Supporting Information

ADP-ribosyl-N_3: A Versatile Precursor for Divergent Syntheses of ADP-ribosylated Compounds

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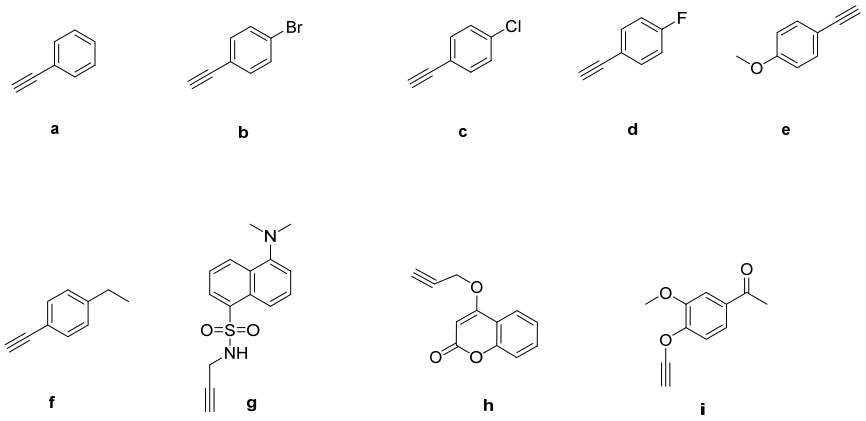
Table 1. The terminal alkynes **a** to **i** used in the CuAAC reaction.



a b c d e f g h i

Alkyne (**a**, **b, c, d, e, f**), $CuSO_4 \cdot 5H_2O$,Sodium ascorbate and copper(0) from Alfa Aesar. Alkynes (**g, h,** and **i**) was prepared with the method used in our previous work. Alkyne **h**, **g** prepared with the method used in our previous work[1]. The compound of **i** were prepared with the following procedure: 4-hydroxy-3-methoxyacetophenone (1 mmol) was added to a stirred suspension of the bromopropyne (1.0 mmol), potassium carbonate (1mmol) in methanol (5 mL). Upon completion of the reaction (TLC), the mixture was concentrated. The crude mixture was purified by silica gel column chromatography using Ethyl acetate/ petroleum ether as eluent to give target compound.

Characterization of compound 7a-7i:

Compound 7a ^{1}H NMR (400 MHz, D_2O) δ 8.38 (s, 1H), 8.03 (s, 1H), 7.59 (d, *J* = 7.0 Hz, 2H), 7.42 – 7.29 (m, 3H), 6.12 (d, *J* = 4.7 Hz, 1H), 5.83 (s, 1H), 4.66 (s, 1H), 4.51-4.56(m, 2H) 4.43 (s, 2H), 4.32 (m, 1H), 4.32-4.18(m, 4H).^{31}P NMR (162 MHz, D_2O): δ -11.55. HRMS (ESI) m/z calculate for($[M+H]^+$):$C_{23}H_{29}N_80_{13}P_2^+$:687.1324, Found: 687.1326.

Compound 7b ^{1}H NMR (600 MHz, D_2O) δ 8.27 (s, 1H), 8.12 (s, 1H), 7.86 (s, 1H), 7.55 (d, *J* = 7.8 Hz, 2H), 7.42 (d, *J* = 7.8 Hz, 2H), 6.44 (d, *J* = 4.8 Hz, 1H), 5.84 (d, *J* = 5.0 Hz, 1H), 4.64 (t, *J* = 4.7 Hz, 1H), 4.57 (s, 1H), 4.50 (d, *J* = 4.7 Hz, 2H), 4.44 (s, 1H), 4.36 (s, 2H), 4.28 (s, 2H), 4.16-4.14 (m, 1H).^{31}P NMR (162 MHz, D_2O): δ -11.71. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{23}H_{28}BrN_8O_{13}P_2^+$: 765.0429, Found: 765.0431.

Compound 7c ^{1}H NMR (600 MHz, D_2O) δ 8.40 (s, 1H), 8.20 (s, 1H), 8.01 (s, 1H), 7.52-7.51 (m, 2H), 7.31-7.30 (m, 2H), 6.15-6.14 (m, 1H), 5.79-5.78 (M, 1H), 4.65 (s, 1H), 4.51 (s, 2H), 4.44 (s, 1H), 4.40 (s, 1H), 4.32 – 4.30 (m, 4H), 4.20-4.18 (m, 1H). ^{31}P NMR (162 MHz, D_2O): δ -11.83. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{23}H_{28}ClN_8O_{13}P_2^+$: 721.0934, Found: 721.0936.

Compound 7d ^{1}H NMR (600 MHz, D_2O) δ 8.32 (s, 1H), 8.05 (s, 1H), 7.85 (s, 1H), 7.55 – 7.53 (m, 2H), 7.17-7.14 (m, 2H), 6.42 (d, *J* = 4.6 Hz, 1H), 5.88 (d, *J* = 5.0 Hz, 1H), 4.63 (t, *J* = 4.7 Hz, 1H), 4.56 (s, 1H), 4.53-4.52 (m, 1H), 4.49-4.16 (m, 2H), 4.39 – 4.31 (m, 2H), 4.28 (s, 2H), 4.16-4.14 (m, 1H).^{31}P NMR (162 MHz, D_2O): δ -11.74. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{23}H_{28}FN_8O_{13}P_2^+$:705.1230, Found: 705.1231.

