

Supporting Information

Enantioselective Synthesis of Functionalized 3,4-Disubstituted Dihydro-2(1*H*)-quinolinones via Michael–Hemiaminalization/Oxidation Reaction

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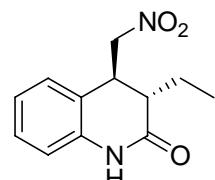
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1. General information

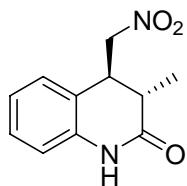
The ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or DMSO at 500 MHz and 125 MHz, respectively, with TMS as the internal standard. GC-MS experiments were performed on a GC system with a mass selective detector. HRMS data were measured on a LC/TOF-MS with ESI source. Column chromatography and flash chromatography experiments were performed on silica gel (200-300 mesh) eluting with ethyl ether and petroleum ether. TLC experiments were carried out on glass-backed silica plates. In each case, enantiomeric ratio was determined on a chiral column in comparison with authentic racemates by chiral HPLC. Chemicals were used without purification as commercially available.

2. Typical procedure for the organocatalytic asymmetric Michael-hemiaminalization/oxidation Reaction

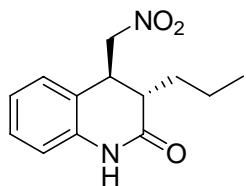
Solvent (0.5 mL) was added to a mixture of nitroolefins **1** (0.1 mmol) with aldehydes **2** (0.3 mmol) in the presence of 20 mol% catalyst **3d** and 20 mol% PhCO₂H **4a** at room temperature under vigorous stirring. After 1 day, the reaction mixture was extracted with DCM, washed with water, dried, and concentrated. The residue was purified by flash chromatography on silica gel (ethyl ether/petroleum ether = 1:4 as eluent) to yield products **5**. Then, **5** and DCM (2 mL) was added to a mixture of PCC (3 equiv.) with CH₃CO₂Na (3 equiv.) or Na₂CO₃ (3 equiv.) at room temperature under vigorous stirring. After reaction completion, the residue was purified by flash chromatography on silica gel (ethyl ether/petroleum ether = 1:2 as eluent) to yield products **6**. Enantiomeric ratio was determined by HPLC analysis on a chiral column.



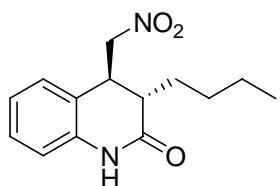
Compound (6a), yield: 20.4 mg, 87 %; 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; t_{major} = 65.672 min, t_{minor} = 71.174; ¹H NMR (500 MHz, CDCl₃): δ = 9.38 (s, 1H), 7.29–7.26 (m, 1H), 7.21–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.92–6.89 (m, 1H), 4.53–4.43 (m, 2H), 3.73–3.70 (m, 1H), 2.51–2.48 (m, 1H), 1.72–1.64 (m, 1H), 1.55–1.46 (m, 1H), 1.06–1.02 (m, 3H) ppm; ¹³C NMR (125 MHz, CDCl₃): δ = 172.2, 135.9, 129.4 (×2), 124.1, 119.7, 116.1, 78.1, 45.6, 40.2, 23.7, 11.6 ppm; HRMS: (ESI+) m/z calcd for C₁₂H₁₅N₂O₃ [M+H]⁺ 235.1083, found 235.1094.



Compound (6b), yield: 13.4 mg, 61 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 50.489\text{min}$; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.99$ (s, 1H), 7.30–7.26 (m, 1H), 7.22–7.20 (m, 1H), 7.08–7.05 (m, 1H), 6.90–6.88 (m, 1H), 4.53–4.42 (m, 2H), 3.60–3.57 (m, 1H), 2.76–2.70 (m, 1H), 1.26–1.25 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 172.7$, 136.6, 129.6, 129.5, 124.2, 119.5, 116.0, 78.0, 42.5, 38.6, 16.4 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{11}\text{H}_{13}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 221.0926, found 221.0930.

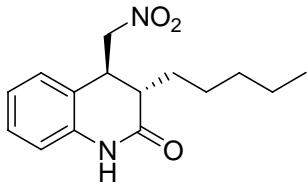


Compound (6c), yield: 15.6 mg, 63 %; 98 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 75.746$ min, $t_{\text{major}} = 66.776$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.37$ (s, 1H), 7.29–7.26 (m, 1H), 7.20–7.19 (m, 1H), 7.07–7.04 (m, 1H), 6.84–6.83 (m, 1H), 4.51–4.41 (m, 2H), 3.70–3.68 (m, 1H), 2.60–2.58 (m, 1H), 1.60–1.56 (m, 2H), 1.45–1.40 (m, 2H), 0.93–0.83 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.9$, 135.9, 129.5, 129.4, 124.1, 119.8, 115.9, 78.1, 43.8, 40.5, 32.4, 20.1, 13.7 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 249.1239, found 249.1235.

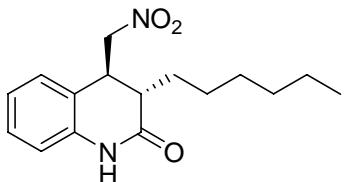


Compound (6d), yield: 20.4 mg, 87 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 46.583$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.44$ (s, 1H), 7.29–7.26 (m, 1H), 7.20–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.92–6.90 (m, 1H), 4.52–4.42 (m, 2H), 3.71–3.68 (m, 1H), 2.58–2.55 (m, 1H), 1.63–1.58 (m, 1H), 1.49–1.36 (m, 3H),

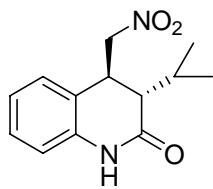
1.33–1.24 (m, 3H), 0.88–0.86 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 172.5, 136.0, 129.4 ($\times 2$), 124.1, 119.7, 116.1, 78.1, 43.9, 40.4, 30.1, 29.0, 22.3, 13.8 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 263.1396, found 263.1401.



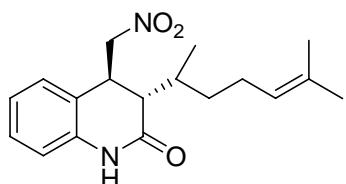
Compound (6e), yield: 20.4 mg, 74 %; > 99 % ee; $> 99:1$ dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 21.425$ min, $t_{\text{major}} = 24.892$ min; ^1H NMR (500 MHz, CDCl_3): δ = 9.57 (s, 1H), 7.29–7.26 (m, 1H), 7.20–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.92–6.91 (m, 1H), 4.52–4.42 (m, 2H), 3.71–3.68 (m, 1H), 2.59–2.56 (m, 1H), 1.64–1.55 (m, 1H), 1.50–1.37 (m, 3H), 1.30–1.26 (m, 4H), 0.87–0.84 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 172.6, 156.0, 136.0, 129.4, 129.3, 124.1, 119.7, 116.1, 78.1, 43.9, 40.4, 31.3, 30.3, 26.5, 22.3, 13.9 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 277.1552, found 277.1549.



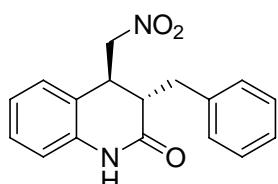
Compound (6f), yield: 22.0 mg, 76 %; 98 % ee; $> 99:1$ dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 75.746$ min, $t_{\text{major}} = 66.776$ min; ^1H NMR (500 MHz, CDCl_3): δ = 9.30 (s, 1H), 7.29–7.26 (m, 1H), 7.20–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.90–6.89 (m, 1H), 4.51–4.41 (m, 2H), 3.71–3.68 (m, 1H), 2.58–2.55 (m, 1H), 1.64–1.57 (m, 1H), 1.49–1.34 (m, 3H), 1.29–1.22 (m, 6H), 0.86–0.84 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 172.4, 135.9, 129.4 ($\times 2$), 124.1, 119.7, 116.0, 78.1, 44.0, 40.4, 31.5, 30.3, 28.8, 26.8, 22.5, 14.0 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{16}\text{H}_{23}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 291.1709, found 291.1709.



Compound (6g), yield: 19.1 mg, 77 %; 95 % ee; > 30:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 63.017$ min, $t_{\text{major}} = 52.155$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.81$ (s, 1H), 7.28–7.25 (m, 1H), 7.20–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.86–6.85 (m, 1H), 4.51–4.42 (m, 2H), 3.87–3.84 (m, 1H), 2.25–2.23 (m, 1H), 1.79–1.71 (m, 1H), 1.03–0.98 (m, 6H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.2, 136.1, 129.4, 129.1, 124.1, 120.4, 115.9, 78.2, 50.8, 39.0, 28.3, 20.8, 20.5$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 249.1239, found 249.1247.

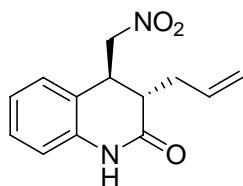


Compound (6h), yield: 23.1 mg, 73 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 33.481$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.47$ (s, 1H), 7.28–7.26 (m, 1H), 7.19–7.17 (m, 1H), 7.05–7.02 (m, 1H), 6.83–6.81 (m, 1H), 5.01–4.98 (m, 1H), 5.50–4.41 (m, 2H), 3.86–3.62 (m, 1H), 2.39–2.36 (m, 1H), 2.08–2.01 (m, 1H), 1.86–1.81 (m, 1H), 1.73–1.67 (m, 1H), 1.62 (s, 3H), 1.54 (s, 3H), 1.52–1.48 (m, 1H), 1.35–1.28 (m, 1H), 0.91–0.88 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.2, 136.0, 131.9, 129.4, 128.9, 124.1, 123.8, 120.6, 115.8, 78.5, 49.3, 38.4, 34.3, 33.3, 25.6, 25.2, 17.6, 16.6$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{18}\text{H}_{25}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 317.1865, found 317.1849.

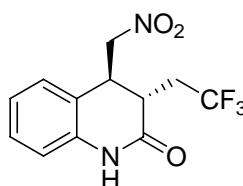


Compound (6i), yield: 22.2 mg, 75 %; 95 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm;

$t_{\text{minor}} = 133.223$ min, $t_{\text{major}} = 167.151$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.02$ (s, 1H), 7.34–7.30 (m, 3H), 7.29–7.26 (m, 1H), 7.16–7.15 (m, 1H), 7.11–7.08 (m, 3H), 6.92–7.90 (m, 1H), 4.43–4.36 (m, 2H), 3.53–3.49 (m, 1H), 3.11–3.07 (m, 1H), 2.89–2.85 (m, 1H), 2.58–2.53 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.5$, 136.8, 136.0, 129.7, 129.6, 129.0 ($\times 2$), 128.9 ($\times 2$), 127.2, 124.4, 119.4, 116.2, 77.8, 45.7, 38.6, 35.8 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{17}\text{H}_{17}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 297.1239, found 297.1243.

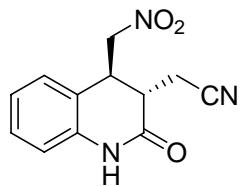


Compound (6j), yield: 18.0 mg, 73 %; 98 % ee; $> 99:1$ dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 26.985$ min, $t_{\text{major}} = 24.238$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.68$ (s, 1H), 7.30–7.27 (m, 1H), 7.19–7.17 (m, 1H), 7.08–7.05 (m, 1H), 6.95–6.93 (m, 1H), 5.81–5.72 (m, 1H), 5.15–5.13 (m, 1H), 5.03–5.00 (m, 1H), 4.52–4.43 (m, 2H), 3.77–3.74 (m, 1H), 2.68–2.65 (m, 1H), 2.48–2.43 (m, 1H), 2.16–2.10 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 172.0$, 135.9, 133.6, 129.5, 129.4, 124.3, 119.3, 118.8, 77.9, 43.4, 39.2, 34.3 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 247.1083, found 247.1079.

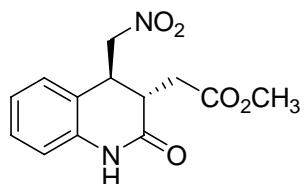


Compound (6k), yield: 20.2 mg, 70 %; 92 % ee; $> 99:1$ dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 40.799$ min, $t_{\text{major}} = 52.021$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.21$ (s, 1H), 7.35–7.32 (m, 1H), 7.26–7.25 (m, 1H), 7.14–7.10 (m, 1H), 6.94–6.92 (m, 1H), 4.57–4.53 (m, 1H), 4.49–4.45 (m, 1H), 3.89–3.86 (m, 1H), 3.03–3.00 (m, 1H), 2.46–2.36 (m, 1H), 2.31–2.20 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 169.2$, 135.5, 130.0 (1C, m), 126.8, 124.9, 124.6, 118.5, 116.5, 77.1, 39.1 (d, $^3J_{\text{C},\text{F}} = 139.6$

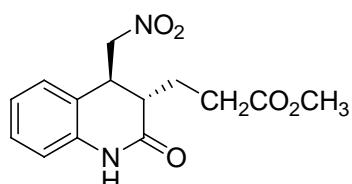
Hz), 33.8 (1C, m), 29.7 ppm; HRMS: (ESI+) m/z calcd for $C_{12}H_{12}F_3N_2O_3$ [M+H]⁺ 289.0800, found 289.0806.



Compound (6l), yield: 16.4 mg, 67 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 38.653$ min; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.65$ (s, 1H), 7.36–7.27 (m, 2H), 7.15–7.09 (m, 1H), 6.97–6.93 (m, 1H), 4.65–4.61 (m, 1H), 4.56–4.52 (m, 1H), 3.90–3.87 (m, 1H), 3.08–3.04 (m, 1H), 2.78–2.73 (m, 1H), 2.61–2.56 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta = 168.4, 135.2, 130.2, 129.4, 125.1, 117.8, 116.7, 116.1, 76.8, 40.3, 39.6, 18.7$ ppm; HRMS: (ESI+) m/z calcd for $C_{12}H_{12}N_3O_3$ [M+H]⁺ 246.0879, found 246.0888.

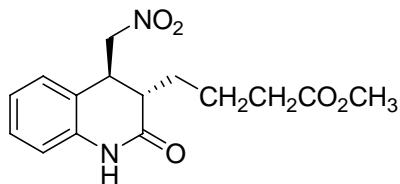


Compound (6m), yield: 18.9 mg, 68 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/i-PrOH (70:30) as the eluent, Flow: 1.0 mL/min; UV = 254 nm; $t_{\text{major}} = 26.057$ min; ¹H NMR (500 MHz, CDCl₃): $\delta = 9.49$ (s, 1H), 7.31–7.28 (m, 1H), 7.22–7.20 (m, 1H), 7.09–7.06 (m, 1H), 6.95–6.94 (m, 1H), 4.61–4.57 (m, 1H), 4.51–4.47 (m, 1H), 3.83–3.80 (m, 1H), 3.70 (s, 3H), 3.14–3.11 (m, 1H), 2.67–2.63 (m, 1H), 2.51–2.45 (m, 1H) ppm; ¹³C NMR (125 MHz, CDCl₃): $\delta = 170.7, 170.5, 135.7, 129.7, 129.6, 124.4, 118.9, 116.3, 77.8, 52.2, 40.4, 39.9, 34.1$ ppm; HRMS: (ESI+) m/z calcd for $C_{13}H_{15}N_2O_5$ [M+H]⁺ 279.0980, found 279.0988.

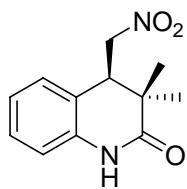


Compound (6n), yield: 19.3 mg, 66 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV =

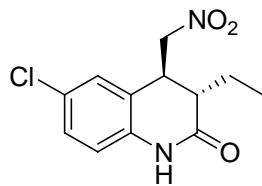
252 nm; $t_{\text{major}} = 91.434$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.22$ (s, 1H), 7.30–7.27 (m, 1H), 7.21–7.20 (m, 1H), 7.08–7.05 (m, 1H), 6.90–6.88 (m, 1H), 4.53–4.49 (m, 1H), 4.46–4.42 (m, 1H), 3.70–3.65 (m, 1H), 3.66 (s, 3H), 3.66–3.62 (m, 1H), 2.57–2.45 (m, 2H), 1.93–1.81 (m, 2H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 172.8$, 171.2, 135.6, 129.6, 129.5, 124.3, 119.4, 116.2, 77.8, 51.8, 43.2, 41.0, 31.2, 25.7 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 293.1137, found 293.1145.



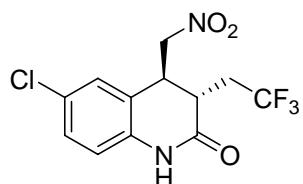
Compound (6o), yield: 21.4 mg, 70 %; 96 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/ethanol (80:20) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 15.732$ min, $t_{\text{major}} = 19.345$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.70$ (s, 1H), 7.29–7.26 (m, 1H), 7.21–7.19 (m, 1H), 7.06–7.03 (m, 1H), 6.93–6.92 (m, 1H), 4.54–4.49 (m, 1H), 4.47–4.43 (m, 1H), 3.72–3.68 (m, 1H), 3.63 (s, 3H), 2.61–2.58 (m, 1H), 2.37–2.27 (m, 2H), 1.88–1.71 (m, 2H), 1.66–1.59 (m, 1H), 1.55–1.48 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 173.4$, 172.0, 135.7, 129.5, 129.4, 124.1, 119.5, 116.2, 77.9, 51.6, 43.6, 40.4, 33.4, 29.7, 22.2 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 307.1294, found 307.1292.



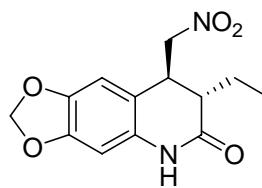
Compound (6p), yield: 11.7 mg, 50 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 51.768$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.97$ (s, 1H), 7.28–7.25 (m, 1H), 7.11–7.09 (m, 1H), 7.03–7.00 (m, 1H), 6.89–6.88 (m, 1H), 4.73–4.69 (m, 1H), 4.37–4.32 (m, 1H), 3.49–3.46 (m, 1H), 1.36 (s, 3H), 1.21 (s, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 174.8$, 135.7, 129.2, 129.0, 123.9, 121.8, 115.6, 76.8, 47.2, 39.8, 25.4, 20.8 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 235.1083, found 235.1077.



Compound (6q), yield: 20.1 mg, 75 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{major}} = 19.025$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.56$ (s, 1H), 7.27–7.21 (m, 2H), 6.89–6.88 (m, 1H), 4.51–4.42 (m, 2H), 3.70–3.67 (m, 1H), 2.49–2.46 (m, 1H), 1.70–1.56 (m, 1H), 1.53–1.44 (m, 1H), 1.04–1.02 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 172.0, 134.6, 129.5, 129.3, 129.0, 121.4, 117.4, 77.6, 45.2, 39.9, 23.7, 11.5$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{12}\text{H}_{14}\text{ClN}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 269.0692, found 269.0687.

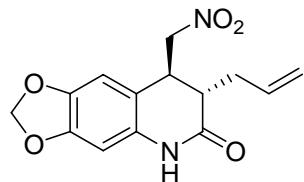


Compound (6r), yield: 24.5 mg, 76 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{minor}} = 10.106$ min, $t_{\text{major}} = 11.612$ min; ^1H NMR (500 MHz, DMSO): $\delta = 10.65$ (s, 1H), 7.36–7.2 (m, 2H), 6.96–6.94 (m, 1H), 4.88–4.86 (m, 1H), 4.67–4.63 (m, 1H), 3.78–3.75 (m, 1H), 2.84–2.82 (m, 1H), 2.58–2.47 (m, 1H), 2.42–2.33 (m, 1H) ppm; ^{13}C NMR (125 MHz, DMSO): $\delta = 167.5, 135.9, 129.1, 129.0, 126.3, 126.3$ (d, $^1\text{J}_{\text{C-F}} = 275.4$ Hz), 121.0, 117.4, 77.0, 39.2, 37.1, 33.3 (1C, m) ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{12}\text{H}_{11}\text{ClF}_3\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 323.0410, found 323.0413.

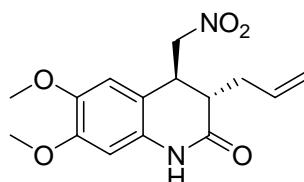


Compound (6s), yield: 18.4 mg, 66 %; 97 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{minor}} = 17.279$ min, $t_{\text{major}} = 26.131$ min; ^1H NMR (500 MHz, DMSO): $\delta = 10.04$ (s, 1H), 6.79 (s, 1H), 6.49 (s, 1H), 5.96 (s, 2H), 4.65–4.61 (m, 1H), 4.53–4.49 (m, 1H),

3.51 (t, $J = 7.5$ Hz, 1H), 2.22 (t, $J = 7.5$ Hz, 1H), 1.44–1.30 (m, 2H), 0.89 (t, $J = 7.5$ Hz, 3H) ppm; ^{13}C NMR (125 MHz, DMSO): $\delta = 169.9, 147.2, 142.4, 131.5, 111.8, 109.1, 101.2, 97.2, 78.2, 44.5, 39.4, 23.1, 11.3$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{13}\text{H}_{15}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 279.0980, found 279.0985.



Compound (6t), yield: 22.6 mg, 78 %; 97 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{minor}} = 19.225$ min, $t_{\text{major}} = 27.705$ min; ^1H NMR (500 MHz, DMSO): $\delta = 10.12$ (s, 1H), 6.75 (s, 1H), 6.52 (s, 1H), 5.98 (d, $J = 3$ Hz, 2H), 5.78–5.70 (m, 1H), 5.07–4.97 (m, 2H), 4.68–4.64 (m, 1H), 4.55–4.51 (m, 1H), 3.50–3.47 (m, 1H), 2.45–2.42 (m, 1H), 2.23–2.18 (m, 1H), 2.06–2.00 (m, 1H) ppm; ^{13}C NMR (125 MHz, DMSO): $\delta = 169.4, 117.4, 112.6, 131.7, 131.6, 117.7, 111.4, 109.0, 101.2, 97.3, 78.1, 42.2, 38.9, 34.08$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{15}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 291.0980, found 291.0985.



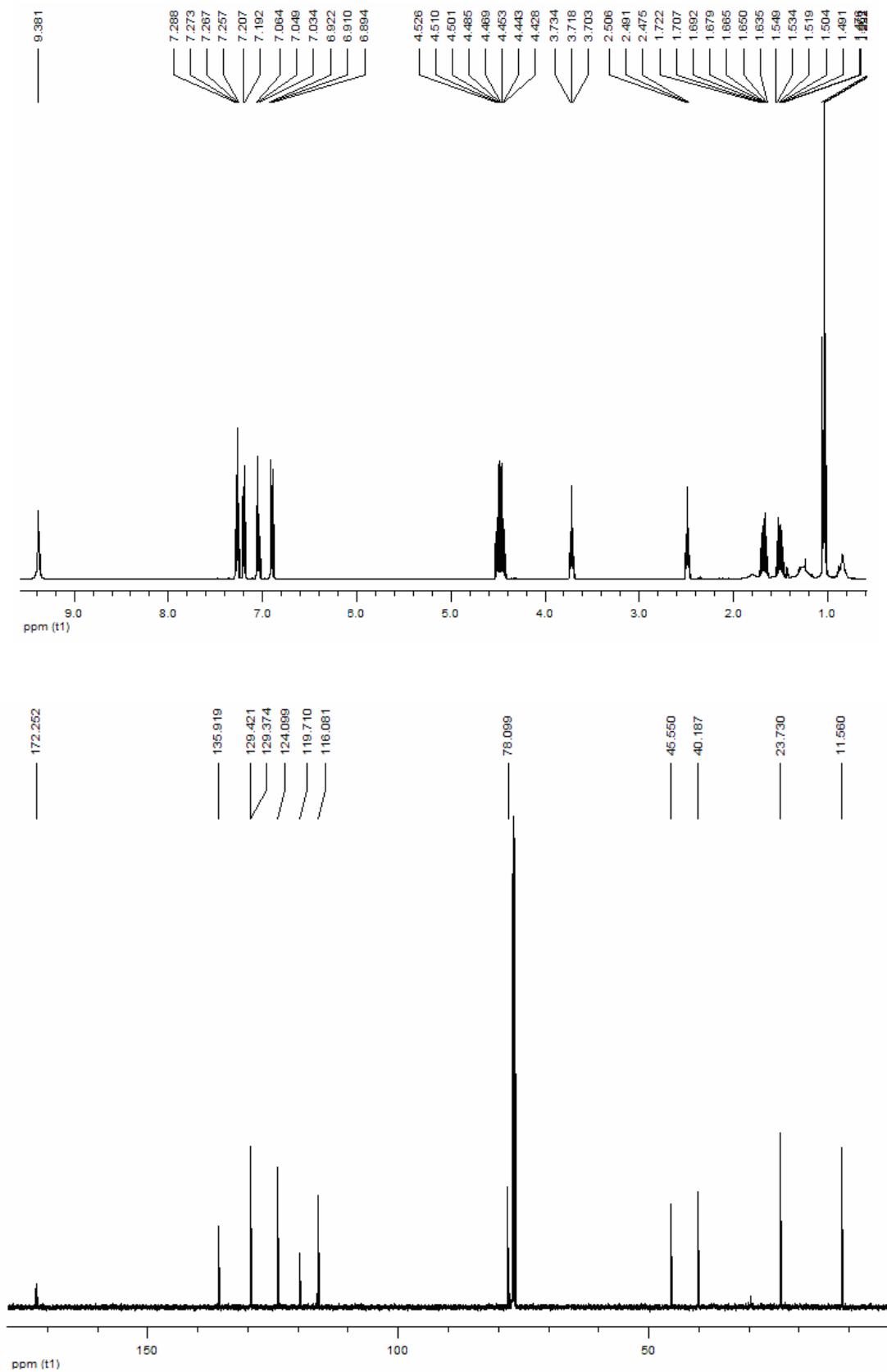
Compound (6u), yield: 22.0 mg, 72 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (50:50) as the eluent, Flow: 0.5 mL/min; UV = 216 nm; $t_{\text{minor}} = 38.491$ min, $t_{\text{major}} = 44.023$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.31$ (s, 1H), 6.66 (s, 1H), 6.45 (s, 1H), 5.80–5.72 (m, 1H), 5.15–5.13 (m, 1H), 5.04–5.01 (m, 1H), 4.49–4.42 (m, 2H), 3.89 (s, 3H), 3.85 (s, 3H), 3.66–3.63 (m, 1H), 2.63–2.60 (m, 1H), 2.47–2.42 (m, 1H), 2.17–2.10 (m, 1H) ppm; ^{13}C NMR (125 MHz, CDCl_3): $\delta = 171.5, 149.9, 145.7, 133.7, 129.6, 118.7, 112.2, 110.3, 100.6, 78.0, 56.4, 56.2, 43.5, 39.1, 34.2$ ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{15}\text{H}_{19}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$ 307.1293, found 307.1289.

