

Supporting Information

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

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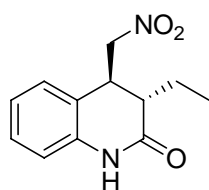
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1. General information

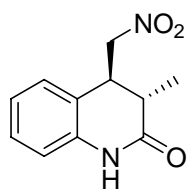
The ^1H NMR and ^{13}C NMR spectra were recorded in CDCl_3 or DMSO at 500 MHz and 125 MHz, respectively, with TMS as the internal standard. GC-MS experiments were performed on a GC system with a mass selective detector. HRMS data were measured on a LC/TOF-MS with ESI source. Column chromatography and 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

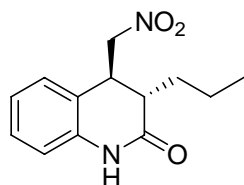
Solvent (0.5 mL) was added to a mixture of nitroolefins **1** (0.1 mmol) with aldehydes **2** (0.3 mmol) in the presence of 20 mol% catalyst **3d** and 20 mol% PhCO₂H **4a** at room temperature under vigorous stirring. After 1 day, the reaction mixture was extracted with DCM, washed with water, dried, 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.



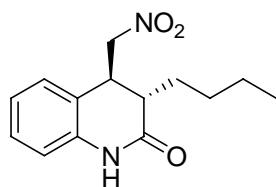
Compound (6a), yield: 20.4 mg, 87 %; 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; t_{major} = 65.672 min, t_{minor} = 71.174; ¹H NMR (500 MHz, CDCl₃): δ = 9.38 (s, 1H), 7.29–7.26 (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 ($\times 2$), 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; $t_{\text{major}} = 50.489$ 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.

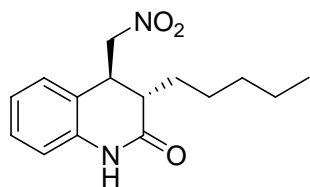


Compound (6c), yield: 15.6 mg, 63 %; 98 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (98:2) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 75.746$ min, $t_{\text{major}} = 66.776$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.37$ (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.

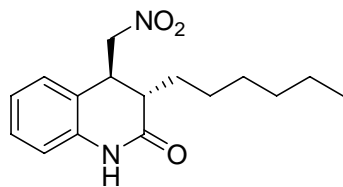


Compound (6d), yield: 20.4 mg, 87 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 46.583$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.44$ (s, 1H), 7.29–7.26 (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),

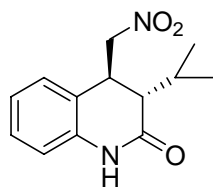
1.33–1.24 (m, 3H), 0.88–0.86 (m, 3H) ppm; ^{13}C NMR (125 MHz, CDCl_3): δ = 172.5, 136.0, 129.4 ($\times 2$), 124.1, 119.7, 116.1, 78.1, 43.9, 40.4, 30.1, 29.0, 22.3, 13.8 ppm; HRMS: (ESI+) m/z calcd for $\text{C}_{14}\text{H}_{19}\text{N}_2\text{O}_3$ $[\text{M}+\text{H}]^+$ 263.1396, found 263.1401.



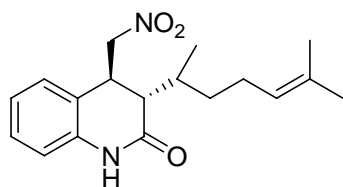
Compound (6e), yield: 20.4 mg, 74 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; t_{minor} = 21.425 min, t_{major} = 24.892 min; ^1H NMR (500 MHz, CDCl_3): δ = 9.57 (s, 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.



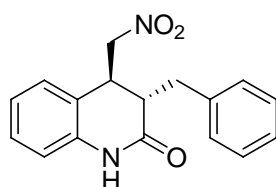
Compound (6f), yield: 22.0 mg, 76 %; 98 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; t_{minor} = 75.746 min, t_{major} = 66.776 min; ^1H NMR (500 MHz, CDCl_3): δ = 9.30 (s, 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_{minor} = 63.017 min, t_{major} = 52.155 min; ^1H NMR (500 MHz, CDCl_3): δ = 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): δ = 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.

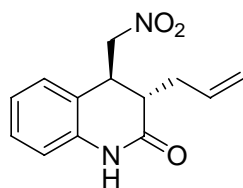


Compound (6h), yield: 23.1 mg, 73 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; t_{major} = 33.481 min; ^1H NMR (500 MHz, CDCl_3): δ = 8.47 (s, 1H), 7.28–7.26 (m, 1H), 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): δ = 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.

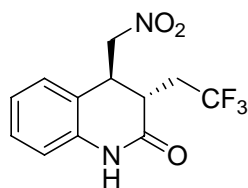


Compound (6i), yield: 22.2 mg, 75 %; 95 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm;

$t_{\text{minor}} = 133.223$ 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.

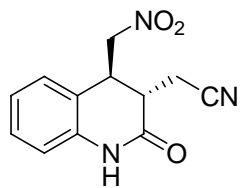


Compound (6j), yield: 18.0 mg, 73 %; 98 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AD-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 26.985$ min, $t_{\text{major}} = 24.238$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.68$ (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.

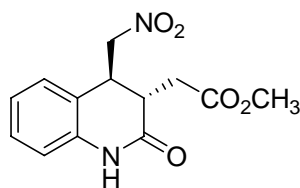


Compound (6k), yield: 20.2 mg, 70 %; 92 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252nm; $t_{\text{minor}} = 40.799$ min, $t_{\text{major}} = 52.021$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.21$ (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, $^3J_{\text{C-F}} = 139.6$

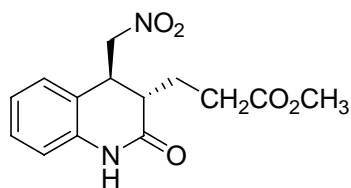
Hz), 33.8 (1C, m), 29.7 ppm; HRMS: (ESI+) m/z calcd for C₁₂H₁₂F₃N₂O₃ [M+H]⁺ 289.0800, found 289.0806.



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_{major} = 38.653 min; ¹H NMR (500 MHz, CDCl₃): δ = 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): δ = 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 C₁₂H₁₂N₃O₃ [M+H]⁺ 246.0879, found 246.0888.

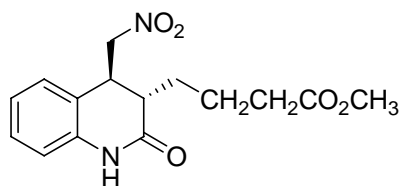


Compound (6m), yield: 18.9 mg, 68 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/i-PrOH (70:30) as the eluent, Flow: 1.0 mL/min; UV = 254 nm; t_{major} = 26.057 min; ¹H NMR (500 MHz, CDCl₃): δ = 9.49 (s, 1H), 7.31–7.28 (m, 1H), 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): δ = 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 C₁₃H₁₅N₂O₅ [M+H]⁺ 279.0980, found 279.0988.

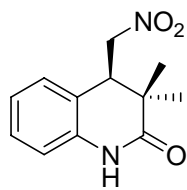


Compound (6n), yield: 19.3 mg, 66 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OD-H with hexane/i-PrOH (95:5) as the eluent, Flow: 1.0 mL/min; UV =

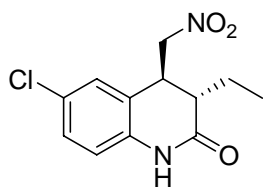
252 nm; $t_{\text{major}} = 91.434$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.22$ (s, 1H), 7.30–7.27 (m, 1H), 7.21–7.20 (m, 1H), 7.08–7.05 (m, 1H), 6.90–6.88 (m, 1H), 4.53–4.49 (m, 1H), 4.46–4.42 (m, 1H), 3.70–3.65 (m, 1H), 3.66 (s, 3H), 3.66–3.62 (m, 1H), 2.57–2.45 (m, 2H), 1.93–1.81 (m, 2H) ppm; ^{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.



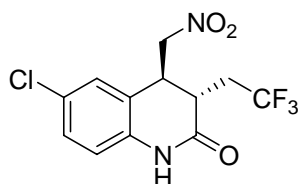
Compound (6o), yield: 21.4 mg, 70 %; 96 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/ethanol (80:20) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{minor}} = 15.732$ min, $t_{\text{major}} = 19.345$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.70$ (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.



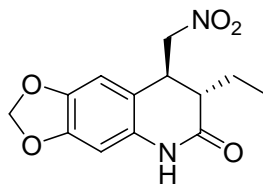
Compound (6p), yield: 11.7 mg, 50 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak OB-H with hexane/i-PrOH (90:10) as the eluent, Flow: 1.0 mL/min; UV = 252 nm; $t_{\text{major}} = 51.768$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 8.97$ (s, 1H), 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.

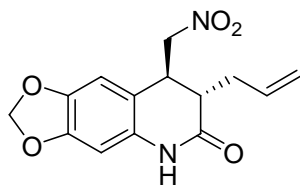


Compound (6r), yield: 24.5 mg, 76 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{minor}} = 10.106$ min, $t_{\text{major}} = 11.612$ min; ^1H NMR (500 MHz, DMSO): $\delta = 10.65$ (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, $^1J_{\text{C-F}} = 275.4$ 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.

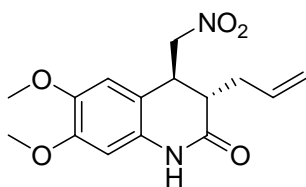


Compound (6s), yield: 18.4 mg, 66 %; 97 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (80:20) as the eluent, Flow: 1.0 mL/min; UV = 216 nm; $t_{\text{minor}} = 17.279$ min, $t_{\text{major}} = 26.131$ min; ^1H NMR (500 MHz, DMSO):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



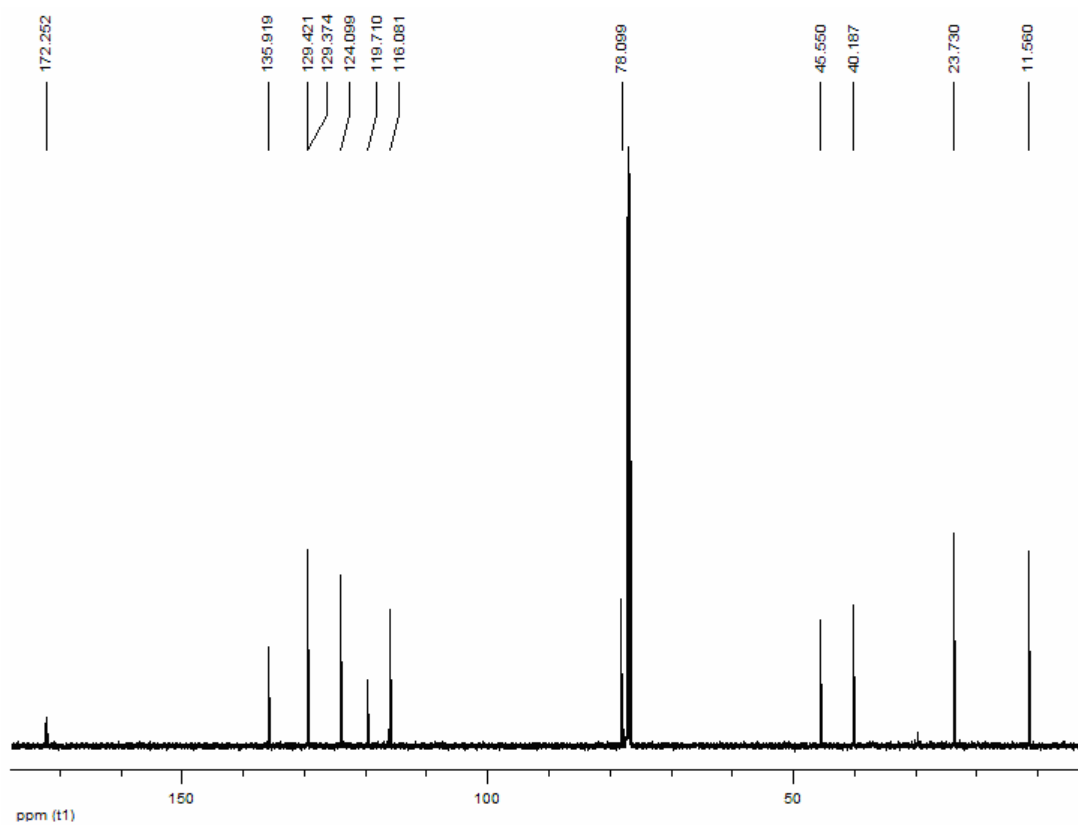
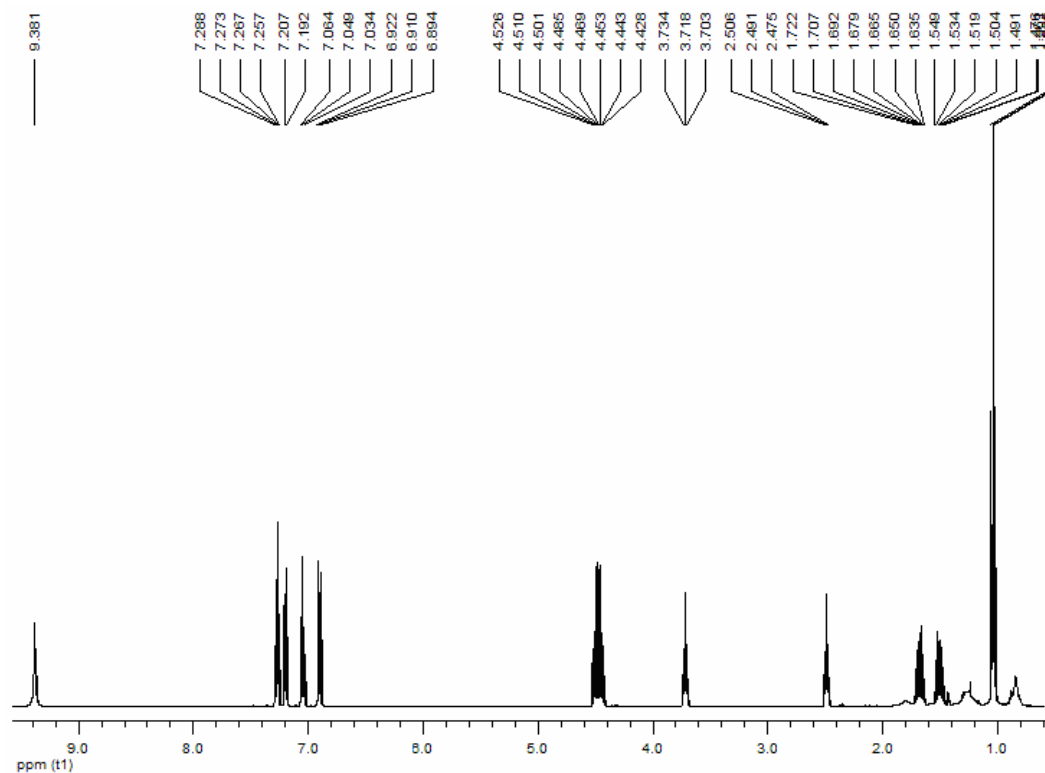
Compound (6u), yield: 22.0 mg, 72 %; > 99 % ee; > 99:1 dr; yellow oil; The enantiomeric excess was determined by HPLC on Daicel Chiralpak AS-H with hexane/EtOH (50:50) as the eluent, Flow: 0.5 mL/min; UV = 216 nm; $t_{\text{minor}} = 38.491$ min, $t_{\text{major}} = 44.023$ min; ^1H NMR (500 MHz, CDCl_3): $\delta = 9.31$ (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**

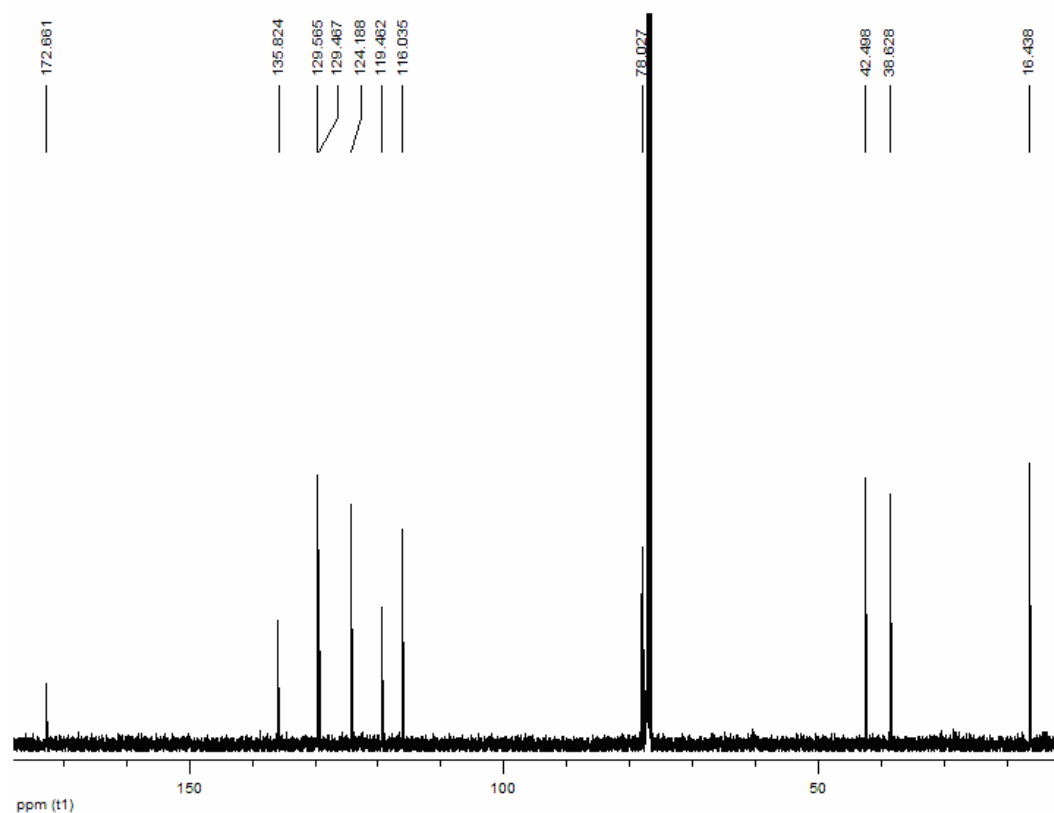
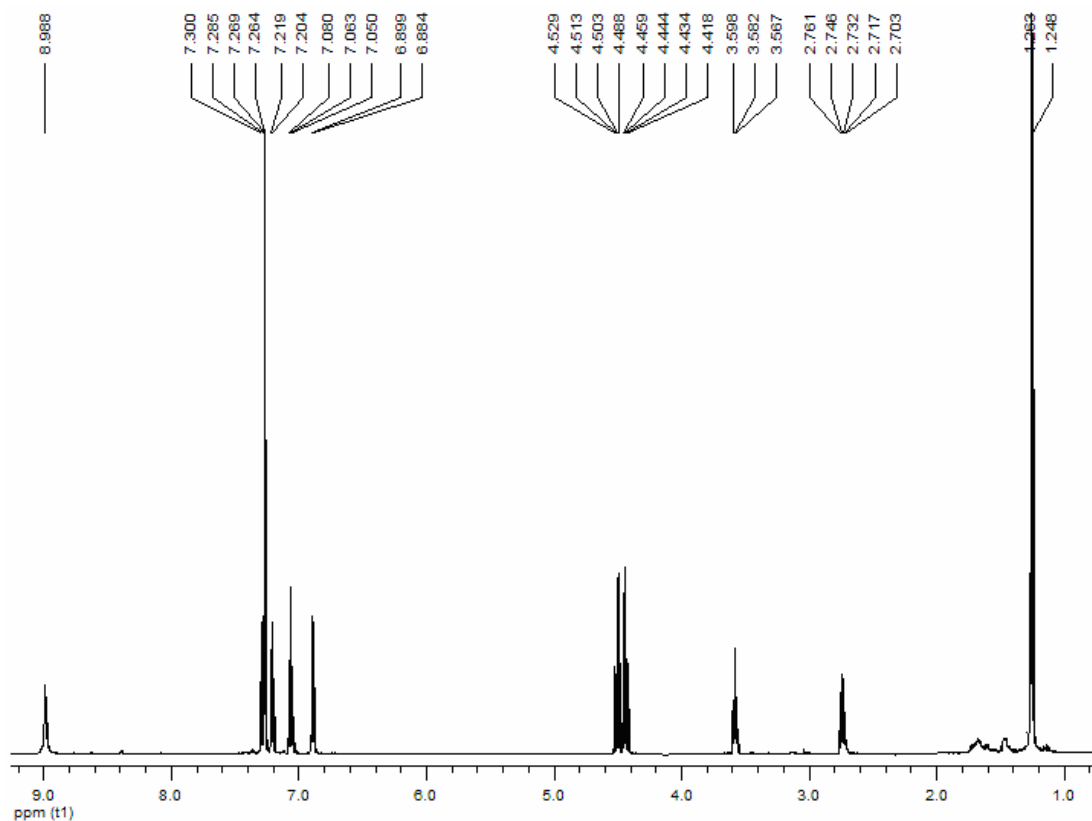
Solvent (1 mL) was added to a mixture of nitroolefins **1** (0.2 mmol) with aldehydes **2** (0.6 mmol) in the presence of 20 mol% catalyst **3d** and 20 mol% PhCO₂H **4a** at room temperature under vigorous stirring. After 1 day, the reaction was quenched by adding aq. HCl, extracted with DCM (3 × 5 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 Chiralpak AD-H.

4. NMR spectra

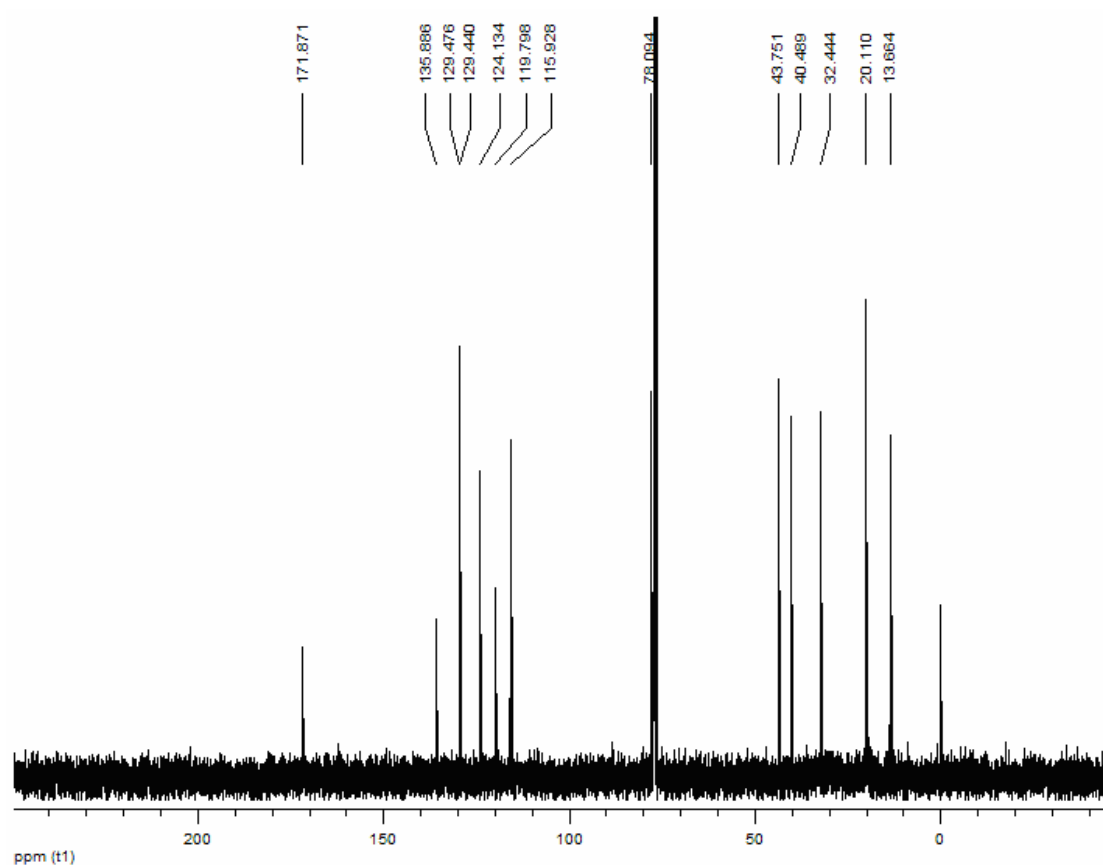
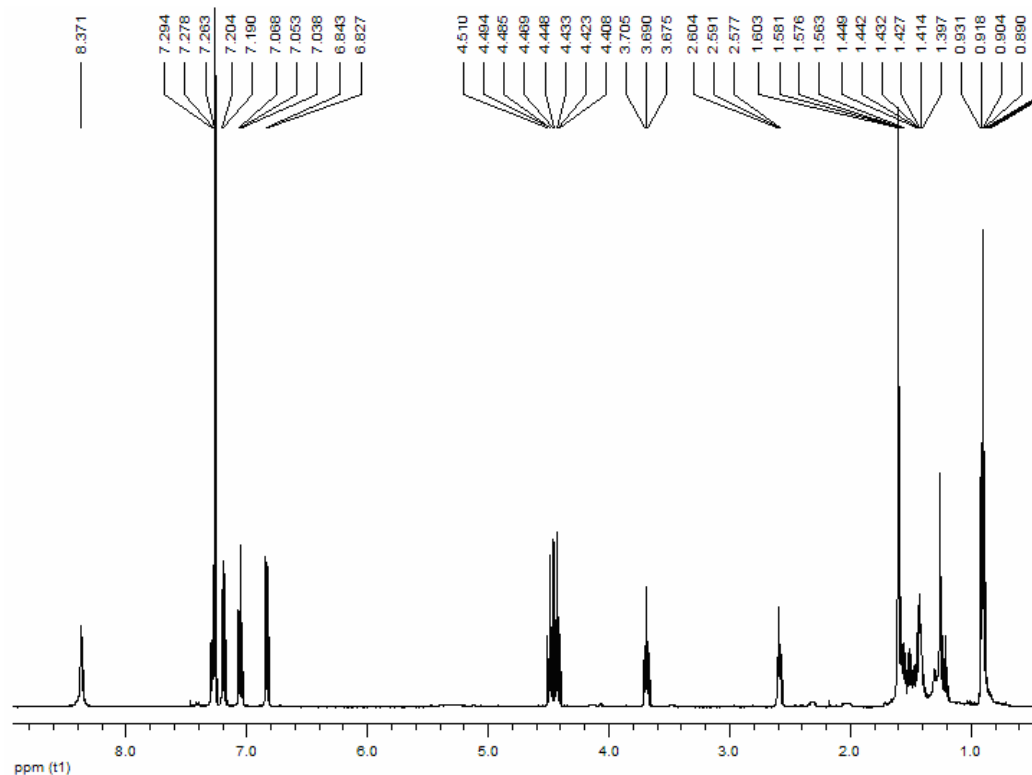
Compound 6a



