Electronic Supplementary Material (ESI) for RSC Advances.

Rh(III)-catalyzed sequential C–H activation and annulation: Access to *N*-fused heterocycles from arylazoles and α-diazocarbonyl compounds

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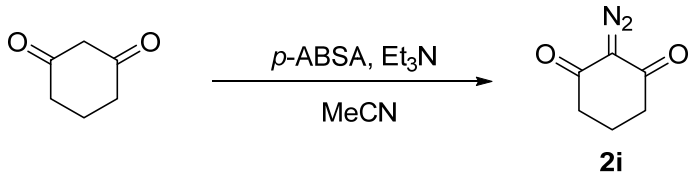
1. General Information

Chemicals were used received without special purification unless stated otherwise. Chemical shifts in ^{1}H NMR (600 MHz or 400 MHz) and ^{13}C NMR (150 MHz or 100 MHz) spectra were expressed in ppm relative to residual chloroform (δ 7.26 ppm for ^{1}H, δ 77.0 ppm for ^{13}C) or tetramethylsilane (δ 0.0 ppm for ^{1}H and ^{13}C). ^{1}H NMR data were reported as follows: chemical shift, multiplicity (s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet), coupling constant (Hz), and relative intensity. ^{13}C NMR spectra were recorded in deuterated solvent. Chemical shifts were reported in ppm with internal solvent signal as a standard. HRMS were obtained on Shimadzu Japan LCMS-IT/TOF.

Substituted pyrazole **1a-o**[1], diazo compounds **2a-i**[2], 3,5-diphenyl-1*H*-1,2,4-triazole **1s**[3], and substituted 2-phenylbenzoimidazole **1p-r**[4] were synthesized according to literature procedures. The rhodium complexes $[Cp^*RhCl_2]_2$ were prepared according to the literature protocols[5].

General procedure for synthesis of 2-Diazocyclohexane-1,3-dione (**2i**)

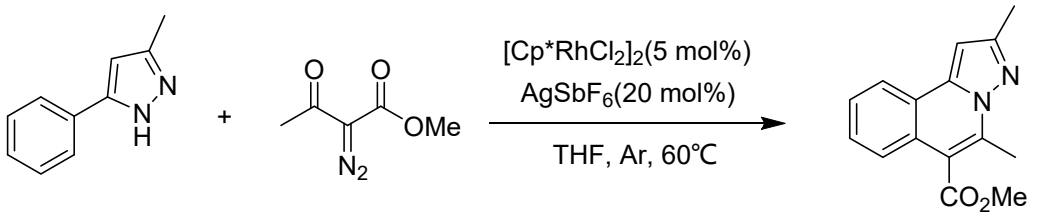


2i

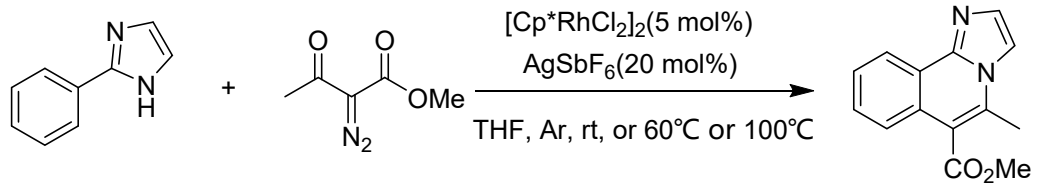
To a solution of cyclohexane-1,3-dione (2.60 mmol) and *p*-ABSA (2.86 mmol) in MeCN (18 mL) at 0℃, Et_3N (1.8 mL) was added dropwise. After stirring at room temperature for 5 hours the reaction mixture was concentrated in vacuo. Water (20 mL) was added. The resulting mixture was extracted with diethyl ether (2 x 20 mL). The combined organic layer was washed with brine (20 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the residue was purified by a silica gel column chromatography with petroleum ether/ ethyl acetate as the eluent to give the 2-Diazocyclohexane-1,3-dione (**2i**).

2. The reactivity comparison of azoles and the DFT calculation

2.1 The reactivity comparison of aryl pyrazole and aryl imidazole



1c **2b** **3cb**, 85%[a,b]



1t **2b** **3tb**, 0%[a,b]

[a]Reaction condition:1 (0.2 mmol), 2 (0.25 mmol), $[Cp^*RhCl_2]_2$ (5 mol%) /$AgSbF_6$ (20 mol%), and THF (2 mL) were stirred under Ar for 24h. [b]Isolated yield.

Scheme 1 The reactivity comparison of aryl pyrazole and aryl imidazole

2.2 Comparison of the activation energy.

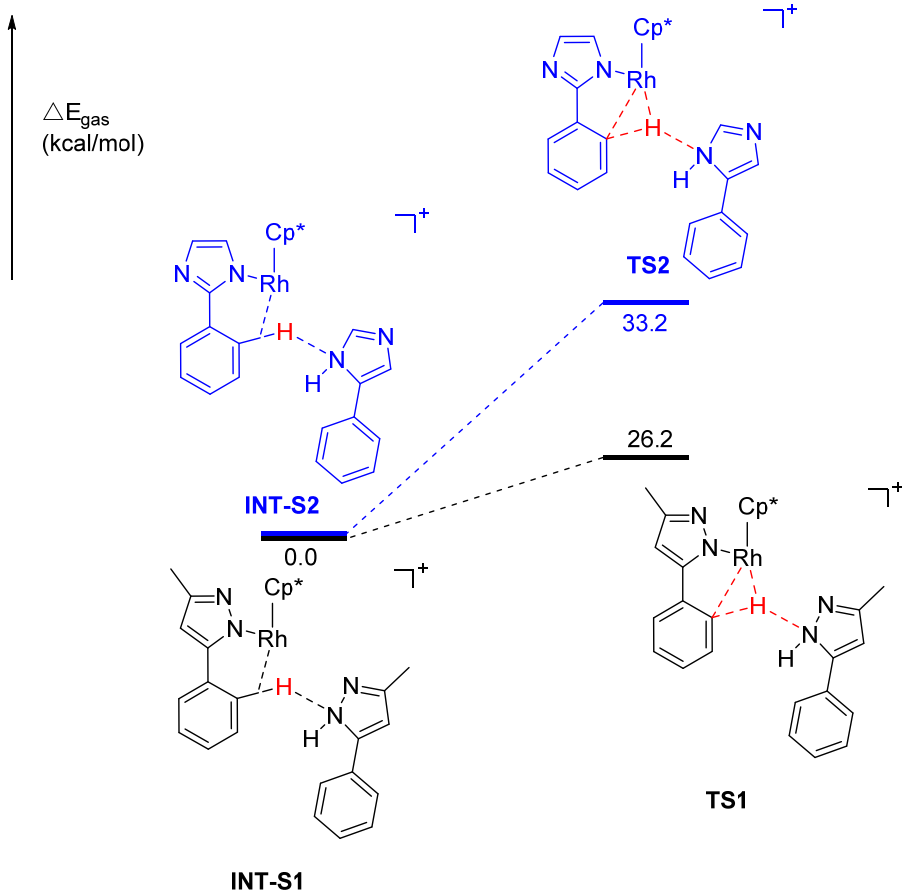
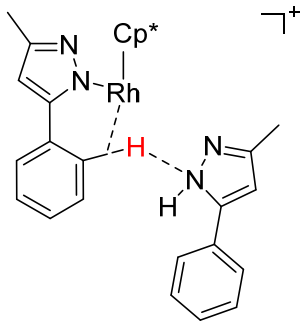


Figure 1 Comparison of the activation energy

2.3 The details of DFT calculation

All the DFT calculations were performed with the Gaussian 09 program package. The geometry optimizations of all minima and transition states involved were performed at the B3LYP levels of theory. The 6-31G basis set was used for C, H, O, and N atoms, while the LANL2DZ basis set was used for Rh.

(1) M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.



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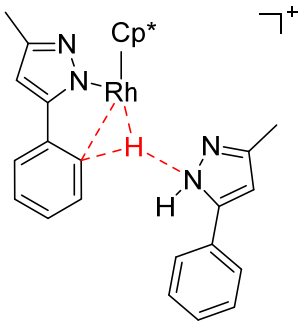

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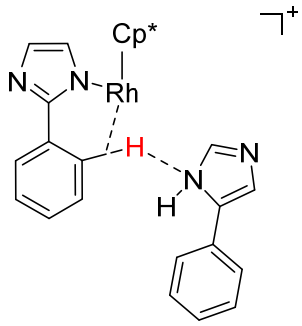

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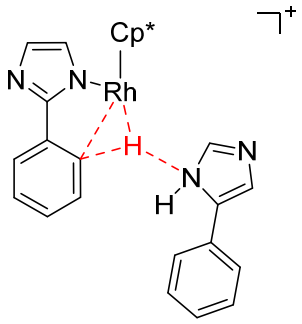

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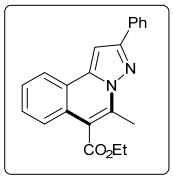
3. Experimental Procedure and Characterization Data of Products 3 and 4a

3.1 General Procedure for the Syntheses of Products 3 and 4a

To a 25 mL Schlenk tube was added substituted pyrazole **1a-o** or 3,5-diphenyl-1*H*-1,2,4-triazole **1s** or substituted 2-phenylbenzoimidazole **1p-r** (0.20 mmol), $[Cp^*RhCl_2]_2$ (7.0 mg, 5.0 mol %), $AgSbF_6$ (14.0 mg, 20.0 mol %), diazo compounds **2a-l** (0.25 mmol) was dissolved with THF (2 mL) and then the solvent was injected into the tube through a syringe, and the tube was purged with Ar for three minutes. Then the formed mixture was stirred at 25℃ or 60℃ or 100℃ under Ar for 24h or 48h (as shown in **Table 2** and **Table 3**). The solvent was then cooled to room temperature and the solvent was removed under vacuum distillation. The crude products were purified by column chromatography on silica gel (eluent: petroleum ether: ethyl acetate= 20:1) to give the desired products **3**.

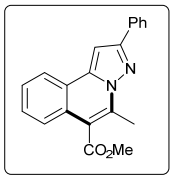
3.2 Experimental Characterization Data of Products 3 and 4a

ethyl 5-methyl-2-phenylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3aa) :



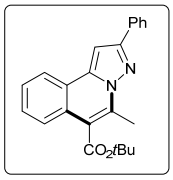
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3aa** (61 mg, 92% yield) as white solid. Melting point: 106-108℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.09 (m, 1H), 8.07 - 8.05 (m, 2H), 7.85 - 7.76 (m, 1H), 7.58 - 7.52 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 7.32 (s, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 2.93 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 153.3, 139.8, 135.9, 133.0, 128.7, 128.5, 128.2, 127.0, 126.4, 126.1, 124.5, 123.6, 123.0, 115.6, 95.4, 61.7, 15.8, 14.3. HRMS m/z (ESI) calcd for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1441, found 331.1442.

methyl 5-methyl-2-phenylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3ab):



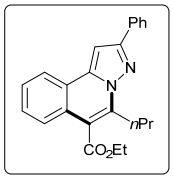
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ab** (74 mg, 94% yield) as white solid. Melting point: 166-168℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 - 8.10 (m, 1H), 8.08 - 8.02 (m, 2H), 7.82 - 7.75 (m, 1H), 7.59 - 7.52 (m, 2H), 7.51 - 7.46 (m, 2H), 7.43 - 7.37 (m, 1H), 7.34 (s, 1H), 4.07 (s, 3H), 2.92 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 153.4, 139.9, 136.3, 133.0, 128.8, 128.5, 128.2, 127.1, 126.4, 126.1, 124.7, 123.7, 123.0, 115.3, 95.5, 52.6, 15.9. HRMS m/z (ESI) calcd for $C_{20}H_{17}N_2O_2$ $[M+H]^+$ 317.1285, found 317.1281.

tert-butyl 5-methyl-2-phenylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3ac):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ac** (82 mg, 92% yield) as white solid. Melting point: 122-124℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 - 8.10 (m, 1H), 8.06 - 8.04 (m, 2H), 7.85 - 7.78 (m, 1H), 7.59 - 7.54 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 7.34 (s, 1H), 2.93 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 153.1, 139.7, 134.8, 133.2, 128.7, 128.4, 128.2, 127.0, 126.4, 126.3, 124.4, 123.7, 123.2, 177.1, 95.3, 82.9, 28.3, 15.5. HRMS m/z (ESI) calcd for $C_{23}H_{23}N_2O_2$ $[M+H]^+$ 359.1754, found 359.1754.

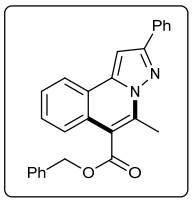
ethyl 2-phenyl-5-propylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3ad):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ad** (60 mg, 84% yield) as white solid. Melting point: 67-69℃. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 3H), 7.80 (d, *J* = 8.0 Hz, 1H), 7.59 - 7.46 (m, 4H), 7.45 - 7.38 (m, 1H), 7.33 (s, 1H), 4.58 (q, *J* = 7.0 Hz, 2H), 3.38 - 3.31 (m, 2H), 2.05 (h, *J* = 7.2 Hz, 2H), 1.53 - 1.49 (m, 3H), 1.18 - 1.14 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 153.0,

139.8, 139.4, 133.1, 128.7, 128.4, 128.1, 127.0, 126.4, 126.2, 124.6, 123.6, 123.2, 115.5, 95.1, 61.6, 31.6, 21.1, 14.3. HRMS m/z (ESI) calcd for $C_{23}H_{23}N_2O_2$ $[M+H]^+$ 359.1754, found 359.1753.

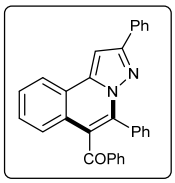
benzyl 5-methyl-2-phenylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3ae):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ae** (77 mg, 99% yield) as white solid. Melting point 143-145℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.3 Hz, 3H), 7.82 - 7.71 (m, 1H), 7.57 - 7.36 (m, 10H), 7.30 (s, 1H), 5.55 (s, 2H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 153.3, 139.7, 136.1, 135.2, 133.0, 128.7, 128.6, 128.5, 128.5, 128.3, 128.1, 127.0, 126.4, 126.1, 124.5, 123.6, 123.0, 115.2, 95.4, 67.5, 15.8. HRMS m/z (ESI) calcd for $C_{26}H_{21}N_2O_2$ $[M+H]^+$ 393.1598, found 393.1597.

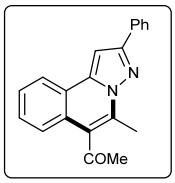
(2,5-diphenylpyrazolo[5,1-*a*]isoquinolin-6-yl)(phenyl) methanone (3af):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3af** (55 mg, 65% yield) as white solid. Melting point 195-197℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.7 Hz, 1H), 7.94 - 7.92 (m, 2H), 7.73 - 7.72 (m, 2H), 7.60 - 7.57 (m, 4H), 7.51 - 7.43 (m, 2H), 7.43 - 7.37 (m, 3H), 7.36 - 7.25 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 153.3, 140.3, 137.8, 136.3, 133.4, 133.0, 131.4, 130.9, 129.5, 129.3, 128.6, 128.4, 128.3, 127.9, 127.3, 126.4, 125.5, 123.9, 122.2, 95.3. HRMS m/z (ESI) calcd for $C_{30}H_{21}N_2O$ $[M+H]^+$ 425.1648, found 425.1648.

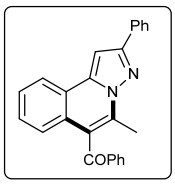
1-(5-methyl-2-phenylpyrazolo [5,1-*a*]isoquinolin-6-yl)ethan-1-one (3ag):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ag** (45 mg, 60% yield) as white solid. Melting point 138-140℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 - 8.10 (m, 1H), 8.04 (d, *J* = 7.9 Hz, 2H), 7.60 - 7.44 (m, 5H), 7.39 (d, *J* = 7.1 Hz, 1H), 7.34 (s, 1H), 2.81 (s, 3H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.4, 153.3, 139.7, 133.2, 132.3, 128.9, 128.6, 128.4, 127.3, 126.5, 125.8, 124.2, 124.1, 123.8, 123.5, 95.5, 33.4, 15.4. HRMS m/z (ESI) calcd for $C_{20}H_{17}N_2O$ $[M+H]^+$ 301.1335, found 301.1338.

(5-methyl-2-phenylpyrazolo [5,1-*a*]isoquinolin-6-yl) (phenyl) methanone (3ah):

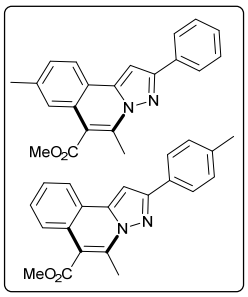


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ah** (83 mg, 92% yield) as white solid. Melting point 205-207℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 8.08 - 8.06 (m, 2H), 7.98 - 7.93 (m, 2H), 7.66 - 7.58 (m, 1H), 7.56 - 7.52 (m, 1H), 7.48 (q, *J* = 7.2 Hz, 4H), 7.43 - 7.38 (m, 4H), 2.70 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 153.1, 139.8, 137.6, 134.2, 133.7, 133.2, 129.9, 129.0, 128.8, 128.5, 128.2, 127.2, 126.4, 125.0, 123.8, 123.3, 120.7, 95.5, 15.8. HRMS m/z (ESI) calcd for $C_{25}H_{19}N_2O$ $[M+H]^+$ 363.1492, found 363.1490.

methyl 5,8-dimethyl-2-phenylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3bb)

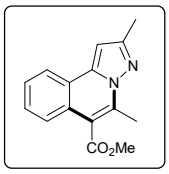
methyl 5-methyl-2-(*p*-tolyl) pyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3bb`):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3bb+3bb`** (78 mg, 97% yield, **3bb:3bb`**= 1:1) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.97 (m, 3H), 7.91 - 7.88 (m, 3H), 7.76 - 7.71 (m, 1H), 7.51 - 7.41 (m, 5H), 7.39 - 7.32 (m, 1H), 7.30 - 7.21 (m, 4H), 7.19 (s, 1H), 4.03 - 4.02 (m, 6H), 2.86 - 2.84 (m, 6H), 2.44 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 168.1, 153.4, 153.2, 139.8, 139.7, 138.3, 138.2, 136.2, 135.9, 133.1, 130.1, 129.4, 128.6, 128.6, 128.4, 128.0, 126.9, 126.3, 126.2, 126.1, 126.0, 124.5, 124.1, 123.6, 123.5, 120.7, 115.1, 115.0, 95.2, 94.9, 52.4, 21.9, 21.3, 15.9. HRMS m/z (ESI) calcd for $C_{21}H_{19}N_2O_2$ $[M+H]^+$ 331.1441, found 331.1439.

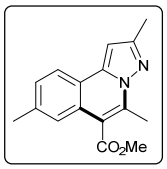
methyl 2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3cb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3cb** (54 mg, 85% yield) as white solid. Melting point 83-85℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 - 7.96 (m, 1H), 7.78 - 7.71 (m, 1H), 7.54 - 7.45 (m, 2H), 6.79 (s, 1H), 4.03 (s, 3H), 2.83 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 151.8, 139.3, 135.8, 128.0, 126.9, 126.1, 124.5, 123.6, 122.7, 114.4, 98.2, 52.4, 16.0, 14.1. HRMS m/z (ESI) calcd for $C_{15}H_{15}N_2O_2$ $[M+H]^+$ 255.1128, found 255.1125.

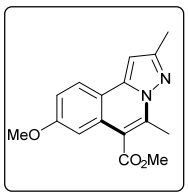
methyl 2,5,8-trimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3db):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3db** (53 mg, 99% yield) as white solid. Melting point 95-97℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 1H), 7.50 (s, 1H), 7.31 (d, *J* = 8.0 Hz, 1H), 6.74 (s, 1H), 4.04 (s, 3H), 2.81 (s, 3H), 2.53 (s, 3H), 2.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 151.7, 139.5, 138.1, 135.5, 128.5, 126.2, 124.1, 123.5, 120.5, 114.3, 97.6, 52.4, 21.9, 16.0, 14.2. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1285, found 269.1288.

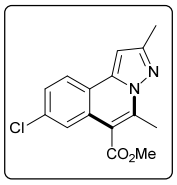
methyl 8-methoxy-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3eb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3eb** (47 mg, 85% yield) as white solid. Melting point 104-106℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.8 Hz, 1H), 7.17 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.65 (s, 1H), 4.02 (s, 3H), 3.87 (s, 3H), 2.81 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 159.3, 151.9, 139.5, 136.5, 127.6, 125.1, 116.8, 116.4, 113.8, 106.0, 97.0, 55.3, 52.3, 16.1, 14.1. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1237.

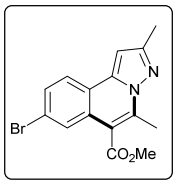
methyl 8-chloro-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3fb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3fb** (45 mg, 79% yield) as white solid. Melting point 145-147℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.6 Hz, 1H), 7.72 (s, 1H), 7.37 (d, *J* = 8.6 Hz, 1H), 6.70 (s, 1H), 4.03 (s, 3H), 2.79 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 152.1, 138.7, 137.4, 133.9, 127.2, 127.2, 124.8, 124.0, 120.9, 113.2, 98.4, 52.5, 16.1, 14.1. HRMS m/z (ESI) calcd for $C_{15}H_{14}ClN_2O_2$ $[M+H]^+$ 289.0738, found 289.0735.

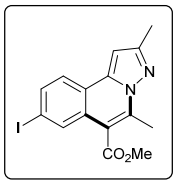
methyl 8-bromo-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3gb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3gb** (60 mg, 91% yield) as white solid. Melting point 155-157℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.89 (m, 1H), 7.77 (d, *J* = 8.6 Hz, 1H), 7.54 - 7.52 (m, 1H), 6.73 (s, 1H), 4.04 (s, 3H), 2.81 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 152.3, 138.9, 137.5, 130.1, 127.6, 127.2, 125.1, 122.3, 121.4, 113.3, 98.6, 52.8, 16.3, 14.3. HRMS m/z (ESI) calcd for $C_{15}H_{14}BrN_2O_2$ $[M+H]^+$ 333.0233, found 333.0231.

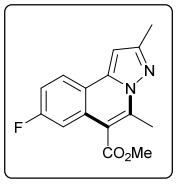
methyl 8-iodo-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3hb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3hb** (66 mg, 87% yield) as white solid. Melting point 155-157℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.71 (d, *J* = 8.4 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 6.74 (s, 1H), 4.04 (s, 3H), 2.80 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 152.1, 138.8, 137.1, 135.5, 133.2, 127.6, 124.8, 121.6, 113.0, 98.5, 93.8, 52.6, 16.1, 14.2. HRMS m/z (ESI) calcd for $C_{15}H_{14}IN_2O_2$ $[M+H]^+$ 381.0095, found 381.0096.

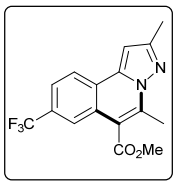
methyl 8-fluoro-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3ib):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3ib** (52 mg, 96% yield) as white solid. Melting point 81-83℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.47 (d, *J* = 10.3 Hz, 1H), 7.21 (s, 1H), 6.72 (s, 1H), 4.04 (s, 3H), 2.83 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 162.0 (d, *J* = 246.9 Hz), 152.2, 139.0, 137.6, 127.8 (d, *J* = 9.5 Hz), 125.7 (d, *J* = 9.1 Hz), 119.3, 115.6 (d, *J* = 23.9 Hz), 113.5 (d, *J* = 3.4 Hz), 110.1 (d, *J* = 24.0 Hz), 98.0, 52.5, 16.2, 14.1. HRMS m/z (ESI) calcd for $C_{15}H_{14}FN_2O_2$ $[M+H]^+$ 272.0961, found 272.0960.

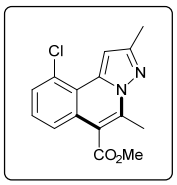
methyl 2,5-dimethyl-8-(trifluoromethyl)pyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3jb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3jb** (58 mg, 91% yield) as white solid. Melting point 103-105℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 8.01 (d, *J* = 8.4 Hz, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 6.83 (s, 1H), 4.06 (s, 3H), 2.83 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 152.3, 138.4, 137.9, 129.6 (q, *J* = 32.4 Hz), 125.8, 124.6, 124.2, 123.9 (q, *J* = 272.3 Hz), 123.0, 122.1 (d, *J* = 4.3 Hz), 113.8, 99.4, 52.6, 16.1, 14.1. HRMS m/z (ESI) calcd for $C_{16}H_{14}F_3N_2O_2$ $[M+H]^+$ 323.1002, found 323.1001.

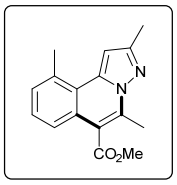
methyl 10-chloro-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3kb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3kb** (52 mg, 91% yield) as white solid. Melting point 126-128℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.56 - 7.53 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 4.03 (s, 3H), 2.80 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.1, 151.5, 136.4, 136.3, 130.4, 128.8, 128.4, 127.6, 123.0, 121.1, 114.5, 104.4, 52.6, 16.3, 14.1. HRMS m/z (ESI) calcd for $C_{15}H_{14}ClN_2O_2$ $[M+H]^+$ 289.0738, found 289.0735.

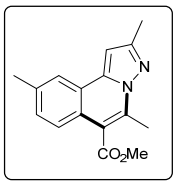
methyl 2,5,10-trimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3lb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3lb** (43 mg, 81% yield) as white solid. Melting point 96-98℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.1 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.2 Hz, 1H), 6.89 (s, 1H), 4.03 (s, 3H), 2.81 (s, 3H), 2.76 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.7, 151.1, 138.4, 134.8, 134.5, 129.2, 127.3, 127.0, 122.5, 122.2, 115.4, 102.9, 52.5, 23.8, 16.2, 14.1. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1285, found 269.1285.

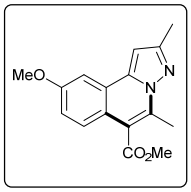
methyl 2,5,9-trimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3mb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3mb** (41 mg, 77% yield) as white solid. Melting point 96-98℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.79 (s, 1H), 4.03 (s, 3H), 2.82 (s, 3H), 2.54 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 151.6, 139.3, 136.9, 135.0, 129.7, 124.4, 123.9, 123.3, 122.8, 114.3, 98.0, 52.4, 21.5, 15.9, 14.2. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_2$ $[M+H]^+$ 269.1285, found 269.1282.

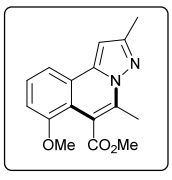
methyl 9-methoxy-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3nb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3nb** (15 mg, 25% yield) as white solid. Melting point 116-118℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 6.7 Hz, 1H), 7.39 (s, 1H), 7.15 (d, *J* = 9.1 Hz, 1H), 6.80 (s, 1H), 4.03 (s, 3H), 3.94 (s, 3H), 2.82 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 158.4, 151.5, 139.2, 133.8, 126.3, 124.0, 120.3, 117.8, 114.3, 104.8, 98.1, 55.5, 52.5, 15.9, 14.2. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1233.

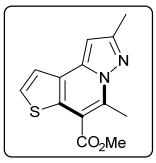
methyl 7-methoxy-2,5-dimethylpyrazolo[5,1-*a*]isoquinoline-6-carboxylate (3nb`):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3nb`** (42 mg, 74% yield) as white solid. Melting point 73-75℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 8.9 Hz, 1H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.80 (s, 1H), 3.98 (s, 3H), 3.93 (s, 3H), 2.74 (s, 3H), 2.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 154.1, 151.4, 138.8, 133.4, 127.8, 124.2, 116.9, 116.4, 112.3, 108.9, 98.3, 56.6, 52.5, 15.2, 14.2. HRMS m/z (ESI) calcd for $C_{16}H_{17}N_2O_3$ $[M+H]^+$ 285.1234, found 285.1230.

