

**Mild Two-Step Process for the Transition-Metal-Free Synthesis of Carbon–Carbon
Bonds from Allylic Alcohols/Ethers and Grignard Reagents**

Xinping Han, Yanhua Zhang, and Jimmy Wu*

Department of Chemistry, Dartmouth College, Hanover, NH 03755

Supporting Information

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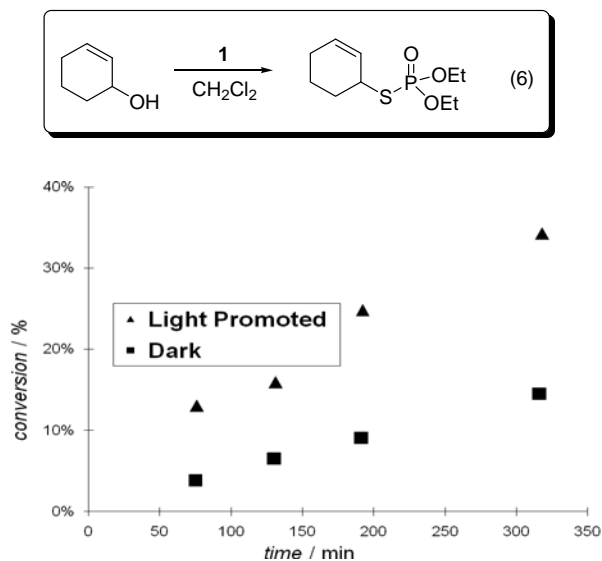
I. General Information

^1H NMR spectra were recorded on a Varian Unity Plus 300 (300 MHz) or 500 (500 MHz) FT spectrometer at ambient temperature. Chemical shift values (δ) are expressed in ppm downfield relative to internal standard (tetramethylsilane at 0 ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet) and br (broad). Coupling constants are reported in hertz. ^{13}C NMR spectra were recorded on a Varian Unity Plus 500 (125 MHz) FT spectrometer at ambient temperature, and are expressed in ppm using solvent as the internal standard (CDCl_3 at 77.0 ppm, C_6D_6 at 128.0 ppm). ^{31}P NMR spectra were recorded on a Varian Unity Plus 300 (121 MHz) or 500 (202 MHz) FT spectrometer at ambient temperature. IR spectra were recorded on a Perkin Elmer FT-IR 1600 Series spectrophotometer, ν_{max} (cm^{-1}) are partially reported. Analytical thin layer chromatography (TLC) was performed on SILICYCLE pre-coated TLC plates (silica gel 60 F-254, 0.25 mm). Flash column chromatography was performed on silica gel 60 (SILICYCLE 230-400 mesh). Visualization was accomplished with UV light and/or with ceric ammonium molybdate (CAM) or KMnO_4 staining solutions. High resolution mass spectra were acquired from the Mass Spectrometry Laboratory of the University of Illinois (Urbana-Champaign, IL).

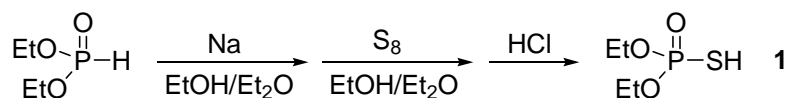
All reactions were carried out in oven-dried glassware with magnetic stirring under nitrogen atmosphere unless otherwise noted. All solvents were freshly distilled. All other reagents and starting materials, unless otherwise noted, were purchased from commercial vendors and used without further purification.

II. Experimental Procedures and Analytical Data

Figure 1. Conversions of Light versus Dark Reactions as a Function of Time for Eq 3



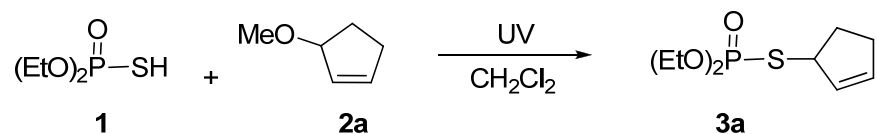
Preparation of *O,O'*-diethyl phosphorothioic acid **2**¹



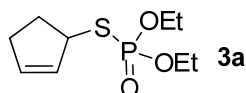
Sodium (0.2 mol, 4.6 g) was dissolved in ethanol (60 mL), and diethyl phosphite (0.2 mol, 26 mL). Diethyl ether (60 mL) was then added to this solution. After stirring for 1 h at rt, sulfur (0.2-0.3 mol, 6.4-9.6 g) was added in portions over 1 h and the reaction was stirred for 2 h. Excess of sulfur was filtered off and the filtrate was concentrated. The residue was dissolved in water (10 mL) and 3 equiv of concentrated HCl (50 mL) was added at 0 °C. The aqueous phase was extracted with ether (3×50 mL) and the combined organic phase was washed with water (3×20 mL). After being dried over MgSO_4 and concentrated with a rotary evaporator, the title compound **1** (31 g, 91% yield) was obtained as light yellow oil and was homogeneous as judged by ^1H NMR spectroscopy: ^1H -NMR (C_6D_6 , 300 MHz) δ 3.98-3.92 (m, 4H), 1.00-0.96 (td, $J = 7.2, 0.6$ Hz, 6H); ^{13}C -NMR (C_6D_6 , 125 MHz) δ 64.4 (d, $J = 5.0$ Hz), 15.8 (d, $J = 7.7$ Hz); ^{31}P -NMR (C_6D_6 , 202 MHz) δ 64.4; IR (film, cm^{-1})

2984, 1476, 1444, 1391, 1163, 1025, 786; **Exact mass calcd for** $[\text{MH}^+]$ requires m/z 171.0245 Found 171.0246 (ES+).

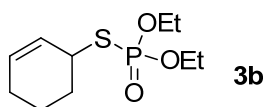
General Procedure A: Preparation of Allylic Phosphorothioate Esters



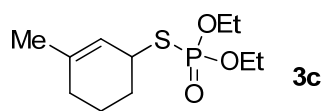
To a round-bottom flask charged with **2a** (16.8 mg, 0.20 mmol) and **1** (36 mg, 0.21 mmol) was added CH_2Cl_2 (1.5 mL). The reaction mixture was placed in either a Rayonet reactor or sunlamp ($\lambda > 300$ nm) and aged at ambient temperature until the reaction was judged complete as determined by thin layer chromatographic analysis (approximately 2 h for compounds **3a**, **3c–3h**, **3j**, **6** and 48 h for compounds **3b**, **3i**, and **3k**). The volatiles were concentrated using a rotary evaporator and the residue purified via silica gel chromatography (EtOAc/hexanes) to afford **3a** (36 mg, 73% yield) as a pale yellow oil.



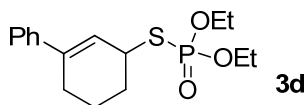
The compound **3a** was prepared from **2a** following General Procedure A and isolated as a light yellow oil in 73% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 300 MHz) δ 5.87-5.85 (m, 1H), 5.60-5.56 (m, 1H), 4.52-4.49 (m, 1H), 4.08-3.91 (m, 4H), 2.27-1.91 (m, 4H), 1.06-1.01 (m, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ 133.9, 132.3 (d, $J = 6.5$ Hz), 63.3 (d, $J = 2.2$ Hz), 63.2 (d, $J = 2.8$ Hz), 51.5 (d, $J = 3.6$ Hz), 33.3 (d, $J = 6.0$ Hz), 31.6, 16.1 (d, $J = 1.9$ Hz), 16.1 (d, $J = 2.2$ Hz); **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.3; **IR** (film, cm^{-1}) 2982, 1443, 1390, 1255, 1161, 1016, 968, 740; **Exact mass calcd for** $[\text{MH}^+]$ requires m/z 237.0714 Found 237.0721 (ES+).



The compound **3b** was prepared from **2b** following General Procedure A and isolated as a light yellow oil in 76% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 5.86-5.84 (m, 1H), 5.57-5.54 (m, 1H), 4.19-4.17 (m, 1H), 4.03-3.89 (m, 4H), 2.00-1.88 (m, 2H), 1.71-1.64 (m, 3H), 1.34-1.31 (m, 1H), 1.02-0.98 (m, 6H); **^{13}C -NMR** (CD_2Cl_2 , 125 MHz) δ 131.0, 127.6 (d, $J = 7.8$ Hz), 63.7 (d, $J = 2.8$ Hz), 63.6 (d, $J = 3.2$ Hz), 42.8 (d, $J = 3.2$ Hz), 31.1 (d, $J = 3.8$ Hz), 24.9, 16.1, 16.0; **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.3; **IR** (film, cm^{-1}) 2933, 1444, 1390, 1255, 1162, 1017, 967, 869, 745; **Exact mass calcd for** $[\text{MH}^+]$ requires m/z 251.0871 Found 251.0859 (ES+).

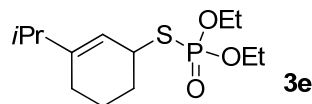


The compound **3c** was prepared from **2c** following the General Procedure A and isolated as a light yellow oil in 93% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 5.62 (bs, 1H), 4.26 (bs, 1H), 4.09-3.94 (m, 4H), 2.04-2.01 (m, 1H), 1.90-1.84 (m, 1H), 1.77-1.73 (m, 1H), 1.62-1.58 (m, 2H), 1.44 (s, 3H), 1.42-1.39 (m, 1H), 1.04 (t, $J = 7.0$ Hz, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ 138.2, 122.7 (d, $J = 8.2$ Hz), 63.2 (d, $J = 6.0$ Hz), 63.1 (d, $J = 6.0$ Hz), 43.9 (d, $J = 3.2$ Hz), 31.0 (d, $J = 3.6$ Hz), 29.7, 23.7, 19.8, 16.2, 16.1; **^{31}P -NMR** (C_6D_6 , 202 MHz) δ 27.8; **IR** (film, cm^{-1}) 2931, 1664, 1443, 1390, 1254, 1162, 1017, 966, 872, 763; **Exact mass calcd for** $[\text{MH}^+]$ requires m/z 265.1027 Found 265.1027 (ES+).

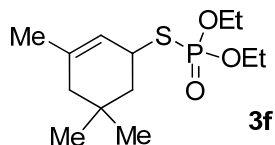


The compound **3d** was prepared from **2d** following General Procedure A and isolated as a light yellow oil in 89% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 7.24-7.21 (m, 2H), 7.12-7.04 (m, 3H), 6.30-6.28 (m, 1H), 4.40-4.35 (m, 1H), 4.06-3.89 (m, 4H), 2.19-1.73 (m, 5H), 1.48-1.41 (m, 1H), 1.06-0.96 (m, 6H); **^{13}C -NMR** (CD_2Cl_2 , 125 MHz) δ 141.5, 140.4, 128.5, 127.7, 125.5, 124.4 (d, $J = 7.9$ Hz), 63.9 (d, $J = 4.5$ Hz), 63.8 (d, $J = 4.1$ Hz), 44.0 (d, $J = 3.3$ Hz), 30.7 (d, $J = 4.1$ Hz), 27.3, 20.0, 16.2, 16.1; **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.4; **IR** (film, cm^{-1}) 2983, 1596, 1494,

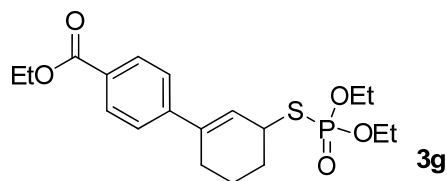
1444, 1390, 1254, 1161, 1017, 967, 879, 753, 698; **Exact mass calcd for** [MH⁺] requires *m/z* 327.1184 Found 327.1180 (ES+).



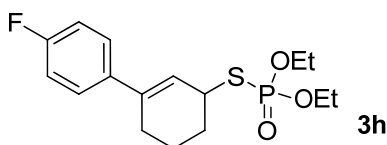
The compound **3e** was prepared from **2e** following General Procedure A and isolated as a light yellow oil in 78% yield that was homogeneous as judged by ¹H NMR spectroscopy: **¹H-NMR** (C₆D₆, 500 MHz) δ 5.65-5.63 (m, 1H), 4.28-4.24 (m, 1H), 4.06-3.91 (m, 4H), 2.01-1.93 (m, 2H), 1.89-1.86 (m, 1H), 1.71-1.62 (m, 3H), 1.42-1.38 (m, 1H), 1.00 (t, *J* = 14.0 Hz, 3H), 1.40 (d, *J* = 7.0 Hz, 6H), 0.85 (d, *J* = 4.0 Hz, 3H), 0.84 (d, *J* = 4.0 Hz, 3H); **¹³C-NMR** (C₆D₆, 125 MHz) δ 147.5 (d, *J* = 0.9 Hz), 120.1 (d, *J* = 7.8 Hz), 63.2 (d, *J* = 6.0 Hz), 63.1 (d, *J* = 6.0 Hz), 43.9 (d, *J* = 3.1 Hz), 35.3, 31.4 (d, *J* = 3.6 Hz), 25.8, 21.2, 21.0, 20.0, 16.0, 15.9; **³¹P-NMR** (C₆D₆, 121 MHz) δ 28.0; **IR** (film, cm⁻¹) 2960, 1443, 1389, 1255, 1162, 1018, 967, 876, 758; **Exact mass calcd for** [MH⁺] requires *m/z* 293.1340 Found 293.1340 (ES+).



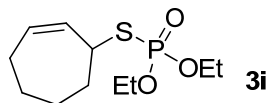
The compound **3f** was prepared from **2f** following General Procedure A and isolated as a light yellow oil in 91% yield and was homogeneous as judged by ¹H NMR spectroscopy: **¹H-NMR** (C₆D₆, 500 MHz) δ 5.62-5.66 (m, 1H), 4.18-4.24 (m, 1H), 4.08-3.93 (m, 4H), 1.95-1.91 (m, 1H), 1.57-1.50 (m, 2H), 1.49 (s, 3H), 1.31-1.25 (m, 1H), 1.05-1.01 (m, 6H), 0.80 (s, 3H), 0.73 (s, 3H); **¹³C-NMR** (C₆D₆, 125 MHz) δ 136.1, 122.2 (d, *J* = 6.4 Hz), 63.1 (d, *J* = 1.4 Hz), 63.0 (d, *J* = 1.4 Hz), 44.5 (d, *J* = 5.5 Hz), 43.3, 42.6 (d, *J* = 3.3 Hz), 31.0, 30.8, 25.3, 23.7, 16.0, 15.9; **³¹P-NMR** (C₆D₆, 121 MHz) δ 27.8; **IR** (film, cm⁻¹) 2954, 2360, 1441, 1390, 1255, 1101, 1021, 968, 909, 801, 608; **Exact mass calcd for** [MH⁺] requires *m/z* 293.1340 Found 293.1352 (ES+).



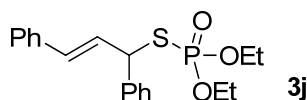
The compound **3g** was prepared from **2g** following General Procedure A and isolated as a light yellow oil in 70% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 8.16-8.14 (d, 2H), 7.20-7.17 (d, 2H), 6.32-6.30 (d, 1H), 4.40-4.35 (m, 1H), 4.16-4.11 (q, 2H), 4.08-3.92 (m, 4H), 2.02-1.97 (m, 2H), 1.92-1.85 (m, 2H), 1.74-1.71 (m, 1H), 1.44-1.40 (m, 1H), 1.04-0.97 (m, 9H); **^{13}C -NMR** (CD_2Cl_2 , 125 MHz) δ 166.4, 145.8, 139.4 (d, $J = 1.0$ Hz), 129.7 (d, $J = 4.5$ Hz), 126.5, 126.4, 125.4, 63.8 (d, $J = 4.1$ Hz), 63.8 (d, $J = 4.1$ Hz), 61.1, 43.7 (d, $J = 2.8$ Hz), 30.6 (d, $J = 4.1$ Hz), 27.2, 20.0, 16.2, 16.1, 14.3; **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.3; **IR** (film, cm^{-1}) 3847, 2930, 1716, 1606, 1446, 1366, 1275, 1184, 1105, 1018, 970, 842, 771, 702; **Exact mass calcd for** $[\text{MNa}^+]$ requires m/z 421.1215 Found 421.1219 (ES+).



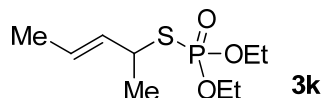
The compound **3h** was prepared from **2h** following General Procedure A and isolated as a light yellow oil in 92% yield that was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 6.99-6.95 (m, 2H), 6.76-6.72 (m, 2H), 6.16-6.14 (m, 1H), 4.37-4.34 (m, 1H), 4.05-3.91 (m, 4H), 2.00-1.96 (m, 2H), 1.90-1.85 (m, 2H), 1.75-1.72 (m, 1H), 1.45-1.41 (m, 1H), 1.03-0.95 (m, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ 162.6 (d, $J = 244.9$ Hz), 138.8, 137.4 (d, $J = 3.3$ Hz), 127.1 (d, $J = 7.8$ Hz), 124.7 (dd, $J = 7.3$ Hz), 115.2 (d, $J = 21.0$ Hz), 63.3 (d, $J = 6.0$ Hz), 63.2 (d, $J = 5.9$ Hz), 43.9 (d, $J = 2.6$ Hz), 30.7 (d, $J = 4.1$ Hz), 27.1, 19.9, 16.0, 15.9; **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.5; **IR** (film, cm^{-1}) 2933, 1600, 1509, 1444, 1390, 1253, 1162, 1099, 1017, 968, 827, 767, 601; **Exact mass calcd for** $[\text{MNa}^+]$ requires m/z 367.0909 Found 367.0911 (ES+).



The compound **3i** was prepared from **2i** following General Procedure A and isolated as a light yellow oil in 74% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 5.95-5.91 (m, 1H), 5.64-5.61 (m, 1H), 4.38-4.34 (m, 1H), 4.05-3.90 (m, 4H), 2.06-1.83 (m, 5H), 1.56-1.46 (m, 2H), 1.27-1.23 (m, 1H), 1.02-0.99 (m, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ 133.8, 132.9 (d, $J = 7.4$ Hz), 63.2, 63.1 (d, $J = 5.9$ Hz), 47.1 (d, $J = 3.1$ Hz), 34.4 (d, $J = 4.1$ Hz), 28.3, 27.1, 26.8, 16.0 (d, $J = 1.4$ Hz), 15.9 (d, $J = 1.4$ Hz); **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.8; **IR** (film, cm^{-1}) 2930, 1652, 1444, 1392, 1254, 1162, 1016, 968, 869, 744, 601, 568; **Exact mass calcd for** $[\text{MH}^+]$ requires m/z 265.1027 Found 265.1033 (ES+).

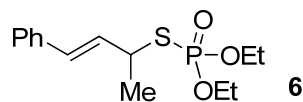


The compound **3j** was prepared from **2i** following General Procedure A and isolated as a light yellow oil in 72% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 7.40-7.38 (d, 2H), 7.14-6.97 (m, 8H), 6.66-6.63 (d, 1H), 6.56-6.50 (m, 1H), 5.49-5.45 (m, 1H), 4.02-3.76 (m, 4H), 0.93-0.87 (m, 6H); **^{13}C -NMR** (CD_2Cl_2 , 125 MHz) δ 141.0 (d, $J = 6.0$ Hz), 136.6, 131.8, 129.5 (d, $J = 5.5$ Hz), 129.0, 128.8, 128.2, 128.0, 128.0, 126.8, 63.8 (d, $J = 3.3$ Hz), 63.7 (d, $J = 3.8$ Hz), 53.2 (d, $J = 3.3$ Hz), 16.0 (d, $J = 2.3$ Hz), 15.9 (d, $J = 2.4$ Hz); **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 25.8; **IR** (film, cm^{-1}) 3028, 2983, 1598, 1493, 1451, 1391, 1254, 1162, 1016, 971, 749, 697; **Exact mass calcd for** $[\text{MNa}^+]$ requires m/z 385.1003 Found 385.1011 (ES+).

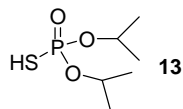


The compound **3k** was prepared from **2k** following General Procedure A and isolated as a light yellow oil in 73% yield and was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 5.50-5.46 (m, 2H), 4.08-3.98 (m, 3H), 3.96-3.88 (m, 2H), 1.43-1.41 (m, 3H), 1.39-1.36 (m, 3H), 1.02-0.98 (m, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ

133.5 (d, $J = 5.4$ Hz), 126.2, 63.3 (d, $J = 2.3$ Hz), 63.2 (d, $J = 1.4$ Hz), 44.3 (d, $J = 3.3$ Hz), 23.0 (d, $J = 6.9$ Hz), 17.5, 15.9, 15.9; **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 27.2; **IR** (film, cm^{-1}) 2981, 1666, 1447, 1391, 1254, 1162, 1018, 967, 791; **Exact mass calcd for $[\text{MH}^+]$** requires m/z 239.0871 Found 239.0868 (ES+).

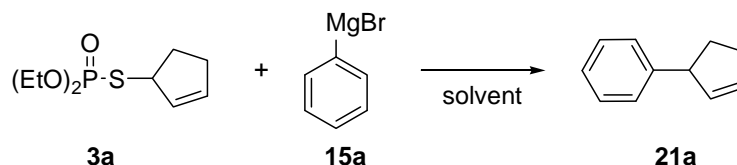


The compound **6** was prepared from **4** following General Procedure A and isolated as a light yellow oil in 72% yield that was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (C_6D_6 , 500 MHz) δ 7.18-6.99 (m, 5H), 6.50 (d, $J = 16.0$ Hz, 1H), 6.20 (dd, $J_1 = 8.5$ Hz, $J_2 = 8.5$ Hz, 1H), 4.24-4.19 (m, 1H), 4.04-3.87 (m, 4H), 1.40 (d, $J = 7.0$ Hz, 3H), 1.00-0.93 (m, 6H); **^{13}C -NMR** (C_6D_6 , 125 MHz) δ 136.9, 131.8 (d, $J = 4.5$ Hz), 130.4, 128.7, 127.8, 126.7, 63.2 (d, $J = 3.8$ Hz), 63.1 (d, $J = 3.3$ Hz), 44.7 (d, $J = 3.3$ Hz), 22.7 (d, $J = 7.8$ Hz), 15.9 (d, $J = 1.8$ Hz), 15.9 (d, $J = 1.8$ Hz); **^{31}P -NMR** (C_6D_6 , 121 MHz) δ 26.4; **IR** (film, cm^{-1}) 2991, 1447, 1391, 1254, 1162, 1019, 968, 752, 695; **Exact mass calcd for $[\text{MH}^+]$** requires m/z 301.1027 Found 301.1030 (ES+).

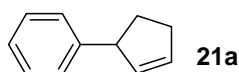


The title compound **13** was prepared following the procedure to make compound **1** but differing in the workup. After the excess sulfur had been filtered off, the filtrate was concentrated, dissolved in water, and washed 4 times with EtOAc. The aqueous layer was acidified with conc. HCl and extracted with EtOAc. The organic layer was dried with Na_2SO_4 , concentrated by rotary evaporator and isolated as yellow oil in 73% yield that was homogeneous as judged by ^1H NMR spectroscopy: **^1H -NMR** (CD_2Cl_2 , 500 MHz) δ 6.80-6.52 (s, 1H), 4.77-4.72 (m, 2H), 1.35-1.33 (dd, $J = 7.2, 0.6$ Hz, 6H); **^{13}C -NMR** (CD_2Cl_2 , 125 MHz) δ 73.8 (d, $J = 5.5$ Hz), 23.4 (dd, $J_1 = 5.1$ Hz, $J_2 = 5.5$ Hz); **^{31}P -NMR** (CD_2Cl_2 , 202 MHz) δ 58.4.

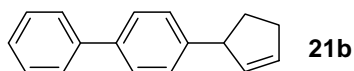
General Procedure B: Cross-coupling Reactions Between Grignard Reagents^{2,3} and Allylic Phosphorothioate Esters



A solution of freshly prepared phenylmagnesium bromide (1.0 M in Et₂O, 1.0 mL) was added to Et₂O (3.5 mL) under N₂ at 0 °C. This was followed by the addition of a solution of cyclopentenyl phosphorothioate ester **3a** (0.5 mmol, 0.118 g) in Et₂O (1.0 mL). The reaction was stirred at rt overnight. The reaction was then quenched with water (10 mL) and the aqueous phase was extracted with Et₂O (3×20 mL). The combined organic phases were sequentially washed with 5% HCl aq. (10 mL), 10% NaOH aq. (10 mL) and saturated NaHCO₃ aq. (10 mL). After being dried over MgSO₄ and concentrated with a rotary evaporator, the residue was purified by silica gel column chromatography (pentane for all compounds).

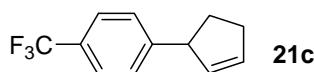


The compound **21a** was prepared following General Procedure B and isolated as a colorless oil in 83% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in Et₂O at rt using I₂ as an initiator. **¹H-NMR** (CDCl₃, 500 MHz) δ 7.32-7.29 (m, 2H), 7.22-7.19 (m, 3H), 5.96-5.95 (m, 1H), 5.80-5.79 (m, 1H), 3.91-3.90 (m, 1H), 2.52-2.41 (m, 3H), 1.75-1.74 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 146.7, 134.4, 132.1, 128.5, 127.3, 126.1, 51.4, 33.9, 32.6; **IR** (film, cm⁻¹) 3055, 2932, 2849, 2360, 1600, 1490, 1452, 1013, 911, 755, 731, 698; **Exact mass calcd for [M⁺]** requires *m/z* 144.0939 Found 144.0941 (EI+).

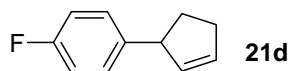


The compound **21b** was prepared following General Procedure B and isolated as a colorless oil in 81% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in THF at rt using I₂ as an initiator. **¹H-NMR**

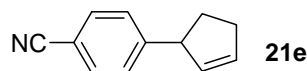
(CDCl₃, 500 MHz) δ 7.60-7.58 (m, 2H), 7.55-7.53 (m, 2H), 7.45-7.42 (m, 2H), 7.35-7.32 (m, 1H), 7.29-7.27 (m, 2H), 5.99-5.97 (m, 1H), 5.83-5.82 (m, 1H), 3.96-3.95 (m, 1H), 2.55-2.43 (m, 3H), 1.81-1.78 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 145.8, 141.2, 139.1, 134.3, 132.2, 128.8, 127.7, 127.3, 127.2, 127.1, 51.1, 33.9, 32.6; **IR** (film, cm⁻¹) 3052, 2939, 2847, 1600, 1485, 1008, 913, 833, 762, 739, 696; **Exact mass calcd for [M⁺]** requires m/z 220.1252 Found 220.1250 (EI+).



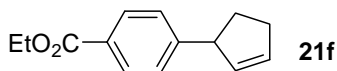
The compound **21c** was prepared following General Procedure B and isolated as a colorless oil in 78% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in Et₂O at rt using I₂ as an initiator. **¹H-NMR** (CDCl₃, 500 MHz) δ 7.54 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.01-5.99 (m, 1H), 5.77-5.75 (m, 1H), 3.96-3.95 (m, 1H), 2.52-2.42 (m, 3H), 1.72-1.71 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 150.7, 133.5, 133.0, 128.5 (q, J = 32 Hz), 127.7, 125.4 (q, J = 3.8 Hz), 124.5 (q, J = 270 Hz) 51.2, 33.8, 32.6; **IR** (film, cm⁻¹) 3056, 2943, 2853, 1617, 1419, 1327, 1164, 1125, 1068, 1016, 913, 836, 723; **Exact mass calcd for [M⁺]** requires m/z 212.0812 Found 212.0813 (EI+).



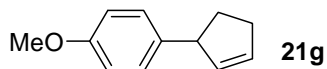
The compound **21d** was prepared following General Procedure B and isolated as a colorless oil in 79% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was purchased from Sigma-Aldrich Co. **¹H-NMR** (CDCl₃, 500 MHz) δ 7.16-7.13 (m, 2H), 6.99-6.96 (m, 2H), 5.96-5.94 (m, 1H), 5.76-5.74 (m, 1H), 3.89-3.87 (m, 1H), 2.50-2.38 (m, 3H), 1.70-1.67 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 161.5 (d, J = 242 Hz), 142.3 (d, J = 3.3 Hz), 134.3, 132.3, 128.6 (d, J = 7.3 Hz), 115.2 (d, J = 21 Hz), 50.6, 34.0, 32.5; **IR** (film, cm⁻¹) 3052, 2942, 2851, 2360, 1602, 1508, 1223, 1156, 830; **Exact mass calcd for [M⁺]** requires m/z 162.0845 Found 162.0846 (EI+).



The compound **21e** was prepared following General Procedure B and isolated by silica gel column chromatography (hexanes/ CH_2Cl_2 8:1) as a colorless oil in 59% yield that was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared via halogen-magnesium exchange.³ **^1H -NMR** (CDCl_3 , 300 MHz) δ 7.57 (dd, J = 6.6, 2.1 Hz, 2H), 7.28 (dd, J = 6.6, 2.1 Hz, 2H), 6.02-5.99 (m, 1H), 5.74-5.71 (m, 1H), 3.93-3.92 (m, 1H), 2.49-2.40 (m, 3H), 1.72-1.66 (m, 1H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 152.3, 133.4, 132.9, 132.4, 128.1, 119.3, 109.9, 51.5, 33.7, 32.5; **IR** (film, cm^{-1}) 2955, 2226, 1606, 1500, 1014, 832; **Exact mass calcd for $[\text{M}^+]$** requires m/z 169.0891 Found 169.0892 (EI+).

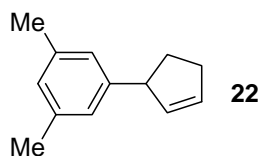


The compound **21f** was prepared following General Procedure B and isolated by silica gel column chromatography (hexanes/ CH_2Cl_2 8:1) as a colorless oil in 57% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared via halogen-magnesium exchange.³ **^1H -NMR** (CDCl_3 , 300 MHz) δ 7.96 (dt, J = 8.4, 1.8 Hz, 2H), 7.24 (dt, J = 8.4, 1.8 Hz, 2H), 5.99-5.96 (m, 1H), 5.77-5.74 (m, 1H), 4.36 (q, J = 6.9 Hz, 2H), 3.95-3.93 (m, 1H), 2.51-2.39 (m, 3H), 1.74-1.69 (m, 1H), 1.38 (t, J = 6.9 Hz, 3H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 166.7, 152.0, 133.6, 132.8, 129.8, 129.6, 128.4, 127.3, 60.9, 51.4, 33.7, 32.6, 14.4; **IR** (film, cm^{-1}) 2956, 1718, 1609, 1366, 1275, 1176, 1102, 1021, 770, 708; **Exact mass calcd for $[\text{M}^+]$** requires m/z 216.1150 Found 216.1149 (EI+).

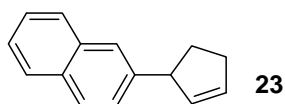


The compound **21g** was prepared following General Procedure B and isolated as a colorless oil in 77% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in refluxing THF using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.12 (d, J = 8.0 Hz, 2H), 6.85 d, J = 8.0 Hz, 2H), 5.94-5.92 (m, 1H), 5.77-5.76 (m, 1H), 3.87-3.85 (m, 1H), 3.80 (s, 3H), 2.50-2.37 (m, 3H), 1.70-1.69 (m, 1H);

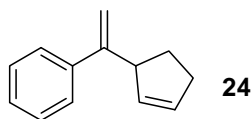
¹³C-NMR (CDCl₃, 125 MHz) δ 158.0, 138.7, 134.7, 131.7, 128.2, 113.8, 55.3, 50.6, 34.0, 32.5; **IR** (film, cm⁻¹) 3052, 2950, 2947, 1611, 1583, 1510, 1463, 1353, 1301, 1244, 1176, 1107, 1038, 913, 827, 715; **Exact mass calcd for [M⁺]** requires *m/z* 174.1045 Found 174.1043 (EI+).



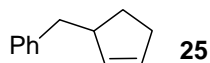
The compound **22** was prepared following General Procedure B and isolated as a colorless oil in 71% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in refluxing THF using I₂ as an initiator. **¹H-NMR** (CDCl₃, 500 MHz) δ 6.85 (s, 1H), 6.83 (s, 2H), 5.95-5.93 (m, 1H), 5.78-5.77 (m, 1H), 3.84-3.83 (m, 1H), 2.52-2.50 (m, 1H), 2.42-2.38 (m, 2H), 2.31 (s, 6H), 1.74-1.72 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 146.6, 138.0, 134.6, 131.8, 127.8, 125.2, 51.3, 33.9, 32.6, 21.4; **IR** (film, cm⁻¹) 2923, 1603, 1460, 1037, 909, 846, 735, 701; **Exact mass calcd for [M⁺]** requires *m/z* 172.1252 Found 172.1251 (EI+).



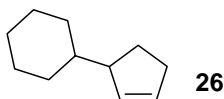
The compound **23** was prepared following General Procedure B and isolated as a colorless oil in 75% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in refluxing THF using I₂ as an initiator. **¹H-NMR** (CDCl₃, 500 MHz) δ 7.81 (t, *J* = 8.5 Hz, 3H), 7.64 (s, 1H), 7.48-7.43 (m, 2H), 7.36 (d, *J* = 8.5 Hz, 1H), 6.03-6.01 (m, 1H), 5.89-5.87 (m, 1H), 4.09 (bs, 1H), 2.58-2.47 (m, 3H), 1.85-1.82 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 144.0, 134.3, 133.7, 132.4, 132.3, 128.2, 127.7, 127.6, 126.3, 126.0, 125.3, 125.2, 51.5, 33.7, 32.7; **IR** (film, cm⁻¹) 3051, 2942, 1599, 1506, 854, 816, 745; **Exact mass calcd for [M⁺]** requires *m/z* 194.1096 Found 194.1094 (EI+).



The compound **24** was prepared following General Procedure B and isolated as a colorless oil in 56% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.45-7.44 (m, 2H), 7.36-7.32 (m, 2H), 7.29-7.26 (m, 1H), 5.92-5.90 (m, 1H), 5.79-5.78 (m, 1H), 5.26 (s, 1H), 5.04 (s, 1H), 3.87-3.86 (m, 1H), 2.39-2.35 (m, 2H), 2.27-2.23 (m, 1H), 1.67-1.63 (m, 1H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 152.4, 142.1, 133.4, 132.0, 128.3, 127.3, 126.5, 110.9, 49.9, 32.1, 31.2; **IR** (film, cm^{-1}) 3054, 2939, 2848, 1625, 1493, 1028, 906, 777, 733, 701; **Exact mass calcd for $[\text{M}^+]$** requires m/z 170.1096 Found 170.1097 (EI+).

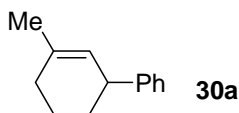


The compound **25** was prepared following General Procedure B and isolated as a colorless oil in 89% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.32-7.29 (m, 2H), 7.23-7.20 (m, 3H), 5.78-5.77 (m, 1H), 5.70-5.68 (m, 1H), 3.01-3.00 (m, 1H), 2.73-2.61 (m, 2H), 2.38-2.29 (m, 2H), 2.04-2.01 (m, 1H), 1.56-1.52 (m, 1H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 141.5, 134.8, 130.8, 129.1, 128.3, 125.8, 47.4, 42.3, 32.0, 29.7; **IR** (film, cm^{-1}) 3027, 2924, 2849, 1603, 1495, 1453, 1357, 1078, 909, 699; **Exact mass calcd for $[\text{M}^+]$** requires m/z 158.1095 Found 158.1094 (EI+).

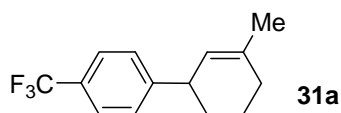


The compound **26** was prepared following General Procedure B and isolated as a colorless oil in 75% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 5.74-5.73 (m, 2H), 2.45-2.43 (m, 1H), 2.29-2.23 (m, 2H), 1.97-1.92 (m, 1H), 1.76-1.63 (m, 5H), 1.54-1.46 (m, 1H), 1.25-1.11 (m, 4H), 0.97-0.91 (m, 2H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 133.6, 130.7, 51.9, 43.1, 32.3, 31.3, 31.2, 27.5, 26.9, 26.7, 26.6;

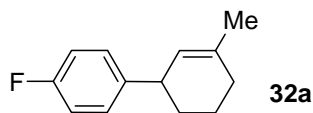
IR (film, cm^{-1}) 3053, 2923, 2850, 1448, 1353, 1265, 1005, 889, 719; **Exact mass calcd for** $[\text{M}^+]$ requires m/z 150.1408 Found 150.1408 (EI+).



The compound **30a** was prepared following General Procedure B. Regioisomer **25b** was not observed in the ^1H NMR spectrum of the unpurified residue following typical workup procedures. The yield is not available due to the instability of this compound. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.31-7.28 (m, 2H), 7.22-7.18 (m, 3H), 5.44 (s, 1H), 3.38-3.37 (m, 1H), 2.02-1.94 (m, 3H), 1.78-1.76 (m, 1H), 1.75 (s, 3H), 1.63-1.62 (m, 1H), 1.51-1.47 (m, 1H).

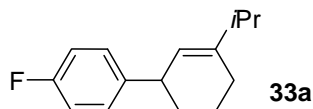


The compound **31a** was prepared following General Procedure B and isolated as colorless oil in 81% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.55 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H), 5.42-5.41 (m, 1H), 3.45-3.43 (m, 1H), 2.05-1.97 (m, 3H), 1.77-1.76 (m, 1H), 1.77 (s, 3H), 1.65-1.64 (m, 1H), 1.48-1.45 (m, 1H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 151.5, 136.4, 128.3 (q, $^2J_{\text{C-F}} = 32.0$ Hz), 128.2, 125.2 (q, $^3J_{\text{C-F}} = 3.6$ Hz), 124.5 (q, $^1J_{\text{C-F}} = 270.0$ Hz), 123.5, 42.2, 32.3, 29.9, 24.1, 21.5; **IR** (film, cm^{-1}) 2931, 1618, 1417, 1325, 1162, 1124, 1068, 1018, 908, 838, 735.

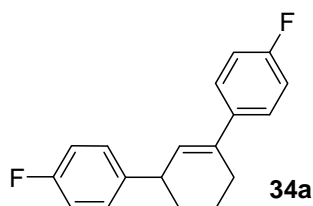


The compound **32a** was prepared following General Procedure B and isolated as colorless oil in 75% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was purchased from Sigma-Aldrich (1.0 M solution in THF). **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.18-7.15 (m, 2H), 6.99-6.96 (m, 2H), 5.41 (bs, 1H), 3.37-3.35 (m, 1H), 2.02-1.93 (m, 3H), 1.75 (s, 3H), 1.75-1.74 (m, 1H), 1.63-1.61 (m, 1H), 1.47-1.42

(m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 161.4 (d, ¹J_{C-F} = 241.6 Hz), 142.9, 135.7, 129.2 (d, ³J_{C-F} = 7.8 Hz), 124.3, 115.0 (d, ²J_{C-F} = 21.1 Hz), 41.5, 32.6, 30.0, 24.1, 21.5; **IR** (film, cm⁻¹) 2929, 2858, 1603, 1507, 1446, 1222, 1156, 1093, 1015, 888, 829; **Exact mass calcd for** [M⁺] requires *m/z* 190.1158 Found 190.1155 (EI+).

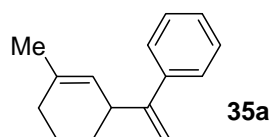


The compound **33a** was prepared following General Procedure B and isolated as light yellow oil in 70% yield that was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was purchased from Sigma-Aldrich (1.0 M solution in THF). **¹H-NMR** (CDCl₃, 500 MHz) δ 7.16-7.13 (m, 2H), 6.99-6.95 (m, 2H), 5.42-5.39 (m, 1H), 3.39-3.35 (m, 1H), 2.26-2.23 (m, 1H), 2.05-2.01 (m, 2H), 1.98-1.94 (m, 1H), 1.76-1.70 (m, 1H), 1.61-1.56 (m, 1H), 1.46-1.40 (m, 1H), 1.06 (d, *J* = 7.0 Hz, 6H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 161.5 (d, *J* = 241.6 Hz), 145.5, 143.3 (d, *J* = 2.8 Hz), 129.3 (d, *J* = 7.8 Hz), 121.7, 115.1 (d, *J* = 21.0 Hz), 41.4, 35.5, 33.2 (d, *J* = 1.0 Hz), 16.1, 21.8, 21.7, 21.7; **IR** (film, cm⁻¹) 2956, 1509, 1230, 822; **Exact mass calcd for** [M⁺] requires *m/z* 218.1471 Found 218.1470 (EI+).

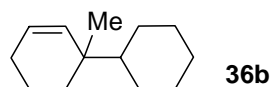


The compound **34a** was prepared following General Procedure B and isolated as light yellow oil in 70% yield that was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard was purchased from Sigma-Aldrich (1.0 M solution in THF). **¹H-NMR** (CDCl₃, 500 MHz) δ 7.43-7.38 (m, 2H), 7.26-7.18 (m, 2H), 7.06-6.97 (m, 4H), 6.07-6.05 (m, 1H), 3.59-3.55 (m, 1H), 2.51-2.45 (m, 2H), 2.10-2.03 (m, 1H), 1.95-1.89 (m, 1H), 1.81-1.75 (m, 1H), 1.62-1.54 (m, 1H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 162.2 (d, *J* = 244 Hz), 161.6 (d, *J* = 242 Hz), 142.4 (d, *J* = 3.1 Hz), 138.4 (d, *J* = 3.1 Hz), 137.2, 129.4 (d, *J* = 7.8 Hz), 127.6 (d, *J* = 1.4 Hz), 126.9 (d, *J* = 7.8 Hz), 115.3 (d, *J* = 21.1 Hz), 115.2 (d, *J* = 21.1 Hz), 42.1, 32.5 (d, *J* = 0.9 Hz), 27.7, 21.8; **IR** (film, cm⁻¹) 2831, 1802, 1508, 1222,

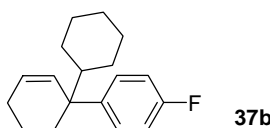
1169, 1094, 824, 537; **Exact mass calcd for** $[M^+]$ requires m/z 270.1220 Found 270.1221 (EI+).



The compound **35a** was prepared following General Procedure B and isolated as colorless oil in 55% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 7.40-7.38 (m, 2H), 7.34-7.31 (m, 2H), 7.28-7.26 (m, 1H), 5.42 (m, 1H), 5.27 (m, 1H), 5.03 (m, 1H), 3.34 (m, 1H), 1.94-1.93 (m, 2H), 1.72 (s, 3H), 1.76-1.68 (m, 2H), 1.55 (m, 1H), 1.38-1.36 (m, 1H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 153.0, 142.3, 135.4, 128.3, 127.3, 126.7, 123.9, 112.9, 40.3, 30.3, 28.3, 24.1, 20.8; **IR** (film, cm^{-1}) 2927, 1623, 1491, 1455, 1120, 1028, 896, 777, 698; **Exact mass calcd for** $[M^+]$ requires m/z 198.1409 Found 198.1410 (EI+).

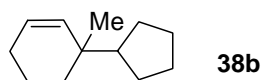


The compound **36b** was prepared following General Procedure B and isolated as a colorless oil in 81% yield and was homogeneous as judged by ^1H NMR spectroscopy. The corresponding Grignard was prepared in Et_2O at rt using I_2 as an initiator. **^1H -NMR** (CDCl_3 , 500 MHz) δ 5.61-5.57 (m, 1H), 5.43 (d, $J = 10.0$ Hz, 1H), 1.91-1.90 (m, 2H), 1.79-1.54 (m, 8H), 1.29-1.08 (m, 5H), 1.03-0.93 (m, 2H), 0.92 (s, 3H); **^{13}C -NMR** (CDCl_3 , 125 MHz) δ 137.1, 125.1, 47.8, 36.9, 31.6, 27.7, 27.4, 27.3, 27.2, 27.0, 25.4, 25.0, 19.5; **IR** (film, cm^{-1}) 3010, 2926, 2851, 1449, 1367, 731; **Exact mass calcd for** $[M^+]$ requires m/z 178.1722 Found 178.1724 (EI+).

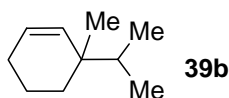


The compound **37b** was prepared following General Procedure B in 47% yield as a mixture of regioisomers (**37a**:**37b** = 15:85). The major regioisomer was separated by AgNO_3

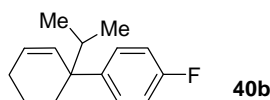
impregnated silica gel⁴ as light yellow oil and was judged homogeneous by ¹H NMR spectroscopy: **¹H-NMR** (CDCl₃, 500 MHz) δ 7.24-7.21 (m, 2H), 6.98-6.94 (m, 2H), 5.86-5.85 (m, 2H), 1.99-1.87 (m, 4H), 1.74-1.71 (m, 2H), 1.64-1.62 (m, 2H), 1.56-1.49 (m, 2H), 1.33-1.30 (m, 1H), 1.26-1.03 (m, 4H), 0.96-0.90 (m, 2H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 160.9 (d, *J* = 242.1 Hz), 144.2 (d, *J* = 3.1 Hz), 132.2, 129.2 (d, *J* = 7.4 Hz), 128.5, 114.6 (d, *J* = 20.5 Hz), 48.3, 45.9, 32.2, 28.3, 27.9, 27.3, 27.3, 27.0, 25.9, 19.2; **IR** (film, cm⁻¹) 2927, 2852, 1801, 1506, 1449, 1231, 1181, 928, 674; **Exact mass calcd for [M⁺]** requires *m/z* 258.1784 Found 258.1787 (EI+).



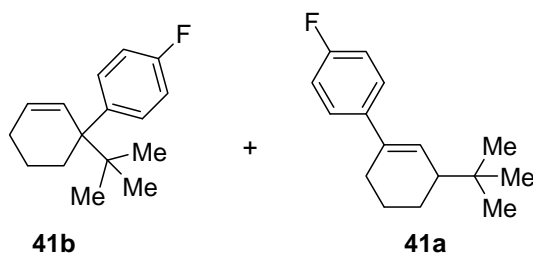
The compound **38b** was prepared following General Procedure B and isolated as a colorless oil in 80% yield as a mixture of regioisomers (**38a:38b** = 13:87) as judged by ¹H NMR spectroscopy. The corresponding Grignard was prepared in Et₂O at rt using I₂ as an initiator. **¹H-NMR** (CDCl₃, 500 MHz) δ 5.62-5.59 (m, 1H), 5.45 (d, *J* = 9.5 Hz, 1H), 5.38 (s, 1H, **22b**), 1.94-1.72 (m, 3H), 1.65-1.45 (m, 9H), 1.38-1.23 (m, 3H), 0.93 (s, 3H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 135.9, 125.6, 50.3, 33.7, 27.1, 27.0, 26.1, 26.0, 25.5, 25.4, 25.2, 19.4; **IR** (film, cm⁻¹) 2951, 1456, 1135, 907, 734; **Exact mass calcd for [M⁺]** requires *m/z* 164.1565 Found 164.1565 (EI+).



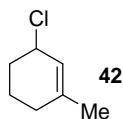
The compound **39b** was prepared following General Procedure B and isolated as a colorless oil in 86% yield and was homogeneous as judged by ¹H NMR spectroscopy. The corresponding Grignard (*i*-PrMgCl) was purchased from Acros Organics (2.0 M solution in THF). **¹H-NMR** (CDCl₃, 500 MHz) δ 5.62-5.58 (m, 1H), 5.44 (dd, *J* = 10.5, 1.0 Hz, 1H), 1.93-1.89 (m, 2H), 1.66-1.48 (m, 4H), 1.31-1.29 (m, 1H), 0.91 (s, 3H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.83 (d, *J* = 6.5 Hz, 3H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 136.8, 125.3, 36.9, 31.1, 25.4, 24.4, 19.4, 17.8, 17.2; **IR** (film, cm⁻¹) 3013, 2958, 1457, 1367, 731, 712; **Exact mass calcd for [M-H⁺]** requires *m/z* 137.1330 Found 137.1328 (EI+).



