Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Iodine-Promoted Sequential Dual Oxidative C_{sp3}-H Amination/ C_{sp3}-H Iodination Reactions: Efficient Synthesis of 1-iodoimidazo[1,5-*a*]pyridines

Yan-Dong Wu, Xiao Gen, Qinghe Gao, Jingjing Zhang, Xia Wu and An-Xin Wu**

Key Laboratory of Pesticide & Chemical Biology, Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, P. R. China

E-mail: chemwuxia@mails.ccnu.edu.cn, chwuax@mail.ccnu.edu.cn;

Table of Contents **page**

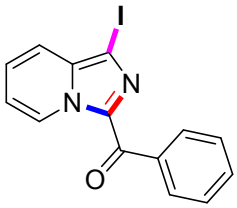
1. General

All substrates and reagents were commercially available and used without further purification. TLC analysis was performed using pre-coated glass plates. Column chromatography was performed using silica gel (200–300 mesh). IR spectra were recorded on a Perkin-Elmer PE-983 infrared spectrometer as KBr pellets with absorption in cm^{-1}. ^1H spectra were recorded in $CDCl_3$ on 300/400/600 MHz NMR spectrometers and resonances (δ) are given in parts per million relative to tetramethylsilane. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constants (Hz) and integration. ^{13}C spectra were recorded in $CDCl_3$ on 75/150 MHz NMR spectrometers and resonances (δ) are given in ppm. HRMS were obtained on a Bruker 7-tesla FT-ICR MS equipped with an electrospray source. The X-ray crystal-structure determinations of **3ma** were obtained on a Bruker SMART APEX CCD system. Melting points were determined using XT-4 apparatus and not corrected.

2. General procedure for the synthesis of 3 (3aa as an example)

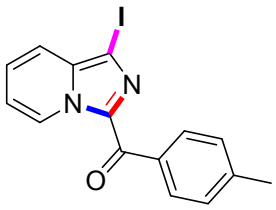
A mixture of acetophenone **1a** (1.0 mmol), pyridin-2-ylmethanamine **2a** (1.0 mmol), HCl (1.0 mmol) and iodine (1.6 mmol) in DMSO (3 mL) was stirred at 110 ℃, till almost completed conversion of the substrates by TLC analysis, then extracted with EtOAc three times (3 × 50 mL). The extract was washed with 10% $Na_2S_2O_3$ solution (w/w). The extract was dried over anhydrous Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography on silica gel (eluent: petroleum ether/EtOAc) to afford the product **3aa**.

3. Characterization data for compounds 3



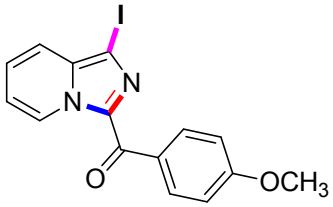
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(phenyl)methanone (3aa):

Yield 74%; 257.5 mg; yellow solid; mp 134–137℃; IR (KBr): 1610, 1448, 1434, 1338, 1227, 883, 753, 707 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.77 (d, J = 7.2 Hz, 1H), 8.38 (d, J = 7.8 Hz, 2H), 7.56 (t, J = 8.4 Hz, 2H), 7.50 (t, J = 7.8 Hz, 2H), 7.24 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.2, 137.4, 136.8, 136.3, 132.3, 130.7, 128.1, 127.1, 125.5, 118.3, 117.1, 78.7; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{14}H_{10}IN_2O$: 348.9832; found: 348.9837.



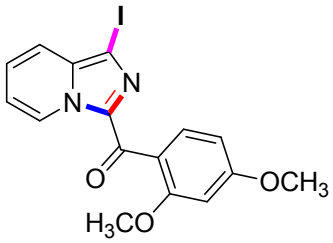
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(p-tolyl)methanone (3ba):

Yield 70%; 253.4 mg; yellow solid; mp 135–138 ℃; IR (KBr): 1618, 1605, 1438, 1336, 1231, 1188, 889, 753 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.80 (d, J = 7.2 Hz, 1H), 8.31 (d, J = 7.8 Hz, 2H), 7.59 (d, J = 8.4 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 7.26 (t, J = 7.8 Hz, 1H), 7.05 (t, J = 6.6 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.2, 143.1, 137.0, 136.3, 134.9, 130.8, 128.7, 127.1, 125.3, 118.4, 116.9, 78.4, 21.7; HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{15}H_{12}IN_2O$: 362.9989; found: 362.9992.



(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(4-methoxyphenyl)methanone (3ca):

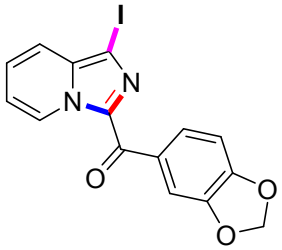
Yield 75%; 283.5 mg; yellow solid; mp 136–139 ℃; IR (KBr): 1632, 1596, 1436, 1174, 765, 751, 616 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.80 (d, J = 7.2 Hz, 1H), 8.49 (d, J = 9.0 Hz, 2H), 7.60 (d, J = 9.0 Hz, 1H), 7.25 (d, J = 9.0 Hz, 1H), 7.05 (t, J = 7.2 Hz, 1H), 7.01 (d, J = 9.0 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 180.1, 163.2, 137.0, 136.1, 133.1, 130.2, 127.4, 125.2, 118.4, 116.8, 113.5, 78.1, 55.5; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{15}H_{12}IN_2O_2$: 378.9938; found: 378.9
946.



(2,4-dimethoxyphenyl)(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3da):

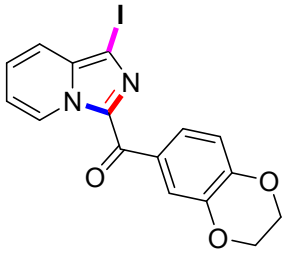
Yield 69%; 281.5 mg; yellow solid; mp 132–136 ℃; IR (KBr): 1633, 1604, 1263, 1097, 1074, 1022, 804 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.71 (d, J = 7.2 Hz, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.51 (d, J = 9.0 Hz, 1H), 7.21-7.16 (m, 1H), 6.98 (t, J = 7.2 Hz, 1H), 6.54-6.47 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 182.2, 163.4, 160.3, 136.3, 133.5, 127.2, 127.0, 125.2, 120.9, 118.4,

116.9, 104.2, 99.3, 78.4, 55.9, 55.5; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}IN_2O_3$: 409.0044; found: 409.0049.



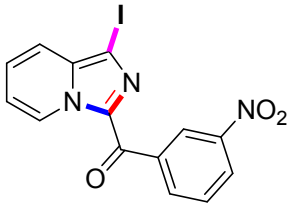
benzo[d][1,3]dioxol-5-yl(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3ea):

Yield 63%; 246.9 mg; yellow solid; mp 236–239 ℃; IR (KBr): 1631, 1590, 1433, 1419, 1257, 1240, 757 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.78 (d, J = 7.2 Hz, 1H), 8.17 (d, J = 8.4 Hz, 1H), 7.96 (s, 1H), 7.61 (d, J = 9.0 Hz, 1H), 7.28 (d, J = 7.2 Hz, 1H), 7.06 (d, J = 7.2 Hz, 1H), 6.94 (d, J = 7.8 Hz, 1H), 6.07 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.5, 151.4, 147.6, 136.3, 131.8, 127.4, 127.3, 125.3, 118.5, 117.0, 110.7, 108.0, 107.9, 101.7, 78.3; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{15}H_9IN_2NaO_3$: 414.9550; found: 414.9556.



(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3fa):

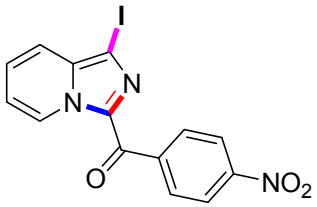
Yield 74%; 300.4 mg; yellow solid; mp 187–190 ℃; IR (KBr): 1606, 1573, 1437, 1322, 1287, 1236, 1219, 1184, 1068, 887, 757 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.78 (d, J = 7.2 Hz, 1H), 8.08-8.00 (m, 2H), 7.59 (d, J = 9.0 Hz, 1H), 7.25 (d, J = 8.4 Hz, 1H), 7.04 (d, J = 6.6 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 4.37-4.30 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.8, 147.7, 142.9, 136.9, 136.2, 131.0, 127.3, 125.2, 125.0, 120.4, 118.4, 117.0, 116.9, 78.2, 64.7, 64.1; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{12}IN_2O_3$: 406.9887; found: 406.9891.



(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(3-nitrophenyl)methanone (3ga):

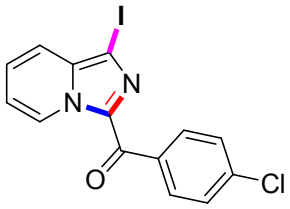
Yield 73%; 286.8 mg; yellow solid; mp 232–235 °C; IR (KBr): 1603, 1530, 1442, 1425, 1348, 1335, 1229, 762, 749, 714 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm)

9.86 (d, J = 6.6 Hz, 1H), 9.25 (s, 1H), 8.81 (d, J = 7.8 Hz, 1H), 8.43 (d, J = 7.8 Hz, 1H), 7.78-7.63 (m, 2H), 7.41 (t, J = 7.8 Hz, 1H), 7.20 (t, J = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 178.1, 148.1, 139.0, 137.1, 136.52, 136.45, 129.3, 127.4, 126.6, 126.5 125.7, 118.8, 118.0, 79.9; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_9IN_3O_3$: 393.9683; found: 393.9687.



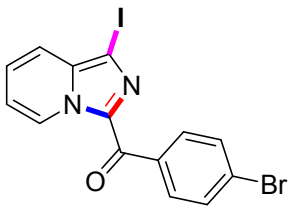
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(4-nitrophenyl)methanone (3ha):

Yield 77%; 302.6 mg; yellow solid; mp 211–214 ℃; IR (KBr): 1629, 1590, 1516, 1441, 1341, 1233, 848, 752, 715 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.87 (d, J = 6.6 Hz, 1H), 8.56 (d, J = 9.0 Hz, 2H), 8.36 (d, J = 8.4 Hz, 2H), 7.70 (d, J = 9.0 Hz, 1H), 7.42 (t, J = 7.2 Hz, 1H), 7.21 (t, J = 6.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 178.7, 149.7, 142.7, 137.1, 136.6, 131.7, 127.4, 126.7, 123.2, 118.7, 118.0, 80.0; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{14}H_9IN_3O_3$: 393.9683; found: 393.9686.



(4-chlorophenyl)(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3ia):

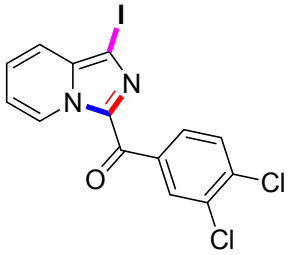
Yield 82%; 313.2 mg; yellow solid; mp 128–131 ℃; IR (KBr): 1613, 1437, 1421, 1332, 1224, 884, 852, 755, 640 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.81 (t, J = 7.8 Hz, 1H), 8.43-8.32 (m, 2H), 7.62 (t, J = 8.4 Hz, 1H), 7.50-7.44 (m, 2H), 7.35-7.28 (m, 1H), 7.13-7.07 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.8, 138.8, 136.7, 136.6, 135.8, 132.2, 128.4, 127.3, 125.9, 118.6, 117.4, 79.0,; HRMS (ESI): m*/z* $[M+H]^+$ calcd for $C_{14}H_9ClIN_2O$: 382.9443; found: 382.9446.



(4-bromophenyl)(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3ja):

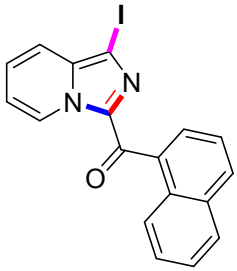
Yield 79%; 336.5 mg; yellow solid; mp 154–157 ℃; IR (KBr): 1610, 1435, 1420, 1333, 1233, 1221, 1176, 1010, 968, 882, 756, 640 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.77 (d, J = 7.2 Hz, 1H), 8.28 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H),

7.59 (d, J = 9.0 Hz, 1H), 7.29 (t, J = 8.4 Hz, 1H), 7.08 (t, J = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 179.7, 136.6, 136.5, 136.1, 132.3, 131.3, 127.5, 127.1, 125.8, 118.5, 117.3, 79.0; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_8BrIN_2NaO$: 448.8757; found: 448.8763.



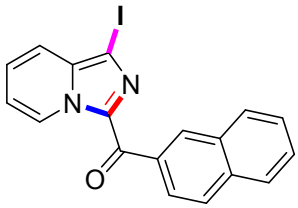
(3,4-dichlorophenyl)(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3ka):

Yield 70%; 291.1 mg; yellow solid; mp 155–158 ℃; IR (KBr): 1612, 1439, 1424, 1334, 1235, 1210, 769, 754 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.77 (d, J = 6.6 Hz, 1H), 8.49 (s, 1H), 8.33 (d, J = 8.4 Hz, 1H), 7.62 (d, J = 9.0 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.33 (t, J = 8.4 Hz, 1H), 7.12 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 178.0, 137.0, 136.7, 136.4, 132.5, 132.4, 130.1, 130.0, 127.4, 127.2, 126.2, 118.6, 117.6, 79.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_7Cl_2IN_2NaO$: 438.8872; found: 438.8875.



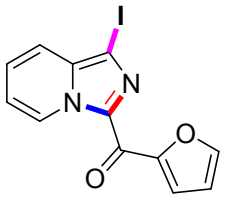
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(naphthalen-1-yl)methanone (3la):

Yield 79%; 314.4 mg; yellow solid; mp 142–145 ℃; IR (KBr): 1600, 1585, 1445, 1435, 1335, 1230, 891, 738, 773, 750 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.91 (d, J = 7.2 Hz, 1H), 8.32-8.27 (m, 1H), 8.04-7.99 (m, 1H), 7.99 (d, J = 8.4 Hz, 1H), 7.91-7.86 (m, 1H), 7.61-7.54 (m, 2H), 7.54-7.47 (m, 2H), 7.31-7.26 (m, 1H), 7.13-7.09 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 184.3, 137.8, 136.8, 135.0, 133.8, 131.5, 131.1, 130.1, 128.4, 127.4, 127.1, 126.0, 125.8, 125.4, 124.4, 118.5, 117.4, 79.4; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{12}IN_2O$: 398.9989; found: 398.9990.



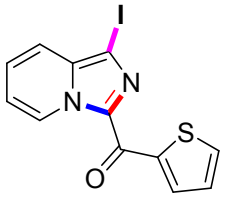
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(naphthalen-2-yl)methanone (3ma):

Yield 72%; 286.6 mg; yellow solid; mp 150–153 ℃; IR (KBr): 1613, 1440, 1420, 1338, 1241, 1220, 1188, 897, 833, 822, 757 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.86 (d, J = 7.2 Hz, 1H), 9.06 (s, 1H), 8.41-8.34 (m, 1H), 8.05 (d, J = 7.8 Hz, 1H), 7.94 (d, J = 9.0 Hz, 1H), 7.89 (d, J = 7.8 Hz, 1H), 7.64-7.55 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.31-7.27 (m, 1H), 7.09 (t, J = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.2, 137.1, 136.5, 135.3, 134.8, 132.91, 132.86, 132.5, 129.9, 128.2, 127.8, 127.6, 126.3, 126.2 125.6, 118.5, 117.2, 78.8; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{18}H_{12}IN_2O$: 398.9989; found: 398.9994.



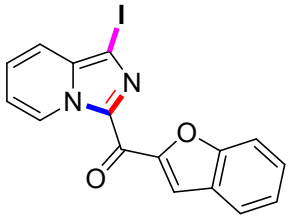
furan-2-yl(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3na):

Yield 62%; 209.5 mg; yellow solid; mp 166–169 ℃; IR (KBr): 1612.3, 1465.3, 1443.4, 1340.5, 1234.8, 1019.6, 844.1, 776.5, 756.0 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.76 (d, J = 7.2 Hz, 1H), 8.19 (d, J = 3.6 Hz, 1H), 7.78-7.70 (m, 1H), 7.55 (d, J = 9.0 Hz, 1H), 7.28-7.16 (m, 1H), 7.10-6.99 (m, 1H), 6.71-6.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 168.2, 150.9, 147.1, 136.4, 135.6, 126.9, 125.3, 122.1, 118.4, 117.1, 112.4, 78.6; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_8IN_2O_2$: 338.9625; found: 338.9622.



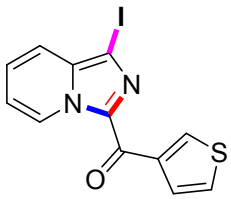
(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(thiophen-2-yl)methanone (3oa):

Yield 60%; 212.4; yellow solid; mp 143–146 ℃; IR (KBr): 1591, 1440, 1409, 1335, 1225, 1038, 814, 753, 711, 643 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.76 (d, J = 7.2 Hz, 1H), 8.64 (d, J = 3.6 Hz, 1H), 7.71 (d, J = 4.2 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.27-7.23 (m, 1H), 7.21 (t, J = 4.2 Hz, 1H), 7.05 (t, J = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 172.7, 142.3, 136.5, 136.0, 135.4, 134.5, 128.1, 127.0, 125.4, 118.5, 117.1, 78.5; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_8IN_2OS$: 354.9397; found: 354.9404.