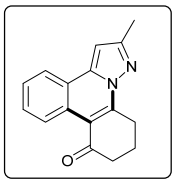
methyl 2,5-dimethylpyrazolo[1,5-*a*] thieno [3,2-c]pyridine-6-carboxylate (3ob):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give 3ob (51 mg, 99% yield) as white solid. Melting point 138-140℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (s, 1H), 7.46 (s, 1H), 6.48 (s, 1H), 4.01 (s, 3H), 3.00 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 153.0, 138.4, 137.0, 132.5, 125.9, 125.5, 125.0, 110.6, 96.2, 52.1, 16.1, 14.2. HRMS m/z (ESI) calcd for $C_{13}H_{13}N_2O_2S$ $[M+H]^+$ 261.0692, found 261.0692.

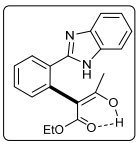
2-methyl-10, 11-dihydropyrazolo [1, 5-*f*] phenanthridin-8(9*H*)-one (3ci):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 20:1) give **3ci** (44 mg, 88% yield) as white solid. Melting point 105-107℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.35 (s, 1H), 7.94 (s, 1H), 7.56 - 7.48 (m, 2H), 6.76 (s, 1H), 3.48 (m, 2H), 2.75 (m, 2H), 2.53 (m, 3H), 2.26 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.3, 153.8, 148.0, 140.5, 128.9, 127.0, 126.9, 126.3, 123.2, 122.6, 113.5, 99.2, 39.7, 25.9, 20.8, 14.2. HRMS m/z (ESI) calcd for $C_{16}H_{15}N_2O$ $[M+H]^+$ 250.1106, found 250.1105.

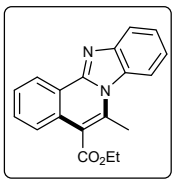
ethyl (*E*)-2-(2-(1H-benzo[*d*]imidazol-2-yl)phenyl)-3-hydroxybut-2-enoate (4a):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **4a** (61 mg, 95% yield) as white solid. Melting point 193-195℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.2 Hz, 1H), 8.09 - 7.99 (m, 1H), 7.79 (d, *J* = 8.7 Hz, 1H), 7.48 - 7.41 (m, 3H), 7.32 - 7.19 (m, 2H), 4.15 - 3.91 (m, 3H), 1.61 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 147.7, 144.2, 133.7, 130.9, 130.3, 130.2, 129.1, 126.0, 125.3, 123.2, 122.6, 119.6, 113.4, 87.3, 62.2, 55.3, 26.6, 13.7. HRMS m/z (ESI) calcd for $C_{19}H_{18}N_2O_3$ $[M+H]^+$ 323.1390, found 323.1389.

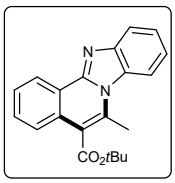
ethyl 6-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline-5-carboxylate (3pa):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3pa** (38 mg, 63% yield) as white solid. Melting point 175-177℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 6.8 Hz, 1H), 8.17 - 7.96 (m, 2H), 7.69 - 7.64 (m, 3H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 1H), 4.57 (q, *J* = 6.6 Hz, 2H), 3.06 (s, 3H), 1.49 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 147.3, 143.8, 134.6, 131.3, 130.5, 128.7, 127.8, 125.3, 124.9, 124.0, 122.3, 121.6, 120.0, 116.5, 114.5, 62.0, 19.2, 14.3. HRMS m/z (ESI) calcd for $C_{19}H_{17}N_2O_2$ $[M+H]^+$ 304.1212, found 304.1213.

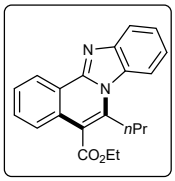
tert-butyl 6-methylbenzo[4,5] imidazo [2,1-*a*]isoquinoline-5-carboxylate (3pc):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3pc** (50 mg, 76% yield) as white solid. Melting point 180-182℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 7.0 Hz, 1H), 8.12 - 7.91 (m, 2H), 7.77 - 7.59 (m, 3H), 7.47 (t, *J* = 6.5 Hz, 1H), 7.31 (d, *J* = 6.9 Hz, 1H), 3.05 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.1, 147.6, 144.5, 133.7, 131.6, 130.4, 128.9, 127.7, 125.3, 124.7, 123.9, 122.1, 120.2, 117.7, 115.4, 114.5, 83.3, 28.4, 19.0. HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2O_2$ $[M+H]^+$ 332.1525, found 332.1528.

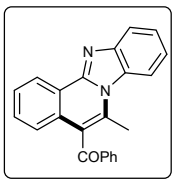
ethyl 6-propylbenzo[4,5] imidazo [2,1-*a*]isoquinoline-5-carboxylate (3pd):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3pd** (20 mg, 30% yield) as white solid. Melting point 181-183℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.72 - 7.61 (m, 3H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.1 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 3.40 - 3.21 (m, 2H), 2.10 - 1.85 (m, 2H), 1.50 (t, *J* = 7.1 Hz, 3H), 1.20 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 147.9, 144.5, 138.0, 130.7, 130.4, 128.7, 127.8, 125.3, 124.7, 124.0, 122.5, 122.1, 120.3, 116.4, 114.1, 62.0, 33.0, 21.4, 14.3, 13.8. HRMS m/z (ESI) calcd for $C_{21}H_{21}N_2O_2$ $[M+H]^+$ 332.1525, found 332.1524.

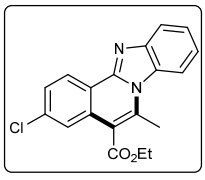
(6-methylbenzo [4,5] imidazo[2,1-*a*]isoquinolin-5-yl)(phenyl)methanone (3ph):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3ph** (26 mg, 39% yield) as white solid. Melting point 185-187℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.93 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.65 (t, *J* = 7.5 Hz, 2H), 7.56 (t, *J* = 7.8 Hz, 2H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.44 - 7.34 (m, 2H), 2.93 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 147.7, 144.4, 137.4, 134.5, 132.7, 131.6, 130.3, 129.9, 129.7, 129.1, 127.8, 125.3, 124.8, 124.5, 122.2, 122.1, 120.8, 120.2, 114.4, 19.2. HRMS m/z (ESI) calcd for $C_{23}H_{17}N_2O$ $[M+H]^+$ 336.1263, found 336.1257.

ethyl 3-chloro-6-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline-5-carboxylate (3qa):

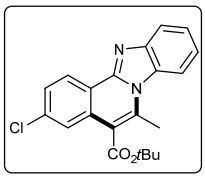


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3qa** (58 mg, 85% yield) as white solid. Melting point 174-176℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.6 Hz, 1H), 8.05 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.57 (d, *J* = 8.6 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.35 (t, *J* = 7.8 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 3.06 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ

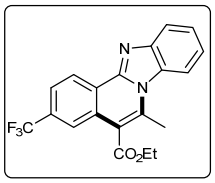
167.1, 146.9, 144.4, 136.6, 136.4, 131.4, 129.7, 128.2, 126.7, 125.0, 123.7, 122.4, 120.2, 120.2, 115.0, 114.5, 62.2, 19.3, 14.3. HRMS m/z (ESI) calcd for $C_{19}H_{16}ClN_2O_2$ $[M+H]^+$ 338.0822, found 338.0824.

tert-butyl 3-chloro-6-methylbenzo[4,5]imidazo[2,1-*a*]isoquinoline-5-carboxylate (3qc):



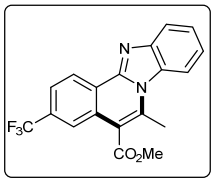
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3qc** (59 mg, 80% yield) as white solid. Melting point 181-183℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.6 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 1H), 7.70 (s, 1H), 7.55 (d, *J* = 8.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.3 Hz, 1H), 3.05 (s, 3H), 1.72 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 166.3, 146.8, 144.3, 136.4, 135.3, 131.4, 129.8, 128.0, 126.6, 124.8, 123.5, 122.2, 120.2, 120.0, 116.4, 114.4, 83.5, 28.2, 18.9. HRMS m/z (ESI) calcd for $C_{21}H_{20}ClN_2O_2$ $[M+H]^+$ 366.1135, found 366.1140.

ethyl 6-methyl-3-(trifluoromethyl)benzo[4,5]imidazo[2,1-*a*]isoquinoline-5-carboxylate (3ra):



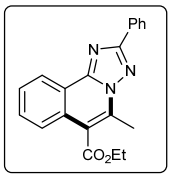
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3ra** (64 mg, 86% yield) as white solid. Melting point 193-195℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.4 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.01-7.99 (m, 2H), 7.82 (d, *J* = 8.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 8.2 Hz, 1H), 4.59 (q, *J* = 7.2 Hz, 2H), 3.08 (s, 3H), 1.51 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.0, 146.3, 144.4, 136.9, 131.8 (q, *J* = 32.9 Hz), 131.5, 128.3, 126.0, 125.8 (q, *J* = 328.3 Hz), 125.2, 124.1, 123.8, 122.9, 121.6 (q, *J* = 4.0 Hz), 120.5, 115.5, 114.7, 62.3, 19.3, 14.2. HRMS m/z (ESI) calcd for $C_{20}H_{16}F_3N_2O_2$ $[M+H]^+$ 372.1086, found 372.1090.

methyl 6-methyl-3-(trifluoromethyl)benzo[4,5]imidazo[2,1-*a*]isoquinoline-5-carboxylate (3rb):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3rb** (59 mg, 86% yield) as white solid. Melting point 160-162℃. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.5 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.96 (s, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.53 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 4.10 (s, 3H), 3.06 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 167.5, 146.2, 144.3, 137.1, 131.8 (q, *J* = 32.7 Hz), 131.4, 128.3, 126.0, 125.2, 124.0, 123.8, 123.8 (q, *J* = 272.6 Hz), 122.9, 121.5 (q, *J* = 3.7 Hz), 120.5, 115.2, 114.7, 53.0, 19.4. HRMS m/z (ESI) calcd for $C_{19}H_{14}F_3N_2O_2$ $[M+H]^+$ 358.0929, found 358.0930.

ethyl 5-methyl-2-phenyl-[1,2,4]triazolo[5,1-*a*]isoquinoline-6-carboxylate (3sa):



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate = 10:1) give **3sa** (34 mg, 51% yield) as white solid. Melting point 110-112℃.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (d, *J* = 7.3 Hz, 1H), 8.38 (d, *J* = 6.8 Hz, 2H), 7.91 (d, *J* = 7.5 Hz, 1H), 7.72 (p, *J* = 7.1 Hz, 2H), 7.58 - 7.42 (m, 3H), 4.58 (q, *J* = 7.1 Hz, 2H), 2.96 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 163.4, 150.1, 134.8, 130.8, 130.4, 130.0, 128.8, 128.7, 127.8, 127.3, 124.6, 124.6, 120.7, 117.4, 62.1, 15.9, 14.3. HRMS m/z (ESI) calcd for $C_{20}H_{18}N_3O_2$ $[M+H]^+$ 331.1321, found 331.1322.

3. References

[1] C. Wiles, P. Watts, S. J. Haswell and E. Pombo-Villar, *Org. Process Res. Dev.*, 2004, **8**, 28.

[2] a) F. Ye, C. Wang, Y. Zhang and J. Wang, *Angew. Chem. Int. Ed.*, 2014, **53**, 11625.

b) Wang J, Wang M, Chen K, Zha S, Song C, Zhu J. *Org. Lett.* 2016, **18**, 1178.

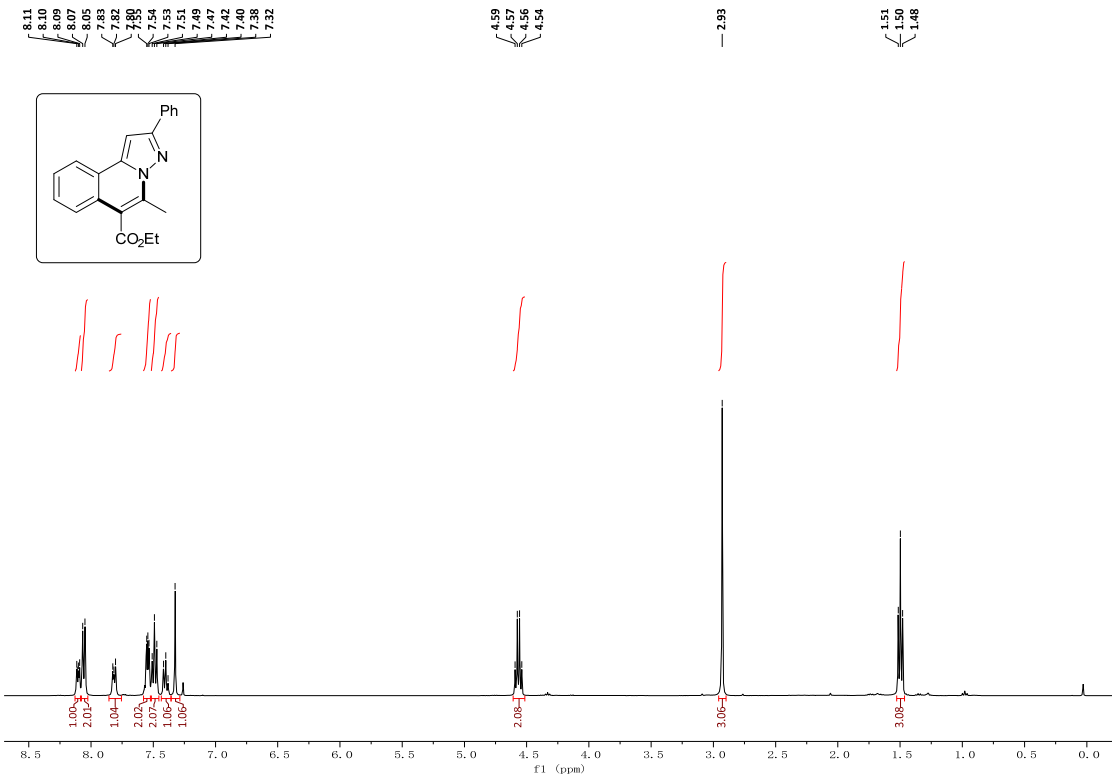
[3] H. Xu, Y. Jiang and H. Fu, *Synlett*, 2013, **24**, 125.

[4] T. Yamashita, S. Yamada, Y. Yamazaki and H. Tanaka, *Synth. Commun.*, 2009, **39**, 2982.

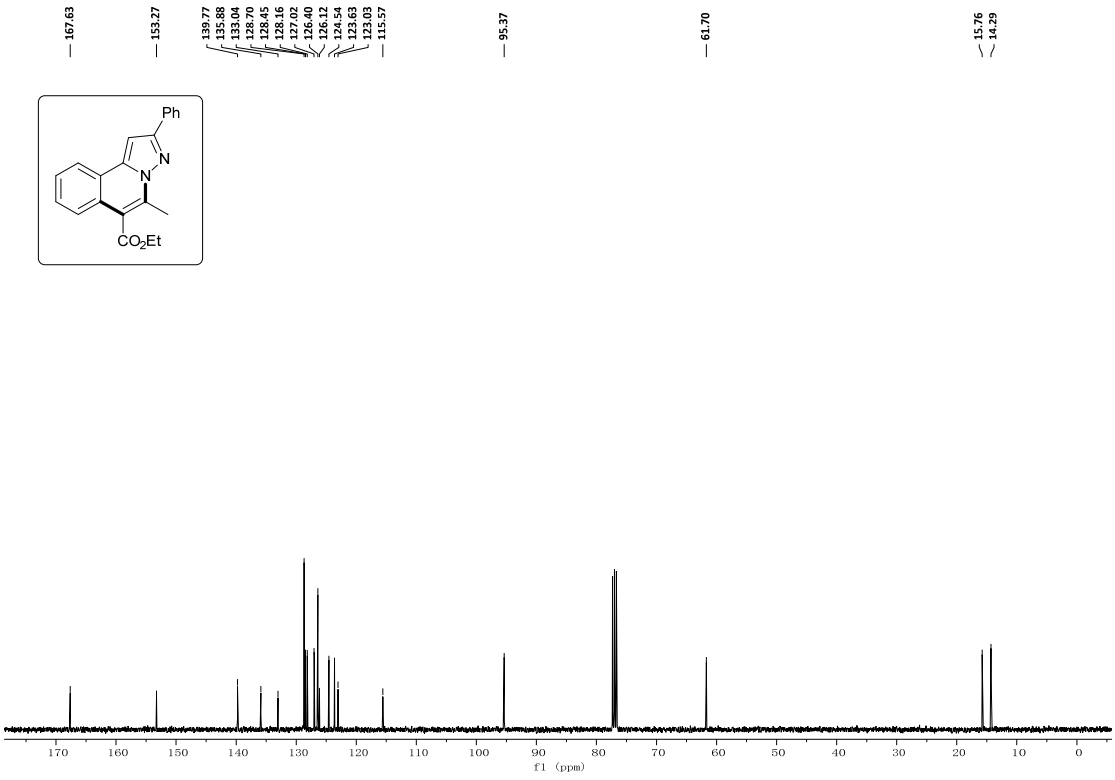
[5] K.-i. Fujita, Y. Takahashi, M. Owaki, K. Yamamoto and R. Yamaguchi, *Org. Lett.*, 2004, **6**, 2785.

4. NMR Spectra

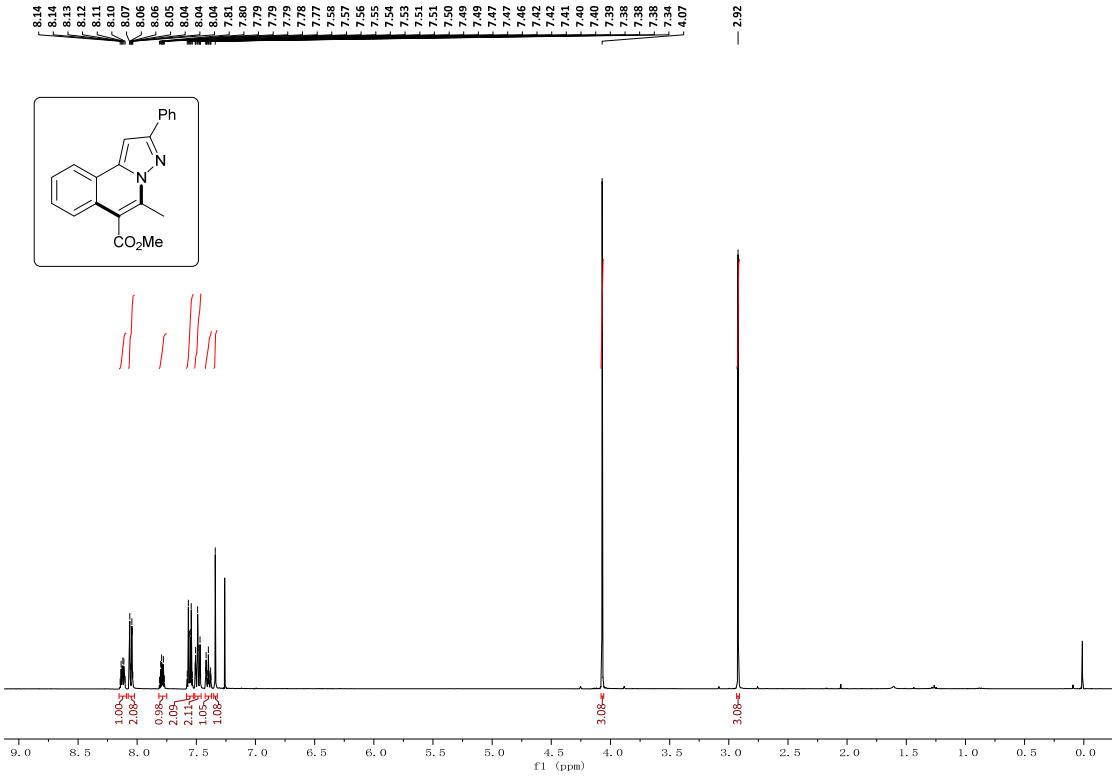
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3aa



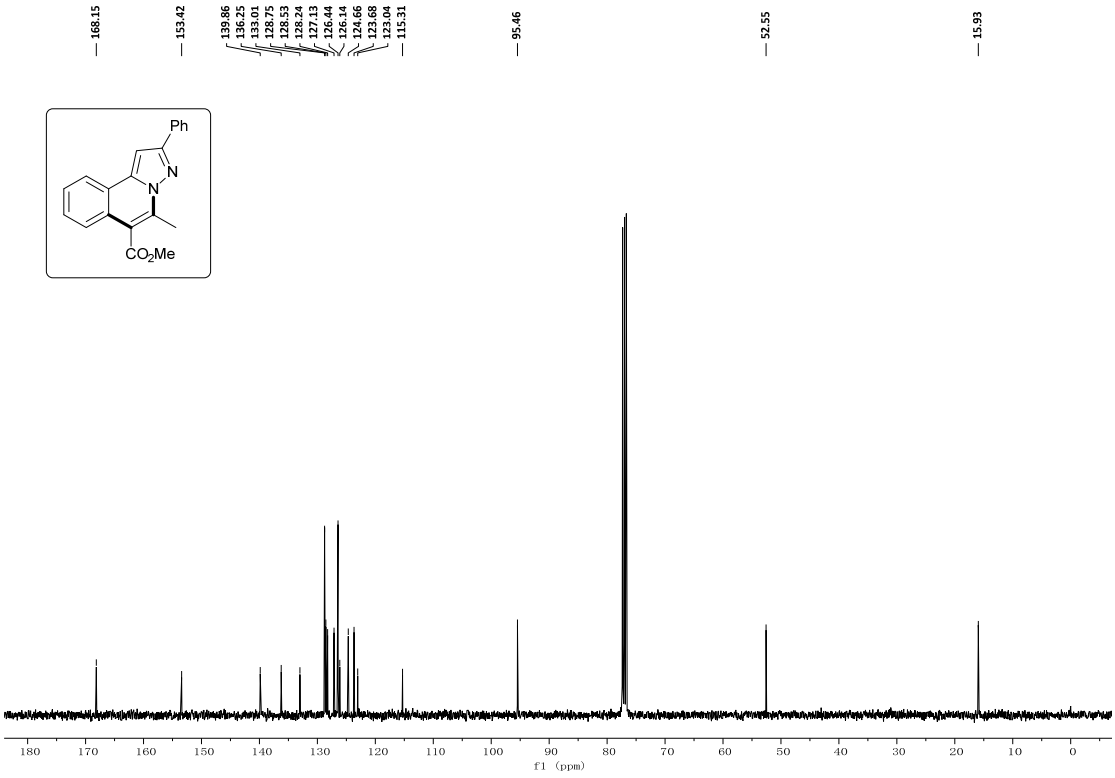
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3aa



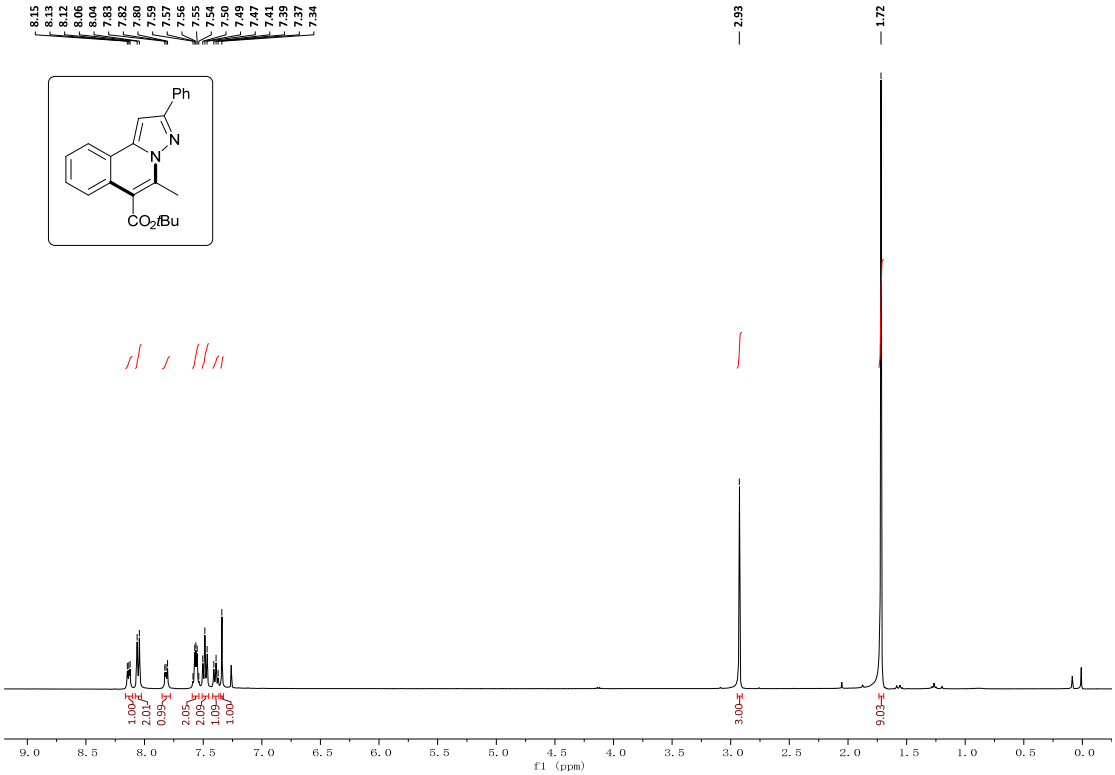
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ab



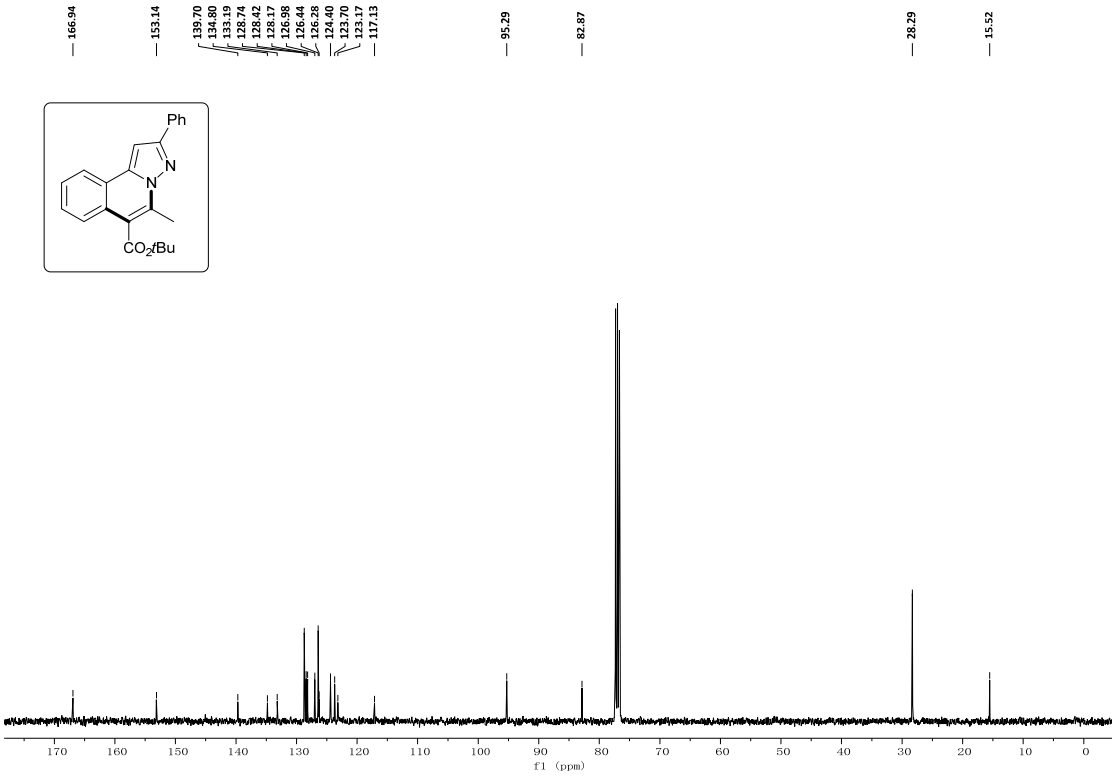
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ab



