Supporting Information for

Chiral Calcium VAPOL-Phosphate Mediated Asymmetric Chlorination and Michael Reactions of 3-Substituted Oxindoles

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General Considerations: All reactions were carried out in flame-dried screw-cap test tubes with magnetic stirring. Toluene, diethyl ether, dichloromethane, and THF were purified by passing through a column of activated alumina under a dry argon atmosphere. Anhydrous *tert*-butyl methyl ether was commercially purchased and used without further purification. Ethyl acetate and isopropyl acetate were dried over 4Å MS. Substituted BINOL phosphoric acids were prepared from commercially available chiral BINOL. Oxindoles were prepared according to known literature procedures.[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. Melting points were determined using a MEL-TEMP 3.0 instrument and are uncorrected. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance DPX-250 (250 MHz for ^{1}H and 62.5 MHz for ^{13}C) instrument. ^{31}P NMR were recorded on a Varian Unity Inova 400 (162 MHz for ^{31}P). ^{1}H and ^{13}C chemical shifts are reported in ppm downfield from tetramethylsilane (TMS). H_3PO_4 was used as an external standard for ^{31}P (σ: 0.00 ppm). The HRMS data were measured on an Agilent 1100 LC/MS ESI/TOF mass spectrometer with electrospray ionization.Compounds described in the literature were characterized by comparing their spectral data to the reported values. The absolute configuration of compound **2a** was determined to be "(*S*)"by comparison of the optical rotation value to the reported literature value.[3]The absolute configuration of compounds **3a**-**3d** was determined to be "(*S*)" by comparison of the observed optical rotation values to the reported literature values.[4]

Catalyst Preparation

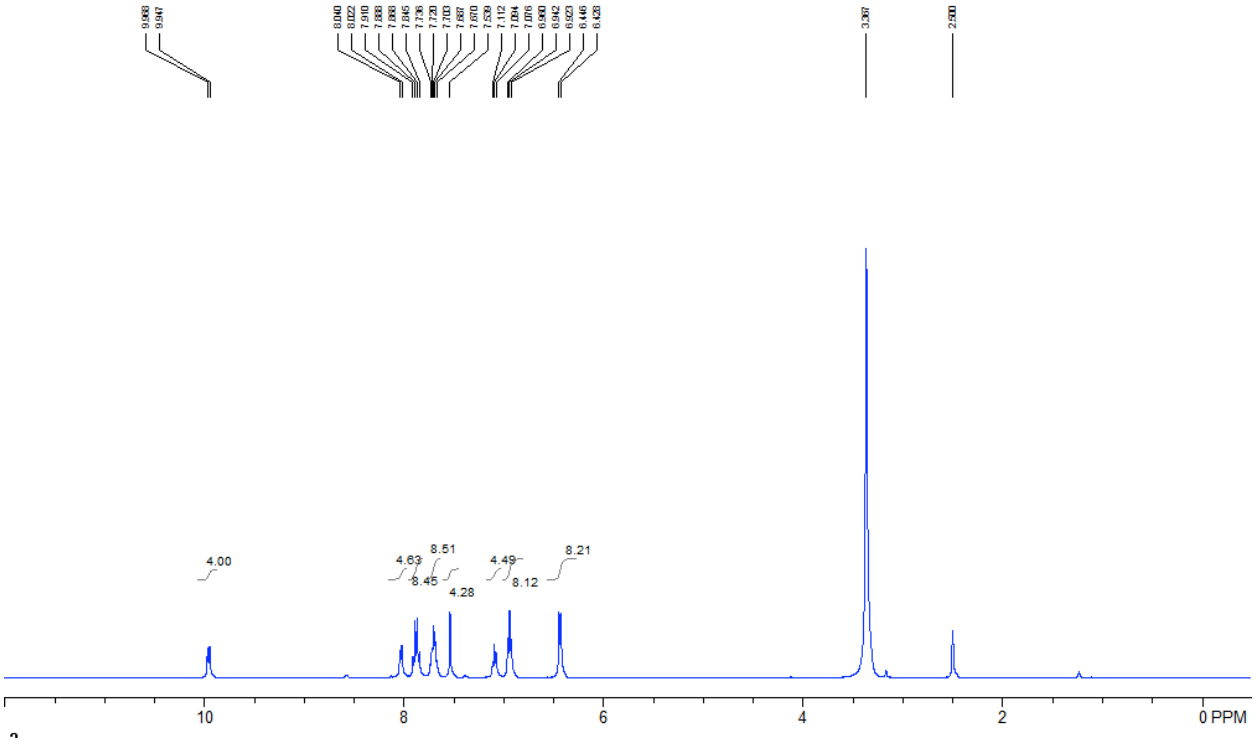
"(*R*) or (*S*)-PA1 (VAPOL-PA) purified on silica gel" (Table 1, entries 2-6): was prepared according to the reported literature procedure.[2]

"PA1 (VAPOL-PA) washed with HCl"(Table 1, entry 8): Prepared in a similar manner to the reported literature procedure[2] but not purified by silica gel column chromatography. The crude (*R*) or (*S*)-VAPOL phosphoric acid was precipitated from EtOH with 6 *N* HCl. The resulting white solid was filtered, and dried overnight under high vacuum to afford acidified chiral VAPOL-PA. The ^{1}H NMR of the title compound is identical to "**PA1 (VAPOL-PA) purified on silica gel."**

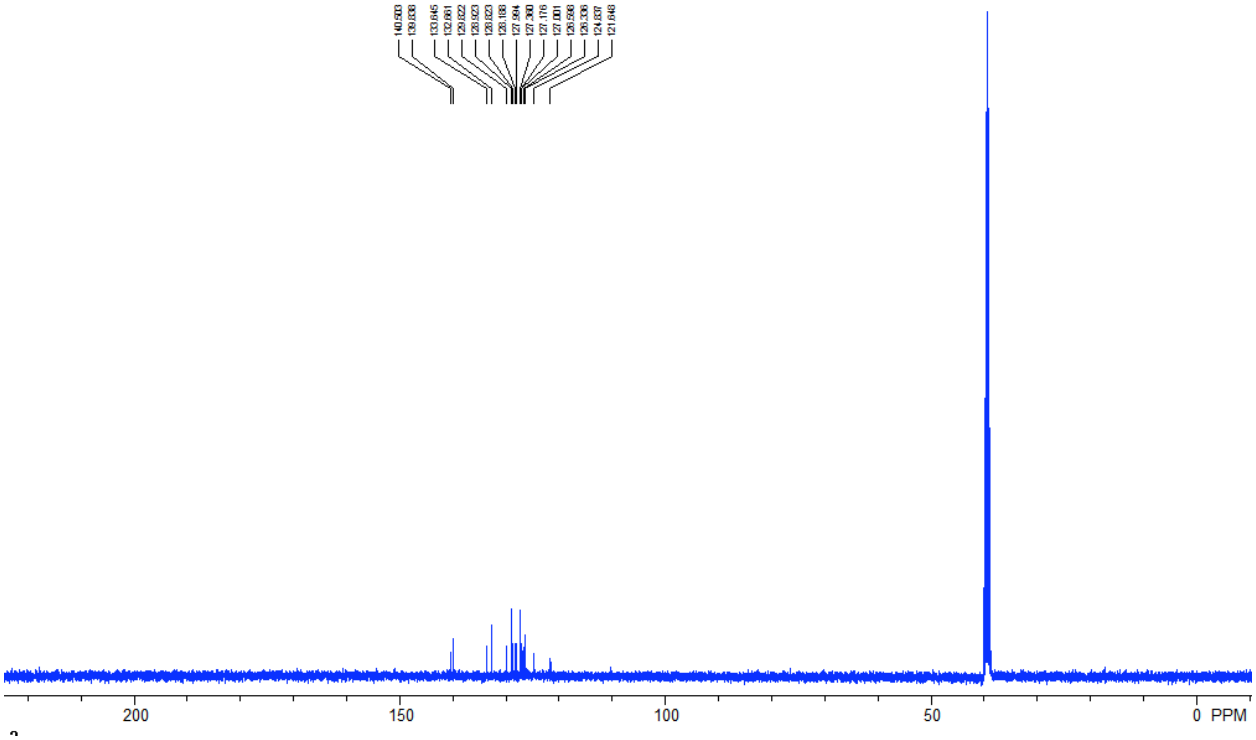
Catalysts M[P1]$_n$: For Na[**P1**] (Table 1, entry 9), K[**P1**] (Table 1, entry 10), Mg[**P1**]$_2$ (Table 1, entry 11), Ca[**P1**]$_2$(Table 1, entries 12 and 15, Table 2, Figure 2), Sr[**P1**]$_2$(Table 1, entry 13), or Ba[**P1**]$_2$(Table 1, entry 14), NaOMe (1.0 equiv), KO*t*Bu (1.0 equiv), Mg(O*t*Bu)$_2$ (0.5 equiv), Ca(OMe)$_2$ (0.5 equiv), Sr(O*i*Pr)$_2$ (0.5 equiv) or Ba(O*t*Bu)$_2$ (0.5 equiv)was combined with "**PA1 (VAPOL-PA) washed with HCl"** (1.0 equiv) in a flame-dried Schlenk tube, under an argon atmosphere. MeOH was added (0.05 M) and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under high vacuum to afford the desired **M**[**P1**]$_n$ as a white solid, which was used directly without further purification. The ^{1}H NMR of these compounds is the same as "**PA1 (VAPOL-PA) purified on silica gel**."

Procedure for the preparation of Ca[(*S*)-VAPOL-Phosphate]$_2$: A flame-dried flask was charged with "PA1 (VAPOL-PA) washed with HCl" (60.0mg, 0.1 mmol) and Ca(OMe)$_2$ (5.1 mg, 0.05 mmol). Methanol (5 mL) was added and the resulting mixture was stirred at room temperature for 1 h. The solvent was removed under high vacuum to afford Ca[(*S*)-VAPOL-Phosphate]$_2$ as a pale yellow solid. ^{1}H NMR (400 MHz, d$_6$-DMSO) δ 9.96 (d, *J* = 8.4 Hz, 4H), 8.03 (d, *J* = 7.2 Hz, 4H), 7.88 (dd, *J* = 16.8, 8.8 Hz, 8H), 7.74-7.67 (m, 8H), 7.54 (s, 4H), 7.09 (t, *J* = 7.2 Hz, 4H), 6.94 (t, *J* = 7.2 Hz, 8H), 6.44 (d, *J* = 7.2 Hz, 8H); ^{13}C NMR (100 MHz, d$_6$-DMSO) δ 140.5, 139.8, 133.7, 132.7, 129.8, 128.9, 128.8, 128.2, 128.0, 127.4, 127.2, 127.0, 126.6, 126.3, 124.8, 121.6(two C not located). ^{31}P NMR (162 MHz, d$_6$-DMSO) δ 1.05.

^{1}H NMR of Ca[(*R*)-VAPOL-Phosphate]$_2$

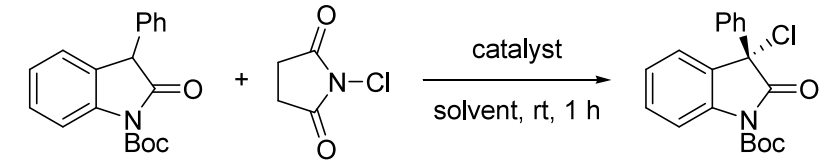


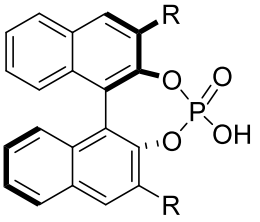
^{13}C NMR of Ca[(*R*)-VAPOL-Phosphate]$_2$



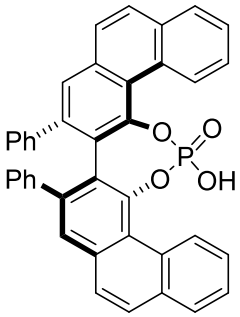
Preliminary Catalyst/Solvent Screening for the Enantioselective Chlorination of Oxindoles

(Catalysts are purified by silica gel column)

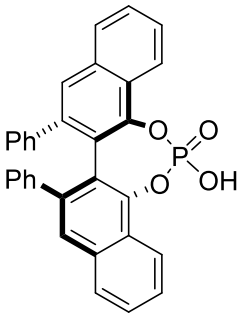




PA1: R = α–naph
PA2: R = $SiPh_3$
PA3: R = 2,4,6-(*i*-Pr)$_3$C$_6$H$_2$
PA4: R = 9-phenylanthryl
PA5: R = 9-anthryl



PA6 (VAPOL-PA)



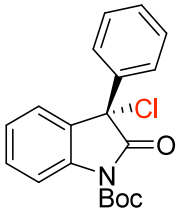
PA7 (VANOL-PA)

entry	catalyst	solvent	conversion (%)[b]	*ee* (%)[c]
1[d]	—	toluene	< 20	—
2	**PA1**	toluene	99	6
3	**PA2**	toluene	99	6
4	**PA3**	toluene	99	1
5	**PA4**	toluene	99	16
6	**PA6**	toluene	99	51
7	**PA6**	DCM	99	48
8	**PA6**	EtOAc	99	50
9	**PA6**	benzene	99	60
10	**PA5**	benzene	99	18
11	**PA7**	benzene	99	2
12	**PA6**	*i*-PrOAc	99	80

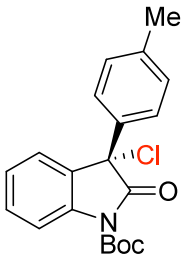
[a] Reaction Conditions: oxindole (0.05 mmol, 1.0 equiv), NCS (0.06 mmol, 1.2 equiv), 5 mol % catalyst in solvent (0.5 mL, 0.1 M). [b] Isolated yield.[c] Enantiomeric excess determined by chiral HPLC analysis. [d] After 24 h.

General procedure for the enantioselective chlorination of oxindoles:

To a flame-dried test tube was added oxindole **1** (0.05 mmol, 1.0 equiv) and Ca[(*S*)-**VAPOL-Phosphate**]$_2$ (2.5 mol %, 1.5 mg). The atmosphere was exchanged with argon three times and isopropyl acetate (1.0 mL) was added. After stirring for 10 min, NCS (0.12 M solution in isopropyl acetate) was added to the mixture of oxindole and catalyst over a period of 20 min. After stirring for an additional 10 min, the reaction mixture was purified directly by silica gel column chromatography (eluent: Hexane / EtOAc = 20/1) to yield product **2**. The *ee* of product **2** was determined by chiral HPLC analysis.

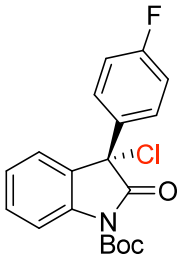


***tert*-butyl 3-chloro-2-oxo-3-phenylindoline-1-carboxylate (2a)**[3]: 99% yield, 94% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.3 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 23.92 min, t_R(minor) = 32.21 min.$[\alpha]^{20}_D$ = +99.16^o (*c* = 0.508, $CHCl_3$) Lit:$[\alpha]^{20}_D$ = -81.9^o (*c* = 0.18, $CHCl_3$, (*R*)-isomer)[3].^{1}H NMR (250 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.25 Hz, 1H), 7.46-7.18 (m, 8H), 1.55 (s, 9H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.0, 149.0, 139.1, 136.4, 130.8, 129.2, 128.9, 128.6, 127.9, 126.5, 125.4, 115.7, 85.2, 66.6, 28.0.HRMS (ESI) calcd for ($[M+Na]^+$)366.0867, found 366.0872.

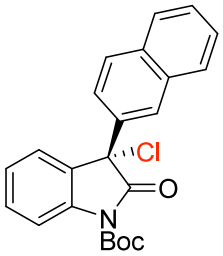


***tert*-butyl 3-chloro-2-oxo-3-p-tolylindoline-1-carboxylate (2b)**: 99% yield, 93% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.5 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 14.63 min, t_R(minor) = 28.28 min;$[\alpha]^{20}_D$ = +78.744^o (*c* = 0.43,

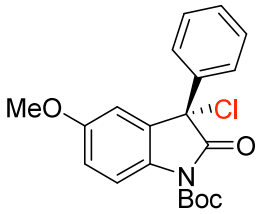
$CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.90 (dt, *J* = 7.75, 1.0 Hz, 1H), 7.38-7.18 (m, 5H), 7.09 (d, *J* = 7.75 Hz, 2H), 2.28 (s, 3H), 1.54 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.0, 149.0, 139.3, 139.1, 133.4, 130.7, 129.3, 129.0, 127.8, 126.1, 125.4, 115.6, 85.1, 66.5, 28.0, 21.1. HRMS (ESI) calcd for ($[M\text{-Boc-Cl+H}]^+$) 222.0913, found 222.0909.



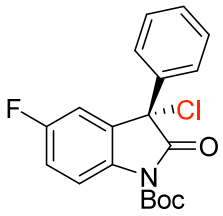
***tert*-butyl 3-chloro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate (2c)**: 99% yield, 96% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.3 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 21.48 min, t_R(minor) = 24.11 min. $[\alpha]^{20}_D$ = +122.21° (*c* = 0.59, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.25 Hz, 1H), 7.45-7.34 (m, 4H), 7.25-7.18 (m, 1H), 6.97 (t, *J* = 8.25 Hz, 2H), 1.55 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.8, 165.2, 161.2, 148.9, 139.1, 132.2, 132.2, 131.0, 130.2, 130.0, 128.5, 126.1, 125.5, 115.8, 115.7, 115.4, 85.3, 65.9, 28.0.HRMS (ESI) calcd for ($[M+Na]^+$)384.0773, found 384.0764.



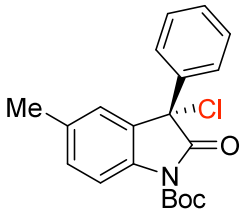
***tert*-butyl 3-chloro-3-(naphthalen-2-yl)-2-oxoindoline-1-carboxylate (2d)**: 99% yield, >99% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.3 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 26.85 min, t_R(minor) = 29.52 min.$[\alpha]^{20}_D$ = +63.36° (*c* = 0.49, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.97-7.91 (m, 1H), 7.82-7.66 (m, 5H), 7.45-7.38 (m, 4H), 7.25 (dt, *J* = 8.25, 1.0 Hz, 1H), 1.55 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.9, 149.0, 139.2 133.6, 133.3, 132.5, 130.9, 128.9, 128.8, 128.5, 127.6, 127.3, 127.2, 126.7, 126.2, 125.5, 125.2, 115.7, 85.2, 66.8, 28.0. HRMS (ESI) calcd for ($[M\text{-Boc-Cl+H}]^+$) 258.0913, found 258.0911.



