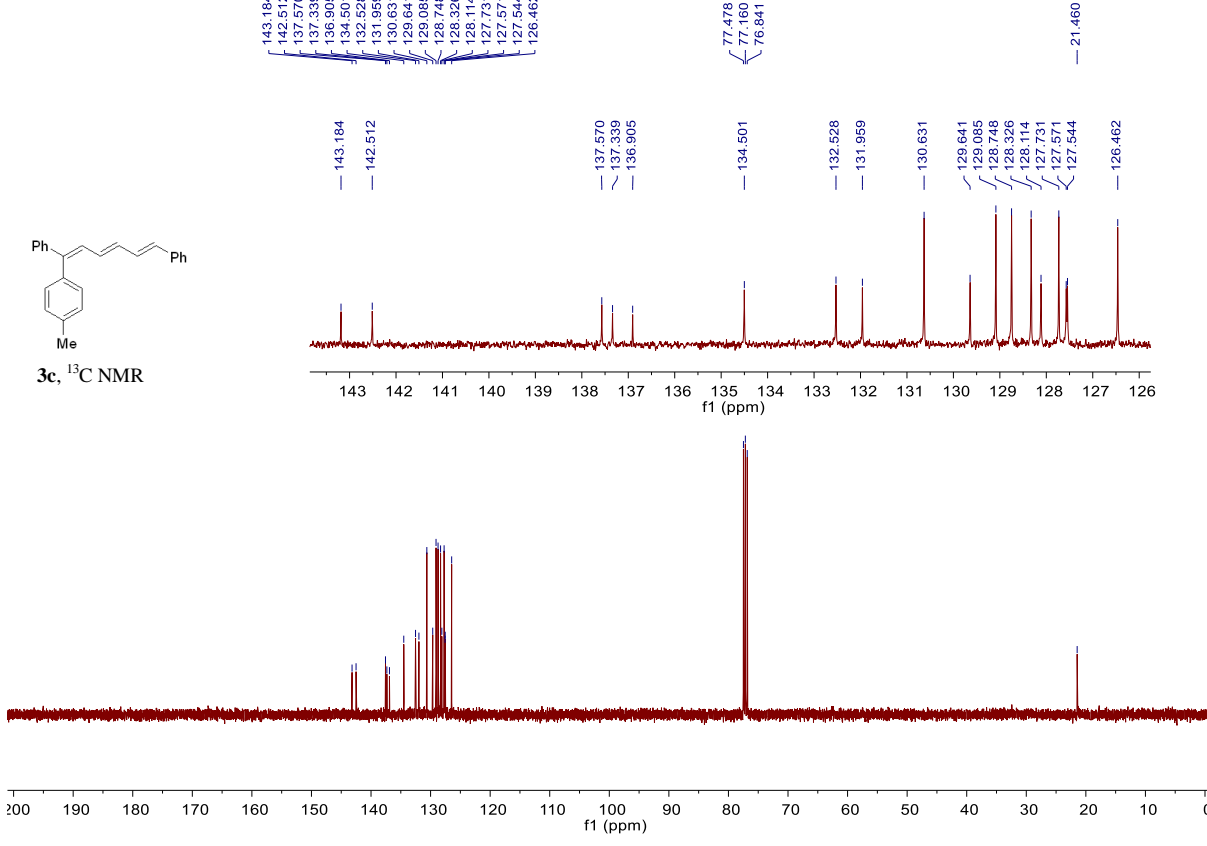
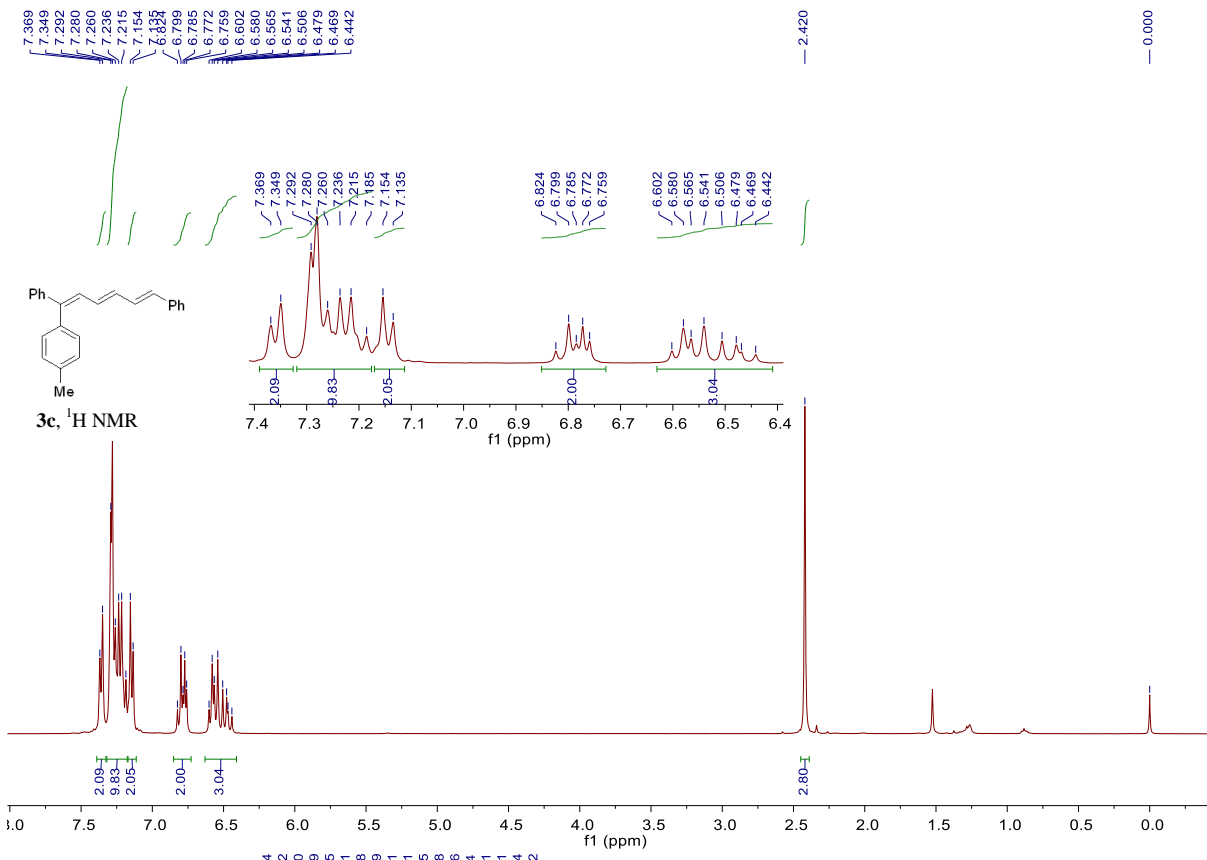
Carpita, A. Ribecai and L. Mannina, *Tetrahedron*, 2001, **57**, 2847. (g) M.-Y. Li, P.-B. Han, T.-J. Hu, D. Wei, G. Zhang, A.-J. Qin, C.-G. Feng, B. Tang and G.-Q. Lin, *iscience*, 2020, **23**, 100966.

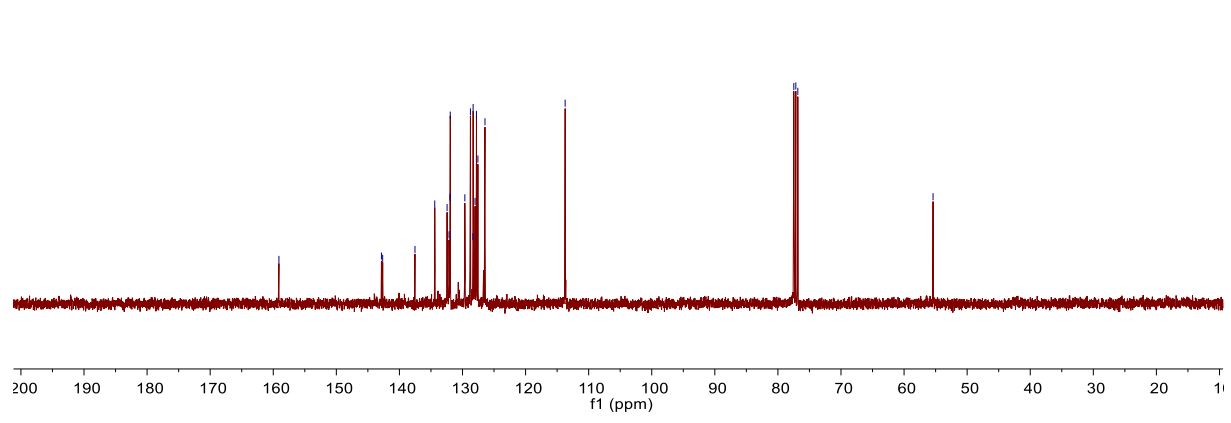
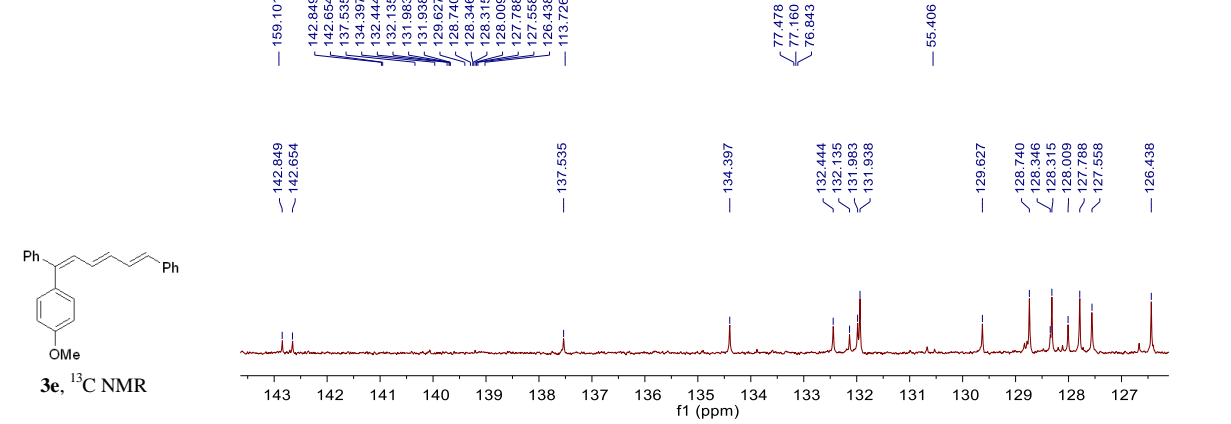
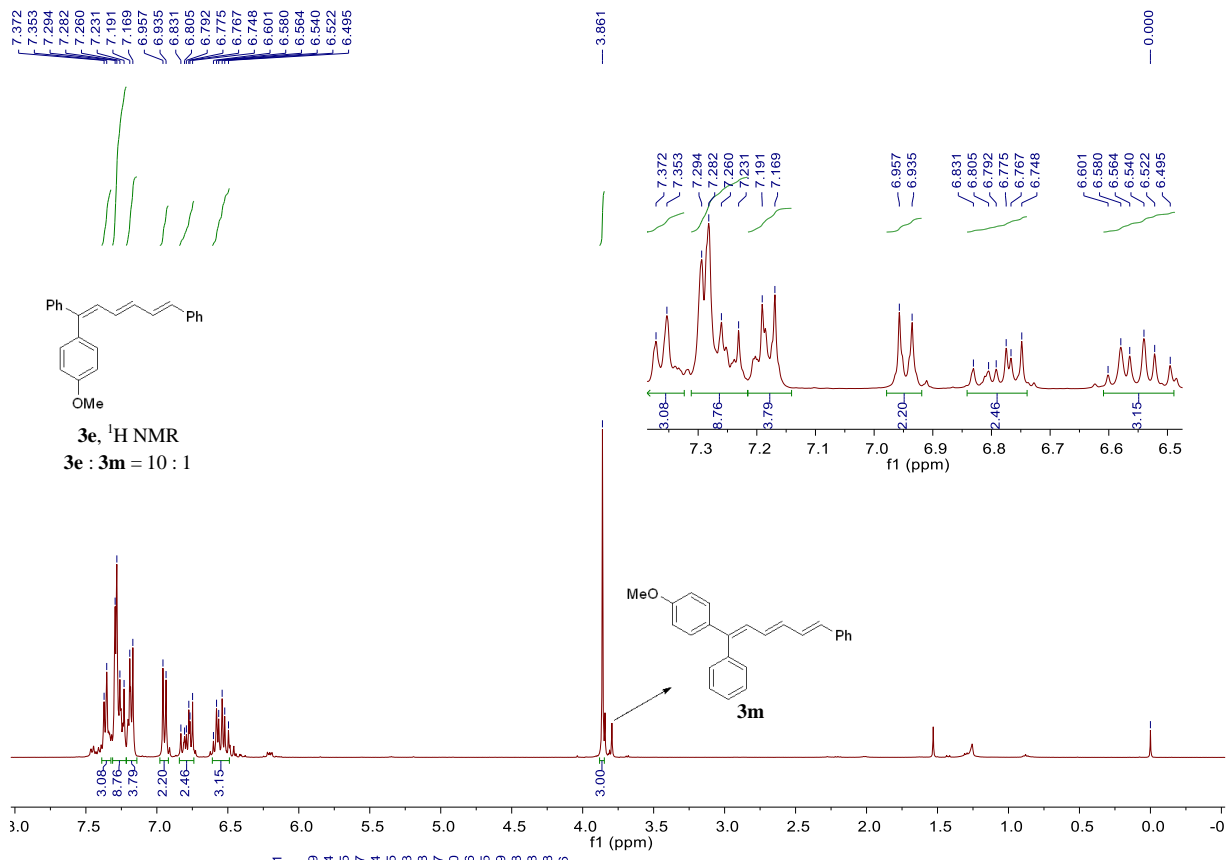
(2) (a) N. Yasukawa, H. Yokoyama, M. Masuda, Y. Monguchi, H. Sajiki and Y. Sawama, *Green Chem.*, 2018, **20**, 1213. (b) R.J. Maza, E. Davenport, N. Miralles, J.J. Carbo and E. Fernandez *Org. Lett.*, 2019, **21**, 2251. (c) B.T. Sargent and E.J. Alexanian *J. Am. Chem. Soc.*, 2017, **139**, 12438.

