Supporting Information

Phosphine-Catalyzed Domino Reactions of Alkynyl Ketones with Sulfonylhydrazones: Construction of Diverse Pyrazoloquinazoline Derivatives

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General Information:

General Methods. All reactions were carried out in flamed-dried or oven-dried round bottomed flasks. All reactions were performed under an N_2 atmosphere. Reactions were monitored through thin-layer chromatography (TLC) on 0.25-mm SiliCycle silica gel plates. Plates were visualized under UV light. Flash column chromatography (FCC) was performed using SiliCycle Silica-P Flash silica gel (60 Å pore size, 40-63 μm). Organic solutions were concentrated through rotary evaporators. Reagents were used as received from commercial sources. THF, Et_2O, and toluene were distilled from K and Na metal, respectively. DMF, CH_2Cl_2 and acetone were distilled from CaH_2. CH_3CN was distilled from P_2O_5. PE refers to petroleum ether (boiling range 60–90 °C). Melting points were obtained on a melting point apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded in DMSO-*d6* using a 300 MHz spectrometer: chemical shifts (δ) are given in parts per million, coupling constants (*J*) in Hz. High-resolution mass spectra were recorded in EI mode on a MS spectrometer.

General procedure for the Synthesis of α, β-unsaturated γ-amino esters.

To the solution of alkynyl ketones (0.24 mmol) and sulfonylhydrazones (0.2 mmol) in dry CH_2Cl_2 (2 mL) was added PBu_3 (12.0 mg, 0.06 mmol). The resulting mixture was stirred at 0 ^oC under nitrogen atmosphere for the required period of time. Upon completion, the solvent was evaporated under reduced pressure and the product was purified by flash column chromatography (eluent: EtOAc/hexane, 1:5~1:1) to provide a pyrazoloquinazoline.

Spectral Data of the products:

1-benzoyl-6-benzylpyrazolo[1,5-c]quinazolin-5(6H)-one (**3a**): yellow solid (45.0 mg, 59% yield); mp 171–173 ^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.73 (d, *J* = 8.1 Hz, 1H), 8.30 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.2 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 3H), 7.48 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.28 (m, 6H), 5.63 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 190.2, 147.2, 145.7, 140.7, 138.9, 136.1, 133.6, 132.5, 129.9, 129.2, 129.1, 127.7, 126.9, 126.7, 123.7, 119.6, 117.7, 116.4, 113.1, 47.5; HRMS (EI) Calcd. for $C_{24}H_{17}N_3NaO_2$: 402.1213; Found:402.1220.

6-benzyl-1-(4-methylbenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3b**): yellow solid (63.2 mg, 50% yield); mp 210–212 ^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.63 (d, *J* = 8.1 Hz, 1H), 8.27 (s, 1H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.45 (d, *J* = 8.5 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 2H), 7.37–7.25(m, 6H), 5.61 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d*6): δ = 189.9, 147.03, 145.7, 144.3, 140.4, 136.3, 136.2, 136.1, 132.4, 130.1, 129.8, 129.1, 127.8, 126.9, 126.6, 123.7, 117.8, 116.4, 113.1, 47.5, 21.6; HRMS (EI) Calcd. for $C_{25}H_{19}N_3NaO_2$: 416.1369; Found: 416.1373.

6-benzyl-1-(4-methoxybenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3c**): yellow solid (45.9 mg, 61% yield); mp 183-185^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*) δ = 8.51 (d, *J* = 8.0 Hz, 2H), 8.30 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.45 (d, *J* = 8.3 Hz, 1H), 7.37 – 7.28 (m, 6H), 7.13 (d, *J* = 8.7 Hz, 2H), 5.62 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ = 188.9, 163.9, 146.6, 145.7, 141.0, 136.1, 136.0, 132.5, 132.2, 131.3, 129.1, 127.8, 126.9, 126.4, 123.7, 117.8, 116.4, 114.6, 113.1, 56.1, 47.4; HRMS (EI) Calcd. for $C_{25}H_{19}N_3NaO_3$: 432.1319; Found: 432.1326.

6-benzyl-1-(4-bromobenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3d**): yellow solid (42.9 mg, 57% yield); mp 244-246^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*) δ = 8.74 (d, *J* = 8.0 Hz, 1H), 8.32 (s, 1H), 7.84–7.80 (m, 4H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.37 – 7.32 (m, 5H), 7.27 (t, *J* =

6.9 Hz, 1H), 5.62 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 189.0, 147.3, 145.7, 141.1, 137.7, 135.9, 134.8, 132.4, 132.0, 131.1, 129.0, 128.3, 127.9, 127.5, 126.59, 123.9, 117.6, 115.5, 113.1, 48.1; HRMS (EI) Calcd. for $C_{24}H_{16}BrN_3NaO_2$: 480.0318; Found: 480.0326.

6-benzyl-1-(4-chlorobenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3e**): yellow solid (41.4 mg, 55% yield); mp 249-251^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*) δ = 8.75 (d, *J* = 7.9 Hz, 1H), 8.34 (s, 1H), 7.92 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.37–7.32 (m, 6H), 5.63 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d*6) δ = 189.1, 147.2, 145.5, 140.8, 138.6, 137.7, 136.2, 136.1, 132.6, 131.8, 129.3, 129.1, 127.7, 126.9, 126.7, 123.7, 117.4, 116.4, 113.0, 47.5. HRMS(EI) Calcd. for $C_{24}H_{16}ClN_3NaO_2$: 436.0823; Found: 436.0832.

6-benzyl-1-(4-fluorobenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3f**): yellow solid (39.2 mg, 52% yield); mp 243-245^{o}C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.68 (d, *J* = 8.0 Hz, 1H), 8.33 (s, 1H), 7.99 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.62 (t, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 8.6 Hz, 1H), 7.43 (t, *J* = 8.8 Hz, 2H), 7.27–7.39 (m, 6H), 5.63 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 188.9, 147.1, 145.6, 140.6, 136.1, 134.6, 132.9, 132.8, 132.5, 129.1, 127.7, 126.9, 126.6, 123.7, 116.4, 116.3, 116.2, 113.0, 109.8, 47.5; HRMS (EI) Calcd. for $C_{24}H_{16}FN_3NaO_2$: 420.1119; Found: 420.1118.

6-benzyl-1-(4-nitrobenzoyl)pyrazolo[1,5-c]quinazolin-5(6H)-one (**3g**): white solid (27.9 mg, 37% yield); mp 260-262^{o}C; ^{1}HNMR (300 MHz, DMSO-*d6*): δ = 8.97 (d, *J* = 8.0 Hz, 1H), 8.42 (d, *J* = 8.6 Hz, 2H), 8.33 (s, 1H), 8.10 (d, *J* = 8.6 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 7.41–7.34 (m, 5H), 7.28 (t, *J* = 6.9 Hz, 1H), 5.65 (s, 2H); ^{13}CNMR (75 MHz, DMSO-*d6*): δ = 188.9, 150.1, 149.6, 147.8, 144.5, 136.4, 136.1, 133.0, 131.0, 129.1, 127.8, 127.1, 126.9, 124.3, 123.8, 117.6, 116.4, 114.5, 113.0, 47.6; HRMS (EI) Calcd. for $C_{24}H_{16}N_4NaO_4$: 440.1109; Found: 440.1103.

1-(2-naphthoyl)-6-benzylpyrazolo[1,5-c]quinazolin-5(6H)-one (**3h**): yellow solid (49.8 mg, 66%

yield); mp 179-180°C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.72 (d, J = 8.1 Hz, 1H), 8.51 (s, 1H), 8.42 (s, 1H), 8.21–7.95 (m, 4H), 7.78–7.57 (m, 4H), 7.52 (t, J = 12.2 Hz, 2H), 7.35 (m, 7H), 7.15–6.99 (m, 1H), 5.66 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d*6): δ = 190.1, 147.39, 145.7, 136.2, 136.2, 136.1, 135.5, 132.5, 132.4, 132.2, 130.1, 129.2, 129.1, 129.0, 128.1, 127.8, 127.5, 126.97, 126.6, 125.9, 125.2, 123.8, 118.0, 116.5, 113.1, 47.5; HRMS (EI) Calcd. for $C_{28}H_{19}N_3NaO_2$: 452.1369; Found: 452.1378.

1-acetyl-6-benzylpyrazolo[1,5-c]quinazolin-5(6H)-one (**3i**): yellow solid (39.9 mg, 53% yield); mp 227-229°C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 9.50 (d, J = 8.1 Hz, 1H), 8.81 (s, 1H), 7.64 (t, J = 7.8 Hz, 1H), 7.45 (d, J = 8.5 Hz, 1H), 7.39 (t, J = 7.6 Hz, 1H), 7.34–7.31 (m, 4H), 7.28–7.25 (m, 1H), 5.60 (s, 2H), 2.69(s, 3H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 193.4, 148.1, 145.6, 140.0, 136.1, 136.0, 132.8, 129.1, 127.9, 127.7, 126.8, 123.6, 116.1, 113.3, 110.0, 47.5, 30.5; HRMS (EI) Calcd. for $C_{19}H_{15}N_3NaO_2$: 340.1056; Found: 340.1061.

1-benzoyl-6-benzyl-9-methylpyrazolo[1,5-c]quinazolin-5(6H)-one (**3j**): yellow solid (36.9 mg, 49% yield); mp 152-153°C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.48 (s, 1H), 8.27 (s, 1H), 7.91–7.88 (m, 2H), 7.72 (t, J = 7.3 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 8.7 Hz, 1H), 7.37–7.27 (m, 6H), 5.60 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (75MHz, DMSO-*d6*): δ = 190.3, 147.2, 145.6, 140.7, 139.0, 136.2, 134.0, 133.6, 133.5, 132.9, 129.9, 129.20 ,129.1, 127.8, 126.9, 126.6, 117.7, 116.3, 112.9, 47.4, 20.7; HRMS (EI) Calcd. for $C_{25}H_{19}N_3NaO_2$: 416.1369; Found: 416.1372.

1-benzoyl-6-benzyl-9-chloropyrazolo[1,5-c]quinazolin-5(6H)-one (**3k**): yellow solid (43.7 mg, 58% yield); mp 197-198°C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.48 (s, 1H), 8.27 (s, 1H), 7.95–7.84 (m, 2H), 7.72 (t, J = 7.3 Hz, 1H), 7.60 (t, J = 7.5 Hz, 2H), 7.42 (d, J = 8.7 Hz, 1H), 7.39–7.23 (m, 6H), 5.60 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 199.4, 147.5, 145.4, 139.9, 138.9, 135.8,

135.1, 133.7, 132.1, 130.4, 129.9, 129.3, 129.1, 128.6, 127.8, 126.9, 125.9, 118.4, 114.6, 47.8; HRMS (EI) Calcd. for $C_{24}H_{16}ClN_3NaO_2$: 436.0823; Found: 436.0829.

1-benzoyl-6-benzyl-9-fluoropyrazolo[1,5-c]quinazolin-5(6H)-one (**3l**): yellow solid (33.9 mg, 45% yield); mp 238-240°C; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 8.67 (d, *J* = 10.0 Hz, 1H), 8.33 (s, 1H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.73 (t, *J* = 7.3 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 2H), 7.54–7.51 (m, 2H), 7.37–7.28 (m, 5H), 5.63 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ =190.4, 159.3, 156.1, 147.5, 145.4, 139.0, 135.9, 133.6, 133.0, 129.9, 129.22, 129.1, 127.8, 126.9, 120.2, 119.9, 118.7, 118.6, 112.2, 47.8; HRMS (EI) Calcd. for $C_{24}H_{16}FN_3NaO_2$: 420.1119; Found: 420.1125.

