Supporting Information

Carvone-Derived P-Stereogenic Phosphines: Design, Synthesis, and Use in Allene–Imine [3 + 2] Annulation

Andrew J. Smaligo, Sriramurthy Vardhineedi, and Ohyun Kwon*

Department of Chemistry and Biochemistry, University of California, Los Angeles, California 90095-1569

*ohyun@chem.ucla.edu

Table of Contents

1. General Information

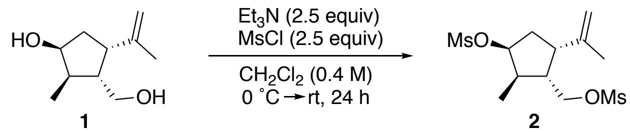
Unless otherwise stated, reactions were performed in flame-dried glassware fitted with rubber septa under an argon atmosphere and were stirred with Teflon-coated magnetic stirring bars. Liquid reagents and solvents were transferred via syringe using standard Schlennk techniques. Benzene and dichloromethane were freshly distilled over calcium hydride. Tetrahydrofuran (THF) was distilled over sodium/benzophenone ketyl. All other solvents and reagents were used as received unless otherwise noted. Reaction temperatures above 23 °C refer to oil bath temperatures. Thin layer chromatography was performed using Silicycle silica gel 60 F-254 precoated plates (0.25 mm) and visualized by UV irradiation and cerium ammonium molybdate stain. SiliCycle Silica-P silica gel (particle size 40-63 μm) was used for flash column chromatography. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AV-500, DRX-500 and AV-400 MHz spectrometers with ^{13}C operating frequencies of 125, 125 and 100 MHz, respectively. Chemical shifts (δ) are reported in ppm relative to the residual solvent $CD(H)Cl_3$ signal (δ = 7.26 for ^{1}H NMR and δ = 77.0 for ^{13}C NMR). Data for ^{1}H NMR spectra are reported as follows: chemical shift, multiplicity, coupling constants (Hz), and number of hydrogens. Data for ^{13}C NMR spectra are reported in terms of chemical shift. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet. HRMS (ESI) was recorded on an IonSpec Ultima 7T FTICR using samples in CH_3CN. MALDI mass data was obtained on an AB/PerSpective DE-STR TOF instrument using samples in CH_3CN with 2,5-dihydroxybenzoic acid as a matrix. X-ray crystallographic data were collected using a Bruker SMART CCD based diffractometer equipped with a low-temperature apparatus operating at 100K. Melting points (mp) are uncorrected and were collected on an Electrothermal® capillary melting point apparatus. Optical rotations were determined using an Autopol IV polarimeter and a 50-mm cell at concentrations close to 1 g/100 mL. All values of ee were determined through chiral HPLC using a Shimadzu CBM Lite system.

Abbreviations. Ms = methanesulfonyl, Ts = *p*-toluenesulfonyl, Ns = *p*-nitrobenzenesulfonyl, Bs = benzenesulfonyl, PMP = *p*-methoxyphenyl, Ar = aryl, THF = tetrahydrofuran, EtOAc = ethyl acetate, MeOH = methanol, Et_3N = triethylamine, HOAc = acetic acid, PhOH = phenol.

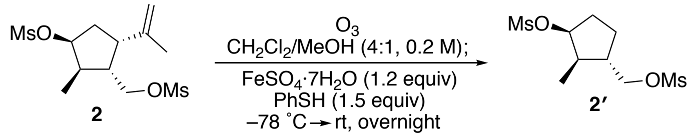
2. Catalyst Preparation

The diol **1** was prepared on 100-g scale following a literature procedure.[1] Only one purification was required: distillation of the ester precursor to the diol **1**.

2.1. Preparation of the Mesylates 2 and 2´

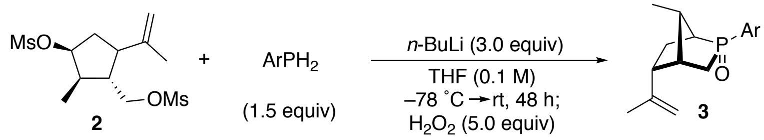


A solution of methanesulfonyl chloride (97.0 mL, 1250 mmol) was added dropwise to a stirred solution of the diol **1** (85 g, 500 mmol) and Et_3N (174 mL, 1250 mmol) in CH_2Cl_2 (0.4 M) at 0 °C. After stirring at 0 °C for 30 min, the mixture was warmed to room temperature and stirred for an additional 24 h. Upon completion (TLC), the reaction was quenched through the addition of saturated aqueous $NaHCO_3$ (400 mL). The aqueous phase was extracted with CH_2Cl_2 (3 × 400 mL); the combined organic phases were washed with brine, dried (anhydrous Na_2SO_4), and concentrated (rotary evaporation) to provide the dimesylate **2** as a viscous liquid (160 g, 98% yield). IR (film) ν_{max} 3355, 2930, 2360, 1646 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.07 (t, J = 3.6 Hz, 1H), 4.93 (s, 1H), 4.73 (s, 1H), 4.10 (dd, J = 10.0, 5.2 Hz, 1H), 3.94 (dd, J = 10.0, 7.2 Hz, 1H), 3.10–3.03 (m, 1H), 3.01 (s, 3H), 2.97 (s, 3H), 2.25–2.12 (m, 3H), 2.06–1.79 (m, 1H), 1.79 (s, 3H), 1.17 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 112.2, 85.6, 70.4, 44.3, 44.2, 42.1, 38.2, 37.1, 23.4, 14.7; LRMS (MALDI) calcd for $C_{12}H_{22}O_6S_2$ m/z 326.09, found 326.1.



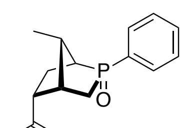
A stirred solution of the dimesylate **2** (16.3 g, 50.0 mmol) in CH_2Cl_2/MeOH (4:1, 0.2 M) was cooled to –78 °C in an acetone/dry ice bath. Ozone was bubbled through the cooled solution until a blue color was observed. The solution was purged with argon for 30 min and then thiophenol (7.65 mL, 75.0 mmol) and iron(II) sulfate heptahydrate (16.7 g, 60.0 mmol) were added sequentially. The cooling bath was removed and the mixture was warmed to room temperature and stirred overnight. Water (100 mL) was added and then the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic phases were washed with saturated aqueous $NaHCO_3$ and brine, dried (anhydrous Na_2SO_4), and concentrated (rotary evaporation). The residue was purified through flash column chromatography (SiO_2; EtOAc/hexanes, 1:2) to give the dimesylate **2´** as a white solid (11.4 g, 80% yield). When performed on 150-mmol scale, a similar procedure was followed, except for purification. The crude product was triturated in diethyl ether for 10 min and the filter cake collected and dried under vacuum to give the dimesylate **2´** as a white solid (*ca*. 65% yield, average from five runs). m.p. 95–96 ˚C (decomp); IR (film) ν_{max} 3027, 2940, 1332, 1171 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 5.04 (s, 1H), 4.26 (dd, J = 4.2, 9.8 Hz, 1H), 4.19 (dd, J = 5.2, 9.7 Hz, 1H), 3.02 (s, 3H), 3.01 (s, 3H), 2.16–1.88 (m, 5H), 1.62–1.54 (m, 1H), 1.14 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 87.8, 71.0, 42.9, 41.3, 38.3, 37.3, 31.8, 25.5, 12.8; HRMS (ESI-TOF) calcd for $HC_9H_{18}O_6S_2$ 287.0623, found 287.0625.

2.2. Dialkylation of the Mesylates to Prepare the Phosphine Oxides 3a, 3e, 3e´, 3f, and 3f´



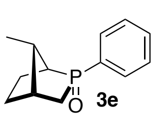
n-Butyllithium (2.1 M solution in hexanes, 3.0 equiv) was added via syringe over 30 min to a stirred solution of arylphosphine (1.5 equiv) in THF (0.1 M) at –78 °C under argon. The orange solution was warmed to room temperature and stirred for 2 h. The resulting bright yellow suspension was cooled to –78 °C and then a solution of the dimesylate **2** (1.0 equiv) in THF (0.5 M) was added dropwise via cannula over 1 h. The resulting mixture was warmed to room temperature and stirred for an additional 48 h. Upon completion (TLC), the reaction was quenched through the addition of half-saturated aqueous NH_4Cl. The THF was removed through rotary evaporation, and the aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were carefully treated with 35% aqueous H_2O_2 (5.0 equiv) and stirred for 1 h.[a] The mixture was washed with saturated aqueous $Na_2S_2O_3$ and extracted three times with CH_2Cl_2. The combined organic phases were washed with brine, dried (anhydrous Na_2SO_4), and concentrated (rotary evaporation). The residue was purified through flash column chromatography (SiO_2; EtOAc/MeOH, 98:2) to give the phosphine oxide **3**. The phosphine oxides **3e**/**3e´** and **3f**/**3f´** were prepared following a similar procedure; the crude products were purified through flash column chromatography (SiO_2; EtOAc/MeOH, 100:0 → 95:5) to give the phosphine oxide **3e/3f** followed by the phosphine oxide **3e´/3f´**.

[a]Hydrogen peroxide is extremely dangerous and care must be taken to avoid generation of highly reactive and potentially explosive organoperoxide compounds. It is important to wash with sodium thiosulfate to quench any such species, as well as use peroxide test strips.



3a

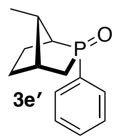
Phosphine Oxide **3a** (85% yield); IR (film) ν_{max} 3387, 2964, 2359, 1653 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.74 (m, 2H), 7.52–7.47 (m, 3H), 5.28 (s, 1H), 5.11 (s, 1H), 2.92–2.90 (m, 1H), 2.66 (ddd, J = 19.5, 14.0, 6.0 Hz, 1H), 2.44 (td, J = 29.5, 5.0 Hz, 1H), 2.33–2.03 (m, 4H), 1.84 (t, J = 13.5 Hz, 1H), 1.77 (s, 3H), 1.08 (d, J = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.5, 134.0 (d, J_{CP} = 89 Hz), 131.3 (d, J_{CP} = 2.7 Hz), 130.2 (d, J_{CP} = 8.8 Hz), 128.5 (d, J_{CP} = 10.8 Hz), 112.6, 45.1, 44.1, 42.4 (d, J_{CP} = 24.6 Hz), 42.1 (d, J_{CP} = 24.6 Hz), 27.3, 26.0, 23.8, 20.2 (d, J_{CP} = 6.6 Hz), 13.6 (d, J_{CP} = 16.0 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 54.8; HRMS (ESI-TOF) calcd for $HC_{16}H_{21}OP$ 261.1408, found 261.1407.



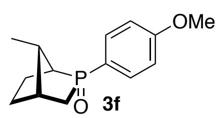
3e

Phosphine Oxide **3e** (54% yield, 80% combined yield); m.p. 79–82 ˚C; IR (film) ν_{max} 2968, 2876, 1436, 1168 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.74 (m, 2H), 7.54–7.45 (m, 3H), 2.53–2.43 (m, 1H), 2.40–2.27 (m, 3H), 2.12–

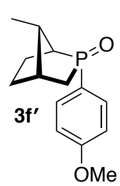
1.95 (m, 3H), 1.72–1.58 (m, 2H), 0.95 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.6 (d, J_{CP} = 89.2 Hz), 131.5 (d, J_{CP} = 2.8 Hz), 130.3 (d, J_{CP} = 9.3 Hz), 128.6 (d, J_{CP} = 11.3 Hz), 42.2 (d, J_{CP} = 46.3), 41.9 (d, J_{CP} = 4.6 Hz), 41.9 (d, J_{CP} = 4.0 Hz), 34.4 (d, J_{CP} = 60.7 Hz), 26.7 (d, J_{CP} = 1.5 Hz), 17.7 (d, J_{CP} = 7.1 Hz), 13.7 (d, J_{CP} = 15.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 56.0; HRMS (ESI-TOF) calcd for $HC_{13}H_{17}OP$ 221.1095, found 221.1095.


3e′

Phosphine Oxide **3e′** (26% yield, 80% combined yield); m.p. 97–98 ˚C; IR (film) ν_{max} 3048, 2963, 2936, 1143 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76–7.67 (m, 2H), 7.55–7.42 (m, 3H), 2.87 (quint, J = 6.8 Hz, 1H), 2.41 (d, J = 31.1 Hz, 1H), 2.18 (t, J = 6.0 Hz, 1H), 2.12–2.03 (m, 2H), 1.91–1.68 (m, 2H), 1.25–1.06 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.7 (d, J_{CP} = 2.8 Hz), 130.9 (d, J_{CP} = 9.0 Hz), 130.4 (d, J_{CP} = 90.8 Hz), 128.5 (d, J_{CP} = 10.9 Hz), 43.2 (d, J_{CP} = 7.2 Hz), 42.4 (d, J_{CP} = 68.5 Hz), 40.2, 36.6 (d, J_{CP} = 58.0 Hz), 25.9, 18.9 (J_{CP} = 3.6 Hz), 13.5 (d, J_{CP} = 13.1 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 57.9; HRMS (ESI-TOF) calcd for $HC_{13}H_{17}OP$ 221.1095, found 221.1096.

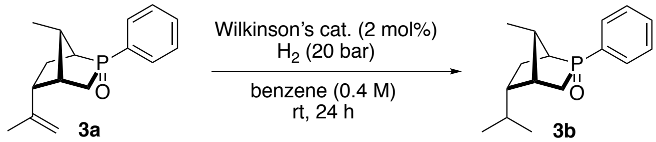

3f

Phosphine Oxide **3f** (53% yield, 82% combined yield); IR (film) ν_{max} 2957, 2878, 1597, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (dd, J = 8.7, 10.4 Hz, 2H), 6.99 (dd, J = 2.0, 8.8 Hz, 2H), 3.85 (s, 3H), 2.50–2.43 (m, 1H), 2.38–2.24 (m, 3H), 2.09–1.95 (m, 3H), 1.69–1.65 (m, 1H), 1.60 (dd, J = 12.3, 13.6 Hz, 1H), 0.95 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1 (d, J_{CP} = 2.8 Hz), 132.2 (J_{CP} = 10.3 Hz), 124.8 (d, J_{CP} = 95.2 Hz), 114.1 (J_{CP} = 12.2 Hz), 55.2, 42.4 (J_{CP} = 68.1 Hz), 42.0 (J_{CP} = 12.9 Hz), 41.9, 34.7 (J_{CP} = 62.0 Hz), 26.7 (d, J_{CP} = 1.5 Hz), 17.8 (J_{CP} = 7.1 Hz), 13.8 (J_{CP} = 15.5 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.4; HRMS (ESI-TOF) calcd for $HC_{14}H_{19}O_2P$ 251.1201, found 251.1206.

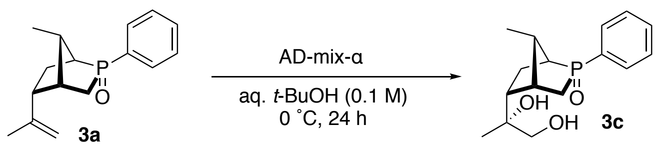

3f′

Phosphine Oxide **3f′** (29% yield, 82% combined yield); IR (film) ν_{max} 3012, 2967, 1597, 1139 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (dd, J = 8.8, 10.4 Hz, 2H), 6.99 (dd, J = 2.2, 8.9 Hz, 2H), 3.85 (s, 3H), 2.84 (quint, J = 7.0 Hz, 1H), 2.40 (d, J = 30.3 Hz, 1H), 2.16 (t, J = 6.2 Hz, 1H), 2.12–2.02 (m, 2H), 1.89–1.72 (m, 2H), 1.26–1.09 (m, 2H), 1.04 (d, J = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.4 (d, J_{CP} = 2.9 Hz), 132.9 (d, J_{CP} = 10.1 Hz), 121.6 (d, J_{CP} = 96.5 Hz), 114.2 (d, J_{CP} = 12.3 Hz), 55.4, 43.3 (d, J_{CP} = 7.2 Hz), 42.7 (d, J_{CP} = 69.4 Hz), 40.4, 37.1 (d, J_{CP} = 36.8 Hz), 26.0, 19.1 (d, J_{CP} = 3.7 Hz), 13.6 (d, J_{CP} = 13.6 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ 57.2; HRMS (ESI-TOF) calcd for $HC_{14}H_{19}O_2P$ 251.1201, found 251.1203.

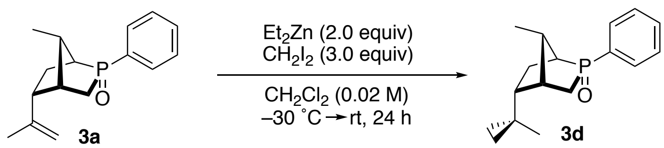
2.3. Preparation of the Phosphine Oxides 3b, 3c, and 3d



A vial equipped with a magnetic stirrer bar was charged with the phosphine oxide **3a** (3.00 g, 11.5 mmol) and Wilkinson's catalyst (212 mg, 0.230 mmol). Dry benzene (30 mL) was added and then the vial placed in a high-pressure hydrogenation apparatus. After purging the system with H_2, the pressure of H_2 gas was adjusted to 20 bar and the mixture stirred for 24 h at room temperature. After releasing the pressure, the solvent was removed through rotary evaporation. The residue was purified through flash column chromatography (SiO_2; EtOAc/MeOH, 98:2) to give the phosphine oxide **3b** (2.7 g, 91% yield) as a white solid. m.p. 91–95 ˚C; IR (film) ν_{max} 2955, 2862, 1435, 1167 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75–7.74 (m, 2H), 7.51–7.47 (m, 3H), 2.34–2.02 (m, 6H), 1.91–1.79 (m, 3H), 1.01 (d, J = 4.5 Hz, 3H), 1.00 (d, J = 6.0 Hz, 3H), 0.88 (d, J = 6.5 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 134.1 (d, J_{CP} = 88.8 Hz), 131.3 (d, J_{CP} = 2.5 Hz), 130.2 (d, J_{CP} = 9.0 Hz), 128.5 (d, J_{CP} = 11.0 Hz), 44.8 (d, J_{CP} = 29 Hz), 42.9 (d, J_{CP} = 13.2 Hz), 42.4 (d, J_{CP} = 67 Hz), 29.3, 27.5 (d, J_{CP} = 61.5 Hz), 23.5 (d, J_{CP} = 6.8 Hz), 22.4, 21.3, 13.5 (d, J_{CP} = 16.2 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 54.8; HRMS (ESI-TOF) calcd for $HC_{16}H_{23}OP$ 263.1565, found 263.1554.

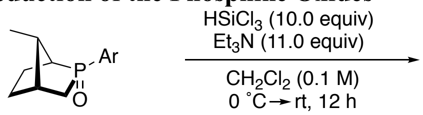


A mixture of AD-mix-α (8.0 g) in 50% aqueous *tert*-butanol (40 mL) was stirred at room temperature until both phases were clear. The mixture was cooled to 0 °C and then a solution of the phosphine oxide **3a** (1.50 g, 5.72 mmol) in 50% aqueous *tert*-butanol (10 mL) was added dropwise. The resulting mixture was stirred vigorously at 0 °C for 24 h before the reaction was quenched through the addition of solid Na_2SO_3 (8.0 g) at 0 °C. After stirring for an additional 30 min at room temperature, the mixture was extracted with EtOAc (3 × 200 mL). The combined organic phases were washed with brine, dried (anhydrous Na_2SO_4), and concentrated (rotary evaporation). The residue was purified through flash column chromatography (SiO_2; EtOAc/MeOH, 92:8) to give the phosphine oxide **3c** (1.58 g, 94% yield) as a white solid. m.p. 167–171 ˚C; IR (film) ν_{max} 3353, 2933, 1435, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.72 (m, 2H), 7.55–7.45 (m, 3H), 4.27 (s, 1H), 3.65 (dd, J = 4.8, 10.8 Hz, 1H), 3.45 (dd, J = 4.8, 10.8 Hz, 1H), 3.24 (dd, J = 4.8, 8.0 Hz, 1H), 2.80 (dd, J = 12.8, 14.8 Hz, 1H), 2.58–2.43 (m, 2H), 2.32–2.10 (m, 4H), 2.03–1.98 (m, 1H), 1.29 (s, 3H), 1.03 (d, J = 6.8 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 132.84 (d, J_{CP} = 90 Hz), 131.7 (d, J_{CP} = 2.5 Hz), 130.3 (d, J_{CP} = 9.3 Hz), 128.6 (d, J_{CP} = 11.3 Hz), 73.7, 69.9, 44.4 (d, J_{CP} = 12.1 Hz), 44.0, 43.3, 42.3 (d, J_{CP} = 66.2 Hz), 29.6 (d, J_{CP} = 61.1 Hz), 26.3, 19.5 (d, J_{CP} = 7.1 Hz), 13.8 (d, J_{CP} = 15.5 Hz); ^{31}P NMR (161 MHz, $CDCl_3$) δ 56.0; HRMS (ESI-TOF) calcd for $HC_{16}H_{23}O_2P$ 295.1463, found 295.1465.



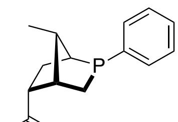
Diethyl zinc (1.13 mL, 11 mmol) was added dropwise to a stirred solution of the phosphine oxide **3a** (1.43 g, 5.5 mmol) in CH_2Cl_2 (300 mL) at –30 °C. After stirring for 10 min, diiodomethane (1.33 mL, 16.5 mmol) was added dropwise. The reaction mixture was slowly warmed to 0 °C and stirred for 2 h, then warmed to room temperature and stirred for 24 h. Upon completion (TLC), the white suspension was hydrolyzed with water, washed with 1.0 M aqueous NaOH and brine, dried (anhydrous Na_2SO_4), and concentrated (rotary evaporation). The residue was purified through flash column chromatography (SiO_2; EtOAc) to give the phosphine oxide **3d** (650 mg, 43% yield) as a white solid. m.p. 98–101 ˚C; IR (film) ν_{max} 3059, 2948, 1487, 1158 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79–7.71 (m, 2H), 7.56–7.43 (m, 3H), 2.66 (quint, J = 5.5 Hz, 1H), 2.45 (dt, J = 4.8, 30.1 Hz, 1H), 2.30–2.03 (m, 4H), 1.92–1.78 (m, 1H), 1.64 (ddd, J = 5.9, 14.0, 19.4 Hz, 1H), 1.52 (dt, J = 4.9, 9.8 Hz, 1H), 1.08 (s, 3H), 1.03 (d, J = 6.8 Hz, 3H), 0.40 (dt, J = 5.1, 10.1 Hz, 1H), 0.28 (dt, J = 4.8, 9.6 Hz, 1H), 0.14 (dt, J = 4.7, 9.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.3 (d, J_{CP} = 89.5 Hz), 131.3 (d, J_{CP} = 2.6 Hz), 130.3 (d, J_{CP} = 9.0 Hz), 128.5 (d, J_{CP} = 11.2 Hz), 45.7, 42.3 (d, J_{CP} = 1.7 Hz), 42.0 (d, J_{CP} = 55.1 Hz), 41.8, 26.8 (d, J_{CP} = 61.3 Hz), 25.3, 18.4 (d, J_{CP} = 6.9 Hz), 13.7, 13.6 (d, J_{CP} = 16.3 Hz), 9.6, 8.8; ^{31}P NMR (202 MHz, $CDCl_3$) δ 55.0; HRMS (ESI-TOF) calcd for $HC_{17}H_{23}OP$ 275.1565, found 275.1566.

2.4. General Procedure for Reduction of the Phosphine Oxides



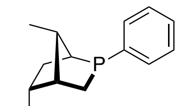
3 **4**

A round-bottom flask equipped with a magnetic stirrer bar was charged with trichlorosilane (10.0 equiv) and Et_3N (11.0 equiv) in CH_2Cl_2 (0.1 M) at 0 °C under argon protection. A solution of the phosphine oxide **3** (1.0 equiv) in CH_2Cl_2 (0.5 M) was added dropwise. The mixture was warmed to room temperature and stirred for 12 h. Upon completion of the reaction (TLC), the mixture was cooled to 0 °C and then the reaction was quenched through the addition of degassed saturated aqueous $NaHCO_3$. After stirring for 5 min, solid K_2CO_3 and anhydrous Na_2SO_4 were added to the mixture with vigorous stirring. The mixture was warmed to room temperature and stirred for 1 h until it became clear. The suspension was filtered through a short plug of silica under argon; the filter cake was rinsed three times with CH_2Cl_2. The combined organic phases were concentrated (rotary evaporation with argon replenishment) to provide the phosphine **4** in a sufficiently pure form to be used directly as a catalyst.



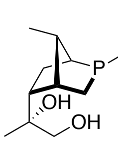
4a

Phosphine **4a** (95% yield); IR (film) ν_{max} 3359, 2967, 1646, 1439 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35–7.30 (m, 4H), 7.26–7.21 (m, 1H), 4.97 (s, 1H), 4.95 (s, 1H), 2.75–2.73 (m, 1H), 2.36 (td, J = 4.5, 14.0 Hz, 1H), 2.26 (dd, J = 6.5, 10.0 Hz, 1H), 2.20–2.06 (m, 2H), 1.94 (dd, J = 13.5, 25.0 Hz, 1H), 1.78–1.68 (m, 2H), 1.73 (s, 3H), 1.04 (d, J = 7.0 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 144.7, 130.2, 129.9, 128.2 (d, J_{CP} = 4.3 Hz), 127.1, 110.2, 45.1 (d, J_{CP} = 3.7 Hz), 44.2 (d, J_{CP} = 4.1 Hz), 40.8 (d, J_{CP} = 5.3 Hz), 25.8, 25.6, 25.0, 24.9, 23.8, 13.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ –7.7; HRMS (ESI-TOF) calcd for $HC_{16}H_{21}P$ 245.1459, found 245.1461.



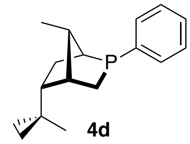
4b

Phosphine **4b** (96% yield); IR (film) ν_{max} 3049, 2951, 2929, 2864, 1719, 1432 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 2H), 7.40–7.33 (m, 3H), 2.42–2.24 (m, 4 H), 2.09–2.03 (m, 1H), 1.98–1.91 (m, 1H), 1.73–1.68 (m, 1H), 1.57–1.48 (m, 1H), 1.44–1.34 (m, 1H), 1.02 (d, J = 6.8 Hz, 3H), 0.95 (d, J = 6.4 Hz, 1H), 0.87 (d, J = 6.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 130.0 (d, J_{CP} = 13.6 Hz), 128.2 (d, J_{CP} = 4.6 Hz), 127.3, 45.5, 45.1, 43.7, 40.5, 29.9, 29.8, 24.8 (d, J_{CP} = 11.0 Hz), 22.3, 21.5, 13.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ –6.0; HRMS (ESI-TOF) calcd for $HC_{16}H_{23}P$ 247.1527, found 247.1520.



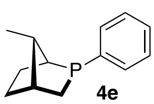
4c

Phosphine **4c** (91% yield); IR (film) ν_{max} 3394, 3052, 2930, 1432 cm^{-1}; ^{1}H (500 MHz, $CDCl_3$) δ 7.30–7.28 (m, 4H), 7.21–7.17 (m, 1H), 3.69 (d, J = 10.5 Hz, 1H), 3.41 (d, J = 10.5 Hz, 1H), 2.73 (dd, J = 12.5, 25.5 Hz, 1H), 2.33 (bs, 1H), 2.33–1.92 (m, 5H), 1.95-1.92 (m, 1H), 1.71–1.62 (m, 2H), 1.24 (s, 3H), 0.96 (d, J = 7.0 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 143.9 (d, J_{CP} = 26.5 Hz), 129.7 (d, J_{CP} = 14.0 Hz), 128.0 (d, J_{CP} = 4.0 Hz), 126.6, 74.2, 69.1, 46.5, 46.4, 43.5, 43.4 (d, J_{CP} = 2.6 Hz), 39.8 (d, J_{CP} = 9.0 Hz), 27.2 (d, J_{CP} = 17.5 Hz), 25.9 (d, J_{CP} = 22.0 Hz), 13.5; ^{31}P NMR (202 MHz, $CDCl_3$) –8.9; HRMS (ESI-TOF) calcd for $HC_{16}H_{23}O_2P$ 279.1514, found 279.1513.



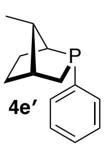
4d

Phosphine **4d** (95% yield); IR (film) ν_{max} 3068, 2930, 2872, 1432 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 4H), 7.23–7.17 (m, 1H), 2.48 (dt, J = 5.4, 10.7 Hz, 1H), 2.40 (dd, J = 13.0, 26.6 Hz, 1H), 2.33 (dt, J = 4.6, 13.3 Hz, 1H), 2.11 (dd, J = 6.7, 10.8 Hz, 1H), 1.98 (dd, J = 6.6, 13.4 Hz, 1H), 1.87 (dddd, J = 6.7, 11.9, 13.7, 35.3 Hz, 1H), 1.71 (dt, J = 6.0, 11.9 Hz, 1H), 1.06 (s, 3H), 0.99 (d, J = 6.8 Hz, 3H), 0.95 (dt, J = 4.8, 9.7 Hz, 1H), 0.72 (ddd, J = 5.7, 13.7, 19.4 Hz, 1H), 0.29 (dt, J = 5.0, 9.9 Hz, 1H), 0.15 (dt, J = 4.8, 9.6 Hz, 1H), 0.09 (dt, J = 4.7, 9.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.1 (d, J_{CP} = 27.0 Hz), 129.8 (d, J_{CP} = 14.1 Hz), 128.1 (d, J_{CP} = 4.0 Hz), 126.5, 46.2 (d, J_{CP} = 4.9 Hz), 44.6 (d, J_{CP} = 2.6 Hz), 41.6, 40.6 (d, J_{CP} = 9.0 Hz), 25.7 (d, J_{CP} = 17.7 Hz), 25.1, 24.3 (d, J_{CP} = 20.4 Hz), 13.5 (d, J_{CP} = 76.2 Hz), 8.6 (d, J_{CP} = 6.8 Hz), 8.4; ^{31}P NMR (202 MHz, $CDCl_3$) δ –9.4; HRMS (ESI-TOF) calcd for $HC_{17}H_{23}P$ 258.1537, found 258.1537.



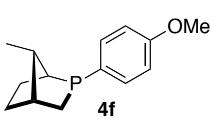
4e

Phosphine **4e** (98% yield); IR (film) ν_{max} 3069, 2952, 2928, 1432 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36–7.28 (m, 4H), 7.24–7.19 (m, 1H), 2.24-2.18 (m, 2H), 2.12–1.98 (m, 1H), 1.94–1.78 (m, 4H), 1.66–1.56 (m, 1H), 1.23–1.16 (m, 1H), 0.92 (d, J = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.9 (d, J_{CP} = 27.0 Hz), 129.9 (d, J_{CP} = 13.9 Hz), 128.1 (d, J_{CP} = 4.0 Hz), 126.6, 44.2 (d, J_{CP} = 5.2 Hz), 41.2 (d, J_{CP} = 2.7 Hz), 40.6 (d, J_{CP} = 9.1 Hz), 32.3 (d, J_{CP} = 17.2 Hz), 27.6, 23.6 (d, J_{CP} = 22.1 Hz), 13.6; ^{31}P NMR (202 MHz, $CDCl_3$) δ –6.59; HRMS (ESI-TOF) calcd for $HC_{13}H_{17}P$ 205.1146, found 205.1146.



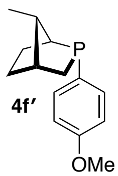
4e′

Phosphine **4e′** (94% yield); IR (film) ν_{max} 2987, 2854, 1490 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39–7.30 (m, 4H), 7.29–7.23 (m, 1H), 2.30–2.16 (m, 3H), 2.13–2.03 (m, 1H), 1.85–1.76 (m, 1H), 1.75–1.67 (m, 1H), 1.54 (dd, J = 5.7, 13.5 Hz, 1H), 1.41 (m, 1H), 1.05 (d, J = 6.7 Hz, 3H), 1.03–0.96 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.7 (d, J_{CP} = 26.1 Hz), 130.8 (d, J_{CP} = 15.2 Hz), 127.9 (d, J_{CP} = 4.4 Hz), 127.0, 45.4 (d, J_{CP} = 19.1 Hz), 42.7 (d, J_{CP} = 2.3 Hz), 39.8 (d, J_{CP} = 13.0 Hz), 27.5 (d, J_{CP} = 8.5 Hz), 27.3 (d, J_{CP} = 1.9 Hz), 23.3 (d, J_{CP} = 4.0 Hz), 14.4 (d, J_{CP} = 13.9 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) –4.79; HRMS (ESI-TOF) calcd for $HC_{13}H_{17}P$ 205.1146, found 205.1149.



4f

Phosphine **4f** (98% yield); IR (film) ν_{max} 3058, 2967, 2853, 1590, 1473 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 6.90 – 6.86 (m, 2H), 3.80 (s, 3H), 2.23 – 2.16 (m, 1H), 2.13 – 1.74 (m, 6H), 1.62 – 1.52 (m, 1H), 1.20 – 1.14 (m, 1H), 0.91 (d, J = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 133.1 (d, J_{CP} = 24.4 Hz), 131.4 (d, J_{CP} = 15.6 Hz), 113.9 (d, J_{CP} = 4.9 Hz), 55.0, 43.8 (d, J_{CP} = 5.0 Hz), 41.1 (d, J_{CP} = 2.6 Hz), 40.9 (d, J_{CP} = 9.4 Hz), 32.0 (d, J_{CP} = 17.4 Hz), 27.5, 23.6 (d, J_{CP} = 22.4 Hz), 13.5; ^{31}P NMR (202 MHz, $CDCl_3$) δ – 8.15; HRMS (ESI-TOF) calcd for $HC_{14}H_{19}OP$ m/z 235.1252, found 235.1252.

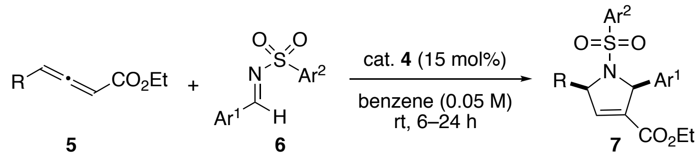


4f′

Phosphine **4f′** (99% yield); IR (film) ν_{max} 2948, 2871, 1595, 1498, 1247 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 6.4, 8.6 Hz, 2H), 6.90 (d, J = 8.1 Hz, 2H), 3.81 (s, 3H), 2.25 (dt, J = 5.6, 11.1 Hz, 1H), 2.21–2.20 (m, 2H), 2.09–1.99 (m, 1H), 1.82–1.69 (m, 2H), 1.48 (dd, J = 5.6, 13.4 Hz, 1H), 1.38–1.32 (m, 1H), 1.06–1.01 (m, 1H), 1.03 (d, J = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.1, 132.4 (d, J_{CP} = 17.4 Hz), 129.7 (d, J_{CP} = 23.6 Hz), 113.7 (d, J_{CP} = 5.7 Hz), 55.0, 45.4 (d, J_{CP} = 18.8 Hz), 42.8 (d, J_{CP} = 2.5 Hz), 40.1 (d, J_{CP} = 13.1 Hz), 27.5 (d, J_{CP} = 8.1 Hz), 27.5 (d, J_{CP} = 2.0 Hz), 22.9 (d, J_{CP} = 4.1 Hz), 14.4 (d, J_{CP} = 13.8 Hz); ^{31}P NMR (202 MHz, $CDCl_3$) δ –6.81; HRMS (ESI-TOF) calcd for $HC_{14}H_{19}OP$ 235.1252, found 235.1251.

3. Allenoate–Imine [3 + 2] Annulation

3.1. General Procedure for Allenoate–Imine [3 + 2] Annulations

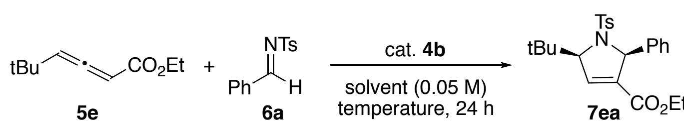


A screw-capped vial equipped with a magnetic stirrer bar was charged with an arylimine **6** (0.1 mmol) and a phosphine **4** (0.015 mmol, added as a stock solution in benzene[a]). An allenoate **5** (0.2 mmol) was added and then the vessel was purged with argon and sealed with a screw cap and Teflon. After stirring at room temperature until completion (indicated by disappearance of the imine via TLC),[b] the mixture was loaded directly onto a silica gel column and purified through flash column chromatography (SiO_2; EtOAc/hexanes, 1:4) to give the pyrroline product **7.**

[a]The phosphine **4** was dissolved in benzene such that the concentration was 1.8 mg/mL. The stock solution was stored in a Schlenk flask at 0 °C under argon protection. Over the course of 2 weeks, there was no appreciable formation of the phosphine oxide, as determined through TLC or NMR spectroscopic analysis.

[b]The phosphines **4e**/**4e′** and **4f**/**4f′** were more reactive relative to the phosphines **4a**, **4b**, **4c**, and **4d**, resulting in reduced reactions times (typically 6–12 hours required for completion).

Table S1. Optimization of the Allene–Imine [3 + 2] Annulation[a]

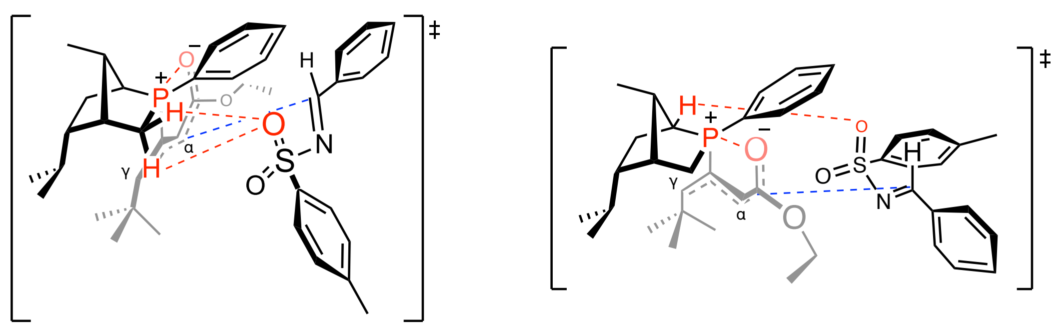


entry	**4b** mol%	solvent	temperature	additive	yield (%)	ee (%)
1	5	benzene	rt	–	58	93
2[b]	5	benzene	rt	–	62	93
3	10	benzene	rt	–	77	92
4[b]	10	benzene	rt	–	89	93
5	15	benzene	rt	–	94	93
6[b]	15	benzene	rt	–	92	93
7	20	benzene	rt	–	93	93
8	15	toluene	rt	–	90	91
9	15	acetonitrile	rt	–	60	40
10	15	dichloromethane	rt	–	96	58
11	15	diethyl ether	rt	–	86	93
12	15	tetrahydrofuran	rt	–	84	83
13	15	methanol	rt	–	NR	N/A
14	15	benzene	0 ˚C	–	78	95
15[c]	15	benzene	0 ˚C	–	82	94
16[d]	15	benzene	40 ˚C	–	90	92
17	15	benzene	rt	H_2O (0.15 equiv)	90	75
18	15	benzene	rt	HOAc (0.15 equiv)	94	90
19	15	benzene	rt	PhOH (0.15 equiv)	92	93

[a]1.0 equiv **6a** (0.1 mmol, 25.9 mg) and 2.0 equiv **5e** (0.2 mmol, 34 µL). [b]1.0 equiv **6a** (3.85 mmol, 1.0 g) and 1.2 equiv **5e** (4.63 mmol, 0.78 mL). [c]Reaction allowed to run for 72 h. [d]Reaction complete within 3 h.

3.2. Proposed Transition States

Displayed below are proposed transition states for the reaction between the allenoate **5e** and the imine **6a** catalyzed by the phosphine **4b**. Calculated transition states are available in reference 2h. The key stabilizing factor in the TS leading to the major *S*-enantiomer is hydrogen bonding between the imino *N*-sulfonyl oxygen atom and the two α-methylene (α to the phosphorous) hydrogen atoms. In contrast, there is only one stabilizing hydrogen bond between the oxygen atom of the sulfonyl group and the α-methine hydrogen in the TS leading to the minor *R*-enantiomer. As the bond between the α-carbon of the phosphonium dienolate and the imino carbon (C_{α}–C_{imine}) forms, the pyramidalization of the C_{α} of the phosphonium enolate bends the bond between the α-carbon and the carbonyl carbon of the ester (C_{α}–C_{ester}) and the bond between the α-carbon and the β-carbon (C_{α}–C_{β}), placing the γ-carbon away from the approaching imine. In the absence of the second stabilizing hydrogen bond, the bond between the α-carbon of the phosphonium enolate and the imino carbon is formed to a lesser extent; at this point, the phosphonium dienolate is still relatively flat, causing greater steric repulsion between the imine and the γ-substituent. This arrangement enhances the preference for the TS leading to the major *S*-enantiomer, resulting in the greater enantioselectivity observed upon increasing the size of the γ-substituent.



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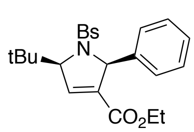
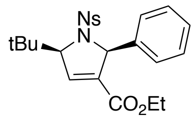
3.3. Analytical Data for the Pyrroline Products

Compounds **7aa**/**7aa′**, **7ba**, **7bp′**, **7ca**, **7da**/**7da′**, **7ea**/**7ea′**, **7eb**, **7ec**, **7ed**, **7ee**, and **7eg** (in racemic form) have been synthesized previously; their spectral data are provided in the pertinent references.[2] Complete spectral data are provided for all new compounds. Compounds **7ba**, **7bh′**, **7bm′**, **7bp′**, **7ca**, **7ch**, **7ci′**, **7cn′**, and **7co′** were obtained as an inseparable mixture of *cis* (major) and *trans* (minor) diastereomers. NMR spectral data are provided for the enantiomerically enriched samples of a mixture of the *cis* (major) and *trans* (minor) diastereomers.



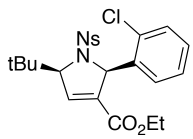
7eb

Pyrroline **7eb** (90% yield, 92% ee); $[\alpha]_D$ +83.9 (c = 1.00, CH_2Cl_2, 23.0 °C)



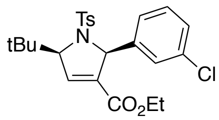
7ec

Pyrroline **7ec** (94% yield, 95% ee); [α]D +85.5 (c = 1.00, CH_2Cl_2, 23.0 °C)



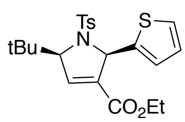
7ed

Pyrroline **7ed** (96% yield, 98% ee); [α]D +129.2 (c = 1.00, CH_2Cl_2, 23.0 °C)



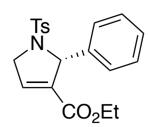
7ee

Pyrroline **7ee** (89% yield, 94% ee); [α]D +106.7 (c = 1.00, CH_2Cl_2, 23.0 °C)



7eg

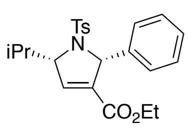
Pyrroline **7eg** (89% yield, 92% ee); [α]D +130.1 (c = 1.00, CH_2Cl_2, 23.0 °C)



7aa′

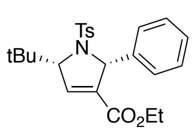
Pyrroline **7aa′** (93% yield, 84% ee); [α]D –162.2 (c = 1.00, CH_2Cl_2, 24.1 °C)

Recrystallization to >99% ee; –193.1 (c = 1.00, CH_2Cl_2, 26.0 °C)



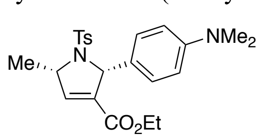
7da′

Pyrroline **7da′** (97% yield, 94% ee); [α]D –96.6 (c = 1.00, CH_2Cl_2, 25.3 °C)



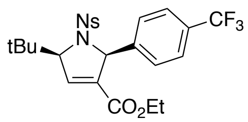
7ea′

Pyrroline **7ea′** (94% yield, 99% ee); [α]D –111.8 (c = 1.00, CH_2Cl_2, 24.7 °C)



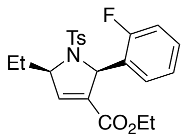
7bp′

Pyrroline **7bp′** (96% yield, 94% ee, 99:1 d.r.); [α]D –151.2 (c = 1.00, CH_2Cl_2, 23.6 ˚C)



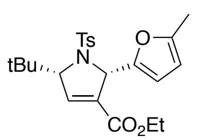
7ef

Pyrroline **7ef** (86% yield, 92% ee); $[\alpha]_D$ +85.1 (c = 1.00, CH_2Cl_2, 23.1 °C); IR (film) ν_{max} 2968, 2362, 1720, 1533, 1326 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 8.34-8.31 (m, 2H), 8.02-7.98 (m, 2H), 7.59 (s, 4H), 6.78-6.77 (m, 1H), 5.92 (s, 1H), 4.41 (dd, *J* = 0.6, 2.6 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.81 (s, 9H); ^{13}C (125 MHz, $CDCl_3$) δ 162.1, 150.4, 142.8, 142.7, 141.2, 141.2, 133.6, 129.2, 128.5, 125.2, 124.3, 78.5, 78.5, 68.3, 68.3, 61.4, 36.1, 27.9, 14.0; LRMS (MALDI) calcd for $C_{24}H_{25}F_3N_2O_6SNa$ $[M + Na]^+$ 549.13, found 549.2.



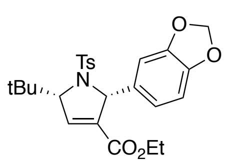
7ch

Pyrroline **7ch** (93% yield, 83% ee, 99:1 d.r.); m.p. 128–132 ˚C; $[\alpha]_D$ +156.2 (c = 1.00, CH_2Cl_2, 23.0 ˚C); IR (film) ν_{max} 2977, 2365, 1717, 1353 cm^{-1}; ^1H (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.32–7.19 (m, 4H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 9.3 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 5.90 (s, 1H), 4.58–4.51 (m, 1H), 4.08–3.89 (m, 2H), 2.40 (s, 3H), 2.30–2.21 (m, 1H), 1.95–1.84 (m, 1H), 1.09 (t, *J* = 7.5 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H); ^{13}C (125 MHz, $CDCl_3$) δ 161.7, 161.4, 143.6, 139.4, 134.3, 133.4, 129.6, 129.4, 129.3, 129.2, 129.2, 127.7, 127.6, 124.0, 123.9, 115.3, 115.1, 68.8, 62.2, 62.1, 60.7, 29.9, 21.4, 13.6, 10.3; HRMS (ESI-TOF) calcd for $HC_{22}H_{25}FNO_4S$ 418.1488, found 418.1489.



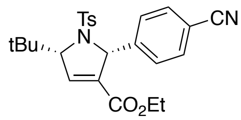
7ei′

Pyrroline **7ei′** (94% yield, 99% ee); $[\alpha]_D$ –20.6 (c = 1.00, CH_2Cl_2, 24.0 ˚C); IR (film) ν_{max} 2963, 2924, 1723, 1167 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 6.76 (t, *J* = 2.0 Hz, 1H), 6.03 (d, *J* = 3.0 Hz, 1H), 5.85 (d, *J* = 2.8 Hz, 1H), 5.80 (s, 1H), 4.52 (t, *J* = 1.2 Hz, 1H), 4.19–4.03 (m, 2H), 2.41 (s, 3H), 2.16 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 151.3, 150.0, 143.7, 140.6, 135.0, 132.1, 129.5, 128.0, 109.5, 106.3, 63.4, 60.6, 36.3, 27.5, 21.4, 13.9, 13.4; HRMS (ESI-TOF) calcd for $HC_{23}H_{29}NO_5S$ 432.1845, found 432.1845.



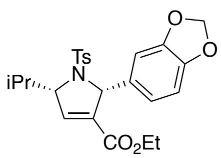
7ej′

Pyrroline **7ej′** (94% yield, 98% ee); m.p. 118–122 ˚C; $[\alpha]_D$ –171.5 (c = 1.00, CH_2Cl_2, 23.2 ˚C); IR (film) ν_{max} 2965, 2905, 1718, 1247, 1165 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 1.6 Hz, 1H), 6.76 (dd, *J* = 1.7, 8.1 Hz, 1H), 6.72–6.68 (m, 2H), 5.94 (s, 2H), 5.79 (s, 1H), 4.33 (d, *J* = 2.6 Hz, 1H), 4.11 (dq, *J* = 1.1, 7.1 Hz, 2H), 2.40 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.5, 147.4, 146.9, 143.8, 141.1, 134.1, 134.0, 133.5, 129.5, 127.9, 121.4, 108.9, 107.4, 100.9, 77.7, 68.2, 60.8, 35.9, 27.9, 21.4, 13.9; HRMS (ESI-TOF) calcd for $HC_{25}H_{29}NO_6S$ 472.1794, found 472.1796.



