Supporting Information

An Efficient Approach toward Formation of Polycyclic Coumarin Derivatives via Carbocation-initiated [4 + 2] Cycloaddition and Atom-Economic Photo-irradiated Cyclization

Ling Chen,[a] Yu-Ming Cui,[a] Zheng Xu,[a] Jian Cao,[a] Zhan-Jiang Zheng,[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

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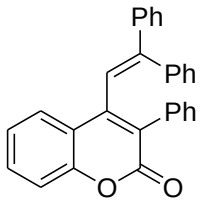
General experimental procedures

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 4-vinylcoumarin 3

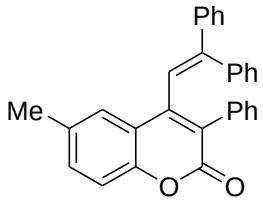


3a

4-(2,2-diphenylvinyl)-3-phenyl-2*H*-chromen-2-one 3a

A vial was charged with and $ZnBr_2$ (67.6 mg, 0.3 mmol), propargyl silyl ether **1b** (116.0 mg, 0.3 mmol) and ynamide **2c** (56.2 mg, 0.3 mmol) and evacuated under high vacuum and backfilled with N_2. CH_2Cl_2 (3 mL) was next added and the solution was stirred at rt. Upon reaction completion (8 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** (88.9 mg, 74%) as a colorless solid, mp 182-184 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73-7.75 (m, 1H), 7.49-7.53 (m, 1H), 7.19-7.31 (m, 11H), 6.99-7.04 (m, 4H), 6.70 (s, 1H), 6.57 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.1, 152.8, 148.4, 148.0, 142.0, 138.5, 134.0, 131.3, 130.4, 129.5, 128.4, 128.3, 128.1, 128.0, 127.65, 127.61, 126.7, 126.5, 124.2, 120.8, 120.4, 116.8. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{29}H_{21}O_2$, 401.1536; found

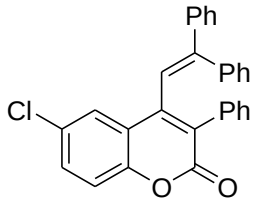
401.1537.



3b

4-(2,2-diphenylvinyl)-6-methyl-3-phenyl-2*H*-chromen-2-one 3b

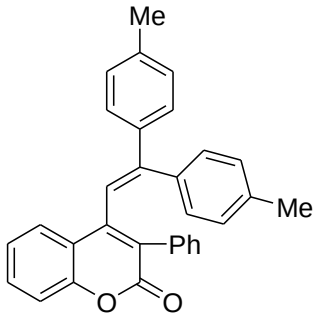
Colorless solid (141.0 mg, 68%), mp 199-201 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (s, 1H), 7.05-7.22 (m, 11H), 6.87-6.94 (m, 4H), 6.60 (s, 1H), 6.46 (d, J = 7.6 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 151.0, 148.3, 148.0, 142.1, 138.6, 134.1, 133.9, 132.4, 130.5, 129.5, 128.5, 128.4, 128.3, 128.1, 128.0, 127.6, 127.5, 126.4, 126.3, 121.0, 120.1, 116.5, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_2$, 437.1512; found 437.1517.



3c

6-chloro-4-(2,2-diphenylvinyl)-3-phenyl-2*H*-chromen-2-one 3c

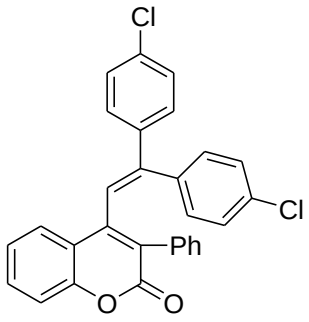
Yellow oil (97.8 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, J = 2.4 Hz, 1H), 7.42-7.46 (m, 1H), 7.18-7.34 (m, 10H), 7.00-7.06 (m, 4H), 6.63 (s, 1H), 6.60 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.6, 151.2, 149.2, 146.9, 141.7, 138.4, 133.5, 131.2, 130.2, 129.6, 129.4, 128.7, 128.4, 128.3, 128.1, 127.9, 127.7, 127.4, 126.1, 121.4, 119.9, 118.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}ClNaO_2$, 457.0966; found 457.0969.



3d

4-(2,2-di*p*-tolylvinyl)-3-phenyl-2*H*-chromen-2-one 3d

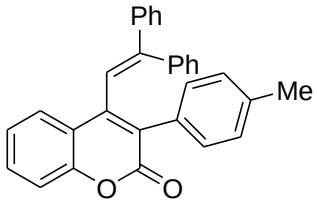
Yellow oil (83.5 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 7.6 Hz, 1H), 7.47-7.49 (m, 1H), 7.34 (d, J = 8.0 Hz, 1H), 7.10-7.23 (m, 8H), 7.01 (d, J = 7.2 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 6.61 (s, 1H), 6.47 (d, J = 8.0 Hz, 2H), 2.34 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.3, 152.8, 148.43, 148.40, 139.4, 138.4, 137.9, 135.8, 134.1, 131.3, 130.4, 129.5, 129.0, 128.6, 128.3, 127.6, 126.8, 126.3, 124.2, 120.5, 119.6, 116.7, 21.25, 21.23. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{24}NaO_2$, 451.1669; found 451.1666.



3e

4-(2,2-bis(4-chlorophenyl)vinyl)-3-phenyl-2*H*-chromen-2-one 3e

Yellow oil (83.1 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.72 (m, 1H), 7.53-7.55 (m, 1H), 7.38 (d, J = 8.4 Hz, 1H), 7.19-7.29 (m, 6H), 7.11 (d, J = 8.4 Hz, 2H), 6.98-7.03 (m, 4H), 6.72 (s, 1H), 6.44 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 152.8, 147.2, 146.1, 139.9, 136.5, 134.8, 134.4, 133.7, 131.6, 130.6, 130.3, 129.5, 128.7, 128.4, 127.8, 127.7, 126.5, 126.3, 124.4, 121.6, 120.2, 116.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{18}Cl_2NaO_2$, 491.0576; found 491.0566.

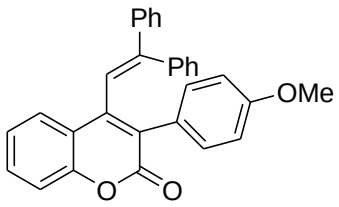


3f

4-(2,2-diphenylvinyl)-3-*p*-tolyl-2*H*-chromen-2-one 3f

Colorless solid (89.5 mg, 72%), mp 185-187 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70-7.72 (m, 1H), 7.46-7.50 (m, 1H), 7.20-7.34 (m, 8H), 7.01-7.05 (m, 4H), 6.93 (d, J = 8.0 Hz, 2H), 6.70 (s, 1H), 6.62 (d, J = 7.2 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.2, 152.8, 148.2, 147.5, 142.1, 138.6, 137.4, 131.1, 131.0, 130.2,

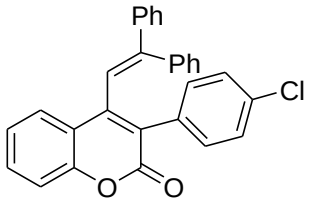
129.4, 128.38. 128.36, 128.35, 128.32, 128.1, 127.9, 126.7, 126.6, 124.1, 121.0, 120.2, 116.7, 21.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_2$, 437.1512; found 437.1513.



3g

4-(2,2-diphenylvinyl)-3-(4-methoxyphenyl)-2*H*-chromen-2-one 3g

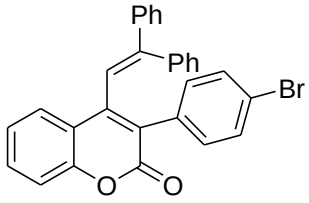
Colorless solid (107.2 mg, 83%), mp 192-194 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 7.2 Hz, 1H), 7.48-7.49 (m, 1H), 7.15-7.34 (m, 8H), 6.96-7.05 (m, 4H), 6.76 (d, J = 8.0 Hz, 2H), 6.71 (s, 1H), 6.62 (d, J = 8.0 Hz, 2H), 3.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 159.1, 152.7, 148.1, 147.3, 142.0, 138.6, 131.7, 131.1, 129.4, 128.4, 128.3, 128.1, 127.9, 126.6, 126.3, 126.1, 124.2, 121.0, 120.4, 116.7, 113.2, 55.2. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{22}O_3$, 431.1642; found 431.1655.



3h

3-(4-chlorophenyl)-4-(2,2-diphenylvinyl)-2*H*-chromen-2-one 3h

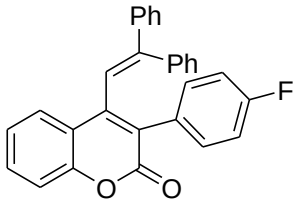
Colorless solid (84.1 mg, 64%), mp 207-209 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H), 7.51-7.55 (m, 1H), 7.14-7.37 (m, 10H), 7.02-7.06 (m, 2H), 6.89-6.91 (m, 2H), 6.71 (s, 1H), 6.57 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 152.8, 148.9, 148.2, 141.8, 138.4, 133.6, 132.4, 131.8, 131.7, 129.4, 128.7, 128.5, 128.3, 128.2, 128.1, 127.8, 126.6, 125.1, 124.4, 120.3, 116.8. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}ClNaO_2$, 457.0966; found 457.0968.



3i

3-(4-bromophenyl)-4-(2,2-diphenylvinyl)-2*H*-chromen-2-one 3i

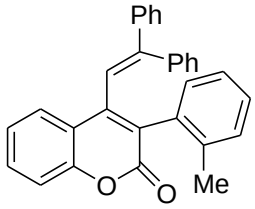
Colorless solid (85.5 mg, 59%), mp 199-201 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75-7.77 (m, 1H), 7.52-7.54 (m, 1H), 7.20-7.37 (m, 10H), 7.03-7.07 (m, 2H), 6.84 (d, J = 8.4 Hz, 2H), 6.71 (s, 1H), 6.57 (d, J = 7.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 152.8, 149.0, 148.1, 141.8, 138.3, 132.9, 132.0, 131.6, 130.8, 129.4, 128.7, 128.4, 128.33, 128.27, 128.1, 126.6, 125.1, 124.4, 121.9, 120.30, 120.27, 116.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}BrNaO_2$, 501.0461; found 501.0482.



3j

4-(2,2-diphenylvinyl)-3-(4-fluorophenyl)-2*H*-chromen-2-one 3j

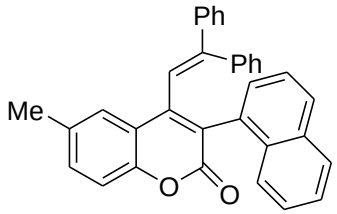
Colorless solid (87.9 mg, 70%), mp 203-205 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.0 Hz, 1H), 7.52-7.54 (m, 1H), 7.17-7.37 (m, 8H), 7.02-7.06 (m, 2H), 6.88-6.94 (m, 4H), 6.71 (d, J = 1.6 Hz, 1H), 6.58 (d, J = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.2 (d, J = 246 Hz), 161.1, 152.8, 148.7, 148.1, 141.9, 138.4, 132.2 (d, J = 9 Hz), 131.5, 129.9 (d, J = 3 Hz), 129.4, 128.6, 128.4, 128.3, 128.2, 128.0, 126.6, 125.3, 124.4, 120.5, 120.4, 116.8, 114.6 (d, J = 21 Hz). HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}FNaO_2$, 441.1261 found 441.1270.



3k

4-(2,2-diphenylvinyl)-3-*o*-tolyl-2*H*-chromen-2-one 3k

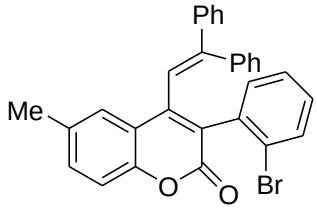
Colorless solid (100.7 mg, 81%), mp 218-220 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 7.6 Hz, 1H), 7.49-7.51 (m, 1H), 7.37 (d, J = 8.4 Hz, 1H), 7.05-7.30 (m, 13H), 6.59-6.66 (m, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 153.0, 149.0, 148.4, 142.3, 138.8, 133.7, 131.4, 130.6, 130.0, 129.8, 128.4, 128.33, 128.30, 128.14, 128.09, 126.9, 126.8, 125.2, 124.3, 120.7, 120.3, 116.9, 19.3. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{30}H_{23}O_2$, 415.1693 found 415.1685.



3l

4-(2,2-diphenylvinyl)-6-methyl-3-(naphthalen-1-yl)-2*H*-chromen-2-one 3l

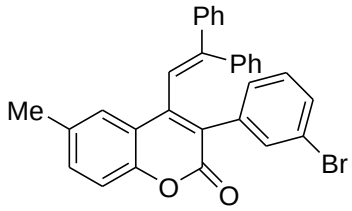
Colorless solid (159.6 mg, 69%), mp 202-204 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 6.8 Hz, 1H), 7.59 (d, J = 8.4 Hz, 1H), 7.45 (s, 1H), 6.40-7.31 (m, 18H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 151.3, 150.2, 148.0, 142.1, 138.7, 134.1, 133.5, 132.7, 131.6, 131.3, 129.6, 128.7, 128.42, 128.38, 128.2, 128.1, 127.8, 126.7, 126.2, 125.4, 125.3, 124.9, 121.3, 120.1, 116.7, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{34}H_{24}NaO_2$, 487.1669 found 487.1664.



3m

3-(2-bromophenyl)-4-(2,2-diphenylvinyl)-6-methyl-2*H*-chromen-2-one 3m

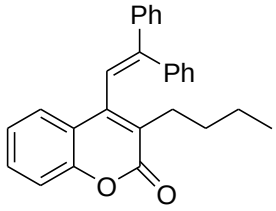
Colorless solid (81.4 mg, 55%), mp 162-164 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.45 (m, 2H), 7.11-7.24 (m, 8H), 6.94-7.01 (m, 4H), 6.10-6.66 (m, 4H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.7, 151.2, 149.8, 148.1, 142.1, 138.6, 135.1, 134.2, 132.9, 132.4, 132.1, 130.0, 129.3, 128.7, 128.5, 128.4, 128.1, 127.2, 126.7, 125.3, 123.5, 120.6, 119.7, 116.7, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{21}BrNaO_2$, 515.0617 found 515.0618.



3n

3-(3-bromophenyl)-4-(2,2-diphenylvinyl)-6-methyl-2*H*-chromen-2-one 3n

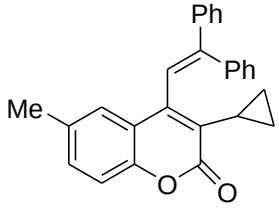
Colorless solid (93.2 mg, 63%), mp 175-177 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (s, 1H), 7.20-7.35 (m, 9H), 7.03-7.09 (m, 3H), 6.97 (s, 1H), 6.89 (d, J = 7.6 Hz, 1H), 6.70 (s, 1H), 6.51 (d, J =7.2 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.9, 150.9, 149.0, 148.7, 141.9, 138.2, 136.1, 134.3, 133.4, 132.8, 130.5, 129.4, 129.1, 128.9, 128.6, 128.5, 128.4, 128.3, 128.1, 126.3, 124.7, 121.4, 120.4, 120.2, 116.6, 21.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{21}BrNaO_2$, 515.0617 found 515.0632.



3o

3-butyl-4-(2,2-diphenylvinyl)-2*H*-chromen-2-one 3o

Yellow oil (63.4 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.60 (m, 1H), 7.37-7.42 (m, 6H), 7.25-7.27 (m, 1H), 7.11-7.17 (m, 4H), 7.04 (d, J = 8.0 Hz, 2H), 6.75 (s, 1H), 2.46 (t, J = 7.6 Hz, 2H), 1.12-1.55 (m, 4H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 152.4, 148.3, 146.7, 141.9, 138.8, 130.4, 129.4, 128.6, 128.5, 128.4, 128.2, 127.0, 126.4, 123.9, 120.7, 119.9, 116.6, 29.8, 28.6, 23.0, 13.9. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}O_2$, 381.1849 found 381.1851.



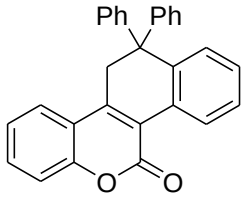
3p

3-cyclopropyl-4-(2,2-diphenylvinyl)-6-methyl-2*H*-chromen-2-one 3p

Colorless solid (53.3 mg, 47%), mp 163-165 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.33-7.38 (m, 6H), 7.05-7.12 (m, 5H), 6.96 (d, J = 7.2 Hz, 2H), 6.78 (s, 1H), 2.25 (s, 3H), 1.18-1.24 (m, 1H), 1.00-1.05 (m, 1H), 0.77-0.79 (m, 1H), 0.62-0.64 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8, 150.2, 148.7, 147.5, 141.9, 139.2, 133.5, 131.3, 129.4, 128.6, 128.5, 128.4, 128.3, 128.2, 126.2, 125.6, 121.1, 119.8, 116.2, 21.0, 12.1, 7.7, 7.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{22}NaO_2$, 401.1512 found 401.1517.

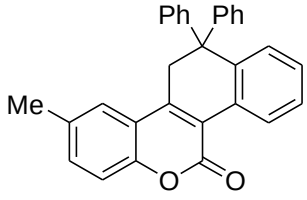
Typical procedure for the synthesis of polycyclic coumarin derivatives 4



4a

12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4a

A solution of **3a** (50.0 mg, 0.125 mmol) in $CDCl_3$ (1 mL) was irradiated using high pressure Hg lamp at rt for 12 h. The solvent was removed to give the pure product **4a** in quantitative yield as a colorless solid, mp 263-265 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 8.0 Hz, 1H), 7.78-7.80 (m, 1H), 7.37-7.47 (m, 2H), 7.18-7.27 (m, 9H), 7.03-7.06 (m, 4H), 6.85 (d, J = 8.0 Hz, 1H), 3.84 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.8, 152.9, 147.3, 144.5, 142.8, 131.4, 130.7, 128.8, 128.3, 128.1, 128.0, 127.2, 126.9, 124.4, 123.8, 119.9, 119.3, 116.9, 51.9, 37.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{20}NaO_2$, 423.1356; found 423.1339.

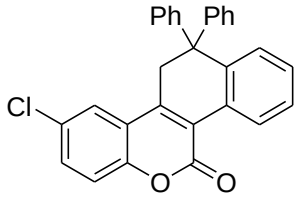


4b

9-methyl-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4b

Colorless solid (50.0 mg, 100%), mp >250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59 (d, J = 7.6 Hz, 1H), 7.57 (s, 1H), 7.36-7.40 (m, 1H), 7.13-7.27 (m, 9H), 7.03-7.06 (m, 4H), 6.86 (d, J = 7.6 Hz, 1H), 3.81 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 151.1, 147.3, 144.5, 142.7, 134.0, 132.6, 130.8, 128.9, 128.8, 128.2, 128.1,

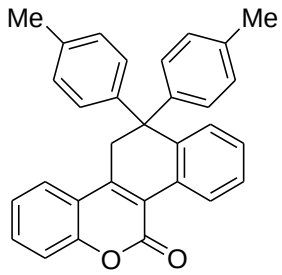
127.9, 127.2, 126.8, 123.6, 119.7, 119.0, 116.6, 51.9, 37.0, 21.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_2$, 437.1512; found 437.1516.



4c

9-chloro-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4c

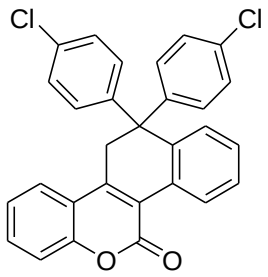
Colorless solid (50.0 mg, 100%), mp >250 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 8.56, (d, J = 8.0 Hz, 1H), 7.76 (d, J = 2.4 Hz, 1H), 7.34-7.43 (m, 2H), 7.19-7.30 (m, 8H), 7.02-7.04 (m, 4H), 6.85 (d, J = 7.6 Hz, 1H), 3.79 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.2, 151.2, 146.0, 144.2, 142.9, 131.3, 130.3, 129.9, 128.9, 128.81, 128.78, 128.2, 128.1, 127.3, 127.0, 123.4, 120.9, 120.5, 118.3, 51.8, 37.0. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}ClNaO_2$, 457.0966; found 457.0968.



4d

12,12-di*p*-tolyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4d

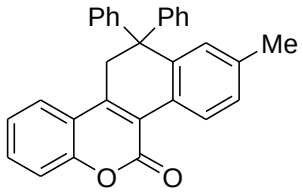
Colorless solid (50.0 mg, 100%), mp >250 ^oC. ^1H NMR (400 MHz, $CDCl_3$): δ 8.58, (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.2 Hz, 1H), 7.21-7.44 (m, 5H), 6.99 (d, J = 8.4 Hz, 4H), 6.91 (d, J = 8.4 Hz, 4H), 6.85 (d, J = 7.6 Hz, 1H), 3.78 (s, 2H), 2.25 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 152.9, 147.5, 143.2, 141.6, 136.4, 131.4, 130.7, 128.8, 128.7, 128.3, 127.9, 127.1, 124.4, 123.9, 119.9, 119.4, 116.9, 51.2, 37.0, 20.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{31}H_{24}NaO_2$, 451.1669; found 451.1681.



4e

12,12-bis(4-chlorophenyl)-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4e

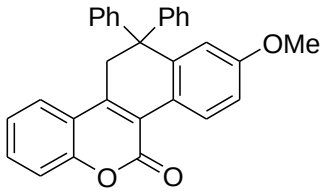
Colorless solid (50.0 mg, 100%), mp >250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.59, (d, J = 7.6 Hz, 1H), 7.77 (d, J = 7.6 Hz, 1H), 7.27-7.51 (m, 5H), 7.19 (d, J = 8.4 Hz, 4H), 6.97 (d, J = 8.4 Hz, 4H), 6.79 (d, J = 7.6 Hz, 1H), 3.77 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.9, 146.7, 142.7, 141.7, 133.1, 131.7, 130.5, 130.1, 128.6, 128.4, 128.3, 127.7, 124.5, 123.7, 119.8, 119.0, 117.1, 51.2, 36.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{18}Cl_2NaO_2$, 491.0576; found 491.0599.



4f

2-methyl-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4f

Colorless solid (50.0 mg, 100%), mp >250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50, (d, J = 8.0 Hz, 1H), 7.77-7.79 (m, 1H), 7.44-7.46 (m, 1H), 7.18-7.30 (m, 9H), 7.03-7.06 (m, 4H), 6.65 (s, 1H), 3.81 (s, 2H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.9, 152.8, 146.4, 144.6, 142.7, 138.4, 131.1, 129.5, 128.8, 128.1, 128.0, 127.9, 126.8, 124.3, 123.7, 120.0, 119.4, 116.9, 51.9, 37.1, 21.6. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_2$, 437.1512; found 437.1519.

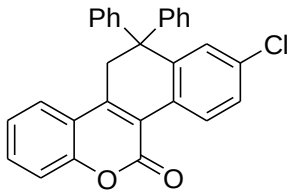


4g

2-methoxy-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4g

Colorless solid (50.0 mg, 100%), mp 232-234 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61,

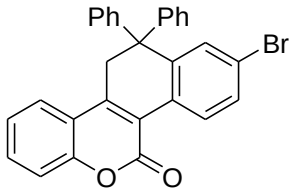
(d, *J* = 9.2 Hz, 1H), 7.76-7.78 (m, 1H), 7.43-7.45 (m, 1H), 7.18-7.28 (m, 8H), 7.03-7.06 (m, 4H), 6.90-6.93 (m, 1H), 6.40 (d, *J* = 2.8 Hz, 1H), 3.82 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 159.0, 152.6, 145.2, 144.9, 144.3, 130.9, 129.6, 128.8, 128.1, 126.9, 124.3, 123.8, 123.6, 119.8, 119.5, 116.8, 116.0, 111.1, 55.2, 52.1, 36.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_3$, 453.1461; found 453.1454.



4h

2-chloro-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4h

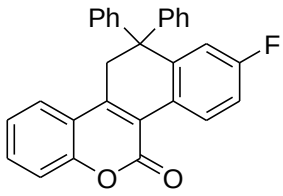
Colorless solid (50.0 mg, 100%), mp 248-250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58, (d, *J* = 8.8 Hz, 1H), 7.78-7.80 (m, 1H), 7.49-7.50 (m, 1H), 7.20-7.30 (m, 9H), 7.01-7.04 (m, 4H), 6.83 (d, *J* = 2.4 Hz, 1H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.9, 147.4, 144.8, 143.7, 134.3, 131.7, 129.4, 129.2, 128.8, 128.7, 128.3, 127.4, 127.2, 124.5, 123.9, 119.10, 119.07, 117.0, 51.9, 36.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}ClNaO_2$, 457.0966; found 457.0986.



4i

2-bromo-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4i

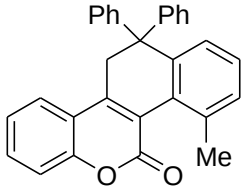
Colorless solid (50.0 mg, 100%), mp 256-258 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.42 (d, *J* = 8.4 Hz, 1H), 7.69-7.72 (m, 1H), 7.39-7.45 (m, 2H), 7.12-7.23 (m, 8H), 6.90-6.95 (m, 5H), 3.74 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 152.9, 147.5, 145.0, 143.7, 137.8, 131.7, 130.4, 129.6, 128.7, 128.3, 127.2, 124.5, 123.9, 122.7, 119.1, 119.0, 117.0, 51.9, 36.9. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}BrNaO_2$, 501.0461; found 501.0475.



4j

2-fluoro-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4i

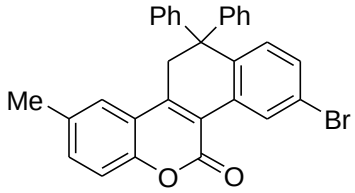
Colorless solid (50.0 mg, 100%), mp 235-237 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.61-8.65 (m, 1H), 7.76-7.79 (m, 1H), 7.45-7.46 (m, 1H), 7.02-7.23 (m, 8H), 7.02-7.04 (m, 5H), 6.56-6.59 (m, 1H), 3.83 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.4 (d, J = 248 Hz), 158.8, 152.8, 146.7, 145.8 (d, J = 6 Hz), 143.8, 131.5, 130.2 (d, J = 8 Hz), 128.7, 128.3, 127.1, 126.9 (d, J = 3 Hz), 124.5, 123.8, 119.2, 116.9, 116.2 (d, J = 24 Hz), 113.9 (d, J = 21 Hz), 52.0, 36.7. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{19}FNaO_2$, 441.1261; found 441.1263.