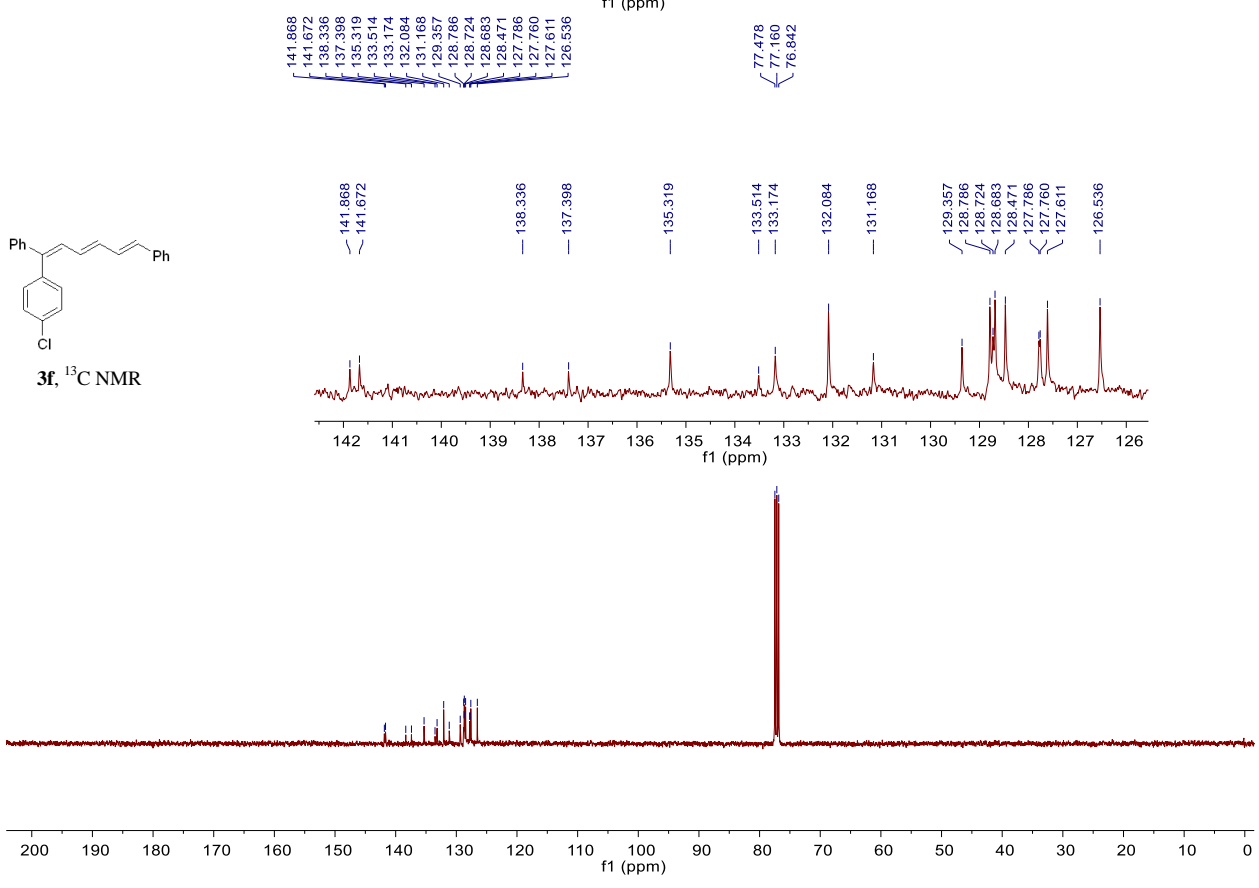
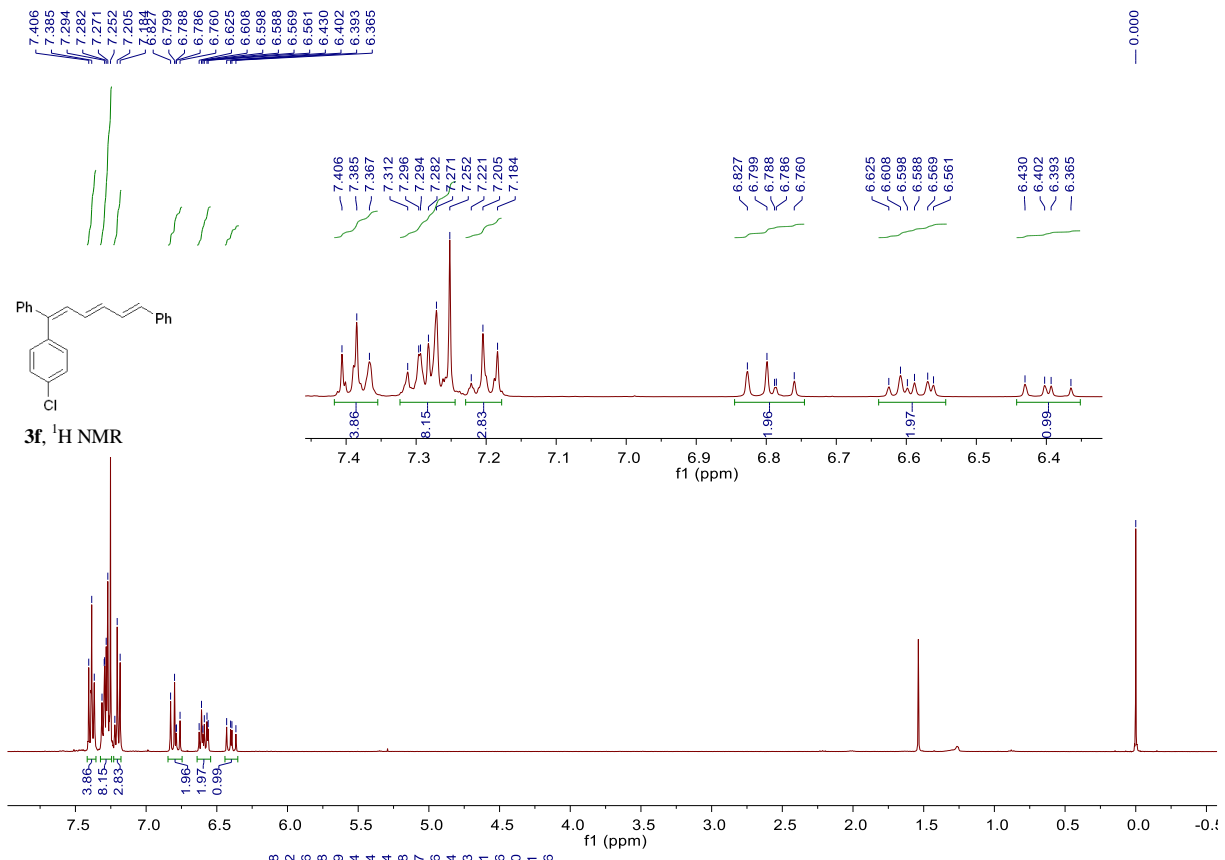
7. ^1H , ^{13}C , and ^{19}F NMR Spectra of Compounds

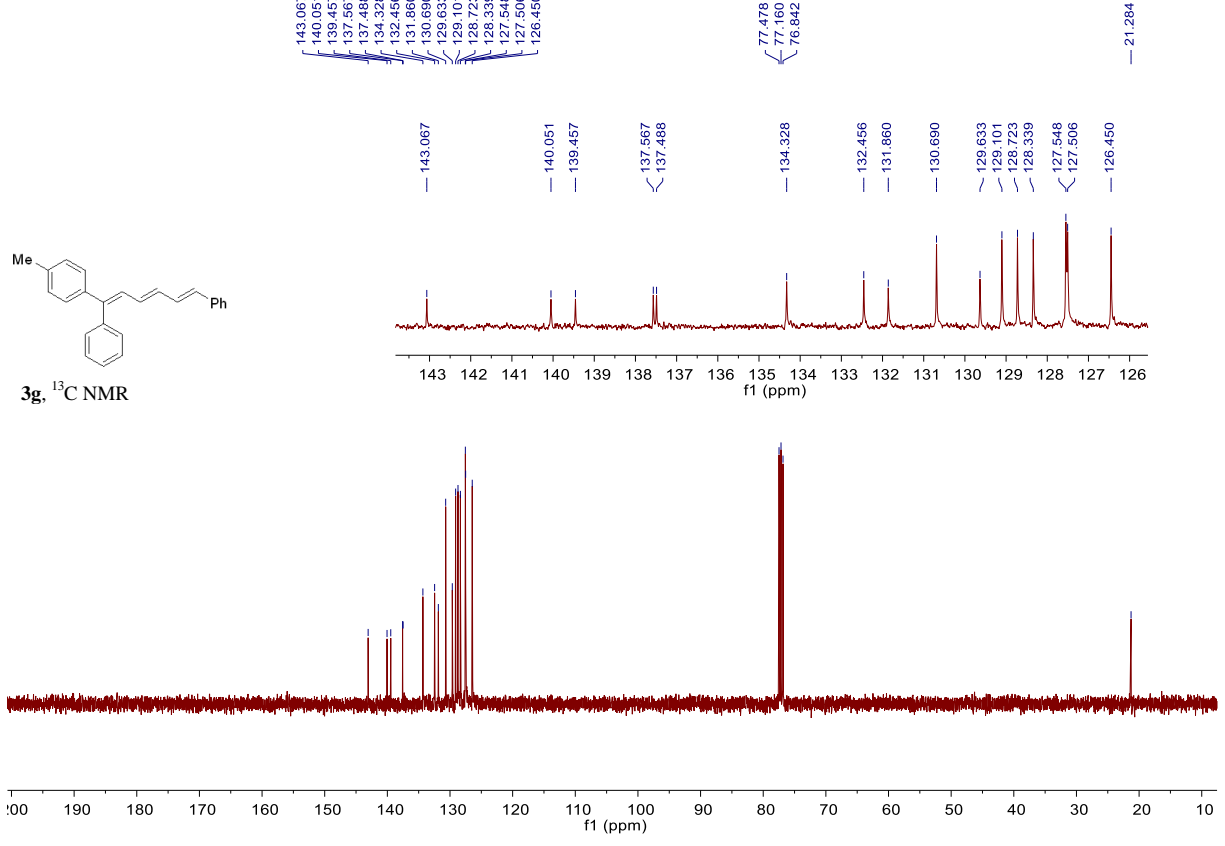
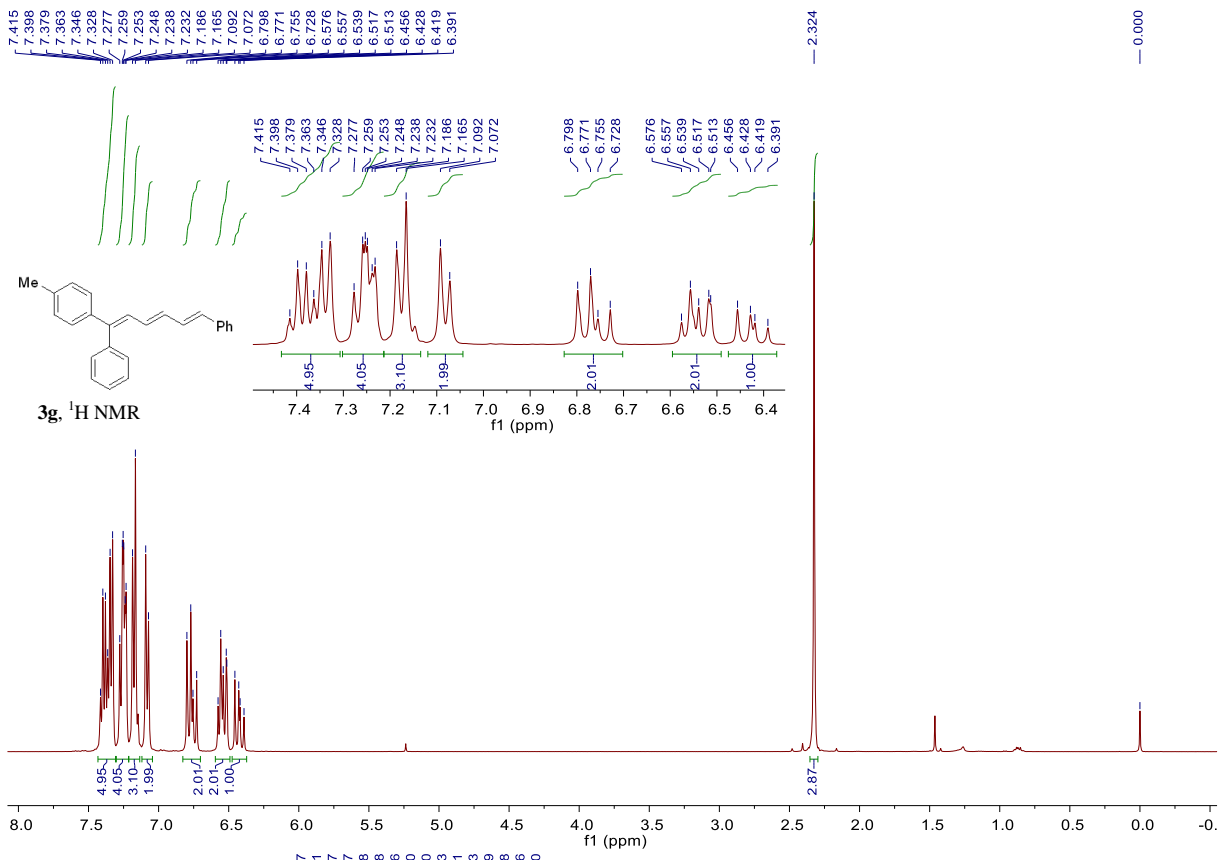