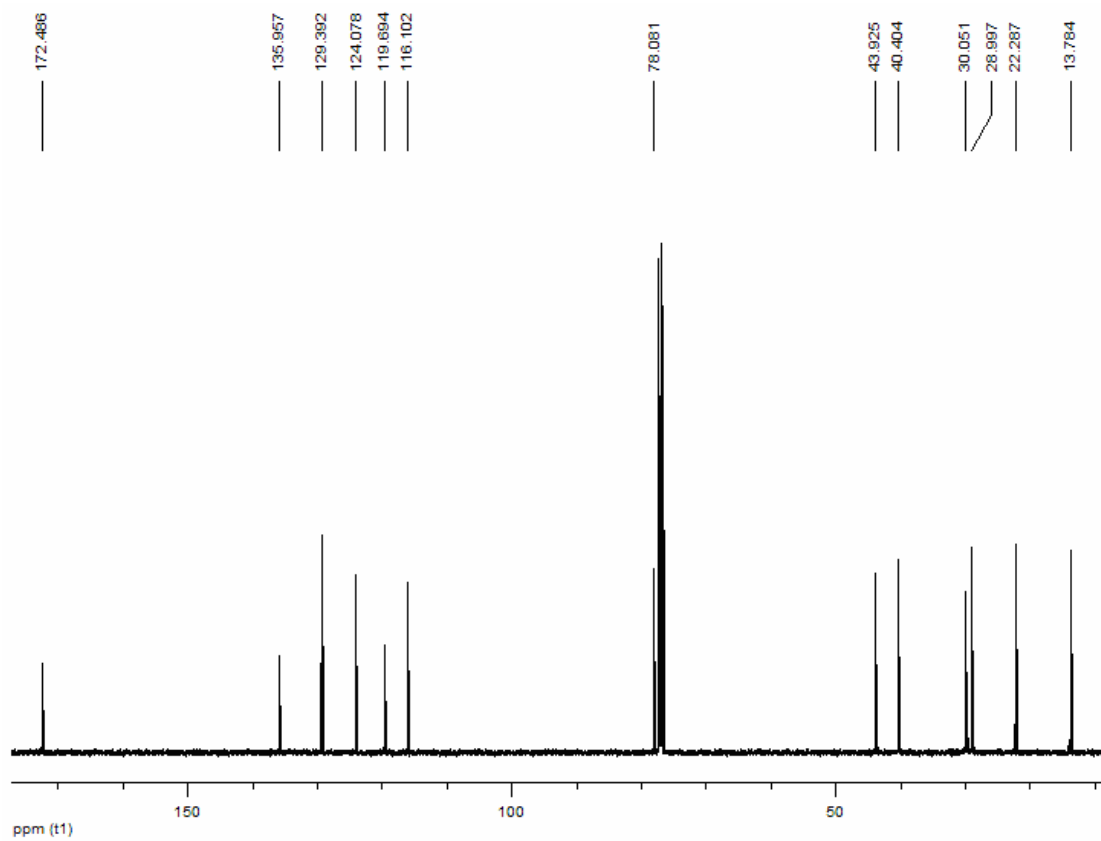
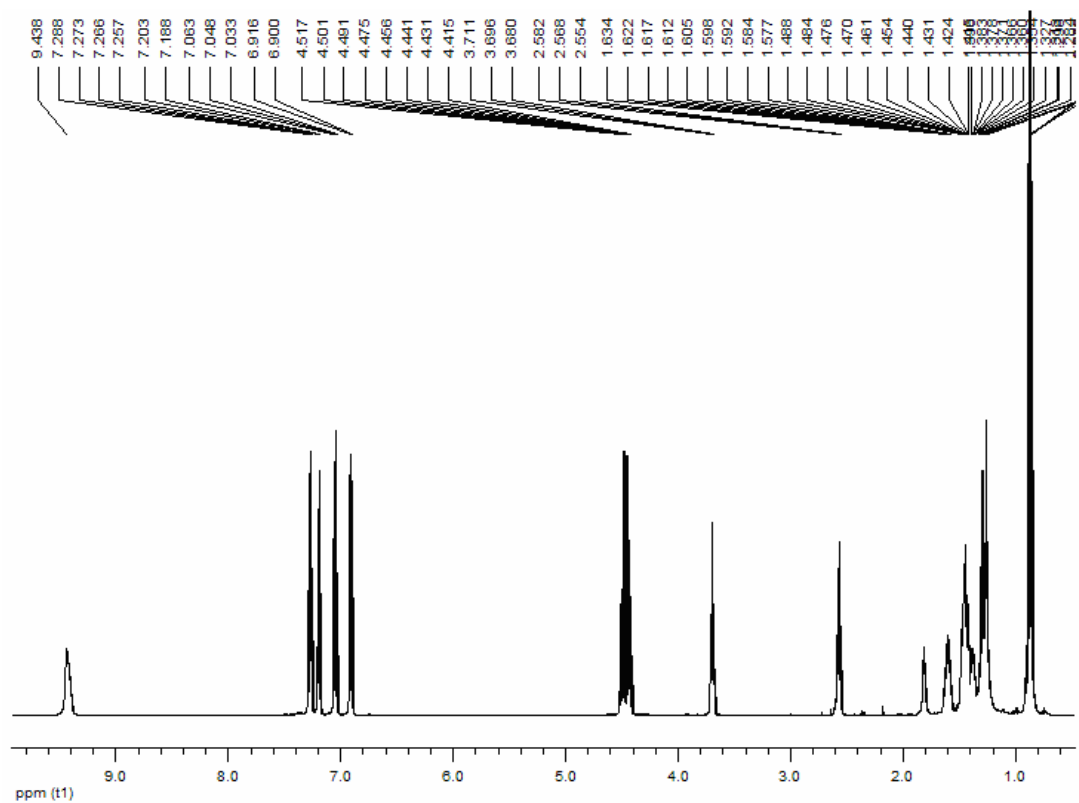
Compound 6b



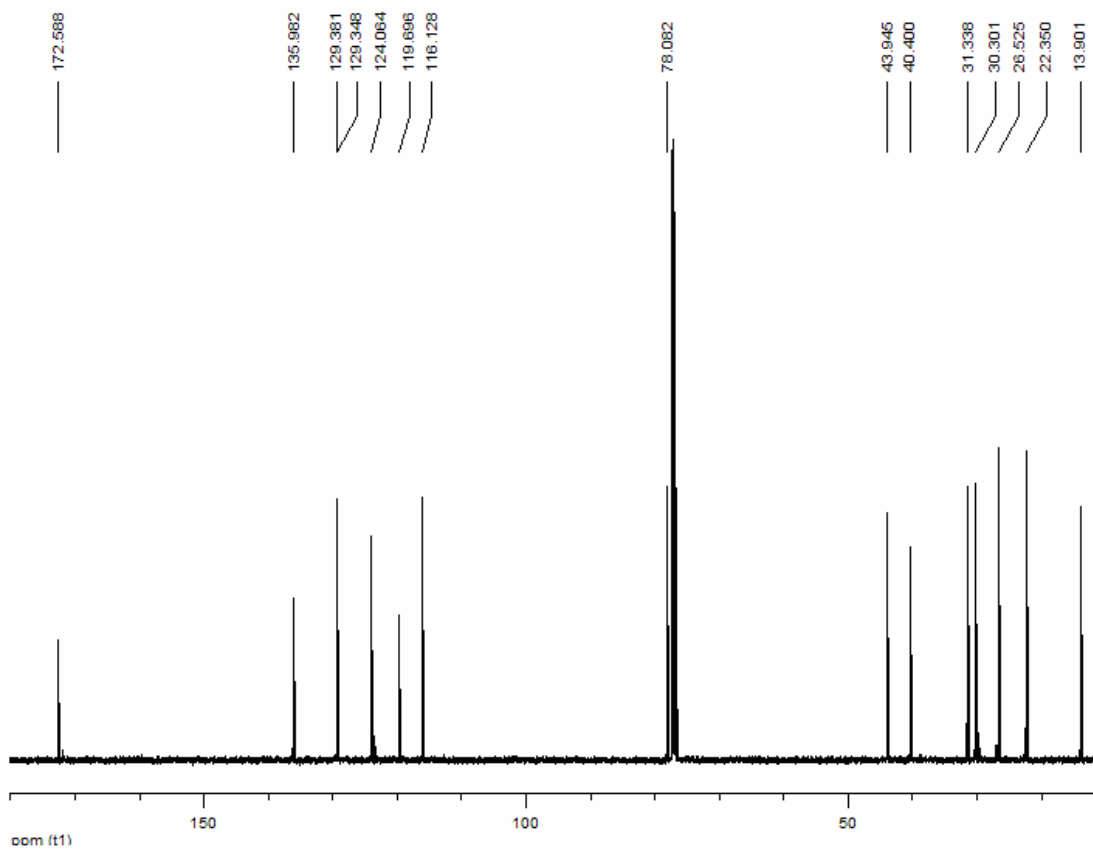
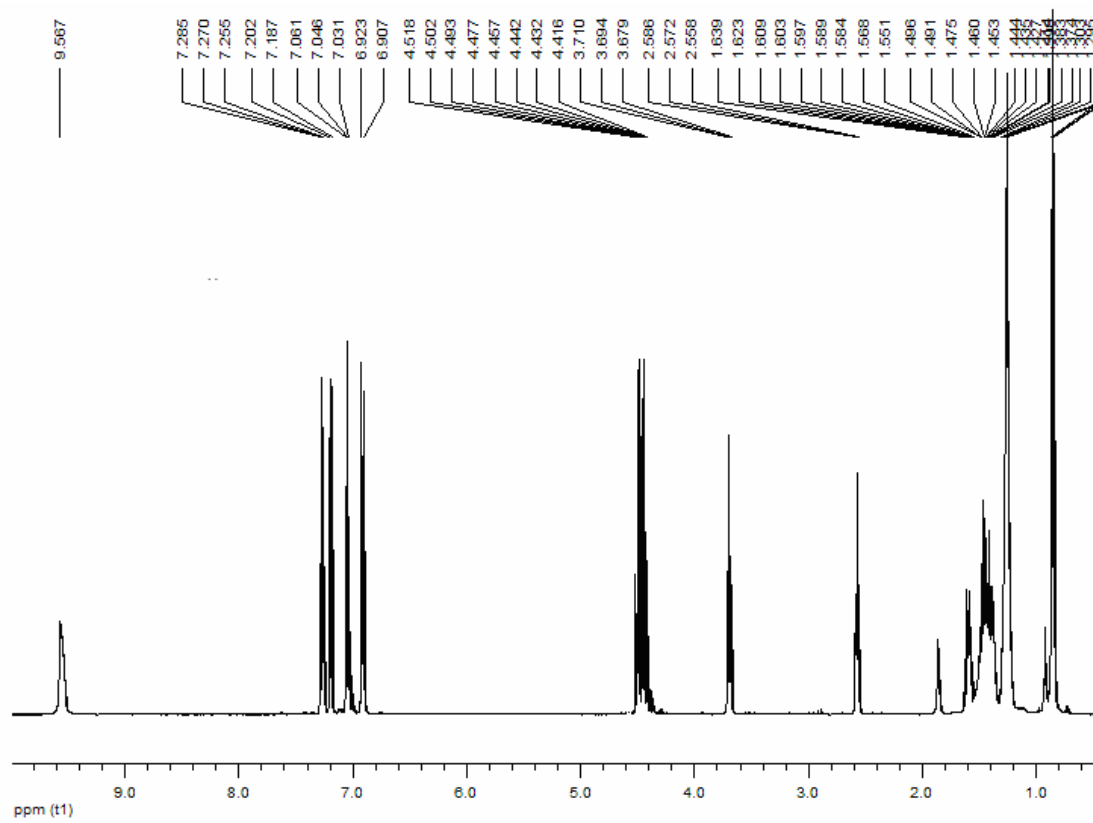
Compound 6c



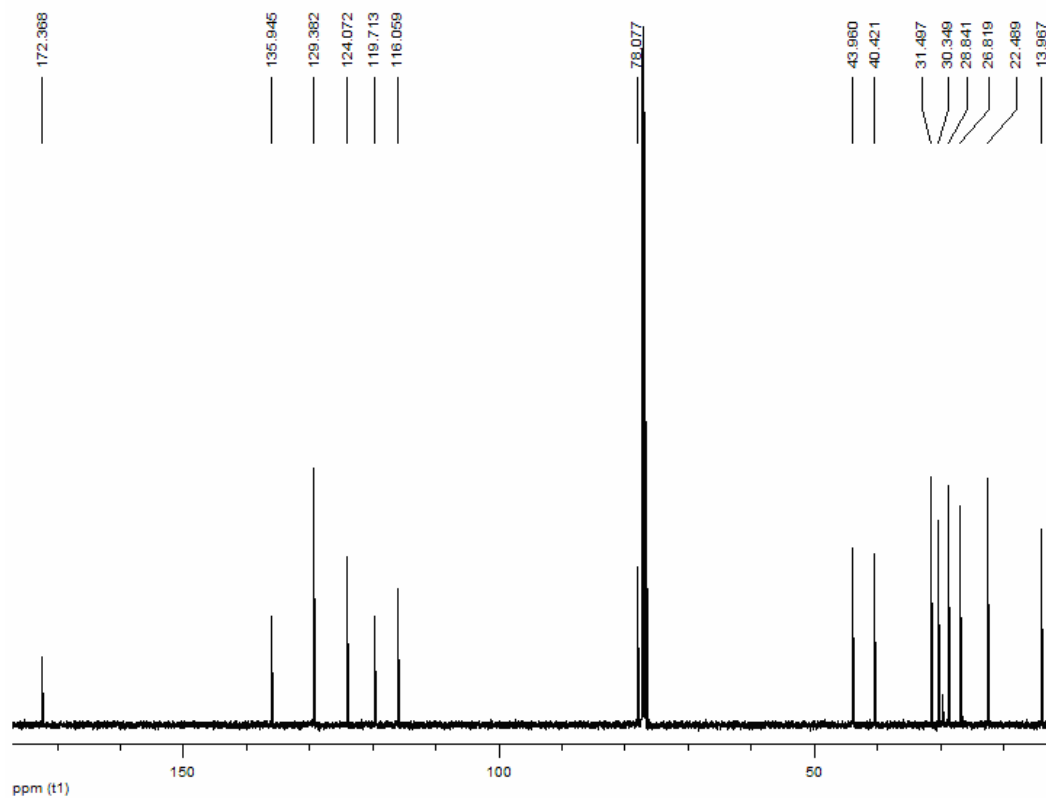
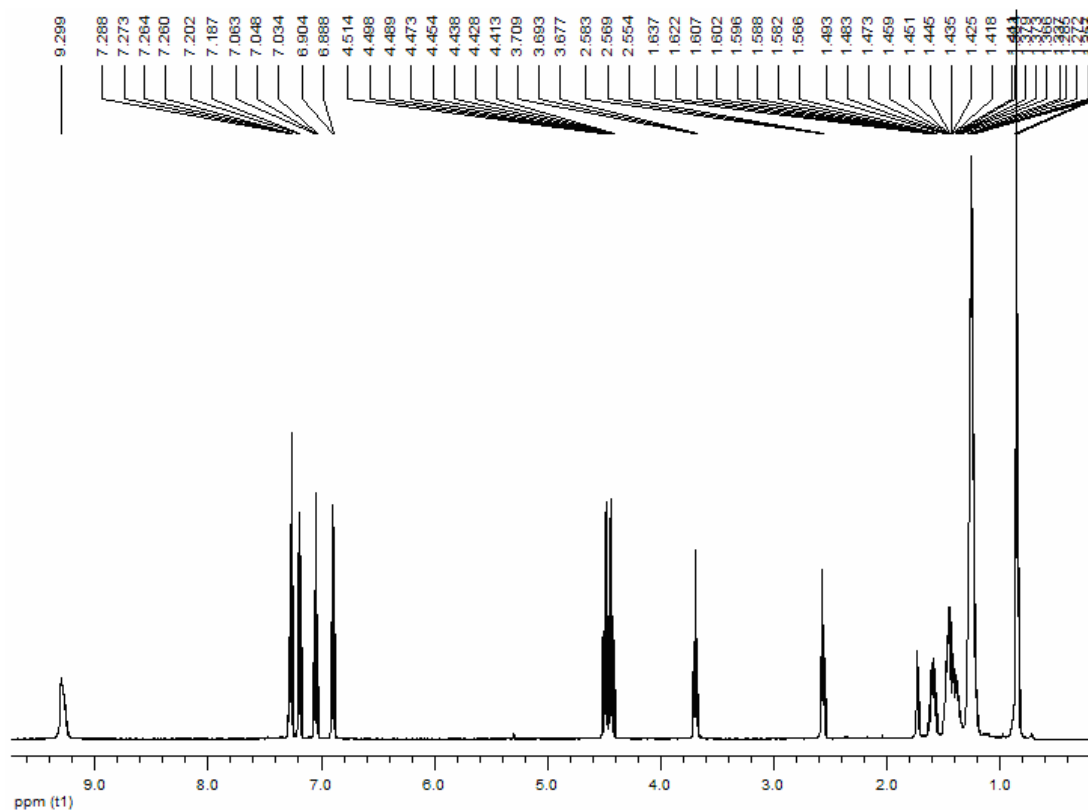
Compound 6d



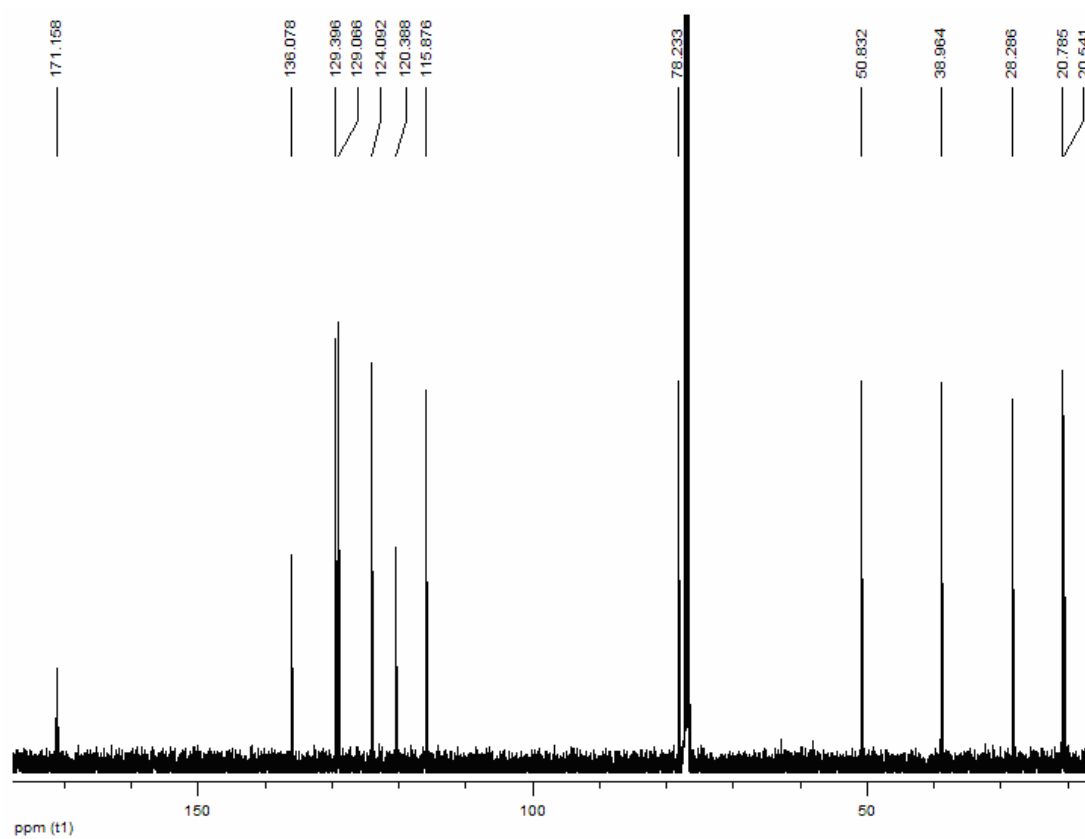
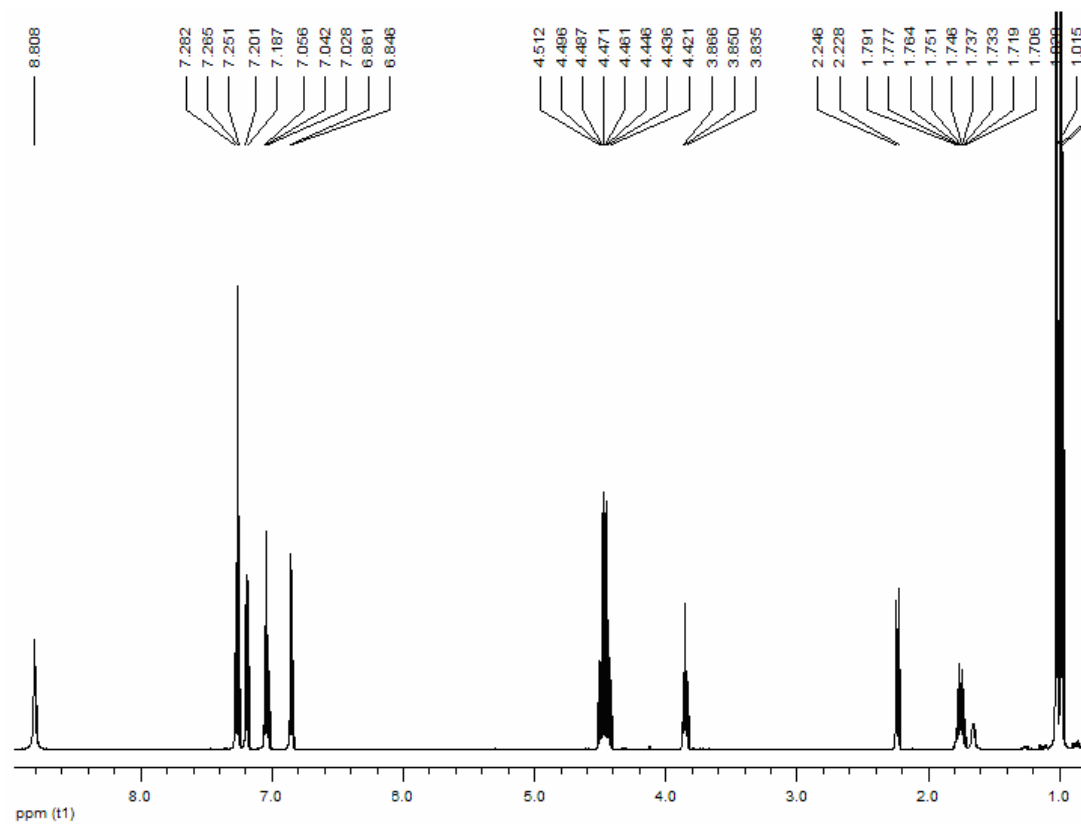
Compound 6e



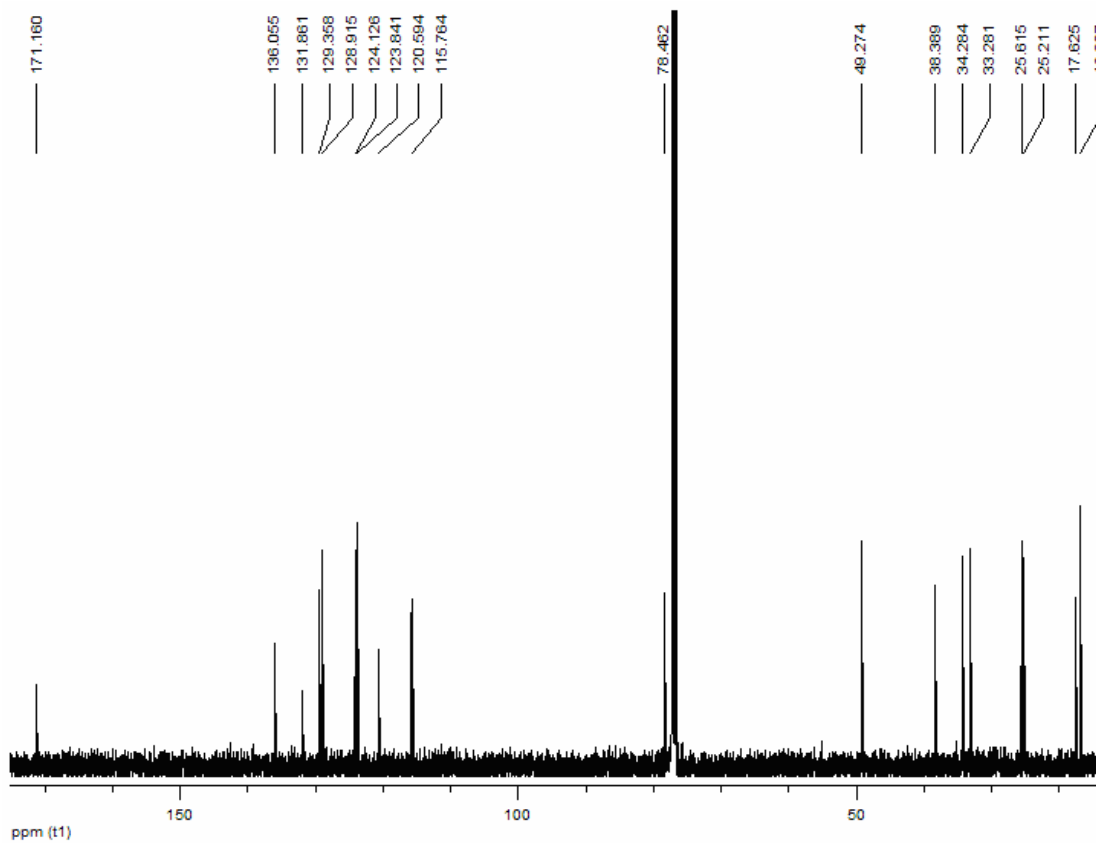
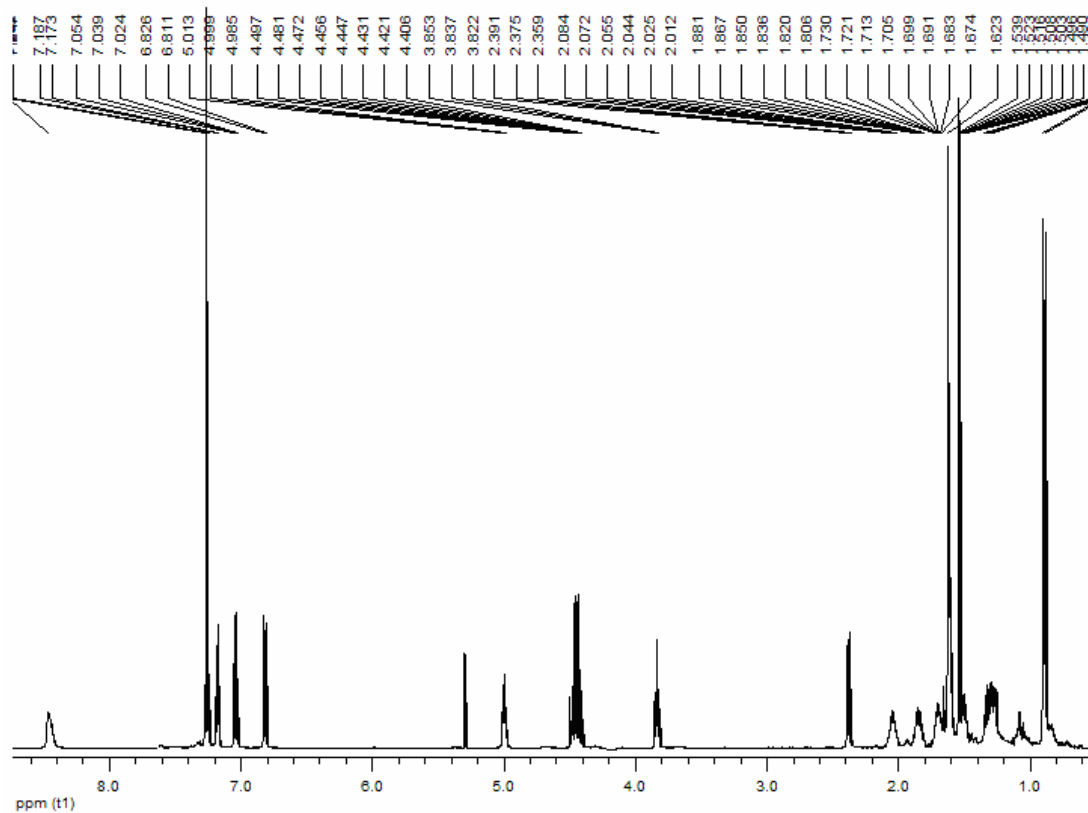
Compound 6f