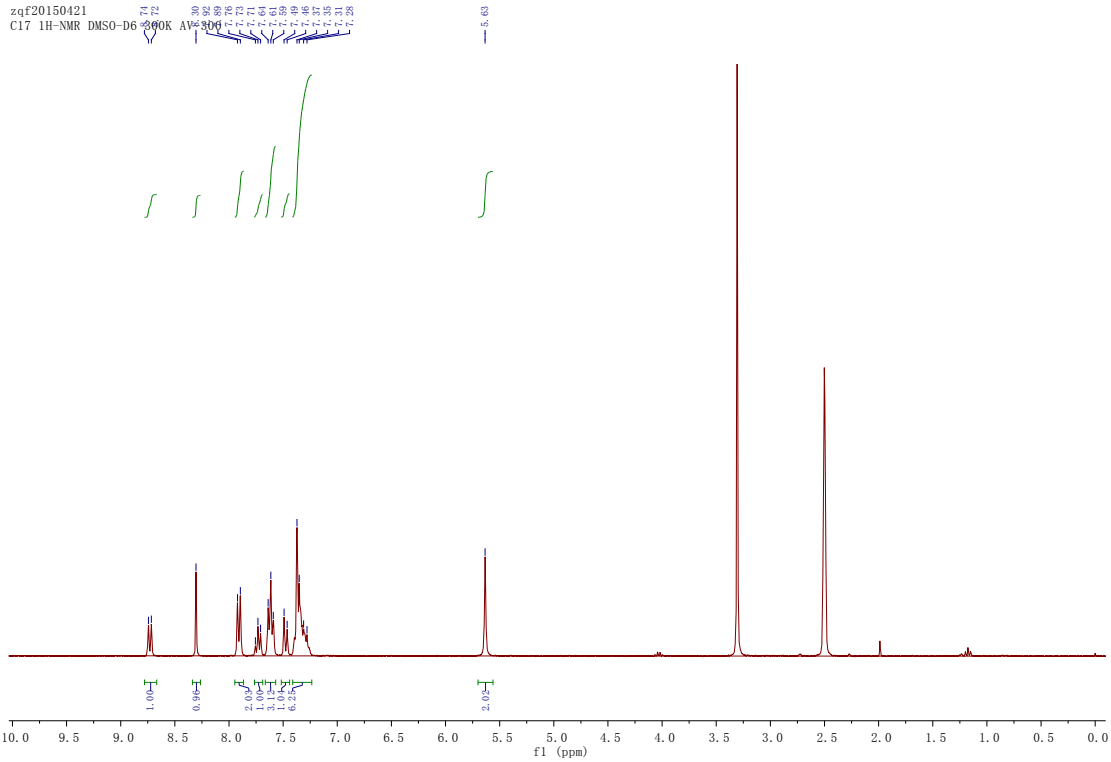
1-benzoyl-6-benzyl-8-chloropyrazolo[1,5-c]quinazolin-5(6H)-one (**3m**): yellow solid (45.2 mg, 60% yield); mp 193-195 °C; ^{1}HNMR (300 MHz, DMSO-*d6*): δ = 8.79 (d, *J* = 8.7 Hz, 1H), 8.30 (s, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.72 (t, *J* = 7.1 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 2H), 7.51 (s, 1H), 7.43 – 7.29 (m, 6H), 5.63 (s, 2H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 190.2, 147.4, 145.5, 140.2, 138.9, 137.5, 136.9, 135.8, 133.7, 129.9, 129.2, 128.4, 127.9, 126.9, 123.8, 117.9, 116.1, 114.5, 112.2, 47.6; HRMS (EI) Calcd. for $C_{24}H_{16}ClN_3NaO_2$: 436.0823; Found: 436.0828.

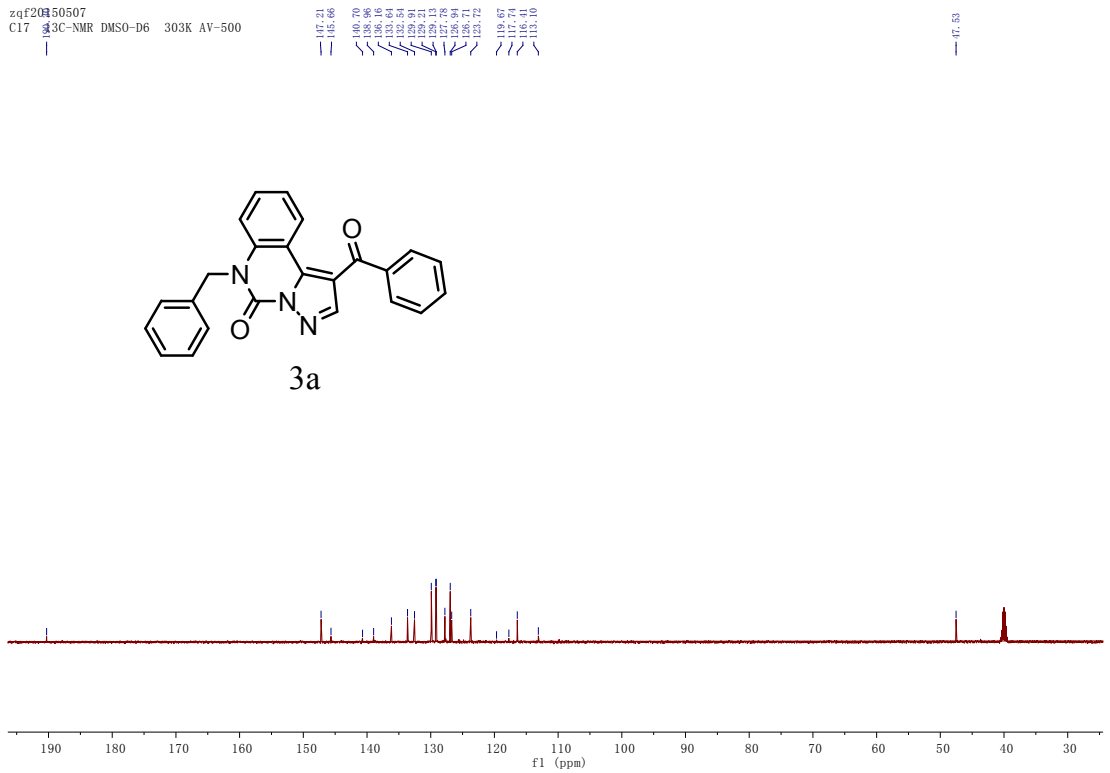
1-benzoyl-6-methylpyrazolo[1,5-c]quinazolin-5(6H)-one(3n): brown solid (42.2 mg, 56% yield); mp.196-198°C; ^{1}HNMR (300 MHz, $CDCl_3$): δ = 9.08 (d, *J* = 7.3 Hz, 1H), 8.18 (s, 1H), 7.92 (d, *J* = 7.1 Hz, 2H), 7.73 – 7.64 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 2H), 7.41 (m, *J* = 14.3, 7.5 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, DMSO-*d6*): δ = 190.2, 147.0, 145.1, 140.6, 139.0, 137.0, 133.6, 132.7, 129.9, 129.2, 126.5, 123.67, 117.6, 116.1, 112.7, 31.6; HRMS(EI) Calcd. For $C_{18}H_{13}N_3NaO_2$: 326.09; Found: 326.0908.

2-benzoyl-6-benzylpyrazolo[1,5-c]quinazolin-5(6H)-one (**5**): yellow solid; mp 199-200°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.51 (d, *J* = 7.3 Hz, 2H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.68 – 7.47 (m, 5H), 7.34 –

7.30 (m, 6H), 7.28 (s, 1H), 5.65 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 187.6, 154.6, 140.5, 136.2, 135.2, 135.1, 133.3, 130.98, 130.91, 129.0, 128.4, 127.8, 126.6, 124.8, 124.1, 115.8, 114.5, 113.5, 102.8, 47.9. HRMS (EI) Calcd. for $C_{24}H_{17}N_3NaO_2$: 402.1213;Found:402.1216.

Copies of ^{1}HNMR and ^{13}CNMR Spectra





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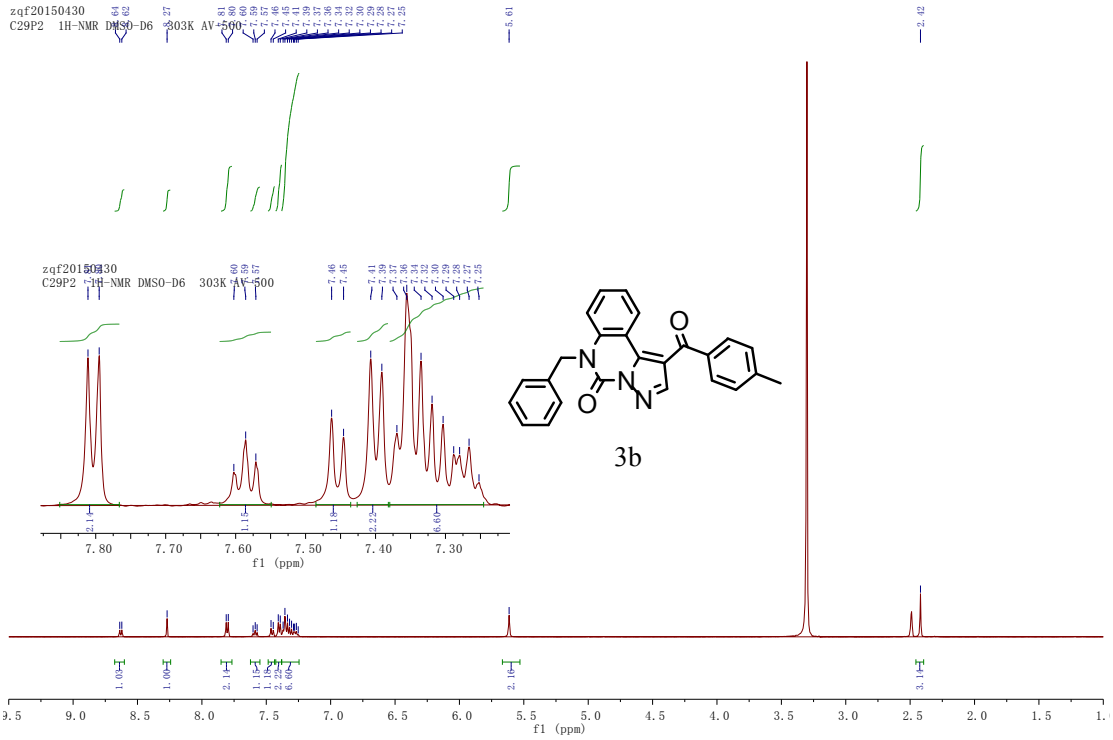
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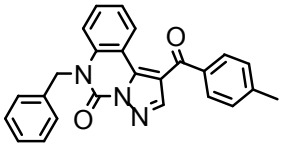