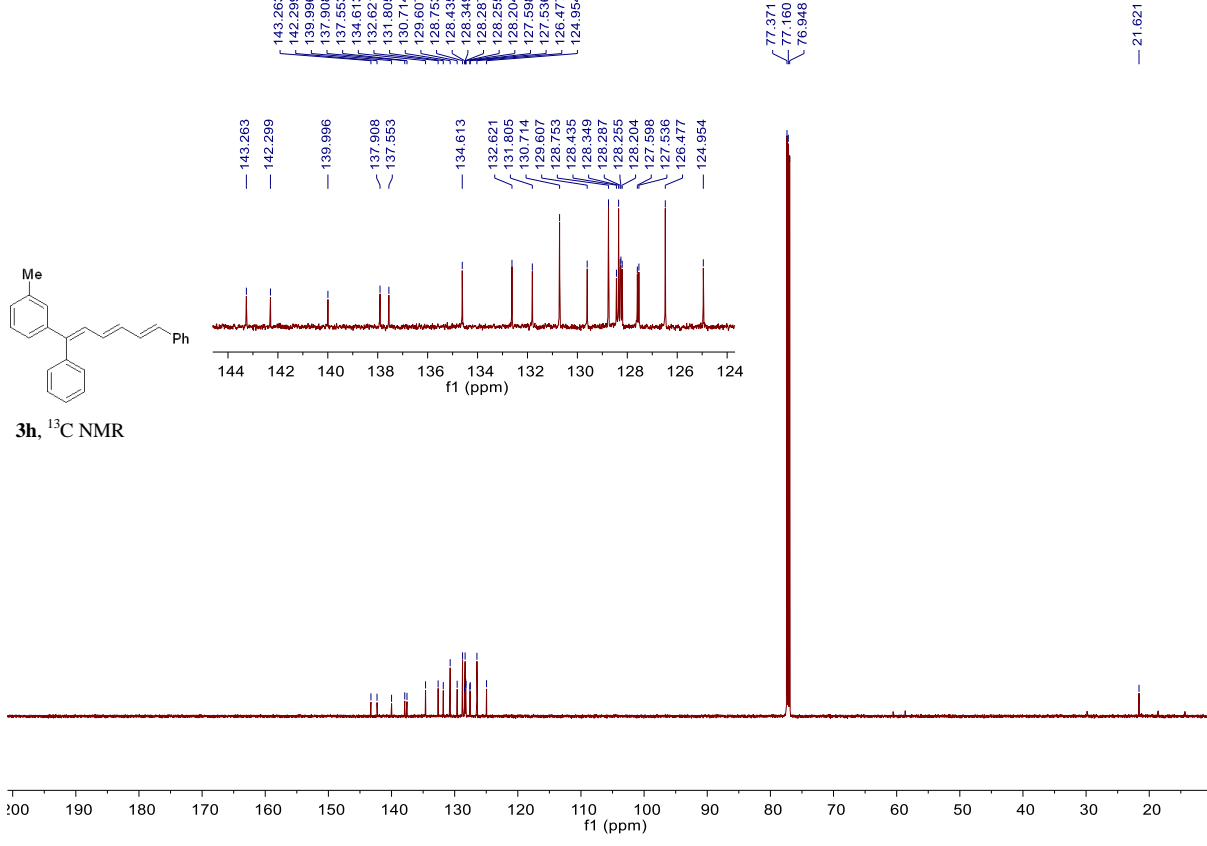
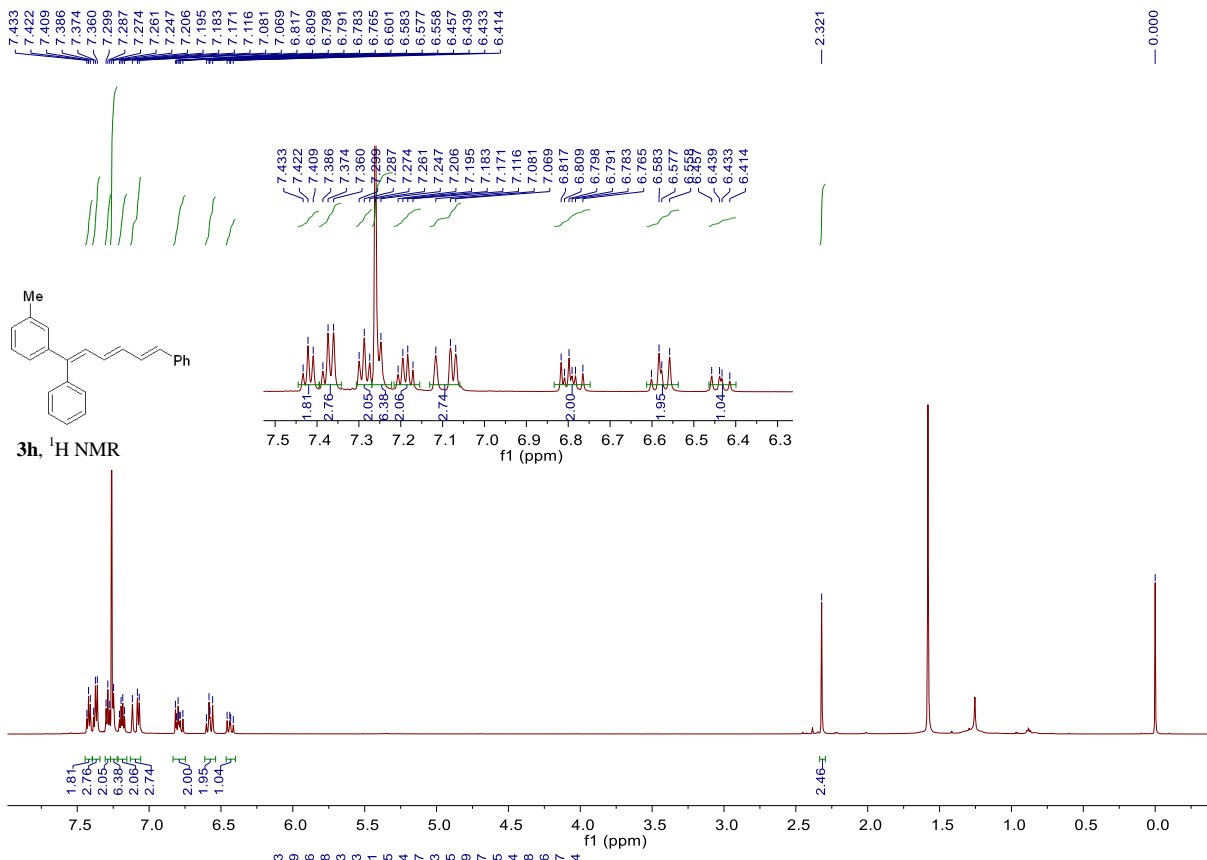


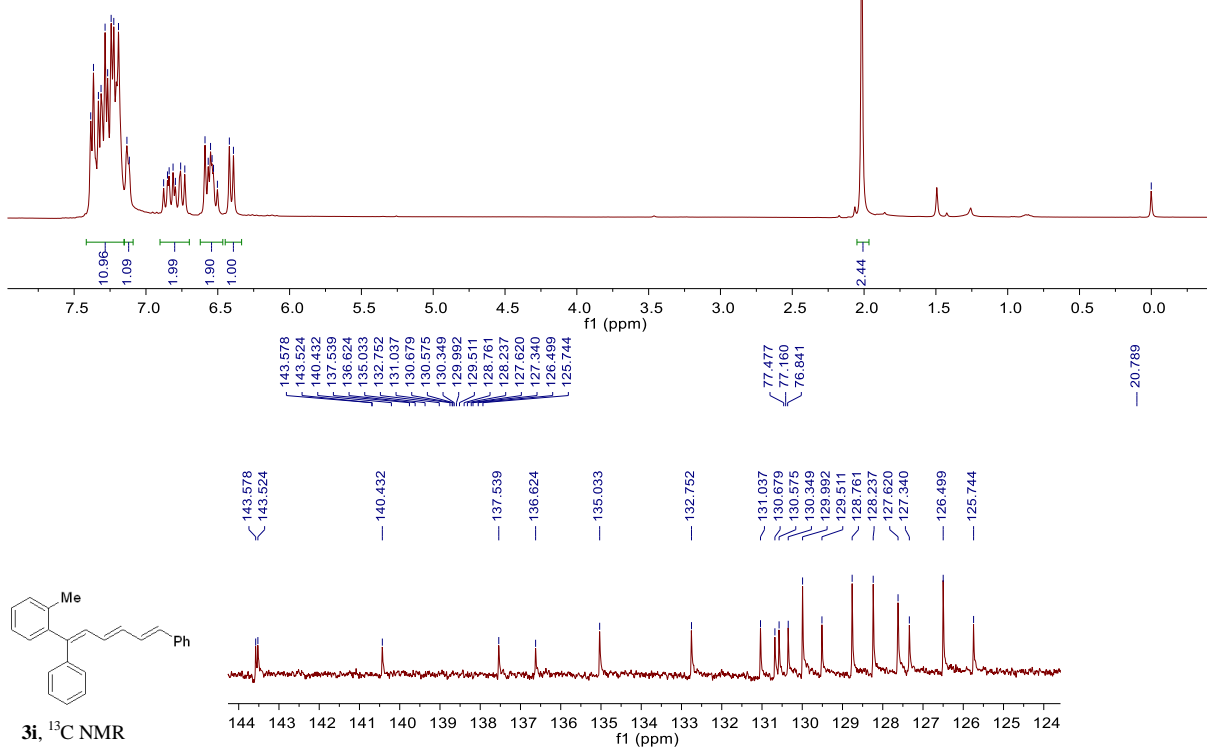
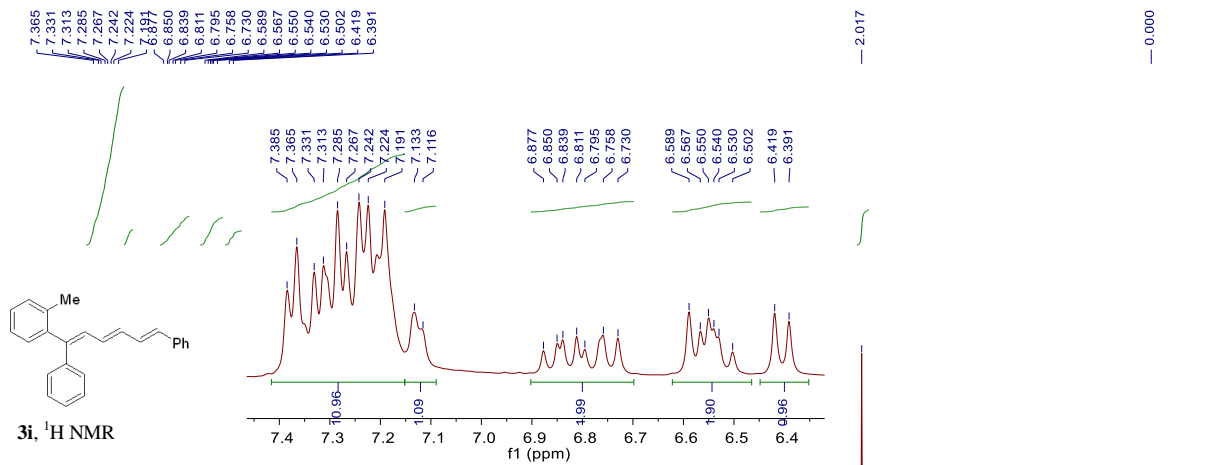


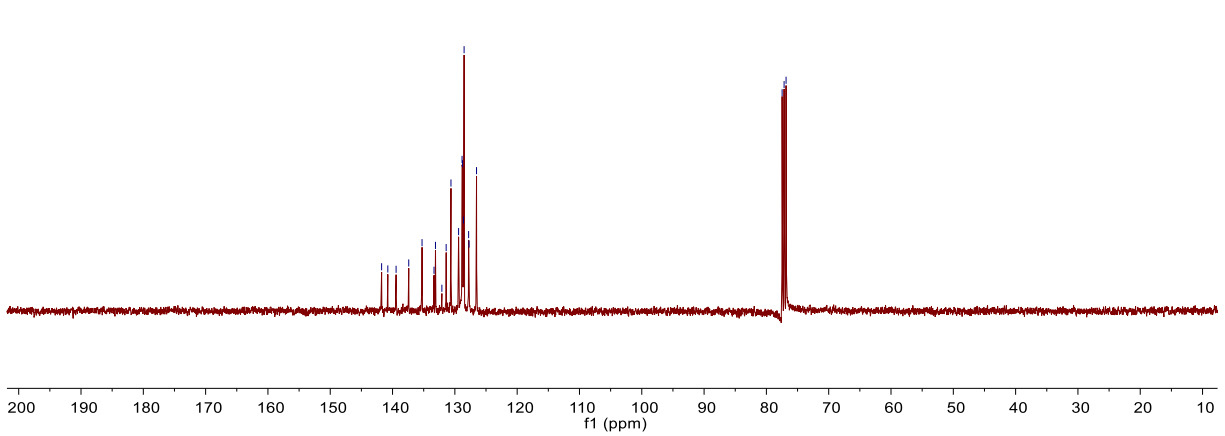
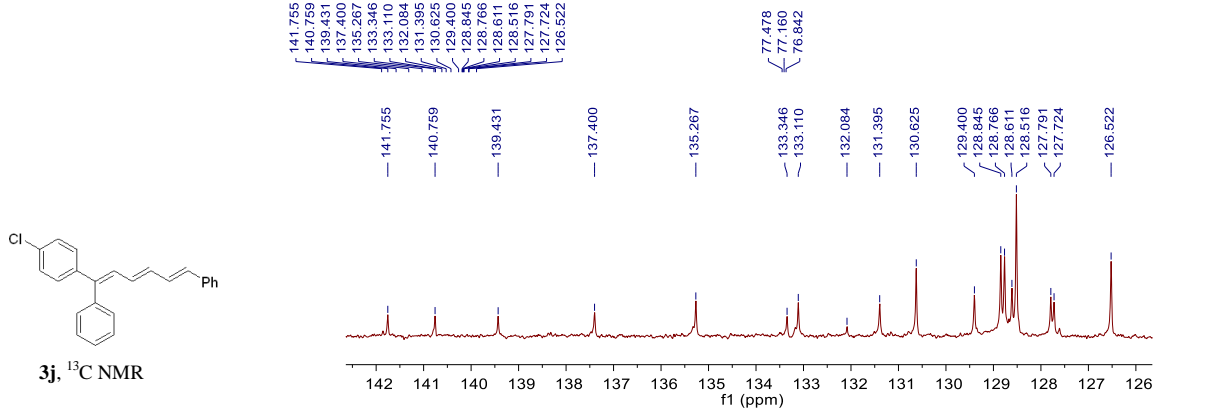
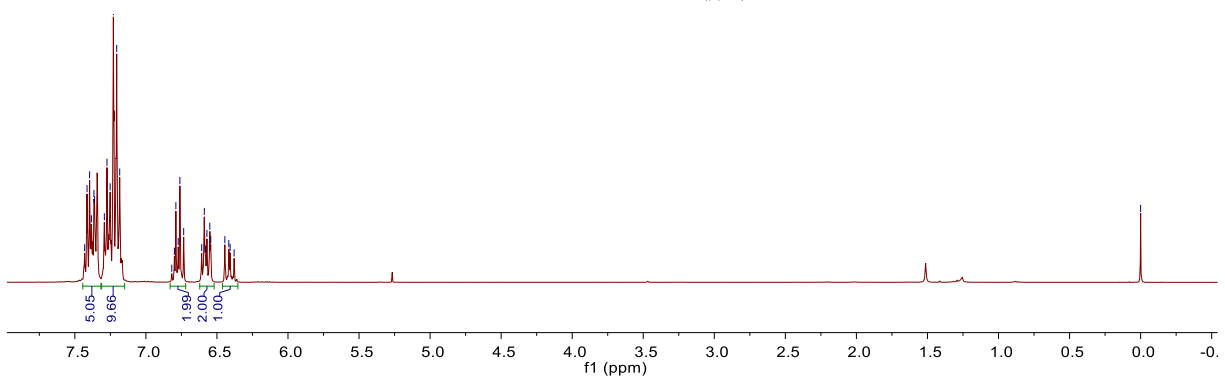
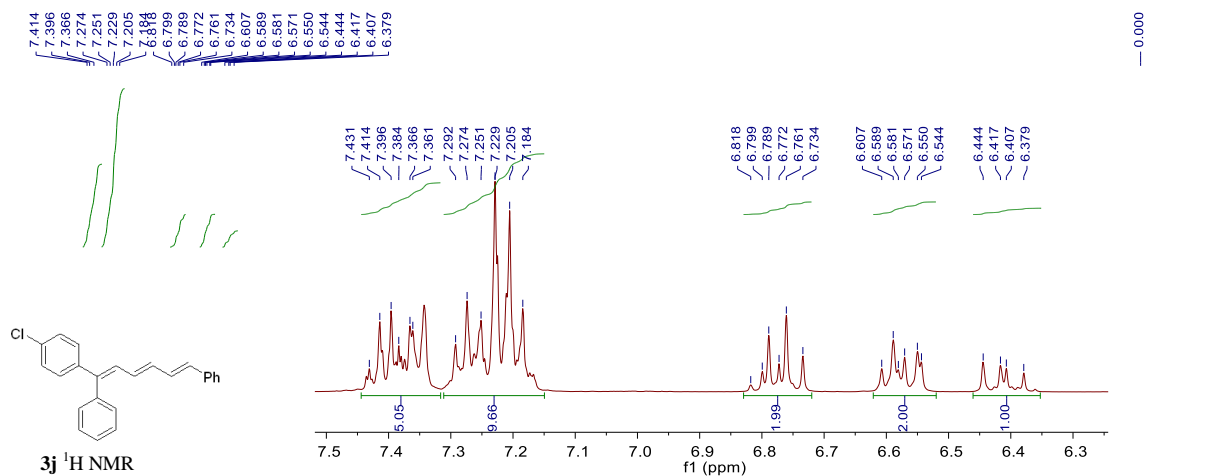