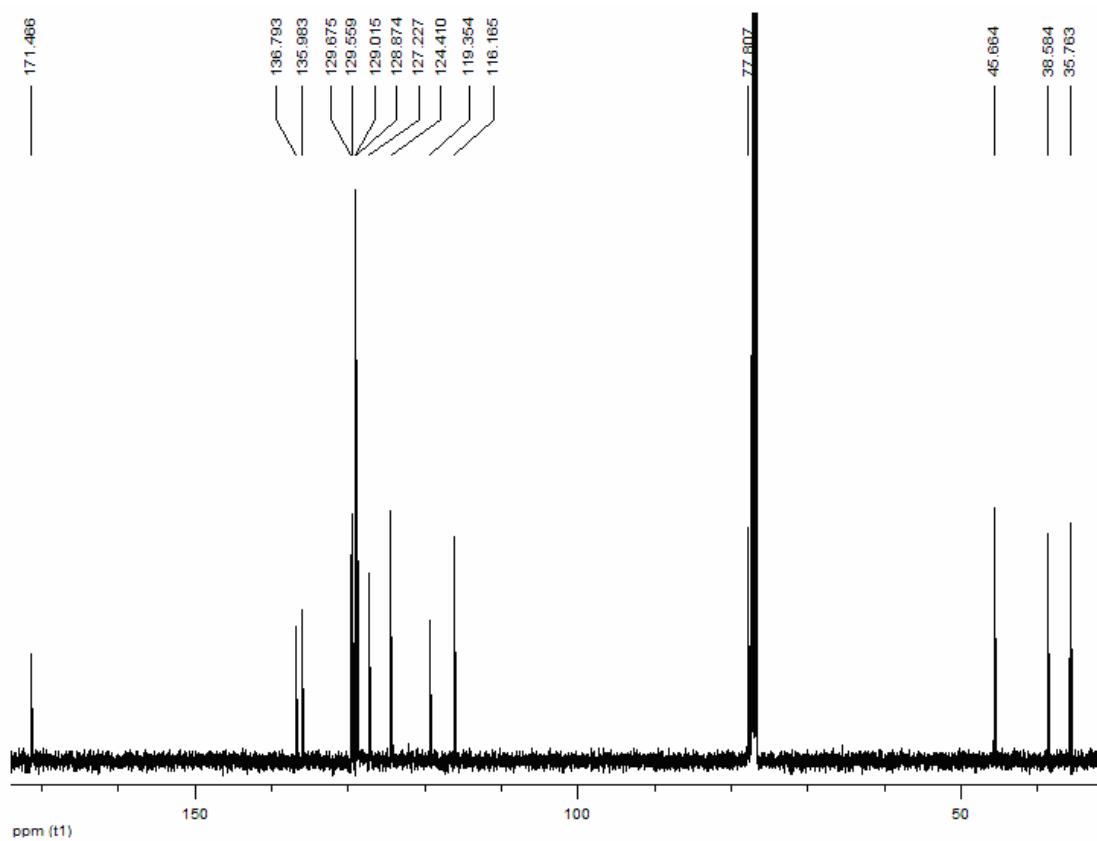
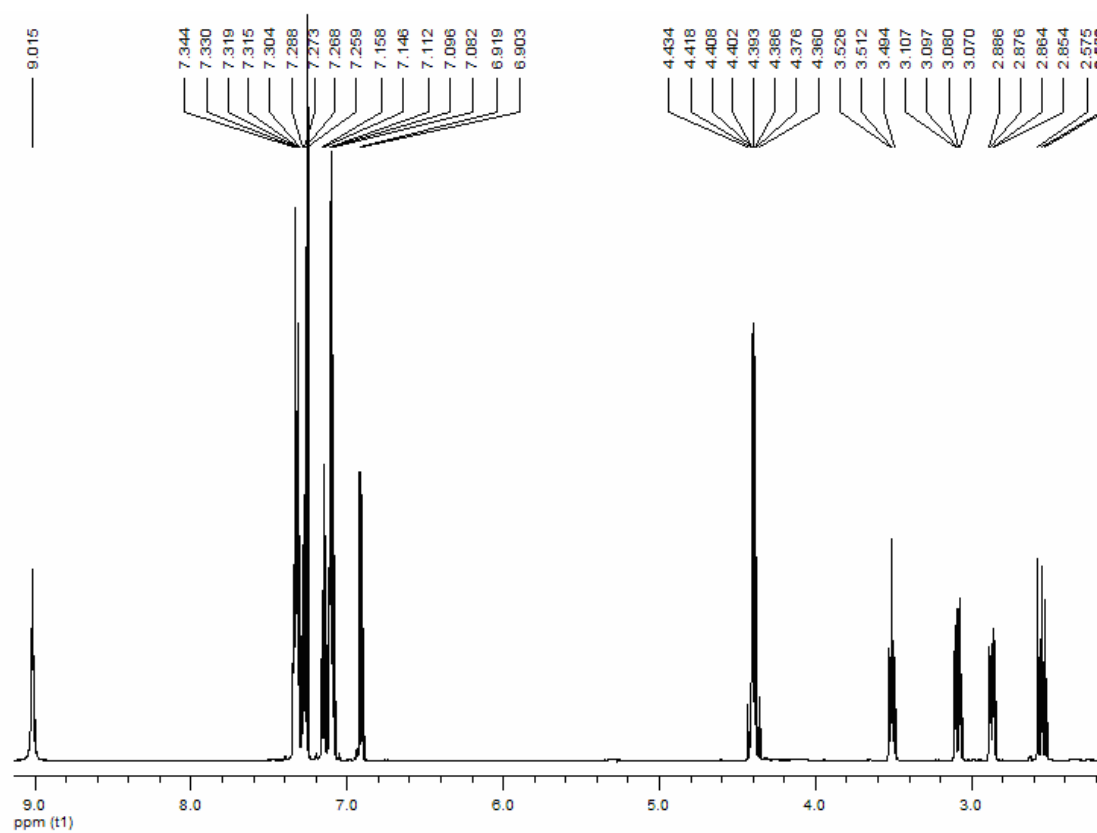
Compound 6g



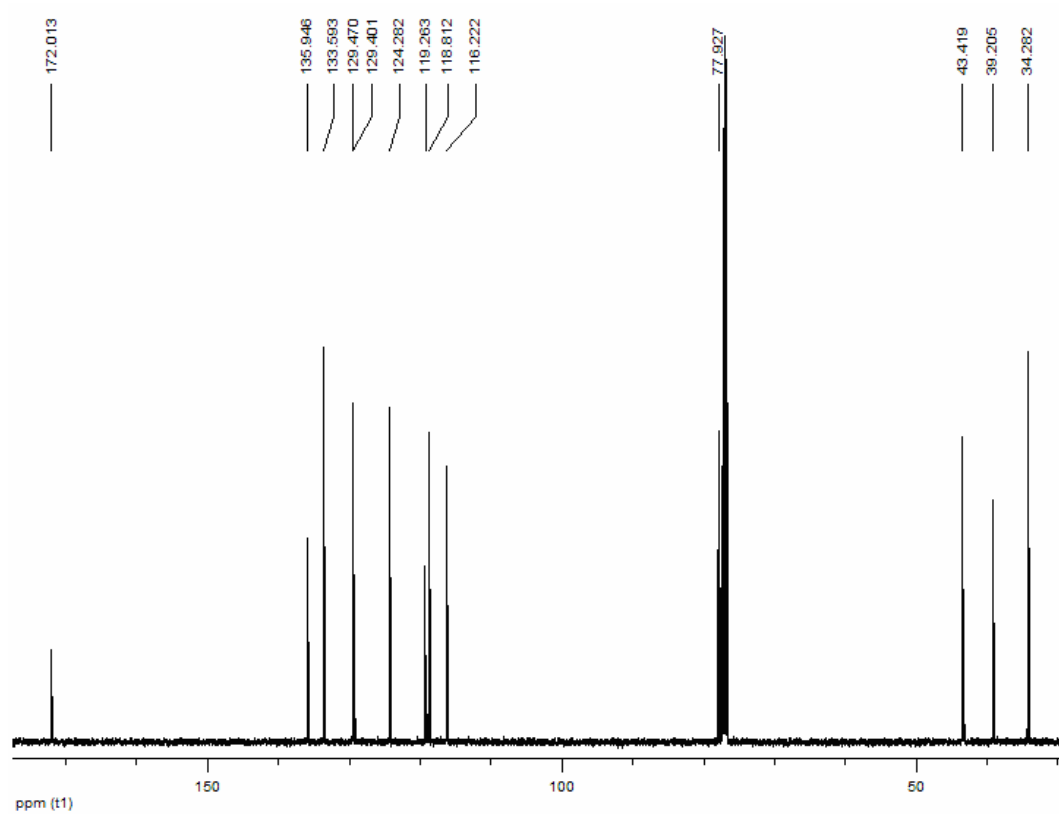
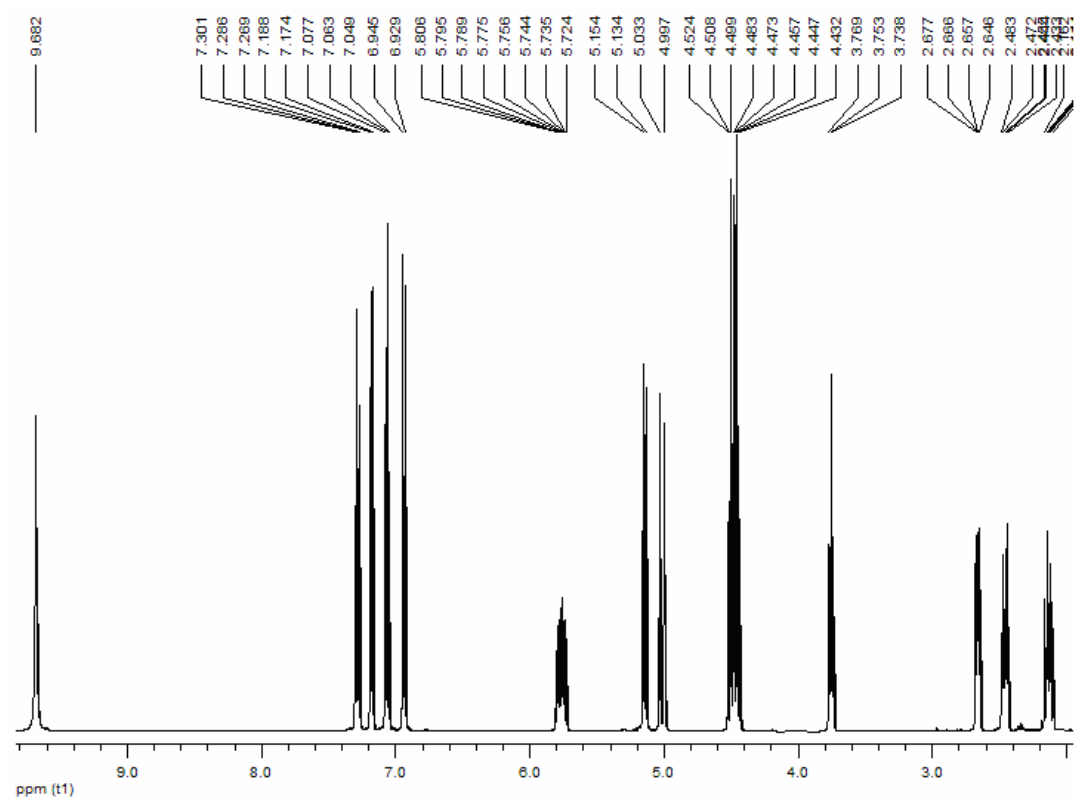
Compound 6h



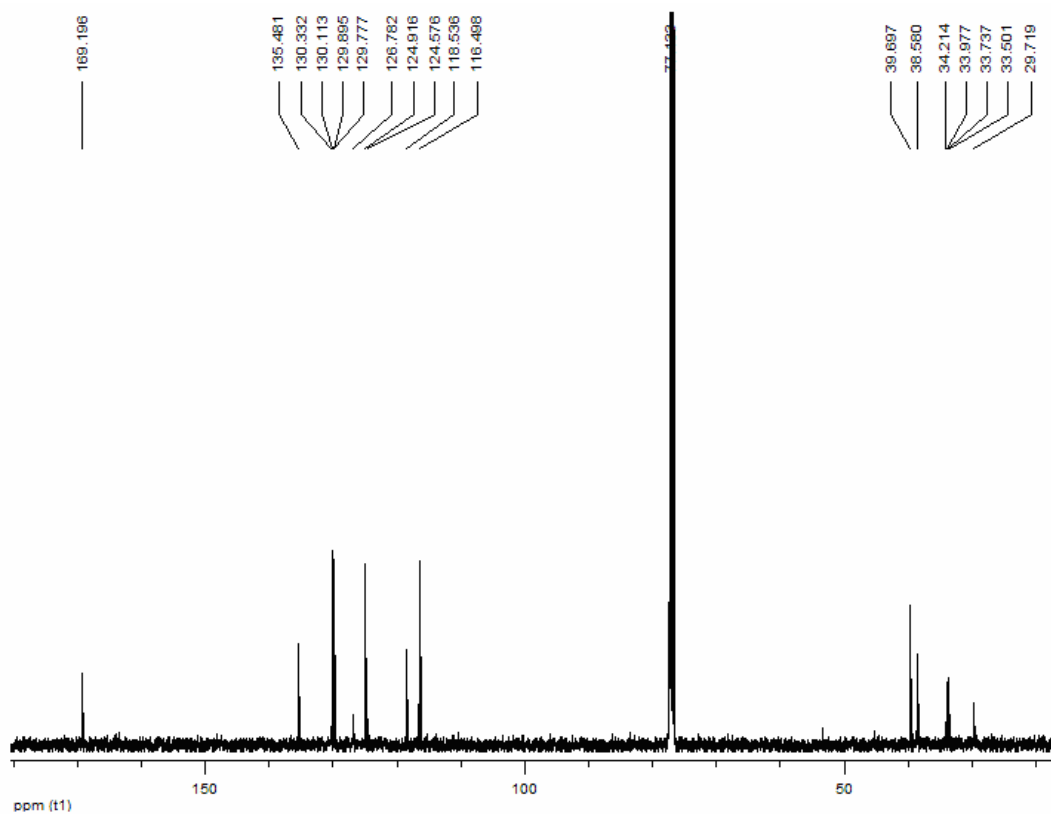
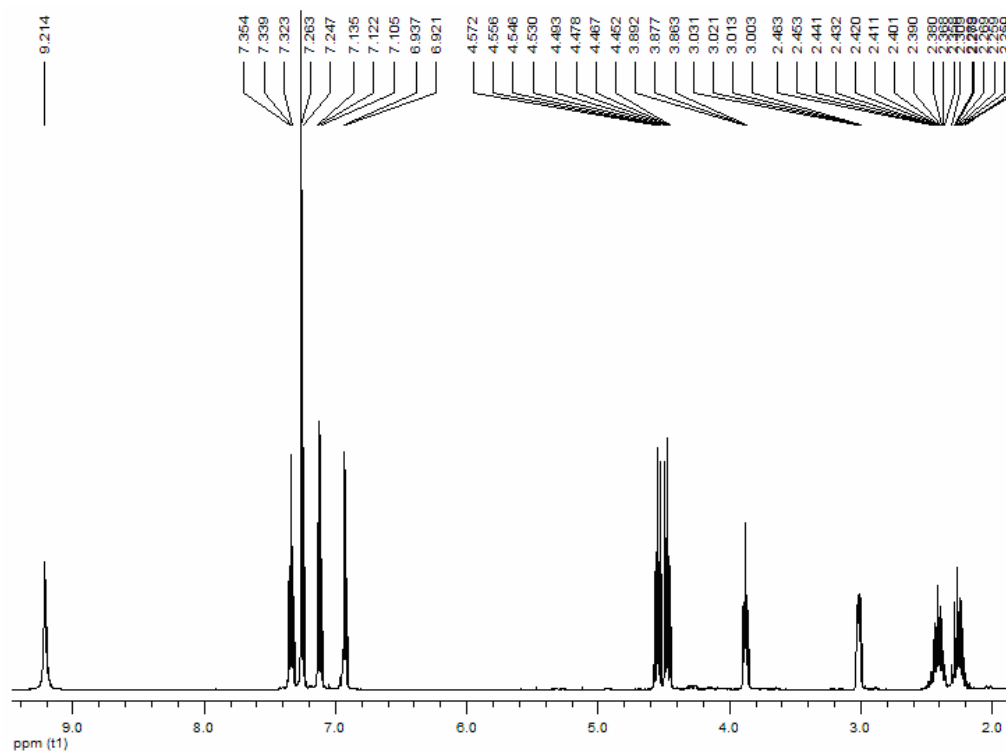
Compound 6i



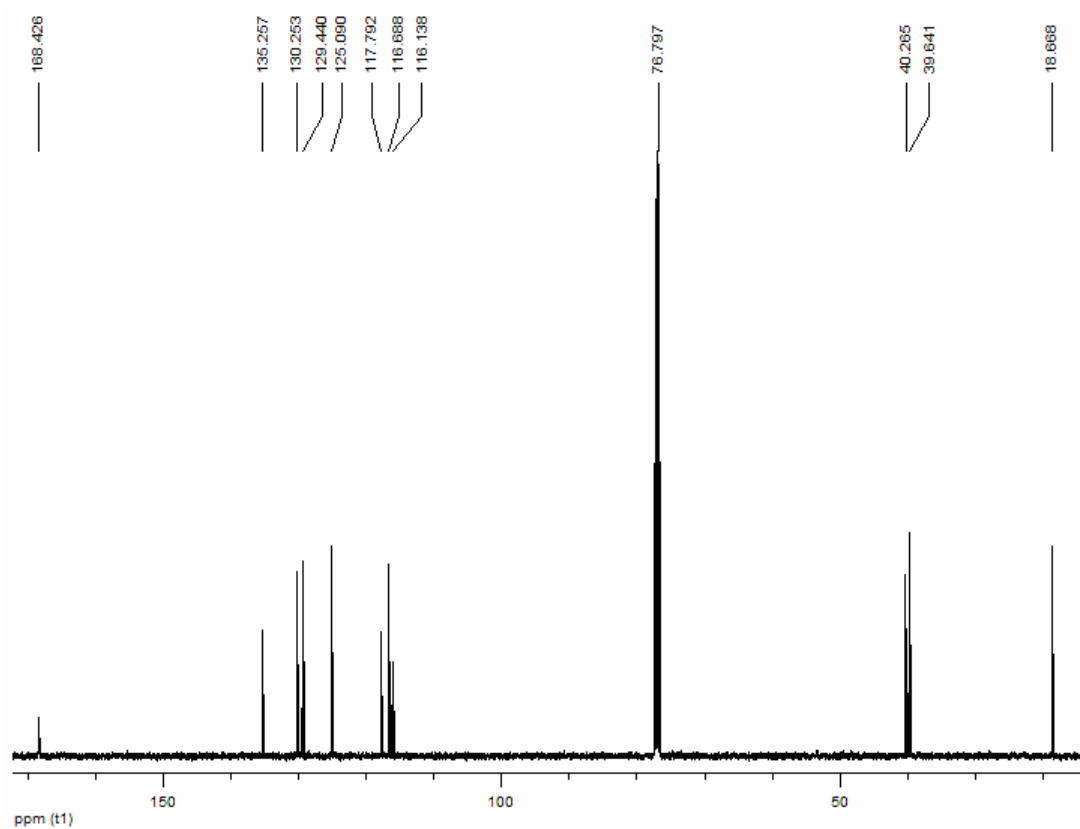
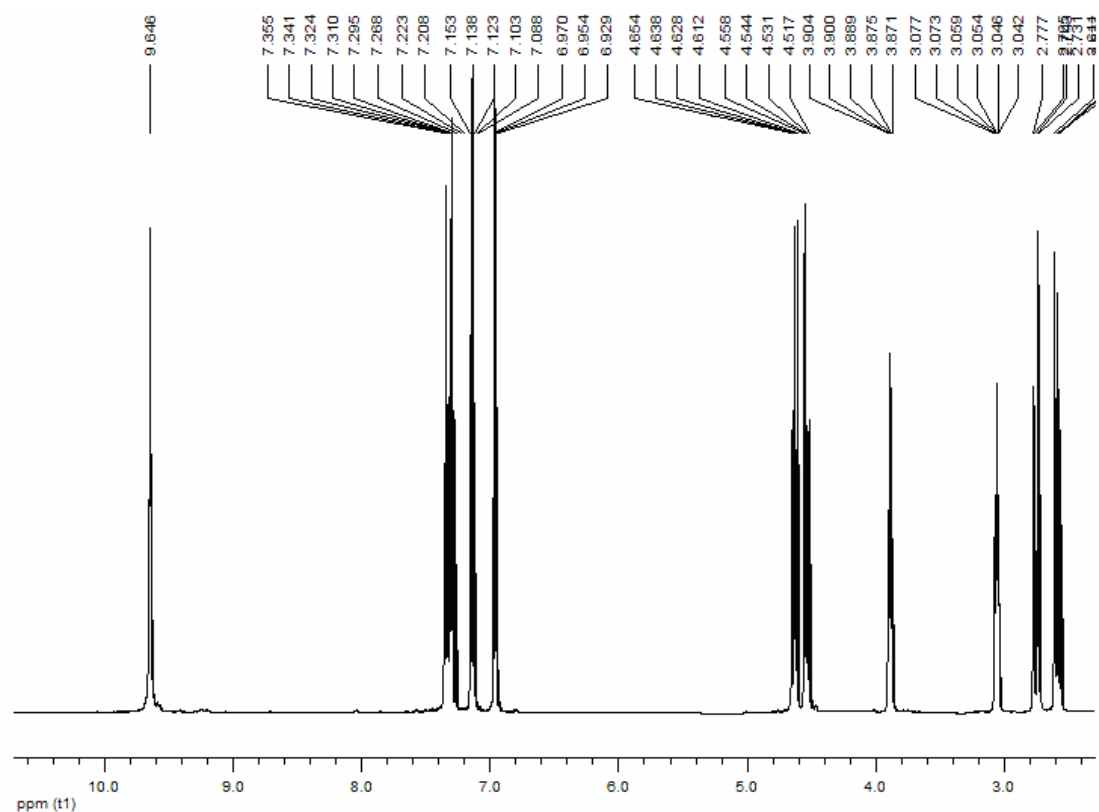
Compound 6j