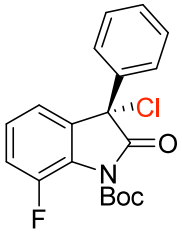
***tert*-butyl 3-chloro-5-methoxy-2-oxo-3-phenylindoline-1-carboxylate (2e)**: 99% yield, 90% *ee.* Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.5 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 26.09 min, t_R(minor) = 19.05 min.$[\alpha]^{20}_D$ = +107.48° (*c* = 0.593, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.25 Hz, 1H), 7.45-7.41 (m, 2H), 7.31-7.27 (m, 3H), 6.92-6.87 (m, 2H), 3.72 (d, *J* = 1.0 Hz, 3H), 1.53 (d, *J* = 1Hz, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.1, 157.4, 149.1, 136.3, 132.4, 130.0, 129.2, 128.6, 127.9, 116.8, 116.4, 111.3, 85.0, 66.9, 55.8, 31.6, 28.0. HRMS (ESI) calcd for ($[M\text{-Boc-Cl}]^+$) 237.0784, found 222.0779.



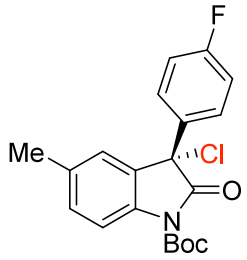
***tert*-butyl 3-chloro-5-fluoro-2-oxo-3-phenylindoline-1-carboxylate (2f)**: 99% yield, 93% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.3 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 25.39 min, t_R(minor) = 20.11 min.$[\alpha]^{20}_D$ = +92.715° (*c* = 0.4225, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.92 (dq, *J* =4.0, 1.0 Hz, 1H), 7.44-7.39 (m, 2H), 7.33-7.26 (m, 3H), 7.12-7.04 (m, 2H), 1.54 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.6, 162.1, 158.2, 148.9, 135.8, 135.1, 135.1, 130.7, 130.5, 129.4, 128.7, 127.7, 117.8, 117.4, 117.3, 117.2, 113.5, 113.1, 85.4, 66.2, 28.0.HRMS (ESI) calcd for ($[M+Na]^+$)384.0773, found 384.0767.



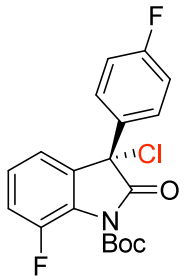
***tert*-butyl 3-chloro-5-methyl-2-oxo-3-phenlindoline-1-carboxylate (2g)**: 99% yield, 86% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (*S*, *S*)-Whelk-O1, 1.0 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 11.61 min, t_R(minor) = 8.19 min. $[\alpha]^{20}_D$ = +96.145° (*c* = 0.48, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.25 Hz, 1H), 7.46-7.42 (m, 2H), 7.32-7.28 (m, 3H), 7.19-7.15 (m, 2H), 2.30 (s, 3H), 1.54 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.1, 149.0, 136.8, 136.5, 135.3, 131.4, 129.1, 128.9, 128.6, 127.9, 126.4, 115.5, 85.0, 66.9, 28.1, 21.1. HRMS (ESI) calcd for ($[M+Na]^+$)384.0773, found 384.0765.



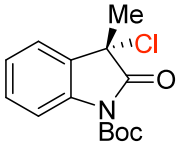
***tert*-butyl 3-chloro-7-fluoro-2-oxo-3-phenylindoline-1-carboxylate (2h)**: 99% yield, 97% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (*S*, *S*)-Whelk-O1, 1.0 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 12.11 min, t_R(minor) = 9.65 min. $[\alpha]^{20}_D$ = +86.923° (*c* = 0.603, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.43-7.39 (m, 2H), 7.28-7.26 (m, 3H), 7.16-7.10 (m, 3H), 1.51 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.6, 150.6, 147.1, 146.6, 135.8, 132.2, 132.1, 129.4, 128.7, 127.7, 126.5, 126.4, 126.2, 126.0, 122.0, 121.9, 119.0, 118.7, 85.9, 66.5, 66.5, 27.7. HRMS (ESI) calcd for ($[M+Na]^+$)384.0773, found 384.0765.



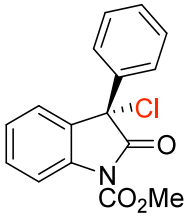
***tert*-butyl 3-chloro-3-(4-fluorophenyl)-5-methyl-2-oxoindoline-1-carboxylate (2i)**: 99% yield, 92% *ee*. Enantiomeric excess was determined by chiral HPLC analysis ((*S*, *S*)-Whelk-O1, 1.0 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 10.61 min, t_R(minor) = 6.69 min. $[\alpha]^{20}_D$ = +97.025° (*c* = 0.825, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.5 Hz, 1H), 7.41 (dd, *J* = 7.0, 1.75 Hz, 2H), 7.20-7.15 (m, 2H), 6.97 (t, *J* = 8.5 Hz, 2H), 2.31 (s, 3H), 1.54 (s, 9H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 171.0, 170.9, 165.1, 161.2, 149.0, 136.7, 135.4, 132.4, 132.3, 131.6, 130.1, 130.0, 128.5, 126.4, 115.7, 115.6, 115.3, 85.1, 66.2, 28.0, 21.1.HRMS (ESI)calcd for ([M-Boc-Cl+H]$^+$) 240.0819, found 240.0815.



***tert*-butyl 3-chloro-7-fluoro-3-(4-fluorophenyl)-2-oxoindoline-1-carboxylate (2j)**: 99% yield, 98% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 1.0 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 9.80 min, t_R(minor) = 22.64 min.$[\alpha]^{20}_D$ = +72.642° (*c* = 0.675, $CHCl_3$). ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 9.0, 5.0 Hz, 2H), 7.20-7.13 (m, 3H), 6.98 (t, *J* = 8.25 Hz, 2H), 1.53 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.4, 170.4, 166.3, 161.3, 150.6, 147.0, 146.6, 131.7, 131.7, 131.6, 131.6, 126.6, 126.5, 126.2, 126.0, 121.9, 121.9, 119.2, 118.9, 115.9, 115.5, 86.0, 65.7, 65.7, 27.7, 27.7.HRMS (ESI) calcd for ([M+Na]$^+$) 402.0679, found 402.0674.



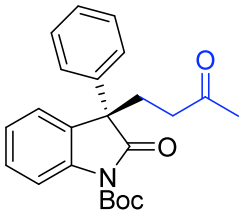
***tert*-butyl 3-chloro-3-methyl-2-oxoindoline-1-carboxylate (2k)**: 99% yield, 62% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralcel OJ-H, 0.3 mL/min, 90:10 hexanes/iPrOH): t_R(major) = 21.73 min, t_R(minor) = 23.61 min.$[\alpha]^{20}_D$ = +30.143° (*c* = 0.48, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.97-7.91 (m, 1H), 7.82-7.66 (m, 5H), 7.45-7.38 (m, 4H), 7.25 (dt, *J* = 8.25, 1.0 Hz, 1H), 1.55 (s, 9H).^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.9, 149.0, 139.2 133.6, 133.3, 132.5, 130.9, 128.9, 128.8, 128.5, 127.6, 127.3, 127.2, 126.7, 126.2, 125.5, 125.2, 115.7, 85.2, 66.8, 28.0. HRMS (ESI) calcd for ($[M+Na]^+$)304.0711, found 304.0708.



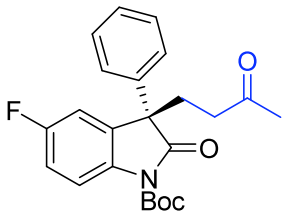
methyl 3-chloro-2-oxo-3-phenylindoline-1-carboxylate (2l): 99% yield, 97% *ee.* Enantiomeric excess was determined by chiral HPLC analysis ((*S*, *S*)-Whelk-O1, 1.0 mL/min, 90:10 hexanes/iPrOH):t_R(major) = 17.36 min, t_R(minor) = 13.93 min. $[\alpha]^{20}_D$ = +116.55° (*c* = 0.77, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 1H), 7.42-7.20 (m, 8H), 3.89 (s, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ 170.9, 151.2, 138.6, 136.2, 133.9, 129.3, 129.1, 128.7, 127.8, 126.2, 125.8, 115.7, 85.2, 66.6, 54.3. HRMS (ESI) calcd for ($[M+H]^+$)302.0579, found 304.0574.

General procedure for the enantioselective Michael reaction of oxindoles:

To a flame-dried test tube was added oxindole **1** (0.05 mmol, 1.0 equiv) and Ca[(*R*)-**VAPOL-Phosphate**]$_2$ (2.5 mol %, 1.5 mg). The atmosphere was exchanged with argon three times and isopropyl acetate (0.5 mL) was added. The mixture was cooled to 0 ^{o}C, and methyl vinyl ketone (12.3 µl, 3.0 equiv) was added. The reaction was continued at 0 ^{o}C, and upon completion purified directly by silica gel column chromatography (eluent: Hexane / EtOAc = 5/1) to yield product **3**. The *ee* of product **3** was determined by chiral HPLC analysis.

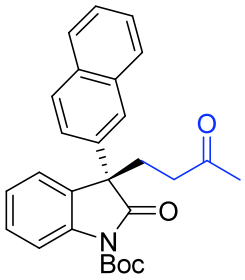


(*S*)-tert-butyl 2-oxo-3-(3-oxobutyl)-3-phenylindoline-1-carboxylate (3a): 97% yield, 90% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralpak AD-H, 1.0 mL/min, 94:6 hexanes/iPrOH):t_R(major) = 7.95 min, t_R(minor) = 10.89 min.$[\alpha]^{20}_D$ = -53.94^{o} (*c* = 0.71, $CHCl_3$) Lit: $[\alpha]^{20}_D$ = -62.02^{o} (*c* = 1.00, $CHCl_3$, (*S*)-isomer).[41]^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.34-7.12 (m, 8H), 2.74-2.62 (m, 1H), 2.47-2.17 (m, 2H), 2.09-1.96 (m, 1H), 1.94 (s, 3H), 1.56 (s, 9H). The spectral data are identical to those in reference 4.

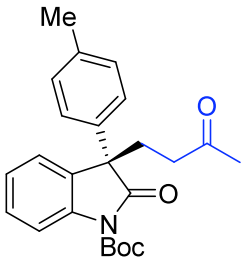


(*S*)-tert-butyl 5-fluoro-2-oxo-3-(3-oxobutyl)-3-phenylindoline-1-carboxylate (3b): 96% yield, 95% *ee*. Enantiomeric excess was determined by chiral HPLC analysis(Chiralpak AD-H, 1.0 mL/min, 94:6 hexanes/iPrOH): t_R(major) = 6.71 min, t_R(minor) = 7.87 min.$[\alpha]^{20}_D$ = -58.64^{o} (*c* = 0.675, $CHCl_3$); ^{1}H NMR (250 MHz, $CDCl_3$) δ 7.88 (dd,*J* = 9.0, 4.5 Hz, 2H), 7.29-7.19 (m, 5H), 7.00 (dt, J = 9.0, 2.75 Hz,1H), 6.83 (dd, J = 7.75, 2.5 Hz, 1H), 2.73-2.63 (m, 1H), 2.44-2.23 (m,

2H), 2.12-2.02 (m, 1H), 1.97 (s, 3H), 1.55 (s, 9H). The spectra data are identical to those in reference 4.

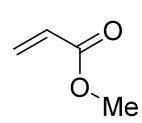


(*S*)-tert-butyl 3-(naphthalen-2-yl)-2-oxo-3-(3-oxobutyl)indoline-1-carboxylate (3c): 95% yield, 95% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralpak AD-H, 1.0 mL/min, 94:6 hexanes/iPrOH): t_R(major) = 9.48 min, t_R(minor) = 14.11 min$[\alpha]^{20}_D$ = -22.195° (*c* = 0.925, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.72-7.65 (m, 4H), 7.40-7.34 (m, 4H), 7.18-7.15 (m, 2H), 2.86-2.75 (m, 1H), 2.58-2.28 (m, 2H), 2.12-1.99 (m, 1H), 1.95 (s, 3H), 1.56 (s, 9H). The spectral data are identical to those in reference 4.

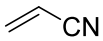


(*S*)-tert-butyl 2-oxo-3-(3-oxobutyl)-3-p-tolylindoline-1-carboxylate (3d): 96% yield, 90% *ee*. Enantiomeric excess was determined by chiral HPLC analysis (Chiralpak AD-H, 1.0 mL/min, 94:6 hexanes/iPrOH): t_R(major) = 7.49 min, t_R(minor) = 11.25 min.$[\alpha]^{20}_D$ = -47.31° (*c* = 0.73, $CHCl_3$).^{1}H NMR (250 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.25 Hz, 1H), 7.30-7.02 (m, 7H), 2.71-2.61 (m, 1H), 2.45-2.28 (m, 2H), 2.23 (s, 3H), 2.05-1.97 (m, 1H), 1.94 (s, 3H), 1.55 (s, 9H). The spectral data are identical to those in reference 4.

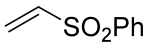
Additional Michael Acceptors were screened with the following results.



No reaction



No reaction



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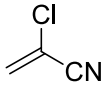
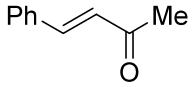


No reaction



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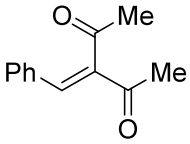

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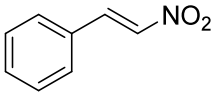

D.r. ~ 1/1
Ee: Less than 10%

References

(1)(a) Hamashima, Y.; Suzuki, T.; Takano, H.; Shimura, Y.; Sodeoka, M. *J. Am. Chem. Soc*. **2005**, *127,* 10164-10165.(b) Rajeswaran, W. G.; Cohen, L. A. *Tetrahedron* **1998**, *54*, 11375-11380.(c) Ishimaru, T.; Shibata, N.; Nagai, J.; Nakamura, S.;Toru, T.; Kanemasa,S. *J. Am. Chem. Soc*. **2006**, *128,* 16488-16489.

(2) Desai, A. A.; Huang, L.; Wulff, W. D.; Rowland, G. B.; Antilla, J. C. *Synthesis,* **2010,***12*, 2106-2109.

(3) Shibata, N.; Kohno, J.; Takai, K.; Nakamura, S.; Toru, T.; Kagemasa, S. *Angew. Chem., Int. Ed.* **2005**, *44*, 4204.

(4)He, R.; Ding, C.; Maruoka, K. *Angew. Chem., Int. Ed.* **2009**, *48*, 4559.

Chiral HPLC analysis of compound **2a**

Chromatogram : WZ-3-40_channel1

System : HPLC
Method : Wenhua
User : User1

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Processed : 4/21/2010 11:18:24 PM
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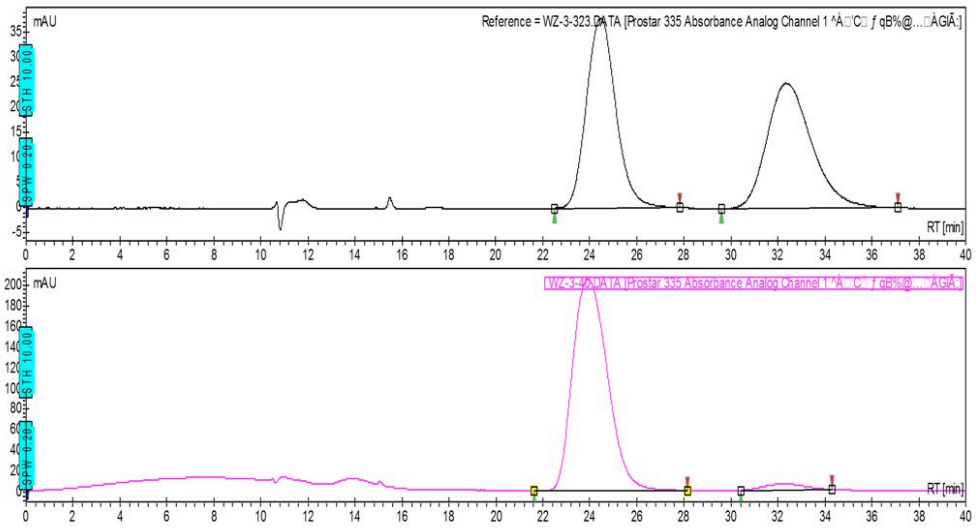

Peak results :

WZ-3-323.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	24.45	49.91	37.8	54.6	49.914
2	UNKNOWN	32.33	50.09	24.9	54.8	50.086
Total			100.00	62.6	109.5	100.000

WZ-3-40.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	23.92	96.78	204.5	350.3	96.781
2	UNKNOWN	32.21	3.22	5.7	11.6	3.219
Total			100.00	210.2	361.9	100.000

Chiral HPLC analysis of compound **2b**

Chromatogram : WZ-3-4-OJ-90-0.5_channel1

System : HPLC
Method : Wenhua
User : User1

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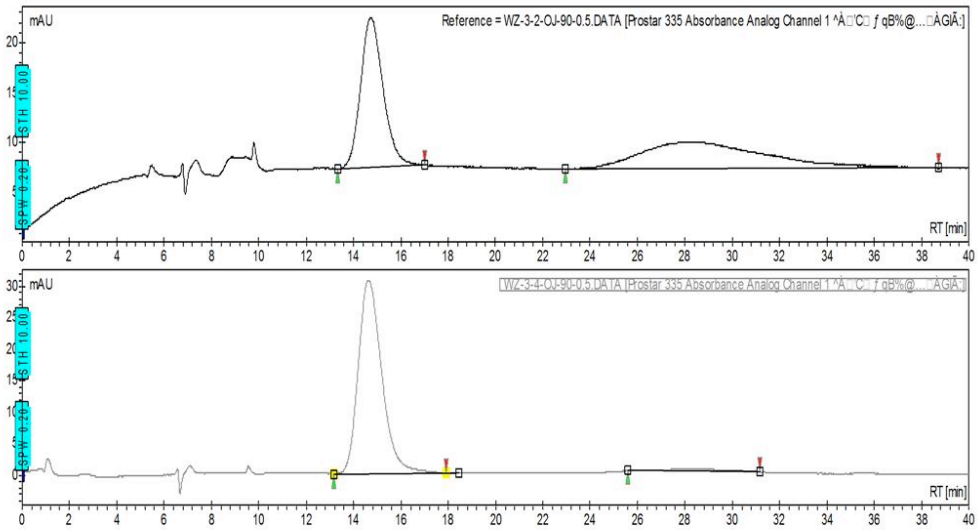

Peak results :

WZ-3-2-OJ-90-0.5.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	14.72	50.12	15.1	16.6	50.122
2	UNKNOWN	27.92	49.88	2.7	16.5	49.878
Total			100.00	17.7	33.0	100.000

