SUPPORTING INFORMATION

Iron-catalyzed [3+2]-cycloaddition of in situ generated *N*-ylides with alkynes or olefins: access to multi-substituted/polycyclic pyrrole derivatives

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General Information

General. All reactions were carried out in oven-dried glassware. Flash column chromatography was performed using silica gel (300-400 mesh) or aluminum oxide (200-300 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 on a 400 or 500 MHz spectrometer; chemical shifts were reported in ppm with the solvent signal as reference, and coupling constants (*J*) were given in Hertz. The peak information was described as: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI or CI Source).

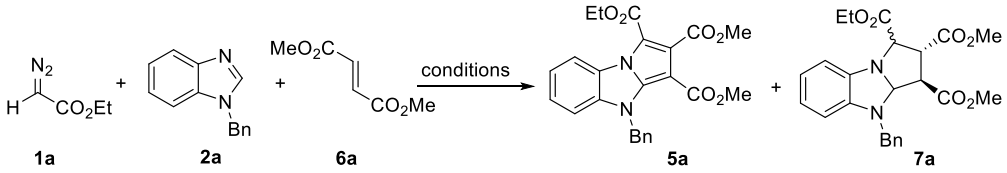
Materials. Anhydrous toluene was distilled from Na by following the standard purification procedure. All catalysts, including [Fe(TPP)Cl], $[(MeCN)_4Cu]PF_6$, $Rh_2(OAc)_4$, CuBr, and CuF_2 were purchased from chemical vendor, and used directly without additional treatment. Diazo compounds **1** were prepared according to the literature.[1] Benzimidazoles **2** were prepared according to the literature[2] or purchased from chemical vendor. Alkynes **3**, alkenes **6**, and other chemicals were purchased from chemical vendor and used as received without further purification.

Condition Optimization

Initially, CuF_2 was used as the catalyst combined with equal amount of triphenylphosphine. However, only slowly decomposition of the diazo compound **1a** occurred at 80 ^{o}C, and neither **5a** or **7a** was formed under these conditions (Table S1, entry 1). Since we have observed the formation of **5a** in the condition optimization for **4a**, then [Fe(TPP)Cl] was chose as the catalyst in the following studies. The screening of different oxidants in dichloromethane (DCM) revealed that DDQ (2,3-dicyano-5,6-dichlorobenzoquinone) is the effective oxidant in this reaction (entry 4), and only cycloaddition adduct **7a** was obtained in the cases with MnO_2 or CrO_3 (entries 2 and 3). The examination of solvents showed that all these tested solvents,

including DCM, 1,4-dioxane, ethyl acetate, and tetrahydrofuran (THF), gave the product in quantitative yields (entries 5-8), thus demonstrating extraordinary robustness of this two-step one-pot process. Above 95% isolated yield was obtained when the reaction was conducted on a 0.2 mmol scale in DCM catalyzed by [Fe(TPP)Cl]] in the presence of 2.2 equiv. of DDQ as oxidant (entry 9).

Table S1 Condition Optimization for the synthesis of polycyclic pyrroles[a]



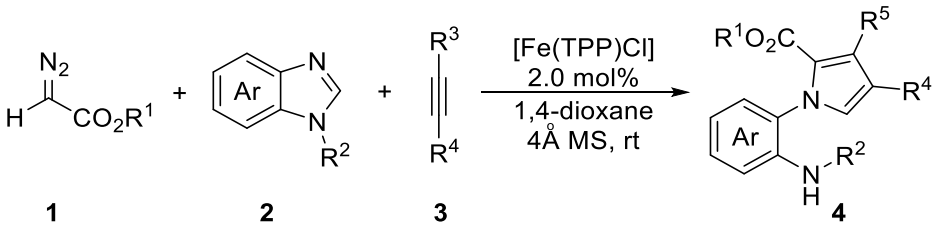
1a 2a 6a 5a 7a

Entry	Cat (x mol%)	Solvent	Oxidant (equiv.)	Yield of **5a** (%)[b]
1[c]	CuF_2 (20) + PPh_3 (20)	DCE	-	ND
2	[Fe(TPP)Cl] (2.0)	DCM	MnO_2 (2.0)	ND(>95[d])
3	[Fe(TPP)Cl] (2.0)	DCM	CrO_3 (2.0)	ND(>95[d])
4	[Fe(TPP)Cl] (2.0)	DCM	DDQ (2.0)	92
5	[Fe(TPP)Cl] (2.0)	DCM	DDQ (2.2)	>95
6	[Fe(TPP)Cl] (2.0)	1,4-dioxane	DDQ (2.2)	>95
7	[Fe(TPP)Cl] (2.0)	EtOAc	DDQ (2.2)	>95
8	[Fe(TPP)Cl] (2.0)	THF	DDQ (2.2)	>95
9	[Fe(TPP)Cl] (2.0)	DCM	DDQ (2.2)	>95[e]

[a]Unless otherwise noted, all reactions were conducted on a 0.1 mmol with **1a**:**2a**:**6a** = 1.5:1.2:1 under air. [b]The yields were determined by proton NMR with *p*-nitrobenzaldehyde as an internal standard. [c]The reaction was carried out at 80 °C, and only decomposition of **1a** was observed. [d]Isolated yields of **7a**. [e]The reaction was conducted on a 0.2 mmol scale and the yield was given in isolated yield. ND = not detected.

Experimental Procedures

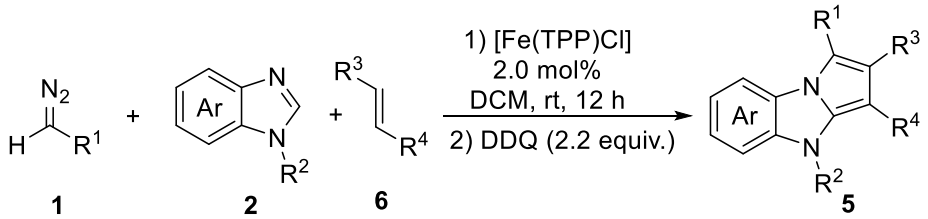
General Procedure for the Synthesis of 4



1 **2** **3** **4**

To a 10-mL oven-dried vial containing a magnetic stirring bar, [Fe(TPP)Cl] (2.7 mg, 2.0 mol%), 100 mg 4 Å MS, alkyne **3** (0.20 mmol), and benzimidazole **2** (0.24 mmol) in 1,4-dioxane (3.0 mL), diazo compound **1** (0.30 mmol) in 1,4-dioxane (1.0 mL) was added slowly *via* a syringe pump over 2 h under argon atmosphere at room temperature, and the reaction mixture was stirred for additional 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by by flash chromatography on silica gel (for 4g, on neutral aluminum oxide) without any additional treatment (eluent: PE/EA = 20:1 ~ 1:1, v/v) to give the pure products **4** in good to high yields.

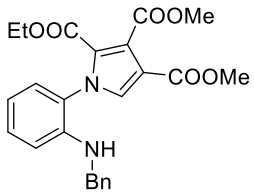
General Procedure for the Synthesis of 5



1 **2** **6** **5**

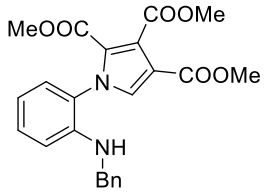
To a 10-mL oven-dried vial containing a magnetic stirring bar, [Fe(TPP)Cl] (2.7 mg, 2.0 mol%), alkene **6** (0.20 mmol), and benzimidazole **2** (0.24 mmol) in DCM (3.0 mL), diazo compound **1** (0.30 mmol) in DCM (1.0 mL) was added slowly *via* a syringe pump over 2 h at room temperature, and the reaction mixture was stirred for additional 12 h. Then, DDQ (99.9 mg, 0.44 mmol) in DCM (1.5 mL) was added to the above reaction mixture, and the reaction mixture was stirred for another 1 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel (for 5b, on neutral aluminum oxide) without any additional treatment (eluent: PE/EA = 10:1 ~ 1:1, v/v) to give the pure products **5** in

moderate to excellent yields.



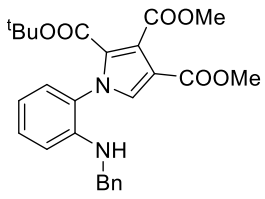
4a

2-Ethyl 3,4-dimethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4a).[3] 72.8 mg, 86% yield. Pale yellow solid; mp = 257.2-258.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.35 – 7.19 (comp, 6H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.73 (t, *J* = 7.4 Hz, 1H), 6.66 (d, *J* = 8.1 Hz, 1H), 4.35 (d, *J* = 5.3 Hz, 2H), 4.13 (q, *J* = 6.8 Hz, 2H), 3.98 (s, 3H), 3.90 (s, 1H), 3.84 (s, 3H), 1.11 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.8, 158.4, 143.8, 138.6, 132.0, 130.5, 128.7, 127.6, 127.2, 126.8, 125.6, 125.1, 122.6, 116.8, 115.2, 111.9, 61.0, 52.9, 51.8, 47.3, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{25}N_2O_6$ $[M+H]^+$: 437.1707, found 437.1705.



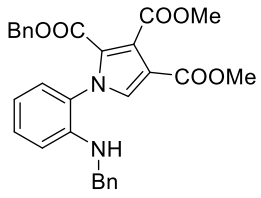
4b

Trimethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4b). 72.8 mg, 88% yield. Pale yellow solid; mp = 259.1-261.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34 – 7.28 (m, 2H), 7.27 – 7.18 (comp, 4H), 7.02 (d, *J* = 7.0 Hz, 1H), 6.73 (t, *J* = 6.7 Hz, 1H), 6.67 (d, *J* = 7.7 Hz, 1H), 4.35 (d, *J* = 4.1 Hz, 2H), 3.98 (s, 3H), 3.90 (s, 1H), 3.83 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 162.7, 158.8, 143.7, 138.6, 132.2, 130.5, 128.6, 127.5, 127.2, 126.7, 125.6, 124.9, 122.2, 116.8, 115.1, 111.9, 52.9, 52.0, 51.8, 47.2; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{23}N_2O_6$ $[M+H]^+$: 423.1551, found 423.1544.



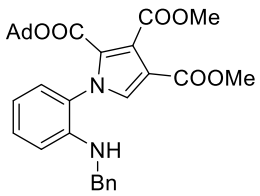
4c

2-(*Tert*-butyl) 3,4-dimethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4c). 75.3 mg, 83% yield. Pale yellow solid; mp = 162.3-164.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (s, 1H), 7.33 – 7.18 (comp, 6H), 7.03 (d, *J* = 7.6 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.35 (d, *J* = 5.7 Hz, 2H), 3.97 (s, 3H), 3.93 (t, *J* = 5.6 Hz, 1H), 3.82 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.8, 157.5, 143.7, 138.6, 131.5, 130.3, 128.6, 127.4, 127.2, 126.7, 125.4, 125.1, 123.9, 116.7, 114.9, 111.7, 82.3, 52.7, 51.7, 47.2, 27.8; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{28}N_2O_6Na$ $[M+Na]^+$: 487.1840, found 487.1838.



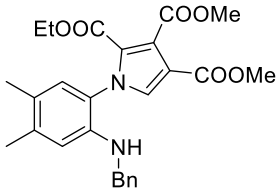
4d

2-Benzyl 3,4-dimethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4d). 82.8 mg, 85% yield. Pale yellow solid; mp = 265.8-267.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.33 – 7.19 (comp, 9H), 7.19 – 7.15 (m, 2H), 7.03 (d, *J* = 7.3 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 5.16 – 5.07 (m, 2H), 4.29 (d, *J* = 5.7 Hz, 2H), 3.92 – 3.86 (m, 1H), 3.82 (s, 3H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 162.7, 158.2, 143.7, 138.5, 134.8, 132.3, 130.5, 128.6, 128.48, 128.45, 128.4, 127.5, 127.2, 126.7, 126.0, 124.9, 122.1, 116.8, 115.2, 112.0, 67.0, 52.7, 51.8, 47.2; HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{27}N_2O_6$ $[M+H]^+$: 499.1864, found 499.1878.



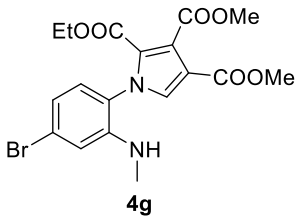
4e

2-((3*r*)-Adamantan-1-yl) 3,4-dimethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4e). 95.9 mg, 90% yield. Pale yellow solid; mp = 182.9-184.6 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.32 – 7.19 (comp, 6H), 7.03 (d, *J* = 7.7 Hz, 1H), 6.72 (t, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.2 Hz, 1H), 4.36 (d, *J* = 5.6 Hz, 2H), 3.98 (s, 3H), 3.94 (t, *J* = 5.2 Hz, 1H), 3.82 (s, 3H), 2.09 (s, 3H), 1.97 (s, 6H), 1.59 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.9, 157.2, 143.7, 138.7, 131.6, 130.3, 128.6, 127.5, 127.2, 126.8, 125.4, 125.1, 123.8, 116.7, 114.9, 111.7, 82.5, 52.8, 51.8, 47.2, 41.1, 36.0, 30.8; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{35}N_2O_6$ $[M+H]^+$: 543.2490, found 543.2485.



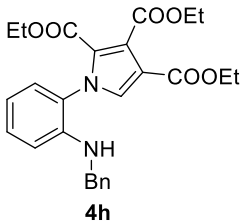
4f

2-Ethyl 3,4-dimethyl 1-(2-(benzylamino)-4,5-dimethylphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4f). 63.6 mg, 70% yield. Pale yellow solid; mp = 336.1-337.4 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (s, 1H), 7.33 – 7.20 (comp, 5H), 6.79 (s, 1H), 6.49 (s, 1H), 4.32 (d, *J* = 5.3 Hz, 2H), 4.21 – 4.10 (m, 2H), 3.96 (s, 3H), 3.82 (s, 3H), 3.67 (s, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 1.16 (t, *J* = 7.1 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 162.9, 158.4, 141.5, 139.1, 138.9, 132.3, 128.6, 128.3, 127.1, 126.8, 125.4, 125.0, 122.8, 122.5, 114.8, 113.5, 61.0, 52.8, 51.8, 47.6, 20.2, 18.6, 13.8; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{29}N_2O_6$ $[M+H]^+$: 465.2020, found 465.2015.



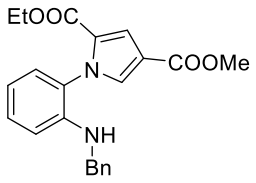
4g

2-Ethyl 3,4-dimethyl 1-(4-bromo-2-(methylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4g). 65.4 mg, 76% yield. Pale yellow solid; mp = 245.2-247.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (s, 1H), 6.90 – 6.82 (comp, 3H), 4.17 – 4.09 (m, 2H), 3.97 (s, 3H), 3.83 (s, 3H), 3.49 (d, *J* = 4.9 Hz, 1H), 2.78 (d, *J* = 5.0 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 162.6, 158.2, 146.1, 131.9, 128.6, 125.7, 124.6, 123.8, 122.2, 119.1, 115.3, 113.7, 61.1, 52.9, 51.8, 30.0, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{19}BrN_2O_6$ $[M+H]^+$: 439.0499, found 439.0502.



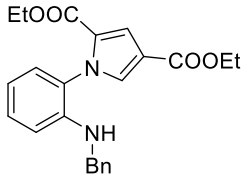
4h

Triethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (4h). 75.6 mg, 83% yield. Pale yellow solid; mp = 190.4-192.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (s, 1H), 7.34 – 7.28 (m, 2H), 7.28 – 7.20 (comp, 4H), 7.05 – 7.01 (m, 1H), 6.75 – 6.69 (m, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.44 (q, *J* = 7.1 Hz, 2H), 4.36 (d, *J* = 5.9 Hz, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 4.21 – 4.08 (m, 2H), 3.94 (t, *J* = 5.8 Hz, 1H), 1.43 (t, *J* = 7.2 Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.10 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 162.3, 158.4, 143.7, 138.6, 132.1, 130.4, 128.6, 127.5, 127.2, 126.7, 125.8, 125.1, 122.3, 116.7, 115.4, 111.8, 61.9, 60.9, 60.6, 47.2, 14.2, 14.1, 13.7; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{29}N_2O_6$ $[M+H]^+$: 465.2020, found 465.2027.



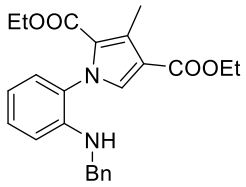
4i

2-Ethyl 4-methyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,4-dicarboxylate (4i). 57.1 mg, 77% yield. Pale yellow solid; mp = 211.3-212.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (s, 1H), 7.32 – 7.28 (m, 2H), 7.27 – 7.23 (comp, 4H), 7.06 (d, *J* = 7.7 Hz, 1H), 6.75 (t, *J* = 7.5 Hz, 1H), 6.69 (d, *J* = 8.2 Hz, 1H), 4.32 (d, *J* = 4.4 Hz, 2H), 4.16 (q, *J* = 6.7 Hz, 2H), 3.84 (s, 3H), 3.75 (s, 1H), 1.15 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 159.5, 143.9, 138.7, 132.9, 130.2, 128.6, 127.4, 127.2, 126.9, 126.0, 125.1, 118.9, 117.0, 116.8, 111.7, 60.4, 51.5, 47.5, 14.0; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{23}N_2O_4$ $[M+H]^+$: 379.1652, found 379.1654.



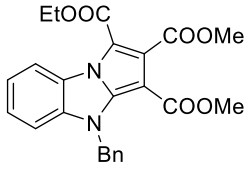
4j

Diethyl 1-(2-(benzylamino)phenyl)-1*H*-pyrrole-2,4-dicarboxylate (4j). 59.9 mg, 78% yield. Pale yellow solid; mp = 179.4-181.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.46 (s, 1H), 7.33 – 7.27 (m, 2H), 7.27 – 7.21 (comp, 4H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.74 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 4.36 – 4.27 (m, 4H), 4.16 (q, *J* = 6.9 Hz, 2H), 3.76 (t, *J* = 5.1 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.16 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 159.6, 143.9, 138.7, 132.8, 130.1, 128.6, 127.4, 127.2, 126.9, 126.0, 125.0, 118.9, 117.4, 116.8, 111.6, 60.4, 60.2, 47.4, 14.4, 14.0; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{25}N_2O_4$ $[M+H]^+$: 393.1809, found 393.1808.



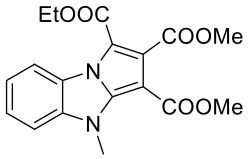
4k

Diethyl 1-(2-(benzylamino)phenyl)-3-methyl-1*H*-pyrrole-2,4-dicarboxylate (4k). 58.1 mg, 73% yield. Pale yellow solid; mp = 187.1-189.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.34 – 7.28 (m, 2H), 7.28 – 7.18 (comp, 4H), 7.07 – 7.03 (m, 1H), 6.77 – 6.71 (m, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.35 – 4.25 (m, 4H), 4.16 – 4.03 (m, 2H), 3.86 (t, *J* = 5.7 Hz, 1H), 2.67 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.01 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 160.6, 144.0, 138.9, 132.9, 132.2, 129.7, 128.6, 127.3, 127.2, 127.1, 126.9, 122.7, 116.7, 116.3, 111.4, 60.0, 59.8, 47.4, 14.4, 13.8, 11.9; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{27}N_2O_4$ $[M+H]^+$: 407.1965, found 407.1958.



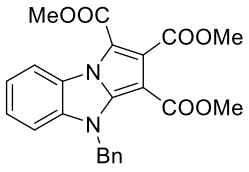
5a

1-Ethyl 2,3-dimethyl 4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5a).[4] 85.7 mg, >95% yield. Pale yellow solid; mp = 177.2-178.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.2 Hz, 1H), 7.34 – 7.22 (comp, 6H), 7.20 – 7.15 (m, 2H), 6.03 (s, 2H), 4.45 – 4.38 (m, 2H), 3.97 (s, 3H), 3.76 (s, 3H), 1.40 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.8, 159.6, 141.9, 136.6, 136.4, 130.5, 128.8, 127.7, 126.62, 126.59, 124.8, 121.8, 116.6, 110.3, 109.7, 90.0, 60.9, 52.6, 51.6, 48.5, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{22}N_2O_6Na$ $[M+Na]^+$: 457.1370, found 457.1361.



