Supporting Information for

Chiral Metal Phosphate Catalysis: Highly Asymmetric Hetero-Diels-Alder Reactions

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General Considerations: All reactions were carried out in screw-cap test tubes with magnetic stirring. Anhydrous dichloromethane and methanol were purchased from sigma-aldrich and used without further purification. Substituted BINOL phosphoric acids were prepared from commercially available chiral BINOL. Molecular Sieves (4Å) were flame-dried under high vacuum before use. Keto eaters and benzyl-protected isatins were purchased from commercial sources or prepared according to the literatures[1].

Thin layer chromatography was performed on Merck TLC plates (silica gel 60 F254). Flash column chromatography was performed with Merck silica gel (230-400 mesh). Enantiomeric excess (ee) was determined using a Varian Prostar HPLC with a 210 binary pump and a 335 diode-array detector. Column conditions are reported in the experimental section below. Optical rotations were performed on a Rudolph Research Analytical Autopol IV polarimeter (λ589) using a 700-μL cell with a path length of 1 dm. ^{1}H NMR was recorded on a Varian Inova 600 Spectrometer (600 MHz for ^{1}H) or a Varian Inova 500 Spectrometer (500 MHz for ^{1}H) or a Varian Inova 400 Spectrometer (400 MHz for ^{1}H) or a Bruker Avance DPX-250 instrument (250 MHz for ^{1}H). ^{13}C NMR was recorded on a Bruker Avance DPX-250 instrument (62.5 MHz for ^{13}C) or a Varian Inova 400 Sectrometer (100 MHz for ^{13}C) or a Varian Inova 500 Spectrometer (125 MHz for ^{13}C). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). The HRMS data were measured on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization. MALDI-MS data was measured on a Bruker Daltconics MALDI/TOF Autoflex spectrometer using Nitrogen laser. Compounds described in the literature were characterized by comparing their spectral data to the reported values. The absolute configurations of compound **3d**, **3i** were determined to be "(R)" by comparison of the optical rotation values to the reported literature value.[2,4] The absolute configuration of compound **3a** was determined to be "(S)" by comparison of the optical rotation value to the reported literature value.[4] The absolute configurations of **5b** was determined by X-ray structure analysis. The absolute configurations of all the other compounds were tentatively assigned by analogy. The SERS experiments were carried out on the Raman setup. The exposure time was 10 s and accumulation number was 3. The Raman spectra were measured in the frequency range from 1400 to 2100 cm^{-1}.

Catalyst Preparation

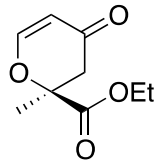
To a flame-dried 50 mL flask was added 120 mg (*R*) 1-naphthyl-BINOL phosphoric acid[3] (0.2 mmol) and 10.2 mg $Ca(OMe)_2$ (0.1 mmol), followed by 10 mL anhydrous MeOH and 10 mL

anhydrous DCM. The mixture was stirred overnight at room temperature. Then solvent was removed to afford the Ca[**P4**]$_2$ as a white solid.

^{1}H NMR (600 MHz, Acetone-d6) δ 8.5 - 7.0 (m,48H) ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 148.62, 148.47, 136.38, 134.11 134.02, 133.54, 133.24, 132.90, 131.40, 129.82, 129.04, 128.96, 127.92, 127.50, 127.07, 126.61, 126.12, 123.63. MALDI-MS $[M+H]^+$: Found 1239.615 with α-cyano-4-hydroxy-cinnamic acid as matrix.

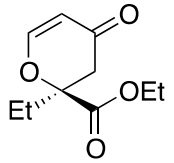
General Procedure for enantioselective HDA reactions of alpha-keto esters and isatins

To a test tube was weighted 80 mg Molecular Sieves (4Å), 6.2 mg Ca[**P4**]$_2$ (2.5 mol%), 0.2 mmol alpha-keto ester **1** or isatin **4**, followed by 4 mL of DCM. Then 0.26 mmol of Danishefsky's diene was added via micro syringe at room temperature. The mixture was stirred at room temperature for indicated time, after which it was cooled down to 0°C and 2 mL of 2.0 M HCl aqueous solution (or two drops of TFA) was added. The mixture was allowed to warm to room temperature in 1 h, and stirred for another 1 hour at room temperature. The reaction was quenched by 1.0 M $NaHCO_3$ aqueous solution and the aqueous layer was washed with DCM (2 x 2.0 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to afford oil, which is purified by silica gel chromatography (6:1 Hexane:EA) to deliver the desired product.



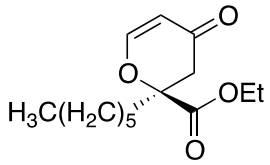
(*S*)-Ethyl 2-methyl-4-oxo-3,4-dihydro-2H-pyran-2-carboxylate (3a)[4]: 95% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 7.52 min, t_R(minor) = 6.89 min. $[\alpha]^{25}_D$= +110.2° (c = 0.293 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.0 Hz, 1H), 5.40 (dd, *J* = 6.0 Hz, 0.8 Hz, 1H), 4.20 (q, *J* = 7.1 Hz, 2H), 2.99 (dd, *J* = 16.5 Hz, 0.8 Hz, 1H), 2.66 (d, *J* = 16.8 Hz, 1H), 1.63 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.4, 170.5, 161.1, 107.3, 83.1, 61.9, 44.4, 24.5, 14.2. ^{1}H NMR and ^{13}C NMR match the reported value.



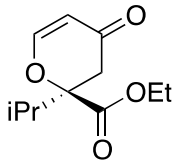
Ethyl 2-ethyl-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3b): 95 % yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 6.67 min, t_R(minor) = 6.20 min. $[\alpha]^{25}_D$= +164.5° (c = 0.295 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 (d, *J* = 6.1 Hz, 1H), 5.37 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.89 (dd, *J* = 16.8, 1.0 Hz, 1H), 2.67 (d, *J* = 16.7 Hz, 1H), 1.94 (q, *J* = 7.5 Hz, 2H), 1.22 (t, *J* = 7.1 Hz, 3H), 0.94 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.42, 170.62, 162.29, 107.55, 86.04, 62.36, 43.12, 30.83, 14.26, 7.73. HRMS (ESI) Calcd for $[M+H]^+$ 199.09649, Found 199.09701.



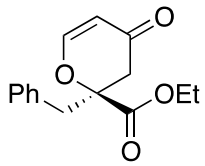
Ethyl 2-hexyl-4-oxo-3,4-dihydro-2H-pyran-2-carboxylate (3c): 94% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 5.69 min, t_R(minor) = 5.11 min. $[\alpha]^{25}_D$= +101.4° (c = 0.455 $CHCl_3$). ^{1}H NMR (600 MHz, CDCl3) δ 7.35 (d, *J* = 6.0 Hz, 1H), 5.38 (d, J = 6.0 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 2.91 (d, J = 16.7 Hz, 1H), 2.69 (d, J = 16.7 Hz, 1H), 1.89 (dd, J = 8.7, 7.2 Hz, 2H), 1.32 – 1.22 (m, 11H), 0.85 (t, J = 6.8 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.47, 170.76, 162.31, 107.59, 85.83, 62.41, 43.56, 37.68, 31.64, 29.21, 23.24, 22.65, 14.31, 14.20. HRMS (ESI) Calcd for $[M+H]^+$ 255.15909, Found 255.15915.



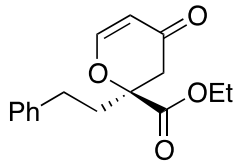
(*R*)-ethyl 2-isopropyl-4-oxo-3,4-dihydro-2H-pyran-2-carboxylate (3d)[2]: 95% yield, 90% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 6.19 min, t_R(minor) = 5.71 min. $[\alpha]^{25}_D$= +155.6° (c = 0.310 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 6.0 Hz, 1H), 5.38 (d, *J* = 6.0 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 2.87 (d, *J* = 16.5 Hz, 1H), 2.73 (d, *J* = 16.5 Hz, 1H), 2.20 (m, 1H),1.24 (t, *J* = 7.2 Hz, 3H), 1.00 (d, *J* = 6.6 Hz, 3H), 0.98 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) *δ* 190.8, 170.6, 162.6, 107.7, 88.8, 62.3, 40.8, 35.0, 17.0, 16.8, 14.4. ^{1}H NMR and ^{13}C NMR match the reported value.



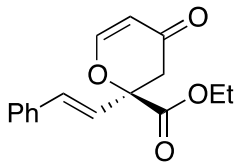
Ethyl 2-benzyl-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3e): 91% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 10.17 min, t_R(minor) = 7.76 min. $[\alpha]^{25}_D$= +103.8° (c = 0.240 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 6.3 Hz, 1H), 7.28b- 7.20 (m, 3H), 7.17 – 7.11 (m, 2H), 5.33 (dd, *J* = 6.1, 1.0 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 3.22 (d, *J* = 14.0 Hz, 1H), 3.09 (d, *J* = 14.0 Hz, 1H), 2.89 (dd, *J* = 16.7, 1.0 Hz, 1H), 2.62 (d, *J* = 16.8 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.14, 170.30, 161.92, 133.58, 130.49, 128.49, 127.64, 107.55, 85.70, 62.42, 43.33, 42.72, 14.02. HRMS (ESI) Calcd for $[M+H]^+$ 261.11214, Found 261.11234.



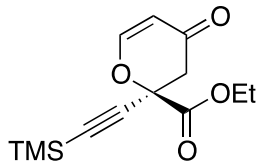
Ethyl 4-oxo-2-phenethyl-3,4-dihydro-2*H*-pyran-2-carboxylate (3f): 94% yield, 96% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 9.08 min, t_R(minor) = 7.64 min. $[\alpha]^{25}_D$= +58.5° (c = 0.520 $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.1 Hz, 1H), 7.27 (t, *J* = 7.2 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.43 (dd, *J* = 6.1, 0.9 Hz, 1H), 4.19 (q, *J* = 6.9 Hz, 2H), 2.97 (d, *J* = 16.7 Hz, 1H), 2.84 -2.78 (m, 1H), 2.76 (d, *J* = 16.8 Hz, 1H), 2.66 – 2.57 (m, 1H), 2.27 – 2.21 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.10, 170.41, 162.21, 140.35, 128.78, 128.49, 126.55, 107.72, 85.33, 62.58, 43.65, 39.42, 29.67, 14.33. HRMS (ESI) Calcd for $[M+H]^+$ 275.12779, Found 275.12848.



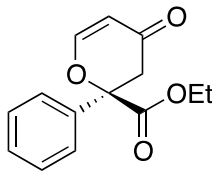
(*E*)-ethyl 4-oxo-2-styryl-3,4-dihydro-2*H*-pyran-2-carboxylate (3g): 92% yield, 98% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 13.04 min, t_R(minor) = 9.61 min. $[\alpha]^{25}_D$= -32.5° (c = 0.305 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 (d, *J* = 6.0 Hz, 1H), 7.38 (d, *J* = 7.8 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 7.8 Hz, 1H), 6.80 (d, *J* = 16.1 Hz, 1H), 6.23 (d, *J* = 16.1 Hz, 1H), 5.47 (d, *J* = 6.1 Hz, 1H), 4.24 (qd, *J* = 7.2, 2.4 Hz, 2H), 3.19 (d, *J* = 16.7 Hz, 1H), 2.90 (d, *J* = 16.7 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.68, 169.16, 161.37, 135.11, 133.05, 128.85, 128.80, 126.94, 124.42, 108.08, 84.71, 62.83, 43.58, 14.10. HRMS (ESI) Calcd for $[M+H]^+$ 273.11214, Found 273.11313.



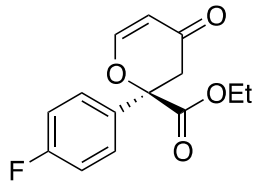
Ethyl 4-oxo-2-((trimethylsilyl)ethynyl)-3,4-dihydro-2*H*-pyran-2-carboxylate (3h): 76% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 99:1 hexanes/iPrOH): t_R(major) = 9.64 min, t_R(minor) = 8.56 min. $[\alpha]^{25}_D$= -90.4° (c = 0.350 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 6.2 Hz, 1H), 5.48 (d, *J* = 6.2 Hz, 1H), 4.30 (qd, *J* = 7.1, 2.3 Hz, 2H), 3.09 (d, *J* = 16.7 Hz, 1H), 2.96 (d, *J* = 16.7 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9H) ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.30, 166,69, 161.04, 108.56, 98.11, 95.12, 78.27, 63.93, 45.21, 14.47, 0.02. HRMS (ESI) Calcd for $[M+H]^+$ 267.10471, Found 267.10469.



(*R*)-Ethyl 4-oxo-2-phenyl-3,4-dihydro-2*H*-pyran-2-carboxylate (3i)[4]: 96% yield, 98% ee.

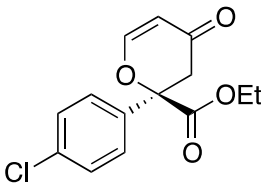
Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 97:3 hexanes/iPrOH): t_R(major) = 14.63 min, t_R(minor) = 13.57 min. $[\alpha]^{25}_D$= +48.6° (c = 0.325 $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) 7.57 – 7.50 (m, 3H), 7.44 – 7.36 (m, 3H), 5.49 (dd, *J* = 6.0, 1.0 Hz, 1H), 4.20 (qd, *J* = 7.2, 1.0 Hz, 2H), 3.51 (dd, *J* = 16.6, 1.0 Hz, 1H), 3.09 (d, *J* = 16.6 Hz, 1H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) *δ* 189.84, 169.55, 161.55, 136.71, 129.17, 128.89, 124.99, 108.37, 85.70, 62.76, 44.34, 13.94. ^{1}H NMR and ^{13}C NMR match the reported value.



Ethyl 2-(4-fluorophenyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3j): 95% yield, 98% ee.

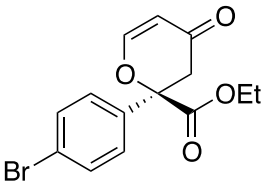
Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 8.67 min, t_R(minor) = 7.88 min. $[\alpha]^{25}_D$= +39.2° (c = 0.405 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.46 (d, *J* = 6.1 Hz, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 5.48 (d, *J* = 6.1 Hz, 1H), 4.17 (qd, *J* = 7.1, 2.0 Hz, 2H), 3.40 (d, *J* = 16.6 Hz, 1H), 3.01 (d, *J* = 16.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.68,

169.54, 165.16, 161.54, 161.20, 132.77, 132.72, 127.30, 127.17, 116.22, 115.88, 108.58, 85.37, 63.02, 44.43, 14.09. HRMS (ESI) Calcd for $[M+H]^+$ 265.08706, Found 265.08835.



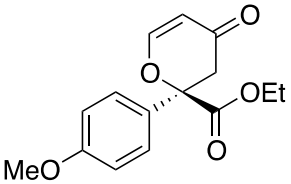
Ethyl 2-(4-chlorophenyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3k): 96% yield, 98% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 9.32 min, t_R(minor) = 8.52 min. $[\alpha]^{25}_D$= +22.7° (c = 0.465 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.46 (d, *J* = 6.1 Hz, 1H), 7.44 (d, *J* = 8.7 Hz, 2H), 7.36 (d, *J* = 8.7 Hz, 2H), 5.49 (d, *J* = 6.0 Hz, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.39 (d, *J* = 16.7 Hz, 1H), 2.99 (d, *J* = 16.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.53, 169.36, 161.47, 135.46, 135.43, 129.26, 126.66, 108.64, 85.36, 63.11, 44.38, 14.10. HRMS (ESI) Calcd for $[M+H]^+$ 281.05751, Found 281.05741.



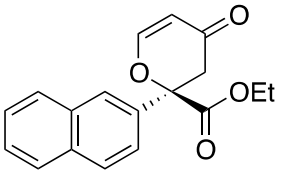
Ethyl 2-(4-bromophenyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3l): 97% yield, 98% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 9.49 min, t_R(minor) = 8.71 min. $[\alpha]^{25}_D$= +12.5° (c = 0.665 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 6.1 Hz, 1H), 7.38 (d, *J* = 8.5 Hz, 2H), 5.49 (d, *J* = 6.1 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.39 (d, *J* = 16.6 Hz, 1H), 2.99 (d, *J* = 16.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.34, 169.14, 161.30, 135.82, 132.08, 126.78, 123.52, 108.50, 85.25, 62.98, 44.20, 13.96. HRMS (ESI) Calcd for $[M+H]^+$ 325.00700, Found 325.00649.



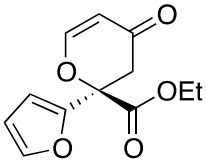
Ethyl 2-(4-methoxyphenyl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3m): 96% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 12.27 min, t_R(minor) = 11.36 min. $[\alpha]^{25}_D$= -26.9° (c = 0.530 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 6.1 Hz, 1H), 7.43 – 7.40 (m, 2H), 6.91 – 6.88 (m, 2H), 5.47 (d, *J* = 6.1 Hz, 1H), 4.20 – 4.13 (m, 2H), 3.78 (s, 3H), 3.38 (d, *J* = 16.6 Hz, 1H), 3.05 (d, *J* = 16.6 Hz, 1H), 1.17 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 190.16, 169.88, 161.74, 160.30, 128.76, 126.71, 114.34, 108.42, 85.57, 62.80, 55.51, 44.21, 14.12. HRMS (ESI) Calcd for $[M+H]^+$ 277.10705, Found 277.10810.



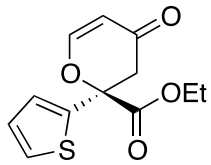
Ethyl 2-(naphthalen-2-yl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3n): 91% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 12.68 min, t_R(minor) = 11.03 min. $[\alpha]^{25}_D$= -30.4° (c = 0.585 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.88 – 7.82 (m, 3H), 7.60 (dd, *J* = 8.8 Hz, 2.0 Hz, 1H), 7.54 – 7.49 (m, 3H), 5.52 (dd, *J* = 6.0 Hz, 0.8 Hz, 1H), 4.19 (qd, *J* = 7.2 Hz, 1.6 Hz 2H), 3.53 (d, *J* = 17.6 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H), 1.18 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.69, 169.46, 161.38, 133.89, 133.25, 132.83, 128.82, 128.43, 127.59, 126.99 126.71, 124.69, 122.21, 108.40, 85.79, 62.79, 44.28, 13.91. HRMS (ESI) Calcd for $[M+H]^+$ 297.11213, Found 297.11195.

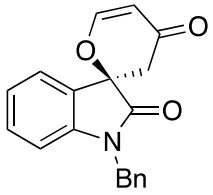


Ethyl 2-(furan-2-yl)-4-oxo-3,4-dihydro-2*H*-pyran-2-carboxylate (3o): 83% yield, 98% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD-H, 1.0 mL/min, 95:5 hexanes/iPrOH): t_R(major) = 16.80 min, t_R(minor) = 18.11 min. $[\alpha]^{25}_D$= -153.2° (c = 0.215 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 2.0 Hz, 0.8 Hz, 1H), 7.35 (d, *J* = 6.0 Hz, 1H), 6.47 (dd, *J* = 3.2 Hz, 0.8 Hz, 1H), 6.39 (dd, *J* = 3.2 Hz, 2.0 Hz, 1H), 5.47 (d, *J* = 6.0 Hz, 1H), 4.31 – 4.23 (m, 2H), 3.27 (d, *J* = 16.8 Hz, 1H), 3.21 (dd, *J* = 16.8 Hz, 0.8 Hz, 1H), 1.25 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.02, 167.46, 160.86, 148.31, 143.93, 110.78, 110.25, 107.85, 81.26, 63.00, 41.45, 13.94. HRMS (ESI) Calcd for $[M+H]^+$ 237.07575, Found 237.07541.

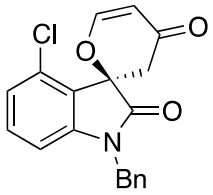


Ethyl 4-oxo-2-(thiophen-2-yl)-3,4-dihydro-2*H*-pyran-2-carboxylate (3p): 99% yield, 99% ee. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD-H, 0.7 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 17.55 min, t_R(minor) = 19.21 min. $[\alpha]^{25}_D$= -41.6° (c = 0.625 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 6.2 Hz, 1.2 Hz, 1H), 7.35 (dt, *J* = 5.2 Hz, 1.2 Hz, 1H), 7.12 (dt, *J* = 3.6 Hz, 1.2 Hz, 1H), 7.00 (ddd, *J* = 5.2 Hz, 2.8 Hz, 0.8 Hz, 1H), 5.49 (d, *J* = 6.0 Hz, 1H), 4.29 – 4.17 (m, 2H), 3.41 (d, *J* = 16.8 Hz, 1H), 3.19 (dd, *J* = 17.6 Hz, 1.2 Hz, 1H), 1.23 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.09, 168.52, 161.03, 139.54, 127.04, 127.01, 126.18, 108.23, 83.82, 62.99, 44.60, 13.88. HRMS (ESI) Calcd for $[M+H]^+$ 253.05290, Found 253.05301.



1-benzylspiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5a): 95% yield, 99% ee.

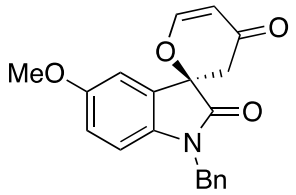
Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 21.57 min, t_R(minor) = 23.61 min. $[\alpha]^{25}_D$= -276.6° (c = 0.430 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (ddd, *J* = 7.5, 1.2, 0.5 Hz, 1H), 7.39 (d, *J* = 6.2 Hz, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.22 (m, 4H), 7.00 (td, *J* = 7.6, 1.0 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 5.61 (dd, *J* = 6.2, 0.7 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 4.85 (d, *J* = 15.7 Hz, 1H), 3.22 (d, *J* = 16.6 Hz, 1H), 2.70 (dd, *J* = 16.6, 0.7 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 189.12, 172.11, 161.33, 142.07, 134.72, 131.19, 128.94, 127.94, 127.41, 127.14, 124.35, 123.59, 110.06, 106.95, 81.36, 43.92, 41.40. HRMS (ESI) Calcd for $[M+H]^+$ 306.11320, Found 306.30841.



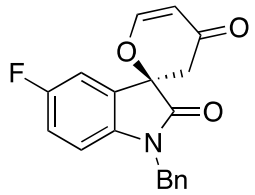
1-benzyl-4-chlorospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5b): 96% yield, 99% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OD-H, 0.7 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 51.07 min, t_R(minor) = 58.12 min. $[\alpha]^{25}_D$= +156.7° (c = 0.570 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.3 Hz, 1H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.26 (d,

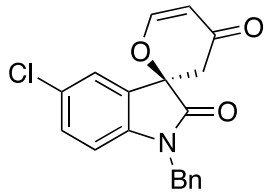
J = 7.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 8.1 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.62 (d, *J* = 7.9 Hz, 1H), 5.58 (d, *J* = 6.3 Hz, 1H), 4.83 (d, *J* = 15.7 Hz, 1H), 4.79 (d, *J* = 15.7 Hz, 1H), 3.74 (d, *J* = 17.2 Hz, 1H), 2.60 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.15, 172.83, 160.87, 144.44, 134.64, 132.46, 132.44, 129.25, 128.32, 127.43, 124.89, 123.05, 108.67, 106.78, 81.42, 44.05, 38.59. HRMS (ESI) Calcd for $[M+H]^+$ 340.07350, Found 340.07278.



1-benzyl-5-methoxyspiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5c): 98% yield, 96% ee.
Enantiomeric excess was determined by chiral HPLC analysis (Regis Pirkle Covalent (*S,S*) Whelk-O1 FEL, 1.0 mL/min, 55:45 hexanes/iPrOH): t_R(major) = 23.35 min, t_R(minor) = 26.56 min. $[\alpha]^{25}_D$= -122.6° (c = 0.910 $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 6.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 7.27 – 7.22 (m, 3H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.75 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.62 (d, *J* = 8.6 Hz, 1H), 5.61 (d, *J* = 6.2 Hz, 1H), 4.87 (d, *J* = 15.7 Hz, 1H), 4.82 (d, *J* = 15.7 Hz, 1H), 3.69 (s, 3H), 3.21 (d, *J* = 16.7 Hz, 1H), 2.70 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 189.14, 171.96, 161.42, 156.42, 135.23, 134.84, 129.00, 128.49, 127.99, 127.20, 115.35, 111.78, 110.69, 107.01, 81.71, 55.87, 44.06, 41.53. HRMS (ESI) Calcd for $[M+H]^+$ 336.12303, Found 336.12247.