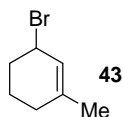
The compound **40b** was prepared following General Procedure B in 61% yield as a mixture of regioisomers (**40a**:**40b** = 15:85). The major regioisomer was separated by AgNO₃ impregnated silica gel⁴ as light yellow oil and was judged homogeneous by ¹H NMR spectroscopy: **¹H-NMR** (CDCl₃, 500 MHz) δ 7.26-7.23 (m, 2H), 6.98-6.94 (m, 2H), 5.94-5.90 (m, 1H), 5.84-5.81 (m, 1H), 1.99-1.95 (m, 2H), 1.88-1.84 (m, 2H), 1.54-1.51 (m, 1H), 1.25-1.21 (m, 2H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.68 (d, *J* = 6.5 Hz, 3H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 160.9 (d, *J* = 241.8 Hz), 144.3, 131.1, 129.1 (d, *J* = 8.6 Hz), 129.1, 114.6 (d, *J* = 20.6 Hz), 40.1, 37.4, 32.6, 30.5, 29.9, 19.2, 18.2, 18.1; **IR** (film, cm⁻¹) 2957, 1509, 1230, 622; **Exact mass calcd for [M⁺]** requires *m/z* 218.1471 Found 218.1473 (EI+).



The compound **41a** and **41b** was prepared following General Procedure B in 48% yield as a 1:1 mixture and separated by AgNO₃ impregnated silica gel.⁴ The products were judged homogeneous by ¹H NMR spectroscopy: For **41a** **¹H-NMR** (CDCl₃, 500 MHz) δ 7.35-7.32 (m, 2H), 7.00-6.97 (m, 2H), 6.06-6.05 (m, 1H), 2.34-2.28 (m, 2H), 2.02-1.97 (m, 2H), 1.86-1.82 (m, 1H), 1.60-1.56 (m, 1H), 1.26-1.23 (m, 1H), 0.93 (s, 9H); **¹³C-NMR** (CDCl₃, 125 MHz) δ 162.0 (d, *J* = 244.0 Hz), 139.1 (d, *J* = 3.3 Hz), 136.3, 128.8 (d, *J* = 1.4 Hz), 126.8 (d, *J* = 7.8 Hz), 115.1 (d, *J* = 21.0 Hz), 42.6, 32.8, 28.1, 25.2, 22.8, 20.1, 19.7; **IR** (film, cm⁻¹) 2957, 2867, 1601, 1509, 1468, 1356, 1221, 1162, 824; **Exact mass calcd for [M⁺]** requires *m/z* 232.1627 Found 232.1631 (EI+). For **41b** **¹H-NMR** (CDCl₃, 500 MHz) δ 7.28-7.24 (m, 2H), 6.96-6.91 (m, 2H), 6.22-6.19 (m, 1H), 5.80-5.77 (1, 2H), 2.33-2.29 (m, 1H), 1.98-1.88 (m, 2H), 1.78-1.72 (m, 1H), 1.22-1.14 (m, 2H), 0.84 (s, 9H).



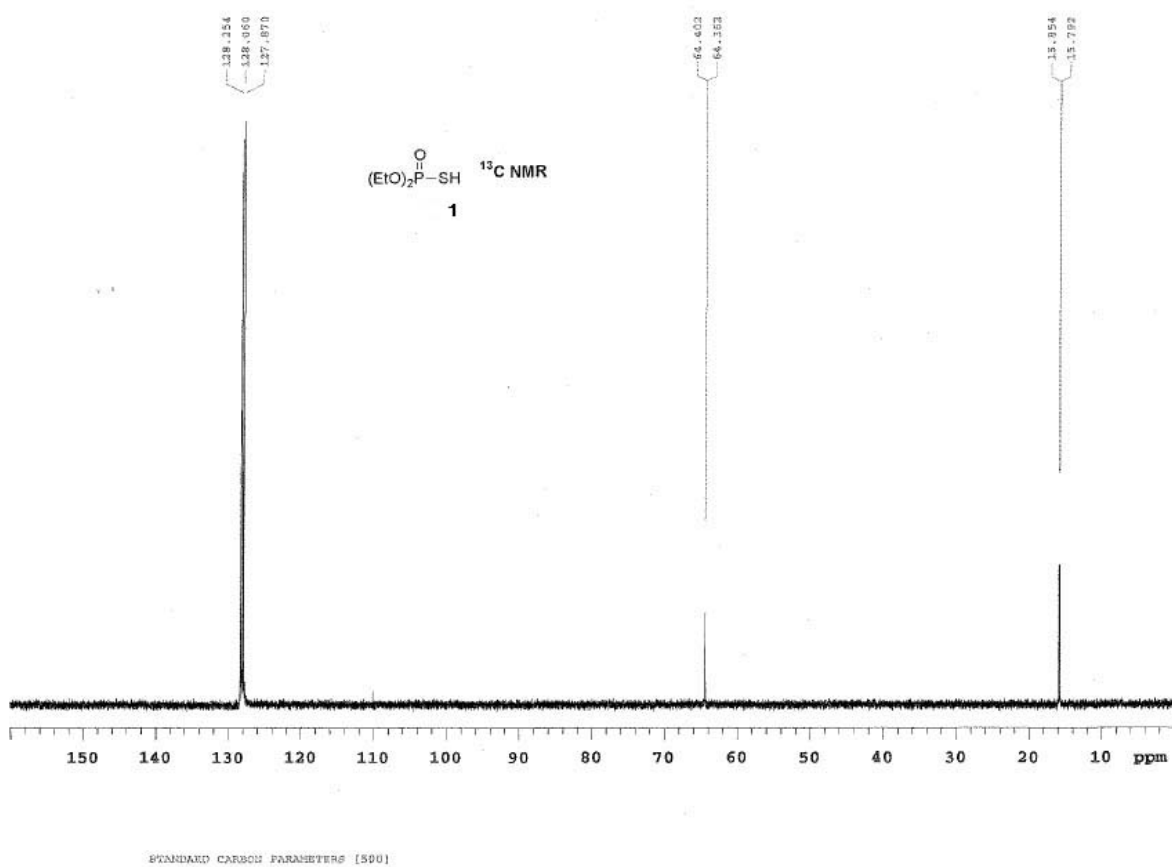
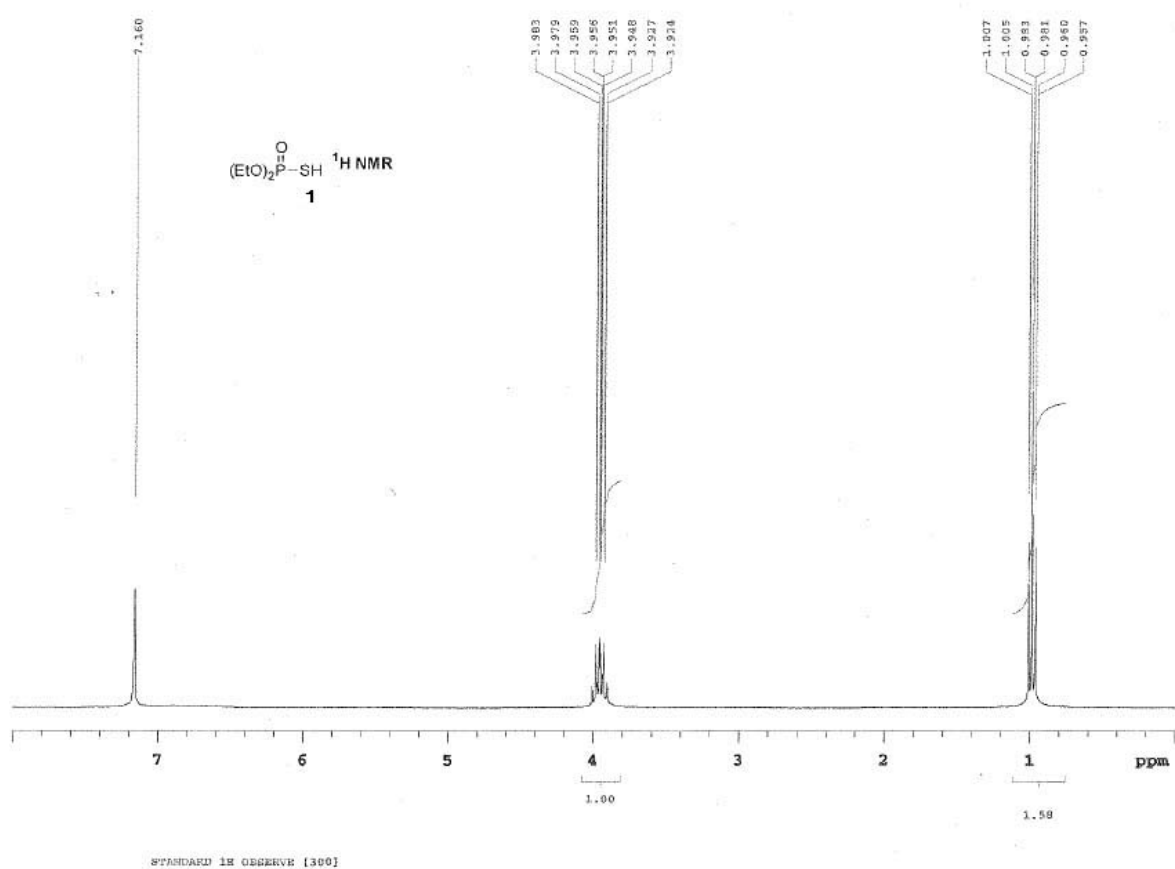
2-cyclohexenone (10 mmol, 0.97 mL) was added to Et₂O (40 mL) under N₂ at 0 °C. This was followed by the addition of a solution of methylmagnesium bromide (1.0 M in THF, 10 mL). The reaction was stirred at rt and monitored by TLC. Upon completion, the reaction was quenched with water (10 mL) and the aqueous phase was extracted with Et₂O (3×30 mL). The combined organic phases were sequentially washed with saturated NH₄Cl aq. (20 mL), saturated NaHCO₃ aq. (20 mL) and saturated NaCl aq. (20 mL). After being dried over MgSO₄ and concentrated by rotary evaporator, the residue was purified by silica gel column chromatography (EtOAc/hexanes) to afford 1-methyl-2-cyclohexenol as colorless oil. Then, 1-methyl-2-cyclohexenol (3 mmol, 0.34mL) was added to 1.2 mL concentrated hydrochloric acid, followed by the addition of 20 mL CH₂Cl₂ to the reaction mixture. The organic phases were separated and were sequentially washed with saturated NaHCO₃ aq. (2×20 mL) and saturated NaCl aq. (20 mL). After being dried over MgSO₄ and concentrated by rotary evaporator, compound **42** was obtained as a light yellow oil that was homogeneous as judged by ¹H NMR spectroscopy. This compound was used without further purification due to its instability towards silica gel: **¹H-NMR** (CD₂Cl₂, 300 MHz) δ 5.59-5.57 (m, 1H), 4.68-4.64 (m, 1H), 2.06-1.90 (m, 6H), 1.71 (s, 3H).

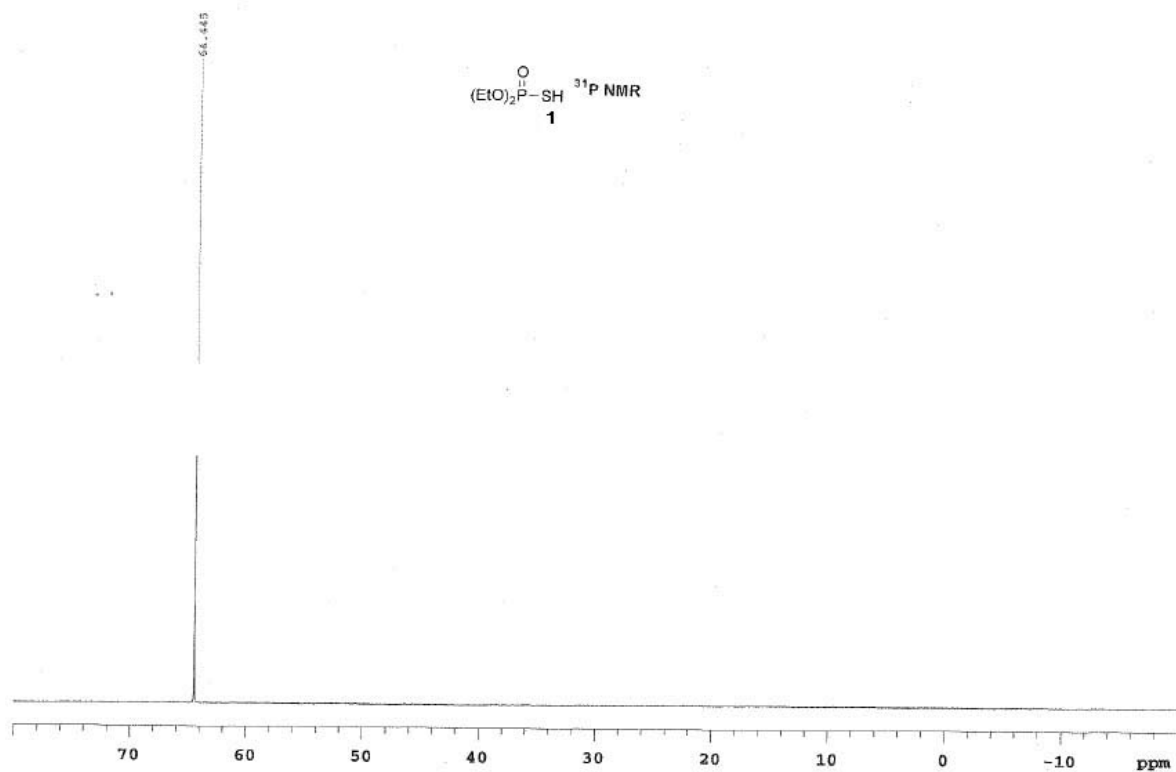


The title compound **43** was prepared following procedure to make **42** with the only difference being the addition of hydrobromic acid instead of hydrochloric acid. Compound **43** was isolated as colorless oil that was homogeneous as judged by ¹H NMR spectroscopy: **¹H-NMR** (CD₂Cl₂, 300 MHz) δ 5.71-5.68 (m, 1H), 4.96-4.92 (m, 1H), 2.20-2.15 (m, 1H), 2.12-2.08 (m, 2H), 2.20-1.93 (m, 2H), 1.73-1.71 (m, 1H), 1.71 (s, 3H).

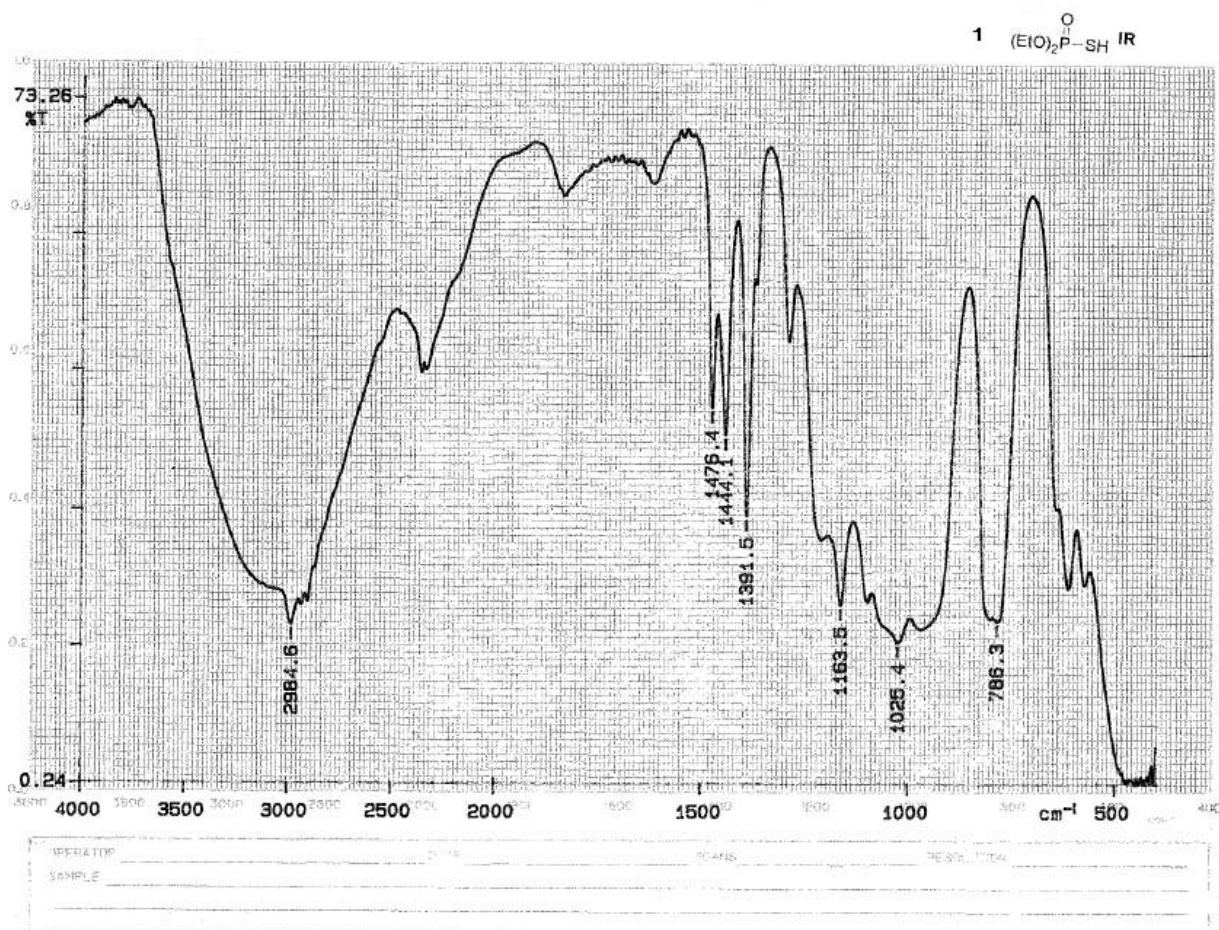
III. References.

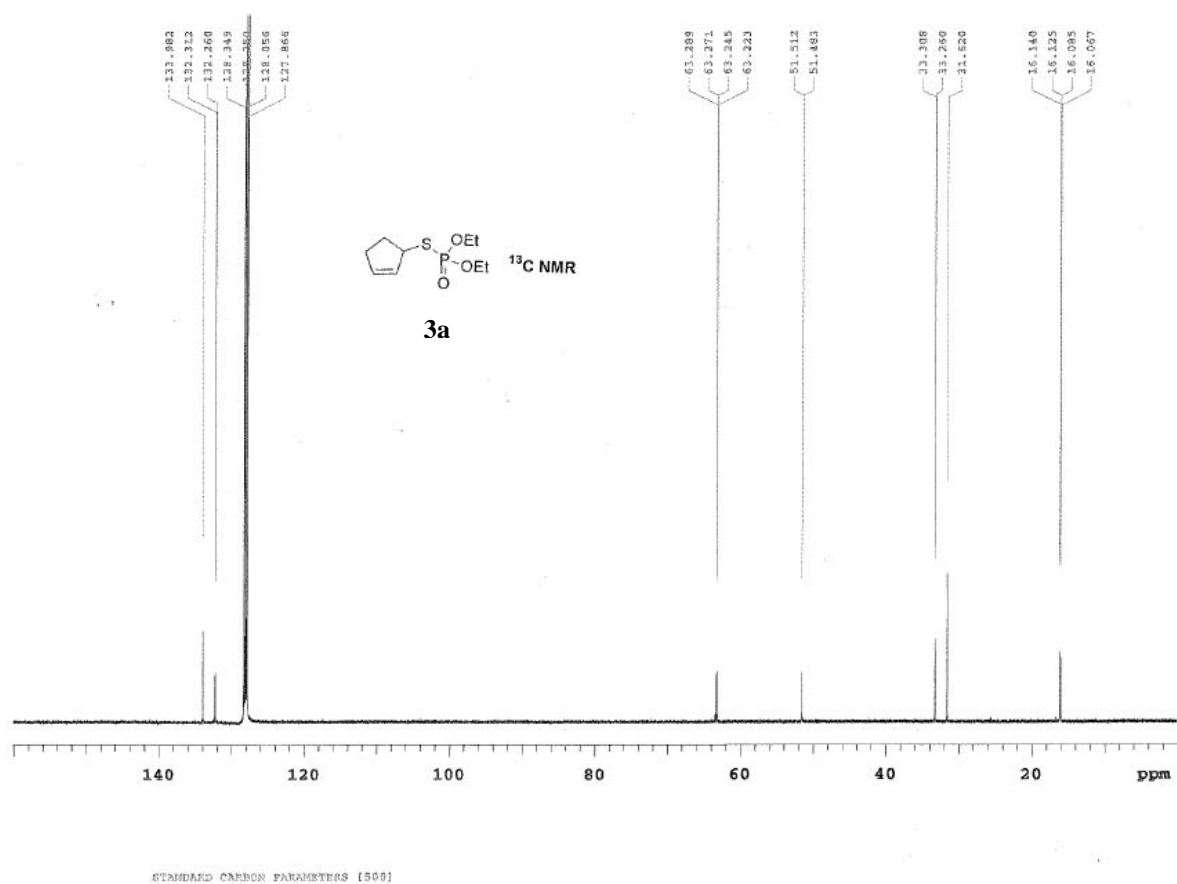
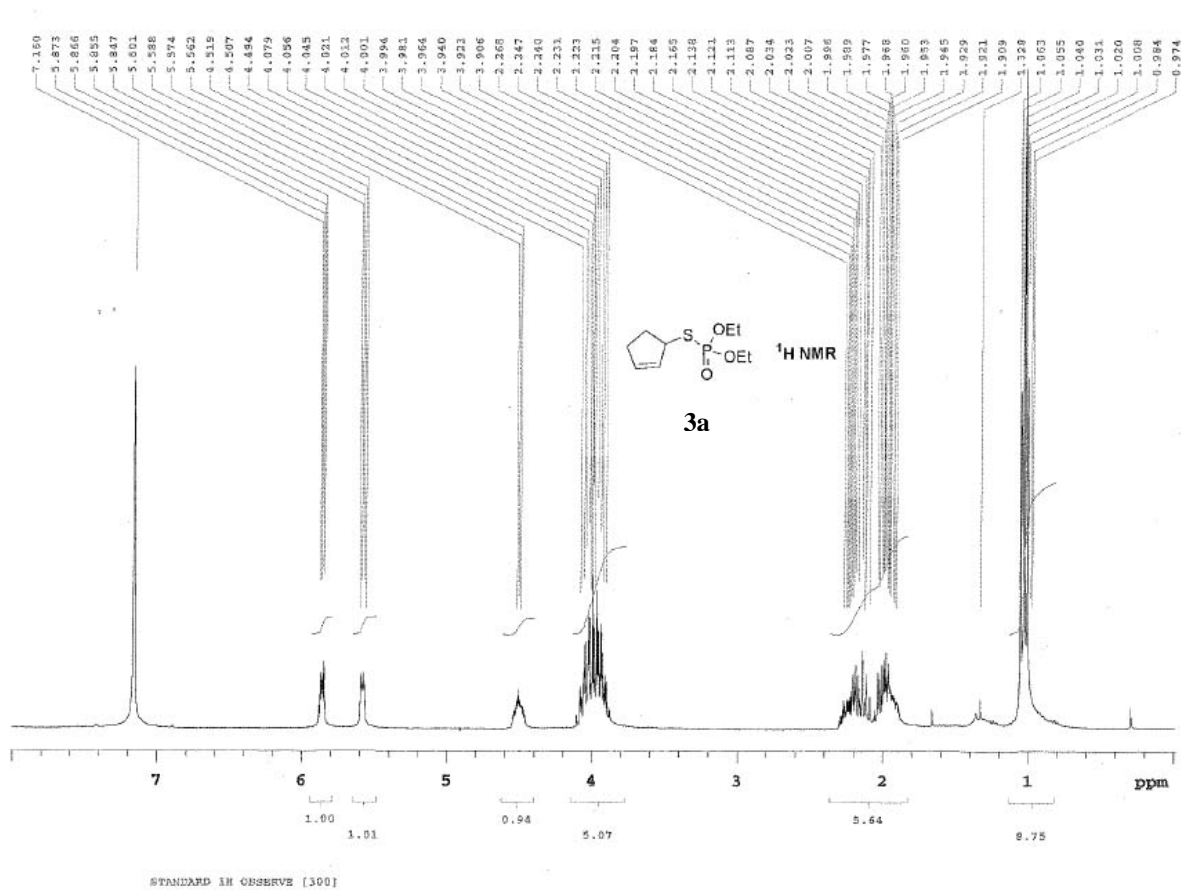
- (1) Foss, O. *Acta Chem. Scand.* **1947**, *1*, 8–31.
- (2) Organ, M. G.; Abdel-Hadi, M.; Avola, S.; Hadei, N.; Nasielski, J.; O'Brien, C. J.; Valente, C. *Chem.—Eur. J.* **2006**, *13*, 150–157.
- (3) Boymond, L.; Rottländer, M.; Cahiez, G.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1701–1703.
- (4) Li, T.-S.; Li, J.-T.; Li, H.-Z. *J. Chromatography A* **1995**, *715*, 372–375.

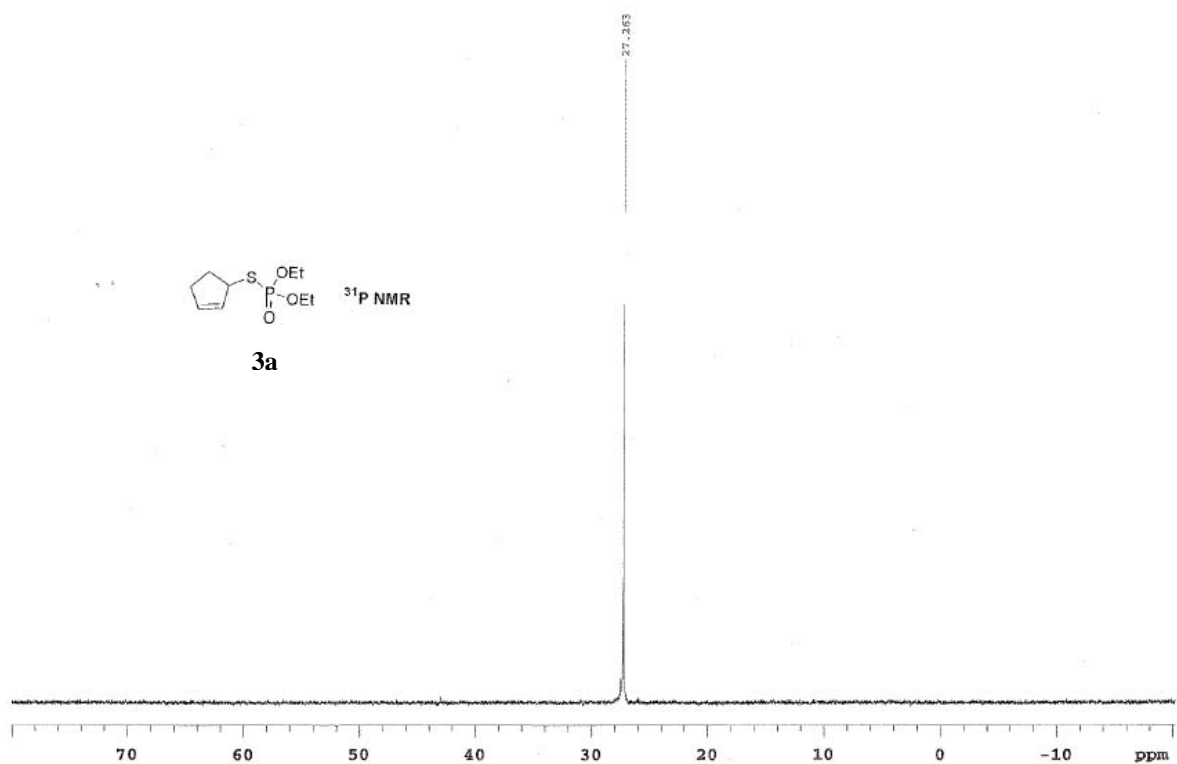




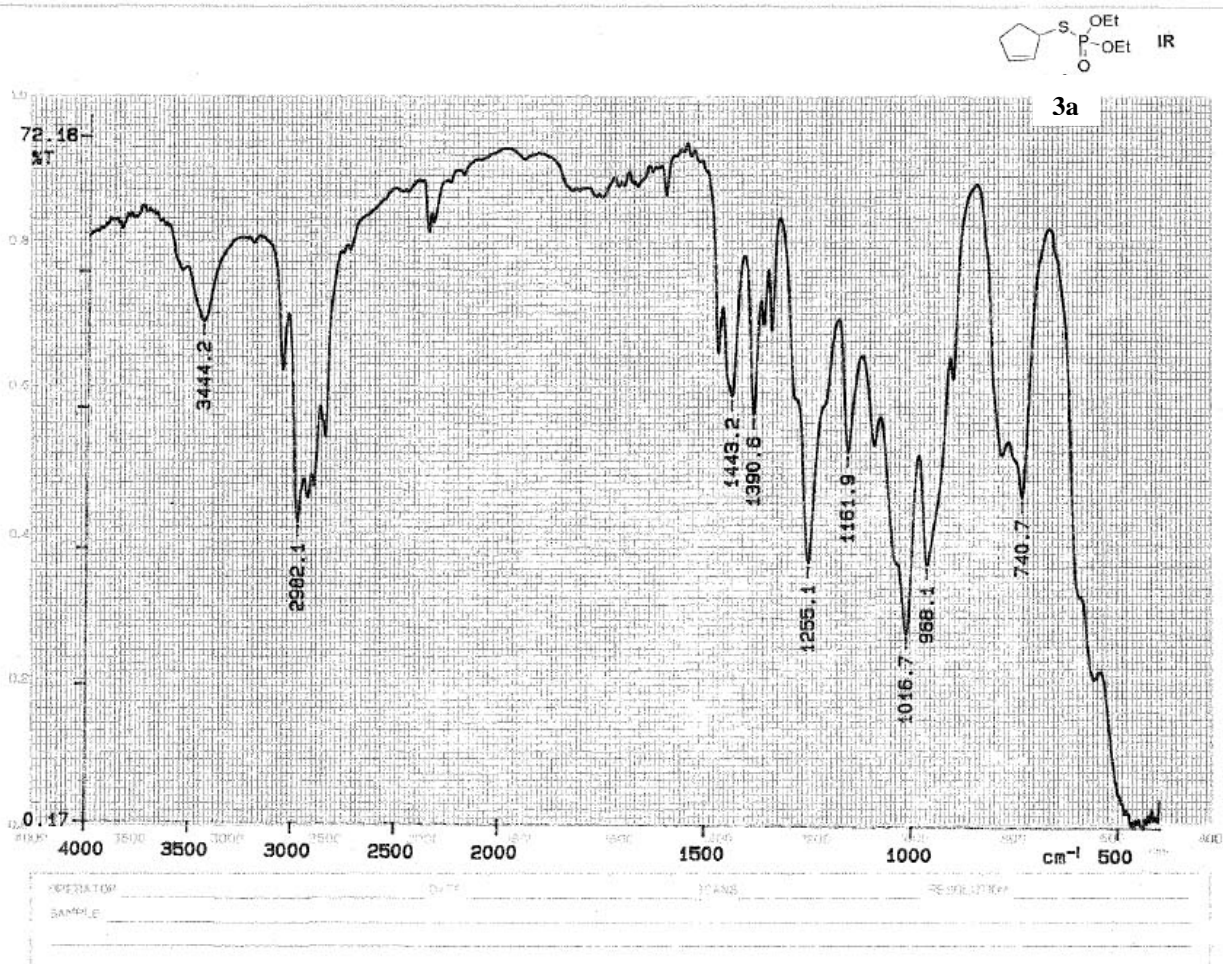
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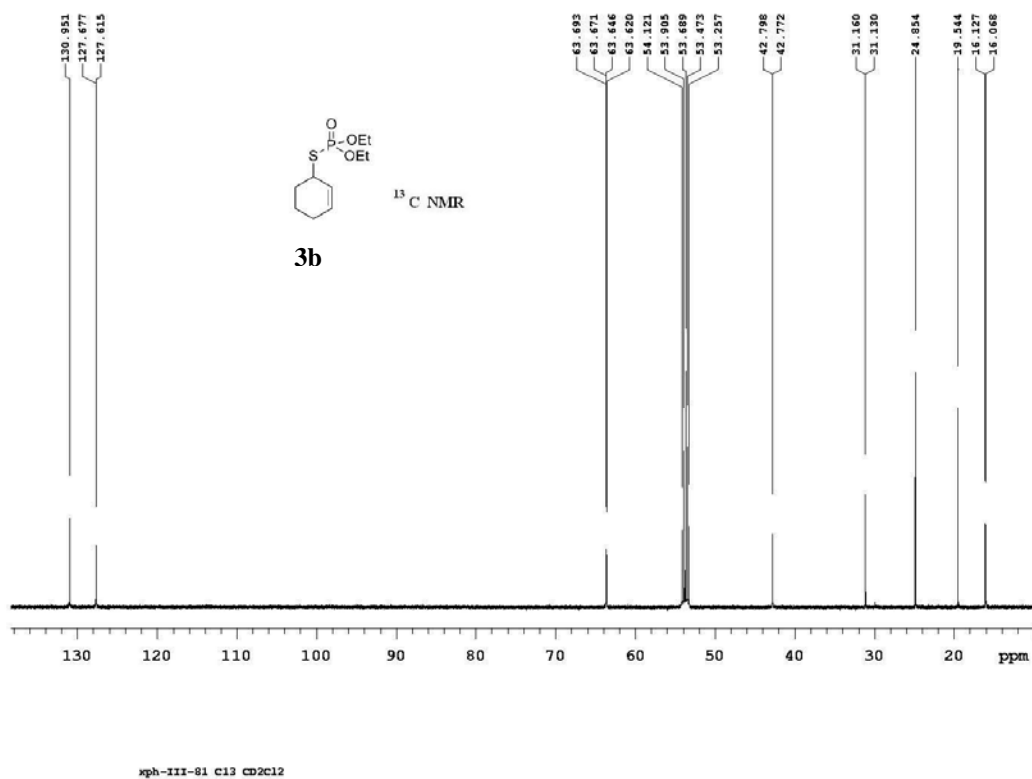
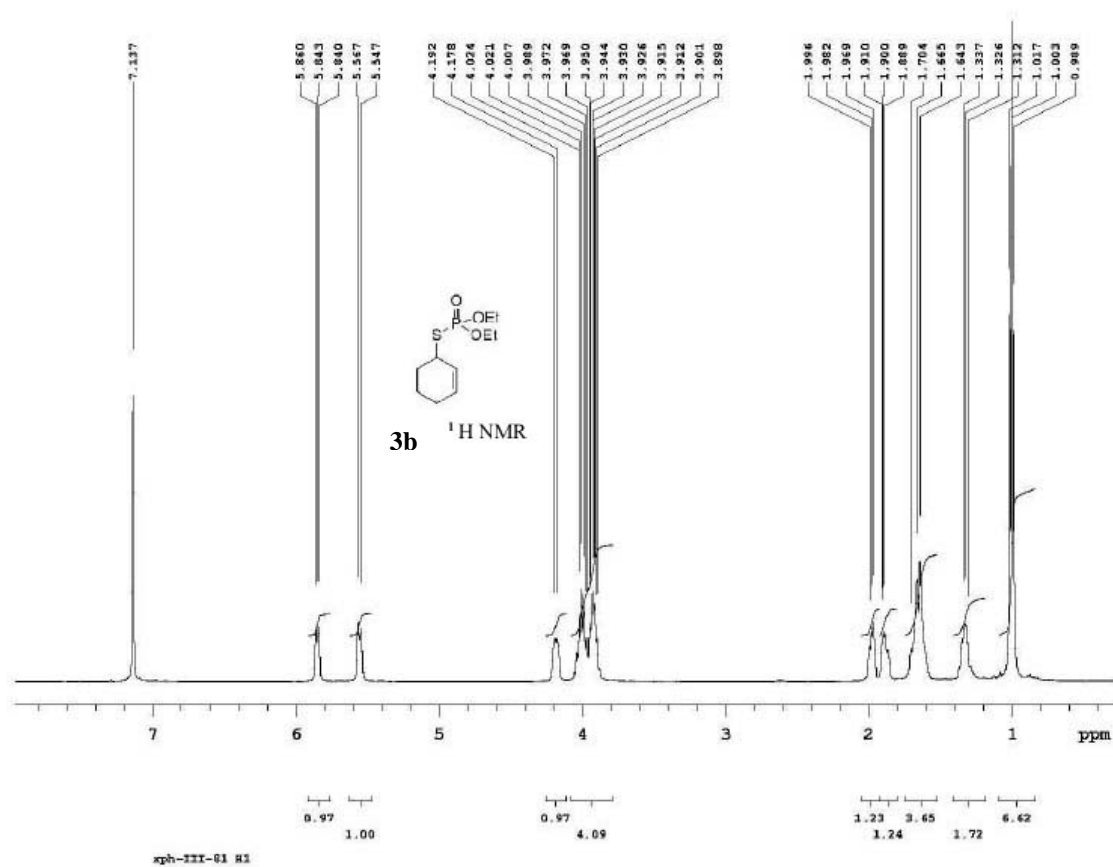


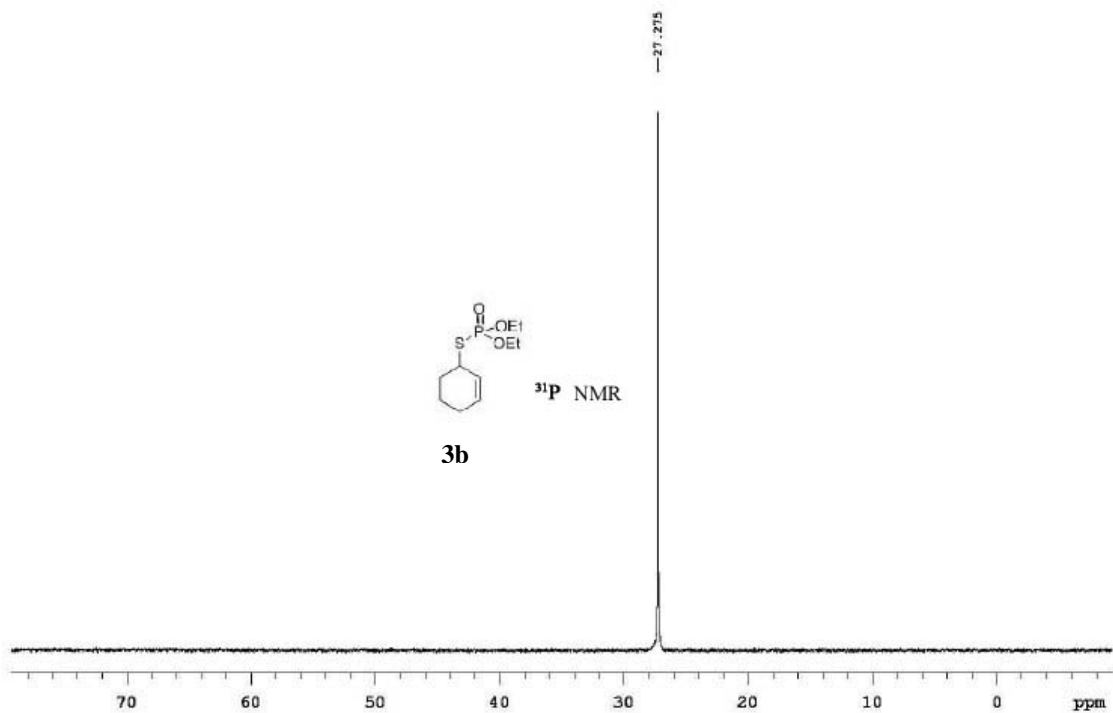




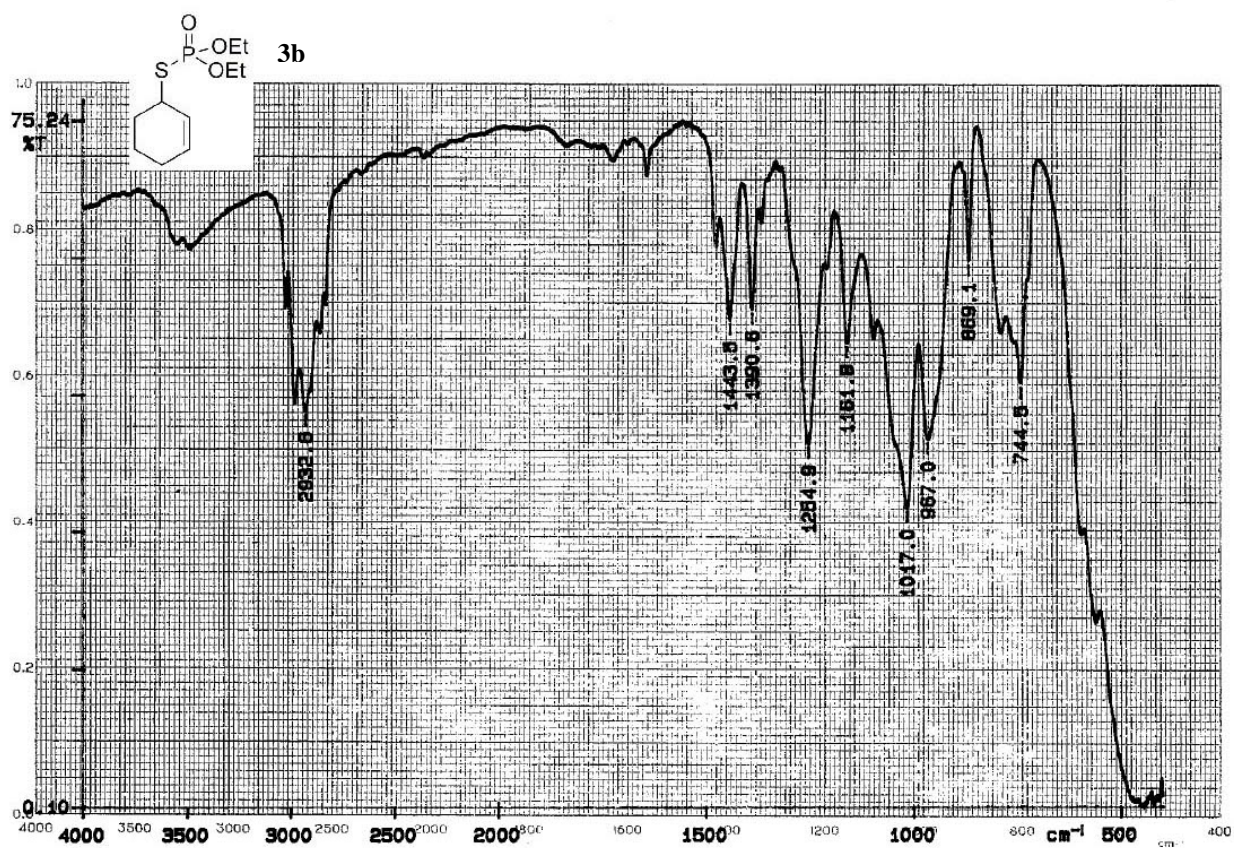
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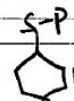


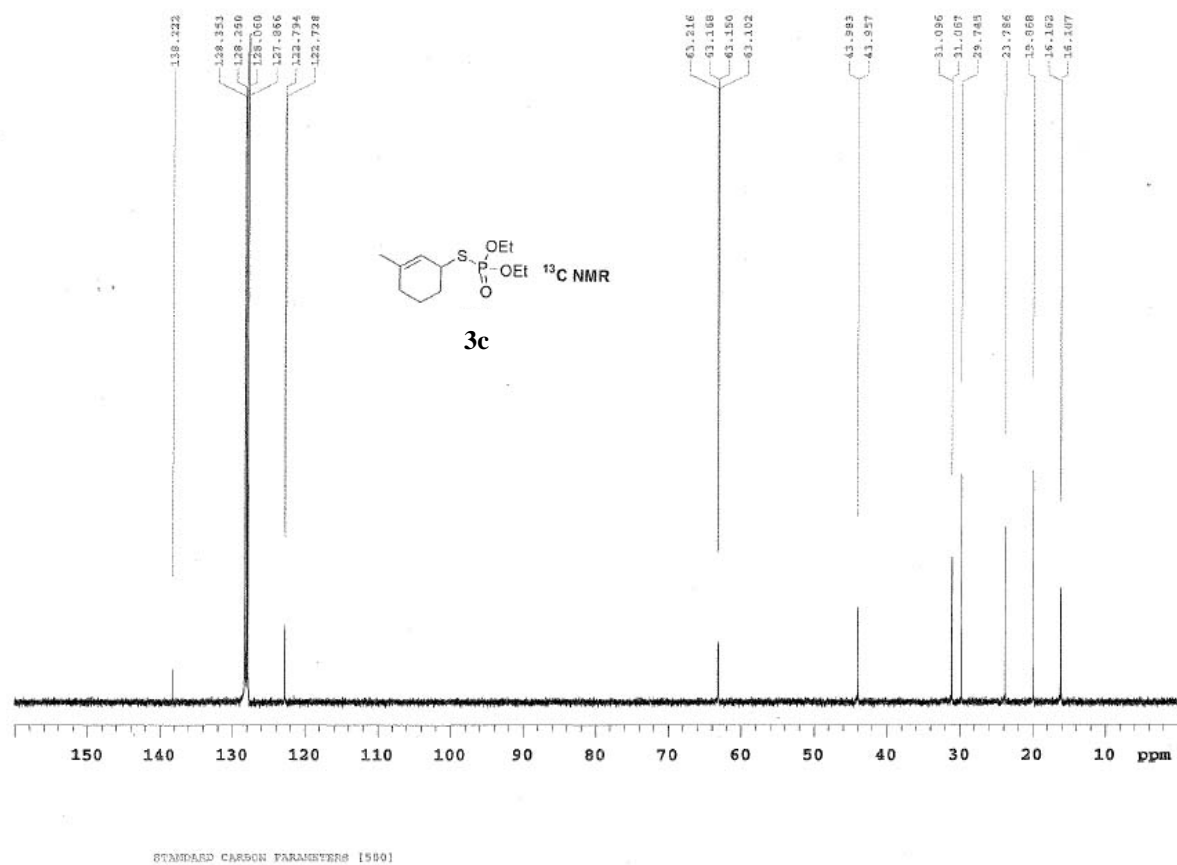
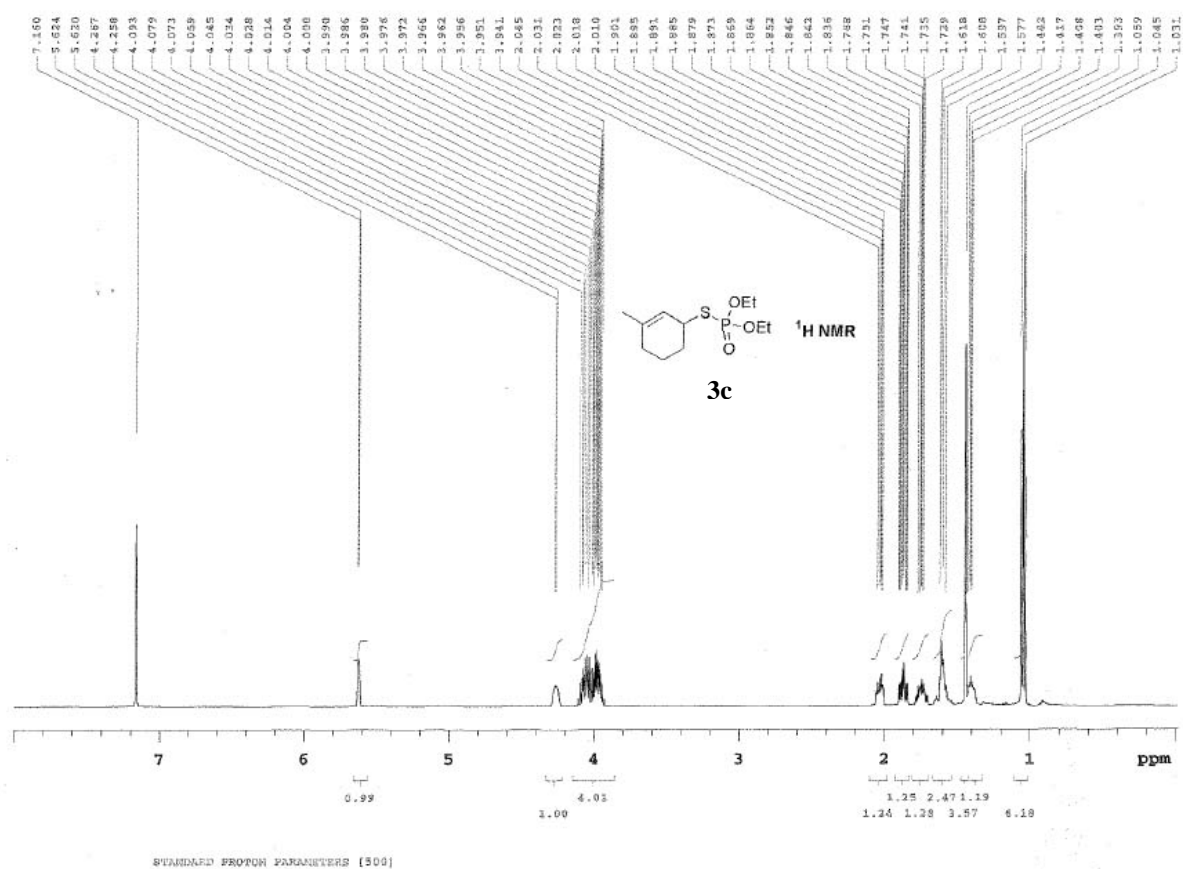


