Supporting Information

Lewis acid catalyzed [2 + 2] cycloaddition of ynamides and propargyl silyl ethers: synthesis of alkylidenecyclobutenones and their reactivity in ring-opening and ring expansion

Ling Chen[a], Jian Cao,[a] Zheng Xu[a], Zhan-Jiang Zheng[a], Yu-Ming Cui[a], and Li-Wen Xu*[a,b]*

[a] Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, No 1378, Wenyi West Road, Science Park of HZNU, Hangzhou 311121, People's Republic of China

[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics (LICP), Chinese Academy of Sciences (CAS), P. R. China

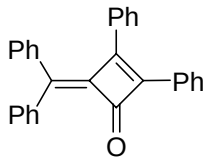
Table of Contents

General experimental procedures

General: ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker Avance (400 MHz) spectrometer, using $CDCl_3$ as the solvent and TMS as internal standard; chemical shifts were quoted in parts per million and *J* values were given in hertz. High resolution mass spectrometry (HRMS) was performed on a Waters Micromass GCT instrument. Melting points were uncorrected. All solvents were dried according to standard procedures. Ynamides **2**[1] and propargylic silyl ether **1**[2] were prepared by reported methods.

1. X. Zhang, Y. Zhang, J. Huang, R.-P. Hsung, K. C. M. Kurtz, J. Oppenheimer, M. E. Petersen, I. K. Sagamanova, L. Shen and M. R. Tracey, *J. Org. Chem.*, 2006, **71**, 4170.
2. T. Ishikawa, S. Manabe, T. Aikawa, T. Kudo and S. Saito, *Org. Lett.*, 2004, **6**, 2361.

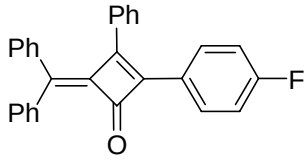
Typical procedure for the synthesis of alkylidenecyclobutenones 3



3a

4-(diphenylmethylene)-2,3-diphenylcyclobut-2-enone 3a

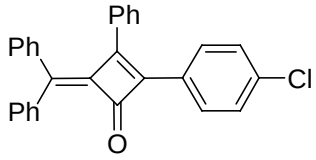
A vial was charged with propargyl silyl ether **1a** (106.9 mg, 0.3 mmol) and ynamide **2a** (56.2 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. CH_2Cl_2 (3 mL) and $BF_3{\cdot}OEt_2$ (8.5 mg, 0.06 mmol) were next added and the solution was stirred at rt. Upon reaction completion (7 h, TLC, eluent: hexane-EtOAc, 15:1), the mixture was filtered over a plug of silica gel (washed with 50 mL EtOAc), and the filtrate was concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 15:1) to afford **3a** (75.0 mg, 65%) as a yellow solid, mp 181-183 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.77 (m, 2H), 7.21-7.41 (m, 9H), 7.02-7.13 (m, 5H), 6.93-6.97 (m, 2H), 6.89 (d, J = 7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 187.6, 176.0, 154.4, 147.3, 138.6, 138.1, 131.9, 130.64, 130.60, 130.56, 129.8, 129.6, 129.4, 128.7, 128.0, 127.9, 127.7, 127.5, 127.42, 127.37, 127.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{21}O$, 385.1587; found 385.1595.



3b

4-(diphenylmethylene)-2-(4-fluorophenyl)-3-phenylcyclobut-2-enone 3b

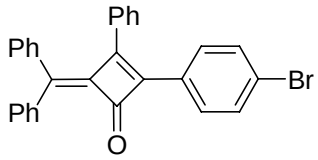
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (142.8 mg, 71%), mp 180-182 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.78 (m, 2H), 7.31-7.39 (m, 5H), 7.20-7.21 (m, 1H), 6.92-7.10 (m, 9H), 6.87 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.4, 175.5 (d, J = 2.1 Hz), 163.3 (d, J = 250.2 Hz), 153.2, 147.2, 138.6, 138.1, 131.8, 130.8, 130.6, 130.5, 129.5, 129.4, 128.1, 127.7, 127.5, 127.4, 127.0, 126.1 (d, J = 3.4 Hz), 116.0 (d, J = 21.7 Hz). HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{20}FO$, 403.1493; found 403.1491.



3c

2-(4-chlorophenyl)-4-(diphenylmethylene)-3-phenylcyclobut-2-enone 3c

The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (152.6 mg, 73%), mp 202-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67-7.69 (m, 2H), 7.21-7.39 (m, 8H), 6.92-7.12 (m, 7H), 6.87 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 176.3, 152.9, 147.1, 138.5, 138.0, 135.5, 131.7, 131.3, 130.6, 129.6, 129.0, 128.6, 128.2, 128.14, 128.07, 127.7, 127.6, 127.4, 127.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{20}ClO$, 419.1197; found 419.1187.

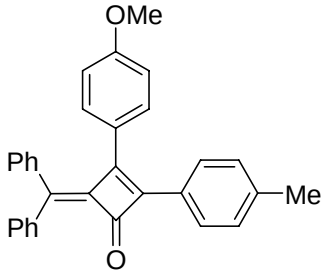


3d

2-(4-bromophenyl)-4-(diphenylmethylene)-3-phenylcyclobut-2-enone 3d

The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (155.2 mg, 67%), mp 209-211 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.62 (m, 2H), 7.32-7.43 (m, 7H), 7.22-7.25 (m, 1H), 7.07-7.13 (m, 3H), 6.93-7.01 (m, 4H), 6.88 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.1, 176.4, 153.0, 147.1, 138.5,

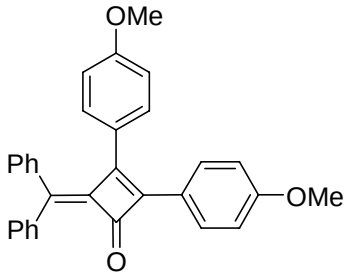
138.0, 132.0, 131.7, 131.4, 130.5, 129.6, 128.8, 128.6, 128.1, 128.0, 127.7, 127.5, 127.4, 127.3, 127.0, 123.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{20}BrO$, 463.0692; found 463.0676.



3e

4-(diphenylmethylene)-3-(4-methoxyphenyl)-2-*p*-tolylcyclobut-2-enone 3e

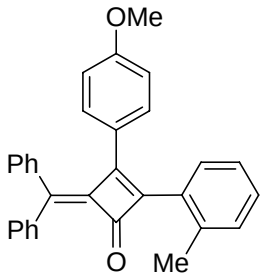
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (126.4 mg, 59%), mp 145-147 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 7.6 Hz, 2H), 7.30-7.38 (m, 5H), 7.09-7.12 (m, 3H), 6.90-7.02 (m, 6H), 6.60 (d, J = 8.4 Hz, 2H), 3.77 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 174.6, 160.6, 153.6, 147.5, 139.7, 138.9, 138.6, 130.8, 130.6, 129.8, 129.4, 129.3, 127.8, 127.6, 127.4, 127.3, 127.2, 124.1, 113.3, 55.4, 21.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}O_2$, 429.1849; found 429.1842.



3f

4-(diphenylmethylene)-2,3-bis(4-methoxyphenyl)cyclobut-2-enone 3f

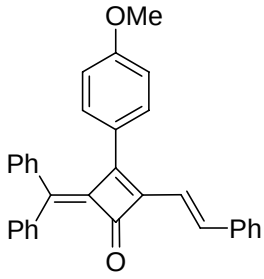
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Red solid (134.0 mg, 60%), mp 178-180 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 2H), 7.27-7.37 (m, 5H), 7.07-7.09 (m, 1H), 6.88-7.00 (m, 6H), 6.82 (d, J = 8.8 Hz, 2H), 6.60 (d, J = 8.4 Hz, 2H), 3.75 (s, 3H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.9, 173.4, 160.6, 160.5, 153.4, 147.6, 139.0, 138.6, 130.8, 130.6, 129.3, 129.0, 127.7, 127.6, 127.4, 127.3, 124.3, 122.8, 114.2, 113.3, 55.4, 55.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}O_3$, 445.1798; found 445.1788.



3g

4-(diphenylmethylene)-3-(4-methoxyphenyl)-2-*o*-tolylcyclobut-2-enone 3g

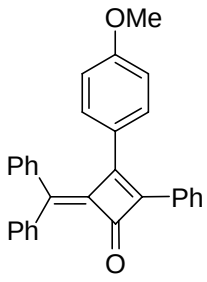
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (162.8 mg, 76%), mp 159-161 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.38 (m, 5H), 7.19-7.21 (m, 4H), 7.07-7.10 (m, 3H), 7.00-7.02 (m, 2H), 6.78-6.80 (m, 2H), 6.49-6.52 (m, 2H), 3.70 (s, 3H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 176.4, 161.2, 156.8, 146.4, 139.3, 138.9, 136.9, 131.0, 130.8, 130.7, 130.5, 130.0, 129.3, 128.9, 128.8, 128.0, 127.75, 127.72, 127.6, 125.6, 123.5, 113.2, 55.3, 20.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}O_2$, 429.1849; found 429.1853.



3h

(*E*)-4-(diphenylmethylene)-3-(4-methoxyphenyl)-2-styrylcyclobut-2-enone 3h

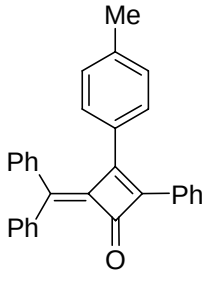
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (76.6 mg, 35%), mp 150-152 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (d, J = 16.0 Hz, 1H), 7.39-7.41 (m, 2H), 7.15-7.31 (m, 8H), 7.06-7.12 (m, 1H), 6.85-7.02 (m, 7H), 6.58 (d, J = 8.4 Hz, 2H), 3.70 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.5, 173.0, 161.0, 152.5, 147.0, 139.2, 138.9, 138.0, 136.8, 130.9, 130.8, 130.3, 130.2, 128.84, 128.79, 127.9, 127.7, 127.5, 127.1, 123.9, 115.5, 113.4, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{25}O_2$, 441.1849; found 441.1834.



3i

4-(diphenylmethylene)-3-(4-methoxyphenyl)-2-phenylcyclobut-2-enone 3i

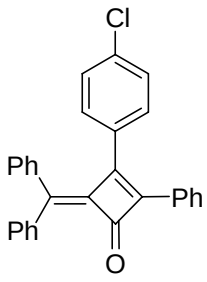
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (78.5 mg, 63%), mp 160-162 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, J = 6.8 Hz, 2H), 7.13-7.26 (m, 8H), 6.96-6.98 (m, 1H), 6.77-6.89 (m, 6H), 6.47 (d, J = 8.4 Hz, 2H), 3.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.6, 175.6, 160.8, 153.5, 147.5, 138.9, 138.5, 130.8, 130.7, 130.5, 130.1, 129.4, 128.7, 127.9, 127.7, 127.54, 127.51, 127.4, 124.0, 113.4, 55.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}NO_2$, 415.1693; found 415.1699.



3j

4-(diphenylmethylene)-2-phenyl-3-*p*-tolylcyclobut-2-enone 3j

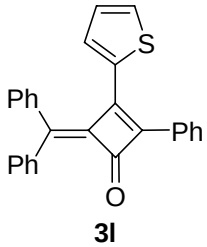
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (129.5 mg, 65%), mp 184-186 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76-7.78 (m, 2H), 7.27-7.39 (m, 8H), 7.07-7.08 (m, 1H), 6.88-6.98 (m, 8H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.7, 176.1, 154.0, 147.4, 139.9, 138.8, 138.4, 130.7, 130.6, 130.5, 129.9, 129.5, 128.9, 128.7, 128.6, 127.9, 127.6, 127.5, 127.4, 127.3, 21.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}O$, 399.1743; found 399.1748.



3k

3-(4-chlorophenyl)-4-(diphenylmethylene)-2-phenylcyclobut-2-enone 3k

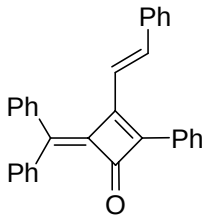
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (115.2 mg, 55%), mp 188-190 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.72 (m, 2H), 7.30-7.40 (m, 8H), 7.07-7.14 (m, 3H), 6.90-7.02 (m, 4H), 6.89 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.2, 174.3, 154.6, 147.1, 138.4, 138.1, 135.4, 130.9, 130.6, 130.5, 130.3, 129.8, 129.5, 128.8, 128.5, 128.3, 128.1, 127.74, 127.68, 127.5, 127.4. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{20}ClO$, 419.1197; found 419.1198.



3l

4-(diphenylmethylene)-2-phenyl-3-(thiophen-2-yl)cyclobut-2-enone 3l

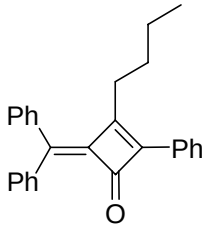
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (56.4 mg, 48%), mp 172-174 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88-7.90 (m, 2H), 7.31-7.39 (m, 9H), 7.21-7.23 (m, 1H), 7.12-7.16 (m, 2H), 7.07 (d, J = 7.6 Hz, 2H), 6.77-6.80 (m, 1H), 6.62 (d, J = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.8, 166.8, 153.3, 146.6, 138.9, 138.8, 132.1, 131.6, 130.9, 130.8, 130.7, 130.4, 129.7, 129.5, 128.6, 128.1, 127.9, 127.8, 127.7, 127.6, 127.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{19}OS$, 391.1151; found 391.1146.



3m

(*E*)-4-(diphenylmethylene)-2-phenyl-3-styrylcyclobut-2-enone 3m

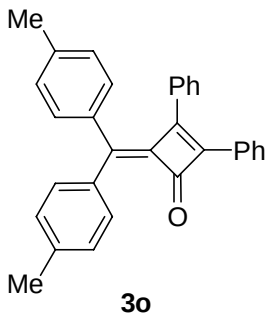
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (99.1 mg, 48%), mp 140-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 2H), 7.21-7.44 (m, 16H), 7.05-7.09 (m, 3H), 6.19 (d, J = 16.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.3, 170.8, 153.5, 146.8, 143.0, 139.9, 138.8, 135.4, 131.2, 130.7, 130.6, 130.4, 129.8, 129.4, 128.9, 128.8, 128.1, 128.0, 127.9, 127.8, 127.6, 117.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{23}O$, 411.1743; found 411.1747.



3n

3-butyl-4-(diphenylmethylene)-2-phenylcyclobut-2-enone 3n

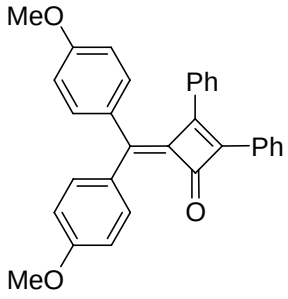
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Colorless oil (40.3 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 7.2 Hz, 2H), 7.36-7.43 (m, 7H), 7.24-7.32 (m, 6H), 2.46 (t, J = 8.0 Hz, 2H), 1.19-1.22 (m, 2H), 1.05-1.08 (m, 2H), 0.69 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 187.8, 183.3, 155.1, 148.8, 139.3, 138.6, 130.4, 130.3, 130.0, 129.8, 129.1, 128.9, 128.1, 127.9, 127.7, 127.3, 29.0, 28.5, 22.9, 13.6. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O$, 365.1900; found 365.1897.



3o

4-(di*p*-tolylmethylene)-2,3-diphenylcyclobut-2-enone 3o

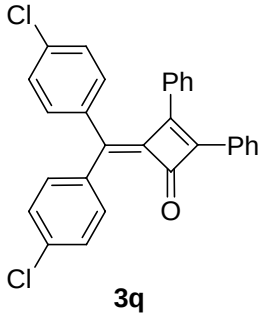
The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (127.9 mg, 62%), mp 162-164 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.76 (m, 2H), 7.02-7.29 (m, 12H), 6.74-6.76 (m, 4H), 2.37 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.0, 176.2, 153.5, 146.5, 137.9, 137.2, 136.0, 135.4, 132.1, 130.7, 130.5, 129.9, 129.4, 129.2, 128.6, 128.4, 127.9, 127.8, 127.4, 127.2, 21.4, 21.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}O$, 413.1900; found 413.1896.



3p

4-(bis(4-methoxyphenyl)methylene)-2,3-diphenylcyclobut-2-enone 3p

The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Red solid (151.1 mg, 68%), mp 171-173 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.76 (m, 2H), 7.21-7.35 (m, 6H), 7.11-7.15 (m, 2H), 7.04 (d, J = 7.6 Hz, 2H), 6.87 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 8.4 Hz, 2H), 3.81 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 188.3, 176.3, 159.6, 159.2, 152.7, 145.4, 132.2, 131.9, 131.9, 131.5, 130.8, 130.0, 129.3, 128.7, 127.9, 127.3, 127.2, 113.2, 112.8, 55.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{25}O_3$, 445.1798; found 445.1813.



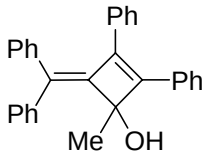
3q

4-(bis(4-chlorophenyl)methylene)-2,3-diphenylcyclobut-2-enone 3q

The mobile phase for flash chromatography: hexane/ethyl acetate = 15:1. Yellow solid (117.9 mg, 52%), mp 190-192 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.76 (m, 2H),

7.29-7.32 (m, 8H), 7.16-7.20 (m, 2H), 7.03 (d, J = 7.2 Hz, 2H), 6.92 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 186.9, 175.5, 155.4, 148.5, 136.6, 136.2, 134.1, 133.7, 131.73, 131.67, 130.0, 129.7, 129.5, 128.8, 128.2, 128.0, 127.8, 127.6, 127.5, 127.0. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{19}Cl_2O$, 453.0807; found 453.0804.

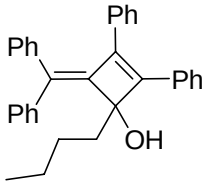
Typical procedure for the synthesis of alkylidenecyclobutenols 4



4a

4-(diphenylmethylene)-1-methyl-2,3-diphenylcyclobut-2-enol 4a

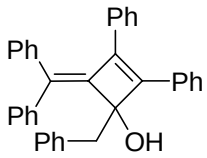
A vial was charged with **3a** (115.4 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. THF (3 mL) was next added to dissolve **3a**. Then MeMgBr (0.45 mmol, 0.45 mL, 1 M in THF) was added and the solution was stirred at rt for 10 min. The resulting mixture was then quenched by saturated aqueous solution of NH_4Cl (20 mL). After extraction with diethyl ether (30 mL), the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1) to afford **4a** (95.8 mg, 80%) as a white solid, mp 140-142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.57 (m, 4H), 7.20-7.32 (m, 6H), 6.94-7.08 (m, 6H), 6.84-6.86 (m, 4H), 2.42 (s, 1H), 1.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 149.9, 144.7, 140.9, 139.6, 133.8, 131.9, 130.4, 129.9, 128.6, 128.5, 128.1, 127.9, 127.8, 127.4, 127.3, 127.1, 126.9, 126.3, 81.5, 23.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{24}NaO$, 423.1719; found 423.1717.



4b

1-butyl-4-(diphenylmethylene)-2,3-diphenylcyclobut-2-enol 4b

The mobile phase for flash chromatography: hexane/ethyl acetate = 9:1. White solid (99.6 mg, 75%), mp 169-171 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43-7.53 (m, 4H), 7.22-7.32 (m, 6H), 6.90-7.15 (m, 6H), 6.85-6.87 (m, 4H), 2.38 (s, 1H), 1.99-2.05 (m, 1H), 1.75-1.82 (m, 1H), 1.23-1.43 (m, 4H), 0.76 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 145.9, 144.9, 141.1, 139.6, 133.7, 132.3, 130.2, 129.6, 128.5, 128.4, 128.0, 127.9, 127.8, 127.3, 127.2, 127.1, 126.9, 126.3, 84.8, 34.6, 27.2, 22.8, 13.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{33}H_{30}NaO$, 465.2189; found 465.2181.

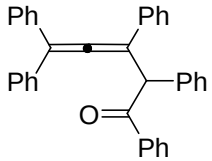


4c

1-benzyl-4-(diphenylmethylene)-2,3-diphenylcyclobut-2-enol 4c

The mobile phase for flash chromatography: hexane/ethyl acetate = 9:1. Colorless oil (109.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52-7.66 (m, 4H), 7.10-7.38 (m, 9H), 6.84-6.96 (m, 6H), 6.71-6.75 (m, 2H), 6.50 (d, J = 7.2 Hz, 2H), 6.42 (d, J = 7.2 Hz, 2H), 3.46 (d, J = 13.2 Hz, 1H), 3.15 (d, J = 13.2 Hz, 1H), 2.83 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 147.1, 144.5, 141.1, 139.4, 137.2, 133.8, 132.6, 130.5, 130.3, 129.9, 128.6, 128.5, 128.4, 128.2, 127.6, 127.5, 127.33, 127.29, 127.0, 126.89, 126.87, 126.4, 126.2, 85.0, 47.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}NaO$, 499.2032; found 499.2028.

Typical procedure for the synthesis of 4,5-dien-2-ones 5

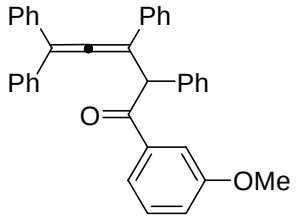


5a

1,2,3,5,5-pentaphenylpenta-3,4-dien-1-one 5a

A vial was charged with **3a** (115.4 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. THF (3 mL) was next added to dissolve **3a**. Then PhMgBr (0.45 mmol, 0.45 mL, 1 M in THF) was added and the solution was stirred at rt for 10

min. The resulting mixture was then quenched by saturated aqueous solution of NH_4Cl (20 mL). After extraction with diethyl ether (30 mL), the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1) to afford **5a** (108.1 mg, 78%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (d, J = 7.6 Hz, 2H), 7.40-7.45 (m, 3H), 7.15-7.33 (m, 18H), 7.03-7.05 (m, 2H), 6.00 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 196.5, 137.1, 136.4, 136.1, 135.5, 135.3, 132.9, 129.6, 128.8, 128.7, 128.6, 128.3, 128.2, 127.9, 127.53, 127.46, 127.37, 127.27, 126.2, 115.3, 109.2, 55.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{27}O$, 463.2056; found 463.2047.

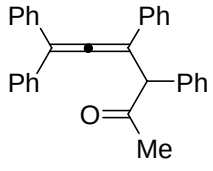


5b

1-(3-methoxyphenyl)-2,3,5,5-tetraphenylpenta-3,4-dien-1-one 5b

The mobile phase for flash chromatography: hexane/ethyl acetate = 9:1. Colorless oil (103.3 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, J = 7.6 Hz, 1H), 7.34-7.36 (m, 3H), 7.07-7.24 (m, 17H), 6.93-6.96 (m, 2H), 6.83-6.86 (m, 1H), 5.92 (s, 1H), 3.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.5, 196.4, 159.8, 137.7, 137.2, 136.1, 135.5, 135.3, 129.6, 128.9, 128.8, 128.7, 128.4, 128.3, 127.9, 127.64, 127.56, 127.47, 127.38, 126.2, 121.3, 119.6, 115.4, 113.1, 109.3, 55.9, 55.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{36}H_{28}NaO_2$, 515.1982; found 515.1987.

Procedure for the synthesis of 3,4,6,6-tetraphenylhexa-4,5-dien-2-one 5c

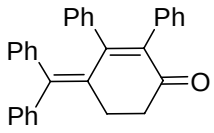


5c

A vial was charged with **4a** (120.1 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. Toluene (3 mL) was next added to dissolve **4a**. Then LDA

(0.9 mmol, 0.45 mL, 2 M in THF) was added and the solution was stirred at rt for 20 min. The resulting mixture was then quenched by saturated aqueous solution of NH_4Cl (20 mL). After extraction with diethyl ether (30 mL), the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1) to afford **5c** (102.1 mg, 85%) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.42 (m, 18H), 7.04-7.07 (m, 2H), 5.12 (s, 1H), 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.1, 205.4, 136.7, 136.0, 135.8, 135.3, 129.3, 128.8, 128.7, 128.6, 128.56, 128.54, 128.4, 128.1, 127.7, 127.6, 127.4, 126.2, 115.1, 108.1, 61.3, 29.4. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{24}NaO$, 423.1719; found 423.1742.

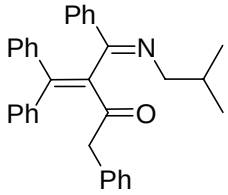
Procedure for the synthesis of 4-(diphenylmethylene)-2,3-diphenylcyclohex-2-enone 6



6

A vial was charged with **3a** (115.4 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. THF (3 mL) was next added to dissolve **3a**. Then C_2H_3MgCl (0.45 mmol, 0.45 mL, 1 M in THF) was added and the solution was stirred at rt for 10 min. The resulting mixture was then quenched by saturated aqueous solution of NH_4Cl (20 mL). After extraction with diethyl ether (30 mL), the organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1) to afford **6** (69.3 mg, 56%) as a colorless solid, mp 176-178 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07-7.33 (m, 8H), 6.84-6.95 (m, 5H), 6.64-6.75 (m, 7H), 3.11 (t, J = 6.4 Hz, 2H), 2.73 (t, J = 6.4 Hz, 2H),; ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.6, 157.2, 147.5, 142.7, 142.5, 139.8, 137.9, 137.1, 135.1, 130.9, 130.7, 130.2, 128.2, 127.8, 127.4, 127.3, 127.0, 126.7, 126.6, 126.5, 39.7, 34.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{24}NaO$, 435.1719; found 435.1752.

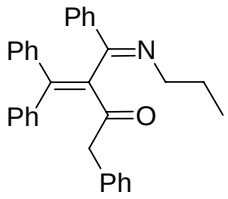
Typical procedure for the synthesis of imines 7



7a

(*Z*)-3-((isobutylimino)(phenyl)methyl)-1,4,4-triphenylbut-3-en-2-one 7a

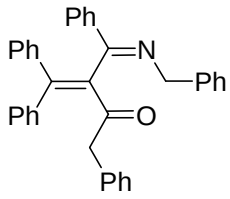
A vial was charged with **3a** (115.4 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. 1,4-Dioxane (3 mL) was next added to dissolve **3a**. Then *i*-$BuNH_2$ (32.8 mg, 0.45 mmol) was added and the solution was stirred at 80 ^oC for 24 h. The resulting mixture was then concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/ethyl acetate = 9:1) to afford **7a** (101.6 mg, 74%) as a colorless solid, mp 135-137 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.6 Hz, 2H), 7.08-7.44 (m, 16H), 6.76-6.78 (m, 2H), 3.05 (s, 2H), 3.31 (dd, J_1 = 6.8 Hz, J_2 = 13.6 Hz, 1H), 2.89 (dd, J_1 = 6.8 Hz, J_2 = 13.6 Hz, 1H), 1.85-1.89 (m, 1H), 0.92 (d, J = 6.8 Hz, 3H), 0.88 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.5, 163.4, 150.9, 140.5, 140.2, 139.5, 137.6, 133.9, 130.3, 129.8, 129.4, 129.3, 129.1, 128.9, 128.4, 128.16, 128.15, 128.0, 126.8, 61.6, 49.0, 29.9, 21.0, 20.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{33}H_{32}NO$, 458.2478; found 458.2471.



7b

(*Z*)-1,4,4-triphenyl-3-(phenyl(propylimino)methyl)but-3-en-2-one 7b

The mobile phase for flash chromatography: hexane/ethyl acetate = 9:1. Colorless oil (110.4 mg, 83%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.81-7.83 (m, 2H), 7.08-7.40 (m, 16H), 6.78-6.79 (m, 2H), 3.47-3.51 (m, 3H), 3.09-3.12 (m, 1H), 1.46-1.62 (m, 2H), 0.90 (t, J = 8.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 163.4, 150.8, 140.5, 140.2, 139.3, 137.5, 133.8, 130.2, 129.85, 129.79, 129.4, 129.2, 129.1, 128.9, 128.4, 128.1, 128.0, 126.8, 55.9, 49.0, 23.9, 12.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{32}H_{30}NO$, 444.2322; found 444.2358.

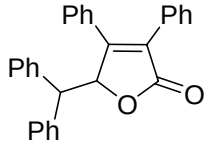


7c

(*Z*)-3-((benzylimino)(phenyl)methyl)-1,4,4-triphenylbut-3-en-2-one 7c

The mobile phase for flash chromatography: hexane/ethyl acetate = 9:1. Colorless oil (100.3 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 6.4 Hz, 2H), 7.12-7.45 (m, 21H), 6.76-6.77 (m, 2H), 4.78 (d, J =16.0 Hz, 1H), 4.25 (d, J =16.0 Hz, 1H), 3.47-3.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 164.3, 151.5, 140.4, 140.1, 140.0, 139.1, 137.1, 133.7, 130.3, 130.2, 129.8, 129.6, 129.3, 129.0, 128.4, 128.32, 128.28, 128.27, 128.21, 128.0, 126.9, 126.6, 57.6, 49.1. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{36}H_{30}NO$, 492.2322; found 492.2336.

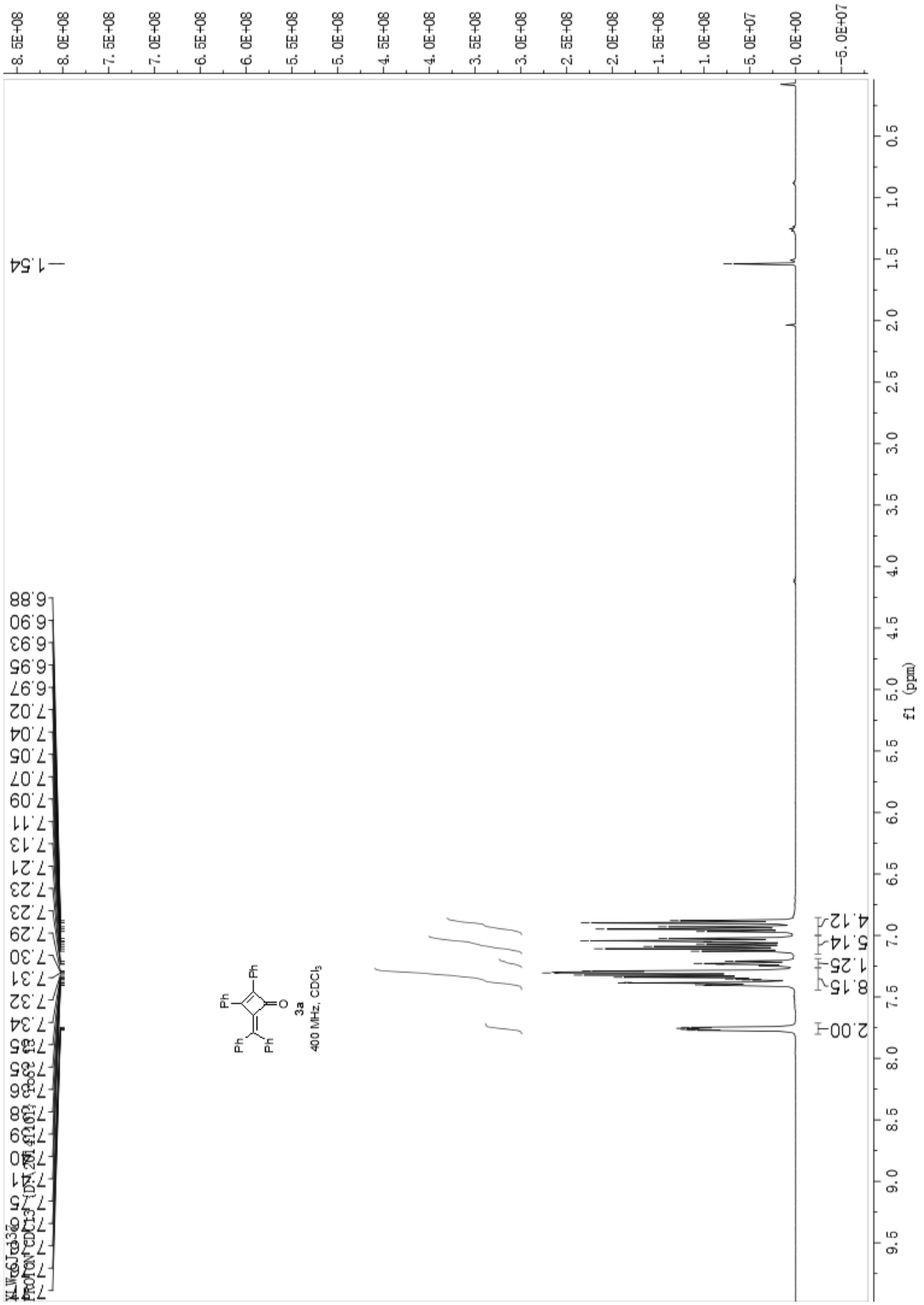
Procedure for the synthesis of 5-benzhydryl-3,4-diphenylfuran-2(5*H*)-one 8