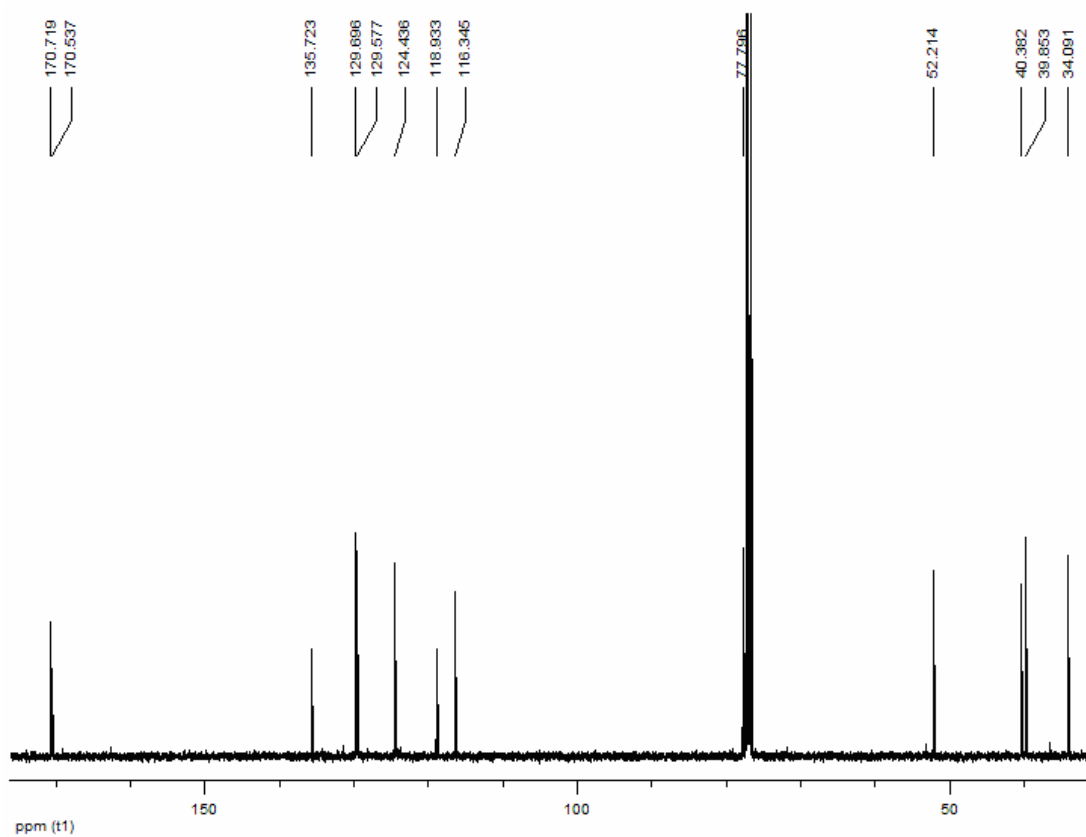
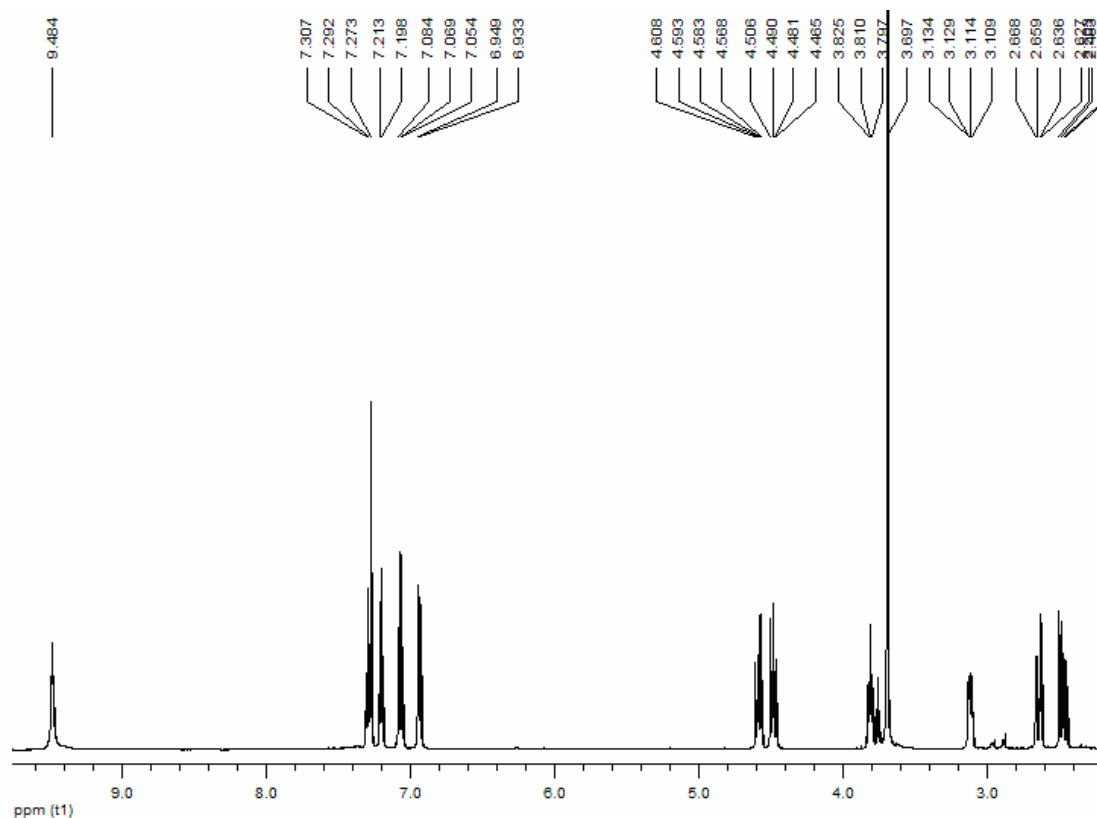
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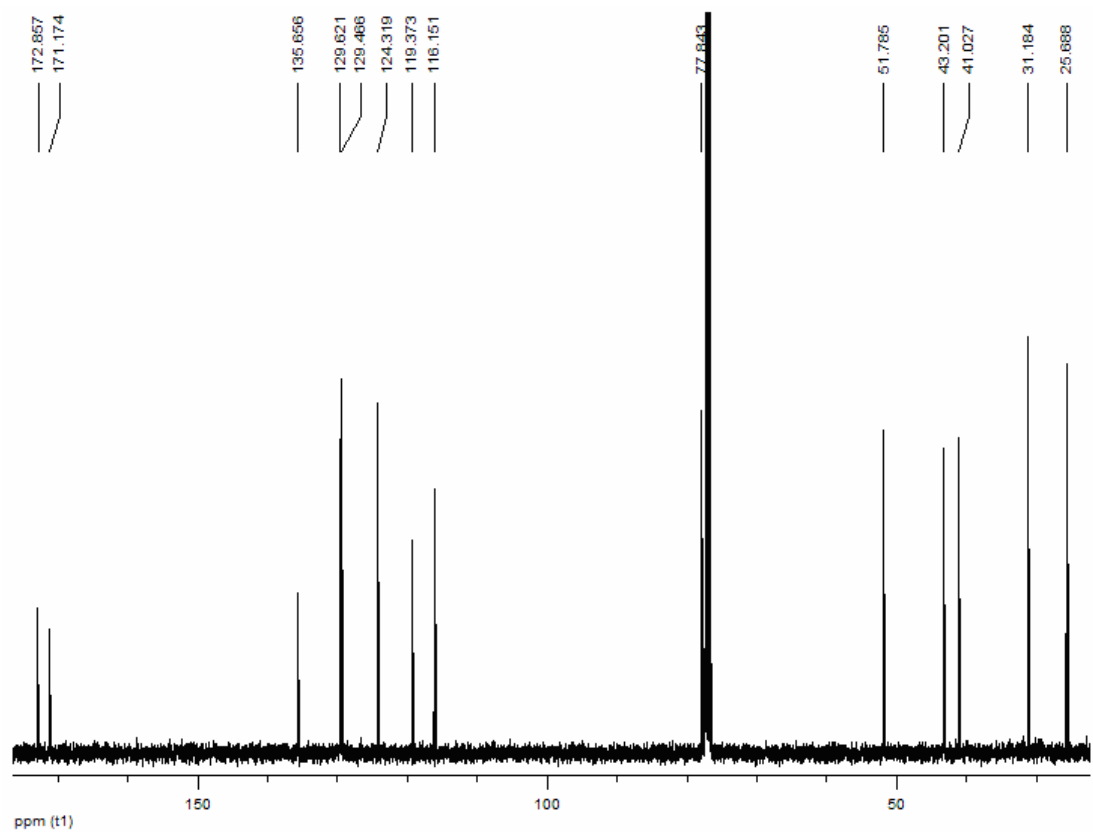
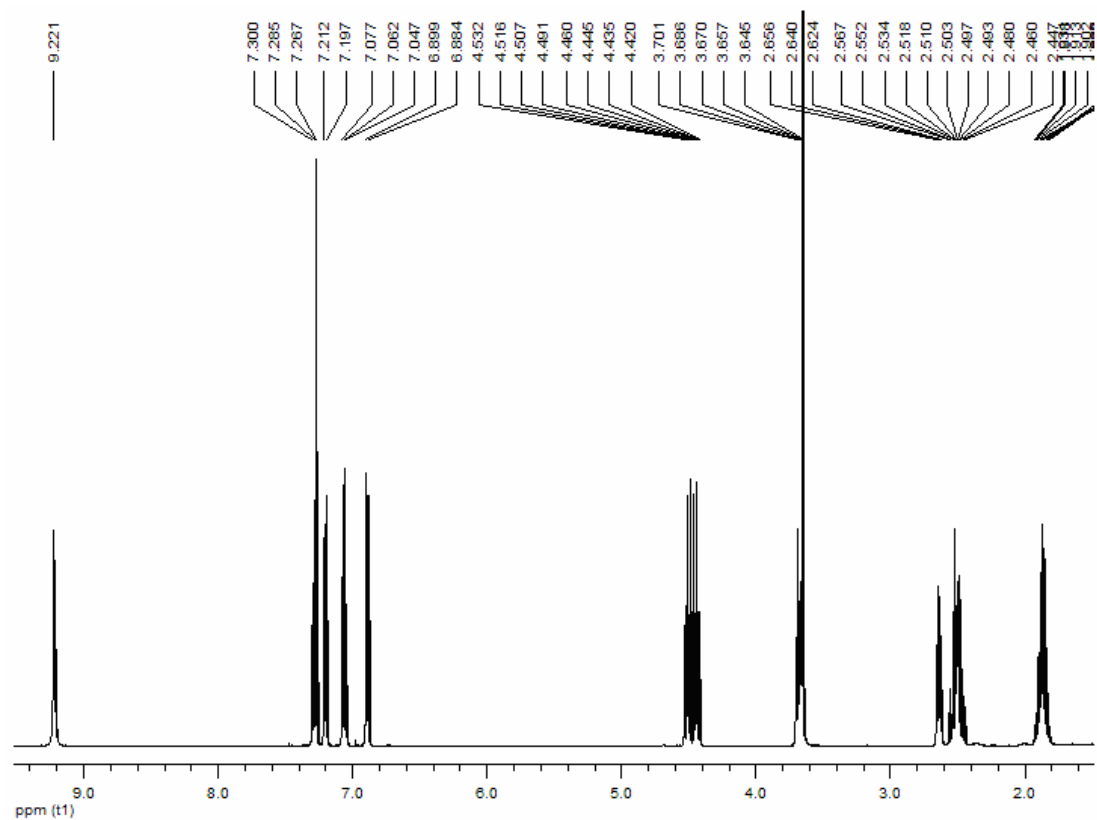
Compound 6l



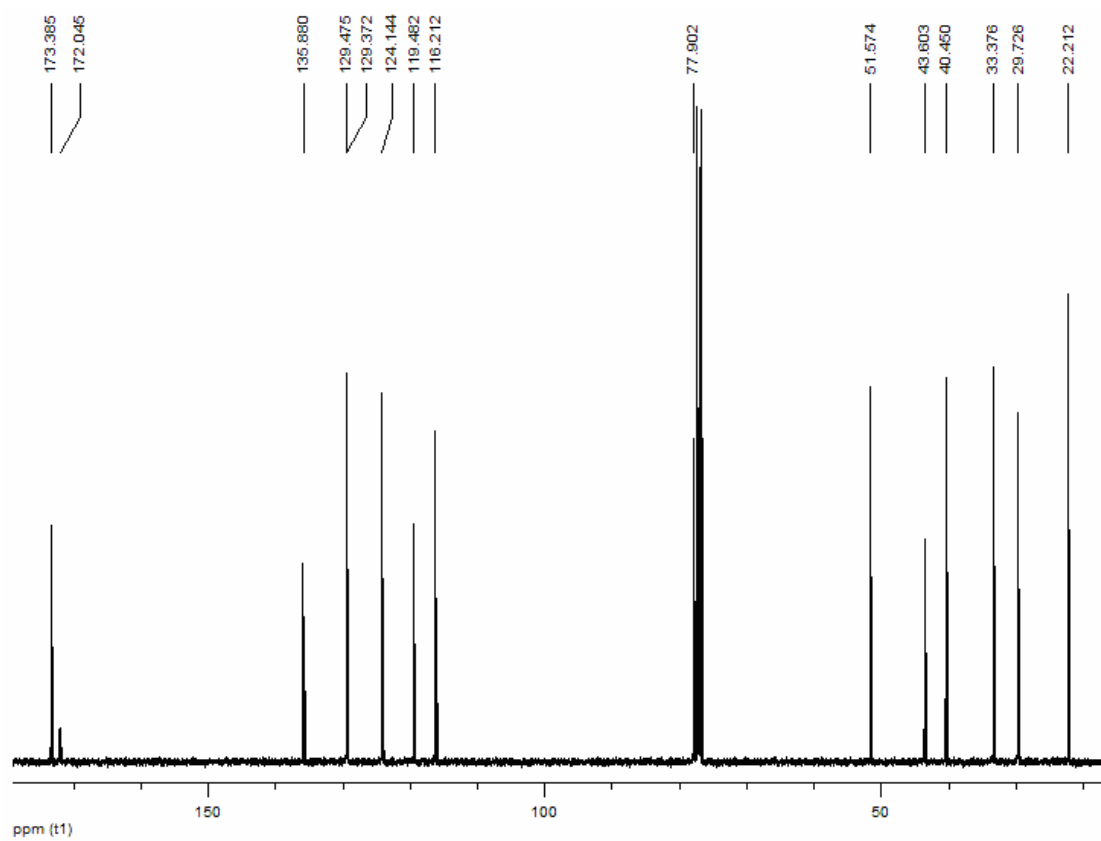
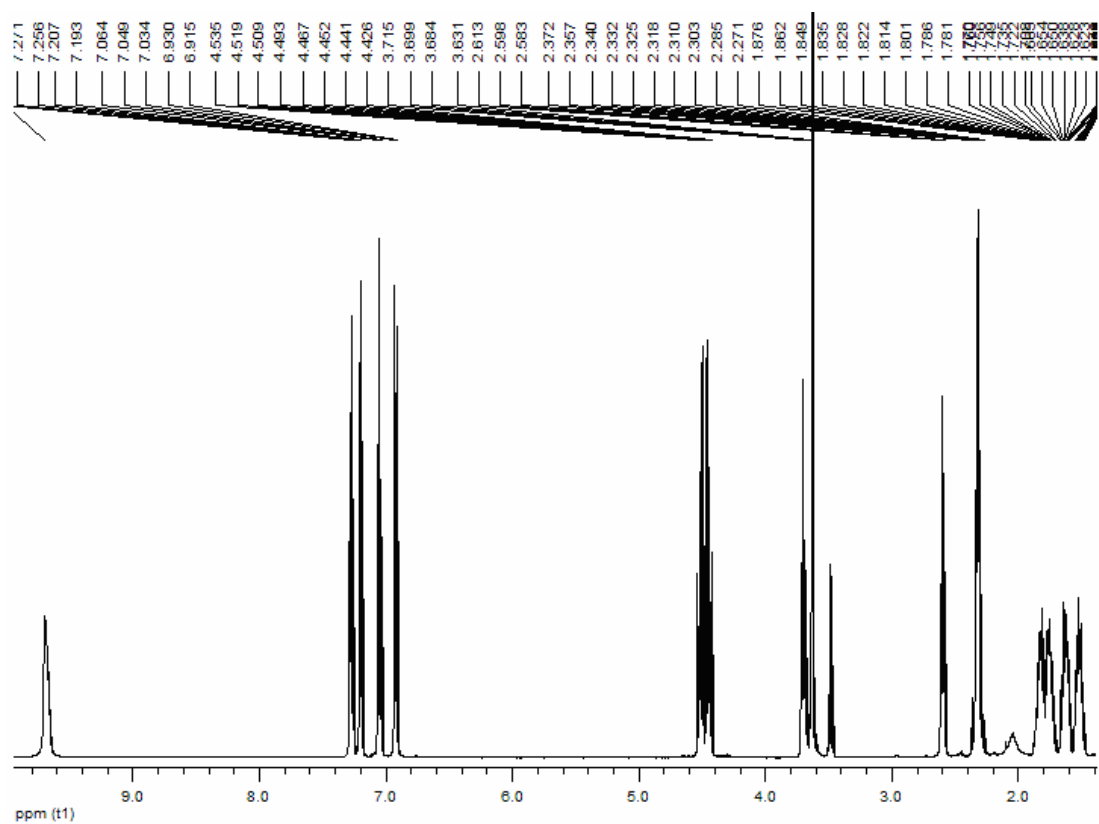
Compound 6m



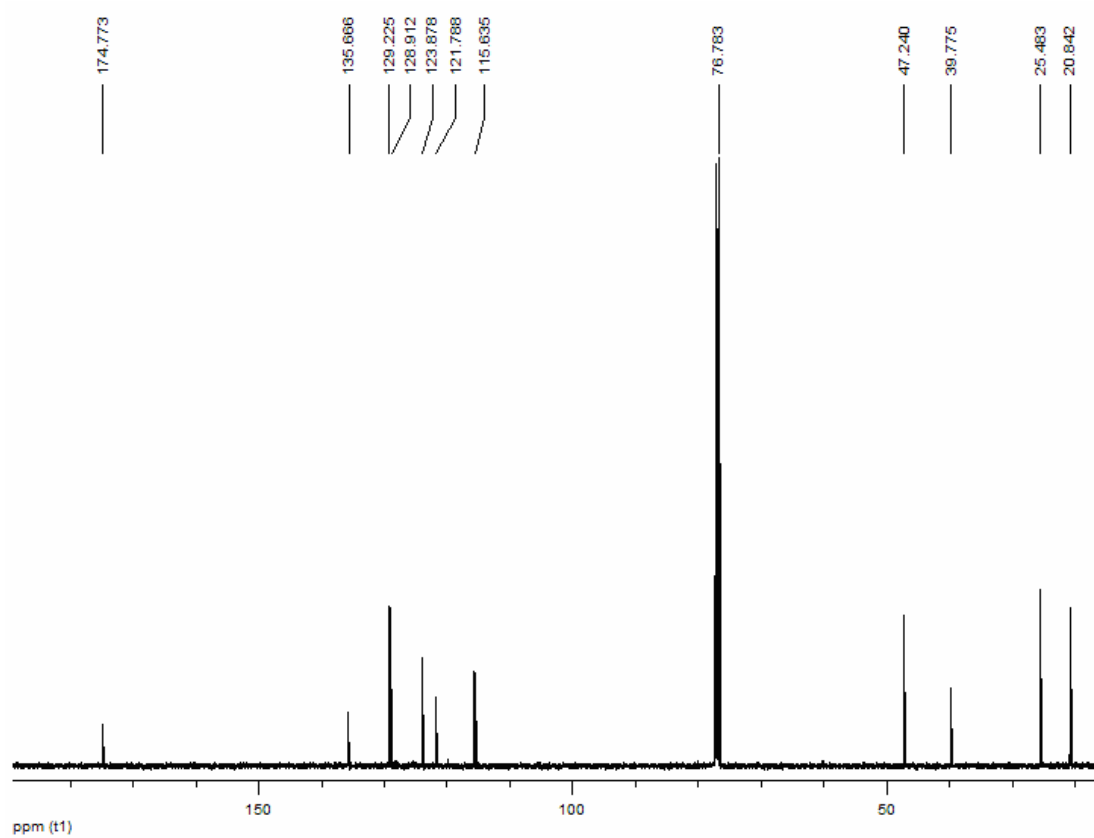
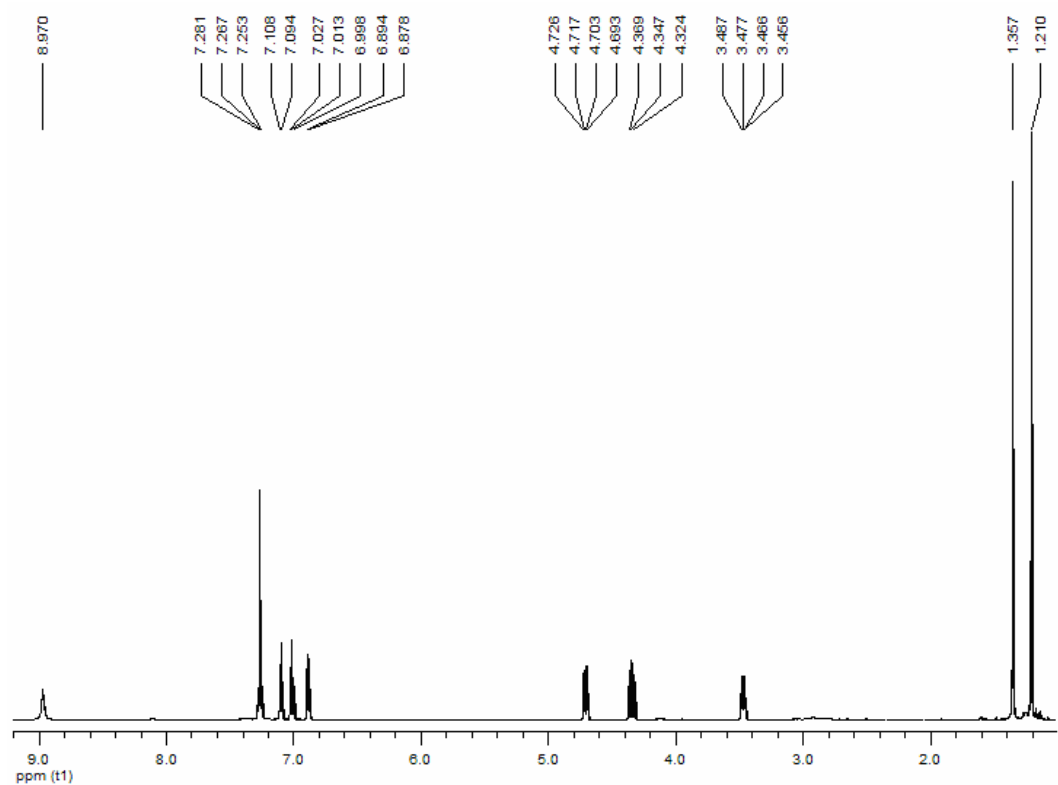
Compound 6n



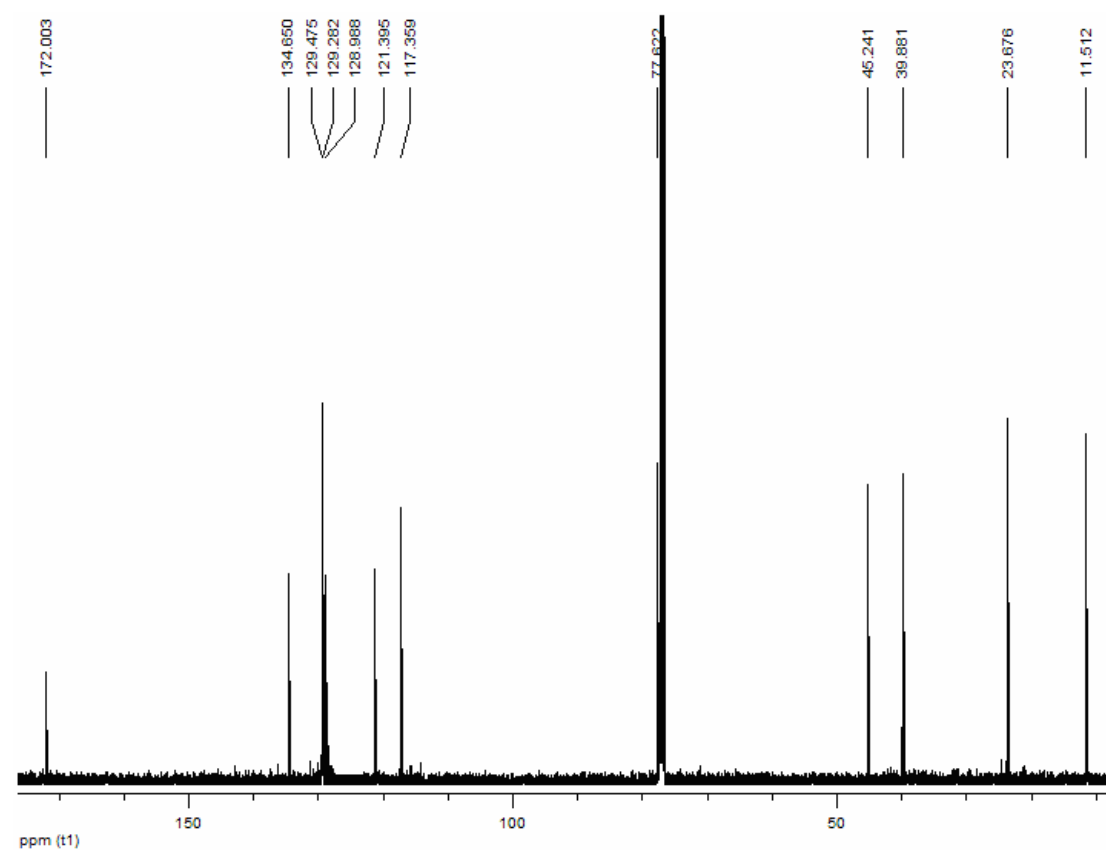
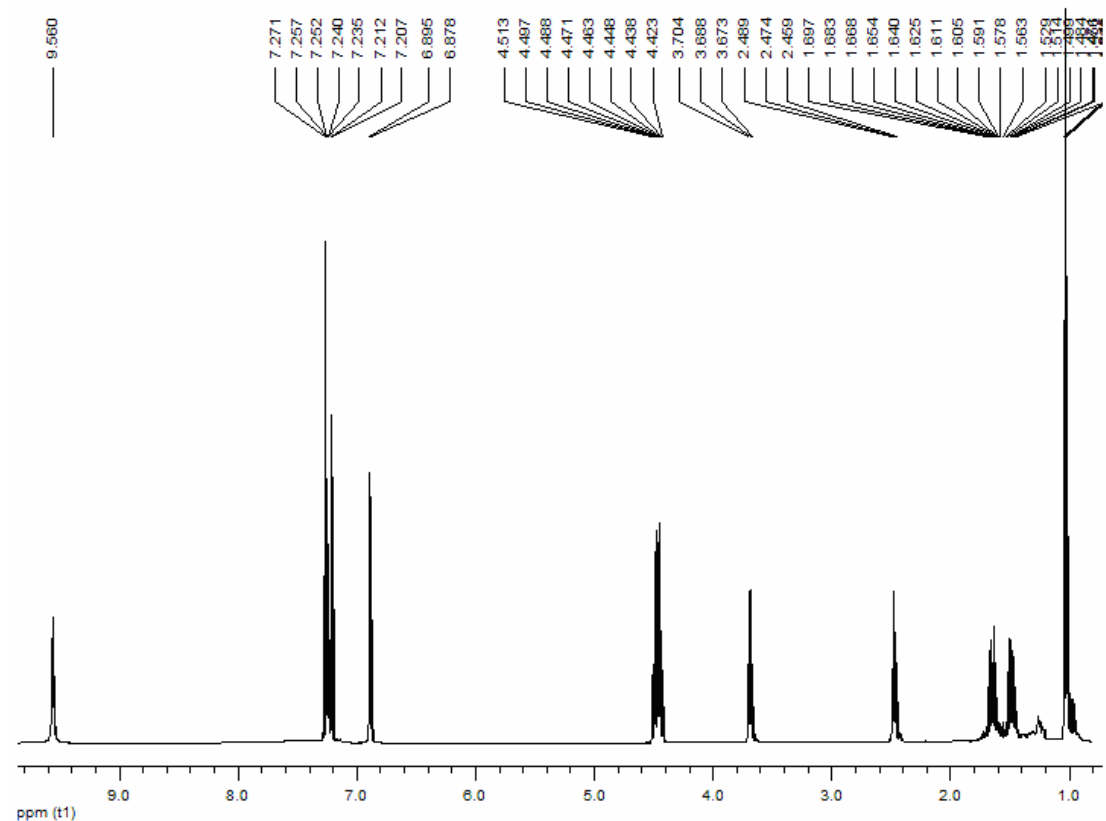
Compound 6o



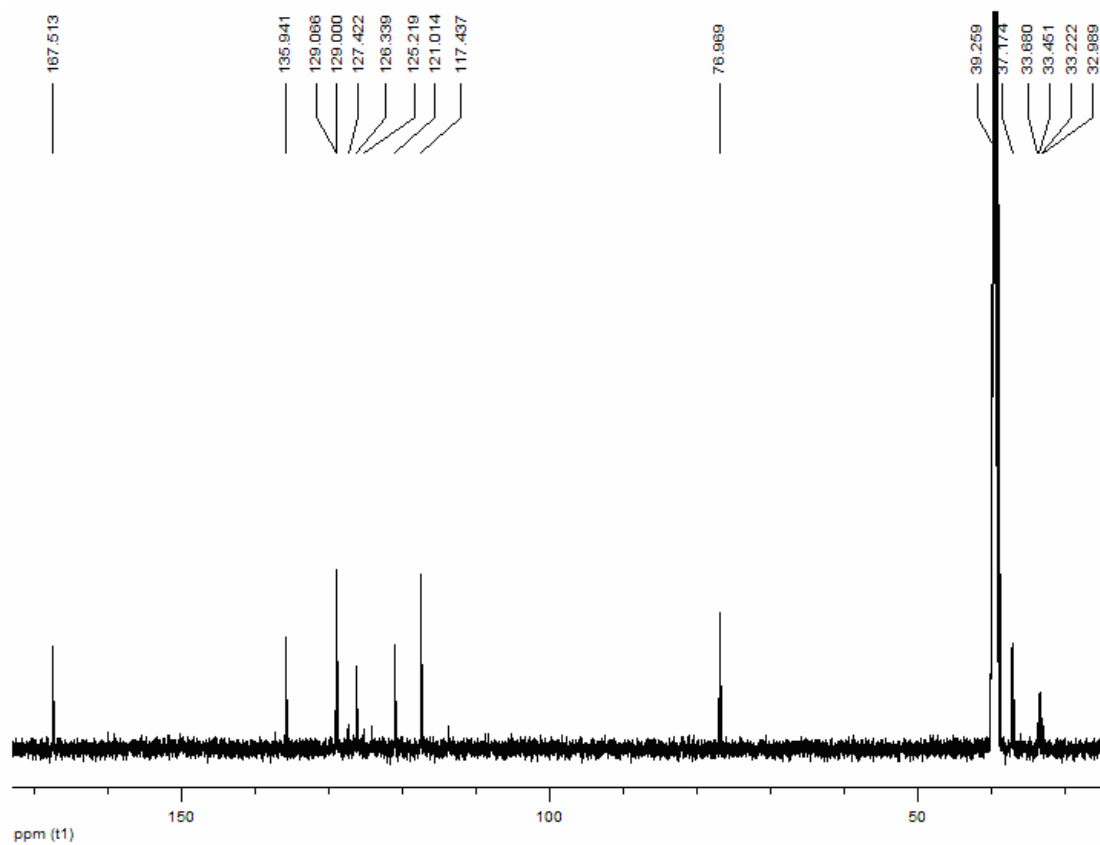
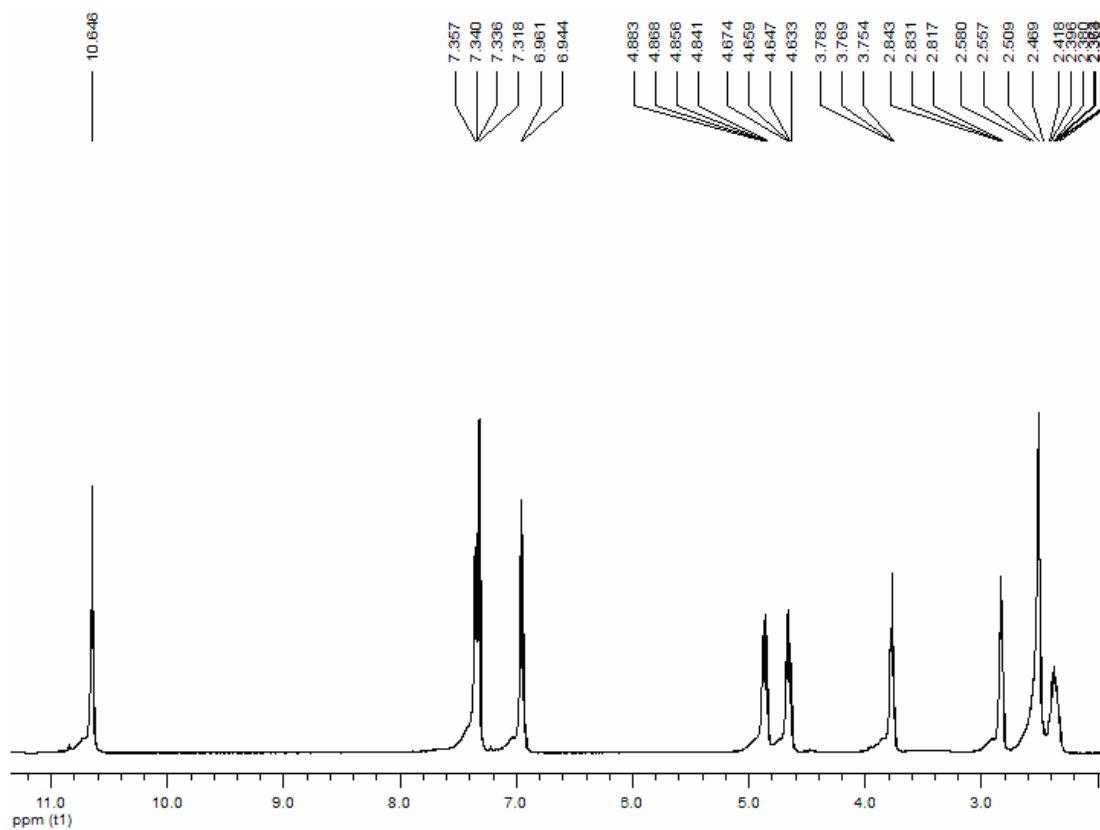
Compound 6p



