

SUPPORTING INFORMATION

A simple and efficient synthesis of highly substituted indeno[1,2-*b*]pyrrole and acenaphtho[1,2-*b*]pyrrole derivatives by tandem three-component reactions

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1. Experimental

1.1. General

Melting points were recorded on an Electrothermal digital melting point apparatus and uncorrected. IR Spectra were recorded on a Nicolet FT-IR500 spectrophotometer using KBr optics. ^1H NMR and ^{13}C MNR spectra were recorded on a JMTC-400/54/SS spectrometer using $\text{DMSO-}d_6$ as solvent and TMS as internal standard. HRMS analyses were conducted on a Bruker micro-TOF-Q-MS analyzer. X-Ray diffraction data were made on a Rigaku Mercury CCD area detector with graphite monochromated Mo-K α radiation.

1.2. Typical experimental procedure

1.2.1 Typical experimental procedure for **4**

A mixture of an equimolar amount of 1,3-dicarbonyl compound **2** (0.5 mmol) and tryptamine **3** (0.5 mmol) was stirred in ethanol at room temperature for 1h. Ninhydrin **1** (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the mixture was poured into cold water, then filtered and washed with EtOH (95%). The precipitate was purified by recrystallization from EtOH to give the product **4**.

1.2.2 Typical experimental procedure for **6**

A mixture of an equimolar amount of 1,3-dicarbonyl compound **2** (0.5 mmol) and tryptamine **3** (0.5 mmol) was stirred in ethanol at room temperature for 1h. Acenaphthenequinone **5** (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the mixture was poured into cold water, then filtered and washed with EtOH (95%). The precipitate was purified by recrystallization from EtOH to give the product **6**.

1.2.3 Typical experimental procedure for **8**

A mixture of an equimolar amount of 1,3-dicarbonyl compound **2** (0.5 mmol) and benzylamine **7** (0.5 mmol) were stirred in ethanol at room temperature for 2h. Ninhydrin **1** (0.5 mmol) was then added to this solution and stirred at room temperature for 0.5-1h. Completion of the reaction was monitored with TLC, the reaction mixture was poured into ice cold water. Then, the addition of brine solution

to the reaction mixture brought the precipitate. The precipitate was filtered, washed with water to give the product **8**. The crystal for X-ray diffraction was developed by recrystallization from EtOH.

2. X-Ray crystallographic data

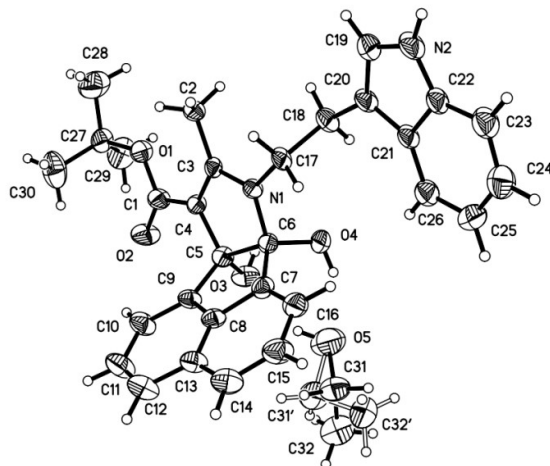
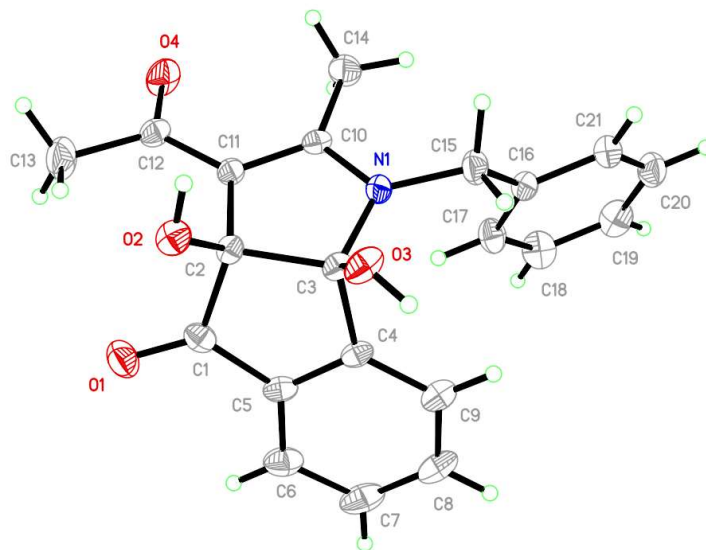


Figure 1. The crystal structure of **6d** with ethanol solvent

Table 1. Crystallographic data of compound **6d** (CCDC: 1866992)

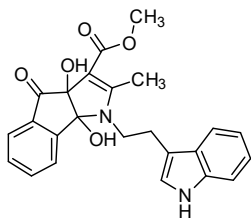
Empirical formula	C ₃₂ H ₃₆ N ₂ O ₅
Formula weight	528.63
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.9141(9) Å alpha = 117.069(3) deg. b = 12.5687(11) Å beta = 93.6000(10) deg. c = 13.6349(12) Å gamma = 107.657(2) deg.
Volume	1400.7(2) Å ³
Z, Calculated density	2, 1.253 Mg/m ³
Absorption coefficient	0.085 mm ⁻¹
F(000)	564
Crystal size	0.30 x 0.18 x 0.14 mm
Theta range for data collection	2.35 to 25.02 deg.
Limiting indices	-11 ≤ h ≤ 11, -11 ≤ k ≤ 14, -16 ≤ l ≤ 15
Reflections collected / unique	6978 / 4822 [R(int) = 0.0878]
Data / restraints / parameters	4822 / 0 / 378
Goodness-of-fit on F ²	0.87
Final R indices [I > 2σ(I)]	R1 = 0.0941, wR2 = 0.2203
R indices (all data)	R1 = 0.2250, wR2 = 0.2842

Largest diff. peak and hole

0.483 and -0.279 e.Å⁻³**Figure 2.** The crystal structure of **8f****Table 2.** Crystallographic data of compound **8f** (CCDC: 1866994)

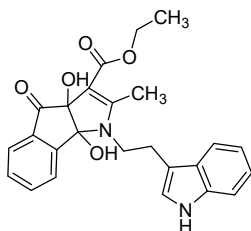
Empirical formula	C ₂₁ H ₁₉ NO ₄
Formula weight	349.37
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P2(1)/n
Unit cell dimensions	a = 8.1950(9) Å alpha = 90 deg. b = 16.7069(15) Å beta = 102.369(2) deg. c = 12.8179(12) Å gamma = 90 deg.
Volume	1714.2(3) Å ³
Z, Calculated density	4, 1.354 Mg/m ³
Absorption coefficient	0.094 mm ⁻¹
F(000)	736
Crystal size	0.45 x 0.21 x 0.18 mm
Theta range for data collection	2.44 to 25.02 deg.
Limiting indices	-9 ≤ h ≤ 8, -19 ≤ k ≤ 18, -15 ≤ l ≤ 15
Reflections collected / unique	8456 / 3003 [R(int) = 0.0420]
Data / restraints / parameters	3003 / 0 / 235
Goodness-of-fit on F ²	1.017
Final R indices [I > 2σ(I)]	R1 = 0.0465, wR2 = 0.1078
R indices (all data)	R1 = 0.0854, wR2 = 0.1269
Largest diff. peak and hole	0.246 and -0.241 e.Å ⁻³

3. Characterization data of compounds



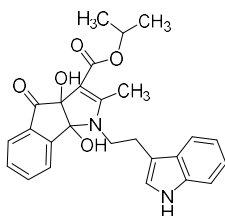
4a) methyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 149-151°C; IR(cm^{-1}): 744, 1194, 1356, 1437, 1551, 1655, 1717, 3410; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 2.22 (s, 3H, CH_3), 2.92-3.00 (m, 1H, CH), 3.14-3.21 (m, 1H, CH), 3.55 (s, 3H, OCH_3), 3.72-3.80 (m, 1H, CH), 3.98-4.06 (m, 1H, CH), 5.67 (s, 1H, OH), 6.77 (s, 1H, OH), 7.02 (t, $J=8.0$ Hz, 1H, ArH), 7.10 (t, $J=8.0$ Hz, 1H, ArH), 7.29 (s, 1H, ArH), 7.37 (d, $J=8.0$ Hz, 1H, ArH), 7.56 (t, $J=8.0$ Hz, 1H, ArH), 7.63 (d, $J=8.0$ Hz, 1H, ArH), 7.70-7.77 (m, 2H, ArH), 7.89 (d, $J=8.0$ Hz, 1H, ArH), 10.92 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.16, 27.45, 43.10, 50.15, 84.97, 94.74, 95.15, 111.74, 111.99, 118.86, 118.97, 121.56, 123.50, 123.72, 124.96, 127.62, 130.64, 135.51, 136.01, 136.73, 148.68, 160.53, 166.27, 198.83. HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 418.1529, found: 418.1545.



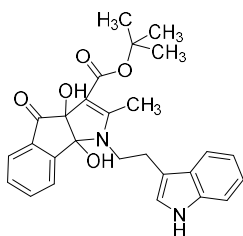
4b) ethyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 121-123°C; IR(cm^{-1}): 744, 1175, 1339, 1414, 1551, 1655, 1717, 3408; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.17 (t, $J=8.0$ Hz, 3H, CH_3), 2.19 (s, 3H, CH_3), 2.87-2.95 (m, 1H, CH), 3.09-3.17 (m, 1H, CH), 3.67-3.75 (m, 1H, CH), 3.91-4.06 (m, 3H, CH_2+CH), 5.55 (s, 1H, OH), 6.74 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.33 (d, $J=8.0$ Hz, 1H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.59 (d, $J=8.0$ Hz, 1H, ArH), 7.67-7.74 (m, 2H, ArH), 7.86 (d, $J=8.0$ Hz, 1H, ArH), 10.89 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.18, 15.13, 27.47, 43.08, 58.28, 84.98, 94.83, 95.10, 111.76, 111.98, 118.86, 118.96, 121.56, 123.49, 123.69, 124.97, 127.62, 130.63, 135.54, 135.98, 136.73, 148.73, 160.18, 166.79, 198.75. HRMS calcd for $\text{C}_{25}\text{H}_{24}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 432.1685, found: 432.1701.



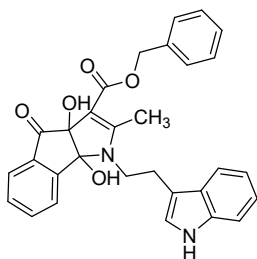
4c) *isopropyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate*

Yellow solid; m.p.: 101-103°C; IR(cm^{-1}): 743, 1107, 1175, 1416, 1553, 1647, 1718, 3412; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm): 1.18 (t, $J=8.0$ Hz, 6H, 2CH_3), 2.20 (s, 3H, CH_3), 2.86-2.94 (m, 1H, CH), 3.10-3.16 (m, 1H, CH), 3.67-3.75 (m, 1H, CH), 3.92-4.00 (m, 1H, CH), 4.81-4.87 (m, 1H, CH), 5.42 (s, 1H, OH), 6.72 (s, 1H, OH), 6.98 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.59 (d, $J=8.0$ Hz, 1H, ArH), 7.67-7.74 (m, 2H, ArH), 7.86 (d, $J=8.0$ Hz, 1H, ArH), 10.88 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm): 13.22, 22.54, 27.50, 43.06, 65.28, 85.00, 95.04, 111.79, 111.98, 118.87, 118.96, 121.56, 123.50, 123.65, 124.98, 127.62, 130.62, 135.55, 135.96, 136.74, 148.83, 159.82, 165.35, 198.77. HRMS calcd for $\text{C}_{26}\text{H}_{26}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 446.1842, found: 446.1838.



4d) *tert-butyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate*

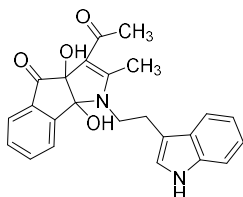
Yellow solid; m.p.: 110-112°C; IR(cm^{-1}): 743, 1153, 1366, 1458, 1560, 1655, 1718, 3410; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm): 1.41 (s, 9H, 3CH_3), 2.18 (s, 3H, CH_3), 2.85-2.92 (m, 1H, CH), 3.08-3.15 (m, 1H, CH), 3.66-3.74 (m, 1H, CH), 3.90-3.98 (m, 1H, CH), 5.28 (s, 1H, OH), 6.69 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.59 (d, $J=8.0$ Hz, 1H, ArH), 7.68-7.74 (m, 2H, ArH), 7.85 (d, $J=8.0$ Hz, 1H, ArH), 10.88 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO-}d_6$; δ , ppm): 13.12, 27.53, 28.95, 43.01, 78.24, 84.97, 94.93, 96.01, 111.81, 111.98, 118.87, 118.96, 121.56, 123.50, 123.62, 124.96, 127.62, 130.60, 135.54, 135.95, 136.74, 148.96, 159.31, 165.47, 198.94. HRMS calcd for $\text{C}_{27}\text{H}_{28}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 460.1998, found: 460.1969.