WZ-3-4-OJ-90-0.5.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	14.63	96.47	30.7	35.6	96.468
2	UNKNOWN	28.28	3.53	0.5	1.3	3.532
Total			100.00	31.1	36.9	100.000

Chiral HPLC analysis of compound **2c**

Chromatogram : WZ-3-43_channel1

System : HPLC
Method : Wenhua
User : User1

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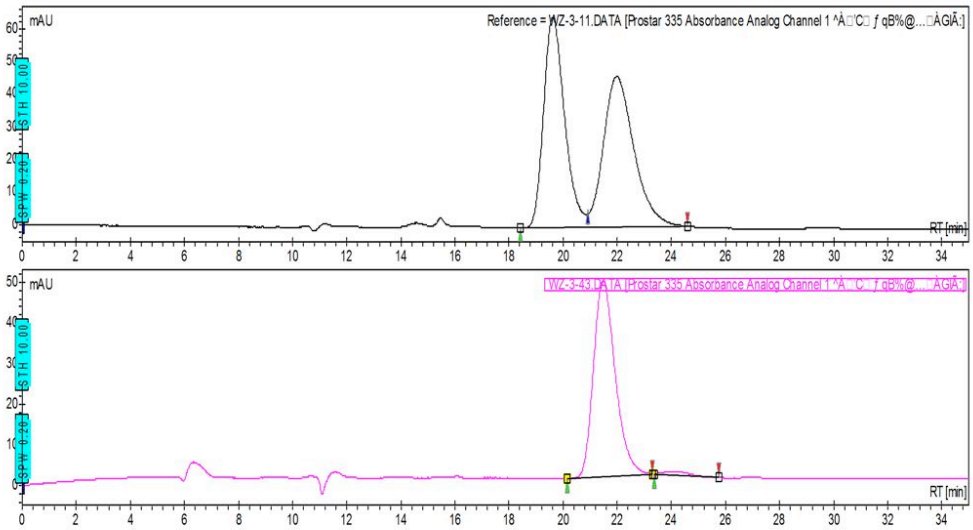

Peak results :

WZ-3-11.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	19.61	49.06	64.5	58.1	49.057
2	UNKNOWN	21.99	50.94	46.2	60.4	50.943
Total			100.00	110.7	118.5	100.000

WZ-3-43.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	21.48	97.86	48.1	44.7	97.862
2	UNKNOWN	24.11	2.14	1.0	1.0	2.138
Total			100.00	49.1	45.7	100.000

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Chiral HPLC analysis of compound **2d**

Chromatogram : WZ-3-41_channel1

System : HPLC
Method : Wenhua
User : User1

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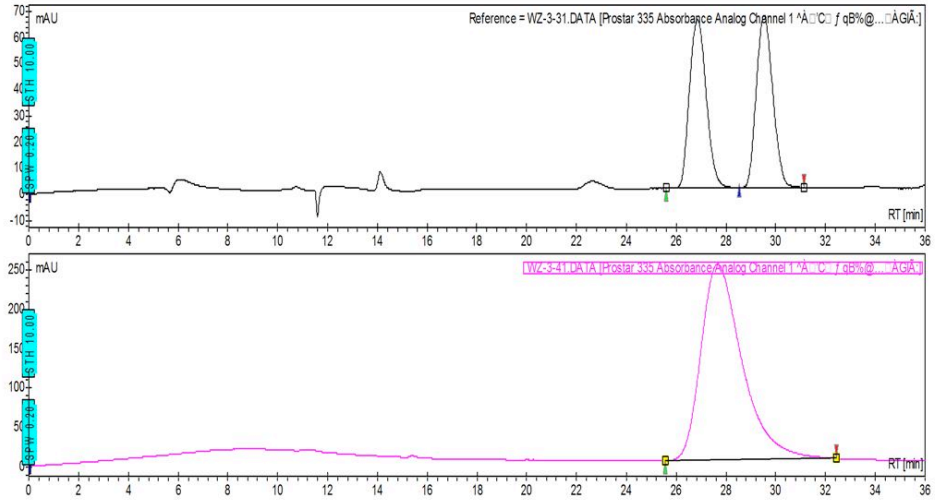

Peak results :

WZ-3-31.DATA [Prostar 335 Absorbance Analog Channel 1 ^Â□'C□ ƒ qB%@…□ÀGIÃ:]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	26.85	49.95	64.4	50.5	49.952
2	UNKNOWN	29.52	50.05	66.0	50.6	50.048
Total			100.00	130.4	101.1	100.000

WZ-3-41.DATA [Prostar 335 Absorbance Analog Channel 1 ^Â□'C□ ƒ qB%@…□ÀGIÃ:]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	27.65	100.00	249.0	477.5	100.000
Total			100.00	249.0	477.5	100.000

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Chiral HPLC analysis of compound **2e**

Chromatogram : WZ-3-46-OJ-90-0.51_channel1

System : HPLC
Method : Wenhua
User : User1

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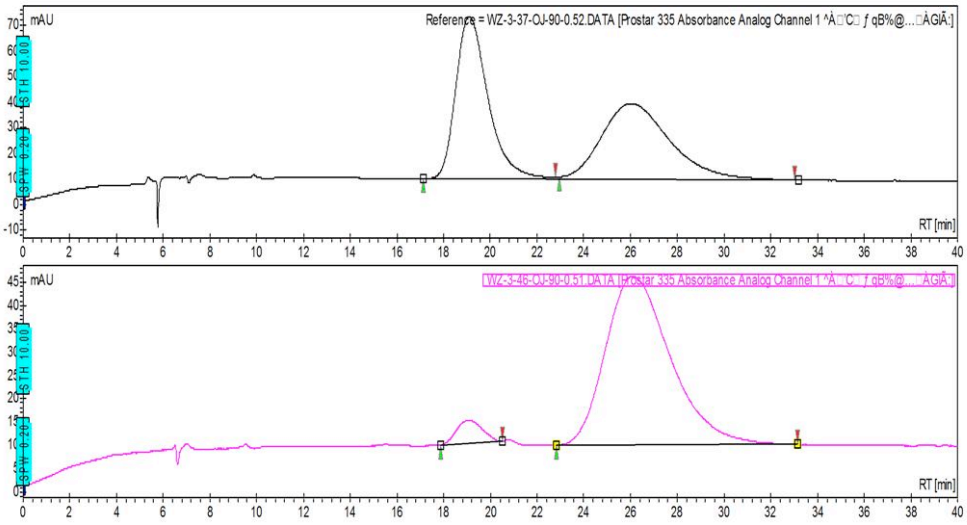

Peak results :

WZ-3-37-OJ-90-0.52.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	19.11	50.25	63.4	101.3	50.250
2	UNKNOWN	26.04	49.75	29.6	100.3	49.750
Total			100.00	93.0	201.7	100.000

WZ-3-46-OJ-90-0.51.DATA [Prostar 335 Absorbance Analog Channel 1 ^À□'C□ ƒ qB%@…□ÀGIÃ:]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	19.05	5.14	5.0	6.3	5.144
1	UNKNOWN	26.09	94.86	36.3	116.8	94.856
Total			100.00	41.4	123.1	100.000

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Chiral HPLC analysis of compound **2f**

Chromatogram : WZ-3-381_channel1

System : HPLC
Method : Wenhua
User : User1

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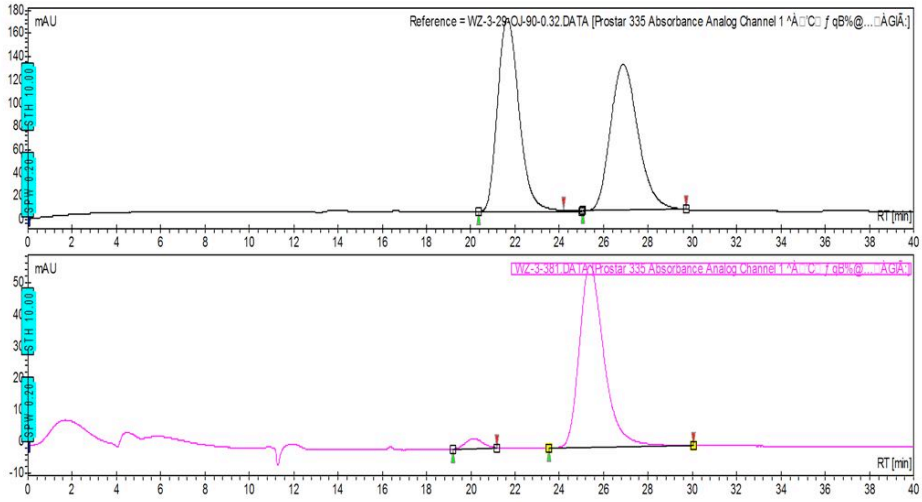

Peak results :

WZ-3-29-OJ-90-0.32.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	21.65	50.63	166.0	185.6	50.635
2	UNKNOWN	26.88	49.37	125.7	180.9	49.365
Total			100.00	291.7	366.5	100.000

WZ-3-381.DATA [Prostar 335 Absorbance Analog Channel 1 ^À□'C□ ƒ qB%@…□ÀGIÃ:]

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
2	UNKNOWN	20.11	3.62	3.1	2.8	3.625
1	UNKNOWN	25.39	96.38	57.5	73.9	96.375
Total			100.00	60.6	76.7	100.000

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Chiral HPLC analysis of compound **2g**

Chromatogram : WZ-3-62-Whelk-O1-90-1.0_channel1

System : HPLC
Method : test
User : User1

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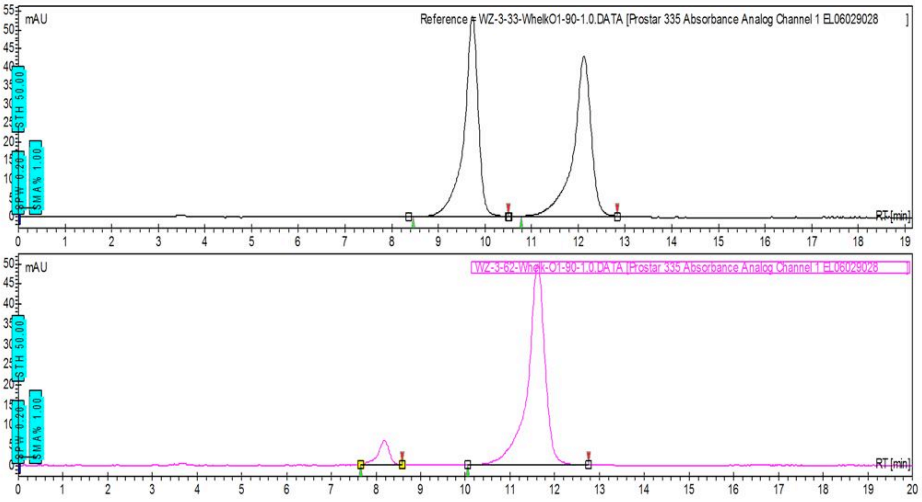

Peak results :

WZ-3-33-WhelkO1-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.73	53.8	0.51	19.2	50.094
2	12.12	42.9	0.63	19.1	49.906
Total		96.7		38.3	100.000

WZ-3-62-Whelk-O1-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	8.19	6.0	0.43	1.7	7.223
2	11.61	49.7	0.64	22.4	92.777
Total		55.8		24.1	100.000

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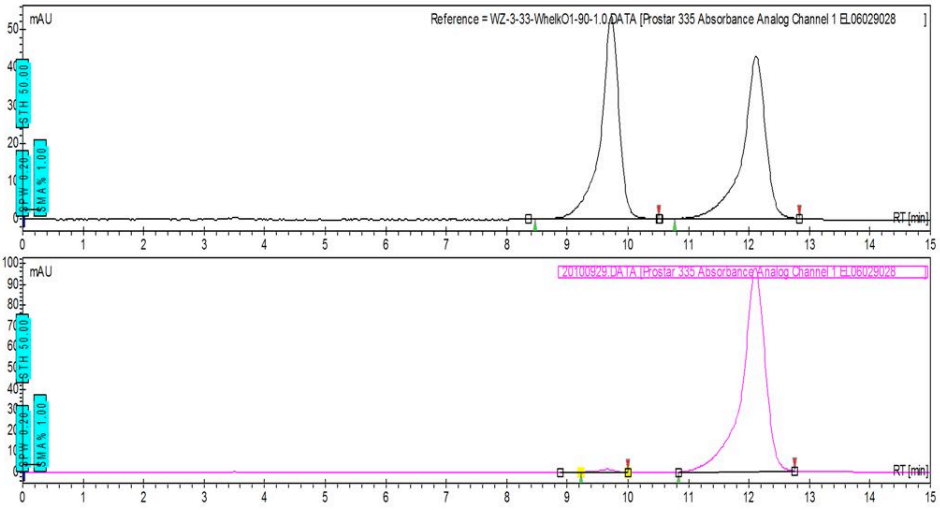
Chiral HPLC analysis of compound **2h**

Chromatogram : 20100929_channel1

System : HPLC
Method : test
User : User1

Acquired : 9/30/2010 12:23:09 AM
Processed : 9/30/2010 12:39:23 AM
Printed : 9/30/2010 12:40:43 AM



Peak results :

WZ-3-33-WhelkO1-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.73	53.8	0.51	19.2	50.094
2	12.12	42.9	0.63	19.1	49.906
Total		96.7		38.3	100.000

20100929.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.65	1.8	0.49	0.6	1.406
2	12.11	97.4	0.63	43.6	98.594
Total		99.1		44.2	100.000

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Chiral HPLC analysis of compound **2i**

Chromatogram : 20101008_channel1

System : HPLC
Method : test
User : User1

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Processed : 10/8/2010 12:23:53 PM
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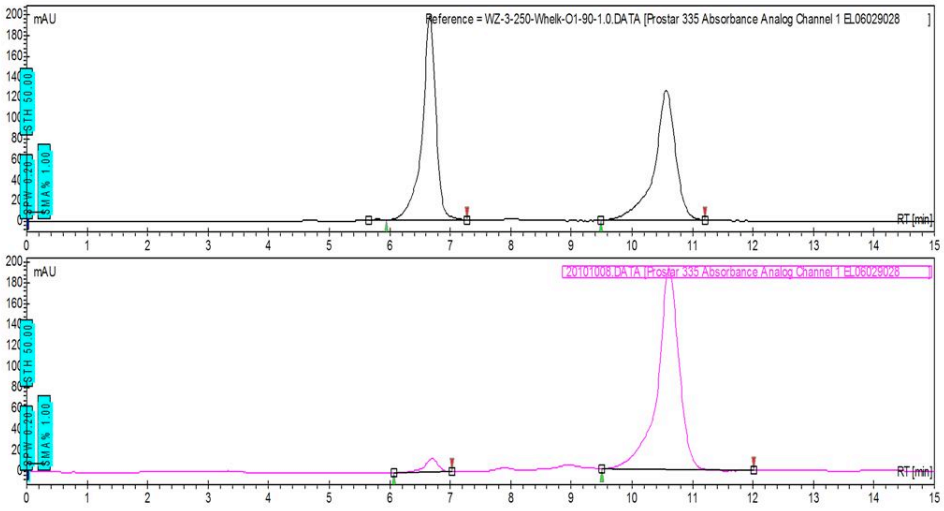

Peak results :

WZ-3-250-Whelk-O1-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.67	197.7	0.37	52.4	50.498
2	10.56	125.1	0.58	51.3	49.502
Total		322.8		103.7	100.000

20101008.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.69	13.0	0.39	3.4	4.098
2	10.61	192.3	0.60	79.1	95.902
Total		205.3		82.5	100.000

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Chiral HPLC analysis of compound **2j**

Chromatogram : WZ-4-13-OJ-90-1.0_channel1

System : HPLC
Method : test
User : User1

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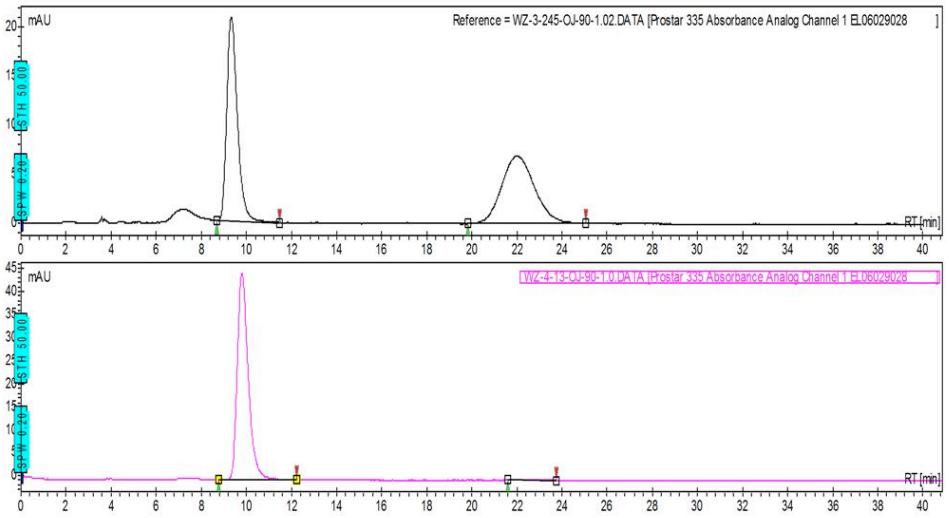

Peak results :

WZ-3-245-OJ-90-1.02.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.33	20.8	0.85	11.4	49.632
2	21.99	6.9	2.67	11.6	50.368
Total		27.7		23.0	100.000

WZ-4-13-OJ-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.80	44.8	0.87	25.3	99.059
2	22.64	0.2	1.38	0.2	0.941
Total		45.0		25.5	100.000

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Chiral HPLC analysis of compound **2k**

Chromatogram : WZ-3-45-repeat_channel1

System : HPLC
Method : test
User : User1

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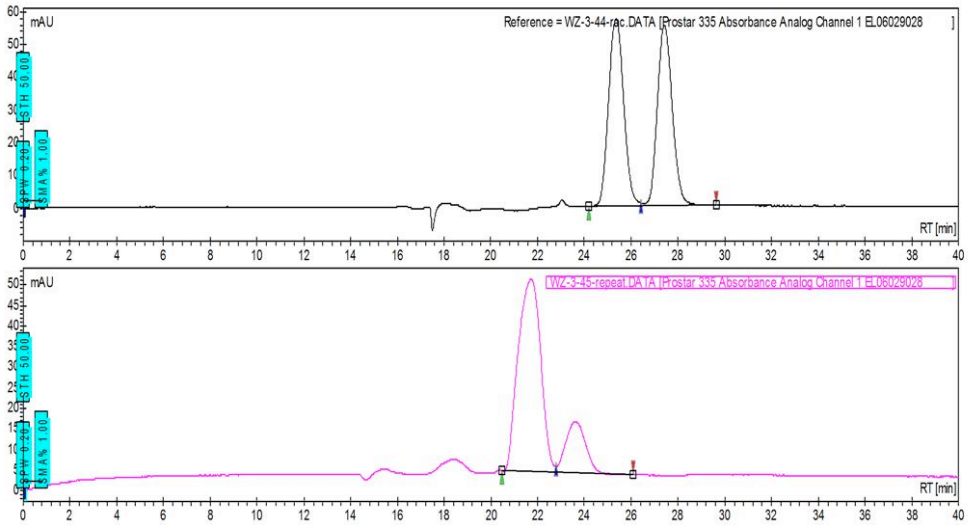