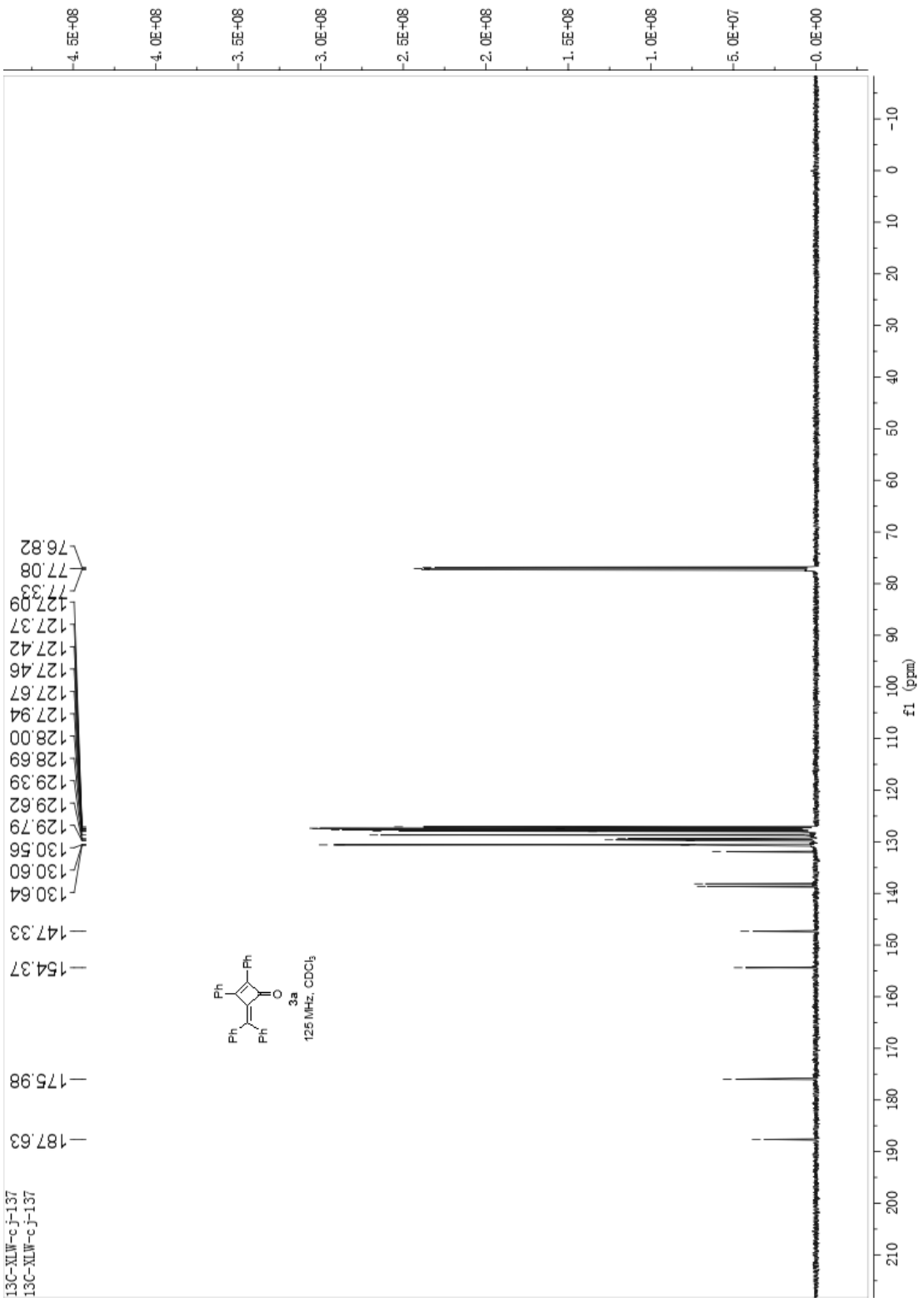


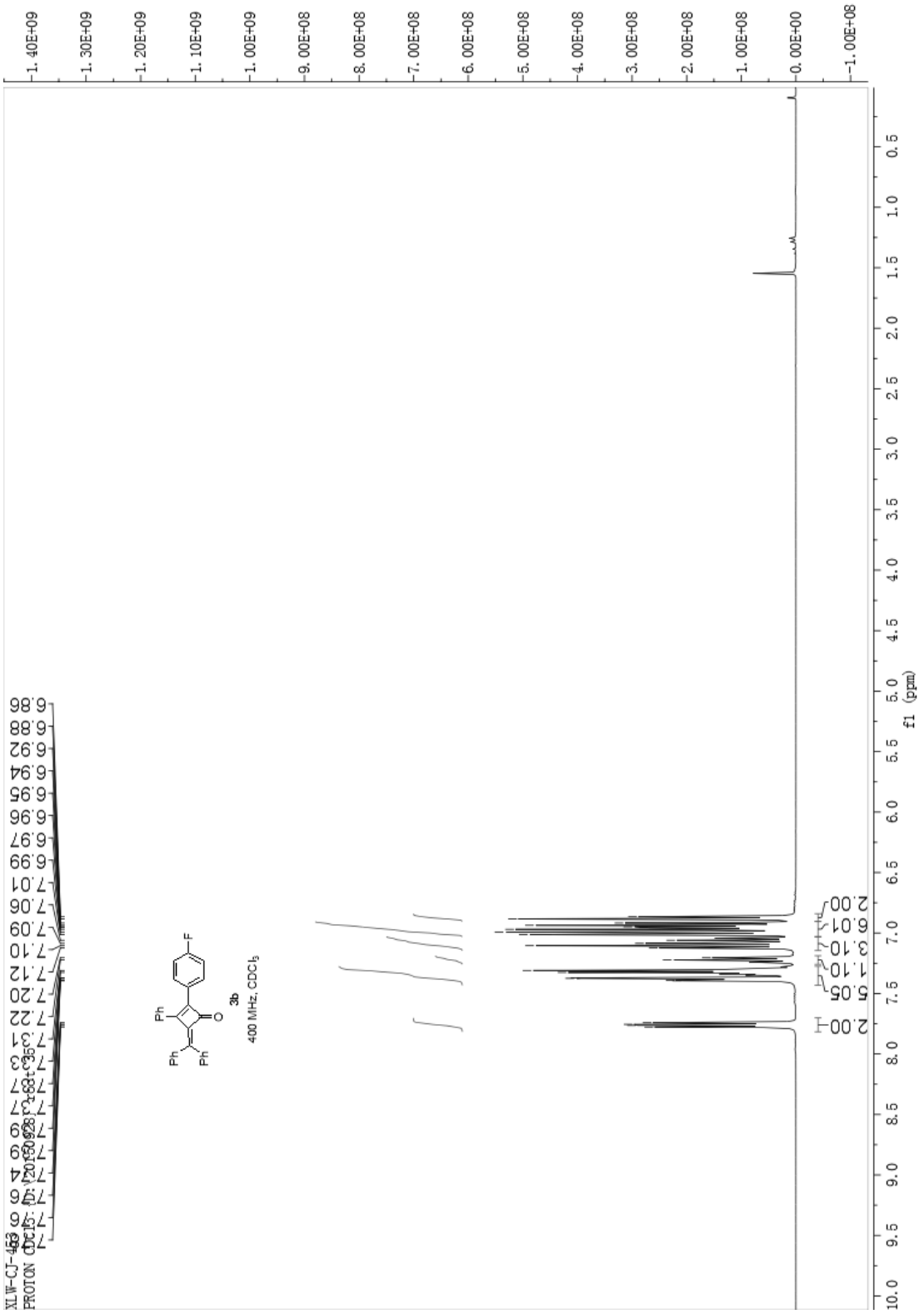
8

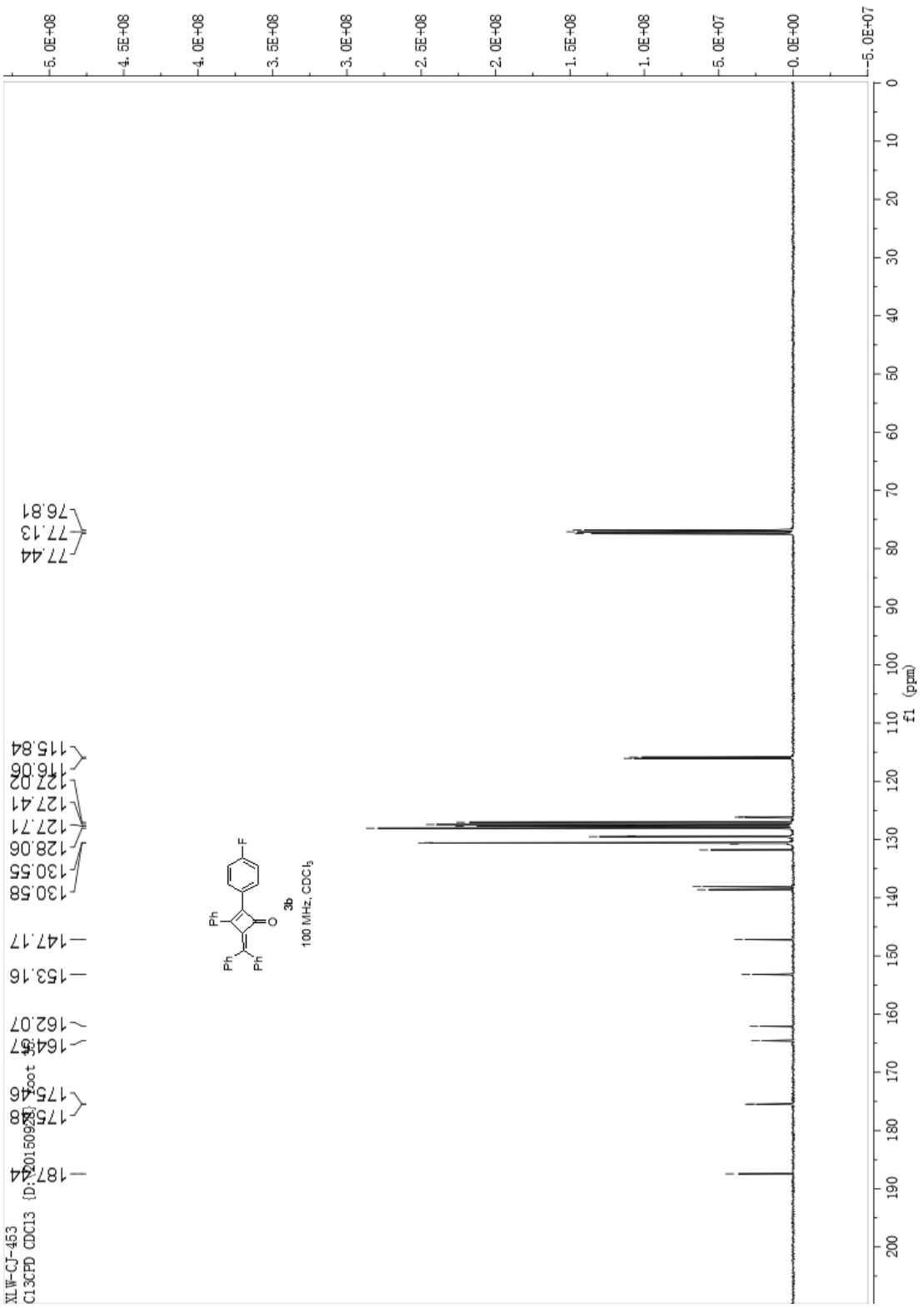
A solution of **3a** (115.4 mg, 0.3 mmol) and 1,4-diaza-bicyclo[2.2.2]octane (33.7 mg, 0.3 mmol) in wet THF (5 mL) was irradiated using high pressure Hg lamp at rt for 3 d. The residue after removal of solvent was subjected to column chromatography on silica gel (hexane–EtOAc = 9:1) to give **8** (61.6 mg, 51%) as a colorless solid, mp 206-208 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, J = 7.6 Hz, 2H), 7.09-7.36 (m, 14H), 6.82-6.91 (m, 4H), 6.11 (s, 1H), 4.21 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 158.8, 141.3, 136.6, 131.1, 130.4, 129.94, 129.88, 129.1, 129.0, 128.7, 128.63, 128.58, 128.52, 128.0, 127.4, 127.0, 82.3, 52.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{22}NaO_2$, 425.1512; found 425.1519.

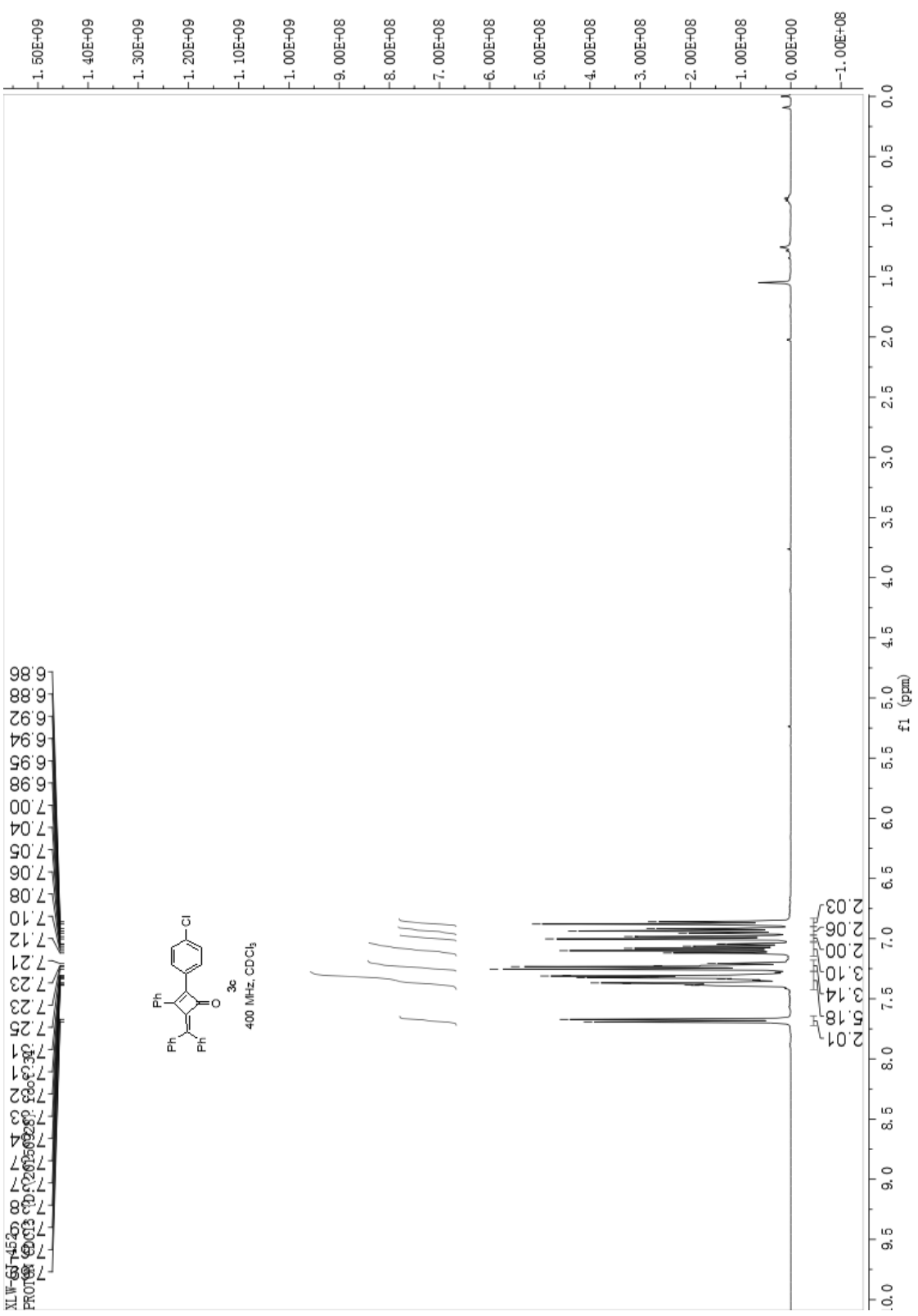
NMR spectra of new compounds

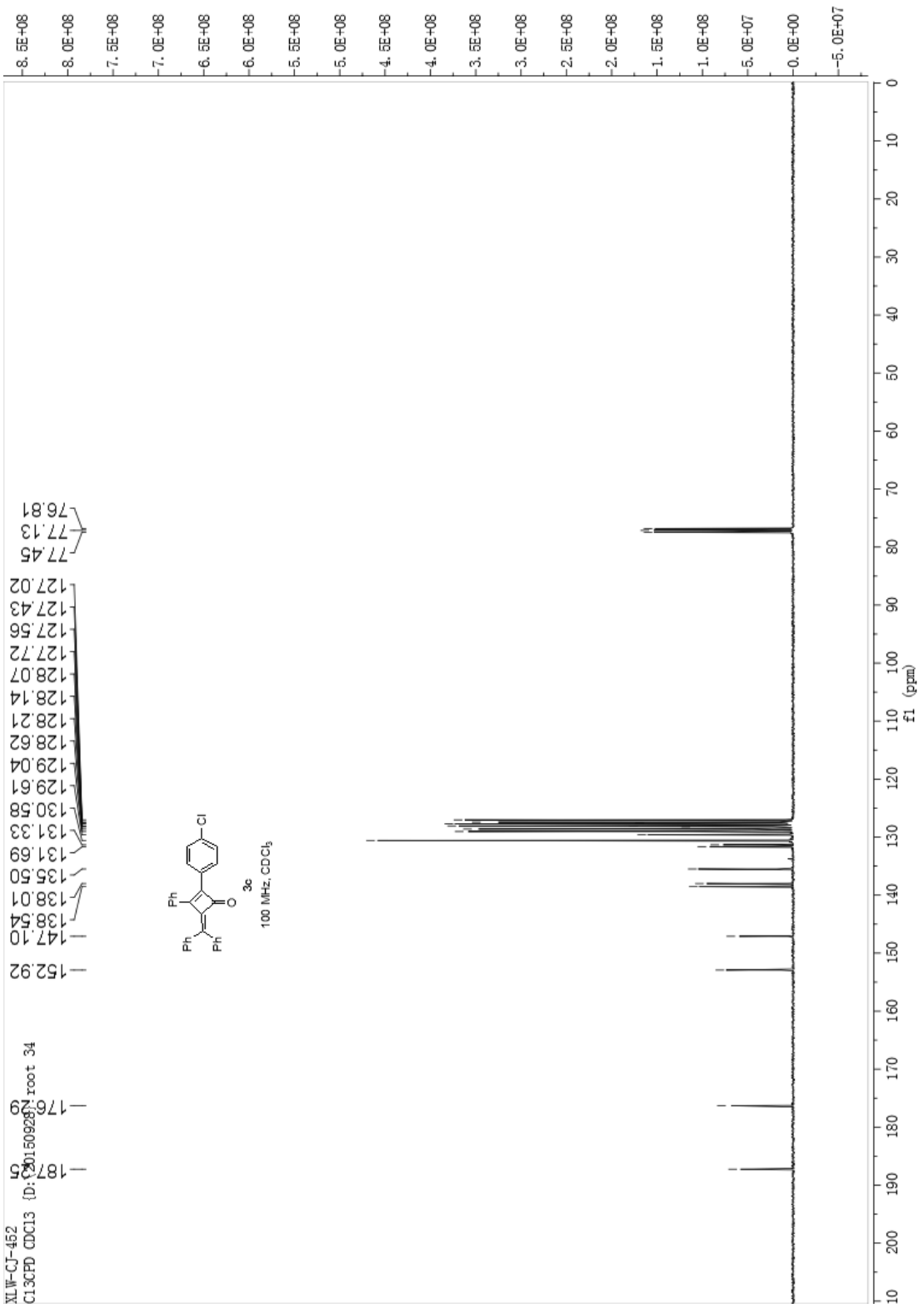


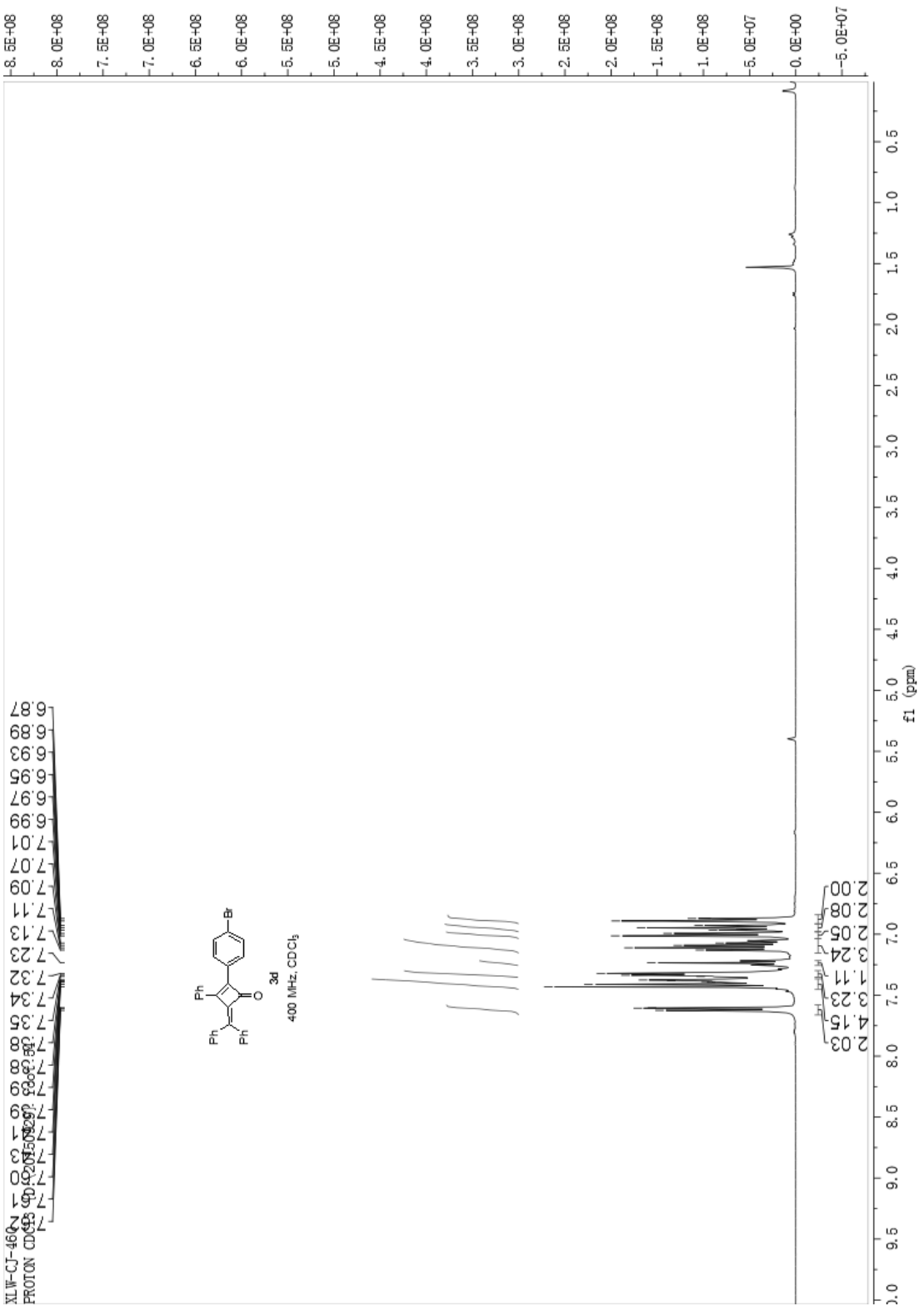

13C-XLW-cj-137
13C-XLW-cj-137
187.63
175.98
154.37
147.33
130.64
130.60
130.56
129.79
129.62
129.39
128.69
128.00
127.94
127.67
127.46
127.42
127.37
127.09
77.33
77.08
76.82
Ph
Ph
Ph
Ph
O
3a
125 MHz, CDCl3
f1 (ppm)

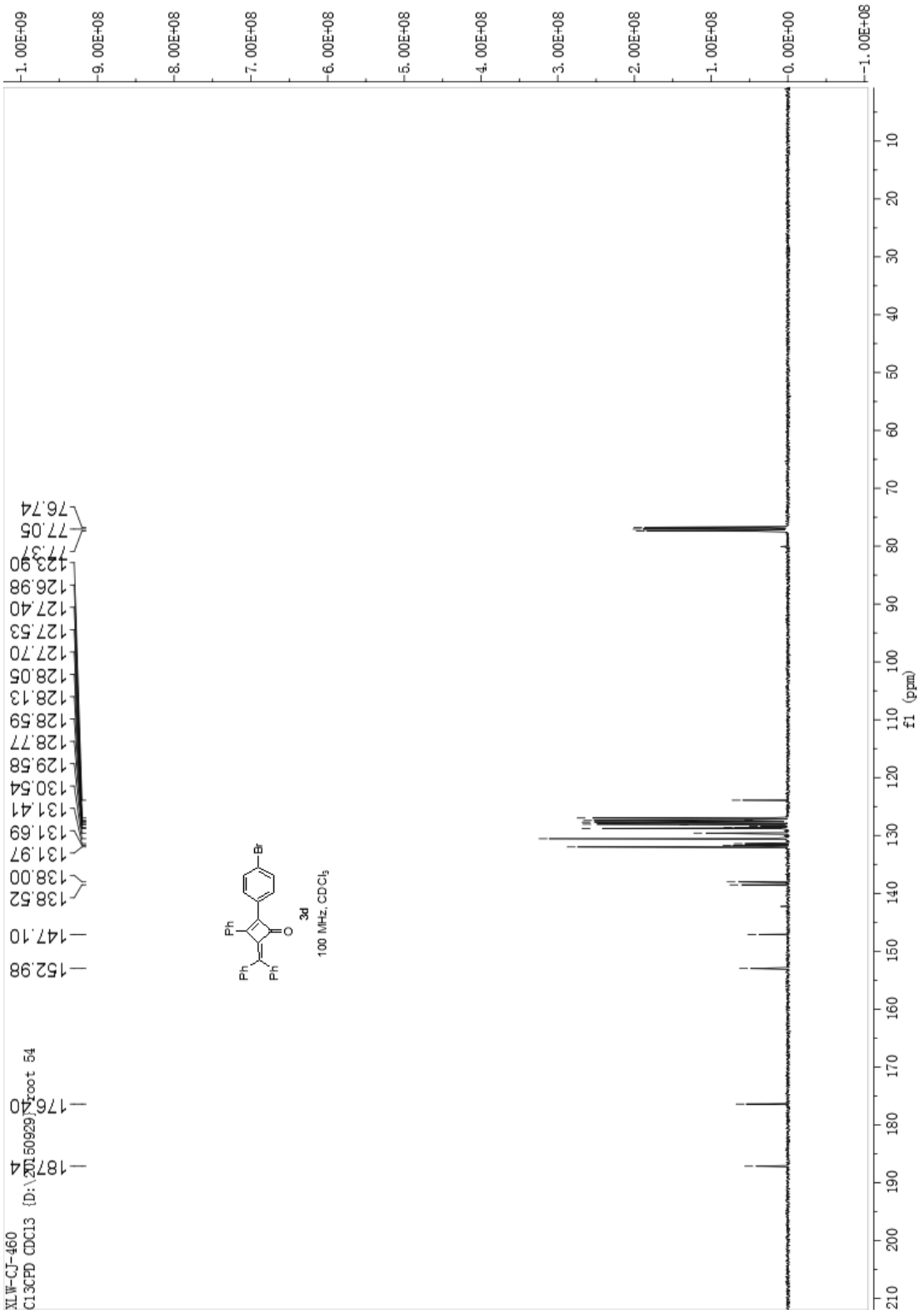

XLW-CJ-463
PROTON CDCl3
3b
400 MHz, CDCl3
f1 (ppm)

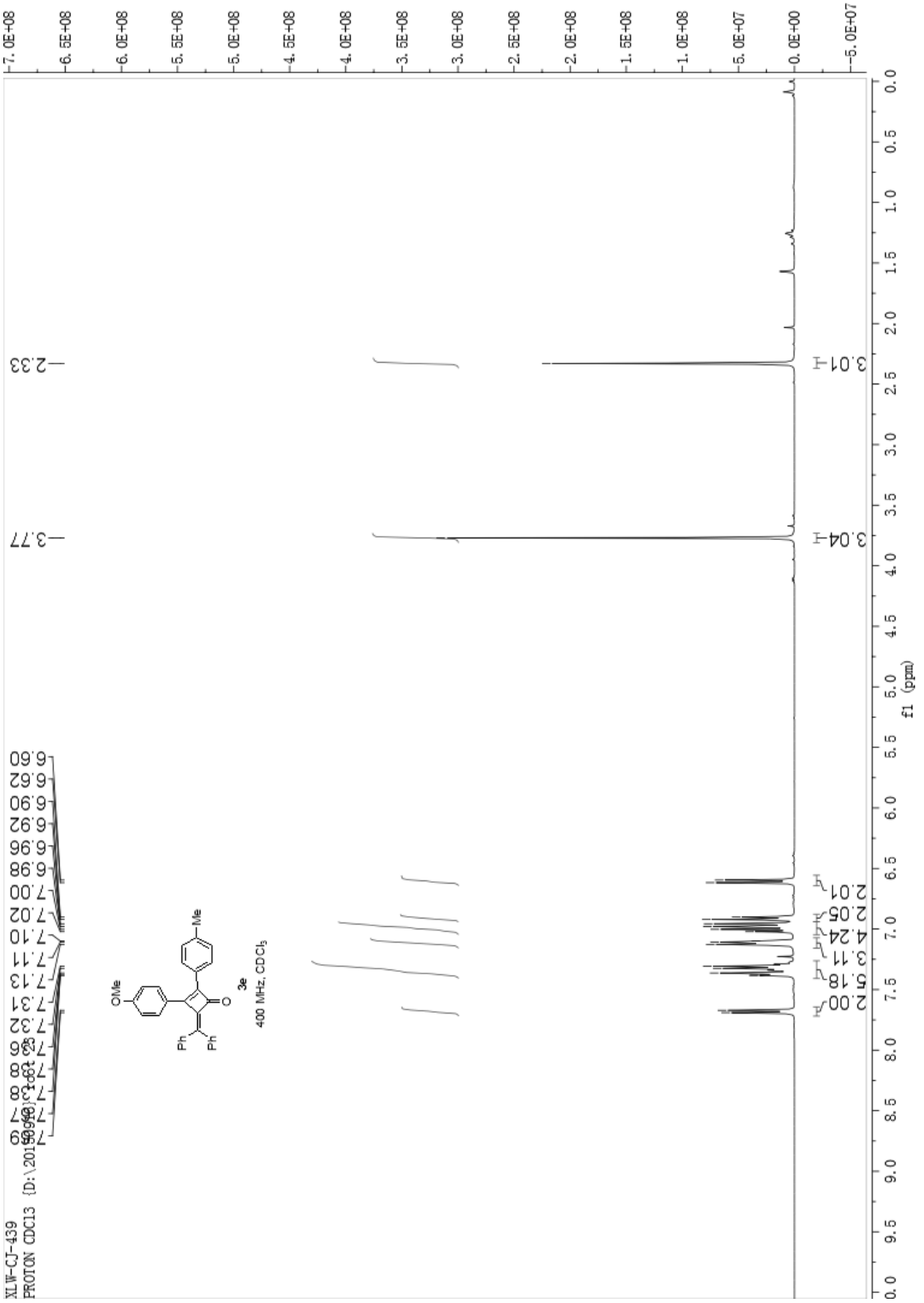

XLW-CJ-453
C13CPD CDCl3 {D:\Data\20150928} root
3b
100 MHz, CDCl3
f1 (ppm)
187.24
175.46
175.28
164.57
162.07
153.16
147.17
130.58
130.55
128.06
127.71
127.41
127.02
116.06
115.84
77.44
77.13
76.81

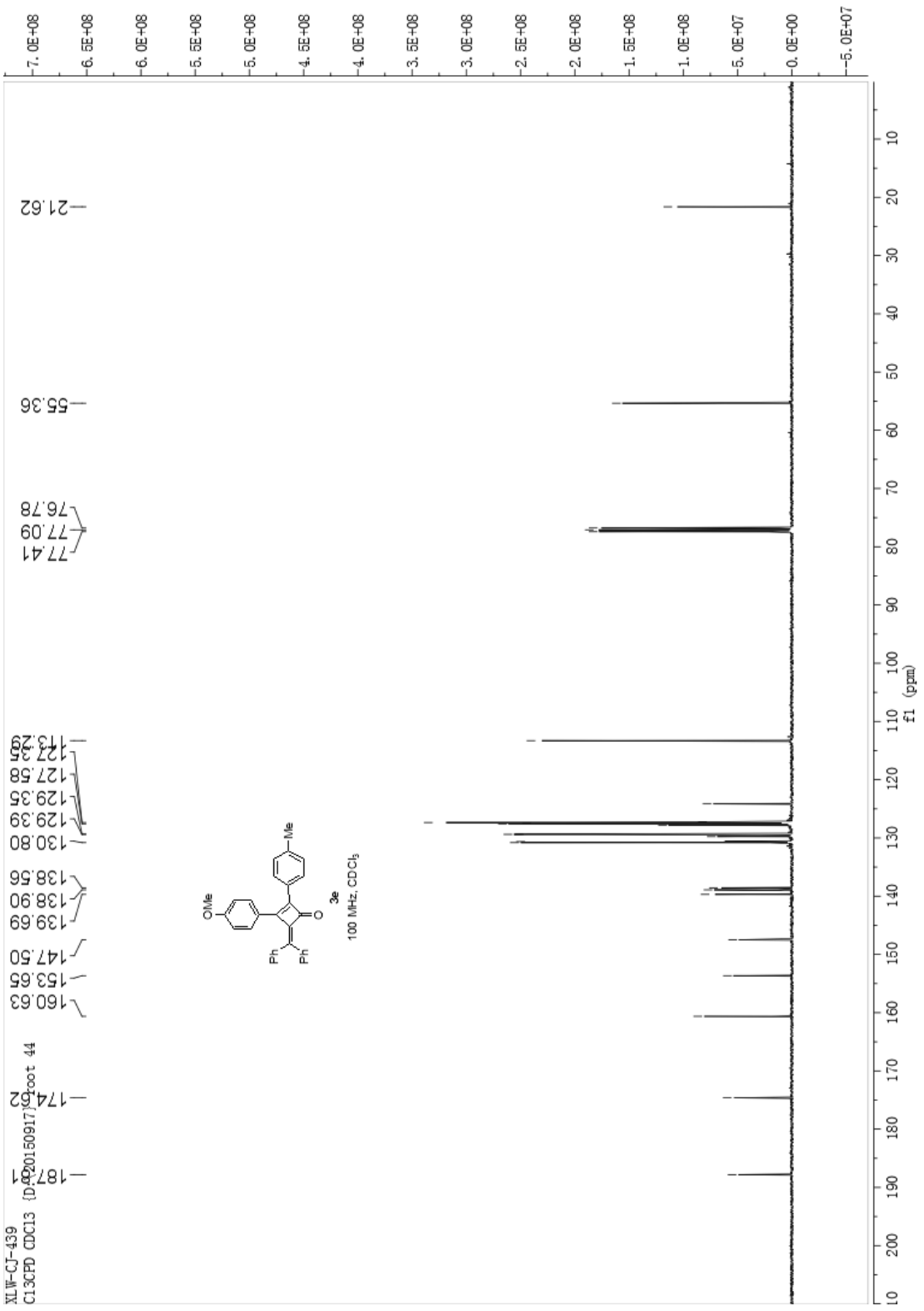

3c
400 MHz, CDCl3
f1 (ppm)

