

## Supplementary data

### Synthesis, antiproliferative and apoptosis-inducing effects of novel asiatic acid derivatives containing $\alpha$ -aminophosphonates

Ri-Zhen Huang<sup>a,†</sup>, Cai-Yi Wang<sup>b,†</sup>, Jian-Fei Li<sup>a</sup>, Gui-Yang Yao<sup>c</sup>, Ying-Ming Pan<sup>a</sup>, Man-Yi Ye<sup>a</sup>, Heng-Shan Wang<sup>a,\*</sup>, Ye Zhang<sup>a,d,\*</sup>

<sup>a</sup> State Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, PR China

<sup>b</sup> College of Chemical and Material Science, Hebei Normal University, Shijiazhuang 050024, China

<sup>c</sup> Department of Pharmaceutical Engineering, School of Chemistry and Chemical Engineering, Southeast University, Nanjing 211189, PR China

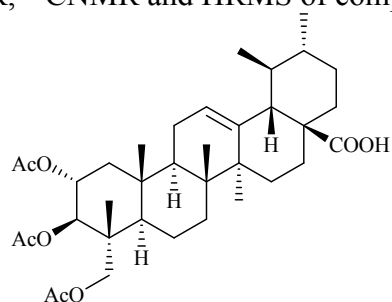
<sup>d</sup> Department of Chemistry & Pharmaceutical Science, Guilin Normal College, Xinyi Road 15, Guangxi 541001, PR China

\* Corresponding author. State Key Laboratory Cultivation Base for the Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry & Pharmaceutical Science of Guangxi Normal University, Yucui Road 15, Guilin 541004, Guangxi, PR China.

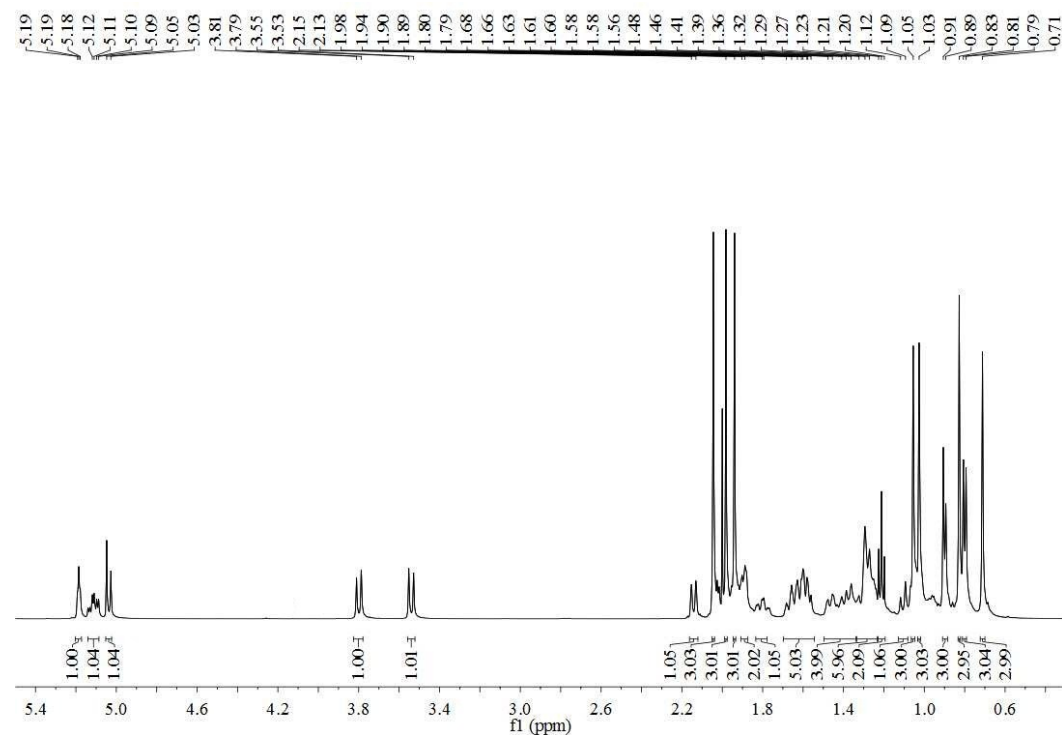
E-mail addresses: [whengshan@163.com](mailto:whengshan@163.com) (H.-S. Wang); [zhangye81@126.com](mailto:zhangye81@126.com) (Y. Zhang)

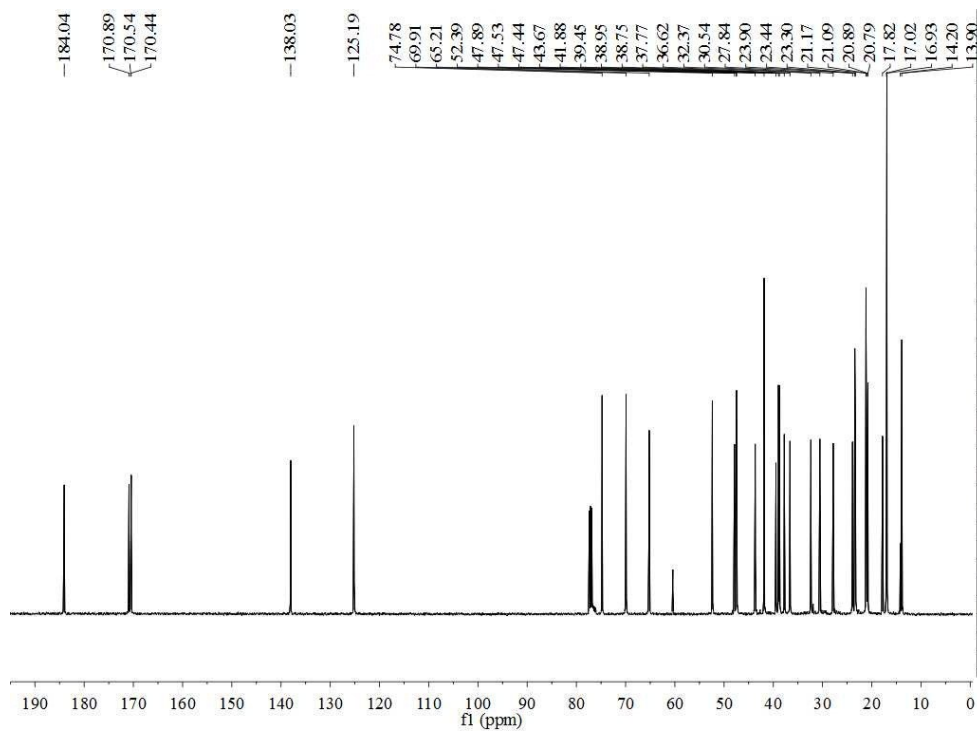
† Co-first author: These authors contributed equally to this work.

$^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and HRMS of compounds **1**, **3a–3r**, **6i** and **6n**:

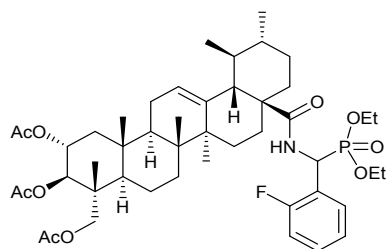
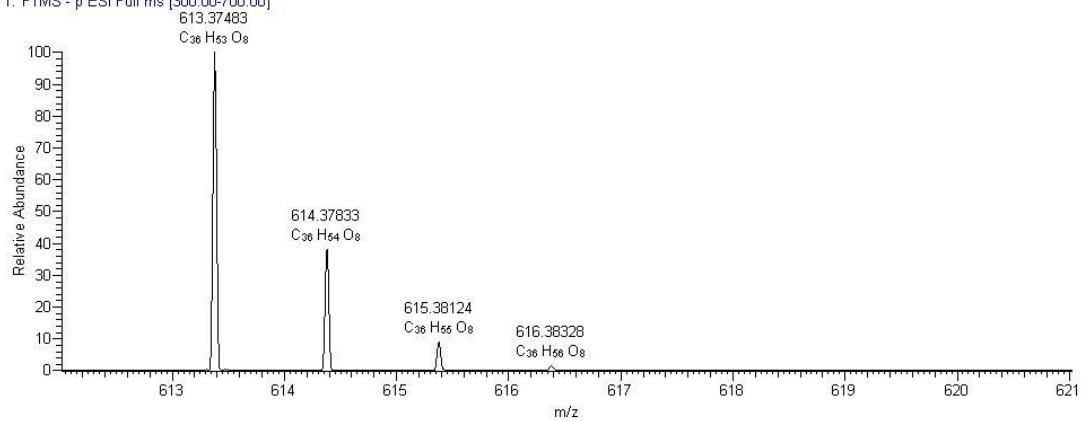


Compound **1**: Yield 85.5%. m.p. 151.2~154.6 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  5.19 (t,  $J = 3.2$  Hz, 1H, H-12), 5.11 (td,  $J = 10.9, 4.6$  Hz, 1H, H-2), 5.04 (d,  $J = 10.3$  Hz, 1H, H-3), 3.80 (d,  $J = 11.8$  Hz, 1H, H-23), 3.54 (d,  $J = 11.9$  Hz, 1H, H-23), 2.14 (d,  $J = 11.3$  Hz, 1H, H-9), 2.04 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.98 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.94 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.89-1.11 (triterpene's H, 19H), 1.05 (s, 3H,  $\text{CH}_3$ -27), 1.03 (s, 3H,  $\text{CH}_3$ -24), 0.90 (s, 3H,  $\text{CH}_3$ -25), 0.83 (s, 3H,  $\text{CH}_3$ -26), 0.80 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ -29), 0.71 (d,  $J = 6.4$  Hz, 3H,  $\text{CH}_3$ -30).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  184.04, 170.89, 170.54, 170.43, 138.03, 125.19, 74.77, 69.91, 65.21, 60.41, 52.39, 47.88, 47.53, 47.43, 43.66, 41.87, 39.45, 38.94, 38.75, 37.77, 36.61, 32.37, 30.54, 27.83, 23.90, 23.43, 23.29, 21.17, 21.09, 20.89, 20.79, 17.81, 17.01, 16.93, 14.19, 13.90; ESI-HRMS  $m/z$  Calc for  $\text{C}_{36}\text{H}_{54}\text{O}_8$   $[\text{M}-\text{H}]^-$ : 613.37459, founded: 613.37483.



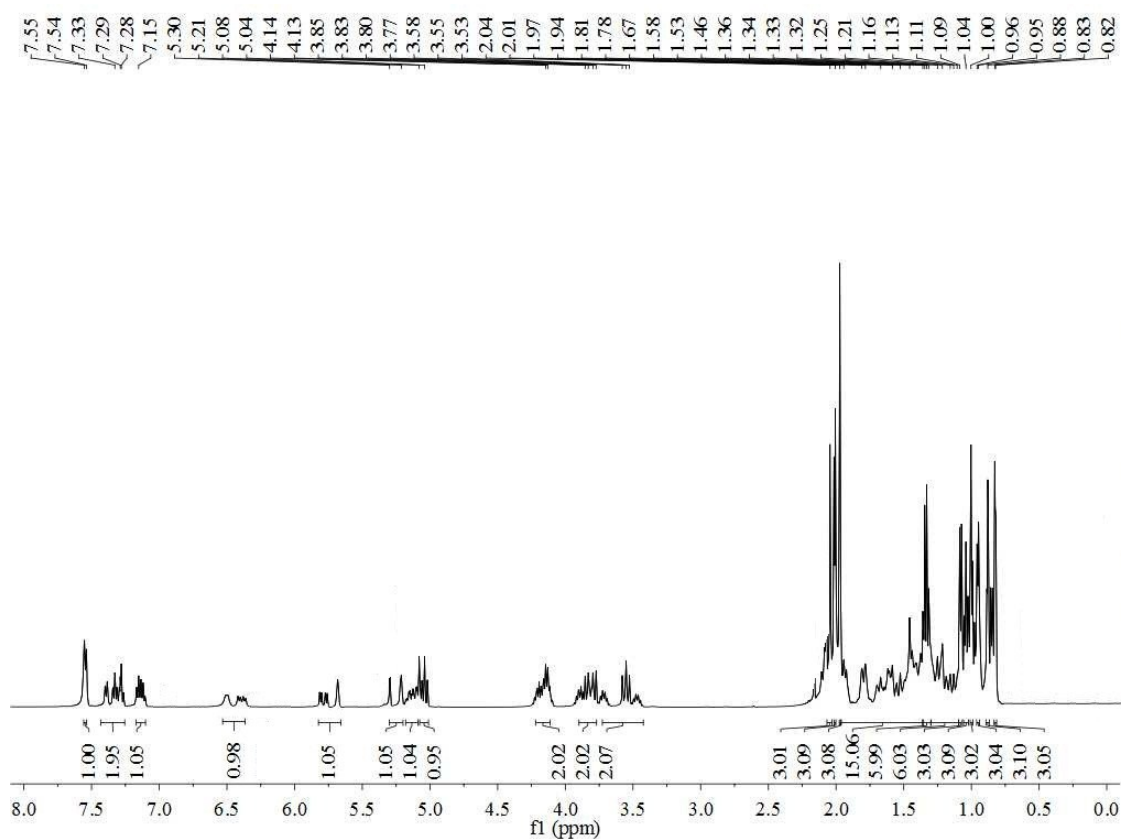


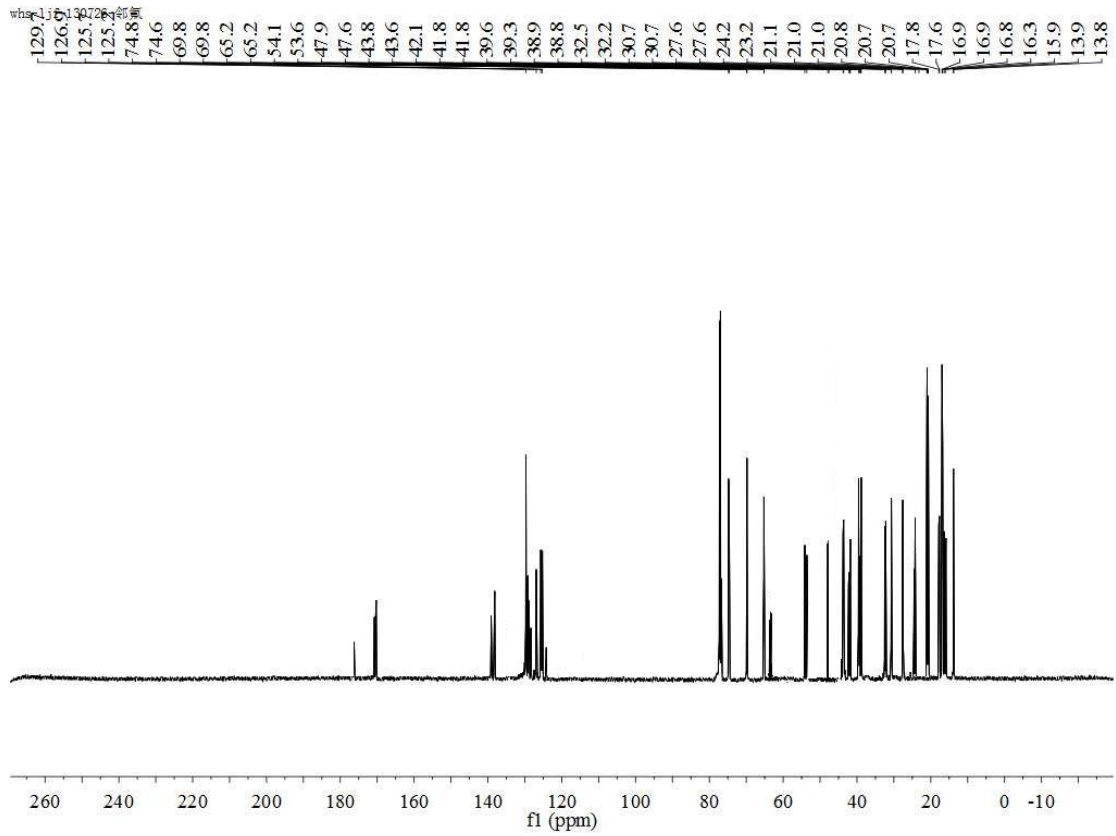
1\_131209152336 #1-11 RT: 0.01-0.04 AV: 11 NL: 7.33E6  
T: FTMS - p ESI Full ms [300.00-700.00]



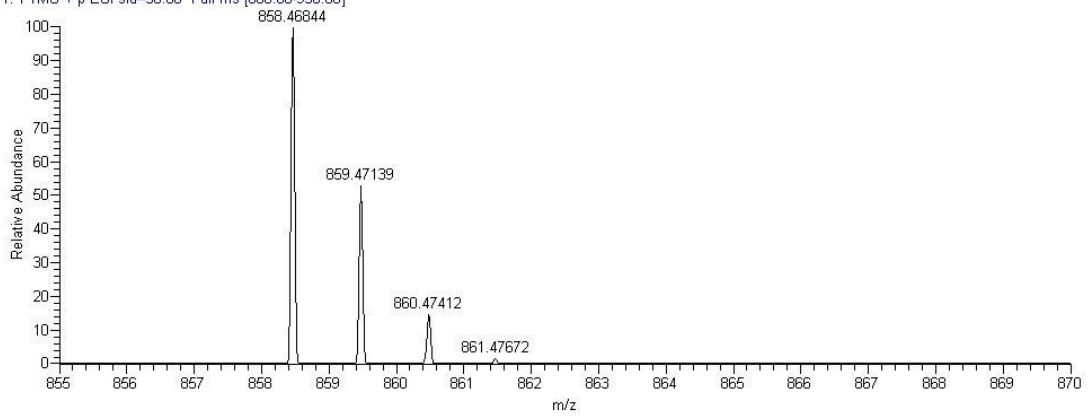
**3a**: Yield 65.5%. m.p. 135.7–139.0 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.55 (d,  $J = 7.2$  Hz, 1H, Ar-H), 7.40–7.27 (m, 2H, Ar-H), 7.17–7.12 (m, 1H, Ar-H), 6.51–6.21 (m, 1H, NH), 5.82–5.67 (m, 1H, H-11), 5.30–5.20 (m, 1H, H-3), 5.16–5.10 (m, 1H, H-2), 5.04 (m, 1H, P-CH), 4.23–4.10 (m, 2H,  $-\text{OCH}_2$ ),

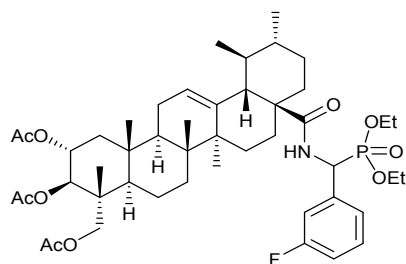
3.40–3.75 (m, 2H, -OCH<sub>2</sub>), 3.73–3.42 (m, 2H, H-23), 2.04 (s, 3H, COCH<sub>3</sub>), 2.01(s, 3H, COCH<sub>3</sub>), 1.97 (s, 3H, COCH<sub>3</sub>), 1.96–1.10 (m, triterpene's H, 21H), 1.33 (t, *J*=5 Hz, 6H, CH<sub>3</sub>×2), 1.10 (s, 3H, CH<sub>3</sub>-27), 1.04 (s, 3H, CH<sub>3</sub>-24), 1.00 (s, 3H, CH<sub>3</sub>-26), 0.95 (d, *J*= 5.5 Hz, 3H, CH<sub>3</sub>-30), 0.88 (s, 3H, CH<sub>3</sub>-25), 0.82 (d, *J*= 3.3 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, DMSO) δ 176.2, 170.7, 170.4, 170.3, 139.1, 138.2, 129.7, 129.2, 128.9, 126.9, 125.7, 125.2, 74.7, 69.8, 65.2, 63.1, 62.8, 54.1, 53.6, 47.9, 47.6, 43.7, 42.3, 42.1, 41.8, 39.6, 39.3, 38.9, 38.8, 32.5, 32.2, 30.7, 29.6, 27.6, 24.2, 23.2, 21.1, 21.0, 20.8, 20.7, 17.8, 17.6, 16.9, 16.8, 16.3, 15.9, 13.8. ESI-HRMS *m/z* Calc for C<sub>47</sub>H<sub>69</sub>FNO<sub>10</sub>P [M+H]<sup>+</sup> : 858.47159 founded: 858.46844.



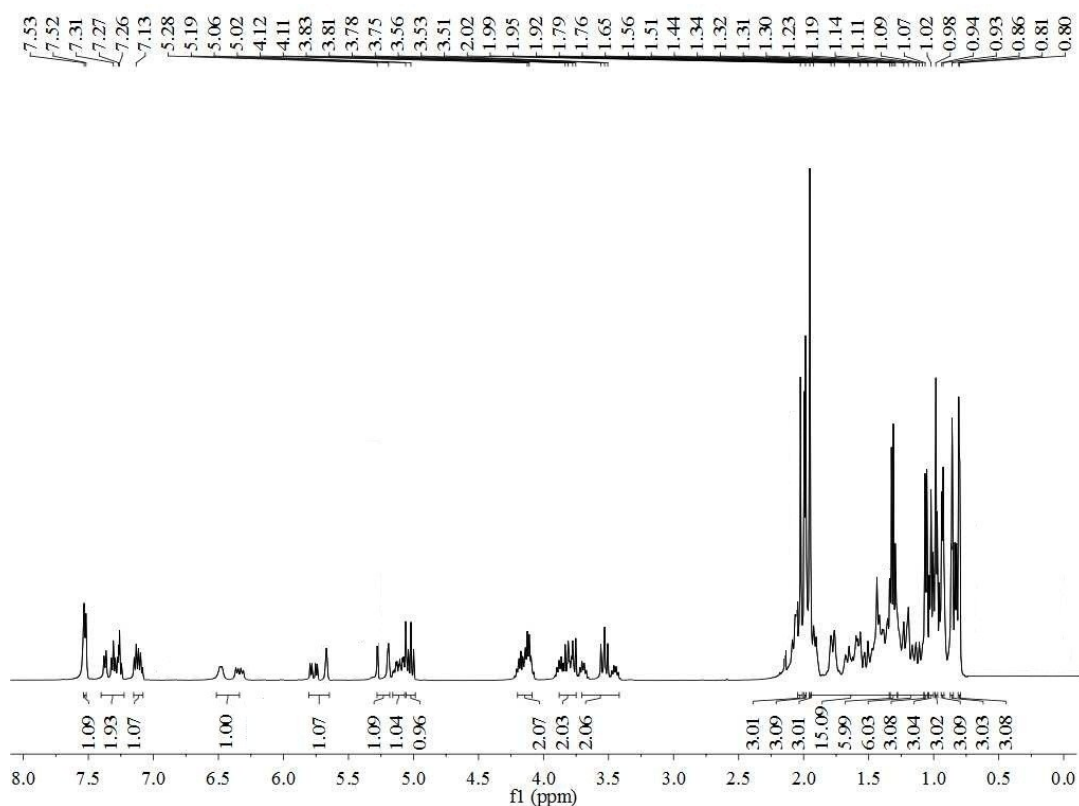


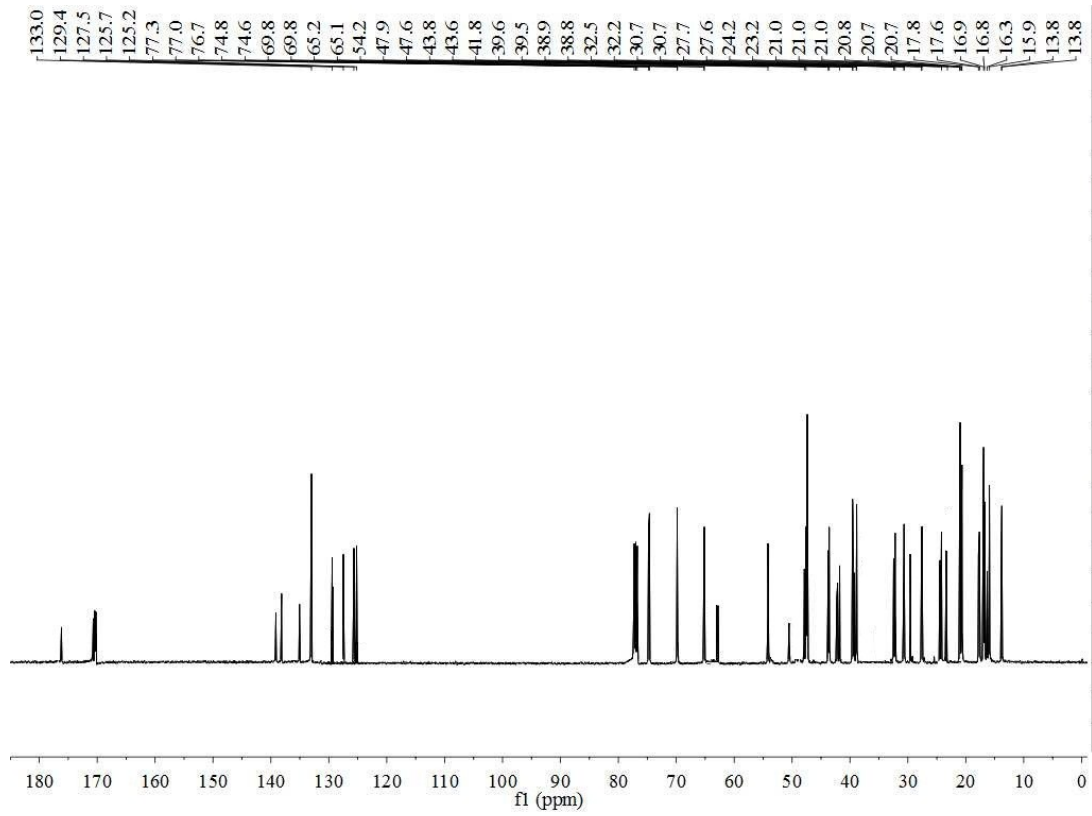
ljf-1 #1-15 RT: 0.01-0.05 AV: 15 NL: 2.49E5  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