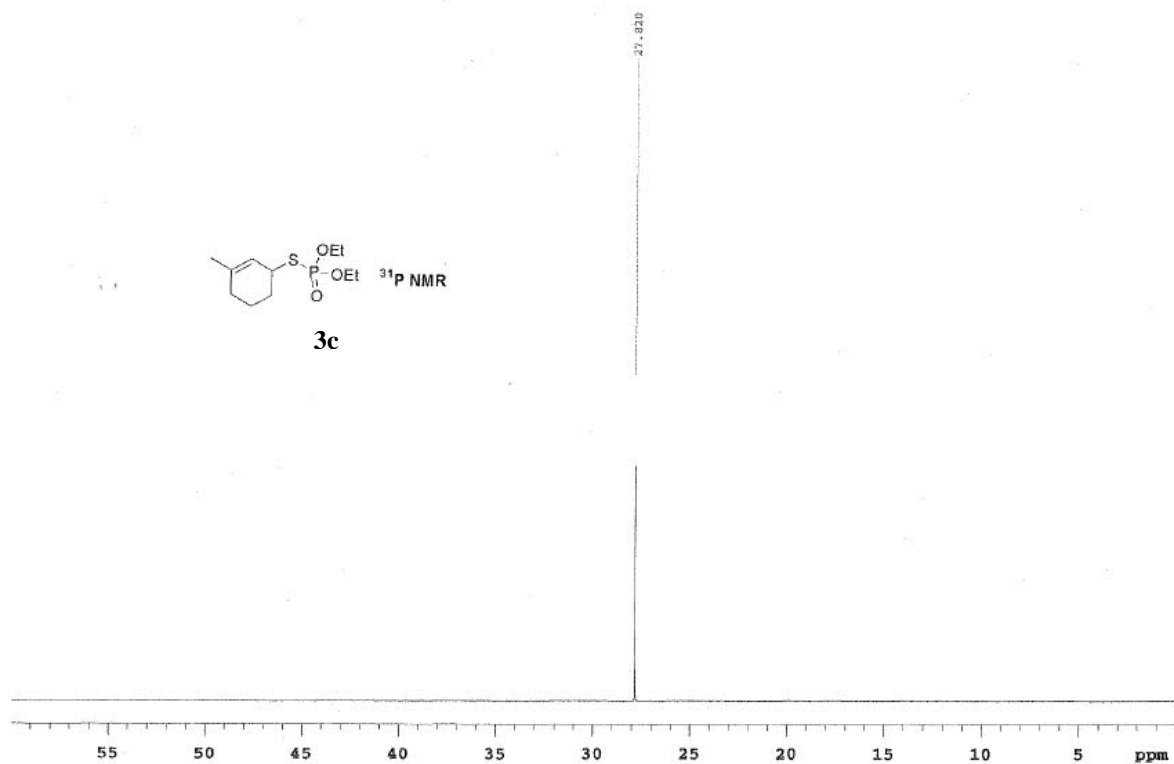
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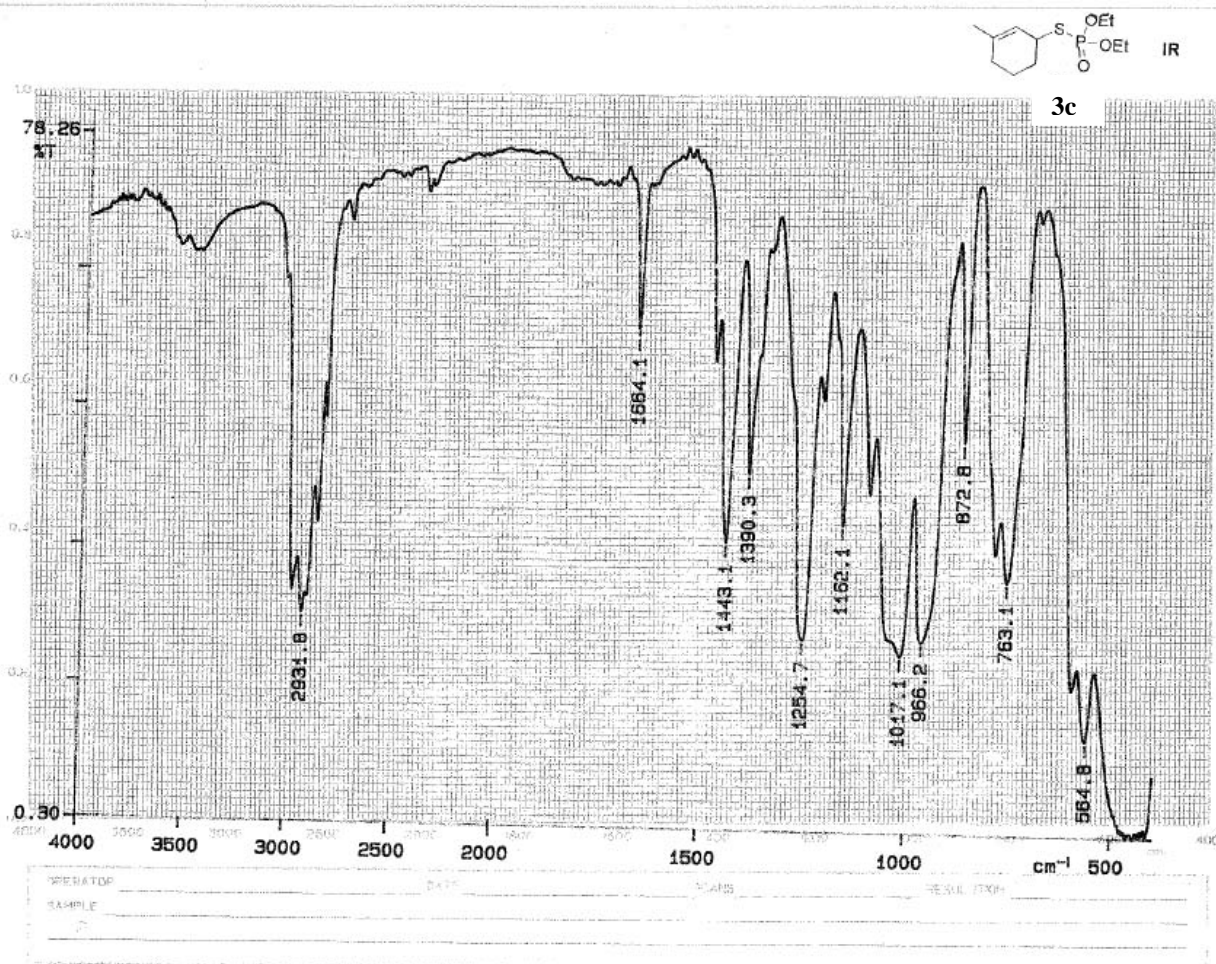
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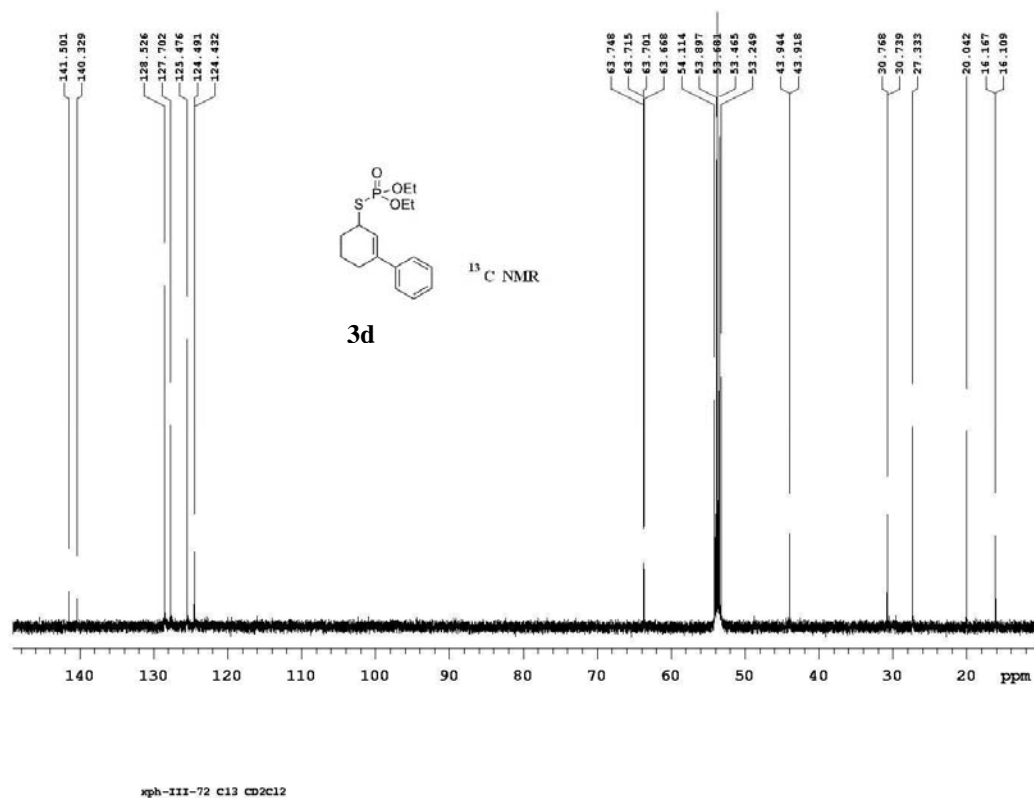
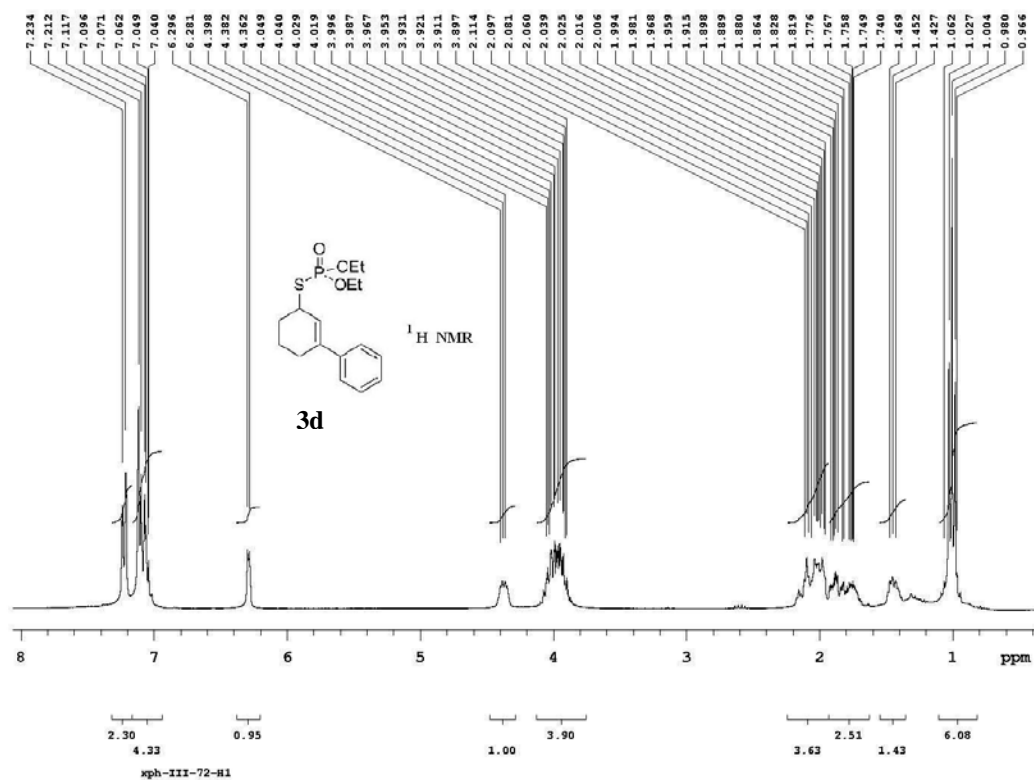


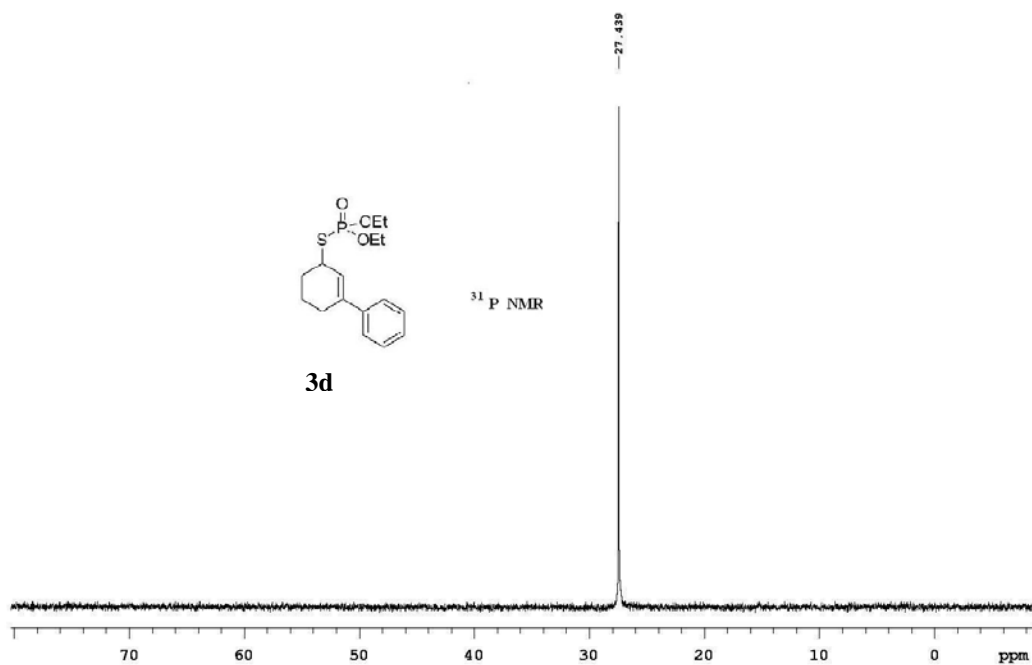




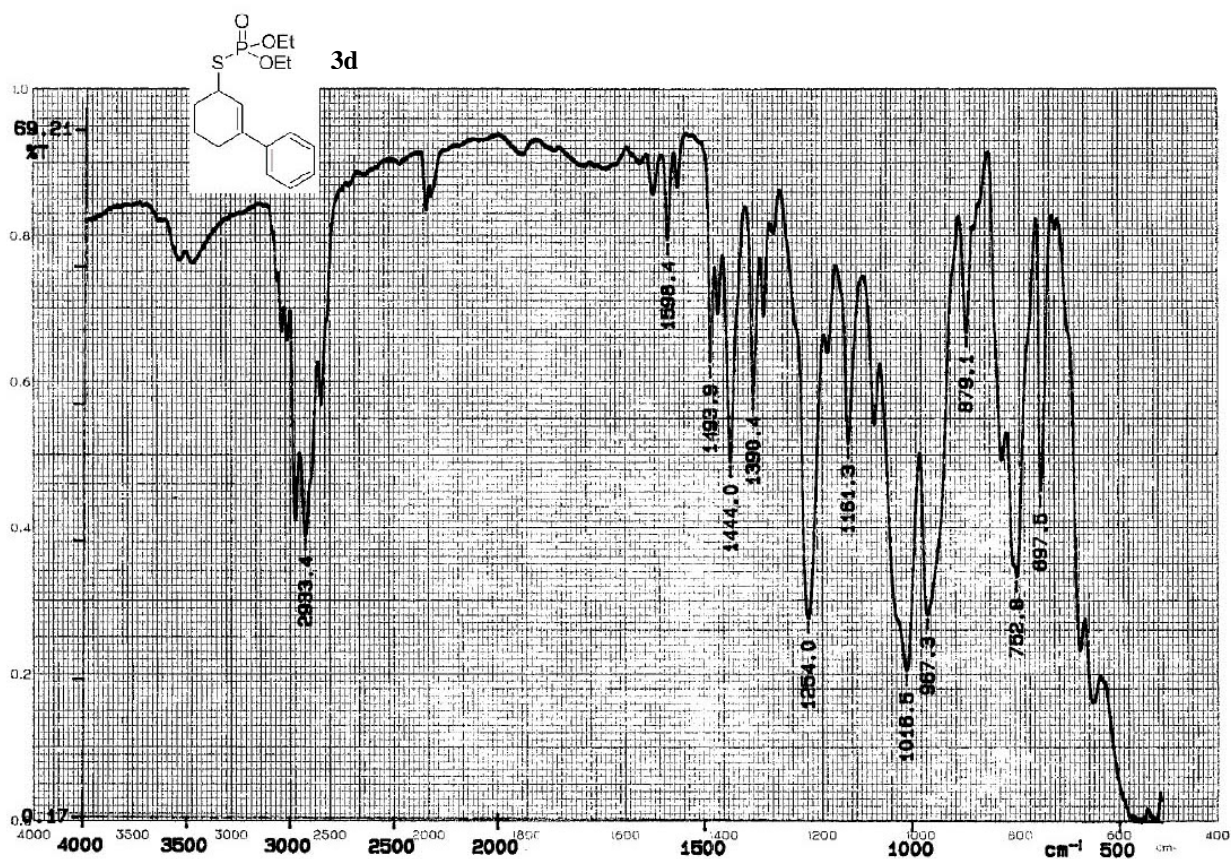
STANDARD P31 PARAMETERS (500)





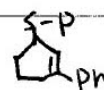


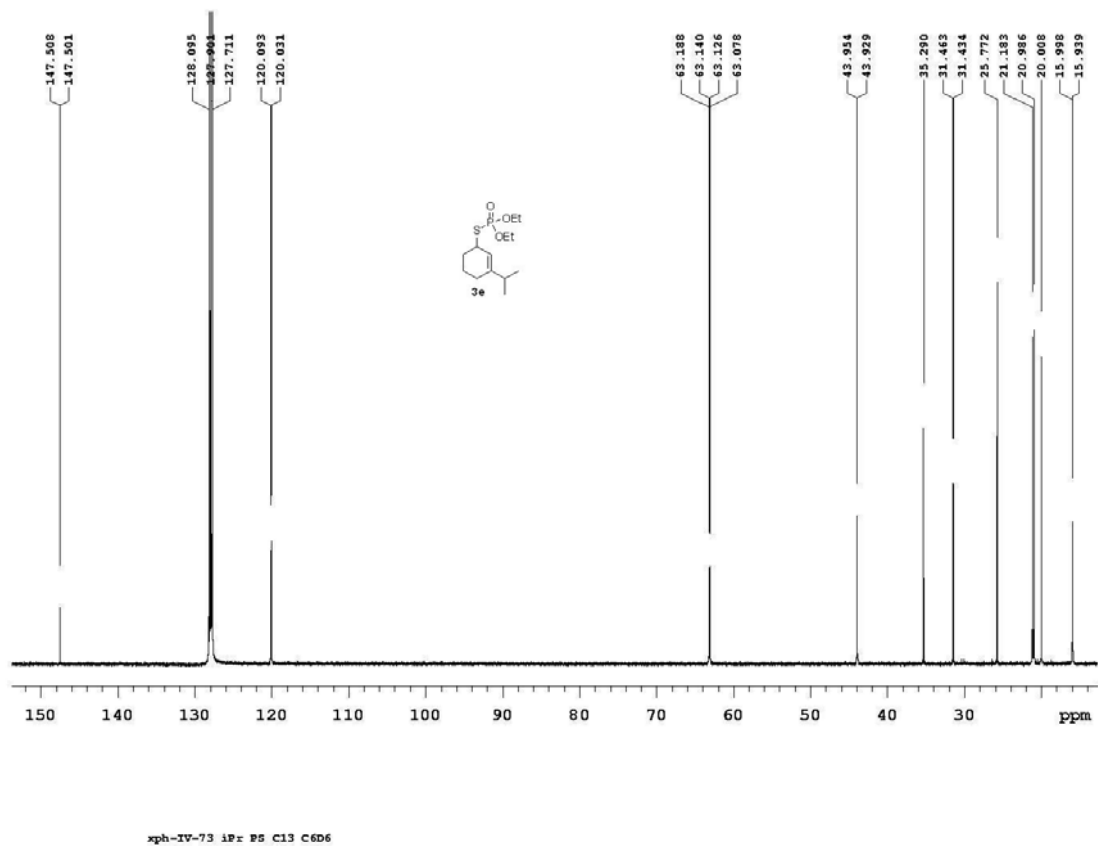
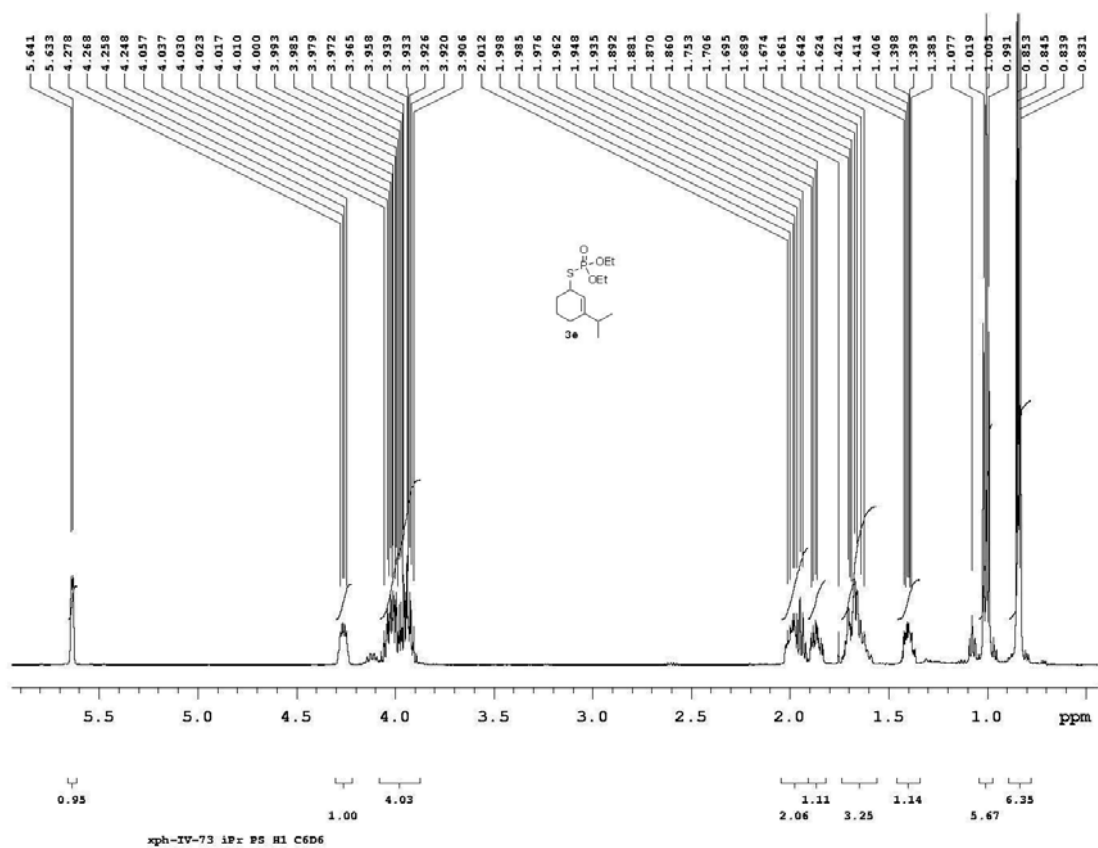
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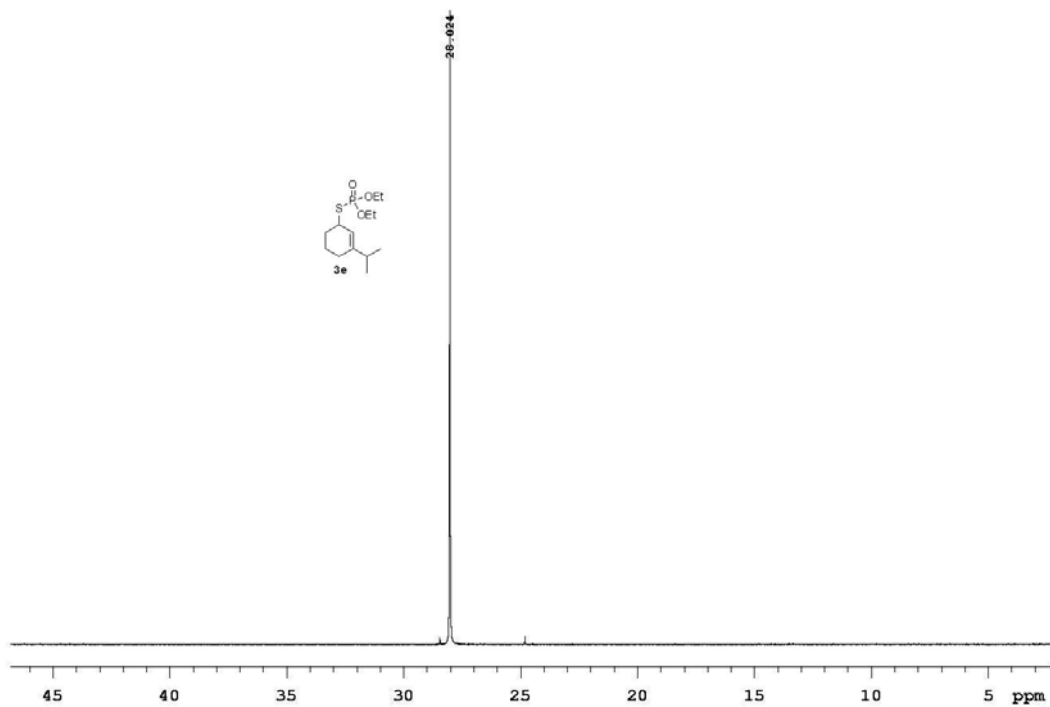


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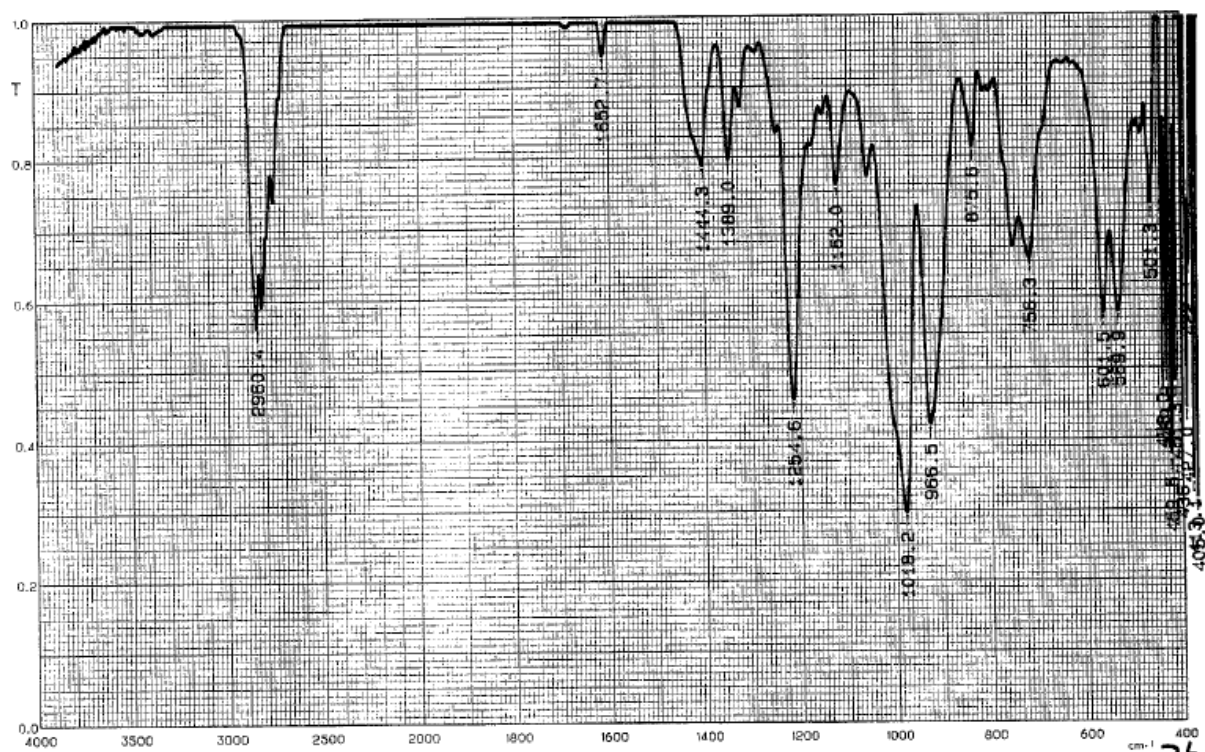
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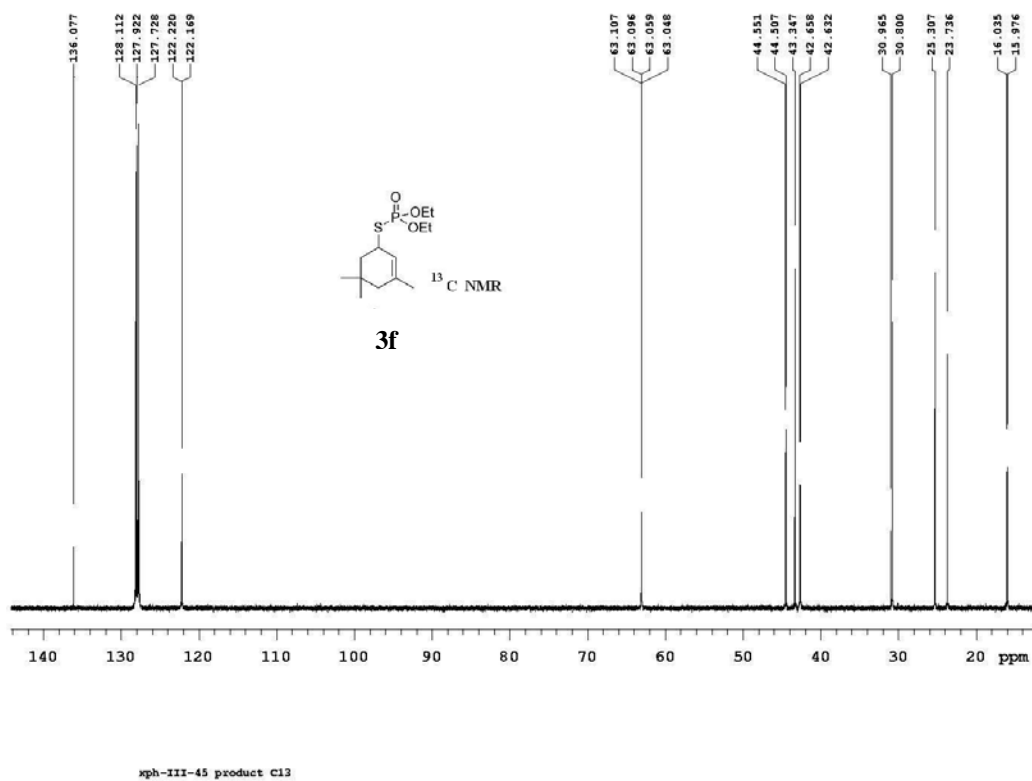
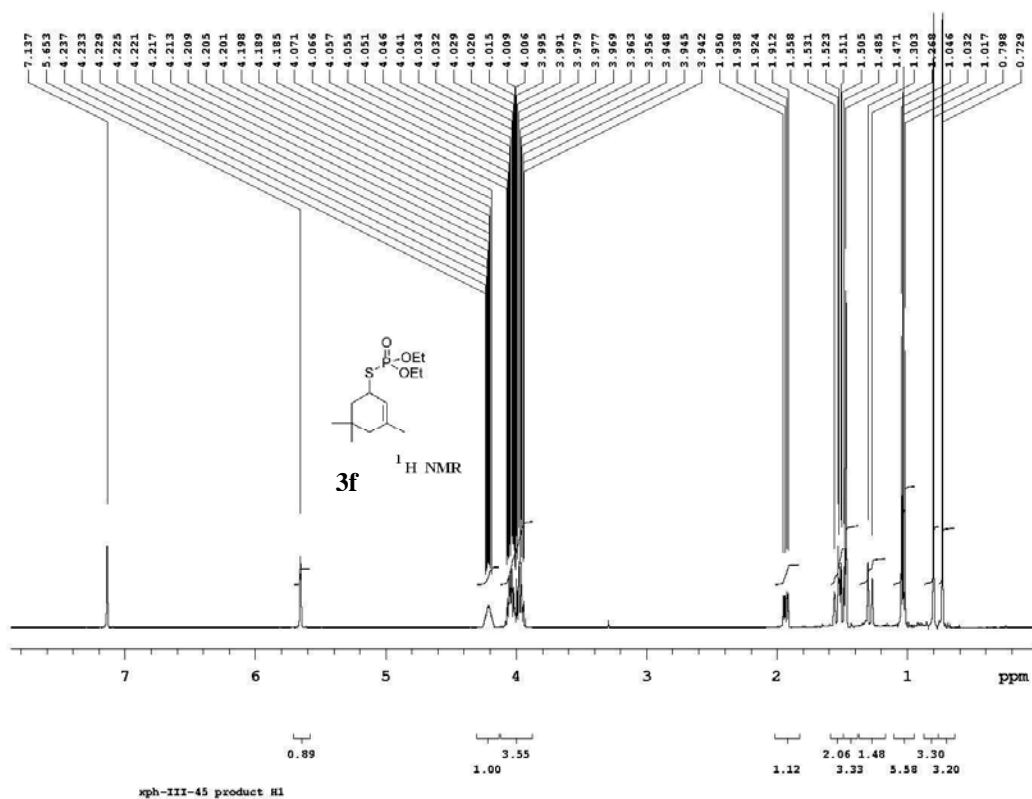


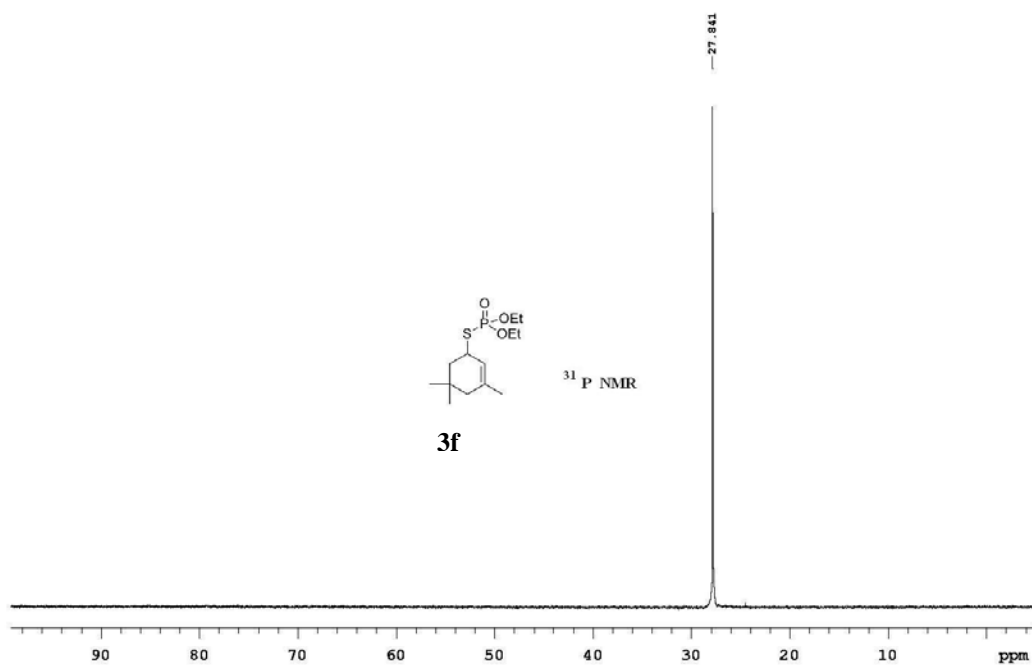
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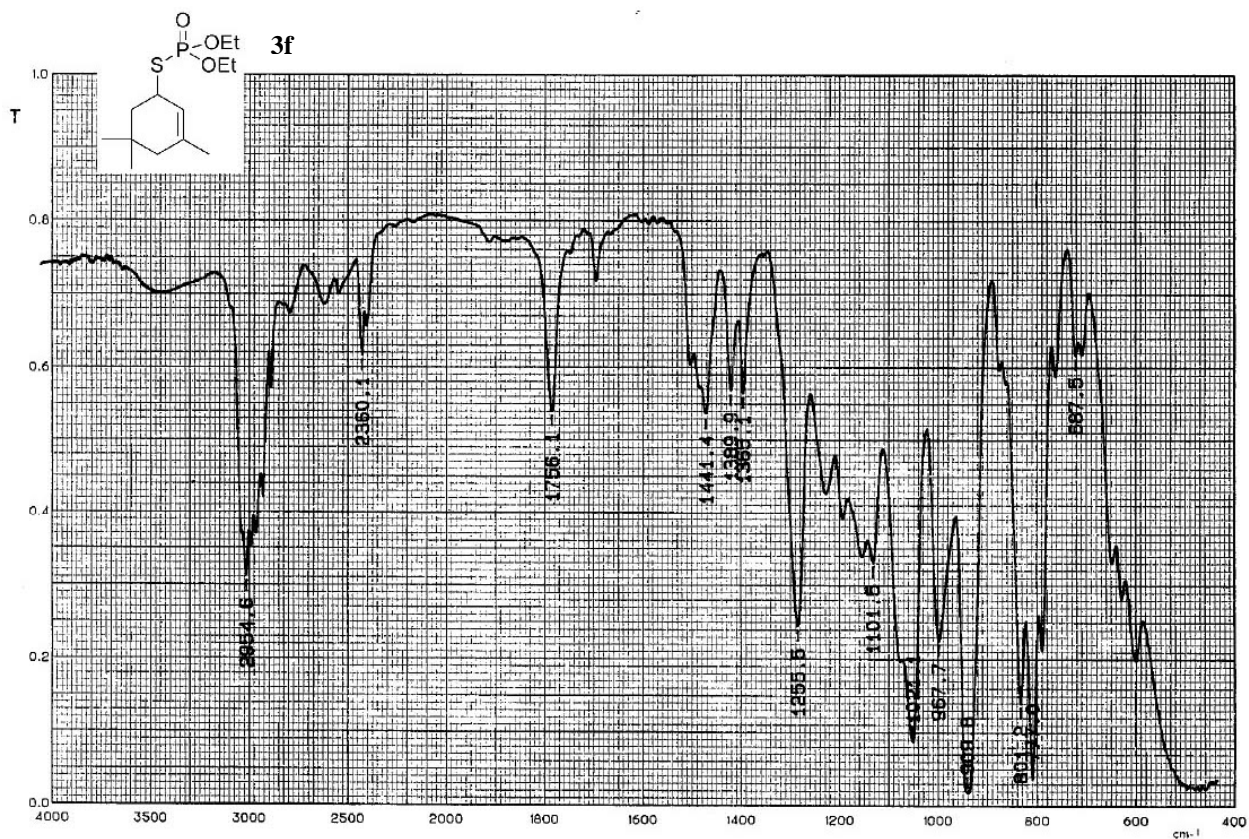
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SAMPLE			

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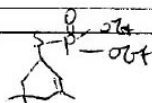


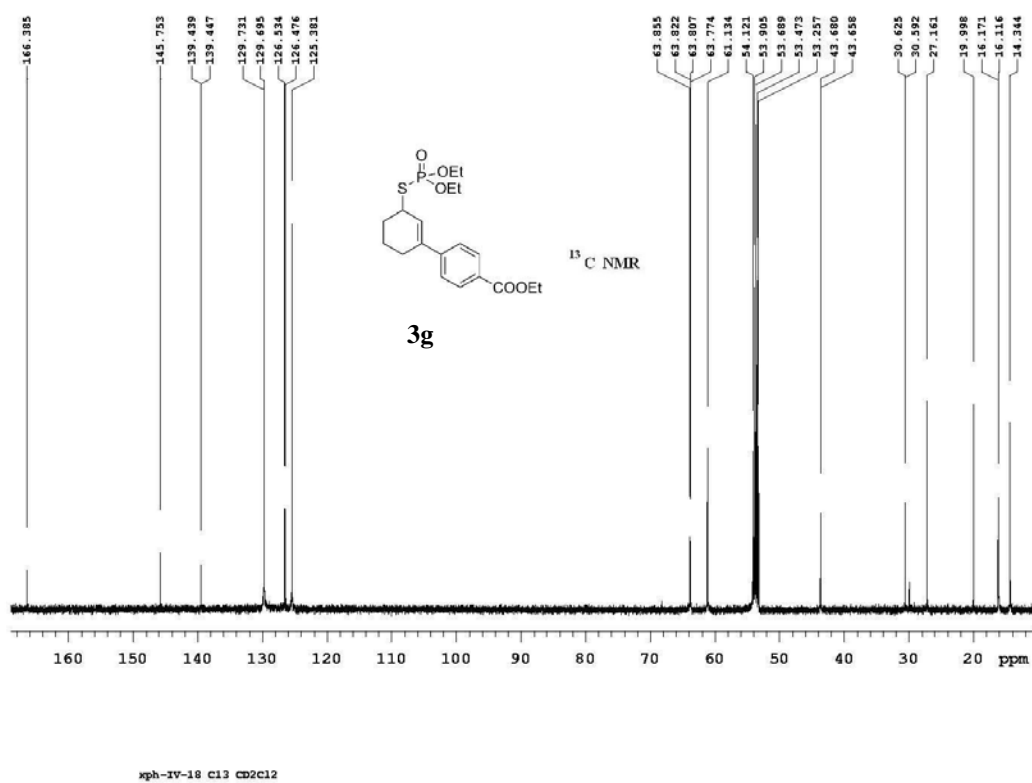
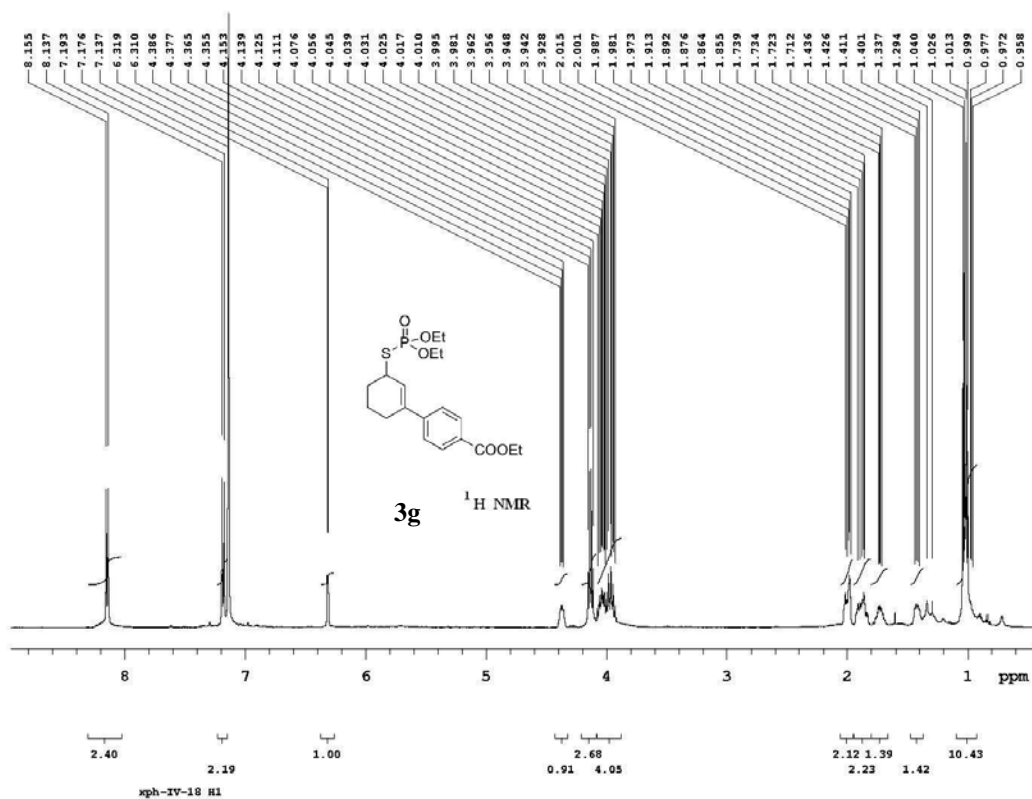