4e) *benzyl 1-(2-(1H-indol-3-yl)ethyl)-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate*

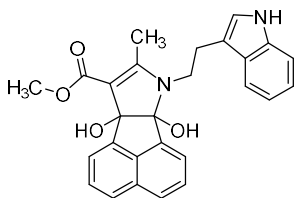
Yellow solid; m.p.: 100-102°C; IR(cm^{-1}): 743, 1157, 1340, 1412, 1547, 1655, 1718, 3423; ^1H NMR (400 MHz, $\text{DMSO-}d_6$; δ , ppm): 2.21 (s, 3H, CH_3), 2.89-2.96 (m, 1H, CH), 3.11-3.18 (m, 1H, CH), 3.70-3.78 (m, 1H, CH), 3.96-4.03 (m, 1H, CH), 5.28 (s, 1H, OH), 6.69 (s, 1H, OH), 5.08 (s, 2H, CH_2), 5.69 (s, 1H, OH), 6.80 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H,

ArH), 7.22-7.26 (m, 2H, ArH), 7.31-7.35 (m, 3H, ArH), 7.46 (d, $J=8.0$ Hz, 1H, ArH), 7.54 (t, $J=8.0$ Hz, 1H, ArH), 7.60 (d, $J=8.0$ Hz, 1H, ArH), 7.69-7.75 (m, 2H, ArH), 7.87 (d, $J=8.0$ Hz, 1H, ArH), 10.89 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO- d_6 ; δ , ppm): 13.33, 27.42, 43.16, 63.97, 85.10, 94.57, 95.20, 111.74, 111.99, 118.87, 118.98, 121.57, 123.54, 123.71, 125.02, 127.63, 127.69, 128.65, 130.69, 135.60, 136.04, 136.74, 138.43, 148.66, 160.99, 166.58, 198.88.; HRMS calcd for $\text{C}_{30}\text{H}_{26}\text{N}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 494.1842, found: 494.1853.



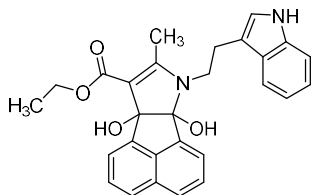
4f) 1-(2-(1H-indol-3-yl)ethyl)-3-acetyl-3a,8b-dihydroxy-2-methyl-3a,8b-dihydroindeno[1,2-b]pyrrol-4(1H)-one

Yellow solid; m.p.: 164-166°C; IR(cm^{-1}): 748, 1356, 1406, 1481, 1601, 1718, 3412; ^1H NMR (400 MHz, DMSO- d_6 ; δ , ppm): 2.26 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.85-2.89 (m, 1H, CH), 3.10-3.15 (m, 1H, CH), 3.71-3.76 (m, 1H, CH), 3.91-3.96 (m, 1H, CH), 6.02 (s, 1H, OH), 6.89 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.26 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.57 (t, $J=8.0$ Hz, 2H, ArH), 7.72-7.79 (m, 2H, ArH), 7.91 (d, $J=8.0$ Hz, 1H, ArH), 10.88 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO- d_6 ; δ , ppm): 13.92, 27.20, 30.08, 42.83, 85.36, 95.25, 106.97, 111.67, 112.02, 118.79, 119.02, 121.61, 123.65, 123.95, 125.16, 127.57, 130.77, 135.25, 136.45, 136.73, 149.34, 160.59, 193.57, 200.43.; HRMS calcd for $\text{C}_{24}\text{H}_{22}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 402.7580, found: 402.1596.



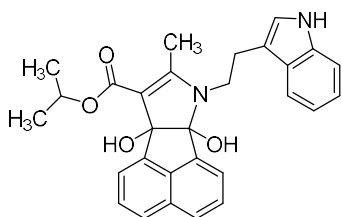
6a) methyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate

White solid; m.p.: 161-163°C; IR(cm^{-1}): 746, 787, 833, 1003, 1080, 1198, 1383, 1439, 1560, 1637, 3421; ^1H NMR (400 MHz, DMSO- d_6 ; δ , ppm): 2.19 (s, 3H, CH_3), 2.84-2.91 (m, 1H, CH), 3.06-3.13 (m, 1H, CH), 3.66 (s, 3H, CH_3), 3.70-3.76 (m, 2H, CH_2), 5.51 (s, 1H, OH), 6.49 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.07 (t, $J=8.0$ Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.52-7.62 (m, 4H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.76-7.82 (m, 2H, ArH), 10.90 (s, 1H, NH); ^{13}C NMR (100 MHz, DMSO- d_6 ; δ , ppm): 13.05, 19.11, 27.00, 43.19, 50.08, 56.58, 87.65, 99.60, 100.90, 111.96, 112.03, 118.75, 118.86, 119.60, 121.57, 123.58, 123.85, 125.27, 127.62, 128.27, 129.10, 131.30, 136.45, 136.75, 142.28, 145.98, 160.48, 166.46. HRMS calcd for $\text{C}_{27}\text{H}_{24}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 440.1736, found: 440.1745.



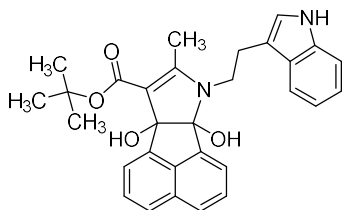
6b) ethyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate

White solid; m.p.: 145-147°C; IR(cm^{-1}): 748, 785, 833, 1080, 1173, 1188, 1339, 1418, 1566, 1618, 3366; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.28 (t, $J=8.0$ Hz, 3H, CH_3), 2.20 (s, 3H, CH_3), 2.83-2.90 (m, 1H, CH), 3.05-3.12 (m, 1H, CH), 3.67-3.78 (m, 2H, CH_2), 4.07-4.19 (m, 2H, CH_2), 5.47 (s, 1H, OH), 6.46 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.52-7.61 (m, 4H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.77 (d, $J=8.0$ Hz, 1H, ArH), 7.85 (d, $J=8.0$ Hz, 1H, ArH), 10.89 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.13, 15.38, 27.01, 43.18, 58.28, 87.67, 99.72, 100.84, 111.96, 112.02, 118.75, 118.97, 119.56, 121.55, 121.71, 123.56, 123.81, 125.24, 127.61, 128.26, 129.03, 131.28, 136.43, 136.73, 142.29, 145.96, 160.24, 166.02. HRMS calcd for $\text{C}_{28}\text{H}_{26}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 454.1893, found: 454.1931.



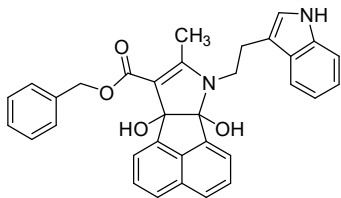
6c) isopropyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho [1,2-b]pyrrole-9-carboxylate

White solid; m.p.: 161-163°C; IR(cm^{-1}): 731, 785, 833, 997, 1080, 1107, 1175, 1400, 1568, 1605, 3325; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.27 (dd, $J_1=8.0$ Hz, $J_2=16.0$ Hz, 6H, 2 CH_3), 2.21 (s, 3H, CH_3), 2.81-2.89 (m, 1H, CH), 3.04-3.11 (m, 1H, CH), 3.69-3.74 (m, 2H, CH_2), 4.97-5.03 (m, 1H, CH), 5.42 (s, 1H, OH), 6.45 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.25 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.52-7.61 (m, 4H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.77 (d, $J=8.0$ Hz, 1H, ArH), 7.90 (d, $J=8.0$ Hz, 1H, ArH), 10.89 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.22, 22.83, 22.91, 27.04, 43.17, 65.10, 87.69, 99.96, 100.80, 111.97, 112.02, 118.75, 118.97, 119.52, 121.55, 121.77, 123.53, 123.80, 125.21, 127.60, 128.24, 128.99, 131.27, 136.43, 136.74, 142.29, 145.98, 159.94, 165.57. HRMS calcd for $\text{C}_{29}\text{H}_{28}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 468.2049, found: 468.2066.



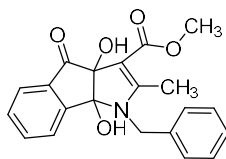
6d) *tert-butyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate*

White solid; m.p.: 112-114°C; IR(cm^{-1}): 741, 785, 833, 1080, 1150, 1366, 1393, 1572, 1649, 3349; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.50 (s, 9H, 3 CH_3), 2.18 (s, 3H, CH_3), 2.81 (s, 1H, CH), 3.05 (s, 1H, CH), 3.68 (s, 2H, CH_2), 5.34 (s, 1H, OH), 6.42 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.24 (s, 1H, ArH), 7.34 (d, $J=8.0$ Hz, 1H, ArH), 7.51-7.60 (m, 4H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.77 (d, $J=8.0$ Hz, 1H, ArH), 7.91 (d, $J=8.0$ Hz, 1H, ArH), 10.89 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.24, 19.10, 27.07, 29.19, 43.11, 56.56, 78.11, 87.72, 100.68, 100.99, 112.00, 118.74, 118.96, 119.45, 121.41, 121.54, 123.49, 123.78, 125.15, 127.59, 128.24, 129.07, 131.29, 136.41, 136.73, 142.34, 146.23, 159.12, 165.79. HRMS calcd for $\text{C}_{30}\text{H}_{30}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 482.2206, found: 482.2245.



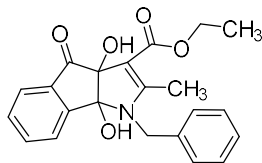
6e) *benzyl 7-(2-(1H-indol-3-yl)ethyl)-6b,9a-dihydroxy-8-methyl-6b,9a-dihydro-7H-acenaphtho[1,2-b]pyrrole-9-carboxylate*

White solid; m.p.: 95-97°C; IR(cm^{-1}): 699, 743, 783, 833, 1080, 1167, 1190, 1346, 1416, 1456, 1560, 1649, 3416; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 2.22 (s, 3H, CH_3), 2.87 (s, 1H, CH), 3.07 (s, 1H, CH), 3.75 (s, 2H, CH_2), 5.21 (s, 2H, CH_2), 5.56 (s, 1H, OH), 6.52 (s, 1H, OH), 6.99 (t, $J=8.0$ Hz, 1H, ArH), 7.06 (t, $J=8.0$ Hz, 1H, ArH), 7.26-7.36 (m, 5H, ArH), 7.41-7.47 (m, 3H, ArH), 7.54-7.62 (m, 3H, ArH), 7.68 (d, $J=8.0$ Hz, 1H, ArH), 7.78 (d, $J=8.0$ Hz, 2H, ArH), 10.90 (s, 1H, NH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.22, 26.97, 43.26, 63.98, 87.73, 99.42, 100.92, 111.95, 112.02, 118.75, 118.98, 119.62, 121.55, 121.87, 123.56, 123.84, 125.29, 127.61, 127.97, 128.22, 128.83, 128.95, 131.27, 136.43, 136.75, 138.47, 142.19, 145.83, 160.85, 165.73. HRMS calcd for $\text{C}_{33}\text{H}_{28}\text{N}_2\text{O}_4$ $[\text{M}+\text{H}]^+$: 516.2049, found: 516.2058.



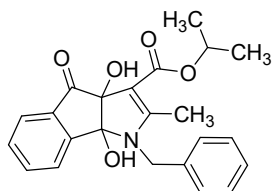
8a) *methyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate*

White solid; m.p.: 154-156°C; IR(cm^{-1}): 784, 823, 1101, 1296, 1427, 1562, 1635, 1721, 3398; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.93 (s, 3H, CH_3), 3.50 (s, 3H, CH_3), 4.75 (d, $J=16.0$ Hz, 1H, CH), 5.12 (d, $J=16.0$ Hz, 1H, CH), 5.70 (s, 1H, OH), 6.79 (s, 1H, OH), 7.19-7.29 (m, 5H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.65-7.70 (m, 2H, ArH), 7.77 (d, $J=8.0$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.65, 45.38, 50.20, 85.04, 94.63, 95.59, 123.46, 125.27, 127.23, 127.37, 128.84, 130.65, 135.49, 135.86, 139.40, 148.54, 160.86, 166.19, 198.81. HRMS calcd for $\text{C}_{21}\text{H}_{19}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 365.1263, found: 365.1279.



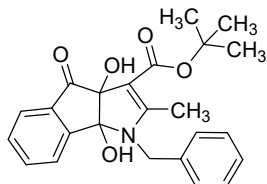
8b) ethyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 72-73°C; IR(cm^{-1}): 765, 852, 1091, 1216, 1437, 1545, 1629, 1743, 3421; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.15 (t, $J=8.0$ Hz, 3H, CH_3), 1.92 (s, 3H, CH_3), 3.90-4.05 (m, 2H, CH_2), 4.75 (d, $J=16.0$ Hz, 1H, CH), 5.10 (d, $J=16.0$ Hz, 1H, CH), 5.61 (s, 1H, OH), 6.78 (s, 1H, OH), 7.20-7.29 (m, 5H, ArH), 7.53 (t, $J=8.0$ Hz, 1H, ArH), 7.64-7.70 (m, 2H, ArH), 7.76 (d, $J=8.0$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.67, 15.08, 45.36, 58.37, 85.07, 94.58, 95.67, 123.45, 125.27, 127.22, 127.36, 128.83, 130.64, 135.52, 135.81, 139.44, 148.56, 160.50, 165.70, 198.73. HRMS calcd for $\text{C}_{22}\text{H}_{21}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 379.1420, found: 379.1438.