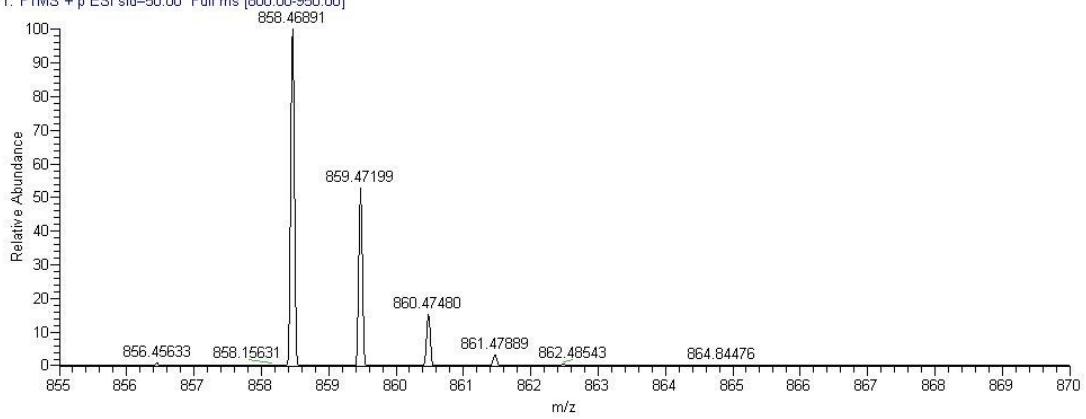


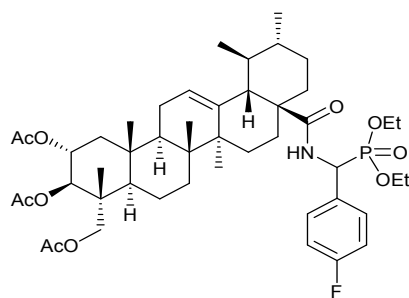
**3b**: Yield 67.5%. m.p. 133.4~135.6 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.53 (d, *J* = 7.2 Hz, 1H, Ar-H), 7.38–7.26 (m, 2H, Ar-H), 7.15–7.10 (m, 1H, Ar-H), 6.49–6.19 (m, 1H, NH), 5.80–5.65 (m, 1H, H-11), 5.28–5.19 (m, 1H, H-3), 5.14–5.08 (m, 1H, H-2), 5.02 (m, 1H, P-CH), 4.21–4.09 (m, 2H, -OCH<sub>2</sub>), 3.88–3.75 (m, 2H, -OCH<sub>2</sub>), 3.71–3.42 (m, 2H, H-23), 2.02 (s, 3H, COCH<sub>3</sub>), 1.99 (s, 3H, COCH<sub>3</sub>), 1.95 (s, 3H, COCH<sub>3</sub>), 1.94–1.08 (m, triterpene's H, 21H), 1.31 (t, *J* = 5 Hz, 6H, CH<sub>3</sub>×2), 1.07 (s, 3H, CH<sub>3</sub>-27), 1.02 (s, 3H, CH<sub>3</sub>-24), 0.98 (s, 3H, CH<sub>3</sub>-26), 0.93 (d, *J* = 5.5 Hz, 3H, CH<sub>3</sub>-30), 0.86 (s, 3H, CH<sub>3</sub>-25), 0.80 (d, *J* = 3.3 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.2, 170.7, 170.4, 170.3, 139.1, 138.2, 135.1, 133.0, 129.4, 127.5, 125.7, 125.2, 74.7, 69.8, 65.2, 63.1, 62.8, 54.2, 50.5, 47.9, 47.6, 43.7, 42.3, 42.1, 41.8, 39.6, 39.3, 38.9, 38.8, 32.5, 32.2, 30.7, 29.6, 27.7, 24.2, 23.2, 21.0, 21.0, 20.8, 20.7, 17.8, 17.6, 16.9, 16.8, 16.4, 15.9, 13.8. ESI-HRMS *m/z* Calc for C<sub>47</sub>H<sub>69</sub>FNO<sub>10</sub>P [M+H]<sup>+</sup>: 858.47159 founded: 858.46891.



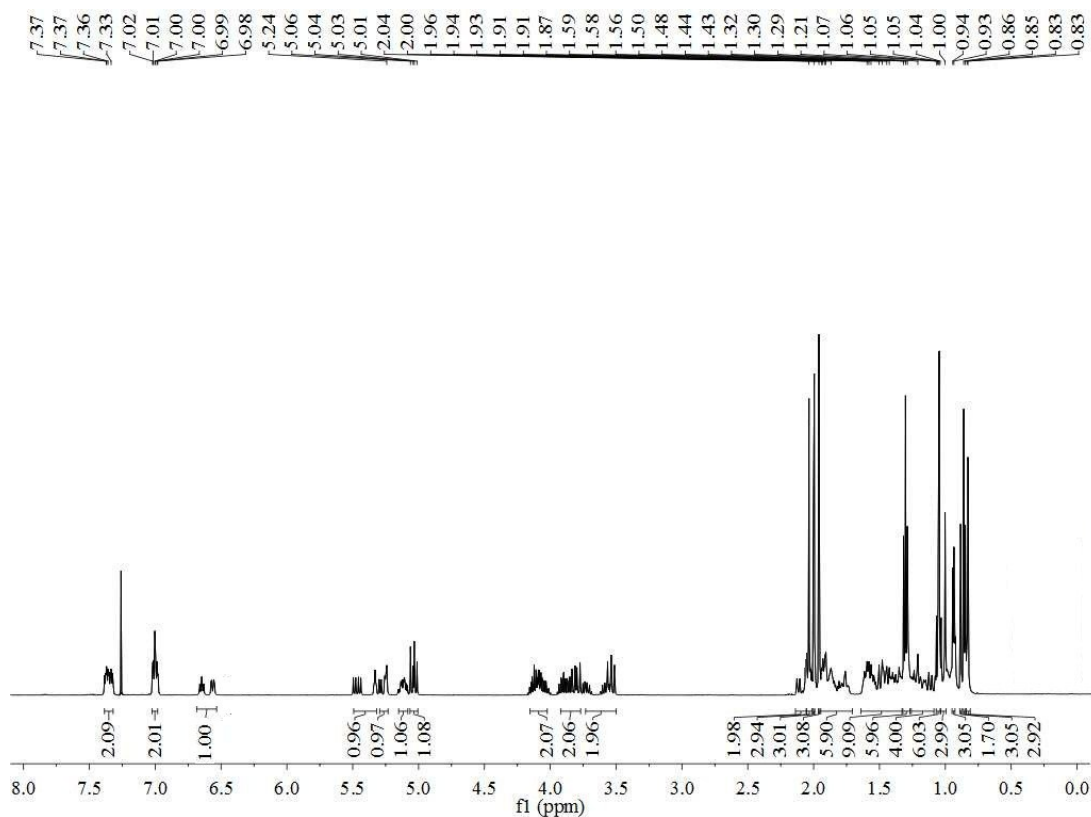


ljf2 #1-14 RT: 0.01-0.05 AV: 14 NL: 1.77E6  
T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]

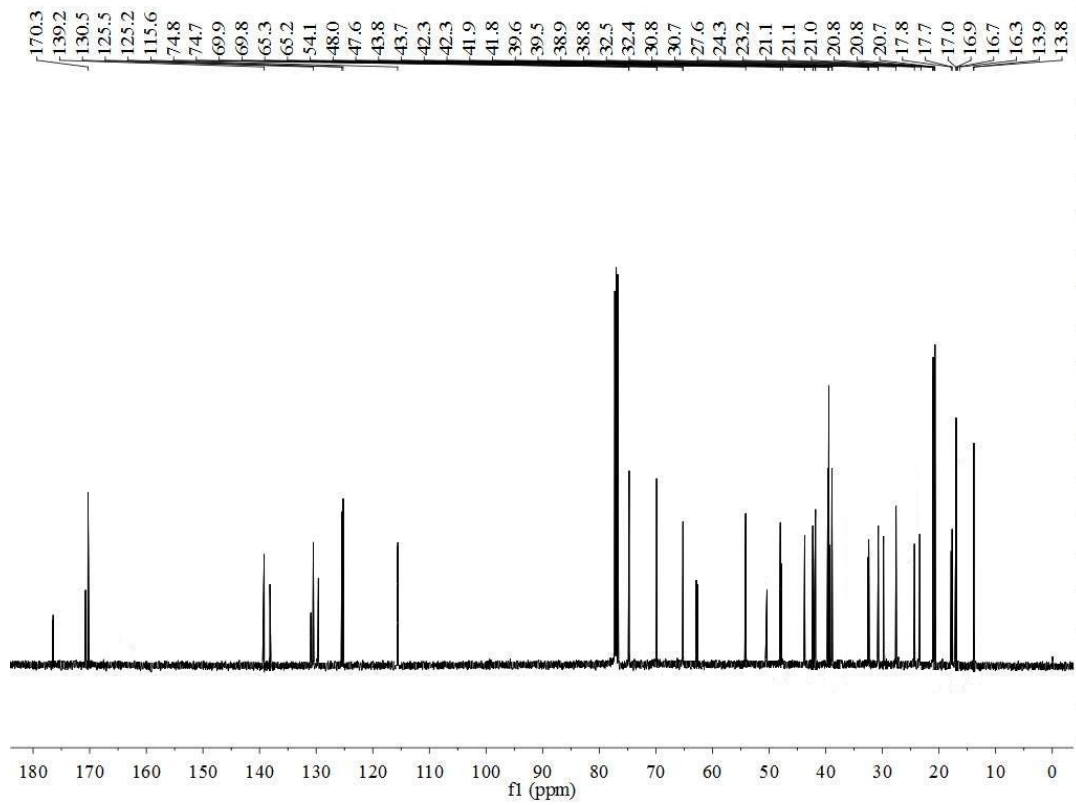




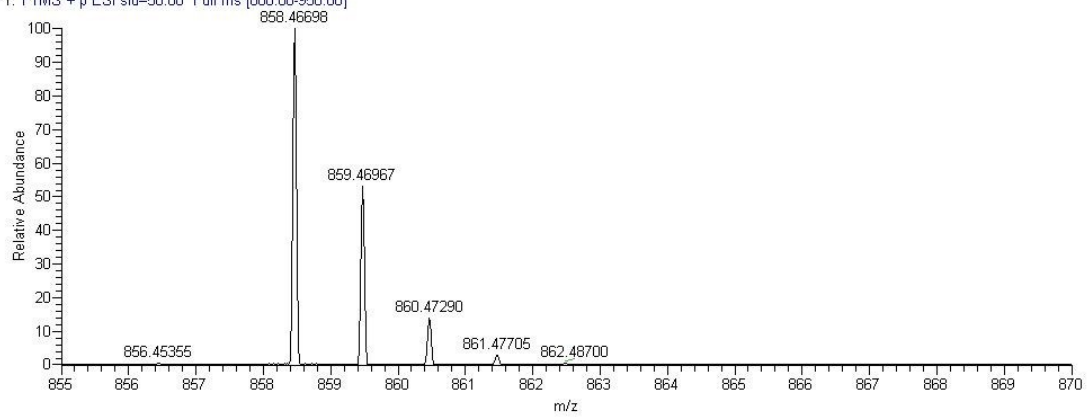
**3c:** Yield 68.1%. m.p. 133.2~135.1 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.39 - 7.32 (m, 2H, Ar-H), 7.02 - 6.98 (m, 2H, Ar-H), 6.67 - 6.43 (m, 1H, NH), 5.51-5.33 (m, 1H, H-11), 5.26 (dd,  $J = 11.3, 9.4$  Hz, 1H, H-3), 5.15 - 5.08 (m, 1H, H-2), 5.04 (dd,  $J = 14.6, 10.3$  Hz, 1H, P-CH), 4.15 - 4.02 (m, 2H,  $-\text{OCH}_2$ ), 3.92 - 3.77 (m, 2H,  $-\text{OCH}_2$ ), 3.73 - 3.50 (m, 2H, H-23), 2.10-1.10 (m, triterpene's H, 21H), 2.04 (s, 3H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 1.96 (s, 3H,  $\text{COCH}_3$ ), (3 $\times$  $\text{CH}_3\text{CO}$ ), 1.30 (td,  $J = 7.1$  Hz, 6H,  $\text{CH}_3\times 2$ ), 1.07 (s, 3H,  $\text{CH}_3$ -27), 1.04 (s, 3H,  $\text{CH}_3$ -24), 1.00 (s, 3H,  $\text{CH}_3$ -26), 0.94 (d,  $J = 4.6$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d,  $J = 3.2$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.50, 170.8, 170.4, 170.3, 139.2, 138.1, 130.9, 130.5, 129.7, 125.5, 125.2, 115.6, 74.8, 69.9, 65.3, 62.9, 62.7, 54.1, 50.4, 48.0, 47.6, 43.8, 42.3, 42.2, 41.8, 39.6, 39.5, 38.9, 38.8, 32.5, 32.4, 30.8, 29.6, 27.6, 24.3, 23.2, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 17.0, 16.7, 16.3, 16.1. 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{FNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 858.47159 founded: 858.46698.

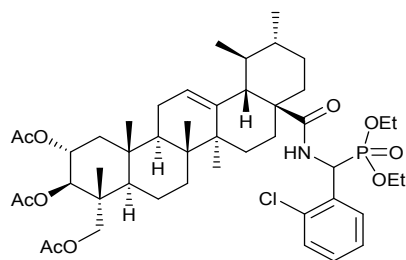




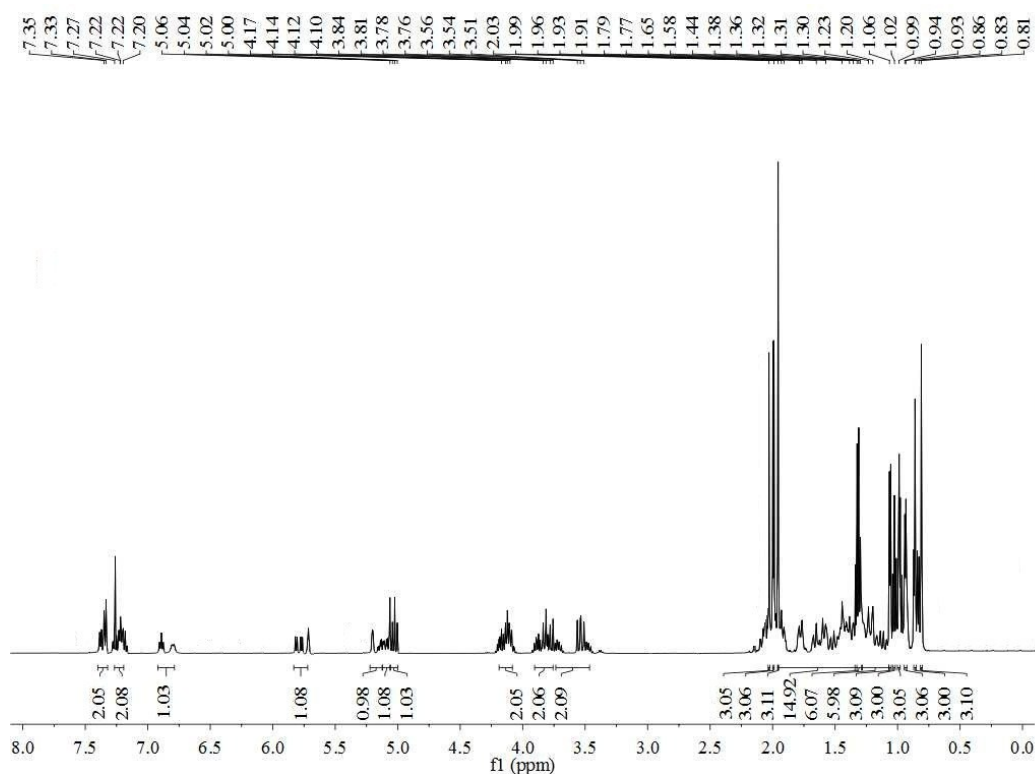


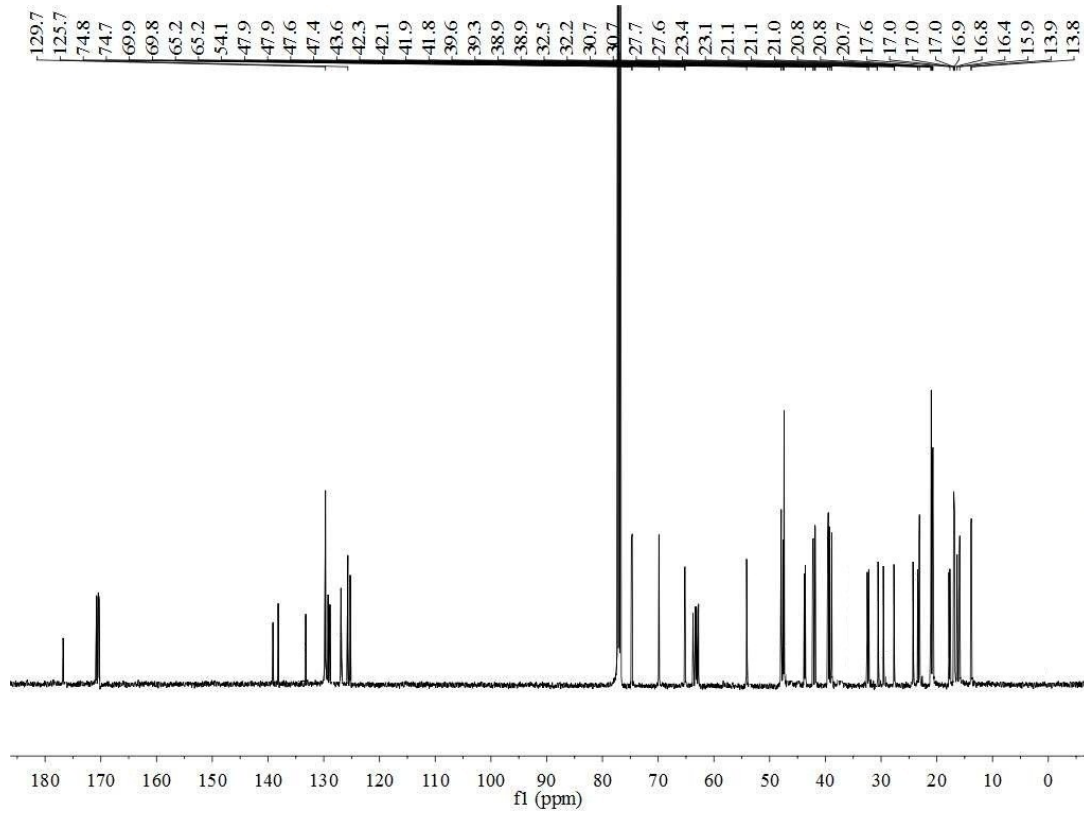
ljf-3 #9 RT: 0.03 AV: 1 NL: 5.07E6  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]





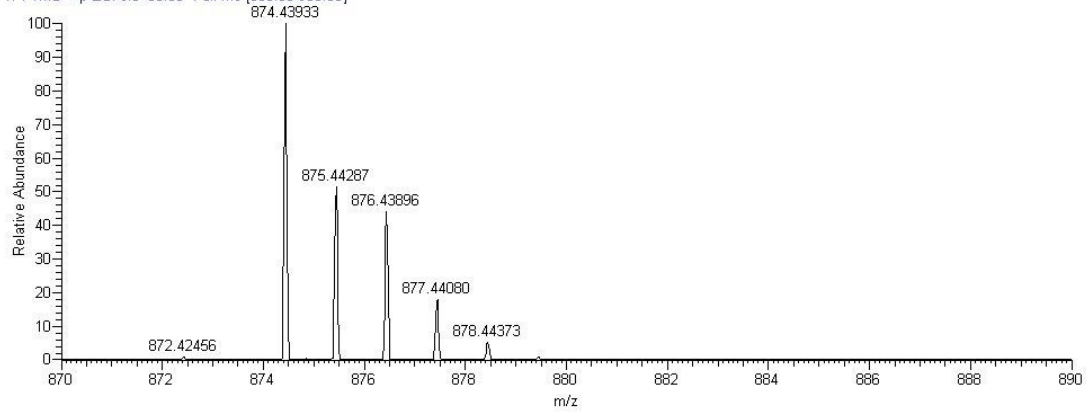
**3d:** Yield 64.9%. m.p. 141.3~144.6 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.39-7.33 (m, 2H, Ar-H), 7.27-7.20 (m, 2H), 6.91-6.79 (m, 1H, NH), 5.82-5.72 (m, 1H, H-11), 5.20-5.13(m, 1H, H-3), 5.12-5.06 (m, 1H, H-2), 5.09-5.06 (m, 1H, P-CH), 4.19-4.09 (m, 2H, -OCH<sub>2</sub>), 3.89-3.72 (m, 2H, -OCH<sub>2</sub>), 3.73-3.47 (m, 2H, H-23), 2.03 (s, 2H, COCH<sub>3</sub>), 1.99 (s, 3H, COCH<sub>3</sub>), 1.96 (s, 3H, COCH<sub>3</sub>), 1.95-1.09 (m, triterpene's H, 21H), 1.34- 1.28 (m, 6H, CH<sub>3</sub>×2), 1.06 (s, 3H, CH<sub>3</sub>-27), 1.02 (s, 1H, CH<sub>3</sub>-24), 0.99 (s, 3H, CH<sub>3</sub>-26), 0.94 (d, *J* = 4.1 Hz, 3H, CH<sub>3</sub>-30), 0.86 (s, 3H, CH<sub>3</sub>-25), 0.81 (s, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.8, 170.8, 170.5, 170.3, 139.1, 138.2, 133.2, 129.7, 129.2, 126.9, 125.7, 125.2, 74.8, 69.9, 65.2, 63.1, 62.8, 54.1, 47.9, 47.6, 47.4, 43.8, 42.3, 42.1, 41.9, 39.6, 39.3, 38.9, 32.5, 32.2, 30.7, 29.6, 27.7, 24.5, 23.4, 23.1, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 16.9, 16.8, 16.4, 15.9, 13.9. ESI-HRMS *m/z* Calc for C<sub>47</sub>H<sub>69</sub>ClNO<sub>10</sub>P [M+H]<sup>+</sup>: 874.44204 founded: 874.43933.