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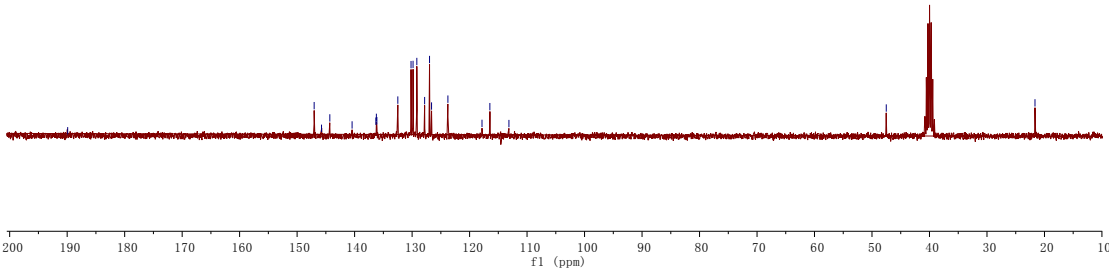
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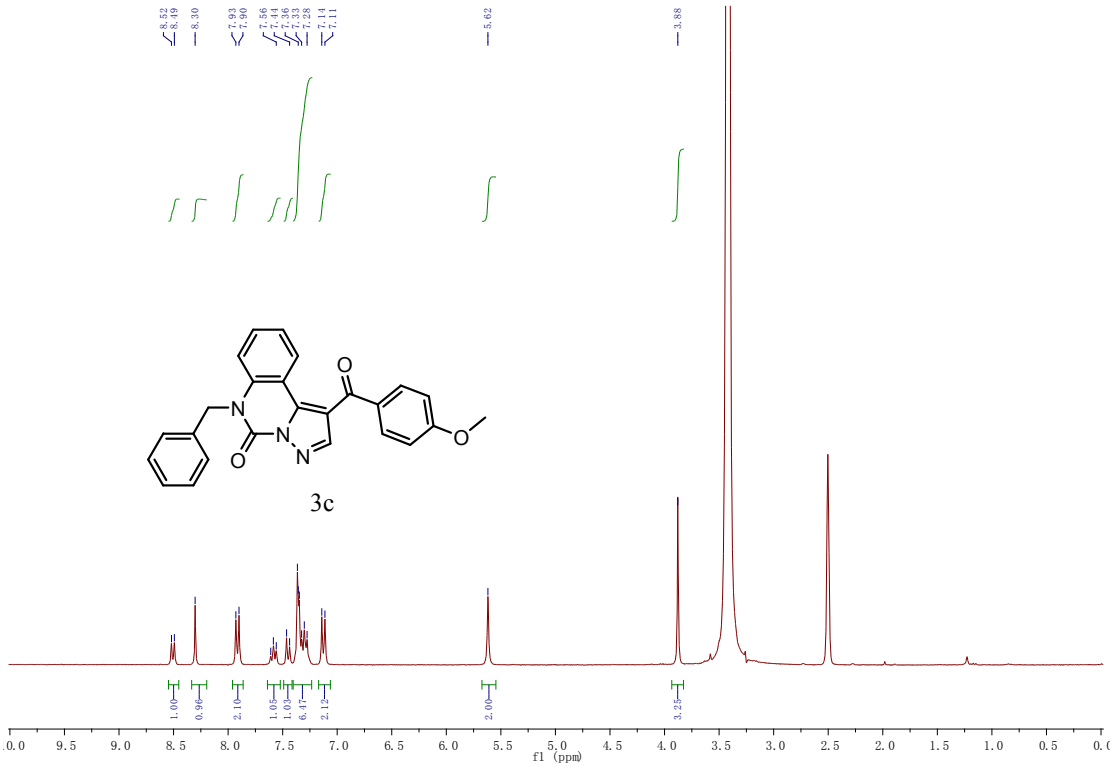
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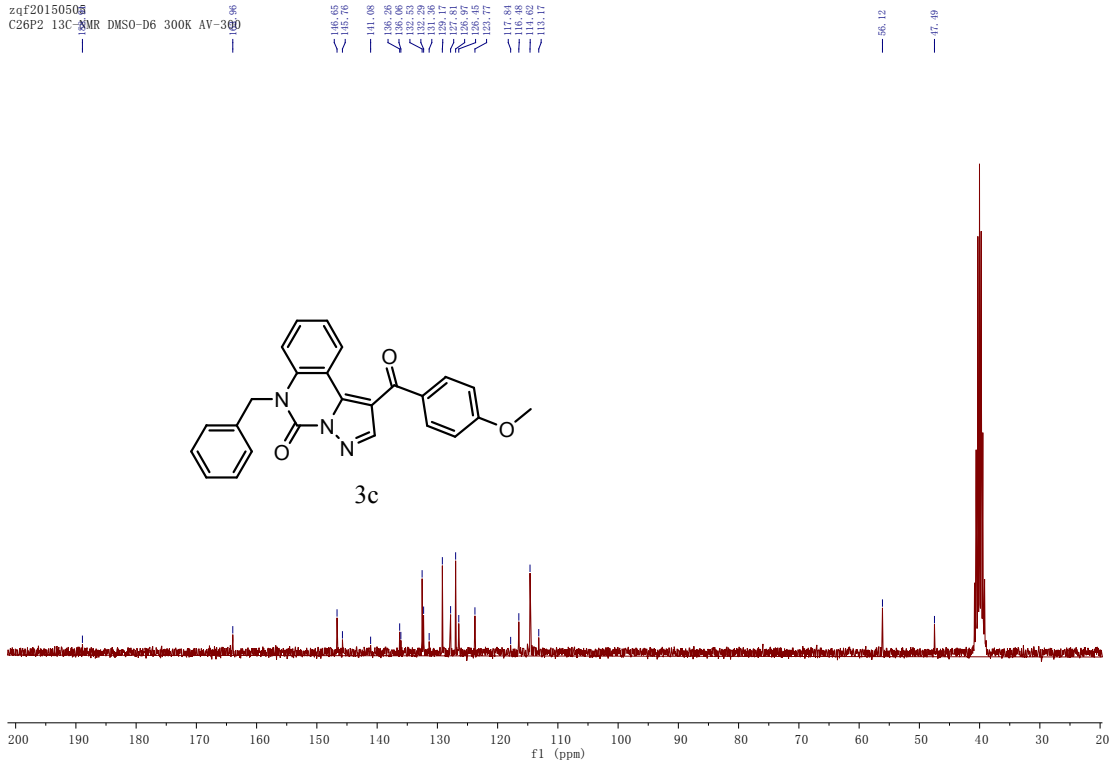
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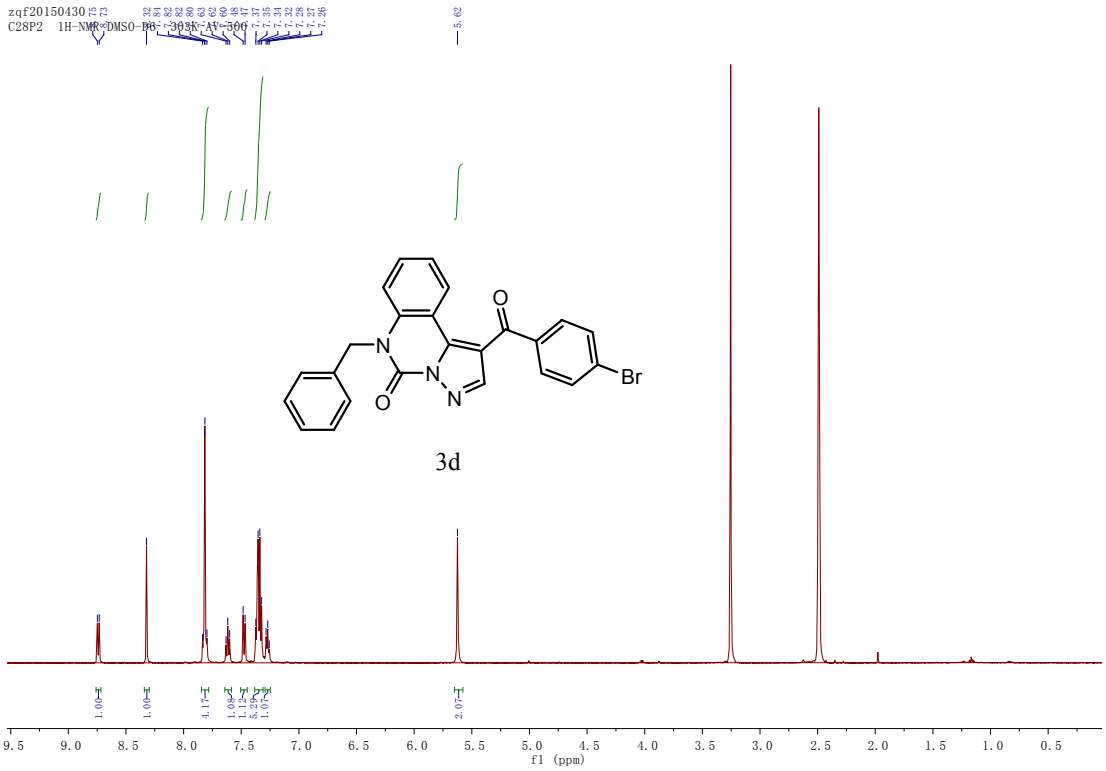
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1.07
2.07
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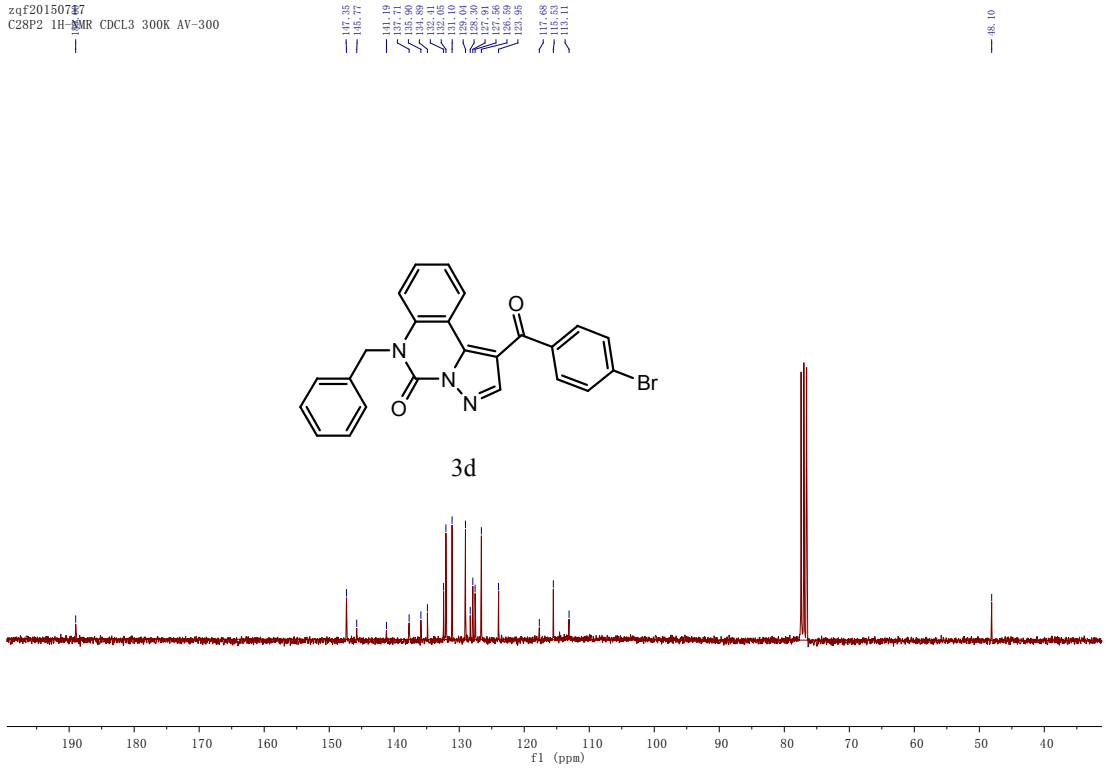
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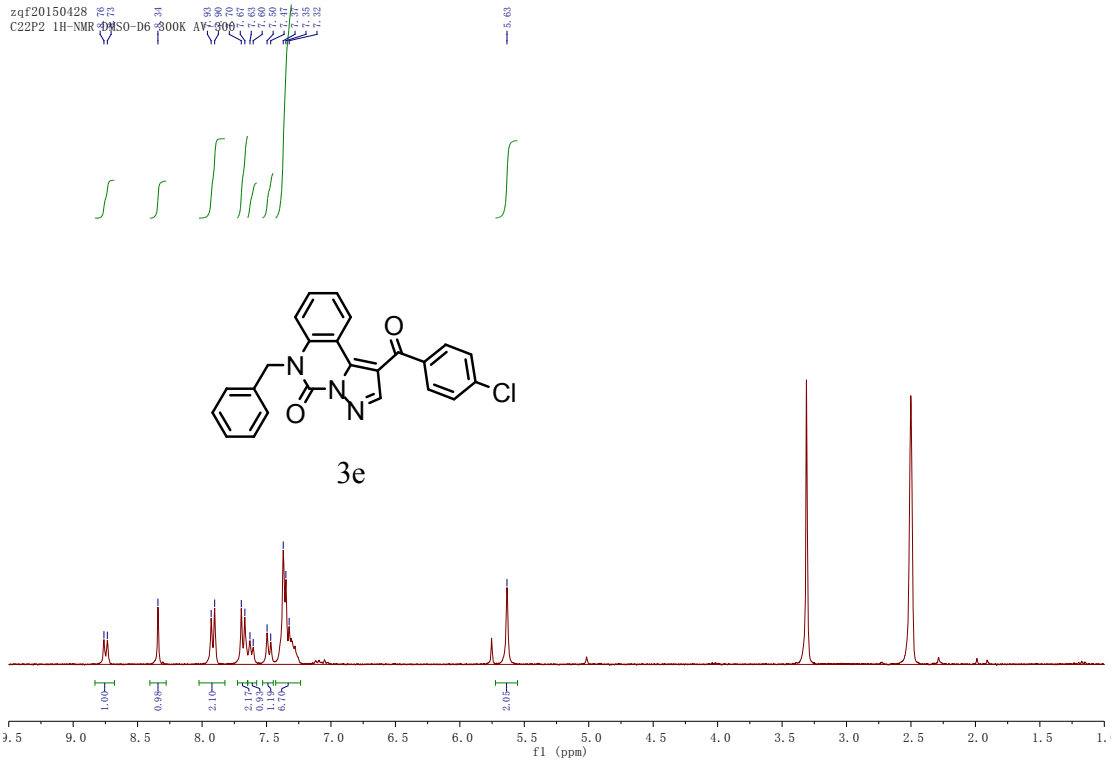
f1 (ppm)