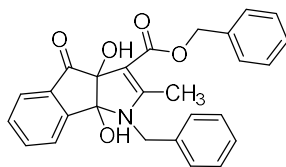
8c) isopropyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Pale yellow solid; m.p.: 71-73°C; IR(cm^{-1}): 756, 918, 1096, 1285, 1408, 1533, 1667, 1715, 3426; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.15 (t, $J=8.0$ Hz, 6H, 2 CH_3), 1.92 (s, 3H, CH_3), 4.73-4.84 (m, 2H, CH_2), 5.08 (d, $J=16.0$ Hz, 1H, CH), 5.50 (s, 1H, OH), 6.77 (s, 1H, OH), 7.19-7.28 (m, 5H, ArH), 7.52 (t, $J=8.0$ Hz, 1H, ArH), 7.64-7.70 (m, 2H, ArH), 7.76 (d, $J=8.0$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.69, 22.59, 45.33, 65.40, 85.08, 94.54, 95.85, 123.44, 125.28, 127.23, 127.35, 128.83, 130.63, 135.54, 135.79, 139.46, 148.62, 160.16, 165.25, 198.74. HRMS calcd for $\text{C}_{23}\text{H}_{23}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 393.1576, found: 393.1561.



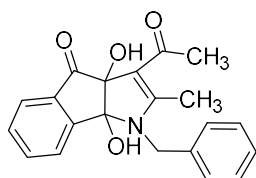
8d) tert-butyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 83-85°C; IR(cm^{-1}): 749, 925, 1163, 1276, 1418, 1556, 1638, 1729, 3398; ^1H NMR (400 MHz, $\text{DMSO}-d_6$; δ , ppm): 1.38 (s, 9H, 3 CH_3), 1.89 (s, 3H, CH_3), 4.74 (d, $J=16.0$ Hz, 1H, CH), 5.06 (d, $J=16.0$ Hz, 1H, CH), 5.37 (s, 1H, OH), 6.74 (s, 1H, OH), 7.18-7.28 (m, 5H, ArH), 7.52 (t, $J=8.0$ Hz, 1H, ArH), 7.65 (t, $J=8.0$ Hz, 1H, ArH), 7.70 (d, $J=8.0$ Hz, 1H, ArH), 7.72 (d, $J=8.0$ Hz, 1H, ArH); ^{13}C NMR (100 MHz, $\text{DMSO}-d_6$; δ , ppm): 13.58, 28.89, 45.28, 78.36, 85.06, 94.46, 96.84, 123.44, 125.26, 127.21, 127.33, 128.82, 130.61, 135.54, 135.77, 139.53, 148.72, 159.64, 165.33, 198.92. HRMS calcd for $\text{C}_{24}\text{H}_{25}\text{NO}_5$ $[\text{M}+\text{H}]^+$: 407.1733, found: 407.1749.



8e) benzyl 1-benzyl-3a,8b-dihydroxy-2-methyl-4-oxo-1,3a,4,8b-tetrahydroindeno[1,2-b]pyrrole-3-carboxylate

Yellow solid; m.p.: 70-71°C; IR(cm⁻¹): 732, 838, 1119, 1239, 1430, 1562, 1669, 1728, 3411; ¹H NMR (400 MHz, DMSO-*d*₆; δ, ppm): 1.94 (s, 3H, CH₃), 4.77 (d, *J*=16.0 Hz, 1H, CH), 5.02-5.14 (m, 3H, CH₂+CH), 5.75 (s, 1H, OH), 6.84 (s, 1H, OH), 7.20-7.33 (m, 8H, ArH), 7.45 (d, *J*=8.0 Hz, 1H, ArH), 7.54 (t, *J*=8.0 Hz, 1H, ArH), 7.65-7.73 (m, 2H, ArH), 7.77 (d, *J*=8.0 Hz, 1H, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆; δ, ppm): 13.81, 45.53, 64.07, 85.16, 94.69, 95.40, 123.50, 125.33, 127.24, 127.38, 127.71, 127.76, 128.64, 128.85, 130.70, 135.58, 135.87, 138.29, 139.31, 148.50, 161.33, 166.52, 198.87. HRMS calcd for C₂₇H₂₃NO₅ [M+H]⁺: 441.1576, found: 441.1589.

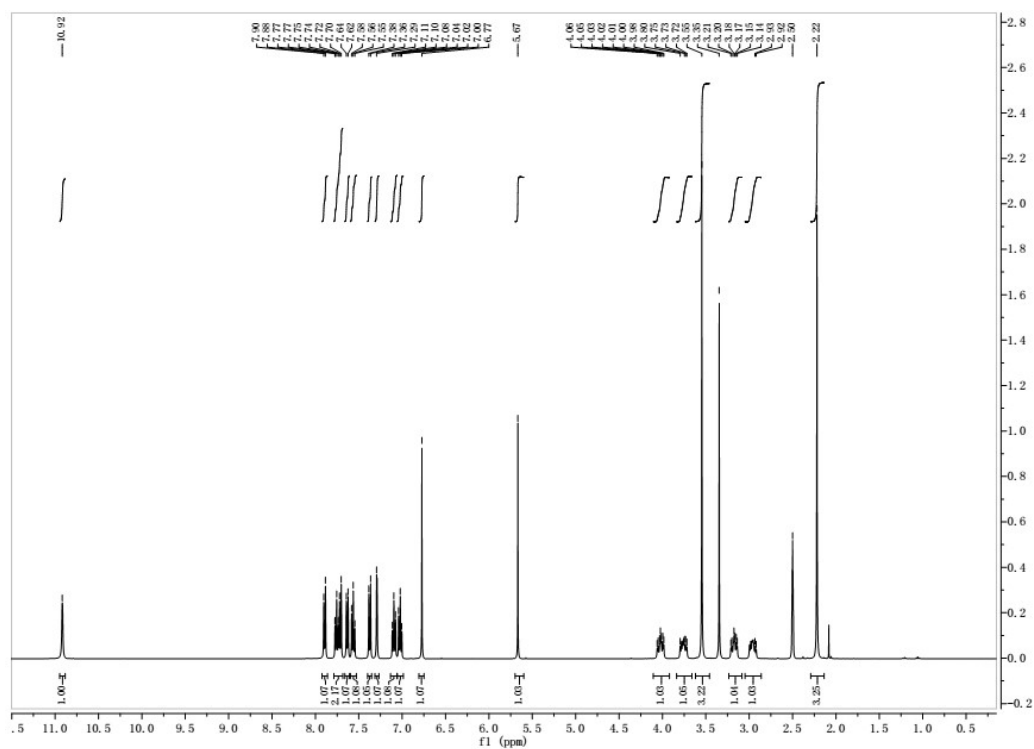


8f) 3-acetyl-1-benzyl-3a,8b-dihydroxy-2-methyl-3a,8b-dihydroindeno[1,2-b]pyrrol-4(1H)-one

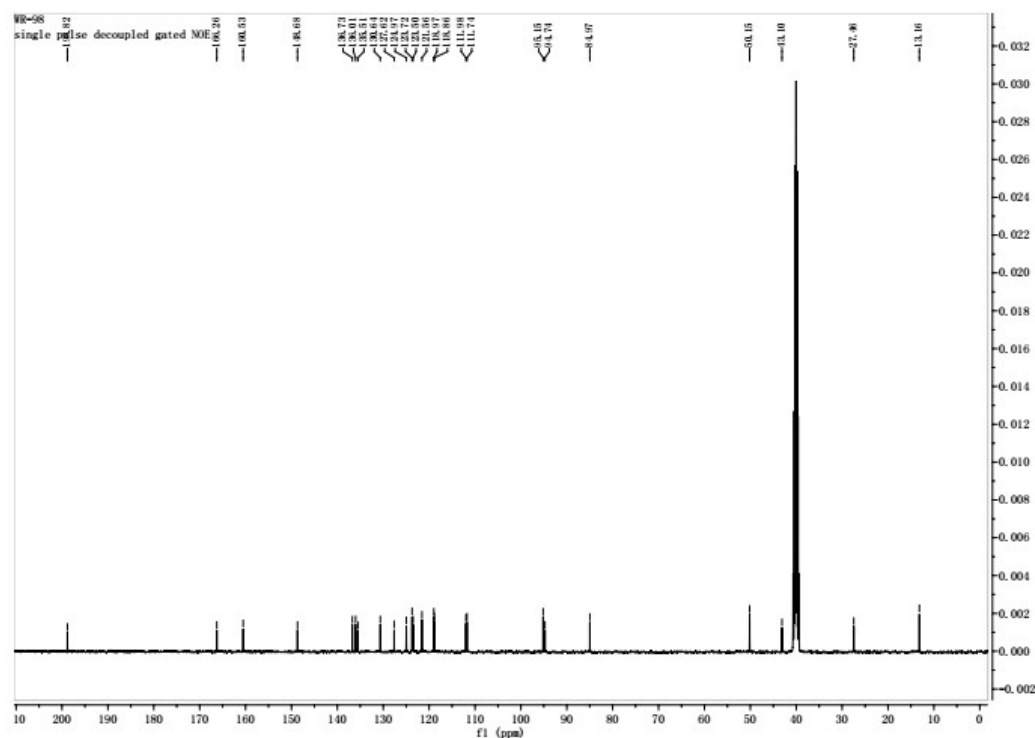
White solid; m.p.: 175-177°C; IR(cm⁻¹): 756, 841, 1093, 1216, 1435, 1562, 1674, 1735, 3417; ¹H NMR (400 MHz, DMSO-*d*₆; δ, ppm): 1.97 (s, 3H, CH₃), 2.31 (s, 3H, CH₃), 4.81 (d, *J*=16.0 Hz, 1H, CH), 5.05 (d, *J*=16.0 Hz, 1H, CH), 6.05 (s, 1H, OH), 6.96 (s, 1H, OH), 7.11 (d, *J*=8.0 Hz, 2H, ArH), 7.16-7.25(m, 3H, ArH), 7.54 (t, *J*=8.0 Hz, 1H, ArH), 7.65 (t, *J*=8.0 Hz, 1H, ArH), 7.73-7.79 (m, 2H, ArH); ¹³C NMR (100 MHz, DMSO-*d*₆; δ, ppm): 14.32, 30.07, 45.21, 85.42, 94.79, 106.51, 123.88, 125.53, 127.05, 127.32, 128.81, 130.73, 135.23, 136.23, 139.04, 149.25, 160.80, 193.76, 200.46. HRMS calcd for C₂₁H₁₉NO₄ [M+H]⁺: 349.1314, found: 349.1325.