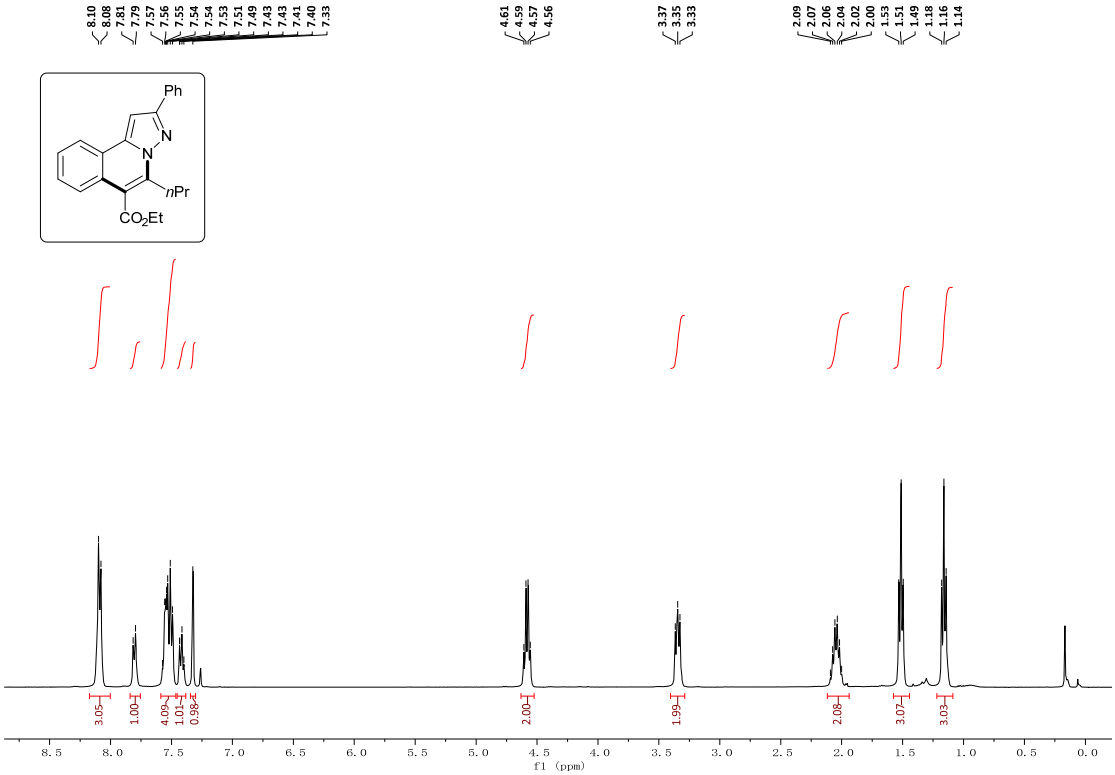
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ac



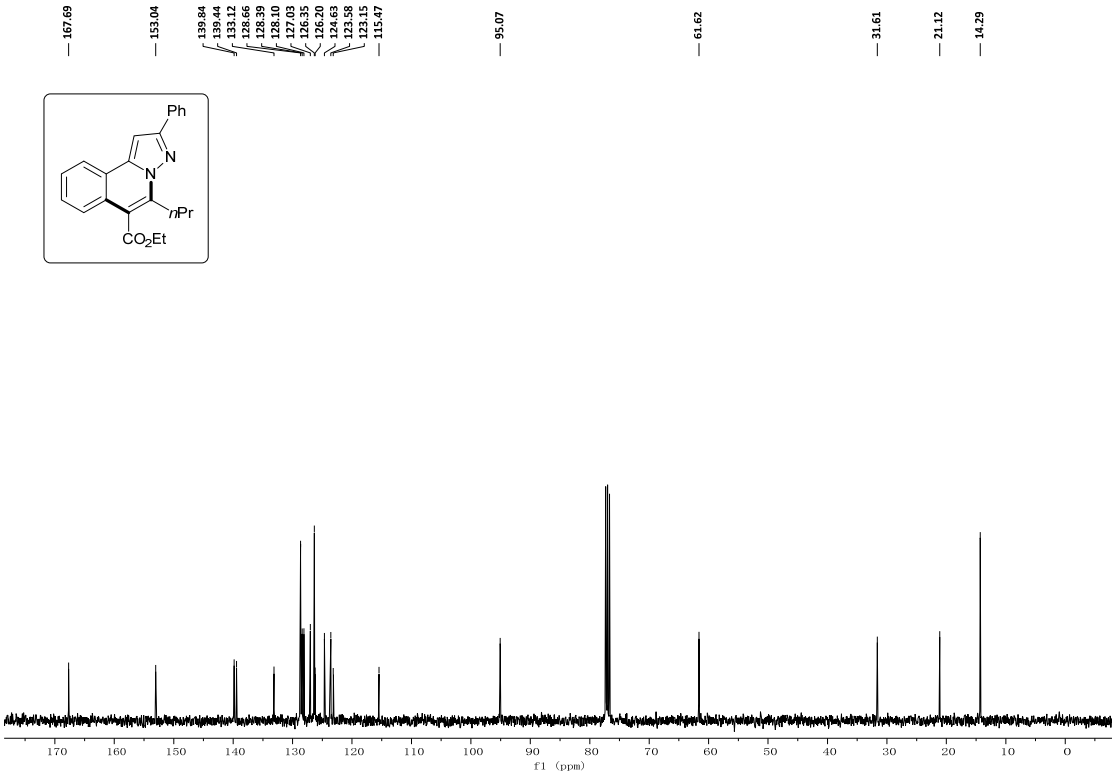
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ac



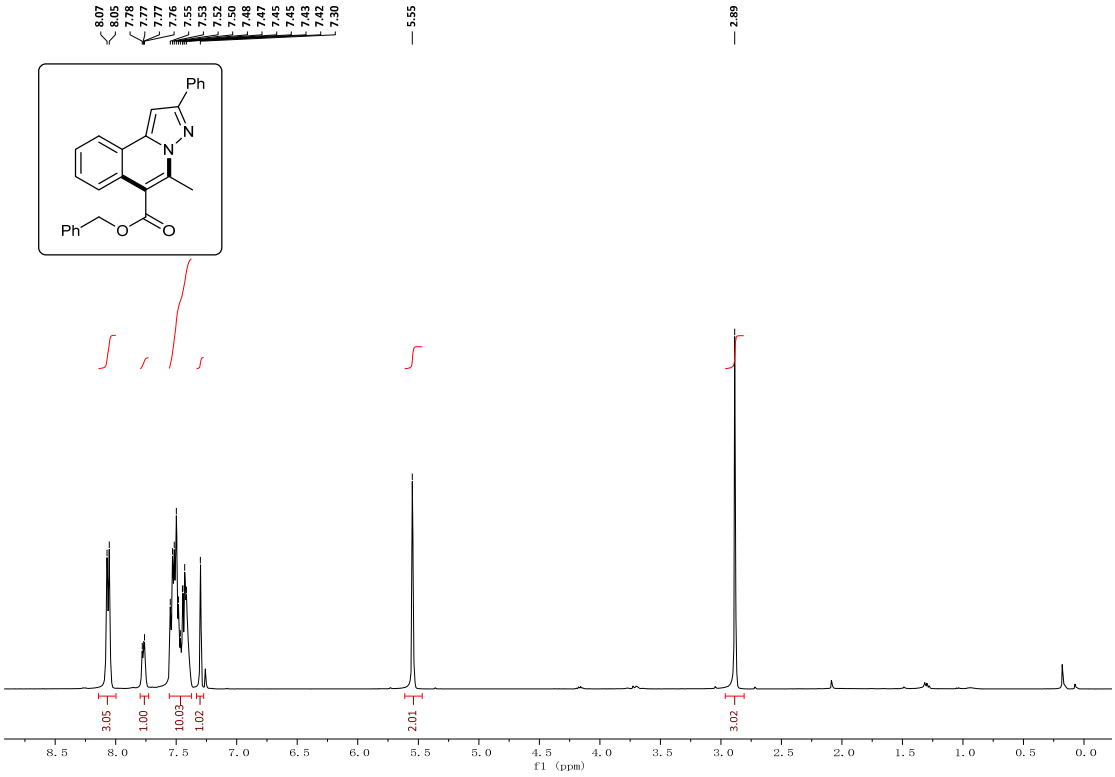
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ad



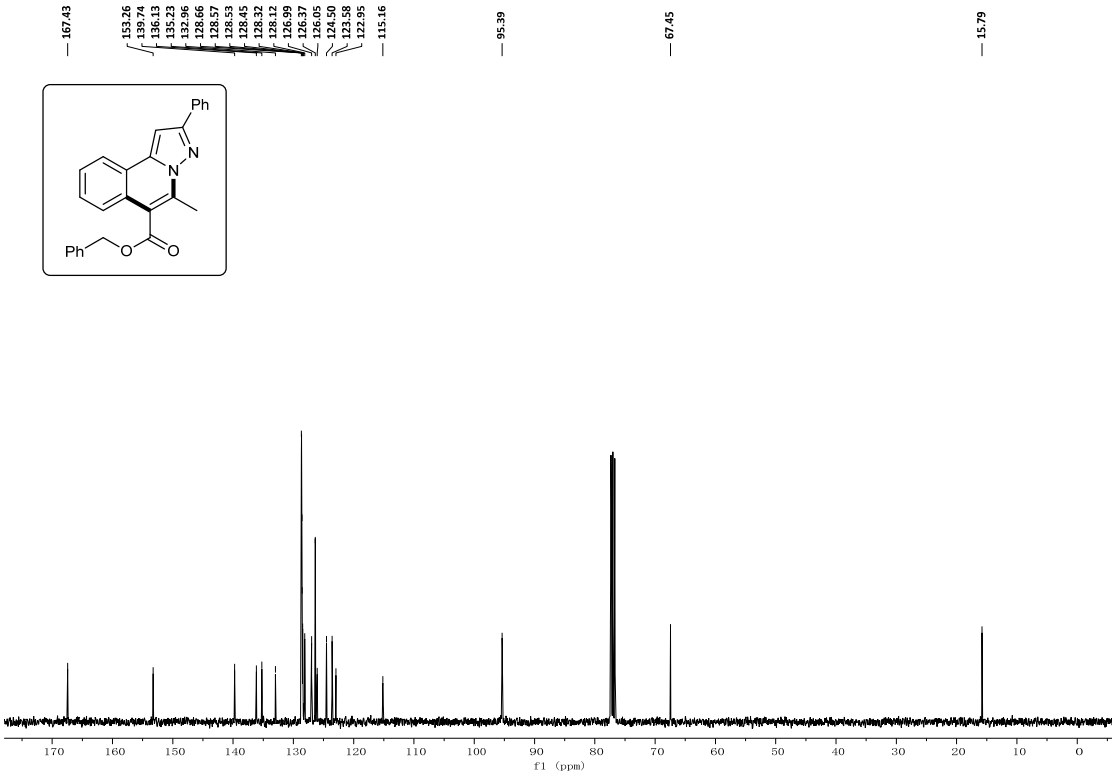
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ad



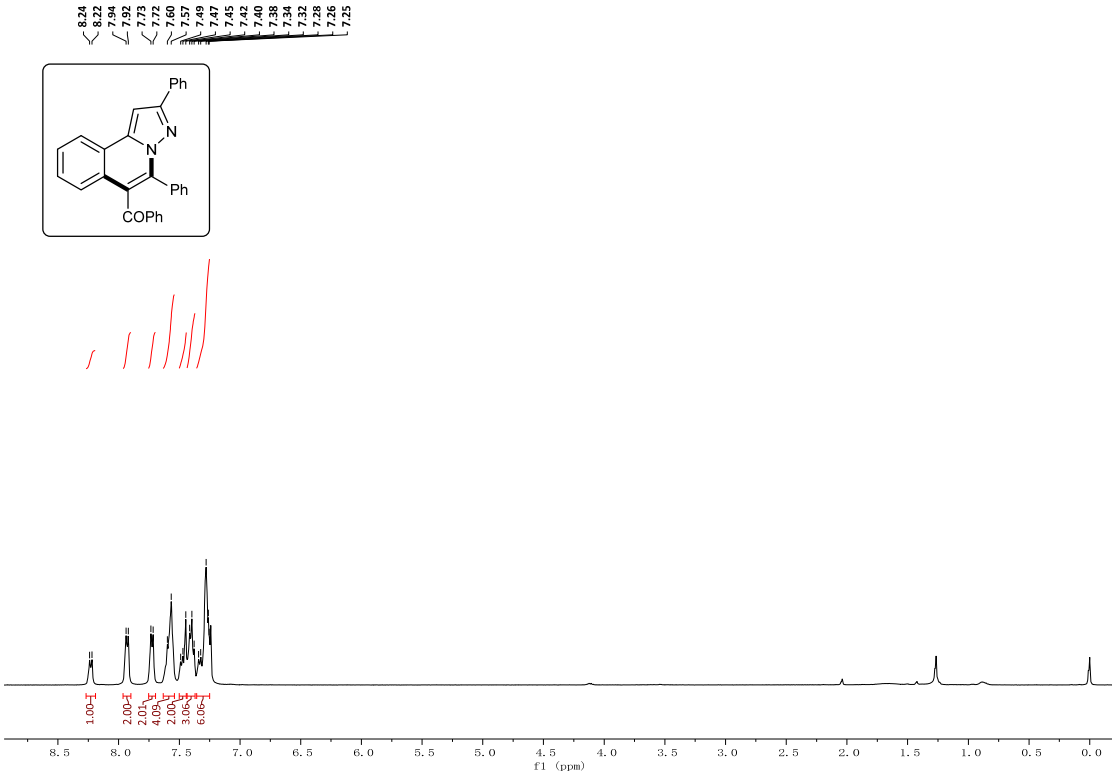
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ae



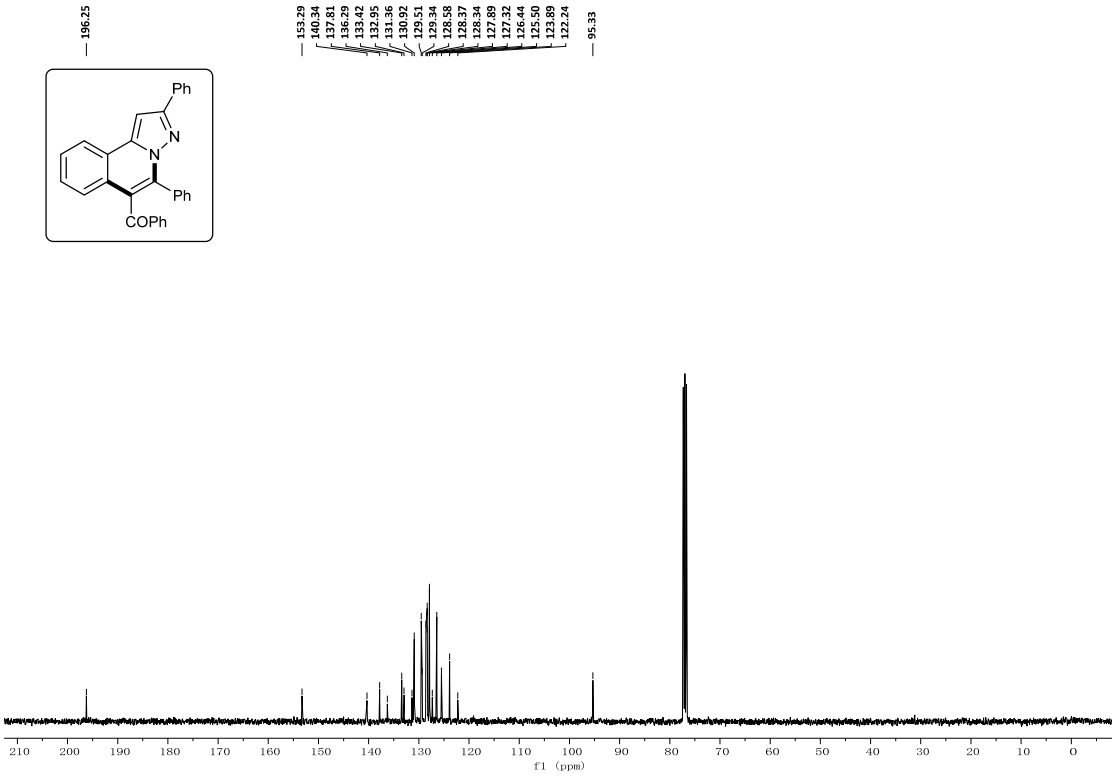
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ae



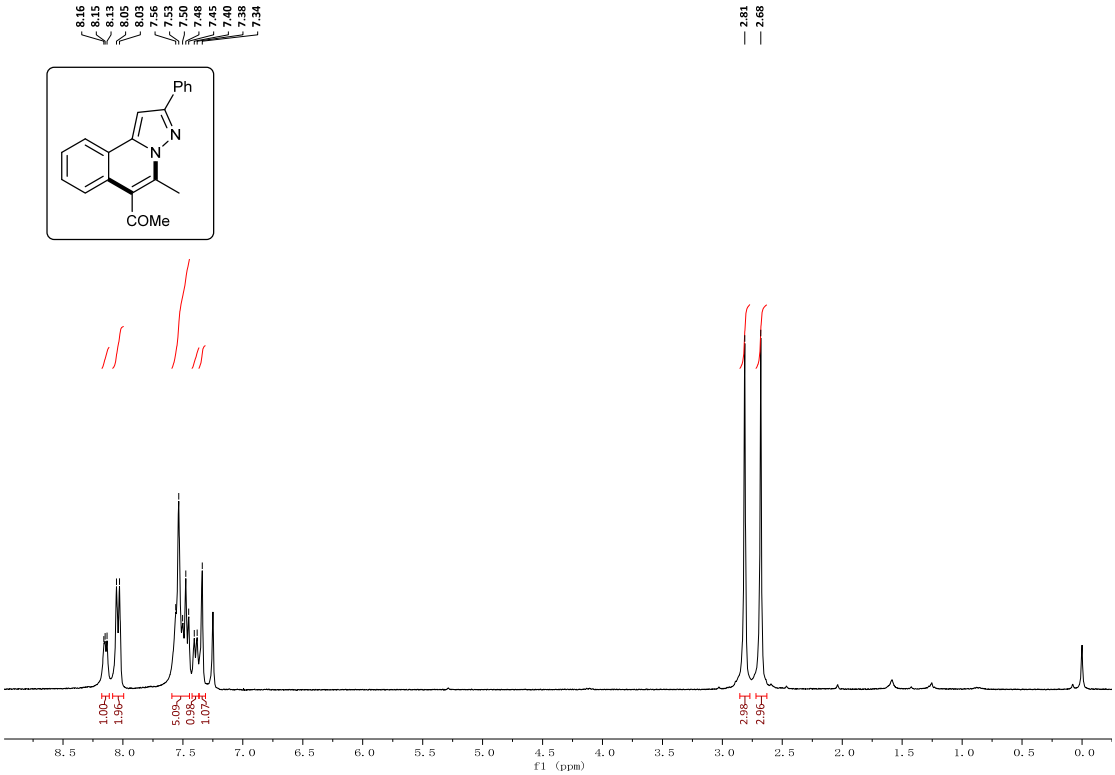
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3af



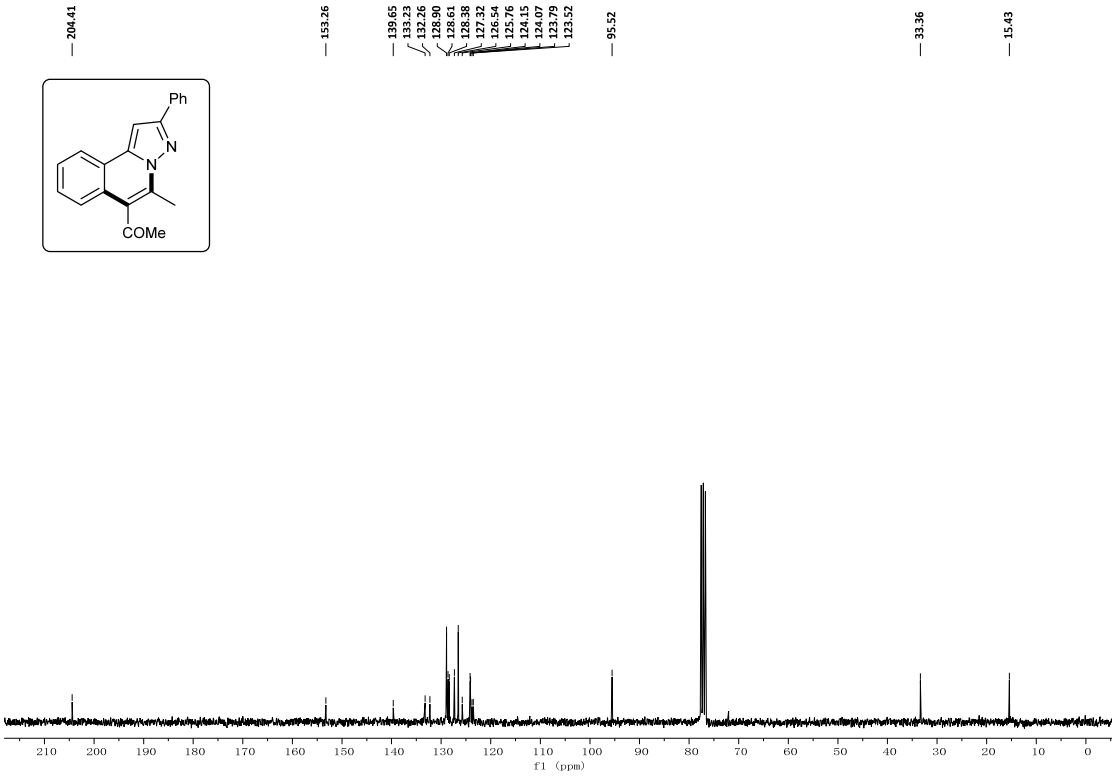
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3af



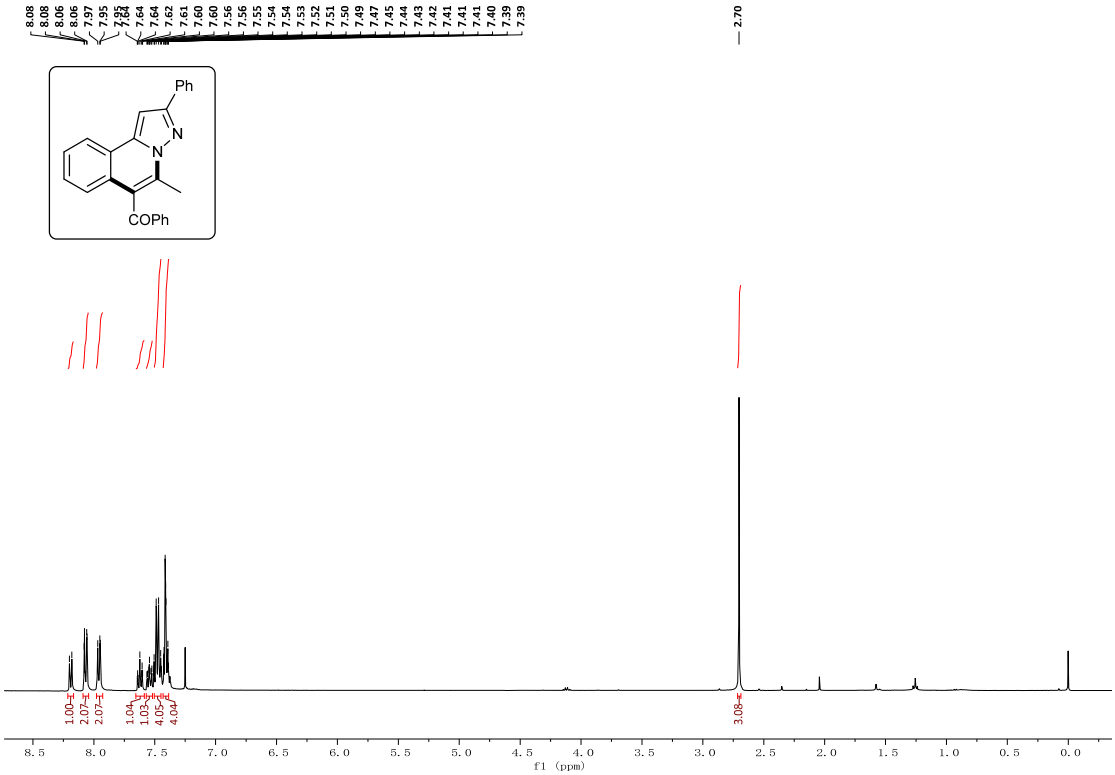
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ag



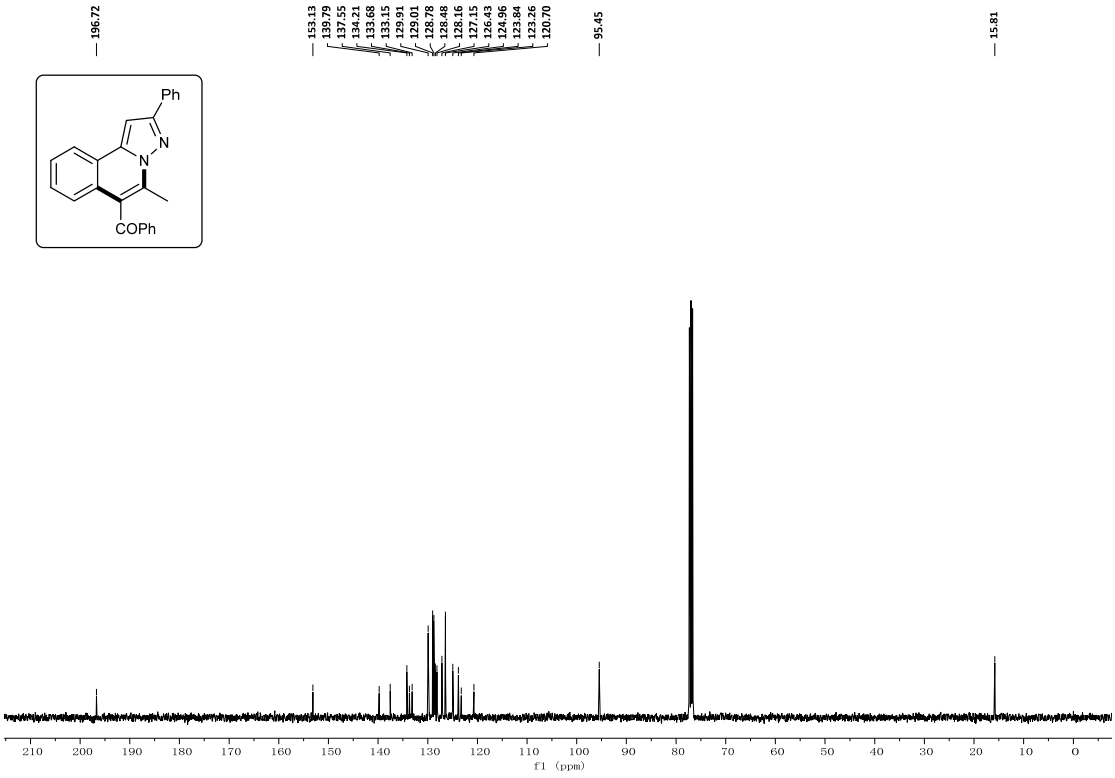
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ag