Compound 7e ^{1}H NMR (600 MHz, D_2O) δ 8.32 (s, 1H), 8.03 (s, 1H), 7.86 (s, 1H), 7.47 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.42 (d, *J* = 4.2 Hz, 1H), 5.86 (d, *J* = 4.6 Hz, 1H), 4.63 (s, 1H), 4.56 (s, 1H), 4.53 – 4.47 (m, 2H), 4.45 (s, 1H), 4.36-4.33 (m, 2H), 4.28 (s, 2H), 4.16-4.14 (m, 1H), 3.89 (s, 3H).^{31}P NMR (162 MHz, D_2O): δ -11.24. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{24}H_{31}N_8O_{14}P_2^+$:717.1429, Found: 717.1431.

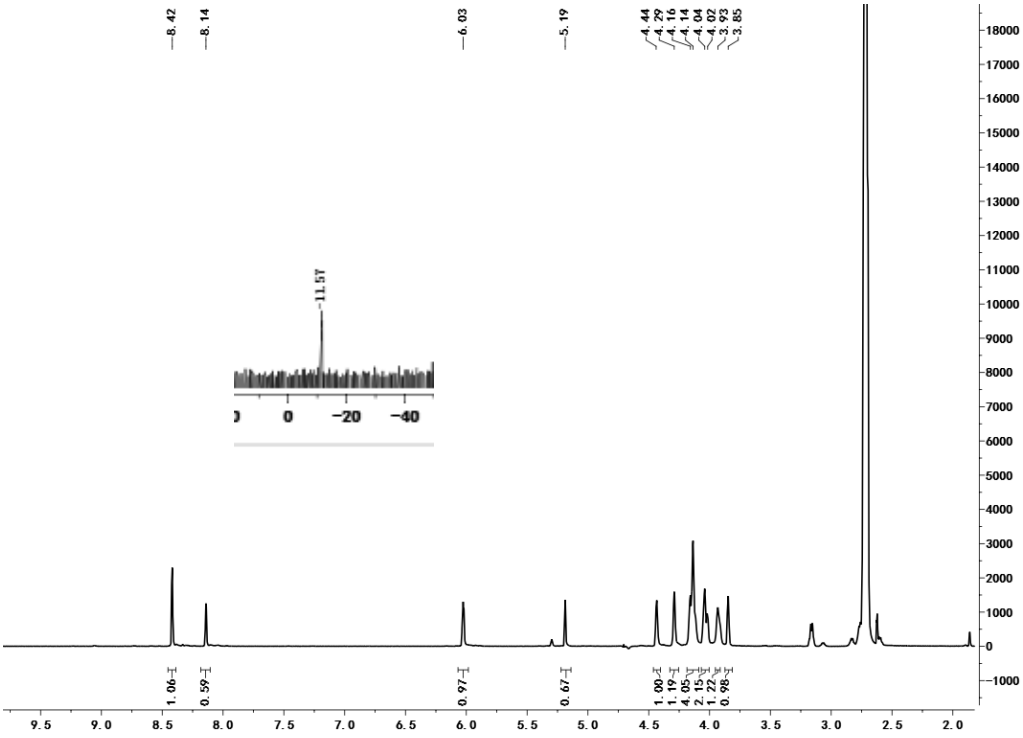
Compound 7f ^{1}H NMR (600 MHz, D_2O) δ 8.35 (s, 1H), 8.21 (s, 1H), 7.98 (s, 1H), 7.49 (d, *J* = 7.7 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 6.12 (d, *J* = 4.9 Hz, 1H), 5.78 (d, *J* = 4.8 Hz, 1H), 4.65 (s, 1H), 4.52 (s, 1H), 4.48 (s, 1H), 4.43 (s, 1H), 4.39 (s, 1H), 4.31 – 4.23 (m, 4H), 4.19-4.17(m, 1H), 2.63-2.59 (m, 2H), 1.34 – 1.24 (m, 3H). ^{31}P NMR (162 MHz, D_2O): δ -11.24. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{25}H_{31}N_8O_{13}P_2^+$: 715.1637, Found: 715.1639.