4. Original ^1H NMR and ^{13}C NMR spectra

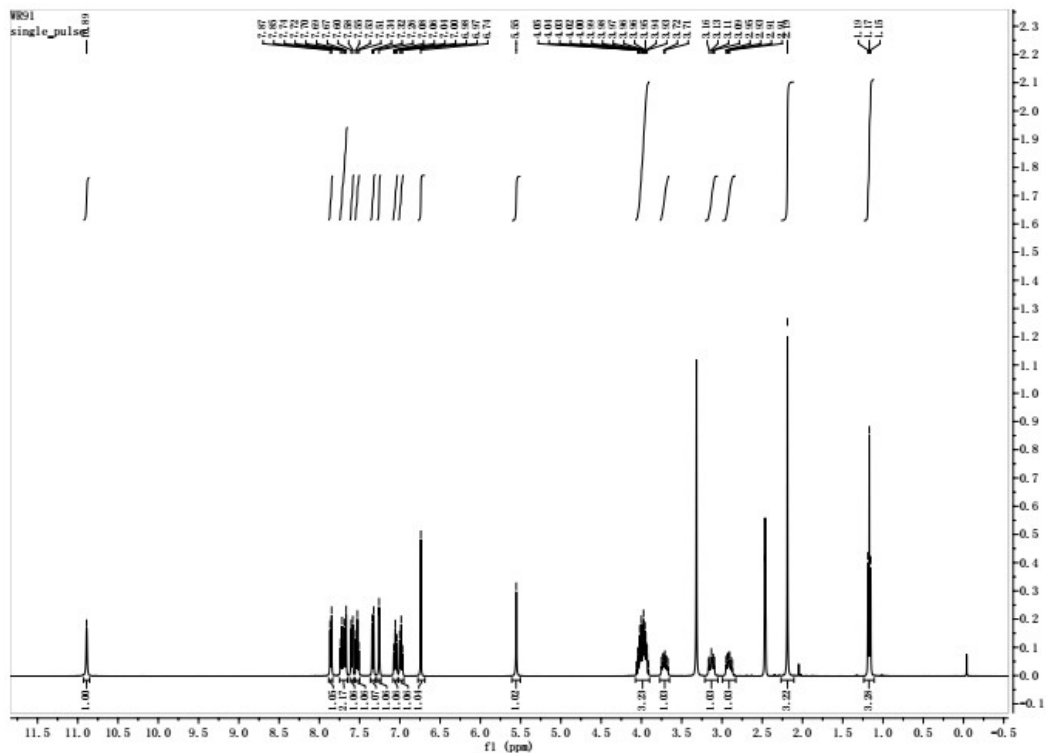
^1H for 4a



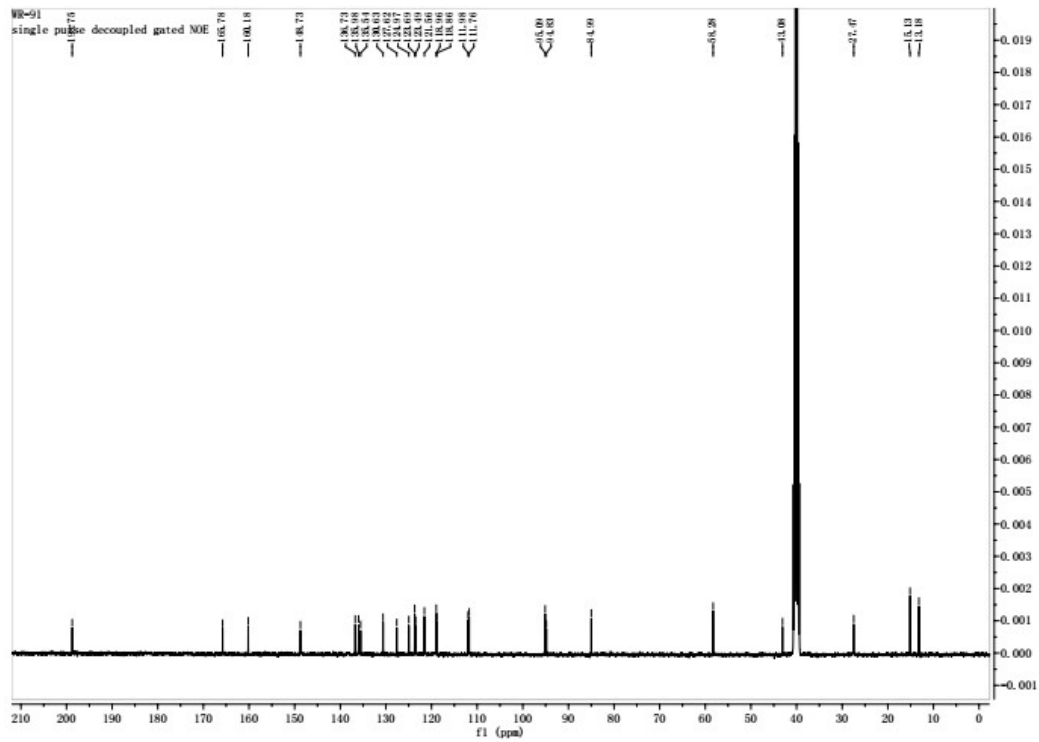
^{13}C for 4a



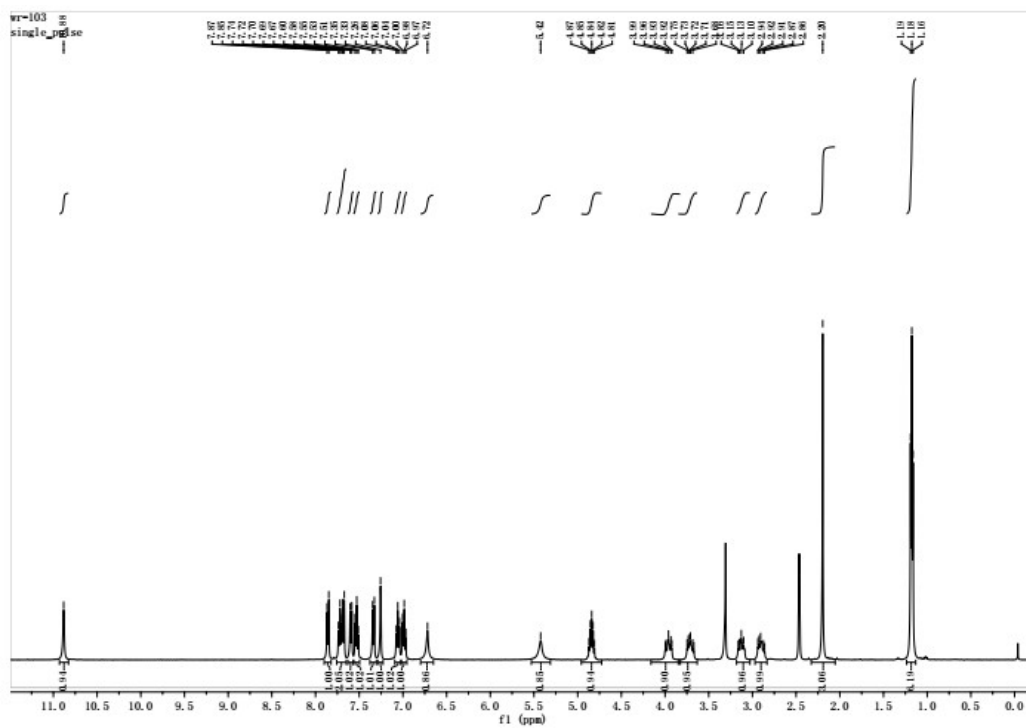
¹H for 4b



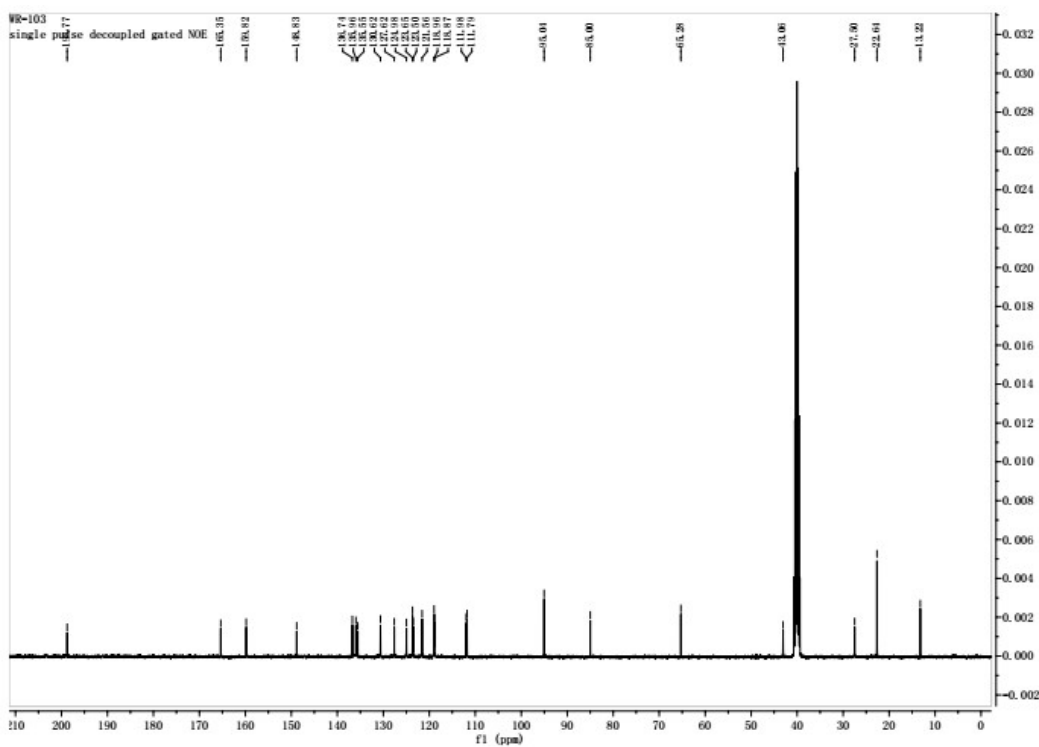
¹³C for 4b



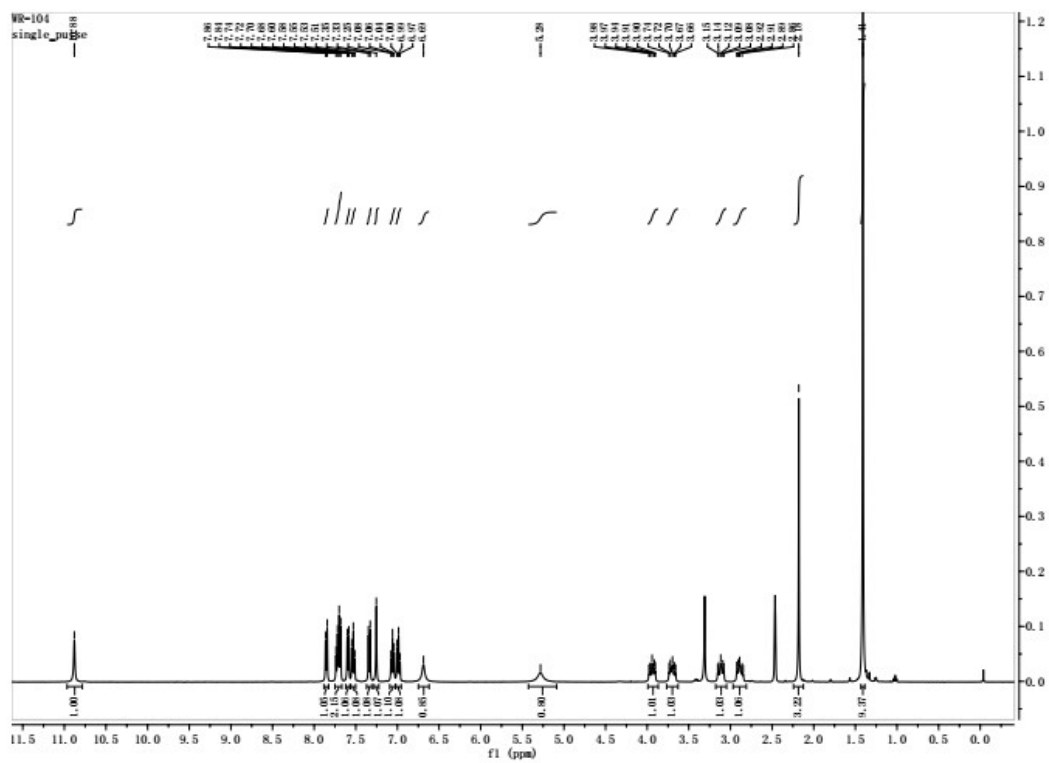