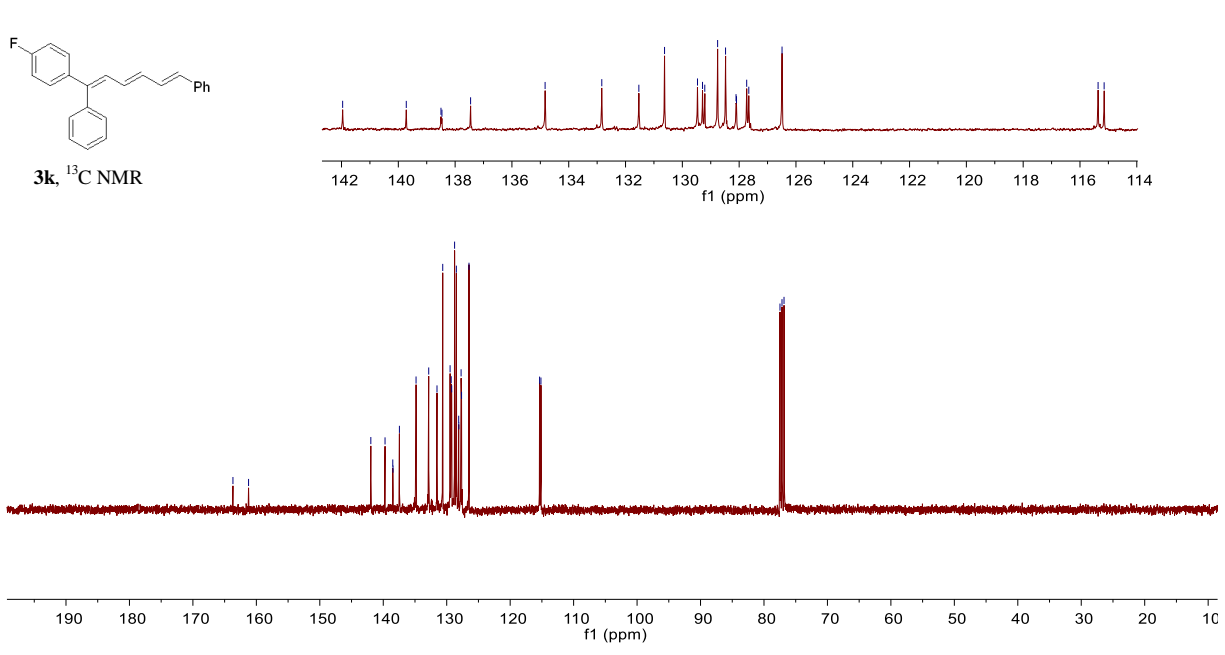
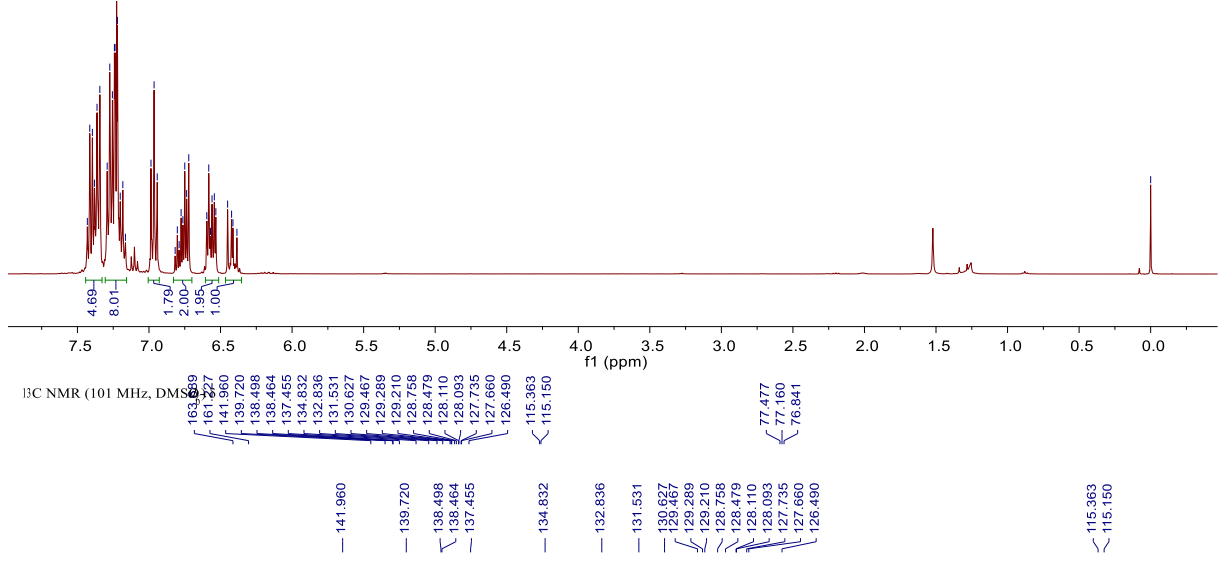
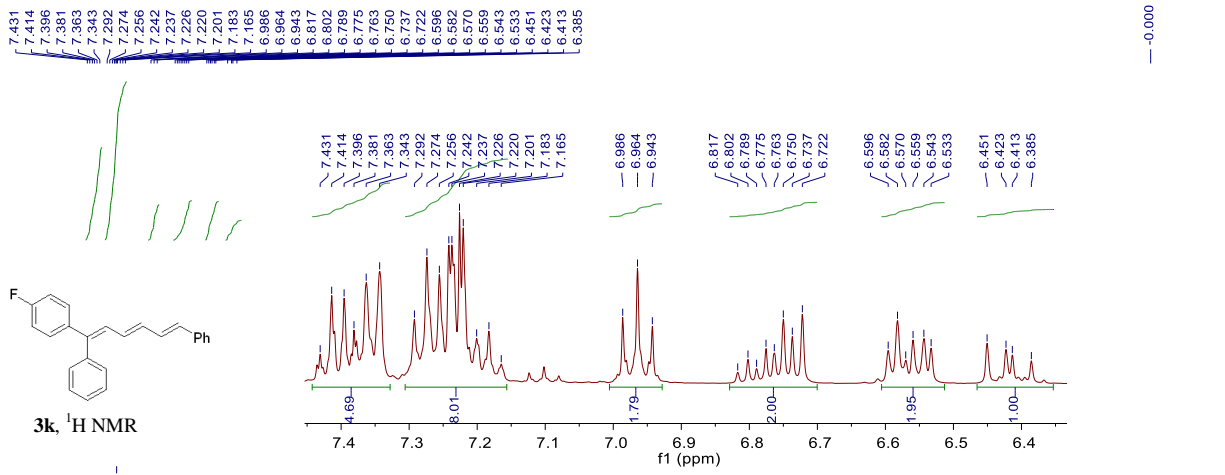


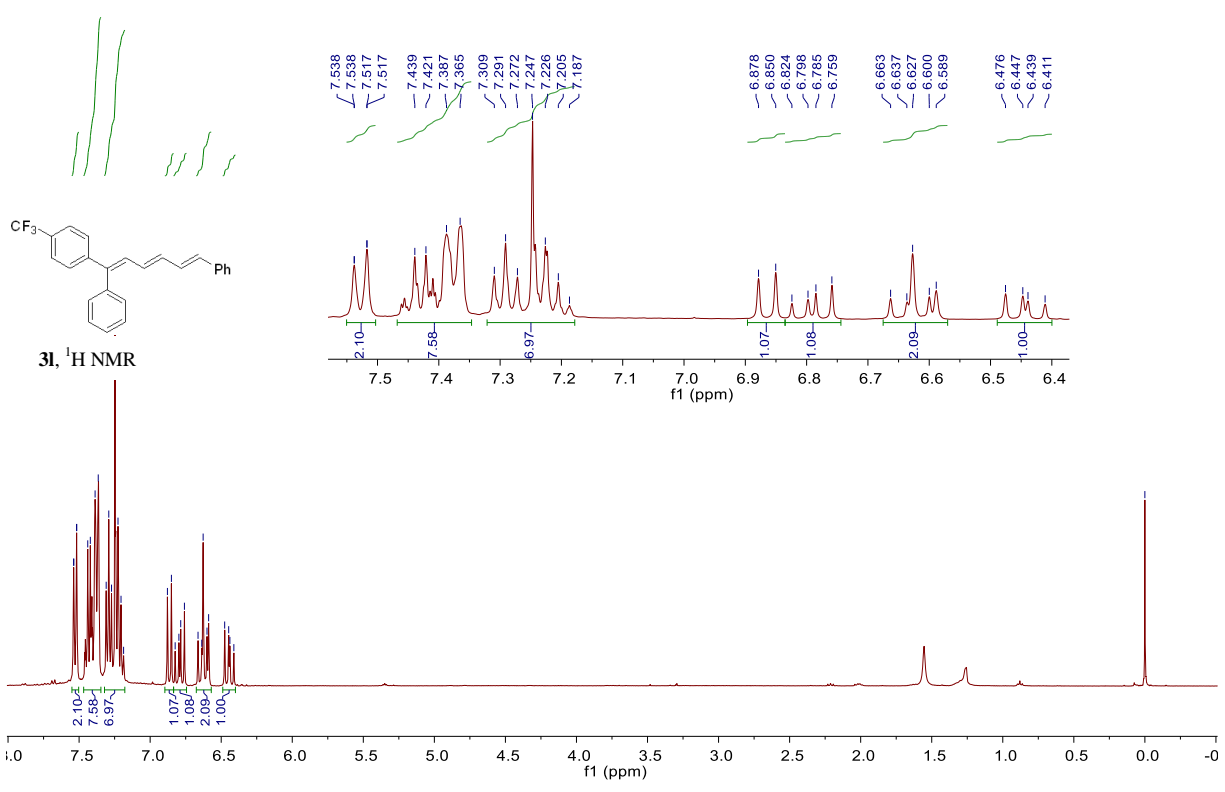
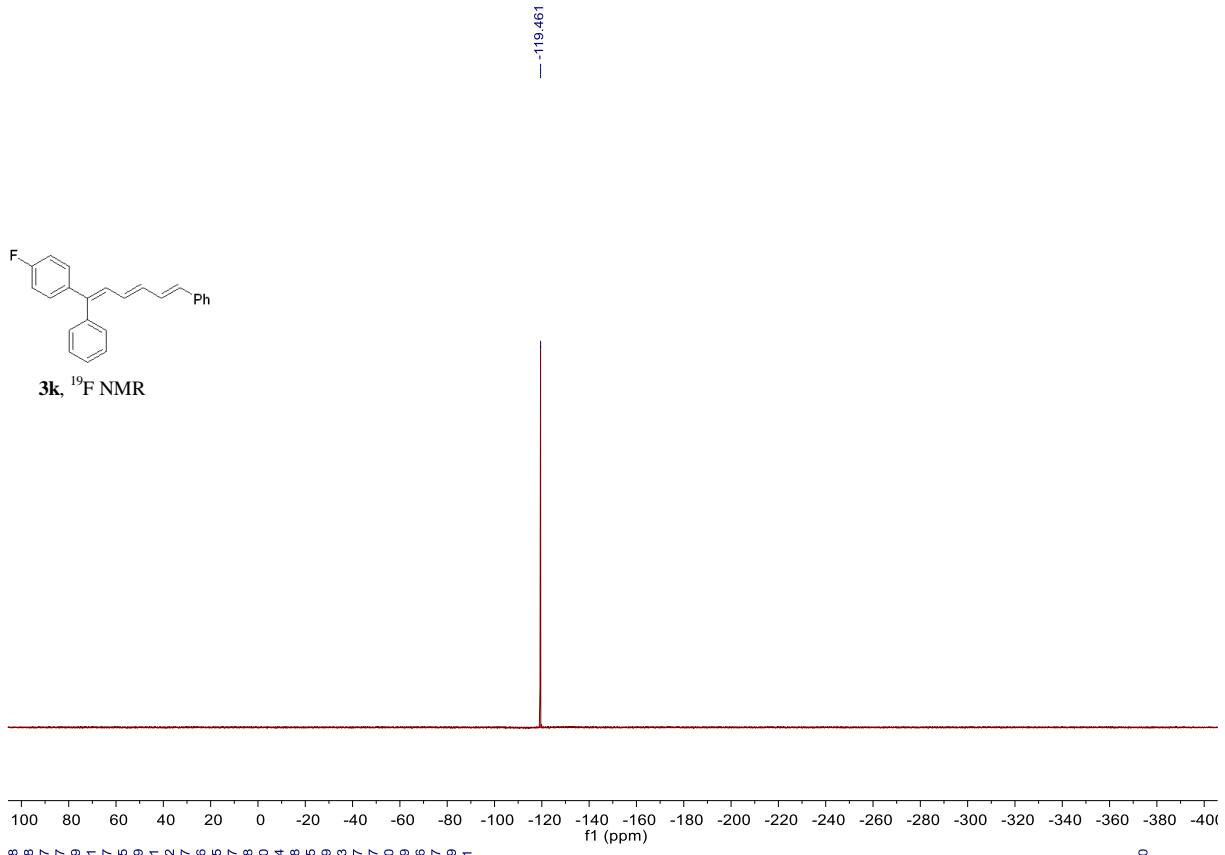