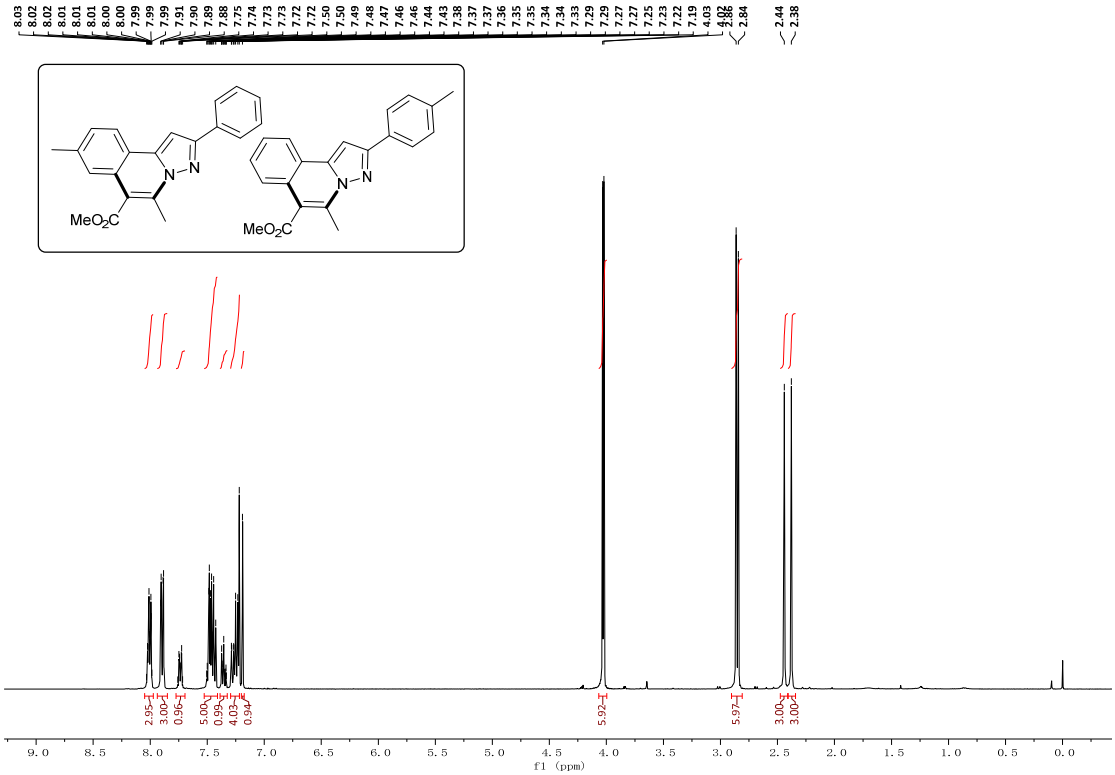
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ah



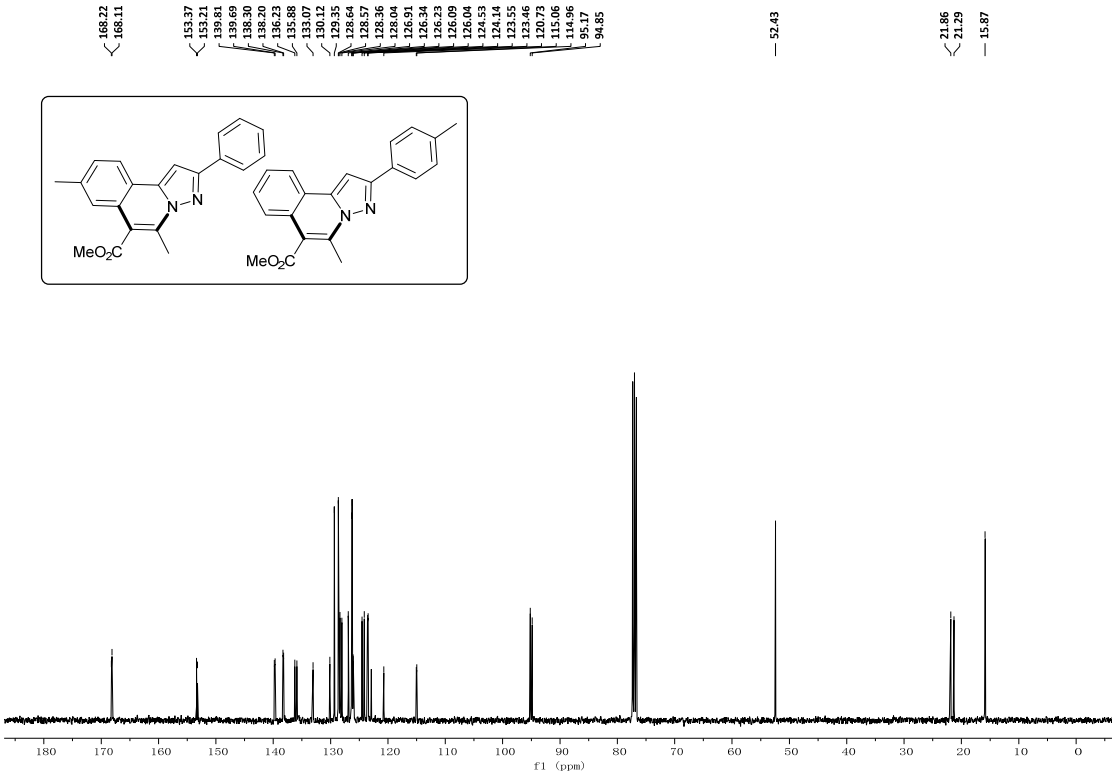
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ah



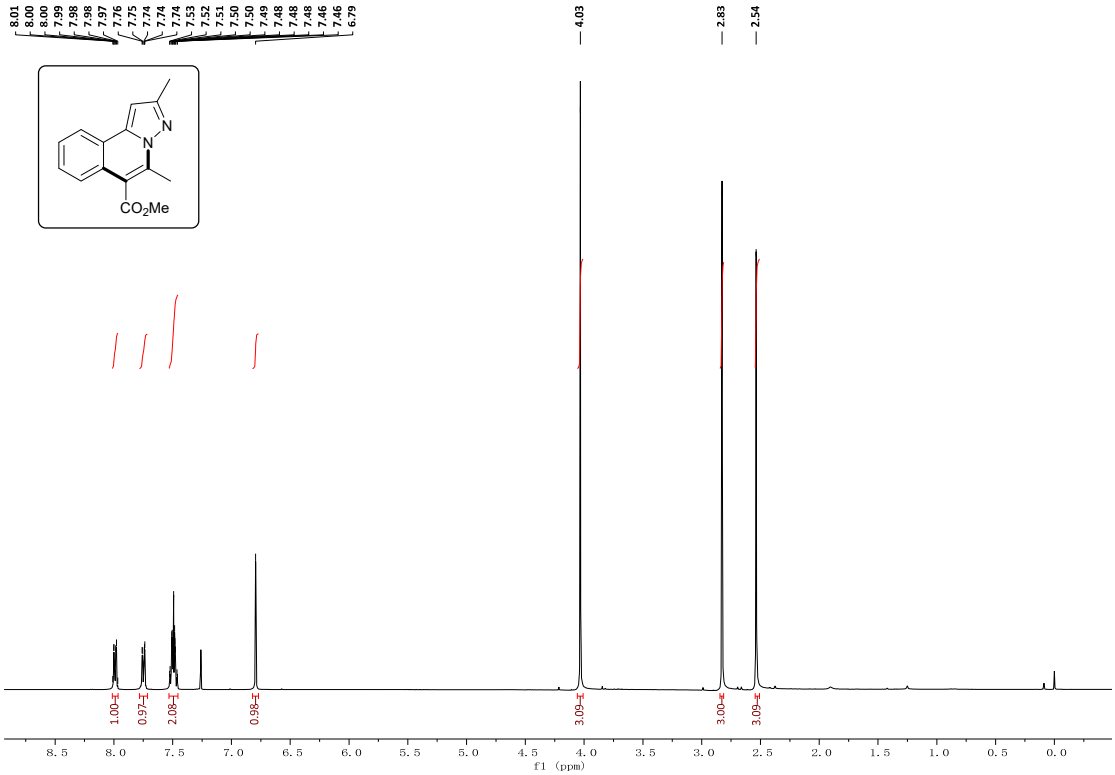
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3bb+3bb`



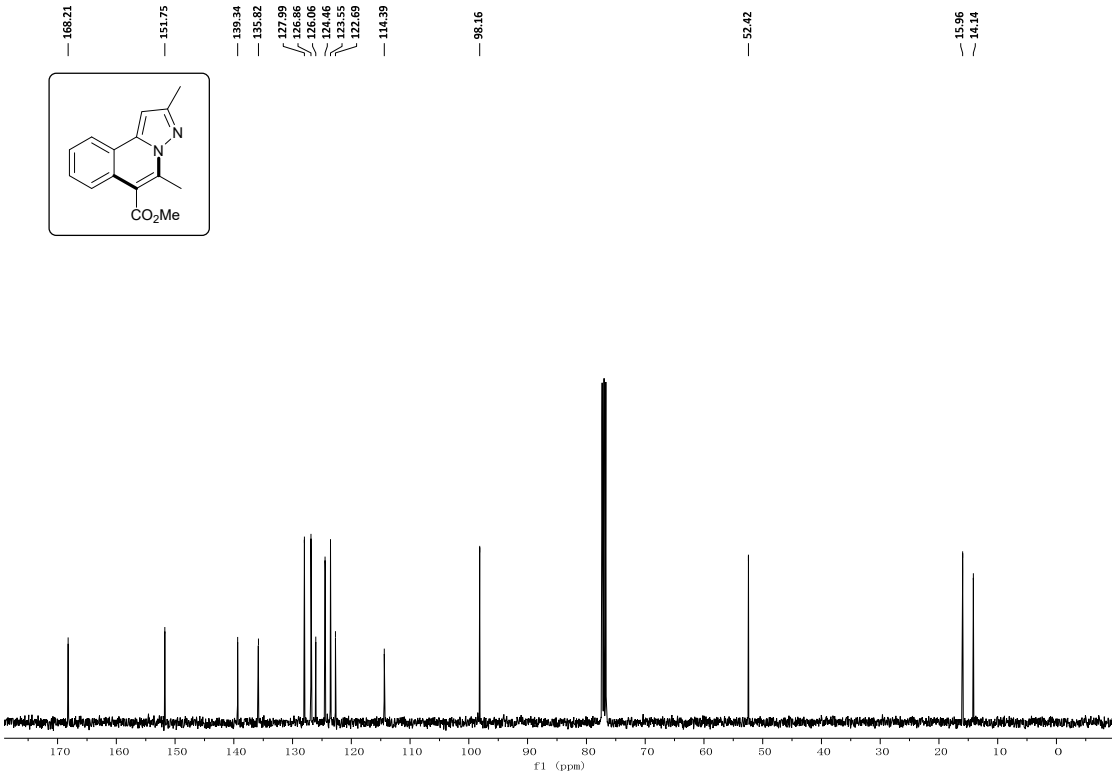
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3bb+3bb`



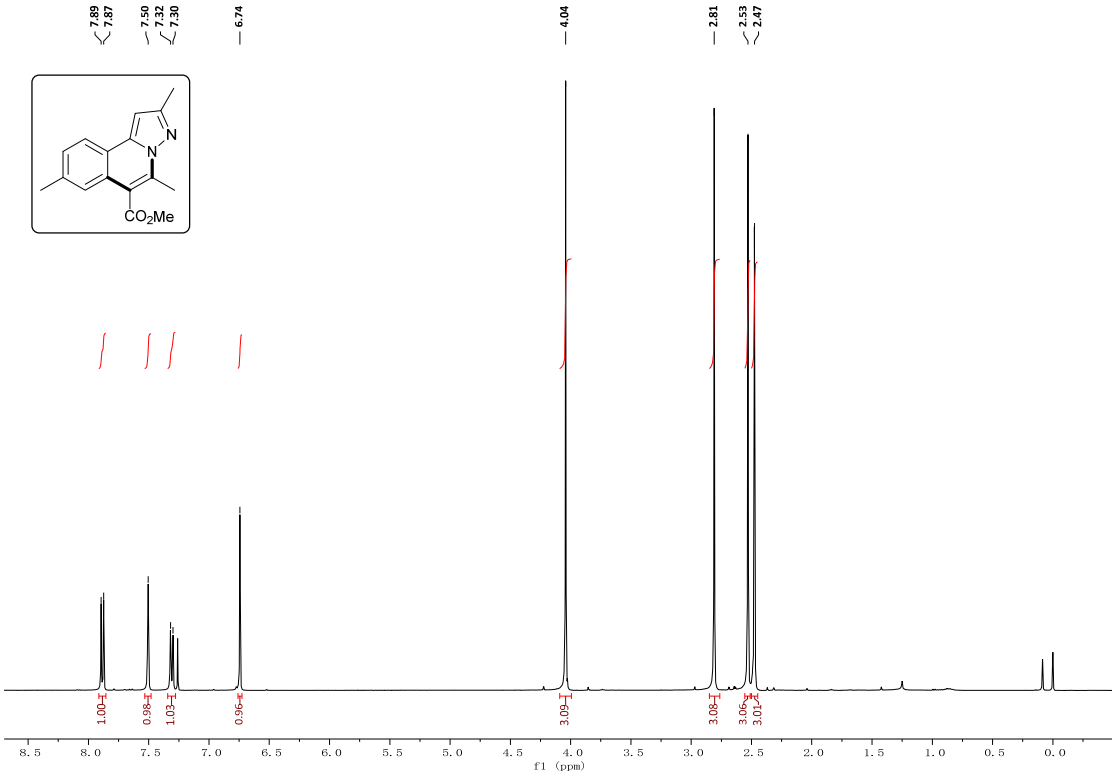
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3cb



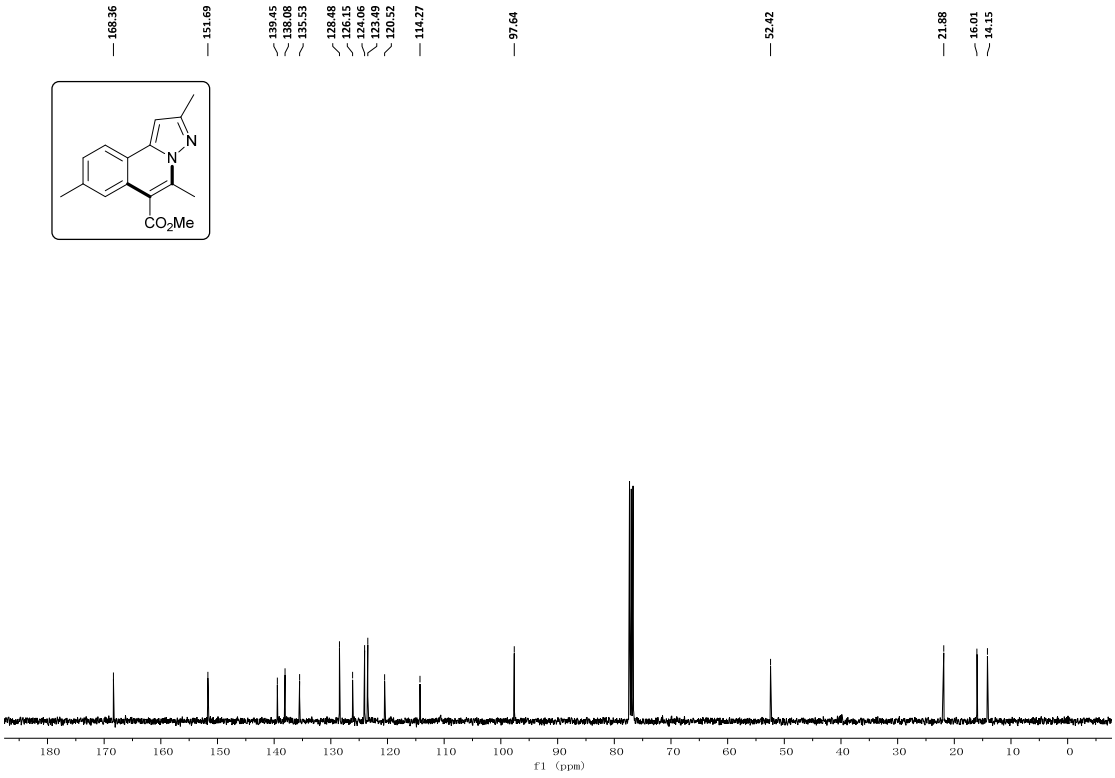
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3cb



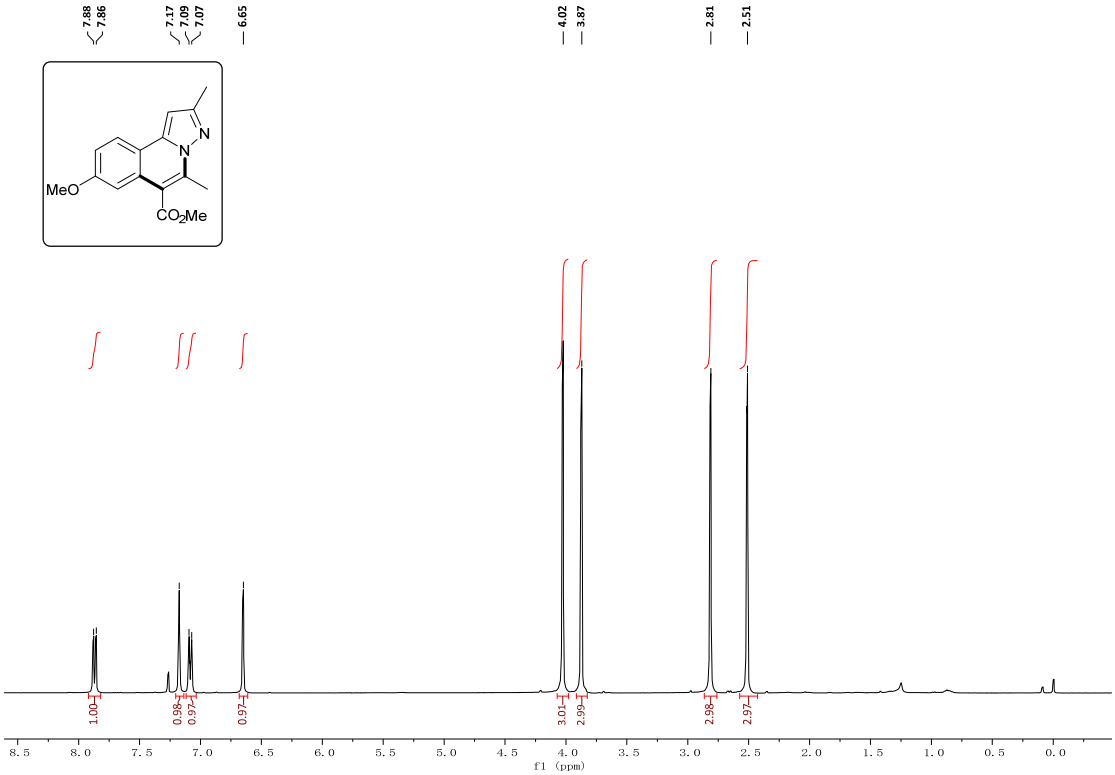
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3db



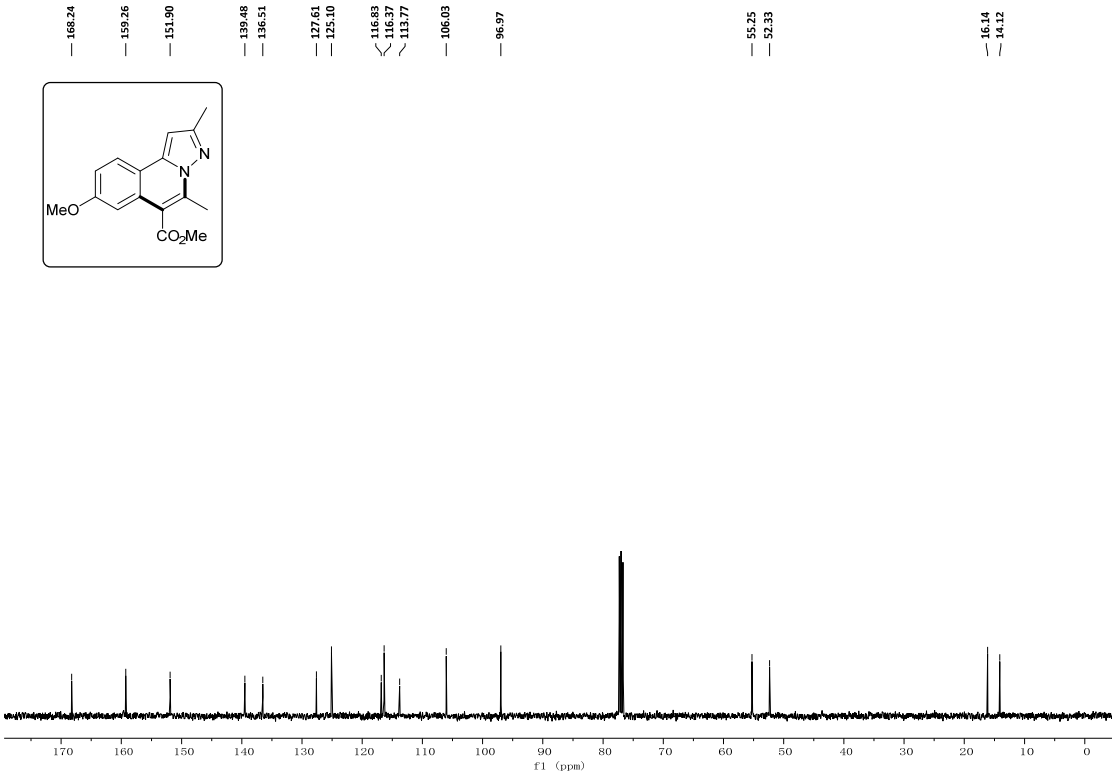
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3db



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3eb



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3eb



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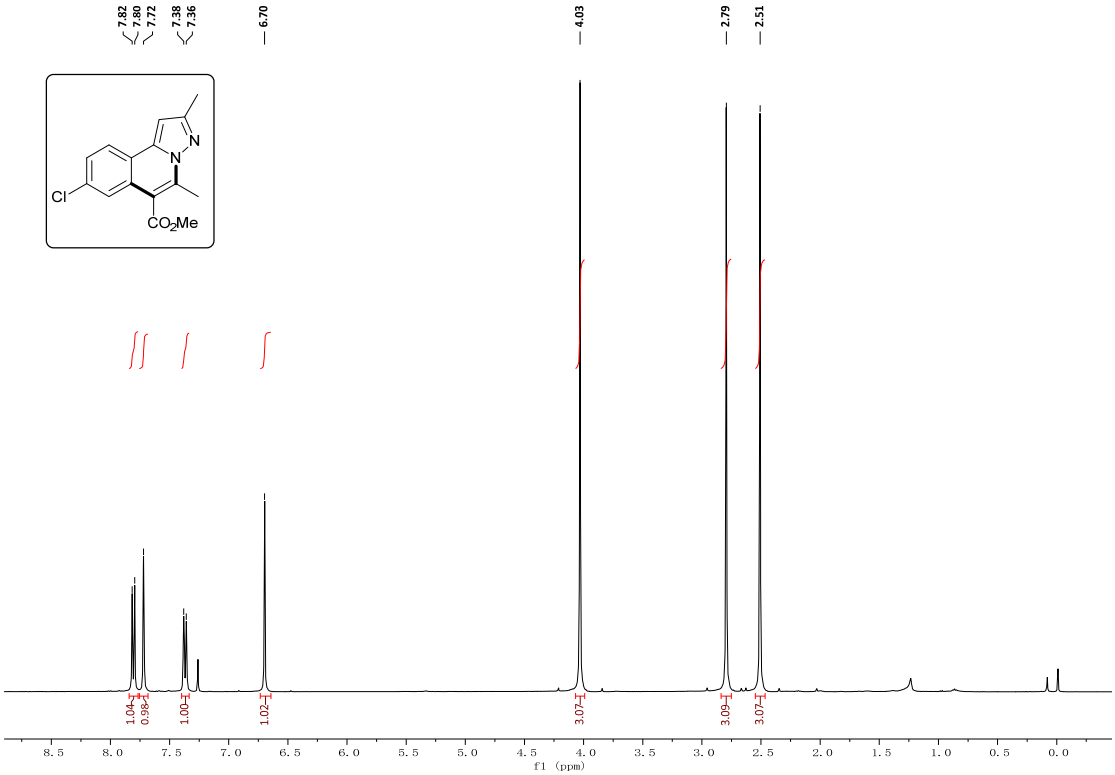
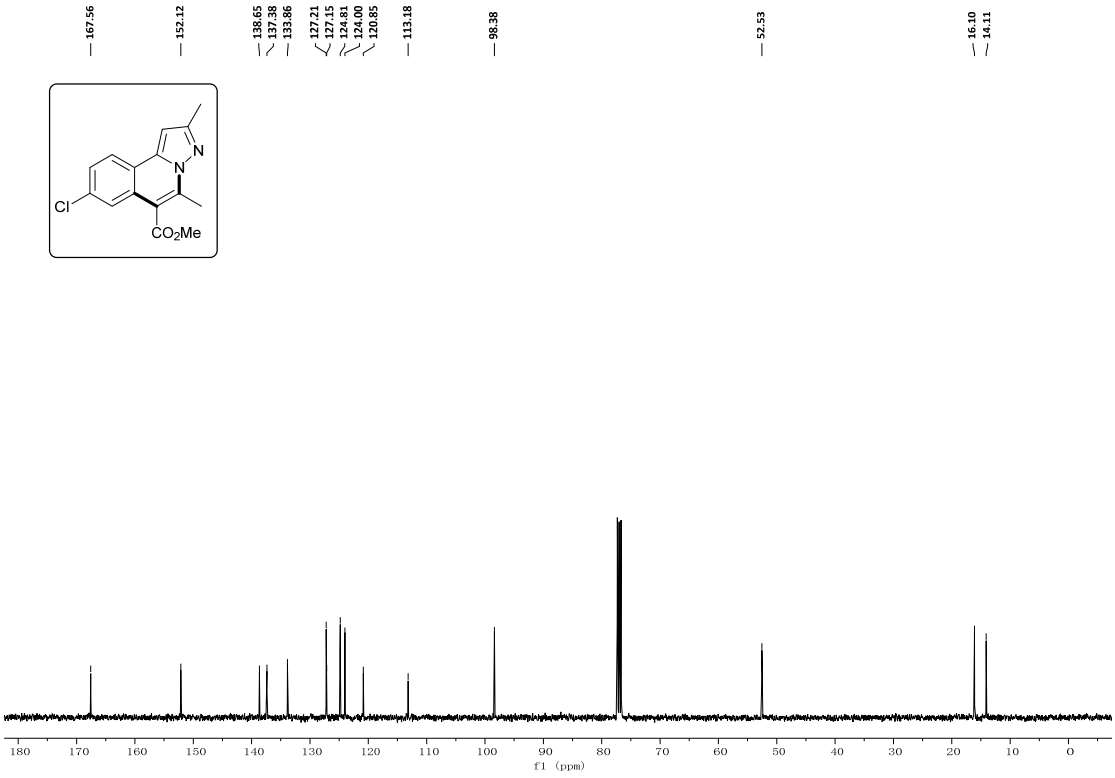
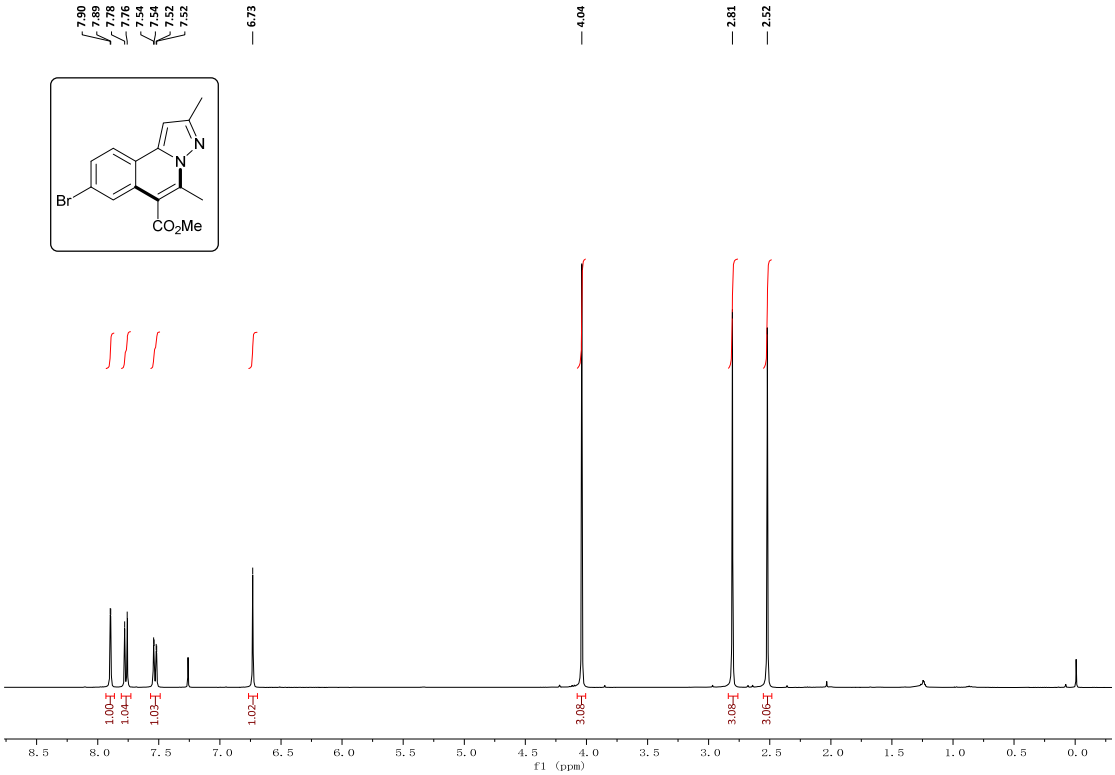