Peak results :

WZ-3-44-rac.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	25.36	56.9	1.19	42.6	51.243
2	27.41	54.9	1.18	40.6	48.757
Total		111.8		83.2	100.000

WZ-3-45-repeat.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	21.73	46.8	1.74	52.4	81.176
2	23.61	12.5	1.55	12.2	18.824
Total		59.3		64.6	100.000

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Chiral HPLC analysis of compound **2l**

Chromatogram : WZ-4-103-SS-Whelk-90-1.0_channel1

System : HPLC
Method : test
User : User1

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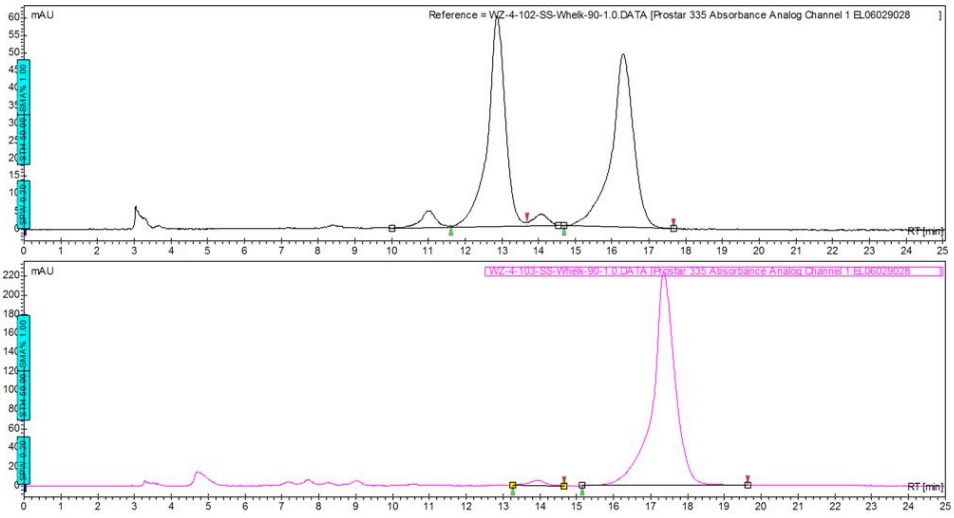

Peak results :

WZ-4-102-SS-Whelk-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	12.88	59.7	0.80	33.3	49.104
1	16.31	49.4	0.98	34.5	50.896
Total		109.1		67.8	100.000

WZ-4-103-SS-Whelk-90-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	13.93	5.2	0.74	2.5	1.576
2	17.36	223.9	1.01	156.6	98.424
Total		229.0		159.1	100.000

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Chiral HPLC analysis of compound **3a**

Chromatogram : WZ-3-282-AD-94-1.0_channel1

System : HPLC
Method : test
User : User1

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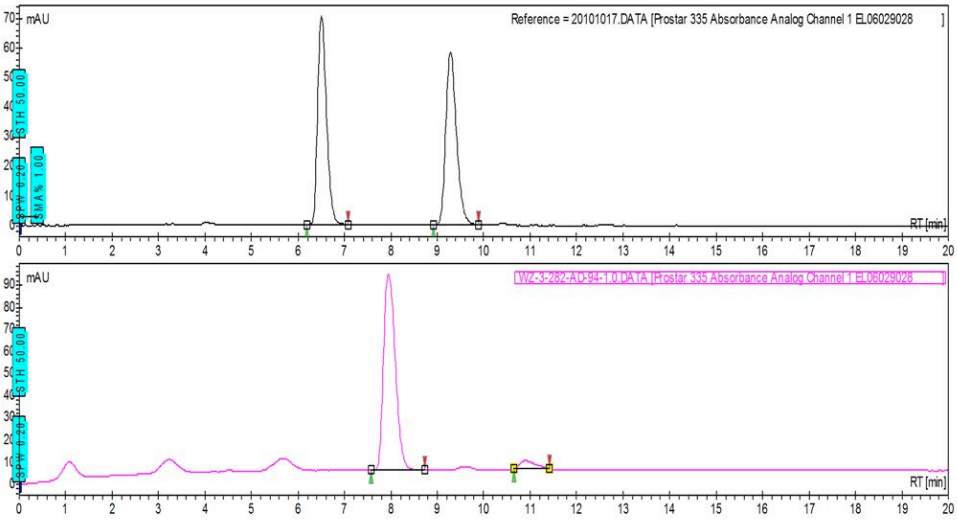

Peak results :

20101017.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.51	71.0	0.35	15.8	50.022
2	9.28	58.8	0.42	15.8	49.978
Total		129.8		31.6	100.000

WZ-3-282-AD-94-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
2	7.95	88.5	0.46	26.2	94.891
1	10.89	3.6	0.65	1.4	5.109
Total		92.1		27.6	100.000

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Chiral HPLC analysis of compound **3b**

Chromatogram : WZ-4-2-AD-94-1.0_channel1

System : HPLC
Method : test
User : User1

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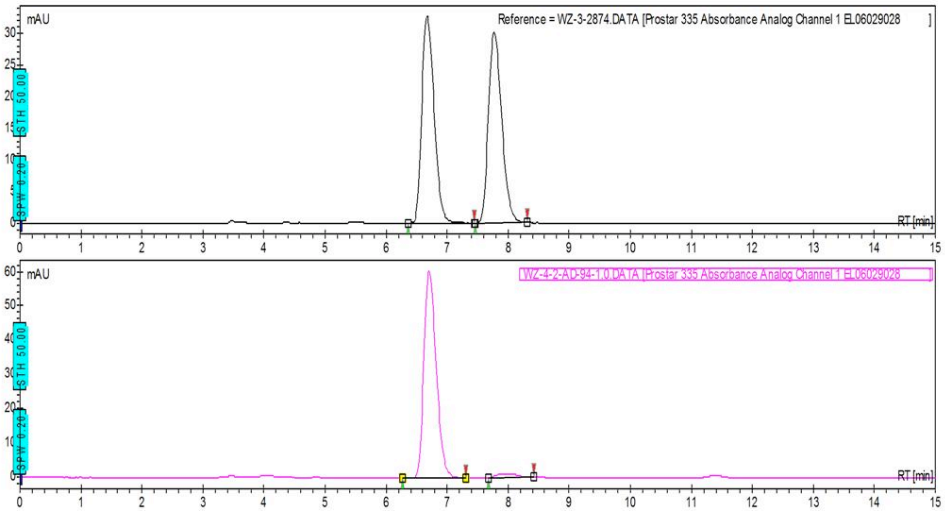
Printed : 10/17/2010 6:24:32 PM



Peak results :

WZ-3-2874.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.67	32.6	0.37	7.7	50.191
2	7.77	30.0	0.40	7.6	49.809
Total		62.6		15.3	100.000

WZ-4-2-AD-94-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	6.71	60.5	0.38	14.2	97.392
2	7.87	1.0	0.55	0.4	2.608
Total		61.5		14.6	100.000

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Chiral HPLC analysis of compound **3c**

Chromatogram : WZ-4-7-AD-94-1.0_channel1

System : HPLC
Method : test
User : User1

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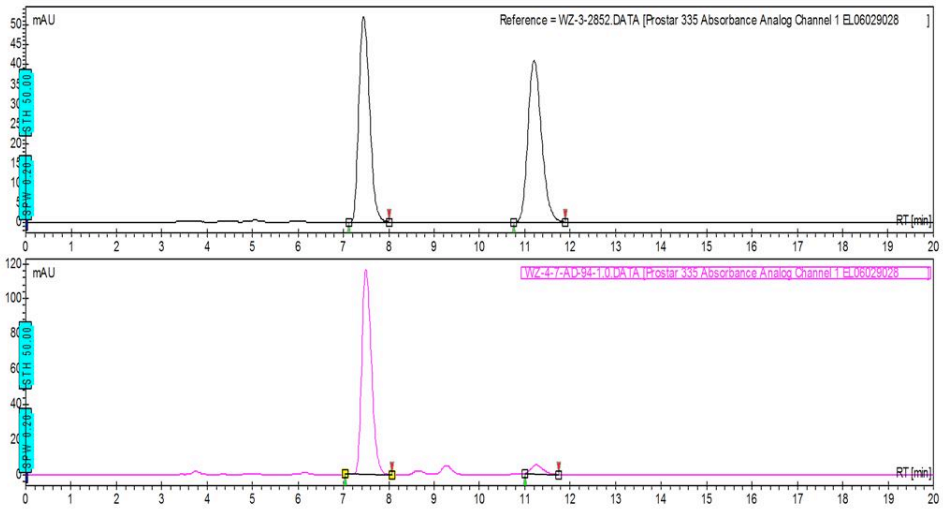

Peak results :

WZ-3-2852.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	7.44	52.1	0.43	14.3	50.066
2	11.20	41.0	0.55	14.3	49.934
Total		93.1		28.6	100.000

WZ-4-7-AD-94-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	7.49	116.5	0.39	28.7	94.815
2	11.25	5.1	0.50	1.6	5.185
Total		121.6		30.3	100.000

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Chiral HPLC analysis of compound **3d**

Chromatogram : WZ-4-6-AD-94-1.0_channel1

System : HPLC
Method : test
User : User1

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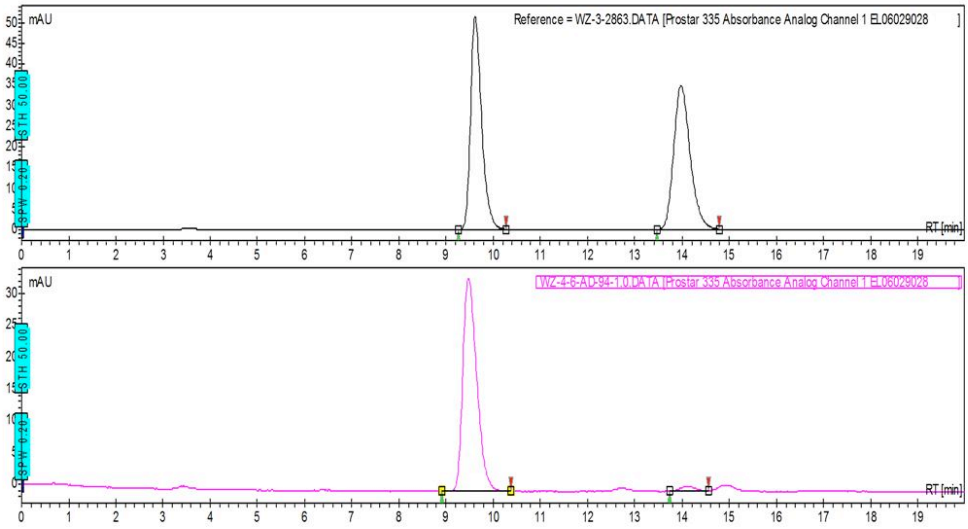

Peak results :

WZ-3-2863.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.61	51.6	0.42	14.0	49.834
2	13.97	34.8	0.63	14.1	50.166
Total		86.3		28.1	100.000

WZ-4-6-AD-94-1.0.DATA [Prostar 335 Absorbance Analog Channel 1 EL06029028]

Index	Time [Min]	Height [mAU]	Width USP [Min]	Area [mAU.Min]	Area % [%]
1	9.48	33.6	0.55	11.5	97.641
2	14.11	0.8	0.65	0.3	2.359
Total		34.4		11.8	100.000

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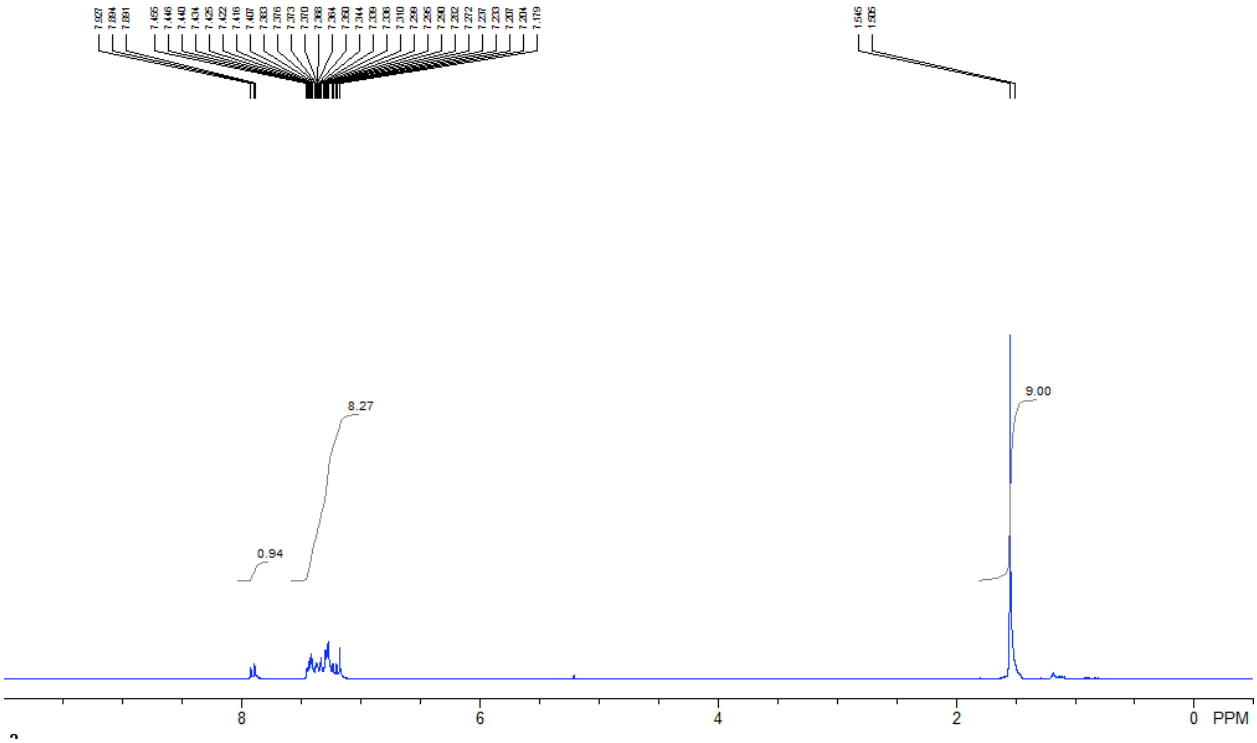
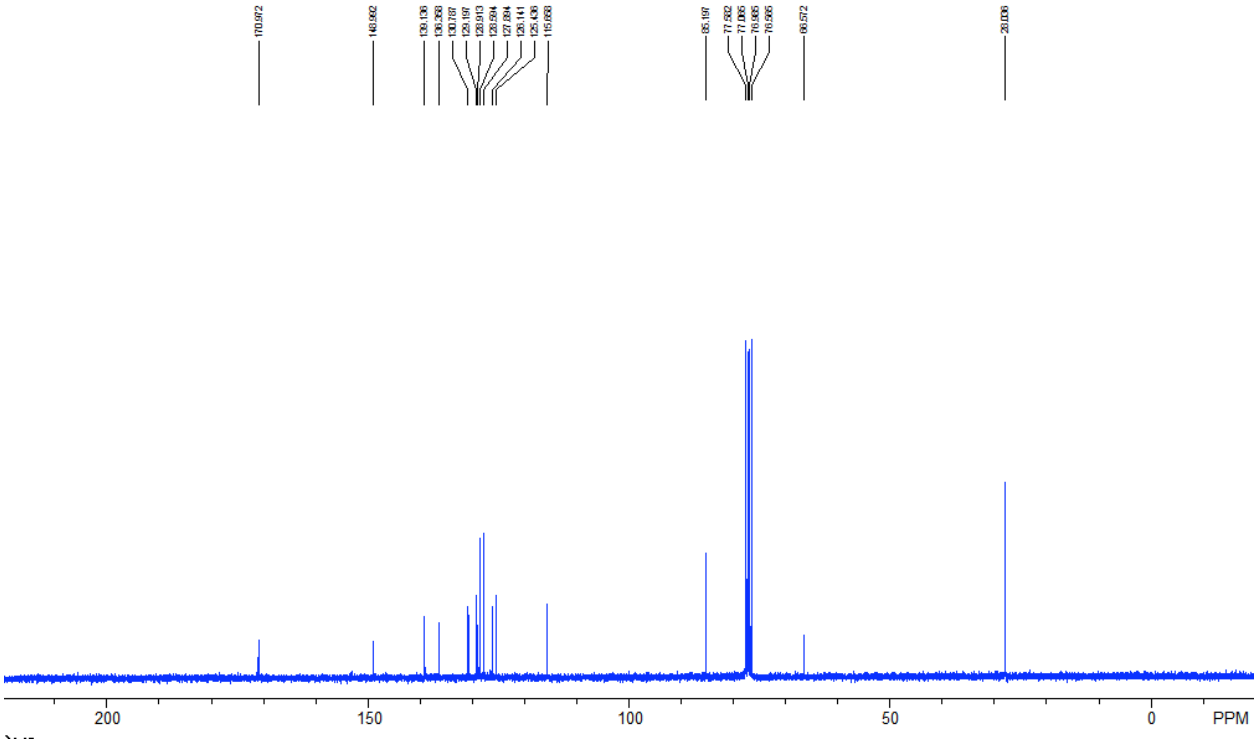
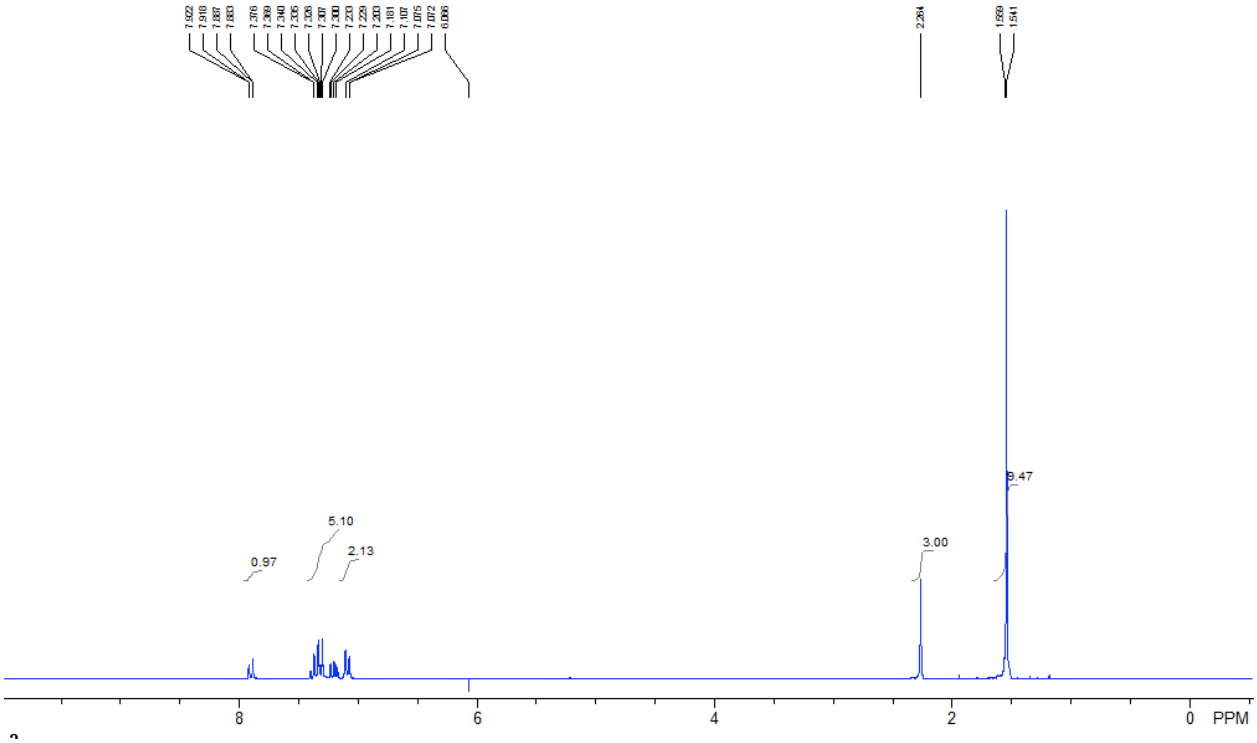
^{1}H NMR of Compound **2a**



