Supporting Information

Lewis Base Catalyzed Regioselective Cyclization of Allene Ketones or α-Methyl Allene Ketone with Unsaturated Pyrazolones

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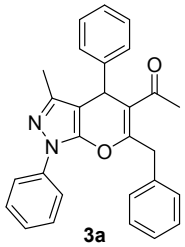
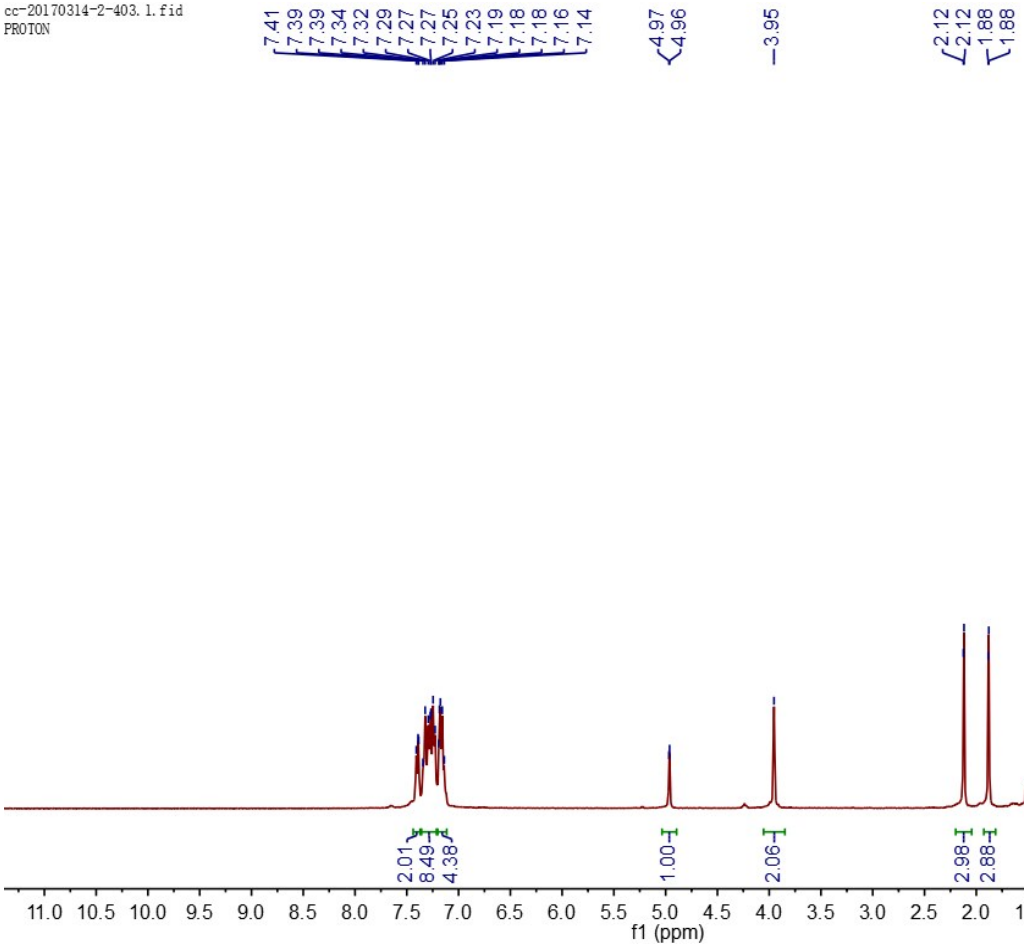
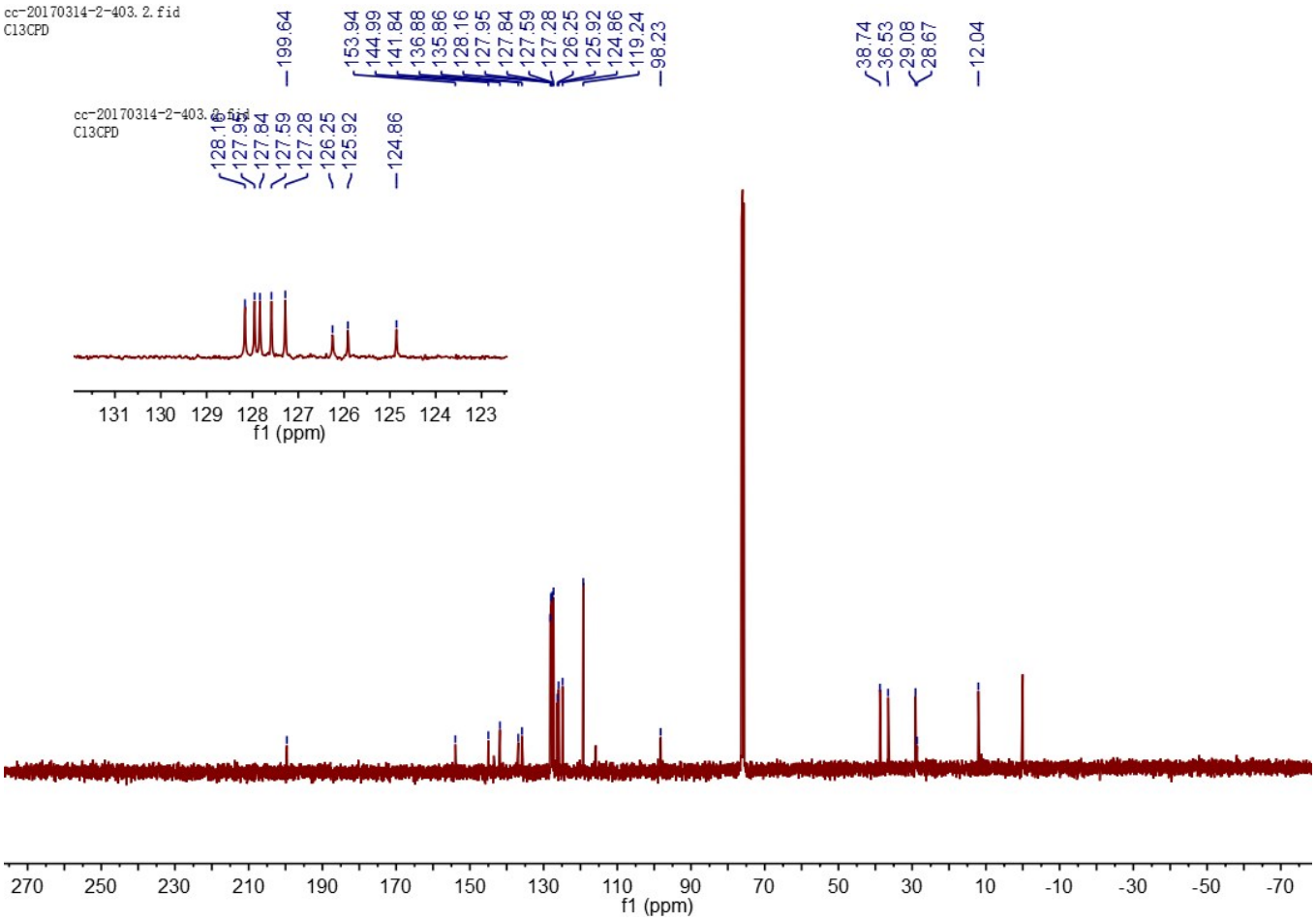
1-(6-Benzyl-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3a):



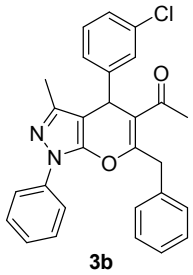
3a

Red solid, m.p. 98-100 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (s, 2H), 7.36-7.22 (m, 9H), 7.20-7.14 (m, 4H), 4.96 (s, 1H), 3.95 (s, 2H), 2.12 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 153.9, 145.0, 141.8, 135.8, 128.1, 127.9, 127.6, 127.3, 126.2, 125.9, 124.8, 119.2, 98.2, 38.7, 36.5, 29.0, 12.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O_2$ $[M + H]^+$ 421.1911, found 421.1914.



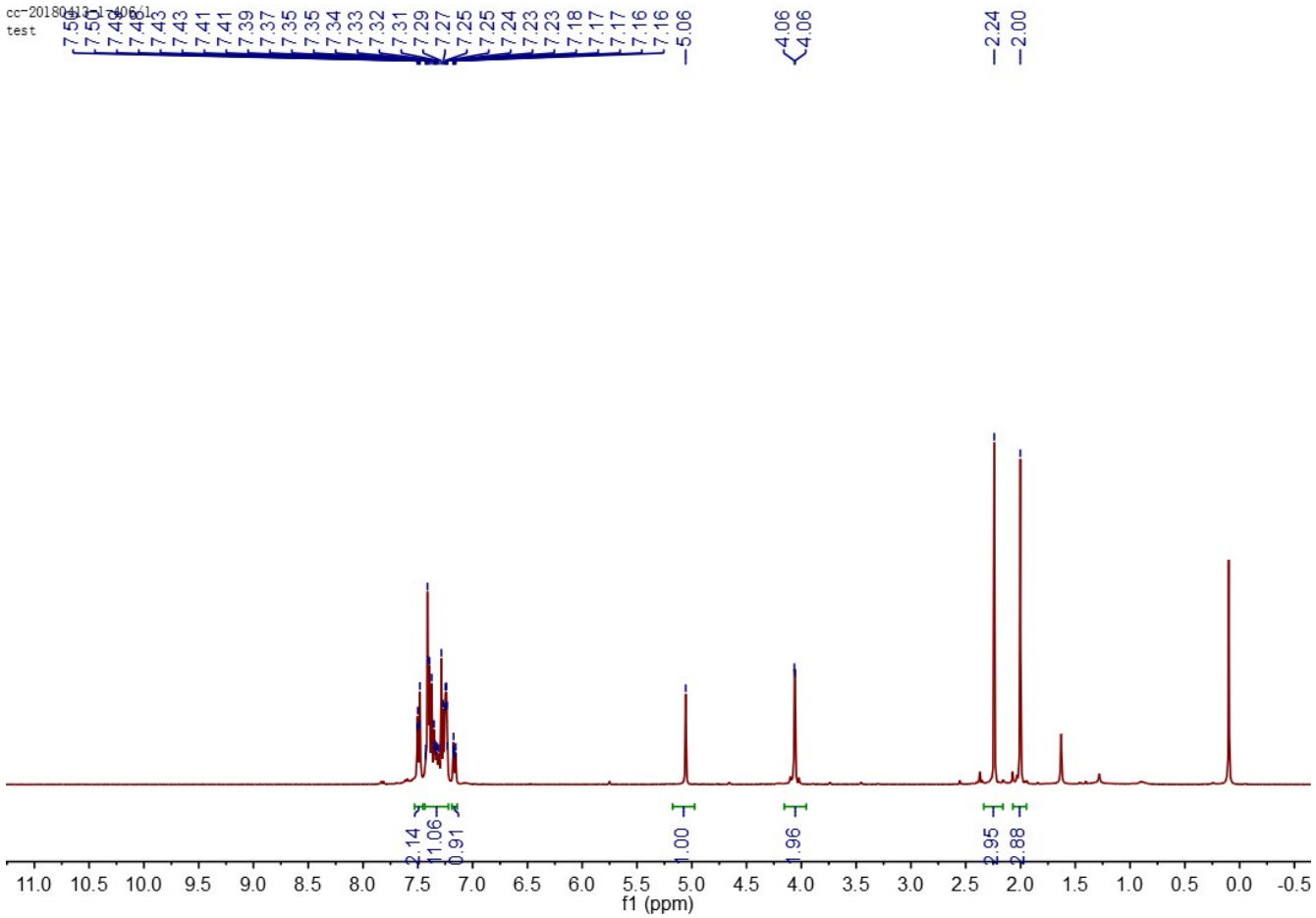


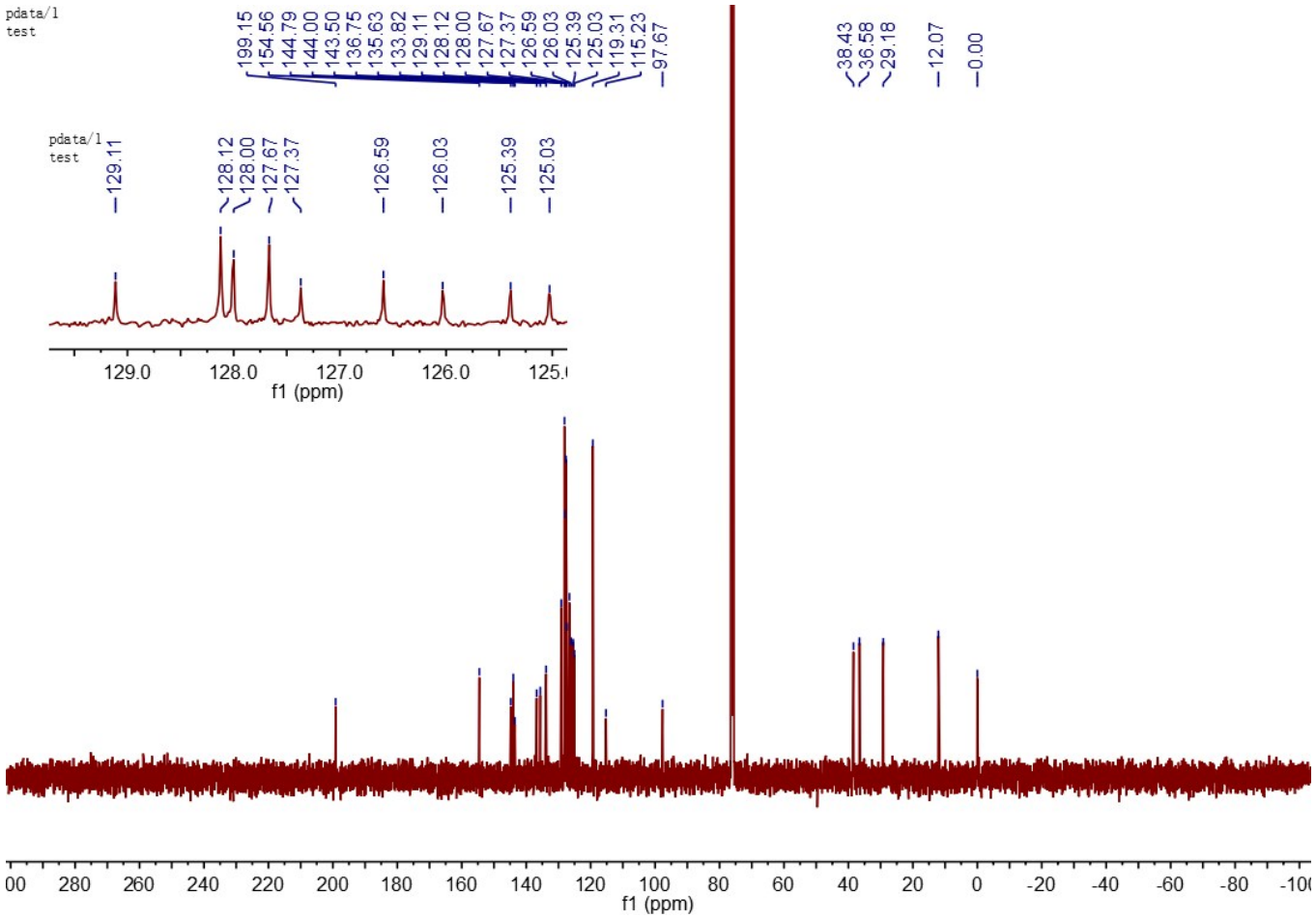
1-(6-Benzyl-4-(3-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3b):



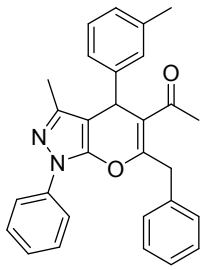
3b

Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49-7.46 (m, 2H), 7.42-7.34 (m, 6H), 7.26-7.23 (m, 5H), 7.17 (s, 1H), 5.06 (s, 1H), 4.06 (s, 2H), 2.24 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 154.5, 144.7, 144.0, 136.7, 135.6, 133.8, 129.1, 128.0, 127.6, 127.3, 126.5, 126.0, 125.3, 125.0, 119.3, 115.2, 97.6, 38.4, 36.5, 29.1, 12.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}ClN_2O_2$ $[M + H]^+$ 455.1521, found 455.1522.


f1 (ppm)

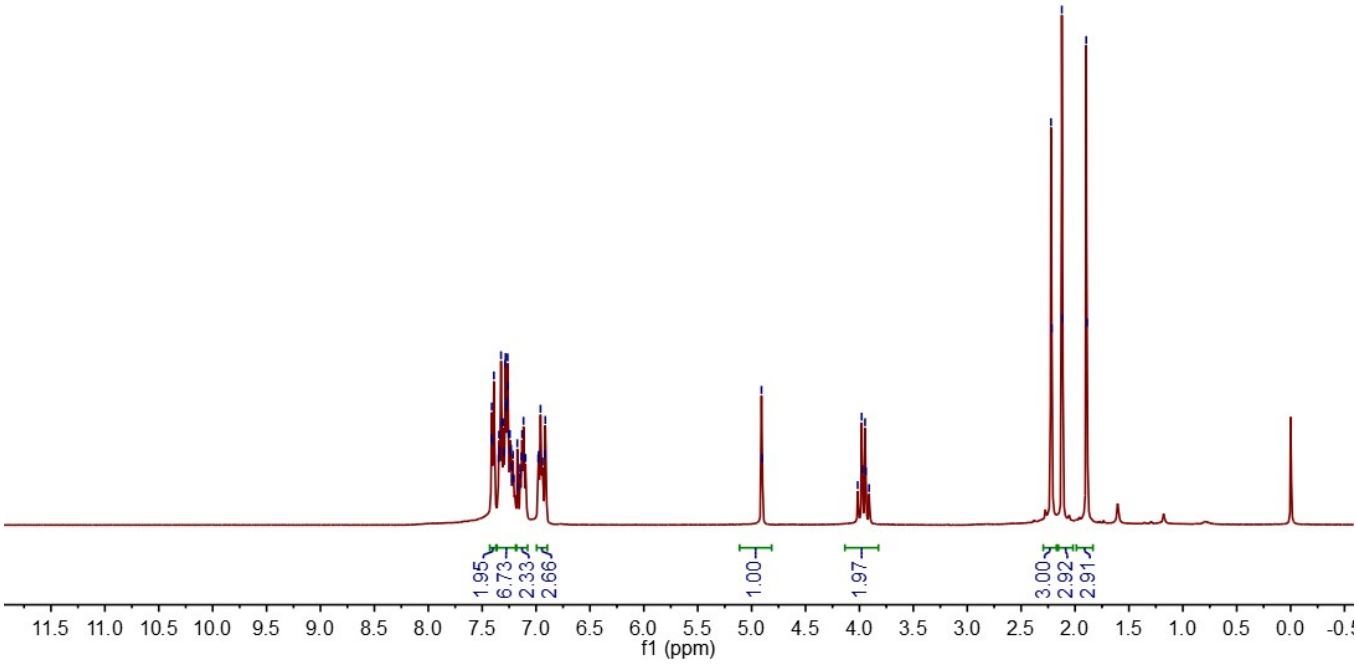

f1 (ppm)

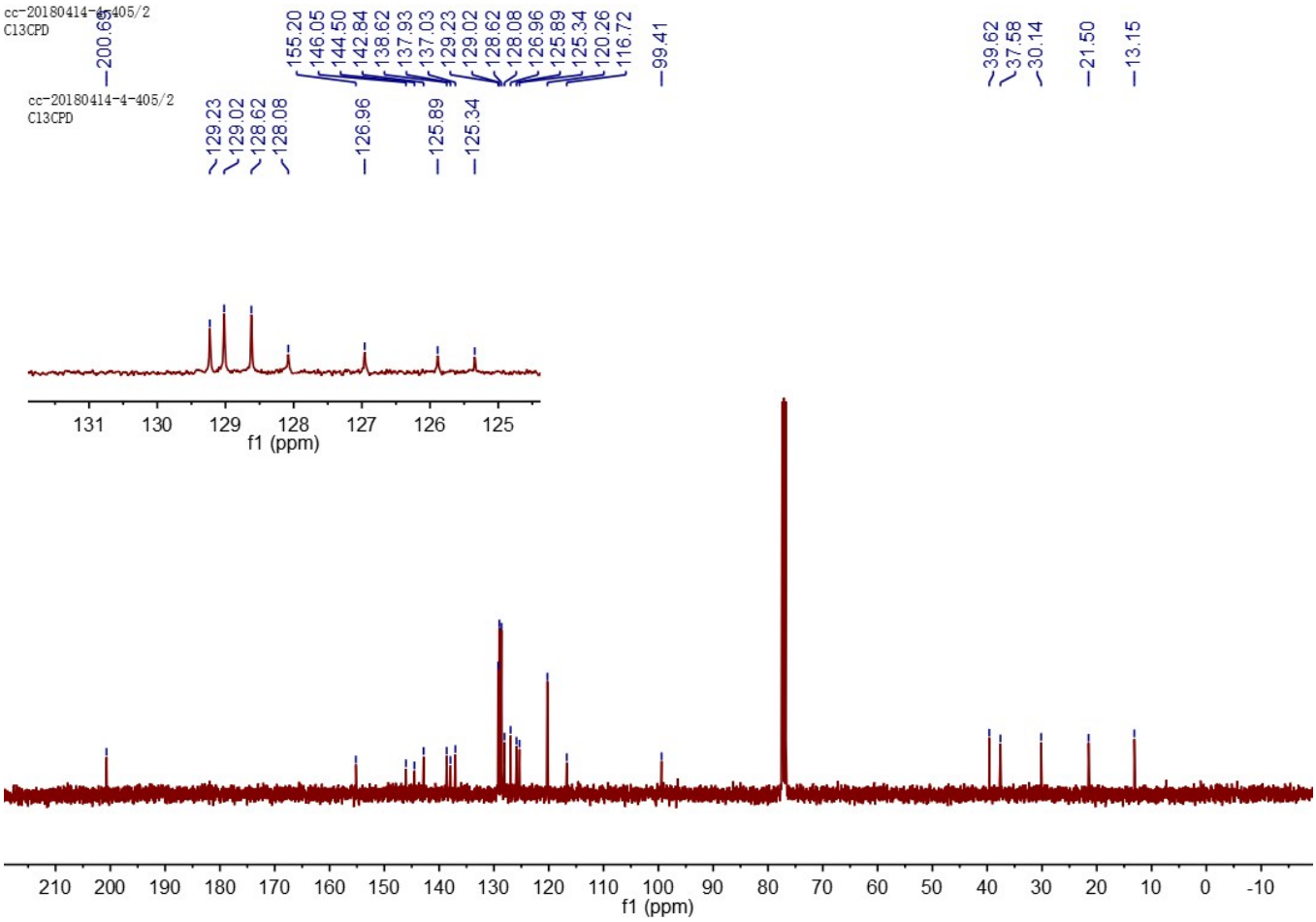
1-(6-Benzyl-3-methyl-1-phenyl-4-(*m*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3c).



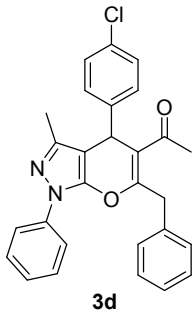
3c

Brown solid, m.p. 103-105 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.35-7.21 (m, 7H), 7.16-7.08 (m, 2H), 6.95-6.90 (m, 3H), 4.91 (s, 1H), 3.96 (q, J = 14.9 Hz, 2H), 2.22 (s, 3H), 2.12 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 155.21, 144.5, 140.7, 137.0, 129.5, 129.4, 129.1, 129.4, 128.1, 127.5, 125.6, 120.2, 116.7, 99.4, 39.6, 37.5, 30.1, 21.5, 13.1. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M+H]^+$ 435.2067, found 435.2066.



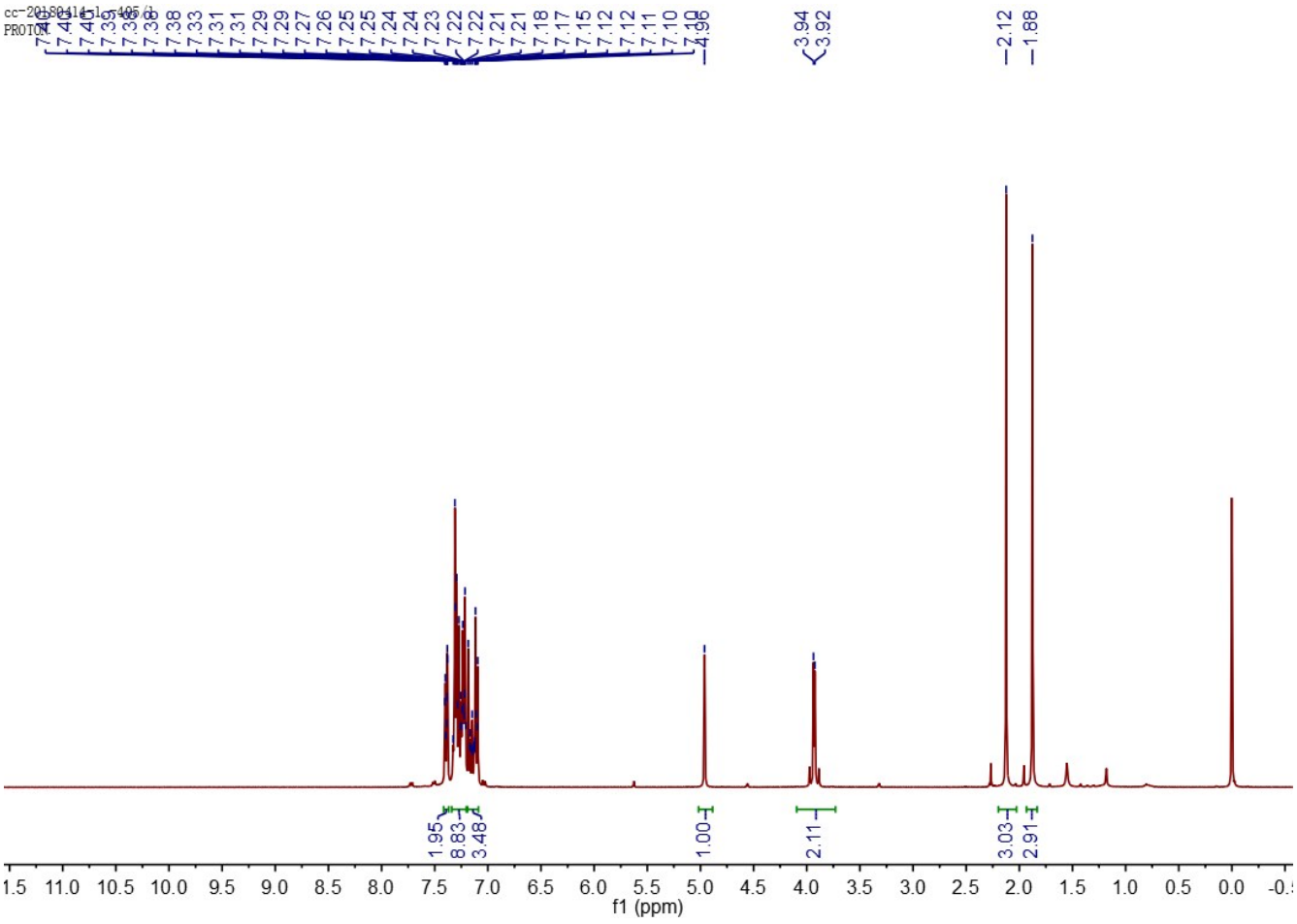


1-(6-Benzyl-4-(4-chlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3d):



3d

Red solid, m.p. 62-63 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.33-7.21 (m, 9H), 7.13-7.11 (m, 3H), 4.96 (s, 1H), 4.00-3.77 (m, 2H), 2.12 (s, 3H), 1.88 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 154.0, 144.8, 143.4, 140.4, 136.7, 135.6, 132.1, 128.5, 128.31, 127.6, 126.0, 125.0, 119.2, 115.5, 97.7, 38.1, 36.5, 29.1, 12.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}ClN_2O_2$ $[M + H]^+$ 455.1521, found 455.1516.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7.29
7.29
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7.24
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7.22
7.21
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7.10
7.10
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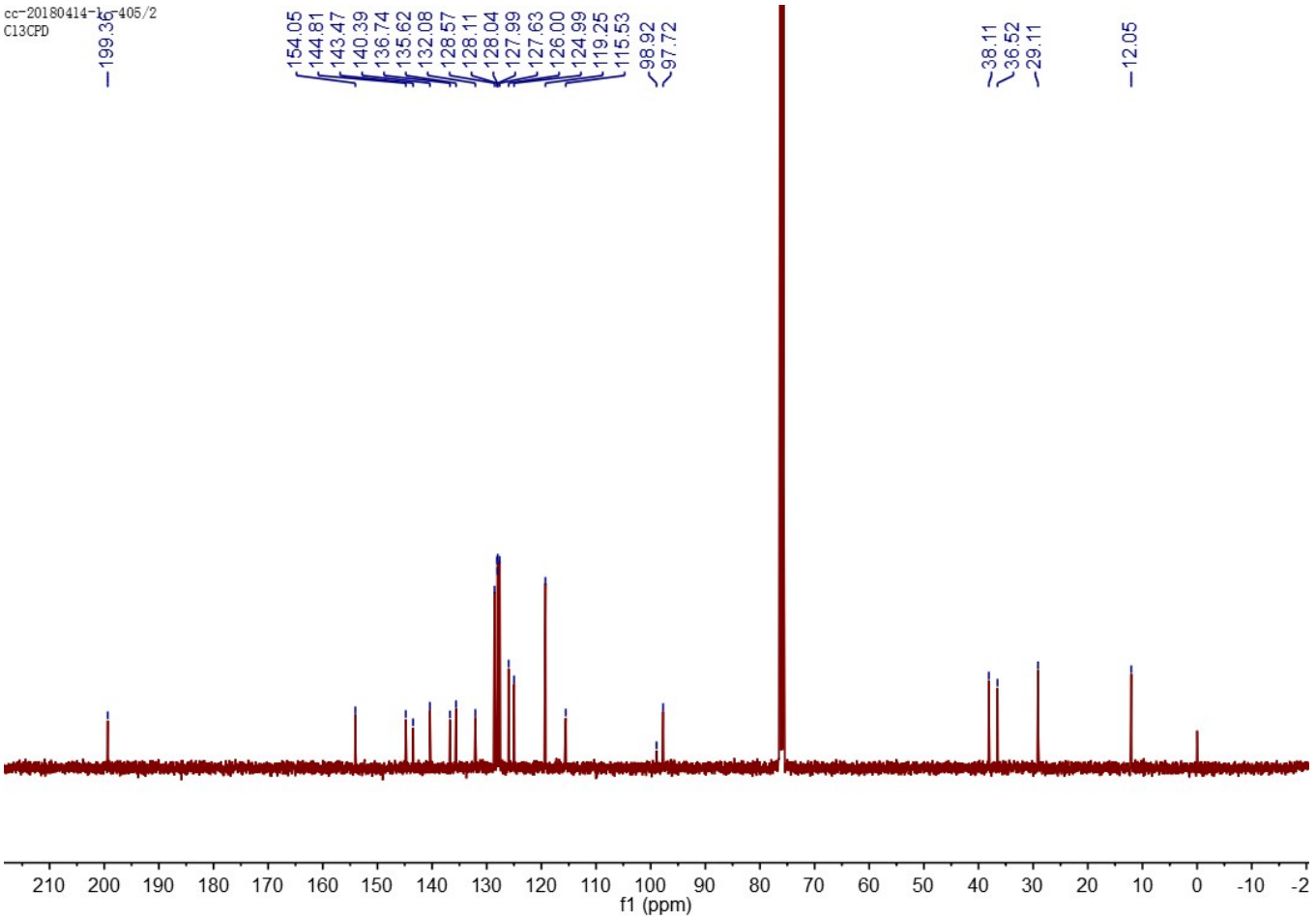
1.00
2.11
3.03
2.91
f1 (ppm)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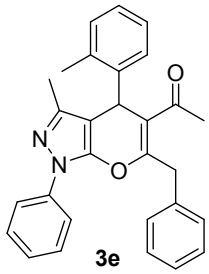
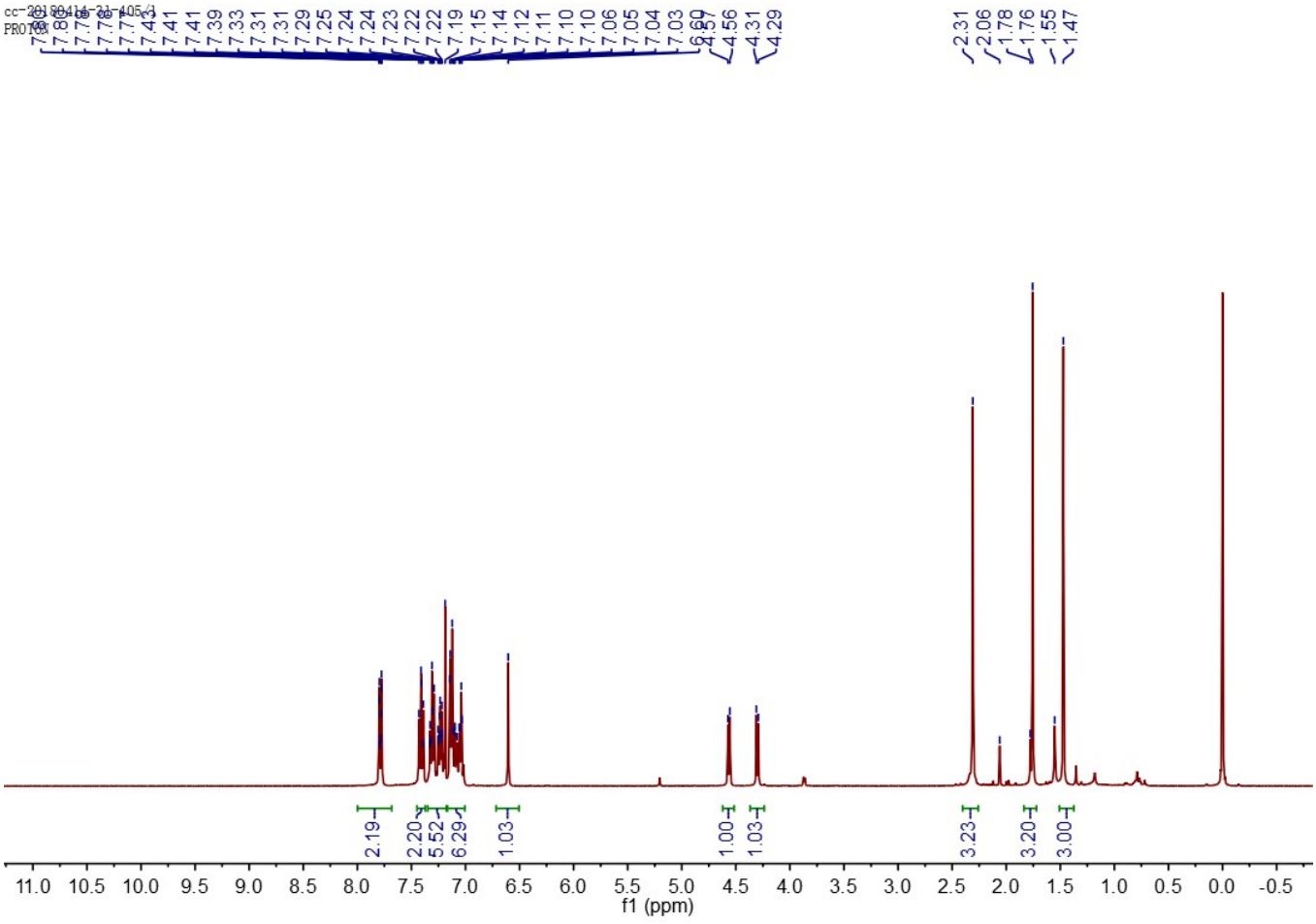
144.81
143.47
140.39
136.74
135.62
132.08
128.57
128.11
128.04
127.99
127.63
126.00
124.99
119.25
115.53
98.92
97.72
38.11
36.52
29.11
12.05
f1 (ppm)

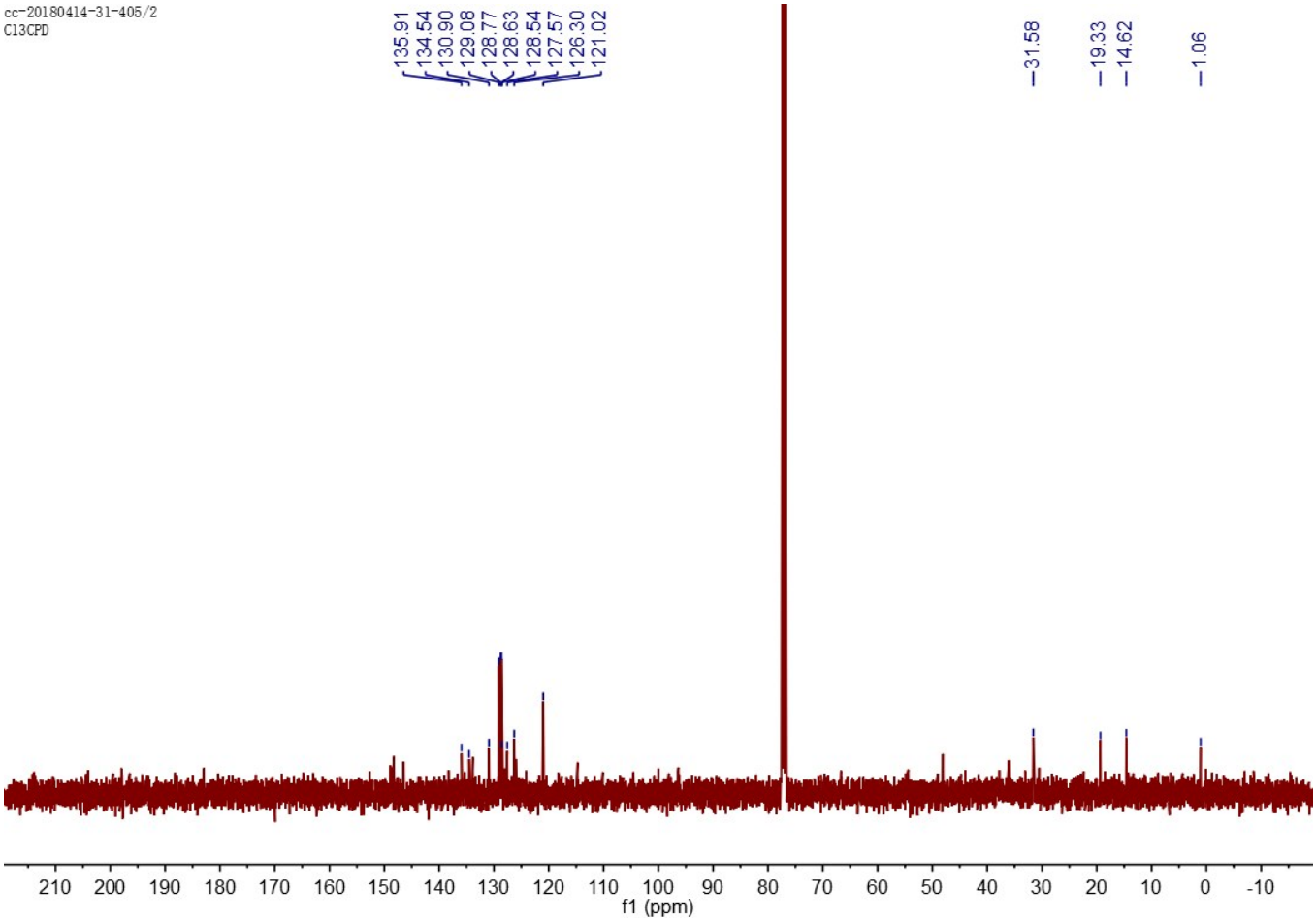
1-(6-Benzyl-3-methyl-1-phenyl-4-(*o*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3e):



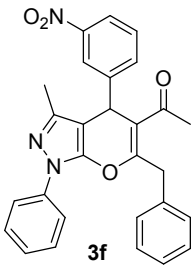
3e

Red solid, m.p. 65-67 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.70 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.27 (ddd, *J* = 13.4, 10.5, 5.3 Hz, 5H), 7.16-7.00 (m, 5H), 6.60 (s, 1H), 4.43 (dd, *J* = 105.2, 7.0 Hz, 2H), 2.30 (d, *J* = 9.6 Hz, 3H), 1.77 (d, *J* = 8.7 Hz, 3H), 1.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.0, 147.8, 147.2, 145.4, 137.2, 134.8, 133.5, 132.8, 129.8, 128.0, 127.7, 127.5, 127.5, 126.5, 126.5, 125.2, 124.9, 119.9, 113.7, 95.3, 47.0, 34.9, 30.5, 18.2, 13.5. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2068.



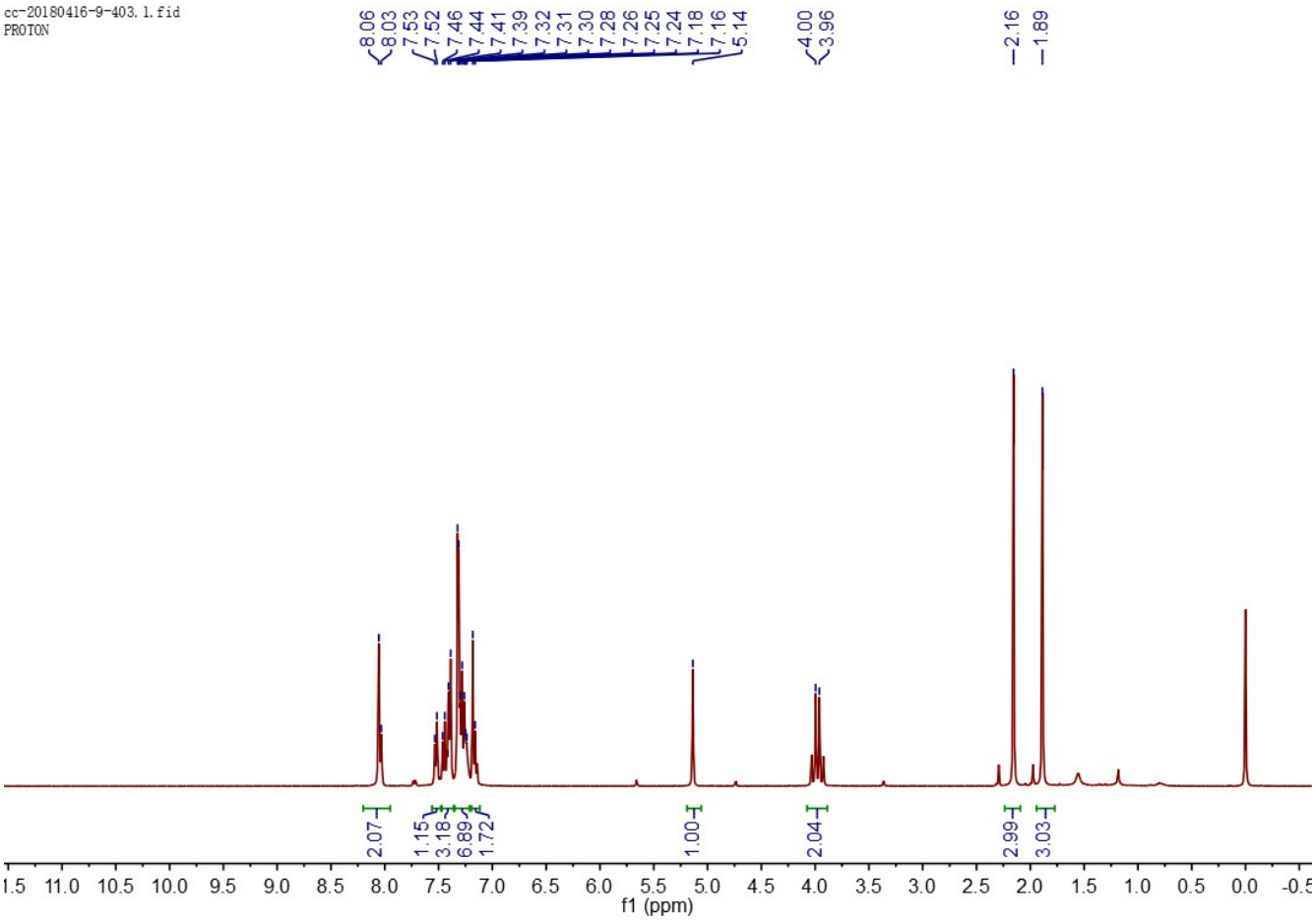


1-(6-Benzyl-3-methyl-4-(3-nitrophenyl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3f):



3f

Red solid, m.p. 124-126 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (s, 2H), 7.52 (s, 1H), 7.46-7.37 (m, 3H), 7.34-7.22 (m, 7H), 7.17 (m, 2H), 5.14 (s, 1H), 3.98 (d, J = 13.7 Hz, 2H), 2.16 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.6, 156.2, 148.6, 145.5, 145.3, 137.7, 136.3, 134.2, 129.9, 129.0, 128.8, 127.2, 126.2, 122.9, 122.4, 120.4, 116.1, 98.2, 39.4, 37.7, 30.2, 13.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}N_3O_4$ $[M + H]^+$ 466.1761; found 466.1758.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7.41
7.39
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7.25
7.24
7.18
7.16
5.14
4.00
3.96
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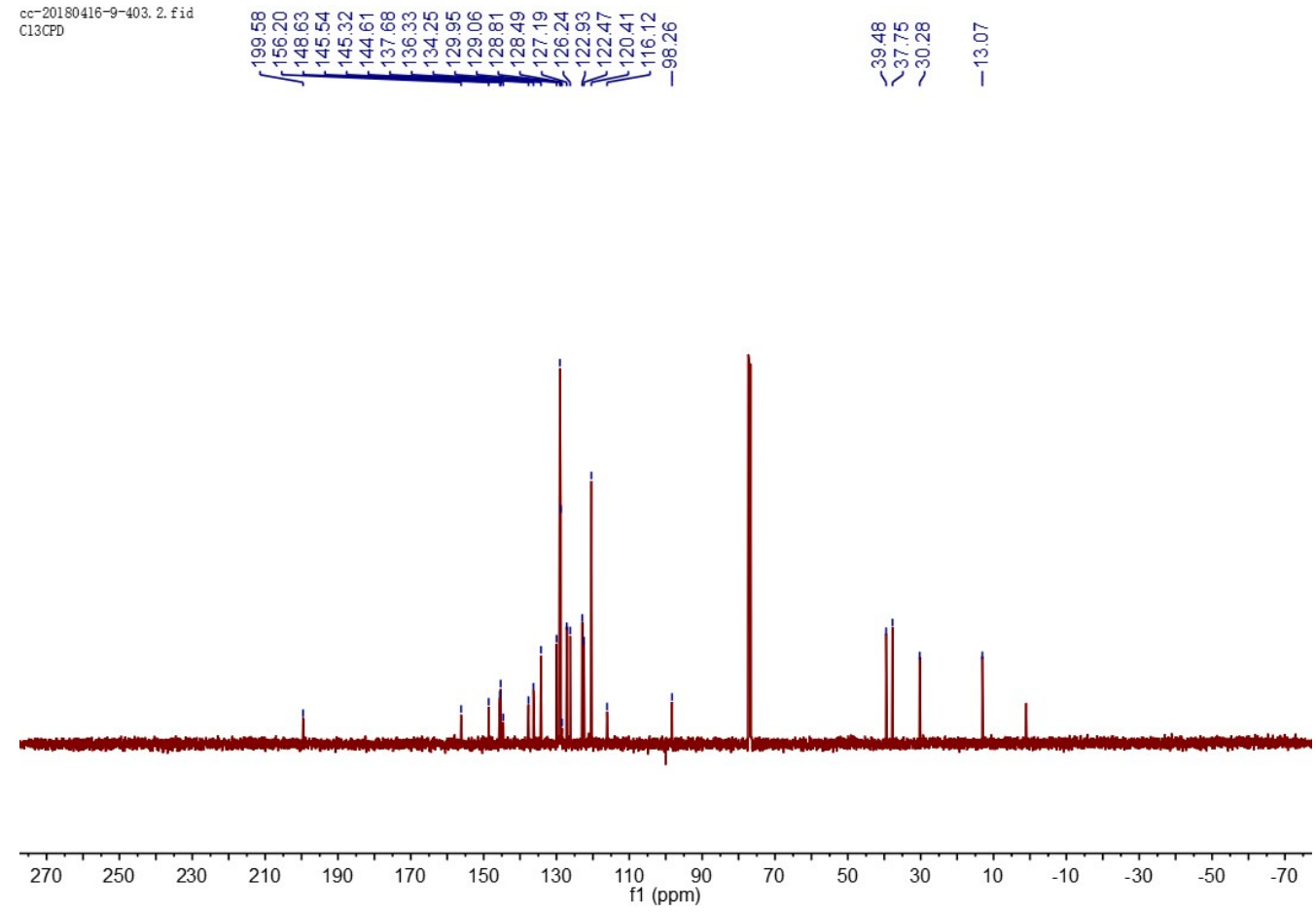
1.72
1.00
2.04
2.99
3.03
f1 (ppm)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148.63
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144.61
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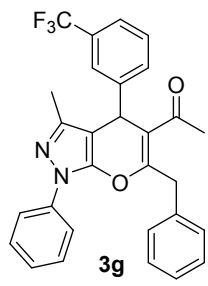
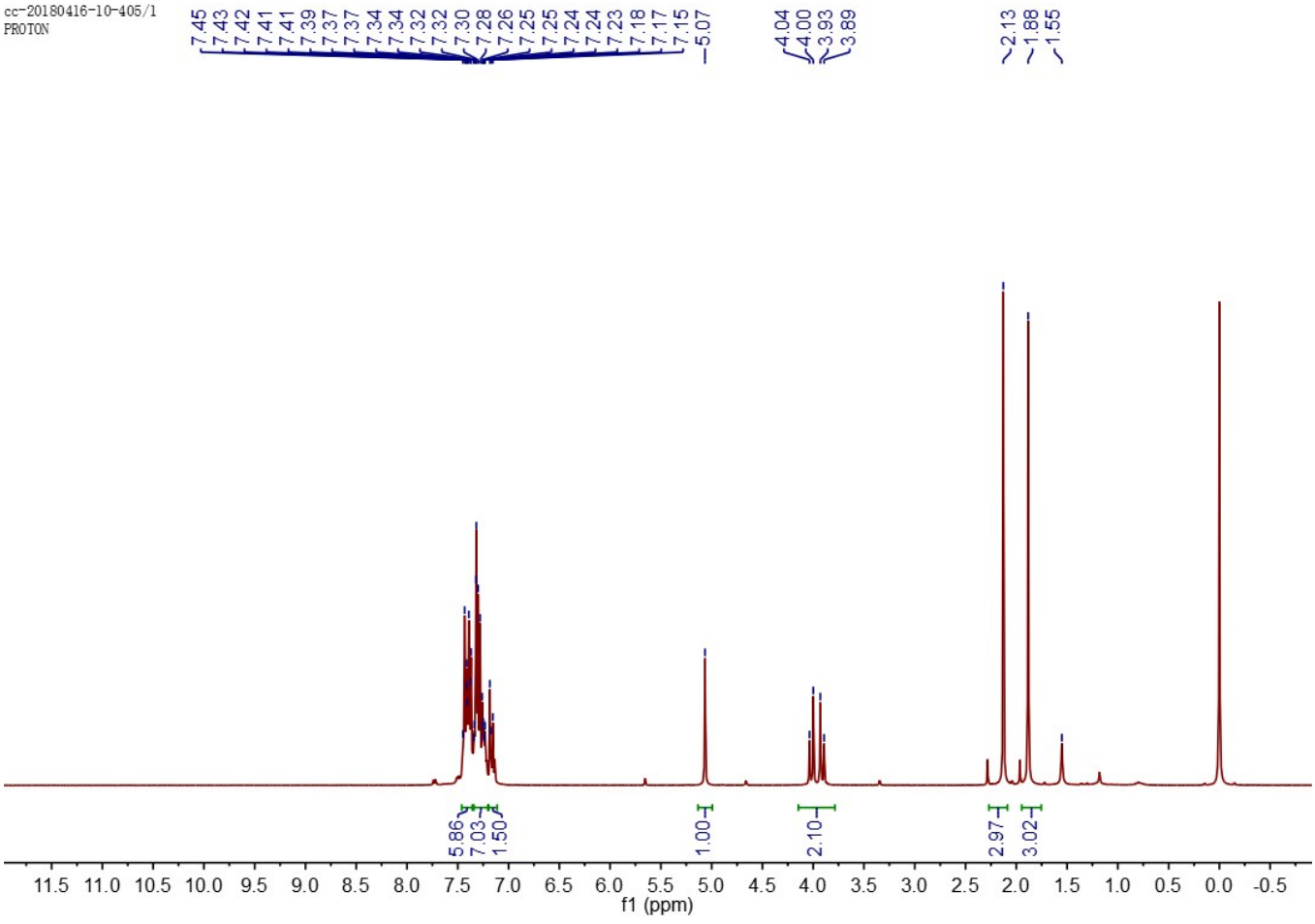
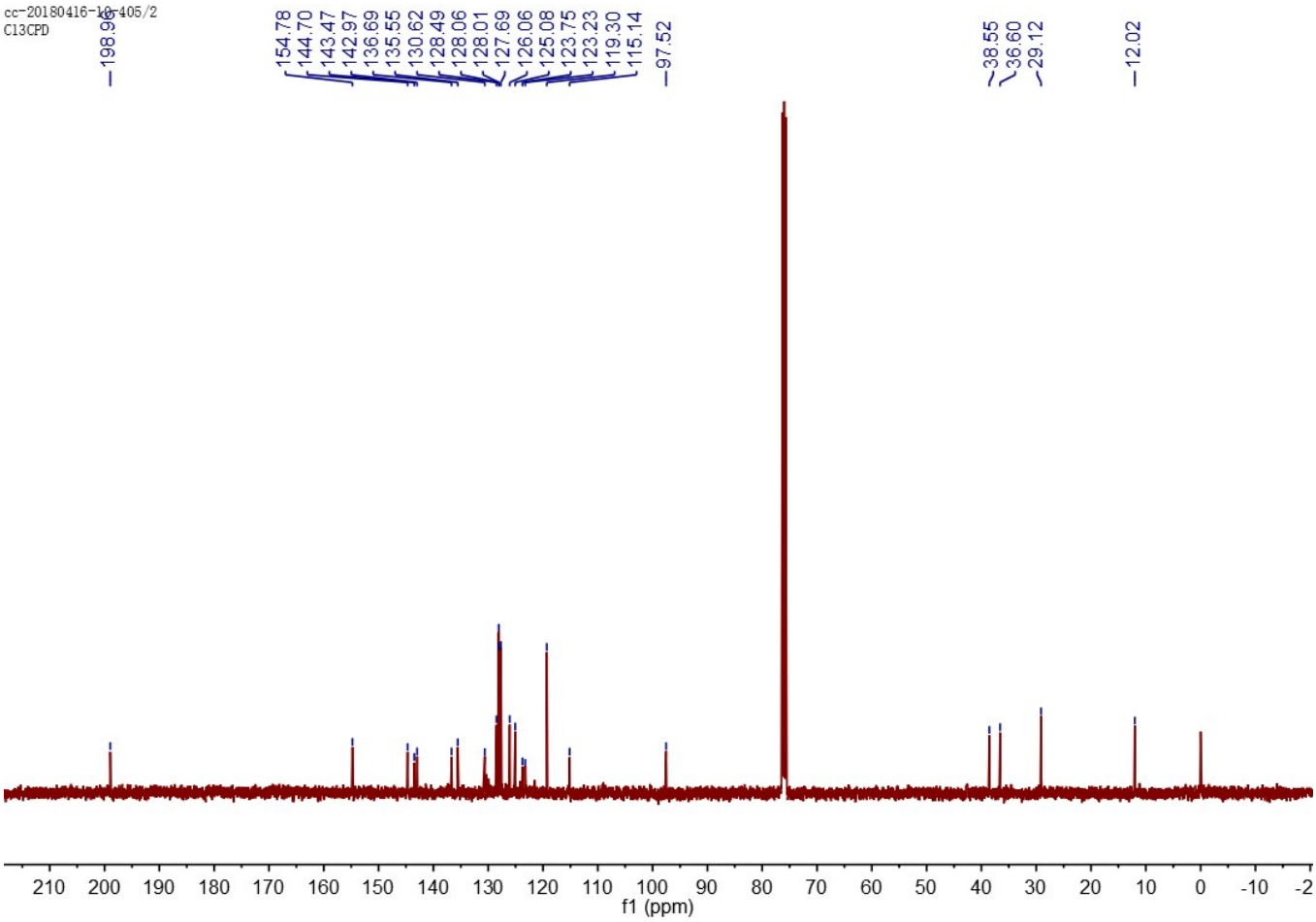
134.25
129.95
129.06
128.81
128.49
127.19
126.24
122.93
122.47
120.41
116.12
98.26
39.48
37.75
30.28
13.07
f1 (ppm)

1-(6-Benzyl-3-methyl-1-phenyl-4-(3-(trifluoromethyl)phenyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3g):

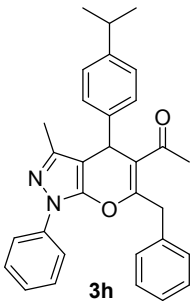


Red liquid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27-8.22 (m, 2H), 7.80 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 7.45-7.34 (m, 4H), 7.30-7.20 (m, 4H), 5.10 (s, 1H), 5.39 (t, *J* = 3.9 Hz, 2H), 3.58 (s, 3H), 3.37 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 154.8, 144.7, 143.4, 142.9, 136.7, 135.5, 130.6, 128.5, 128.0, 127.7, 126.0, 125.0, 123.5 (dd, *J* = 3.0 Hz, *J* = 52.0 Hz), 119.3, 115.1, 97.5, 38.5, 36.6, 29.1, 12.0. HRMS (ESI) *m/z* calcd for $C_{29}H_{24}F_3N_2O_2$ $[M + H]^+$ 489.1784, found 489.1782.

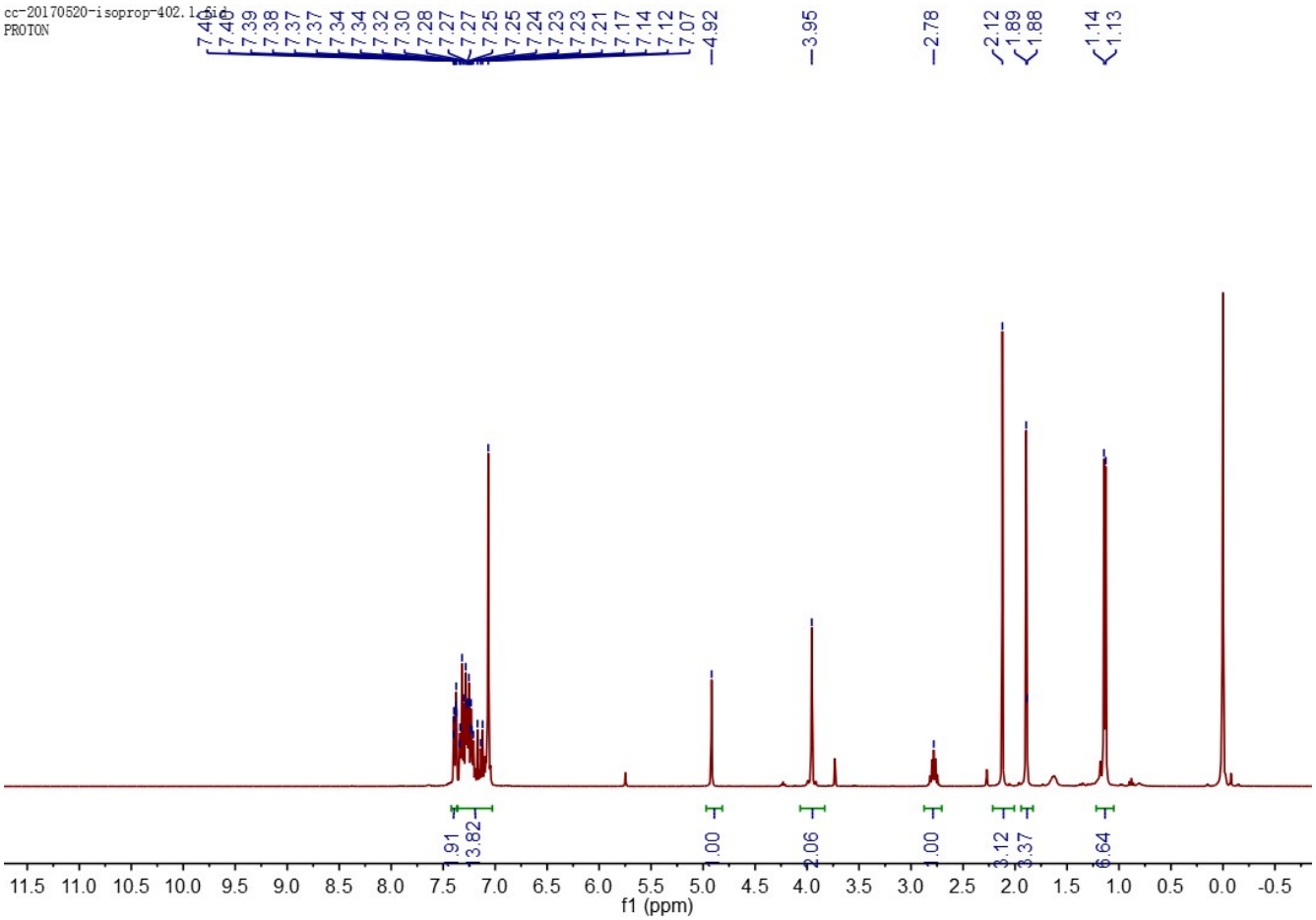




1-(6-Benzyl-4-(4-isopropylphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3h):



Red solid, m.p. 65-67 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.25 (m, 10H), 7.07 (s, 4H), 4.92 (s, 1H), 3.95 (s, 2H), 2.78 (d, *J* = 6.9 Hz, 1H), 2.12 (s, 3H), 1.89 (d, *J* = 3.6 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 154.0, 146.7, 145.0, 143.47, 139.1, 136.9, 135.9, 128.8, 128.2, 127.8, 127.5, 127.3, 127.1, 125.8, 124.8, 119.2, 115.8, 98.5, 38.2, 36.5, 32.6, 29.0, 22.8, 12.0. HRMS (ESI) *m/z* calcd for $C_{31}H_{31}N_2O_2$ $[M + H]^+$ 463.2380, found 463.2382.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7.24
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3.91
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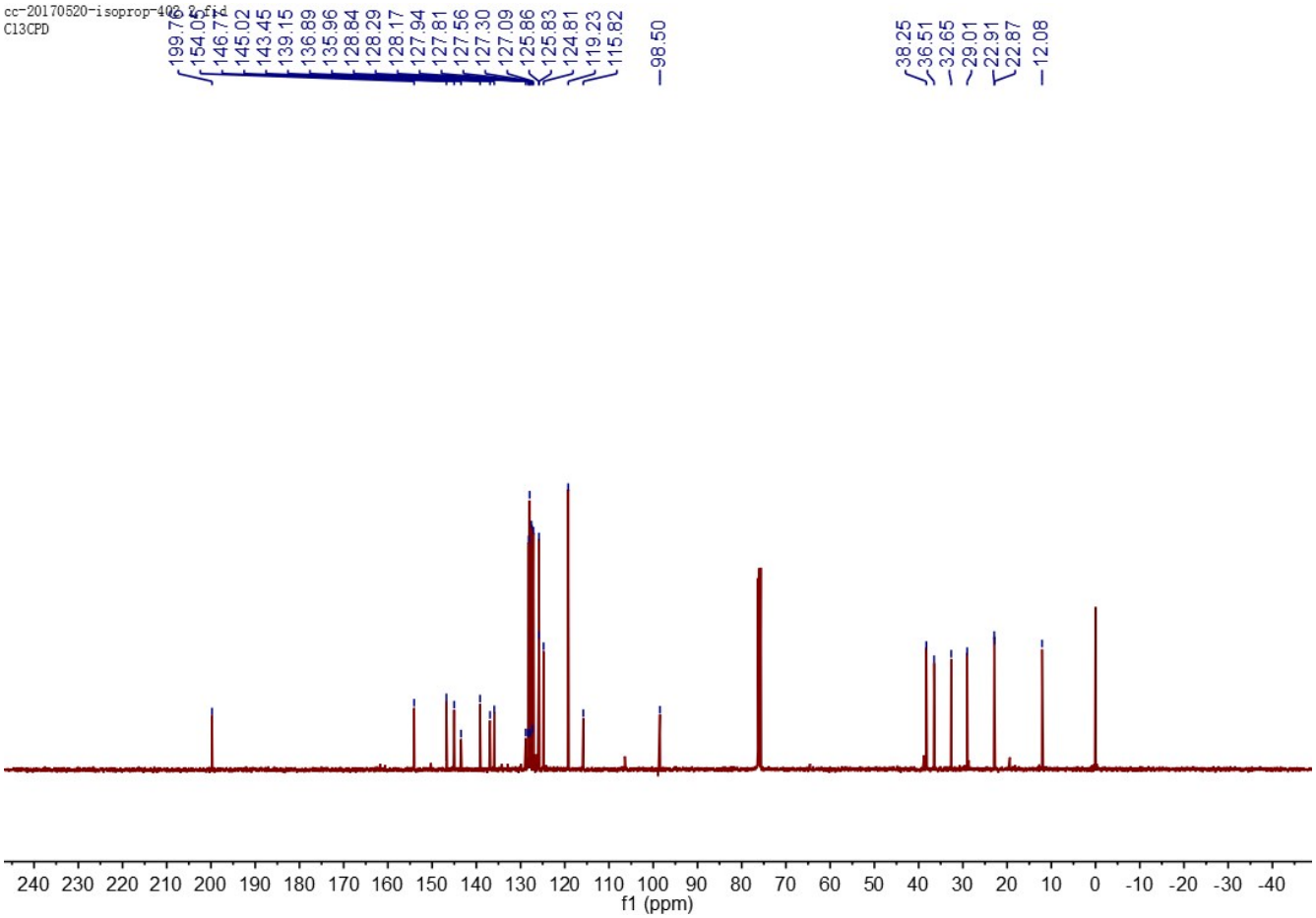
3.12
3.37
6.64
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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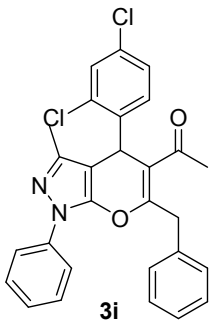
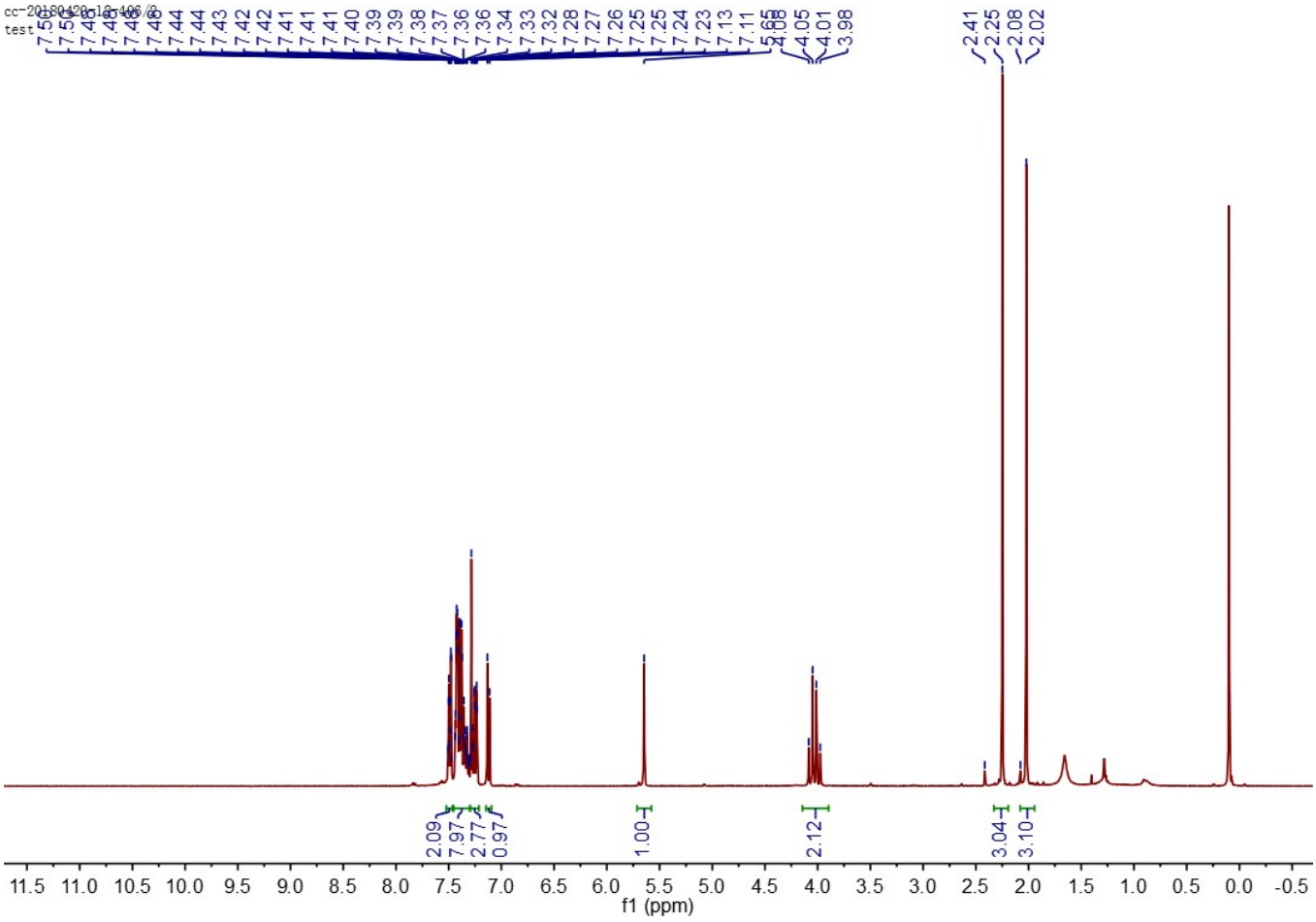
145.02
143.45
139.15
136.89
135.96
128.84
128.29
128.17
127.94
127.81
127.56
127.30
127.09
125.86
125.83
124.81
119.23
115.82
98.50
38.25
36.51
32.65
29.01
22.91
22.87
12.08
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

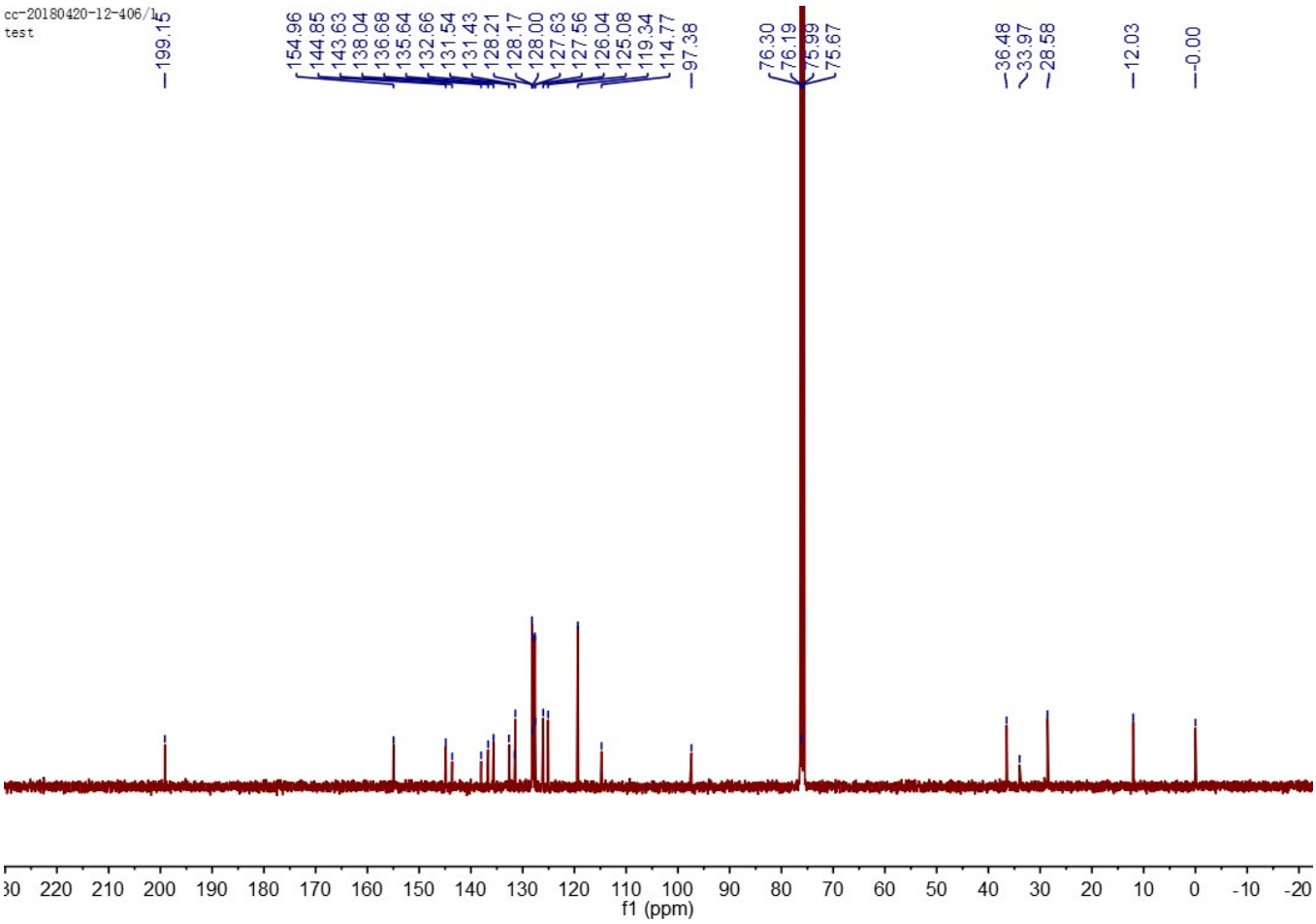
1-(6-Benzyl-4-(2,6-dichlorophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3i):



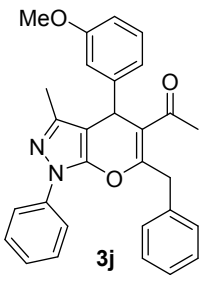
3i

Red solid, m.p. 59-61 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (s, 2H), 7.45-7.33 (m, 8H), 7.25-7.23 (m, 2H), 7.12 (s, 1H), 5.65 (s, 1H), 4.03 (d, J = 14.2 Hz, 2H), 2.25 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.17, 154.98, 144.87, 143.64, 138.05, 136.69, 135.65, 132.66, 131.44, 128.22, 128.02, 127.64, 127.57, 126.05, 125.10, 119.36, 114.77, 97.39, 36.49, 33.98, 28.59, 12.03. HRMS (ESI) *m/z* calcd for $C_{28}H_{23}Cl_2N_2O_2$ $[M + H]^+$ 489.1127, found 489.1131.