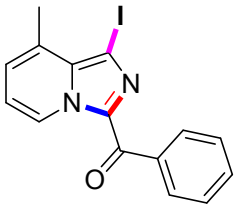
benzofuran-2-yl(1-iodoimidazo[1,5-*a*]pyridin-3-yl)methanone (3pa):

Yield 59%; 228.9 mg; yellow solid; mp 207–210 ℃; IR (KBr): 1626,1613, 1550, 1442, 1338, 1236, 1167, 765, 757, 745 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.79 (d, J = 6.6 Hz, 1H), 8.57 (s, 1H), 7.77 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 8.4 Hz, 1H), 7.56 (d, J = 9.0 Hz, 1H), 7.45 (t, J = 7.8 Hz, 1H), 7.30 (t, J = 7.2 Hz, 1H), 7.25 (t, J = 7.8 Hz, 1H), 7.07 (t, J = 7.2, Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 169.3, 155.6, 151.0, 136.6, 135.9, 127.9, 127.7, 127.2, 126.9, 125.7, 123.6, 118.5, 117.9, 117.4, 112.2, 79.2; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{16}H_{10}IN_2O_2$: 388.9781; found: 388.9782.



(1-iodoimidazo[1,5-*a*]pyridin-3-yl)(thiophen-3-yl)methanone (3qa):

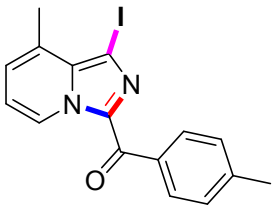
Yield 57%; 201.7 mg; yellow solid; mp 165–168 ℃; IR (KBr): 1589, 1443, 1333, 1229, 1170, 839, 798, 757, 707, 652 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.78 (d, J = 7.2 Hz, 1H), 9.04 (s, 1H), 7.98 (d, J = 4.8 Hz, 1H), 7.56 (d, J = 8.4 Hz, 1H), 7.36-7.31 (m, 1H), 7.23 (t, J = 7.8 Hz, 1H), 7.03 (t, J = 6.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 174.5, 140.5, 136.3, 135.53, 135.48, 128.8, 127.0, 125.3, 125.1, 118.5, 117.0, 78.5; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{12}H_8IN_2OS$: 354.9397; found: 354.9395.



(1-iodo-8-methylimidazo[1,5-*a*]pyridin-3-yl)(phenyl)methanone (3ab):

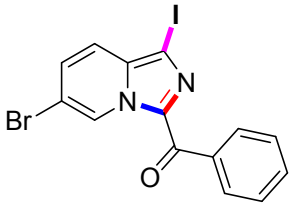
Yield 61%; 220.8 mg; yellow solid; mp 145–148 ℃; IR (KBr): 1623, 1615, 1446, 1426, 1359, 1244, 934, 782, 713 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.81 (d, J = 6.6 Hz, 1H), 8.35 (d, J = 7.2 Hz, 2H), 7.57 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 7.2 Hz, 2H), 6.98 (d, J = 6.6 Hz, 1H), 6.93 (t, J = 7.2 Hz, 1H), 2.92 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.5, 137.8, 137.1, 134.3, 132.3, 130.8, 128.9, 128.1, 125.9,

125.5, 116.9, 75.2, 20.2; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{12}IN_2O$: 362.9989; found: 362.9988.

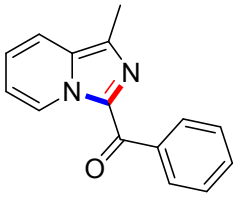


(1-iodo-8-methylimidazo[1,5-*a*]pyridin-3-yl)(p-tolyl)methanone (3bb):

Yield 67%; 251.9 mg; yellow solid; mp 114–117 ℃; IR (KBr): 1614, 1599, 1427, 1351, 1319, 1248, 1184, 929, 770, 735 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.78 (d, J = 7.2 Hz, 1H), 8.27 (d, J = 7.8 Hz, 2H), 7.31 (d, J = 7.8 Hz, 2H), 6.95 (d, J = 6.6 Hz, 1H), 6.90 (t, J = 7.2 Hz, 1H), 2.90 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.3, 143.0, 137.2, 135.1, 134.1, 130.9, 129.7, 128.8, 125.7, 125.3, 116.7, 74.9, 21.7, 20.3; HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}IN_2O$: 377.0145; found: 377.0145.



(6-bromo-1-iodoimidazo[1,5-*a*]pyridin-3-yl)(phenyl)methanone (3ac):
Yield 50%; 212.9 mg; yellow oil, IR (KBr): 1634.4, 1608.6, 1448.0, 1424.9, 1284.6, 1222.1, 965.6, 794.4 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 10.00 (s, 1H), 8.40-8.34 (m, 2H), 7.60-7.43 (m, 4H), 7.33-7.27 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 181.5, 137.1, 136.7, 134.8, 132.7, 130.8, 128.9, 128.2, 127.1, 118.9, 113.2, 79.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{14}H_8BrIN_2NaO$: 448.8757; found: 448.8764.



(1-methylimidazo[1,5-*a*]pyridin-3-yl)(phenyl)methanone (3ad):
Yield 75%; 177.1 mg; yellow oil; IR (KBr): 1610, 1454, 1438, 1418, 1324, 1247, 1230, 1095, 883 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 9.81 (d, J = 7.2 Hz, 1H), 8.37 (d, J = 7.2 Hz, 2H), 7.62 (d, J = 9.0 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.50 (t, J = 7.8 Hz, 2H), 7.15 (t, J = 8.4 Hz, 1H), 6.99 (t, J = 6.6 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 181.8, 138.5, 132.7, 132.1, 131.8, 130.6, 128.0, 127.0, 126.8, , 123.4, 117.4, 116.3, 13.1; HRMS (ESI): *m/z* $[M+Na]^+$ calcd for $C_{15}H_{12}N_2NaO$: 259.0842; found: 259.0846.

4. Crystallographic data and molecular structure of compounds 3ma

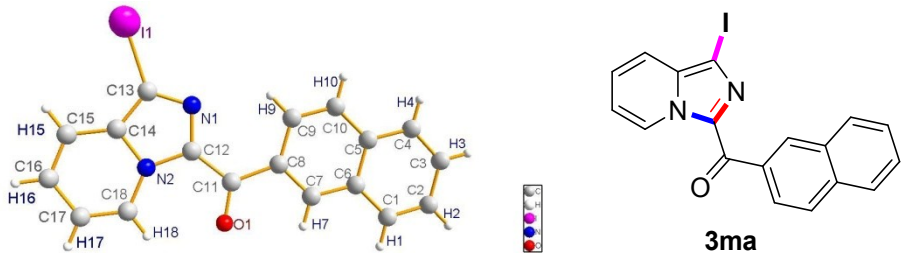
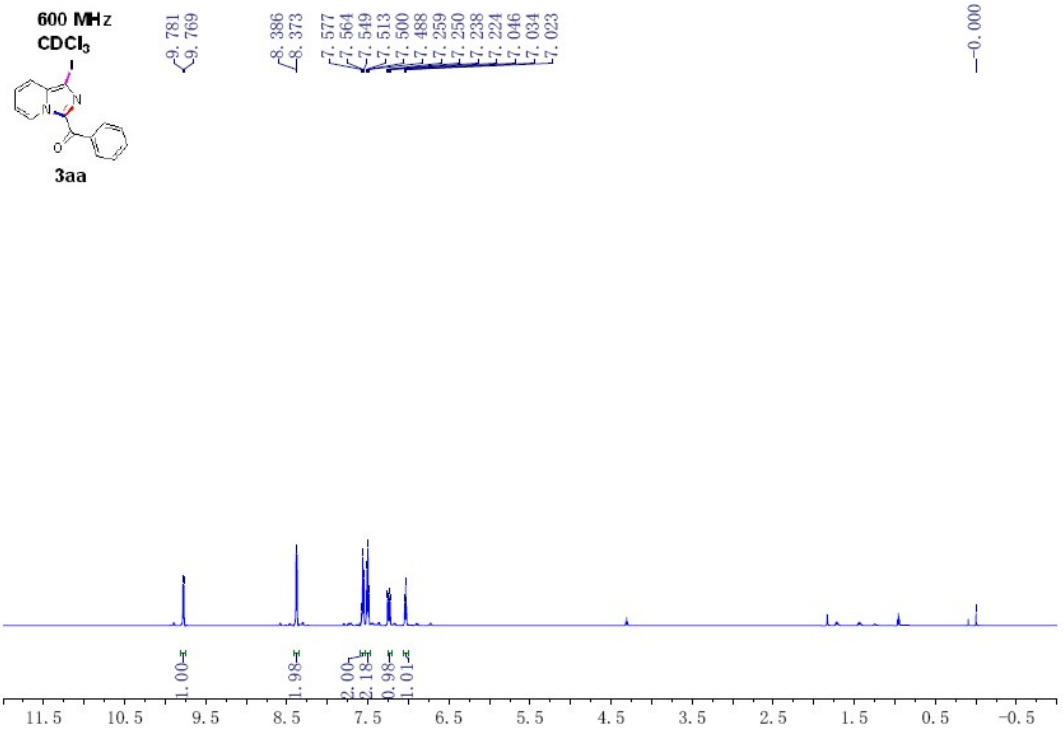
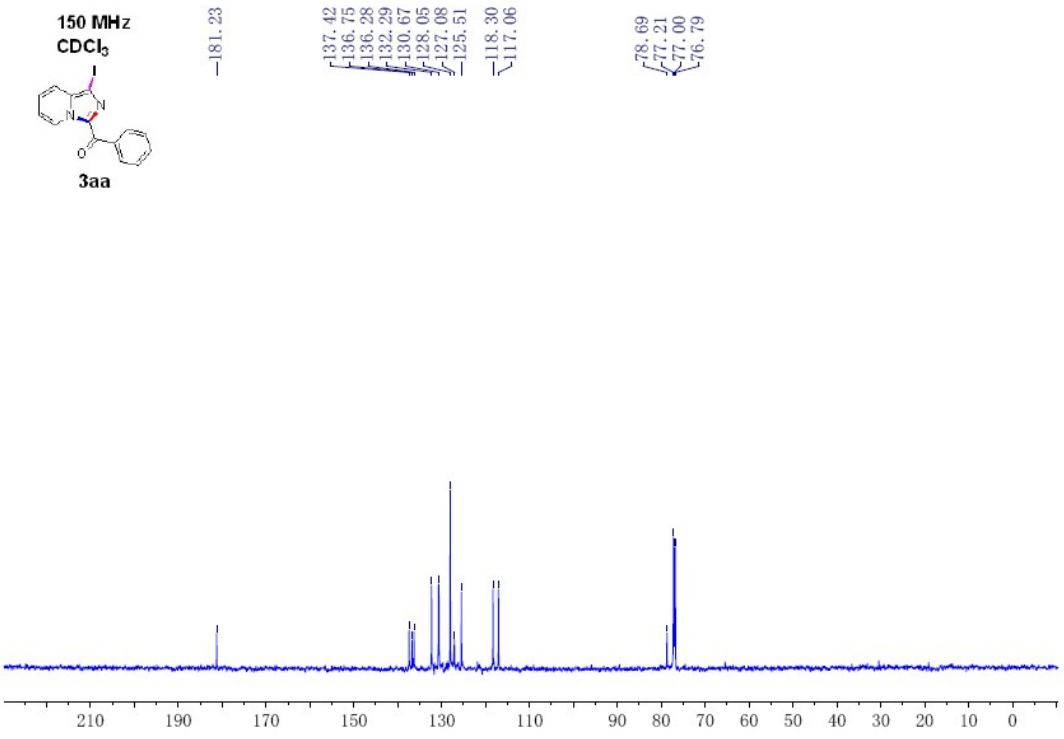


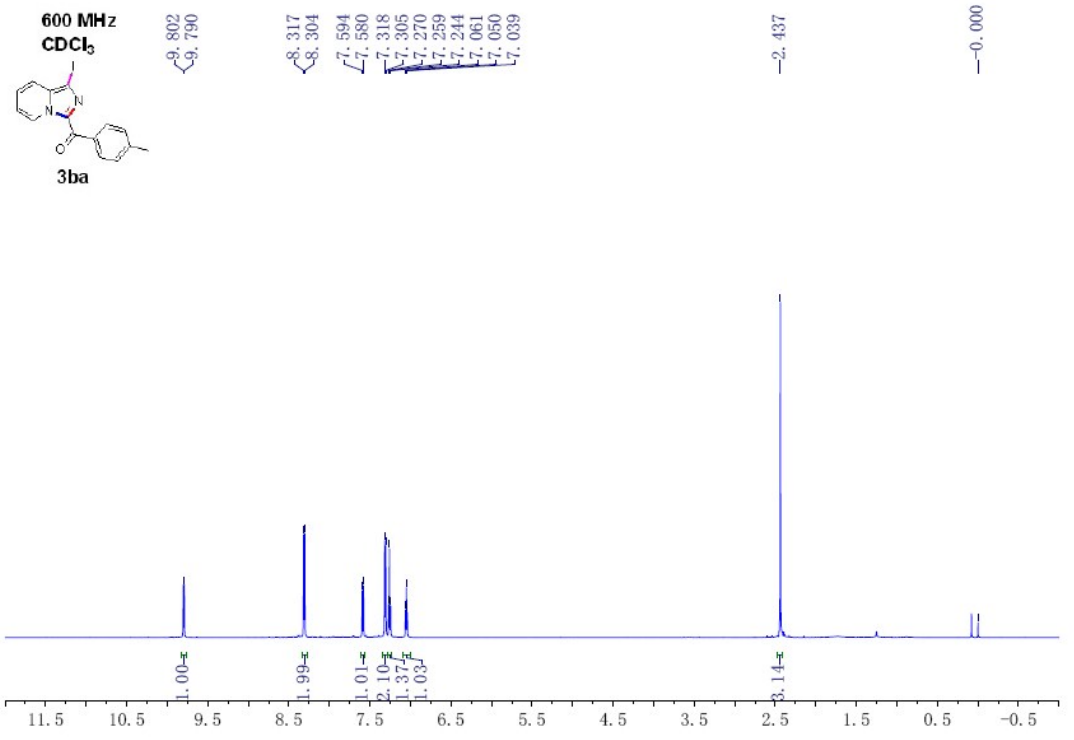
Figure S1. X-ray crystal structure of **3ma**

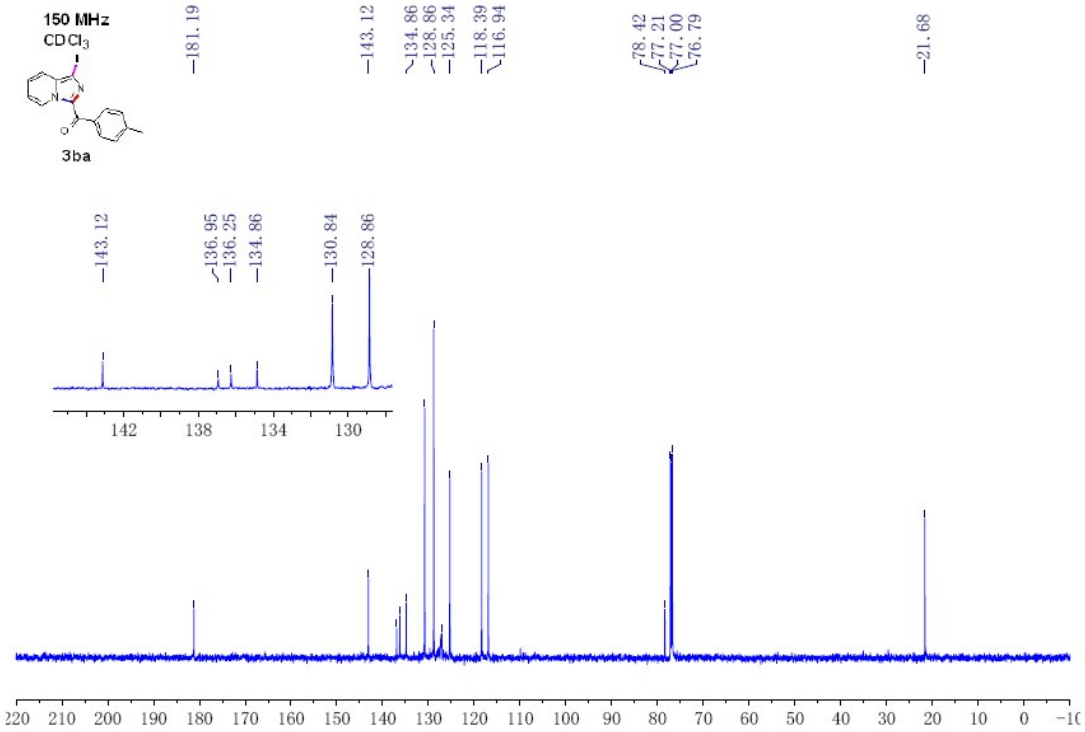
Crystal Data for Compound **3ma**: $C_{18}H_{11}IN_2O$, MW=398.19, Triclinic, a=7.504(11) Å, b=8.467(12) Å, c=13.179(18) Å, α= 95.607(18)°, β=102.60(2)°, γ=110.95(2)°, V= 748.8(18) Å3, T = 296(2) K , space group P-1, Z=2, m(Mo–Ka) = 2.141 mm^{-1}, 10330 Reflections collected, 33963 [R(int) = 0.0244] which were used in all calculations. The final wR2 (F^2) was 1.141. CCDC 1485477 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