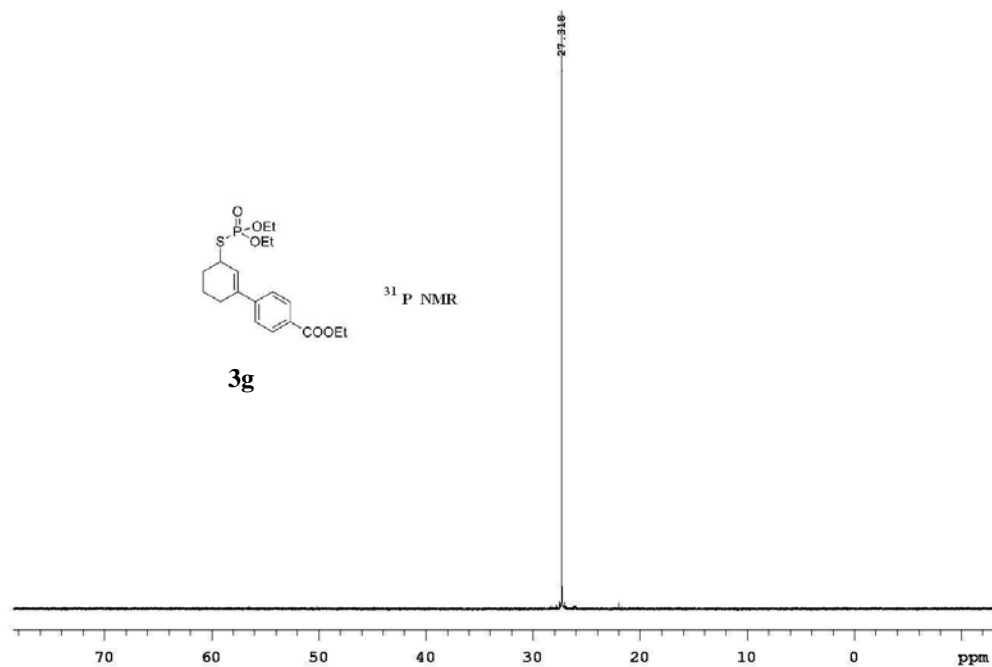
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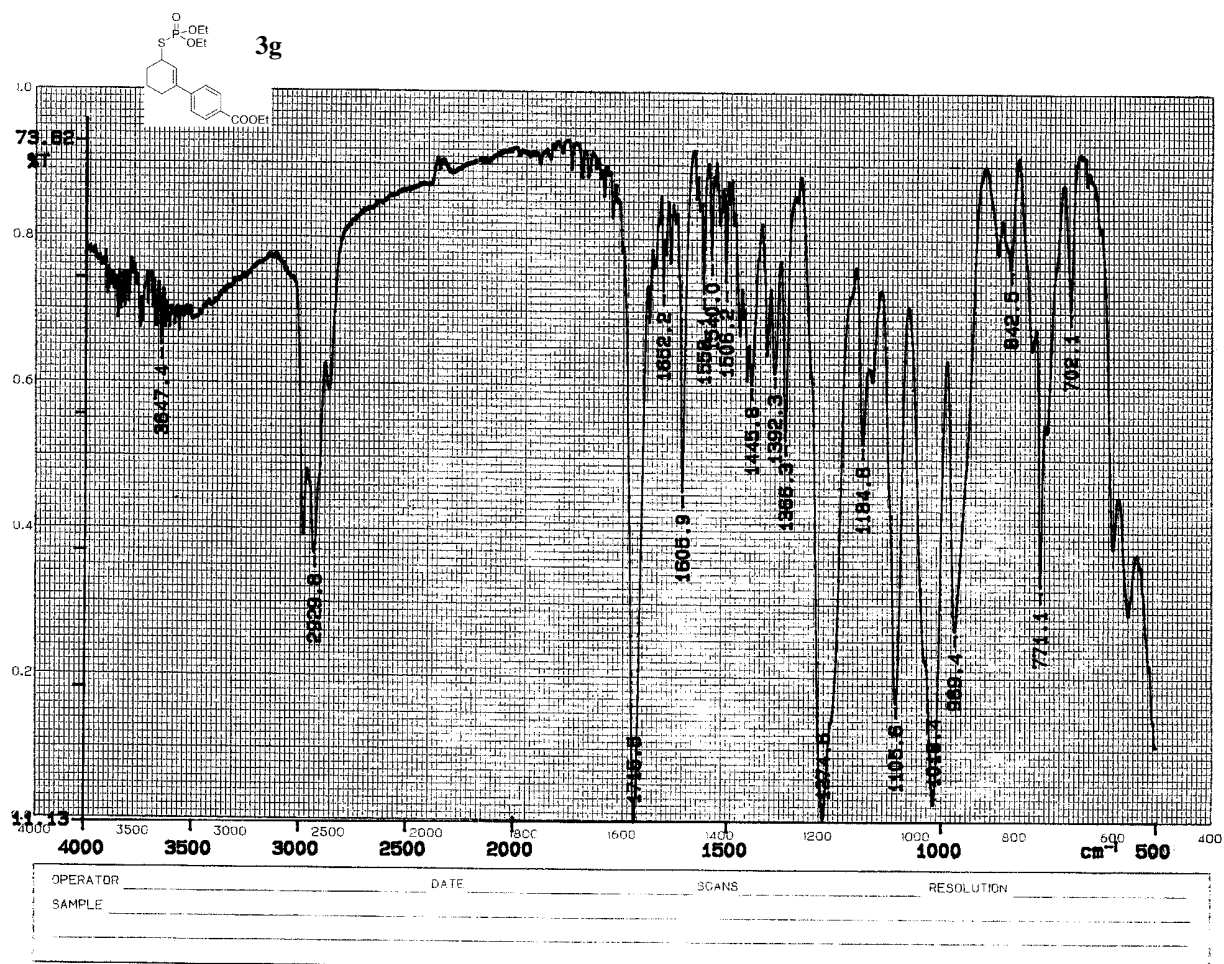
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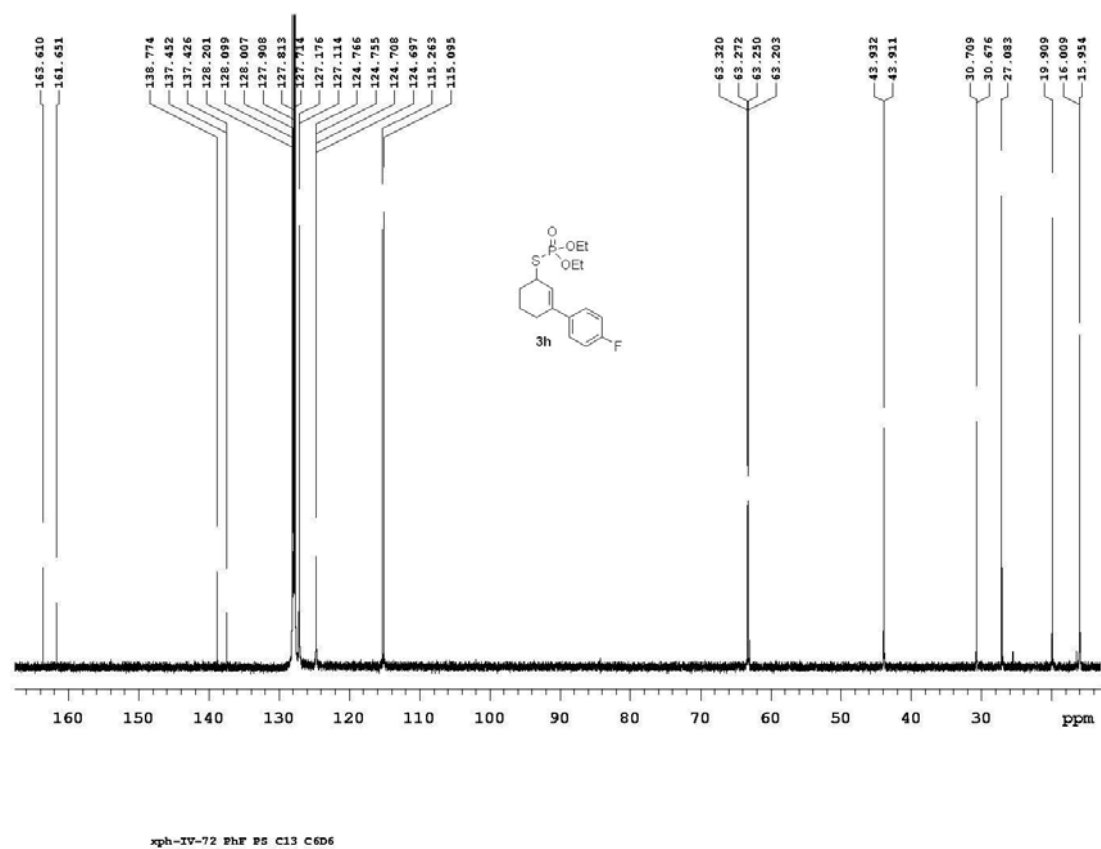
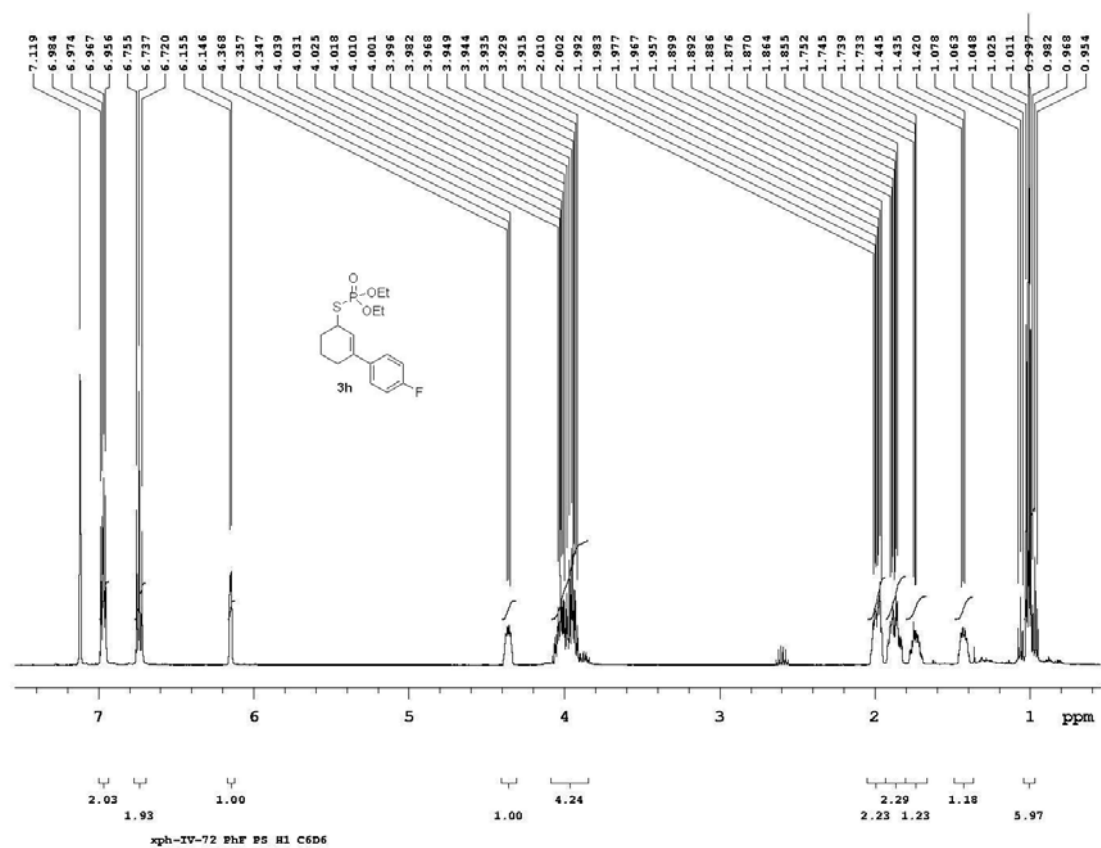


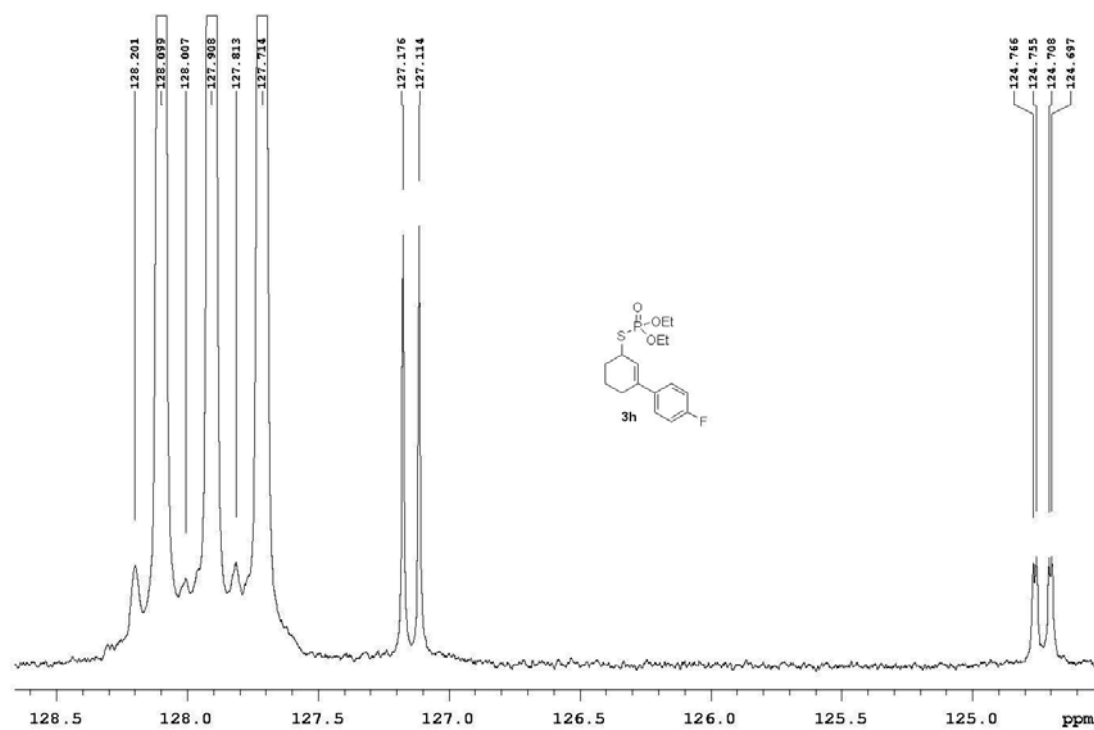




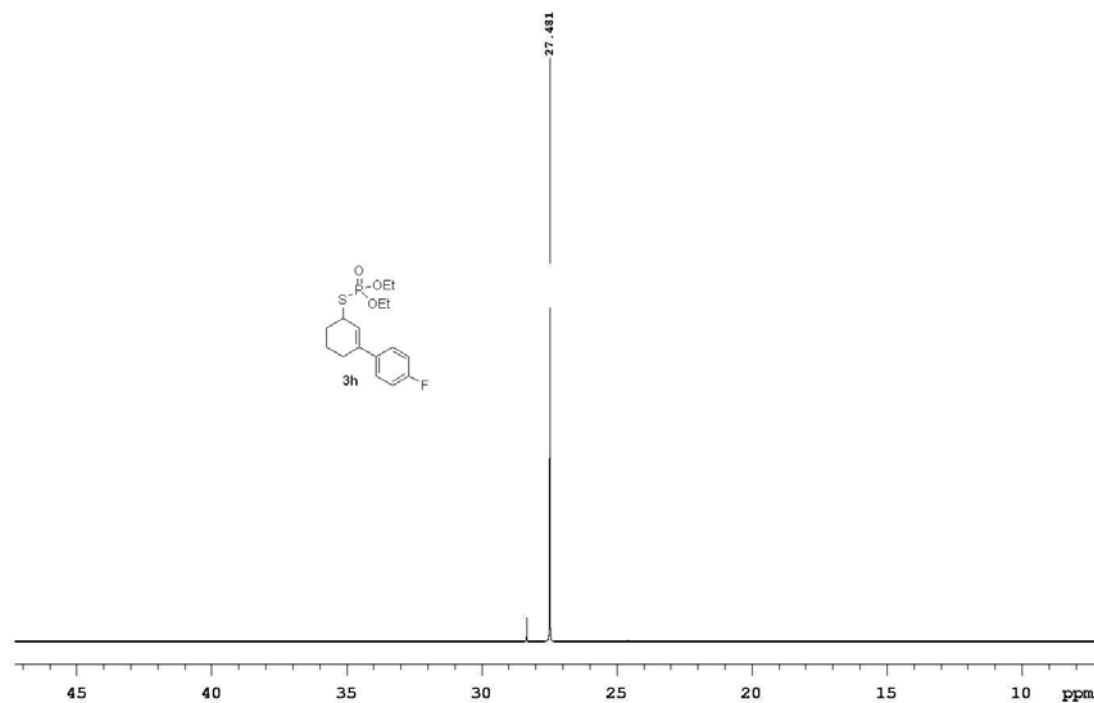
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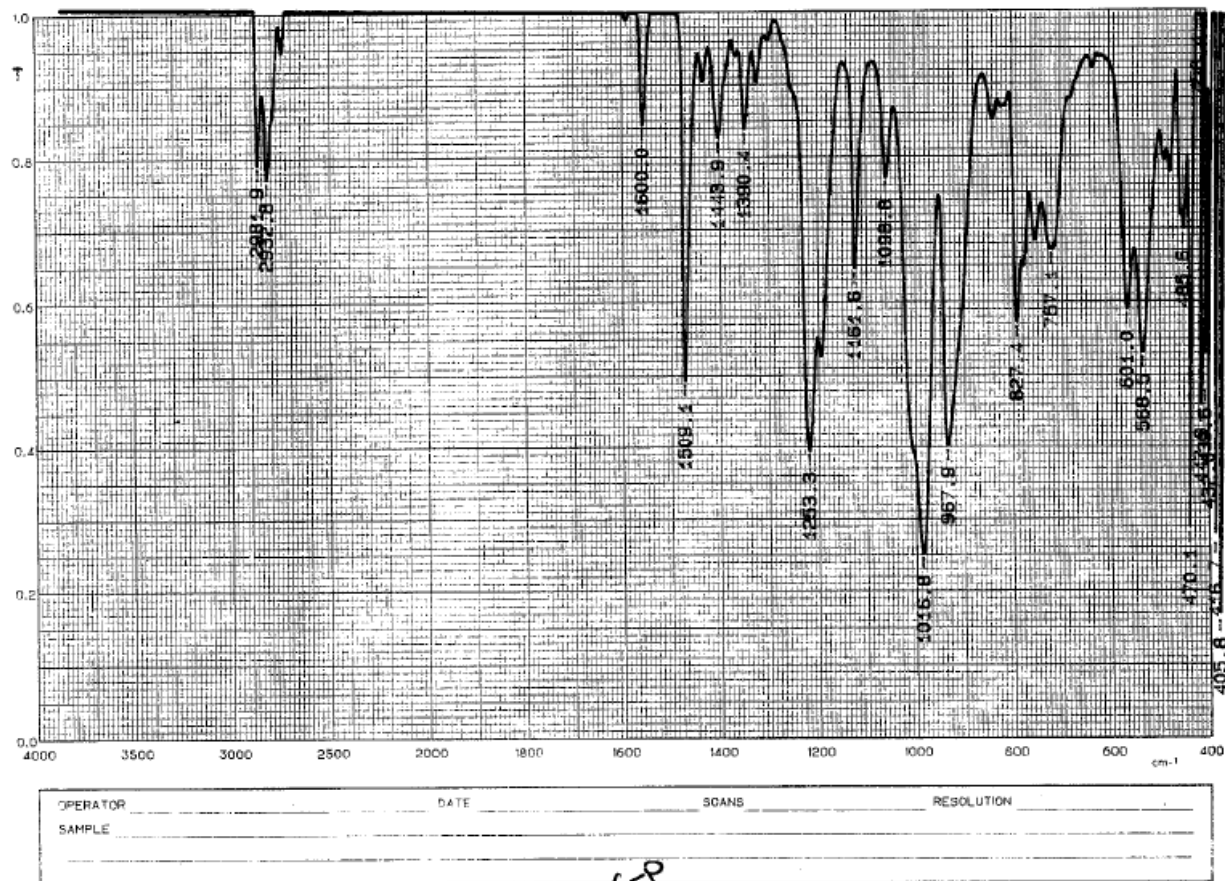




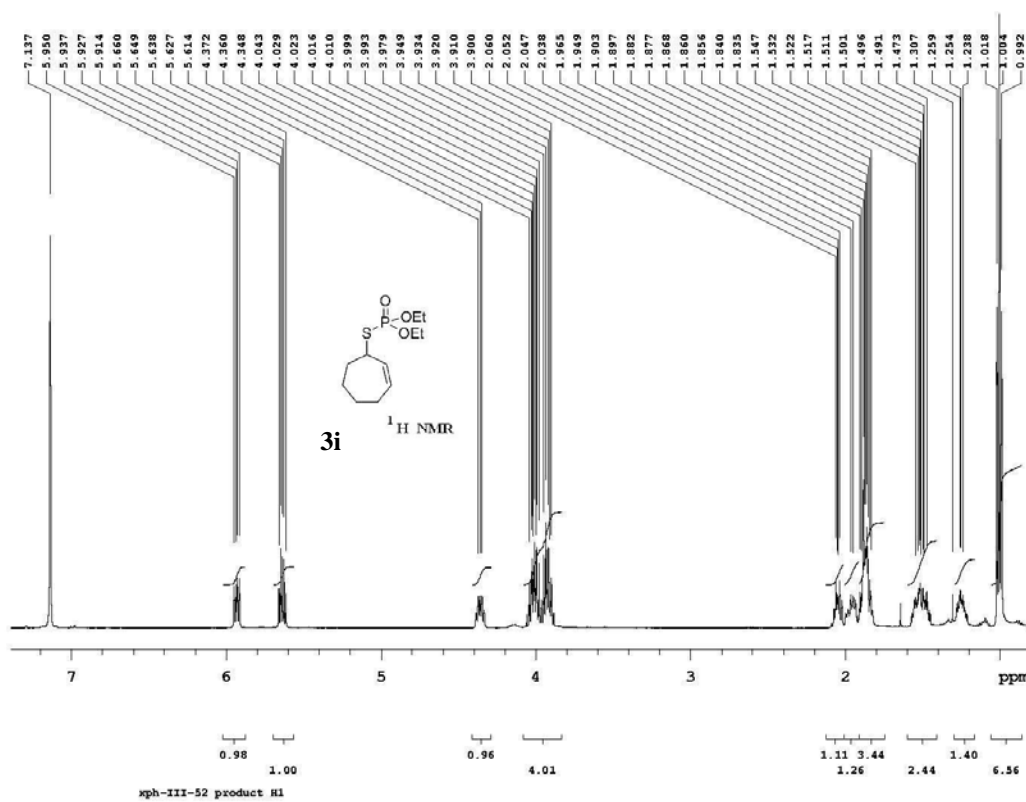
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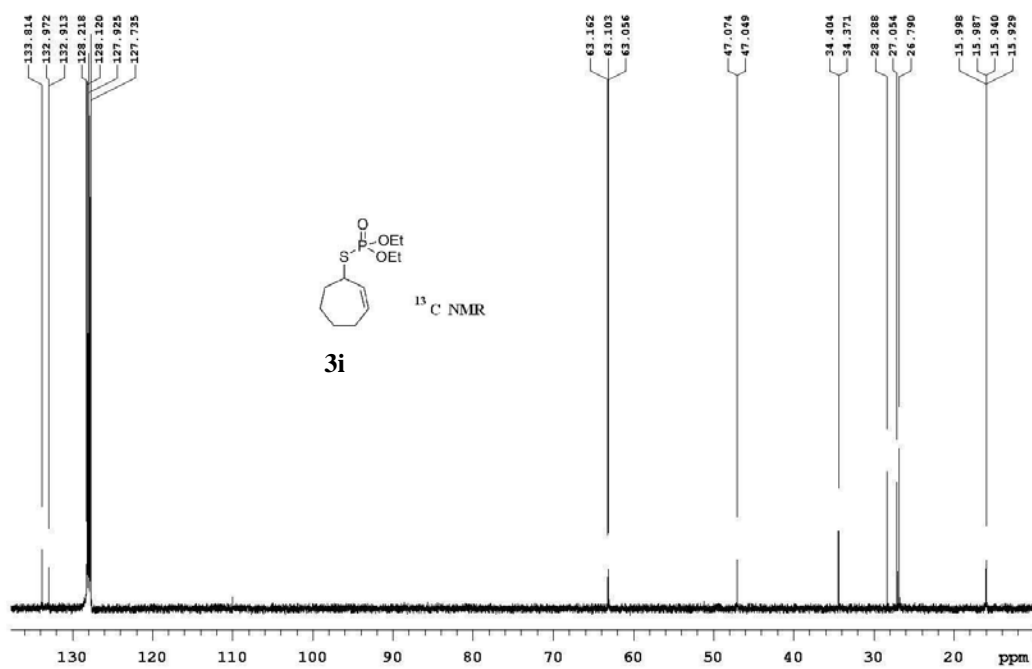


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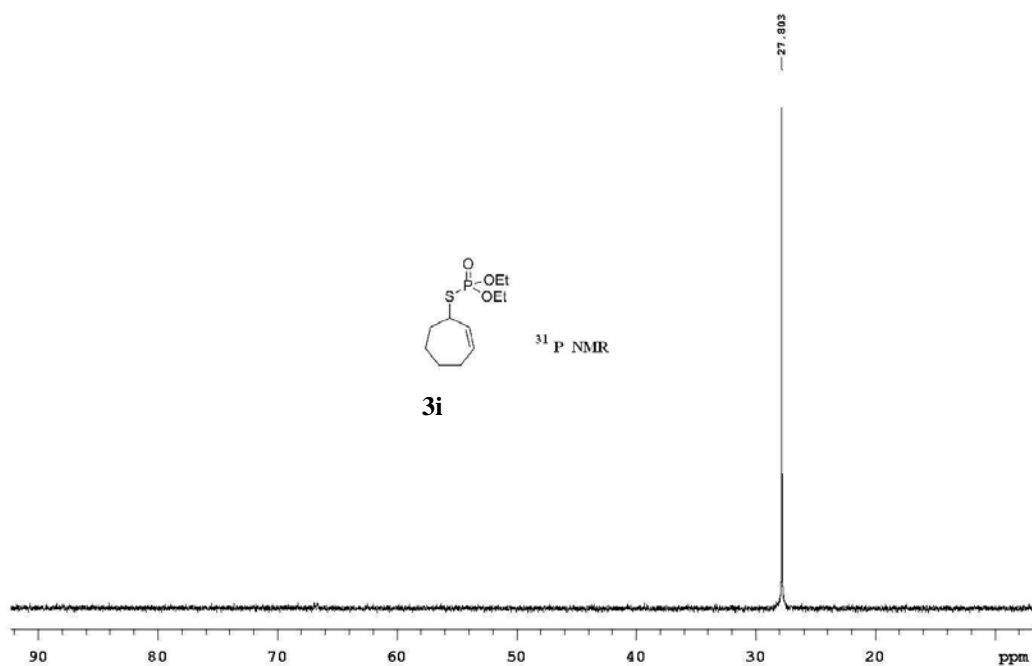


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CH₂PT 3h

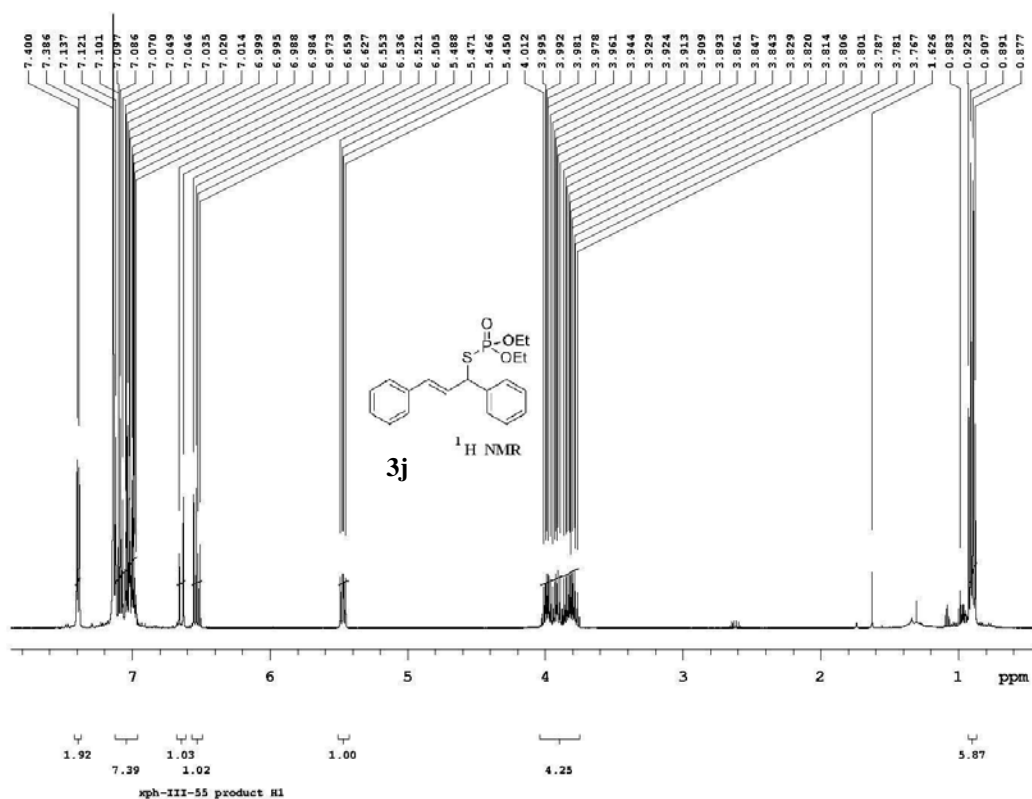
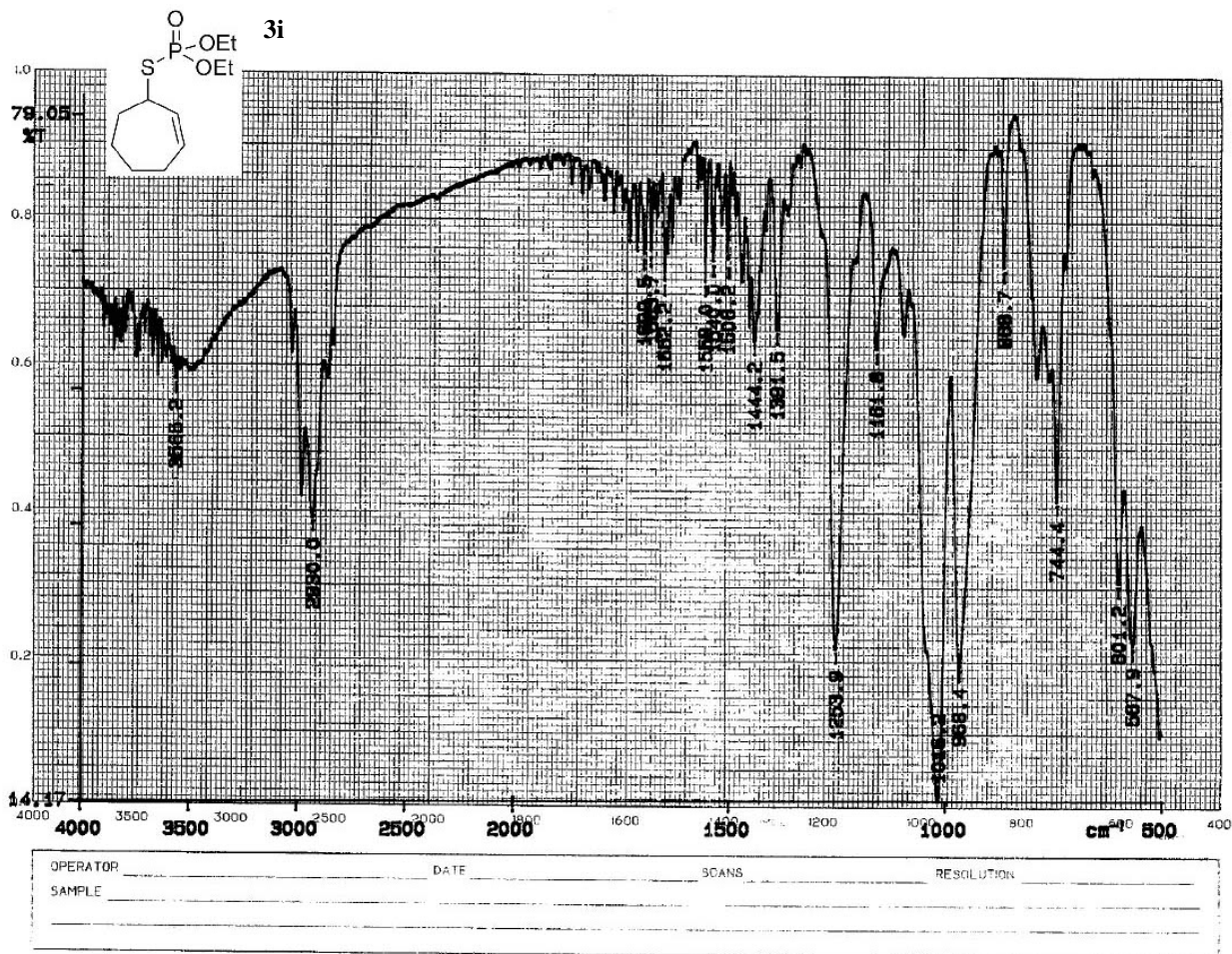


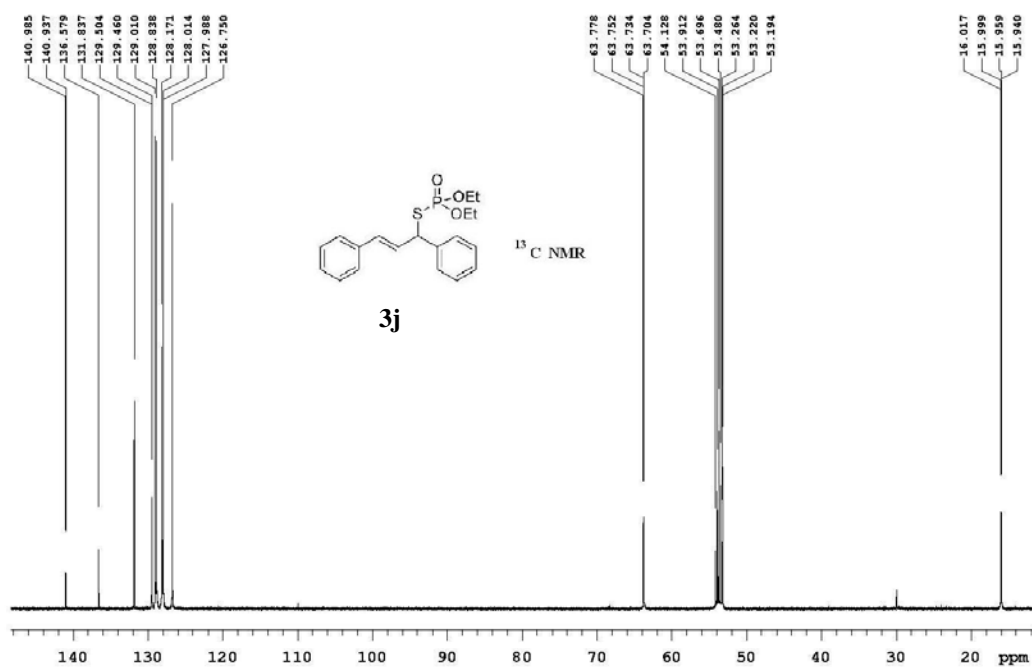


xph-III-52 product C13

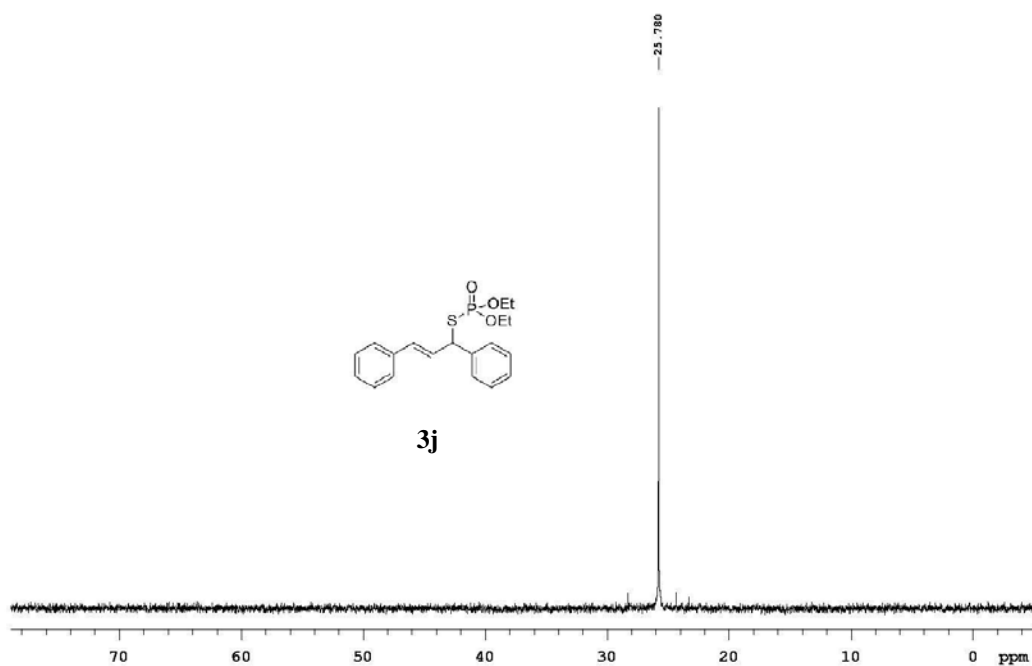


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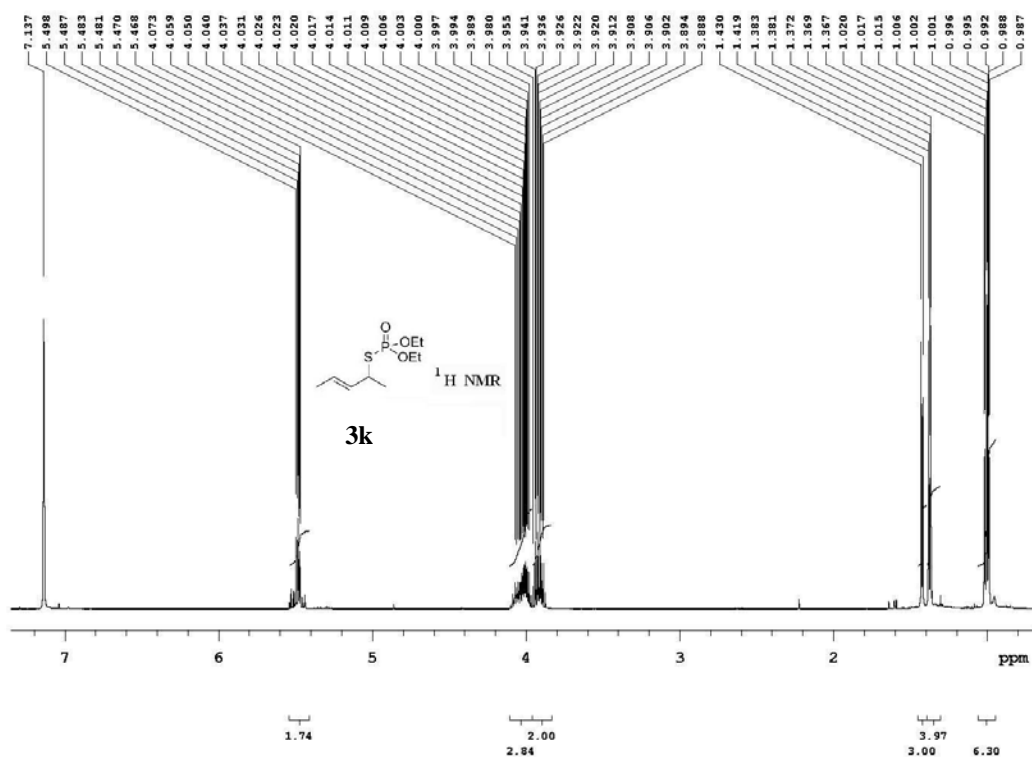
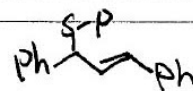
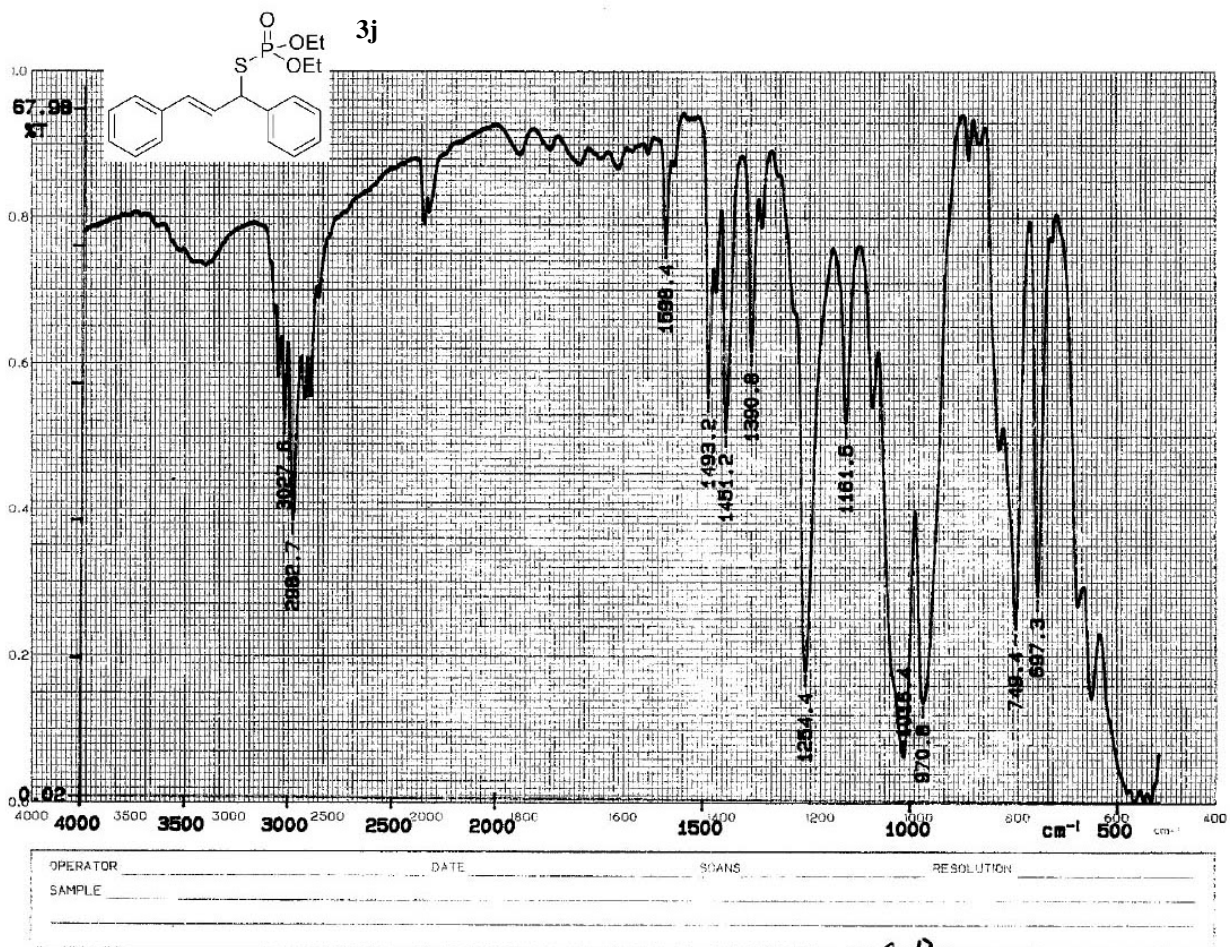


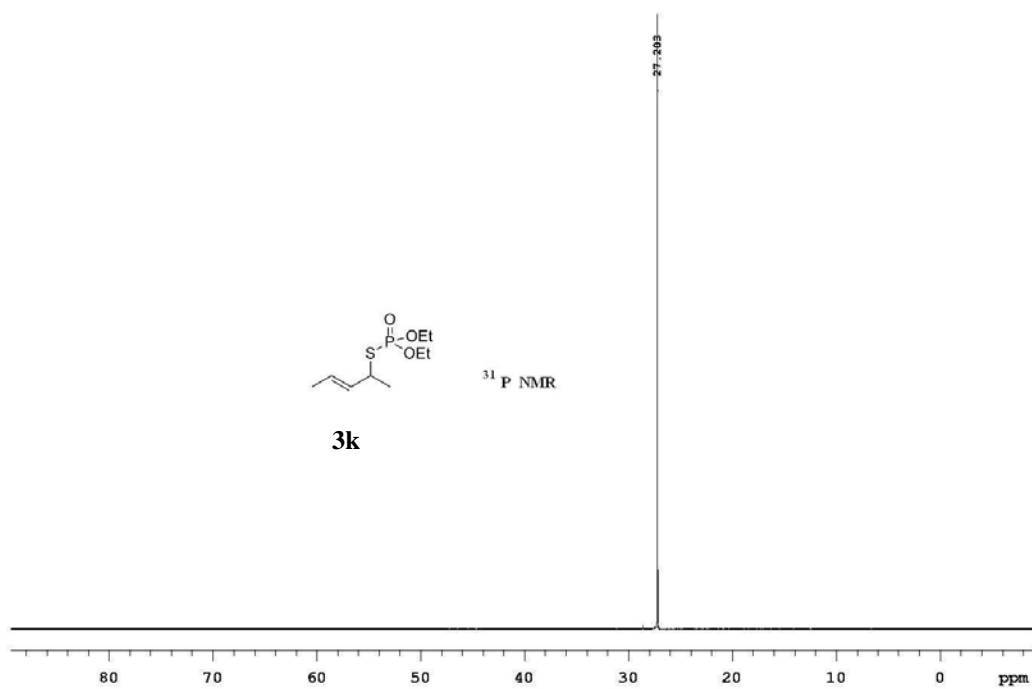
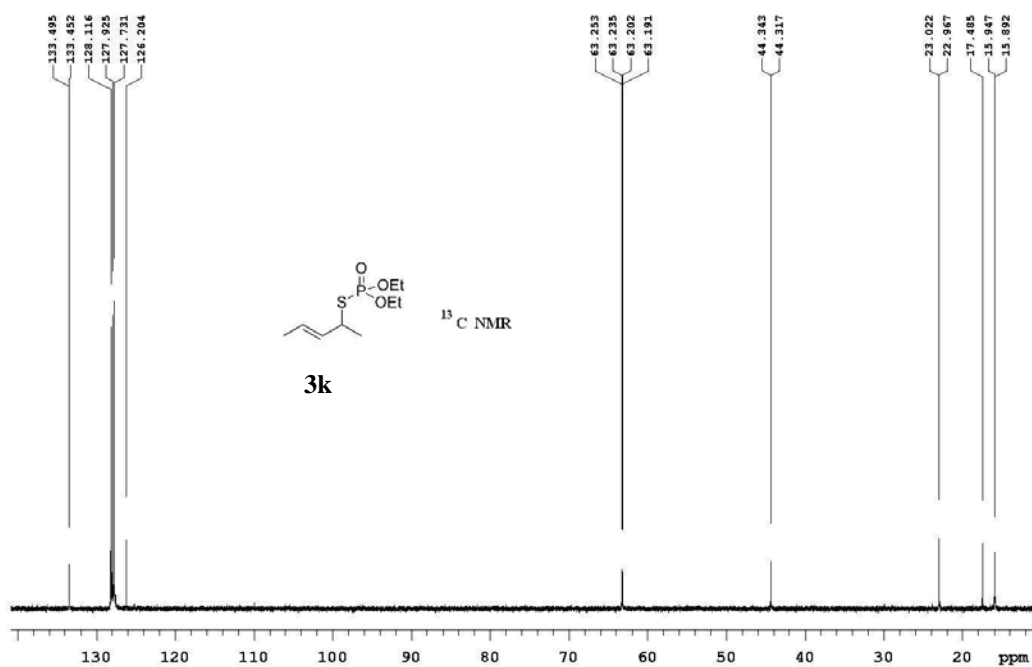