¹H for 4c



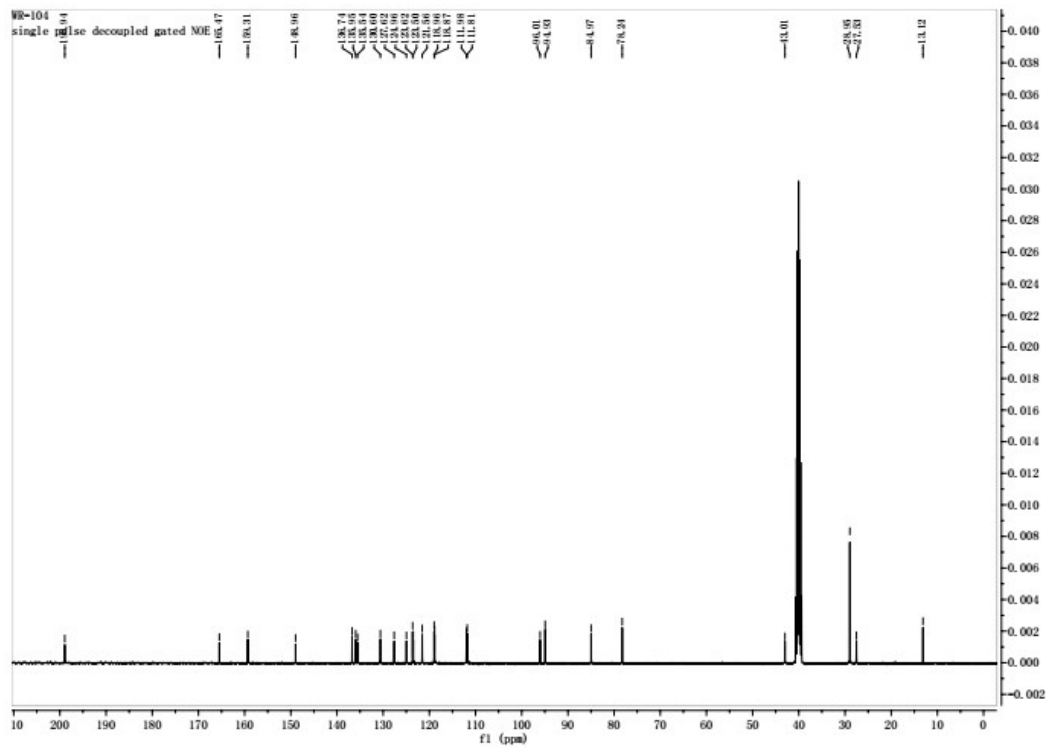
¹³C for 4c



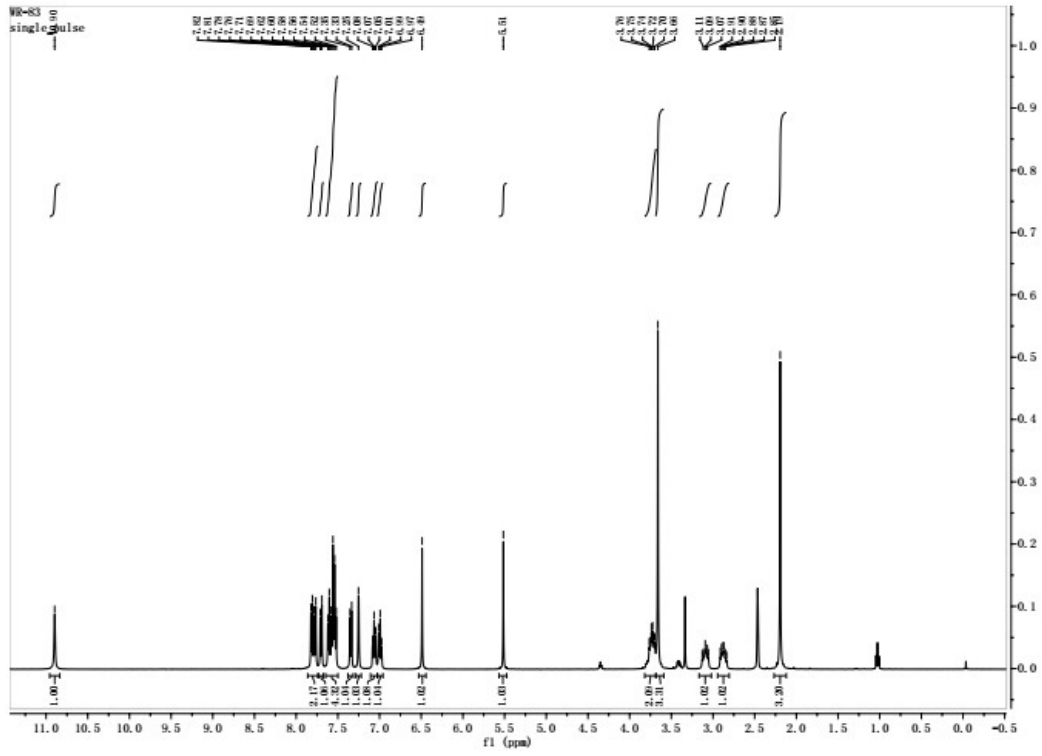
¹H for 4d



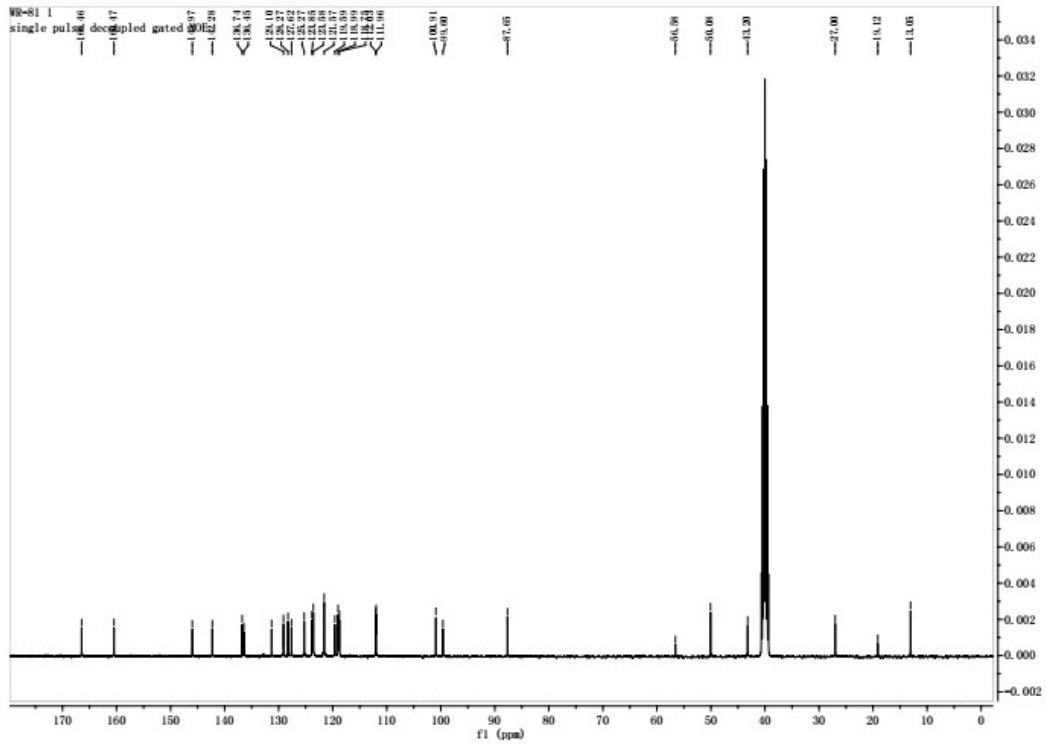
¹³C for 4d



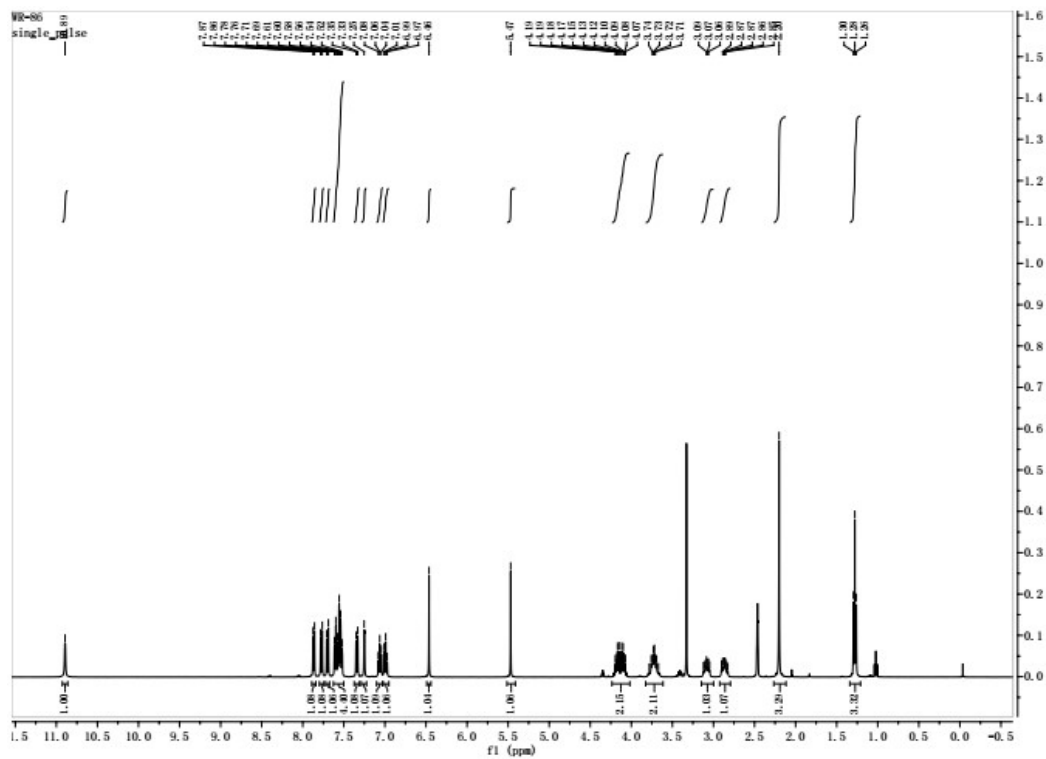
¹H for 6a



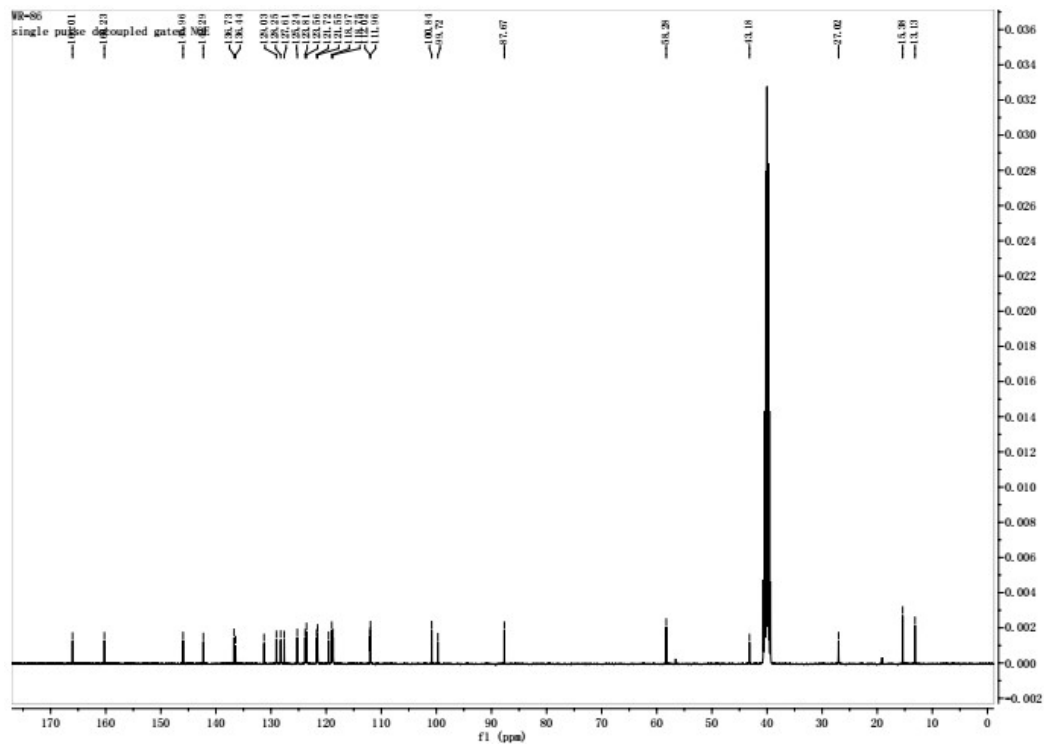
¹³C for 6a



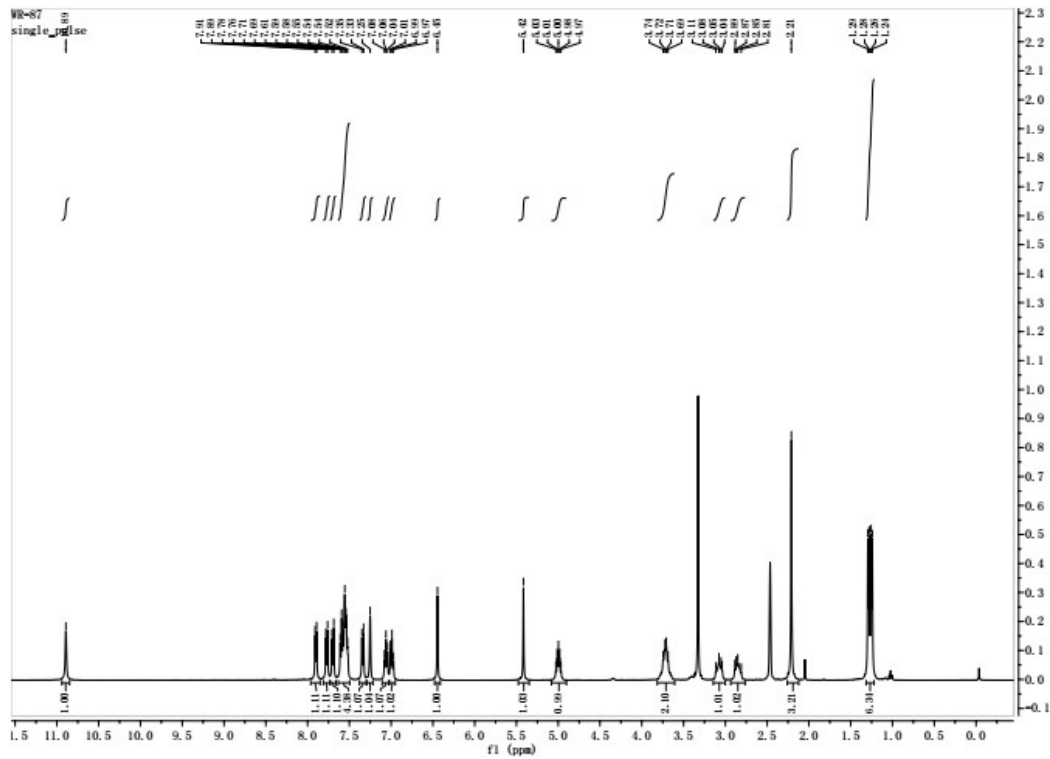