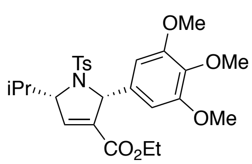
7ek′

Pyrroline **7ek′** (98% yield, 98% ee); m.p. 92–95 ˚C; $[\alpha]_D$ –107.0 (c = 1.00, CH_2Cl_2, 23.8 ˚C); IR (film) ν_{max} 2966, 2229, 1719, 1166 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.63–7.56 (m, 4H), 7.29 (d, *J* = 8.1 Hz, 2H), 6.76 (q, *J* = 1.3 Hz, 1H), 5.85 (s, 1H), 4.35 (d, *J* = 2.7 Hz, 1H), 4.13 (q, *J* = 7.1 Hz, 2H), 2.42 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.79 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 144.9, 144.2, 142.3, 133.4, 133.1, 131.8, 129.7, 128.8, 127.9, 118.6, 111.5, 78.0, 67.8, 61.1, 35.8, 27.7, 21.5, 13.9; HRMS (ESI-TOF) calcd for $HC_{25}H_{28}N_2O_4S$ 453.1848, found 453.1848.



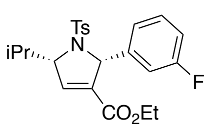
7dj′

Pyrroline **7dj′** (92% yield, 93% ee); m.p. 90–95 ˚C; $[\alpha]_D$ –183.1 (c = 1.00, CH_2Cl_2, 23.8 ˚C); IR (film) ν_{max} 2962, 2927, 1718, 1164 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.24 (t, *J* = 8.7 Hz, 2H), 6.89–6.83 (m, 2H), 6.75–6.71 (m, 2H), 5.93 (s, 2H), 5.63 (t, *J* = 2.0 Hz, 1H), 4.44 (dt, *J* = 2.5, 5.7 Hz, 1H), 4.10–3.99 (m, 2H), 2.39 (s, 3H), 2.13 (sex, *J* = 6.7 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 1.06 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 147.3, 147.2, 143.5, 138.5, 135.0, 134.3, 133.8, 129.5, 127.6, 122.0, 108.6, 107.7, 100.9, 73.2, 69.0, 60.7, 32.9, 21.4, 20.1, 18.0, 13.8; HRMS (ESI-TOF) calcd for $HC_{24}H_{27}NO_6S$ 458.1637, found 458.1642.



7dl′

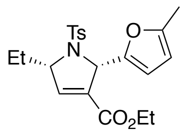
Pyrroline **7dl′** (95% yield, 95% ee); m.p. 118–121 ˚C; $[\alpha]_D$ –202.5 (c = 1.00, CH_2Cl_2, 23.7 ˚C); IR (film) ν_{max} 2961, 2935, 1720, 1164, 1125 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.73 (t, *J* = 2.0 Hz, 1H), 6.59 (s, 2H), 5.71 (t, *J* = 2.1 Hz, 1H), 4.53 (quint, *J* = 2.6 Hz, 1H), 4.12–3.99 (m, 2H), 3.82 (s, 3H), 3.78 (s, 6H), 2.37 (s, 3H), 2.16 (sex, *J* = 6.7 Hz, 1H), 1.10 (q, *J* = 7.1 Hz, 6H), 0.91 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 152.7, 143.5, 138.2, 137.5, 135.5, 135.2, 134.4, 129.3, 127.4, 105.4, 73.1, 69.3, 60.7, 55.9, 32.7, 21.4, 20.0, 17.9, 13.9; HRMS (ESI-TOF) calcd for $HC_{26}H_{33}NO_7S$ 504.2056, found 504.2056.



7dm′

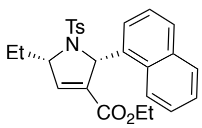
Pyrroline **7dm′** (97% yield, 93% ee); m.p. 109–110 ˚C; $[\alpha]_D$ –102.5 (c = 1.00, CH_2Cl_2, 25.5 ˚C); IR (film) ν_{max} 2963, 2930, 1720, 1260, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.2 Hz, 2H), 7.29–7.21 (m, 3H), 7.18 (d, *J* = 7.8 Hz, 1H), 7.07 (d, *J* = 9.9 Hz, 1H), 6.96 (td, *J* = 1.9, 8.3 Hz, 1H), 6.77 (t, *J* = 1.8 Hz, 1H), 5.69 (s, 1H), 4.48 (dt, *J* = 2.3, 5.8 Hz, 1H), 4.11–3.96 (m, 2H), 2.39 (s, 3H), 2.13 (sex, *J* = 6.7 Hz, 1H), 1.11–1.05 (m, 6H), 0.91 (d, *J* = 6.8

Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 143.7, 142.4, 142.3, 139.1, 134.8, 134.0, 129.5, 129.5, 127.6, 124.0, 115.2, 115.1, 114.9, 114.7, 73.3, 68.6, 60.8, 32.8, 21.4, 20.1, 17.9, 13.8; HRMS (ESI-TOF) calcd for $HC_{23}H_{26}FNO_4S$ 432.1645, found 432.1646.



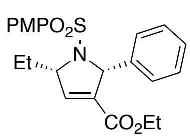
7ci′

Pyrroline **7ci′** (95% yield, 90% ee, 98:2 d.r.); $[\alpha]_D$ –136.3 (c = 1.00, CH_2Cl_2, 23.5 ˚C); IR (film) ν_{max} 2974, 2924, 1720, 1162 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.75 (t, *J* = 1.9 Hz, 1H), 6.16 (d, *J* = 3.1 Hz, 1H), 5.85 (d, *J* = 2.2 Hz, 1H), 5.72 (s, 1H), 4.63–4.57 (m, 1H), 4.15–4.03 (m, 2H), 2.39 (s, 3H), 2.17 (s, 3H), 1.96–1.89 (m, 1H), 1.81–1.75 (m, 1H), 1.16 (t, *J* = 7.1 Hz, 3H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 151.7, 150.1, 143.3, 140.4, 135.9, 131.9, 129.4, 127.3, 109.3, 106.4, 68.1, 62.4, 60.7, 28.9, 21.4, 13.9, 13.4, 9.7; HRMS (ESI-TOF) calcd for $HC_{21}H_{25}NO_5S$ 404.1532, found 404.1528.



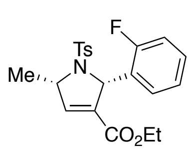
7cn′

Pyrroline **7cn′** (93% yield, 97% ee, >99:1 d.r.); m.p. 105–108 ˚C; $[\alpha]_D$ –41.3 (c = 1.00, CH_2Cl_2, 23.3 ˚C); IR (film) ν_{max} 3063, 2925, 1719, 1597, 1568, 1156 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.34 (d, *J* = 8.6 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.40–7.29 (m, 4H), 6.89 (t, *J* = 7.3 Hz, 3H), 6.61 (s, 1H), 4.87–4.80 (m, 1H), 3.89–3.76 (m, 2H), 2.37–2.28 (m, 1H), 2.22 (s, 3H), 2.01–1.89 (m, 1H), 1.15 (t, *J* = 7.5 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.1, 143.0, 138.4, 136.4, 135.5, 135.2, 133.3, 131.4, 128.8, 128.2, 128.2, 127.4, 126.1, 125.8, 125.3, 124.9, 123.3, 68.5, 63.8, 60.5, 29.8, 21.2, 13.4, 10.5; HRMS (ESI-TOF) calcd for $HC_{26}H_{27}NO_4S$ 450.1739, found 450.1732.



7co′

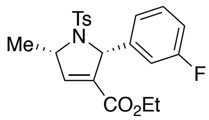
Pyrroline **7co′** (99% yield, 92% ee, >99:1 d.r.); m.p. 88–92 ˚C; $[\alpha]_D$ –96.1 (c = 1.00, CH_2Cl_2, 23.0 ˚C); IR (film) ν_{max} 2977, 2931, 1719, 1260, 1159 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62–7.58 (m, 2H), 7.33–7.30 (m, 2H), 7.29–7.23 (m, 3H), 6.88–6.83 (m, 2H), 6.78 (t, *J* = 2.0 Hz, 1H), 5.67 (t, *J* = 1.9 Hz, 1H), 4.62–4.56 (m, 1H), 4.09–3.94 (m, 2H), 3.83 (s, 3H), 2.12–2.03 (m, 1H), 1.80–1.70 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 162.1, 140.0, 139.3, 134.2, 130.2, 129.5, 128.1, 127.9, 127.8, 114.0, 69.3, 68.6, 60.7, 55.4, 29.7, 13.8, 10.3; HRMS (ESI-TOF) calcd for $HC_{22}H_{25}NO_5S$ 416.1532, found 416.1533.



7bh′

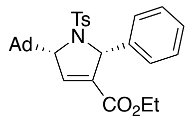
Pyrroline **7bh′** (95% yield, 90% ee, 96:4 d.r.); m.p. 87–93 ˚C; $[\alpha]_D$ –191.8 (c = 1.00, CH_2Cl_2, 22.9 ˚C); IR (film) ν_{max}

2979, 2931, 1720, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2, 2H), 7.26–7.19 (m, 4H), 7.07 (t, J = 7.5 Hz, 1H), 6.97 (t, J = 9.3 Hz, 1H), 5.89 (s, 1H), 4.82–4.72 (m, 1H), 4.07–3.91 (m, 2H), 2.39 (s, 3H), 1.64 (d, J = 6.7 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 159.5, 143.6, 141.0, 134.5, 132.8, 129.6, 129.4, 129.4, 129.4, 128.9, 127.6, 127.5, 126.6, 124.0, 124.0, 115.3, 115.1, 62.9, 62.5, 62.5, 60.7, 22.3, 21.4, 13.6; HRMS (ESI-TOF) calcd for $HC_{21}H_{22}FNO_4S$ 404.1332, found 404.1333.



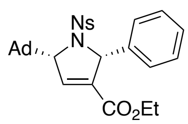
7bm′

Pyrroline **7bm′** (95% yield, 91% ee, 96:4 d.r.); $[\alpha]_D$ –137.8 (c = 1.00, CH_2Cl_2, 23.4 °C); IR (film) ν_{max} 2979, 2926, 1719, 1263, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J = 8.2 Hz, 2H), 7.26–7.10 (m, 4H), 7.02–6.91 (m, 2H), 6.65 (t, J = 1.8 Hz, 1H), 5.63 (s, 1H), 4.82–4.74 (m, 1H), 4.08–3.97 (m, 2H), 2.38 (s, 3H), 1.56 (d, J = 6.7 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 161.8, 161.6, 143.6, 142.6, 142.5, 141.0, 135.2, 133.3, 129.6, 129.5, 127.4, 123.7, 123.6, 114.9, 114.8, 114.7, 114.6, 69.0, 62.8, 60.8, 22.3, 21.4, 13.8; HRMS (ESI-TOF) calcd for $HC_{21}H_{22}FNO_4S$ 404.1332, found 404.1329.



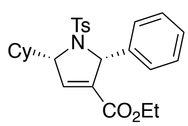
7fa′

Pyrroline **7fa′** (95% yield, 98% ee); m.p. 144–146 °C; $[\alpha]_D$ –31.5 (c = 1.00, CH_2Cl_2, 25.5 °C); IR (film) ν_{max} 2903, 2849, 1718, 1165 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 7.5 Hz, 2H), 7.32–7.25 (m, 5H), 6.76 (q, J = 1.3 Hz, 1H), 5.86 (s, 1H), 4.19 (d, J = 2.6 Hz, 1H), 4.10 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 1.84 (br s, 3H), 1.57 (d, J = 11.7 Hz, 3H), 1.47 (d, J = 12.0 Hz, 6H), 1.32 (d, J = 12.2 Hz, 3H), 1.13 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.6, 143.7, 140.7, 139.5, 134.1, 134.0, 129.5, 128.0, 127.9, 127.9, 127.5, 78.4, 68.2, 60.7, 39.9, 37.7, 36.4, 28.2, 21.4, 13.9; HRMS (ESI-TOF) calcd for $HC_{30}H_{35}NO_4S$ 506.2365, found 503.2369.



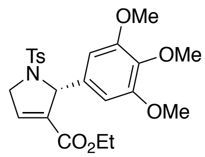
7fc′

Pyrroline **7fc′** (88% yield, 92% ee); m.p. 210–212 °C (decomp); $[\alpha]_D$ –20.4 (c = 1.00, CH_2Cl_2, 23.8 °C); IR (film) ν_{max} 2904, 2849, 1955, 1718, 1531 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, J = 8.8 Hz, 2H), 7.95 (d, J = 8.8 Hz, 2H), 7.42 (d, J = 7.3 Hz, 2H), 7.35–7.29 (m, 3H), 6.79 (q, J = 1.3 Hz, 1H), 5.92 (s, 1H), 4.28, (d, J = 2.4 Hz, 1H), 4.11 (q, J = 3.4 Hz, 2H), 1.86 (br s, 3H), 1.73–1.65 (m, 3H), 1.46 (d, J = 12.7 Hz, 6H), 1.35 (d, J = 12.0 Hz, 3H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 150.0, 143.4, 139.8, 138.6, 134.0, 128.9, 128.1, 128.1, 124.0, 78.8, 68.7, 61.0, 42.5, 39.9, 37.9, 36.4, 36.3, 28.5, 28.1, 13.9; HRMS (ESI-TOF) calcd for $HC_{29}H_{32}N_2O_6S$ 537.2059, found 537.2063.



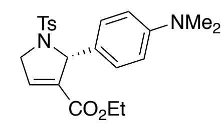
7ga′

Pyrroline **7ga′** (91% yield, 94% ee); m.p. 114–116 ˚C; $[\alpha]_D$ –52.8 (c = 1.00, CH_2Cl_2, 23.1 ˚C); IR (film) ν_{max} 2928, 2852, 1720, 1165 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 1.7, 8.0 Hz, 2H), 7.31–7.26 (m, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.77 (t, *J* = 1.9 Hz, 1H), 5.72 (t, *J* = 1.9 Hz, 1H), 4.49 (dt, *J* = 2.6, 5.1 Hz, 1H), 4.08–3.93 (m, 2H), 2.38 (s, 3H), 1.86 (d, *J* = 11.4 Hz, 1H), 1.81–1.63 (m, 5H), 1.23–1.08 (m, 4H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.99–0.88 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.2, 143.4, 139.7, 139.2, 135.2, 133.9, 129.4, 128.3, 128.0, 127.8, 127.5, 72.6, 69.0, 60.6, 42.4, 30.6, 28.7, 26.2, 25.8, 21.4, 13.8; HRMS (ESI-TOF) calcd for $HC_{26}H_{31}NO_4S$ 454.2052, found 452.2054.



7al′

Pyrroline **7al′** (91% yield, 87% ee); $[\alpha]_D$ –105.3 (c = 1.00, CH_2Cl_2, 23.5 ˚C); IR (film) ν_{max} 2928, 2853, 1721, 1163, 1126 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.79 (d, *J* = 1.8 Hz, 1H), 6.32 (s, 2H), 5.70 (dt, *J* = 1.8, 5.8 Hz, 1H), 4.57 (dt, *J* = 2.3, 17.0 Hz, 1H), 4.36 (ddd, *J* = 1.9, 5.9, 17.0 Hz, 1H), 4.11–4.01 (m, 2H), 3.81 (s, 3H), 3.71 (s, 6H), 2.35 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.7, 152.8, 143.1, 137.6, 136.0, 135.8, 135.2, 134.4, 129.1, 126.9, 104.8, 69.0, 60.8, 60.7, 55.8, 54.7, 21.3, 13.9; HRMS (ESI-TOF) calcd for $HC_{23}H_{27}NO_7S$ 462.1587, found 462.1591.



7ap′

Pyrroline **7ap′** (90% yield, 92% ee); $[\alpha]_D$ –29.300 (c = 1.00, CH_2Cl_2, 24.1 ˚C); IR (film) ν_{max} 2923, 2853, 1719, 1162 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.2 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.7 Hz, 2H), 6.73 (d, *J* = 1.6 Hz, 1H), 6.55 (d, *J* = 8.7 Hz, 2H), 5.68 (d, *J* = 5.5 Hz, 1H), 4.46 (dt, *J* = 2.2, 16.9 Hz, 1H), 4.33 (ddd, *J* = 1.8, 5.7, 16.9 Hz, 1H), 4.07–3.99 (m, 2H), 2.92 (s, 6H), 2.36 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.9, 150.2, 142.7, 136.1, 135.8, 134.6, 129.2, 128.4, 127.0, 112.1, 68.6, 60.6, 54.5, 40.5, 21.4, 13.8; HRMS (ESI-TOF) calcd for $HC_{22}H_{26}N_2O_4S$ 415.1692, found 415.1692.

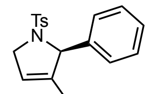
4. Separation of Enantiomers

4.1. HPLC Conditions

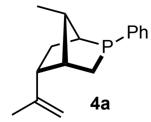
Table S2. Separation of Enantiomers

Compound	Column	Solvents	Flow Rate
7aa	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ba	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ca	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7da	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ea	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7eb	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ec	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ed	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ee	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ef	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7eg	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ch	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7da	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ei	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ej	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ek	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7dl	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7dm	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7dj	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ch	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7cn	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ci	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7co	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7bh	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7bm	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7bp	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7fa	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (40:60)	2.0 mL/min
7fc	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ga	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7ap	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (60:40)	2.0 mL/min
7al	Regis (*R*,*R*)-DACH DNB	CH_2Cl_2/Hexanes (40:60)	2.0 mL/min

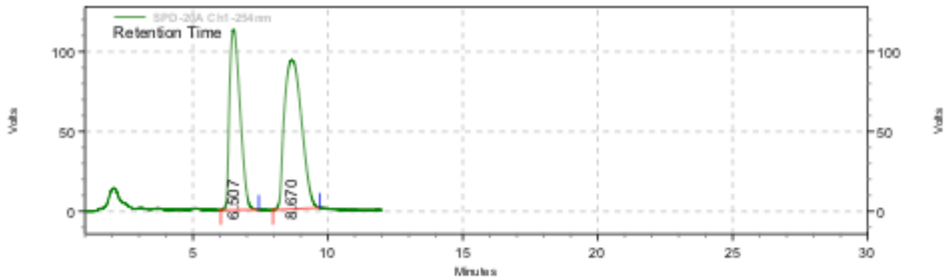
4.2. Copies of HPLC Traces



7aa from the reaction catalyzed by

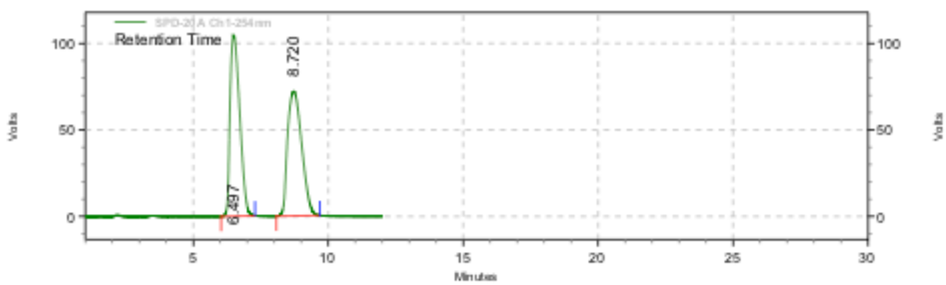


4a



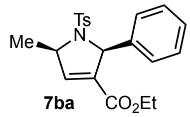
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.507	3069630	42.57	112957	54.76
8.670	4140658	57.43	93314	45.24
Totals	7210288	100.00	206271	100.00

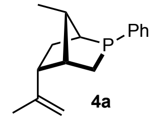


SPD-20A
Ch1-254nm
Results

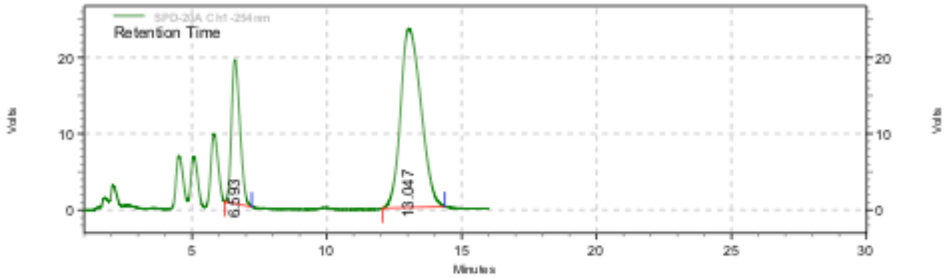
Retention Time	Area	Area %	Height	Height %
6.497	2618856	50.00	104665	59.26
8.720	2618481	50.00	71946	40.74
Totals	5237337	100.00	176611	100.00



7ba from the reaction catalyzed by

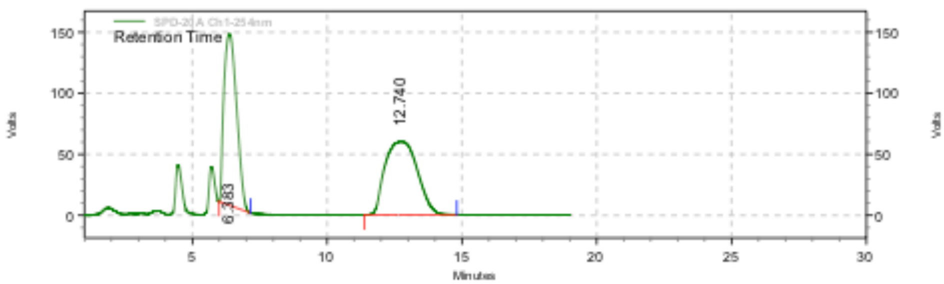


4a



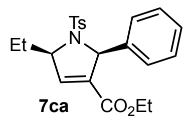
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.593	408918	24.91	18887	44.60
13.047	1232546	75.09	23456	55.40
Totals	1641464	100.00	42343	100.00

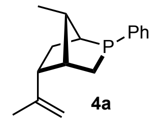


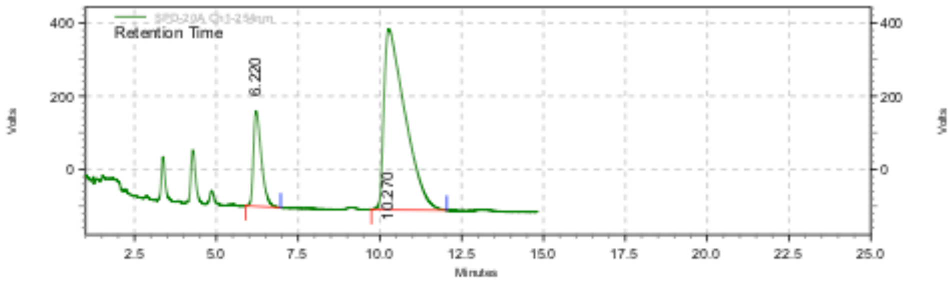
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.383	4603965	47.74	140516	70.07
12.740	5040441	52.26	60014	29.93
Totals	9644406	100.00	200530	100.00



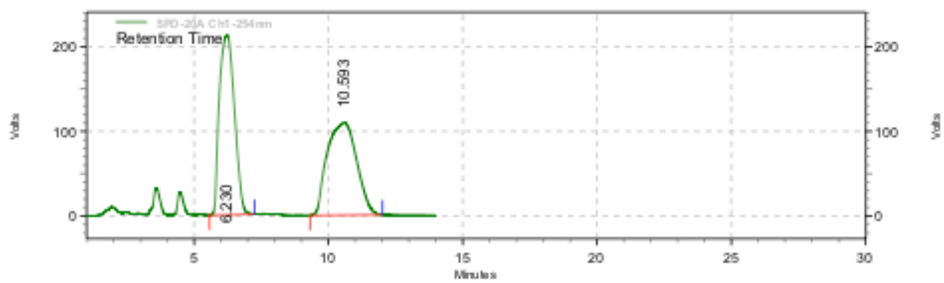
from the reaction catalyzed by





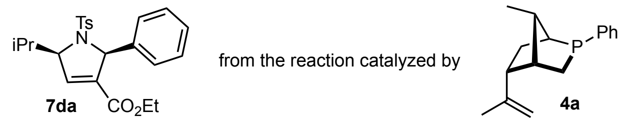
SPD-20A
Ch1-254nm
Results

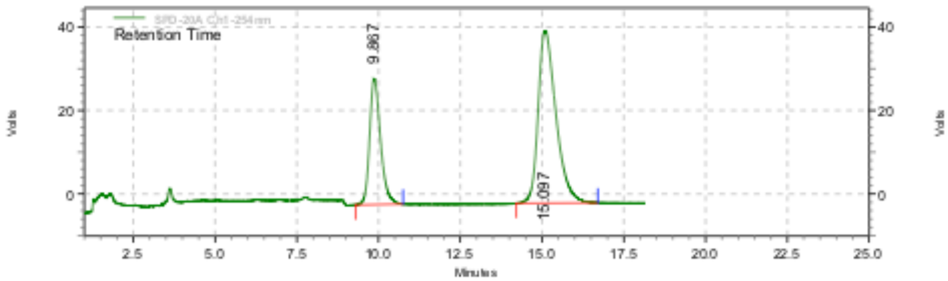
Retention Time	Area	Area %	Height	Height %
6.220	4388368	16.54	258996	34.49
10.270	22140925	83.46	491916	65.51
Totals	26529293	100.00	750912	100.00



SPD-20A
Ch1-254nm
Results

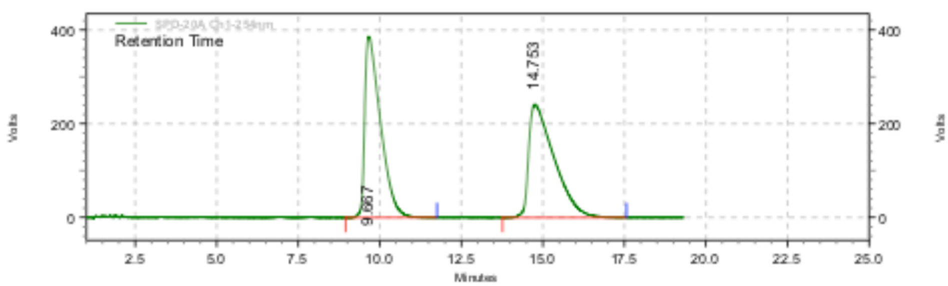
Retention Time	Area	Area %	Height	Height %
6.230	8282768	49.86	212639	66.04
10.593	8328054	50.14	109370	33.96
Totals	16610822	100.00	322009	100.00





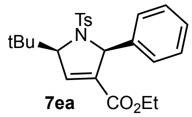
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.867	703582	31.04	30165	42.20
15.097	1563015	68.96	41323	57.80
Totals	2266597	100.00	71488	100.00

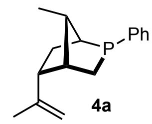


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.667	12996234	49.87	387103	61.62
14.753	13063679	50.13	241091	38.38
Totals	26059913	100.00	628194	100.00



7ea from the reaction catalyzed by



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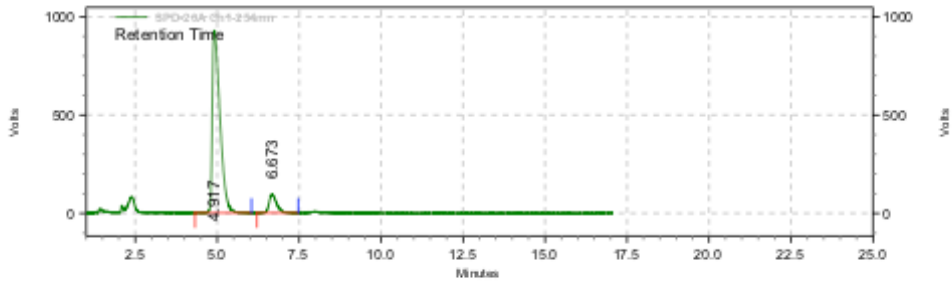
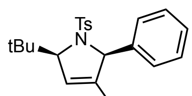


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
4.917	15082326	90.76	929794	90.78
6.673	1535470	9.24	94395	9.22
Totals	16617796	100.00	1024189	100.00



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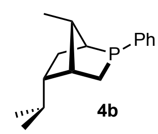

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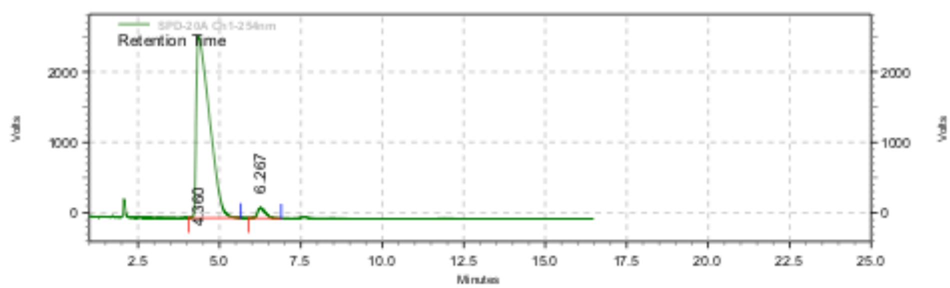
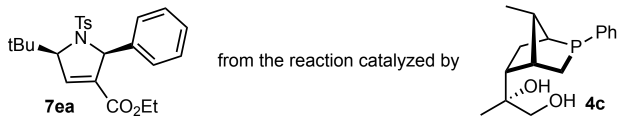
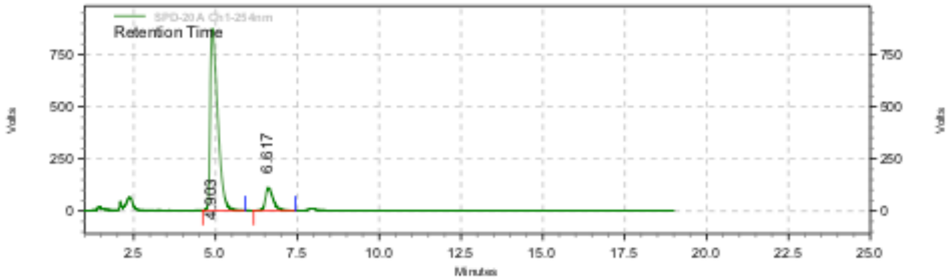


SPD-20A
Ch1-254nm
Results

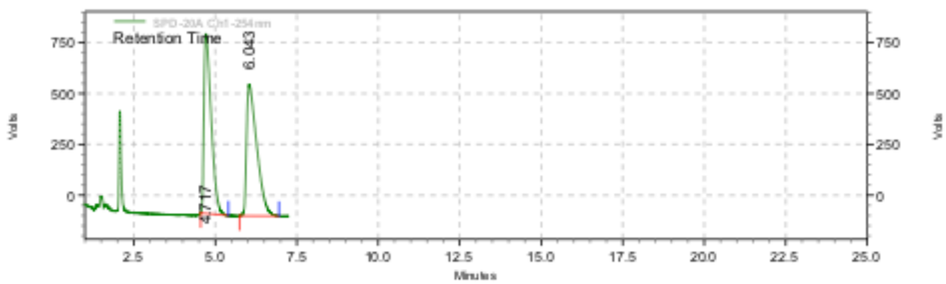
Retention Time	Area	Area %	Height	Height %
4.360	72210140	96.66	2566107	94.62
6.267	2491808	3.34	146041	5.38
Totals	74701948	100.00	2712148	100.00





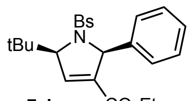
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
4.903	13854871	88.60	871622	88.87
6.617	1782417	11.40	109194	11.13
Totals	15637288	100.00	980816	100.00



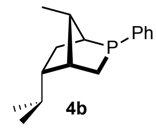
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
4.717	13668933	49.13	881958	57.72
6.043	14151739	50.87	646067	42.28
Totals	27820672	100.00	1528025	100.00



7eb

from the reaction catalyzed by



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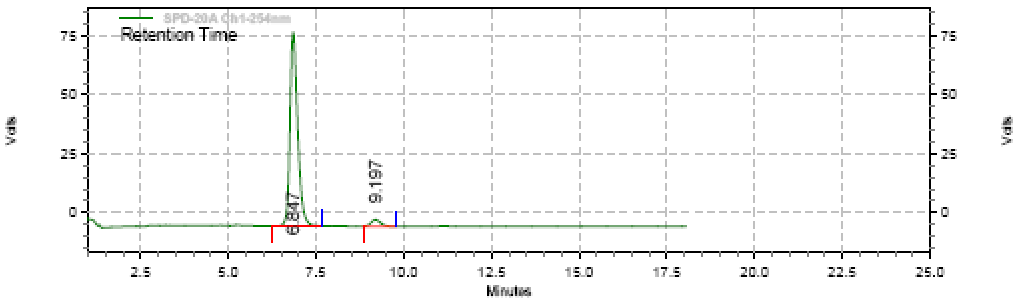
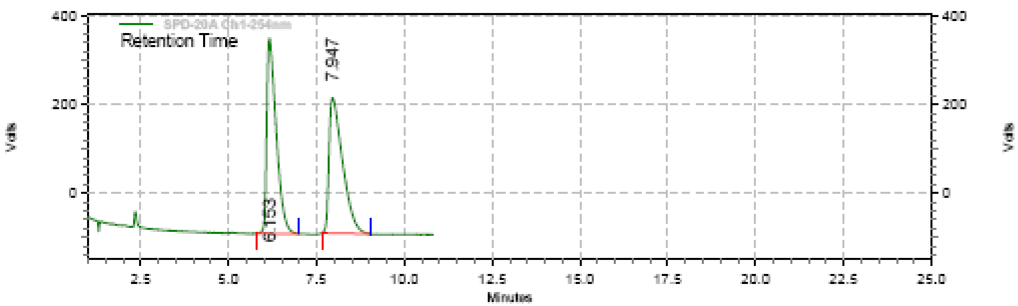


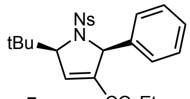
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.847	1258725	95.93	82201	96.67
9.197	53352	4.07	2833	3.33
Totals	1312077	100.00	85034	100.00



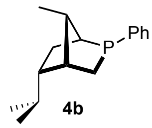
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.153	8302511	50.21	440485	59.13
7.947	8232872	49.79	304454	40.87
Totals	16535383	100.00	744939	100.00



7ec

from the reaction catalyzed by



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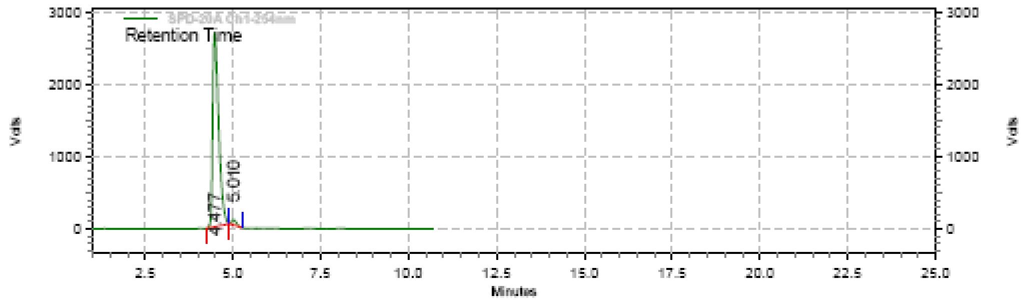
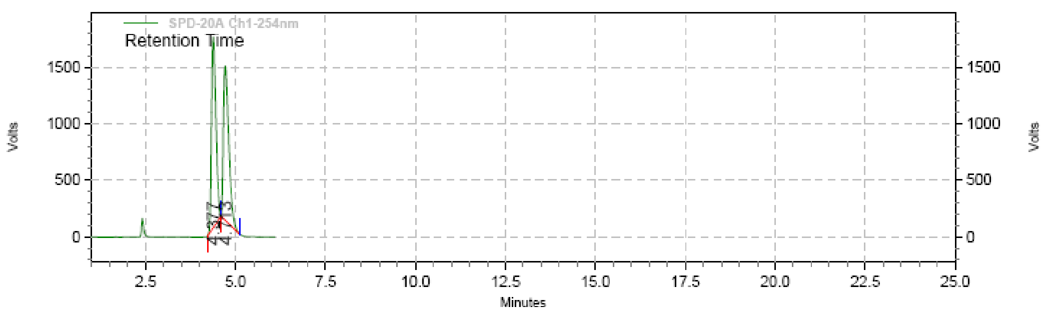


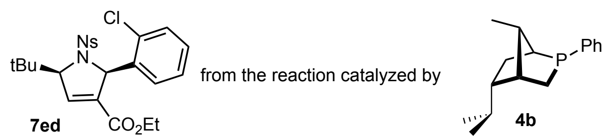
SPD-20A
Ch1-254nm
Results

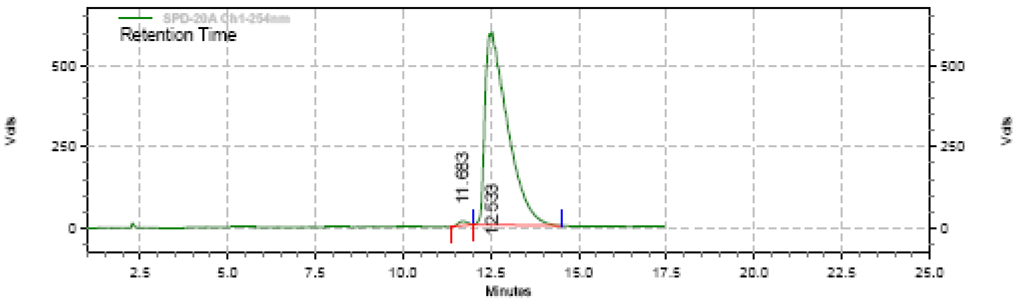
Retention Time	Area	Area %	Height	Height %
4.477	31819255	97.89	2686659	97.29
5.010	684526	2.11	74762	2.71
Totals	32503781	100.00	2761421	100.00



SPD-20A
Ch1-254nm
Results

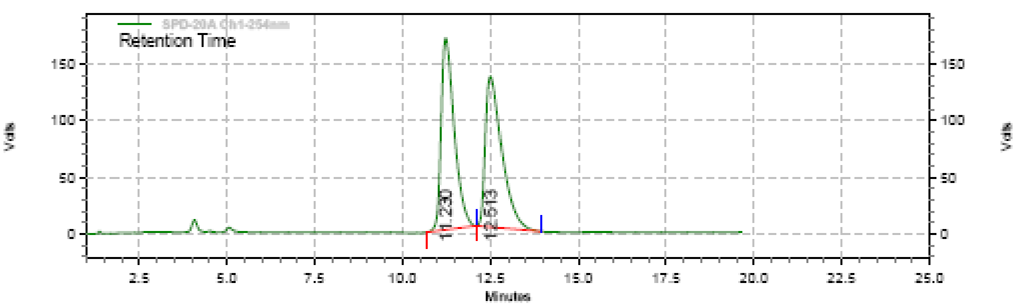
Retention Time	Area	Area %	Height	Height %
4.377	14131165	50.35	1682716	55.27
4.713	13935292	49.65	1361600	44.73
Totals	28066457	100.00	3044316	100.00





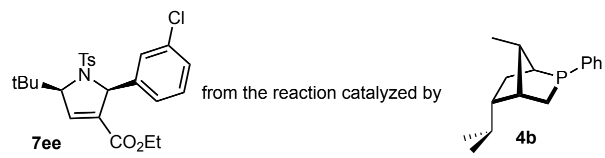
SPD-20A
Ch1-254nm
Results

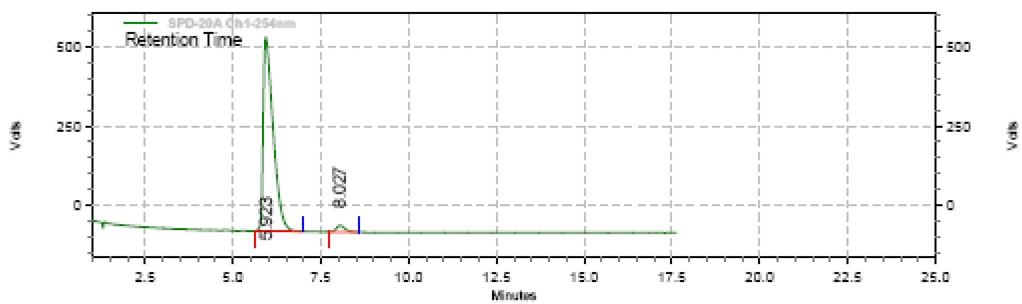
Retention Time	Area	Area %	Height	Height %
11.683	231650	0.88	13562	2.24
12.533	26169097	99.12	591990	97.76
Totals				
	26400747	100.00	605552	100.00



SPD-20A
Ch1-254nm
Results

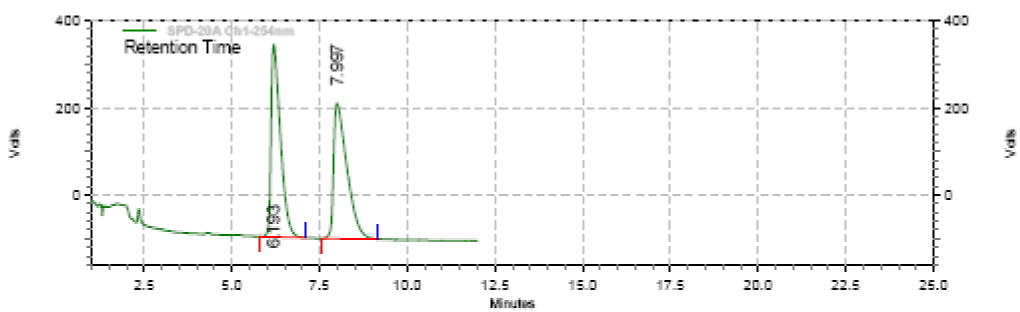
Retention Time	Area	Area %	Height	Height %
11.230	4401168	50.50	169184	55.99
12.513	4313846	49.50	132991	44.01
Totals				
	8715014	100.00	302175	100.00





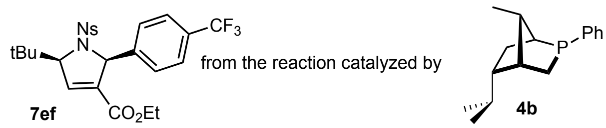
SPD-20A
Ch1-254nm
Results

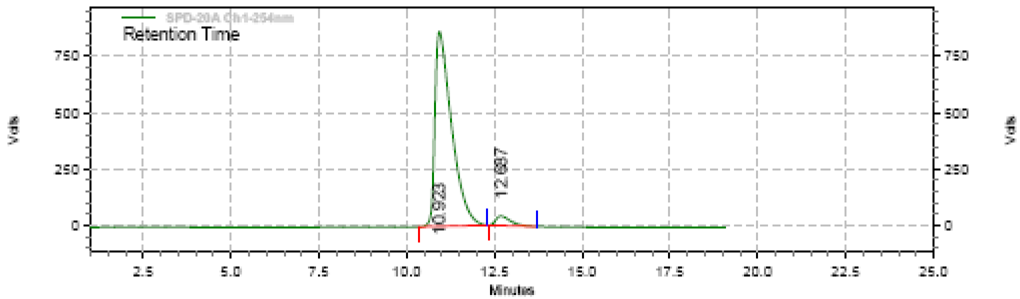
Retention Time	Area	Area %	Height	Height %
5.923	12029945	97.20	609447	96.86
8.027	345949	2.80	19756	3.14
Totals	12375894	100.00	629203	100.00



SPD-20A
Ch1-254nm
Results

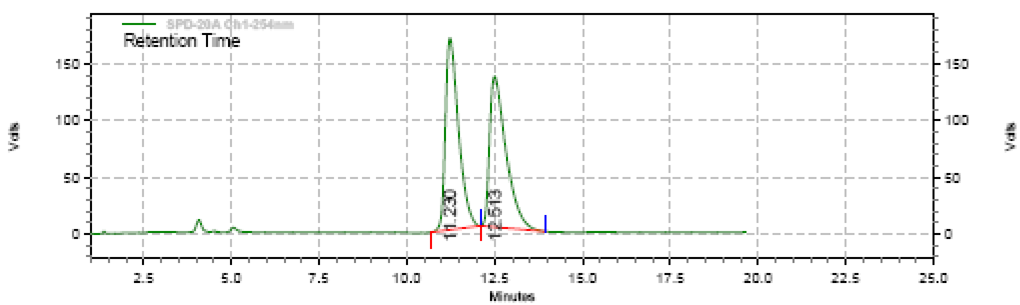
Retention Time	Area	Area %	Height	Height %
6.193	8197320	49.93	440782	58.69
7.997	8219674	50.07	310244	41.31
Totals	16416994	100.00	751026	100.00





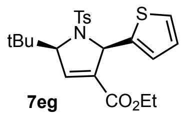
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.923	28610663	95.93	862511	95.34
12.687	1212393	4.07	42111	4.66
Totals	29823056	100.00	904622	100.00

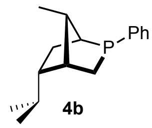


SPD-20A
Ch1-254nm
Results

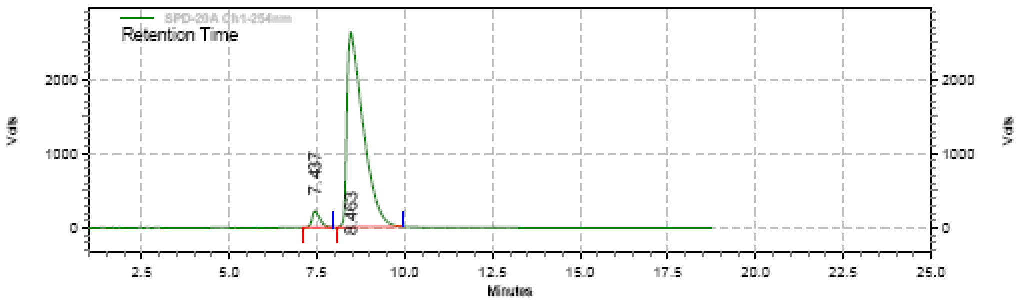
Retention Time	Area	Area %	Height	Height %
11.230	4401168	50.50	169184	55.99
12.513	4313846	49.50	132991	44.01
Totals	8715014	100.00	302175	100.00



7eg from the reaction catalyzed by

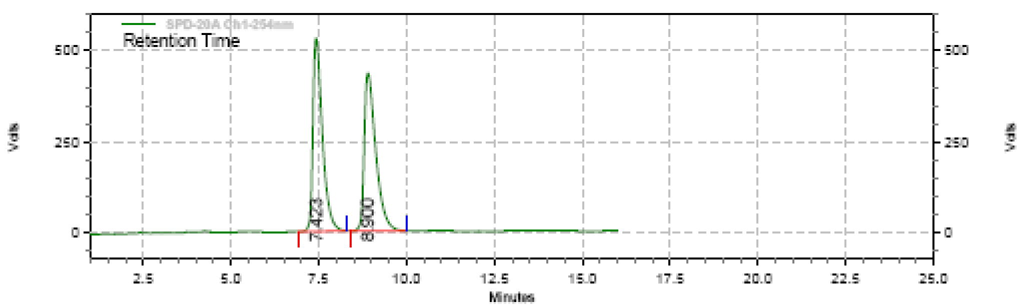


4b



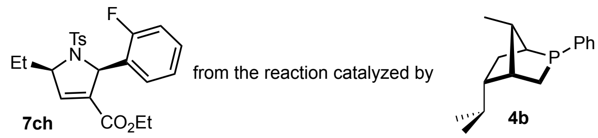
SPD-20A
Ch1-254nm
Results

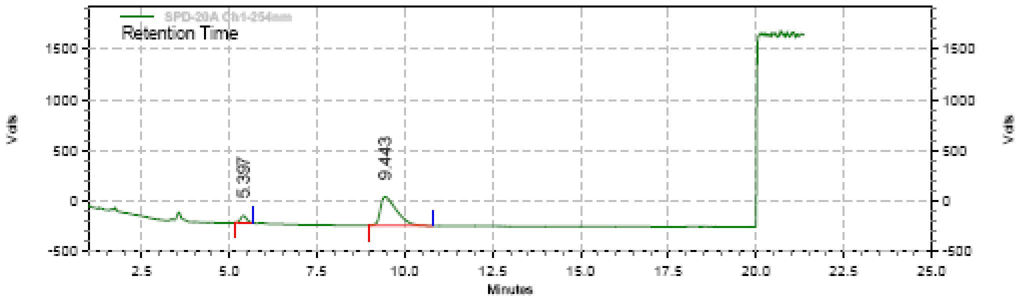
Retention Time	Area	Area %	Height	Height %
7.437	3539450	4.01	220894	7.78
8.463	84712090	95.99	2619906	92.22
Totals	88251540	100.00	2840800	100.00