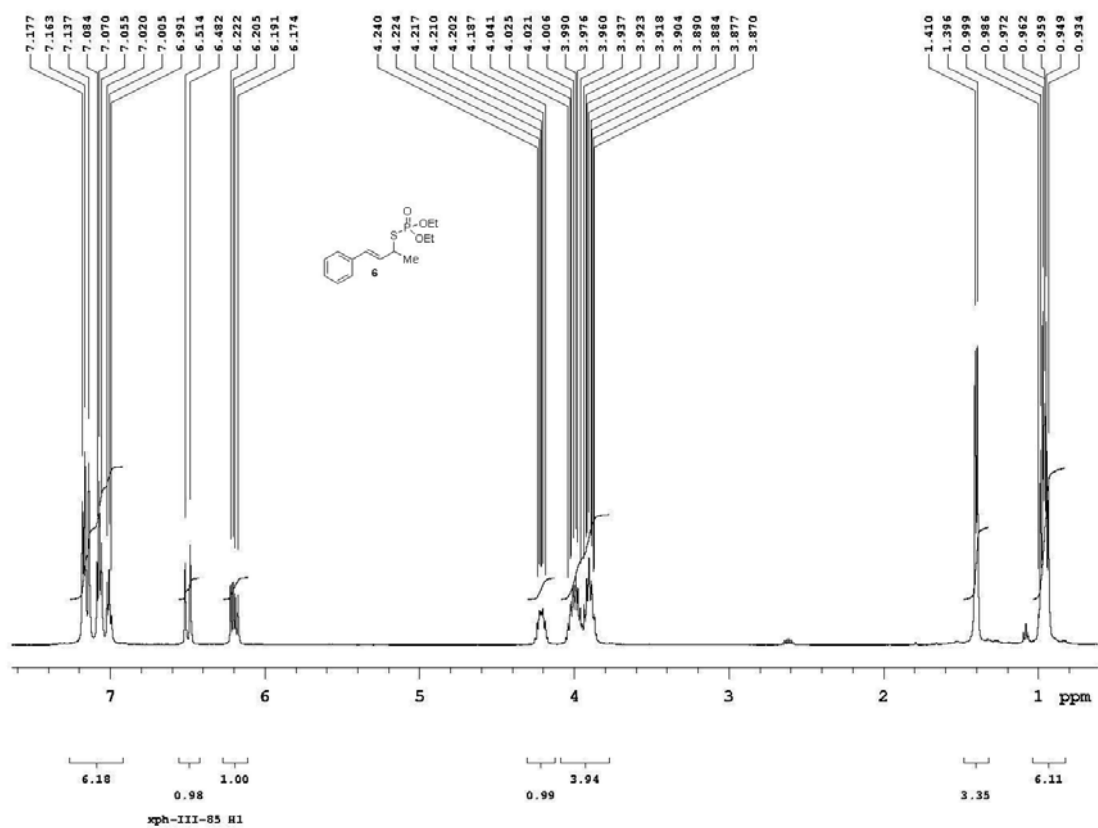
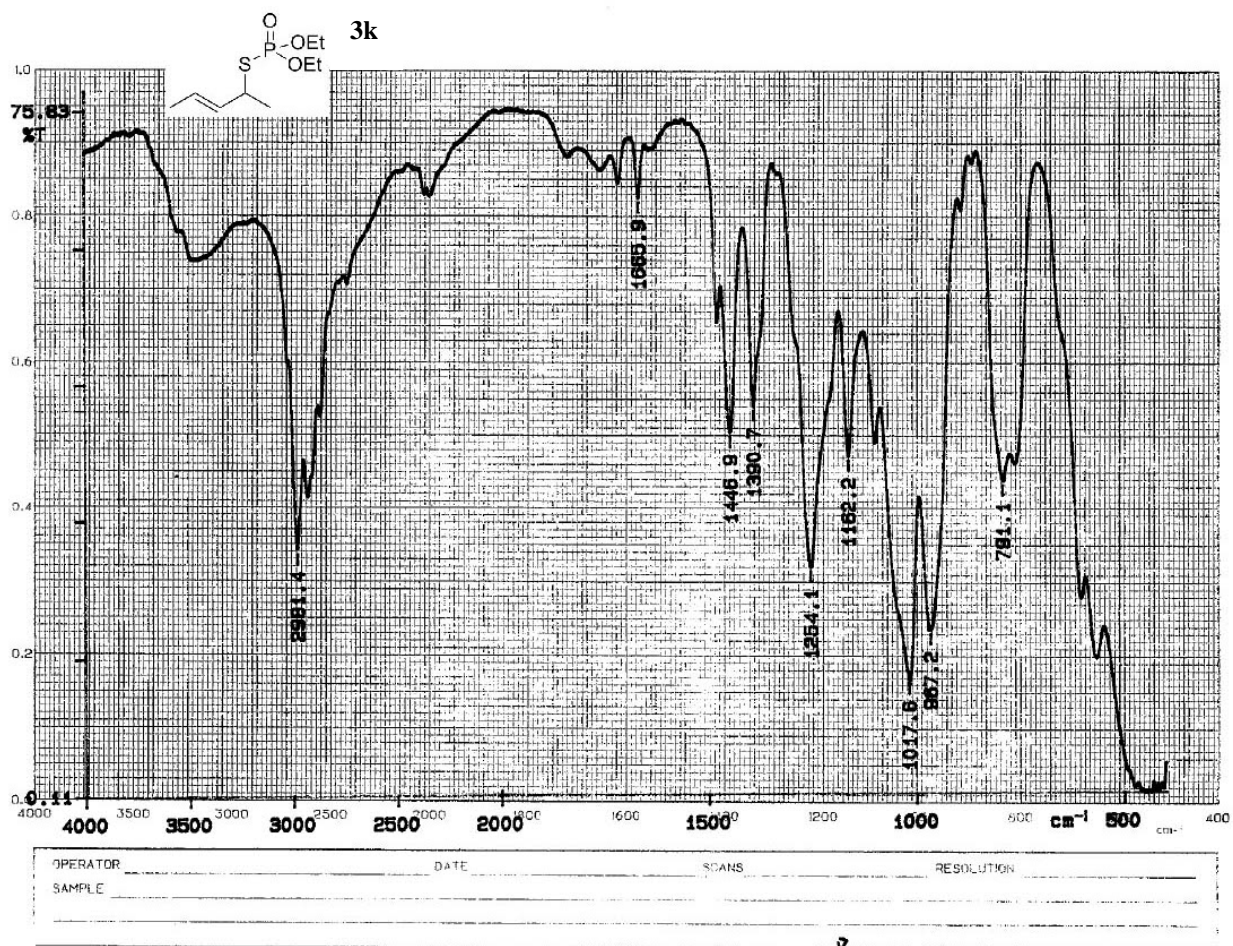
xph-III-55 C13 CD2Cl2

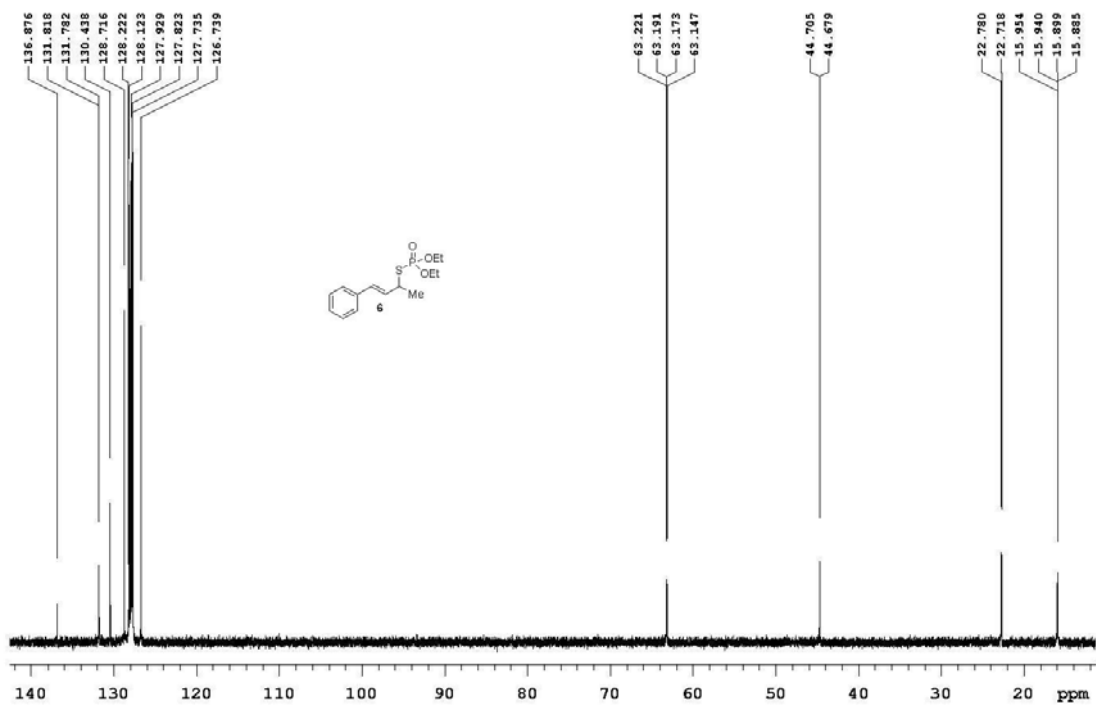


xph-III-55 product P31

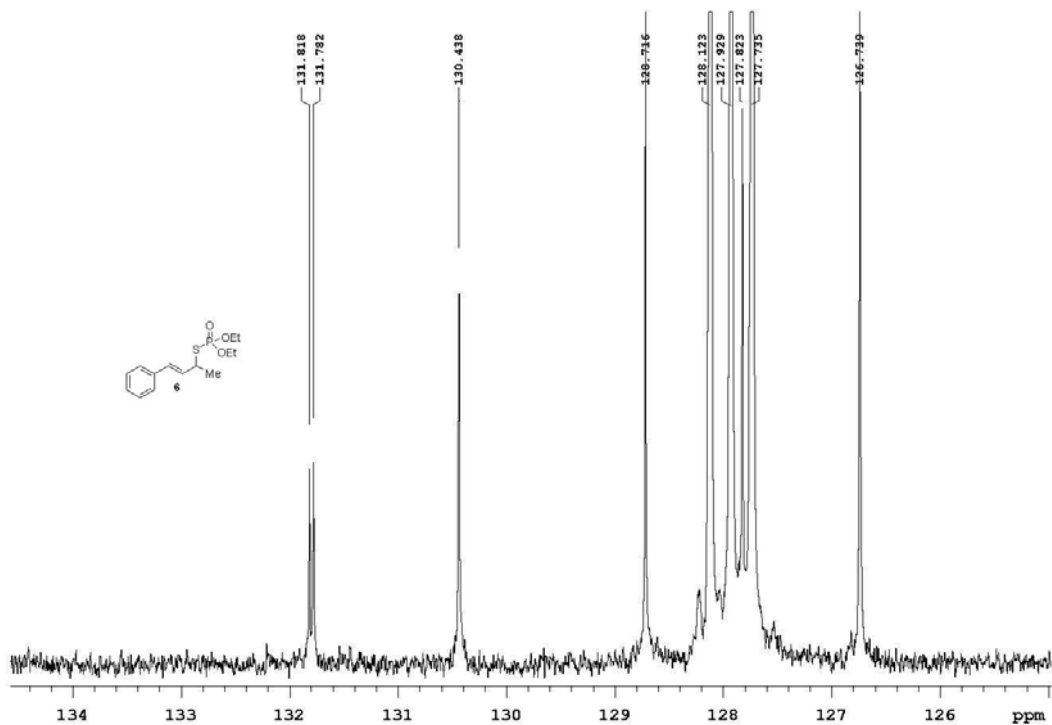




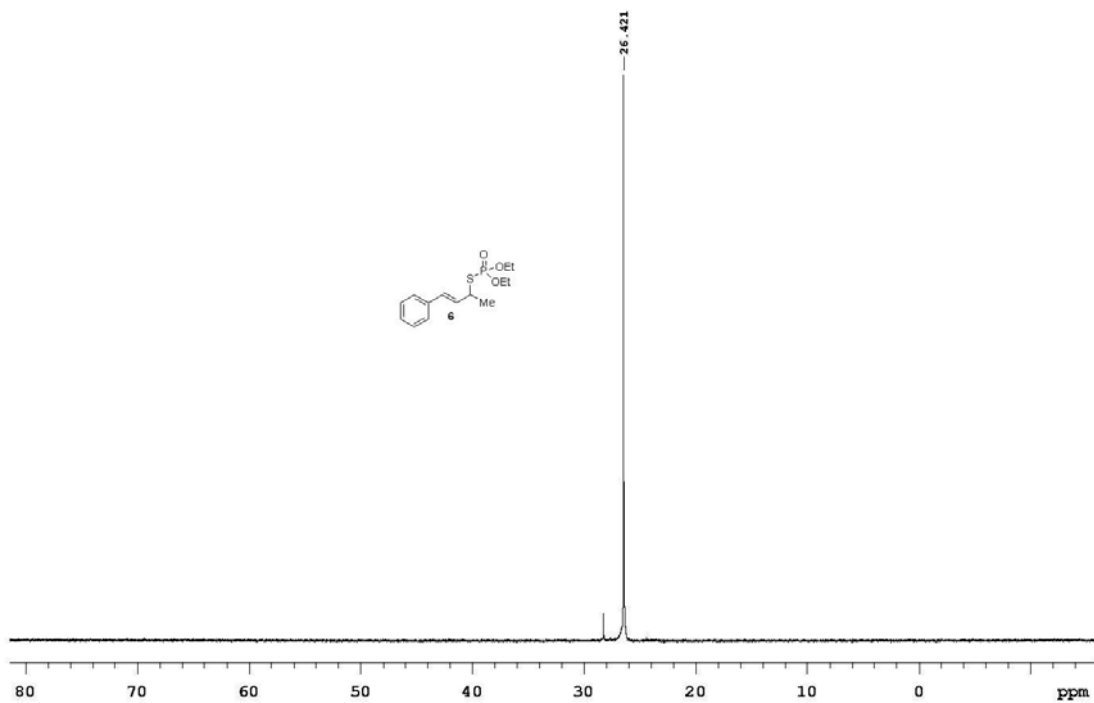




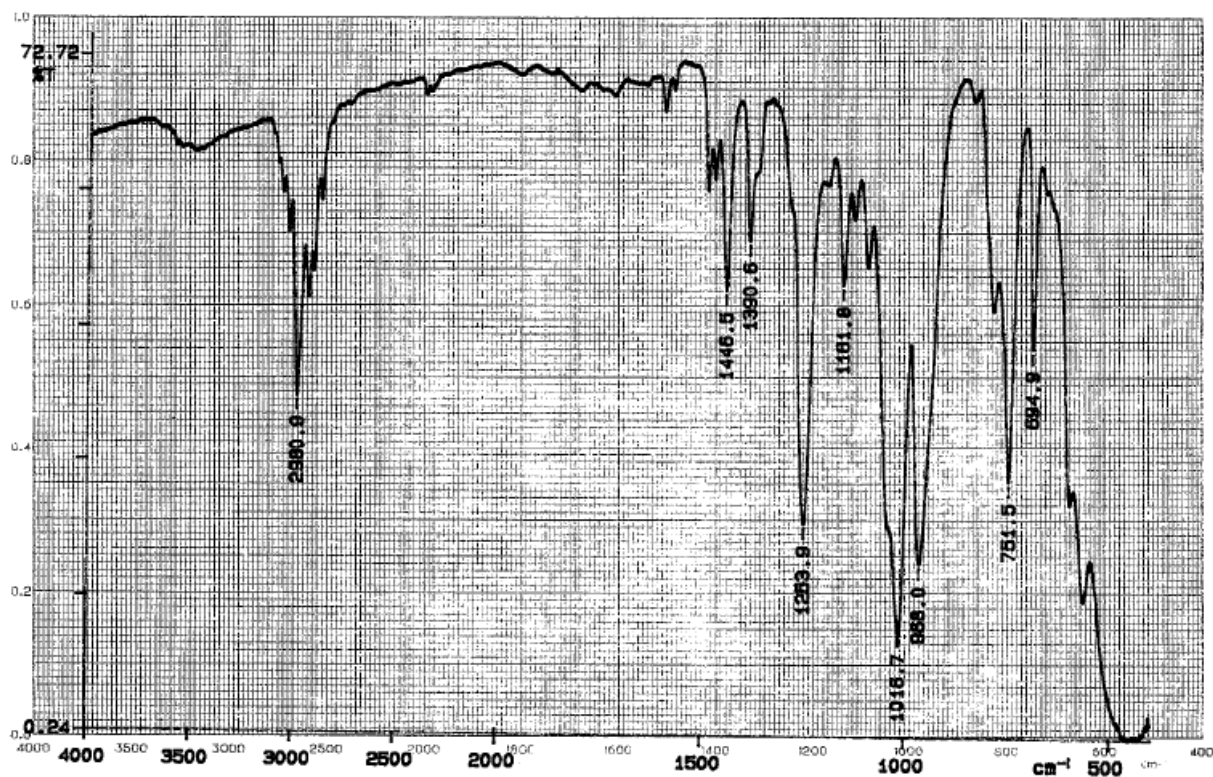
xph-III-85 C13



xph-III-85 C13

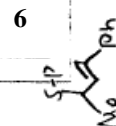


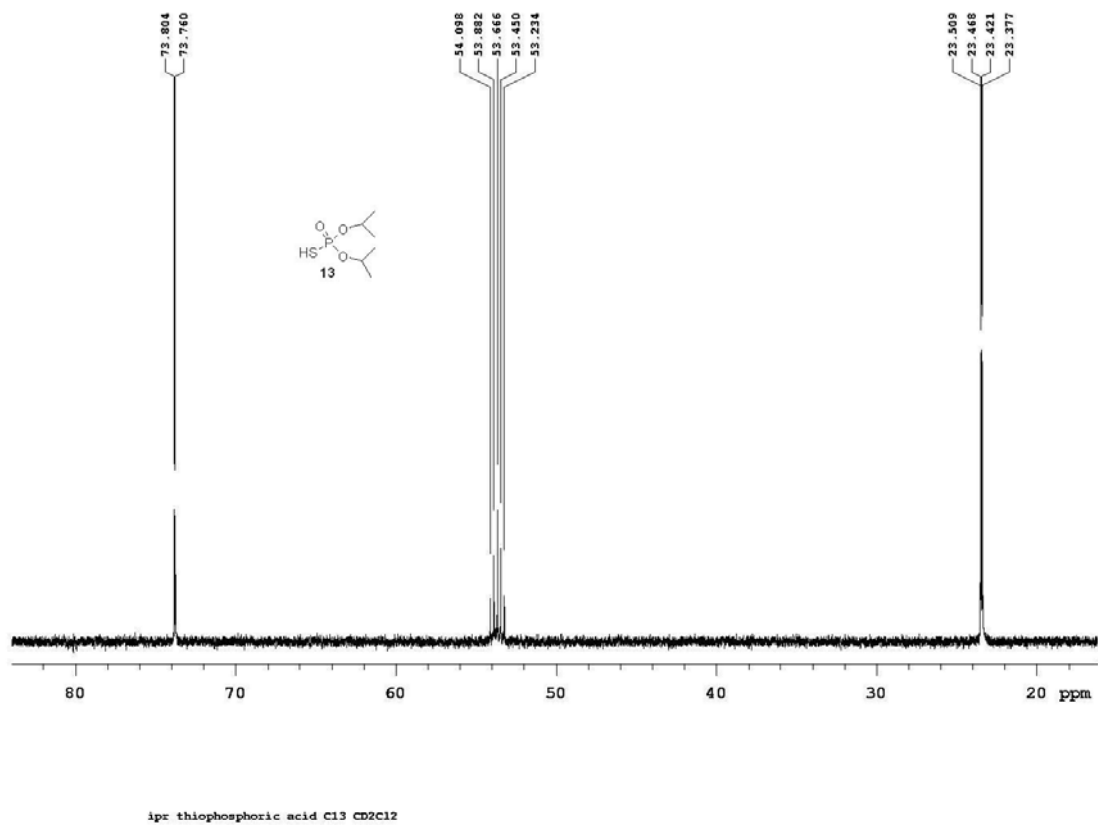
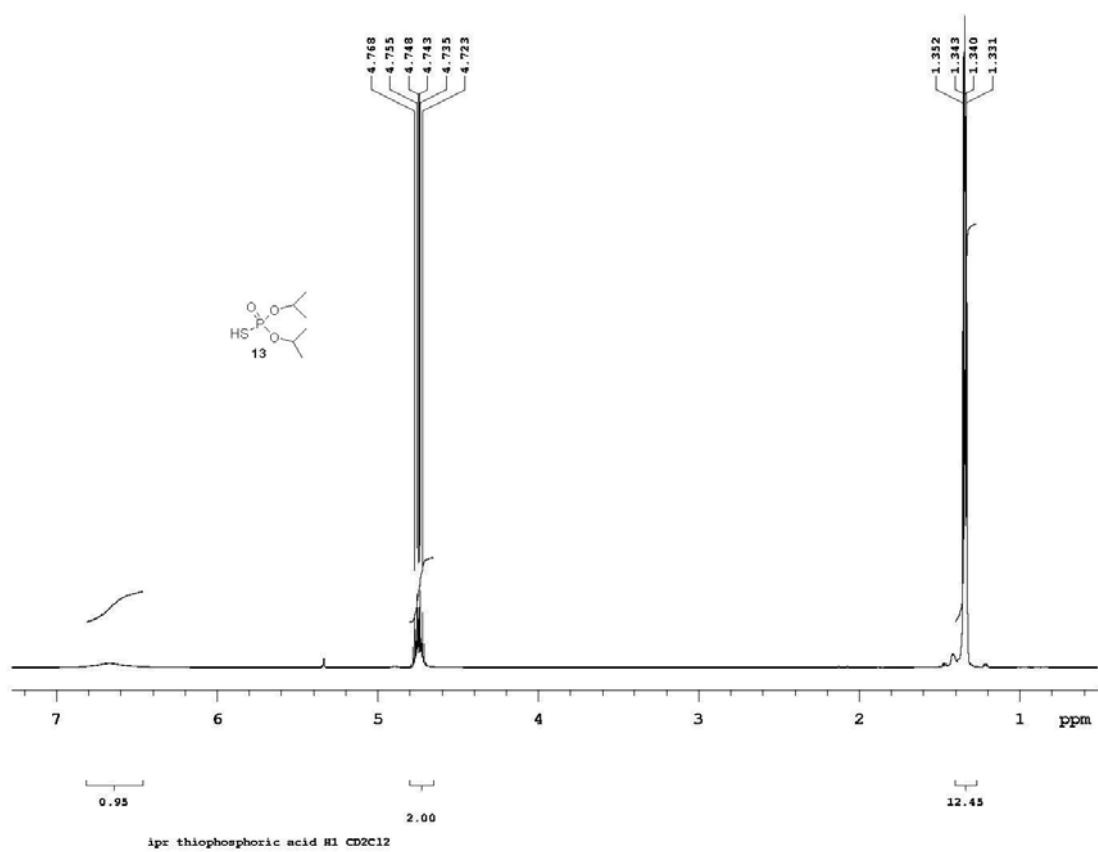
xph-III-85 P31

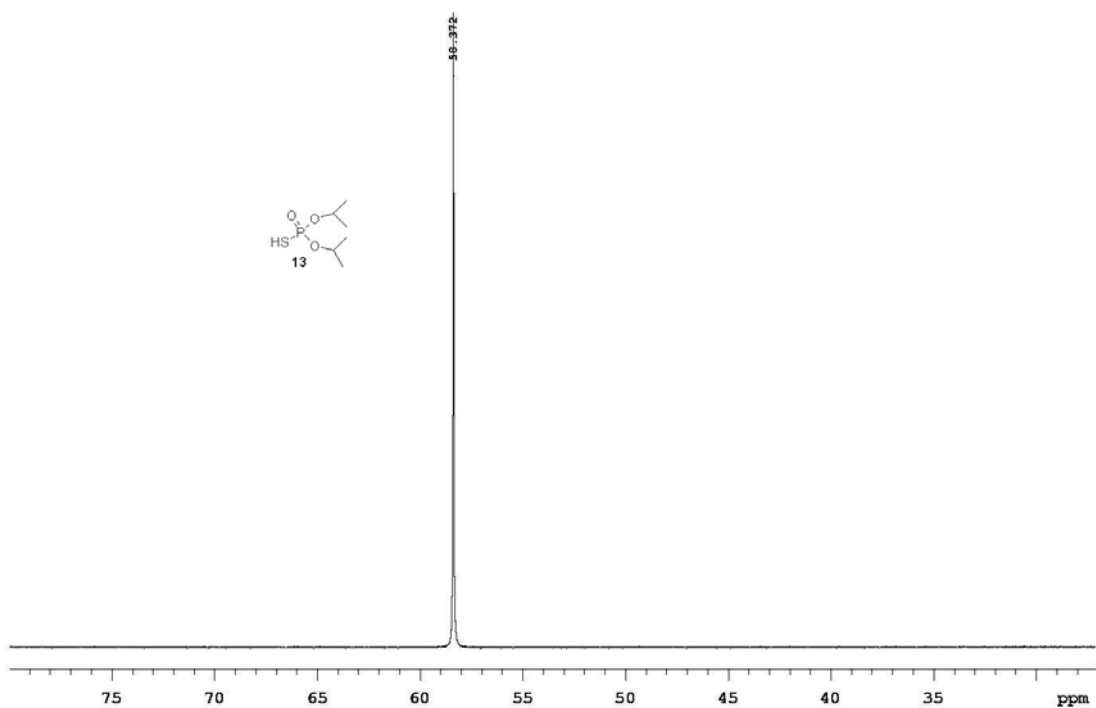


OPERATOR _____ DATE _____ SCANS _____ RESOLUTION _____

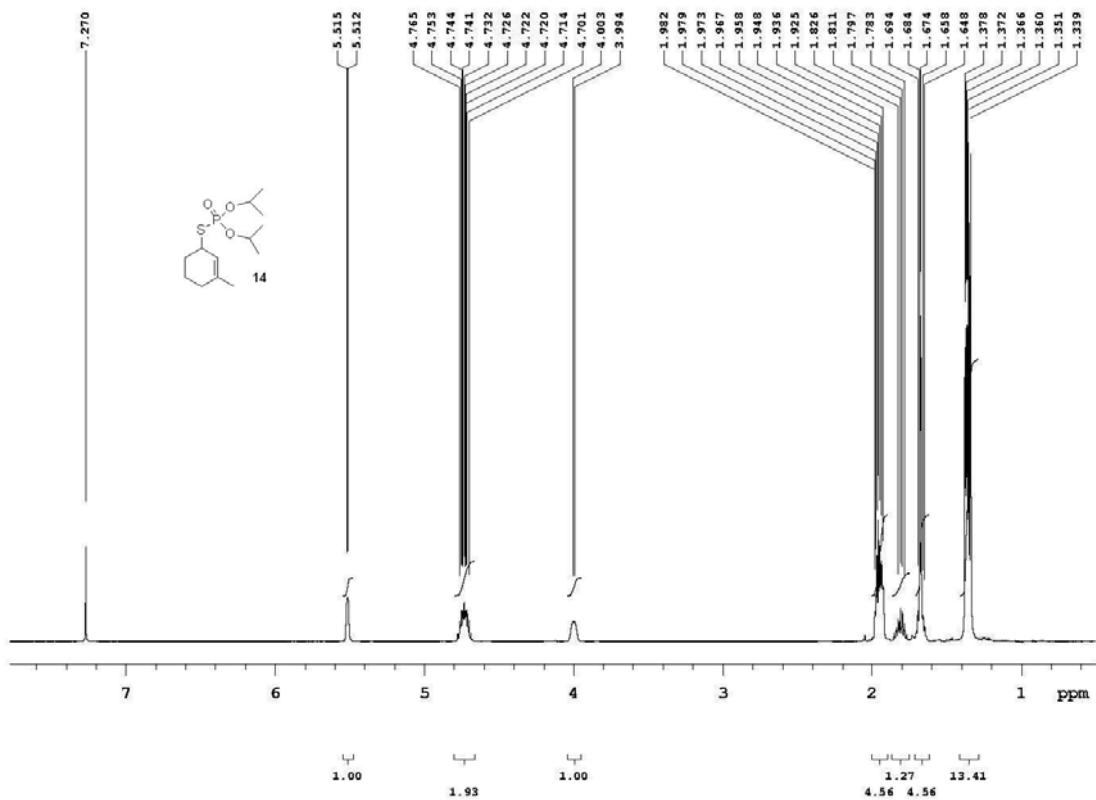
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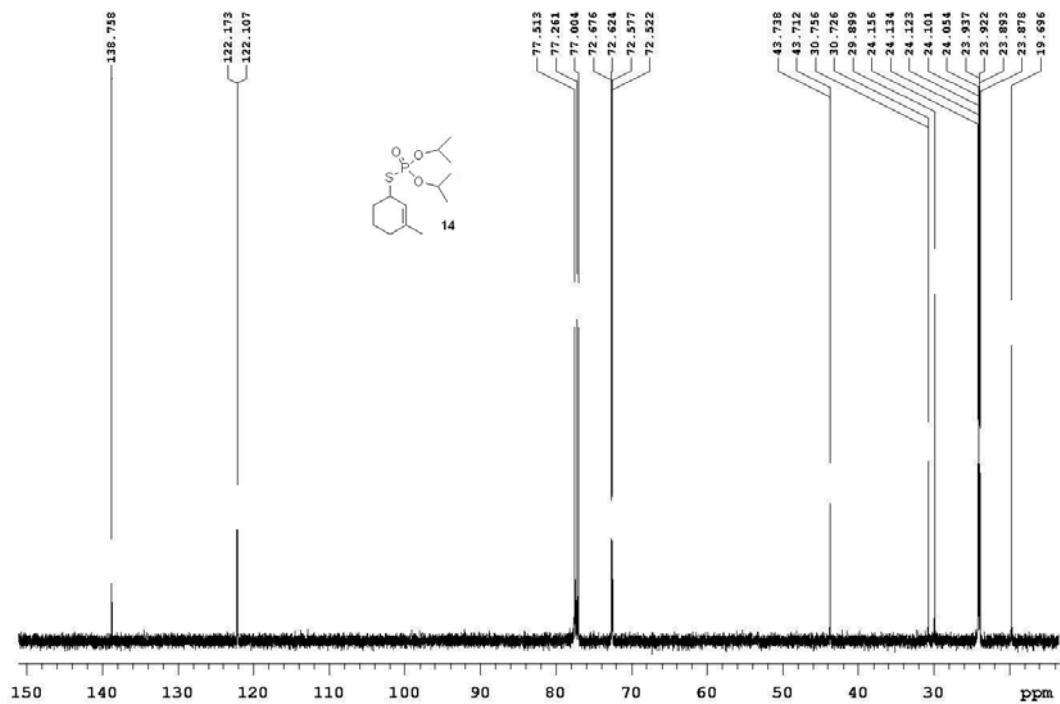




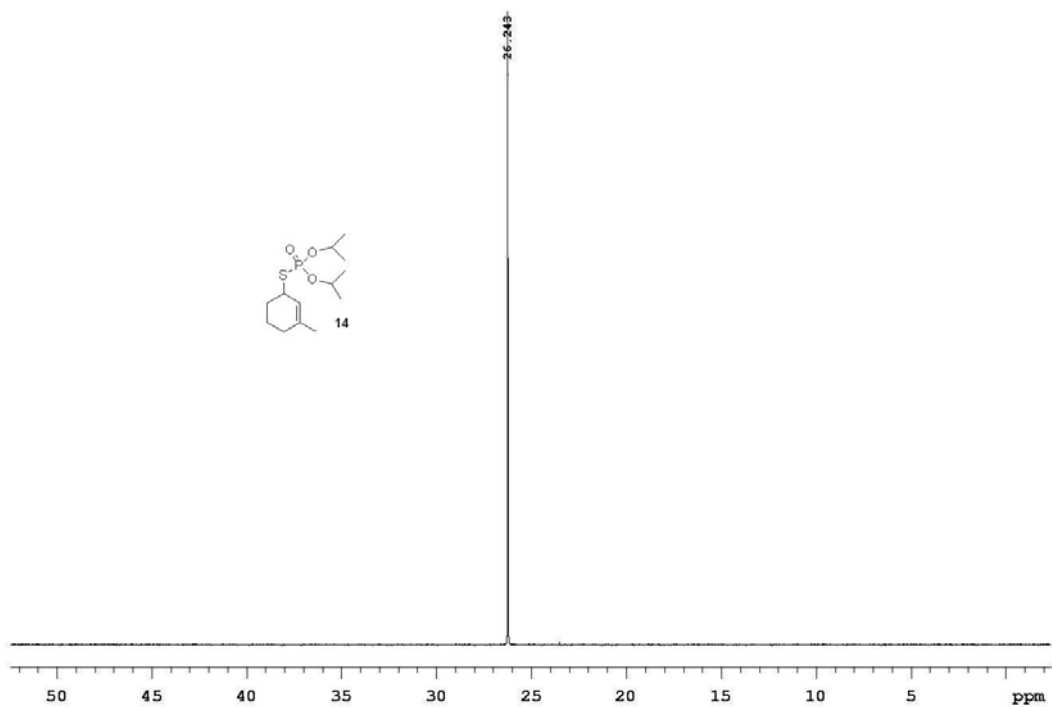
ipr thiophosphoric acid **13** CD₂Cl₂



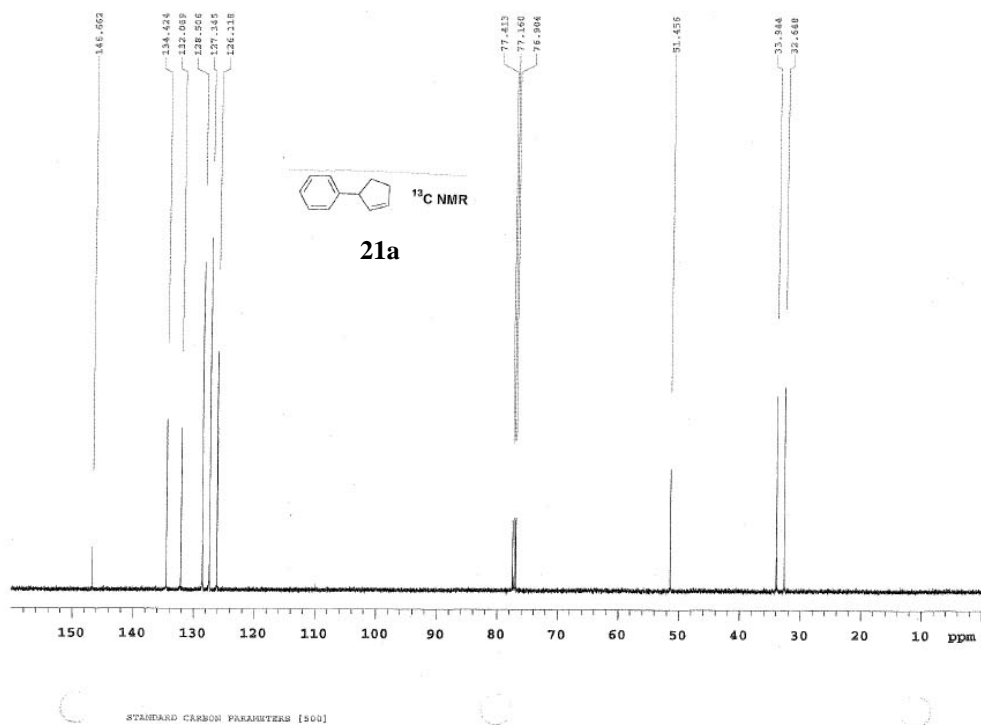
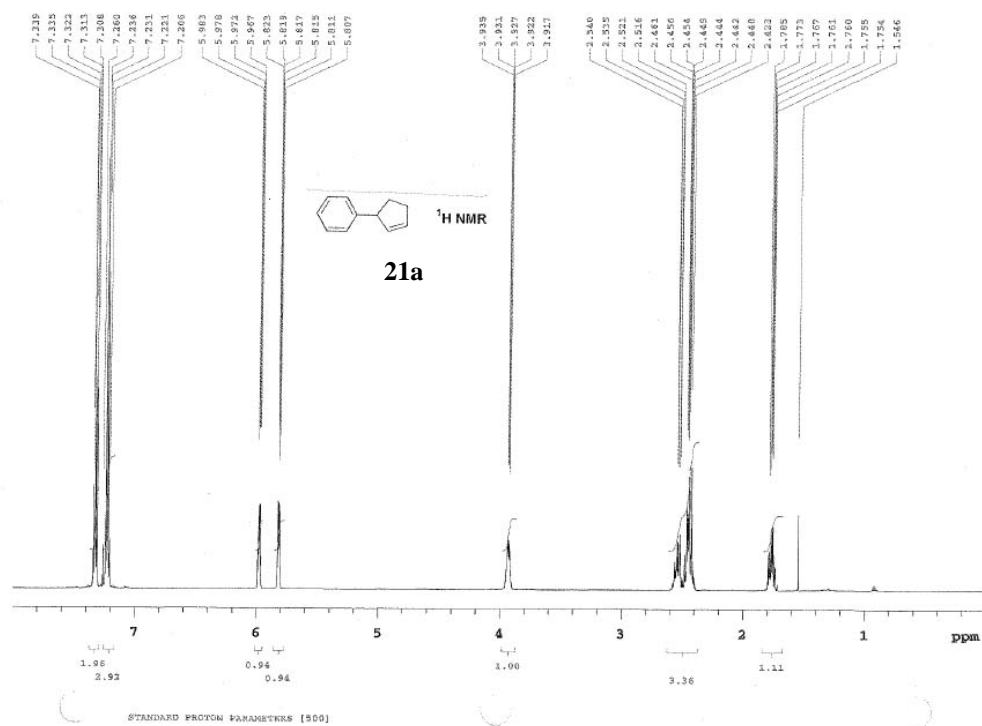
FOR-8-64_columned




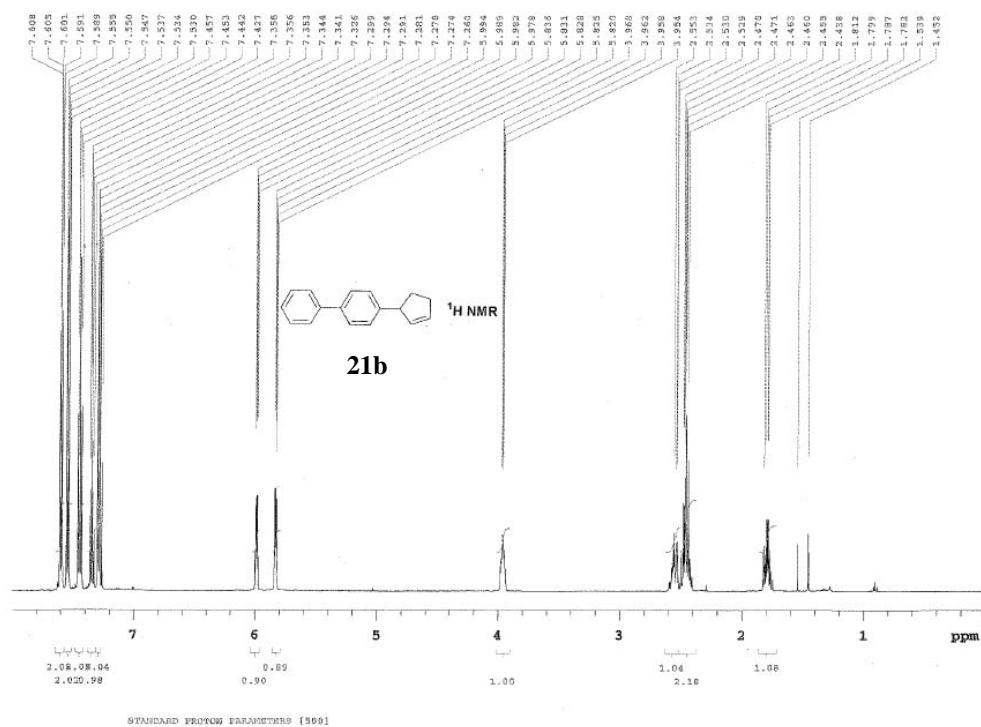
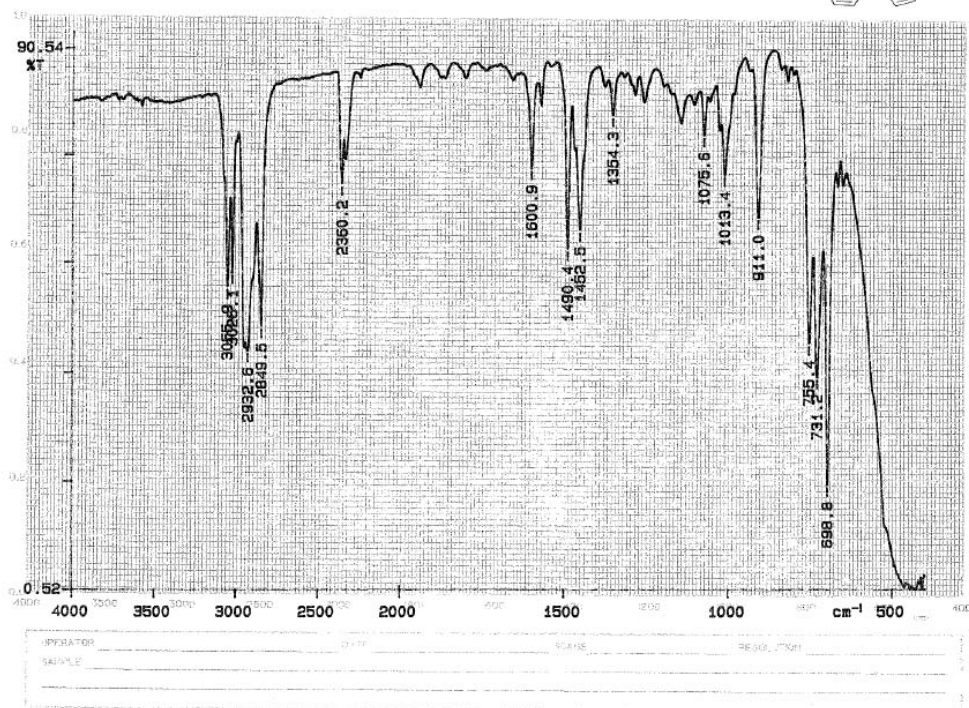
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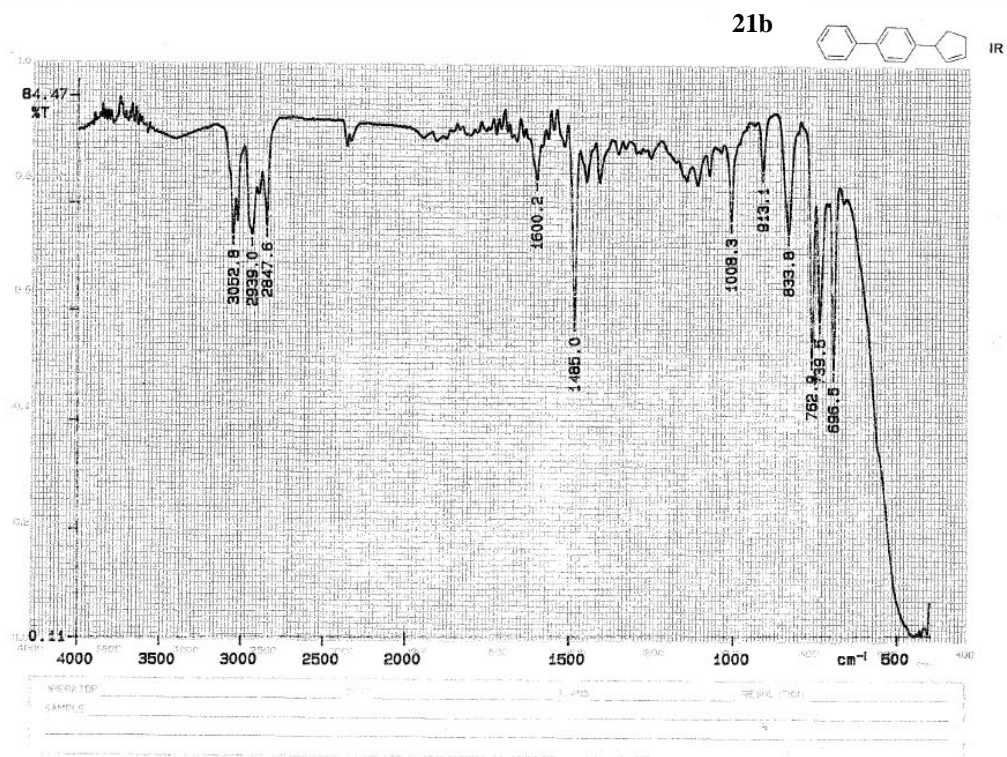
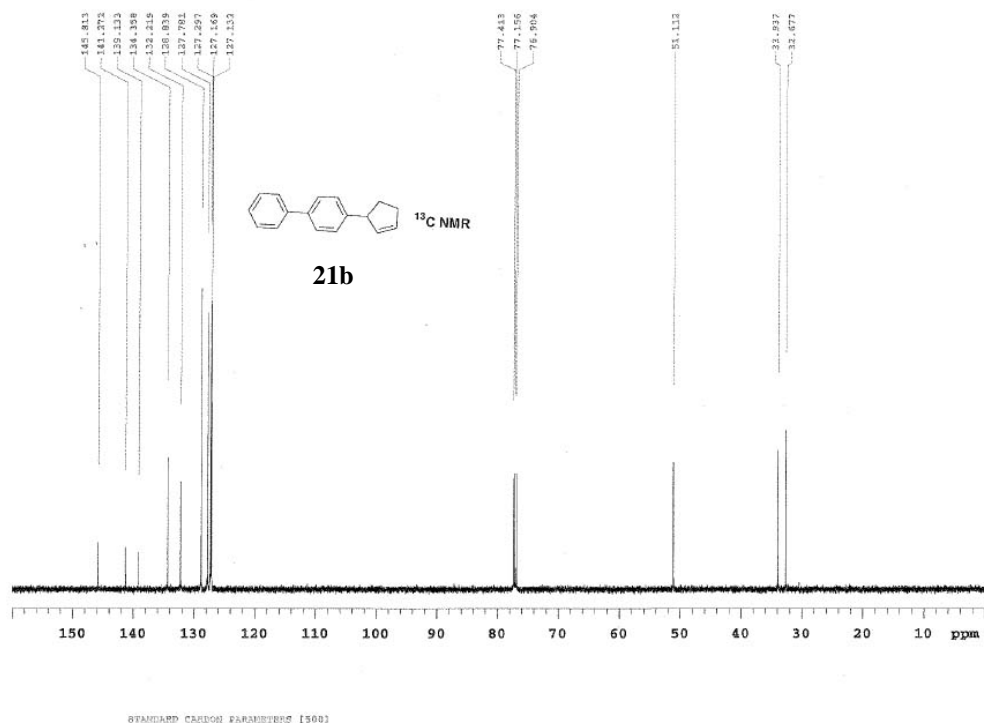