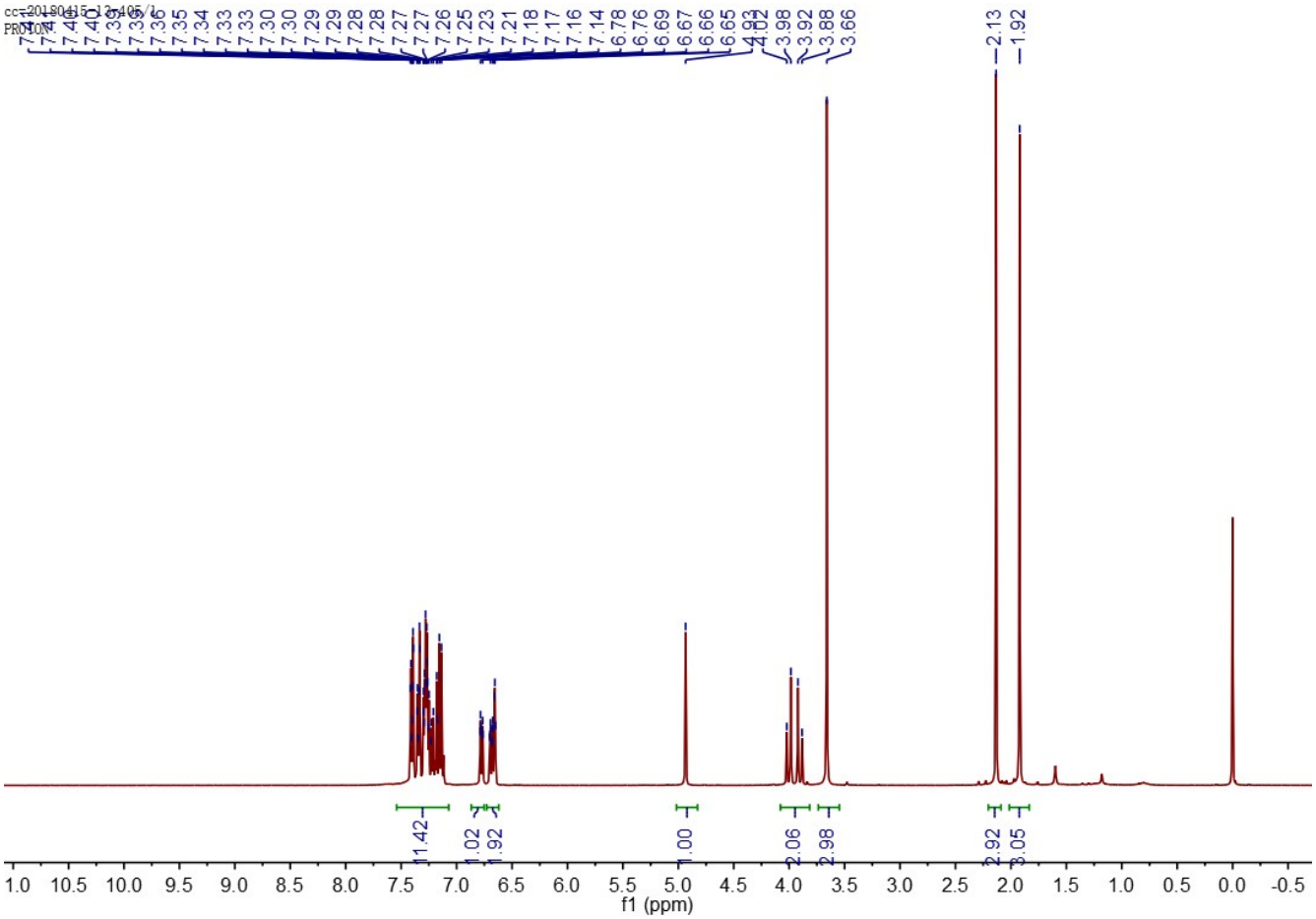


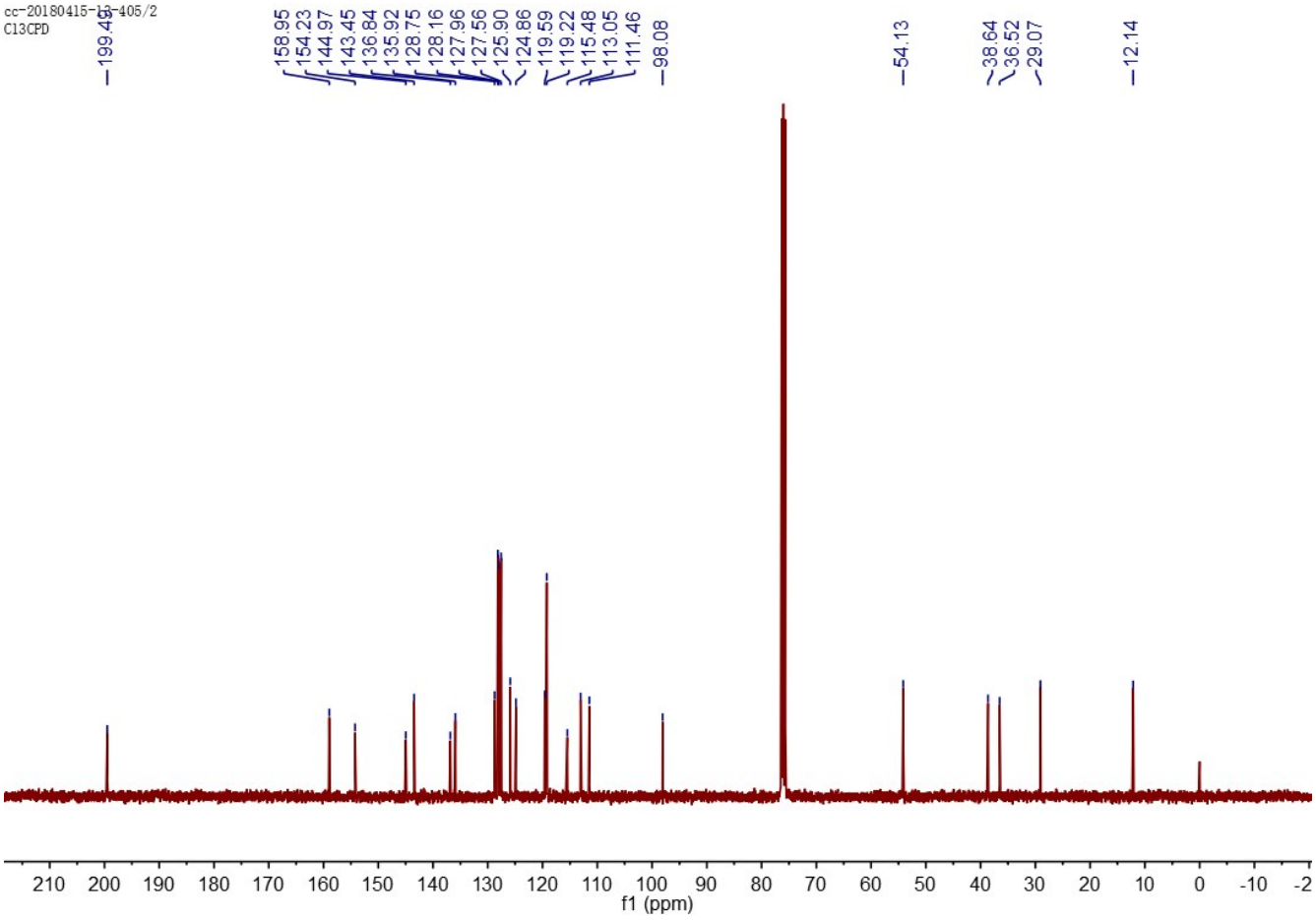
1-(6-Benzyl-4-(3-methoxyphenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3j):



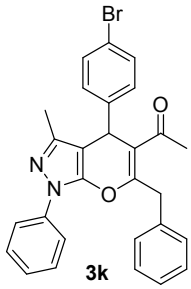
3j

Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.13 (m, 11H), 6.70-6.68 (m, 3H), 4.93 (s, 1H), 3.95 (dd, *J* = 40.3, 14.8 Hz, 2H), 3.66 (s, 3H), 2.13 (s, 3H), 1.92 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.51, 158.97, 154.25, 144.98, 143.46, 136.85, 135.94, 128.76, 128.17, 127.97, 127.57, 125.91, 124.87, 119.60, 119.24, 115.49, 113.07, 111.47, 98.09, 54.14, 38.65, 36.52, 29.08, 12.14. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_3$ $[M + H]^+$ 451.2016, found 451.2015.


PROTON
7.44
7.40
7.39
7.36
7.35
7.34
7.33
7.33
7.30
7.30
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.23
7.21
7.18
7.17
7.16
7.14
6.78
6.76
6.69
6.67
6.66
6.65
4.02
3.98
3.92
3.88
3.66
2.13
1.92
11.42
1.02
1.92
1.00
2.06
2.98
2.92
3.05
f1 (ppm)

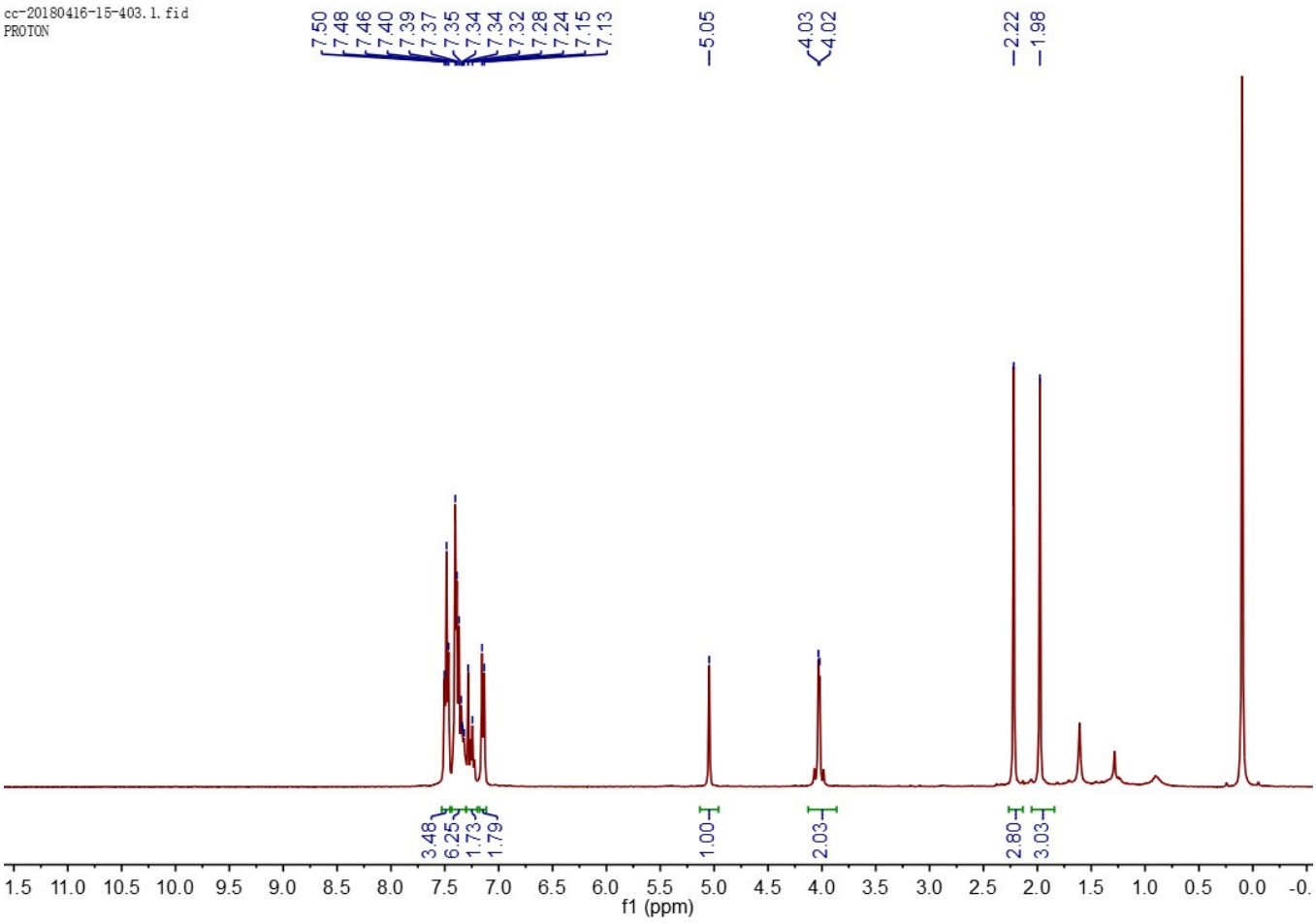

C13CPD
199.45
158.95
154.23
144.97
143.45
136.84
135.92
128.75
128.16
127.96
127.56
125.90
124.86
119.59
119.22
115.48
113.05
111.46
98.08
54.13
38.64
36.52
29.07
12.14
f1 (ppm)

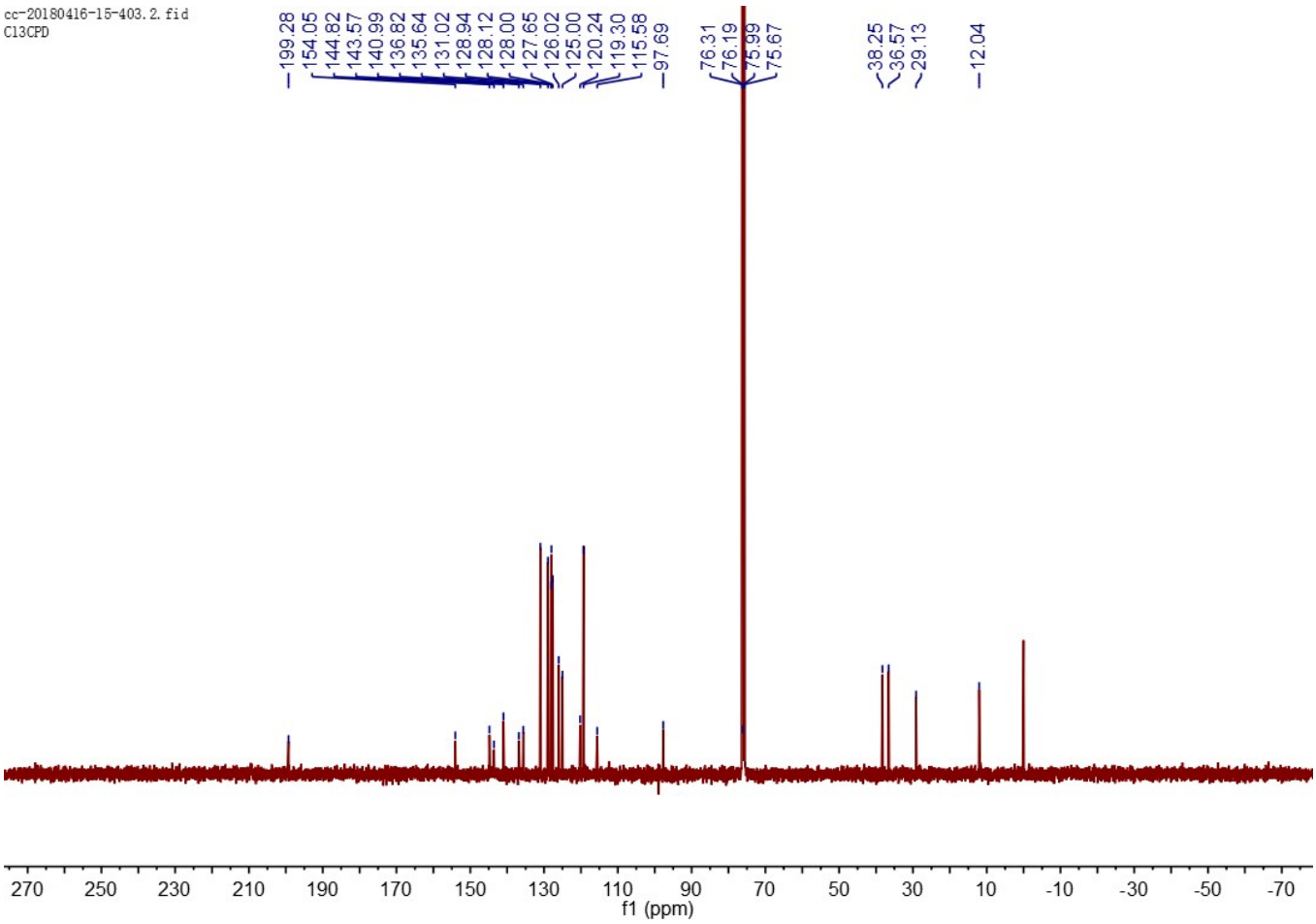
1-(6-Benzyl-4-(4-bromophenyl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3k):



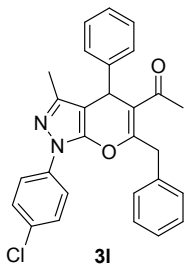
3k

Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48-7.45 (m, 4H), 7.42-7.23 (m, 8H), 7.14 (s, 2H), 5.05 (s, 1H), 4.08-3.95 (s, 2H), 2.22 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2, 154.0, 144.8, 141.0, 136.8, 135.6, 131.0, 128.9, 128.0, 127.6, 126.0, 125.0, 120.2, 119.3, 115.5, 97.7, 38.2, 36.5, 29.1, 12.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}BrN_2O_2$ $[M + H]^+$ 499.1016, found 499.1020.



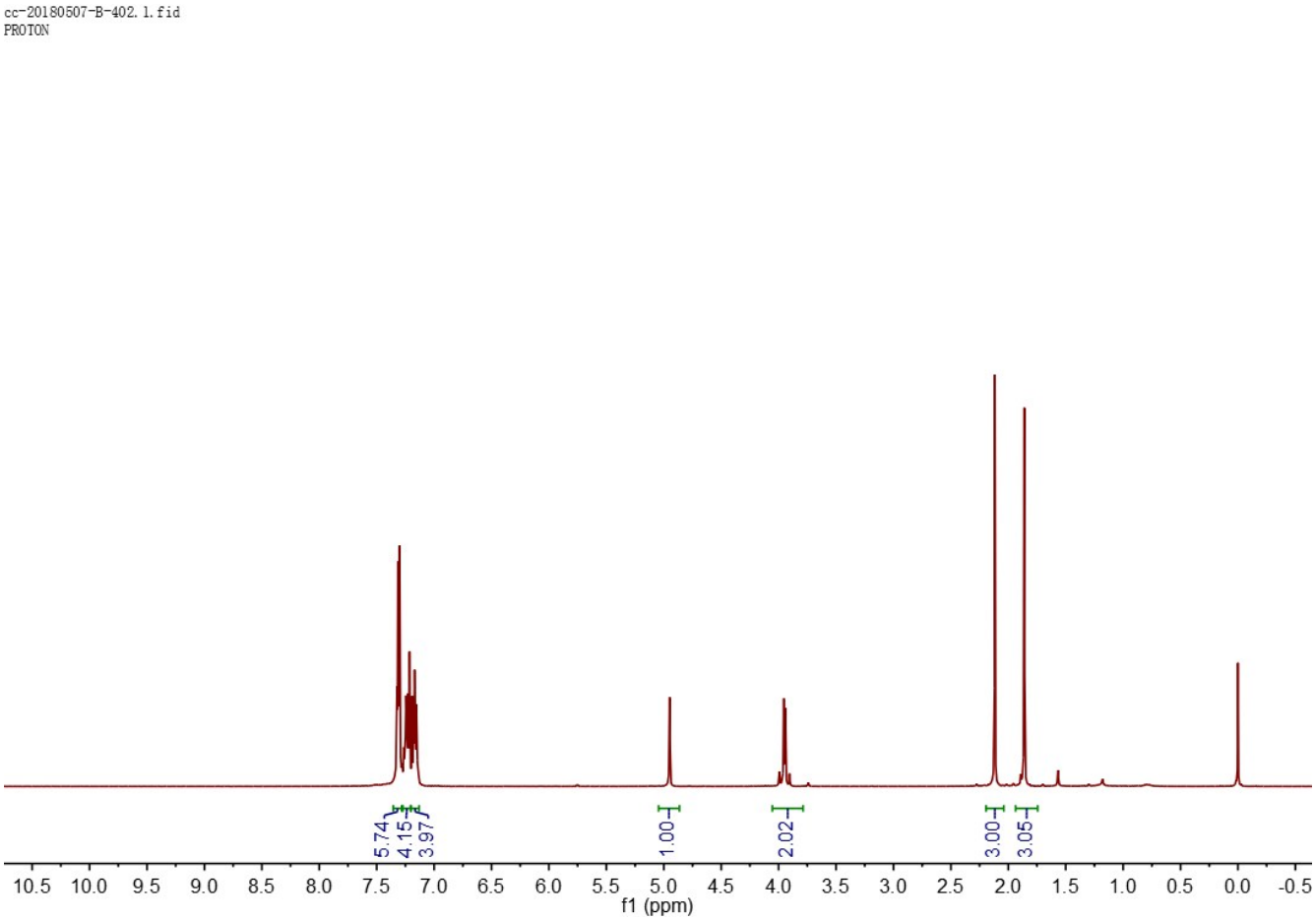


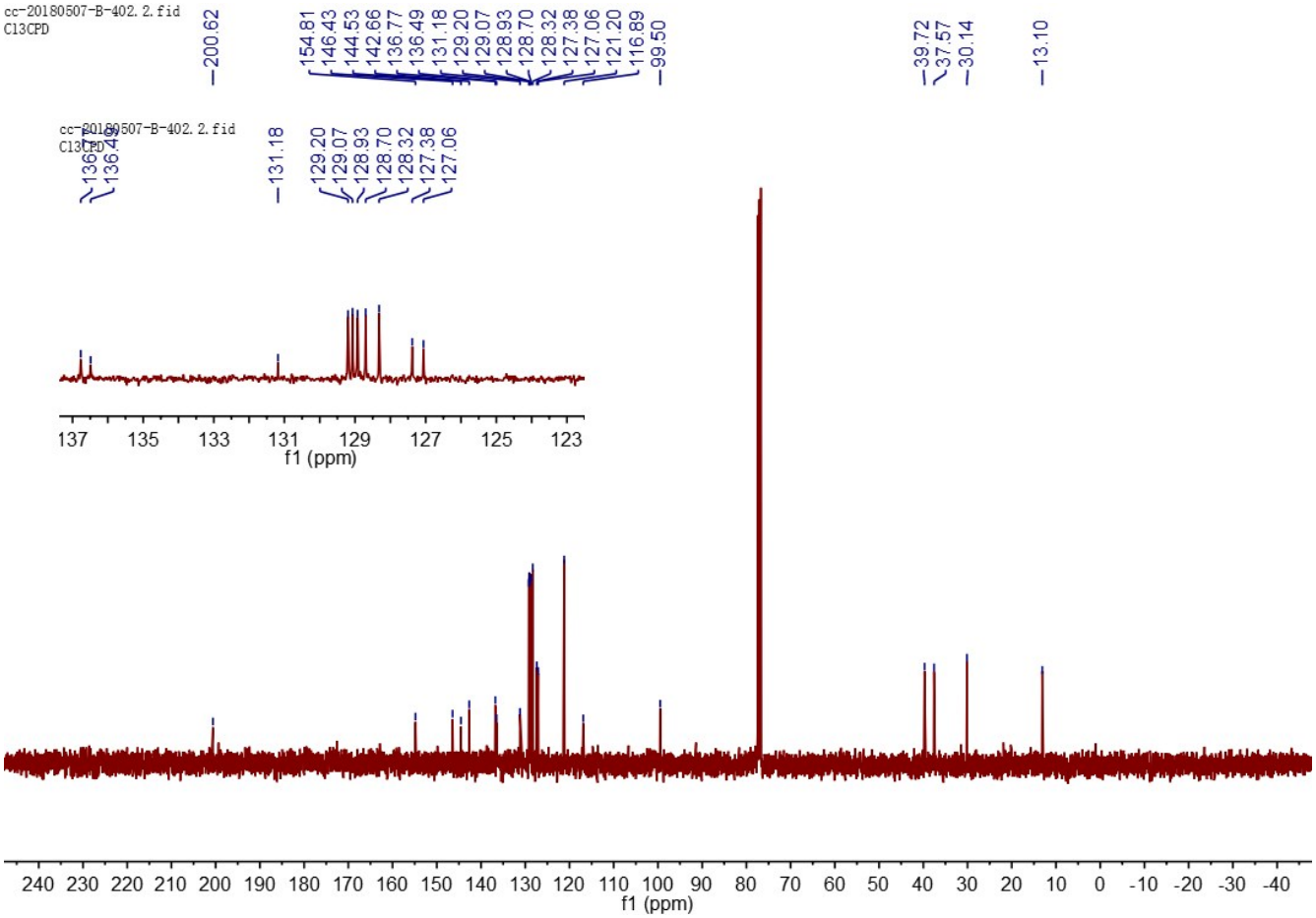
1-(6-Benzyl-1-(4-chlorophenyl)-3-methyl-4-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3l):



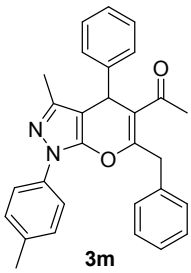
3l

Yellow solid, m.p. 104-105 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.29 (m, 6H), 7.27-7.21 (m, 4H), 7.17-7.08 (m, 4H), 4.95 (s, 1H), 4.05 (s, 2H), 2.12 (s, 3H), 1.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 155.0, 154.7, 146.7, 144.6, 142.6, 136.7, 131.2, 129.2, 129.0, 128.9, 128.1, 128.3, 127.3, 127.0, 121.2, 116.8, 99.5, 39.7, 37.5, 30.1, 13.1. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}ClN_2O_2$ $[M + H]^+$ 455.1521, found 455.1527.


cc-20180507-B-402.1.fid
PROTON
5.74
4.15
3.97
1.00
2.02
3.00
3.05
f1 (ppm)

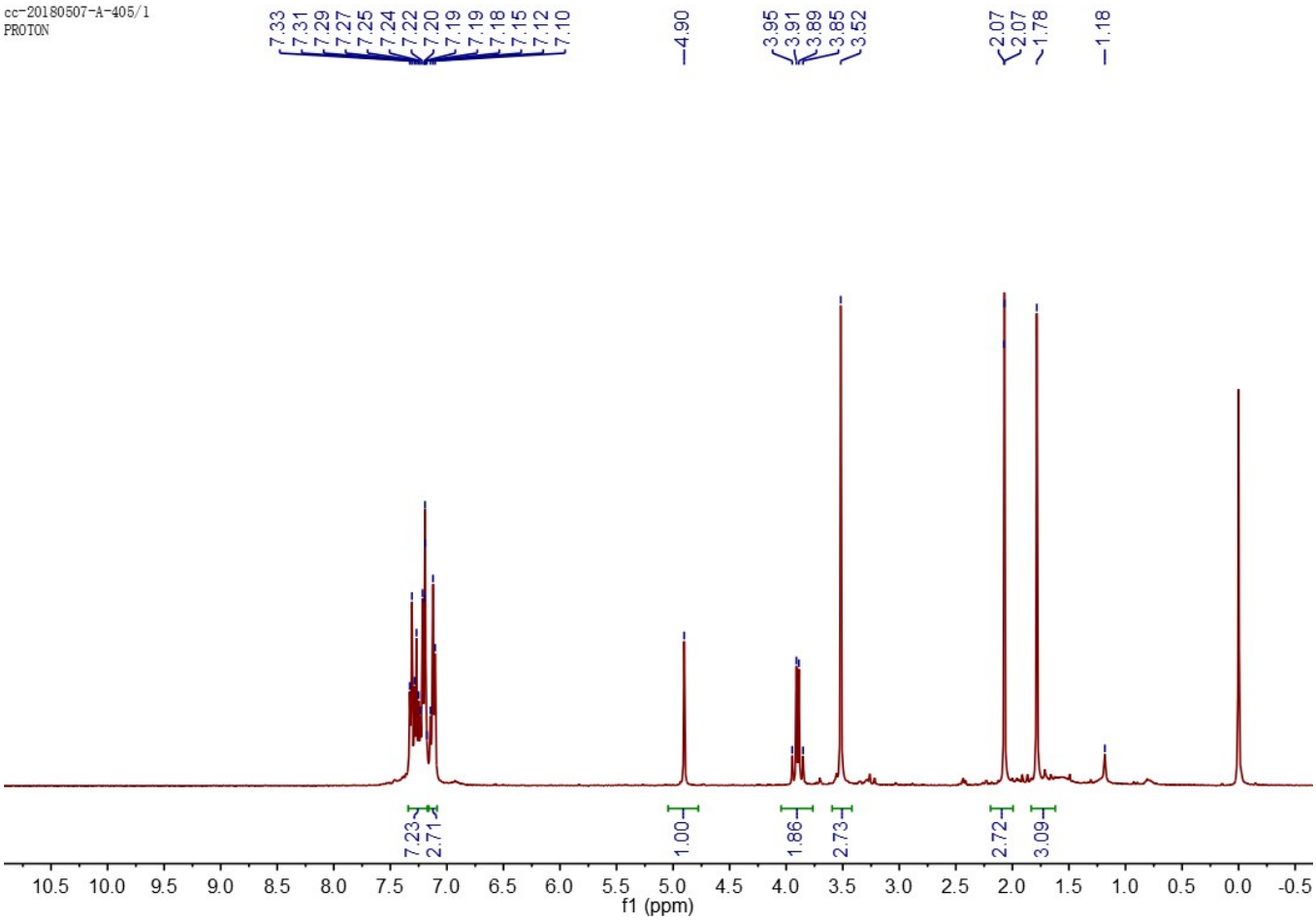

cc-20180507-B-402.2.fid
C13CPD
200.62
154.81
146.43
144.53
142.66
136.77
136.49
131.18
129.20
129.07
128.93
128.70
128.32
127.38
127.06
121.20
116.89
99.50
39.72
37.57
30.14
13.10
cc-20180507-B-402.2.fid
C13CPD
136.77
136.49
131.18
129.20
129.07
128.93
128.70
128.32
127.38
127.06
f1 (ppm)
f1 (ppm)

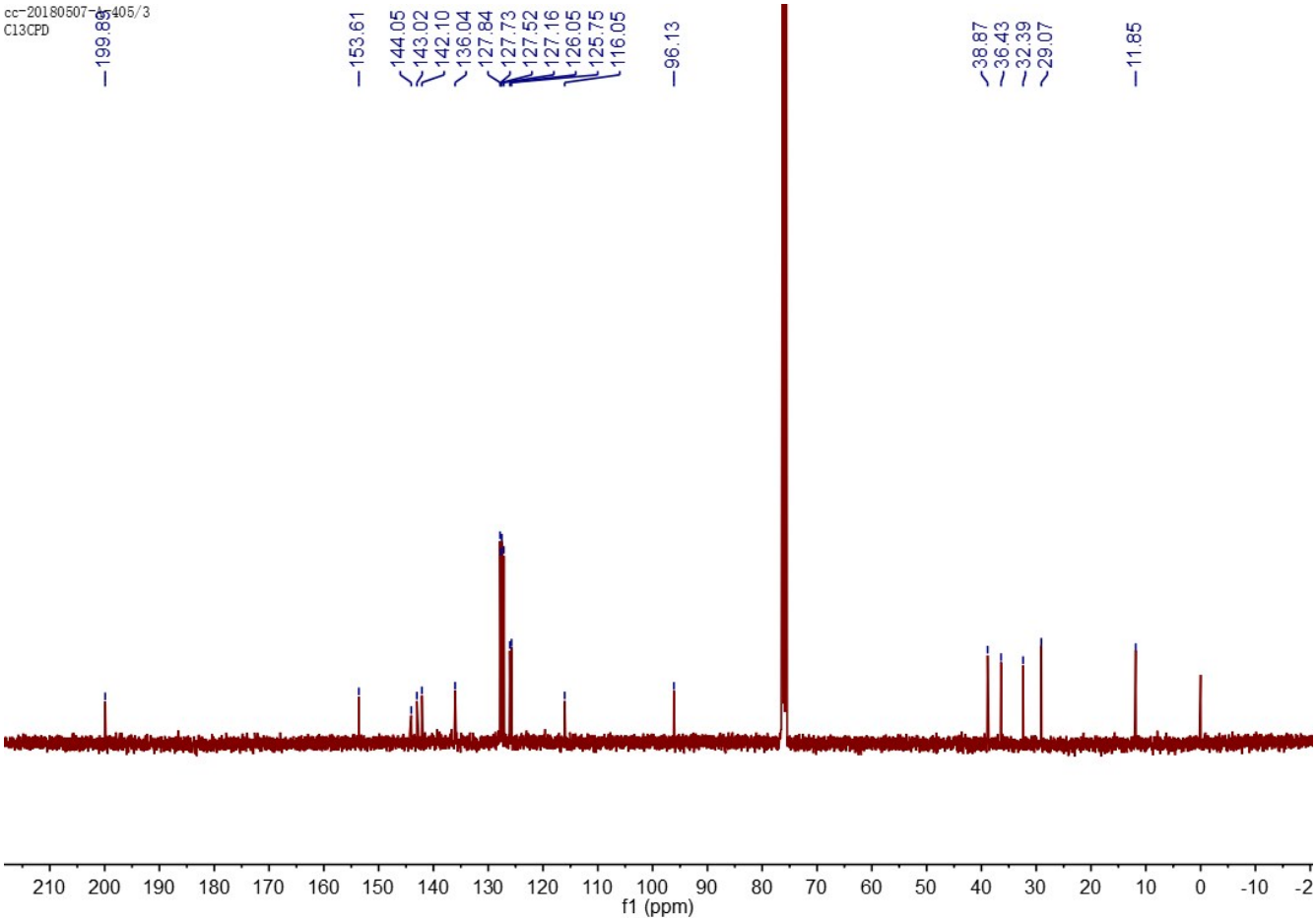
1-(6-Benzyl-3-methyl-4-phenyl-1-(*p*-tolyl)-1,4-dihydropyrano[2,3-c]pyrazol-5-yl)ethan-1-one (3m):



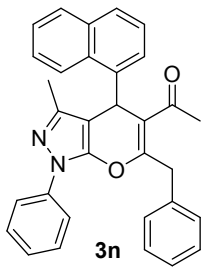
3m

Red solid, m.p. 100-102 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.08 (m, 14H), 4.90 (s, 1H), 3.90 (q, *J* = 14.6 Hz, 2H), 3.52 (s, 3H), 2.07 (s, 3H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.9, 153.6, 143.0, 142.1, 136.0, 127.8, 127.7, 127.5, 127.1, 126.0, 125.7, 116.0, 96.1, 38.8, 36.4, 32.3, 29.0, 11.8. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2071.



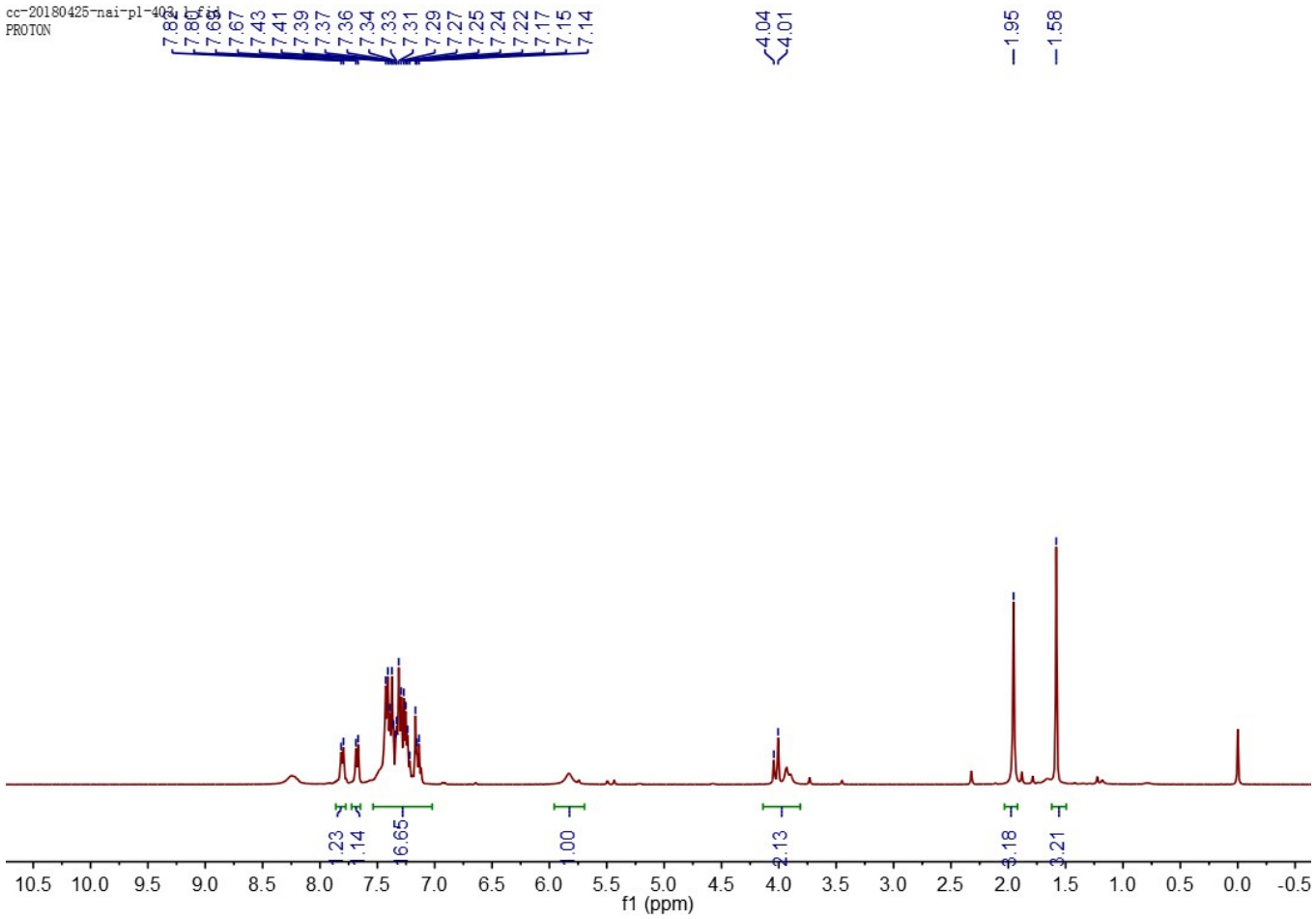


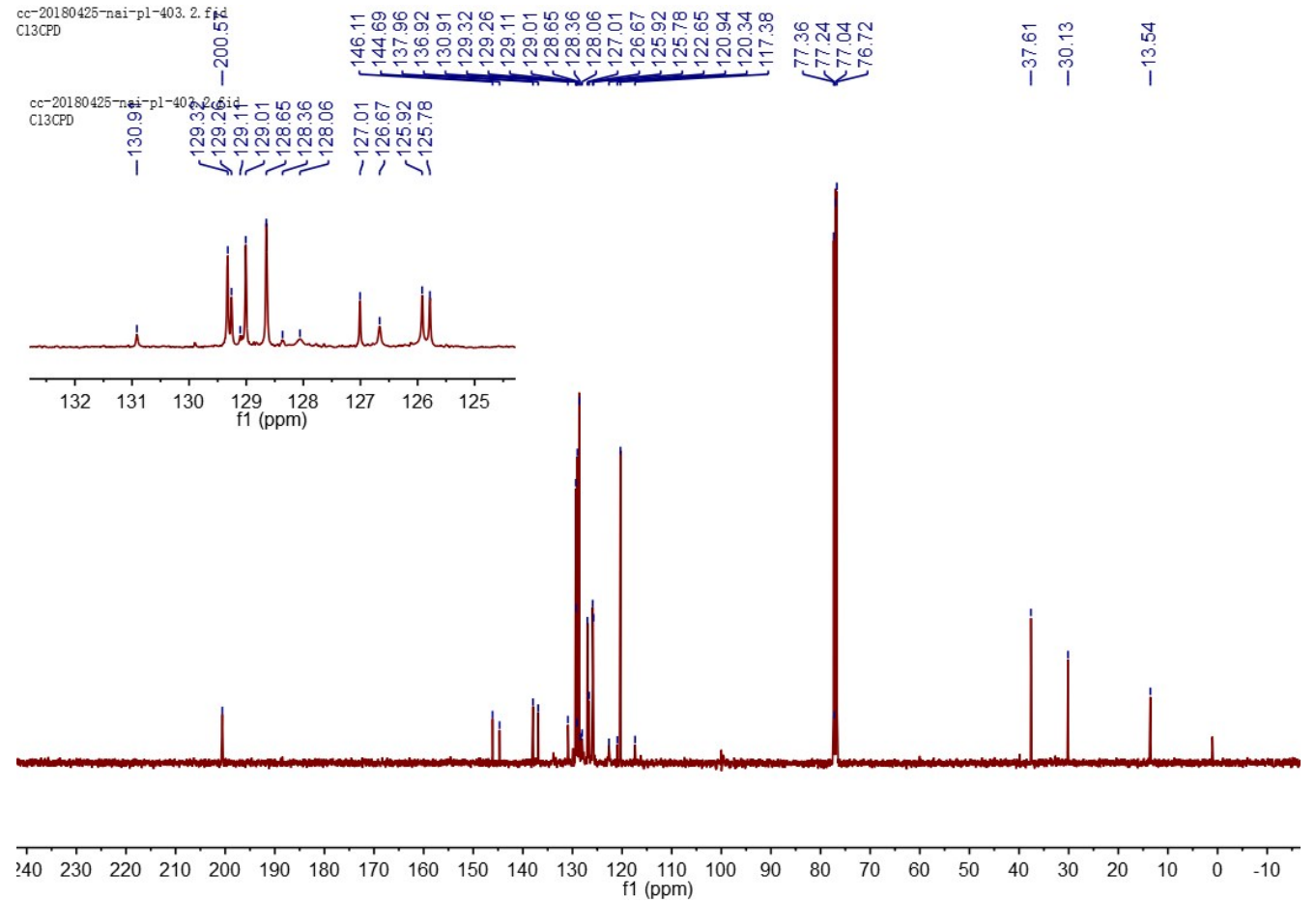
1-(6-Benzyl-3-methyl-4-(naphthalen-1-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3n):



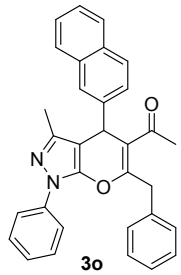
3n

Red solid, m.p. 135-137 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.76 (m, 3H), 7.47-7.21 (m, 12H), 7.14 (s, 2H), 5.83 (s, 1H), 3.97 (dd, *J* = 44.1, 14.6 Hz, 2H), 1.95 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 146.1, 144.7, 137.9, 136.9, 130.9, 129.9, 129.3, 129.2, 129.0, 128.6, 128.3, 128.0, 127.0, 126.6, 125.9, 125.8, 122.6, 120.9, 120.3, 117.3, 39.7, 37.6, 30.1, 13.5. HRMS (ESI) *m/z* calcd for $C_{32}H_{27}N_2O_2$ $[M + H]^+$ 471.2067, found 471.2066.

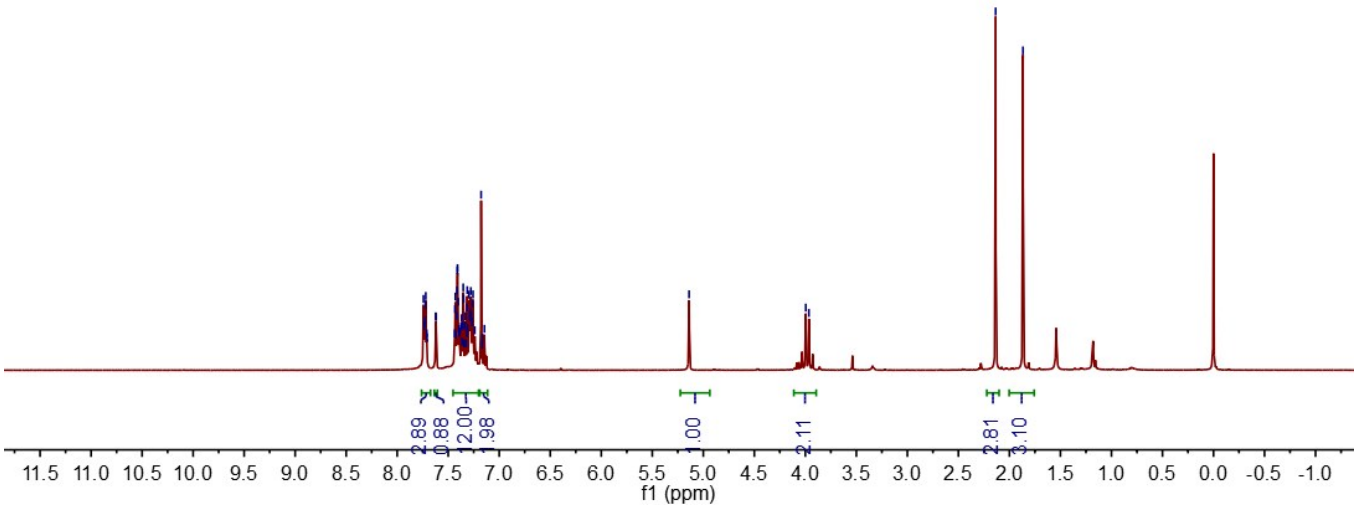

PROTON
7.82
7.80
7.68
7.67
7.43
7.41
7.39
7.37
7.36
7.34
7.33
7.31
7.29
7.27
7.25
7.24
7.22
7.17
7.15
7.14
4.04
4.01
1.95
1.58
1.23
1.14
16.65
1.00
2.13
3.18
3.21
f1 (ppm)

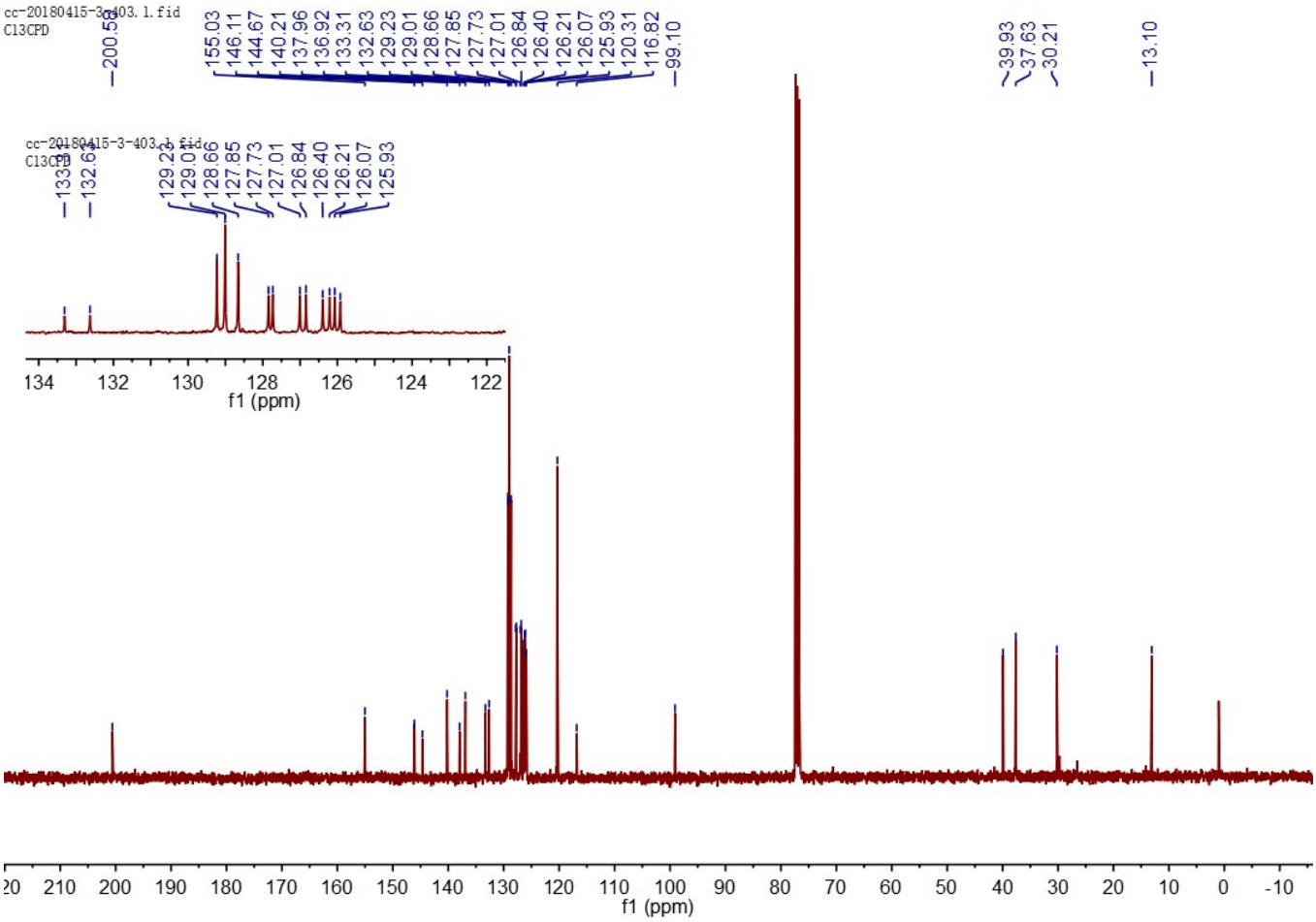

C13CPD
200.51
146.11
144.69
137.96
136.92
130.91
129.32
129.26
129.11
129.01
128.65
128.36
128.06
127.01
126.67
125.92
125.78
122.65
120.94
120.34
117.38
77.36
77.24
77.04
76.72
37.61
30.13
13.54
f1 (ppm)

1-(6-Benzyl-3-methyl-4-(naphthalen-2-yl)-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3o):

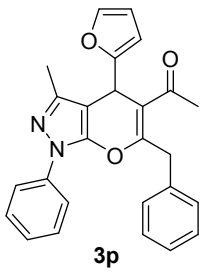


Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.70 (m, 3H), 7.62 (s, 1H), 7.46-7.21 (m, 12H), 7.15 (s, 1H), 5.14 (s, 1H), 3.98 (q, J = 14.9 Hz, 2H), 2.14 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 155.0, 146.1, 144.6, 140.2, 137.9, 136.9, 133.3, 132.6, 129.2, 129.0, 128.6, 127.8, 127.7, 127.0, 126.8, 126.4, 126.2, 126.0, 125.9, 120.3, 116.8, 99.1, 39.9, 37.6, 30.2, 13.1. HRMS (ESI) *m/z* calcd for $C_{32}H_{27}N_2O_2$ $[M + H]^+$ 471.2067, found 471.2061.



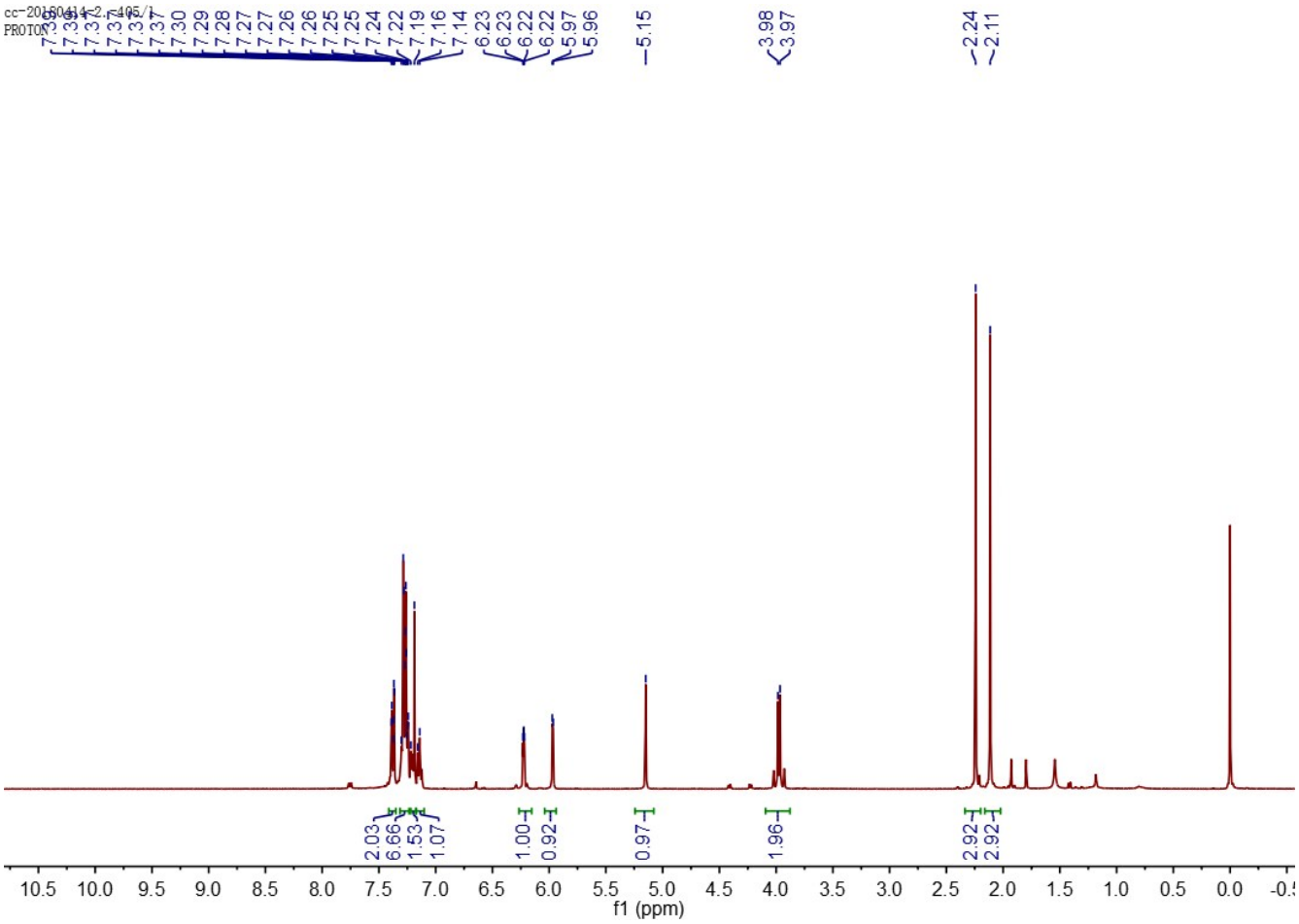


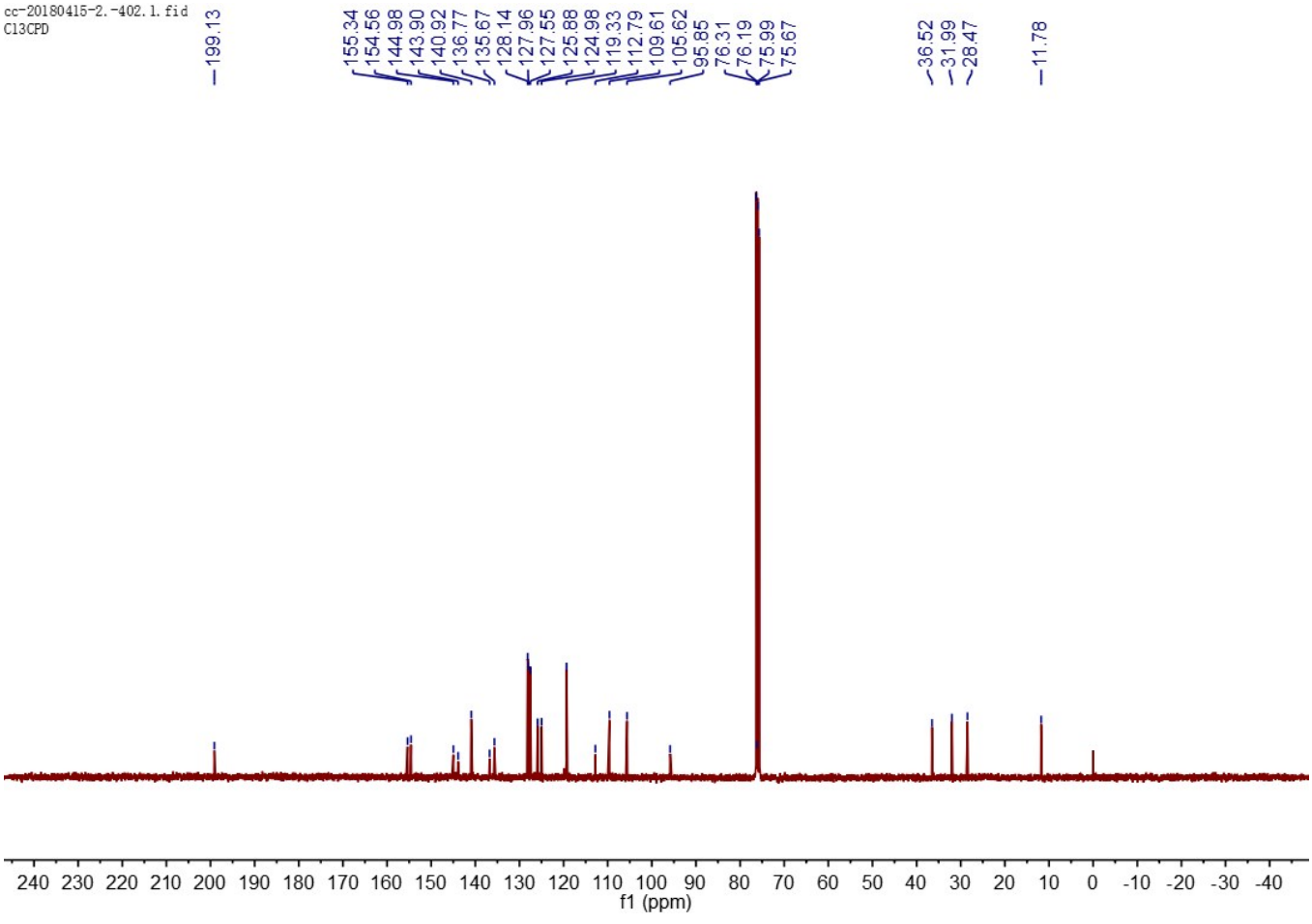
1-(6-Benzyl-4-(furan-2-yl)-3-methyl-1-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3p):



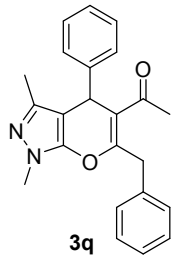
3p

Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.31-7.20 (m, 8H), 7.14 (s, 1H), 6.22 (dd, *J* = 3.1, 1.9 Hz, 1H), 5.97 (d, *J* = 3.2 Hz, 1H), 5.15 (s, 1H), 3.97 (d, *J* = 7.4 Hz, 2H), 2.24 (s, 3H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 155.3, 154.5, 144.9, 143.9, 140.9, 136.7, 135.6, 128.1, 127.9, 127.5, 125.9, 124.9, 119.3, 112.8, 109.6, 105.6, 95.8, 36.5, 31.9, 28.4, 11.7. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_2O_3$ $[M+H]^+$ 411.1703, found 411.1701.