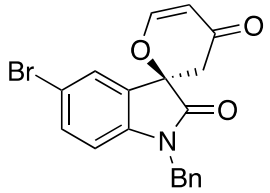


1-benzyl-5-fluorospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5d): 95% yield, 93% ee.
Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 34.05 min, t_R(minor) = 23.16 min. $[\alpha]^{25}_D$= -218.6° (c = 1.400 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (d, *J* = 6.1 Hz, 1H), 7.31 (t, *J* = 7.0 Hz, 2H), 7.27 (d, *J* = 6.9 Hz, 1H), 7.25 – 7.20 (m, 3H), 6.95 (t, *J* = 8.7 Hz, 1H), 6.65 (dd, *J* = 8.3, 3.7 Hz, 1H), 5.63 (d, *J* = 6.1 Hz, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 4.85 (d, *J* = 15.7 Hz, 1H), 3.22 (d, *J* = 16.6 Hz, 1H), 2.69 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 188.70, 171.94, 161.24, 161.15, 157.27, 138.02, 137.98, 134.44, 129.10, 128.65, 128.53, 128.16, 127.17, 117.79, 117.42, 112.92, 112.52, 111.03, 110.91, 107.16, 81.31, 44.13, 41.34. HRMS (ESI) Calcd for $[M+H]^+$ 324.10305, Found 324.10286.



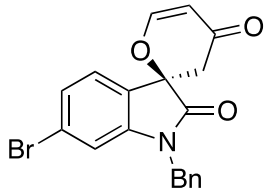
1-benzyl-5-chlorospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5e): 96% yield, 93% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 32.16 min, t_R(minor) = 21.67 min. $[\alpha]^{25}_D$= -291.1° (c = 0.620 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (s, 1H), 7.40 (d, *J* = 6.2 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 6.7 Hz, 1H), 7.25 – 7.20 (m, 3H), 6.65 (d, *J* = 8.4 Hz, 1H), 5.64 (d, *J* = 6.2 Hz, 1H), 4.89 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 3.21 (d, *J* = 16.7 Hz, 1H), 2.70 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 188.62, 171.76, 161.25, 140.61, 134.30, 131.16, 129.13, 129.04, 128.83, 128.21, 127.16, 124.92, 111.22, 107.21, 81.15, 44.11, 41.28. HRMS (ESI) Calcd for $[M+H]^+$ 340.07350, Found 340.07305.



1-benzyl-5-bromospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5f): 95% yield, 93% ee.

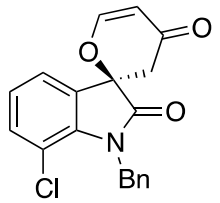
Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 33.09 min, t_R(minor) = 22.08 min. $[\alpha]^{25}_D$= -299.1° (c = 0.650 $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.40 (d, *J* = 6.2 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 1H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.24 – 7.20 (m, 3H), 6.60 (d, *J* = 8.3 Hz, 1H), 5.64 (d, *J* = 6.0 Hz, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.84 (d, *J* = 15.7 Hz, 1H), 3.21 (d, *J* = 16.7 Hz, 1H), 2.70 (d, *J* = 16.7 Hz, 1H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 188.58, 171.65, 161.22, 141.12, 134.26, 134.09, 129.19, 129.13, 128.21, 127.61, 127.15, 116.23, 111.66, 107.22, 81.09, 44.09, 41.27. HRMS (ESI) Calcd for $[M+H]^+$ 384.02298, Found 384.02338.



1-benzyl-6-bromospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5g): 96% yield, 97% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 19.81 min, t_R(minor) = 22.60 min. $[\alpha]^{25}_D$= -238.9° (c = 0.820

$CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 6.4 Hz, 1H), 7.36 – 7.28 (m, 4H), 7.25 – 7.24 (m, 1H), 7.24 – 7.23 (m, 1H), 7.15 (dd, *J* = 8.0, 1.6 Hz, 1H), 6.88 (d, *J* = 1.6 Hz, 1H), 5.62 (d, *J* = 6.4 Hz, 1H), 4.88 (d, *J* = 16.0 Hz, 1H), 4.82 (d, *J* = 16.0 Hz, 1H), 3.20 (d, *J* = 16.8 Hz, 1H), 2.68 (d, *J* = 17.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.64, 171.93, 161.12, 143.46, 134.18, 129.10, 128.19, 127.10, 126.49, 126.22, 125.58, 125.11, 113.46, 107.06, 80.87, 44.04, 41.18. HRMS (ESI) Calcd for $[M+H]^+$ 384.02298, Found 384.02311.



1-benzyl-7-chlorospiro[indoline-3,2'-pyran]-2,4'(3'*H*)-dione (5h): 97% yield, 98% ee.

Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel AD-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 20.07 min, t_R(minor) = 22.84 min. $[\alpha]^{25}_D$= -148.3° (c = 0.775 $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.38 (d, *J* = 6.4 Hz, 1H), 7.32 – 7.24 (m, 3H), 7.23 – 7.17 (m, 3H), 6.97 (t, *J* = 8.0 Hz, 1H), 5.62 (d, *J* = 6.4 Hz, 1H), 5.34 (d, *J* = 16.0 Hz, 1H), 5.29 (d, *J* = 16.4 Hz, 1H), 3.17 (d, *J* = 16.8 Hz, 1H), 2.75 (d, *J* = 16.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.57, 172.86, 161.03, 138.32, 136.39, 133.76, 130.18, 128.72, 127.48, 126.31, 124.63, 122.93, 116.40, 106.94, 80.47, 45.06, 41.45. HRMS (ESI) Calcd for $[M+H]^+$ 340.07350, Found 340.07352.

References:

(1) (a) Hu, S.; Neckers, D. C. *J. Org. Chem*. **1996**, *61*, 6407. (b) Autrey, R. L.; Tahk, F. C. *Tetrahedron* **1967**, *23*, 901. (c) Rambaud, M.; Bakasse, M.; Duguay, G.; Villieras, J. *Synthesis* **1988**, 564. (d) Meng, Q.; Zhu, L.; Zhang, Z. *J. Org. Chem.* **2008***, 73,* 7209. (e) Bagley, M. C.; Brace, C.; Dale, J. W.; Ohnesorge, M.; Phillips, N. G.; Xiong, X.; Bower, J. *J. Chem. Soc., Perkin trans 1* **2002***,* 1663.

(2) Akullian, L. C.; Snapper, M.; Hoveyda, A. H. *J. Am. Chem. Soc*. **2006**, *128*, 6532.

(3) Liang, T.; Zhang, Z.; Antilla, J. C. *Angew. Chem., Int. Ed*. **2010**, *49*, 9734.

(4) Yao, S.; Johannsen, M.; Audrain, H.; Hazell, R. G.; Jørgensen, K. A. *J. Am. Chem. Soc*. **1998** *120*, 8599.

Chiral HPLC analysis of compound **3a**

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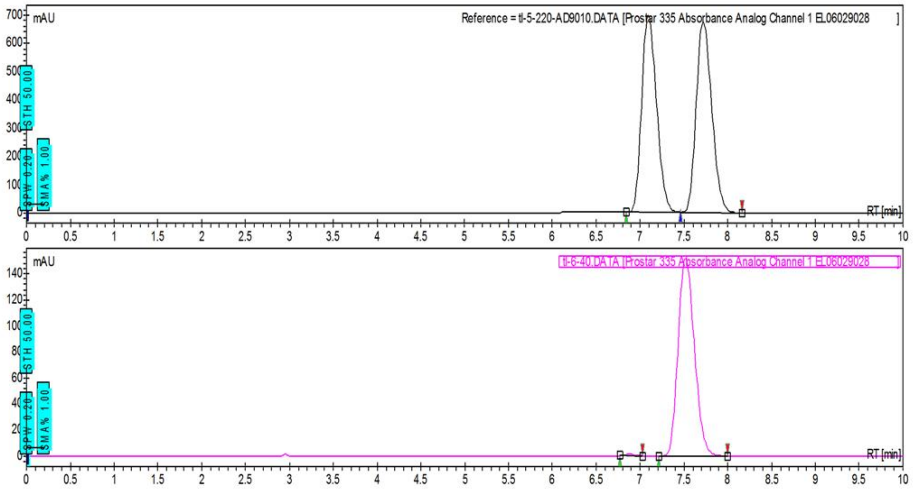

Peak results :

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tl-6-40.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

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2	6.89	1.1	0.25	0.2	0.493
1	7.52	152.2	0.35	32.8	99.507
Total		153.3		33.0	100.000

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Chiral HPLC analysis of compound **3b**

Chromatogram : tl-6-47_channel1

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Method : test
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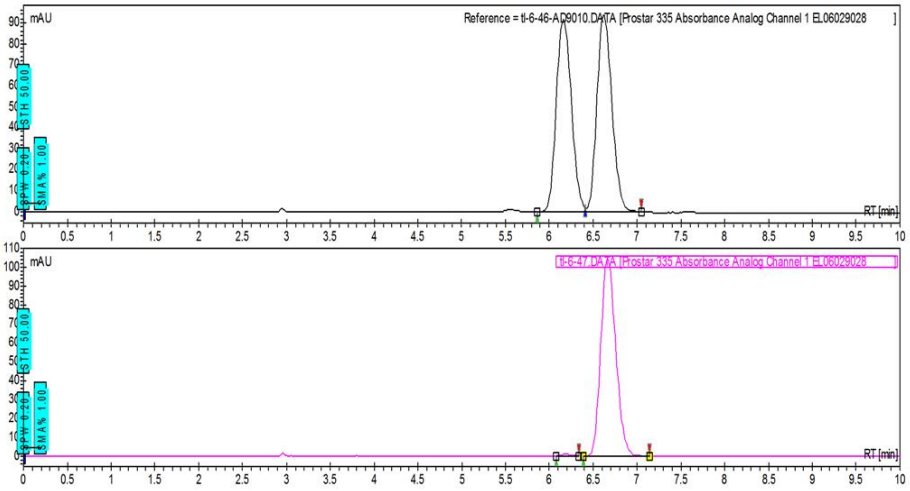

Peak results :

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1	6.16	91.9	0.32	18.5	49.829
2	6.63	93.7	0.32	18.6	50.171
Total		185.6		37.1	100.000

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2	6.20	0.8	0.25	0.1	0.550
1	6.67	105.0	0.32	20.8	99.450
Total		105.7		20.9	100.000

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Chiral HPLC analysis of compound **3c**

Chromatogram : tl-6-66_channel1

System : HPLC
Method : test
User : User1

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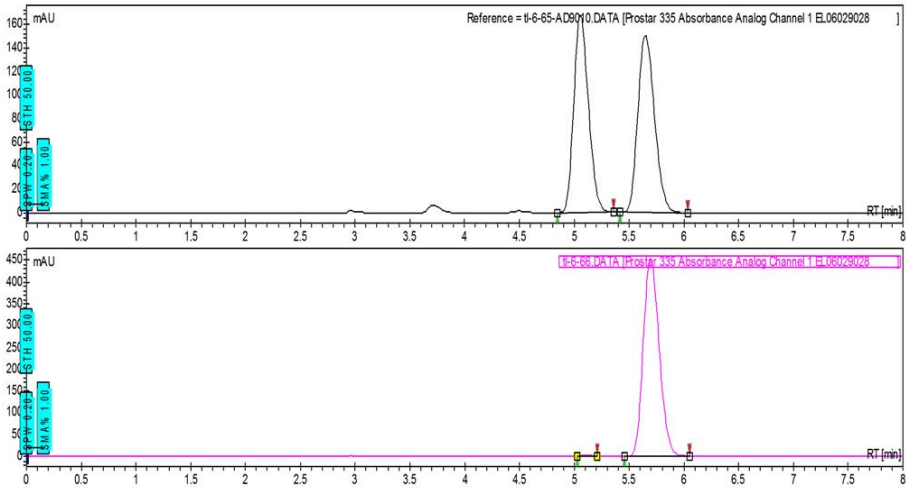

Peak results :

tl-6-65-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	5.05	167.5	0.25	26.1	49.481
2	5.65	150.0	0.29	26.6	50.519
Total		317.5		52.6	100.000

tl-6-66.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	5.11	1.2	0.00	0.1	0.160
2	5.69	453.8	0.27	76.5	99.840
Total		454.9		76.6	100.000

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Chiral HPLC analysis of compound **3d**

Chromatogram : tl-6-51-c-2_channel1

System : HPLC
Method : test
User : User1

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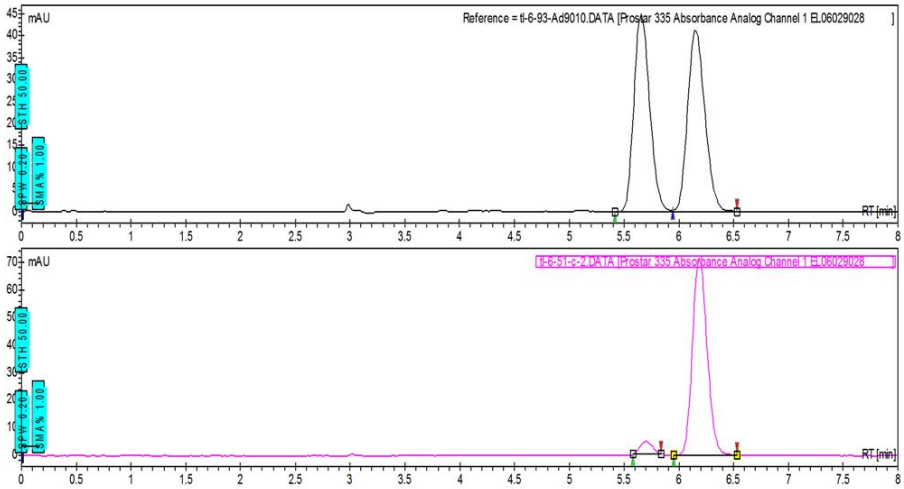
Printed : 5/14/2012 2:15:11 PM



Peak results :

tl-6-93-Ad9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	5.65	44.8	0.27	7.5	49.889
2	6.15	41.2	0.30	7.6	50.111
Total		86.0		15.1	100.000

tl-6-51-c-2.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	5.71	4.6	0.22	0.6	5.212
1	6.19	71.2	0.25	11.0	94.788
Total		75.8		11.6	100.000

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Chiral HPLC analysis of compound **3e**

Chromatogram : tl-6-54_channel1

System : HPLC
Method : test
User : User1

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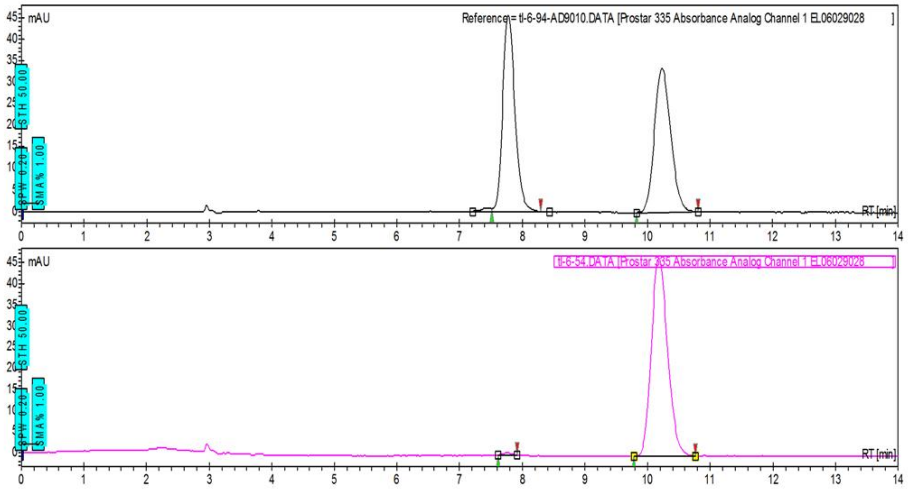
Processed : 4/28/2012 2:29:09 PM
Printed : 5/14/2012 2:17:46 PM



Peak results :

tl-6-94-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	7.77	45.6	0.36	10.3	50.535
2	10.23	33.3	0.49	10.1	49.465
Total		78.9		20.5	100.000

tl-6-54.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	7.76	0.4	0.26	0.1	0.473
1	10.17	46.7	0.48	14.1	99.527
Total		47.2		14.1	100.000

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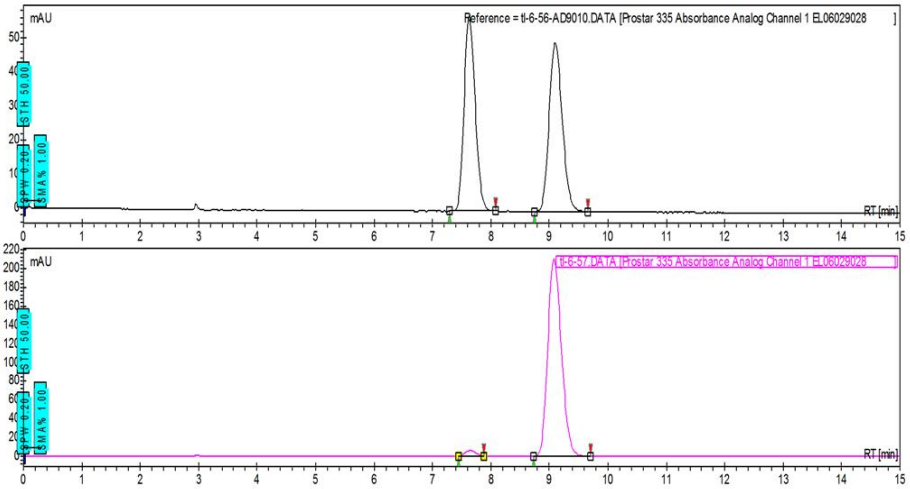
Chiral HPLC analysis of compound **3f**

Chromatogram : tl-6-57_channel1

System : HPLC
Method : test
User : User1

Acquired : 4/29/2012 12:18:42 PM
Processed : 4/29/2012 12:44:06 PM
Printed : 5/14/2012 2:19:14 PM



Peak results :

tl-6-56-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	7.63	57.8	0.35	12.7	49.398
2	9.09	49.8	0.42	13.0	50.602
Total		107.6		25.8	100.000

tl-6-57.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	7.64	5.9	0.34	1.2	2.090
2	9.08	211.6	0.43	57.2	97.910
Total		217.5		58.4	100.000

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Chiral HPLC analysis of compound **3g**

Chromatogram : tl-6-63-1_channel1

System : HPLC
Method : test
User : User1

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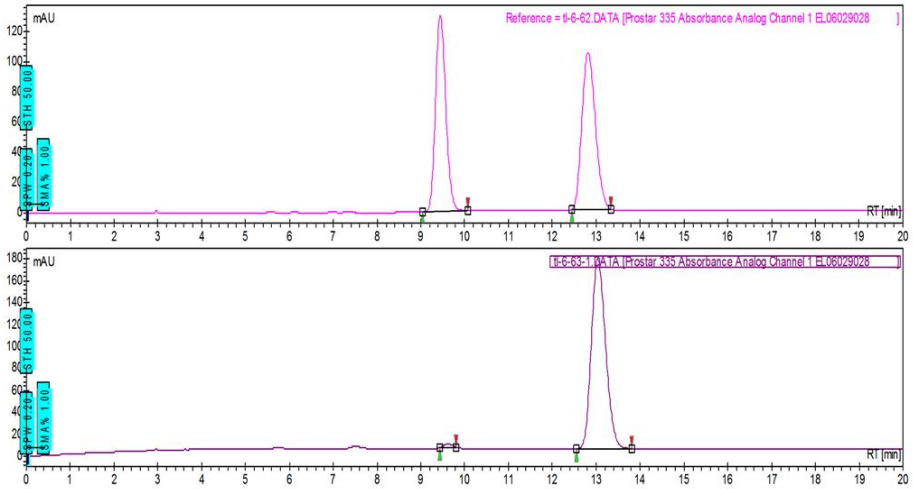

Peak results :

tl-6-62.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.44	129.6	0.43	35.1	48.860
2	12.81	103.5	0.57	36.7	51.140
Total		233.1		71.8	100.000

tl-6-63-1.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	9.61	3.3	0.35	0.7	1.049
1	13.04	173.2	0.60	64.7	98.951
Total		176.4		65.3	100.000

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Chiral HPLC analysis of compound **3h**

Chromatogram : tl-6-70-AD9901_channel1

System : HPLC
Method : test
User : User1

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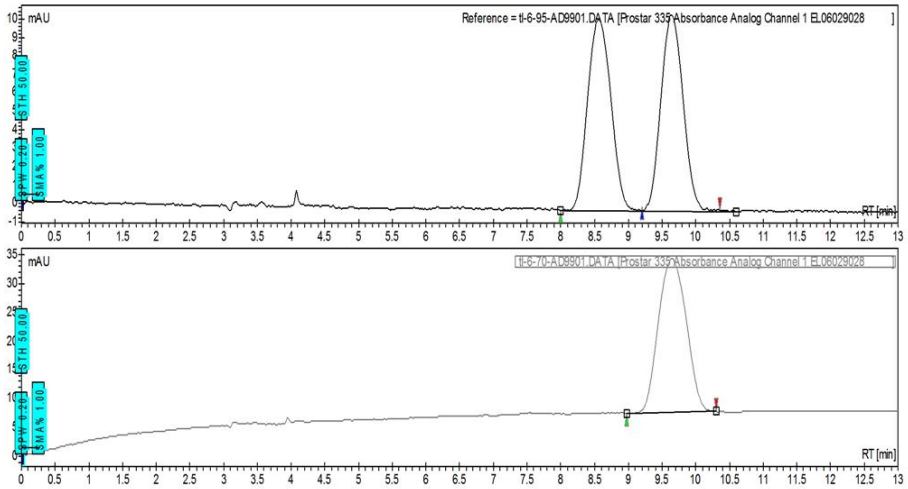
Printed : 5/14/2012 2:28:24 PM



Peak results :

tl-6-95-AD9901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.56	10.4	0.64	4.1	49.820
2	9.64	10.6	0.62	4.2	50.180
Total		21.0		8.3	100.000

tl-6-70-AD9901.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.64	26.7	0.78	13.0	100.000
Total		26.7		13.0	100.000

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Chiral HPLC analysis of compound **3i**

Chromatogram : tl-6-145-AD9703_channel1

System : HPLC
Method : test
User : User1

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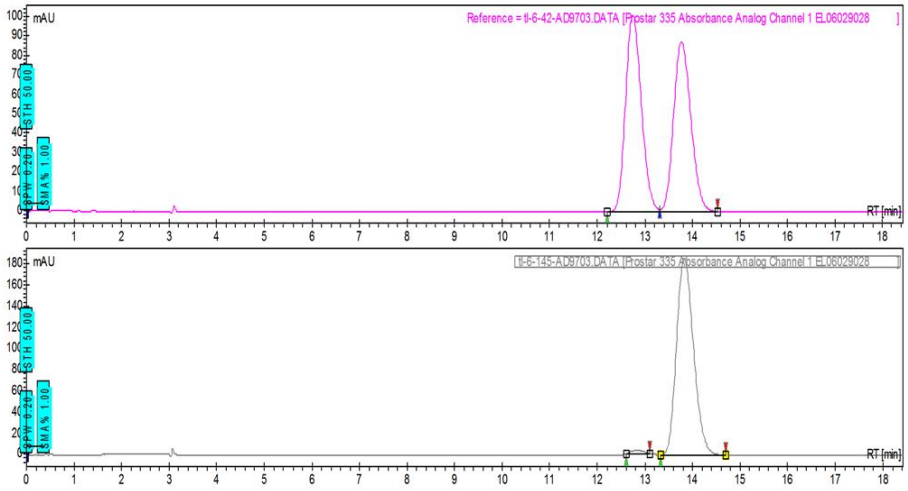
Printed : 6/12/2012 11:59:46 AM



Peak results :

tl-6-42-AD9703.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	12.75	101.0	0.62	39.0	51.379
2	13.77	87.1	0.68	36.9	48.621
Total		188.1		75.9	100.000

tl-6-145-AD9703.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	12.83	3.3	0.48	0.9	1.201
1	13.83	185.5	0.66	77.0	98.799
Total		188.8		77.9	100.000

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Chiral HPLC analysis of compound **3j**

Chromatogram : tl-6-79_channel1

System : HPLC
Method : test
User : User1

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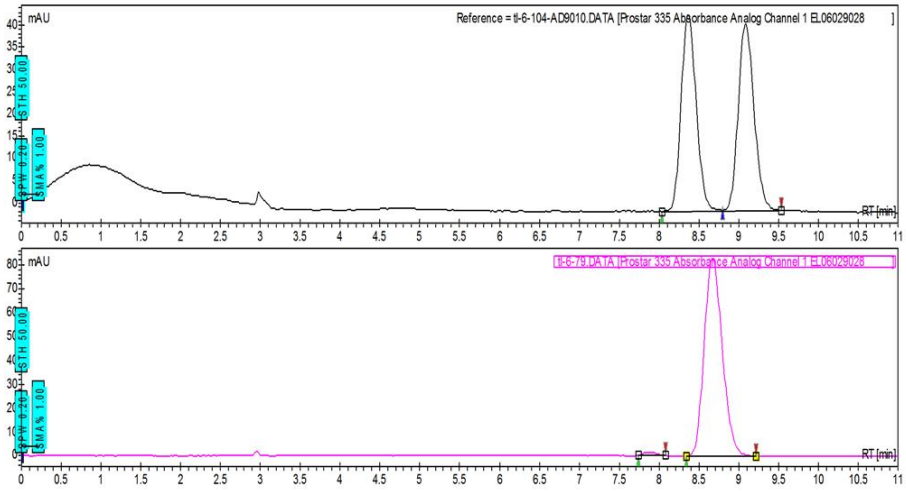