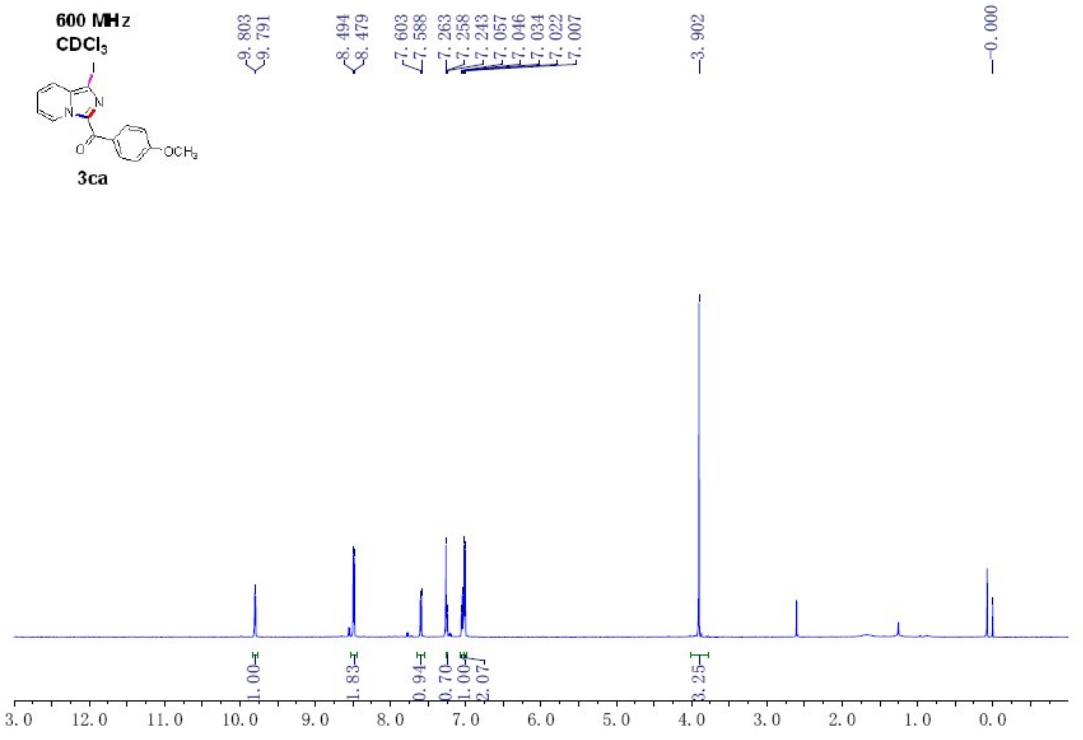
5.^{1}H and ^{13}C NMR spectra of compounds 3

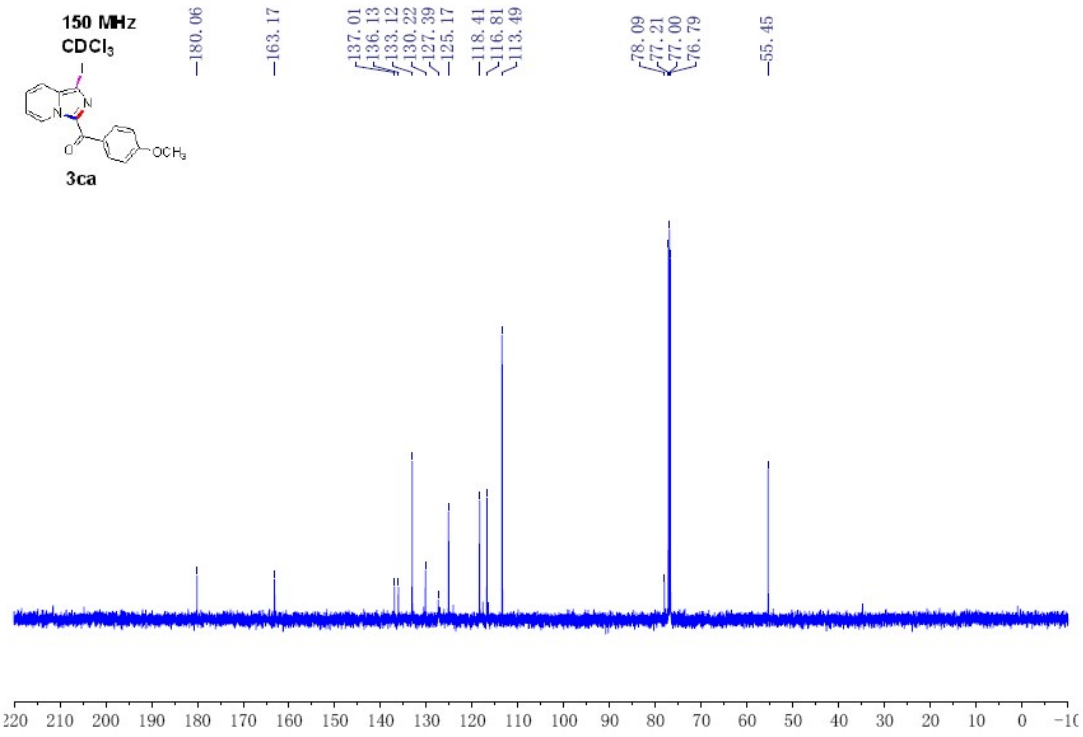

600 MHz
CDCl3
3aa
9.781
9.769
8.386
8.373
7.577
7.564
7.549
7.513
7.500
7.488
7.259
7.250
7.238
7.224
7.046
7.034
7.023
-0.000
1.00
1.98
2.00
2.18
0.98
1.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

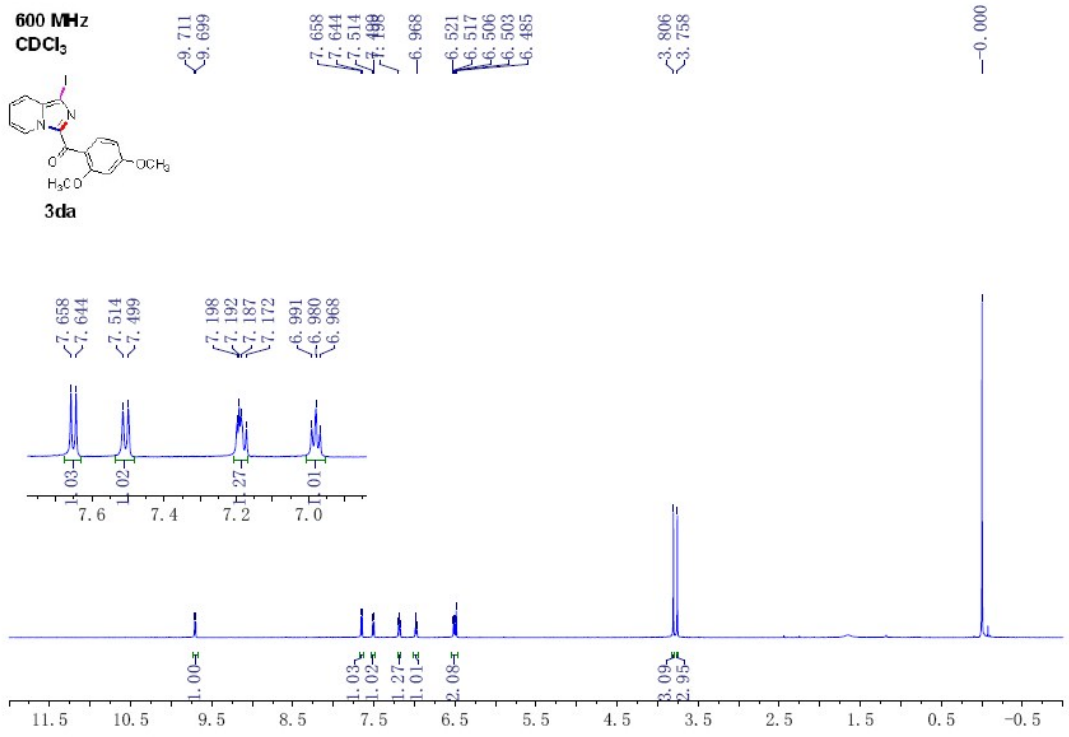

150 MHz
CDCl3
3aa
181.23
137.42
136.75
136.28
132.29
130.67
128.05
127.08
125.51
118.30
117.06
78.69
77.21
77.00
76.79
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

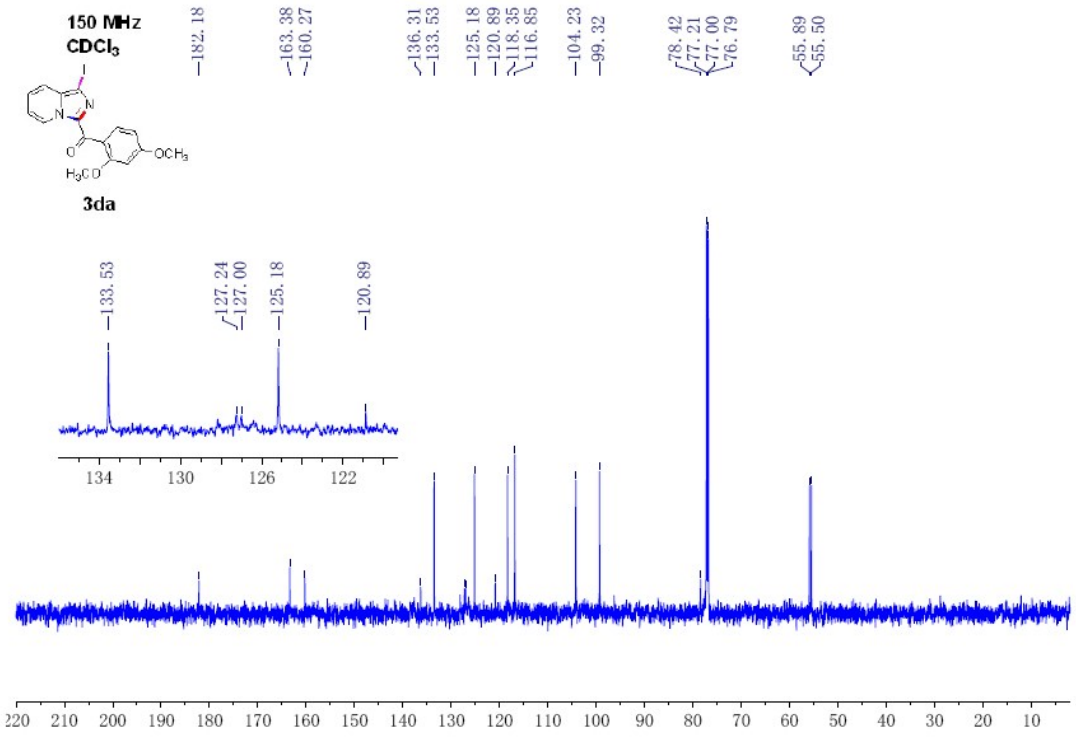

600 MHz
CDCl3
3ba
9.802
9.790
8.317
8.304
7.594
7.580
7.318
7.305
7.270
7.259
7.244
7.061
7.050
7.039
2.437
0.000
1.00
1.99
1.01
2.10
1.37
1.03
3.14
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

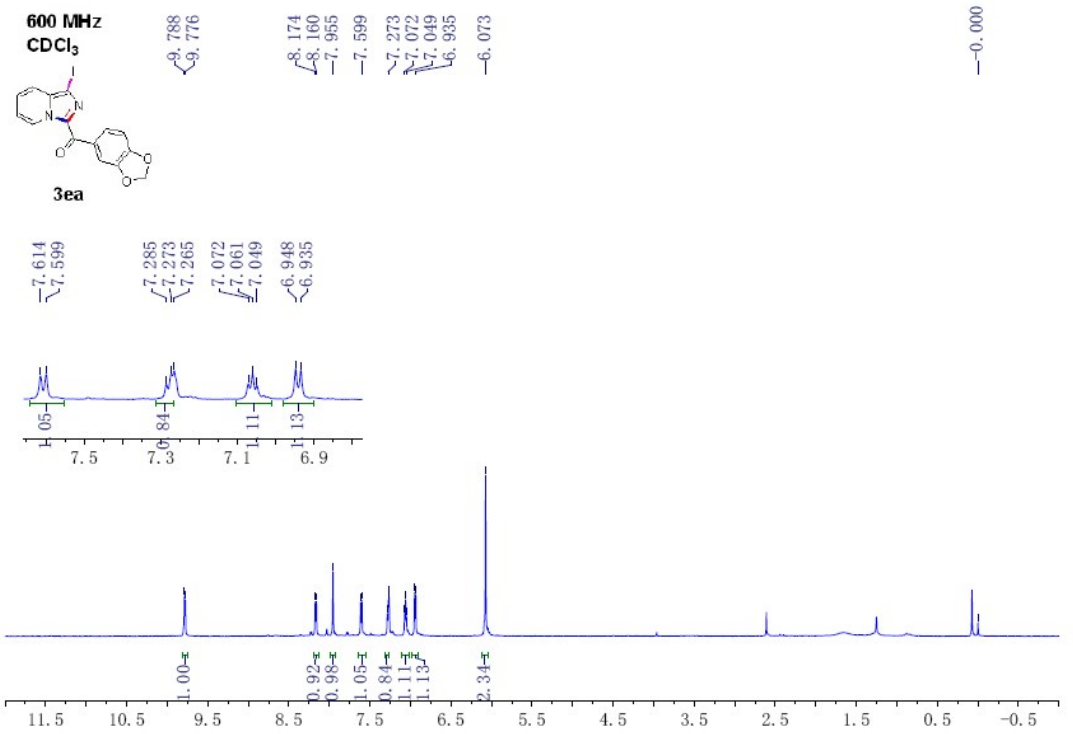

150 MHz
CDCl3
3ba
181.19
143.12
134.86
128.86
125.34
118.39
116.94
78.42
77.21
77.00
76.79
21.68
143.12
136.95
136.25
134.86
130.84
128.86
142
138
134
130
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

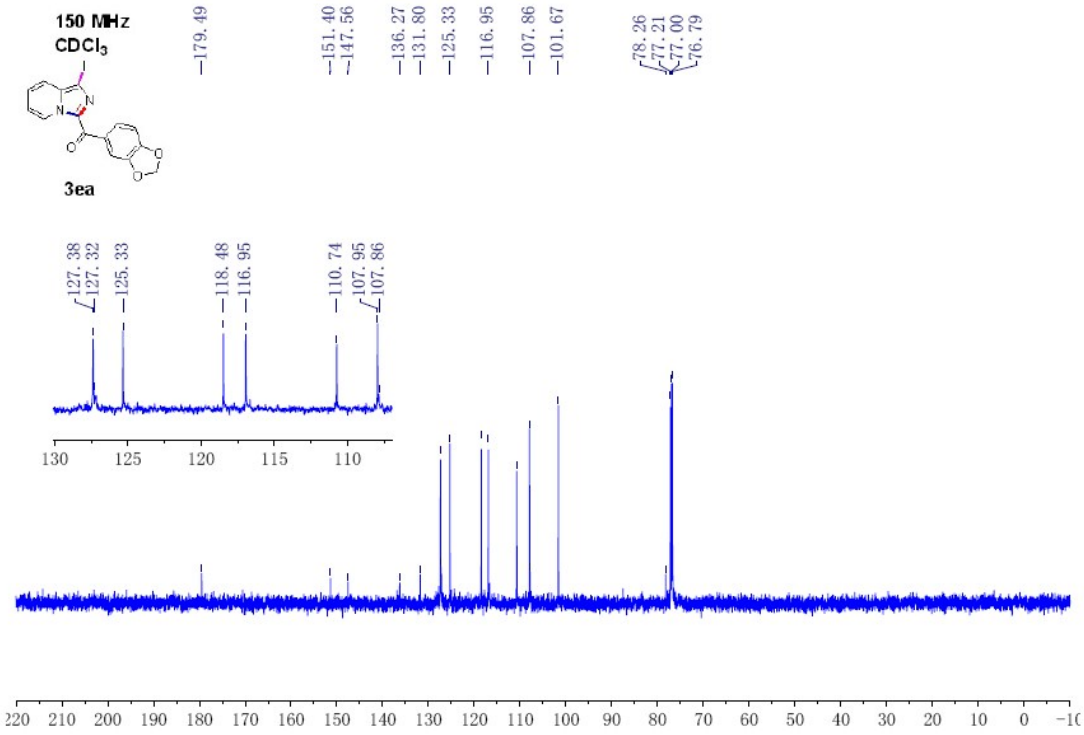

600 MHz
CDCl3
9.803
9.791
8.494
8.479
7.603
7.588
7.263
7.258
7.243
7.057
7.046
7.034
7.022
7.007
3.902
0.000
3ca

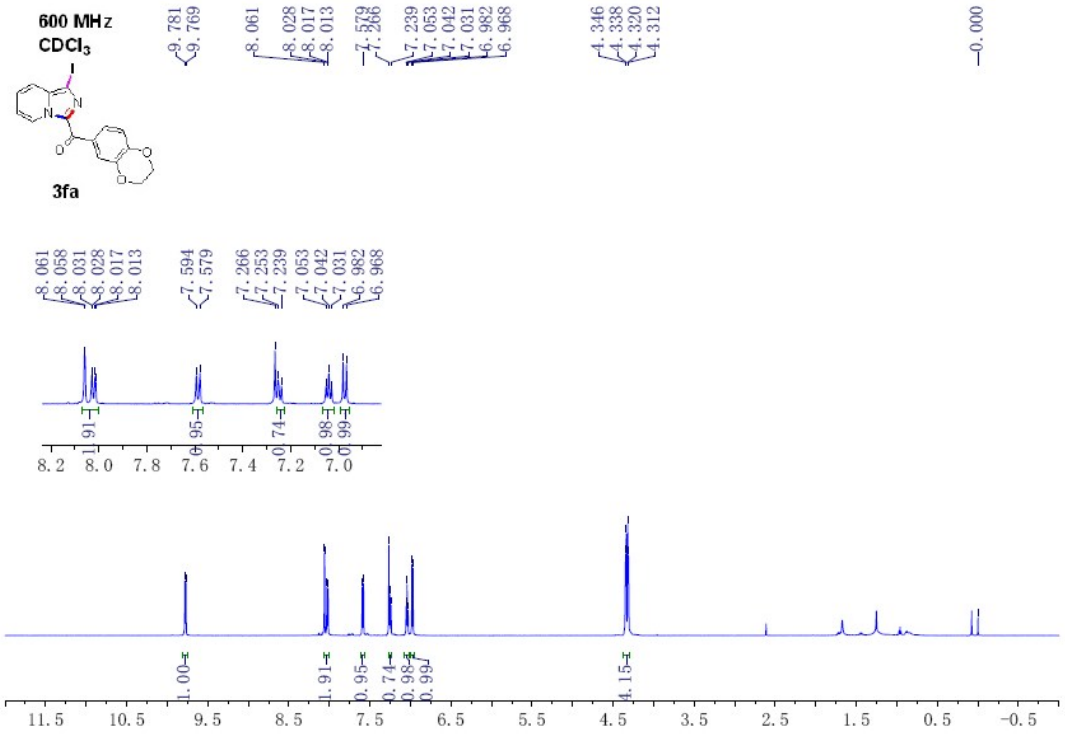

150 MHz
CDCl3
180.06
163.17
137.01
136.13
133.12
130.22
127.39
125.17
118.41
116.81
113.49
78.09
77.21
77.00
76.79
55.45
3ca