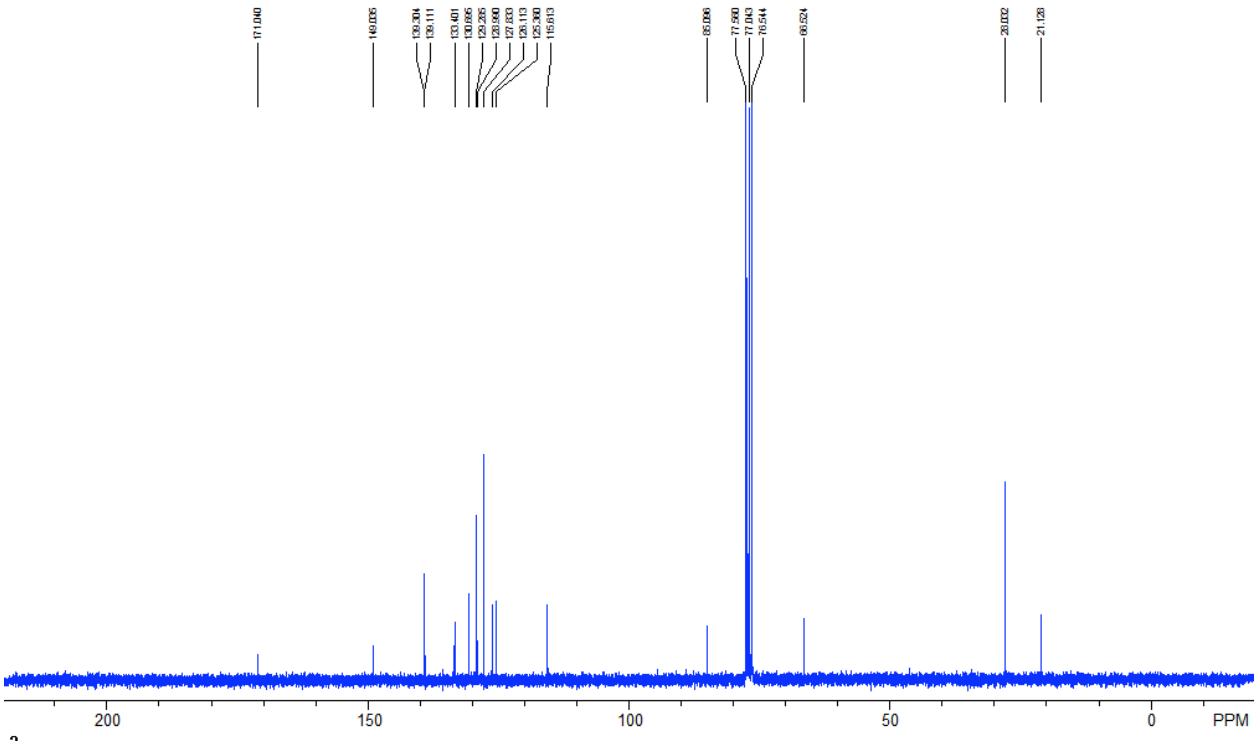
^{13}C NMR of Compound **2a**



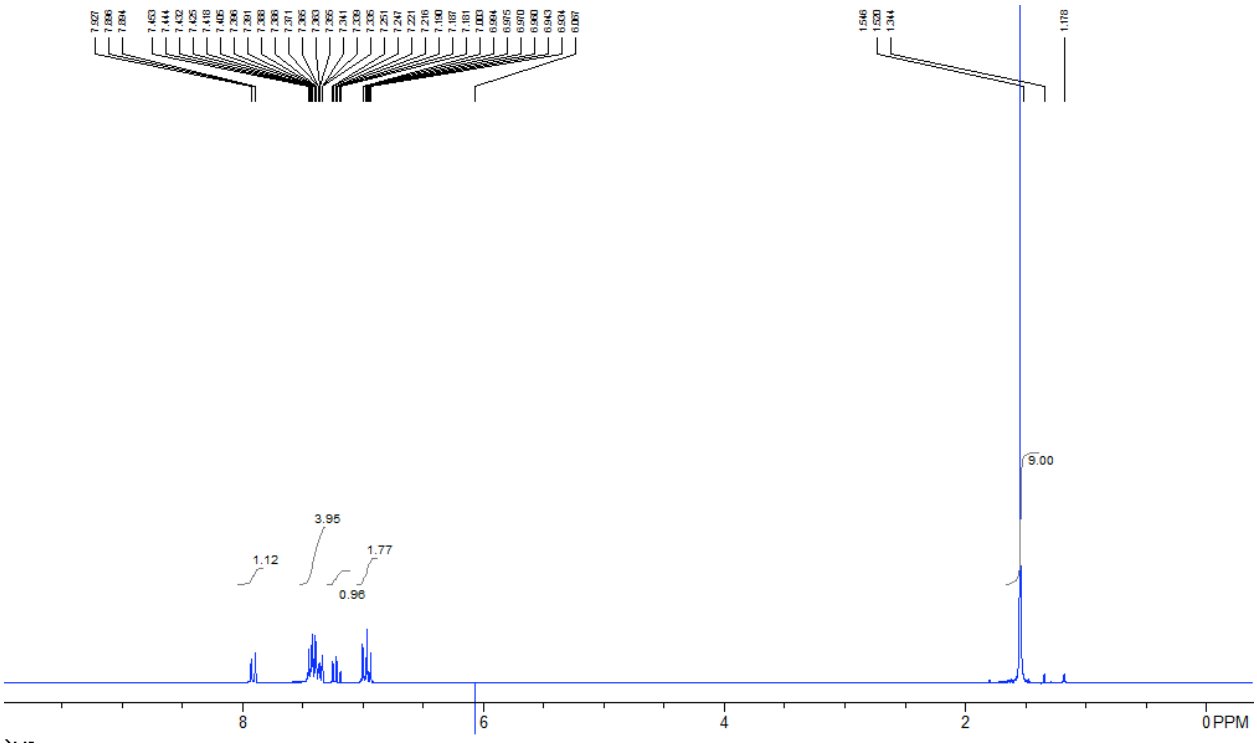
[1]H NMR of Compound **2b**



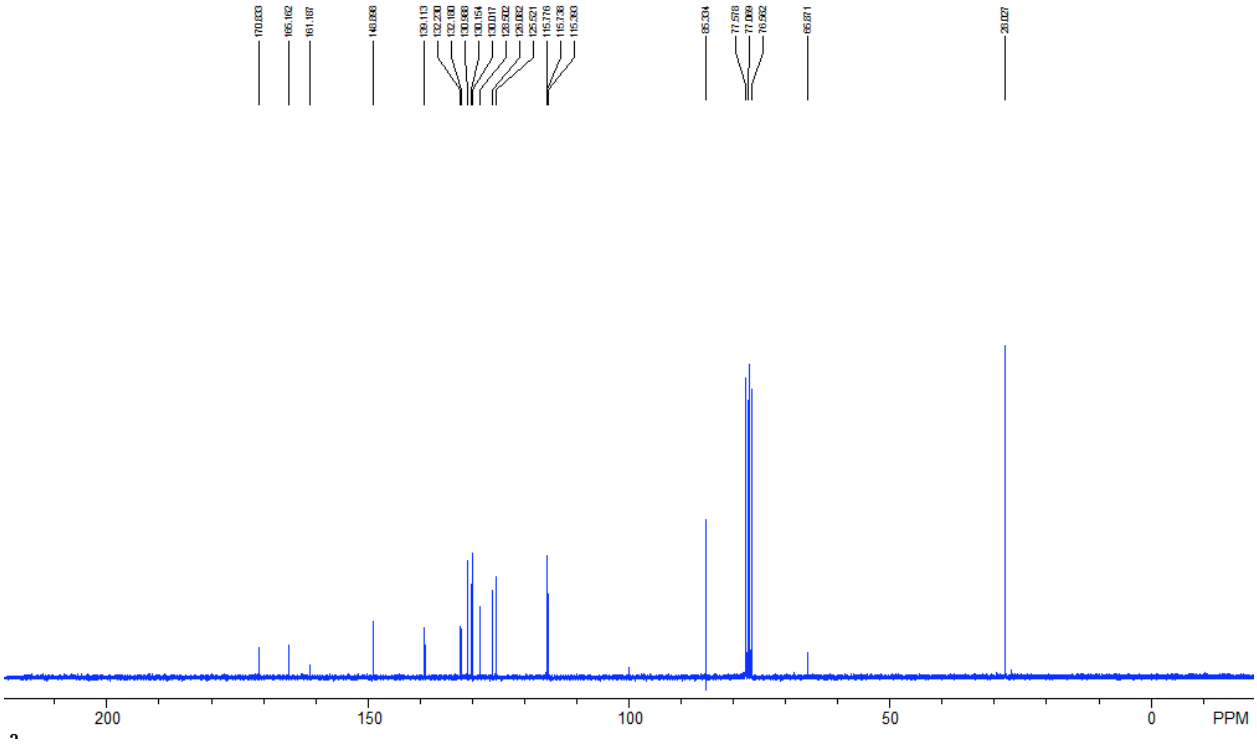
[13]C NMR of Compound **2b**



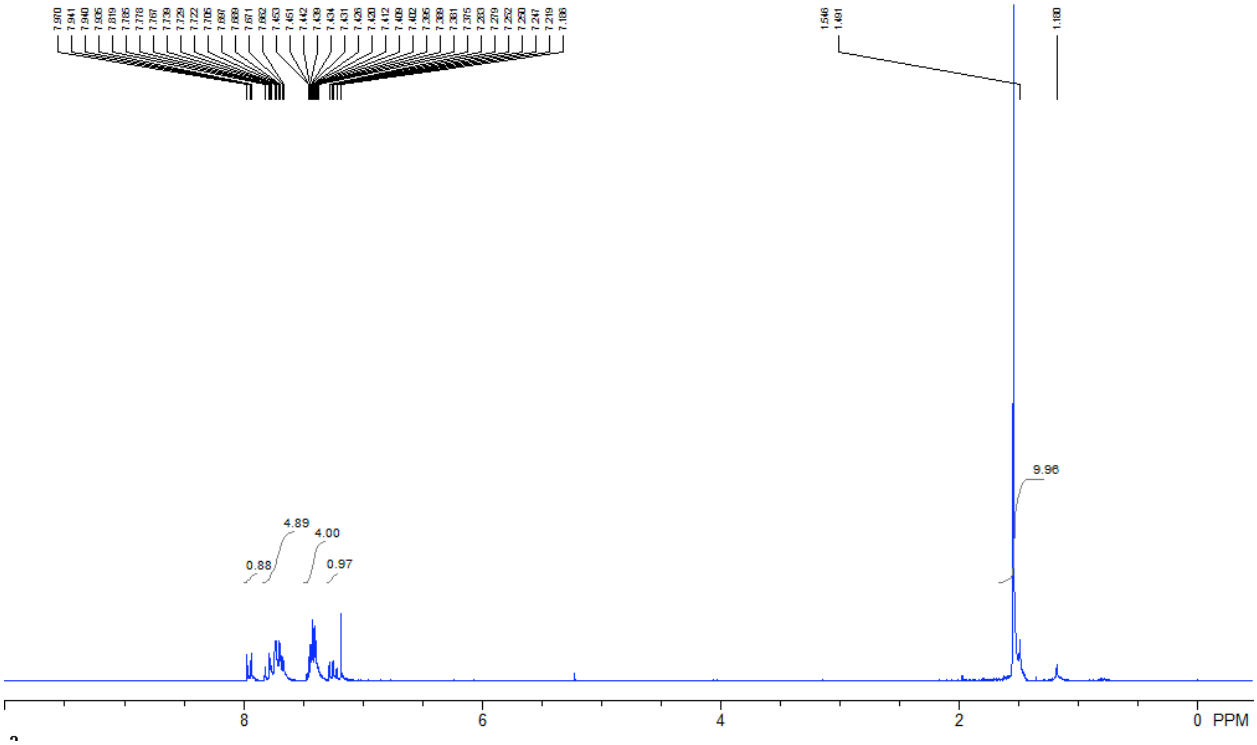
^{1}H NMR of Compound **2c**



^{13}C NMR of Compound **2c**



^{1}H NMR of Compound **2d**



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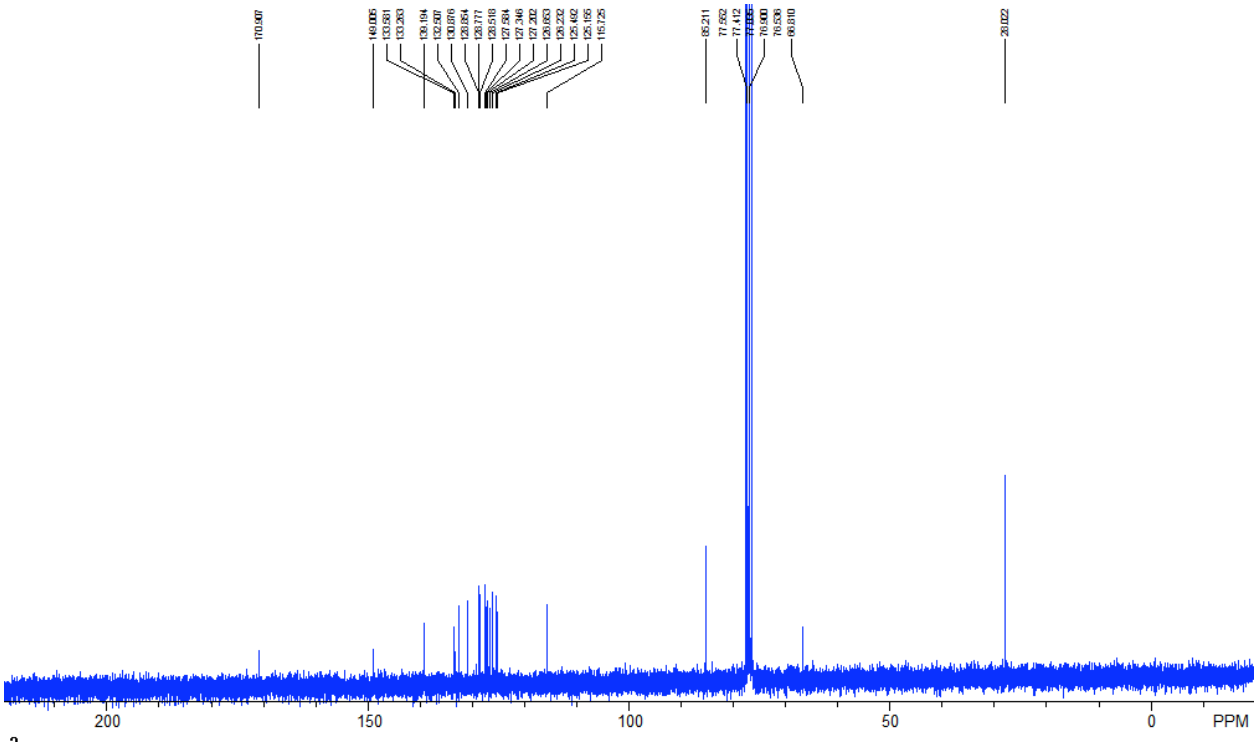