3.Typical procedure for one-pot synthesis of **6a**

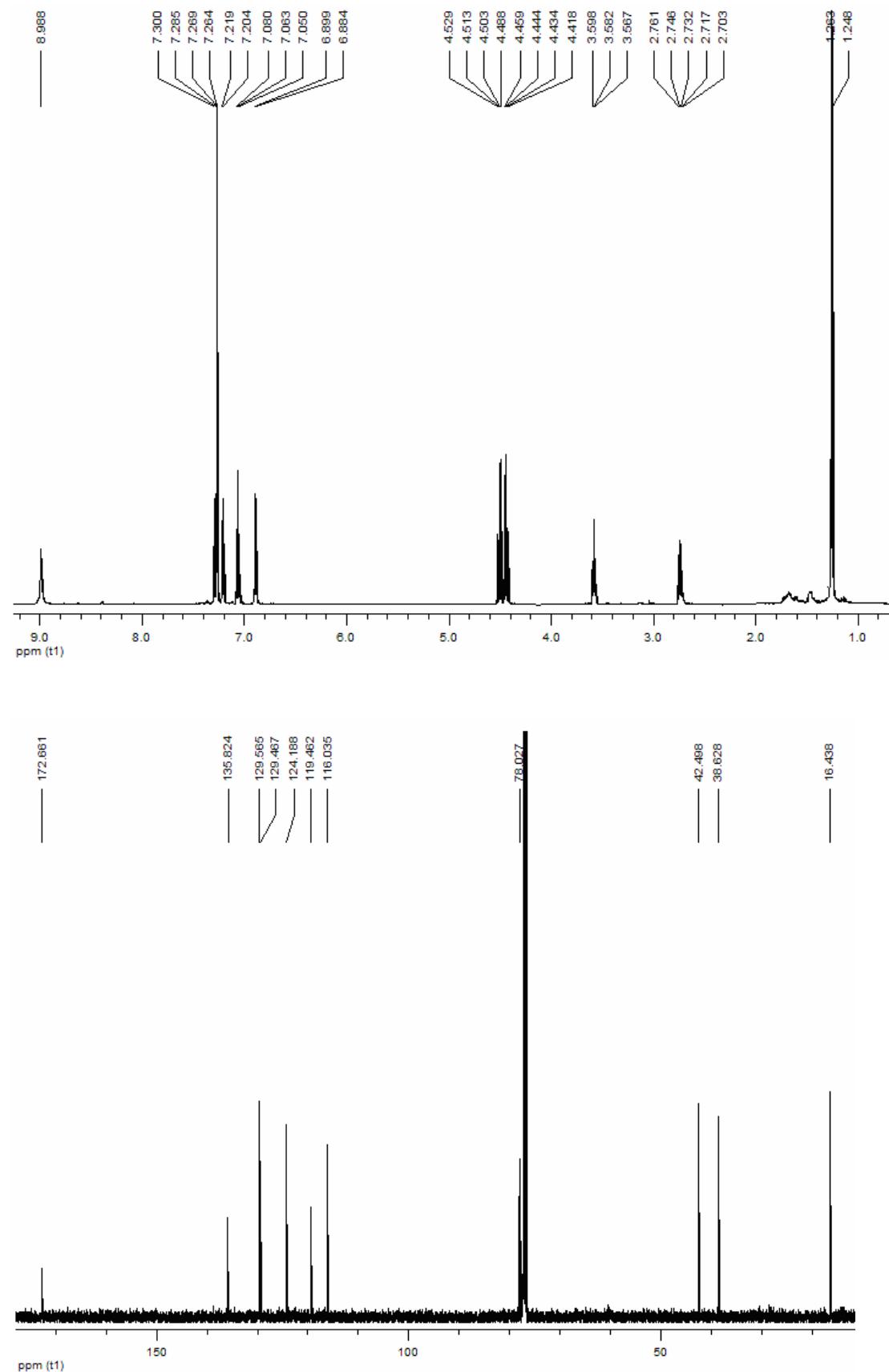
Solvent (1 mL) was added to a mixture of nitroolefins **1** (0.2 mmol) with aldehydes **2** (0.6 mmol) in the presence of 20 mol% catalyst **3d** and 20 mol% PhCO₂H **4a** at room temperature under vigorous stirring. After 1 day, the reaction was quenched by adding aq. HCl, extracted with DCM (3 × 5 mL), washed with aq. Na₂CO₃, and concentrated. DCM (8 mL) and a mixture of PCC (8 equiv.) with CH₃CO₂Na (8 equiv.) were added to the residue at room temperature under vigorous stirring. After reaction completion, the residue was purified by flash chromatography on silica gel (ethyl ether/petroleum ether = 1:2 as eluent) to yield product **6a**. Enantiomeric ratio was determined by HPLC analysis on a Daicel Chiraldpak AD-H.

4. NMR spectra

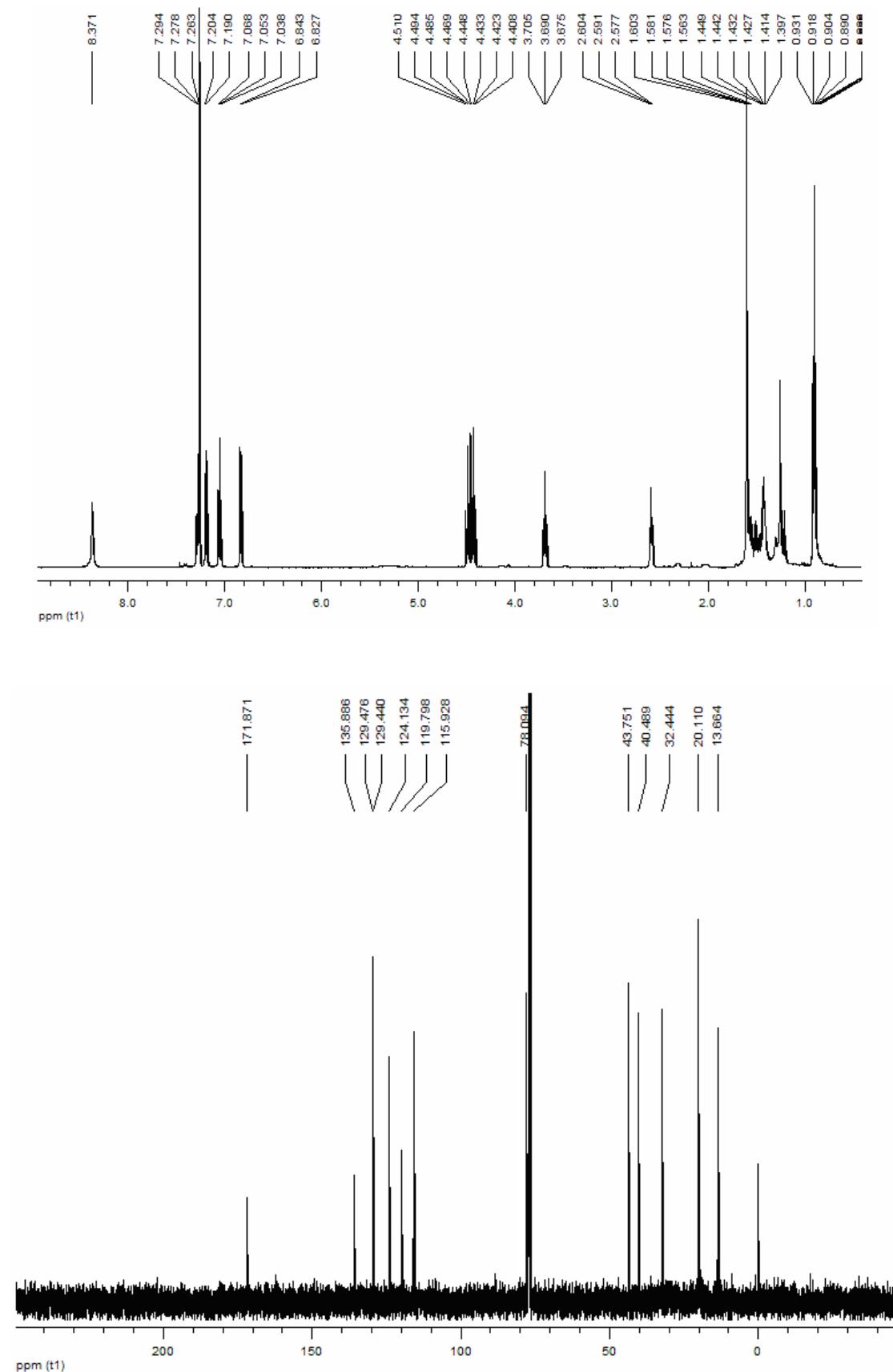
Compound 6a



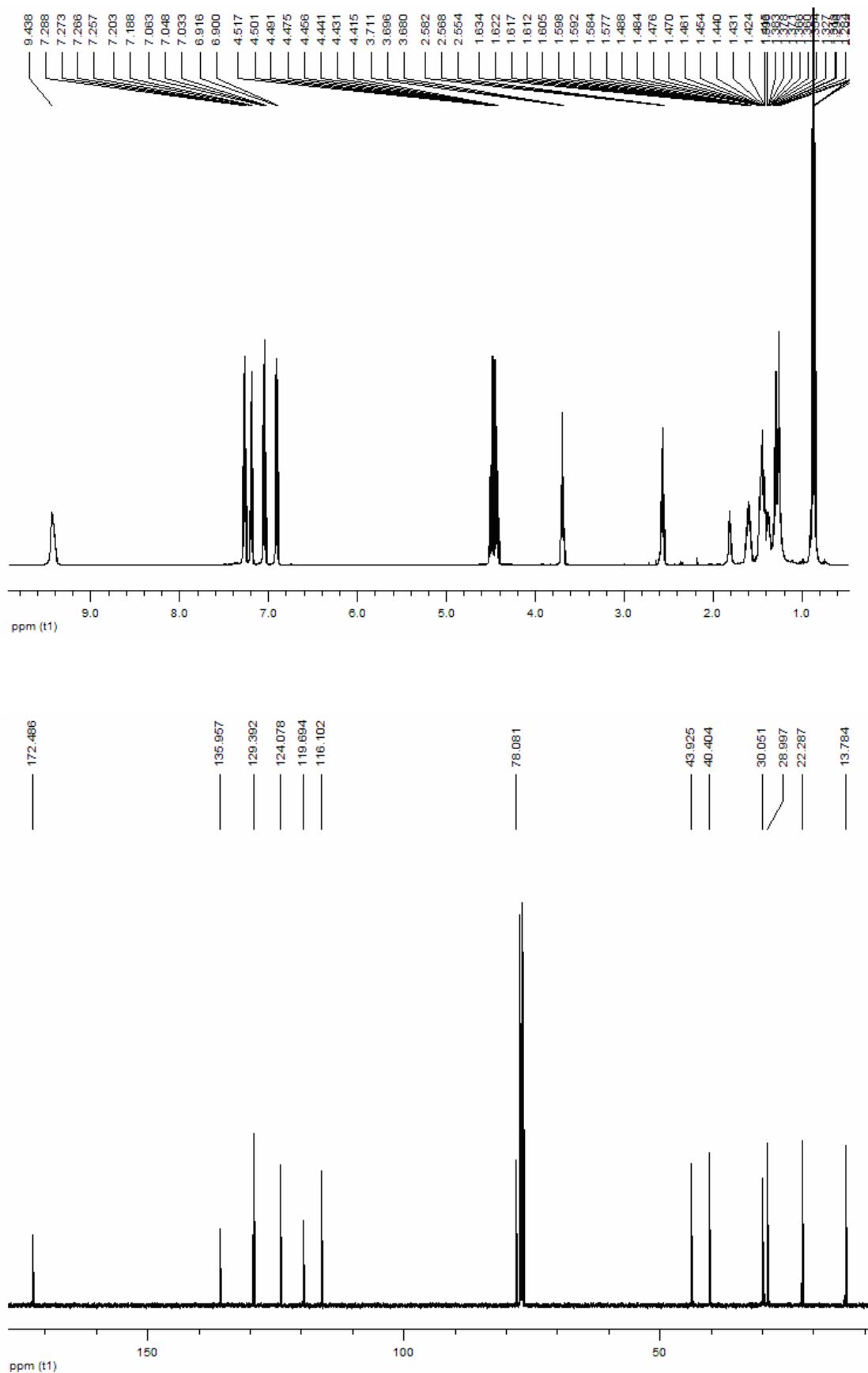
Compound 6b



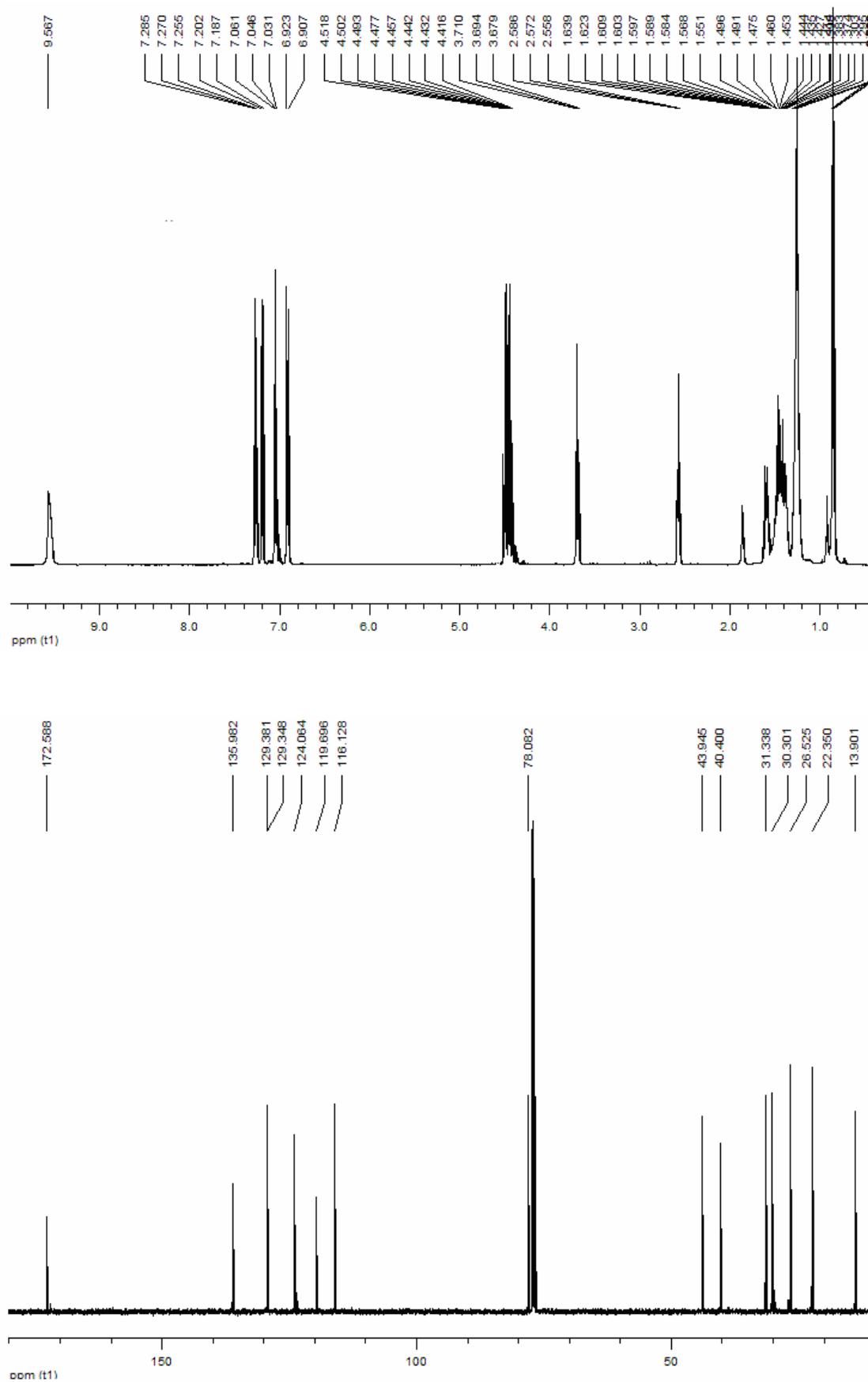
Compound 6c



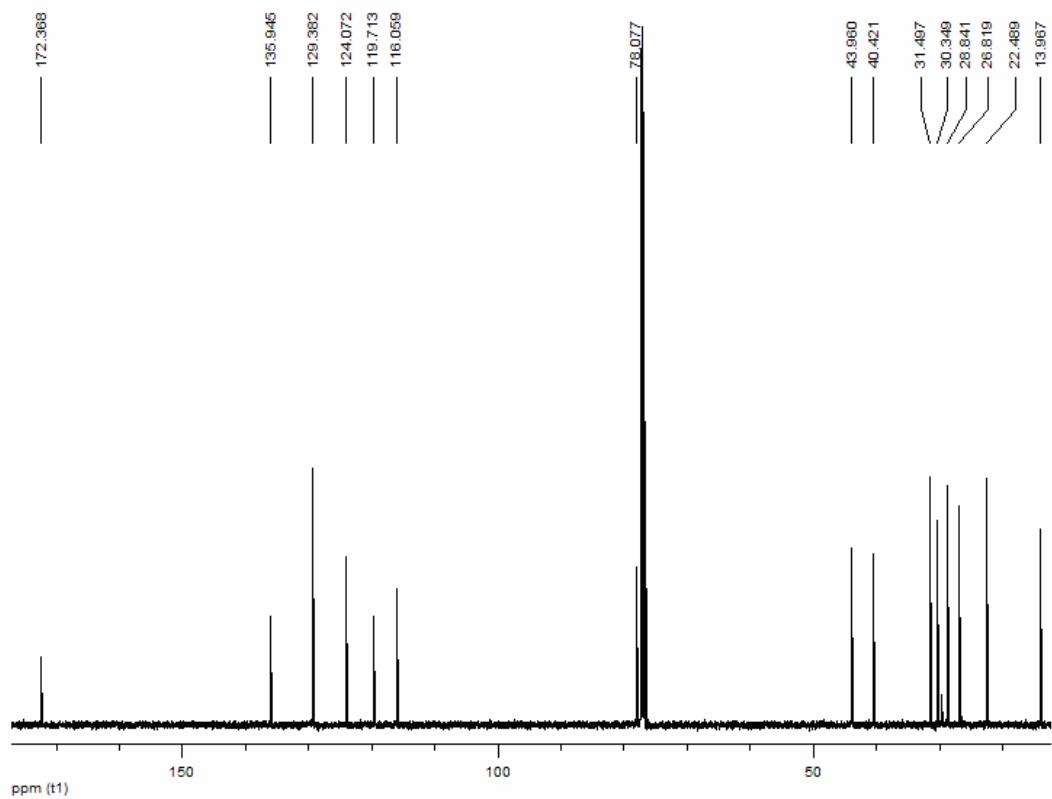
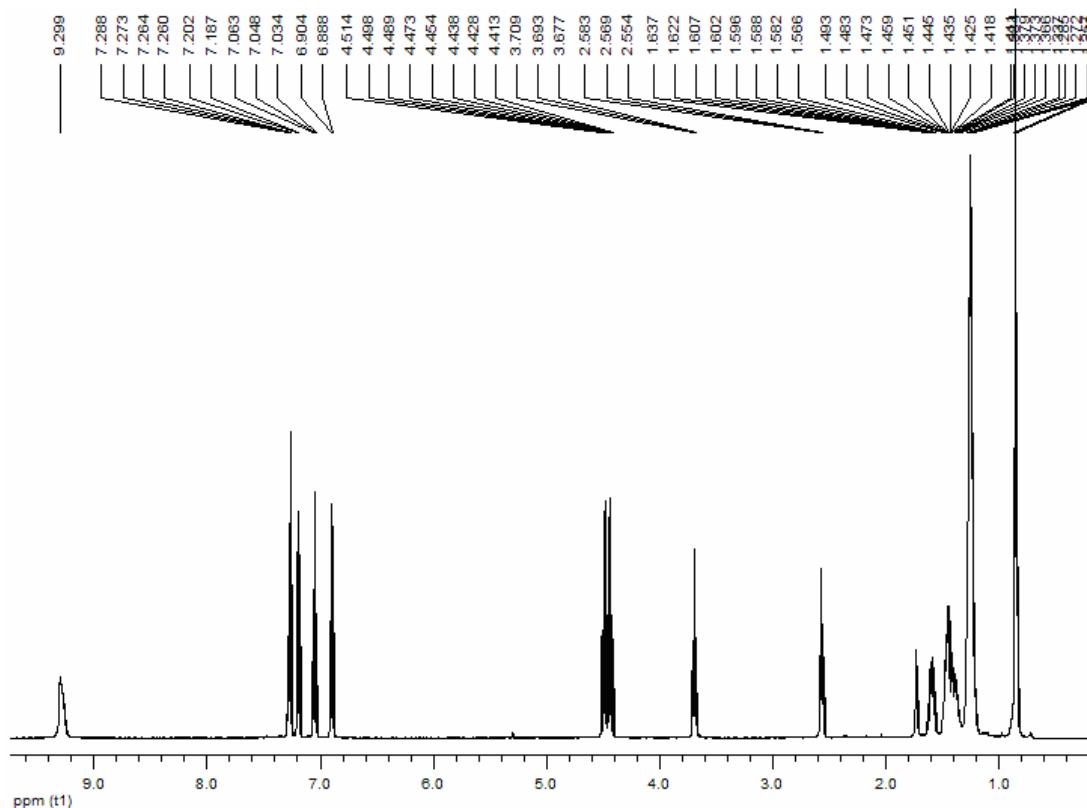
Compound 6d