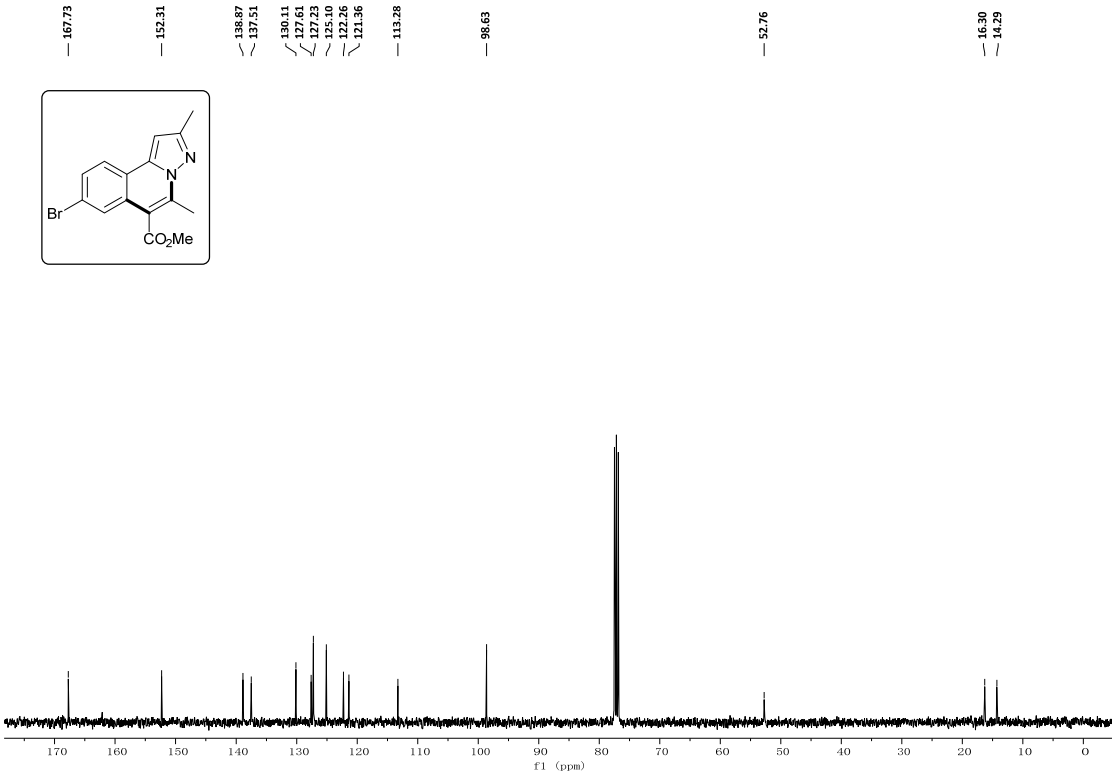
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3fb



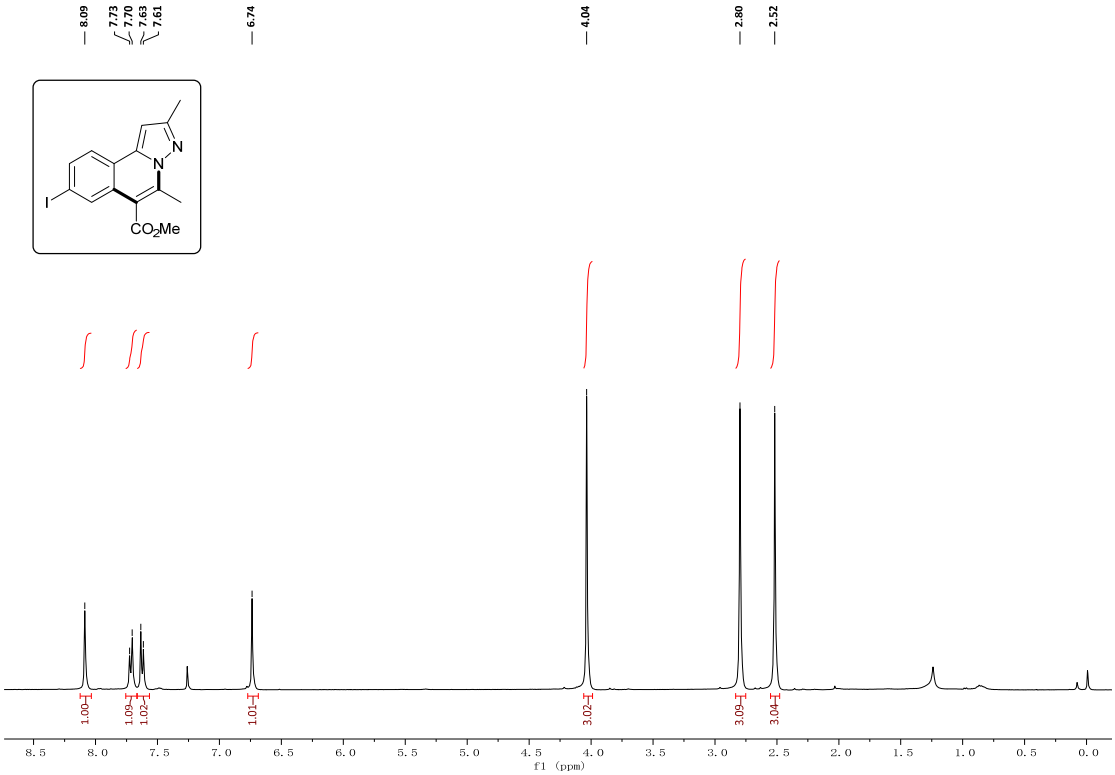
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3gb



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3gb



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3hb



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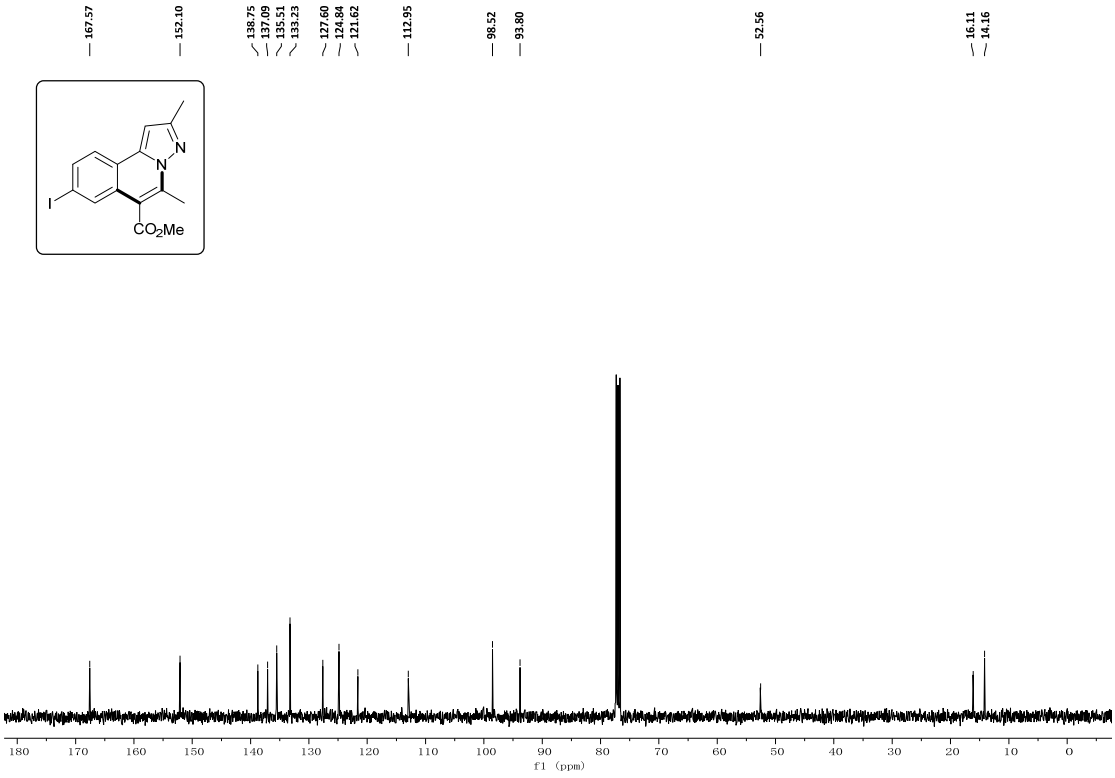
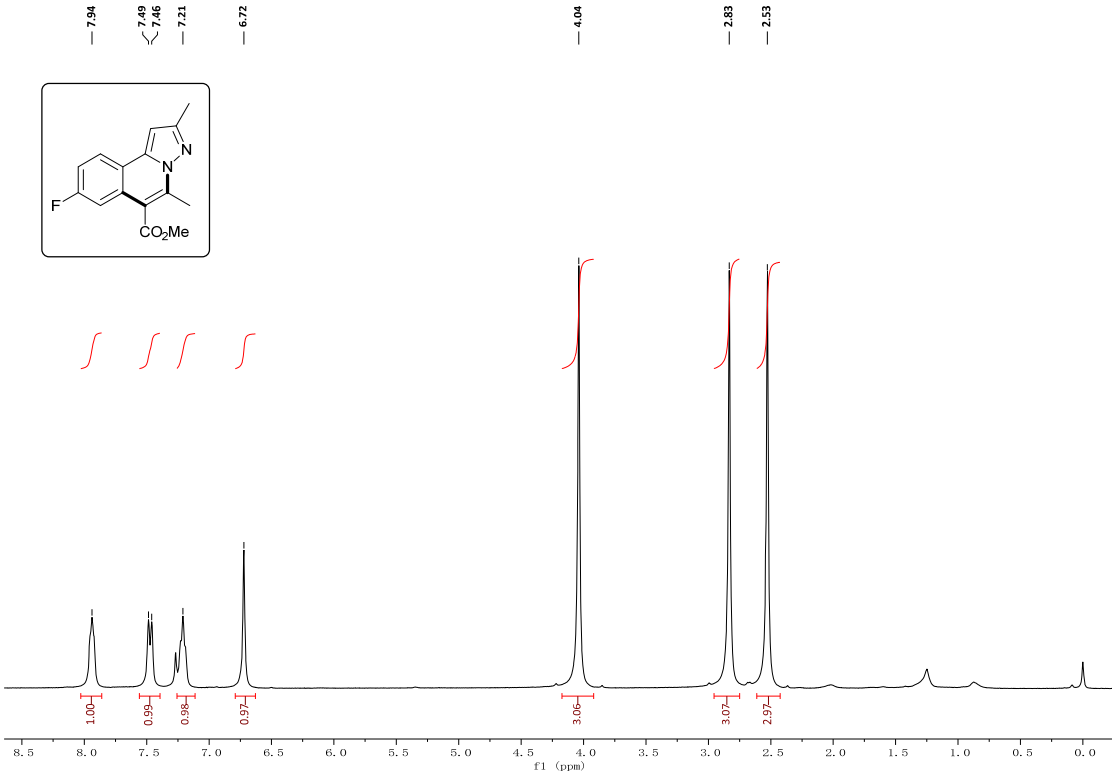
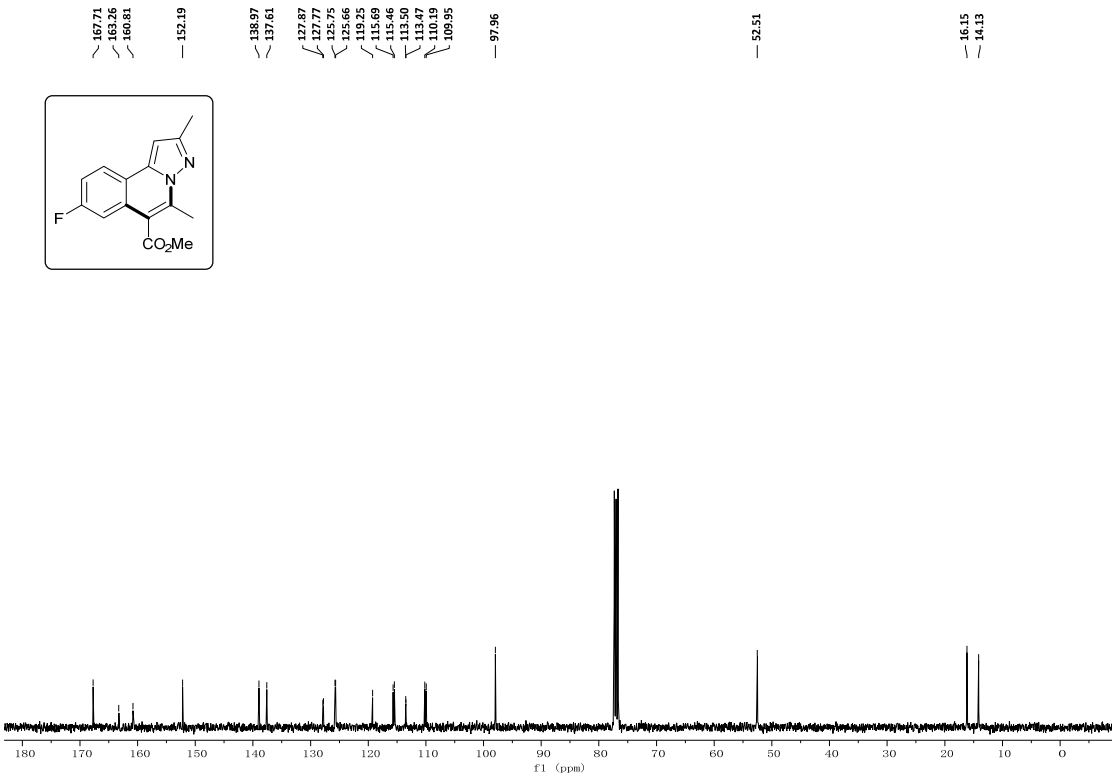


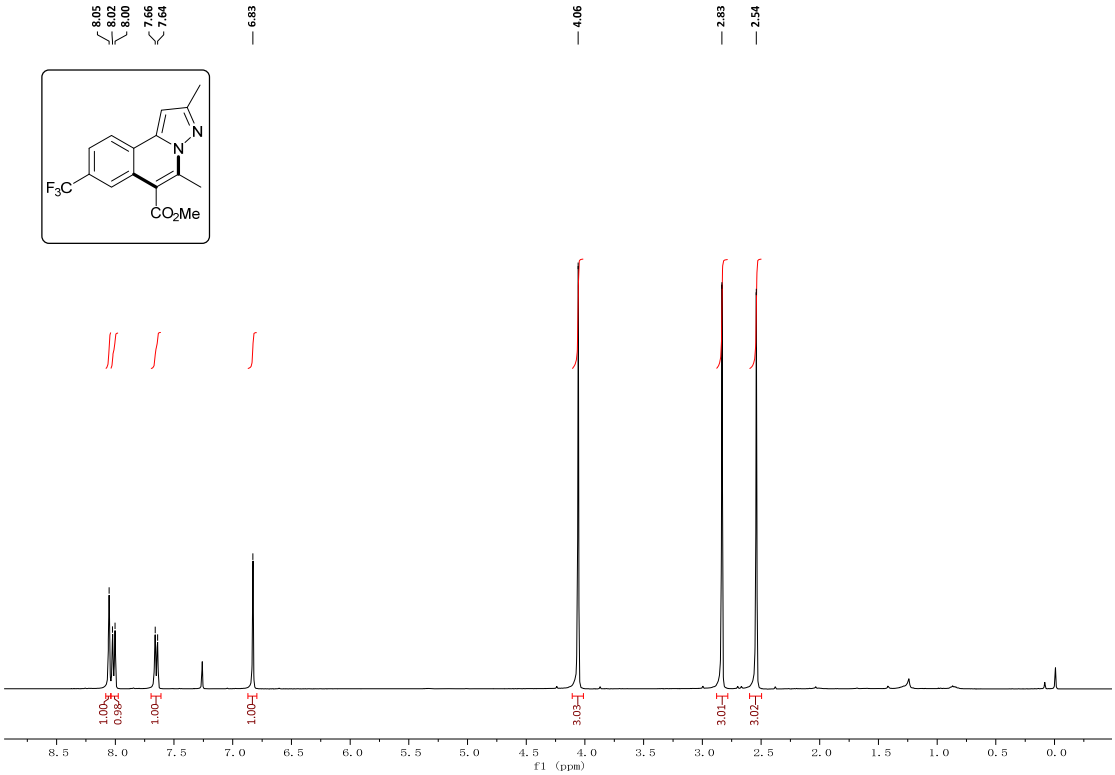
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ib



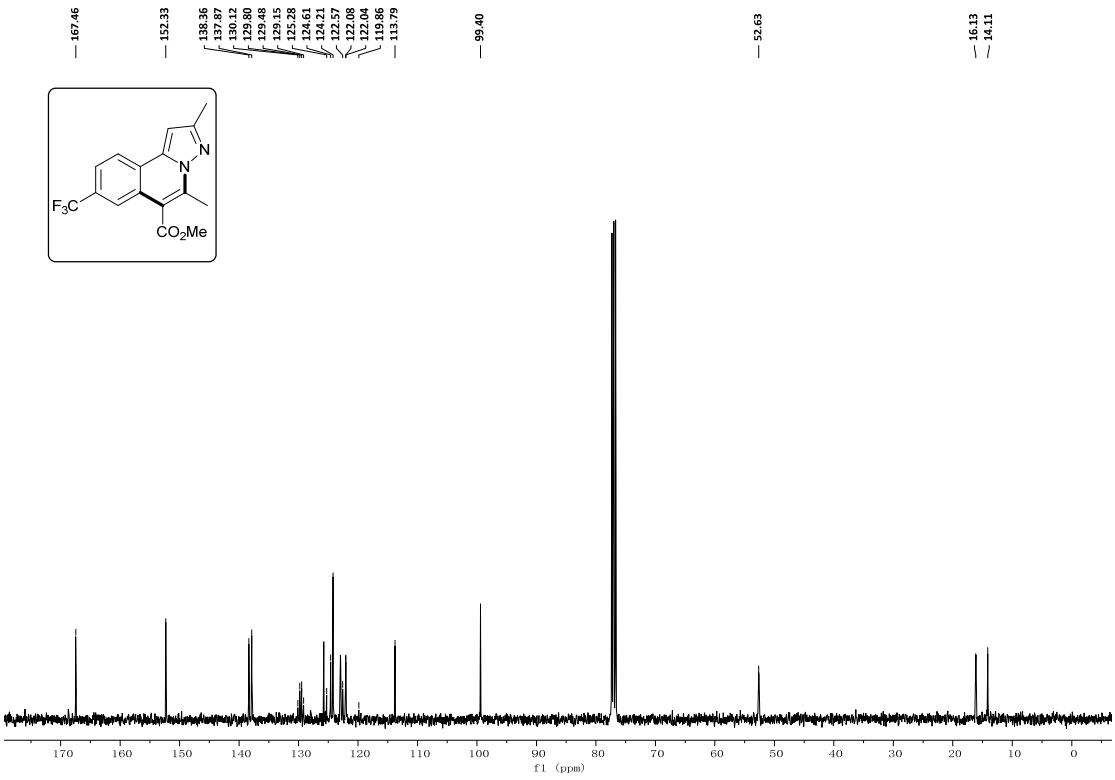
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ib



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3jb



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3jb



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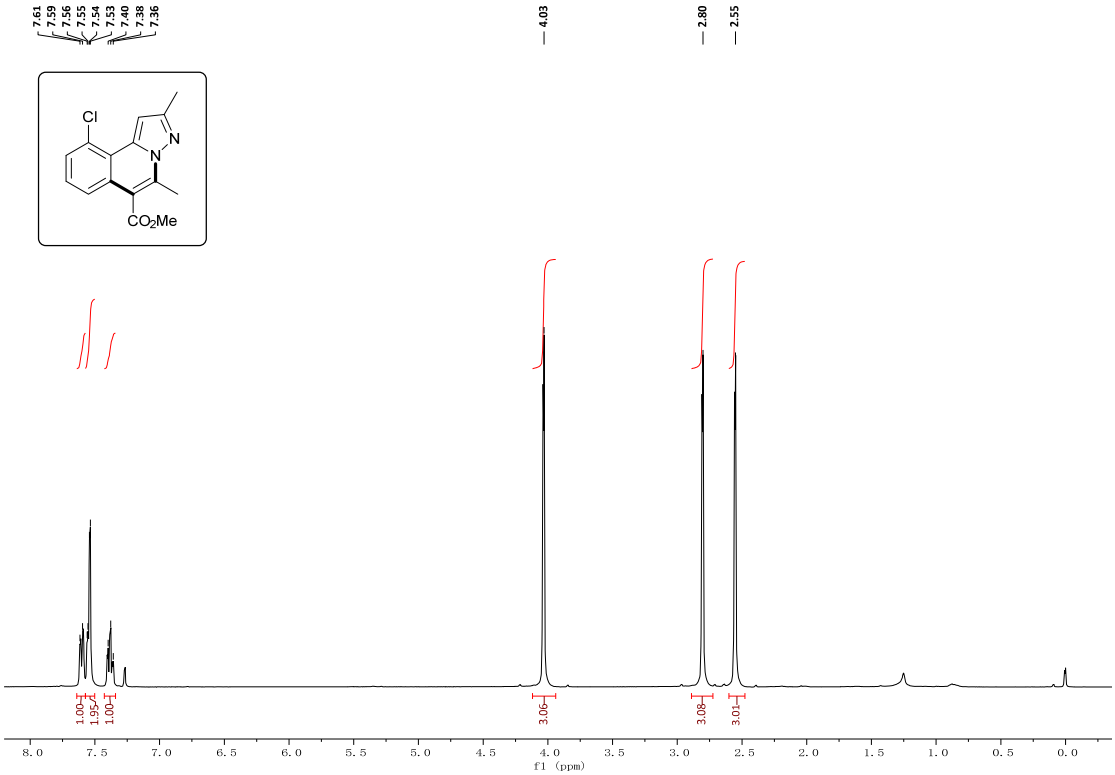
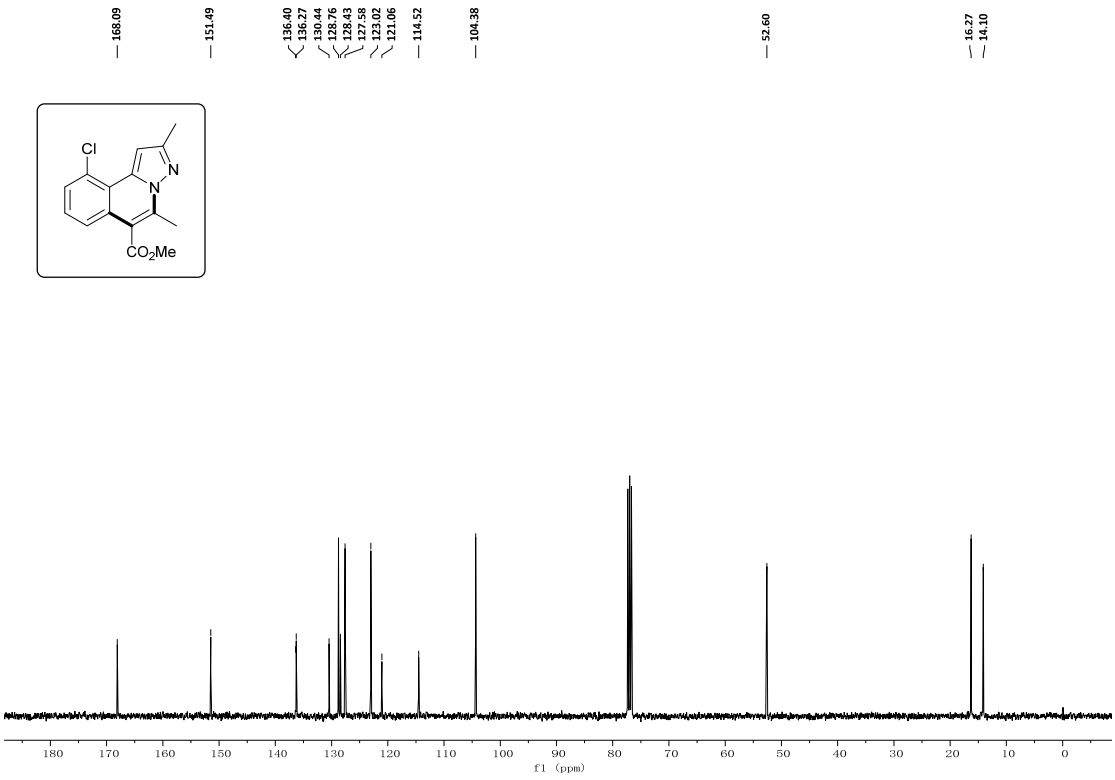
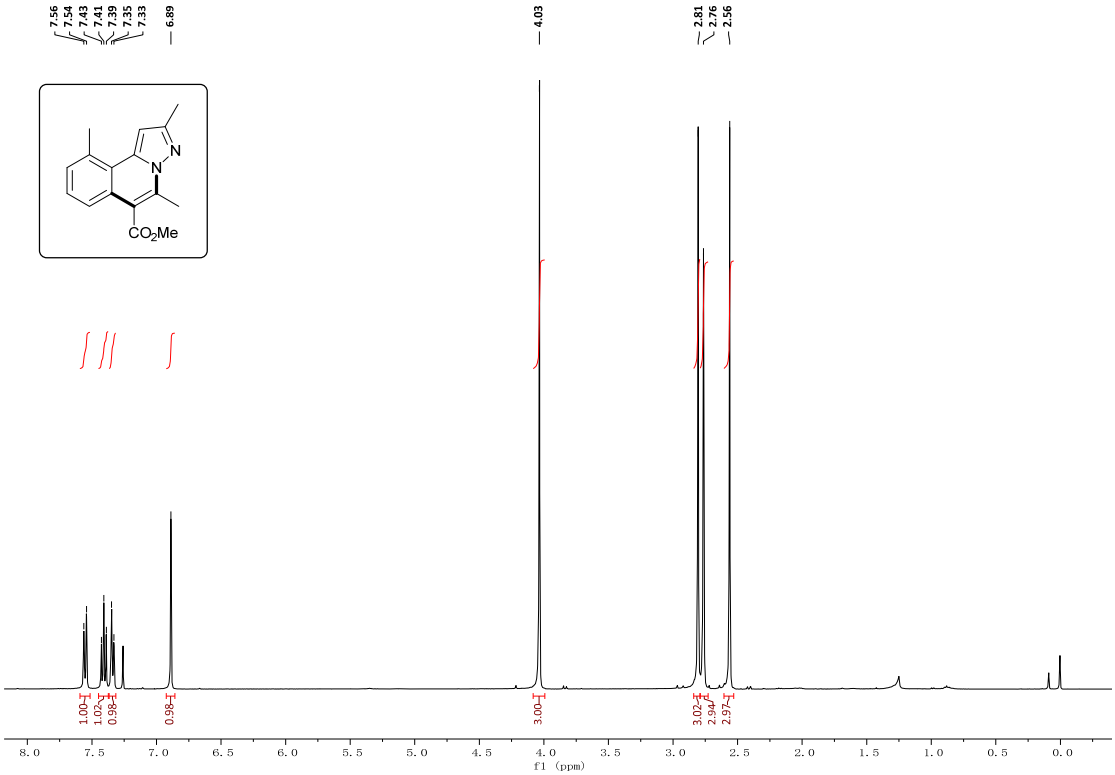