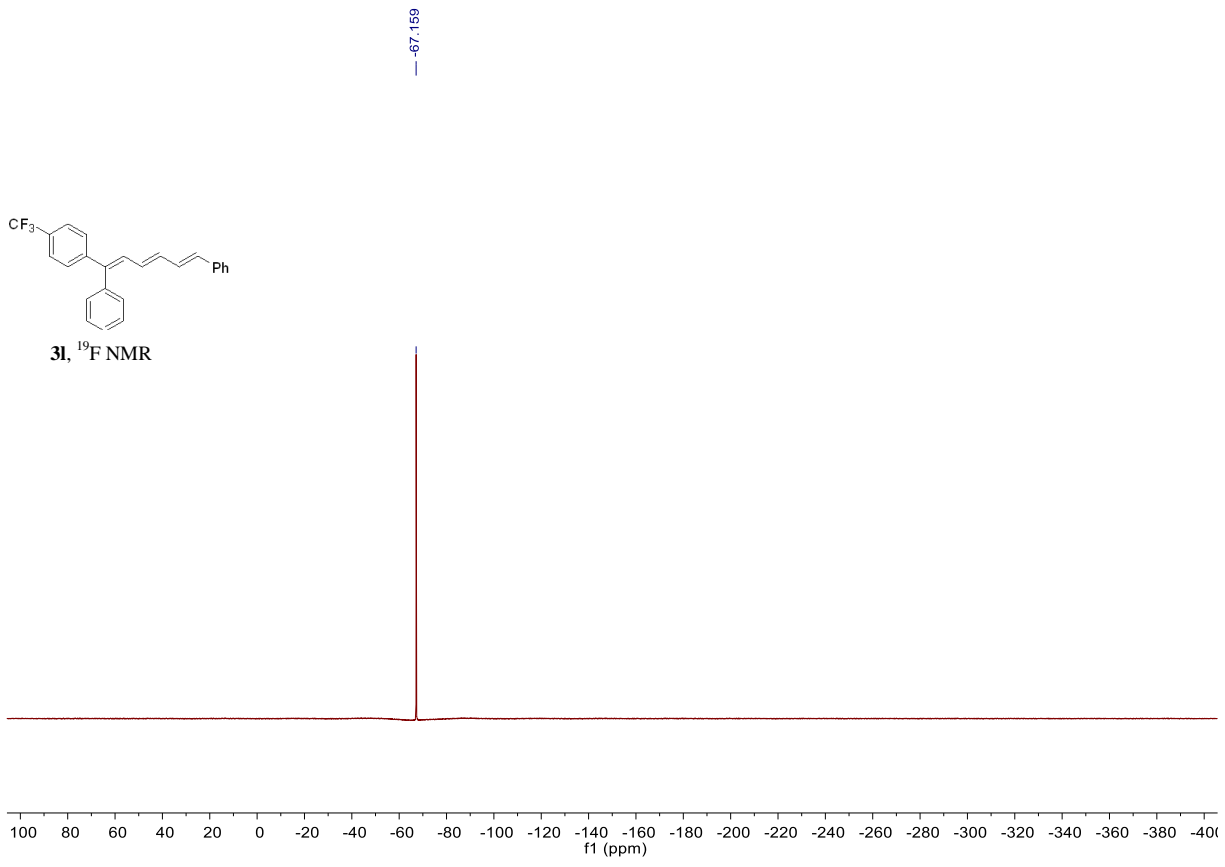
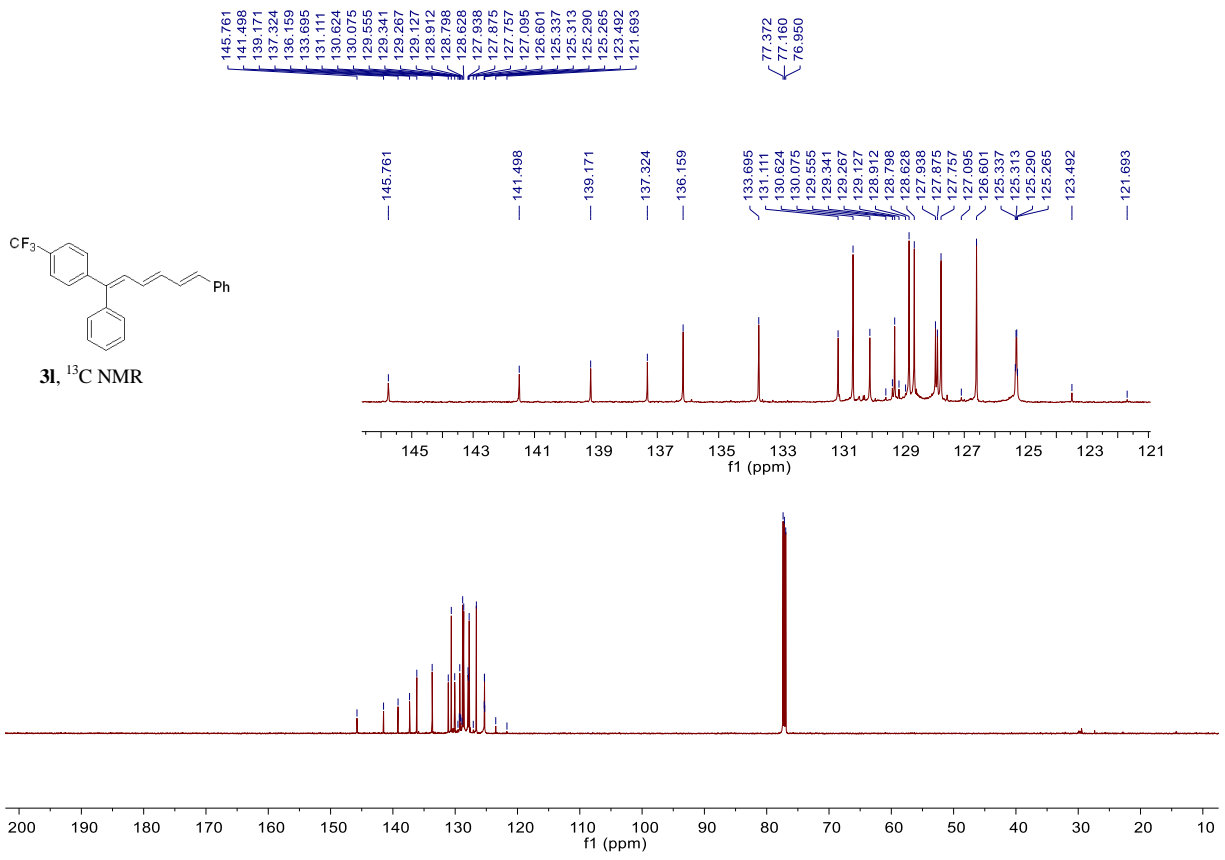


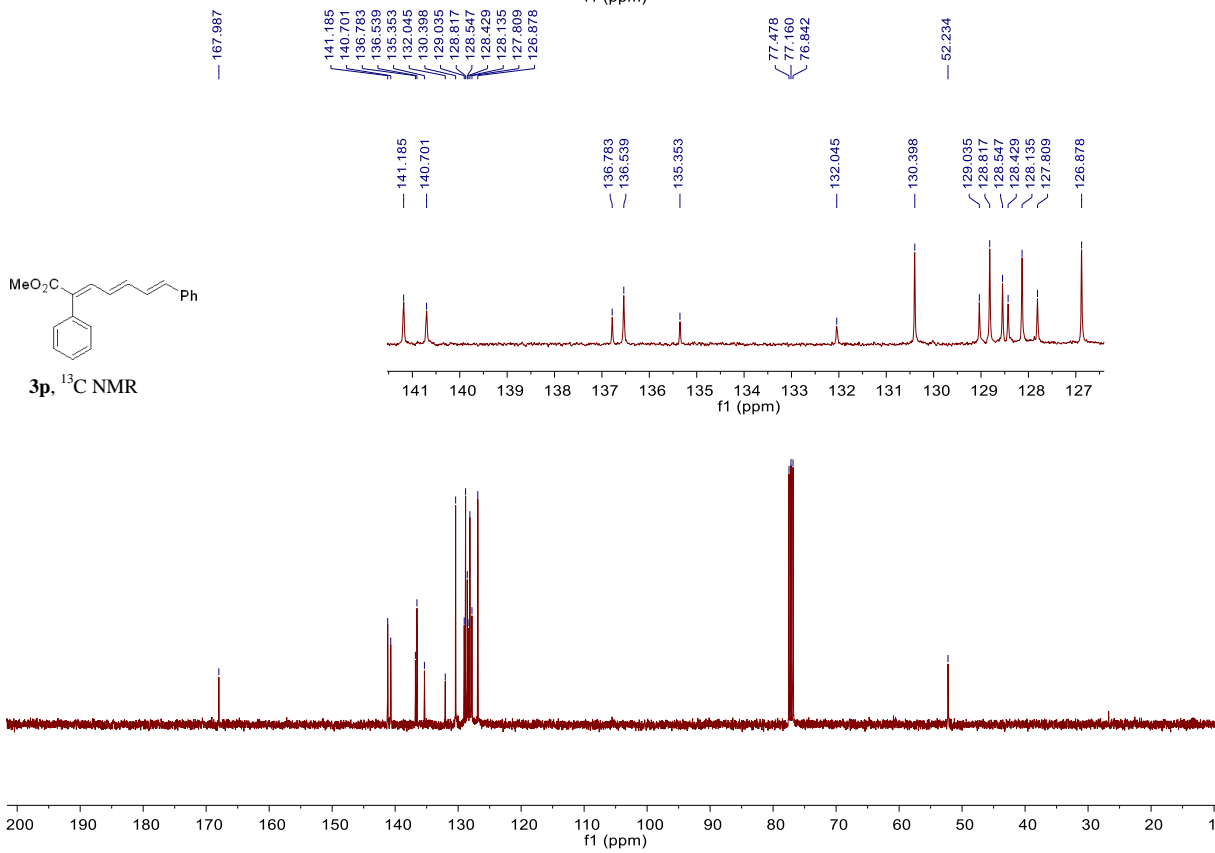
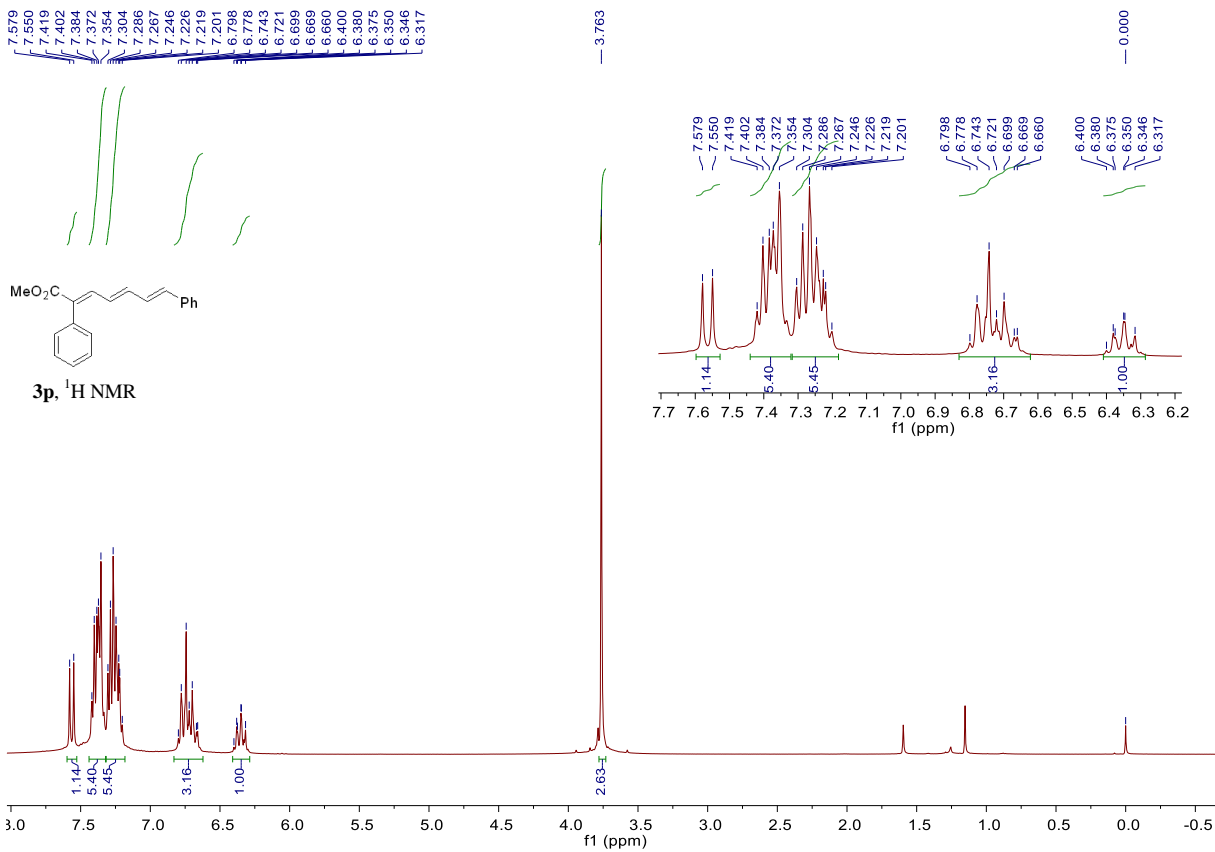


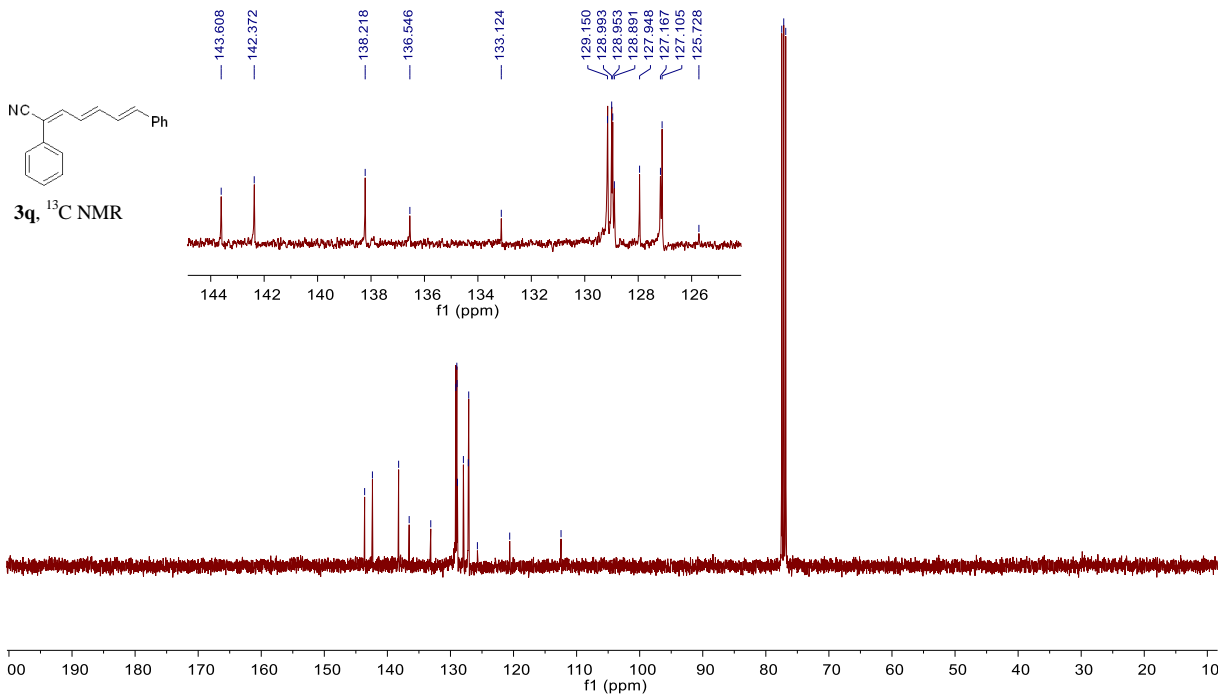
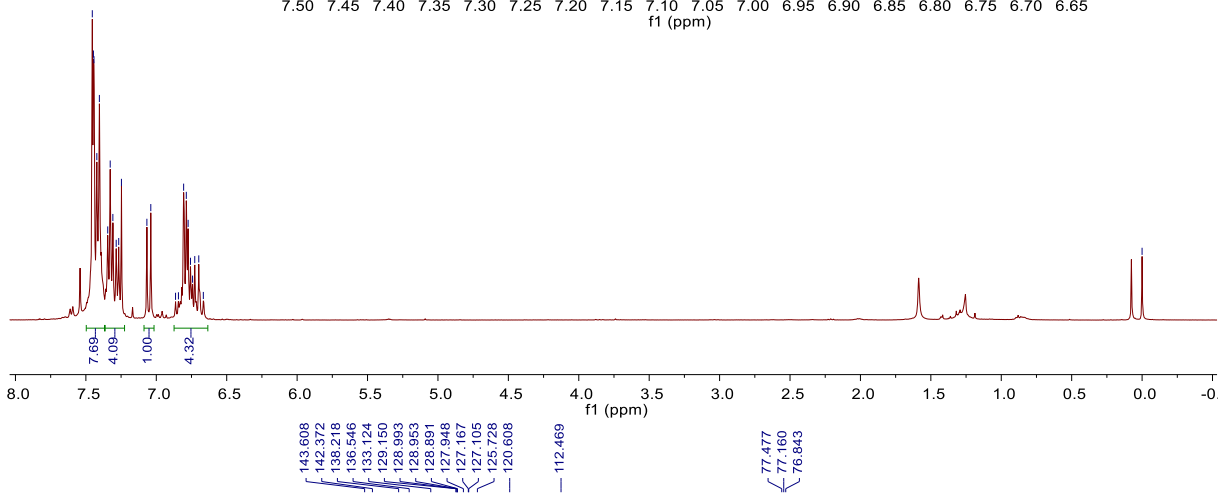
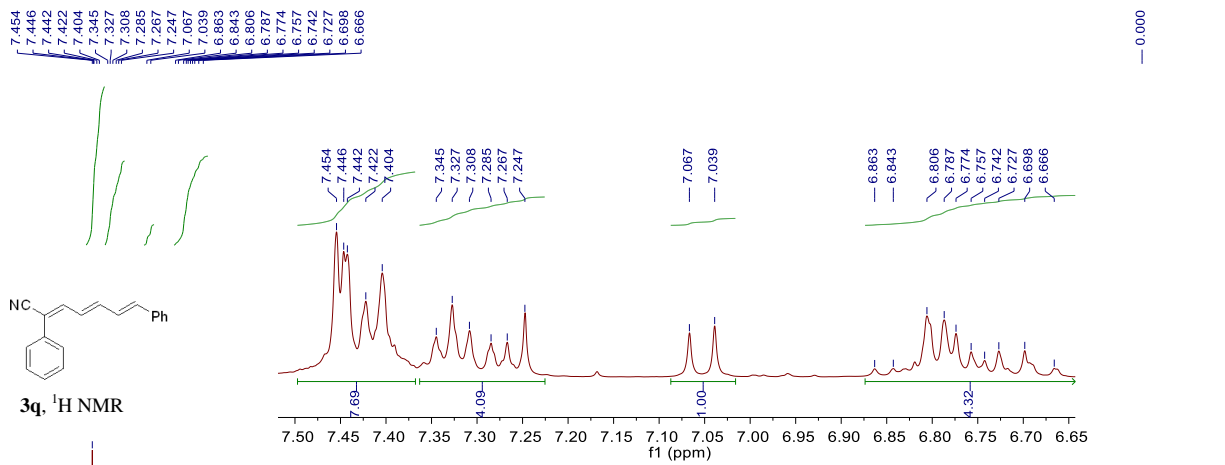