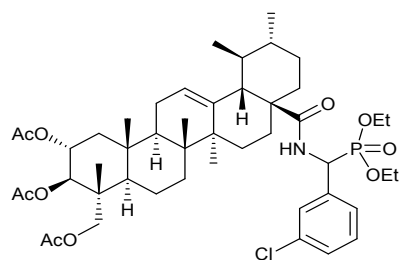




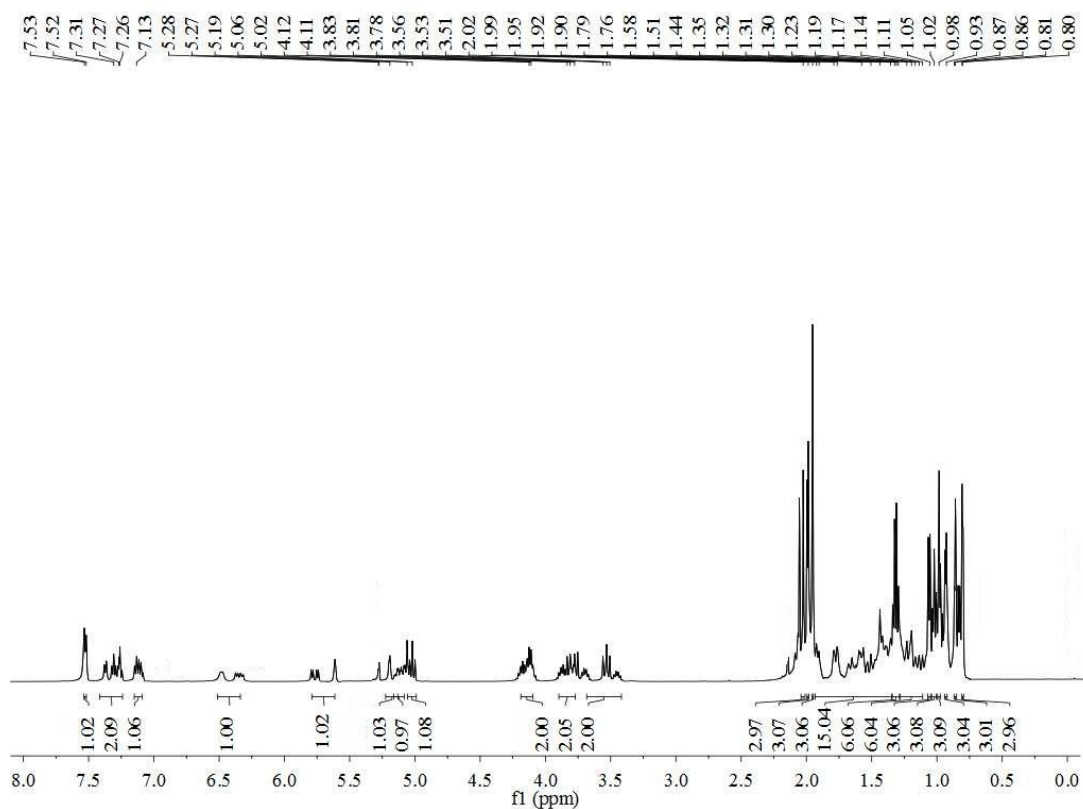
ljf-4 #8 RT: 0.03 AV: 1 NL: 2.72E6

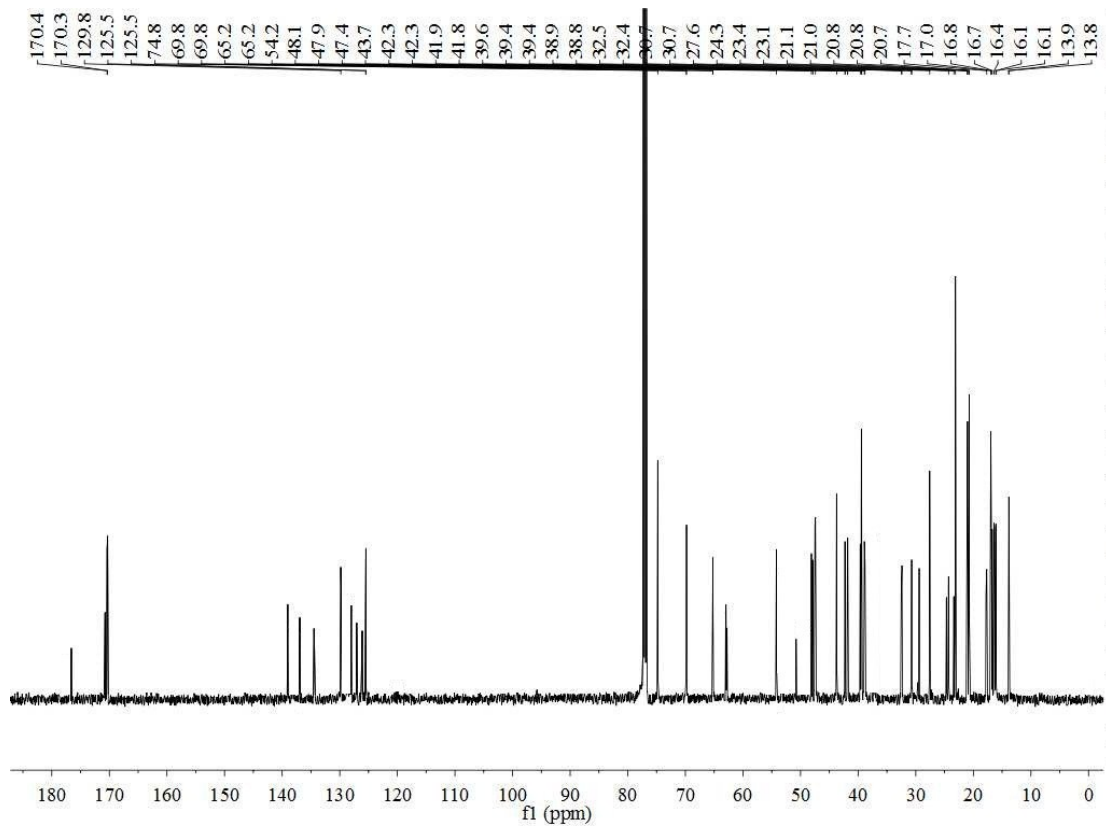
T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



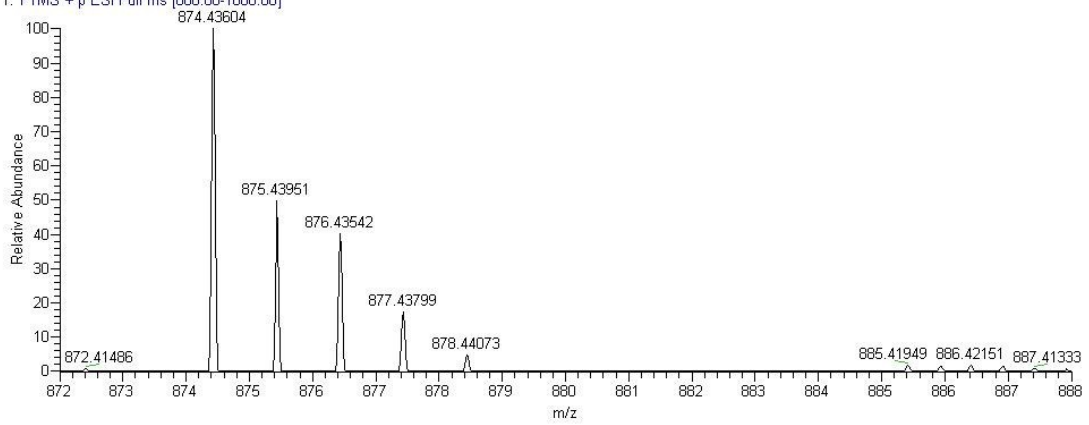


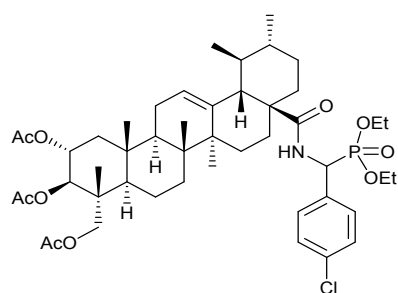
**3e**: Yield 68.3%. m.p. 132.9~135.7 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 15.0$  Hz, 1H, Ar-H), 7.25 (m, 3H, Ar-H), 6.70–6.44 (m, 1H, NH), 5.49–5.33 (m, 1H, H-11), 5.28–5.22 (m, 1H, H-3), 5.15–5.10 (m, 1H, H-2), 5.06–5.01 (m, 1H, P-CH), 4.18–4.00 (m, 2H,  $-\text{OCH}_2$ ), 3.95–3.77 (m, 2H,  $-\text{OCH}_2$ ), 3.63–3.51 (m, 2H, H-23), 1.93–1.01 (m, triterpene's H, 21H), 2.03 (s, 3H,  $\text{COCH}_3$ ), 1.99 (s, 3H,  $\text{COCH}_3$ ), 1.96 (s, 3H,  $\text{COCH}_3$ ), 1.30 (t,  $J = 7.1$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.07 (s, 3H,  $\text{CH}_3$ -27), 1.05 (s, 3H,  $\text{CH}_3$ -24), 0.94 (s, 3H,  $\text{CH}_3$ -26), 0.90 (d,  $J = 3.4$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d, 3H,  $J = 4.3$  Hz,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 170.8, 170.4, 170.3, 139.0, 136.9, 134.5, 129.8, 128.3, 127.0, 126.1, 125.5, 74.8, 69.8, 65.2, 63.0, 62.8, 54.2, 50.8, 48.0, 47.4, 43.7, 42.3, 41.9, 41.8, 39.6, 39.4, 38.9, 32.5, 32.4, 30.7, 29.6, 27.6, 24.3, 23.4, 23.1, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 17.0, 16.8, 16.4, 16.1, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{ClNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$  : 874.44204 founded: 874.43604.



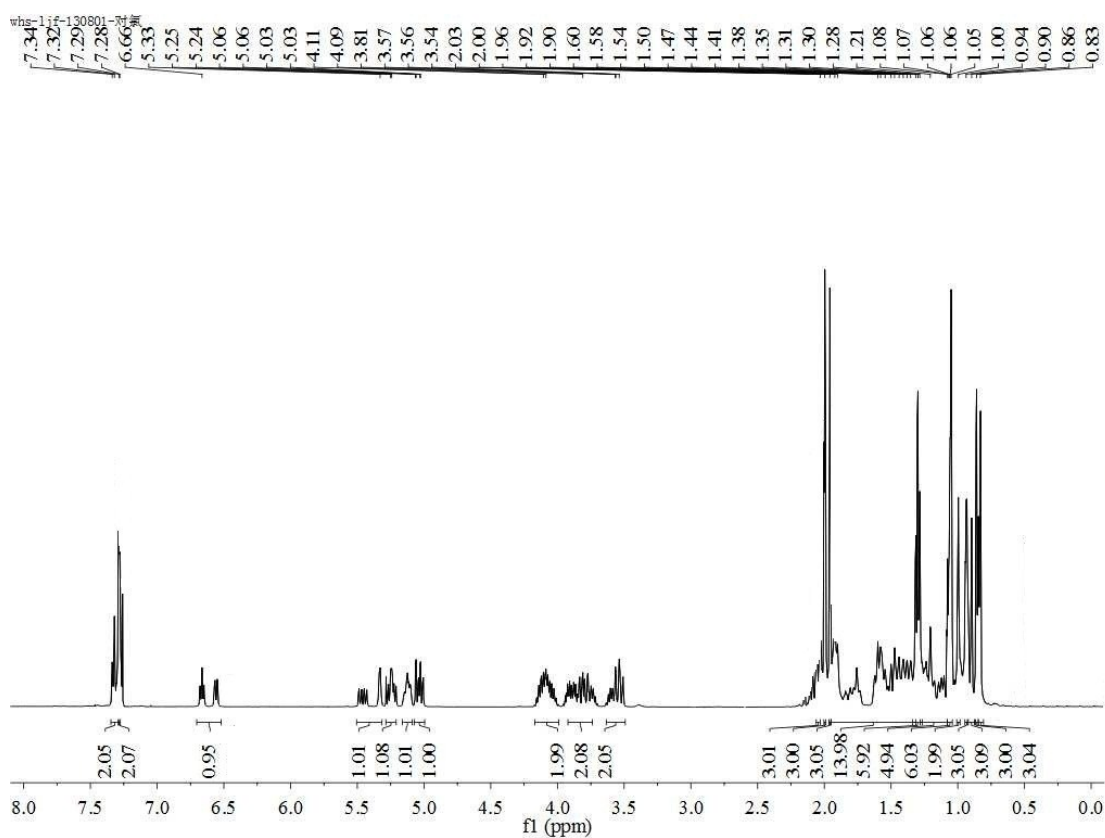


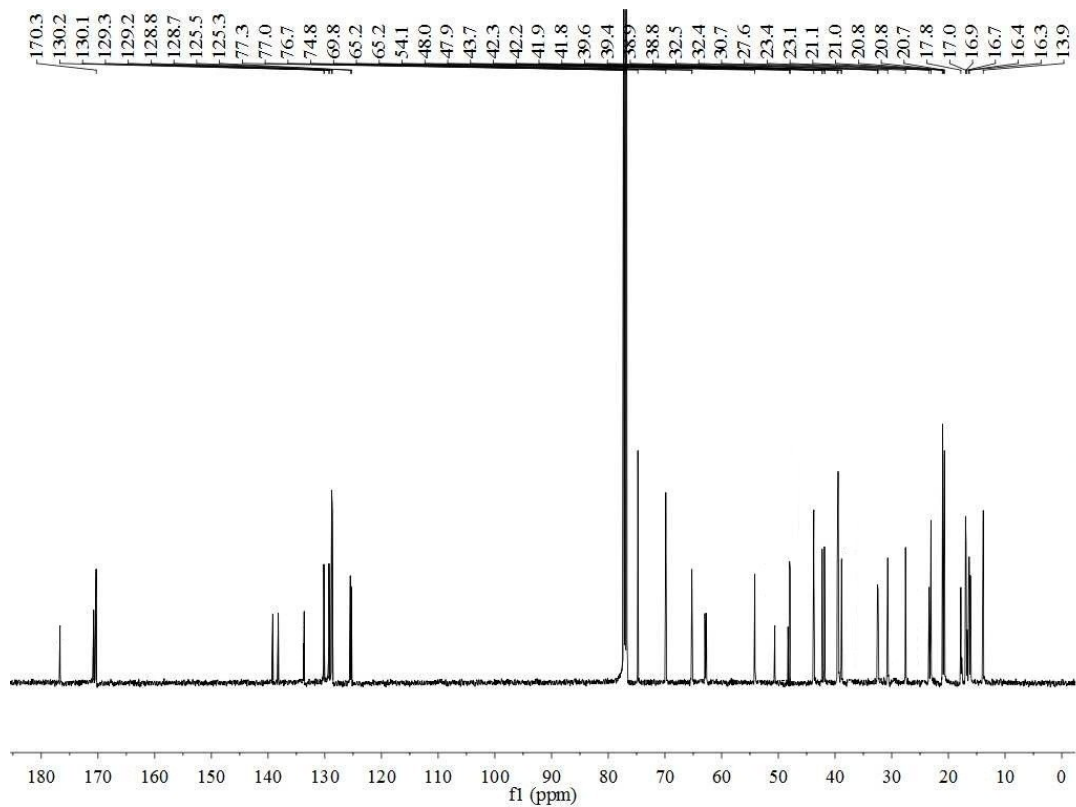
ljf-130721 #7 RT: 0.03 AV: 1 NL: 8.00E5  
T: FTMS + p ESI Full ms [800.00-1000.00]



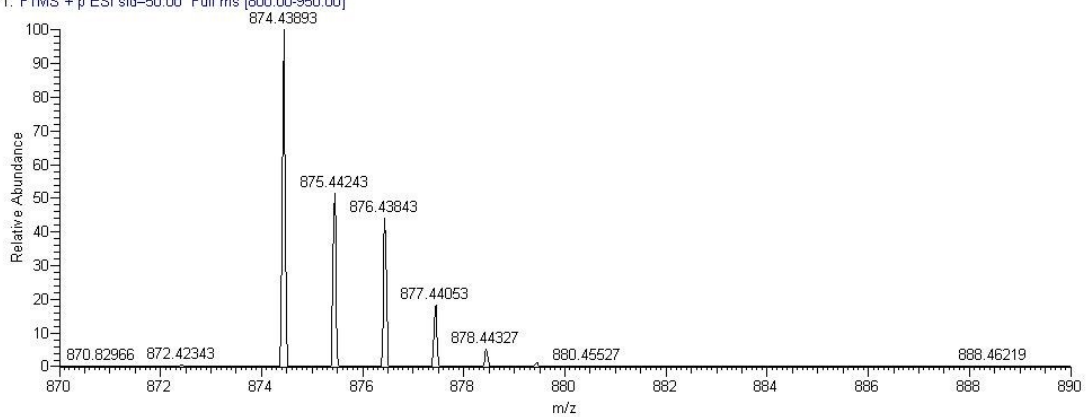


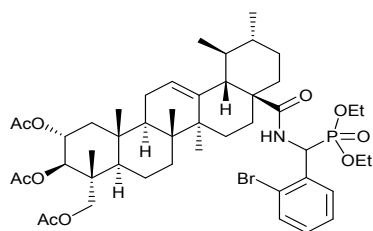
**3f:** Yield 65.6%. m.p. 139.2~140.8 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.33 (d,  $J = 8.3$  Hz, 2H, Ar-H), 7.28 (d,  $J = 2.8$  Hz, 2H, Ar-H), 6.69–6.42 (m, 1H, NH), 5.49–5.33 (m, 1H, H-11), 5.28–5.21 (m, 1H, H-3), 5.13–5.10 (m, 1H, H-2), 5.06–5.03 (m, 1H, P-CH), 4.13–4.06 (m, 2H,  $-\text{OCH}_2$ ), 3.92–3.75 (m, 2H,  $-\text{OCH}_2$ ), 3.57–3.51 (m, 1H, H-23), 2.03 (s, 3H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 1.96 (s, 3H,  $\text{COCH}_3$ ), 1.95–1.00 (m, triterpene's H, 21H), 1.30 (t,  $J = 7.0$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.08–1.05 (m, 6H,  $\text{CH}_3$ -24/27), 0.94 (s, 3H,  $\text{CH}_3$ -26), 0.90 (d,  $J = 3.9$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d,  $J = 4.1$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 170.8, 170.4, 170.3, 139.2, 138.2, 133.6, 130.2, 129.2, 128.8, 125.5, 125.3, 74.8, 69.8, 65.2, 63.0, 62.7, 54.1, 50.6, 48.0, 47.9, 43.7, 42.3, 41.9, 39.6, 39.4, 38.9, 38.8, 32.5, 32.4, 30.7, 29.6, 27.6, 23.4, 23.2, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 17.0, 16.9, 16.7, 16.4, 16.3, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{ClNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 874.44204 founded: 874.43893.



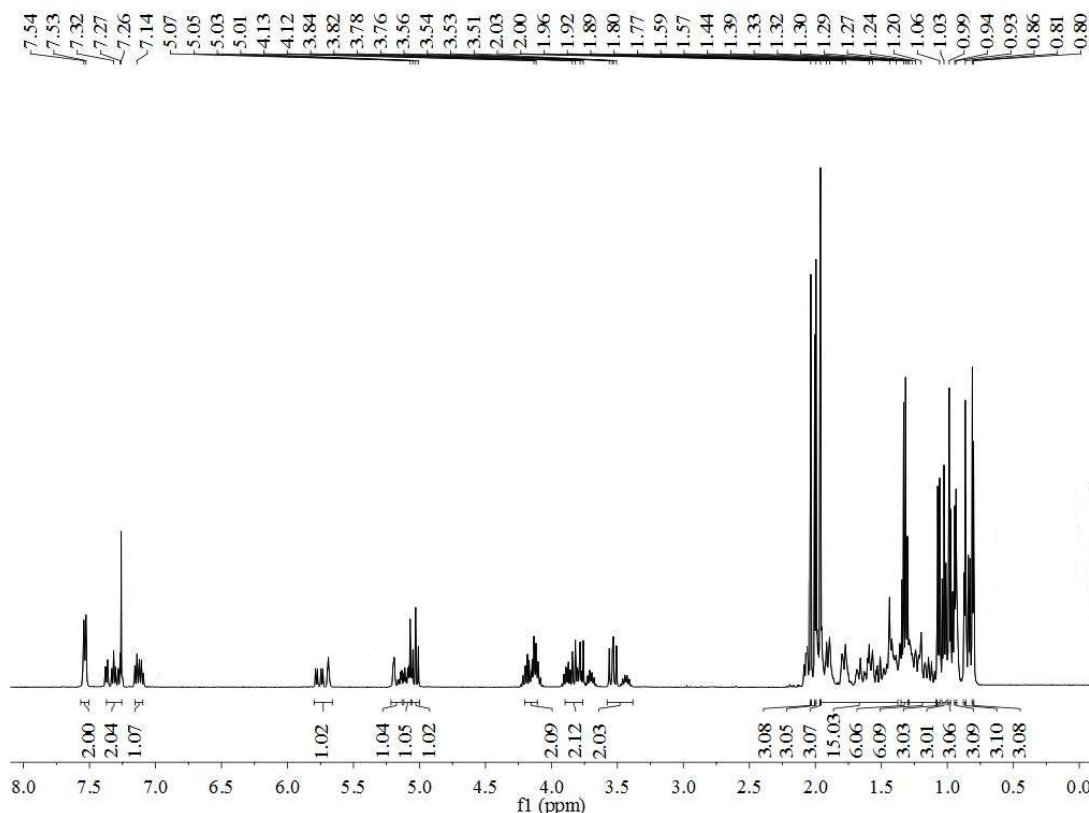


ljf6 #3-15 RT: 0.01-0.05 AV: 13 NL: 2.70E6  
T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]

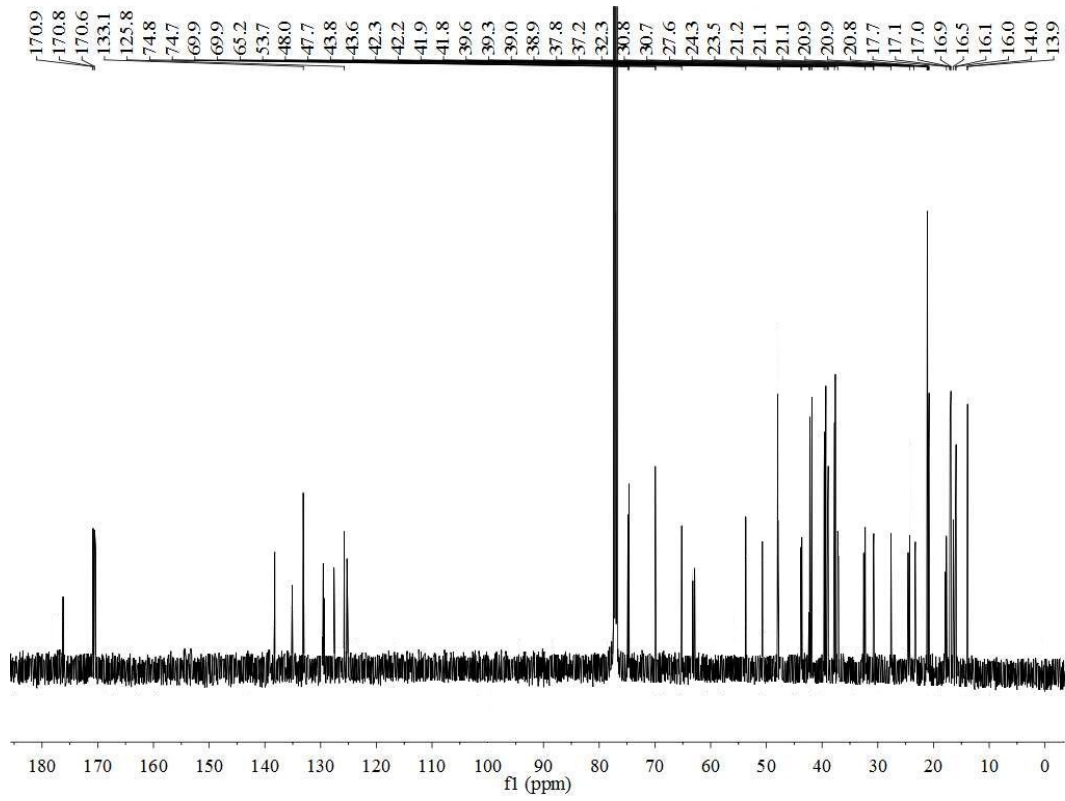




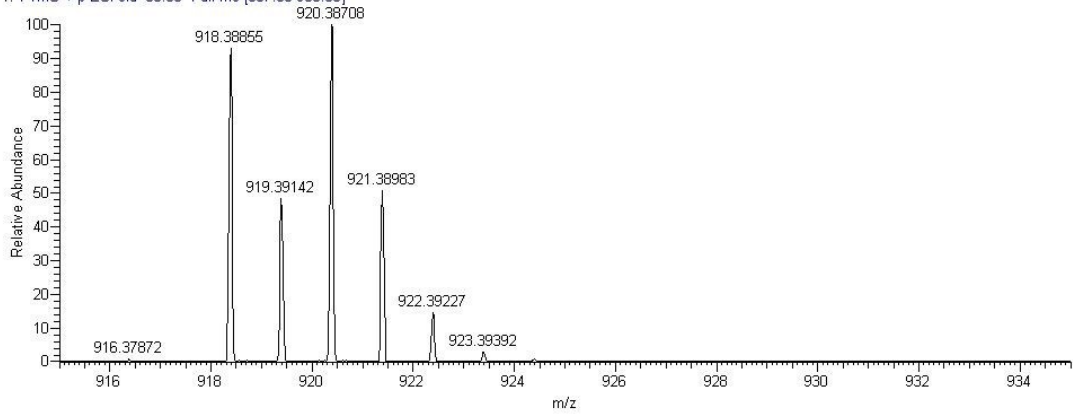
**3g**: Yield 68.9%. m.p. 147.3~150.3 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.53 (d,  $J = 8.0$  Hz, 2H, Ar-H), 7.38–7.25 (m, 2H, Ar-H), 7.16–7.09 (m, 1H, NH), 5.79–5.67 (m, 1H, H-11), 5.19–5.13 (m, 1H, H-3), 5.12–5.06 (m, 1H, H-2), 5.06–5.01 (m, 1H, P-CH), 4.22–4.09 (m, 2H,  $-\text{OCH}_2$ ), 3.89–3.76 (m, 2H,  $-\text{OCH}_2$ ), 3.56–3.39 (m, 2H, H-23), 2.03 (s, 2H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 1.96 (s, 3H,  $\text{COCH}_3$ ), 1.96–1.10 (m, triterpene's H, 21H), 1.35–1.30 (m, 6H,  $\text{CH}_3 \times 2$ ), 1.06 (s, 3H,  $\text{CH}_3$ -27), 1.03 (s, 3H,  $\text{CH}_3$ -24), 0.99 (s, 3H,  $\text{CH}_3$ -26), 0.94 (d,  $J = 4.9$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.81 (d,  $J = 4.9$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 170.9, 170.6, 170.4, 138.2, 135.1, 133.1, 129.5, 129.2, 127.6, 125.8, 125.3, 74.8, 69.9, 65.3, 63.3, 62.9, 53.7, 50.6, 48.00, 47.7, 43.8, 42.3, 42.2, 41.9, 39.6, 39.0, 37.8, 32.5, 32.3, 30.8, 27.7, 24.6, 24.3, 23.5, 21.2, 21.1, 20.9, 20.8, 17.9, 17.7, 17.1, 16.9, 16.5, 16.0, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{BrNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 918.39152 founded: 918.38855.