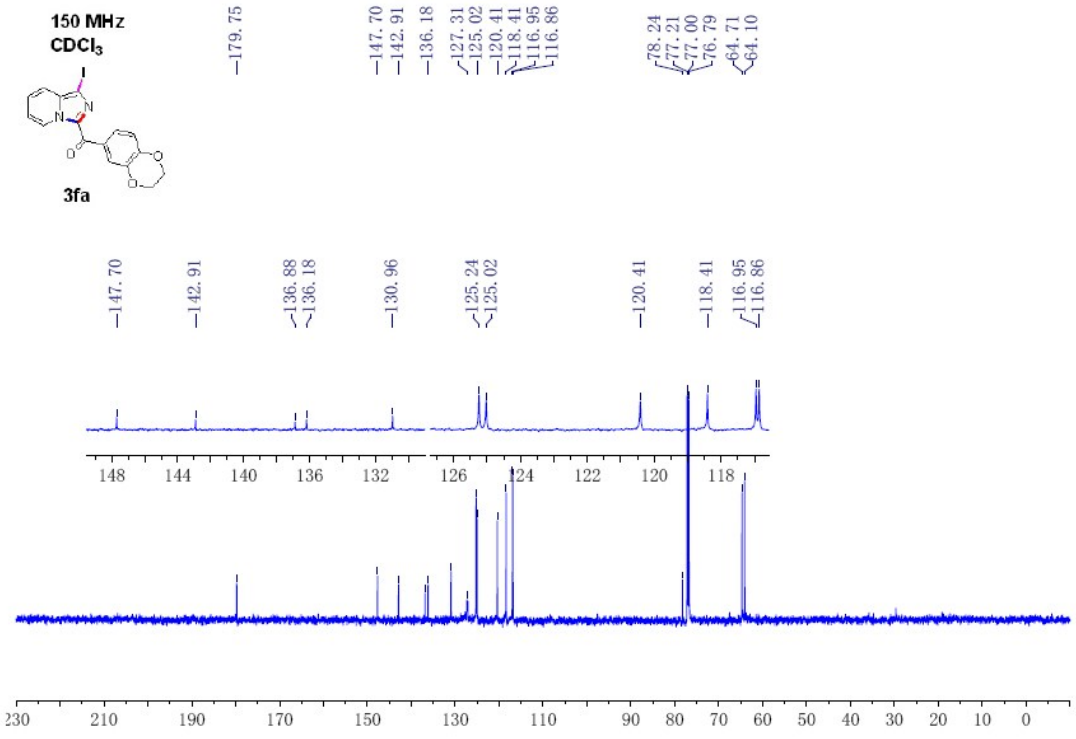

600 MHz
CDCl3
3da

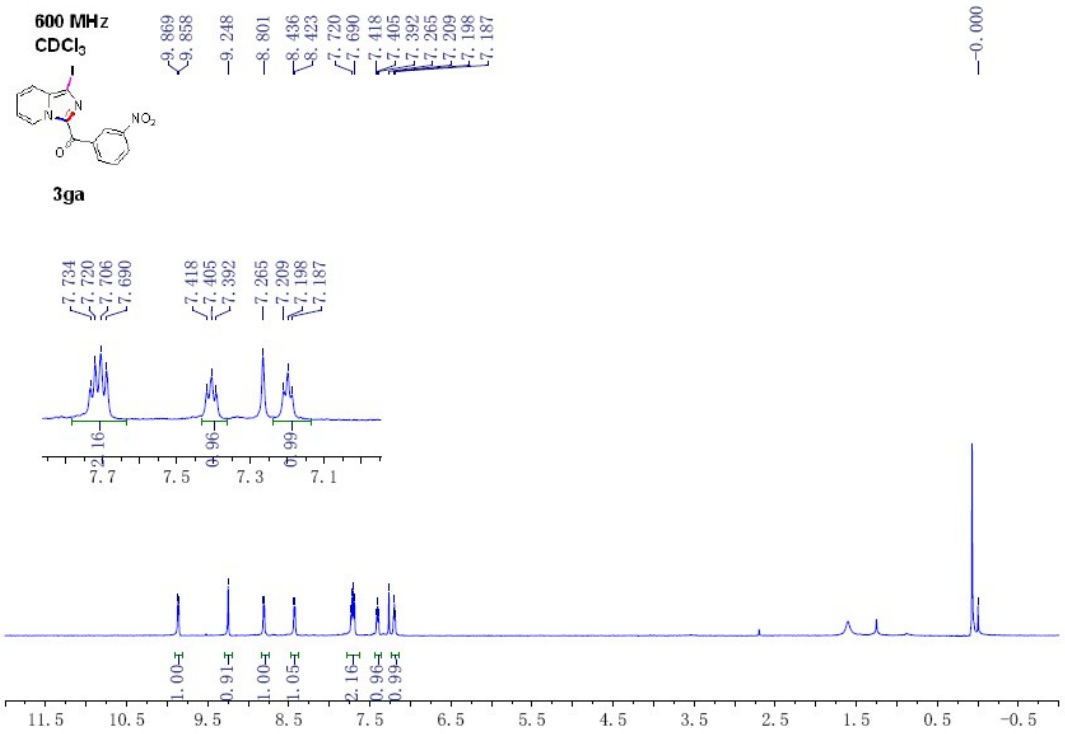

150 MHz
CDCl3
3da

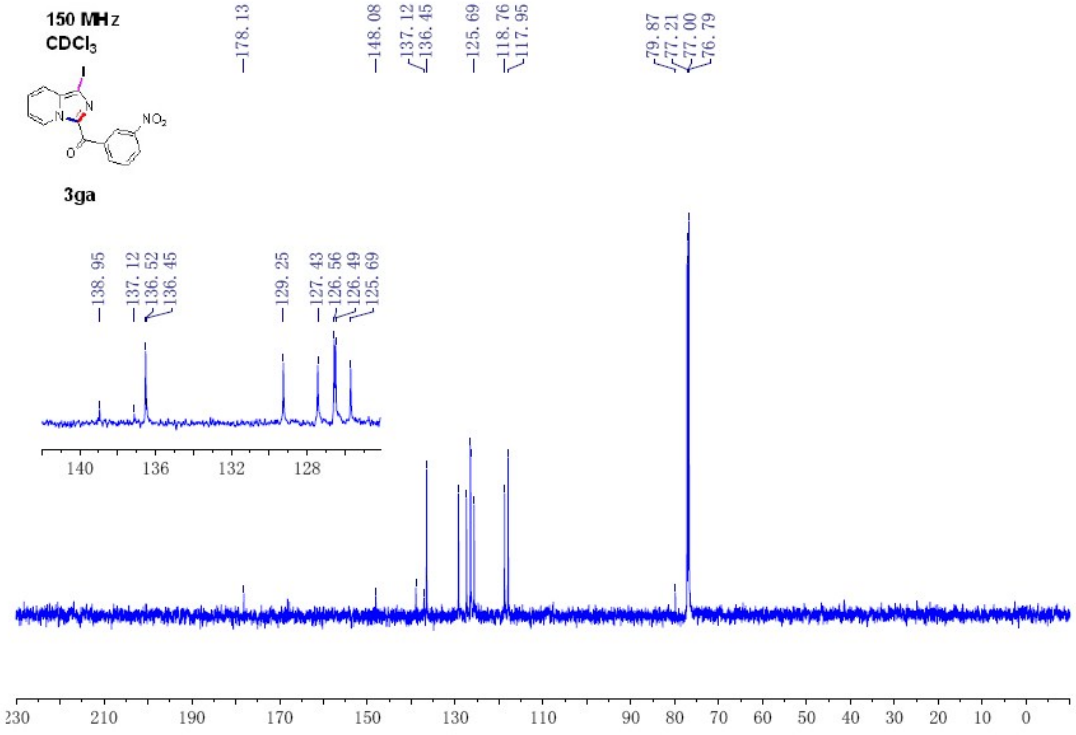

600 MHz
CDCl3
3ea
9.788
9.776
8.174
8.160
7.955
7.599
7.273
7.072
7.049
6.935
6.073
-0.000
7.614
7.599
7.285
7.273
7.265
7.072
7.061
7.049
6.948
6.935
1.00
0.92
0.98
1.05
0.84
1.11
1.13
2.34

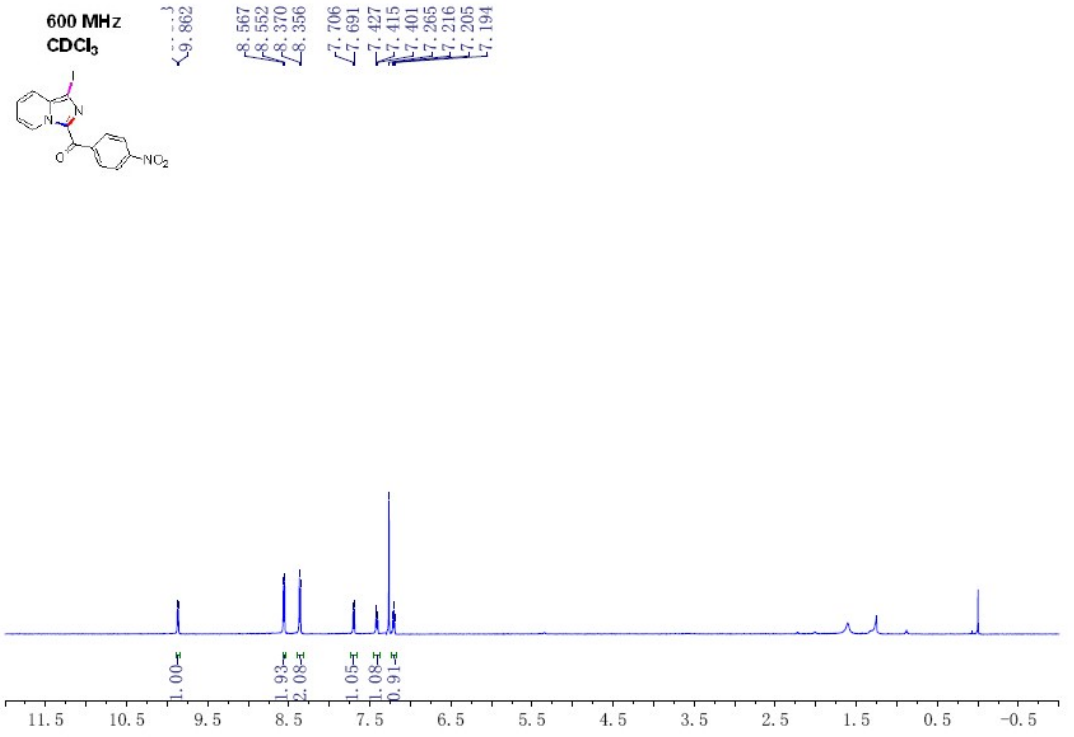

150 MHz
CDCl3
3ea
179.49
151.40
147.56
136.27
131.80
125.33
116.95
107.86
101.67
78.26
77.21
77.00
76.79
127.38
127.32
125.33
118.48
116.95
110.74
107.95
107.86