¹H for 6b



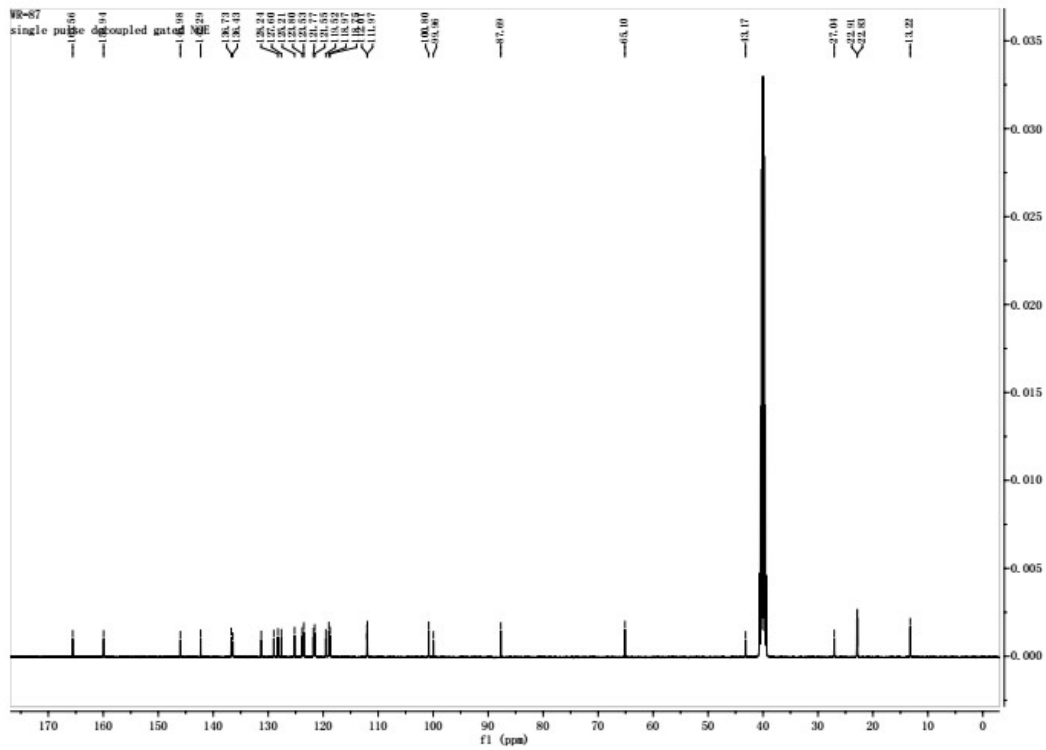
¹³C for 6b



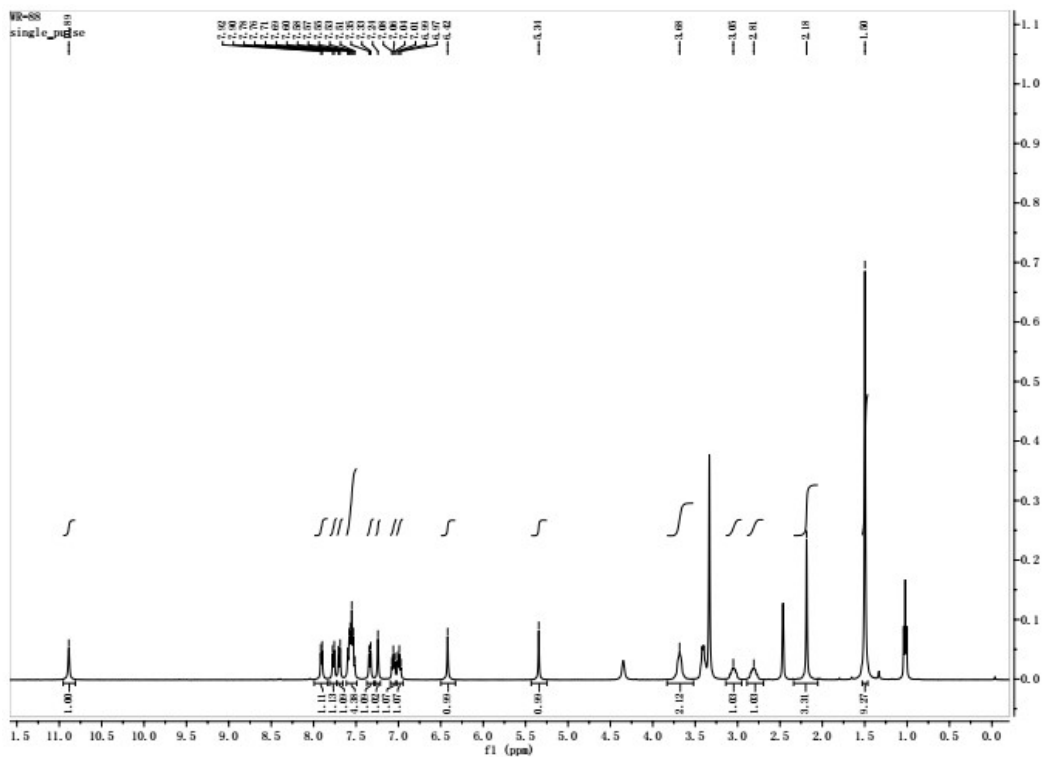
¹H for 6c



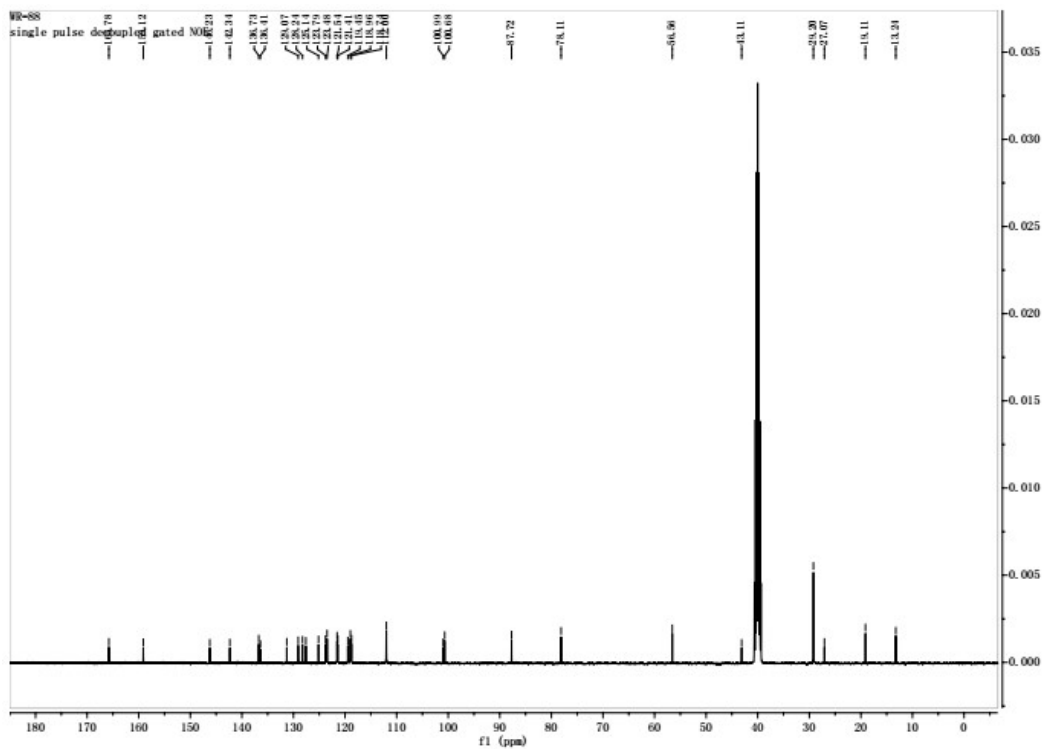
¹³C for 6c



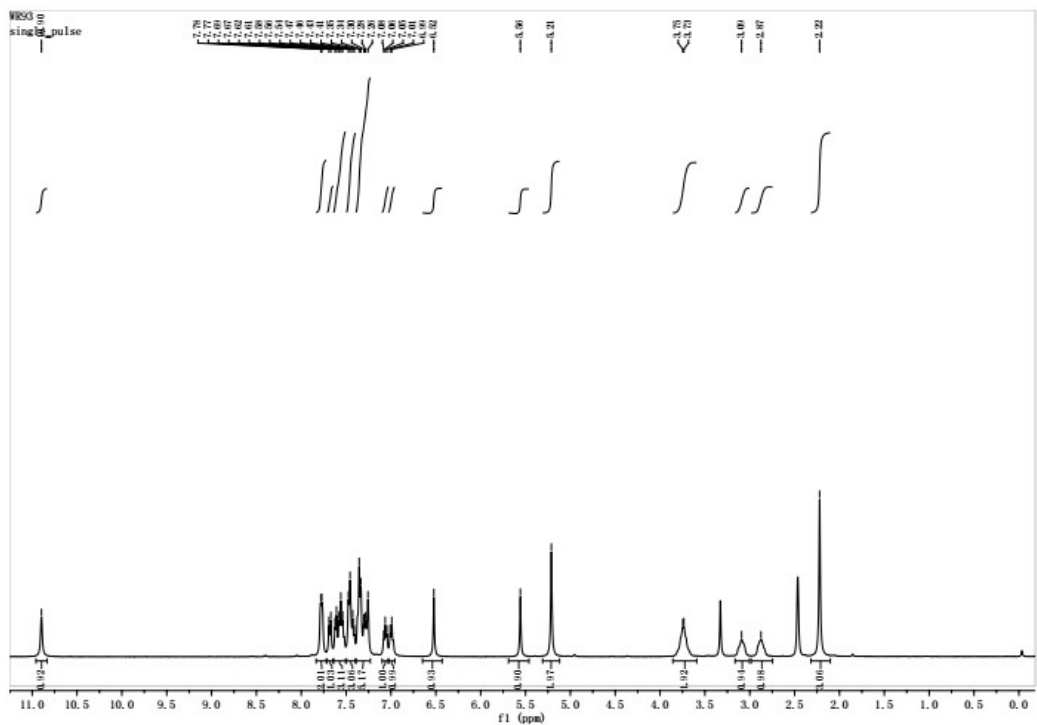
¹H for 6d



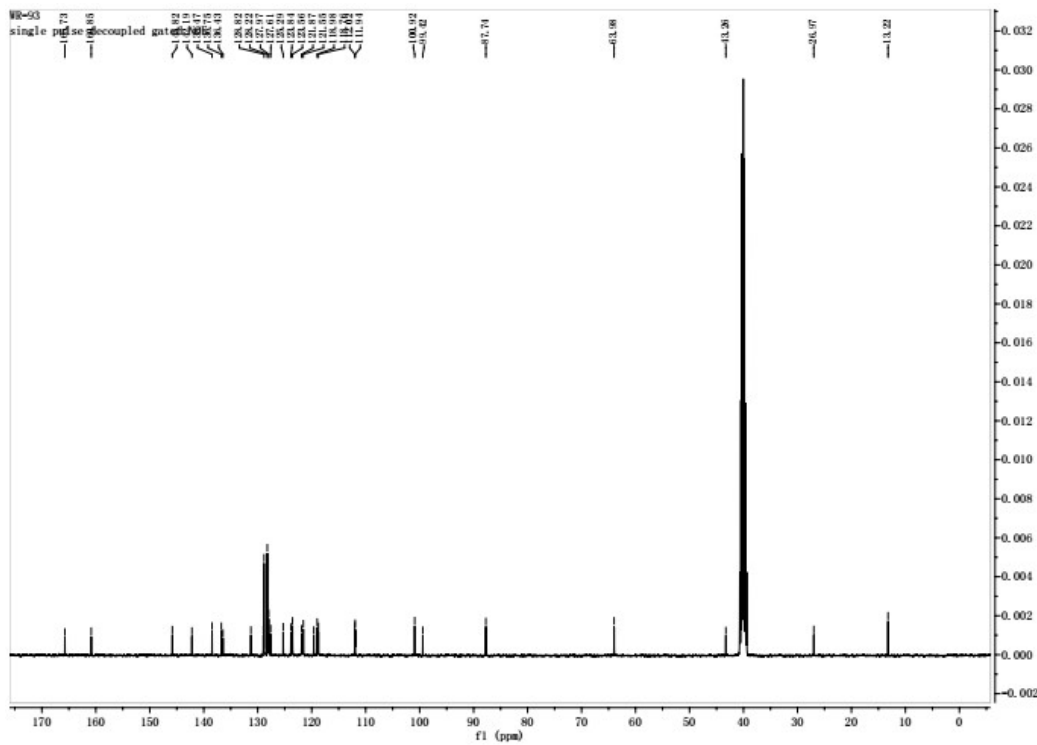
¹³C for 6d