PROTON
7.39 7.37 7.30 7.29 7.28 7.27 7.27 7.26 7.26 7.25 7.25 7.24 7.22 7.19 7.16 7.14
6.23 6.23 6.22 6.22 5.97 5.96
5.15
3.98 3.97
2.24 2.11
2.03 6.66 1.53 1.07 1.00 0.92 0.97 1.96 2.92 2.92
10.5 10.0 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
f1 (ppm)

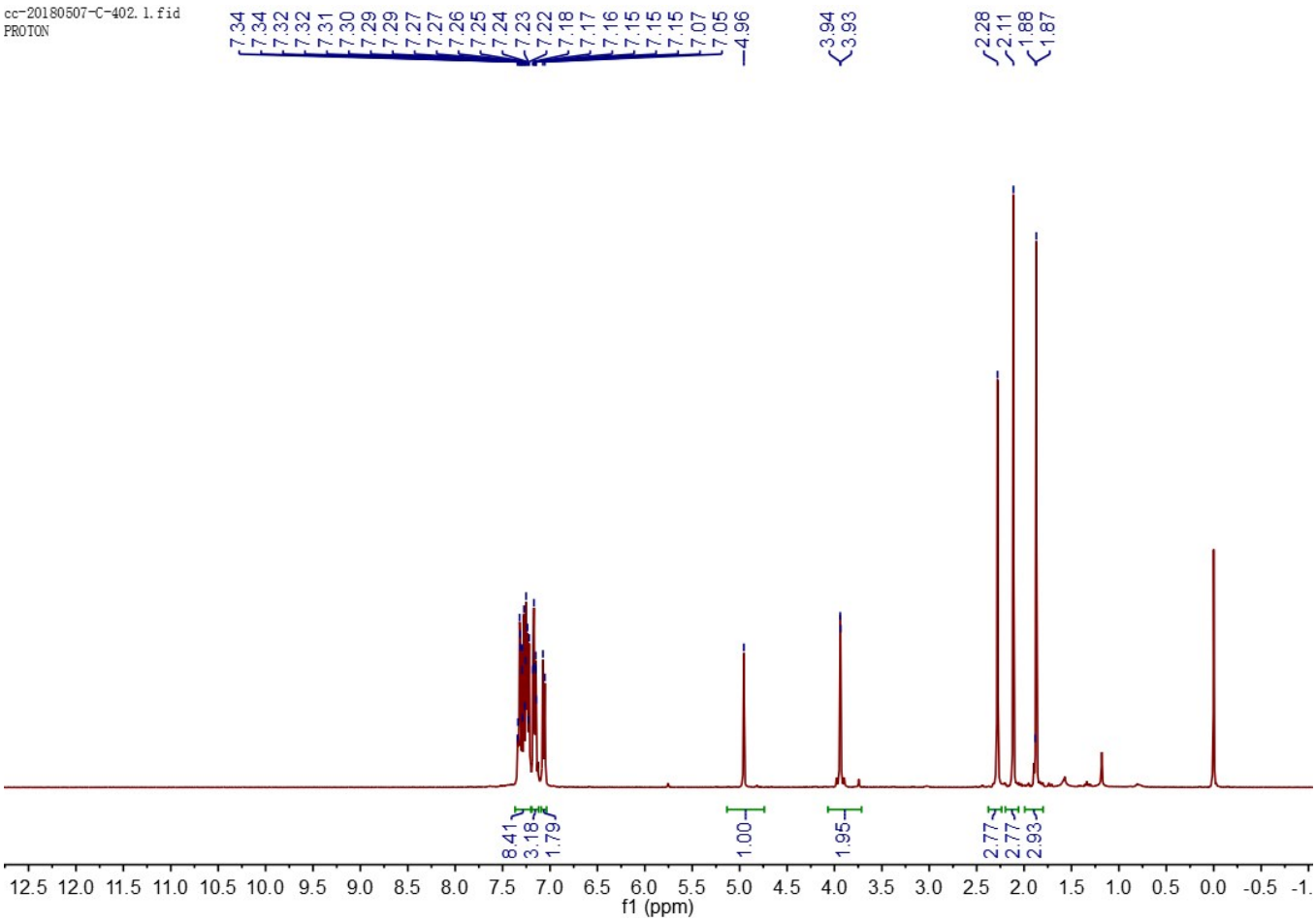

C13CPD
199.13
155.34 154.56 144.98 143.90 140.92 136.77 135.67 128.14 127.96 127.55 125.88 124.98 119.33 112.79 109.61 105.62 95.85 76.31 76.19 75.99 75.67
36.52 31.99 28.47
11.78
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

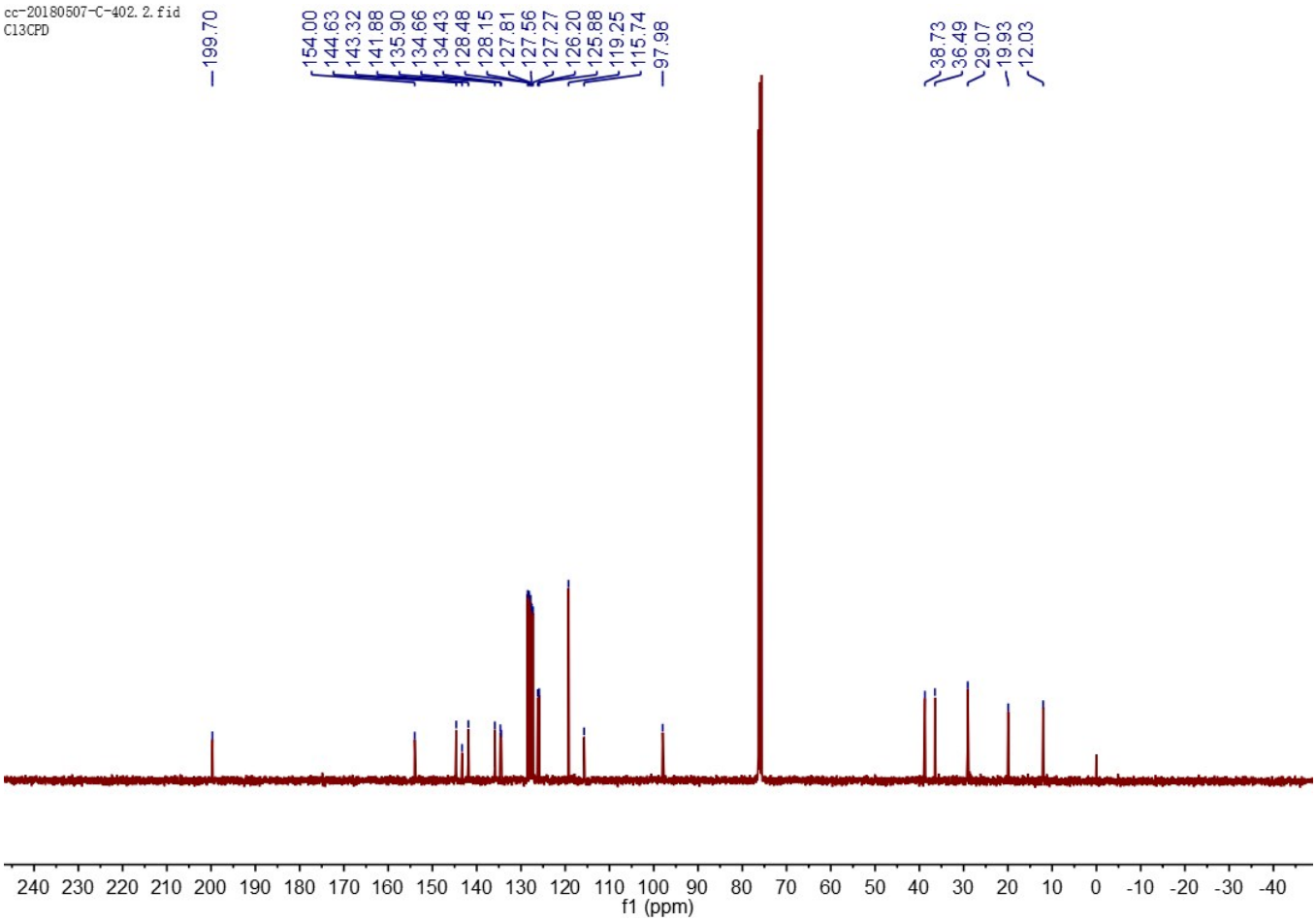
1-(6-Benzyl-1,3-dimethyl-4-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3q):



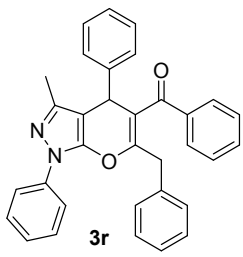
3q

Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.21 (m, 5H), 7.17-7.09 (m, 3H), 7.06 (s, 2H), 4.96 (s, 1H), 3.94 (s, 2H), 2.28 (s, 3H), 2.11 (s, 3H), 1.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.7, 154.0, 144.6, 143.3, 141.8, 135.9, 134.6, 134.4, 128.5, 128.1, 127.8, 127.5, 127.2, 126.2, 125.9, 119.2, 115.7, 97.9, 38.7, 36.4, 29.0, 19.9, 12.0. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}N_2O_2$ $[M + H]^+$ 359.1754, found 359.1756.

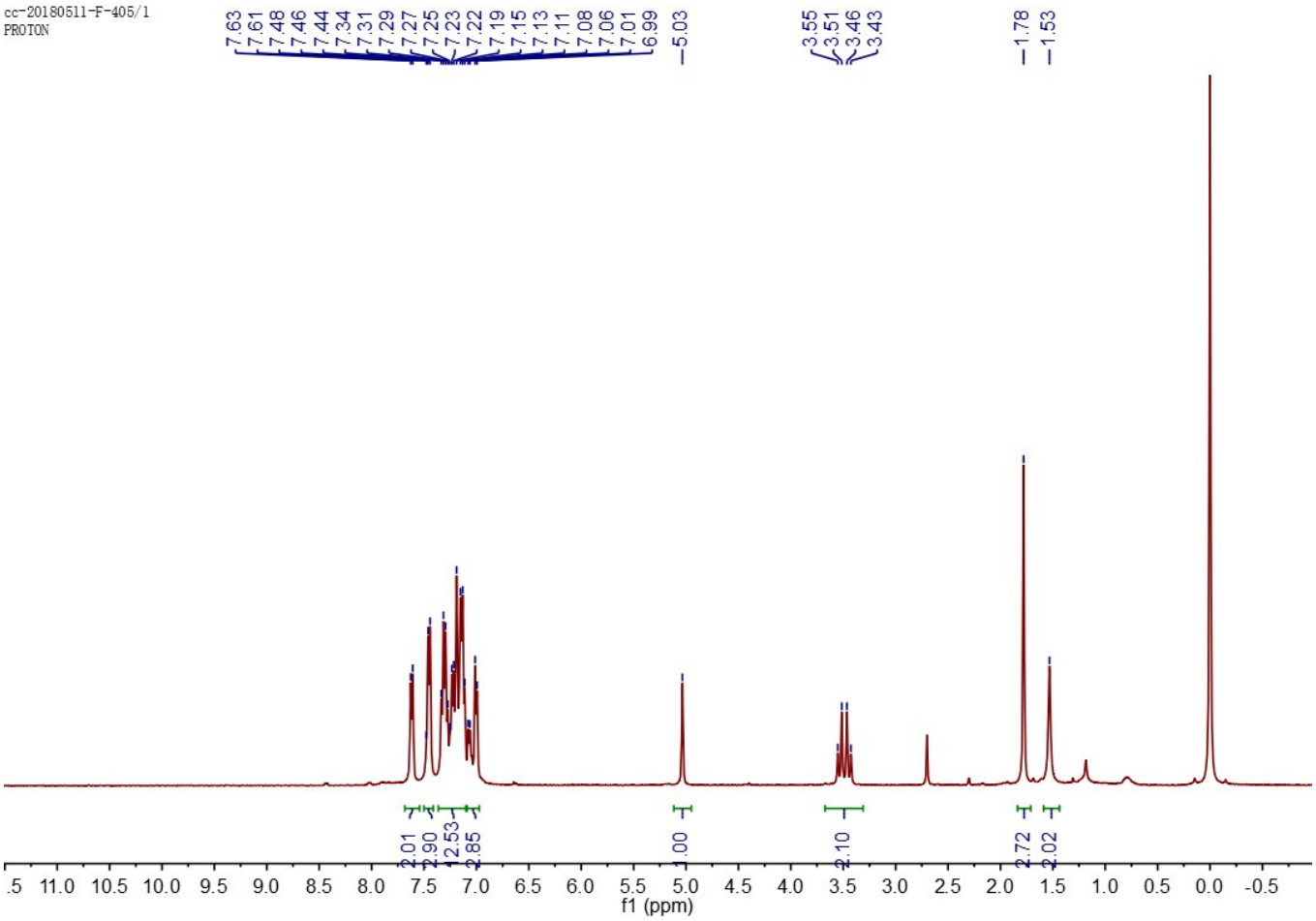


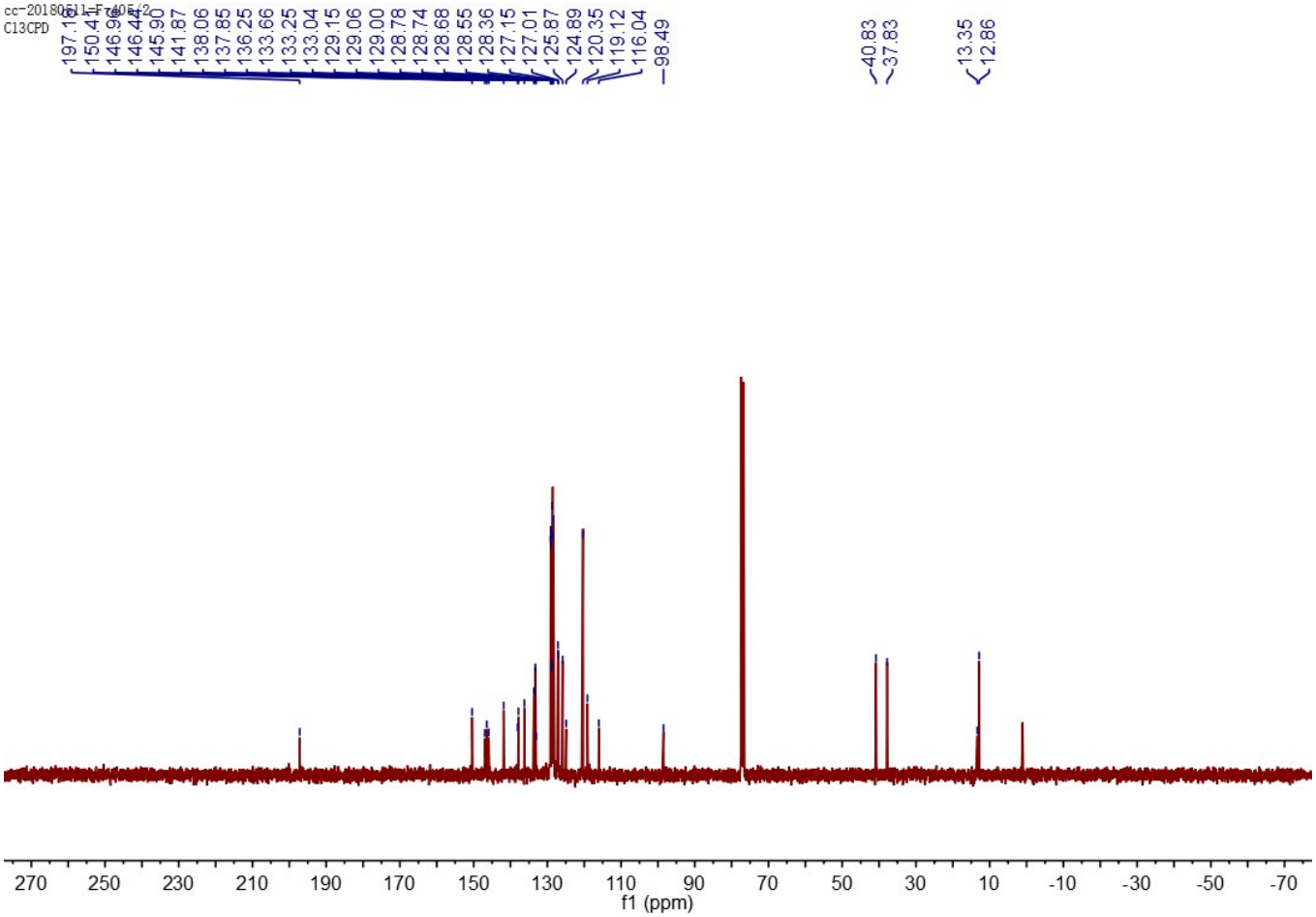


(6-Benzyl-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)(phenyl)methanone (3r):

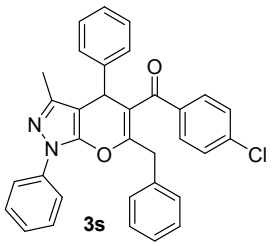


Red solid, m.p. 193-195 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.3 Hz, 3H), 7.30 (dd, *J* = 16.0, 7.9 Hz, 4H), 7.25-7.10 (m, 12H), 7.00 (d, *J* = 7.2 Hz, 2H), 5.03 (s, 1H), 3.49 (dd, *J* = 35.1, 15.0 Hz, 2H), 1.78 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2, 150.4, 146.9, 146.4, 145.9, 141.8, 138.8, 137.8, 136.2, 133.6, 133.2, 133.1, 133.0, 129.0, 128.7, 128.5, 128.5, 128.3, 124.9, 119.1, 116.5, 98.4, 40.8, 37.8, 12.8. HRMS (ESI) *m/z* calcd for $C_{33}H_{27}N_2O_2^+$ $[M + H]^+$ 483.2067, found 483.2069.


cc-20180511-F-405/1
PROTON
7.63
7.61
7.48
7.46
7.44
7.34
7.31
7.29
7.27
7.25
7.23
7.22
7.19
7.15
7.13
7.11
7.08
7.06
7.01
6.99
5.03
3.55
3.51
3.46
3.43
1.78
1.53
2.01
2.90
2.53
2.85
1.00
2.10
2.72
2.02
f1 (ppm)


C13CPD
197.16
150.47
146.96
146.44
145.90
141.87
138.06
137.85
136.25
133.66
133.25
133.04
129.15
129.06
129.00
128.78
128.74
128.68
128.55
128.36
127.15
127.01
125.87
124.89
120.35
119.12
116.04
98.49
40.83
37.83
13.35
12.86
f1 (ppm)

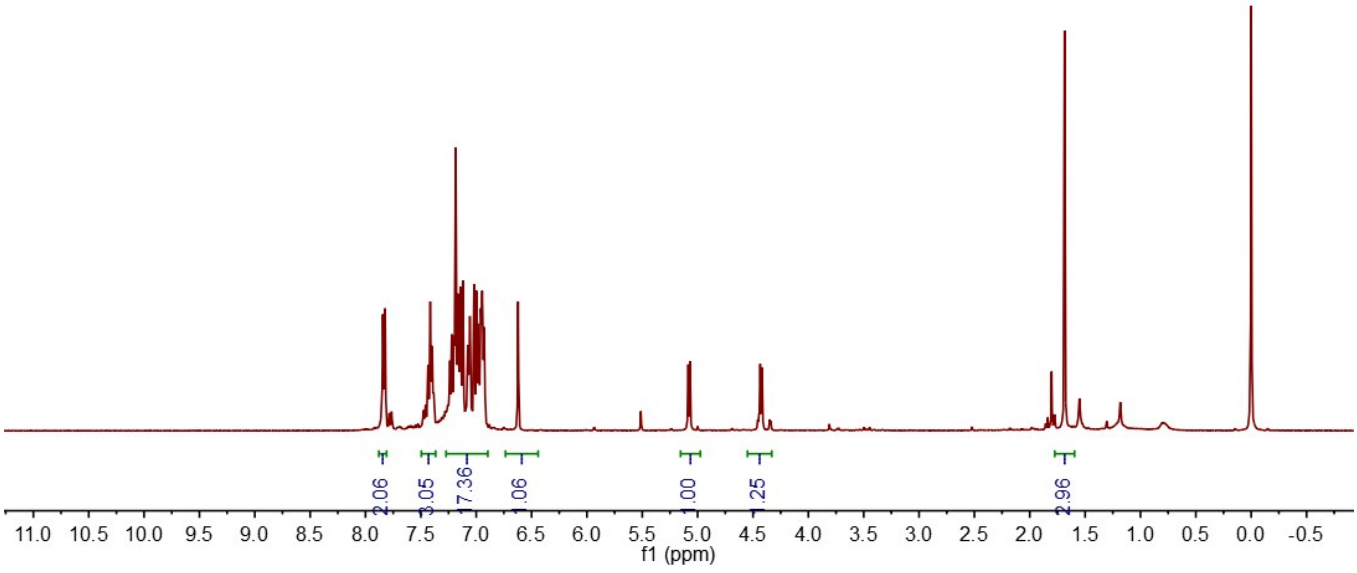
(6-Benzyl-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)(4-chlorophenyl) methanonee (3s):

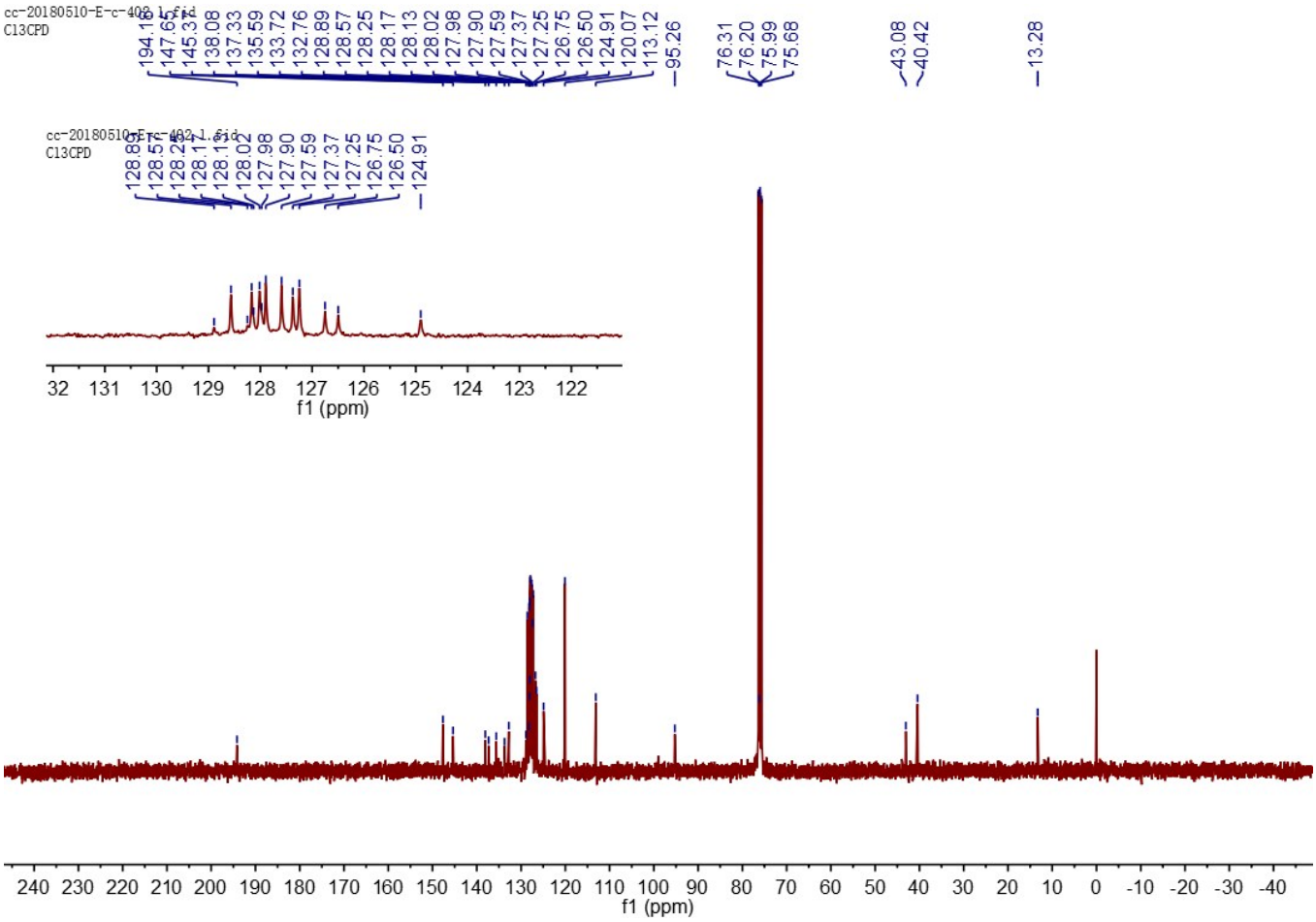


3s

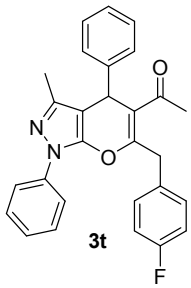
Red solid, m.p. 161-163 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2H), 7.42-7.39 (m, 3H), 7.17-6.89 (m, 14H), 6.62 (s, 1H), 5.08 (d, *J* = 6.7 Hz, 1H), 4.43 (d, *J* = 6.7 Hz, 1H), 1.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.2, 147.6, 145.3, 138.09, 135.6, 132.7, 128.5, 128.1, 128.0, 127.9, 127.6, 127.3, 127.2, 126.7, 126.5, 124.9, 120.0, 113.1, 95.2, 43.0, 40.4, 13.2. HRMS (ESI) *m/z* calcd for $C_{33}H_{26}ClN_2O_2$ $[M + H]^+$ 517.1677, found 517.1678.

cc-20180507-E-405/1
PROTON



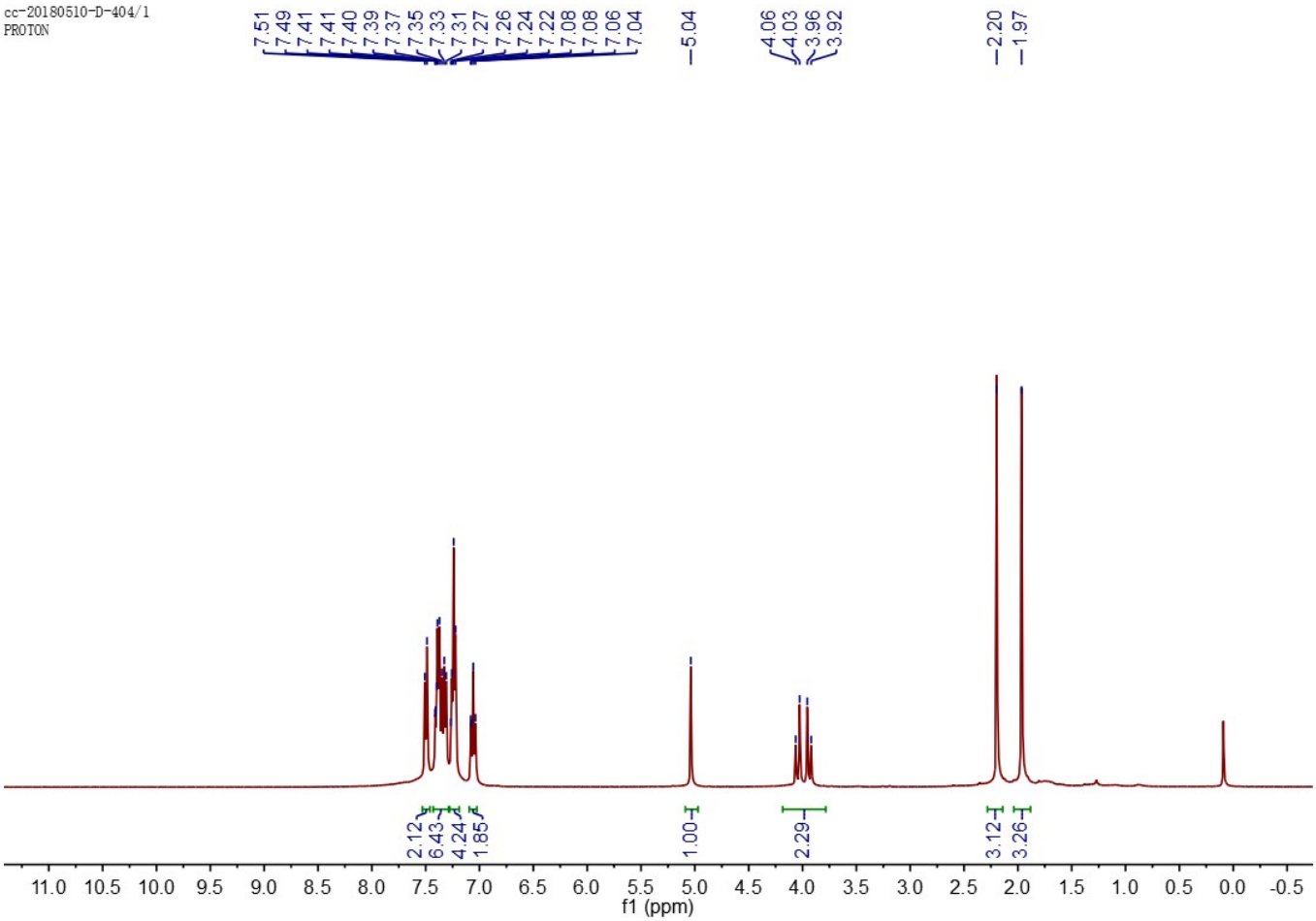


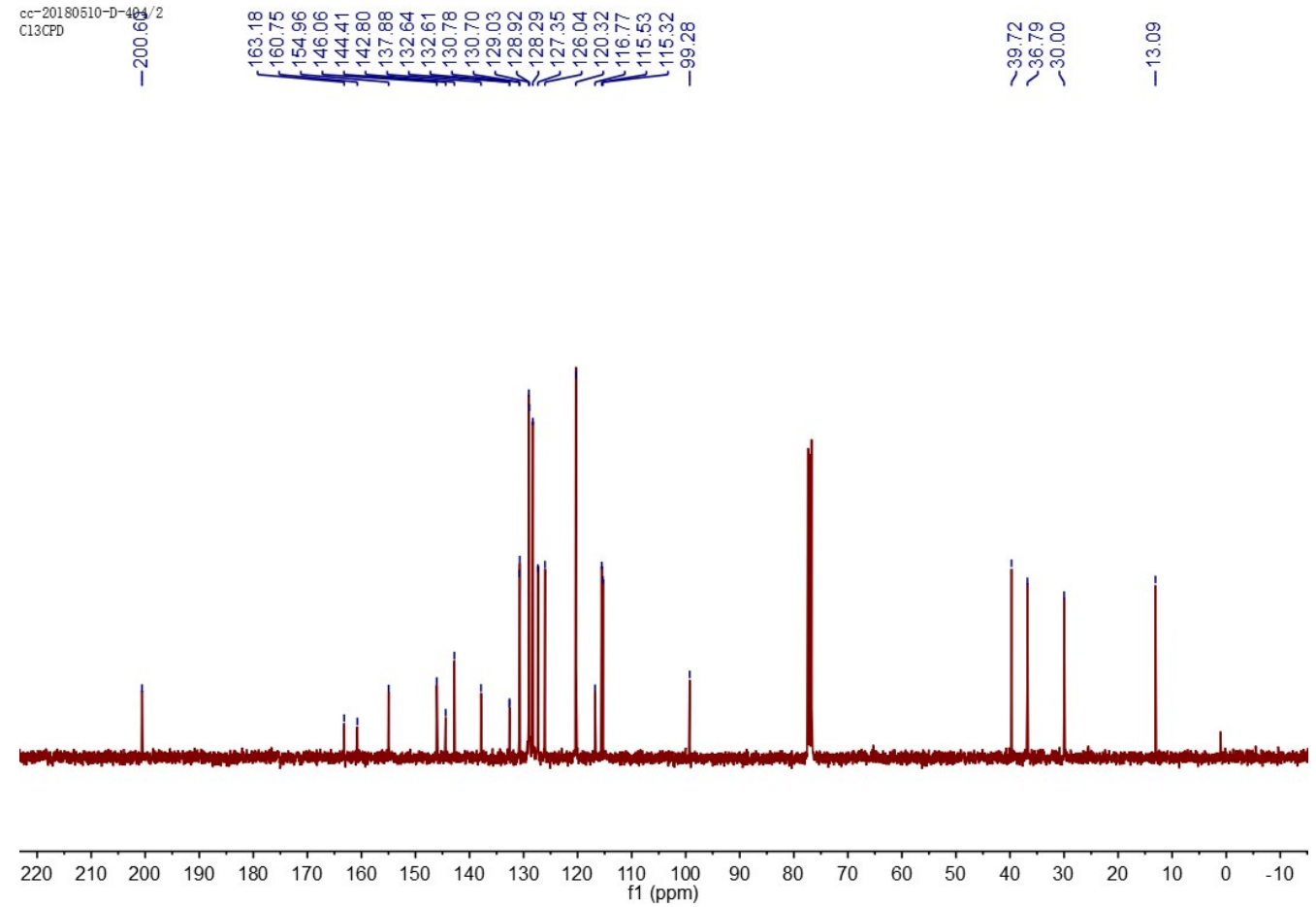
1-(6-(4-Fluorobenzyl)-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)ethan-1-one (3t):



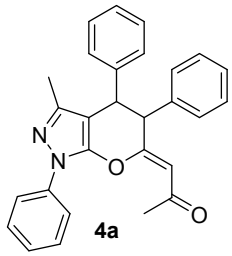
3t

Red solid, m.p. 108-110 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 2H), 7.36-7.33 (m, 6H), 7.24-7.21 (m, 4H), 7.06 (s, 2H), 5.04 (s, 1H), 3.99 (dd, *J* = 42.8, 14.9 Hz, 2H), 2.20 (s, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.6, 163.2, 160.7, 154.9, 146.0, 144.4, 142.8, 137.9, 132.6 (d, J = 3.0 Hz), 130.7 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 11.0 Hz), 127.3, 126.0, 120.3, 116.7, 115.5 (d, *J* = 22.0 Hz), 99.2, 39.7, 36.7, 30.0, 13.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}FN_2O_2^+$ $[M + H]^+$ 439.1816, found 439.1817.

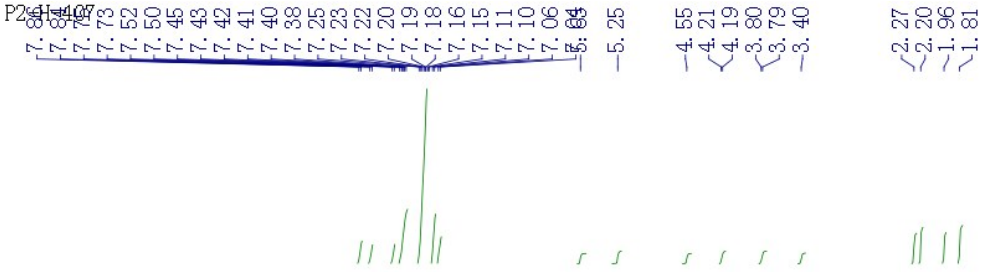

cc-20180510-D-404/1
PROTON
7.51
7.49
7.41
7.41
7.40
7.39
7.37
7.35
7.33
7.31
7.27
7.26
7.24
7.22
7.08
7.08
7.06
7.04
5.04
4.06
4.03
3.96
3.92
2.20
1.97
2.12
6.43
4.24
1.85
1.00
2.29
3.12
3.26
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

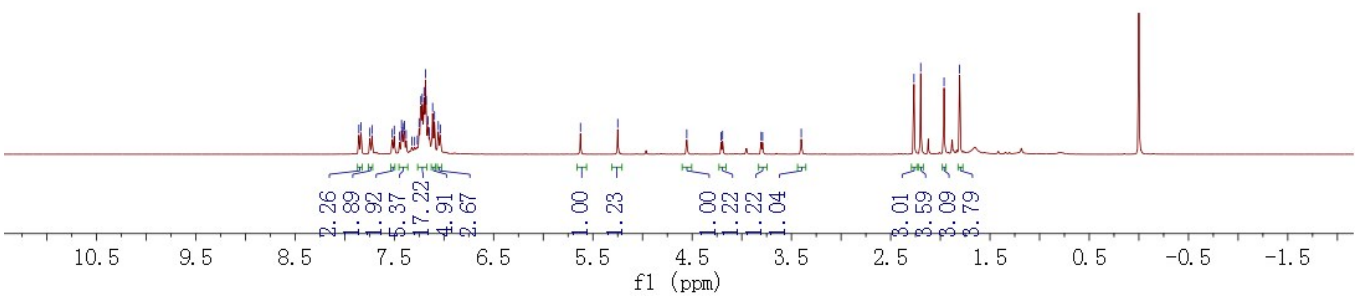

cc-20180510-D-404/2
C13CPD
200.65
163.18
160.75
154.96
146.06
144.41
142.80
137.88
132.64
132.61
130.78
130.70
129.03
128.92
128.29
127.35
126.04
120.32
116.77
115.53
115.32
99.28
39.72
36.79
30.00
13.09
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

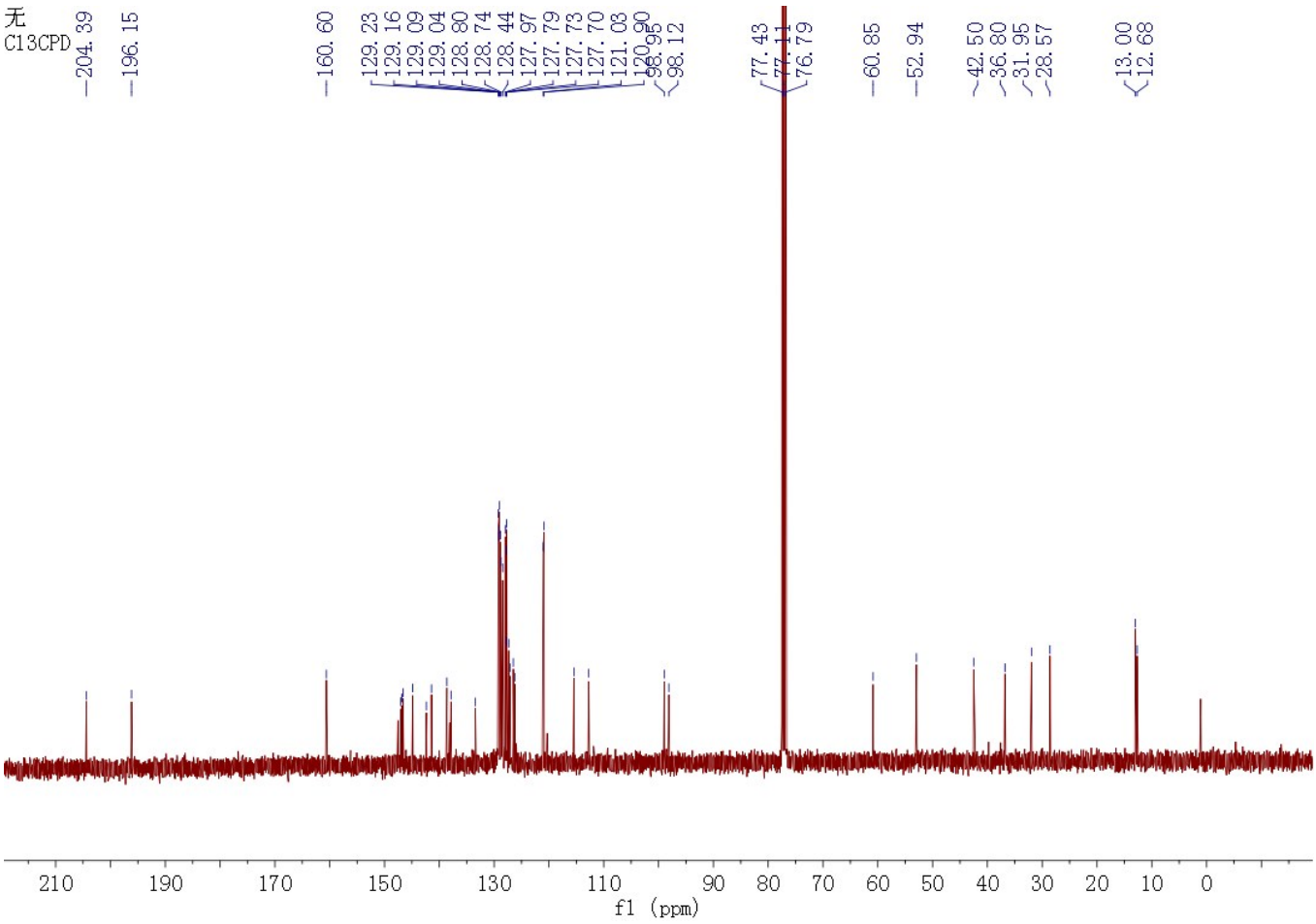
(*Z*)-1-(3-Methyl-1,4,5-triphenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)propan-2-one (4a):



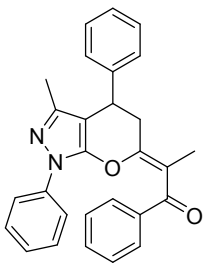
Red solid, m.p. 160-162 ˚C. Major diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 1H), 7.74 (s, 1H), 7.51-7.49 (m,1H), 7.41-7.38 (m, 3H), 7.21-7.18 (m, 6H), 7.10-7.07 (m, 2H), 7.05-7.03 (m, 1H), 5.25 (s, 1H), 3.80 (d, *J* = 5.5 Hz, 1H), 3.40 (s, 1H), 2.20 (s, 3H), 1.81 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.3, 160.6, 147.3, 144.8, 142.3, 141.4, 138.6, 133.4, 129.2, 129.0, 128.8, 127.9, 127.7, 127.1, 126.5 121.0, 120.9, 115.4, 98.9, 60.8, 42.5, 31.9, 13.0. Minor diastereoisomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.83 (m, 1H), 7.74 (s, 1H), 7.51-7.49 (m, 1H), 7.41-7.38 (m, 2H), 7.21-7.18 (m, 5H), 7.10-7.07 (m, 3H), 7.05-7.03 (m, 2H), 5.63 (s, 1H), 4.55 (s, 1H), 4.20 (d, *J* = 5.5 Hz, 1H), , 2.27 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.1, , 146.8, 146.6, 137.8, 129.1, 129.0, 128.7, 128.4, 127.7, 127.7, 127.3, 126.2, 112.7, 98.1, 52.9, 36.8, 28.5, 12.6. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O_2$ $[M + H]^+$ 421.1911, found 421.1914.





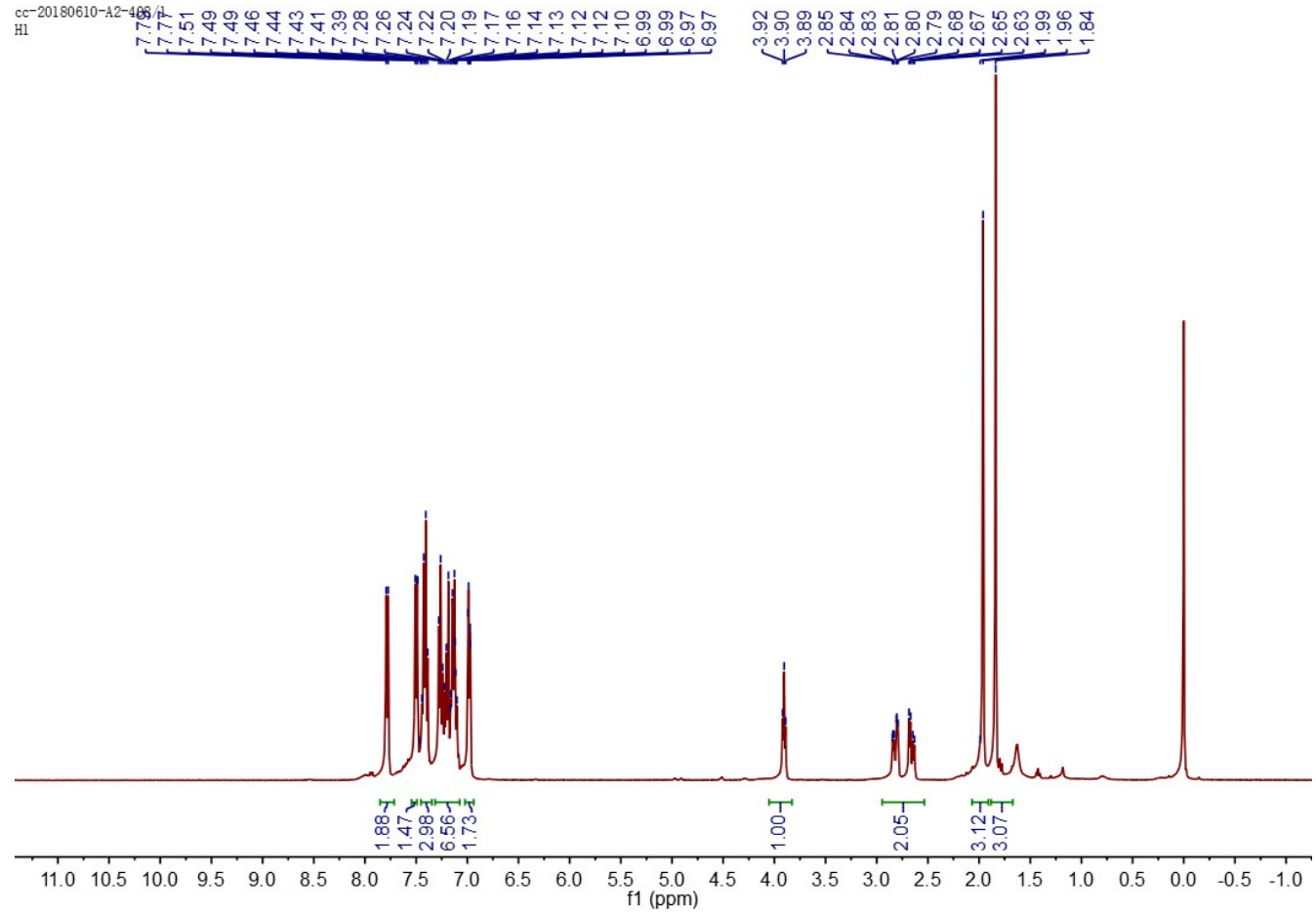


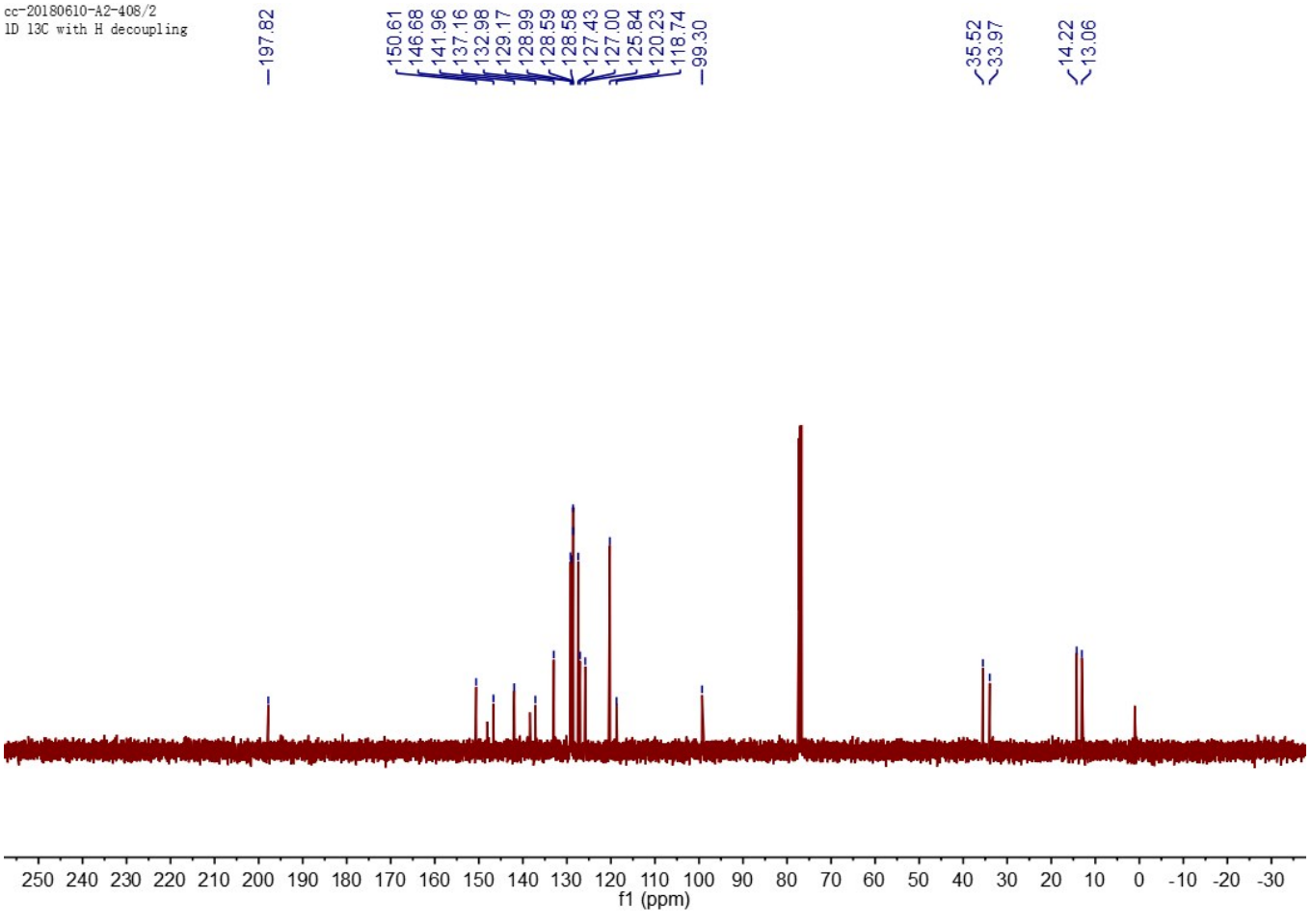
(*E*)-2-(3-Methyl-1,4-diphenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4b):



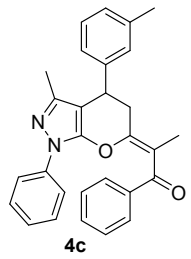
4b

Orange solid, m.p. 131-133 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.54-7.36 (m, 4H), 7.31-7.08 (m, 7H), 6.98 (d, *J* = 5.9 Hz, 2H), 3.90 (t, *J* = 5.9 Hz, 1H), 2.74 (ddd, *J* = 64.3, 14.8, 5.9 Hz, 2H), 1.96 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 150.6, 148.1, 146.6, 141.9, 138.4, 137.1, 132.9, 129.1, 129.0, 128.6, 127.4, 127.0, 125.8, 120.2, 118.7, 99.3, 35.2, 33.9, 14.2, 13.0. HRMS (ESI) *m/z* calcd for $C_{28}H_{25}N_2O_2$ $[M+H]^+$ 421.1911, found 421.1914.

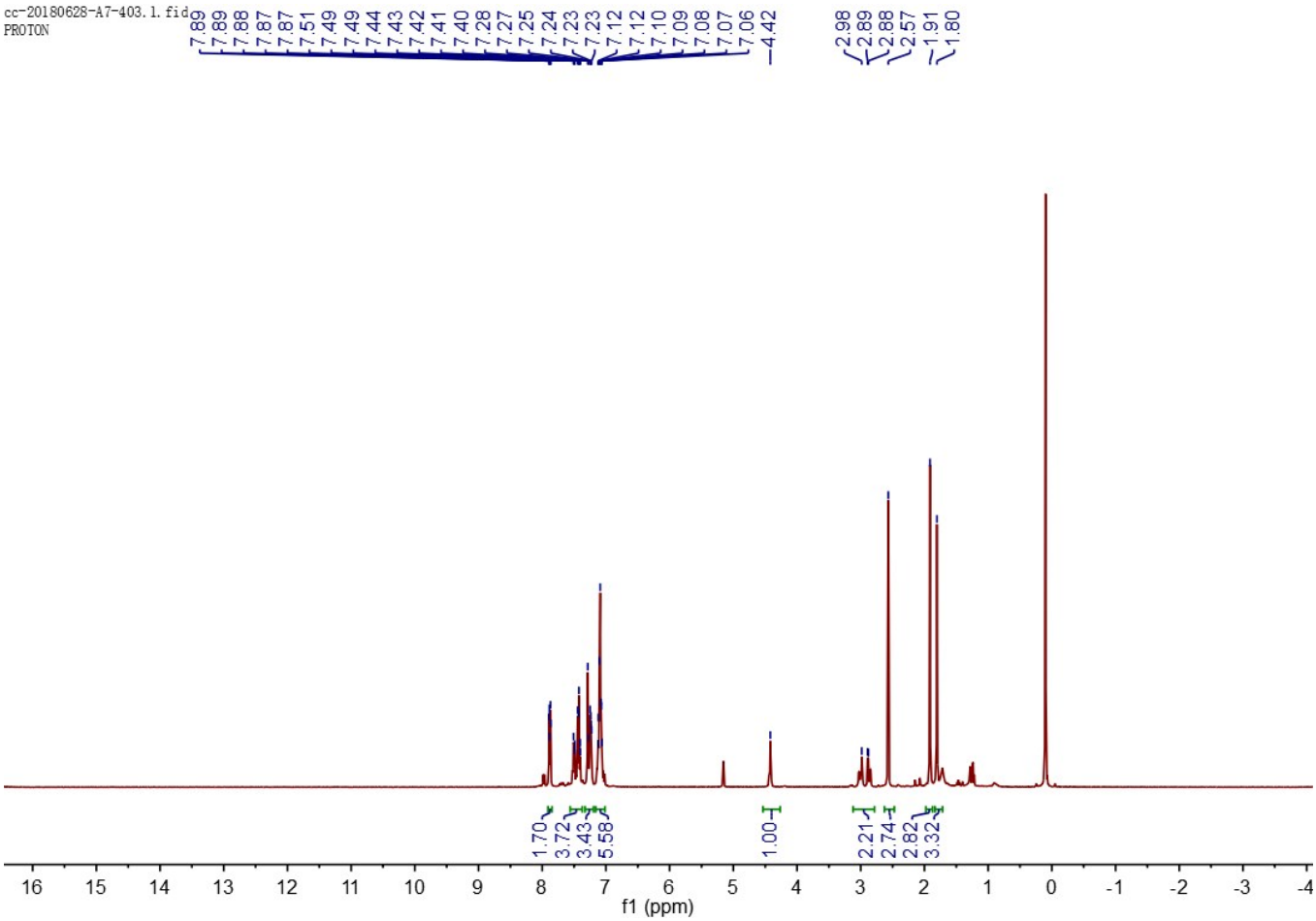

cc-20180610-A2-408/1
H1
7.78
7.77
7.51
7.49
7.49
7.46
7.44
7.43
7.41
7.39
7.28
7.26
7.24
7.22
7.20
7.19
7.17
7.16
7.14
7.13
7.12
7.12
7.10
6.99
6.99
6.97
6.97
3.92
3.90
3.89
2.85
2.84
2.83
2.81
2.80
2.79
2.68
2.67
2.65
2.63
1.99
1.96
1.84
1.88
1.47
2.98
6.56
1.73
1.00
2.05
3.12
3.07
11.0 10.5 10.0 9.5 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)

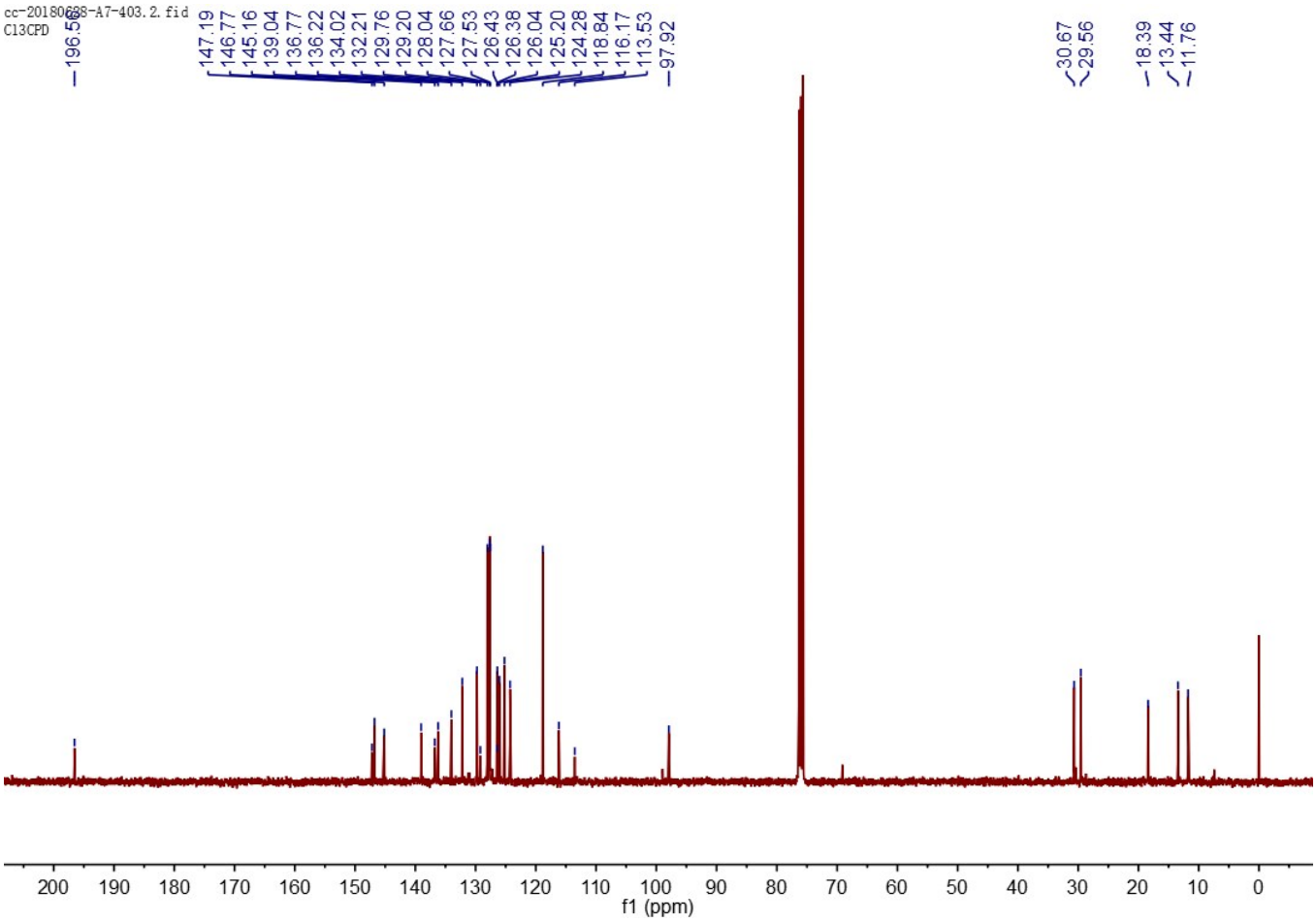

cc-20180610-A2-408/2
1D 13C with H decoupling
197.82
150.61
146.68
141.96
137.16
132.98
129.17
128.99
128.59
128.58
127.43
127.00
125.84
120.23
118.74
99.30
35.52
33.97
14.22
13.06
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)

(*E*)-2-(3-Methyl-1-phenyl-4-(*p*-tolyl)-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4c):

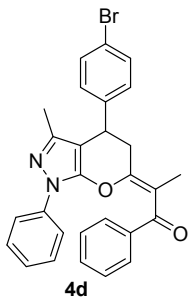


Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.45-7.43 (m,3H), 7.33-7.20 (m, 4H), 7.16-7.07 (m, 5H), 4.42 (t, J = 5.6 Hz, 1H), 3.07-2.79 (m, 2H), 2.57 (s, 3H), 1.91 (s, 3H), 1.80 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.58, 147.21, 146.78, 145.17, 139.05, 136.79, 136.23, 134.03, 132.23, 129.78, 129.22, 128.05, 127.68, 127.54, 126.40, 126.05, 125.21, 124.29, 118.85, 116.18, 113.54, 97.93, 30.67, 29.56, 18.39, 13.44, 11.76. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2072.