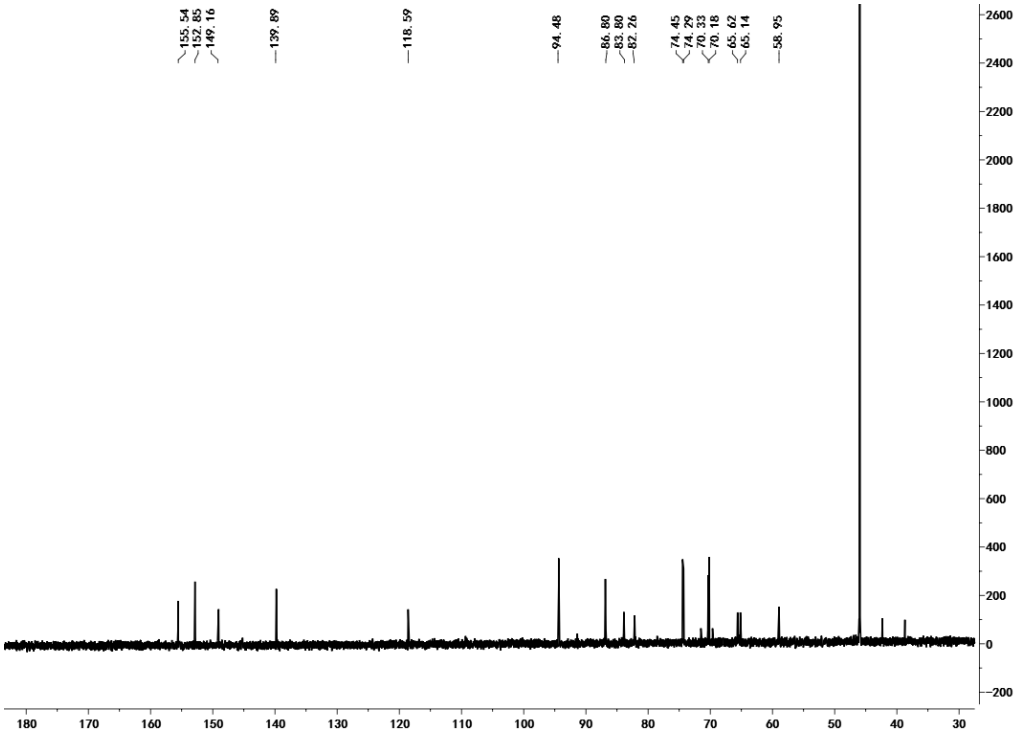
Compound 7g ^{1}H NMR (600 MHz, D_2O) δ 8.45 (s, 1H), 8.31-8.32 (m, 1H), 8.18-8.17 (m, 1H), 8.14-8.12 (m, 2H), 7.57 (s, 2H), 7.29-7.25(m, 1H), 6.06 (s, 1H), 5.90 (s, 1H), 4.52 (s, 1H), 4.43-4.39 (m, 2H), 4.30-4.29 (m, 3H), 4.17 (s, 2H), 4.11-4.06 (m, 2H), 3.28-3.25(m, 6H).^{31}P NMR (162 MHz, D_2O): δ -11.55. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{30}H_{39}N_{10}O_{15}P_2S^+$: 873.1787, Found: 873.1790

Compound 7h ^{1}H NMR (600 MHz, D_2O) δ 8.32 (s, 1H), 7.72-7.67 (m, 2H), 7.56 (s, 1H), 7.37-7.36 (m, 1H), 7.33 (s, 1H), 7.21-7.20 (m, 1H), 6.50 (s, 1H), 5.94 (s, 1H), 5.90 (s, 1H), 5.30 (s, 2H), 4.60 (s, 1H), 4.55 (s, 1H), 4.47-4.48 (m, 2H), 4.33 (s, 1H), 4.27 (s, 1H), 4.24 (s, 2H), 4.14 (s, 2H).^{31}P NMR (162 MHz, D_2O): δ -11.59. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{27}H_{31}N_8O_{16}P_2^+$: 785.1328, Found:785.1329.

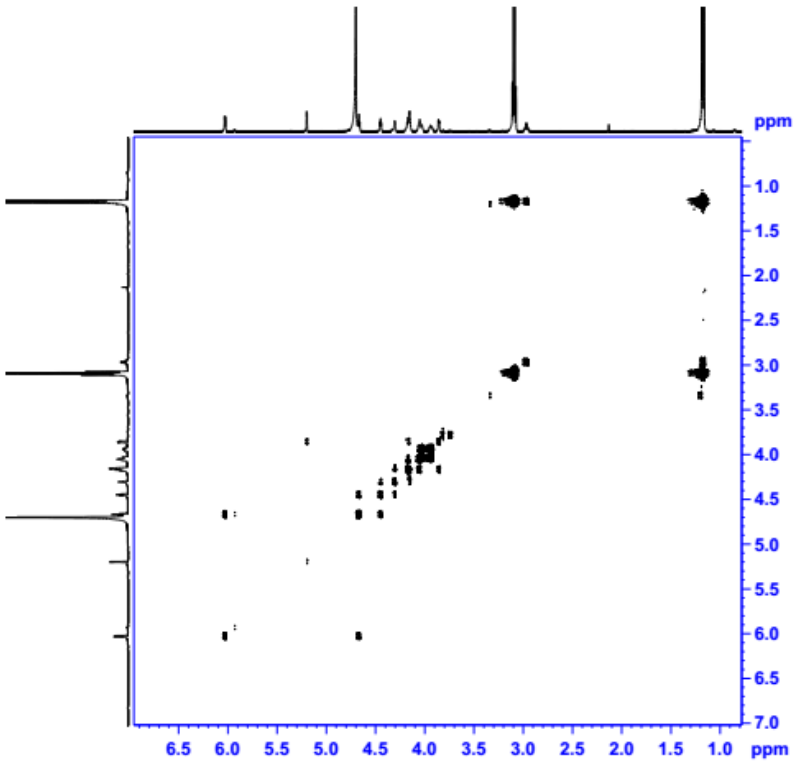
Compound 7i ^{1}H NMR (400 MHz, D_2O): δ 8.39 (s, 1H), 8.20 (s, 1H),8.10(s, 1H), 7.66-7.64(m, 1H), 6.01-5.99 (m, 1H), 5.24 (s, 2H), 4.66-4.64 (m, 2H), 4.53–4.49 (m, 2H), 4.45-4.42 (m, 1H), 4.36 (s, 1H), 4.28–4.24 (m, 3H), 4.12-4.11 (m, 1H), 3.91-3.87 (m, 3H), 2.64-2.62 (m, 3H). ^{31}P NMR (162 MHz, D_2O): δ -11.56. HRMS (ESI) m/z calculate for ($[M+H]^+$): $C_{27}H_{35}N_8O_{16}P_2^+$: 789.1641, Found: 789.1642.