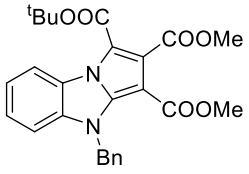
5b

1-Ethyl 2,3-dimethyl 4-methyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5b).[4] 70.0 mg, >95% yield. Pale yellow solid; mp = 166.4-167.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.2 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.28 – 7.23 (m, 1H), 4.36 (q, *J* = 6.8 Hz, 2H), 4.18 (s, 3H), 3.96 (s, 3H), 3.83 (s, 3H), 1.39 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.9, 159.6, 142.1, 137.0, 130.5, 126.3, 124.7, 121.5, 116.5, 109.5, 109.3, 89.7, 60.8, 52.6, 51.5, 31.9, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{18}N_2O_6Na$ [M+Na]$^+$: 381.1057, found 381.1046.



5c

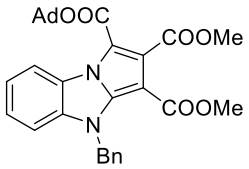
Trimethyl 4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5c).[4] 84.3 mg, >95% yield. Grey solid; mp = 169.2-171.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 7.0 Hz, 1H), 7.33 – 7.21 (comp, 6H), 7.18 (s, 2H), 6.02 (s, 2H), 3.98 (s, 3H), 3.92 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 162.7, 160.0, 141.9, 136.5, 136.4, 130.7, 128.8, 127.7, 126.6, 124.9, 121.8, 116.5, 110.4, 109.4, 90.1, 52.8, 52.0, 51.7, 48.5; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{20}N_2O_6Na$ [M+Na]$^+$: 443.1214, found 443.1219.



5d

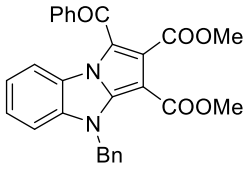
1-(*Tert*-butyl) 2,3-dimethyl 4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5d). 87.6 mg, 95% yield. Grey solid; mp = 232.1-233.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.82 (d, *J* = 7.2 Hz, 1H), 7.32 – 7.21 (comp, 6H), 7.19 – 7.12 (m,

2H), 6.02 (s, 2H), 3.96 (s, 3H), 3.75 (s, 3H), 1.60 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.1, 162.9, 159.1, 141.8, 136.7, 136.4, 129.7, 128.8, 127.6, 126.7, 126.6, 124.7, 121.6, 116.8, 111.1, 110.2, 89.5, 82.0, 52.5, 51.6, 48.5, 28.3; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{26}N_2O_6Na$ [M+Na]$^+$: 485.1683, found 485.1686.



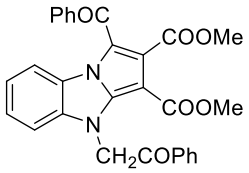
5e

1-((3*r*)-Adamantan-1-yl) 2,3-dimethyl 4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*] imidazole-1,2,3-tricarboxylate (5e). 107.1 mg, >95% yield. Pale yellow solid; mp = 336.3-337.1 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.81 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.21 (comp, 6H), 7.16 (d, *J* = 6.9 Hz, 2H), 6.02 (s, 2H), 3.96 (s, 3H), 3.75 (s, 3H), 2.28 (s, 6H), 2.23 (s, 3H), 1.80 – 1.65 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 162.9, 158.8, 141.8, 136.7, 136.4, 129.7, 128.8, 127.6, 126.7, 126.6, 124.7, 121.6, 116.9, 111.1, 110.1, 89.6, 82.2, 52.6, 51.6, 48.5, 41.6, 36.2, 31.0; HRMS (TOF MS ESI$^+$) calculated for $C_{32}H_{32}N_2O_6Na$ [M+Na]$^+$: 563.2153, found 563.2154.



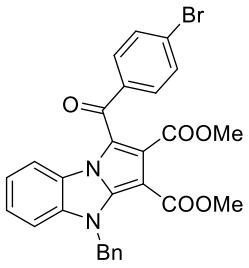
5f

Dimethyl 1-benzoyl-4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (5f). 92.6 mg, >95% yield. Pale yellow solid; mp = 165.6-166.5 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.1 Hz, 1H), 7.79 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.2 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.39 – 7.19 (comp, 8H), 6.05 (s, 2H), 3.71 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 185.0, 165.1, 162.9, 142.3, 139.1, 136.6, 136.5, 131.9, 131.7, 129.0, 128.8, 128.1, 127.7, 126.60, 126.56, 125.0, 121.8, 118.8, 116.7, 110.5, 91.0, 52.1, 51.6, 48.6; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{22}N_2O_5Na$ [M+Na]$^+$: 489.1421, found 489.1413.



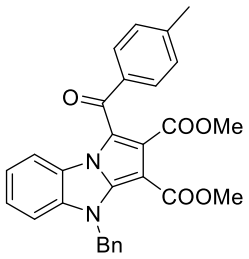
5g

Dimethyl 1-benzoyl-4-(2-oxo-2-phenylethyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*] imidazole-2,3-dicarboxylate (5g). 96.5 mg, >95% yield. Pale yellow solid; mp = 169.2-170.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 7.4 Hz, 2H), 7.80 (d, *J* = 7.3 Hz, 2H), 7.67 (t, *J* = 6.9 Hz, 1H), 7.56 (t, *J* = 7.2 Hz, 3H), 7.46 (t, *J* = 7.1 Hz, 2H), 7.33 (t, *J* = 7.1 Hz, 1H), 7.29 – 7.22 (m, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 6.23 (s, 2H), 3.55 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 191.5, 185.1, 165.0, 163.0, 142.7, 139.2, 137.0, 134.3, 134.1, 131.9, 131.5, 129.1, 129.0, 128.2, 128.1, 126.6, 125.0, 121.9, 119.0, 116.8, 109.3, 91.2, 52.0, 51.6, 51.4; HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{22}N_2O_6Na$ $[M+Na]^+$: 517.1370, found 517.1360.



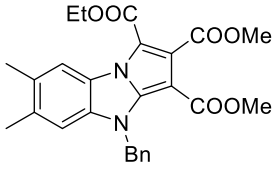
5h

Dimethyl 4-benzyl-1-(4-bromobenzoyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (5h). 104.7 mg, >95% yield. White solid; mp = 231.9-232.8 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 8.1 Hz, 1H), 7.66 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 2H), 7.38 – 7.33 (m, 1H), 7.32 – 7.24 (comp, 5H), 7.22 (d, *J* = 7.0 Hz, 2H), 6.04 (s, 2H), 3.72 (s, 3H), 3.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 183.7, 165.1, 162.8, 142.3, 138.0, 136.6, 136.4, 131.9, 131.3, 130.5, 128.9, 127.8, 126.7, 126.60, 126.55, 125.2, 121.9, 118.4, 116.8, 110.6, 91.3, 52.2, 51.7, 48.7; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{21}BrN_2O_5Na$ $[M+Na]^+$: 567.0526, found 567.0530.



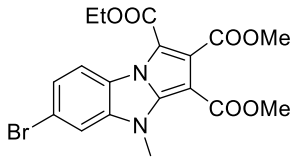
5i

Dimethyl 4-benzyl-1-(4-methylbenzoyl)-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-2,3-dicarboxylate (5i). 94.2 mg, >95% yield. Pale yellow solid; mp = 185.4-185.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 8.1 Hz, 1H), 7.71 (d, *J* = 7.5 Hz, 2H), 7.35 – 7.21 (comp, 10H), 6.04 (s, 2H), 3.71 (s, 3H), 3.30 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 184.9, 165.2, 163.0, 142.7, 142.3, 136.7, 136.5, 136.4, 131.2, 129.2, 128.83, 128.76, 127.7, 126.6, 126.5, 125.0, 121.8, 119.0, 116.6, 110.5, 90.7, 52.1, 51.6, 48.6, 21.7; HRMS (TOF MS ESI$^+$) calculated for $C_{29}H_{24}N_2O_5Na$ $[M+Na]^+$: 503.1577, found 503.1589.



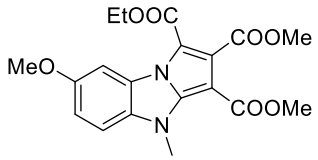
5j

1-Ethyl 2,3-dimethyl 4-benzyl-6,7-dimethyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5j). 87.7 mg, 95% yield. Black gray solid; mp = 205.0-206.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H), 7.30 – 7.23 (comp, 3H), 7.15 (d, *J* = 7.0 Hz, 2H), 7.01 (s, 1H), 5.97 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.96 (s, 3H), 3.74 (s, 3H), 2.37 (s, 3H), 2.31 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.3, 162.8, 159.7, 141.6, 136.9, 134.8, 133.9, 130.7, 130.2, 128.7, 127.5, 126.4, 124.9, 116.8, 110.7, 109.3, 89.9, 60.8, 52.6, 51.5, 48.3, 20.5, 20.2, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{26}N_2O_6Na$ $[M+Na]^+$: 485.1683, found 485.1697.



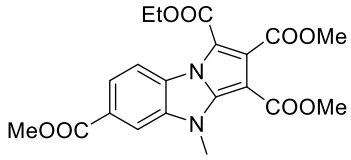
5k

1-Ethyl 2,3-dimethyl 6-bromo-4-methyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5k). 87.2 mg, >95% yield. Grey solid; mp = 207.1-208.5 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.7 Hz, 1H), 7.47 (s, 1H), 7.35 (d, *J* = 8.7 Hz, 1H), 4.35 (q, *J* = 7.0 Hz, 2H), 4.16 (s, 3H), 3.95 (s, 3H), 3.83 (s, 3H), 1.38 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.8, 162.7, 159.4, 142.0, 138.0, 130.4, 125.3, 124.5, 118.0, 117.7, 112.5, 109.6, 90.0, 61.0, 52.6, 51.6, 32.1, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{18}H_{17}BrN_2O_6Na$ $[M+Na]^+$: 459.0162, found 459.0164.



5l

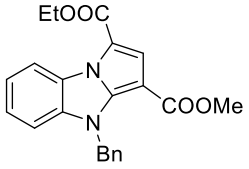
1-Ethyl 2,3-dimethyl 7-methoxy-4-methyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5l). 77.1 mg, 95% yield. Pale yellow solid; mp = 169.4-170.7 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.40 (s, 1H), 7.19 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 8.2 Hz, 1H), 4.35 (d, *J* = 6.7 Hz, 2H), 4.15 (s, 3H), 3.96 (s, 3H), 3.90 (s, 3H), 3.83 (s, 3H), 1.39 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.2, 162.8, 159.6, 155.1, 142.6, 131.3, 130.7, 126.8, 113.4, 109.8, 109.1, 100.7, 89.5, 60.8, 56.1, 52.6, 51.5, 31.9, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{19}H_{20}N_2O_7Na$ $[M+Na]^+$: 411.1163, found 411.1162.



5m

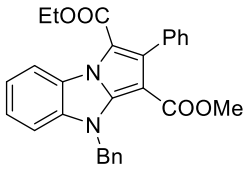
1-Ethyl 2,3-dimethyl 7-methoxy-4-methyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2,3-tricarboxylate (5m). 79.1 mg, 95% yield. Pale yellow solid; mp = 179.3-181.1 ^{o}C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.6 Hz, 1H), 8.03 (s, 1H), 7.95 (d, *J* =

8.6 Hz, 1H), 4.40 – 4.32 (m, 2H), 4.23 (s, 3H), 3.97 (d, *J* = 8.1 Hz, 6H), 3.84 (s, 3H), 1.39 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 166.6, 165.7, 162.6, 159.4, 143.0, 136.9, 131.2, 129.1, 126.6, 123.1, 116.2, 111.1, 109.7, 90.0, 61.0, 52.6, 52.4, 51.7, 32.2, 14.2; HRMS (TOF MS ESI$^+$) calculated for $C_{20}H_{20}N_2O_8Na$ $[M+Na]^+$: 439.1112, found 439.1111.



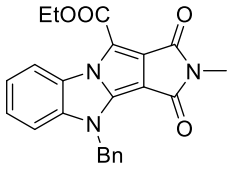
5n

1-Ethyl 3-methyl 4-benzyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,3-dicarboxylate (5n).[5] 73.8 mg, >95% yield. White solid; mp = 140.3-142.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 7.6 Hz, 1H), 7.71 (s, 1H), 7.29 – 7.17 (comp, 8H), 6.06 (s, 2H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.80 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.0, 160.6, 143.1, 136.9, 136.2, 128.7, 127.6, 127.0, 126.8, 125.1, 124.2, 121.4, 116.2, 112.4, 110.2, 91.3, 60.2, 51.2, 48.4, 14.6; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{20}N_2O_4Na$ $[M+Na]^+$: 399.1315, found 399.1313.



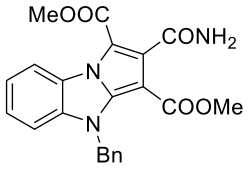
5o

1-Ethyl 3-methyl 4-benzyl-2-phenyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,3-dicarboxylate (5o). 84.6 mg, 88% yield. White solid; mp = 95.1-97.2 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.21 (comp, 13H), 6.01 (s, 2H), 4.05 (q, *J* = 6.8 Hz, 2H), 3.41 (s, 3H), 0.87 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 161.4, 142.7, 140.0, 137.0, 136.6, 136.5, 129.6, 128.7, 127.5, 127.0, 126.8, 126.7, 126.6, 124.2, 121.4, 116.5, 110.9, 110.1, 92.2, 59.9, 50.7, 48.5, 13.5; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}N_2O_4Na$ $[M+Na]^+$: 475.1628, found 475.1637.



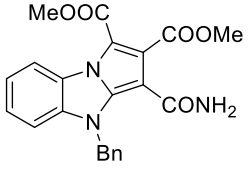
5p

Ethyl 4-benzyl-2-methyl-1,3-dioxo-1,2,3,4-tetrahydrobenzo[*d*]pyrrolo[3',4':3,4] pyrrolo[1,2-*a*]imidazole-10-carboxylate (5p). 34.3 mg, 44% yield. Pale yellow solid; mp = 242.1-243.7 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.27 (comp, 8H), 5.57 (s, 2H), 4.52 – 4.44 (m, 2H), 3.12 (s, 3H), 1.51 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.5, 162.8, 159.6, 136.3, 135.7, 134.9, 129.7, 129.1, 128.5, 127.7, 127.6, 125.3, 122.1, 117.2, 110.3, 110.1, 93.2, 61.4, 49.4, 24.2, 14.4; HRMS (TOF MS ESI$^+$) calculated for $C_{23}H_{19}N_3O_4Na$ $[M+Na]^+$: 424.1268, found 424.1270.



5q

Dimethyl 4-benzyl-2-carbamoyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,3-dicarboxylate (5q). 50.4 mg, 62% yield. Soft red solid; mp = 228.1-230.1 ºC; ^{1}H NMR (500 MHz, DMSO) δ 8.66 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 8.2 Hz, 2H), 7.45 – 7.15 (comp, 8H), 6.07 (s, 2H), 3.83 (s, 3H), 3.68 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 166.2, 163.2, 160.7, 141.9, 137.6, 136.7, 135.8, 129.1, 127.9, 127.0, 126.3, 125.2, 122.0, 116.1, 111.6, 108.6, 90.1, 52.0, 51.6, 47.8; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{19}N_3O_5Na$ $[M+Na]^+$: 428.1217, found 428.1216.

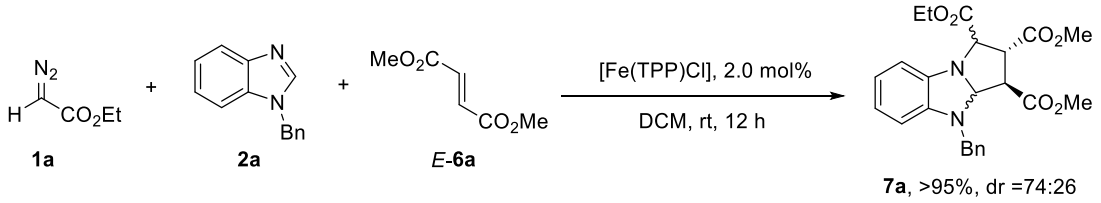


5q'

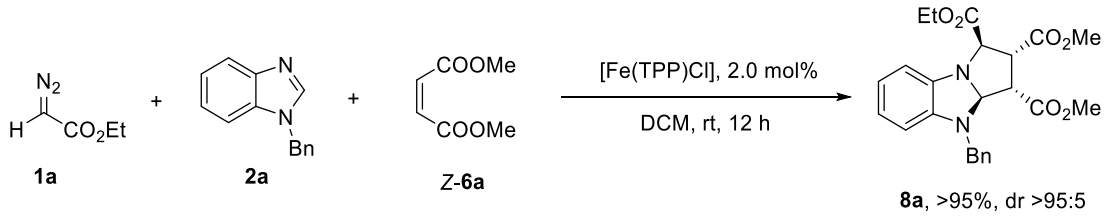
Dimethyl 4-benzyl-3-carbamoyl-4*H*-benzo[*d*]pyrrolo[1,2-*a*]imidazole-1,2-dicarboxylate (5q'). 6.4 mg, 8% yield. Pale yellow solid; mp = 215.6-217.9 ºC; ^{1}H

NMR (500 MHz, DMSO) δ 8.62 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 6.9 Hz, 1H), 7.35 – 7.16 (comp, 6H), 5.93 (s, 2H), 3.86 (s, 6H); ^{13}C NMR (125 MHz, DMSO) δ 166.3, 164.3, 160.1, 140.3, 137.3, 136.8, 129.2, 128.2, 128.1, 127.5, 126.2, 125.5, 121.7, 116.0, 111.5, 107.8, 95.6, 53.3, 52.4, 47.3; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{19}N_3O_5Na$ [M+Na]$^+$: 428.1217, found 428.1218.

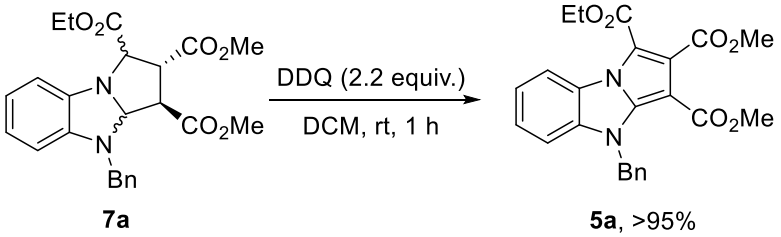
Control Experiments



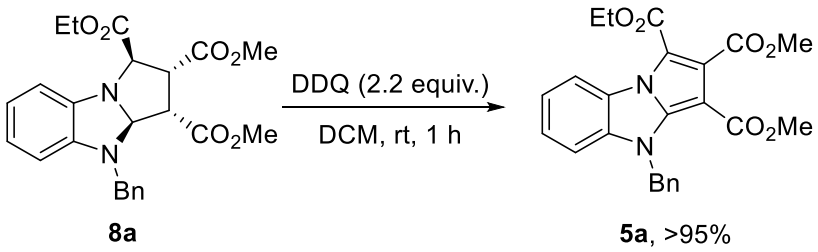
To a 10-mL oven-dried vial containing a magnetic stirring bar, [Fe(TPP)Cl] (2.7 mg, 2.0 mol%), alkene *E*-**6a** (28.8 mg, 0.20 mmol) and benzimidazole **2a** (50.0 mg, 0.24 mmol) in DCM (3.0 mL), diazo compound **1a** (34.3 mg, 0.30 mmol) in DCM (1.0 mL) was added slowly *via* a syringe pump over 2 h at room temperature, and the reaction mixture was stirred for additional 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel without any additional treatment (eluent: PE/EA = 10:1 ~ 1:1, v/v) to give 86.8 mg of the product **7a** as a mixture of two diastereomers in combined >95% yield. 74:26 *dr*. Dark green oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (comp, 4.43H), 7.27 – 7.15 (comp, 5.54H), 6.78 – 6.72 (comp, 0.62H), 6.72 – 6.66 (comp, 3.09H), 6.37 (d, *J* = 7.4 Hz, 0.36H), 6.26 – 6.18 (comp, 1.04H), 5.64 (d, *J* = 6.7 Hz, 1.06H), 5.43 (d, *J* = 6.8 Hz, 0.34H), 4.49 – 4.38 (m, 2.68H), 4.37 – 4.26 (m, 1.15H), 4.25 – 4.15 (m, 3.23H), 3.99 – 3.92 (m, 1.06H), 3.82 – 3.78 (m, 0.36H), 3.69 (s, 2.99H), 3.67 (s, 0.95H), 3.53 (s, 0.91H), 3.42 (s, 3.00H), 1.36 – 1.27 (m, 5.35H);^{13}C NMR (125 MHz, $CDCl_3$) δ 170.01, 169.98, 169.9, 169.5, 169.4, 169.1, 143.4, 141.1, 140.62, 140.55, 136.9, 136.8, 127.6, 127.5, 126.4, 126.3, 126.14, 126.09, 121.9, 121.3, 119.0, 118.3, 110.7, 109.6, 107.8, 105.8, 88.6, 86.2, 68.1, 67.3, 60.9, 60.6, 53.6, 53.2, 51.6, 51.3, 51.22, 51.18, 51.0, 47.9, 46.1, 13.09, 13.12; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{27}N_2O_6$ [M+H]$^+$: 439.1864, found 439.1861.