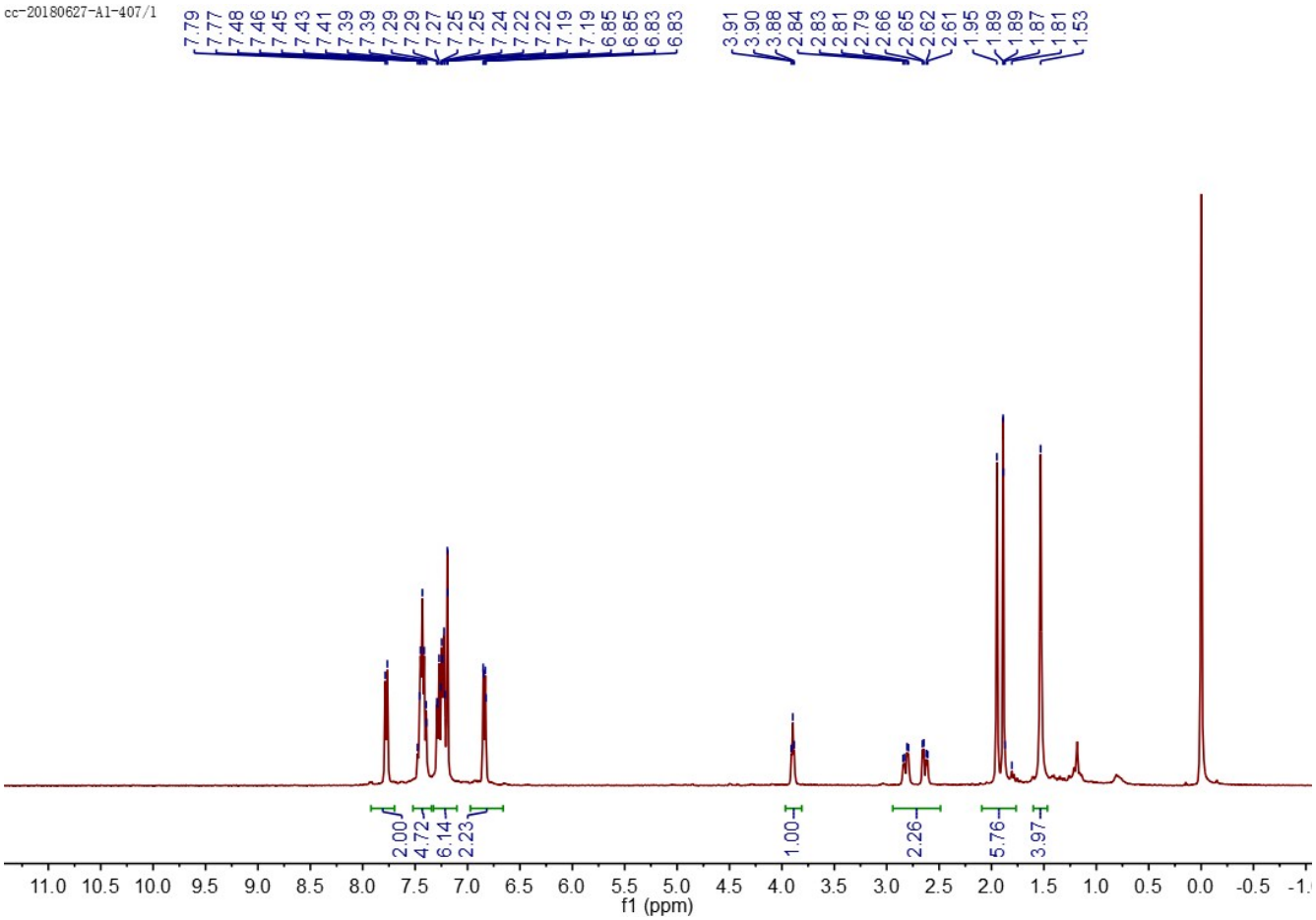


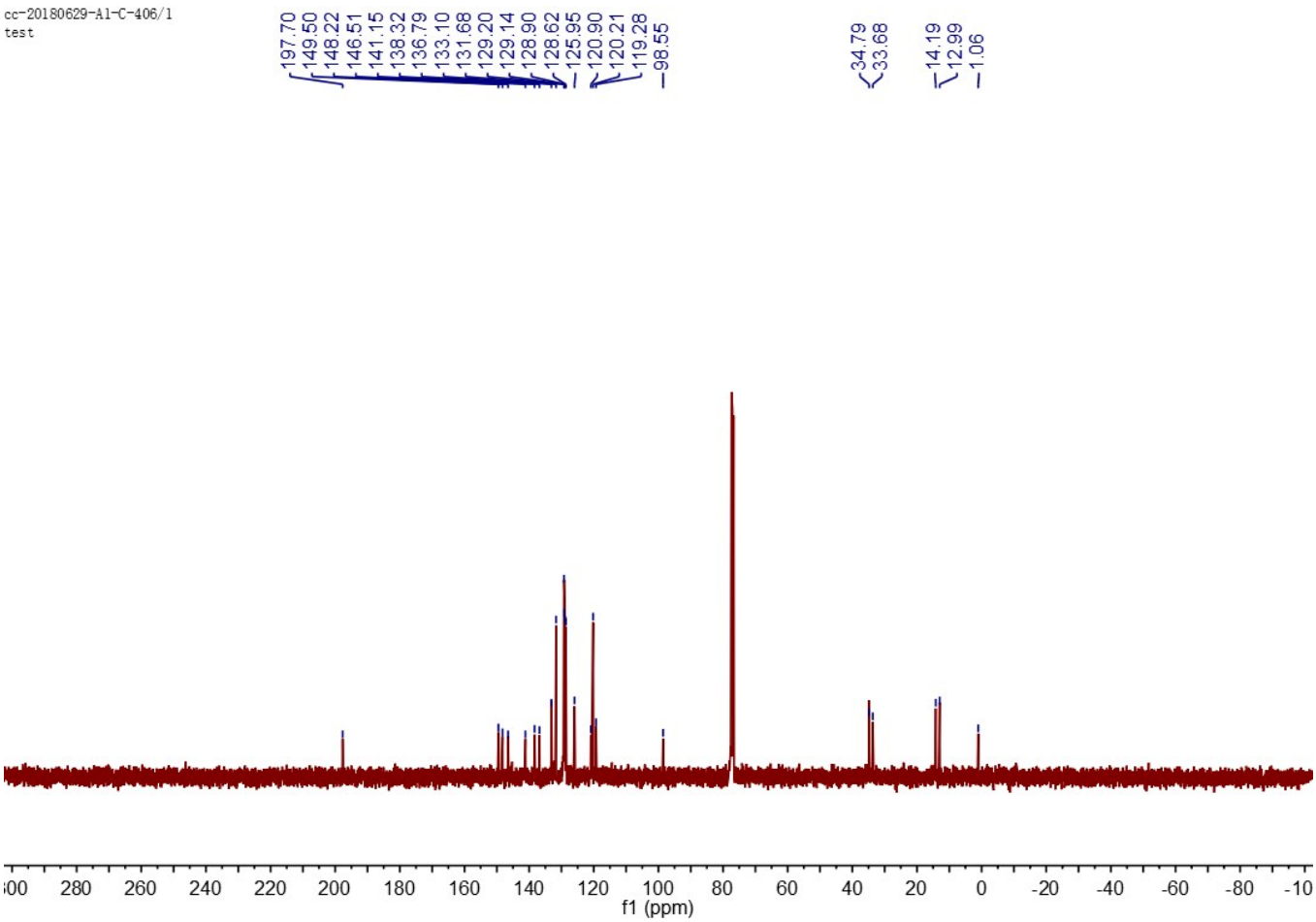


(*E*)-2-(4-(4-Bromophenyl)-3-methyl-1-phenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4d):

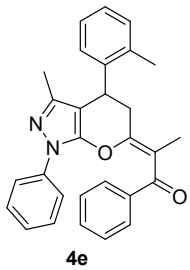


Red solid, m.p. 179-181 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (m, 2H), 7.50-7.36 (m, 5H), 7.26 (dd, *J* = 18.0, 8.1 Hz, 5H), 6.84 (d, *J* = 8.0 Hz, 2H), 3.90 (t, *J* = 5.1 Hz, 1H), 2.94-2.57 (m, 2H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 149.5, 148.2, 146.5, 141.1, 138.3, 136.8, 133.1, 131.6, 129.2, 129.1, 128.9, 128.6, 125.9, 120.9, 120.2, 119.2, 98.5, 34.7, 33.6, 14.1, 12.9. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}BrN_2O_2$ $[M + H]^+$ 499.1016, found 499.1018.


cc-20180627-A1-407/1
7.79
7.77
7.48
7.46
7.45
7.43
7.41
7.39
7.39
7.29
7.29
7.27
7.25
7.25
7.24
7.22
7.22
7.19
7.19
6.85
6.85
6.83
6.83
3.91
3.90
3.88
2.84
2.83
2.81
2.79
2.66
2.65
2.62
2.61
1.95
1.89
1.89
1.87
1.81
1.53
2.00
4.72
6.14
2.23
1.00
2.26
5.76
3.97
f1 (ppm)

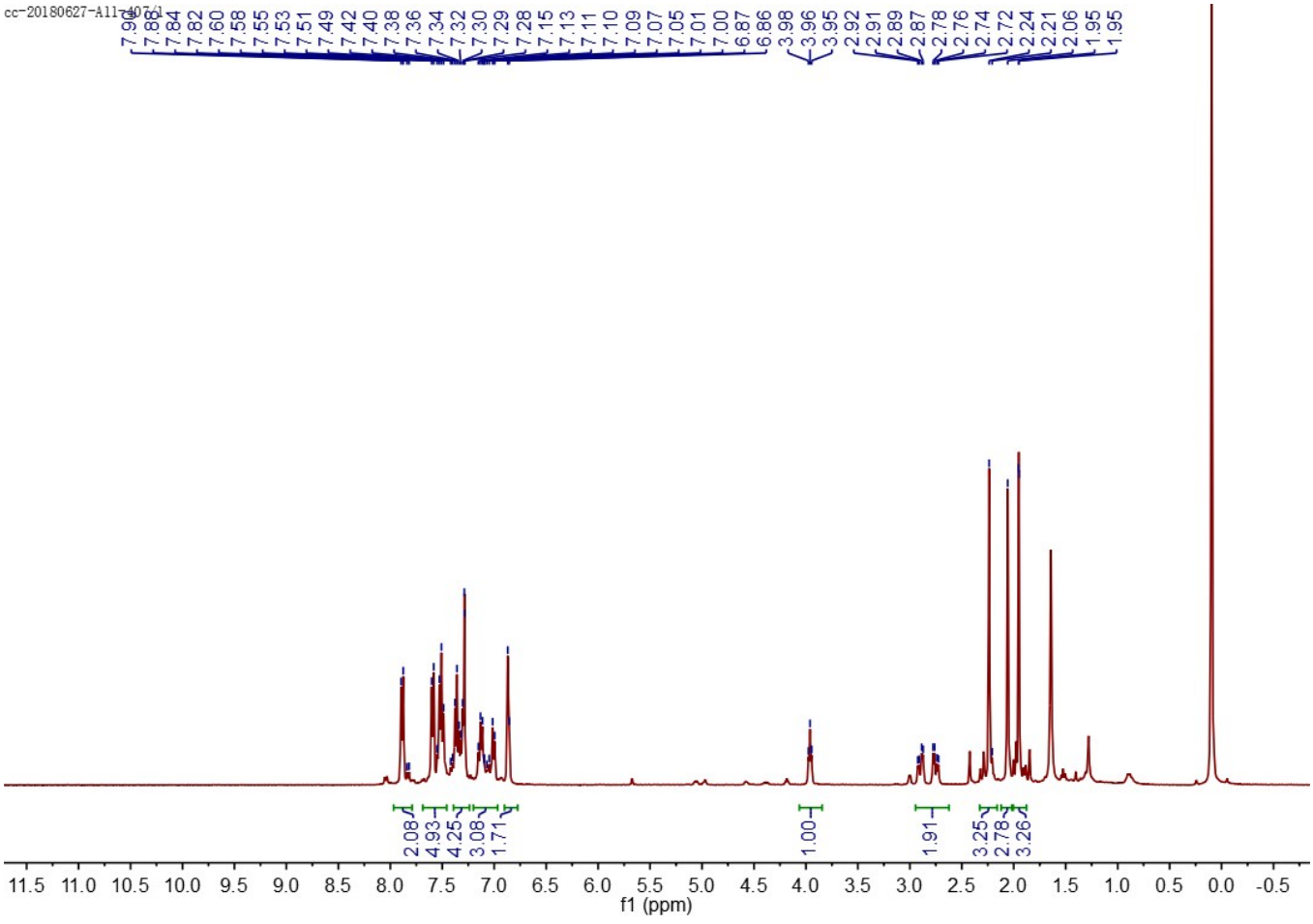

cc-20180629-A1-C-406/1
test
197.70
149.50
148.22
146.51
141.15
138.32
136.79
133.10
131.68
129.20
129.14
128.90
128.62
125.95
120.90
120.21
119.28
98.55
34.79
33.68
14.19
12.99
1.06
f1 (ppm)

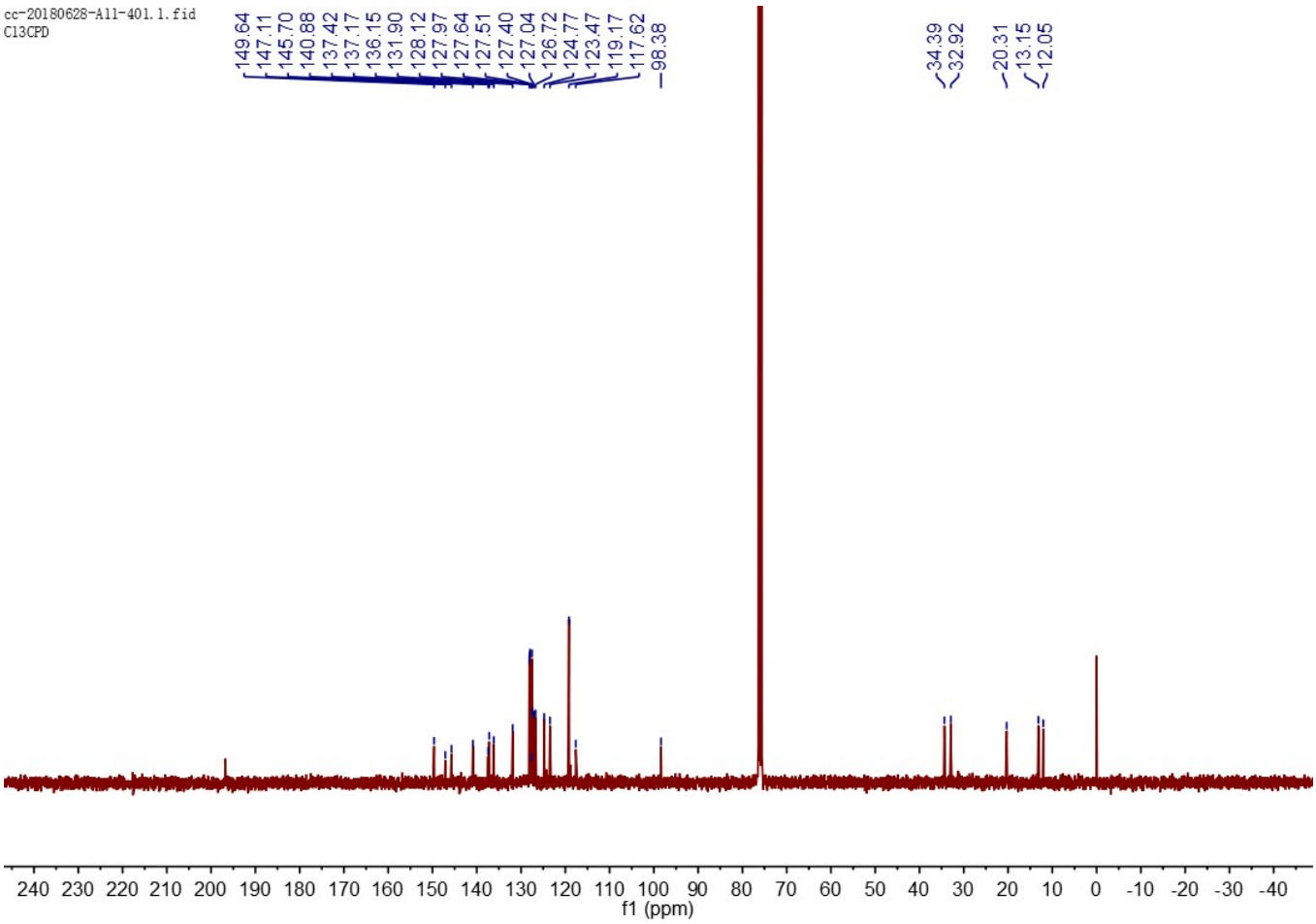
(*E*)-2-(3-Methyl-1-phenyl-4-(*o*-tolyl)-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4e):



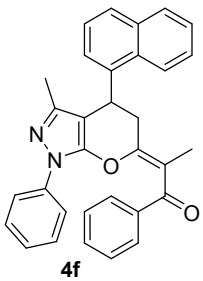
4e

Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 7.9 Hz, 2H), 7.63-7.45 (m, 4H), 7.41-7.31 (m, 3H), 7.18-7.07 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.87 (s, 2H), 3.96 (t, *J* = 5.7 Hz, 1H), 2.82 (ddd, *J* = 20.7, 14.6, 5.5 Hz, 2H), 2.24 (s, 3H), 2.06 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 149.6, 145.7, 140.8, 137.8, 136.1, 131.9, 128.1, 127.9, 127.5, 127.4, 127.0, 126.7, 124.7, 123.4, 119.1, 117.6, 98.3, 34.3, 32.9, 20.3, 13.1, 12.0. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2071.



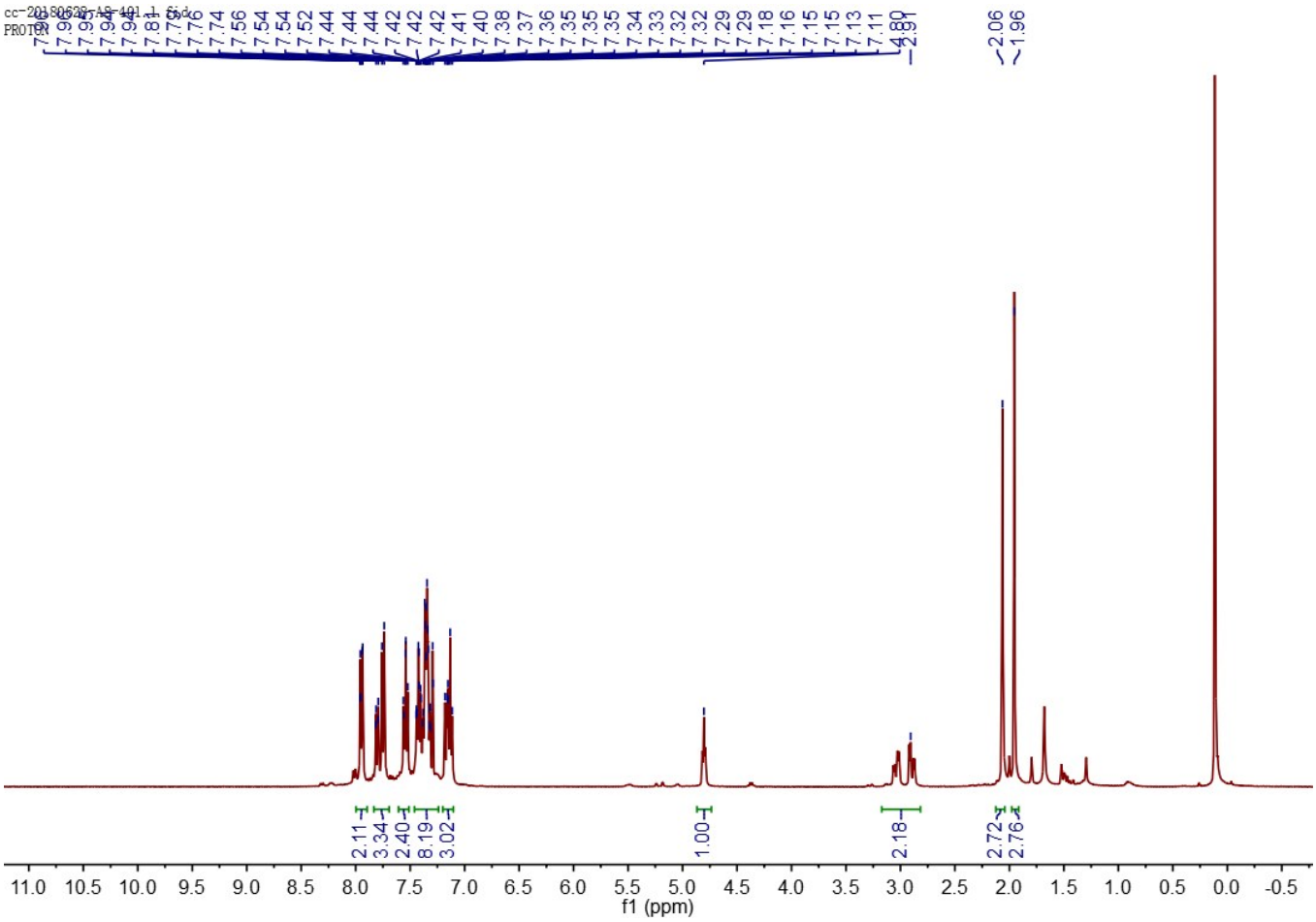


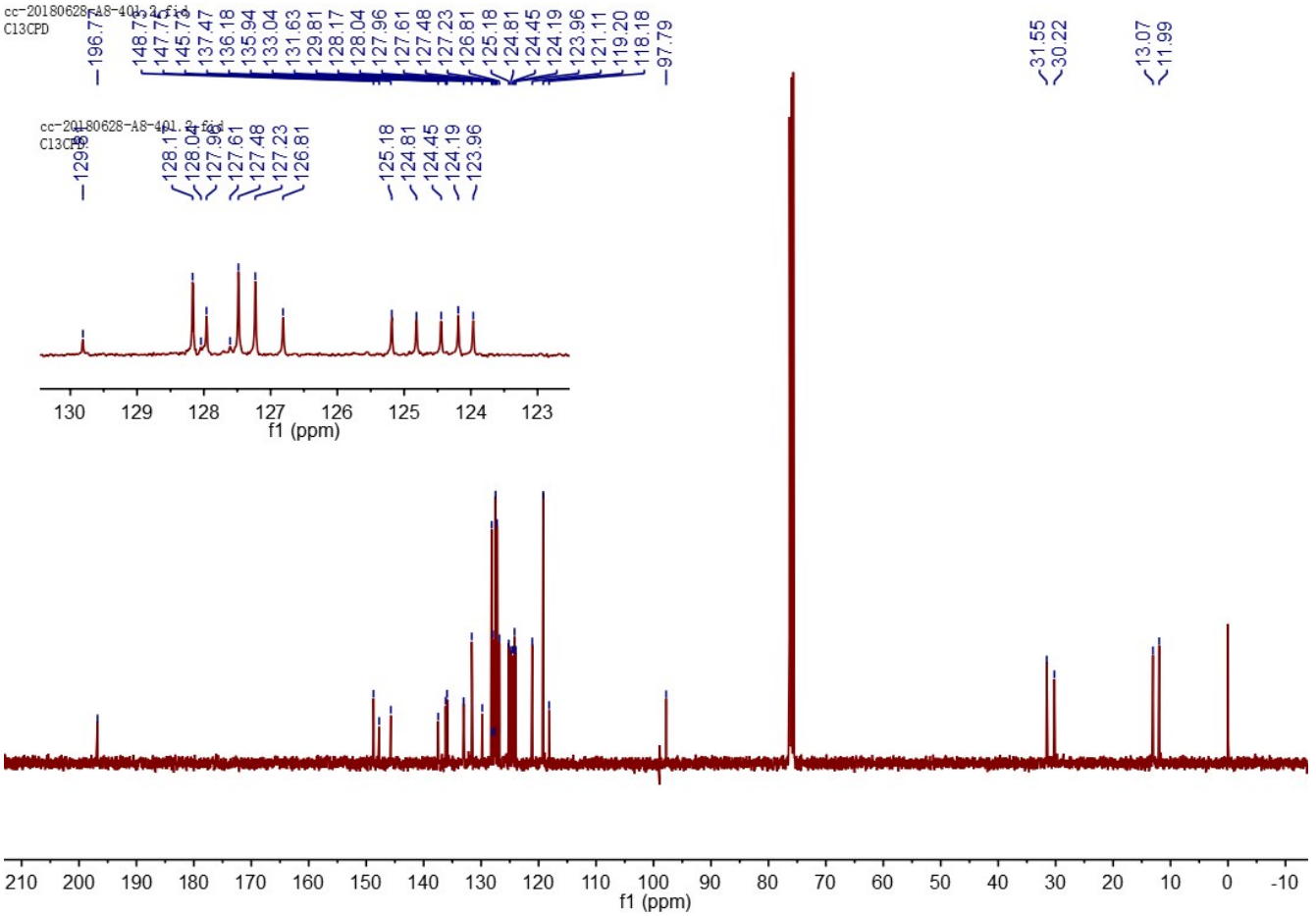
(*E*)-2-(3-Methyl-4-(naphthalen-1-yl)-1-phenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4f):



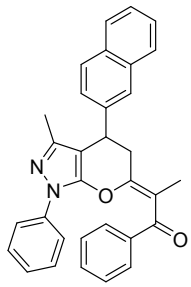
4f

Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 2H), 7.78-7.76 (m, 3H), 7.54-7.52 (m, 3H), 7.38-7.36 (m, 5H), 7.21-7.07 (m, 4H), 4.80 (t, *J* = 5.5 Hz, 1H), 2.97 (ddd, *J* = 19.8, 14.8, 5.5 Hz, 2H), 2.06 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.7, 148.7, 147.7, 145.7, 137.4, 136.1, 135.9, 133.0, 131.6, 129.8, 128.1, 127.9, 127.4, 127.2, 126.8, 125.2, 124.8, 124.4, 124.2, 123.9, 121.1, 119.2, 118.1, 97.8, 31.5, 30.2, 13.0, 11.9. HRMS (ESI) *m/z* calcd for $C_{32}H_{27}N_2O_2$ $[M + H]^+$ 471.2067, found 471.2070.


PROTON
f1 (ppm)

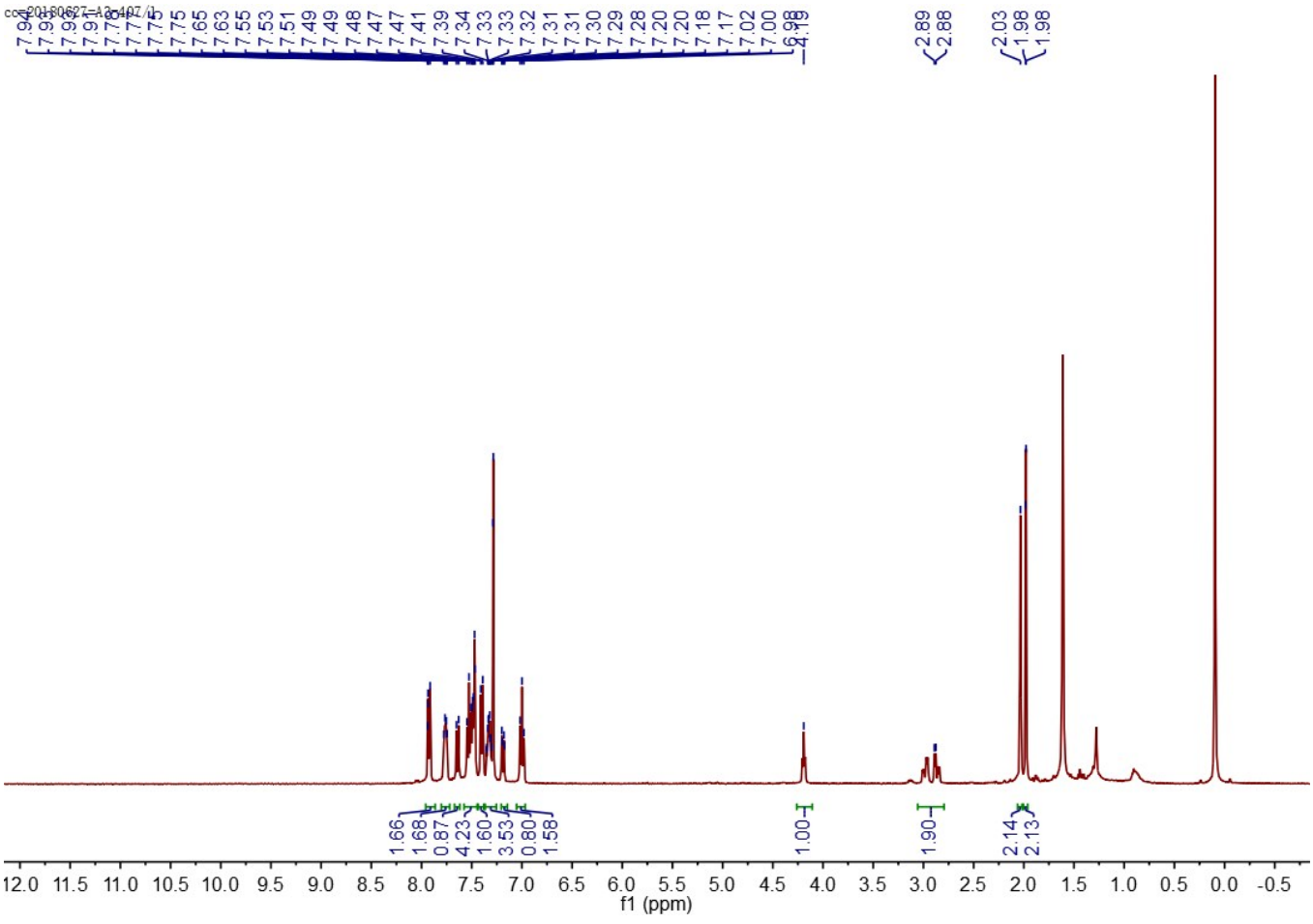

C13CPD
f1 (ppm)

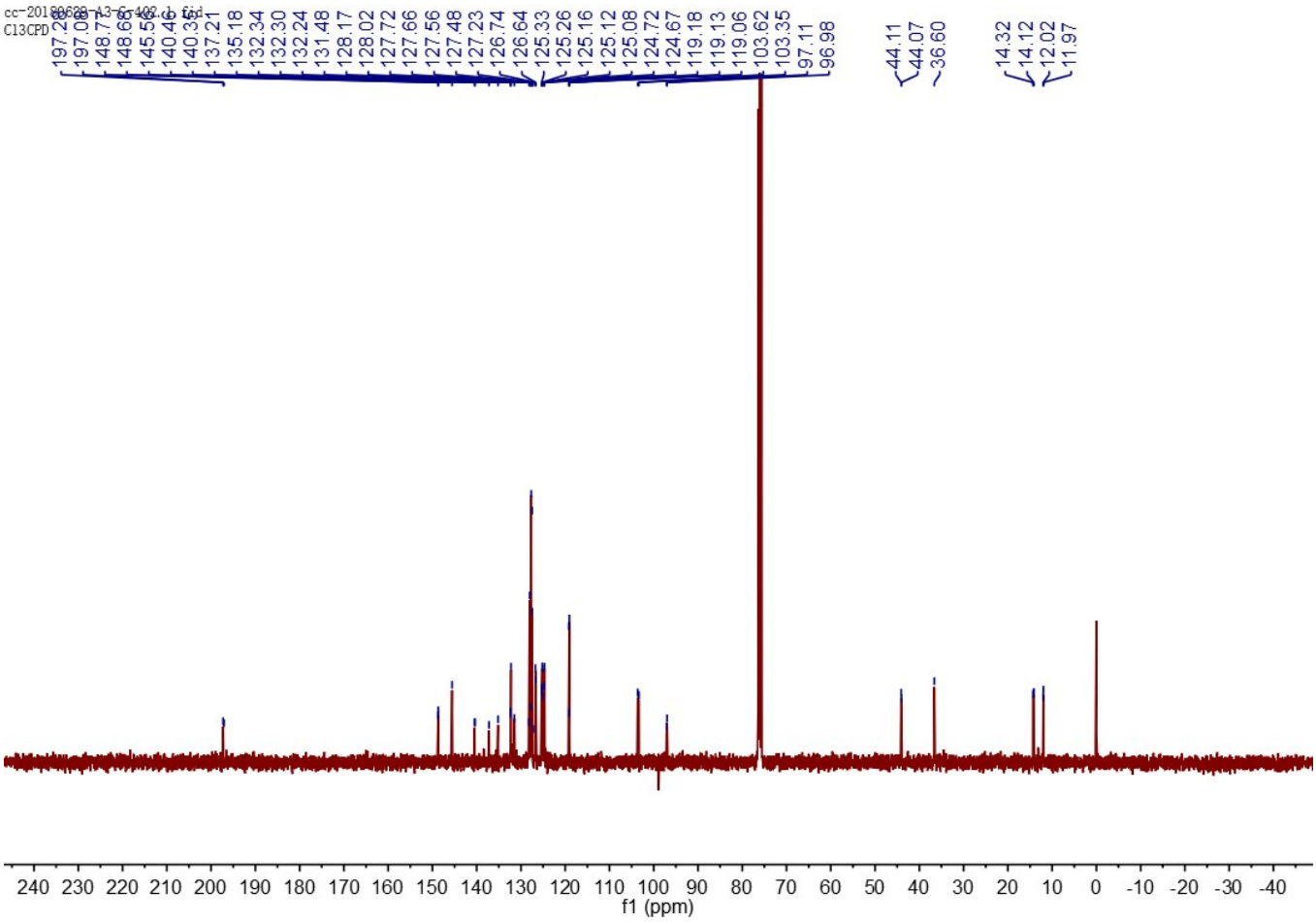
(*E*)-2-(3-Methyl-4-(naphthalen-2-yl)-1-phenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4g):



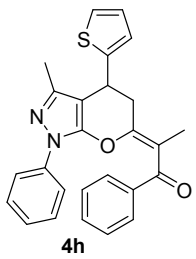
4g

Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.88 (m, 2H), 7.76-7.74 (m, 2H), 7.64 (s, 1H), 7.56-7.45 (m, 5H), 7.40-7.38 (m, 2H), 7.33-7.31 (*m*, 2H), 7.19-7.17 (m, 1H), 7.02-7.00 (m, 2H), 4.19 (t, *J* = 5.5 Hz, 1H), 2.92 (ddd, *J* = 46.9, 14.8, 5.5 Hz, 2H), 2.03 (s, 3H), 1.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 197.1, 148.7, 148.7, 145.5, 140.4, 137.2, 135.1, 132.2, 131.4, 128.0, 127.6, 127.5, 127.4, 126.7, 126.6, 125.3, 125.2, 125.1, 124.6, 119.1, 119.0, 103.6, 103.3, 96.9, 44.1, 36.6, 14.3, 12.0. HRMS (ESI) *m/z* calcd for $C_{32}H_{27}N_2O_2$ $[M + H]^+$ 471.2067, found 471.2071.

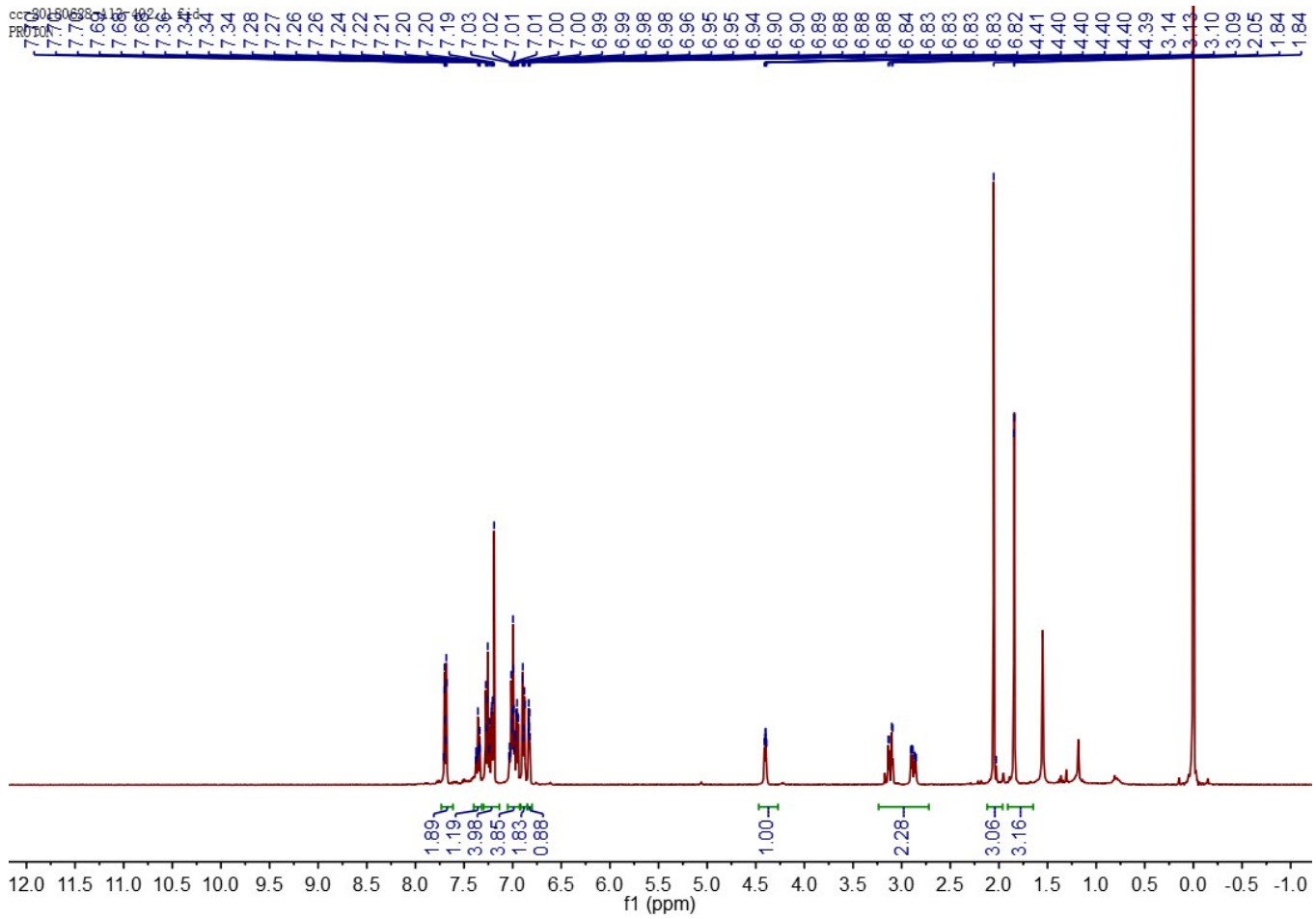


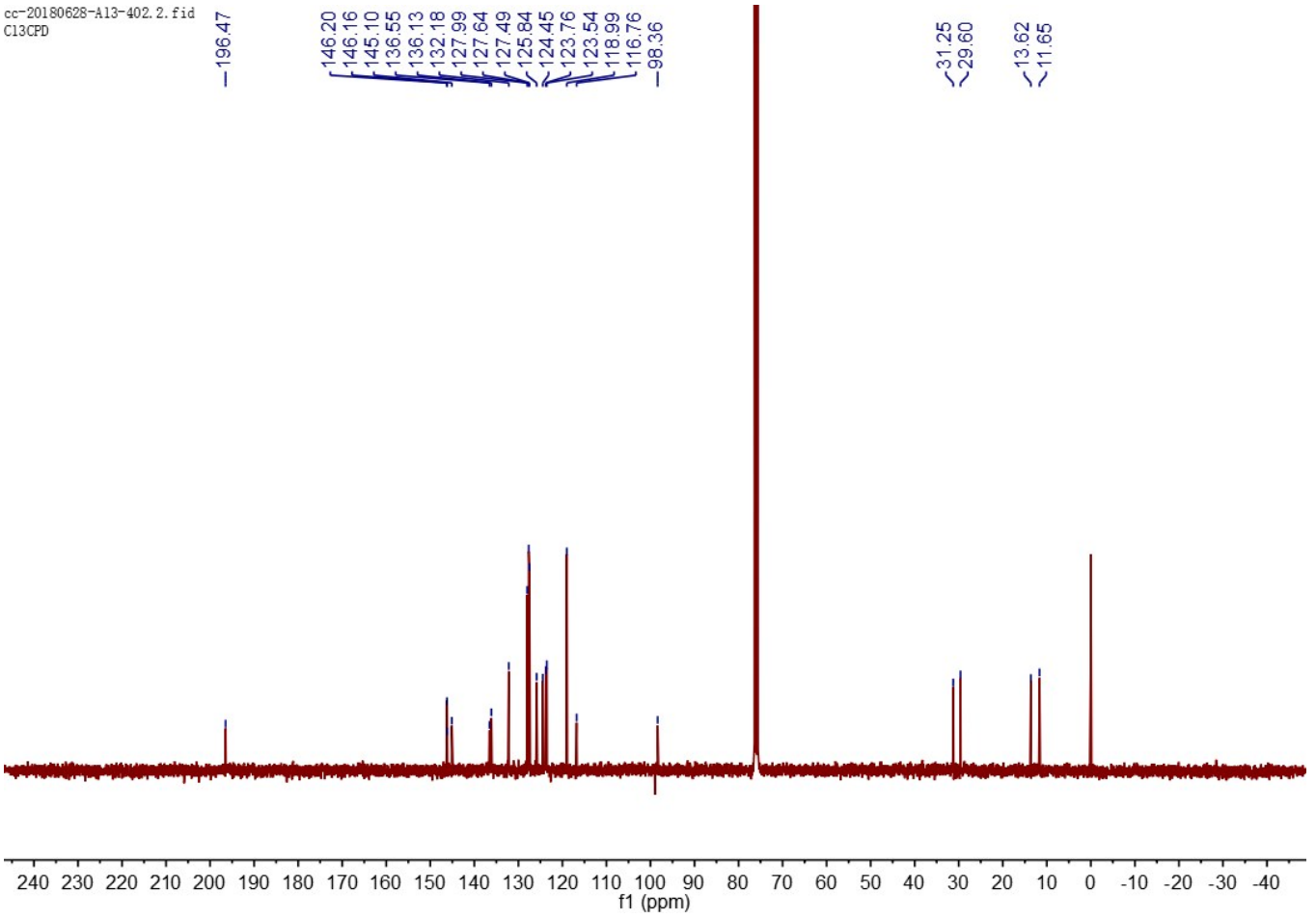


(*E*)-2-(3-Methyl-1-phenyl-4-(thiophen-2-yl)-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4h):

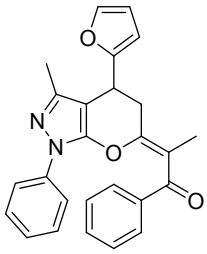


Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.64 (m, 2H), 7.42-7.20 (m, 5H), 7.07-6.79 (m, 6H), 4.43-4.38 (m, 1H), 3.11 (dd, *J* = 14.3, 3.5 Hz, 1H), 2.88 (dd, *J* = 14.3, 4.5 Hz, 1H), 2.05 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 146.2, 145.1, 136.5, 136.1, 132.1, 128.0, 127.6, 127.5, 125.8, 124.4, 123.7, 123.5, 119.0, 116.7, 98.3, 31.2, 29.6, 13.6, 11.6. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_2O_2$ $[M + H]^+$ 427.1475, found 427.1477.


PROTON
1.89
1.19
3.98
3.85
1.83
0.88
1.00
2.28
3.06
3.16
f1 (ppm)

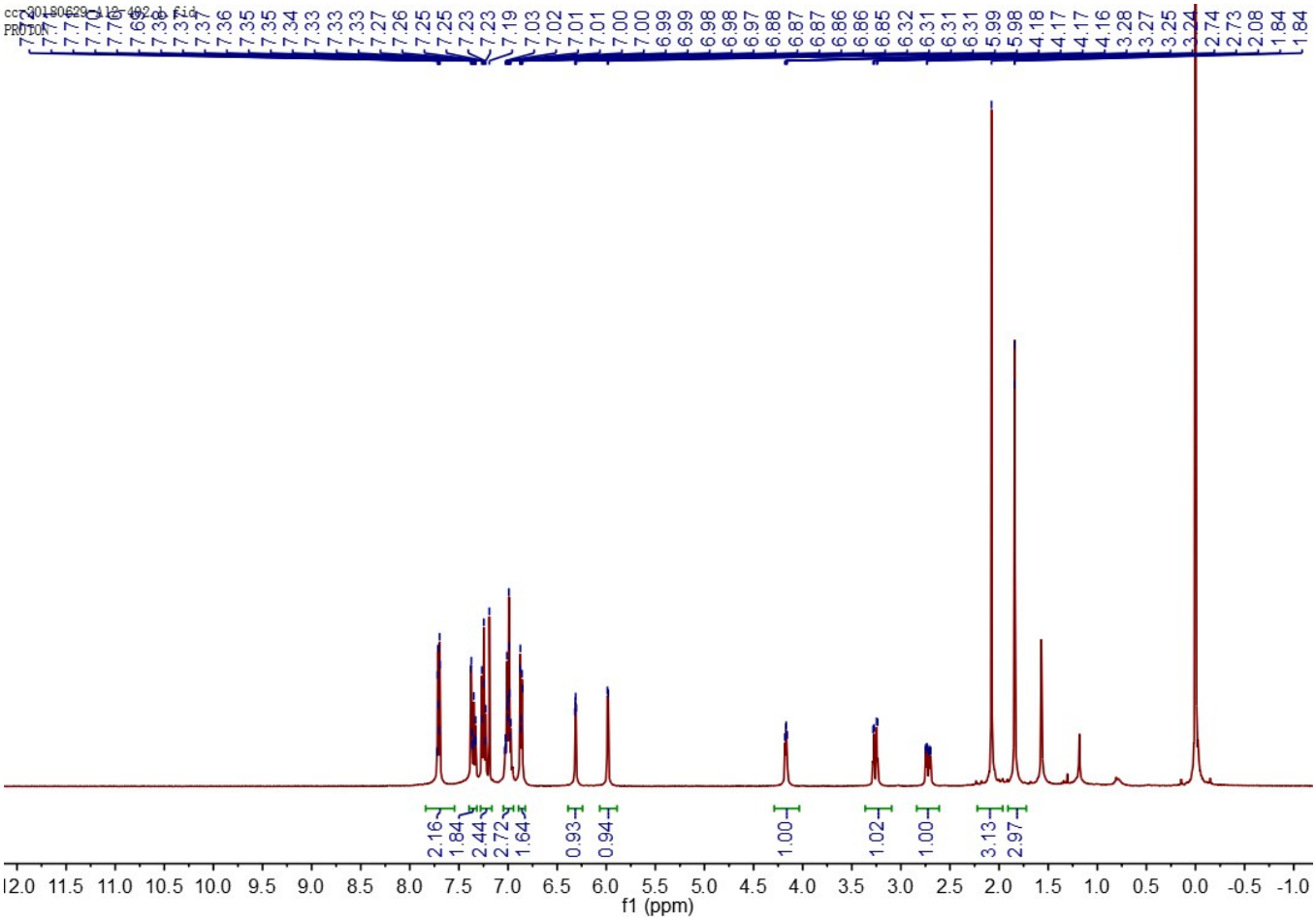

C13CPD
196.47
146.20
146.16
145.10
136.55
136.13
132.18
127.99
127.64
127.49
125.84
124.45
123.76
123.54
118.99
116.76
98.36
31.25
29.60
13.62
11.65
f1 (ppm)

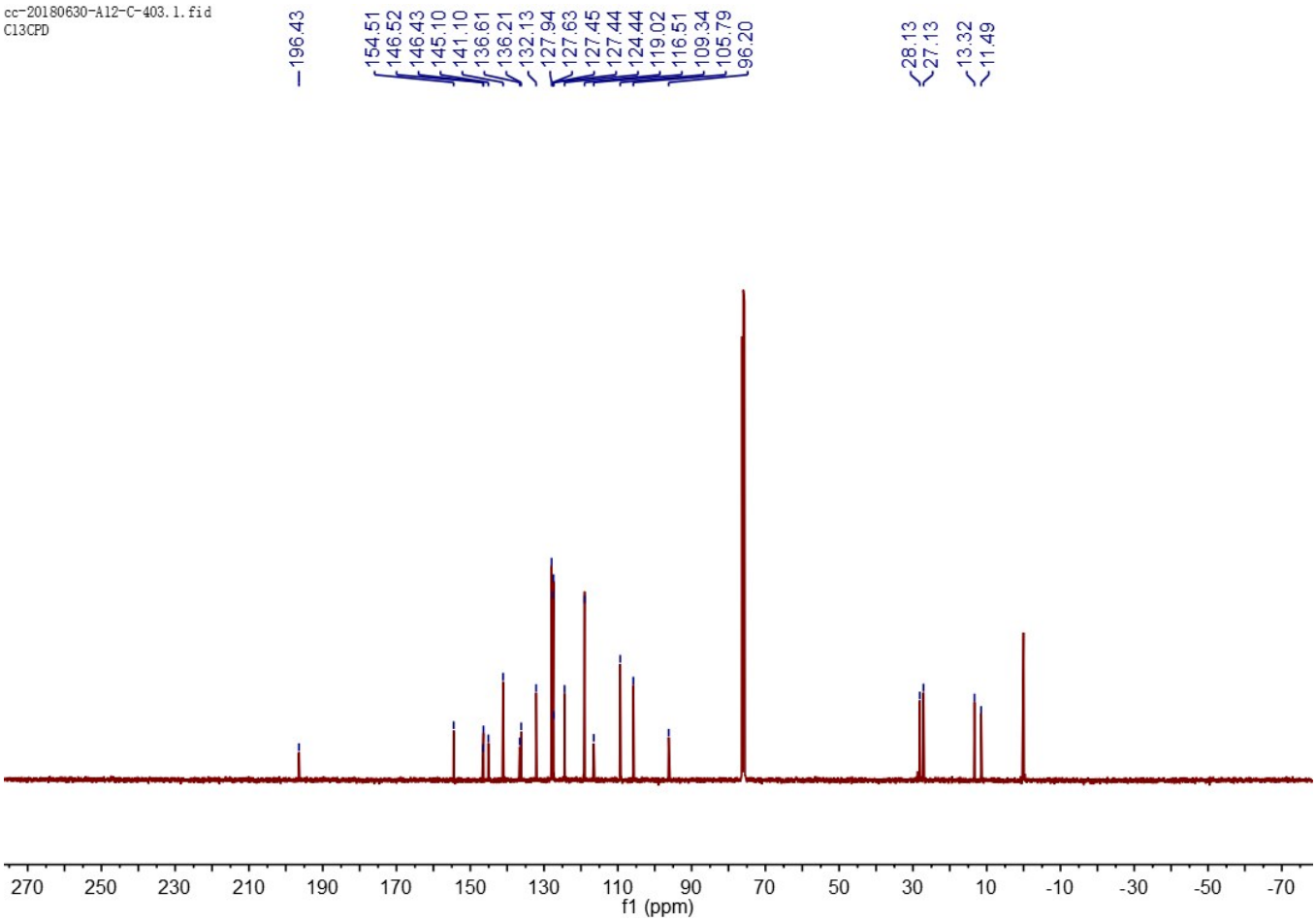
(*E*)-2-(4-(Furan-2-yl)-3-methyl-1-phenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4i):



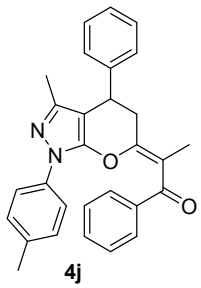
4i

Brown liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.31 (m, 2H), 7.25-7.22 (m, 3H), 7.05-6.94 (m, 3H), 6.87 (dd, *J* = 8.1, 1.5 Hz, 3H), 6.31 (dd, *J* = 3.0, 1.9 Hz, 1H), 5.98 (d, *J* = 3.1 Hz, 1H), 4.20-4.13 (m, 1H), 3.26 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.72 (dd, *J* = 14.2, 5.6 Hz, 1H), 2.08 (s, 3H), 1.84 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.4, 154.5, 146.5, 146.4, 145.1, 141.1, 136.6, 136.2, 132.1, 127.9, 127.6, 127.4, 124.4, 119.0, 116.5, 109.3, 105.8, 96.2, 28.1, 27.1, 13.3, 11.4. HRMS (ESI) *m/z* calcd for $C_{26}H_{23}N_2O_3$ $[M + H]^+$ 411.1703, found 411.1706.



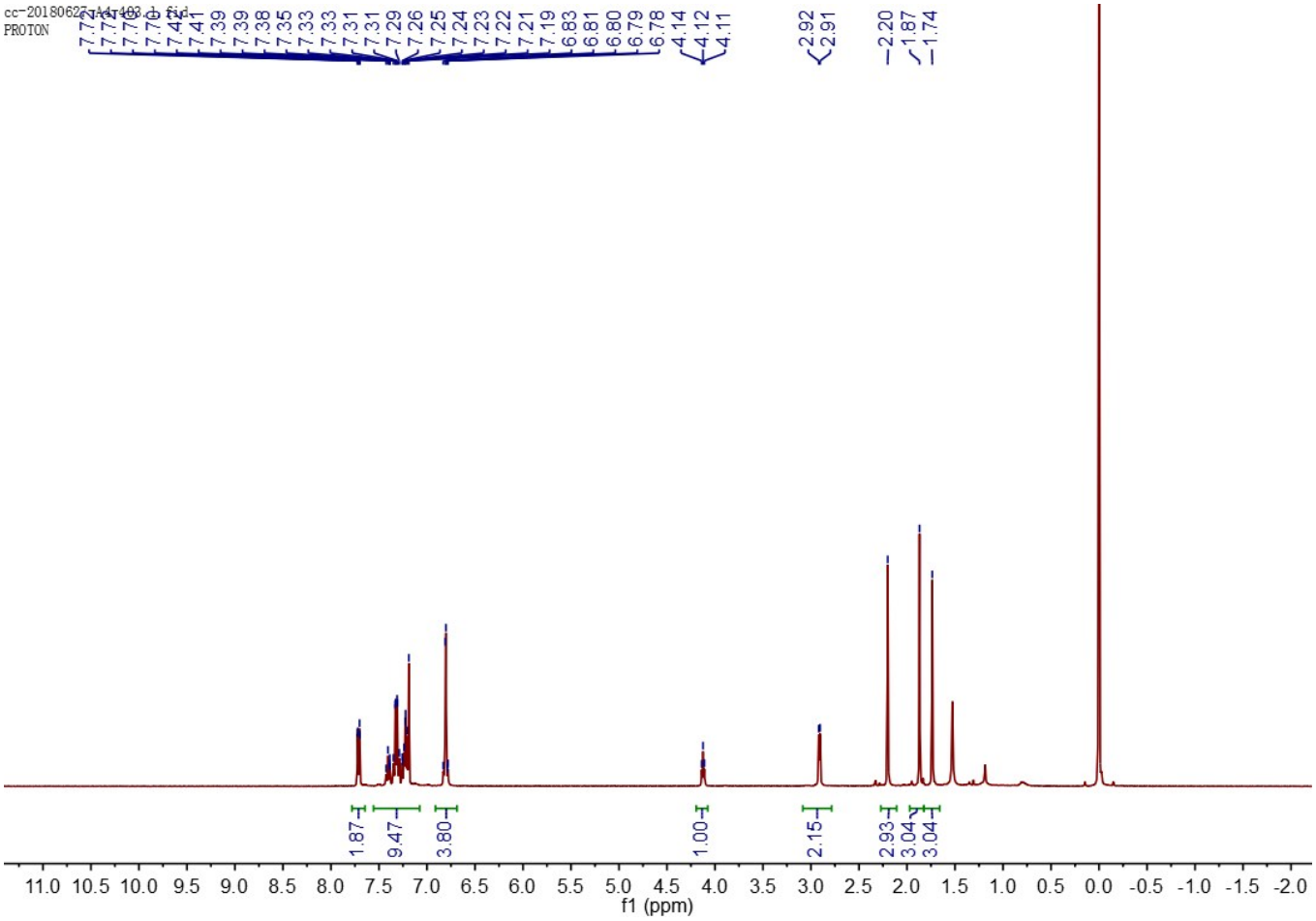


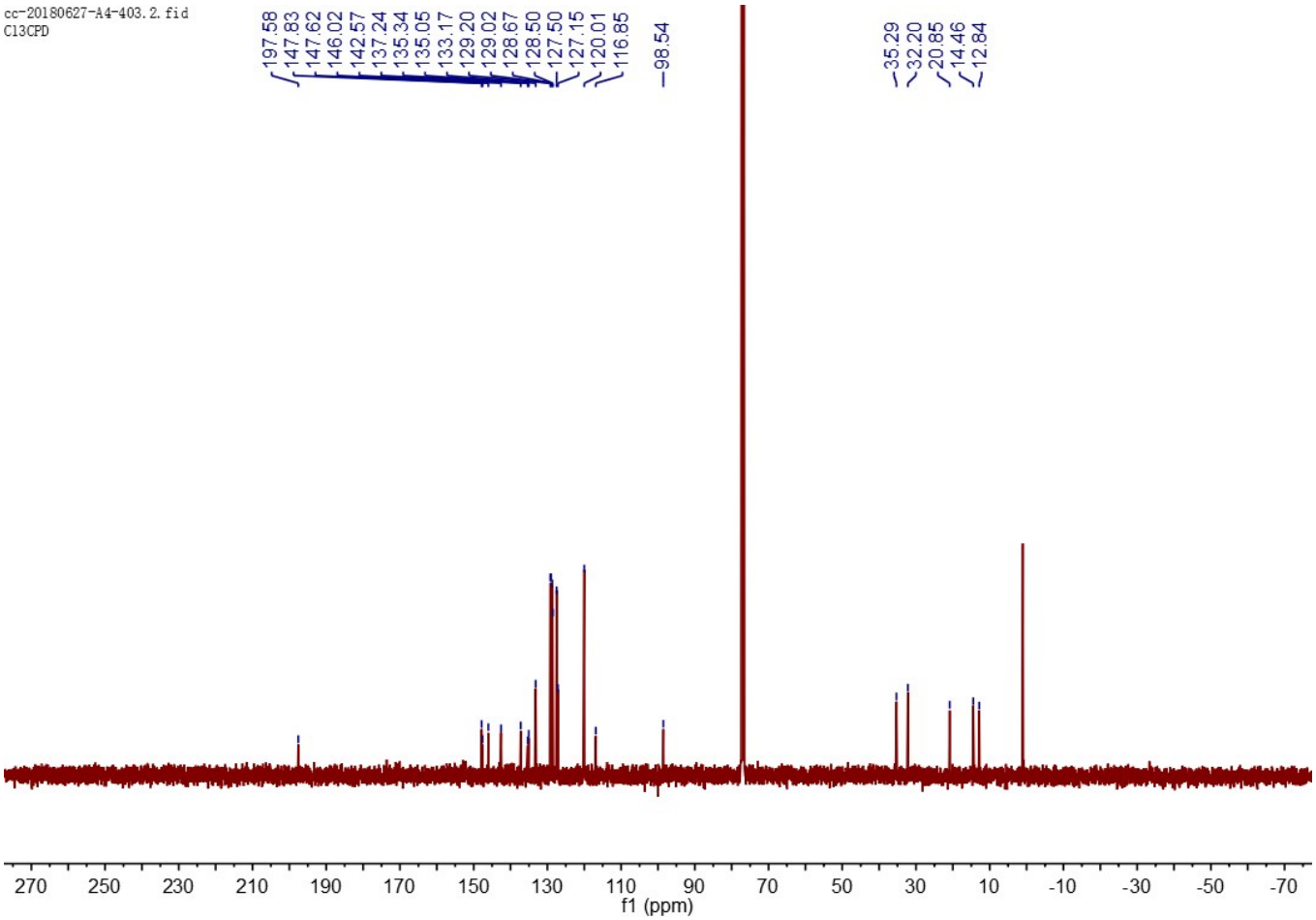
(*E*)-2-(3-Methyl-4-phenyl-1-(*p*-tolyl)-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4j):



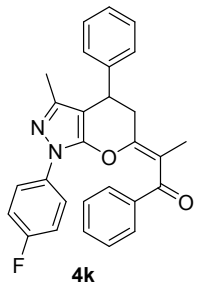
4j

Red liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 1H), 7.46-7.20 (m, 6H), 6.80 (t, *J* = 5.4 Hz, 3H), 4.12 (d, *J* = 5.4 Hz, 1H), 2.91 (d, *J* = 5.3 Hz, 2H), 2.20 (s, 3H), 1.87 (s, 3H), 1.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.0, 142.5, 137.2, 135.0, 133.1, 129.2, 129.0, 128.6, 128.5, 127.5, 127.1, 120.0, 116.8, 98.5, 35.3, 32.2, 20.8, 14.4, 12.8. HRMS (ESI) *m/z* calcd for $C_{23}H_{23}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2073.


cc-20180627-A4-403.1.fid
PROTON
7.77
7.76
7.44
7.41
7.39
7.38
7.35
7.33
7.31
7.29
7.26
7.25
7.24
7.23
7.22
7.21
7.19
6.83
6.81
6.80
6.79
6.78
4.14
4.12
4.11
2.92
2.91
2.20
1.87
1.74
1.87
9.47
3.80
1.00
2.15
2.93
3.04
3.04
11.0 10.5 10.0 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 -1.5 -2.0
f1 (ppm)

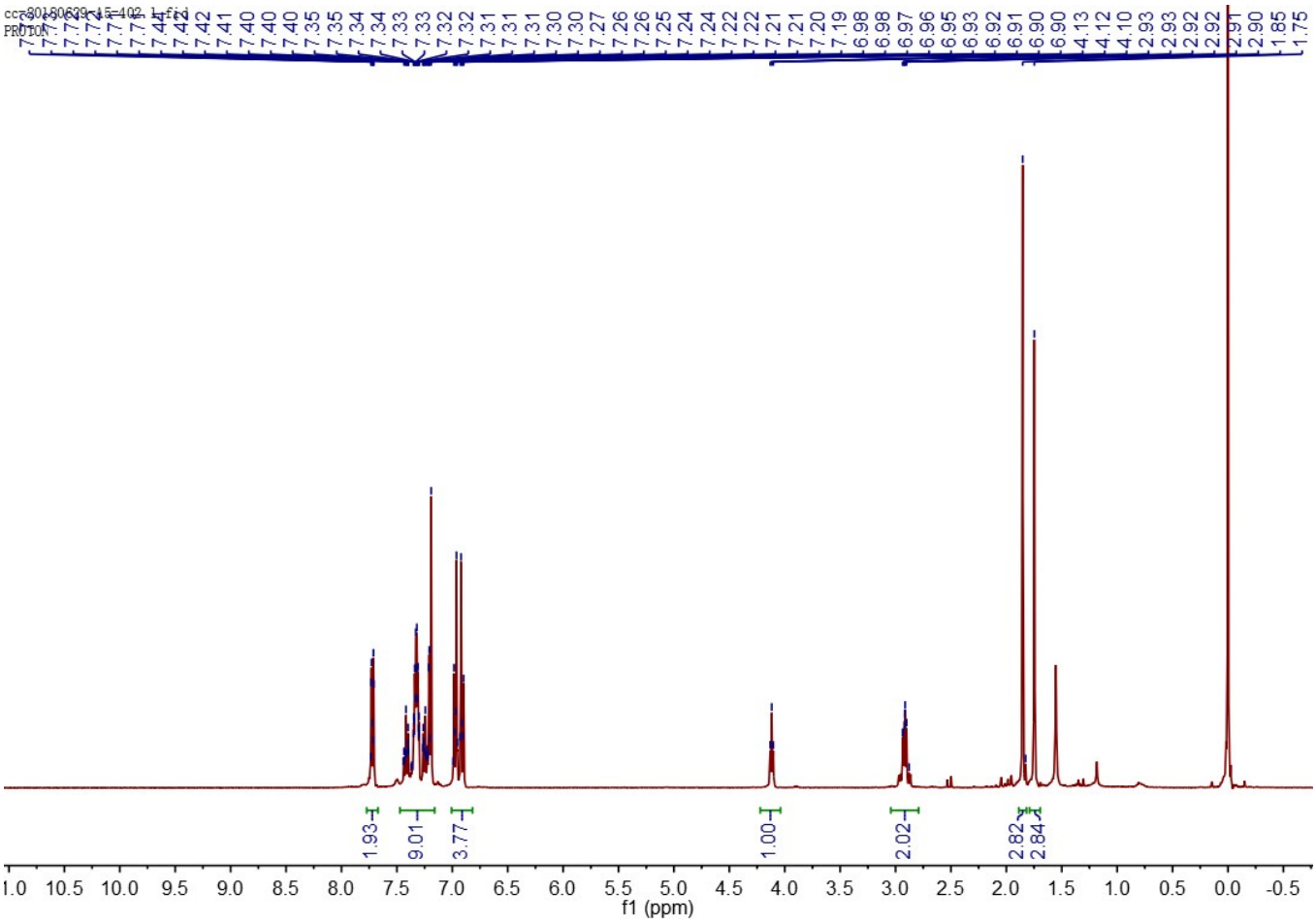

cc-20180627-A4-403.2.fid
C13CPD
197.58
147.83
147.62
146.02
142.57
137.24
135.34
135.05
133.17
129.20
129.02
128.67
128.50
127.50
127.15
120.01
116.85
98.54
35.29
32.20
20.85
14.46
12.84
270 250 230 210 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70
f1 (ppm)

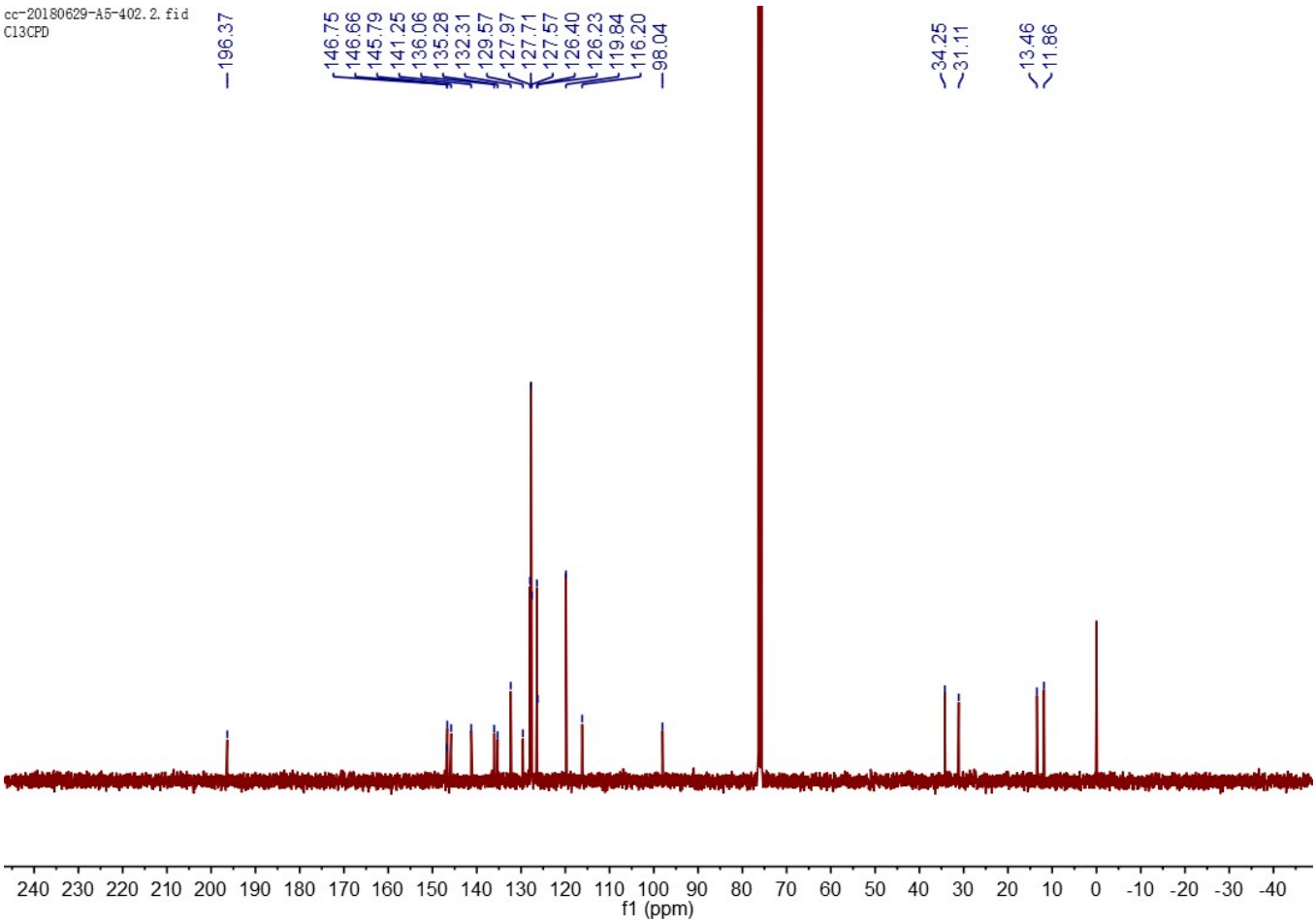
(*E*)-2-(1-(4-Fluorophenyl)-3-methyl-4-phenyl-4,5-dihydropyrano[2,3-*c*]pyrazol-6(1H)-ylidene)-1-phenylpropan-1-one (4k):



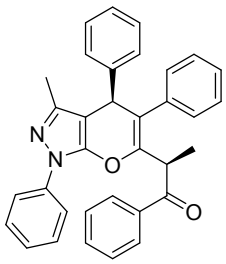
4k

Red solid, m.p. 136-138 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.68 (m, 2H), 7.46-7.21 (m, 8H), 7.01-6.88 (m, 4H), 4.12 (t, *J* = 5.5 Hz, 1H), 2.99-2.88 (m, 2H), 1.84 (s, 3H), 1.75 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 146.6, 145.8, 141.2, 136.0, 135.2, 132.3, 129.5, 127.9, 127.7, 127.5, 126.4, 126.2, 119.8, 116.2, 98.0, 34.2, 31.1, 13.4, 11.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{24}FN_2O_2$ $[M + H]^+$ 439.1816, found 439.1818.