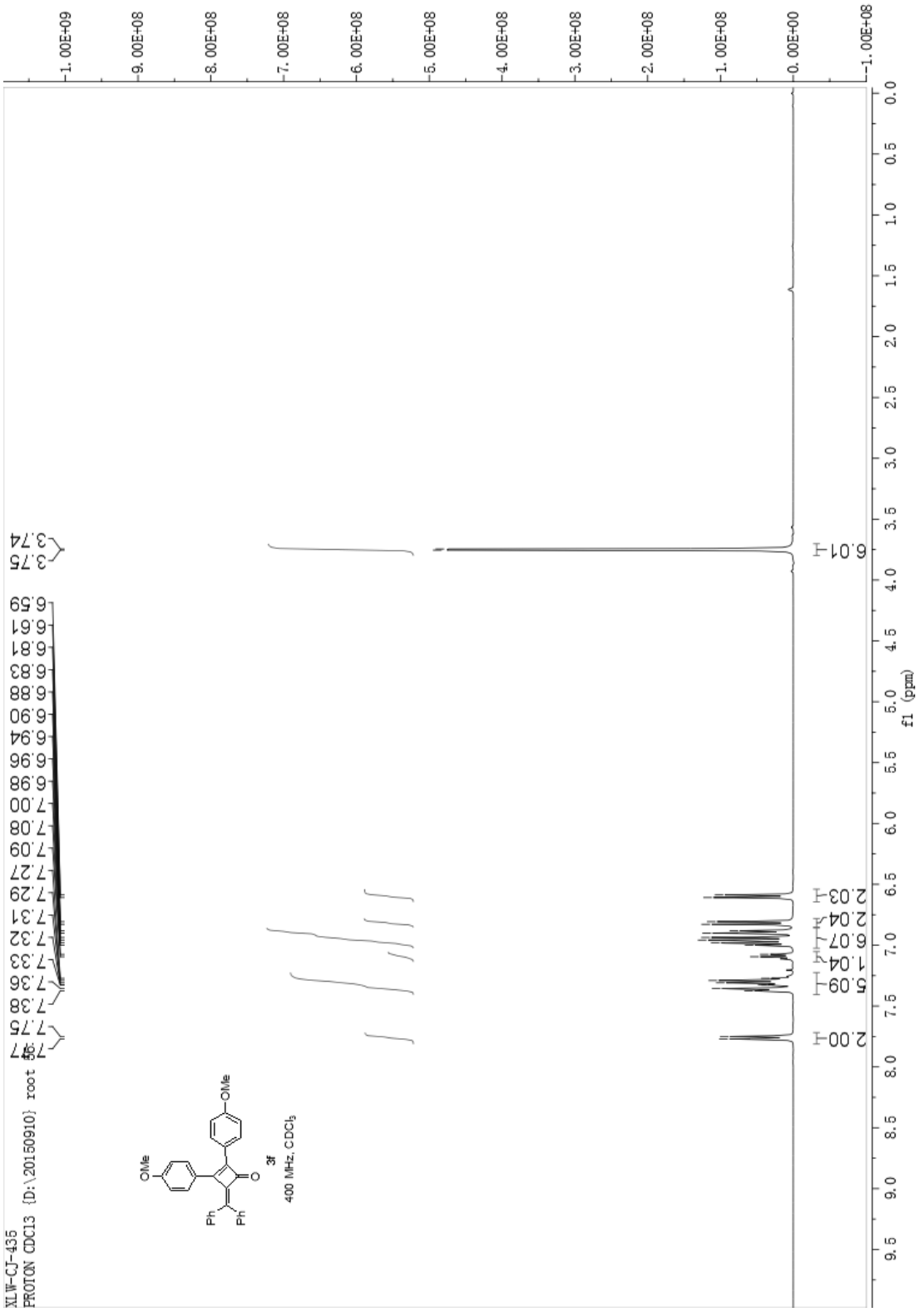

XLW-CJ-452
C13CPD CDCl3 {D:\20150928\root 34
3c
100 MHz, CDCl3
f1 (ppm)

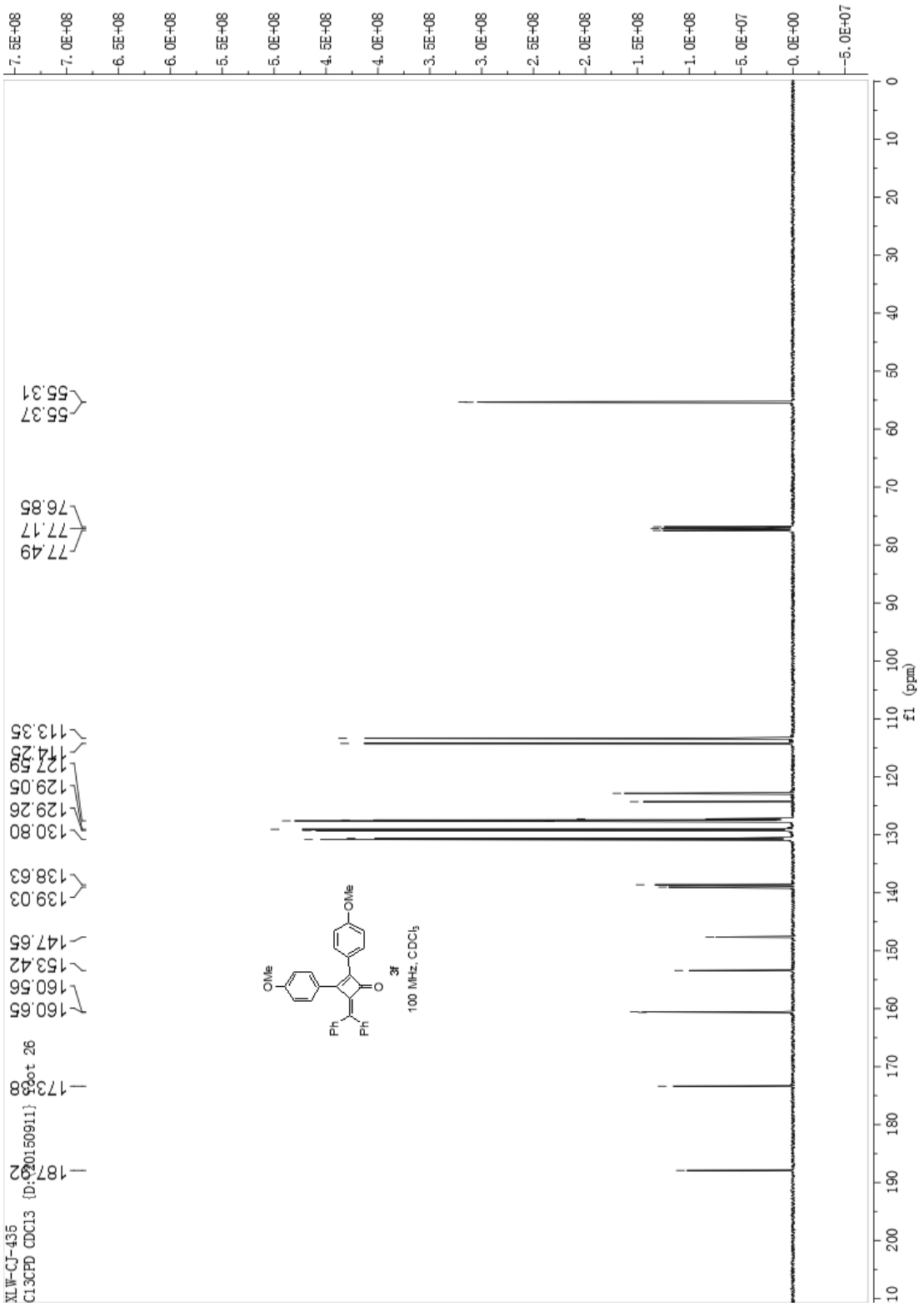

Br
Ph
Ph
Ph
O
3d
400 MHz, CDCl3
f1 (ppm)

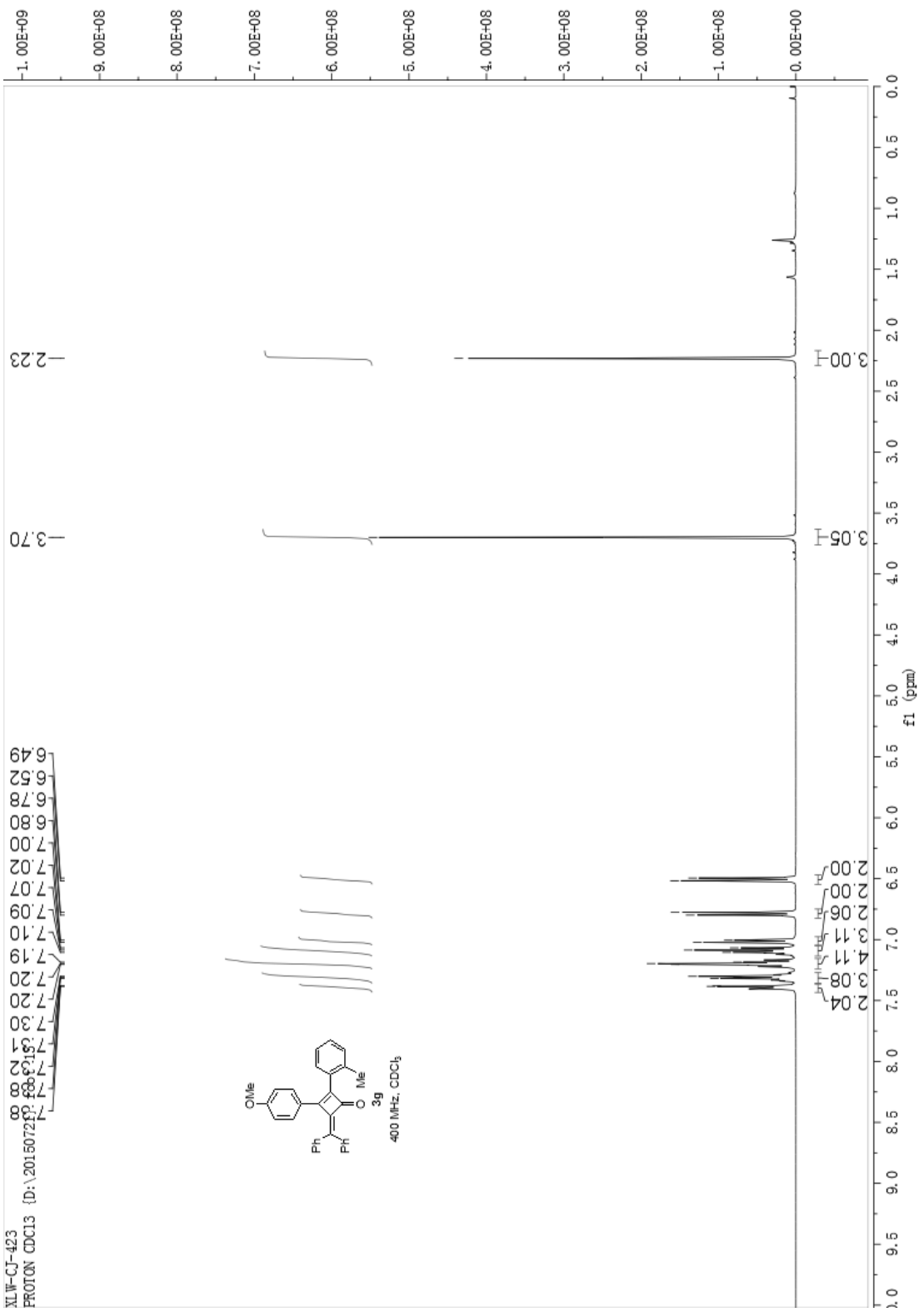

XLW-CJ-460
C13CPD CDCl3 {D:\2015\150929} root 54
f1 (ppm)
3d
100 MHz, CDCl3

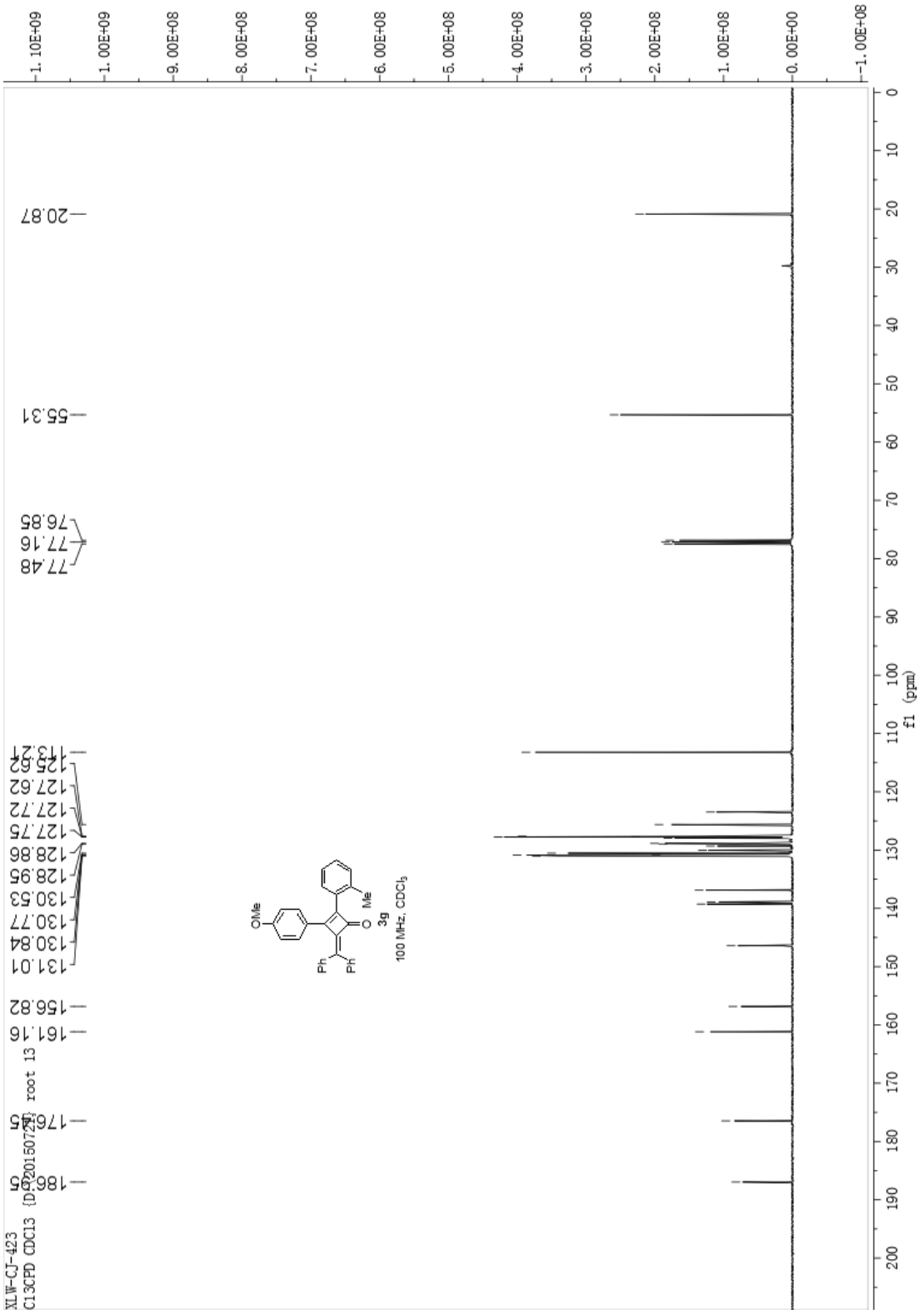

XLW-CJ-439
PROTON CDCl3 {D:\2019\
OMe
Me
Ph
Ph
O
3e
400 MHz, CDCl3
f1 (ppm)

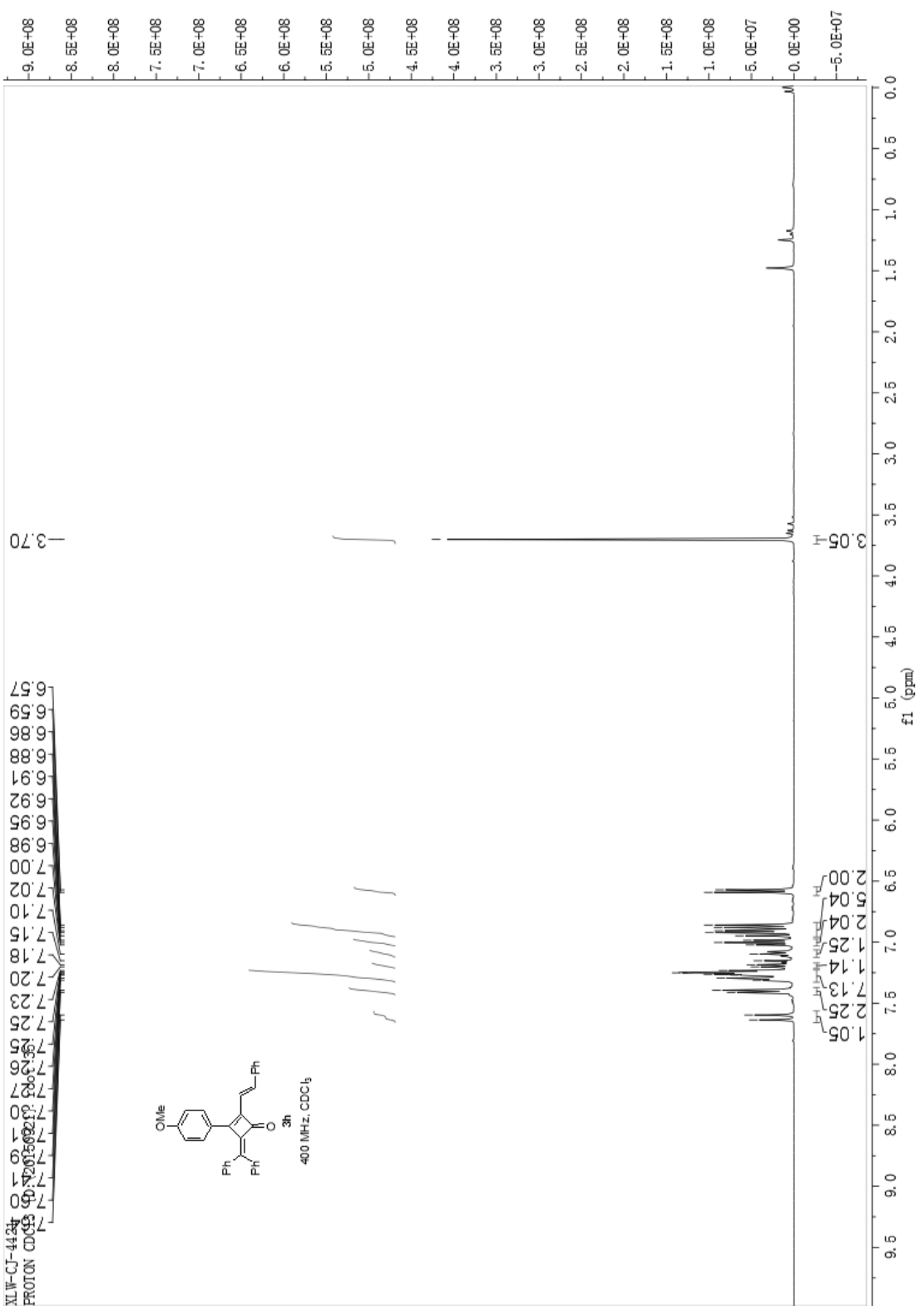

XLW-CJ-439
C13CPD CDCl3 {D:\20150917} root 44
21.62
55.36
76.78
77.09
77.41
113.29
127.35
127.58
129.35
129.39
130.80
138.56
138.90
139.69
147.50
153.65
160.63
174.52
187.91
OMe
Me
Ph
Ph
O
3e
100 MHz, CDCl3
f1 (ppm)

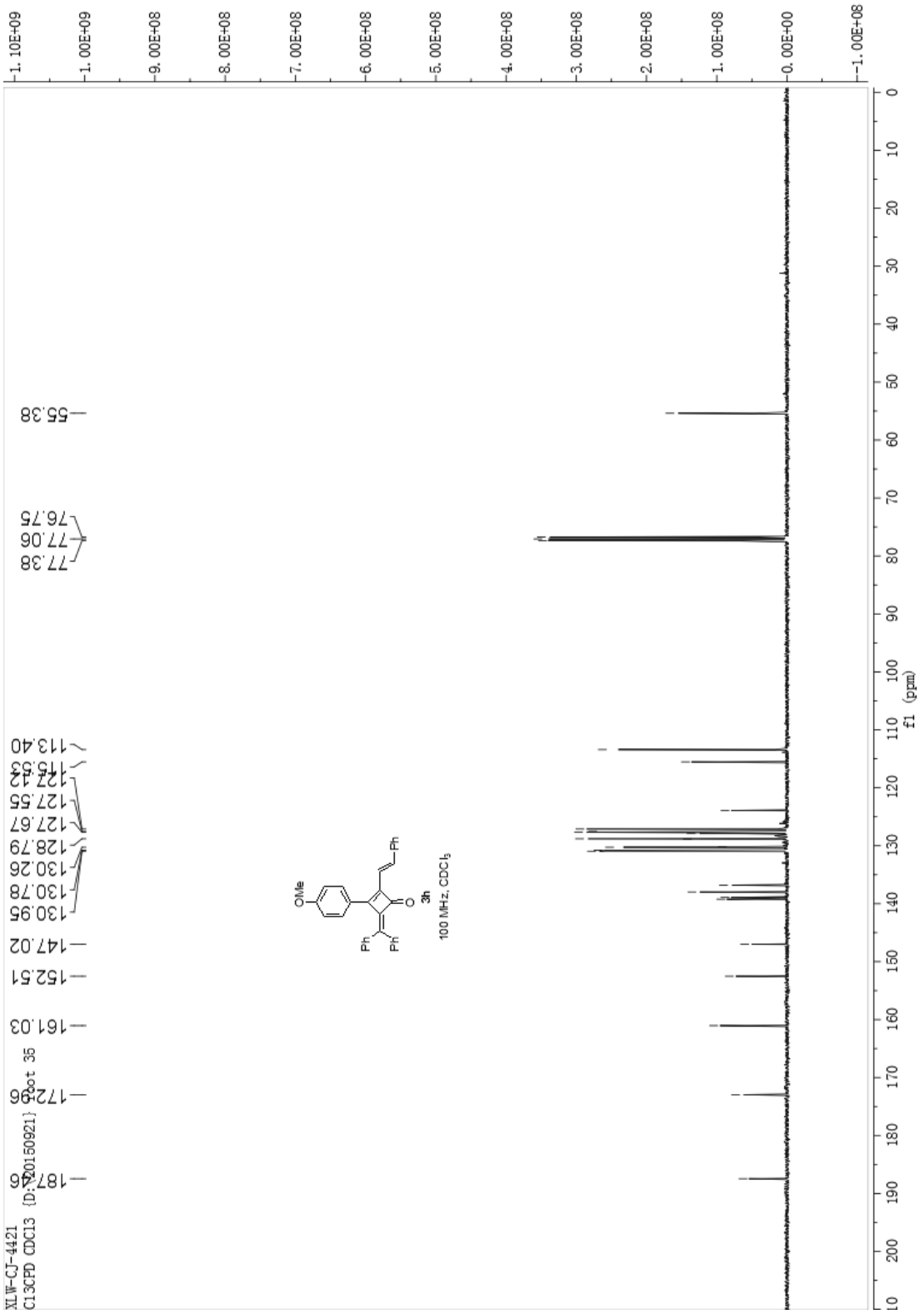

XLW-CJ-435
PROTON CDCl3 {D:\20150910} root
3f
400 MHz, CDCl3
OMe
OMe
Ph
Ph
O
f1 (ppm)

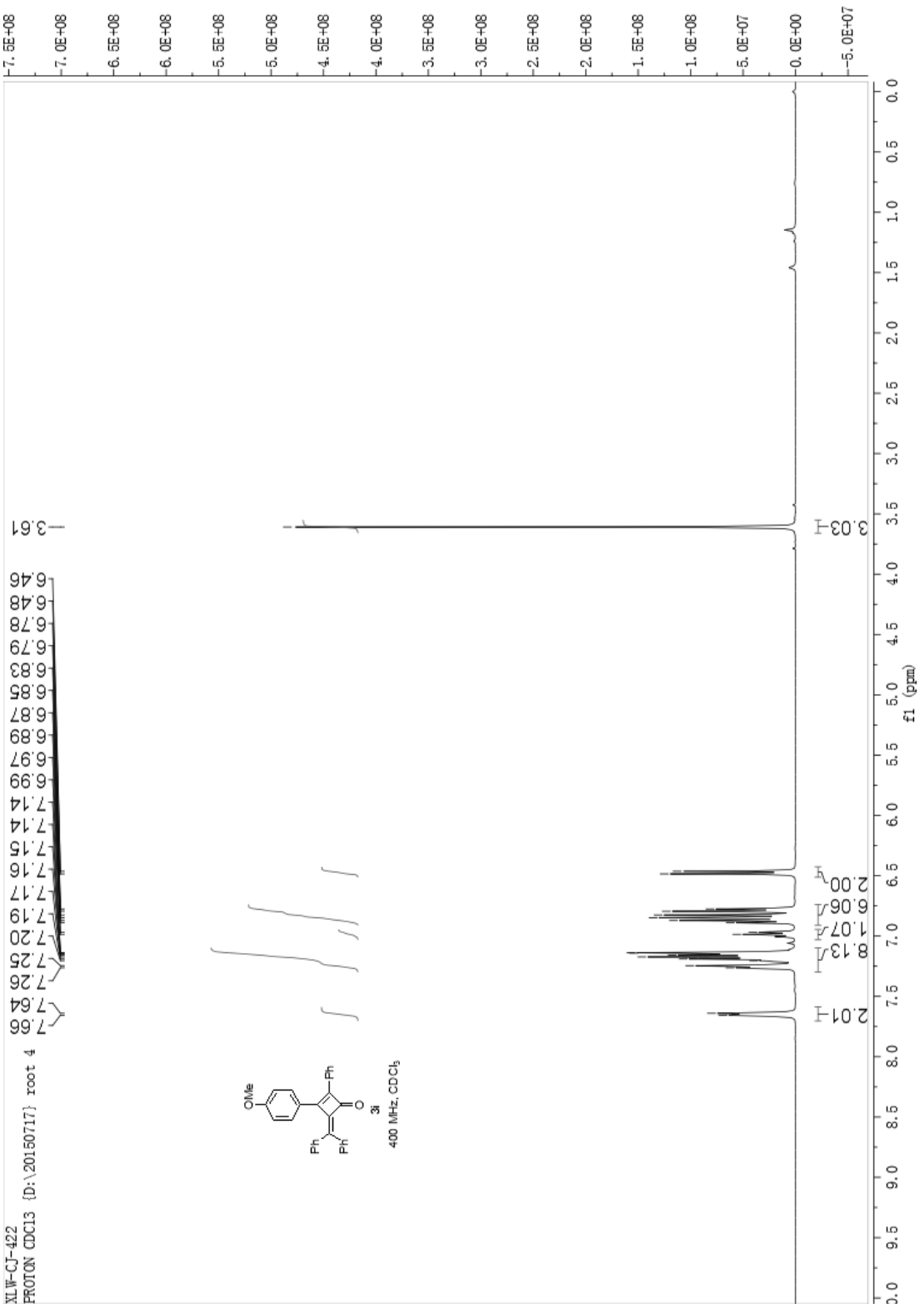

XLW-CJ-435
C13CPD CDCl3 {D:\20150911} root 26
187.92
173.88
160.65
160.56
153.42
147.65
139.03
138.63
130.80
129.26
129.05
127.59
114.25
113.35
77.49
77.17
76.85
55.37
55.31
OMe
OMe
Ph
Ph
O
3f
100 MHz, CDCl3
f1 (ppm)

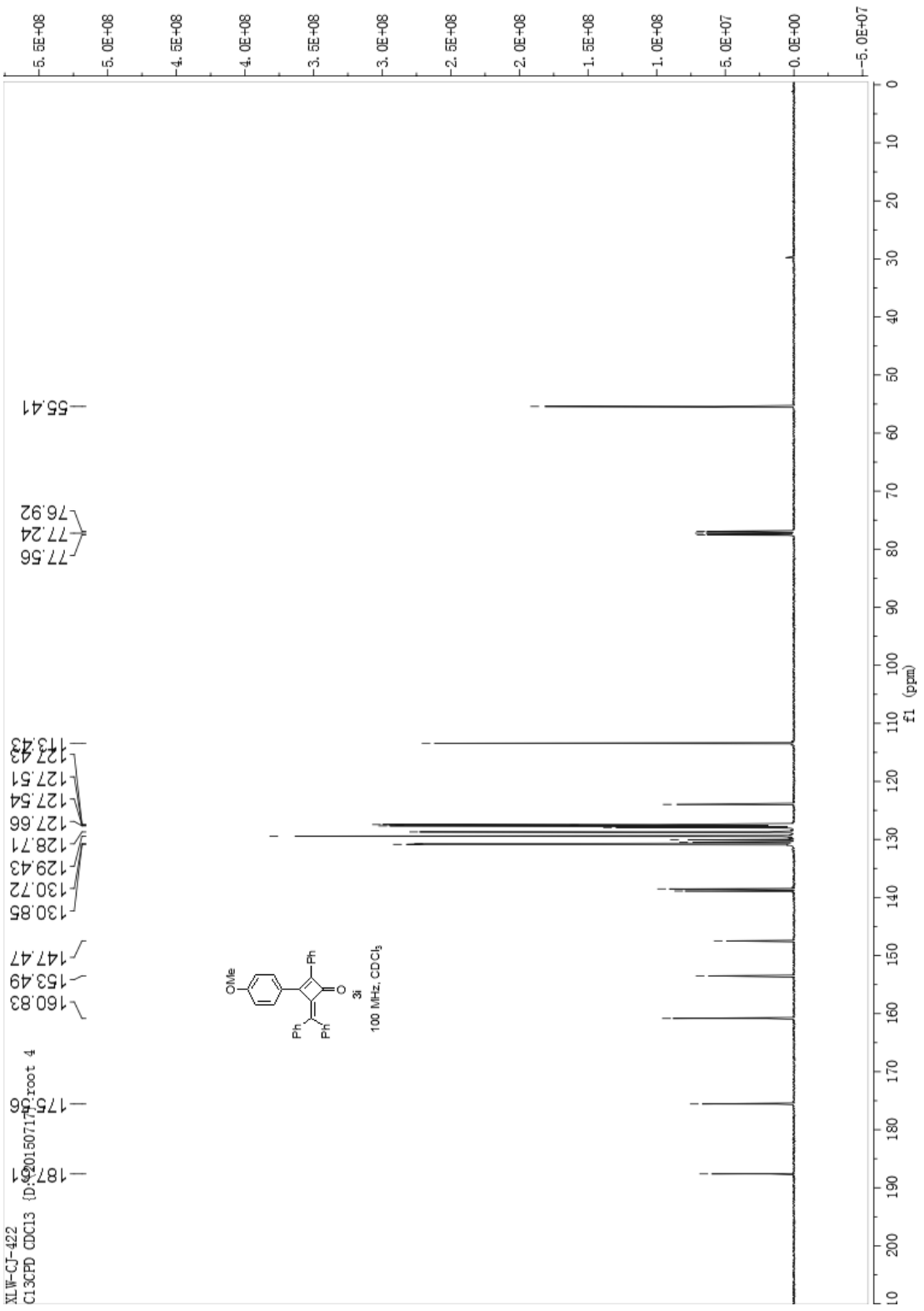

XLW-CJ-423
PROTON CDC13 {D:\20150725}
OMe
Me
O
Ph
Ph
3g
400 MHz, CDCl3
f1 (ppm)

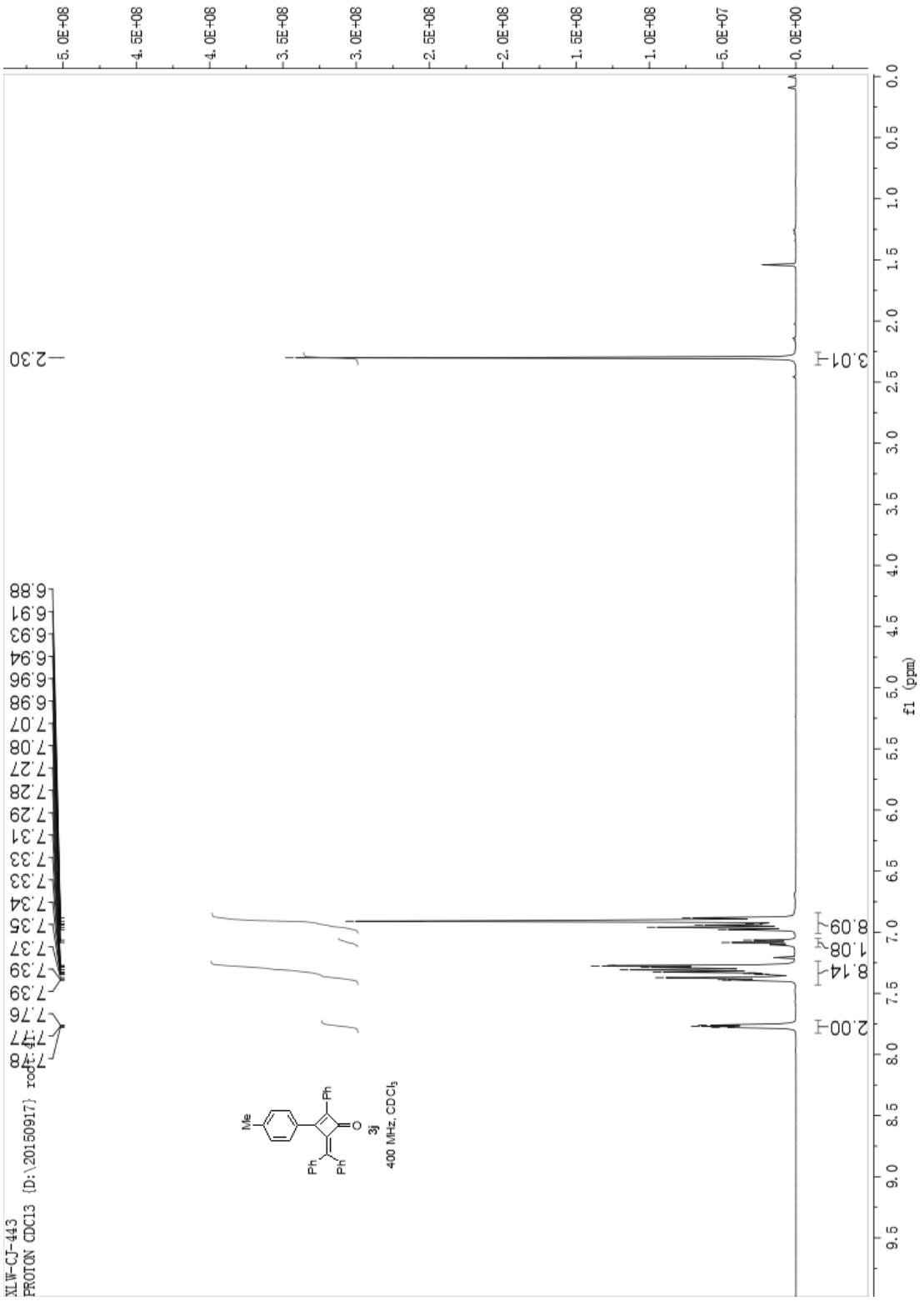

XLW-CJ-423
C13CPD CDC13 (DG20150724) root 13
186.95
176.45
161.16
156.82
131.01
130.84
130.77
130.53
128.95
128.86
127.75
127.72
127.62
125.62
113.27
77.48
77.16
76.85
55.31
20.87
OMe
Me
O
Ph
Ph
3g
100 MHz, CDCl3
f1 (ppm)