To a 10-mL oven-dried vial containing a magnetic stirring bar, [Fe(TPP)Cl] (2.7 mg, 2.0 mol%), alkene *Z*-**6a** (28.8 mg, 0.20 mmol) and benzimidazole **2a** (50.0 mg, 0.24 mmol) in DCM (3.0 mL), diazo compound **1a** (34.3 mg, 0.30 mmol) in DCM (1.0 mL) was added slowly *via* a syringe pump over 2 h at room temperature, and the reaction mixture was stirred for additional 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel without any additional treatment (eluent: PE/EA = 10:1 ~ 1:1, v/v) to give 85.4 mg of the product **8a** as a single diastereomer in >95% yield. Dark green oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (comp, 6H), 6.77 (d, *J* = 6.8 Hz, 1H), 6.70 – 6.60 (m, 2H), 6.31 (d, *J* = 6.8 Hz, 1H), 5.41 (d, *J* = 5.2 Hz, 1H), 4.57 (d, *J* = 9.2 Hz, 1H), 4.49 – 4.31 (comp, 4H), 3.83 – 3.76 (m, 1H), 3.64 (s, 3H), 3.36 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.0, 169.8, 169.2, 141.6, 140.8, 136.0, 127.6, 127.1, 126.5, 120.1, 118.2, 108.0, 104.7, 85.9, 65.3, 60.8, 51.4, 50.7, 50.4, 50.0, 46.1, 13.2; HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{27}N_2O_6$ $[M+H]^+$: 439.1864, found 439.1869.



To a 10-mL oven-dried vial containing a magnetic stirring bar, **7a** (87.6 mg, 0.2 mmol), DDQ (99.9 mg, 0.44 mmol) in DCM (4.0 mL) were added sequentially at room temperature. Then the reaction mixture was stirred for 1 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel without any additional treatment (eluent: PE/EA = 10:1 ~ 1:1, v/v) to give 85.3 mg of the pure product **5a** as pale yellow solid in >95% yield.



8a **5a**, >95%

To a 10-mL oven-dried vial containing a magnetic stirring bar, **8a** (87.6 mg, 0.2 mmol), DDQ (99.9 mg, 0.44 mmol) in DCM (4.0 mL) were added sequentially at room temperature. Then the reaction solution was stirred for 1 h. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel without any additional treatment (eluent: PE/EA = 10:1 ~ 1:1, v/v) to give 83.1 mg of the pure product **5a** as pale yellow solid in >95% yield.

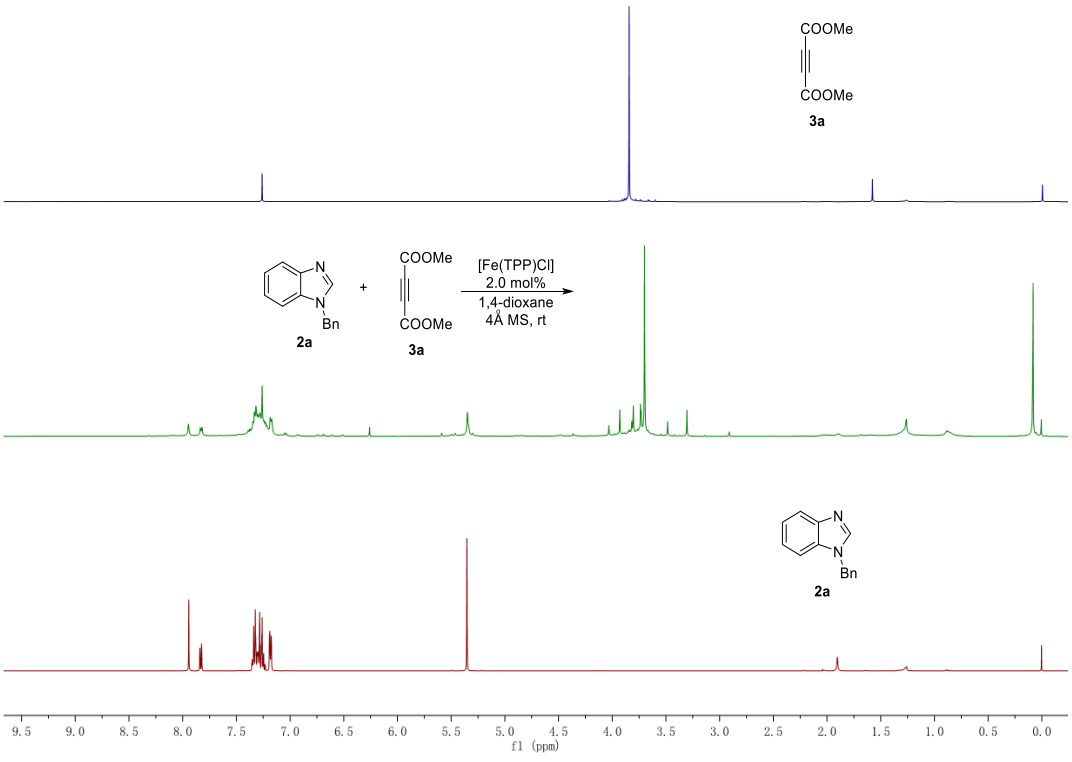


Figure S1. Proton NMR spectra of the crude reaction mixture of **2a** with **3a**.

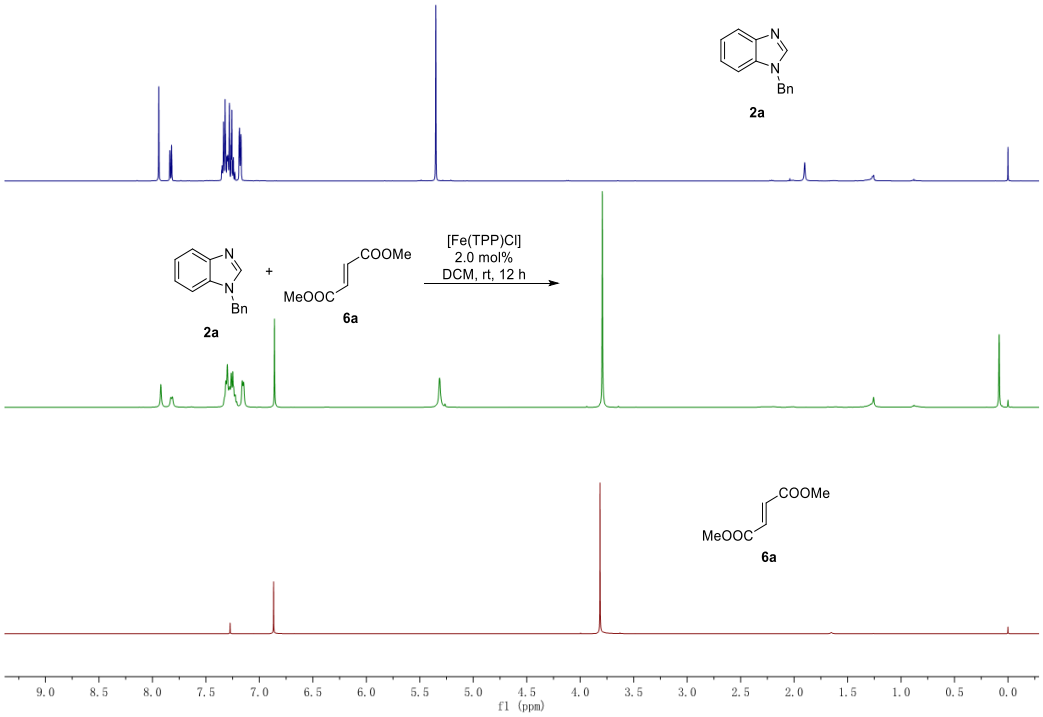


Figure S2. Proton NMR spectra of the crude reaction mixture of **2a** with **6a**.

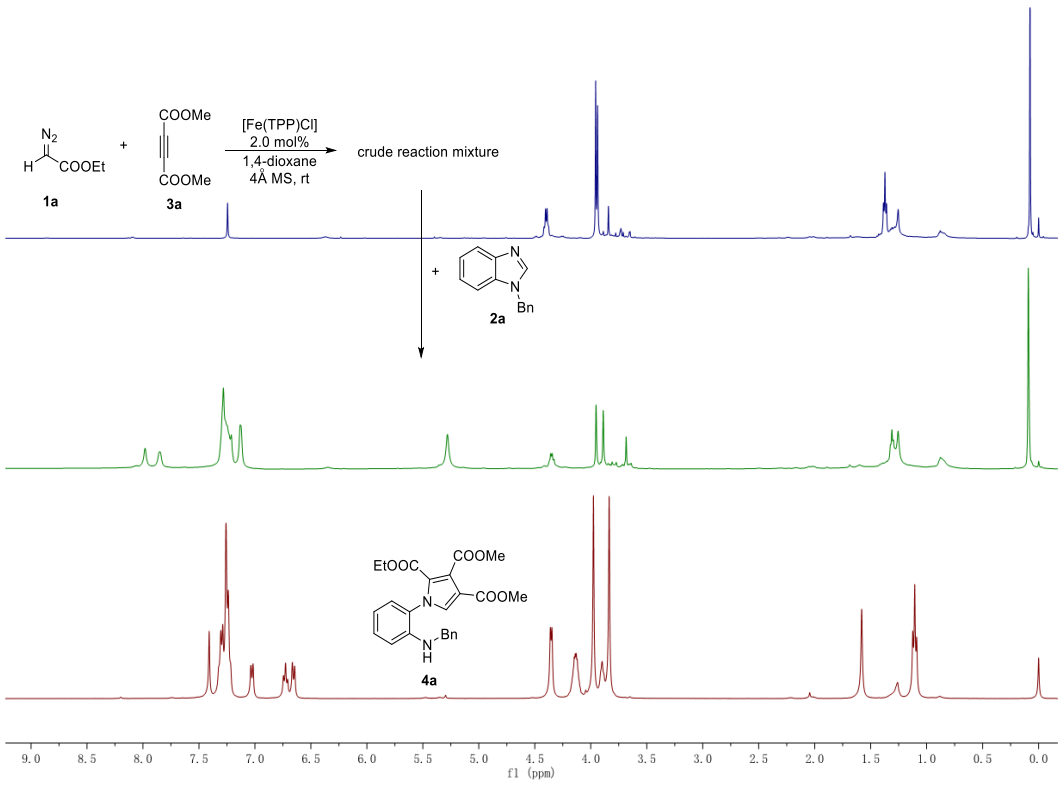


Figure S3. Proton NMR spectra of the crude reaction mixture of **5q**.

1D-NOE NMR Analysis

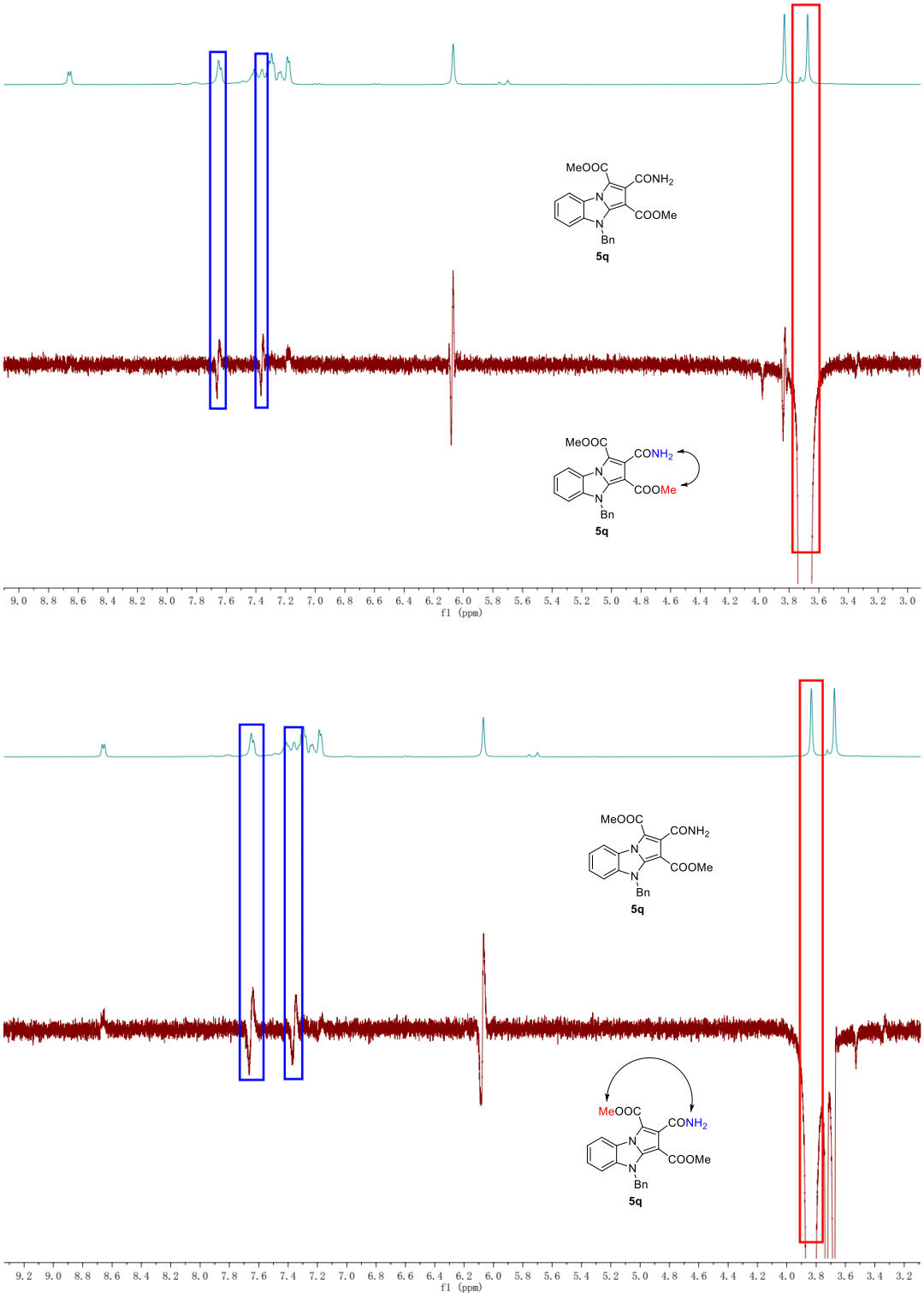


Figure S4. NOE NMR spectra of **5q**.

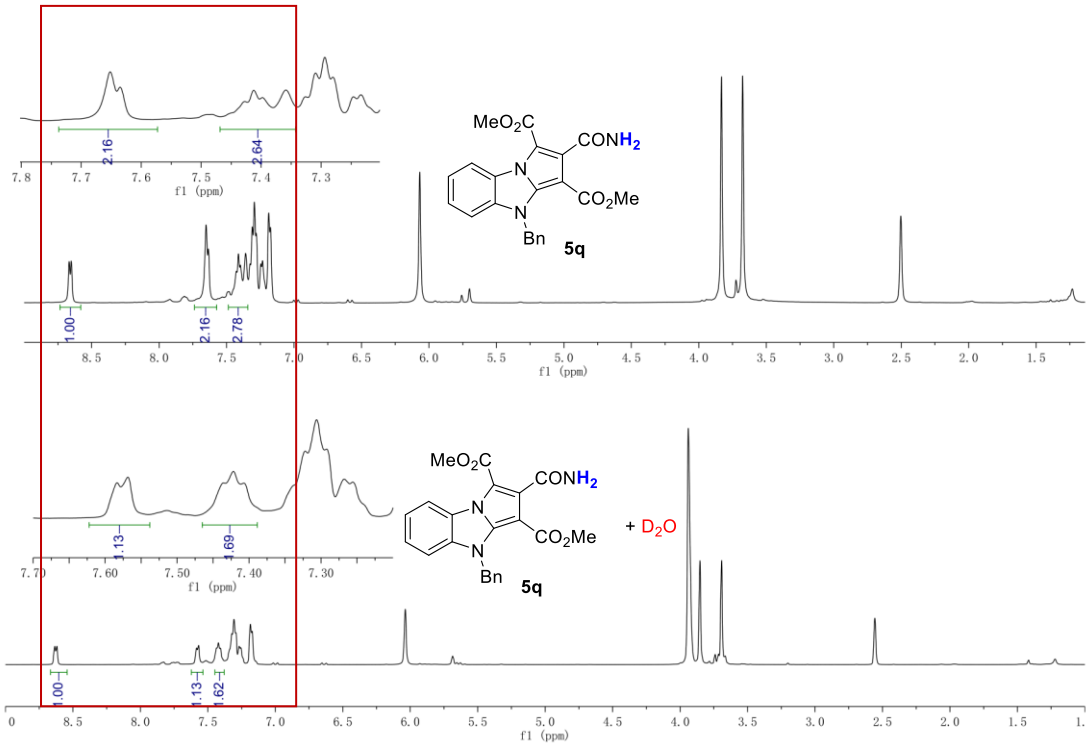
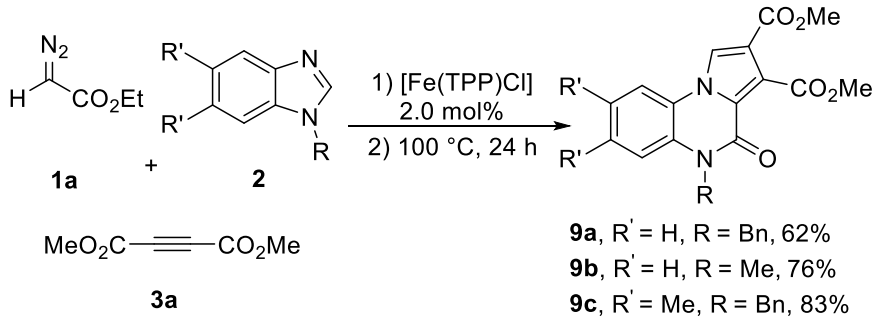
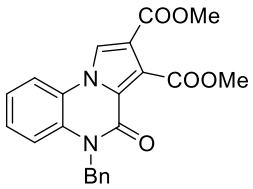


Figure S5. NMR Spectra of D_2O exchange experiment of **5q**.

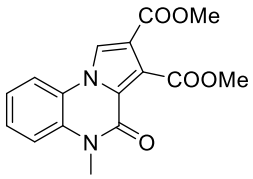
Derivatizations:



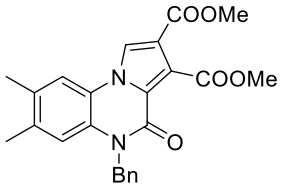
Synthesis of 9: To a 10-mL oven-dried vial containing a magnetic stirring bar, [Fe(TPP)Cl] (2.7 mg, 2.0 mol%), 100 mg 4 Å MS, alkyne **3a** (28.4 mg, 0.20 mmol), and benzimidazole **2** (0.24 mmol) in 1,4-dioxane (3.0 mL), diazo compound **1a** (34.3 mg, 0.30 mmol) in 1,4-dioxane (1.0 mL) was added slowly *via* a syringe pump over 2 h at room temperature under argon atmosphere, and the reaction solution was stirred for another 12 h. Then the reaction solution was stirred for additional 24 h at 100 °C. After the completion of the reaction (monitored by TLC), the reaction mixture was purified by flash chromatography on silica gel without any additional treatment (eluent: PE/EA = 20:1 ~ 1:1, v/v) to give the pure products **9** in 62-83% yields.



Dimethyl 5-benzyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (9a).[6] 47.5 mg, 62% yield. White solid; mp = 259.2-261.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 (s, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.34 – 7.24 (comp, 8H), 5.47 (s, 2H), 4.04 (s, 3H), 3.90 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 162.9, 154.5, 135.6, 129.9, 128.9, 127.6, 127.5, 126.6, 123.6, 122.7, 121.2, 120.8, 118.9, 117.9, 117.1, 115.2, 53.1, 52.1, 45.2; HRMS (TOF MS ESI$^+$) calculated for $C_{22}H_{19}N_2O_5$ $[M+H]^+$: 391.1288, found 391.1287.