Peak results :

tl-6-104-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.37	44.2	0.35	9.7	49.953
2	9.09	42.1	0.37	9.7	50.047
Total		86.4		19.4	100.000

tl-6-79.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	7.88	1.3	0.30	0.2	1.063
1	8.67	83.0	0.42	21.9	98.937
Total		84.3		22.1	100.000

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Chiral HPLC analysis of compound **3k**

Chromatogram : tl-6-100_channel1

System : HPLC
Method : test
User : User1

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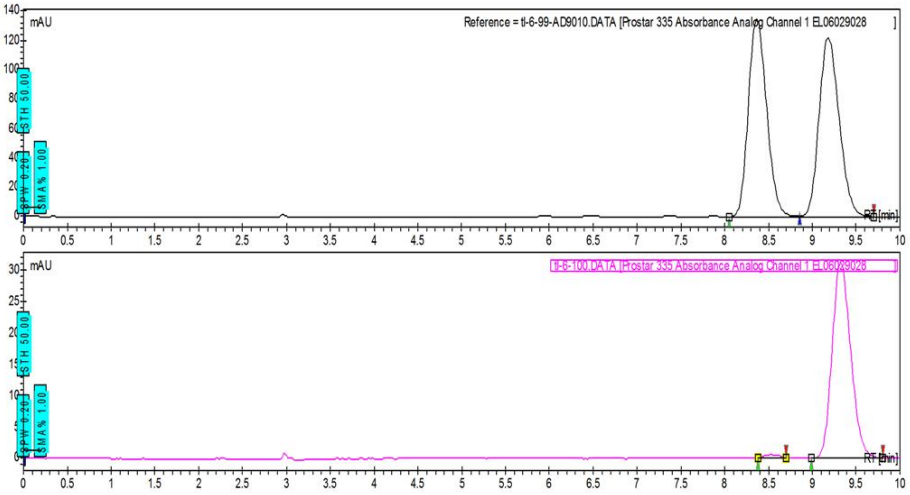
Printed : 5/14/2012 2:33:05 PM



Peak results :

tl-6-99-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.36	134.9	0.39	32.7	50.058
2	9.19	122.1	0.43	32.6	49.942
Total		257.0		65.3	100.000

tl-6-100.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.52	0.5	0.30	0.1	1.067
2	9.32	31.2	0.39	7.7	98.933
Total		31.7		7.7	100.000

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Chiral HPLC analysis of compound **3l**

Chromatogram : tl-6-90_channel1

System : HPLC
Method : test
User : User1

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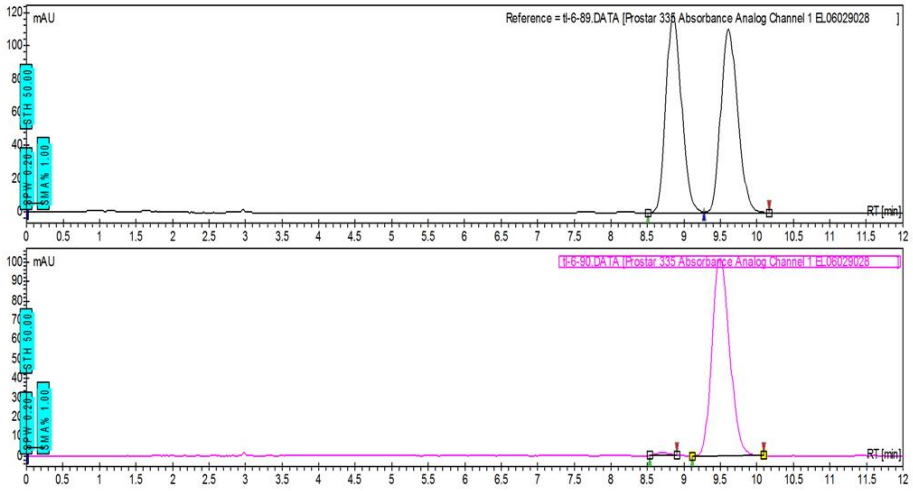
Printed : 5/14/2012 2:34:41 PM



Peak results :

tl-6-89.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.85	119.1	0.40	29.9	50.072
2	9.61	110.2	0.43	29.8	49.928
Total		229.3		59.6	100.000

tl-6-90.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	8.71	1.4	0.34	0.3	0.988
1	9.49	102.1	0.45	28.6	99.012
Total		103.5		28.9	100.000

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Chiral HPLC analysis of compound **3m**

Chromatogram : tl-6-98_channel1

System : HPLC
Method : test
User : User1

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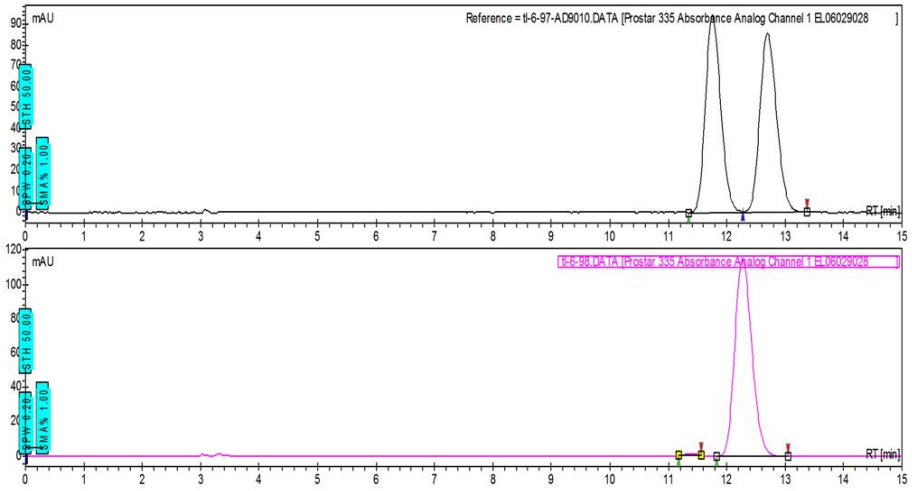
Processed : 5/9/2012 12:50:32 PM
Printed : 5/14/2012 2:35:44 PM



Peak results :

tl-6-97-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	11.76	94.5	0.48	28.6	49.990
2	12.69	85.7	0.53	28.7	50.010
Total		180.1		57.3	100.000

tl-6-98.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	11.36	1.1	0.35	0.2	0.631
2	12.27	115.6	0.54	39.1	99.369
Total		116.7		39.4	100.000

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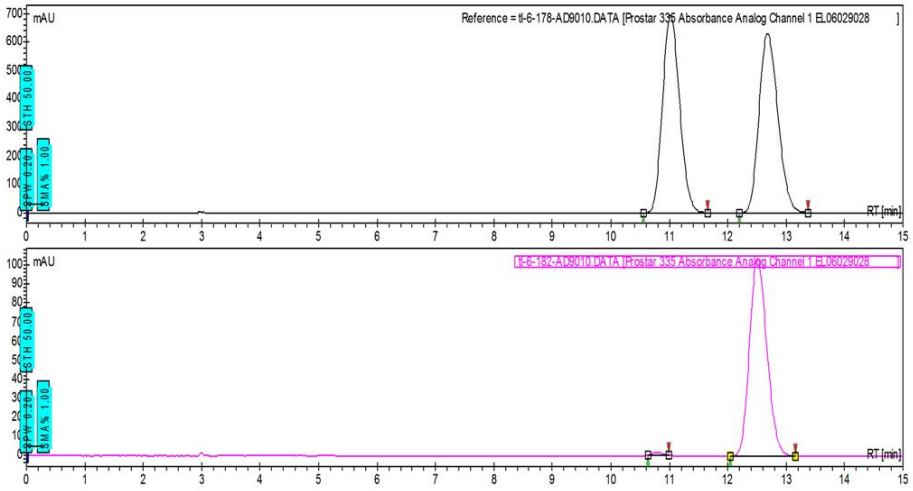
Chiral HPLC analysis of compound **3n**

Chromatogram : tl-6-182-AD9010_channel1

System : HPLC
Method : test
User : User1

Acquired : 6/27/2012 11:15:14 AM
Processed : 6/27/2012 11:32:07 AM
Printed : 6/29/2012 1:39:23 PM



Peak results :

tl-6-178-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	11.03	694.3	0.54	236.1	50.020
2	12.68	629.4	0.60	235.9	49.980
Total		1323.8		472.0	100.000

tl-6-182-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	10.80	1.2	0.34	0.3	0.693
1	12.51	104.0	0.55	36.0	99.307
Total		105.2		36.2	100.000

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Chiral HPLC analysis of compound **3o**

Chromatogram : tl-6-165-OD9505_channel1

System : HPLC
Method : test
User : User1

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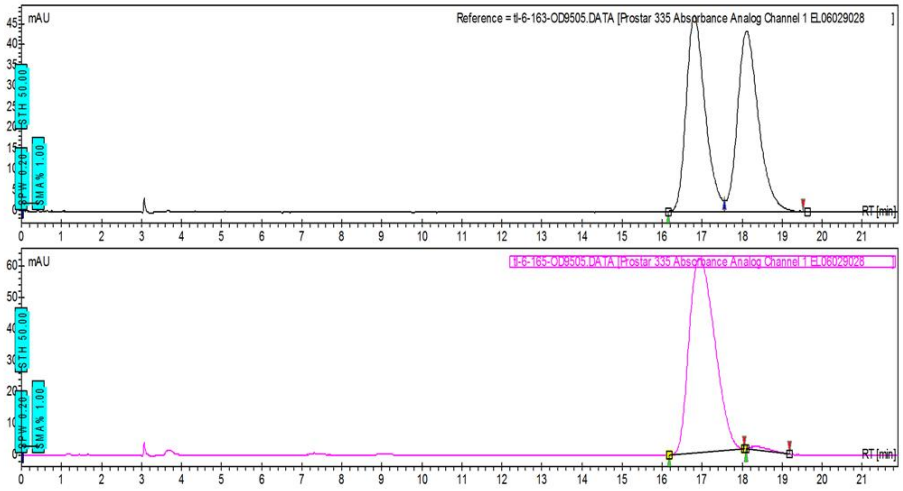
Printed : 6/29/2012 1:34:32 PM



Peak results :

tl-6-163-OD9505.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	16.80	47.2	0.85	25.7	49.431
2	18.11	43.3	0.94	26.3	50.569
Total		90.4		52.1	100.000

tl-6-165-OD9505.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	16.93	61.6	1.19	45.7	98.756
2	18.41	1.1	0.82	0.6	1.244
Total		62.7		46.2	100.000

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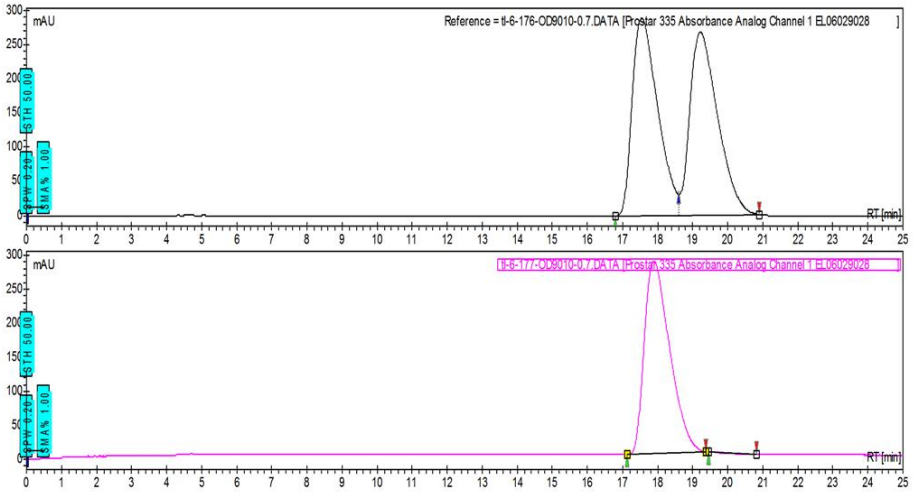
Chiral HPLC analysis of compound **3p**

Chromatogram : tl-6-177-OD9010-0.7_channel1

System : HPLC
Method : test
User : User1

Acquired : 6/24/2012 12:22:25 PM
Processed : 6/24/2012 12:53:30 PM
Printed : 6/29/2012 1:38:08 PM



Peak results :

tl-6-176-OD9010-0.7.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	17.55	288.9	1.36	243.9	49.706
2	19.21	268.1	1.47	246.8	50.294
Total		557.0		490.8	100.000

tl-6-177-OD9010-0.7.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	17.89	282.0	1.35	236.8	99.949
2	20.41	0.4	0.00	0.1	0.051
Total		282.3		236.9	100.000

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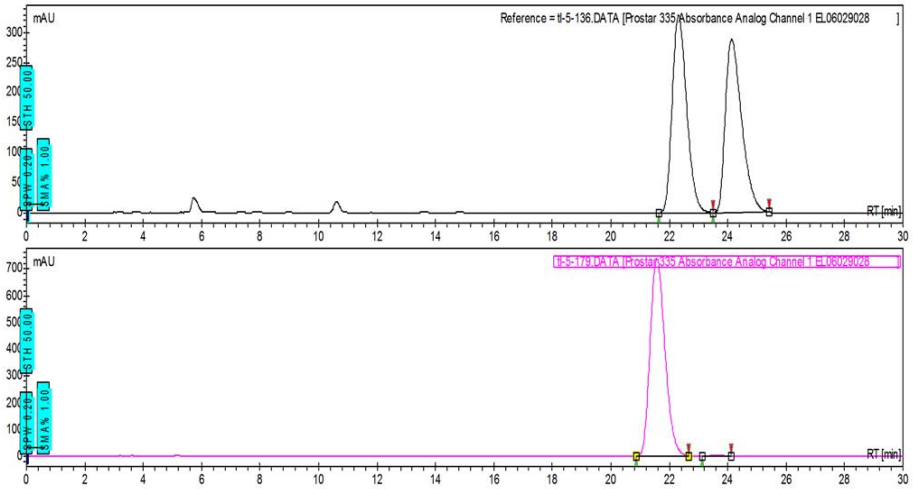
Chiral HPLC analysis of compound **5a**

Chromatogram : tl-5-179_channel1

System : HPLC
Method : test
User : User1

Acquired : 2/17/2012 4:22:57 PM
Processed : 2/17/2012 4:55:20 PM
Printed : 5/14/2012 2:40:41 PM



Peak results :

tl-5-136.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	22.32	329.5	0.91	189.1	50.150
2	24.13	289.1	1.03	188.0	49.850
Total		618.6		377.1	100.000

tl-5-179.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	21.57	738.7	0.93	434.9	99.585
2	23.61	3.5	0.83	1.8	0.415
Total		742.2		436.7	100.000

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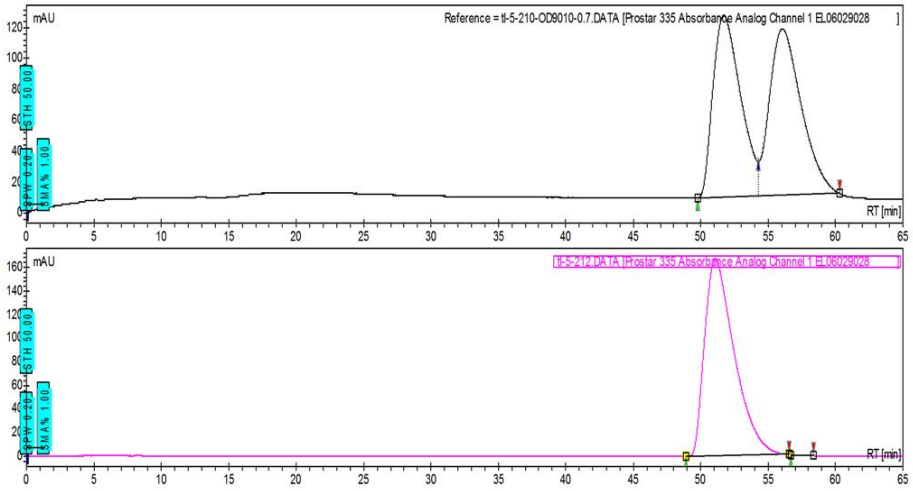
Chiral HPLC analysis of compound **5b**

Chromatogram : tl-5-212_channel1

System : HPLC
Method : test
User : User1

Acquired : 3/5/2012 1:08:54 PM
Processed : 3/5/2012 2:20:32 PM
Printed : 5/14/2012 2:43:23 PM



Peak results :

tl-5-210-OD9010-0.7.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	51.69	117.6	3.97	278.8	48.446
2	56.05	107.7	4.42	296.6	51.554
Total		225.3		575.4	100.000

tl-5-212.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	51.07	167.7	4.09	428.5	99.998
2	58.12	0.1	0.77	0.0	0.002
Total		167.8		428.5	100.000

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Chiral HPLC analysis of compound **5c**

Chromatogram : tl-5-196-whelk5545-1_channel1

System : HPLC
Method : test
User : User1

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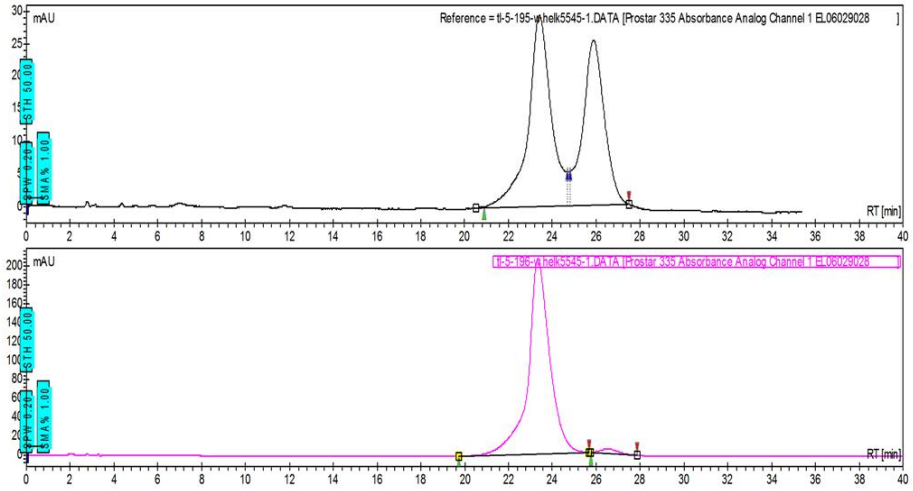
Processed : 2/27/2012 8:12:31 PM
Printed : 5/14/2012 2:46:18 PM



Peak results :

tl-5-195-whelk5545-1.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	23.41	29.4	1.70	35.9	54.958
2	24.81	5.3	0.00	0.6	0.969
3	25.88	25.4	1.68	28.8	44.074
Total		60.2		65.4	100.000

tl-5-196-whelk5545-1.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	23.35	206.6	1.71	235.8	98.110
2	26.56	5.1	1.53	4.5	1.890
Total		211.7		240.4	100.000

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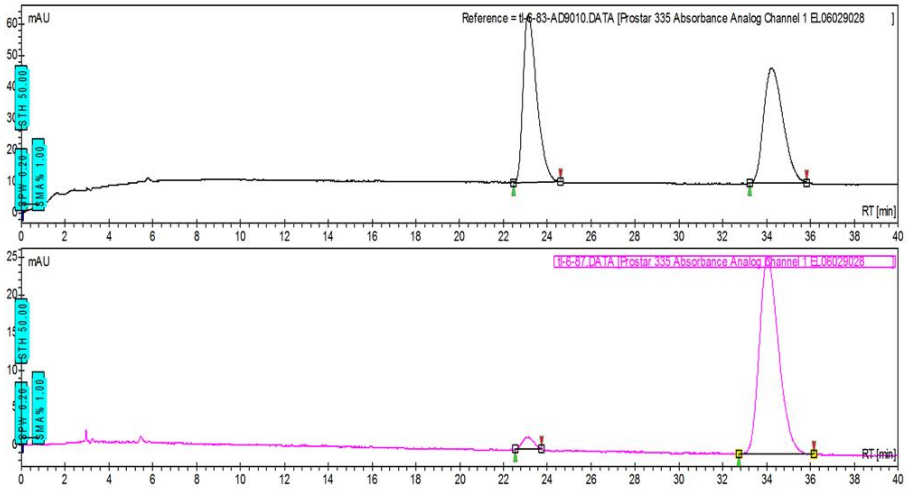
Chiral HPLC analysis of compound **5d**

Chromatogram : tl-6-87_channel1

System : HPLC
Method : test
User : User1

Acquired : 5/6/2012 8:59:27 PM
Processed : 5/6/2012 9:42:41 PM
Printed : 5/14/2012 2:47:48 PM



Peak results :

tl-6-83-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	23.13	53.1	1.13	38.4	50.623
2	34.24	36.6	1.63	37.5	49.377
Total		89.7		75.9	100.000

tl-6-87.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	23.16	1.7	0.91	0.9	3.429
1	34.05	26.2	1.62	26.7	96.571
Total		27.8		27.7	100.000

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Chiral HPLC analysis of compound **5e**

Chromatogram : tl-6-96_channel1

System : HPLC
Method : test
User : User1

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Processed : 5/7/2012 5:59:50 PM
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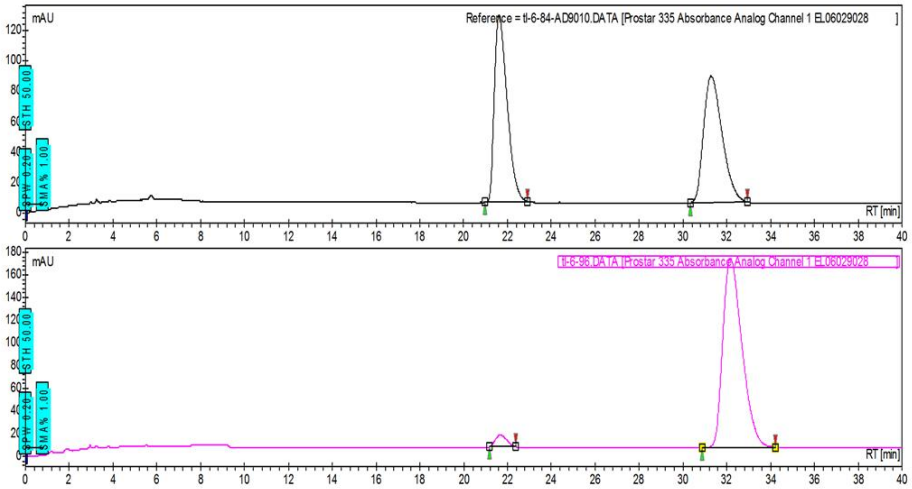

Peak results :

tl-6-84-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	21.63	122.6	1.07	82.5	50.296
2	31.28	82.8	1.56	81.5	49.704
Total		205.4		164.0	100.000

tl-6-96.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	21.67	10.4	1.00	6.2	3.549
1	32.16	167.4	1.61	169.7	96.451
Total		177.7		175.9	100.000

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Chiral HPLC analysis of compound **5f**

Chromatogram : tl-6-129_channel1

System : HPLC
Method : test
User : User1

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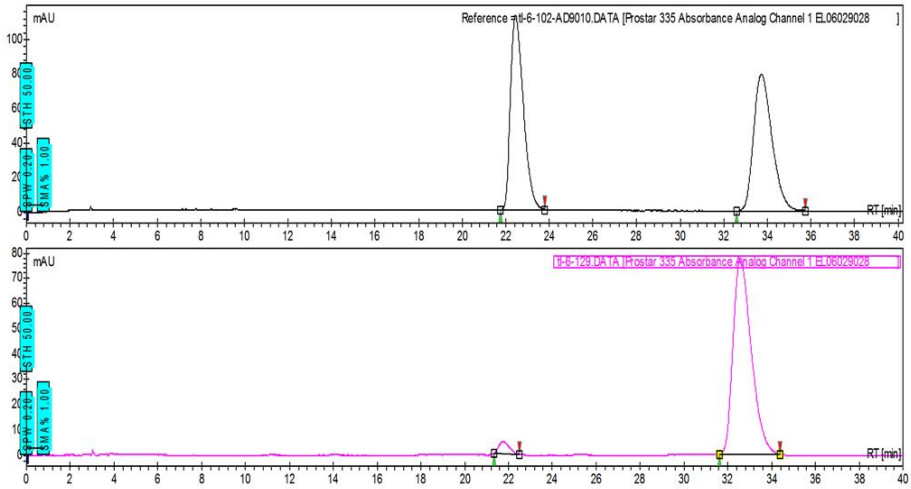