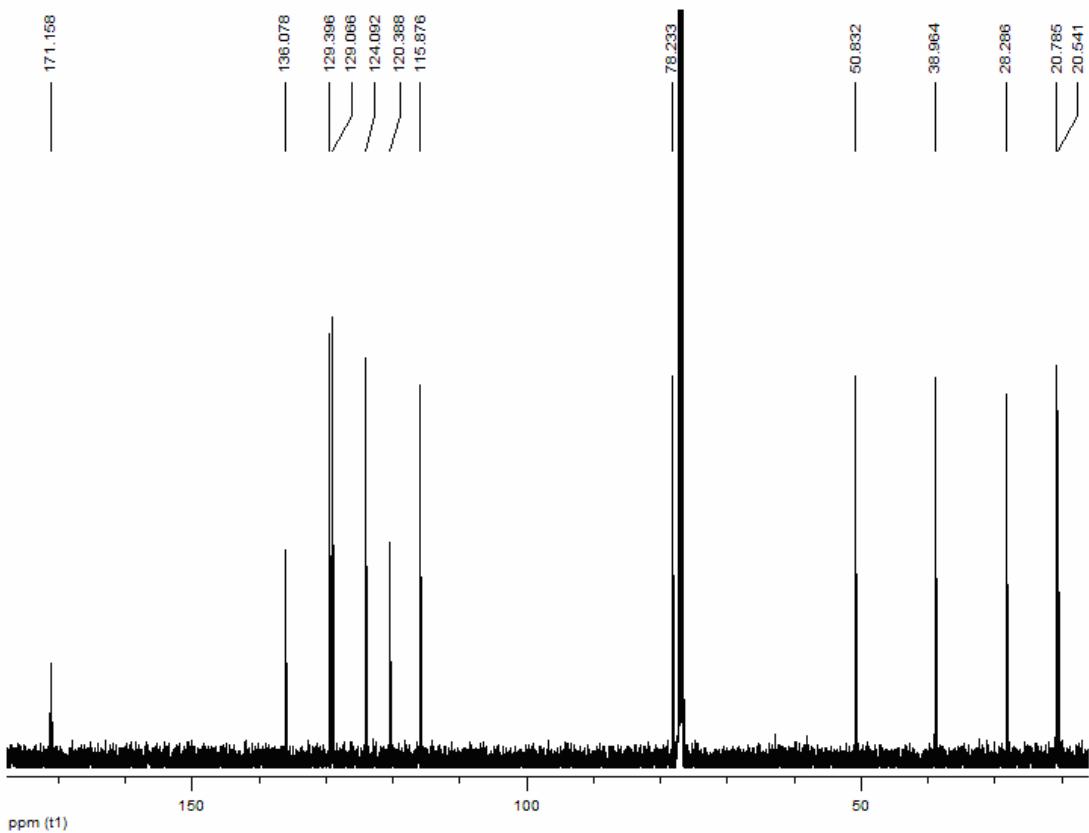
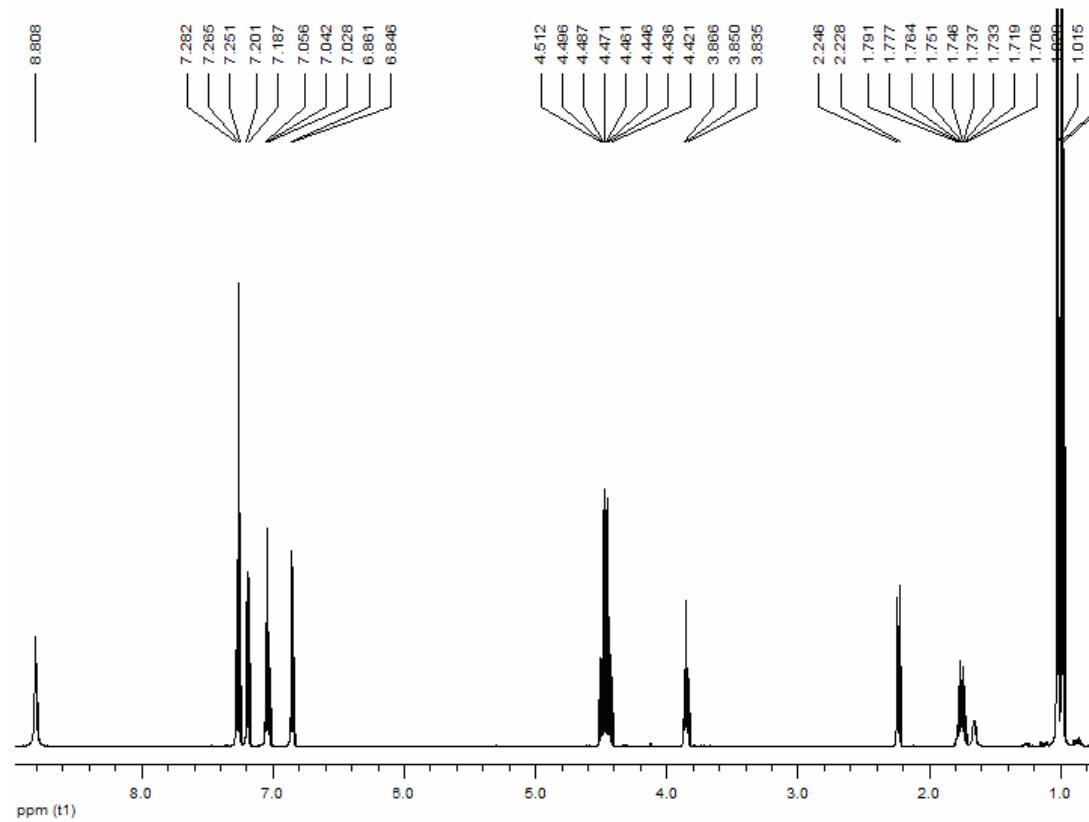
Compound 6e



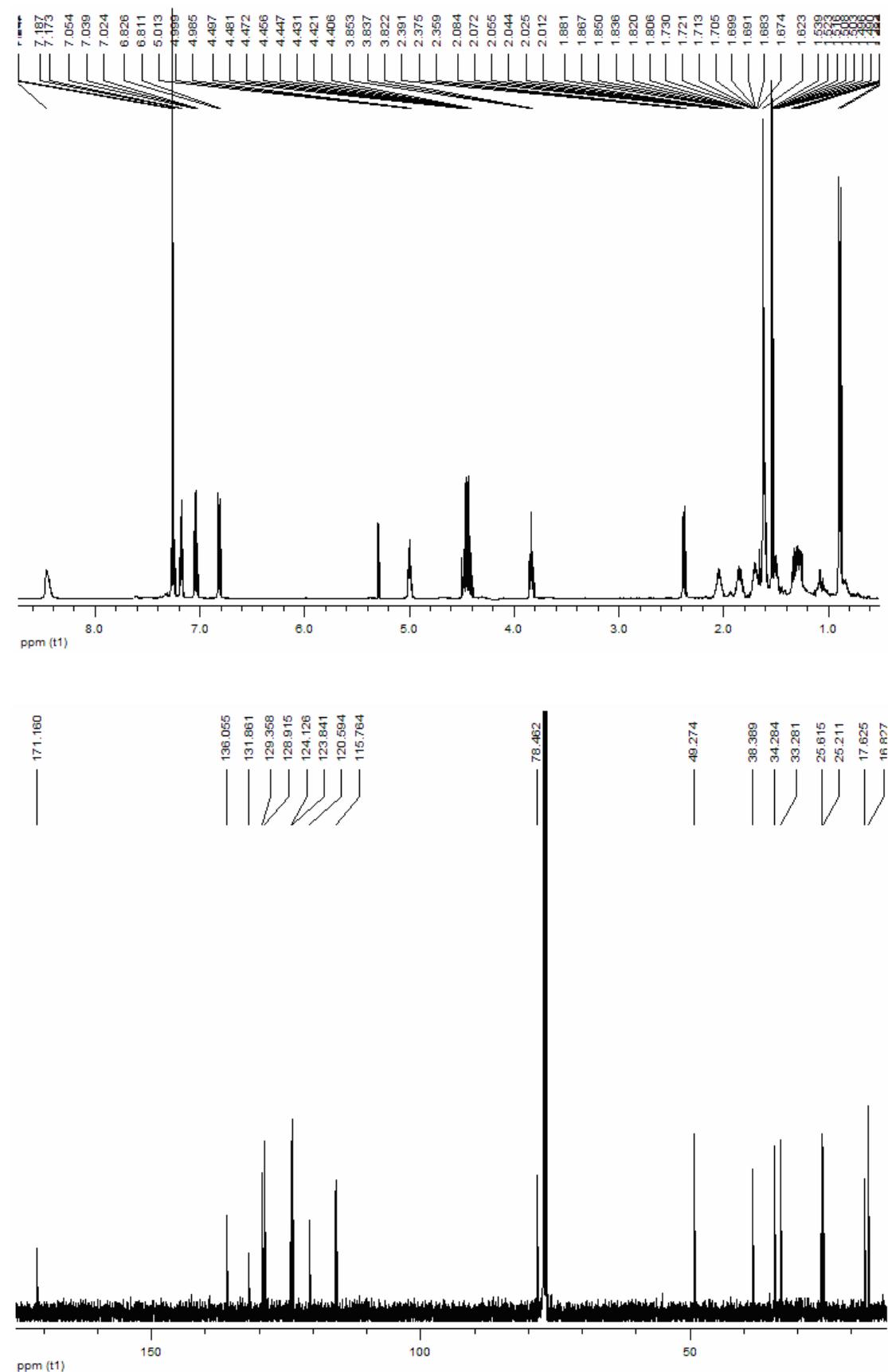
Compound 6f



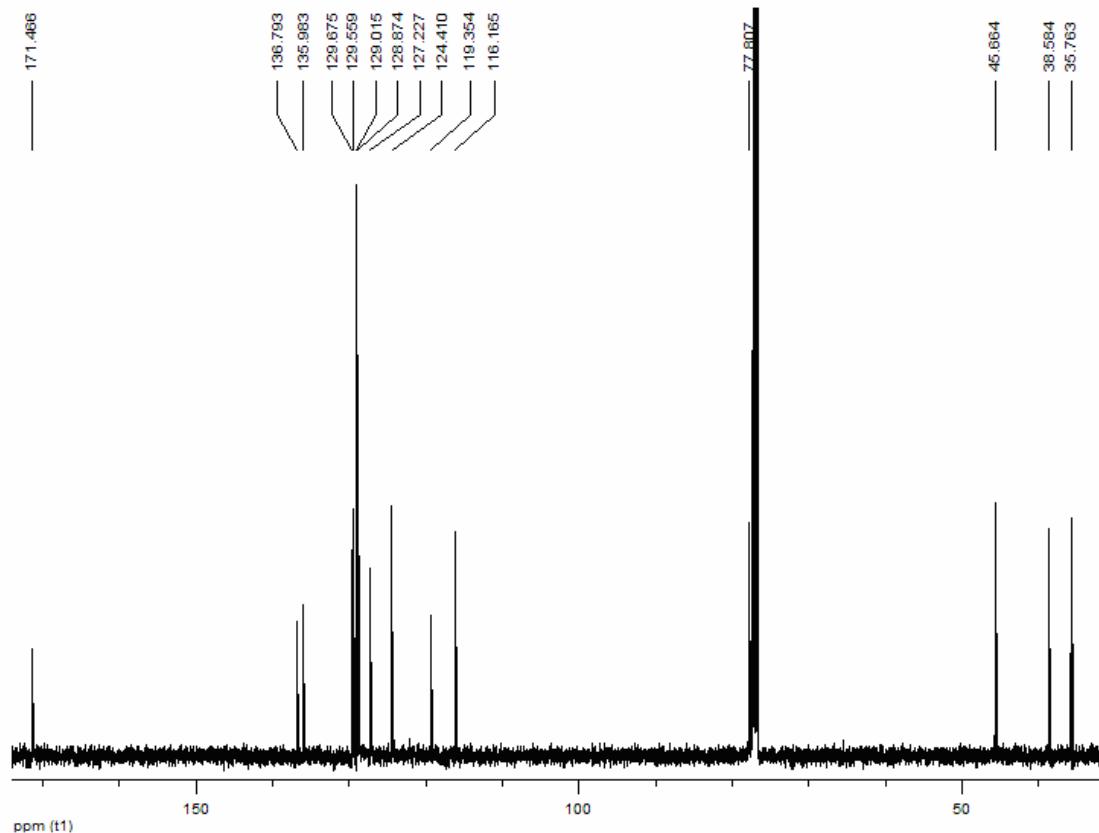
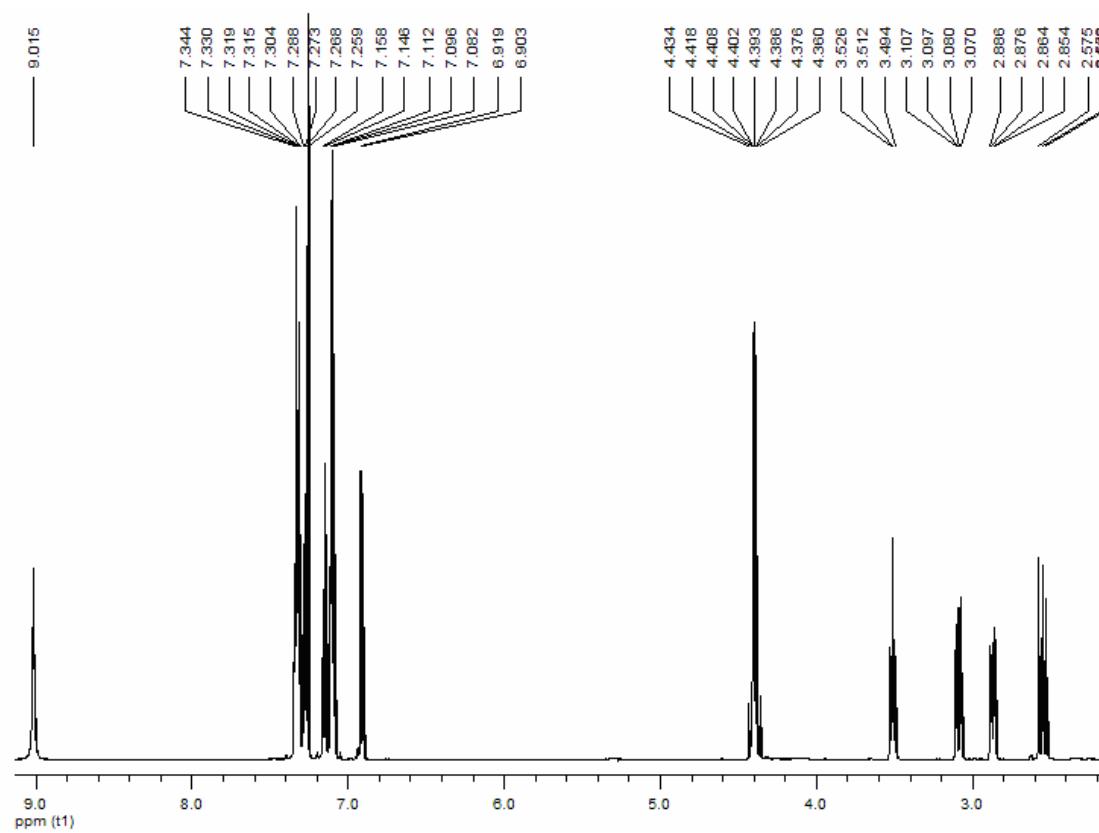
Compound 6g