3d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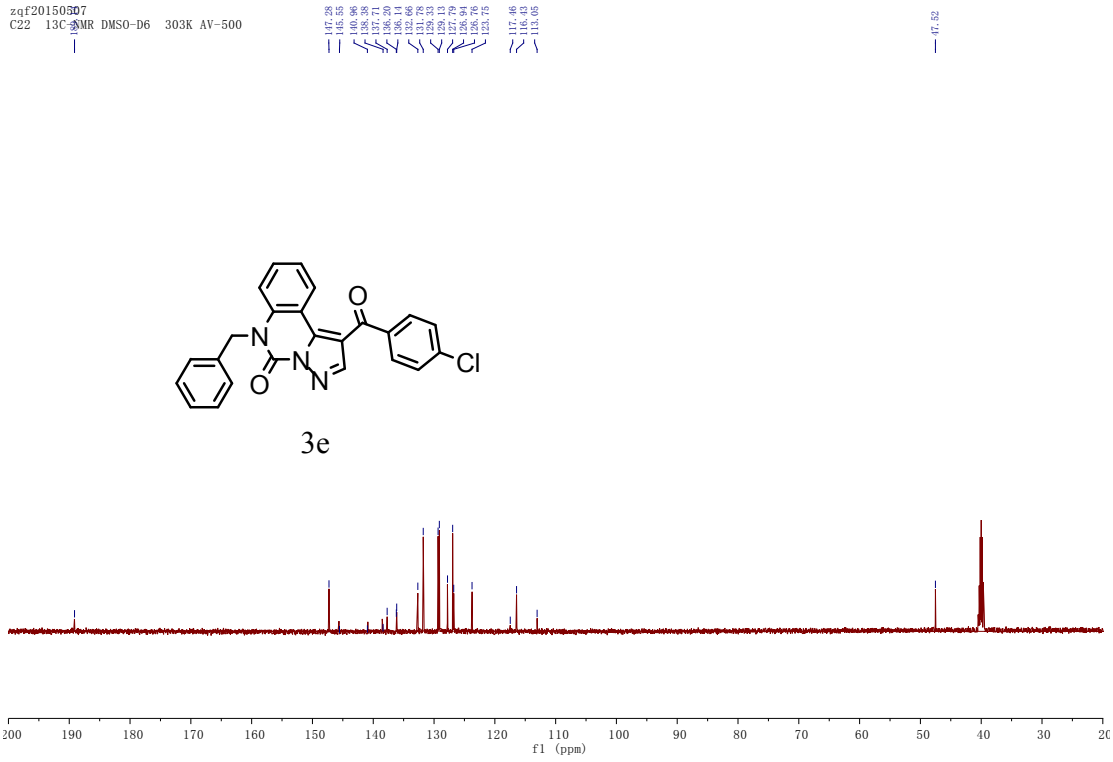
3e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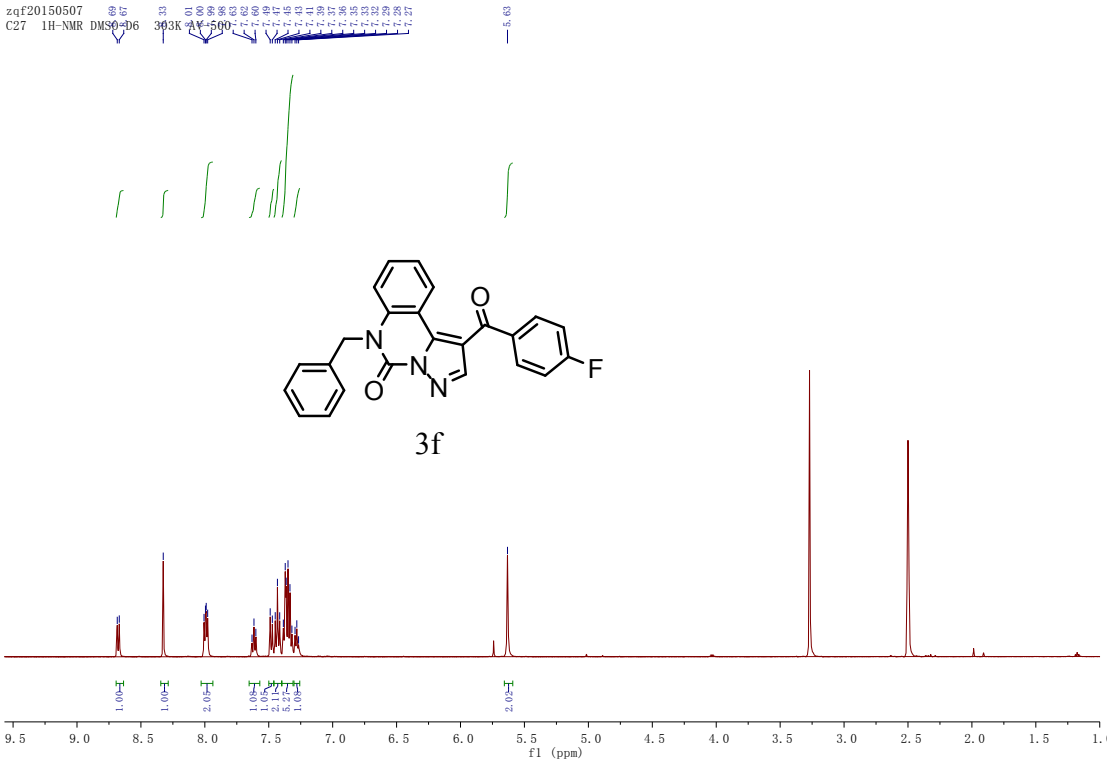
3e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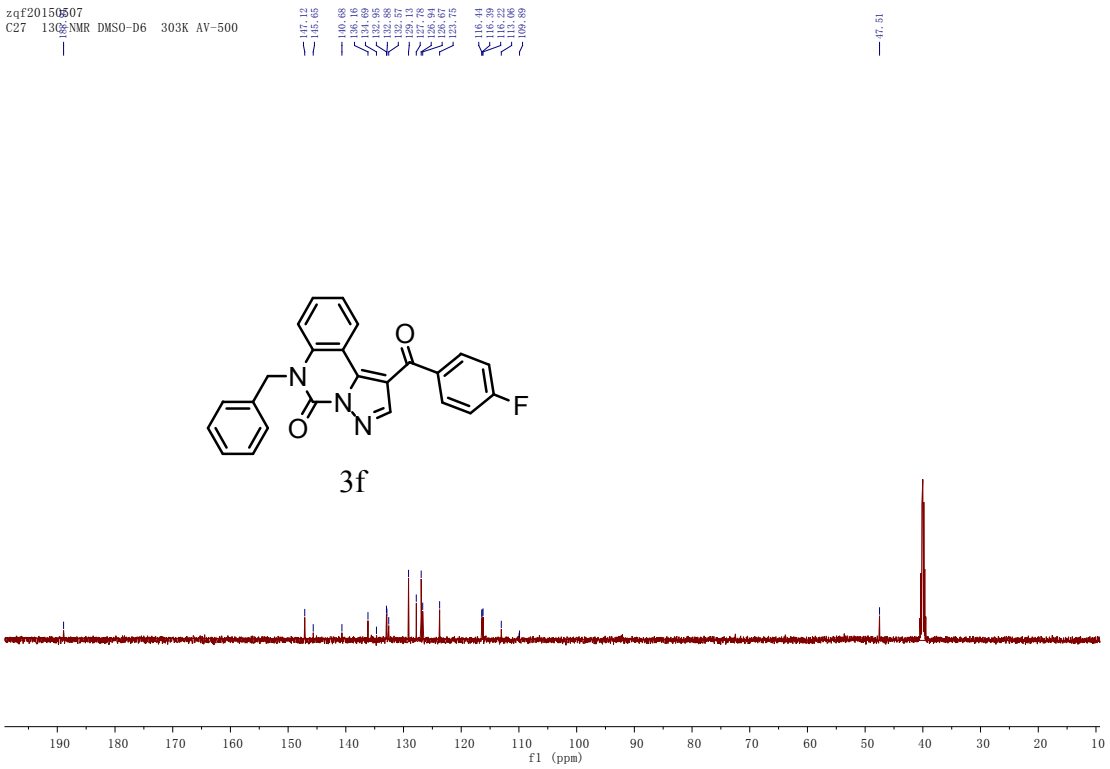
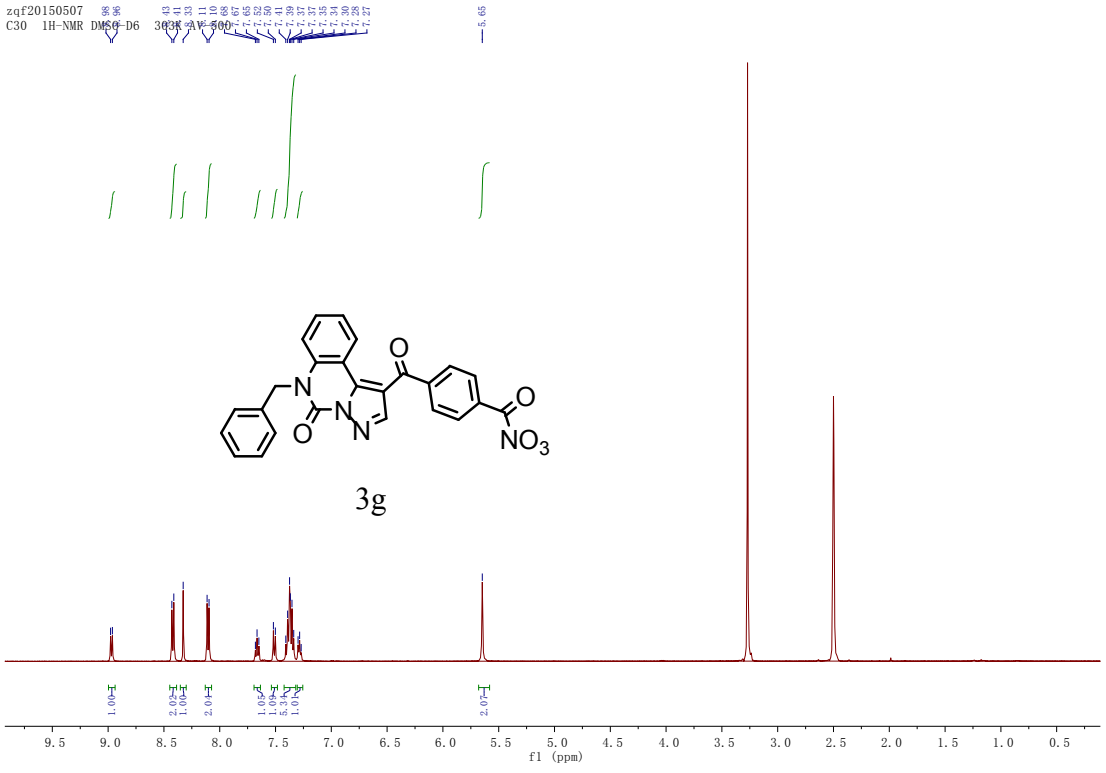
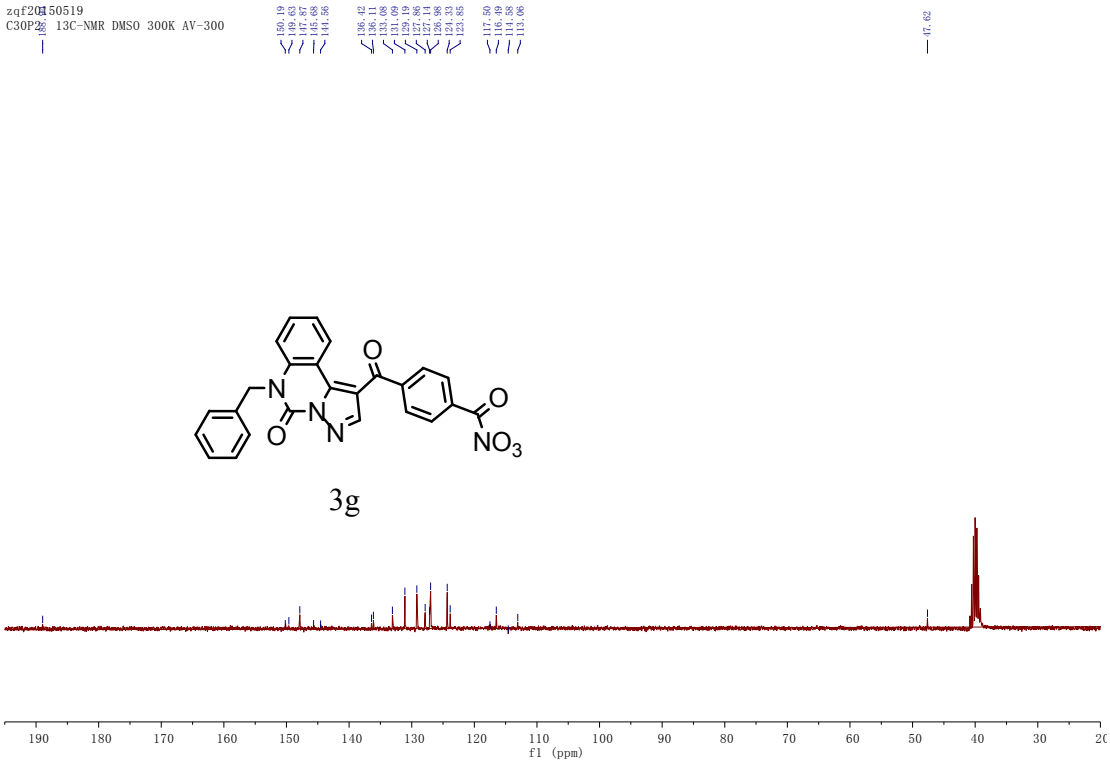
3f
f1 (ppm)