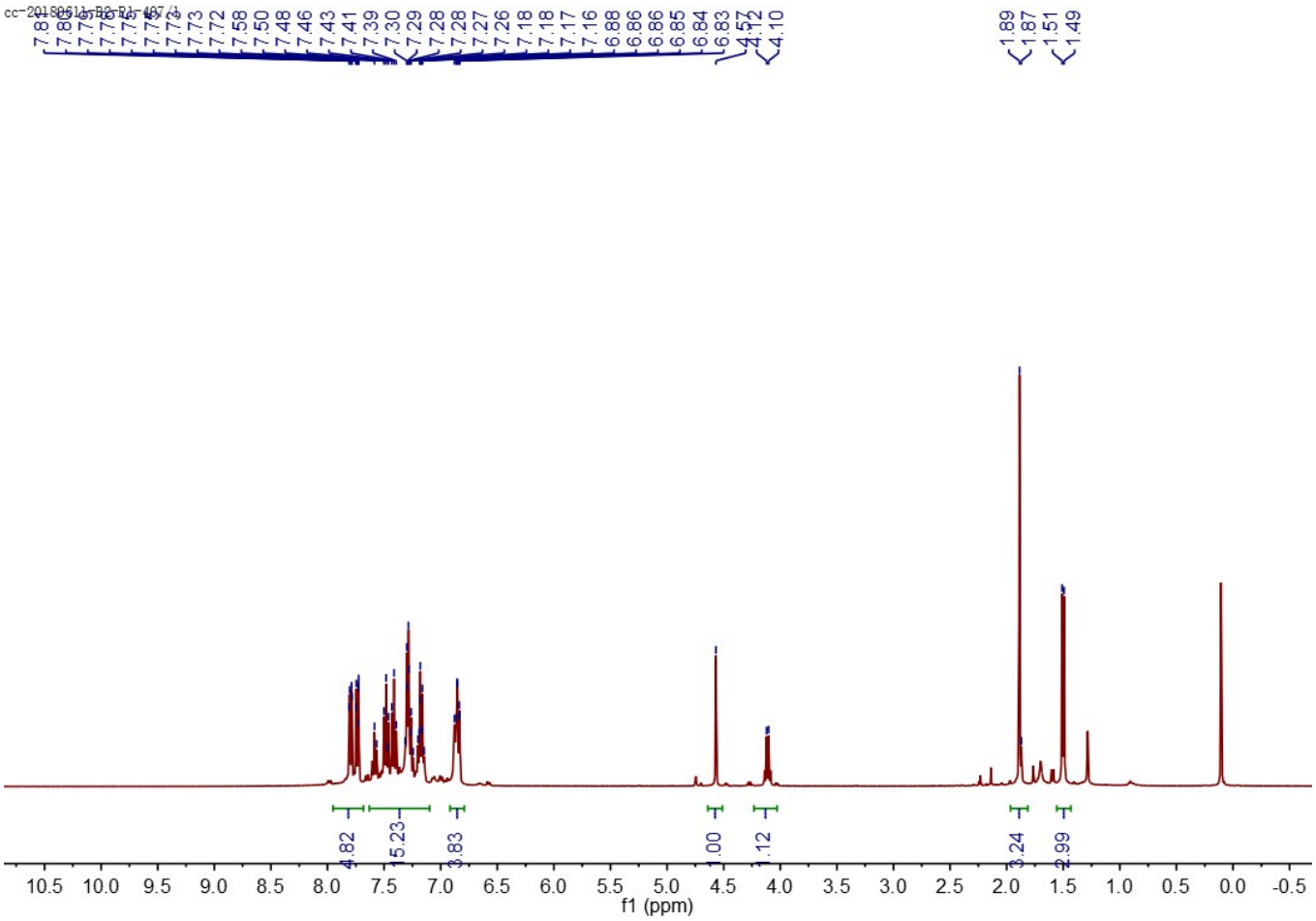


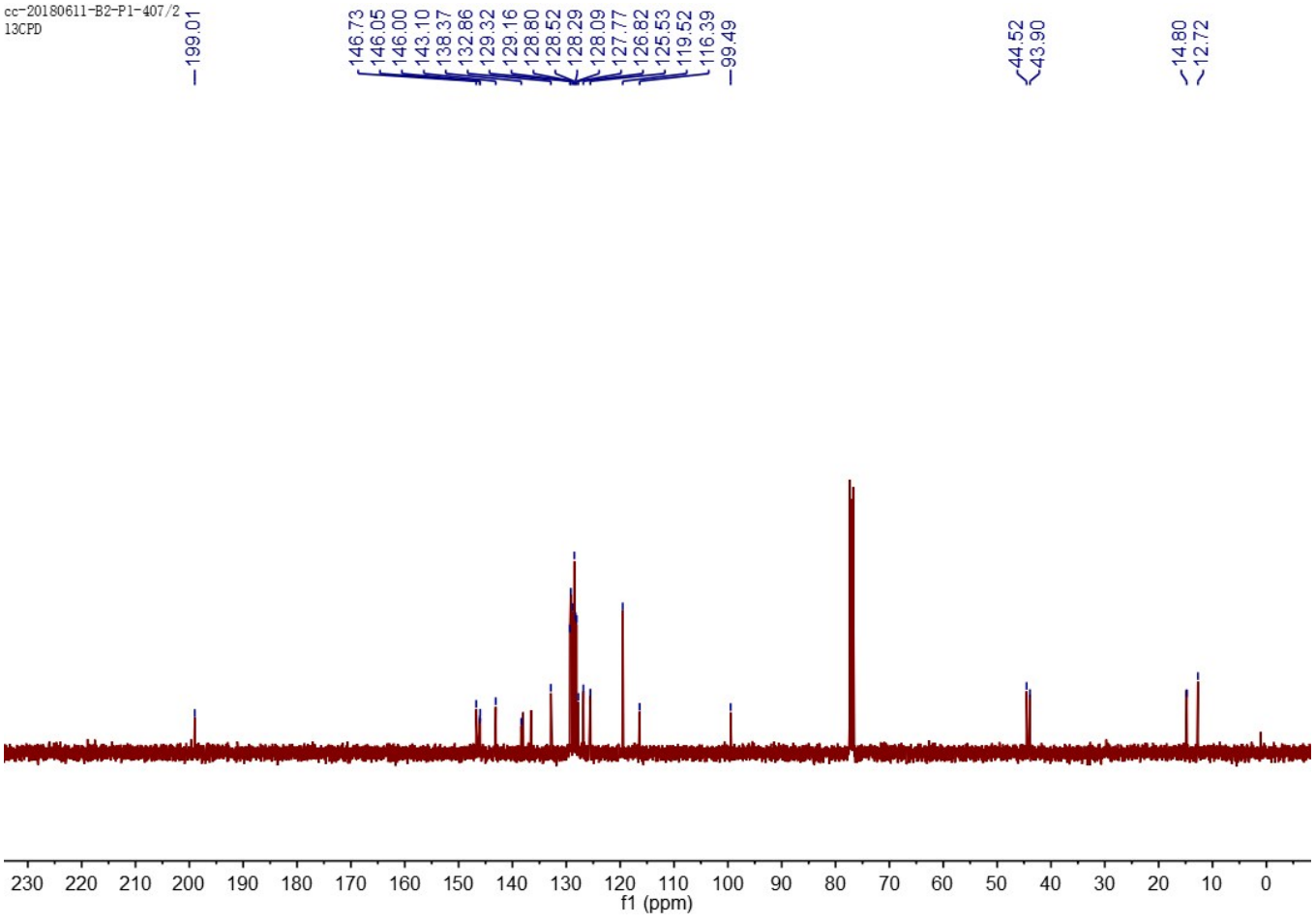
(*R*)-2-((*S*)-3-Methyl-1,4,5-triphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'a):



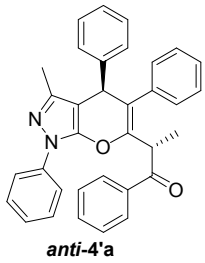
***syn*-4'a**

Orange solid, m.p. 141-142 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 4H), 7.58-7.56 (m, 1H), 7.48 (m, 2H), 7.41-7.39 (m, 2H), 7.32-7.26 (m, 4H), 7.18-7.16 (m, 3H), 6.85-6.81 (m, 4H), 4.57 (s, 1H), 4.11 (q, J = 6.8 Hz, 1H), 1.89 (s, 3H), 1.50 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 146.7, 146.0, 143.1, 138.3, 138.0, 136.5, 132.8, 129.3, 129.1, 128.8, 128.5, 128.3, 128.1, 127.7, 126.8, 125.5, 119.5, 116.3, 99.5, 44.5, 43.9, 14.8, 12.7. HRMS (ESI) *m/z* calcd for $C_{34}H_{29}N_2O_2$ $[M + H]^+$ 497.2224, found 497.2226.


cc-20180611-B2-P1-407/1
7.83
7.81
7.79
7.77
7.75
7.73
7.72
7.58
7.50
7.48
7.46
7.43
7.41
7.39
7.30
7.29
7.28
7.28
7.27
7.26
7.18
7.17
7.16
6.88
6.86
6.86
6.85
6.84
6.83
4.57
4.10
1.89
1.87
1.51
1.49
4.82
15.23
3.83
1.00
1.12
3.24
2.99
f1 (ppm)


cc-20180611-B2-P1-407/2
13CPD
199.01
146.73
146.05
146.00
143.10
138.37
132.86
129.32
129.16
128.80
128.52
128.29
128.09
127.77
126.82
125.53
119.52
116.39
99.49
44.52
43.90
14.80
12.72
f1 (ppm)

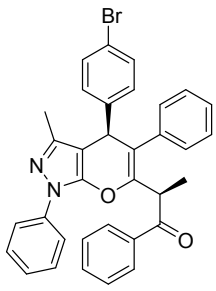
(*S*)-2-((*S*)-3-Methyl-1,4,5-triphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'a):



anti-4'a

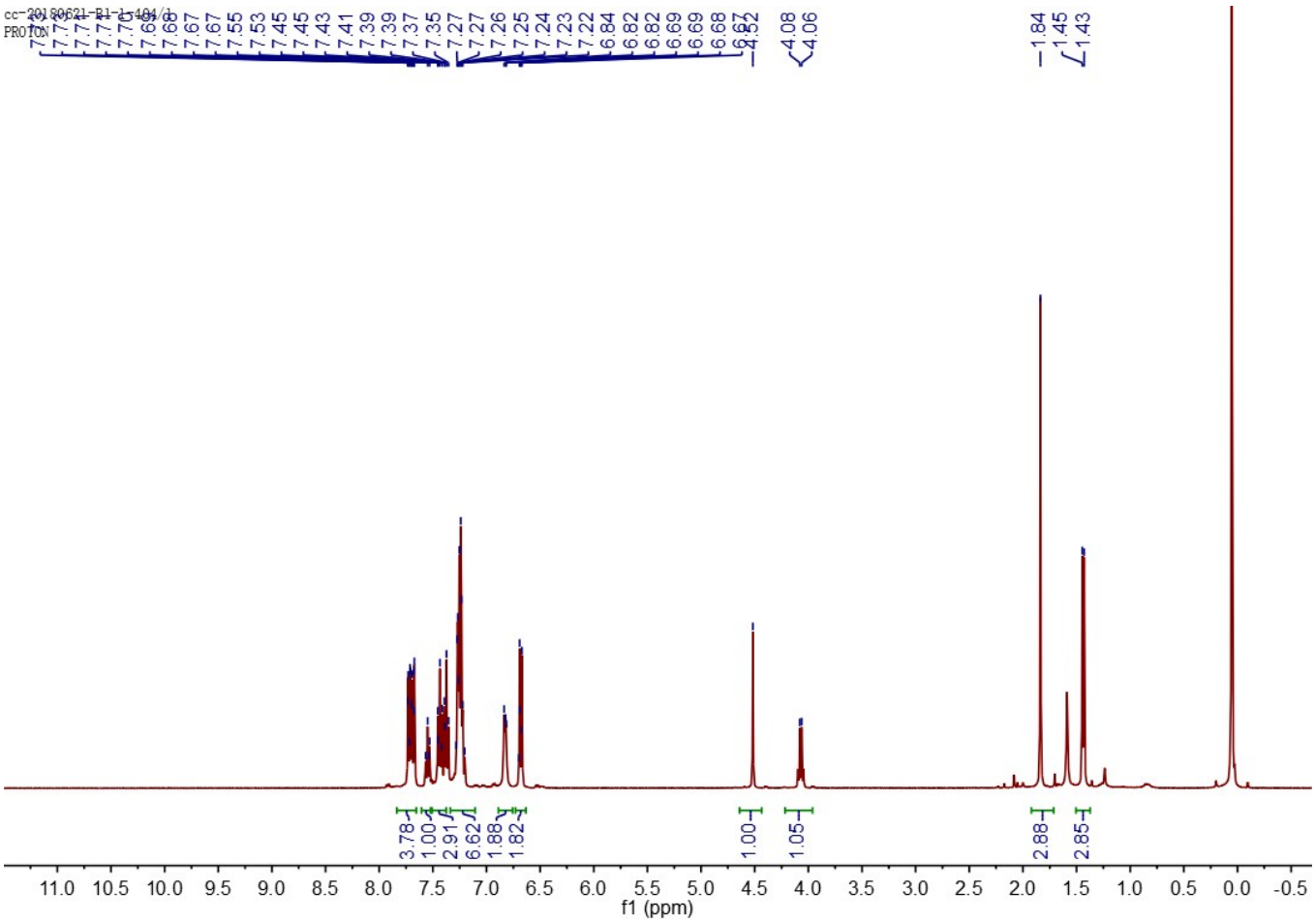
Orange solid, m.p. 168-169 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 4H), 7.58-7.56 (m, 1H), 7.48-7.43 (m, 2H), 7.41-7.39 (m, 2H), 7.32-7.26 (m, 4H), 7.18-7.16 (m, 3H), 6.85-6.81 (m, 4H), 4.57 (s, 1H), 4.11 (q, *J* = 6.8 Hz, 1H), 1.89 (s, 3H), 1.50 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.0, 146.7, 146.0, 143.1, 138.3, 138.0, 136.5, 132.8, 129.3, 129.1, 128.8, 128.5, 128.3, 128.1, 127.7, 126.8, 125.5, 119.5, 116.3, 99.5, 44.5, 43.9, 14.8, 12.7.

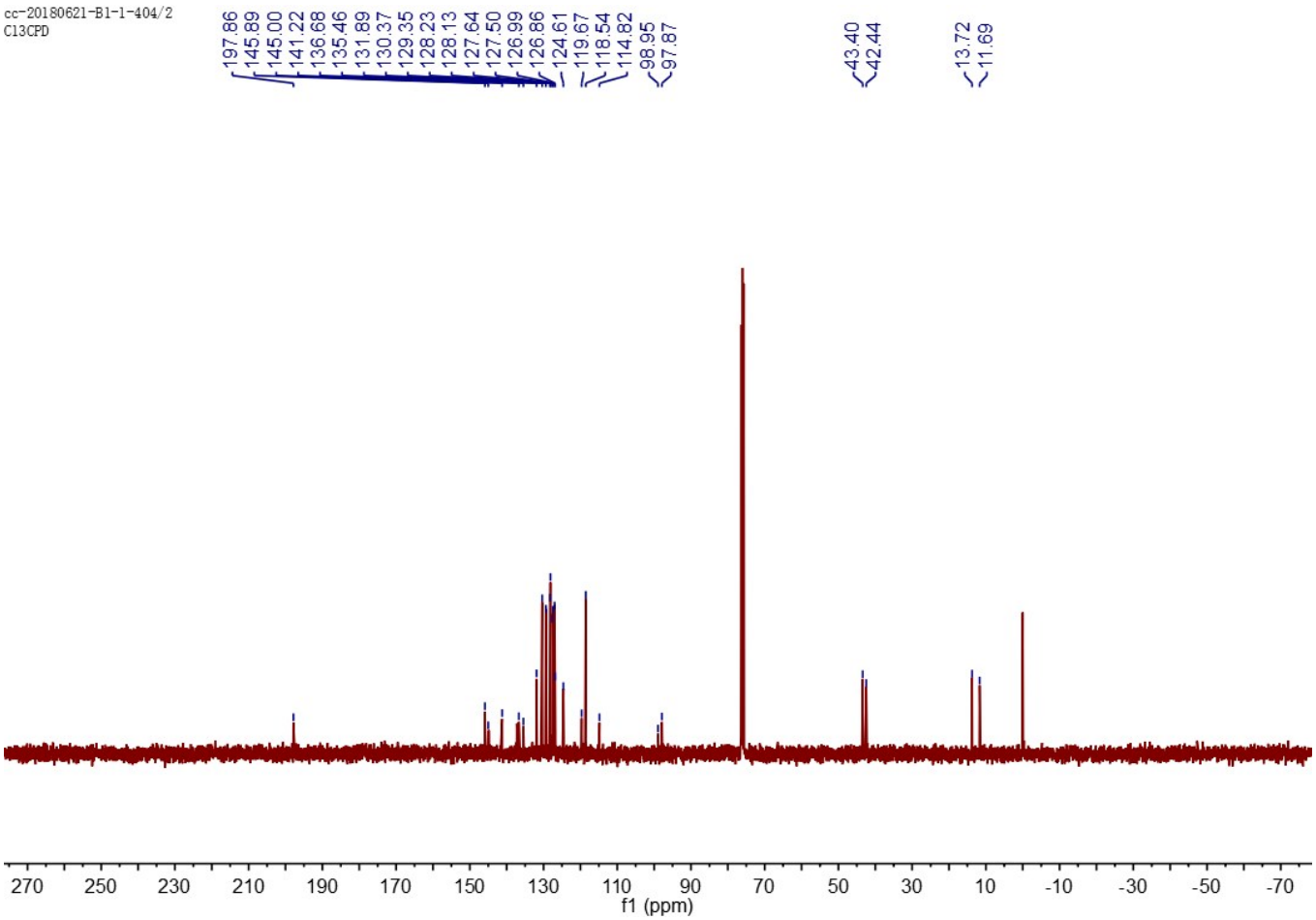
(*R*)-2-((*S*)-4-(4-Bromophenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'b):



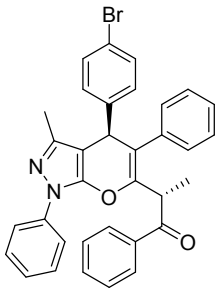
***syn*-4'b**

Yellow solid, m.p. 132-132 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 4H), 7.45-7.43 (m, 6H), 7.29-7.21 (m, 5H), 6.83-6.81 (m, 2H), 6.68-6.66 (m, 2H), 4.52 (s, 1H), 4.07 (q, *J* = 6.8 Hz, 1H), 1.84 (s, 3H), 1.44 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 145.9, 141.2, 137.2, 136.6, 131.9, 130.3, 129.3, 128.2, 128.14 127.6, 127.5, 127.0, 126.8, 124.6, 119.6, 118.5, 114.8, 97.8, 43.4, 42.4, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{34}H_{28}BrN_2O_2$ $[M + H]^+$ 575.1329, found 575.1332.


cc-20180621-B1-1-404/1
PROTON
f1 (ppm)

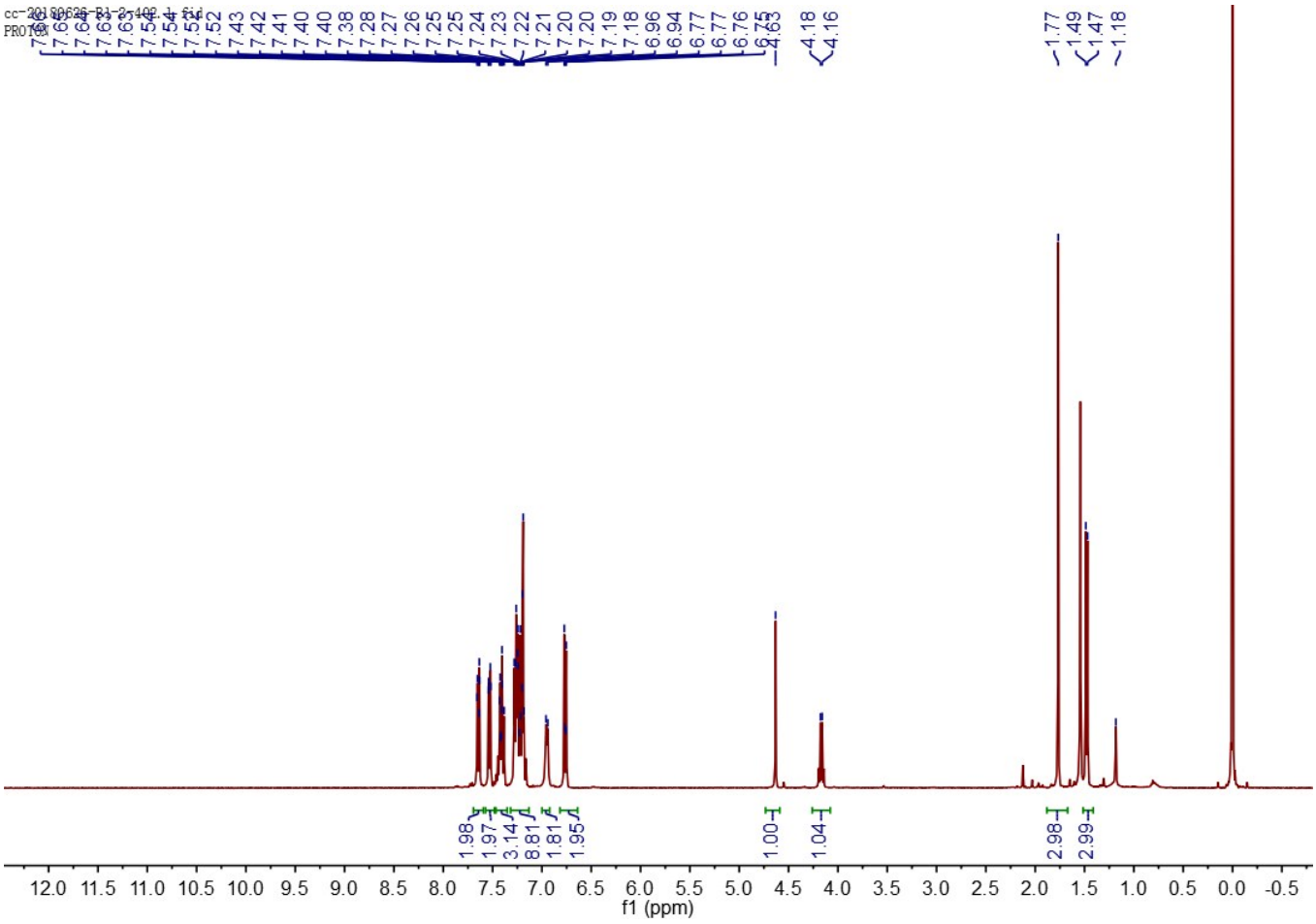

cc-20180621-B1-1-404/2
C13CPD
f1 (ppm)

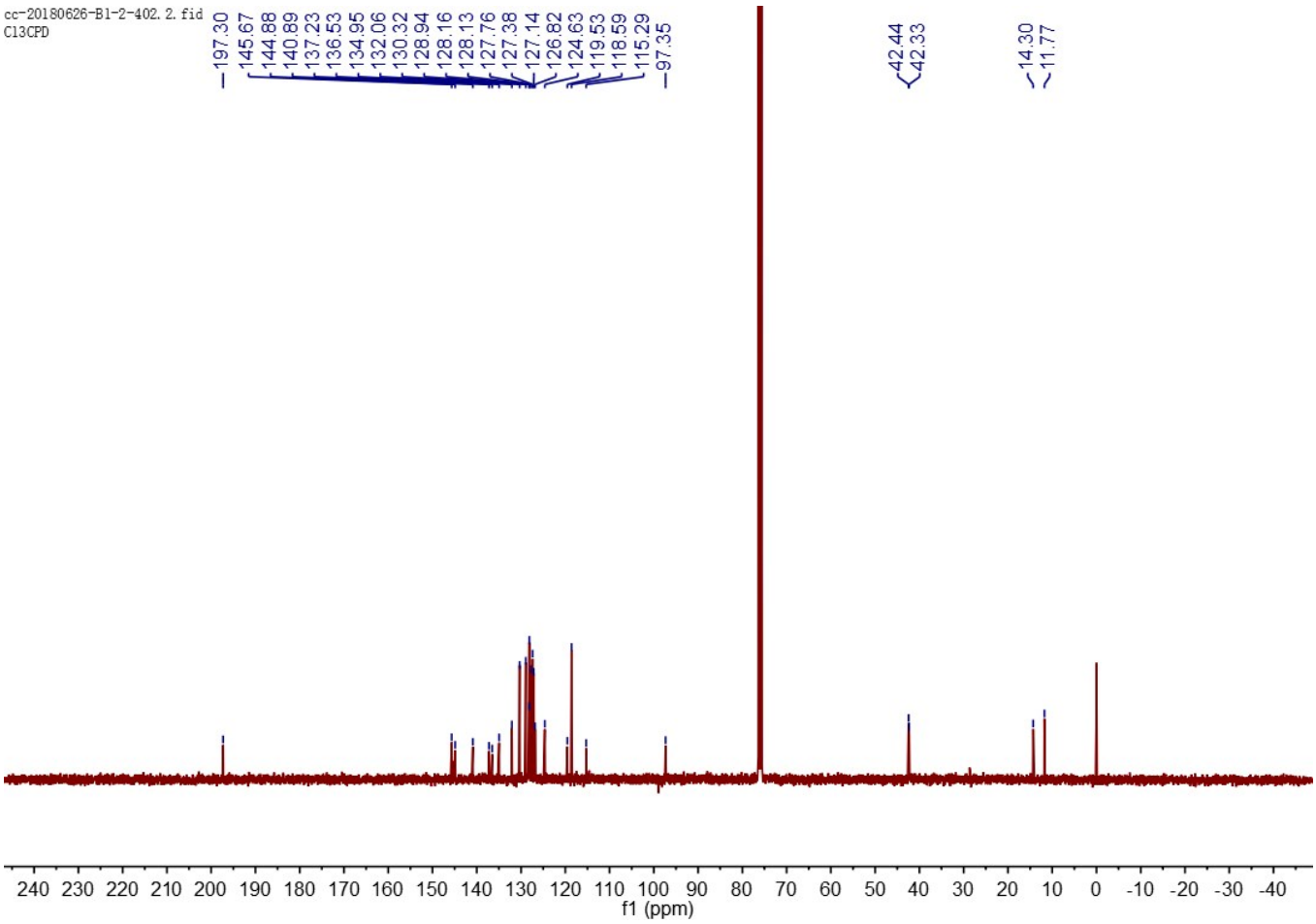
(*S*)-2-((*S*)-4-(4-Bromophenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'b):



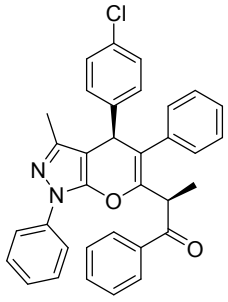
***anti*-4'b**

White solid, m.p. 207-209 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (m, 2H), 7.53-7.50 (m, 2H), 7.42-7.40 (m, 3H), 7.23-7.21 (m, 8H), 6.95-6.93 (m, 2H), 6.76-6.74 (m, 2H), 4.63 (s, 1H), 4.17 (q, *J* = 6.8 Hz, 1H), 1.77 (s, 3H), 1.48 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 145.6, 144.9, 140.9, 137.2, 136.5, 134.9, 132.0, 130.3, 128.9, 128.1, 127.7, 127.3, 127.1, 126.8, 124.6, 119.5, 118.6, 115.3, 97.3, 42.4, 42.3, 14.3, 11.7.



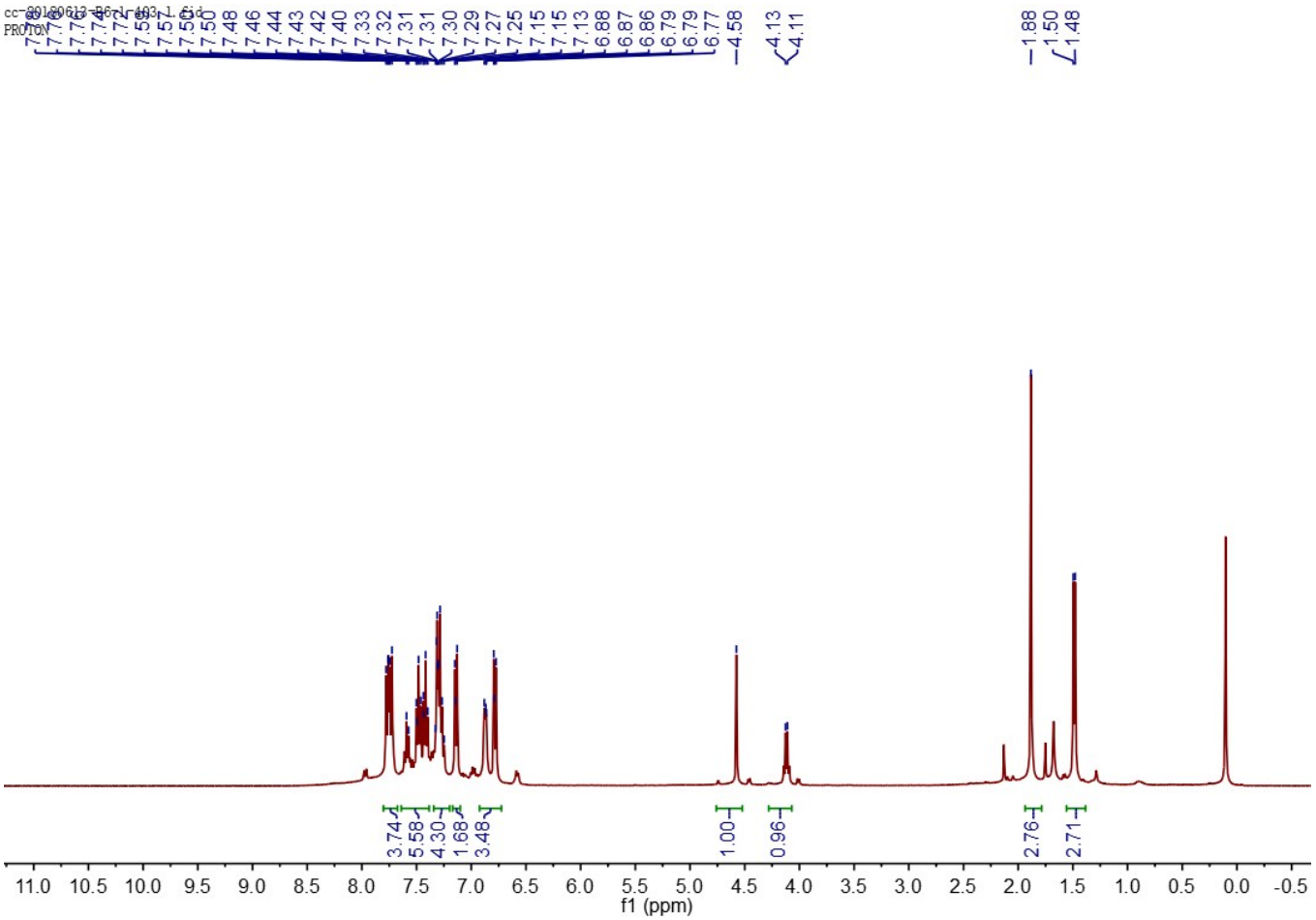


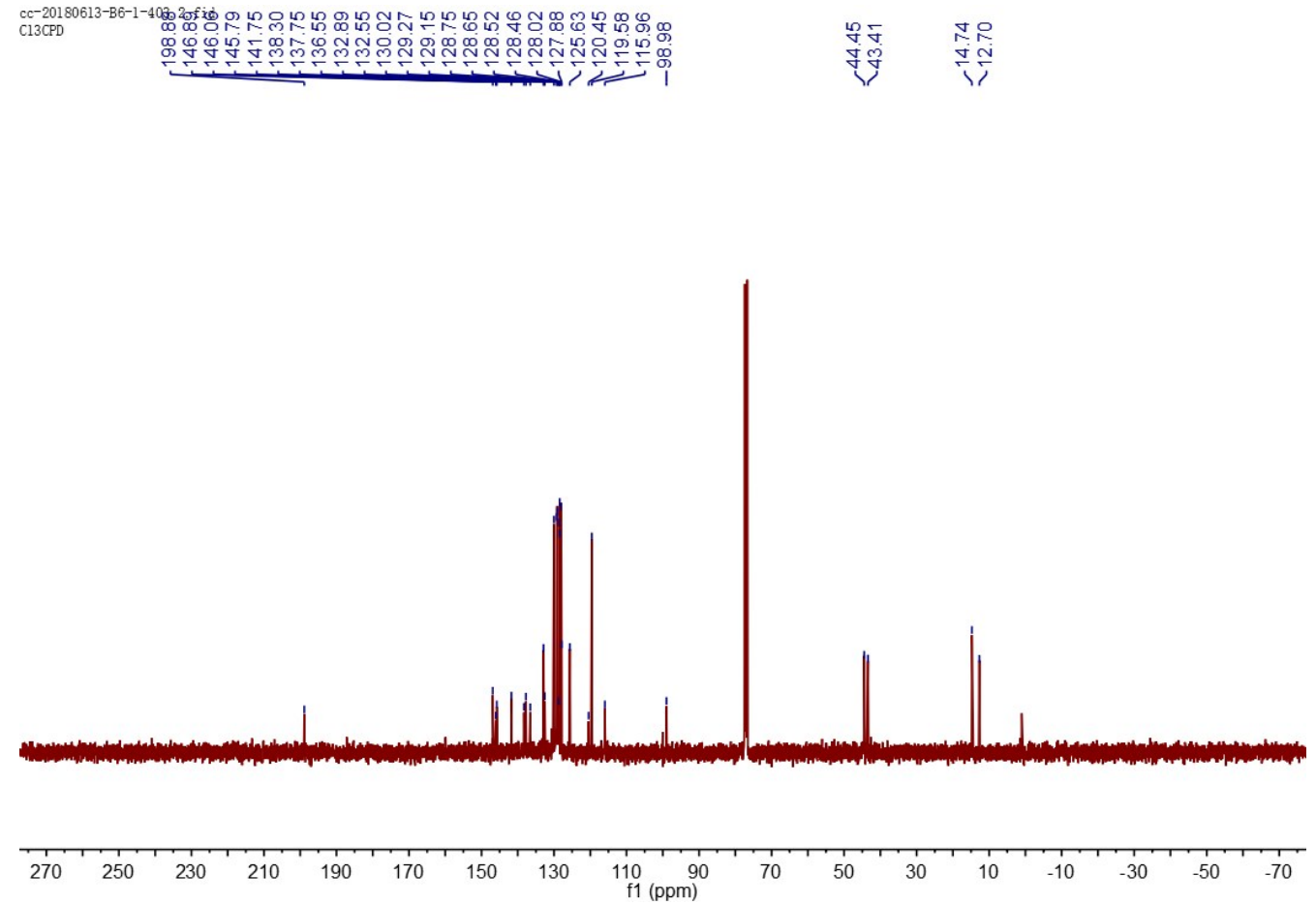
(*R*)-2-((*S*)-4-(4-Chlorophenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'c):



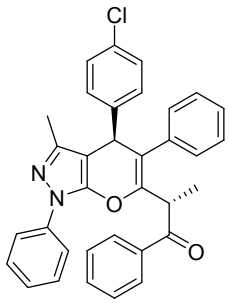
***syn*-4'c**

Yellow solid, m.p. 154-156 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.70 (m, 3H), 7.6-7.38 (m, 6H), 7.35-7.22 (m, 4H), 7.14-7.12 (m, 2H), 6.83-6.81 (m, 4H), 4.58 (s, 1H), 4.12 (q, J = 6.8 Hz, 1H), 1.88 (s, 3H), 1.49 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 146.9, 145.8, 141.7, 137.7, 136.5, 132.9, 132.5, 130.0, 129.2, 129.1, 128.6, 128.5, 128.4, 128.0, 127.8, 125.6, 119.5, 115.9, 98.9, 44.4, 43.4, 14.7, 12.7. HRMS (ESI) *m/z* calcd for $C_{34}H_{28}ClN_2O_2$ $[M + H]^+$ 531.1834, found 531.1837.


PROTON
f1 (ppm)

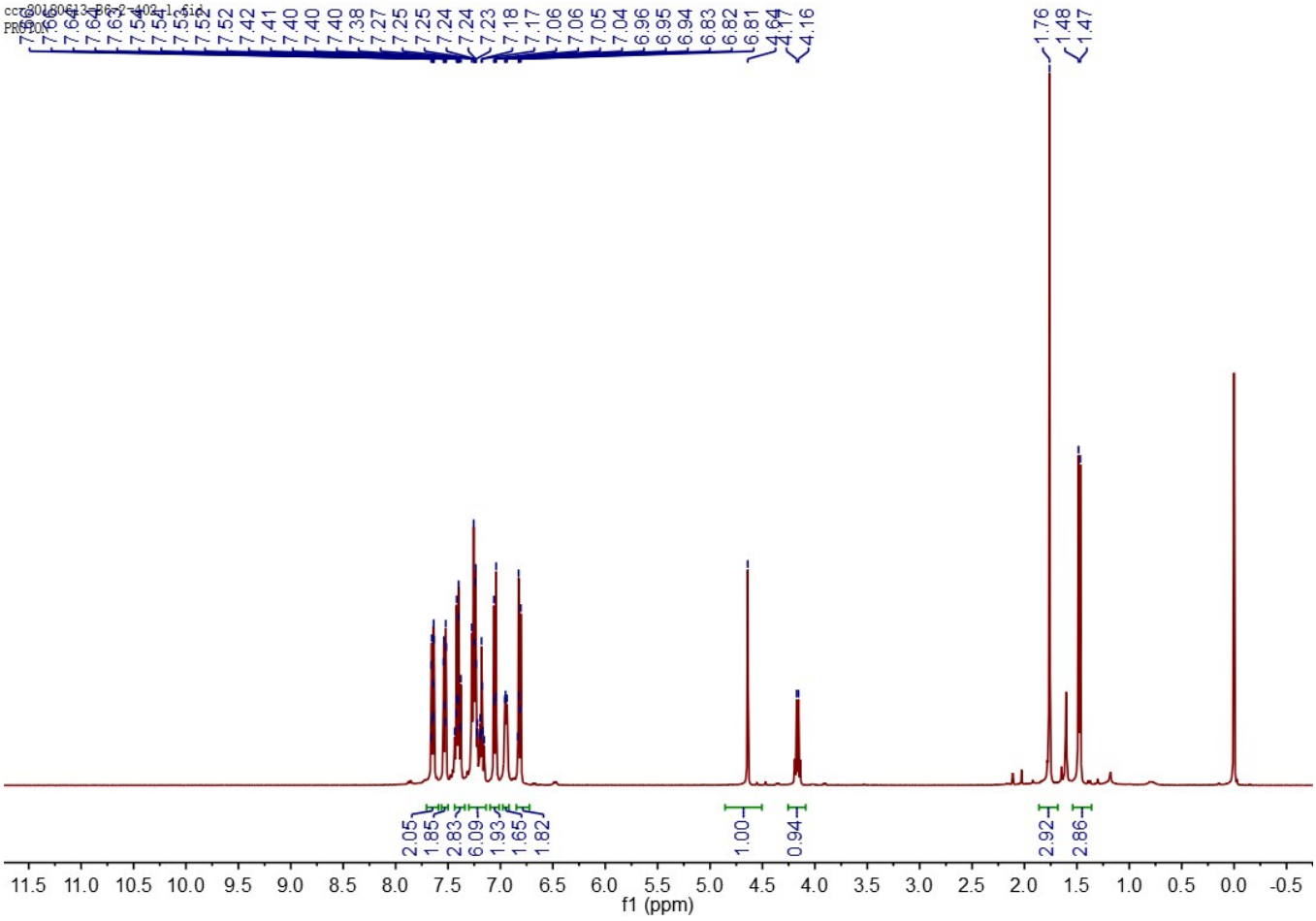

C13CPD
f1 (ppm)

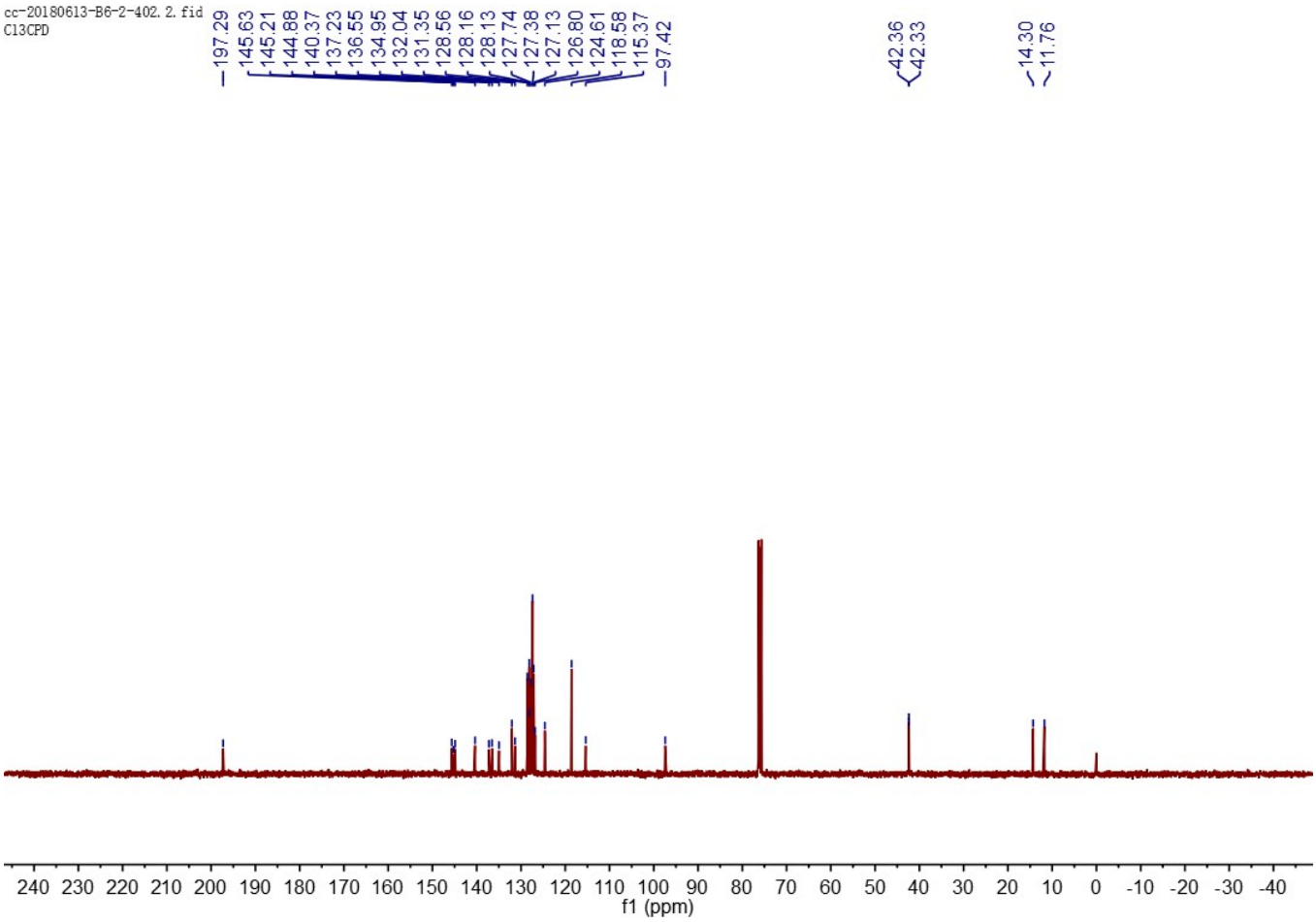
(*S*)-2-((*S*)-4-(4-Chlorophenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'c):



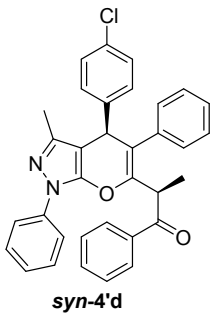
***anti*-4'c**

Yellow solid, m.p. 192-193 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.61 (m, 2H), 7.55-7.50 (m, 2H), 7.45-7.36 (m, 3H), 7.30-7.14 (m, 6H), 7.05-7.03 (m, 2H), 6.95-6.90 (m, 2H), 6.82-6.80 (m, 2H), 4.64 (s, 1H), 4.16 (q, J = 6.8 Hz, 1H), 1.76 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 145.6, 145.2, 144.8, 140.3, 137.2, 136.5, 134.9, 132.0, 131.3, 128.5, 128.1, 127.7, 127.3, 127.1, 126.8, 124.6, 118.5, 115.3, 97.4, 42.3, 14.3, 11.7.



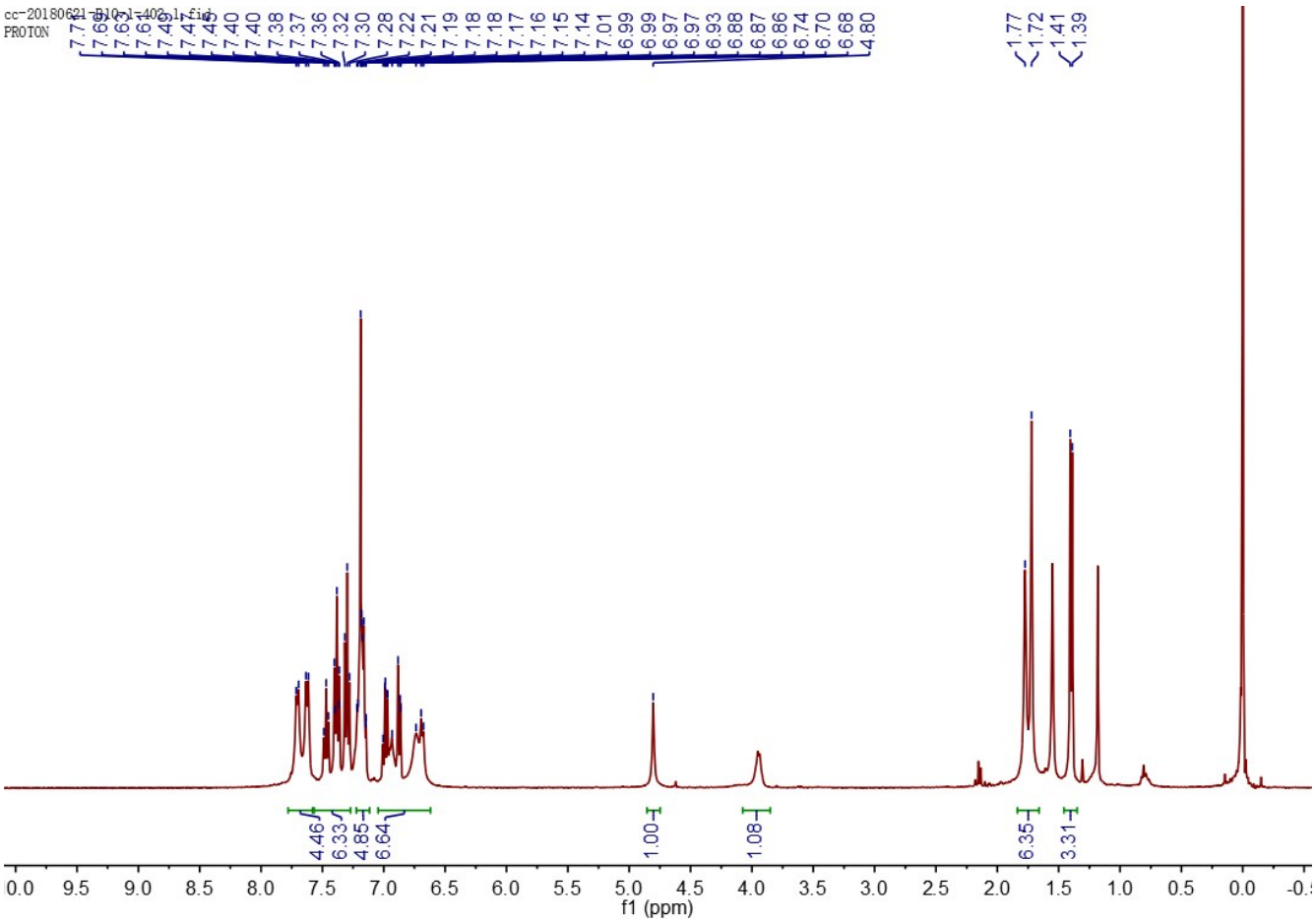


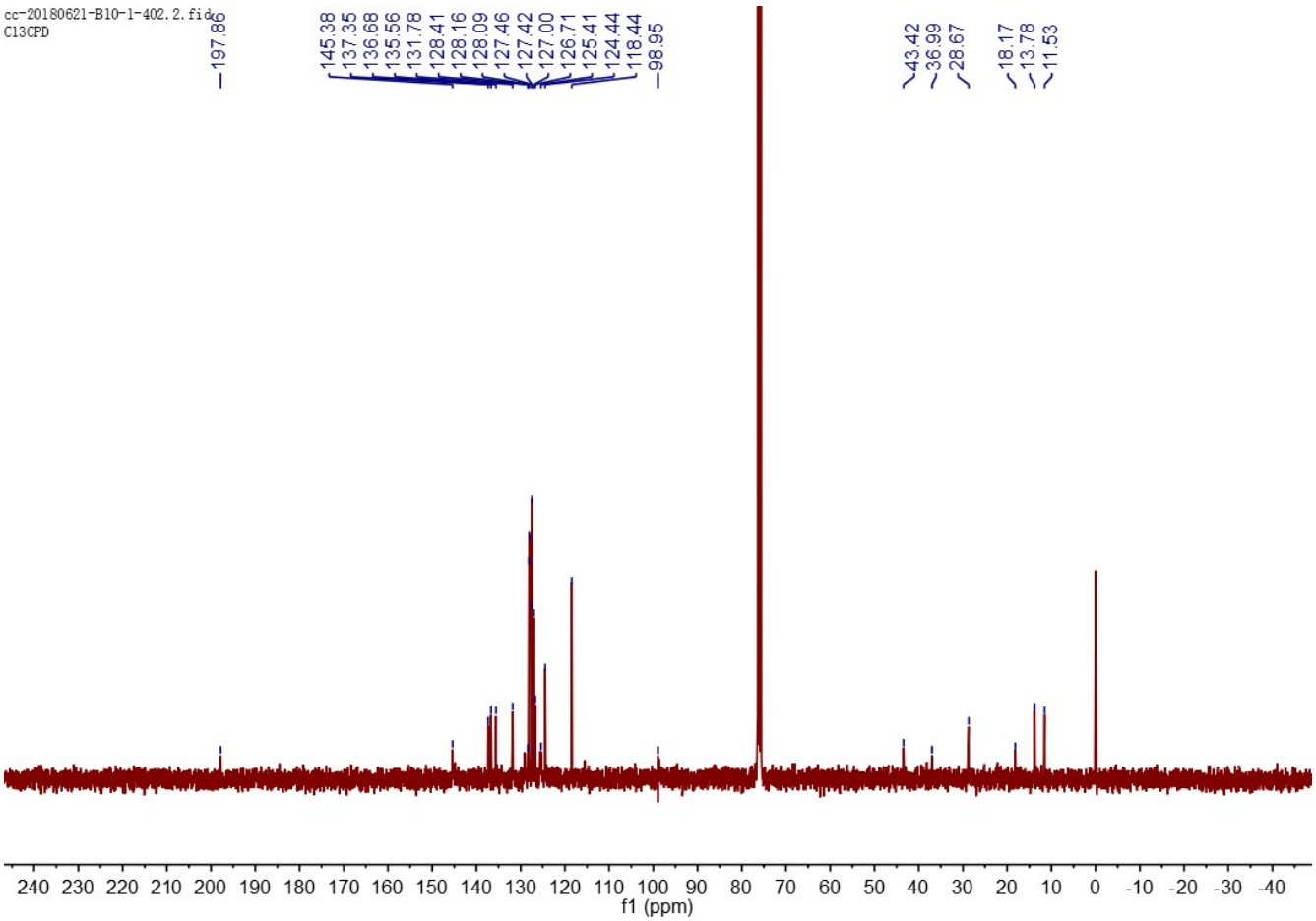
(*R*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(*o*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'd):



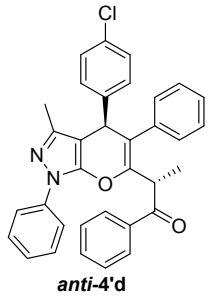
syn-4'd

White solid, m.p. 186-187 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.26 (m, 10H), 7.15 (s, 2H), 6.95-6.92 (m, 4H), 6.79-6.61 (m, 3H), 4.80 (s, 1H), 3.95 (s, 1H), 1.77 (s, 3H), 1.72 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.3, 137.3, 136.7, 135.5, 131.7, 128.1, 128.1, 127.4, 127.0, 126.7, 124.4, 118.4, 43.4, 28.6, 18.1, 13.7, 11.5. HRMS (ESI) *m/z* calcd for $C_{35}H_{31}N_2O_2$ $[M + H]^+$ 511.2380, found 511.2385.


cc-20180621-B10-1-402.1.fid
PROTON
7.74 7.66 7.63 7.61 7.47 7.45 7.40 7.40 7.38 7.37 7.36 7.32 7.30 7.28 7.22 7.21 7.19 7.18 7.18 7.17 7.16 7.15 7.14 7.01 6.99 6.99 6.97 6.97 6.93 6.88 6.87 6.86 6.74 6.70 6.68 4.80
1.77 1.72 1.41 1.39
4.46 6.33 4.85 6.64 1.00 1.08 6.35 3.31
0.0 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
f1 (ppm)

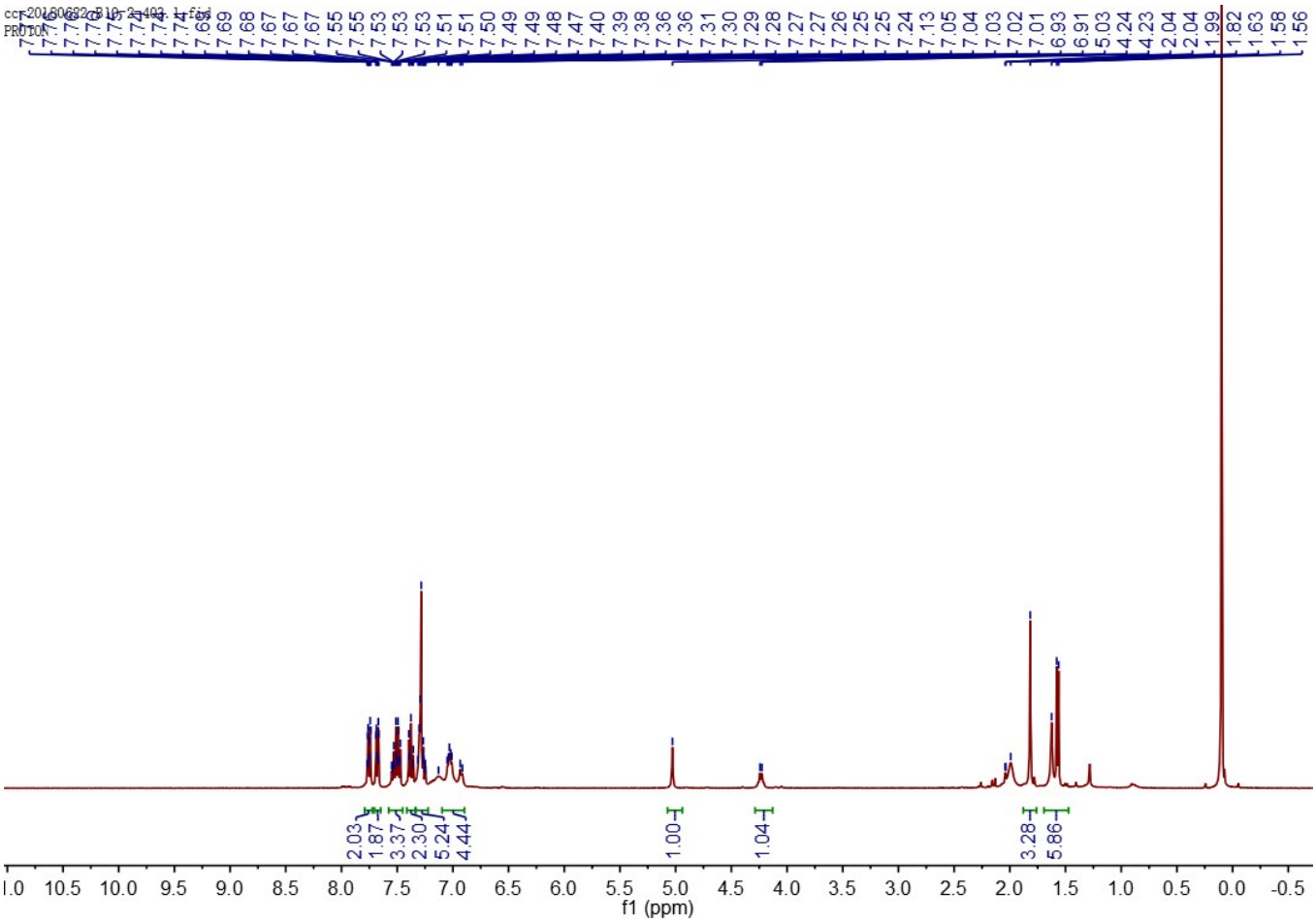

cc-20180621-B10-1-402.2.fid
C13CPD
197.86
145.38 137.35 136.68 135.56 131.78 128.41 128.16 128.09 127.46 127.42 127.00 126.71 125.41 124.44 118.44 98.95
43.42 36.99 28.67 18.17 13.78 11.53
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

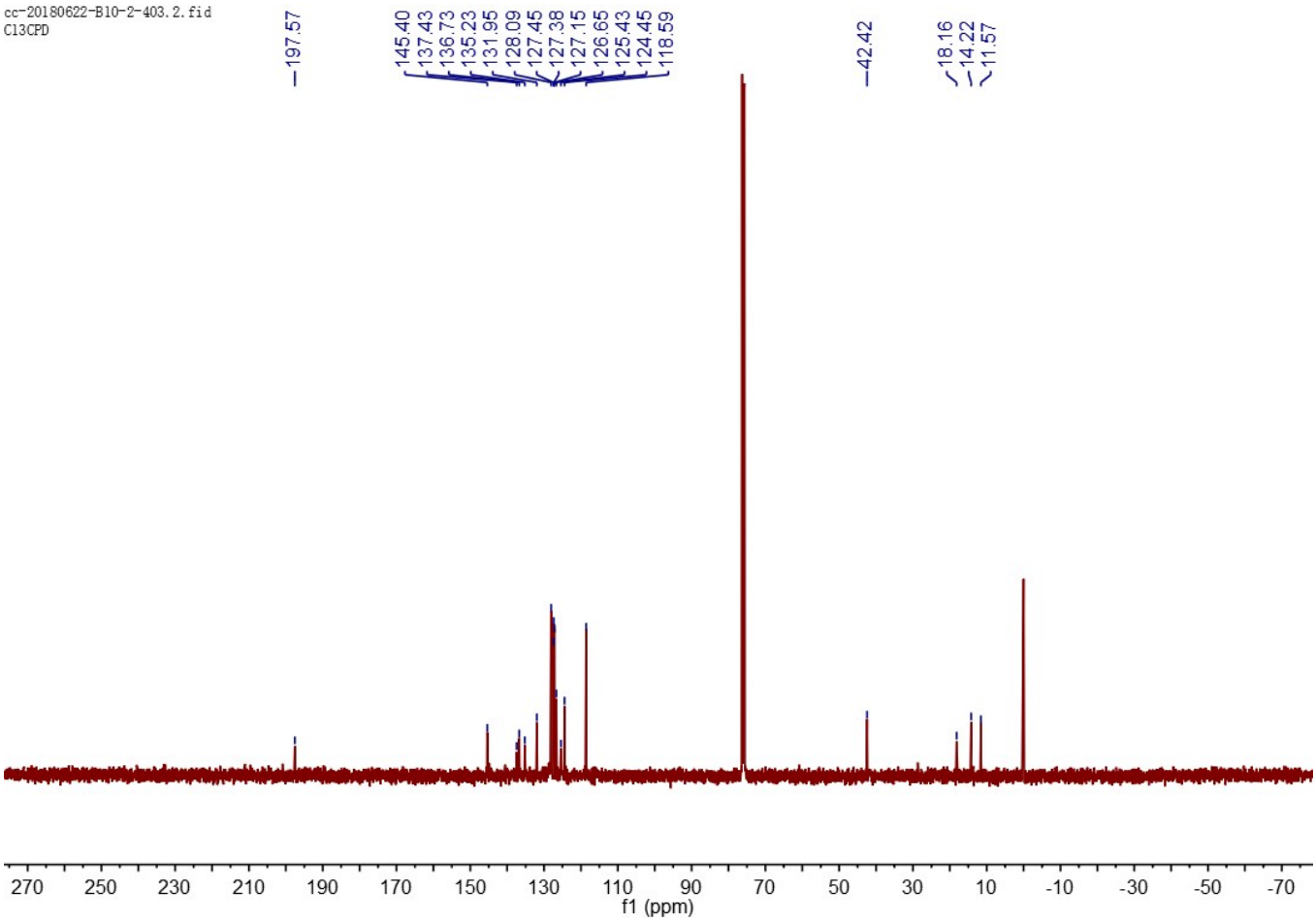
(*S*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(*o*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'd):



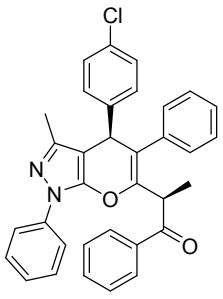
anti-4'd

White solid. m.p. 202-203 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.65 (m, 6H), 7.51-7.49 (m, 5H), 7.38 (s, 4H), 7.07-6.89 (m, 4H), 5.03 (s, 1H), 4.23 (d, *J* = 6.6 Hz, 1H), 1.99 (s, 3H), 1.82 (s, 3H), 1.57 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 145.4, 136.7, 135.2, 131.9, 128.1, 127.4, 127.3, 127.1, 126.6, 124.4, 118.6, 42.4, 28.1, 18.1, 14.2, 11.5.



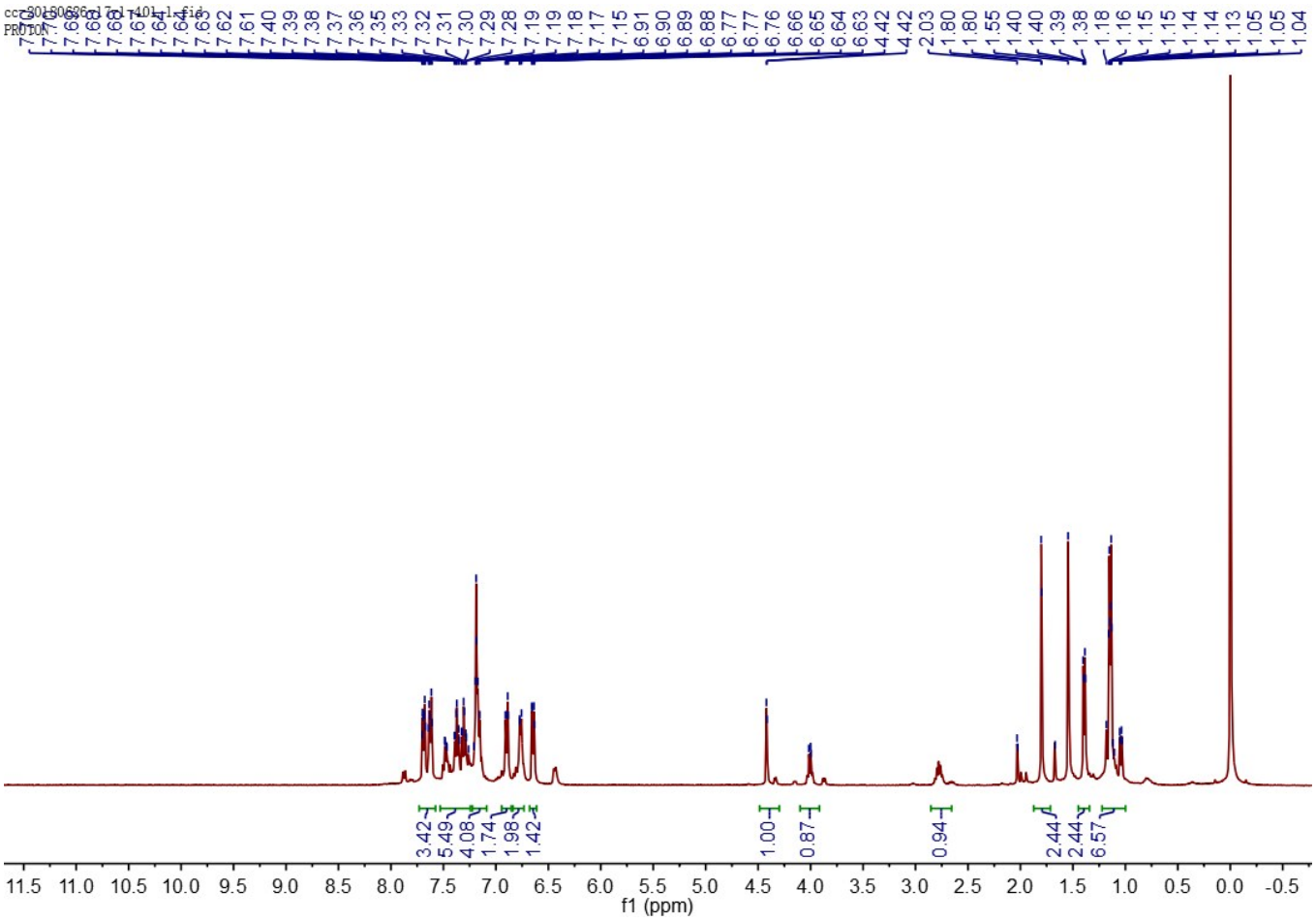


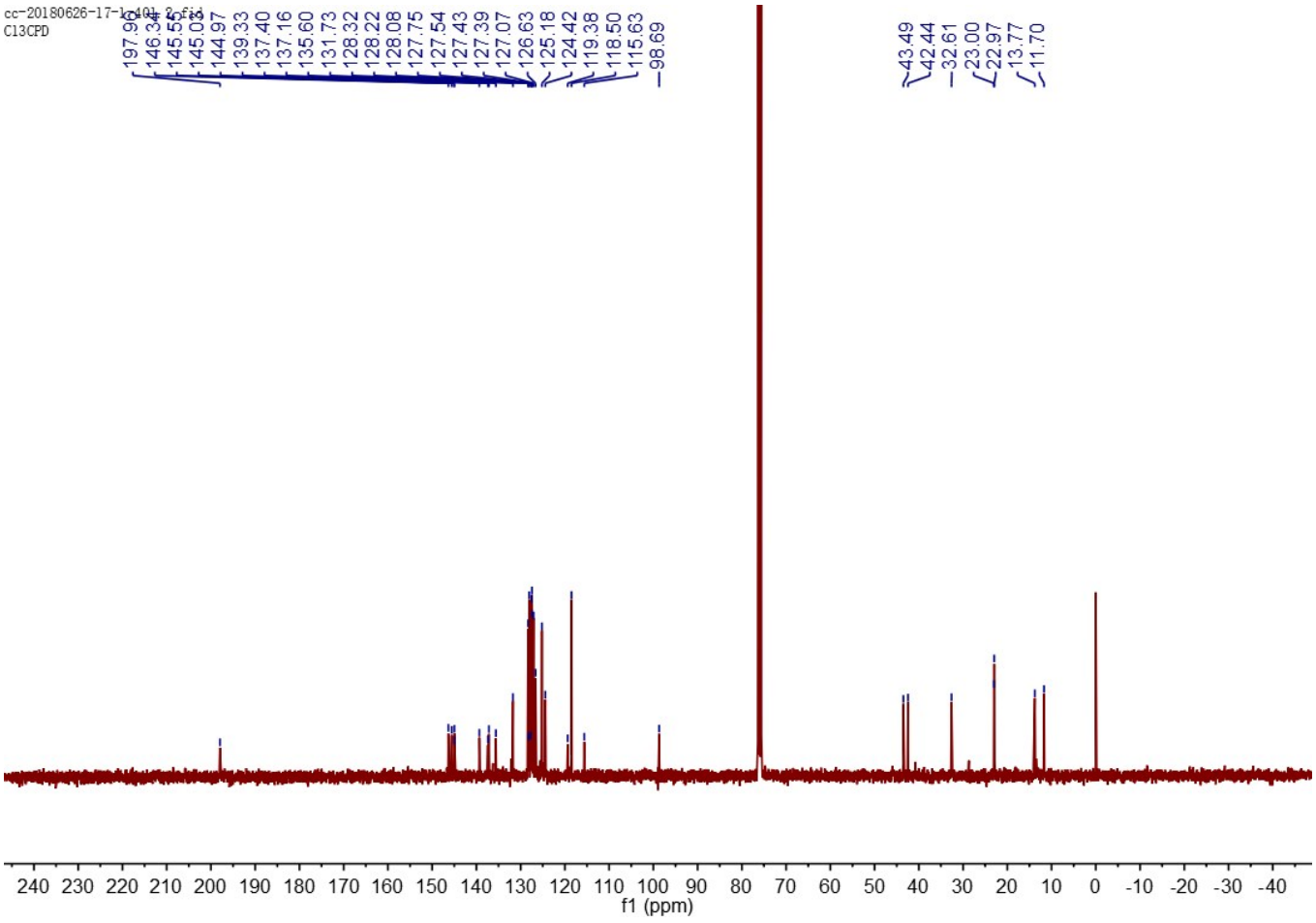
(*R*)-2-((*S*)-4-(4-Isopropylphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'e):



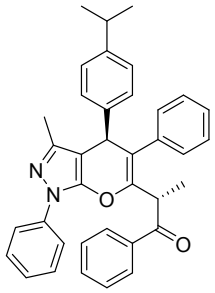
***syn*-4'e**

Yellow solid, m.p. 165-167 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 5H), 7.51-7.23 (m, 7H), 6.90-6.88 (m, 2H), 6.76-7.74 (m, 3H), 6.65-6.63 (m, 2H), 4.42 (s, 1H), 4.01 (q, *J* = 6.7 Hz, 1H), 2.77 (dd, *J* = 13.6, 6.8 Hz, 1H), 1.80 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H), 1.14 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 146.3, 145.5, 144.9, 139.3, 137.4, 137.1, 135.6, 131.7, 128.3, 128.0, 127.7, 127.5, 127.4, 127.4, 127.0, 126.6, 125.2, 124.4, 119.4, 118.5, 115.6, 98.7, 43.4, 42.4, 32.6, 23.0, 22.9, 13.7, 11.7. HRMS (ESI) *m/z* calcd for $C_{37}H_{35}N_2O_2$ $[M + H]^+$ 539.2693, found 539.2691.