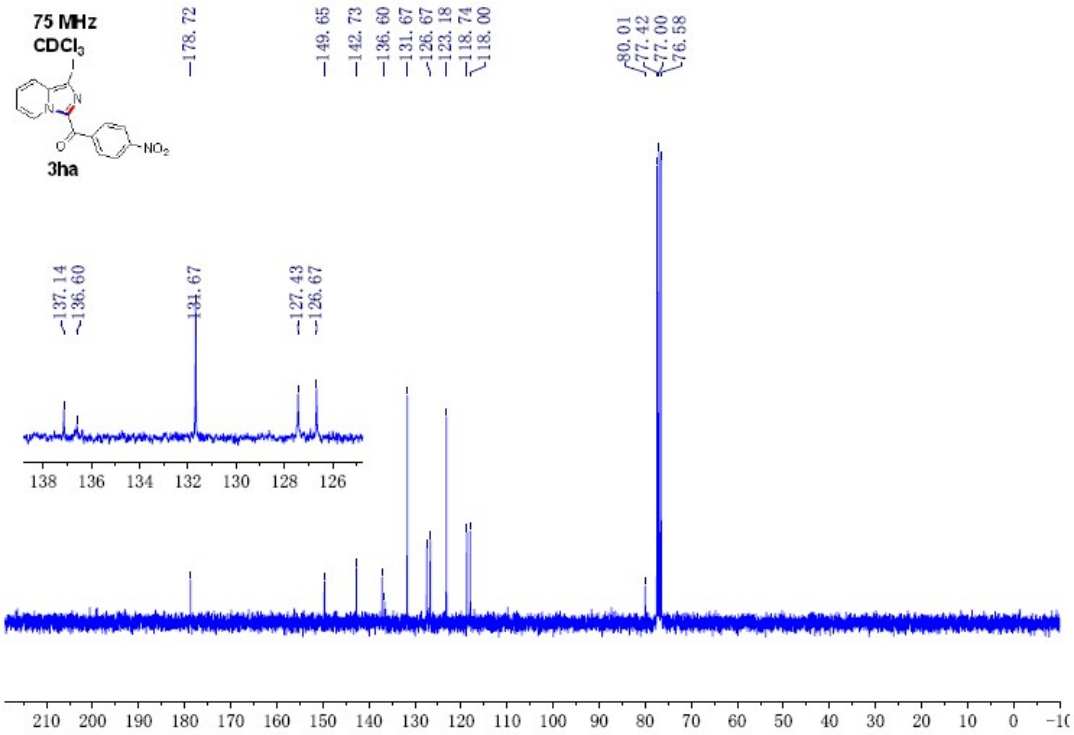

600 MHz
CDCl3
3fa

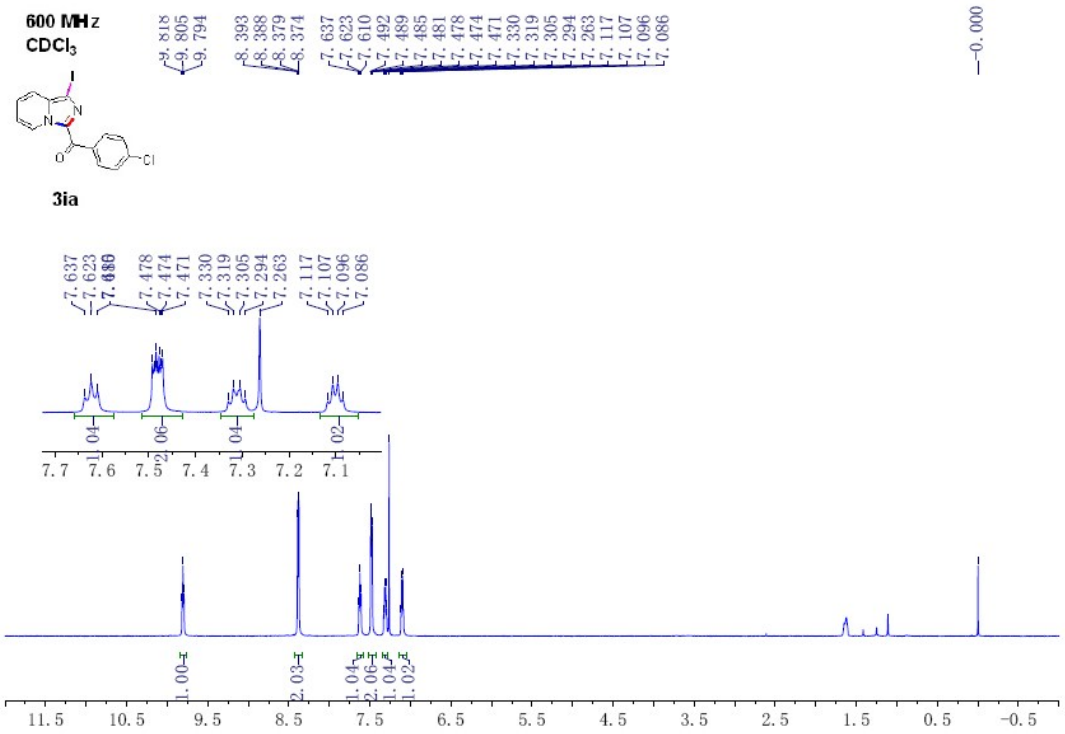

150 MHz
CDCl3
3fa

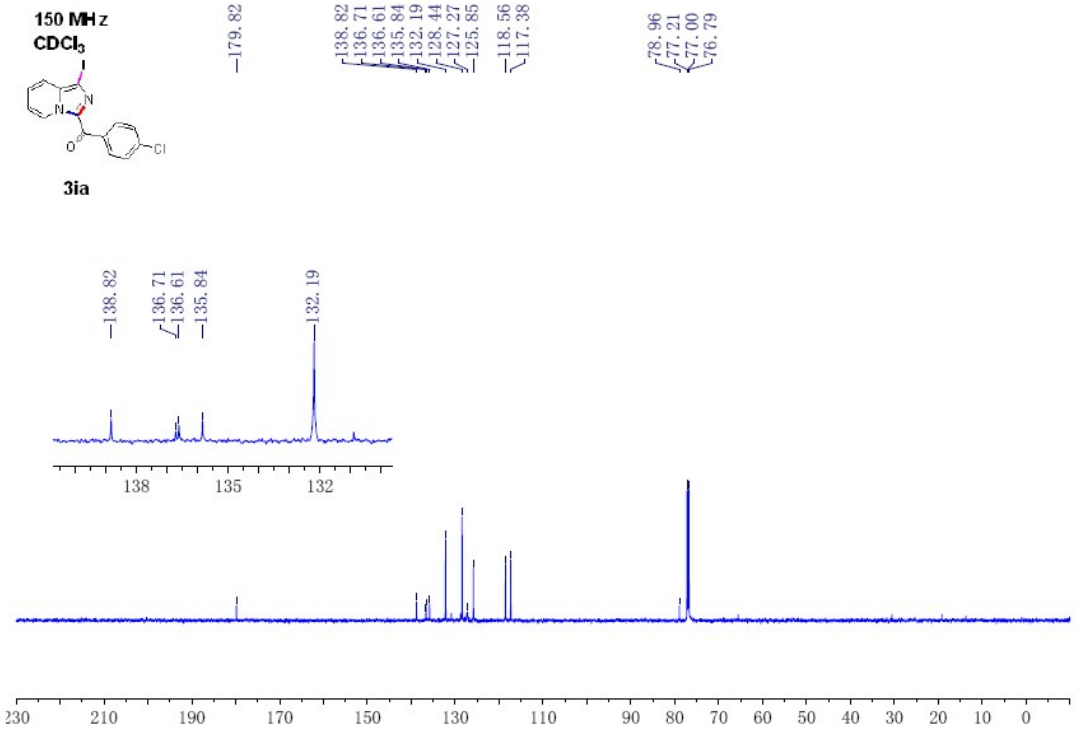

600 MHz
CDCl3
3ga
9.869
9.858
9.248
8.801
8.436
8.423
7.720
7.690
7.418
7.405
7.392
7.265
7.209
7.198
7.187
0.000
7.734
7.720
7.706
7.690
7.418
7.405
7.392
7.265
7.209
7.198
7.187
1.00
0.91
1.00
1.05
2.16
0.96
0.99

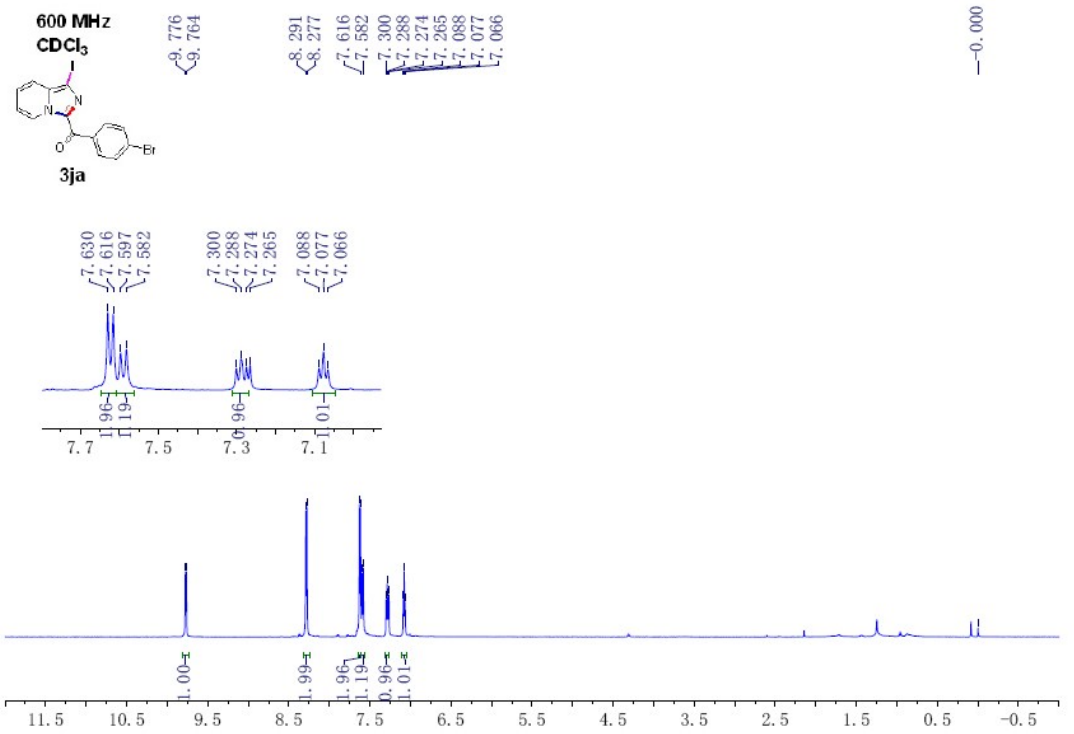

150 MHz
CDCl3
3ga
178.13
148.08
137.12
136.45
125.69
118.76
117.95
79.87
77.21
77.00
76.79
138.95
137.12
136.52
136.45
129.25
127.43
126.56
126.49
125.69

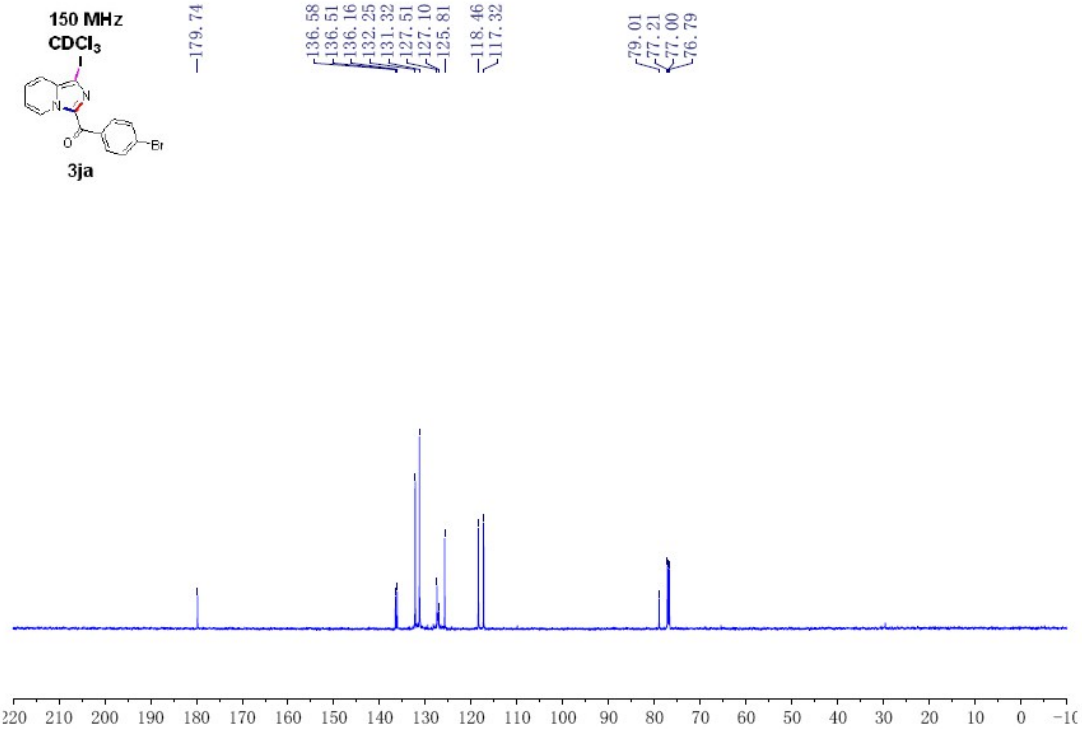

600 MHz
CDCl3
9.862
8.567
8.552
8.370
8.356
7.706
7.691
7.427
7.415
7.401
7.265
7.216
7.205
7.194
1.00
1.93
2.08
1.05
1.08
0.91
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

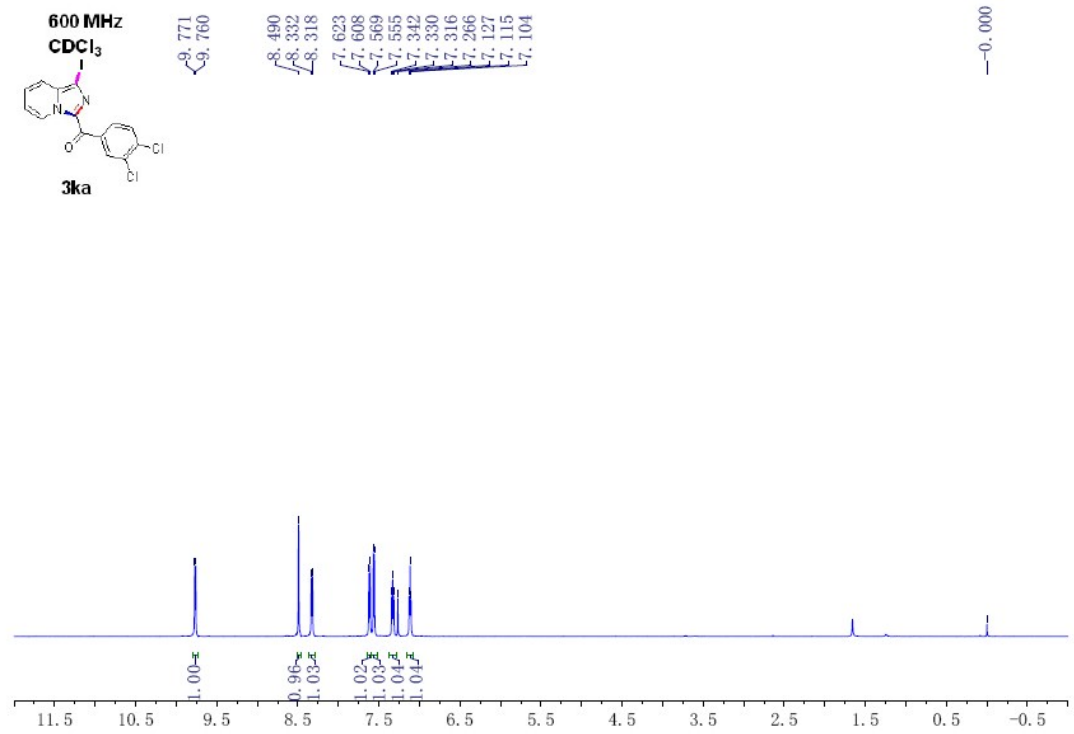

75 MHz
CDCl3
3ha
178.72
149.65
142.73
136.60
131.67
126.67
123.18
118.74
118.00
80.01
77.42
77.00
76.58
137.14
136.60
131.67
127.43
126.67
138
136
134
132
130
128
126
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

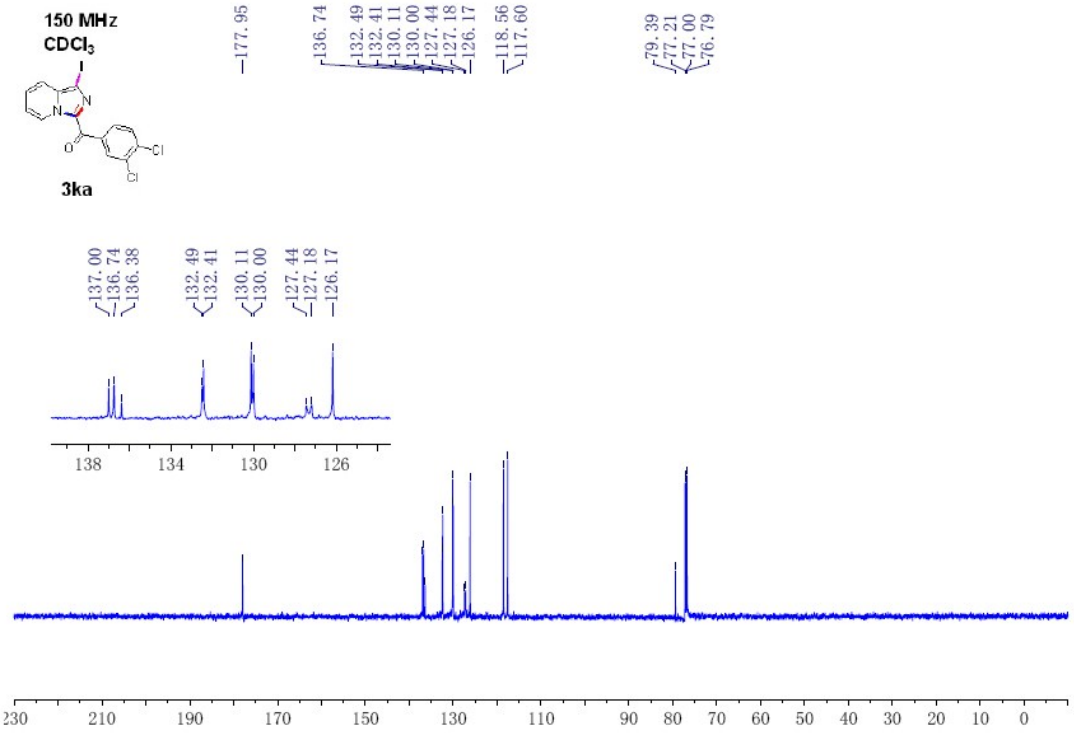

600 MHz
CDCl3
3ia

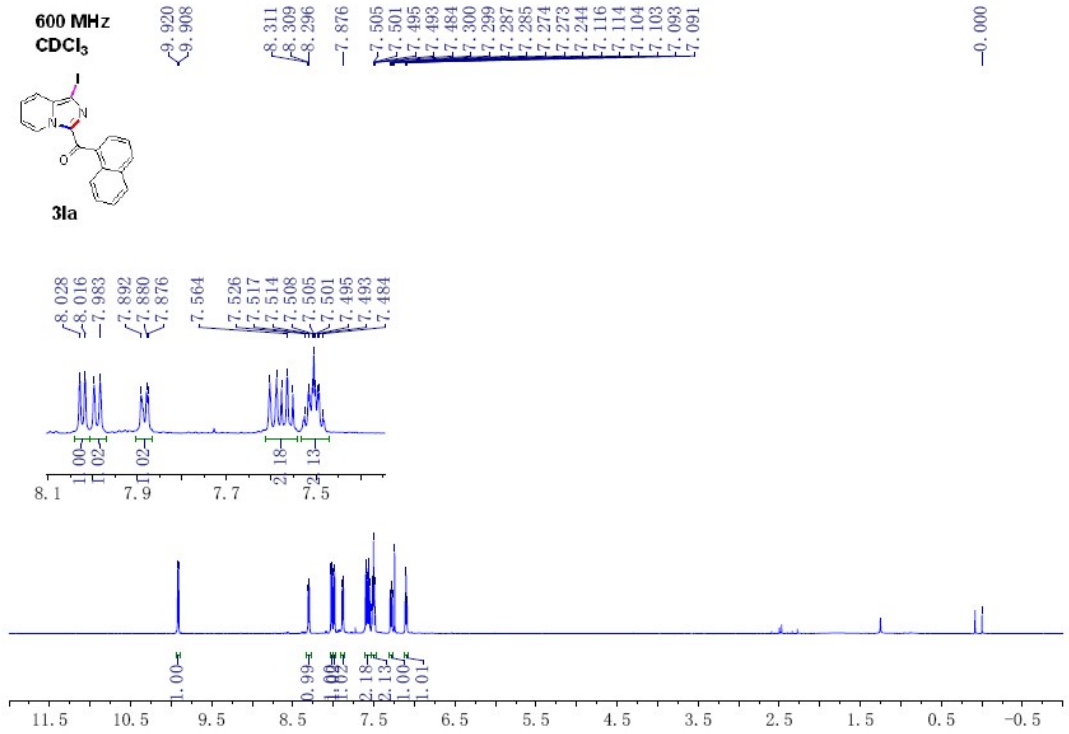

150 MHz
CDCl3
3ia

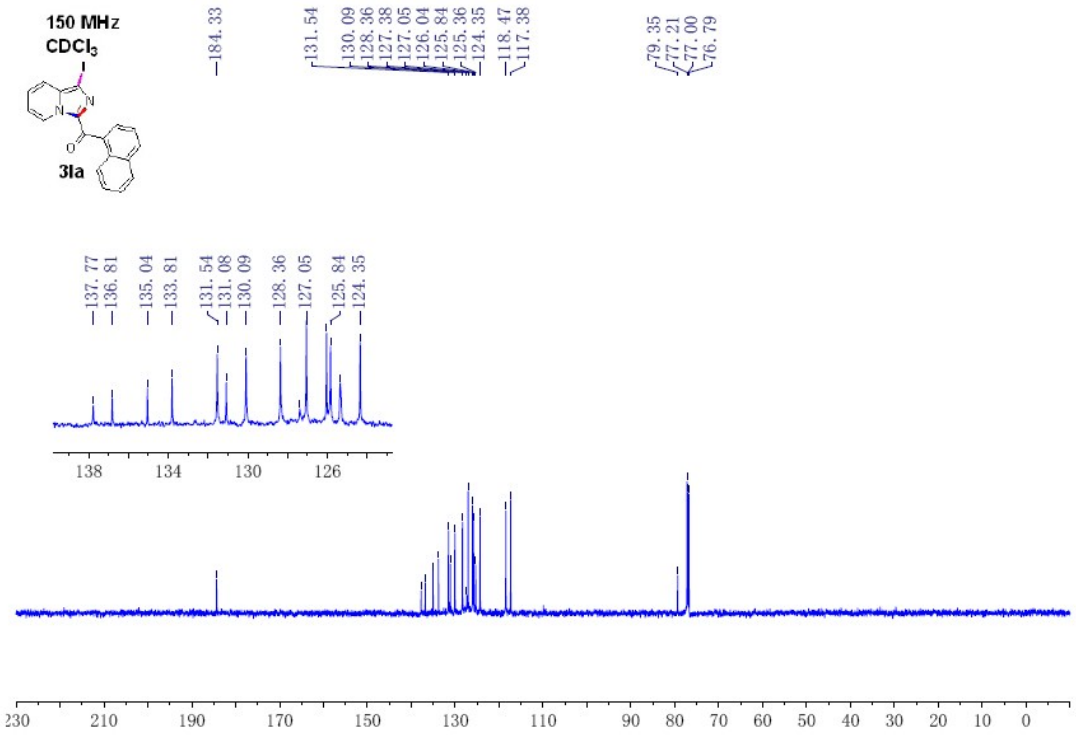

600 MHz
CDCl3
3ja
9.776
9.764
8.291
8.277
7.616
7.582
7.300
7.288
7.274
7.265
7.088
7.077
7.066
-0.000
7.630
7.616
7.597
7.582
7.300
7.288
7.274
7.265
7.088
7.077
7.066
1.96
1.19
0.96
1.01
7.7
7.5
7.3
7.1
1.00
1.99
1.96
1.19
0.96
1.01
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