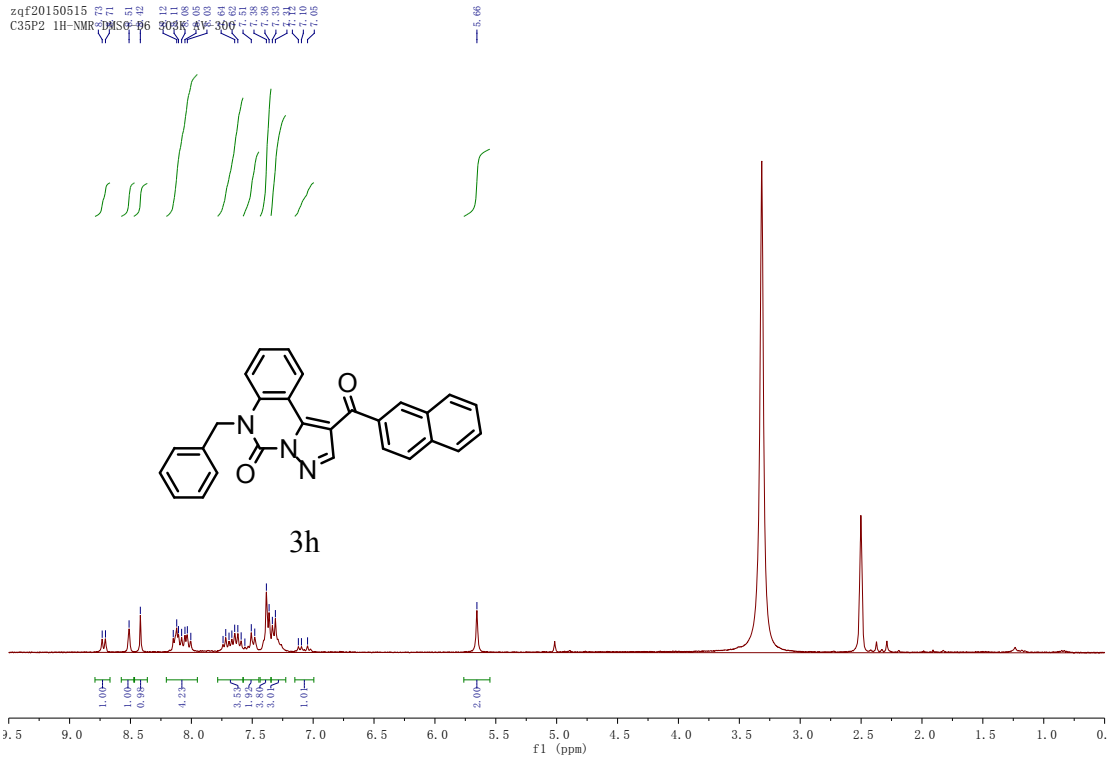

zqf20150507
C27 13C-NMR DMSO-D6 303K AV-500
O
N
N
N
O
F
3f
f1 (ppm)

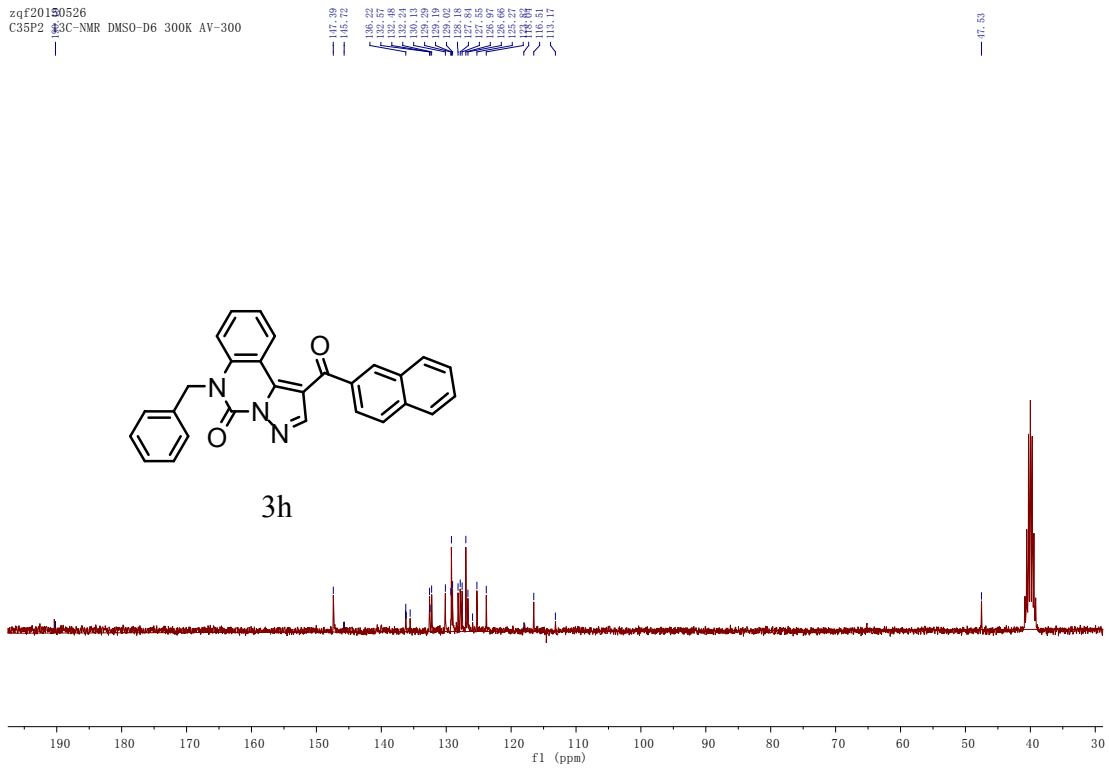

zqf20150507
C30 1H-NMR DMSO-D6 303K AV-500
f1 (ppm)

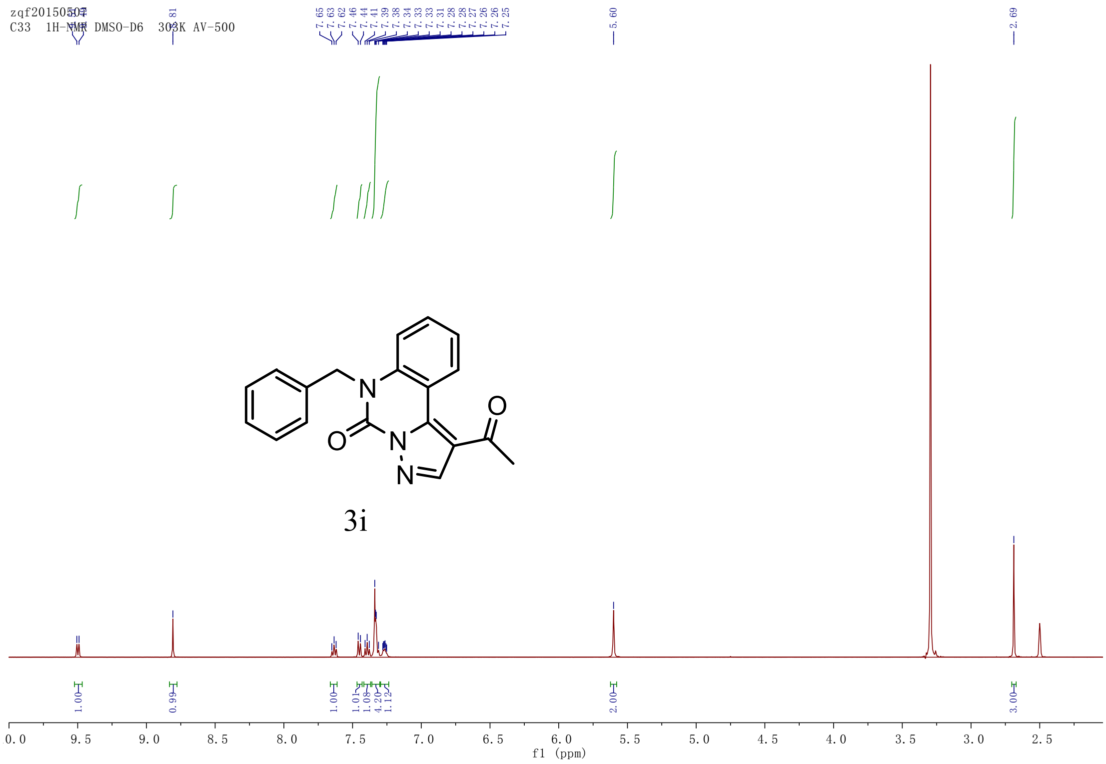
3g

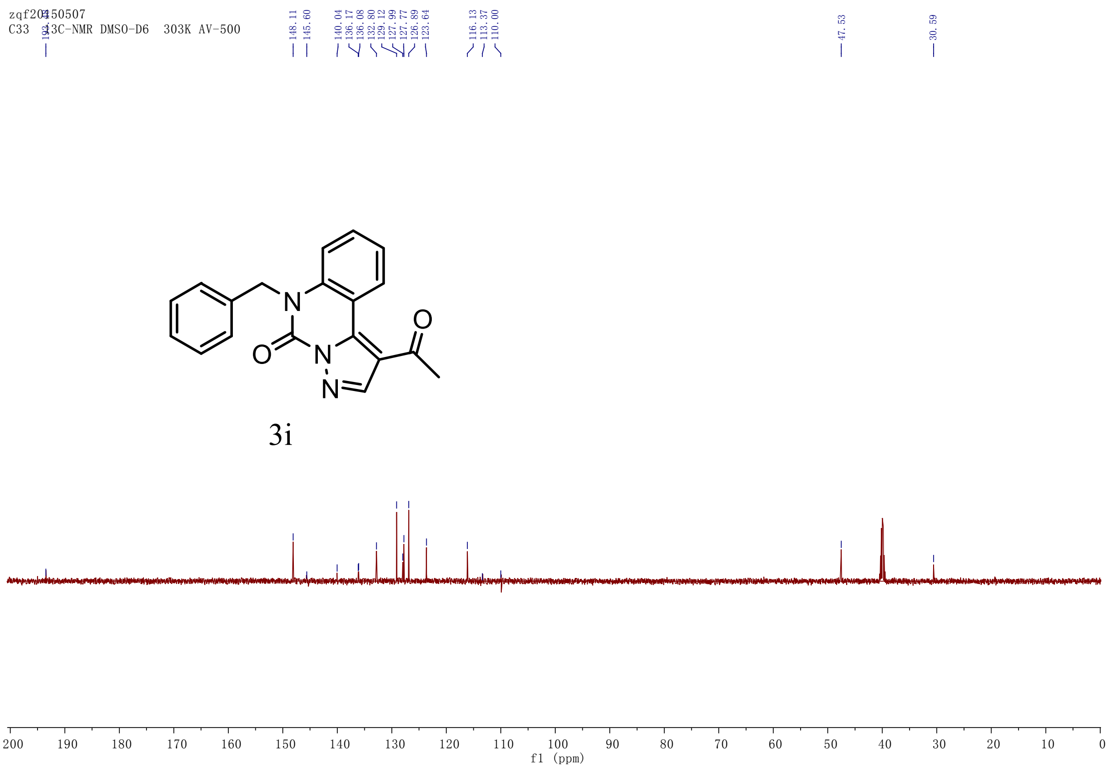

zqf20150519
C30P2 13C-NMR DMSO 300K AV-300
f1 (ppm)