4k

4-methyl-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4k

Colorless solid (50.0 mg, 100%), mp >250 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74-7.76 (m, 1H), 7.44-7.46 (m, 1H), 7.23-7.28 (m, 5H), 6.70-7.20 (m, 9H), 6.57 (d, J = 7.6 Hz, 1H), 3.82 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.8, 153.1, 149.9, 144.8, 136.6, 131.3, 130.33, 130.27, 128.4, 128.2, 128.1, 127.9, 126.8, 126.0, 124.1, 123.9, 121.4, 119.4, 116.8, 53.7, 37.3, 22.3. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{22}NaO_2$, 437.1512; found 437.1533.



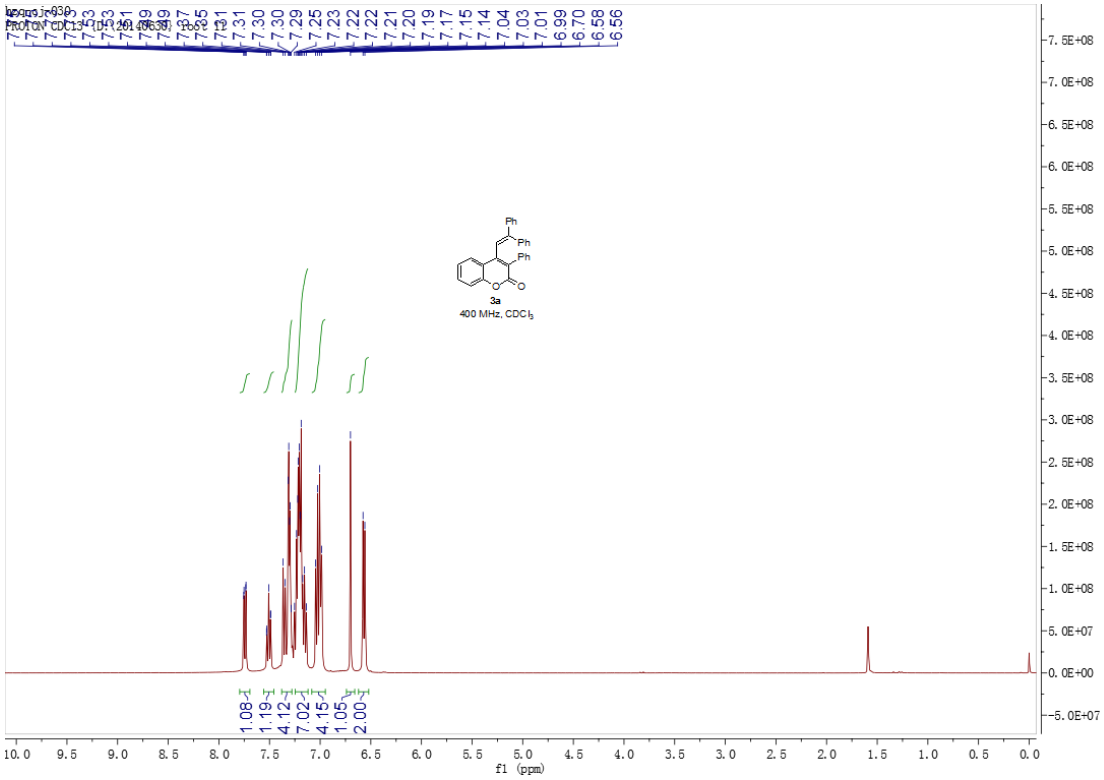
4n

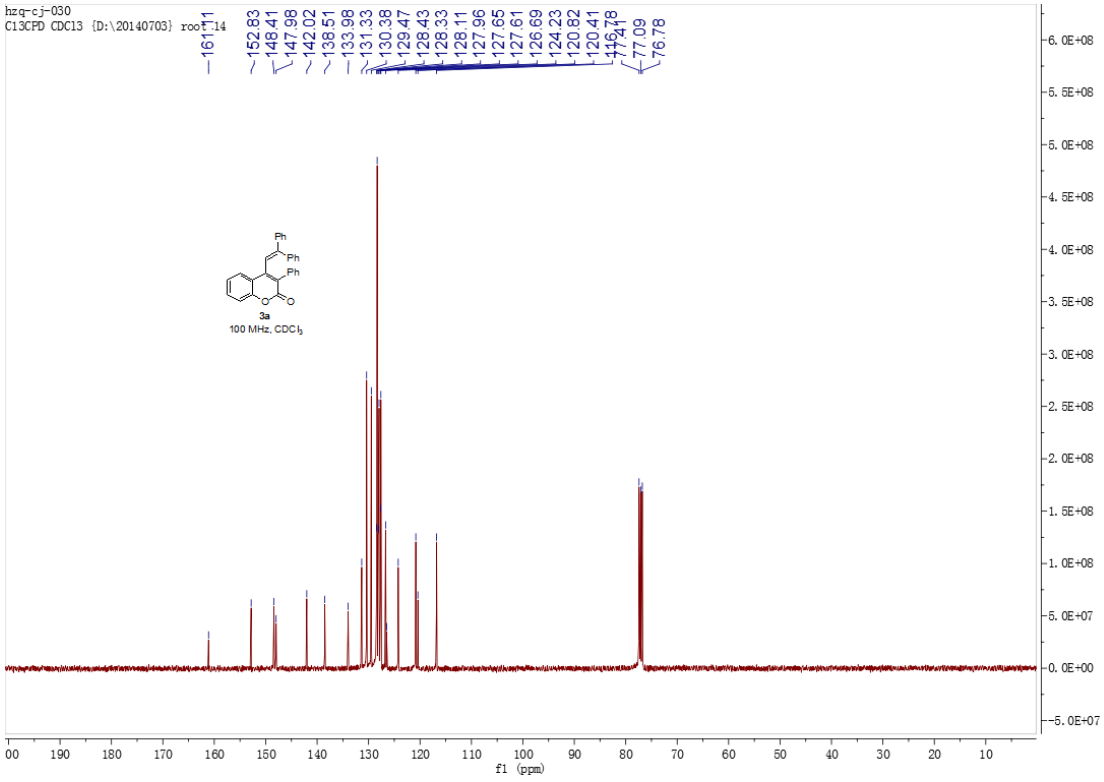
3-bromo-9-methyl-12,12-diphenyl-11,12-dihydronaphtho[1,2-*c*]chromen-5-one 4n

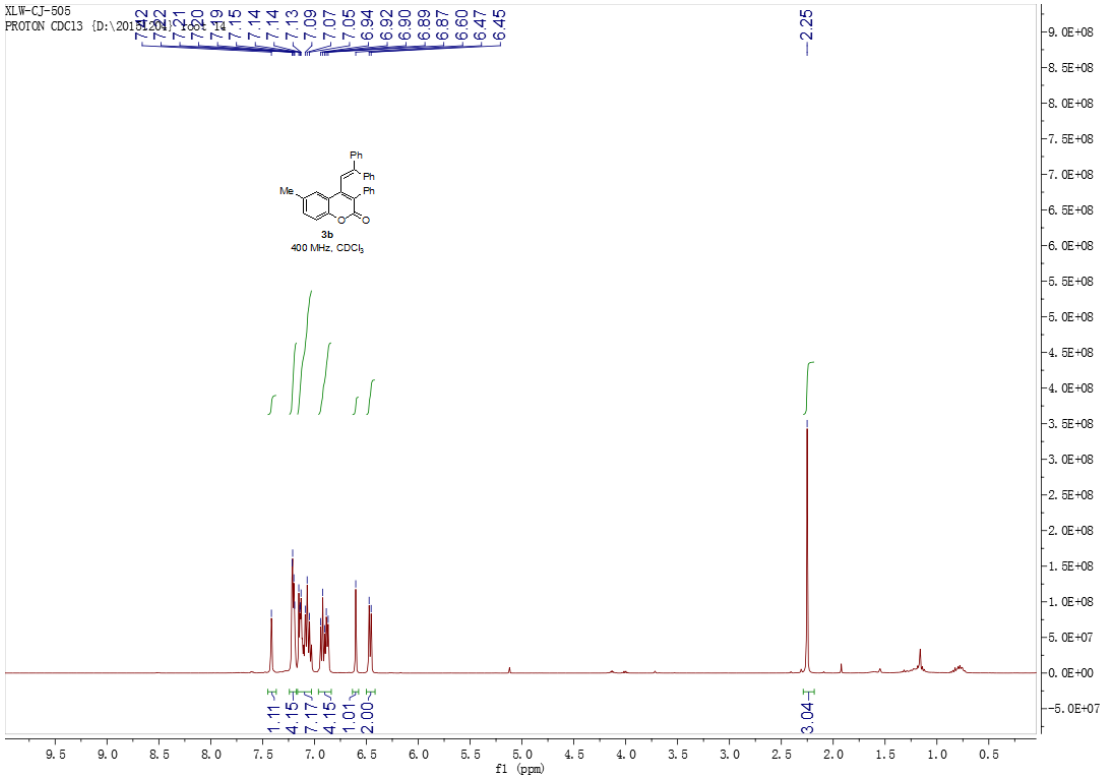
Colorless solid (Purified by crystallization, 41.0 mg, 82%), mp >250 ^{o}C. ^{1}H NMR

(400 MHz, $CDCl_3$): δ 8.78 (d, J = 2.0 Hz, 1H), 7.58 (s, 1H), 7.36-7.39 (m, 2H), 7.17-7.31 (m, 7H), 7.02-7.04 (m, 4H), 6.73 (d, J = 8.4 Hz, 1H), 3.82 (s, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 151.2, 148.2, 143.9, 141.6, 134.2, 133.1, 132.6, 131.0, 130.7, 130.4, 128.7, 128.3, 127.1, 123.8, 121.5, 118.7, 118.6, 116.8, 51.6, 36.9, 21.2. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{21}BrNaO_2$, 515.0617; found 515.0614.

NMR spectra of new compounds



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7.05
6.94
6.92
6.90
6.89
6.87
6.60
6.47
6.45
2.25
Ph
Ph
Ph
Me
O
O
3b
400 MHz, CDCl3
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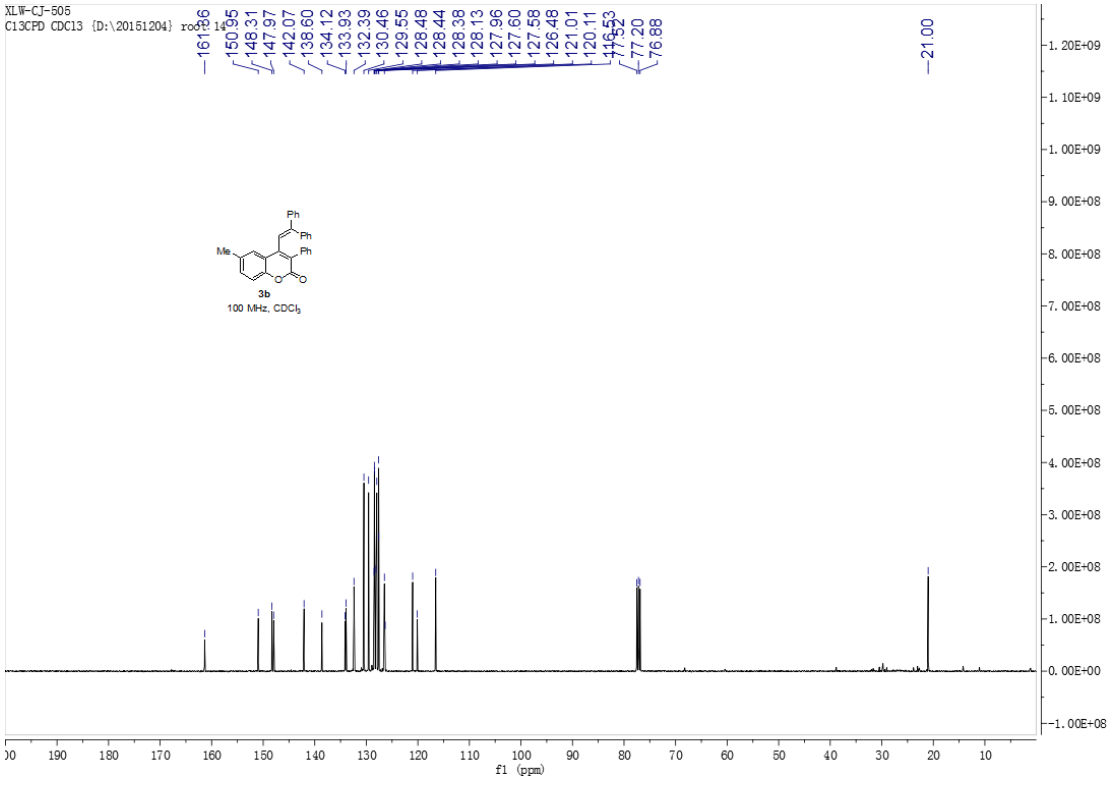
4.15
1.01
2.00
3.04
f1 (ppm)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127.60
127.58
126.48
121.01
120.11
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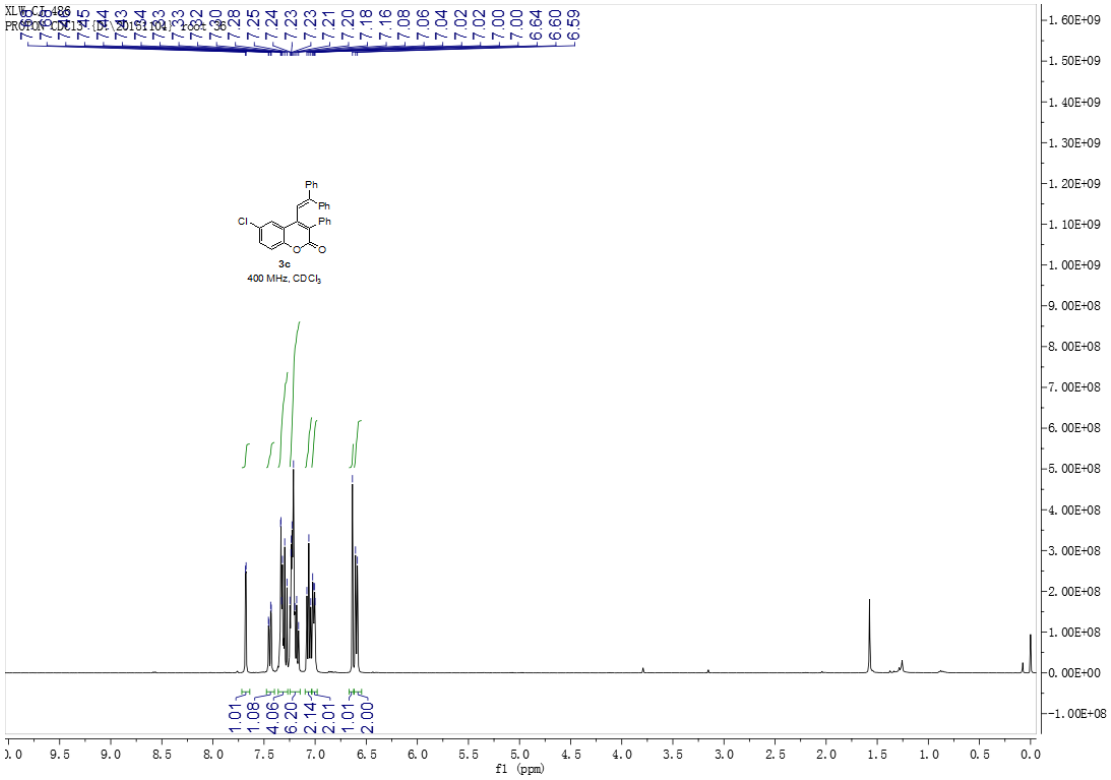
Ph
Ph
Ph
Me
O
O
3b
100 MHz, CDCl3
f1 (ppm)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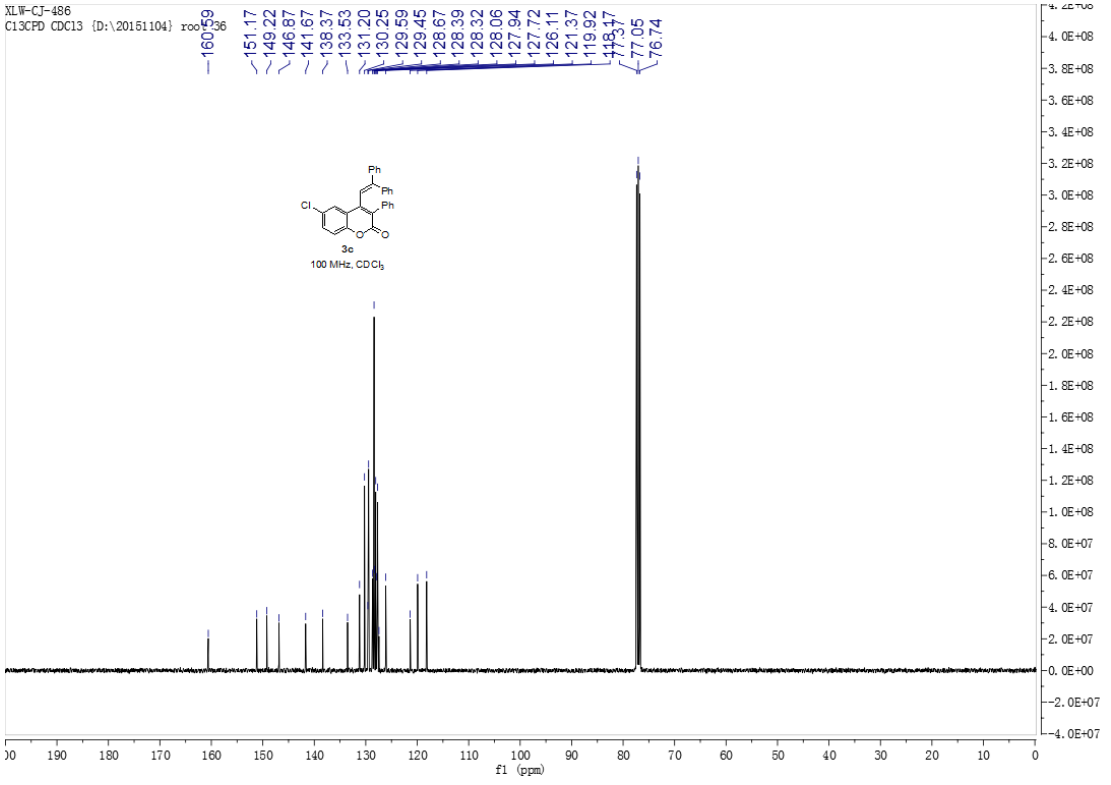
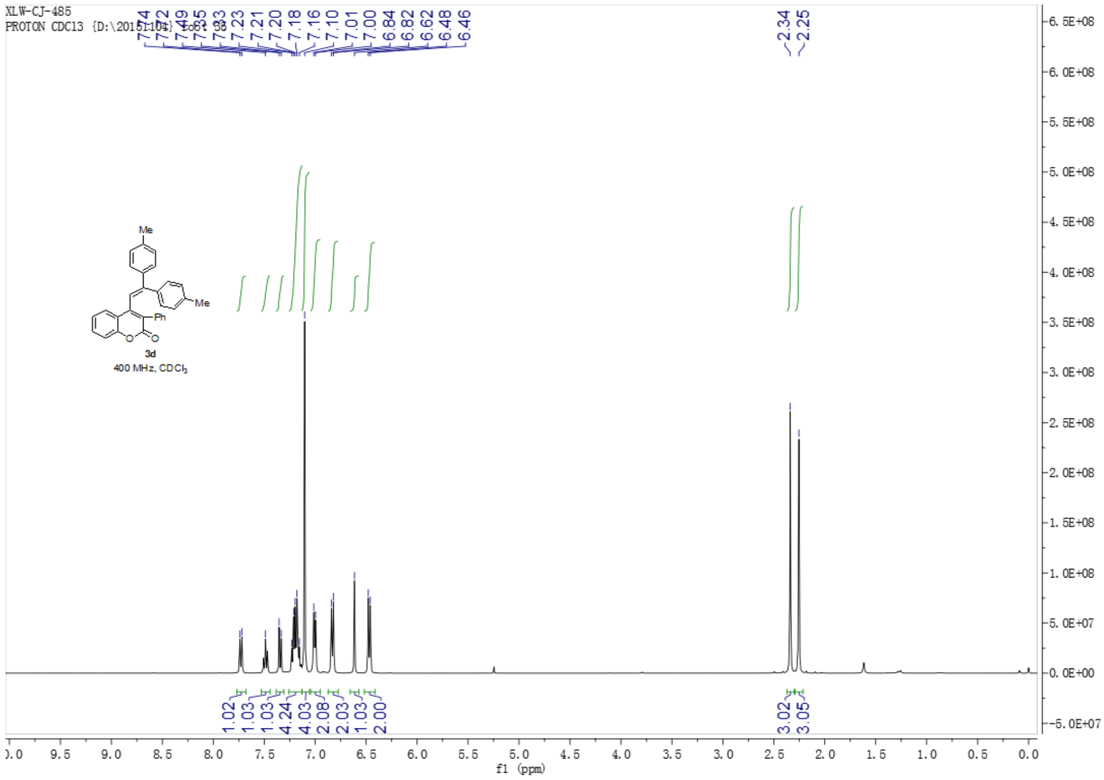
f1 (ppm)