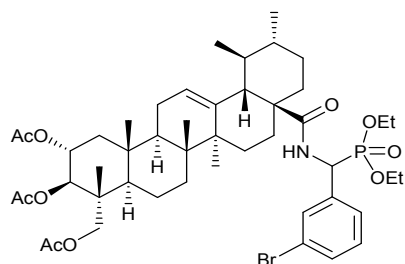




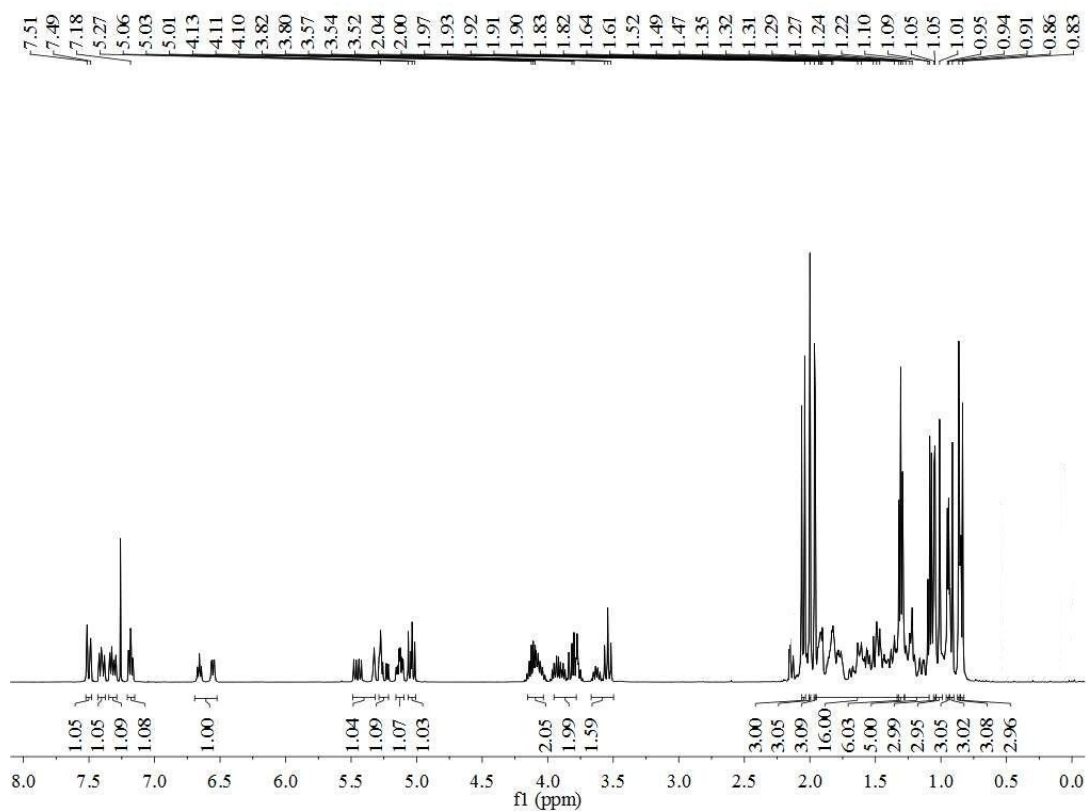


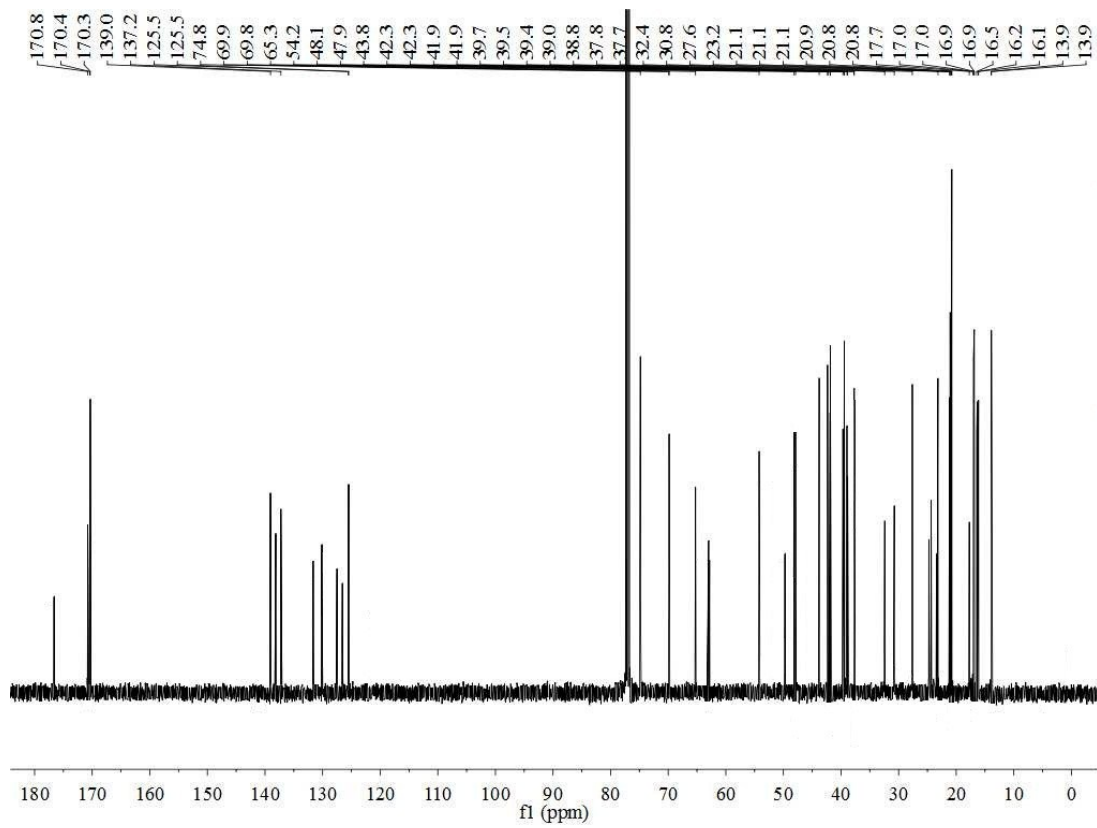
ljf-8 #12 RT: 0.04 AV: 1 NL: 2.38E6  
 T: FTMS + p ESI sid=50.00 Full ms [857.00-950.00]



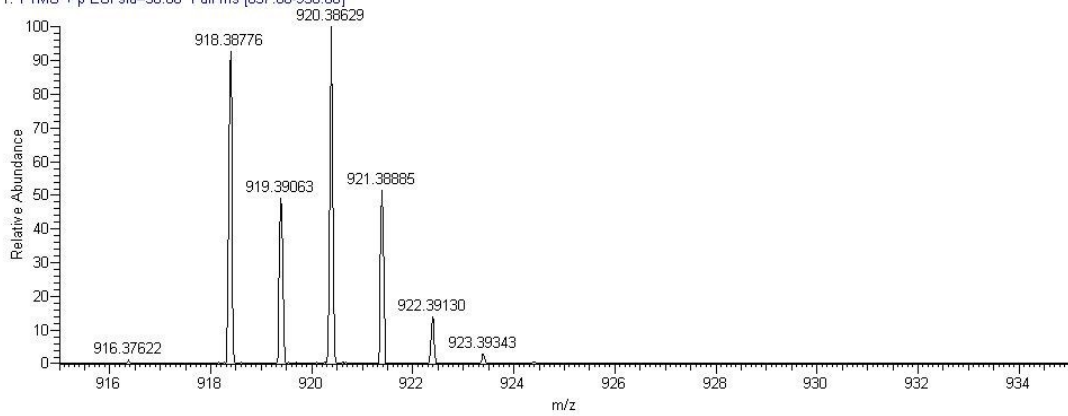


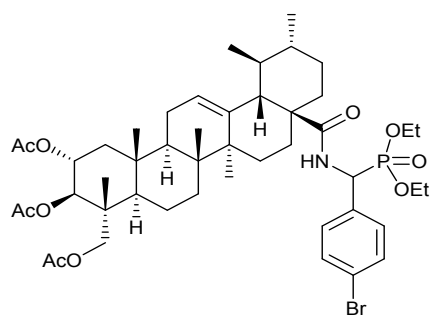
**3h**: Yield 62.9%. m.p. 136.2~139.7 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 13.6$  Hz, 1H, Ar-H), 7.41 (t,  $J = 10.0$  Hz, 1H, Ar-H), 7.32 (dd,  $J = 15.6, 7.7$  Hz, 1H, ArH), 7.18 (t,  $J = 7.8$  Hz, 1H, Ar-H), 6.68–6.44 (m, 1H, NH), 5.48–5.32 (m, 1H, H-11), 5.28–5.22 (m, 1H, H-3), 5.13 (td,  $J = 11.0, 4.5$  Hz, 1H, H-2), 5.06–5.01 (m, 1H, P-CH), 4.16–4.02 (m, 2H,  $-\text{OCH}_2$ ), 3.95–3.80 (m, 2H,  $-\text{OCH}_2$ ), 3.67–3.52 (m, 2H, H-23), 2.04 (s, 3H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 1.97 (s, 3H,  $\text{COCH}_3$ ), 1.95–1.09 (m, triterpene's H, 21H), 1.31 (t,  $J = 7.1$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.05 (s, 3H,  $\text{CH}_3$ -27), 1.01 (s, 3H,  $\text{CH}_3$ -24), 0.95 (s, 3H,  $\text{CH}_3$ -26), 0.91 (d, 3H,  $J = 3.5$  Hz,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d,  $J = 3.6$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 170.8, 170.4, 170.3, 139.0, 138.1, 137.2, 131.6, 130.1, 127.5, 126.6, 125.5, 74.8, 69.9, 65.3, 63.0, 62.9, 54.2, 49.9, 48.1, 47.9, 43.8, 42.3, 41.9, 39.7, 39.5, 38.9, 37.8, 32.6, 32.4, 30.8, 27.6, 24.8, 23.4, 23.2, 21.1, 21.1, 20.9, 20.8, 17.9, 17.7, 17.0, 16.9, 16.5, 16.2, 16.1, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{BrNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 918.39152 founded: 918.38776.



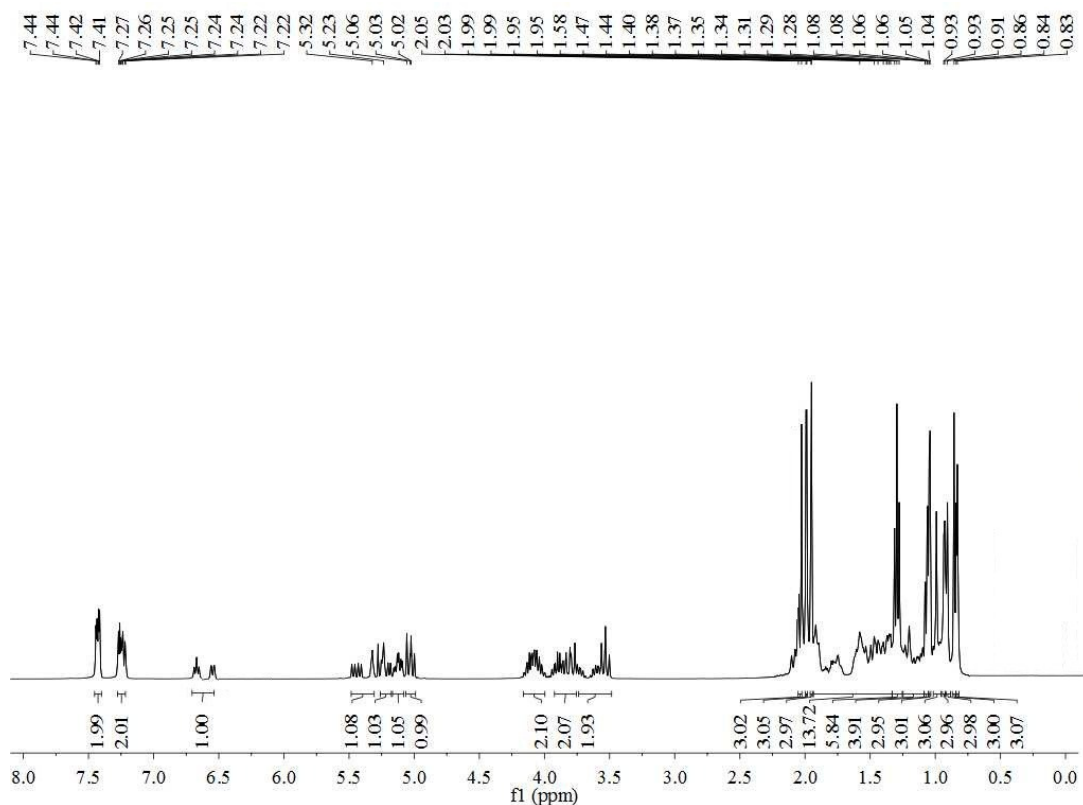


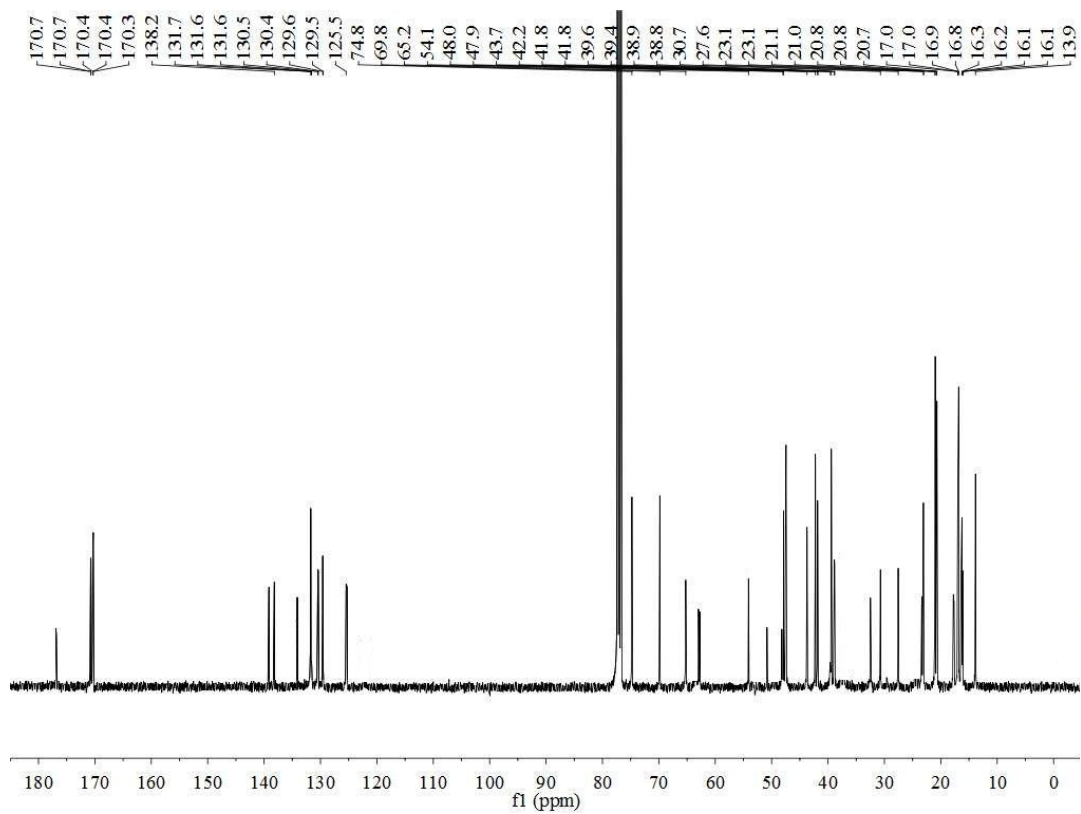
ljf-8 #18 RT: 0.06 AV: 1 NL: 3.97E6  
 T: FTMS + p ESI sid=50.00 Full ms [857.00-950.00]



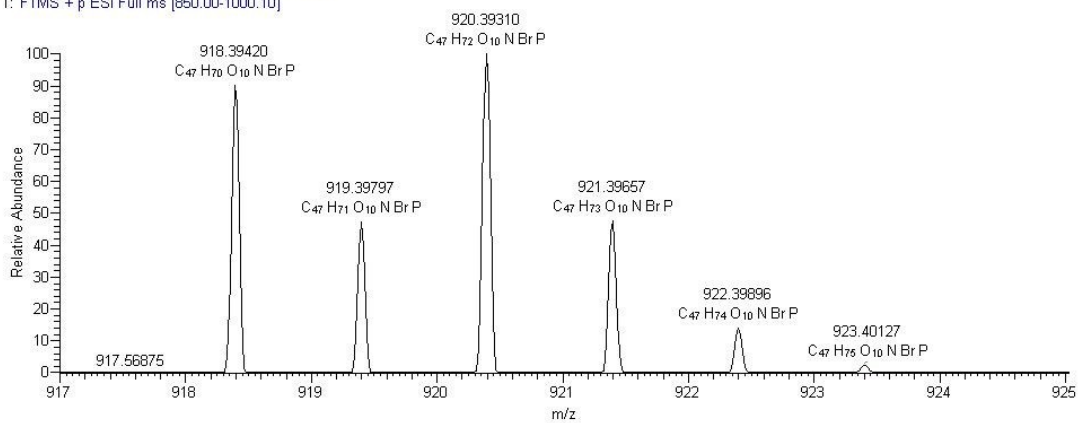


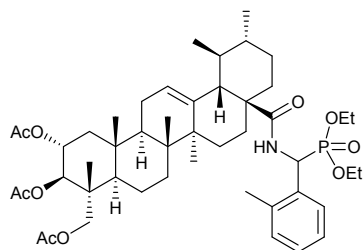
**3i:** Yield 66.5%. m.p. 142.1~144.6 °C.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.43 (dd,  $J = 8.2, 3.4$  Hz, 2H, Ar-H), 7.28 - 7.22 (m, 2H, Ar-H), 6.71-6.42 (m, 1H, NH), 5.48 - 5.31 (m, 1H, H-11), 5.26 - 5.18 (m, 1H, H-3), 5.12 (td,  $J = 10.9, 4.5$  Hz, 1H, H-2), 5.03 (dd,  $J = 13.0, 10.4$  Hz, 1H, P-CH), 4.16 - 4.00 (m, 2H,  $-\text{OCH}_2$ ), 3.92 - 3.76 (m, 2H,  $-\text{OCH}_2$ ), 3.74 - 3.48 (m, 2H, H-23), 2.04 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.99 (d,  $J = 2.7$  Hz, 3H,  $\text{CH}_3\text{CO}$ ), 1.95 (s, 3H,  $\text{CH}_3\text{CO}$ ), ( $3 \times \text{CH}_3\text{CO}$ ), 1.93-0.99 (m, triterpene's H, 21H), 1.29 (t,  $J = 7.1$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.07 (s, 3H,  $\text{CH}_3$ -27), 1.04 (s, 3H,  $\text{CH}_3$ -24), 0.93 (s, 3H,  $\text{CH}_3$ -26), 0.91 (d,  $J = 4.5$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.84 (d,  $J = 3.4$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 170.7, 170.4, 170.3, 139.1, 138.2, 134.1, 131.6, 130.5, 129.6, 125.5, 125.3, 74.8, 69.8, 65.2, 63.0, 62.7, 54.1, 50.8, 48.0, 47.9, 43.7, 42.2, 41.8, 39.6, 39.4, 38.9, 38.8, 32.5, 32.4, 30.7, 29.6, 27.6, 23.4, 23.1, 21.1, 21.0, 20.8, 20.7, 17.8, 17.6, 17.0, 16.9, 16.8, 16.3, 16.1, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{69}\text{BrNO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 918.39152 founded: 918.39420.



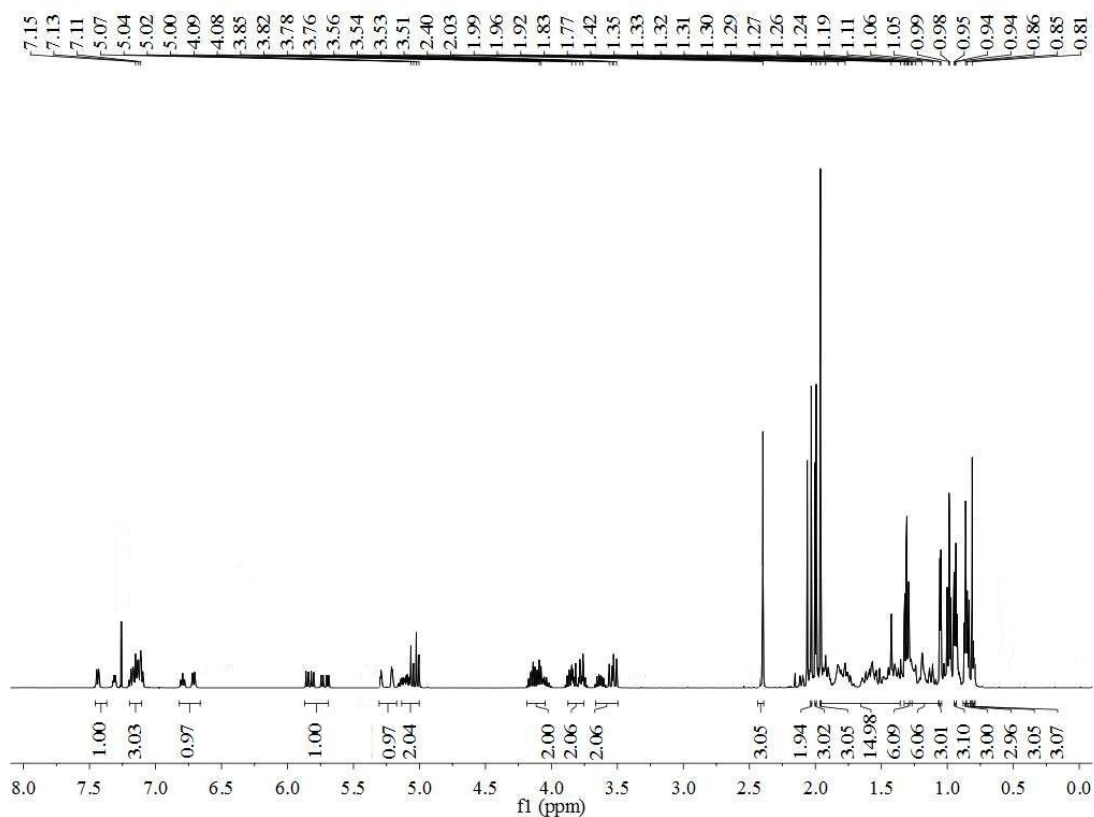


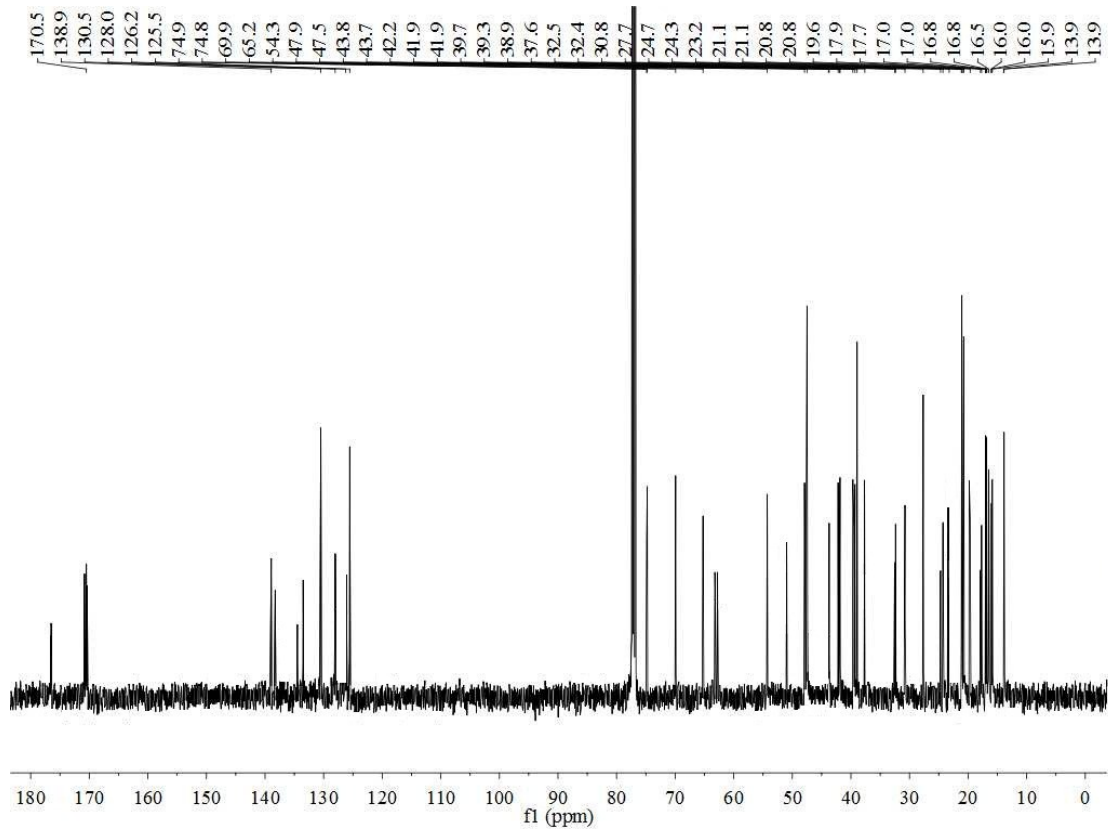
ijf-p-Br #2-33 RT: 0.01-0.11 AV: 32 NL: 3.77E6  
 T: FTMS + p ESI Full ms [850.00-1000.10]