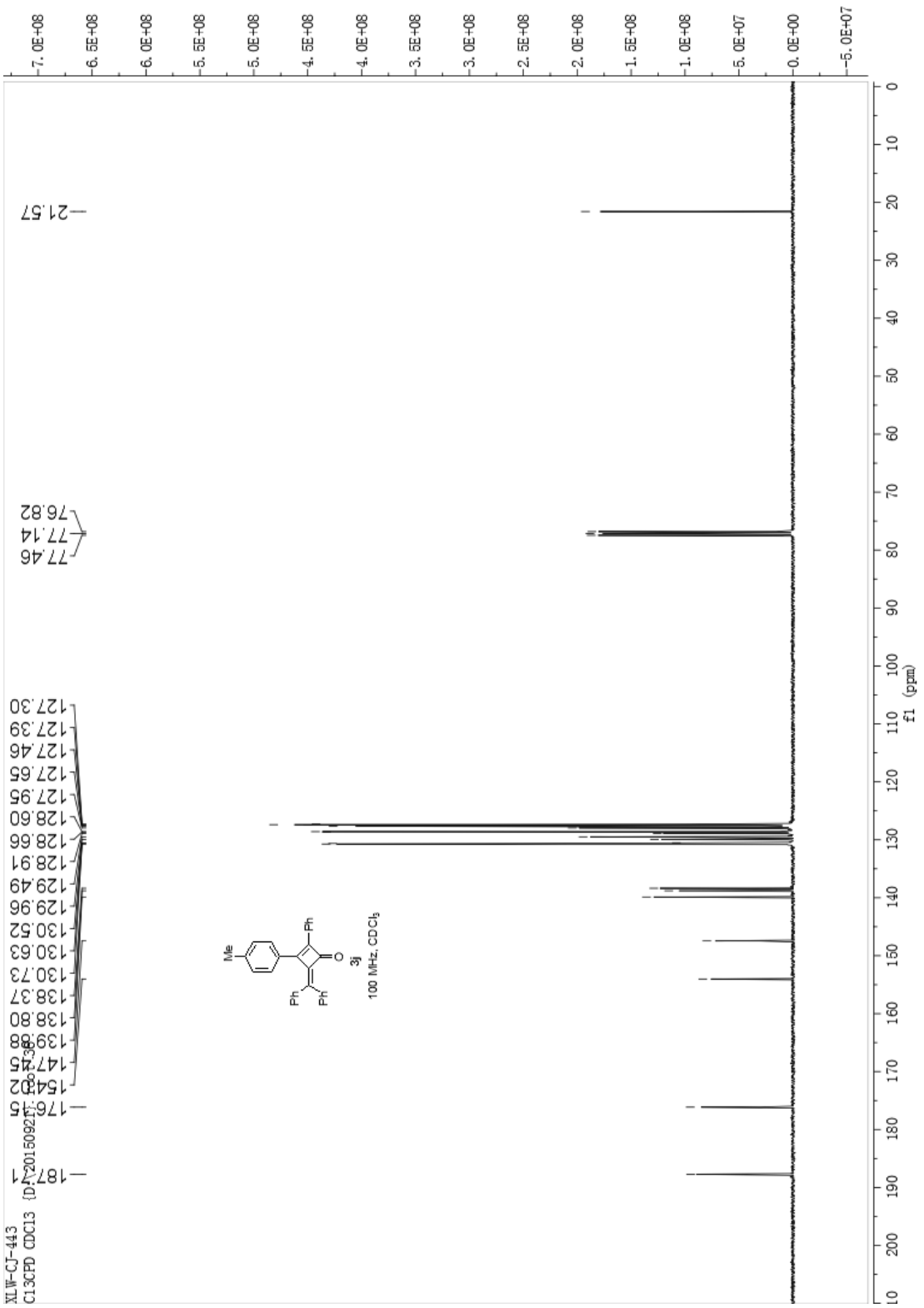

OMe
Ph
Ph
Ph
O
3h
400 MHz, CDCl3
3.70
3.05
1.05
2.25
7.13
1.14
1.25
2.04
5.04
2.00
f1 (ppm)

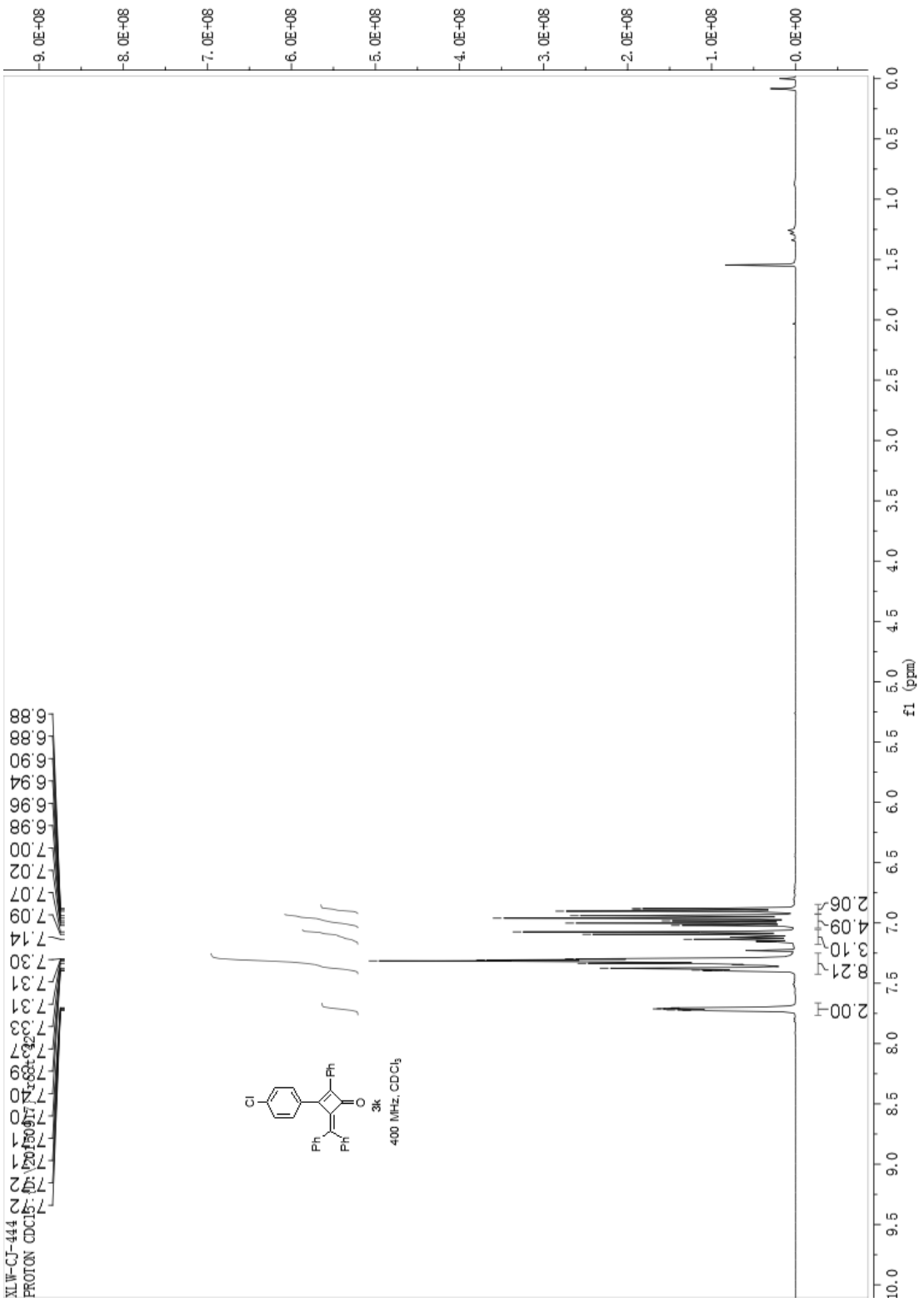

XLW-CJ-4421
C13CPD CDCl3 {D:\20150921} root 36
OMe
Ph
Ph
Ph
O
3h
100 MHz, CDCl3
f1 (ppm)

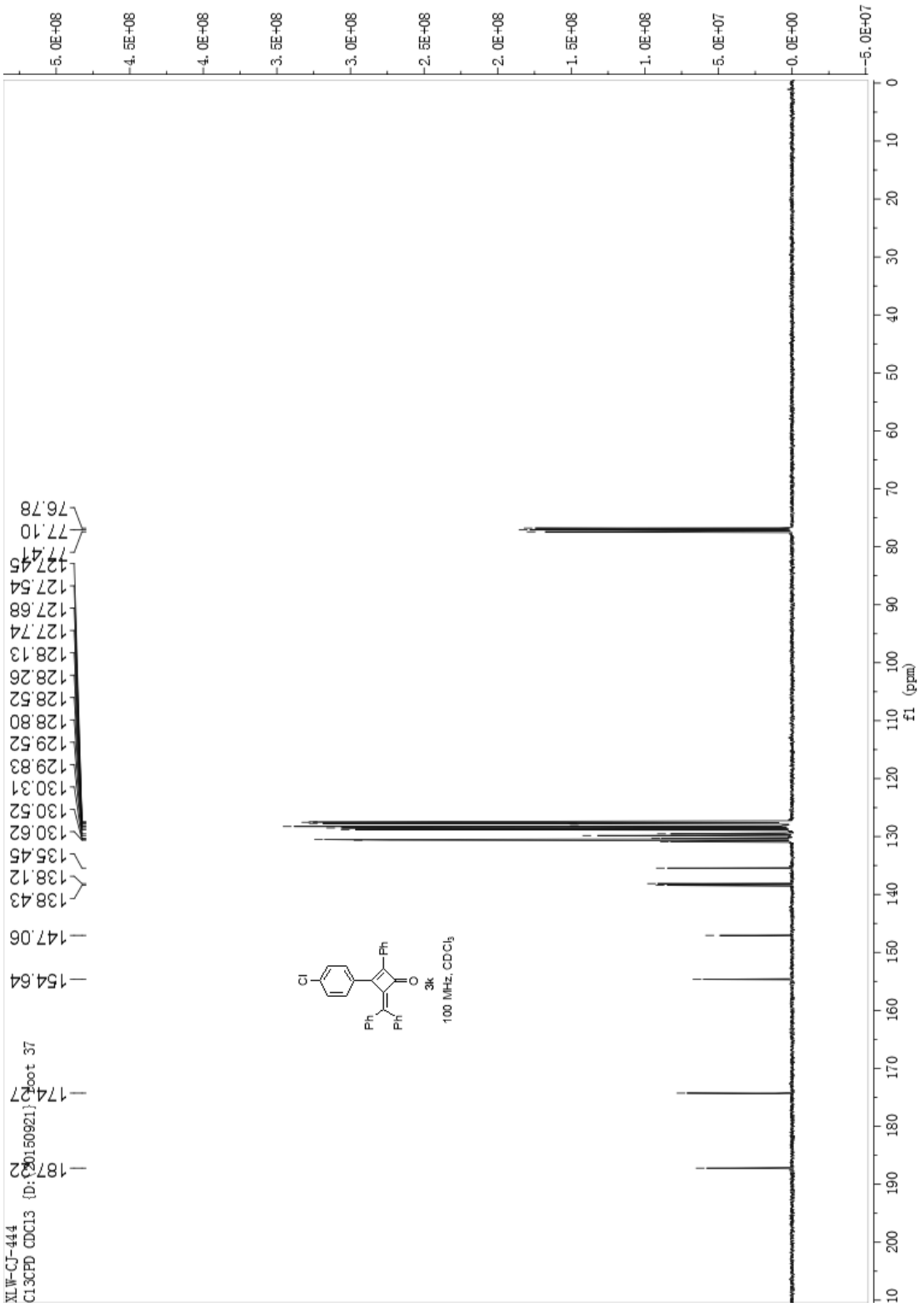

XLW-CJ-422
PROTON CDCl3 {D:\20150717} root 4
3i
400 MHz, CDCl3
f1 (ppm)

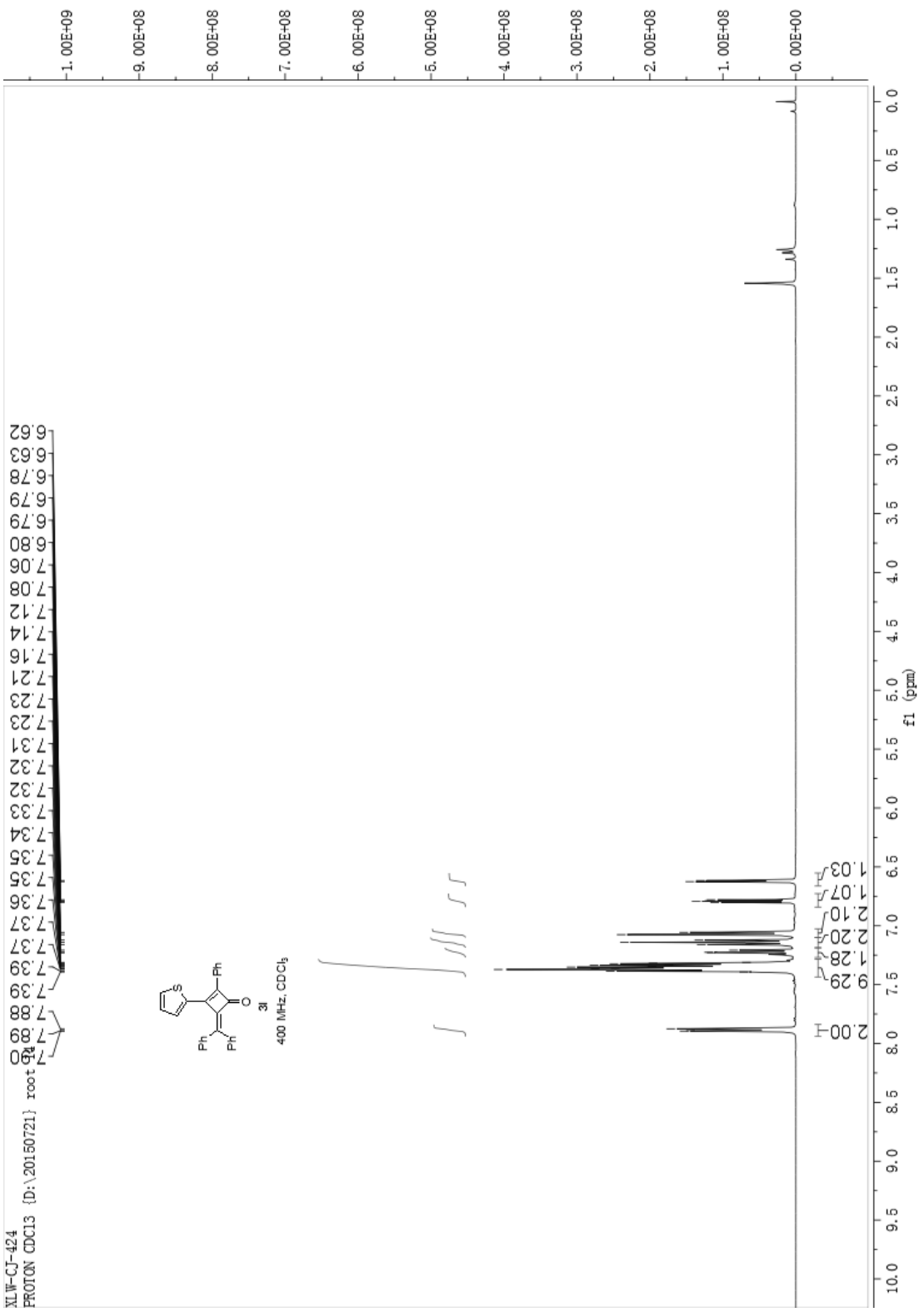

XLW-CJ-422
C13CPD CDCl3 {D:\20150717\2\root 4
187.91
175.56
160.83
153.49
147.47
130.85
130.72
129.43
128.71
127.66
127.54
127.51
127.43
113.43
77.56
77.24
76.92
55.41
OMe
Ph
Ph
Ph
O
3i
100 MHz, CDCl3
f1 (ppm)

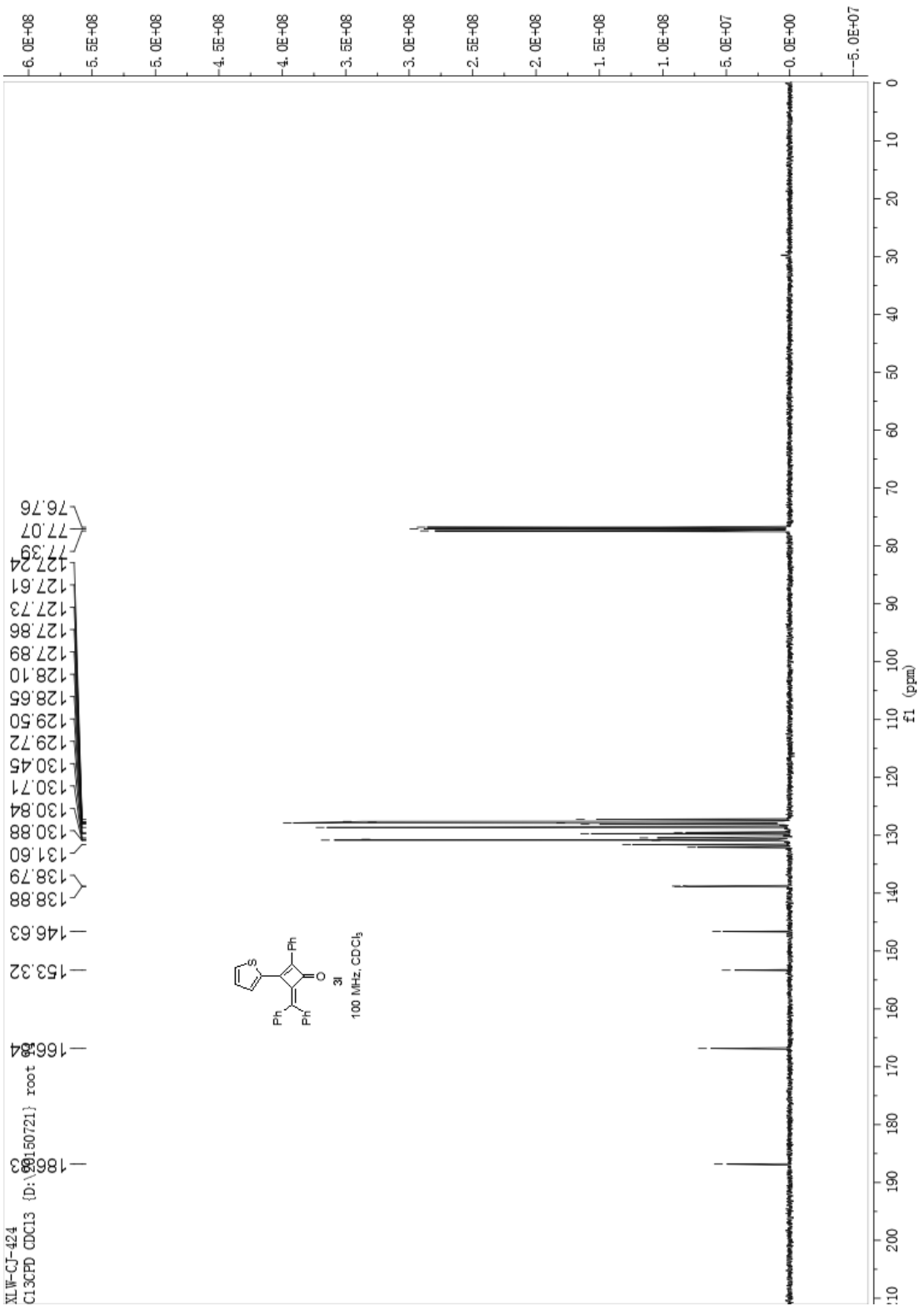

XLW-CJ-443
PROTON CDCl3 {D:\20150917} rod
Me
Ph
Ph
Ph
O
3j
400 MHz, CDCl3
f1 (ppm)

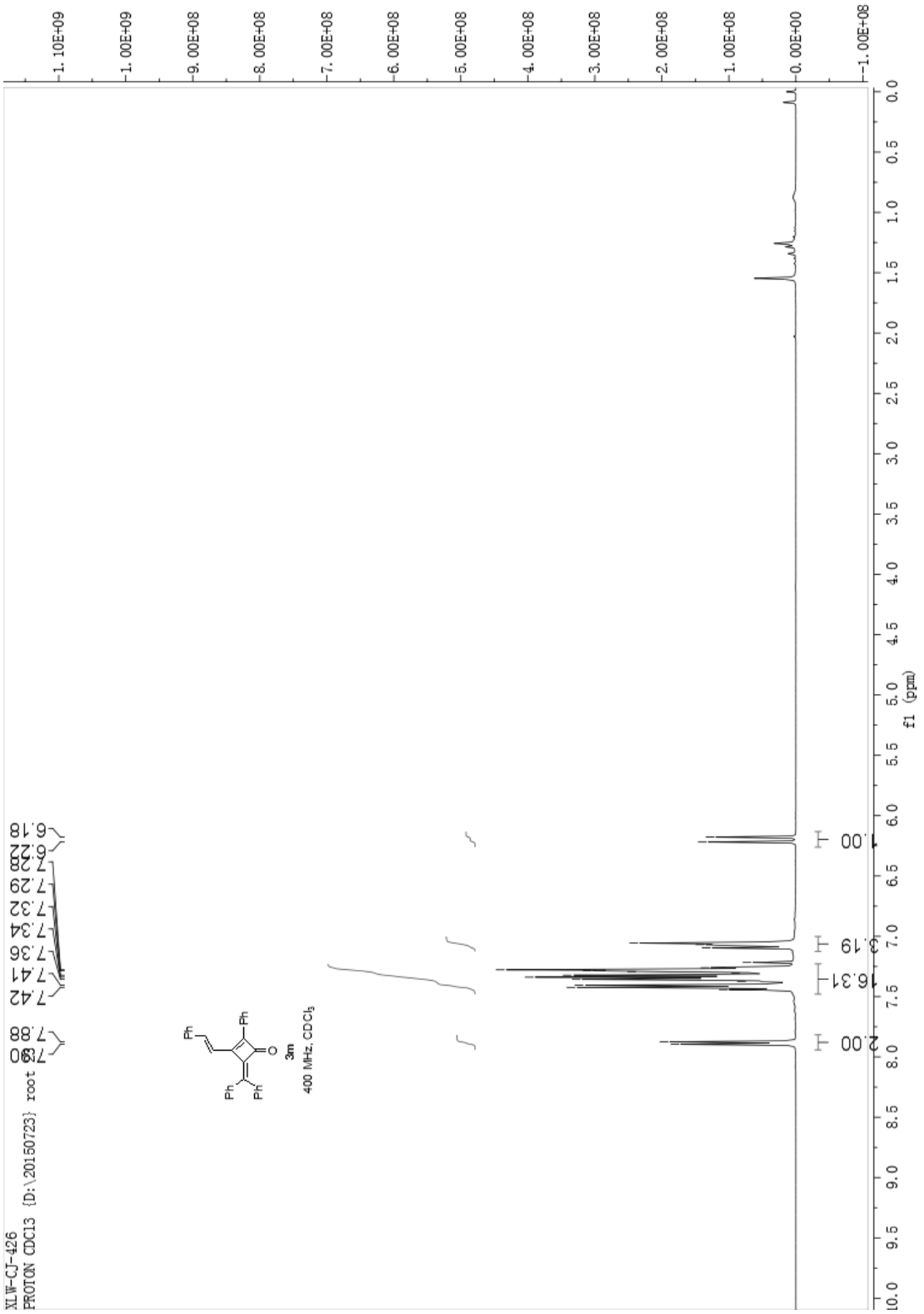

XLW-CJ-443
C13CPD CDCl3 {DA}-20150925
21.57
76.82
77.14
77.46
127.30
127.39
127.46
127.65
127.95
128.60
128.66
128.91
129.49
129.96
130.52
130.63
130.73
138.37
138.80
139.08
147.38
154.02
176.45
187.71
Me
Ph
Ph
Ph
O
3j
100 MHz, CDCl3
f1 (ppm)

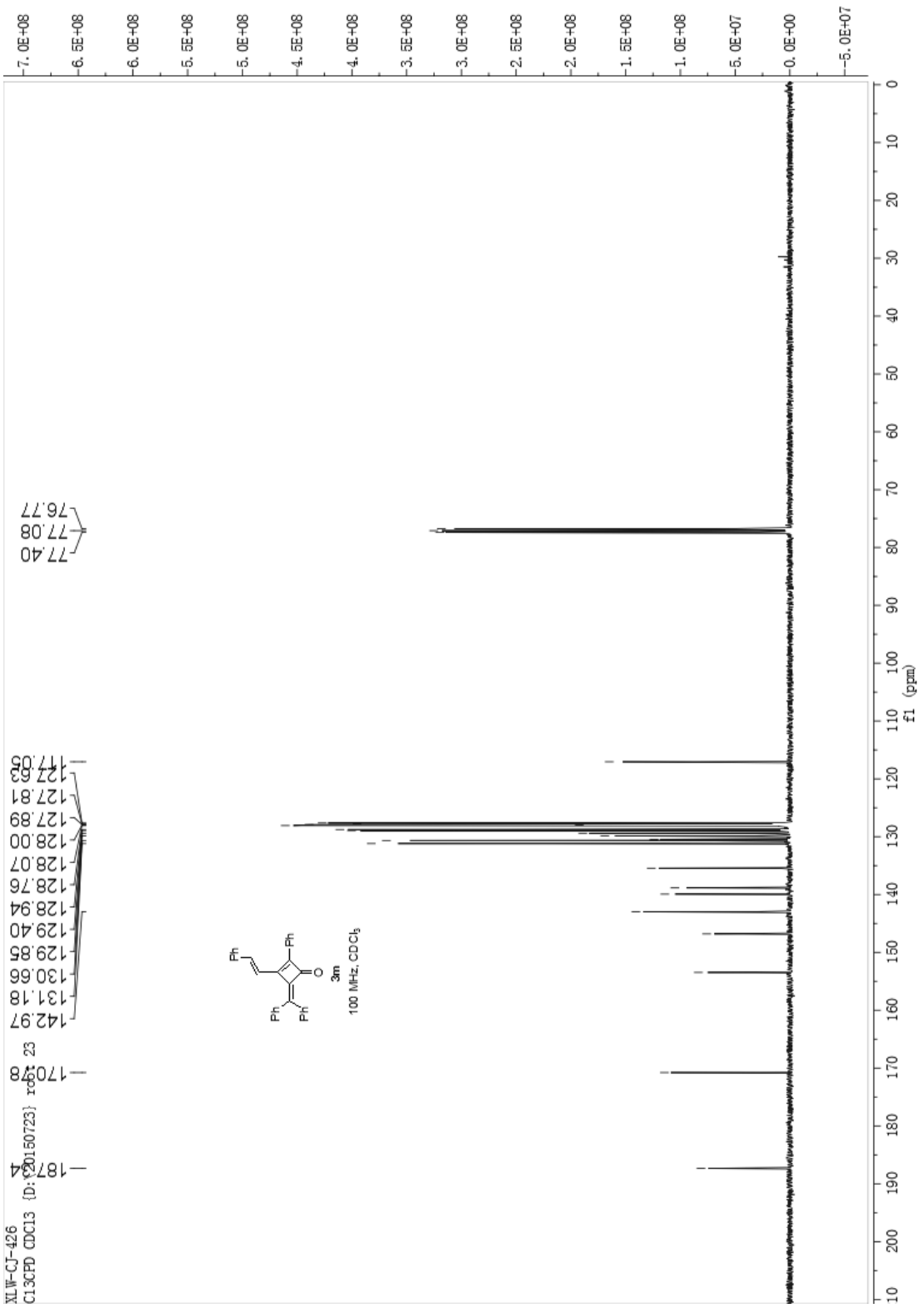

XLW-CJ-444
PROTON CDCl3
400 MHz, CDCl3
3k
Cl
Ph
Ph
Ph
O
2.00
8.21
3.10
4.09
2.06
f1 (ppm)

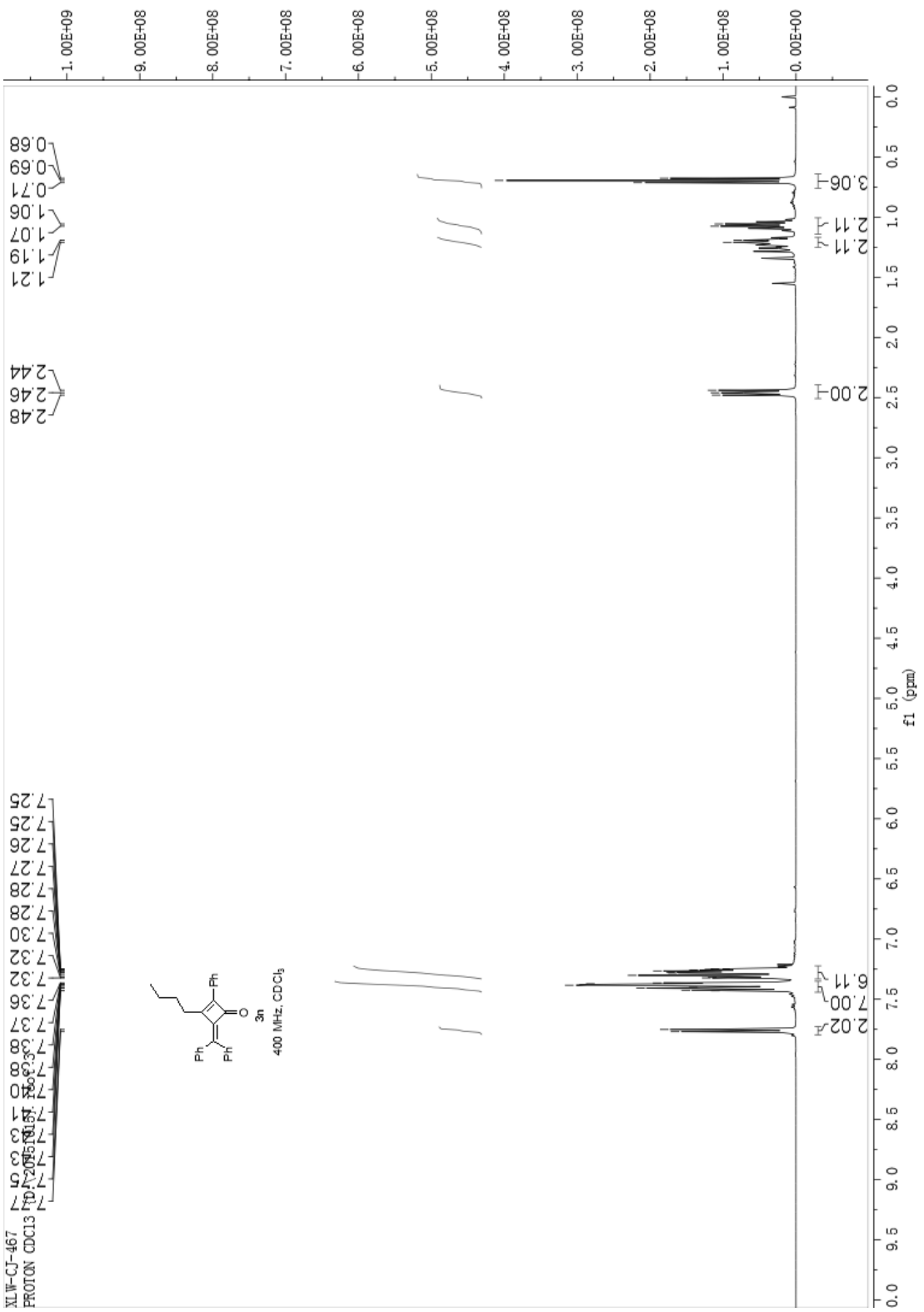

XLW-CJ-444
C13CPD CDCl3 {D:\20150921} {Root 37
3k
100 MHz, CDCl3
f1 (ppm)

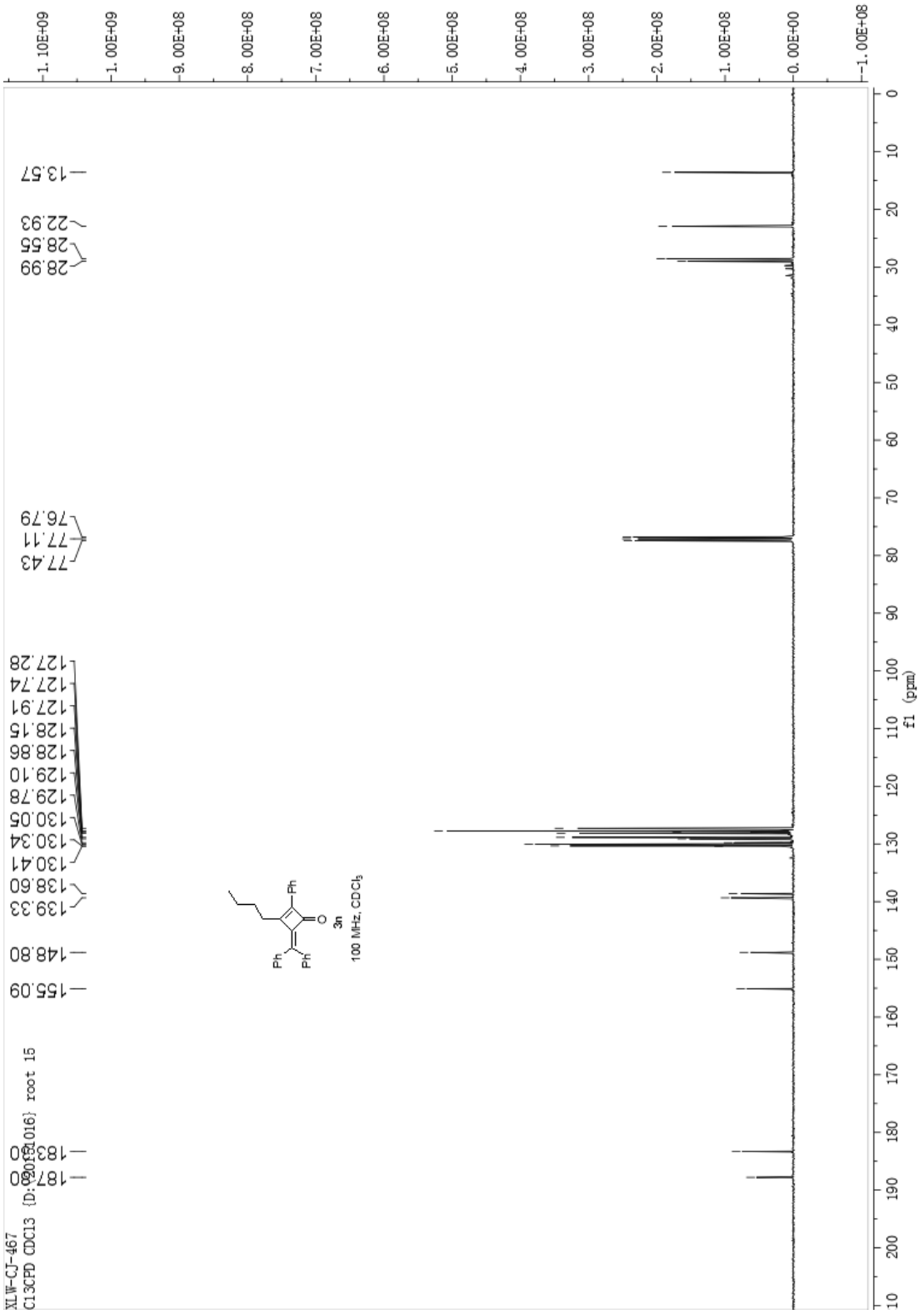

XLW-CJ-424
PROTON CDCl3 {D:\20150721} root
3l
400 MHz, CDCl3
f1 (ppm)