3c
100 MHz, CDCl3
f1 (ppm)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Ph
Me
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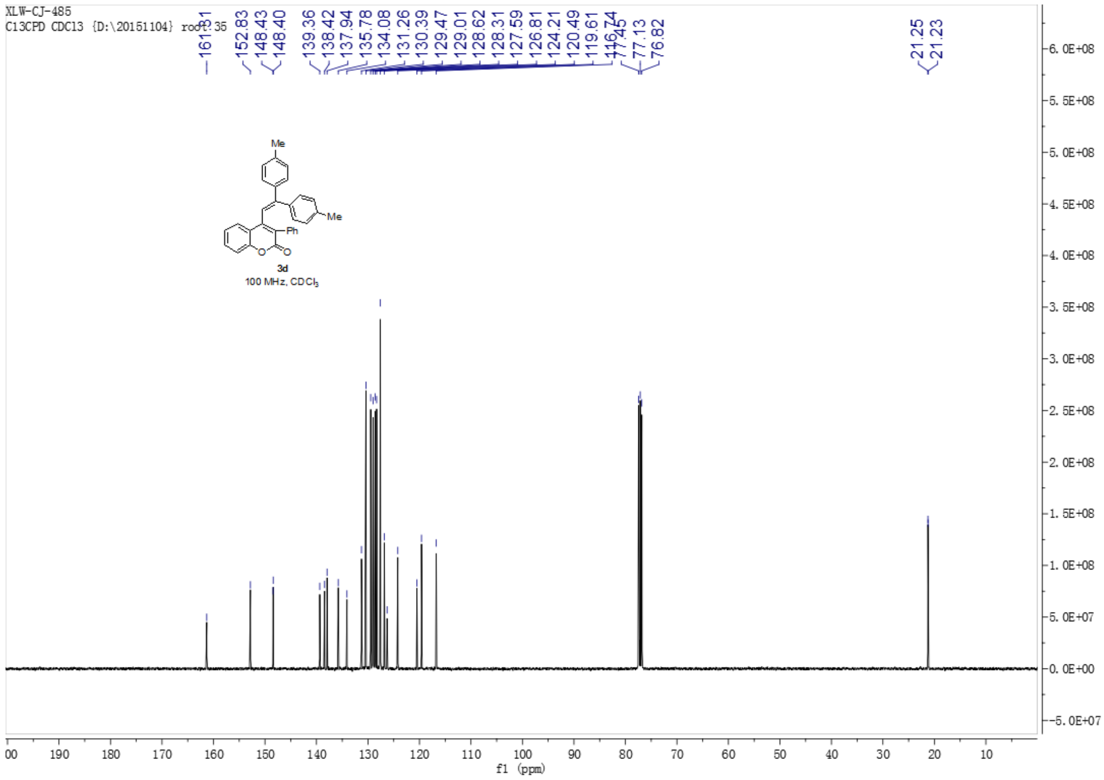
f1 (ppm)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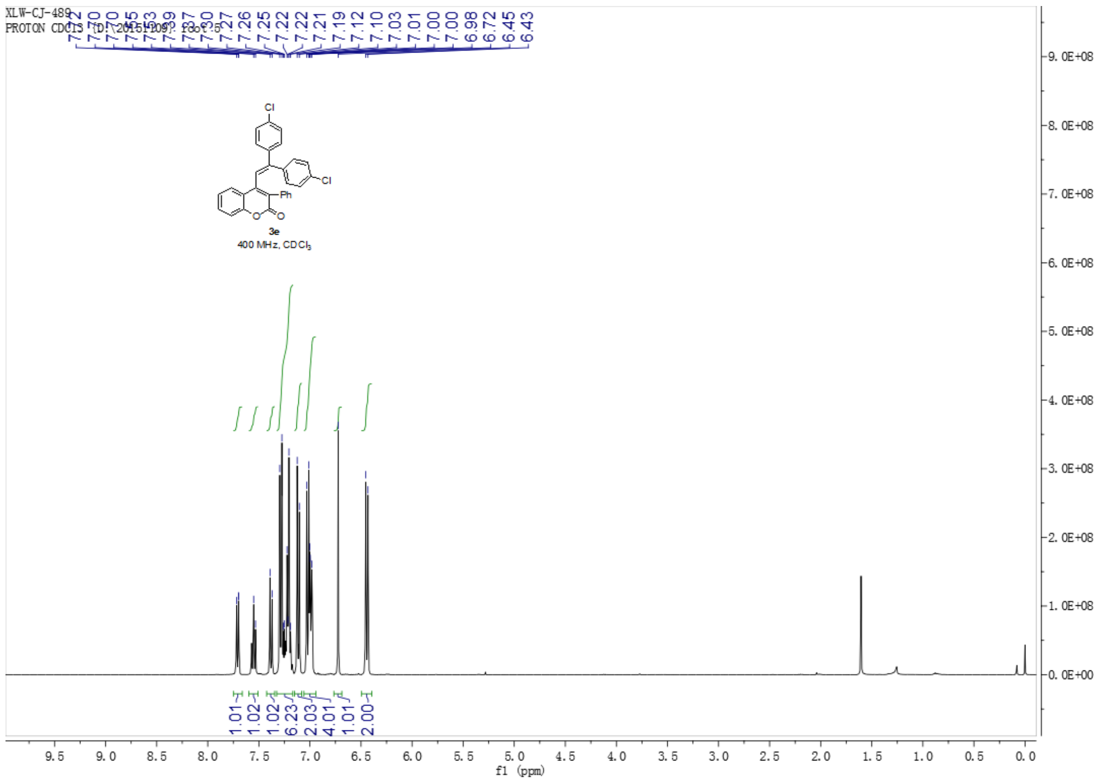
f1 (ppm)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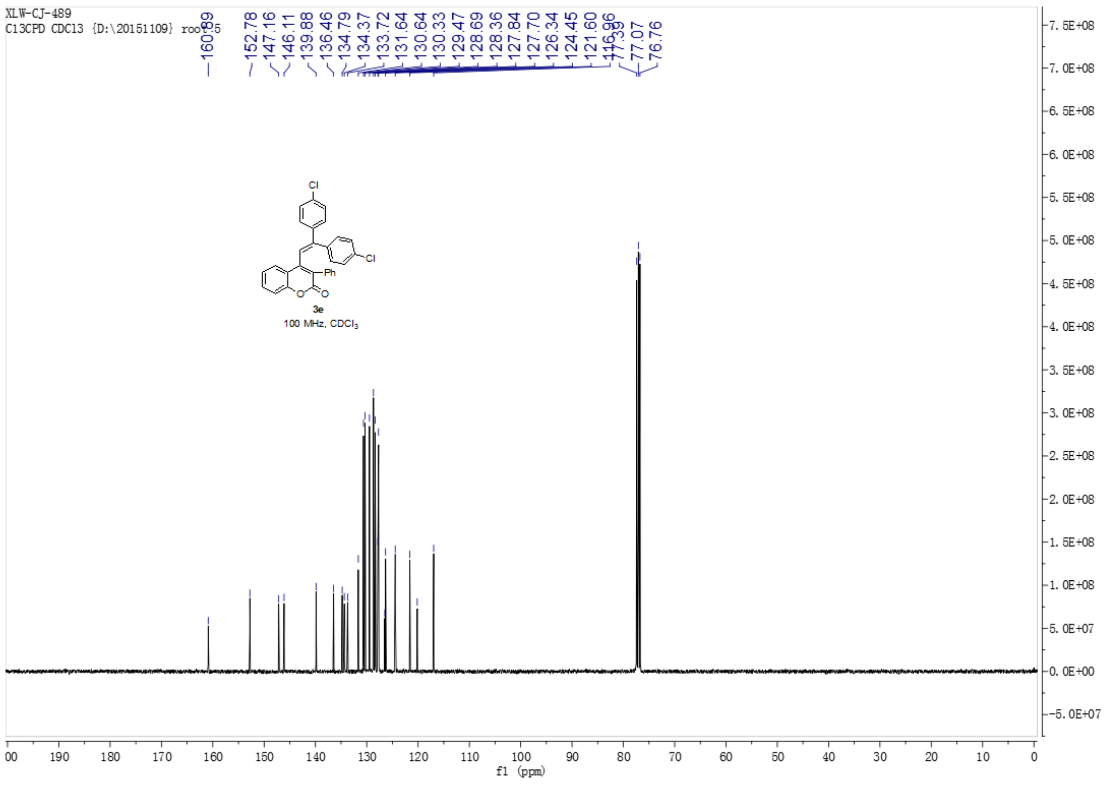
f1 (ppm)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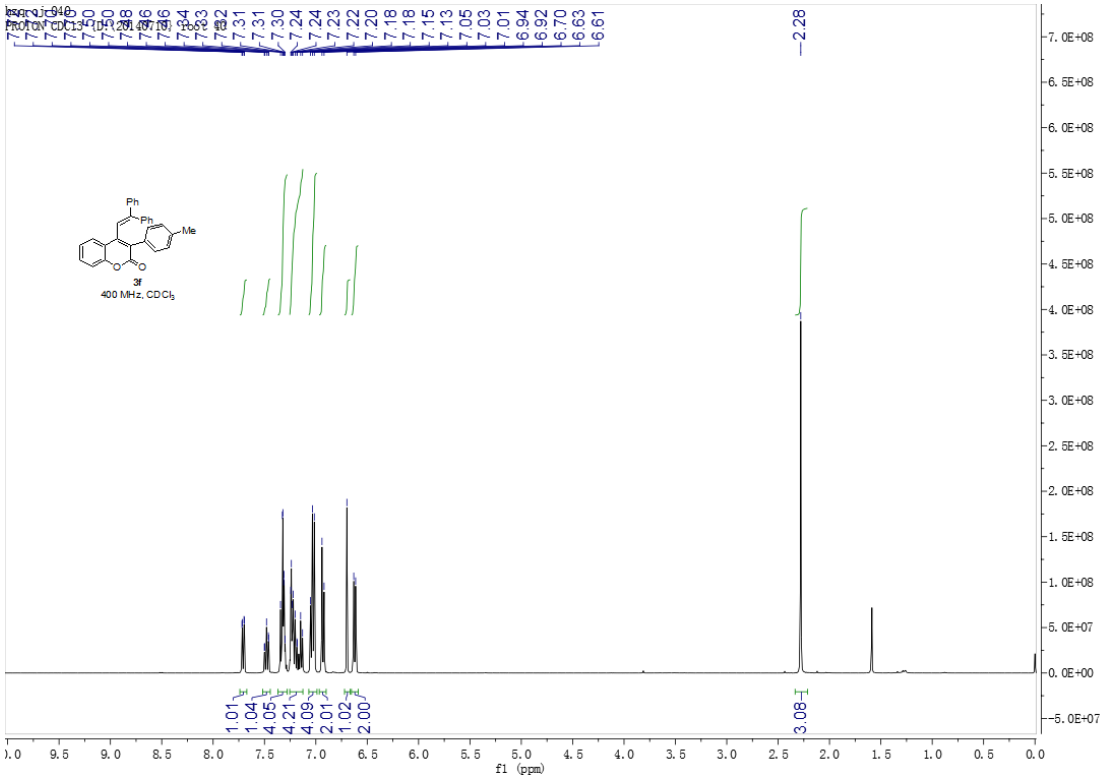
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7.15
7.13
7.05
7.03
7.01
6.94
6.92
6.70
6.63
6.61
2.28
Ph
Ph
Me
O
O
3f
400 MHz, CDCl3
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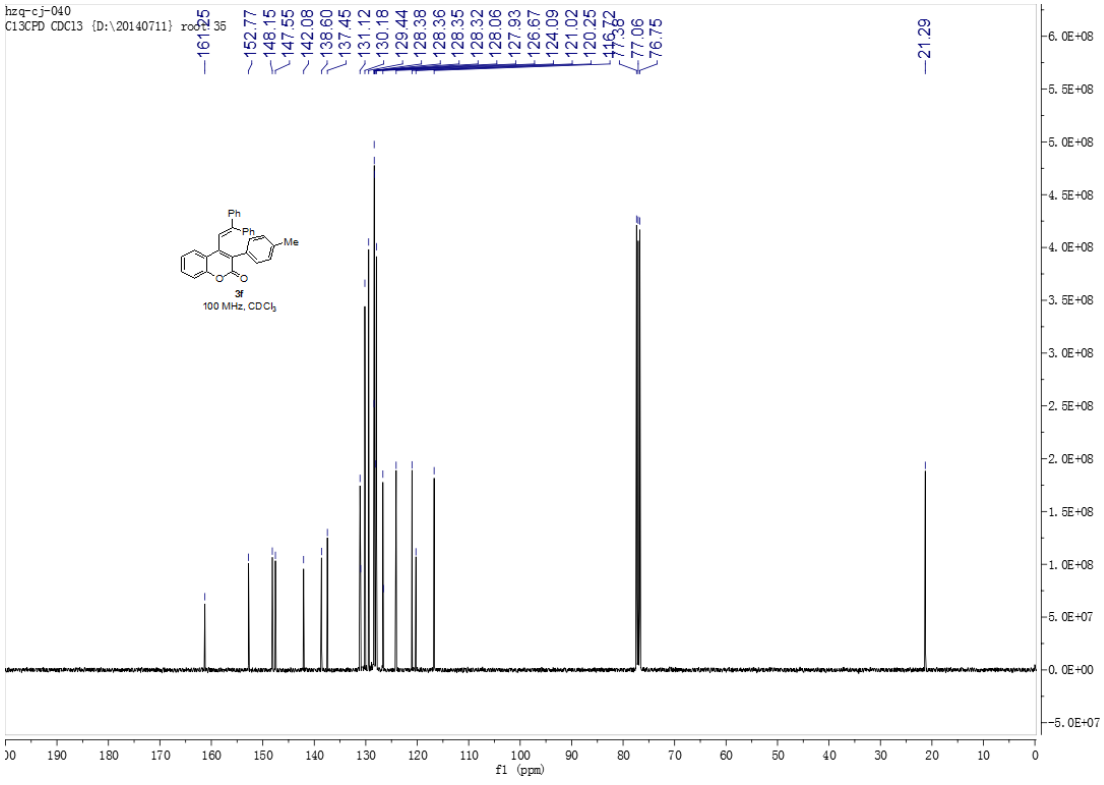
1.04
4.05
4.21
4.09
2.01
1.02
2.00
3.08
f1 (ppm)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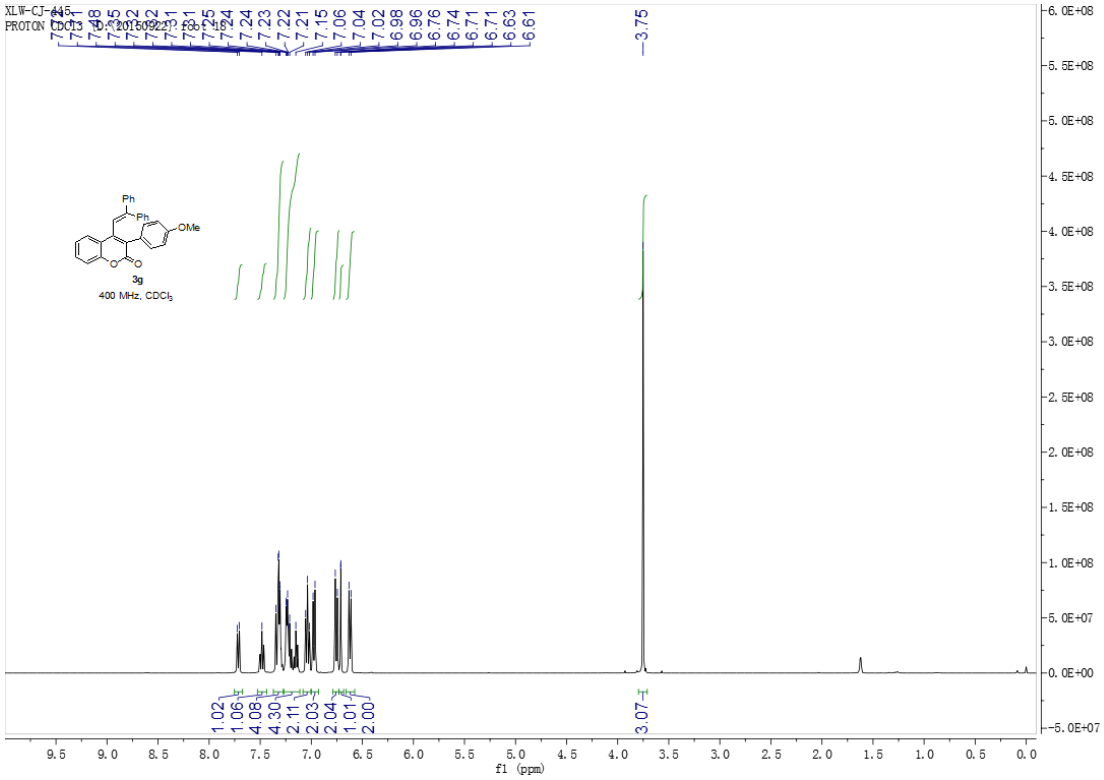
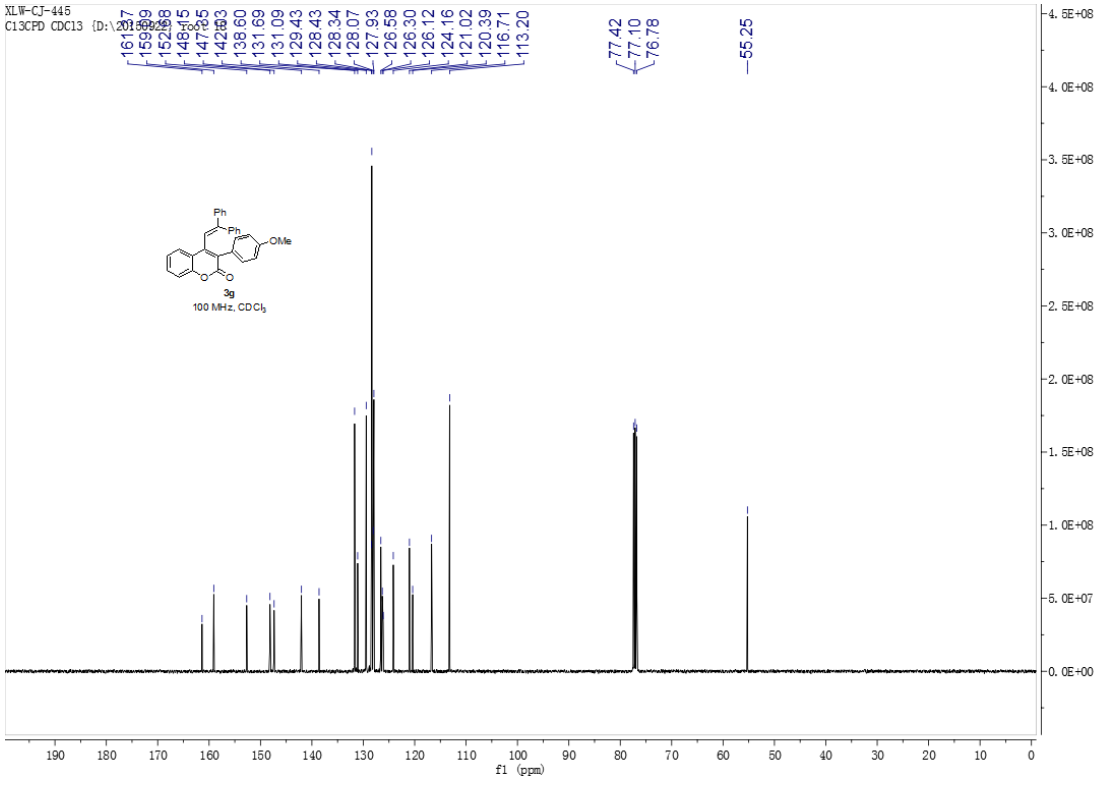
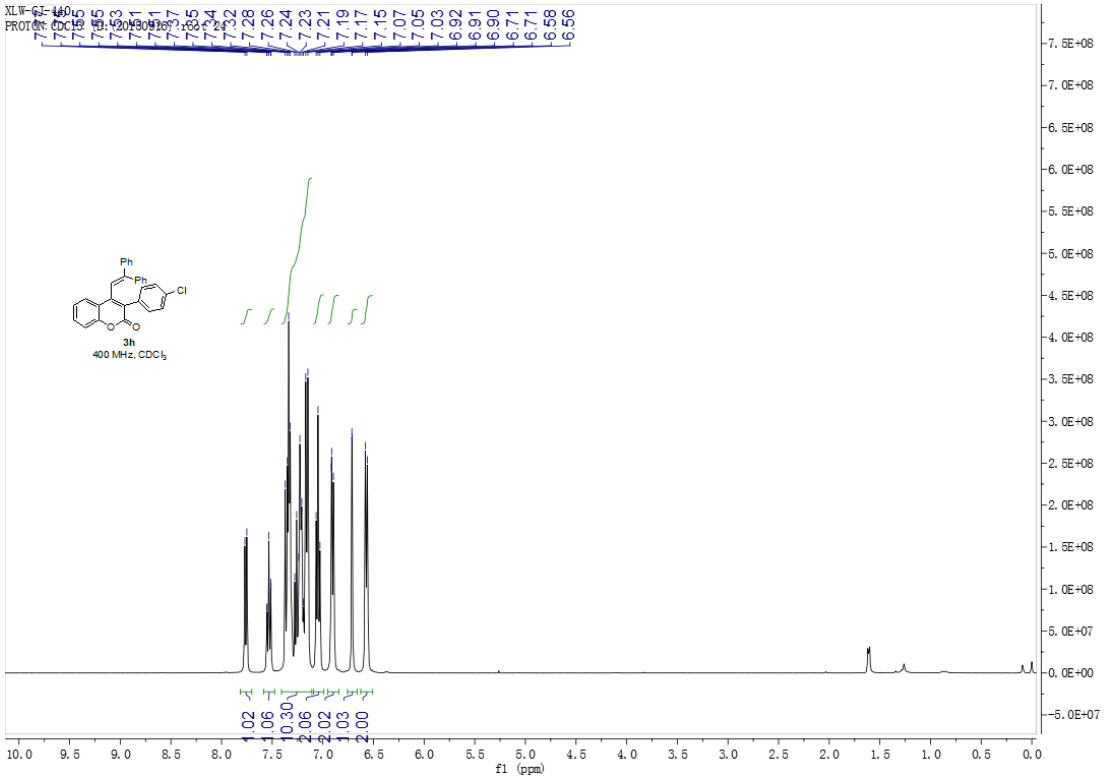
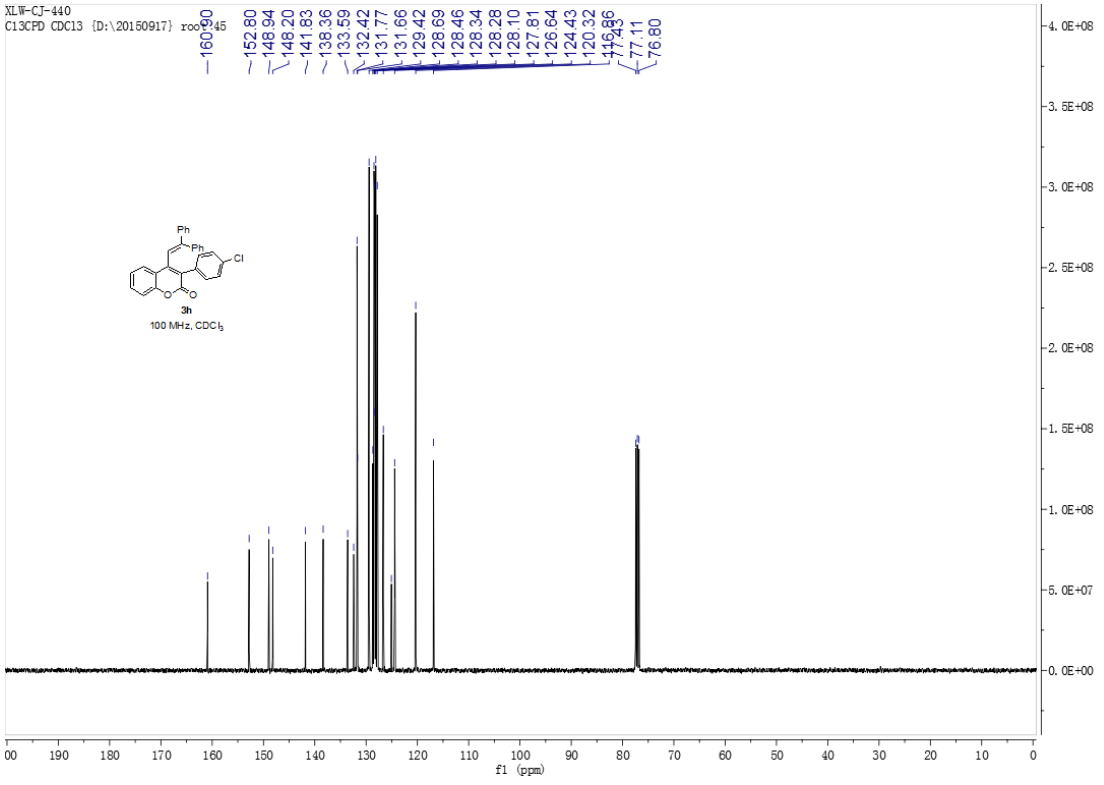
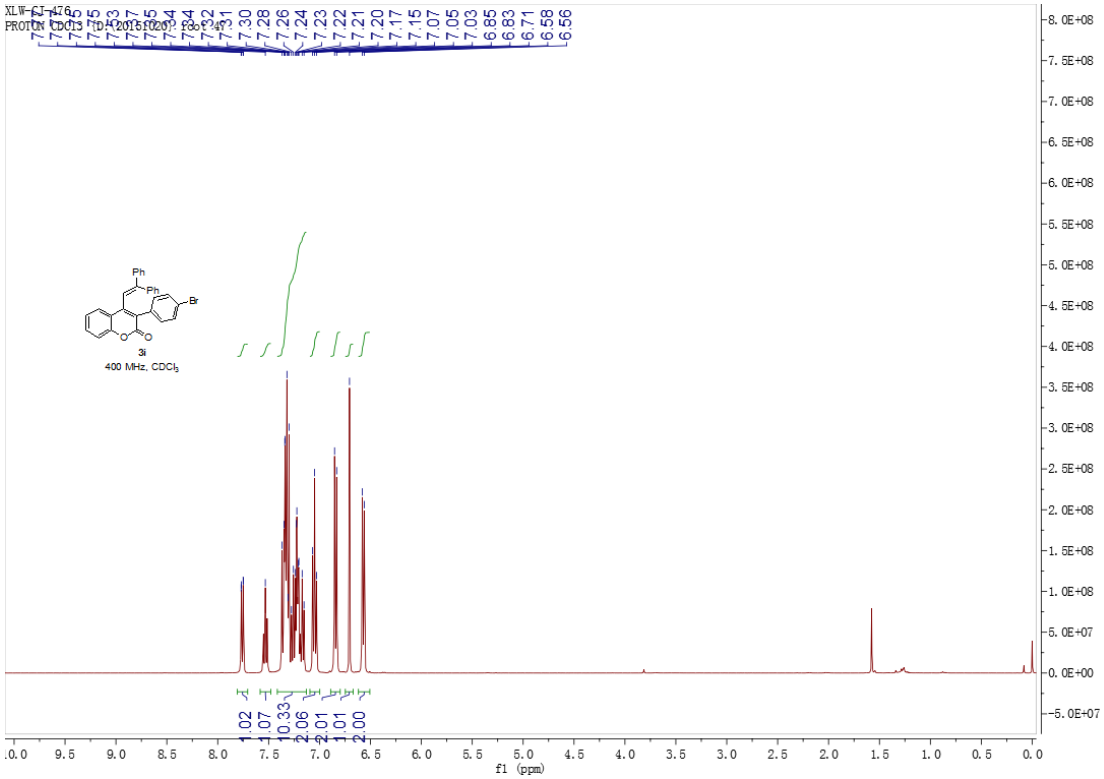
128.35
128.32
128.06
127.93
126.67
124.09
121.02
120.25
77.38
77.06
76.75
21.29
Ph
Ph
Me
O
O
3f
100 MHz, CDCl3
f1 (ppm)

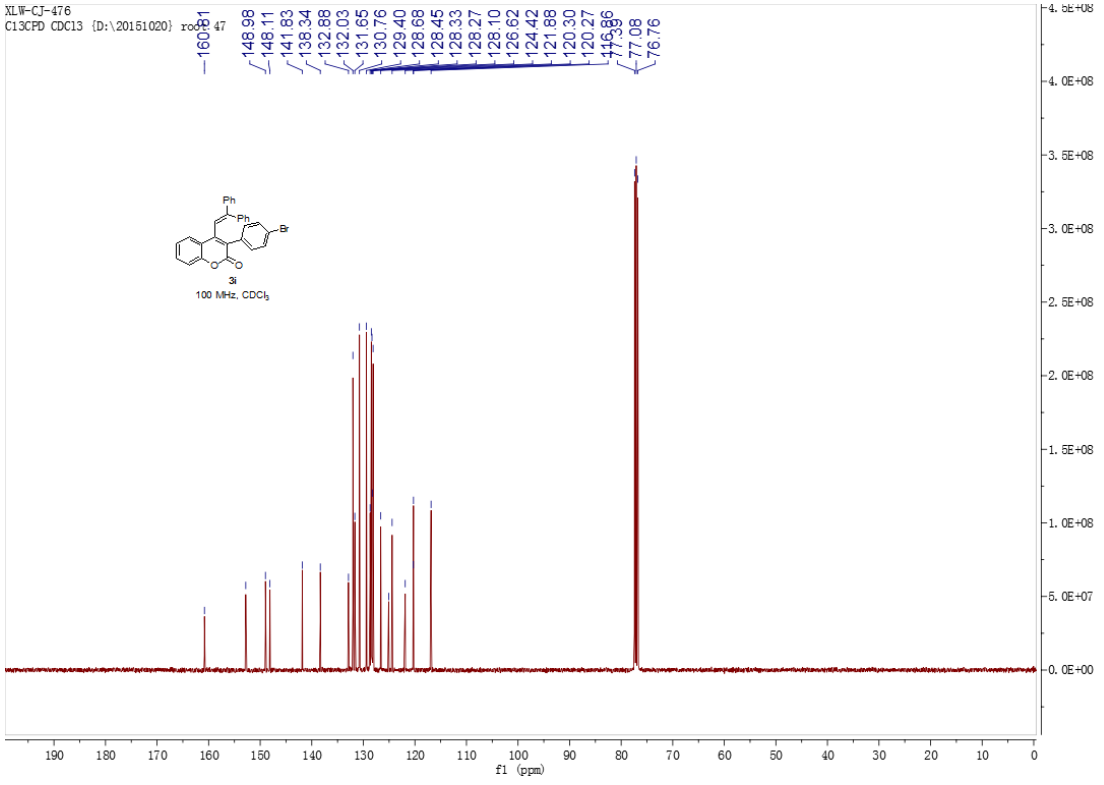

XLW-CJ-445
PROTON CDCl3
3g
400 MHz, CDCl3
3.75
1.02
1.06
4.08
4.30
2.11
2.03
2.04
1.01
2.00
3.07
f1 (ppm)