PROTON
3.42
5.49
4.08
1.74
1.98
1.42
1.00
0.87
0.94
2.44
2.44
6.57
f1 (ppm)

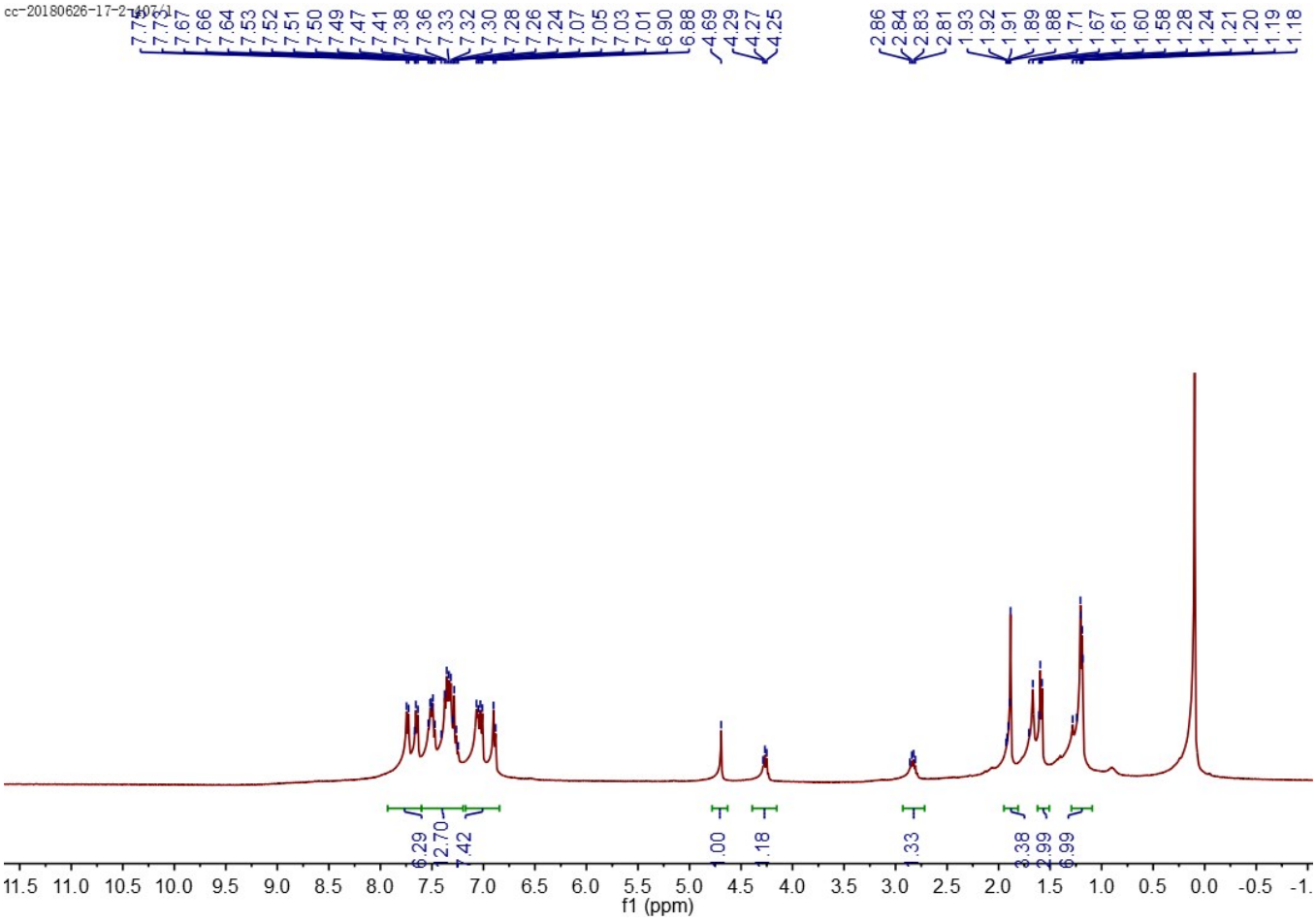

C13CPD
f1 (ppm)

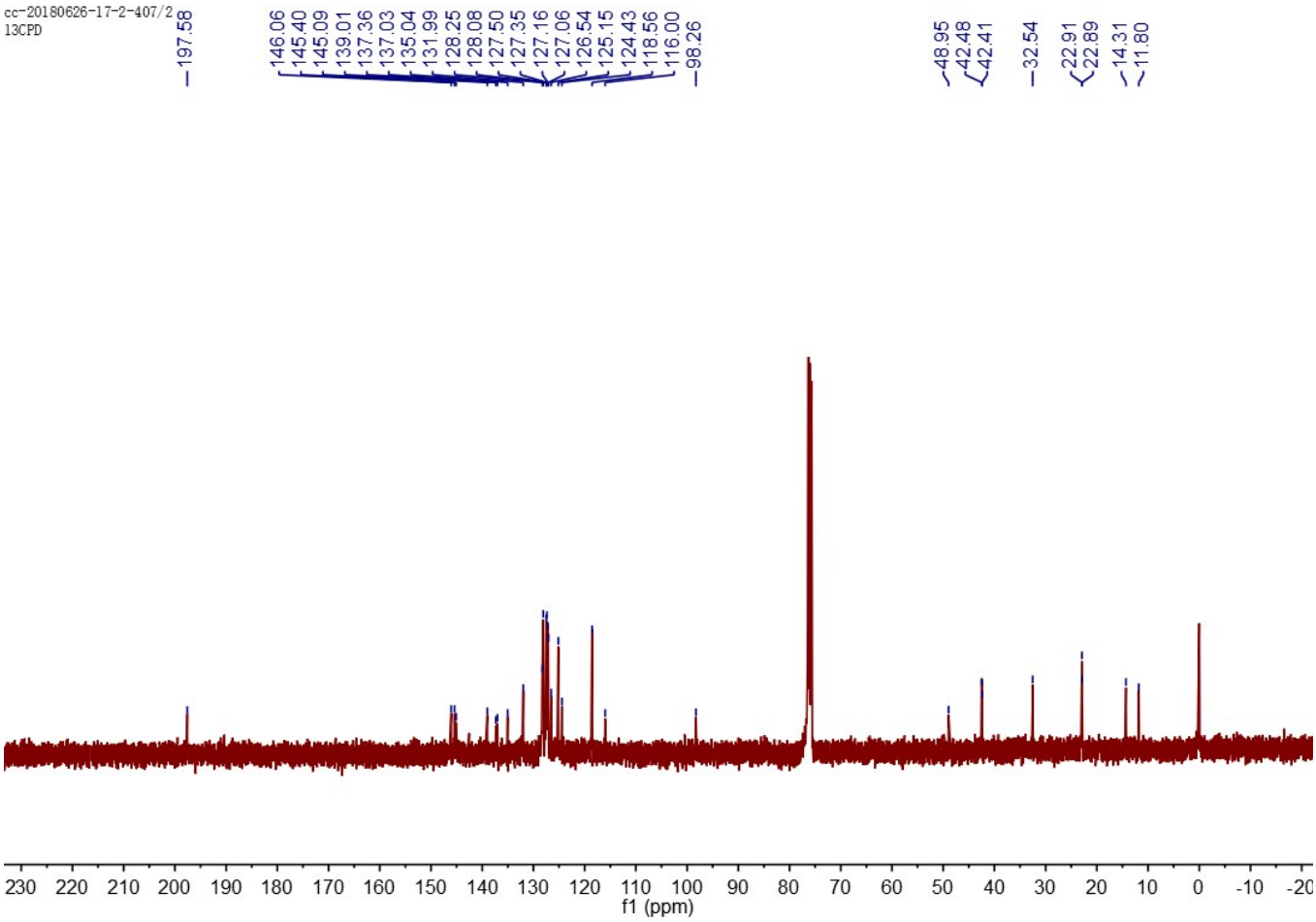
(*S*)-2-((*S*)-4-(4-Isopropylphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'e):



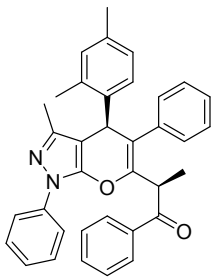
***anti*-4'e**

Yellow solid, m.p. 180-182 ˚C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 3H), 7.65-7.63 (m, 2H), 7.50-7.40 (m, 3H), 7.35-7.31 (m, 2H), 7.04-6.90 (m, 6H), 6.89-6.86 (m, 3H), 4.69 (s, 1H), 4.26 (dd, *J* = 13.4, 6.7 Hz, 1H), 2.92-2.67 (m, 1H), 1.88 (s, 3H), 1.59 (d, *J* = 6.7 Hz, 3H), 1.20 (d, *J* = 6.8 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 145.4, 139.0, 137.3, 137.0, 135.0, 132.0, 128.2, 128.0, 127.5, 127.3, 127.1, 127.0, 126.5, 125.1, 118.5, 116.1, 98.2, 42.4, 42.4, 32.5, 22.9, 14.3, 11.8.



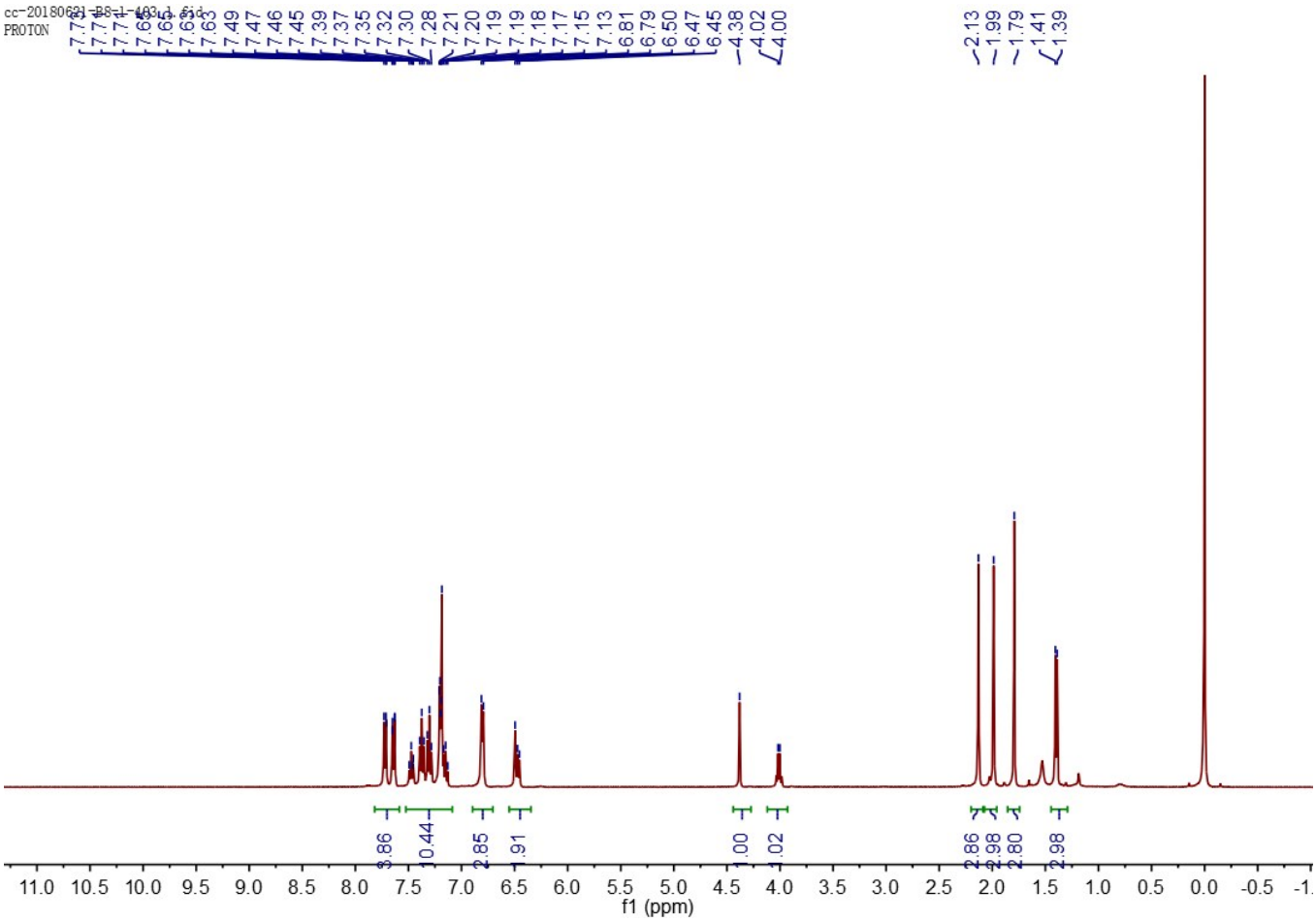


(*R*)-2-((*S*)-4-(2,4-Dimethylphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'f):



***syn*-4'f**

White solid, m.p. 165-167 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.64 (m, 4H), 7.47-7.45 (m, 1H), 7.34-7.31 (m, 3H), 7.23-7.11 (m, 5H), 6.80-6.77 (m, 3H), 6.53-6.44 (m, 2H), 4.38 (s, 1H), 4.01 (q, J = 6.8 Hz, 1H), 2.13 (s, 3H), 1.99 (s, 3H), 1.79 (s, 3H), 1.40 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.6, 145.0, 139.4, 137.4, 137.2, 135.5, 133.8, 131.8, 128.8, 128.4, 128.3, 128.1, 127.4, 127.1, 126.6, 125.1, 124.8, 118.4, 115.5, 98.7, 43.4, 42.5, 18.7, 18.4, 13.8, 11.7. HRMS (ESI) *m/z* calcd for $C_{36}H_{33}N_2O_2$ $[M + H]^+$ 525.2537, found 525.2538.


cc-20180621-B8-1-403.1.fid
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7.74
7.63
7.49
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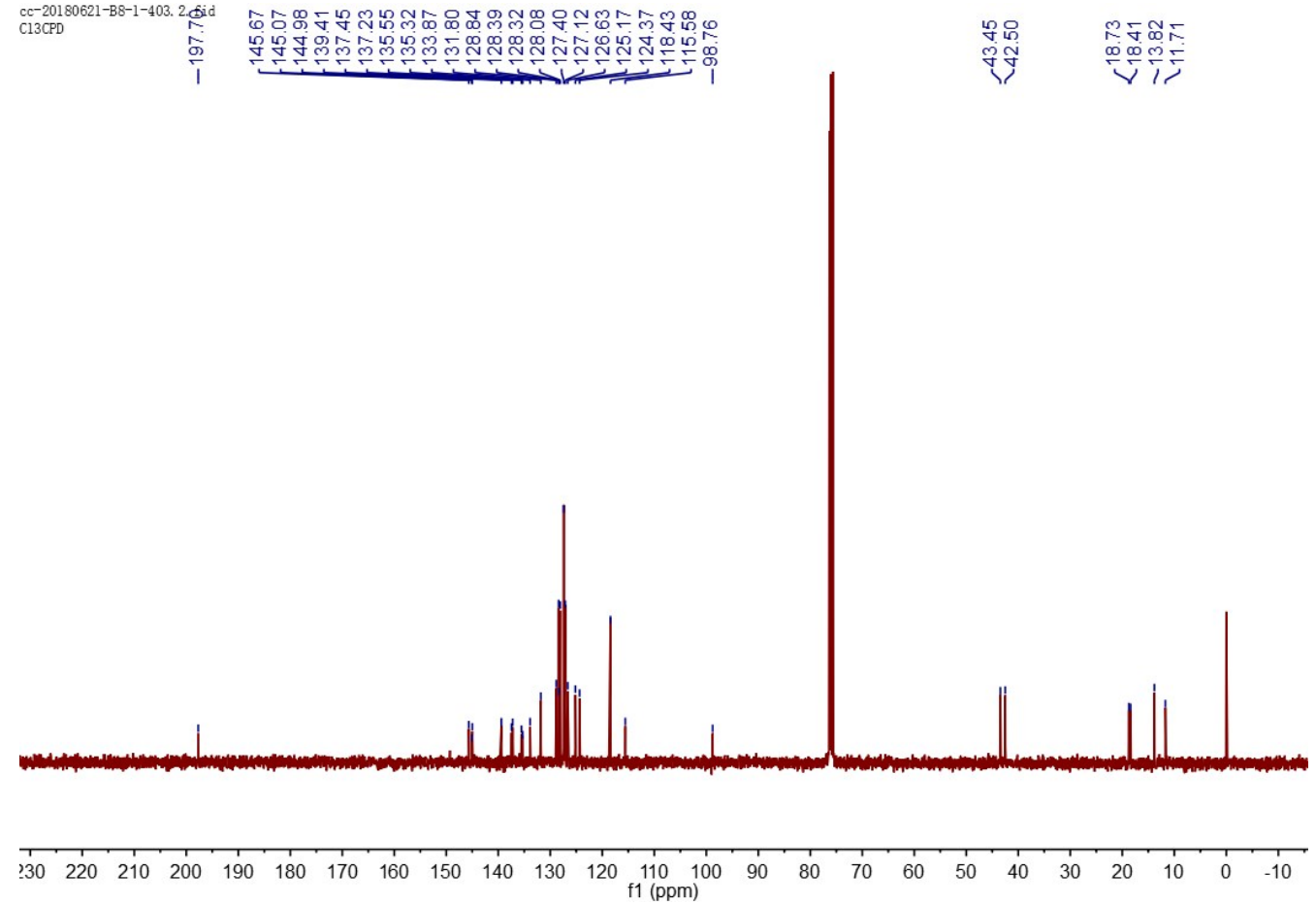
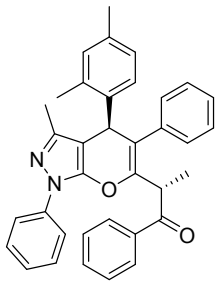
7.46
7.45
7.39
7.37
7.35
7.32
7.30
7.28
7.21
7.20
7.19
7.19
7.18
7.17
7.15
7.13
6.81
6.79
6.50
6.47
4.38
4.02
4.00
2.13
1.99
1.79
1.41
1.39
3.86
10.44
2.85
1.91
1.00
1.02
2.86
2.98
2.80
2.98
f1 (ppm)

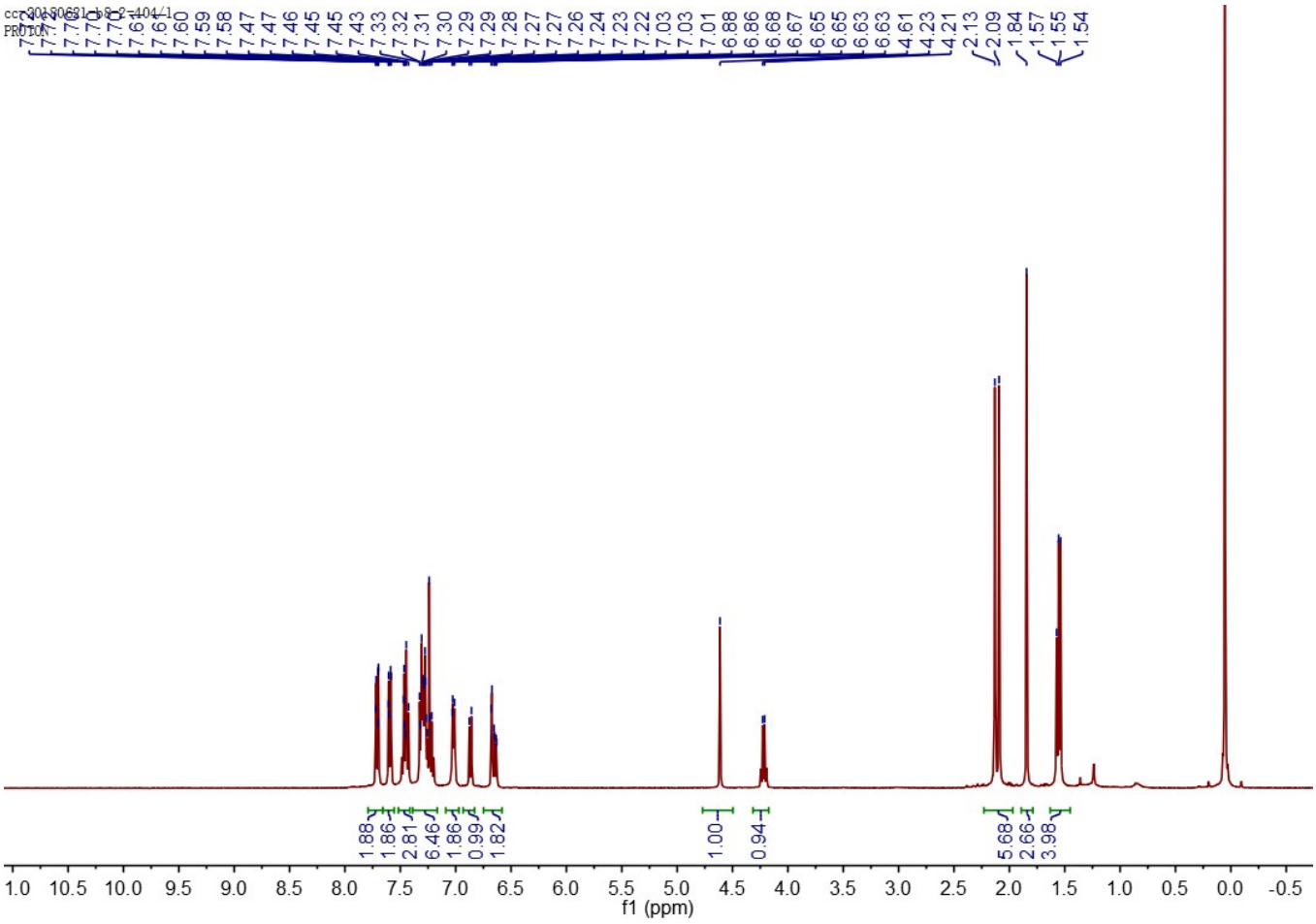

cc-20180621-B8-1-403.2.fid
C13CPD
145.67
145.07
144.98
139.41
137.45
137.23
135.55
135.32
133.87
131.80
128.84
128.39
128.32
128.08
127.40
127.12
126.63
125.17
124.37
118.43
115.58
98.76
43.45
42.50
18.73
18.41
13.82
11.71
f1 (ppm)

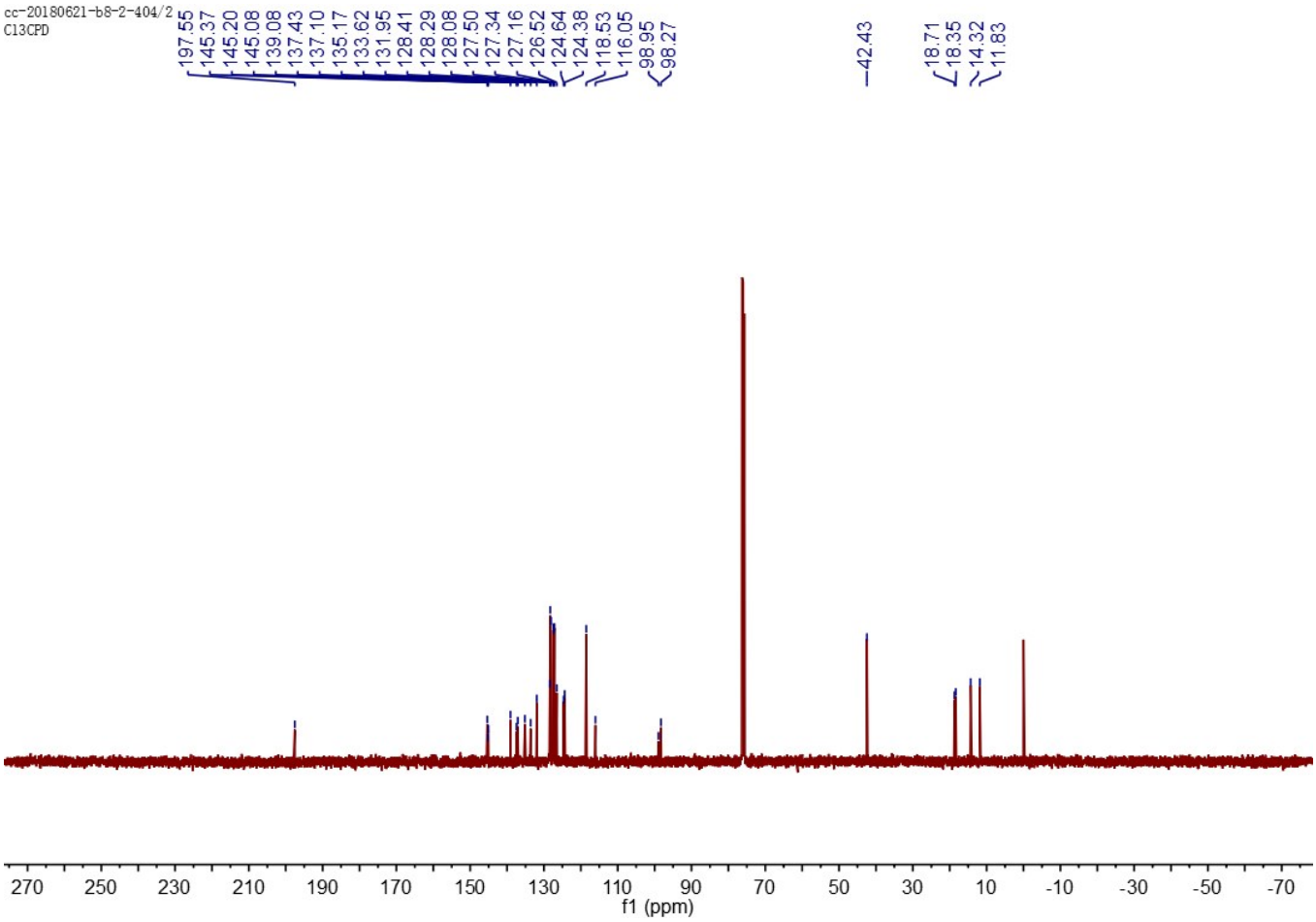
(*S*)-2-((*S*)-4-(2,4-Dimethylphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'f):



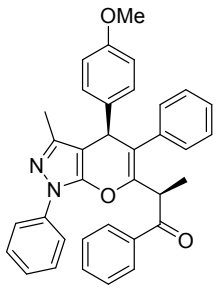
***anti*-4'f**

White solid, m.p. 157-159 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.63-7.56 (m, 2H), 7.46-7.43 (m, 4H), 7.29-7.26 (m, 5H), 7.02-7.00 (m, 2H), 6.87 (s, 1H), 6.71-6.60 (m, 2H), 4.61 (s, 1H), 4.22 (q, *J* = 6.8 Hz, 1H), 2.13 (s, 3H), 2.09 (s, 3H), 1.84 (s, 3H), 1.55 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 145.3, 145.1, 139.1, 137.4, 137.1, 135.1, 133.6, 131.9, 128.4, 128.3, 128.0, 127.5, 127.3, 127.1, 126.5, 124.6, 124.4, 118.5, 116.0, 98.2, 42.4, 42.3, 18.7, 18.3, 14.3, 11.8.



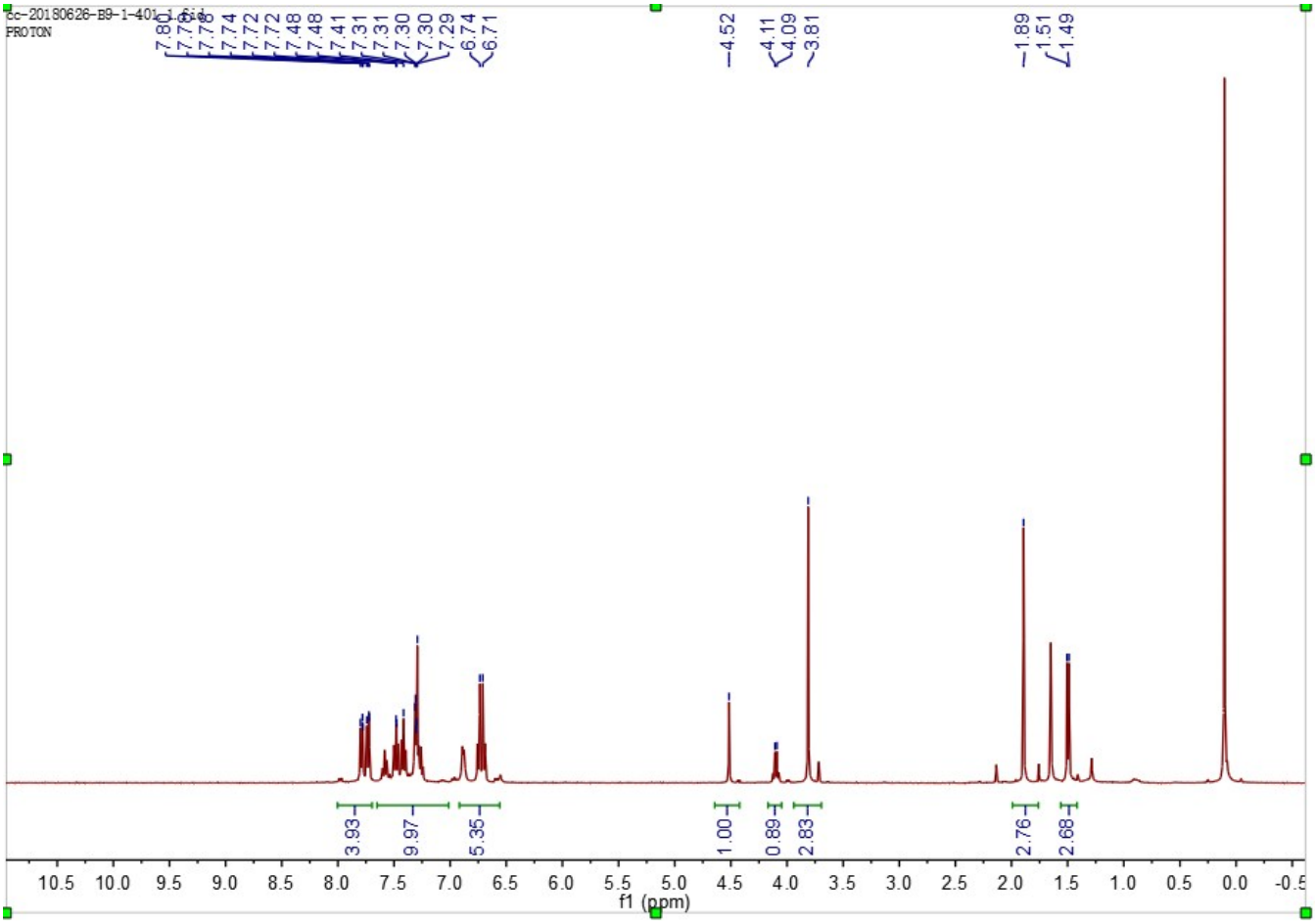


(*R*)-2-((*S*)-4-(4-Methoxyphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'g):



***syn*-4'g**

Yellow solid, m.p. 127-129 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.74 (m, 4H), 7.48-7.44 (m, 5H), 7.31 (s, 2H), 7.25 (s, 1H), 6.88-6.84 (m, 2H), 6.72-6.70 (m, 5H), 4.52 (s, 1H), 4.10 (q, *J* = 6.8 Hz, 1H), 3.81 (s, 3H), 1.89 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 157.3, 145.4, 144.9, 137.3, 137.1, 135.6, 134.3, 131.7, 128.7, 128.3, 128.1, 127.4, 127.0, 126.6, 124.4, 118.4, 115.6, 112.5, 98.5, 54.1, 43.4, 42.0, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{35}H_{31}N_2O_3$ $[M + H]^+$ 527.2329, found 527.2331.


cc-20180626-B9-1-401.1.fid
PROTON
7.80
7.78
7.78
7.74
7.72
7.72
7.48
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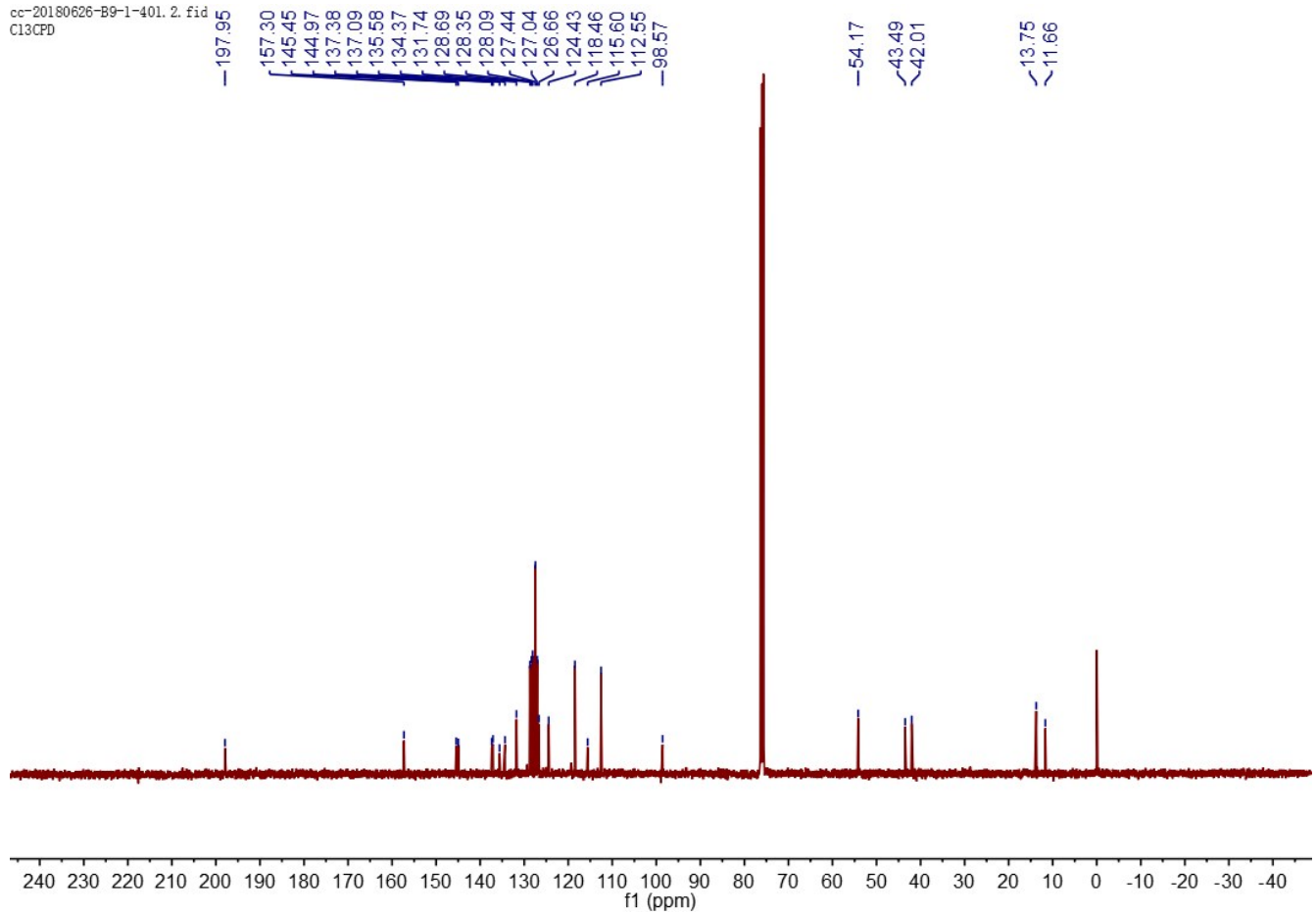
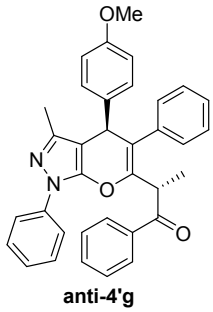
7.30
7.30
7.29
6.74
6.71
4.52
4.11
4.09
3.81
1.89
1.51
1.49
3.93
9.97
5.35
1.00
0.89
2.83
2.76
2.68
f1 (ppm)

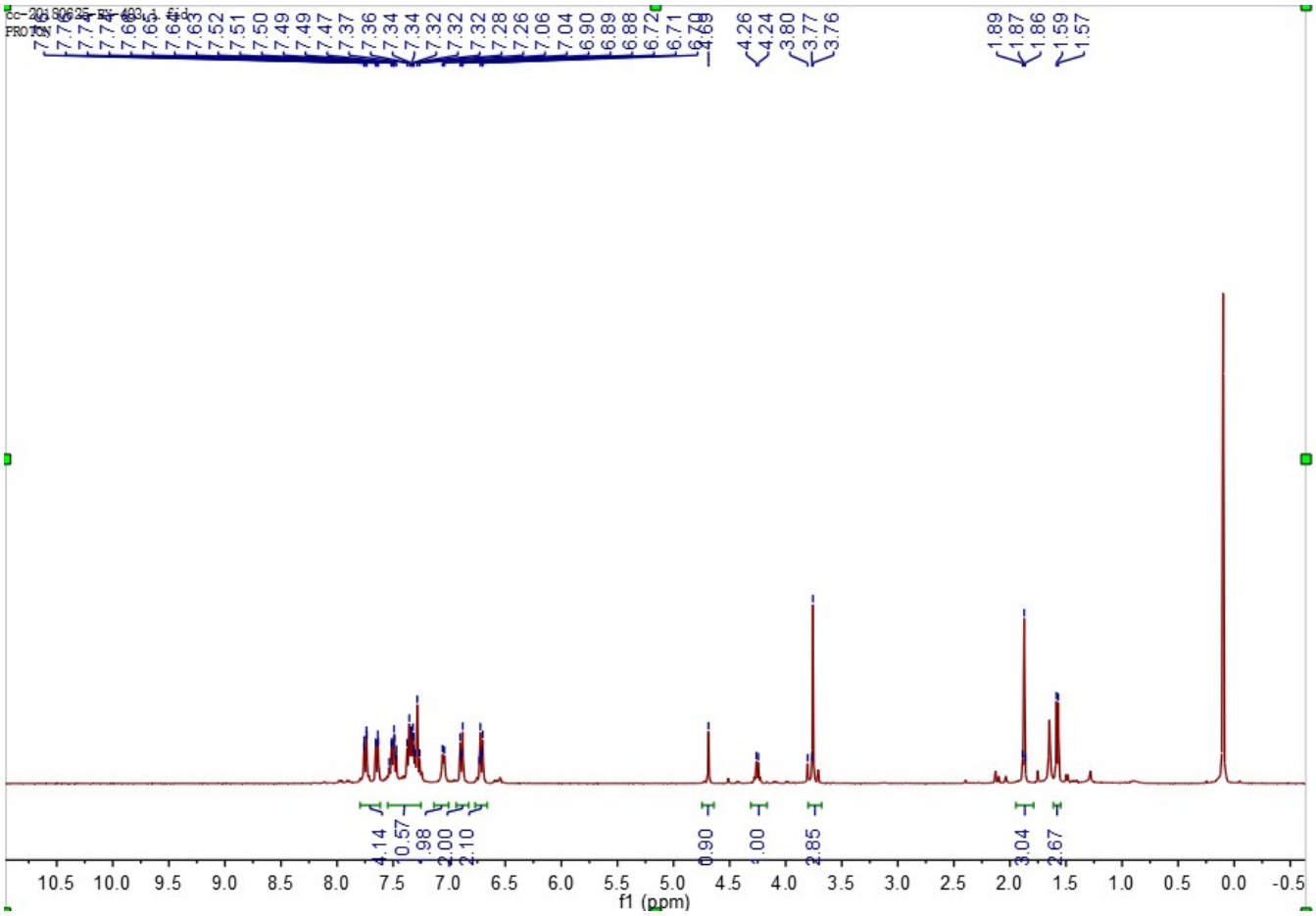

cc-20180626-B9-1-401.2.fid
C13CPD
197.95
157.30
145.45
144.97
137.38
137.09
135.58
134.37
131.74
128.69
128.35
128.09
127.44
127.04
126.66
124.43
118.46
115.60
112.55
98.57
54.17
43.49
42.01
13.75
11.66
f1 (ppm)

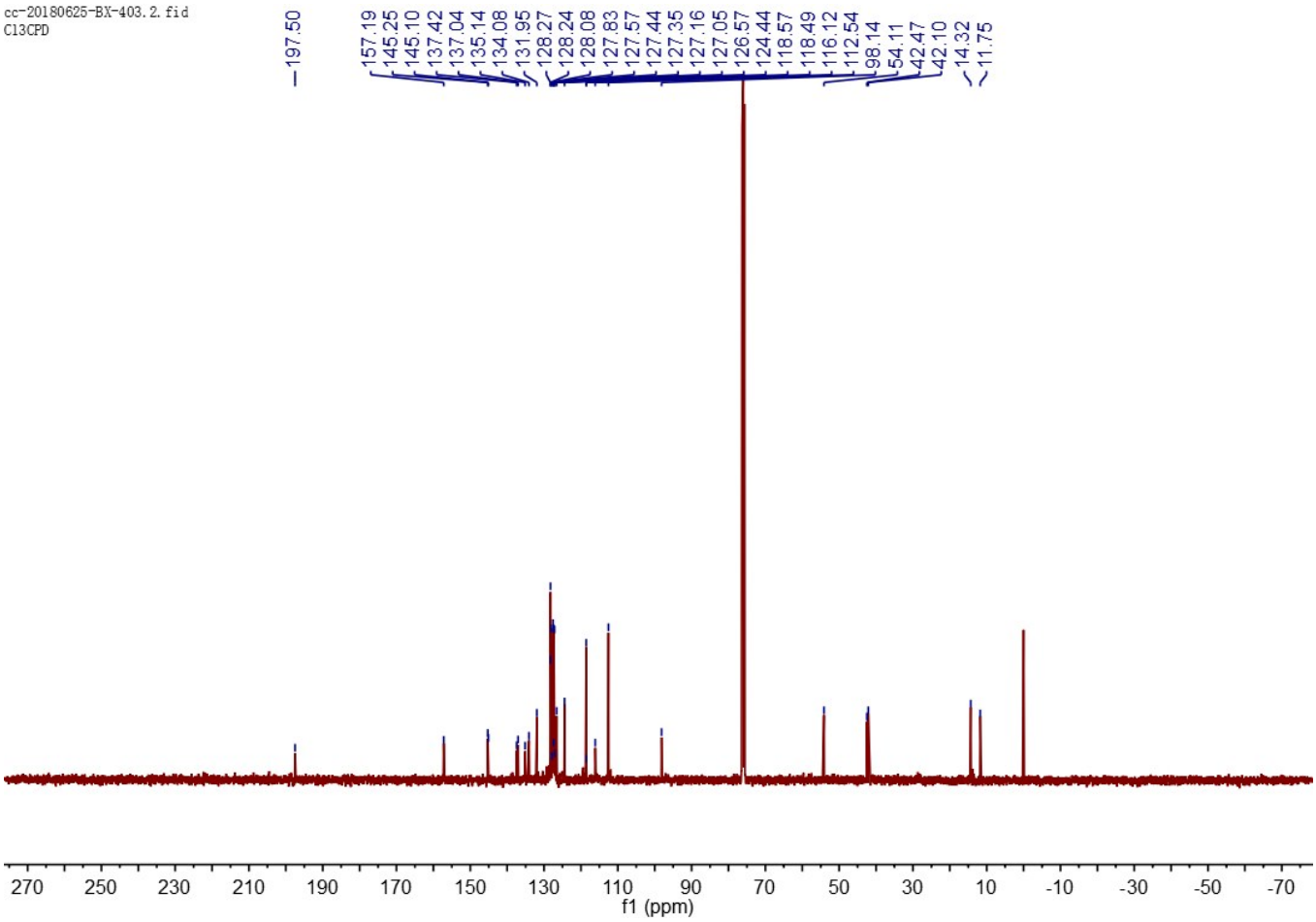
(*S*)-2-((*S*)-4-(4-Methoxyphenyl)-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'g):



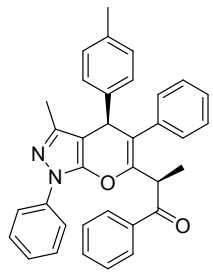
anti-4'g

Yellow solid. m.p. 179-181 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70-7.68 (m, 4H), 7.51-7.49 (m, 3H), 7.35-7.33 (m, 4H), 7.05-7.03 (m, 2H), 6.89-6.86 (m, 3H), 6.71-6.69 (m, 3H), 4.69 (s, 1H), 4.25 (q, J = 6.8 Hz, 1H), 3.76 (s, 3H), 1.87 (s, 3H), 1.65 (s, 3H), 1.58 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 157.2, 145.2, 145.1, 137.4, 137.0, 135.1, 134.1, 131.9, 128.2, 128.1, 127.5, 127.4, 127.3, 127.1, 126.5, 124.4, 118.5, 116.1, 112.5, 98.1, 54.1, 42.4, 42.1, 14.3, 11.7.



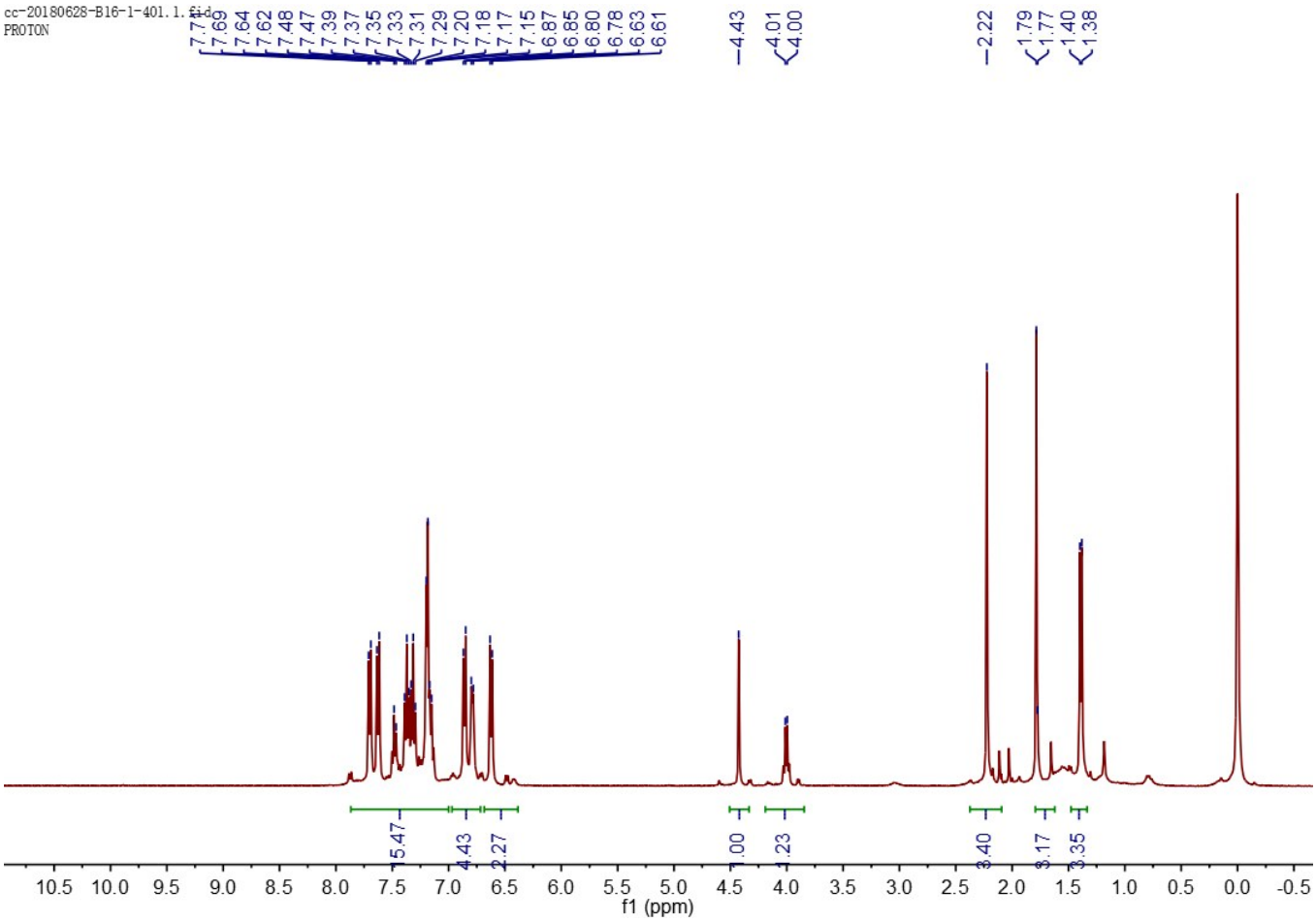


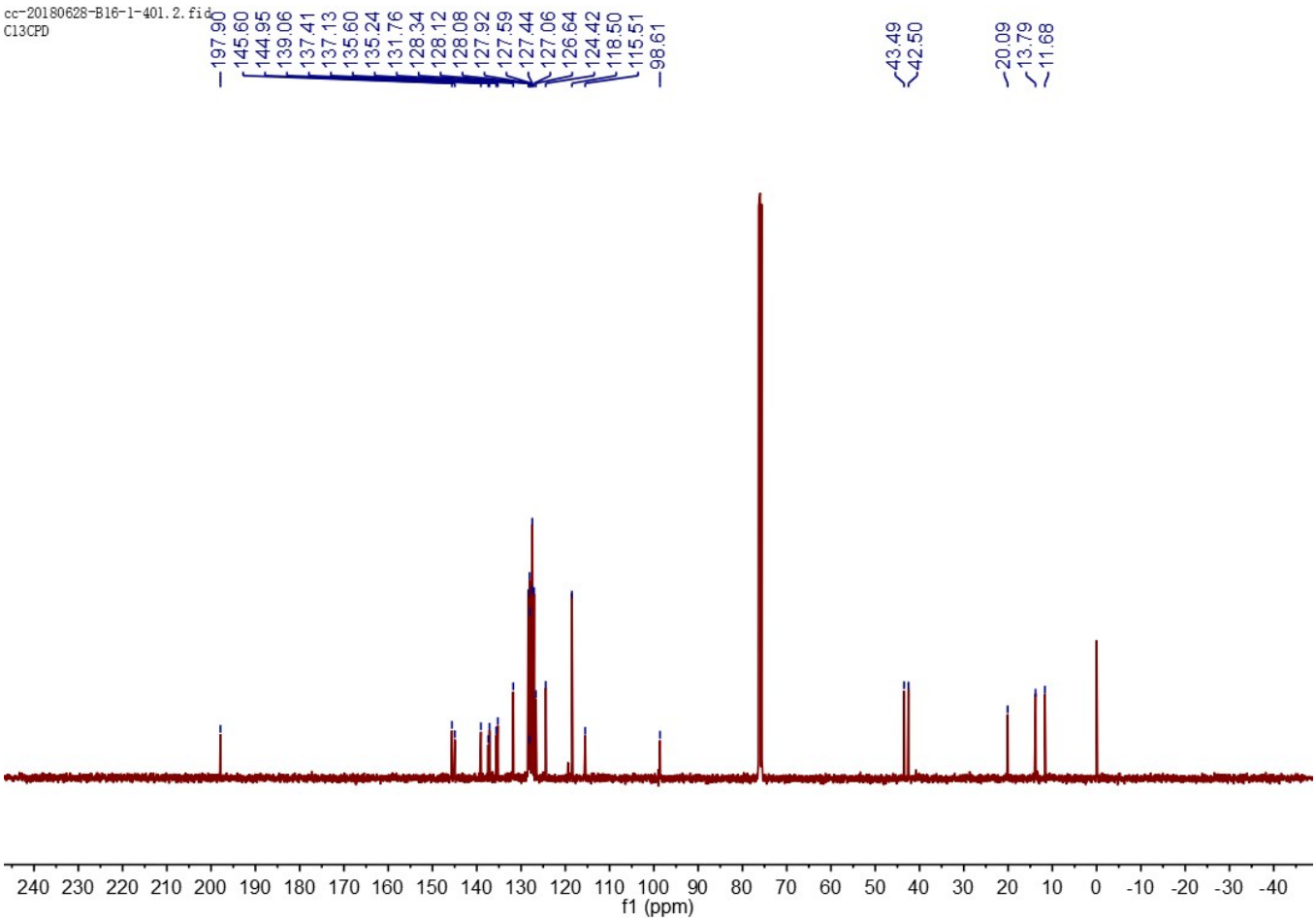
(*R*)-2-((*S*)-4-Methyl-1,5-diphenyl-4-(*p*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'h):



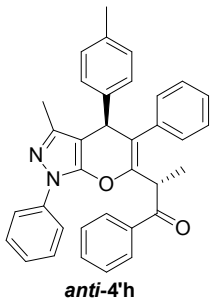
***syn*-4'h**

Yellow solid, m.p. 136-138 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 3H), 7.48-7.45 (m, 1H), 7.34-7.31 (m, 3H), 7.21-7.12 (m, 5H), 6.82-6.79 (m, 5H), 6.62-6.59 (m, 2H), 4.43 (s, 1H), 4.00 (q, *J* = 6.8 Hz, 1H), 2.22 (s, 3H), 1.79 (s, 3H), 1.39 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 145.6, 145.0, 144.9, 139.0, 137.4, 137.1, 135.6, 135.2, 131.7, 128.3, 128.0, 127.9, 127.6, 127.4, 127.0, 126.6, 124.4, 118.5, 115.5, 98.6, 43.4, 42.5, 20.0, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{35}H_{31}N_2O_2$ $[M + H]^+$ 511.2380, found 511.2383.


cc-20180628-B16-1-401.1.fid
PROTON
7.71
7.69
7.64
7.62
7.48
7.47
7.39
7.37
7.35
7.33
7.31
7.29
7.20
7.18
7.17
7.15
6.87
6.85
6.80
6.78
6.63
6.61
4.43
4.01
4.00
2.22
1.79
1.77
1.40
1.38
5.47
4.43
2.27
1.00
1.23
3.40
3.17
3.35
f1 (ppm)

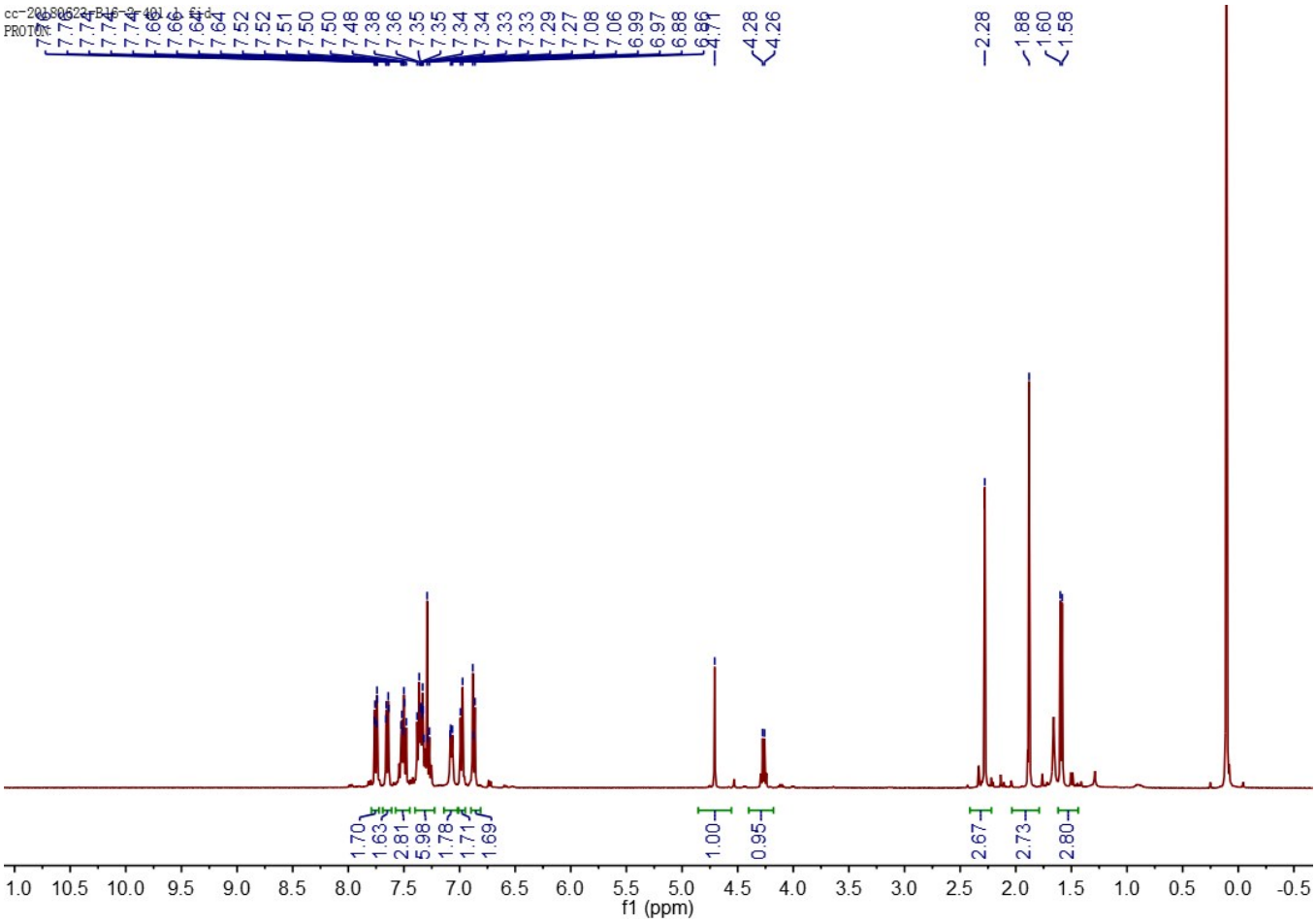

cc-20180628-B16-1-401.2.fid
C13CPD
197.90
145.60
144.95
139.06
137.41
137.13
135.60
135.24
131.76
128.34
128.12
128.08
127.92
127.59
127.44
127.06
126.64
124.42
118.50
115.51
98.61
43.49
42.50
20.09
13.79
11.68
f1 (ppm)

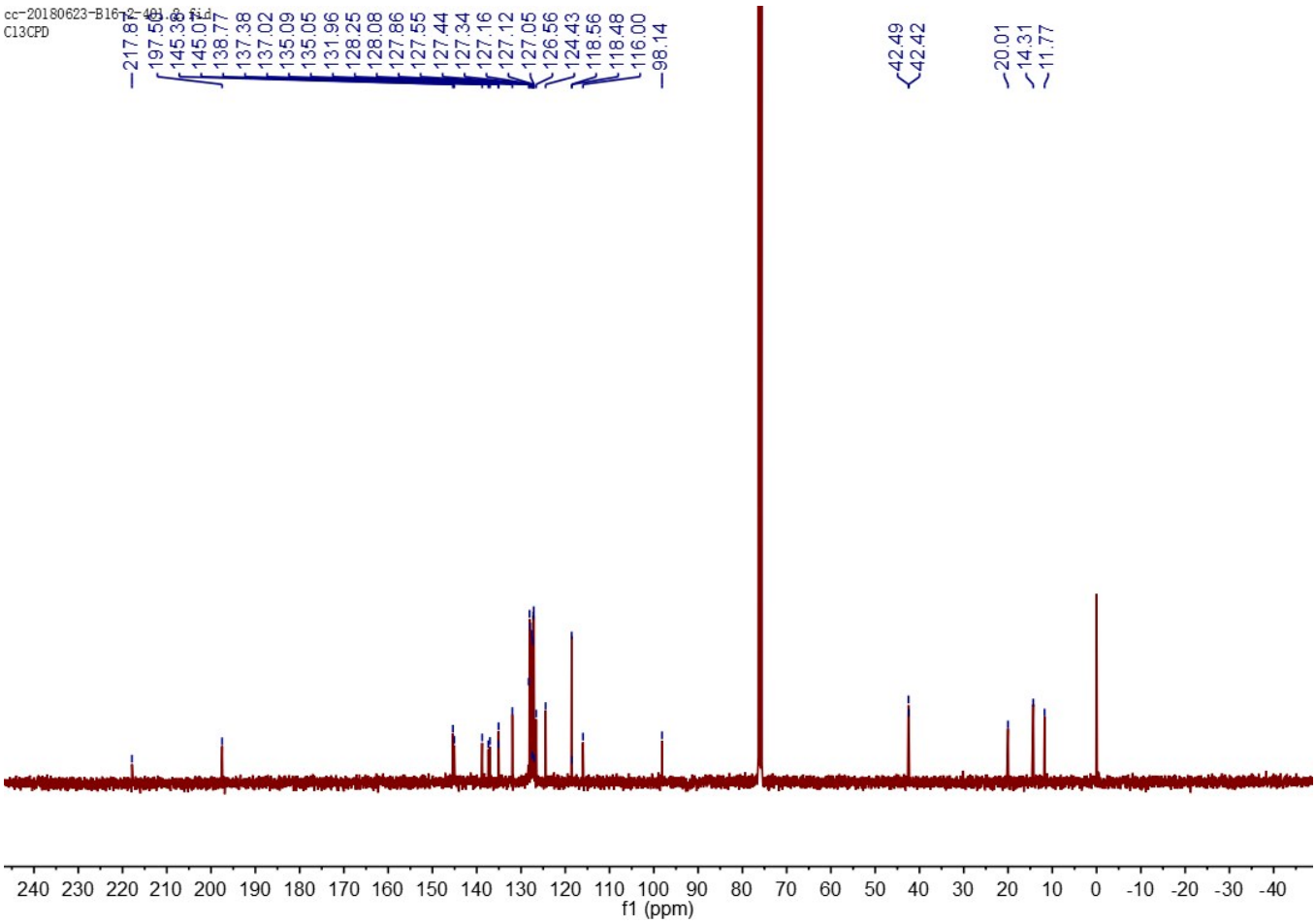
(*S*)-2-((*S*)-4-Methyl-1,5-diphenyl-4-(*p*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'h):



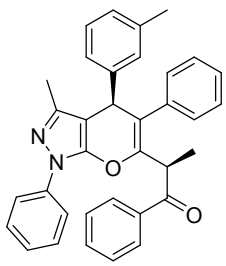
anti-4'h

Yellow solid, m.p. 173-175 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2H), 7.68-7.62 (m, 2H), 7.51-7.49 (m, 4H), 7.35-7.33 (m, 4H), 7.27 (s, 1H), 7.07-7.05 (m, 2H), 6.98-6.96 (m, 2H), 6.87-6.85 (m, 2H), 4.71 (s, 1H), 4.27 (q, J = 6.8 Hz, 1H), 2.28 (s, 3H), 1.88 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 145.3, 145.0, 138.7, 137.4, 137.0, 135.0, 131.9, 128.2, 128.0, 127.8, 127.5, 127.3, 127.1, 127.1, 126.5, 124.4, 118.5, 116.0, 98.1, 42.5, 42.4, 20.0, 14.3, 11.7.



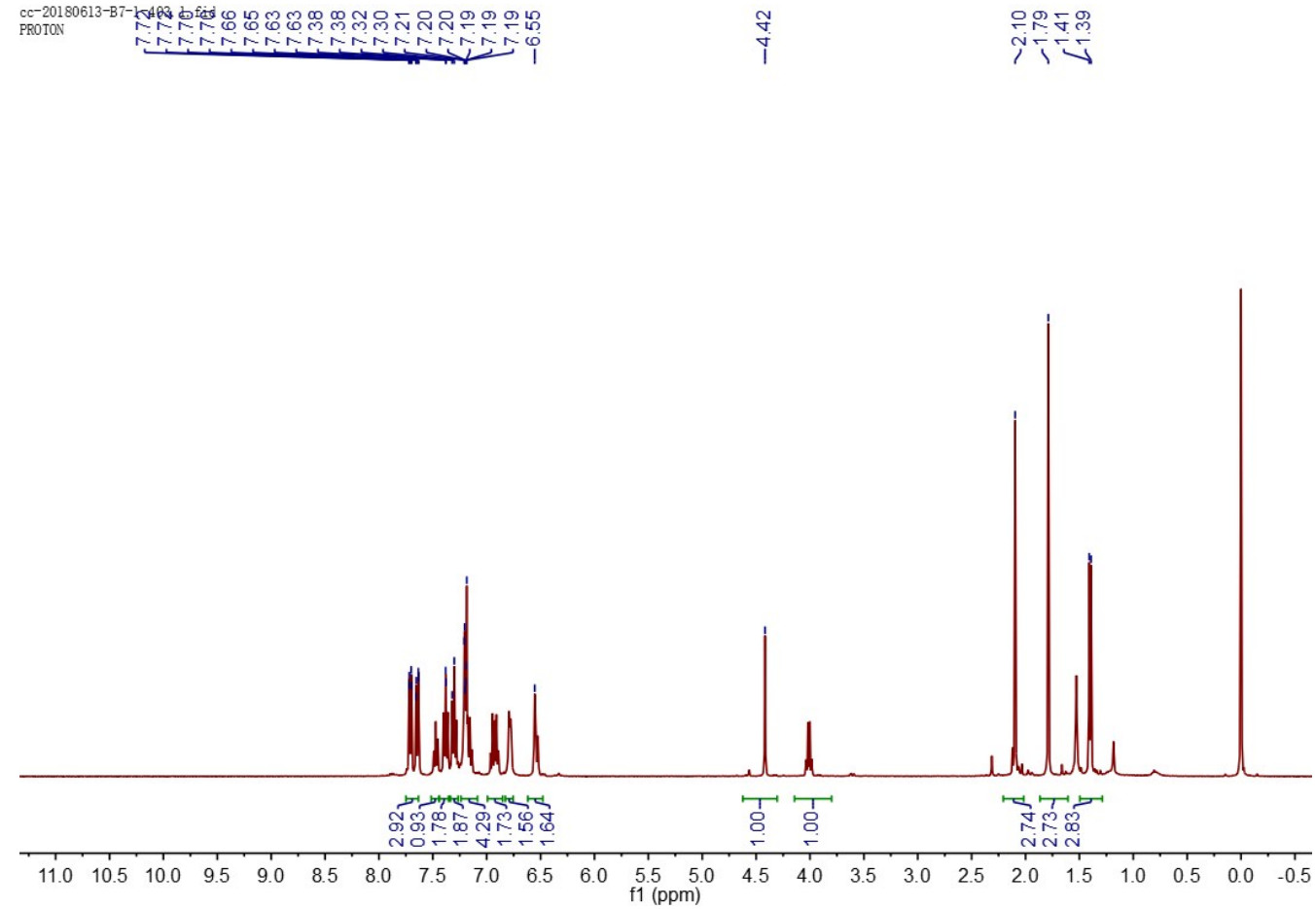


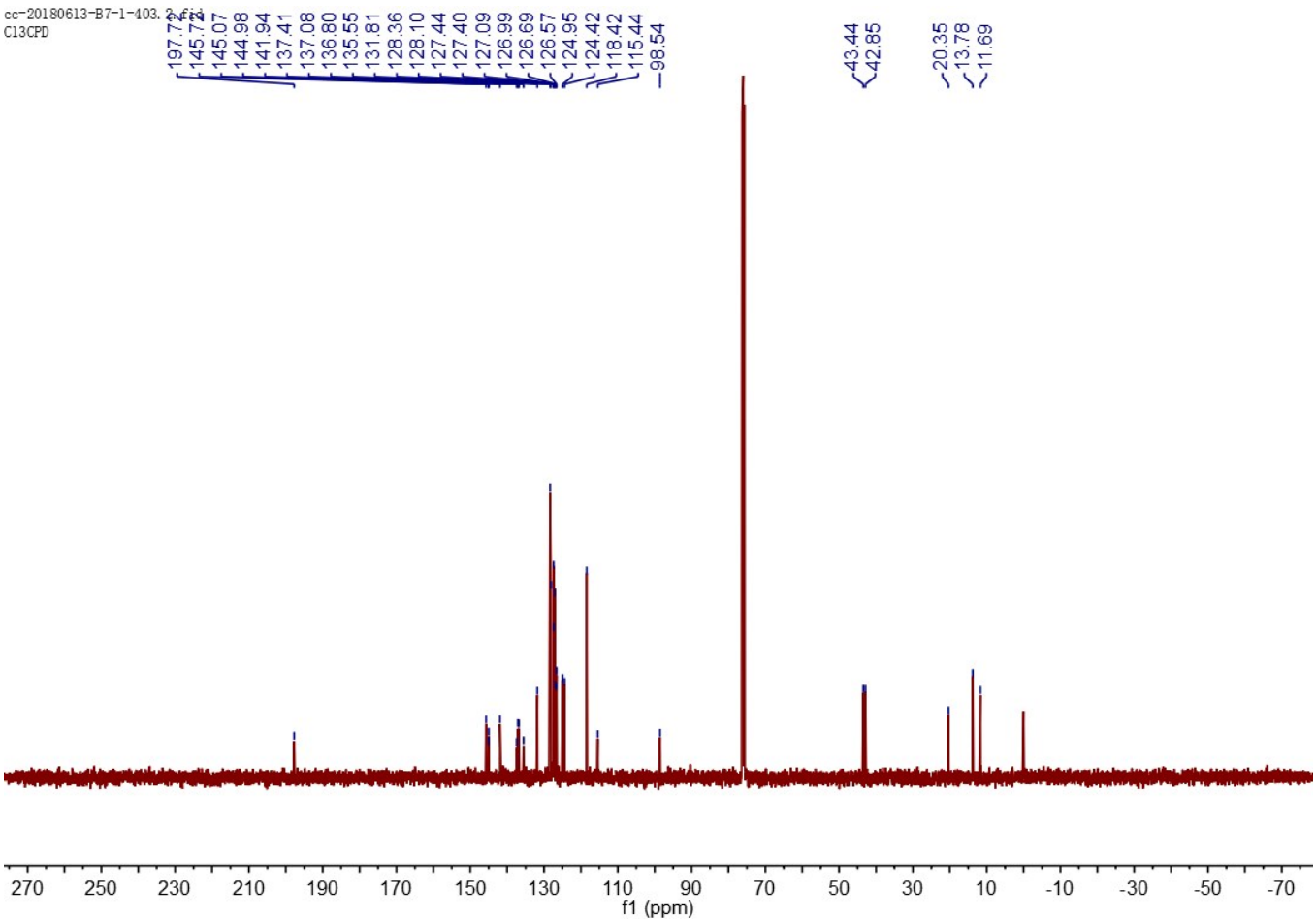
(*R*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(*p*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'i):



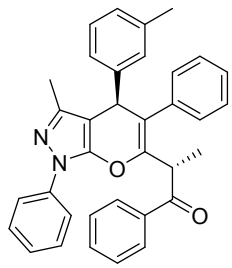
***syn*-4'i**

Yellow solid. m.p. 121-123 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.66 (m, 4H), 7.50-7.12 (m, 9H), 6.98-6.86 (m, 2H), 6.79-6.76 (m, 2H), 6.54-6.50 (m, 2H), 4.42 (s, 1H), 4.01 (q, *J* = 6.8 Hz, 1H), 2.10 (s, 3H), 1.79 (s, 3H), 1.40 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.7, 145.0, 141.9, 137.0, 136.8, 135.5, 131.8, 128.3, 128.1, 127.4, 127.4, 127.1, 127.0, 126.7, 126.5, 124.9, 124.4, 118.4, 115.4, 98.5, 43.4, 42.8, 20.3, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{35}H_{31}N_2O_2$ $[M + H]^+$ 511.2380, found 511.2835.