SPD-20A
Ch1-254nm
Results

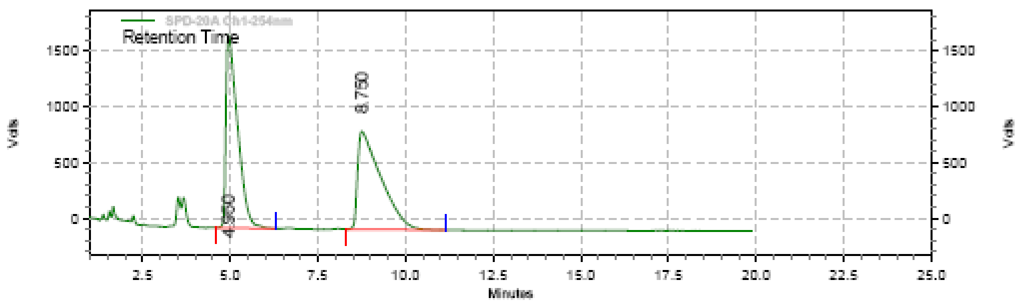
Retention Time	Area	Area %	Height	Height %
7.423	9976100	50.06	530690	55.04
8.900	9951664	49.94	433445	44.96
Totals	19927764	100.00	964135	100.00





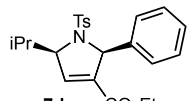
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.397	842451	8.46	70128	19.75
9.443	9113483	91.54	284974	80.25
Totals	9955934	100.00	355102	100.00

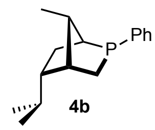


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
4.950	40093741	49.68	1729410	66.43
8.750	40615019	50.32	873905	33.57
Totals	80708760	100.00	2603315	100.00



7da from the reaction catalyzed by



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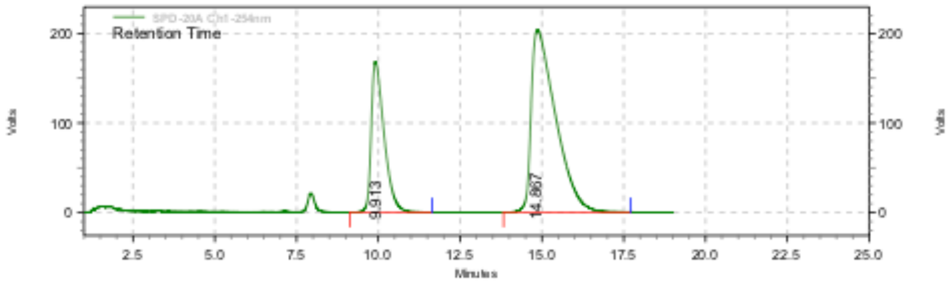
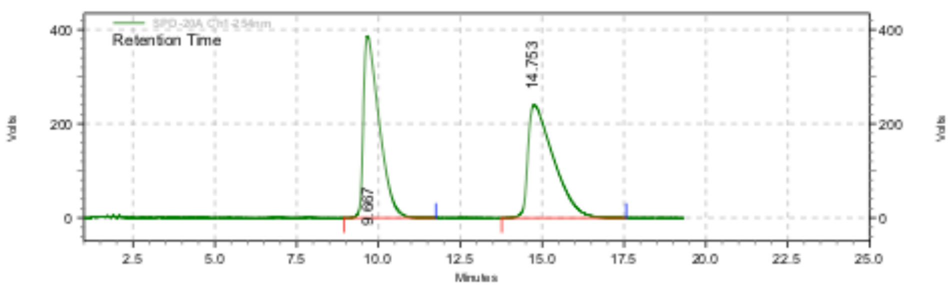


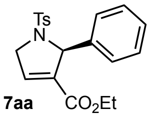
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.913	4621420	30.34	168202	45.21
14.867	10608999	69.66	203832	54.79
Totals	15230419	100.00	372034	100.00

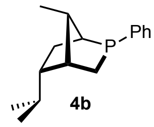


SPD-20A
Ch1-254nm
Results

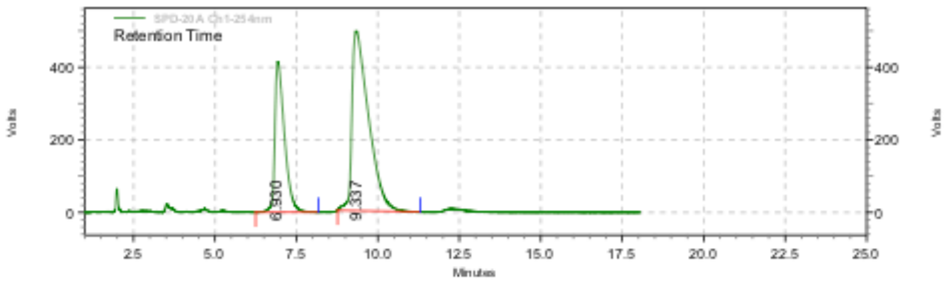
Retention Time	Area	Area %	Height	Height %
9.667	12996234	49.87	387103	61.62
14.753	13063679	50.13	241091	38.38
Totals	26059913	100.00	628194	100.00



7aa from the reaction catalyzed by

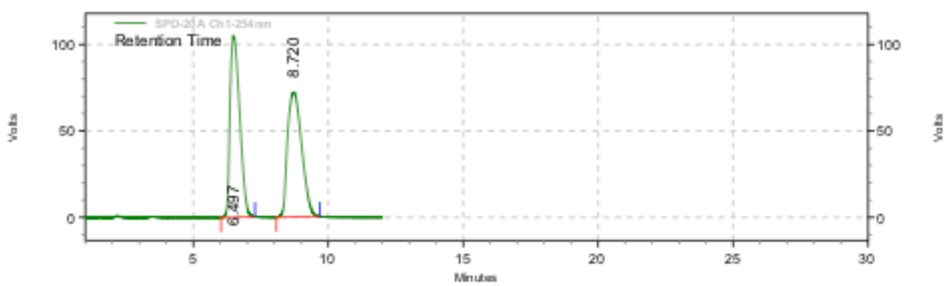


4b



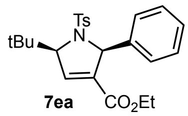
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.930	8507418	32.59	413956	45.51
9.337	17598834	67.41	495606	54.49
Totals	26106252	100.00	909562	100.00

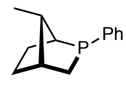


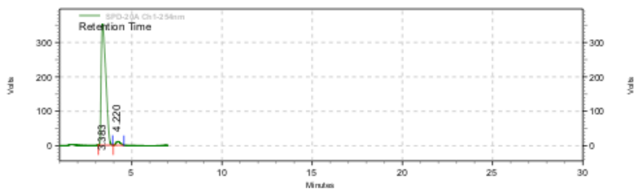
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.497	2618856	50.00	104665	59.26
8.720	2618481	50.00	71946	40.74
Totals	5237337	100.00	176611	100.00



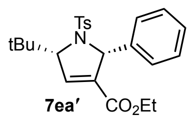
from the reaction catalyzed by



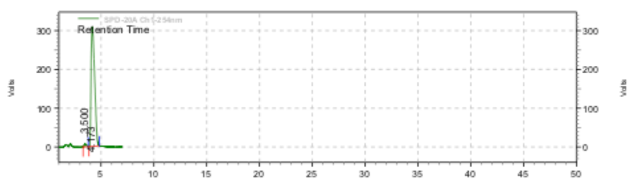


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.383	6198912	97.05	351499	97.10
4.220	188749	2.95	10484	2.90
Totals	6387661	100.00	361983	100.00

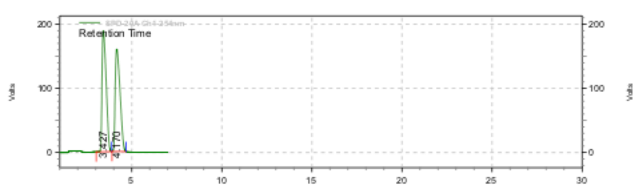


from the reaction catalyzed by



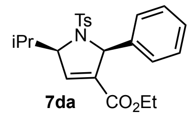
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.500	109508	1.48	7515	2.38
4.173	7268655	98.52	307881	97.62
Totals	7378163	100.00	315396	100.00



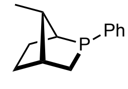
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.427	3014446	50.09	187998	54.04
4.170	3003197	49.91	159891	45.96
Totals	6017643	100.00	347889	100.00

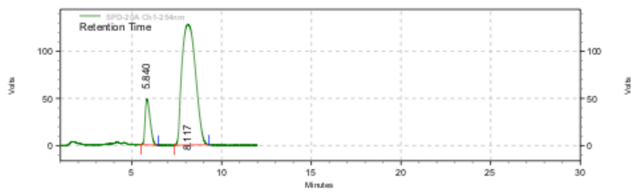


7da

from the reaction catalyzed by

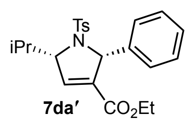


4e



SPD-20A
Ch1-254nm
Results

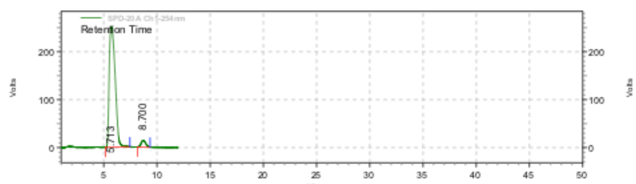
Retention Time	Area	Area %	Height	Height %
5.840	924101	12.03	48153	27.35
8.117	6757407	87.97	127937	72.65
Totals	7681508	100.00	176090	100.00



7da′

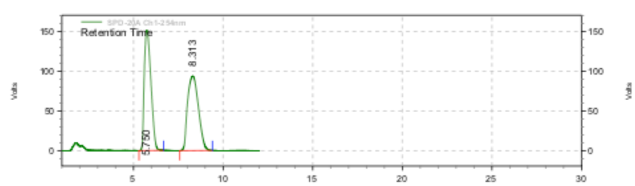
from the reaction catalyzed by

4e′



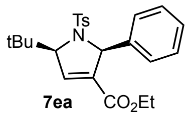
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.713	9808649	95.94	251748	94.70
8.700	415199	4.06	14093	5.30
Totals	10223848	100.00	265841	100.00

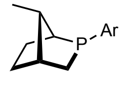


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.750	3923692	49.88	151166	61.78
8.313	3942748	50.12	93536	38.22
Totals	7866440	100.00	244702	100.00



7ea from the reaction catalyzed by



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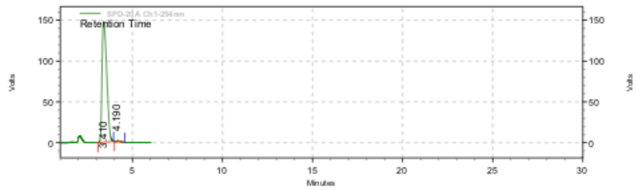
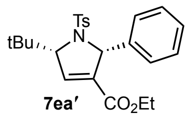
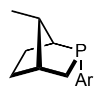


SPD-20A
Ch1-254nm
Results

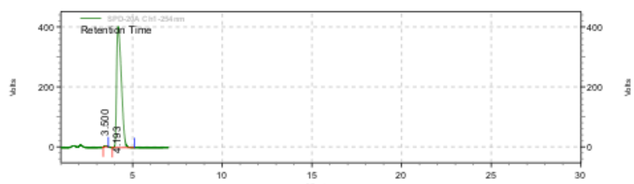
Retention Time	Area	Area %	Height	Height %
3.410	2683633	99.20	147296	99.14
4.190	21684	0.80	1272	0.86
Totals	2705317	100.00	148568	100.00



7ea′ from the reaction catalyzed by

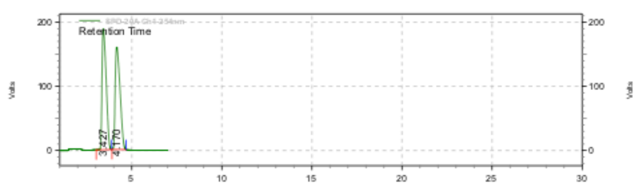


4f′



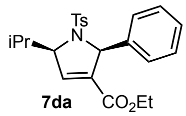
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.500	38664	0.52	3563	0.88
4.193	7382990	99.48	403033	99.12
Totals	7421654	100.00	406596	100.00



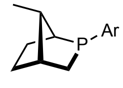
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.427	3014446	50.09	187998	54.04
4.170	3003197	49.91	159891	45.96
Totals	6017643	100.00	347889	100.00



7da

from the reaction catalyzed by



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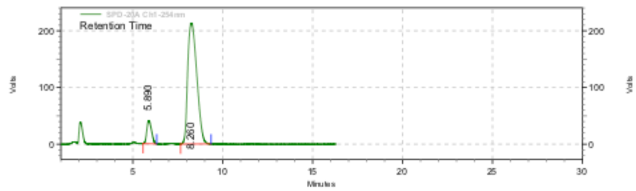
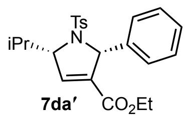


SPD-20A
Ch1-254nm
Results

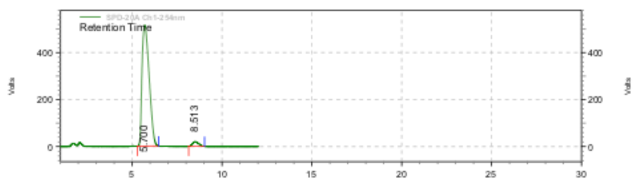
Retention Time	Area	Area %	Height	Height %
5.890	744831	9.03	40403	15.92
8.260	7501981	90.97	213424	84.08
Totals	8246812	100.00	253827	100.00



7da′

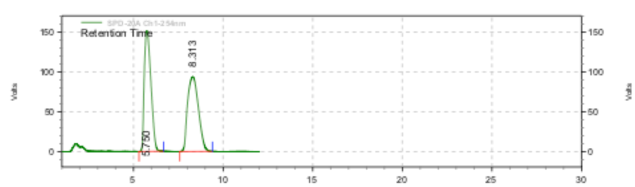
from the reaction catalyzed by

4f′



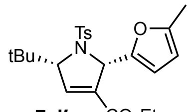
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.700	14227978	96.87	514492	96.42
8.513	459037	3.13	19110	3.58
Totals	14687015	100.00	533602	100.00

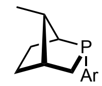


SPD-20A
Ch1-254nm
Results

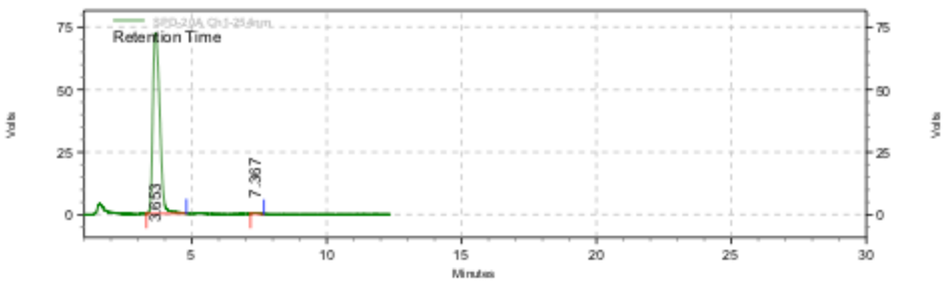
Retention Time	Area	Area %	Height	Height %
5.750	3923692	49.88	151166	61.78
8.313	3942748	50.12	93536	38.22
Totals	7866440	100.00	244702	100.00



7ei′ from the reaction catalyzed by

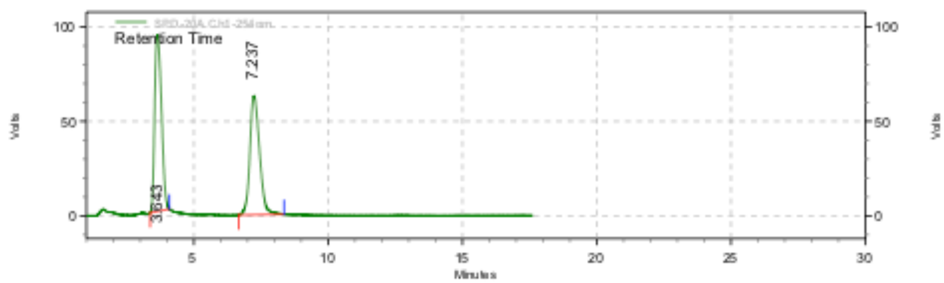


4f′



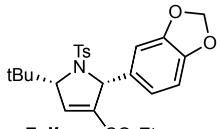
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.653	1293151	99.42	72141	99.39
7.367	7486	0.58	446	0.61
Totals	1300637	100.00	72587	100.00



SPD-20A
Ch1-254nm
Results

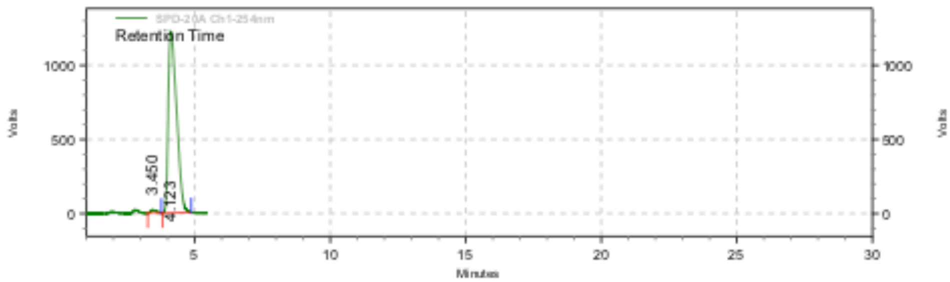
Retention Time	Area	Area %	Height	Height %
3.643	1654361	51.15	93573	59.68
7.237	1580197	48.85	63219	40.32
Totals	3234558	100.00	156792	100.00



7ej′

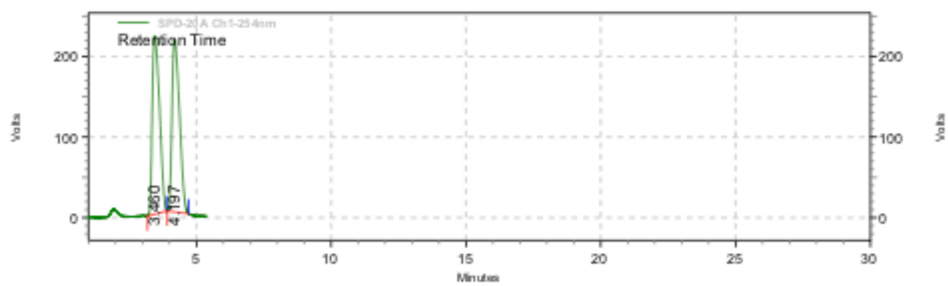
from the reaction catalyzed by

4f′



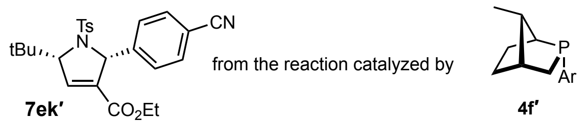
SPD-20A
Ch1-254nm
Results

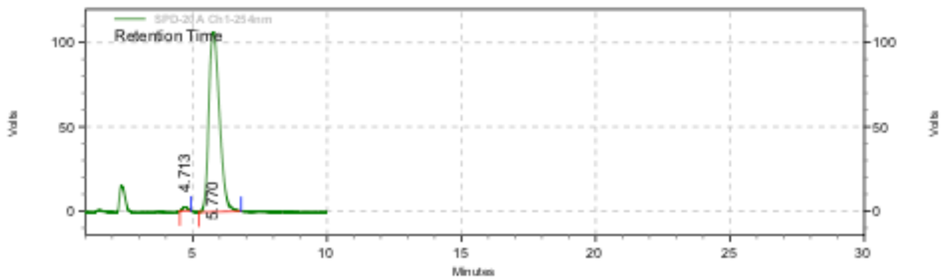
Retention Time	Area	Area %	Height	Height %
3.450	327082	1.23	19989	1.61
4.123	26269502	98.77	1224846	98.39
Totals	26596584	100.00	1244835	100.00



SPD-20A
Ch1-254nm
Results

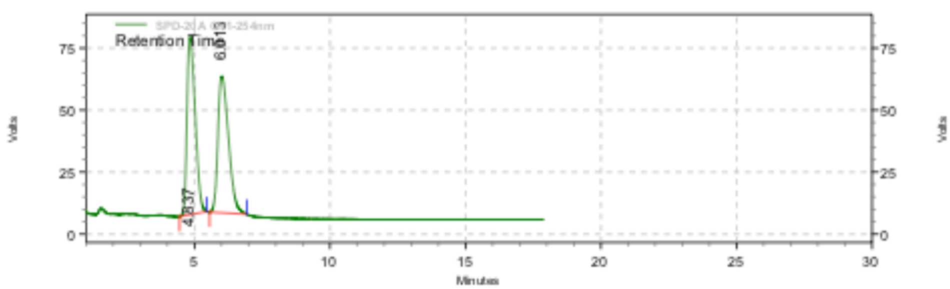
Retention Time	Area	Area %	Height	Height %
3.460	4154710	50.10	221338	50.85
4.197	4137637	49.90	213901	49.15
Totals	8292347	100.00	435239	100.00





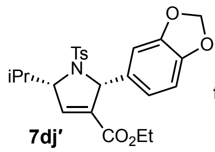
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
4.713	33065	1.11	2234	2.05
5.770	2938637	98.89	106849	97.95
Totals	2971702	100.00	109083	100.00

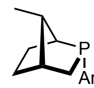


SPD-20A
Ch1-254nm
Results

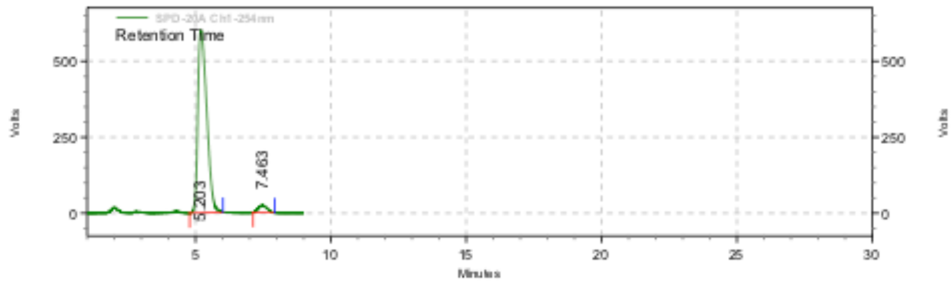
Retention Time	Area	Area %	Height	Height %
4.837	1505679	49.99	71535	56.43
6.013	1506561	50.01	55243	43.57
Totals	3012240	100.00	126778	100.00



7dj' from the reaction catalyzed by

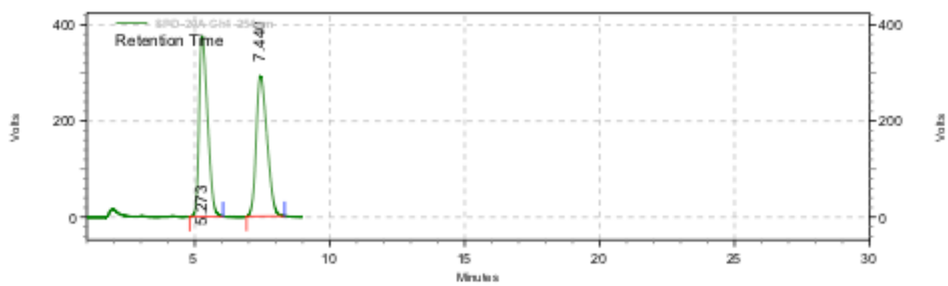


4f'



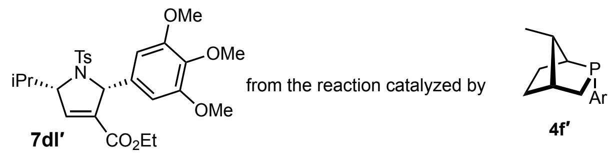
SPD-20A
Ch1-254nm
Results

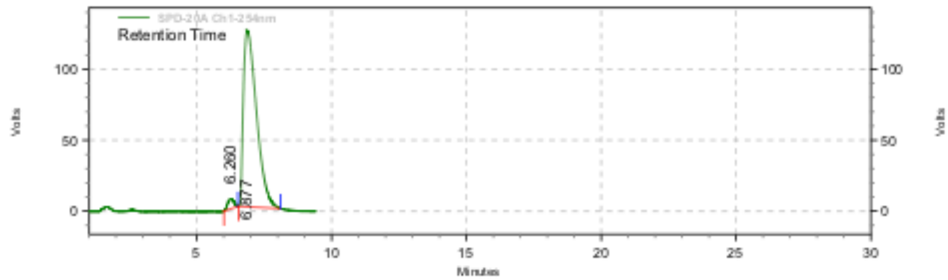
Retention Time	Area	Area %	Height	Height %
5.203	13698617	96.29	599826	96.19
7.463	528220	3.71	23753	3.81
Totals	14226837	100.00	623579	100.00



SPD-20A
Ch1-254nm
Results

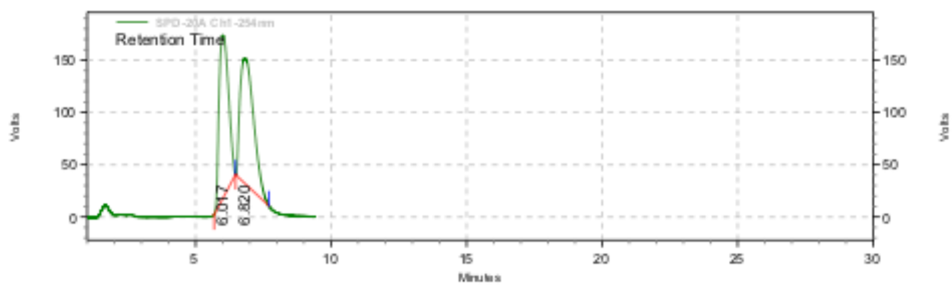
Retention Time	Area	Area %	Height	Height %
5.273	8205105	50.11	376109	56.31
7.440	8170433	49.89	291776	43.69
Totals	16375538	100.00	667885	100.00





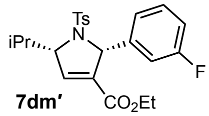
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.260	111244	2.58	6795	5.18
6.877	4208417	97.42	124288	94.82
Totals	4319661	100.00	131083	100.00

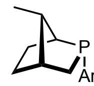


SPD-20A
Ch1-254nm
Results

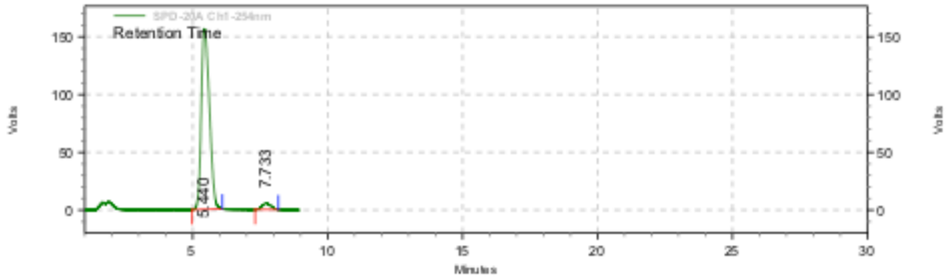
Retention Time	Area	Area %	Height	Height %
6.017	3787159	47.21	155848	56.53
6.820	4233973	52.79	119858	43.47
Totals	8021132	100.00	275706	100.00



7dm′ from the reaction catalyzed by

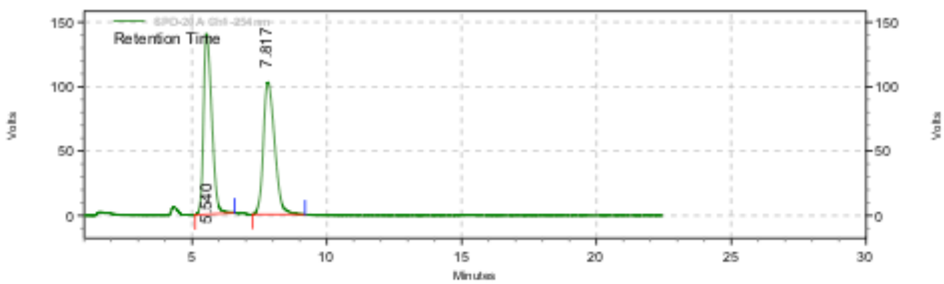


4f′



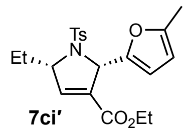
SPD-20A
Ch1-254nm
Results

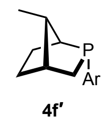
Retention Time	Area	Area %	Height	Height %
5.440	3290787	96.31	156474	96.57
7.733	125924	3.69	5554	3.43
Totals	3416711	100.00	162028	100.00

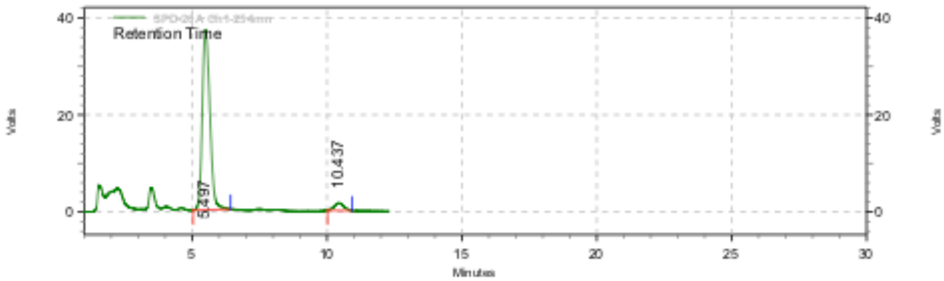


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.540	2970920	49.79	140039	57.70
7.817	2996141	50.21	102683	42.30
Totals	5967061	100.00	242722	100.00

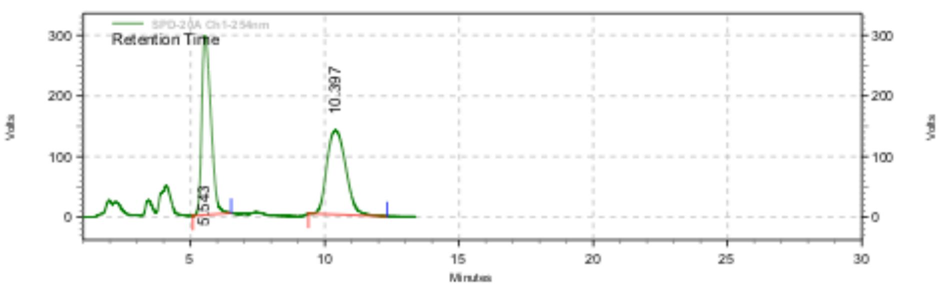






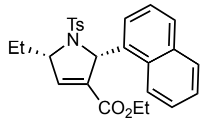
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.497	730756	95.04	37086	96.08
10.437	38125	4.96	1515	3.92
Totals	768881	100.00	38601	100.00



SPD-20A
Ch1-254nm
Results

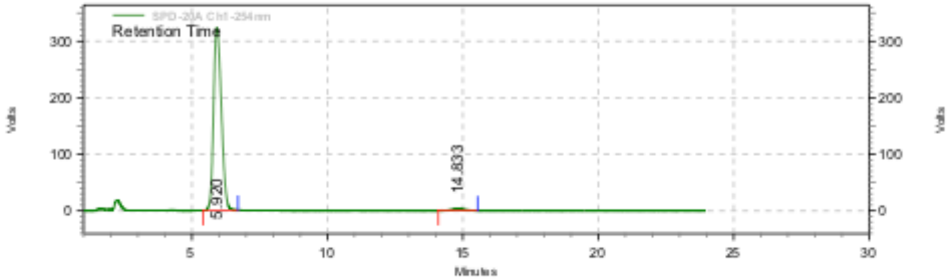
Retention Time	Area	Area %	Height	Height %
5.543	6943028	50.54	294663	67.93
10.397	6795940	49.46	139140	32.07
Totals	13738968	100.00	433803	100.00



7cn′

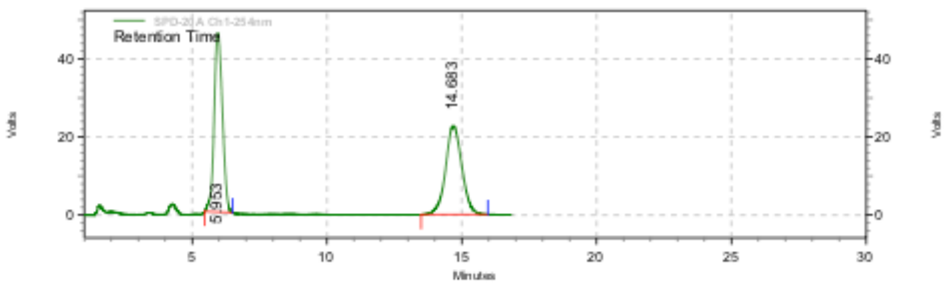
from the reaction catalyzed by

4f′



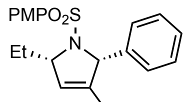
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.920	6516266	98.47	322970	99.16
14.833	101442	1.53	2723	0.84
Totals	6617708	100.00	325693	100.00

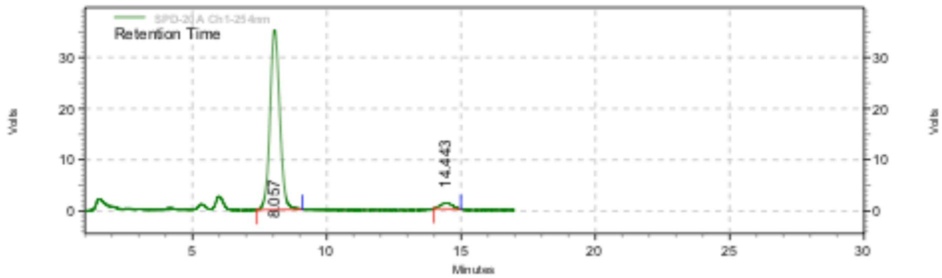


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.953	983983	50.74	45761	66.82
14.683	955173	49.26	22728	33.18
Totals	1939156	100.00	68489	100.00

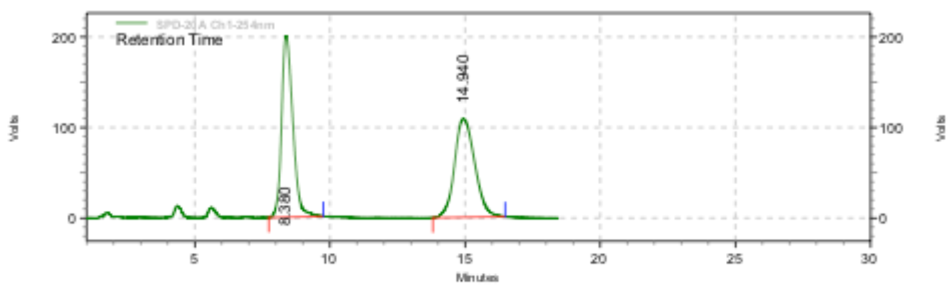


7co′ from the reaction catalyzed by **4f′**



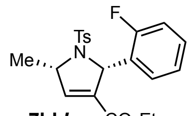
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.057	881487	96.02	35060	96.80
14.443	36492	3.98	1158	3.20
Totals	917979	100.00	36218	100.00



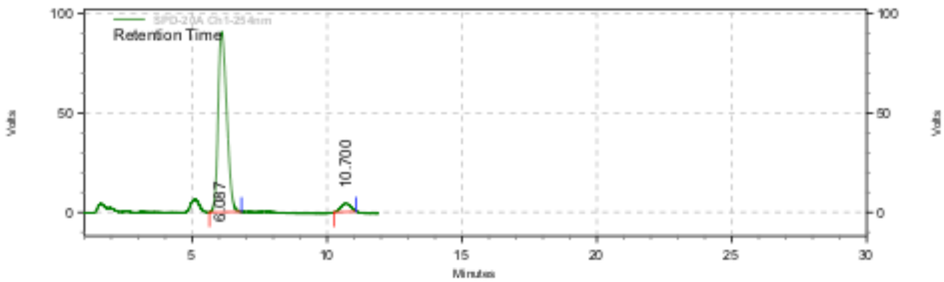
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.380	5801634	50.61	200224	64.73
14.940	5661510	49.39	109082	35.27
Totals	11463144	100.00	309306	100.00



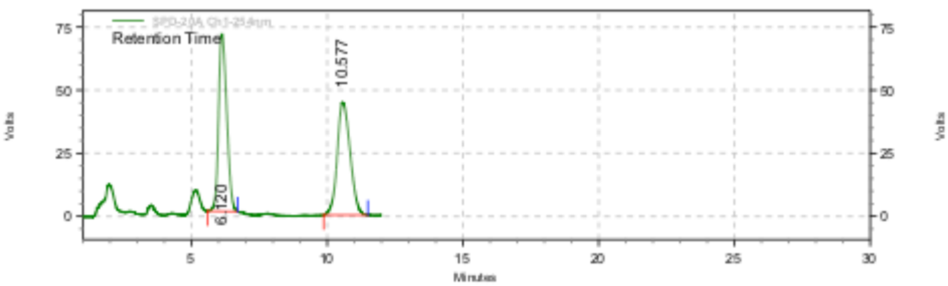
7bh' from the reaction catalyzed by

4f'



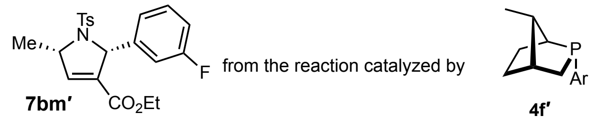
SPD-20A
Ch1-254nm
Results

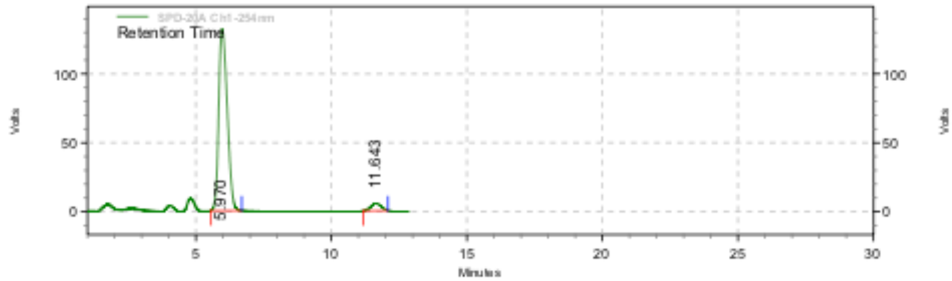
Retention Time	Area	Area %	Height	Height %
6.087	2011991	94.91	90648	95.47
10.700	107838	5.09	4297	4.53
Totals	2119829	100.00	94945	100.00



SPD-20A
Ch1-254nm
Results

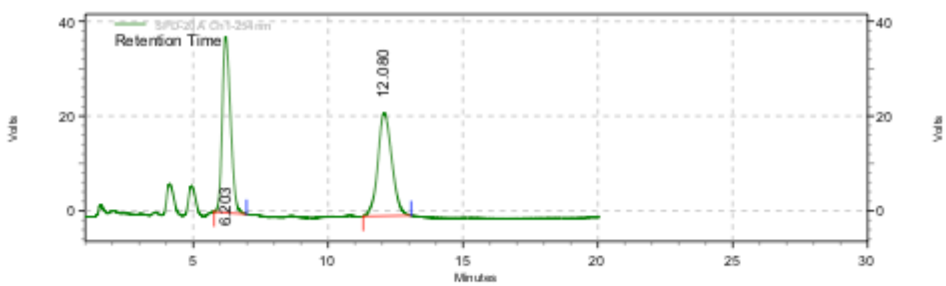
Retention Time	Area	Area %	Height	Height %
6.120	1473238	49.96	70461	61.22
10.577	1475491	50.04	44638	38.78
Totals	2948729	100.00	115099	100.00





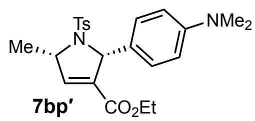
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.970	2888601	95.29	131580	96.14
11.643	142883	4.71	5287	3.86
Totals	3031484	100.00	136867	100.00

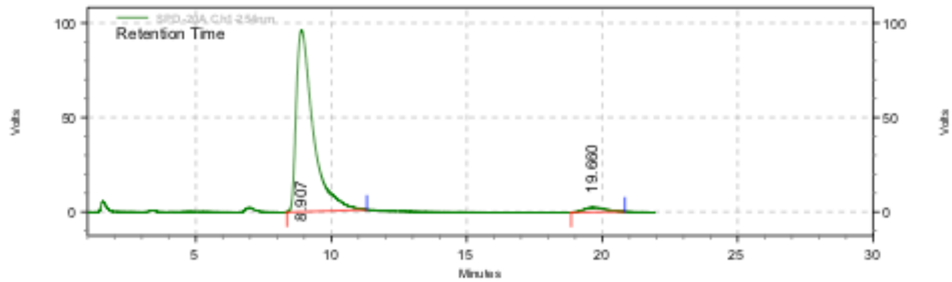


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.203	791048	50.22	37145	63.02
12.080	783962	49.78	21796	36.98
Totals	1575010	100.00	58941	100.00

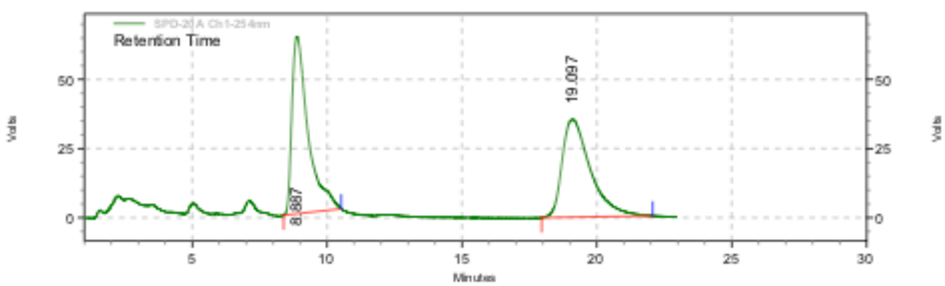


from the reaction catalyzed by



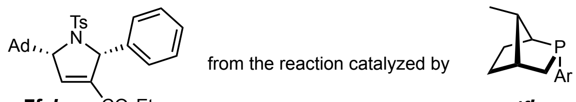
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.907	4170662	96.82	96008	97.51
19.660	137008	3.18	2451	2.49
Totals	4307670	100.00	98459	100.00

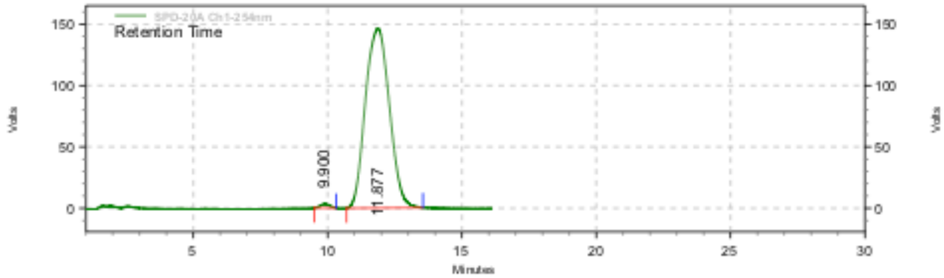


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
8.887	2683893	50.94	64126	64.40
19.097	2584768	49.06	35441	35.60
Totals	5268661	100.00	99567	100.00

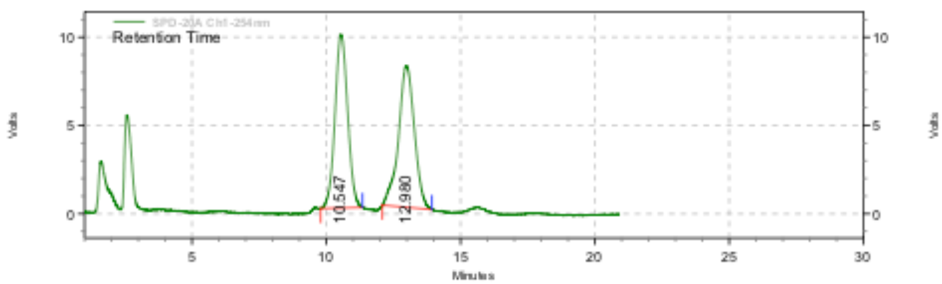


7fa′ from the reaction catalyzed by **4f′**



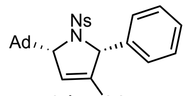
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.900	83728	0.91	3267	2.18
11.877	9071094	99.09	146340	97.82
Totals	9154822	100.00	149607	100.00



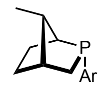
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
10.547	323233	49.42	9831	55.09
12.980	330792	50.58	8015	44.91
Totals	654025	100.00	17846	100.00

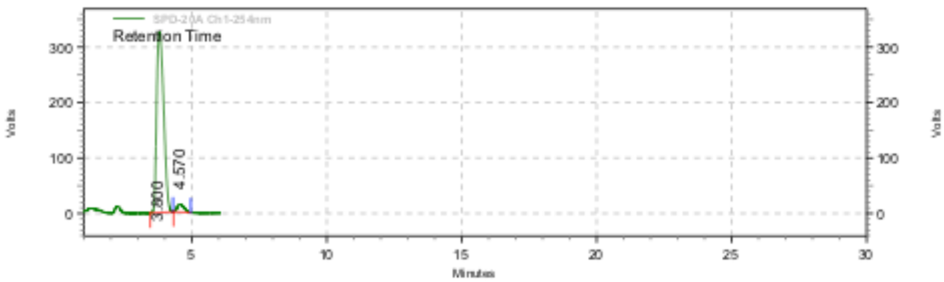


7fc′

from the reaction catalyzed by

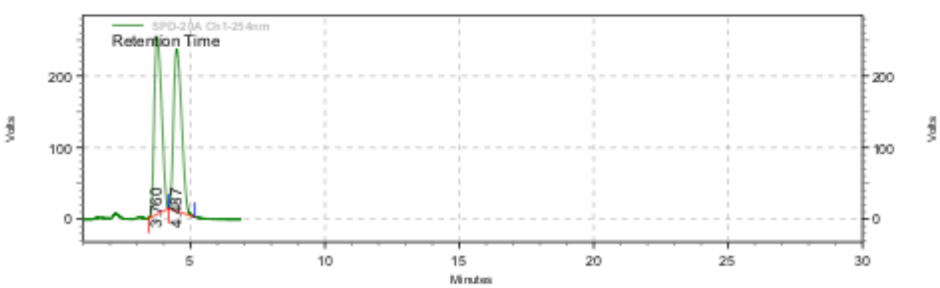


4f′



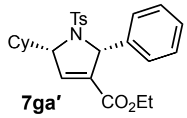
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.800	5921427	95.97	326938	95.88
4.570	248457	4.03	14034	4.12
Totals	6169884	100.00	340972	100.00



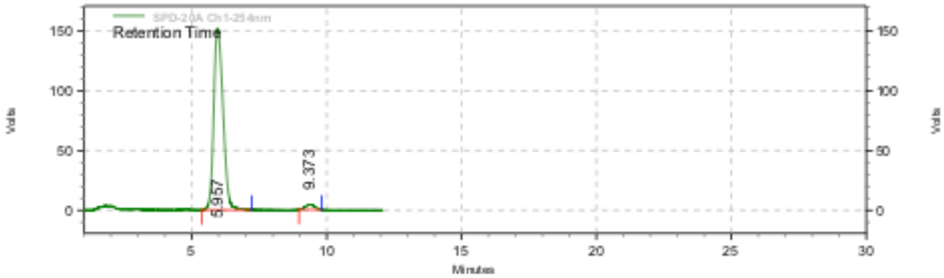
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
3.760	4718386	49.99	246267	52.18
4.487	4719521	50.01	225714	47.82
Totals	9437907	100.00	471981	100.00