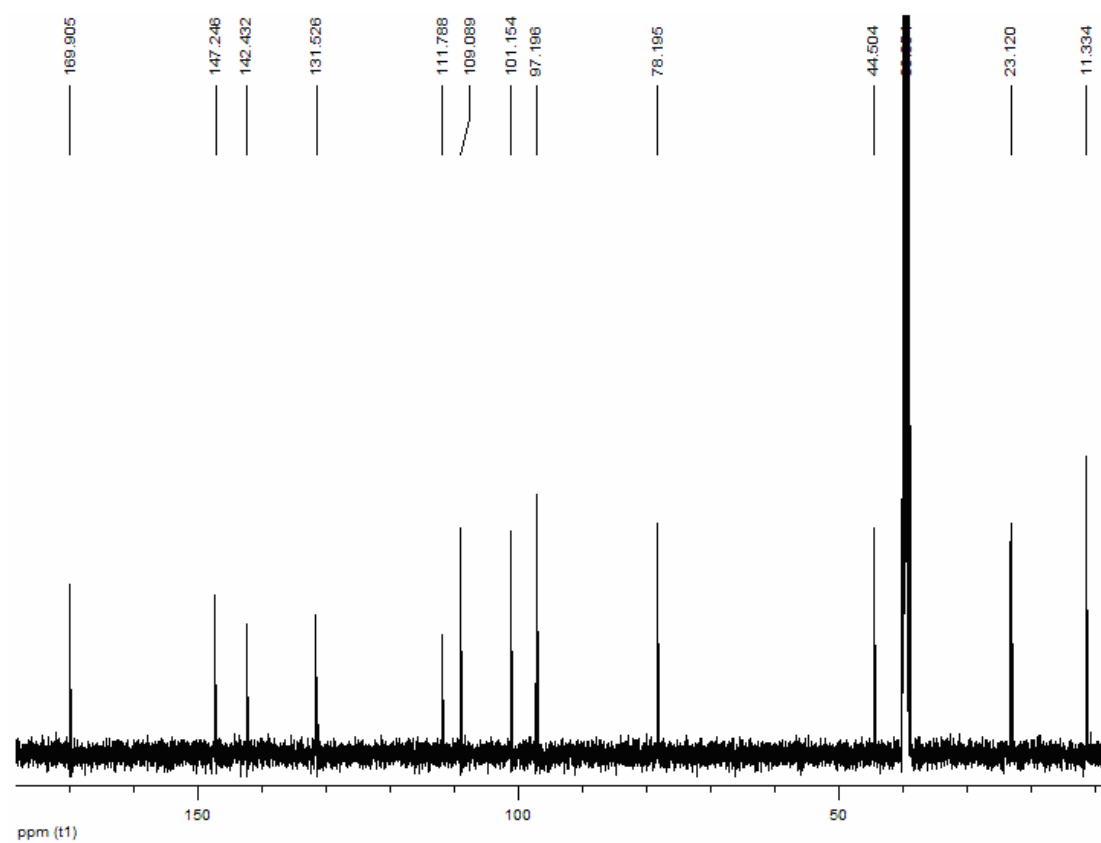
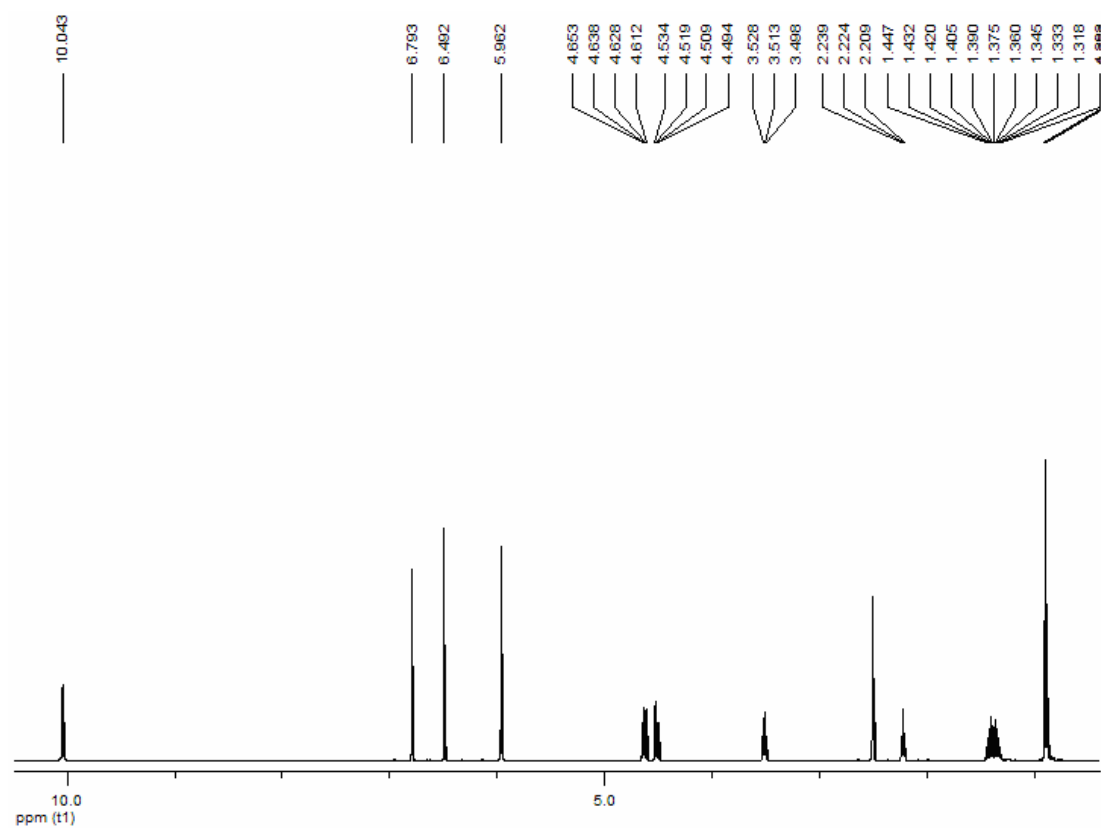
Compound 6q



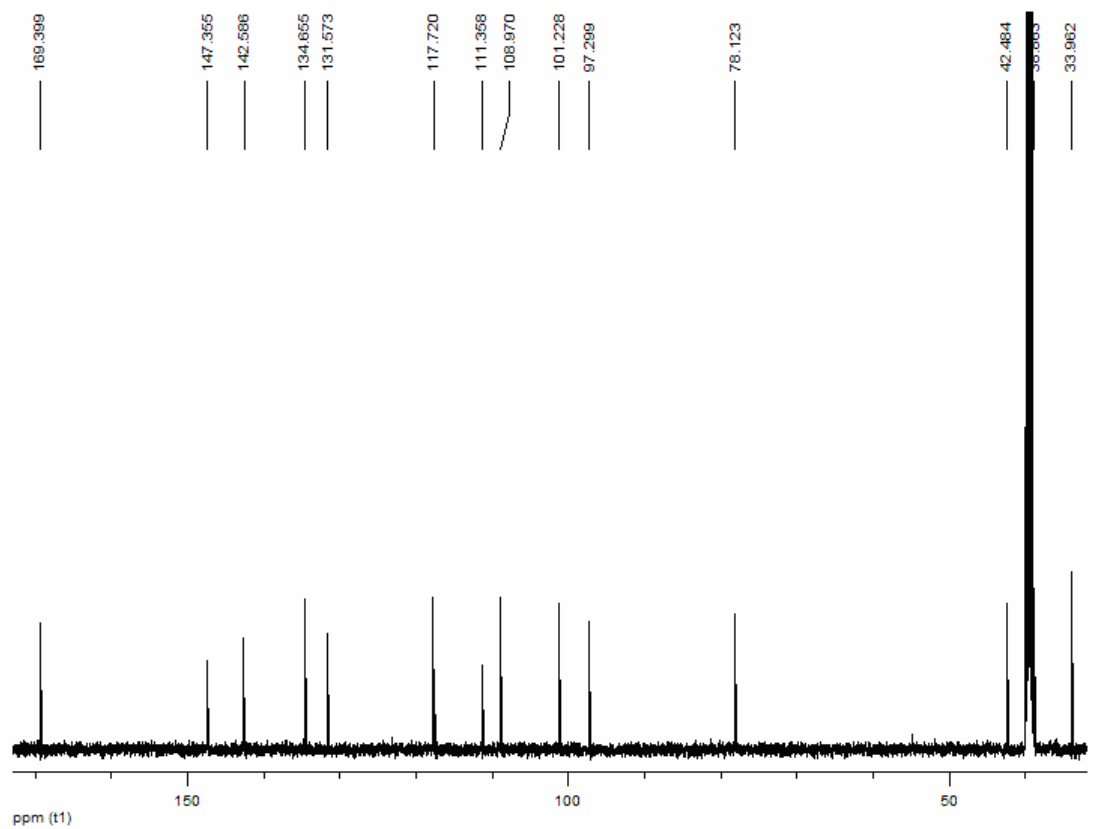
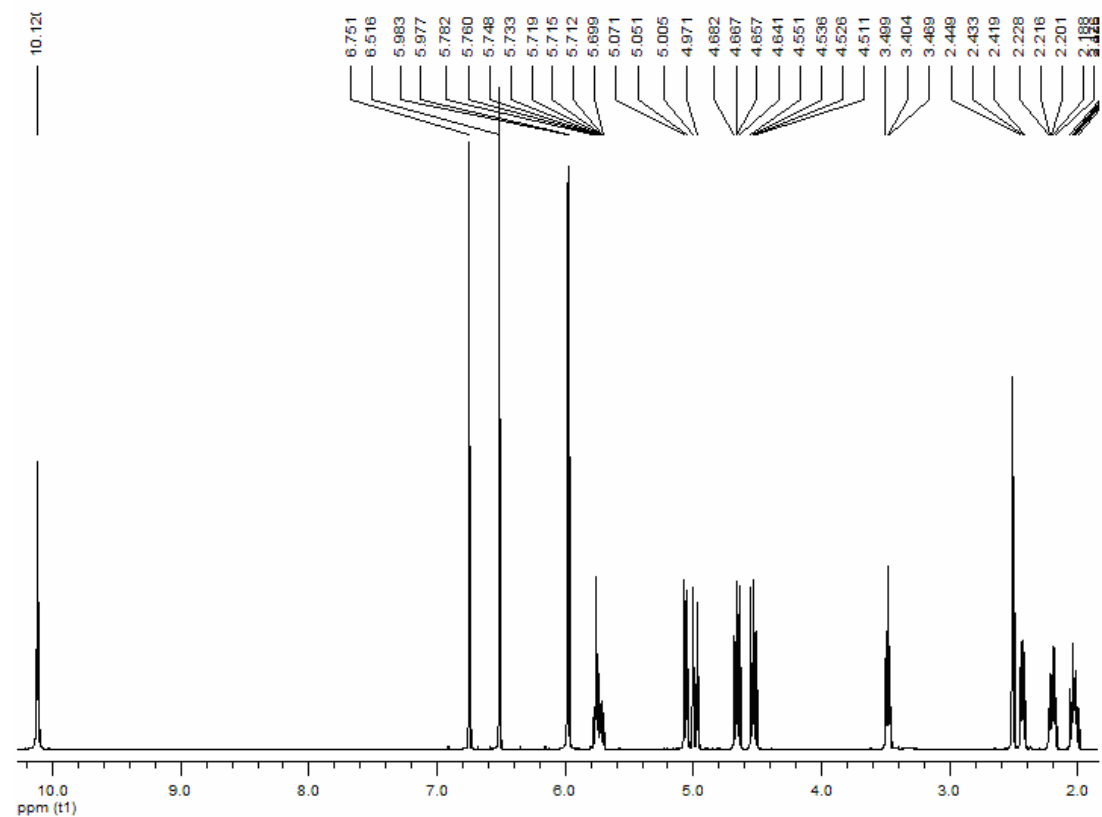
Compound 6r



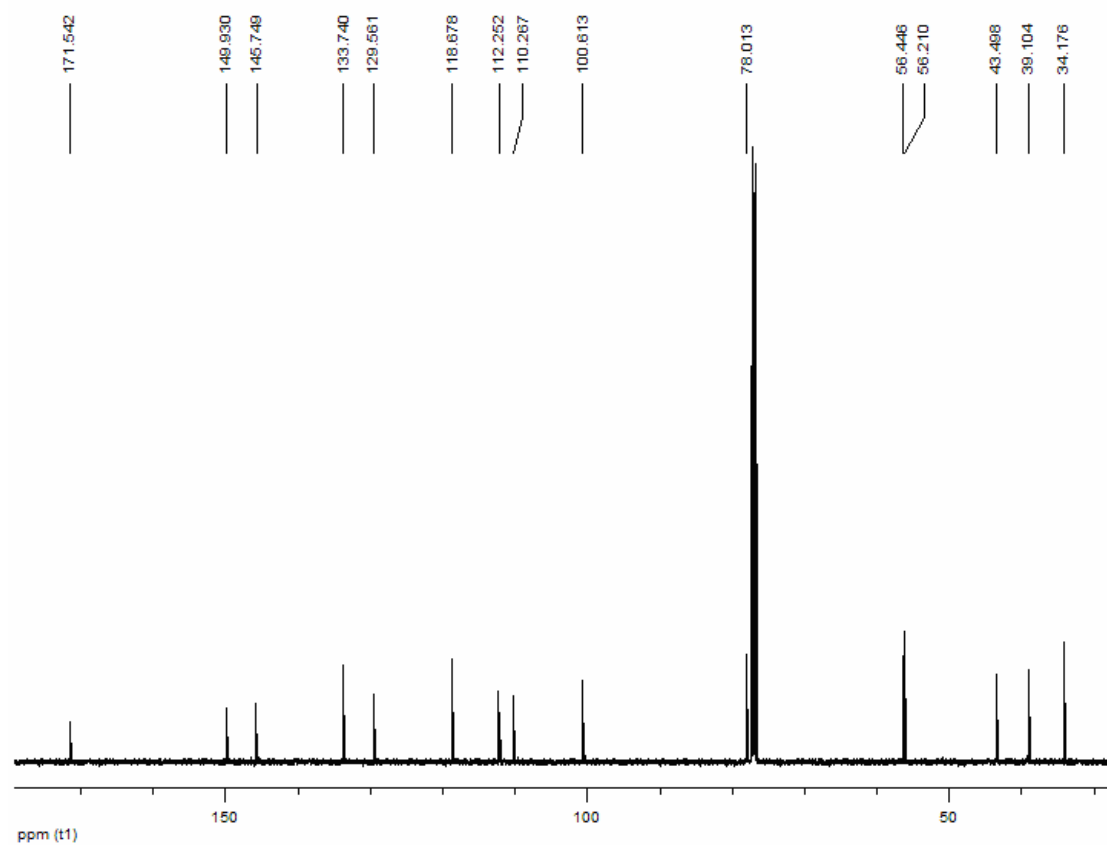
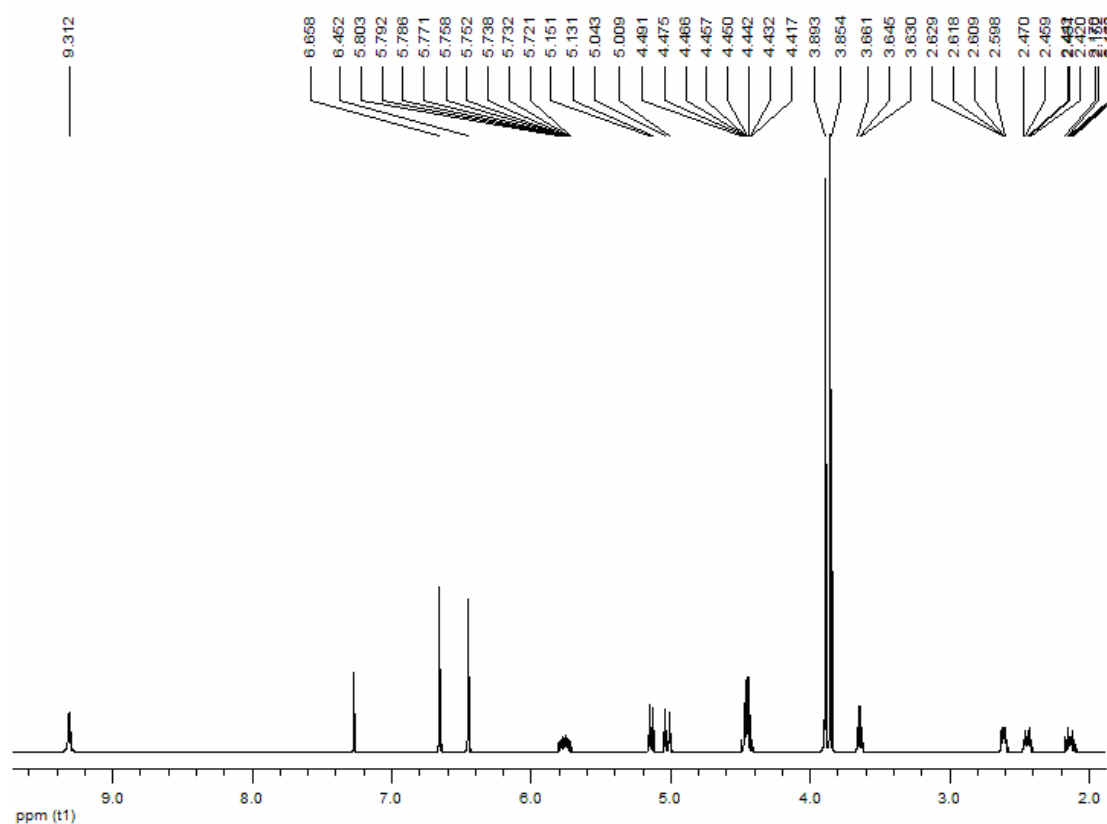
Compound 6s



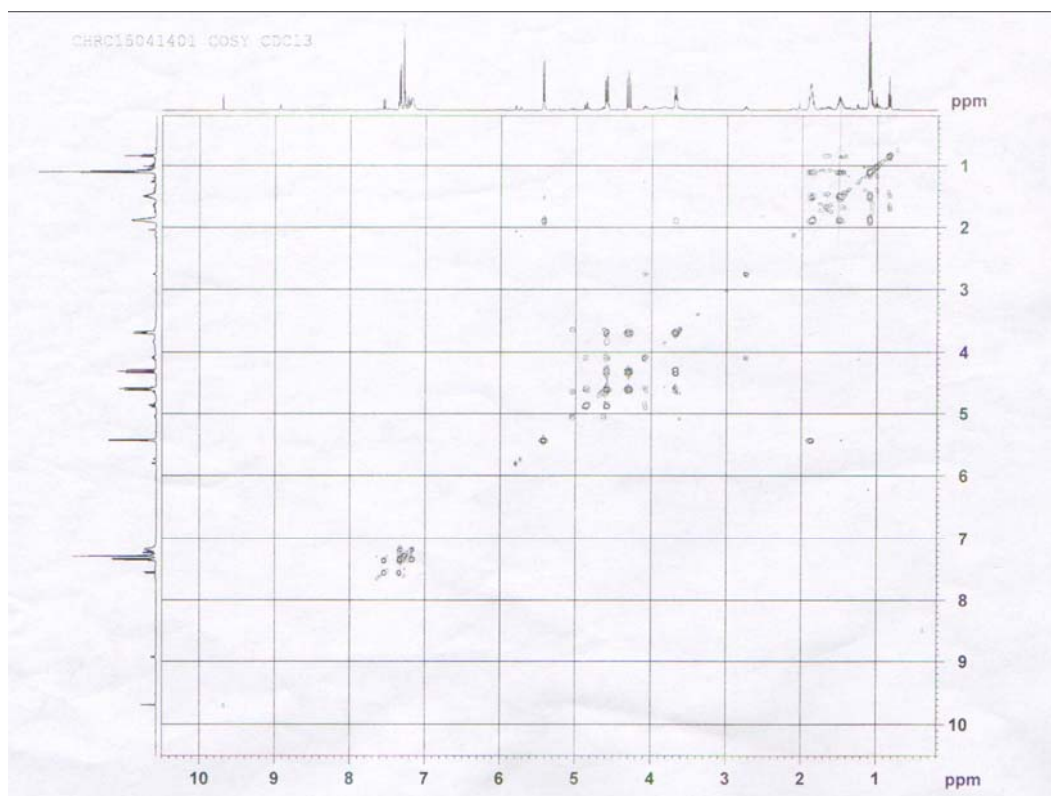
Compound 6t



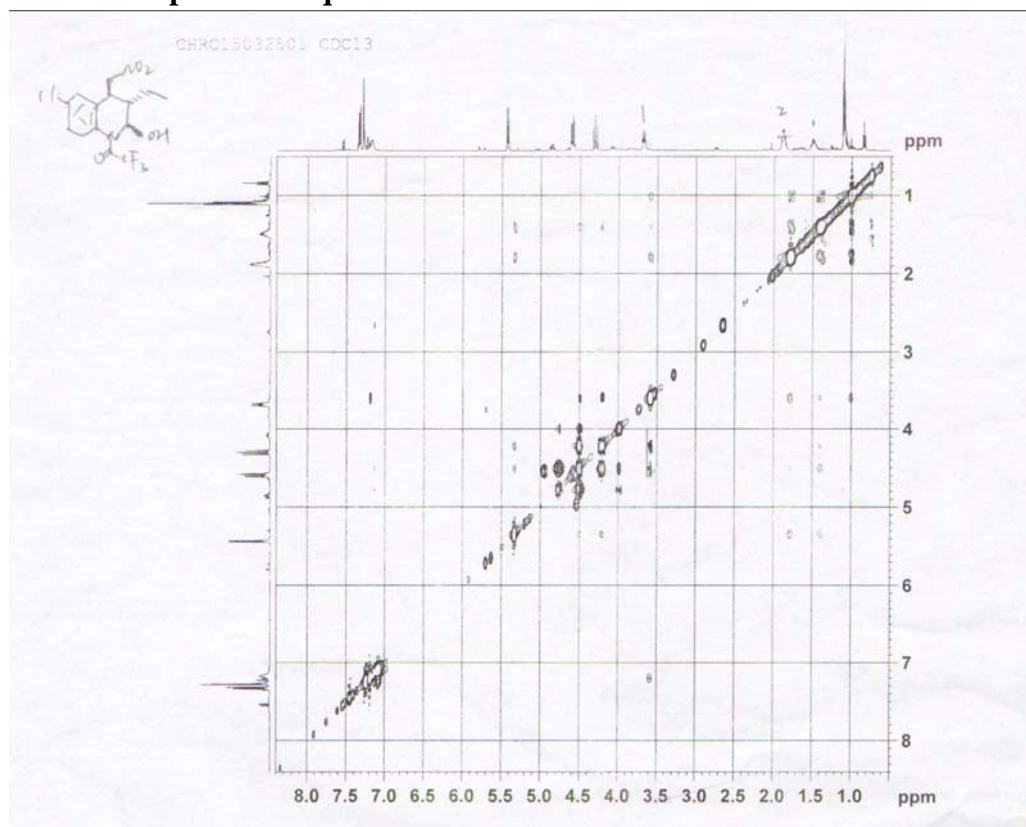
Compound 6u



H-H COSY spectra of 5q



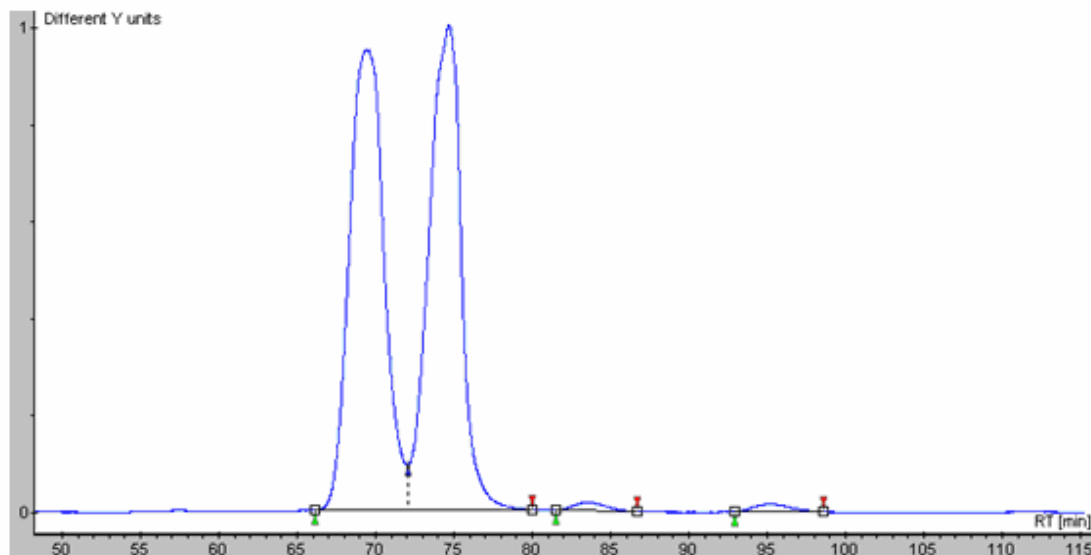
H-H NOESY spectra of 5q



5. HPLC spectra of Michael adducts

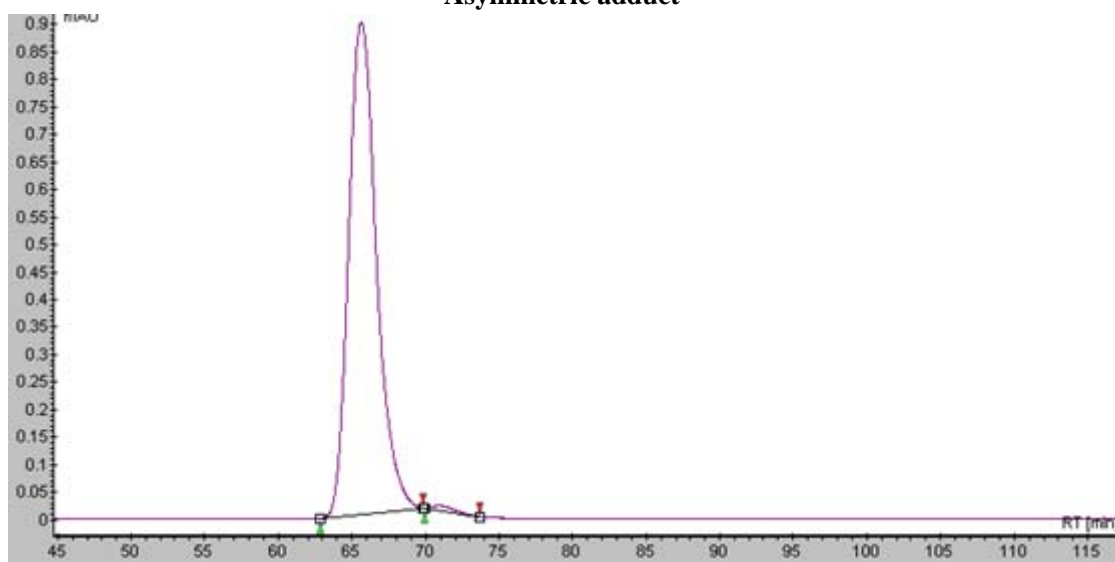
Compound 6a

Racemic adduct

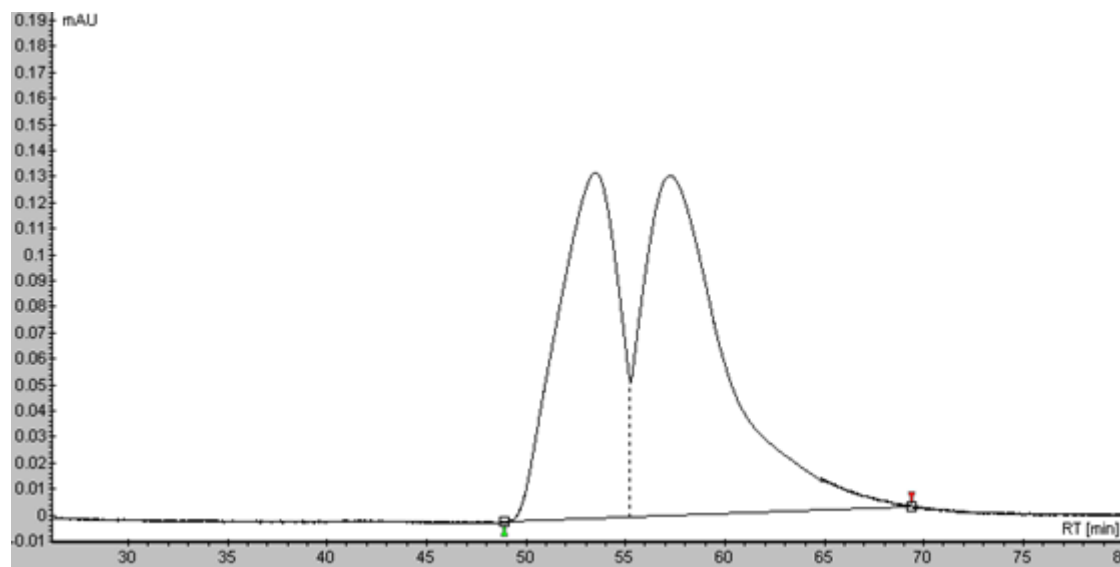


#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	66.057	69.442	72.015	49.754
2	72.015	74.667	79.957	48.564
3	81.480	83.530	86.643	0.813
4	92.865	95.099	98.557	0.869