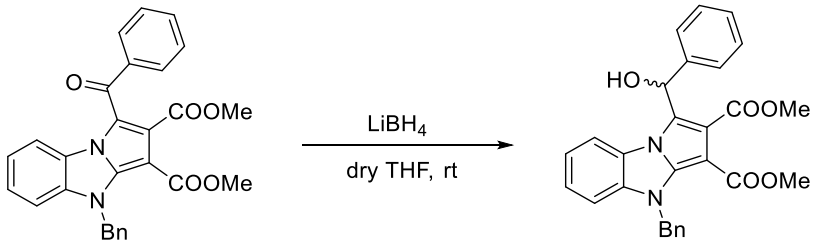


Dimethyl 5-methyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (9b).[7] 46.8 mg, 76% yield. White solid; mp = 245.4-246.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.73 (s, 1H), 7.44 (s, 1H), 7.38 – 7.23 (m, 2H), 4.04 (s, 3H), 3.89 (s, 3H), 3.63 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.5, 162.9, 154.2, 130.7, 127.5, 123.6, 122.5, 121.0, 120.8, 118.6, 117.7, 116.1, 115.1, 53.1, 52.1, 28.5; HRMS (TOF MS ESI$^+$) calculated for $C_{16}H_{14}N_2O_5Na$ $[M+Na]^+$: 337.0795, found 337.0794.



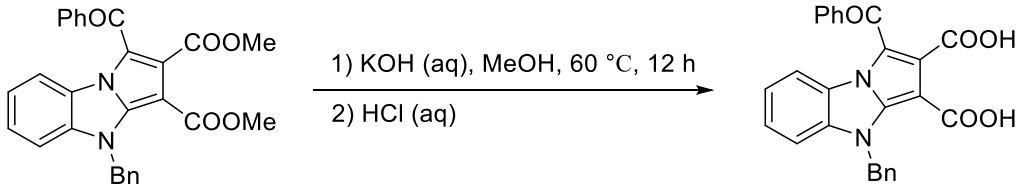
Dimethyl 5-benzyl-7,8-dimethyl-4-oxo-4,5-dihydropyrrolo[1,2-*a*]quinoxaline-2,3-dicarboxylate (9c).[6] 67.7 mg, 83% yield. Pale yellow solid; mp = 275.3-276.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.46 (s, 1H), 7.32 – 7.22 (comp, 5H), 7.00 (s, 1H), 5.42 (s, 2H), 4.04 (s, 3H), 3.89 (s, 3H), 2.30 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.6, 163.0, 154.4, 136.4, 135.9, 132.5, 128.9, 127.7, 127.5, 126.7, 120.81, 120.80, 120.4, 118.5, 117.8, 117.4, 115.9, 53.1, 52.0, 45.1, 20.1, 19.4;

HRMS (TOF MS ESI$^+$) calculated for $C_{24}H_{23}N_2O_5$ $[M+H]^+$: 419.1601, found 419.1610.



5f **10f**, 77%

Synthesis of 10f: To a 25-mL oven-dried round-bottom flask containing a magnetic stirring bar, **5f** (93.3 mg, 0.2 mmol), $LiBH_4$ (21.3 mg, 1.2 mmol), and dry THF (15.0 mL) were added sequentially at room temperature, and the reaction mixture was stirred for 1.0 h. After the completion of the reaction (monitored by TLC), the reaction was quenched by saturated aqueous NH_4Cl (5.0 mL), and extracted with EtOAc (10 mL X 3). The combined organic layer was washed with brine, drying over anhydrous $MgSO_4$ and concentration in vacuo after filtration, the crude product was purified by flash chromatography on silica gel (eluent: PE/EA= 10:1 ~ 5:1, v/v) to afford the pure product **10f** (71.7mg, 77% yield). White solid; mp = 109.3-111.2 ^oC; ^1H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.9 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.32 – 7.21 (comp, 8H), 7.18 – 7.07 (m, 2H), 6.97 (t, *J* = 7.0 Hz, 1H), 6.43 (s, 1H), 5.93 – 5.81 (m, 2H), 3.83 (s, 3H), 3.73 (s, 3H), 3.40 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.1, 163.9, 141.4, 140.0, 137.0, 136.9, 128.7, 128.5, 127.6, 127.5, 126.8, 126.2, 125.5, 124.1, 122.5, 120.9, 120.4, 114.7, 109.9, 86.6, 67.4, 52.4, 51.3, 48.4; HRMS (TOF MS ESI$^+$) calculated for $C_{28}H_{24}N_2O_5Na$ $[M+Na]^+$: 491.1577, found 491.1574.



5f **11f**, 63%

Synthesis of 11f: To a 25-mL oven-dried round-bottom flask containing a magnetic

stirring bar, **5f** (140.0 mg, 0.3 mmol), 1N aqueous KOH (10 mL, 10 mmol), and MeOH (20 mL) were added sequentially at room temperature and stirred for 12.0 h at 60 ℃. After the completion of the reaction (monitored by TLC), the methanol was removed in vacuo and the remaining residue was dissolved in water (30 mL). This aqueous solution was acidified with 2 N HCl until it became acidic (pH ≈ 1). Then the mixture was extracted with ethyl acetate (25 mL X 2) and the combined organic layer was washed with water (10 mL) and dried over anhydrous Na_2SO_4. The solvent was concentrated in vacuo after filtration and the crude product was purified by flash chromatography on silica gel (eluent: PE/EA = 10:1 ~ 1:1, v/v) to afford the pure product **11f** (82.8mg, 63% yield). Pale yellow solid; mp = 244.3-246.1 ^{o}C; ^{1}H NMR (500 MHz, DMSO) δ 7.96 – 7.79 (m, 2H), 7.62 – 7.51 (m, 2H), 7.51 – 7.43 (m, 2H), 7.38 (s, 1H), 7.36 – 7.25 (comp, 5H), 7.22 (s, 1H), 7.09 (s, 1H), 6.36 (s, 2H); ^{13}C NMR (125 MHz, DMSO) δ 189.5, 166.6, 166.2, 141.1, 139.1, 138.3, 136.9, 132.6, 129.0, 128.6, 128.4, 127.3, 124.7, 124.6, 120.7, 119.0, 112.6, 111.4, 93.1, 47.4; HRMS (TOF MS ESI$^+$) calculated for $C_{26}H_{18}N_2O_5Na$ $[M+Na]^+$: 461.1108, found 461.1111.

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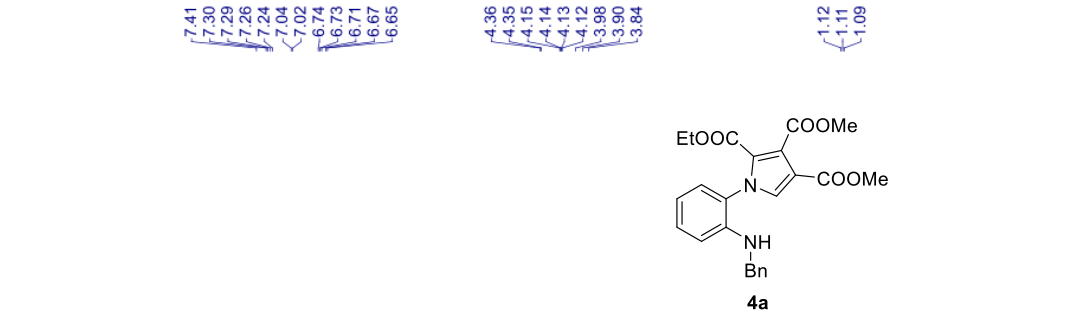
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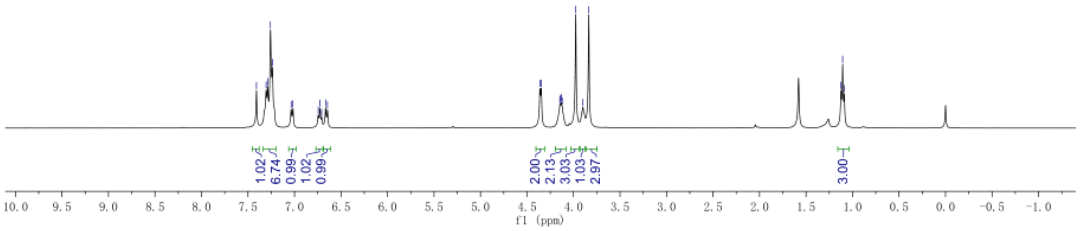
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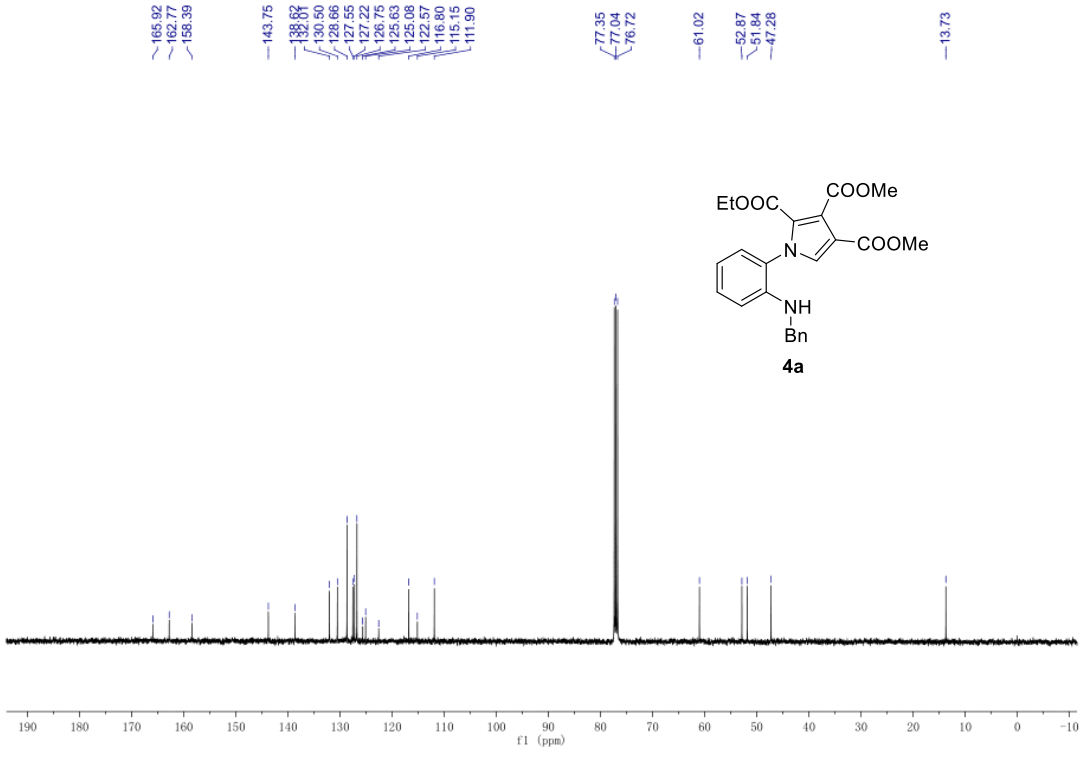
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127.22
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125.63
125.08
122.57
116.80
115.15
111.90
77.35
77.04
76.72
61.02
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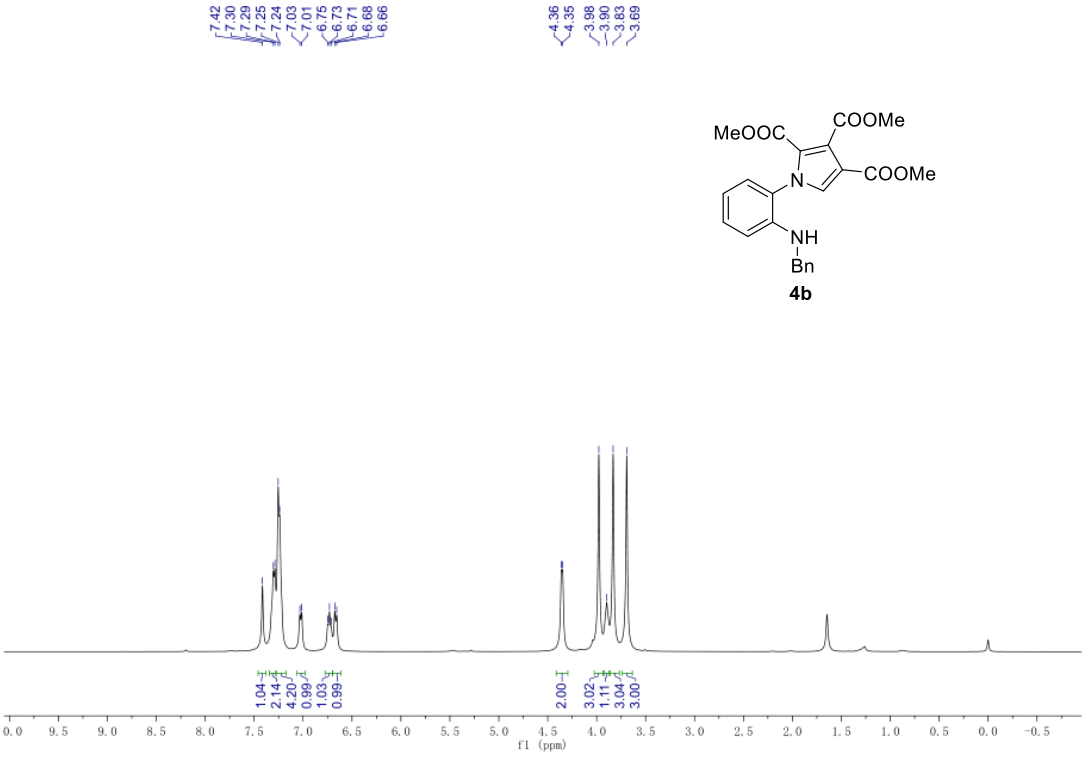
51.84
47.28
13.73
EtOOC
COOMe
COOMe
N
NH
Bn
4a
f1 (ppm)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7.03
7.01
6.75
6.73
6.71
6.68
6.66
4.36
4.35
3.98
3.90
3.83
3.69
MeOOC
COOMe
COOMe
N
NH
Bn
4b
1.04
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4.20
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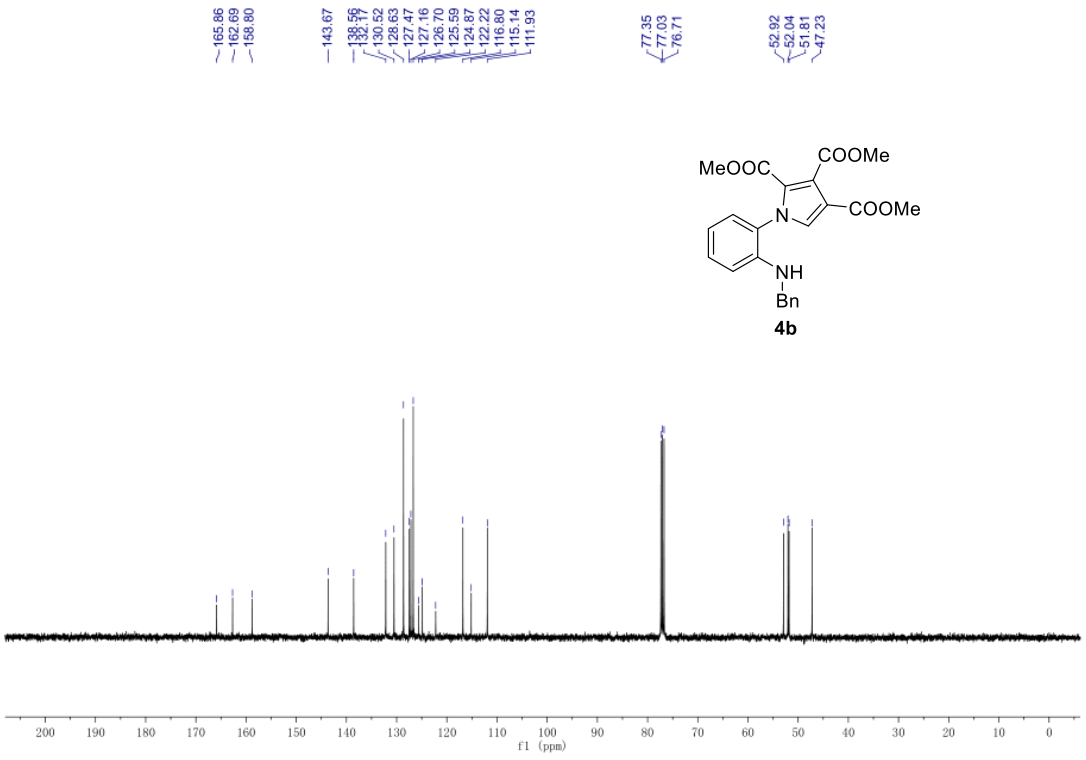
1.03
0.99
2.00
3.02
1.11
3.04
3.00
f1 (ppm)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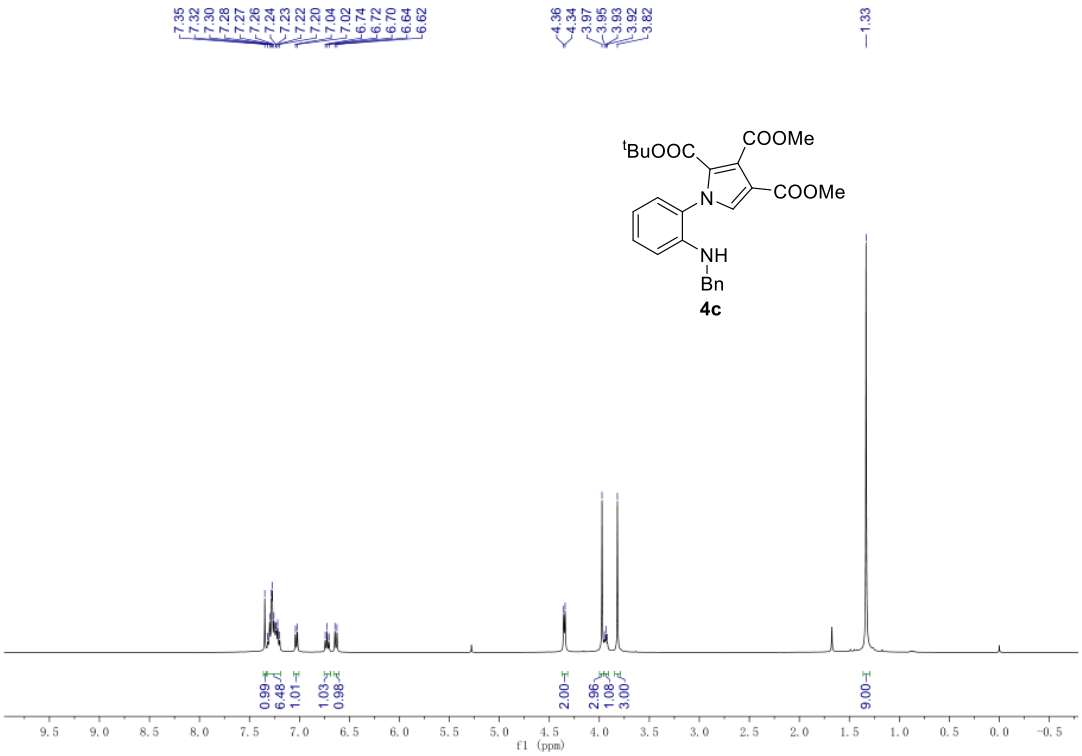
125.59
124.87
122.22
116.80
115.14
111.93
77.35
77.03
76.71
52.92
52.04
51.81
47.23
MeOOC
COOMe
COOMe
N
NH
Bn
4b
f1 (ppm)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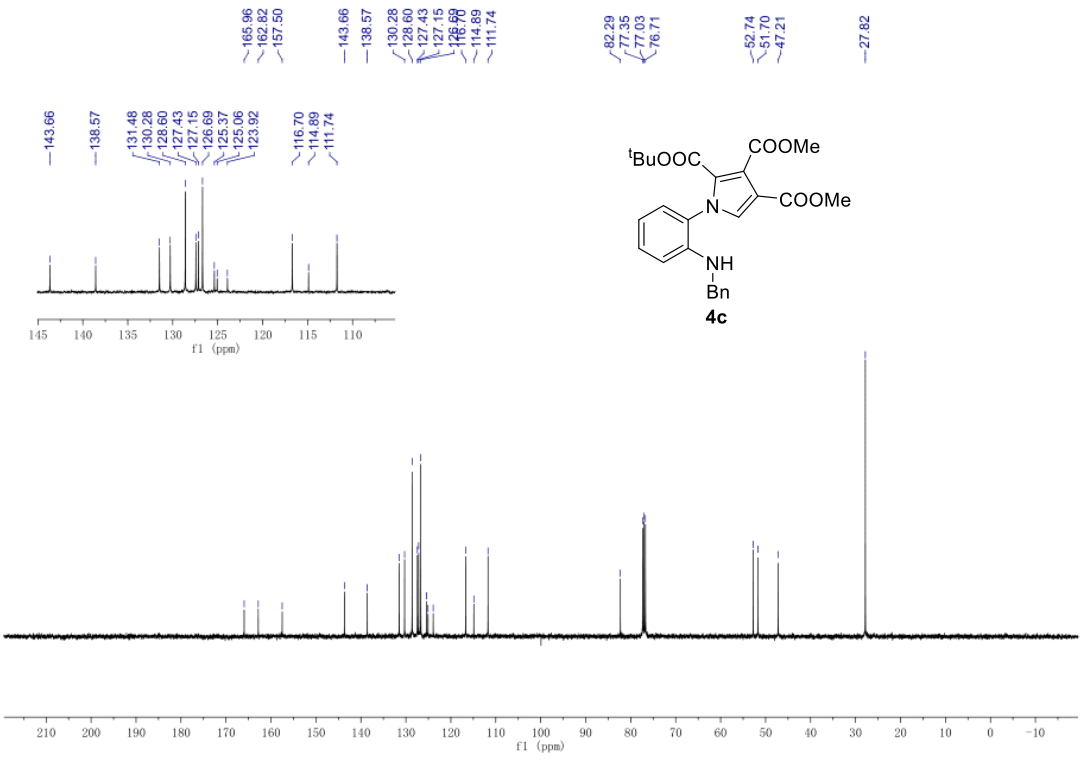
7.23
7.22
7.20
7.04
7.02
6.74
6.72
6.70
6.64
6.62
4.36
4.34
3.97
3.95
3.93
3.92
3.82
1.33
tBuOOC
COOMe
COOMe
N
NH
Bn
4c
0.99
6.48
1.01
1.03
0.98
2.00
2.96
1.08
3.00
9.00
f1 (ppm)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82.29
77.35
77.03
76.71
52.74
51.70
47.21
27.82
143.66
138.57
131.48
130.28
128.60
127.43
127.15
126.69
125.37
125.06
123.92
116.70
114.89
111.74
tBuOOC
COOMe
COOMe
N
NH
Bn
4c
f1 (ppm)
f1 (ppm)