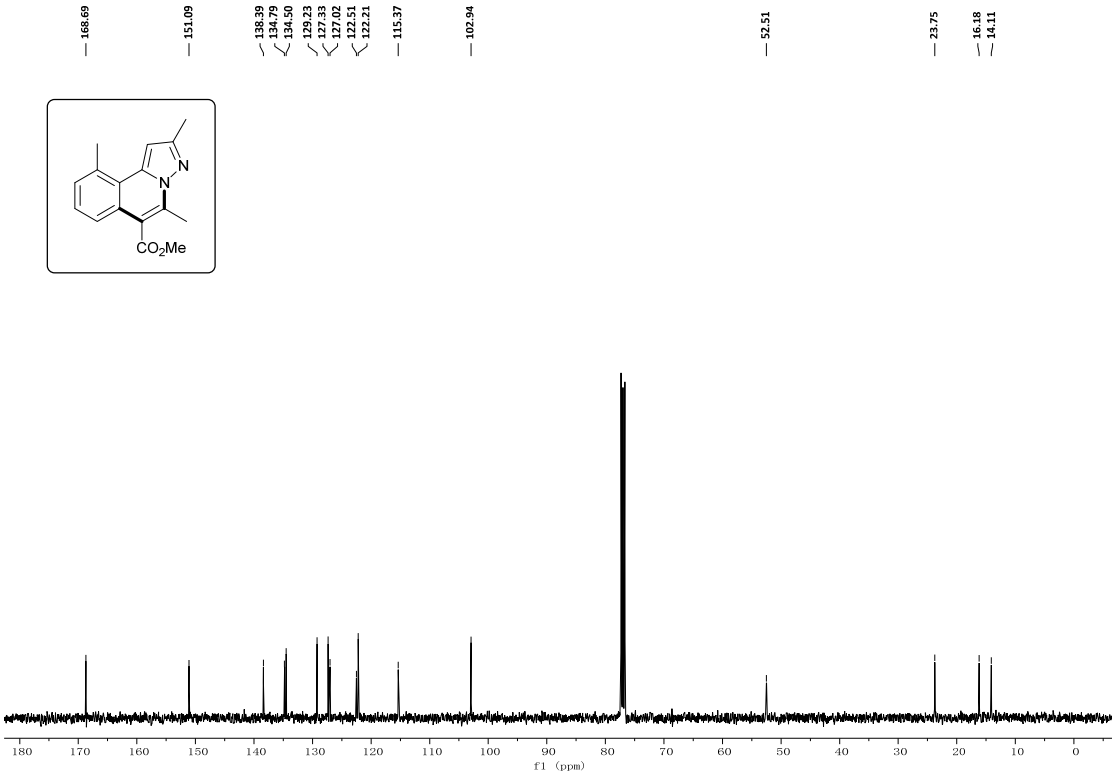
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3kb



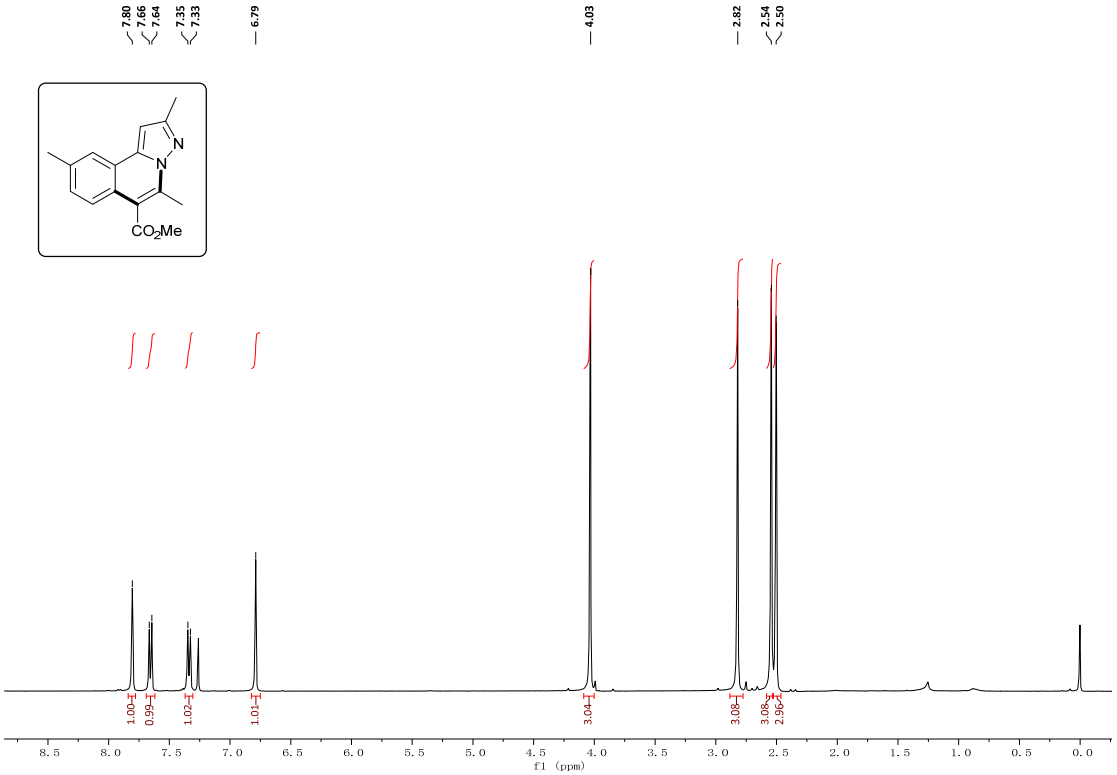
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3lb



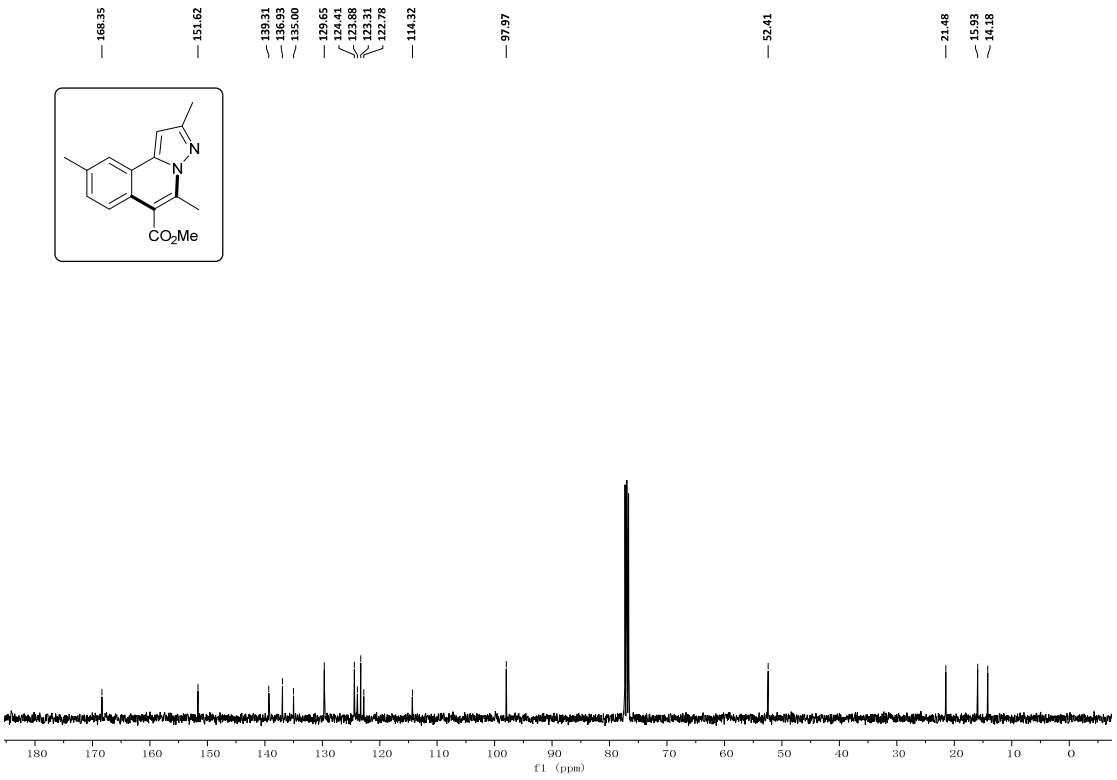
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3lb



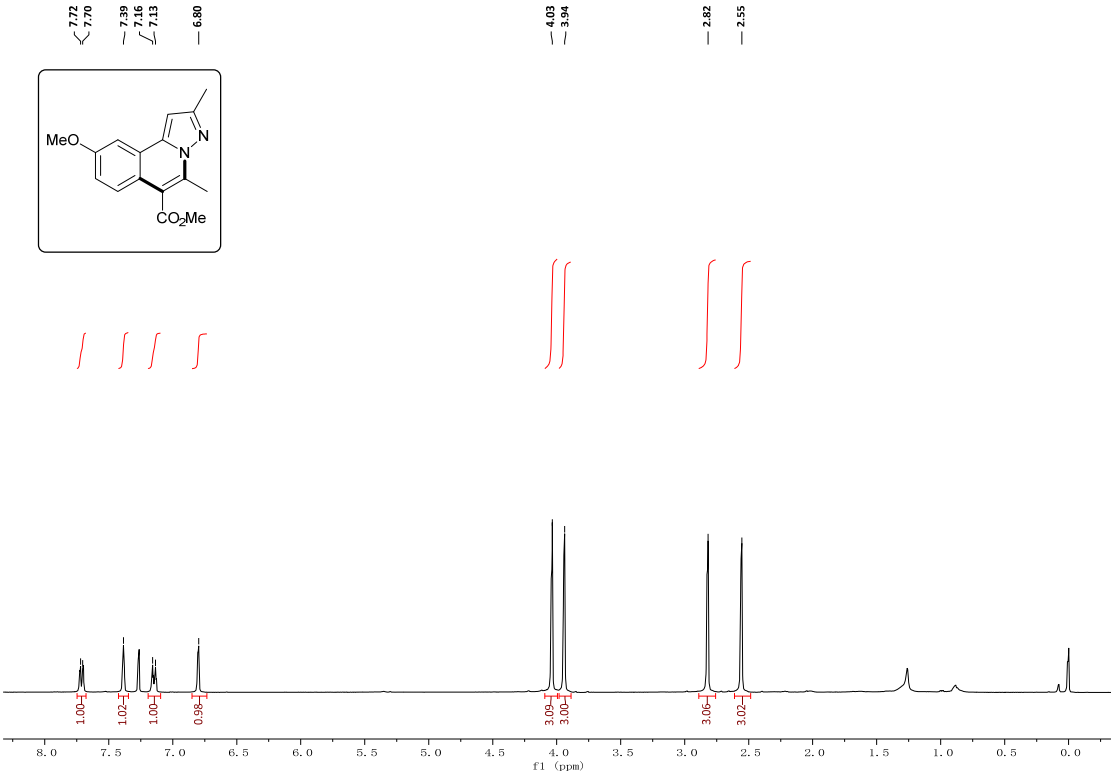
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3mb



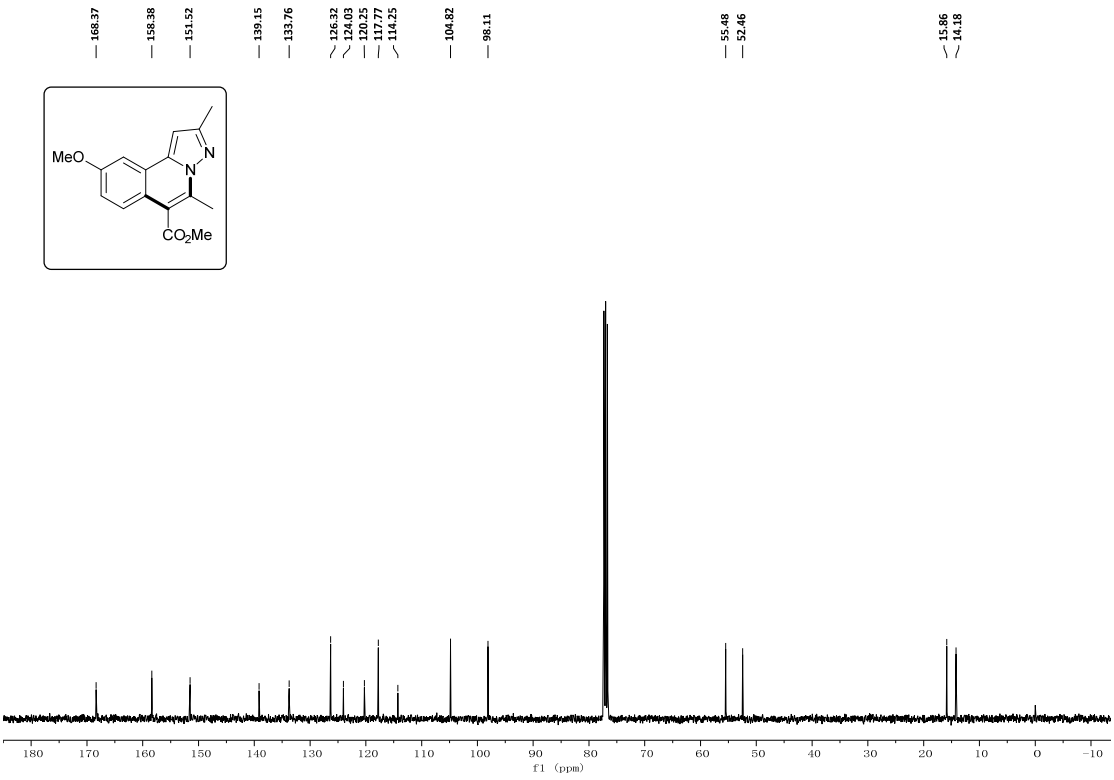
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3mb



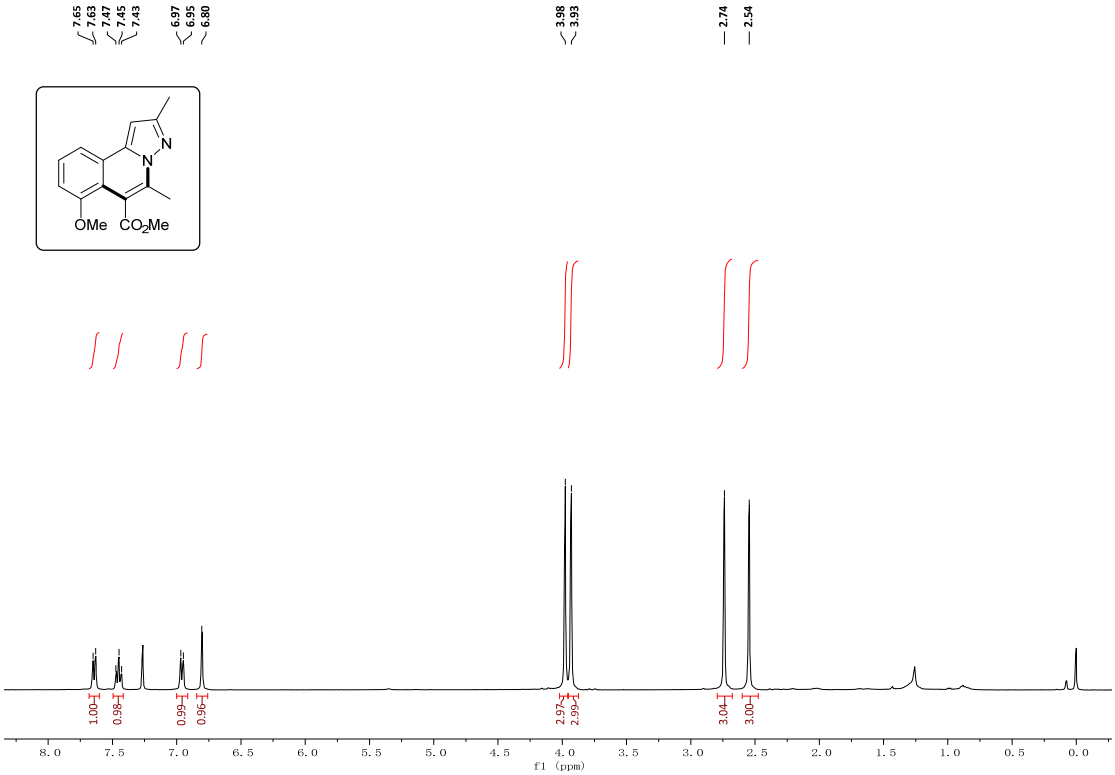
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3nb



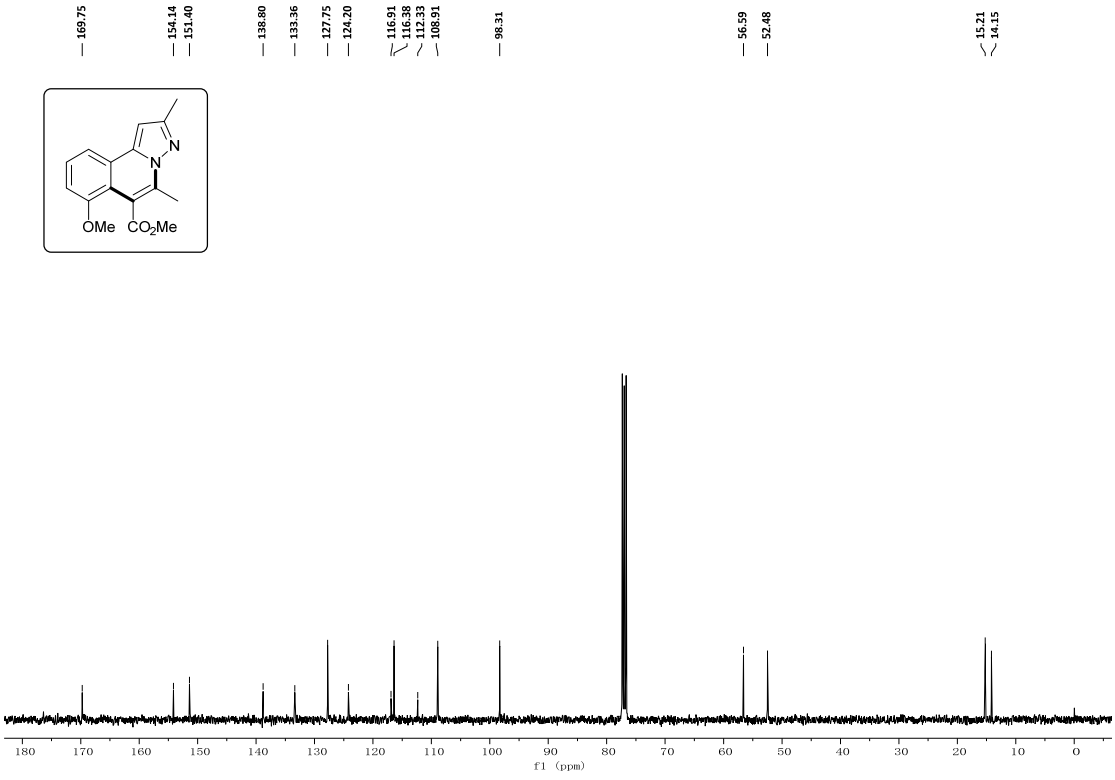
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3nb



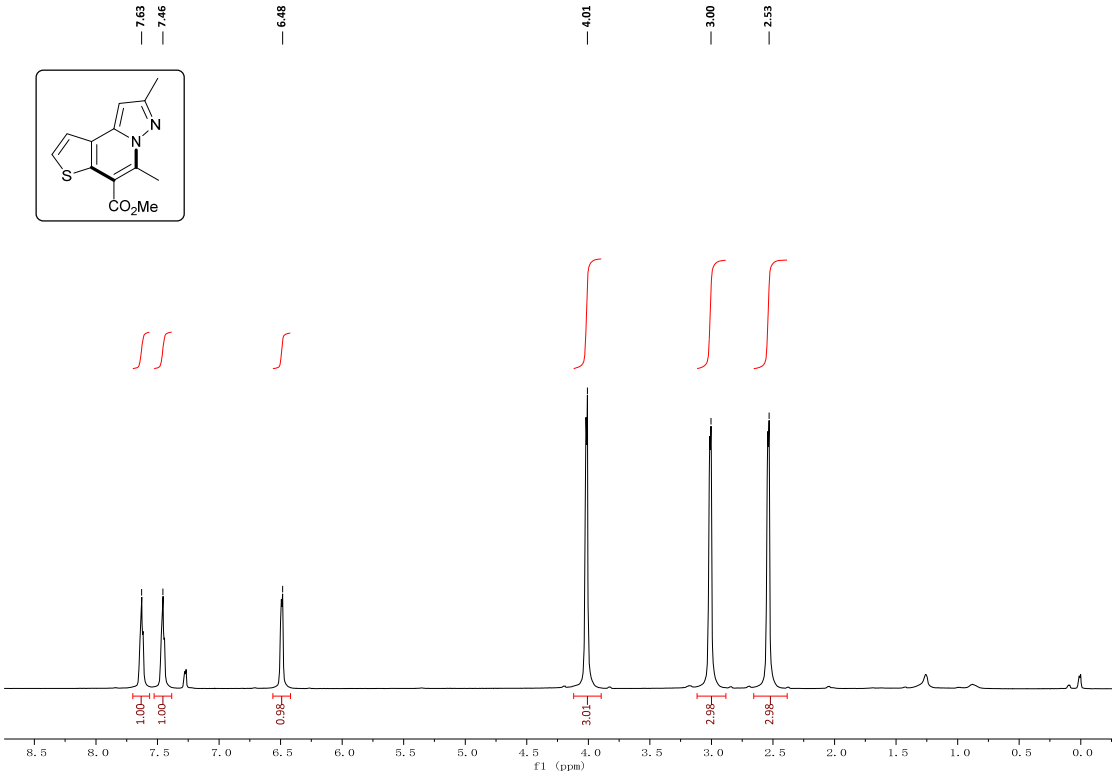
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3nb`



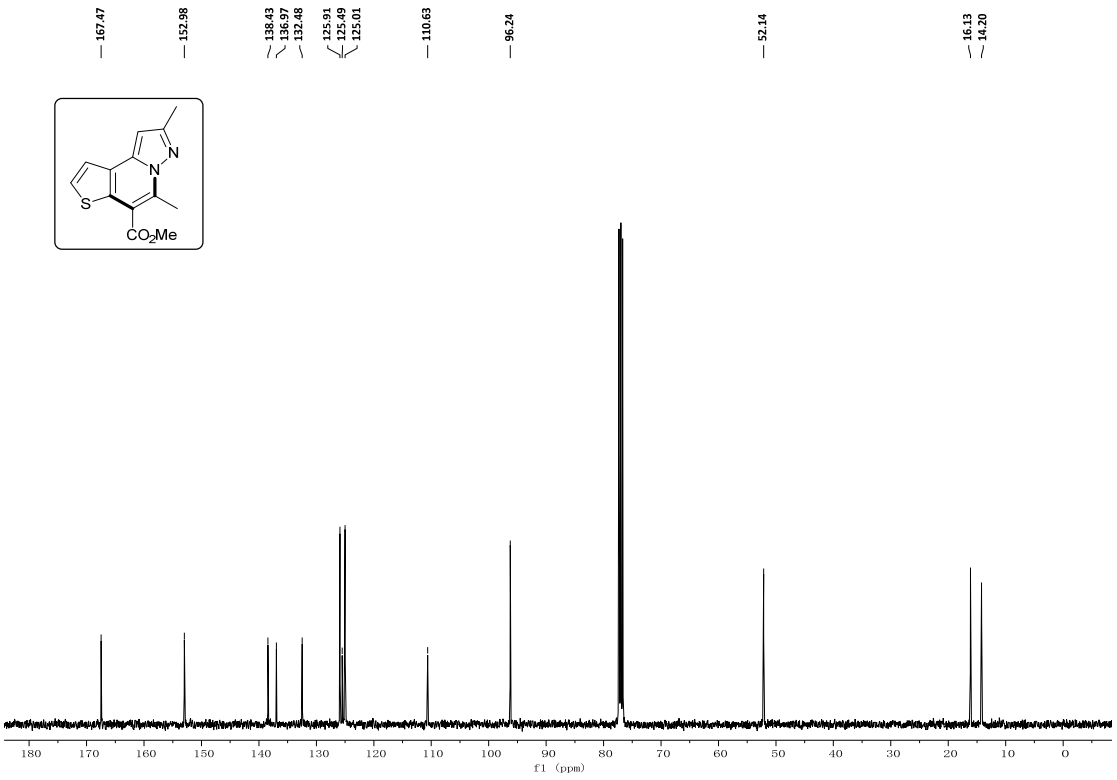
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3nb`



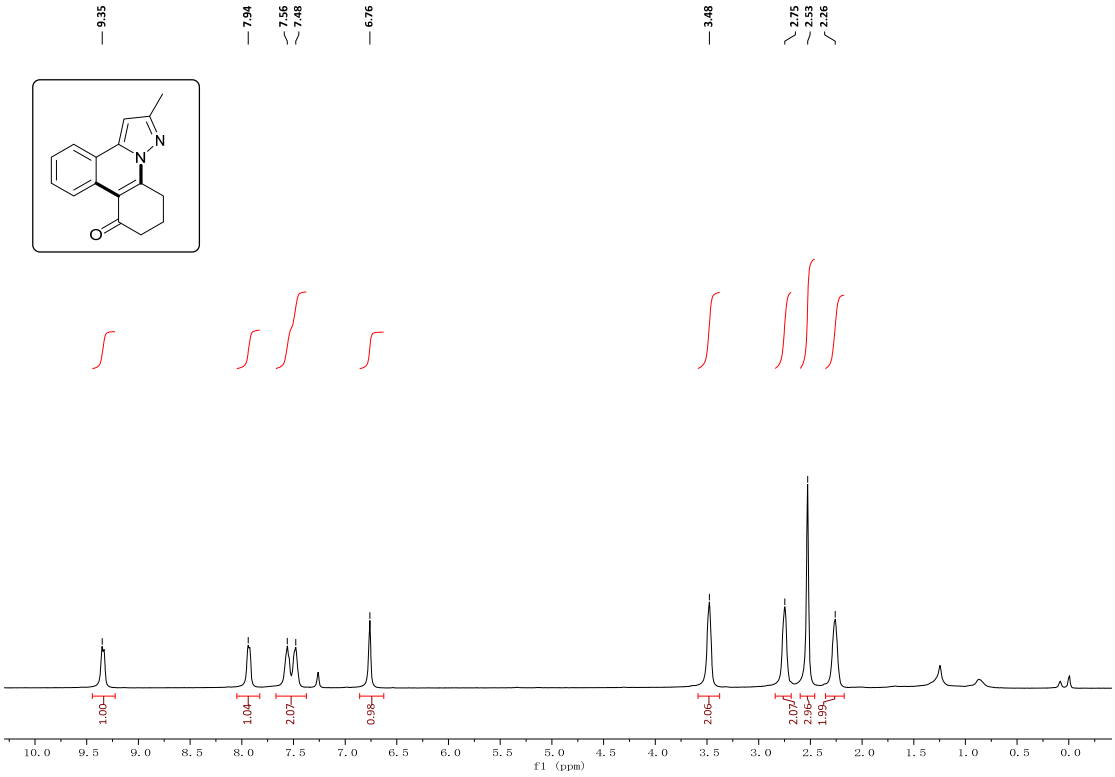
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ob