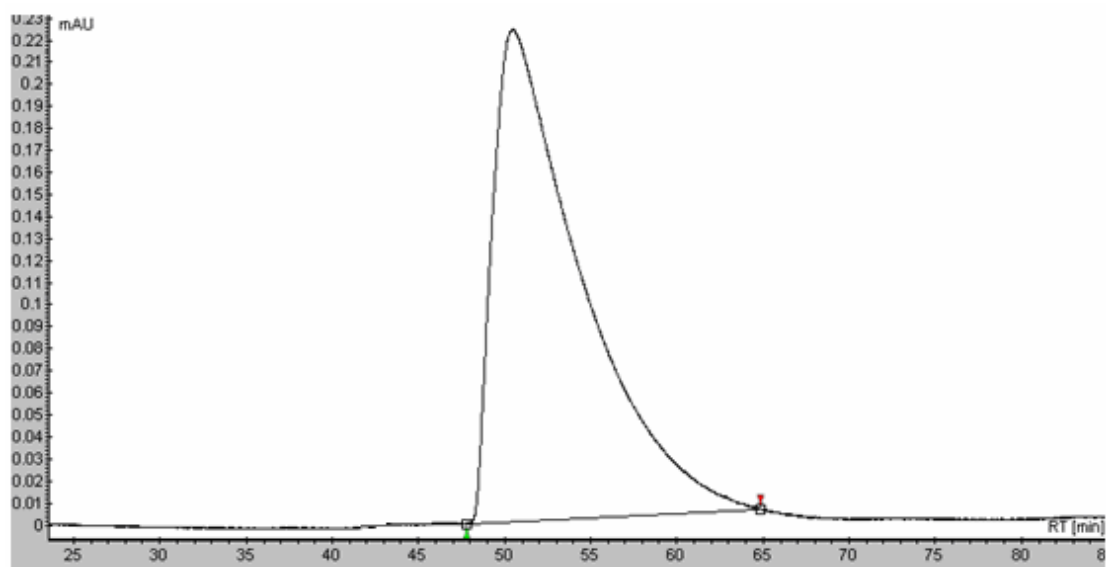
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	62.811	65.672	69.874	99.289
2	69.981	71.174	73.661	0.711

Compound 6b**Racemic adduct**

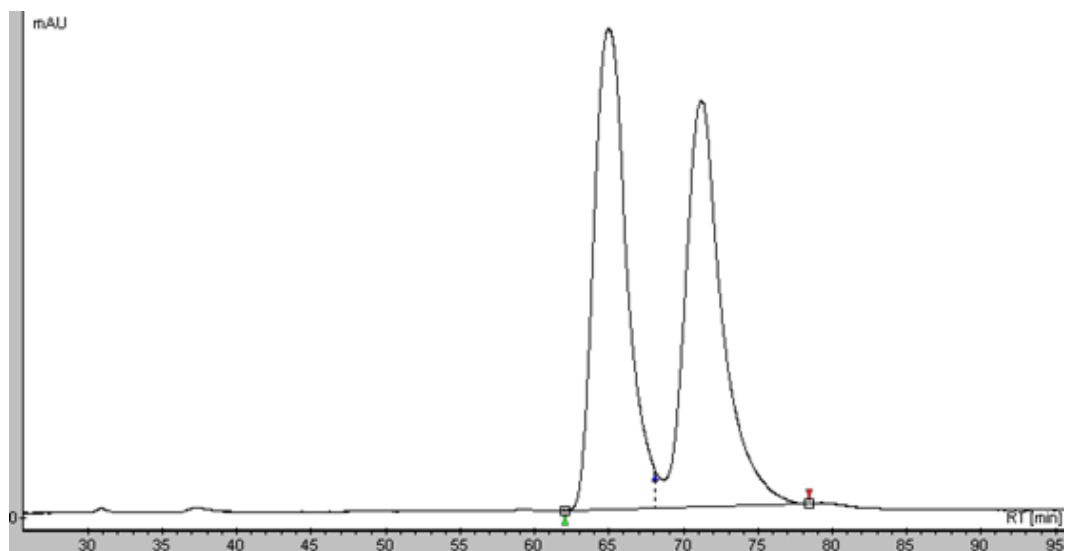
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	48.905	52.697	55.222	48.025
2	55.222	57.940	69.358	51.975

Asymmetric adduct

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

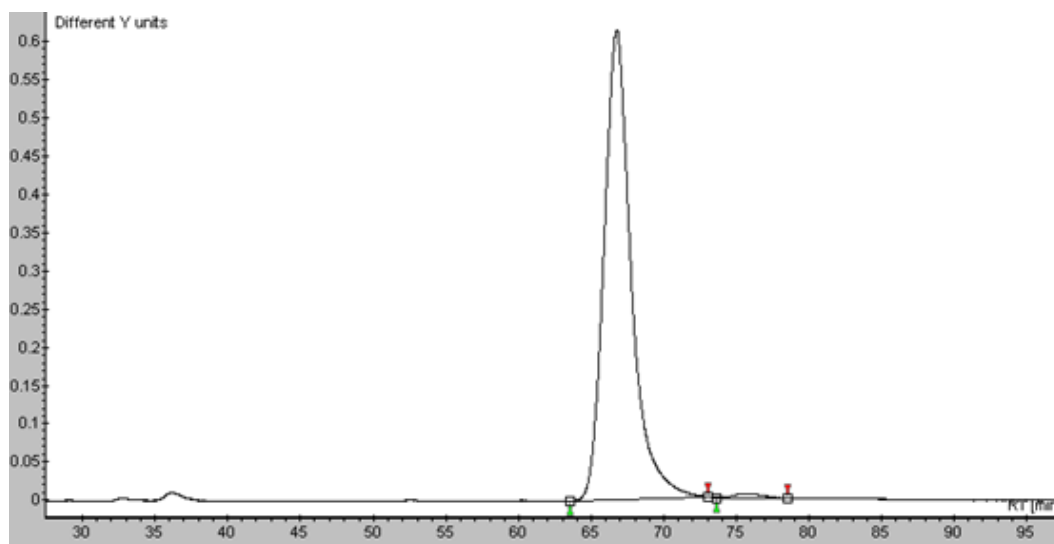
Compound 6c

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

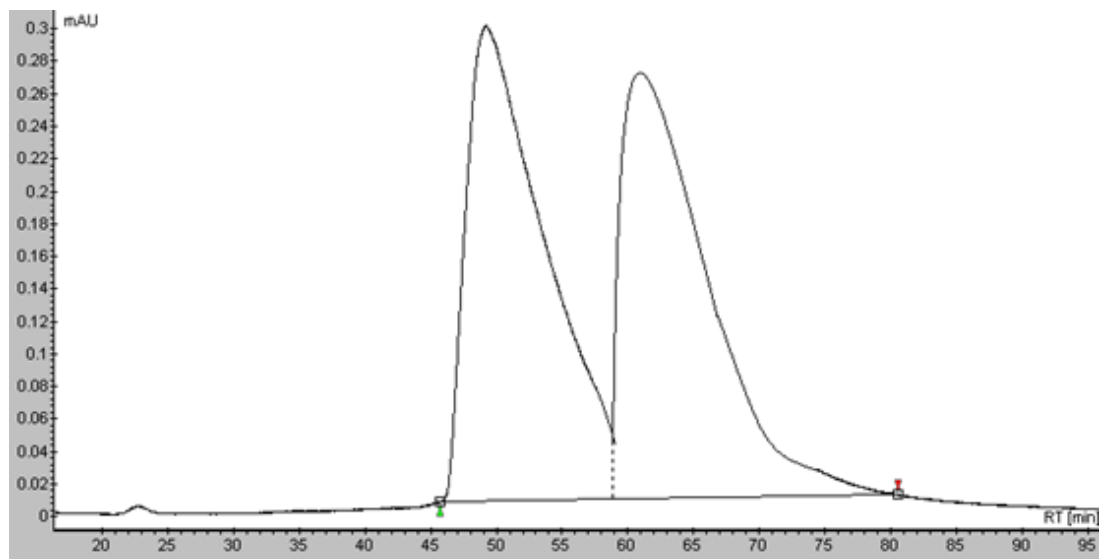
Asymmetric adduct



#	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

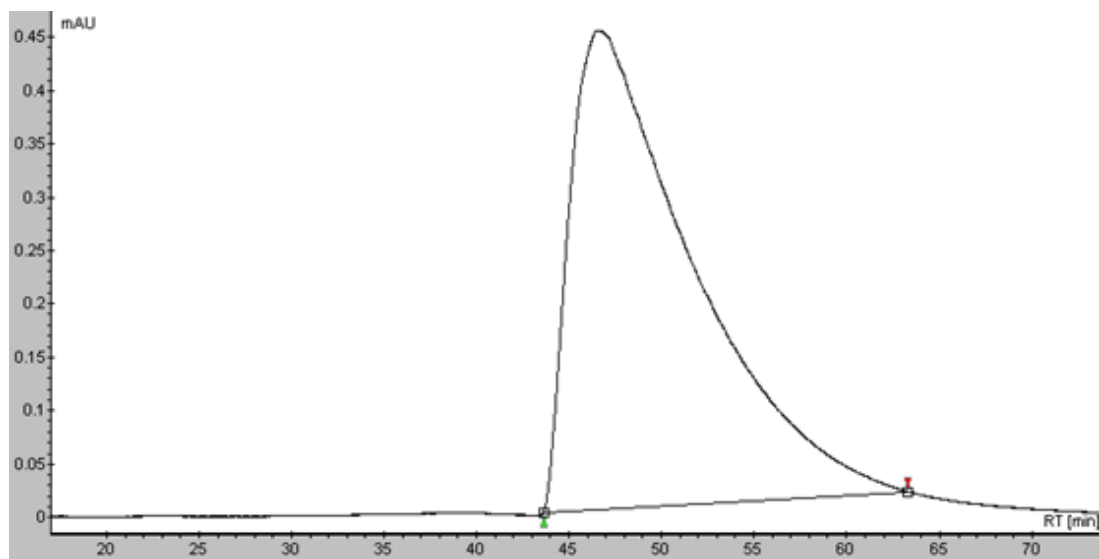
Compound 6d

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

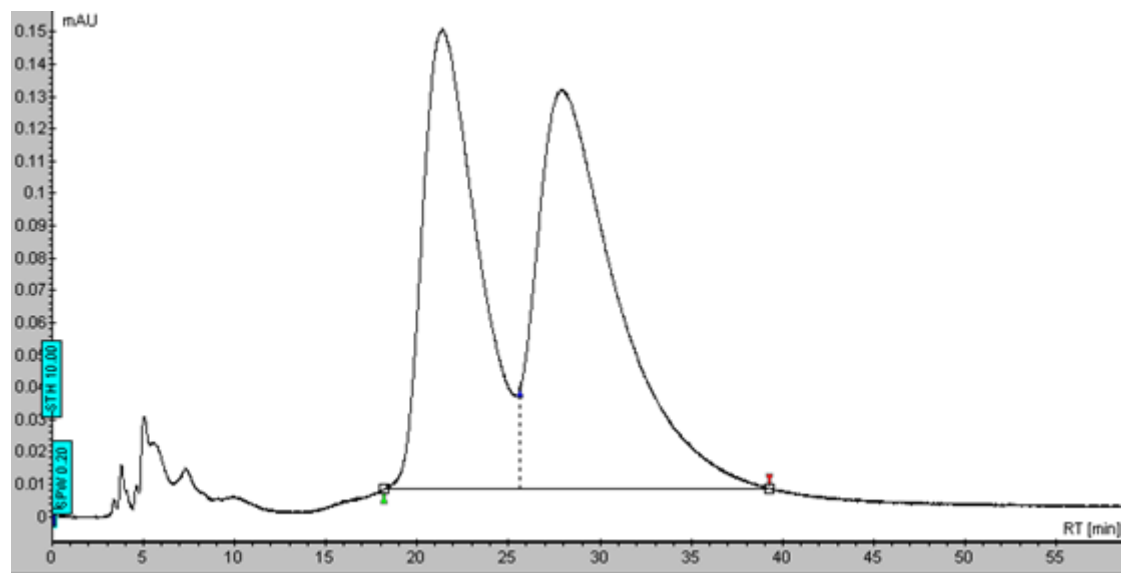
Asymmetric adduct



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

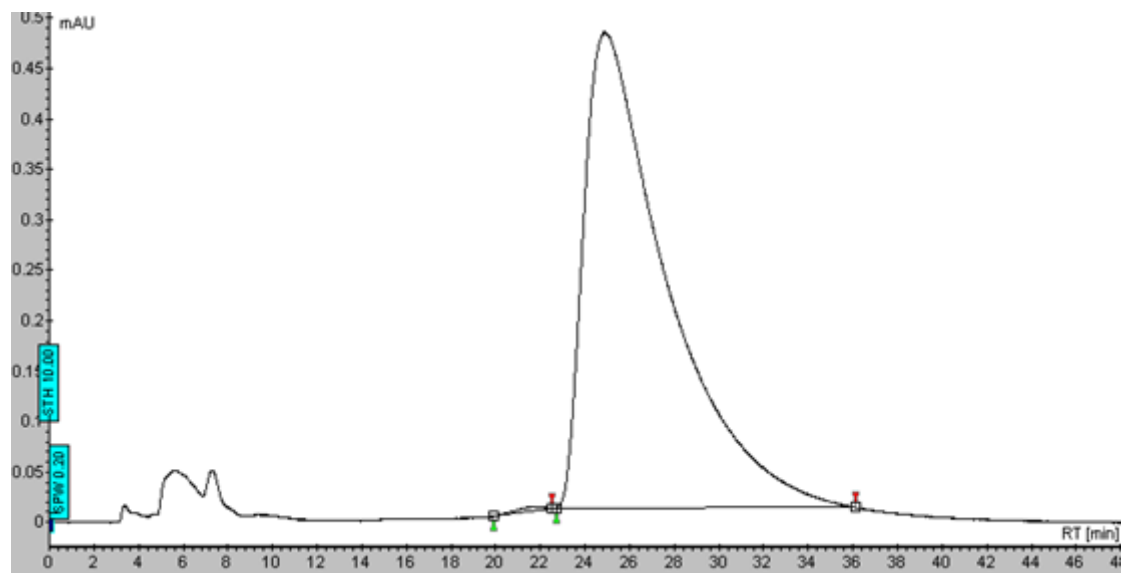
Compound 6e

Racemic adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	18.168	21.358	25.615	44.285
2	25.615	27.918	39.282	55.715

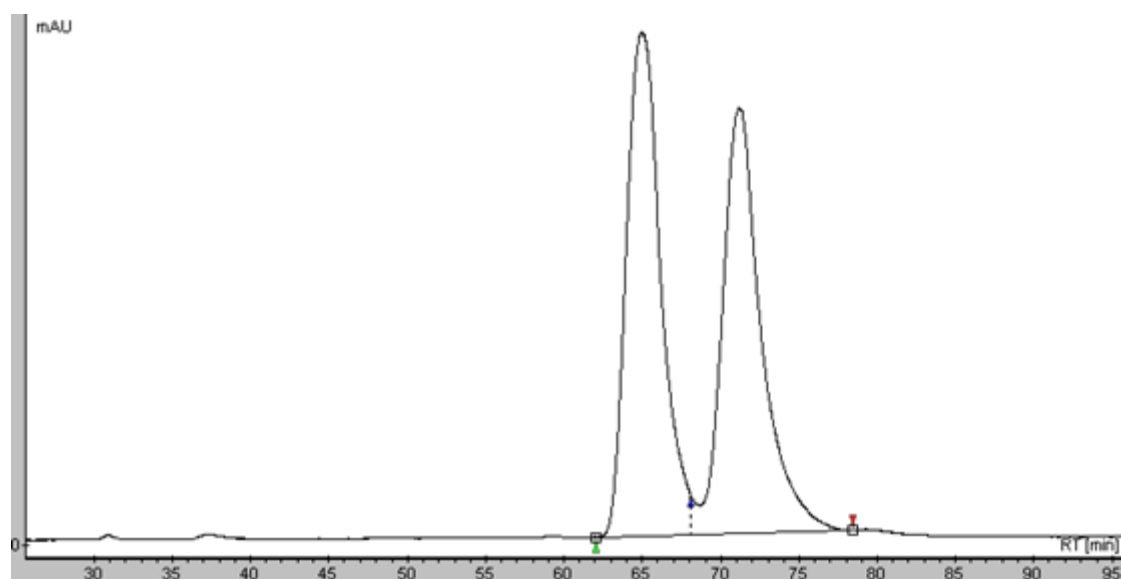
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	19.897	21.425	22.530	0.299
2	22.691	24.892	36.112	99.701