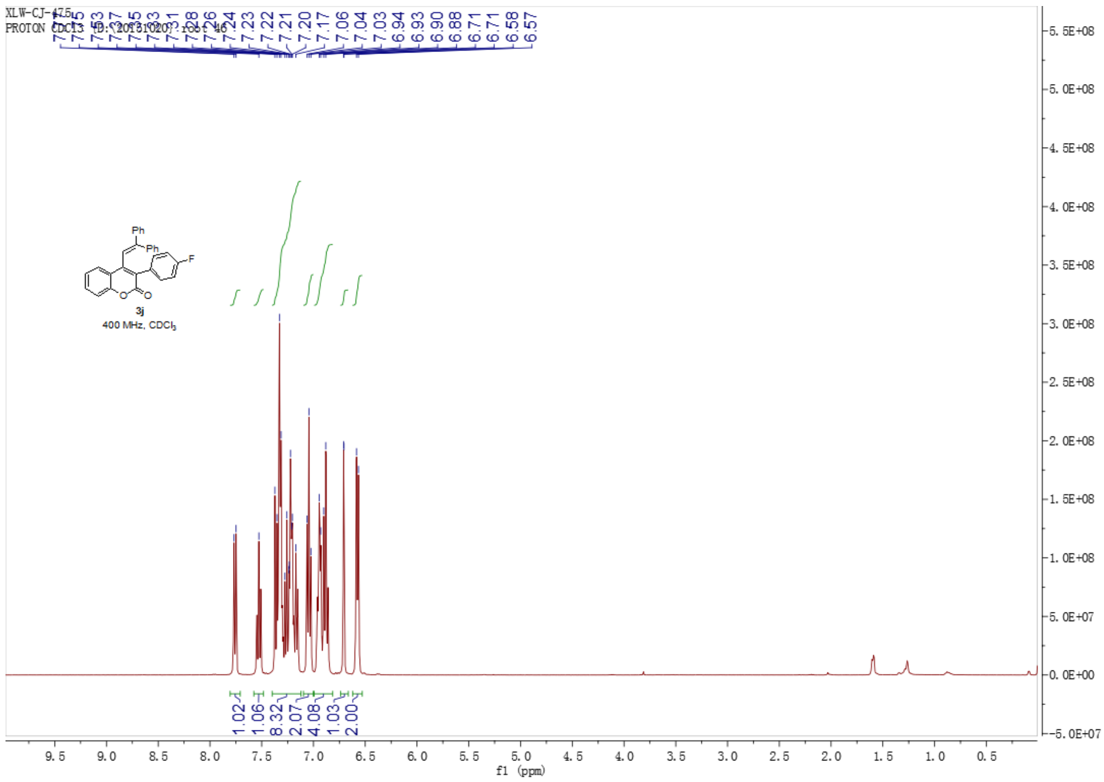

XLW-CJ-445
C13CPD CDCl3
77.42
77.10
76.78
55.25
3g
100 MHz, CDCl3
f1 (ppm)

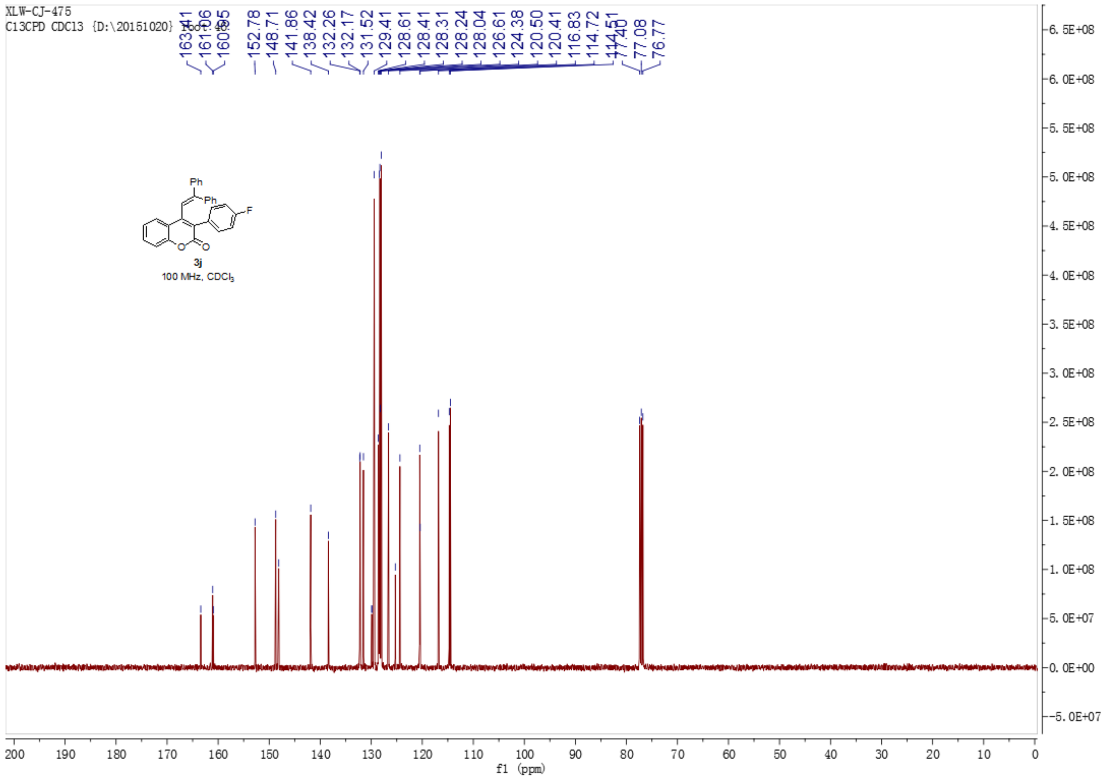

XLW-CJ-440
7.45
7.43
7.41
7.39
7.37
7.35
7.34
7.32
7.28
7.26
7.24
7.23
7.21
7.19
7.17
7.15
7.07
7.05
7.03
6.92
6.91
6.90
6.71
6.71
6.58
6.56
Ph
Ph
Cl
O
O
3h
400 MHz, CDCl3
1.02
1.06
10.30
2.06
2.02
1.03
2.00
f1 (ppm)

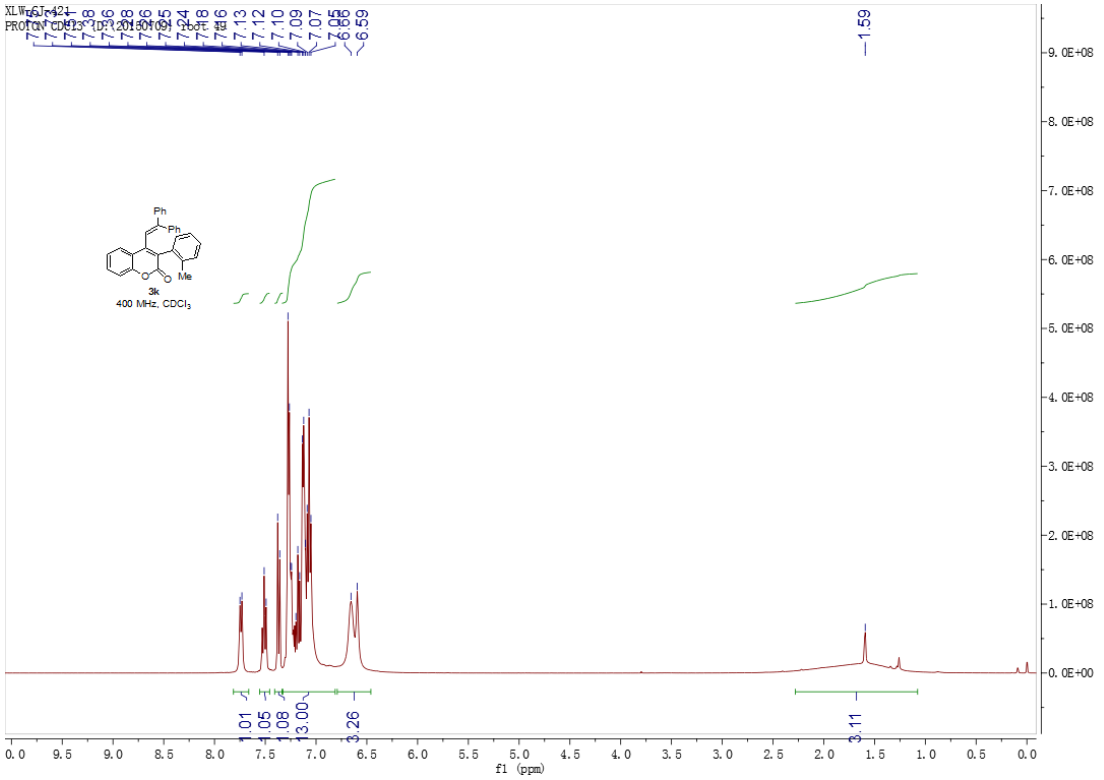

XLW-CJ-440
C13CPD CDCl3 {D:\20150917} roo
160.90
152.80
148.94
148.20
141.83
138.36
133.59
132.42
131.77
131.66
129.42
128.69
128.46
128.34
128.28
128.10
127.81
126.64
124.43
120.32
77.43
77.11
76.80
Ph
Ph
Cl
O
O
3h
100 MHz, CDCl3
f1 (ppm)

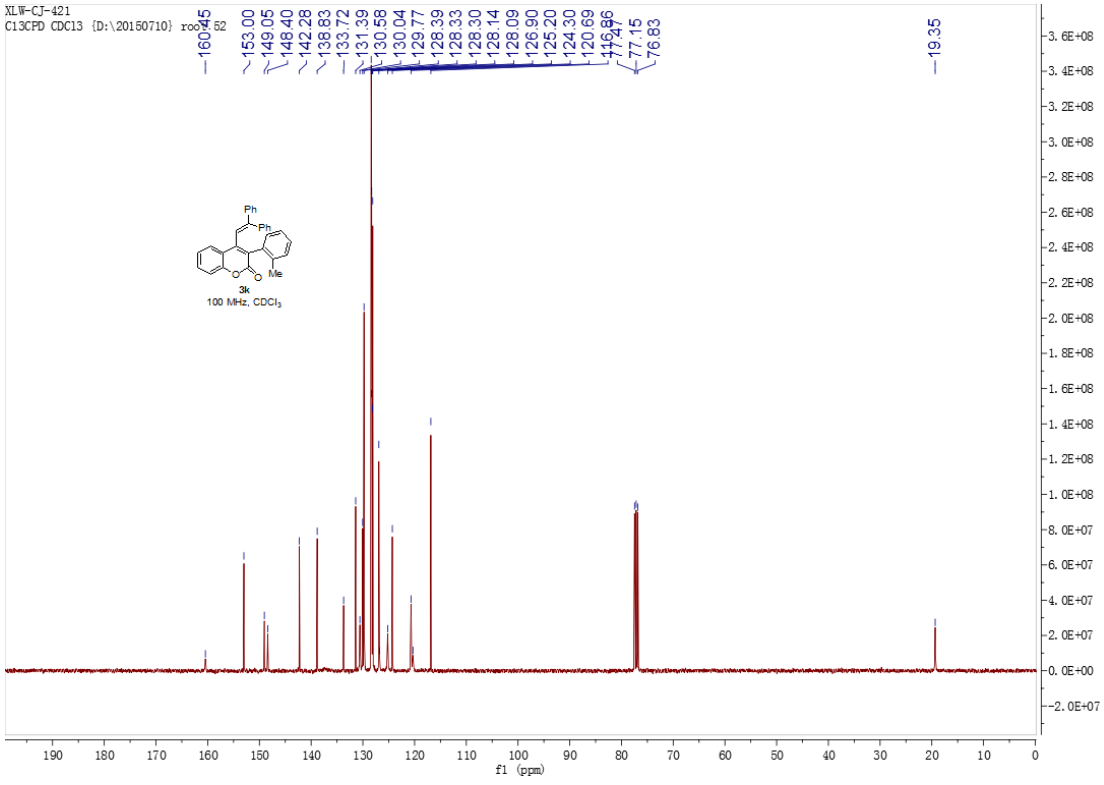

XLW-CJ-476
PROTON CDCl3 {D:\20151020} root 47
7.75 7.73 7.37 7.35 7.34 7.31 7.30 7.28 7.26 7.24 7.23 7.22 7.21 7.20 7.17 7.15 7.07 7.05 7.03 6.85 6.83 6.71 6.58 6.56
Ph
Ph
Br
O
O
3i
400 MHz, CDCl3
1.02 1.07 10.33 2.06 2.01 1.01 2.00
f1 (ppm)

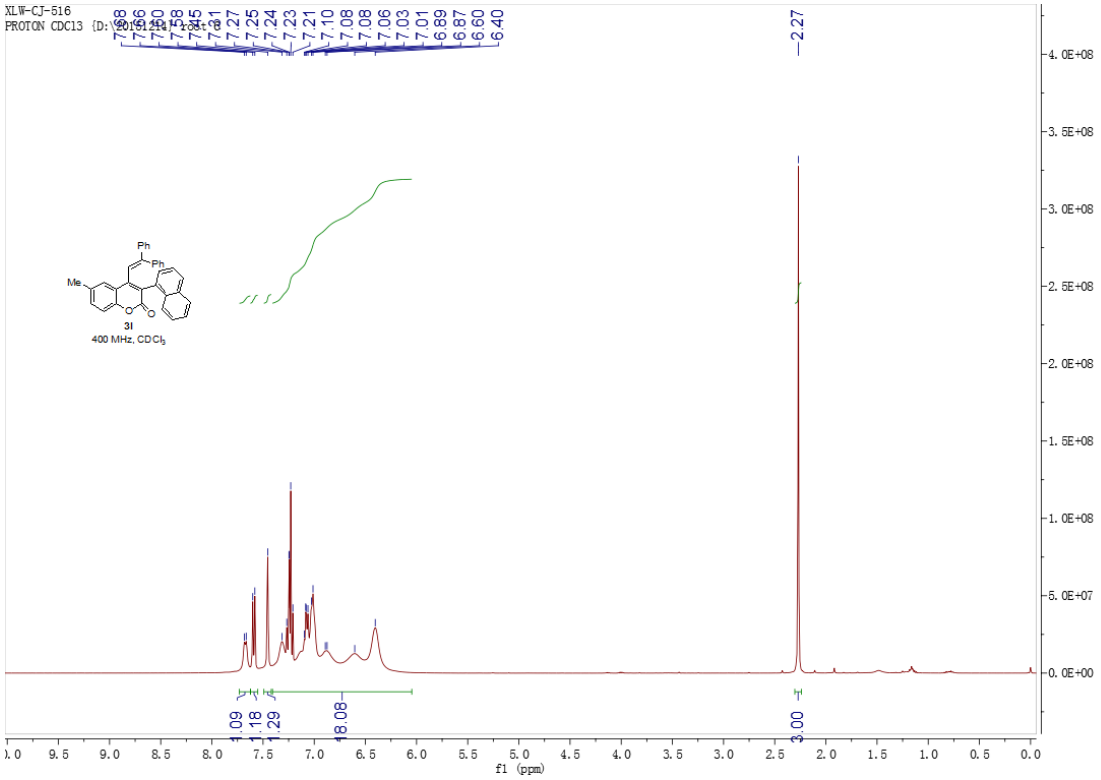

XLW-CJ-476
C13CPD CDCl3 {D:\20151020} root 47
160.81
148.98
148.11
141.83
138.34
132.88
132.03
131.65
130.76
129.40
128.68
128.45
128.33
128.27
128.10
126.62
124.42
121.88
120.30
120.27
77.39
77.08
76.76
Ph
Ph
Br
O
O
3i
100 MHz, CDCl3
f1 (ppm)

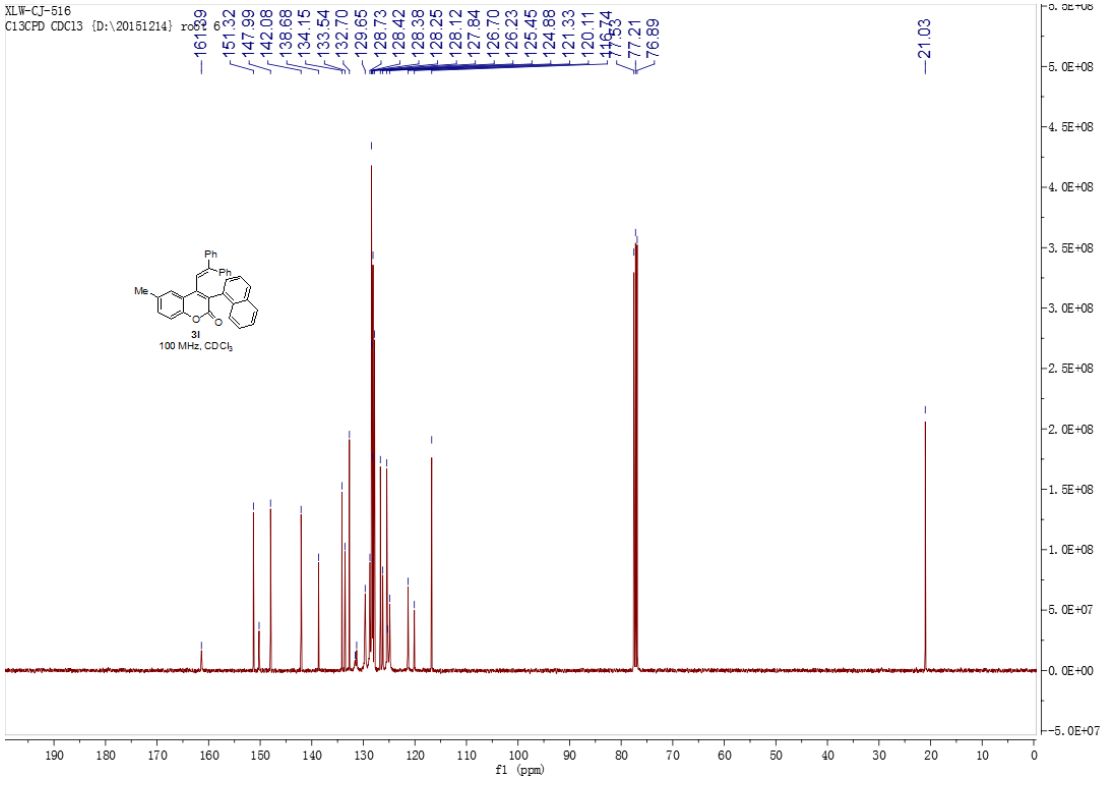

XLW-CJ-475
PROTON CDCl3 {D:\20151020} root 40
3j
400 MHz, CDCl3
1.02
1.06
8.32
2.07
4.08
1.03
2.00
f1 (ppm)

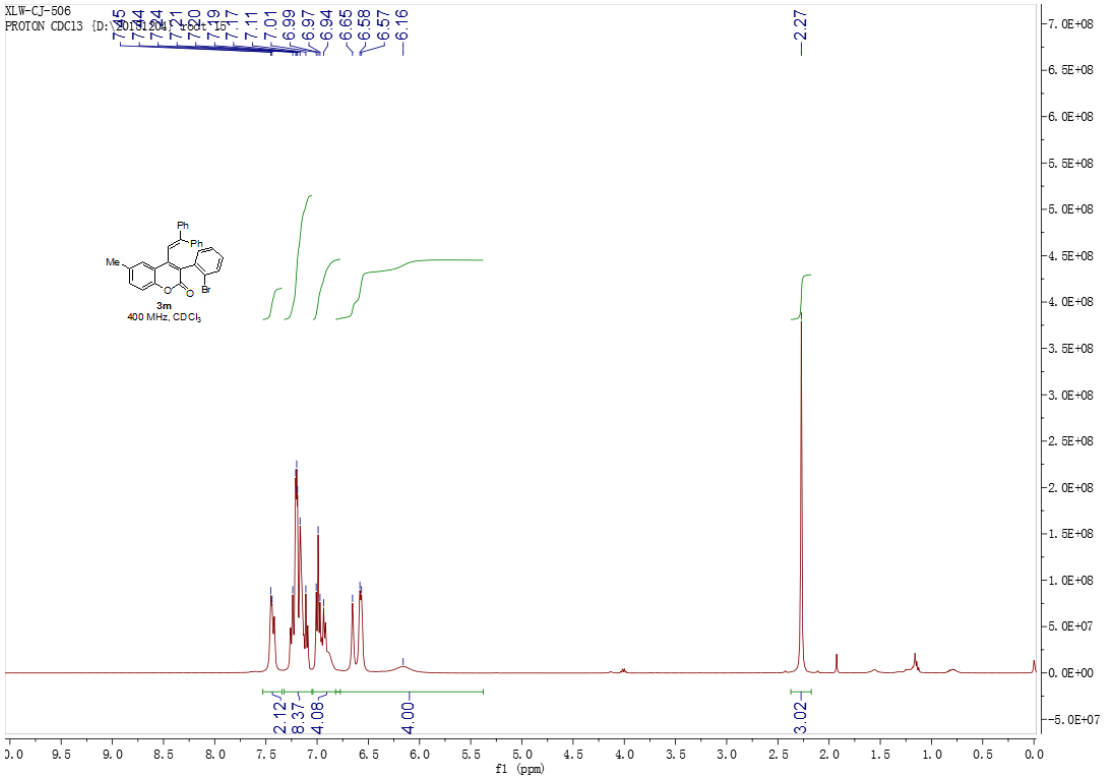

XLW-CJ-475
C13CPD CDCl3 {D:\20151020} root 40
163.11
161.06
160.95
152.78
148.71
141.86
138.42
132.26
132.17
131.52
129.41
128.61
128.41
128.31
128.24
128.04
126.61
124.38
120.50
120.41
116.83
114.72
114.51
77.40
77.08
76.77
3j
100 MHz, CDCl3
f1 (ppm)

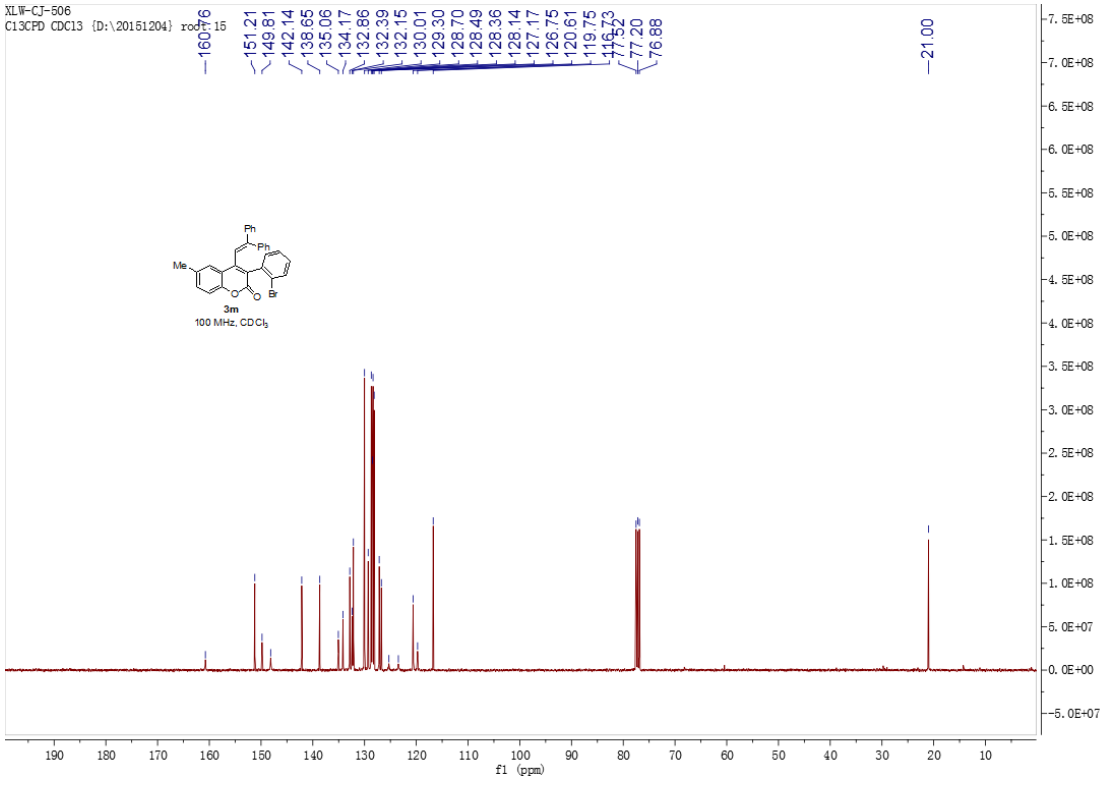

XLW-CJ-421
PROTON CDCl3 {D:\20150709} root
7.38
7.36
7.18
7.16
7.13
7.12
7.10
7.09
7.07
7.05
6.59
1.59
Ph
Ph
Me
O
O
3k
400 MHz, CDCl3
1.01
1.05
1.08
3.00
3.26
3.11
f1 (ppm)

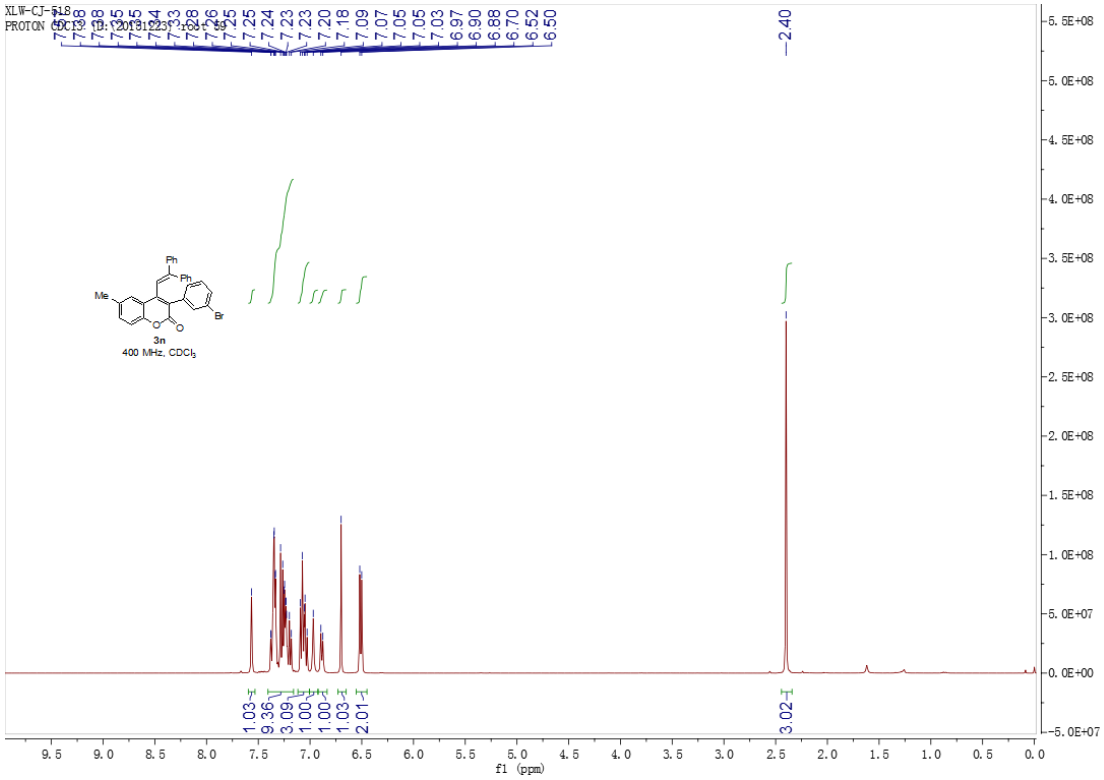

XLW-CJ-421
C13CPD CDCl3 {D:\20150710} root
160.45
153.00
149.05
148.40
142.28
138.83
133.72
131.39
130.58
130.04
129.77
128.39
128.33
128.30
128.14
128.09
126.90
125.20
124.30
120.69
77.47
77.15
76.83
19.35
Ph
Ph
Me
O
O
3k
100 MHz, CDCl3
f1 (ppm)