Compound **6** ^{1}H, ^{31}P and ^{13}C NMR

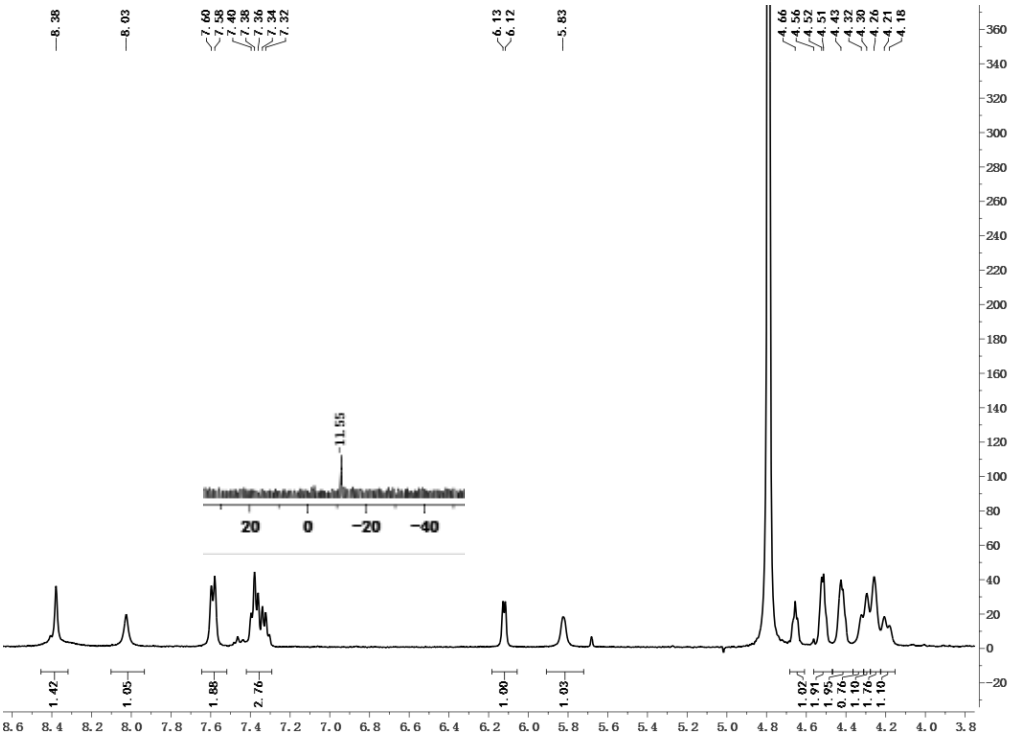




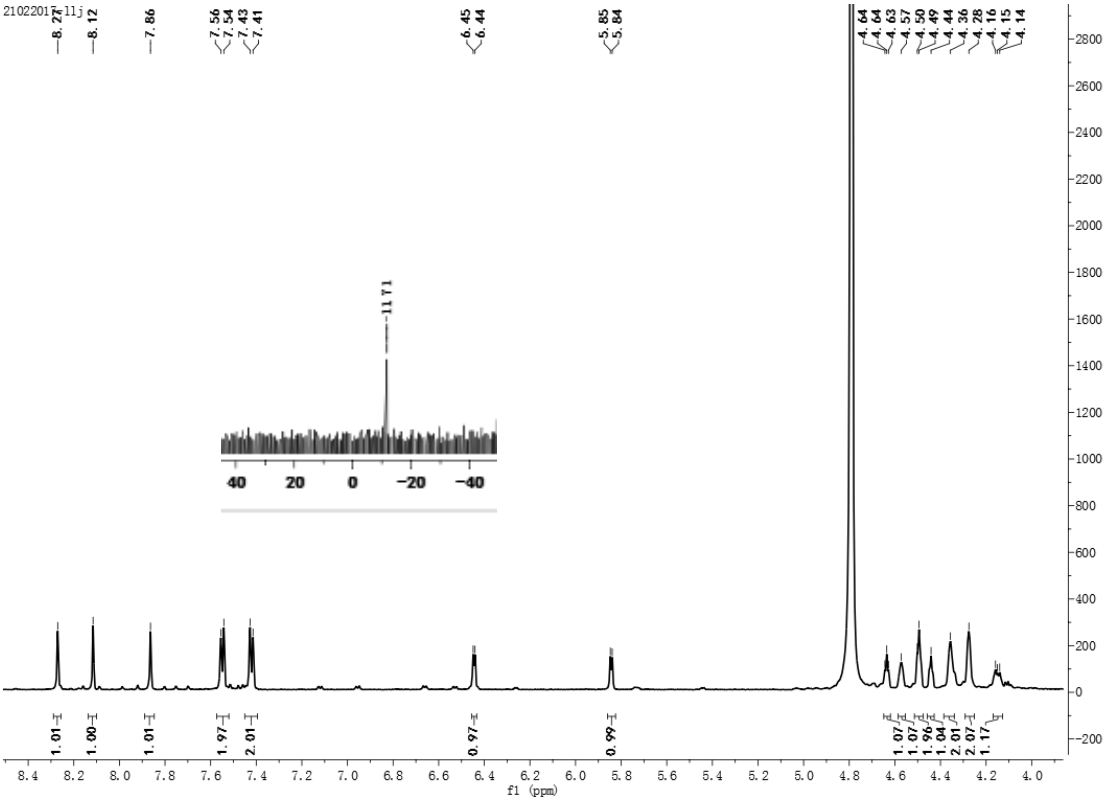
Compound **6** ^{1}H-^{1}H COSY



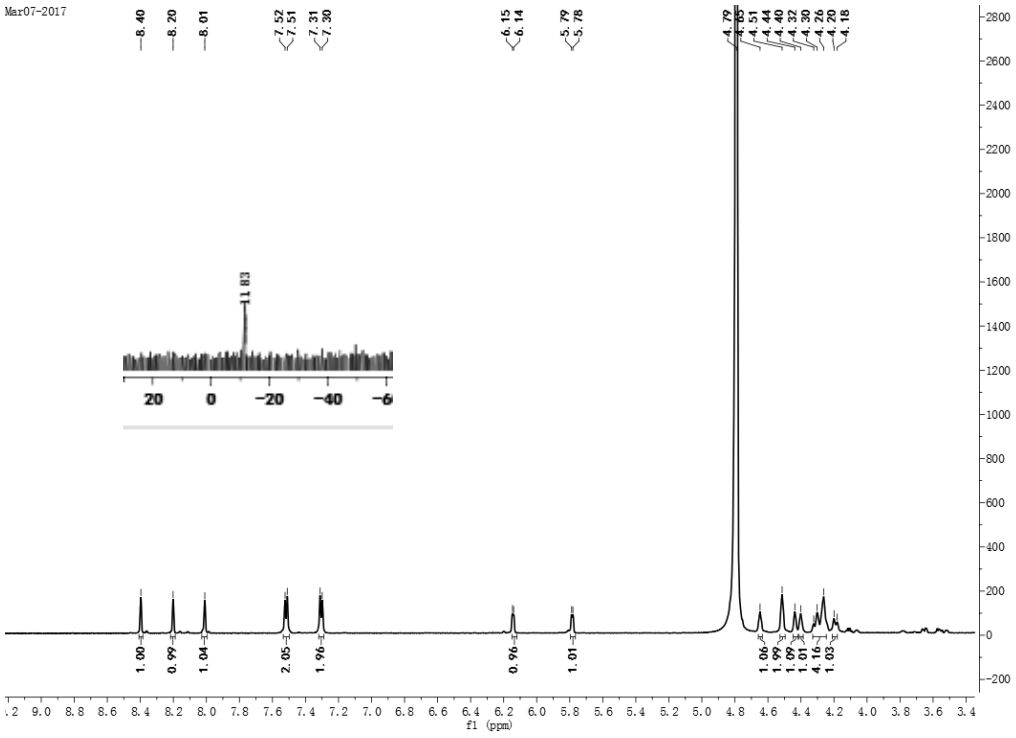