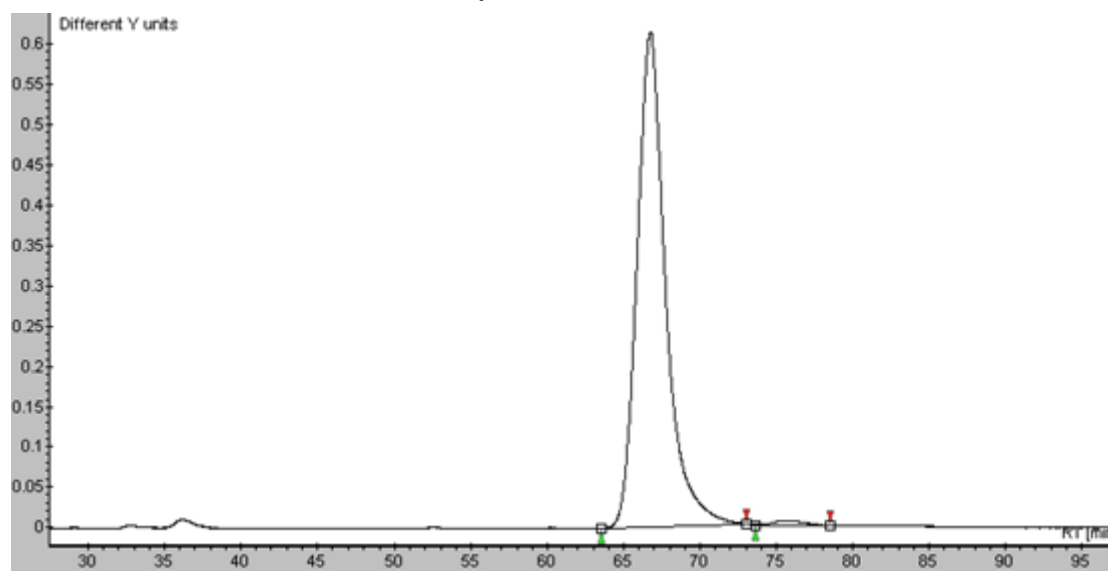
Compound 6f

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

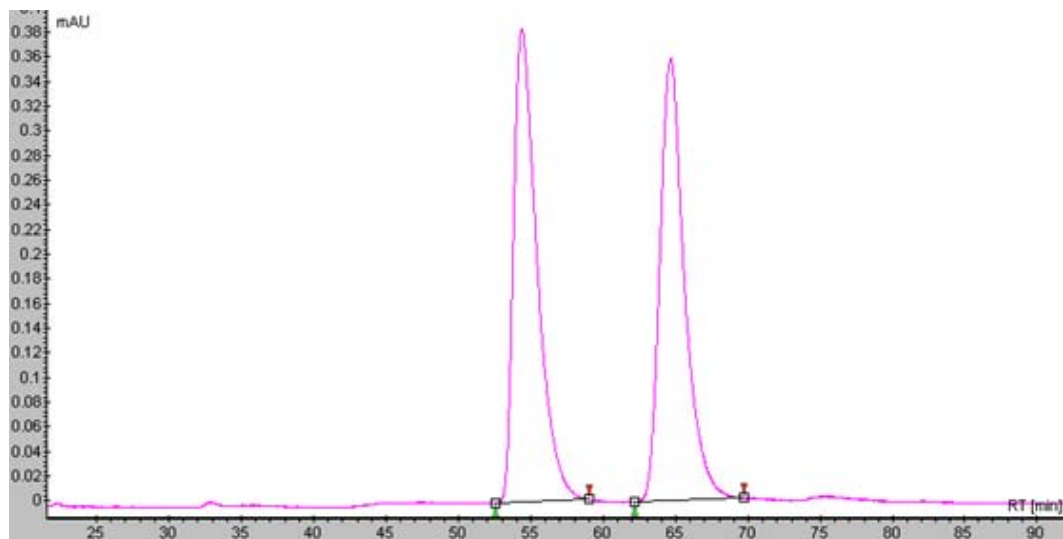
Asymmetric adduct



#	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

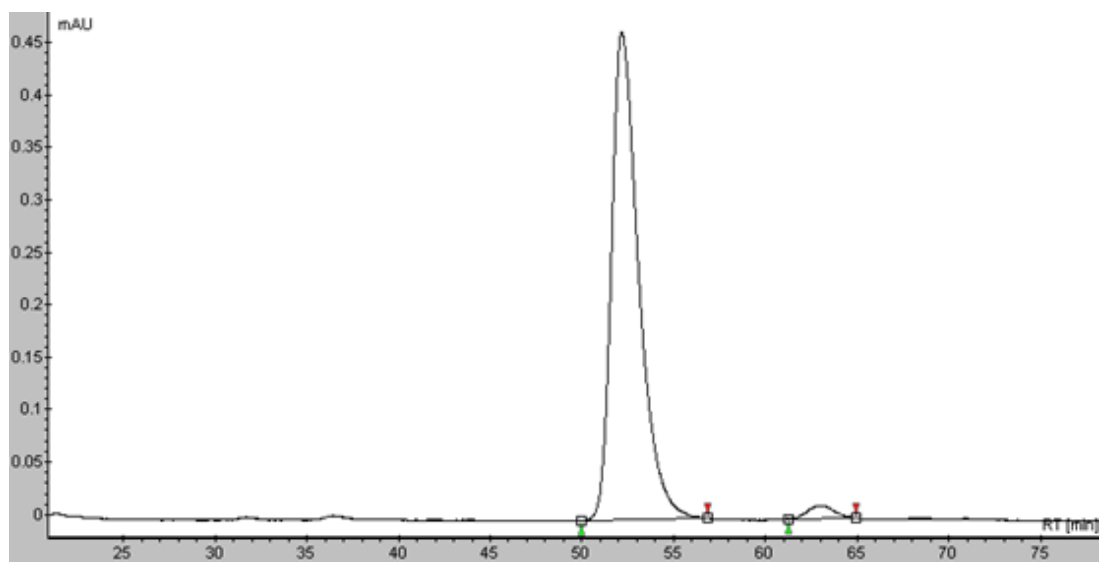
Compound 6g

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

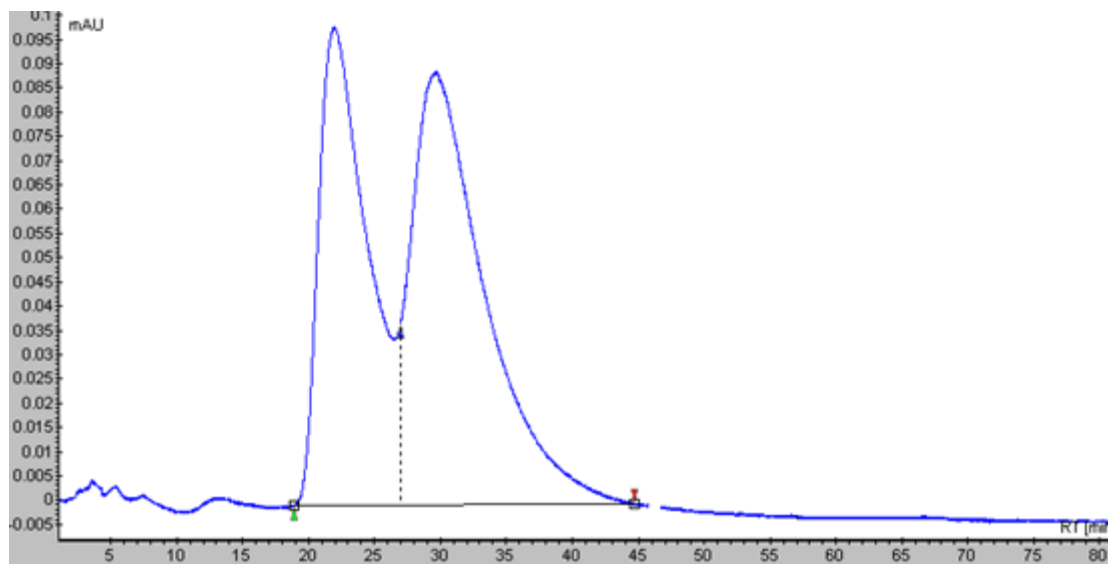
Asymmetric adduct



#	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

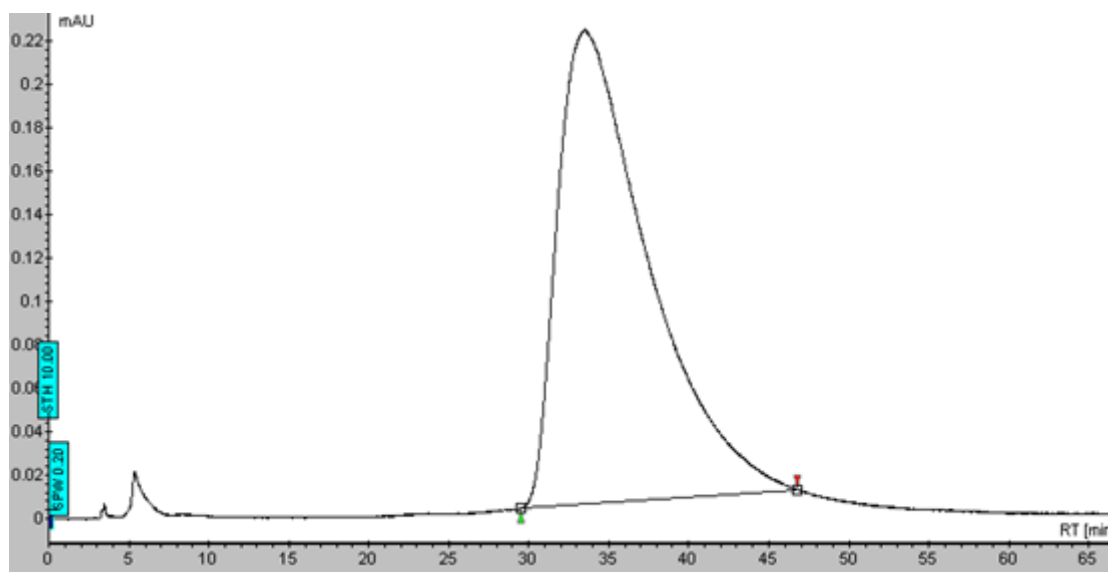
Compound 6h

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

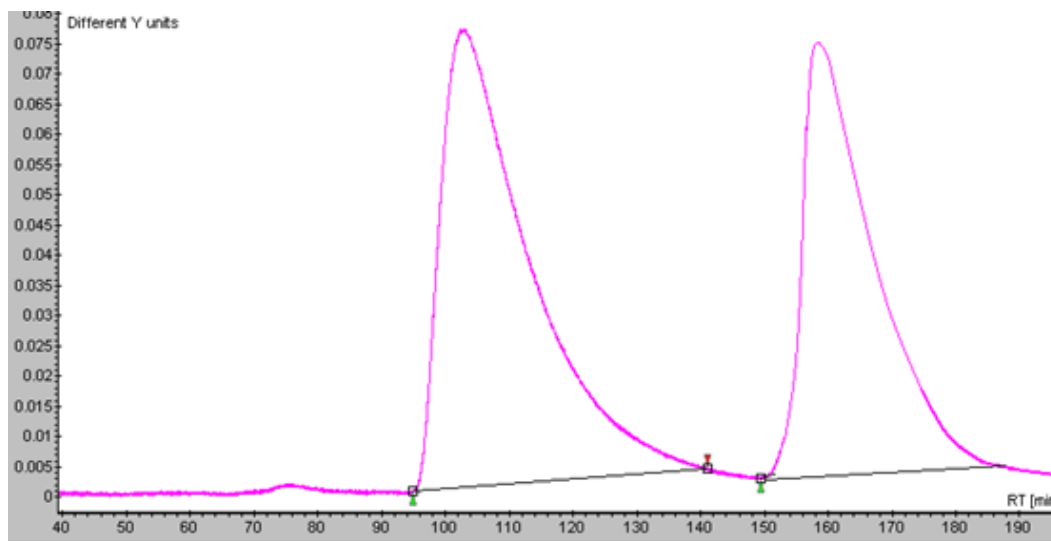
Asymmetric adduct



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

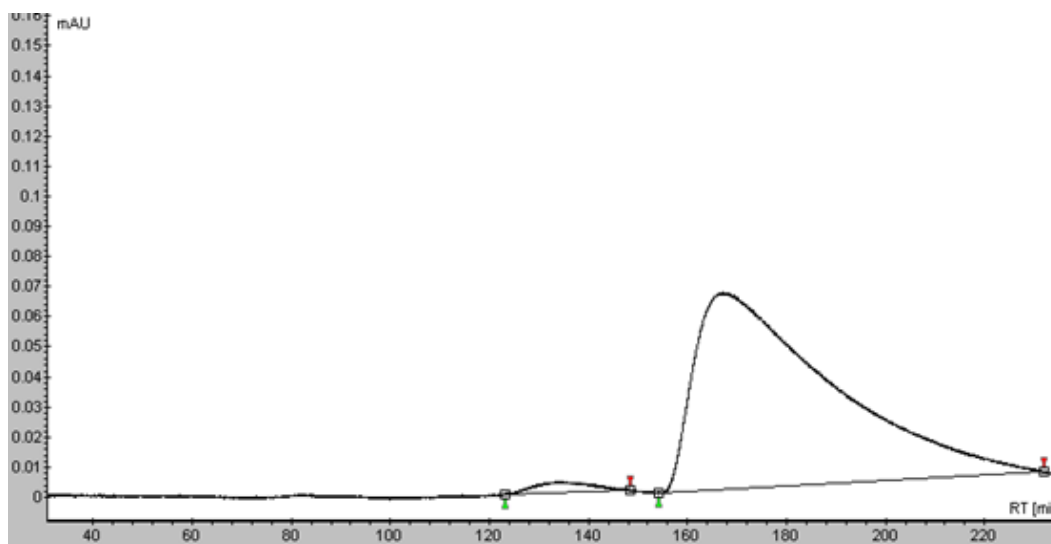
Compound 6i

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

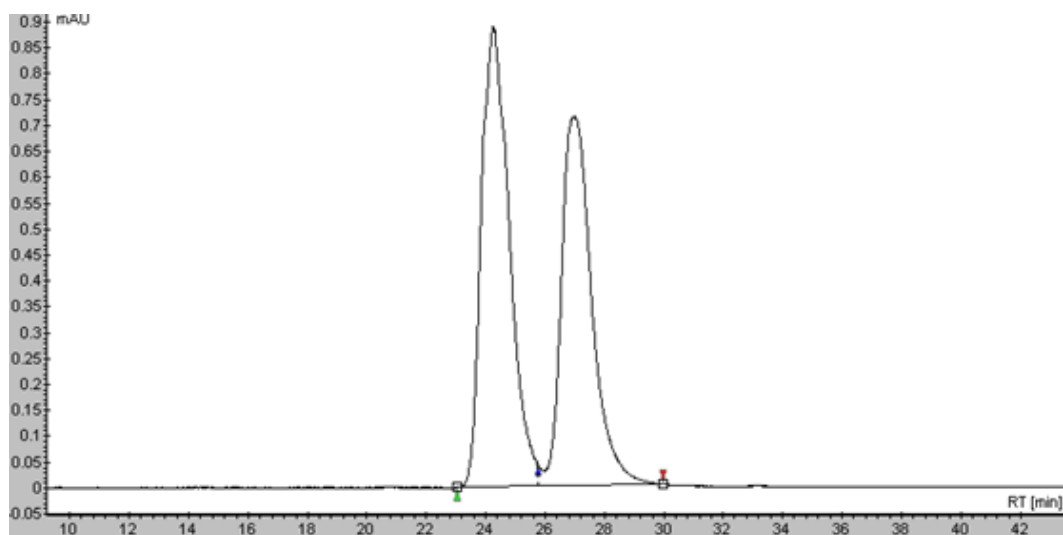
Asymmetric adduct



#	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

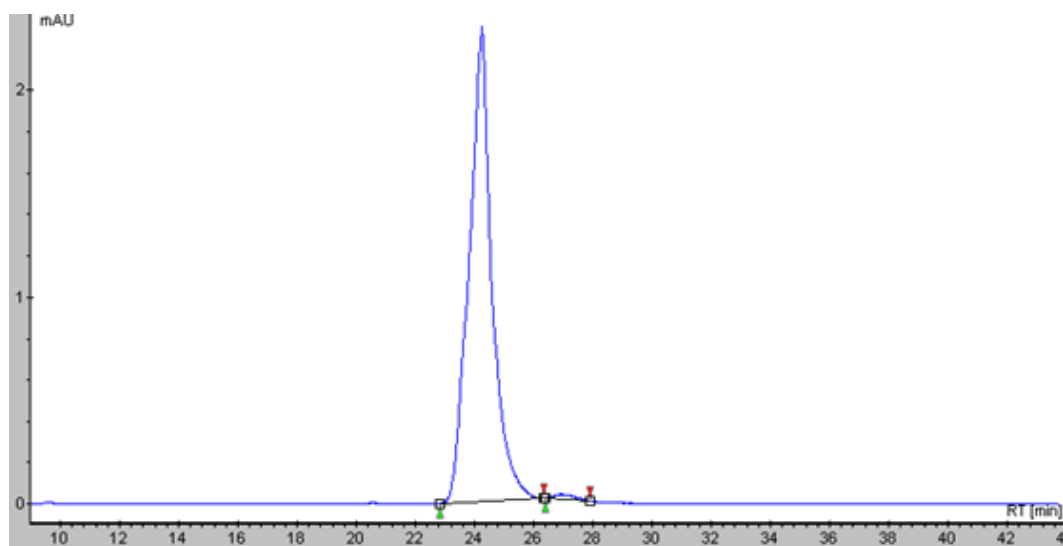
Compound 6j

Racemic adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	23.047	24.252	25.776	53.417
2	25.776	26.998	29.961	46.583

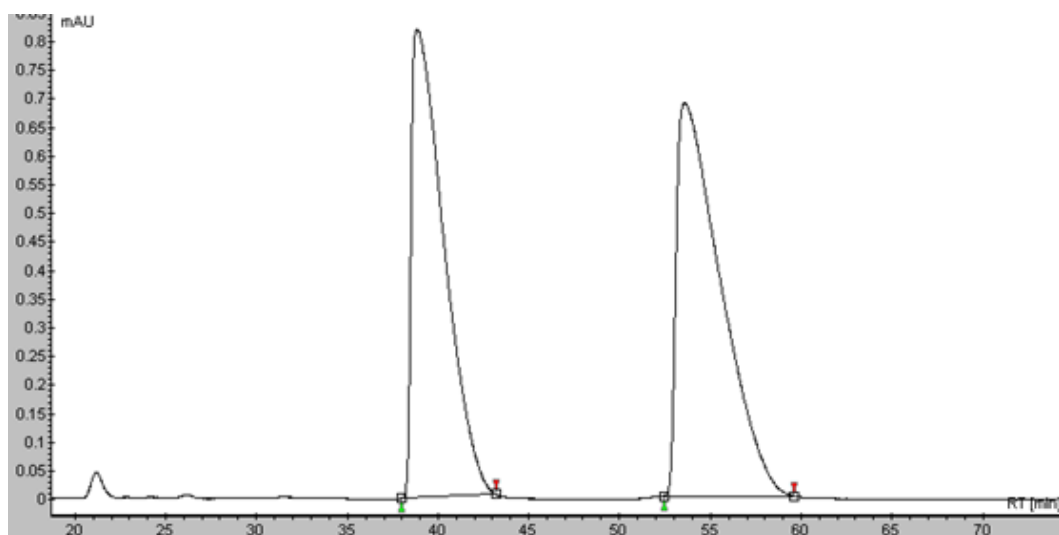
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	22.832	24.238	26.328	99.064
2	26.408	26.985	27.918	0.936

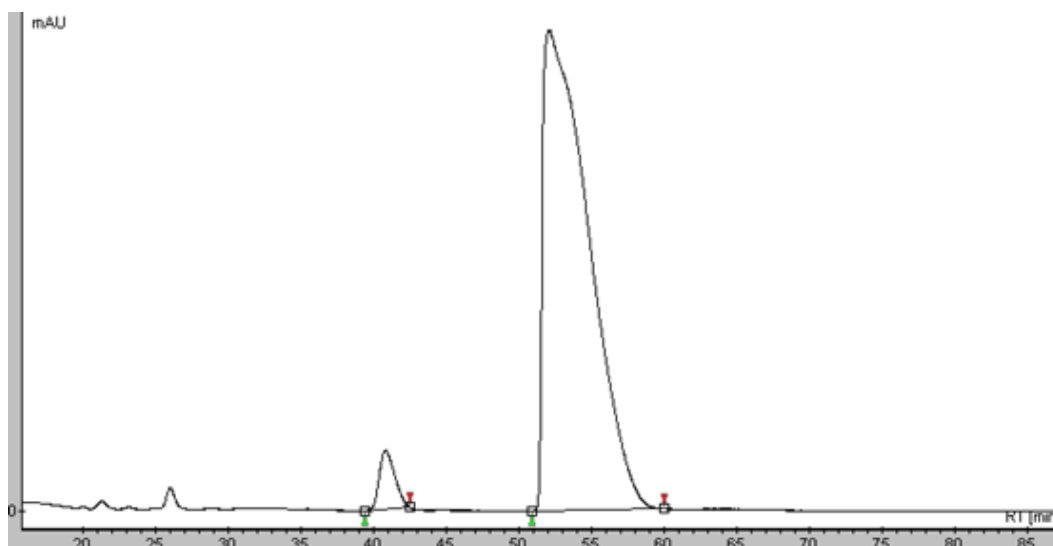
Compound 6k

Racemic adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	37.996	38.799	43.158	46.765
2	52.451	53.581	59.575	53.235

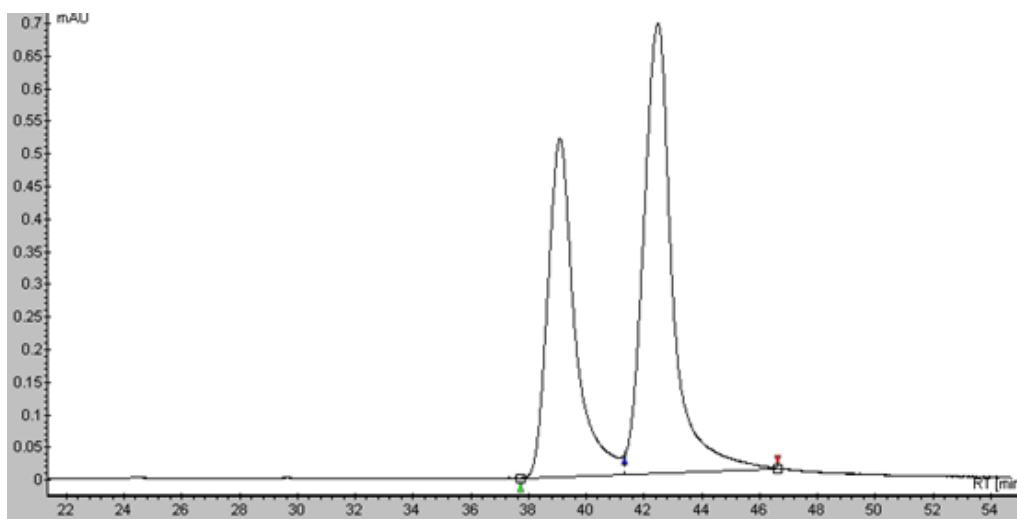
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	39.410	40.799	42.483	3.984
2	50.899	52.021	59.983	96.016

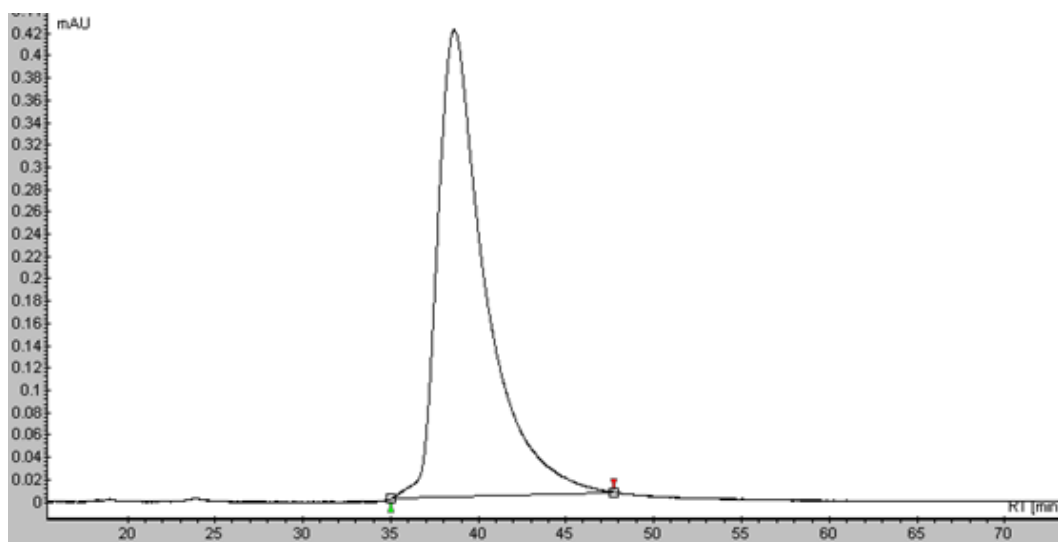
Compound 6l

Racemic adduct

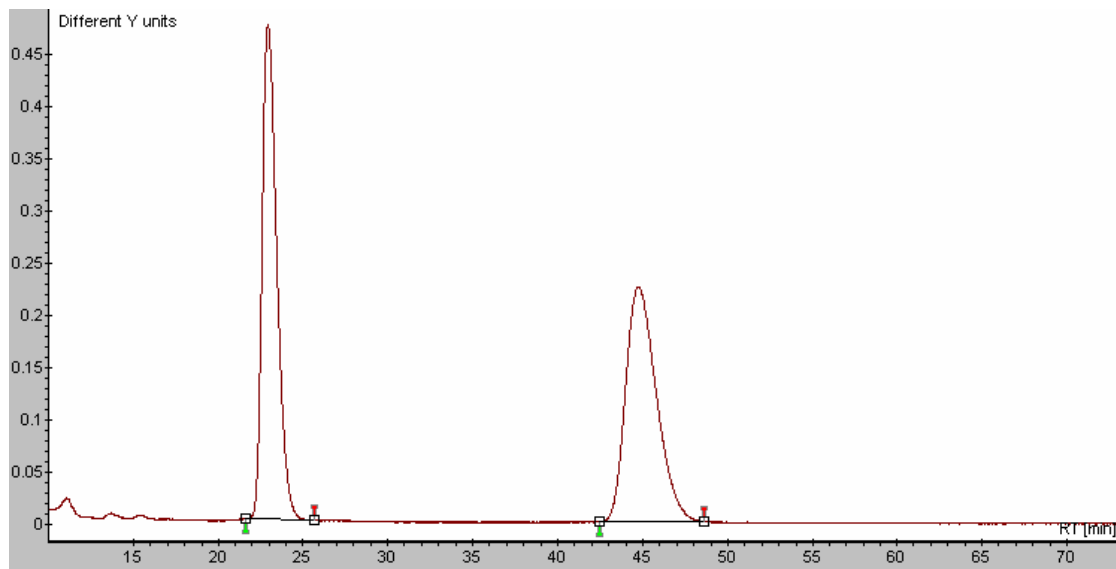


#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	37.725	39.077	41.317	41.494
2	41.317	42.464	46.642	58.506

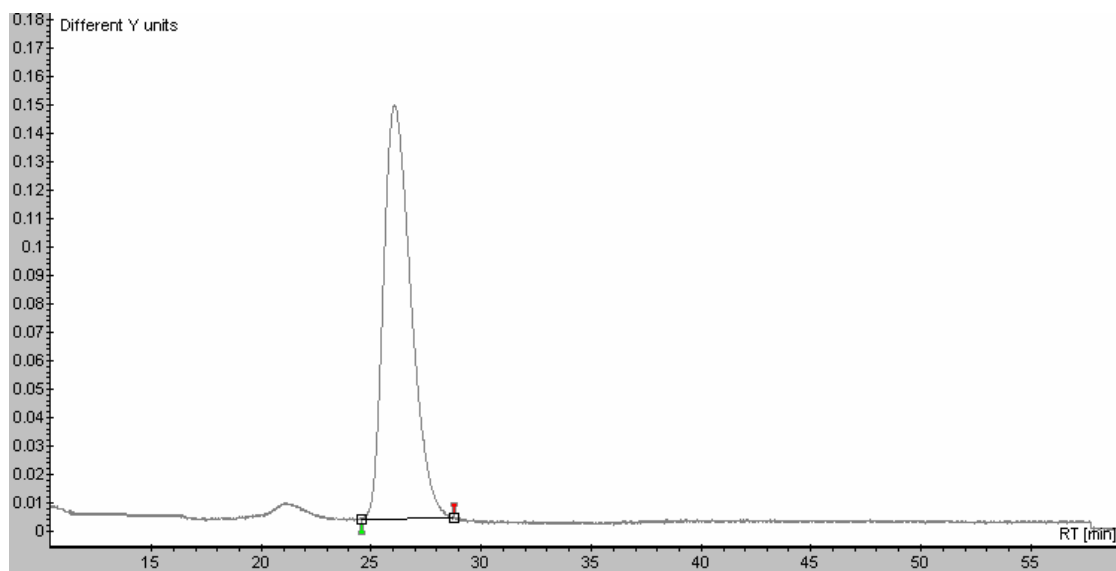
Asymmetric adduct



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

Compound 6m**Racemic adduct**

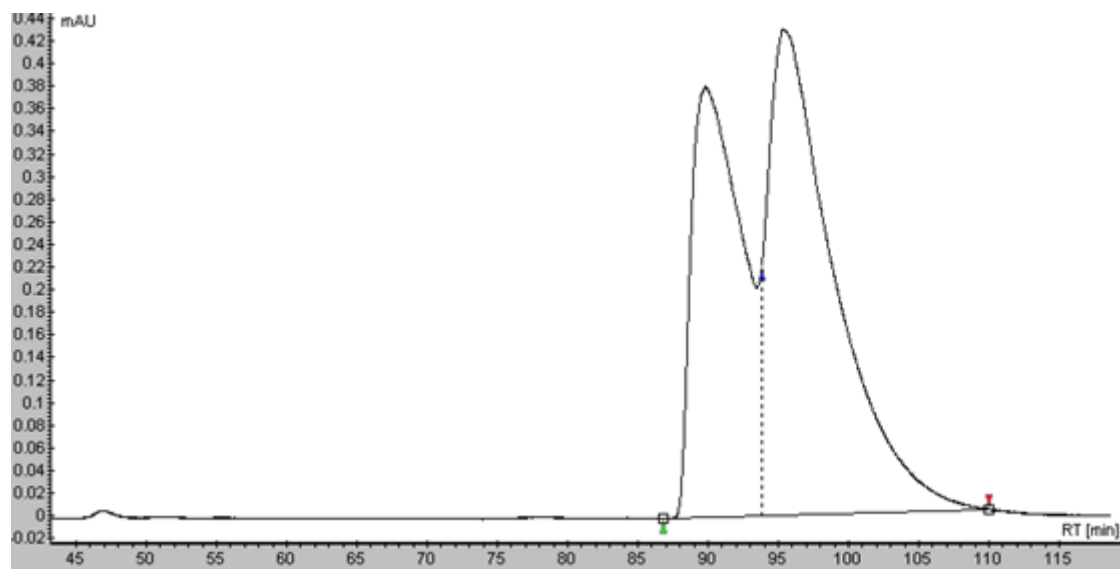
#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	21.626	22.952	25.671	50.101
2	42.464	44.731	48.619	49.899