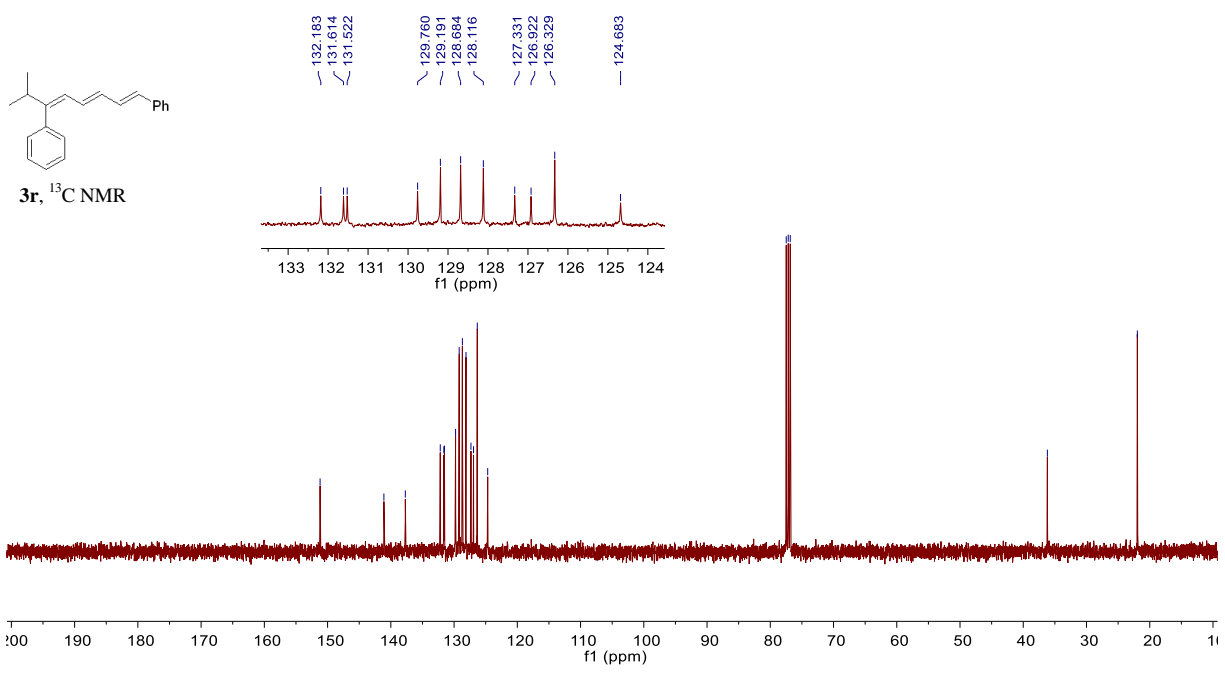
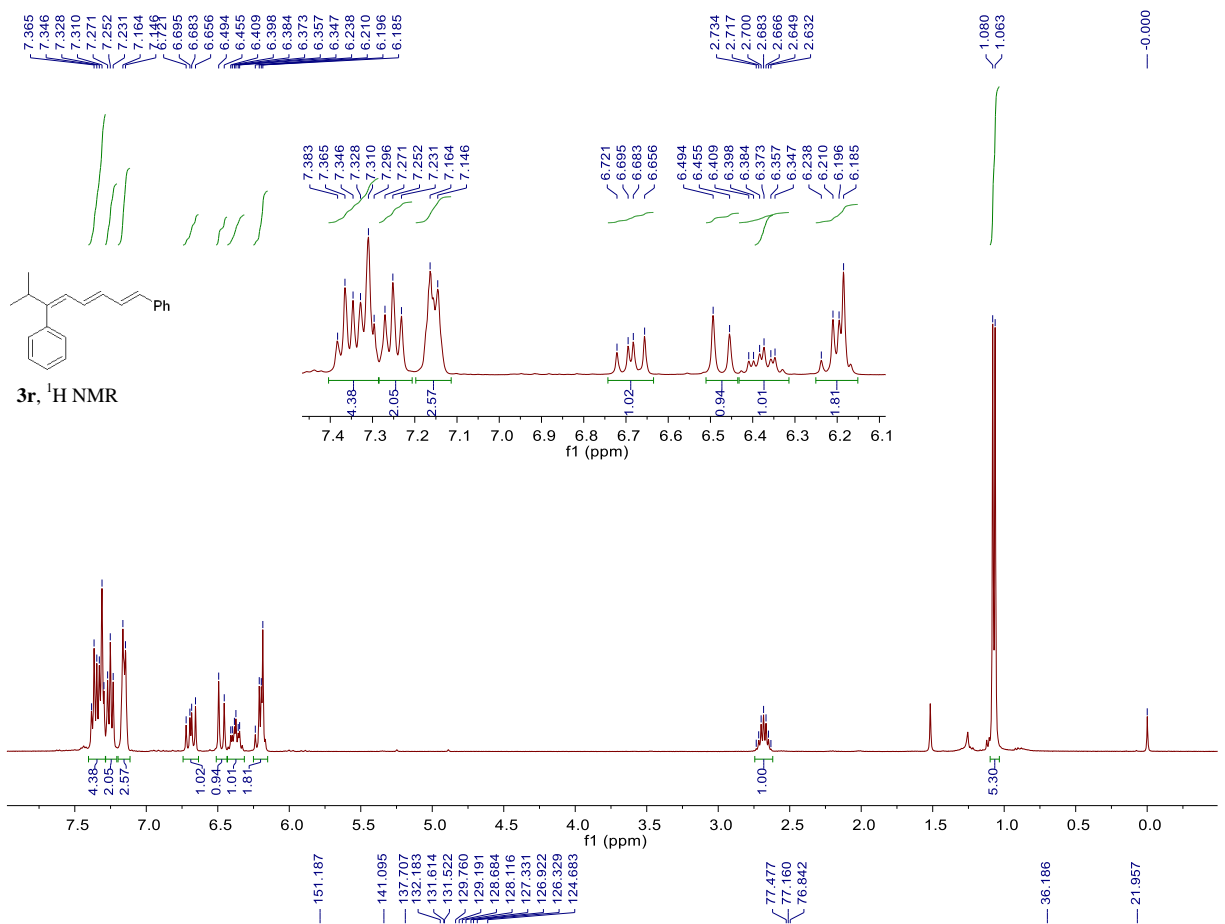


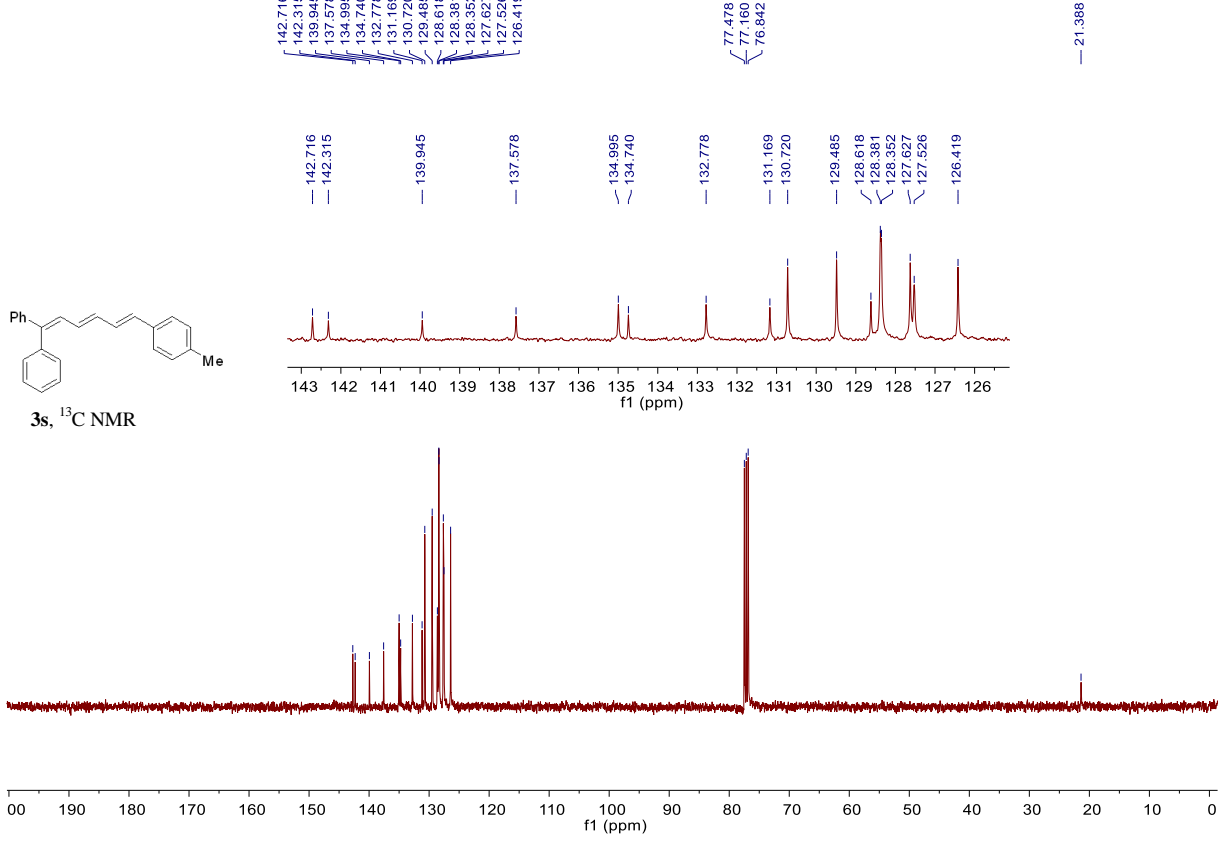
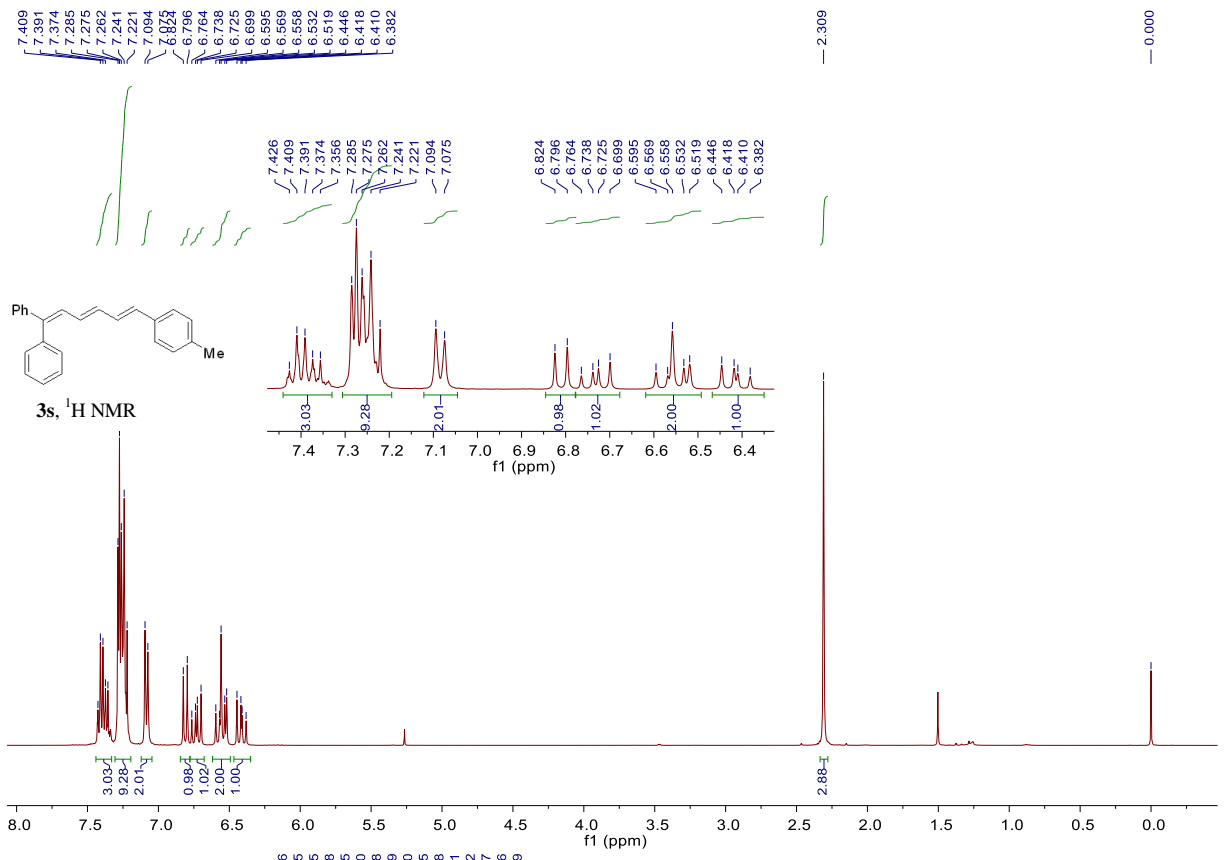