7.41
7.30
7.29
7.28
7.26
7.24
7.22
7.21
7.18
7.17
7.16
7.04
7.02
6.74
6.72
6.70
6.64
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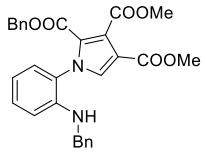
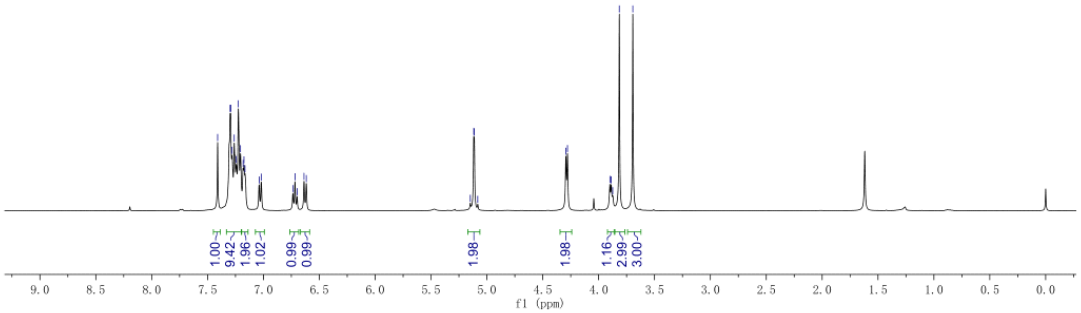
3.87
3.82
3.69


BnOOC
COOMe
COOMe
N
NH
Bn

4d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1.98
1.98
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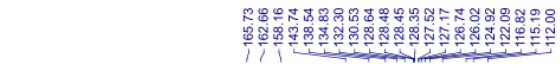
2.99
3.00
f1 (ppm)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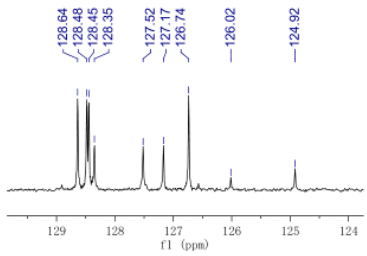
132.30
130.53
128.64
128.48
128.45
128.35
127.52
127.17
126.74
126.02
124.92
122.09
116.82
115.19
112.00
77.35
77.03
76.71
67.00
52.68
51.81
47.24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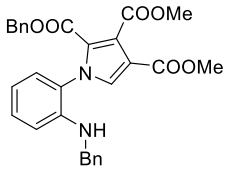
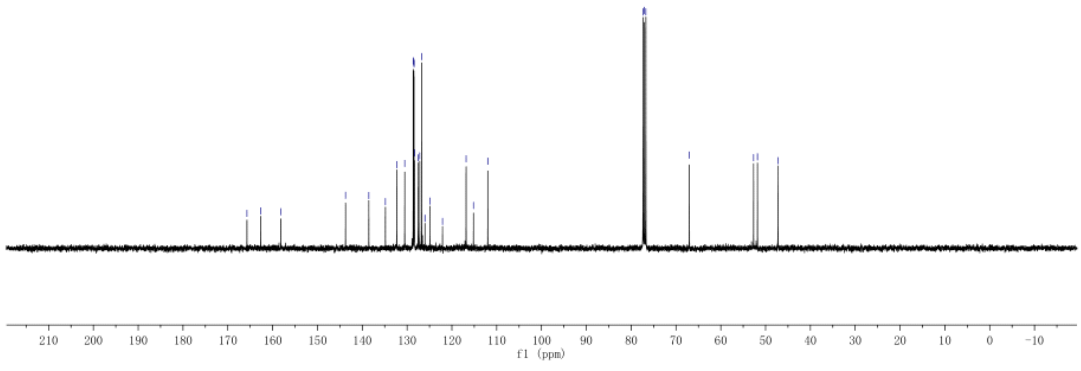
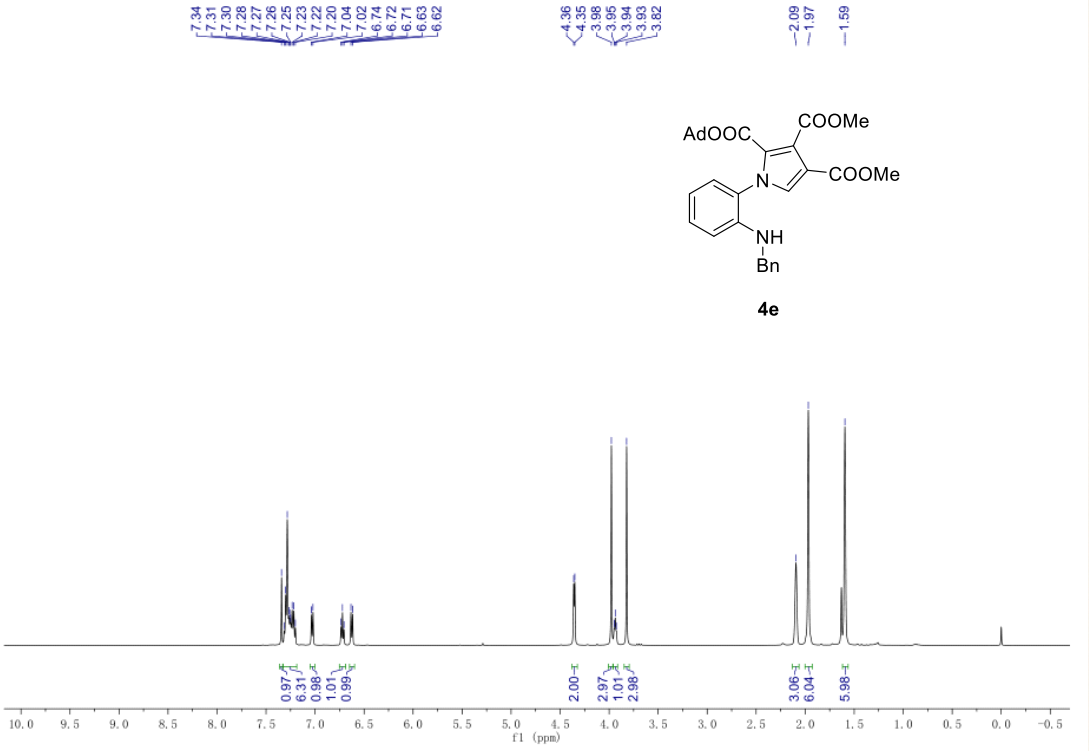
128.48
128.45
128.35
127.52
127.17
126.74
126.02
124.92
f1 (ppm)


BnOOC
COOMe
COOMe
N
NH
Bn

4d


f1 (ppm)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7.23
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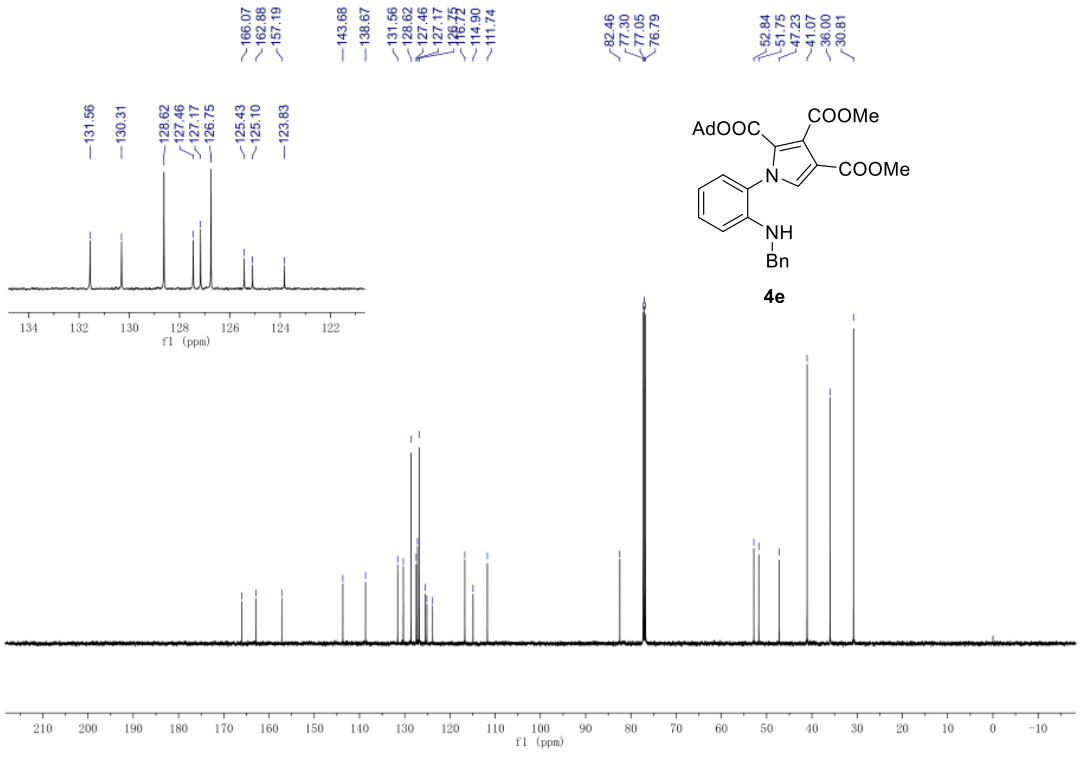
7.20
7.04
7.02
6.74
6.72
6.71
6.63
6.62
4.36
4.35
3.98
3.95
3.94
3.93
3.82
2.09
1.97
1.59
AdOOC
COOMe
COOMe
N
NH
Bn
4e
0.97
6.31
0.98
1.01
0.99
2.00
2.97
1.01
2.98
3.06
6.04
5.98
f1 (ppm)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126.75
125.43
125.10
123.83
114.90
111.74
82.46
77.30
77.05
76.79
52.84
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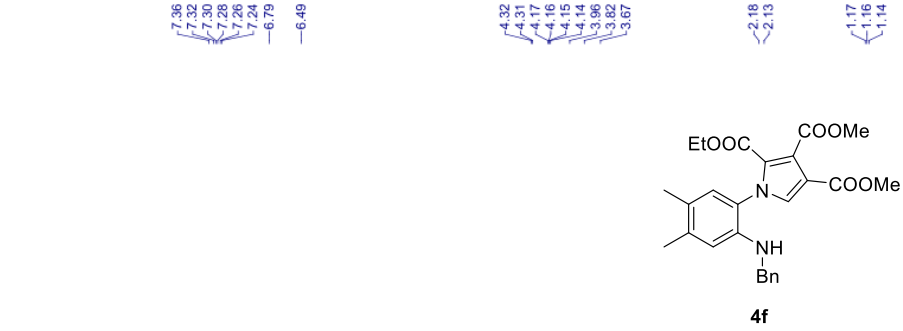
COOMe
N
NH
Bn
4e
f1 (ppm)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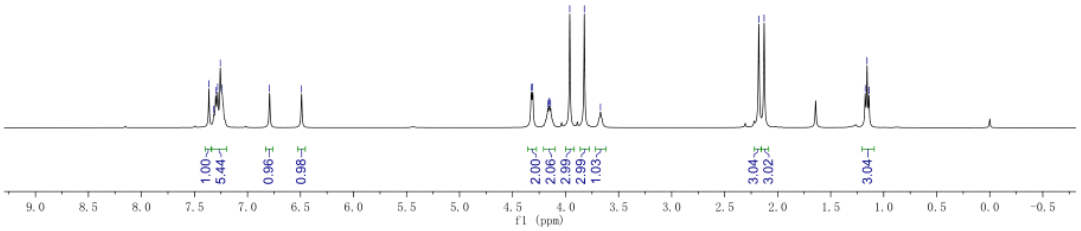
7.24
6.79
6.49
4.32
4.31
4.17
4.16
4.15
4.14
3.96
3.82
3.67
2.18
2.13
1.17
1.16
1.14
EtOOC
COOMe
COOMe
N
NH
Bn

4f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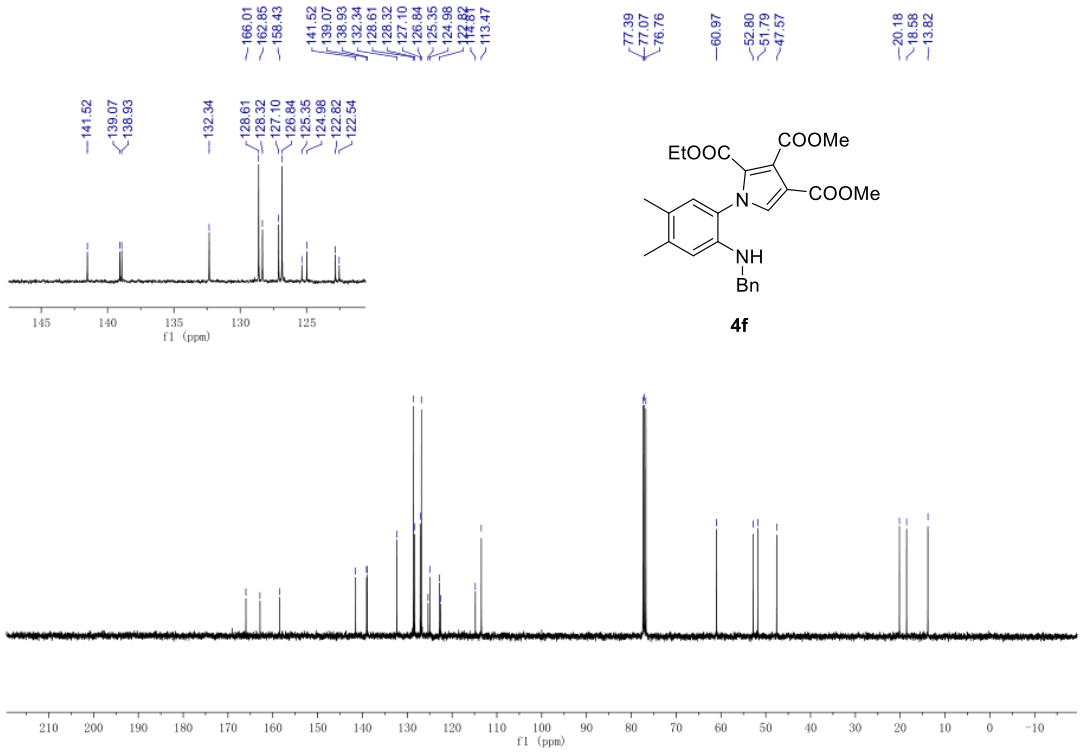
2.06
2.99
2.99
1.03
3.04
3.02
3.04
f1 (ppm)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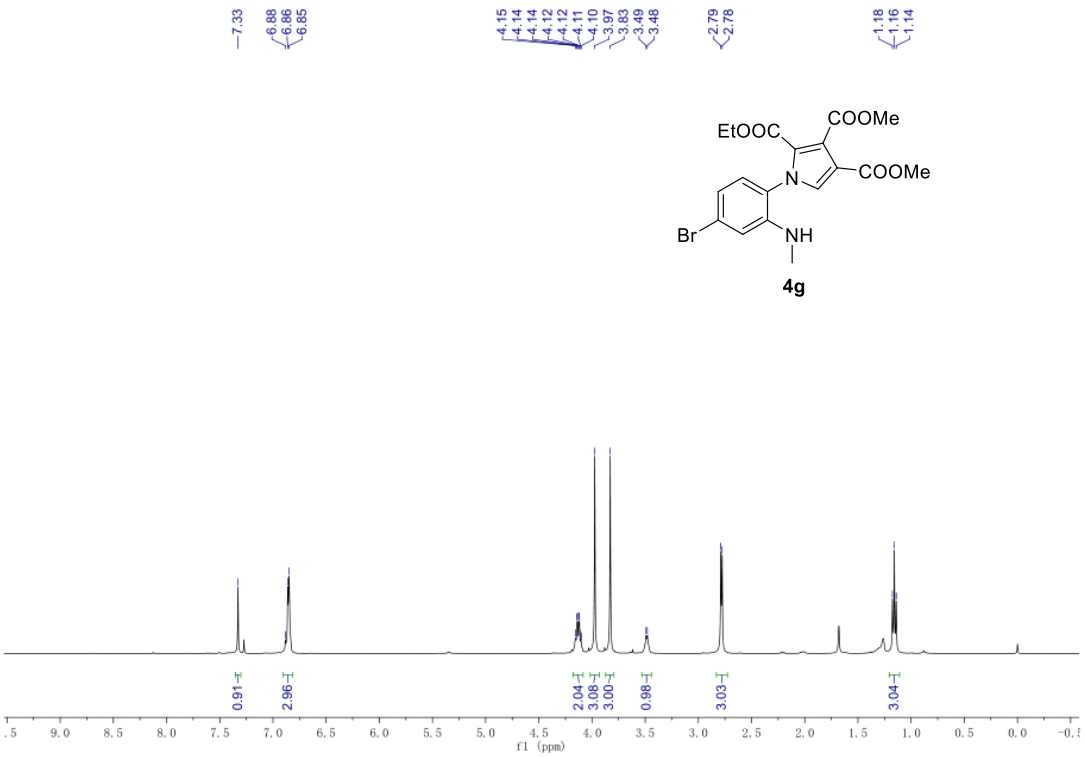
138.93
132.34
128.61
128.32
127.10
126.84
125.35
124.98
122.82
122.54
113.47
77.39
77.07
76.76
60.97
52.80
51.79
47.57
20.18
18.58
13.82
EtOOC
COOMe
COOMe
N
NH
Bn
f1 (ppm)