Peak results :

tl-6-102-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	22.45	112.1	1.09	77.2	50.007
2	33.73	78.7	1.54	77.1	49.993
Total		190.8		154.3	100.000

tl-6-129.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	21.75	4.9	0.89	2.7	3.494
1	32.57	77.6	1.54	75.0	96.506
Total		82.5		77.7	100.000

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Chiral HPLC analysis of compound **5g**

Chromatogram : tl-6-150-AD9010_channel1

System : HPLC
Method : test
User : User1

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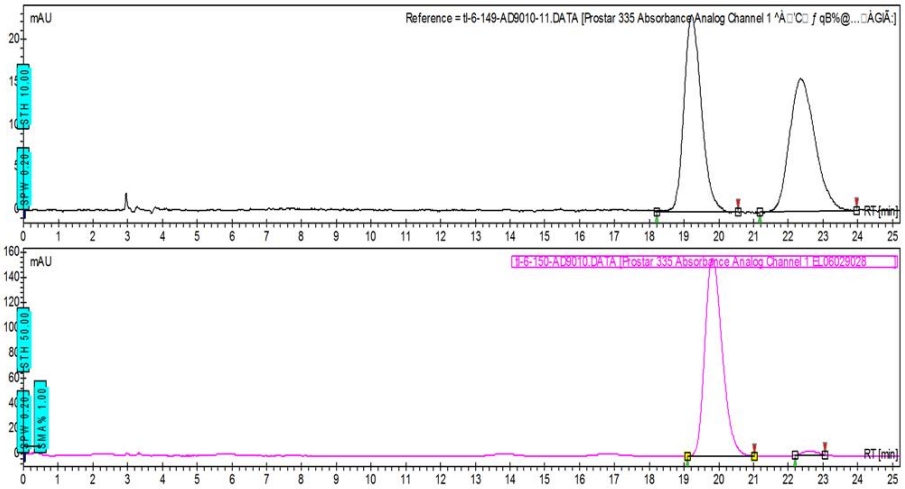

Peak results :

tl-6-149-AD9010-11.DATA [Prostar 335 Absorbance Analog Channel 1 ^À□'C□ ƒ qB%@...□ÀGIÃ:]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	19.21	50.23	23.2	13.5	50.229
2	UNKNOWN	22.36	49.77	15.7	13.4	49.771
Total			100.00	39.0	26.9	100.000

tl-6-150-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	19.81	156.8	0.91	90.7	98.447
2	22.60	2.9	0.81	1.4	1.553
Total		159.7		92.1	100.000

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Chiral HPLC analysis of compound **5h**

Chromatogram : tl-6-156-AD9010_channel1

System : HPLC
Method : test
User : User1

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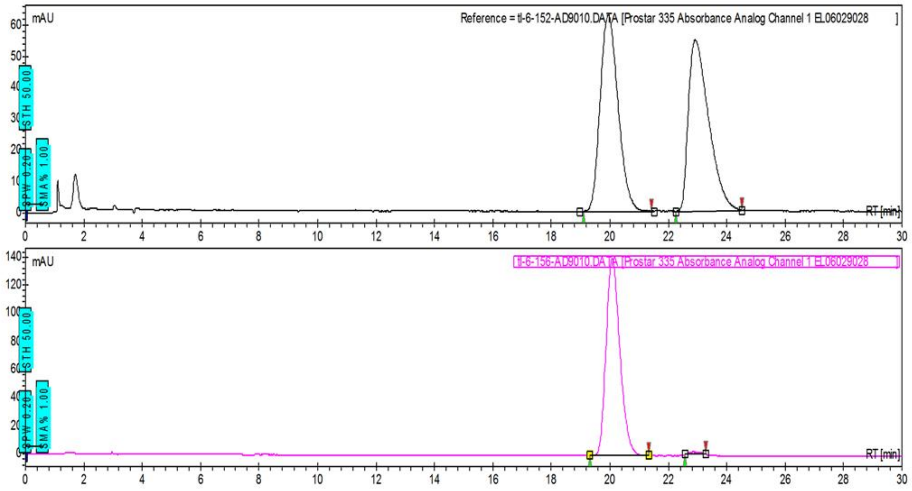
Processed : 6/14/2012 11:00:53 AM
Printed : 6/14/2012 11:14:15 AM



Peak results :

tl-6-152-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	19.95	62.9	1.12	44.5	50.147
2	22.92	54.8	1.28	44.2	49.853
Total		117.7		88.6	100.000

tl-6-156-AD9010.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	20.07	140.4	0.86	76.5	99.028
2	22.84	1.7	0.67	0.8	0.972
Total		142.1		77.2	100.000

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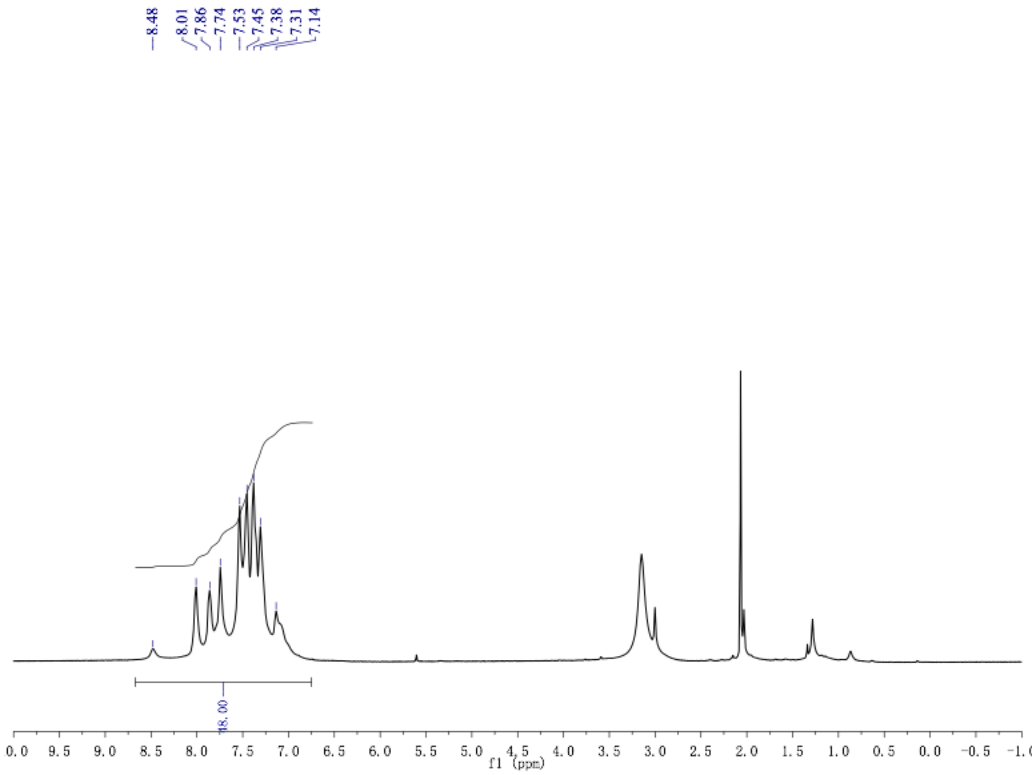
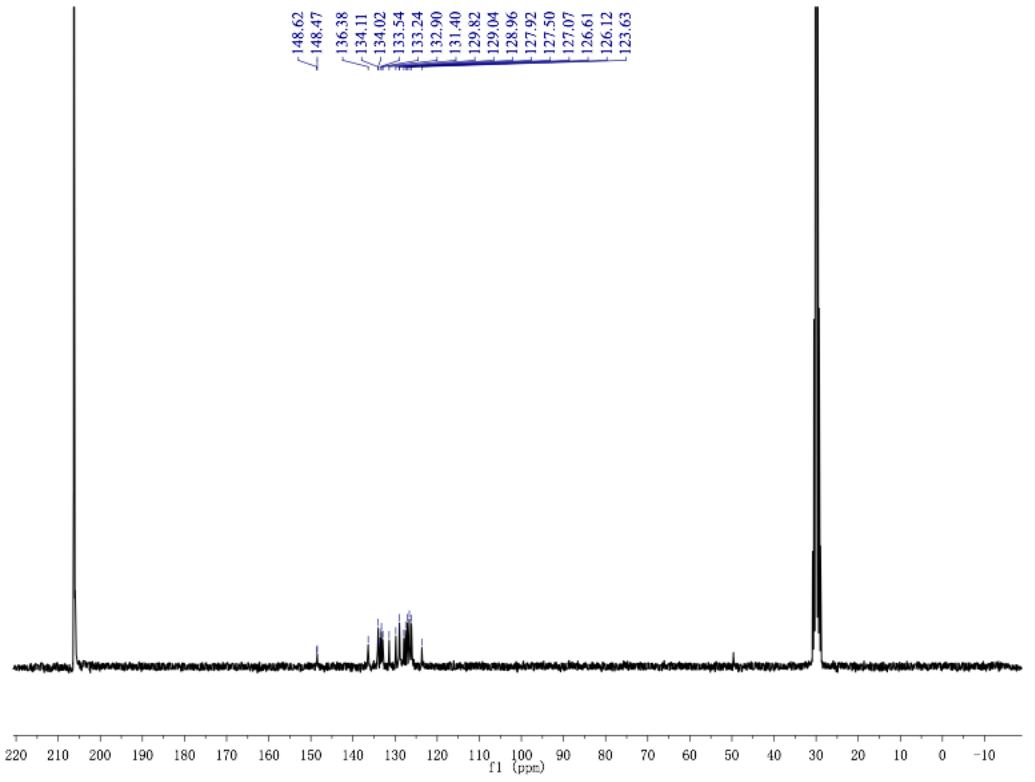
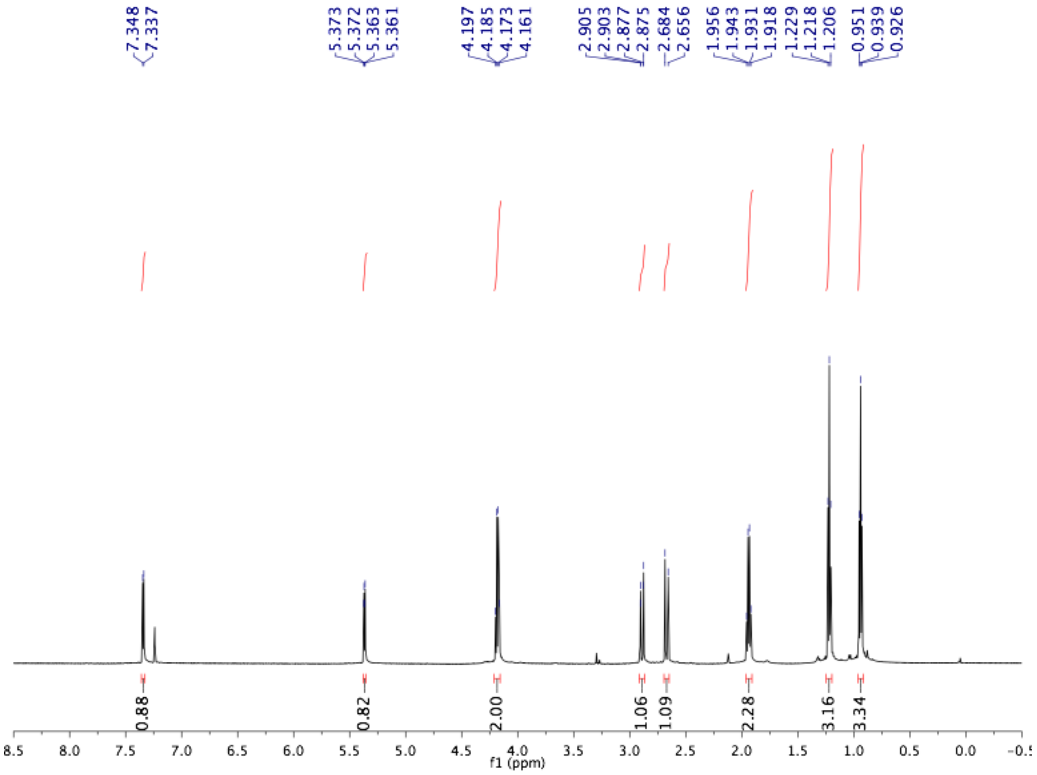
^{1}H NMR of Catalyst Ca[**P4**]$_2$



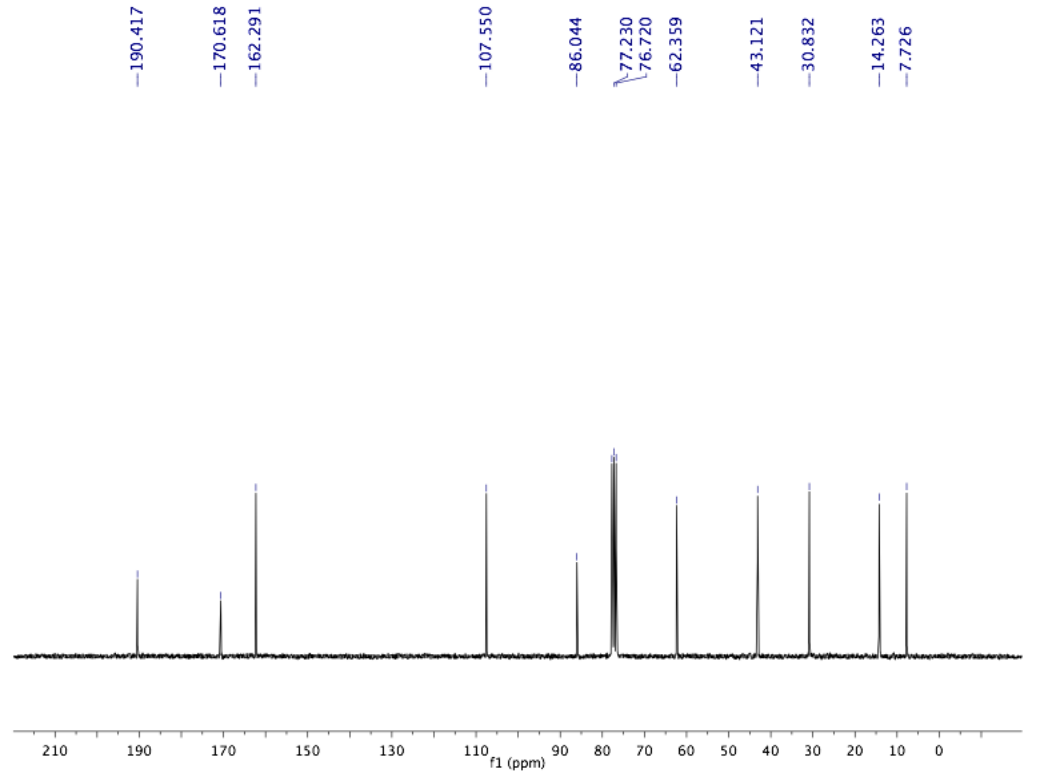
^{13}C NMR of Catalyst Ca[**P4**]$_2$



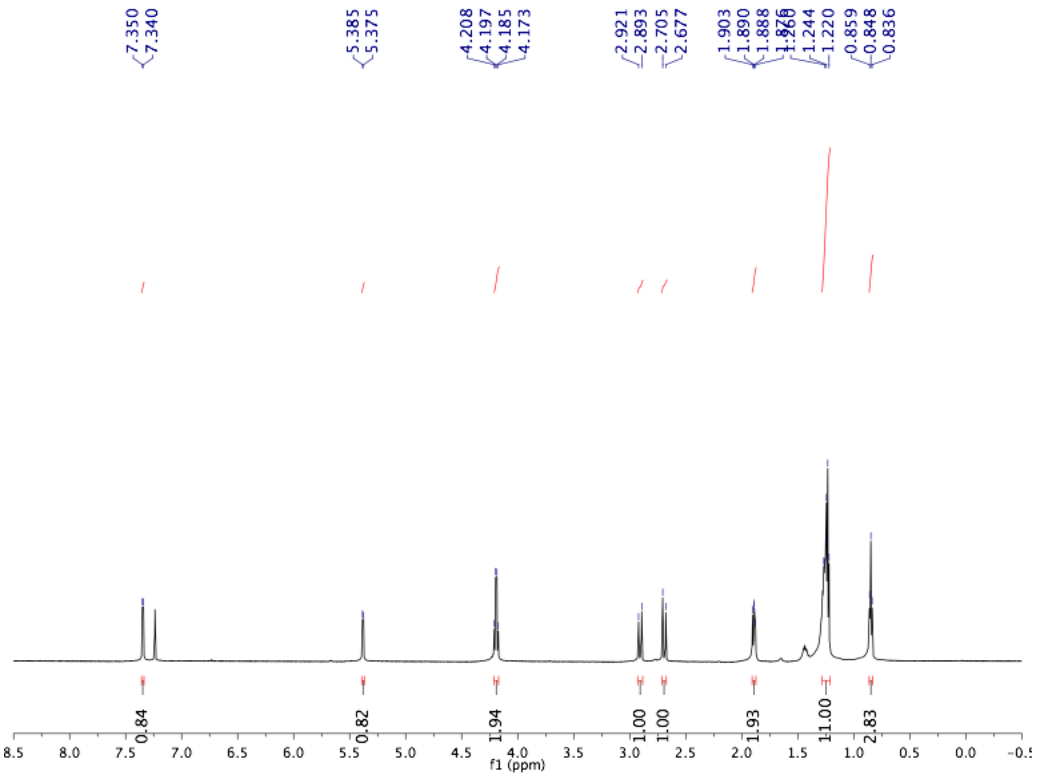
^{1}H NMR of Compound **3b**



^{13}C NMR of Compound **3b**



^{1}H NMR of Compound **3c**



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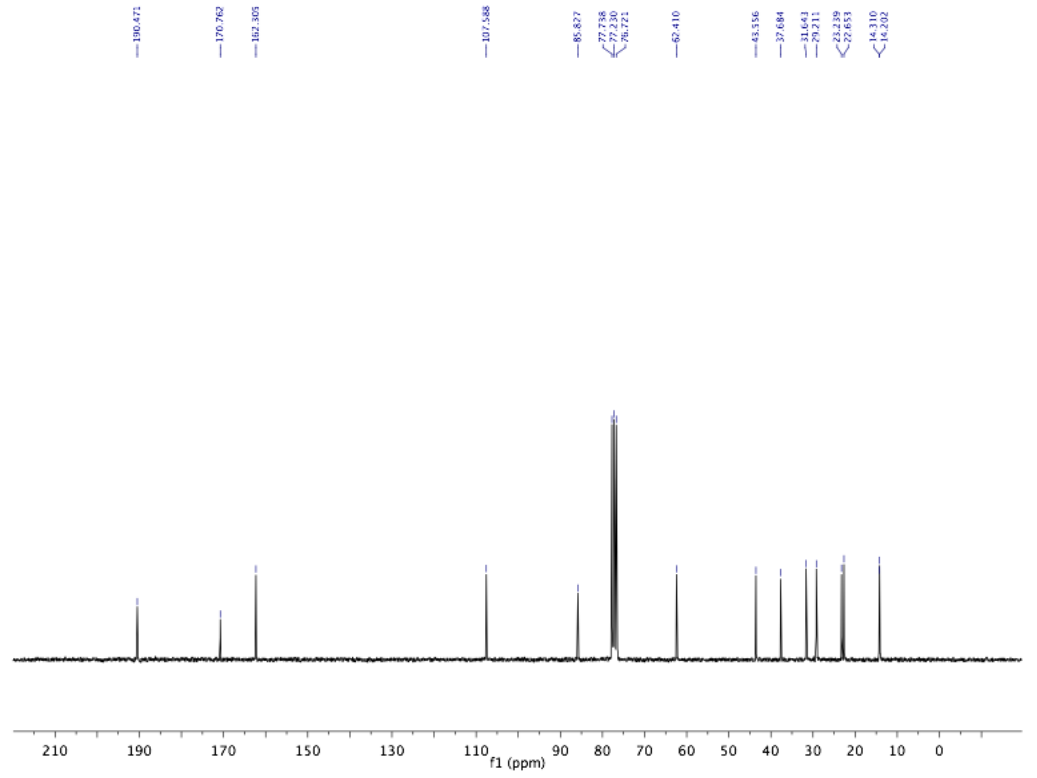
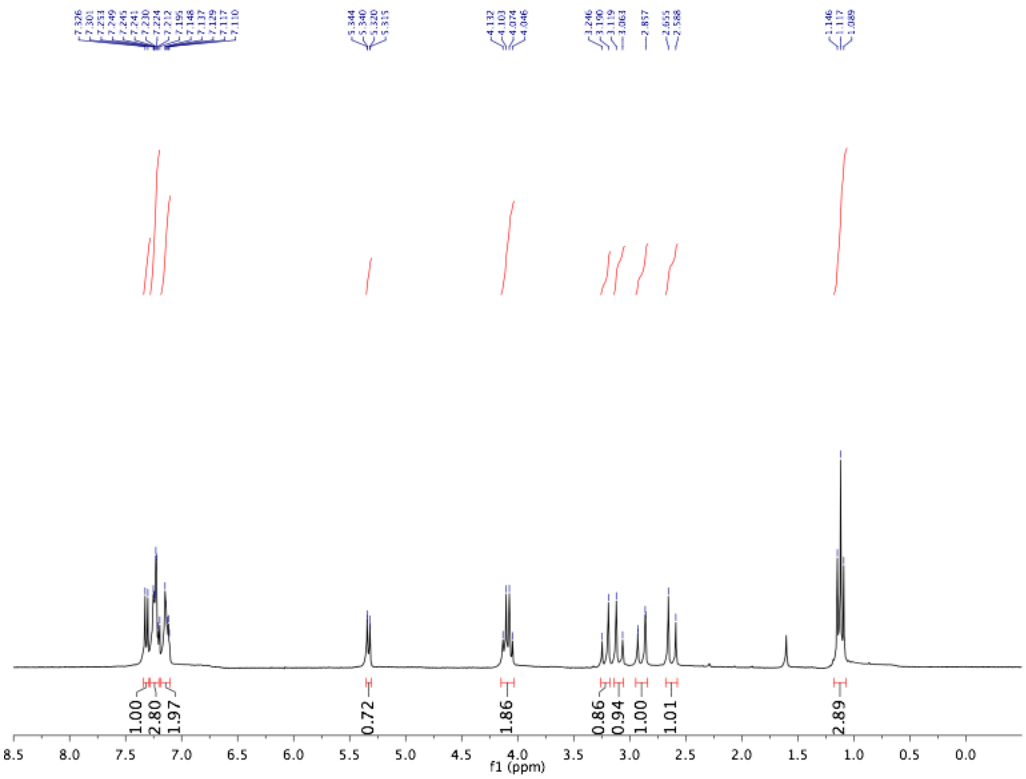