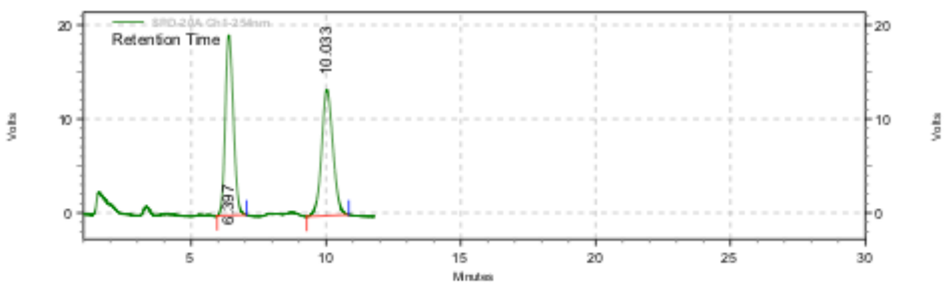
from the reaction catalyzed by

4f′



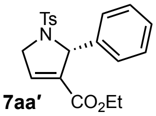
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
5.957	3657089	97.19	151877	97.31
9.373	105851	2.81	4191	2.69
Totals	3762940	100.00	156068	100.00



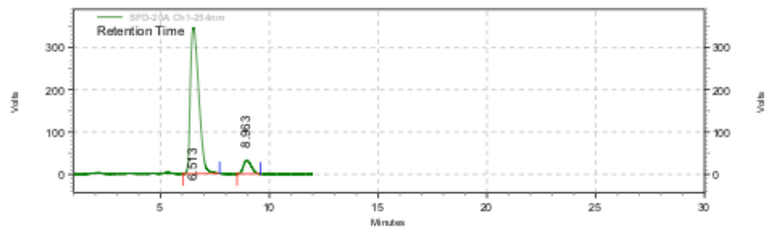
SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.397	401445	50.55	19222	58.99
10.033	392659	49.45	13361	41.01
Totals	794104	100.00	32583	100.00



7aa′ from the reaction catalyzed by

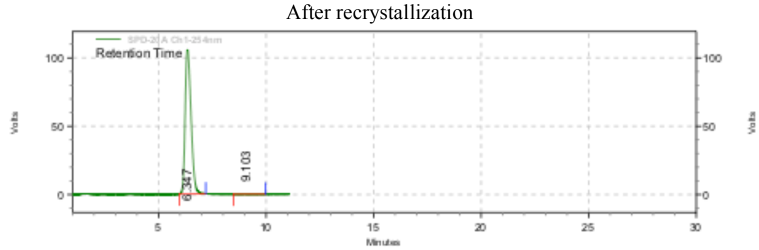
4f′



SPD-20A
Ch1-254nm
Results

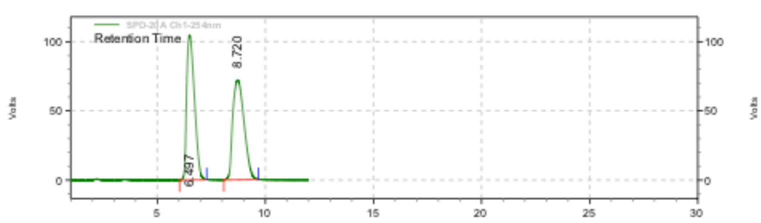
Retention Time	Area	Area %	Height	Height %
6.513	9244532	91.74	345295	91.34
8.963	832089	8.26	32727	8.66
Totals	10076621	100.00	378022	100.00

After recrystallization



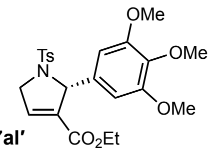
SPD-20A
Ch1-254nm
Results

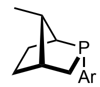
Retention Time	Area	Area %	Height	Height %
6.347	2016379	99.82	105699	99.94
9.103	3711	0.18	66	0.06
Totals	2020090	100.00	105765	100.00

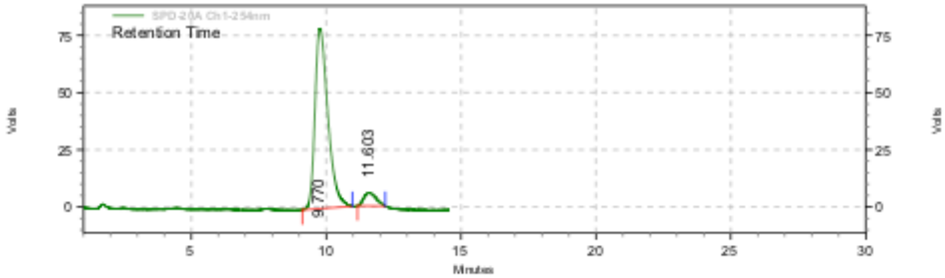


SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
6.497	2618856	50.00	104665	59.26
8.720	2618481	50.00	71946	40.74
Totals	5237337	100.00	176611	100.00

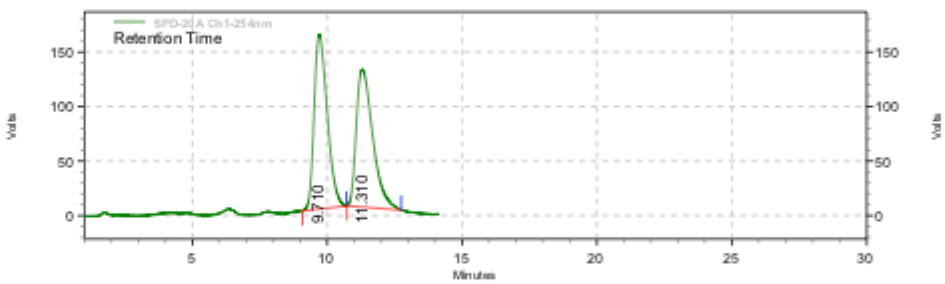


7al′ from the reaction catalyzed by  4f′



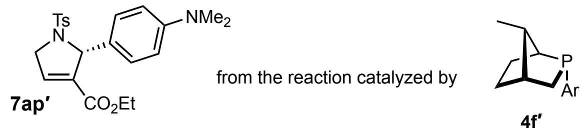
SPD-20A
Ch1-254nm
Results

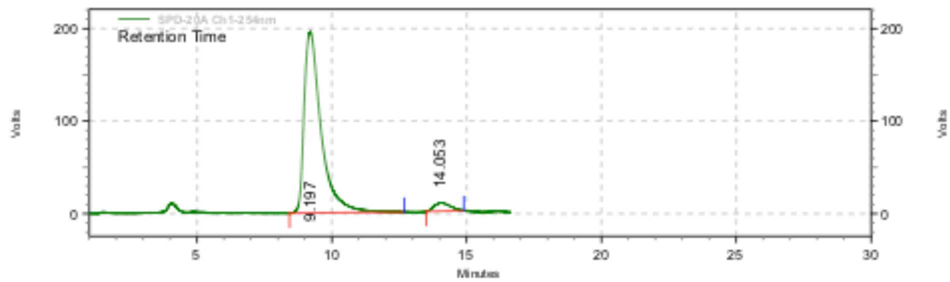
Retention Time	Area	Area %	Height	Height %
9.770	2624074	93.46	78767	93.16
11.603	183629	6.54	5779	6.84
Totals	2807703	100.00	84546	100.00



SPD-20A
Ch1-254nm
Results

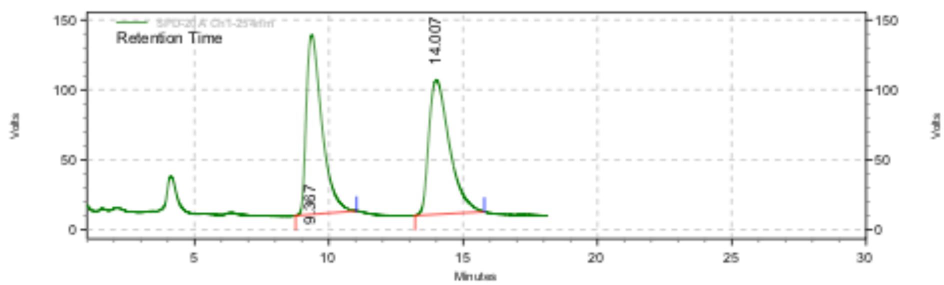
Retention Time	Area	Area %	Height	Height %
9.710	5430661	50.35	160058	55.88
11.310	5354979	49.65	126356	44.12
Totals	10785640	100.00	286414	100.00





SPD-20A
Ch1-254nm
Results

Retention Time	Area	Area %	Height	Height %
9.197	8573443	95.85	195763	95.64
14.053	371576	4.15	8923	4.36
Totals	8945019	100.00	204686	100.00



SPD-20A
Ch1-254nm
Results

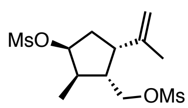
Retention Time	Area	Area %	Height	Height %
9.367	5188678	50.25	128350	57.14
14.007	5136133	49.75	96290	42.86
Totals	10324811	100.00	224640	100.00

5. References

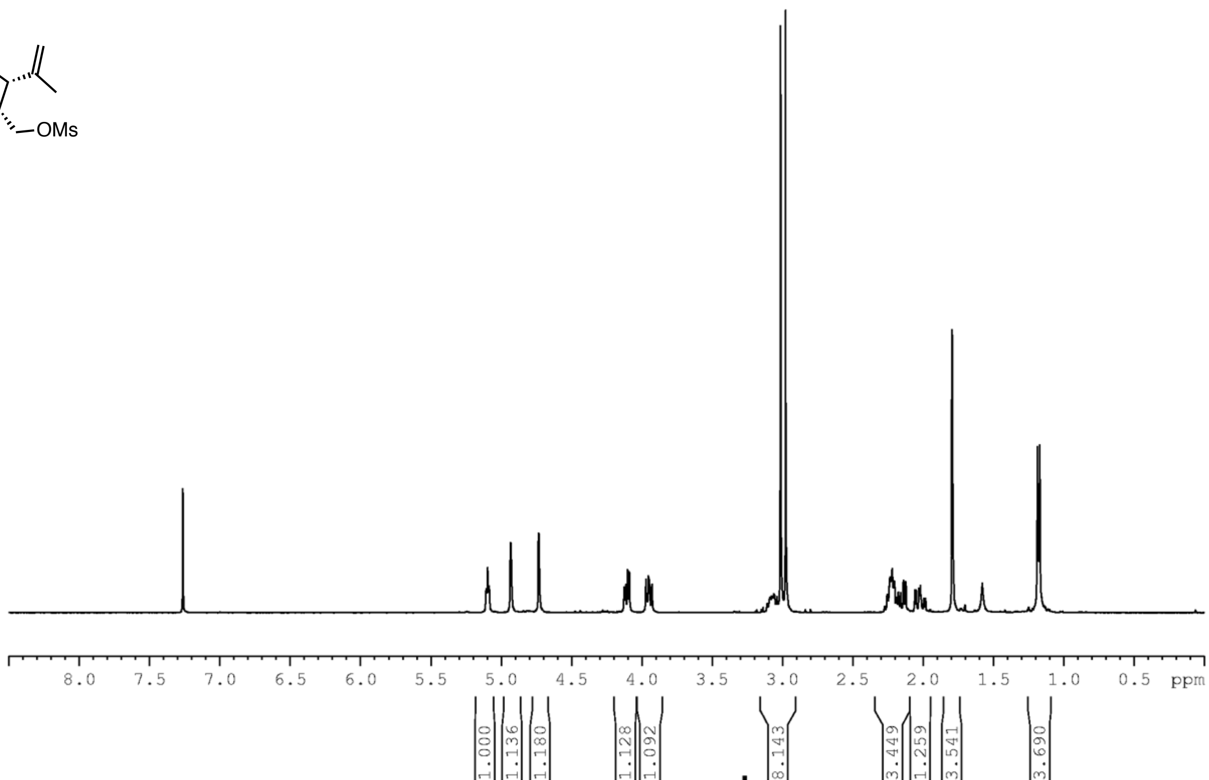
(1) Yang, H.; Gao, Y.; Qiao, X.; Xie, L.; Xu, X. Concise Total Synthesis of (–)-8-Epigrosheimin. *Org. Lett.* **2011**, *13*, 3670–3673.

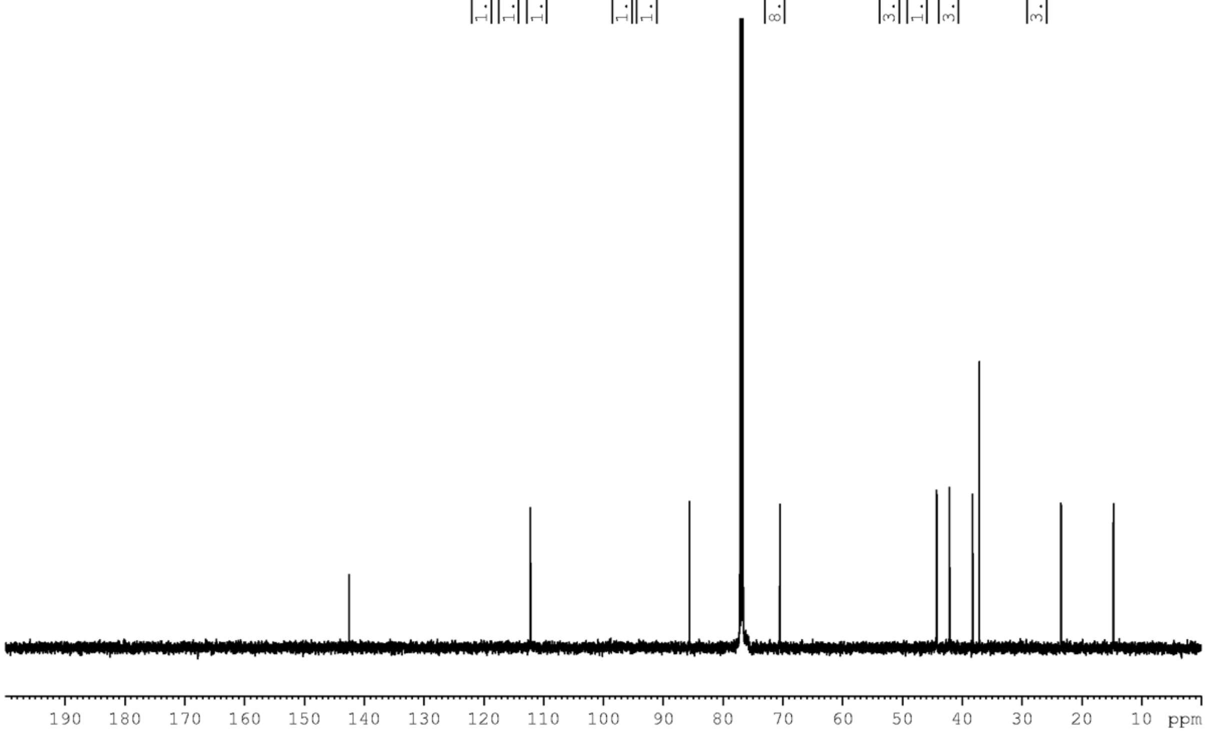
(2) (a) Xu, Z.; Lu, X. A Novel [3+2] Cycloaddition Approach to Nitrogen Heterocycles via Phosphine-Catalyzed Reactions of 2,3-Butadienoates or 2-Butynoates and Dimethyl Acetylenedicarboxylate with Imines: A Convenient Synthesis of Pentabromopseudilin. *J. Org. Chem.* **1998**, *63*, 5031–5041. (b) Zhu, X.; Henry, C. E.; Kwon, O. A Highly Diastereoselective Synthesis of 3-Carbethoxy-2,5-disubstituted-3-pyrrolines by Phosphine Catalysis. *Tetrahedron* **2005**, *61*, 6276–6282. (c) Zhao, G.; Shi, M. Aza-Baylis–Hillman Reactions of *N*-Tosylated Aldimines with Activated Allenes and Alkynes in the Presence of Various Lewis Base Promoters. *J. Org. Chem.* **2005**, *70*, 9975–9984. (d) Tang, X.; Zhang, B.; He, Z.; Gao, R.; He, Z. 1,3,5-Triaza-7-phosphaadamantane (PTA): A Practical and Versatile Nucleophilic Phosphine Organocatalyst. *Adv. Synth. Catal.* **2007**, *349*, 2007–2017. (e) Zheng, S.; Lu, X. A Phosphine-Catalyzed [3 + 2] Annulation Reaction of Modified Allylic Compounds and *N*-Tosylimines. *Org. Lett.* **2008**, *10*, 4481–4484. (f) Watanabe, M.; Fiji, H. D.; Guo, L.; Chang, L.; Kinderman, S. S.; Slamon, D. J.; Kwon, O. Tamanoi, F. Inhibitors of Protein Geranylgeranyltransferase I and Rab Geranylgeranyltransferase Identified from a Library of Allenoate-derived Compounds. *J. Biol. Chem.* **2008**, *283*, 9571–9579. (g) Fang, Y.; Jacobsen, E. N. Cooperative, Highly Enantioselective Phosphinothiourea Catalysis of Imine–Allene [3 + 2] Cycloadditions. *J. Am. Chem. Soc.* **2008**, *130*, 5660–5661. (h) Henry, C. E.; Xu, Q.; Fan, Y. C.; Martin, T. J.; Belding, L.; Dudding, T.; Kwon, O. Hydroxyproline-Derived Pseudoenantiomeric [2.2.1] Bicyclic Phosphines: Asymmetric Synthesis of (+)- and (–)-Pyrrolines. *J. Am. Chem. Soc.* **2014**, *136*, 11890–11893.

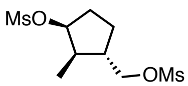
6. Copies of ^{1}H, ^{13}C, and ^{31}P NMR Spectra



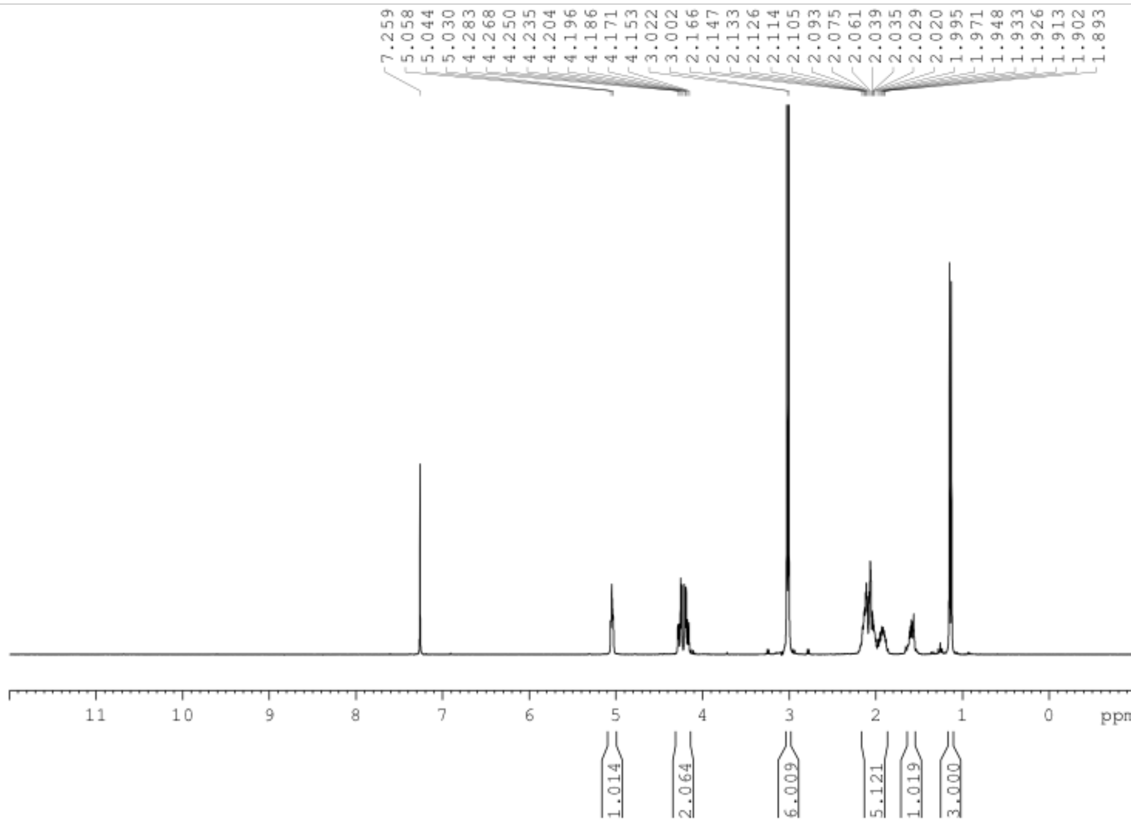
2






MsO
OMs

2′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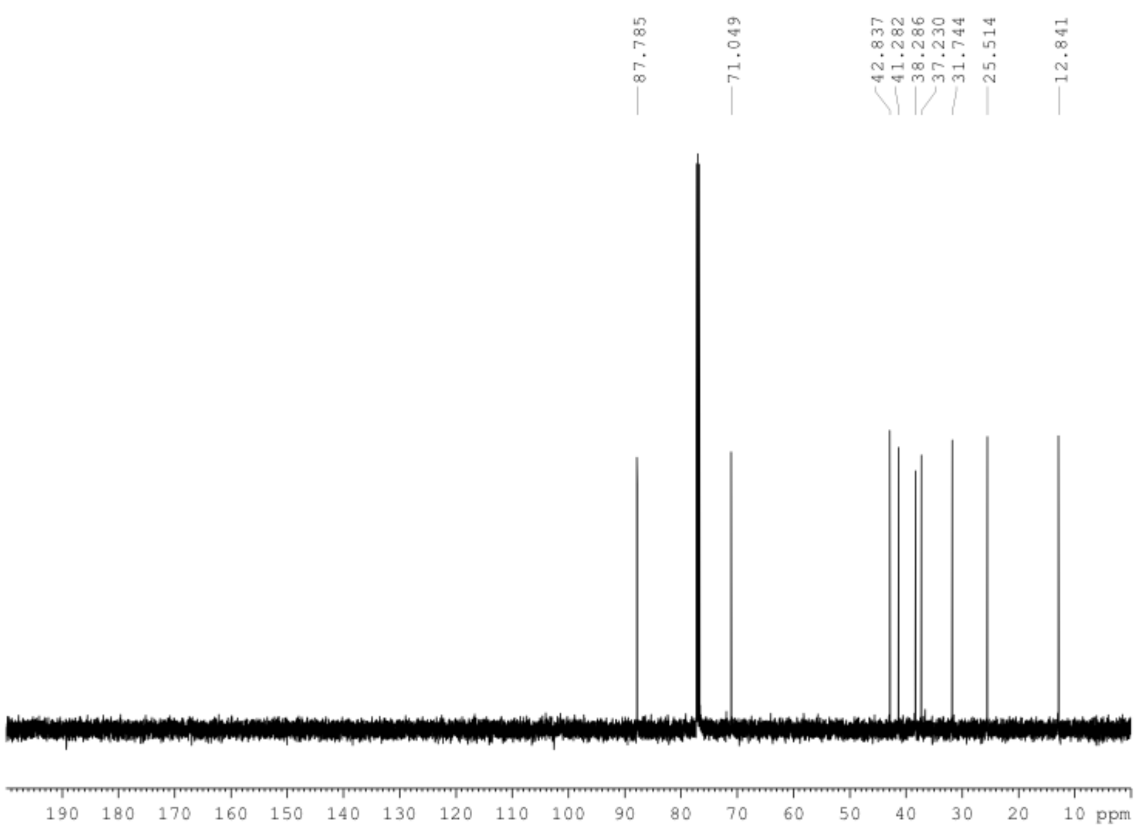
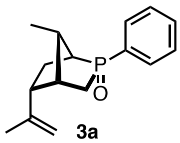
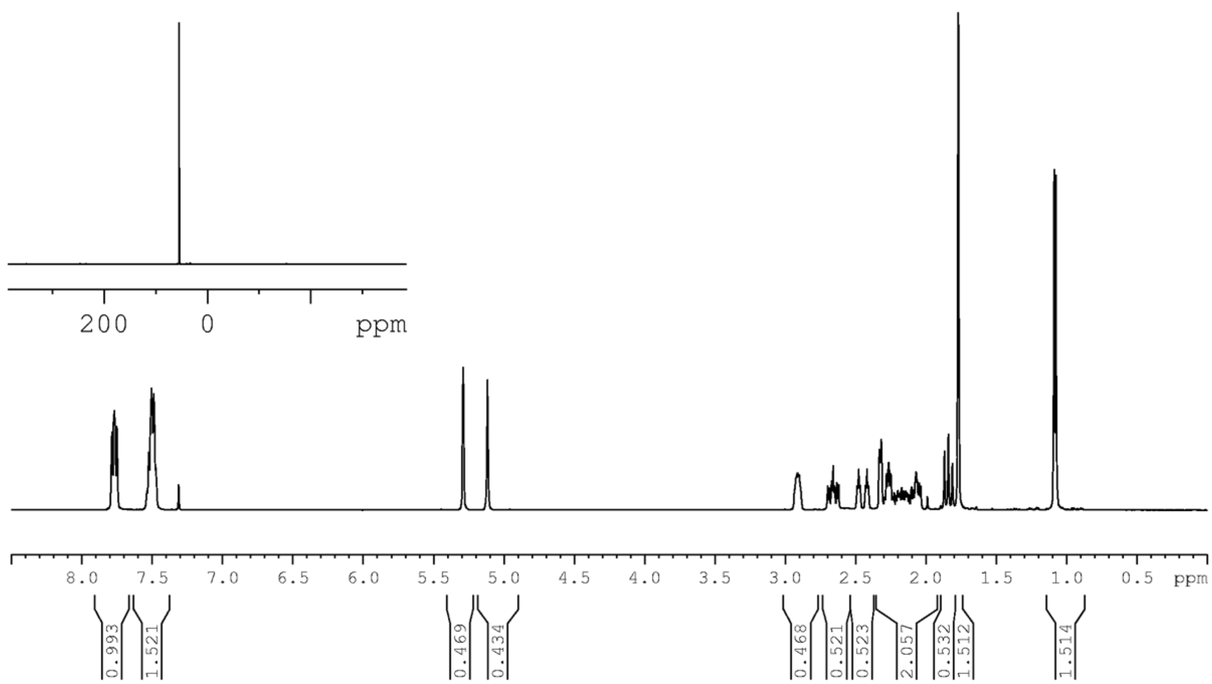
5.058
5.044
5.030
4.283
4.268
4.250
4.235
4.204
4.196
4.186
4.171
4.153
3.022
3.002
2.166
2.147
2.133
2.126
2.114
2.105
2.093
2.075
2.061
2.039
2.035
2.029
2.020
1.995
1.971
1.948
1.933
1.926
1.913
1.902
1.893
11 10 9 8 7 6 5 4 3 2 1 0 ppm
1.014
2.064
6.009
5.121
1.019
3.000


87.785
71.049
42.837
41.282
38.286
37.230
31.744
25.514
12.841
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


P
O

3a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0
ppm
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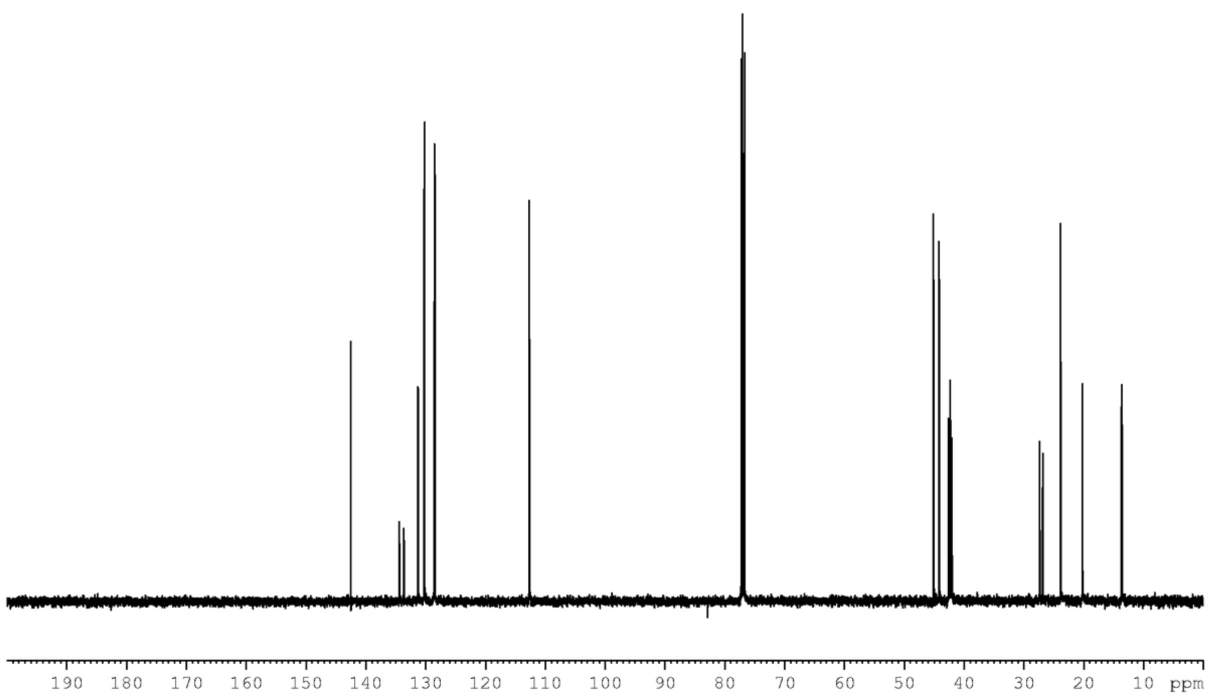
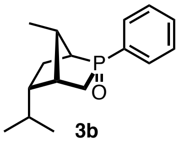
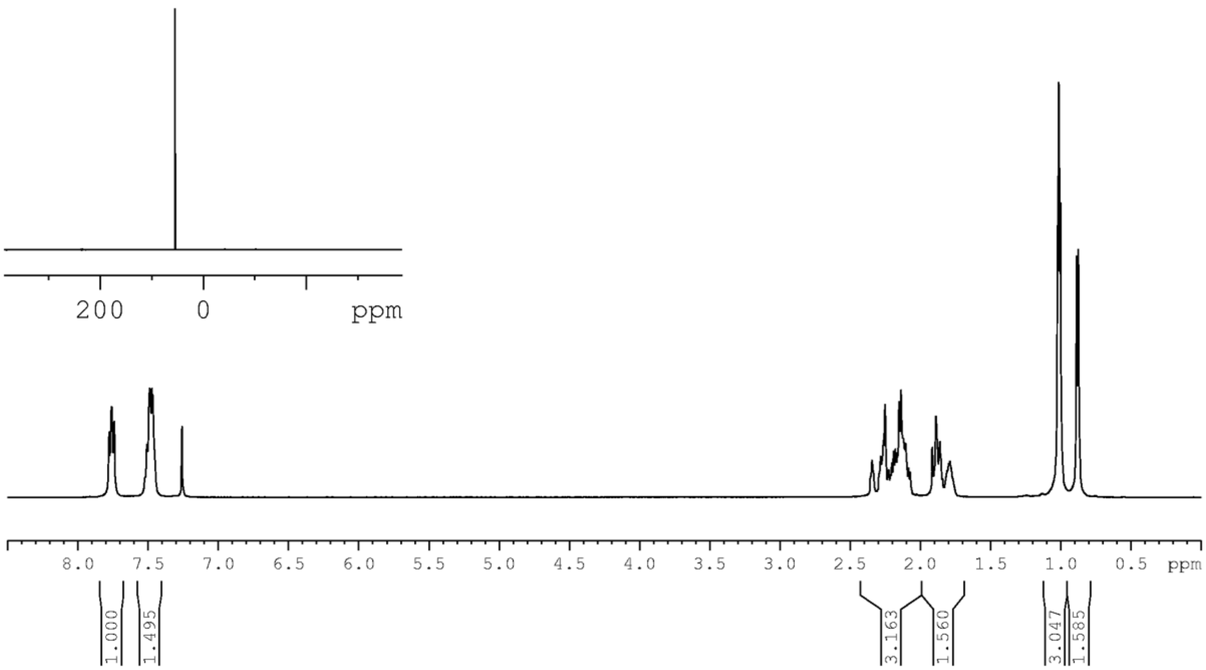
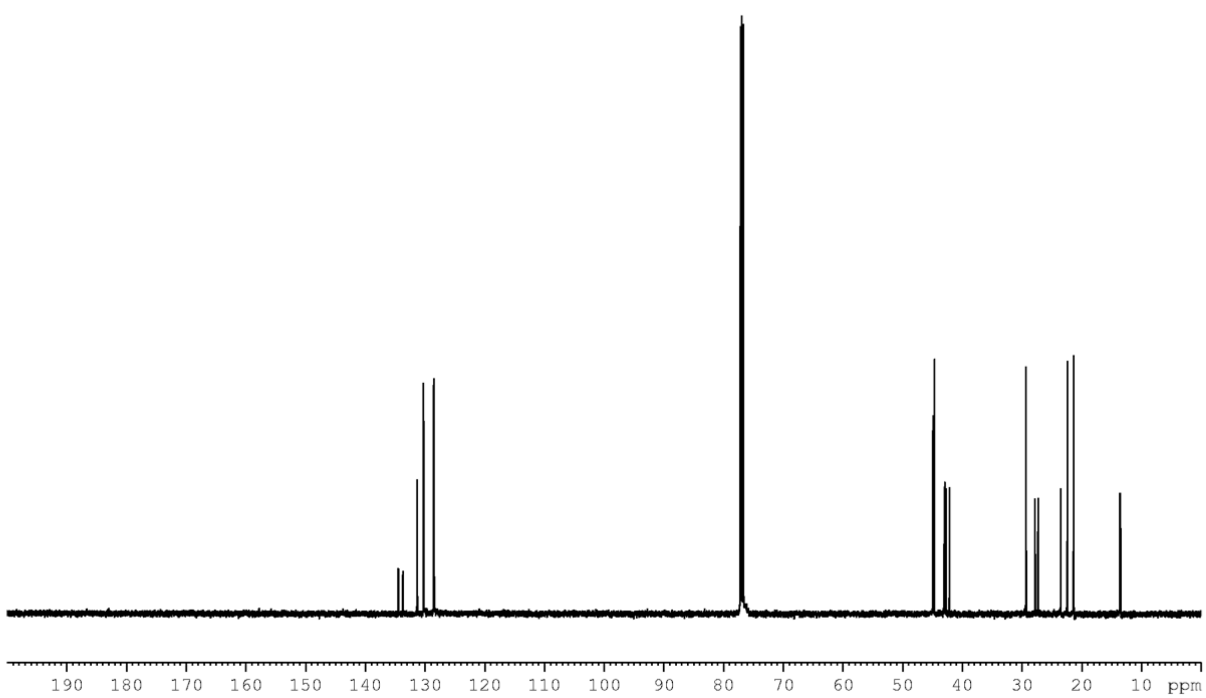
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
0.993
1.521
0.469
0.434
0.468
0.521
0.523
2.057
0.532
1.512
1.514

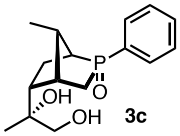

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



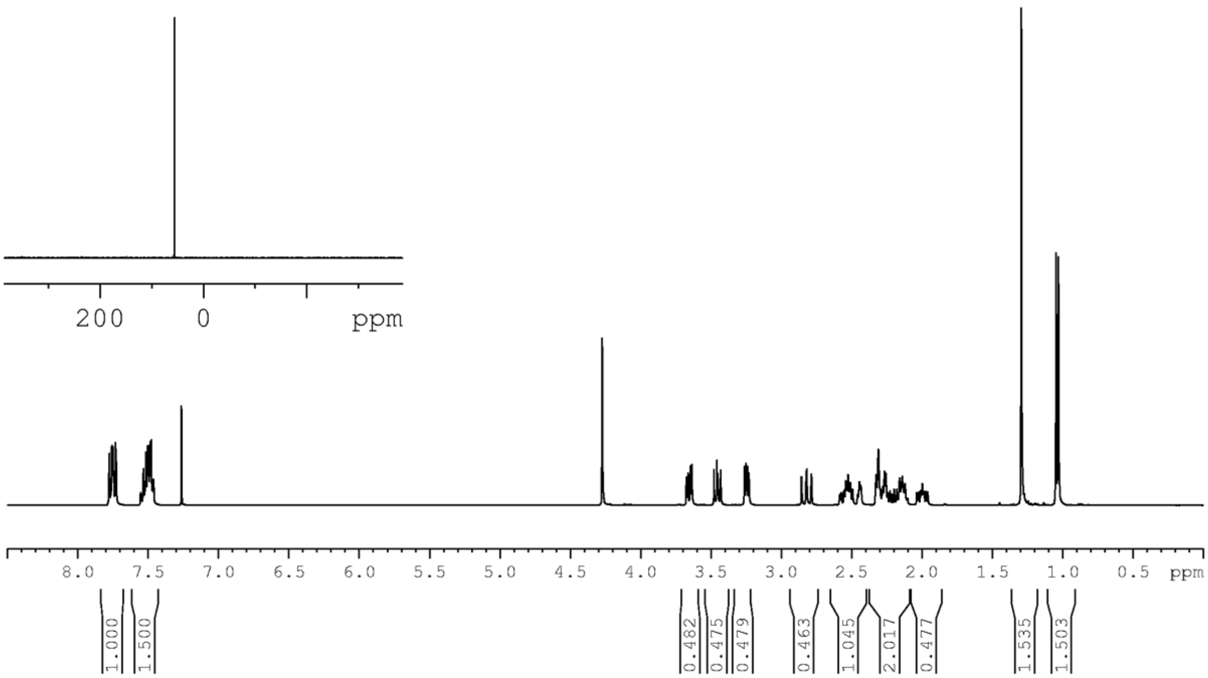
3b

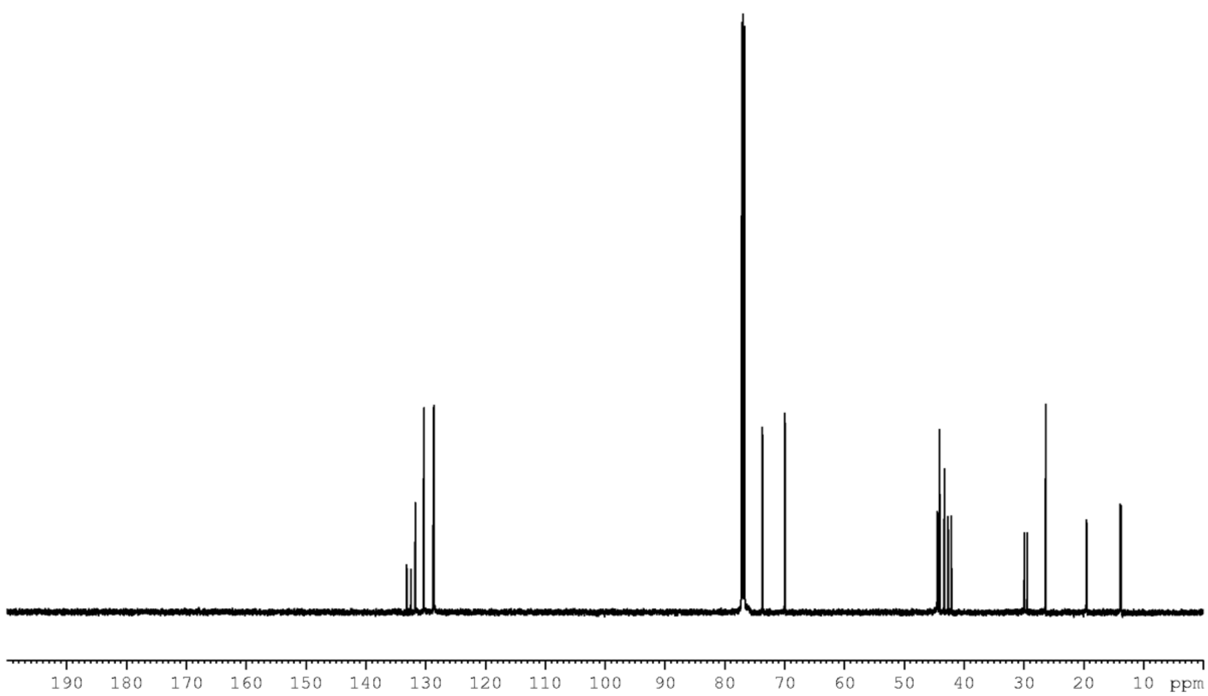

200
0
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.495
3.163
1.560
3.047
1.585