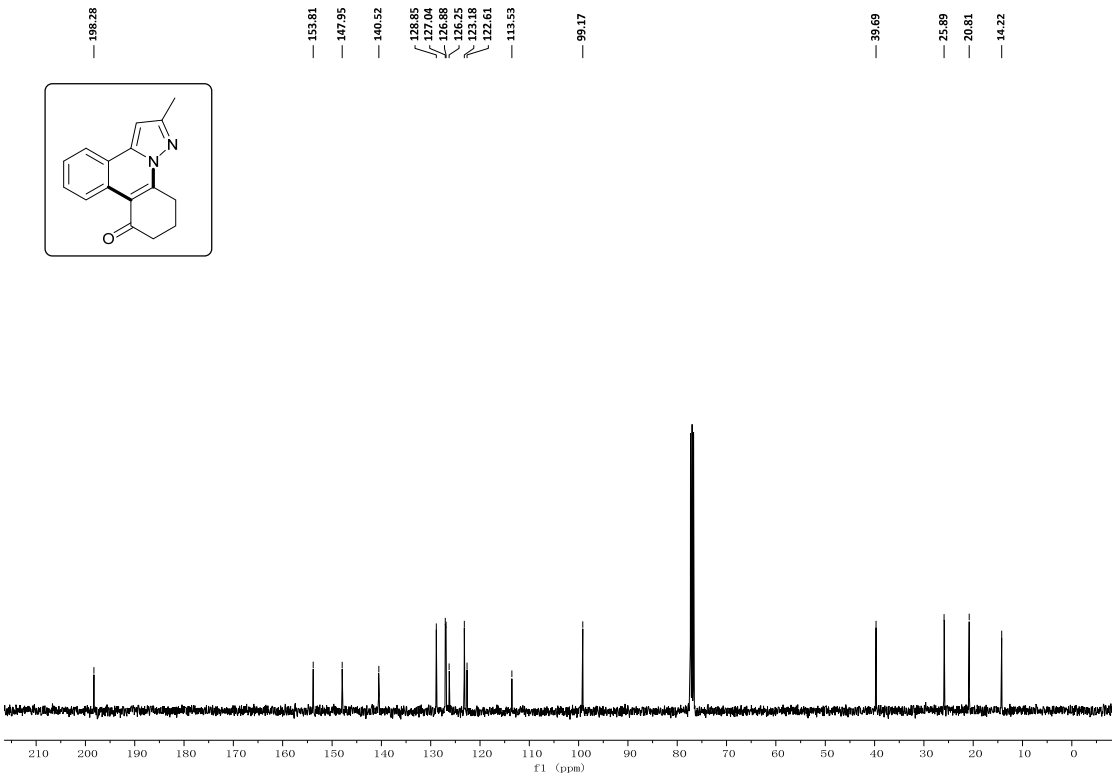
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ob



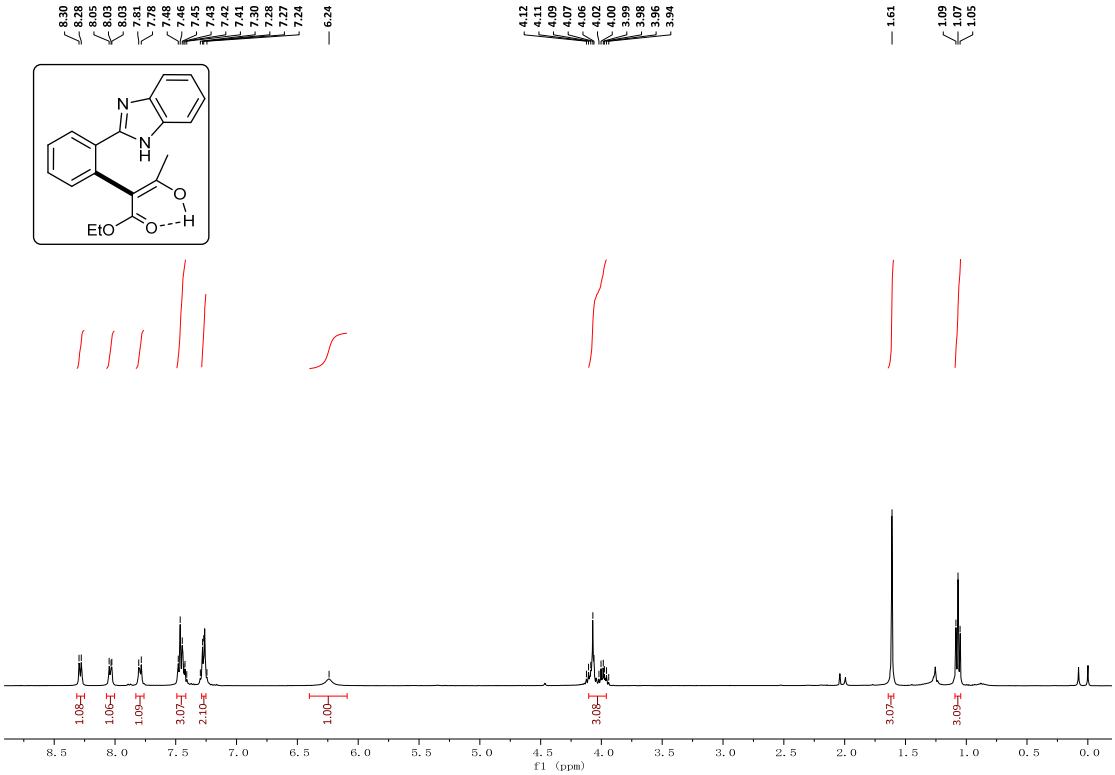
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ci



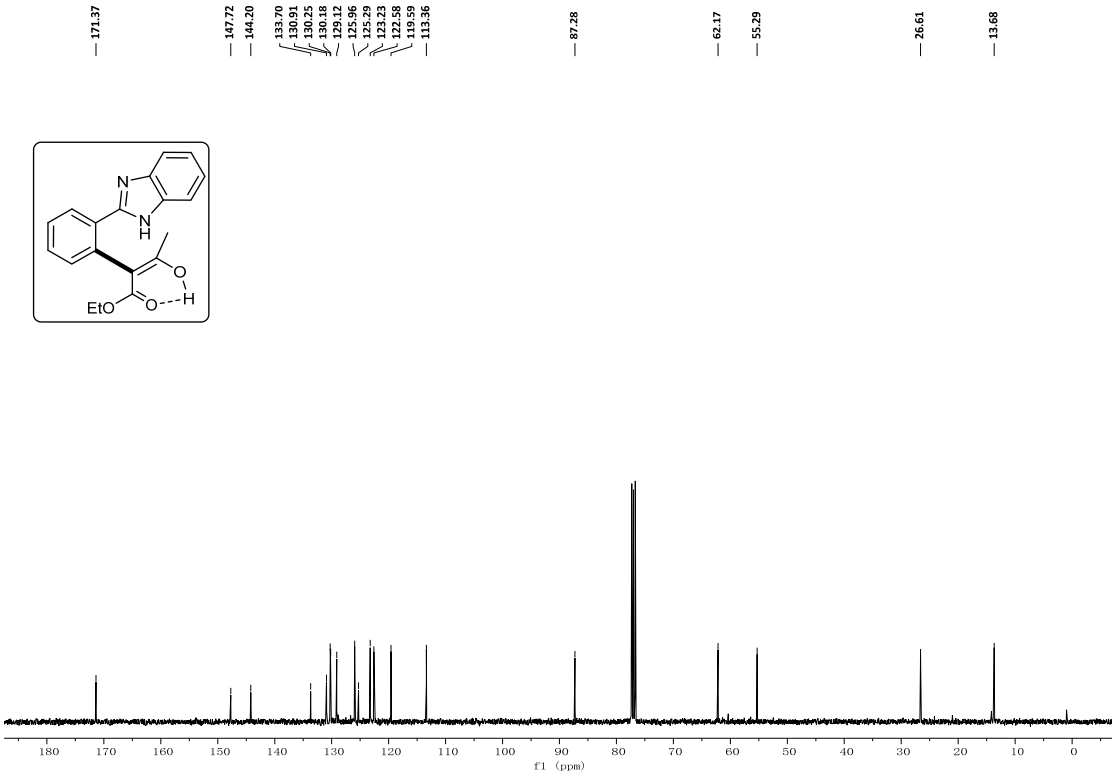
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ci



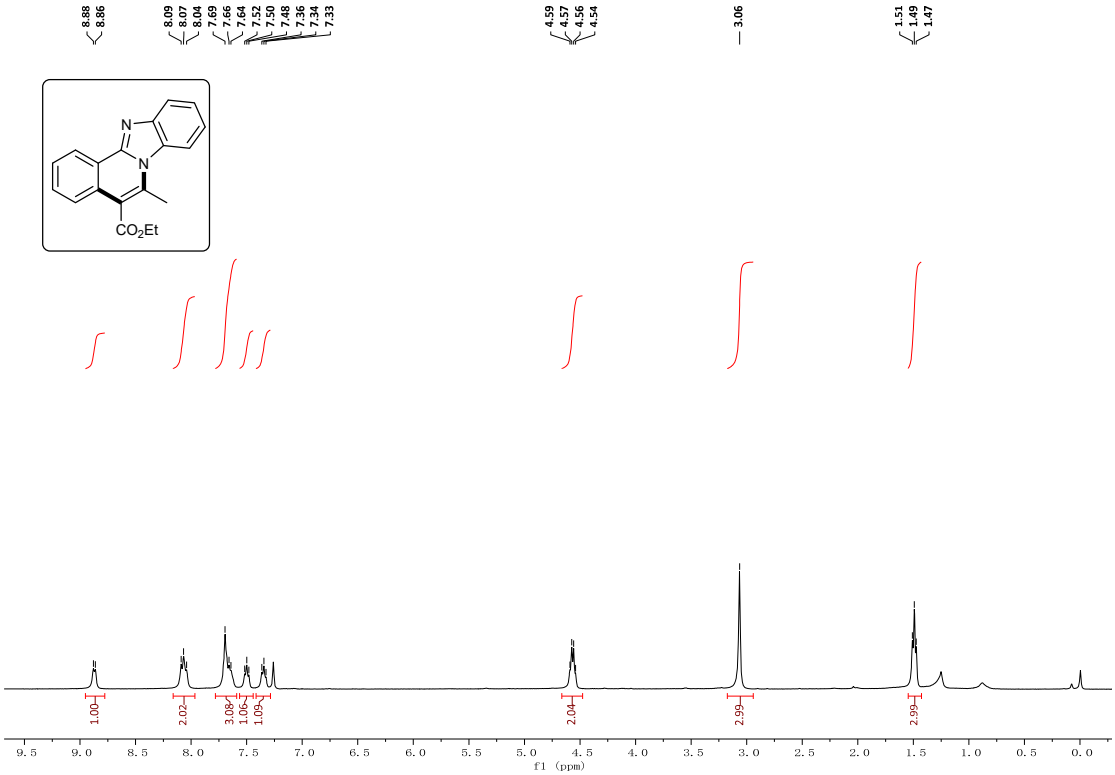
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4a



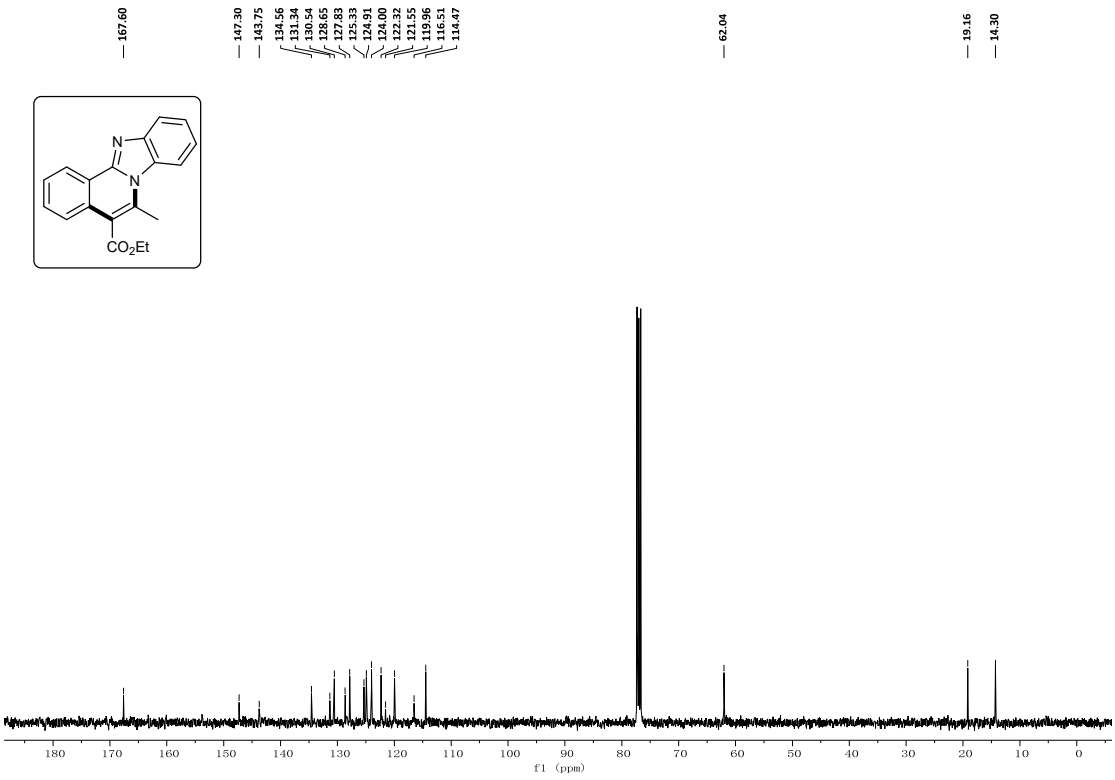
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 4a



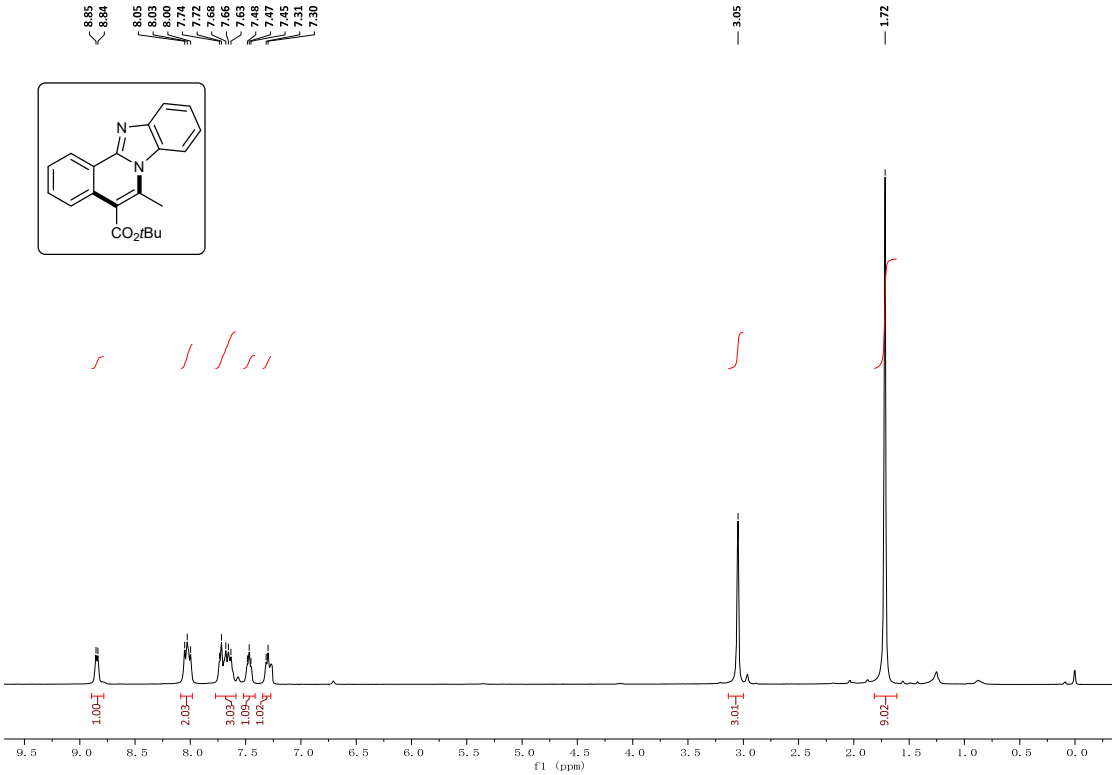
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3pa



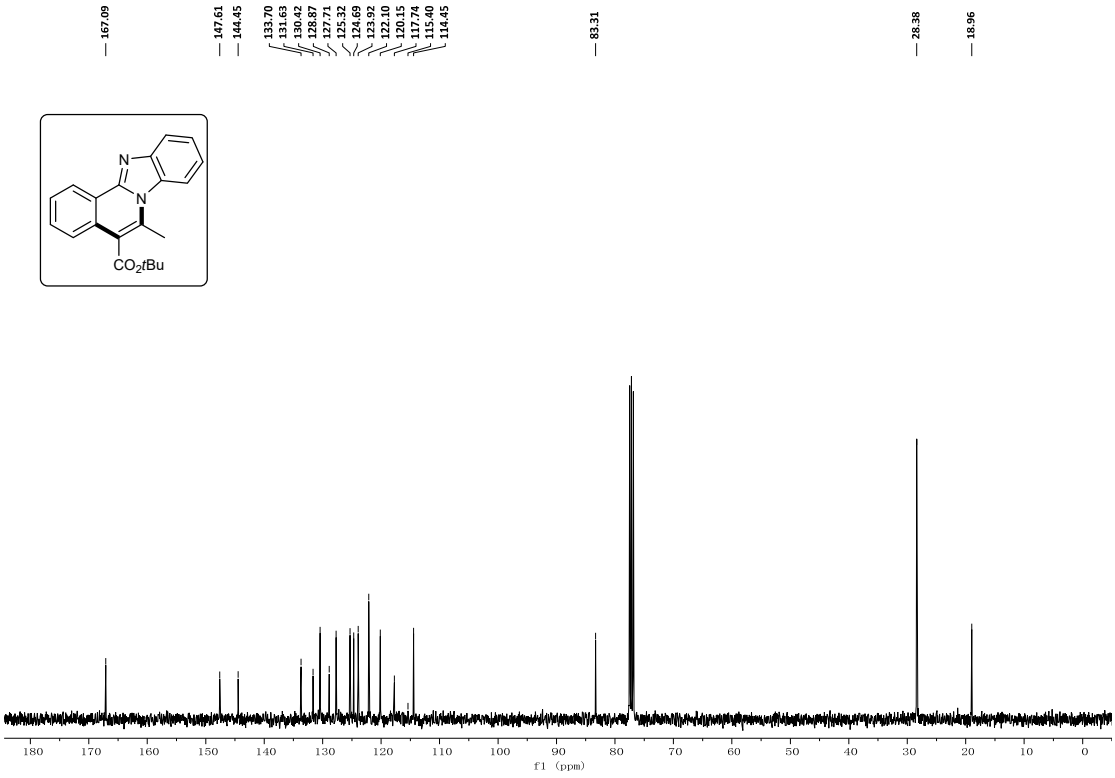
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3pa



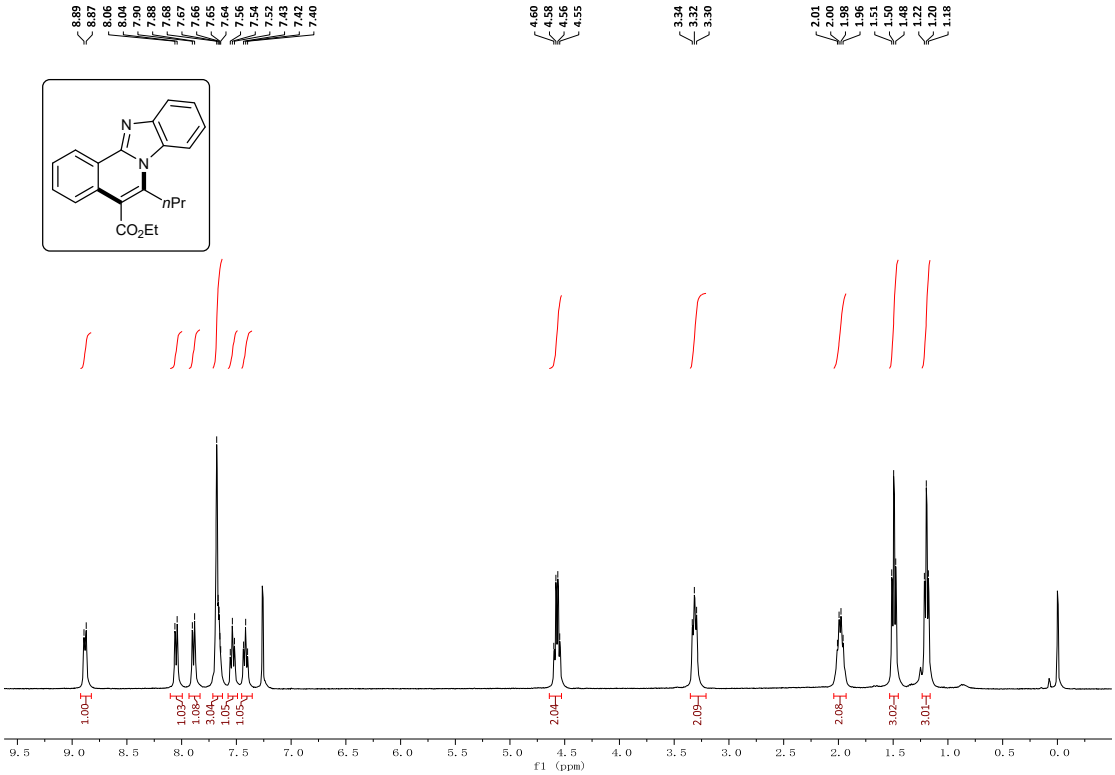
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3pc



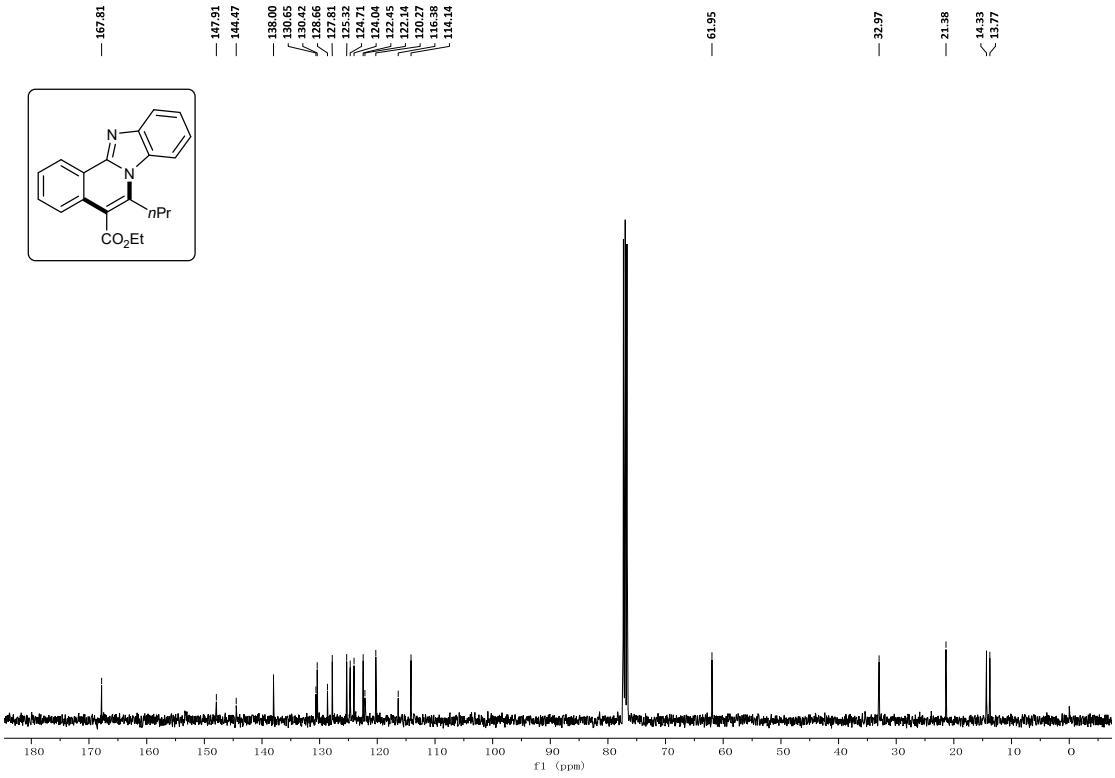
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3pc



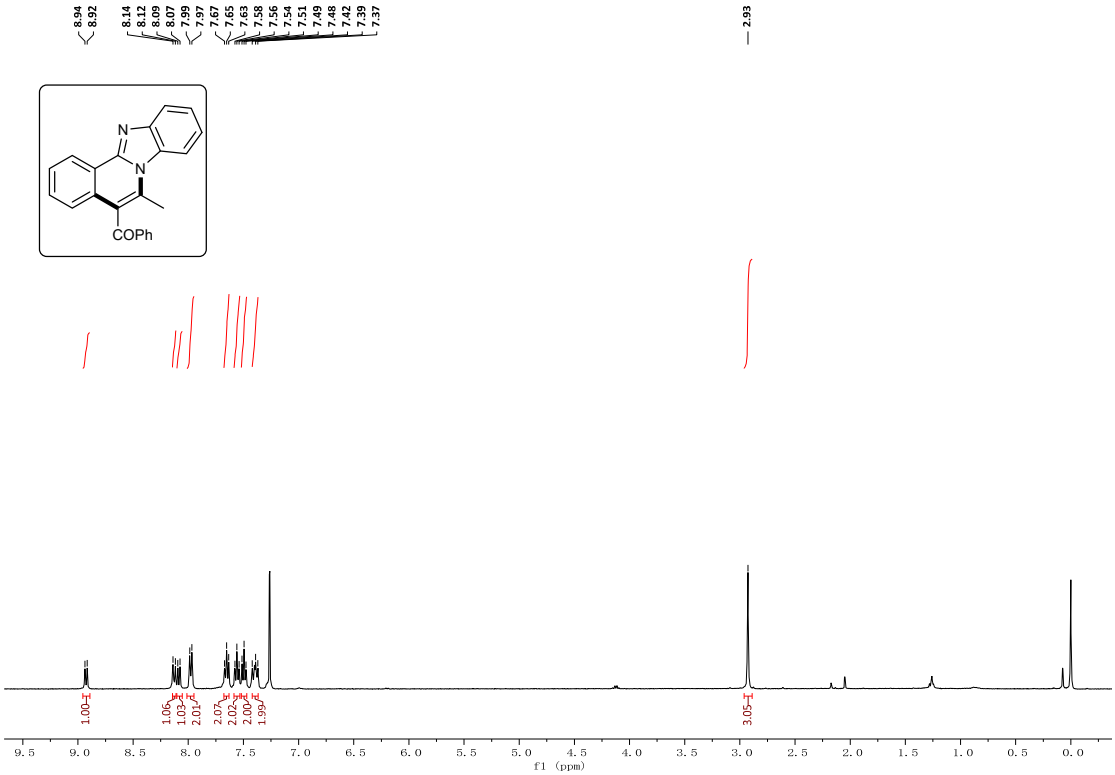
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3pd