4f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6.86
6.85
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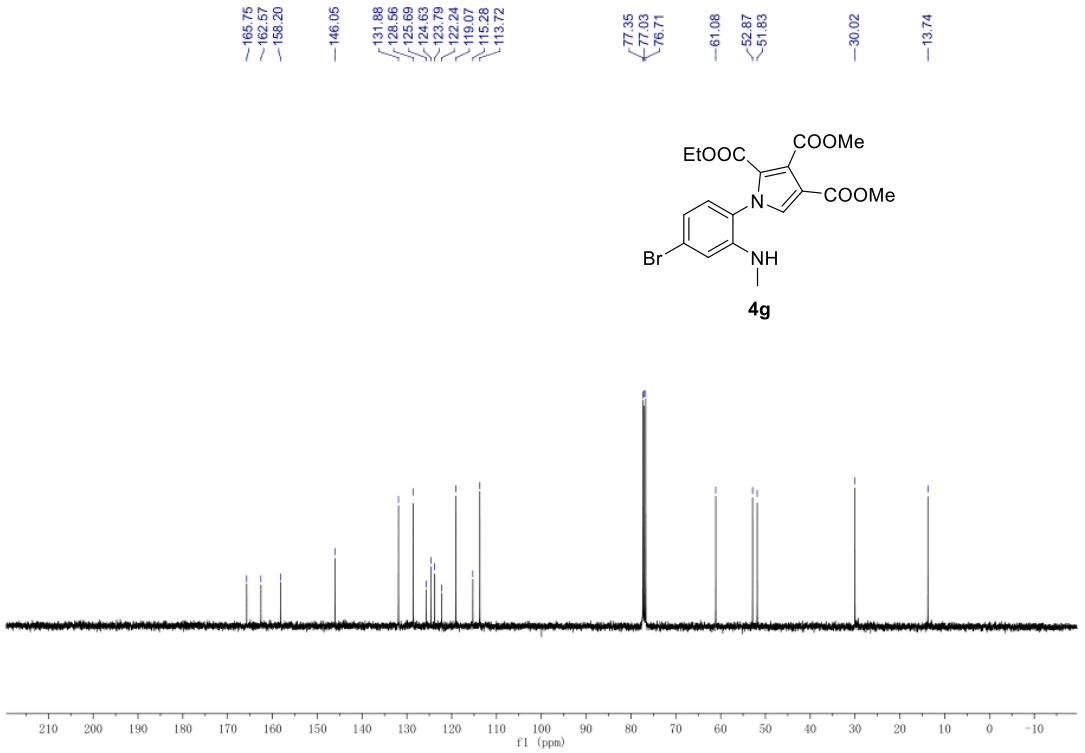
4.14
4.14
4.12
4.12
4.11
4.10
3.97
3.83
3.49
3.48
2.79
2.78
1.18
1.16
1.14
EtOOC
COOMe
COOMe
N
Br
NH
4g
0.91
2.96
2.04
3.08
3.00
0.98
3.03
3.04
f1 (ppm)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123.79
122.24
119.07
115.28
113.72
77.35
77.03
76.71
61.08
52.87
51.83
30.02
13.74
EtOOC
COOMe
COOMe
N
Br
NH
4g
f1 (ppm)


7.42
7.32
7.31
7.29
7.29
7.26
7.25
7.24
7.23
7.23
7.21
7.04
7.04
7.02
7.02
6.74
6.74
6.72
6.72
6.70
6.70
6.66
6.64
4.47
4.45
4.43
4.41
4.36
4.35
4.33
4.31
4.29
4.27
4.20
4.18
4.17
4.16
4.16
4.15
4.14
4.13
4.12
4.11
4.10
4.08
3.95
3.94
3.92
1.45
1.43
1.41
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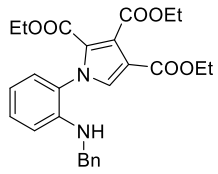
1.33
1.31
1.12
1.10
1.09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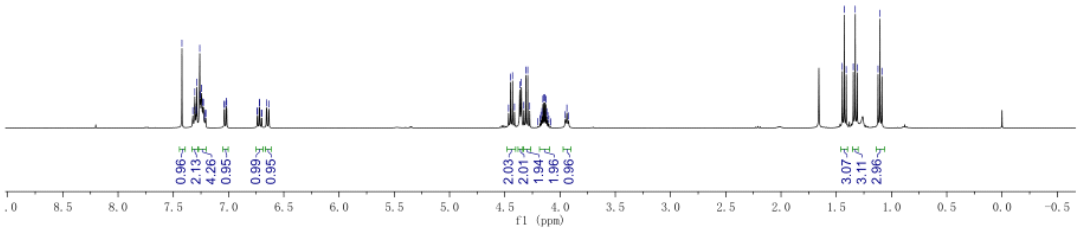
COOEt
COOEt
N
NH
Bn

4h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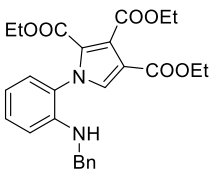
0.95
0.99
0.95
2.03
2.01
1.94
1.96
0.96
3.07
3.11
2.96
f1 (ppm)


165.50
162.34
158.44
143.72
138.63
132.05
130.40
128.61
127.51
127.15
126.71
125.84
125.13
122.32
116.71
115.44
111.80
77.35
77.03
76.71
61.87
60.91
60.61
47.20
14.24
14.12
13.73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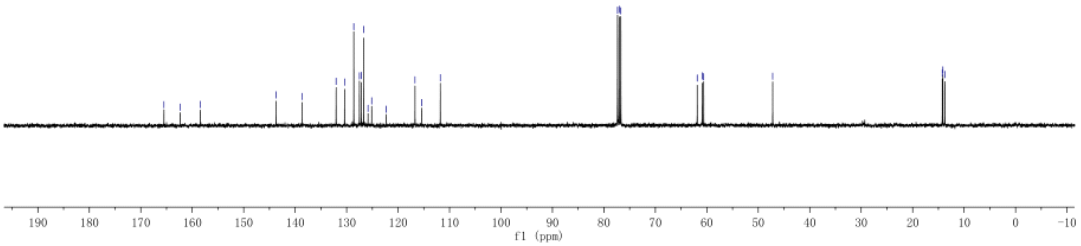
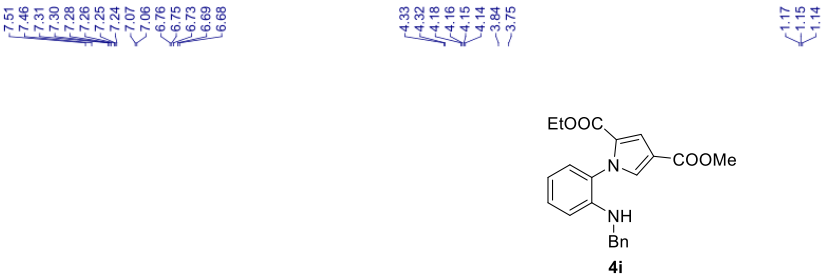
COOEt
COOEt
N
NH
Bn

4h


f1 (ppm)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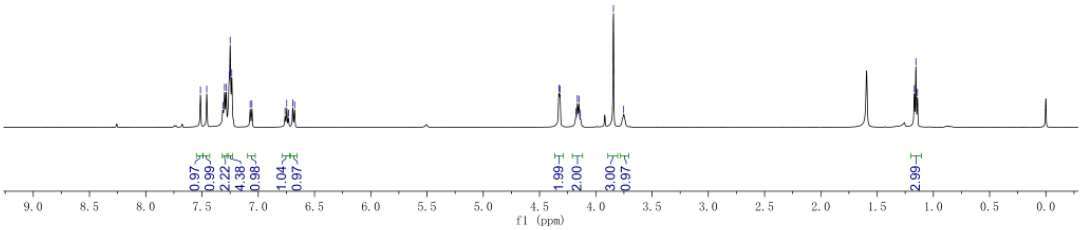
7.24
7.07
7.06
6.76
6.75
6.73
6.69
6.68
4.33
4.32
4.18
4.16
4.15
4.14
3.84
3.75
1.17
1.15
1.14
EtOOC
COOMe
N
NH
Bn

4i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1.04
0.97
1.99
2.00
3.00
0.97
2.99
f1 (ppm)


164.12
159.53
143.93
138.73
132.87
130.15
128.63
127.37
127.21
126.88
125.96
125.13
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117.01
116.79
111.67
77.35
77.03
76.71
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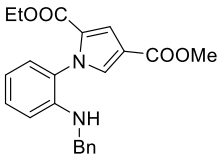
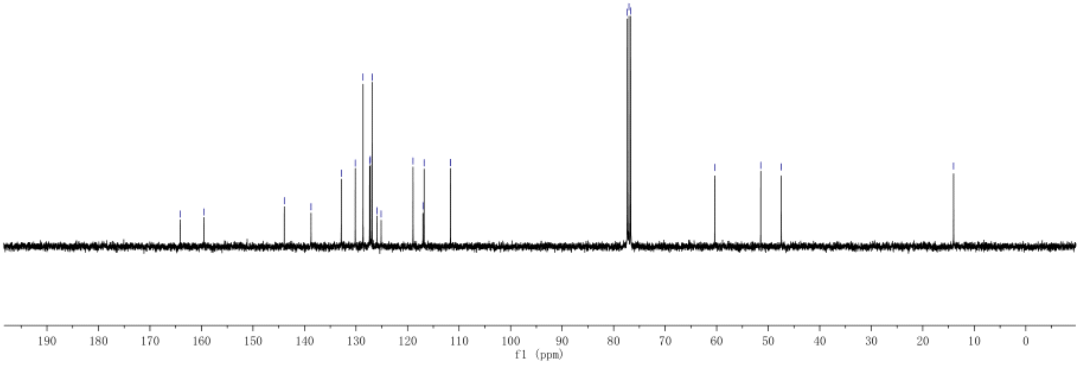
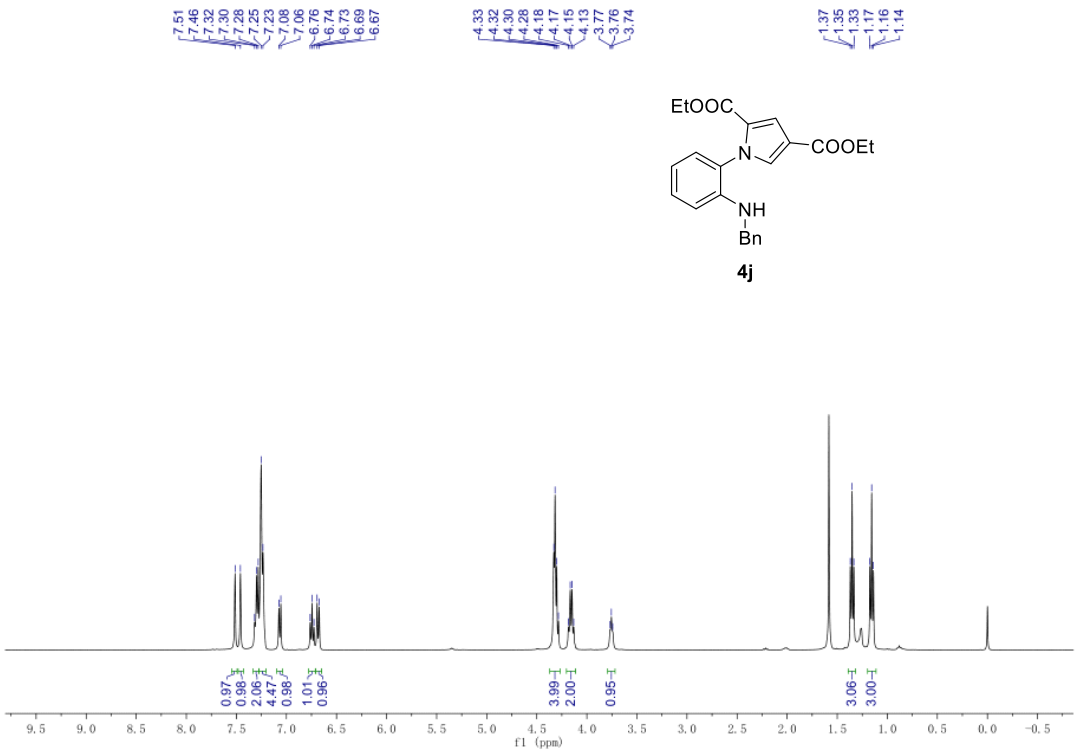
51.46
47.46
14.02