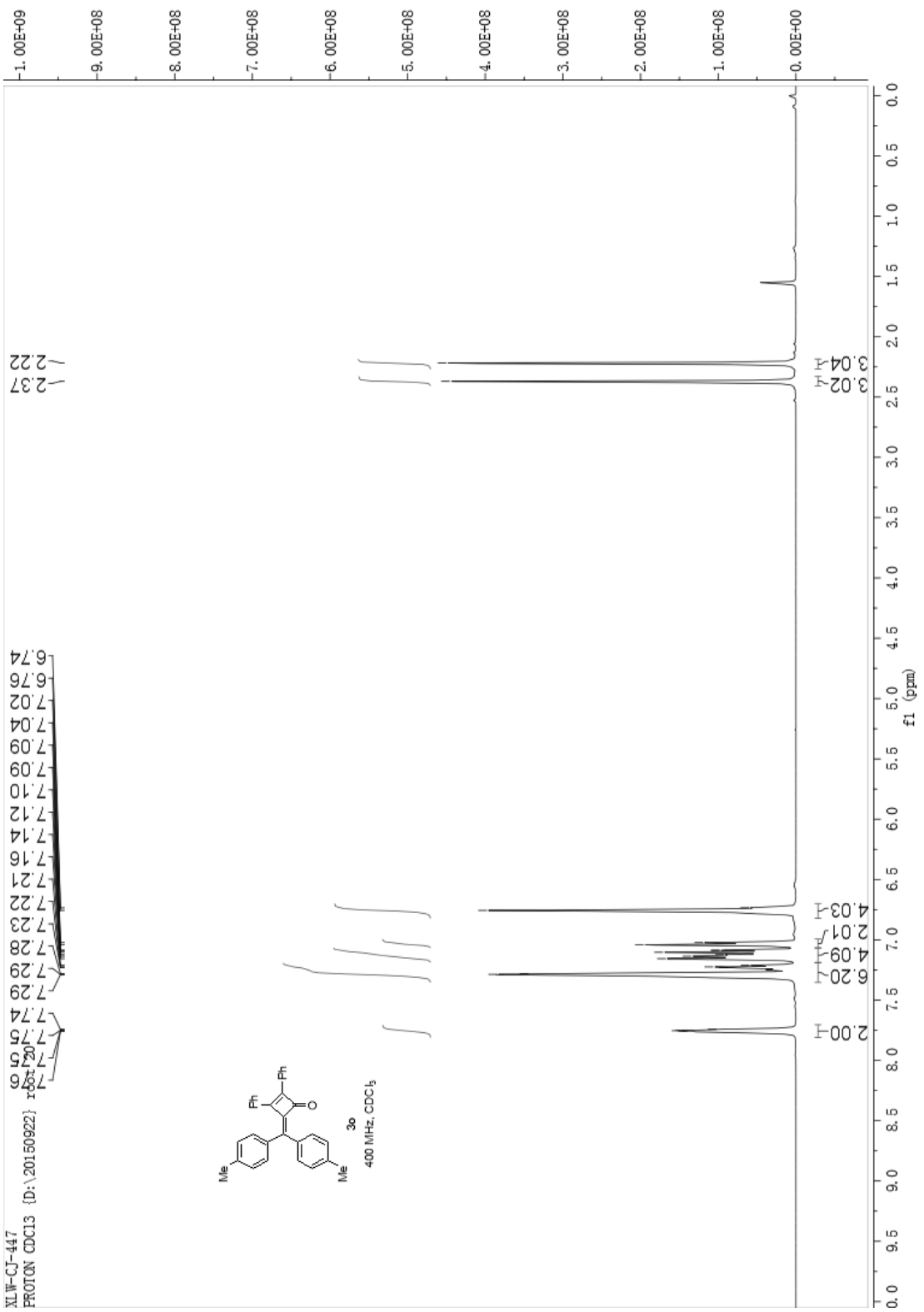

XLW-CJ-424
C13CPD CDCl3 {D:\data\20150721} root 84
3l
100 MHz, $CDCl_3$
f1 (ppm)

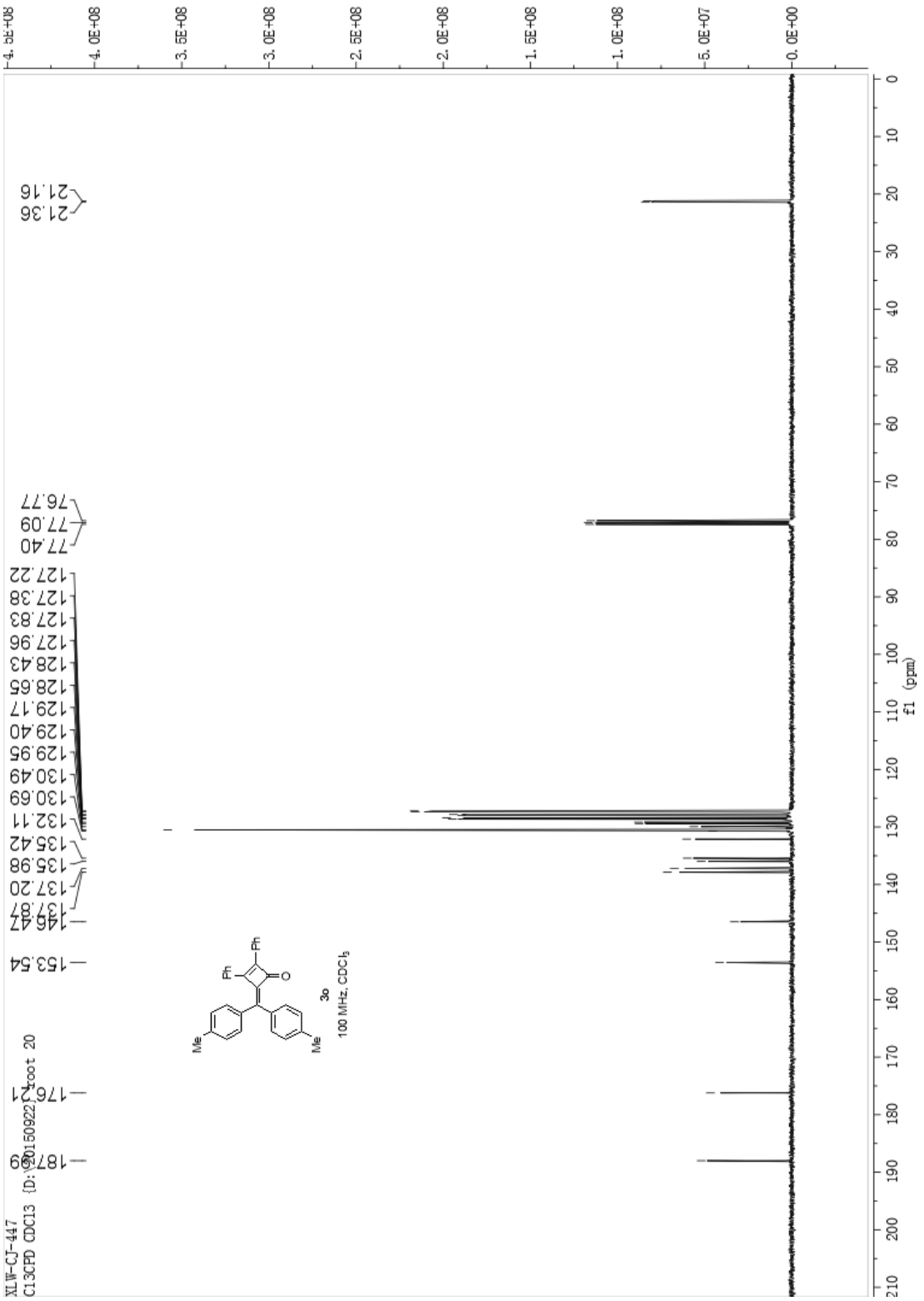

XLW-CJ-426
PROTON CDCl3 {D:\20150723} root
3m
400 MHz, CDCl3
f1 (ppm)

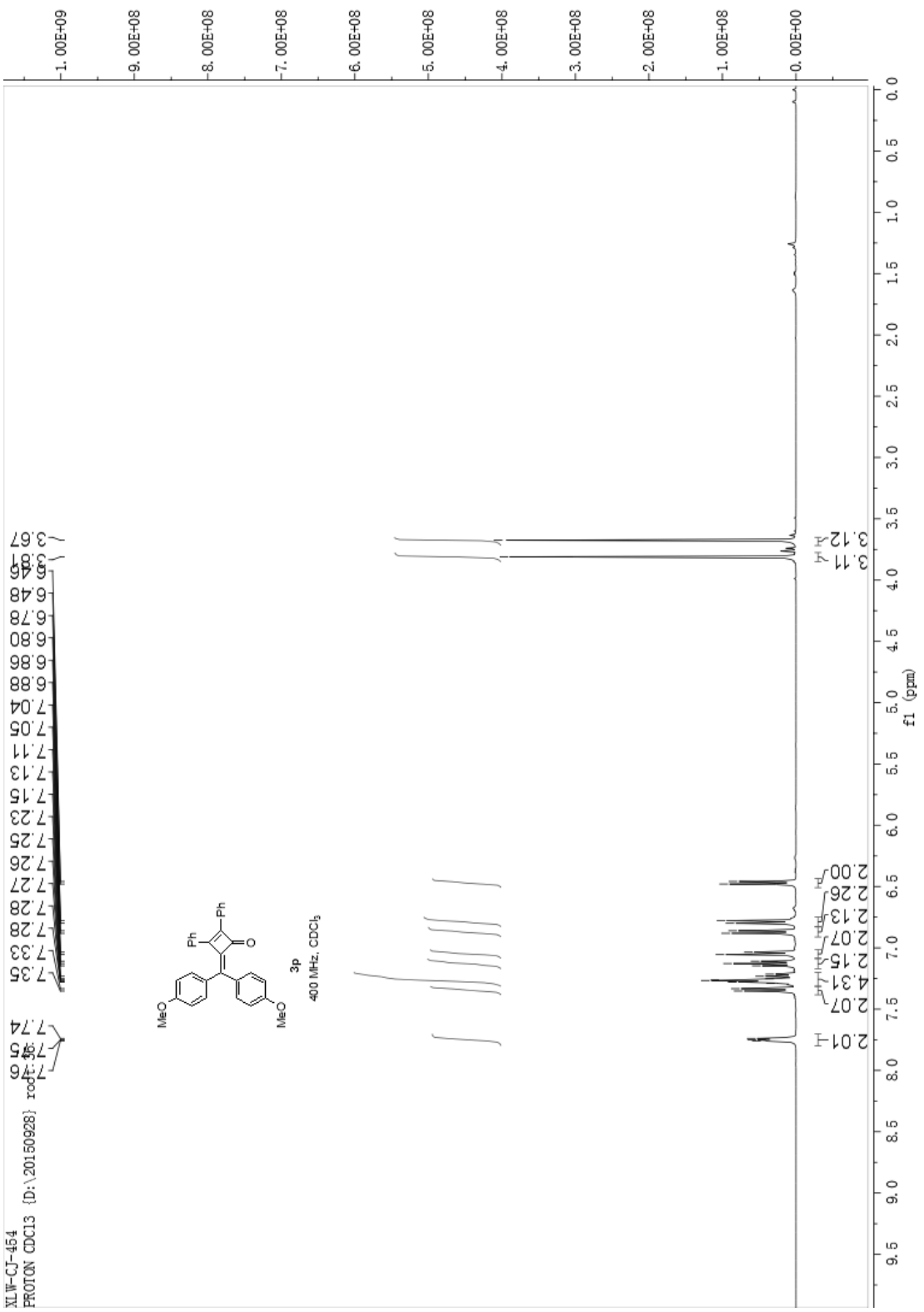

XLW-CJ-426
C13CPD CDCl3 {D:\20150723}
rcc 23
3m
100 MHz, CDCl3
f1 (ppm)

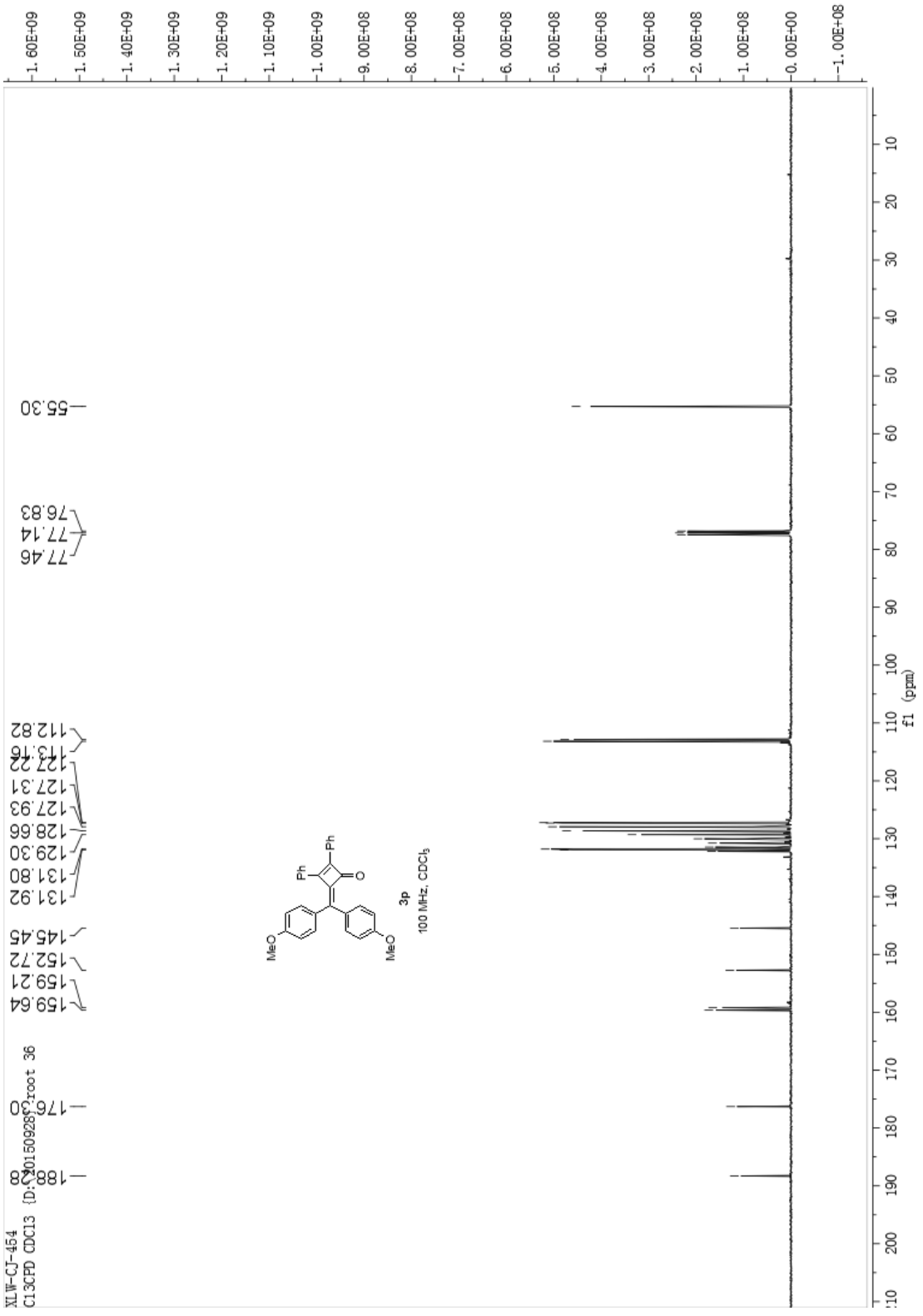

XLW-CJ-467
PROTON CDCl3
3n
400 MHz, CDCl3
Ph
Ph
Ph
O
f1 (ppm)

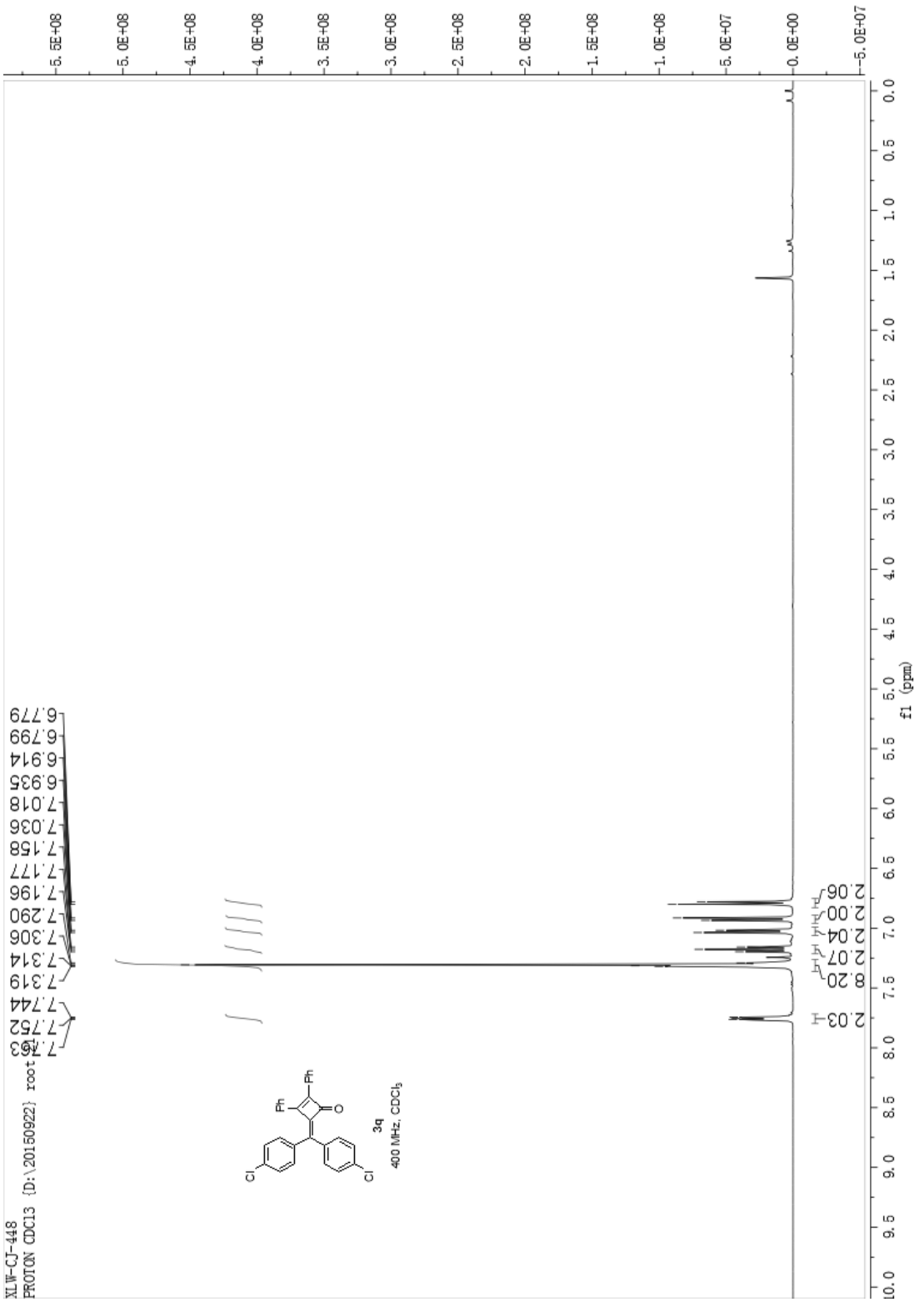

XLW-CJ-467
C13CPD CDCl3 {D:\Data\2016} root 15
187.80
183.30
155.09
148.80
139.33
138.60
130.41
130.34
130.05
129.78
129.10
128.86
128.15
127.91
127.74
127.28
77.43
77.11
76.79
28.99
28.55
22.93
13.57
Ph
Ph
Ph
O
3n
100 MHz, CDCl3
f1 (ppm)

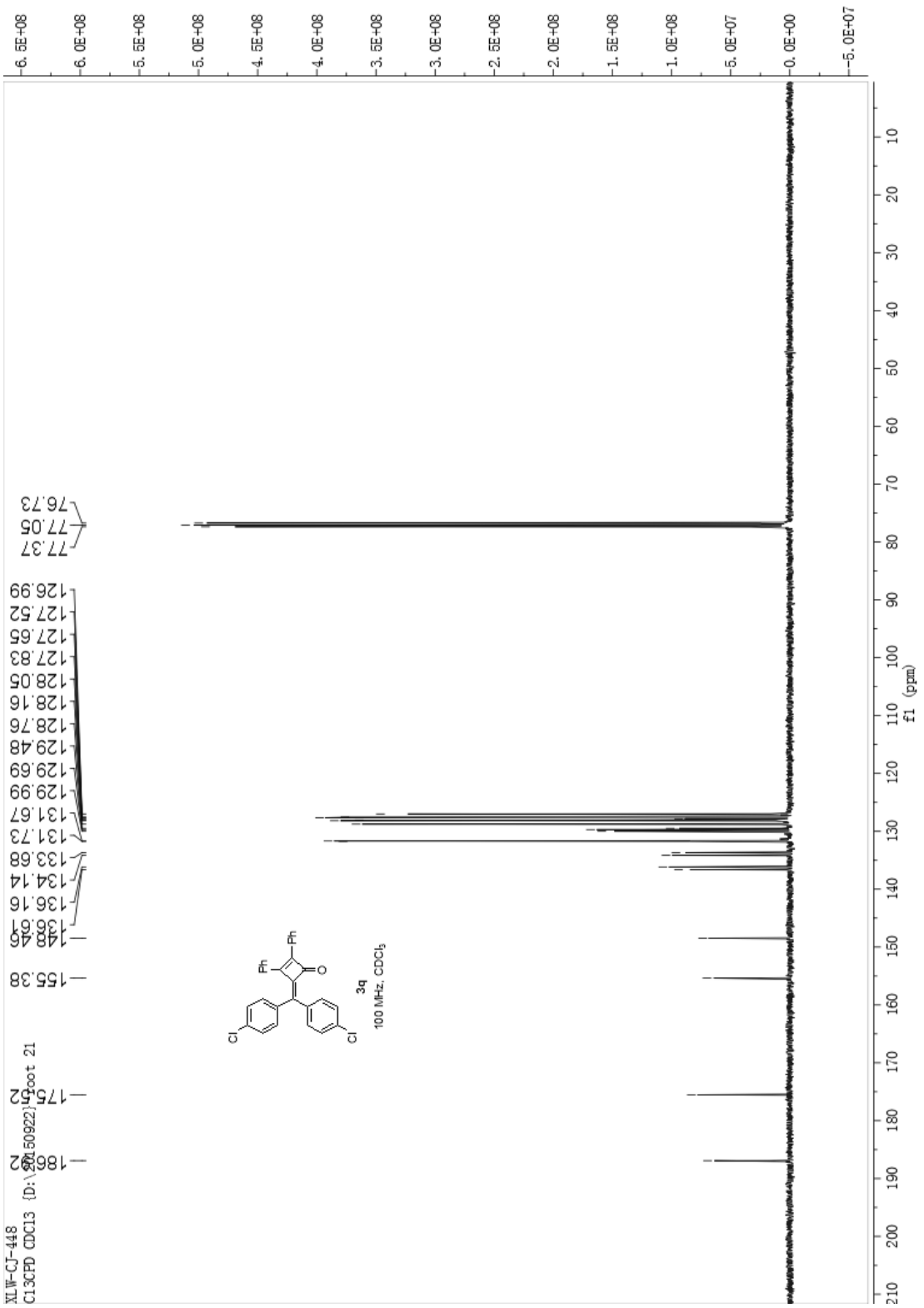

XLW-CJ-447
PROTON CDCl3 {D:\20150922}
3o
400 MHz, CDCl3
Ph
Ph
O
Me
Me
f1 (ppm)

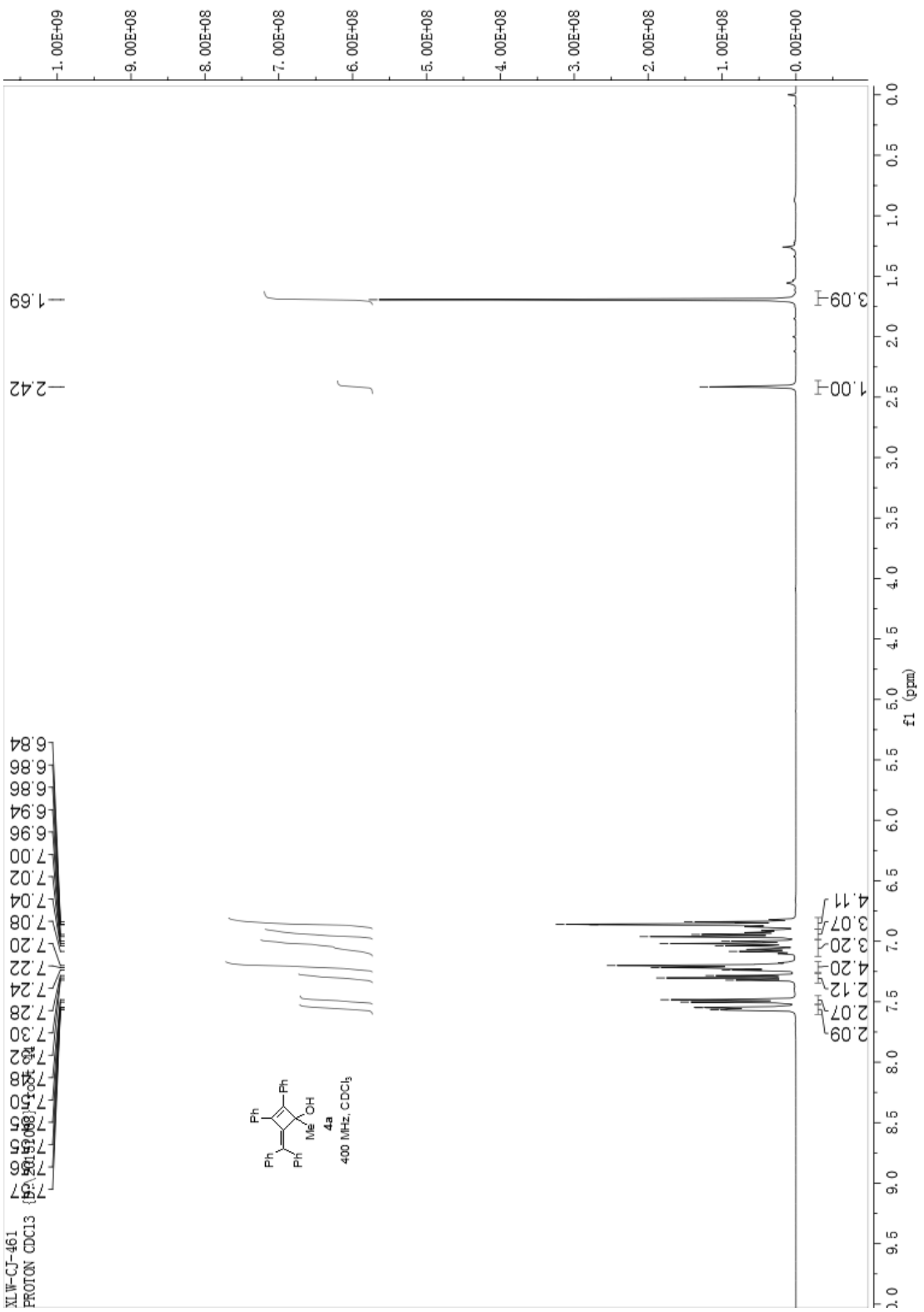

XLW-CJ-447
C13CPD CDCl3 {D:\20150922\root 20
21.16
21.36
76.77
77.09
77.40
127.22
127.38
127.83
127.96
128.43
128.65
129.17
129.40
129.95
130.49
130.69
132.11
135.42
135.98
137.20
137.87
146.47
153.54
176.21
187.99
Ph
Ph
O
Me
Me
3o
100 MHz, CDCl3
f1 (ppm)

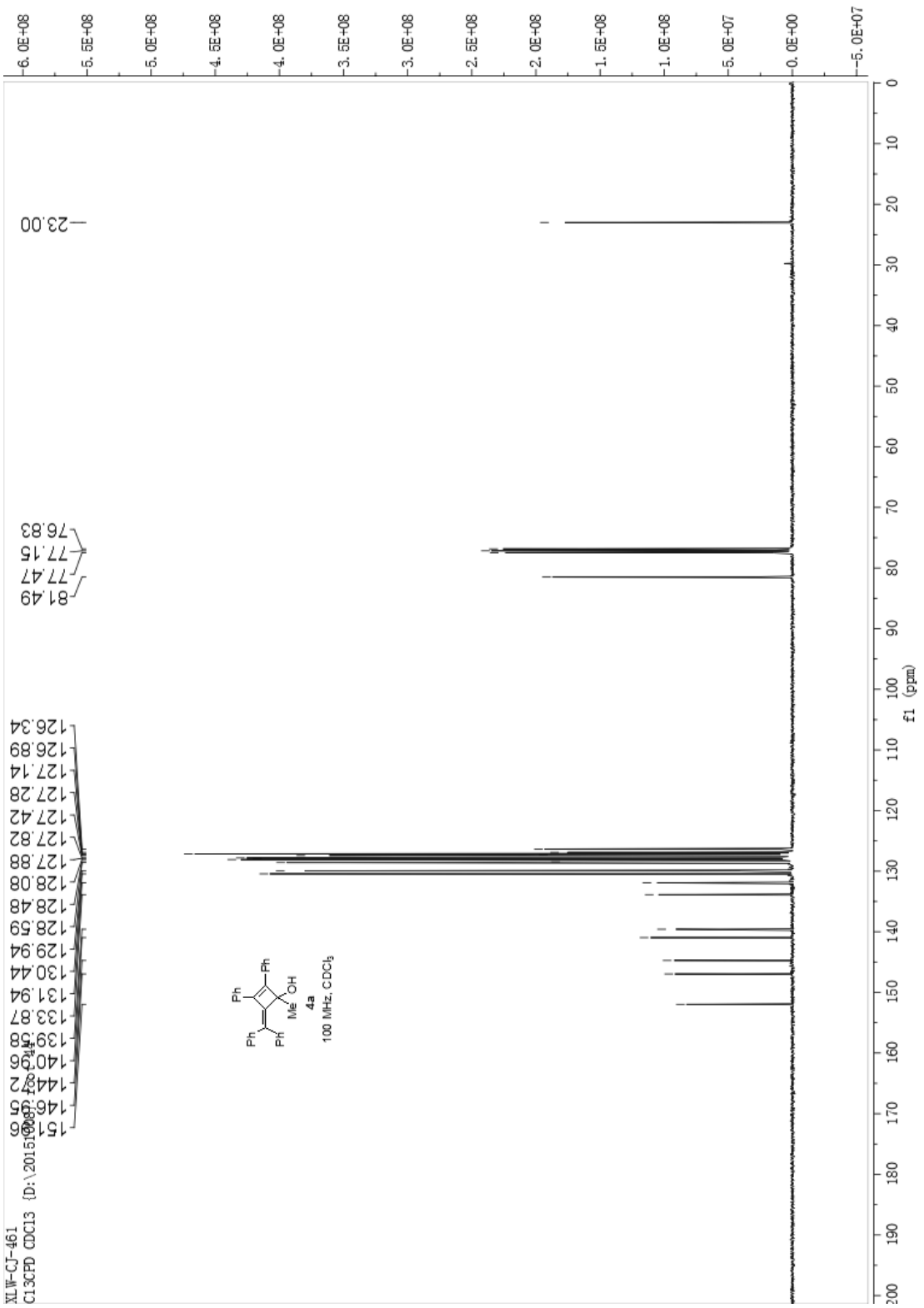

XLW-CJ-454
PROTON CDC13 {D:\20150928} rod
3p
400 MHz, CDCl3
f1 (ppm)