Compound **7a** ^{1}H and ^{31}P NMR



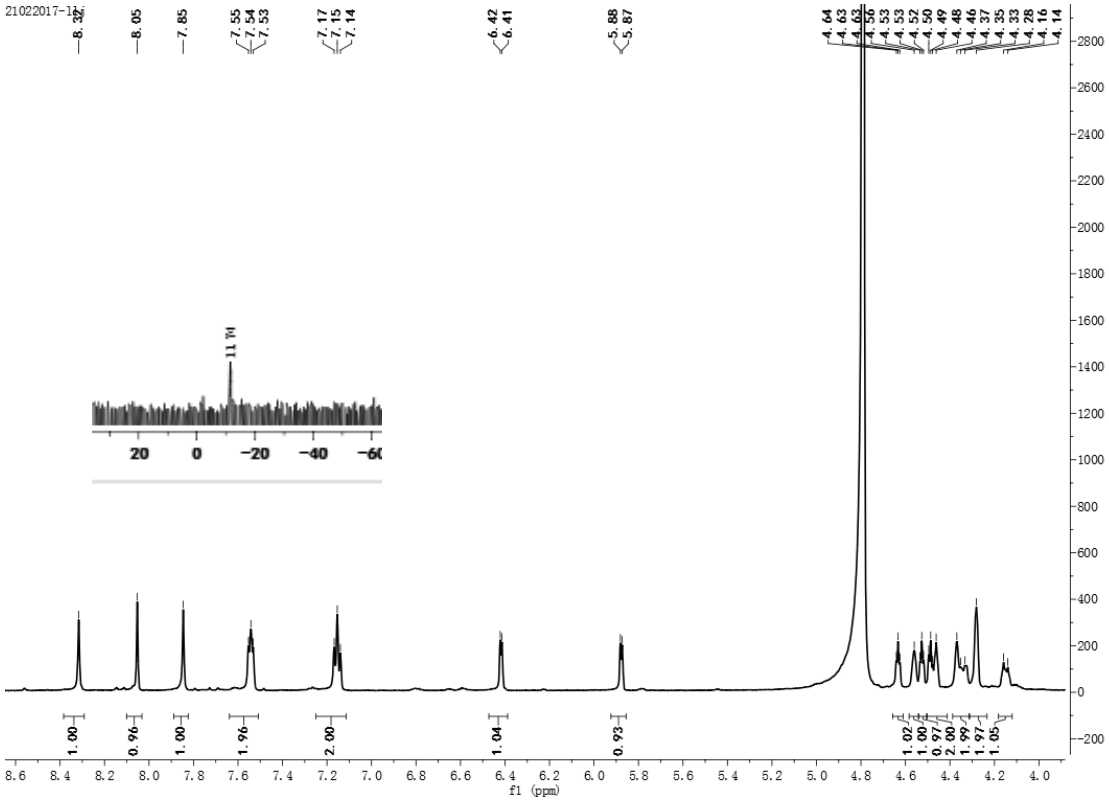
Compound **7b** ^{1}H and ^{31}P NMR



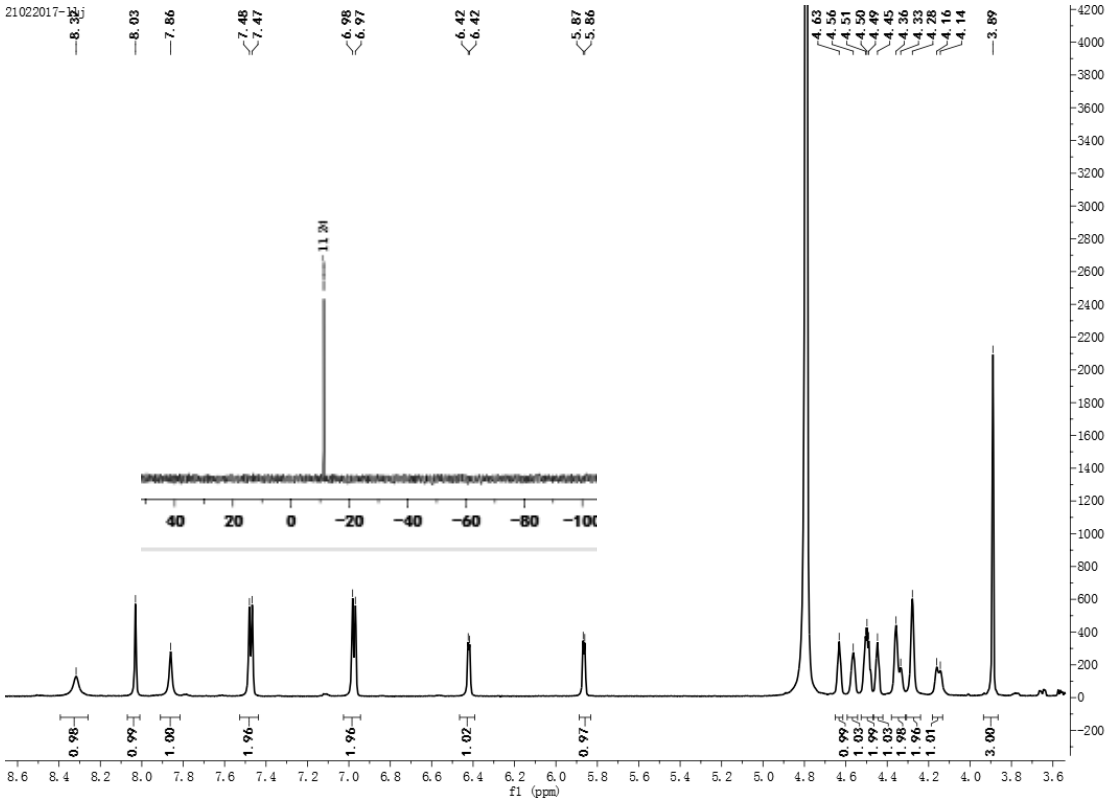
Compound **7c** ^{1}H and ^{31}P NMR