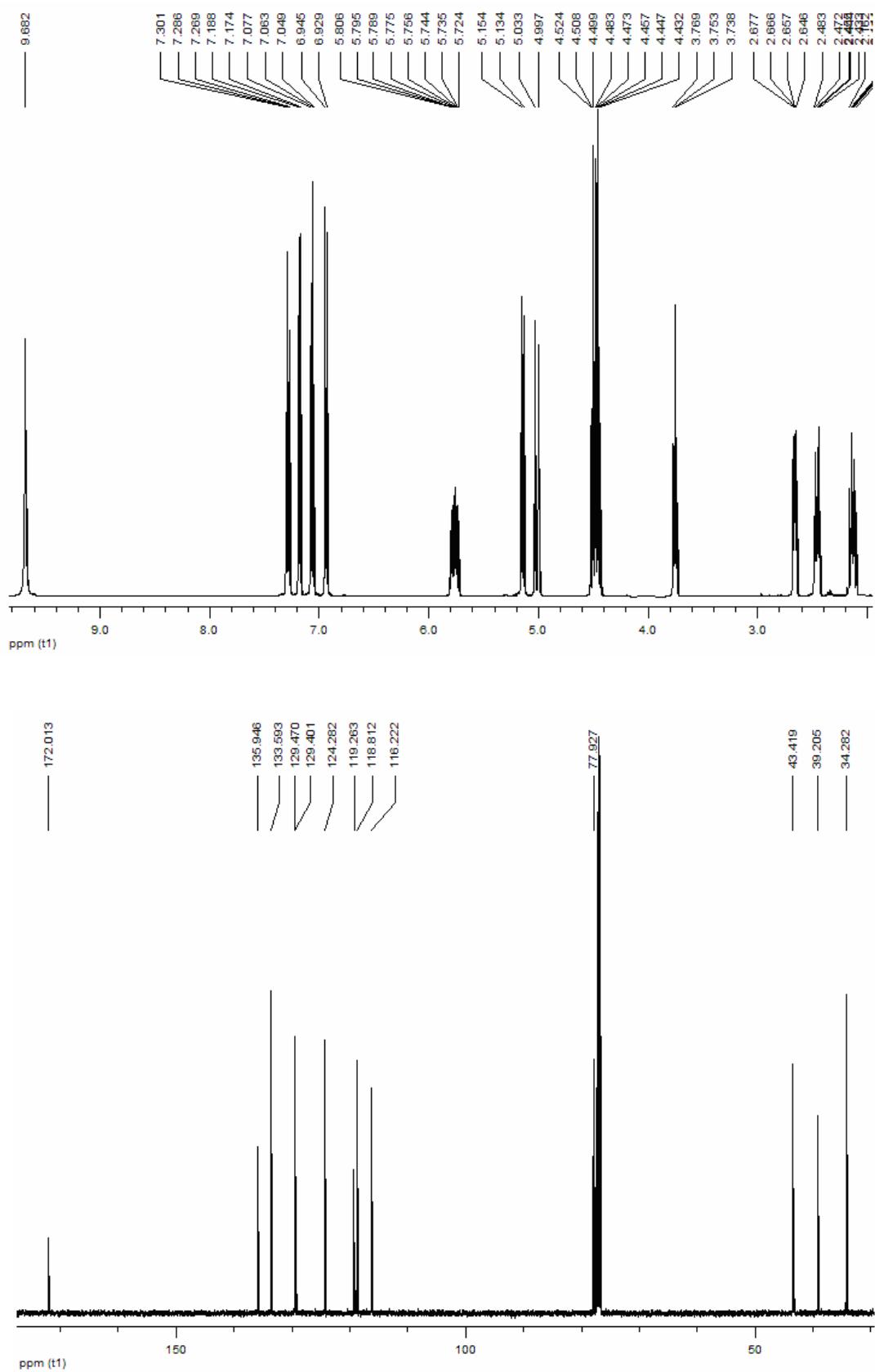
Compound 6h



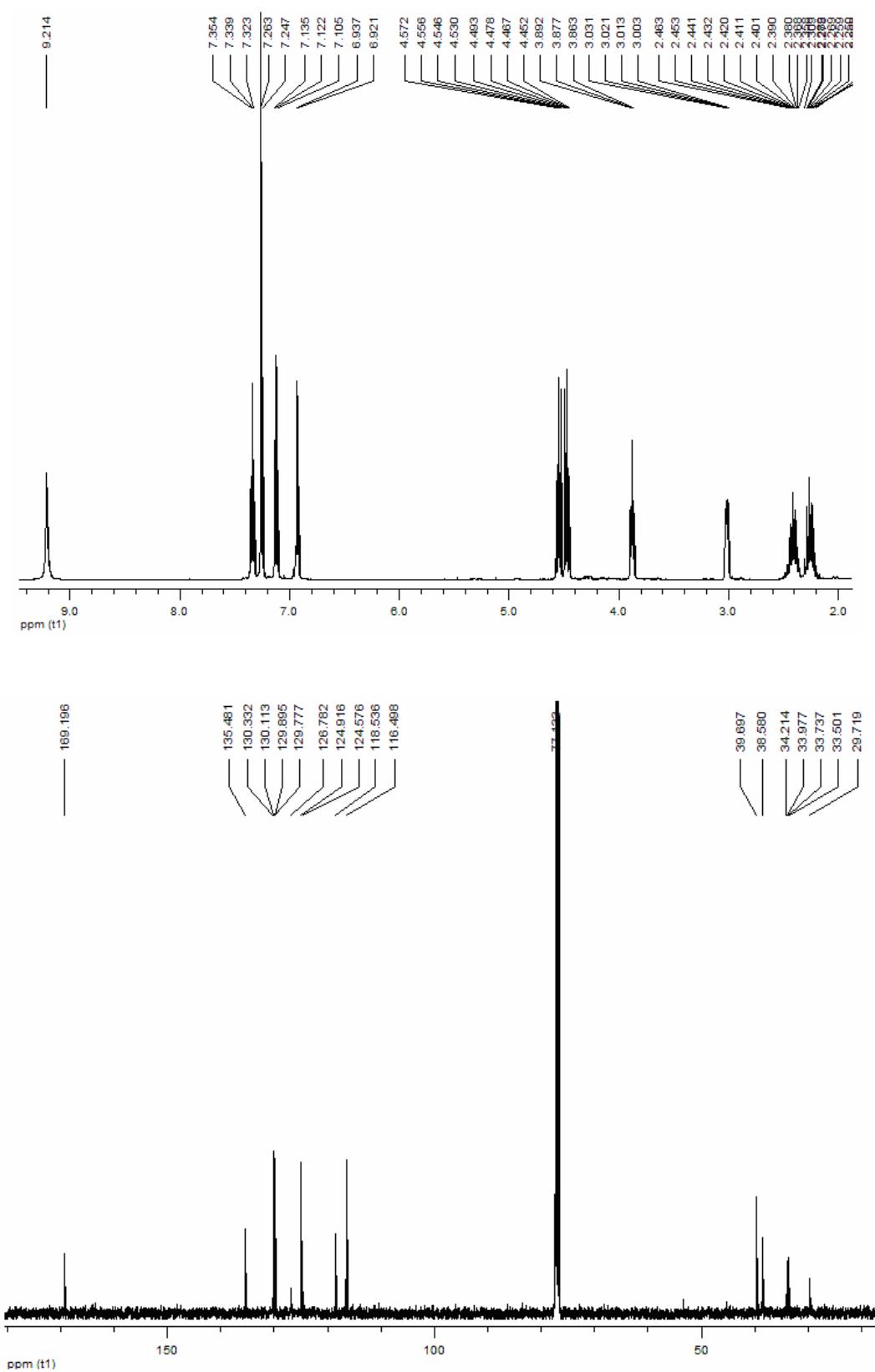
Compound 6i



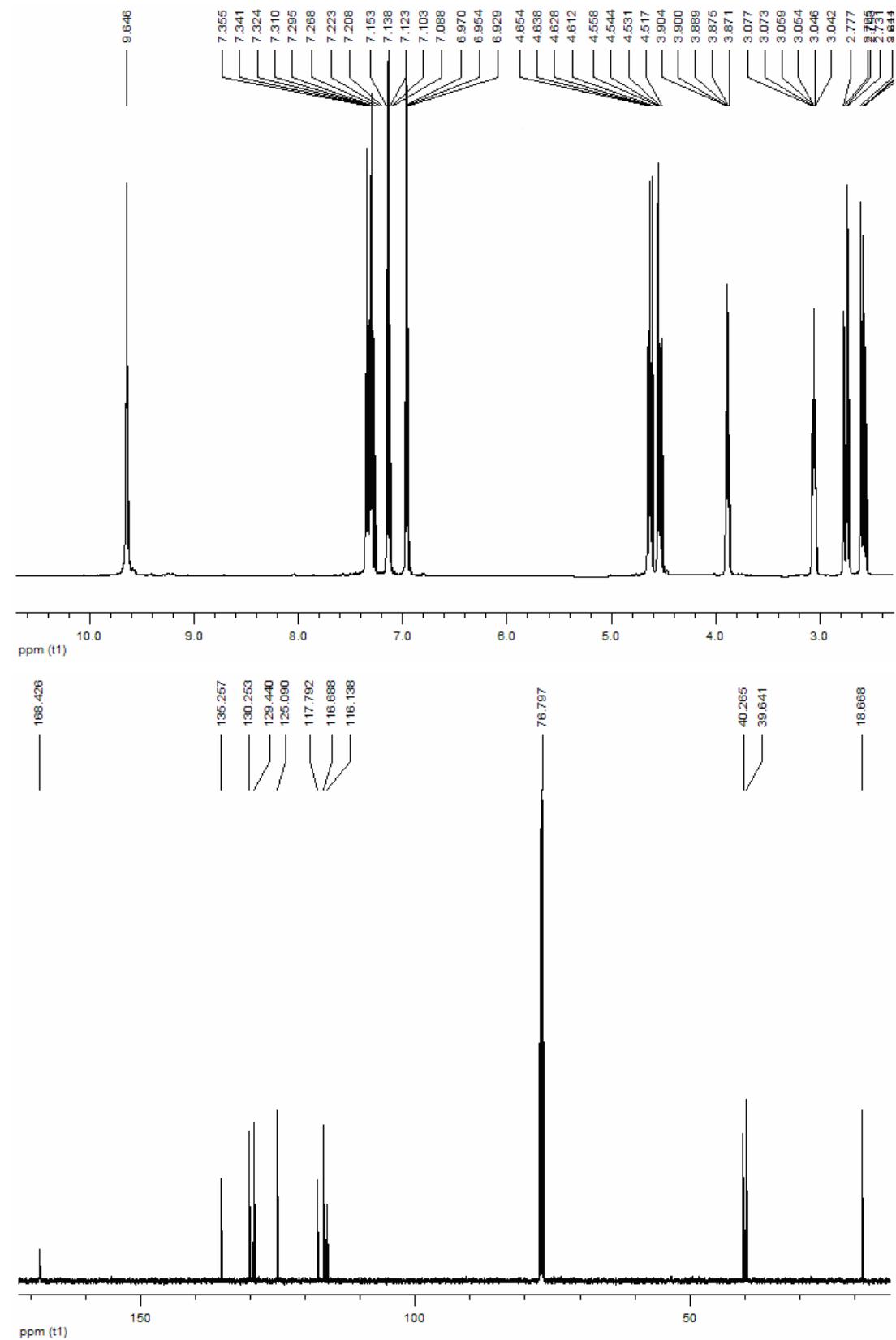
Compound 6j



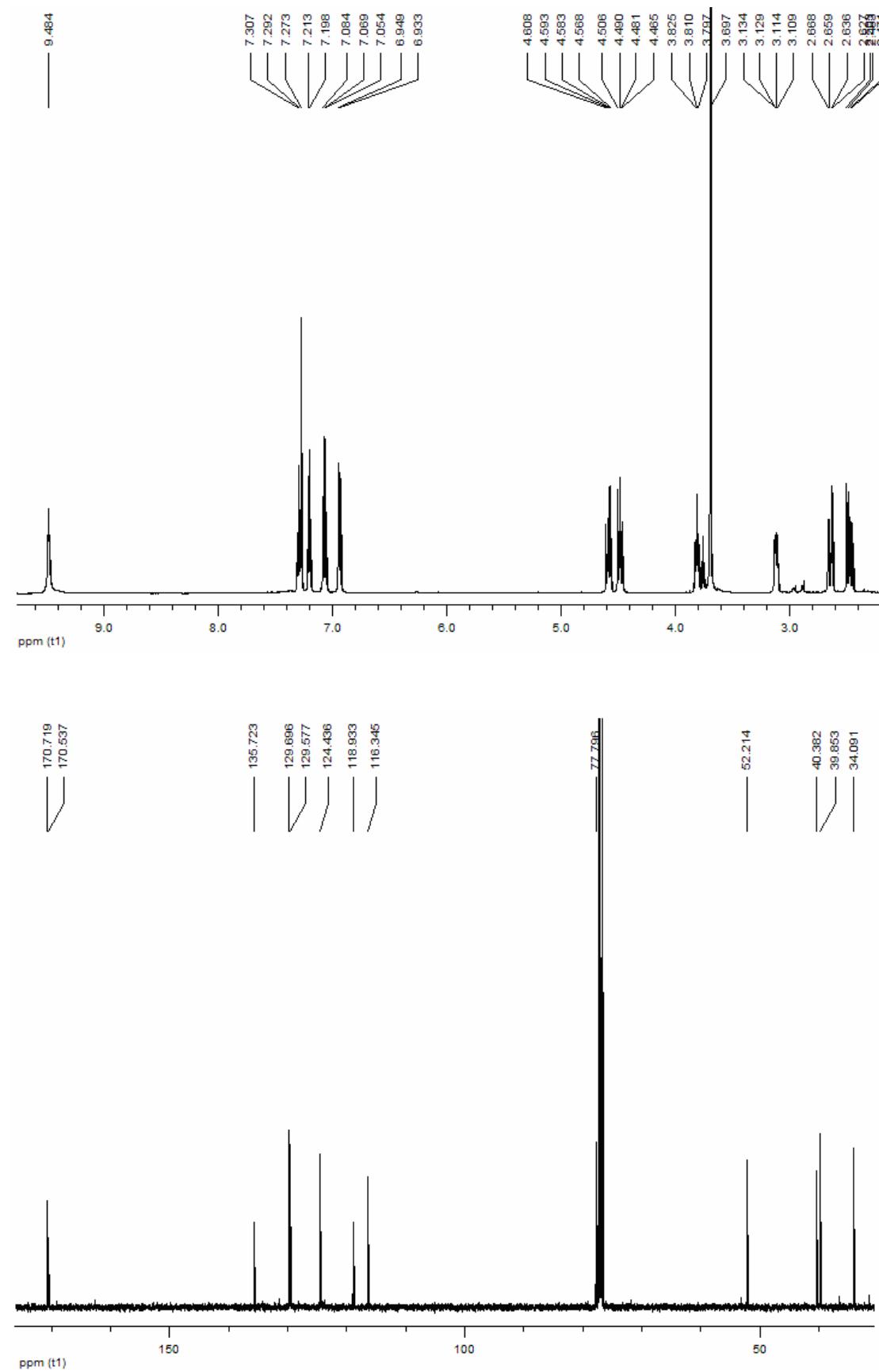
Compound 6k



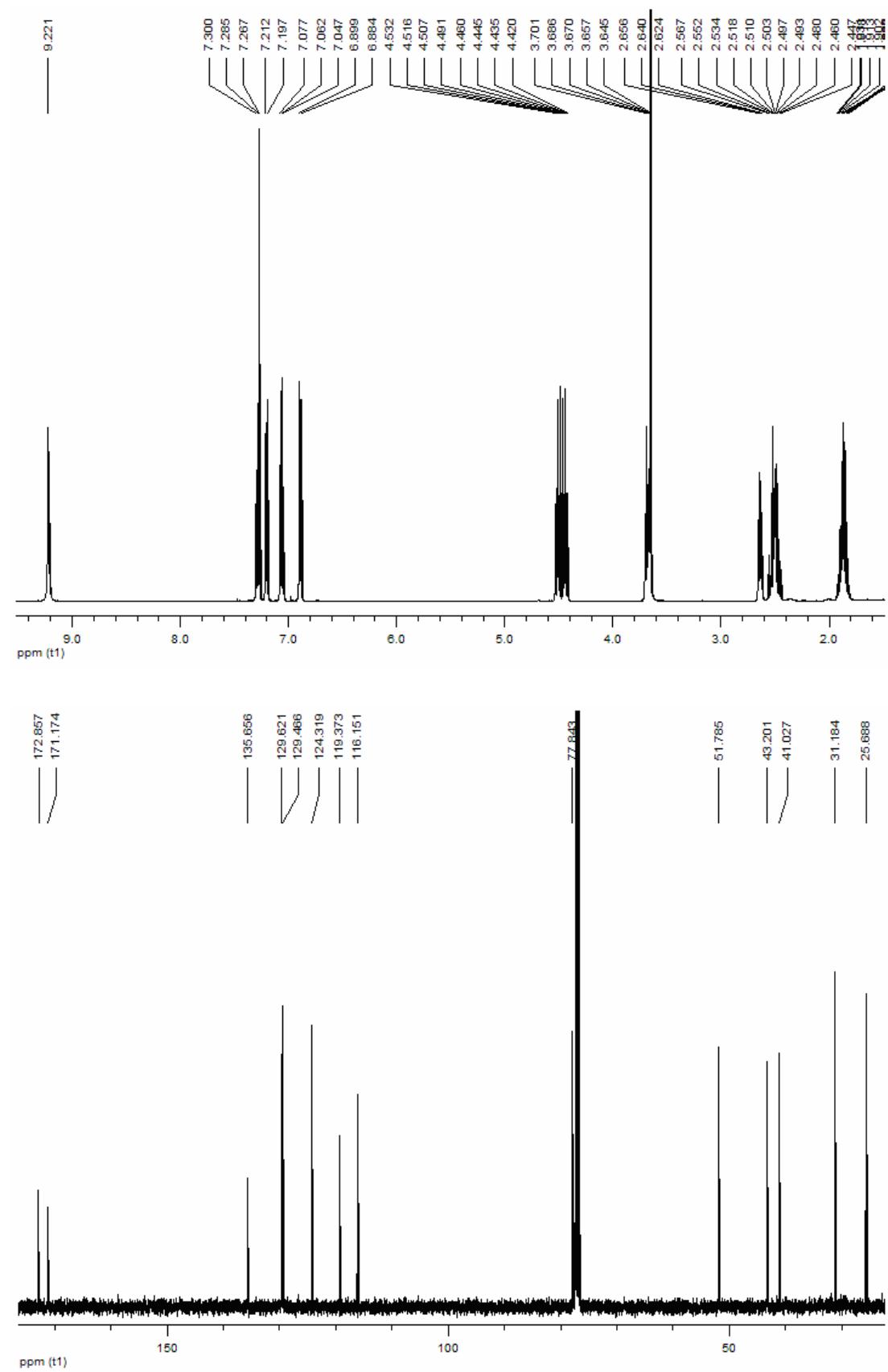
Compound 6l



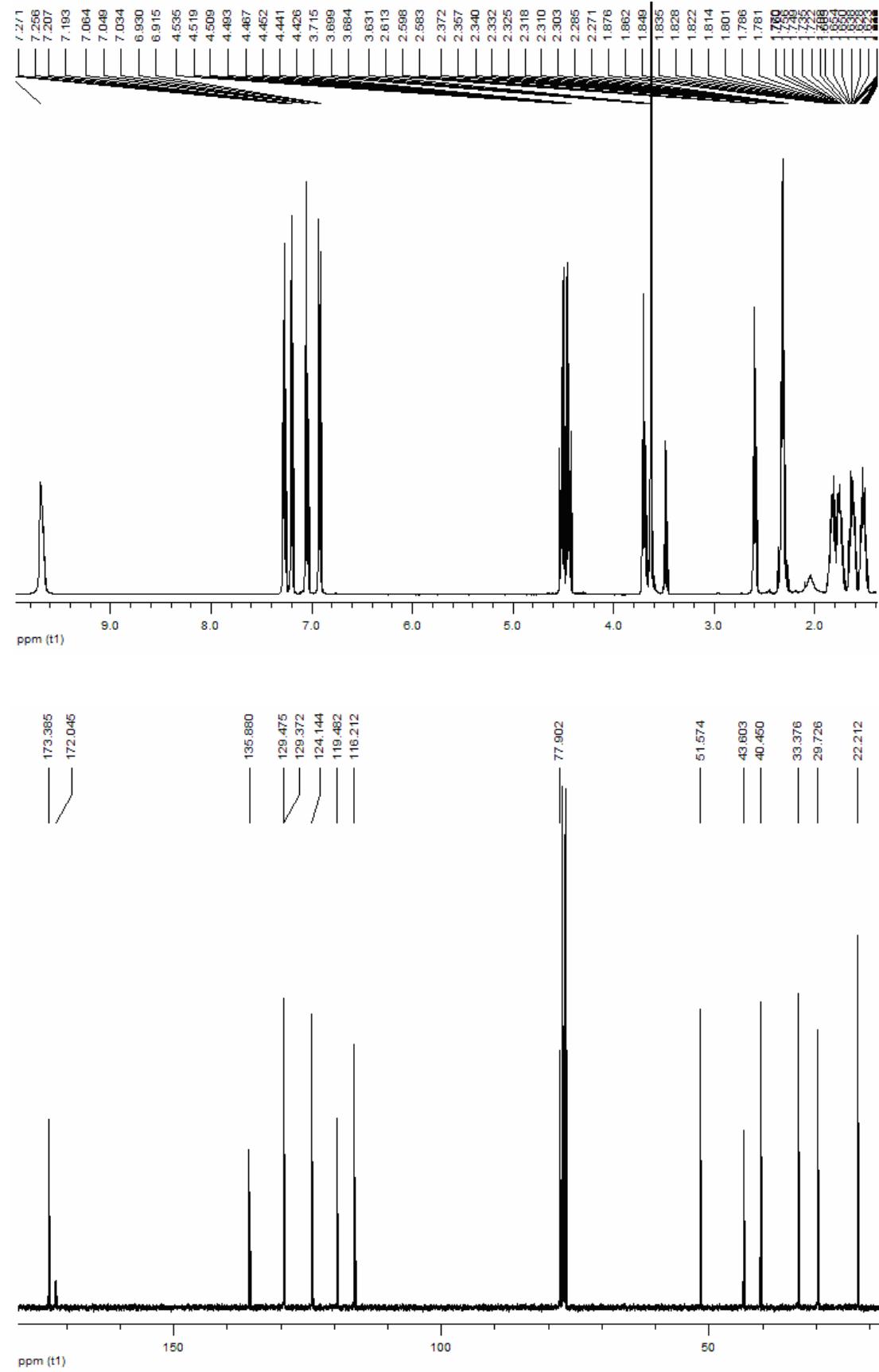
Compound 6m



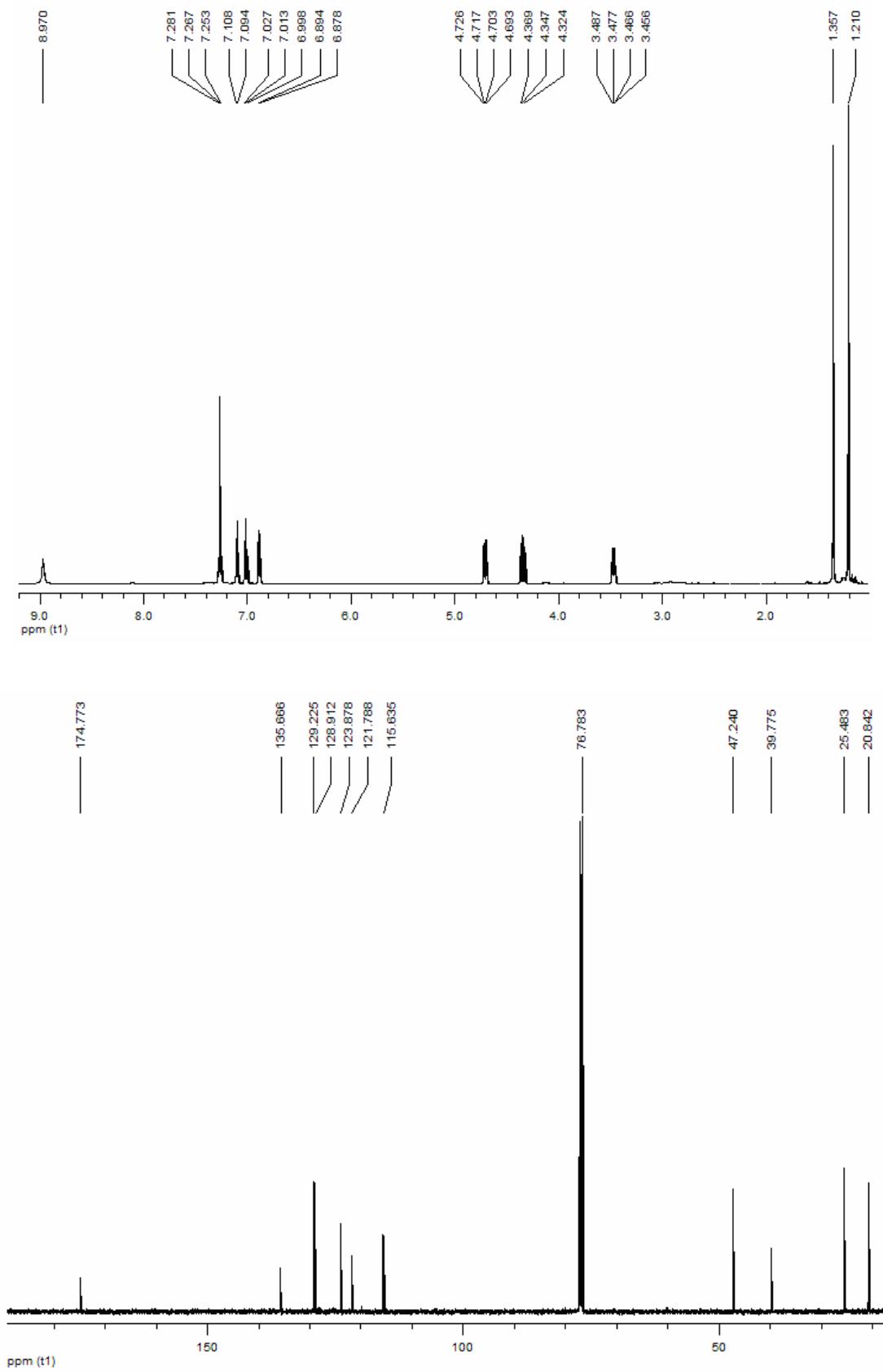
Compound 6n



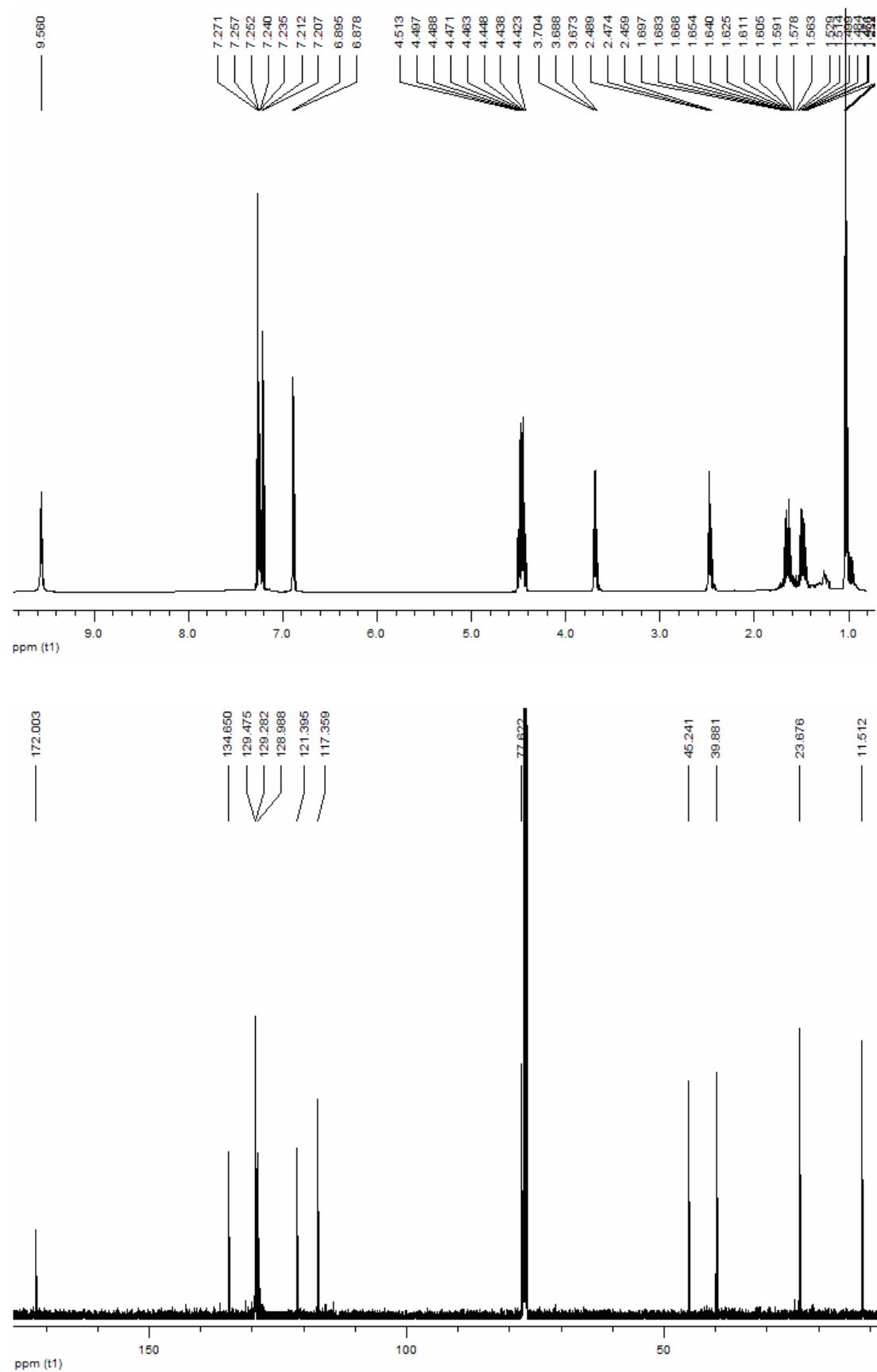
Compound 6o



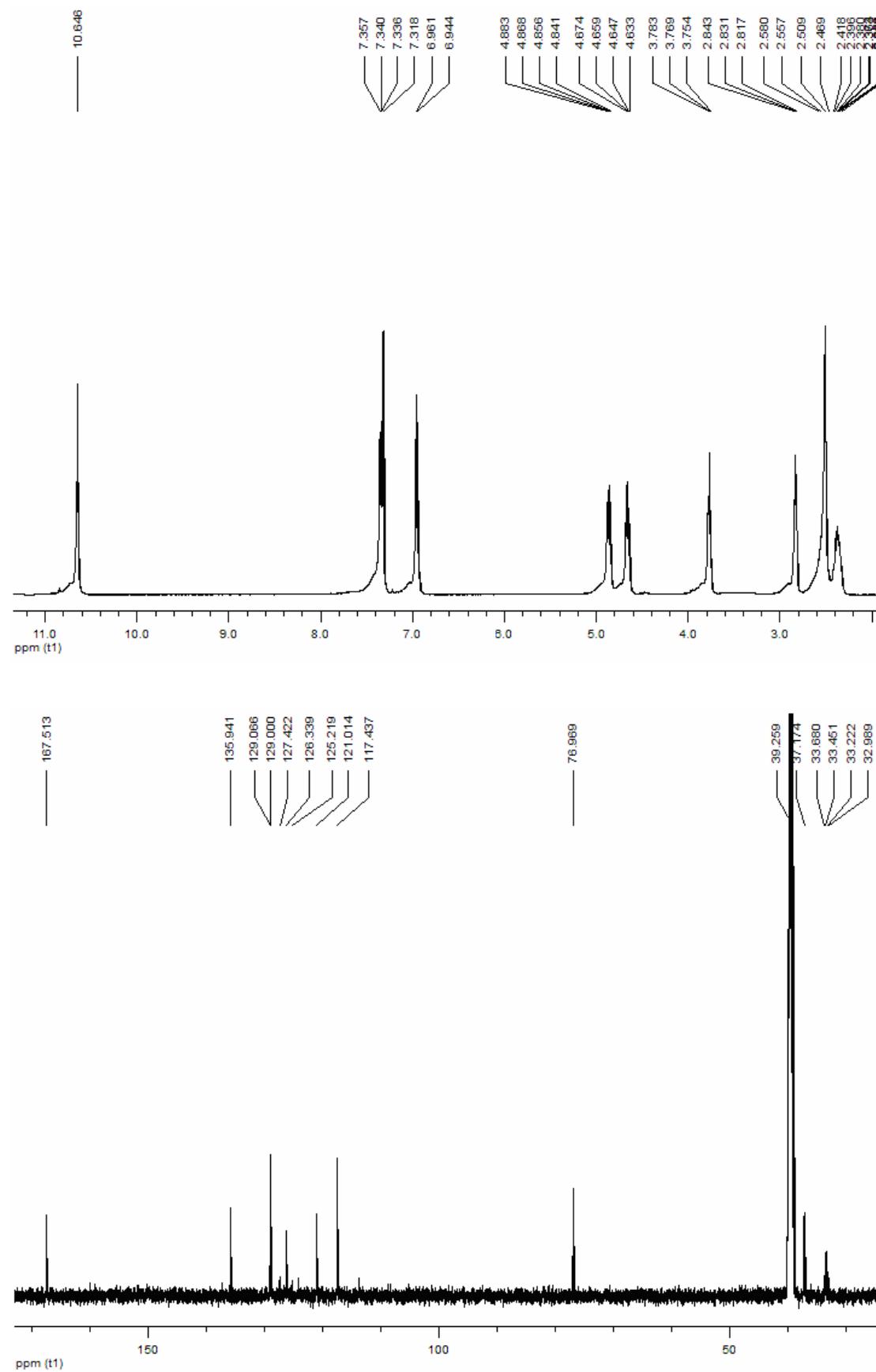
Compound 6p



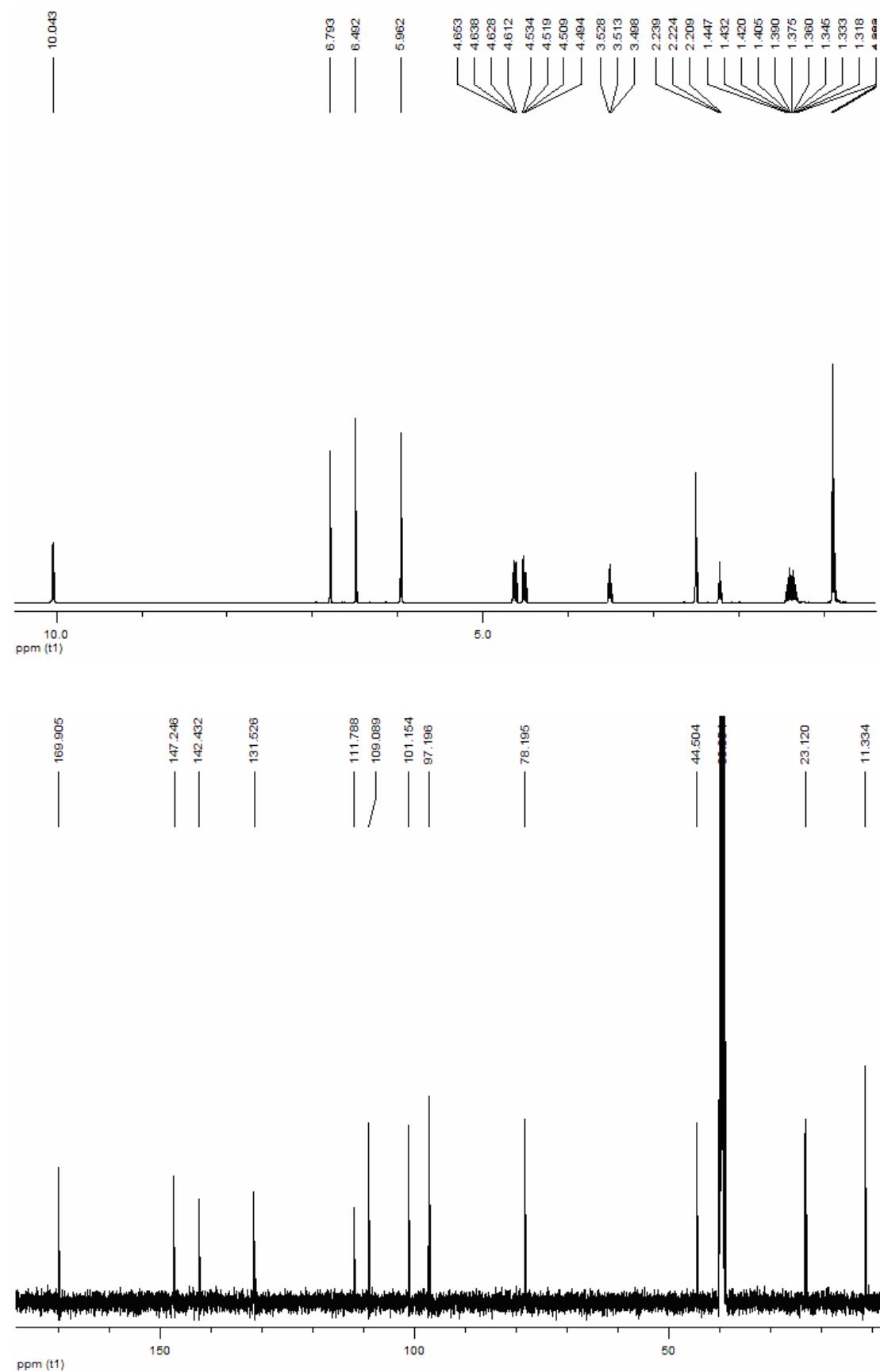
Compound 6q



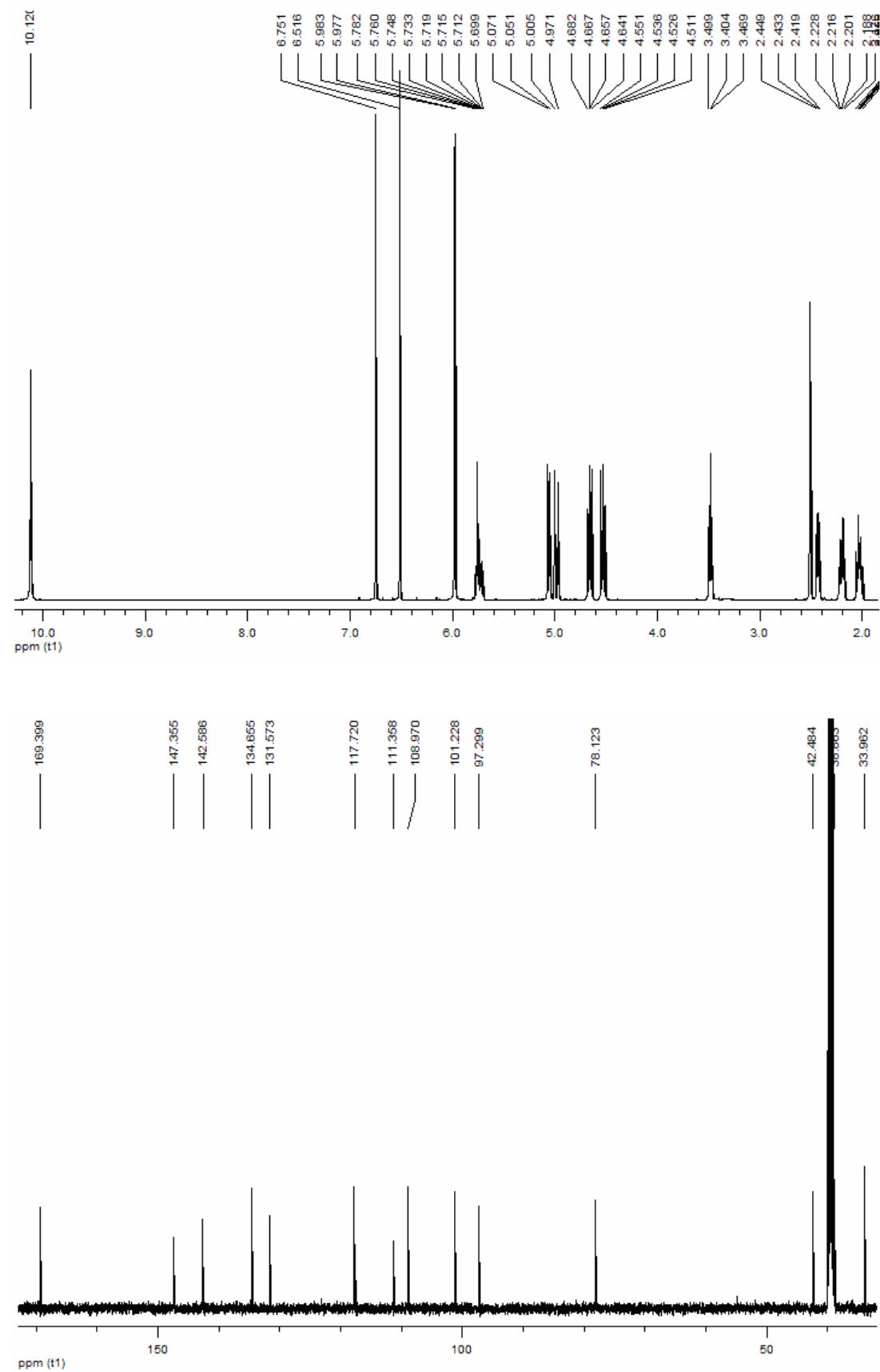
Compound 6r



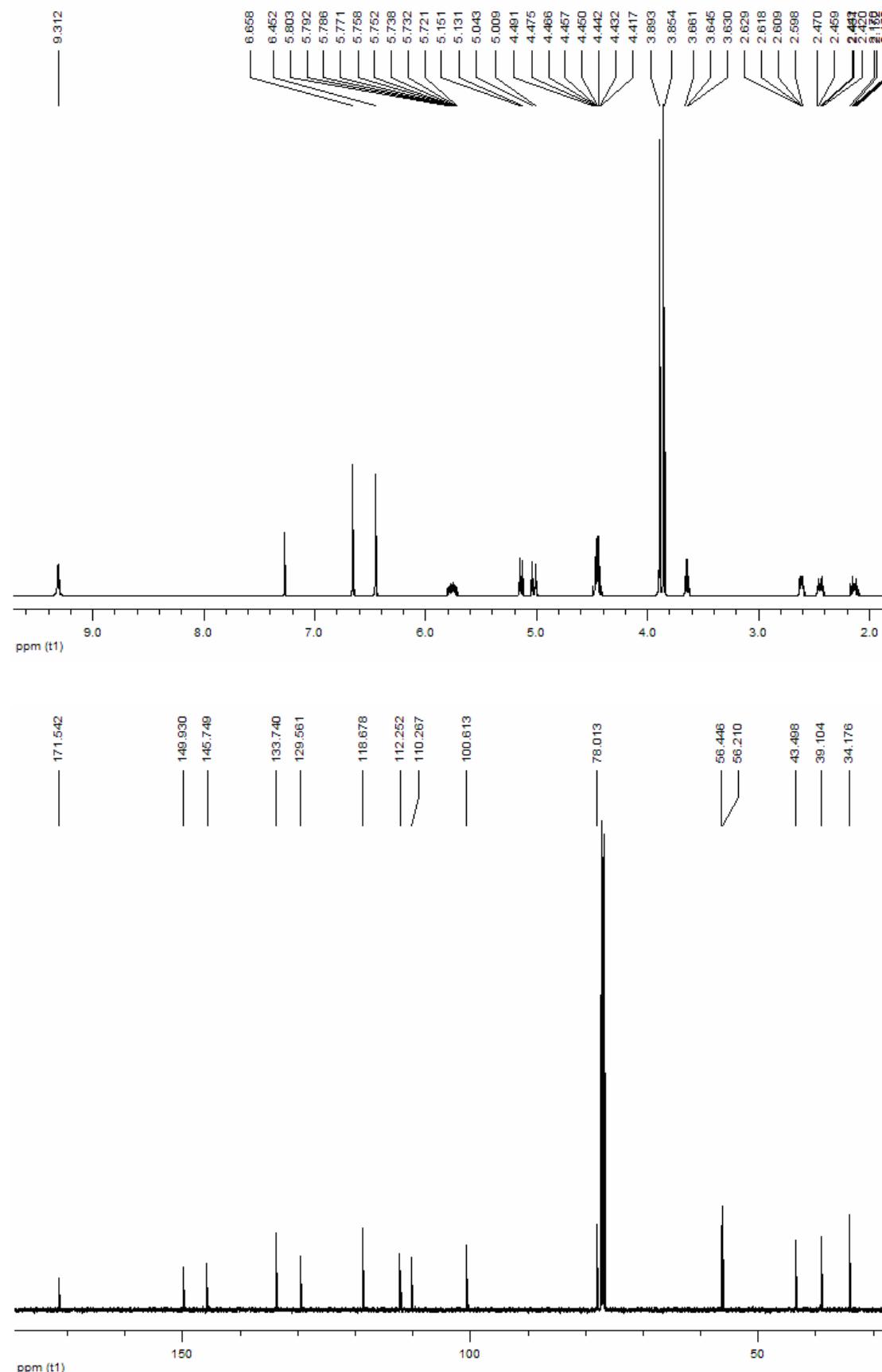