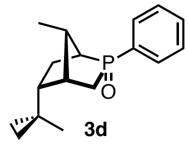

190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



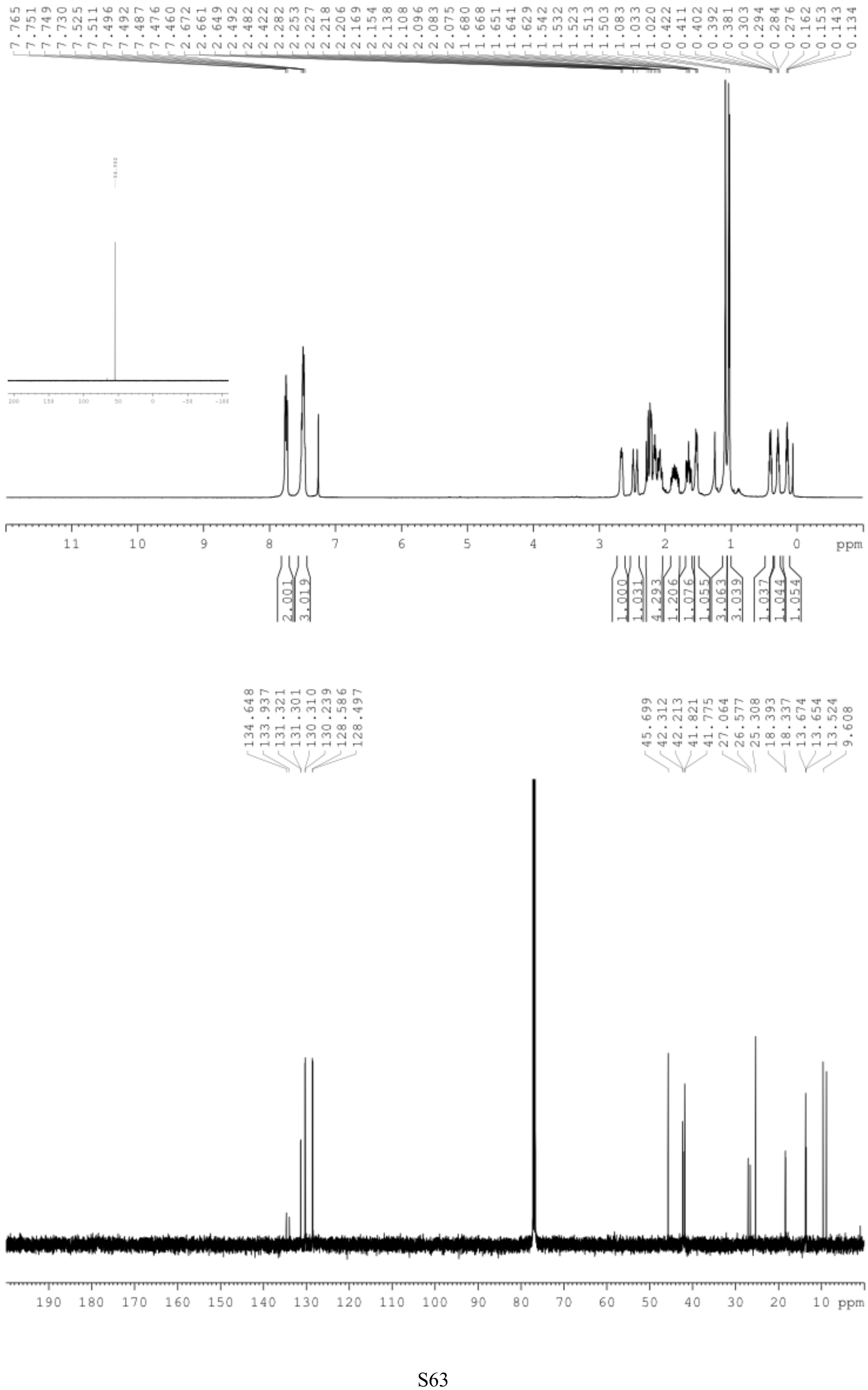
3c

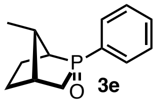




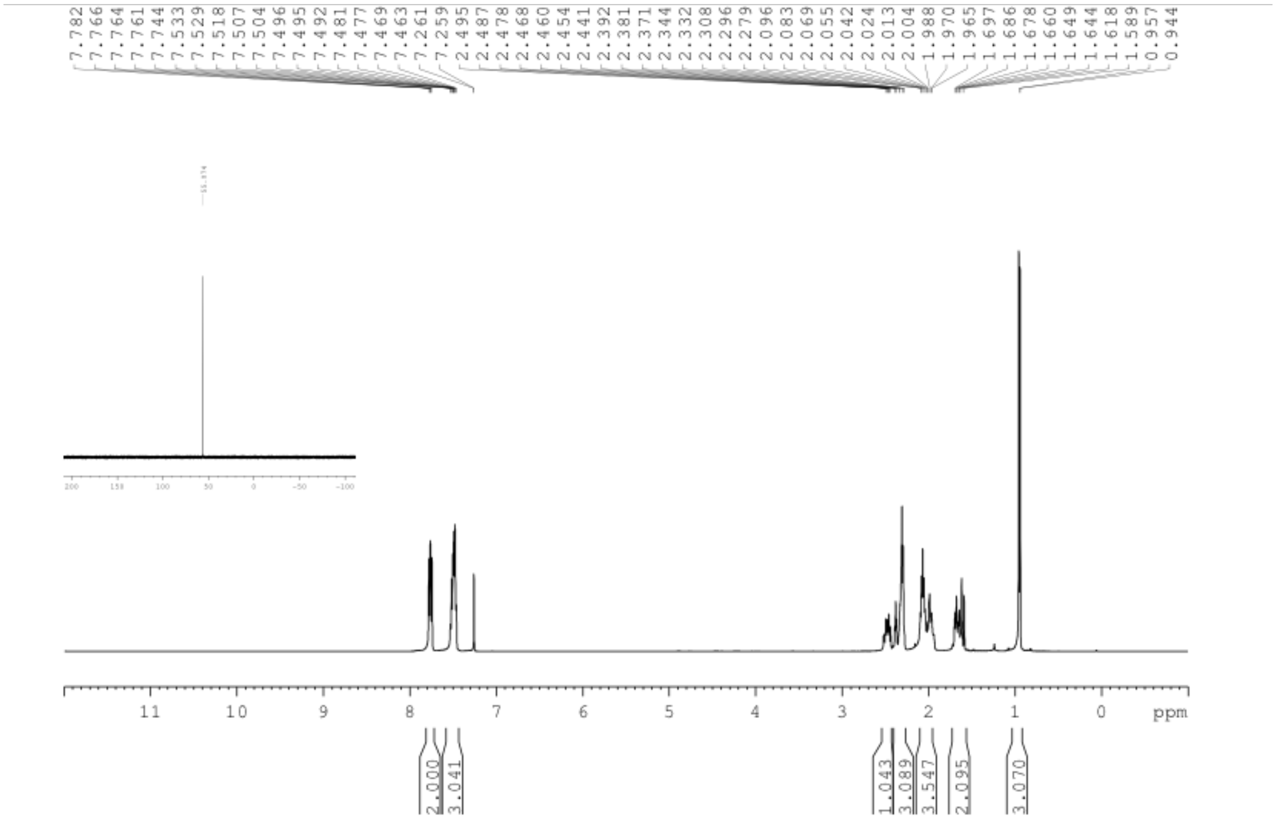


3d





3e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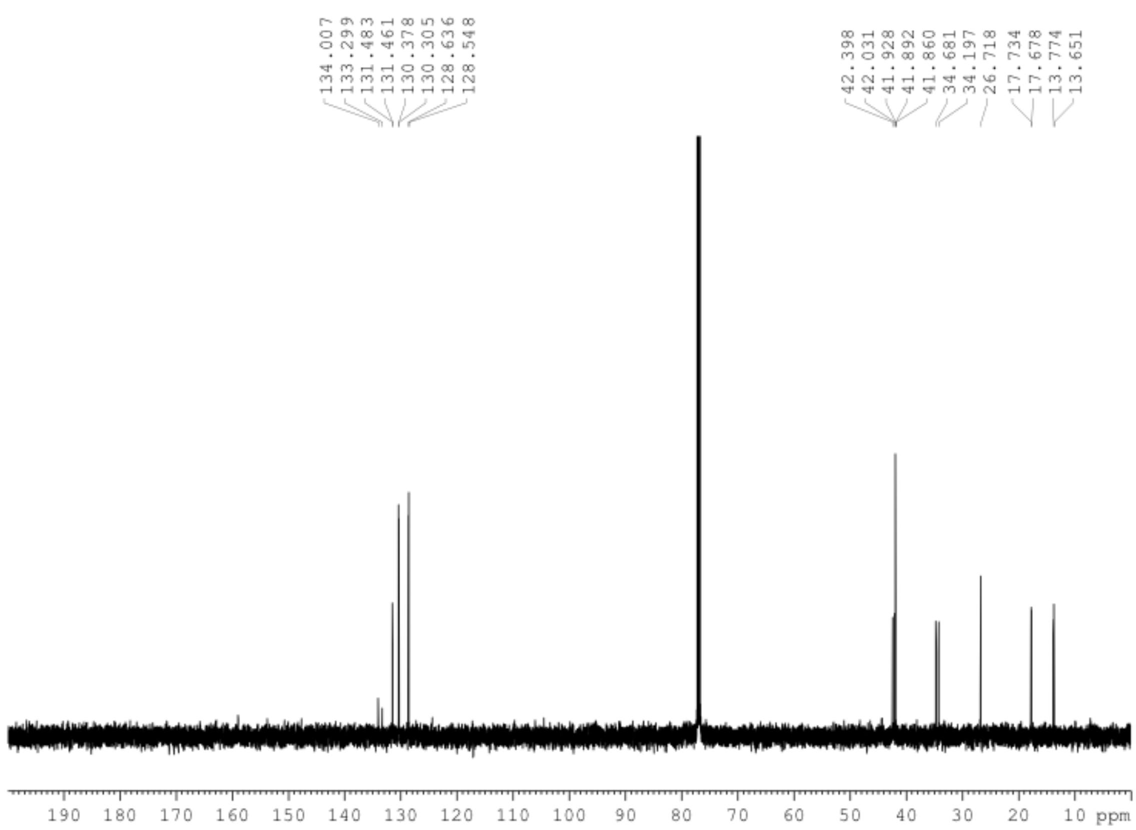
7.764
7.761
7.744
7.533
7.529
7.518
7.507
7.504
7.496
7.495
7.492
7.481
7.477
7.469
7.463
7.261
7.259
2.495
2.487
2.478
2.468
2.460
2.454
2.441
2.392
2.381
2.371
2.344
2.332
2.308
2.296
2.279
2.096
2.083
2.069
2.055
2.042
2.024
2.013
2.004
1.988
1.970
1.965
1.697
1.686
1.678
1.660
1.649
1.644
1.618
1.589
0.957
0.944
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
3.041
1.043
3.089
3.547
2.095
3.070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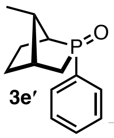
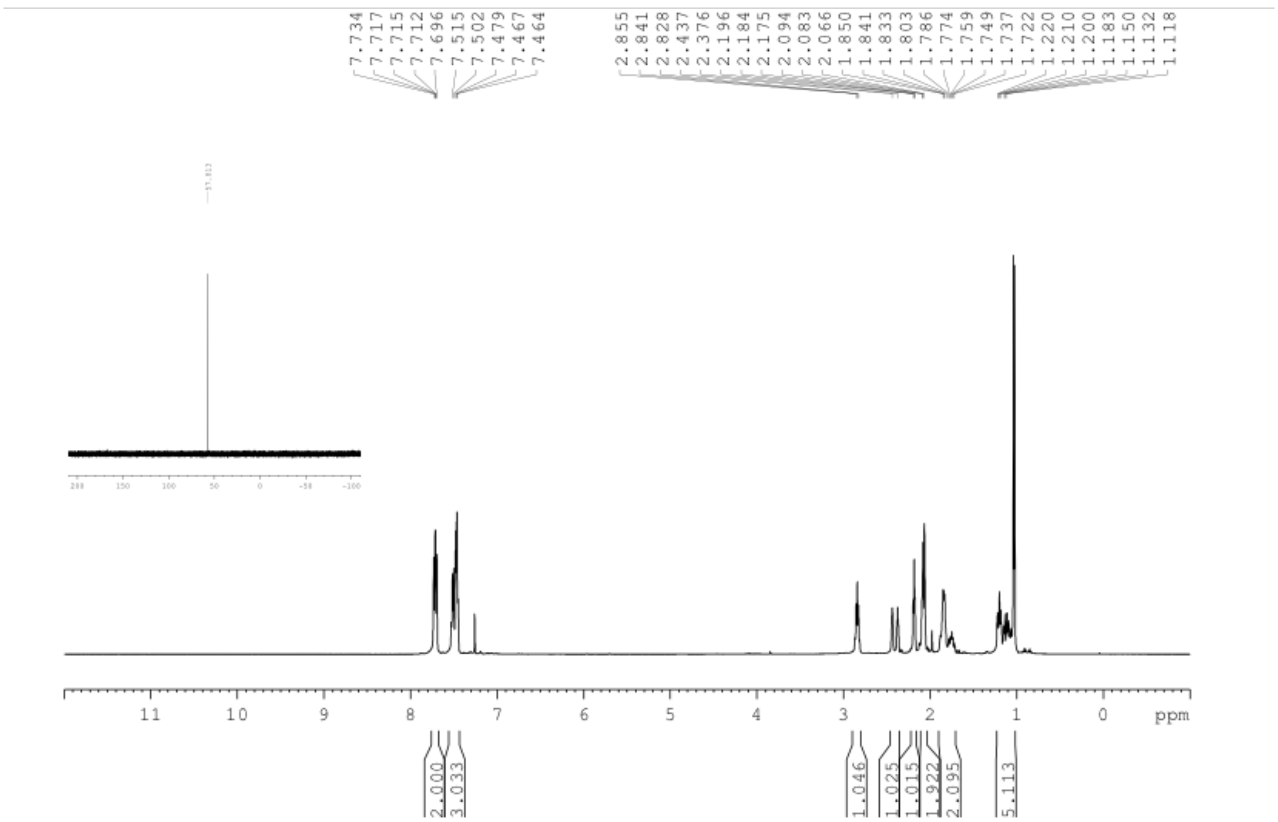
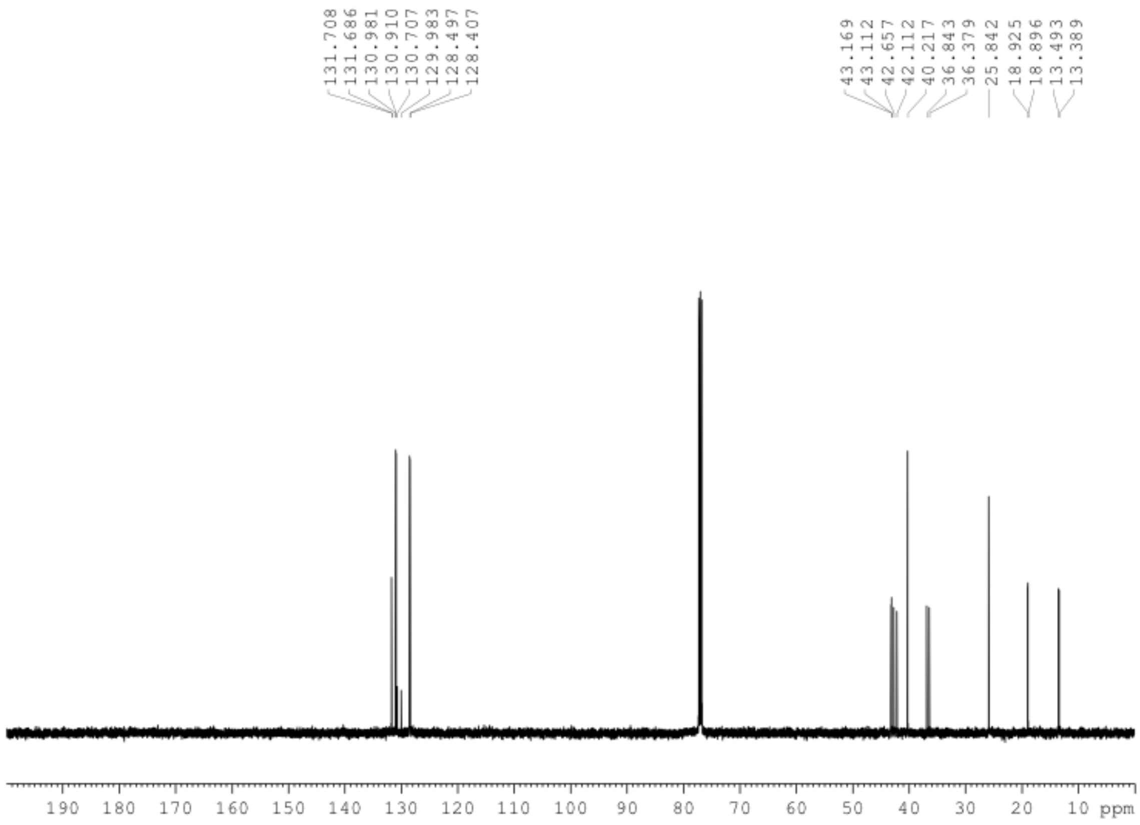
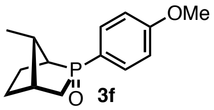
133.299
131.483
131.461
130.378
130.305
128.636
128.548
42.398
42.031
41.928
41.892
41.860
34.681
34.197
26.718
17.734
17.678
13.774
13.651
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
P

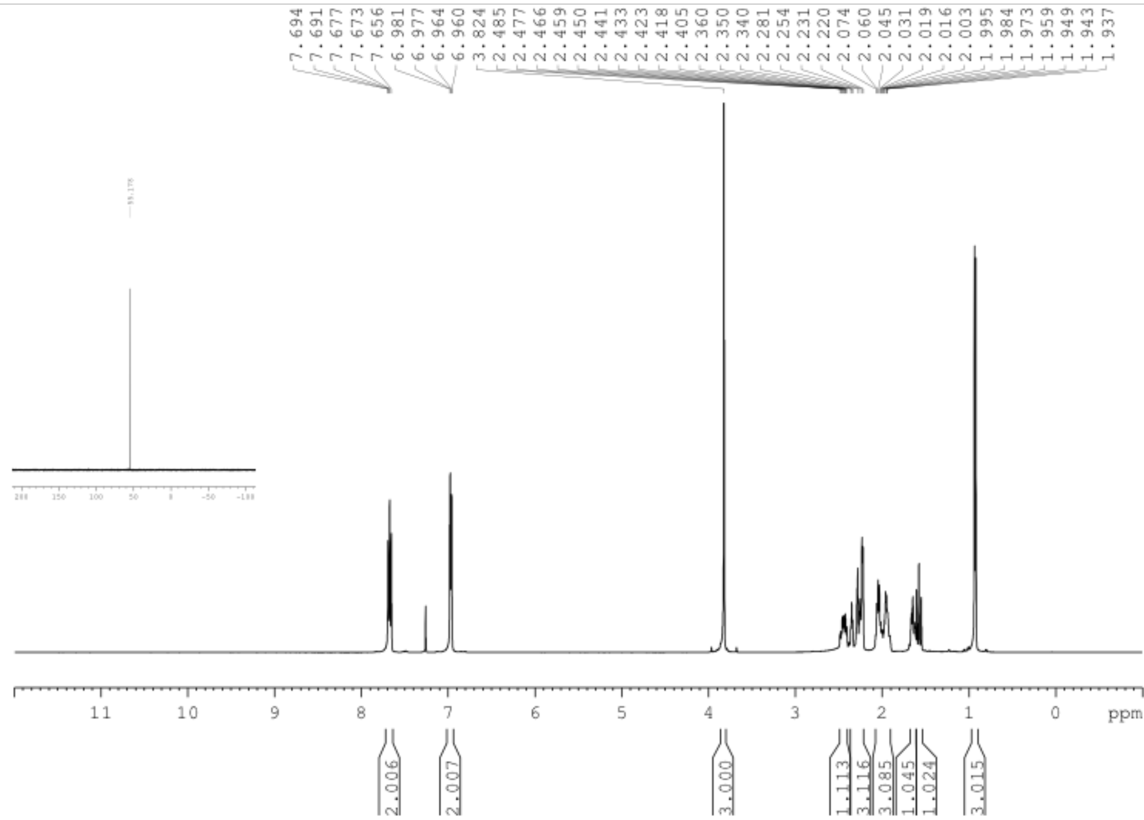
3e′

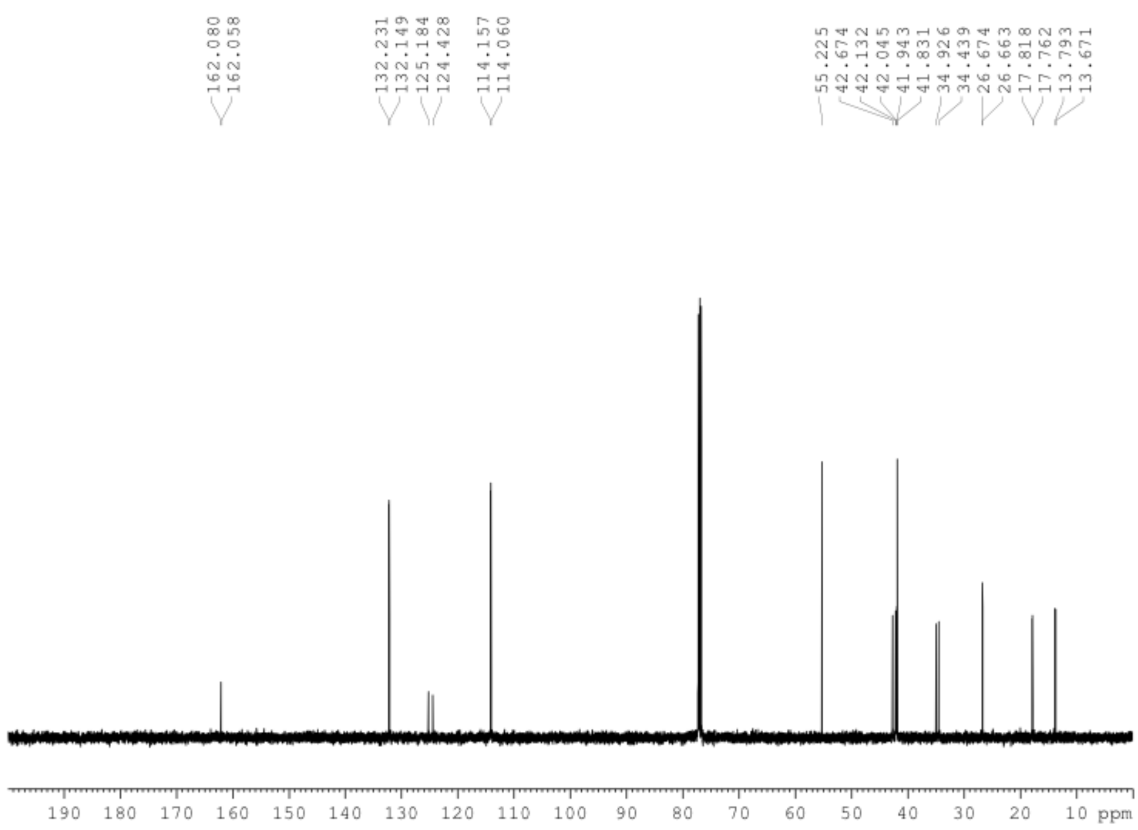

7.734
7.717
7.715
7.712
7.696
7.515
7.502
7.479
7.467
7.464
2.855
2.841
2.828
2.437
2.376
2.196
2.184
2.175
2.094
2.083
2.066
1.850
1.841
1.833
1.803
1.786
1.774
1.759
1.749
1.737
1.722
1.220
1.210
1.200
1.183
1.150
1.132
1.118
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
3.033
1.046
1.025
1.015
1.922
2.095
5.113


131.708
131.686
130.981
130.910
130.707
129.983
128.497
128.407
43.169
43.112
42.657
42.112
40.217
36.843
36.379
25.842
18.925
18.896
13.493
13.389
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



3f


7.694
7.691
7.677
7.673
7.656
6.981
6.977
6.964
6.960
3.824
2.485
2.477
2.466
2.459
2.450
2.441
2.433
2.423
2.418
2.405
2.360
2.350
2.340
2.281
2.254
2.231
2.220
2.074
2.060
2.045
2.031
2.019
2.016
2.003
1.995
1.984
1.973
1.959
1.949
1.943
1.937
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.006
2.007
3.000
1.113
3.116
3.085
1.045
1.024
3.015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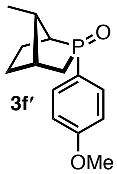
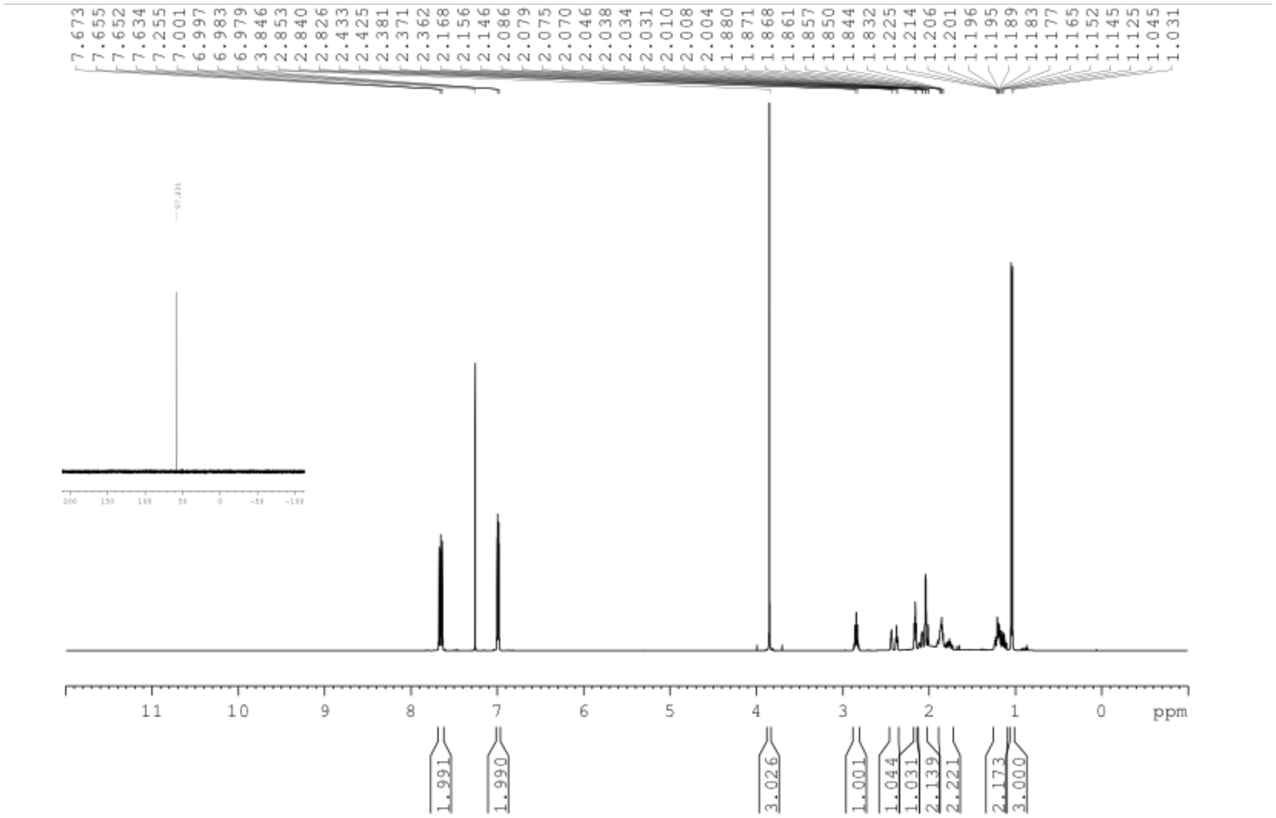
162.058
132.231
132.149
125.184
124.428
114.157
114.060
55.225
42.674
42.132
42.045
41.943
41.831
34.926
34.439
26.674
26.663
17.818
17.762
13.793
13.671
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


O
P
OMe

3f′


7.673
7.655
7.652
7.634
7.255
7.001
6.997
6.983
6.979
3.846
2.853
2.840
2.826
2.433
2.425
2.381
2.371
2.362
2.168
2.156
2.146
2.086
2.079
2.075
2.070
2.046
2.038
2.034
2.031
2.010
2.008
2.004
1.880
1.871
1.868
1.861
1.857
1.850
1.844
1.832
1.225
1.214
1.206
1.201
1.196
1.195
1.189
1.183
1.177
1.165
1.152
1.145
1.125
1.045
1.031
11
10
9
8
7
6
5
4
3
2
1
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1.031
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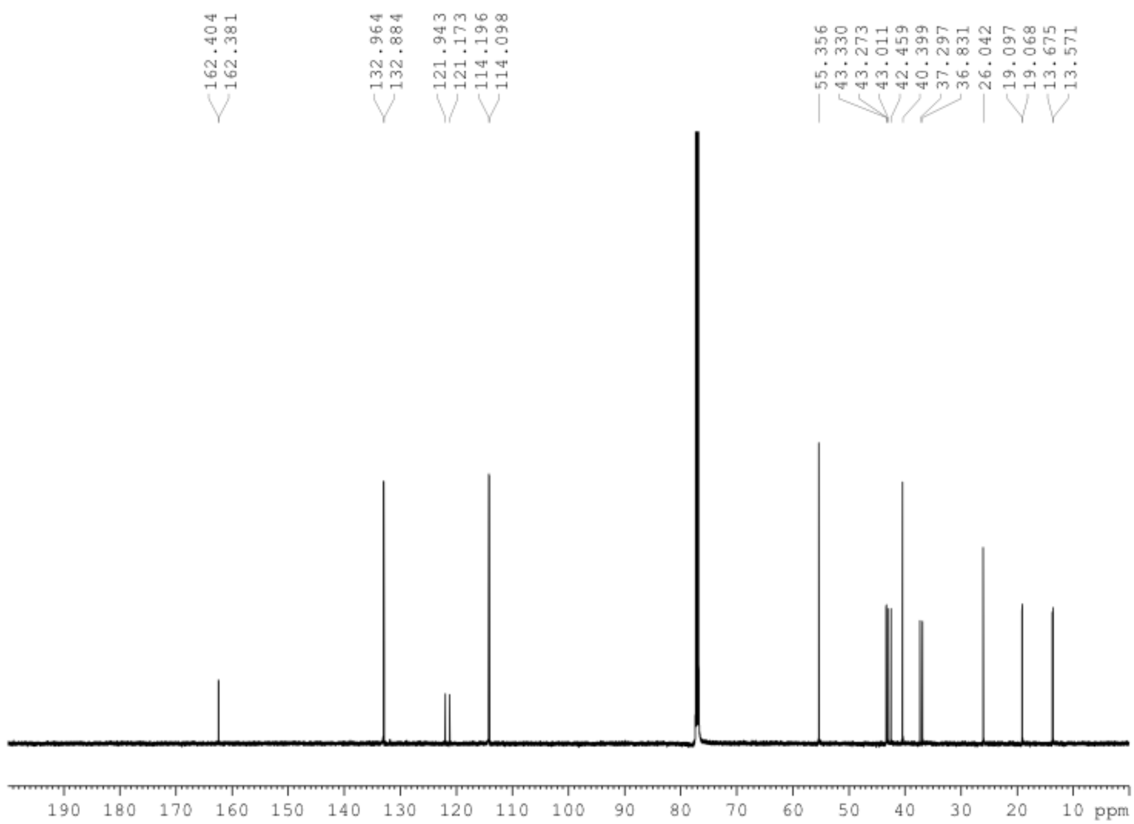
2.221
2.173
3.000


162.404
162.381
132.964
132.884
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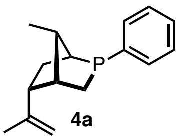
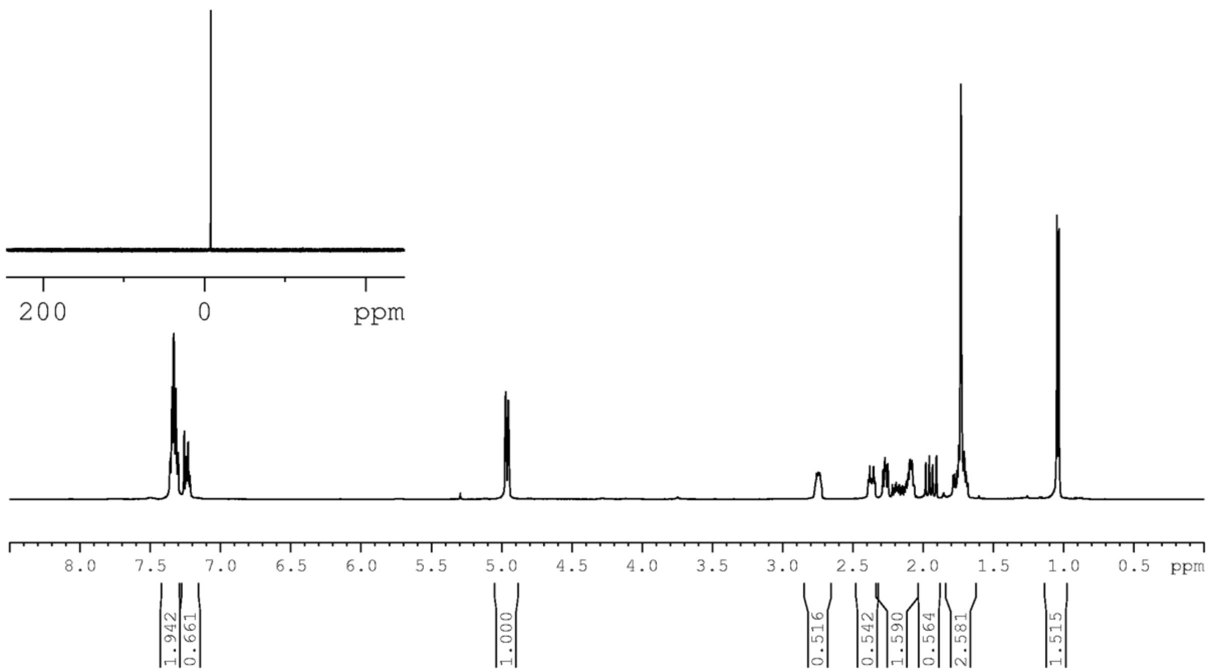
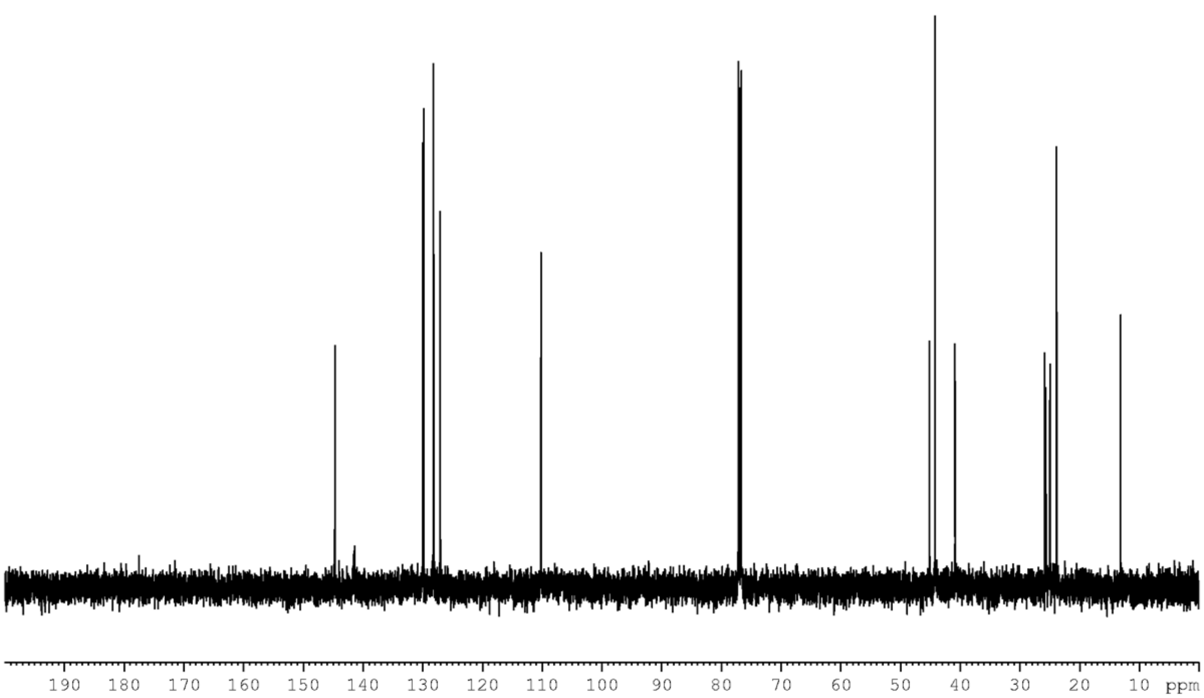
121.173
114.196
114.098
55.356
43.330
43.273
43.011
42.459
40.399
37.297
36.831
26.042
19.097
19.068
13.675
13.571
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



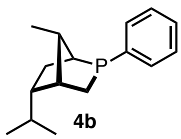
4a



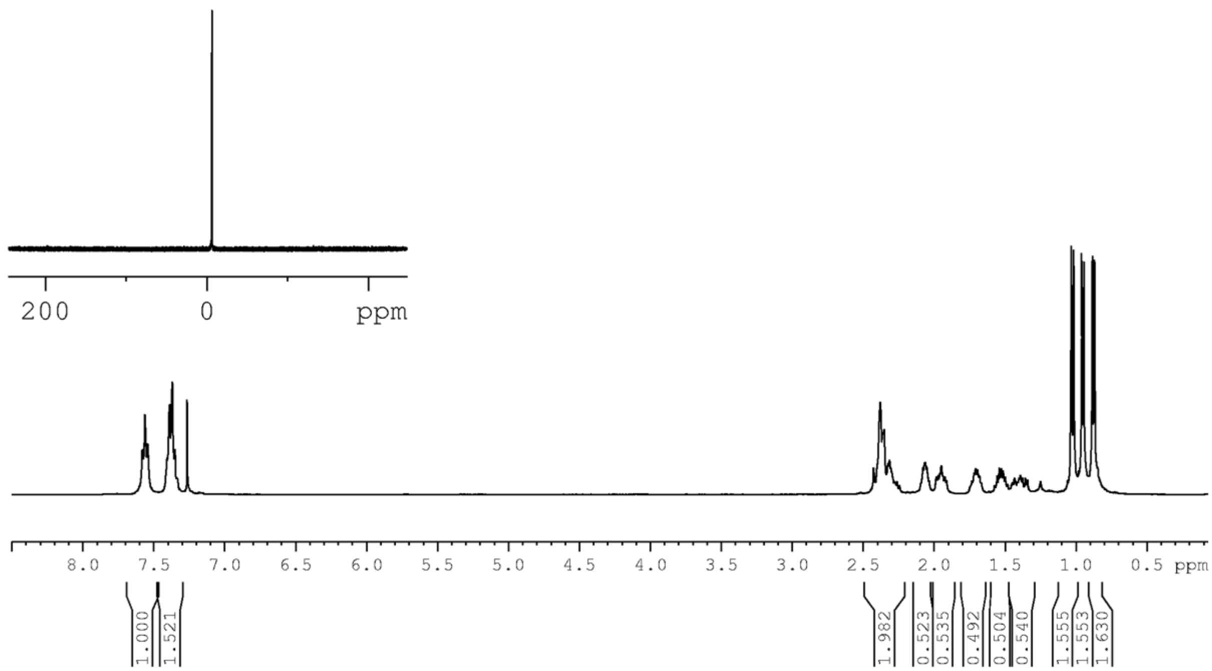
200
0
ppm
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.942
0.661
1.000
0.516
0.542
1.590
0.564
2.581
1.515



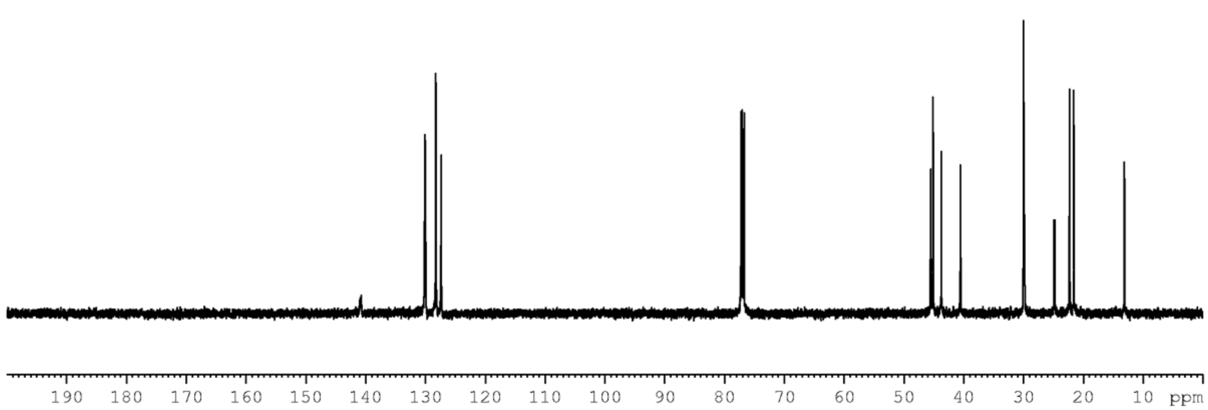
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



4b



200
0
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.000
1.521
1.982
0.523
0.535
0.492
0.504
0.540
1.555
1.553
1.630



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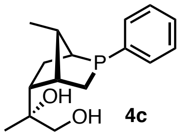
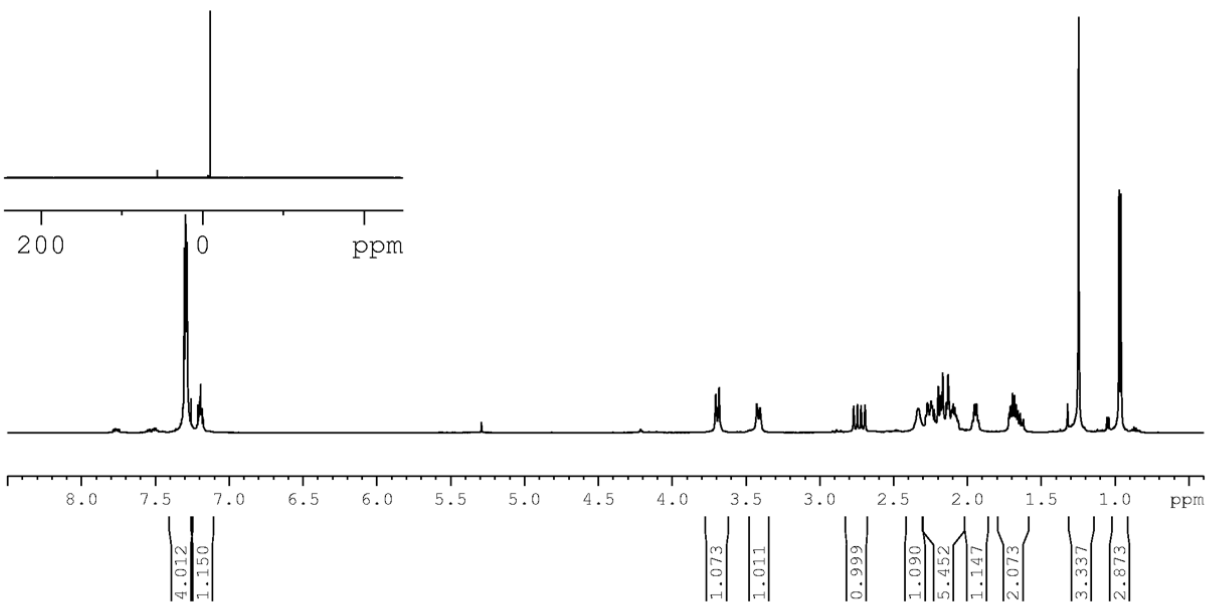
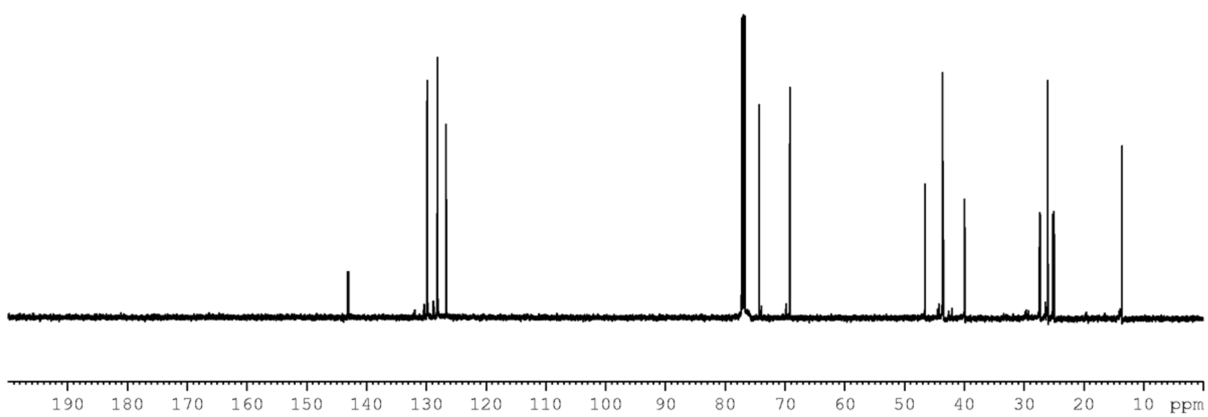
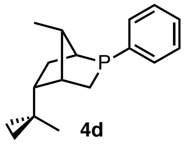

OH
OH
P

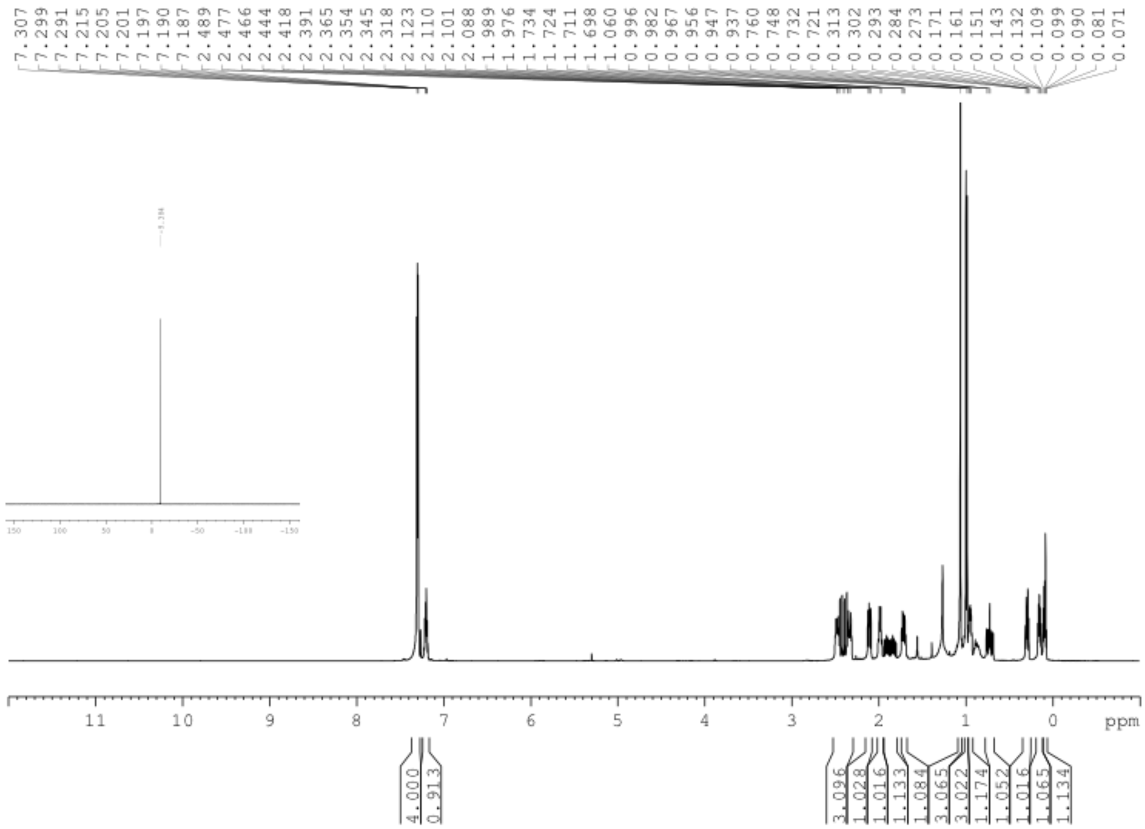
4c

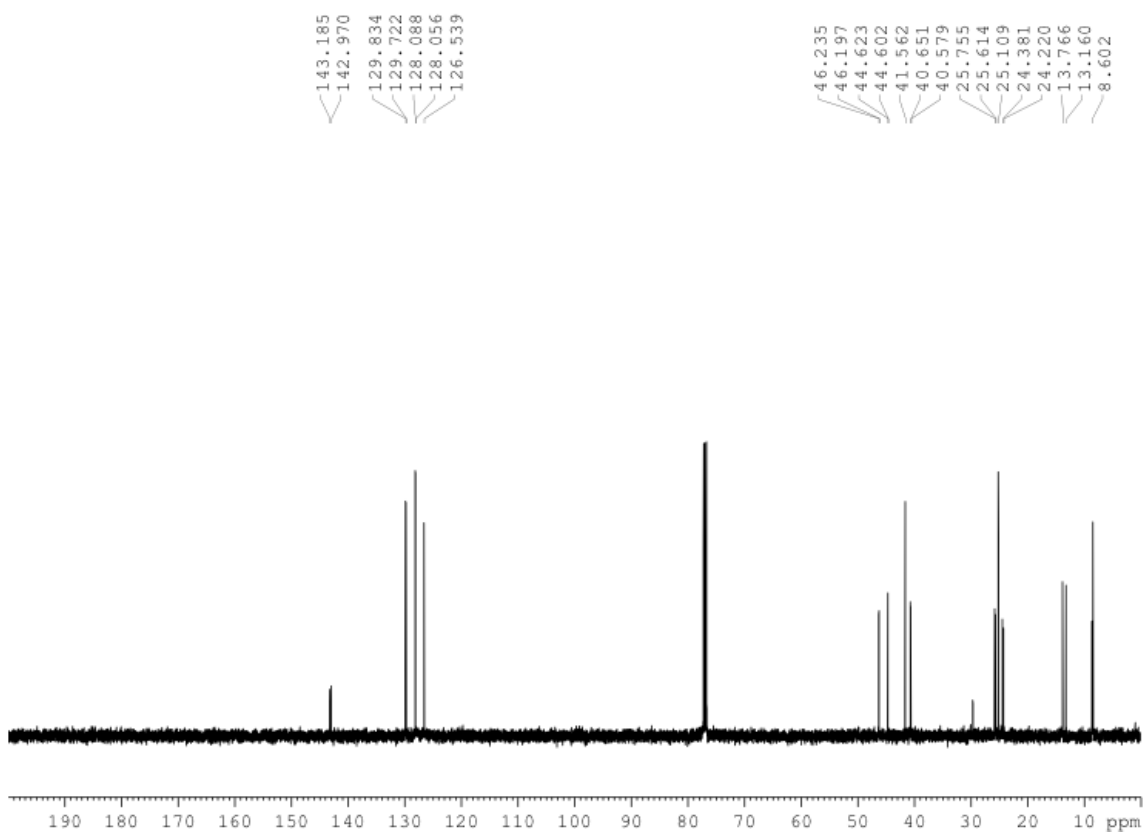

200
0
ppm
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
4.012
1.150
1.073
1.011
0.999
1.090
5.452
1.147
2.073
3.337
2.873


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



4d


7.307
7.299
7.291
7.215
7.205
7.201
7.197
7.190
7.187
2.489
2.477
2.466
2.444
2.418
2.391
2.365
2.354
2.345
2.318
2.123
2.110
2.101
2.088
1.989
1.976
1.734
1.724
1.711
1.698
1.060
0.996
0.982
0.967
0.956
0.947
0.937
0.760
0.748
0.732
0.721
0.313
0.302
0.293
0.284
0.273
0.171
0.161
0.151
0.143
0.132
0.109
0.099
0.090
0.081
0.071
11
10
9
8
7
6
5
4
3
2
1
0
ppm
4.000
0.913
3.096
1.028
1.016
1.133
1.084
3.065
3.022
1.174
1.052
1.016
1.065
1.134
150
100
50
0
-50
-100
-150


143.185
142.970
129.834
129.722
128.088
128.056
126.539
46.235
46.197
44.623
44.602
41.562
40.651
40.579
25.755
25.614
25.109
24.381
24.220
13.766
13.160
8.602
190
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170
160
150
140
130
120
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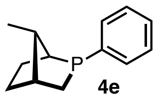
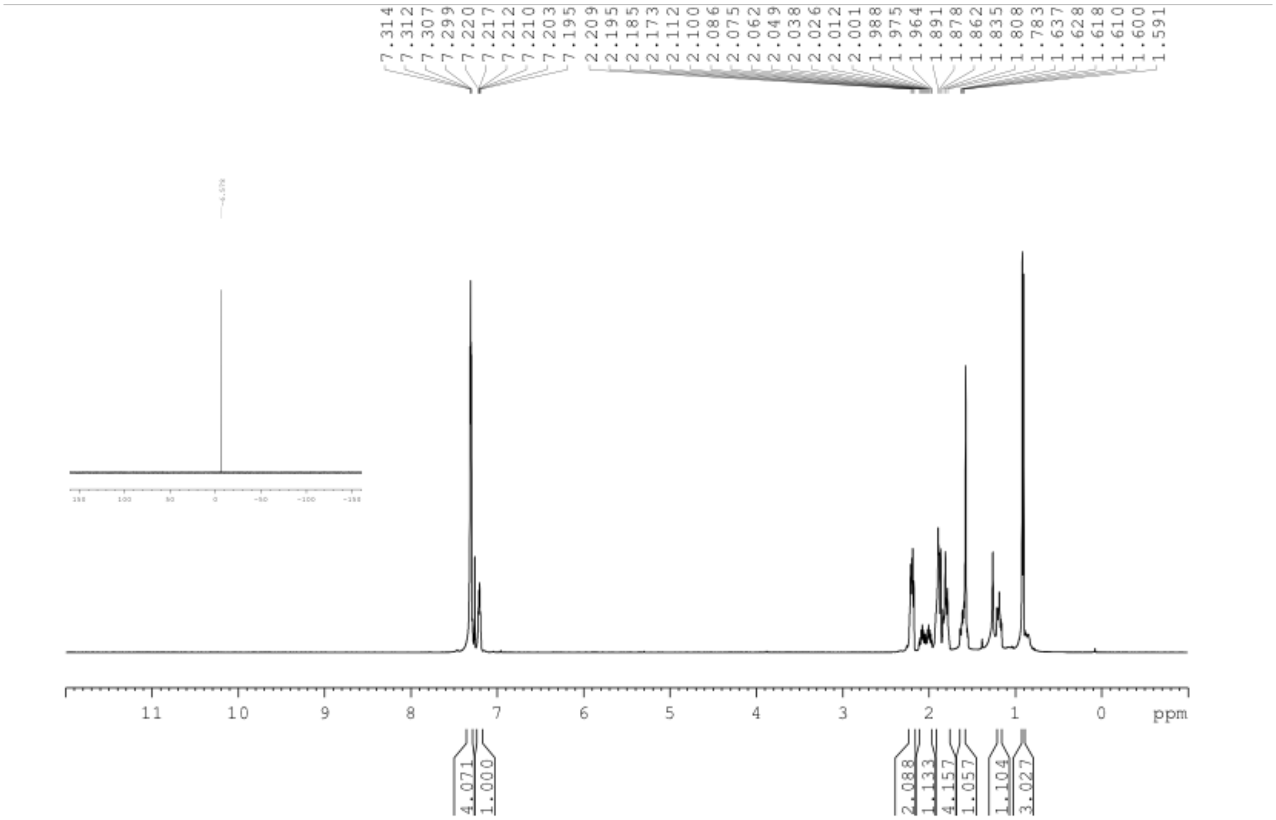
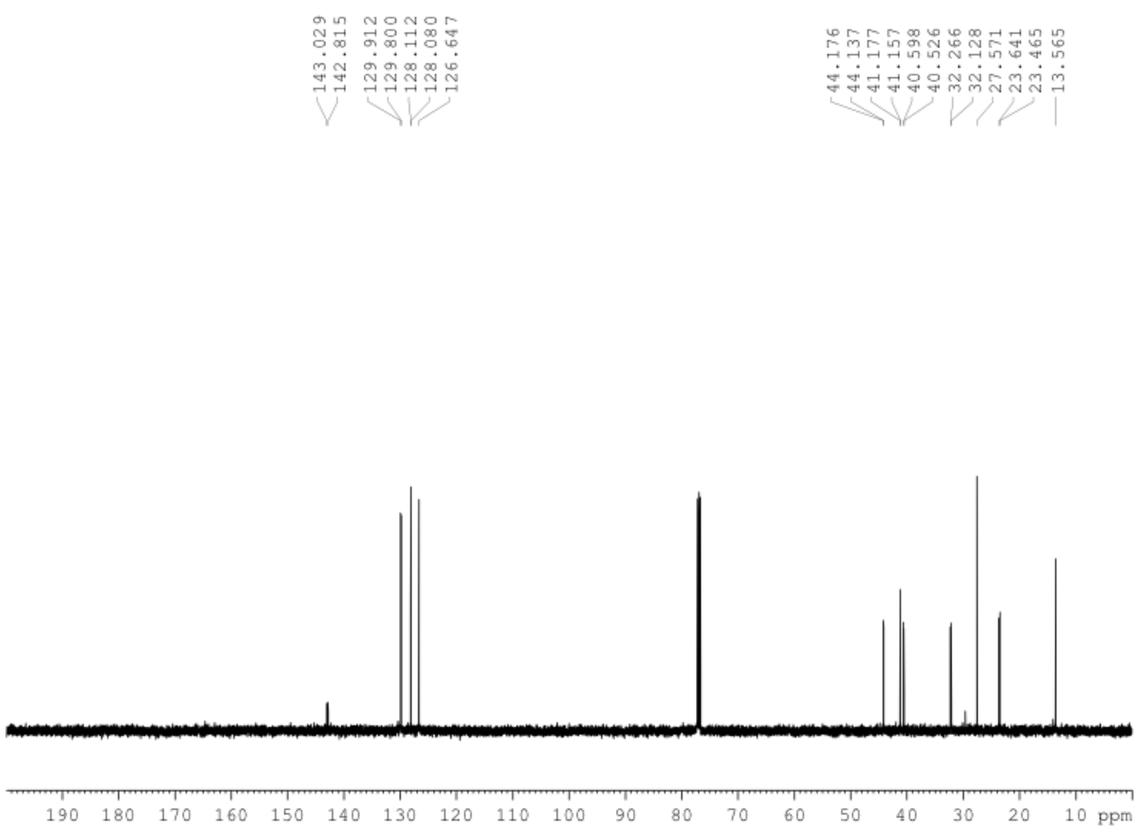
40
30
20
10
ppm