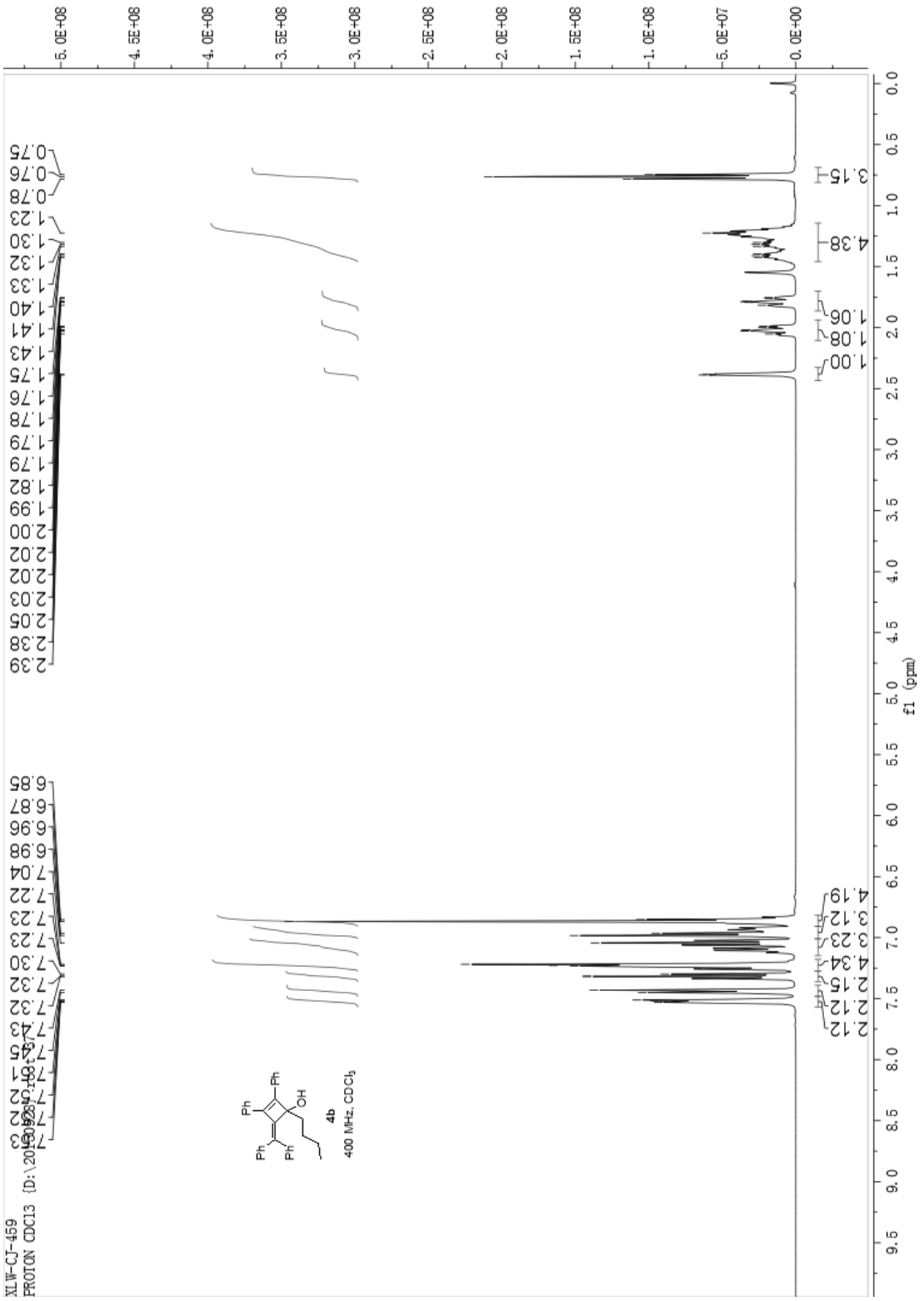

XLW-CJ-454
C13CPD CDCl3 {D:\20150928\root 36
188.28
176.30
159.64
159.21
152.72
145.45
131.92
131.80
129.30
128.66
127.93
127.31
127.22
113.16
112.82
77.46
77.14
76.83
55.30
Ph
Ph
O
MeO
MeO
3p
100 MHz, CDCl3
f1 (ppm)

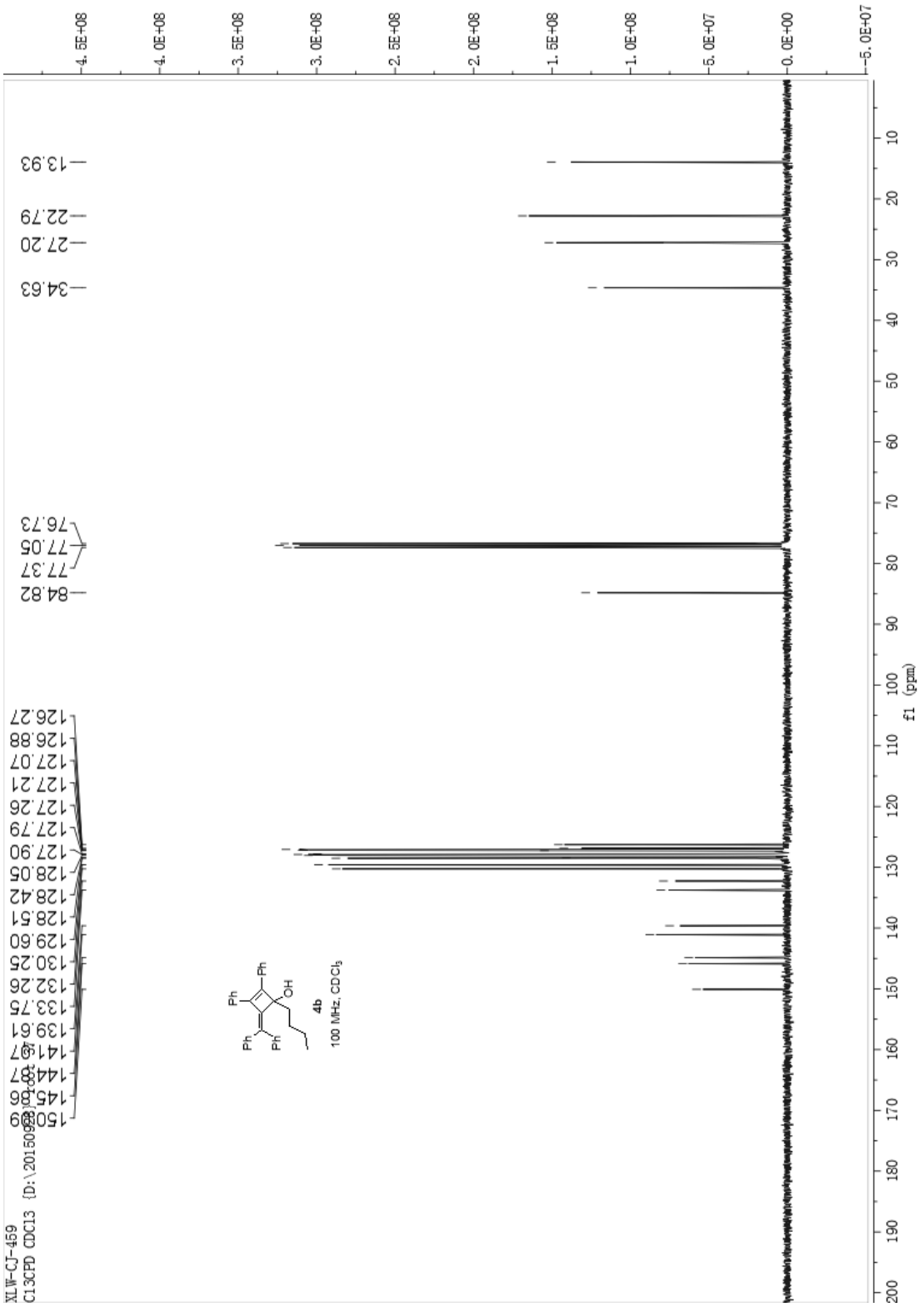

XLW-CJ-448
PROTON CDCl3 {D:\20150922} root
3q
400 MHz, CDCl3
f1 (ppm)

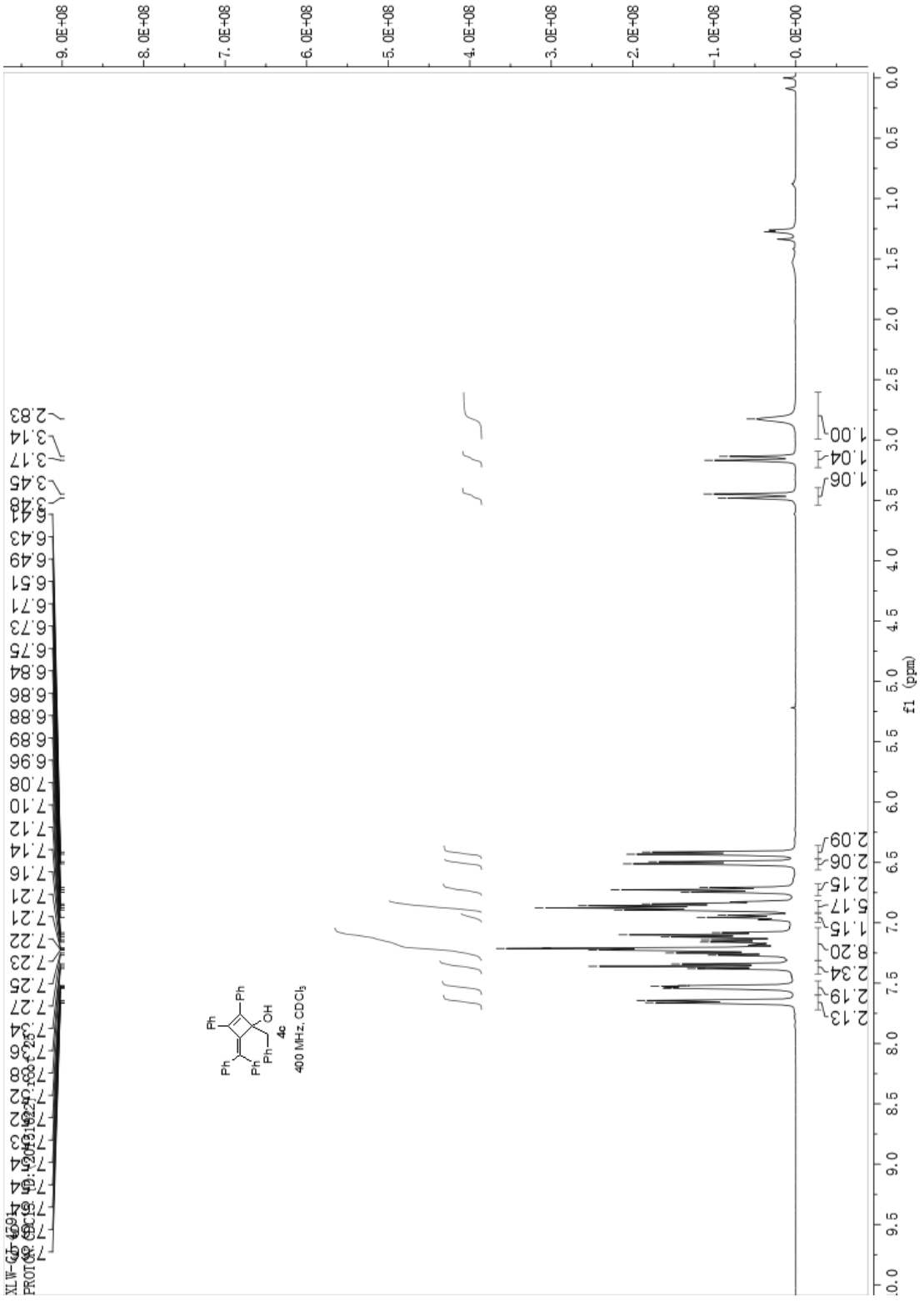

XLW-CJ-448
C13CPD CDCl3 {D:\20150922} root 21
186.92
175.52
155.38
148.45
136.61
136.16
134.14
133.68
131.73
131.67
129.99
129.69
129.48
128.76
128.16
128.05
127.83
127.65
127.52
126.99
77.37
77.05
76.73
Ph
Ph
O
Cl
Cl
3q
100 MHz, CDCl3
f1 (ppm)

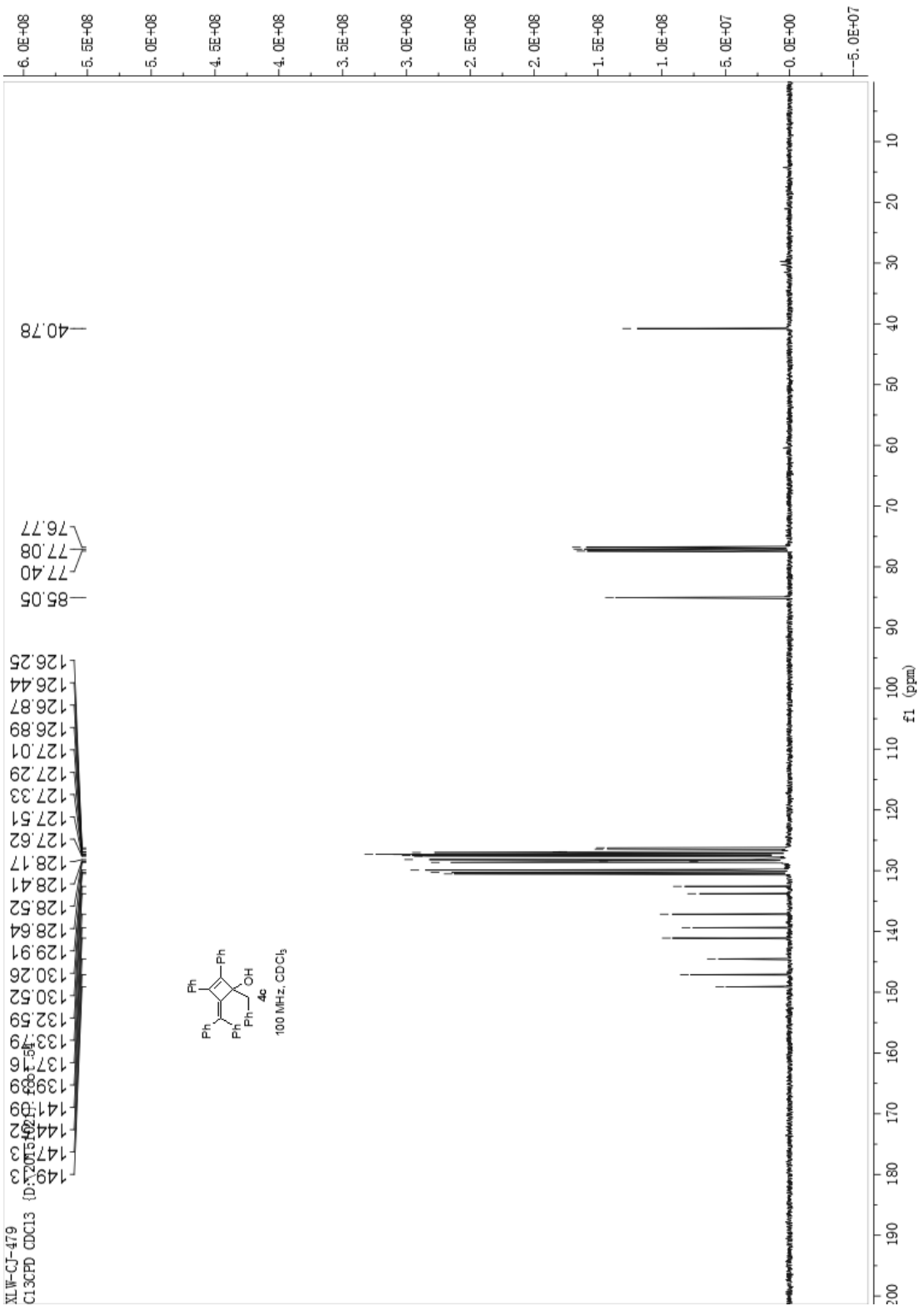

XLW-CJ-461
PROTON CDCl3
Ph
Ph
Ph
Ph
Me
OH
4a
400 MHz, CDCl3
f1 (ppm)

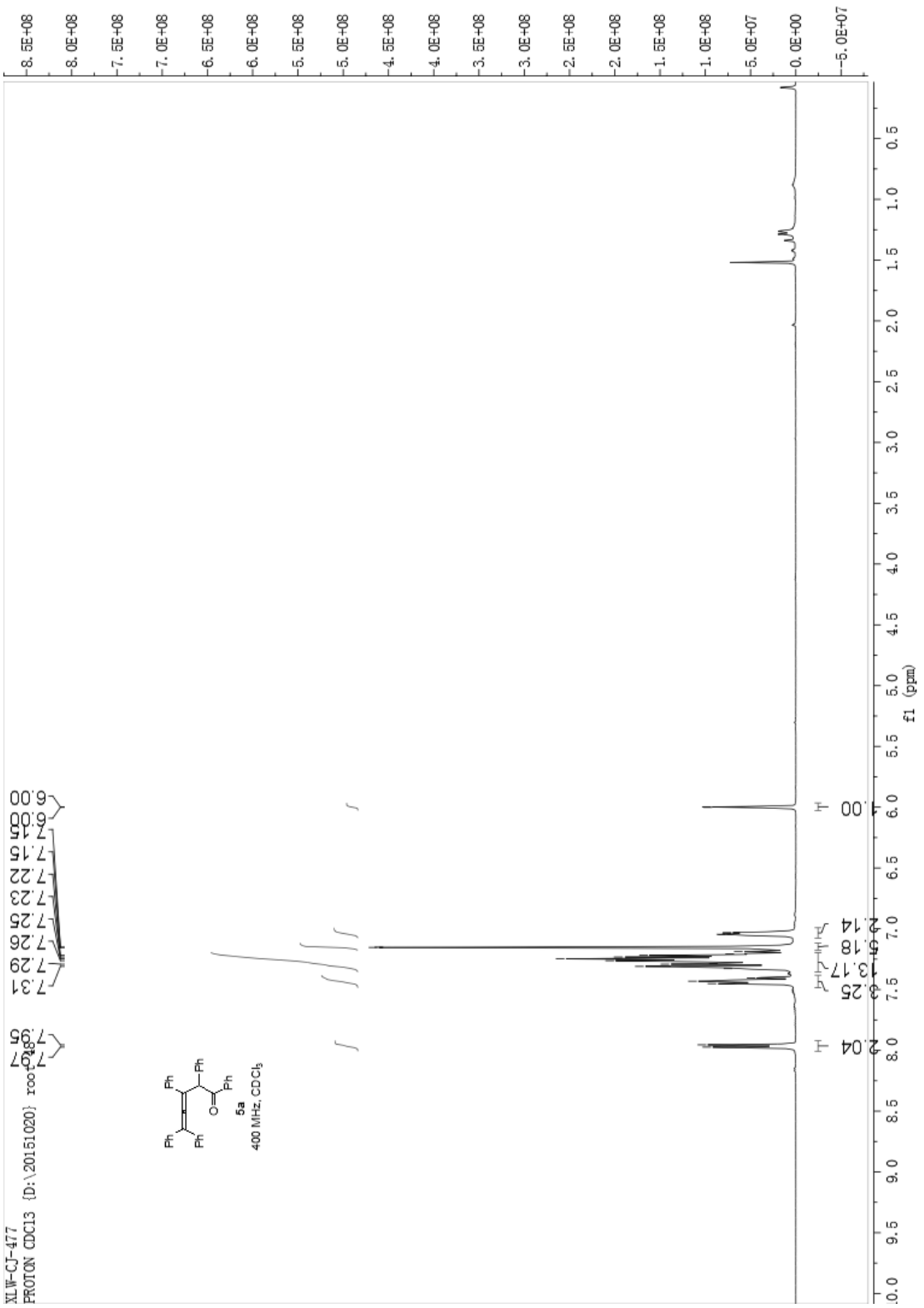

XLW-CJ-461
C13CPD CDCl3 {D:\2015\
23.00
76.83
77.15
77.47
81.49
126.34
126.89
127.14
127.28
127.42
127.82
127.88
128.08
128.48
128.59
129.94
130.44
131.94
133.87
139.58
140.96
144.72
146.95
151.06
Ph
Ph
Me
OH
Ph
Ph
4a
100 MHz, CDCl3
f1 (ppm)

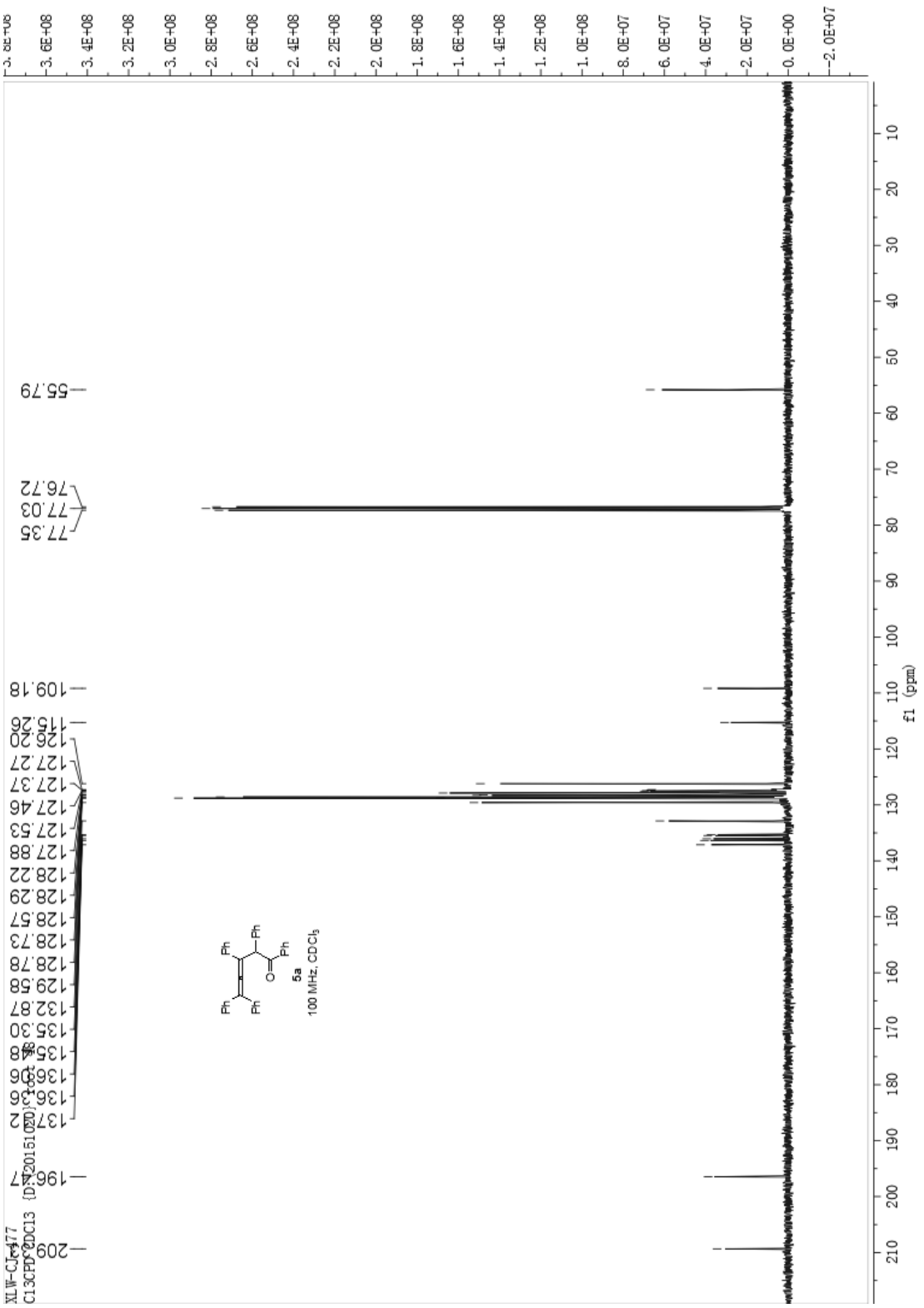

XLW-CJ-459
PROTON CDC13
Ph
Ph
Ph
Ph
OH
4b
400 MHz, CDCl3
f1 (ppm)

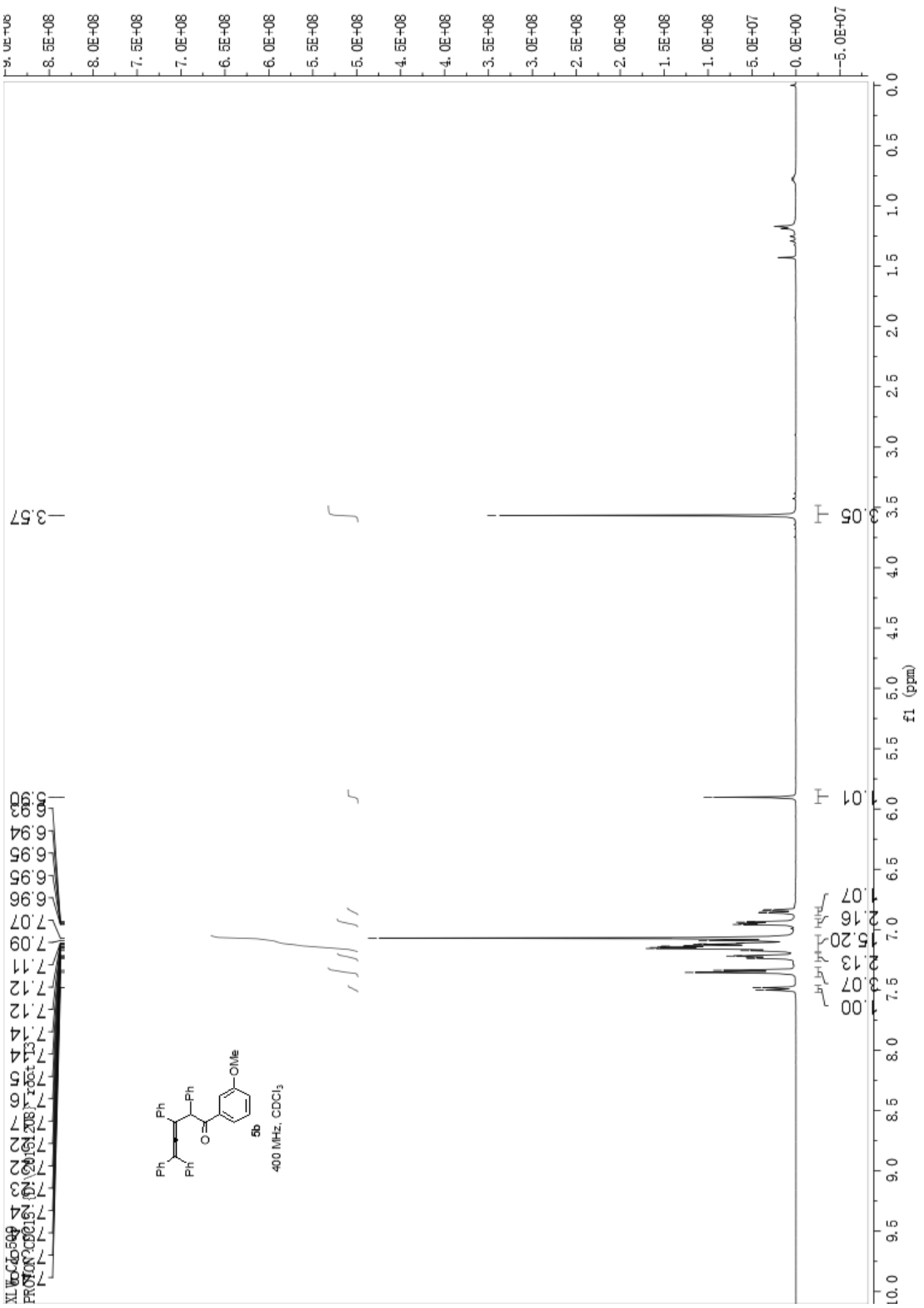

XLW-CJ-459
C13CPD CDCl3 {D:\20150928\1}
13.93
22.79
27.20
34.63
76.73
77.05
77.37
84.82
126.27
126.88
127.07
127.21
127.26
127.79
127.90
128.05
128.42
128.51
129.60
130.25
132.26
133.75
139.61
141.97
144.87
145.06
150.99
Ph
Ph
Ph
Ph
OH
4b
100 MHz, CDCl3
f1 (ppm)

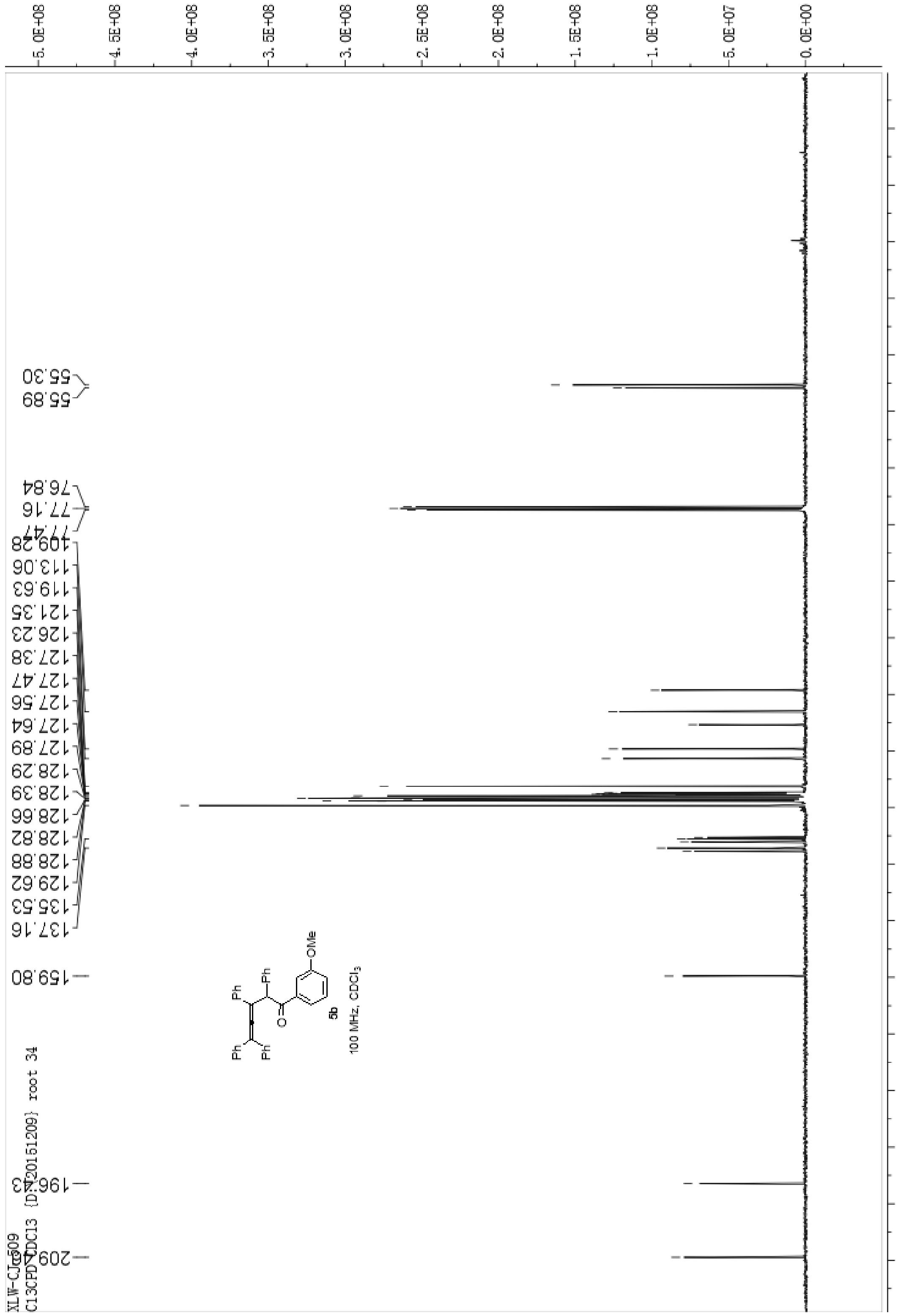

Ph
Ph
Ph
Ph
OH
4c
400 MHz, CDCl3
f1 (ppm)

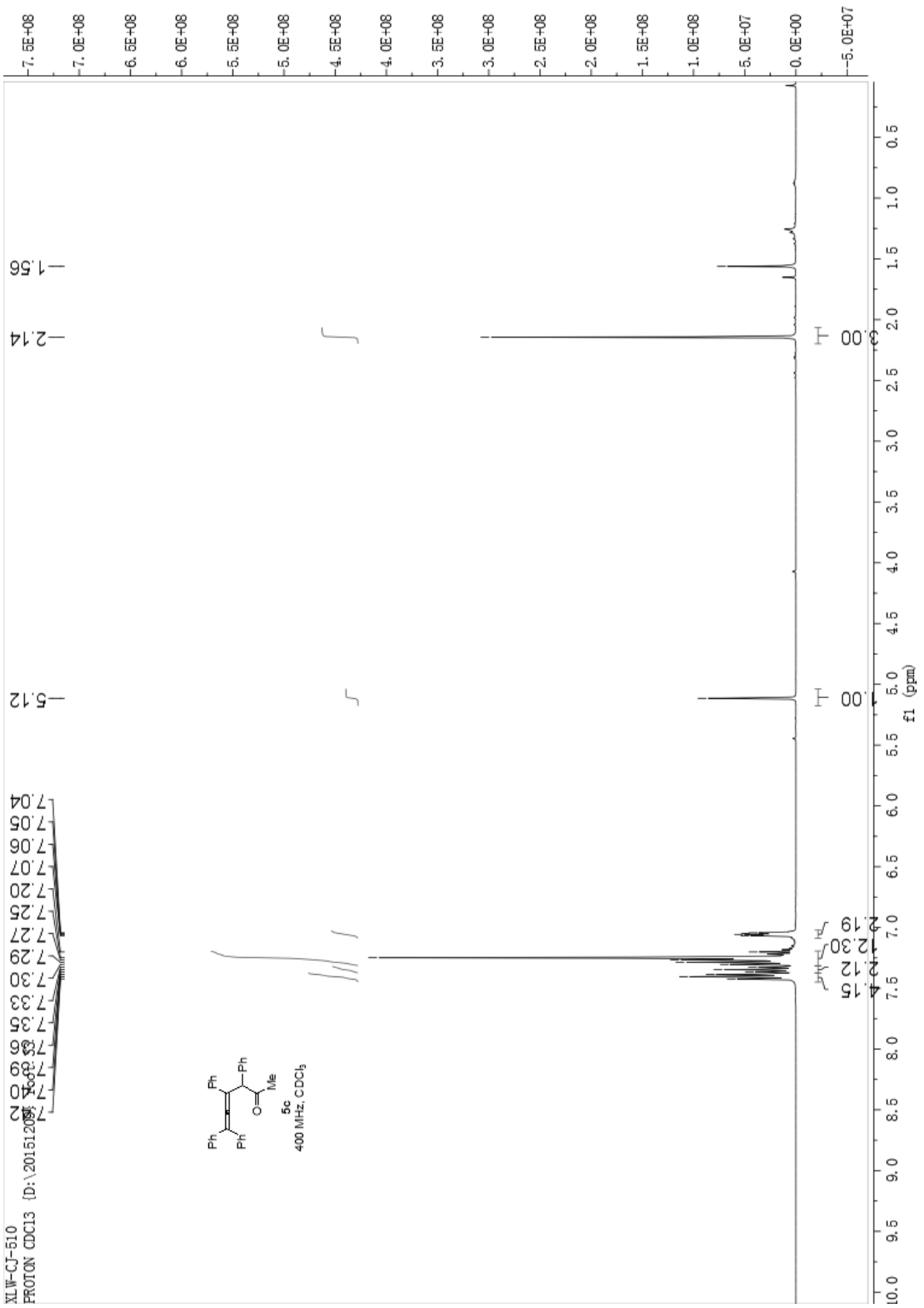

XLW-CJ-479
C13CPD CDCl3
Ph
Ph
Ph
Ph
OH
4o
100 MHz, CDCl3
f1 (ppm)