^{1}H NMR of Compound **3e**



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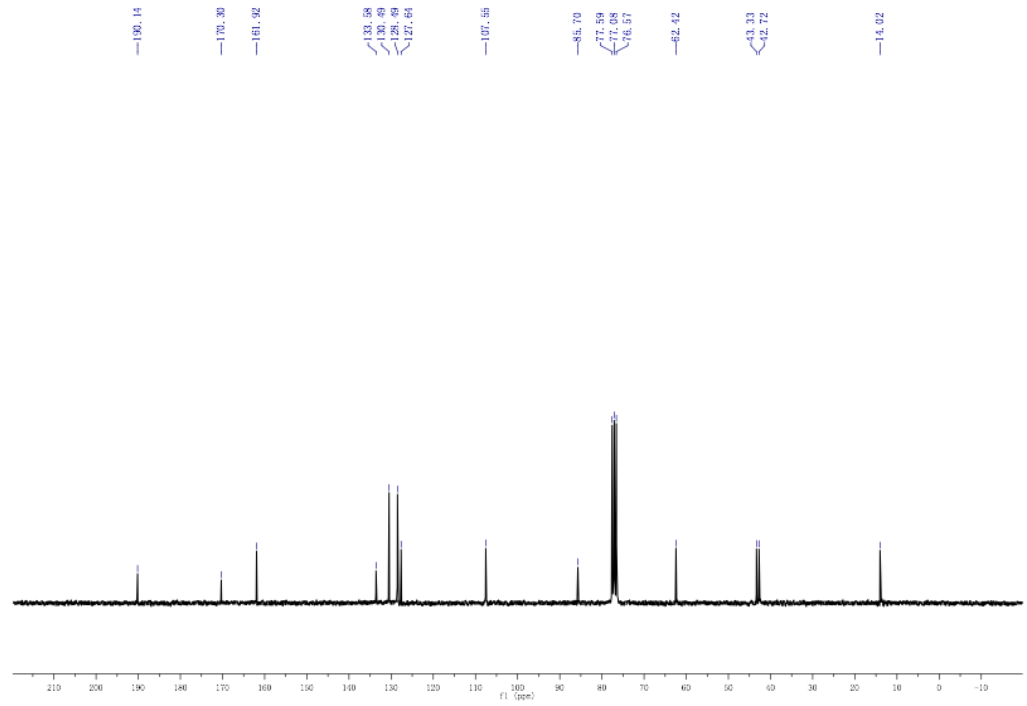
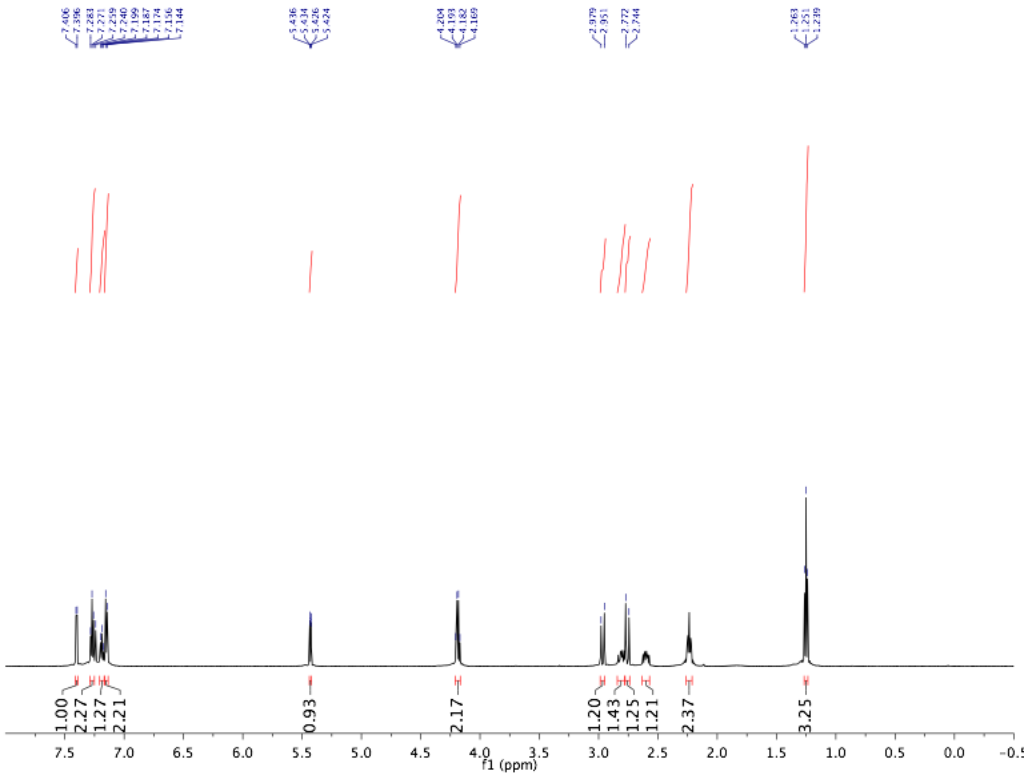
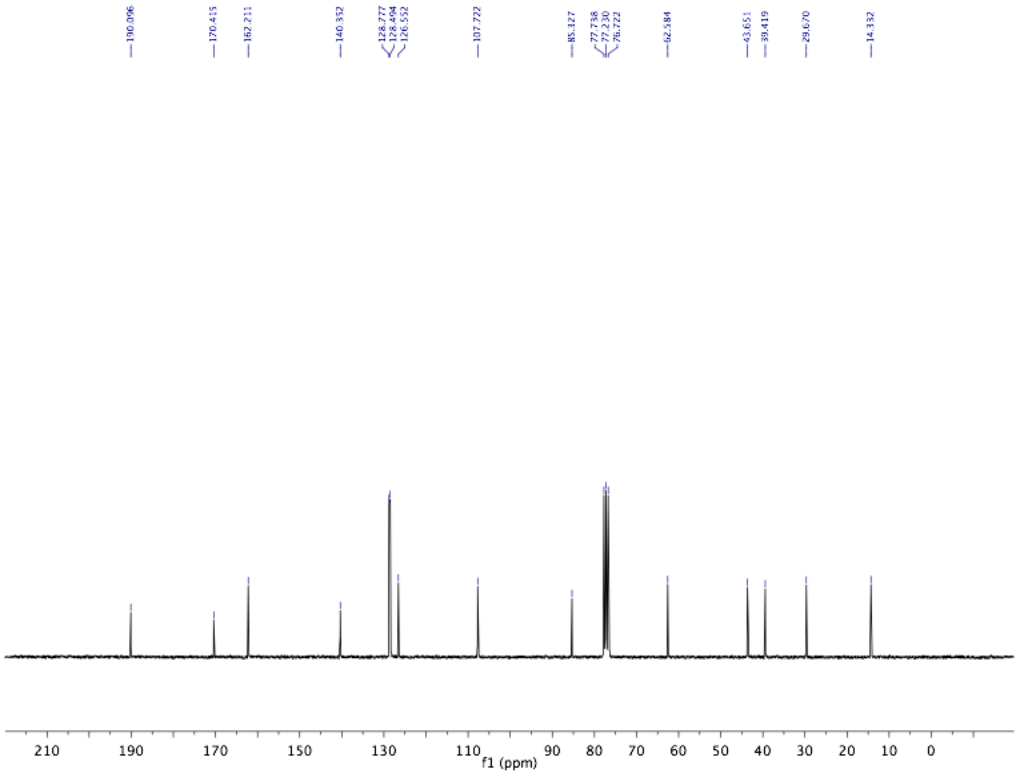


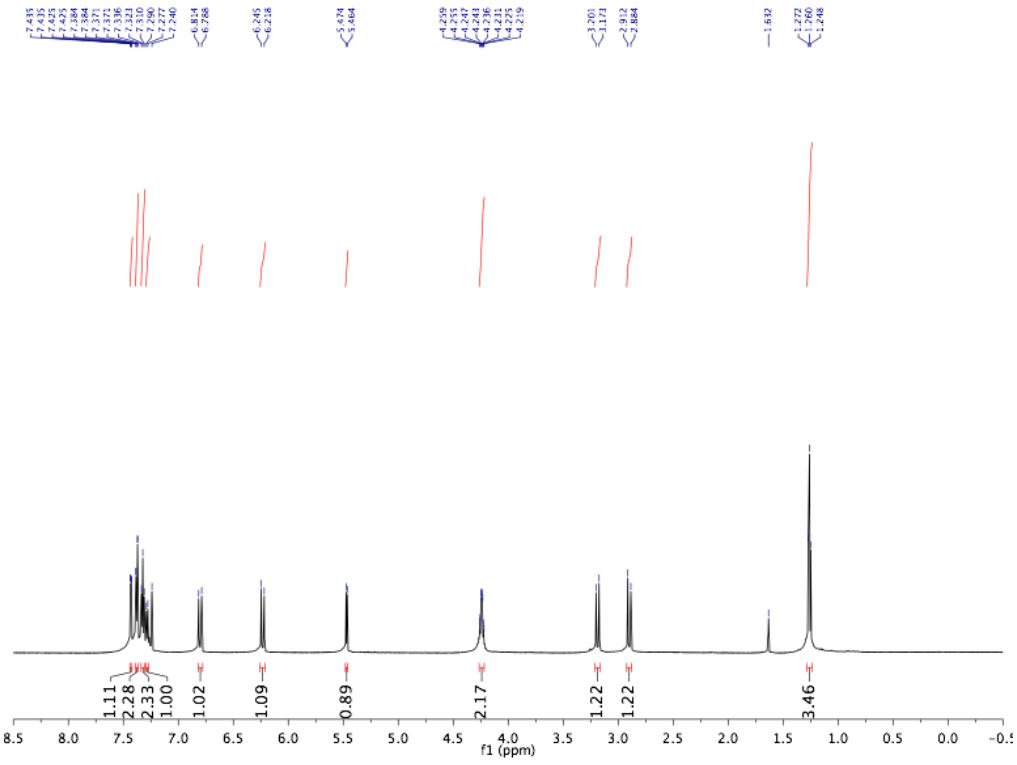
^{1}H NMR of Compound **3f**



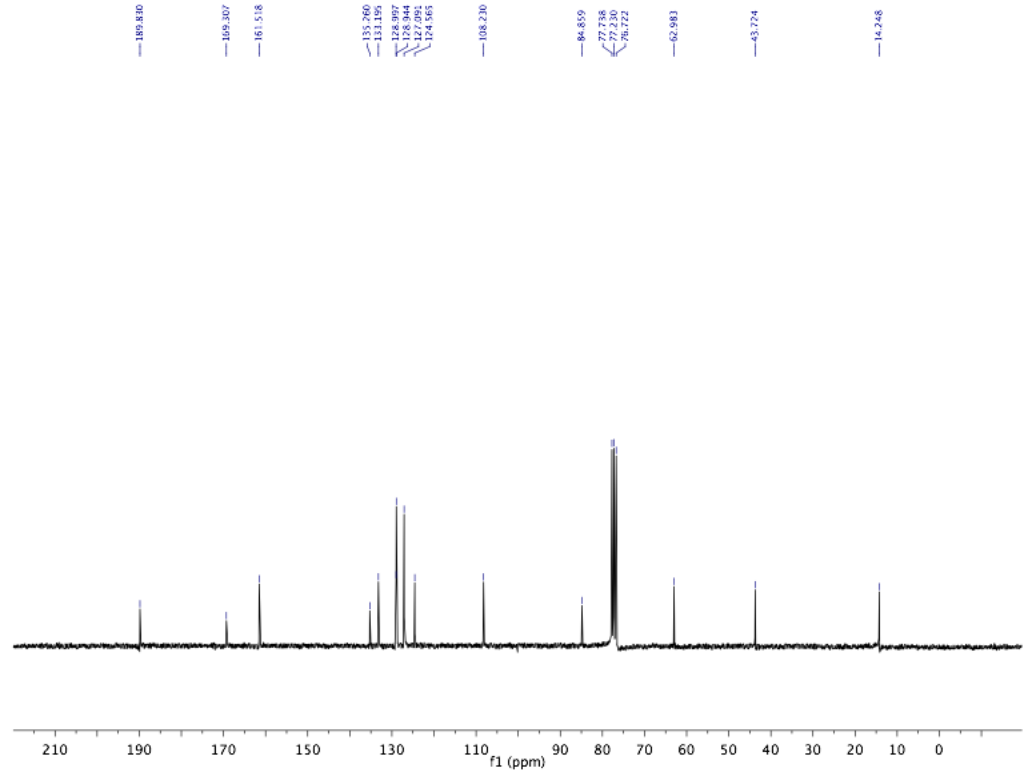
^{13}C NMR of Compound **3f**



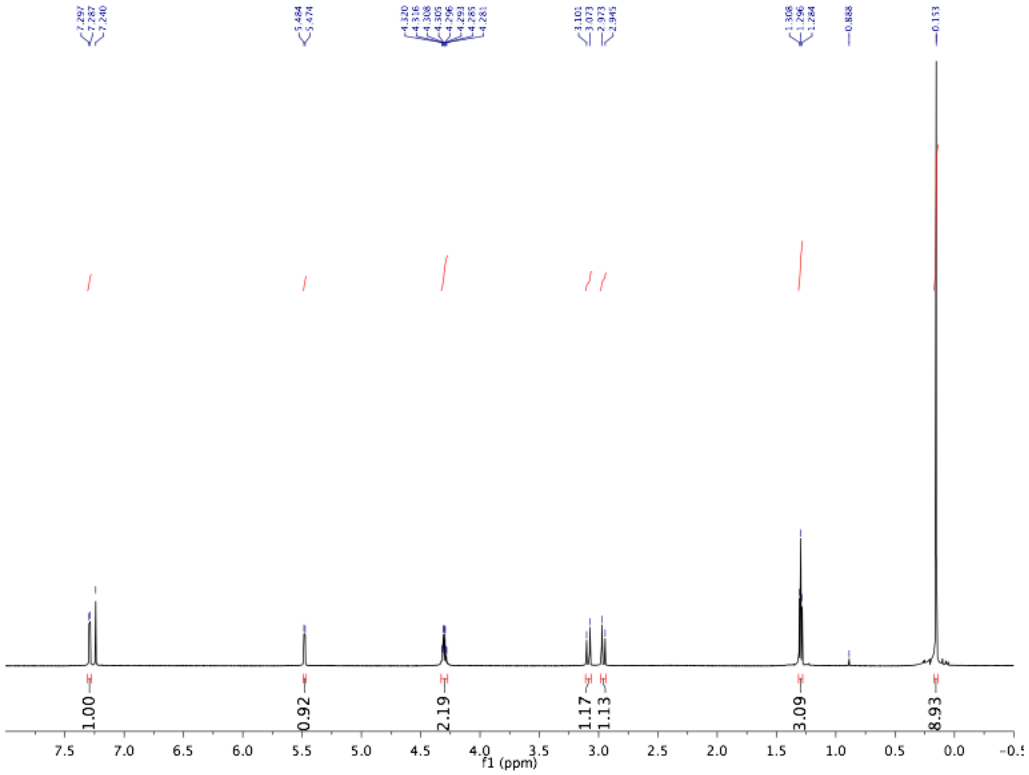
^{1}H NMR of Compound **3g**



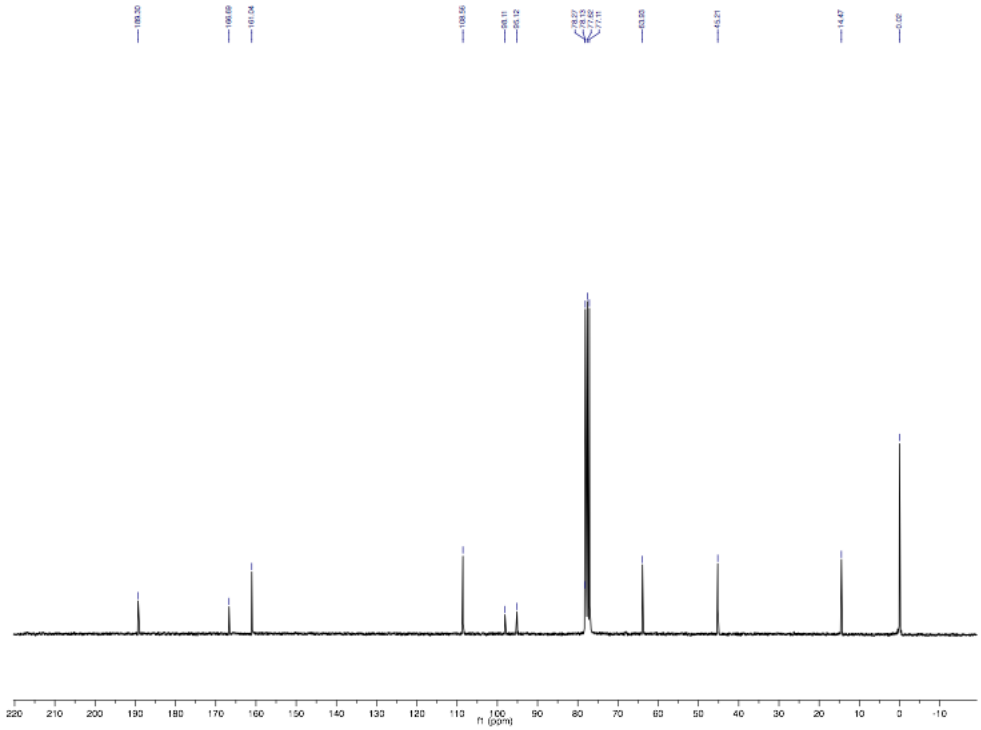
^{13}C NMR of Compound **3g**



^{1}H NMR of Compound **3h**



^{13}C NMR of Compound **3h**



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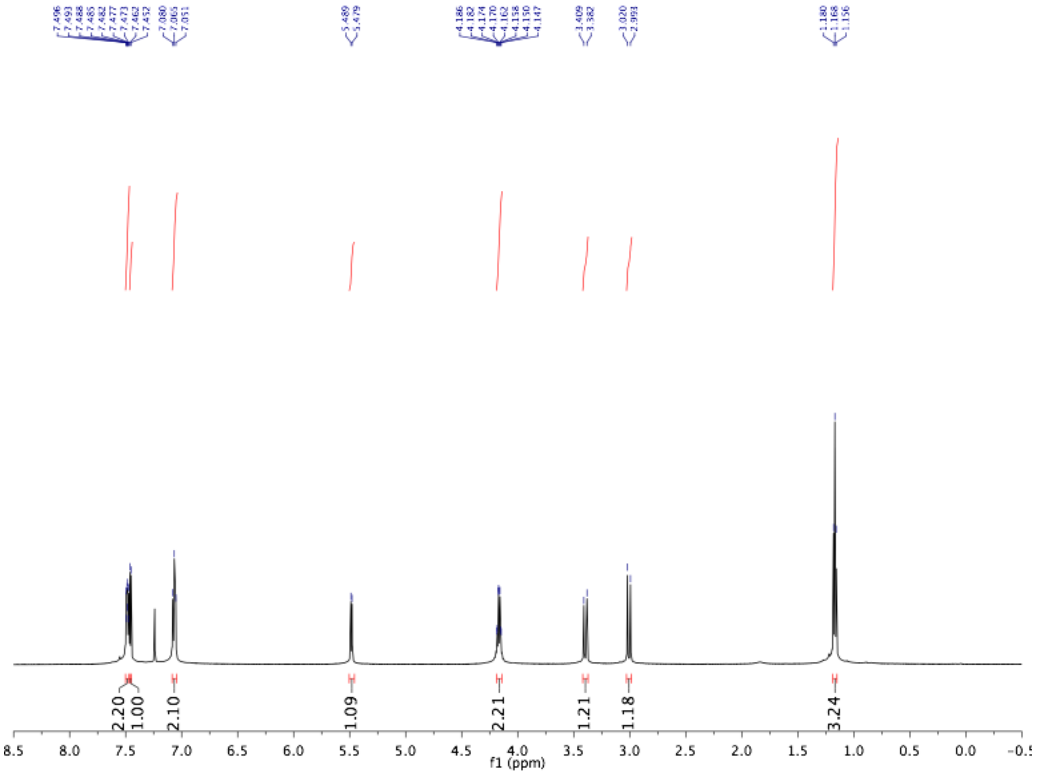
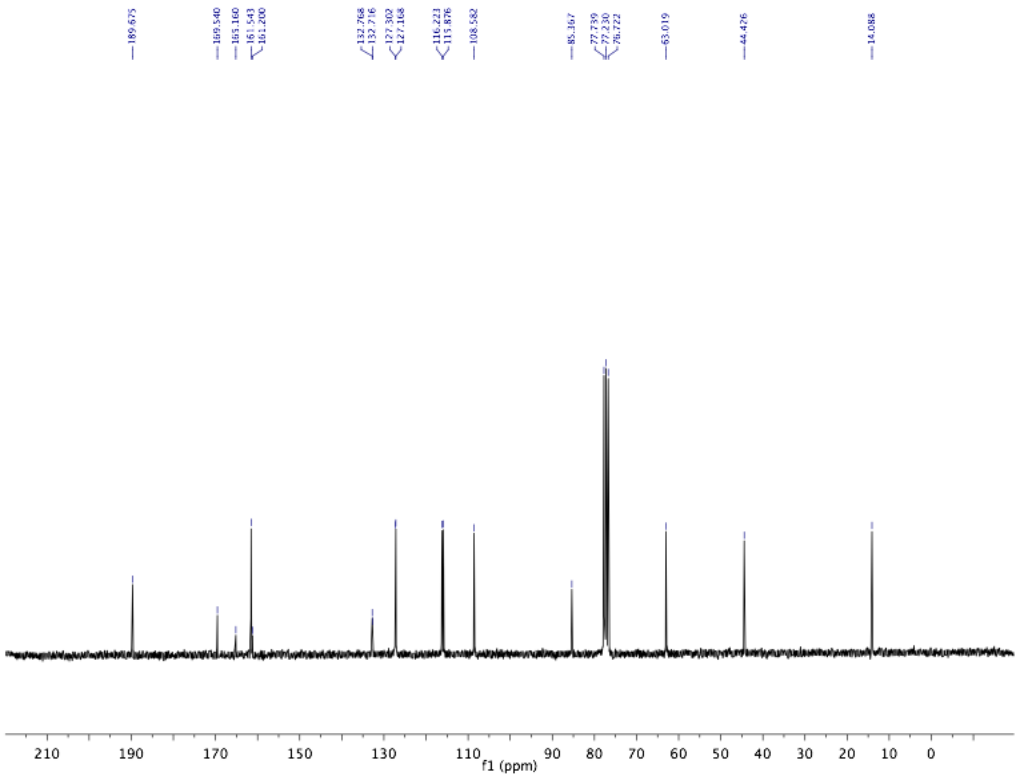
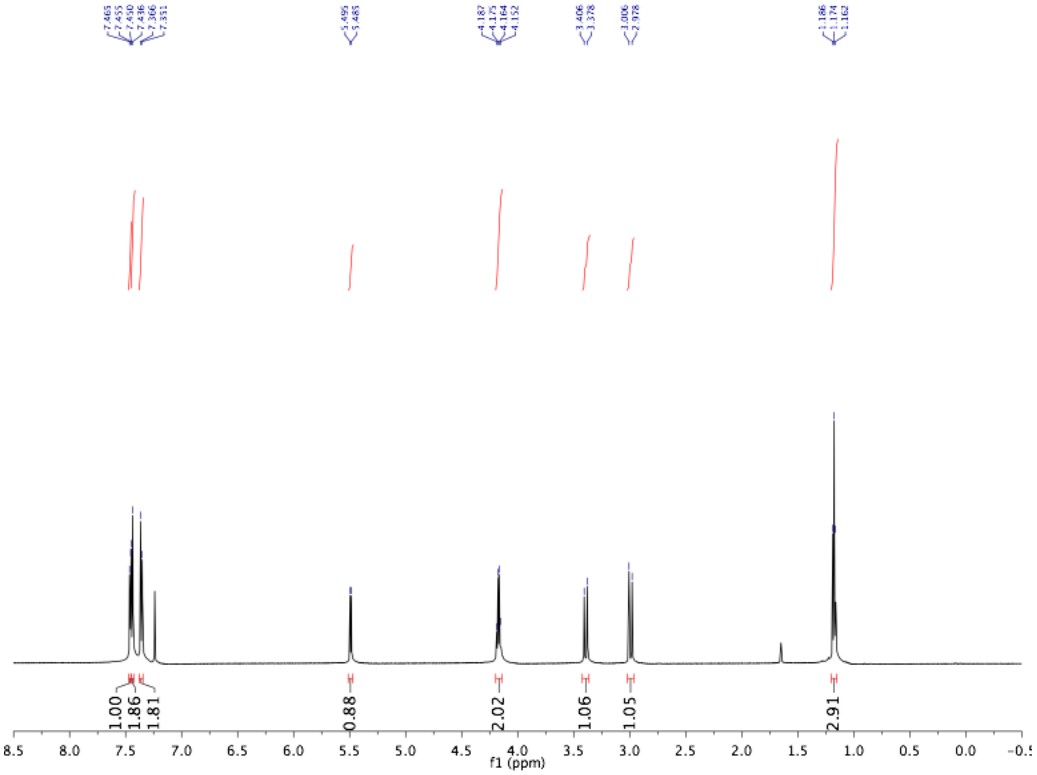