Compound 6s



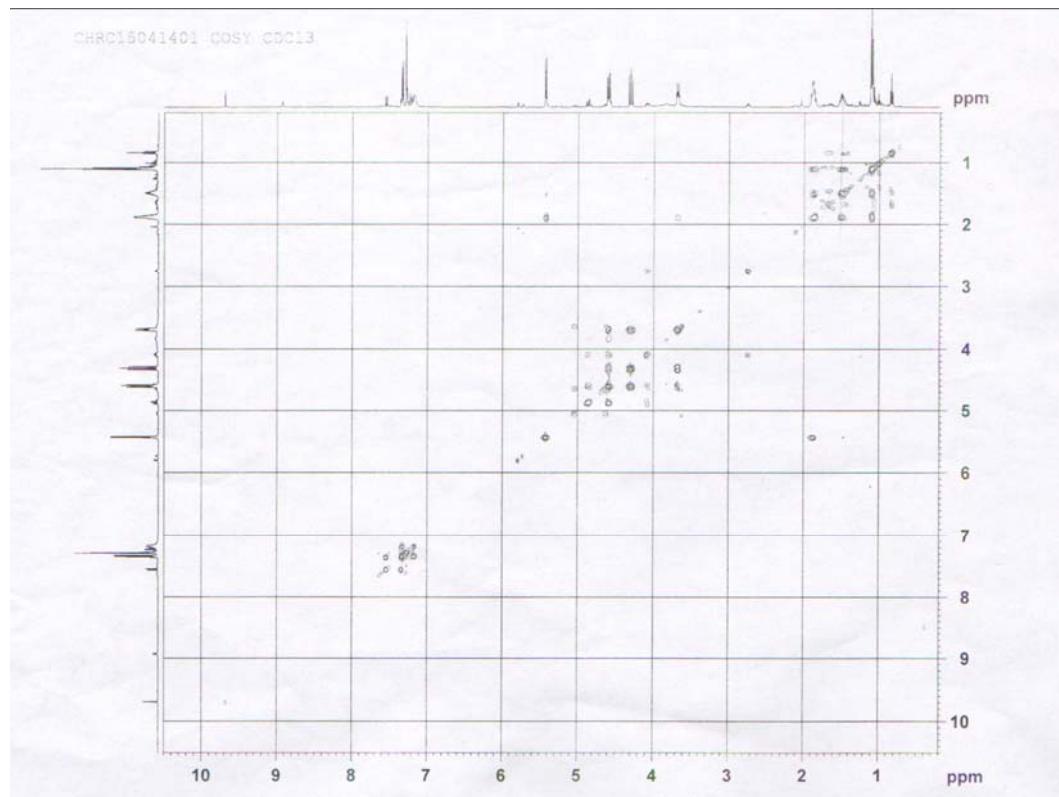
Compound 6t



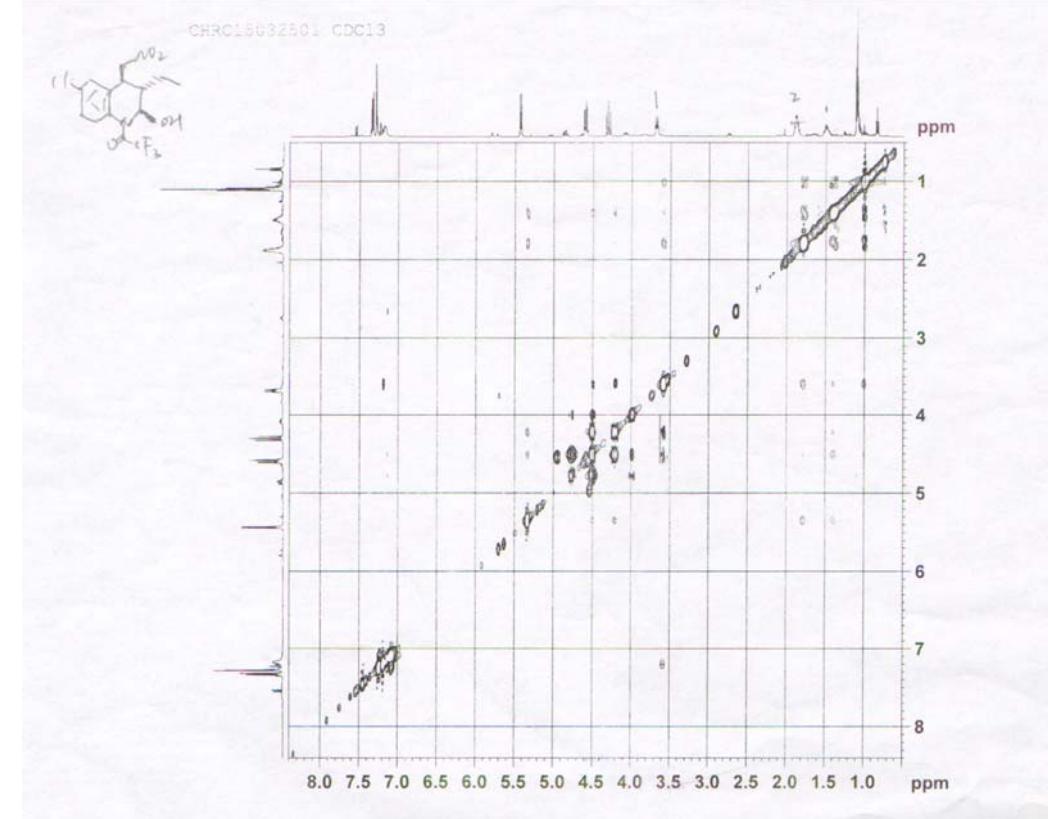
Compound 6u



H-H COSY spectra of 5q



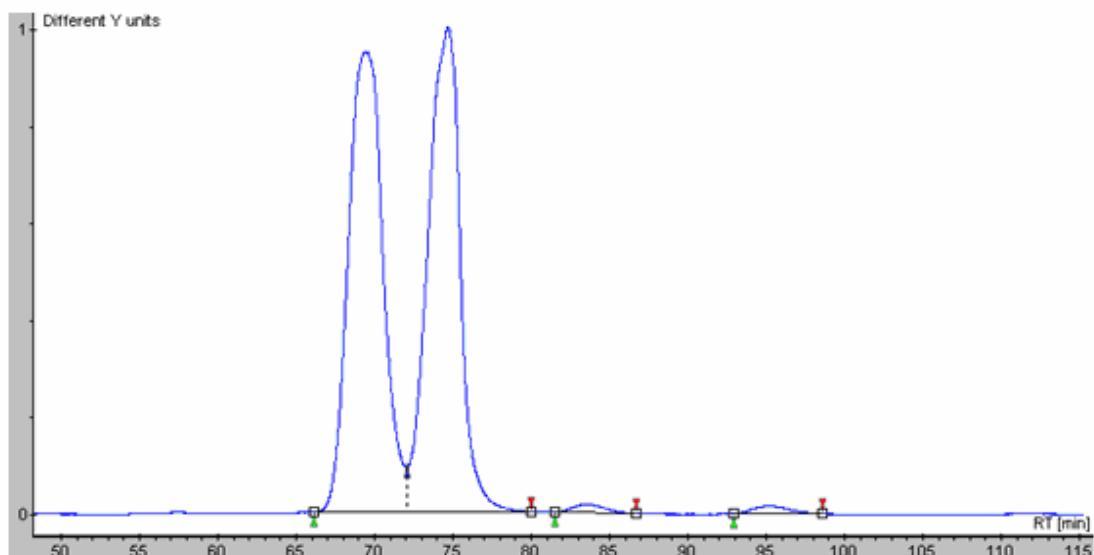
H-H NOESY spectra of 5q



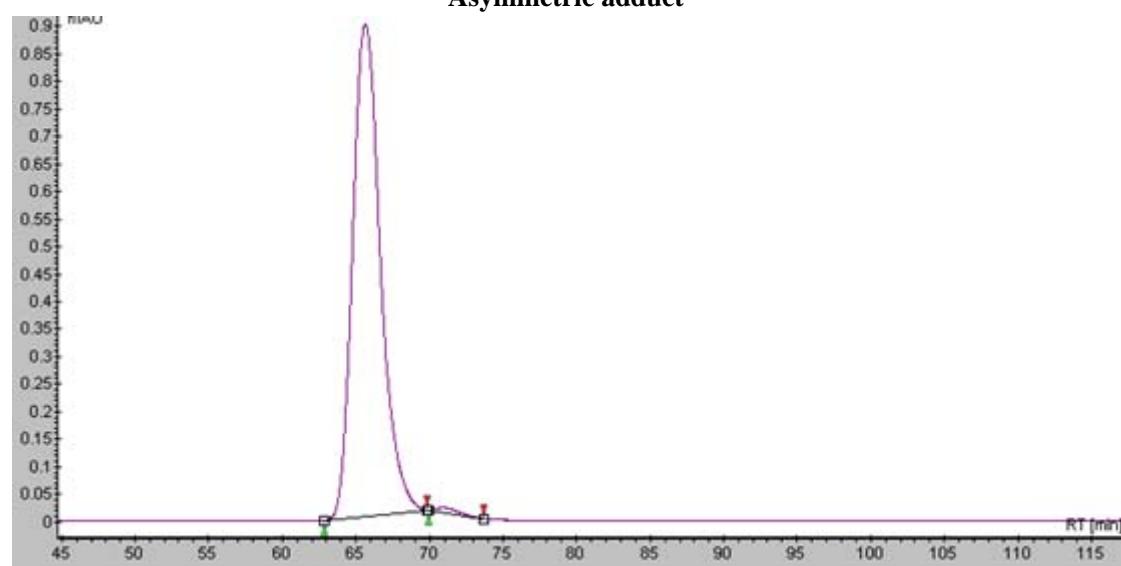
5. HPLC spectra of Michael adducts

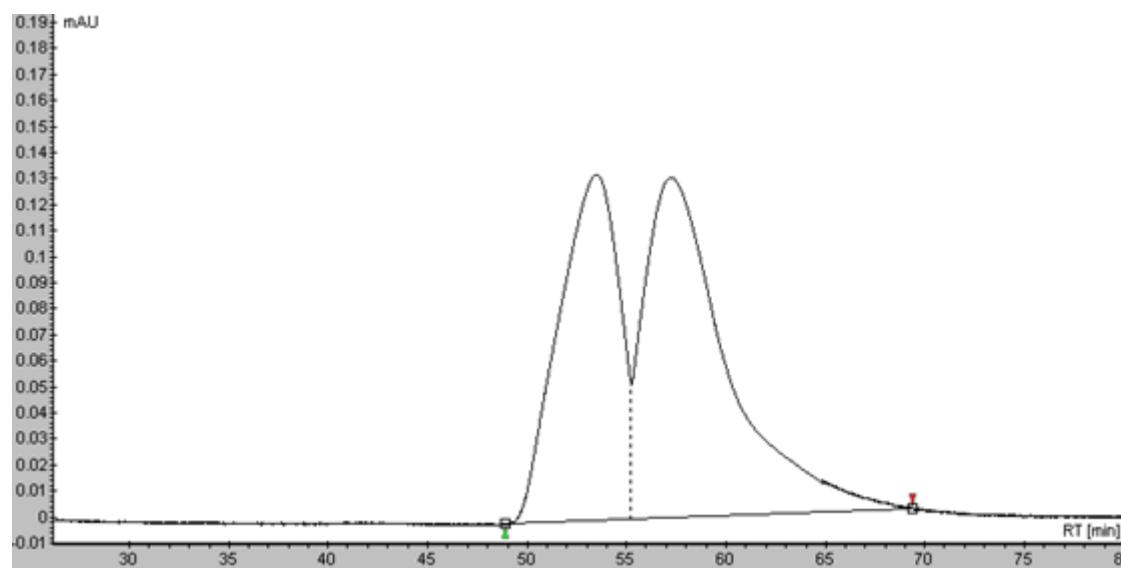
Compound 6a

Racemic adduct

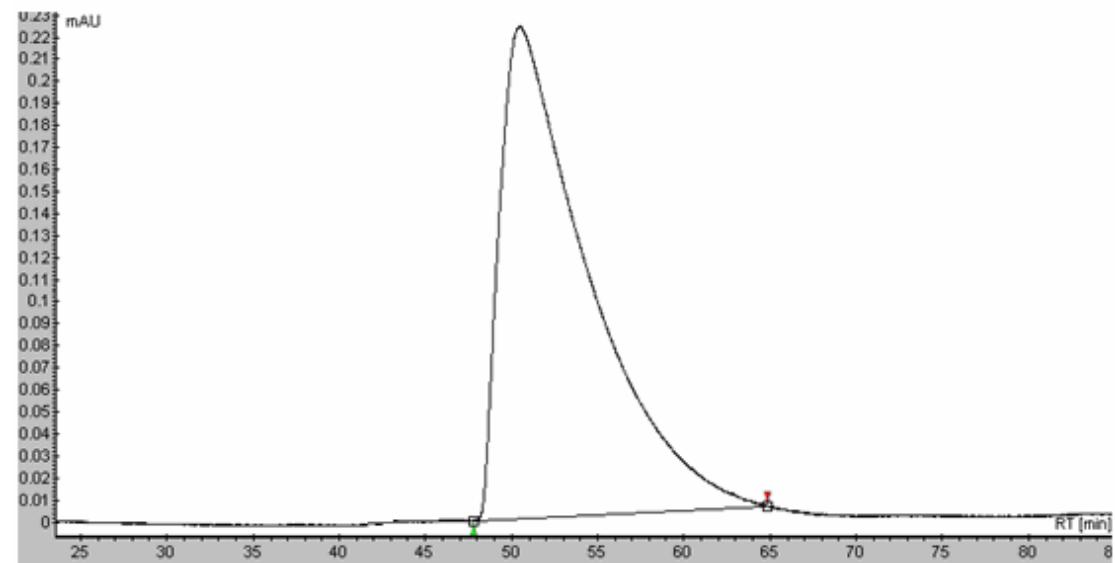


Asymmetric adduct

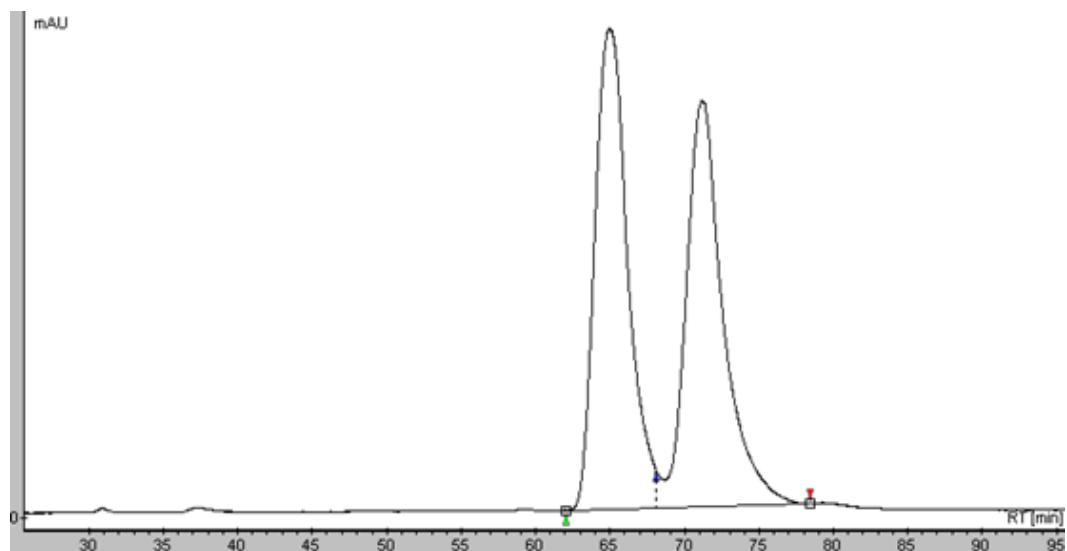


Compound 6b**Racemic adduct**

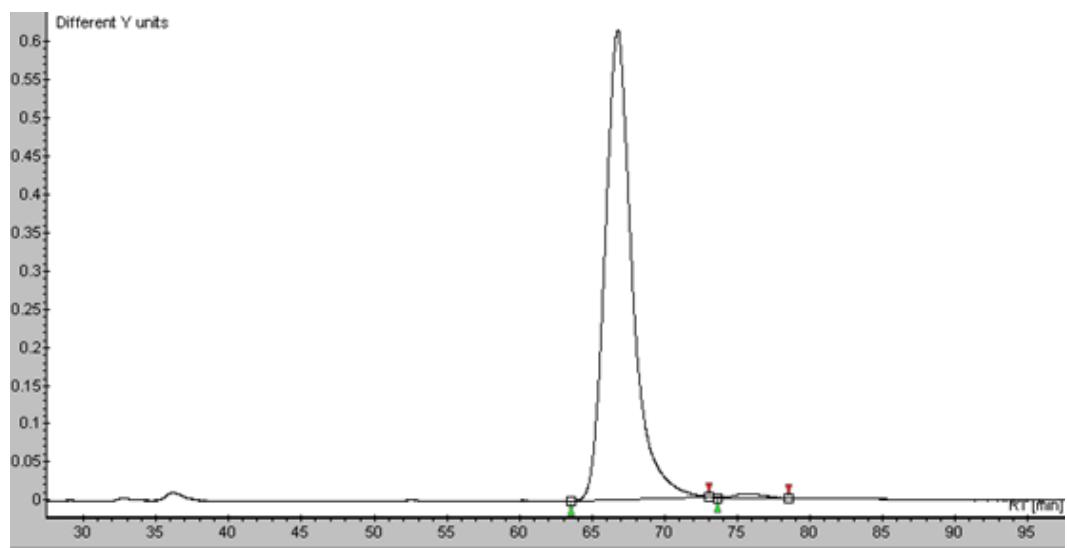
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	48.905	52.697	55.222	48.025
2		55.222	57.940	51.975