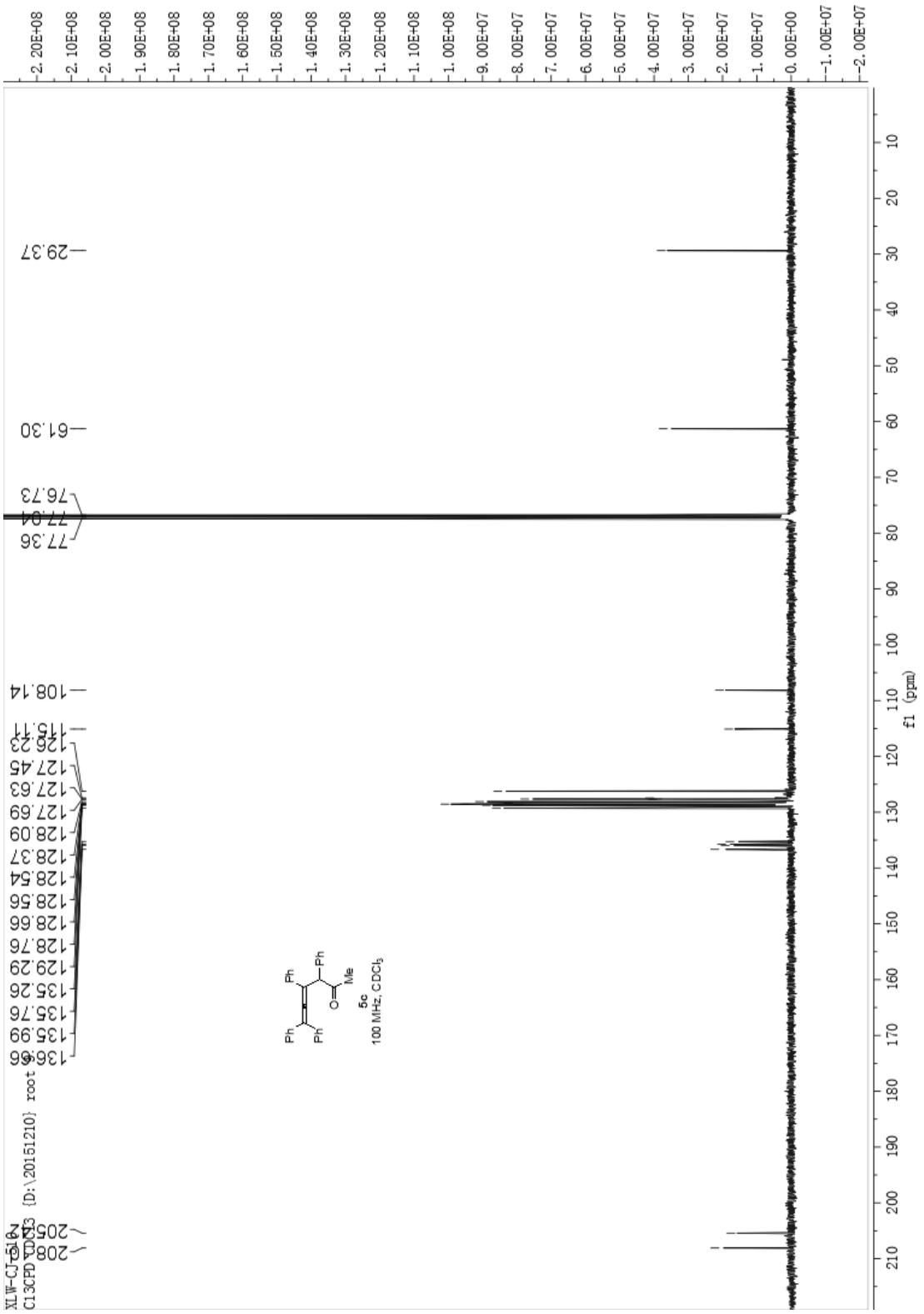

XLW-CJ-477
PROTON CDCl3 {D:\20151020} root
5a
400 MHz, CDCl3
Ph
Ph
Ph
Ph
O
7.95
7.97
7.31
7.29
7.26
7.25
7.23
7.22
7.15
7.15
6.00
6.00
2.04
1.00
f1 (ppm)

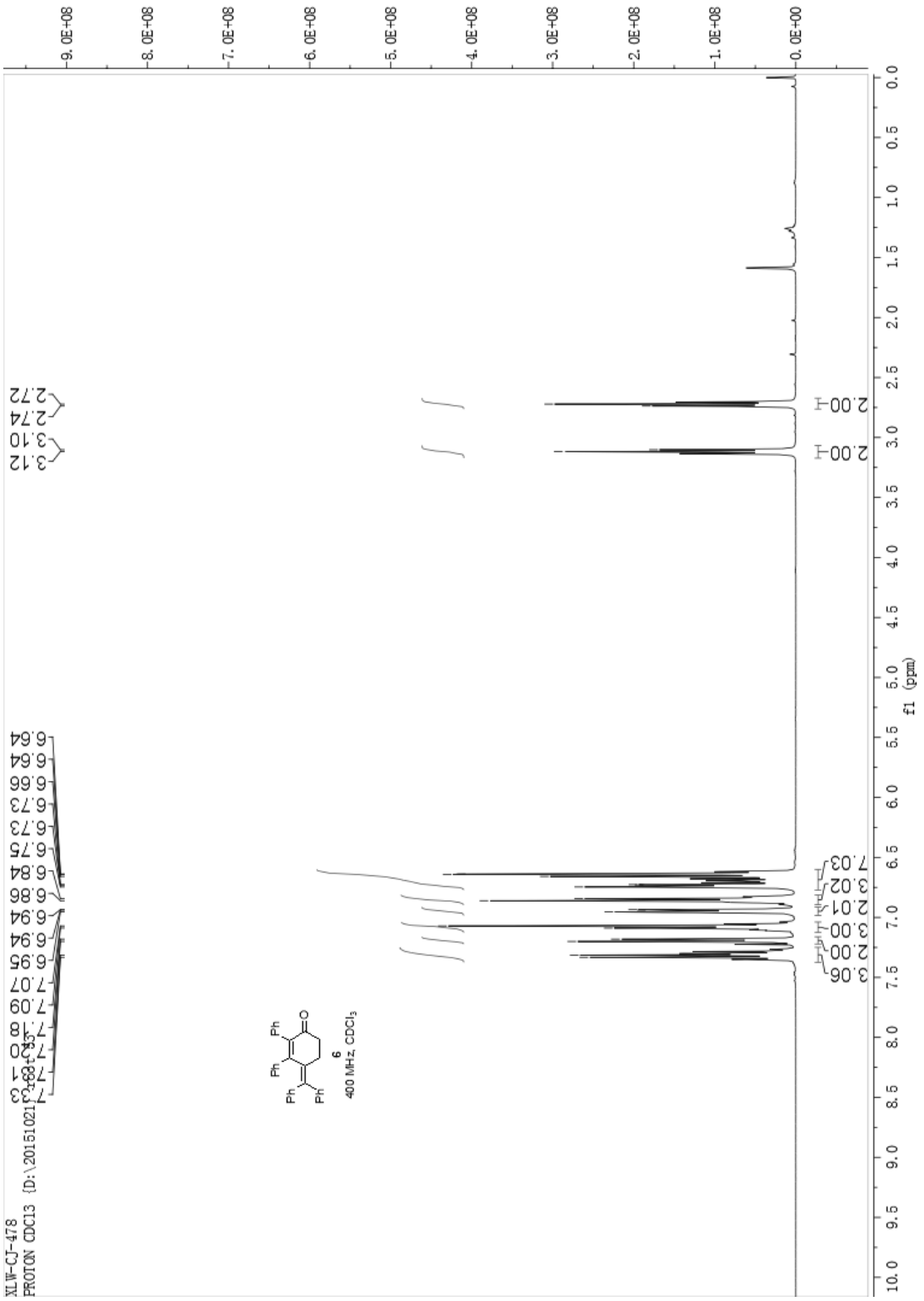

XLW-CJ-r477
C13CPD 2DC13 (DS 20151102)
209.47
196.87
137.02
136.36
136.06
135.48
135.30
132.87
129.58
128.78
128.73
128.57
128.29
128.22
127.88
127.53
127.46
127.37
127.27
126.20
115.26
109.18
77.35
77.03
76.72
55.79
Ph
Ph
Ph
Ph
O
5a
100 MHz, CDCl3
f1 (ppm)

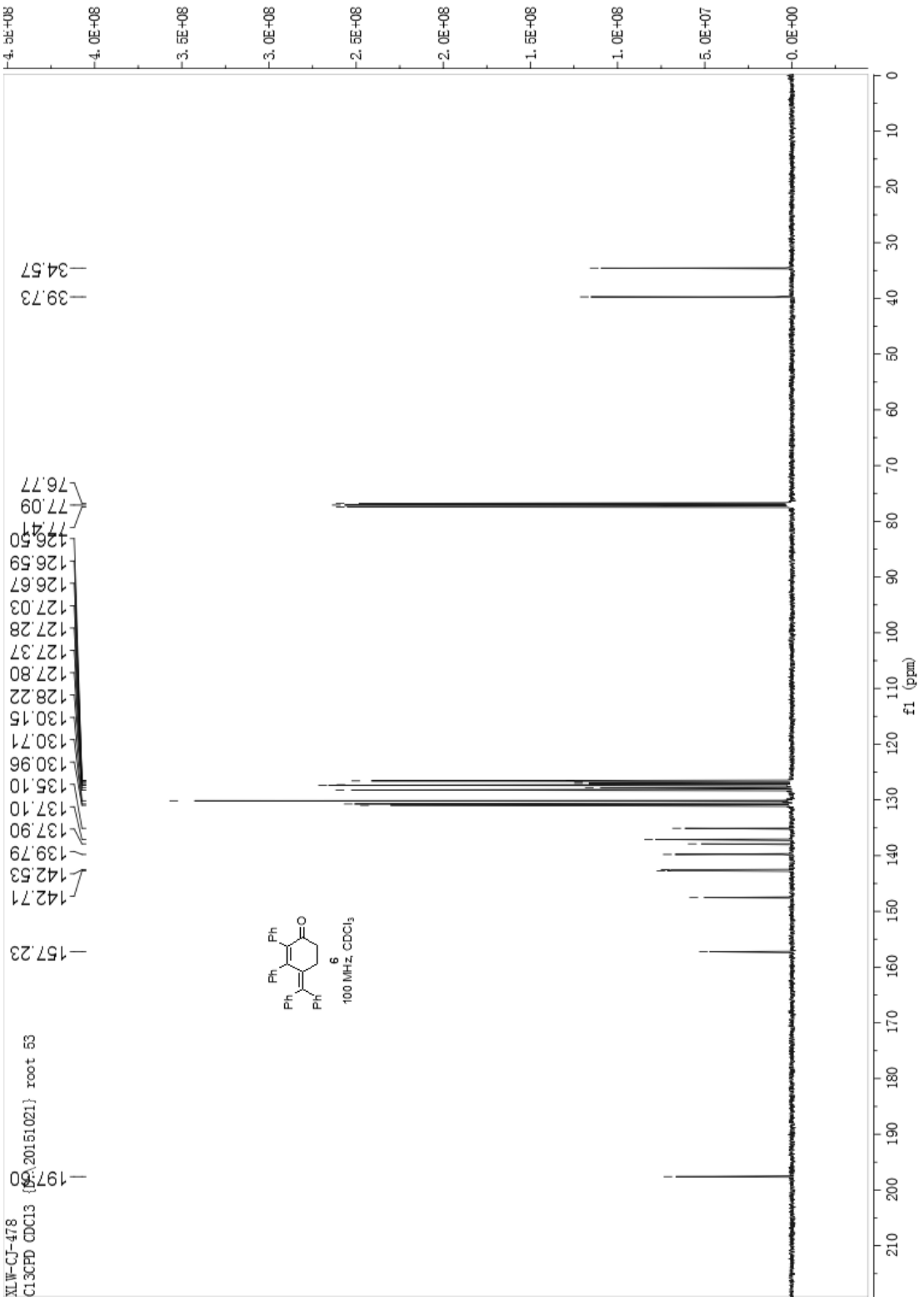

OMe
Ph
Ph
Ph
Ph
O
5b
400 MHz, CDCl3
3.57
f1 (ppm)

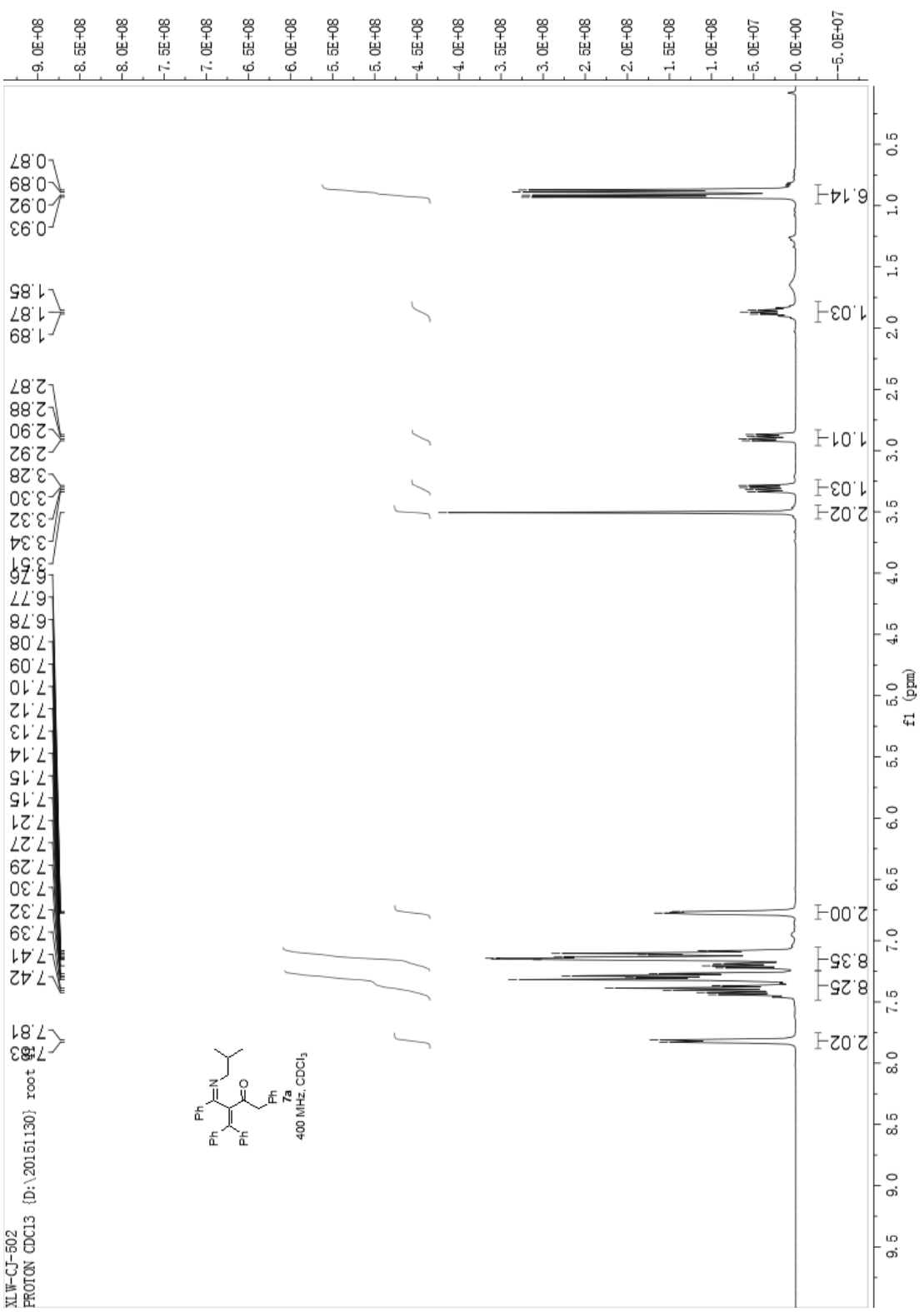

XLW-CJ-509
C13CPD CDCl3 {D:\20151209} root 34
209.
196.43
159.80
137.16
135.53
129.62
128.88
128.82
128.66
128.39
128.29
127.89
127.64
127.56
127.47
127.38
126.23
121.35
119.63
113.06
109.28
77.47
77.16
76.84
55.89
55.30
OMe
Ph
Ph
Ph
Ph
O
5b
100 MHz, CDCl3
f1 (ppm)

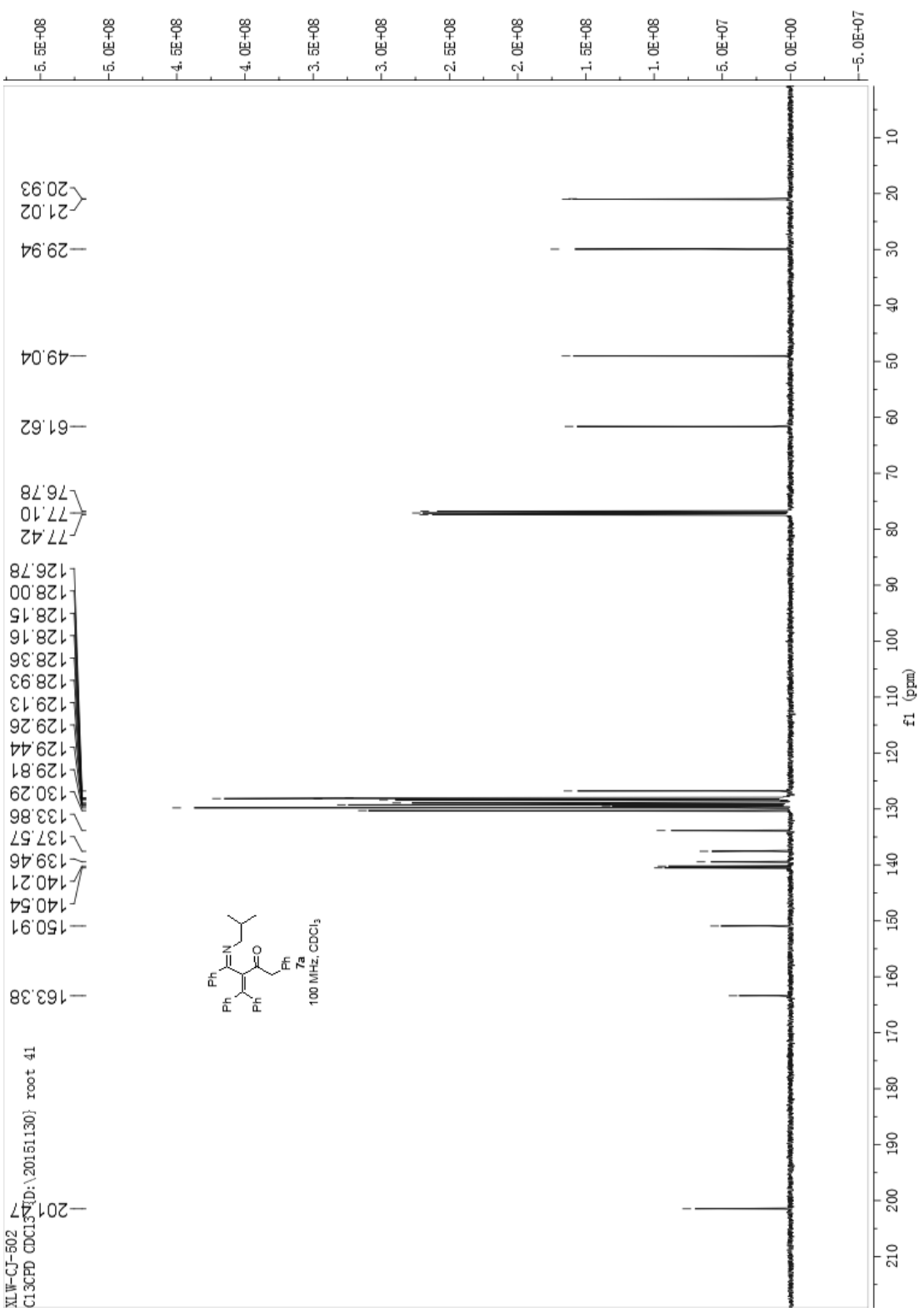

XLW-CJ-510
PROTON CDCl3 {D:\20151209}
Ph
Ph
Ph
O
Me
5c
400 MHz, CDCl3
1.56
2.14
5.12
7.04
7.05
7.06
7.07
7.20
7.25
7.27
7.29
7.30
7.33
7.35
7.36
7.39
7.40
7.42
2.19
12.30
12.12
12.15
1.00
1.00
f1 (ppm)

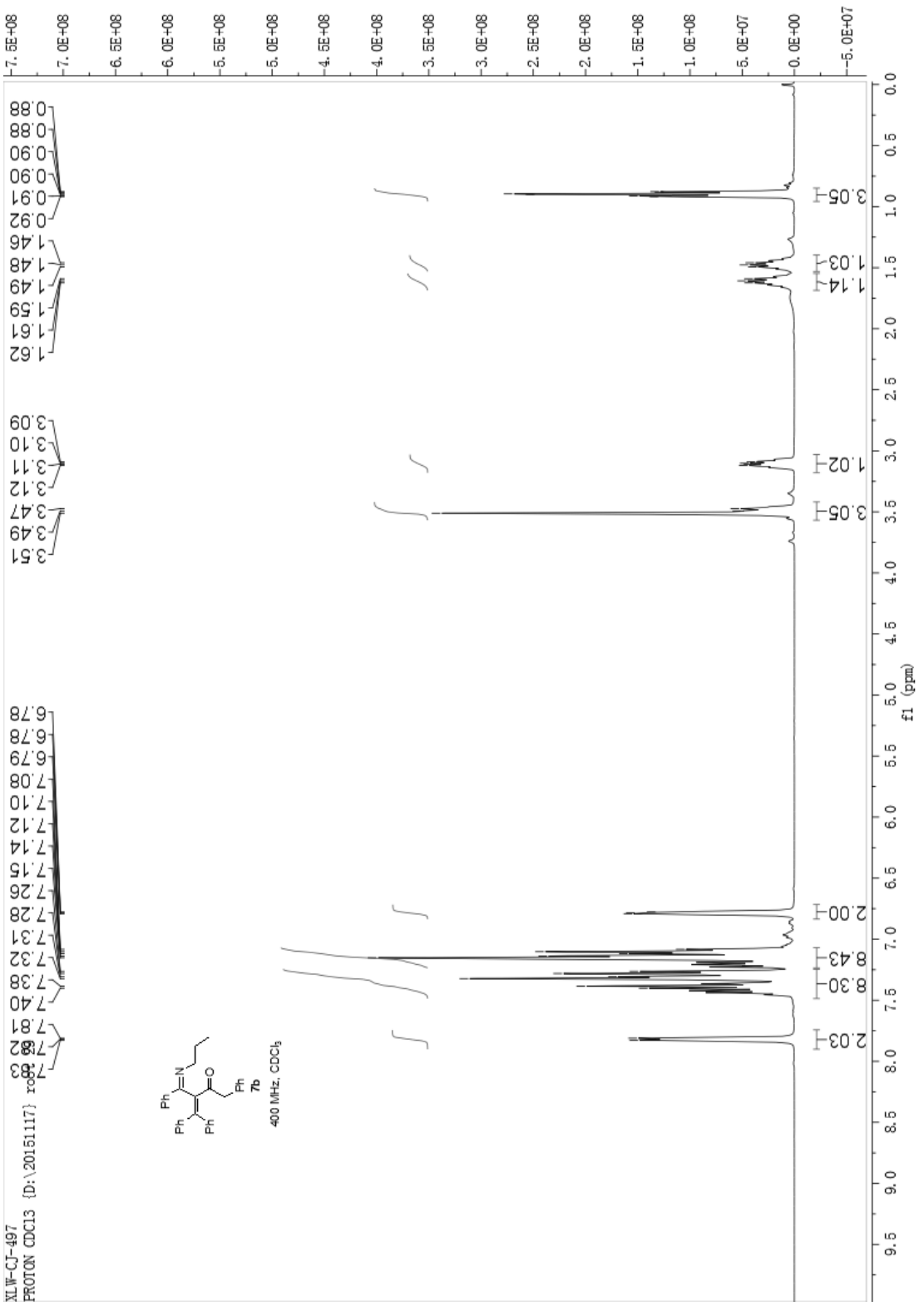

XLW-CJ-5(A)
C13CPD CDCl3 {D:\20151210} root
29.37
61.30
76.73
77.04
77.36
108.14
115.11
126.23
127.45
127.63
127.69
128.09
128.37
128.54
128.56
128.66
128.76
129.29
135.26
135.76
135.99
136.66
205.72
208.
Ph
Ph
Ph
O
Me
5o
100 MHz, CDCl3
f1 (ppm)

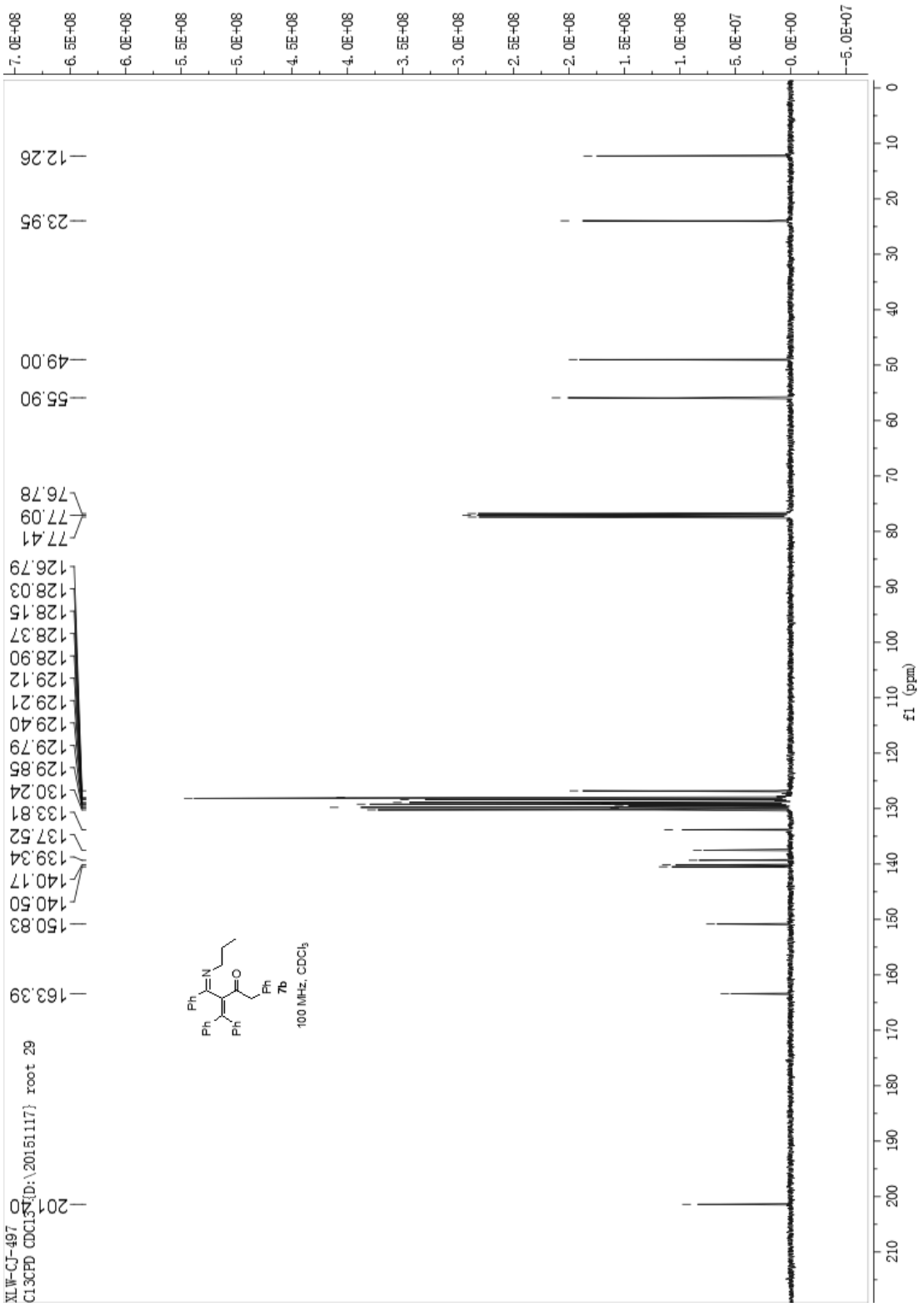

XLW-CJ-478
PROTON CDCl3 {D:\20151021\
6
400 MHz, CDCl3
Ph
Ph
Ph
Ph
O
f1 (ppm)

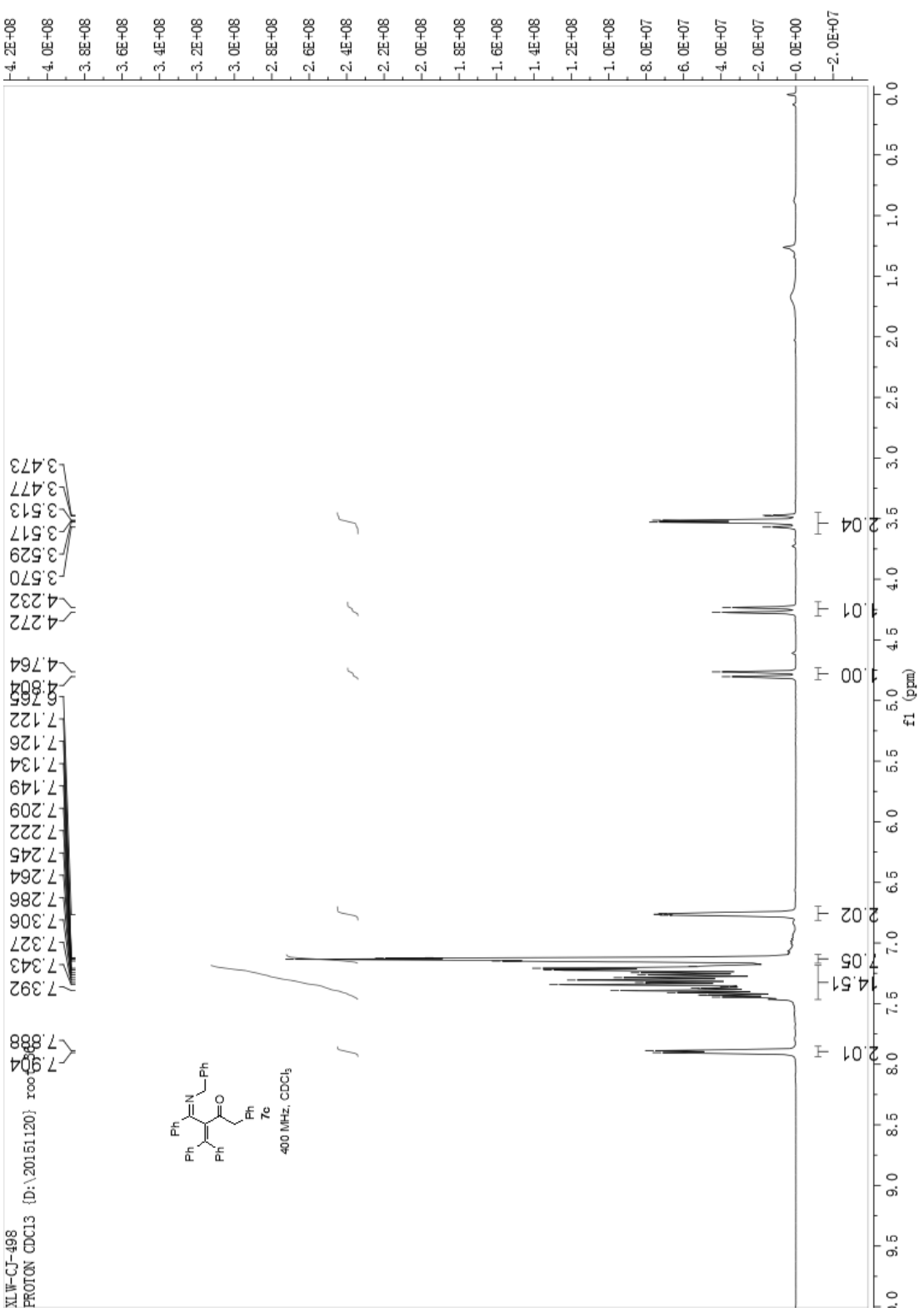

XLW-CJ-478
C13CPD CDCl3 {D:\20151021} root 53
197.80
157.23
142.71
142.53
139.79
137.90
137.10
135.10
130.96
130.71
130.15
128.22
127.80
127.37
127.28
127.03
126.67
126.59
126.50
77.47
77.09
76.77
39.73
34.57
Ph
Ph
Ph
Ph
O
6
100 MHz, CDCl3
f1 (ppm)