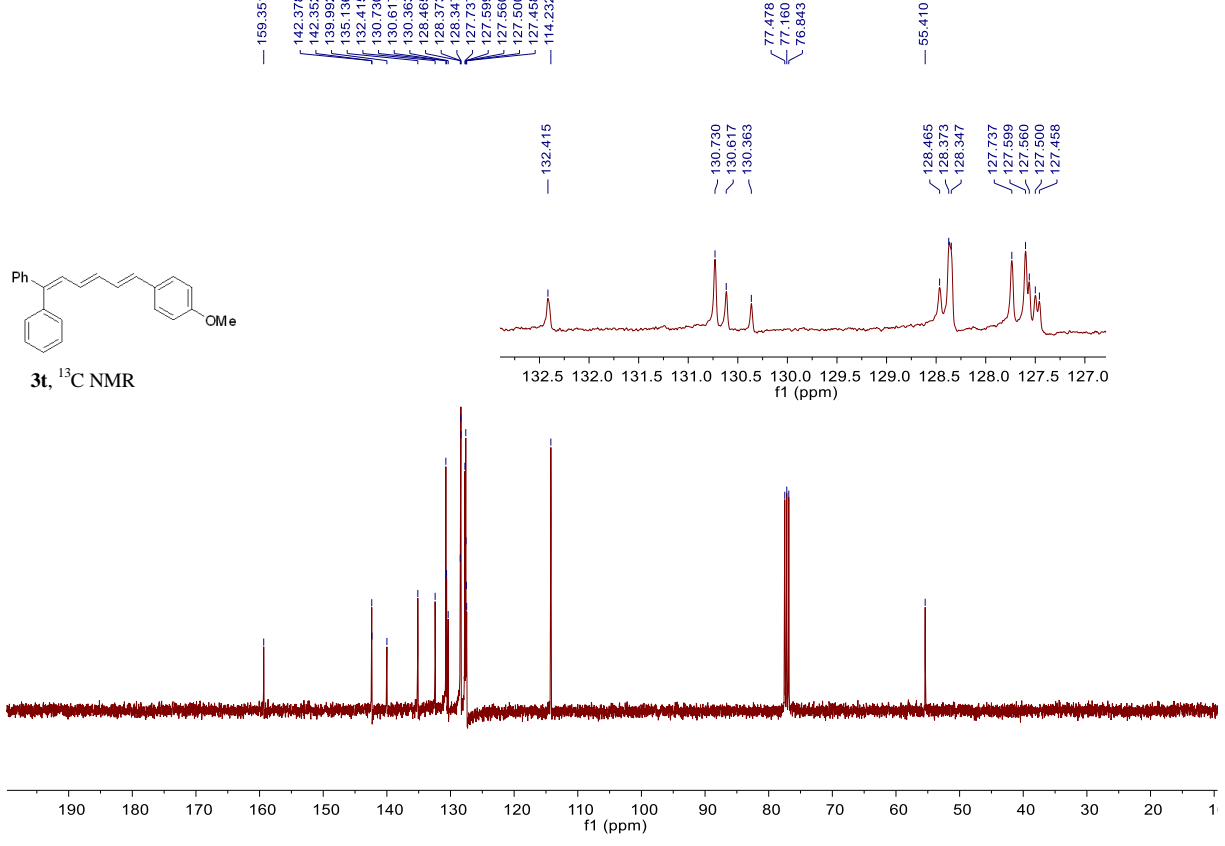
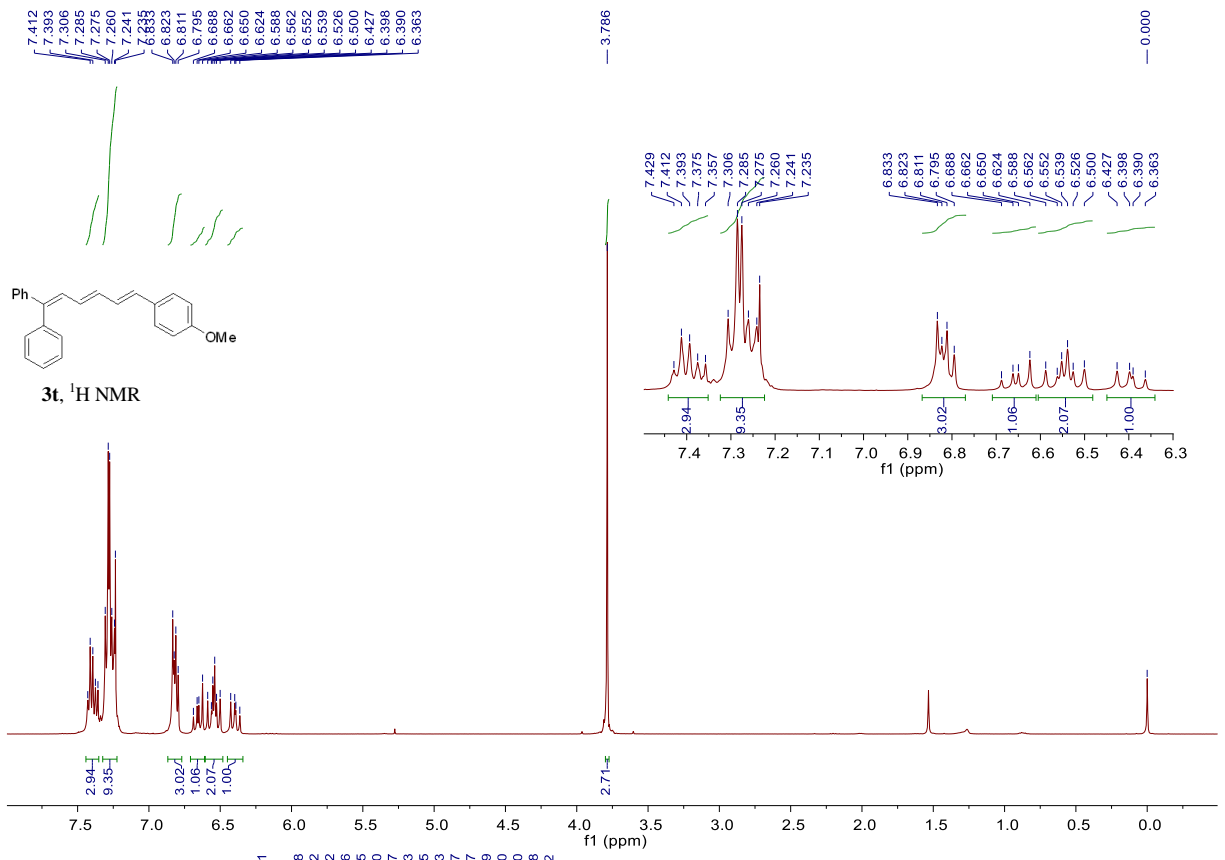


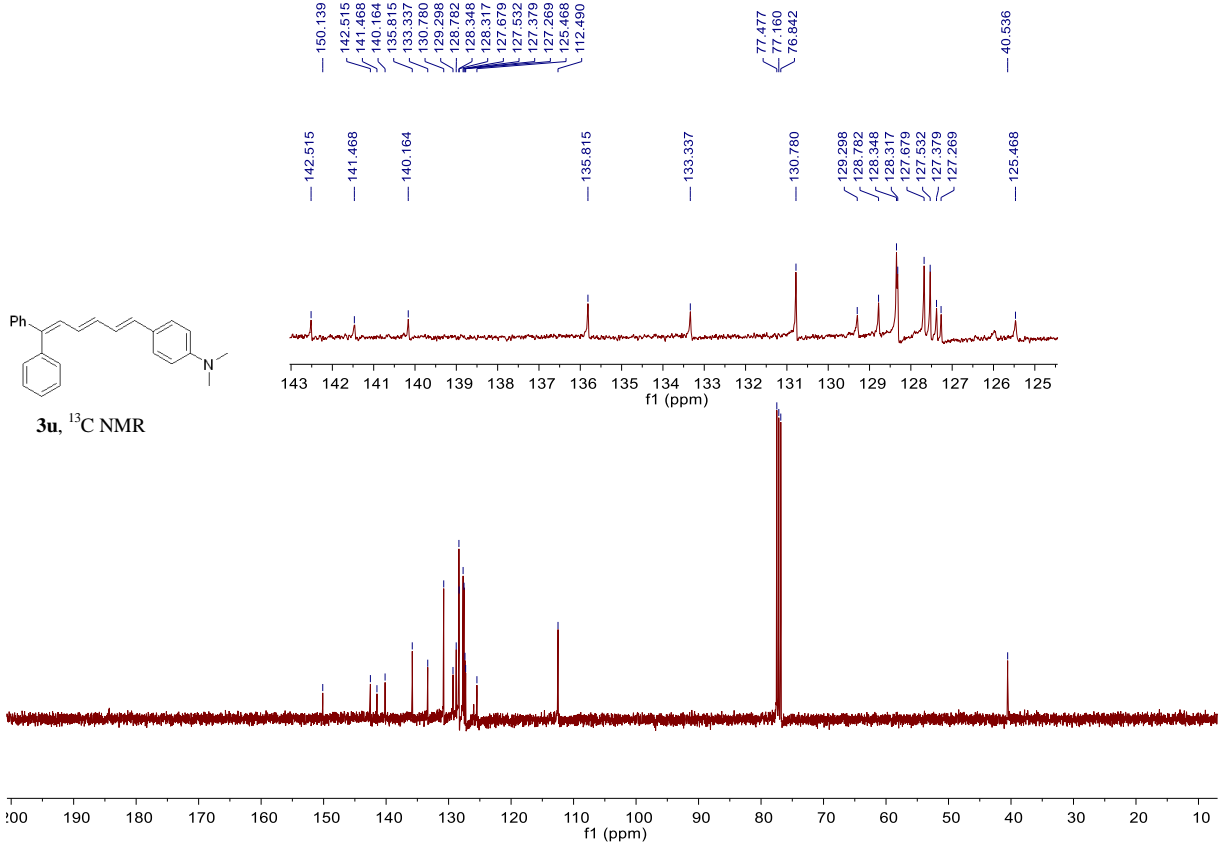
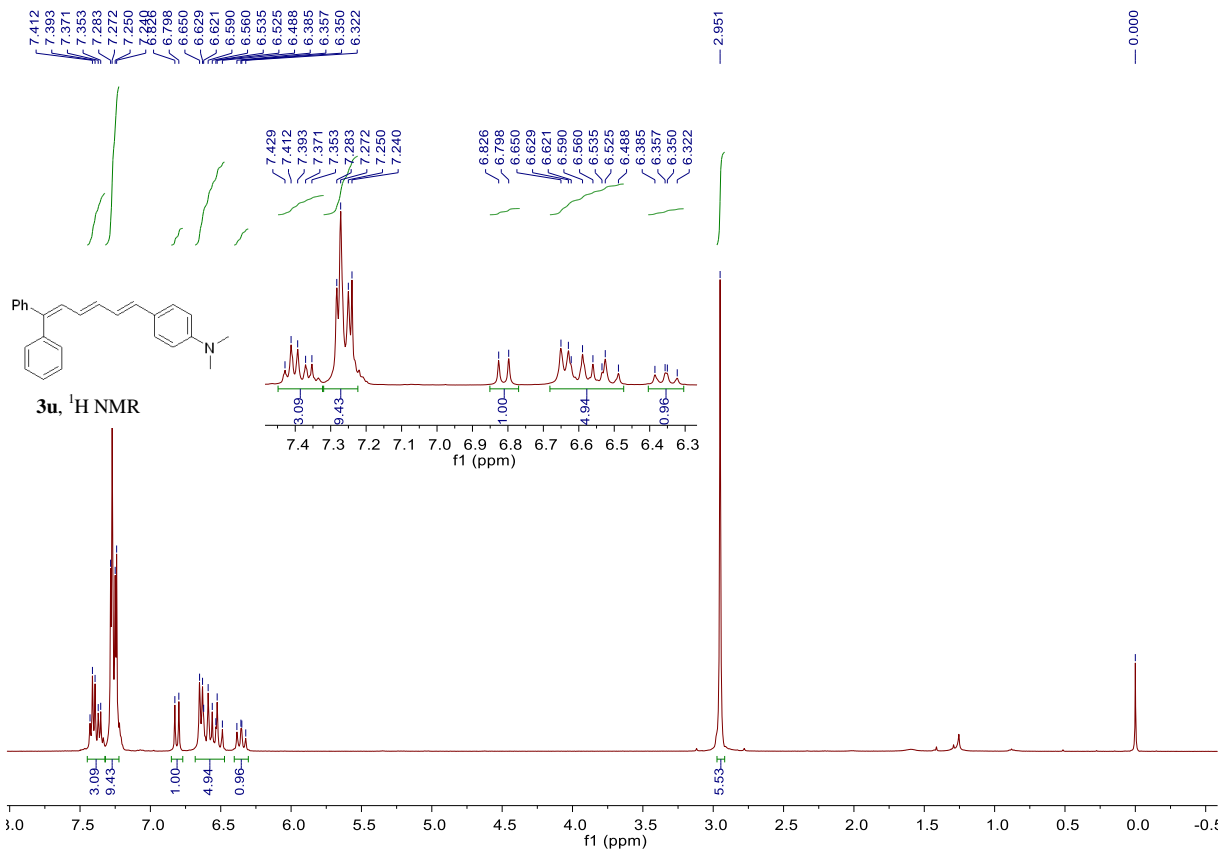