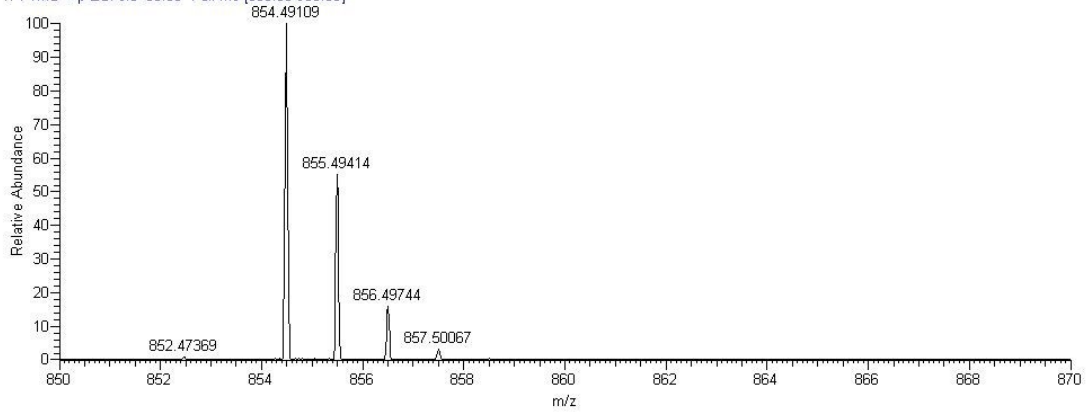


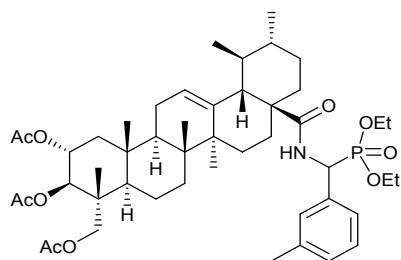
**3j**: Yield 61.9%. m.p. 130.9~134.1 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.45-7.32 (m, 1H, Ar-H), 7.20-7.10 (m, 3H, Ar-H), 6.81- 6.47 (m, 1H, NH), 5.86-5.56 (m, 1H, H-11), 5.29 (d, *J* = 80.5 Hz, 1H, H-3), 5.21-5.00 (m, 2H, H-2, P-CH), 4.17-4.04 (m, 2H, -OCH<sub>2</sub>), 3.88-3.76 (m, 2H, -OCH<sub>2</sub>), 3.65-3.51 (m, 2H, H-23), 2.40 (s, 3H, Ar-CH<sub>3</sub>), 2.03 (s, 3H, COCH<sub>3</sub>), 1.99 (s, 3H, COCH<sub>3</sub>), 1.96 (s, 3H, COCH<sub>3</sub>), 1.96-1.06 (m, triterpene's H, 21H), 1.35-1.26 (m, 6H, CH<sub>3</sub>×2), 1.05 (s, 3H, CH<sub>3</sub>-27), 0.94 (s, 3H, CH<sub>3</sub>-24), 0.86 (s, 3H, CH<sub>3</sub>-26), 0.85 (d, *J* = 5.0 Hz, 3H, CH<sub>3</sub>-30), 0.81 (s, 3H, CH<sub>3</sub>-25), 0.80 (d, *J* = 3.3 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.5, 170.8, 170.5, 170.4, 138.9, 138.3, 134.5, 133.5, 130.5, 128.0, 126.2, 125.5, 74.9, 69.9, 65.2, 62.8, 62.4, 54.3, 50.6, 47.9, 47.5, 43.8, 42.2, 41.9, 39.7, 39.3, 38.9, 37.6, 32.5, 32.4, 30.8, 27.7, 24.7, 24.3, 23.2, 21.1, 21.1, 20.8, 20.8, 19.6, 17.9, 17.7, 17.0, 16.8, 16.5, 16.0, 15.9, 13.9. ESI-HRMS *m/z* Calc for C<sub>48</sub>H<sub>72</sub>NO<sub>10</sub>P [M+H]<sup>+</sup> : 854.49666 founded: 854.49109.



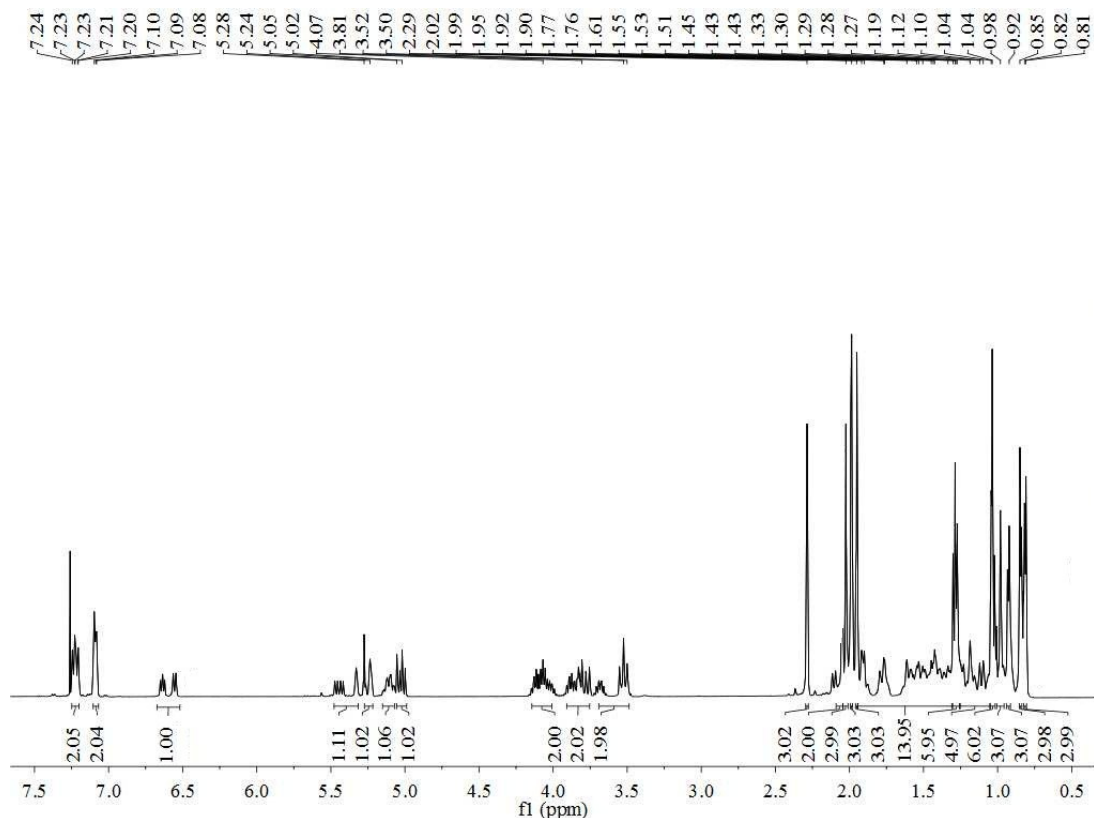


ljf-10 #13 RT: 0.05 AV: 1 NL: 7.24E6  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]

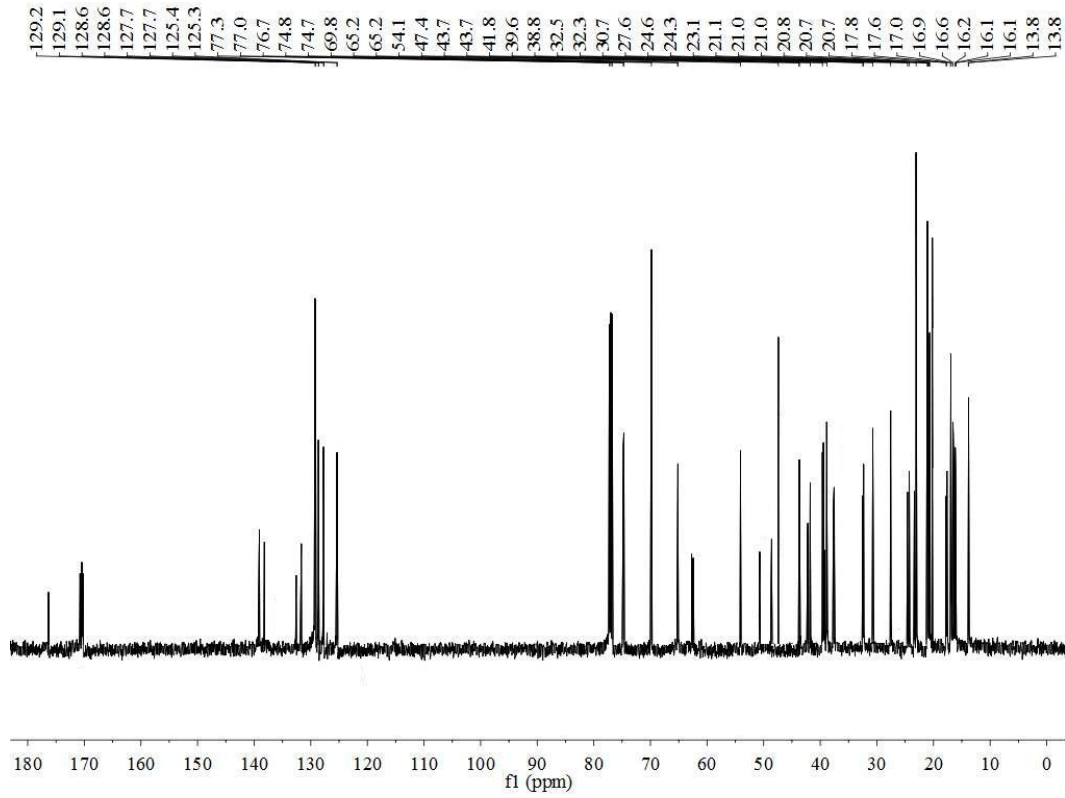




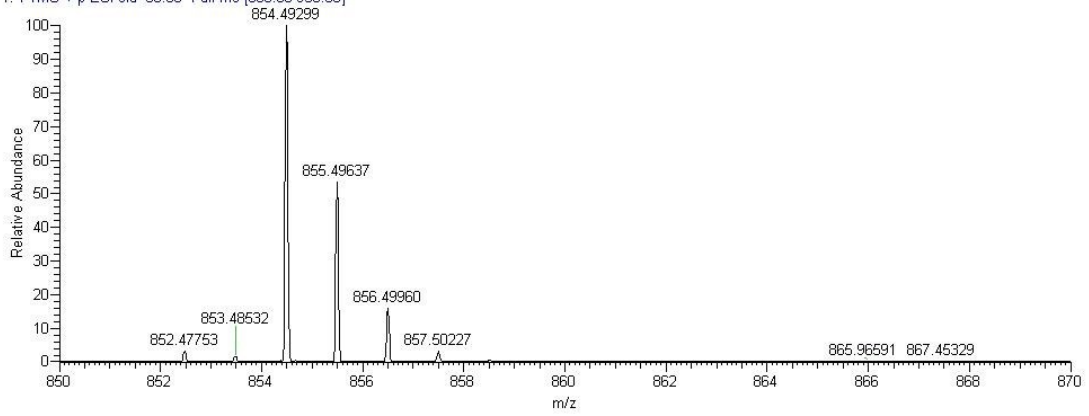
**3k**: Yield 68.5%. m.p. 134.8~136.9 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.25 - 7.20 (m, 2H, Ar-H), 7.10-7.07 (m, 2H, Ar-H), 6.66 - 6.42 (m, 1H, NH), 5.47-5.33 (m, 1H, H-11), 5.27 - 5.22 (m, 1H, H-3), 5.15 - 5.07 (m, 1H, H-2), 5.03 (dd,  $J = 17.7, 10.3$  Hz, 1H, P-CH), 4.11-4.05 (m, 2H,  $-\text{OCH}_2$ ), 3.91 - 3.75 (m, 2H,  $-\text{OCH}_2$ ), 3.73-3.50 (m, 2H, H-23), 2.29 (s, 3H, Ar- $\text{CH}_3$ ), 2.02 (s, 3H,  $\text{COCH}_3$ ), 1.99 (s, 3H,  $\text{COCH}_3$ ), 1.95 (s, 3H,  $\text{COCH}_3$ ), ( $3 \times \text{CH}_3\text{CO}$ ), ( $3 \times \text{CH}_3\text{CO}$ ), 2.08-1.10 (m, triterpene's H, 21H), 1.29 (td,  $J = 8.3, 5.8$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.04 (d,  $J = 3.7$  Hz, 6H,  $\text{CH}_3$ -24/27), 0.98 (s, 3H,  $\text{CH}_3$ -26), 0.92 (d,  $J = 3.9$  Hz, 3H,  $\text{CH}_3$ -30), 0.85 (s, 3H,  $\text{CH}_3$ -25), 0.81 (d,  $J = 4.7$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 170.8, 170.4, 170.3, 139.1, 138.2, 132.6, 131.7, 129.2, 128.6, 127.7, 125.4, 74.8, 69.8, 65.2, 62.7, 62.5, 54.1, 50.7, 48.6, 47.4, 43.7, 42.2, 41.8, 39.6, 39.3, 38.8, 37.7, 32.5, 32.3, 30.7, 27.6, 24.6, 24.3, 23.1, 21.1, 21.0, 20.8, 20.7, 19.9, 17.8, 17.6, 17.0, 16.9, 16.6, 16.2, 16.1, 13.8. ESI-HRMS  $m/z$  Calc for  $\text{C}_{48}\text{H}_{72}\text{NO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 854.49666 founded: 854.49299.

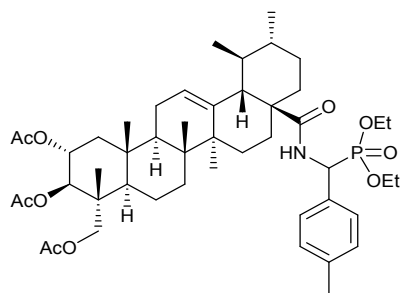




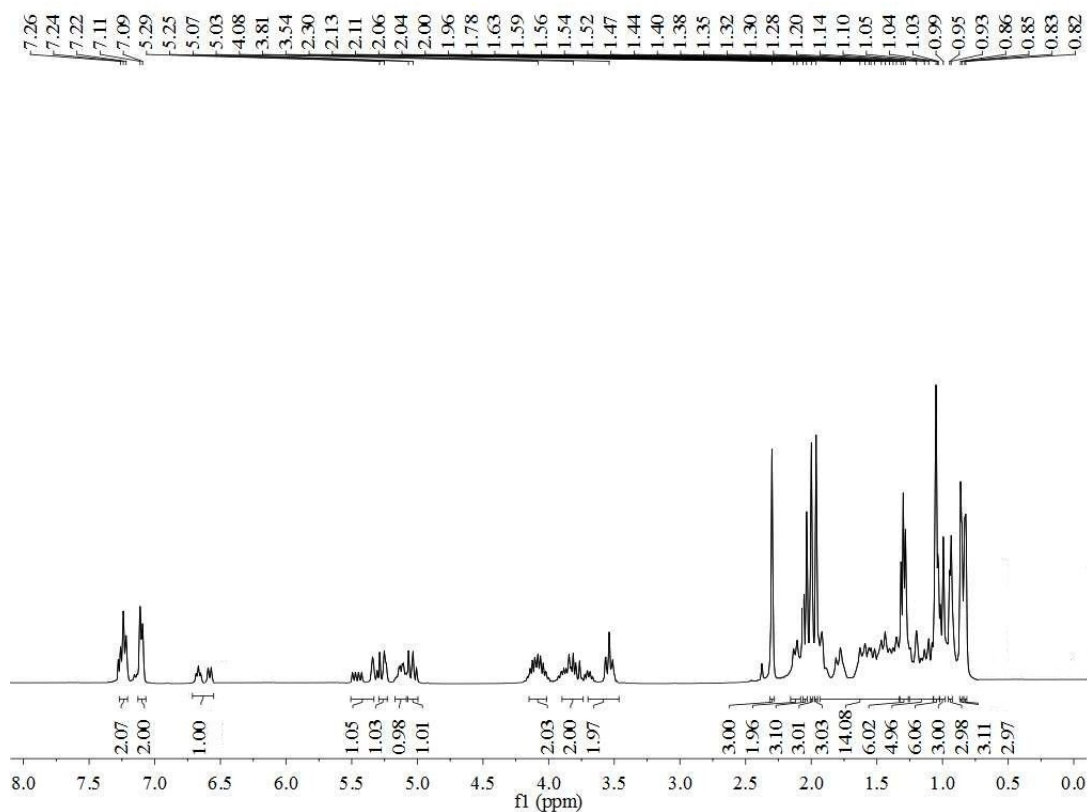


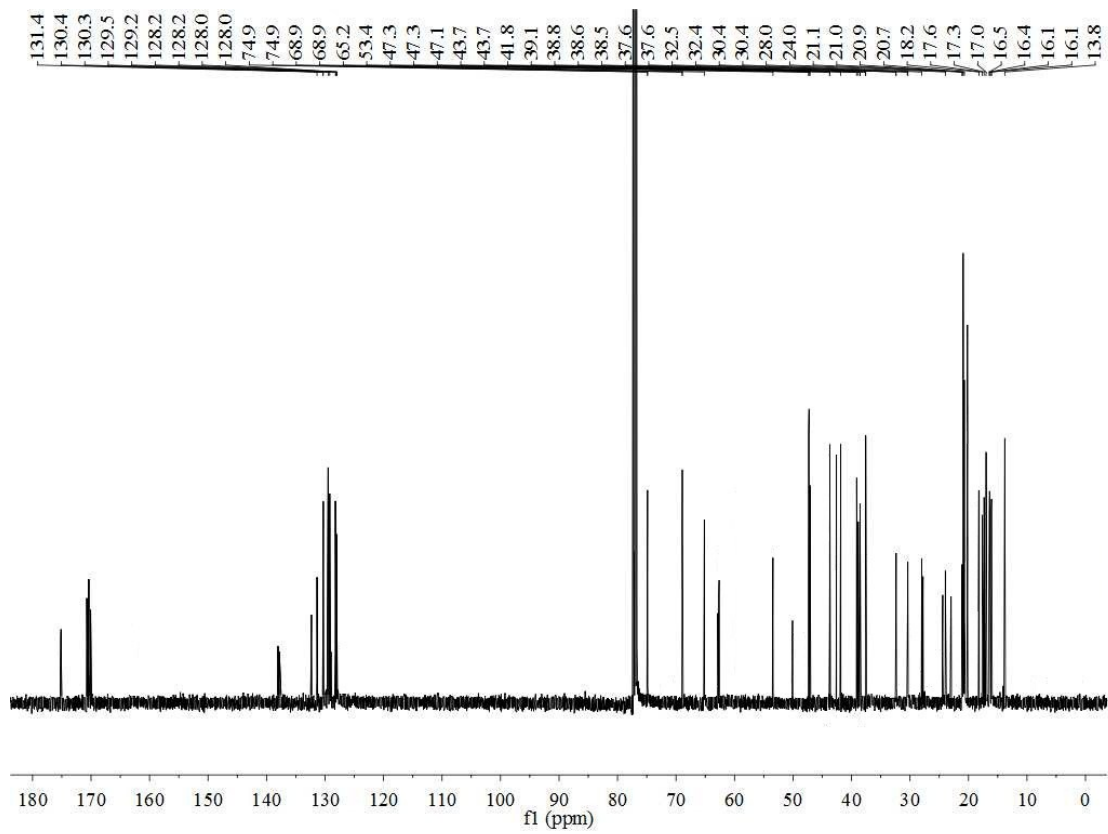
Ijif-11 #1-14 RT: 0.01-0.05 AV: 14 NL: 3.28E6  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



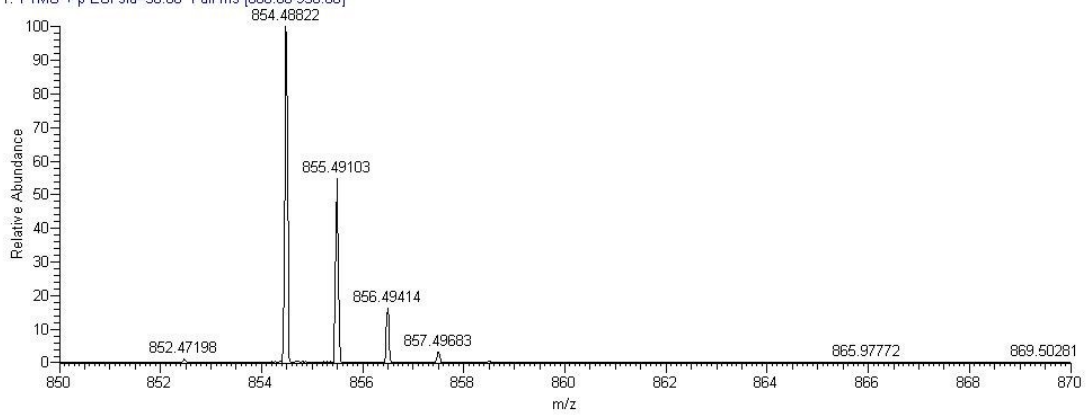


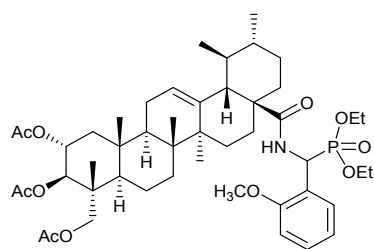
**31:** Yield 64.3%. m.p. 138.1~141.6 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.24 (dd,  $J = 8.5$  Hz, 2H, Ar-H), 7.10 (d,  $J = 7.6$  Hz, 2H, Ar-H), 6.71 - 6.42 (m, 1H, NH), 5.51 - 5.33 (m, 1H, H-11), 5.29 - 5.23 (m, 1H, H-3), 5.12 (m, 1H, H-2), 5.07 - 5.00 (m, 1H, P-CH), 4.15 - 4.02 (m, 2H,  $-\text{OCH}_2$ ), 3.84-3.76 (m, 2H,  $-\text{OCH}_2$ ), 3.57-3.51 (m, 2H, H-23), 2.30 (s, 3H, Ar- $\text{CH}_3$ ), 2.05 (s, 3H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 2.15-1.10 (m, triterpene's H, 21H), 1.96 (s, 3H,  $\text{COCH}_3$ ), ( $3 \times \text{CH}_3\text{CO}$ ), 1.33 - 1.26 (m, 6H,  $\text{CH}_3 \times 2$ ), 1.07 (s, 3H,  $\text{CH}_3$ -27), 1.02 (s, 3H,  $\text{CH}_3$ -24), 0.99 (s, 3H,  $\text{CH}_3$ -26), 0.94 (d,  $J = 4.5$  Hz, 3H,  $\text{CH}_3$ -30), 0.86 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d,  $J = 3.5$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  175.2, 170.7, 170.4, 170.1, 138.0, 132.3, 131.4, 130.4, 129.5, 129.2, 128.2, 128.0, 74.9, 68.9, 65.2, 62.9, 62.7, 53.4, 50.1, 47.3, 47.1, 43.7, 42.4, 41.8, 39.1, 38.8, 38.5, 37.6, 32.5, 32.4, 30.4, 28.0, 24.4, 24.0, 23.2, 21.1, 21.0, 20.9, 20.7, 20.5, 18.2, 17.6, 17.3, 17.0, 16.5, 16.4, 16.1, 13.8. ESI-HRMS  $m/z$  Calc for  $\text{C}_{48}\text{H}_{72}\text{NO}_{10}\text{P}$   $[\text{M}+\text{H}]^+$ : 854.49666 founded: 854.48822.