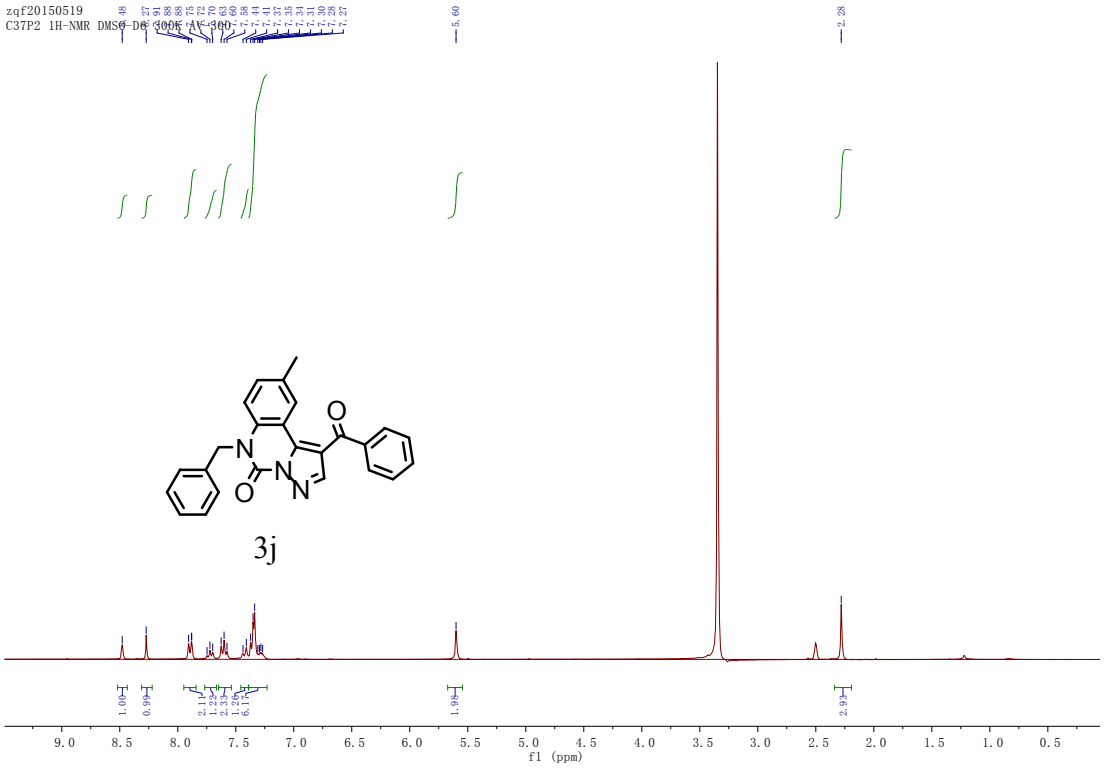
3g

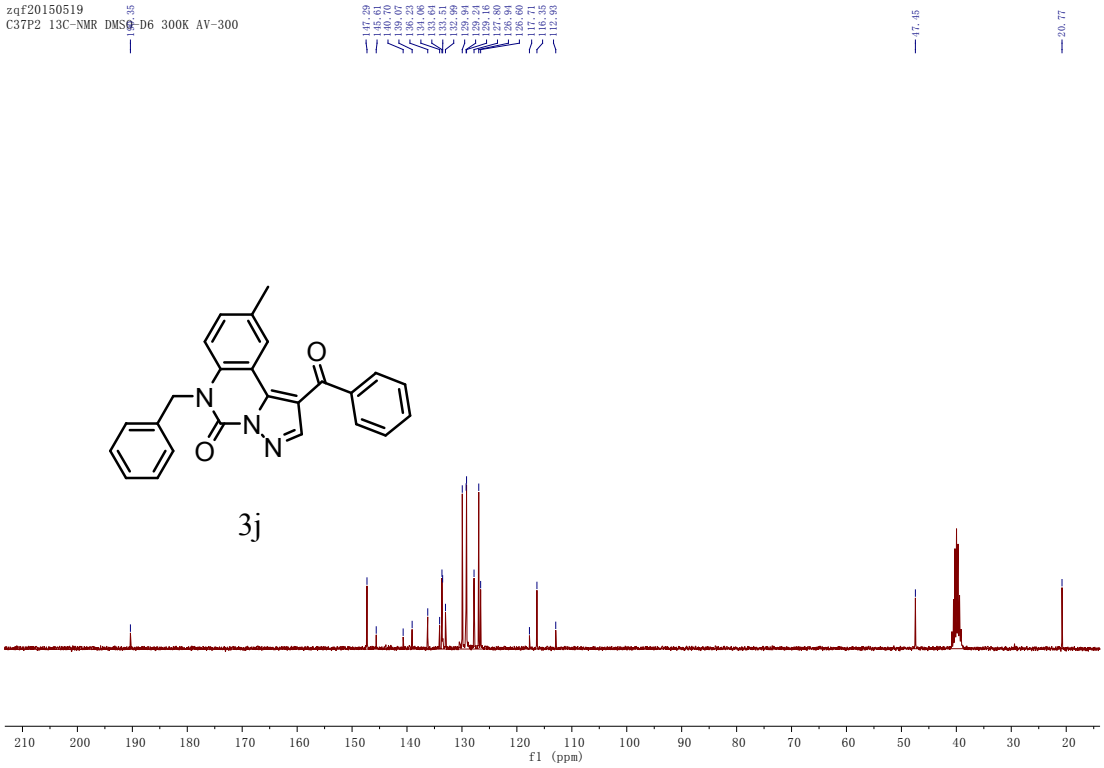

zqf20150515
C35P2 1H-NMR-DMSO-D6 300K AV-300
5.66
3h
1.00
1.00
0.98
4.23
3.54
1.92
3.86
3.01
1.01
2.04
f1 (ppm)

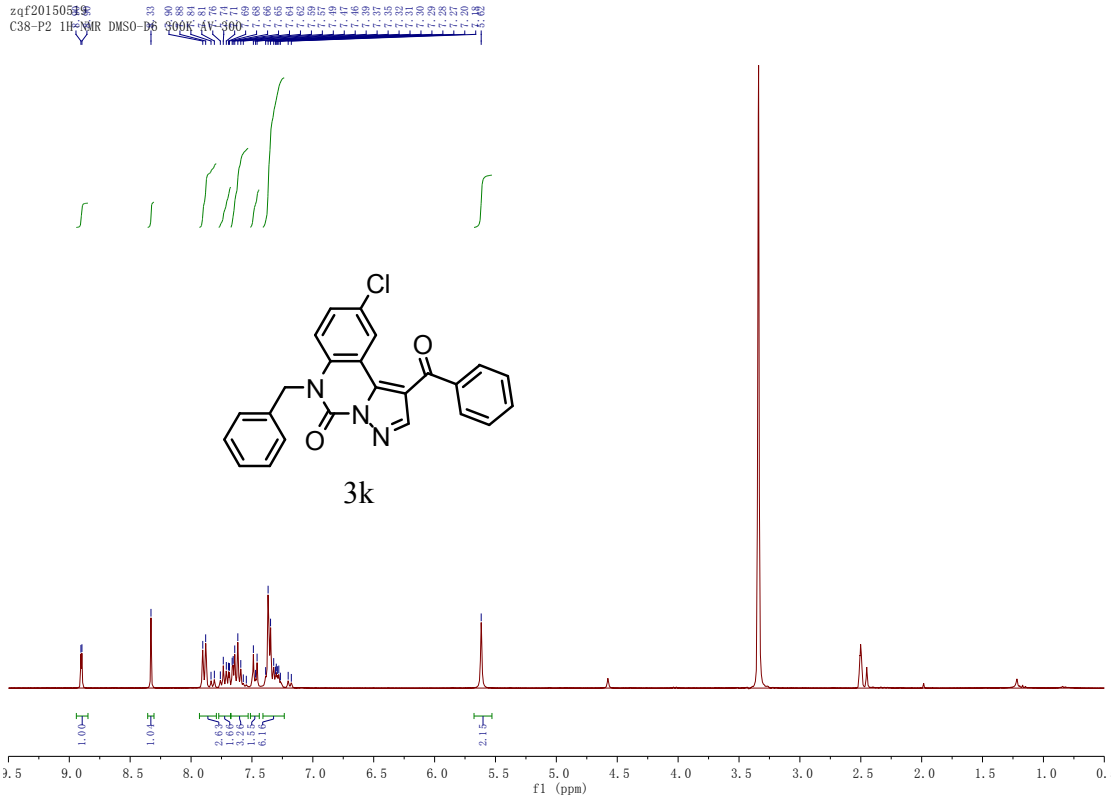

zqf20150526
C35P2 13C-NMR DMSO-D6 300K AV-300
147.39
145.72
136.22
132.57
131.48
132.24
130.13
129.29
129.19
129.02
128.18
127.84
127.65
126.87
126.66
125.27
116.51
113.17
47.53
3h
f1 (ppm)

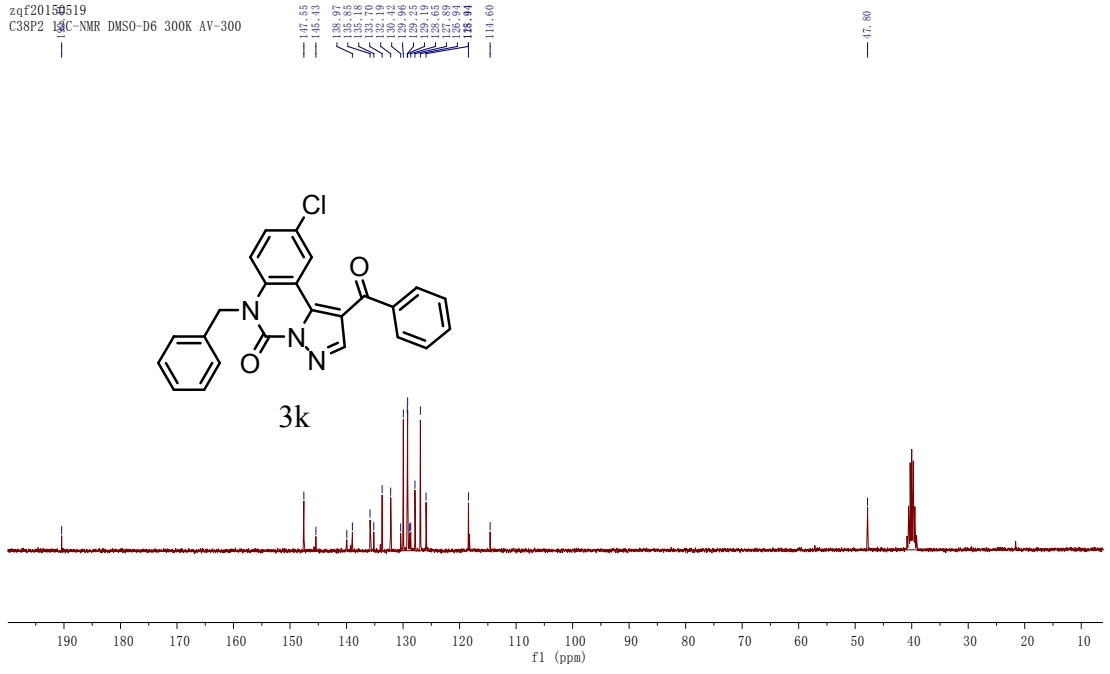

zqf20150507
C33 1H-NMR DMSO-D6 303K AV-500
7.65
7.63
7.62
7.46
7.44
7.41
7.39
7.38
7.34
7.33
7.31
7.28
7.28
7.27
7.26
7.26
7.25
5.60
2.69
3i
1.00
0.99
1.00
1.01
1.08
4.20
1.12
2.00
3.00
f1 (ppm)