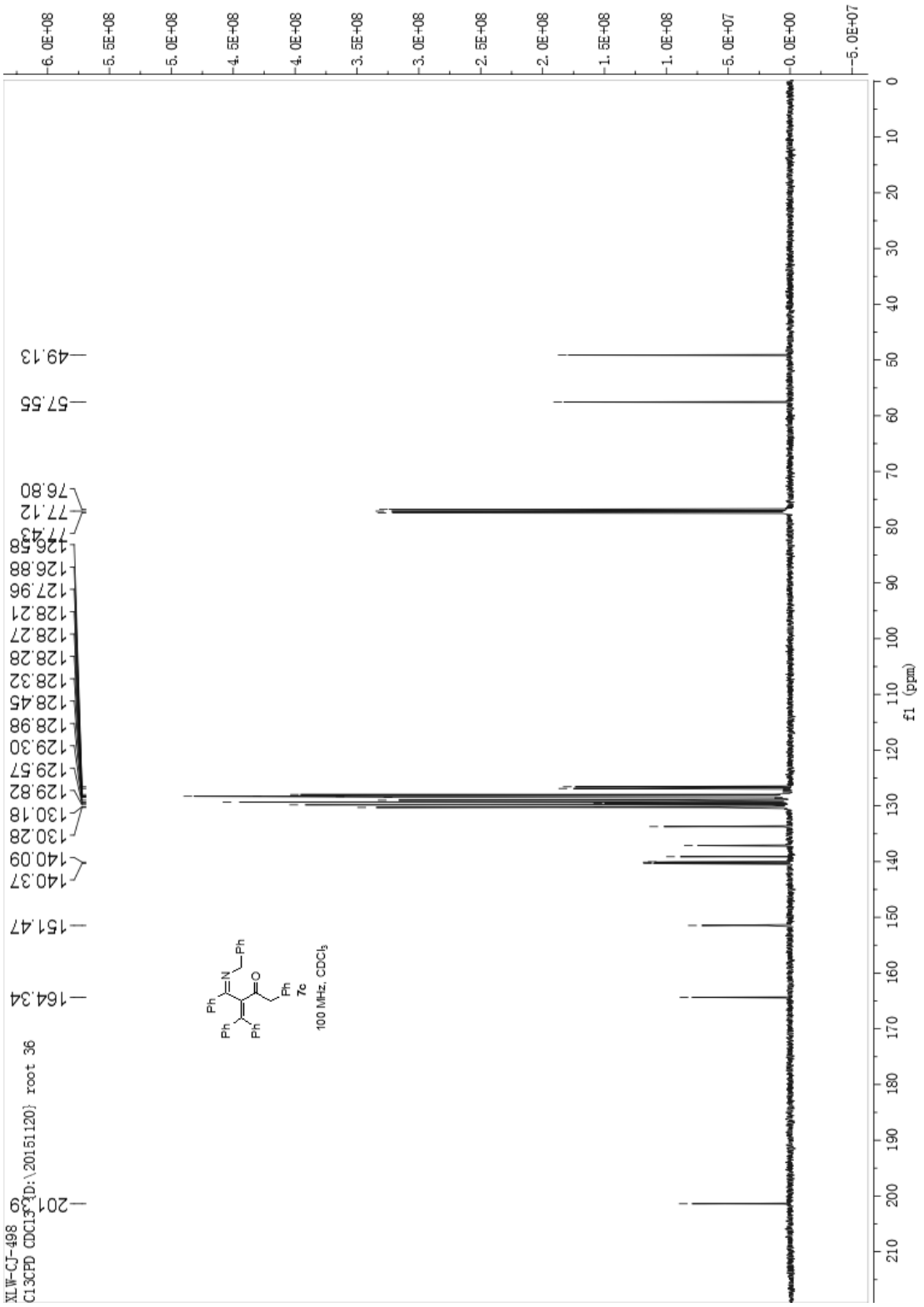

XLW-CJ-502
PROTON CDC13 {D:\20151130} root
400 MHz, CDCl3
7a
f1 (ppm)

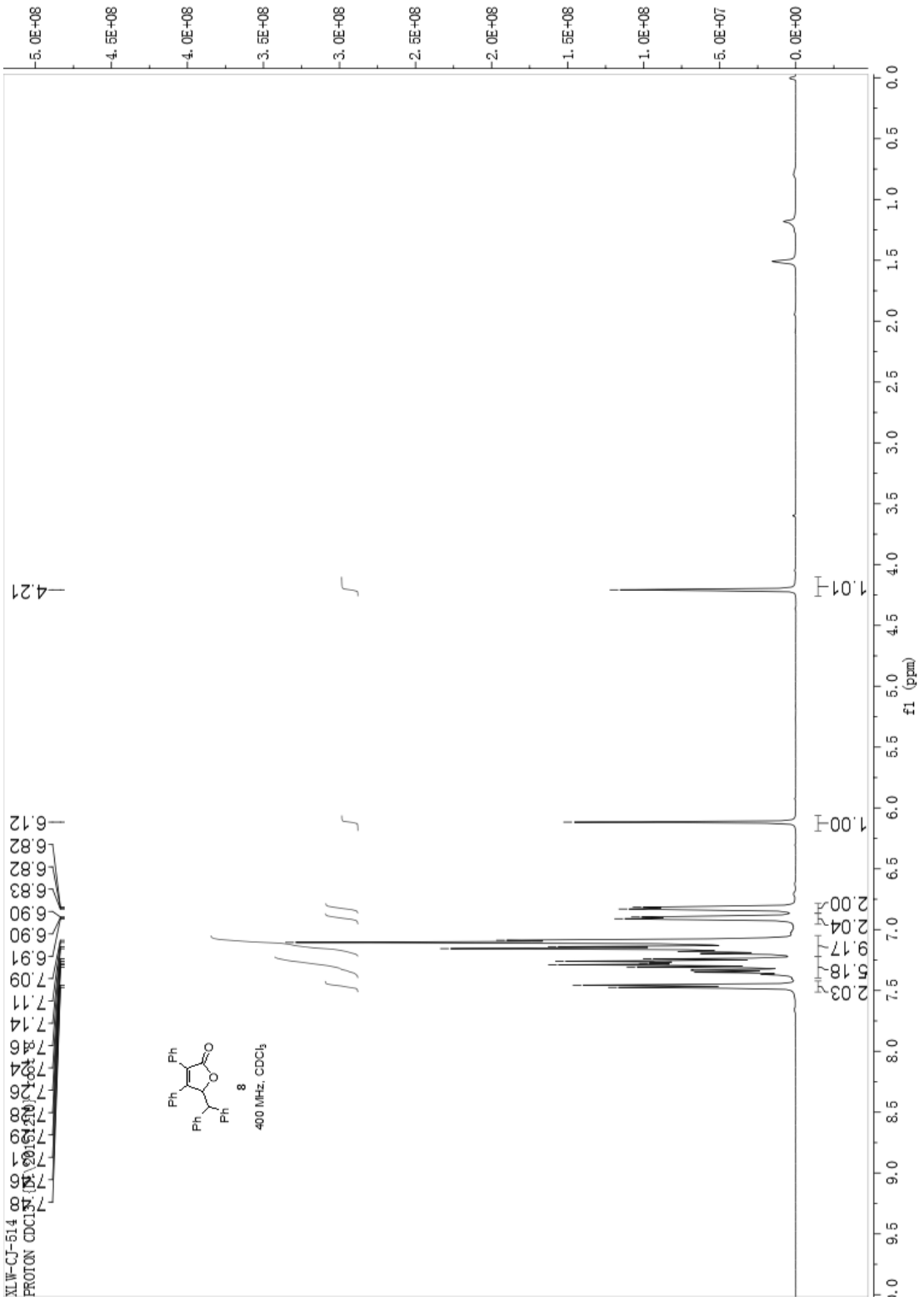

XLW-CJ-502
C13CPD CDCl3 {D:\20151130} root 41
20.93
21.02
29.94
49.04
61.62
76.78
77.10
77.42
126.78
128.00
128.15
128.16
128.36
128.93
129.13
129.26
129.44
129.81
130.29
133.86
137.57
139.46
140.21
140.54
150.91
163.38
201.77
Ph
N
O
Ph
Ph
Ph
7a
100 MHz, CDCl3
f1 (ppm)

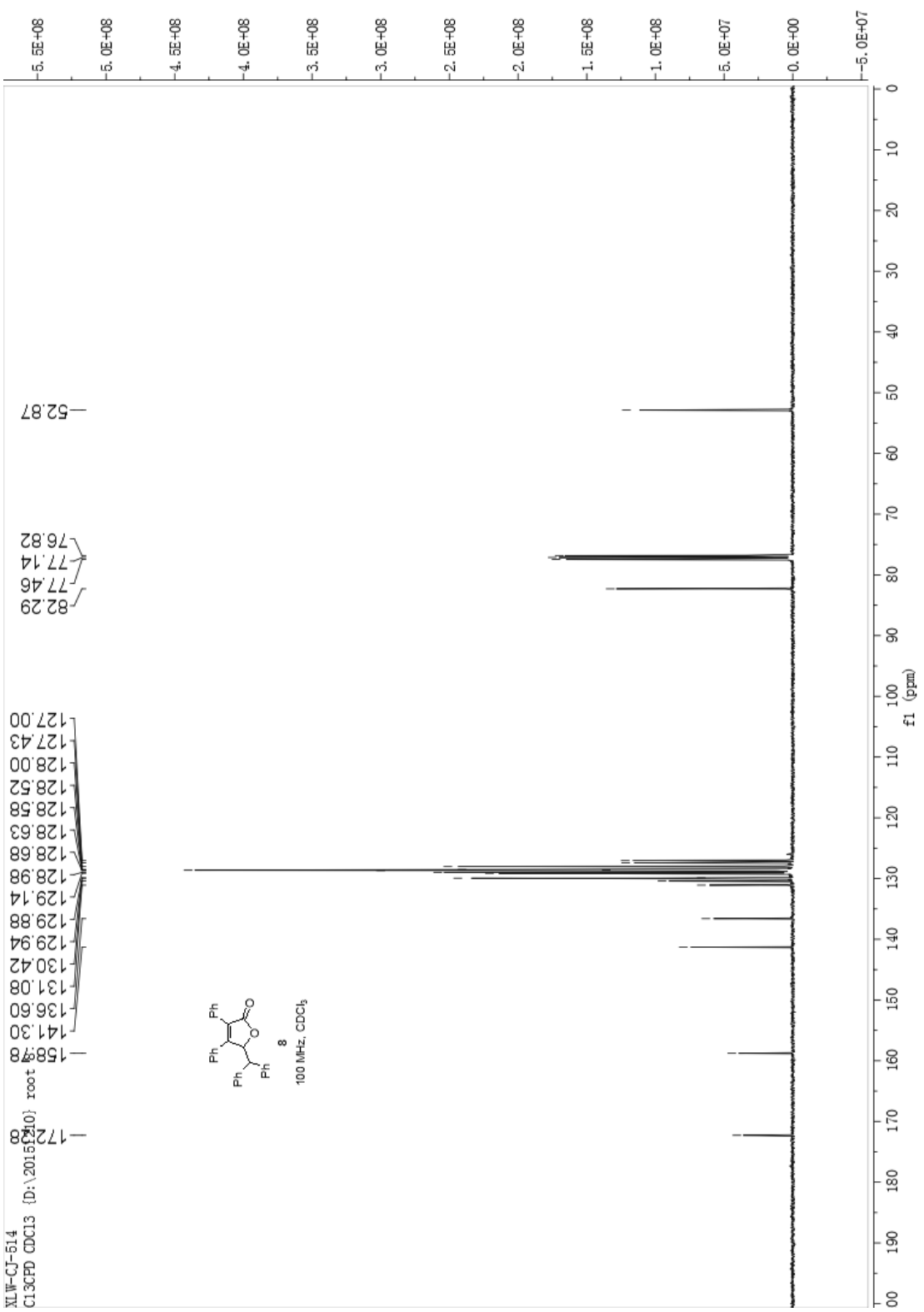

XLW-CJ-497
PROTON CDCl3 {D:\20151117} rob
7b
400 MHz, CDCl3
f1 (ppm)


XLW-CJ-497
C13CPD CDCl3 {D:\20151117} root 29
201.40
163.39
150.83
140.50
140.17
139.34
137.52
133.81
130.24
129.85
129.79
129.40
129.21
129.12
128.90
128.37
128.15
128.03
126.79
77.41
77.09
76.78
55.90
49.00
23.95
12.26
Ph
N
O
Ph
Ph
Ph
7b
100 MHz, CDCl3
f1 (ppm)


XLW-CJ-498
PROTON CDC13 {D:\20151120} roo
400 MHz, CDCl3
7e
Ph
Ph
Ph
Ph
O
N
7.888
7.904
7.392
7.343
7.327
7.306
7.286
7.264
7.245
7.222
7.209
7.149
7.134
7.126
7.122
6.765
4.804
4.764
4.272
4.232
3.570
3.529
3.517
3.513
3.477
3.473
2.01
14.51
7.05
2.02
1.00
1.01
2.04
f1 (ppm)

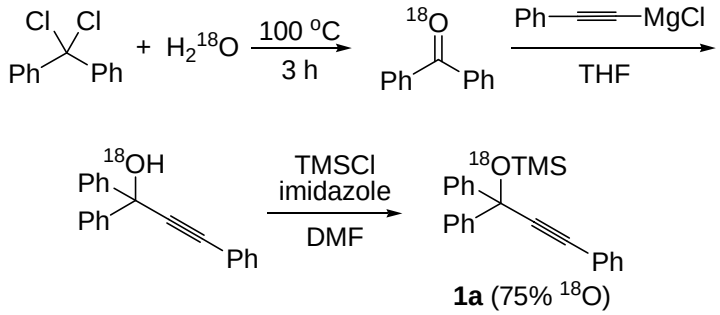

XLW-CJ-498
C13CPD CDCl3 1D:\20151120\ root 36
201.69
164.34
151.47
140.37
140.09
130.28
130.18
129.82
129.57
129.30
128.98
128.45
128.32
128.28
128.27
128.21
127.96
126.88
126.58
77.43
77.12
76.80
57.55
49.13
Ph
N
Ph
O
Ph
Ph
Ph
7e
100 MHz, CDCl3
f1 (ppm)


XLW-CJ-514
PROTON CDCl3
8
400 MHz, CDCl3
f1 (ppm)


XLW-CJ-514
C13CPD CDCl3 {D:\2016\210} root
8
100 MHz, CDCl3
f1 (ppm)
52.87
76.82
77.14
77.46
82.29
127.00
127.43
128.00
128.52
128.58
128.63
128.68
128.98
129.14
129.88
129.94
130.42
131.08
136.60
141.30
158.78
172.28

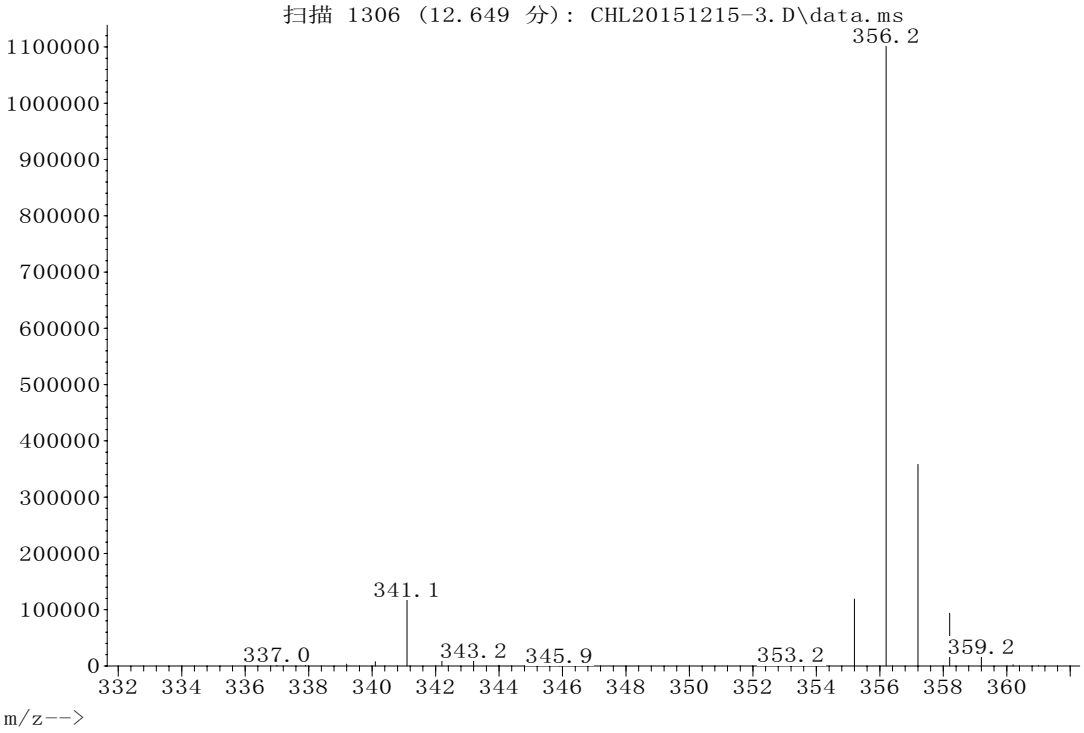
^{18}O-Labeling Experiments

^{18}O-labelled **1a** was prepared from dichlorodiphenylmethane and $H_2{}^{18}O$ (90% ^{18}O).[1]

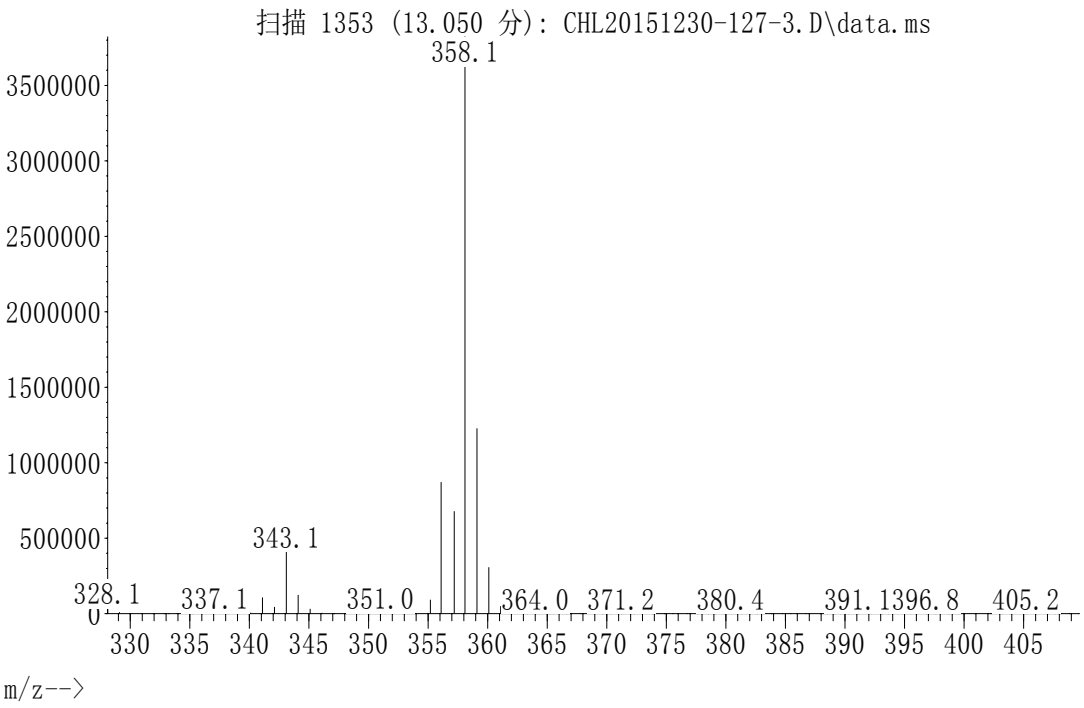


[1] (a) J. M. Risley and R. L. Van Etten, *J. Am. Chem. Soc.*, 1980, **102**, 4609; (b) H. Zheng, M. Lejkowski and D. G. Hall, *Chem. Sci.*, 2011, **2**, 1305.

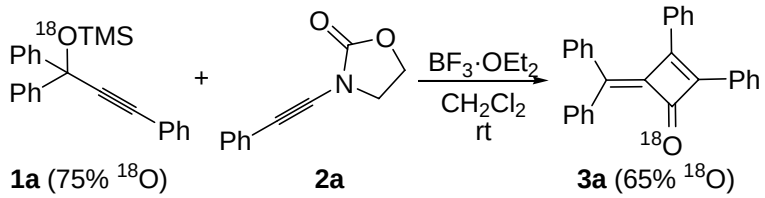
Mass Analysis of **1a**:



Mass Analysis of **1a** (^{18}O labelled):

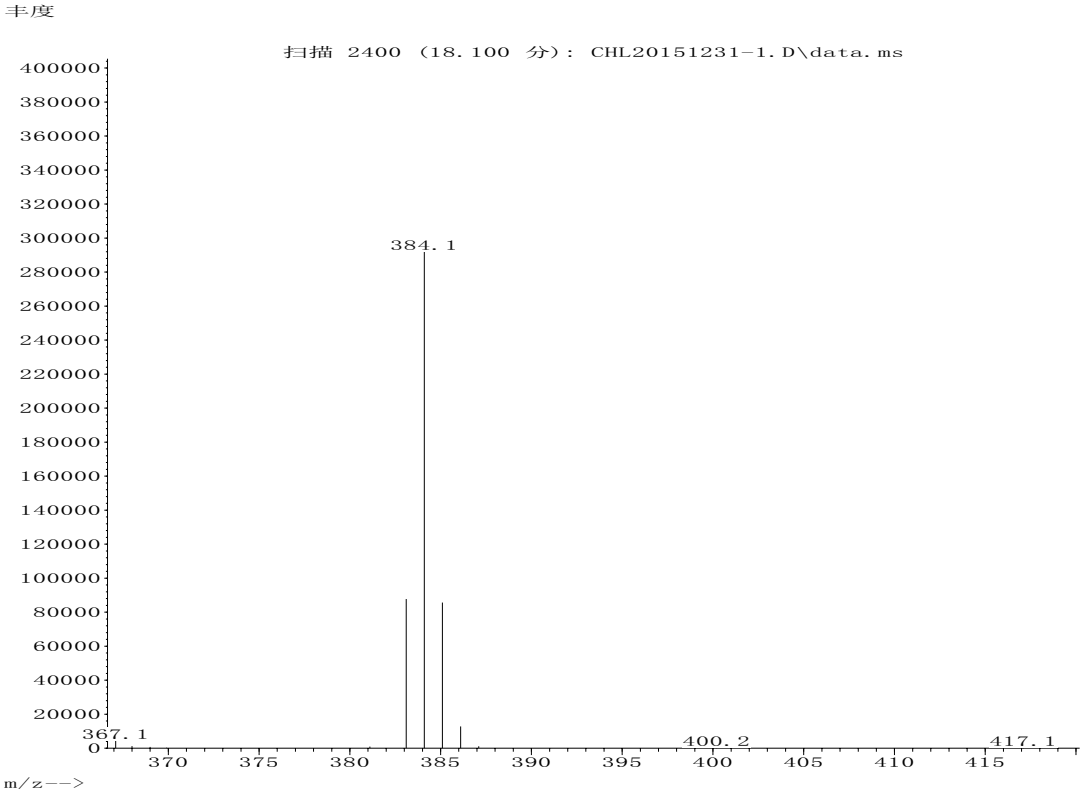


The synthesis of ^{18}O-labelled alkylidenecyclobutenone **3a**.

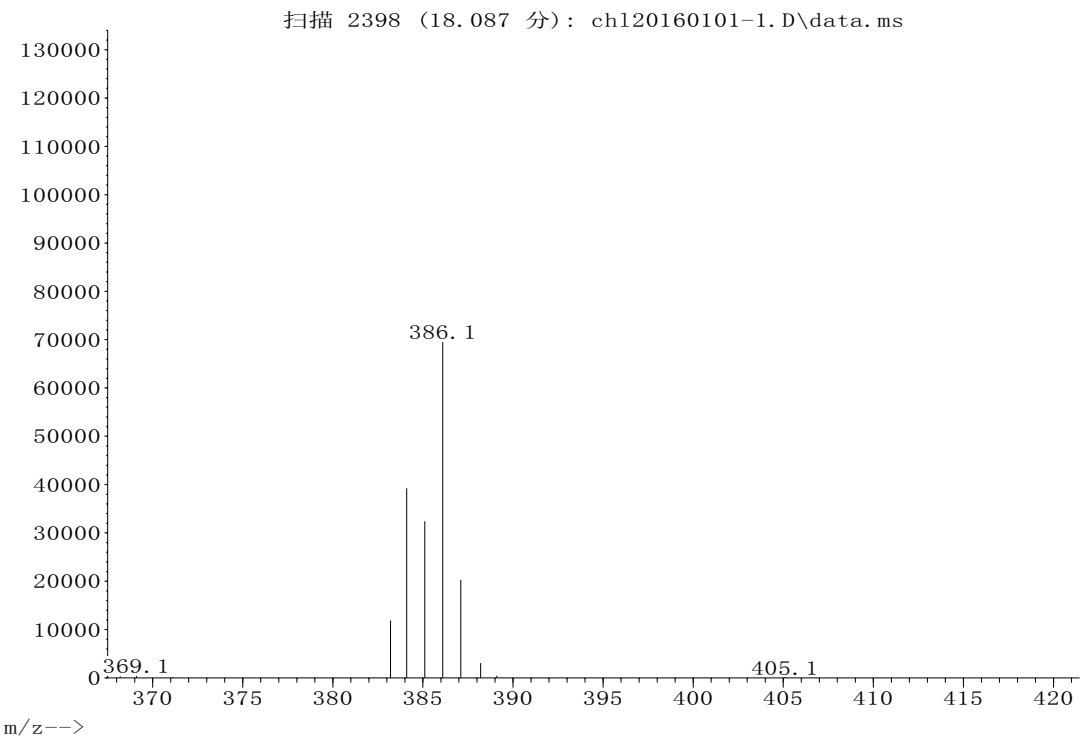


1a (75% ^{18}O) **2a** **3a** (65% ^{18}O)

Mass Analysis of **3a**:



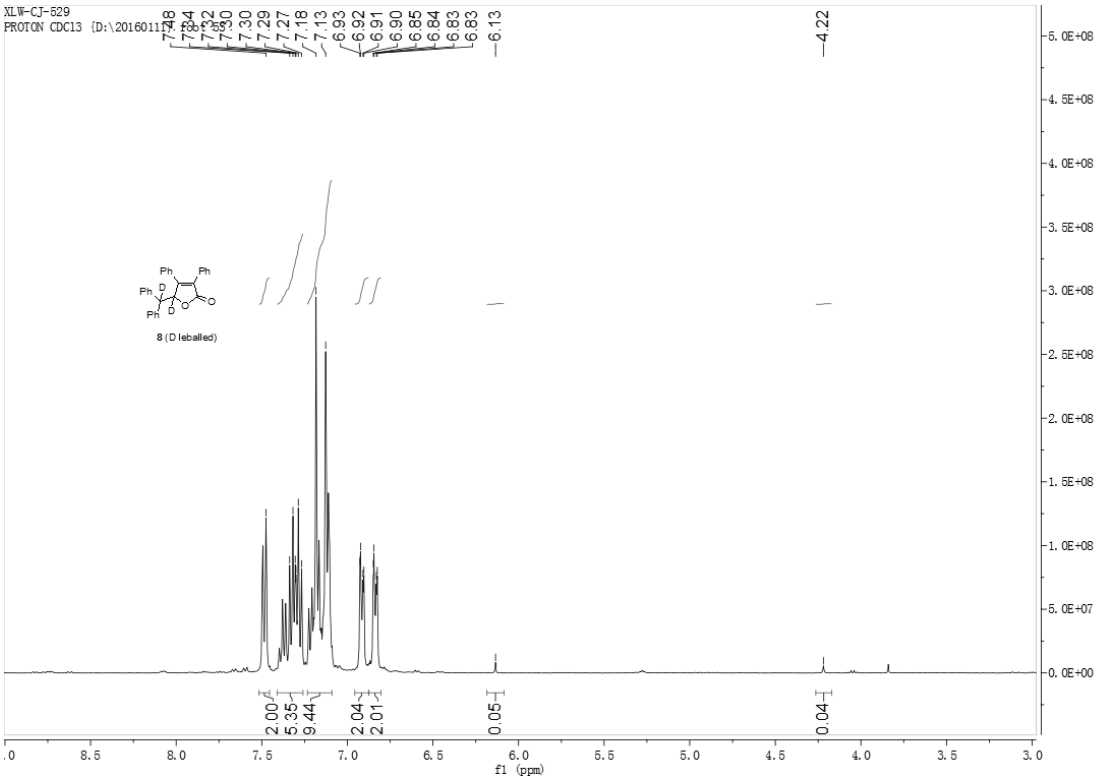
Mass Analysis of **3a** (^{18}O labelled):



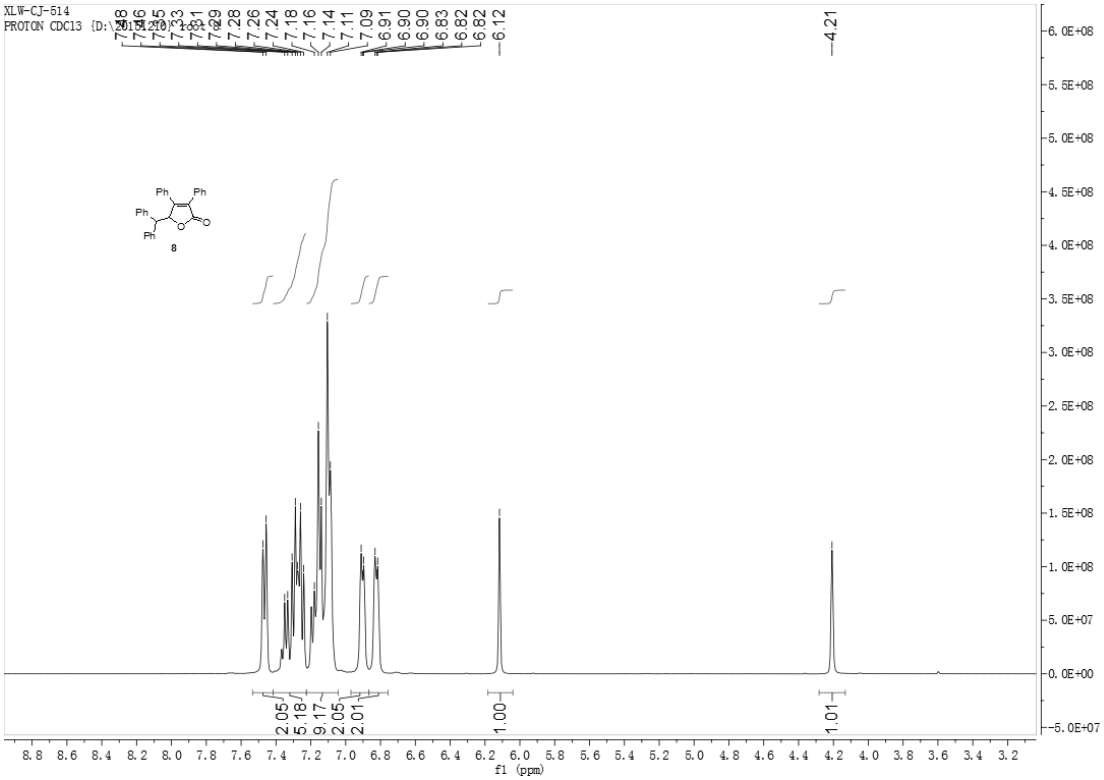
D-Labeling Experiments

D-Labelled 8 was prepared according to the procedure for the synthesis of 5-benzhydryl-3,4-diphenylfuran-2(5*H*)-one **8** except that 0.1 mL D_2O (99% D) was added.

^{1}H NMR of **D-Labelled 8:**

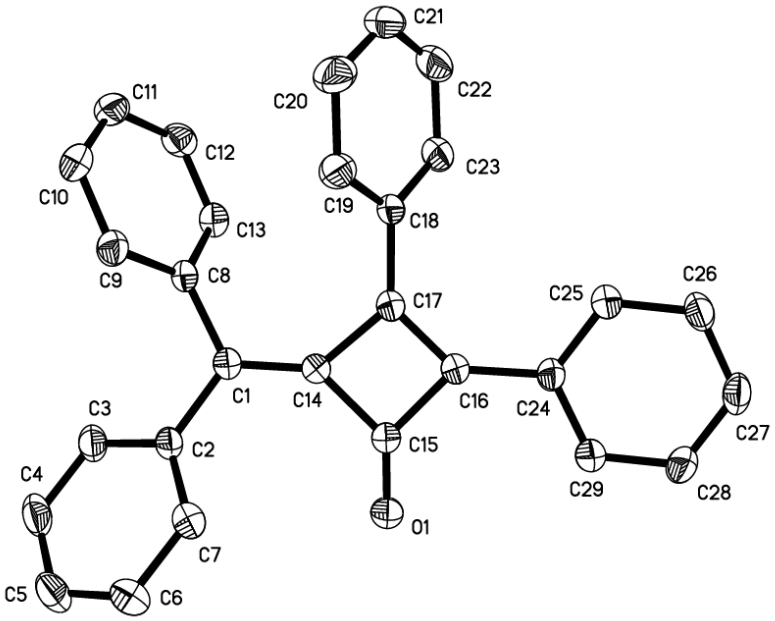


^{1}H NMR of **8:**



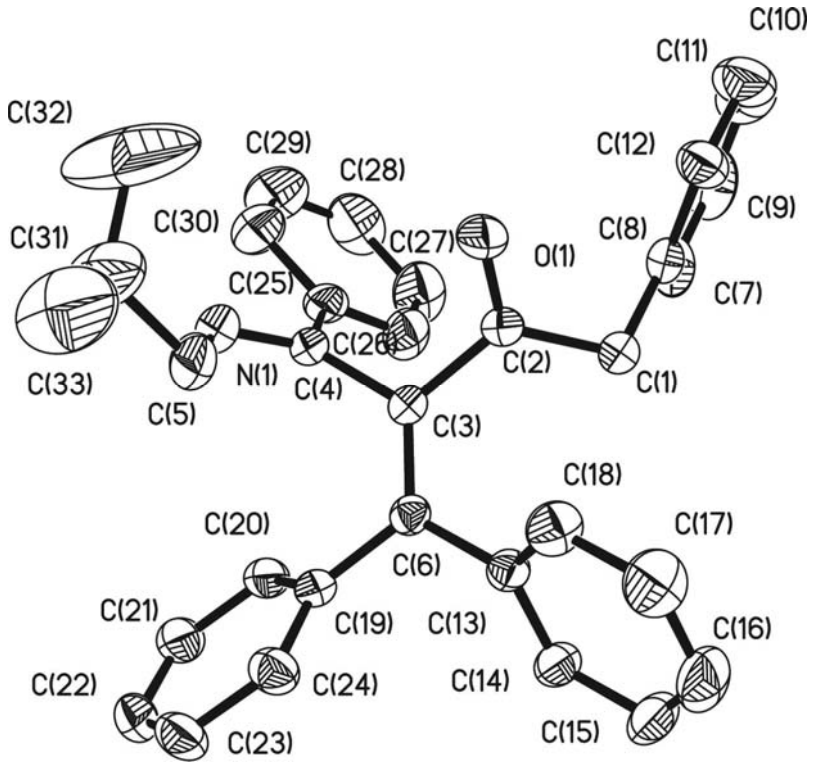
Crystal Structure of **3a**.

This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1446541. Further information can be found in the CIF file.



Crystal Structure of **7a**.

This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1446542. Further information can be found in the CIF file.



Crystal Structure of **8**.

This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1446543. Further information can be found in the CIF file.