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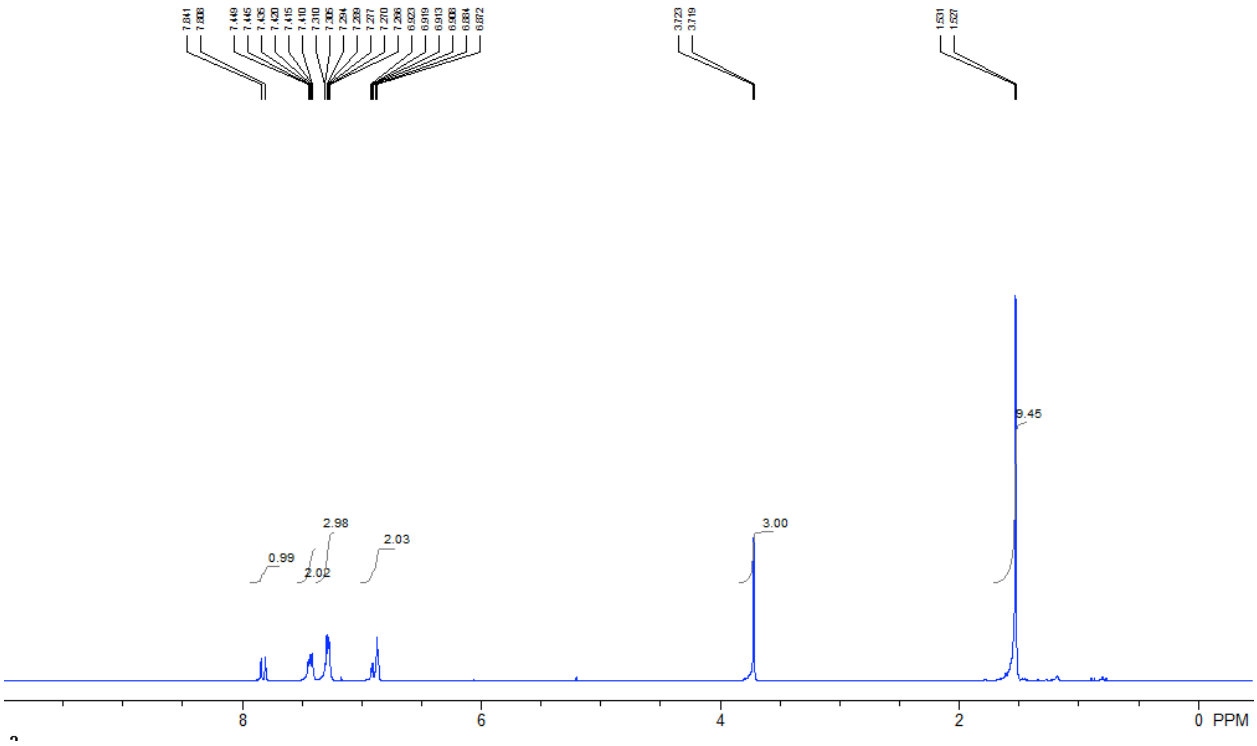

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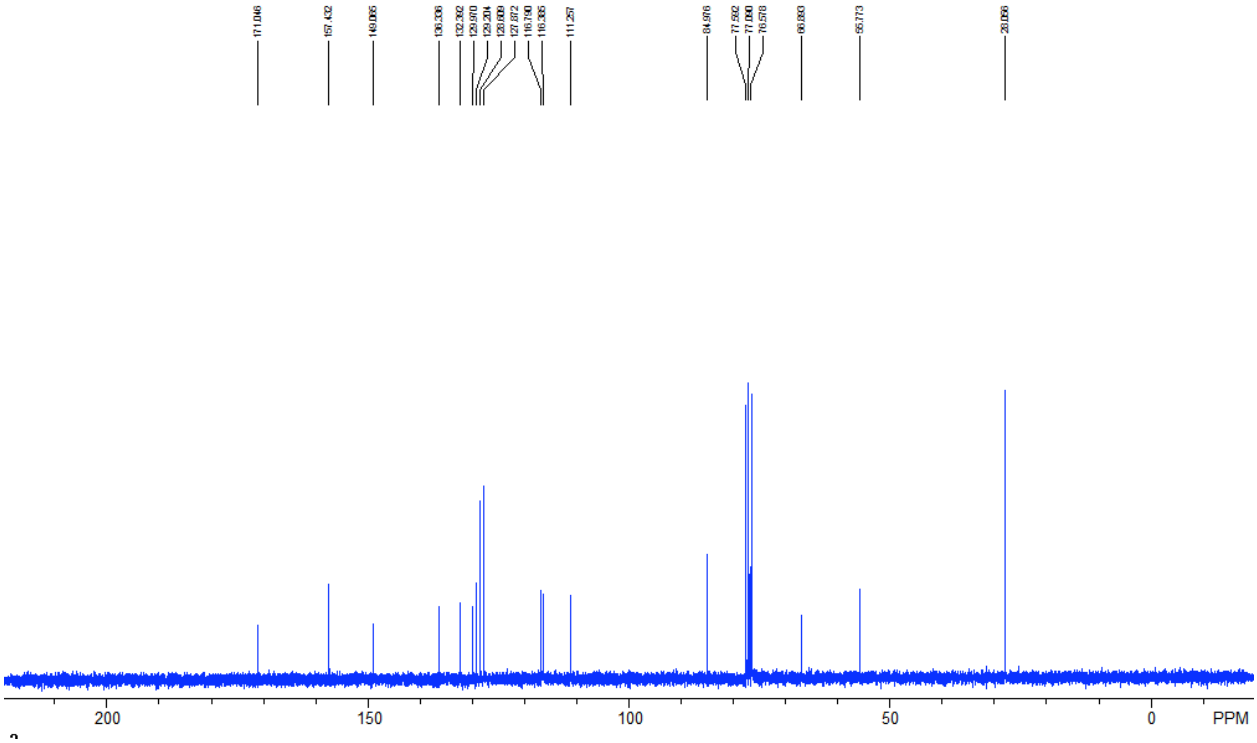
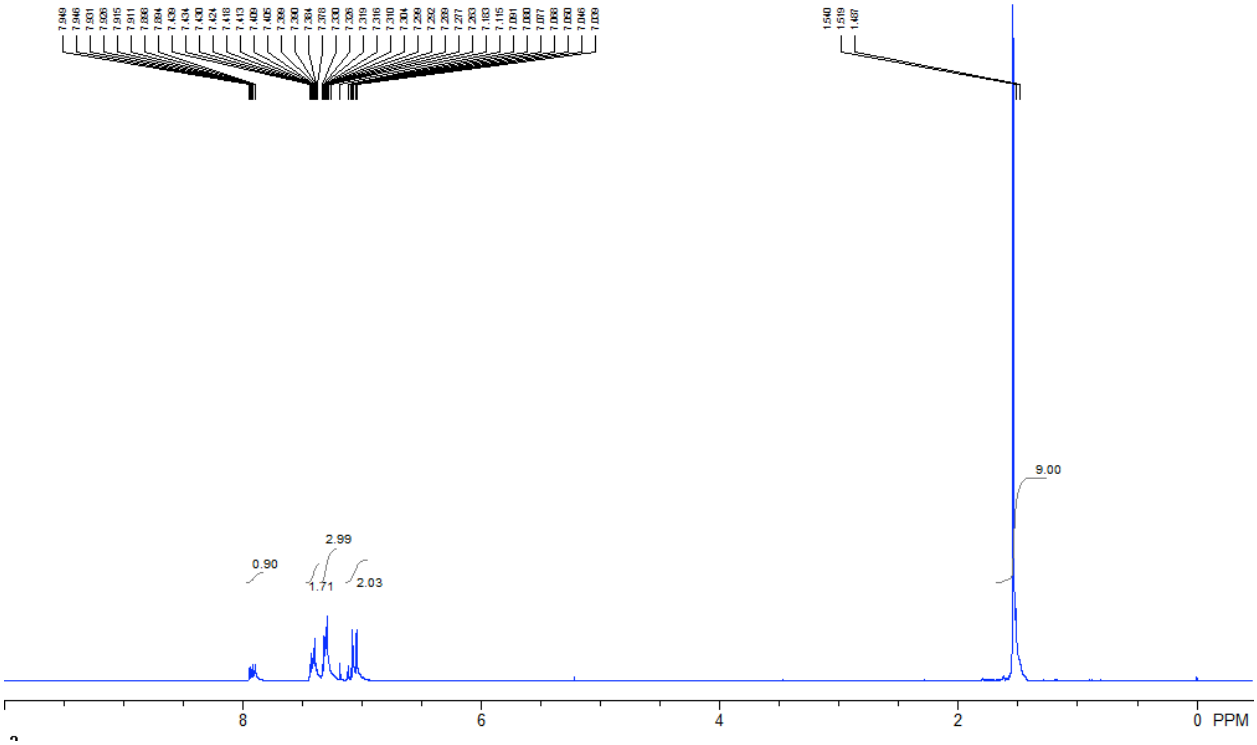
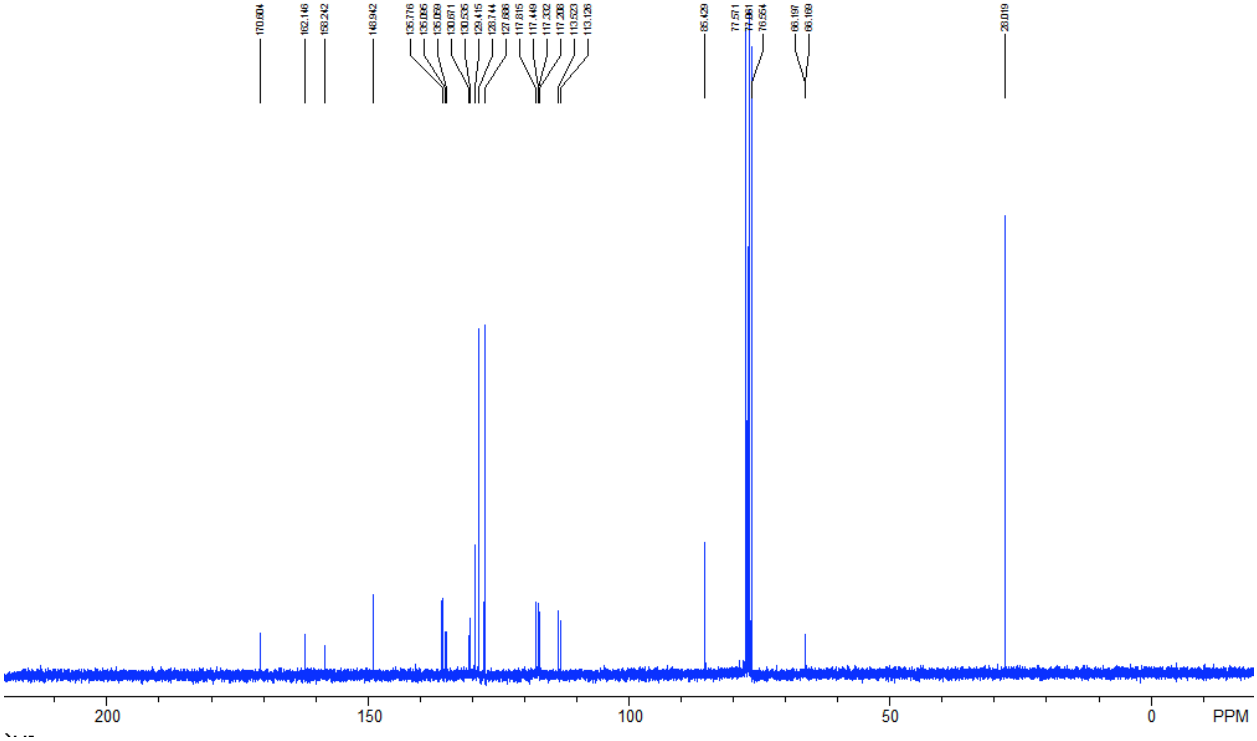