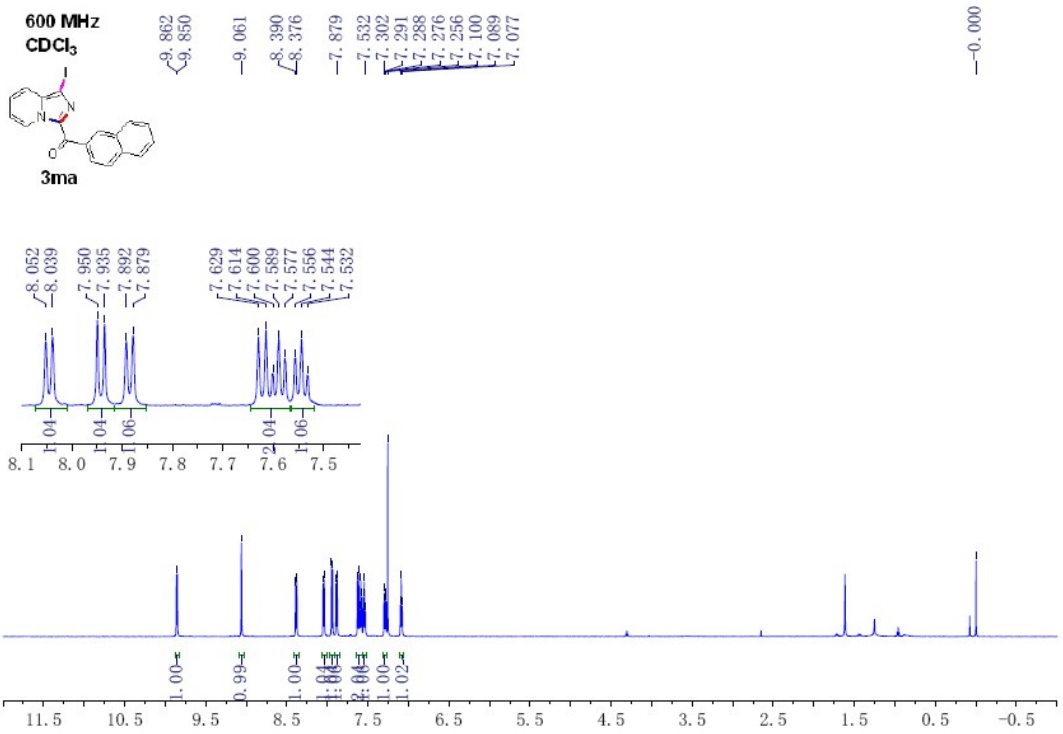

150 MHz
CDCl3
3ja
179.74
136.58
136.51
136.16
132.25
131.32
127.51
127.10
125.81
118.46
117.32
79.01
77.21
77.00
76.79
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

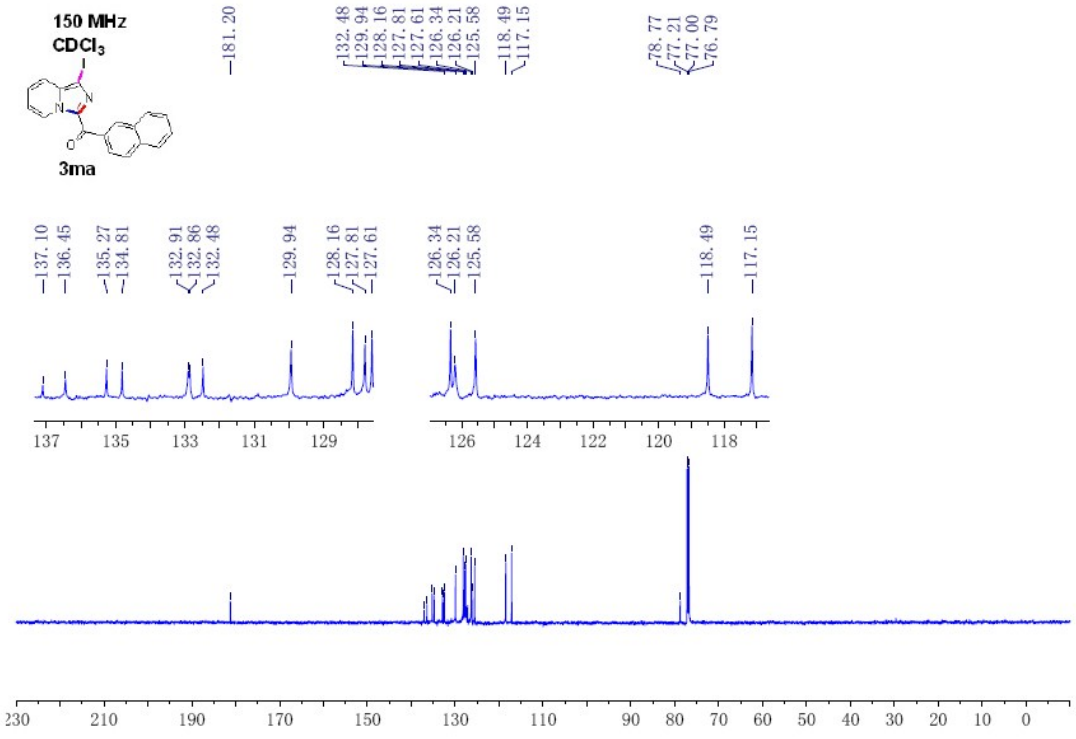

600 MHz
CDCl3
3ka
9.771
9.760
8.490
8.332
8.318
7.623
7.608
7.569
7.555
7.342
7.330
7.316
7.266
7.127
7.115
7.104
-0.000
1.00
0.96
1.03
1.02
1.03
1.04
1.04
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

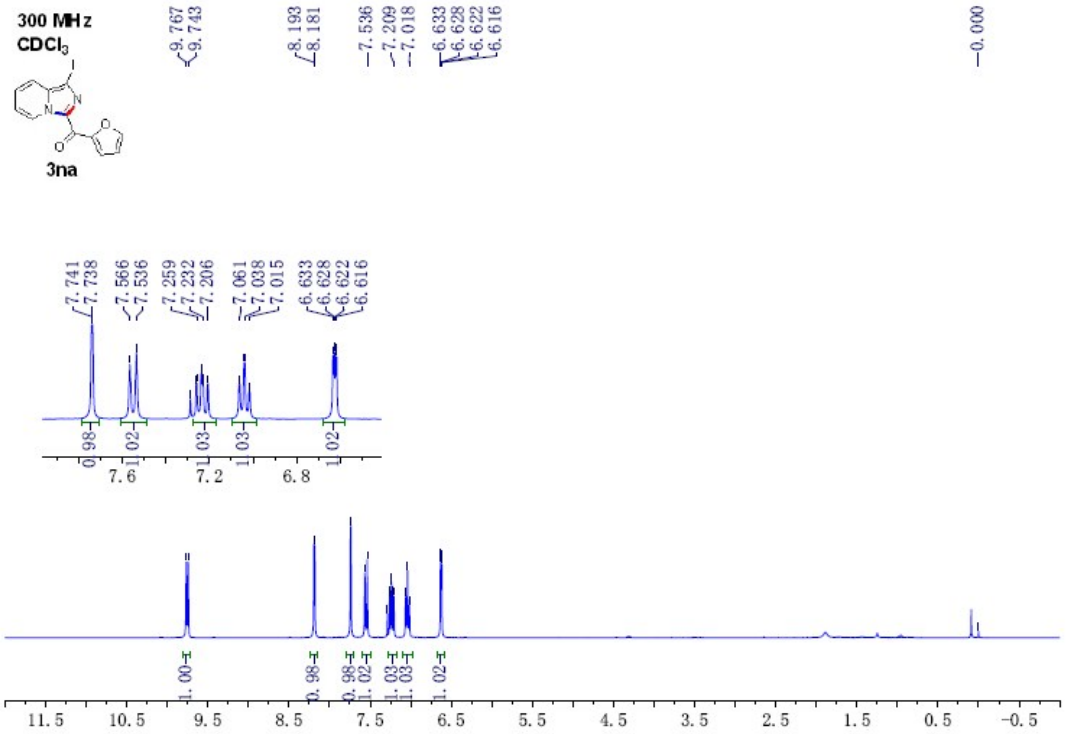

150 MHz
CDCl3
3ka
177.95
136.74
132.49
132.41
130.11
130.00
127.44
127.18
126.17
118.56
117.60
79.39
77.21
77.00
76.79
137.00
136.74
136.38
132.49
132.41
130.11
130.00
127.44
127.18
126.17
138
134
130
126
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0

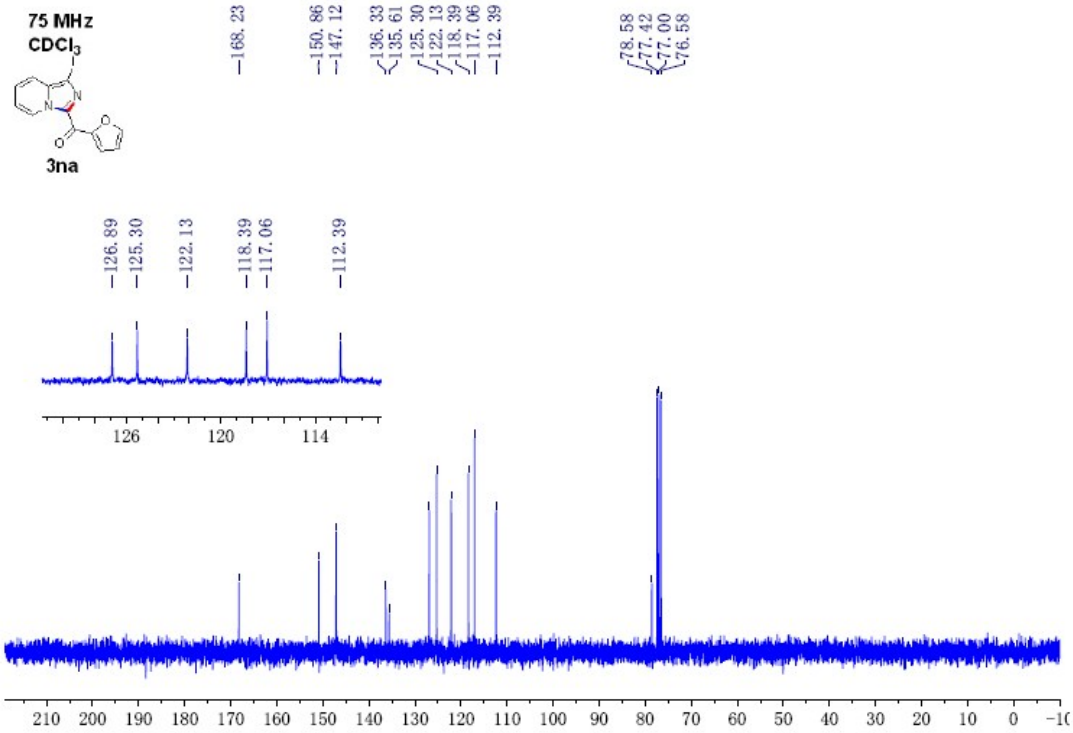

600 MHz
CDCl3
3la

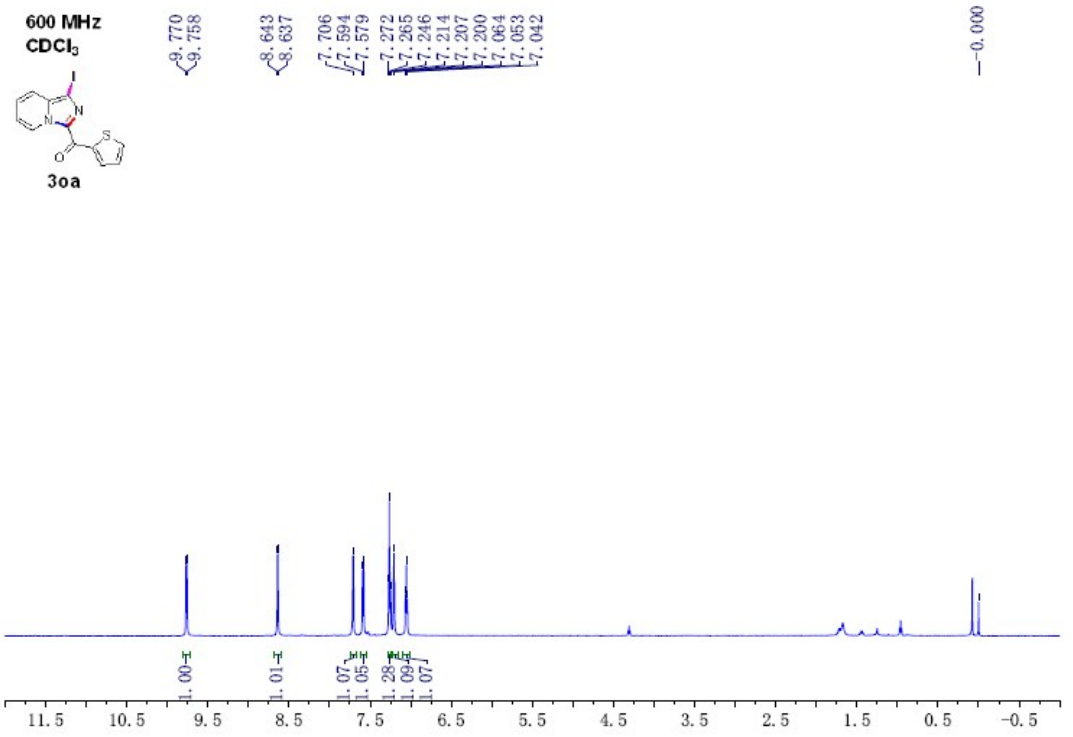

150 MHz
CDCl3
3la

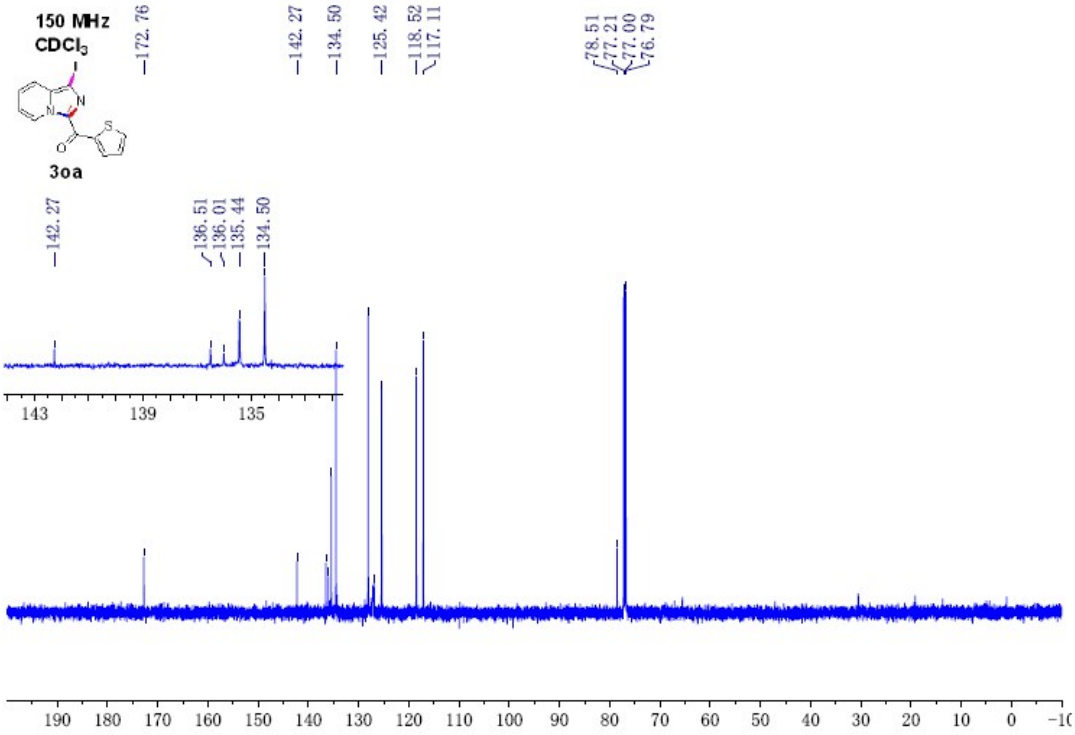

600 MHz
CDCl3
3ma
9.862
9.850
9.061
8.390
8.376
7.879
7.532
7.302
7.291
7.288
7.276
7.256
7.100
7.089
7.077
-0.000
8.052
8.039
7.950
7.935
7.892
7.879
7.629
7.614
7.600
7.589
7.577
7.556
7.544
7.532