EtOOC
COOMe
N
NH
Bn

4i


f1 (ppm)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7.08
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6.76
6.74
6.73
6.69
6.67
4.33
4.32
4.30
4.28
4.18
4.17
4.15
4.13
3.77
3.76
3.74
1.37
1.35
1.33
1.17
1.16
1.14
EtOOC
COOEt
N
NH
Bn
4j
0.97
0.98
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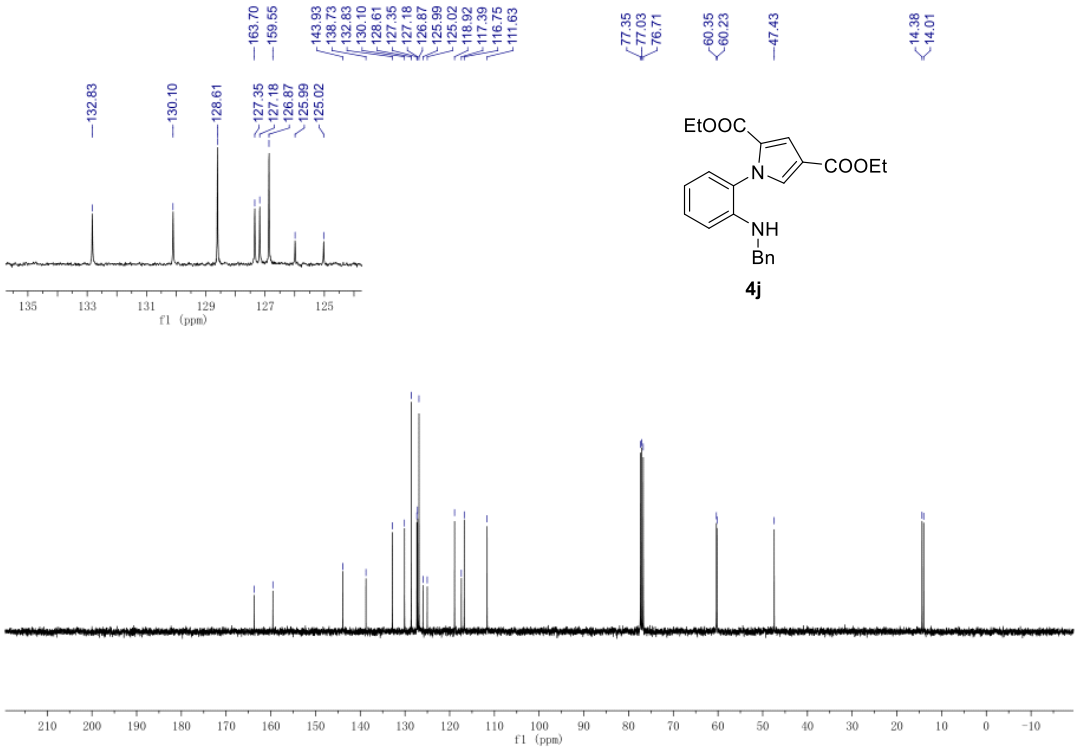
0.98
1.01
0.96
3.99
2.00
0.95
3.06
3.00
f1 (ppm)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130.10
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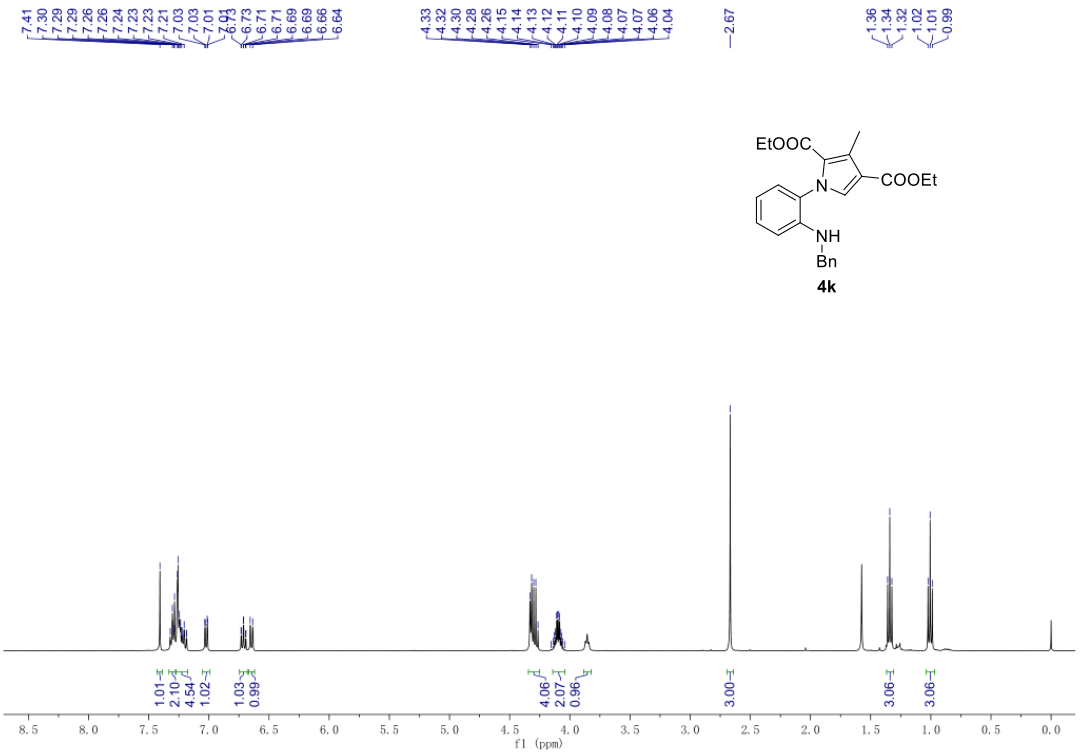
127.35
127.18
126.87
125.99
125.02
118.92
117.39
116.75
111.63
77.35
77.03
76.71
60.35
60.23
47.43
14.38
14.01
132.83
130.10
128.61
127.35
127.18
126.87
125.99
125.02
EtOOC
COOEt
N
NH
Bn
4j
f1 (ppm)
f1 (ppm)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7.01
6.74
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6.71
6.69
6.69
6.66
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4.32
4.30
4.28
4.26
4.15
4.14
4.13
4.12
4.11
4.10
4.09
4.08
4.07
4.07
4.06
4.04
2.67
1.36
1.34
1.32
1.02
1.01
0.99
EtOOC
COOEt
N
NH
Bn
4k
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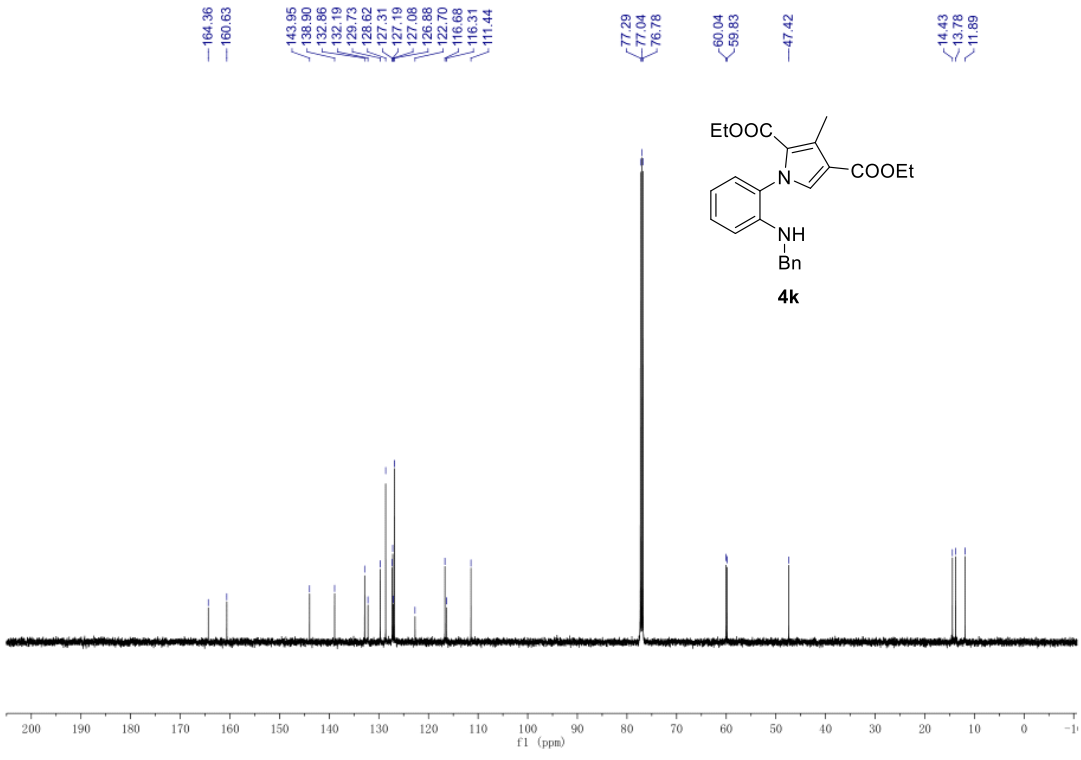
1.03
0.99
4.06
2.07
0.96
3.00
3.06
3.06
f1 (ppm)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127.08
126.88
122.70
116.68
116.31
111.44
77.29
77.04
76.78
60.04
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13.78
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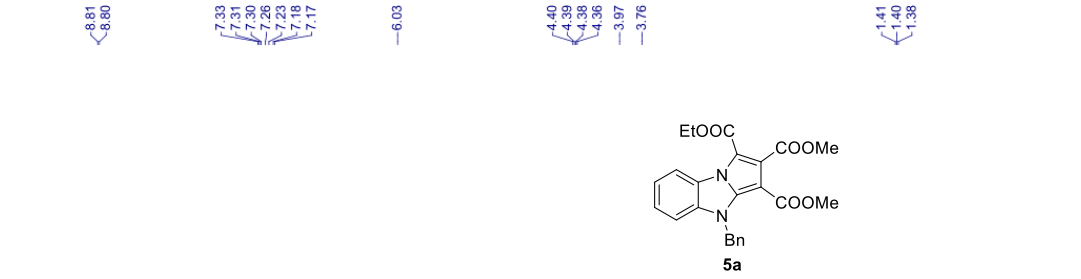
EtOOC
COOEt
N
NH
Bn
4k
f1 (ppm)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7.18
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6.03
4.40
4.39
4.38
4.36
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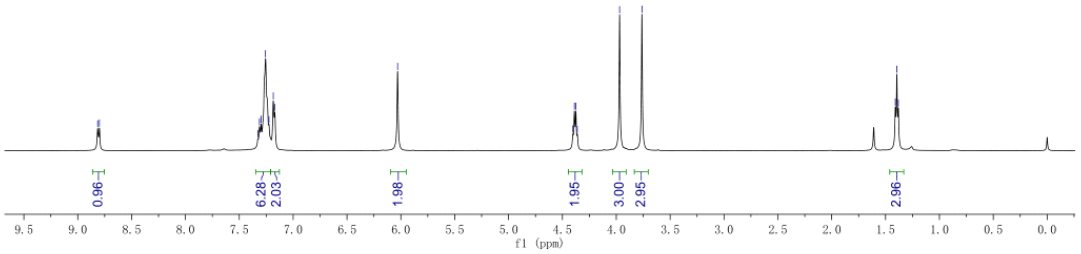
3.76
1.41
1.40
1.38
EtOOC
COOMe
COOMe
N
N
Bn
5a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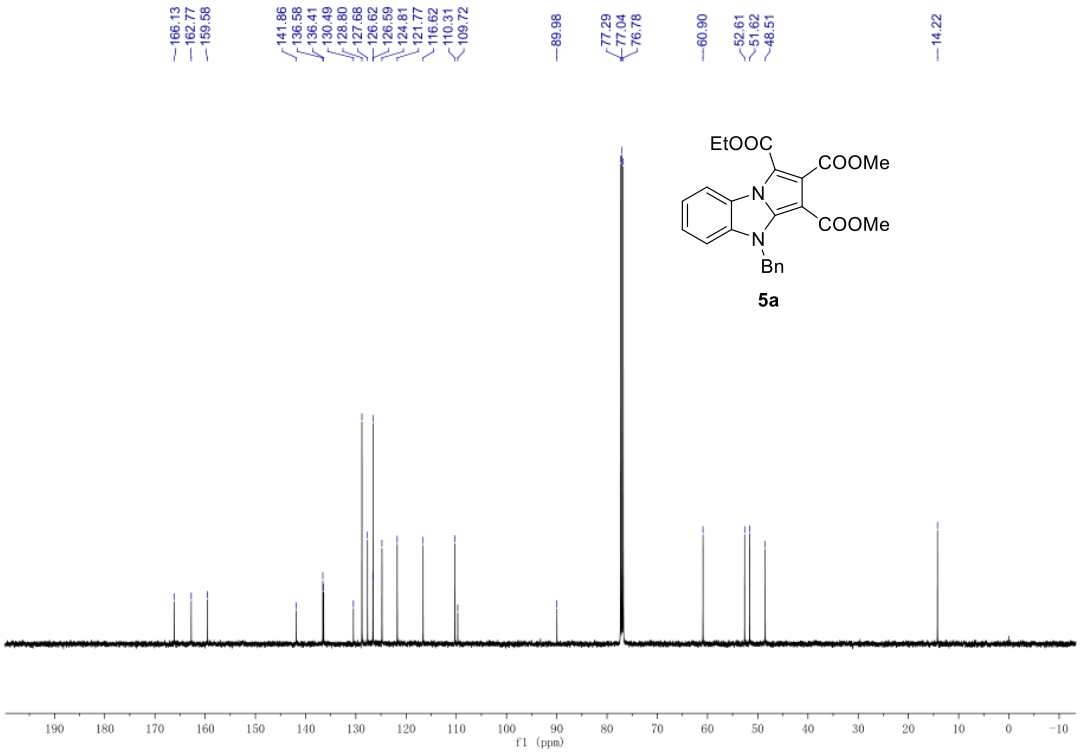
6.28
2.03
1.98
1.95
3.00
2.95
2.96
f1 (ppm)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128.80
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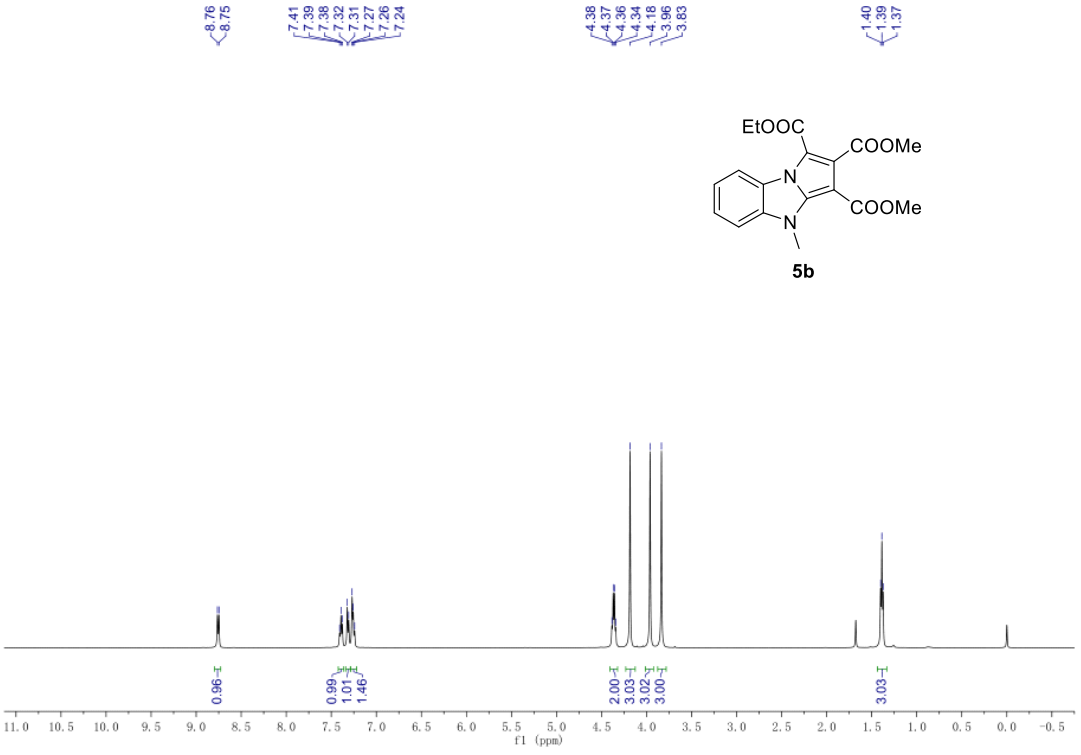
126.59
124.61
121.77
116.62
110.31
109.72
89.98
77.29
77.04
76.78
60.90
52.61
51.62
48.51
14.22
EtOOC
COOMe
COOMe
N
N
Bn
5a
f1 (ppm)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8.75
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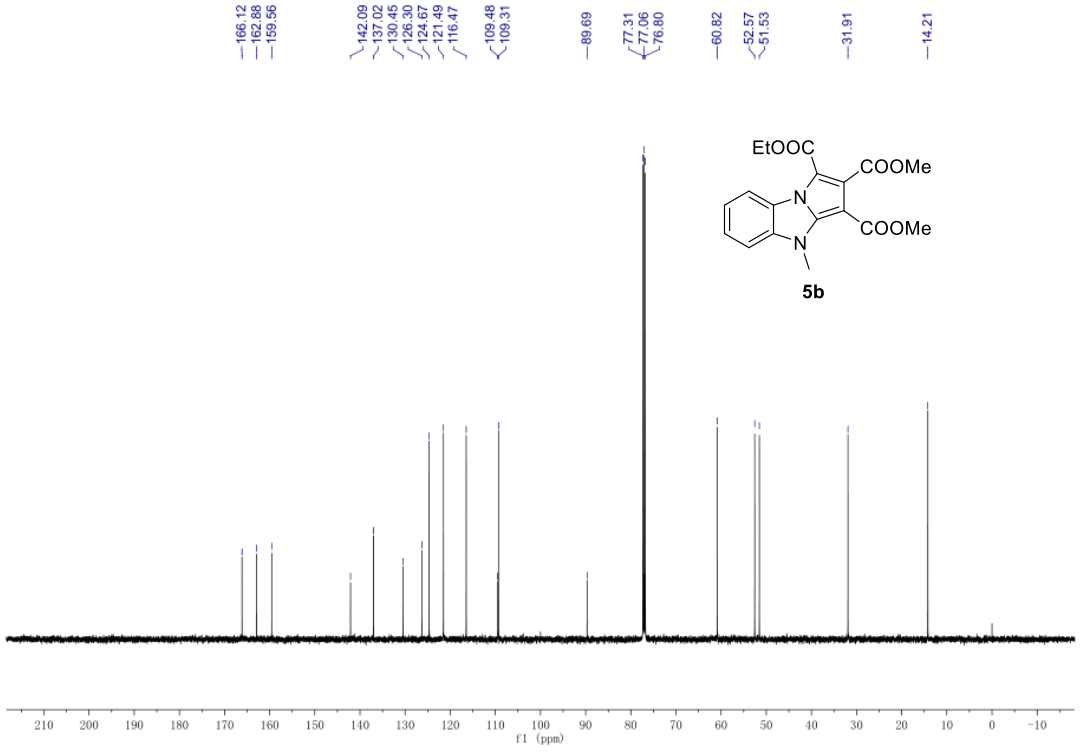
7.31
7.27
7.26
7.24
4.38
4.37
4.36
4.34
4.18
3.96
3.83
1.40
1.39
1.37
EtOOC
COOMe
COOMe
N
N
5b
0.96
0.99
1.01
1.46
2.00
3.03
3.02
3.00
3.03
f1 (ppm)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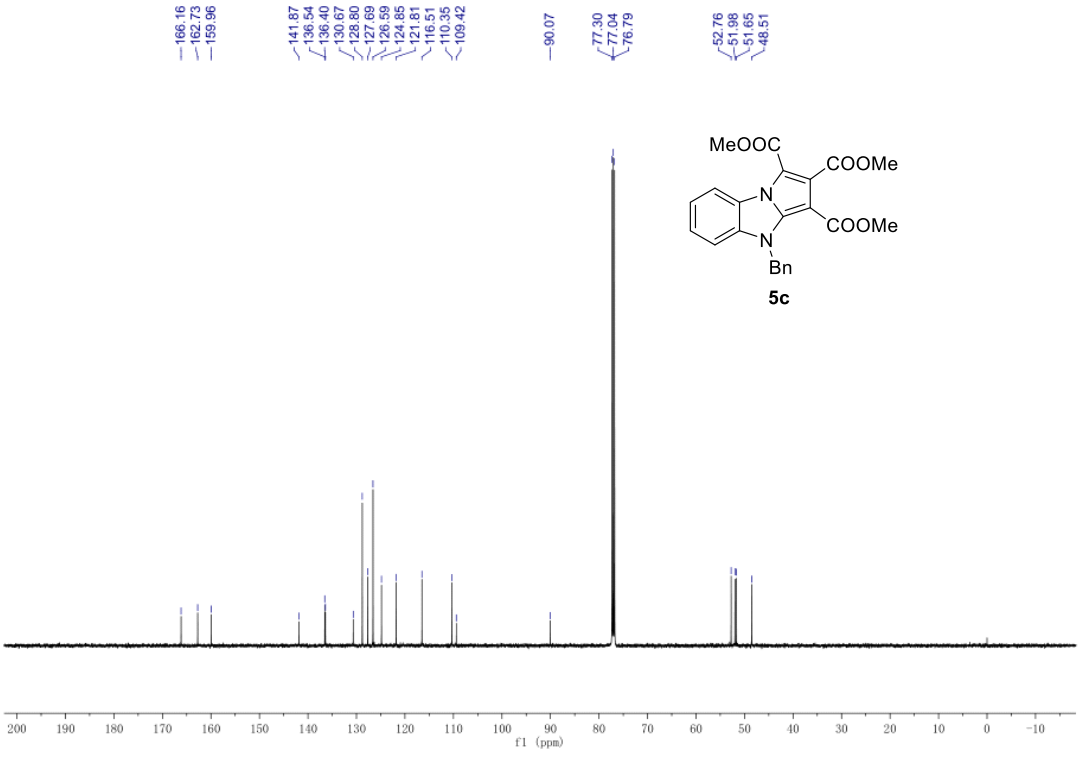
126.30
124.67
121.49
116.47
109.48
109.31
89.69
77.31
77.06
76.80
60.82
52.57
51.53
31.91
14.21
EtOOC
COOMe
COOMe
N
N
5b
f1 (ppm)