Asymmetric adduct

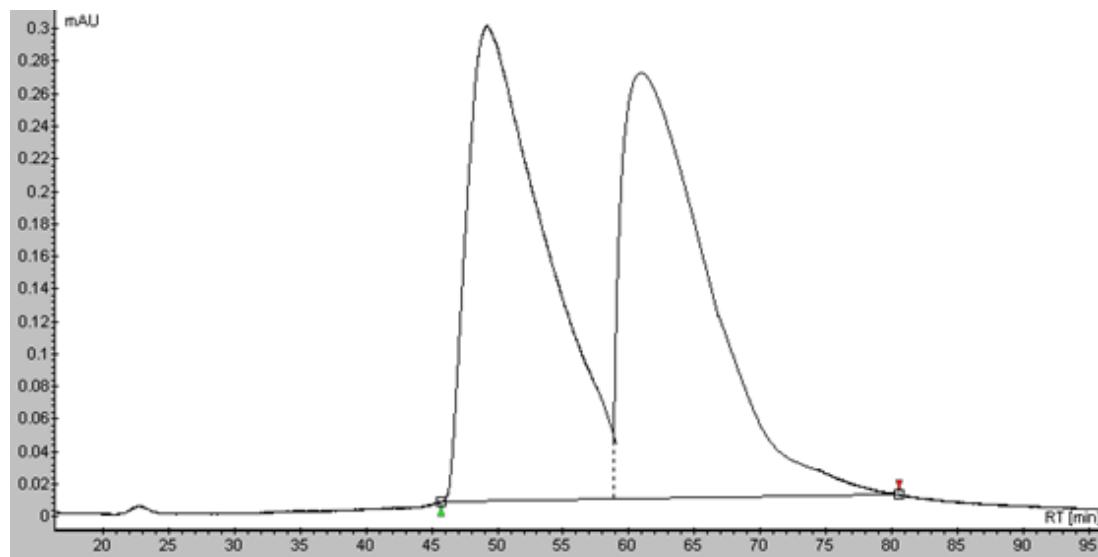
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	47.770	50.489	64.881	100.000

Compound 6c**Racemic adduct**

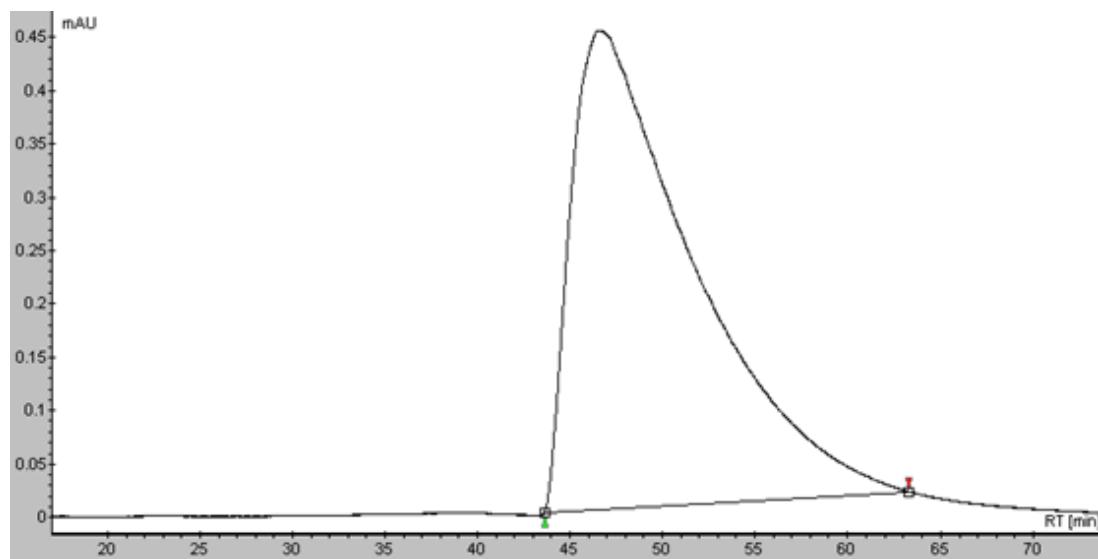
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	62.037	64.950	68.105	50.975
2	68.105	71.214	78.419	49.025

Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	63.588	66.776	73.049	98.981
2	73.646	75.746	78.504	1.019

Compound 6d**Racemic adduct**

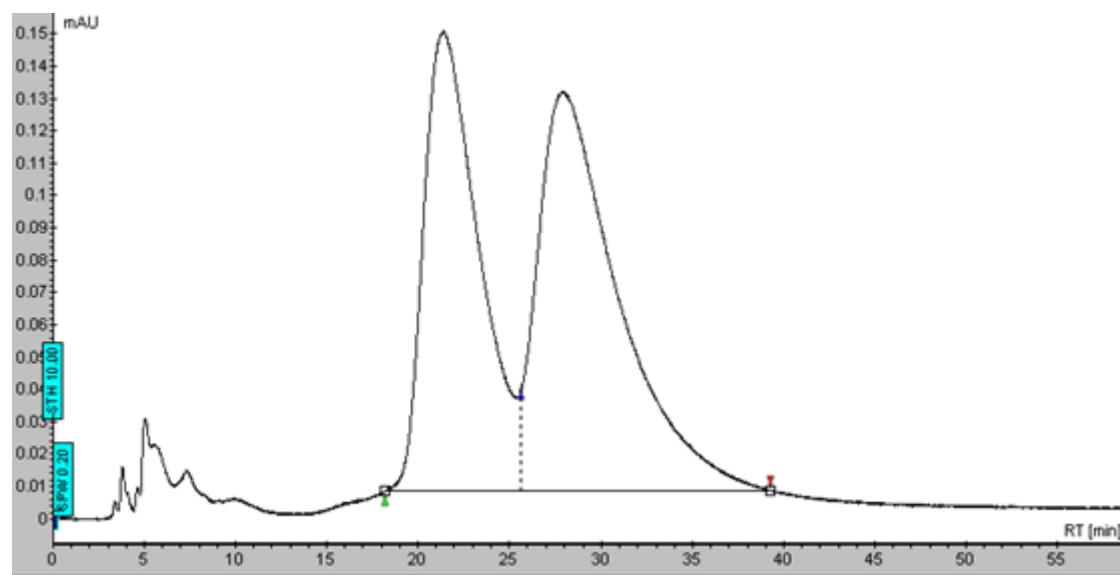
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	45.671	49.249	58.799	51.399
2	58.799	61.578	80.587	48.601

Asymmetric adduct

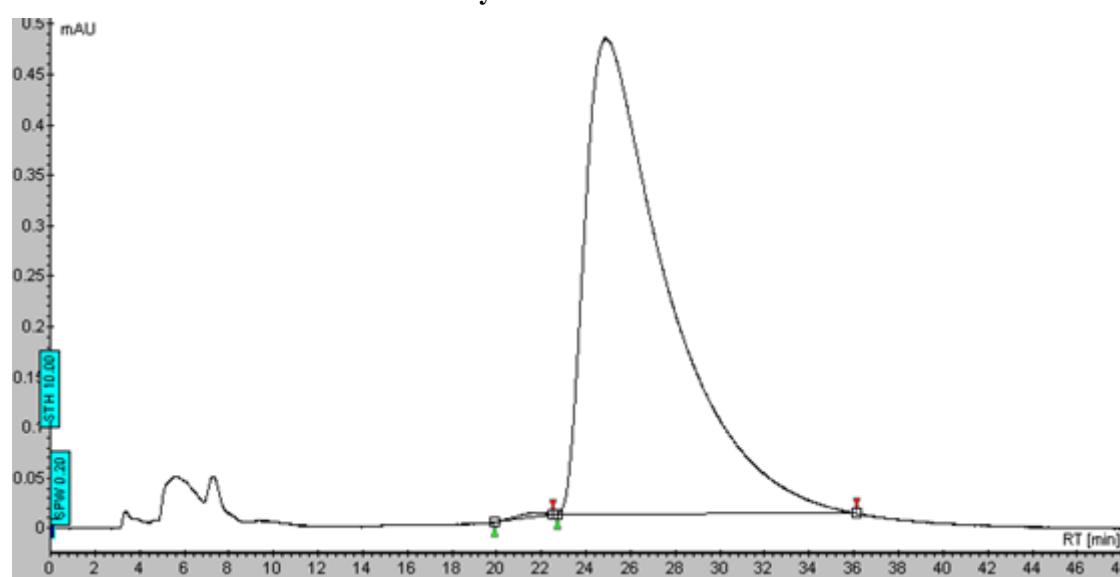
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	43.604	46.583	63.293	100.000

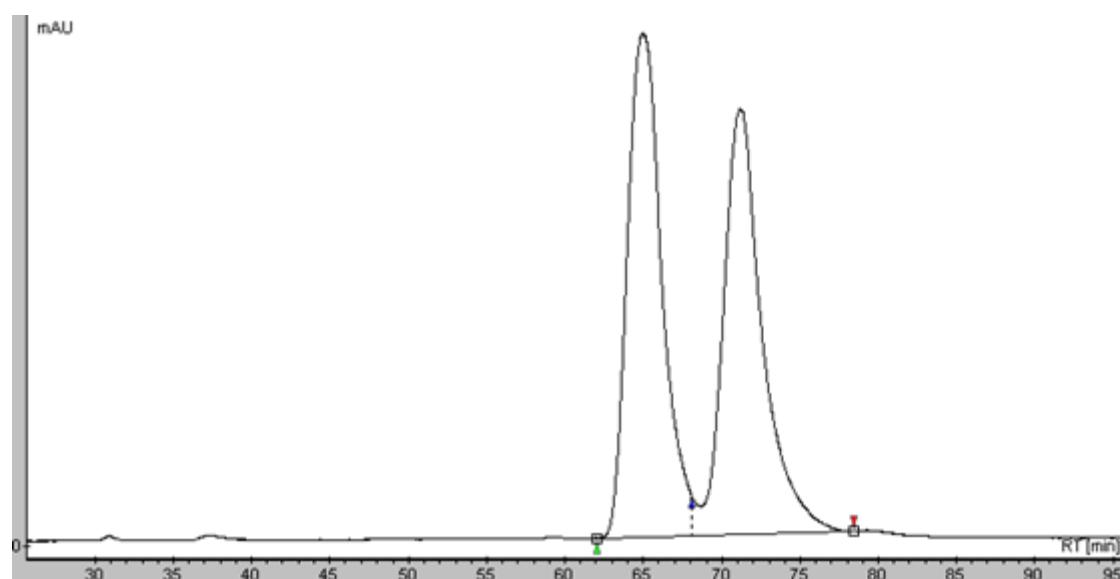
Compound 6e

Racemic adduct

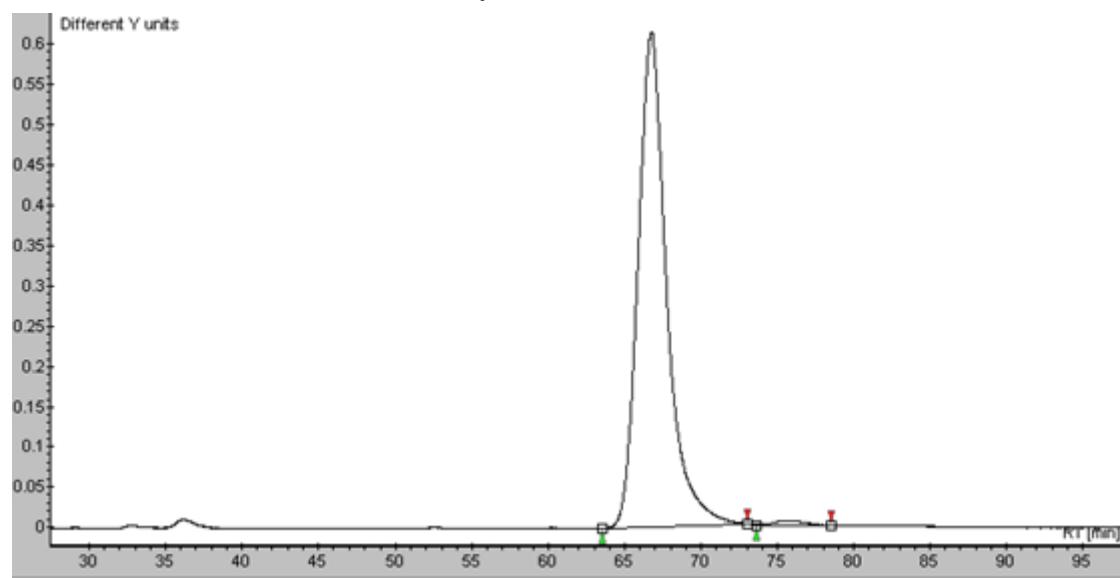


Asymmetric adduct

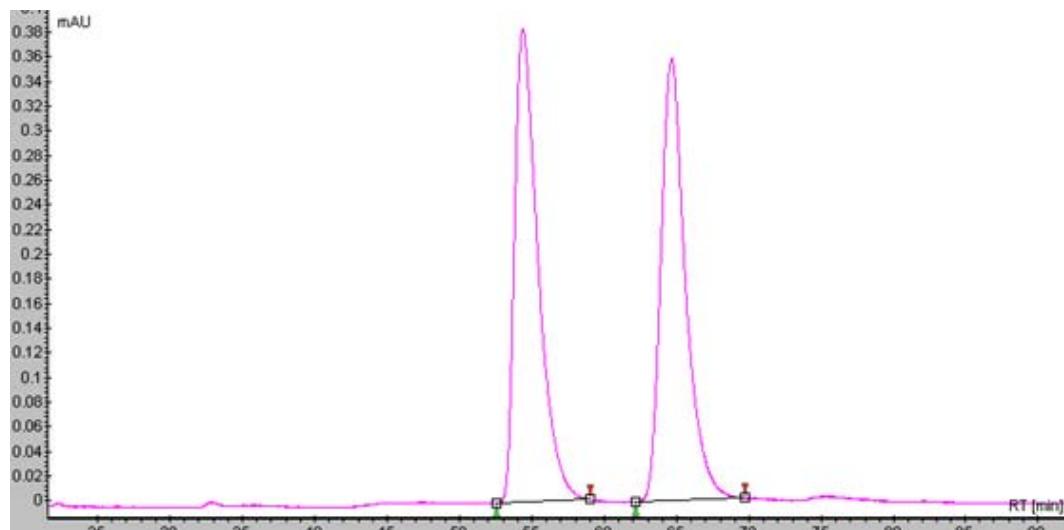


Compound 6f**Racemic adduct**

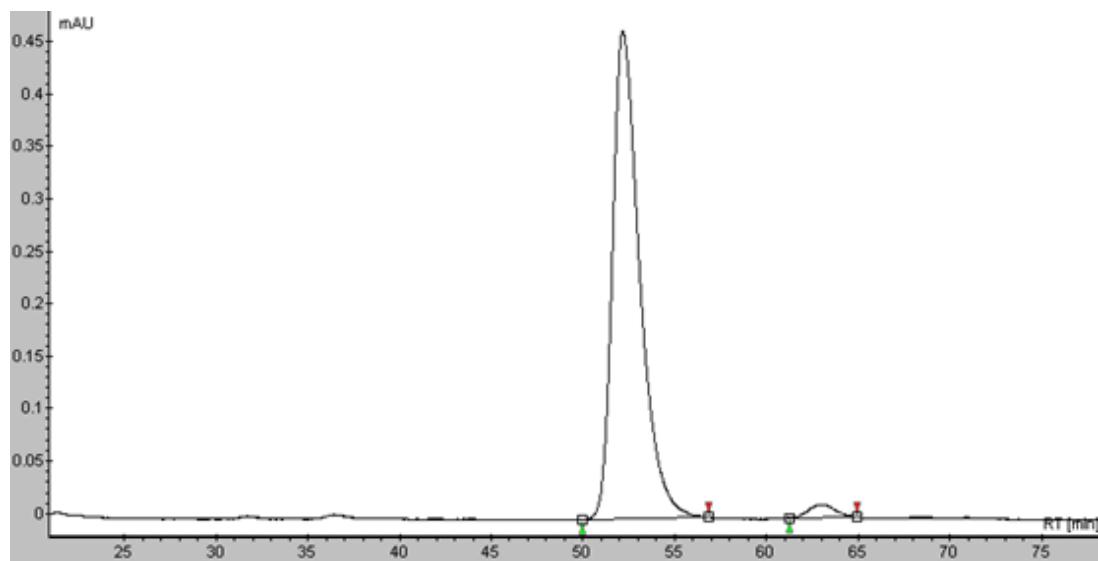
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	62.037	64.950	68.105	50.975
2	68.105	71.214	78.419	49.025

Asymmetric adduct

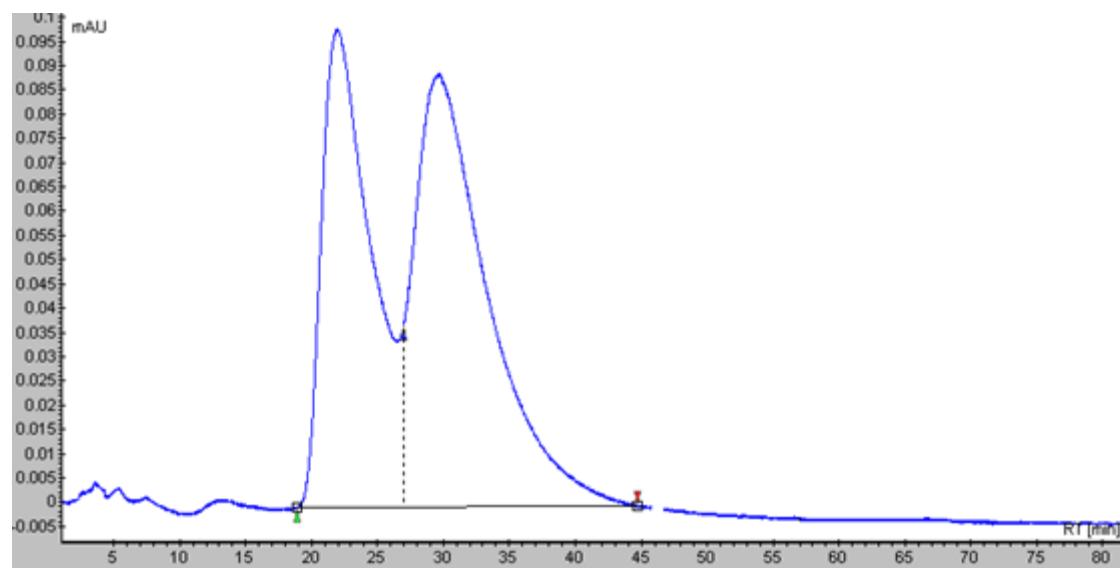
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	63.588	66.776	73.049	98.981
2	73.646	75.746	78.504	1.019

Compound 6g**Racemic adduct**

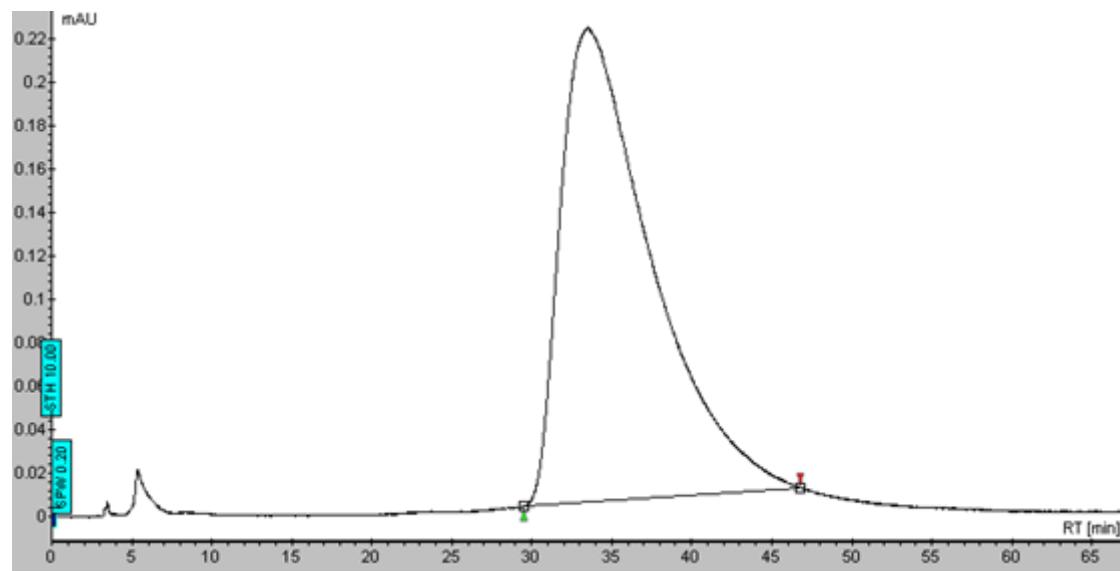
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	52.545	54.380	59.005	50.518
2	62.164	64.697	69.773	49.482

Asymmetric adduct

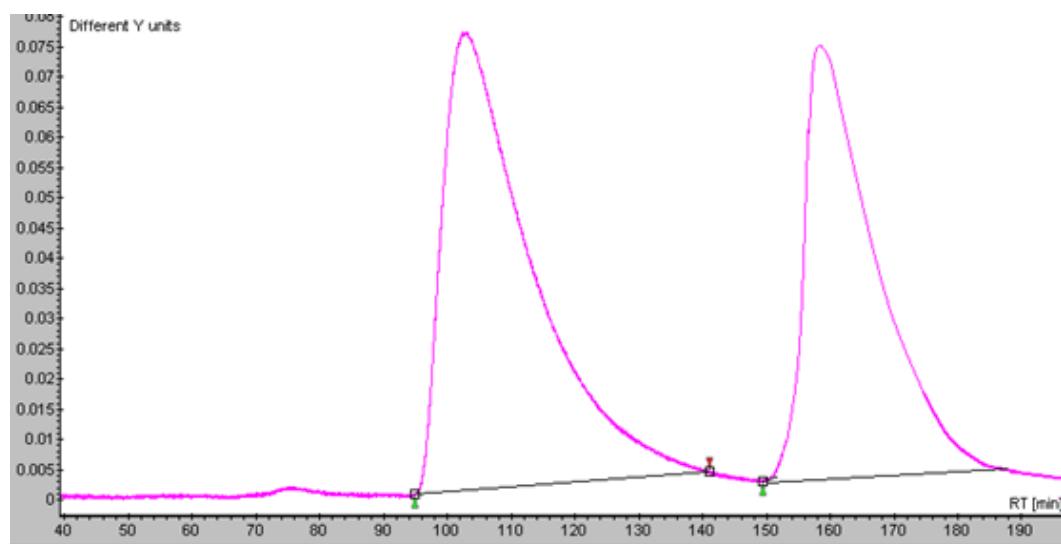
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	49.969	52.155	56.857	97.414
2	61.231	63.017	64.948	2.586

Compound 6h**Racemic adduct**

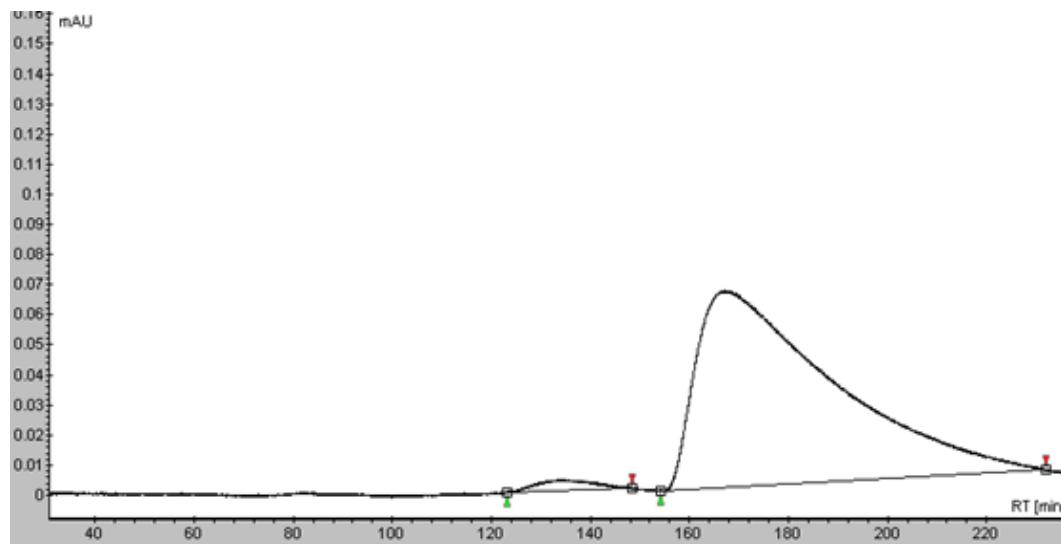
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	18.901	21.940	26.939	42.872
2	26.939	29.679	44.754	57.128