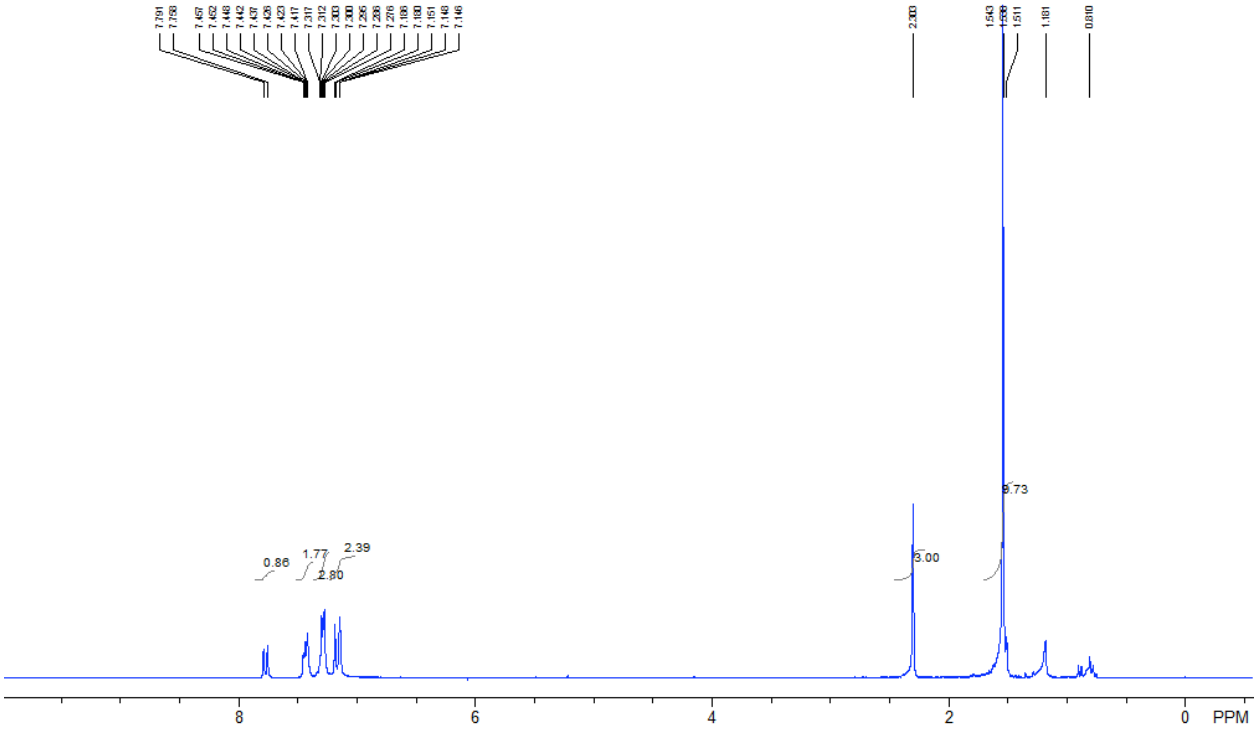
^{1}H NMR of Compound **2f**



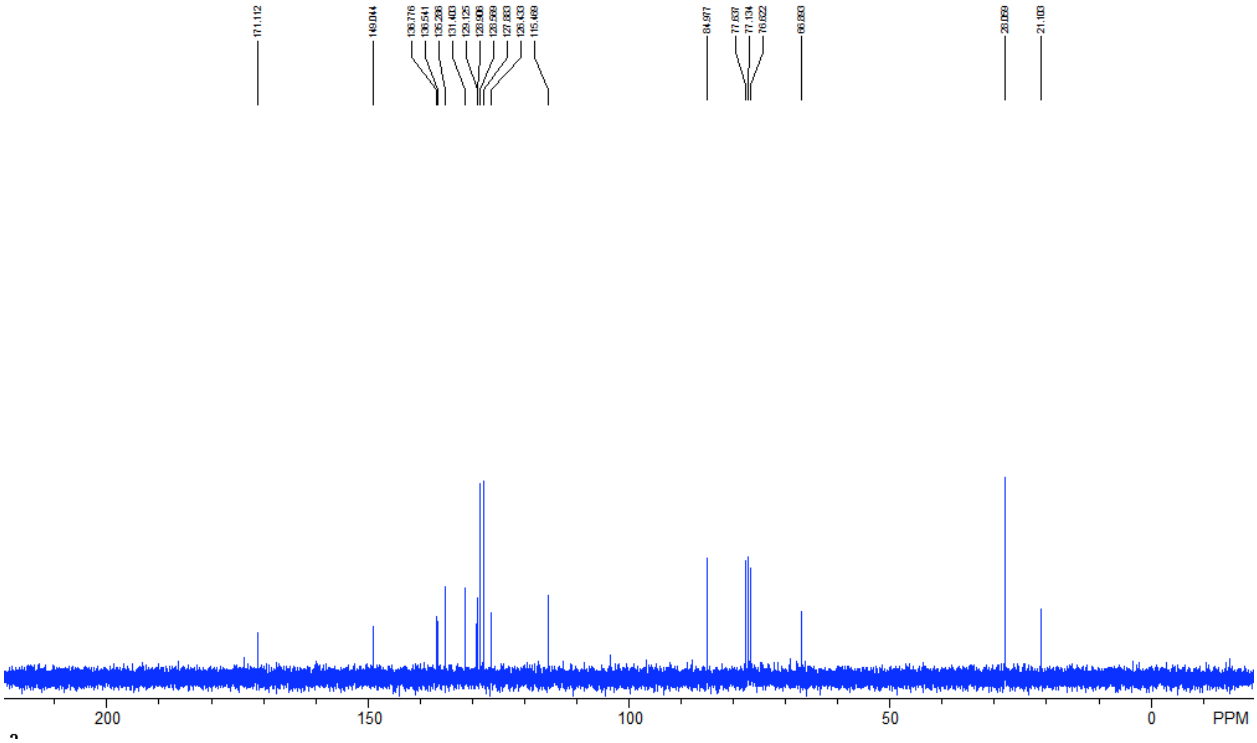
^{13}C NMR of Compound **2f**



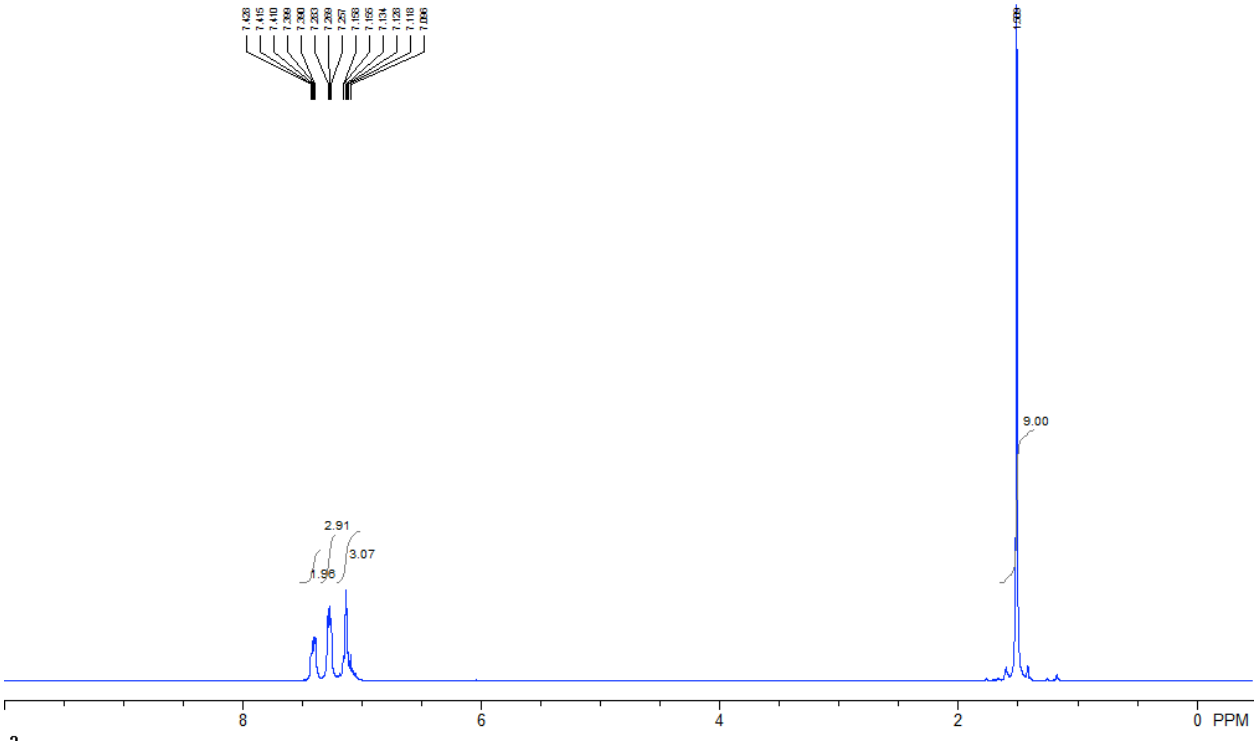
^{1}H NMR of Compound **2g**



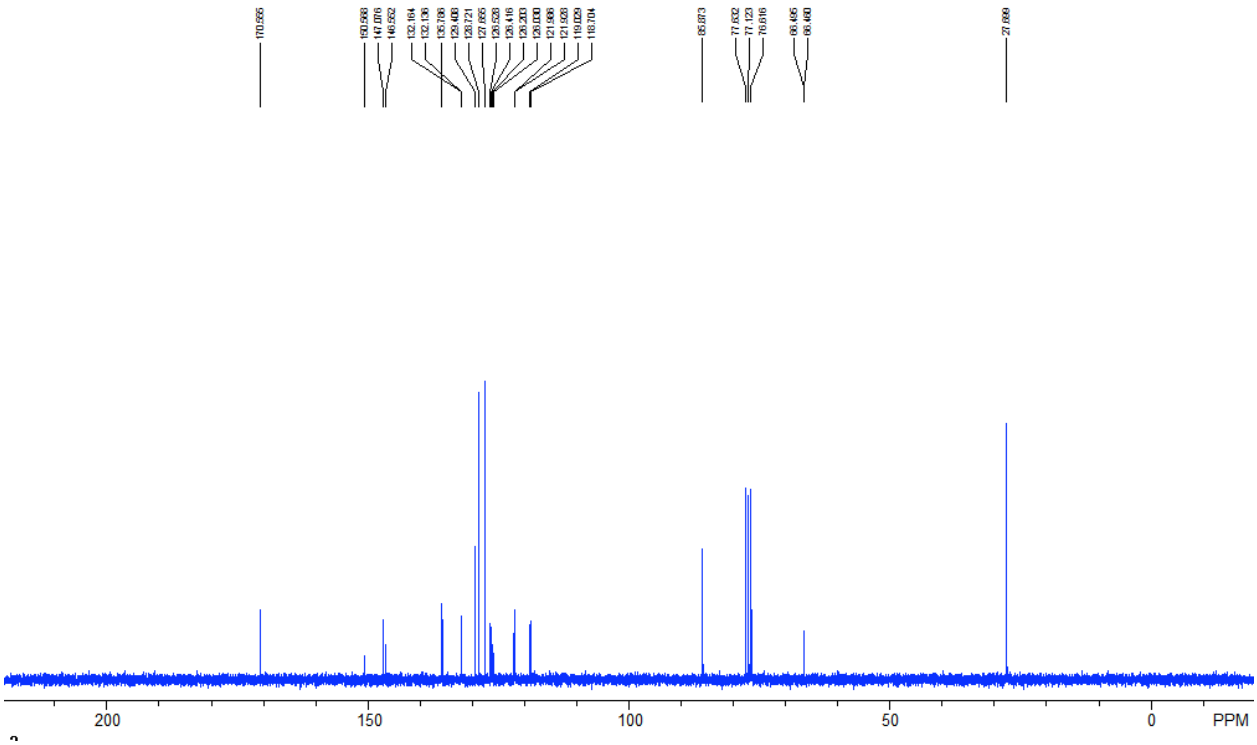
^{13}C NMR of Compound **2g**



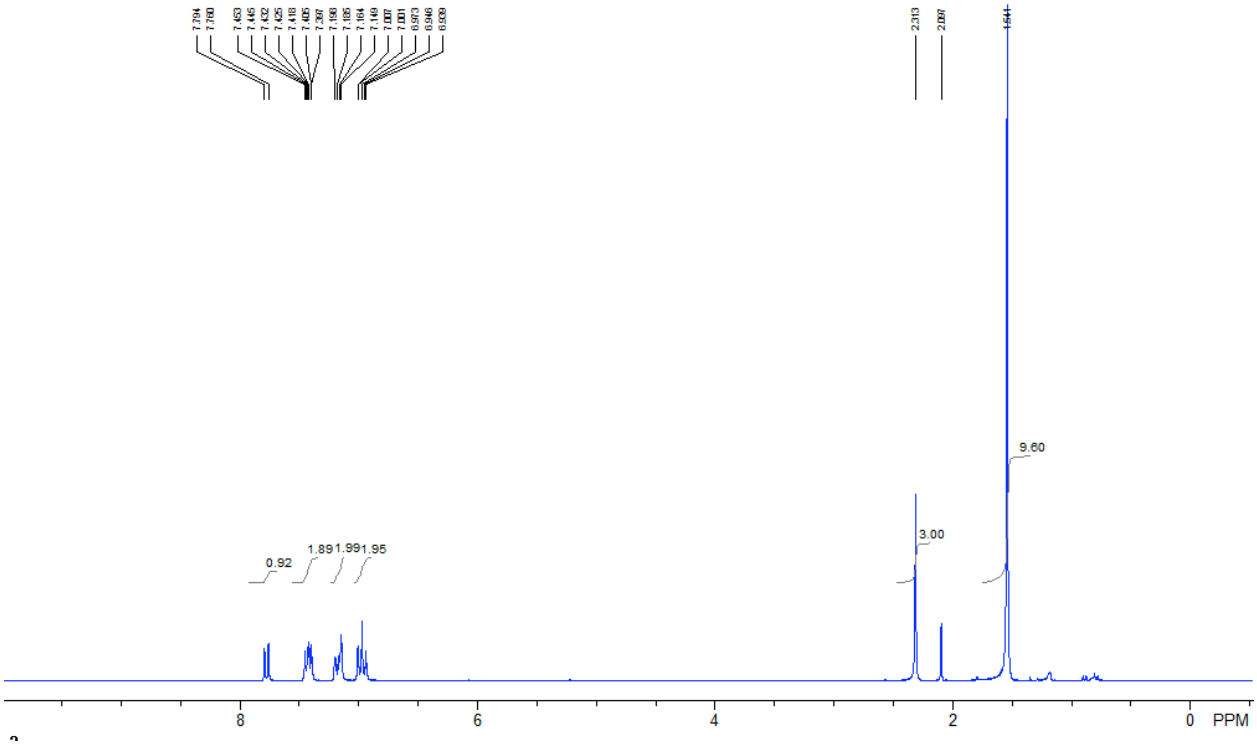
^{1}H NMR of Compound **2h**



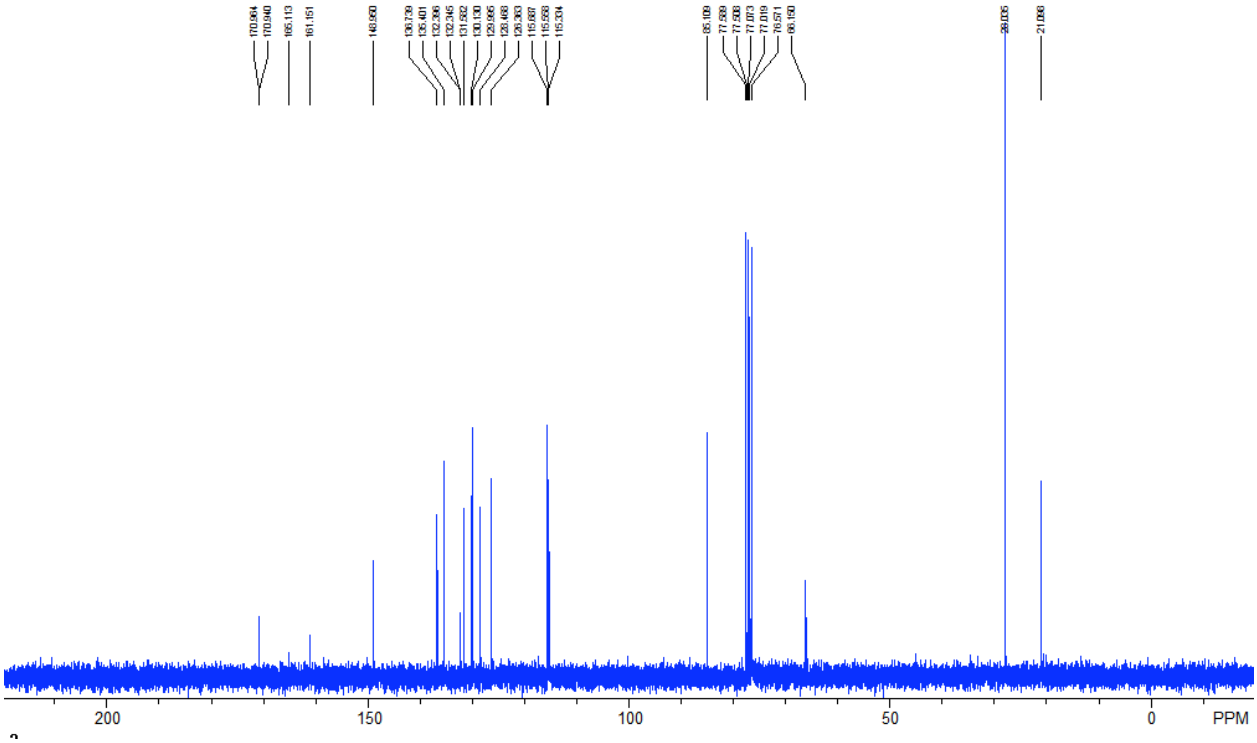
^{13}C NMR of Compound **2h**



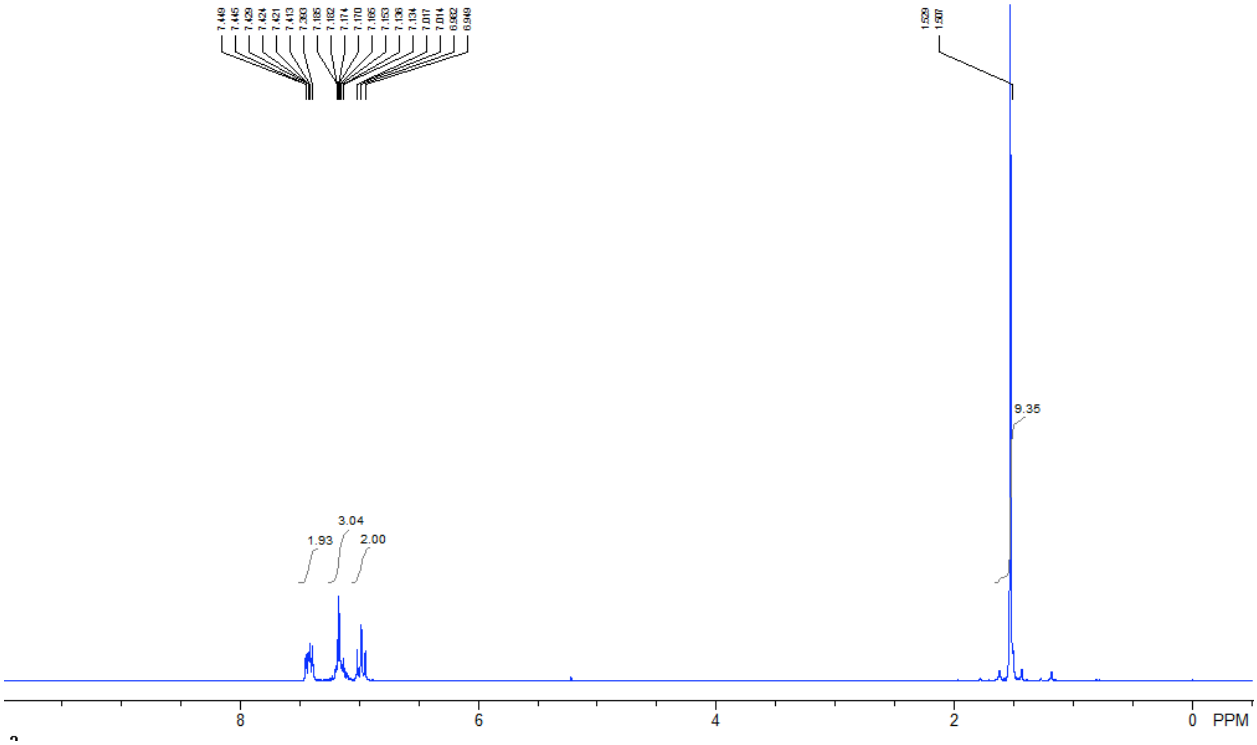
^{1}H NMR of Compound **2i**



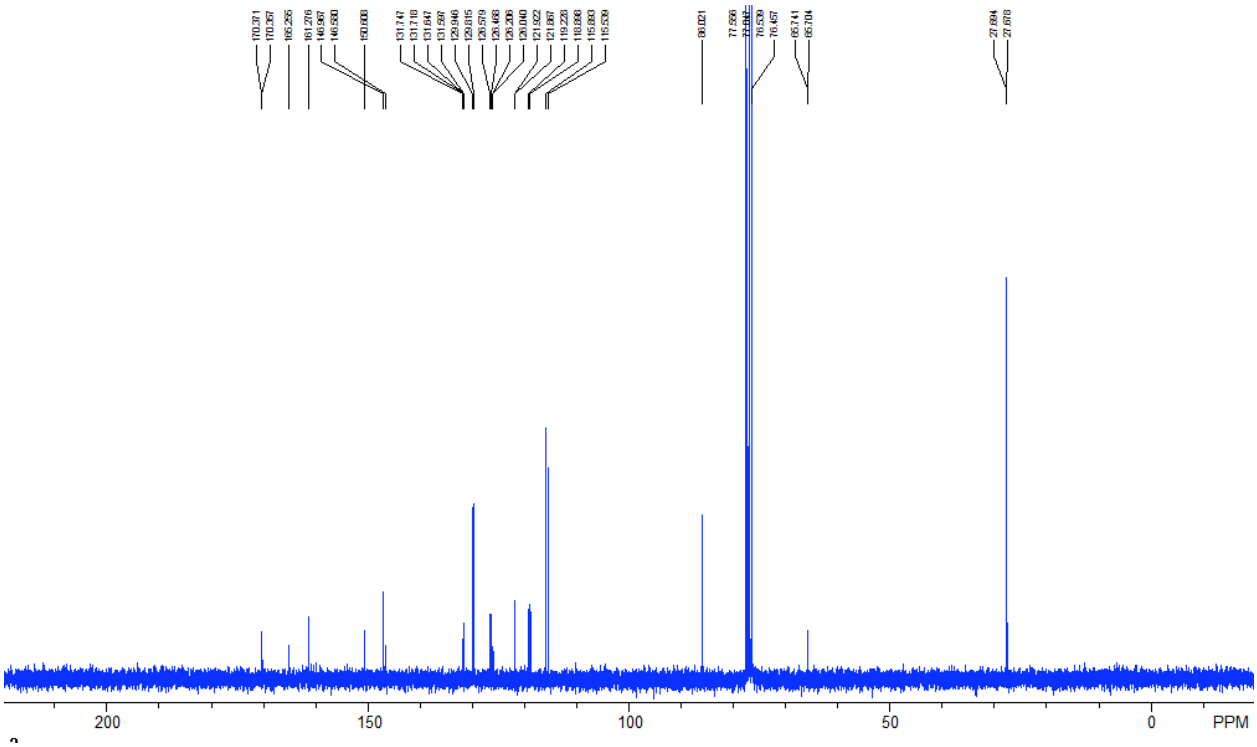
^{13}C NMR of Compound **2i**