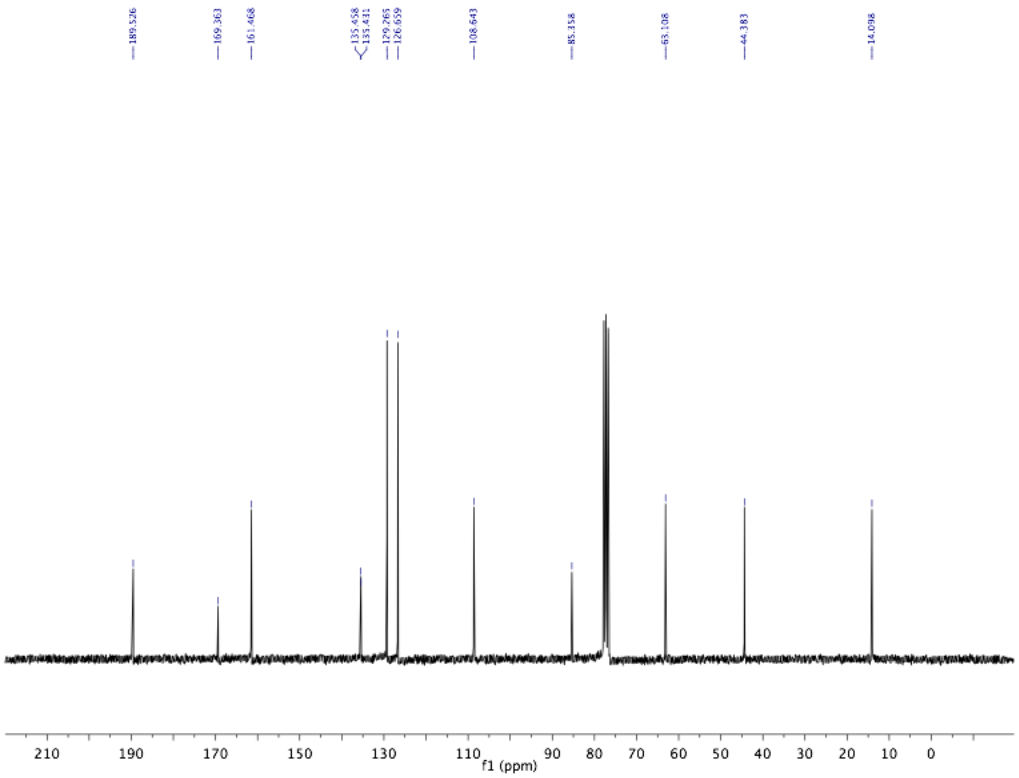
^{13}C NMR of Compound **3j**



^{1}H NMR of Compound **3k**



^{13}C NMR of Compound **3k**



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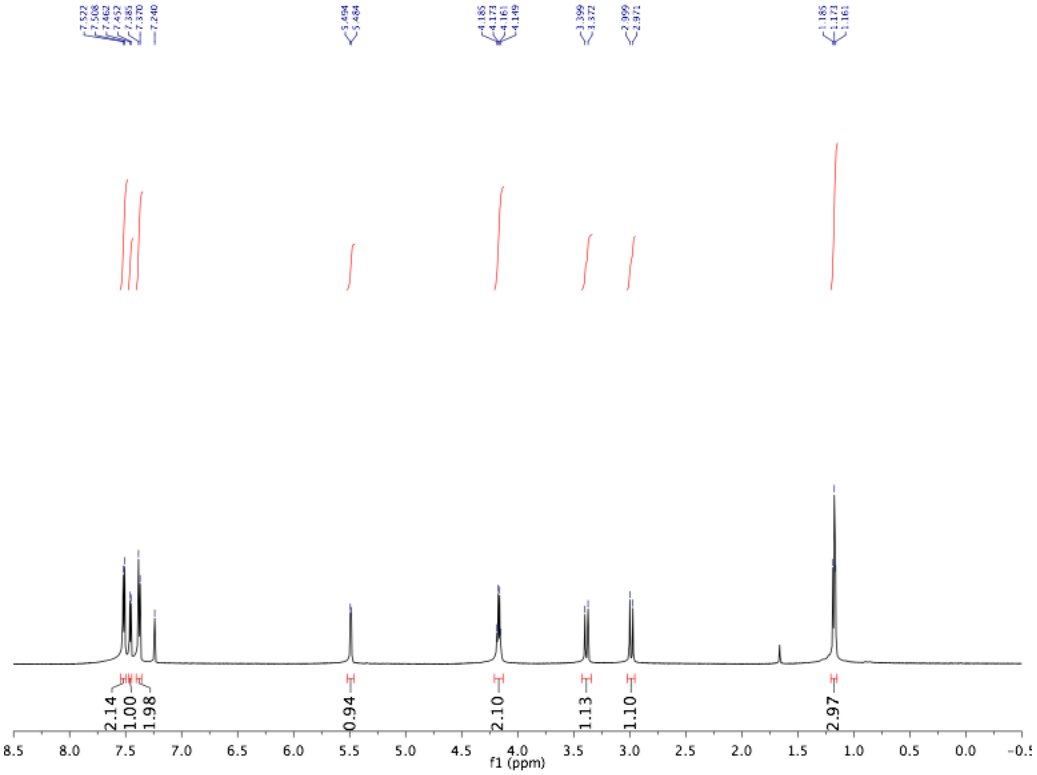
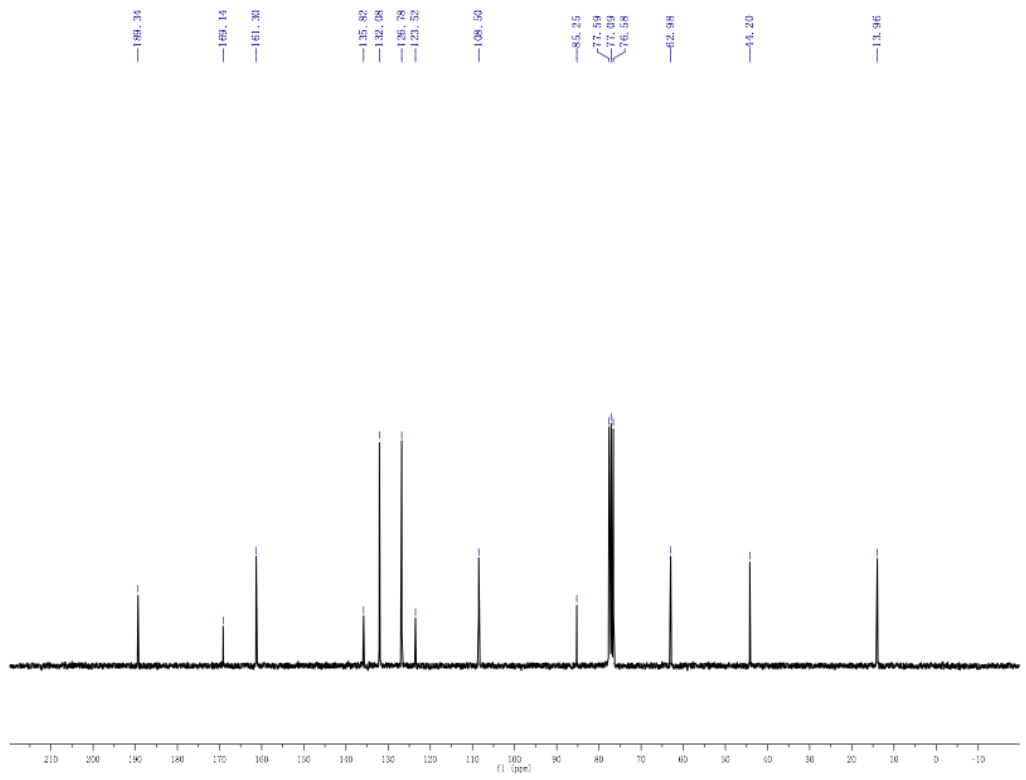
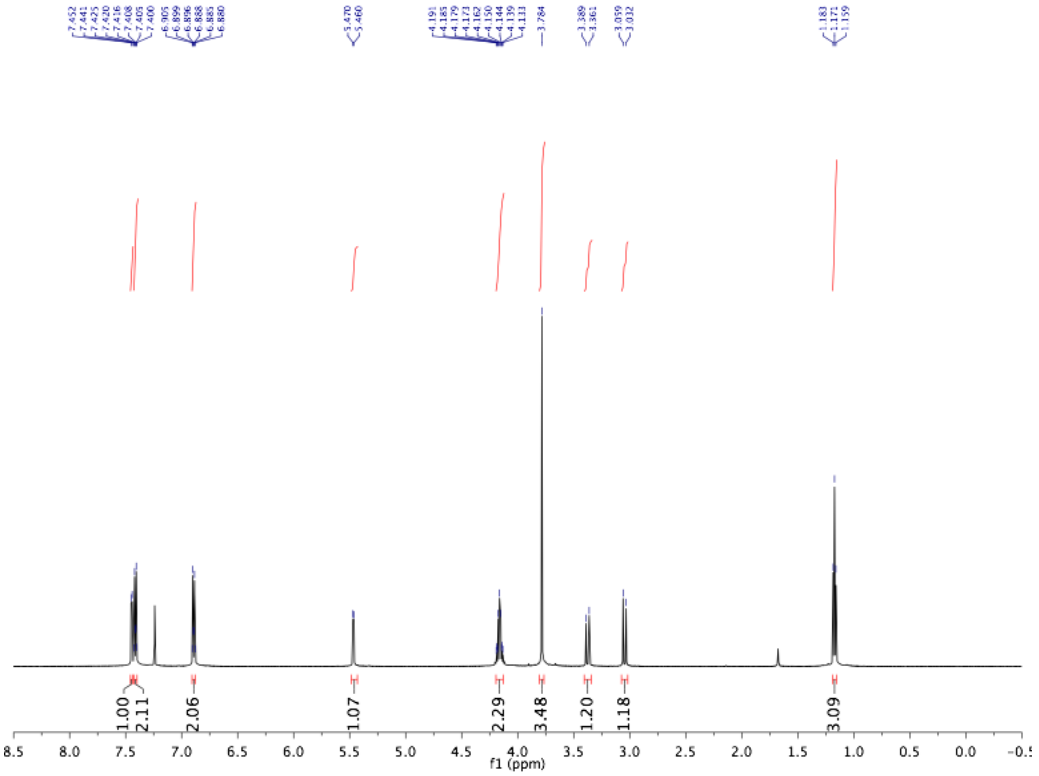


^{13}C NMR of Compound **3l**



^{1}H NMR of Compound **3m**



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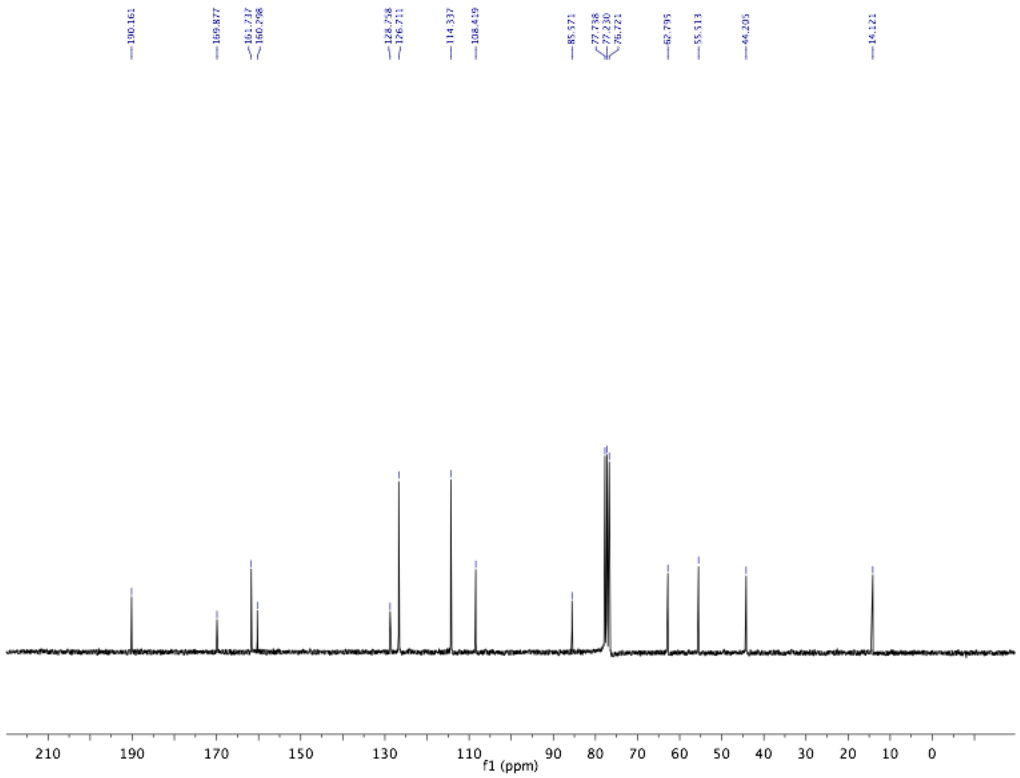
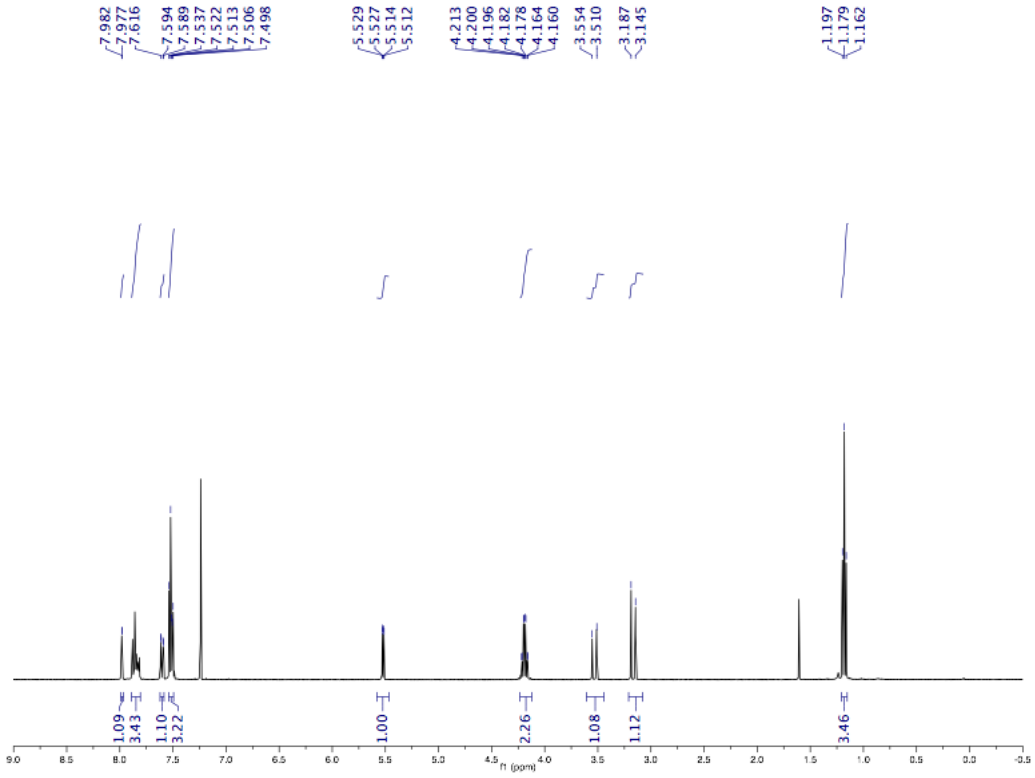
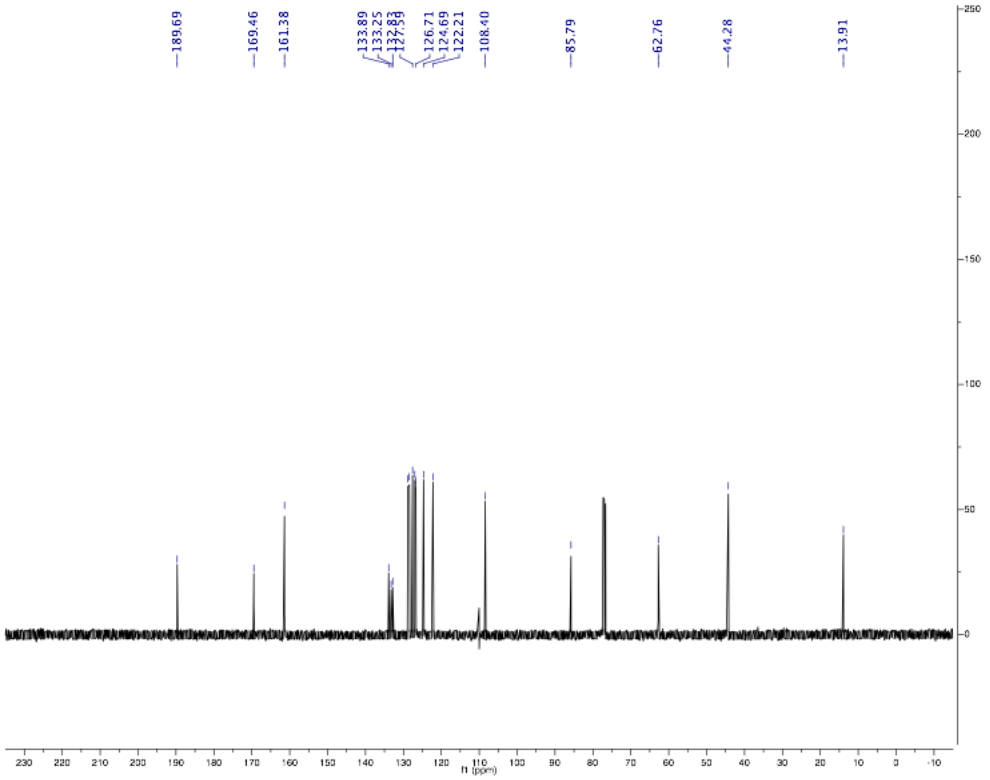


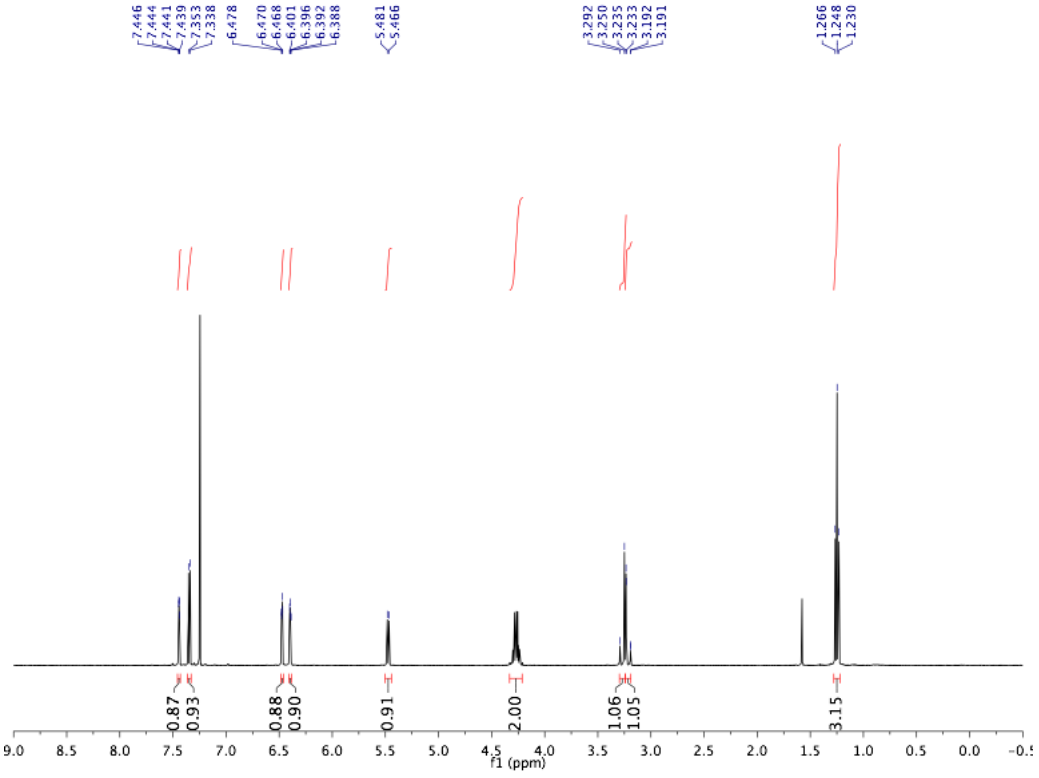
^{1}H NMR of Compound **3n**



^{13}C NMR of Compound **3n**



^{1}H NMR of Compound **3o**



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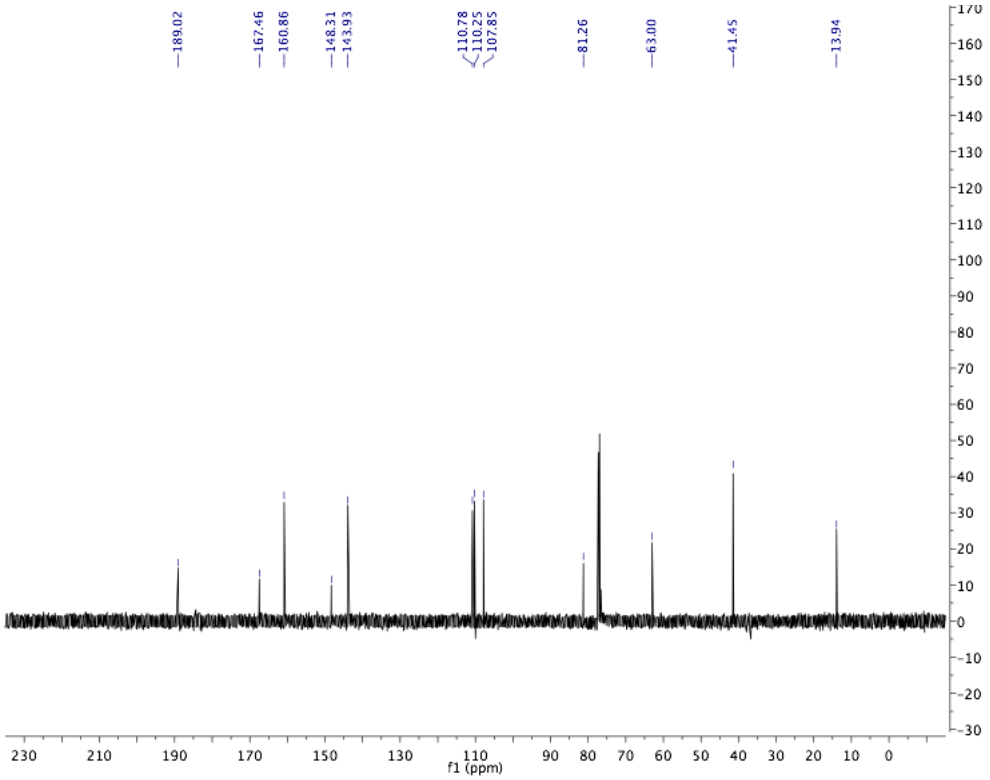
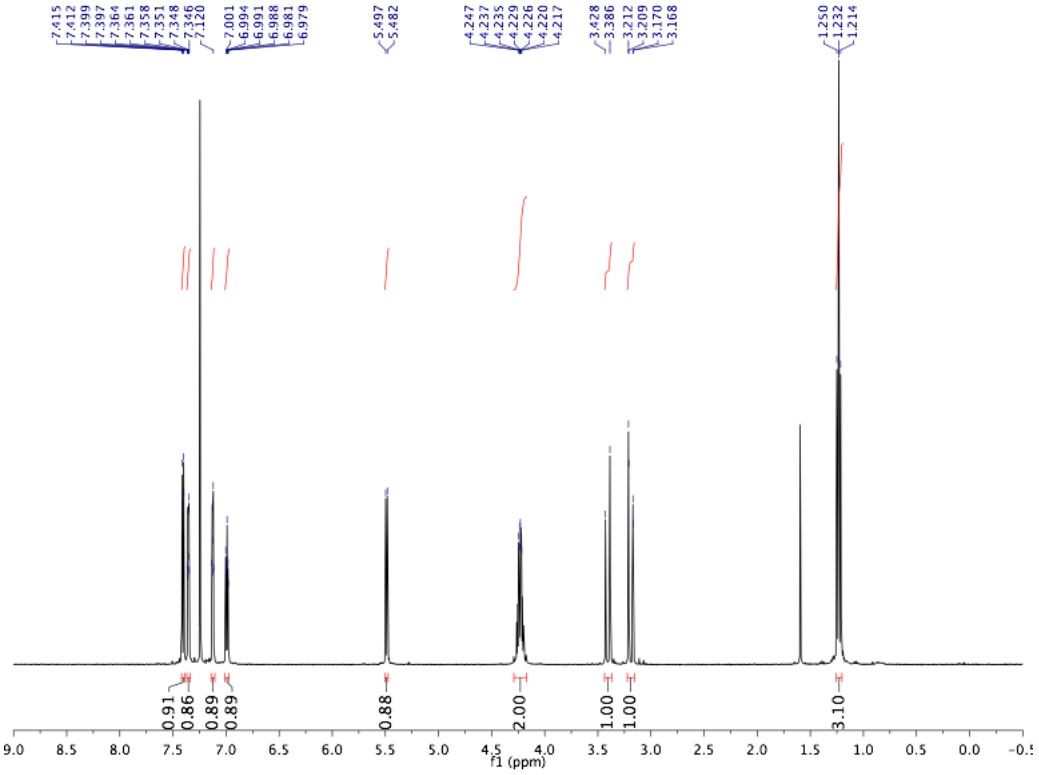
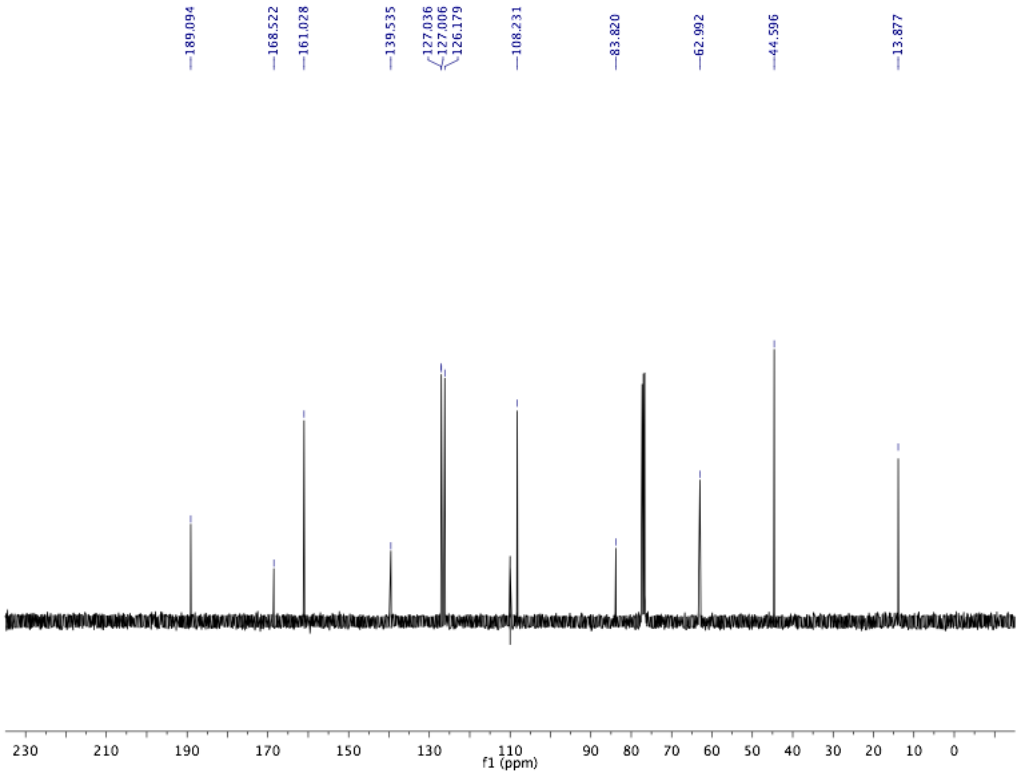