Asymmetric adduct

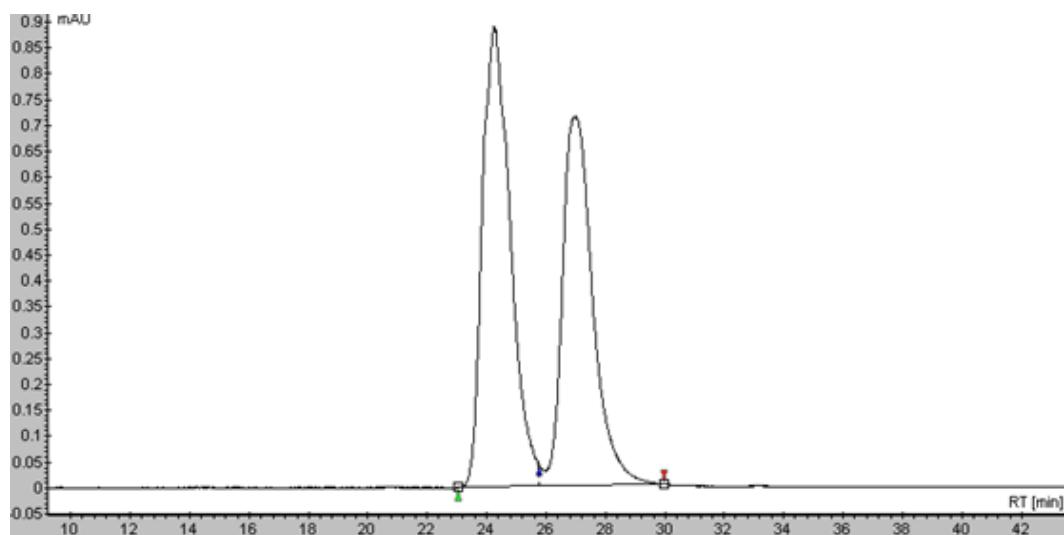
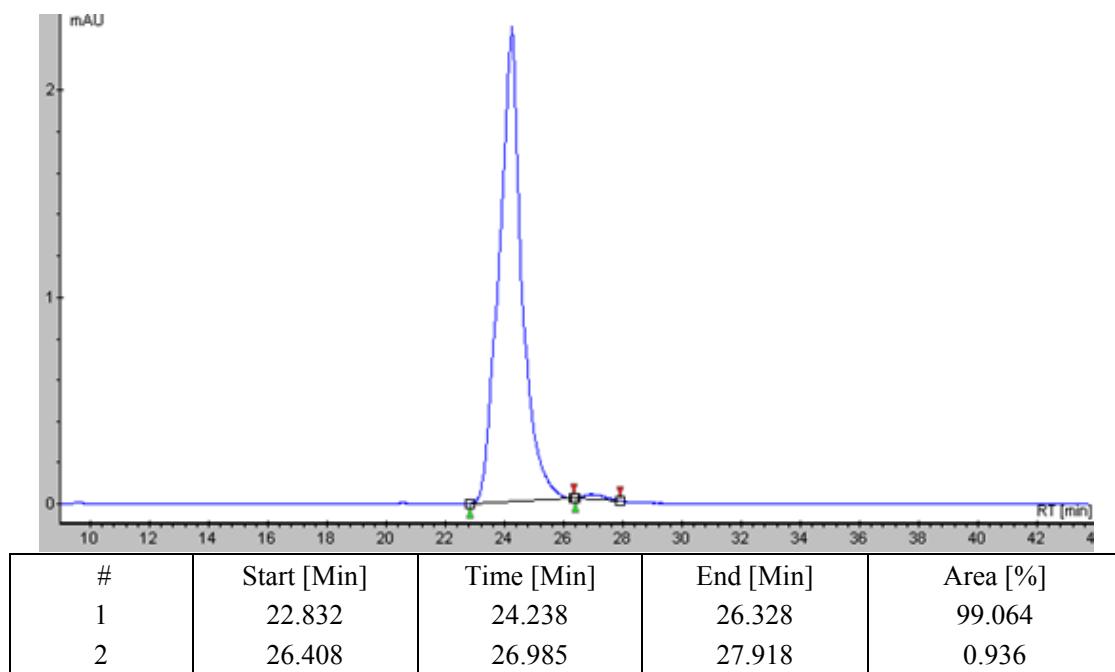
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	29.505	33.481	46.779	100.000

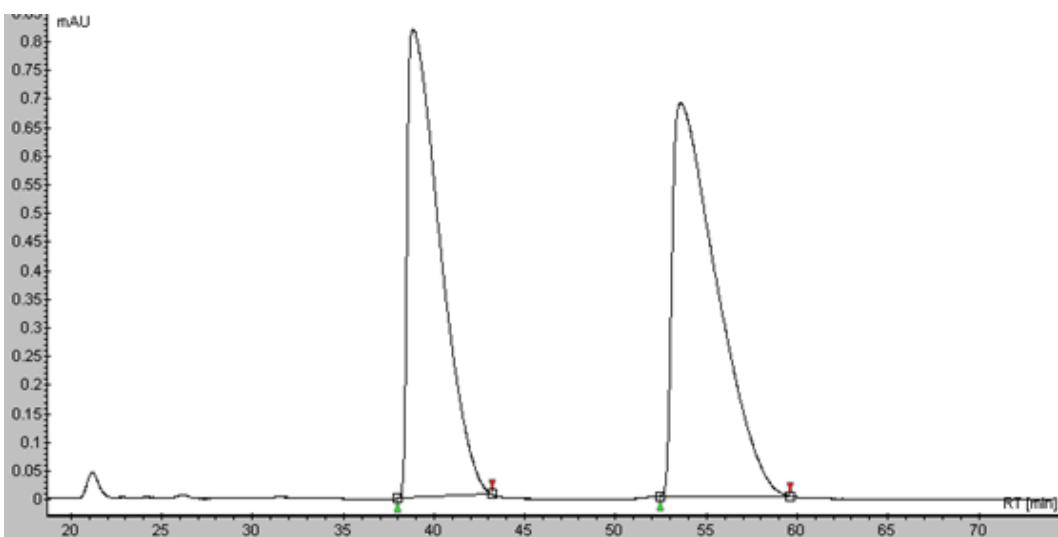
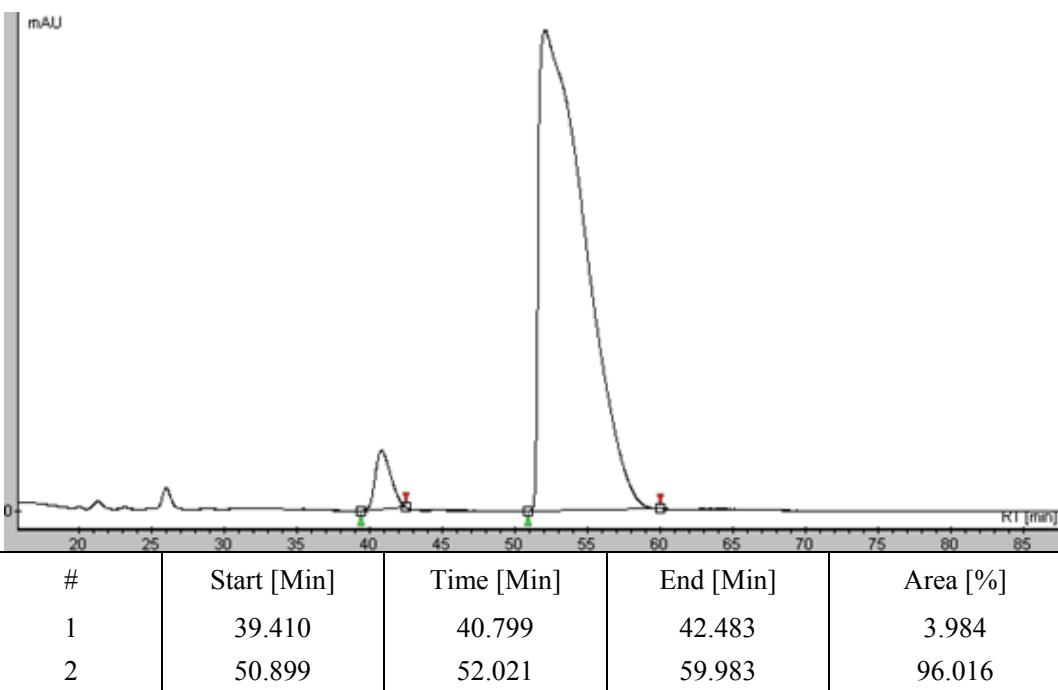
Compound 6i**Racemic adduct**

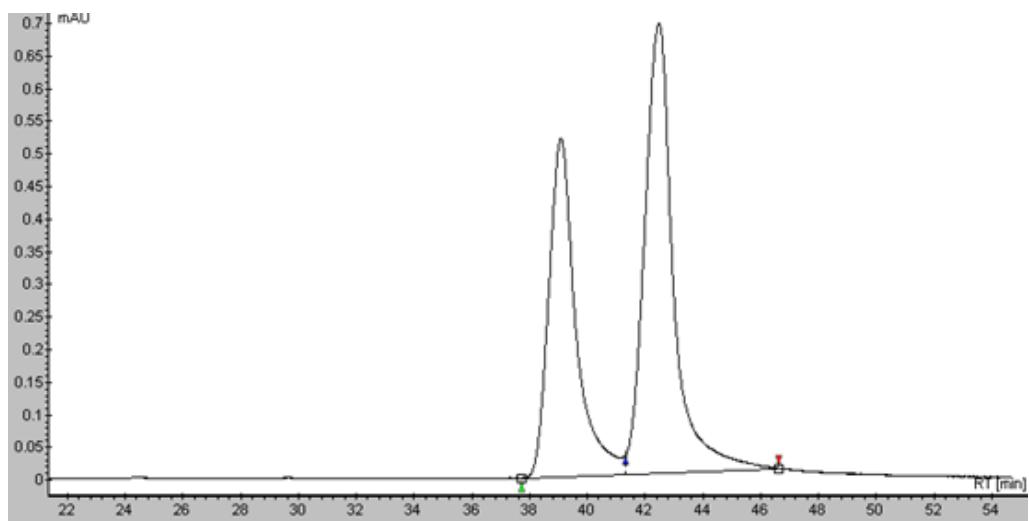
#	Start [Min]	Time [Min]	End [Min]	Area [%]
2	94.894	103.091	140.977	56.657
1	149.430	161.769	187.606	43.343

Asymmetric adduct

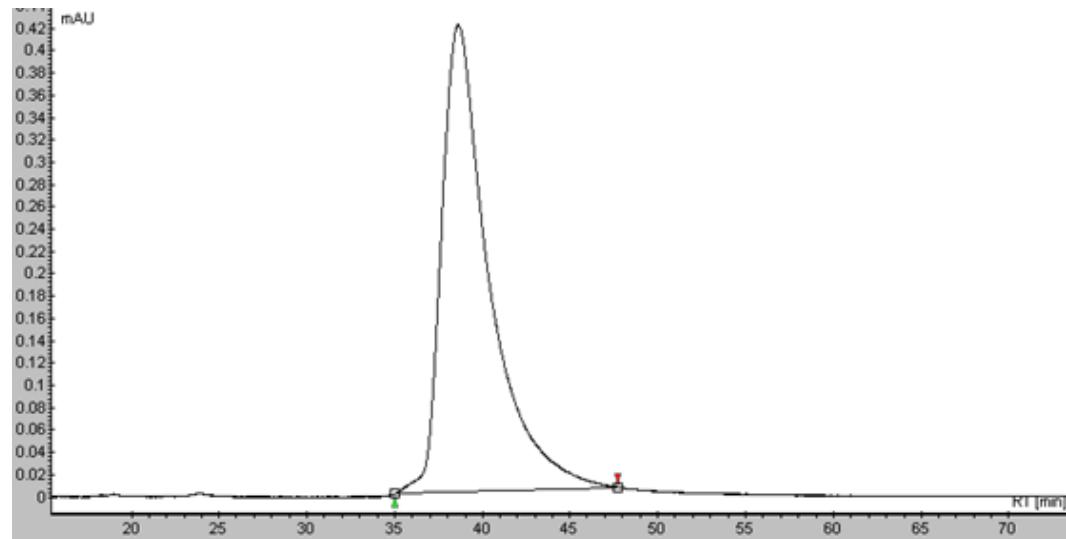
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	123.052	133.223	148.454	2.302
2	154.062	167.151	231.918	97.698

Compound 6j**Racemic adduct****Asymmetric adduct**

Compound 6k**Racemic adduct****Asymmetric adduct**

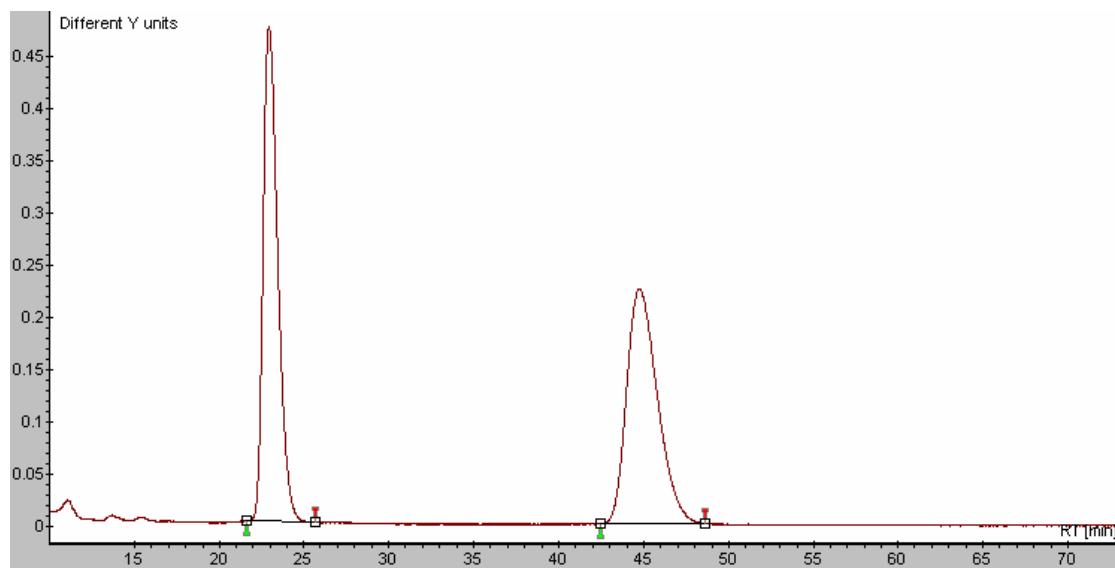
Compound 6l**Racemic adduct**

#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	37.725	39.077	41.317	41.494
2	41.317	42.464	46.642	58.506

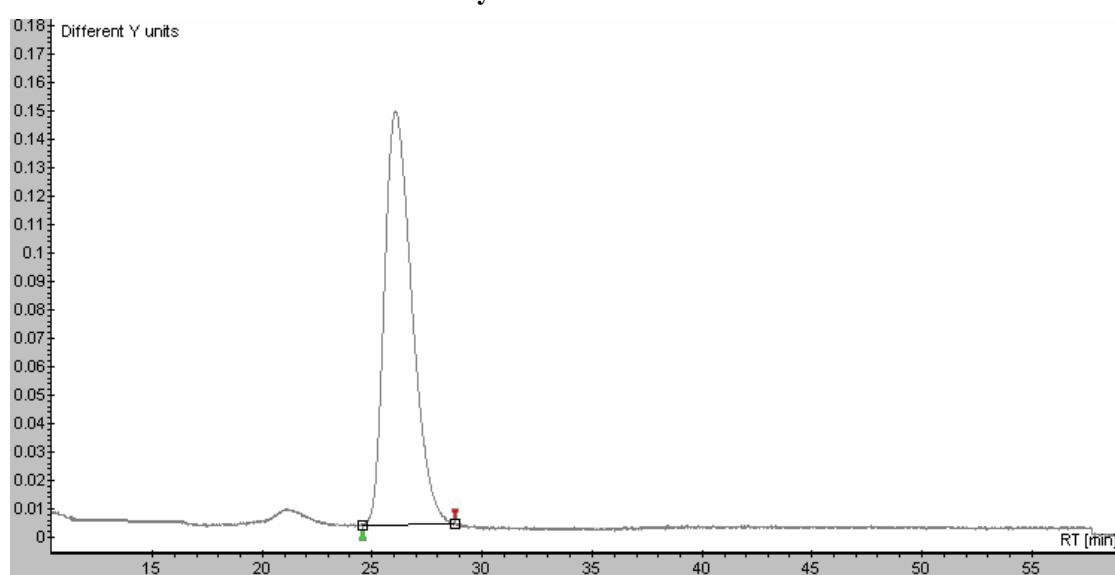
Asymmetric adduct

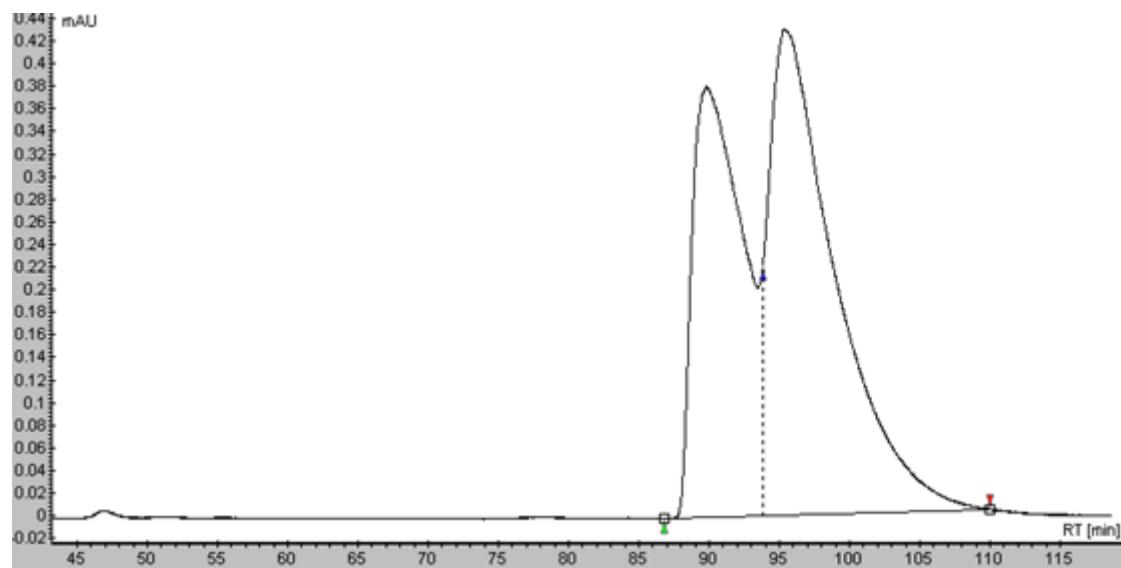
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	34.979	38.653	47.719	100.000

Compound 6m
Racemic adduct

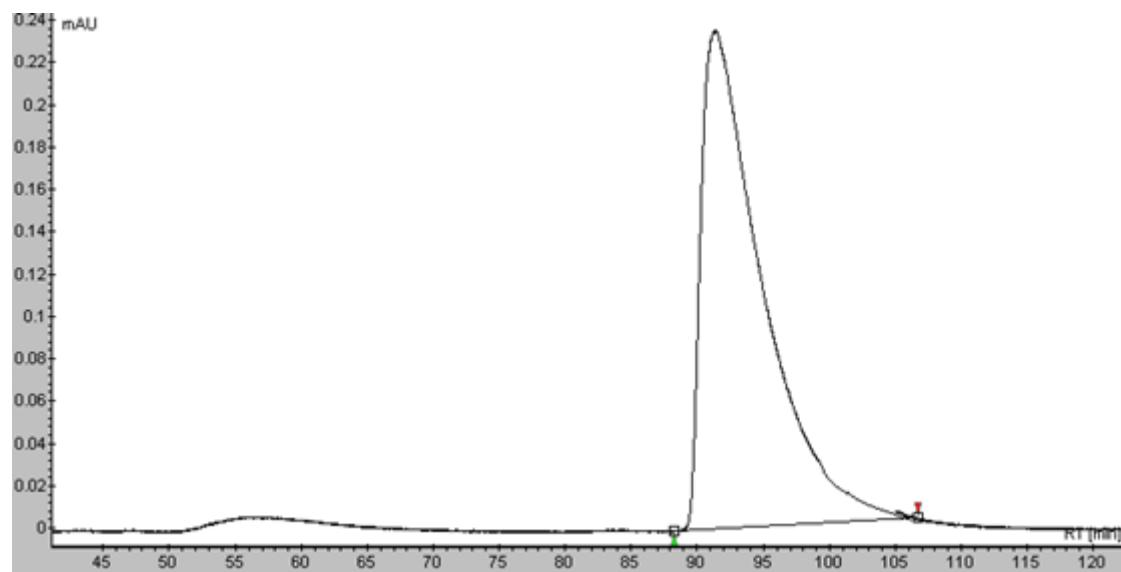


Asymmetric adduct

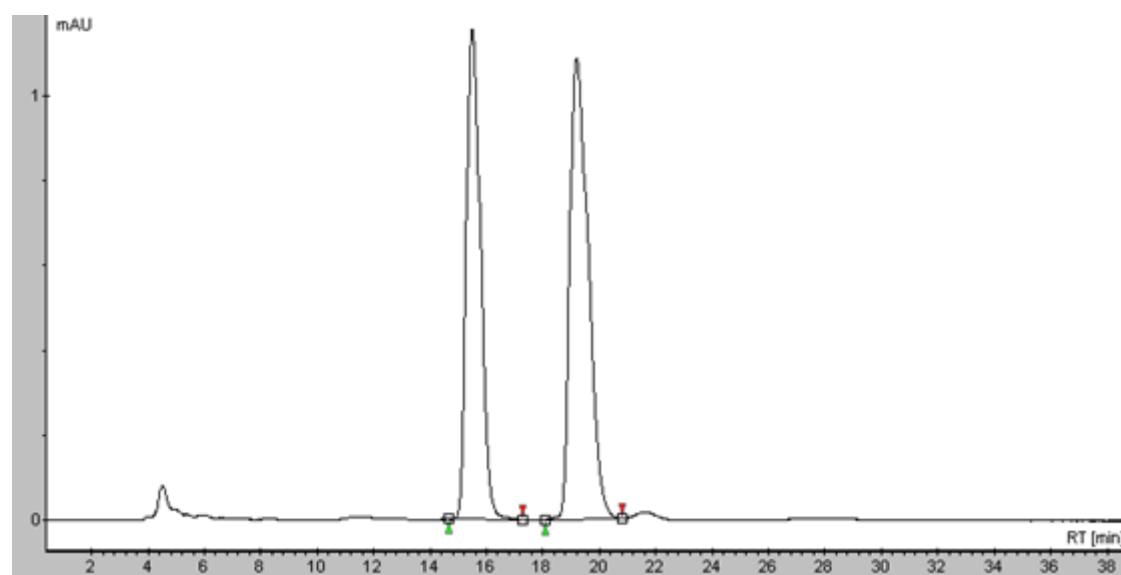


Compound 6n**Racemic adduct**

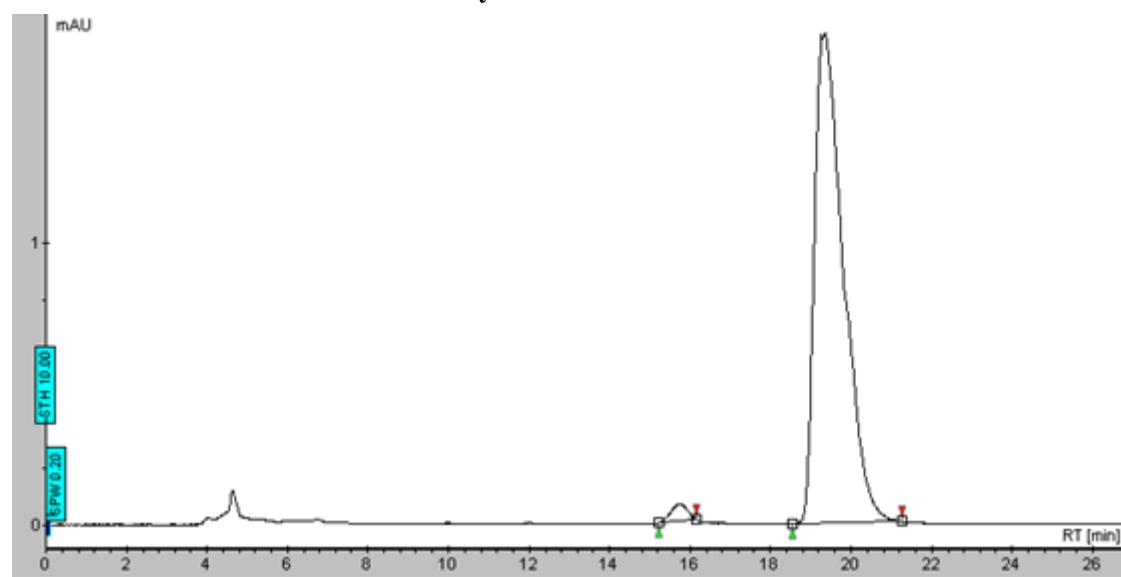
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	86.798	89.781	93.742	40.233
2	93.742	95.312	109.944	59.767