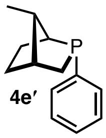
4e



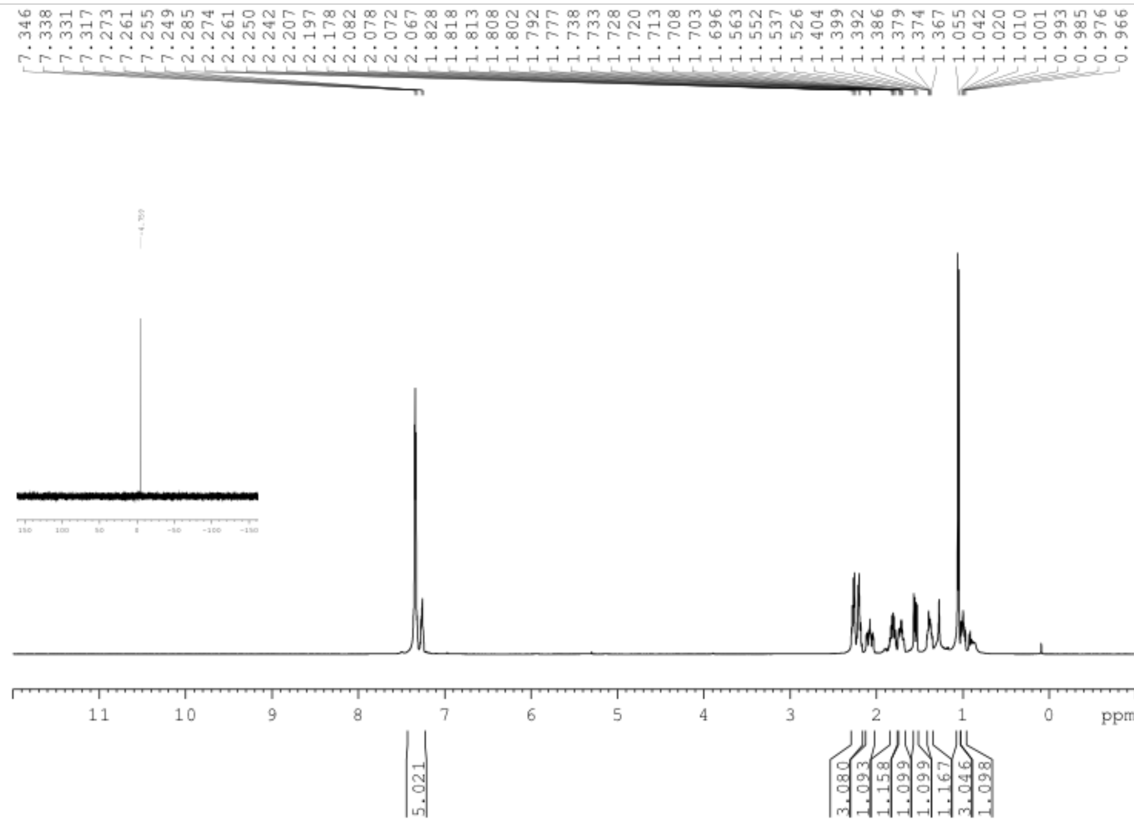
7.314
7.312
7.307
7.299
7.220
7.217
7.212
7.210
7.203
7.195
2.209
2.195
2.185
2.173
2.112
2.100
2.086
2.075
2.062
2.049
2.038
2.026
2.012
2.001
1.988
1.975
1.964
1.891
1.878
1.862
1.835
1.808
1.783
1.637
1.628
1.618
1.610
1.600
1.591
4.071
1.000
2.088
1.133
4.157
1.057
1.104
3.027
ppm

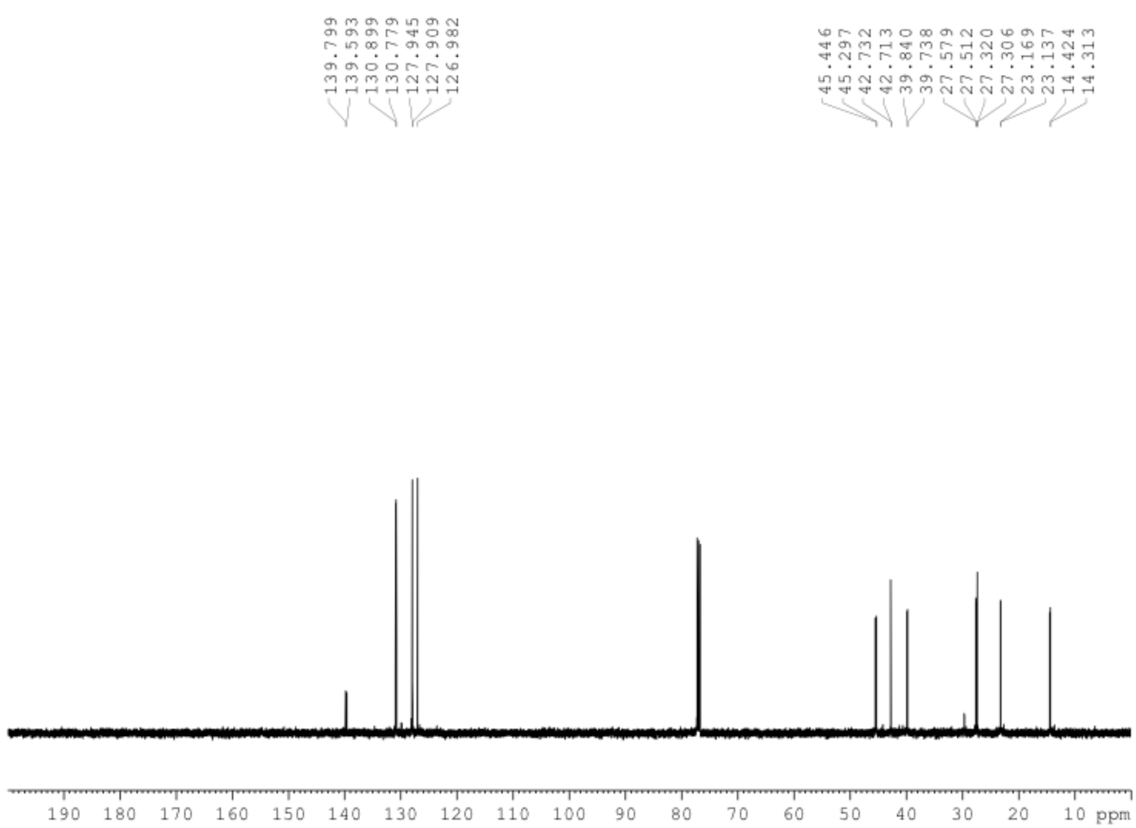


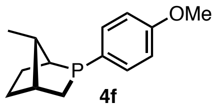
143.029
142.815
129.912
129.800
128.112
128.080
126.647
44.176
44.137
41.177
41.157
40.598
40.526
32.266
32.128
27.571
23.641
23.465
13.565
ppm



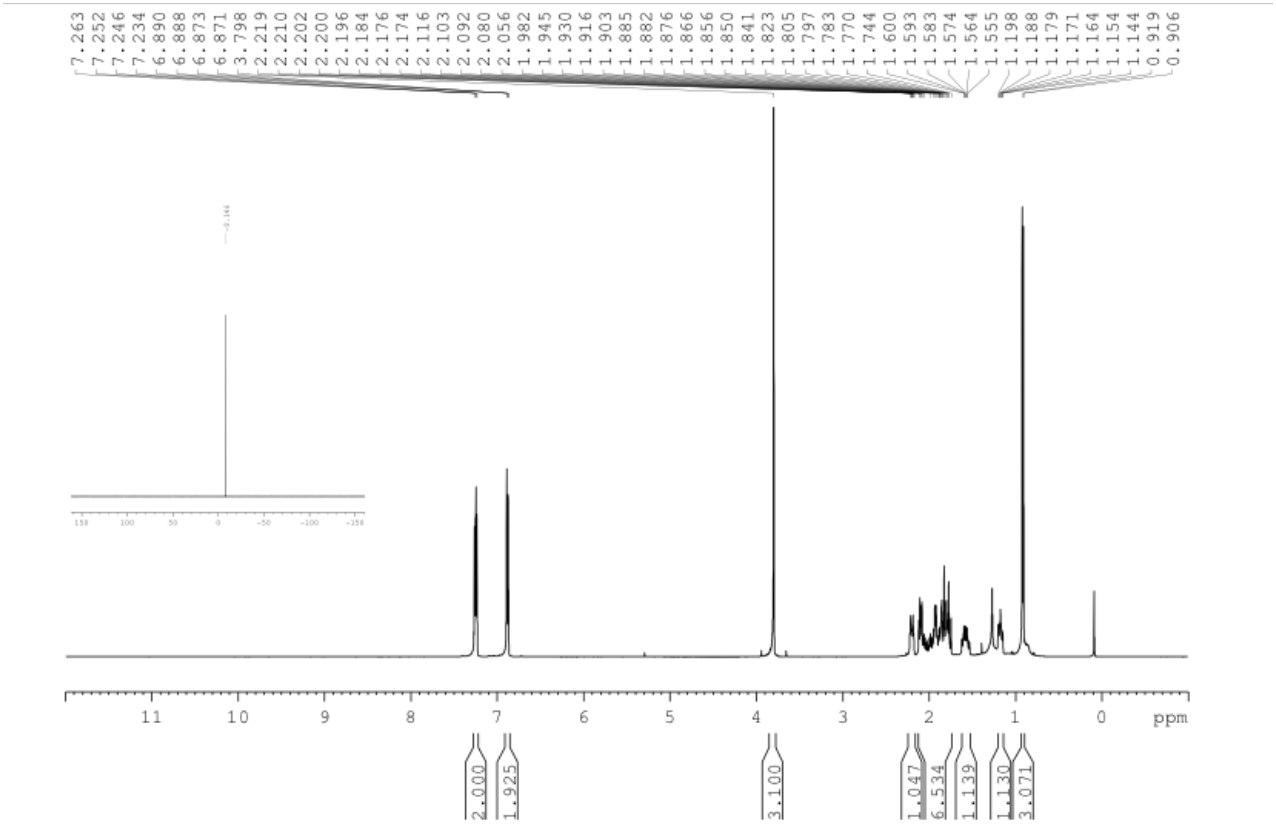
4e′

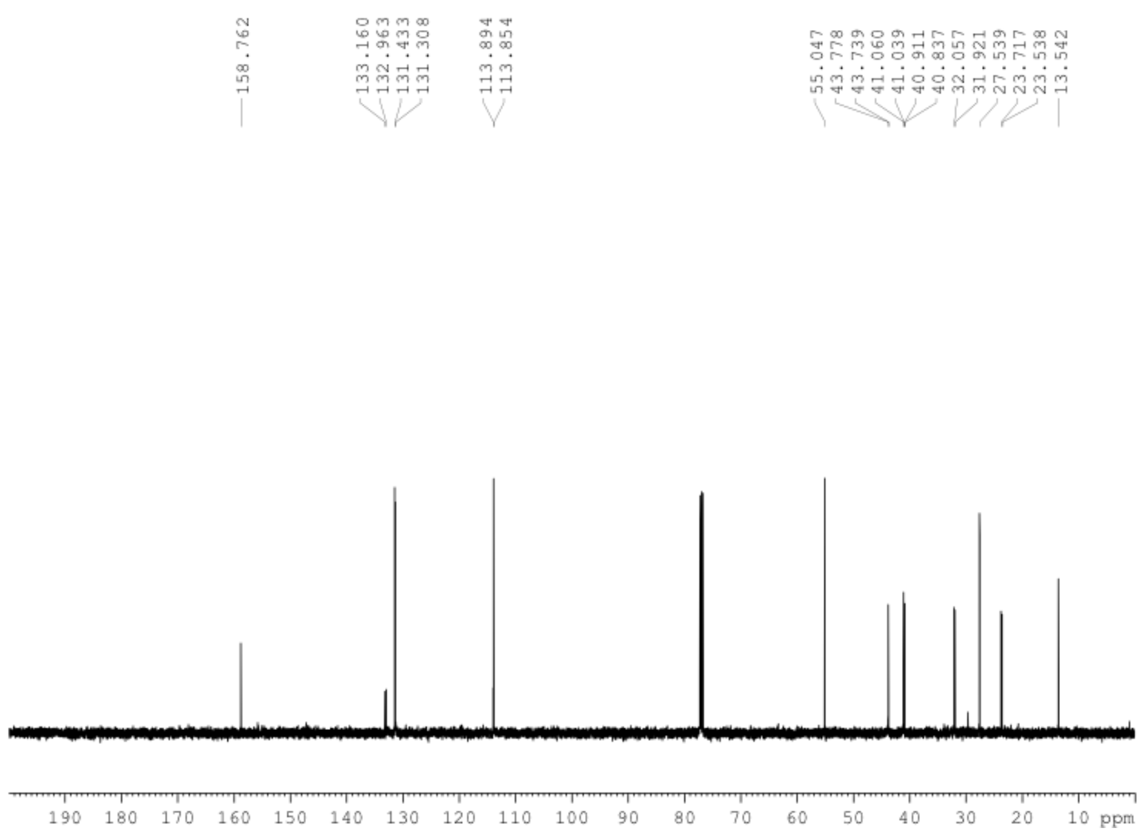

7.346
7.338
7.331
7.317
7.273
7.261
7.255
7.249
2.285
2.274
2.261
2.250
2.242
2.207
2.197
2.178
2.082
2.078
2.072
2.067
1.828
1.818
1.813
1.808
1.802
1.792
1.777
1.738
1.733
1.728
1.720
1.713
1.708
1.703
1.696
1.563
1.552
1.537
1.526
1.404
1.399
1.392
1.386
1.379
1.374
1.367
1.055
1.042
1.020
1.010
1.001
0.993
0.985
0.976
0.966
ppm
5.021
3.080
1.093
1.158
1.099
1.099
1.167
3.046
1.098

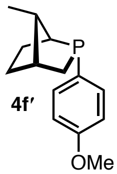

139.799
139.593
130.899
130.779
127.945
127.909
126.982
45.446
45.297
42.732
42.713
39.840
39.738
27.579
27.512
27.320
27.306
23.169
23.137
14.424
14.313
ppm


OMe
P

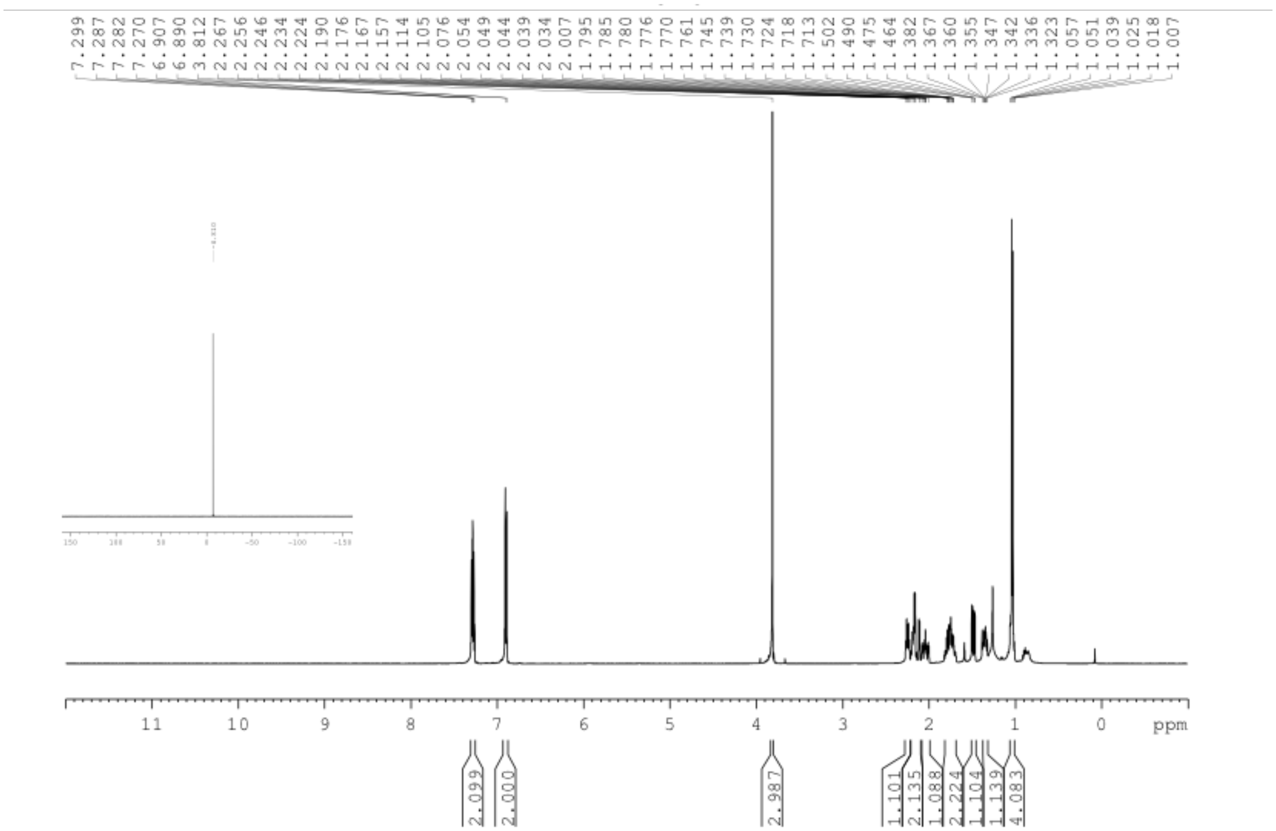
4f

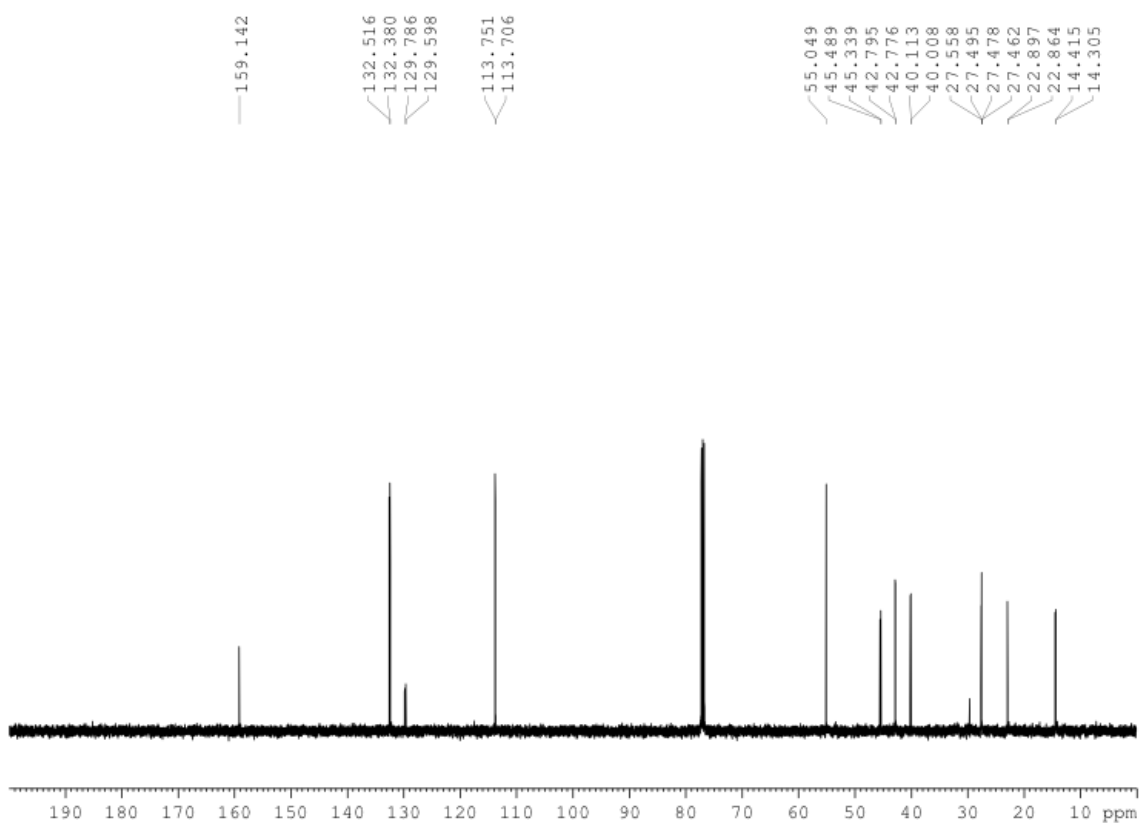

7.263
7.252
7.246
7.234
6.890
6.888
6.873
6.871
3.798
2.219
2.210
2.202
2.200
2.196
2.184
2.176
2.174
2.116
2.103
2.092
2.080
2.056
1.982
1.945
1.930
1.916
1.903
1.885
1.882
1.876
1.866
1.856
1.850
1.841
1.823
1.805
1.797
1.783
1.770
1.744
1.600
1.593
1.583
1.574
1.564
1.555
1.198
1.188
1.179
1.171
1.164
1.154
1.144
0.919
0.906
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
1.925
3.100
1.047
6.534
1.139
1.130
3.071

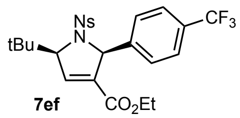

158.762
133.160
132.963
131.433
131.308
113.894
113.854
55.047
43.778
43.739
41.060
41.039
40.911
40.837
32.057
31.921
27.539
23.717
23.538
13.542
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



4f′

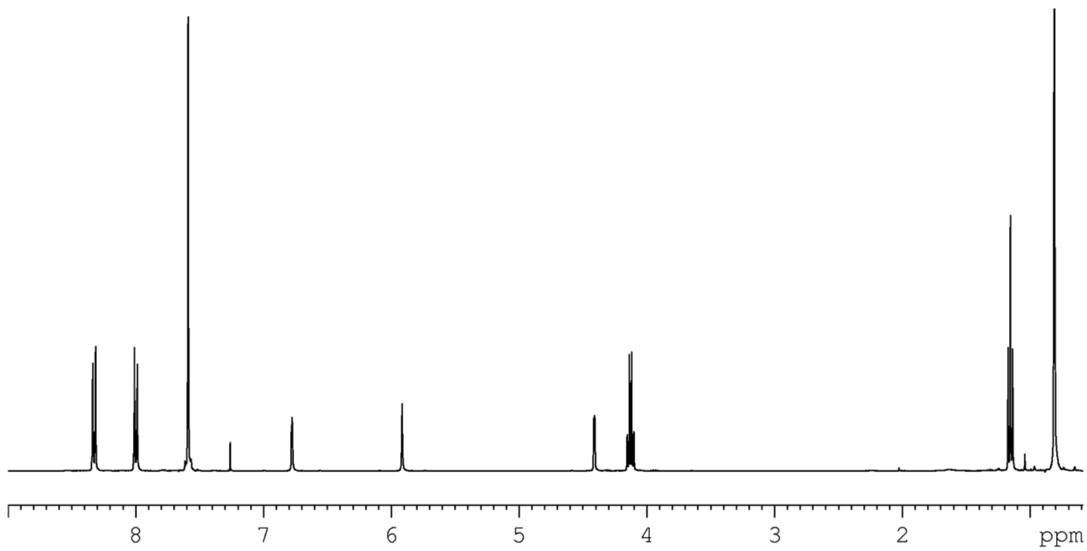




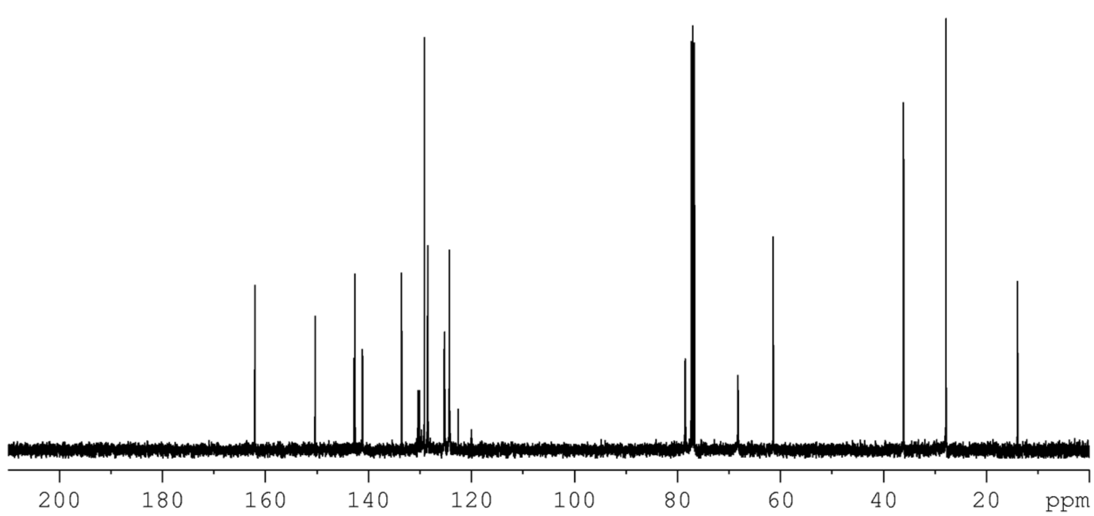


Ns
N
tBu
CF3
CO2Et

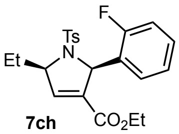
7ef



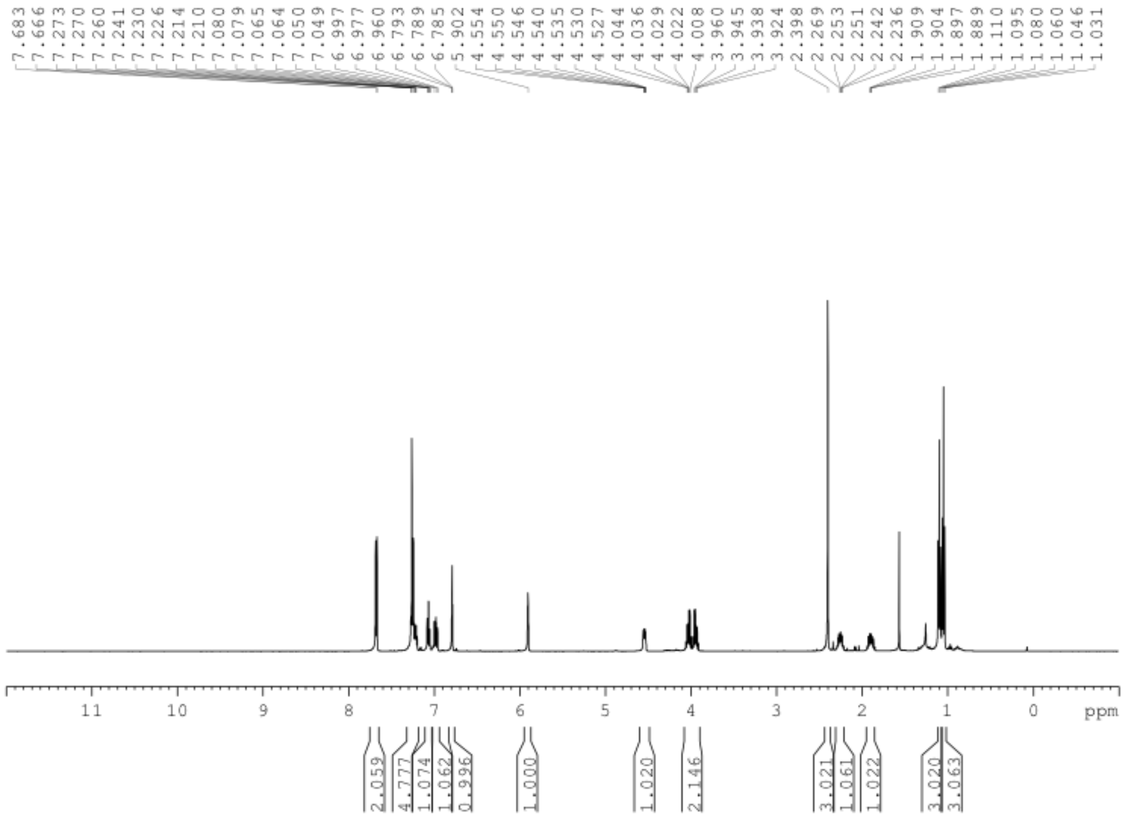
8
7
6
5
4
3
2
ppm



200
180
160
140
120
100
80
60
40
20
ppm


F
Ts
N
Et
CO2Et

7ch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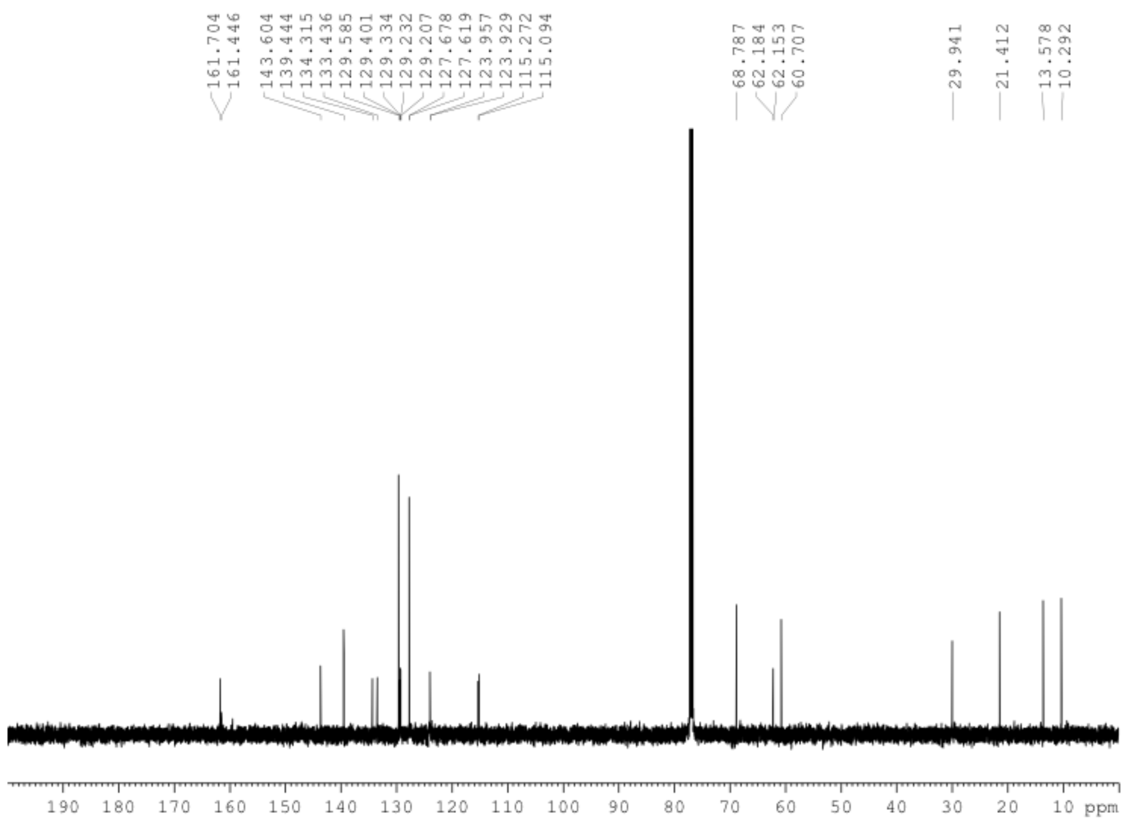
7.273
7.270
7.260
7.241
7.230
7.226
7.214
7.210
7.080
7.079
7.065
7.064
7.050
7.049
6.997
6.977
6.960
6.793
6.789
6.785
5.902
4.554
4.550
4.546
4.540
4.535
4.530
4.527
4.044
4.036
4.029
4.022
4.008
3.960
3.945
3.938
3.924
2.398
2.269
2.253
2.251
2.242
2.236
1.909
1.904
1.897
1.889
1.110
1.095
1.080
1.060
1.046
1.031
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.059
4.777
1.074
1.062
0.996
1.000
1.020
2.146
3.021
1.061
1.022
3.020
3.063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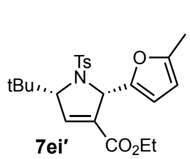
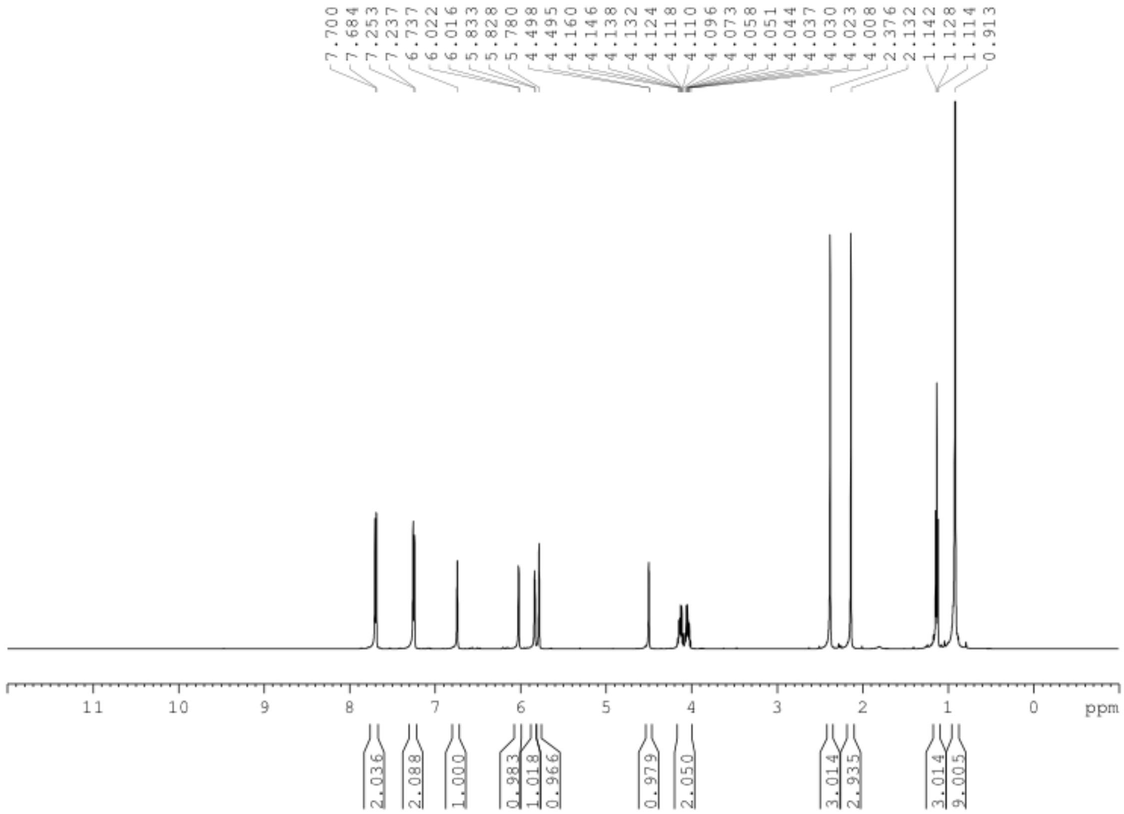
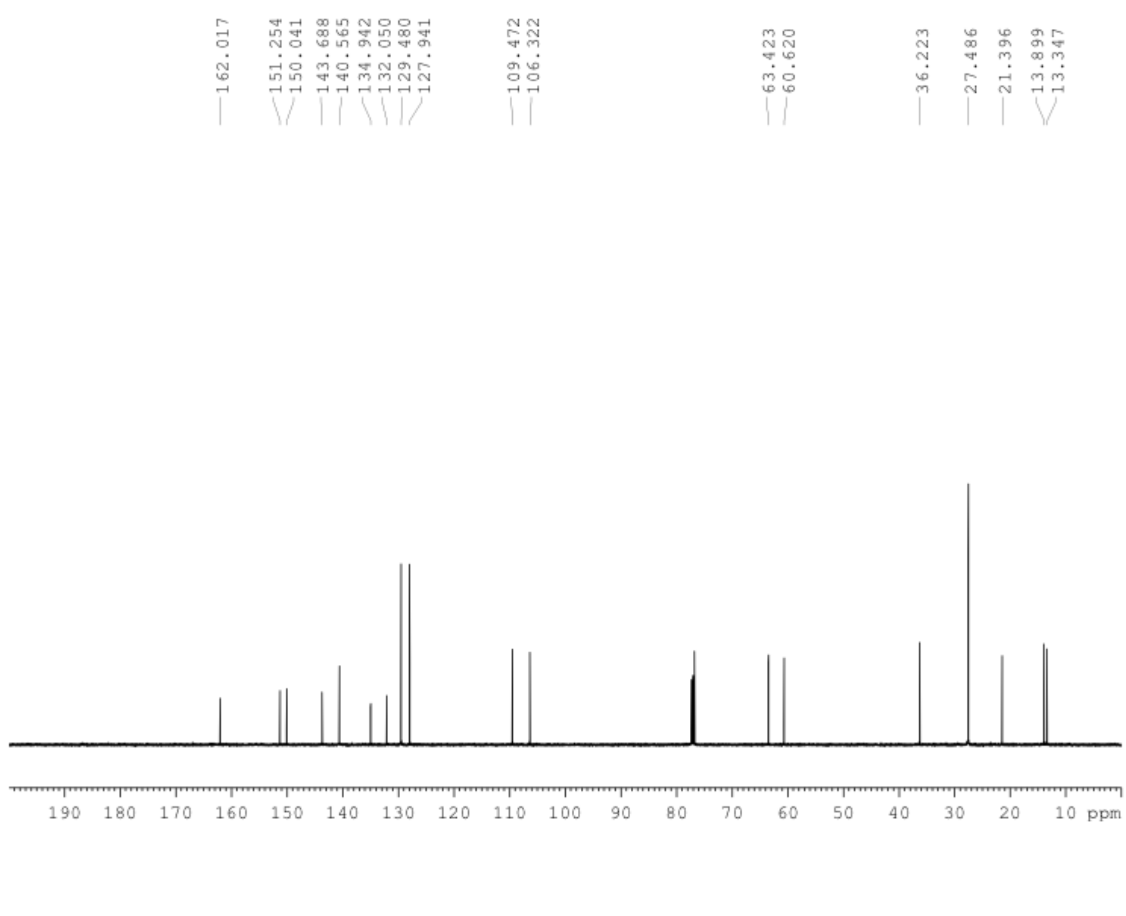
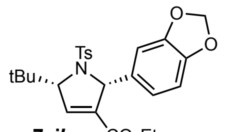
143.604
139.444
134.315
133.436
129.585
129.401
129.334
129.232
129.207
127.678
127.619
123.957
123.929
115.272
115.094
68.787
62.184
62.153
60.707
29.941
21.412
13.578
10.292
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
O
tBu
CO2Et

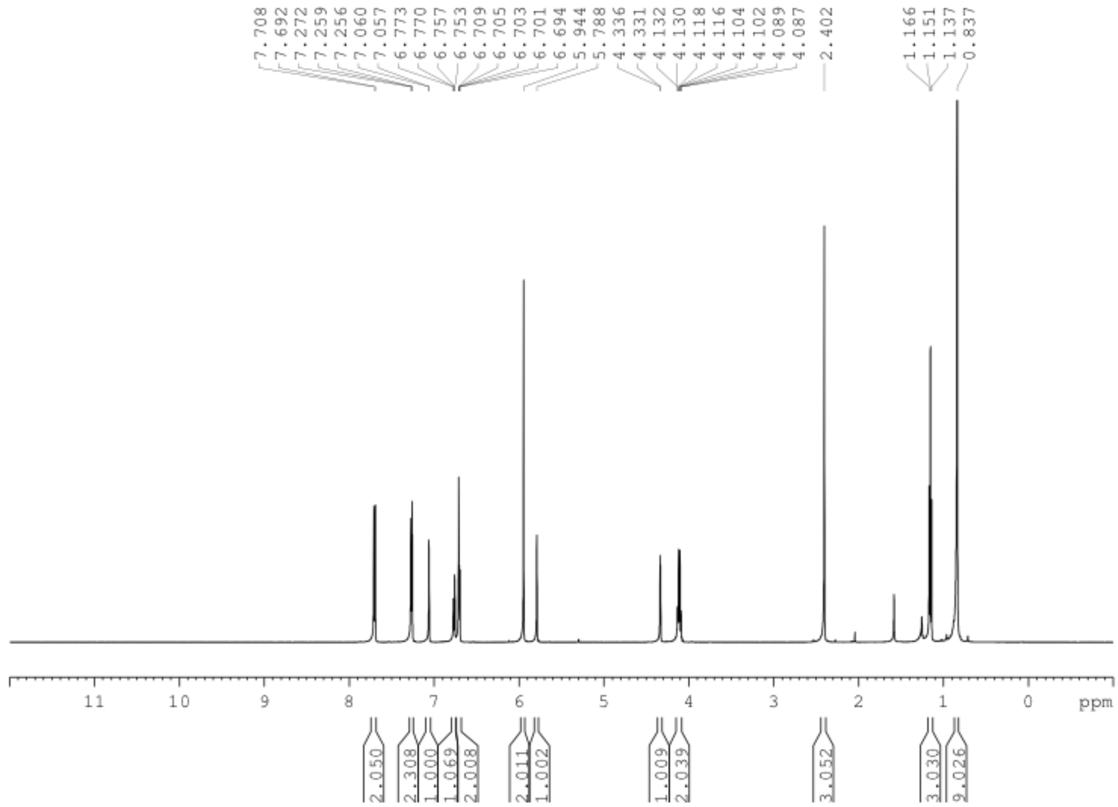
7ei′


7.700
7.684
7.253
7.237
6.737
6.022
6.016
5.833
5.828
5.780
4.498
4.495
4.160
4.146
4.138
4.132
4.124
4.118
4.110
4.096
4.073
4.058
4.051
4.044
4.037
4.030
4.023
4.008
2.376
2.132
1.142
1.128
1.114
0.913
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.036
2.088
1.000
0.983
1.018
0.966
0.979
2.050
3.014
2.935
3.014
9.005


162.017
151.254
150.041
143.688
140.565
134.942
132.050
129.480
127.941
109.472
106.322
63.423
60.620
36.223
27.486
21.396
13.899
13.347
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
tBu
O
O
CO2Et

7ej'