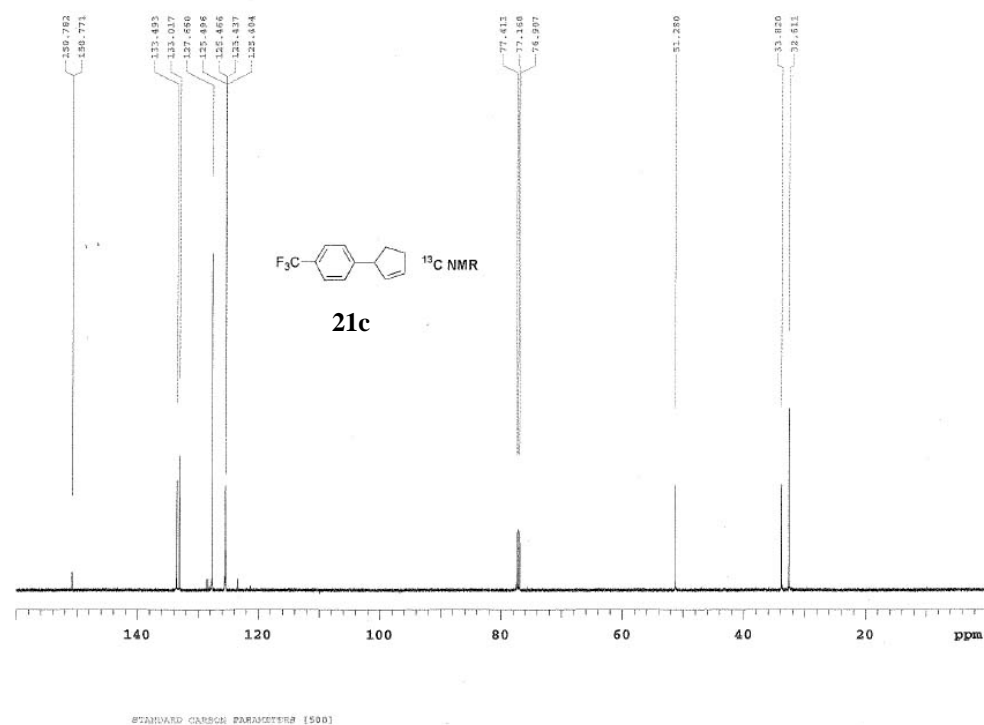
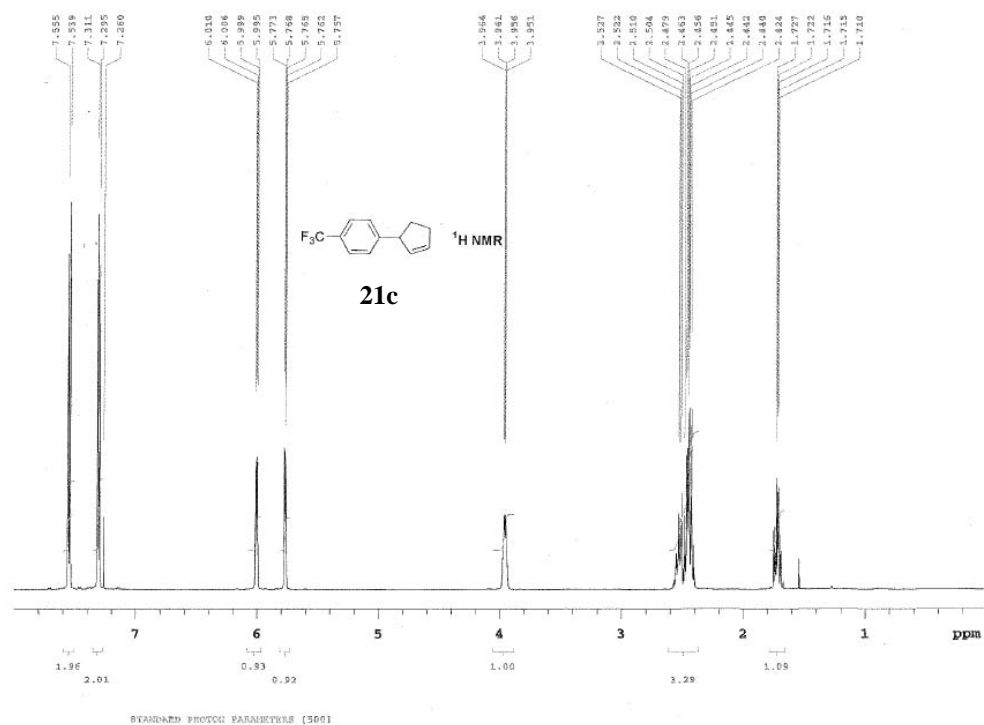
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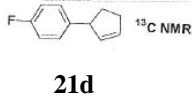
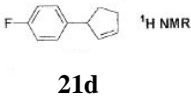


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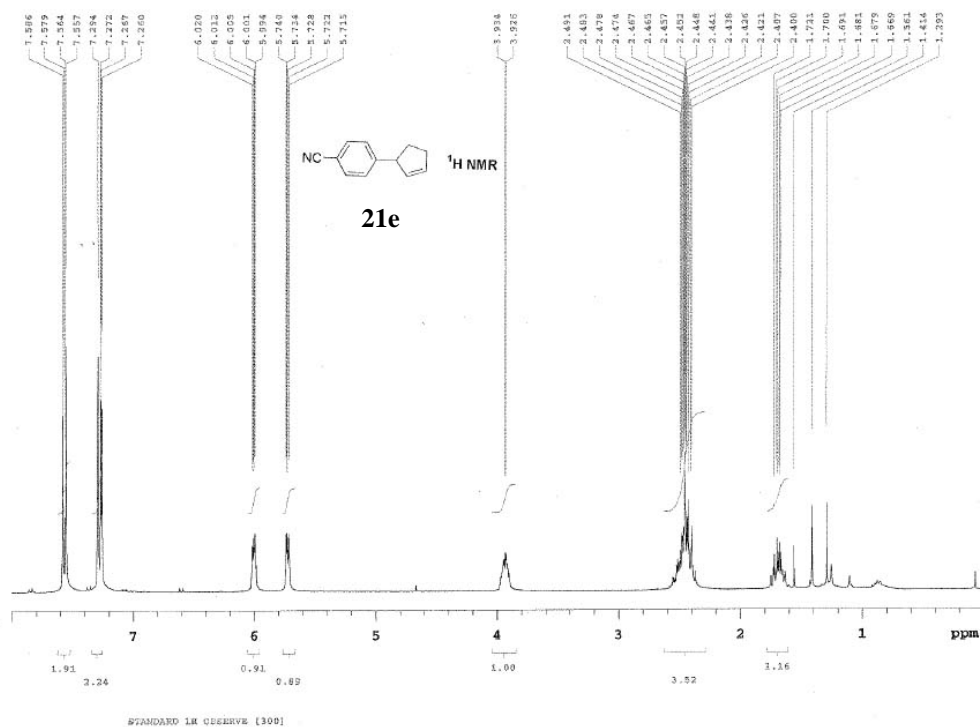
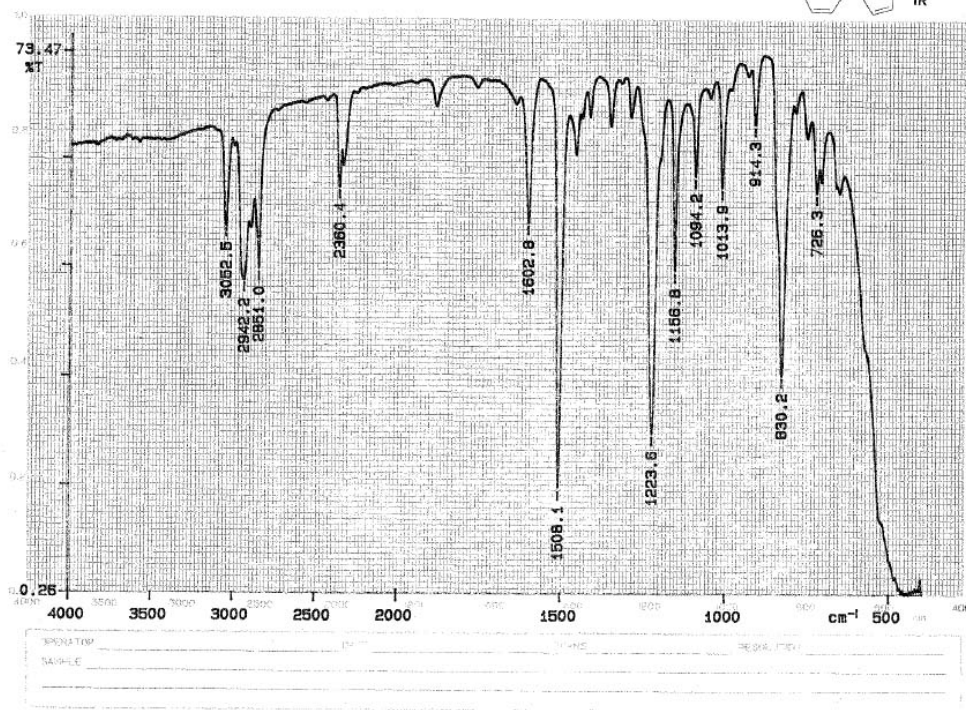
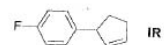


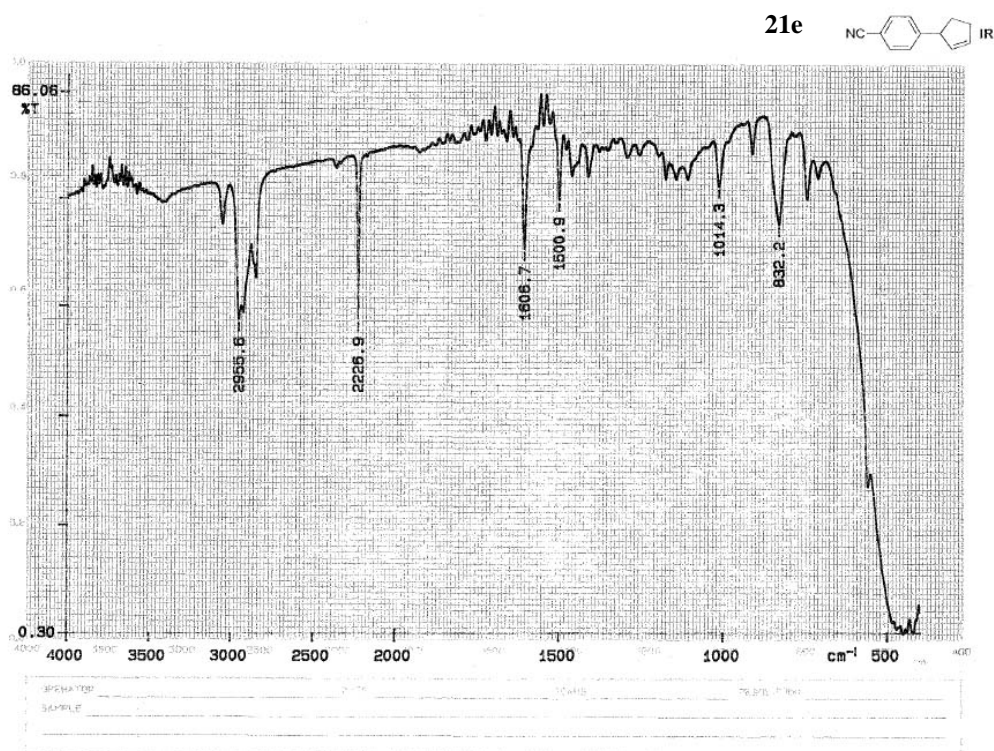
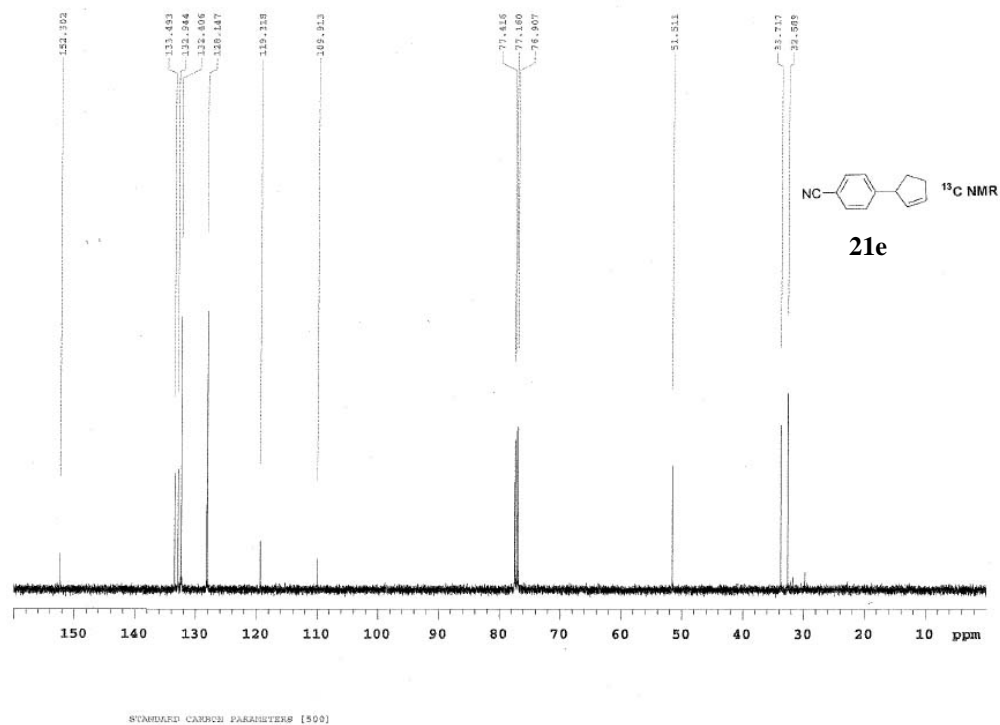


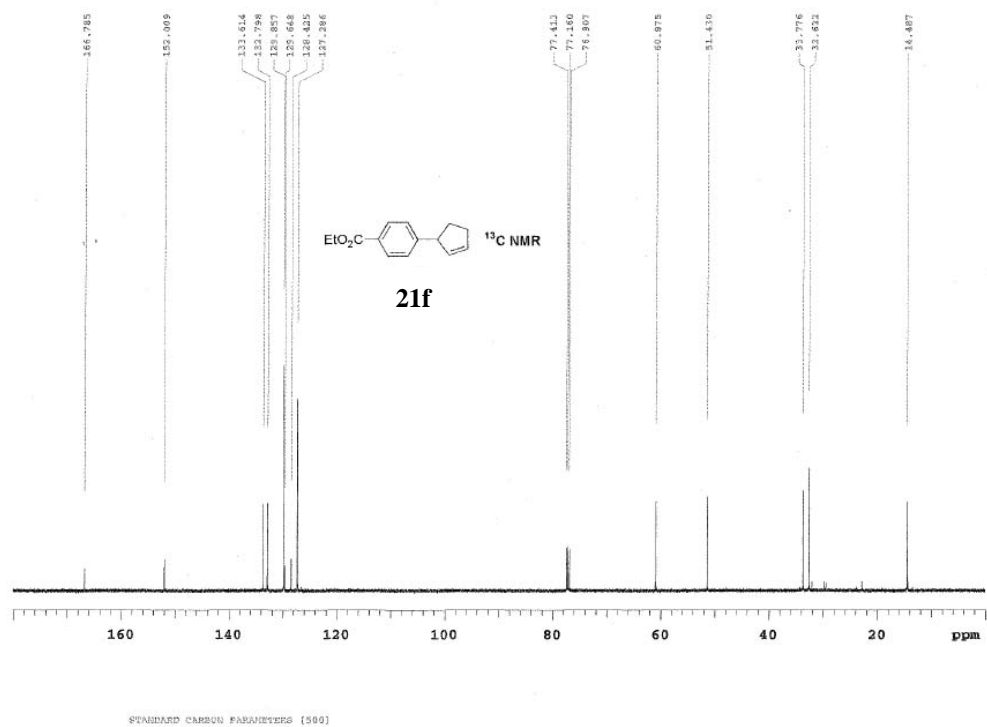
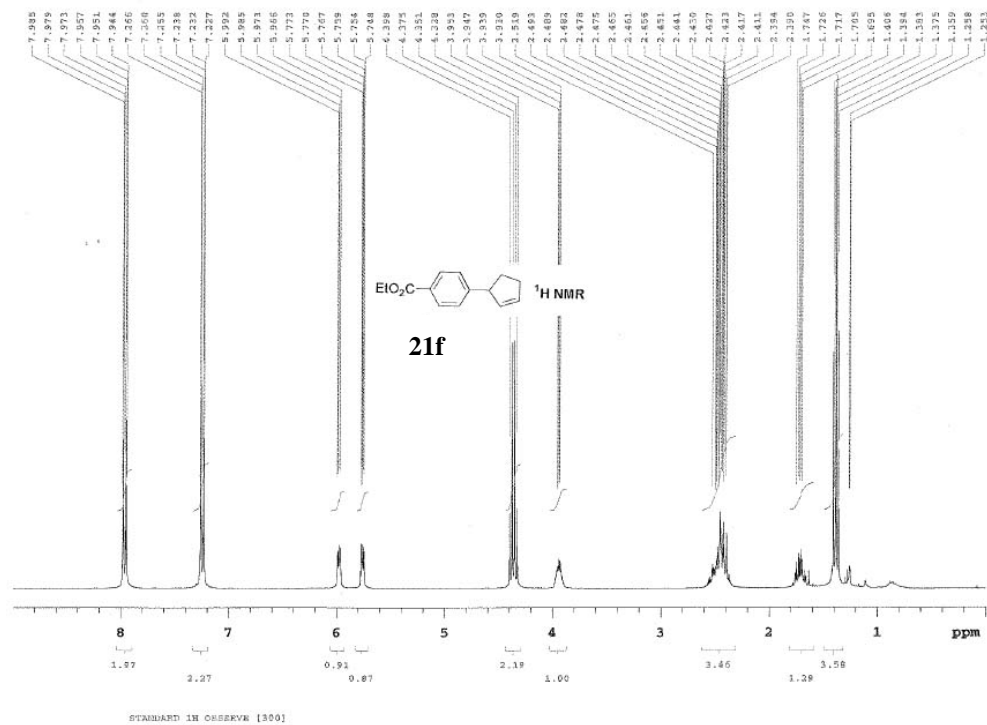




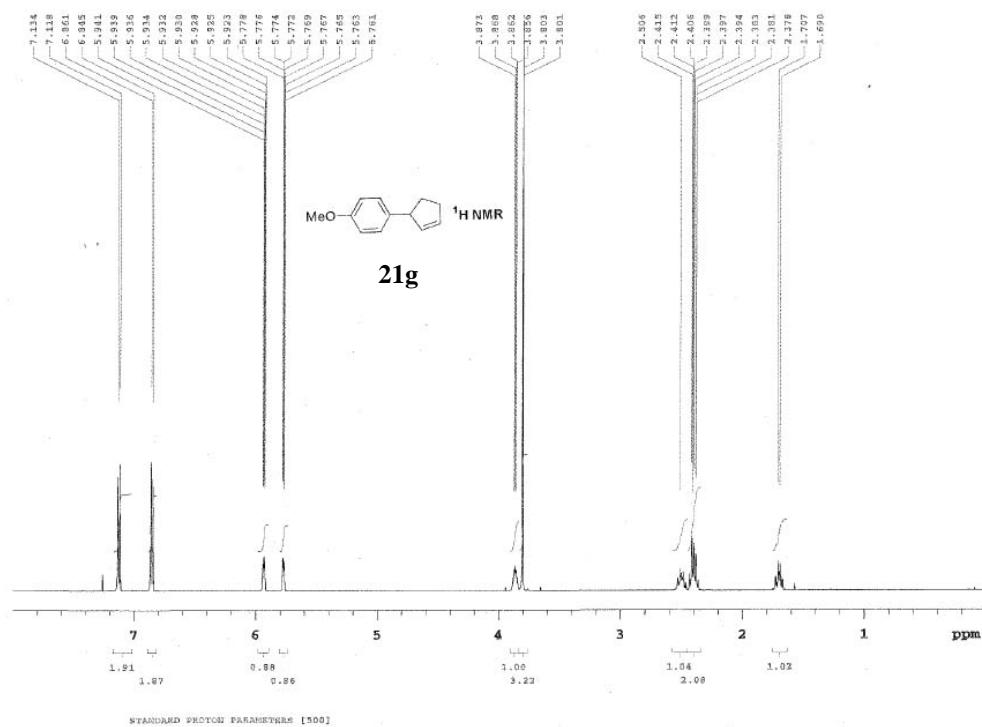
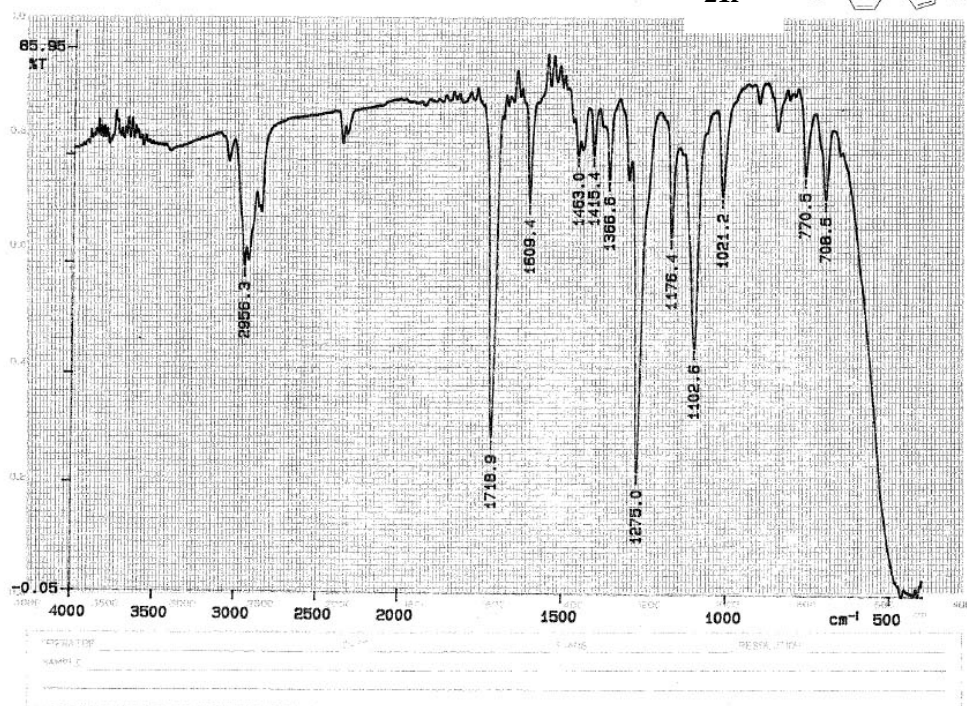
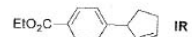
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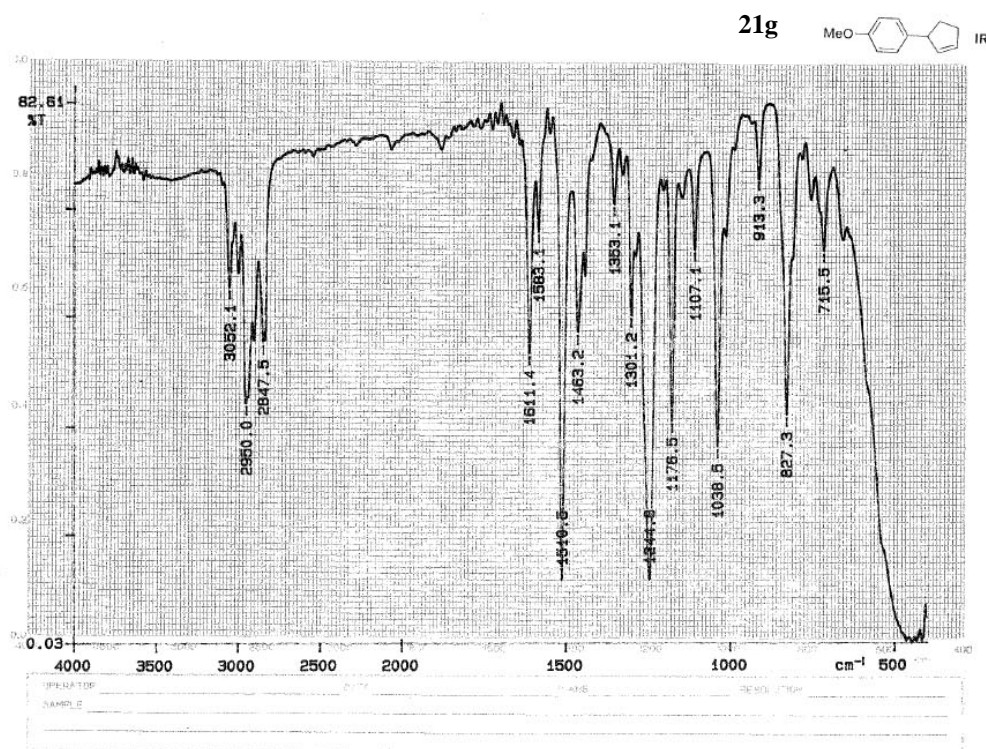
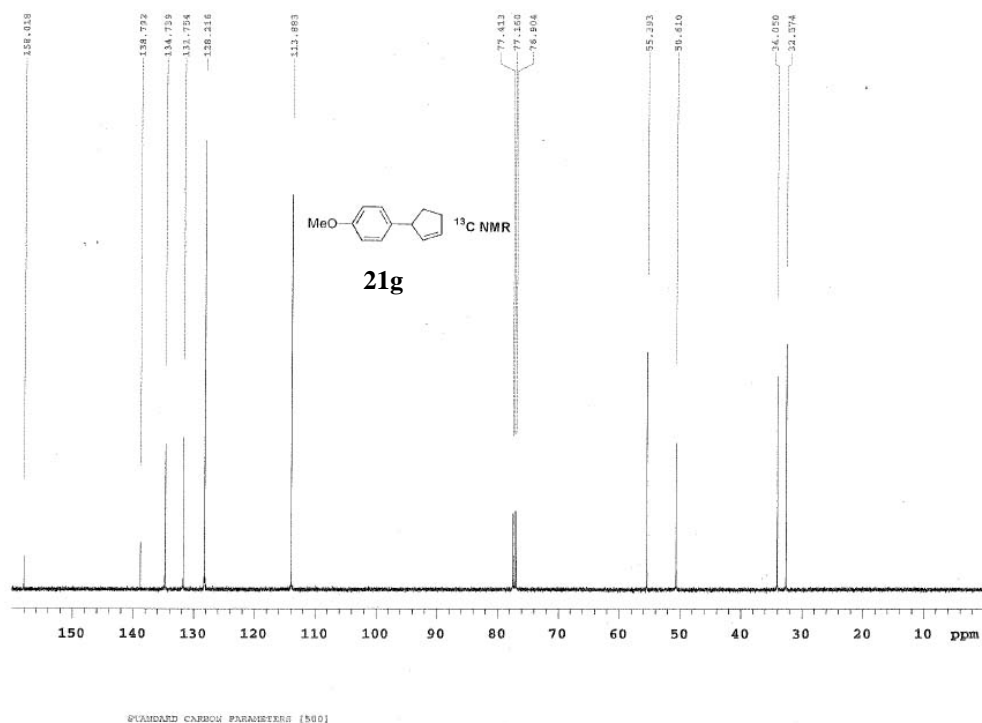


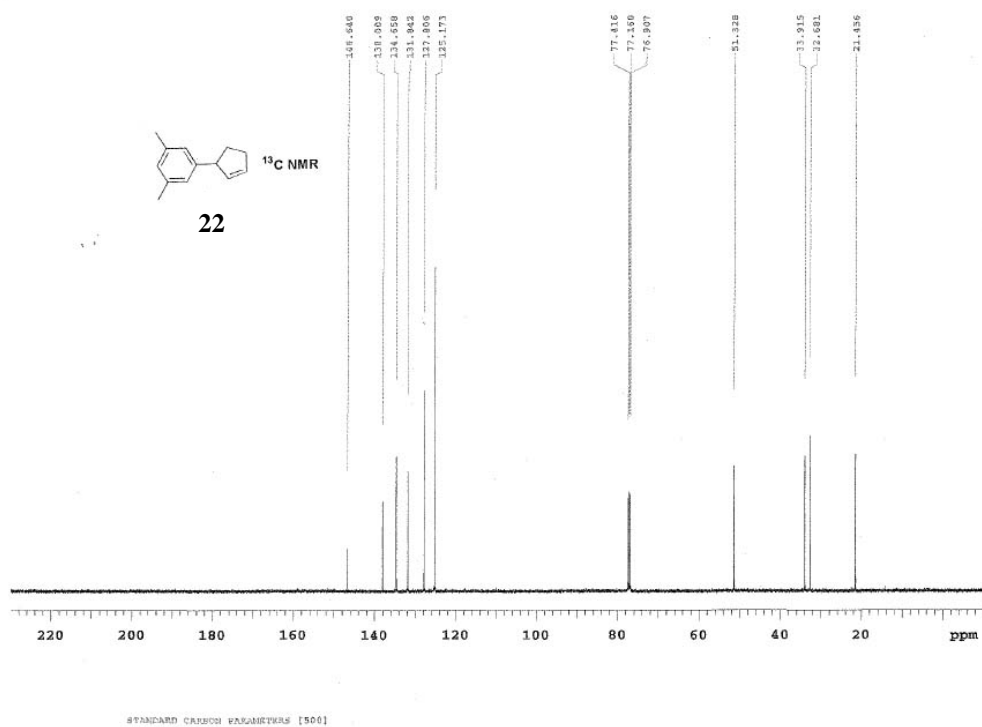
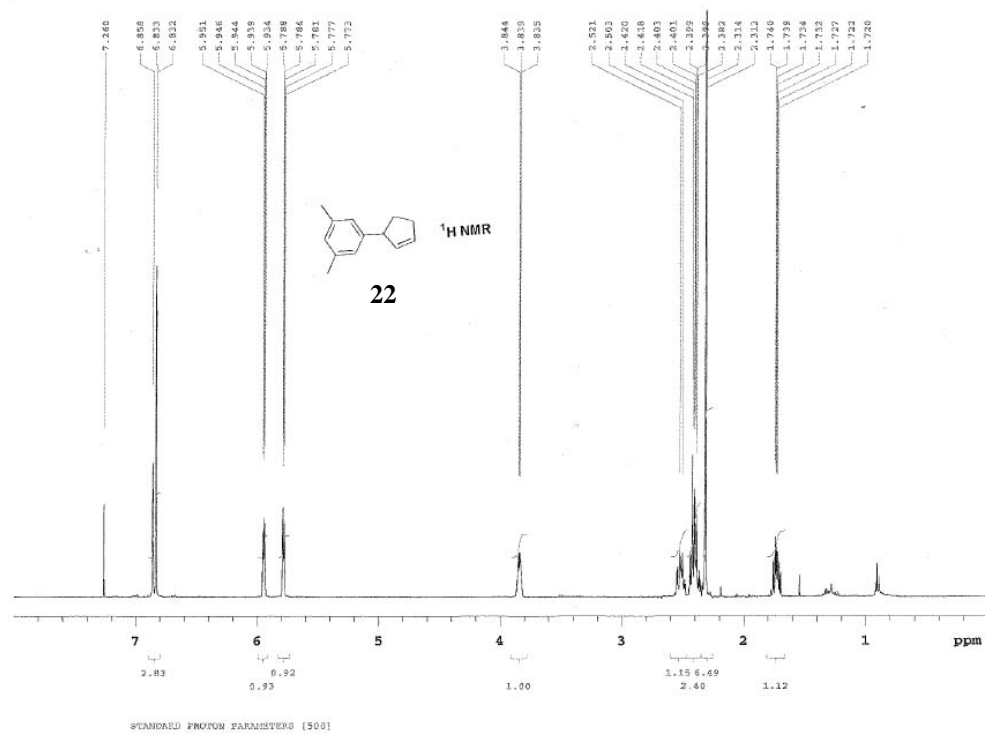


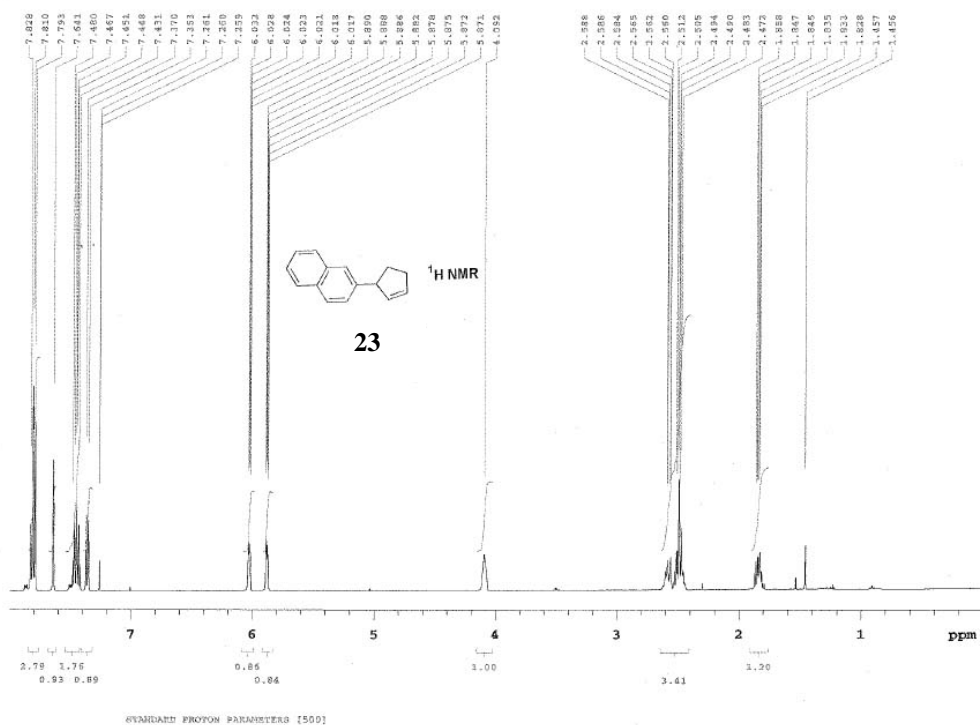
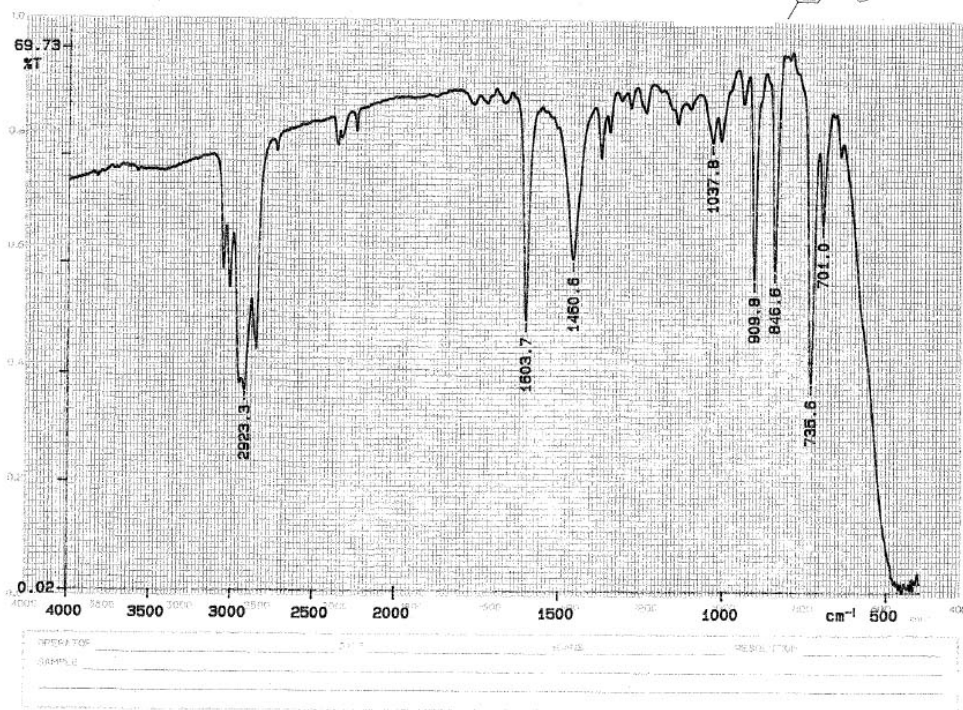
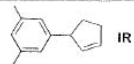


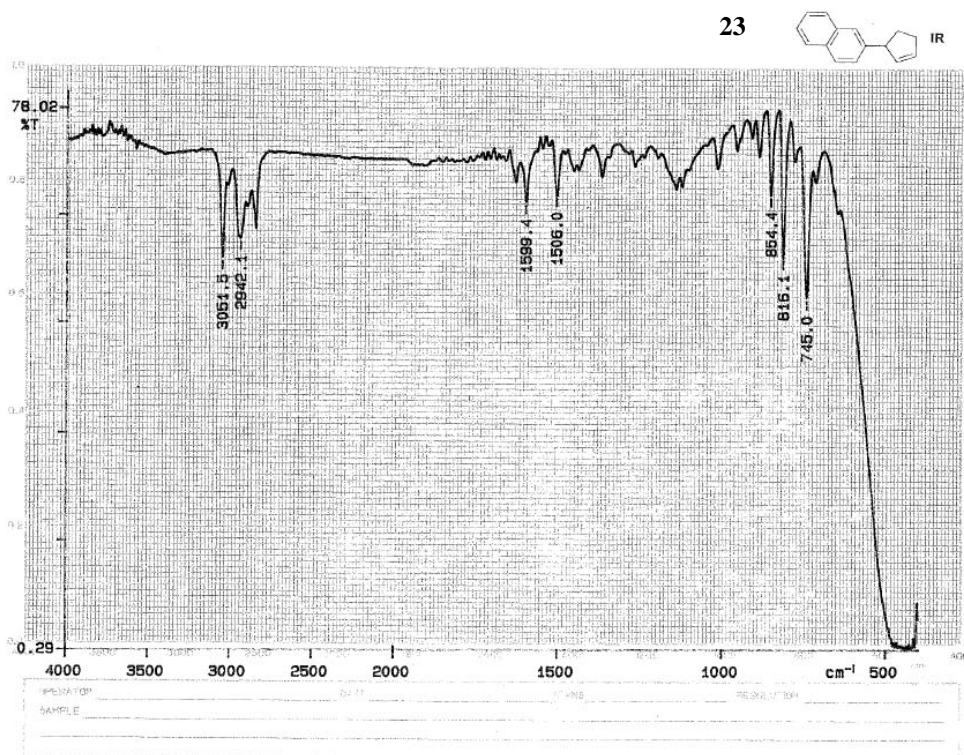
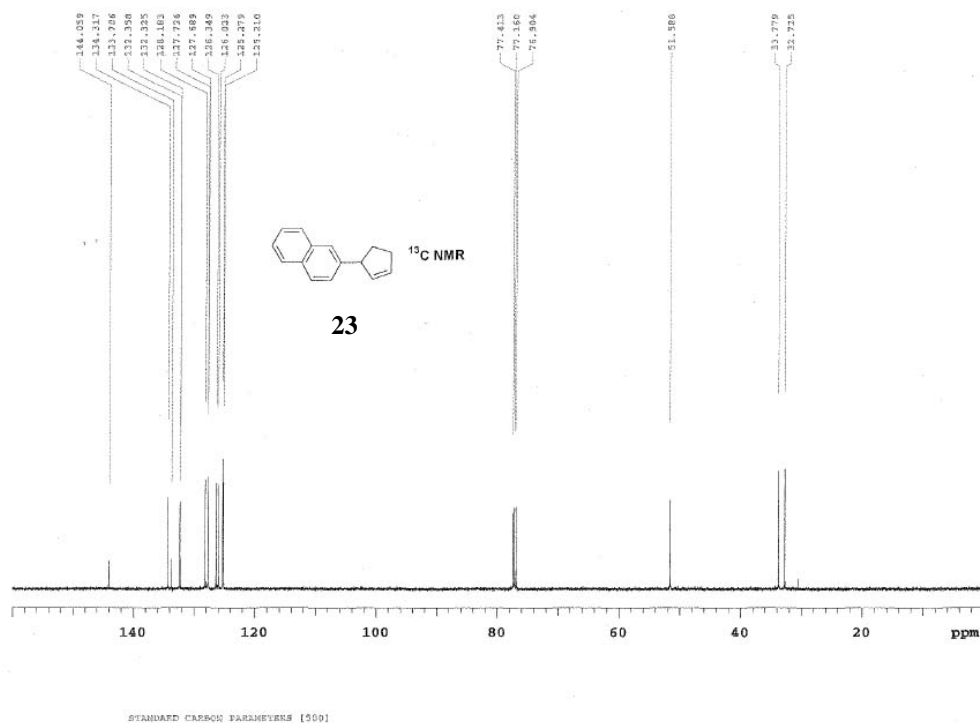
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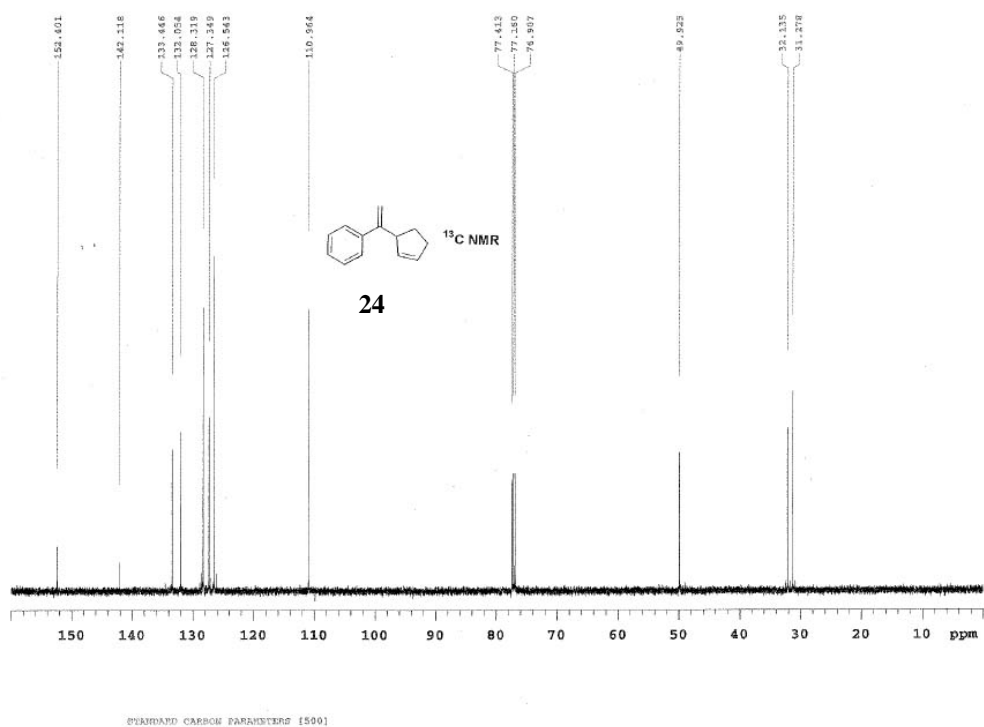
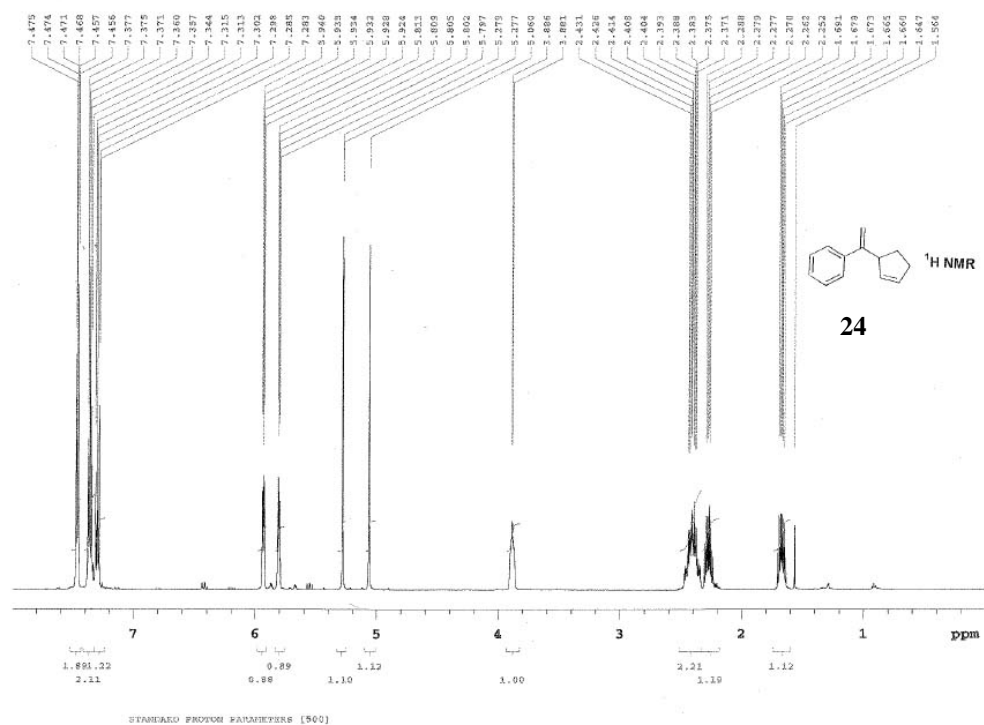


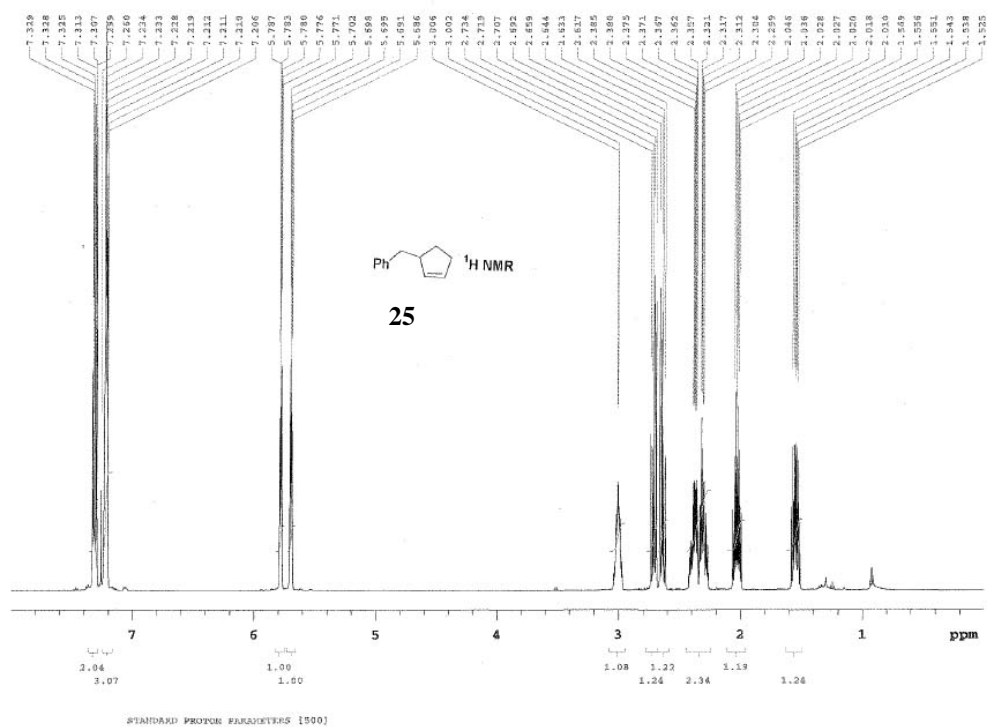
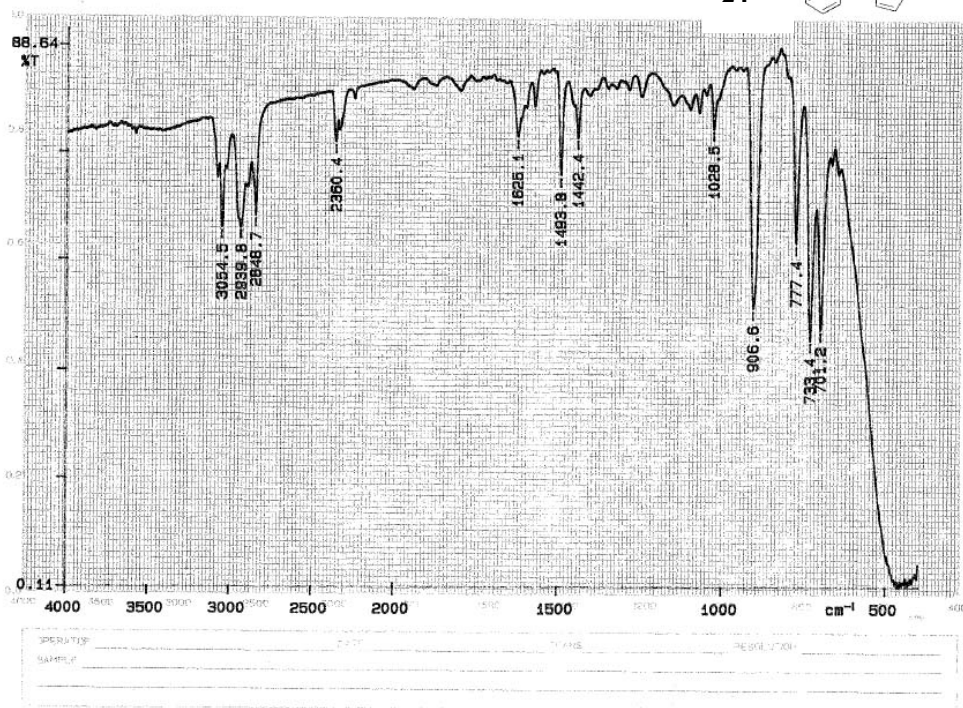
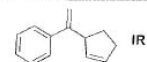