PROTON
7.74
7.66
7.65
7.63
7.63
7.38
7.38
7.32
7.30
7.21
7.20
7.20
7.19
7.19
7.19
6.55
4.42
2.10
1.79
1.41
1.39
2.92
0.93
1.78
1.87
4.29
1.73
1.56
1.64
1.00
1.00
2.74
2.73
2.83
f1 (ppm)

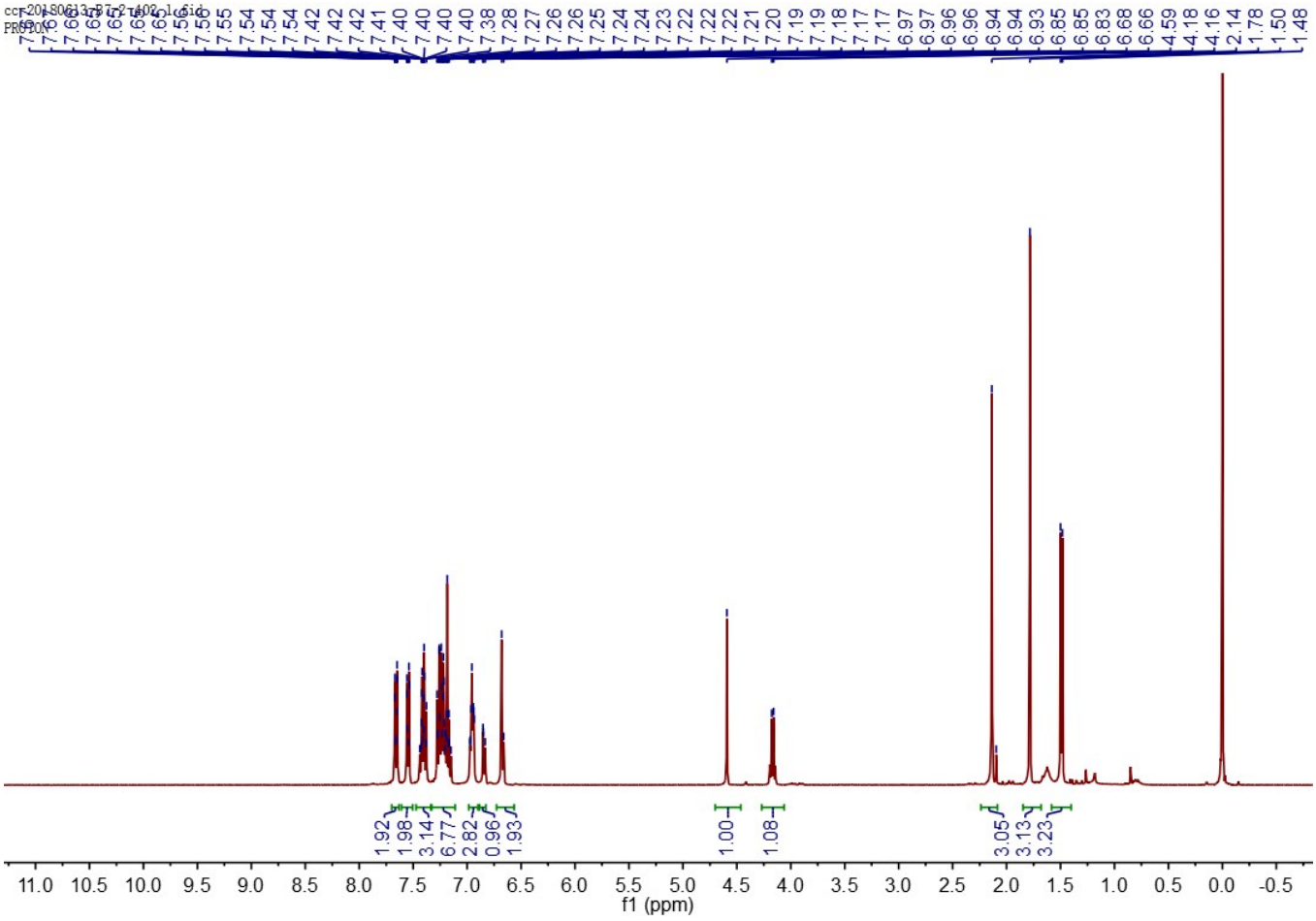

C13CPD
197.72
145.72
145.07
144.98
141.94
137.41
137.08
136.80
135.55
131.81
128.36
128.10
127.44
127.40
127.09
126.99
126.69
126.57
124.95
124.42
118.42
115.44
98.54
43.44
42.85
20.35
13.78
11.69
f1 (ppm)

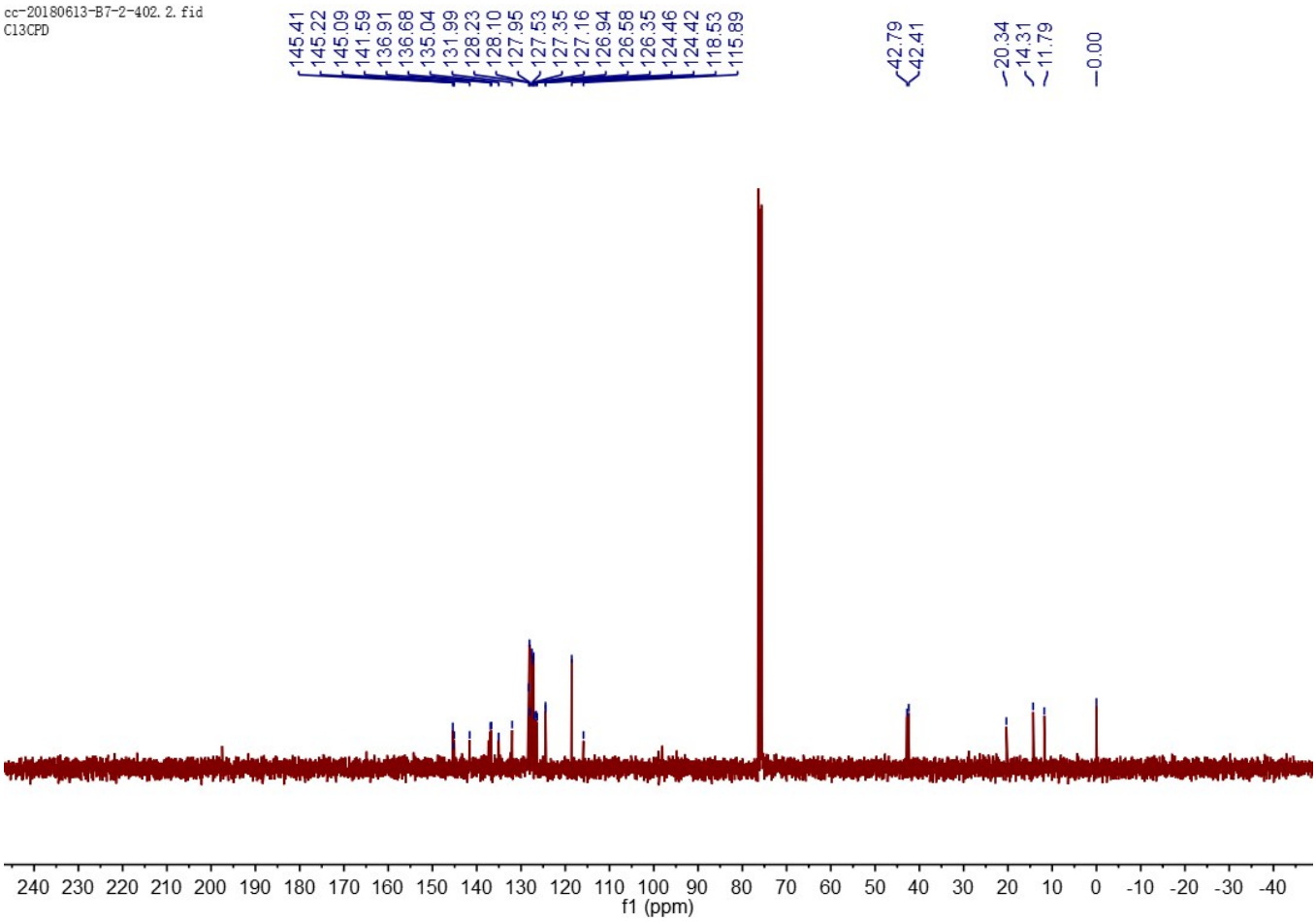
(*S*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(*p*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'i):



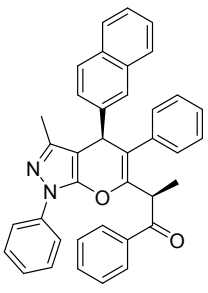
***anti*-4'i**

White solid, m.p. 160-162 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.51 (m, 4H), 7.41-7.39 (m, 3H), 7.31-7.20 (m, 5H), 6.96-6.92 (m, 3H), 6.84-6.82 (m, 2H), 6.67-6.65 (m, 2H), 4.59 (s, 1H), 4.17 (q, J = 6.8 Hz, 1H), 2.14 (s, 3H), 1.78 (s, 3H), 1.49 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 145.4, 136.9, 132.0, 128.2, 128.1, 127.9, 127.5, 127.3, 127.1, 126.9, 126.5, 124.4, 118.5, 42.8, 42.4, 20.3, 14.3, 11.7.



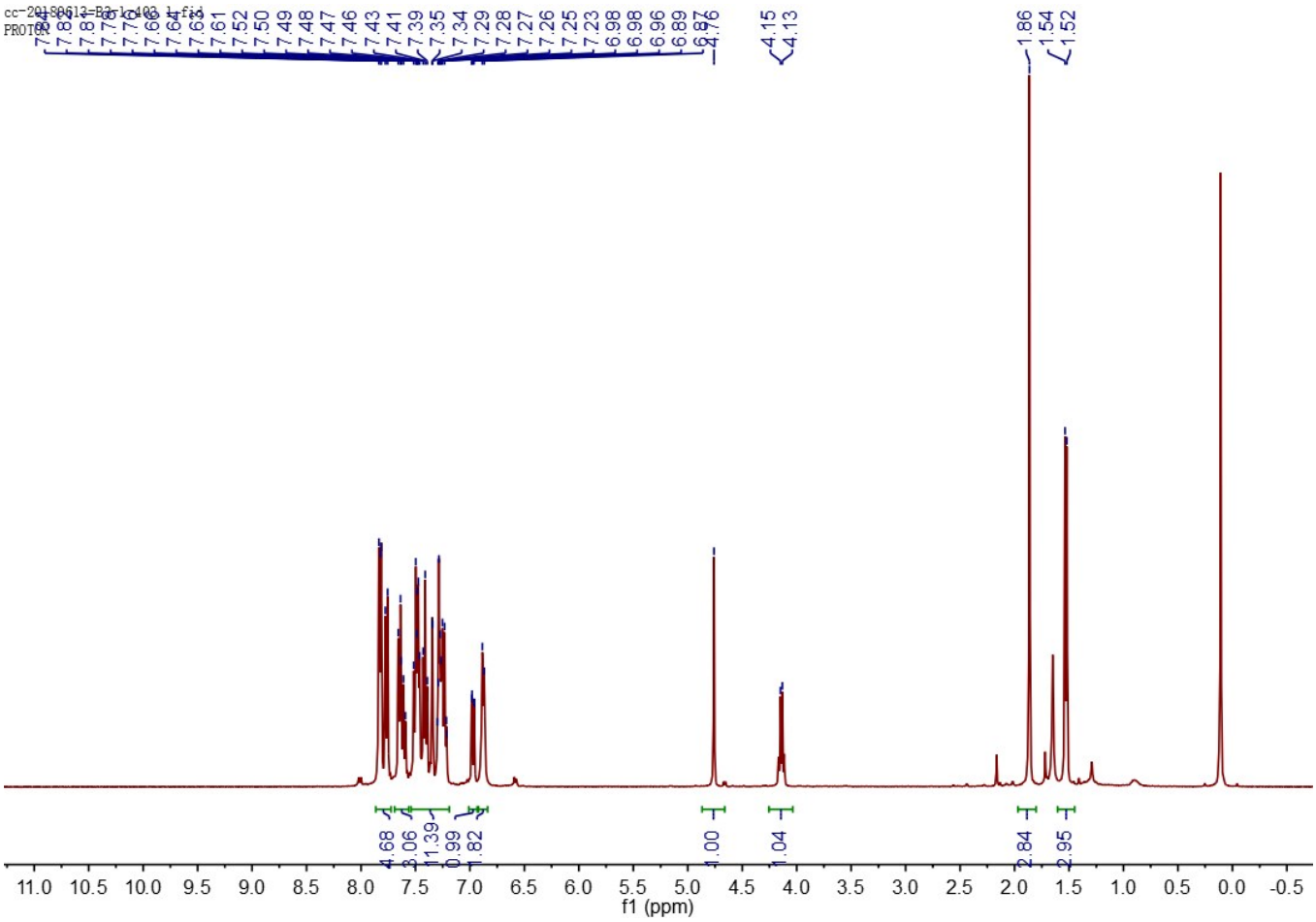


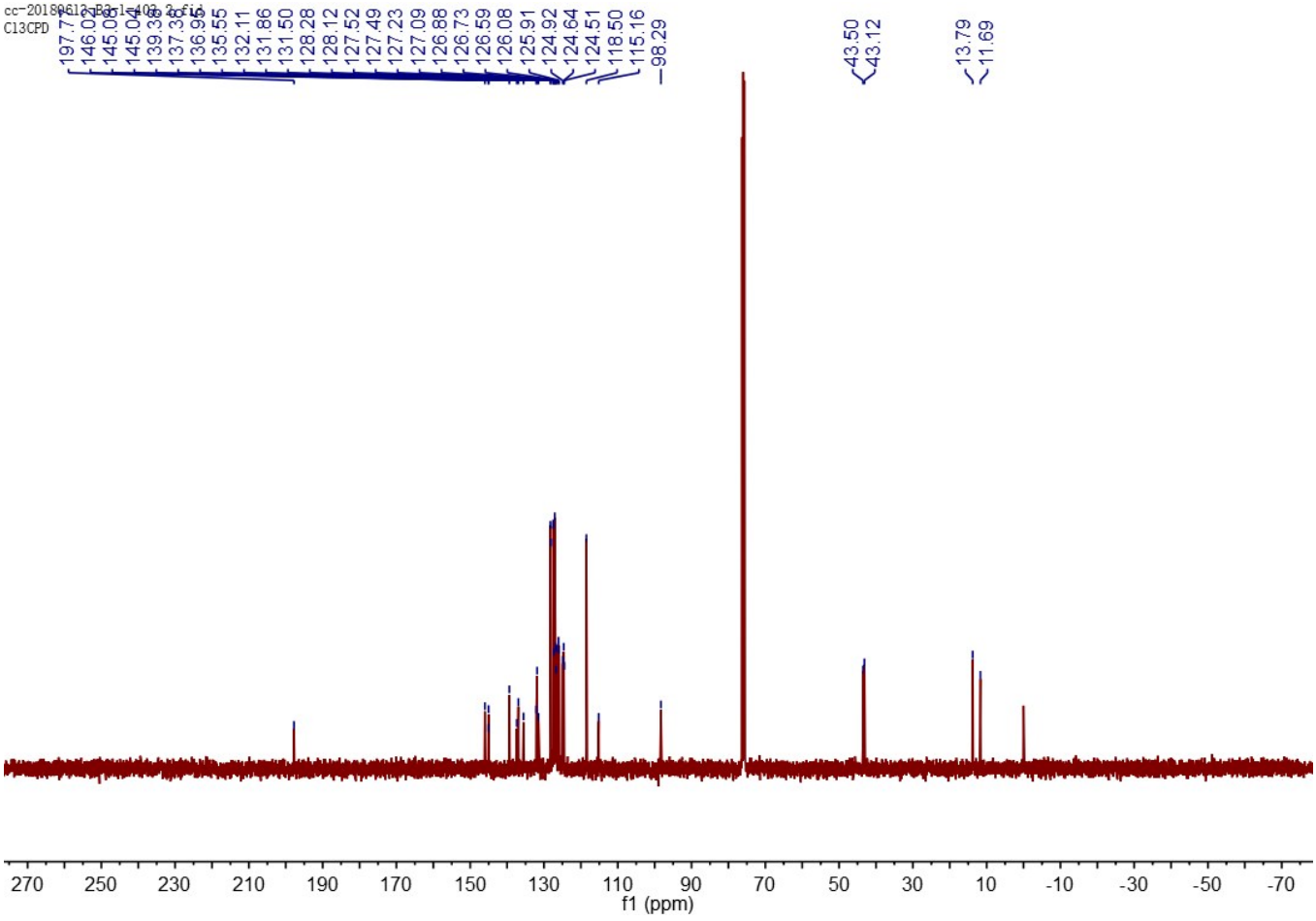
(*R*)-2-((*S*)-3-Methyl-4-(naphthalen-2-yl)-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'j):



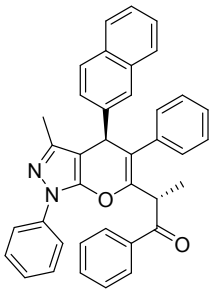
***syn*-4'j**

Yellow solid, m.p. 159-161 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.64 (m, 7H), 7.53-7.51 (m, 4H), 7.47-7.34 (m, 5H), 7.28 (s, 3H), 7.21-7.19 (m, 1H), 7.07-7.05 (m, 2H), 4.76 (s, 1H), 4.13 (q, J = 6.8 Hz, 1H), 1.86 (s, 3H), 1.52 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 145.7, 145.2, 145.1, 139.0, 137.3, 136.8, 135.0, 132.1, 132.0, 131.3, 128.1, 128.1, 127.6, 127.3, 127.1, 126.7, 126.6, 126.5, 125.7, 125.4, 124.8, 124.5, 118.6, 115.6, 98.2, 43.5, 42.1, 13.8, 11.7. HRMS (ESI) *m/z* calcd for $C_{38}H_{31}N_2O_2$ [M + H]$^+$ 547.2380, found 547.2381.


PROTON
7.82
7.81
7.80
7.77
7.76
7.66
7.64
7.63
7.61
7.52
7.50
7.49
7.48
7.47
7.46
7.43
7.41
7.39
7.35
7.34
7.29
7.28
7.27
7.26
7.25
7.23
6.98
6.96
6.89
6.87
4.76
4.15
4.13
1.86
1.54
1.52
4.68
3.06
11.39
0.99
1.82
1.00
1.04
2.84
2.95
11.0 10.5 10.0 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
f1 (ppm)

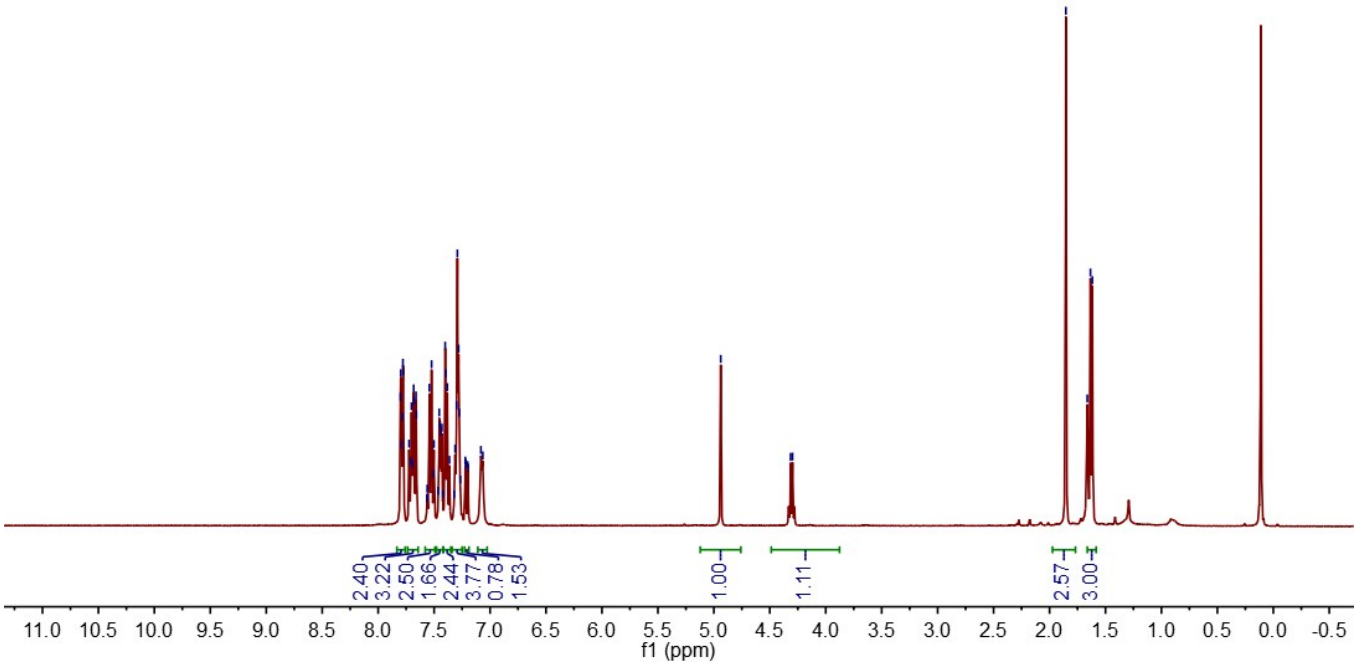

C13CPD
197.77
146.02
145.08
145.04
139.38
137.36
136.96
135.55
132.11
131.86
131.50
128.28
128.12
127.52
127.49
127.23
127.09
126.88
126.73
126.59
126.08
125.91
124.92
124.64
124.51
118.50
115.16
98.29
43.50
43.12
13.79
11.69
270 250 230 210 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70
f1 (ppm)

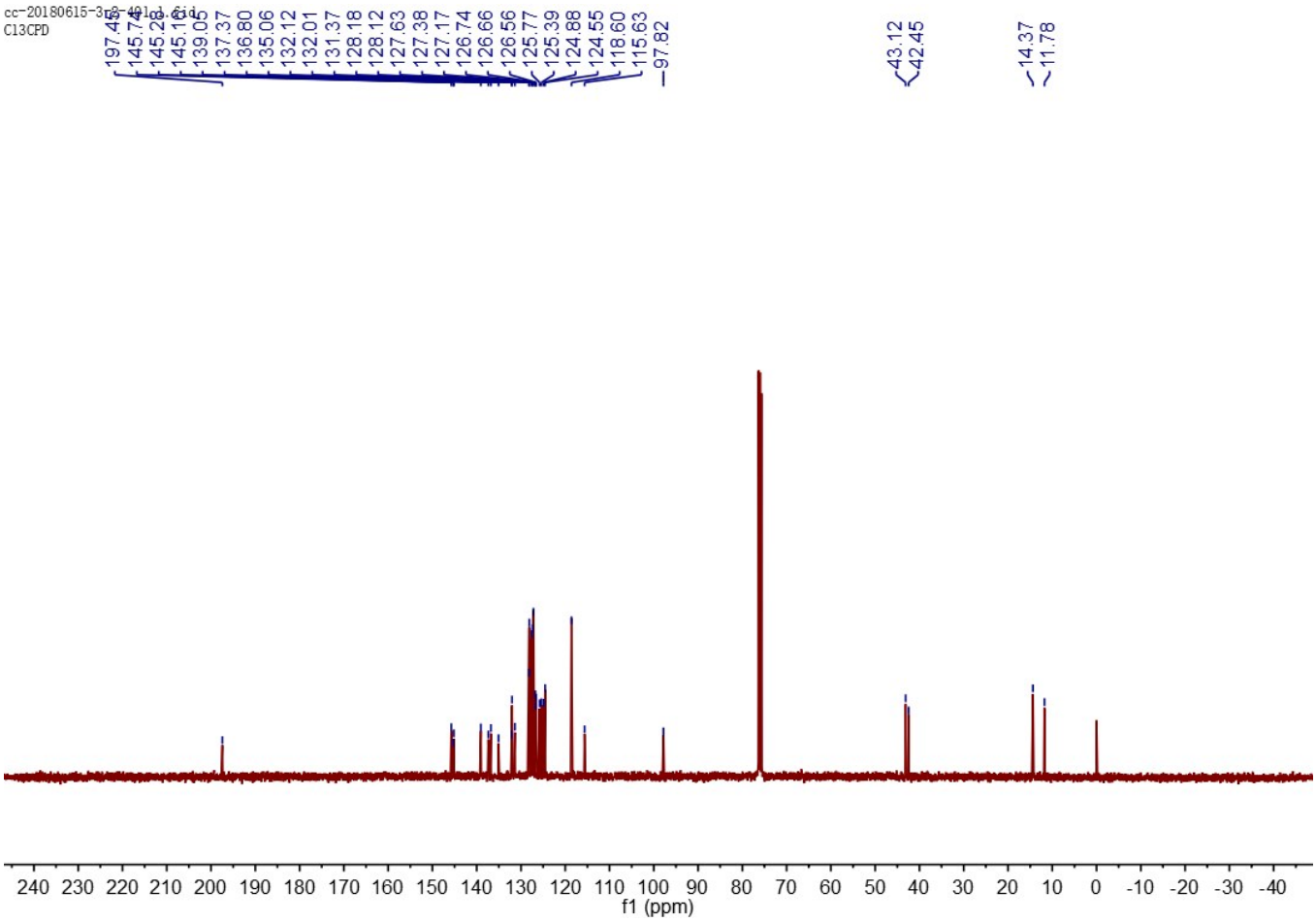
(*S*)-2-((*S*)-3-Methyl-4-(naphthalen-2-yl)-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'j):



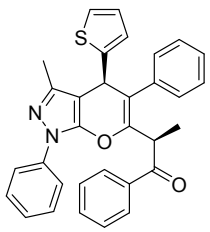
***anti*-4'i**

White solid, m.p. 197-199 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82-7.64 (m, 7H), 7.53-7.51 (m, 4H), 7.47-7.34 (m, 5H), 7.28 (s, 3H), 7.21-7.19 (m, 1H), 7.07-7.05 (m, 2H), 4.94 (s, 1H), 4.31 (q, J = 6.8 Hz, 1H), 1.85 (s, 3H), 1.63 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 145.7, 145.2, 145.1, 139.0, 137.3, 136.8, 135.0, 132.1, 132.0, 131.3, 128.1, 128.1, 127.6, 127.3, 127.1, 126.7, 126.6, 126.5, 125.7, 125.4, 124.8, 124.5, 118.6, 115.6, 97.8, 43.1, 42.4, 14.3, 11.7.



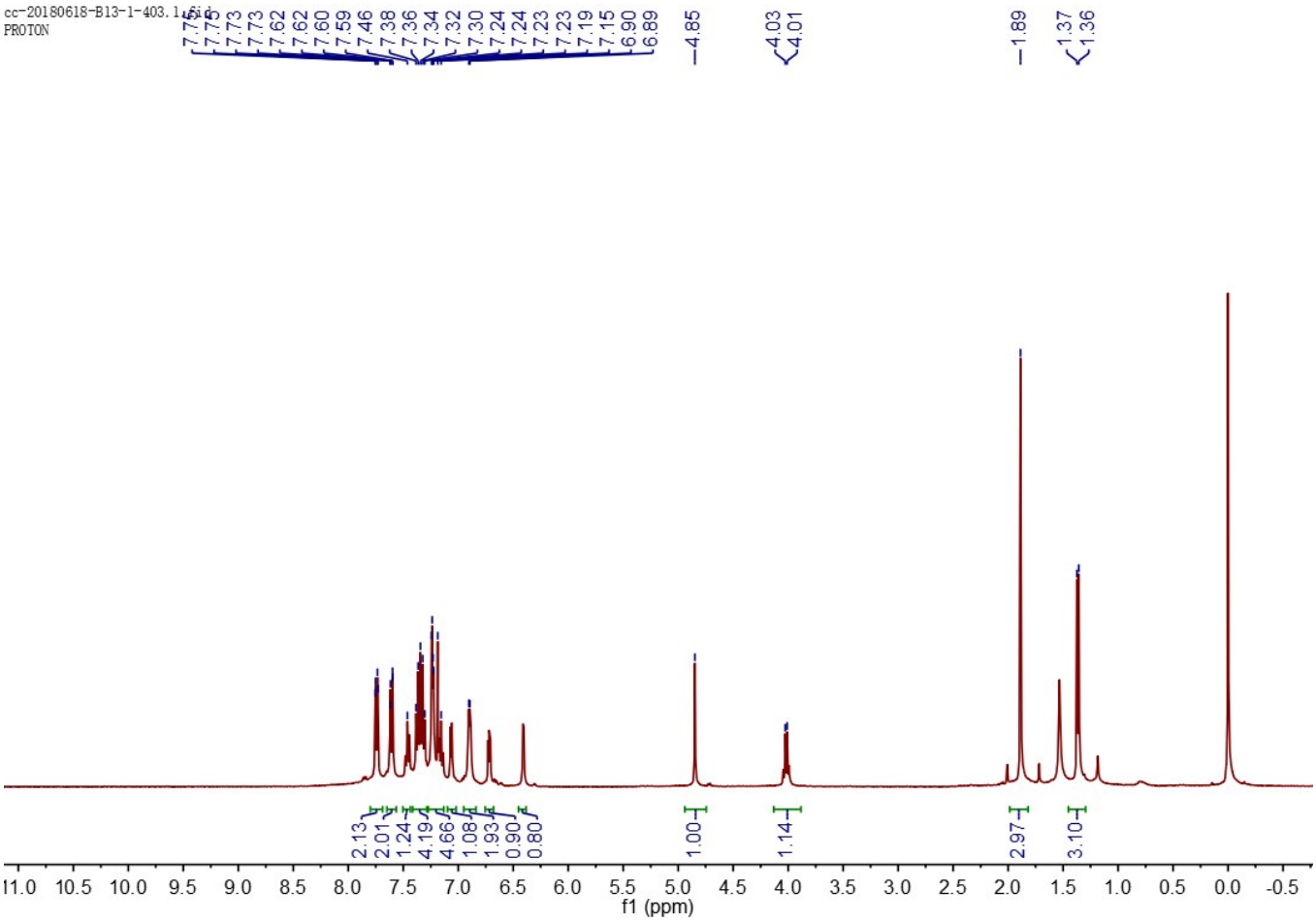


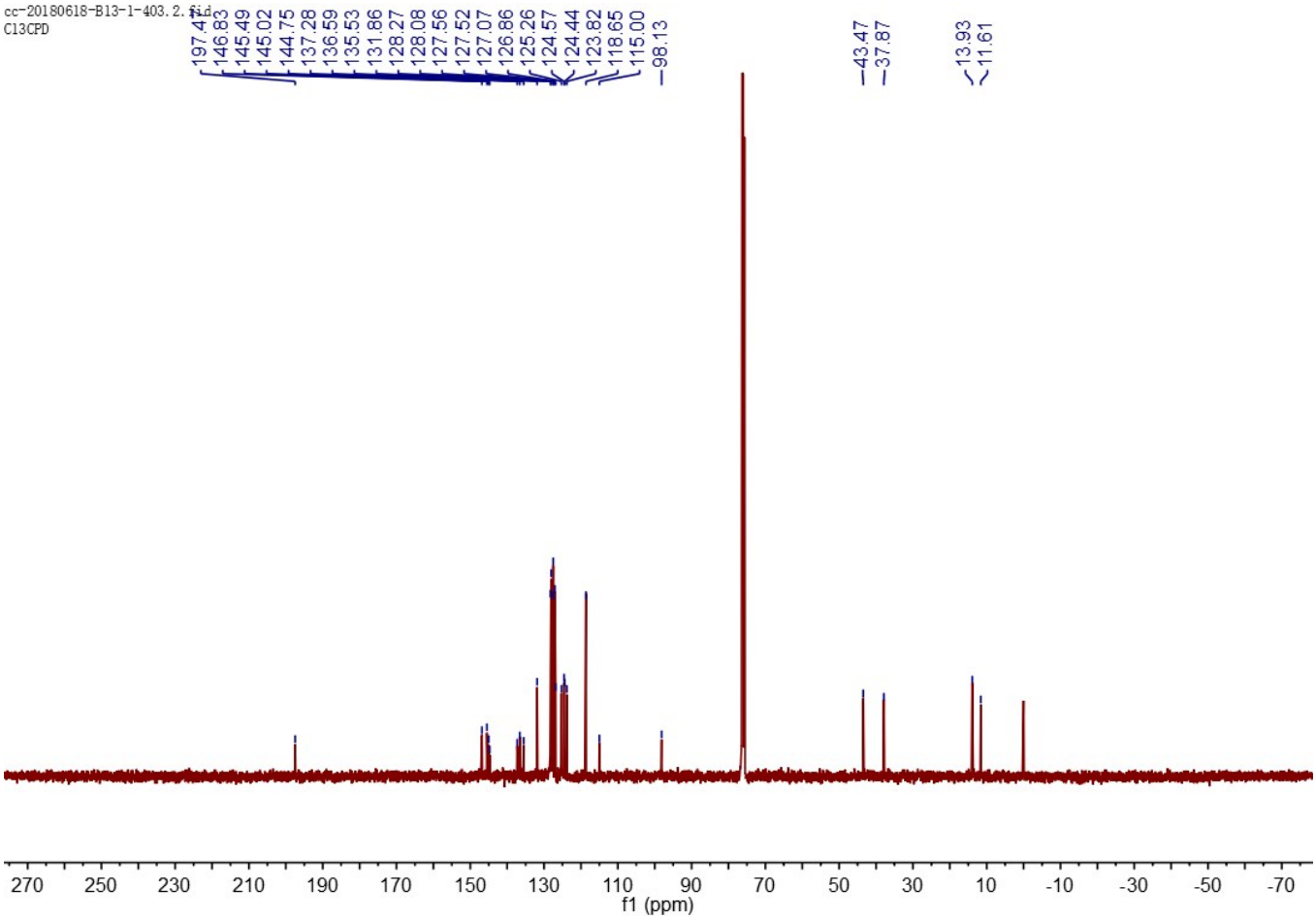
(*R*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'k):



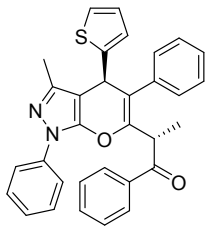
syn-4'k

Yellow solid, m.p. 143-144 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2H), 7.61-7.59 (m, 2H), 7.39-7.37 (m, 6H), 7.27-7.22 (m, 3H), 7.06-7.04 (m, 1H), 6.94-6.86 (m, 2H), 6.72-6.70 (m, 1H), 6.41-6.39 (m, 1H), 4.85 (s, 1H), 4.02 (q, J = 6.8 Hz, 1H), 1.89 (s, 3H), 1.37 (d, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 146.8, 145.5, 145.0, 137.3, 136.6, 135.5, 131.8, 128.2, 128.0, 127.5, 127.5, 127.0, 126.8, 125.2, 124.5, 124.4, 123.8, 118.6, 115.0, 98.1, 43.4, 37.8, 13.9, 11.6. HRMS (ESI) m/z calcd for $C_{32}H_{27}SN_2O_2$ $[M + H]^+$ 503.1788, found 503.1791.


cc-20180618-B13-1-403.1.fid
PROTON
7.76
7.75
7.73
7.73
7.62
7.62
7.60
7.59
7.46
7.38
7.36
7.34
7.32
7.30
7.24
7.24
7.23
7.23
7.19
7.15
6.90
6.89
4.85
4.03
4.01
1.89
1.37
1.36
2.13
2.01
1.24
4.19
4.66
1.08
1.93
0.90
0.80
1.00
1.14
2.97
3.10
f1 (ppm)

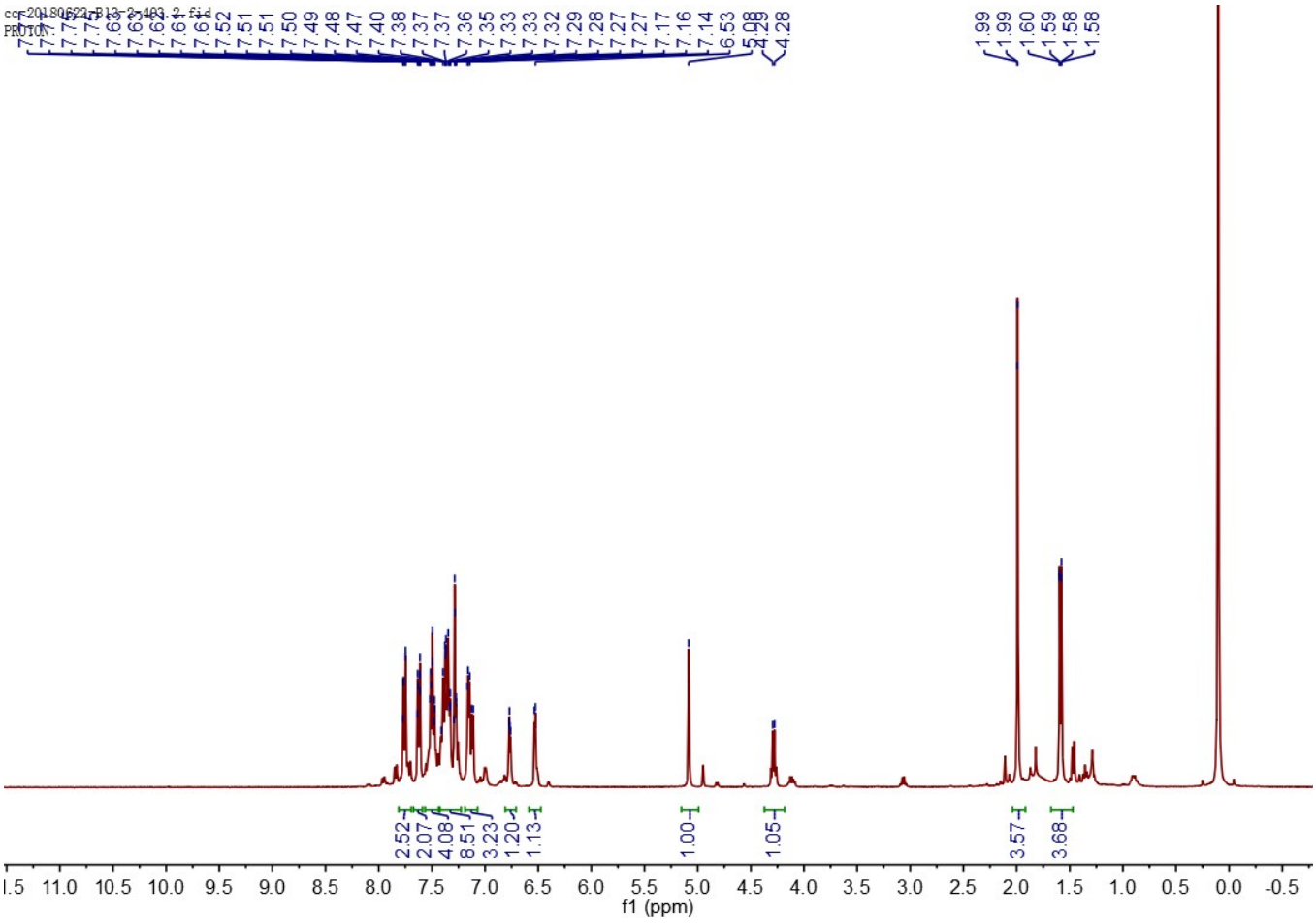

cc-20180618-B13-1-403.2.fid
C13CPD
197.41
146.83
145.49
145.02
144.75
137.28
136.59
135.53
131.86
128.27
128.08
127.56
127.52
127.07
126.86
125.26
124.57
124.44
123.82
118.65
115.00
98.13
43.47
37.87
13.93
11.61
f1 (ppm)

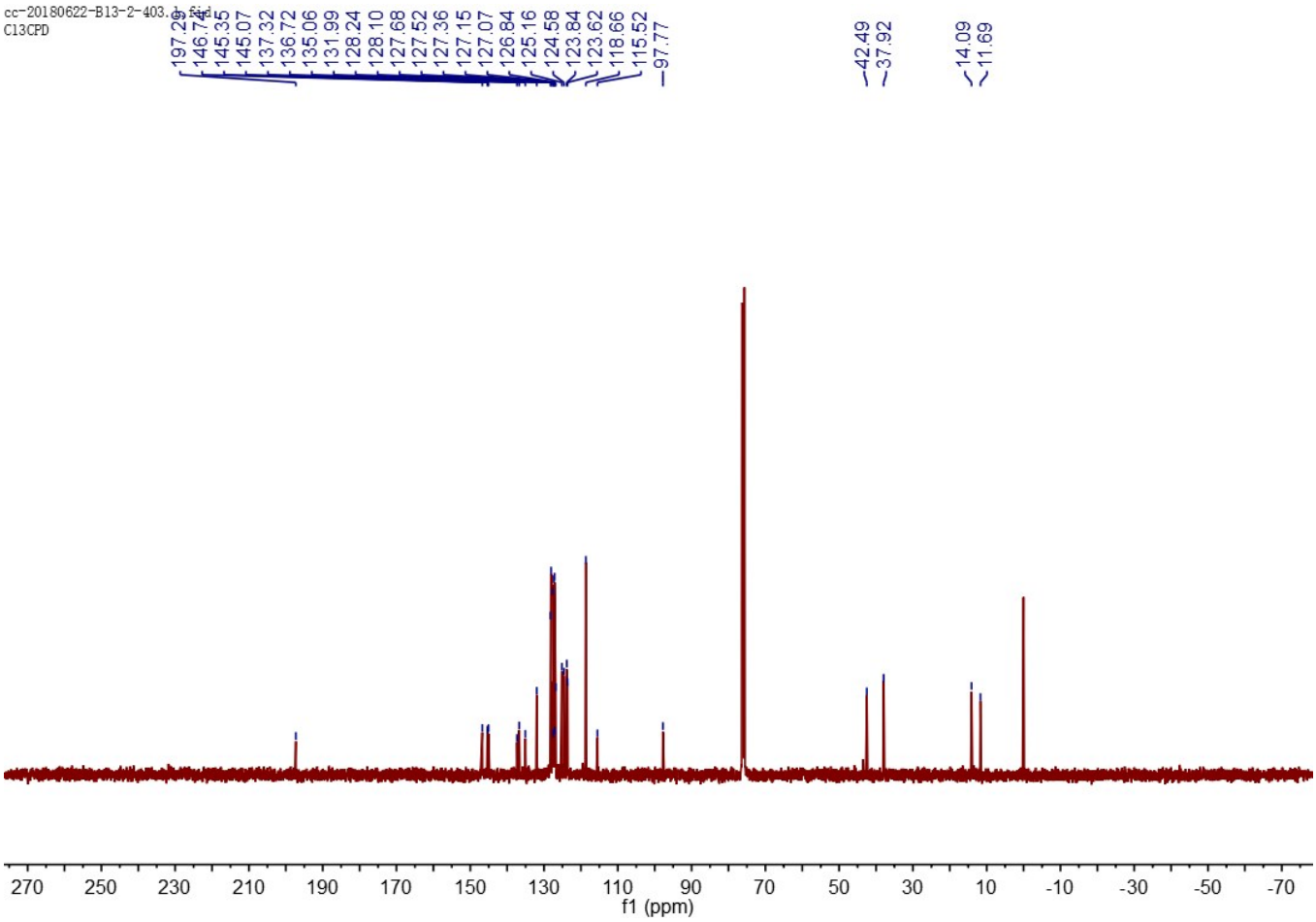
(*S*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-(thiophen-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'k):



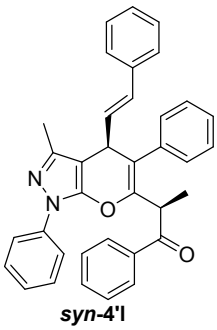
***anti*-4'k**

Yellow solid. m.p. 98-100 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.72 (m, 2H), 7.62-7.59 (m, 2H), 7.50-7.47 (m, 3H), 7.37-7.34 (m, 6H), 7.14-7.11 (m, 3H), 6.79-6.74 (m, 1H), 6.53 (s, 1H), 5.08 (s, 1H), 4.28 (q, J = 6.8 Hz, 1H), 1.99 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 146.7, 145.3, 145.0, 137.3, 136.7, 135.0, 132.0, 128.2, 128.1, 127.6, 127.3, 127.1, 126.8, 125.1, 124.5, 123.8, 123.6, 118.6, 115.5, 97.7, 42.4, 37.9, 14.0, 11.6.



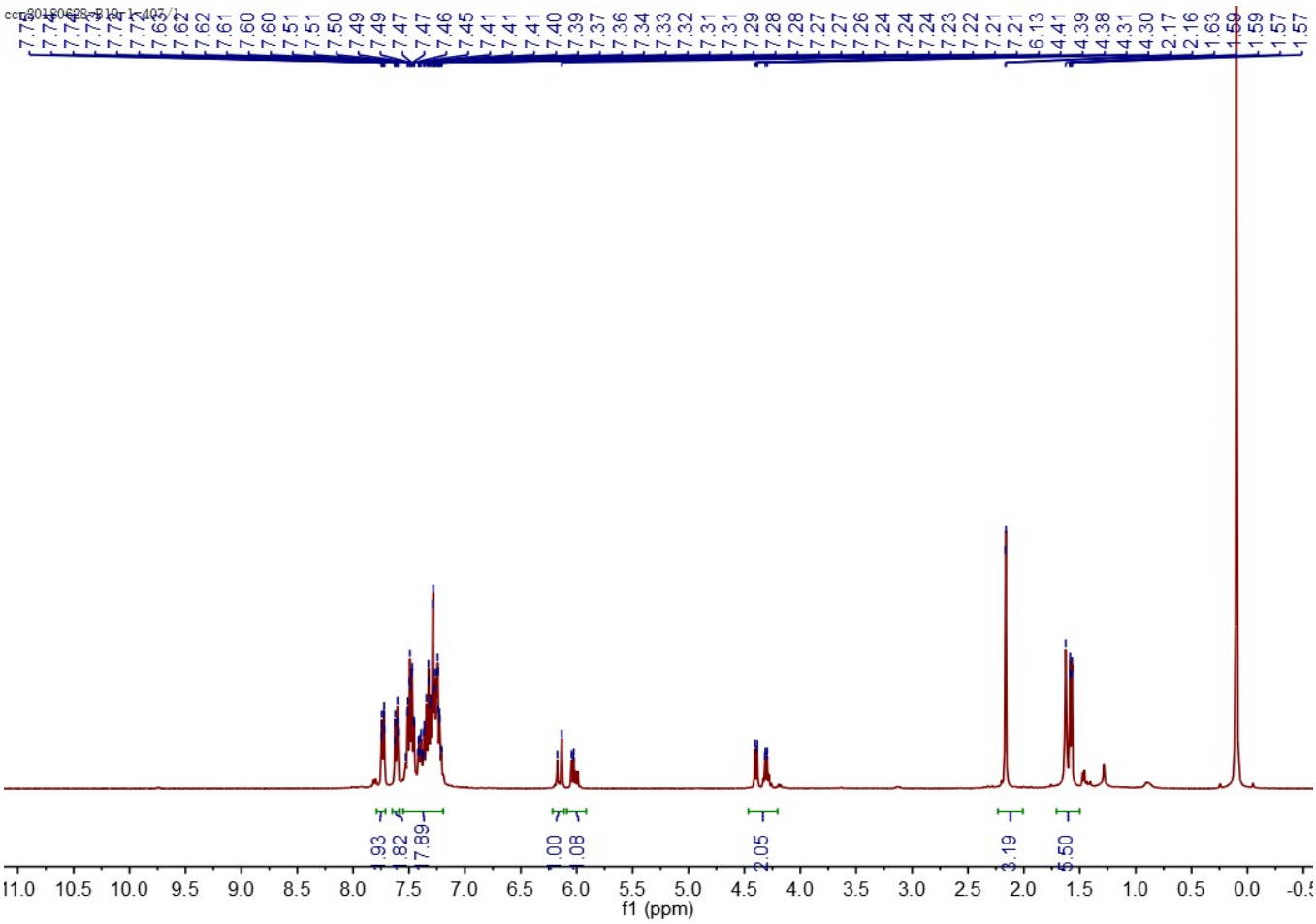


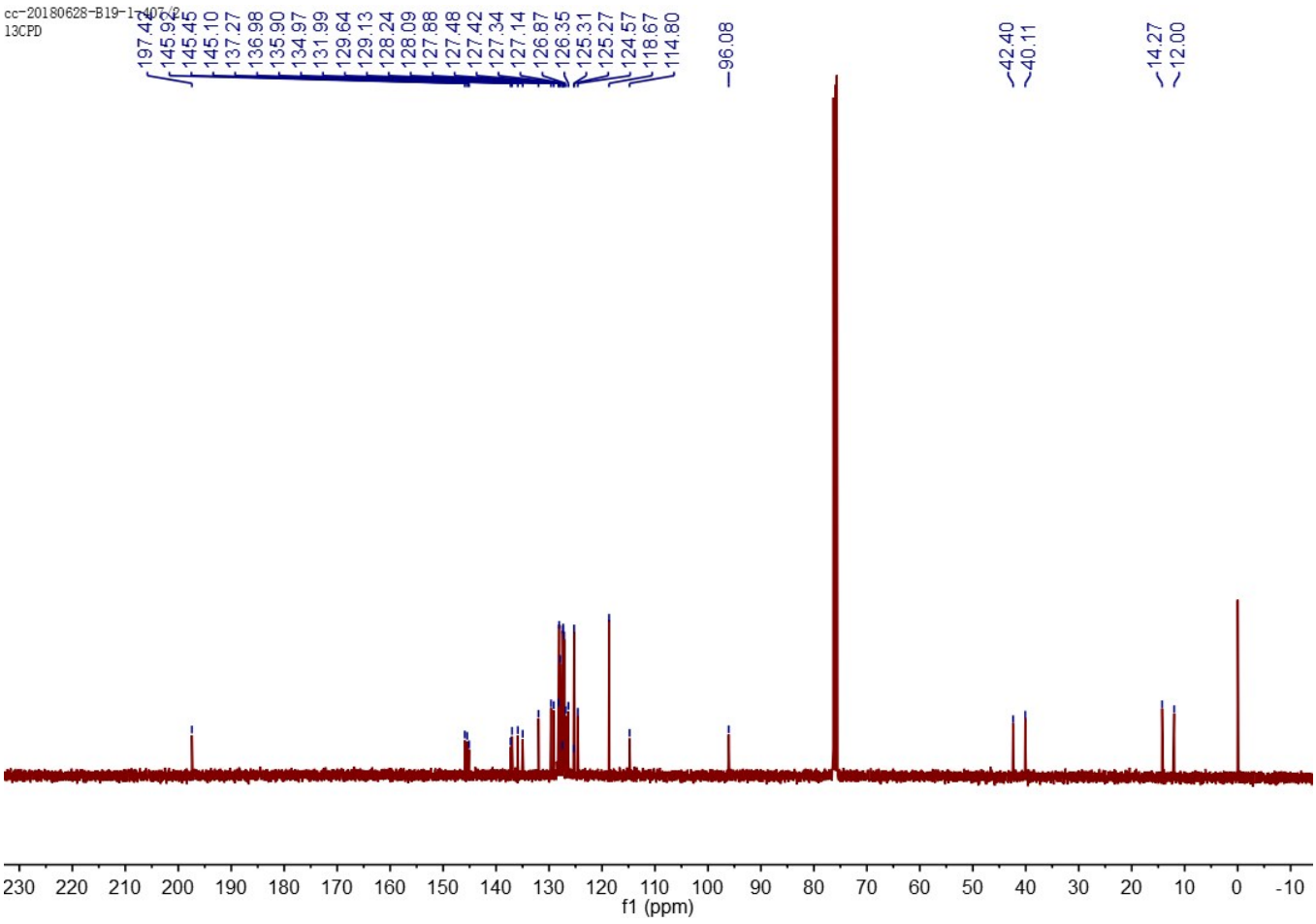
(*R*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-((*E*)-styryl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'l):



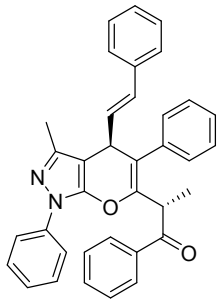
syn-4'l

Yellow solid, m.p. 133-135 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.61-7.59 (m, 2H), 7.48-7.43 (m, 3H), 7.42-7.30 (m, 7H), 7.23-7.21 (m, 6H), 6.15 (d, *J* = 15.7 Hz, 1H), 6.02 (dd, *J* = 15.7, 7.9 Hz, 1H), 4.39 (d, *J* = 7.9 Hz, 1H), 4.30 (q, *J* = 6.8 Hz, 1H), 2.16 (s, 3H), 1.58 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 145.9, 145.4, 145.1, 137.2, 136.9, 135.9, 134.9, 132.0, 129.6, 129.1, 128.2, 128.1, 127.8, 127.4, 127.3, 127.1, 126.8, 126.3, 125.2, 124.5, 118.6, 114.8, 96.0, 42.4, 40.1, 14.2, 11.9. HRMS (ESI) m/z calcd for $C_{36}H_{31}N_2O_2$ $[M + H]^+$ 523.2380, found 523.2382.


f1 (ppm)

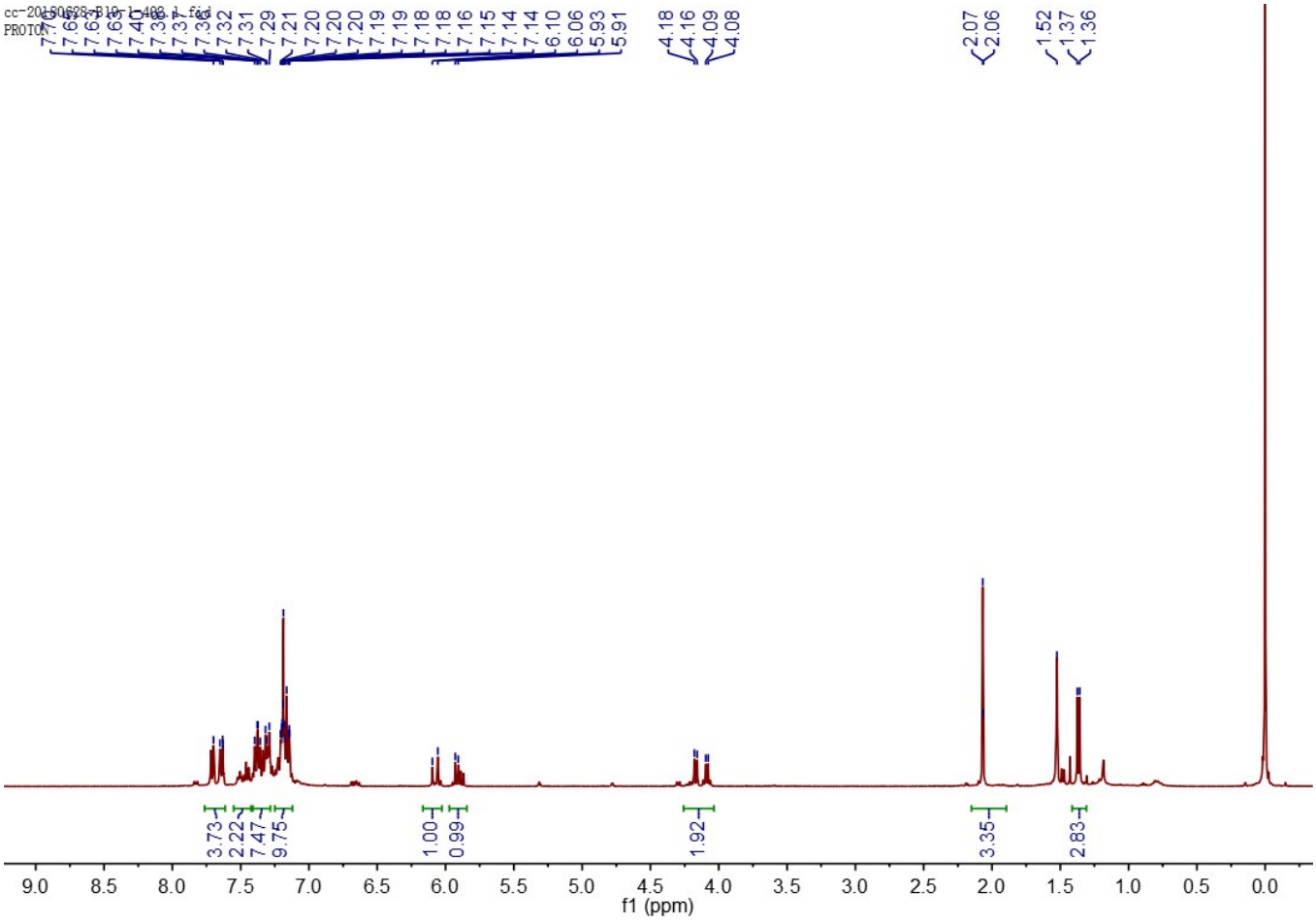

13CPD
f1 (ppm)

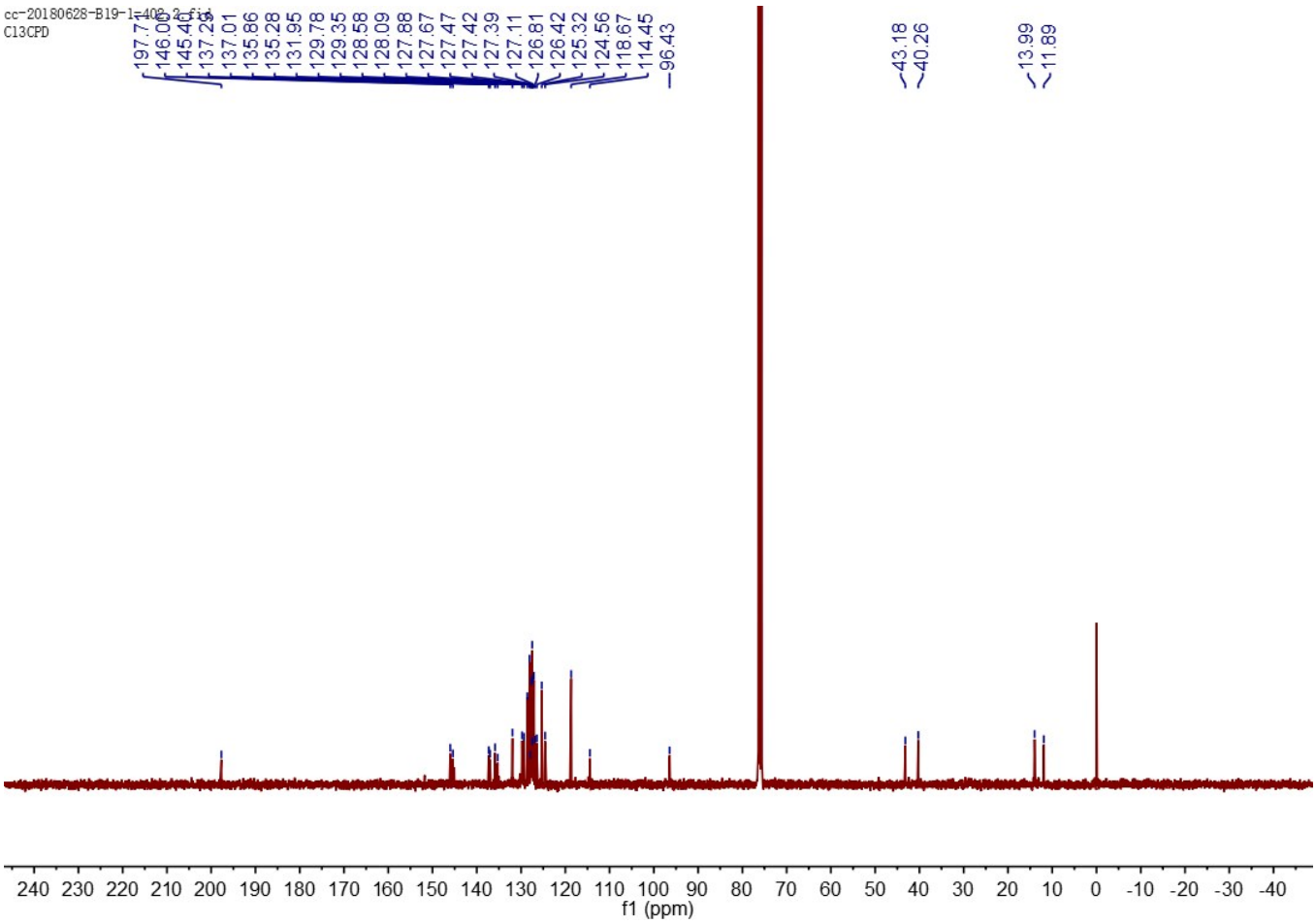
(*S*)-2-((*S*)-3-Methyl-1,5-diphenyl-4-((*E*)-styryl)-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'l):



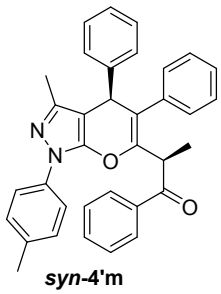
***anti*-4'l**

Red solid, m.p. 87-89 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73-7.68 (m, 2H), 7.67-7.61 (m, 2H), 7.53-7.43 (m, 3H), 7.41-7.35 (m, 4H), 7.35-7.27 (m, 4H), 7.15-7.13 (m, 5H), 6.08 (d, *J* = 15.8 Hz, 1H), 5.90 (dd, *J* = 15.7, 8.5 Hz, 1H), 4.17 (d, *J* = 8.5 Hz, 1H), 4.09 (q, *J* = 6.9 Hz, 1H), 2.07 (s, 3H), 1.37 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 146.0, 145.4, 137.3, 137.0, 135.8, 135.3, 131.9, 129.7, 129.3, 128.5, 128.1, 127.8, 127.6, 127.4, 127.4, 127.1, 126.8, 126.4, 125.3, 124.5, 118.6, 114.4, 96.4, 43.1, 40.2, 13.9, 11.8.