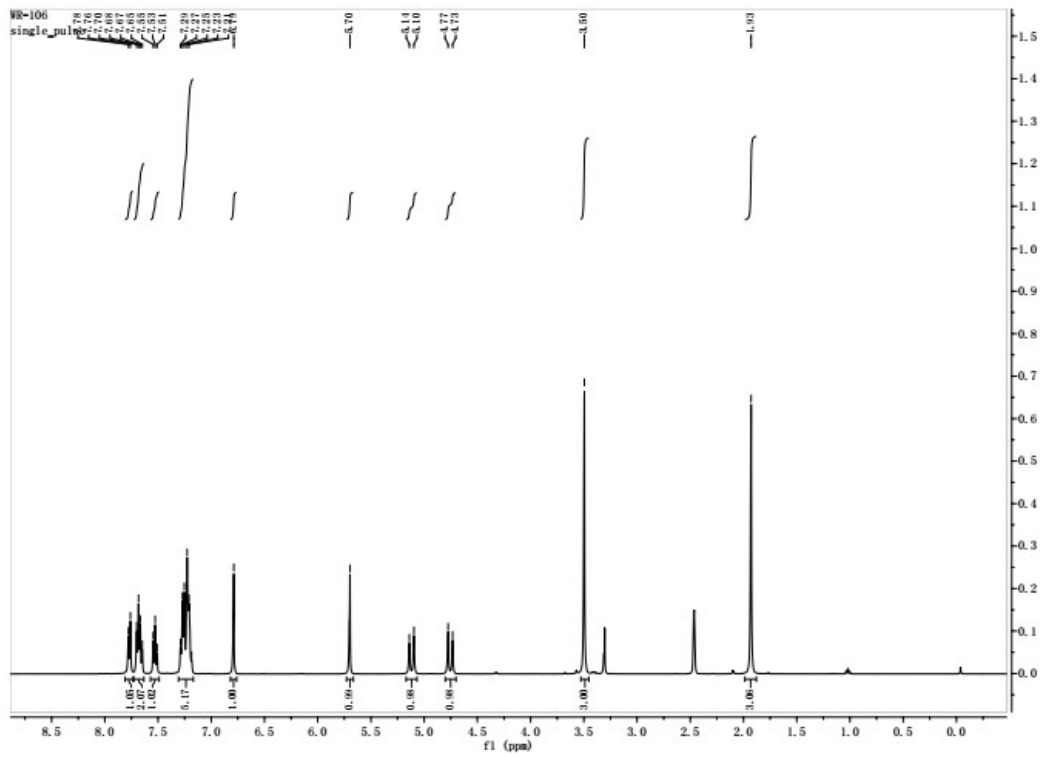
¹H for 6c



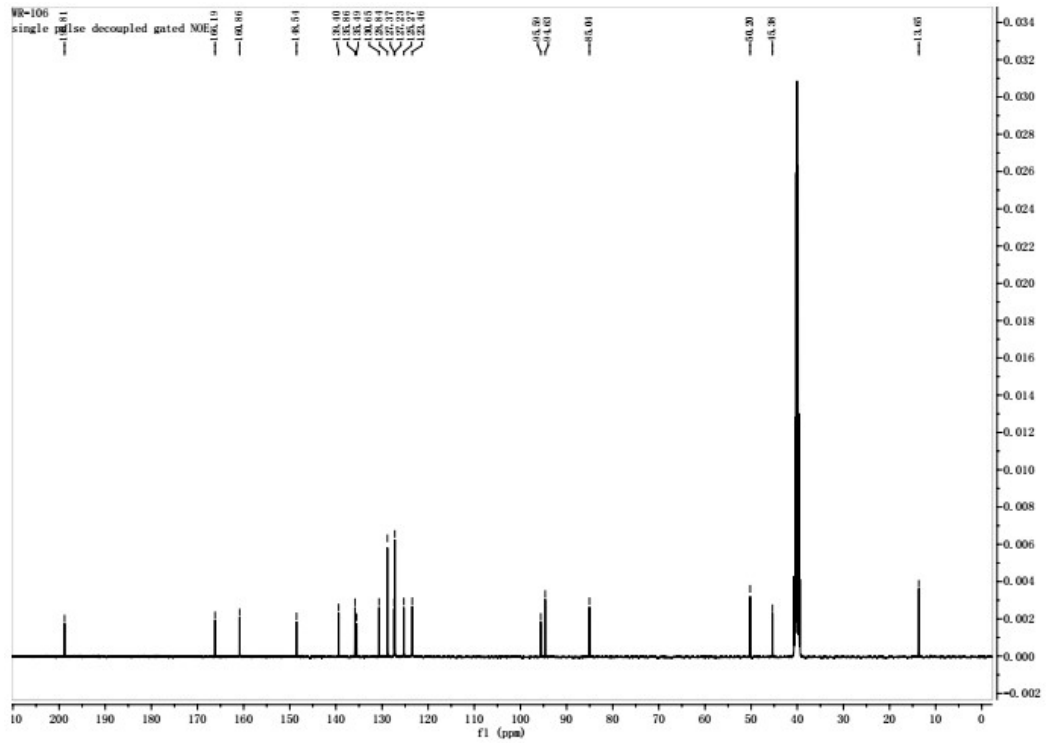
¹³C for 6c



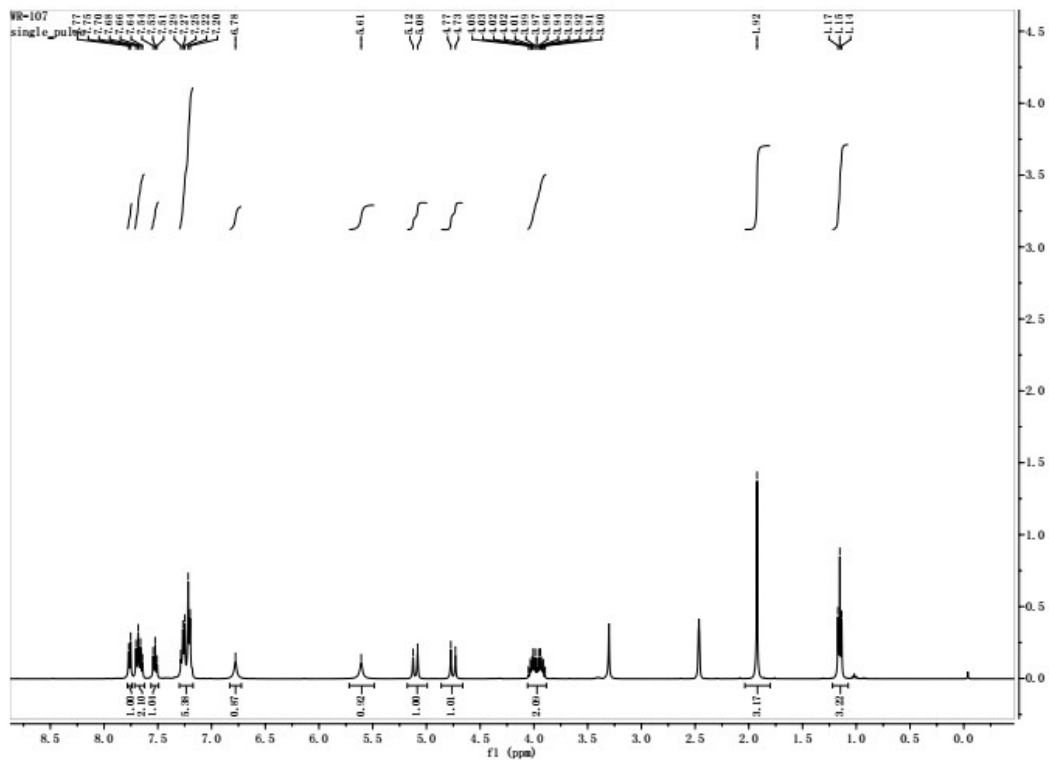
¹H for 8a



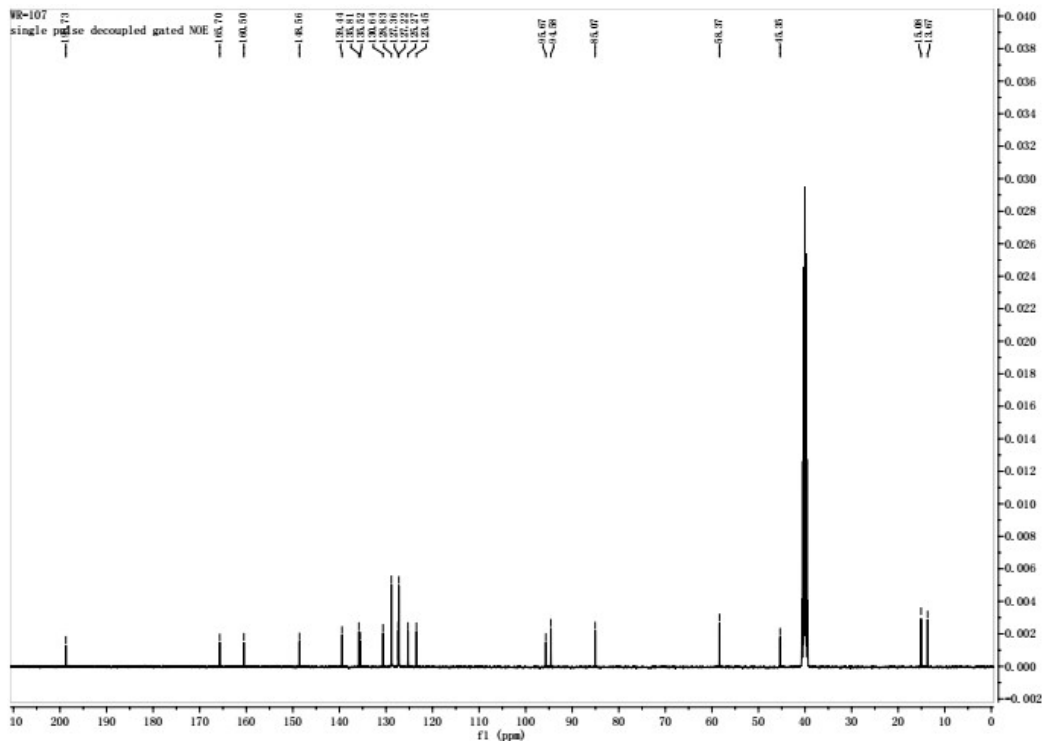
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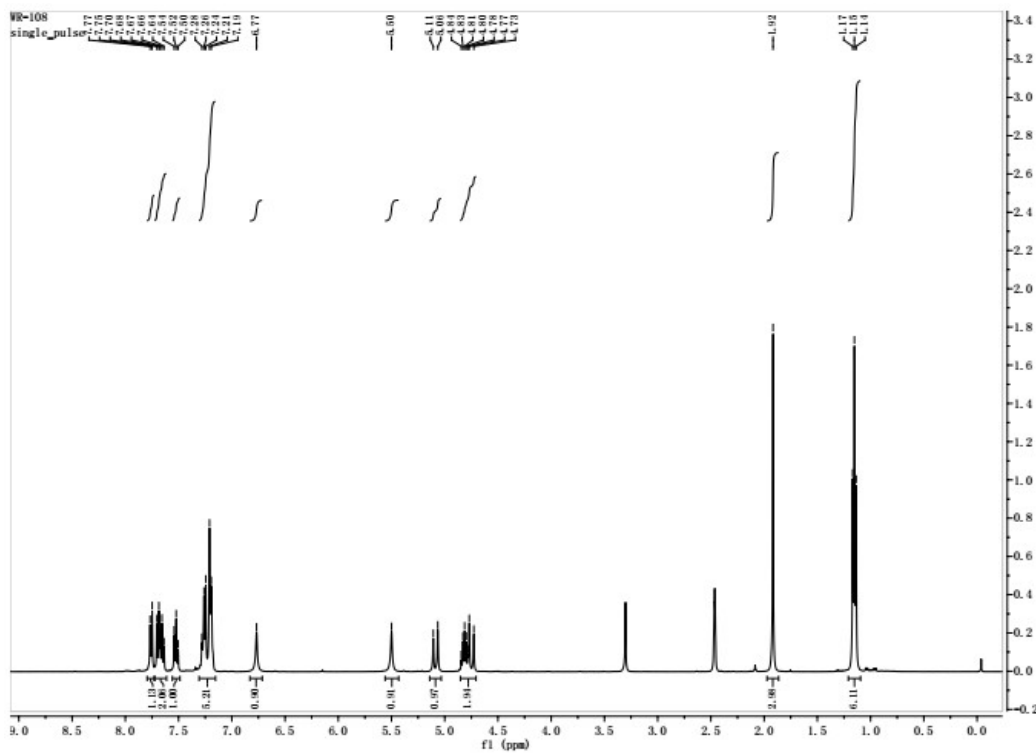
¹H for 8b