Asymmetric adduct

#	Start [Min]	Time [Min]	End [Min]	Area [%]
1	24.561	26.057	28.764	100.000

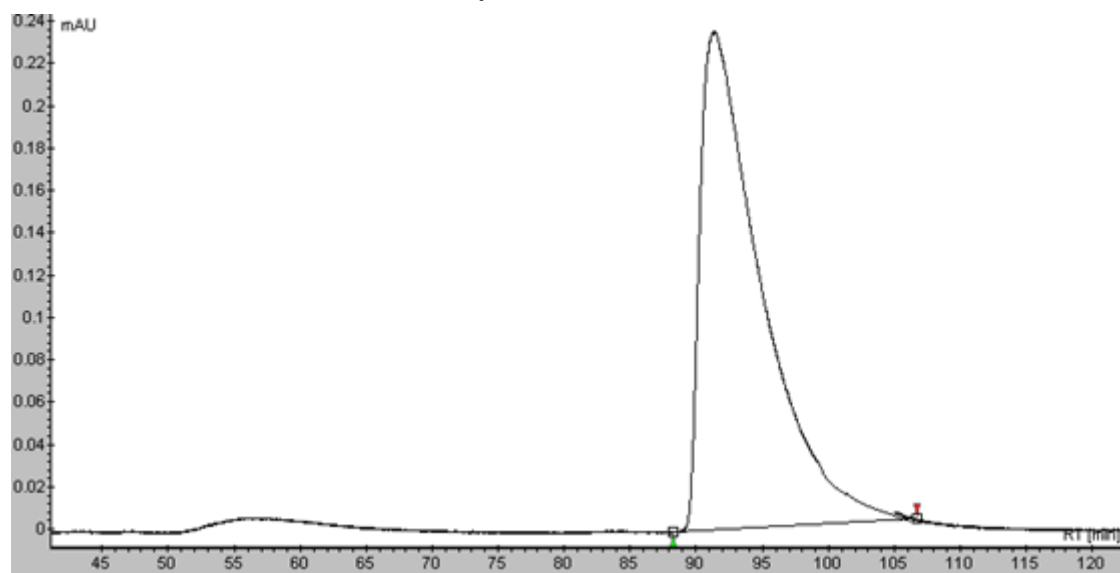
Compound 6n

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

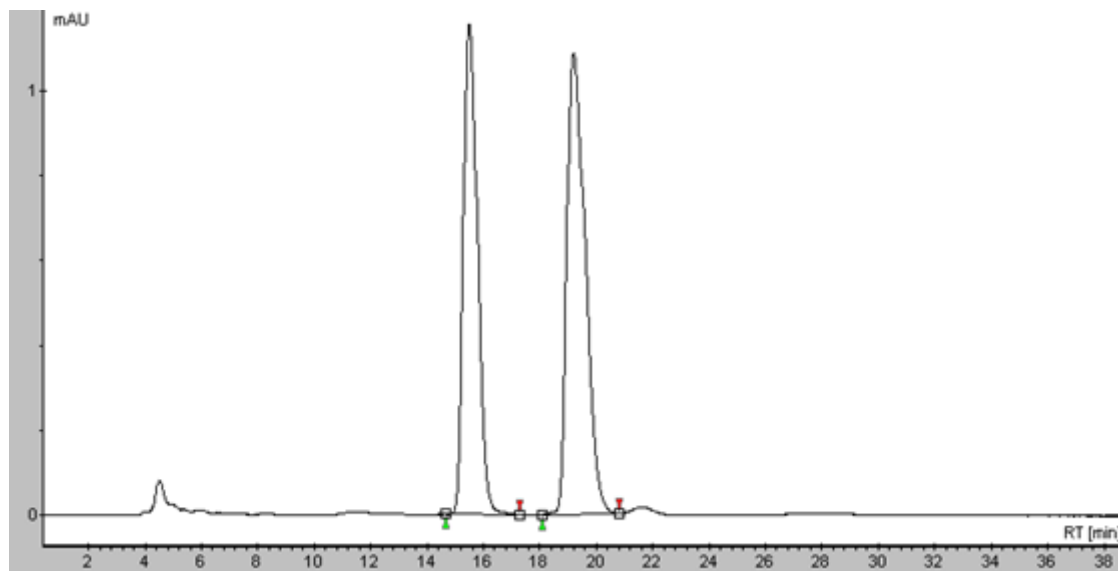
Asymmetric adduct



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

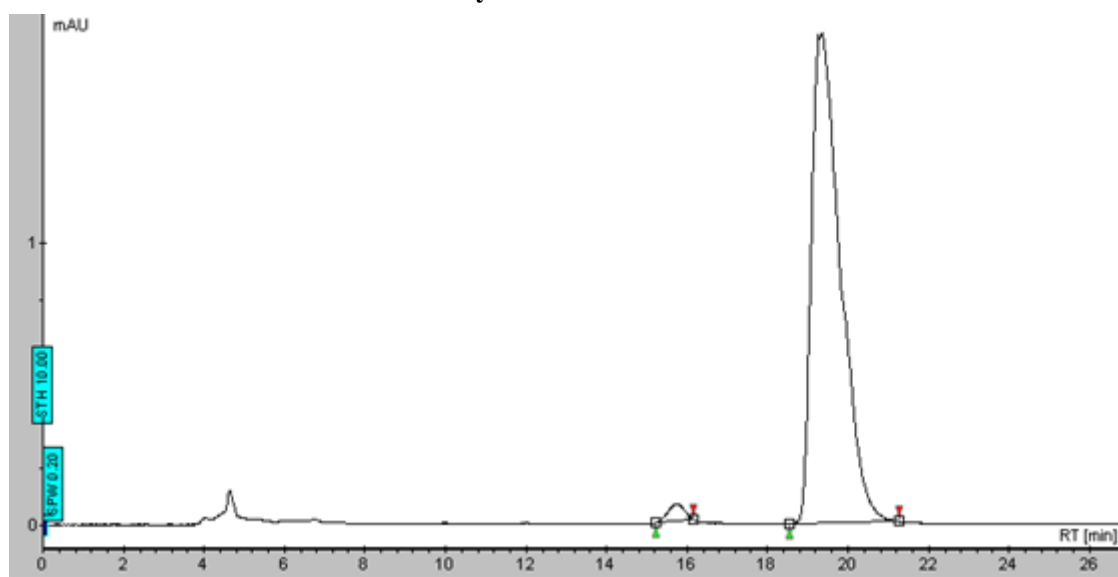
Compound 6o

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

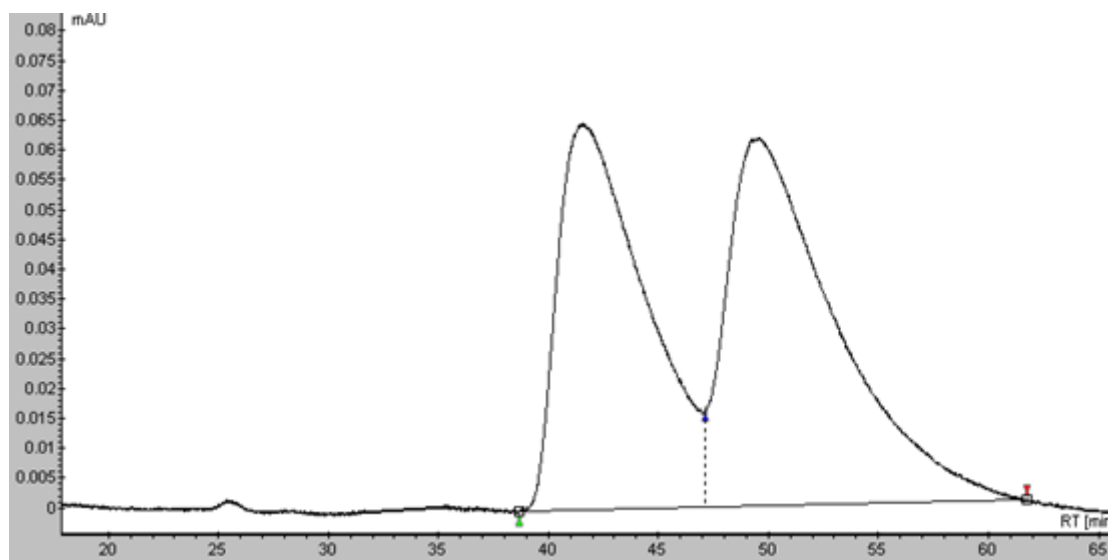
Asymmetric adduct



#	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

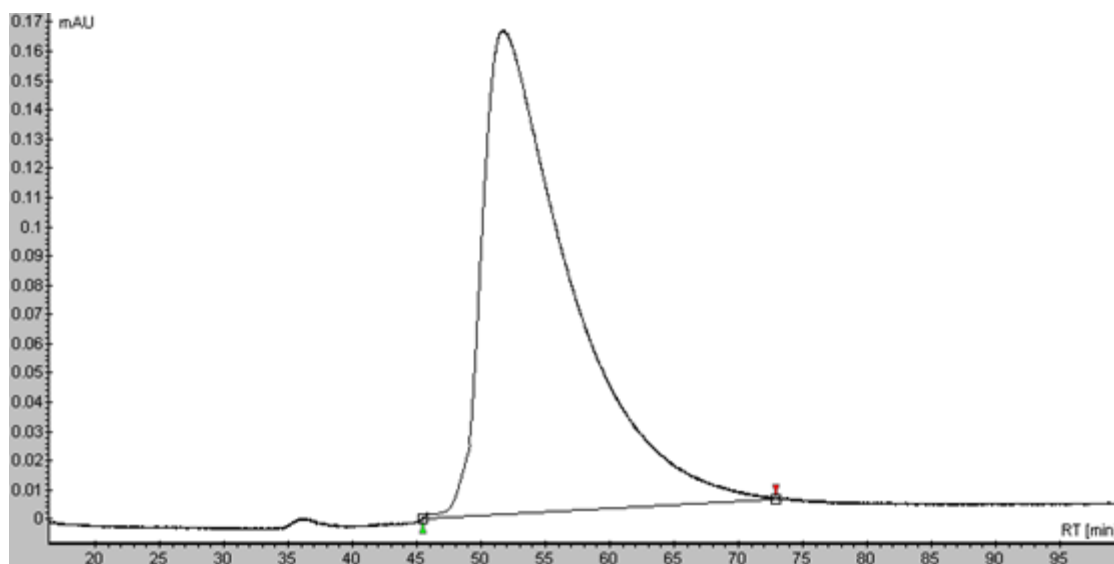
Compound 6p

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

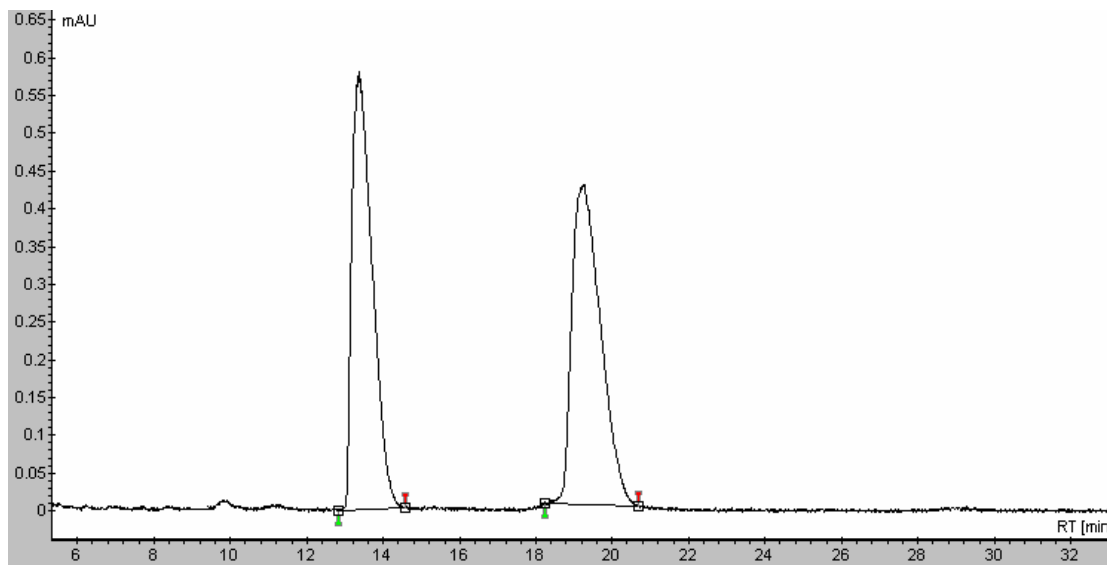
Asymmetric adduct



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

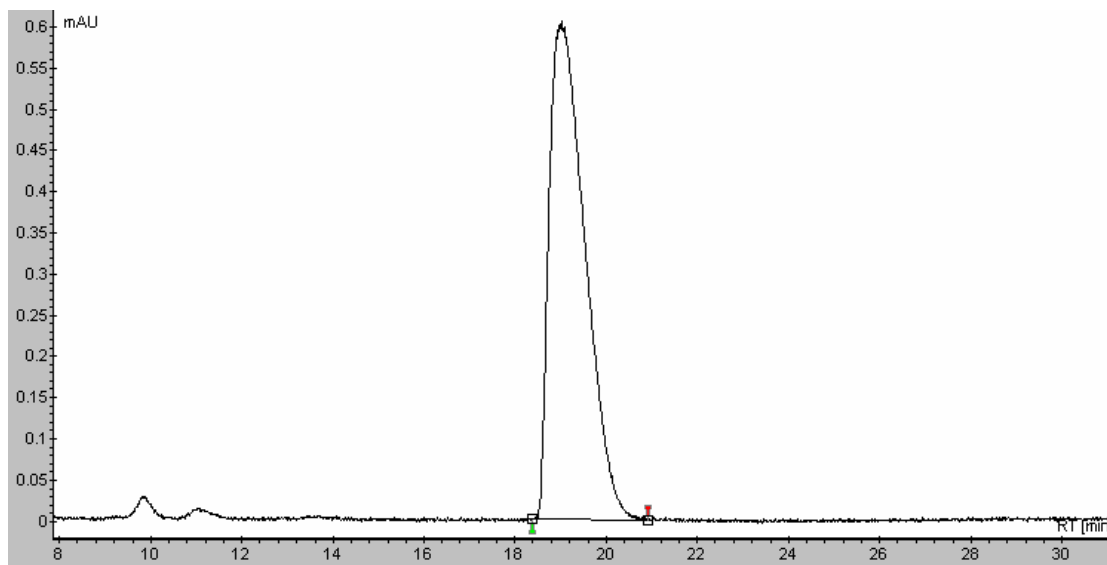
Compound 6q

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

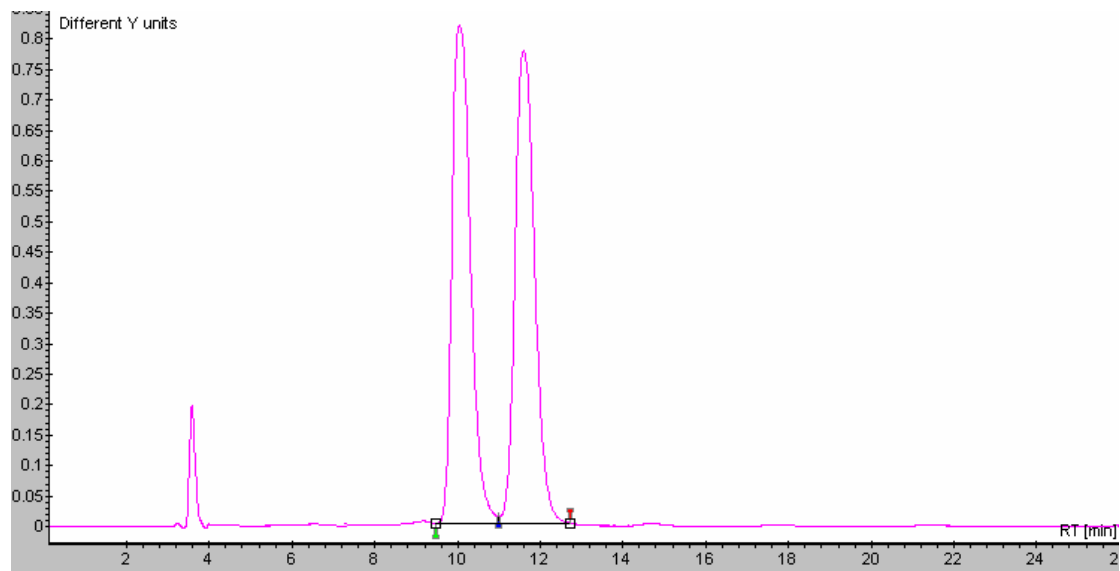
Asymmetric adduct



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

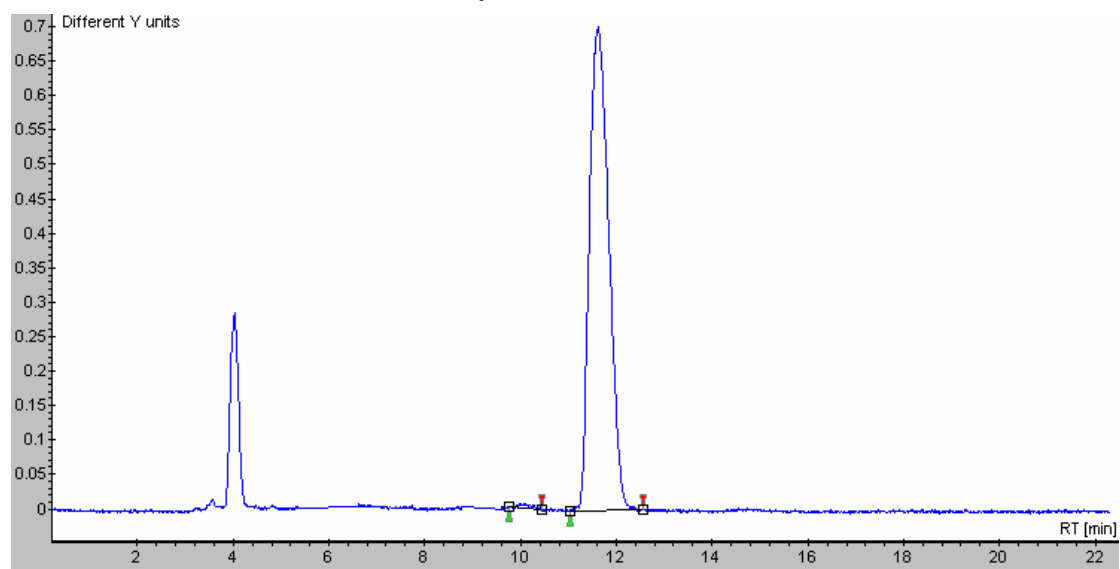
Compound 6r

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

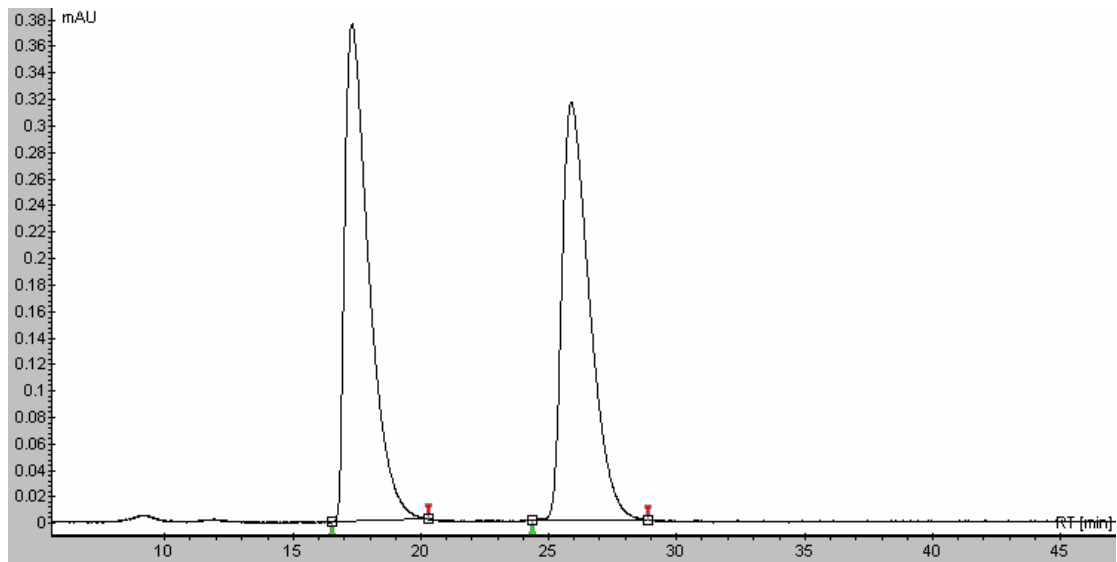
Asymmetric adduct



#	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

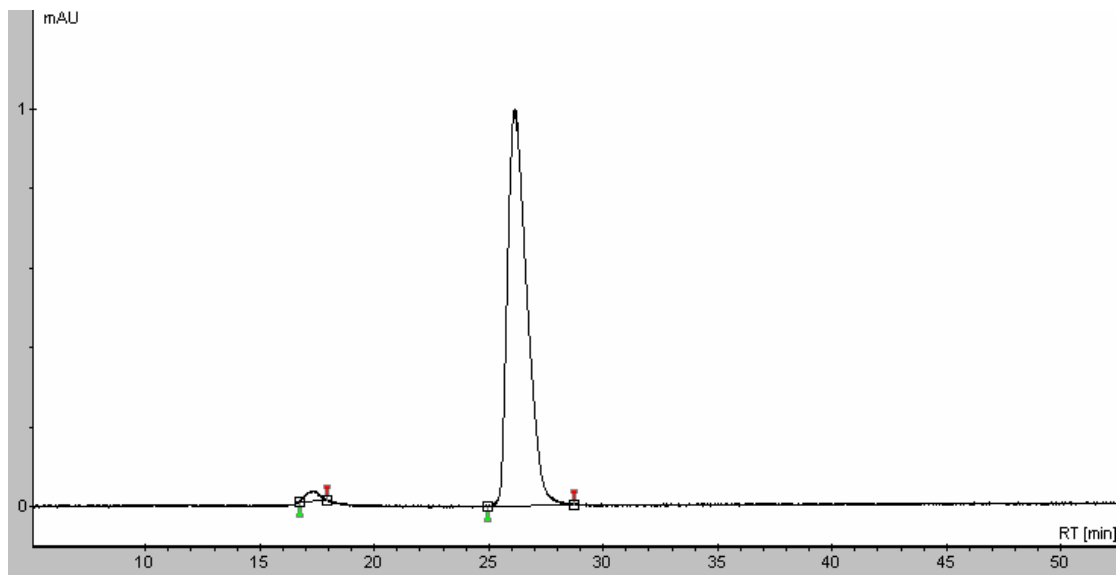
Compound 6s

Racemic adduct



#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	16.522	17.319	20.286	50.997
2	24.330	25.878	28.861	49.003

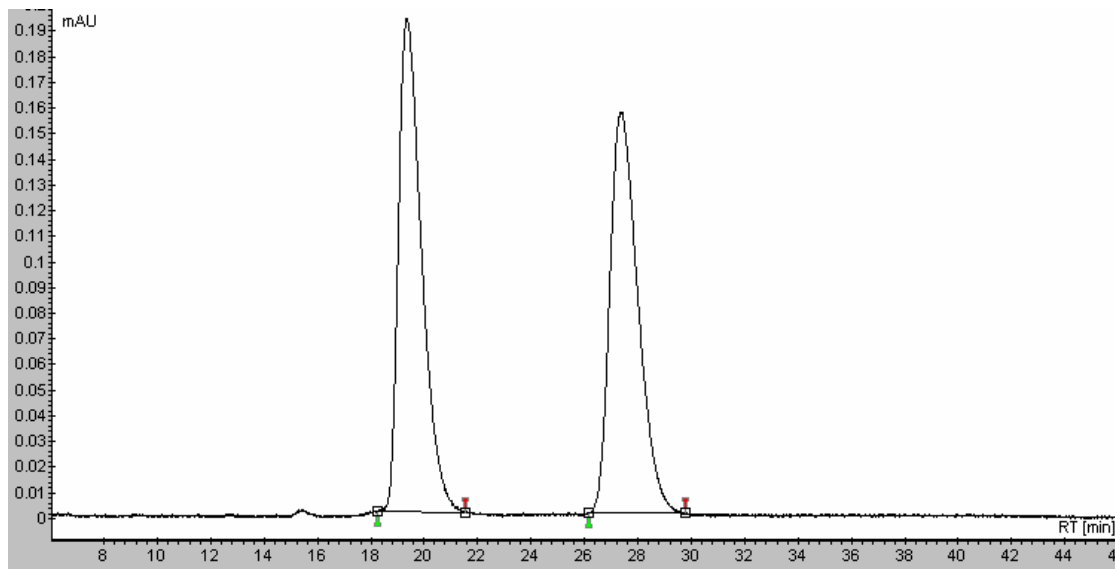
Asymmetric adduct



#	Start [Min]	Time [Min]	End [Min]	Area % [%]
1	16.719	17.279	17.914	1.608
2	24.976	26.131	28.751	98.392

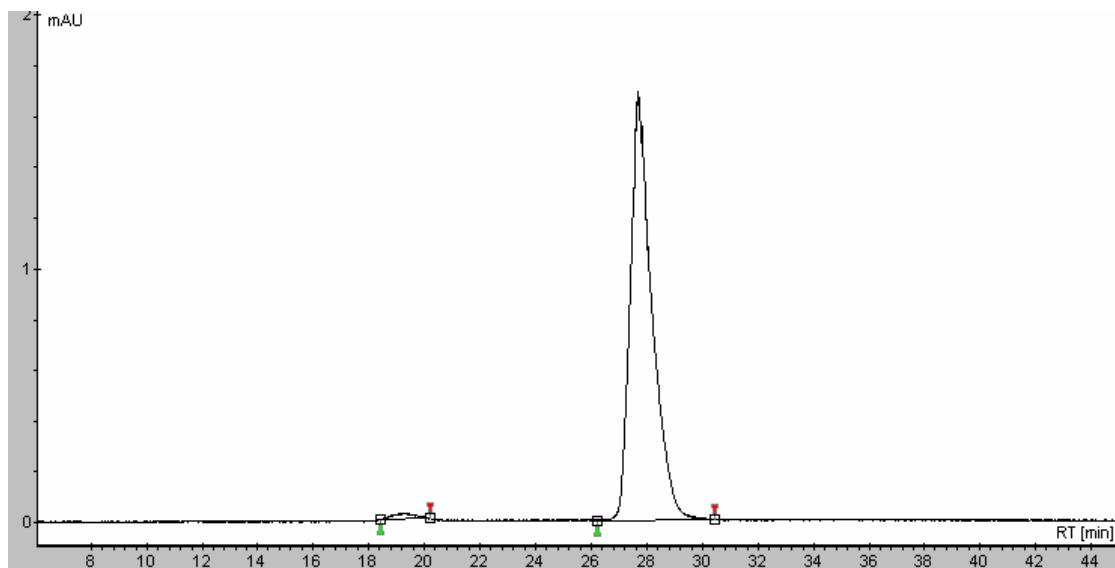
Compound 6t

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

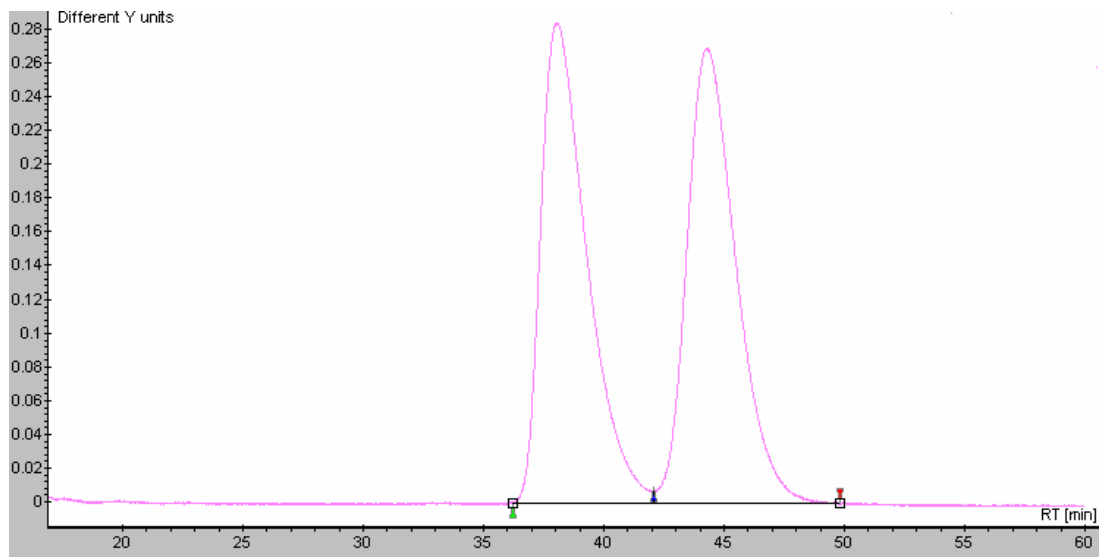
Asymmetric adduct



#	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

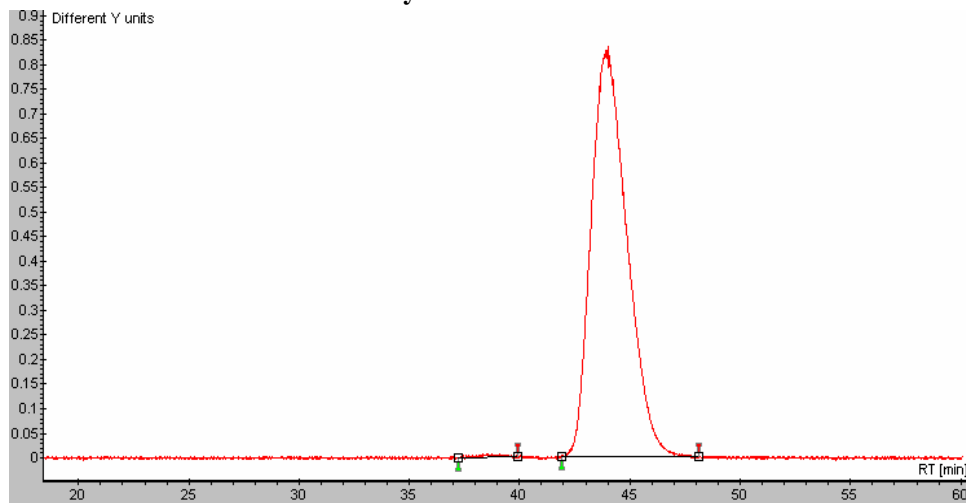
Compound 6u

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