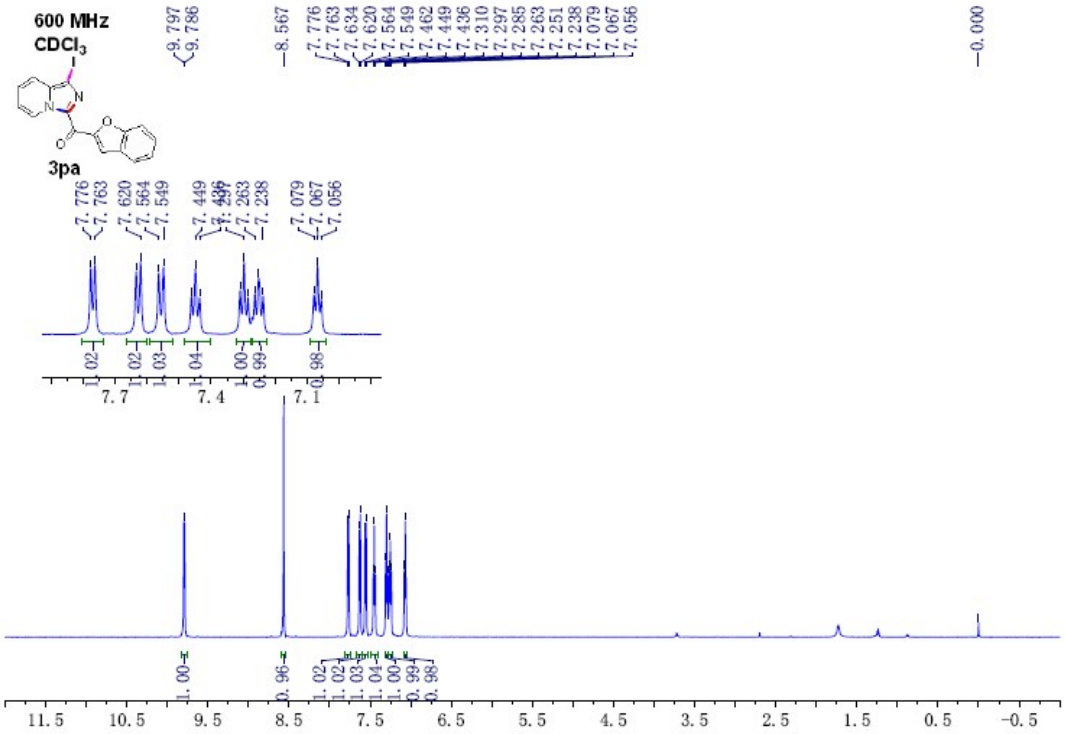

150 MHz
CDCl3
3ma
181.20
132.48
129.94
128.16
127.81
127.61
126.34
126.21
125.58
118.49
117.15
78.77
77.21
77.00
76.79
137.10
136.45
135.27
134.81
132.91
132.86
132.48
129.94
128.16
127.81
127.61
126.34
126.21
125.58
118.49
117.15

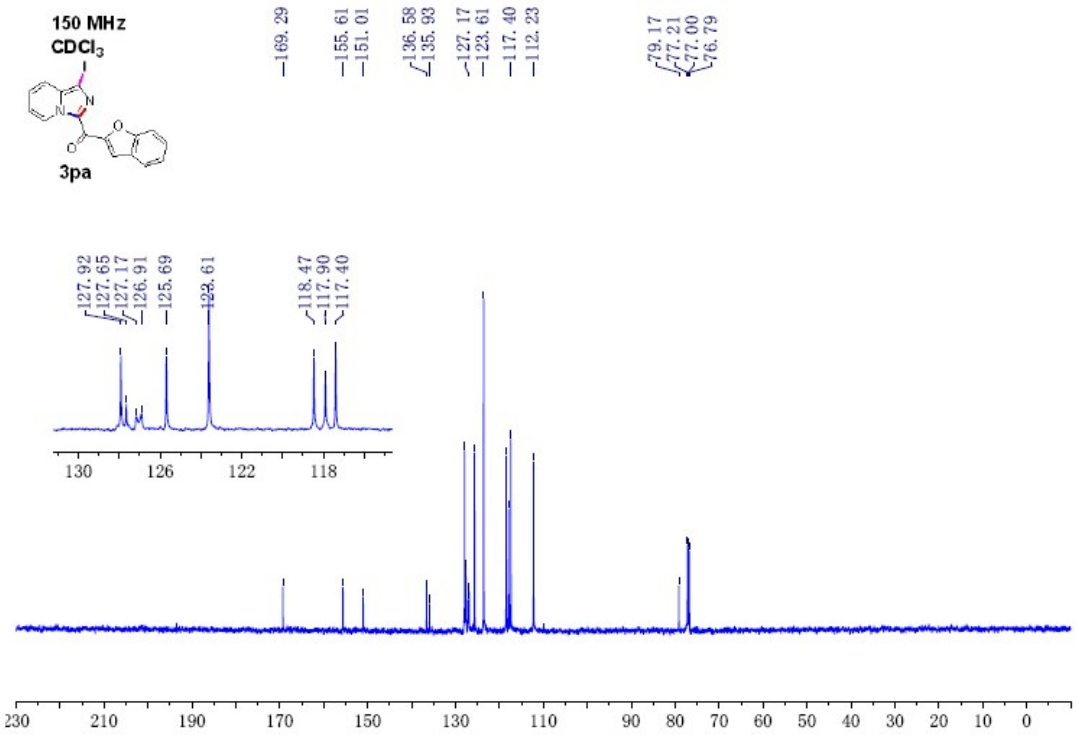

300 MHz
CDCl3
3na
9.767
9.743
8.193
8.181
7.536
7.209
7.018
6.633
6.628
6.622
6.616
0.000
7.741
7.738
7.566
7.536
7.259
7.232
7.206
7.061
7.038
7.015
6.633
6.628
6.622
6.616
0.98
1.02
1.03
1.03
1.02
7.6
7.2
6.8
1.00
0.98
0.98
1.02
1.03
1.03
1.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

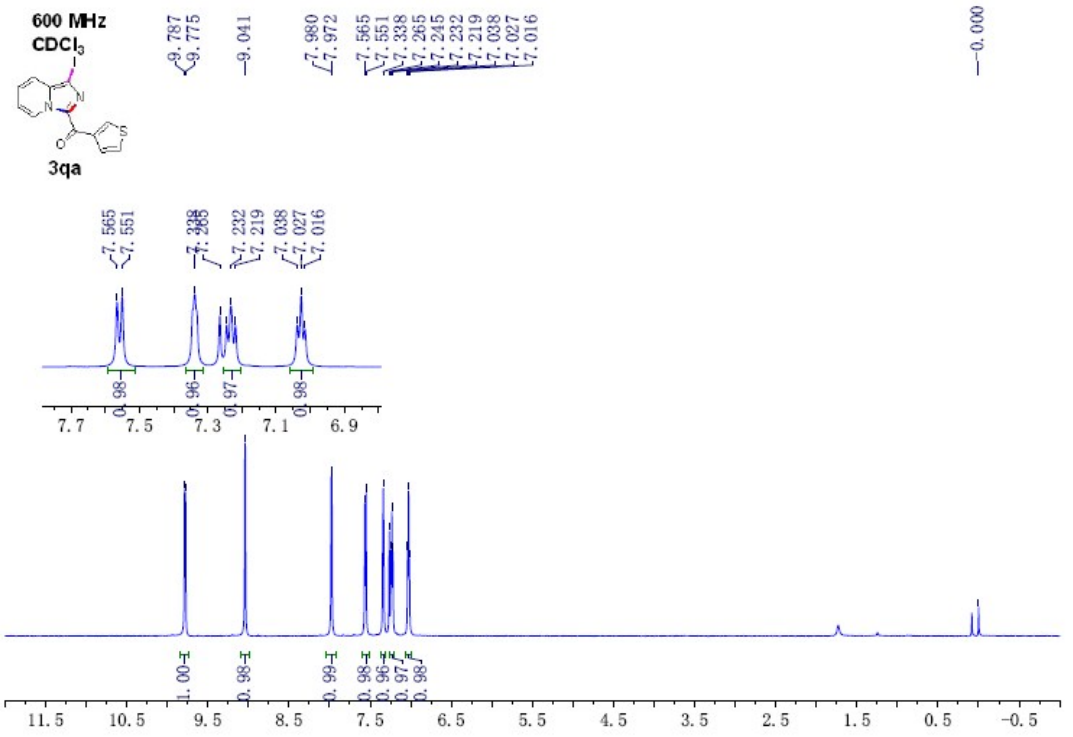

75 MHz
CDCl3
3na
168.23
150.86
147.12
136.33
135.61
125.30
122.13
118.39
117.06
112.39
78.58
77.42
77.00
76.58
126.89
125.30
122.13
118.39
117.06
112.39
126
120
114
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10

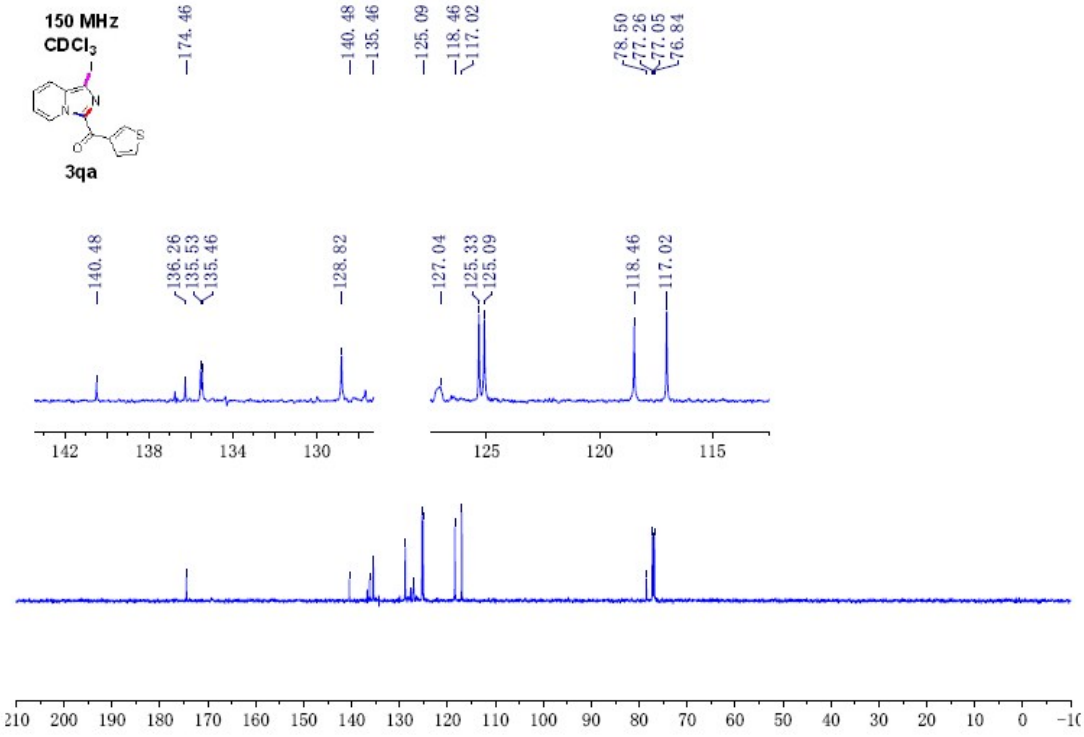

600 MHz
CDCl3
3oa
9.770
9.758
8.643
8.637
7.706
7.594
7.579
7.272
7.265
7.246
7.214
7.207
7.200
7.064
7.053
7.042
-0.000
1.00
1.01
1.07
1.05
1.28
1.09
1.07
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5

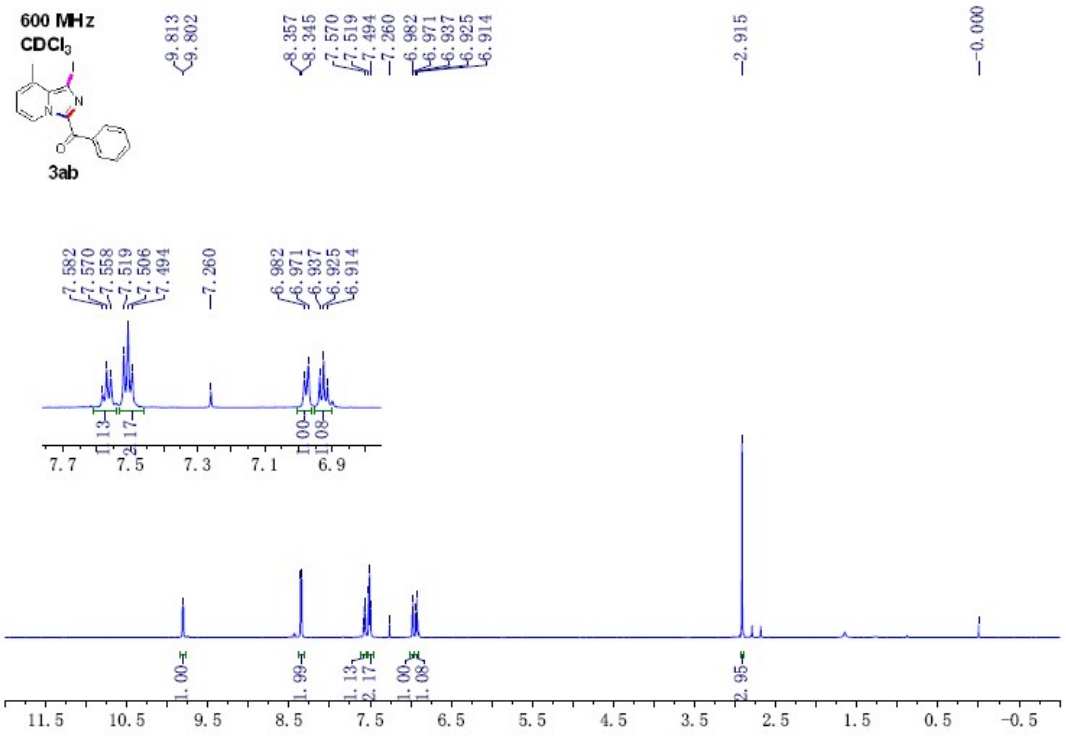

150 MHz
CDCl3
3oa
172.76
142.27
134.50
125.42
118.52
117.11
78.51
77.21
77.00
76.79
142.27
136.51
136.01
135.44
134.50
143
139
135
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