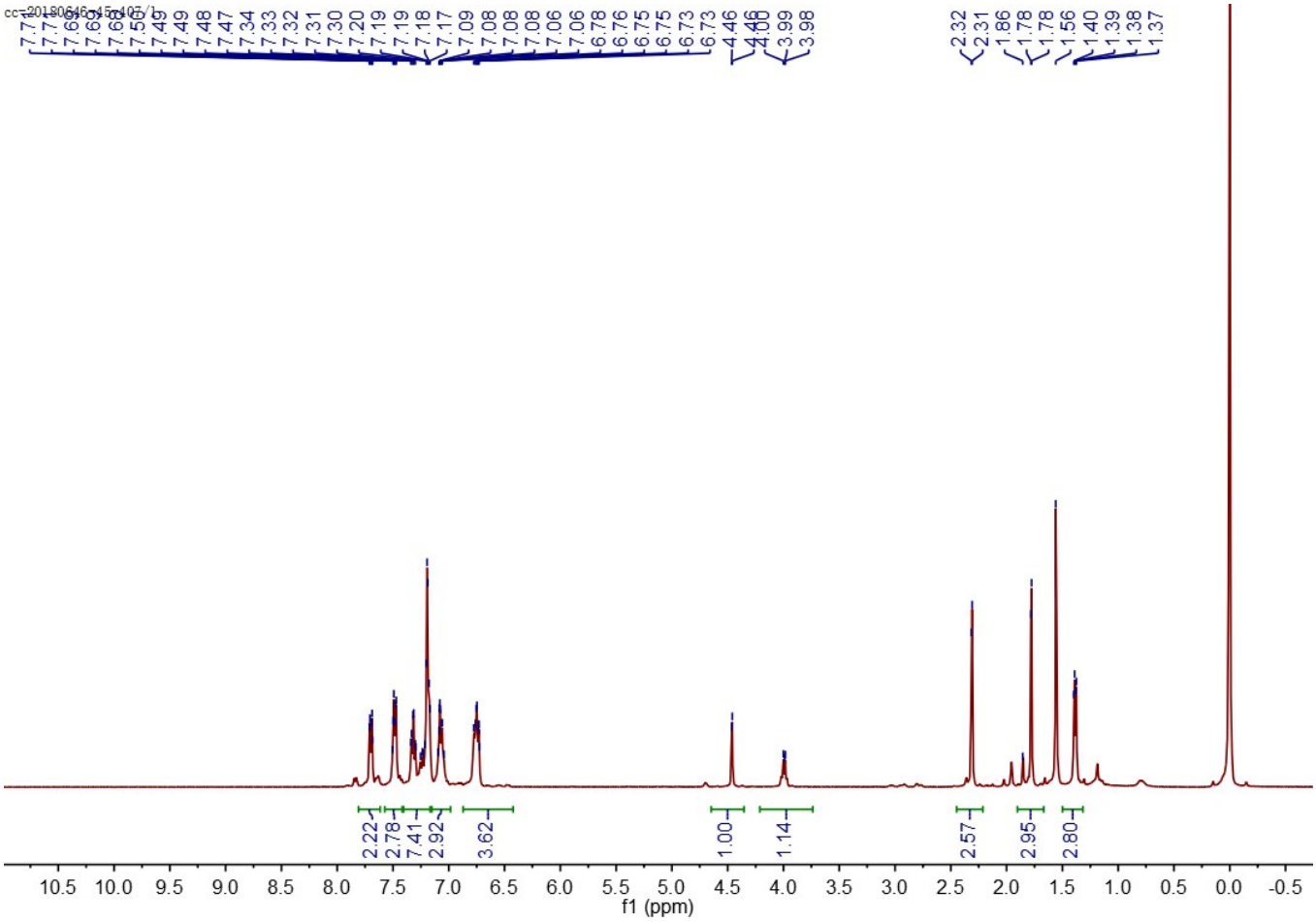


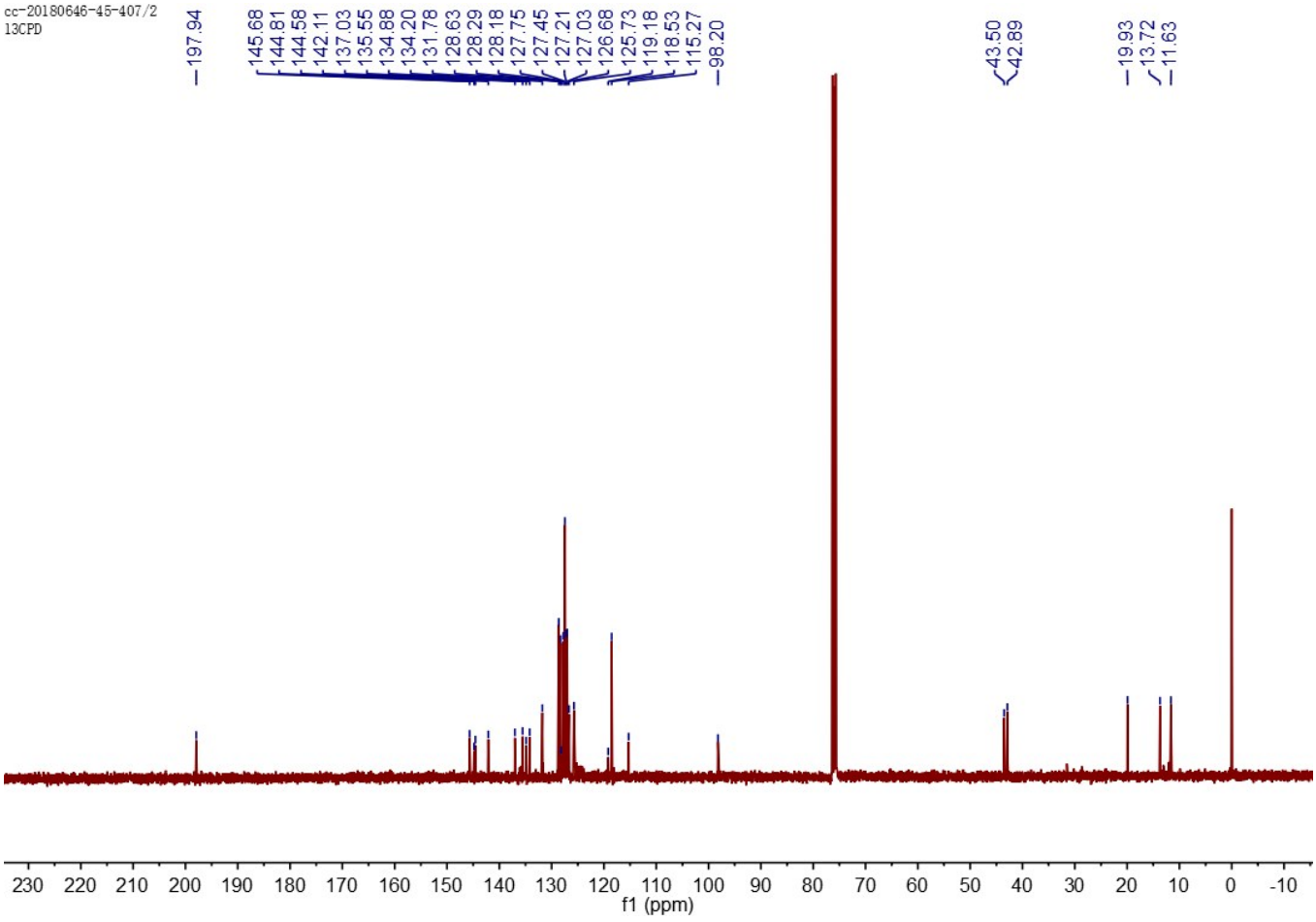


(*R*)-2-((*S*)-1,3-Mimethyl-4,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'm):

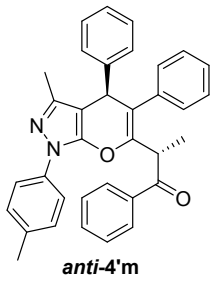


White solid, m.p. 154-156 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 -7.68 (m, 2H), 7.53-7.46 (m, 3H), 7.32-7.30 (m, 3H), 7.07-7.05 (m, 3H), 6.81-6.69 (m, 4H), 4.46 (s, 1H), 3.99 (q, J = 6.7 Hz, 1H), 2.31 (s, 3H), 1.78 (s, 3H), 1.38 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9, 145.6, 144.8, 144.5, 142.1, 137.0, 135.5, 134.8, 134.2, 131.7, 128.6, 128.2, 128.1, 127.7, 127.4, 127.2, 127.0, 126.6, 125.7, 119.1, 118.5, 115.2, 98.2, 43.5, 42.8, 19.9, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{29}H_{27}N_2O_2$ $[M + H]^+$ 435.2067, found 435.2065.


7.71
7.69
7.64
7.56
7.49
7.48
7.47
7.34
7.33
7.32
7.31
7.30
7.20
7.19
7.19
7.18
7.17
7.09
7.08
7.08
7.08
7.06
7.06
6.78
6.76
6.75
6.75
6.73
4.46
4.00
3.99
3.98
2.32
2.31
1.86
1.78
1.78
1.56
1.40
1.39
1.38
1.37
2.22
2.78
7.41
2.92
3.62
1.00
1.14
2.57
2.95
2.80
10.5 10.0 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
f1 (ppm)

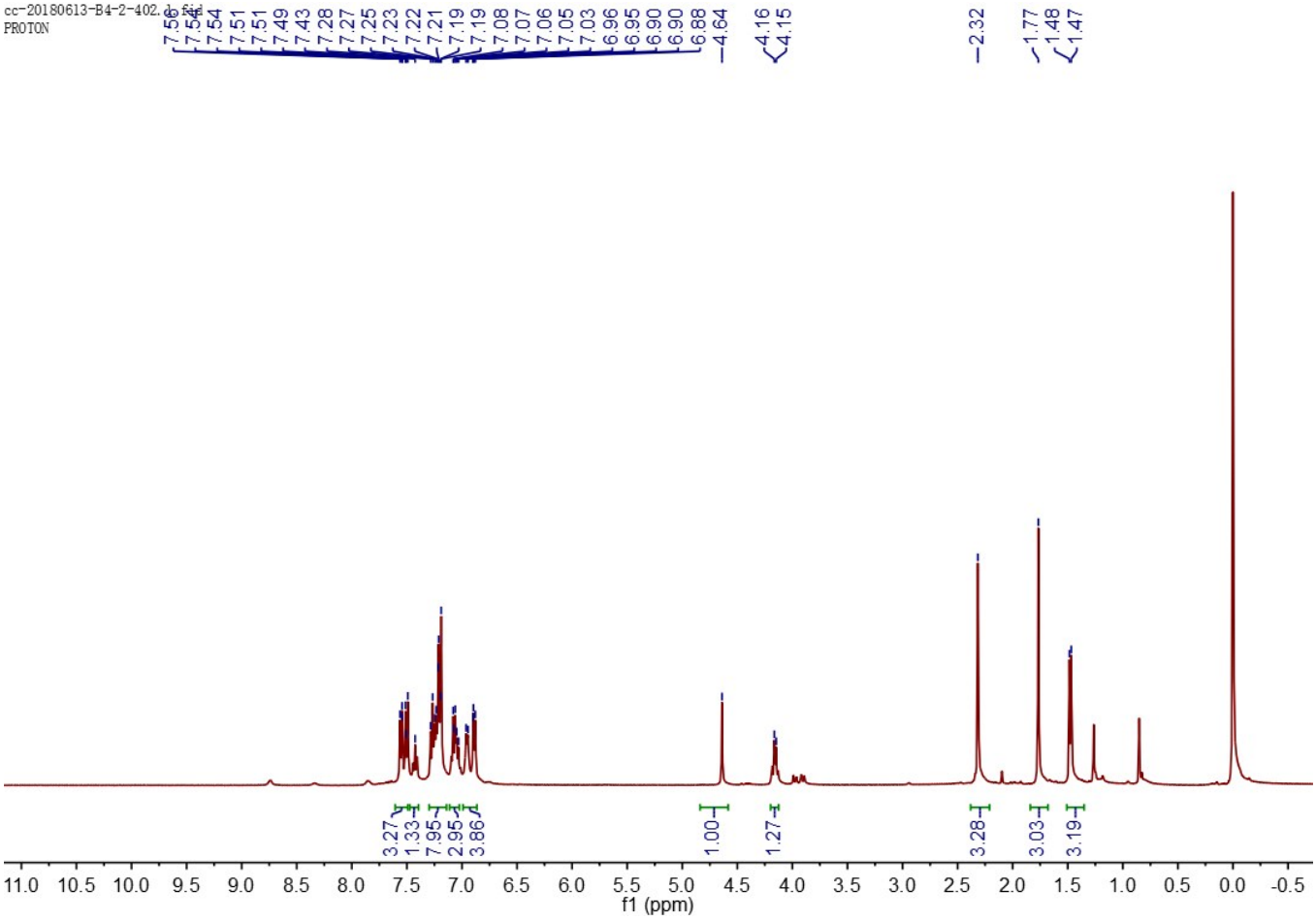

cc-20180646-45-407/2
13CPD
197.94
145.68
144.81
144.58
142.11
137.03
135.55
134.88
134.20
131.78
128.63
128.29
128.18
127.75
127.45
127.21
127.03
126.68
125.73
119.18
118.53
115.27
98.20
43.50
42.89
19.93
13.72
11.63
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

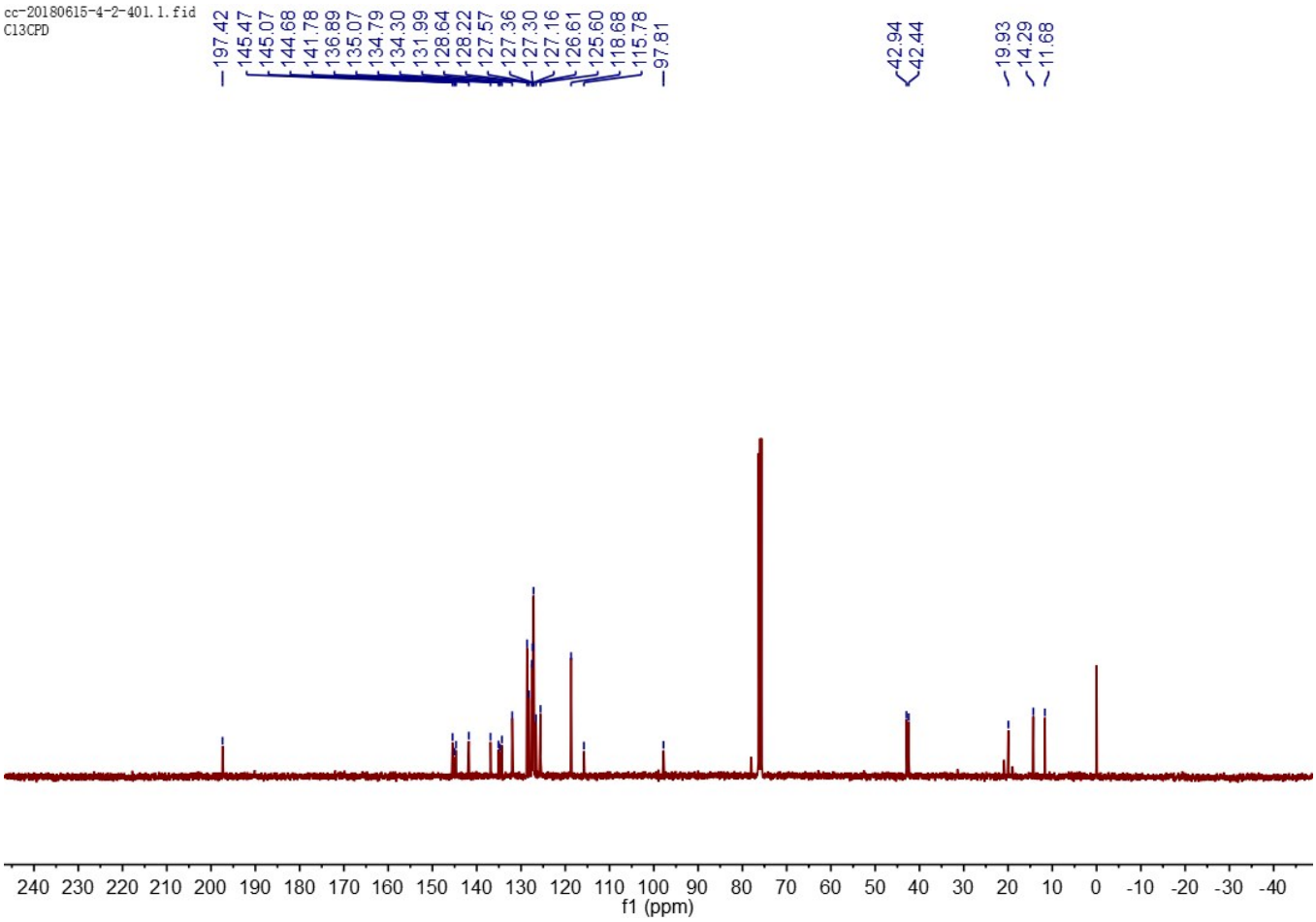
(*S*)-2-((*S*)-1,3-Dimethyl-4,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'm):



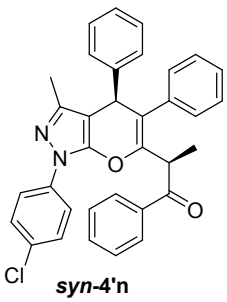
anti-4'm

Yellow solid. m.p. 139-141 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53-7.50 (m, 4H), 7.43-7.41 (m, 2H), 7.29-7.24 (m, 2H), 7.05-7.03 (m, 3H), 6.92-6.90 (m, 4H), 4.64 (s, 1H), 4.16 (d, J = 6.7 Hz, 1H), 2.32 (s, 3H), 1.77 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4, 145.4, 145.0, 144.7, 141.7, 136.9, 135.0, 134.8, 134.3, 132.0, 128.6, 128.2, 127.5, 127.3, 127.3, 127.1, 126.6, 125.6, 118.9, 115.7, 97.8, 42.9, 42.4, 19.9, 14.2, 11.6.



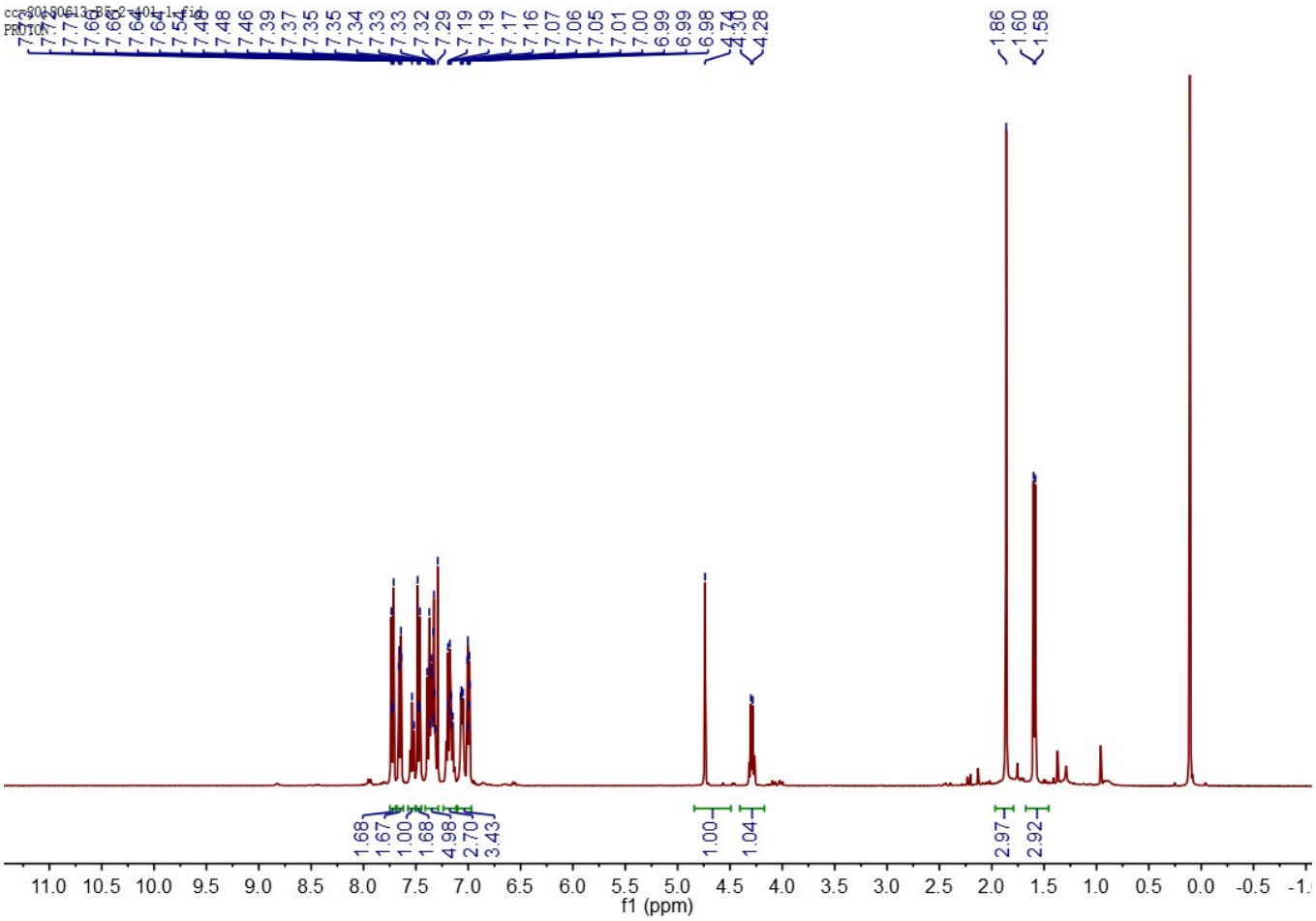


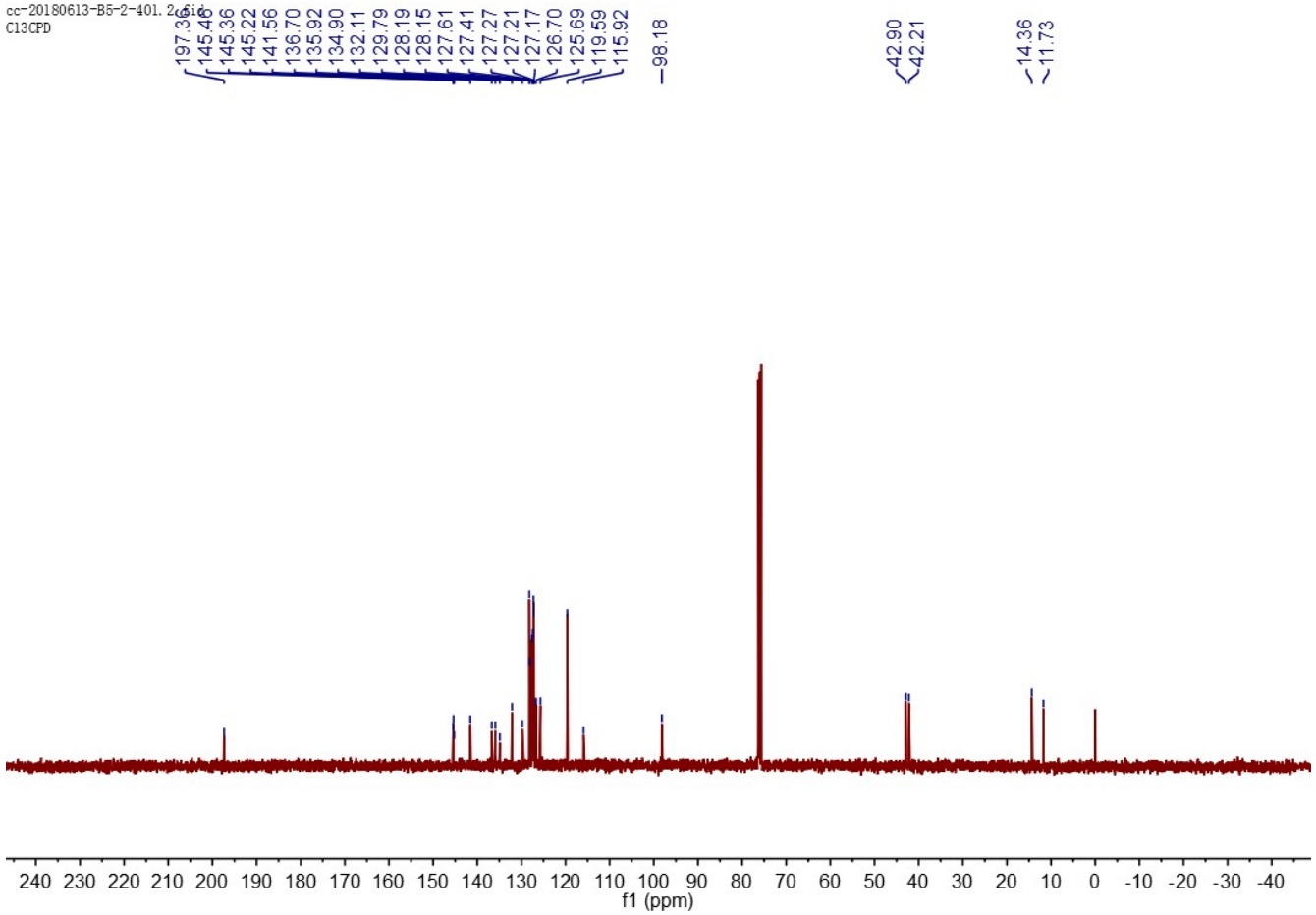
(*R*)-2-((*S*)-1-(4-Fluorophenyl)-3-methyl-4,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'n):



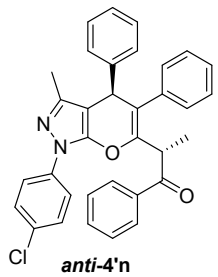
***syn*-4'n**

Yellow solid, m.p. 136-138 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.65-7.60 (m, 2H), 7.54-7.52 (m, 1H), 7.47-7.45 (m, 2H), 7.35-7.33 (m, 5H), 7.18-7.15 (m, 3H), 7.06-7.04 (m, 2H), 7.00-6.98 (m, 2H), 4.74 (s, 1H), 4.29 (q, *J* = 6.8 Hz, 1H), 1.86 (s, 3H), 1.59 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 145.4, 145.3, 145.2, 141.5, 136.7, 135.9, 134.9, 132.1, 129.8, 128.2, 127.6, 127.4, 127.2, 127.2, 127.1, 126.7, 125.7, 119.6, 115.9, 98.1, 42.9, 42.2, 14.3, 11.7. HRMS (ESI) *m/z* calcd for $C_{34}H_{28}FN_2O_2$ $[M + H]^+$ 515.2129, found 515.2132.


PROTON
1.86
1.60
1.58
1.68
1.67
1.00
1.68
4.98
2.70
3.43
1.00
1.04
2.97
2.92
f1 (ppm)

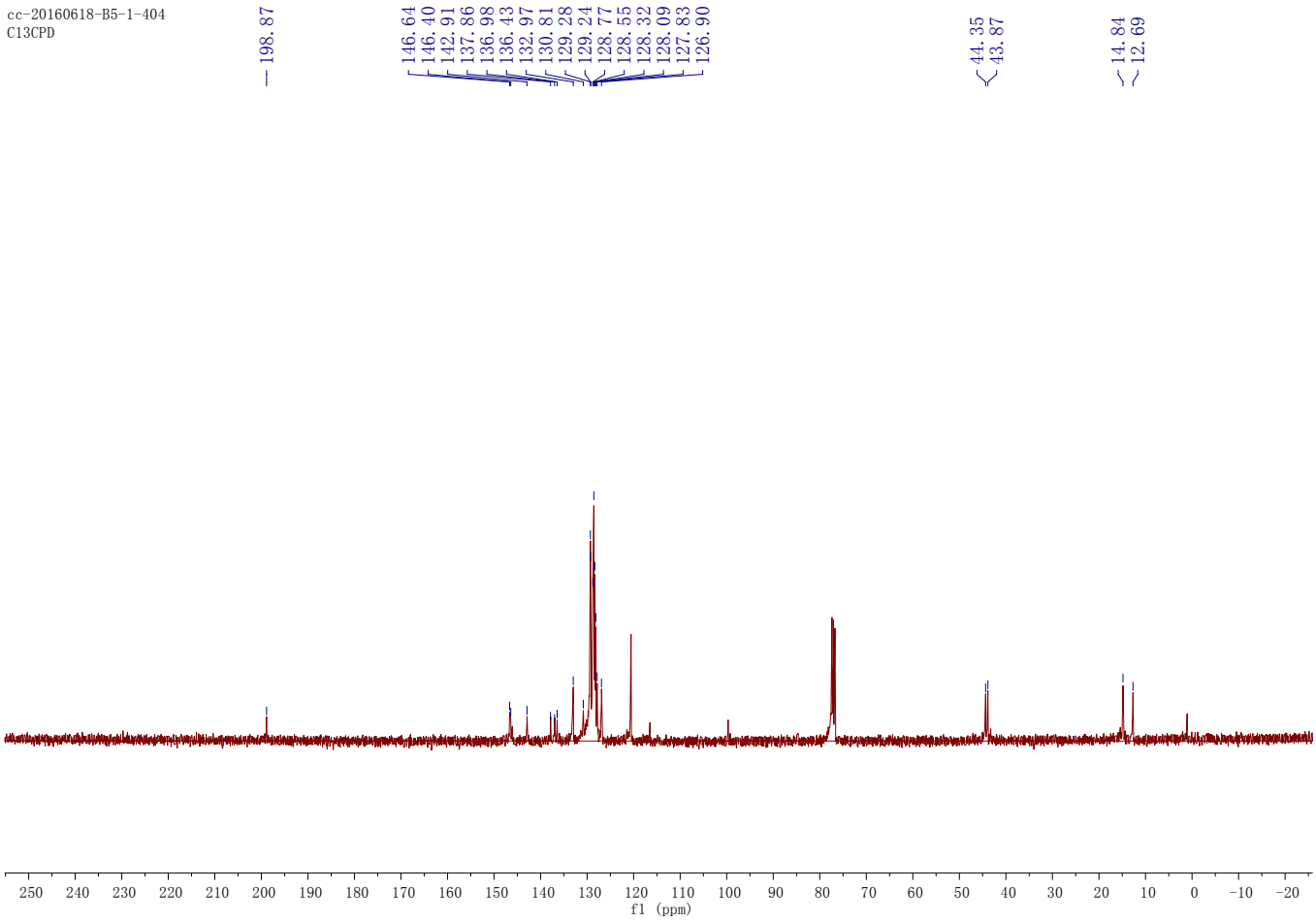

C13CPD
98.18
42.90
42.21
14.36
11.73
f1 (ppm)

(*S*)-2-((*S*)-1-(4-Fluorophenyl)-3-methyl-4,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'n):

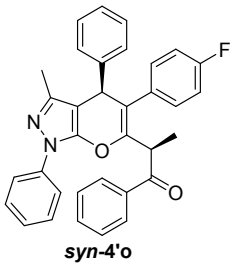


anti-4'n

Yellow solid, m.p. 157-158 ˚C. 1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.65-7.60 (m, 2H), 7.54-7.52 (m, 1H), 7.47-7.45 (m, 2H), 7.35-7.33 (m, 5H), 7.18-7.15 (m, 3H), 7.06-7.04 (m, 2H), 7.00-6.98 (m, 2H), 4.74 (s, 1H), 4.29 (q, J = 6.8 Hz, 1H), 1.86 (s, 3H), 1.59 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9, 146.6, 146.4, 142.9, 137.9, 137.0, 136.4, 133.0, 130.8, 129.3, 129.2, 128.8, 128.6, 128.3, 128.1, 127.8, 126.9, 44.4, 43.9, 14.84, 12.7.

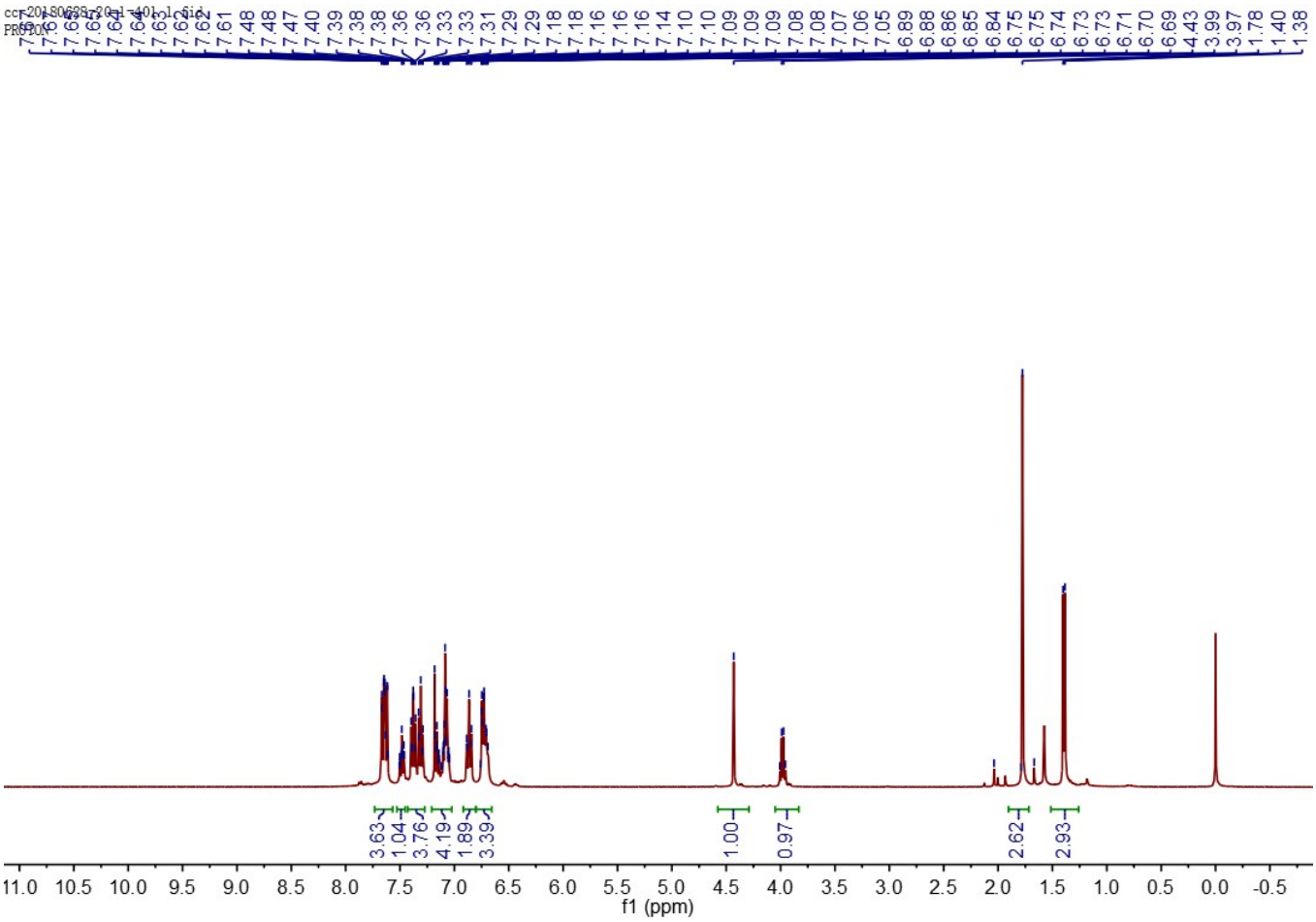


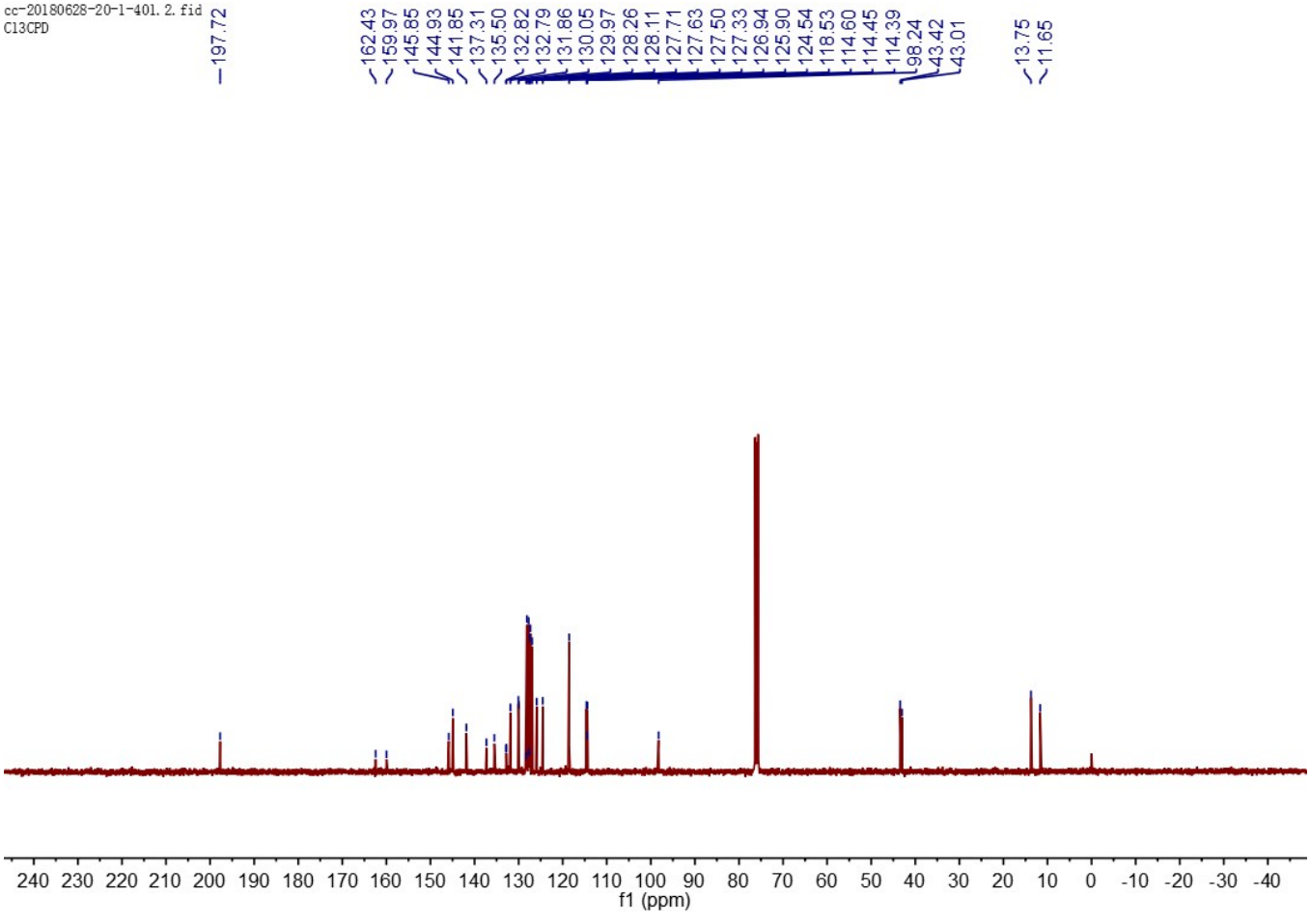
(*R*)-2-((*S*)-5-(4-Fluorophenyl)-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*syn*-4'o):



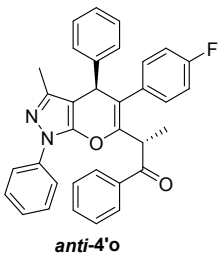
syn-4'o

Orange solid, m.p. 153-155 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.60 (m, 4H), 7.48-7.44 (m, 1H), 7.34-7.31 (m, 5H), 7.07-7.05 (m, 3H), 6.87-6.85 (m, 2H), 6.77-6.67 (m, 4H), 4.43 (s, 1H), 3.98 (q, *J* = 6.8 Hz, 1H), 1.78 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 162.4, 159.9, 145.8, 144.9, 141.8, 137.3, 135.2, 132.8 (d, *J* = 4.0 Hz), 131.8, 130.0 (d, *J* = 8.0 Hz), 128.2, 127.7, 127.5, 127.3, 126.9, 125.9, 124.5, 118.5, 114.6, 114.4 (d, *J* = 6.0 Hz), 98.2, 43.4, 43.0, 13.7, 11.6. HRMS (ESI) *m/z* calcd for $C_{34}H_{28}FN_2O_2$ $[M + H]^+$ 515.2129, found 515.2133.


cc-20180628-20-1-401.1.fid
PROTON
7.66 7.65 7.64 7.64 7.63 7.62 7.61 7.48 7.48 7.47 7.40 7.39 7.38 7.38 7.36 7.36 7.33 7.31 7.29 7.29 7.18 7.16 7.16 7.16 7.14 7.10 7.09 7.09 7.09 7.08 7.07 7.06 7.05 6.89 6.88 6.86 6.85 6.84 6.75 6.74 6.73 6.73 6.71 6.70 6.69 4.43 3.99 3.97 1.78 1.40 1.38
3.63 1.04 3.76 4.19 1.89 3.39 1.00 0.97 2.62 2.93
11.0 10.5 10.0 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
f1 (ppm)

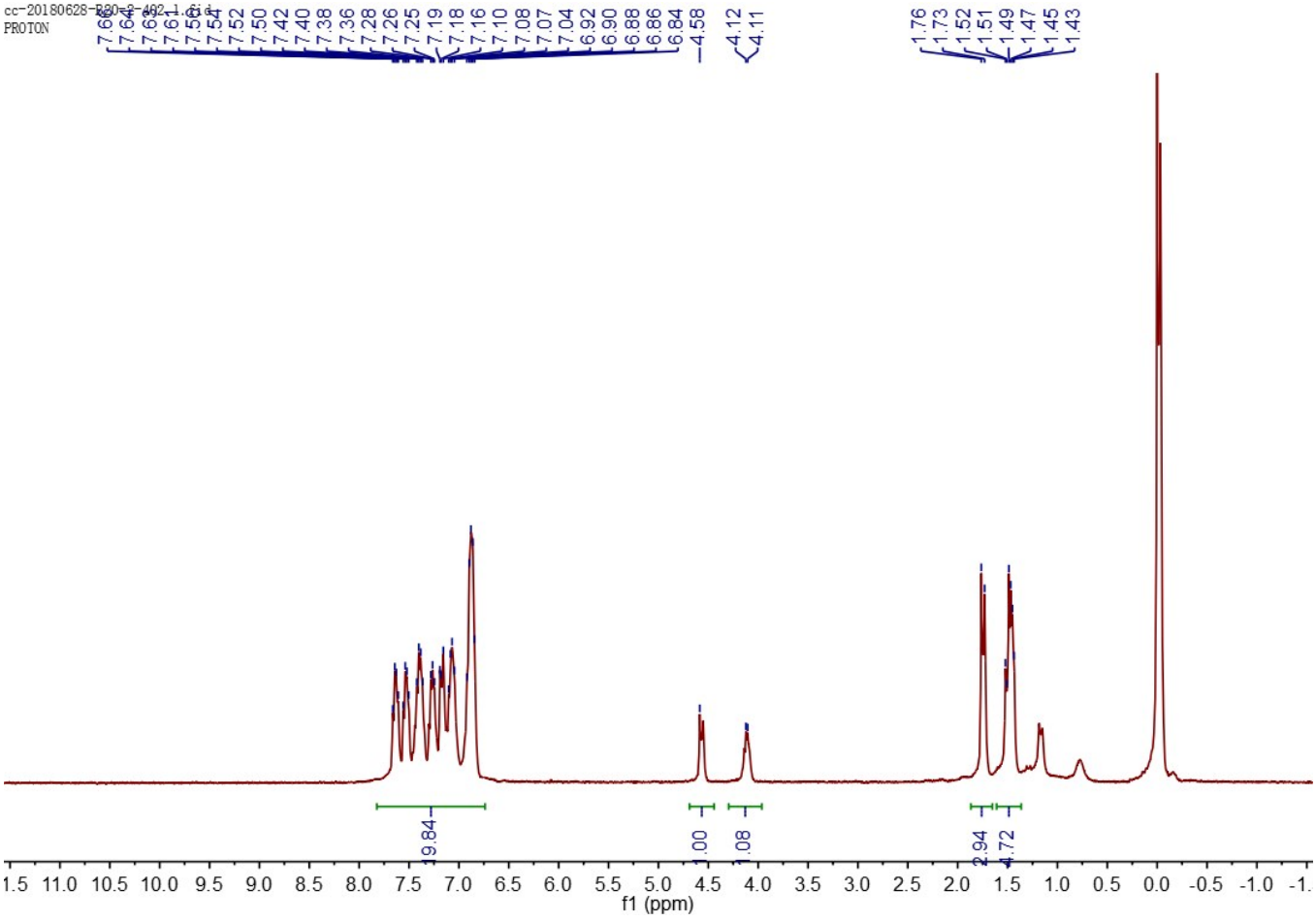

cc-20180628-20-1-401.2.fid
C13CPD
197.72
162.43 159.97 145.85 144.93 141.85 137.31 135.50 132.82 132.79 131.86 130.05 129.97 128.26 128.11 127.71 127.63 127.50 127.33 126.94 125.90 124.54 118.53 114.60 114.45 114.39 98.24 43.42 43.01
13.75 11.65
240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40
f1 (ppm)

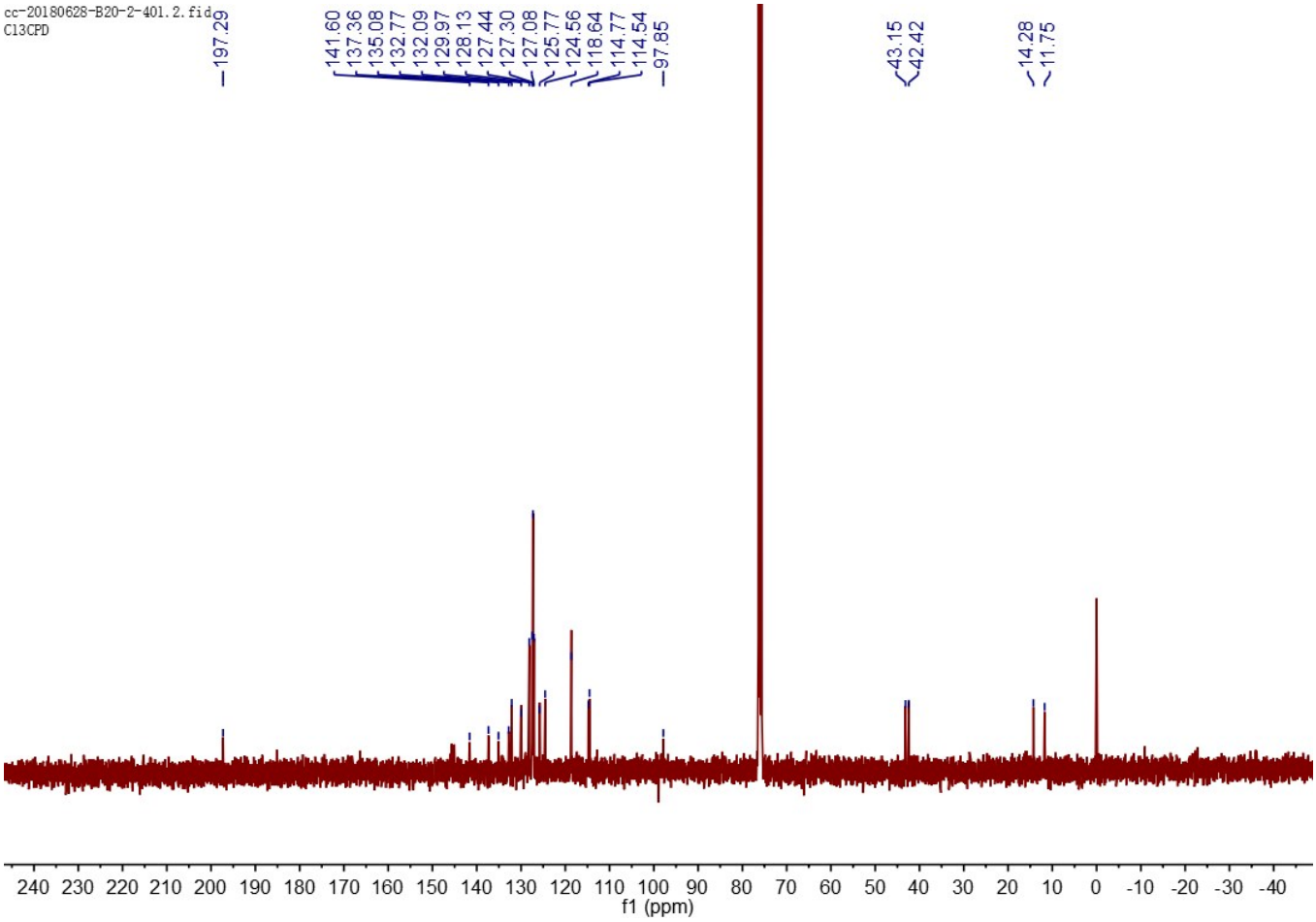
(*S*)-2-((*S*)-5-(4-Fluorophenyl)-3-methyl-1,4-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazol-6-yl)-1-phenylpropan-1-one (*anti*-4'o):



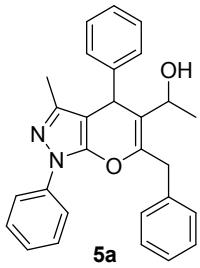
anti-4'o

Yellow solid, m.p. 185-187 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.60 (m, 3H), 7.54 (s, 1H), 7.38 (m, 3H), 7.71-6.97 (m, 4H), 7.27-7.25 (m, 1H), 7.21-7.13 (m, 2H), 6.97-6.95 (m, 3H), 6.88 (s, 2H), 4.58 (s, 1H), 4.11 (q, *J* = 6.9 Hz, 1H), 1.76 (s, 3H), 1.48 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3, 145.6, 145.1, 145.0, 141.6, 137.3, 135.1, 132.7 (d, *J* = 2.0 Hz), 132.1, 129.9 (d, *J* = 7.0 Hz), 128.1, 127.4, 127.3, 127.0, 125.9, 125.7, 124.5, 118.6,114.7 (d, *J* = 2.0 Hz), 114.5, 97.8, 43.1, 42.4, 14.2, 11.7.



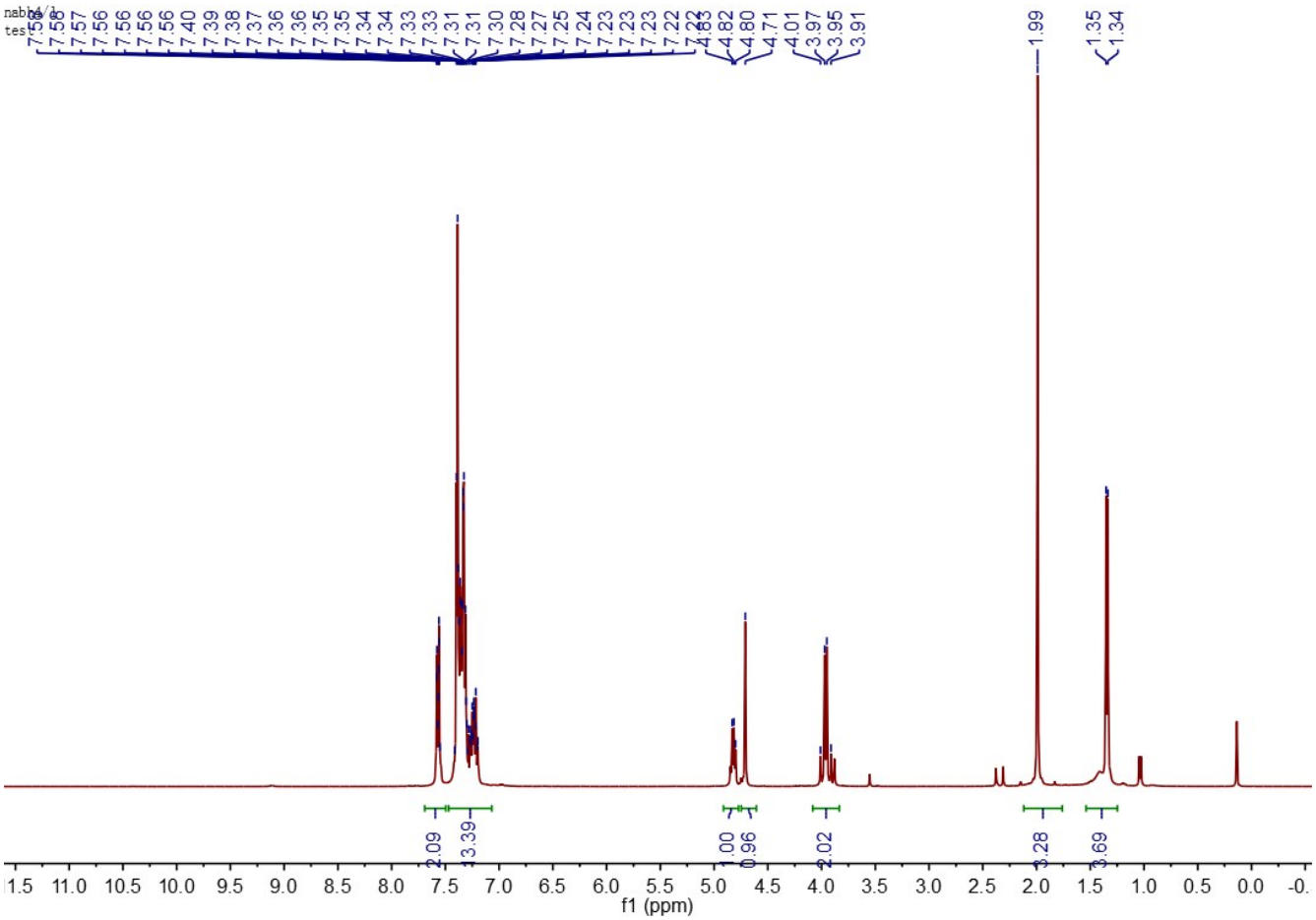


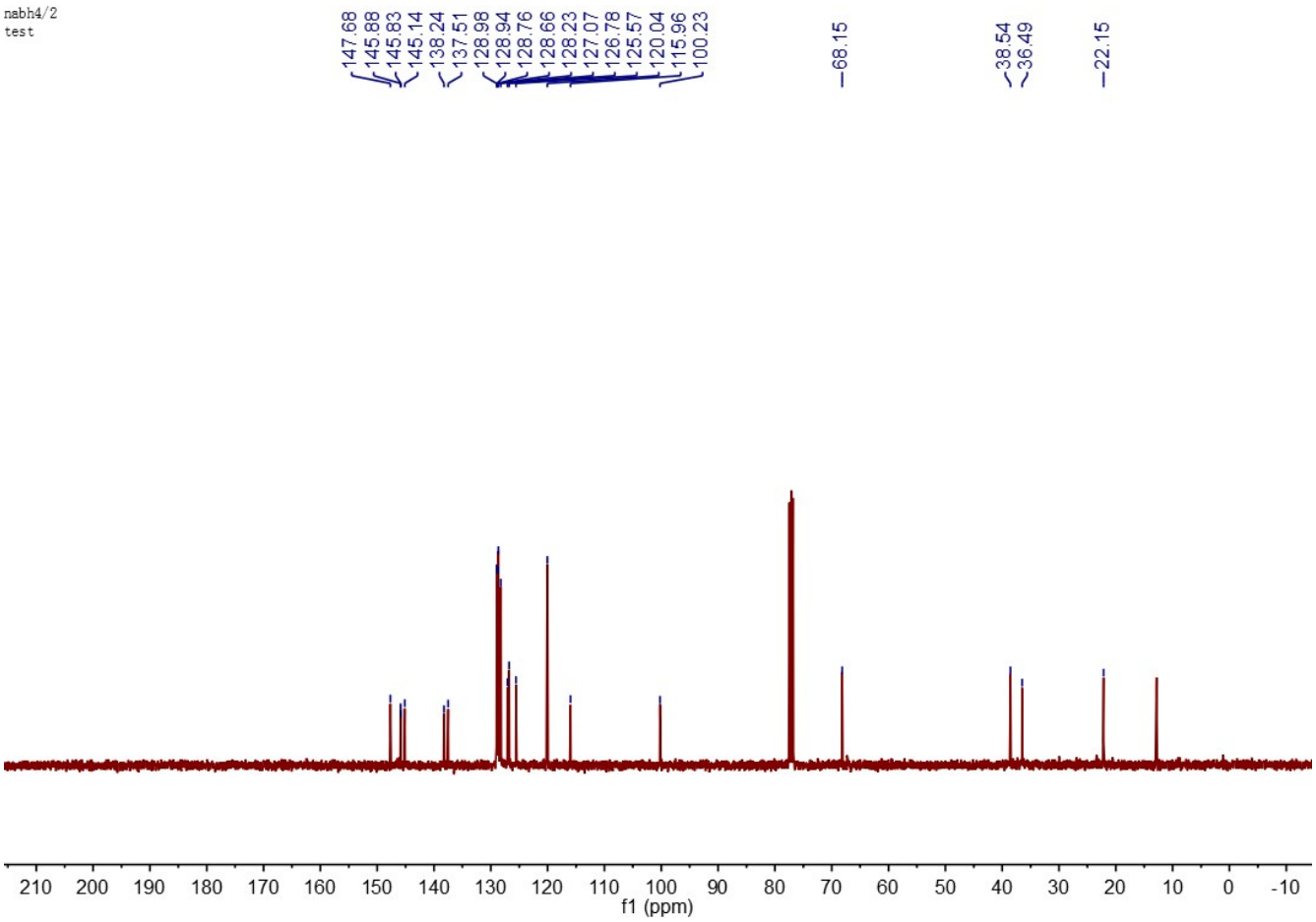
1-(2-Benzyl-5-methyl-4,7-diphenyl-4,7-dihydropyrano[2,3-*b*]pyrrol-3-yl)ethan-1-ol (5a).



5a

Red oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 3H), 7.41-7.18 (m, 13H), 4.82 (dd, *J* = 12.8, 6.3 Hz, 1H), 4.71 (s, 1H), 4.04-3.85 (m, 2H), 1.99 (s, 3H), 1.34 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 145.8, 145.8, 145.1, 138.2, 137.5, 128.9, 128.9, 128.7, 128.6, 128.2, 127.0, 126.7, 125.5, 120.0, 115.9, 100.2, 68.1, 38.5, 36.4, 22.1, 12.8. HRMS (ESI) *m/z* calcd calculated for $C_{28}H_{27}N_2O_2$ $[M + H]^+$ 423.2067, found 423.2066.


nabh4/1
test
7.58 7.58 7.57 7.56 7.56 7.56 7.56 7.40 7.39 7.38 7.37 7.36 7.36 7.35 7.35 7.34 7.34 7.33 7.33 7.31 7.31 7.30 7.28 7.27 7.25 7.24 7.23 7.23 7.23 7.22 4.83 4.82 4.80 4.71 4.01 3.97 3.95 3.91
1.99 1.35 1.34
2.09 3.39 1.00 0.96 2.02 3.28 3.69
1.5 11.0 10.5 10.0 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.
f1 (ppm)


nabh4/2
test
147.68 145.88 145.83 145.14 138.24 137.51 128.98 128.94 128.76 128.66 128.23 127.07 126.78 125.57 120.04 115.96 100.23
68.15
38.54 36.49
22.15
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

X-ray crystallographic data of compound 3a

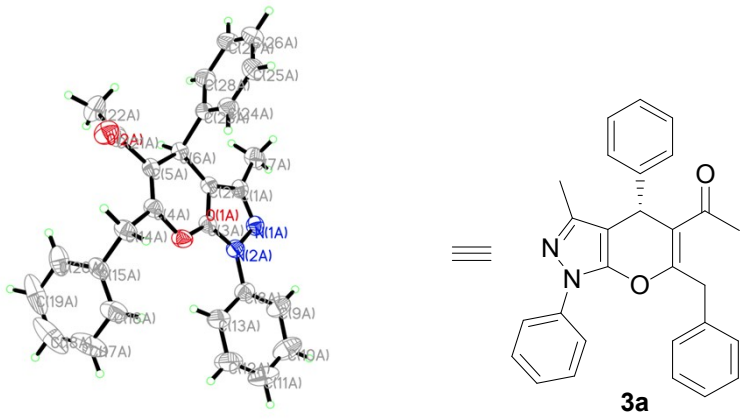


Figure S1 X-ray crystal structure of **3a**

Displacement ellipsoids are shown at the 50% probability level.

Table S1 Crystal data and structure refinement for compound **3a**

Name	Compound **3a**
Empirical formula	C28H24N2O2
Formula weight	420.49
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	12.5063(3)
b/Å	13.3807(2)
c/Å	16.7023(3)
α/°	68.356(2)
β/°	80.275(2)
γ/°	62.538(2)
Volume/Å3	2305.20(9)
Z	4
ρcalcg/cm^3	1.212

μ/mm^{-1}	0.605
F(000)	888.0
Crystal size/mm^3	0.34 × 0.28 × 0.26
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.692 to 158.468
Index ranges	-15 ≤ h ≤ 13, -17 ≤ k ≤ 16, -21 ≤ l ≤ 21
Reflections collected	77402
Independent reflections	9542 [R_{int} = 0.0176, R_{sigma} = 0.0087]
Data/restraints/parameters	9542/8/613
Goodness-of-fit on F^2	1.069
Final R indexes [I>=2σ (I)]	R_1 = 0.0479, wR_2 = 0.1371
Final R indexes [all data]	R1 = 0.0502, wR2 = 0.1395
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.26

X-ray crystallographic data of compound 4a

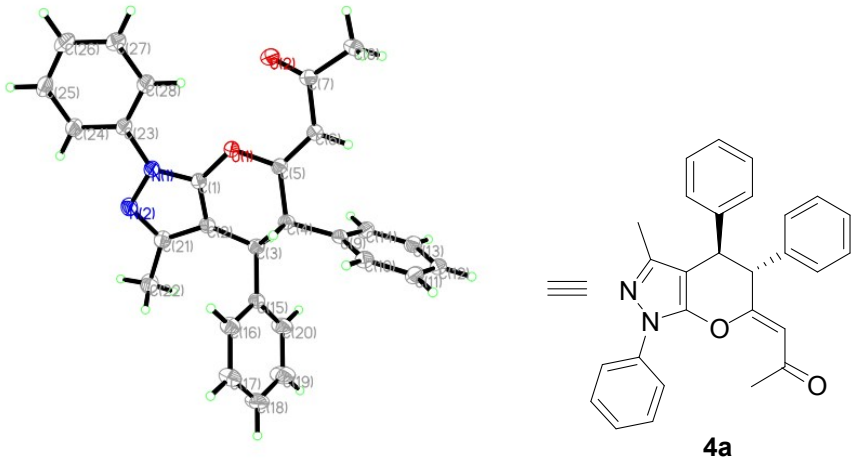


Figure S2 X-ray crystal structure of **4a**

Displacement ellipsoids are shown at the 50% probability level.

Table S2 Crystal data and structure refinement for compound **4a**

Name	Compound **4a**
Empirical formula	C28H24N2O2
Formula weight	420.49
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	13.785(3)
b/Å	9.6814(19)
c/Å	17.390(4)
α/°	90
β/°	106.75(3)
γ/°	90
Volume/Å3	2222.4(8)
Z	4
ρcalcg/cm^3	1.257

μ/mm^{-1}	0.079
F(000)	888.0
Crystal size/mm^3	0.2 × 0.18 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.34 to 55.614
Index ranges	$-18 \leq h \leq 18$, $-12 \leq k \leq 12$, $-22 \leq l \leq 22$
Reflections collected	25893
Independent reflections	5256 [R_{int} = 0.0649, R_{sigma} = 0.0507]
Data/restraints/parameters	5256/0/292
Goodness-of-fit on F^2	0.995
Final R indexes [I>=2σ (I)]	R_1 = 0.0625, wR_2 = 0.1468
Final R indexes [all data]	R_1 = 0.0929, wR_2 = 0.1663
Largest diff. peak/hole / e $Å^{-3}$	0.29/-0.30

X-ray crystallographic data of compound 4b

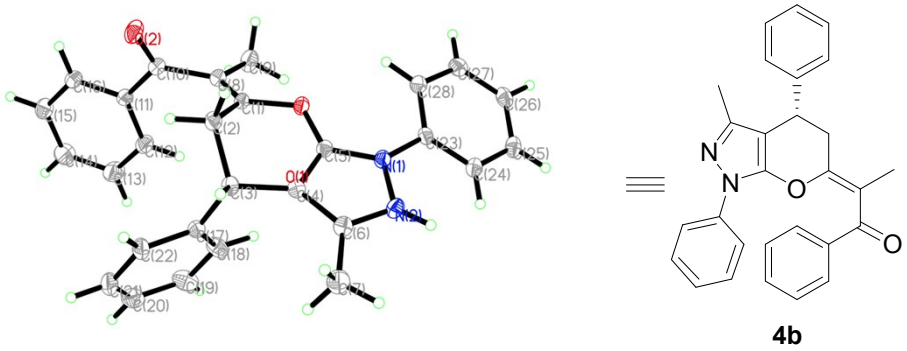


Figure S3 X-ray crystal structure of **4b**

Displacement ellipsoids are shown at the 50% probability level.

Table S3 Crystal data and structure refinement for compound **4b**

Name	Compound **4b**
Empirical formula	C28H25N2O2
Formula weight	421.50
Temperature/K	113.15
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	9.1355(4)
b/Å	13.6330(5)
c/Å	18.2466(7)
α/°	90
β/°	101.056(4)
γ/°	90
Volume/Å3	2230.33(16)
Z	4
ρcalcg/cm^3	1.255

μ/mm^{-1}	0.079
F(000)	892.0
Crystal size/mm^3	0.22 × 0.18 × 0.14
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.754 to 54.204
Index ranges	-9 ≤ h ≤ 11, -17 ≤ k ≤ 17, -23 ≤ l ≤ 23
Reflections collected	19706
Independent reflections	4844 [Rint = 0.0496, Rsigma = 0.0366]
Data/restraints/parameters	4844/0/292
Goodness-of-fit on F^2	1..086
Final R indexes [I>=2σ (I)]	R1 = 0.0536, wR2 = 0.1458
Final R indexes [all data]	R1 = 0.0658, wR2 = 0.1548
Largest diff. peak/hole / e $Å^{-3}$	0.31/-0.57

X-ray crystallographic data of compound 4'a

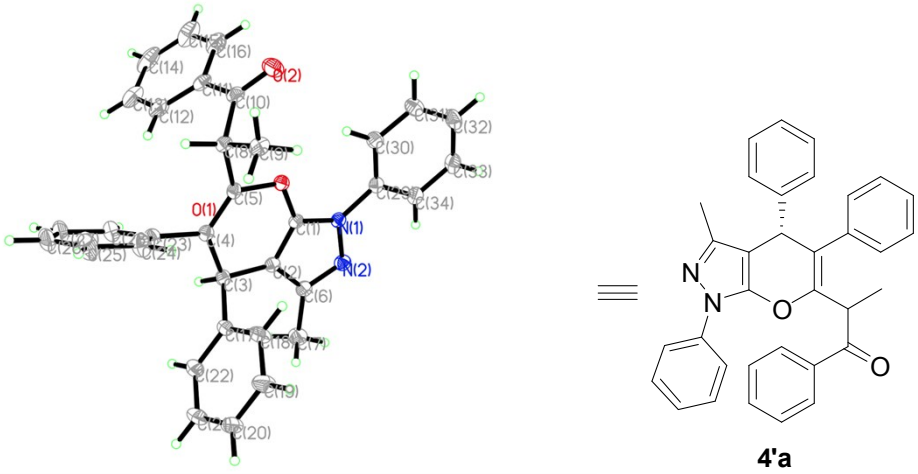


Figure S4 X-ray crystal structure of **4'a**

Displacement ellipsoids are shown at the 50% probability level.

Table S4 Crystal data and structure refinement for compound **4'a**

Name	Compound **6'a**
Empirical formula	C34H28N2O2
Formula weight	496.58
Temperature/K	113.15
Crystal system	triclinic
Space group	P-1
a/Å	10.4057(5)
b/Å	10.8124(8)
c/Å	13.1072(8)
α/°	103.696(6)
β/°	104.327(5)
γ/°	102.121(5)
Volume/Å3	1330.51(15)
Z	2

ρcalcg/cm^3	1.240
μ/mm^{-1}	0.077
F(000)	524.0
Crystal size/mm^3	0.22 × 0.18 × 0.16
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.216 to 52.742
Index ranges	-12≤ h ≤ 13, -13 ≤ k ≤ 13, -16≤ l ≤ 16
Reflections collected	13896
Independent reflections	5404 [Rint = 0.0498, Rsigma = 0.0542]
Data/restraints/parameters	5404/0/346
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R1 = 0.0491, wR2 = 0.1152
Final R indexes [all data]	R1 = 0.0689, wR2 = 0.1274
Largest diff. peak/hole / e Å^{-3}	0.24/-0.23