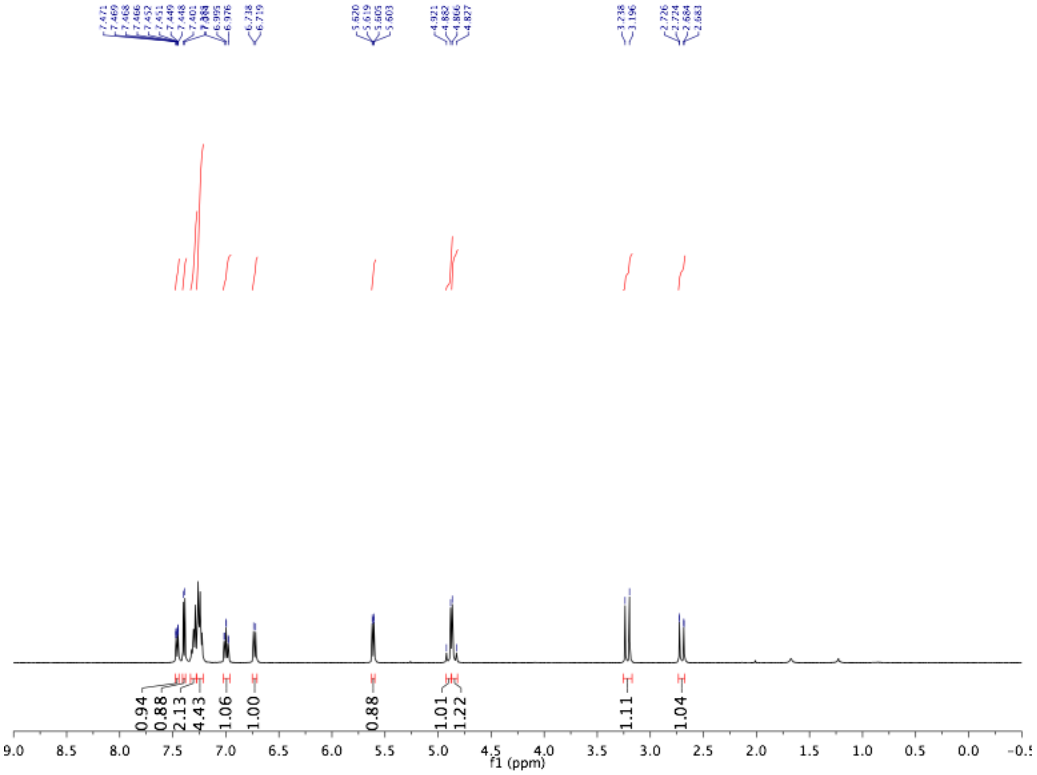
^{1}H NMR of Compound **3p**



^{13}C NMR of Compound **3p**



^{1}H NMR of Compound **5a**



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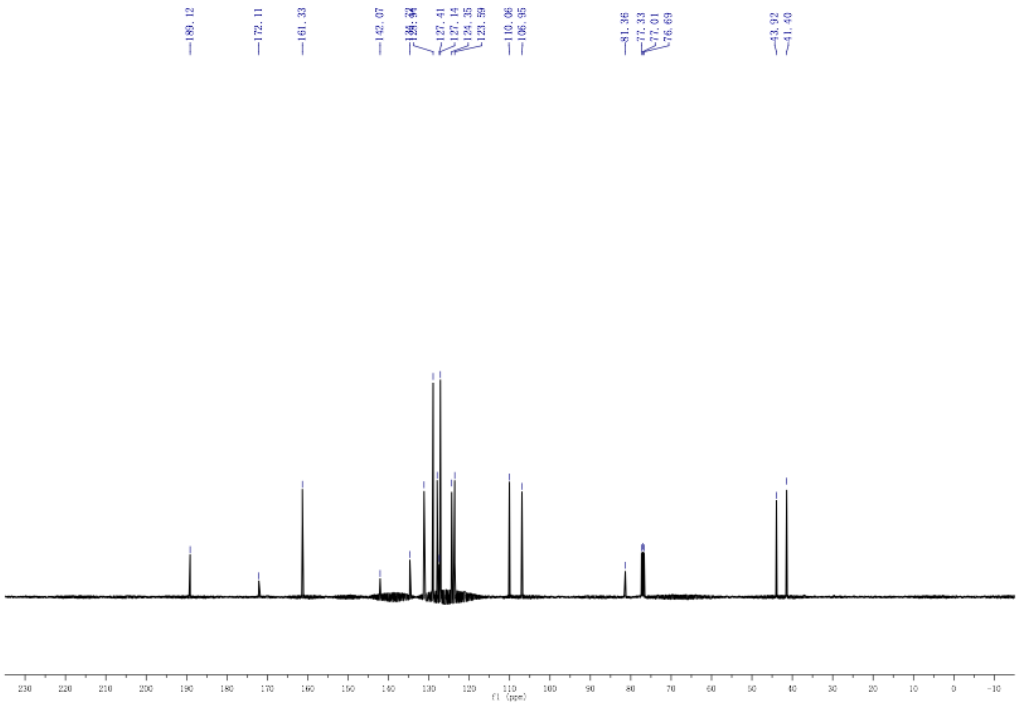
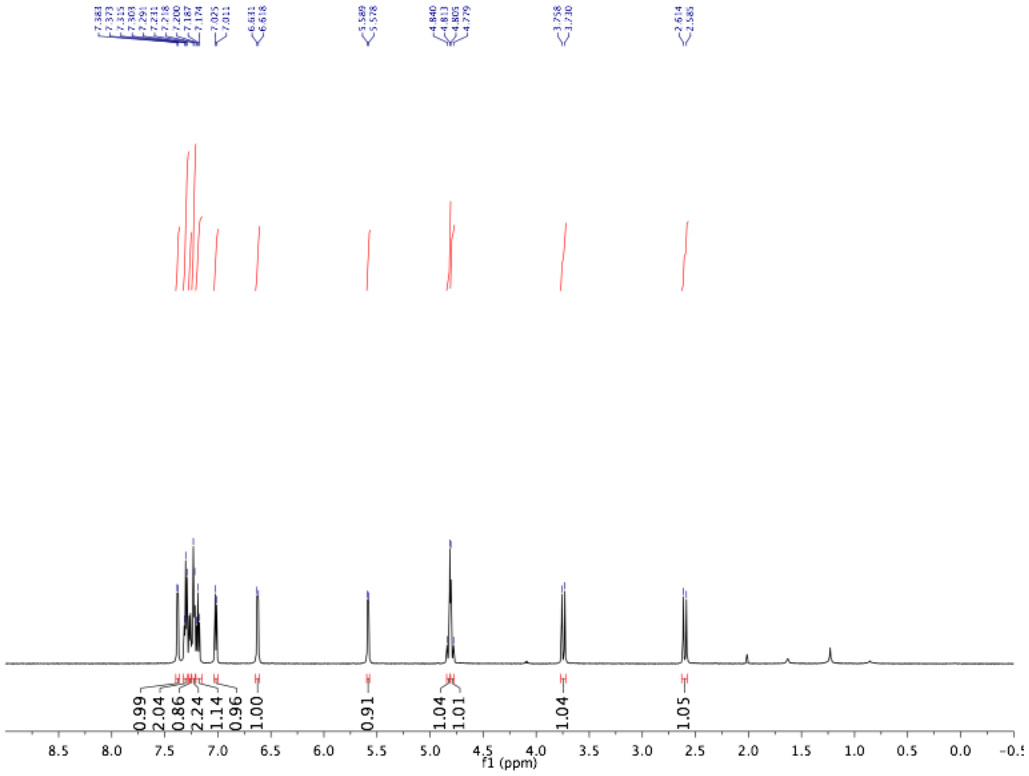


^{1}H NMR of Compound **5b**



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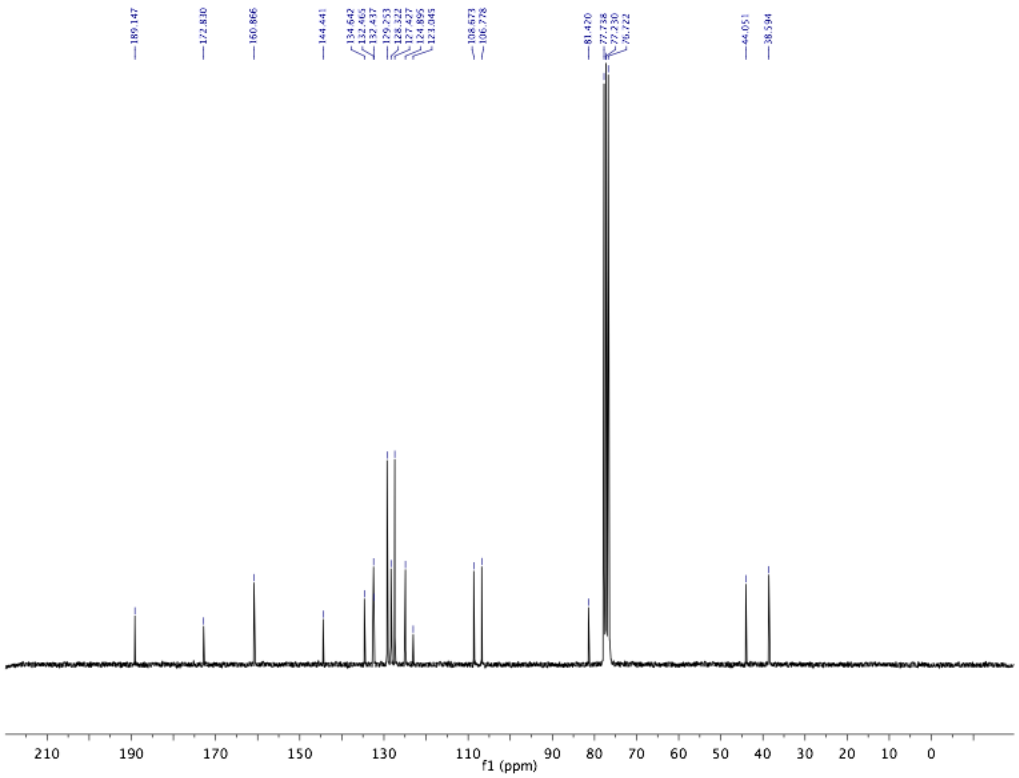
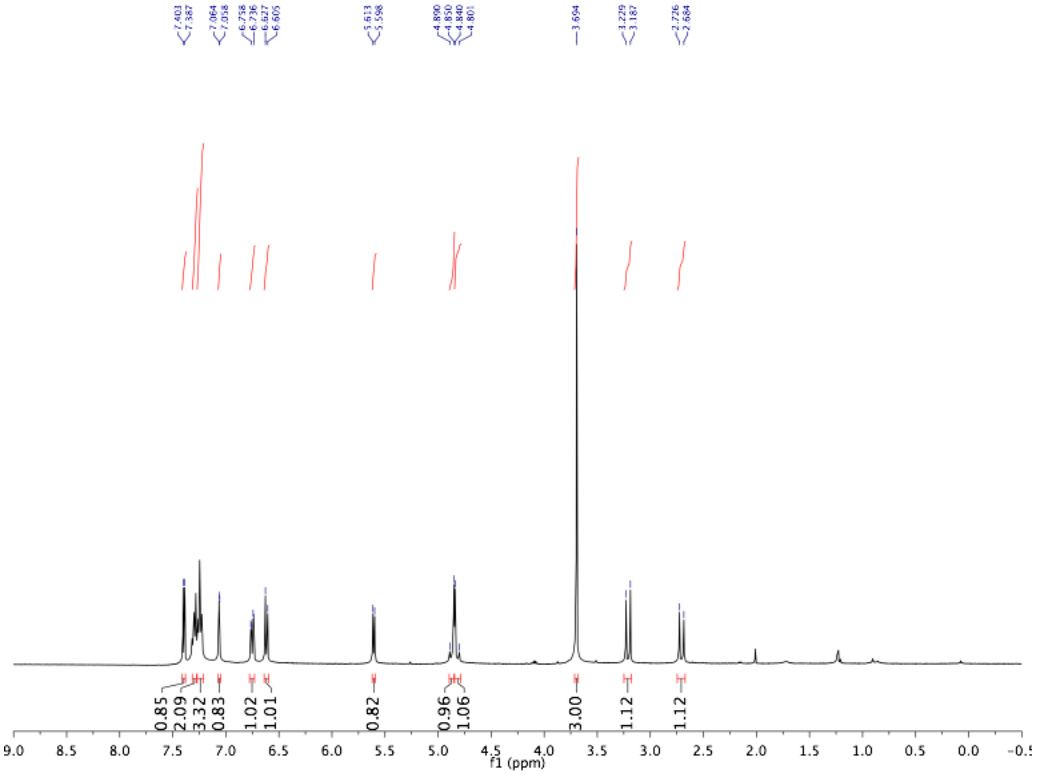
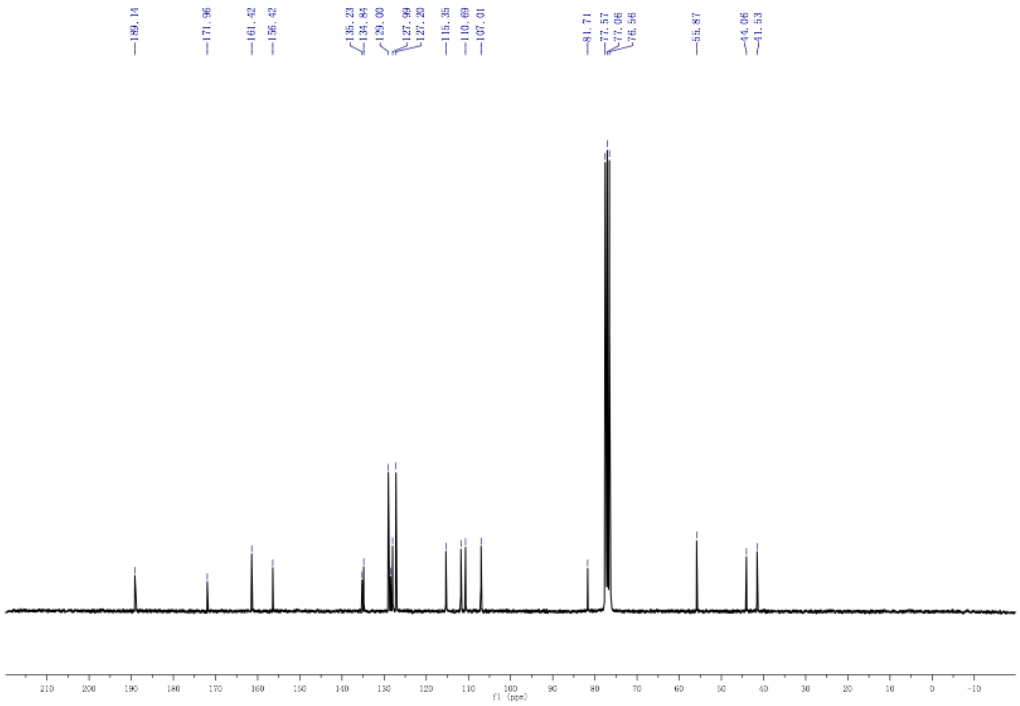