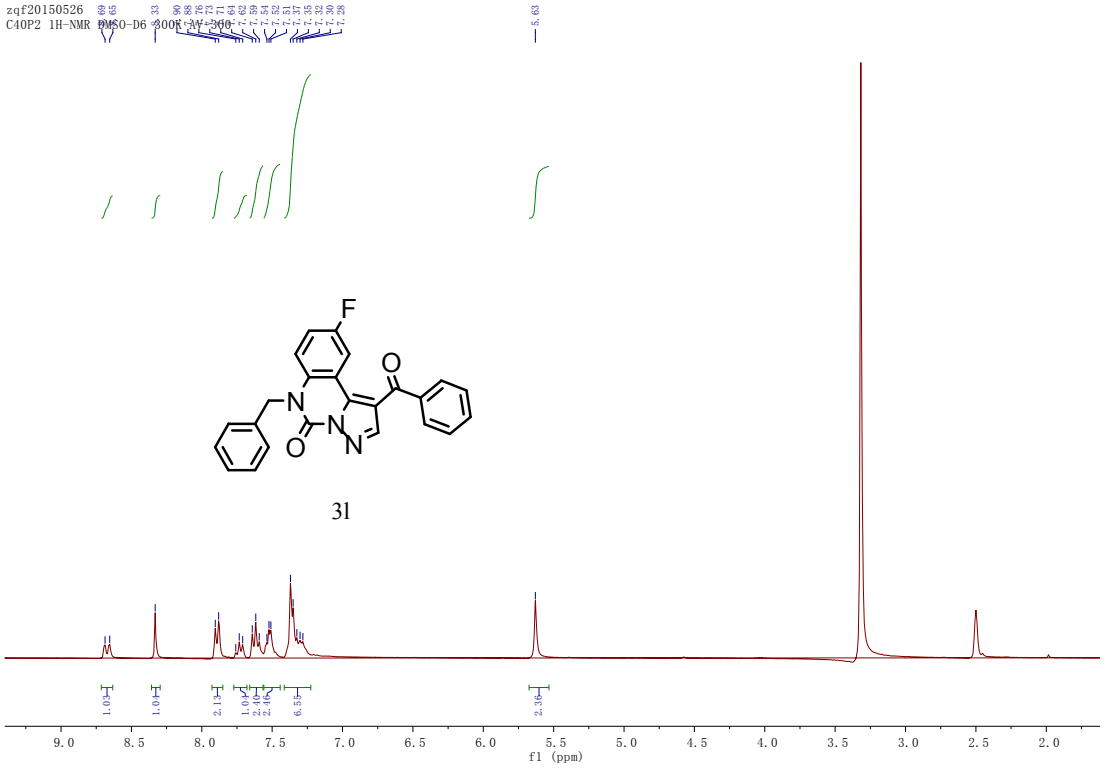

zqf20150507
C33 13C-NMR DMSO-D6 303K AV-500
148.11
145.60
140.04
136.17
136.08
132.80
129.12
127.99
127.77
126.89
123.64
116.13
113.37
110.00
47.53
30.59
3i
f1 (ppm)


zqf20150519
C37P2 1H-NMR DMSO-D6 300K AV-300
3j
f1 (ppm)

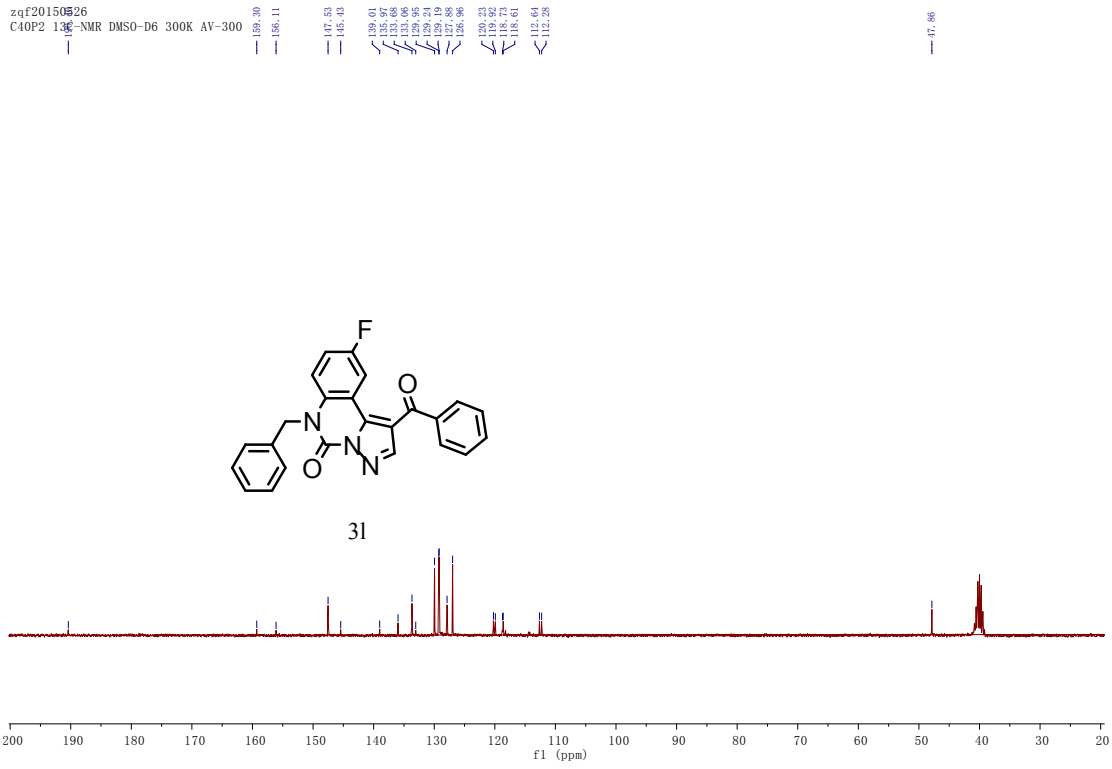

zqf20150519
C37P2 13C-NMR DMSO-D6 300K AV-300
3j
f1 (ppm)


zqf20150519
C38-P2 1H-NMR DMSO-D6 300K AV-300
Cl
O
N
N
O
3k
f1 (ppm)

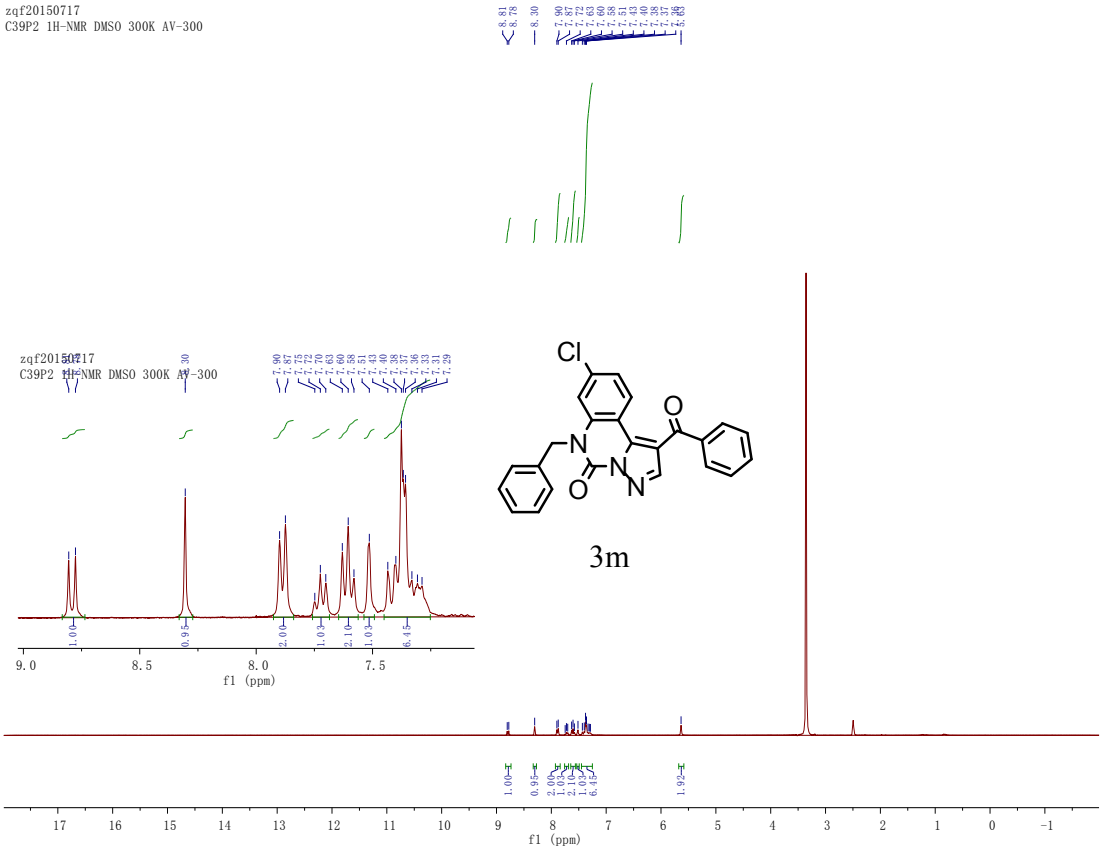

zqf20150519
C38P2 13C-NMR DMSO-D6 300K AV-300
Cl
O
N
N
O
3k
f1 (ppm)

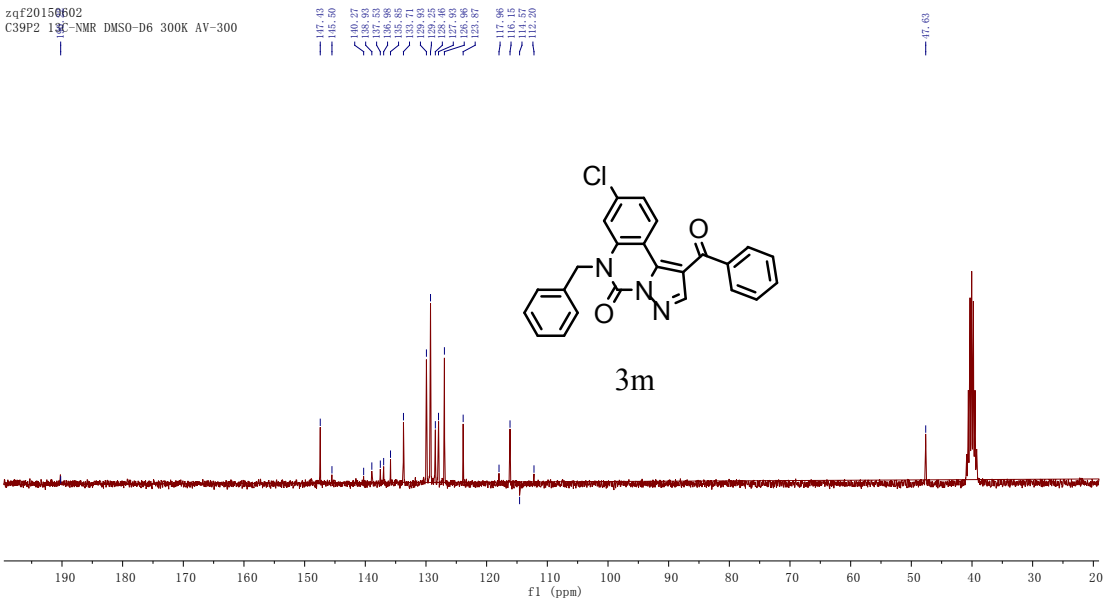

zqf20150526
C40P2 1H-NMR DMSO-D6 300K AV-300
F
O
N
N
N
O
f1 (ppm)