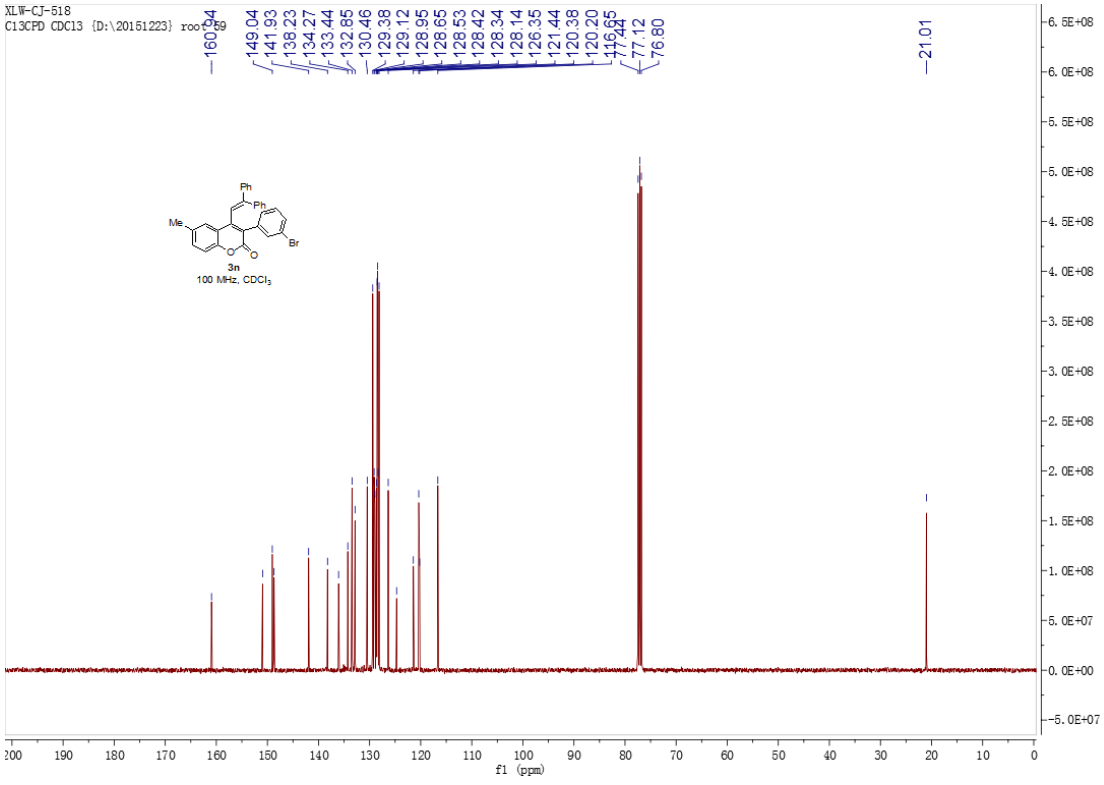

XLW-CJ-516
PROTON CDCl3
2.27
3l
400 MHz, CDCl3
1.09
1.18
1.29
18.08
3.00
f1 (ppm)

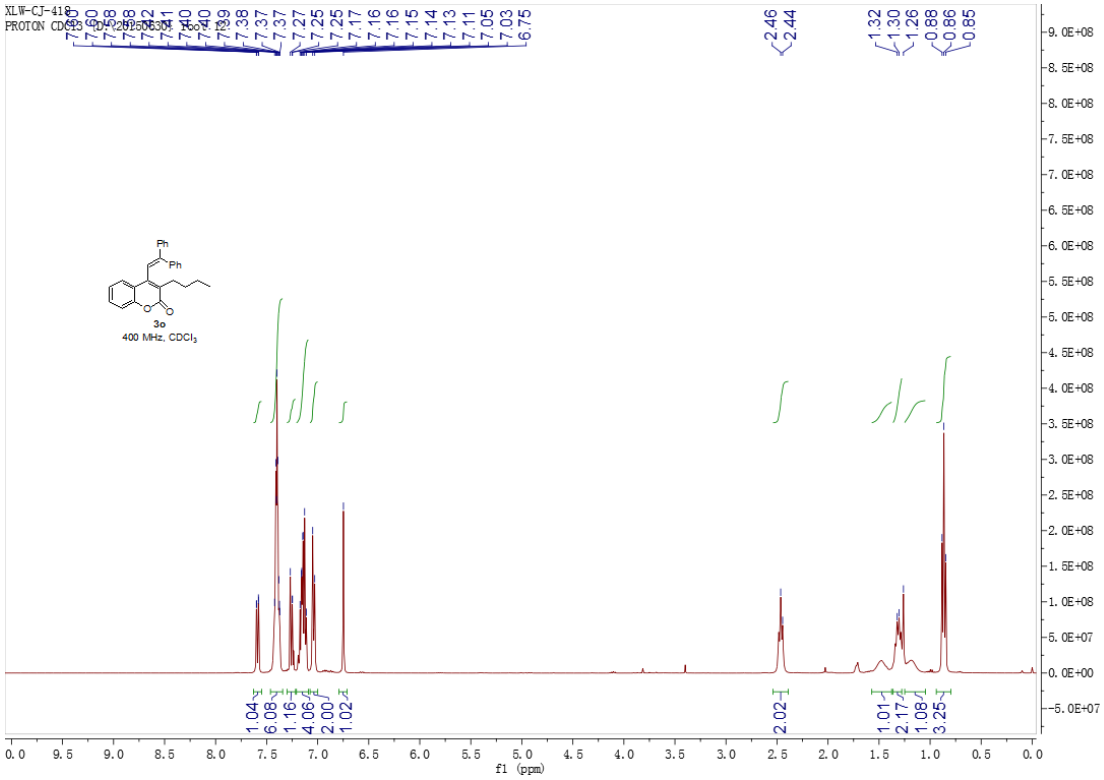

XLW-CJ-516
C13CPD CDCl3
21.03
3l
100 MHz, CDCl3
f1 (ppm)

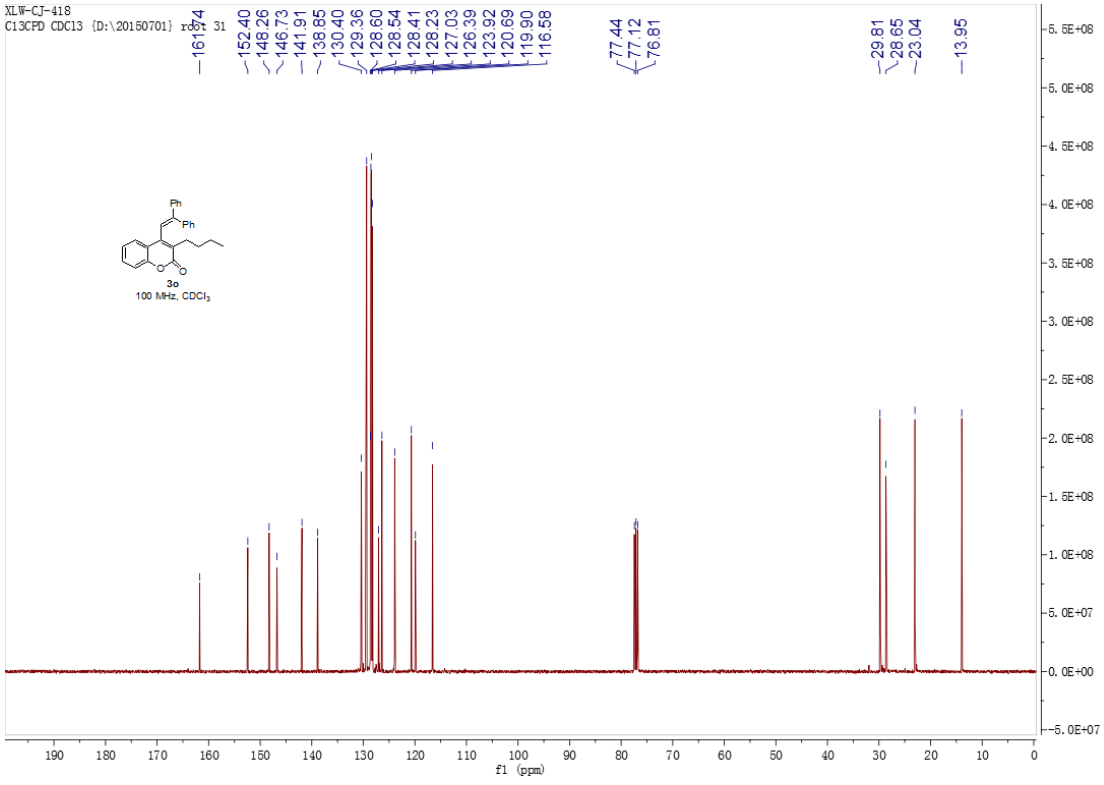

XLW-CJ-506
PROTON CDCl3
7.35
7.34
7.24
7.21
7.20
7.19
7.17
7.11
7.01
6.99
6.97
6.94
6.65
6.58
6.57
6.16
2.27
Ph
Ph
Me
O
O
Br
3m
400 MHz, CDCl3
2.12
8.37
4.08
4.00
3.02
f1 (ppm)

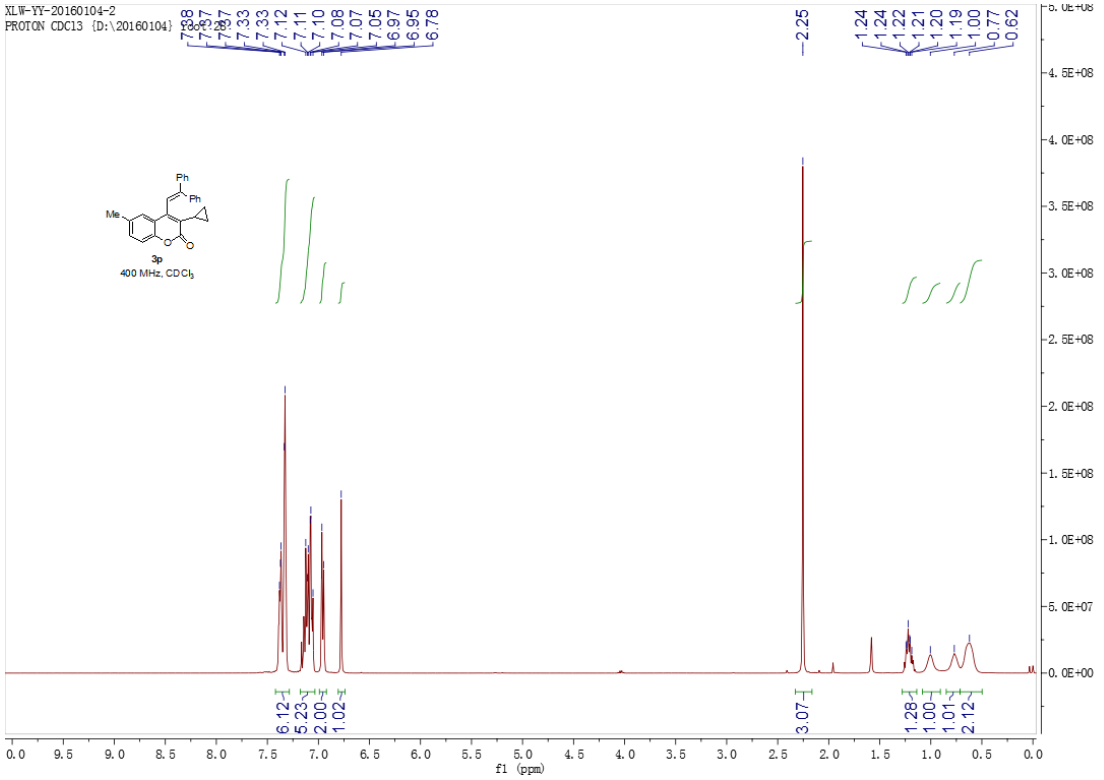

XLW-CJ-506
C13CPD CDCl3
160.76
151.21
149.81
142.14
138.65
135.06
134.17
132.86
132.39
132.15
130.01
129.30
128.70
128.49
128.36
128.14
127.17
126.75
120.61
119.75
116.73
77.52
77.20
76.88
21.00
Ph
Ph
Me
O
O
Br
3m
100 MHz, CDCl3
f1 (ppm)

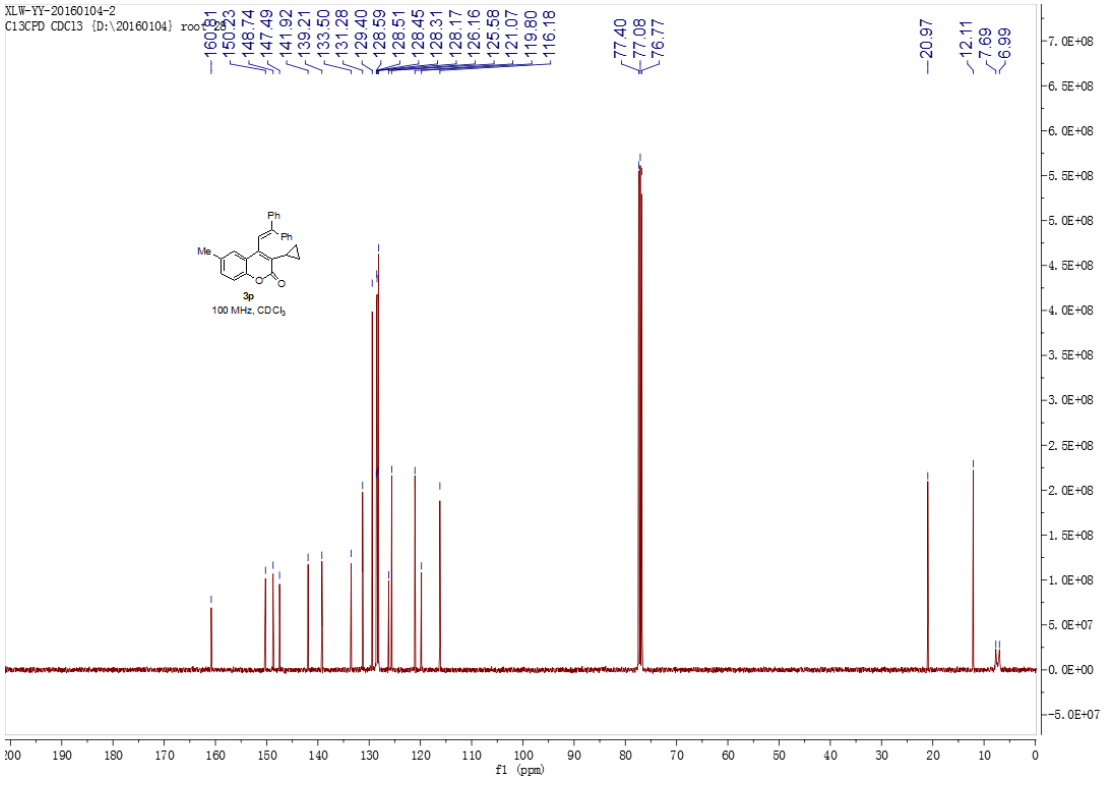

XLW-CJ-518
PROTON CDCl3 {D:\20151223} root 59
2.40
Ph
Ph
Me
Br
O
O
3n
400 MHz, CDCl3
1.03
9.36
3.09
1.00
1.00
1.03
2.01
3.02
f1 (ppm)

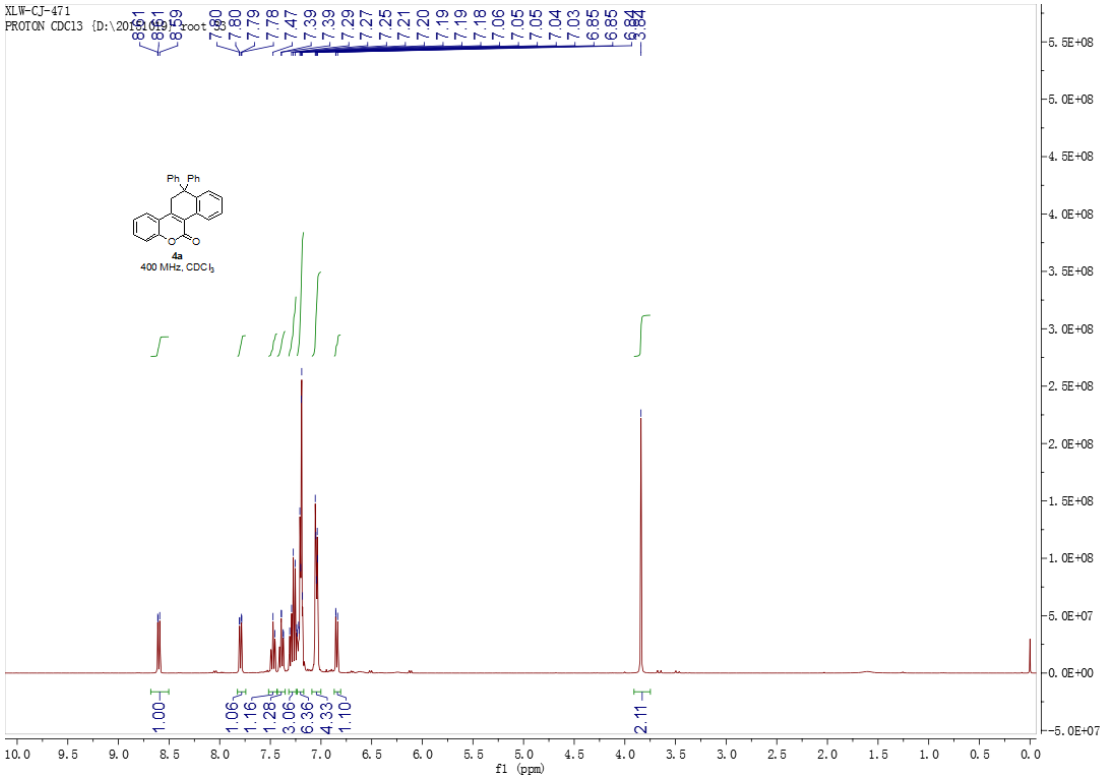

XLW-CJ-518
C13CPD CDCl3 {D:\20151223} root 59
160.04
149.04
141.93
138.23
134.27
133.44
132.85
130.46
129.38
129.12
128.95
128.65
128.53
128.42
128.34
128.14
126.35
121.44
120.38
120.20
116.65
77.44
77.12
76.80
21.01
Ph
Ph
Me
Br
O
O
3n
100 MHz, CDCl3
f1 (ppm)

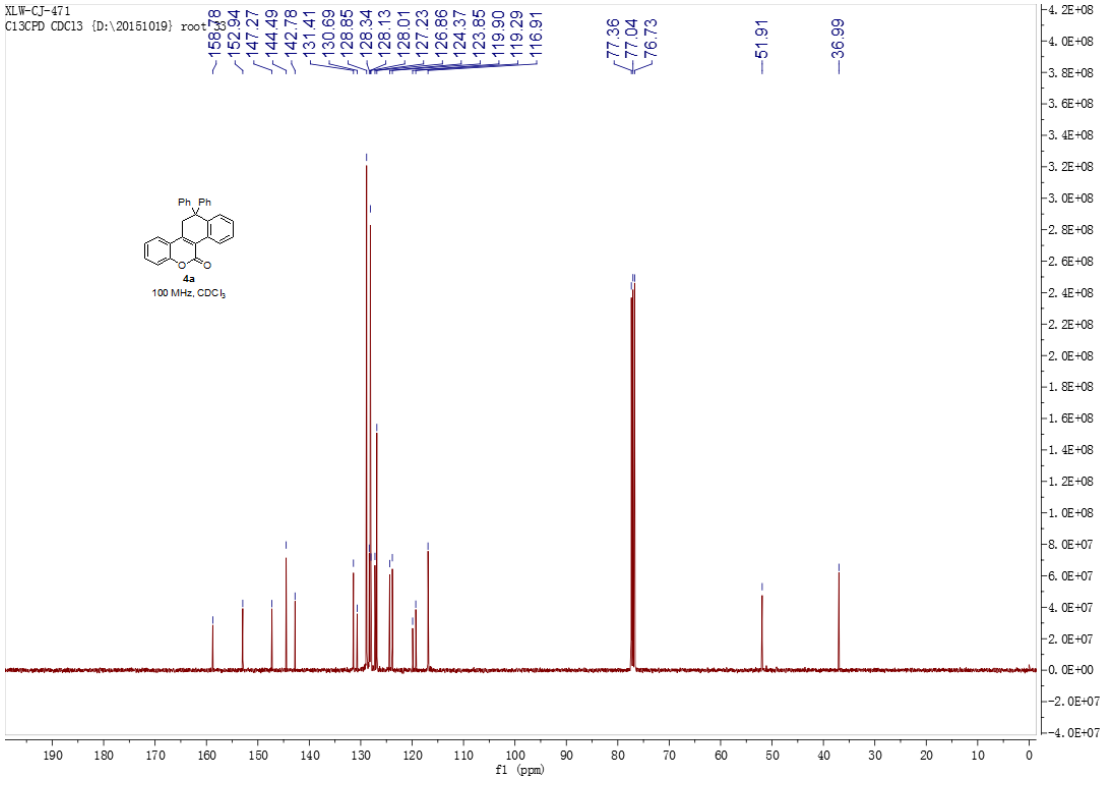

XLW-CJ-418
PROTON CDCl3
7.60 7.58 7.42 7.41 7.40 7.39 7.38 7.37 7.37 7.27 7.25 7.25 7.17 7.16 7.16 7.15 7.14 7.13 7.11 7.05 7.03 6.75
2.46 2.44
1.32 1.30 1.26 0.88 0.86 0.85
Ph
Ph
O
O
3o
400 MHz, CDCl3
1.04 6.08 1.16 4.06 2.00 1.02
2.02
1.01 2.17 1.08 3.25
f1 (ppm)

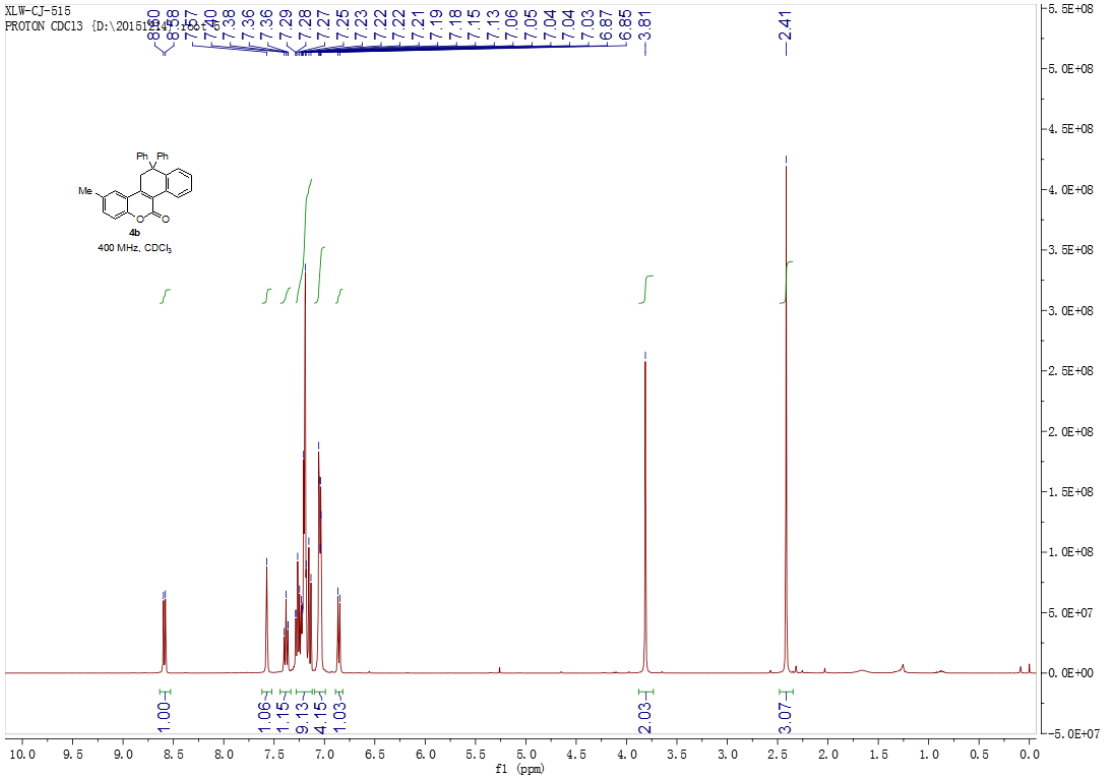

XLW-CJ-418
C13CPD CDCl3
161.74
152.40 148.26 146.73 141.91 138.85 130.40 129.36 128.60 128.54 128.41 128.23 127.03 126.39 123.92 120.69 119.90 116.58
77.44 77.12 76.81
29.81 28.65 23.04 13.95
Ph
Ph
O
O
3o
100 MHz, CDCl3
f1 (ppm)

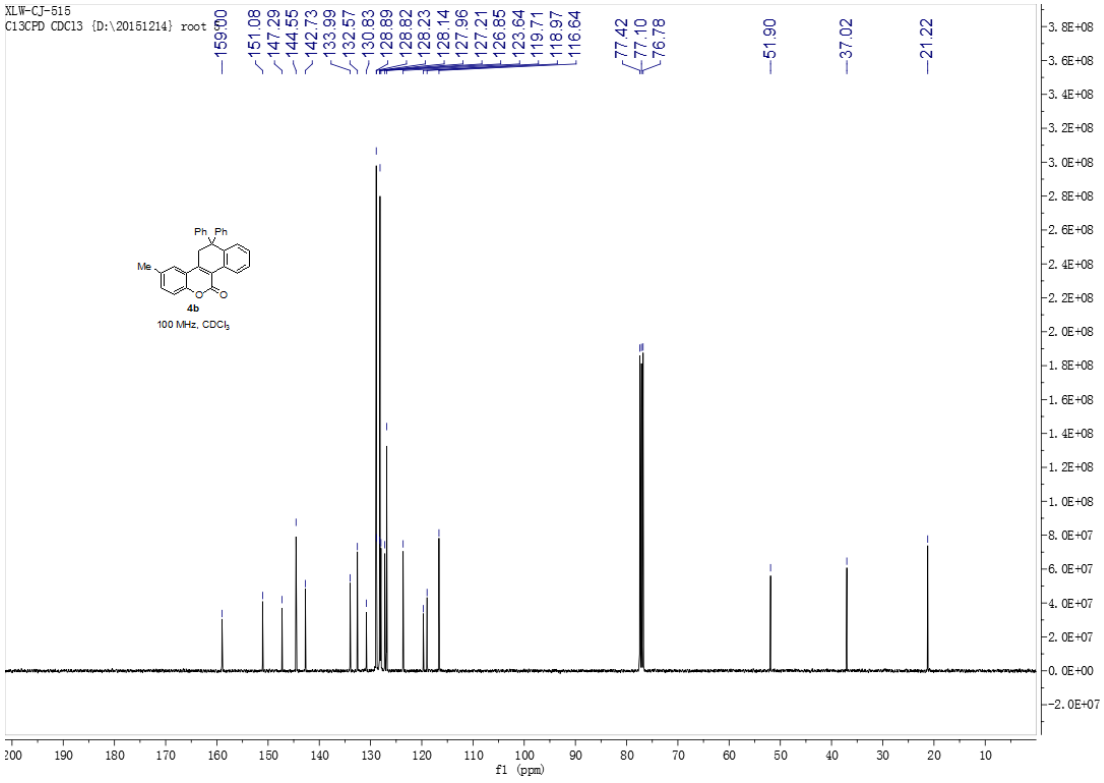

XLW-YY-20160104-2
PROTON CDCl3 {D:\20160104} root 28
7.38
7.37
7.33
7.33
7.12
7.11
7.10
7.08
7.07
7.05
6.97
6.95
6.78
2.25
1.24
1.24
1.22
1.21
1.20
1.19
1.00
0.77
0.62
Ph
Ph
Me
O
O
3p
400 MHz, CDCl3
6.12
5.23
2.00
1.02
3.07
1.28
1.00
1.01
2.12
f1 (ppm)