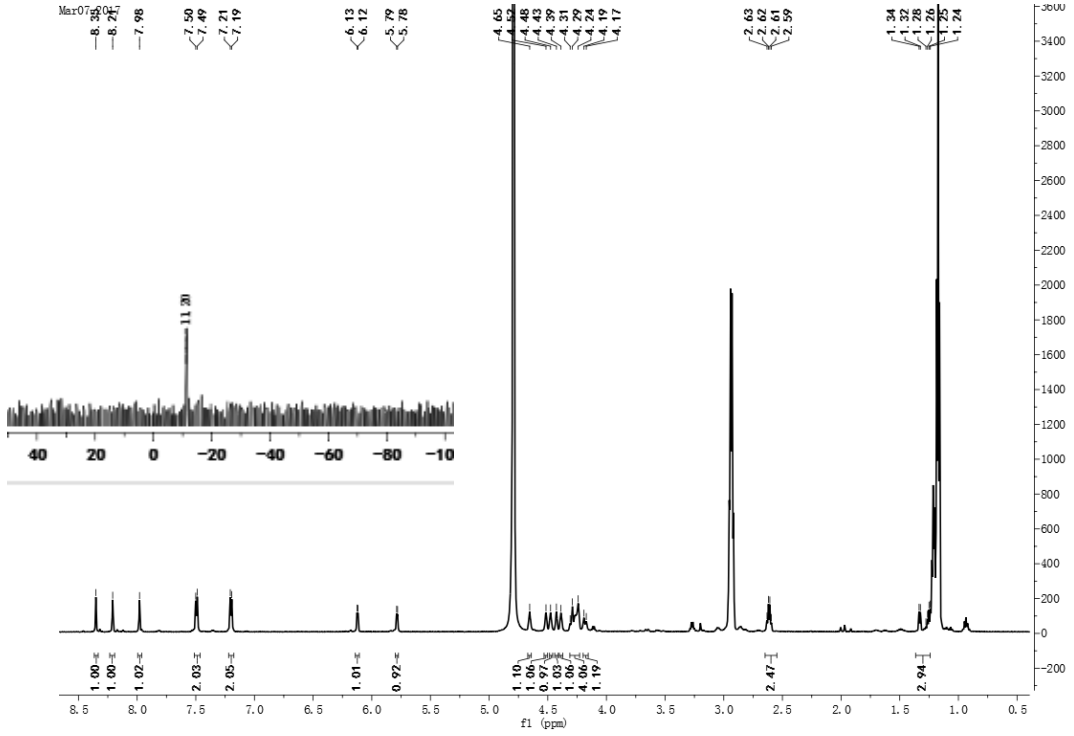
Compound **7d** ^{1}H and ^{31}P NMR



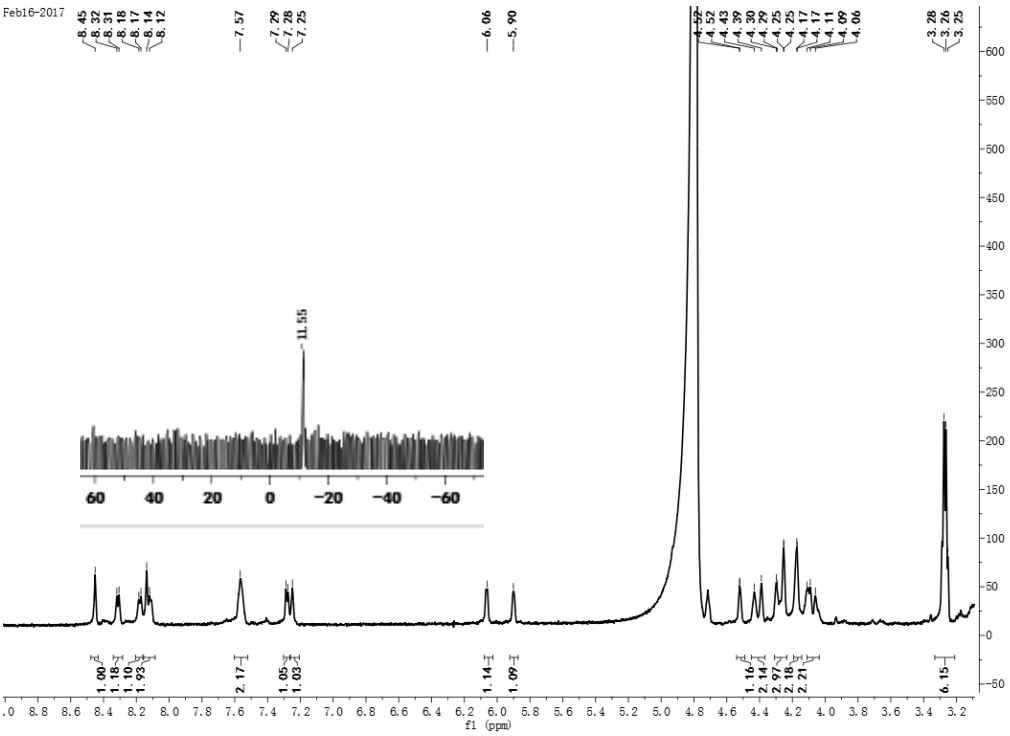
Compound **7e** ^{1}H and ^{31}P NMR



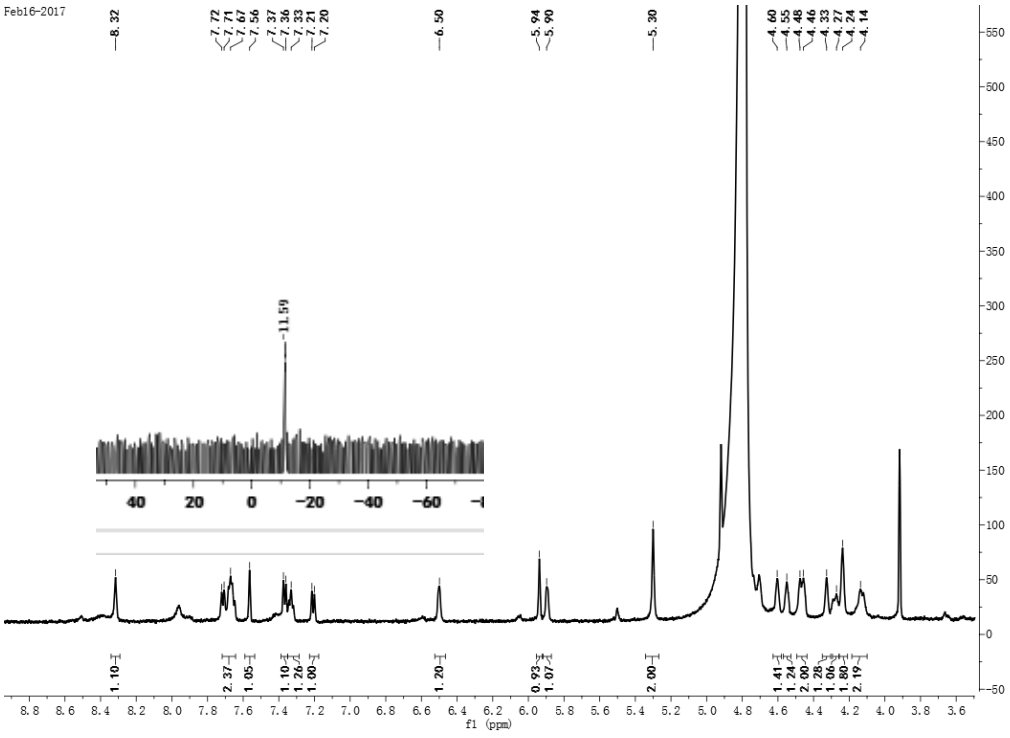