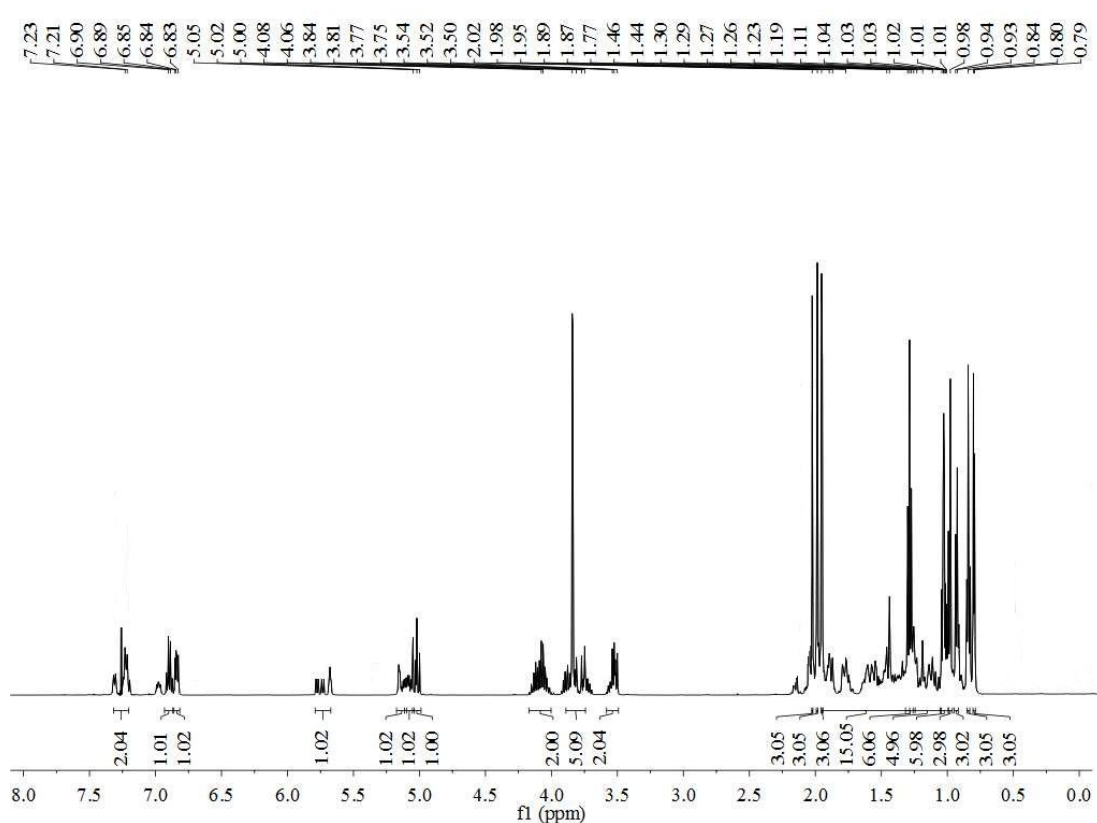


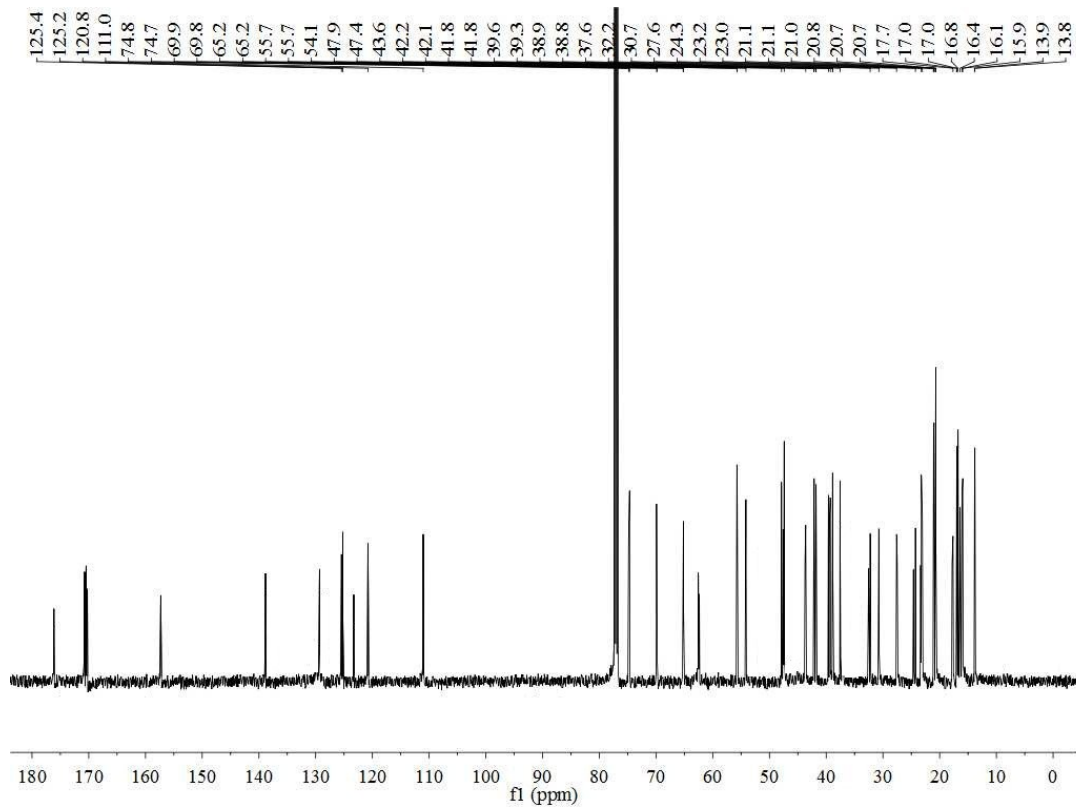
ljf-12 #2 RT: 0.01 AV: 1 NL: 1.63E7  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



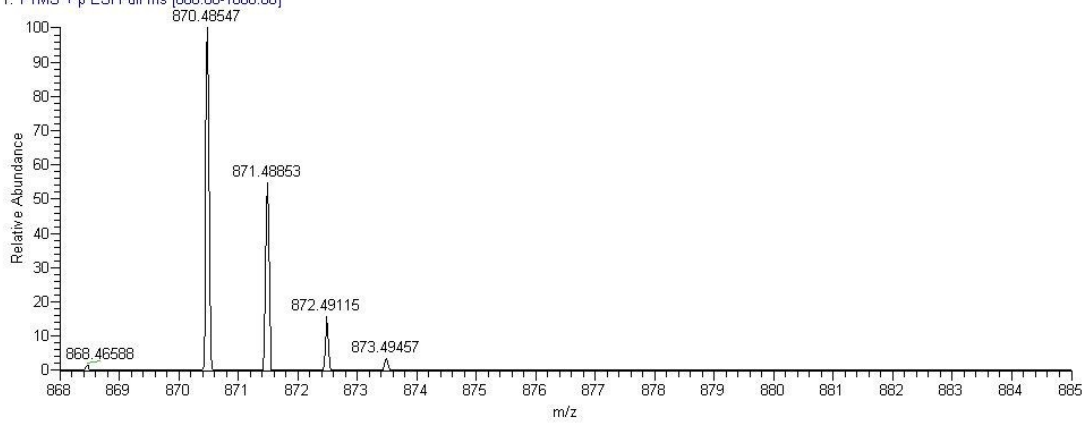


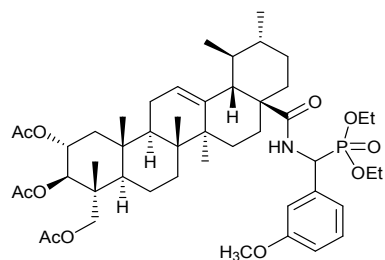
**3m**: Yield 69.0%. m.p. 132.3~135.2 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.32-7.20 (t, 2H, Ar-H), 6.92-6.87 (m, 1H, Ar-H), 6.84 (m, 1H, NH), 5.78-5.67 (m, 1H, H-11), 5.16-5.11 (m, 1H, H-3), 5.10-5.08 (m, 1H, H-2), 5.03-5.00 (m, 1H, P-CH), 4.15-4.01 (m, 2H, -OCH<sub>2</sub>), 3.90-3.75 (m, 5H, -OCH<sub>2</sub>, Ar-OCH<sub>3</sub>), 3.57-3.50 (m, 1H, H-23), 2.02 (s, 2H, COCH<sub>3</sub>), 1.98 (s, 3H, COCH<sub>3</sub>), 1.95 (s, 3H, COCH<sub>3</sub>), 1.95-1.06 (m, triterpene's H, 21H), 1.28 (m, 6H, CH<sub>3</sub>×2), 1.05-0.99 (m, 6H, CH<sub>3</sub>-27/24), 0.98 (s, 3H, CH<sub>3</sub>-26), 0.93 (d, *J* = 6.3 Hz, 3H, CH<sub>3</sub>-30), 0.84 (s, 3H, CH<sub>3</sub>-25), 0.80 (d, *J* = 4.4 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.1, 170.8, 170.5, 170.3, 157.3, 138.8, 129.3, 125.4, 125.2, 123.3, 120.8, 111.0, 74.8, 69.9, 65.2, 62.6, 62.4, 55.7, 54.1, 47.9, 47.4, 43.7, 42.2, 41.8, 39.6, 39.3, 38.9, 37.6, 32.5, 32.2, 30.8, 27.6, 24.6, 24.3, 23.2, 23.0, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 17.0, 16.8, 16.4, 16.1, 15.9, 13.9. ESI-HRMS *m/z* Calc for C<sub>48</sub>H<sub>72</sub>NO<sub>11</sub>P [M+H]<sup>+</sup>: 870.49158 founded: 870.48547.



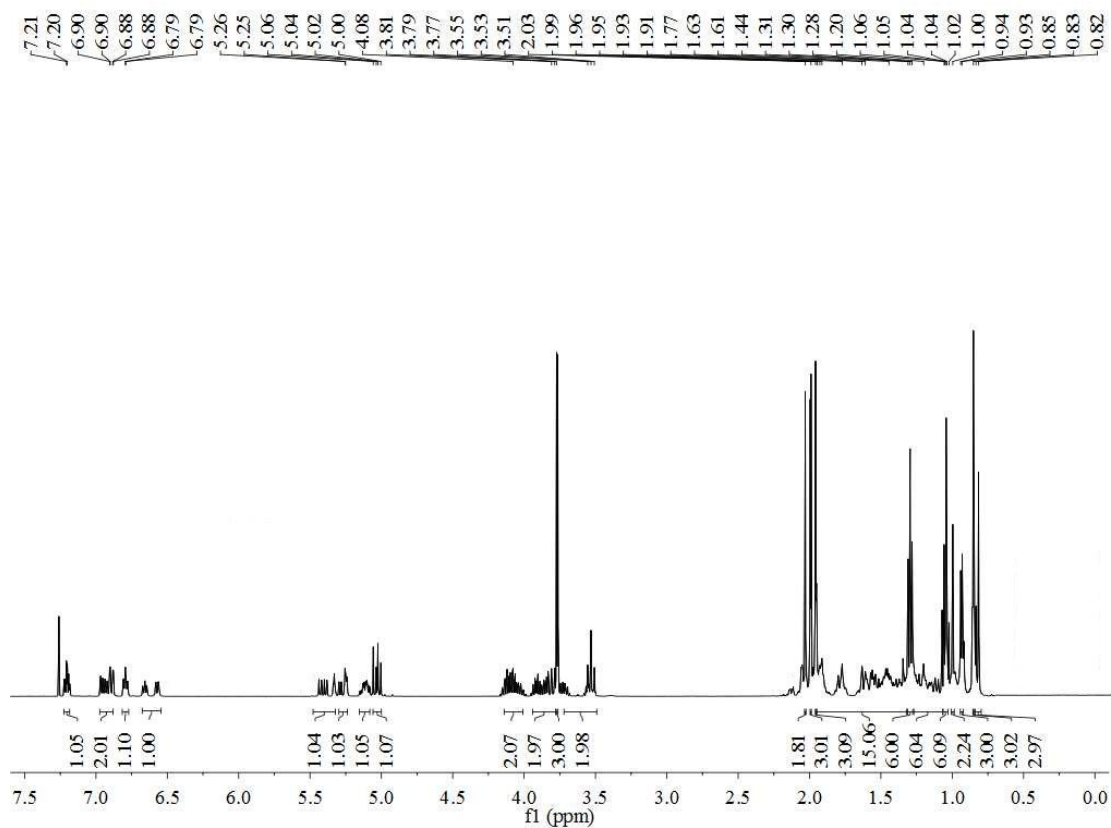


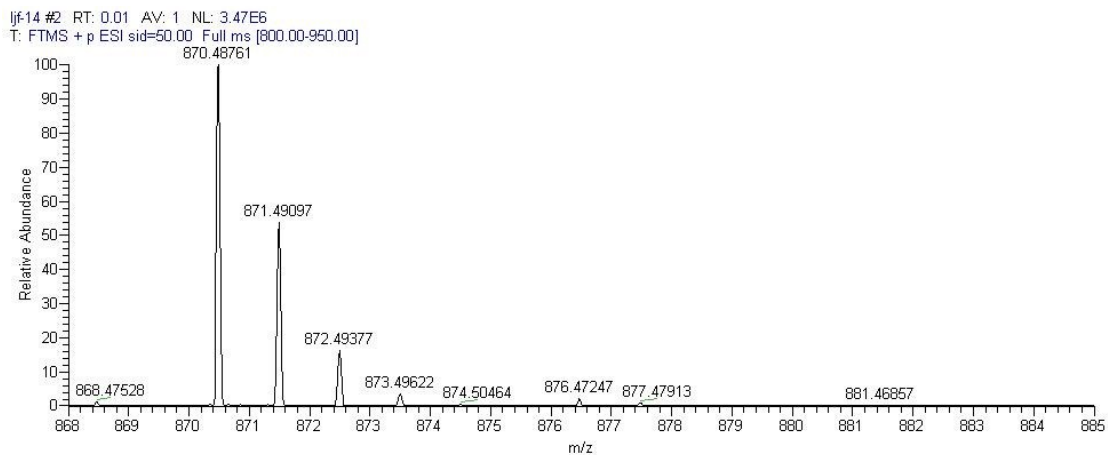
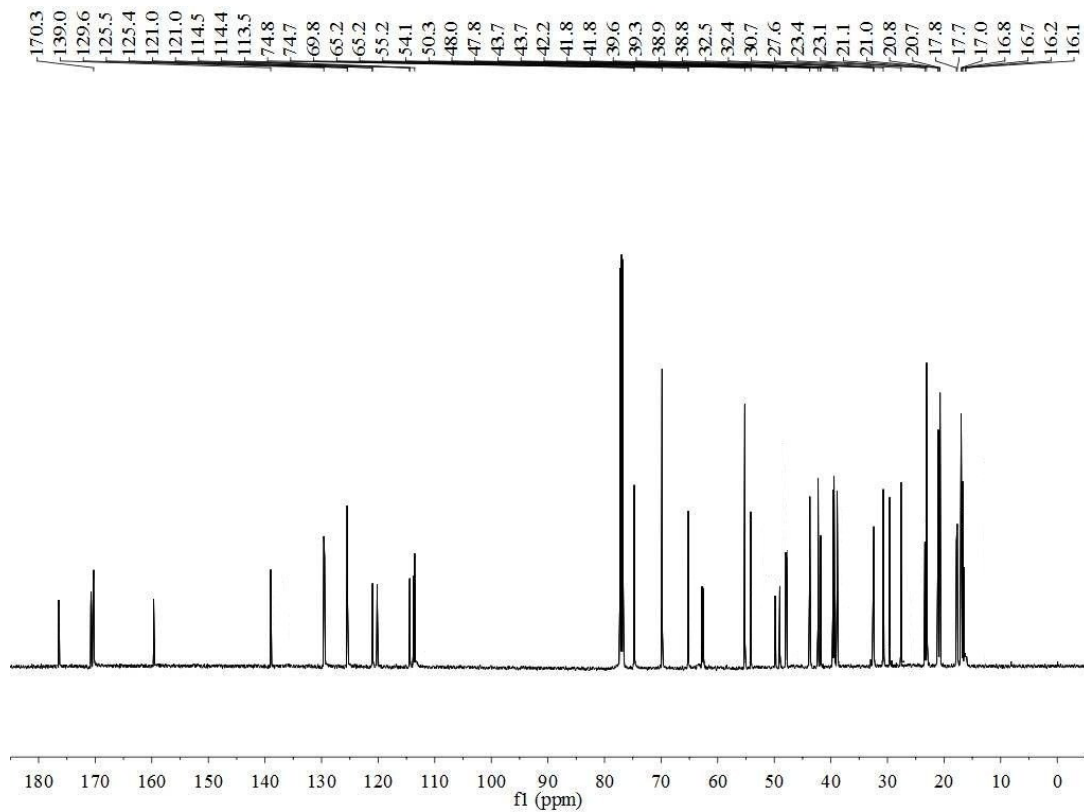
ljf-130722 #2 RT: 0.01 AV: 1 NL: 7.66E5  
 T: FTMS + p ESI Full ms [800.00-1000.00]

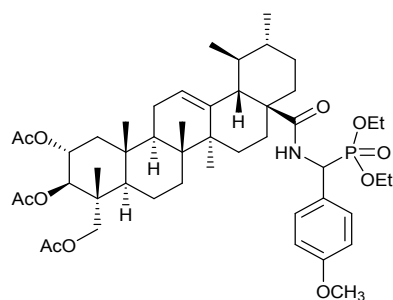




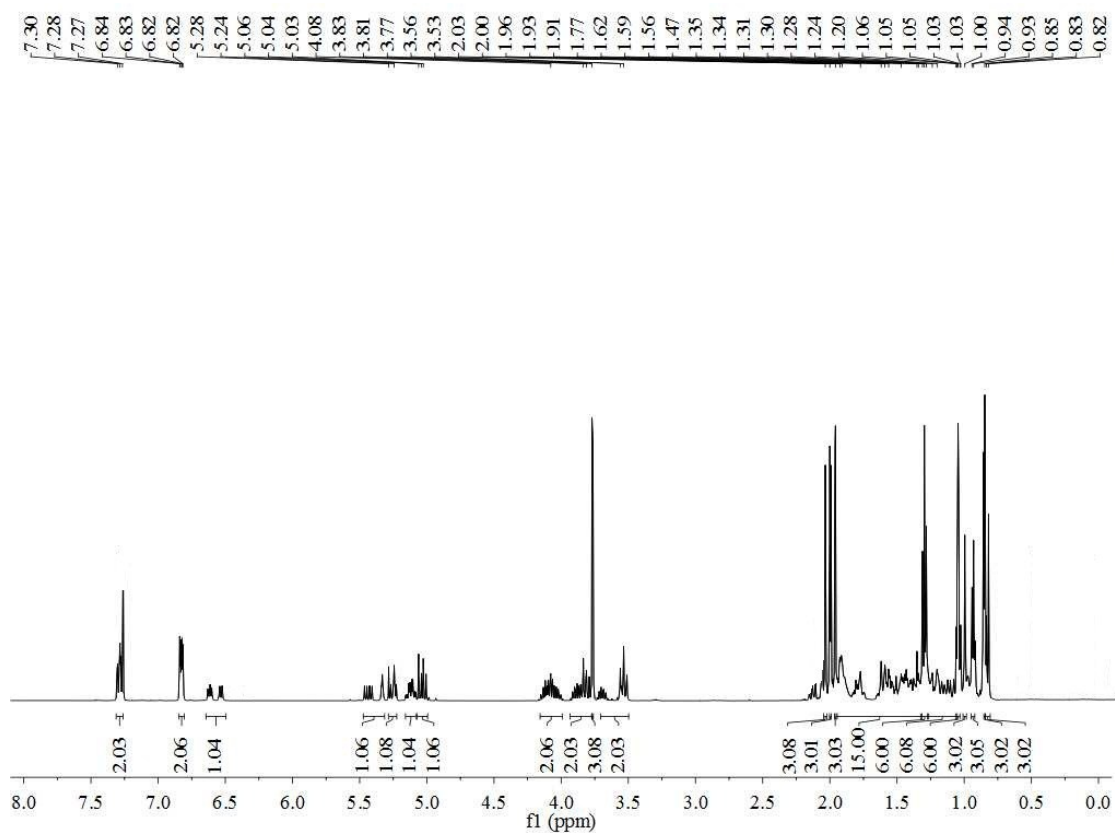
**3n:** Yield 65.7%. m.p. 131.2~134.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.20 (td, *J* = 7.9, 3.2 Hz, 1H, Ar-H), 6.97 - 6.88 (m, 2H, Ar-H), 6.79 (t, *J* = 8.2, 6.7 Hz, 1H), 6.68 - 6.44 (m, 1H, NH), 5.48 - 5.32 (m, 1H, H-11), 5.30 - 5.24 (m, 1H, H-3), 5.15 - 5.08 (m, 1H, H-2), 5.03 (dd, *J* = 16.2, 10.3 Hz, 1H, P-CH), 4.14 - 4.01 (m, 2H, -OCH<sub>2</sub>), 3.94-3.79 (m, 2H, -OCH<sub>2</sub>), 3.77 (d, *J* = 4.2 Hz, 3H, Ar-OCH<sub>3</sub>), 3.73-3.53 (m, 2H, H-23), 2.04 (d, *J* = 12.5 Hz, 3H, COCH<sub>3</sub>), 1.99 (d, *J* = 2.7 Hz, 3H, COCH<sub>3</sub>), 1.96 (d, *J* = 2.6 Hz, 3H, COCH<sub>3</sub>), 1.30 (t, *J* = 7.1 Hz, 6H, CH<sub>3</sub>×2), 1.07 (s, 3H, CH<sub>3</sub>-27), 1.04 (s, 3H, CH<sub>3</sub>-24), 1.00 (s, 3H, CH<sub>3</sub>-26), 0.94 (d, *J* = 5.3 Hz, 3H, CH<sub>3</sub>-30), 0.85 (s, 3H, CH<sub>3</sub>-25), 0.82 (d, *J* = 9.0 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.4 (C-28), 170.7 (COCH<sub>3</sub>), 170.4 (COCH<sub>3</sub>), 170.3 (COCH<sub>3</sub>), 159.7 (Ar-C), 139.0 (C-13), 129.6 (Ar-C), 125.5 (C-12), 121.0 (Ar-C), 120.2 (Ar-C), 114.5 (Ar-C), 113.5 (Ar-C), 74.8 (C-3), 69.8 (C-2), 65.2 (C-23), 62.7 (-OCH<sub>2</sub>), 62.6 (-OCH<sub>2</sub>), 55.2 (-OCH<sub>3</sub>), 54.1 (P-CH), 50.3 (C-18), 48.0 (C-9), 47.8 (C-5), 43.7 (C-4), 42.3 (C-1), 41.9 (C-17), 41.8 (C-10), 39.60 (C-8), 39.3 (C-19), 38.9 (C-14), 38.8 (C-20), 32.5 (C-7), 32.4 (C-22), 30.7 (C-16), 29.6 (C-15), 27.6 (C-21), 23.4 (C-11), 23.1 (C-27), 21.1 (C-29), 21.0 (COCH<sub>3</sub>), 20.8 (COCH<sub>3</sub>), 20.7 (COCH<sub>3</sub>), 17.8 (C-25), 17.7 (C-30), 17.0 (C-26), 16.8 (C-6), 16.7 (C-24), 16.2 (CH<sub>3</sub>), 16.1 (CH<sub>3</sub>). ESI-HRMS *m/z* Calc for C<sub>48</sub>H<sub>72</sub>NO<sub>11</sub>P [M+H]<sup>+</sup>: 870.49158 founded: 870.48761.