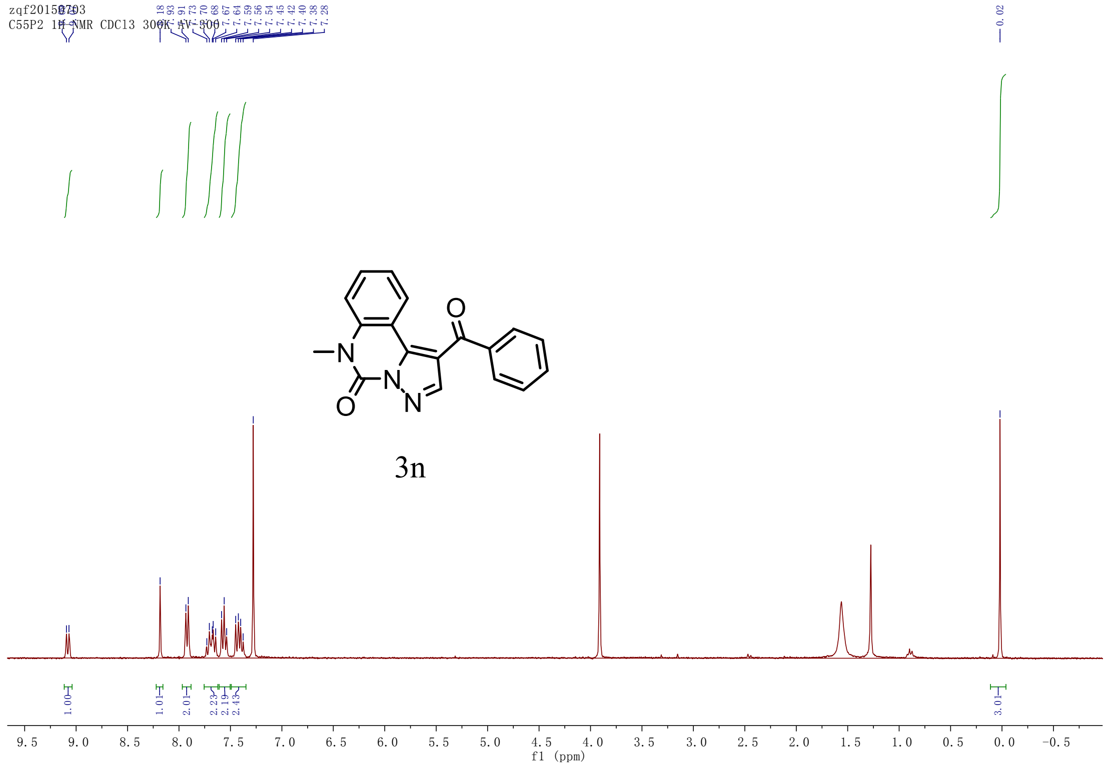
31

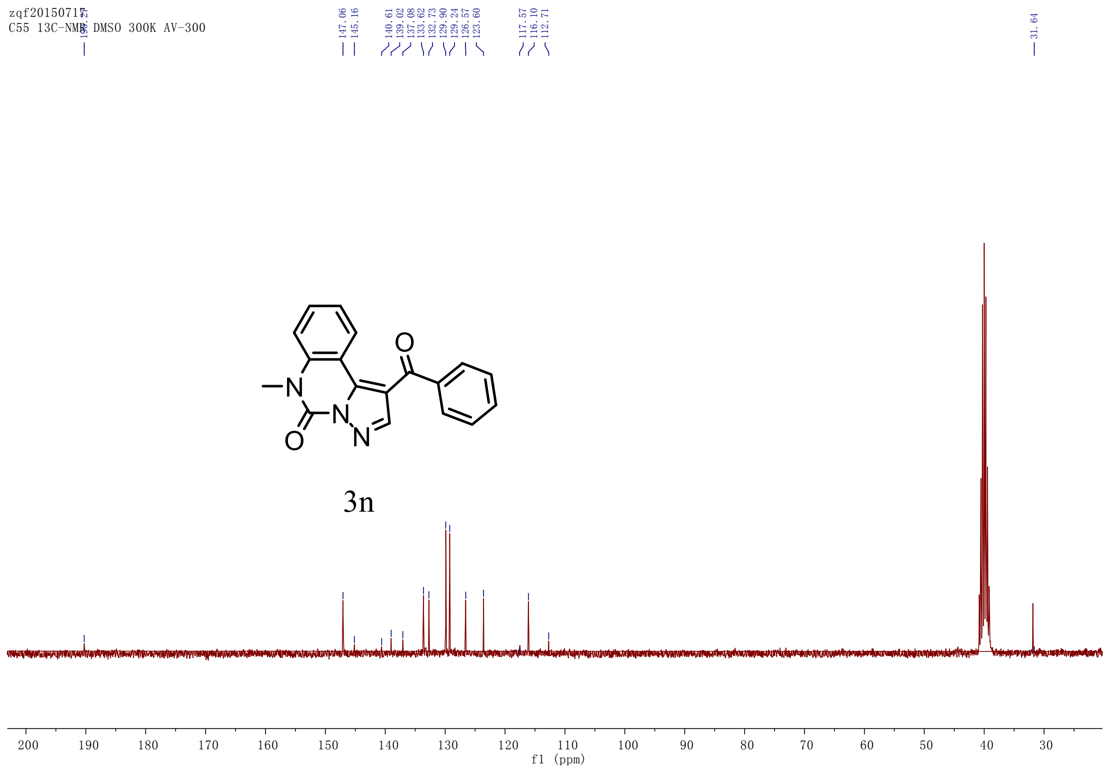

zqf20150526
C40P2 13C-NMR DMSO-D6 300K AV-300
F
O
N
N
N
O
f1 (ppm)

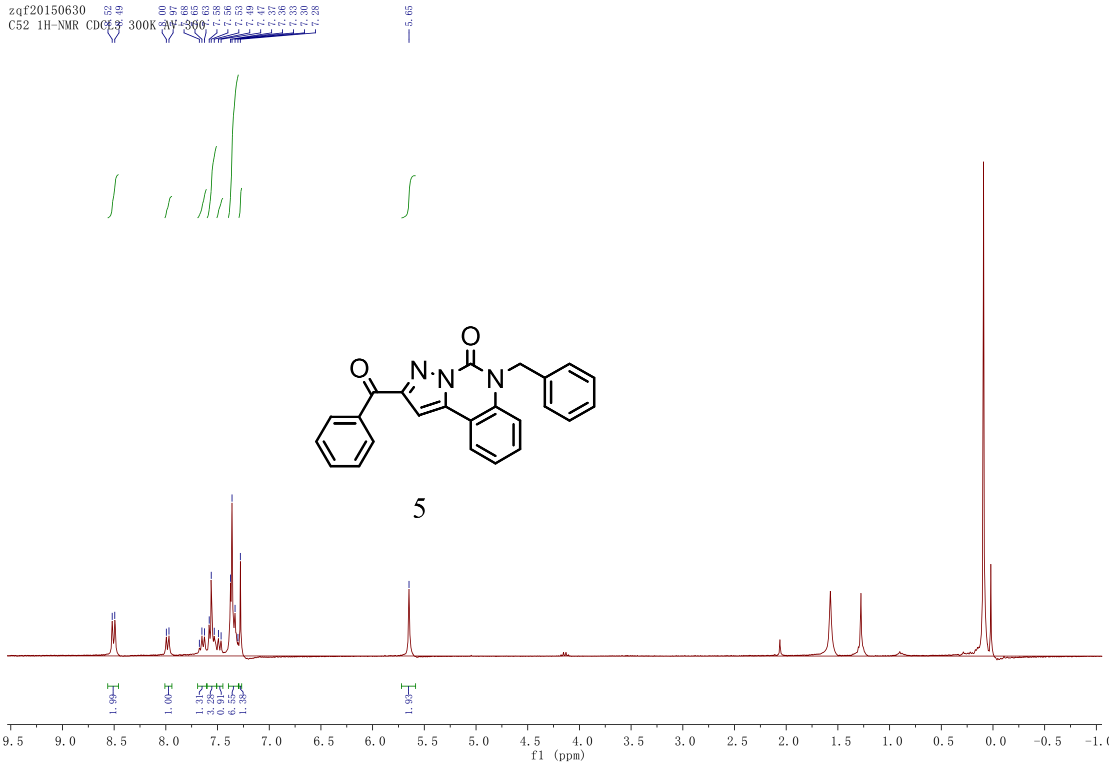
31

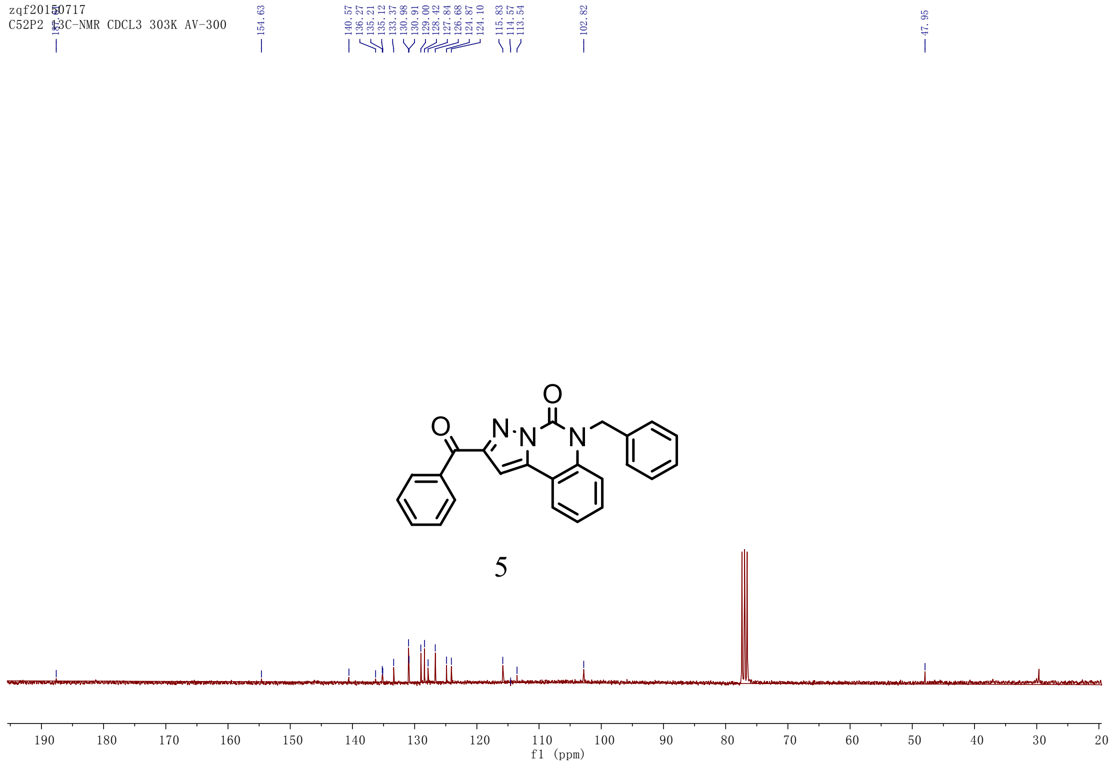

zqf20150717
C39P2 1H-NMR DMSO 300K AV-300
Cl
O
N
N
O
N
3m
f1 (ppm)


zqf20150602
C39P2 13C-NMR DMSO-D6 300K AV-300
Cl
O
N
N
O
N
3m
f1 (ppm)


C55P2 1H-NMR CDCl3 300K AV-300
8.18
7.73
7.70
7.68
7.67
7.64
7.59
7.56
7.54
7.45
7.42
7.40
7.38
7.28
0.02
1.00
1.01
2.01
2.23
2.19
2.43
3.01
3n
f1 (ppm)


zqf20150717
C55 13C-NMR DMSO 300K AV-300
147.06
145.16
140.61
139.02
137.08
133.62
132.73
129.90
129.24
126.57
123.60
117.57
116.10
112.71
31.64
3n
f1 (ppm)


zqf20150630
C52 1H-NMR CDCL3 300K AV-300
8.52
8.49
8.00
7.97
7.68
7.65
7.63
7.58
7.56
7.53
7.49
7.47
7.37
7.36
7.33
7.30
7.28
5.65
5
1.99
1.00
1.31
3.28
0.91
6.55
1.38
1.93
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


zqf20150717
C52P2 13C-NMR CDCL3 303K AV-300
154.63
140.57
136.27
135.21
135.12
133.37
130.98
130.91
129.00
128.42
127.84
126.68
124.87
124.10
115.83
114.57
113.54
102.82
47.95
5
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)