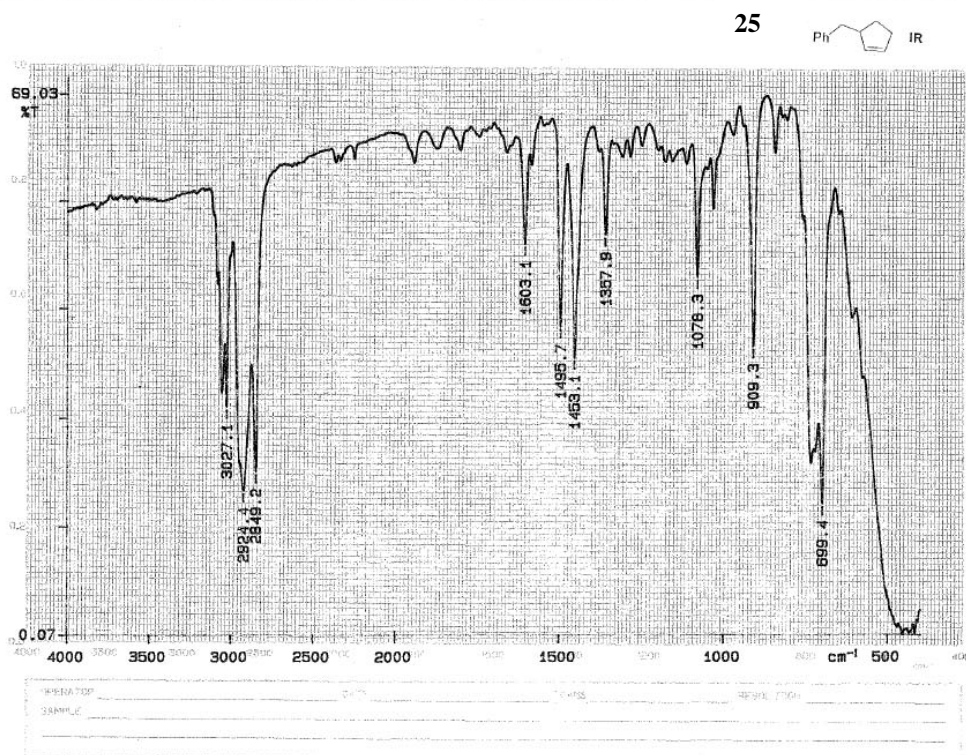
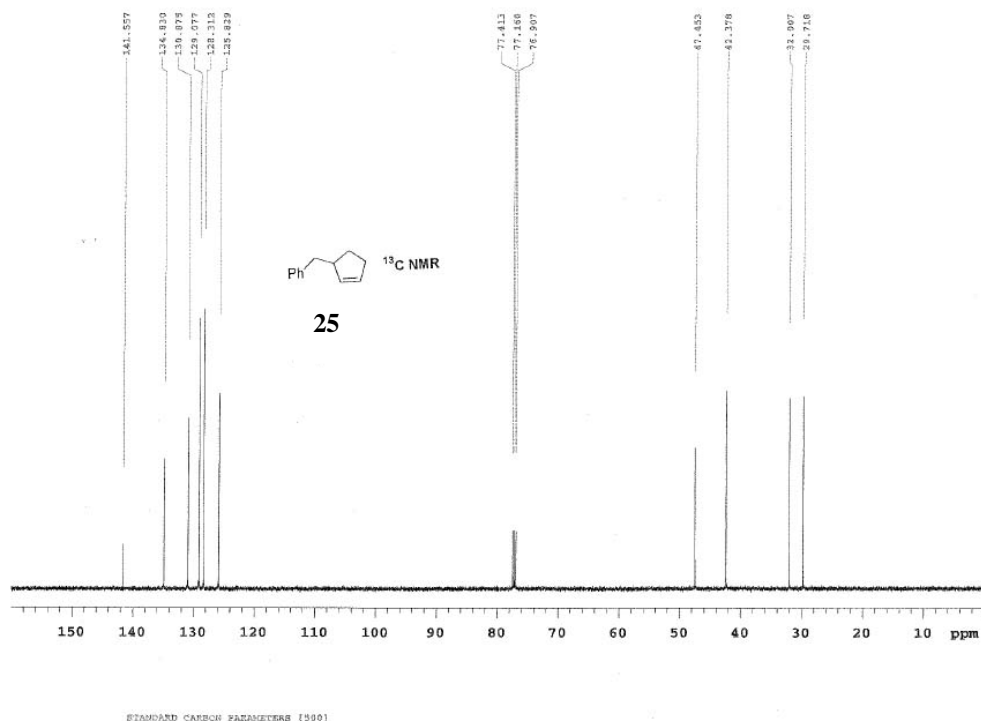


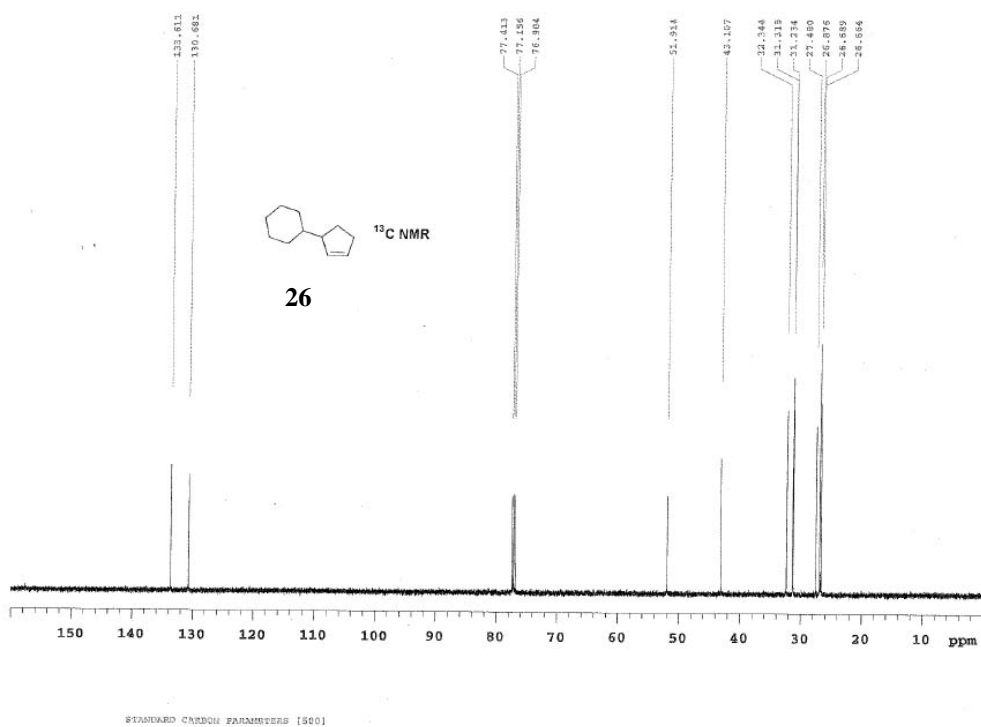
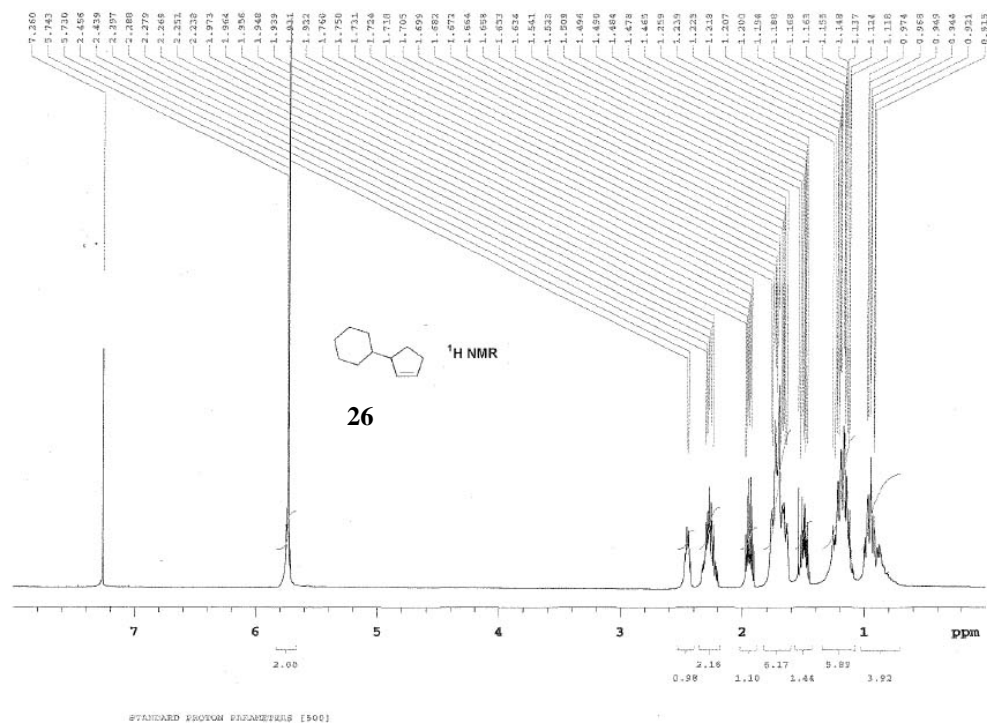


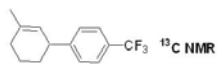
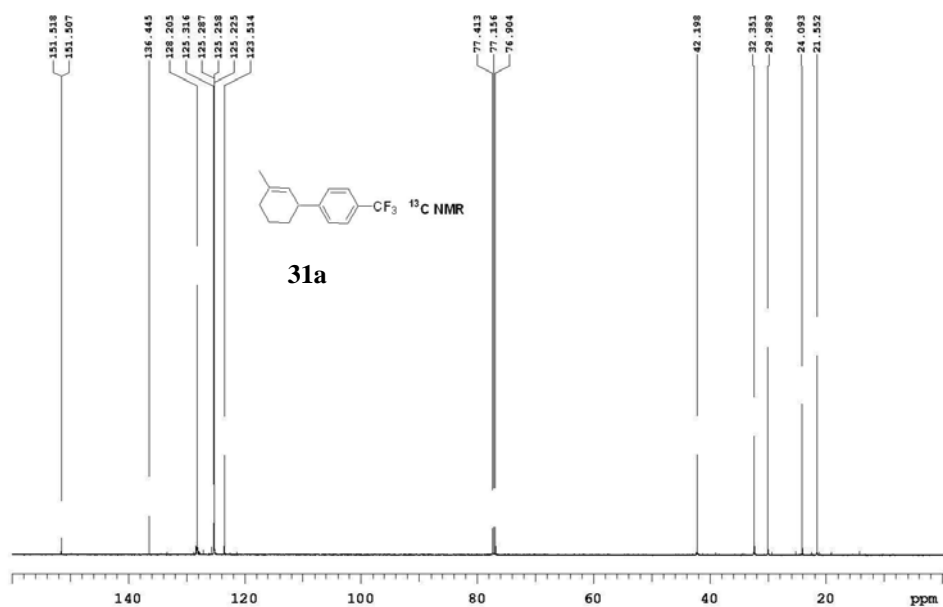
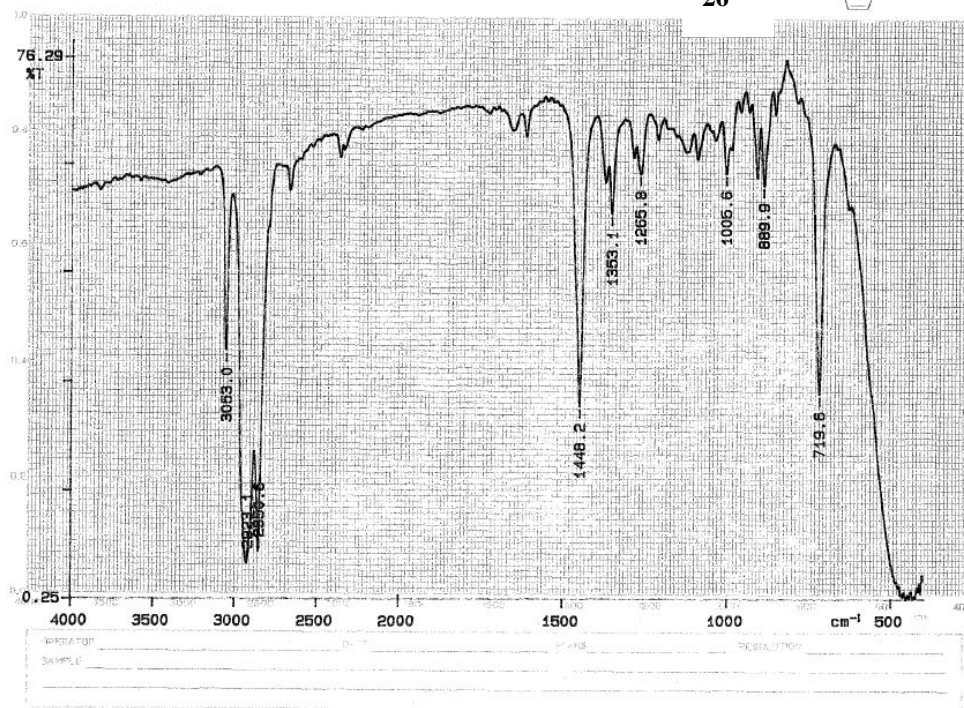
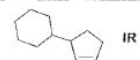






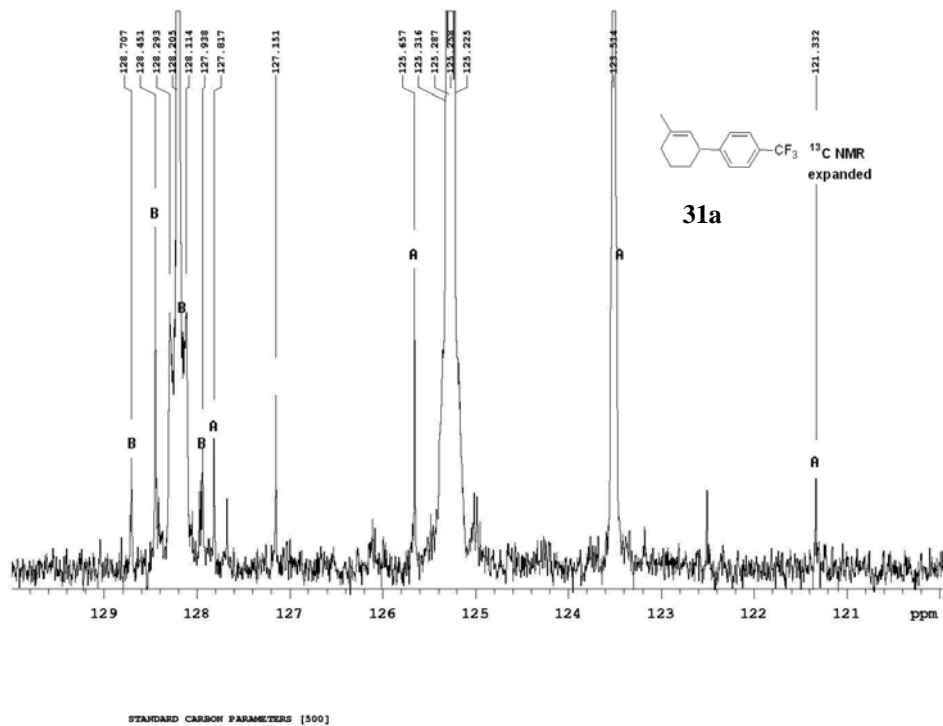
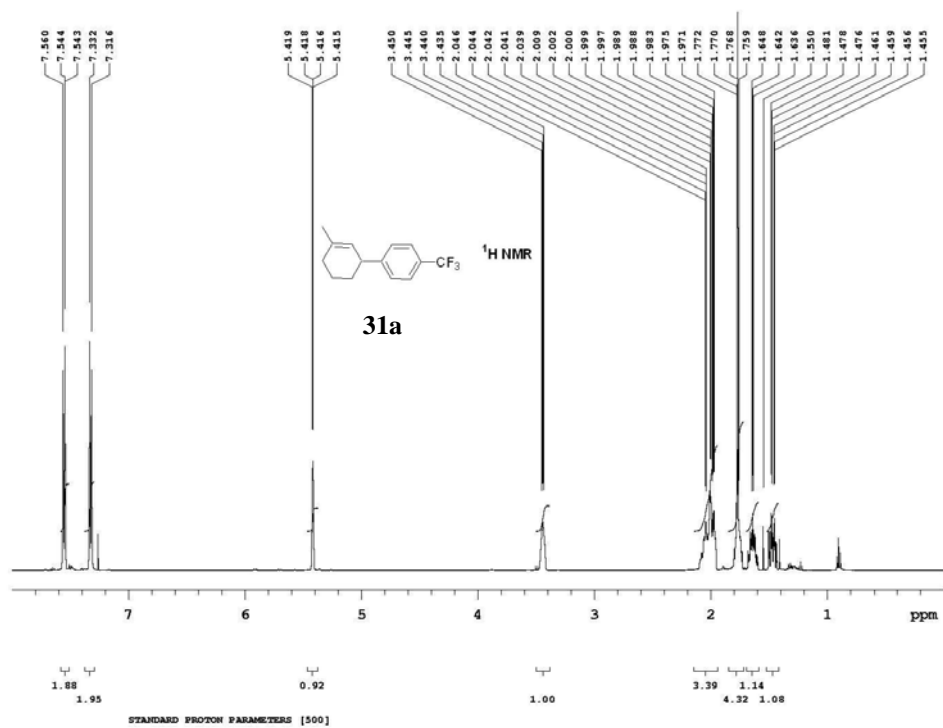


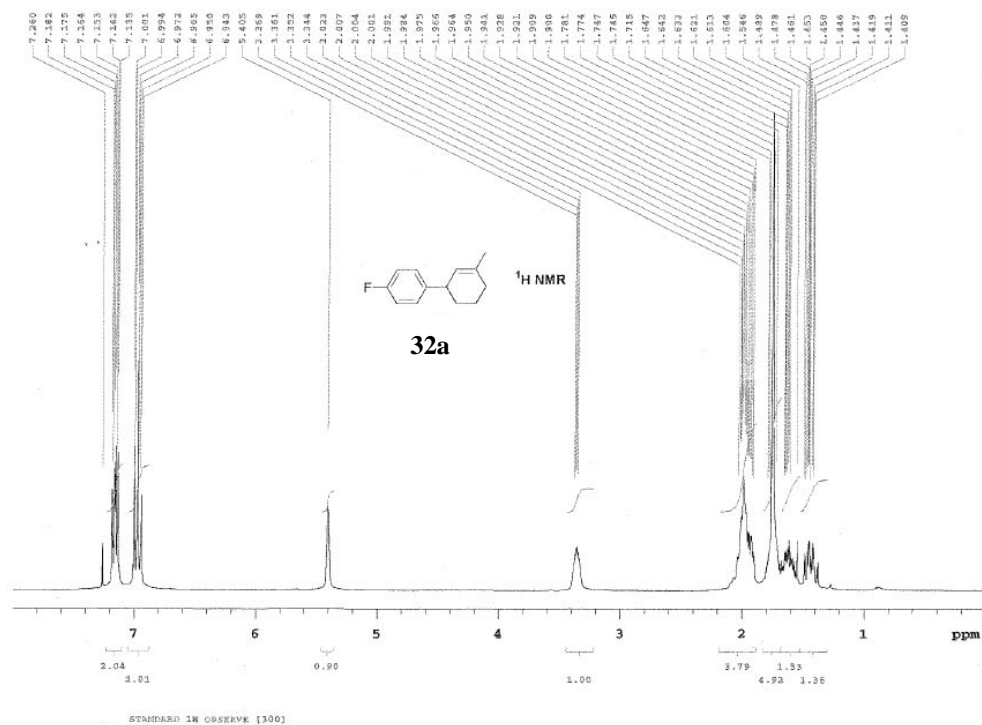
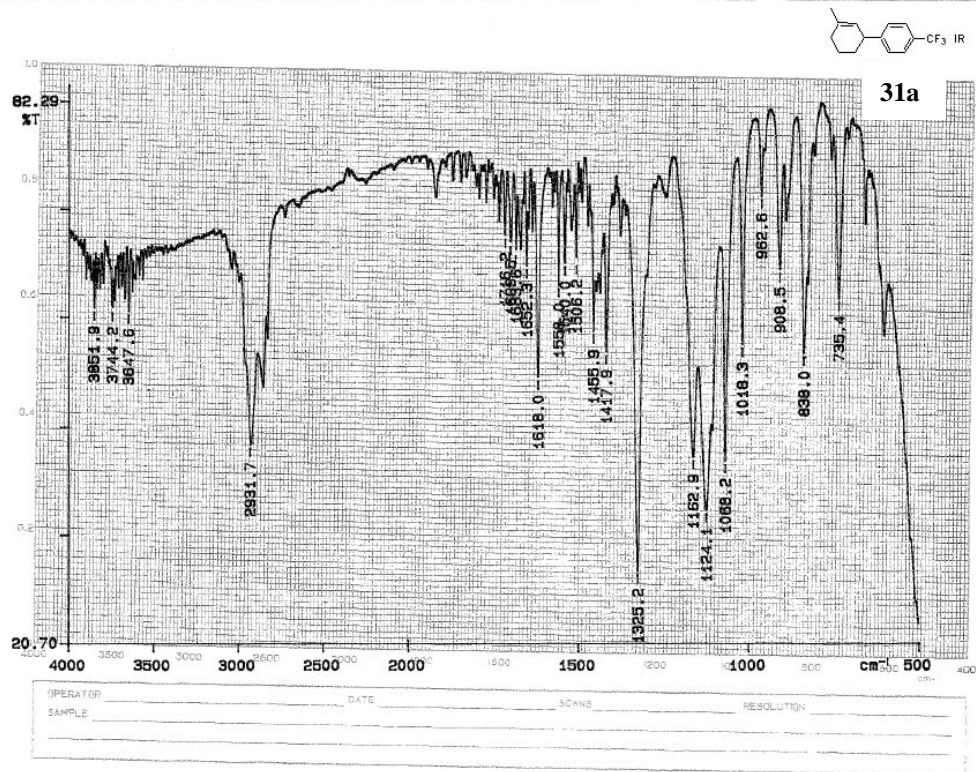


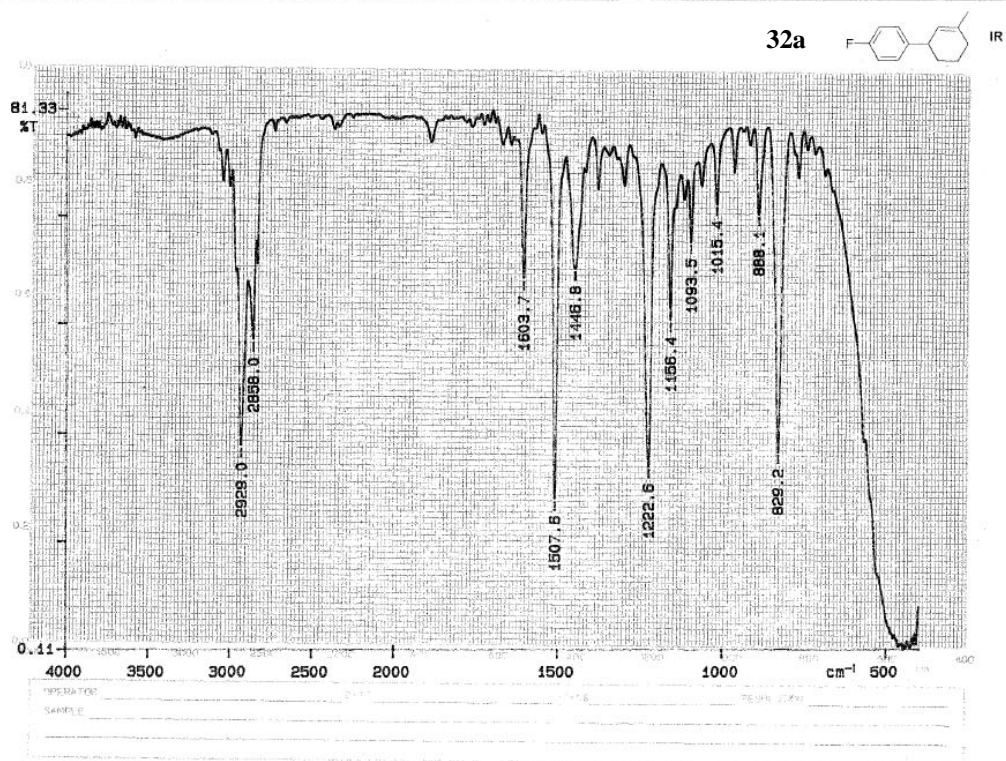
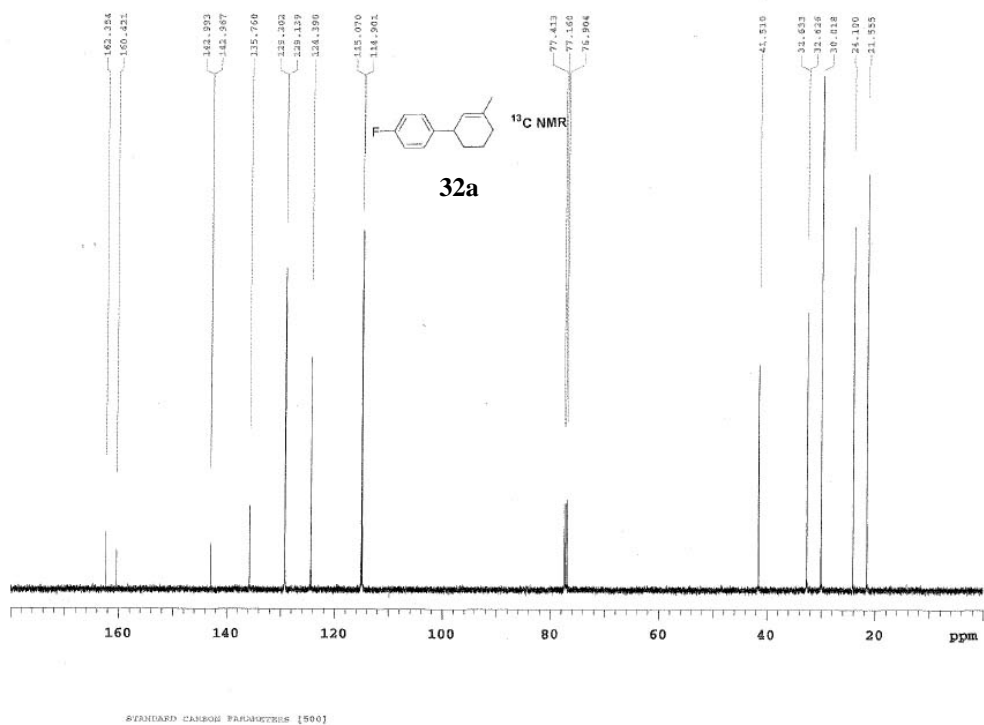


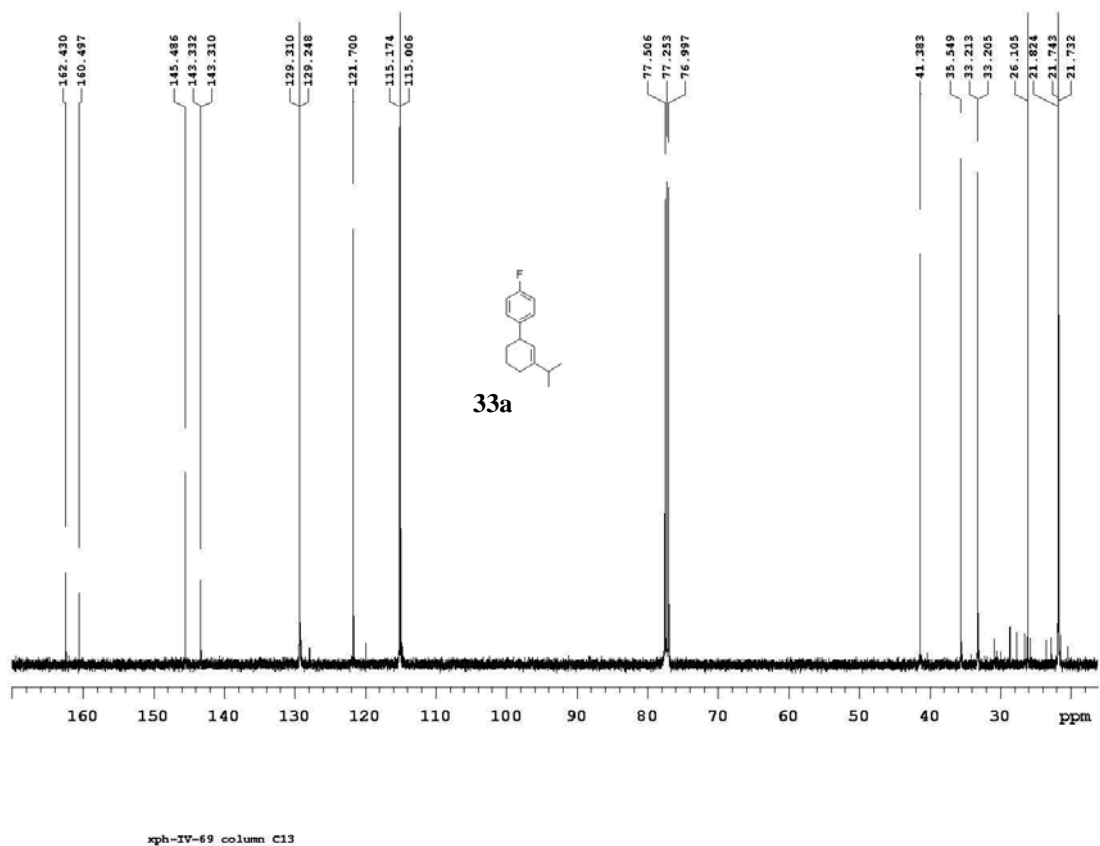
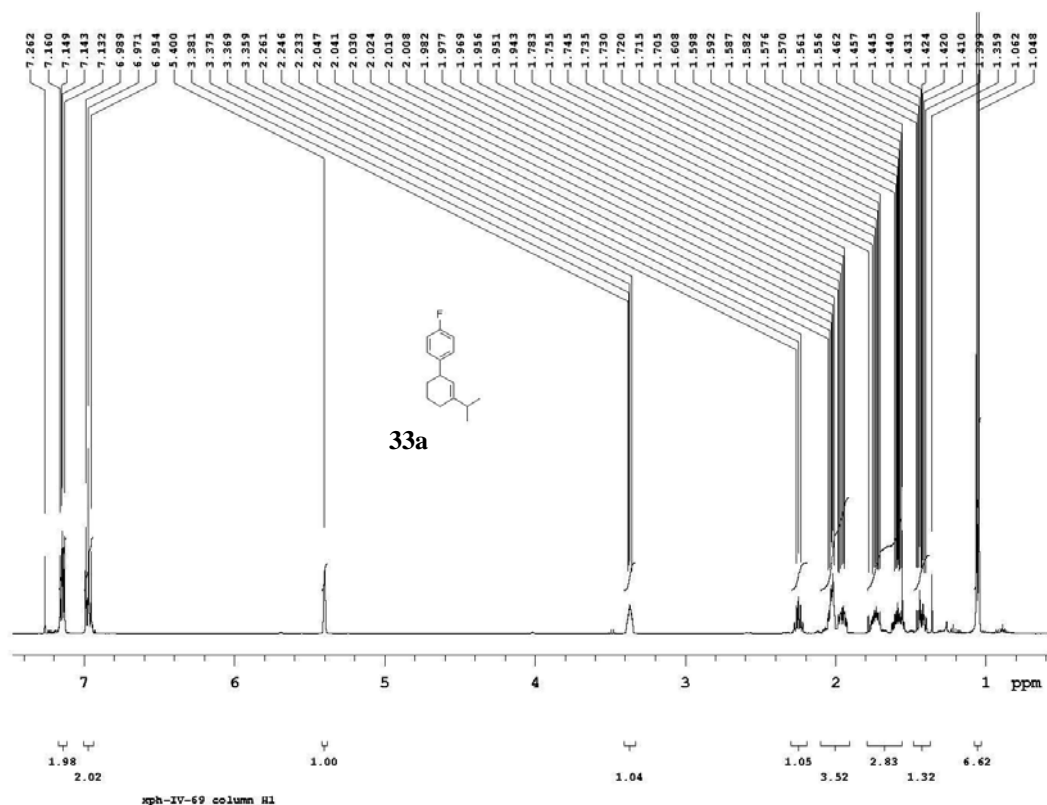
31a

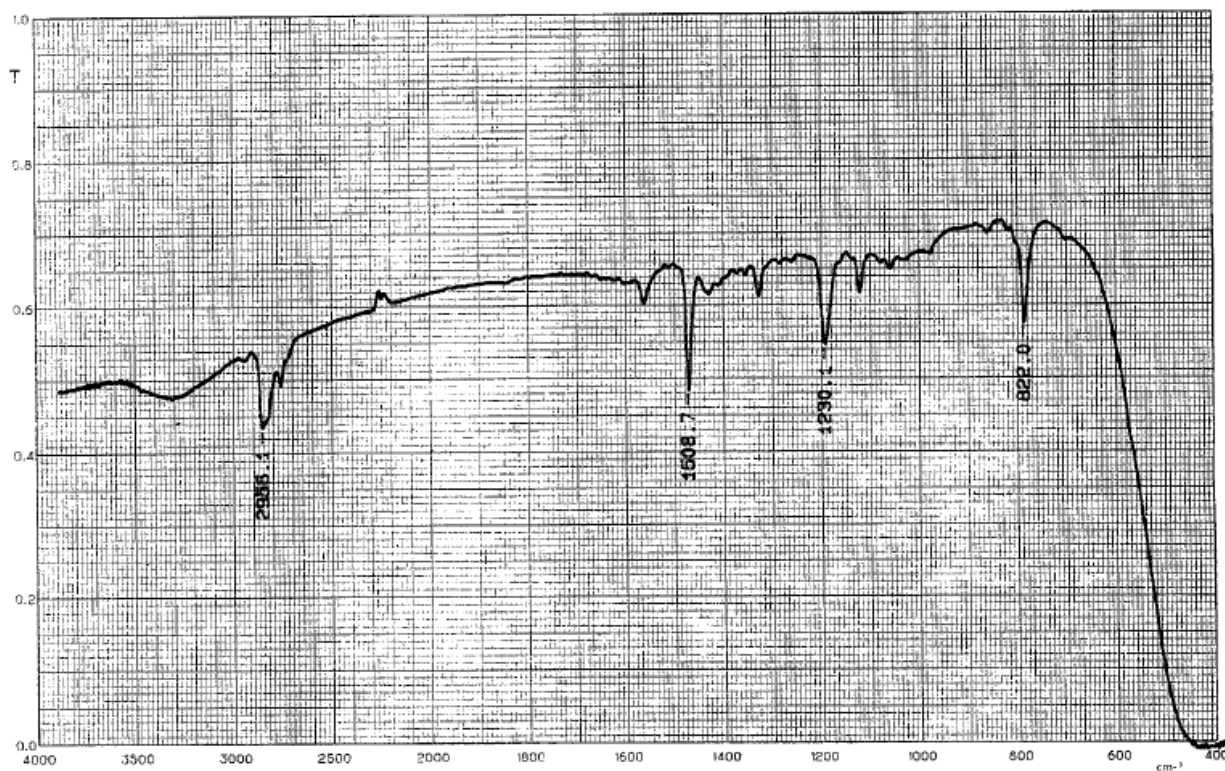
STANDARD CARBON PARAMETERS [500]



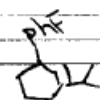




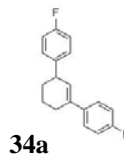
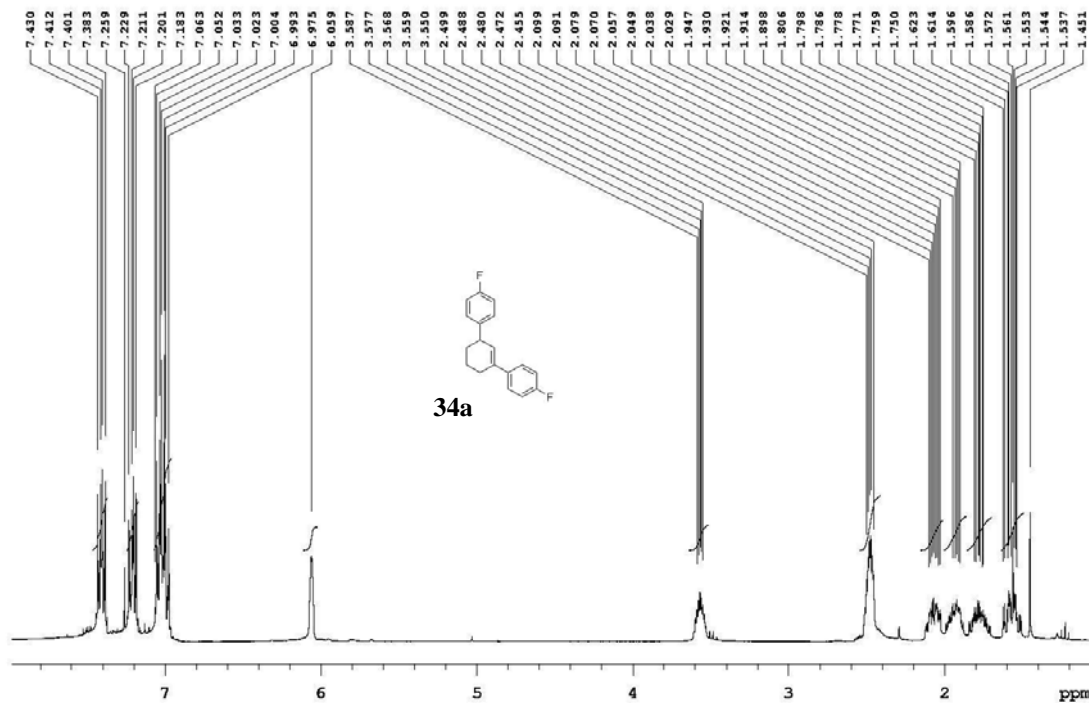




OPERATOR _____	DATE _____	SCANS _____	RESOLUTION _____
SAMPLE _____			



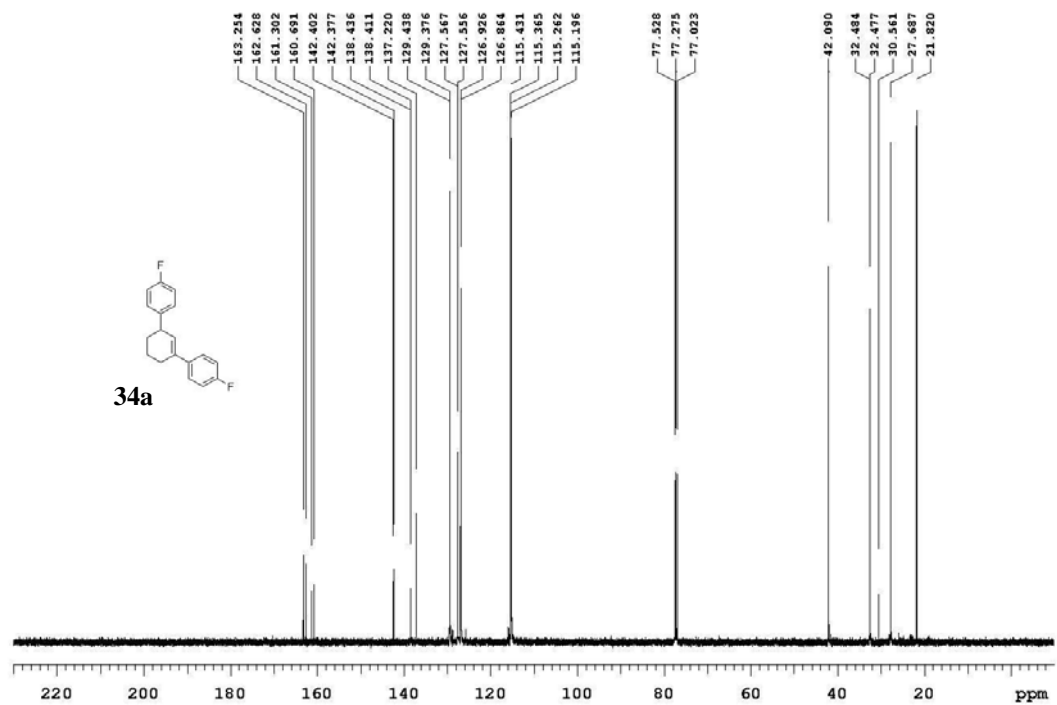
33a



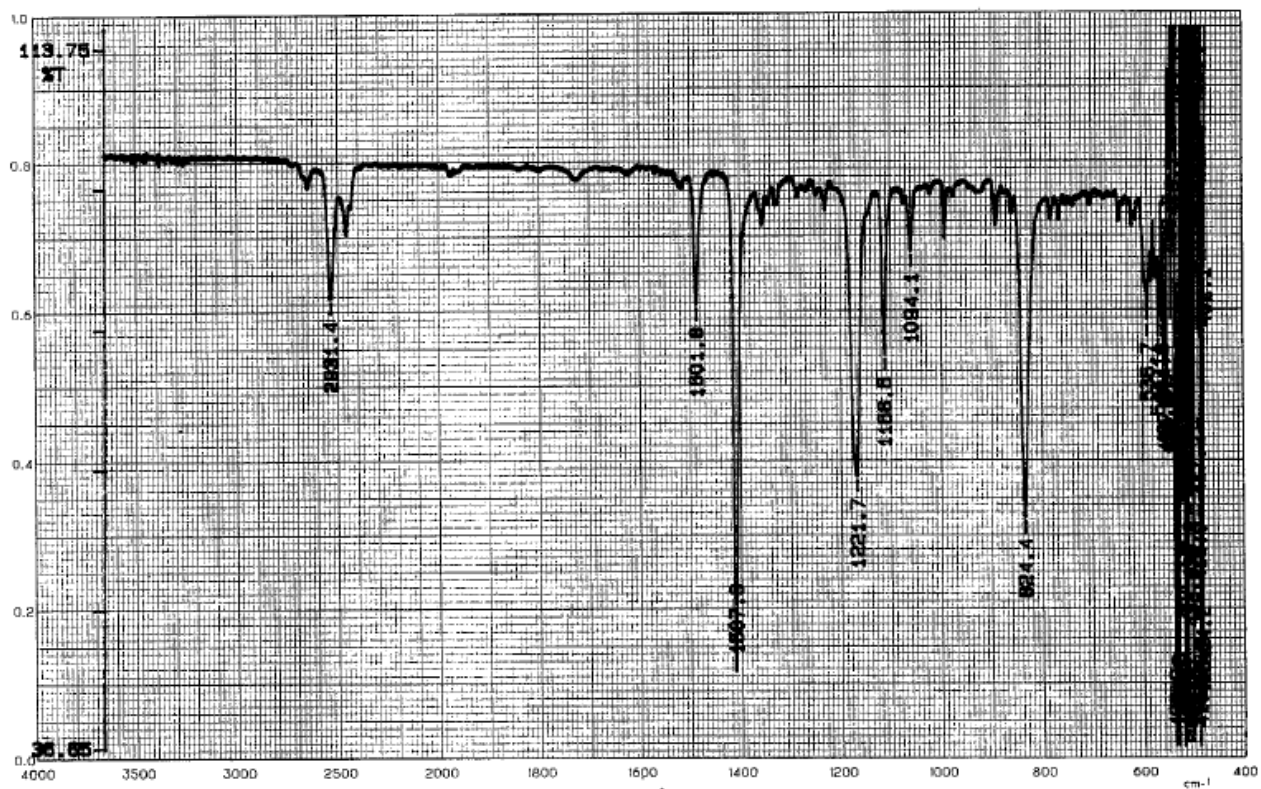
34a

2.07 3.57 0.92
1.91
xph-IV-51 column

1.00 2.16 1.19 1.35 1.30 1.46

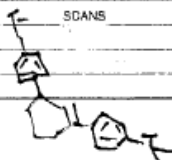


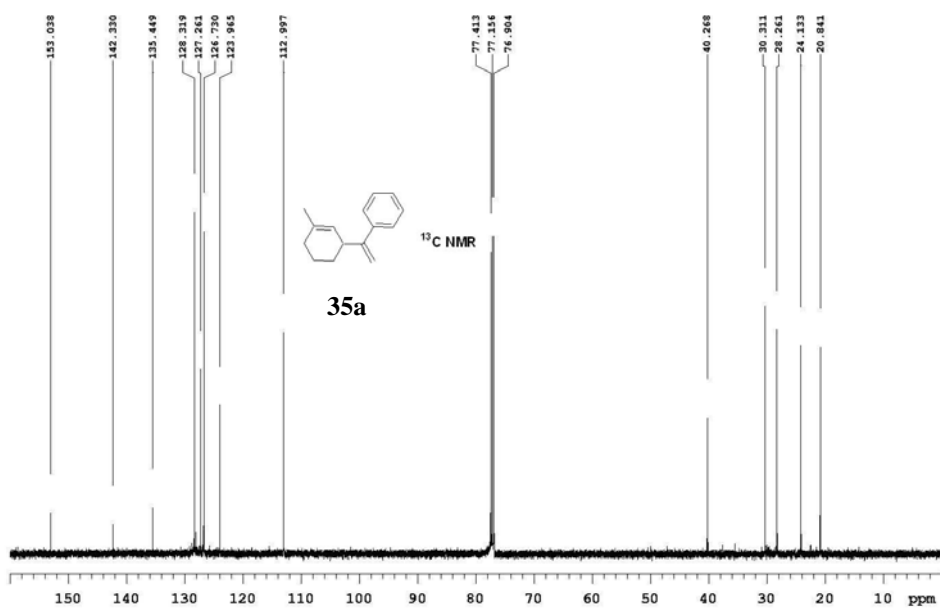
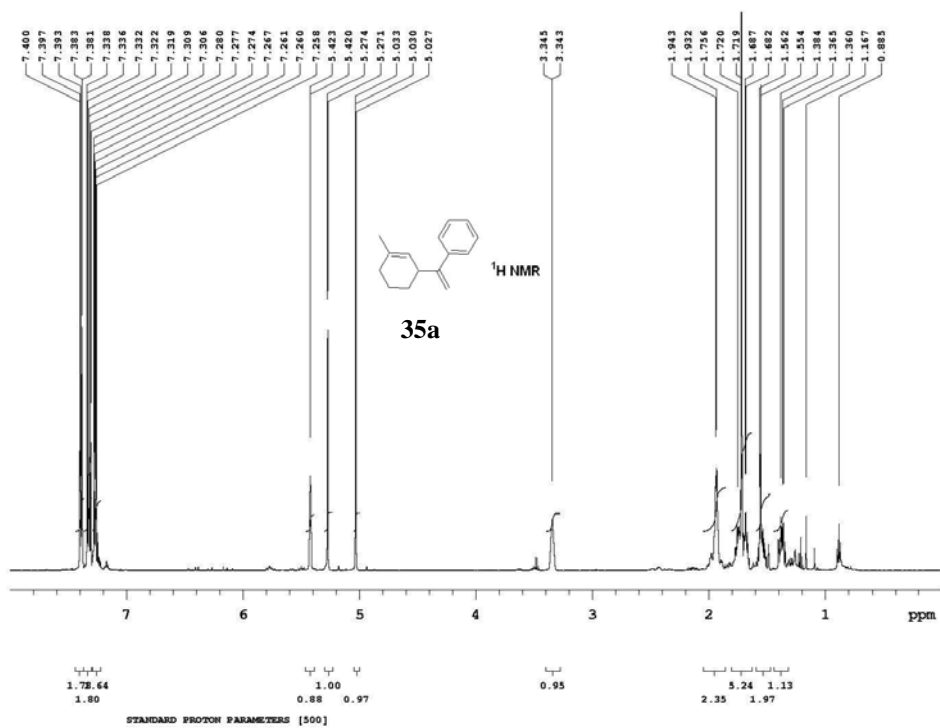
xph-IV-51 C13