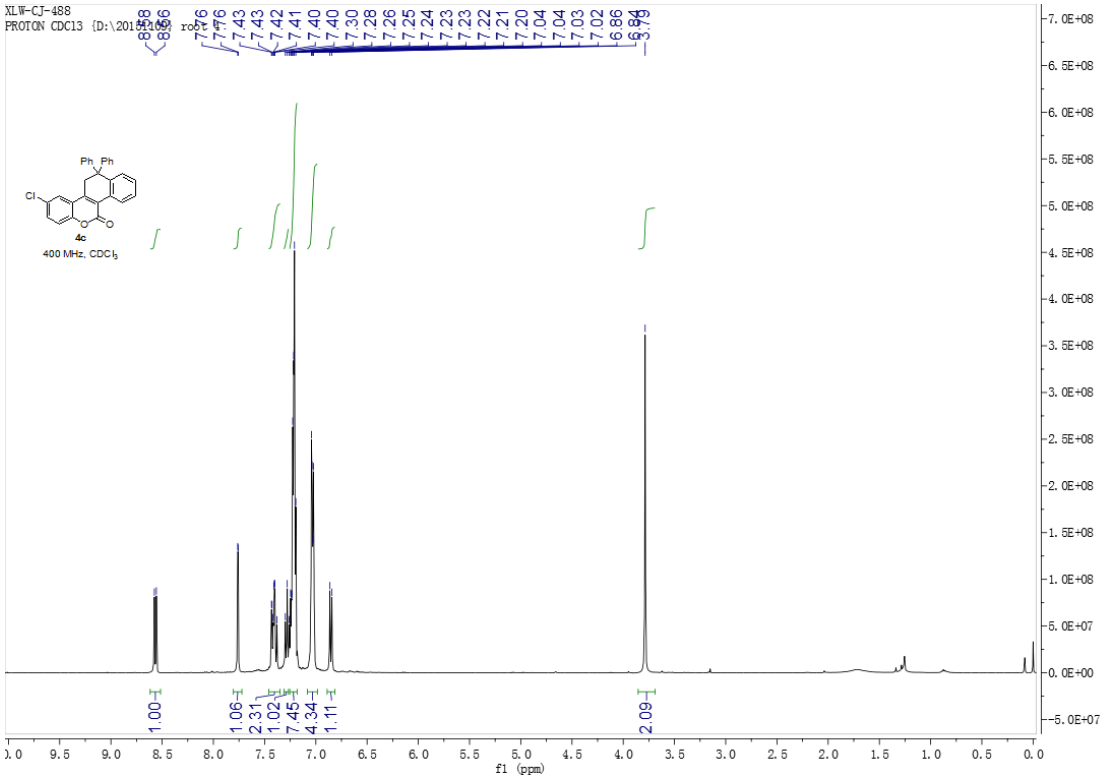

XLW-YY-20160104-2
C13CPD CDCl3 {D:\20160104} root 28
160.11
150.23
148.74
147.49
141.92
139.21
133.50
131.28
129.40
128.59
128.51
128.45
128.31
128.17
126.16
125.58
121.07
119.80
116.18
77.40
77.08
76.77
20.97
12.11
7.69
6.99
Ph
Ph
Me
O
O
3p
100 MHz, CDCl3
f1 (ppm)

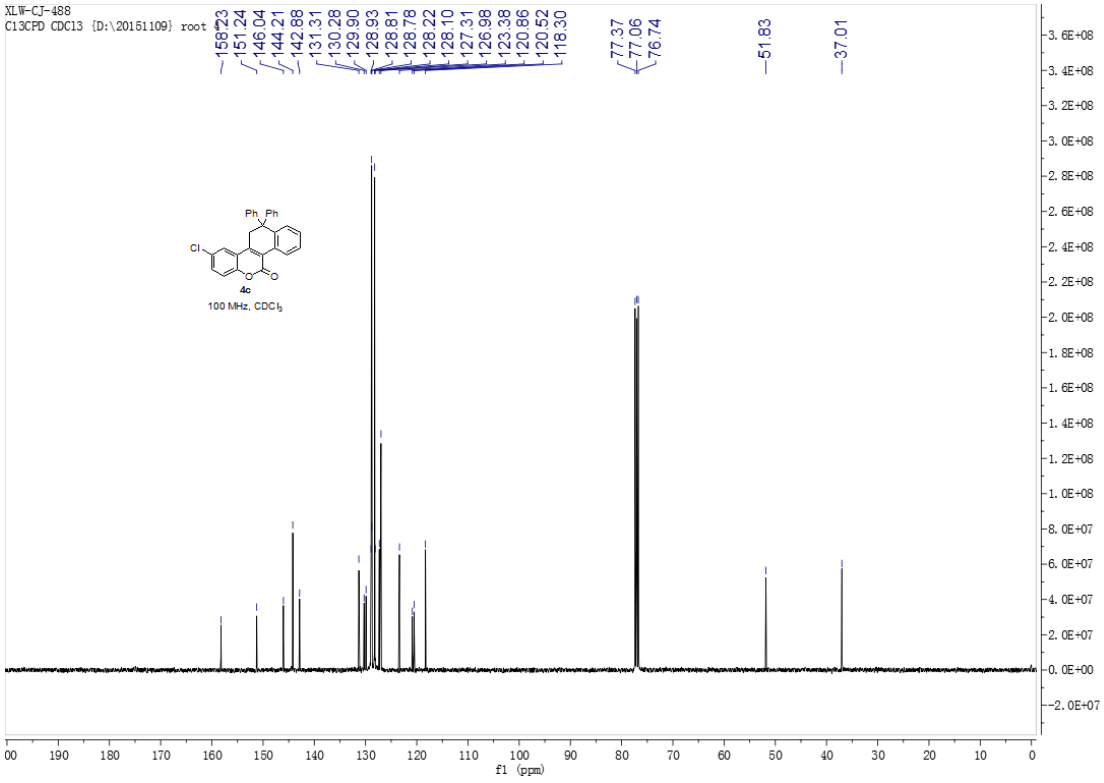

XLW-CJ-471
PROTON CDCl3 {D:\20151019} root 33
8.61
8.61
8.59
7.80
7.80
7.79
7.78
7.47
7.39
7.39
7.29
7.27
7.25
7.21
7.20
7.19
7.19
7.18
7.06
7.05
7.05
7.04
7.03
6.85
6.85
6.84
6.84
Ph Ph
O
O
4a
400 MHz, CDCl3
1.00
1.06
1.16
1.28
3.06
6.36
4.33
1.10
2.11
f1 (ppm)

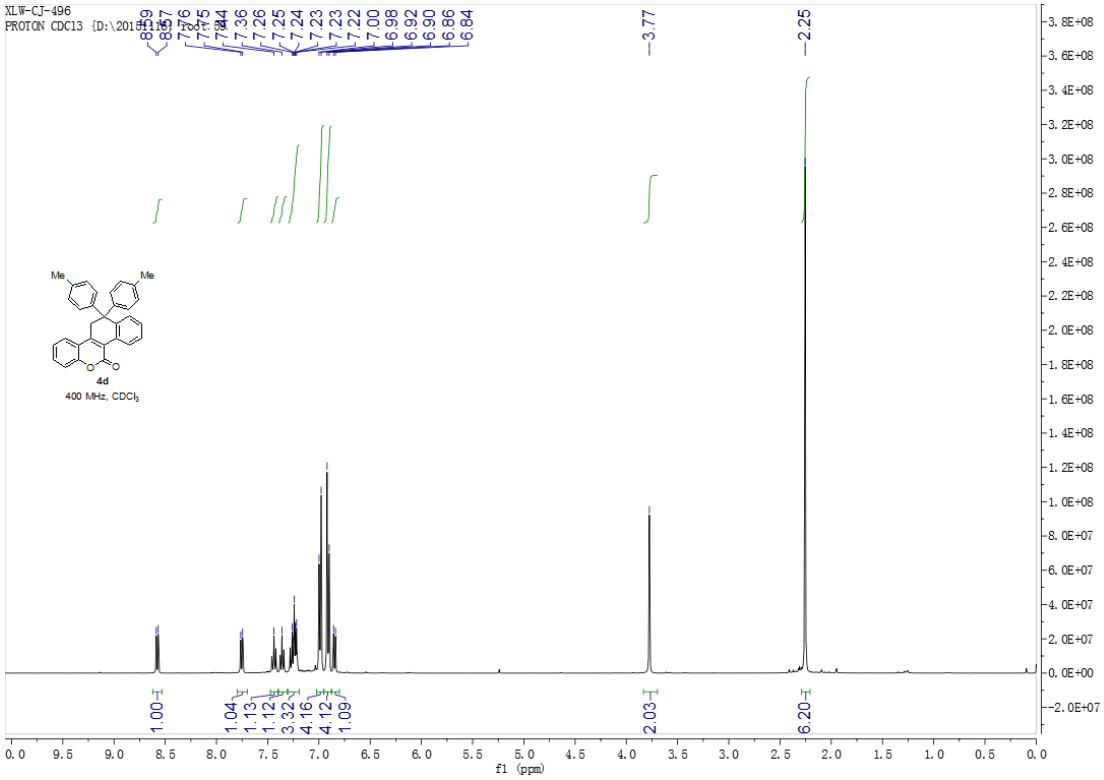

XLW-CJ-471
C13CPD CDCl3 {D:\20151019} root 33
158.78
152.94
147.27
144.49
142.78
131.41
130.69
128.85
128.34
128.13
128.01
127.23
126.86
124.37
123.85
119.90
119.29
116.91
77.36
77.04
76.73
51.91
36.99
Ph Ph
O
O
4a
100 MHz, CDCl3
f1 (ppm)

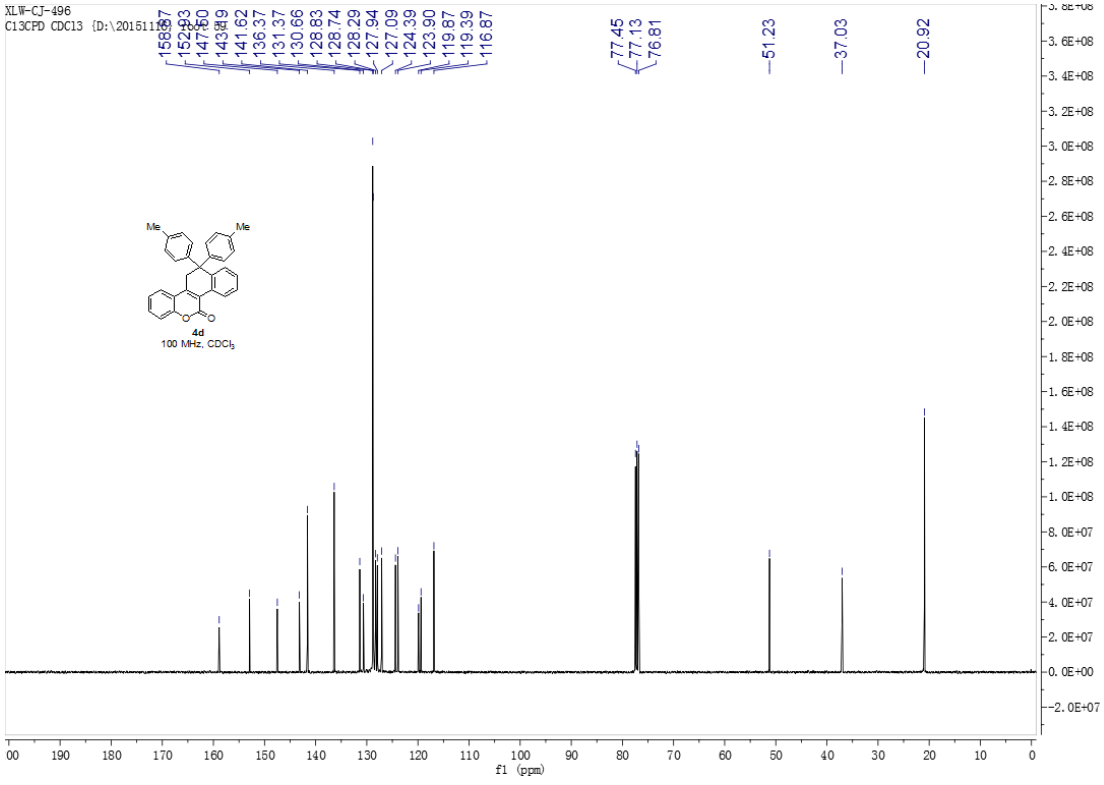

XLW-CJ-515
PROTON CDCl3 {D:\20151214} root
8.50
8.38
8.37
7.40
7.38
7.36
7.29
7.28
7.27
7.25
7.23
7.22
7.22
7.21
7.19
7.18
7.15
7.13
7.06
7.05
7.04
7.04
7.03
6.87
6.85
3.81
2.41
Ph Ph
Me
O
O
4b
400 MHz, CDCl3
1.00
1.06
1.15
9.13
4.15
1.03
2.03
3.07
f1 (ppm)

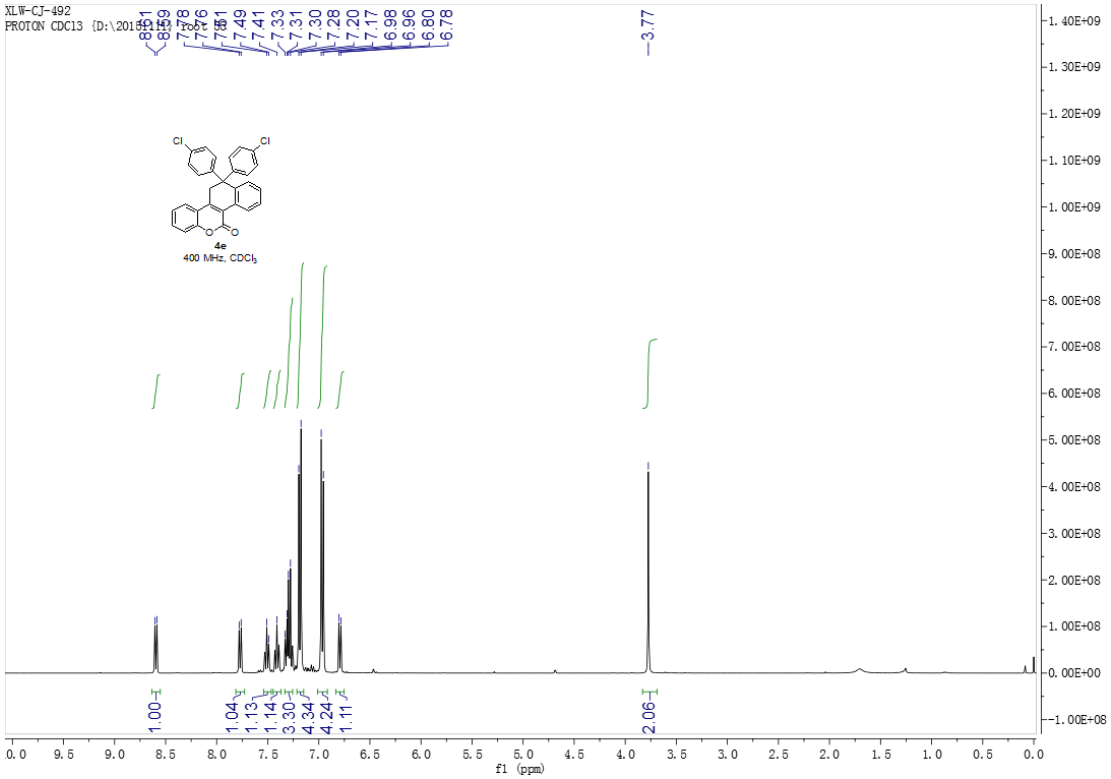

XLW-CJ-515
C13CPD CDCl3 {D:\20151214} root
159.00
151.08
147.29
144.55
142.73
133.99
132.57
130.83
128.89
128.82
128.23
128.14
127.96
127.21
126.85
123.64
119.71
118.97
116.64
77.42
77.10
76.78
51.90
37.02
21.22
Ph Ph
Me
O
O
4b
100 MHz, CDCl3
f1 (ppm)


XLW-CJ-488
PROTON CDCl3 {D:\20151109} root
8.48
8.46
7.76
7.76
7.43
7.43
7.42
7.41
7.40
7.40
7.30
7.28
7.26
7.25
7.24
7.23
7.23
7.22
7.21
7.20
7.04
7.04
7.03
7.02
6.86
6.84
3.79
Ph Ph
Cl
O
O
4c
400 MHz, CDCl3
1.00
1.06
2.31
1.02
7.45
4.34
1.11
2.09
f1 (ppm)


XLW-CJ-488
C13CPD CDCl3 {D:\20151109} root
158.23
151.24
146.04
144.21
142.88
131.31
130.28
129.90
128.93
128.81
128.78
128.22
128.10
127.31
126.98
123.38
120.86
120.52
118.30
77.37
77.06
76.74
51.83
37.01
Ph Ph
Cl
O
O
4c
100 MHz, CDCl3
f1 (ppm)


XLW-CJ-496
PROTON CDCl3
8.59
8.57
7.76
7.75
7.44
7.36
7.26
7.25
7.24
7.23
7.23
7.22
7.00
6.98
6.92
6.90
6.86
6.84
3.77
2.25
Me
Me
4d
400 MHz, CDCl3
1.00
1.04
1.13
1.12
3.32
4.16
4.12
1.09
2.03
6.20
f1 (ppm)