Compound **7f** ^{1}H and ^{31}P NMR



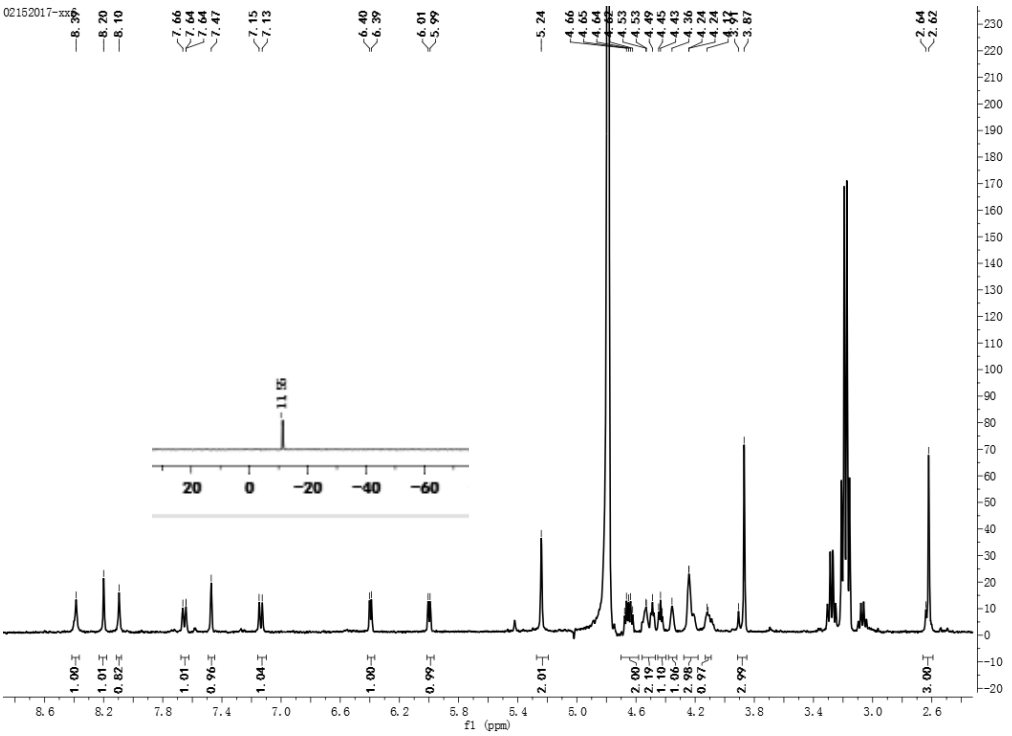
Compound **7g** ^{1}H and ^{31}P NMR



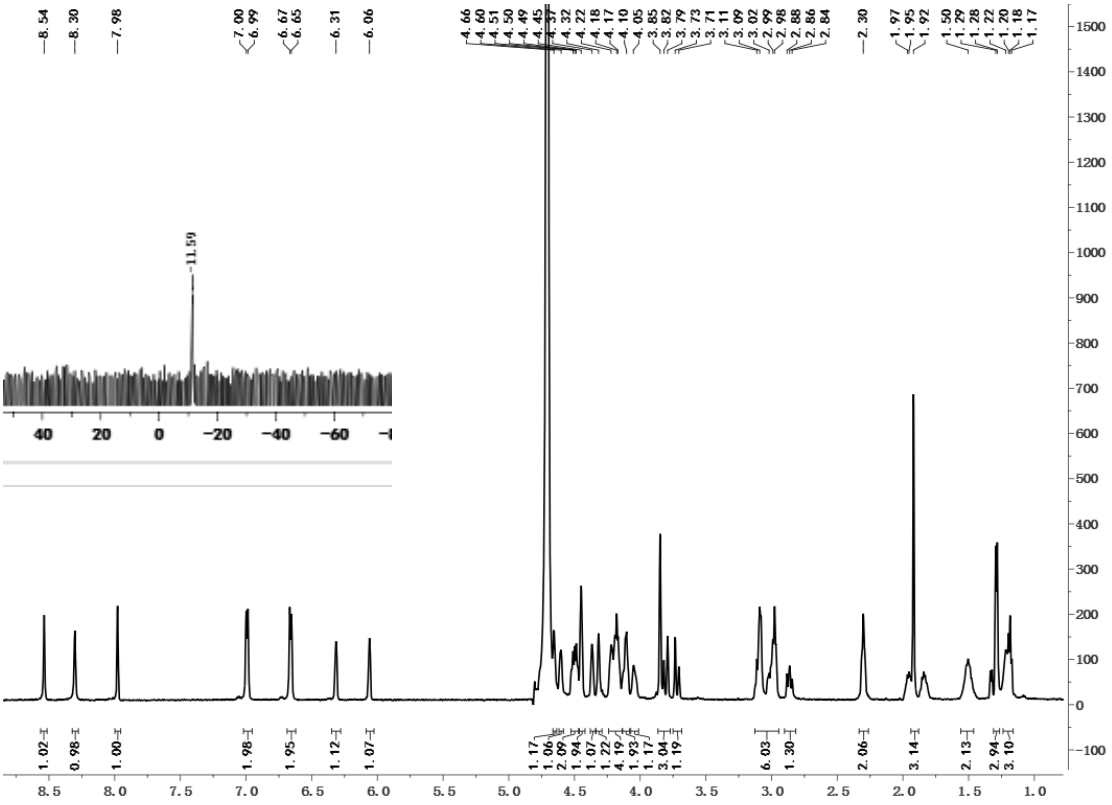
Compound **7h** ^{1}H and ^{31}P NMR



Compound **7i** ^{1}H and ^{31}P NMR



Compound **9** ^{1}H NMR and ^{31}P NMR



Reference

[1] L. Li, S. Ding, Y. Yang, A. Zhu, *Chem.Eur.J.*, **2017**, *23*, 1166-1172.