7.708
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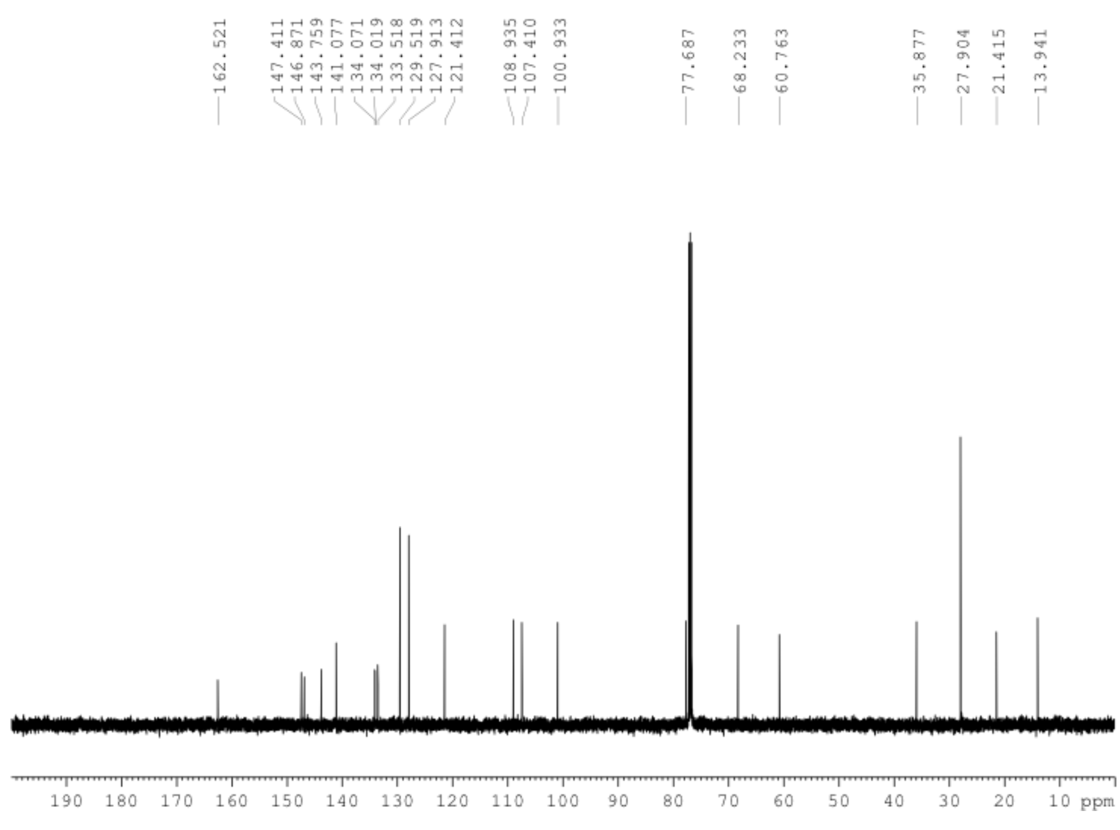
7.272
7.259
7.256
7.060
7.057
6.773
6.770
6.757
6.753
6.709
6.705
6.703
6.701
6.694
5.944
5.788
4.336
4.331
4.132
4.130
4.118
4.116
4.104
4.102
4.089
4.087
2.402
1.166
1.151
1.137
0.837
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.050
2.308
1.000
1.069
2.008
2.011
1.002
1.009
2.039
3.052
3.030
9.026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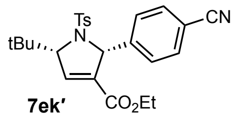
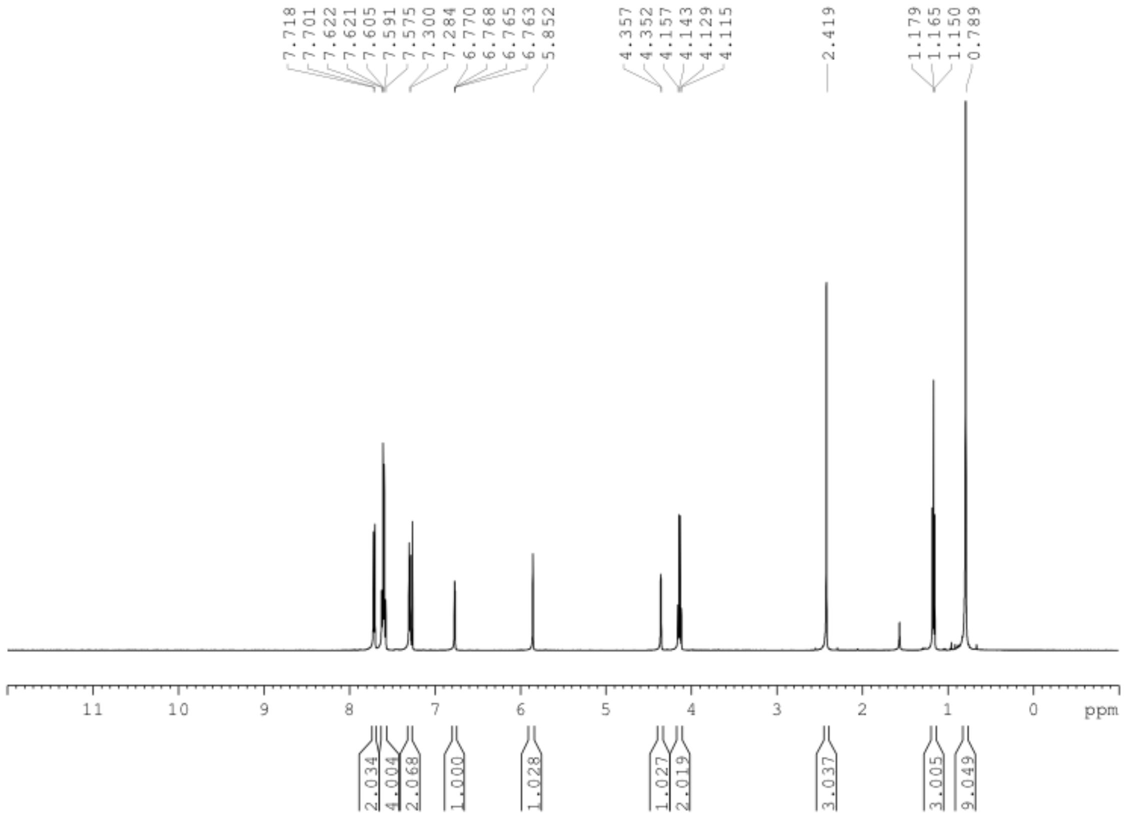
147.411
146.871
143.759
141.077
134.071
134.019
133.518
129.519
127.913
121.412
108.935
107.410
100.933
77.687
68.233
60.763
35.877
27.904
21.415
13.941
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
tBu
CN
CO2Et

7ek'


7.718
7.701
7.622
7.621
7.605
7.591
7.575
7.300
7.284
6.770
6.768
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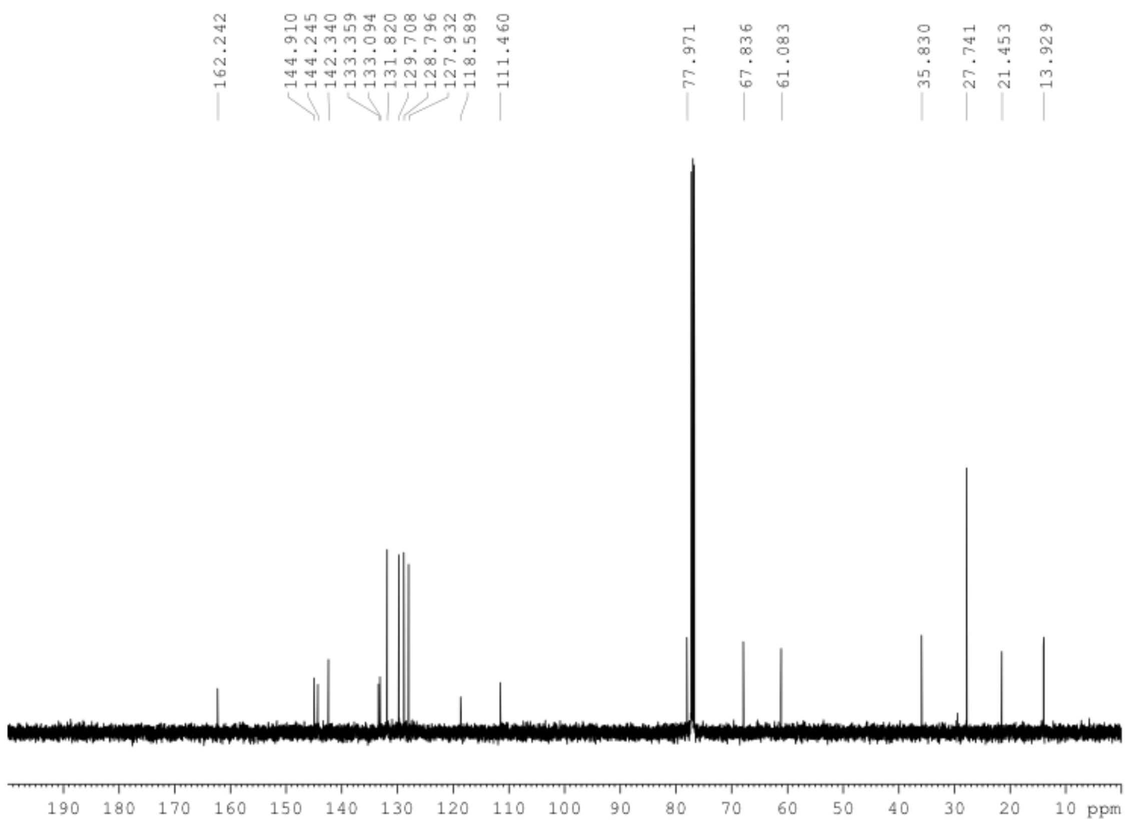
6.763
5.852
4.357
4.352
4.157
4.143
4.129
4.115
2.419
1.179
1.165
1.150
0.789
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.034
4.004
2.068
1.000
1.028
1.027
2.019
3.037
3.005
9.049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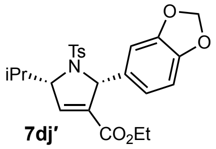
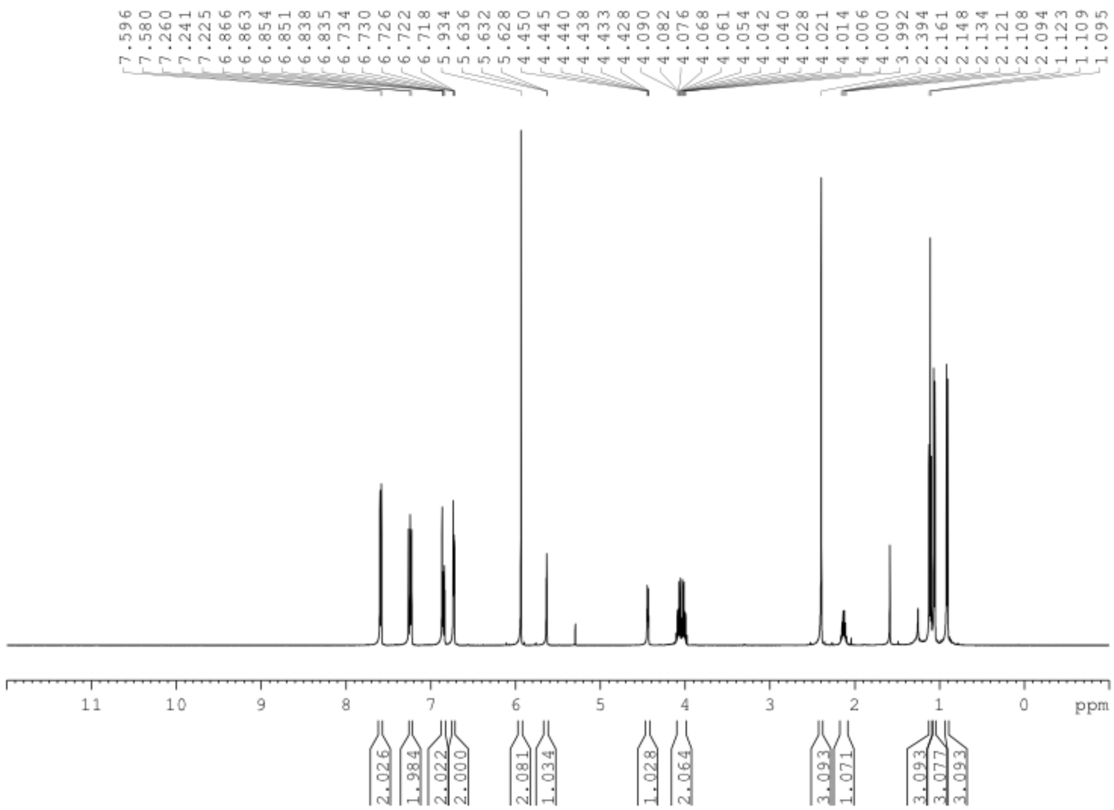
144.245
142.340
133.359
133.094
131.820
129.708
128.796
127.932
118.589
111.460
77.971
67.836
61.083
35.830
27.741
21.453
13.929
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
iPr
CO2Et

7dj'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7.580
7.260
7.241
7.225
6.866
6.863
6.854
6.851
6.838
6.835
6.734
6.730
6.726
6.722
6.718
5.934
5.636
5.632
5.628
4.450
4.445
4.440
4.438
4.433
4.428
4.090
4.082
4.076
4.068
4.061
4.054
4.042
4.040
4.028
4.021
4.014
4.006
4.000
3.992
2.394
2.161
2.148
2.134
2.121
2.108
2.094
1.123
1.109
1.095
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.026
1.984
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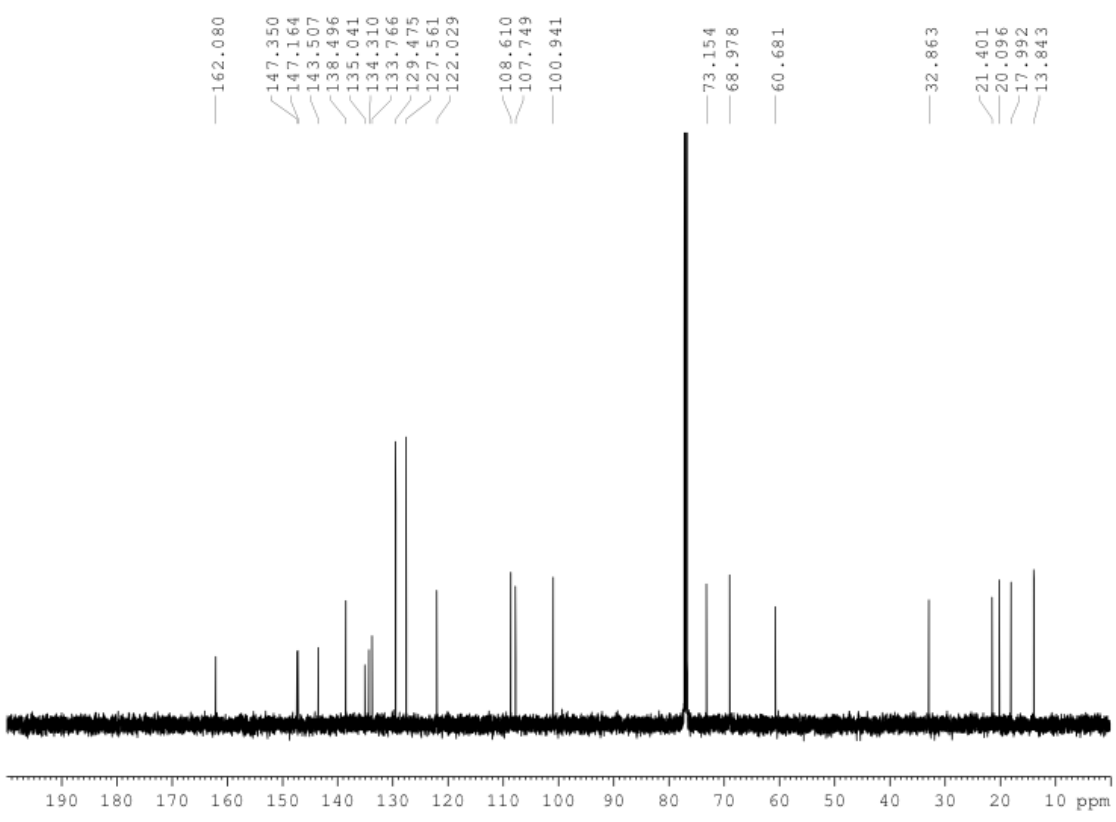
2.000
2.081
1.034
1.028
2.064
3.093
1.071
3.093
3.077
3.093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147.350
147.164
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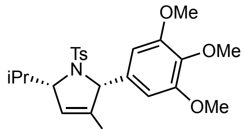
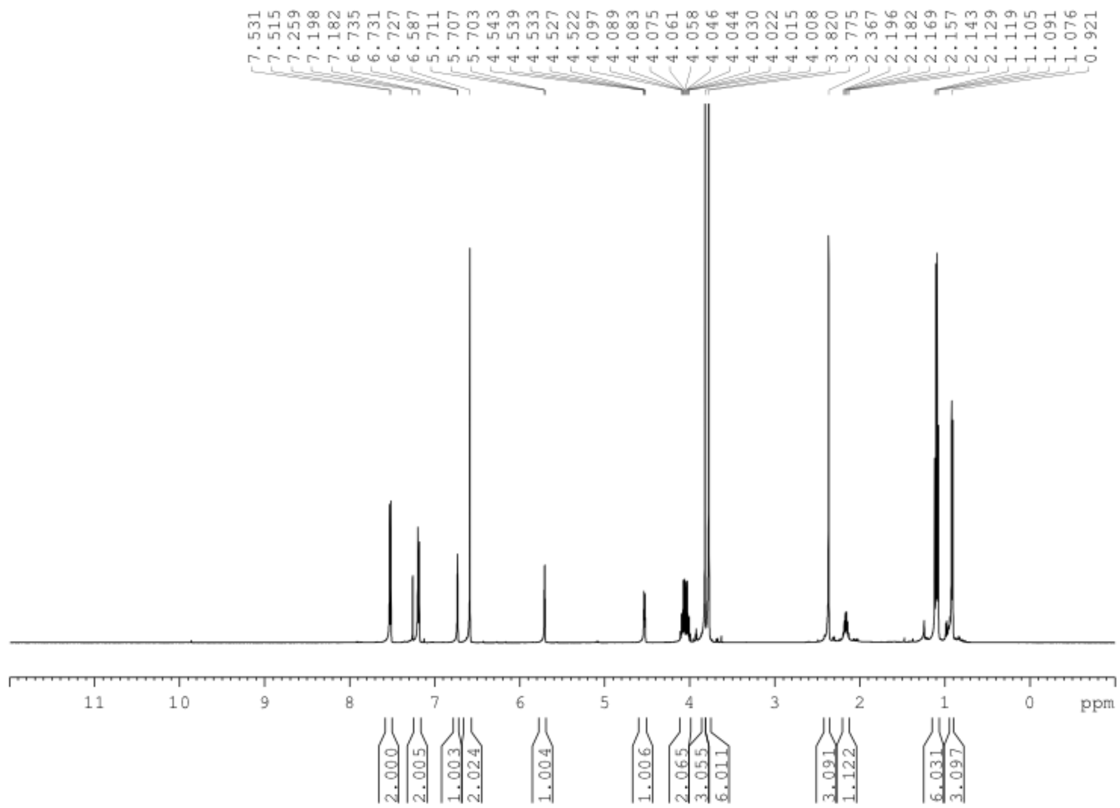
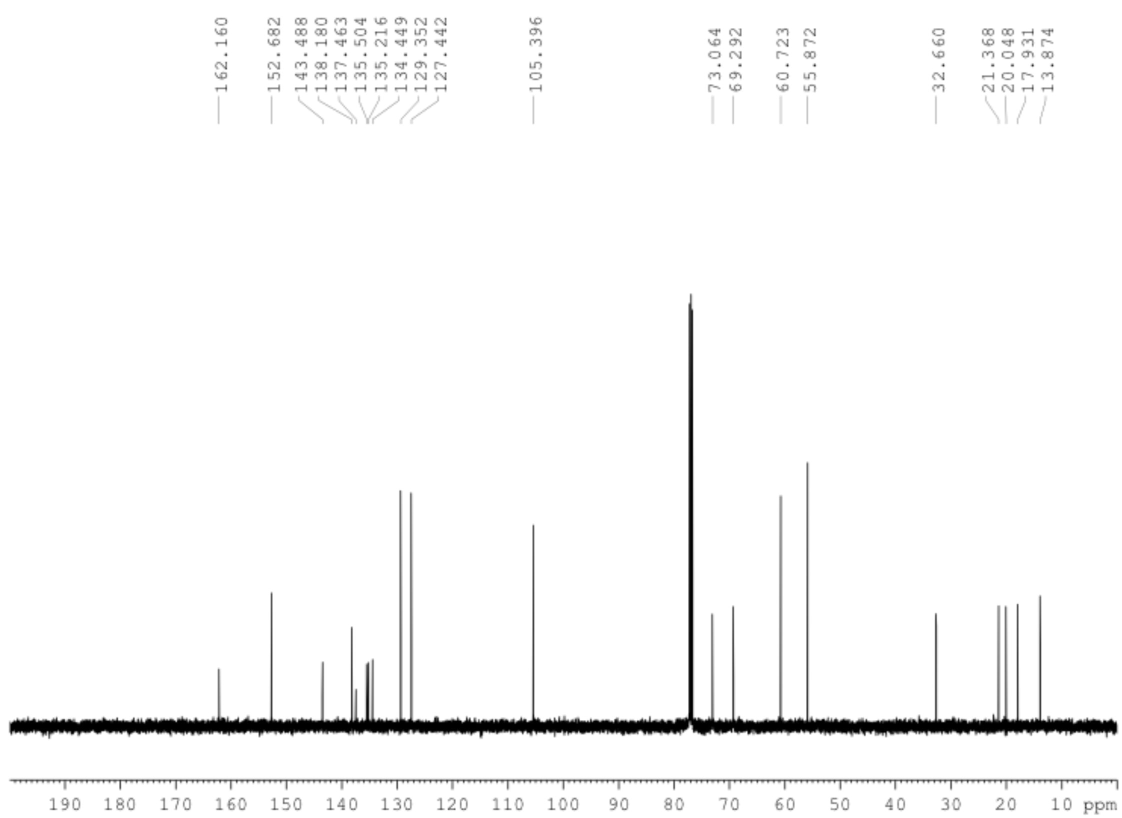
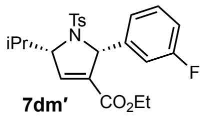
138.496
135.041
134.310
133.766
129.475
127.561
122.029
108.610
107.749
100.941
73.154
68.978
60.681
32.863
21.401
20.096
17.992
13.843
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm



7dl'

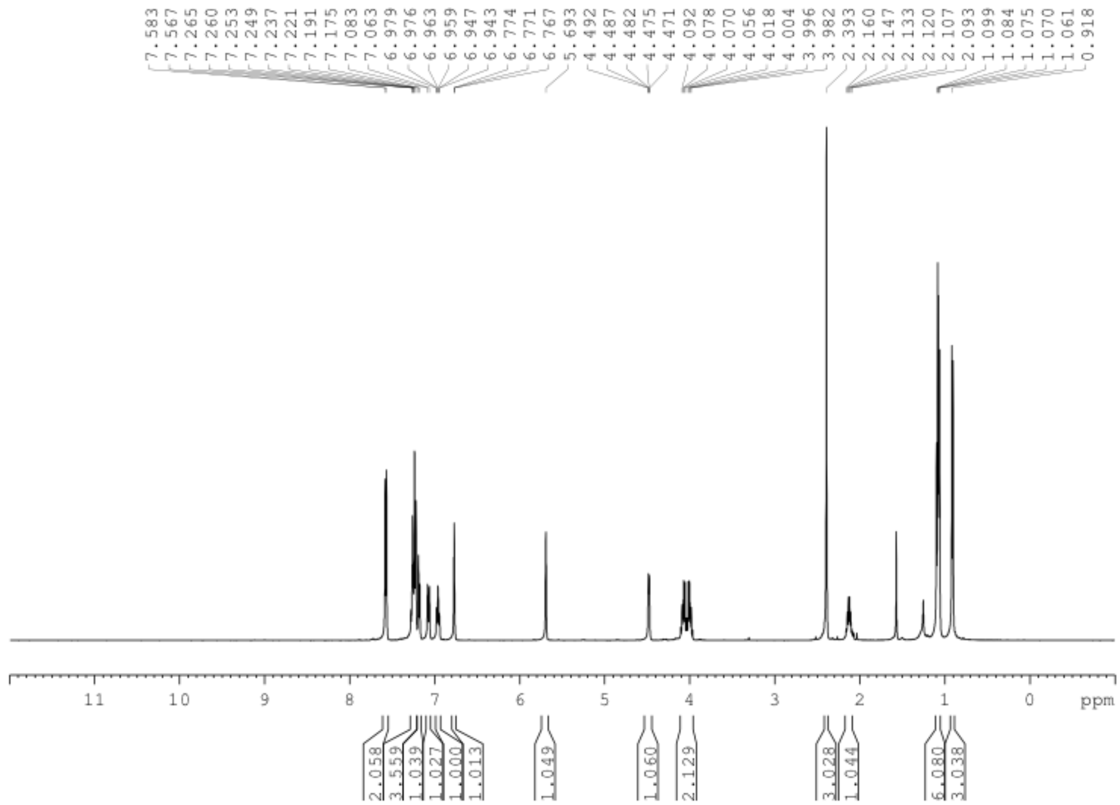




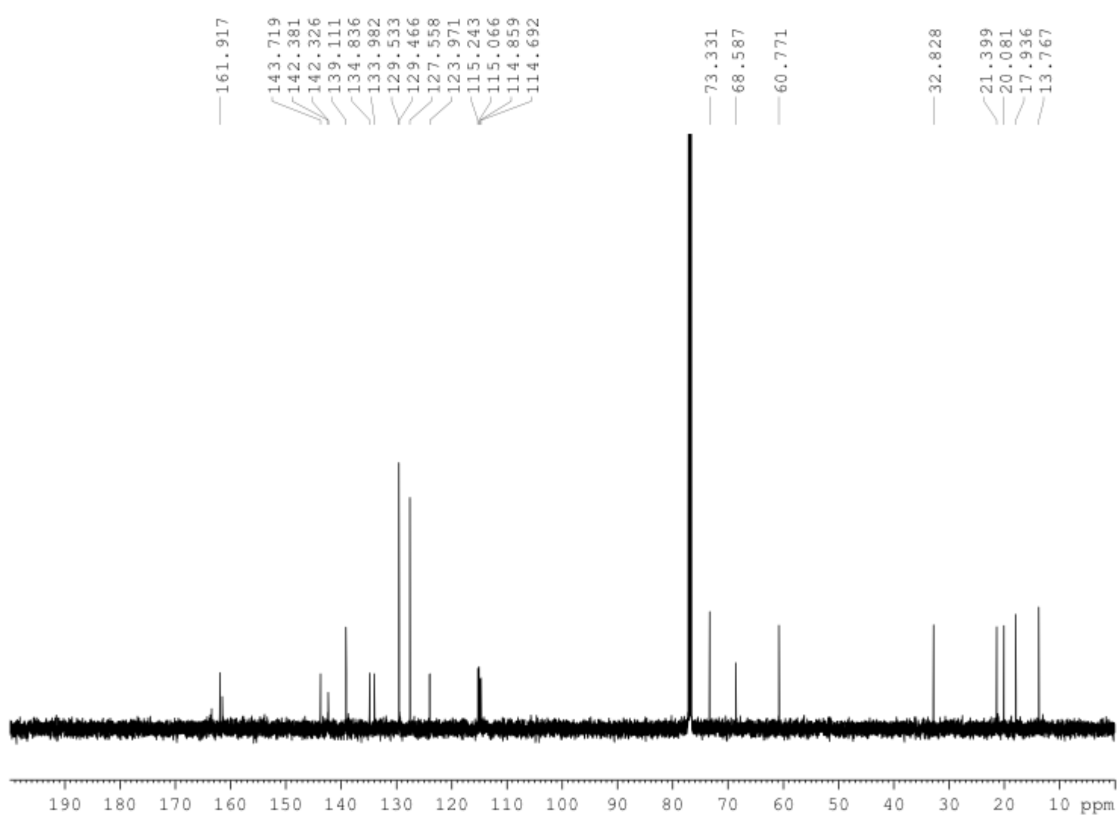


iPr
N
Ts
F
CO2Et

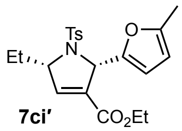
7dm′



7.583
7.567
7.265
7.260
7.253
7.249
7.237
7.221
7.191
7.175
7.083
7.063
6.979
6.976
6.963
6.959
6.947
6.943
6.774
6.771
6.767
5.693
4.492
4.487
4.482
4.475
4.471
4.092
4.078
4.070
4.056
4.018
4.004
3.996
3.982
2.393
2.160
2.147
2.133
2.120
2.107
2.093
1.099
1.084
1.075
1.070
1.061
0.918
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.058
3.559
1.039
1.027
1.000
1.013
1.049
1.060
2.129
3.028
1.044
6.080
3.038

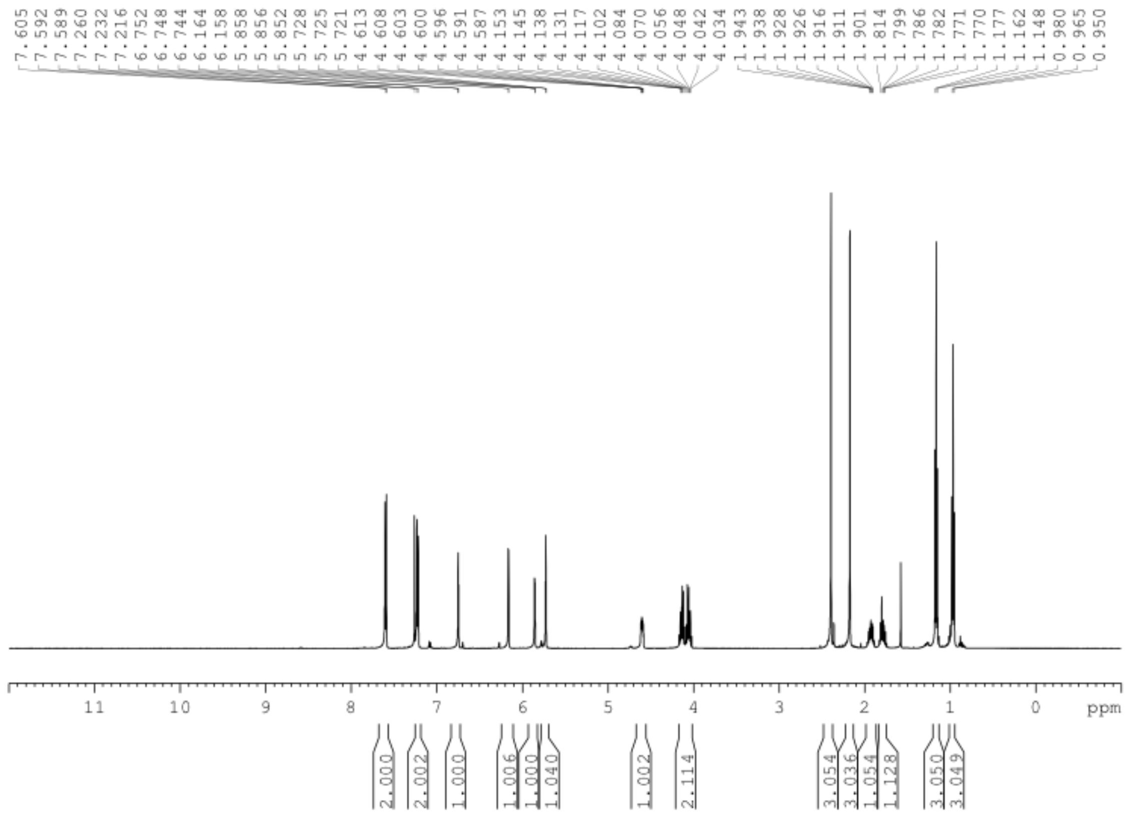


161.917
143.719
142.381
142.326
139.111
134.836
133.982
129.533
129.466
127.558
123.971
115.243
115.066
114.859
114.692
73.331
68.587
60.771
32.828
21.399
20.081
17.936
13.767
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

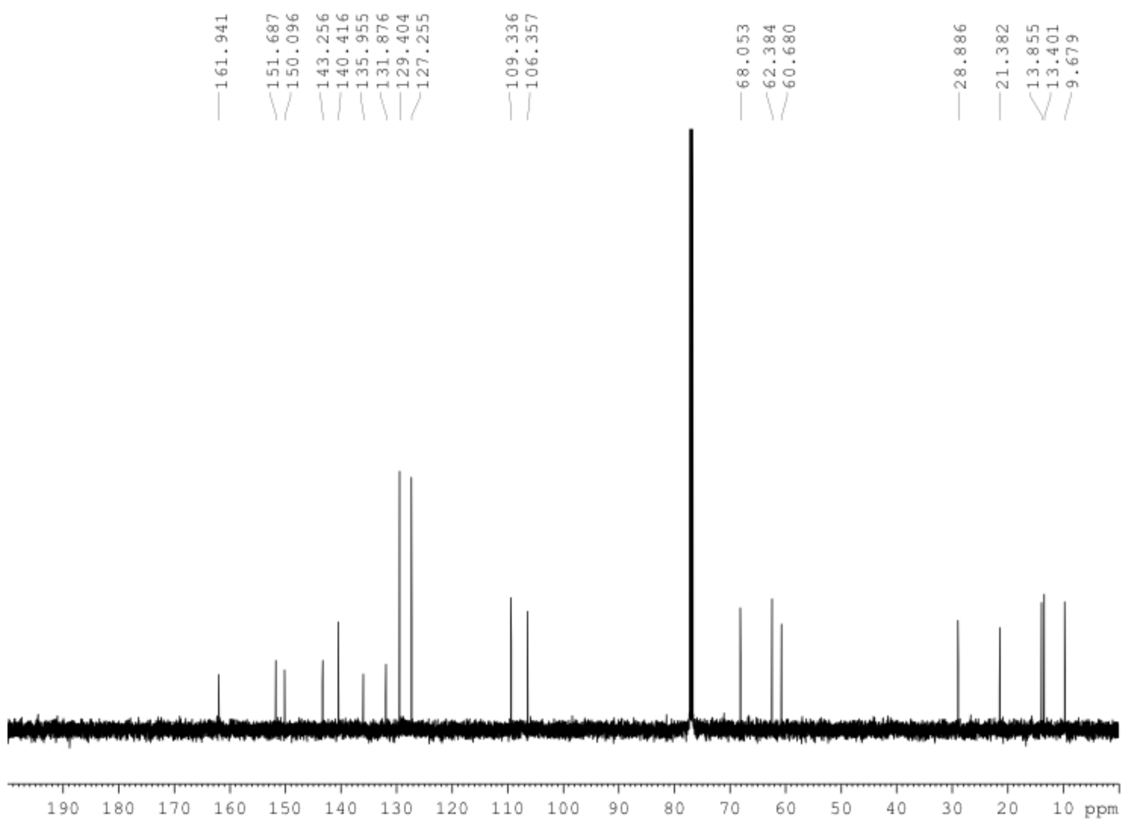


Ts
N
O
Et
CO$_2$Et

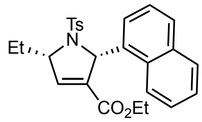
7ci'



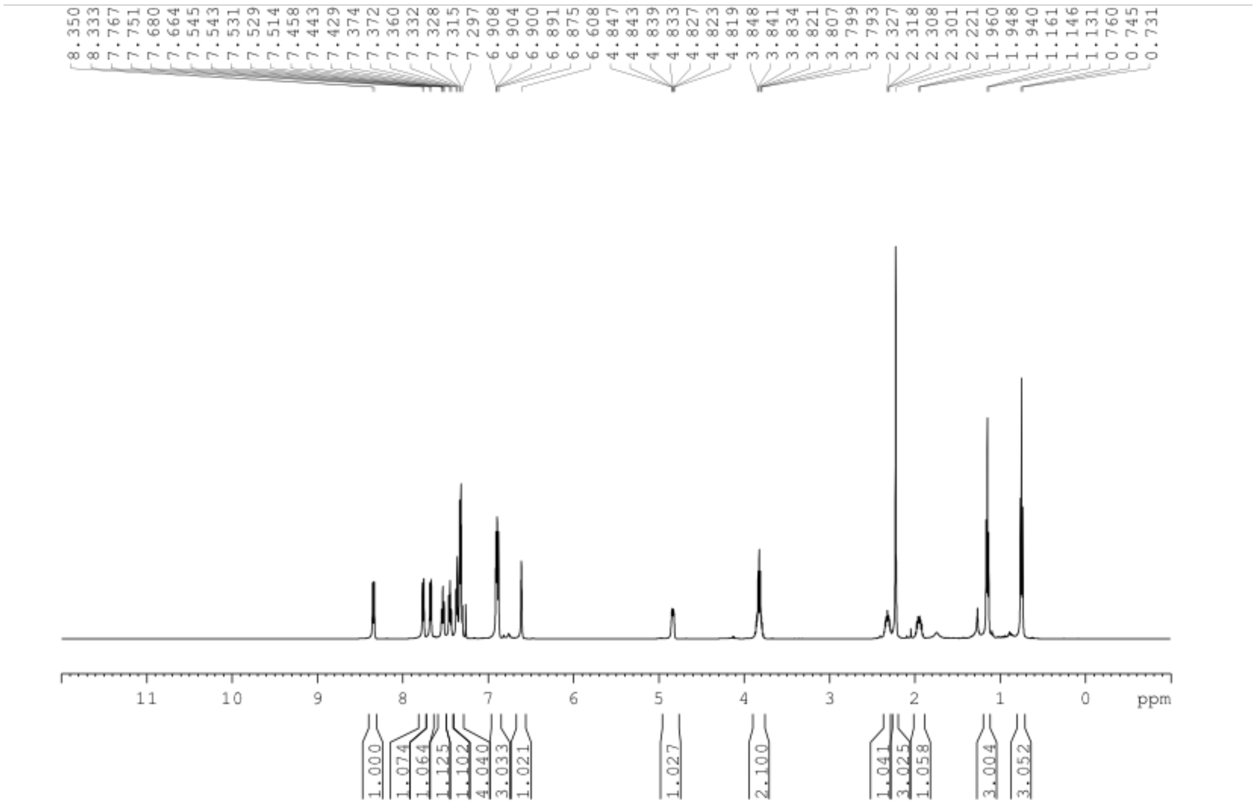
7.605 7.592 7.589 7.260 7.232 7.216 6.752 6.748 6.744 6.164 6.158 5.858 5.856 5.852 5.728 5.725 5.721 4.613 4.608 4.603 4.600 4.596 4.591 4.587 4.153 4.145 4.138 4.131 4.117 4.102 4.084 4.070 4.056 4.048 4.042 4.034 1.943 1.938 1.928 1.926 1.916 1.911 1.901 1.814 1.799 1.786 1.782 1.771 1.770 1.177 1.162 1.148 0.980 0.965 0.950
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.000 2.002 1.000 1.006 1.000 1.040 1.002 2.114 3.054 3.036 1.054 1.128 3.050 3.049



161.941 151.687 150.096 143.256 140.416 135.955 131.876 129.404 127.255 109.336 106.357 68.053 62.384 60.680 28.886 21.382 13.855 13.401 9.679
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
Et
CO2Et

7cn′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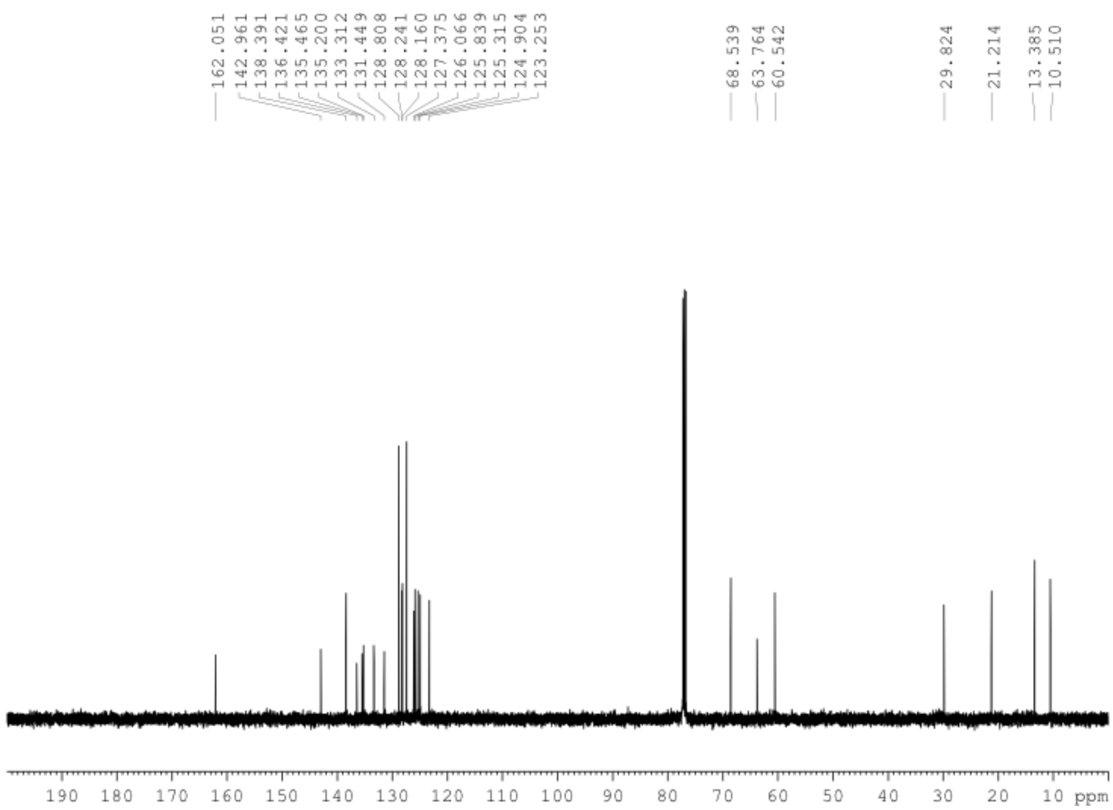
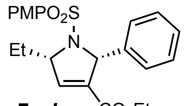
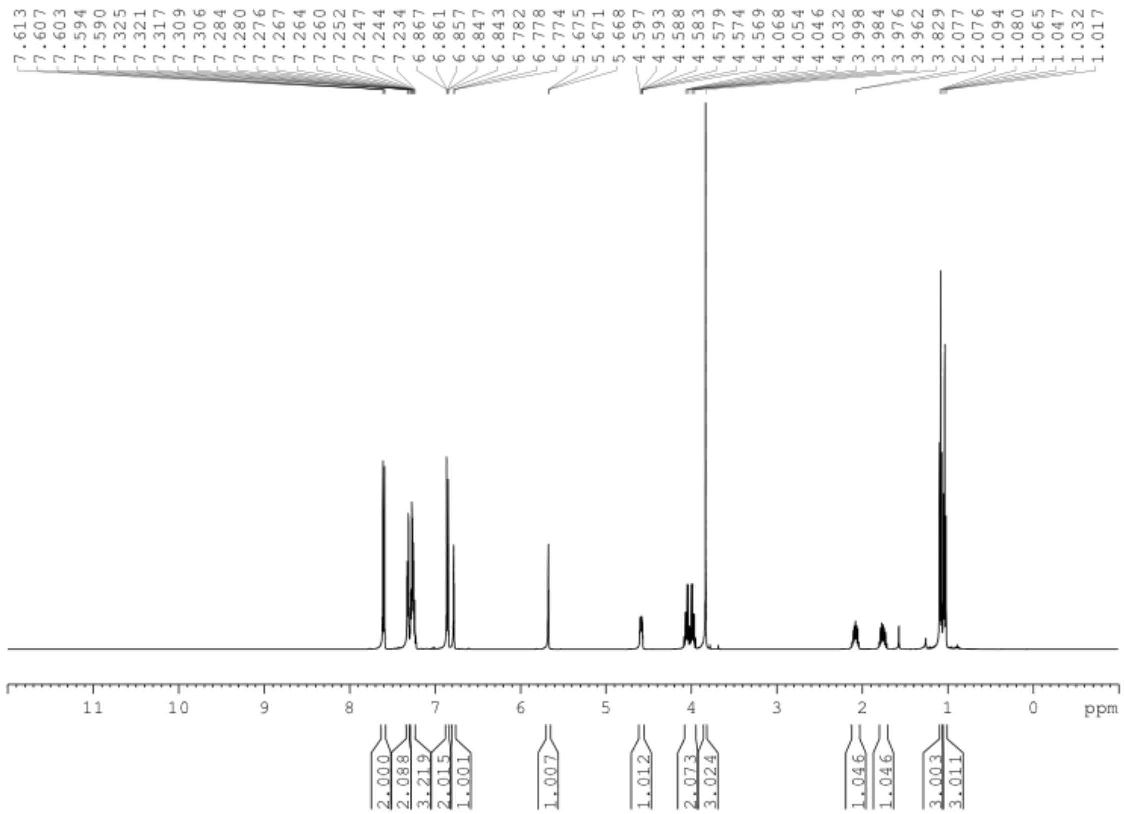
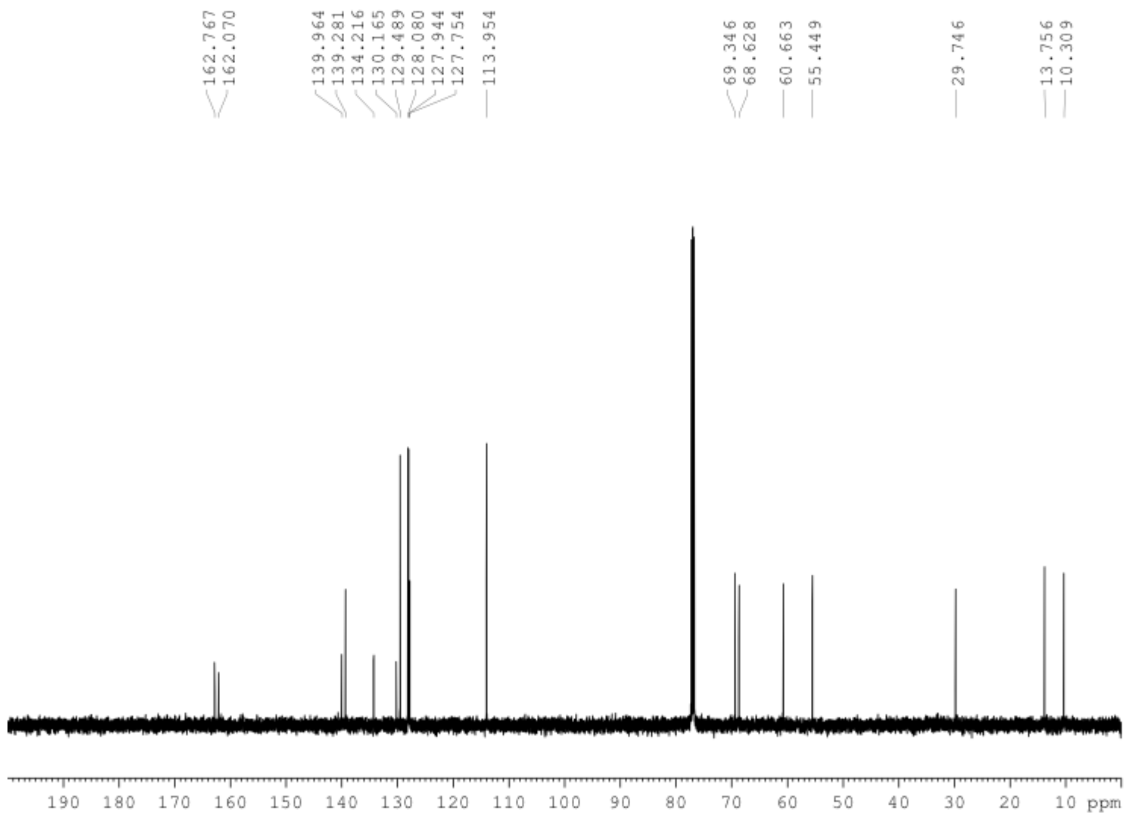
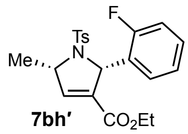
8.333
7.767
7.751
7.680
7.664
7.545
7.543
7.531
7.529
7.514
7.458
7.443
7.429
7.374
7.372
7.360
7.332
7.328
7.315
7.297
6.908
6.904
6.900
6.891
6.875
6.608
4.847
4.843
4.839
4.833
4.827
4.823
4.819
3.848
3.841
3.834
3.821
3.807
3.799
3.793
2.327
2.318
2.308
2.301
2.221
1.960
1.948
1.940
1.161
1.146
1.131
0.760
0.745
0.731
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.000
1.074
1.064
1.125
1.102
4.040
3.033
1.021
1.027
2.100
1.041
3.025
1.058
3.004
3.052


162.051
142.961
138.391
136.421
135.465
135.200
133.312
131.449
128.808
128.241
128.160
127.375
126.066
125.839
125.315
124.904
123.253
68.539
63.764
60.542
29.824
21.214
13.385
10.510
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

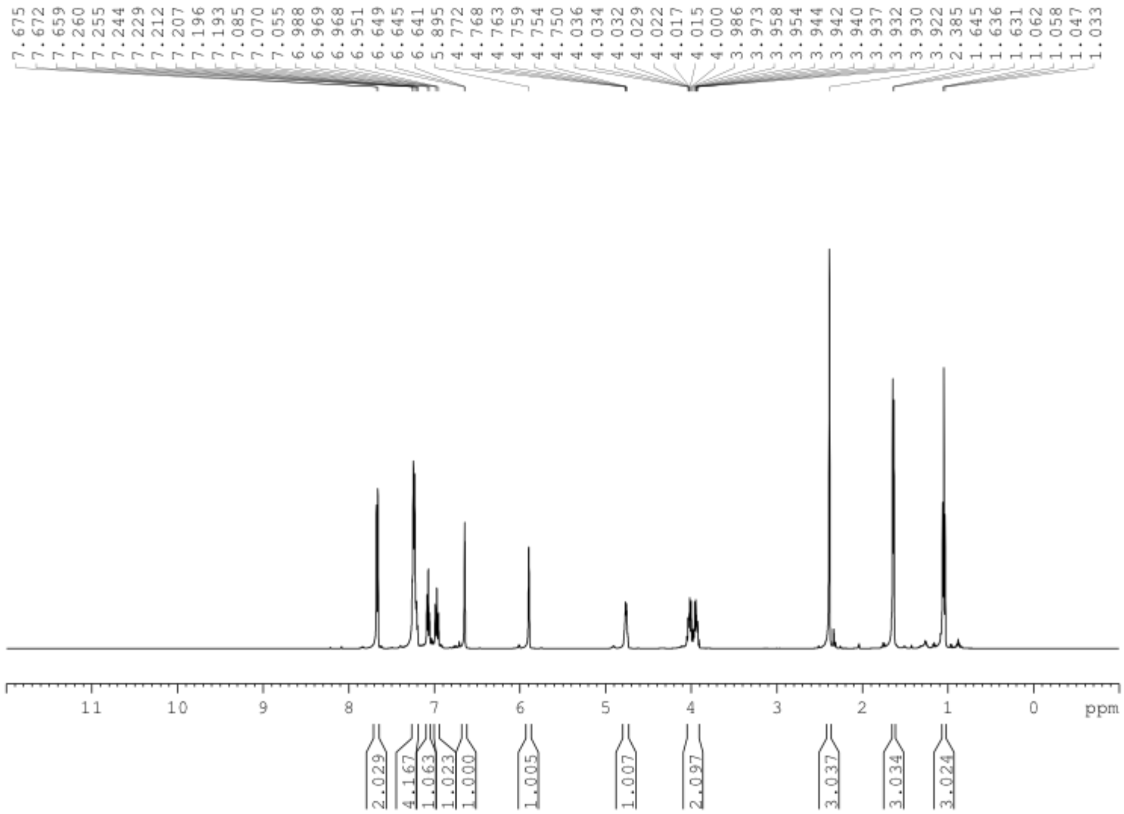

PMPO2S
N
Et
CO2Et
7co'