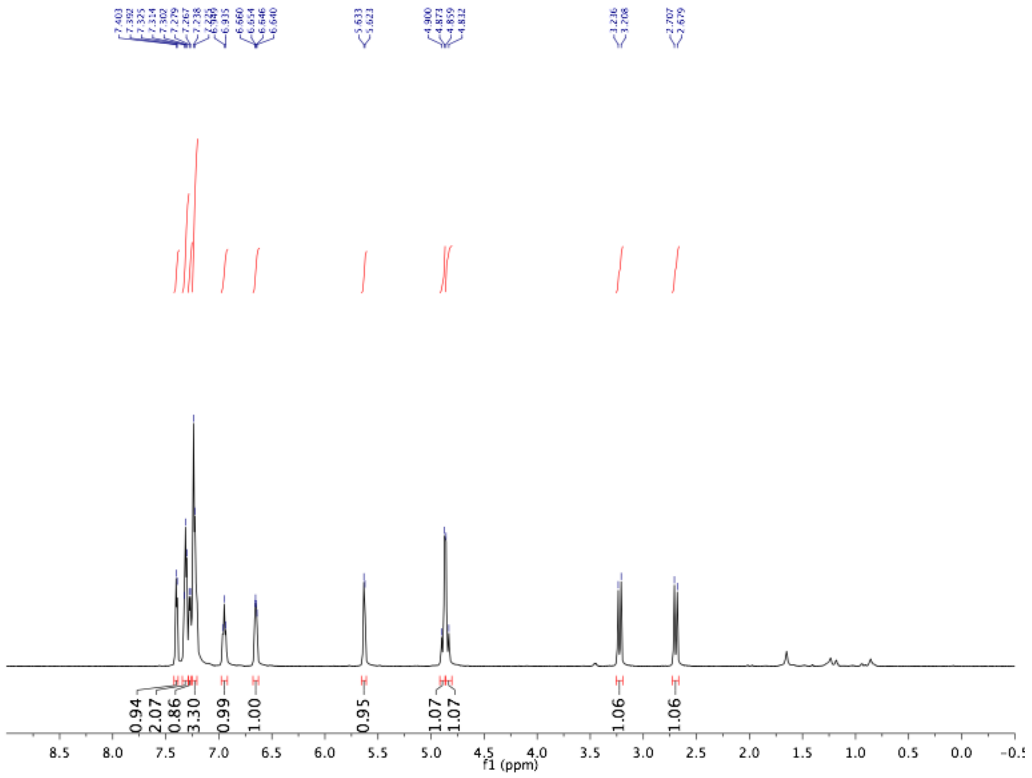
^{1}H NMR of Compound **5c**



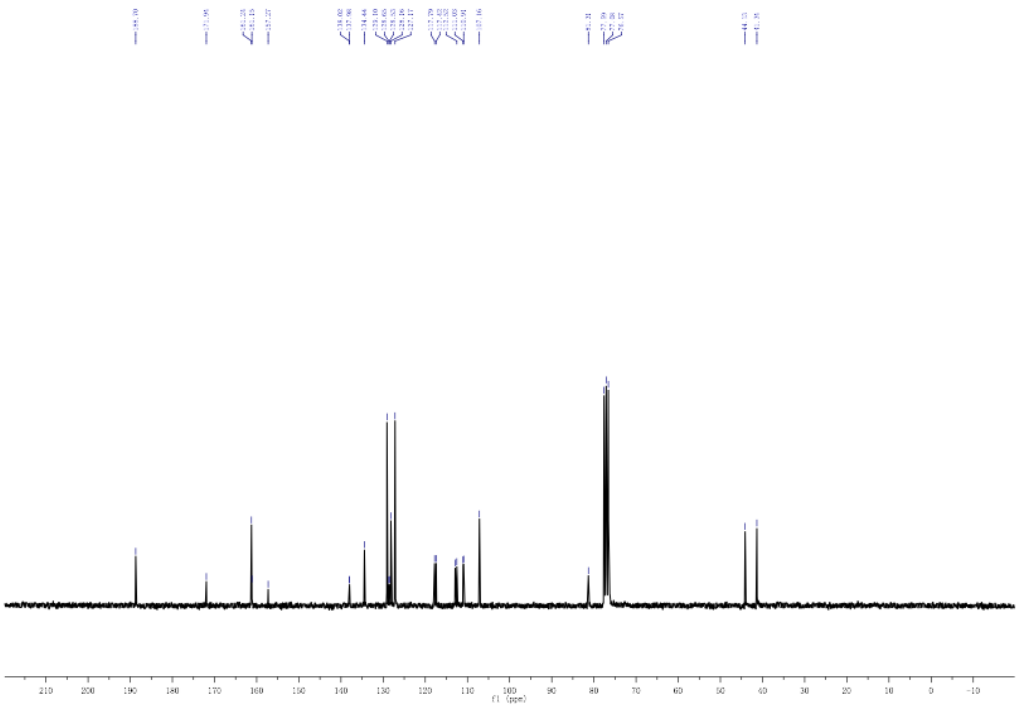
^{13}C NMR of Compound **5c**



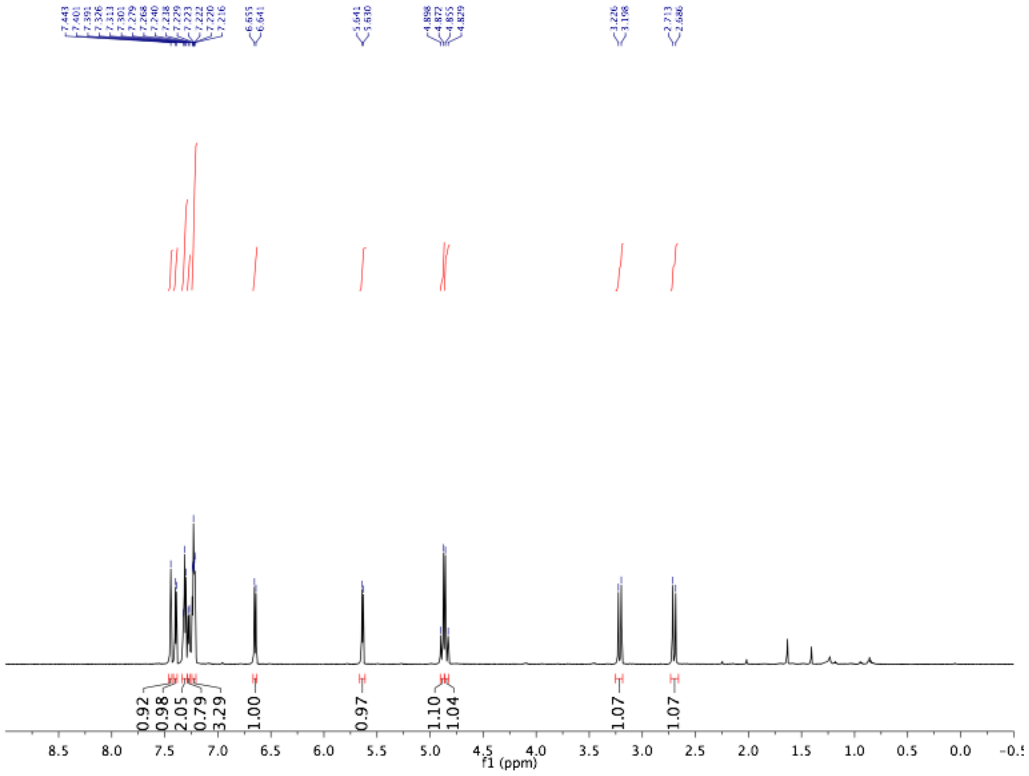
^{1}H NMR of Compound **5d**



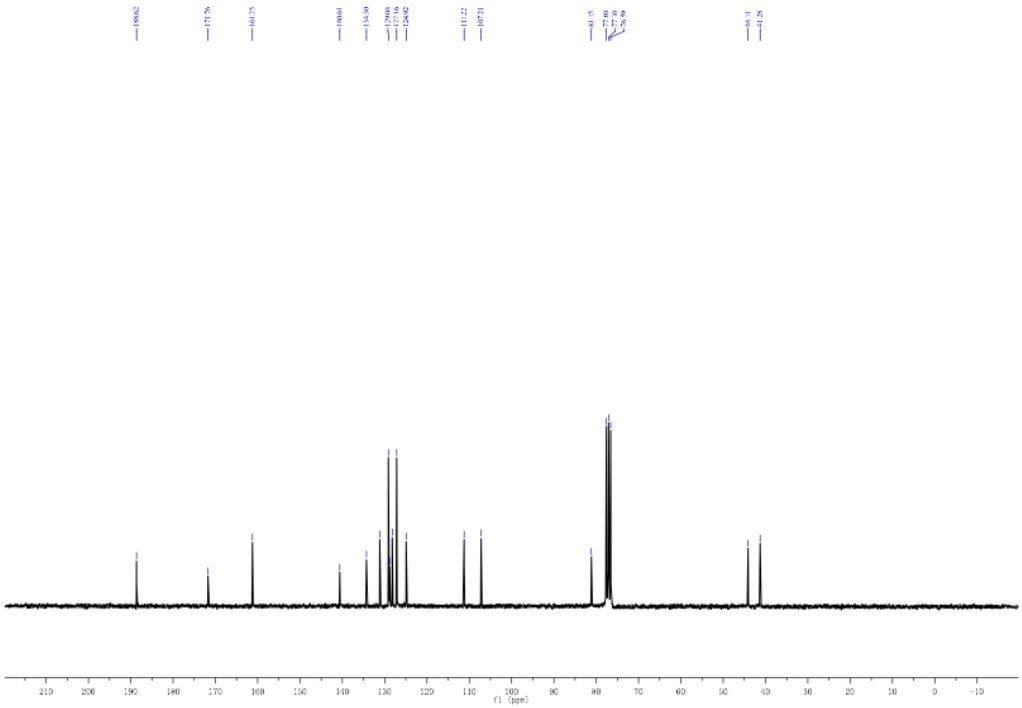
^{13}C NMR of Compound **5d**



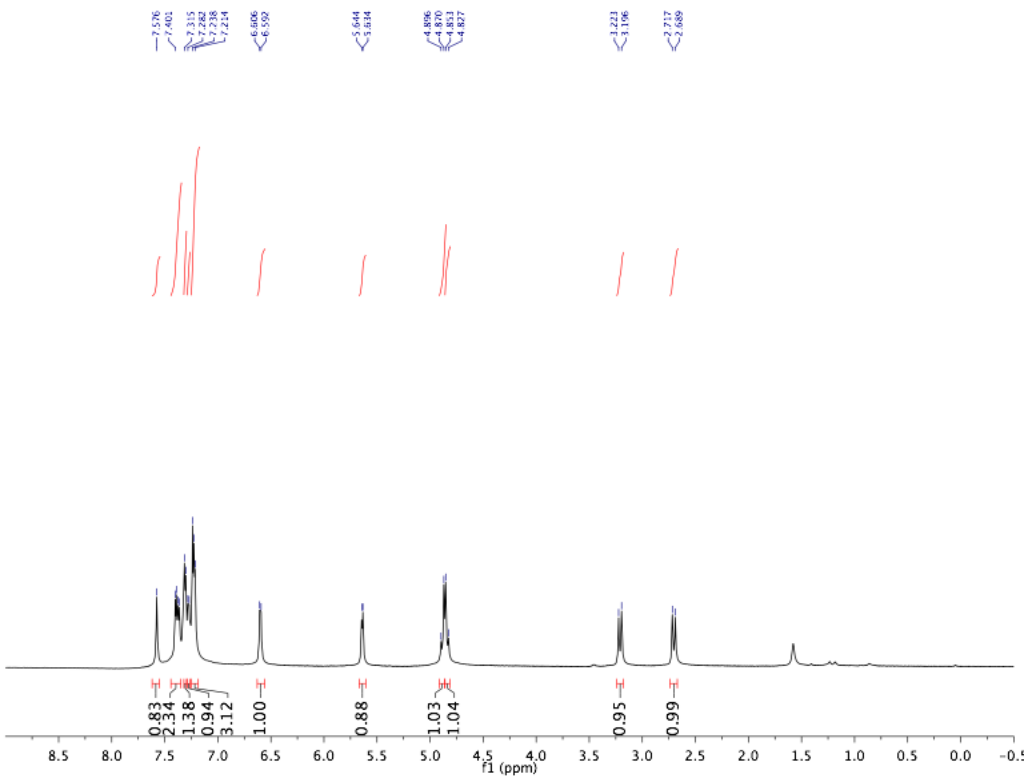
^{1}H NMR of Compound **5e**



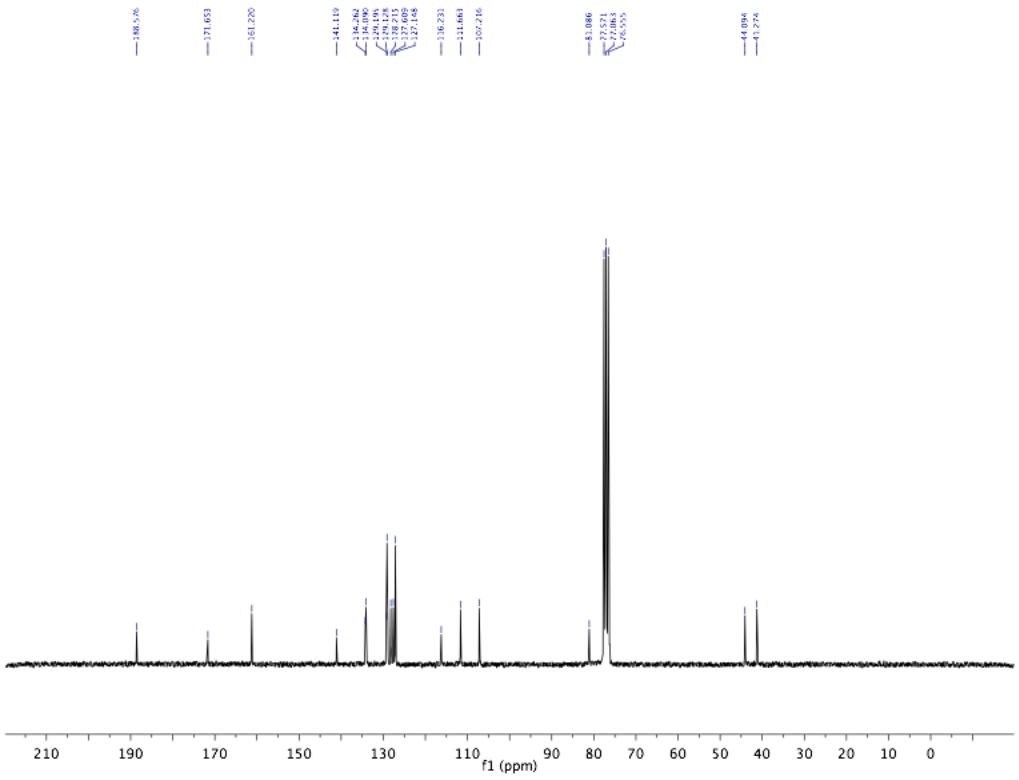
^{13}C NMR of Compound **5e**



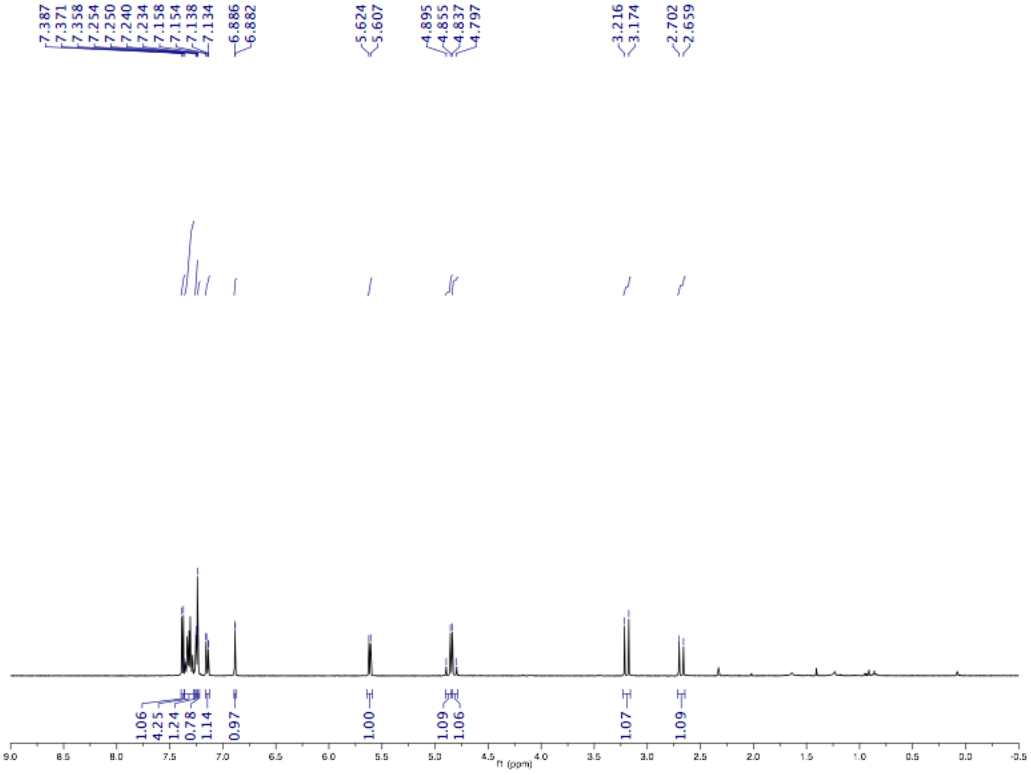
^{1}H NMR of Compound **5f**



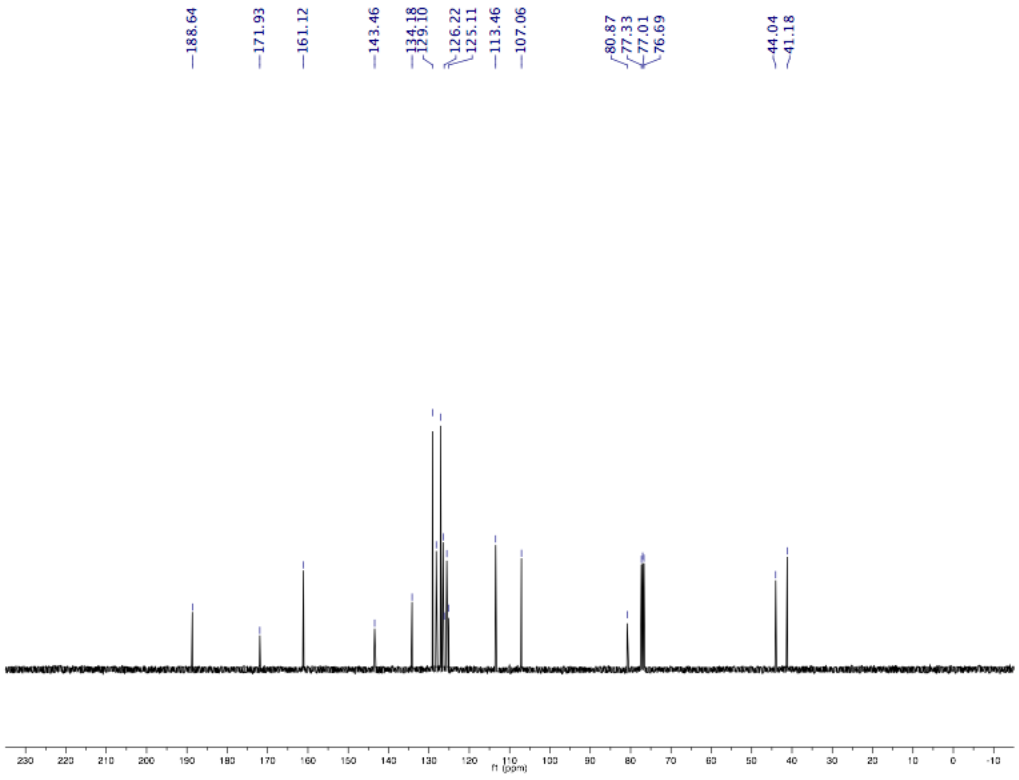
^{13}C NMR of Compound **5f**



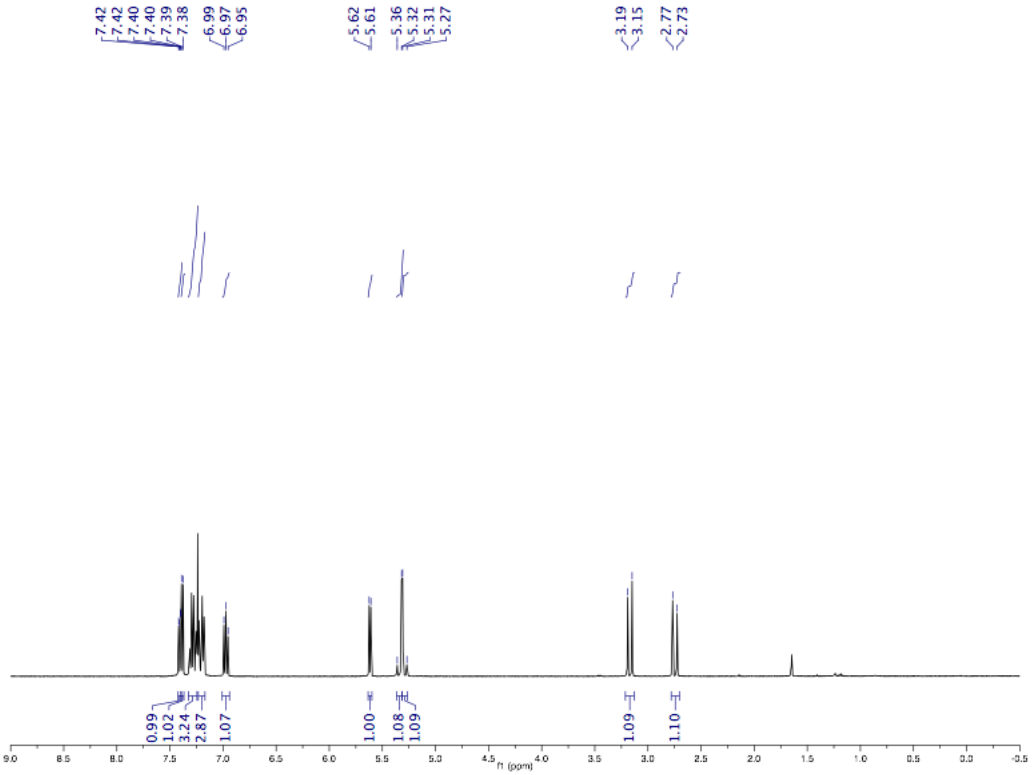
^{1}H NMR of Compound **5g**



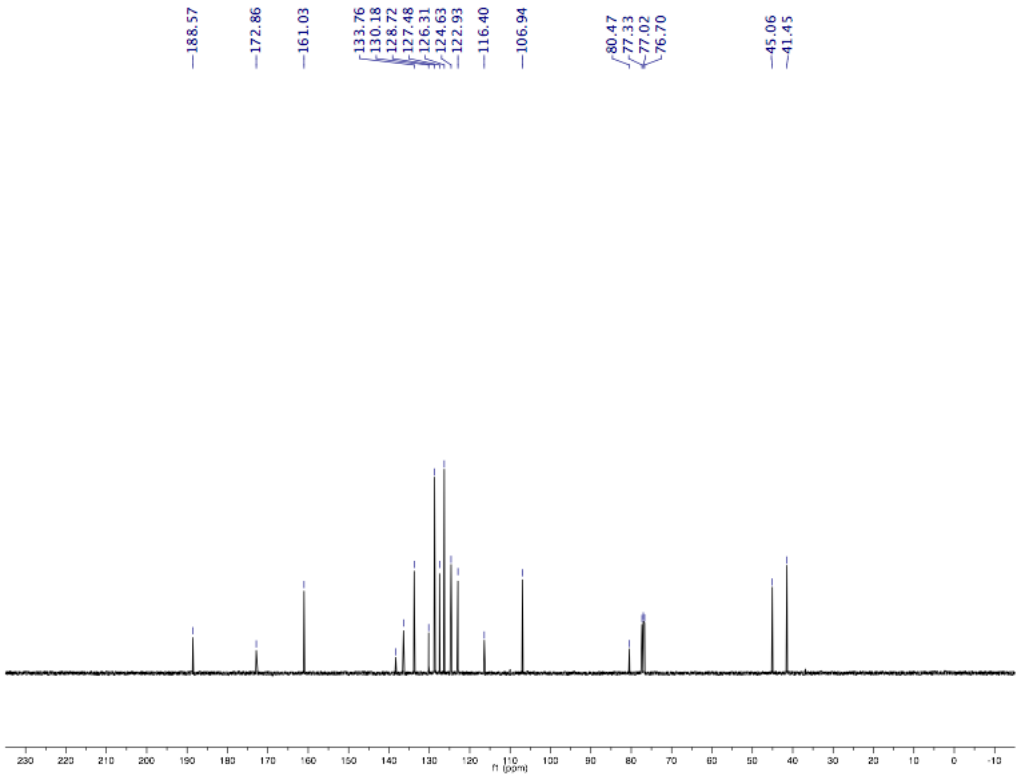
^{13}C NMR of Compound **5g**



^{1}H NMR of Compound **5h**



^{13}C NMR of Compound **5h**



X-ray Crystallography

The X-ray intensity data for **Ca[P4]2** were measured on a Bruker D8 Venture PHOTON 100 CMOS system equipped with a Cu K_α INCOATEC Imus micro-focus source (λ = 1.54178 Å). The X-ray diffraction data for compound **5b** were collected using Bruker-AXS SMART-APEXII CCD diffractometer (CuKα, λ = 1.54178 Å). Indexing was performed using *APEX2* [1] (Difference Vectors method). Data integration and reduction were performed using SaintPlus [2]. Absorption correction was performed by multi-scan method implemented in SADABS [3]. Space groups were determined using XPREP implemented in APEX2 [1]. The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL97 (**5b**) SHELXL-2012 Beta version (**Ca[P4]2**) contained in OLEX2 [9] and WinGX v1.70.01 [4,5,6,7] programs.

5b: CCDC 1009077. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms of groups were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Crystal data and refinement conditions are shown in Table 1.

Ca[P4]2: CCDC 1009078. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of –CH groups were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH). Hydrogen atoms of methanol molecules have been refined using DFIX and DANG

restraints and Uiso(H) = 1.5Ueq(-OH). Hydrogen atoms of water molecule have been refined using DFIX and DANG restraints and Uiso(H) = 1.5Ueq(-OH). Atoms C22, C25 and C26 have been refined using restraints for ADP's (SIMU, ISOR). Crystal was a pseudo-merohedral twin (β~90) with 2-fold axis along [100 or 001] acting as twinning operator (1/0/0 0/-1/0 0/0/-1). BASF = 0.15. One molecule of methanol is disordered over two positions. Crystal data and refinement conditions are shown in Table 2.

[1] Bruker (2012). *APEX2* . Bruker AXS Inc., Madison, Wisconsin, USA.

[2] Bruker (20012). SAINT. Data Reduction Software.

[3] Sheldrick, G. M. (1996). *SADABS. Program for Empirical Absorption Correction.* University of Gottingen, Germany.

[4] Farrugia L.J. Appl. Cryst. (1999). 32, 837±838

[5] Sheldrick, G.M. (2012 Beta) SHELXL-97. Program for the Refinement of Crystal

[6] Sheldrick, G.M. (1990) Acta Cryst. A46, 467-473

[7] Sheldrick, G. M. (2008). Acta Cryst. A64, 112-122.

[8] Dolomanov, O.V.; Bourhis, L.J.; Gildea, R.J.; Howard, J.A.K.; Puschmann, H., OLEX2: A complete structure solution, refinement and analysis program (2009). J. Appl. Cryst., 42, 339-341.

Table 1 Crystal data and structure refinement for **5b**

Identification code	**5b**
Empirical formula	C19 H14 Cl N O3
Formula weight	339.76
Temperature	228(2) K
Wavelength	1.54178 A
Crystal system, space group	Orthorhombic, P212121
Unit cell dimensions	a = 5.70670(10) A alpha = 90 deg. b = 13.4355(2) A beta = 90 deg. c = 20.8250(3) A gamma = 90 deg.
Volume	1596.70(4) A^3
Z, Calculated density	4, 1.413 Mg/m^3
Absorption coefficient	2.265 mm^-1
F(000)	704
Crystal size	0.40 x 0.12 x 0.08 mm
Theta range for data collection	3.92 to 68.38 deg.
Limiting indices	-5<=h<=6, -15<=k<=16, -25<=l<=24

Reflections collected / unique	19107 / 2884 [R(int) = 0.0322]
Completeness to theta = 68.38	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8396 and 0.4644
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2884 / 0 / 218
Goodness-of-fit on F^2	1.047
Final R indices [I>2sigma(I)]	R1 = 0.0281, wR2 = 0.0726
R indices (all data)	R1 = 0.0293, wR2 = 0.0736
Absolute structure parameter	0.009(13)
Extinction coefficient	0.0020(3)
Largest diff. peak and hole	0.145 and -0.159 e.A^-3

Table 2 Crystal data and structure refinement for **Ca[P4]2**	
Identification code	**$Ca[P4]_2$**
Empirical formula	$C_{86}H_{74}CaO_{15}P_2$
Moiety formula	$C_{84}H_{64}CaO_{12}P_2$,2 (CH_4O), H_2O
Formula weight	1449.47
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.2594(3)
b/Å	13.6877(5)
c/Å	32.5308(11)
α/°	90
β/°	90.290(2)
γ/°	90
Volume/Å3	3677.6(2)
Z	2
ρcalcmg/mm3	1.309
m/mm 1	1.708
F(000)	1520.0
Crystal size/mm3	0.1 × 0.03 × 0.02
2Θ range for data collection	7.006 to 133°
Index ranges	$-9 \leq h \leq 9$, $-16 \leq k \leq 16$, $-38 \leq l \leq 38$
Reflections collected	52231
Independent reflections	52231[R(int) = ?]
Data/restraints/parameters	52231/37/962
Goodness-of-fit on F2	1.055
Final R indexes [I>=2σ (I)]	$R_1 = 0.0756$, $wR_2 = 0.1641$
Final R indexes [all data]	$R_1 = 0.0908$, $wR_2 = 0.1736$
Largest diff. peak/hole / e Å-3	0.76/-0.44
Flack parameter	0.036(6)

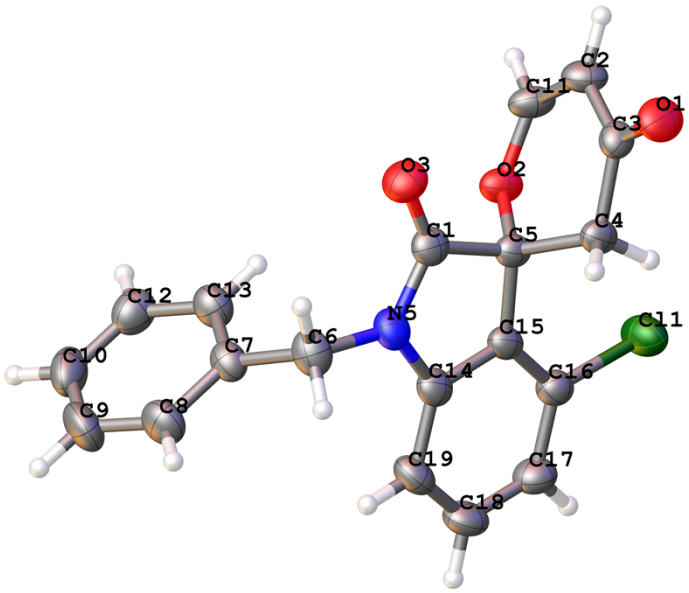


Fig 1. Asymmetric unit of **5b**. Ellipsoids drawn at 50% probability level.