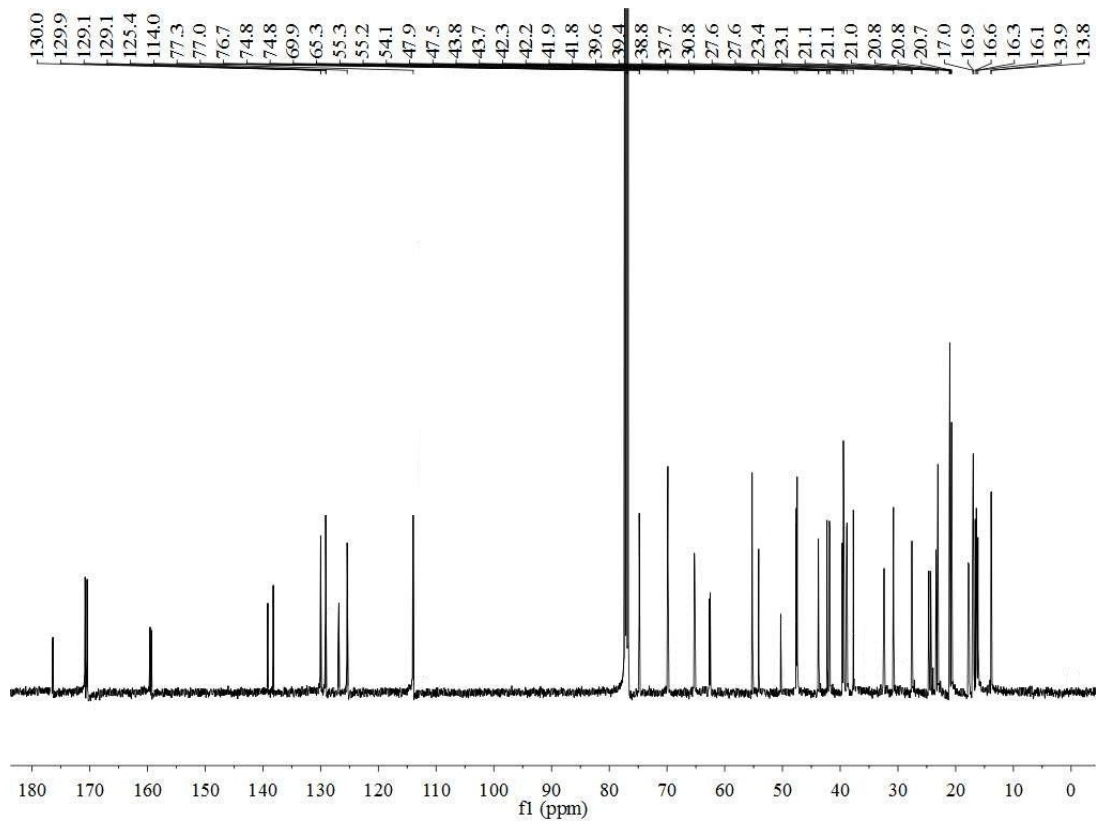




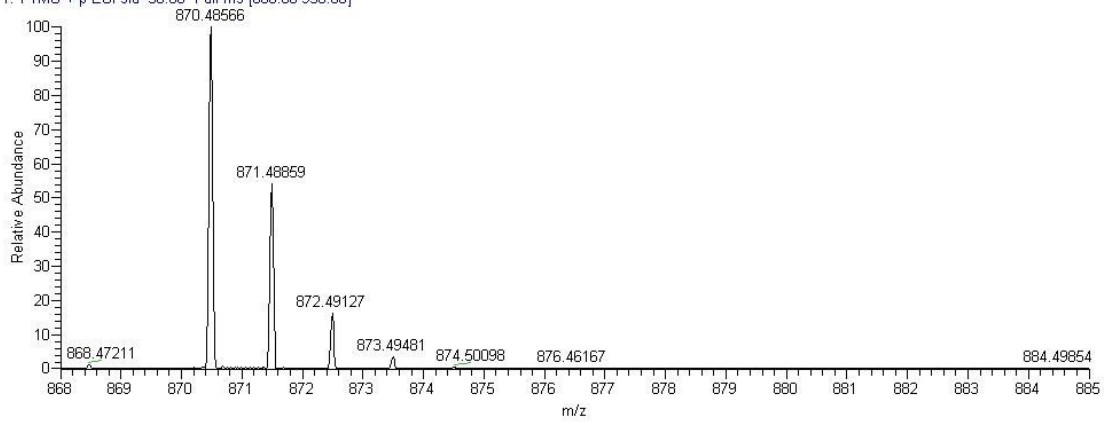
**3o:** Yield 61.9%. m.p. 133.4–135.8 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30–7.27 (m, 2H, Ar-H), 6.83 (dd,  $J = 8.7, 3.3$  Hz, 2H, Ar-H), 6.63–6.50 (m, 1H, NH), 5.46–5.33 (m, 1H, H-11), 5.28–5.23 (m, 1H, H-3), 5.16–5.08 (m, 1H, H-2), 5.06–5.01 (m, 1H, P-CH), 4.15–4.00 (m, 2H,  $-\text{OCH}_2$ ), 3.91–3.79 (m, 2H,  $-\text{OCH}_2$ ), 3.77 (s, 3H, Ar- $\text{OCH}_3$ ), 3.70–3.51 (m, 2H, H-23), 2.03 (s, 3H,  $\text{COCH}_3$ ), 2.00 (s, 3H,  $\text{COCH}_3$ ), 1.96 (s, 3H,  $\text{COCH}_3$ ), 1.95–1.08 (m, triterpene's H, 21H), 1.30 (t,  $J = 7.0$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.06–1.03 (m, 6H,  $\text{CH}_3$ -27/24), 1.00 (s, 3H,  $\text{CH}_3$ -26), 0.94 (d,  $J = 5.9$  Hz, 3H,  $\text{CH}_3$ -30), 0.85 (s, 3H,  $\text{CH}_3$ -25), 0.83 (d,  $J = 7.4$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  176.3, 170.8, 170.4, 170.3, 159.4, 139.2, 138.2, 130.0, 129.1, 126.8, 125.4, 114.0, 74.8, 69.9, 65.3, 62.7, 62.5, 55.3, 54.1, 47.9, 47.5, 43.8, 42.3, 41.9, 39.6, 39.4, 38.8, 37.7, 32.5, 32.4, 30.8, 27.6, 24.6, 24.3, 23.4, 23.1, 21.1, 21.0, 20.8, 20.7, 17.8, 17.7, 17.0, 16.9, 16.6, 16.3, 16.1, 13.9. ESI-HRMS  $m/z$  Calc for  $\text{C}_{48}\text{H}_{72}\text{NO}_{11}\text{P}$   $[\text{M}+\text{H}]^+$  : 870.49158 founded: 870.48566.

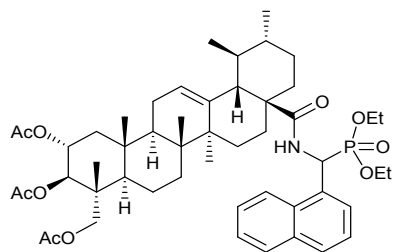




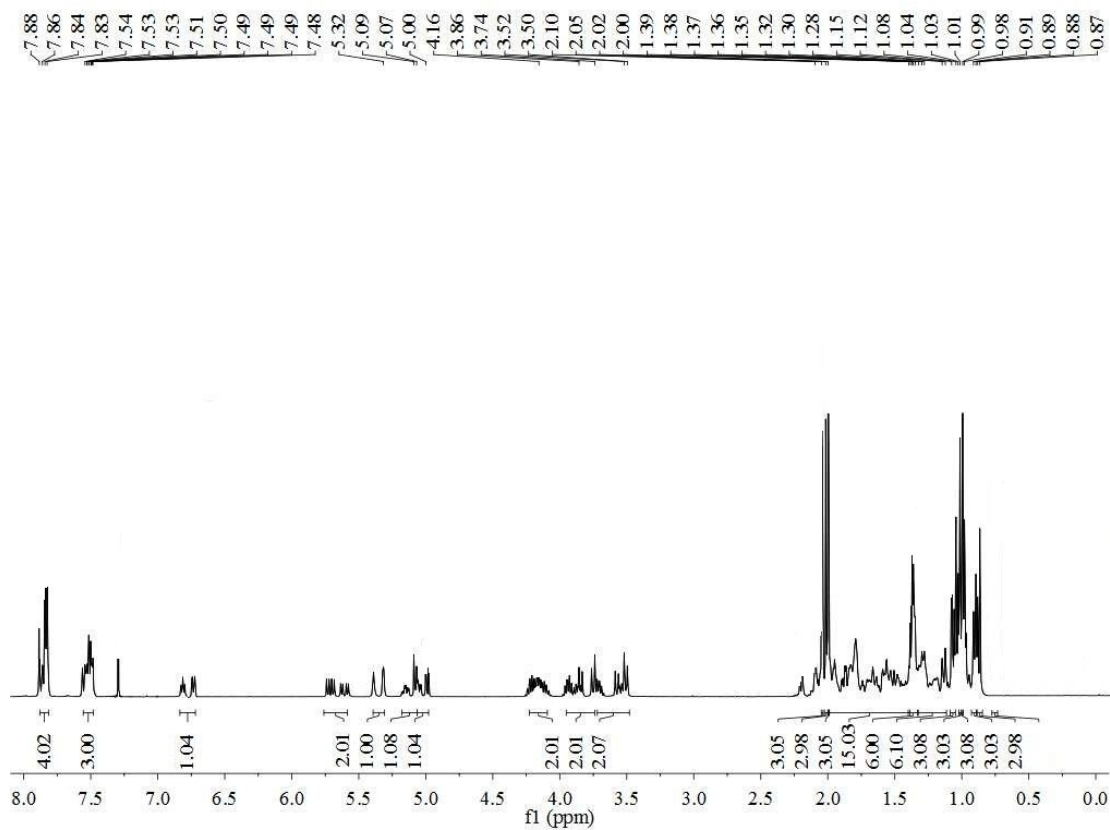


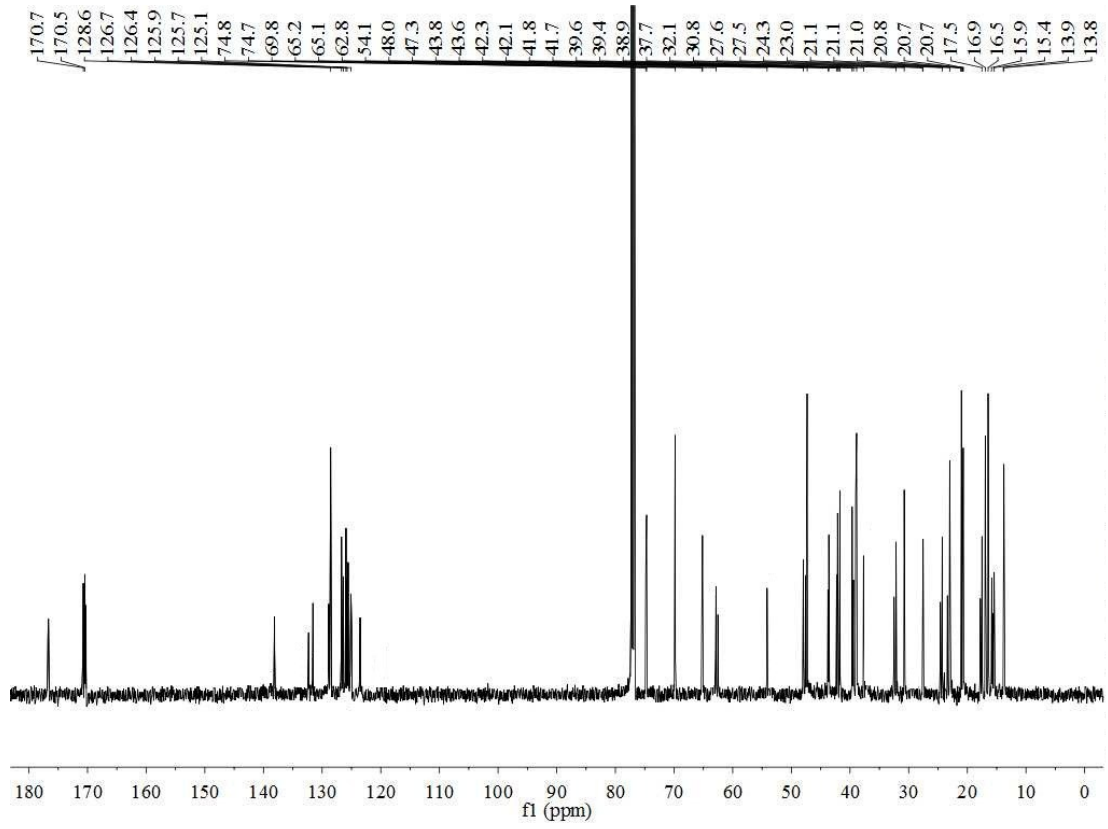
ljf-15 #2 RT: 0.01 AV: 1 NL: 1.44E7  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



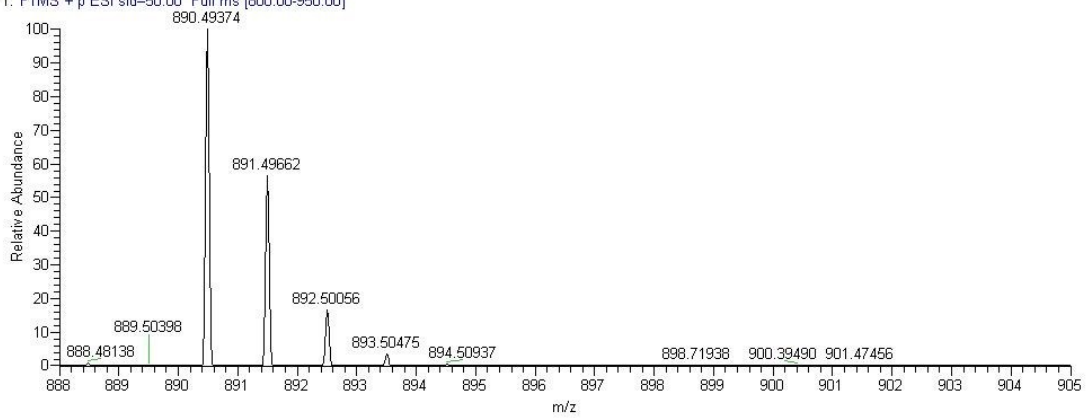


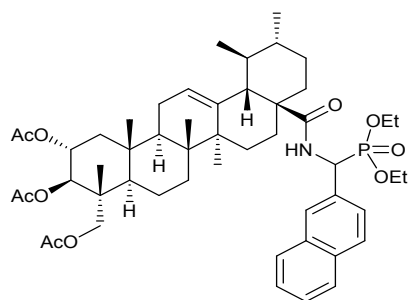
**3p**: Yield 66.2%. m.p. 129.8~132.1 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.35 (td, *J* = 8.2, 3.9 Hz, 2H, Ar-H), 7.32-7.26 (m, 3H, Ar-H), 6.74-6.49 (m, 1H, NH), 5.47 - 5.31 (m, 1H, H-11), 5.31 - 5.21 (m, 1H, H-3), 5.14 - 5.07 (m, 1H, H-2), 5.05 - 4.99 (m, 1H, H-2, P-CH), 4.16 - 4.03 (m, 2H, -OCH<sub>2</sub>), 3.89 - 3.75 (m, 2H, -OCH<sub>2</sub>), 3.68 - 3.46 (m, 2H, H-23), 2.04 (d, *J* = 8.0 Hz, 3H, COCH<sub>3</sub>), 1.99 (d, *J* = 2.7 Hz, 3H, COCH<sub>3</sub>), 1.95 (d, *J* = 2.3 Hz, 3H, COCH<sub>3</sub>), 1.32 - 1.26 (m, 6H, CH<sub>3</sub>×2), 1.05 (s, 3H, CH<sub>3</sub>-27), 1.00 (m, 3H, CH<sub>3</sub>-24), 0.99 (s, 3H, CH<sub>3</sub>-26), 0.93 (d, *J* = 6.1 Hz, 3H, CH<sub>3</sub>-30), 0.84 (d, *J* = 1.9 Hz, 3H, CH<sub>3</sub>-25), 0.81 (d, *J* = 4.8 Hz, 3H, CH<sub>3</sub>-29). ESI-HRMS *m/z* Calc for C<sub>47</sub>H<sub>70</sub>NO<sub>10</sub>P [M+H]<sup>+</sup> : 840.48101 founded: 840.47461.



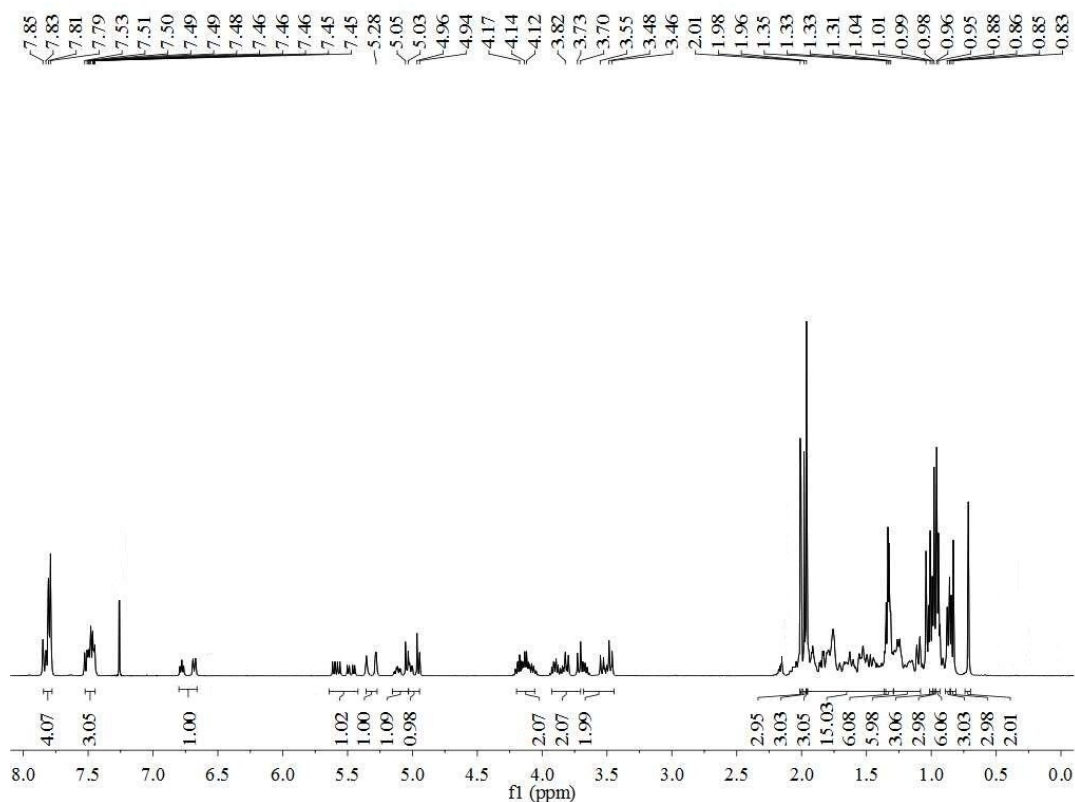


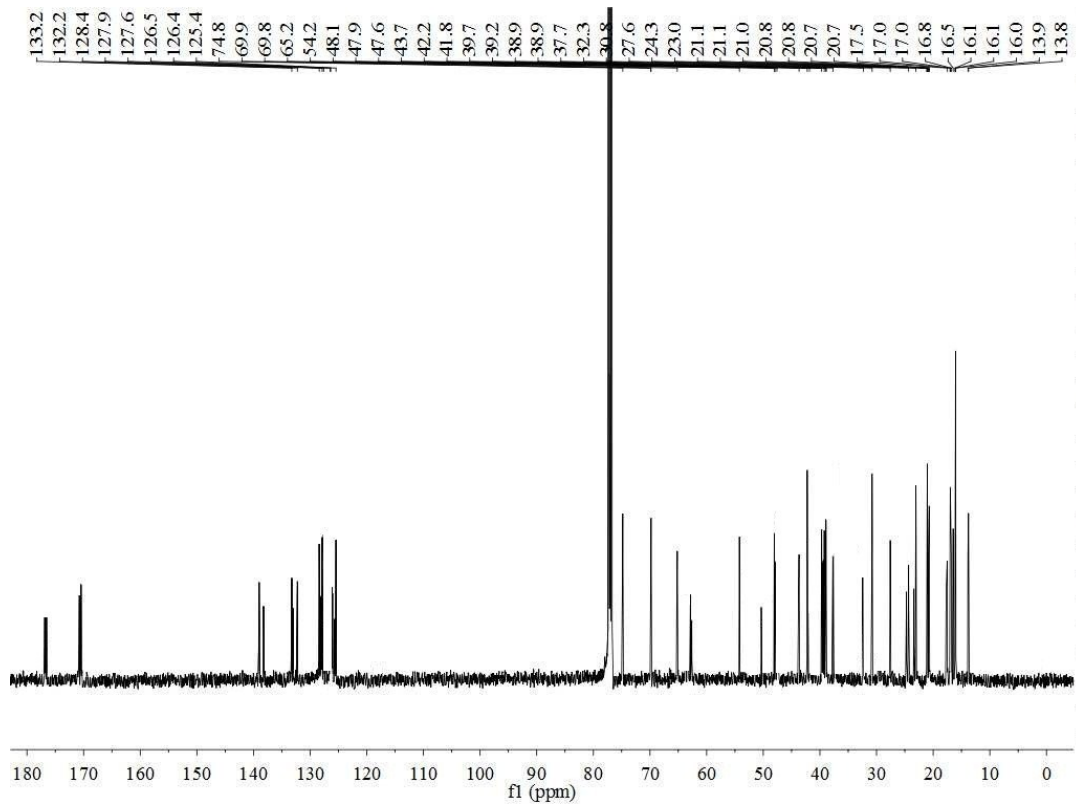
ljf-16 #2-16 RT: 0.01-0.06 AV: 15 NL: 2.67E6  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



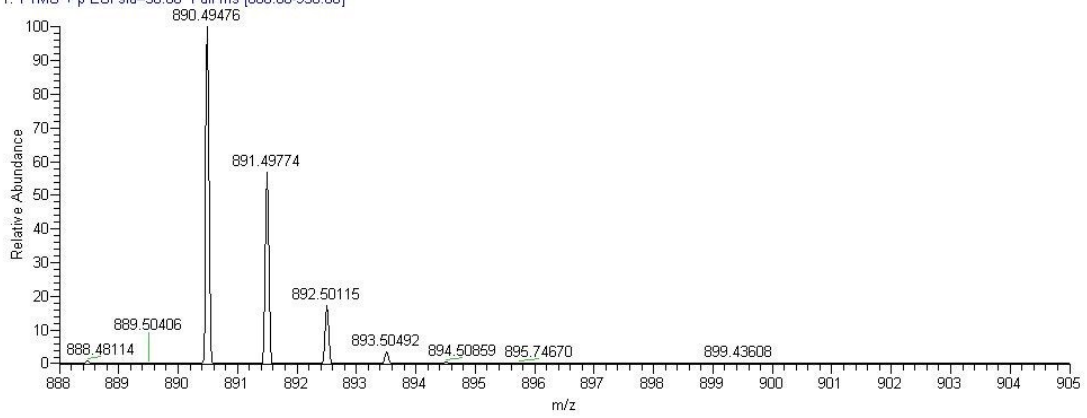


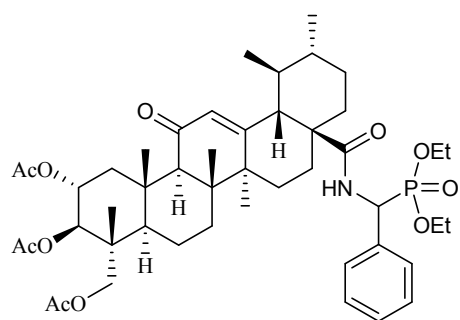
**3q:** Yield 61.2%. m.p. 141.2~144.8 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.88–7.83 (m, 4H, Ar-H), 7.56–7.48 (m, 3H, Ar-H), 6.82–6.63 (m, 1H, NH), 5.74–5.53 (m, 1H, H-11), 5.39–5.31 (m, 1H, H-3), 5.18–5.12 (m, 1H, H-2), 5.09–4.98 (m, 1H, P-CH), 4.23–4.06 (m, 2H, -OCH<sub>2</sub>), 3.96–3.72 (m, 2H, -OCH<sub>2</sub>), 3.75–3.49 (m, 2H, H-23), 2.09 (s, 3H, COCH<sub>3</sub>), 2.04 (s, 3H, COCH<sub>3</sub>), 2.01 (s, 3H, COCH<sub>3</sub>), 1.99–1.12 (m, triterpene's H, 21H), 1.39–1.32 (m, 6H, CH<sub>3</sub>×2), 1.08 (s, 3H, CH<sub>3</sub>-27), 1.01 (s, 3H, CH<sub>3</sub>-24), 0.99 (s, 3H, CH<sub>3</sub>-26), 0.99 (d, *J* = 6.7 Hz, 3H, CH<sub>3</sub>-30), 0.91 (s, 3H, CH<sub>3</sub>-25), 0.87 (d, *J* = 8.2 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.7, 170.8, 170.5, 170.3, 138.1, 132.3, 131.6, 128.9, 128.6, 126.7, 126.4, 125.9, 125.7, 125.1, 125.0, 123.5, 74.8, 69.8, 65.2, 62.9, 62.5, 54.1, 48.0, 47.3, 43.7, 42.2, 41.8, 39.6, 39.4, 38.9, 37.7, 32.5, 32.2, 30.8, 27.6, 24.6, 24.3, 23.4, 23.0, 21.1, 21.0, 20.8, 20.7, 17.8, 17.5, 16.9, 16.5, 15.9, 15.7, 15.4, 13.8. ESI-HRMS *m/z* Calc for C<sub>51</sub>H<sub>72</sub>NO<sub>10</sub>P [M+H]<sup>+</sup>: 890.49666 founded: 890.49374.