XLW-CJ-496
C13CPD CDCl3
158.87
152.93
147.60
143.49
141.62
136.37
131.37
130.66
128.83
128.74
128.29
127.94
127.09
124.39
123.90
119.87
119.39
116.87
77.45
77.13
76.81
51.23
37.03
20.92
Me
Me
4d
100 MHz, CDCl3
f1 (ppm)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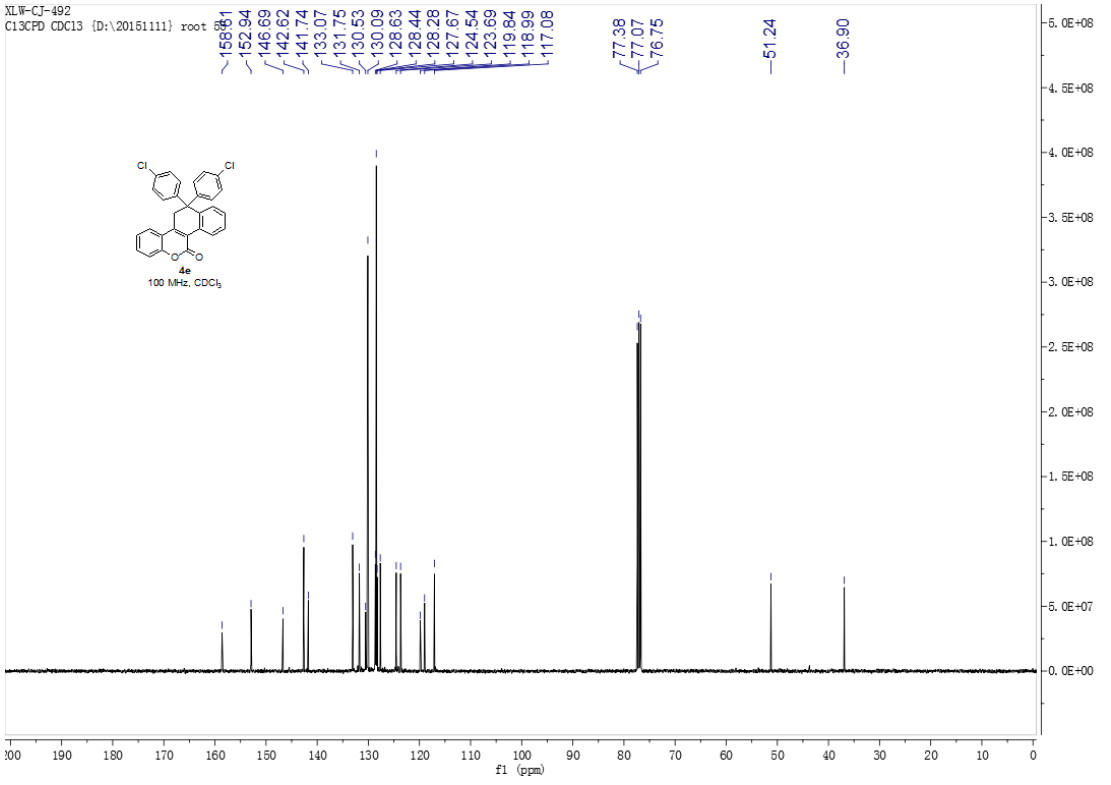
7.51
7.49
7.41
7.33
7.31
7.30
7.28
7.20
7.17
6.98
6.96
6.80
6.78
3.77
4e
400 MHz, CDCl3
1.00
1.04
1.13
1.14
3.30
4.34
4.24
1.11
2.06
f1 (ppm)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152.94
146.69
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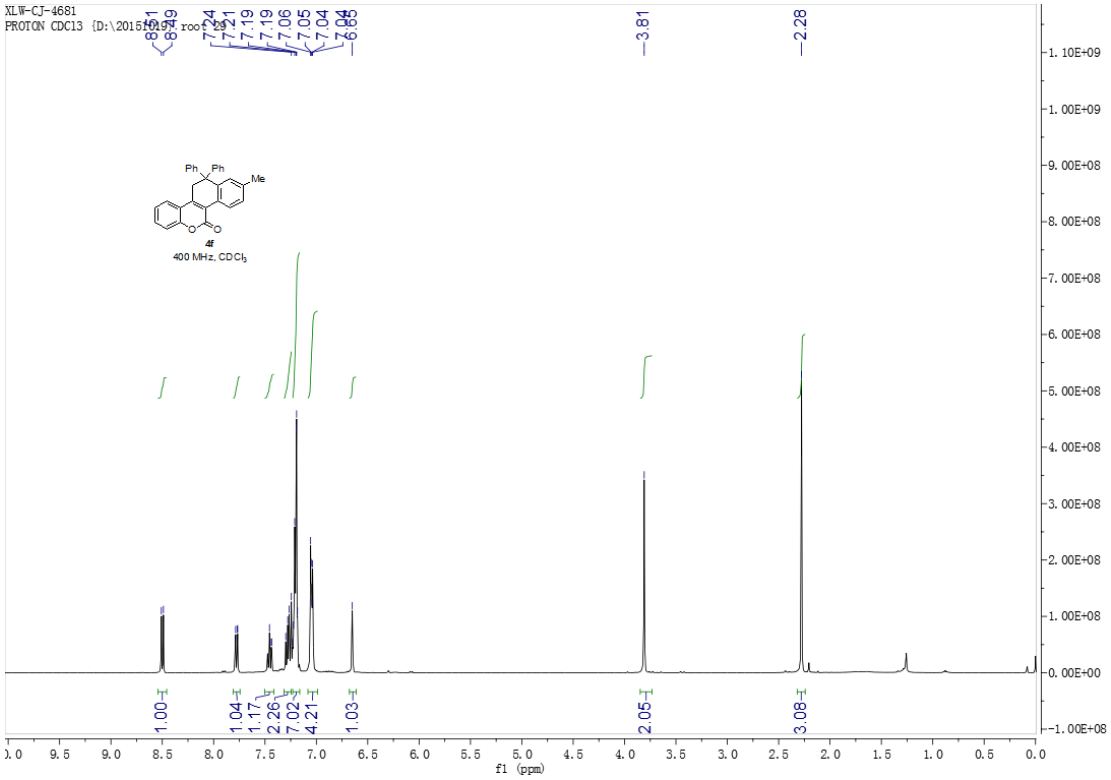
141.74
133.07
131.75
130.53
130.09
128.63
128.44
128.28
127.67
124.54
123.69
119.84
118.99
117.08
77.38
77.07
76.75
51.24
36.90
4e
100 MHz, CDCl3
f1 (ppm)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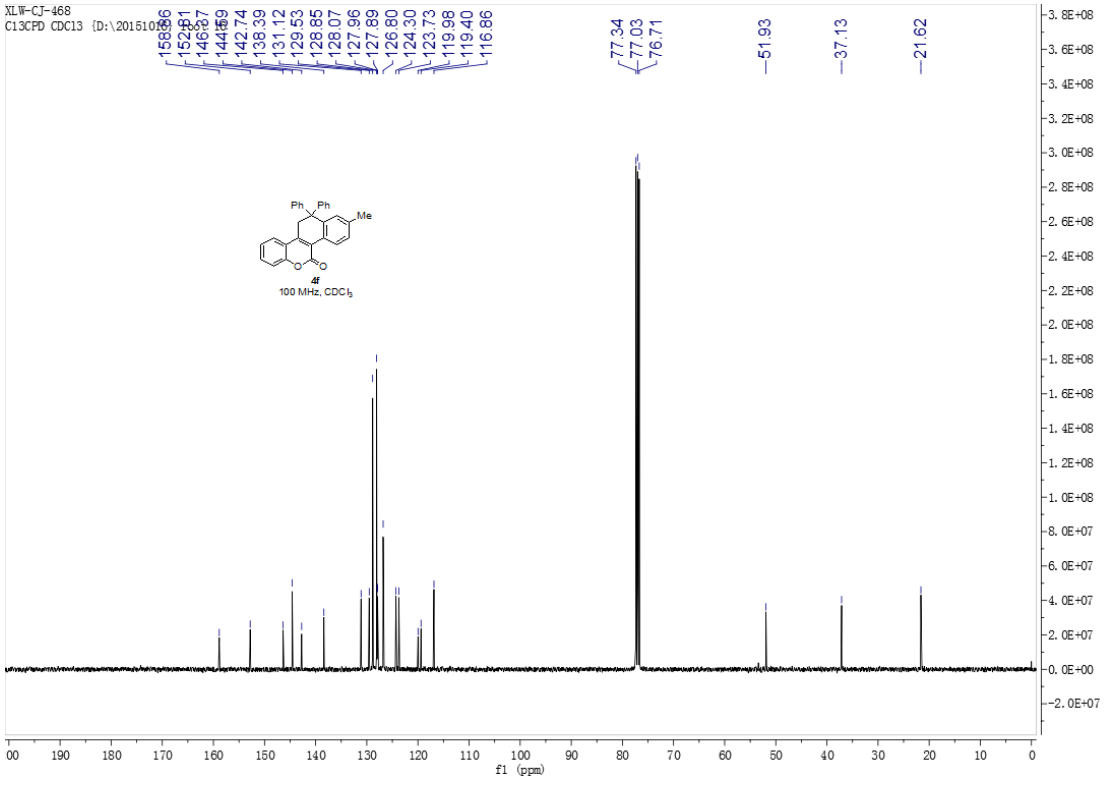
8.39
7.24
7.21
7.19
7.19
7.06
7.05
7.04
7.04
6.85
3.81
2.28
Ph
Ph
Me
O
O
4f
400 MHz, CDCl3
1.00
1.04
1.17
2.26
7.02
4.21
1.03
2.05
3.08
f1 (ppm)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152.81
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144.59
142.74
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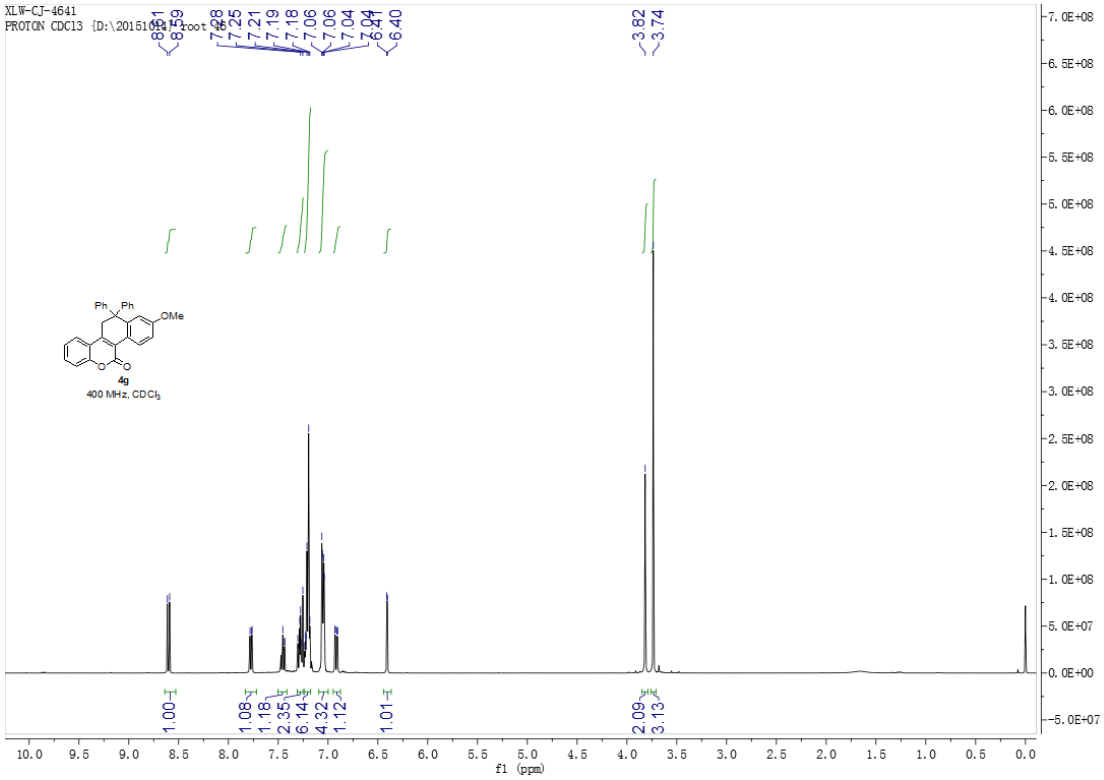
131.12
129.53
128.85
128.07
127.96
127.89
126.80
124.30
123.73
119.98
119.40
116.86
77.34
77.03
76.71
51.93
37.13
21.62
Ph
Ph
Me
O
O
4f
100 MHz, CDCl3
f1 (ppm)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8.39
7.28
7.25
7.21
7.19
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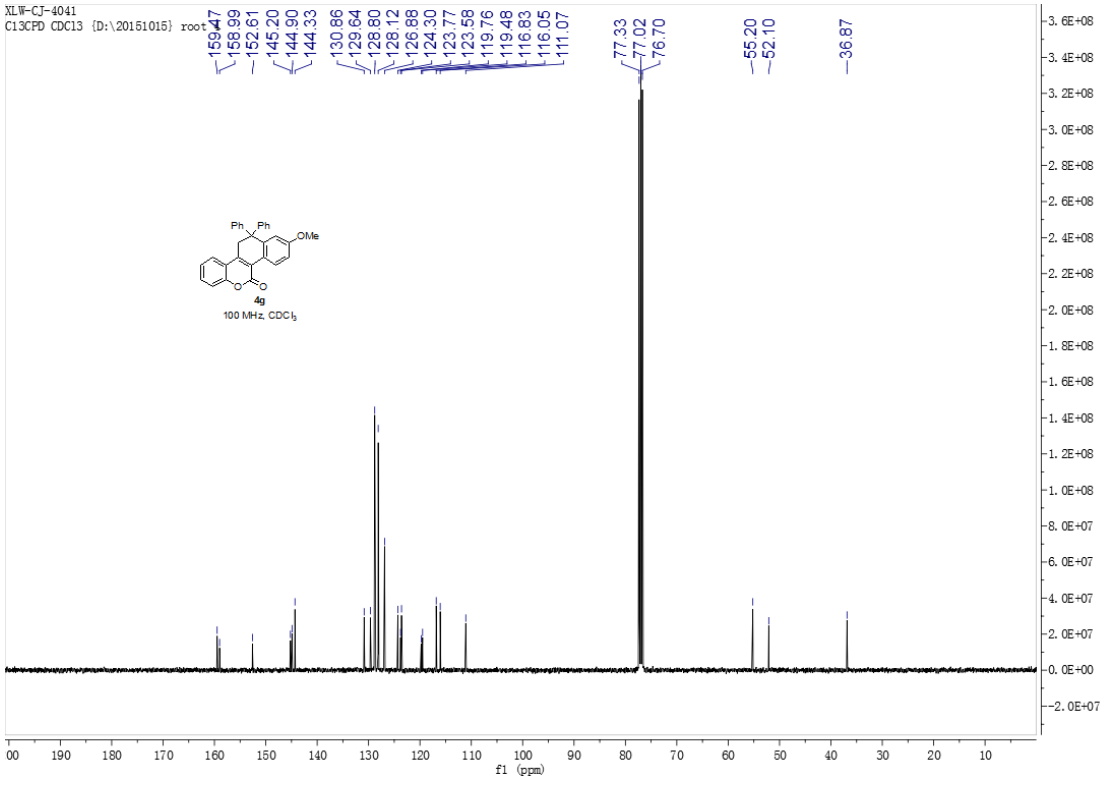
7.06
7.04
6.41
6.40
3.82
3.74
Ph
Ph
OMe
O
O
4g
400 MHz, CDCl3
1.00
1.08
1.18
2.35
6.14
4.32
1.12
1.01
2.09
3.13
f1 (ppm)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152.61
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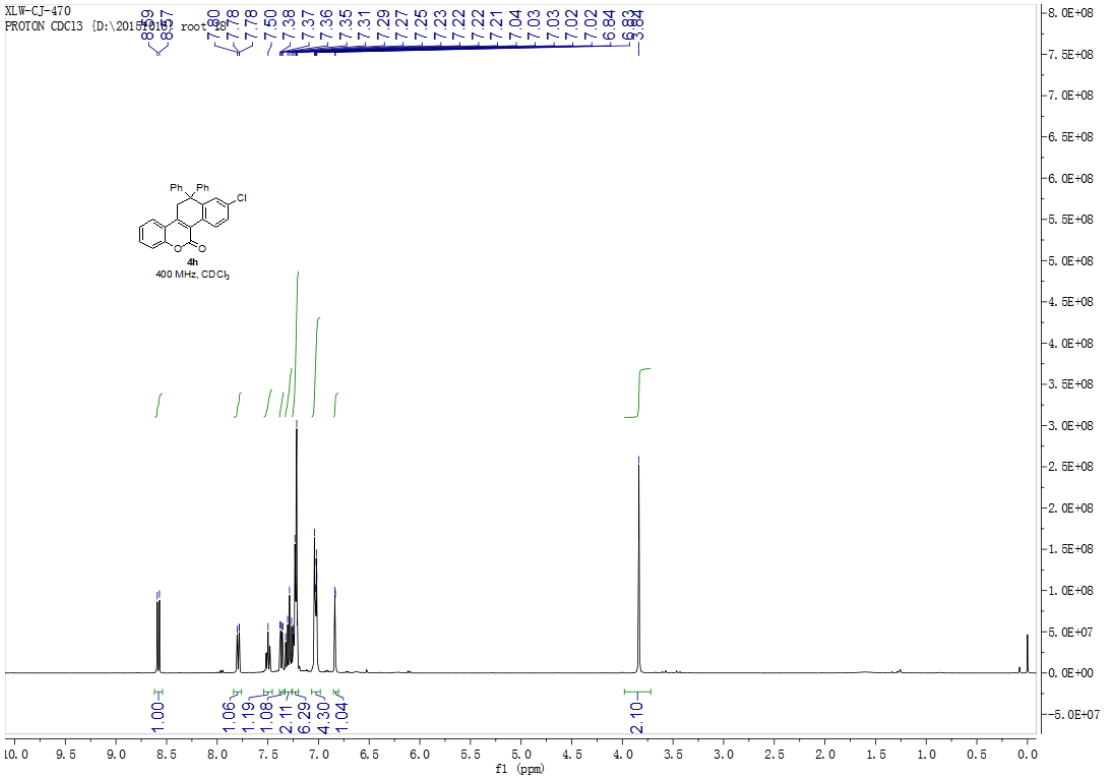
144.90
144.33
130.86
129.64
128.80
128.12
126.88
124.30
123.77
123.58
119.76
119.48
116.83
116.05
111.07
77.33
77.02
76.70
55.20
52.10
36.87
Ph
Ph
OMe
O
O
4g
100 MHz, CDCl3
f1 (ppm)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8.47
7.80
7.78
7.78
7.50
7.38
7.37
7.36
7.35
7.31
7.29
7.27
7.25
7.23
7.22
7.22
7.21
7.04
7.03
7.02
7.02
6.84
6.83
3.84
Ph
Ph
Cl
O
O
4h
400 MHz, CDCl3
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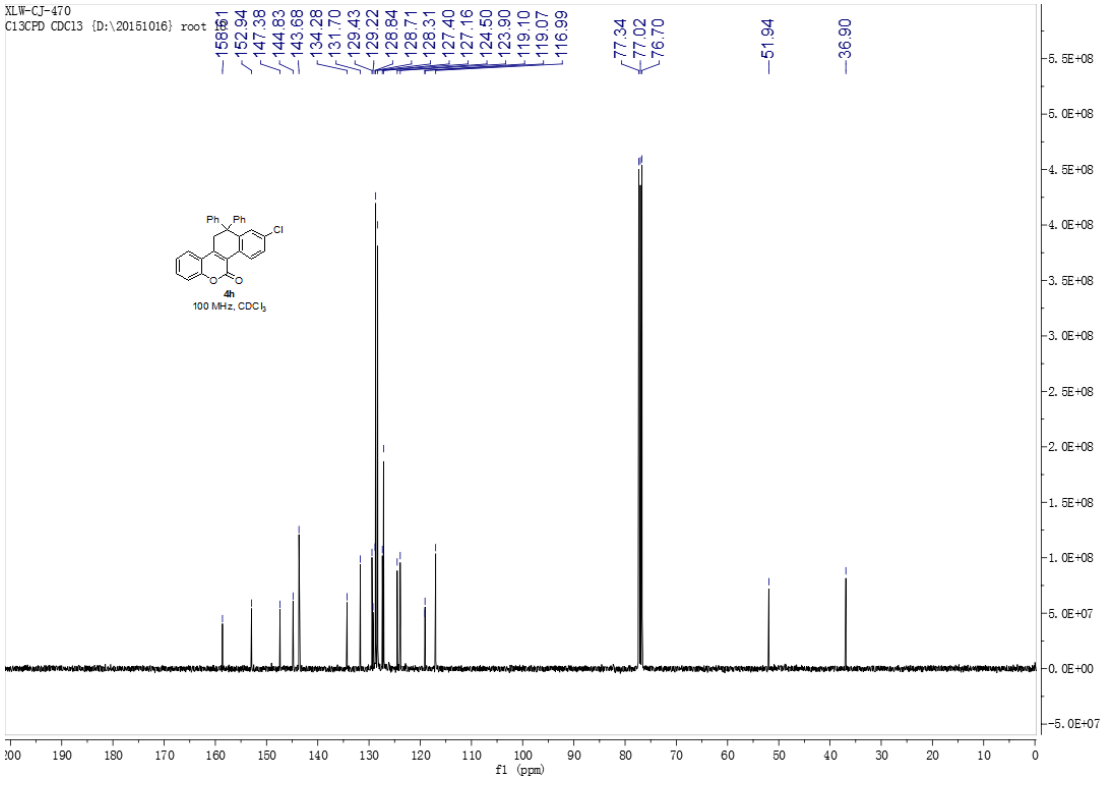
1.06
1.19
1.08
2.11
6.29
4.30
1.04
2.10
f1 (ppm)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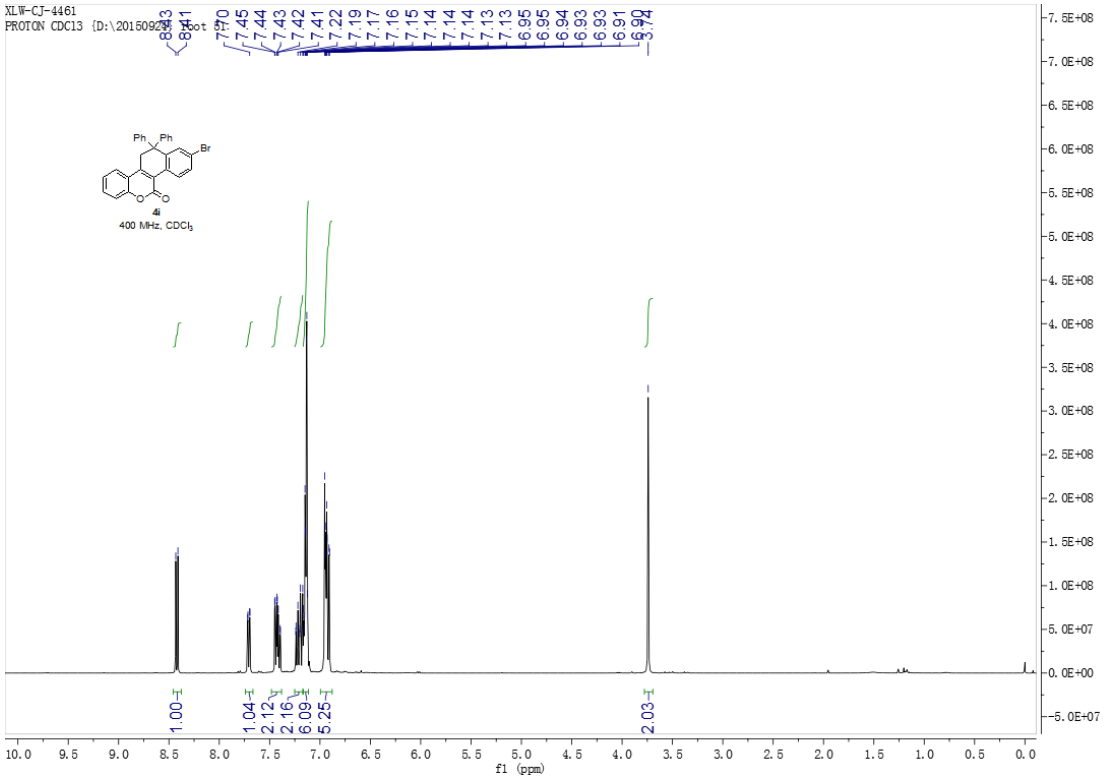
129.43
129.22
128.84
128.71
128.31
127.40
127.16
124.50
123.90
119.10
119.07
116.99
77.34
77.02
76.70
51.94
36.90
Ph
Ph
Cl
O
O
4h
100 MHz, CDCl3
f1 (ppm)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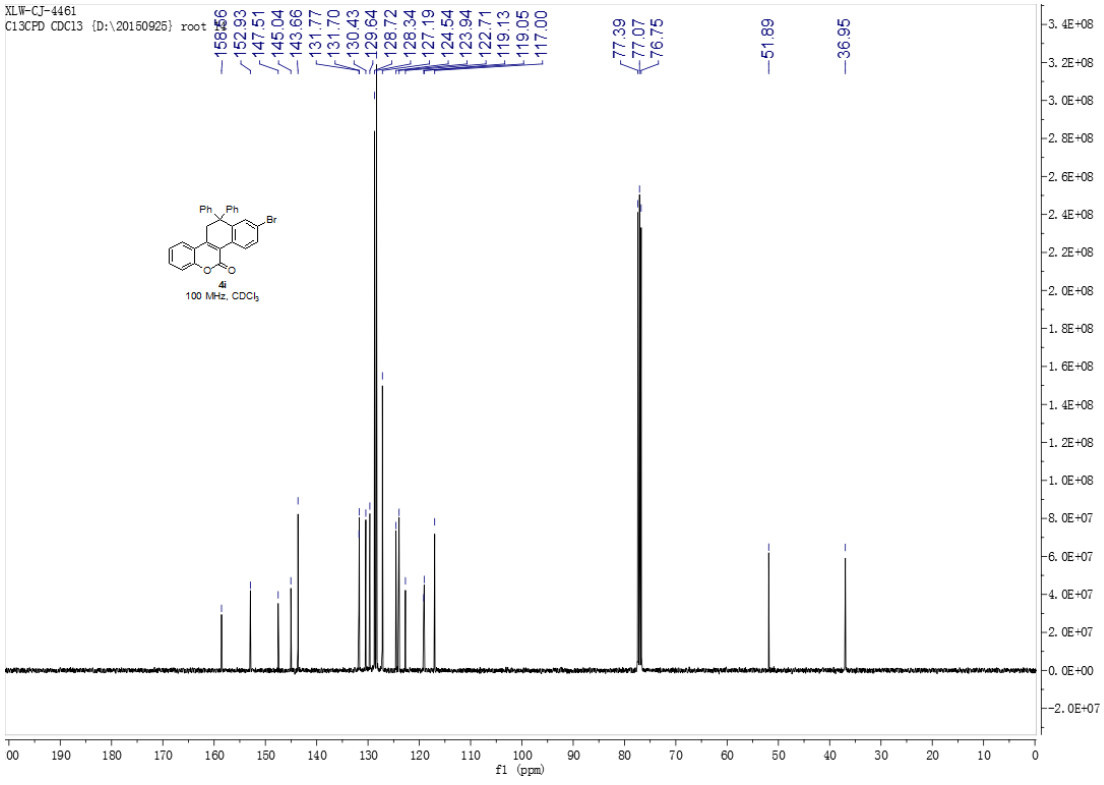
7.42
7.41
7.22
7.19
7.17
7.16
7.15
7.14
7.14
7.14
7.13
7.13
6.95
6.95
6.94
6.93
6.93
6.91
6.90
3.74
Ph
Ph
Br
O
O
4i
400 MHz, CDCl3
1.00
1.04
2.12
2.16
6.09
5.25
2.03
f1 (ppm)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147.51
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143.66
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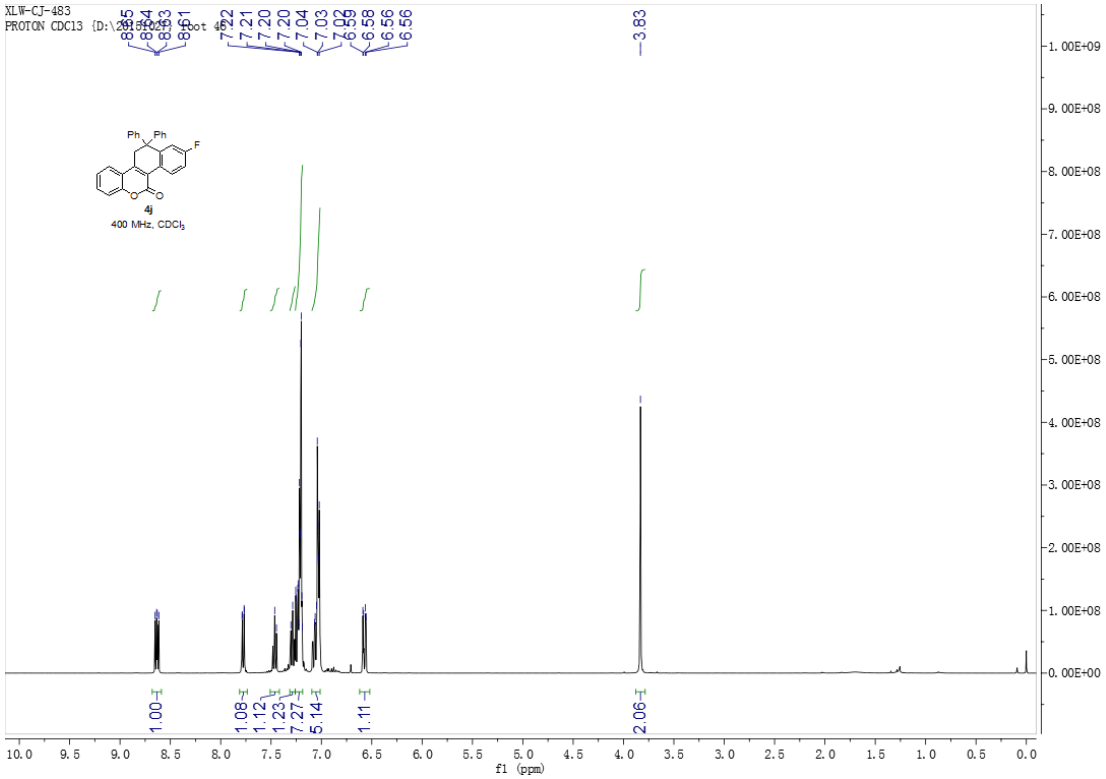
131.70
130.43
129.64
128.72
128.34
127.19
124.54
123.94
122.71
119.13
119.05
117.00
77.39
77.07
76.75
51.89
36.95
Ph
Ph
Br
O
O
4i
100 MHz, CDCl3
f1 (ppm)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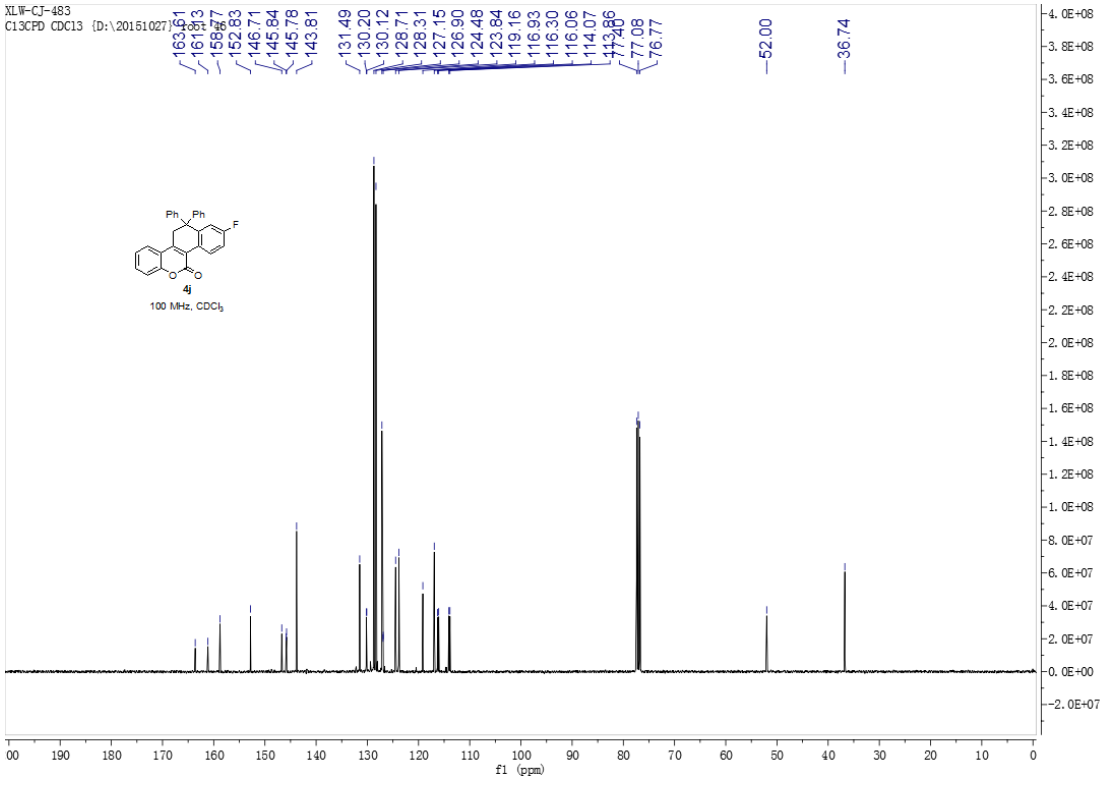
8.54
8.53
8.51
7.22
7.21
7.20
7.20
7.04
7.03
7.02
6.59
6.58
6.56
6.56
3.83
Ph
Ph
F
O
O
4j
400 MHz, CDCl3
1.00
1.08
1.12
1.23
7.27
5.14
1.11
2.06
f1 (ppm)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C13CPD CDCl3
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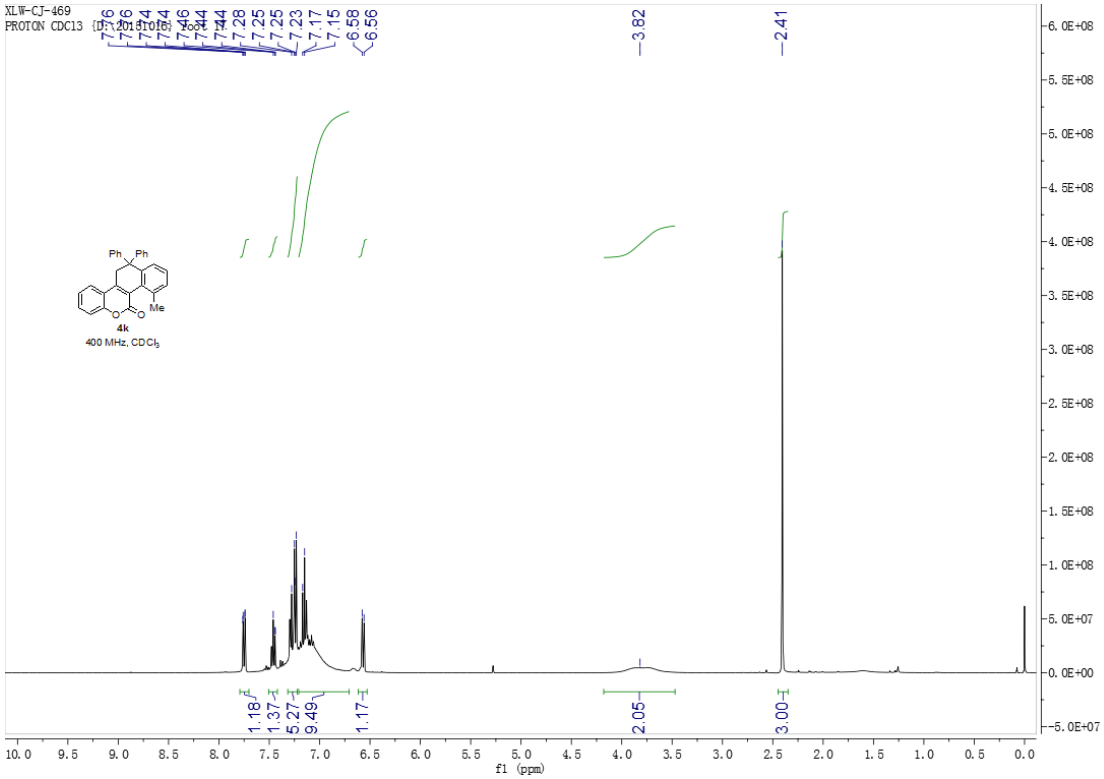
161.13
158.47
152.83
146.71
145.84
145.78
143.81
131.49
130.20
130.12
128.71
128.31
127.15
126.90
124.48
123.84
119.16
116.93
116.30
116.06
114.07
113.86
77.40
77.08
76.77
52.00
36.74
Ph
Ph
F
O
O
4j
100 MHz, CDCl3
f1 (ppm)