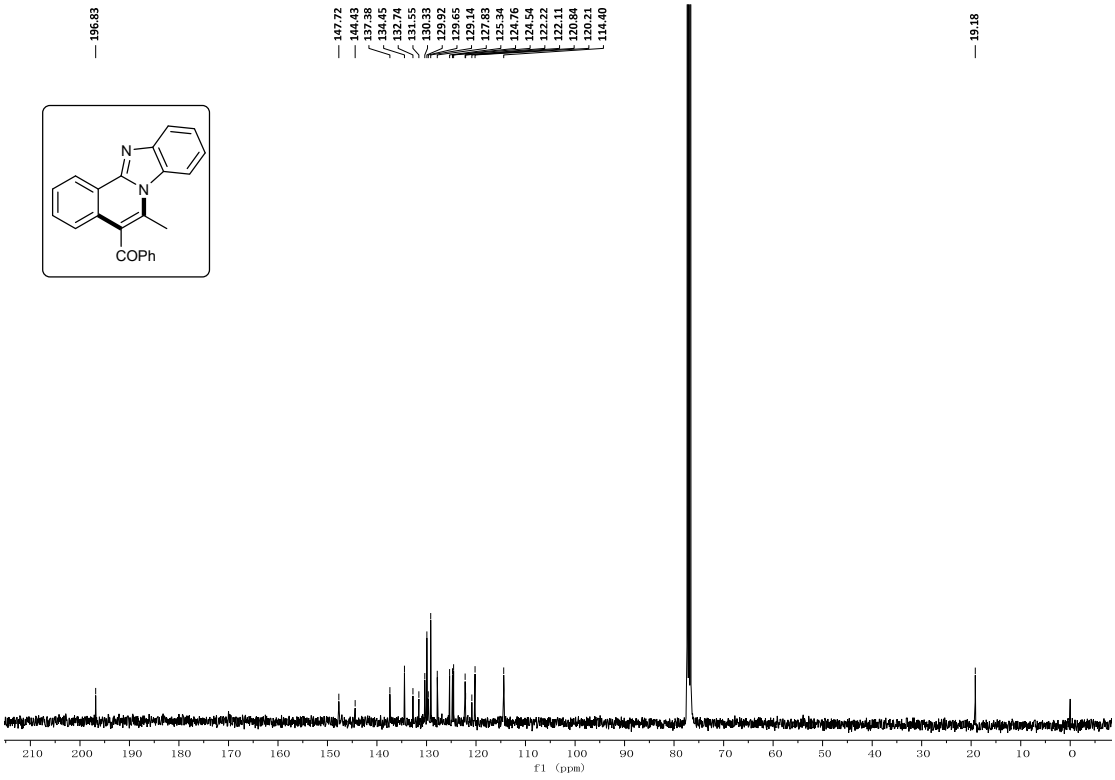
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3pd



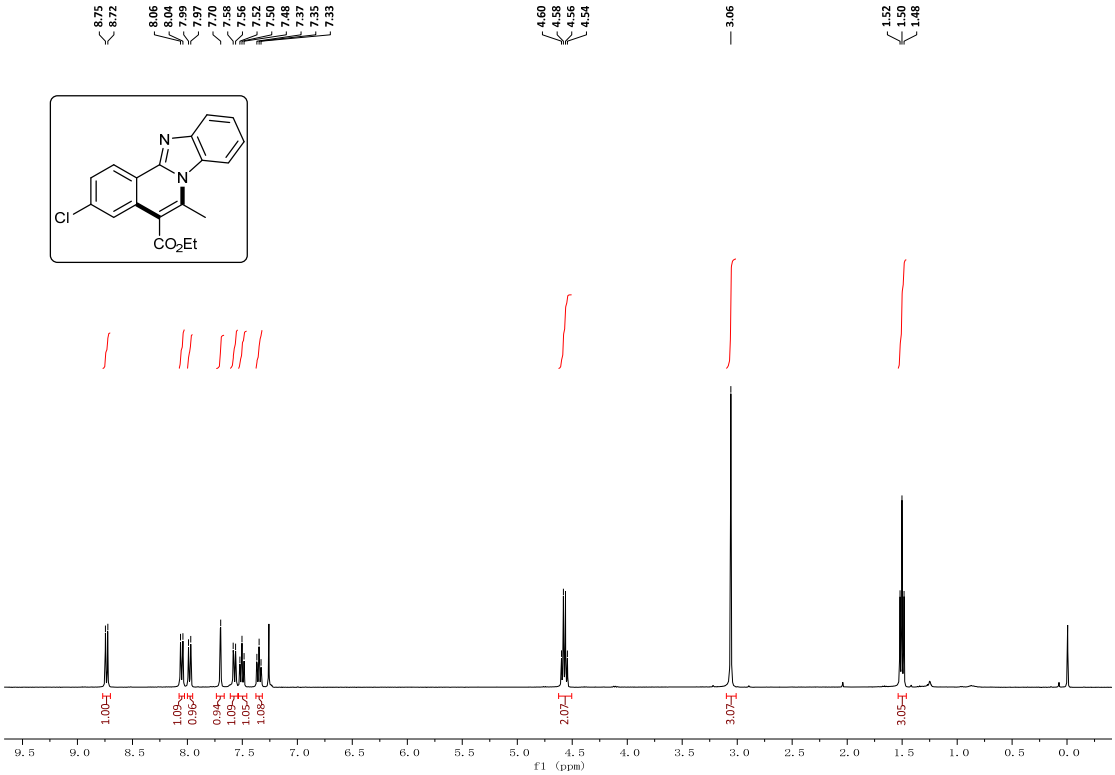
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3ph



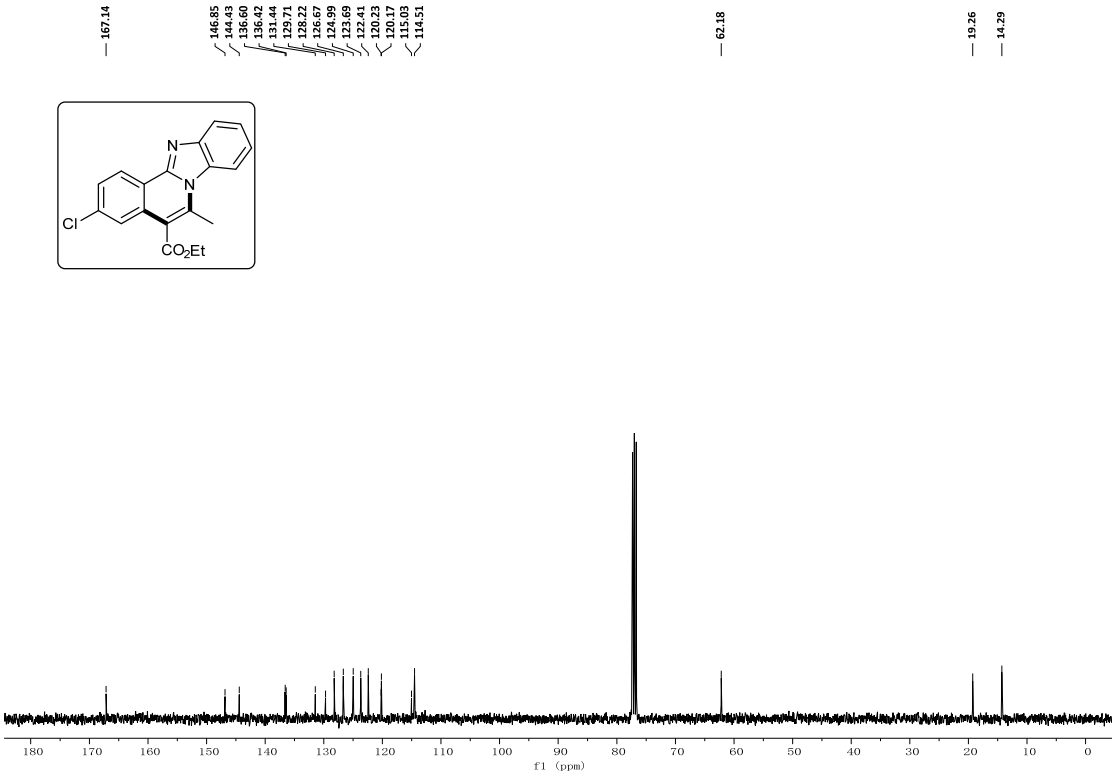
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3ph



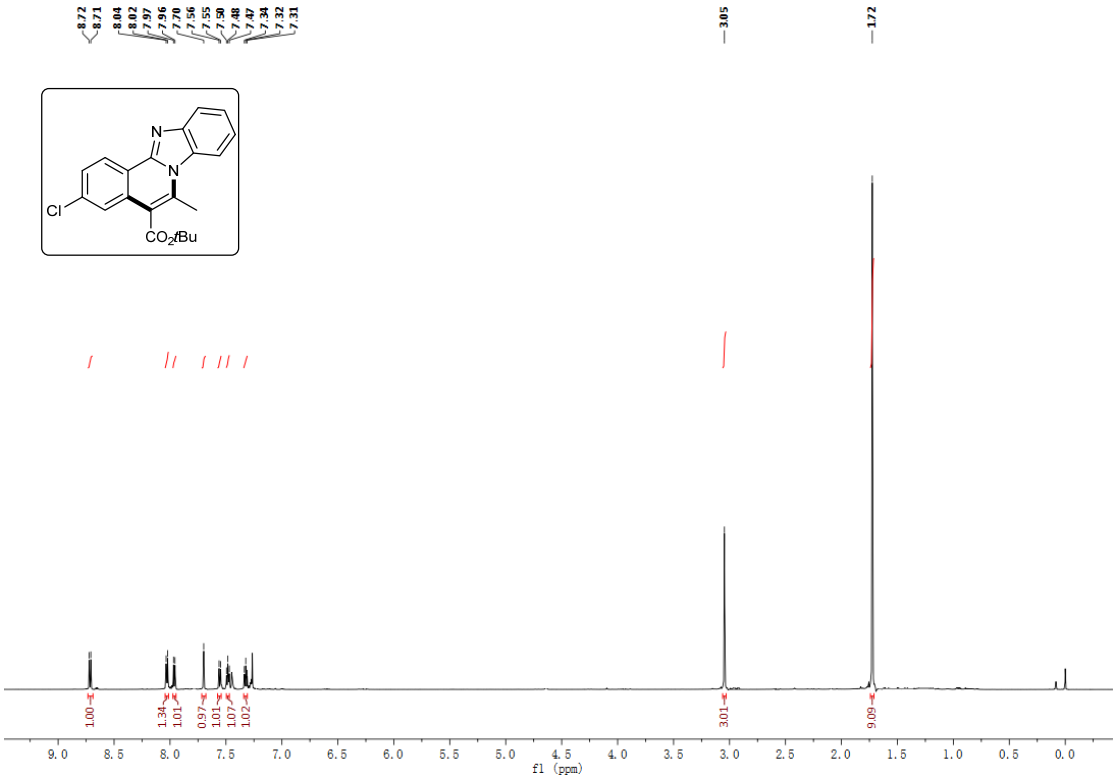
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3qa



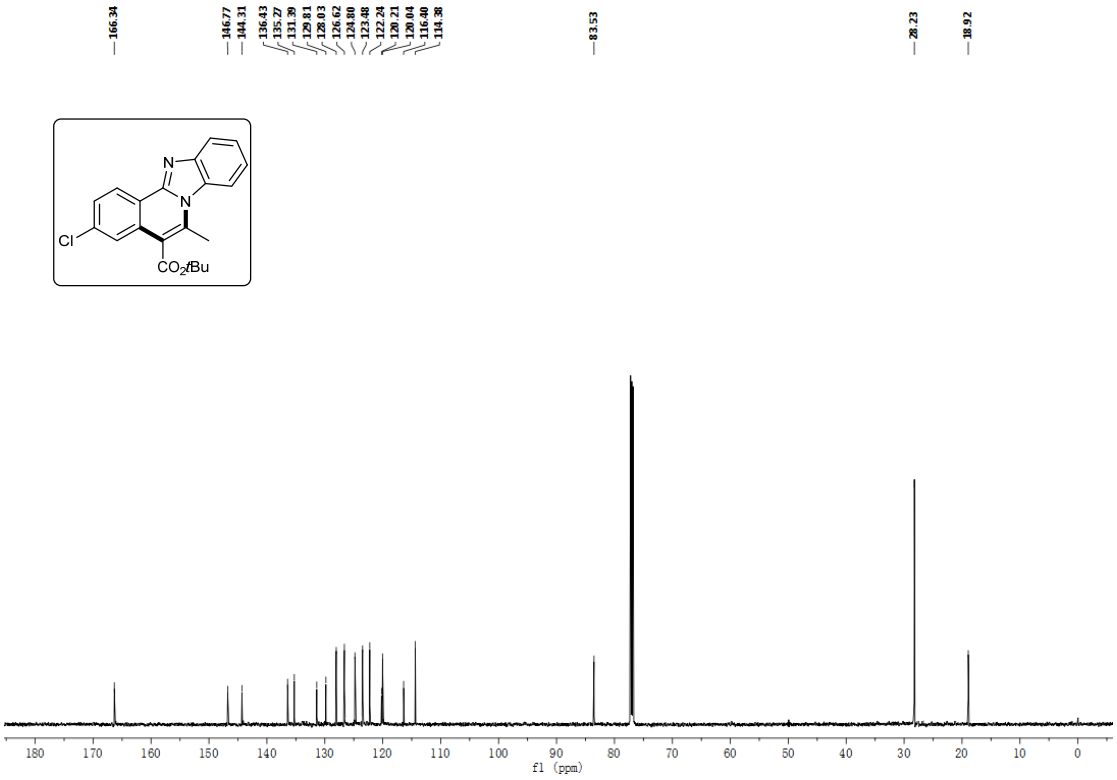
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3qa



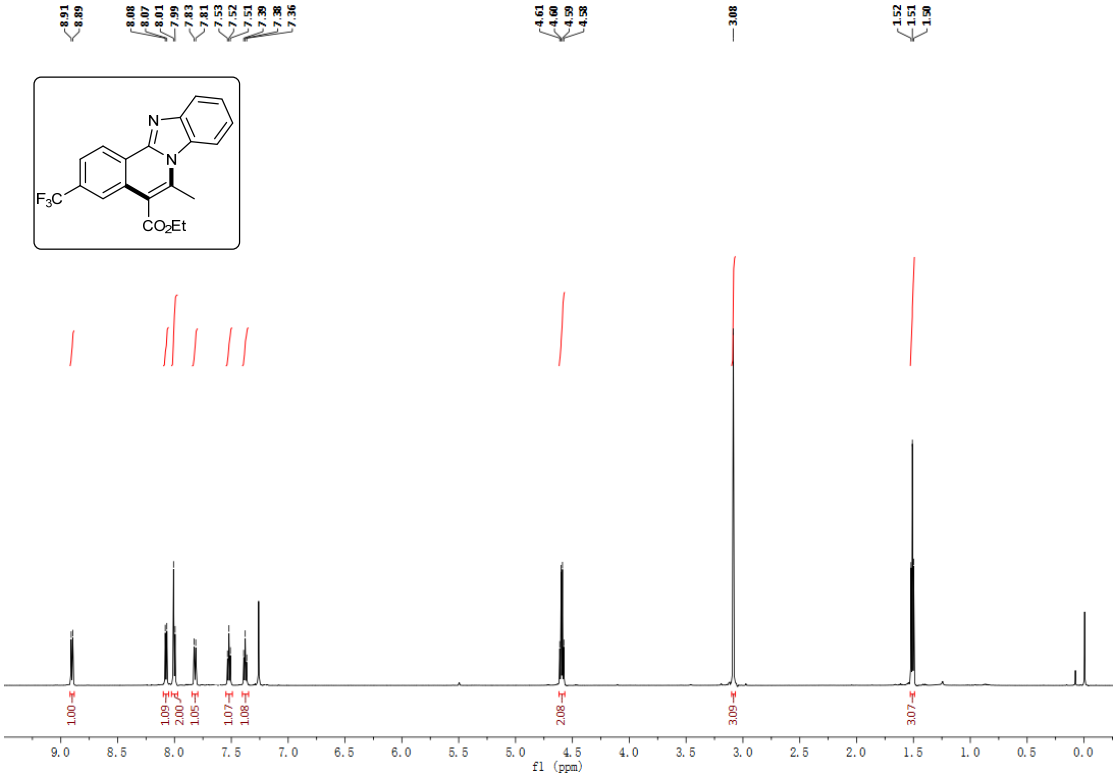
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3qc



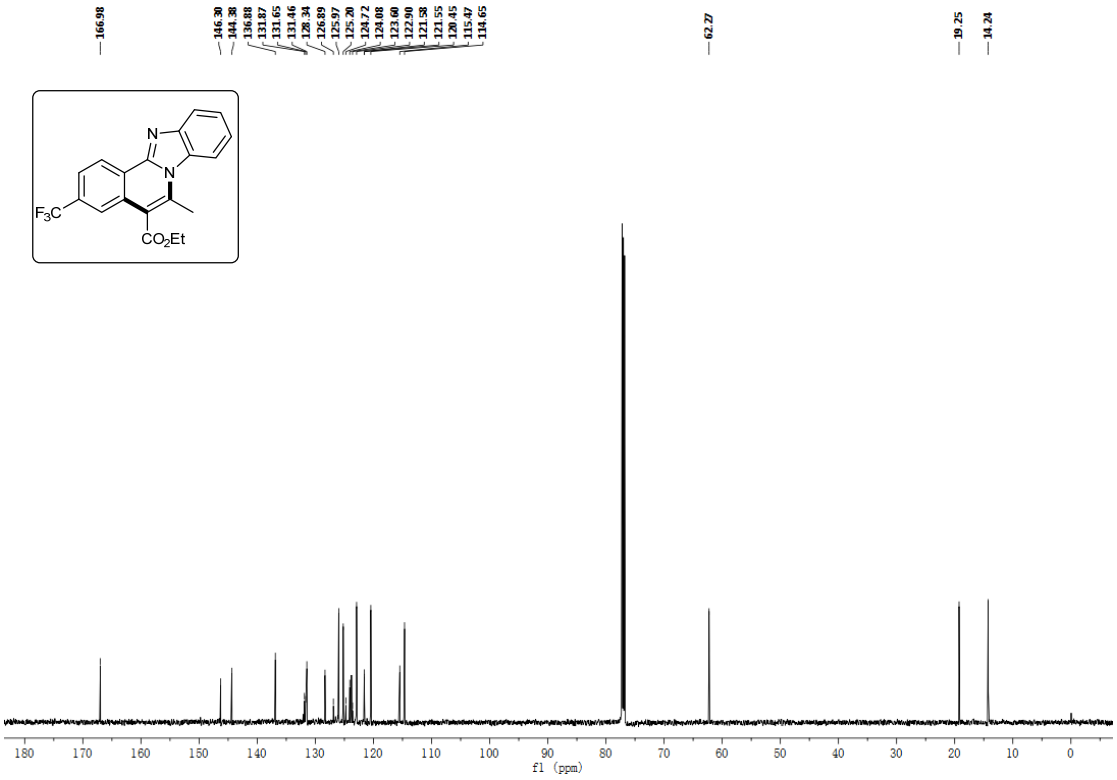
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3qc



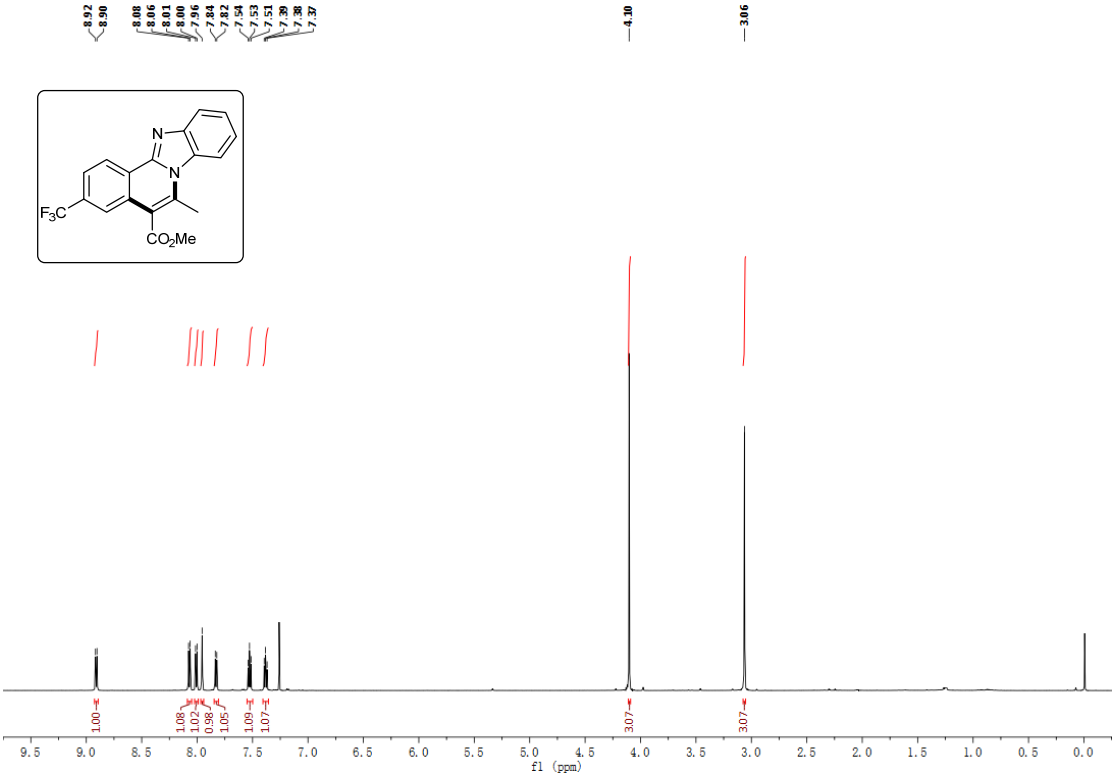
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3ra



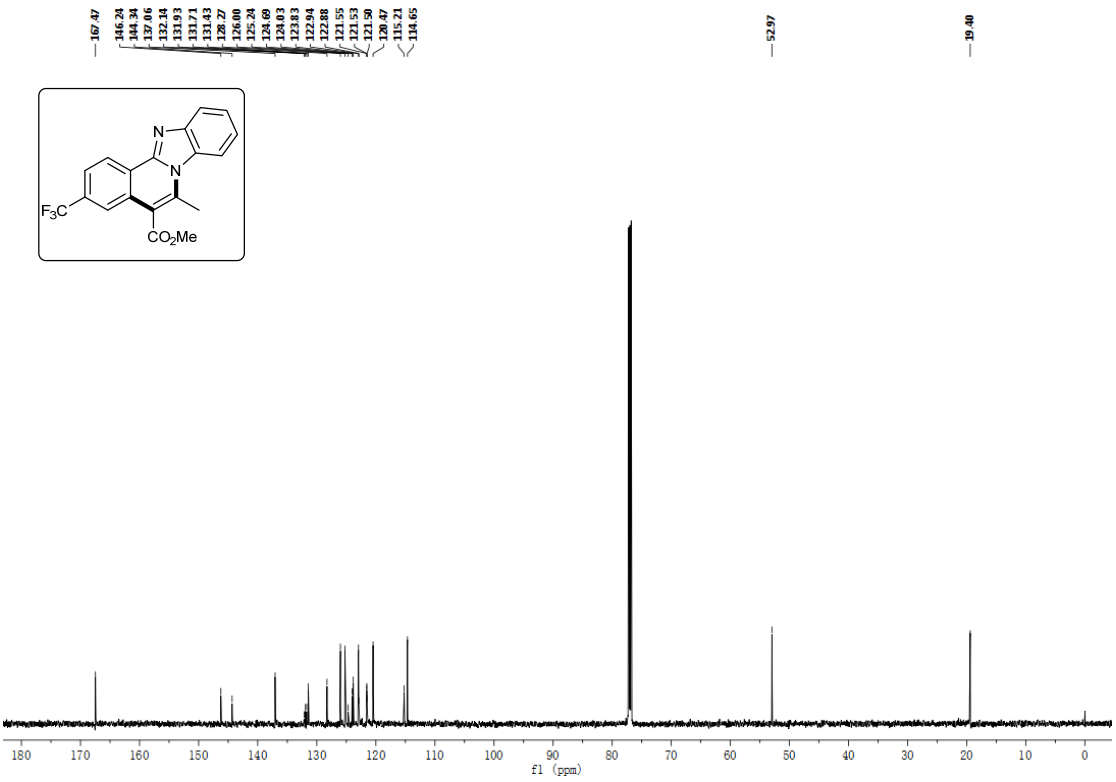
^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3ra



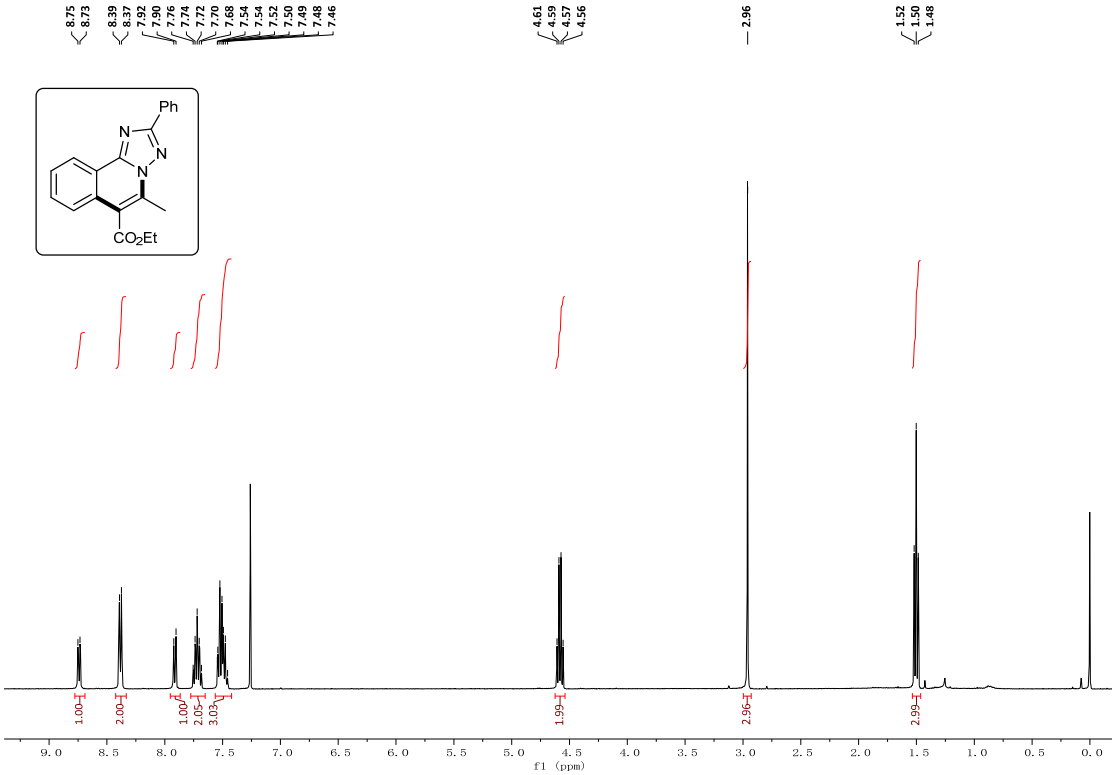
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 3rb



^{13}C NMR spectrum (150 MHz, $CDCl_3$) of 3rb



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 3sa



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of 3sa