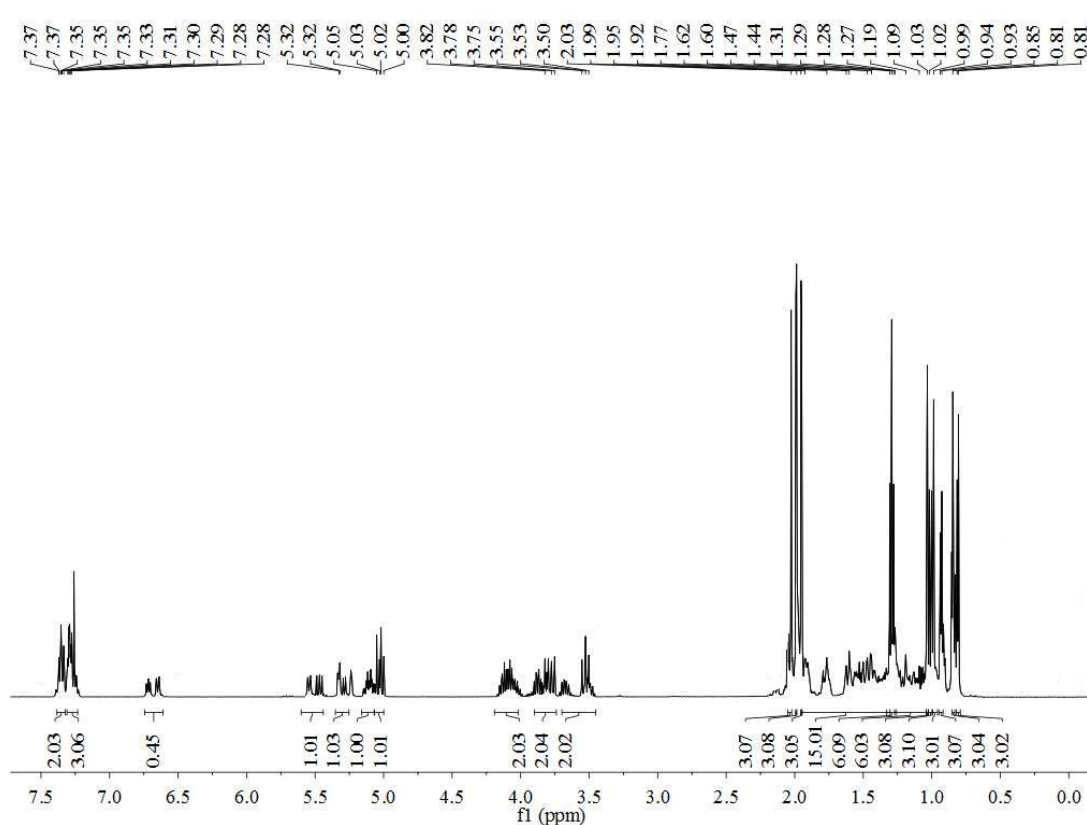


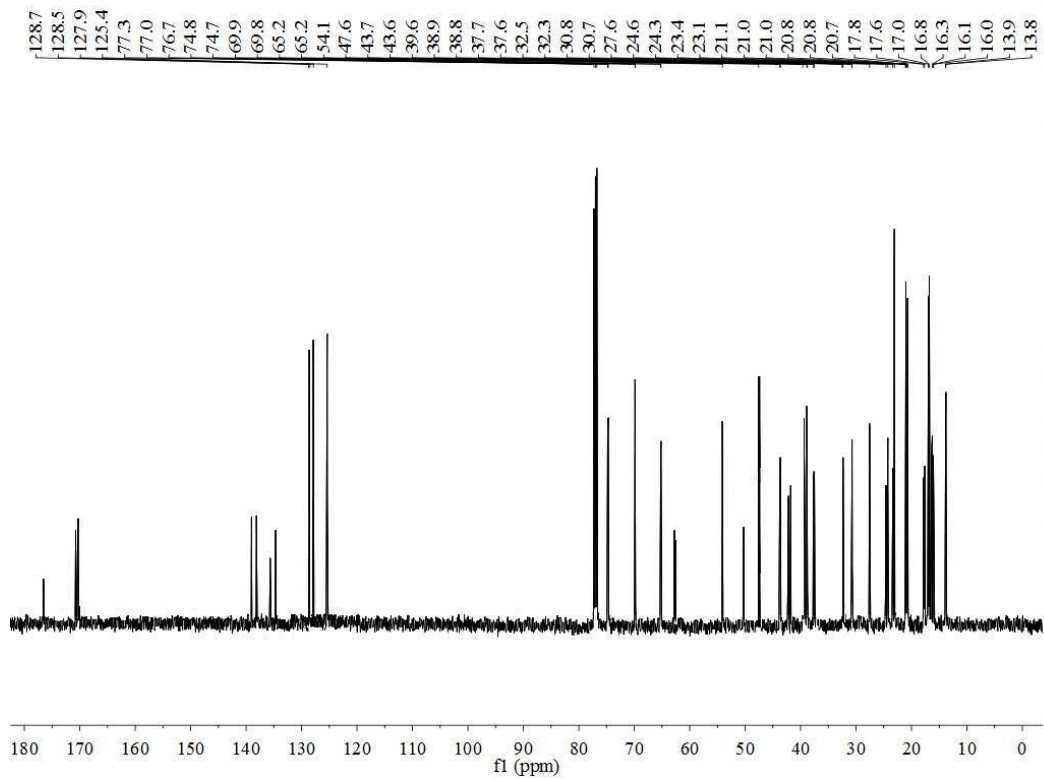
ljf-17 #2-13 RT: 0.01-0.05 AV: 12 NL: 1.14E6  
 T: FTMS + p ESI sid=50.00 Full ms [800.00-950.00]



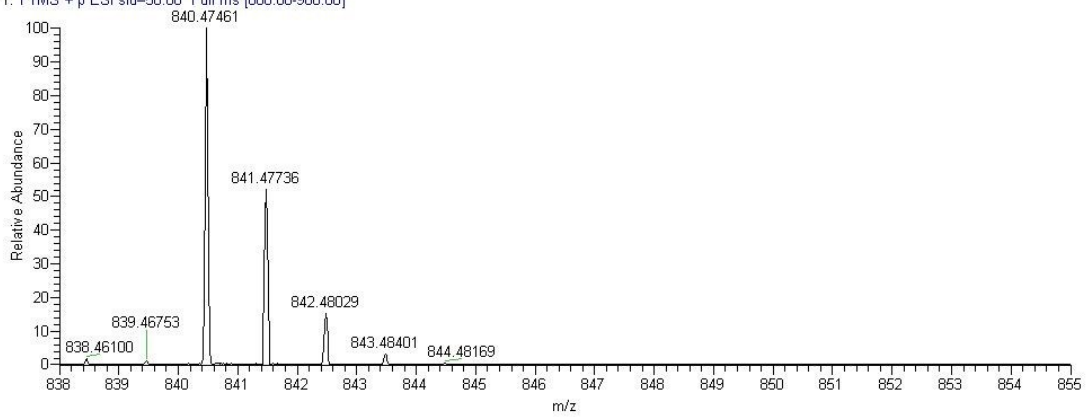


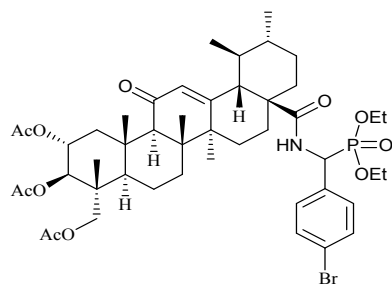
**3r:** Yield 69.0%. m.p. 137.1~140.2 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.84–7.78 (m, 4H, Ar-H), 7.52–7.45 (m, 3H, Ar-H), 6.81–6.56 (m, 1H, NH), 5.71–5.44 (m, 1H, H-11), 5.35–5.28 (m, 1H, H-3), 5.14–5.03 (m, 1H, H-2), 5.03–4.94 (m, 1H, P-CH), 4.19–4.06 (m, 2H, -OCH<sub>2</sub>), 3.93–3.73 (m, 2H, -OCH<sub>2</sub>), 3.67–3.46(m, 2H, H-23), 2.01 (s, 3H, COCH<sub>3</sub>), 1.98 (s, 3H, COCH<sub>3</sub>), 1.96 (s, 3H, COCH<sub>3</sub>), 1.95–1.08 (m, 21H), 1.35–1.31 (m, 6H, CH<sub>3</sub>×2), 1.00 (s, 3H, CH<sub>3</sub>-27), 0.98 (s, 3H, CH<sub>3</sub>-24), 0.95–0.97 (m, 6H, CH<sub>3</sub>-26/30), 0.87 (s, 3H, CH<sub>3</sub>-25), 0.84 (d, *J* = 8.2 Hz, 3H, CH<sub>3</sub>-29). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 176.6, 170.8, 170.5, 170.3, 139.0, 138.2, 133.2, 133.0, 132.2, 128.4, 127.9, 127.6, 126.5, 126.4, 126.1, 125.4, 74.8, 69.9, 65.3, 62.9, 62.7, 54.2, 48.0, 47.6, 43.8, 42.2, 41.8, 39.7, 39.2, 38.9, 37.7, 32.4, 32.3, 30.8, 27.6, 24.7, 24.3, 23.4, 23.0, 21.1, 21.0, 20.8, 20.7, 17.7, 17.5, 17.0, 16.8, 16.5, 16.1, 16.0, 13.8. ESI-HRMS *m/z* Calc for C<sub>51</sub>H<sub>72</sub>NO<sub>10</sub>P [M+H]<sup>+</sup>: 890.49666 founded: 890.49476.



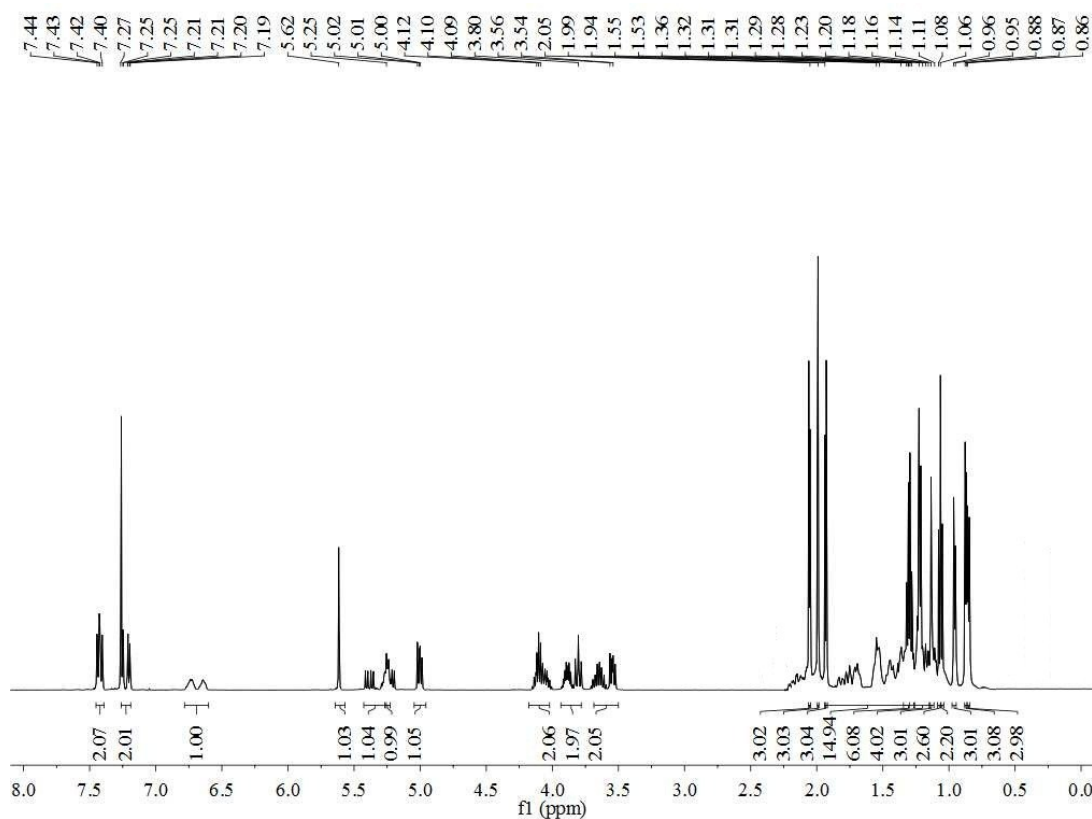


ljf-18 #9 RT: 0.03 AV: 1 NL: 2.79E7  
T: FTMS + p ESI sid=50.00 Full ms [800.00-900.00]

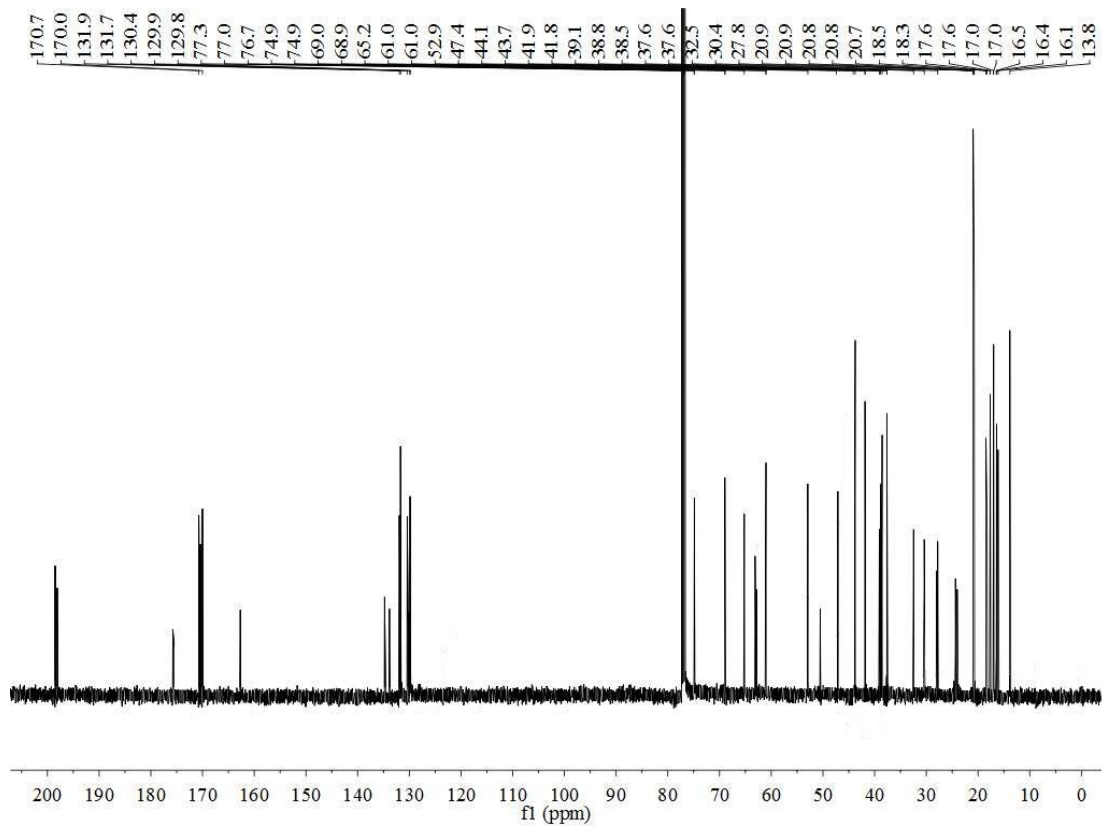




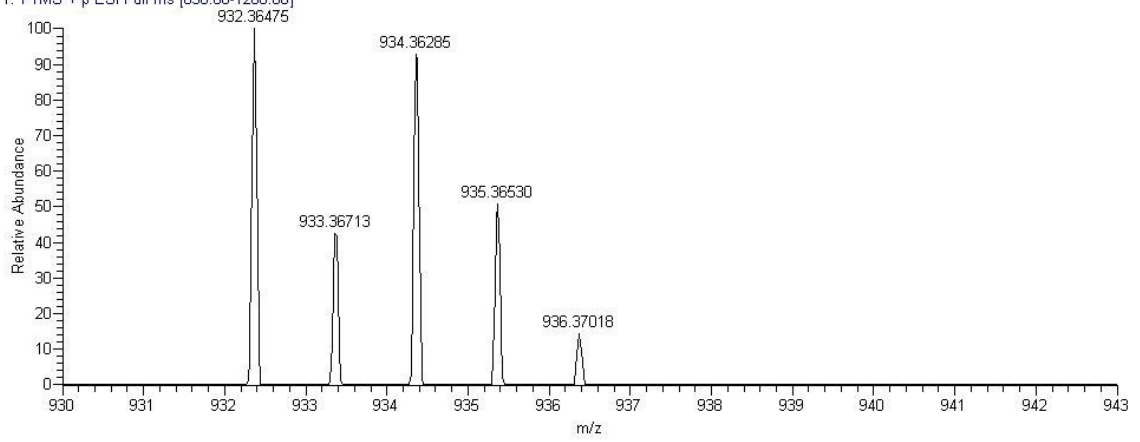
**6i:** Yield 62.0%. m.p. 157.1~160.0 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.42 (dd,  $J = 11.2, 8.5$  Hz, 2H, Ar-H), 7.27–7.19 (m, 2H, Ar-H), 6.69 (d,  $J = 47.9$  Hz, 1H), 5.62 (s, 1H, H-12), 5.41–5.28 (m, 1H, H-3), 5.25 (m, 1H, H-2), 5.00 (dd,  $J = 10.2, 7.0$  Hz, 1H, P-CH), 4.15–4.02 (m, 2H,  $-\text{OCH}_2$ ), 3.92–3.78 (m, 2H,  $-\text{OCH}_2$ ), 3.69–3.52 (m, 2H, H-23), 2.05 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.99 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.94 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.93–1.30 (m, 19H), 1.30 (t,  $J = 12.9, 6.5$  Hz, 6H,  $\text{CH}_3 \times 2$ ), 1.14 (s, 3H,  $\text{CH}_3$ -27), 1.08 (s, 3H,  $\text{CH}_3$ -24), 1.06 (s, 3H,  $\text{CH}_3$ -26), 0.96 (d,  $J = 5.0$  Hz, 3H,  $\text{CH}_3$ -30), 0.88 (s, 3H,  $\text{CH}_3$ -25), 0.86 (d,  $J = 5.2$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.1, 175.7, 170.7, 170.4, 170.0, 162.6, 134.8, 133.9, 131.9, 131.7, 130.4, 130.3, 130.0, 129.8, 74.9, 68.9, 65.2, 63.1, 62.9, 61.0, 52.9, 50.5, 47.4, 44.1, 43.7, 41.9, 39.1, 38.8, 38.6, 37.6, 32.5, 30.4, 27.9, 24.4, 24.0, 20.9, 20.9, 20.8, 20.7, 18.5, 18.3, 17.6, 17.0, 16.9, 16.5, 16.4, 16.1, 13.8. ESI-HRMS  $m/z$  Calc for  $\text{C}_{47}\text{H}_{67}\text{BrNO}_{11}\text{P}$   $[\text{M}+\text{H}]^+$  : 932.37079 founded: 932.36475.

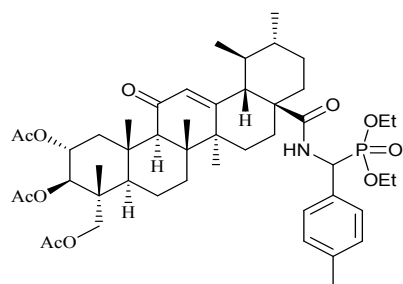




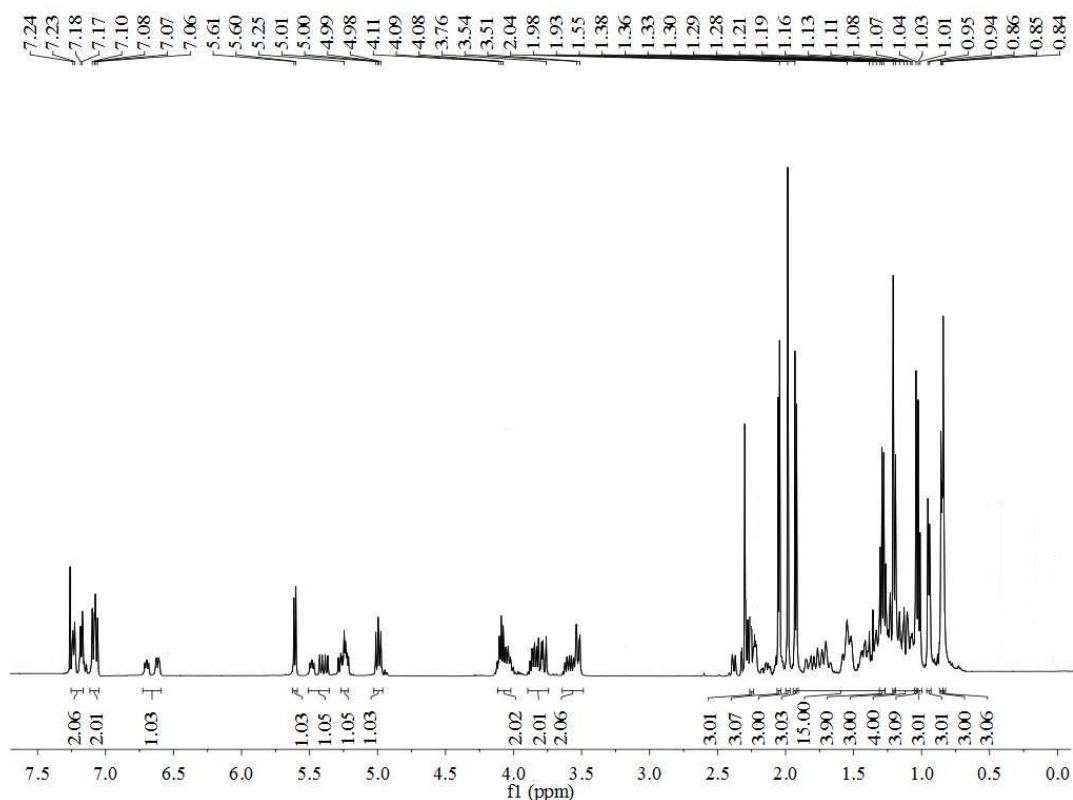


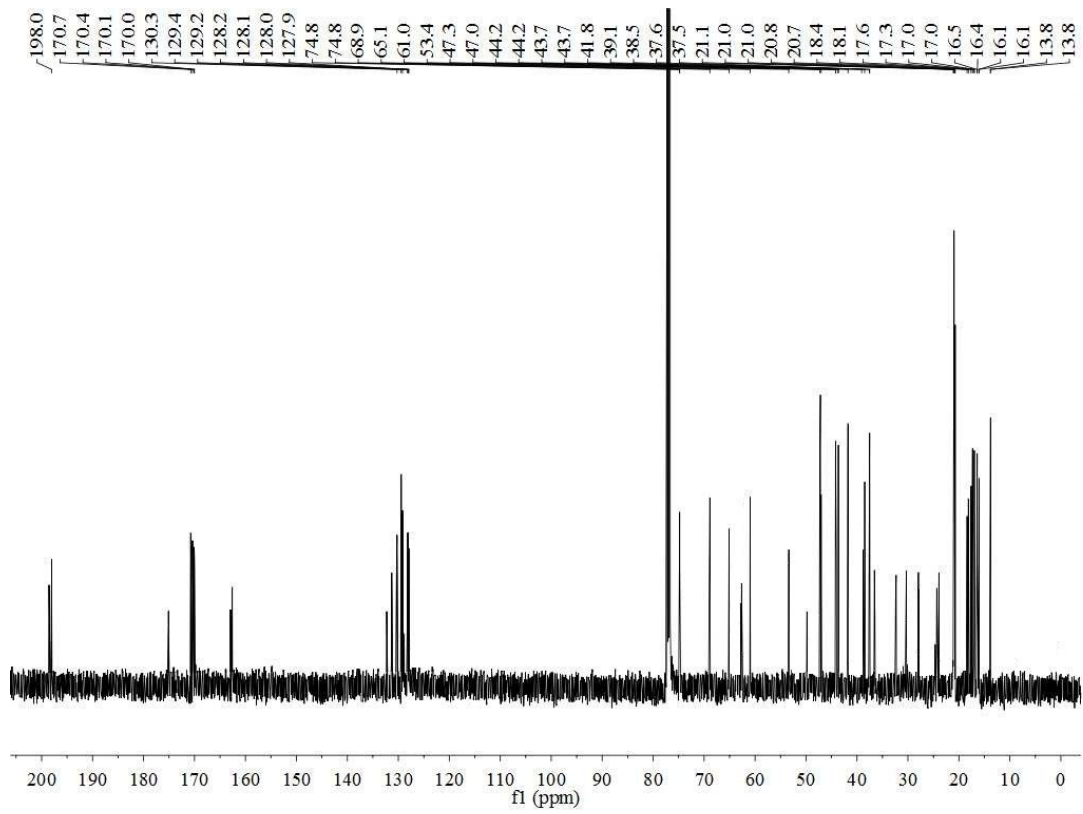
ijf-130723 #12 RT: 0.04 AV: 1 NL: 9.66E4  
T: FTMS + p ESI Full ms [850.00-1200.00]





**6n**: Yield 65.1%. m.p. 161.2~164.8 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.21 (dd,  $J = 28.2, 6.7$  Hz, 2H, Ar-H), 7.08 (dd,  $J = 11.3, 8.0$  Hz, 2H, Ar-H), 6.71-6.60 (m, 1H, NH), 5.61 (d,  $J = 7.0$  Hz, 1H, H-12), 5.51-5.36 (m, 1H, H-3), 5.27-5.22 (m, 1H, H-2), 4.99 (dd,  $J = 10.2, 8.1$  Hz, 1H, P-CH), 4.12-4.02 (m, 2H,  $-\text{OCH}_2$ ), 3.88-3.76 (m, 2H,  $-\text{OCH}_2$ ), 3.64-3.51 (m, 2H, H-23), 2.3 (s, 3H, Ar- $\text{CH}_3$ ), 2.04 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.98 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.93 (s, 3H,  $\text{CH}_3\text{CO}$ ), 1.92-1.06 (m, 19H), 1.31-1.28 (m, 6H,  $\text{CH}_3 \times 2$ ), 1.21 (s, 3H,  $\text{CH}_3$ -27), 1.03 (s, 3H,  $\text{CH}_3$ -24), 1.01 (s, 3H,  $\text{CH}_3$ -26), 0.95 (d,  $J = 6.3$  Hz, 3H,  $\text{CH}_3$ -30), 0.85 (s, 3H, C-25), 0.84 (d,  $J = 3.7$  Hz, 3H,  $\text{CH}_3$ -29).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  198.0, 175.1, 170.7, 170.4, 170.1, 162.7, 132.3, 131.3, 130.3, 129.4, 129.2, 128.2, 128.0, 74.8, 68.9, 65.1, 62.8, 62.7, 61.0, 53.4, 50.0, 47.2, 44.2, 43.7, 41.8, 39.1, 38.5, 37.6, 36.6, 32.4, 32.3, 30.4, 27.7, 24.3, 23.9, 21.1, 21.0, 20.8, 20.7, 18.4, 18.1, 17.6, 17.3, 17.0, 16.5, 16.4, 16.1, 13.8. ESI-HRMS  $m/z$  Calc for  $\text{C}_{48}\text{H}_{70}\text{NO}_{11}\text{P}$   $[\text{M}+\text{H}]^+$ : 868.47593 founded: 868.47266.





ljf-130619 #2 RT: 0.01 AV: 1 NL: 6.24E5  
 T: FTMS + p ESI Full ms [820.00-885.00]