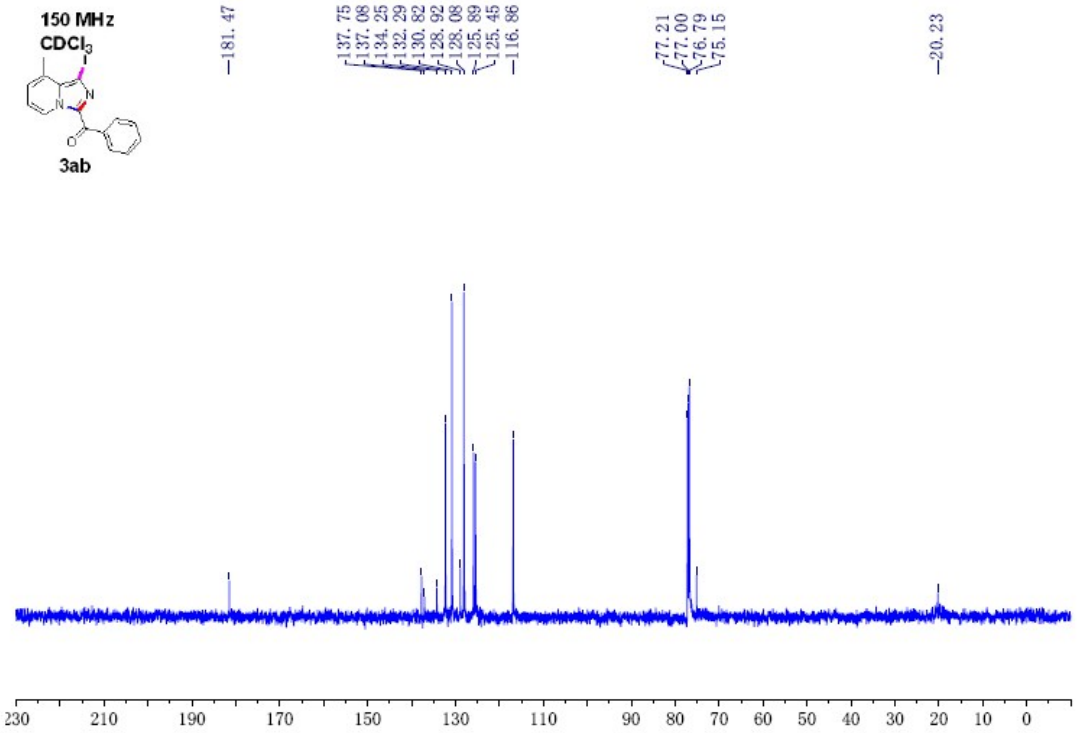

600 MHz
CDCl3
3pa

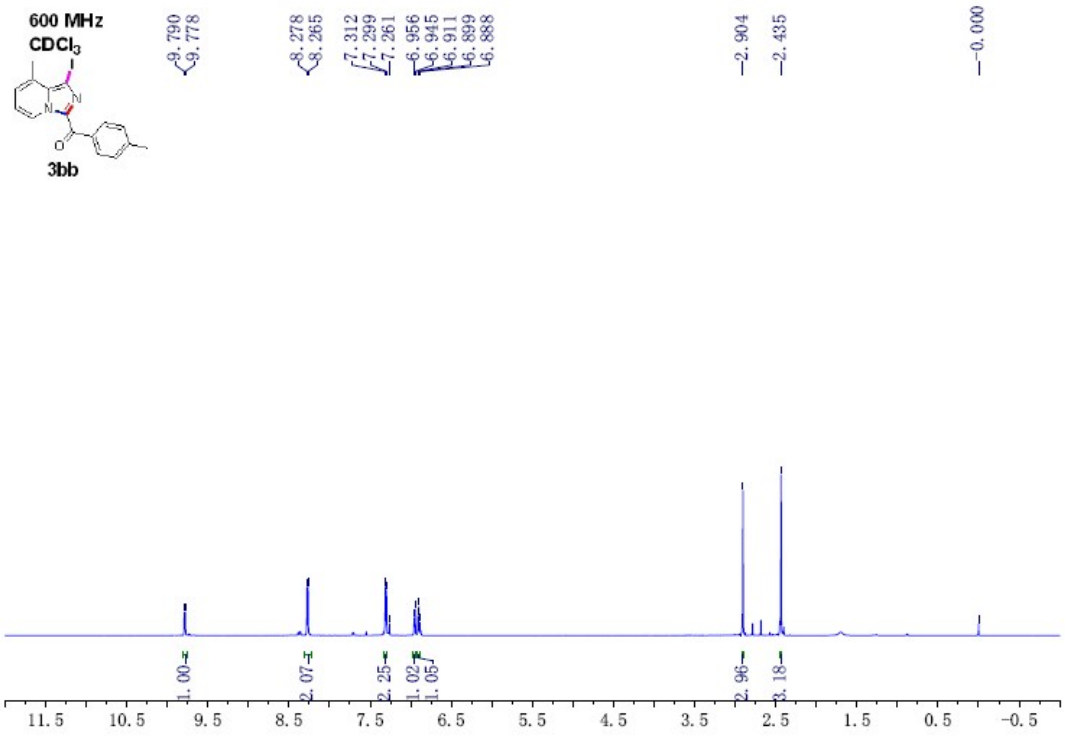

150 MHz
CDCl3
3pa

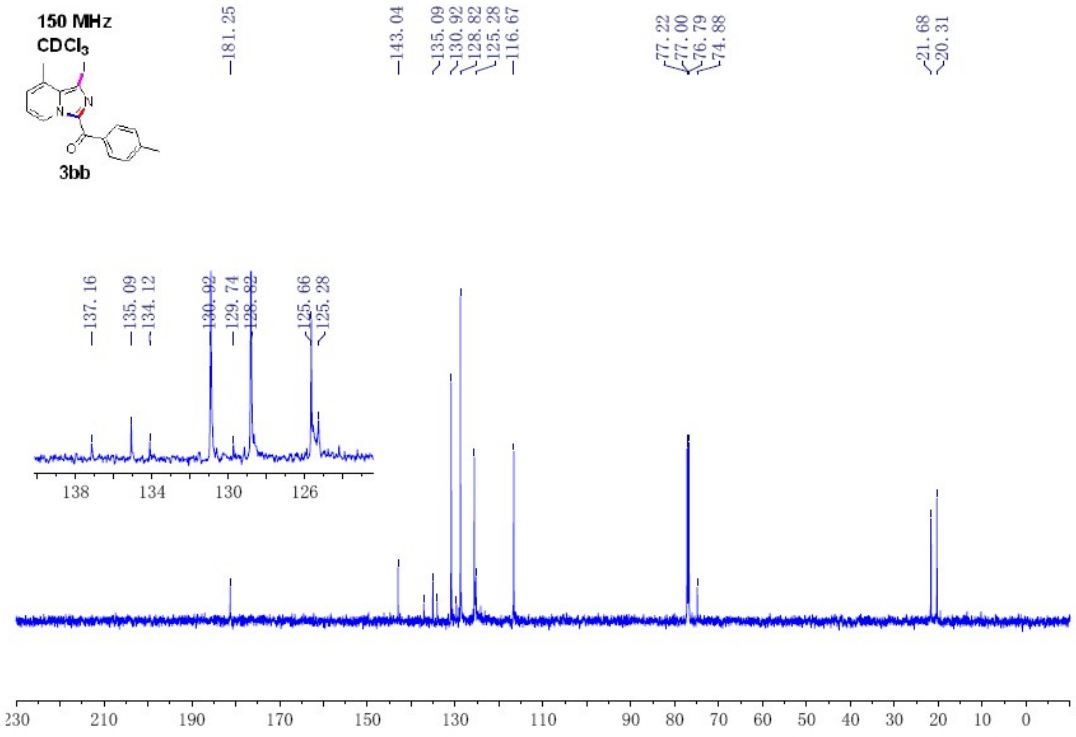

600 MHz
CDCl3
3qa

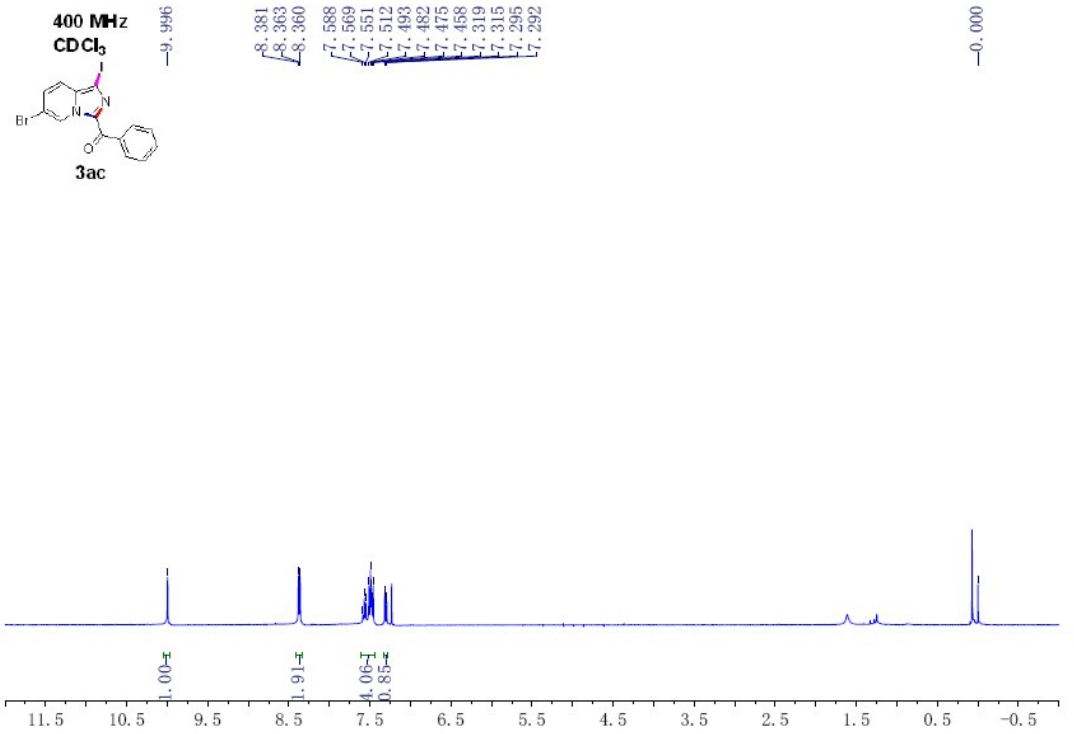

150 MHz
CDCl3
3qa

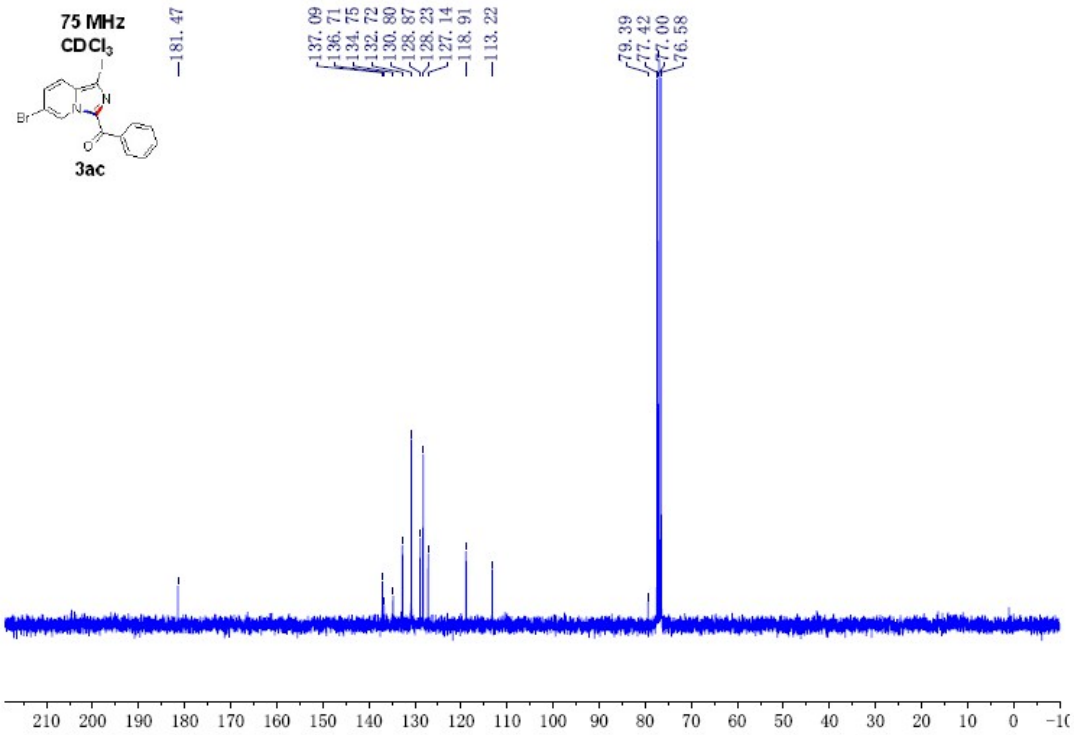

600 MHz
CDCl3
3ab
9.813
9.802
8.357
8.345
7.582
7.570
7.558
7.570
7.519
7.506
7.494
7.260
6.982
6.971
6.937
6.925
6.914
2.915
0.000
1.00
1.99
1.13
2.17
1.00
1.08
2.95

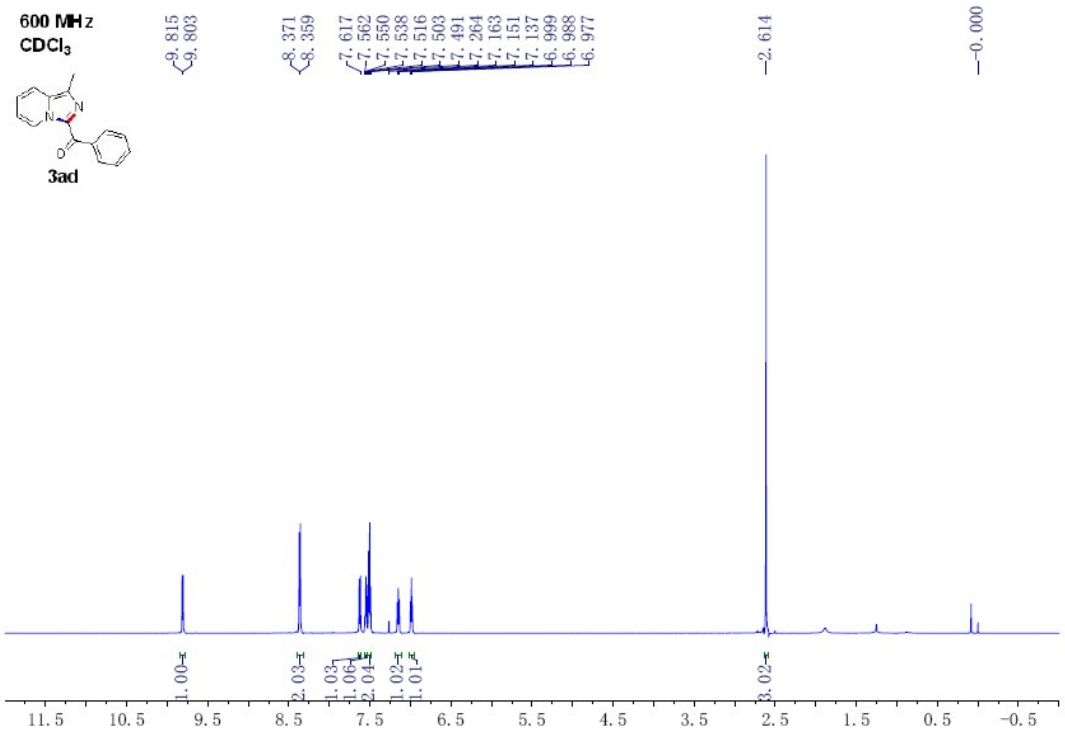

150 MHz
CDCl3
3ab
181.47
137.75
137.08
134.25
132.29
130.82
128.92
128.08
125.89
125.45
116.86
77.21
77.00
76.79
75.15
20.23

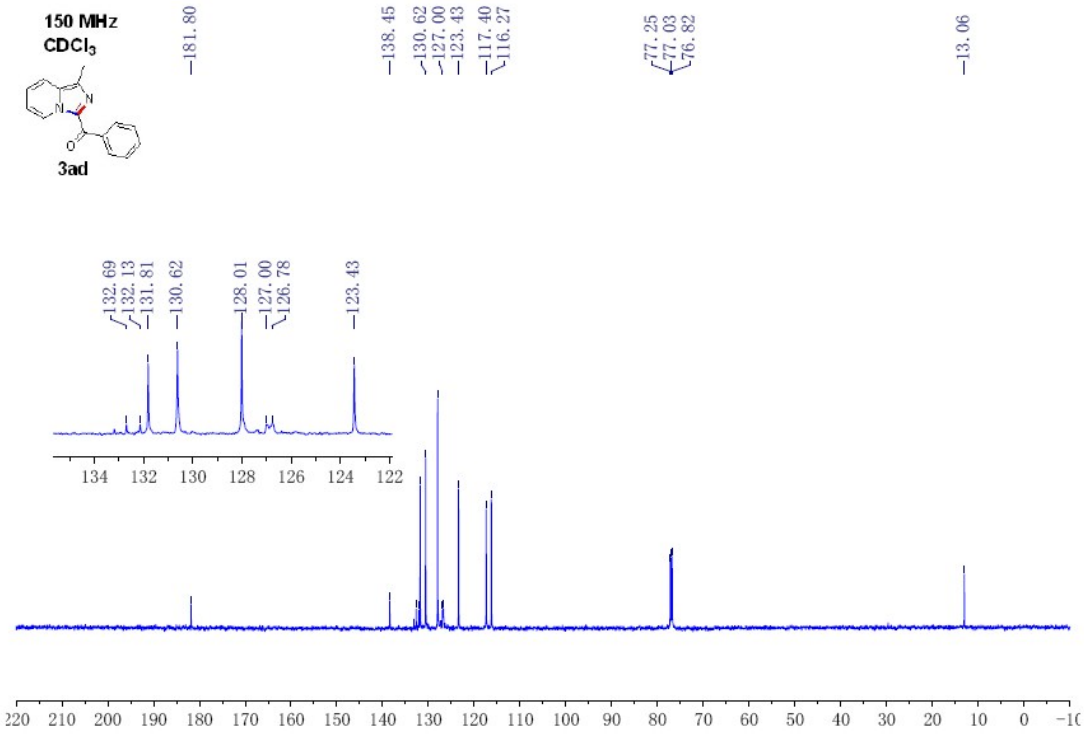

600 MHz
CDCl3
3bb
9.790
9.778
8.278
8.265
7.312
7.299
7.261
6.956
6.945
6.911
6.899
6.888
2.904
2.435
0.000
1.00
2.07
2.25
1.02
1.05
2.96
3.18
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


150 MHz
CDCl3
3bb
181.25
143.04
135.09
130.92
128.82
125.28
116.67
77.22
77.00
76.79
74.88
21.68
20.31
137.16
135.09
134.12
130.92
129.74
128.82
125.66
125.28
138
134
130
126
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0


400 MHz
CDCl3
3ac
9.996
8.381
8.363
8.360
7.588
7.569
7.551
7.512
7.493
7.482
7.475
7.458
7.319
7.315
7.295
7.292
0.000
1.00
1.91
4.06
0.85
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


75 MHz
CDCl3
3ac
181.47
137.09
136.71
134.75
132.72
130.80
128.87
128.23
127.14
118.91
113.22
79.39
77.42
77.00
76.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


600 MHz
CDCl3
3ad
9.815
9.803
8.371
8.359
7.617
7.562
7.550
7.538
7.516
7.503
7.491
7.264
7.163
7.151
7.137
6.999
6.988
6.977
2.614
0.000
1.00
2.03
1.03
1.06
2.04
1.02
1.01
3.02
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5


150 MHz
CDCl3
3ad
181.80
138.45
130.62
127.00
123.43
117.40
116.27
77.25
77.03
76.82
13.06
132.69
132.13
131.81
130.62
128.01
127.00
126.78
123.43
134
132
130
128
126
124
122
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0