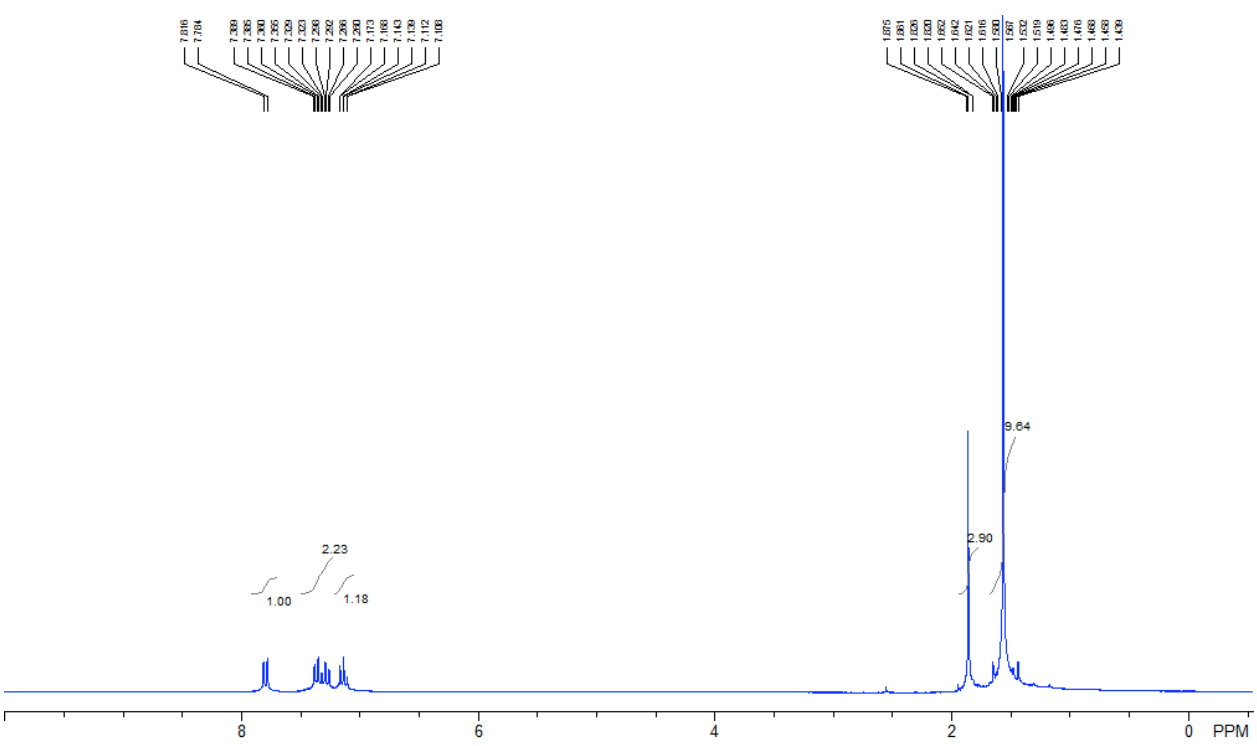
^{1}H NMR of Compound **2j**



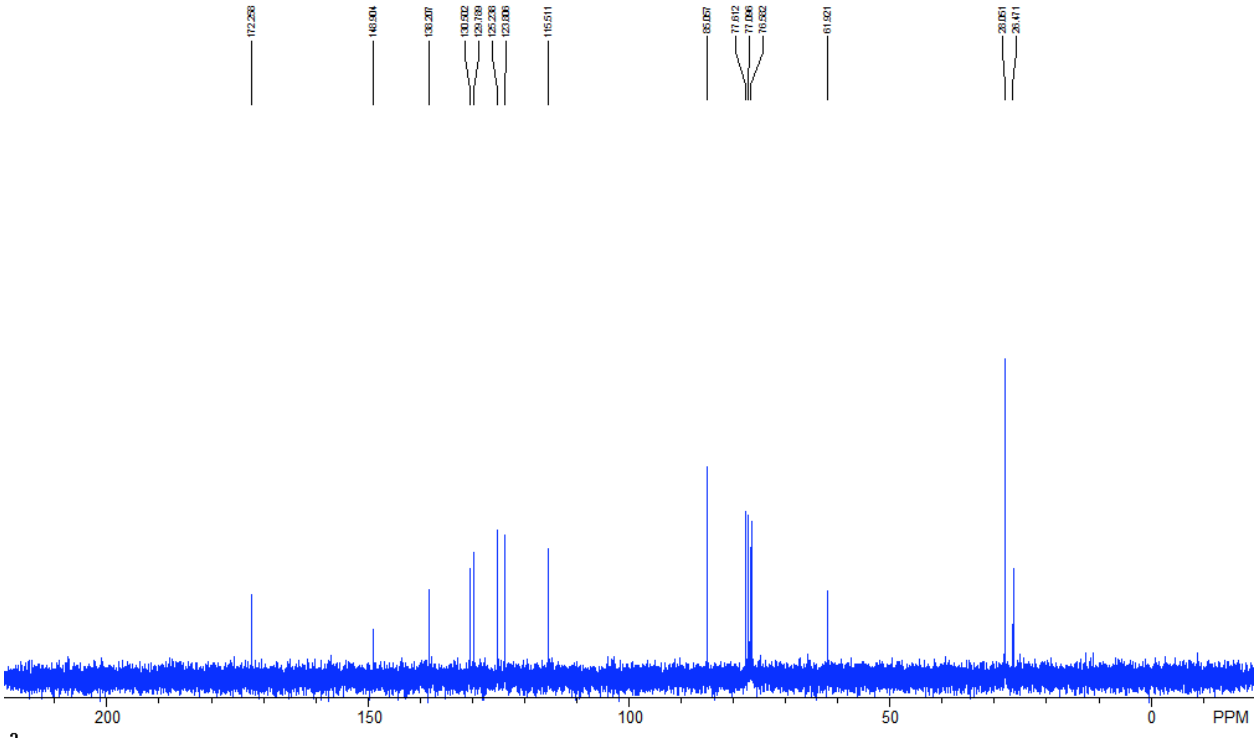
^{13}C NMR of Compound **2j**



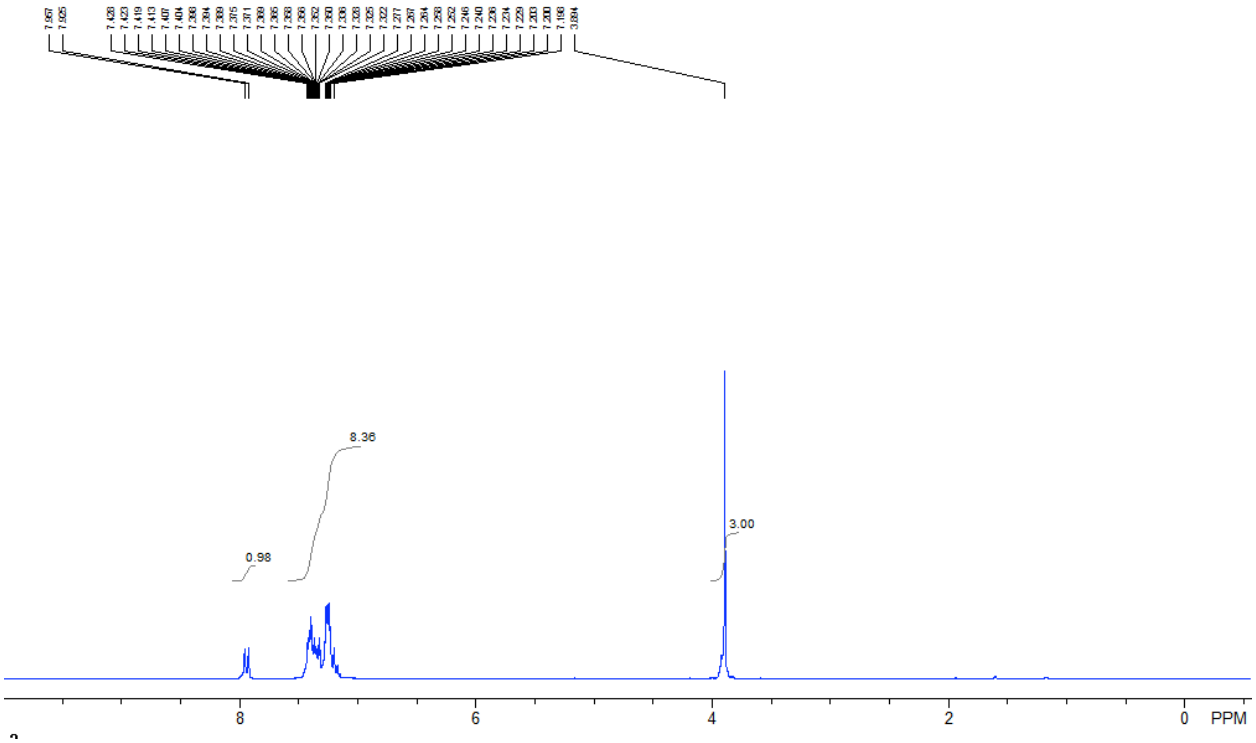
^{1}H NMR of Compound **2k**



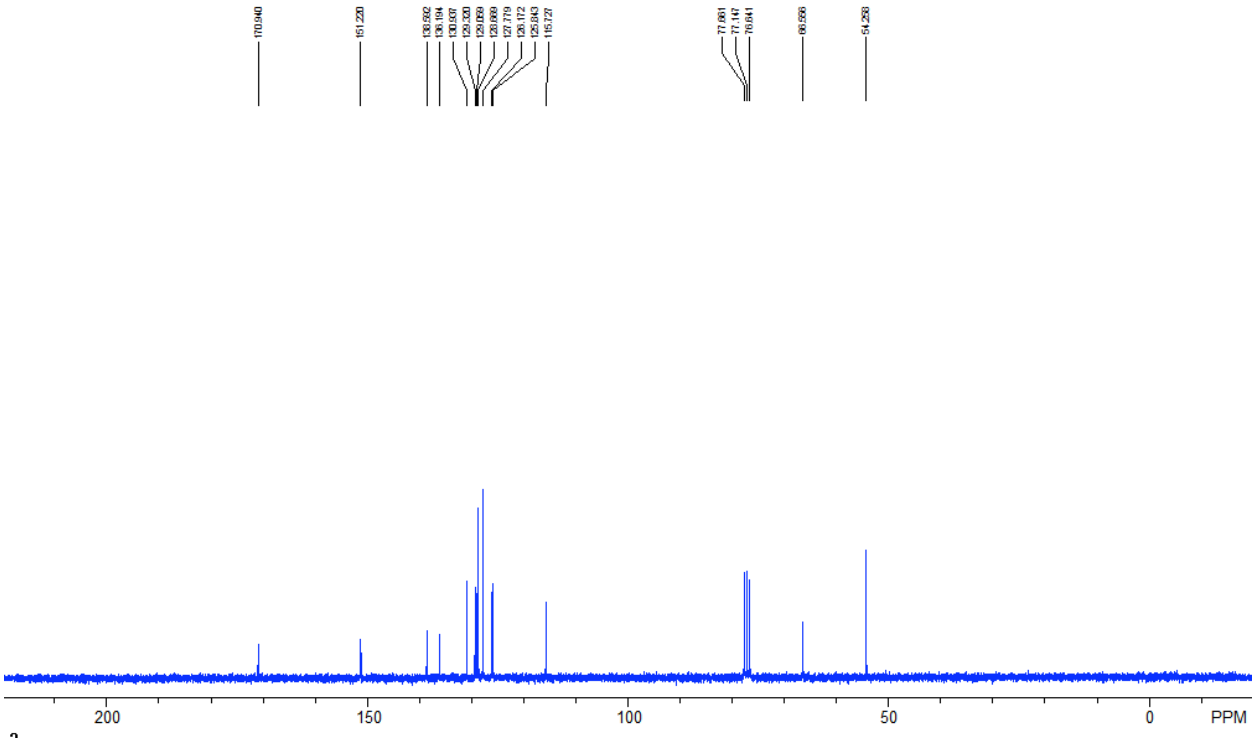
^{13}C NMR of Compound **2k**



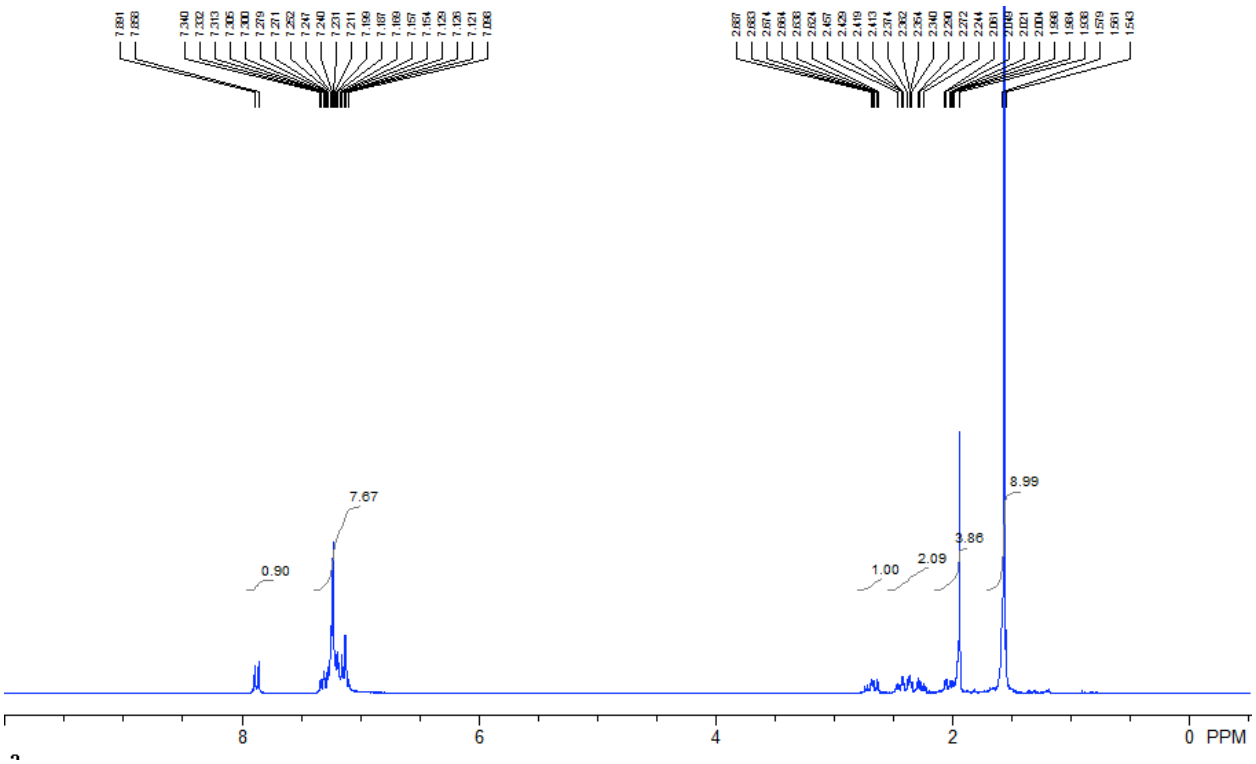
[1]H NMR for compound **2l**



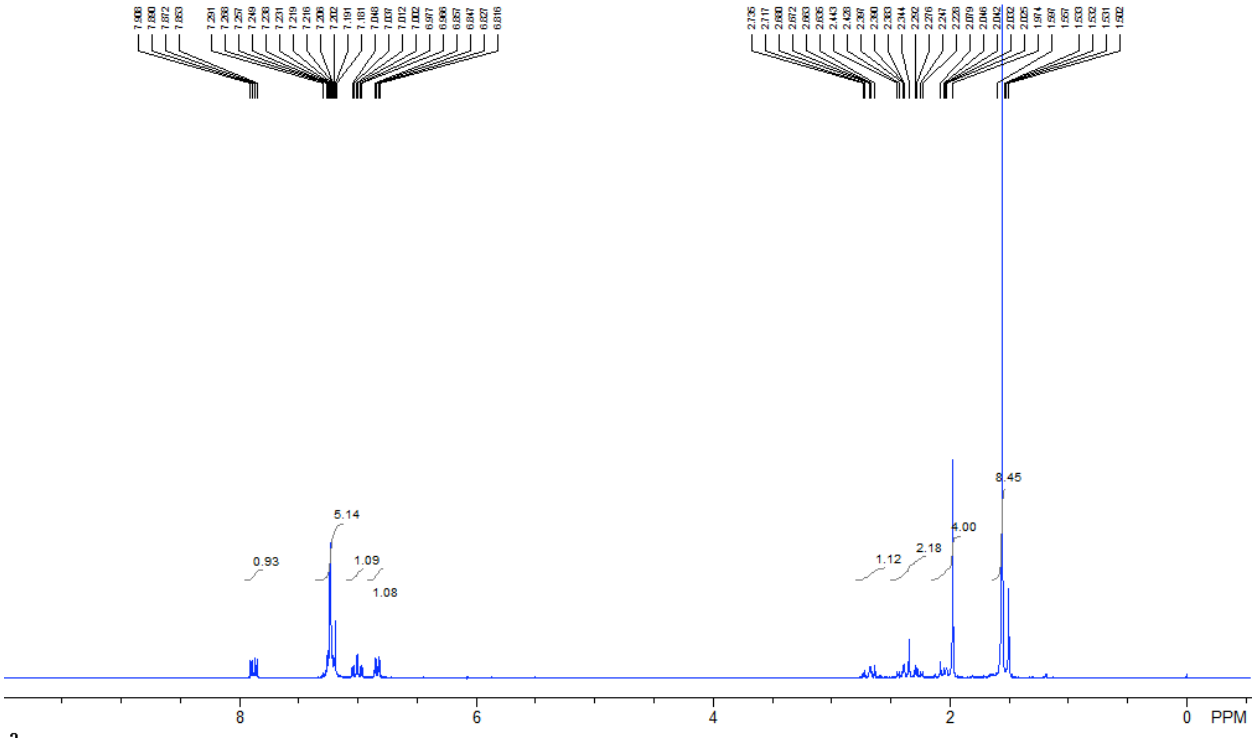
[13]C NMR of Compound **2l**



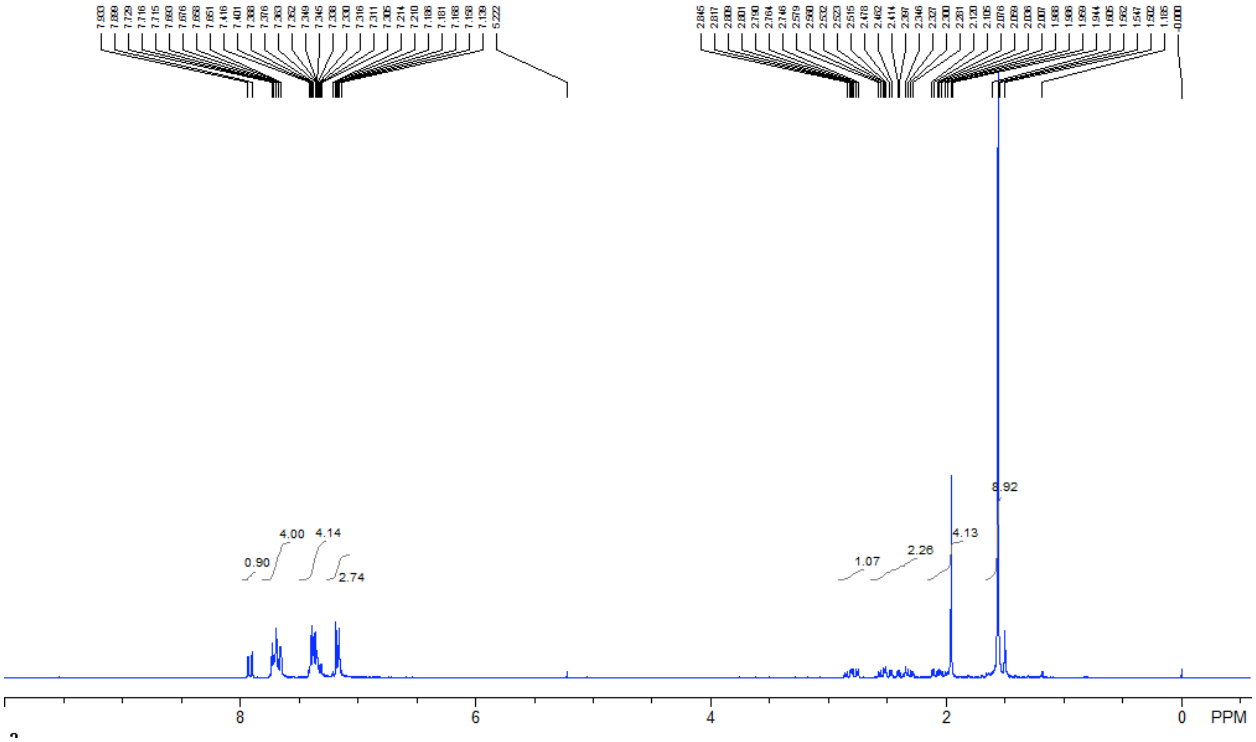
^{1}H NMR for compound **3a**



^{1}H NMR for compound **3b**



^{1}H NMR for compound **3c**



^{1}H NMR for compound **3d**