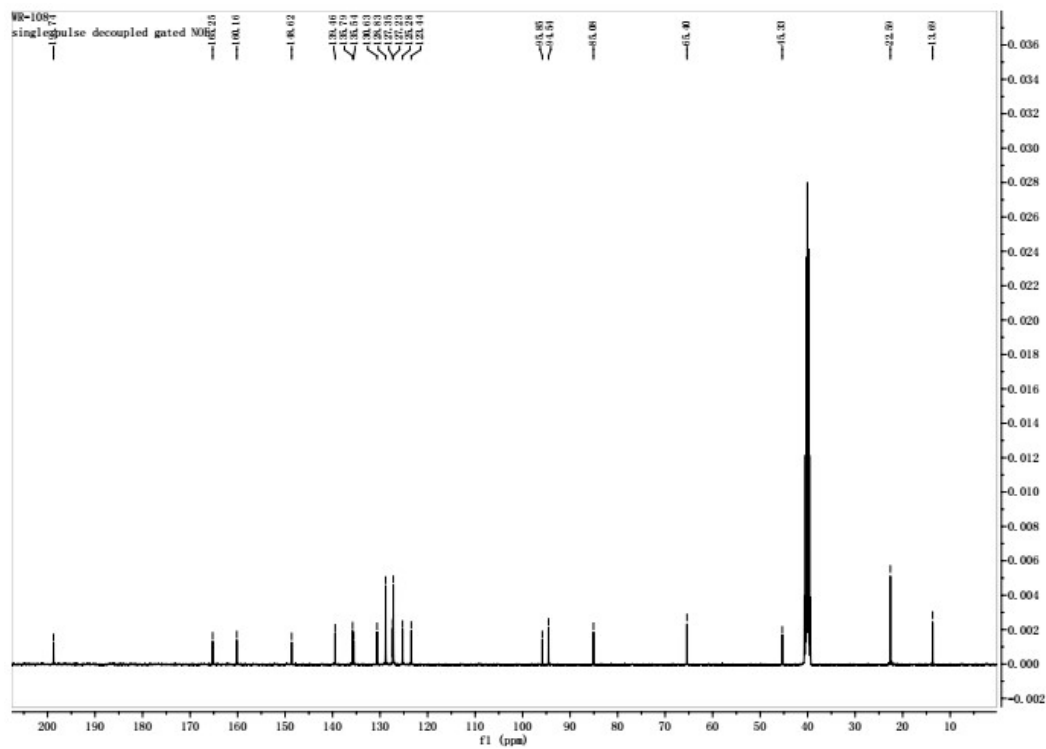
¹³C for 8b



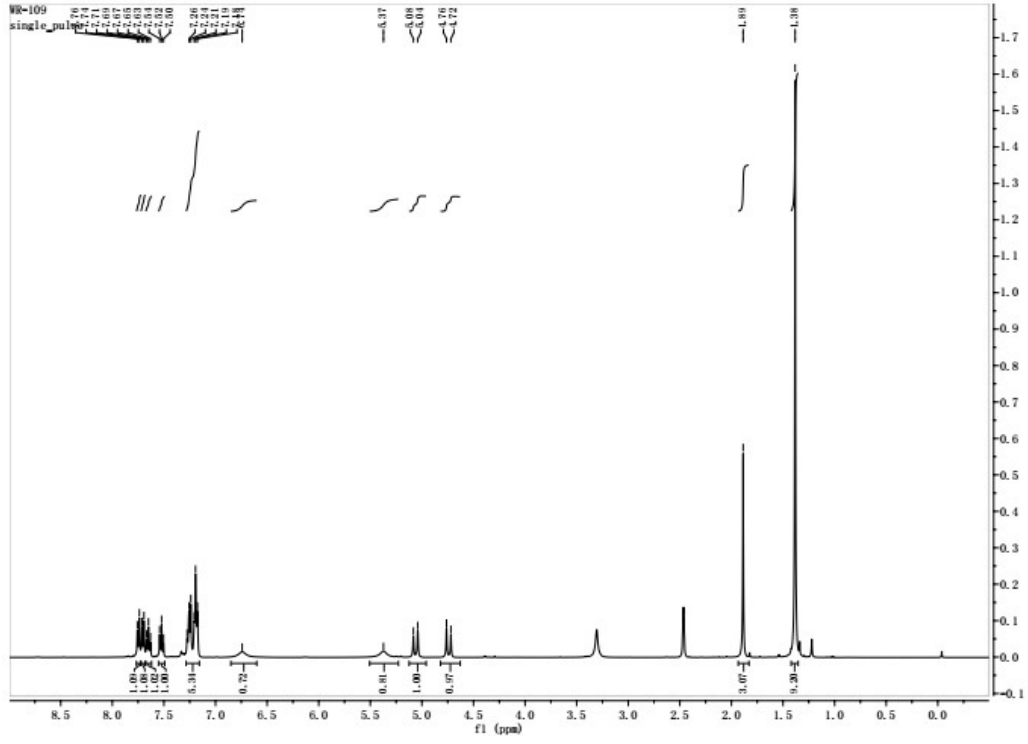
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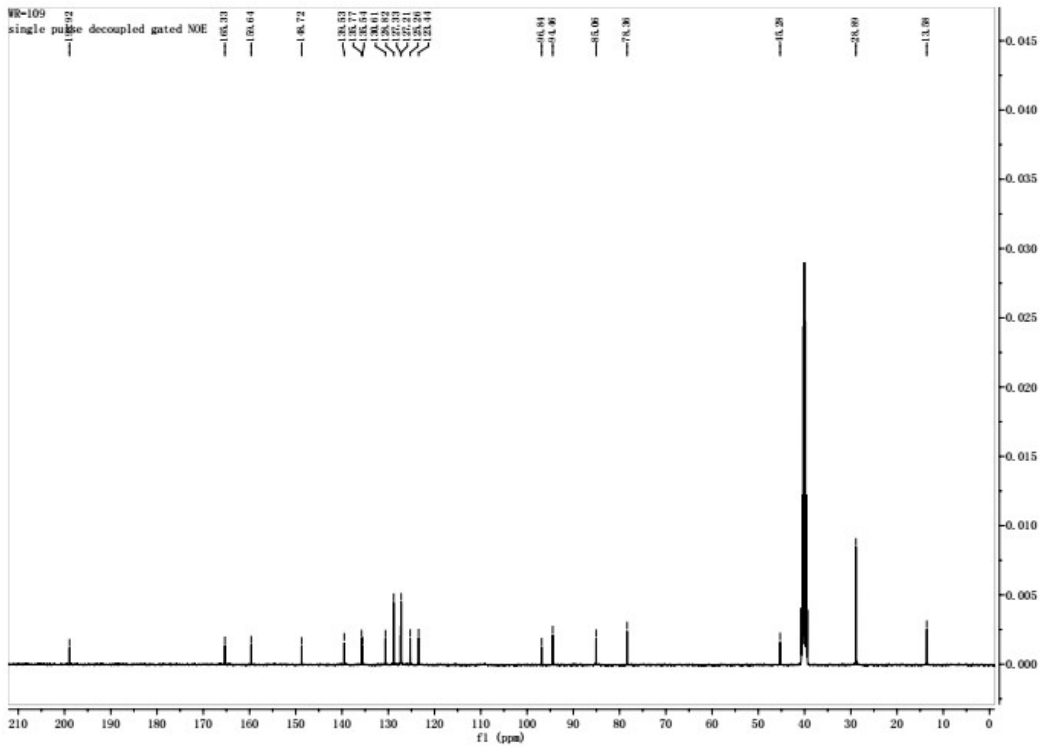
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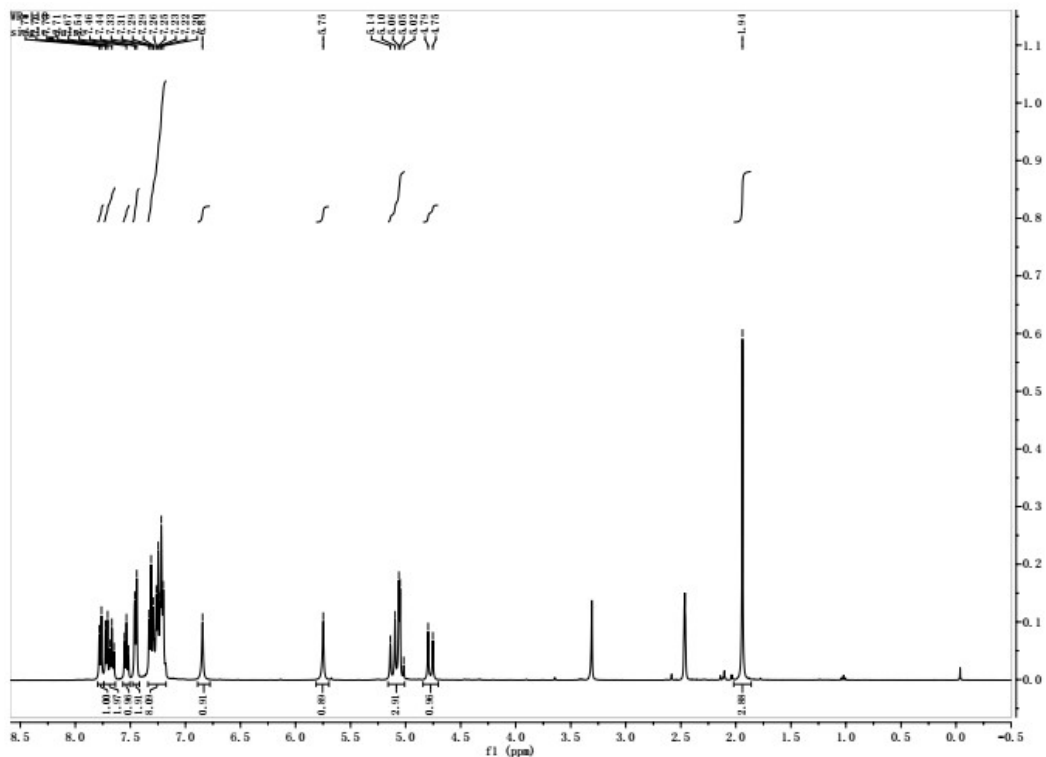
¹H for 8d



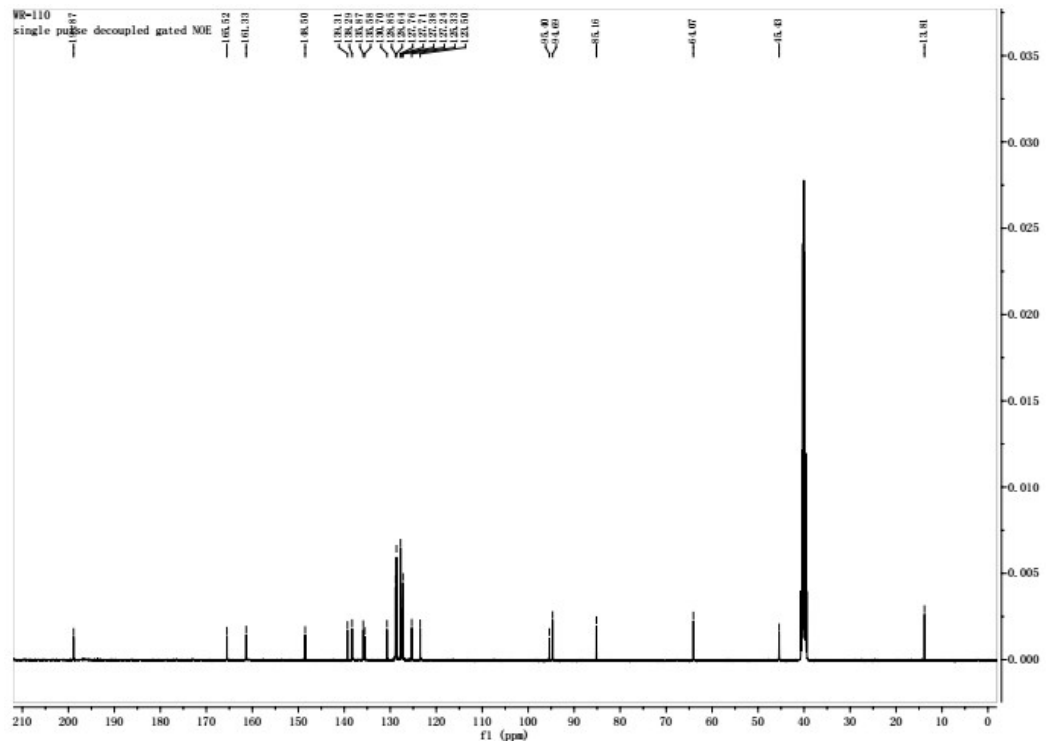
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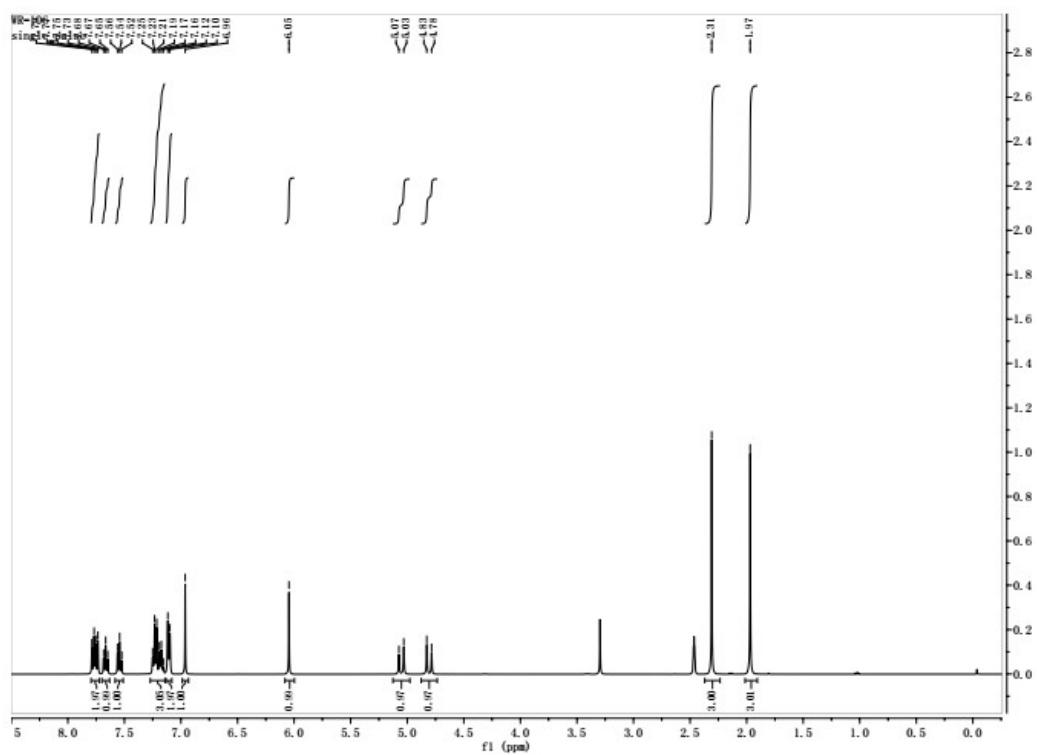
¹H for 8c



¹³C for 8c



¹H for 8f



¹³C for 8f