Asymmetric adduct

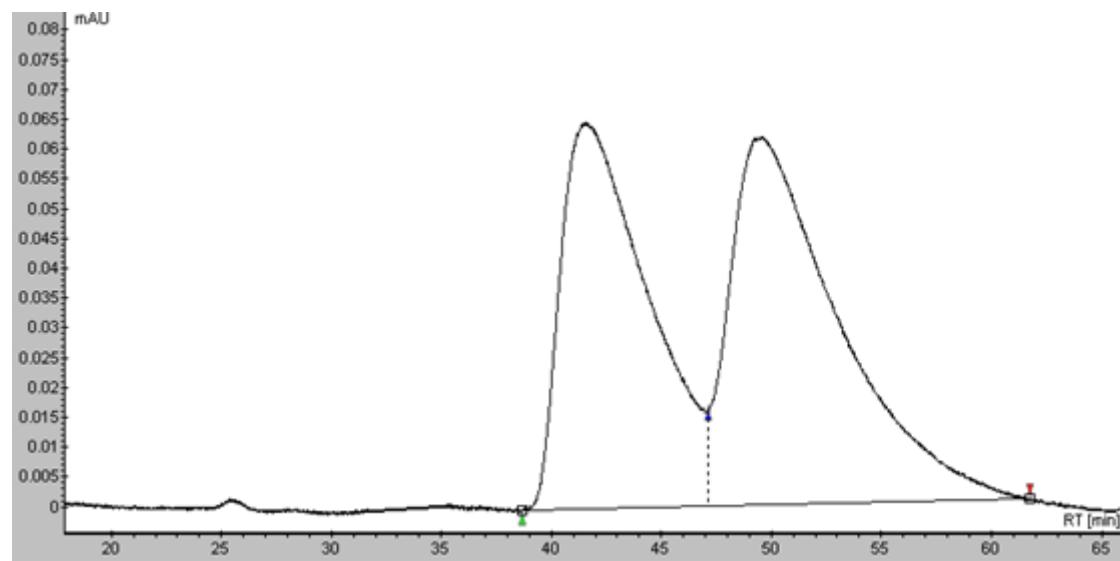
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	88.215	91.434	106.714	100.000

Compound 6o**Racemic adduct**

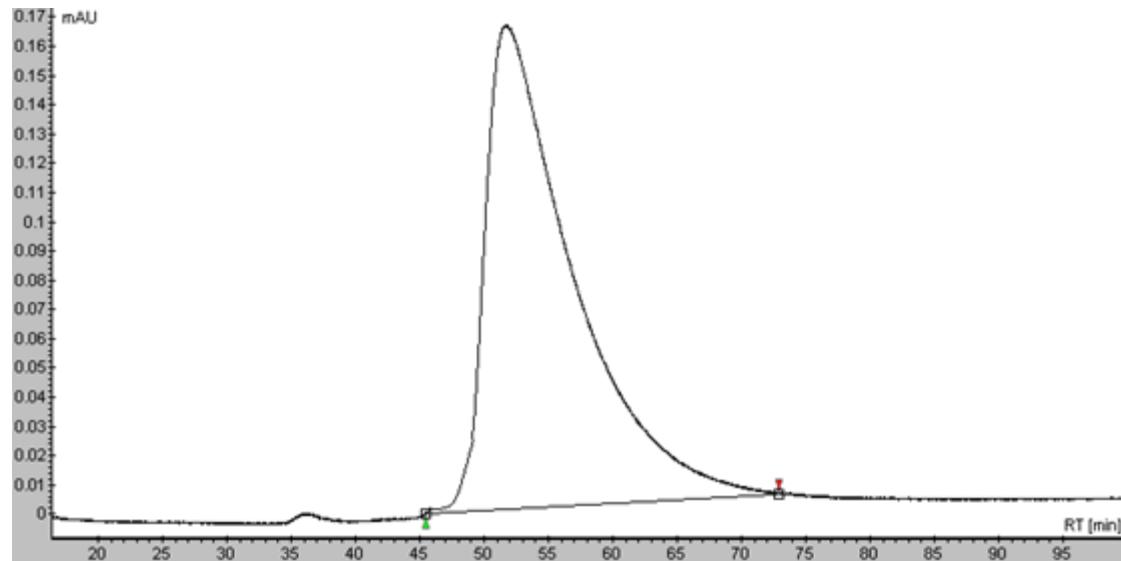
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	14.686	15.488	17.284	45.173
2	18.076	19.206	20.801	54.827

Asymmetric adduct

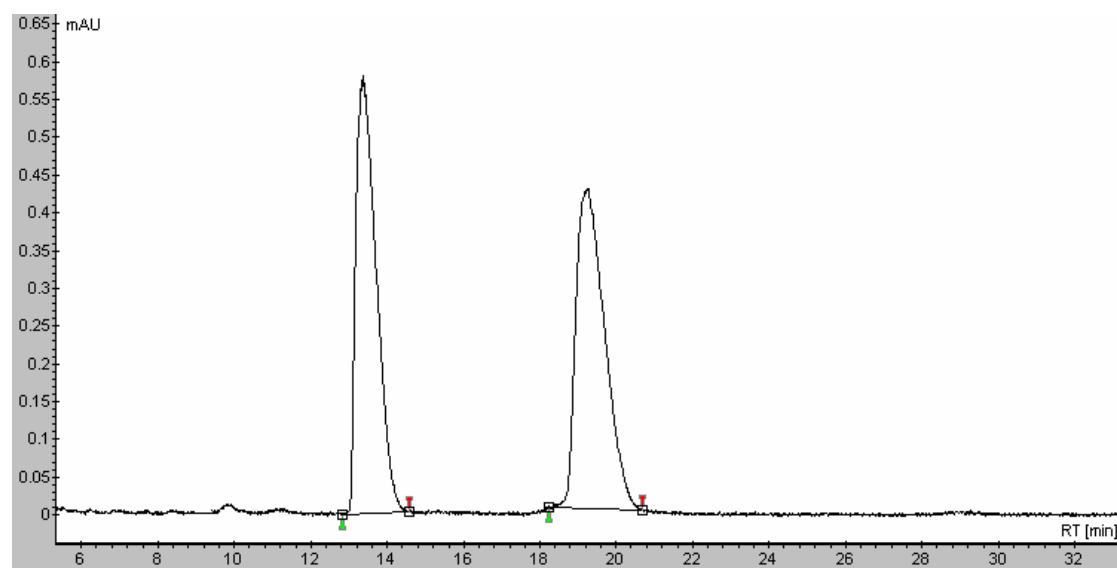
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	15.221	15.732	16.154	1.959
2	18.542	19.345	21.265	98.041

Compound 6p**Racemic adduct**

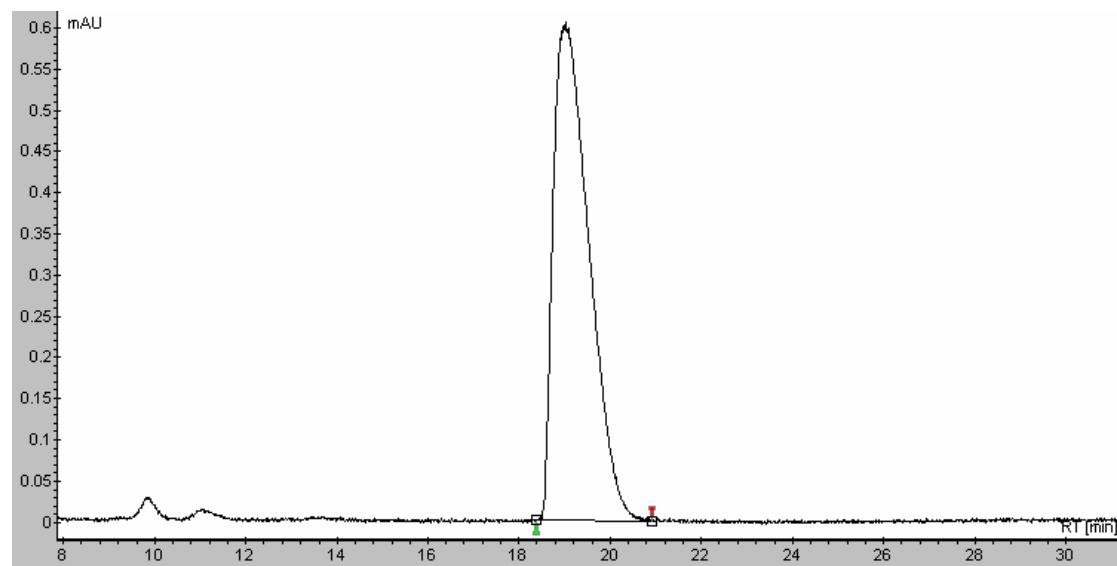
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	38.705	41.558	47.143	45.773
2	47.143	49.556	61.726	54.227

Asymmetric adduct

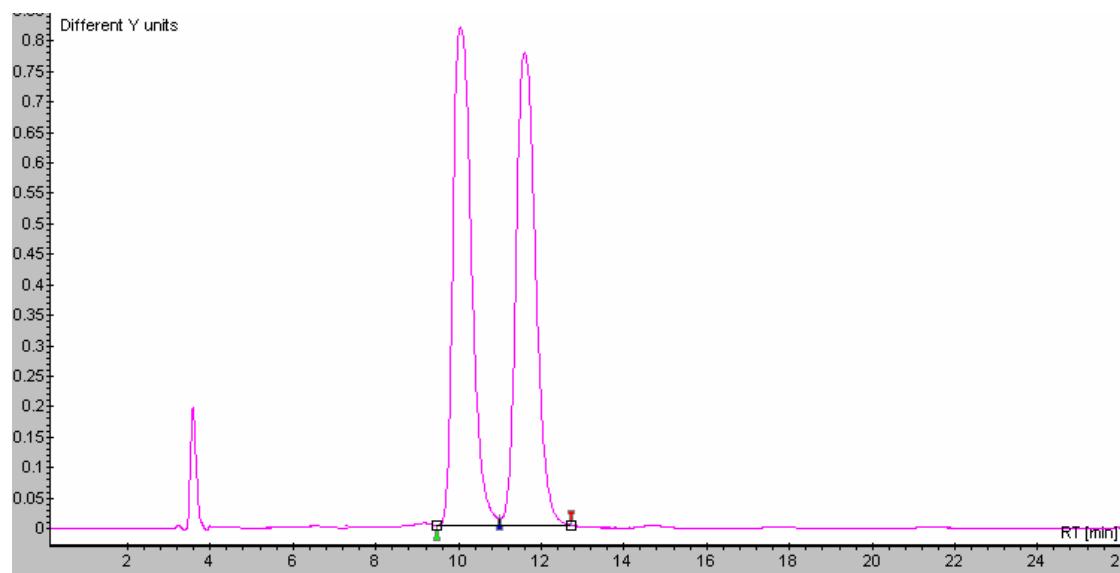
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	45.525	51.768	72.931	100.000

Compound 6q**Racemic adduct**

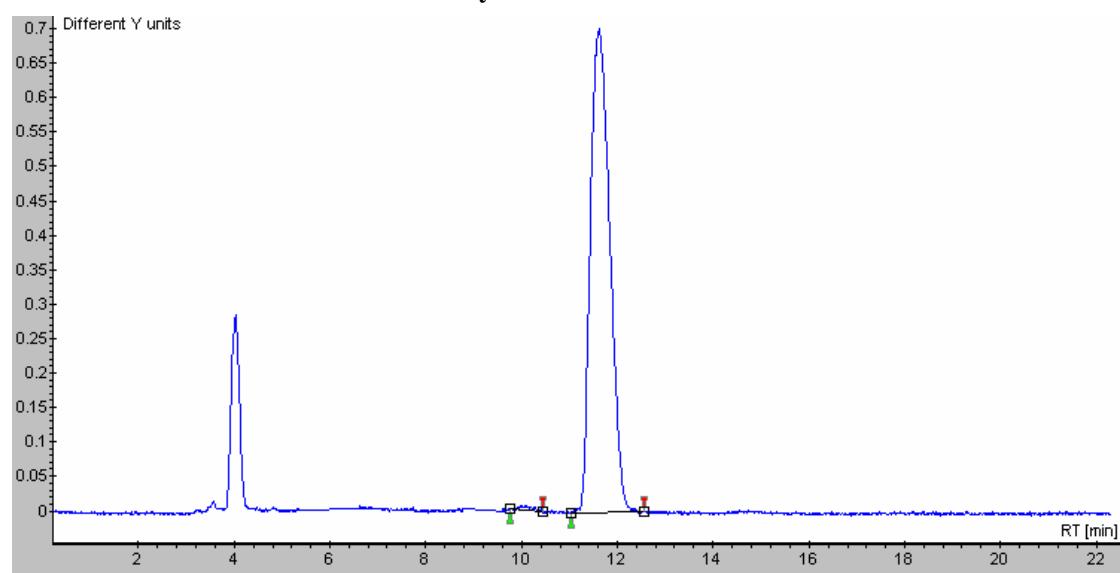
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	12.833	13.359	14.581	49.080
2	18.233	19.252	20.681	50.920

Asymmetric adduct

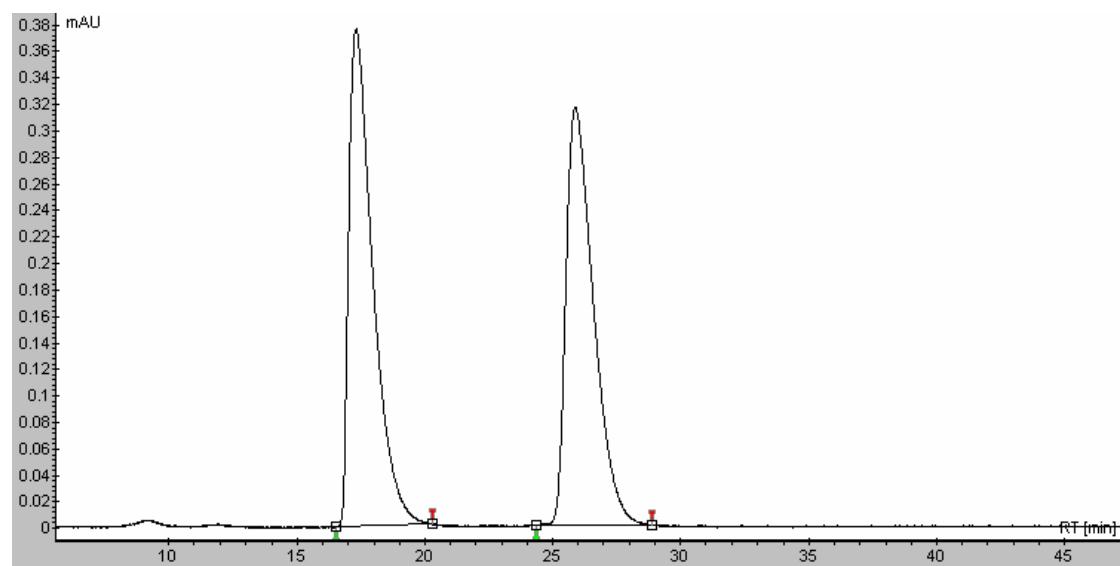
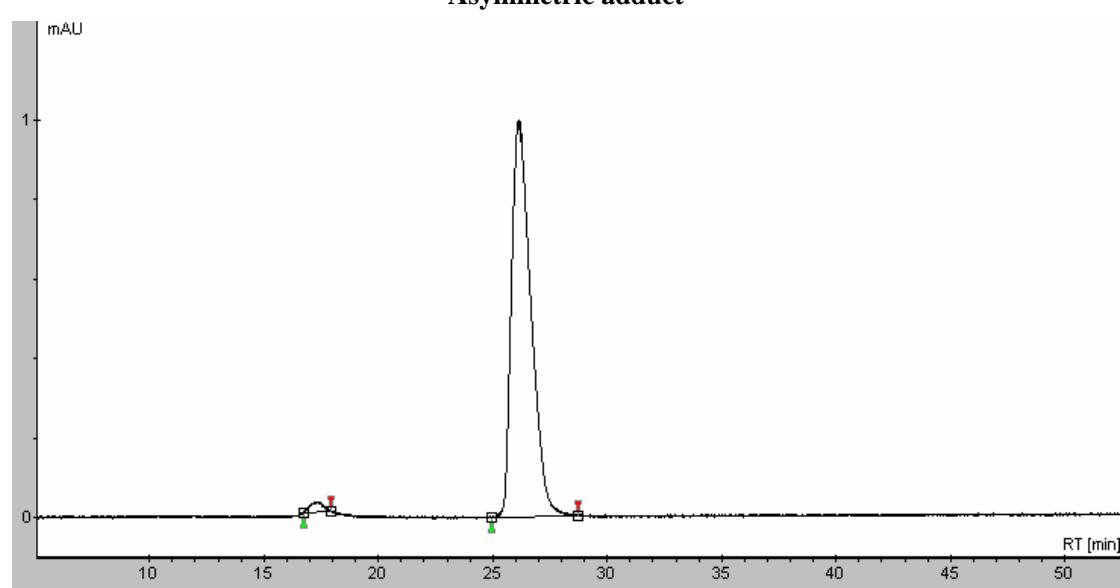
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	18.363	19.025	20.910	100.000

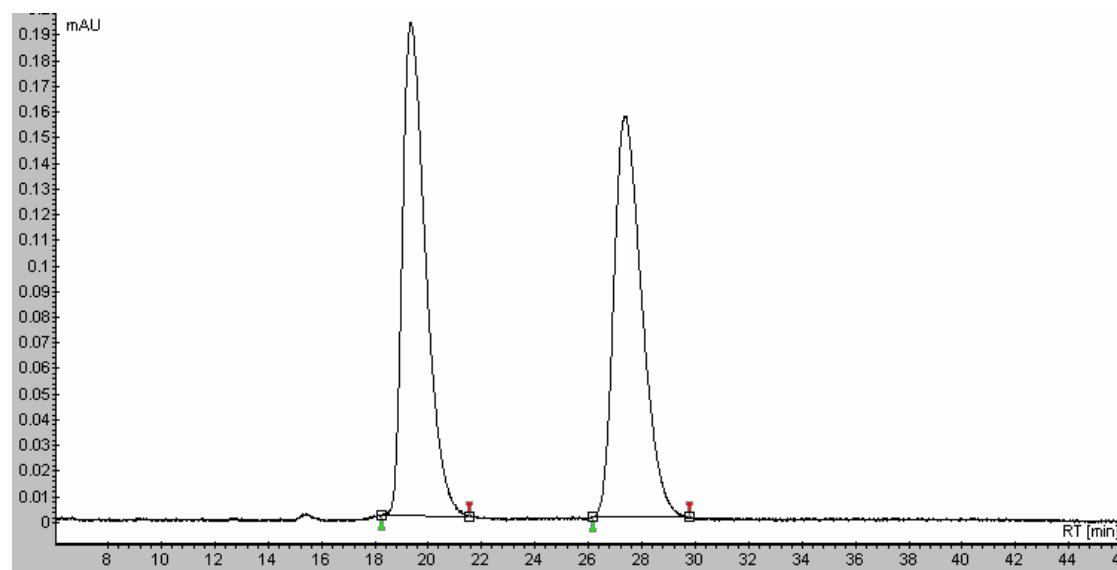
Compound 6r**Racemic adduct**

#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	9.477	10.039	10.998	49.941
2	10.998	11.586	12.717	50.059

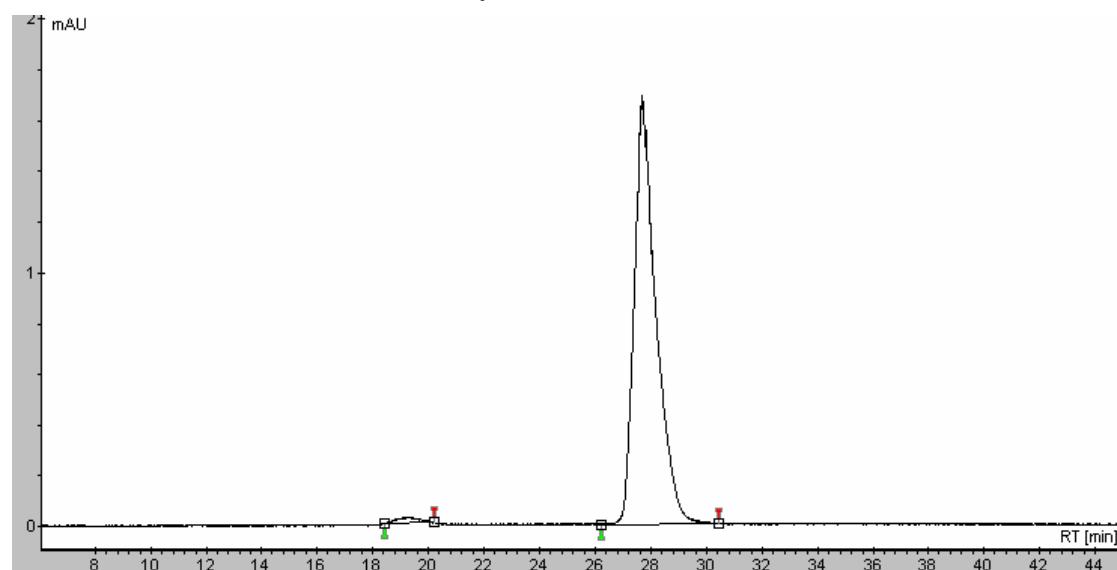
Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	9.748	10.106	10.438	0.707
2	11.037	11.612	12.554	99.293

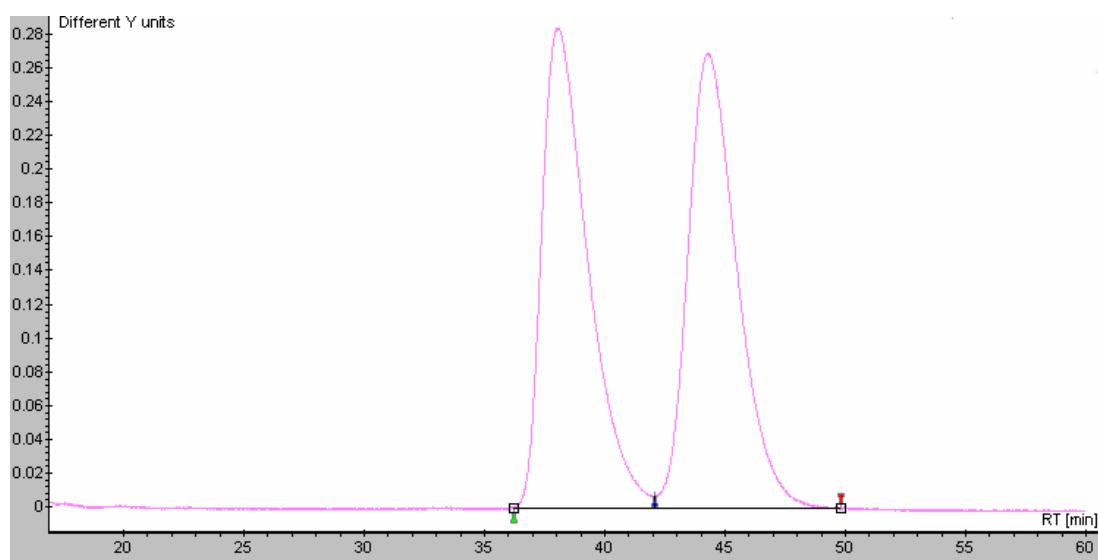
Compound 6s**Racemic adduct****Asymmetric adduct**

Compound 6t**Racemic adduct**

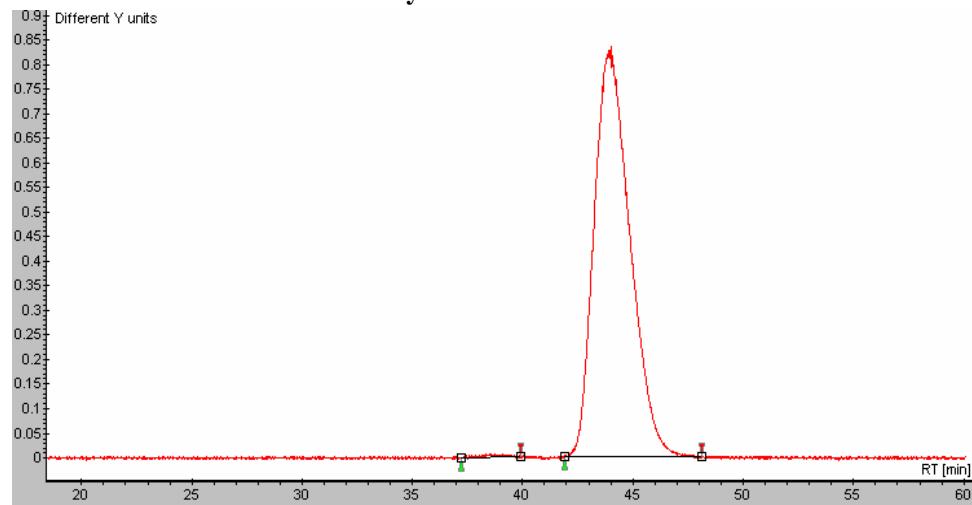
#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	18.264	19.345	21.543	50.546
2	26.173	27.371	29.775	49.454

Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	18.427	19.225	20.181	1.453
2	26.195	27.705	30.430	98.547

Compound 6u**Racemic adduct**

#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	36.175	38.011	42.061	49.765
2	42.061	44.263	49.804	50.235

Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area % [%]
2	37.227	38.491	39.918	0.455
1	41.913	44.023	48.104	99.545