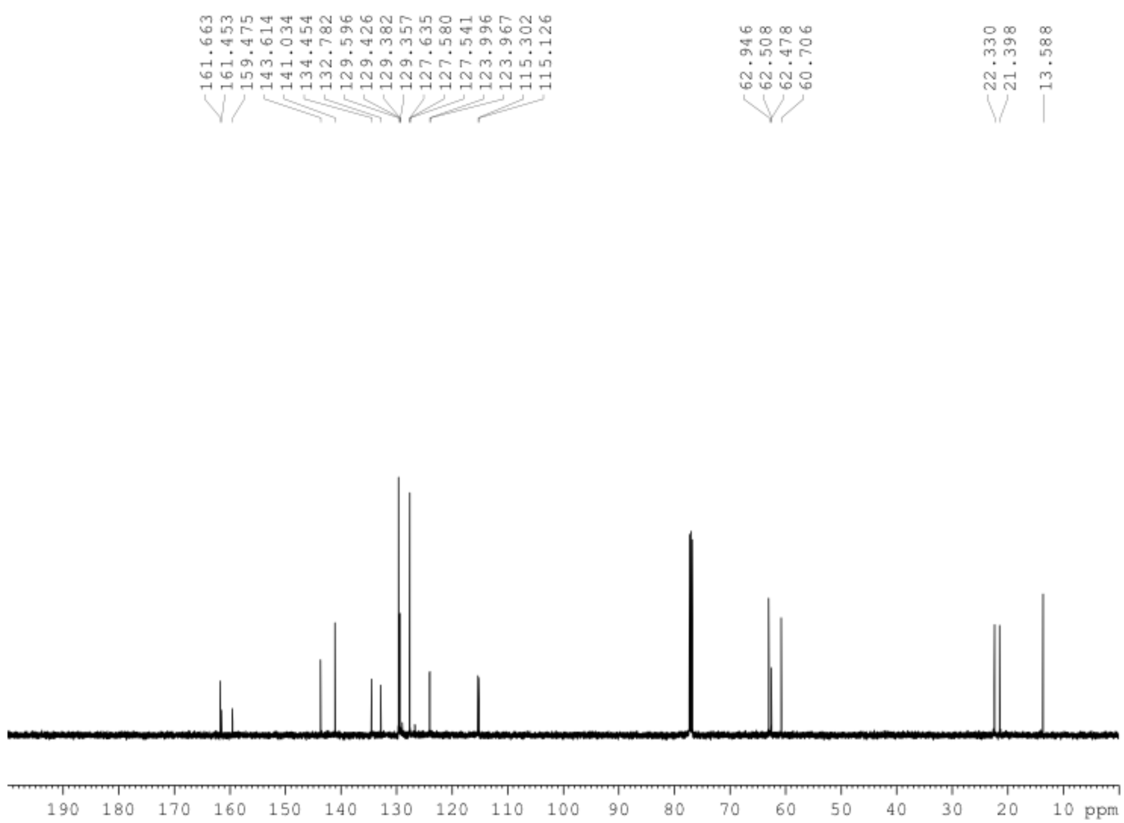

7.613
7.607
7.603
7.594
7.590
7.325
7.321
7.317
7.309
7.306
7.284
7.280
7.276
7.267
7.264
7.260
7.252
7.247
7.244
7.234
6.867
6.861
6.857
6.847
6.843
6.782
6.778
6.774
5.675
5.671
5.668
4.597
4.593
4.588
4.583
4.579
4.574
4.569
4.068
4.054
4.046
4.032
3.998
3.984
3.976
3.962
3.829
2.077
2.076
1.094
1.080
1.065
1.047
1.032
1.017
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.000
2.088
3.219
2.015
1.001
1.007
1.012
2.073
3.024
1.046
1.046
3.003
3.011

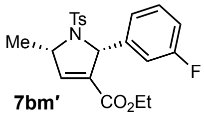

162.767
162.070
139.964
139.281
134.216
130.165
129.489
128.080
127.944
127.754
113.954
69.346
68.628
60.663
55.449
29.746
13.756
10.309
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


F
Ts
N
Me
CO2Et

7bh′

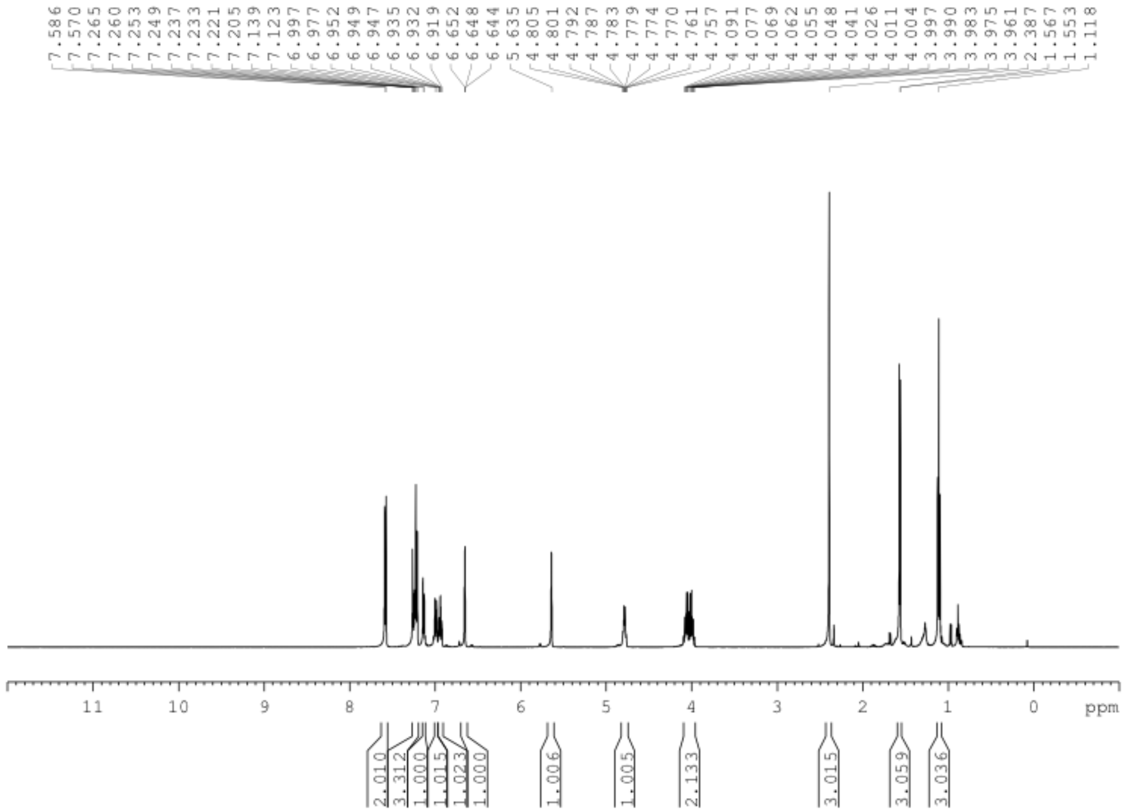

7.675
7.672
7.659
7.260
7.255
7.244
7.229
7.212
7.207
7.196
7.193
7.085
7.070
7.055
6.988
6.969
6.968
6.951
6.649
6.645
6.641
5.895
4.772
4.768
4.763
4.759
4.754
4.750
4.036
4.034
4.032
4.029
4.022
4.017
4.015
4.000
3.986
3.973
3.958
3.954
3.944
3.942
3.940
3.937
3.932
3.930
3.922
2.385
1.645
1.636
1.631
1.062
1.058
1.047
1.033
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.029
4.167
1.063
1.023
1.000
1.005
1.007
2.097
3.037
3.034
3.024


161.663
161.453
159.475
143.614
141.034
134.454
132.782
129.596
129.426
129.382
129.357
127.635
127.580
127.541
123.996
123.967
115.302
115.126
62.946
62.508
62.478
60.706
22.330
21.398
13.588
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

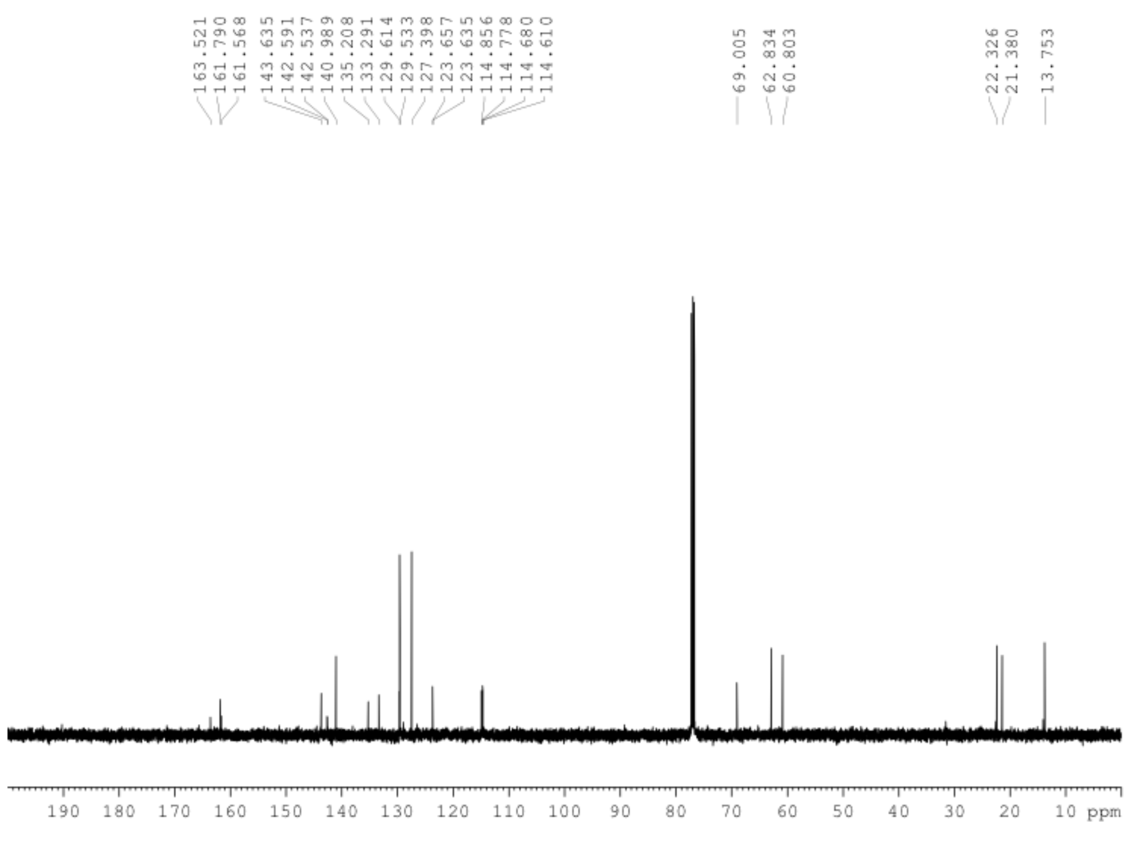


Ts
N
Me
F
CO_2Et

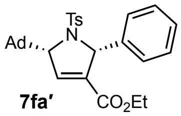
7bm′



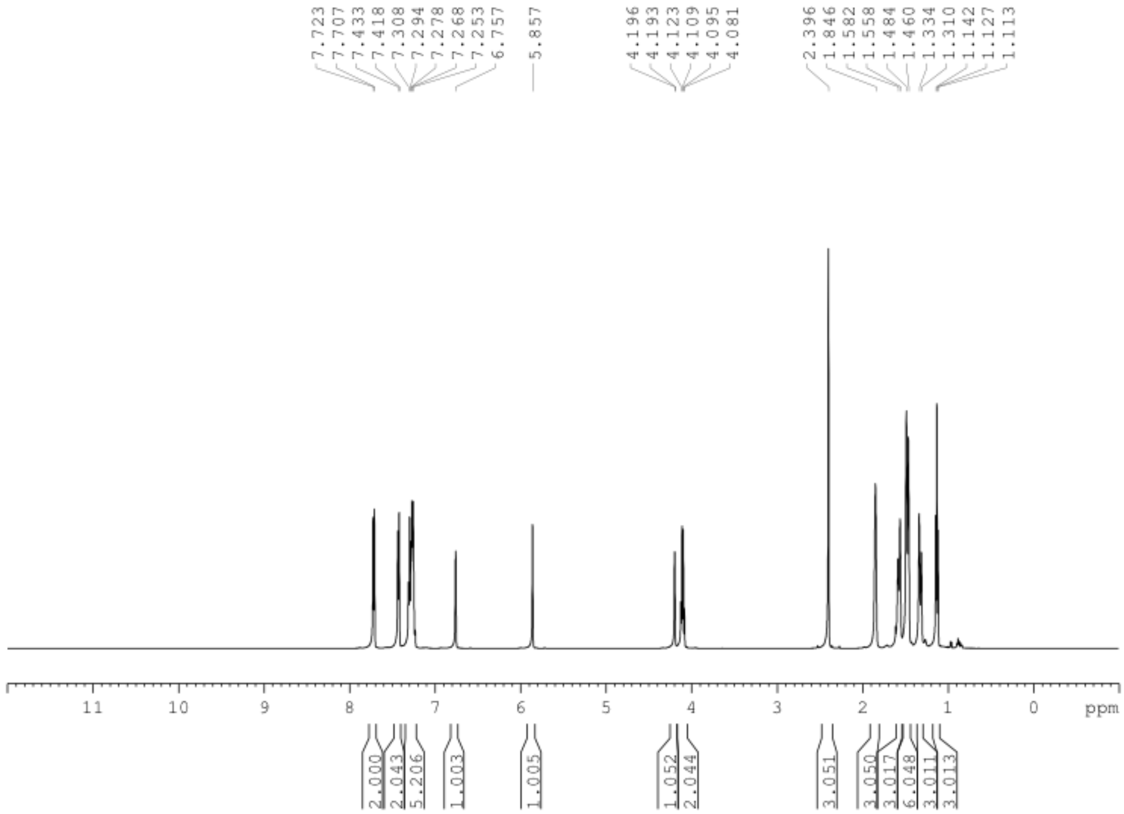
7.586
7.570
7.265
7.260
7.253
7.249
7.237
7.233
7.221
7.205
7.139
7.123
6.997
6.977
6.952
6.949
6.947
6.935
6.932
6.919
6.652
6.648
6.644
5.635
4.805
4.801
4.792
4.787
4.783
4.779
4.774
4.770
4.761
4.757
4.091
4.077
4.069
4.062
4.055
4.048
4.041
4.026
4.011
4.004
3.997
3.990
3.983
3.975
3.961
2.387
1.567
1.553
1.118
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.010
3.312
1.000
1.015
1.023
1.000
1.006
1.005
2.133
3.015
3.059
3.036



163.521
161.790
161.568
143.635
142.591
142.537
140.989
135.208
133.291
129.614
129.533
127.398
123.657
123.635
114.856
114.778
114.680
114.610
69.005
62.834
60.803
22.326
21.380
13.753
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ad
Ts
N
CO2Et

7fa'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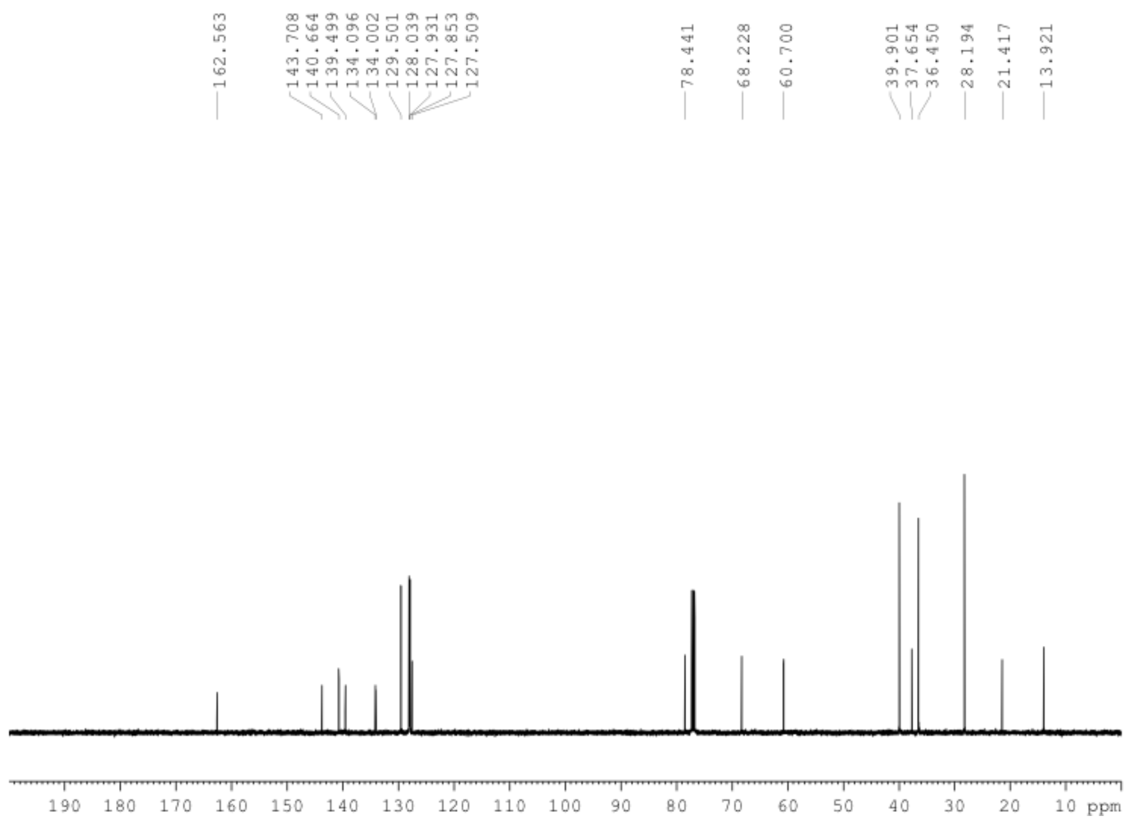
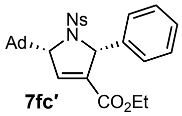
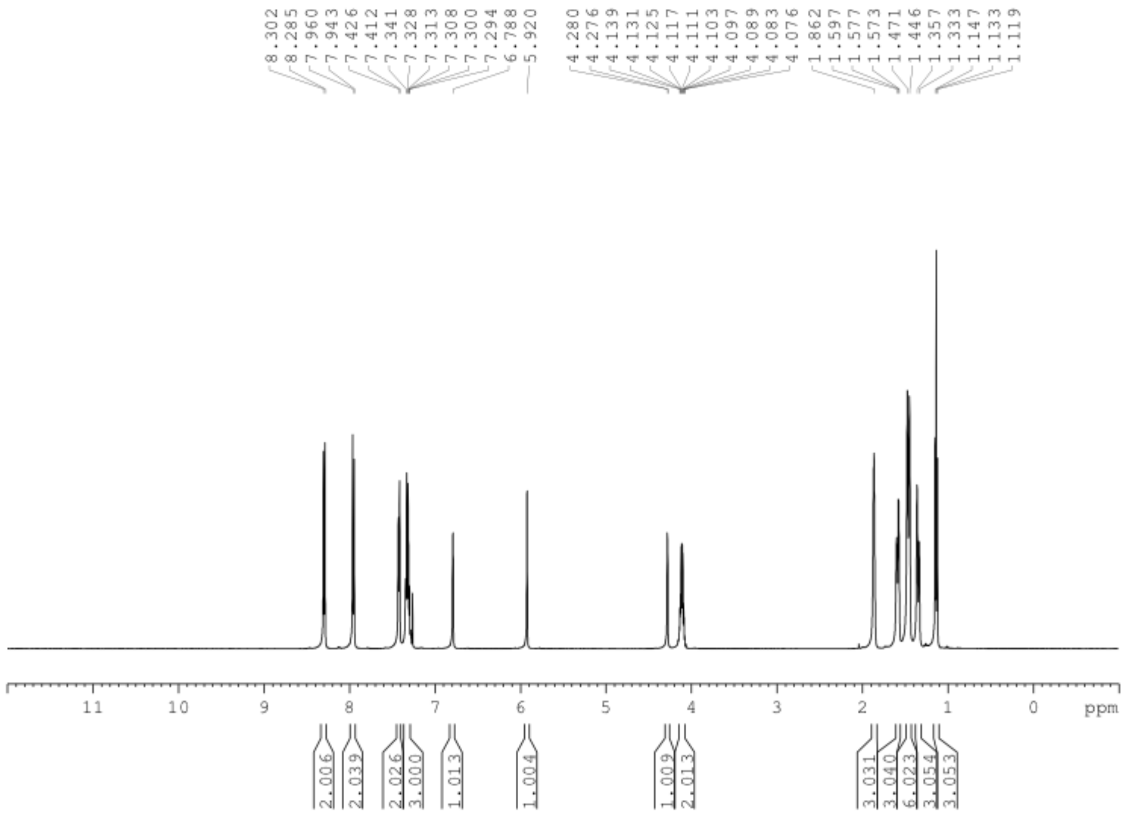
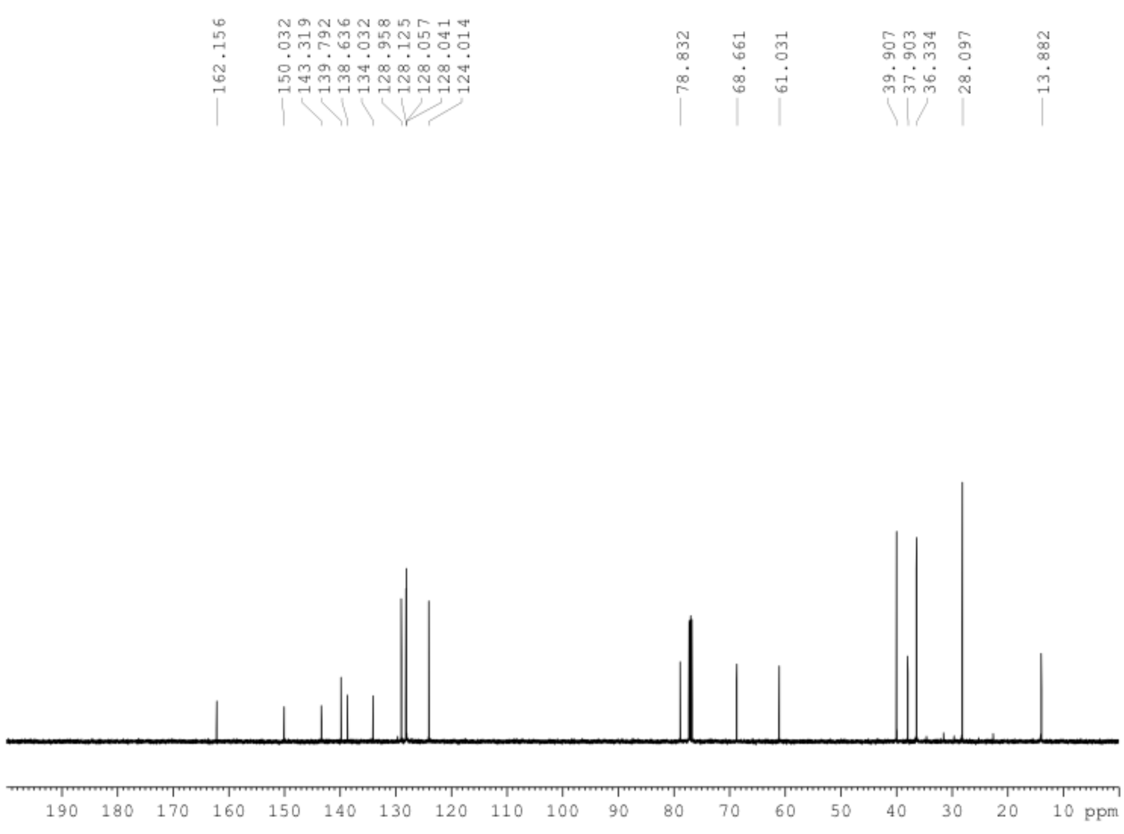
7.707
7.433
7.418
7.308
7.294
7.278
7.268
7.253
6.757
5.857
4.196
4.193
4.123
4.109
4.095
4.081
2.396
1.846
1.582
1.558
1.484
1.460
1.334
1.310
1.142
1.127
1.113
2.000
2.043
5.206
1.003
1.005
1.052
2.044
3.051
3.050
3.017
6.048
3.011
3.013
ppm


162.563
143.708
140.664
139.499
134.096
134.002
129.501
128.039
127.931
127.853
127.509
78.441
68.228
60.700
39.901
37.654
36.450
28.194
21.417
13.921
ppm


Ns
N
Ad
CO2Et

7fc′


8.302
8.285
7.960
7.943
7.426
7.412
7.341
7.328
7.313
7.308
7.300
7.294
6.788
5.920
4.280
4.276
4.139
4.131
4.125
4.117
4.111
4.103
4.097
4.089
4.083
4.076
1.862
1.597
1.577
1.573
1.471
1.446
1.357
1.333
1.147
1.133
1.119
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.006
2.039
2.026
3.000
1.013
1.004
1.009
2.013
3.031
3.040
6.023
3.054
3.053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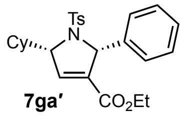
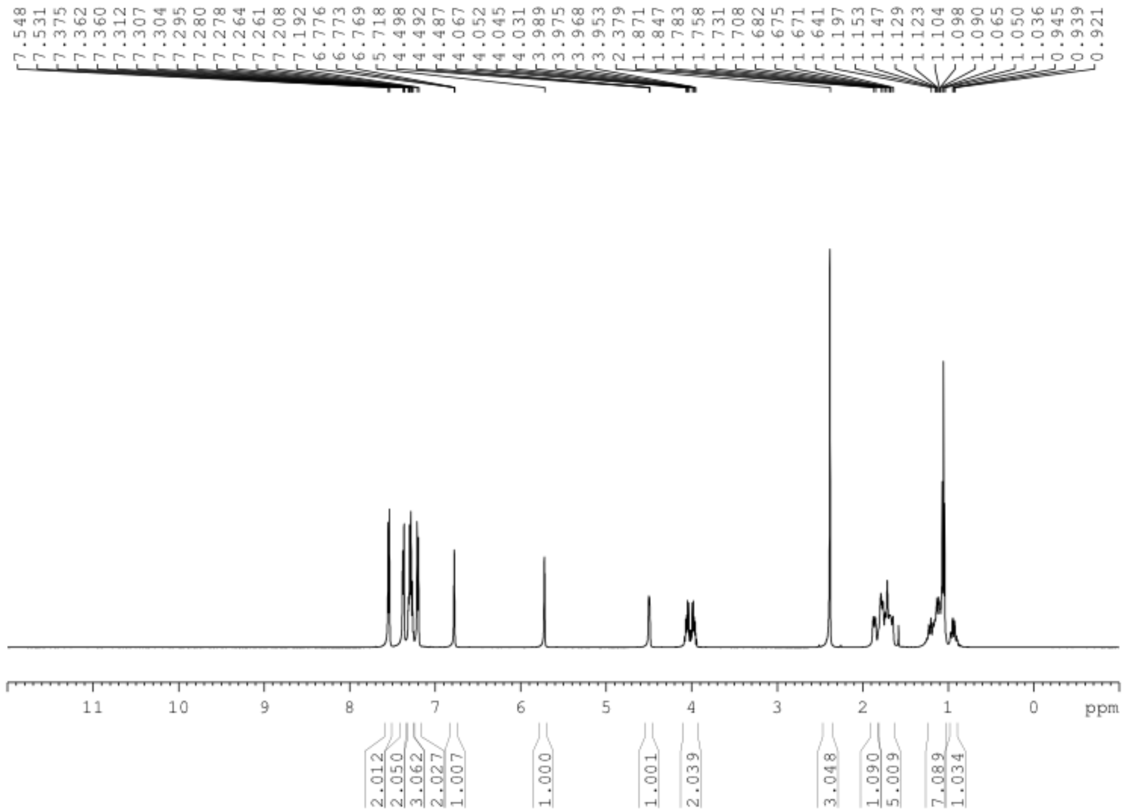
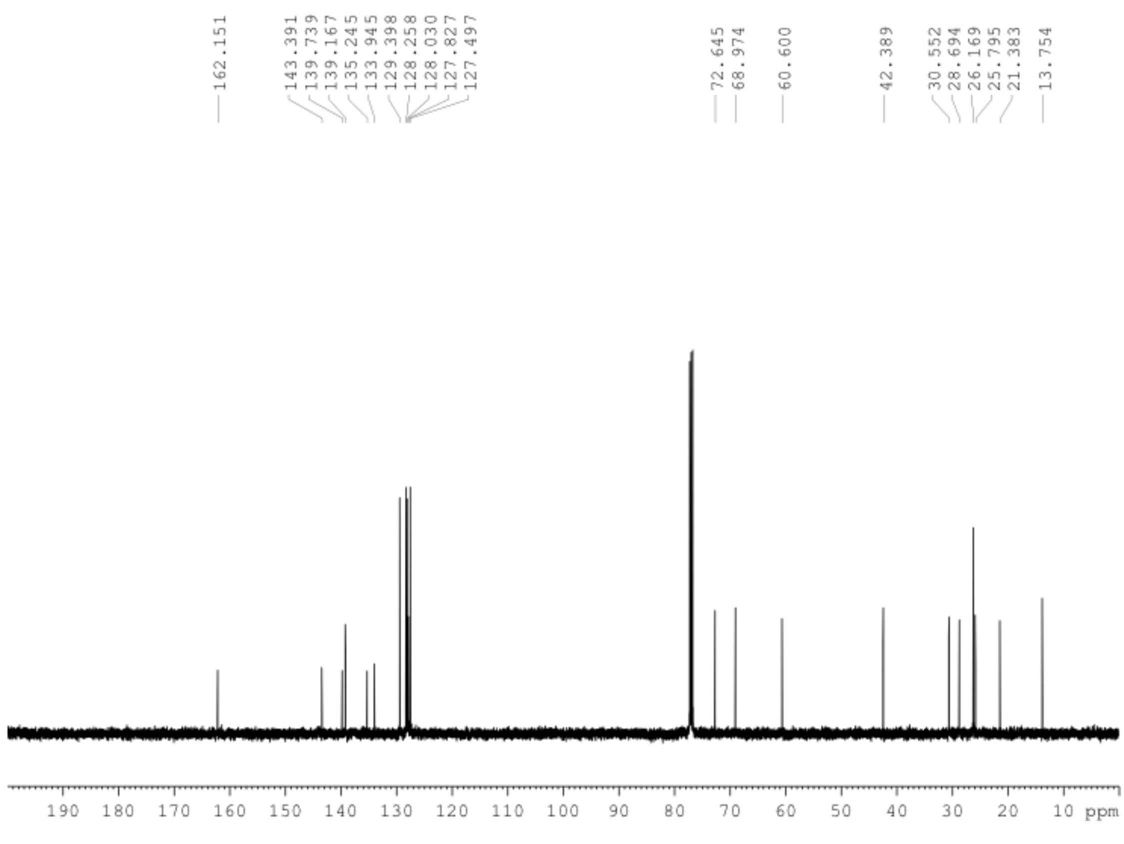
150.032
143.319
139.792
138.636
134.032
128.958
128.125
128.057
128.041
124.014
78.832
68.661
61.031
39.907
37.903
36.334
28.097
13.882
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm


Cy
Ts
N
CO2Et

7ga'


7.548
7.531
7.375
7.362
7.360
7.312
7.307
7.304
7.295
7.280
7.278
7.264
7.261
7.208
7.192
6.776
6.773
6.769
5.718
4.498
4.492
4.487
4.067
4.052
4.045
4.031
3.989
3.975
3.968
3.953
2.379
1.871
1.847
1.783
1.758
1.731
1.708
1.682
1.675
1.671
1.641
1.197
1.153
1.147
1.129
1.123
1.104
1.098
1.090
1.065
1.050
1.036
0.945
0.939
0.921
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.012
2.050
3.062
2.027
1.007
1.000
1.001
2.039
3.048
1.090
5.009
7.089
1.034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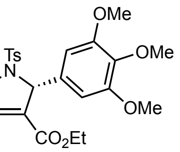
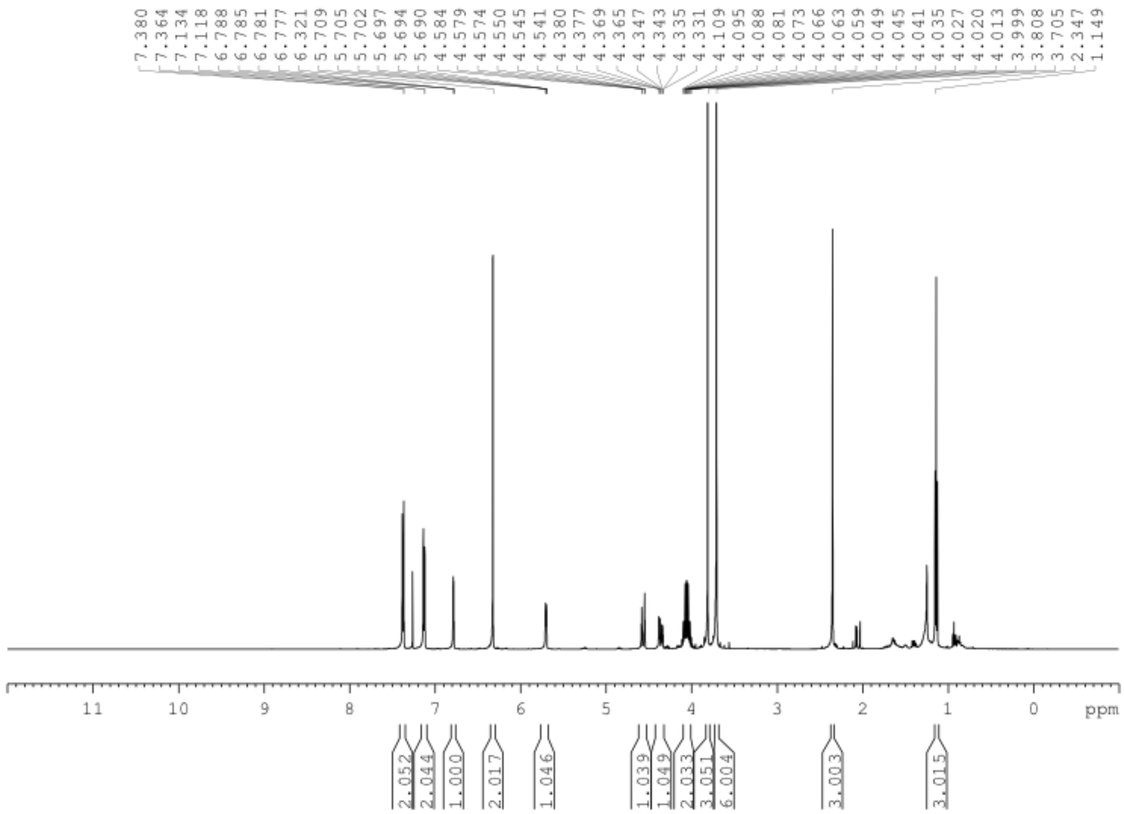
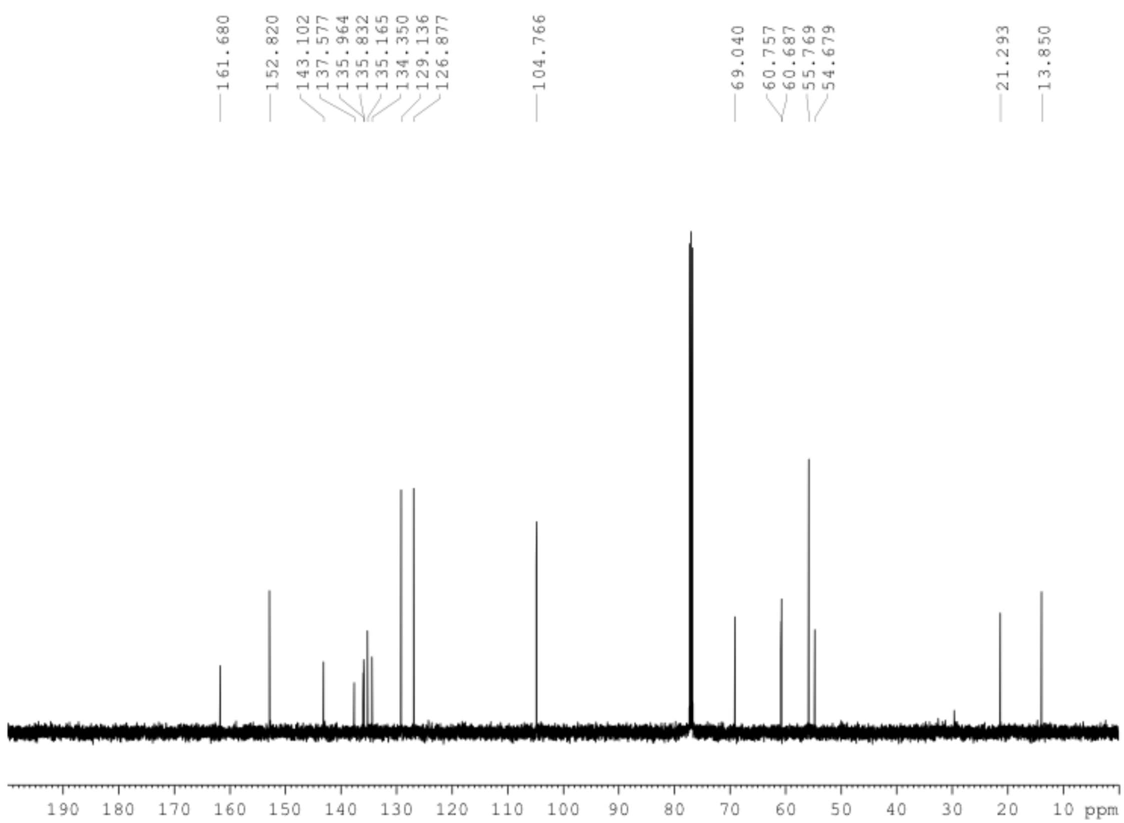
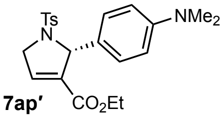
139.739
139.167
135.245
133.945
129.398
128.258
128.030
127.827
127.497
72.645
68.974
60.600
42.389
30.552
28.694
26.169
25.795
21.383
13.754
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
OMe
OMe
OMe
CO2Et

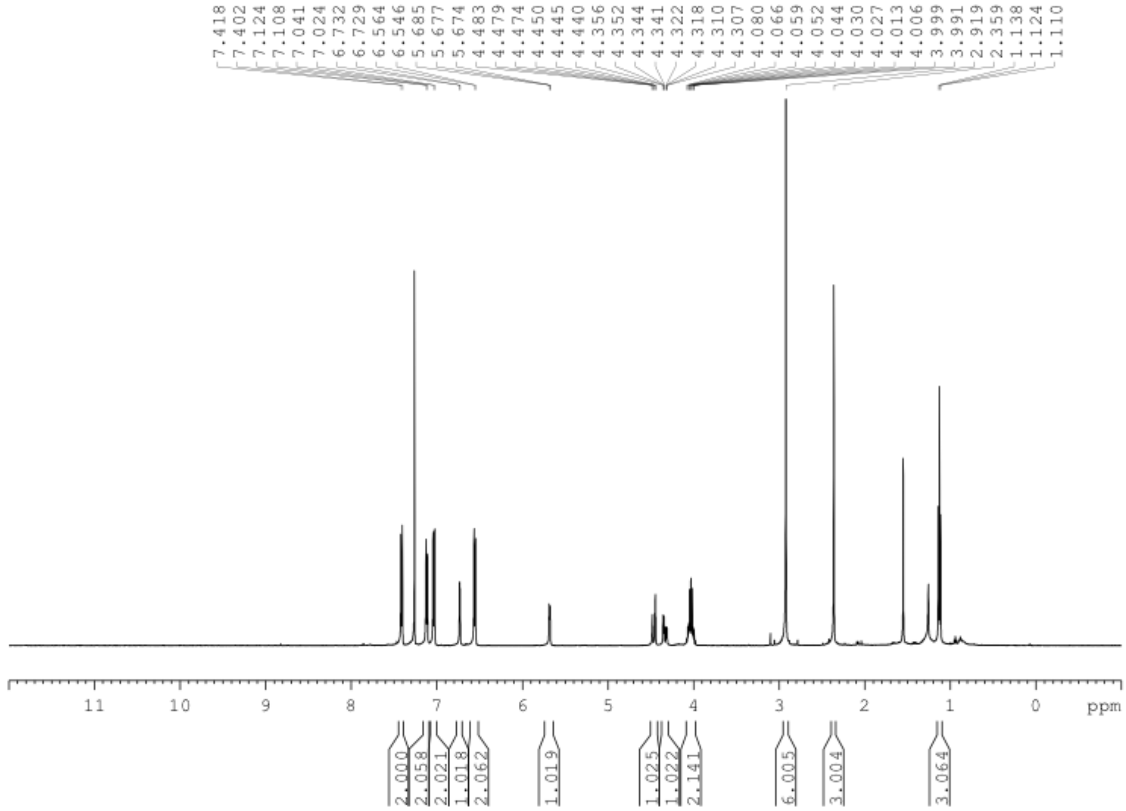
7al′


7.380 7.364 7.134 7.118 6.788 6.785 6.781 6.777 6.321 5.709 5.705 5.702 5.697 5.694 5.690 4.584 4.579 4.574 4.550 4.545 4.541 4.380 4.377 4.369 4.365 4.347 4.343 4.335 4.331 4.109 4.095 4.088 4.081 4.073 4.066 4.063 4.059 4.049 4.045 4.041 4.035 4.027 4.020 4.013 3.999 3.808 3.705 2.347 1.149
11 10 9 8 7 6 5 4 3 2 1 0 ppm
2.052 2.044 1.000 2.017 1.046 1.039 1.049 2.033 3.051 6.004 3.003 3.015


161.680 152.820 143.102 137.577 135.964 135.832 135.165 134.350 129.136 126.877 104.766 69.040 60.757 60.687 55.769 54.679 21.293 13.850
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts
N
NMe2
CO2Et

7ap′


7.418
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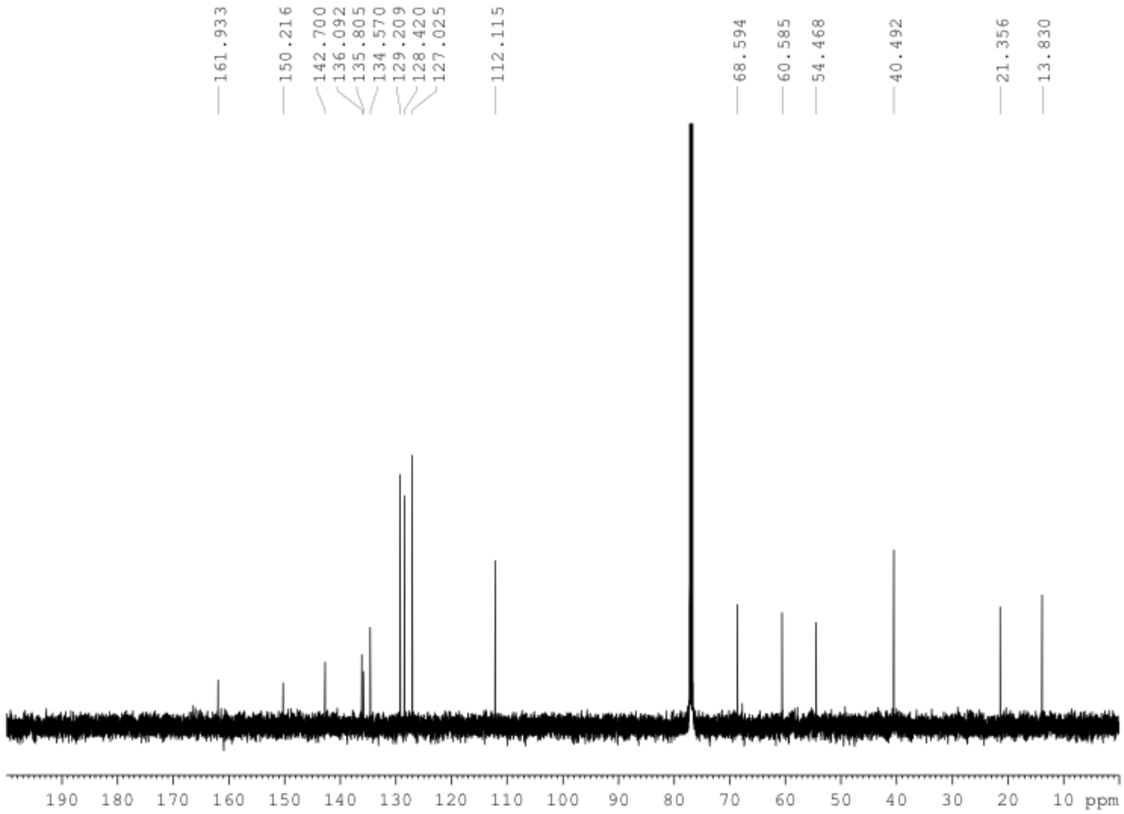
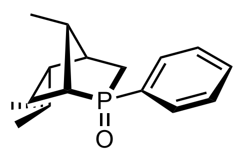
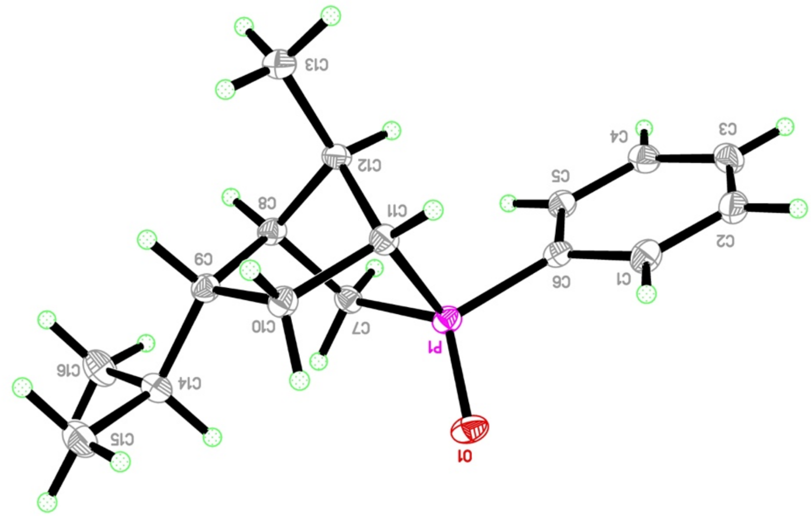
7.108
7.041
7.024
6.732
6.729
6.564
6.546
5.685
5.677
5.674
4.483
4.479
4.474
4.450
4.445
4.440
4.356
4.352
4.344
4.341
4.322
4.318
4.310
4.307
4.080
4.066
4.059
4.052
4.044
4.030
4.027
4.013
4.006
3.999
3.991
2.919
2.359
1.138
1.124
1.110
11
10
9
8
7
6
5
4
3
2
1
0
ppm
2.000
2.058
2.021
1.018
2.062
1.019
1.025
1.022
2.141
6.005
3.004
3.064

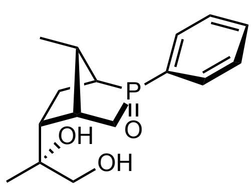

161.933
150.216
142.700
136.092
135.805
134.570
129.209
128.420
127.025
112.115
68.594
60.585
54.468
40.492
21.356
13.830
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

7. ORTEP Representations of the Phosphine Oxides 3b and 3c



3b derived from (*S*)-carvone





3c derived from (*R*)-carvone