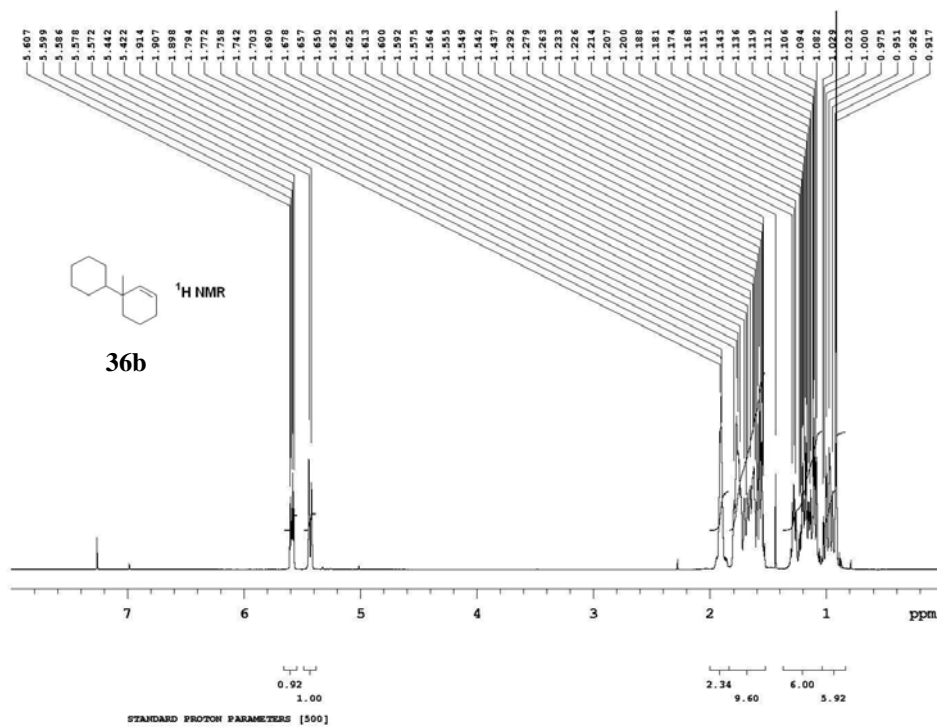
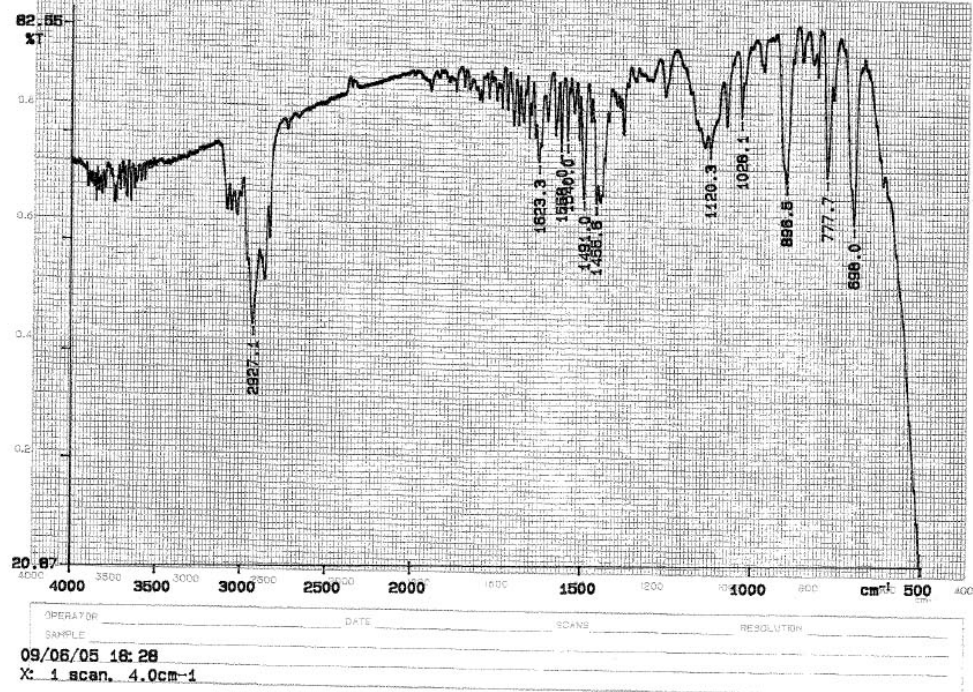
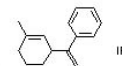


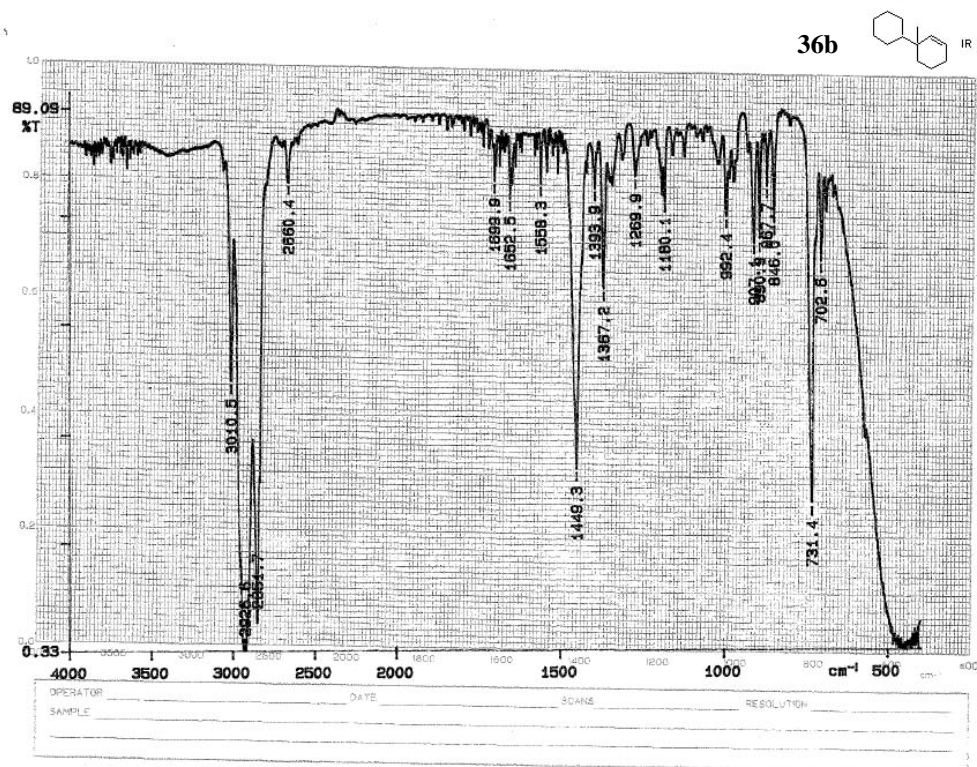
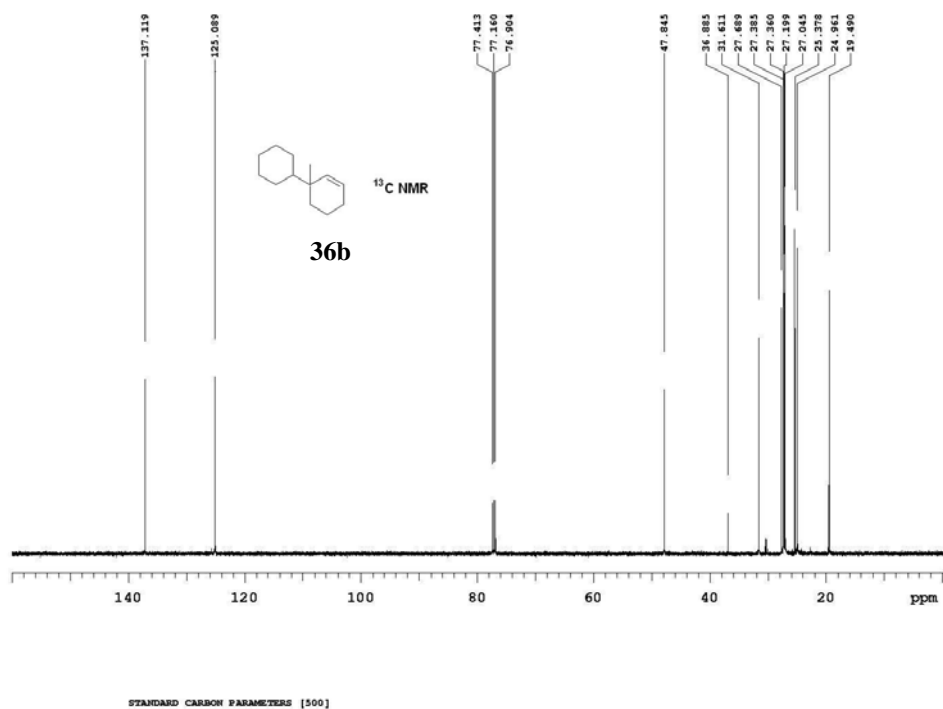
OPERATOR	DATE	SCANS	RESOLUTION
SAMPLE			

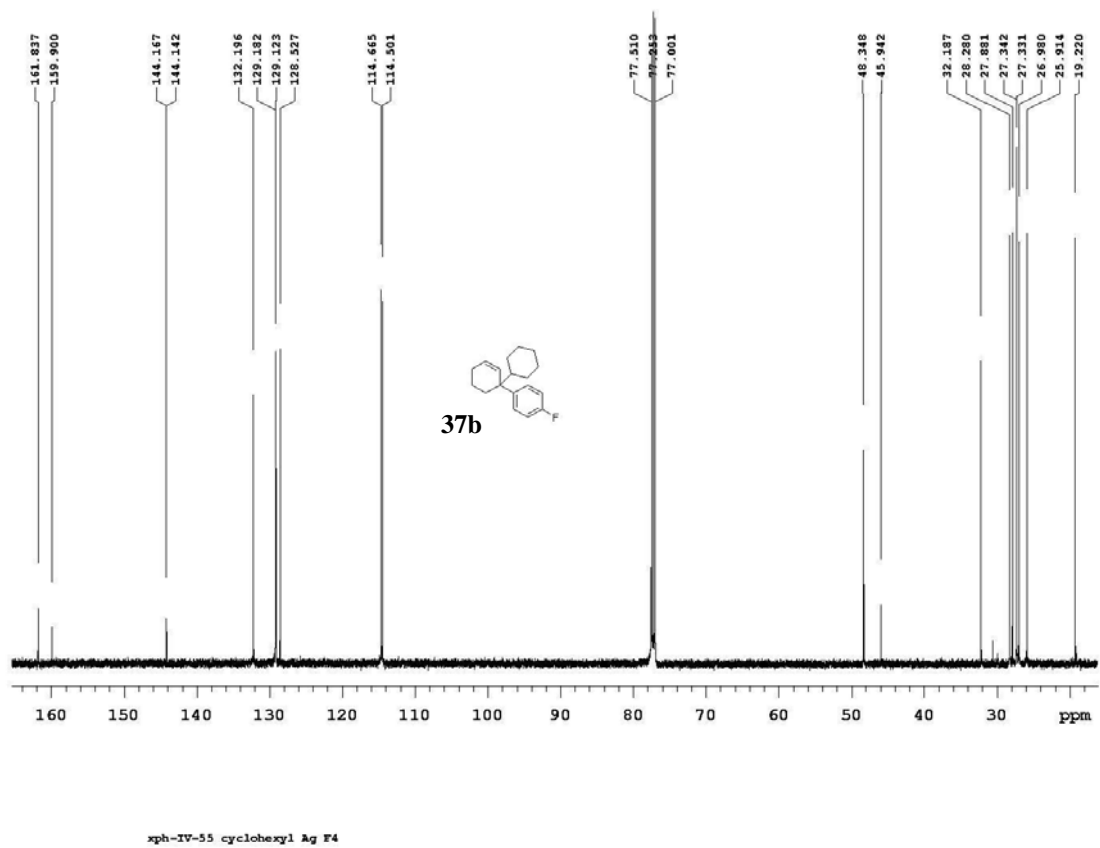
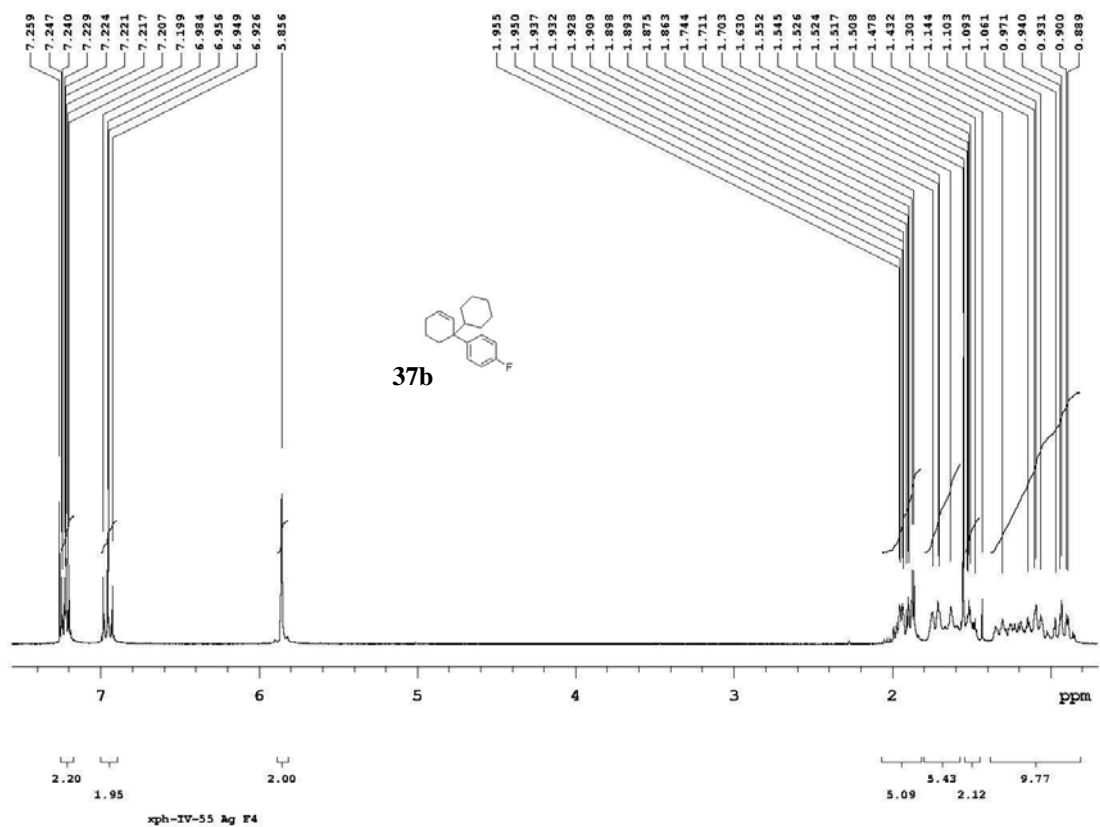
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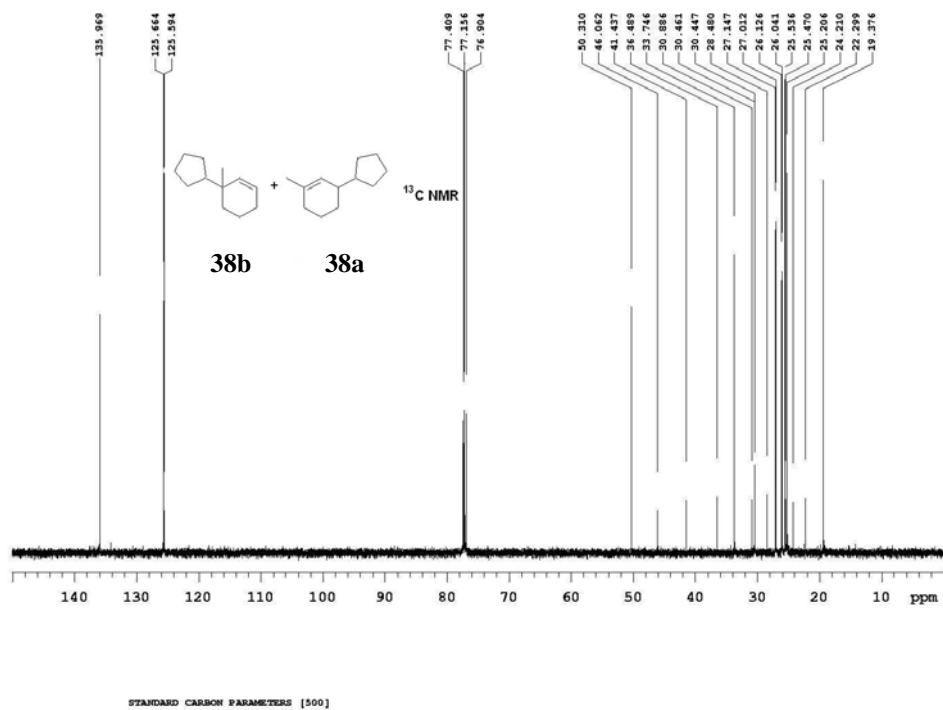
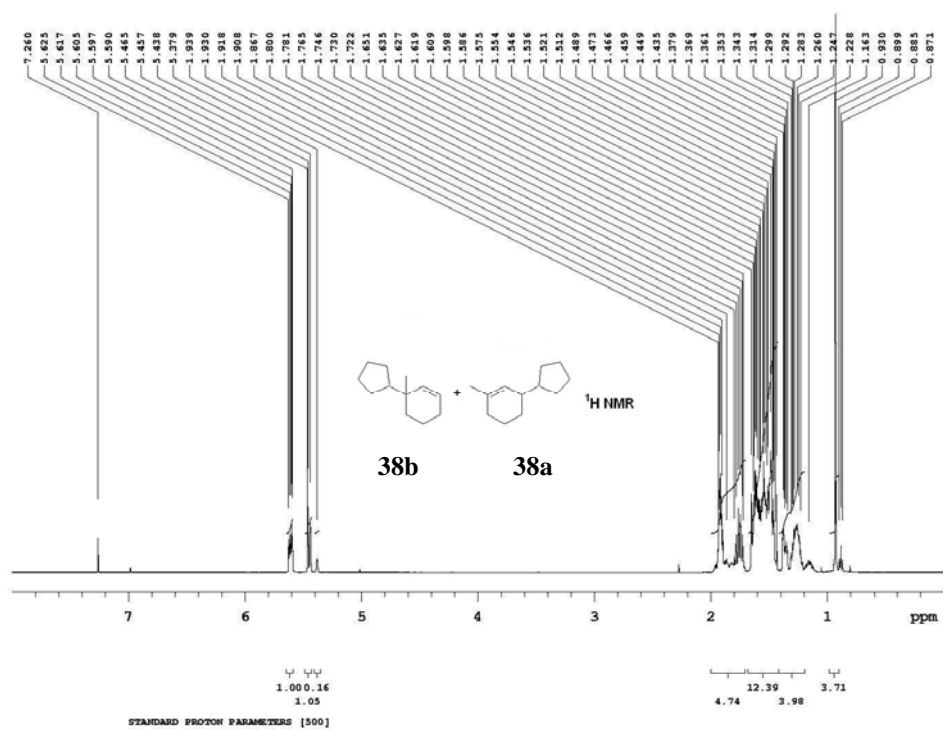


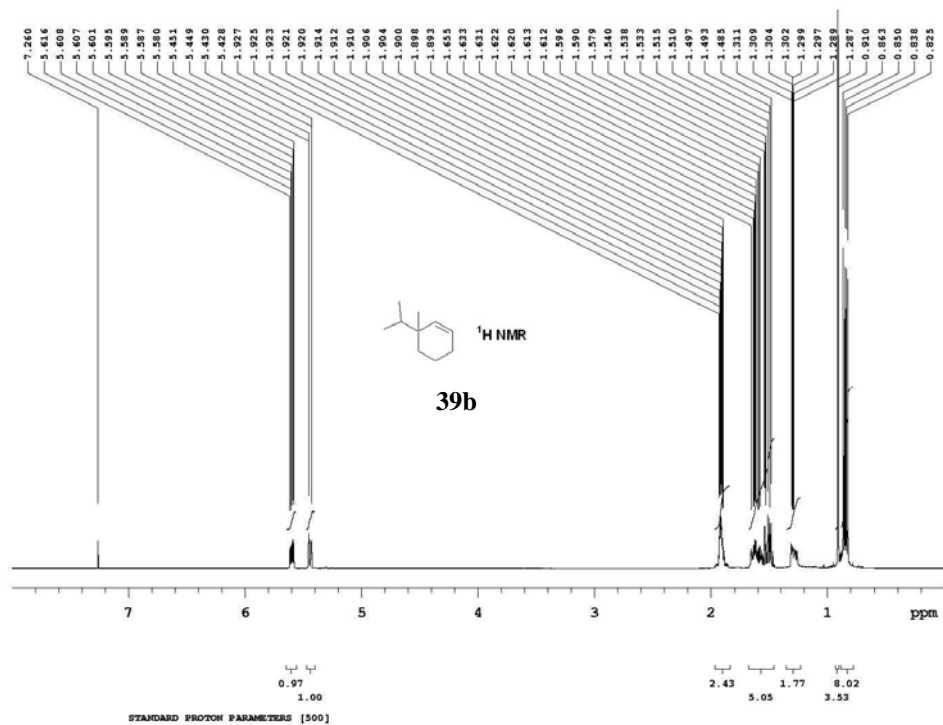
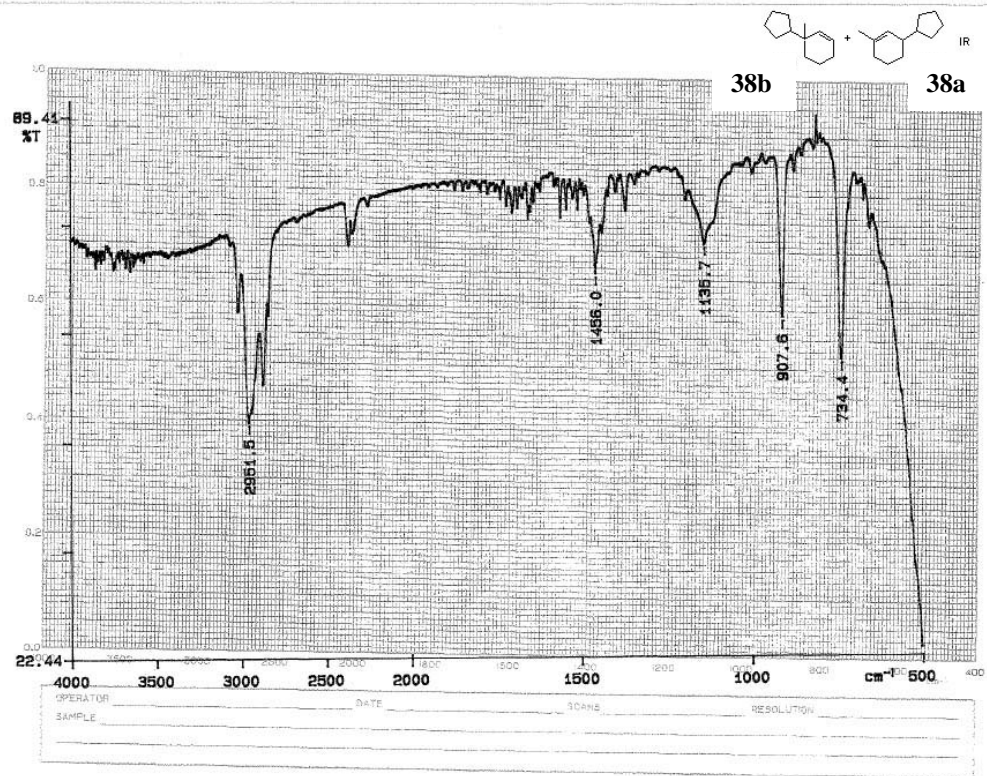


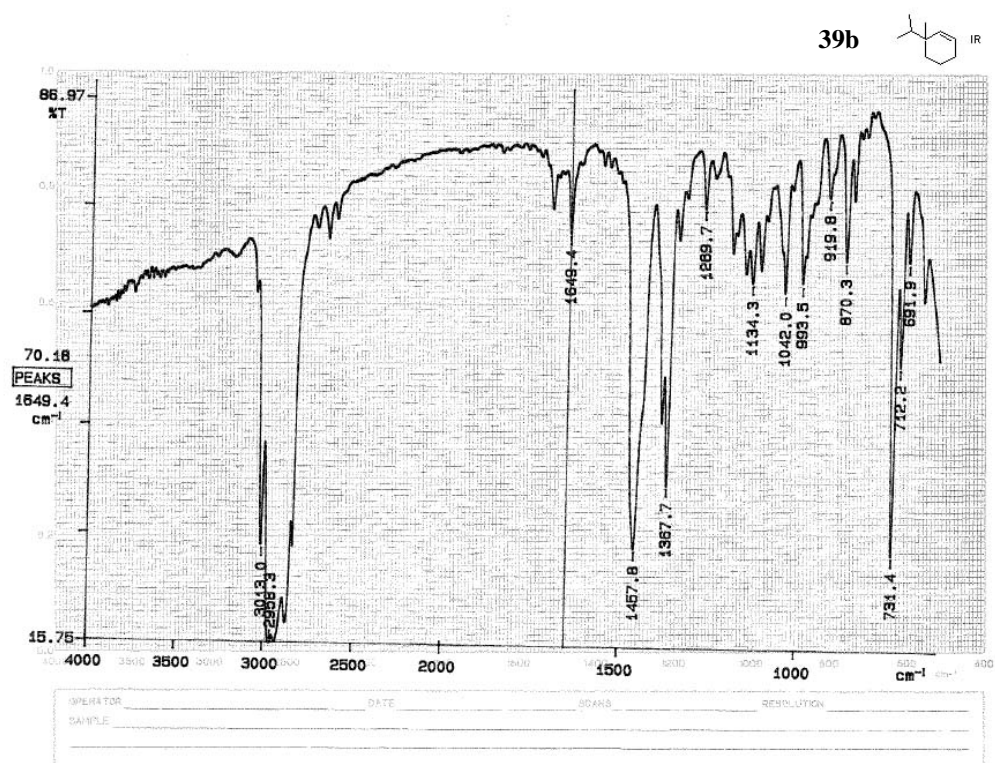
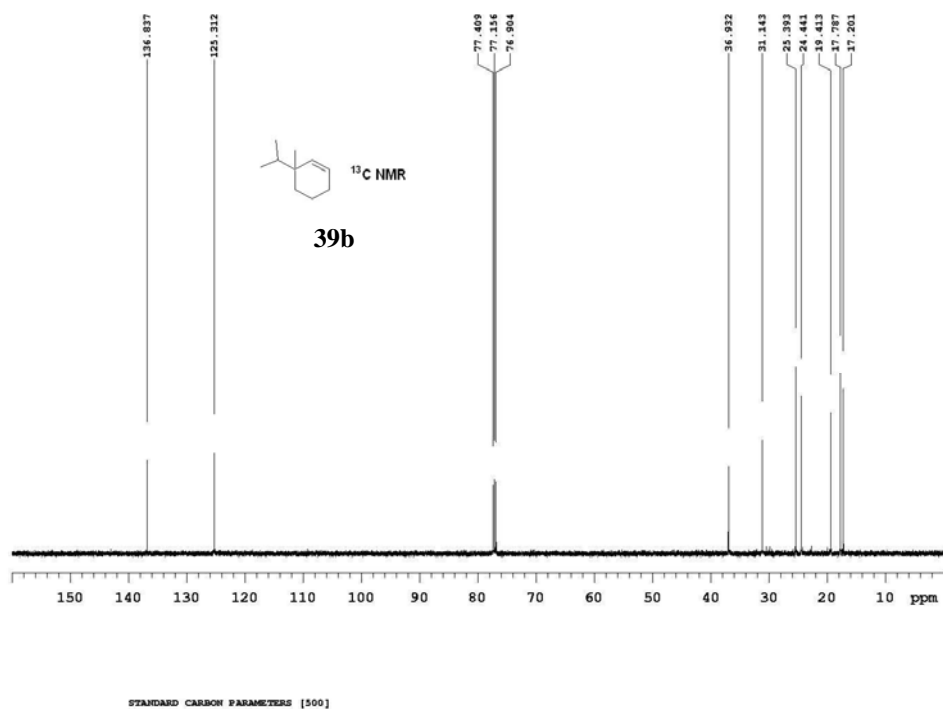


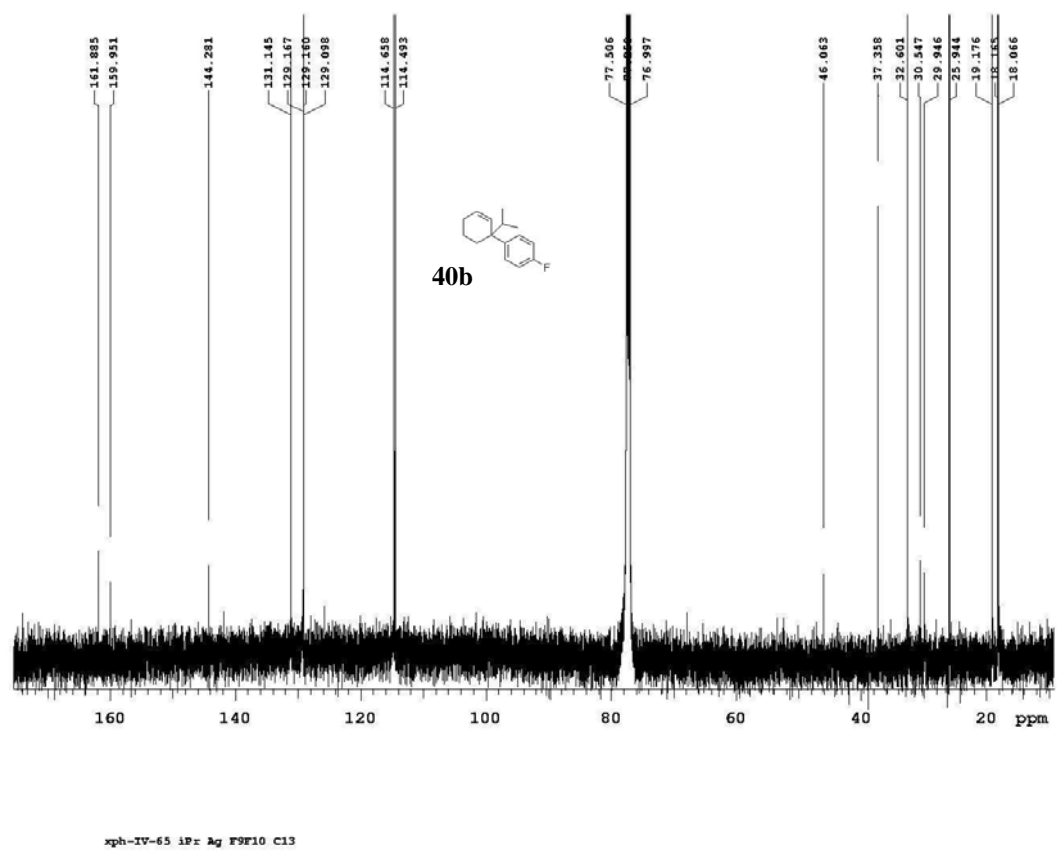
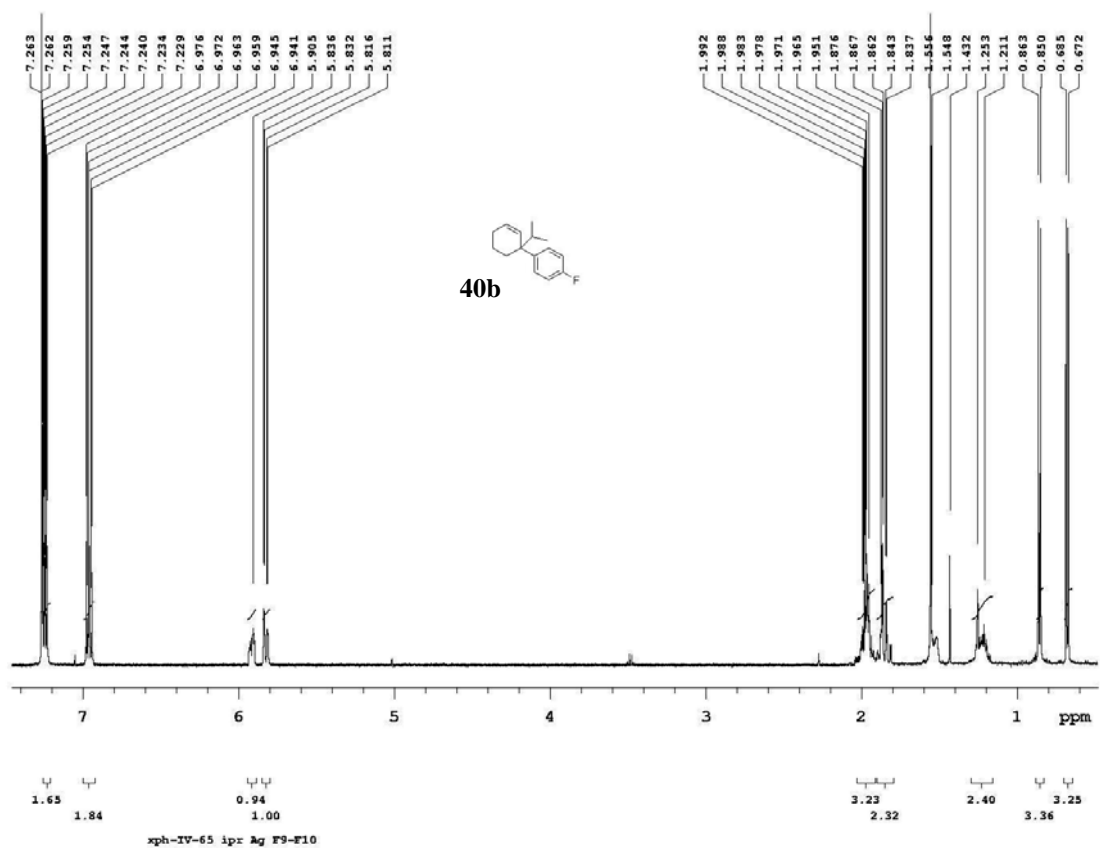


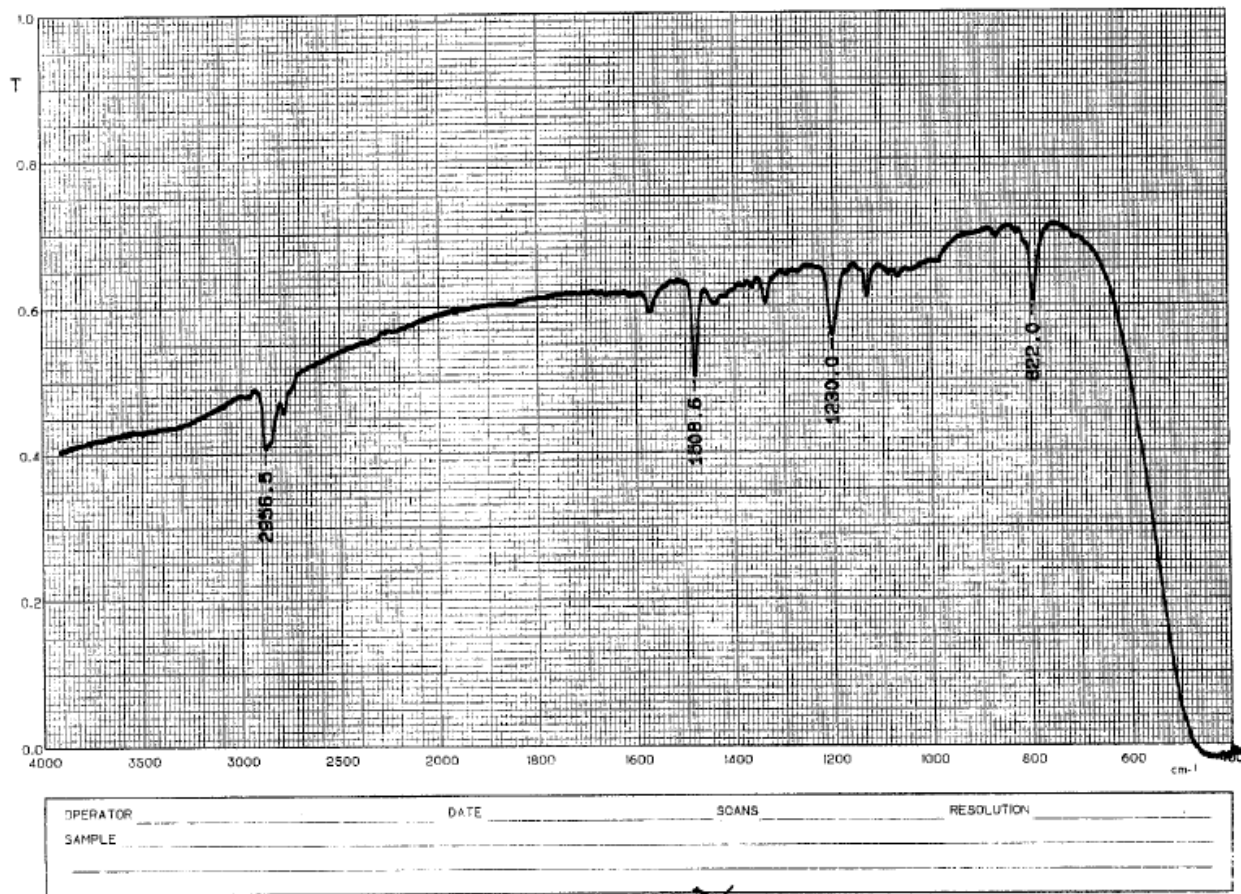




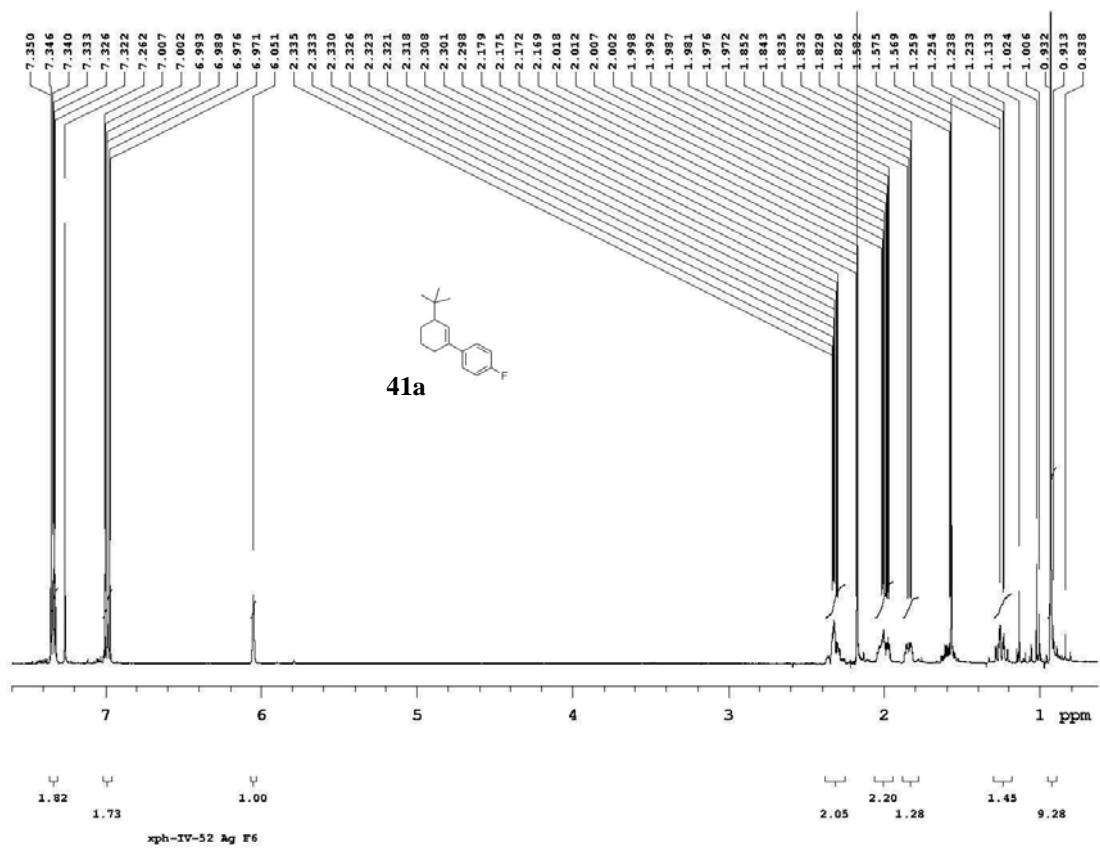


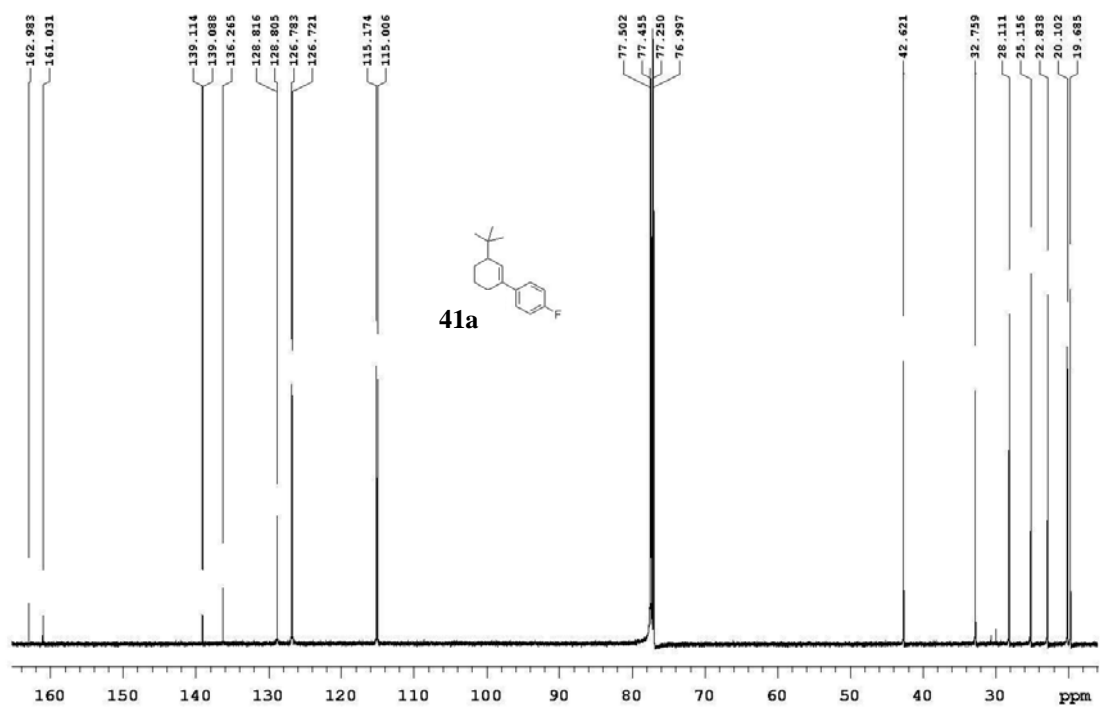




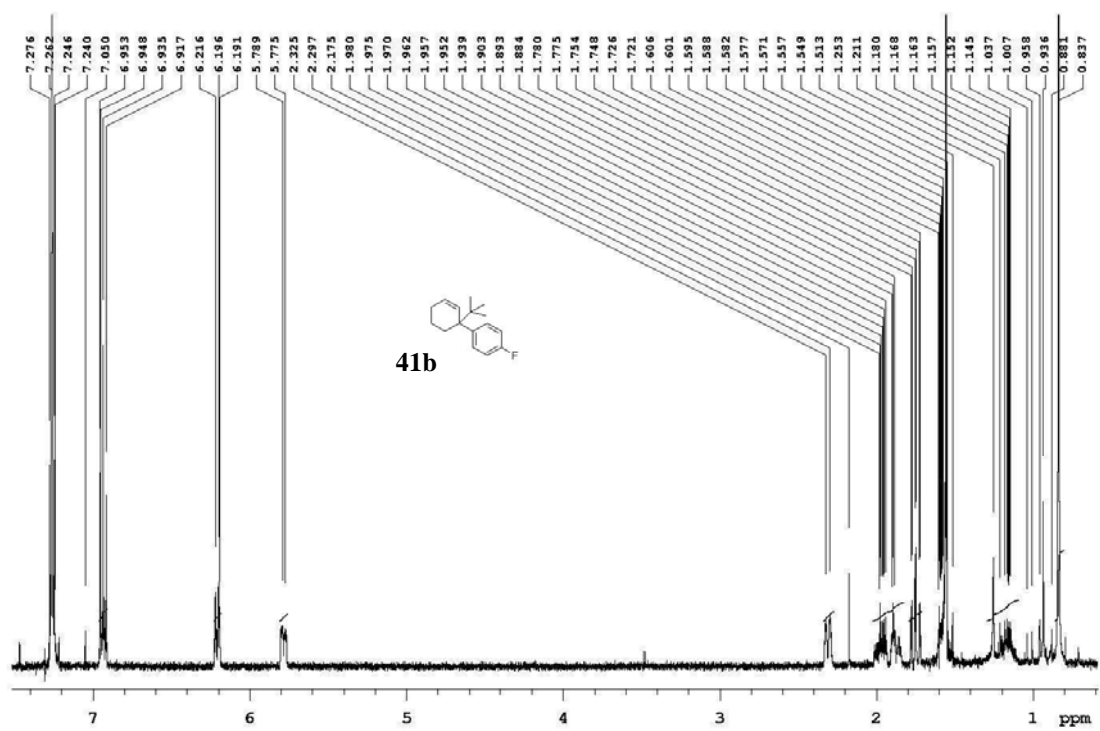


~~40a~~ + CC(C)(C)c1ccc(cc1)-c2ccc(F)cc2 40b





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xph-IV-52 Ag F9