XLW-CJ-469
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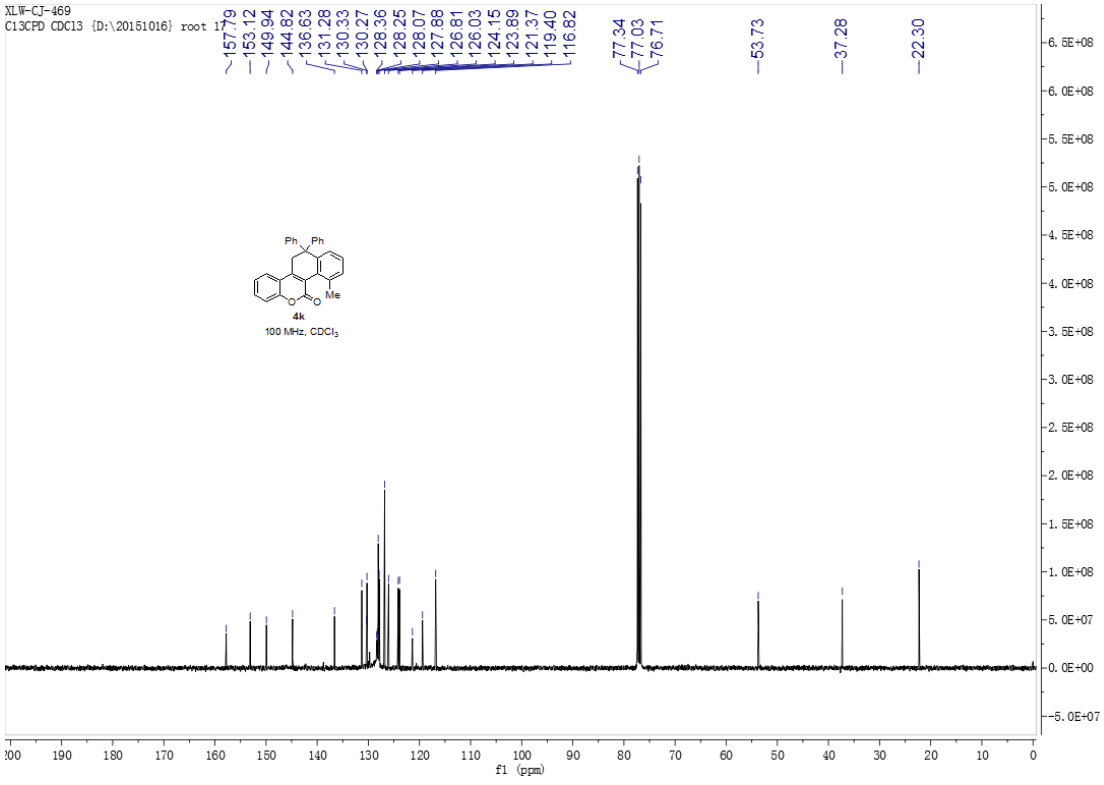
7.46
7.44
7.28
7.25
7.23
7.17
7.15
6.58
6.56
3.82
2.41
Ph
Ph
Me
O
O
4k
400 MHz, CDCl3
1.18
1.37
5.27
9.49
1.17
2.05
3.00
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


XLW-CJ-469
C13CPD CDCl3 {D:\20151016} root 17
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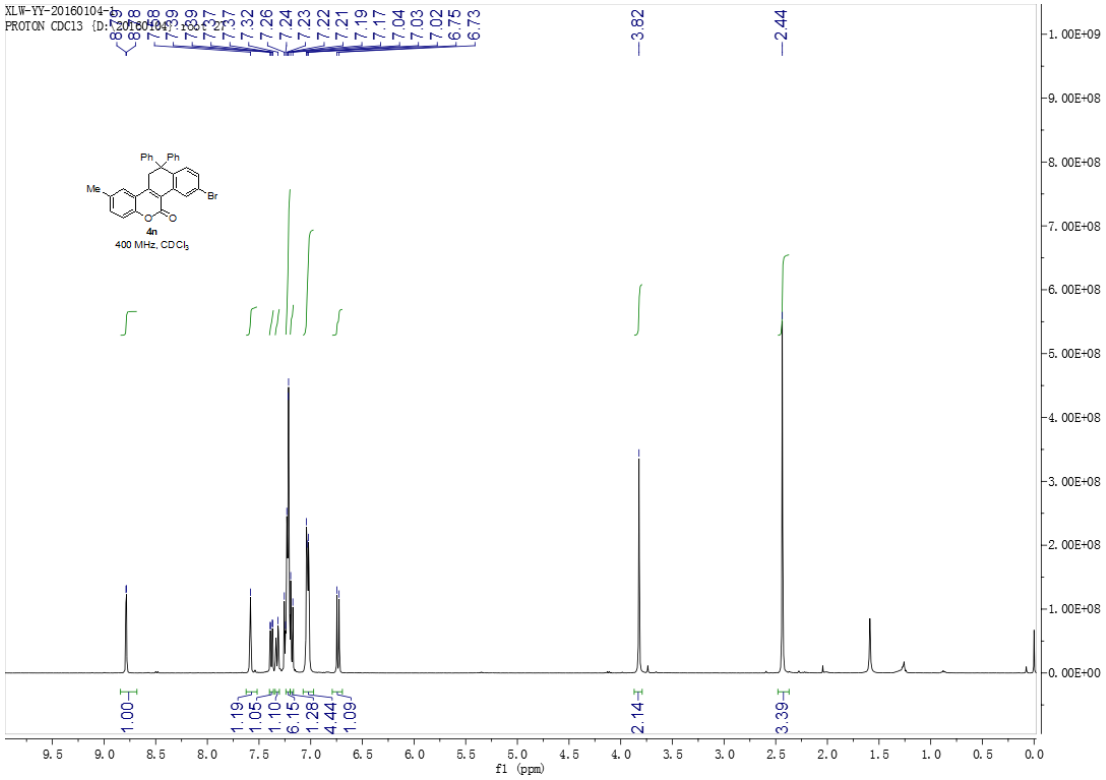
153.12
149.94
144.82
136.63
131.28
130.33
130.27
128.36
128.25
128.07
127.88
126.81
126.03
124.15
123.89
121.37
119.40
116.82
77.34
77.03
76.71
53.73
37.28
22.30
Ph
Ph
Me
O
O
4k
100 MHz, CDCl3
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00
-5.0E+07
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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6.67
7.39
7.38
7.37
7.32
7.26
7.24
7.23
7.22
7.21
7.19
7.17
7.04
7.03
7.02
6.75
6.73
3.82
2.44
Ph
Ph
Me
Br
O
O
4n
400 MHz, CDCl3
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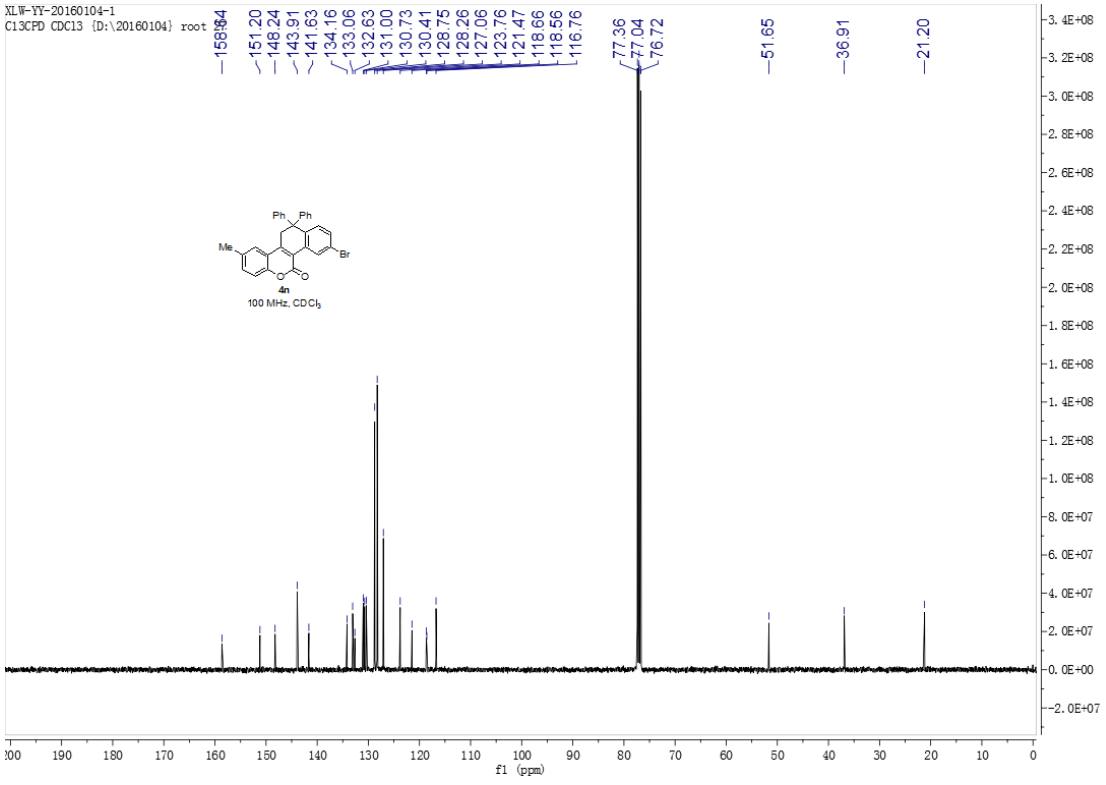
1.19
1.05
1.10
6.15
1.28
4.44
1.09
2.14
3.39
f1 (ppm)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143.91
141.63
134.16
133.06
132.63
131.00
130.73
130.41
128.75
128.26
127.06
123.76
121.47
118.66
118.56
116.76
77.36
77.04
76.72
51.65
36.91
21.20
Ph
Ph
Me
Br
O
O
4n
100 MHz, CDCl3
f1 (ppm)

Figure S1. Fluorescent analysis of 4-vinylcoumarin **3a** in different solvents.

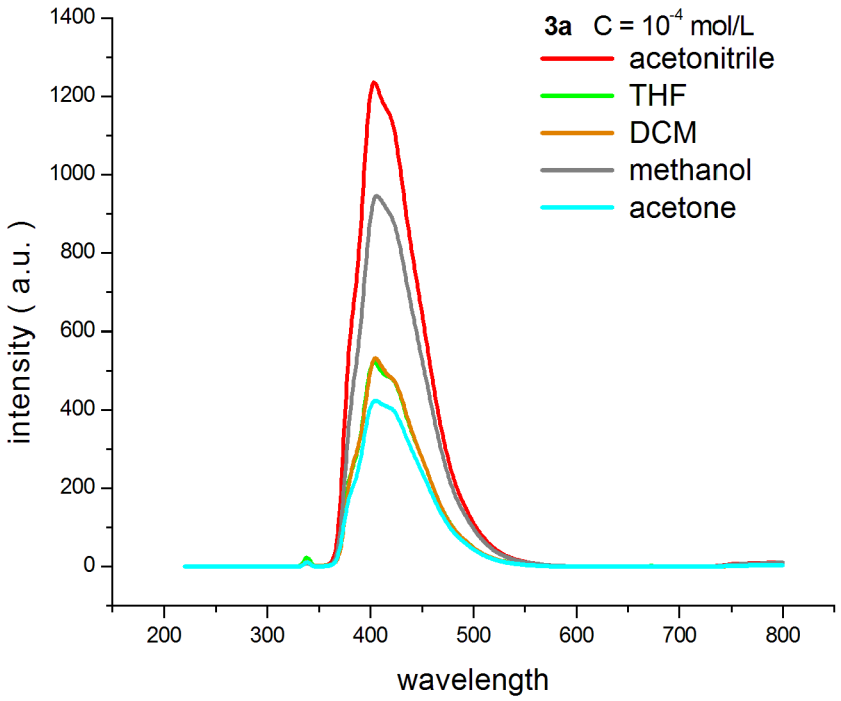


Figure S2. Fluorescent spectra of the solution of 4-vinylcoumarin **3a** in acetonitrile at different concentration.

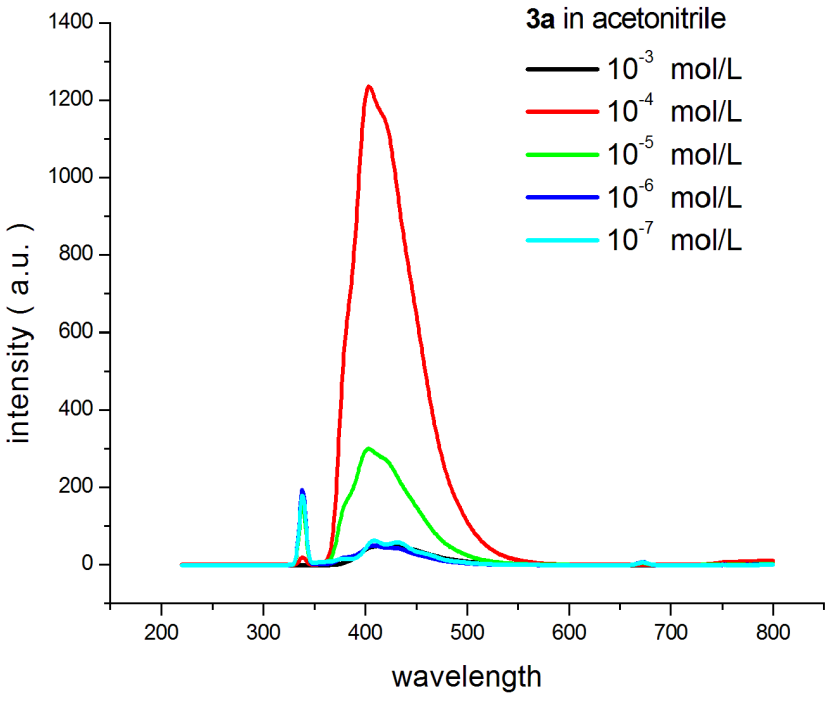


Figure S3. Fluorescent analysis of 4-vinylcoumarin **4a** in different solvents.

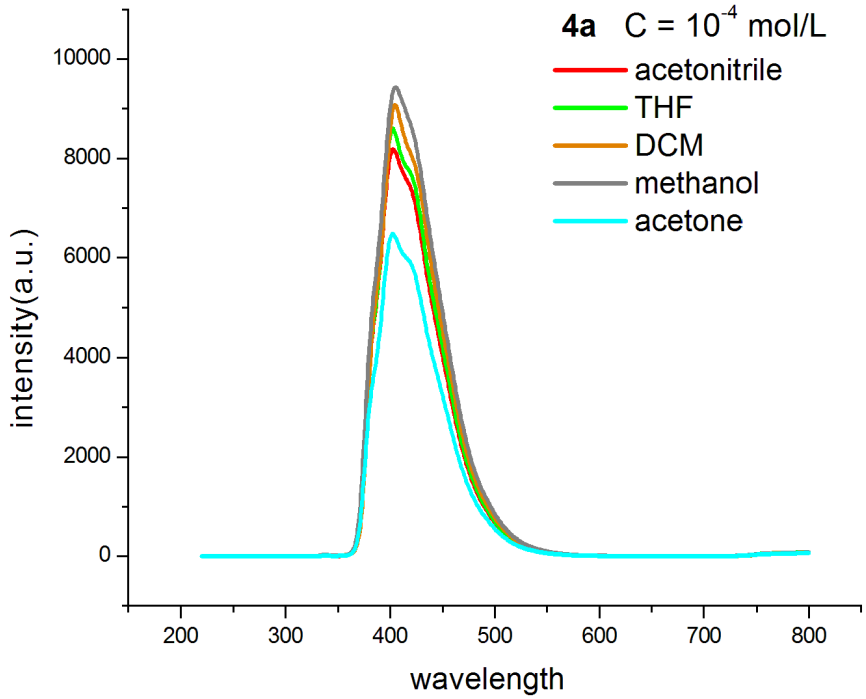


Figure S4. Fluorescent spectra of the solution of 4-vinylcoumarin **4a** in acetonitrile at different concentration.

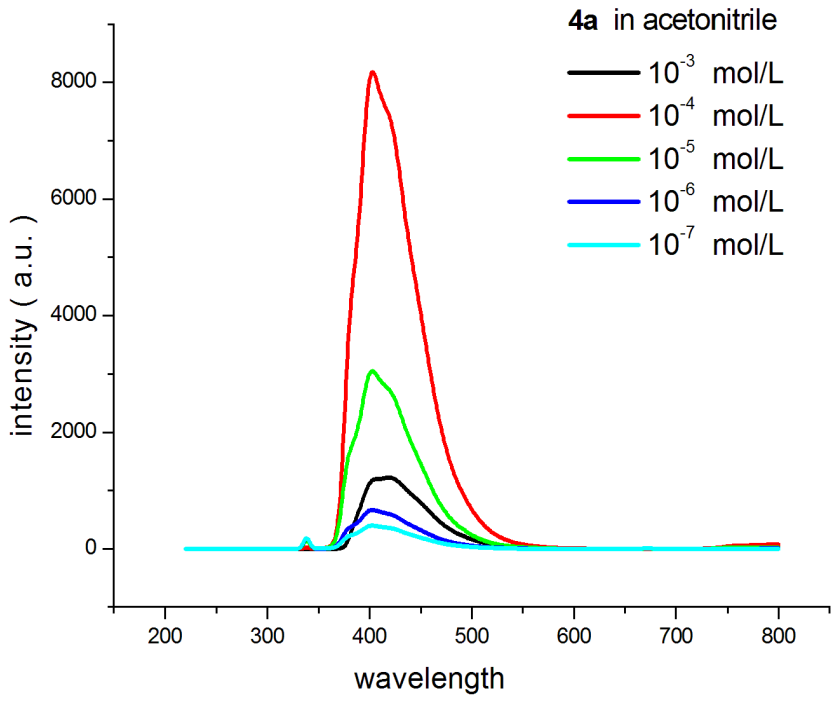
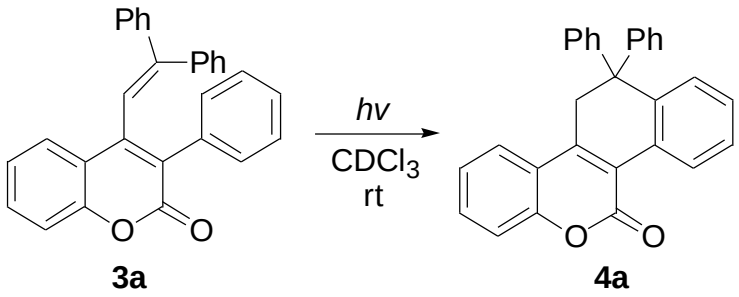


Figure S5. Fluorescent monitoring of transformations of 4-vinylcoumarin **3a** under UV irradiation.



3a **4a**

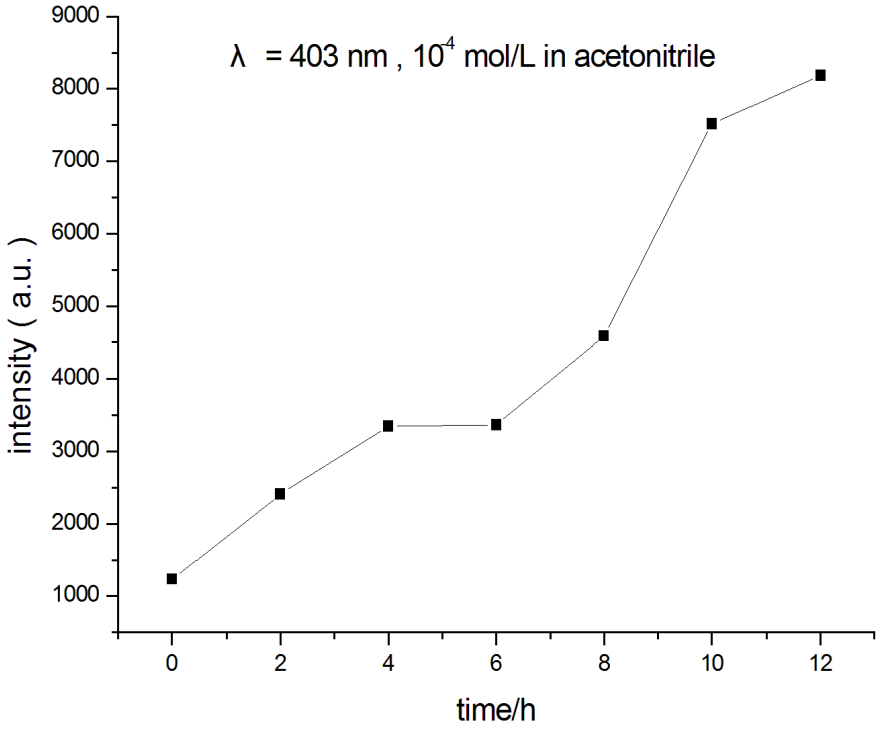
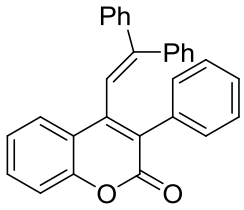
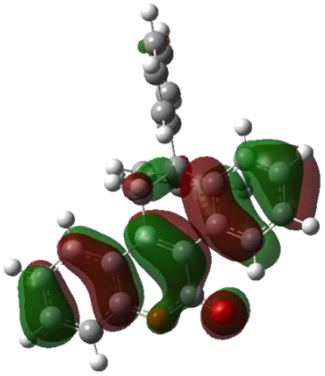
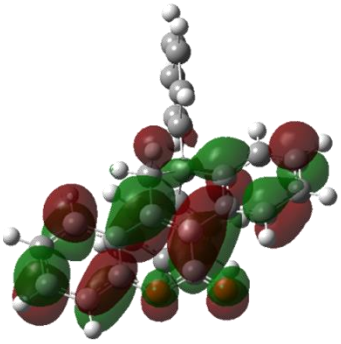
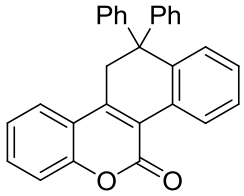
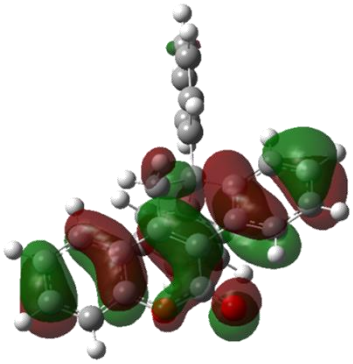
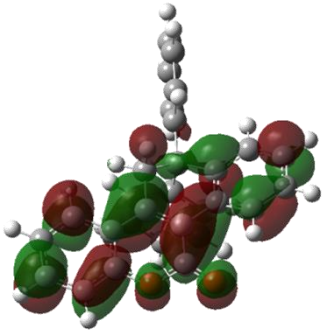


Figure S6. Frontier orbital energy (in eV) calculated at B3LYP/6-31G(d,p) level of theory

	HOMO(eV)	**LUMO(eV)**	**Δ**
3a 	**-5.84** 	**-1.92** 	**3.92**
4a 	**-5.80** 	**-2.03** 	**3.77**

Note: To obtain useful information for the better understanding of the observed fluorescence intensity of **3a** and **4a**, we performed the theoretical calculations using Gaussian 09 software package. Figure S5 gives the electron density diagrams for HOMO and LUMO orbitals of **3a** and **4a**. Interestingly, **3a** has the lower HOMO and the higher LUMO level (-5.84/-1.92 ev respectively), and **4a** has the higher HOMO and the lower LUMO level (-5.80/-2.03 ev respectively). By reference to **3a**, the reduced energy gap of **4a** predominantly derives from the decrease of LUMO level due to diminishing of conjugated 4-vinyl region. These calculation outcomes of frontier orbital energy reasonably account for the difference and spectra performance of **3a** and **4a**.

References: Frisch, M. J. et al. J. Gaussian 09, Revision C. 01. (Gaussian, Wallingford, 2010).

Figure S7. Crystal Structure of **4a**.

This crystal was deposited in the Cambridge Crystallographic Data Centre and assigned as CCDC 1490150. Further information can be found in the CIF file.