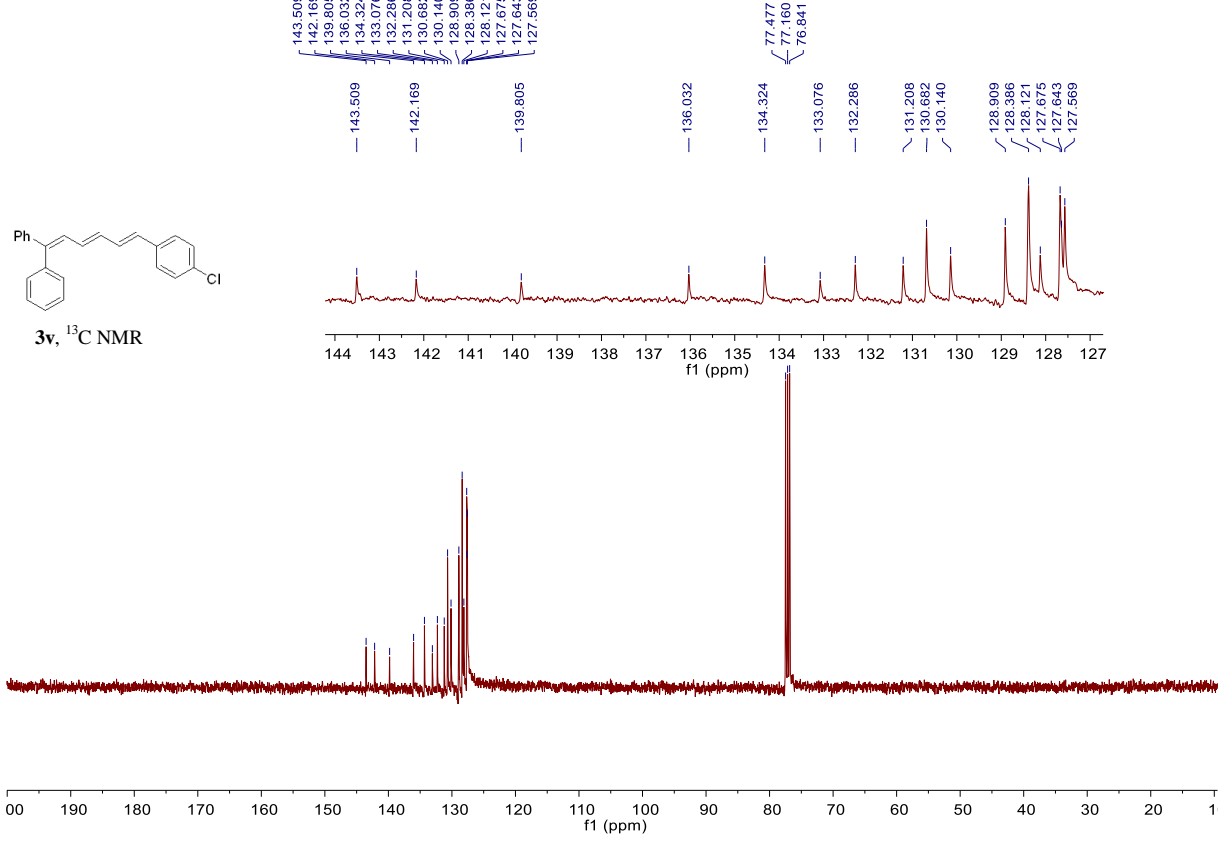
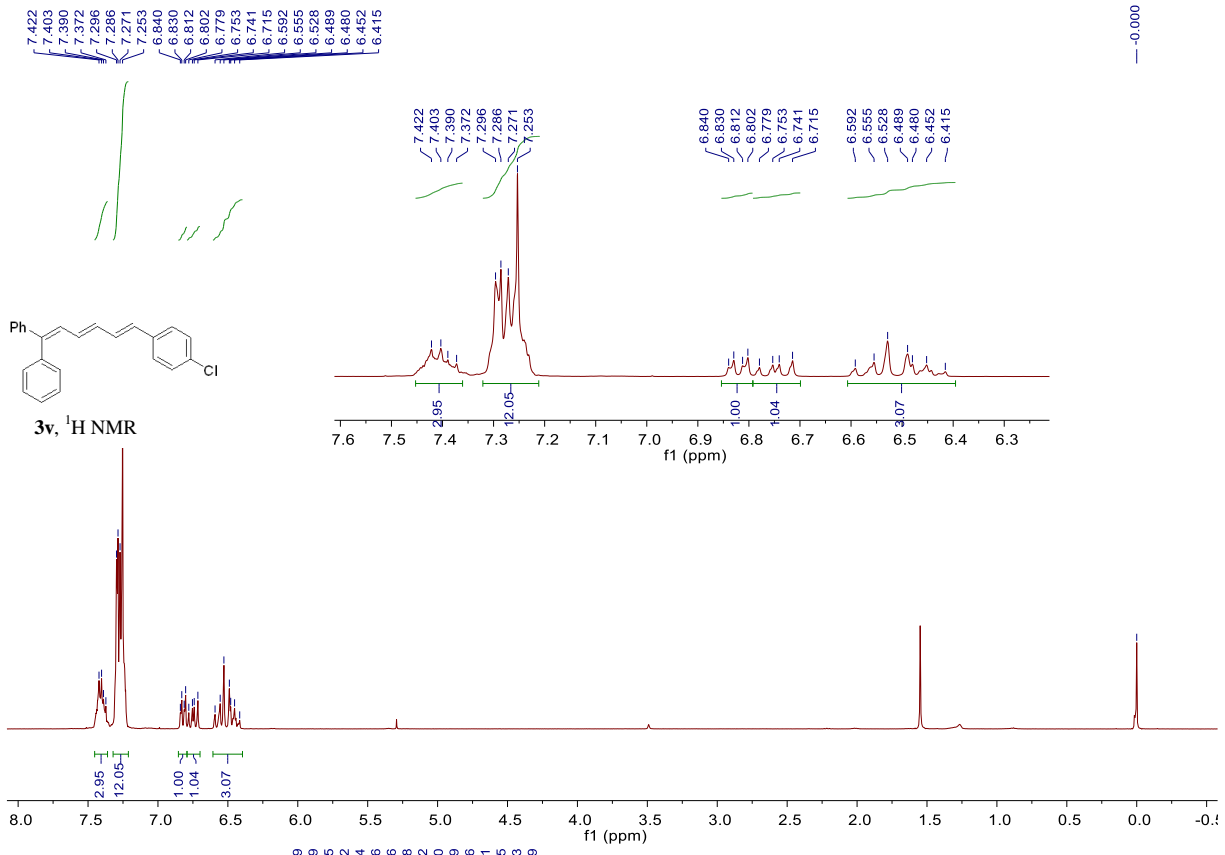


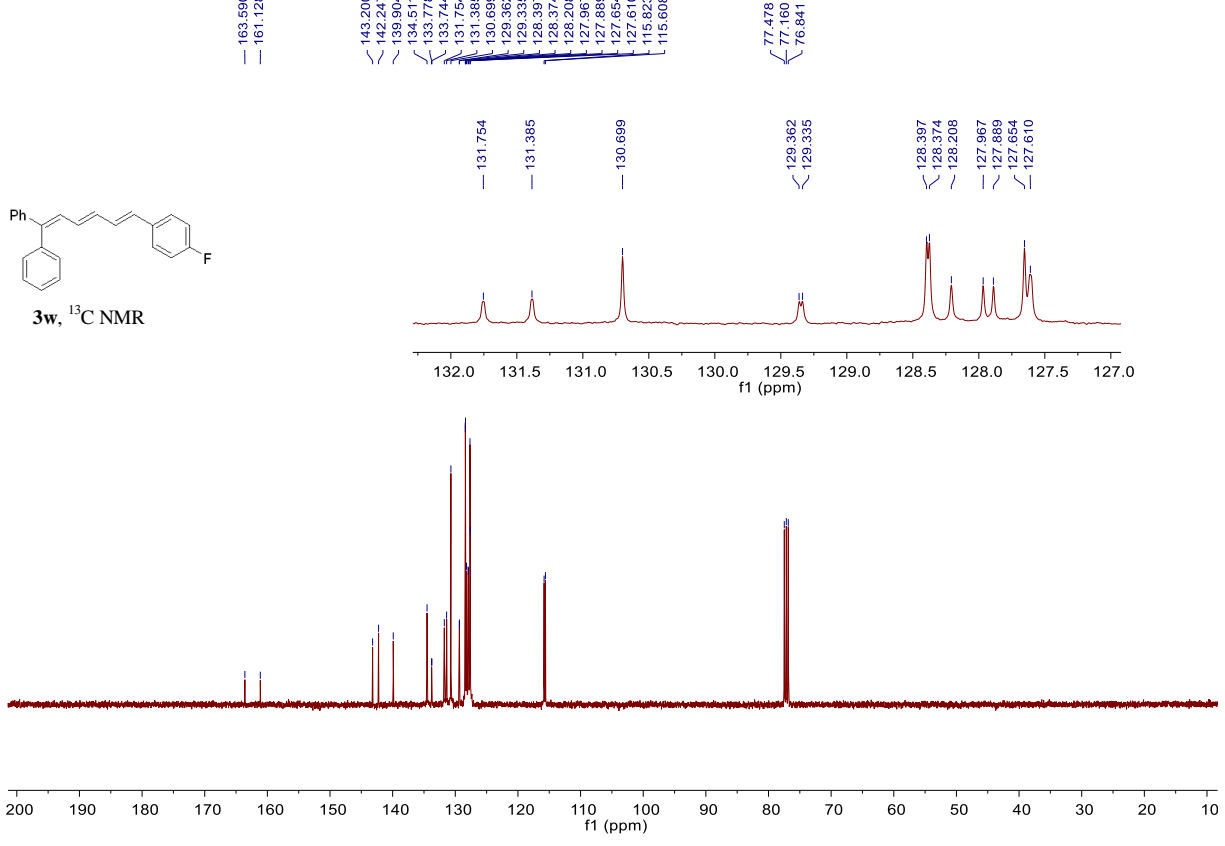
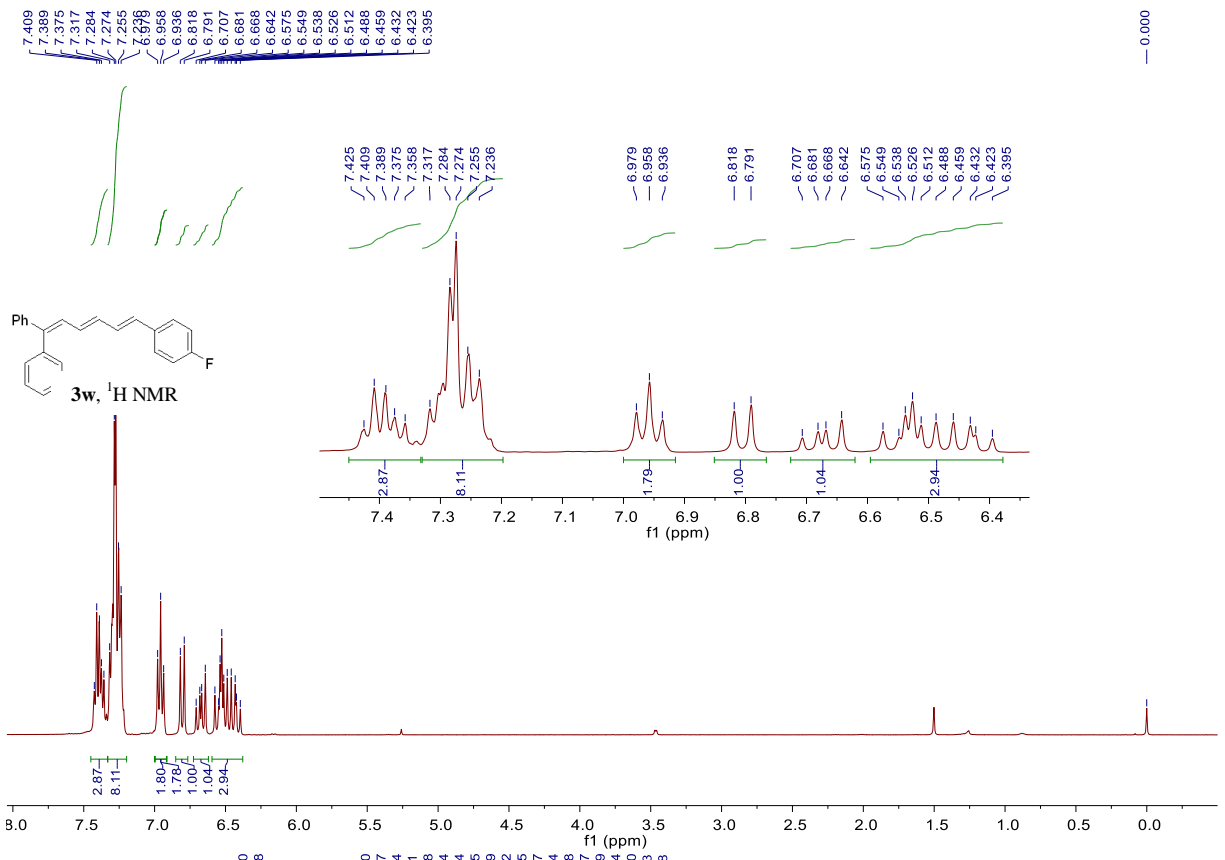


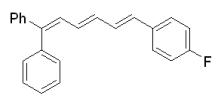




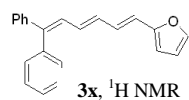
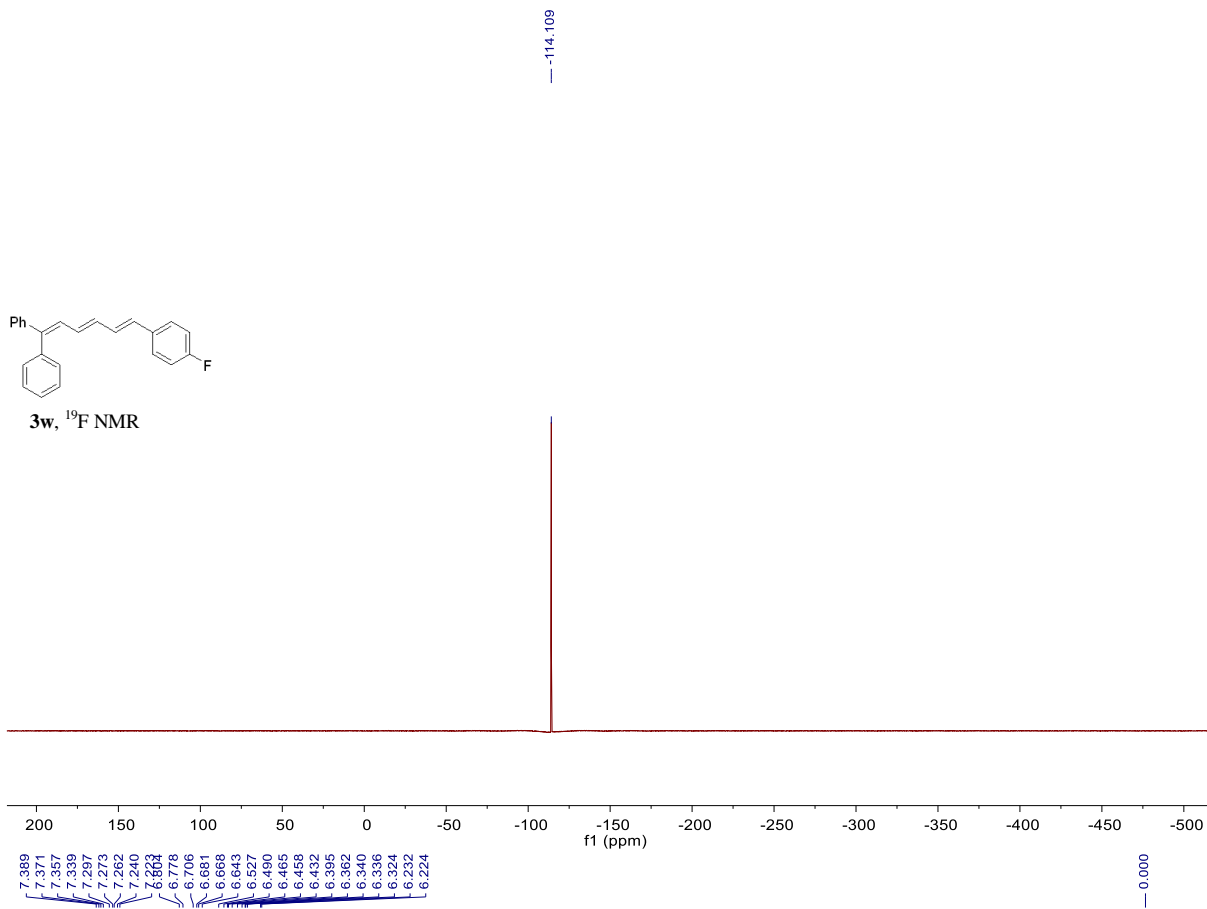








3w, ^{19}F NMR



3x, ^1H NMR