8.78
8.76
7.31
7.30
7.26
7.18
6.02
3.98
3.92
3.76
MeOOC
COOMe
COOMe
N
N
Bn
5c
0.99
6.32
1.93
1.98
2.98
3.00
3.00
f1 (ppm)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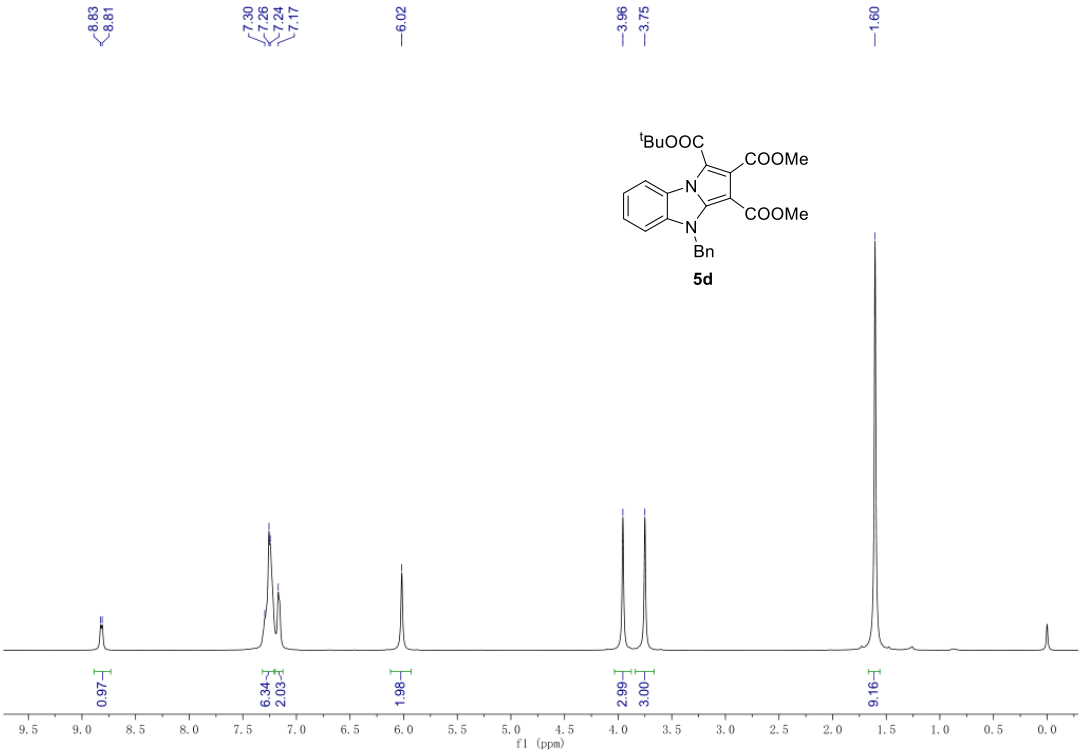
121.81
116.51
110.35
109.42
90.07
77.30
77.04
76.79
52.76
51.98
51.65
48.51
MeOOC
COOMe
COOMe
N
N
Bn
5c
f1 (ppm)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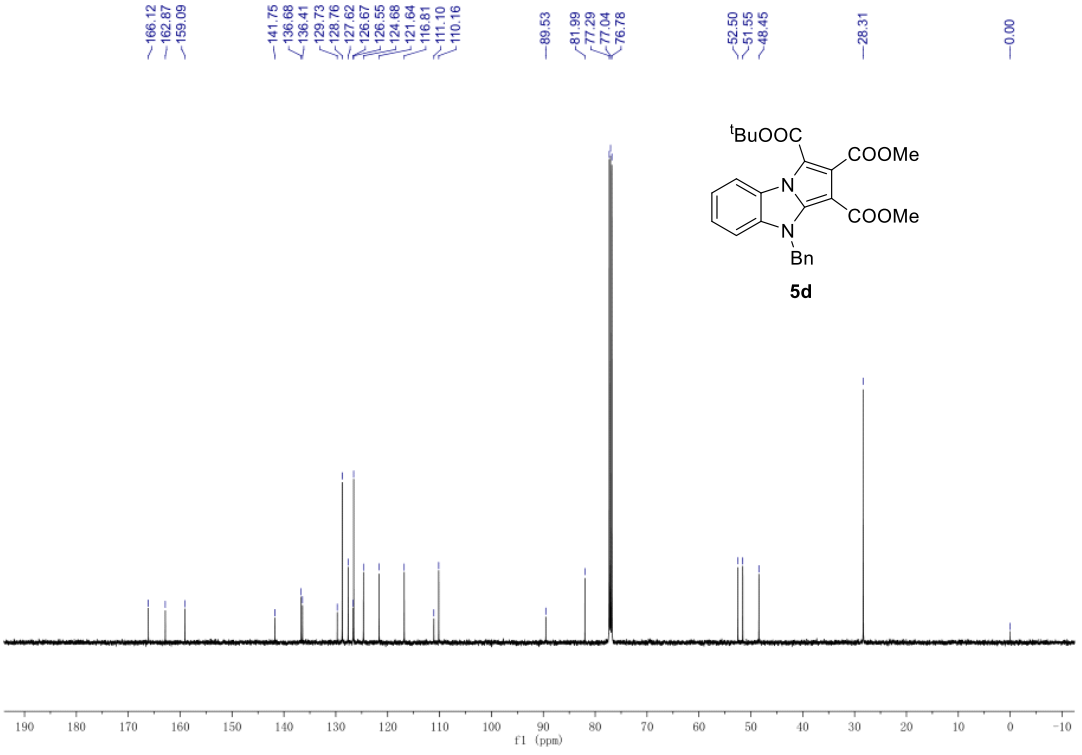
7.30
7.26
7.24
7.17
6.02
3.96
3.75
1.60
tBuOOC
COOMe
COOMe
N
N
Bn
5d
0.97
6.34
2.03
1.98
2.99
3.00
9.16
f1 (ppm)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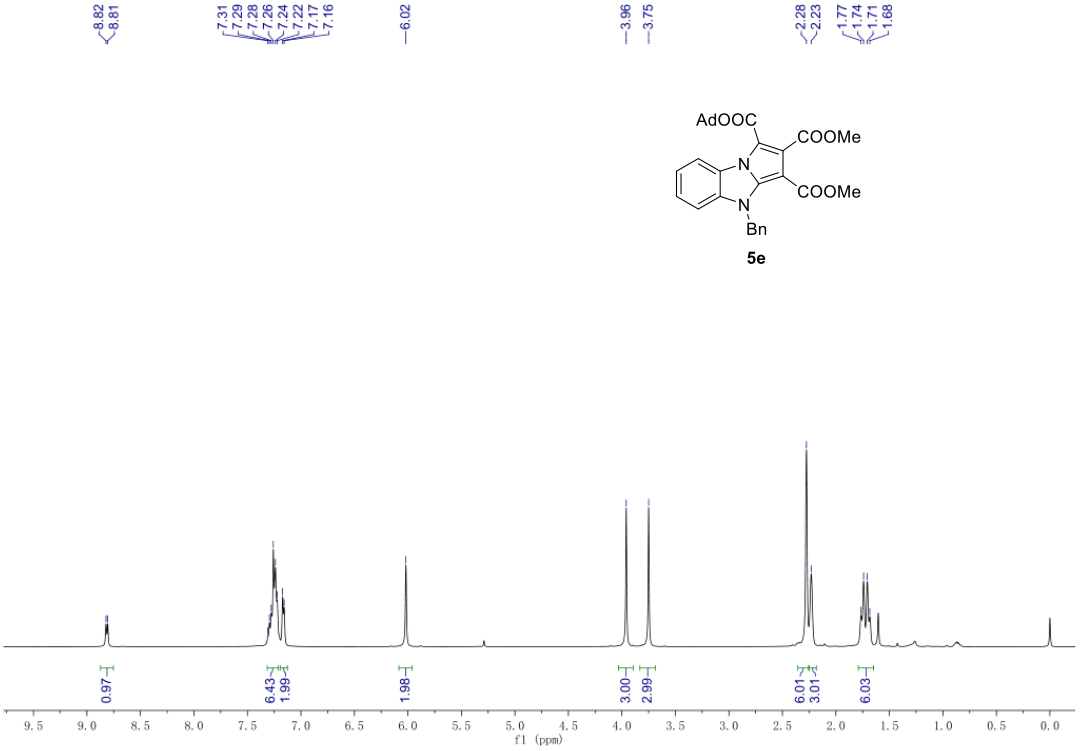
126.55
124.68
121.64
116.81
111.10
110.16
89.53
81.99
77.29
77.04
76.78
52.50
51.55
48.45
28.31
0.00
tBuOOC
COOMe
COOMe
N
N
Bn
5d
f1 (ppm)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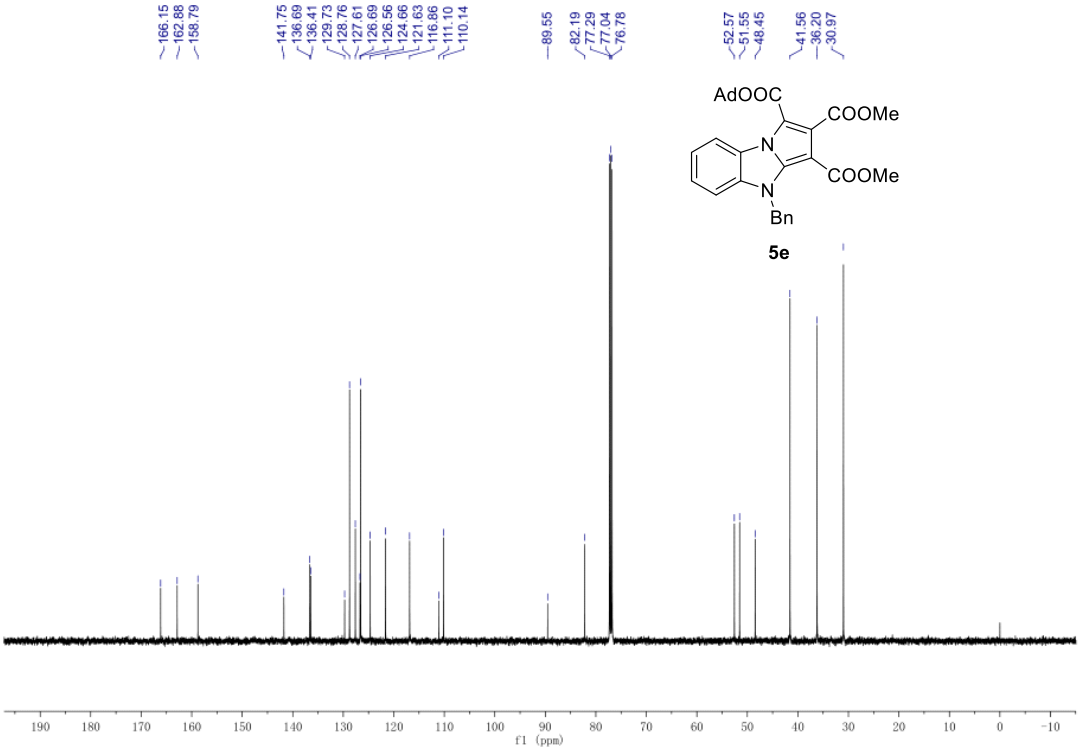
8.81
7.31
7.29
7.28
7.26
7.24
7.22
7.17
7.16
6.02
3.96
3.75
2.28
2.23
1.77
1.74
1.71
1.68
AdOOC
COOMe
COOMe
N
N
Bn
5e
0.97
6.43
1.99
1.98
3.00
2.99
6.01
3.01
6.03
f1 (ppm)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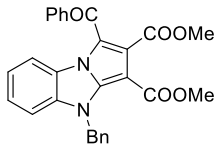
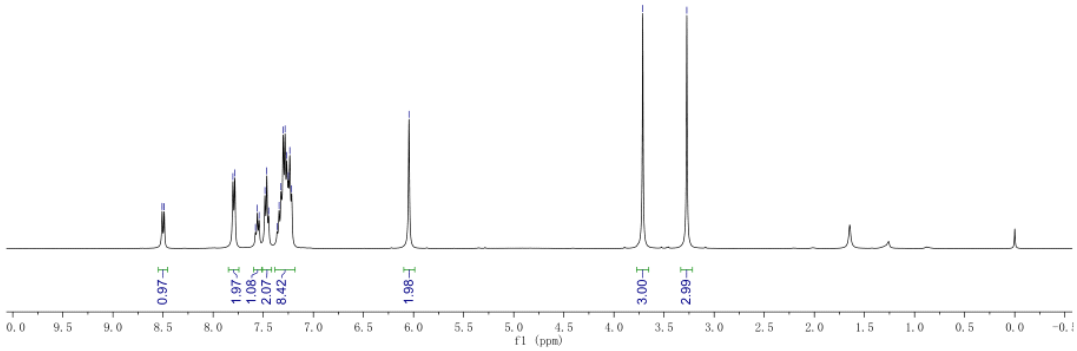
136.69
136.41
129.73
128.76
127.61
126.69
126.56
124.66
121.63
116.86
111.10
110.14
89.55
82.19
77.29
77.04
76.78
52.57
51.55
48.45
41.56
36.20
30.97
AdOOC
COOMe
COOMe
N
N
Bn
5e
f1 (ppm)


8.51
8.49
7.80
7.78
7.56
7.48
7.46
7.45
7.34
7.32
7.30
7.28
7.27
7.25
7.24
7.22
6.05
3.71
3.27


PhOC
COOMe
COOMe
N
N
Bn

5f


0.97
1.97
1.08
2.07
8.42
1.98
3.00
2.99
f1 (ppm)


185.03
165.14
162.88
142.29
139.14
136.64
136.46
131.92
131.70
128.95
128.83
128.08
127.74
126.60
126.56
125.03
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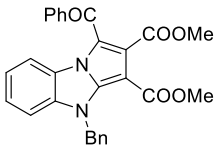
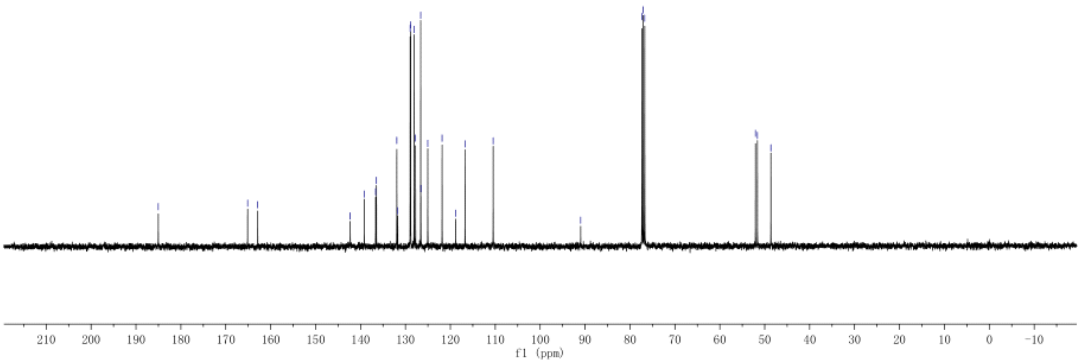
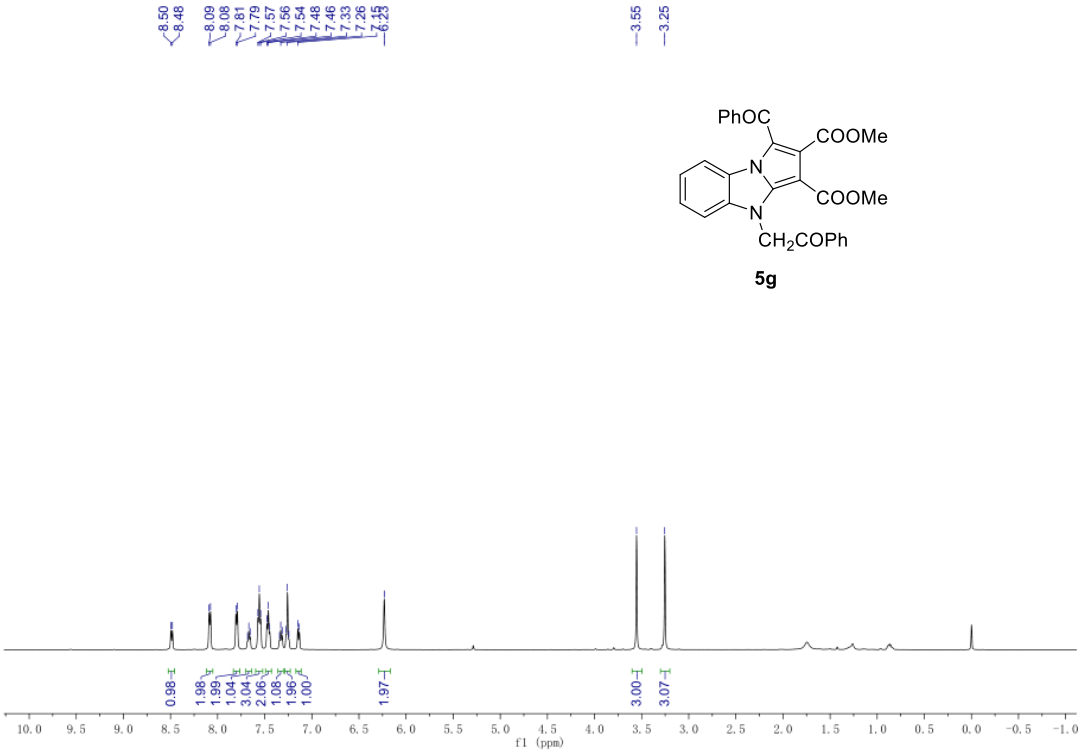
118.83
116.74
110.47
90.98
77.36
77.04
76.72
52.08
51.63
48.63


PhOC
COOMe
COOMe
N
N
Bn

5f


f1 (ppm)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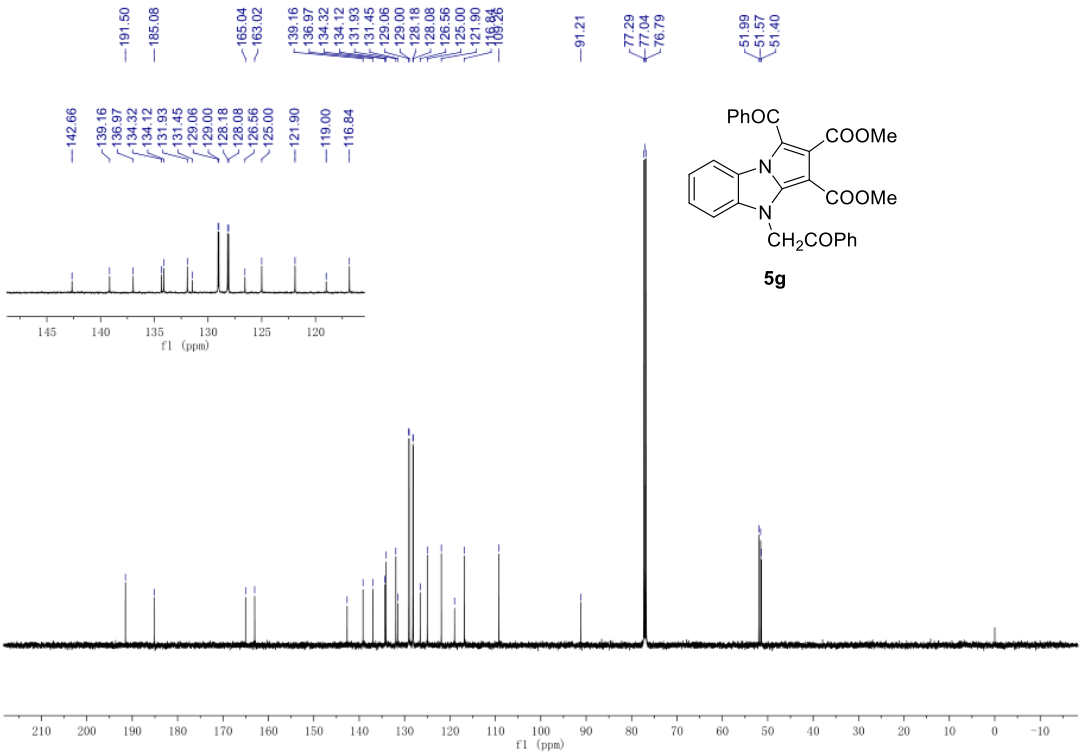
8.48
8.09
8.08
7.81
7.79
7.57
7.56
7.54
7.48
7.46
7.33
7.26
3.55
3.25
PhOC
COOMe
COOMe
N
N
CH2COPh
5g
0.98
1.98
1.99
1.04
3.04
2.06
1.08
1.96
1.00
1.97
3.00
3.07
f1 (ppm)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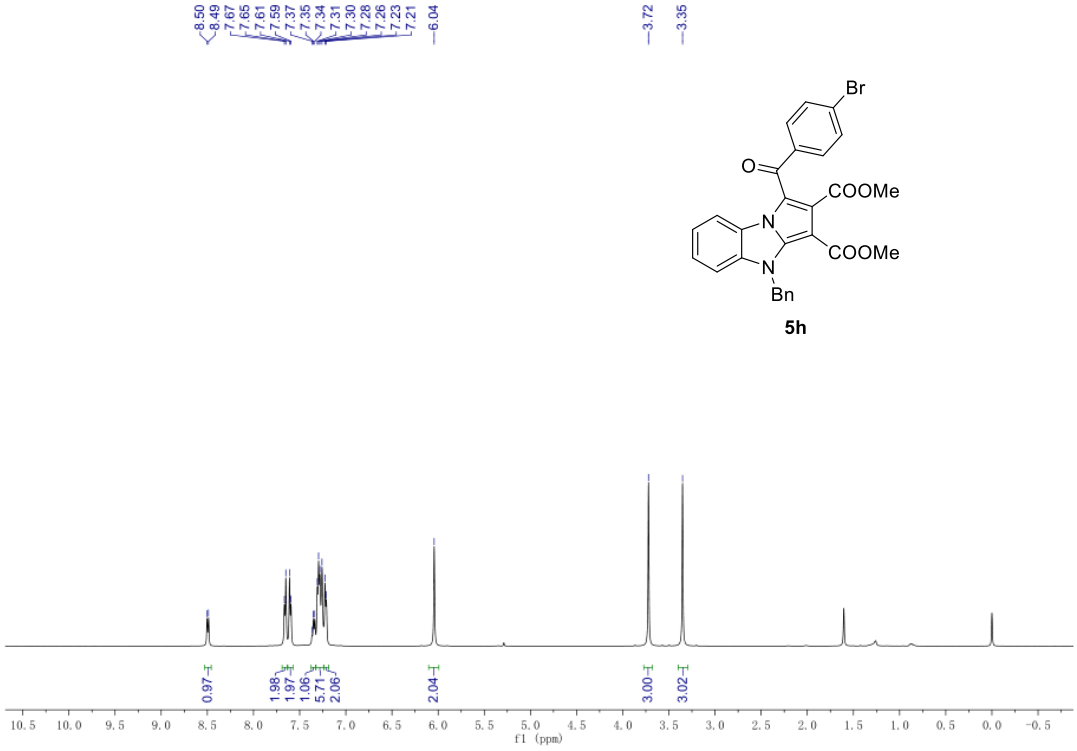
163.02
139.16
136.97
134.32
134.12
131.93
131.45
129.06
129.00
128.18
128.08
126.56
125.00
121.90
119.00
116.84
91.21
77.29
77.04
76.79
51.99
51.57
51.40
142.66
139.16
136.97
134.32
134.12
131.93
131.45
129.06
129.00
128.18
128.08
126.56
125.00
121.90
119.00
116.84
PhOC
COOMe
COOMe
N
N
CH2COPh
5g
f1 (ppm)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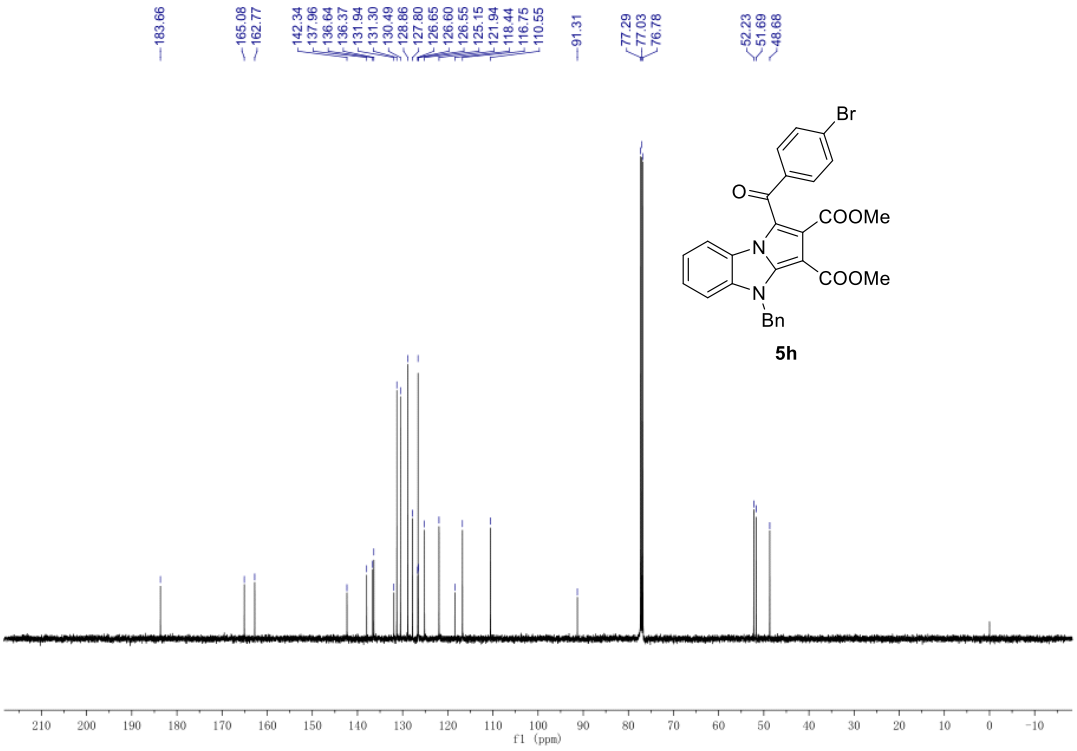
7.65
7.61
7.59
7.37
7.35
7.34
7.31
7.30
7.28
7.26
7.23
7.21
6.04
3.72
3.35
Br
O
COOMe
COOMe
N
N
Bn
0.97
1.98
1.97
1.06
5.71
2.06
2.04
3.00
3.02
f1 (ppm)

5h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136.64
136.37
131.94
131.30
130.49
128.86
127.60
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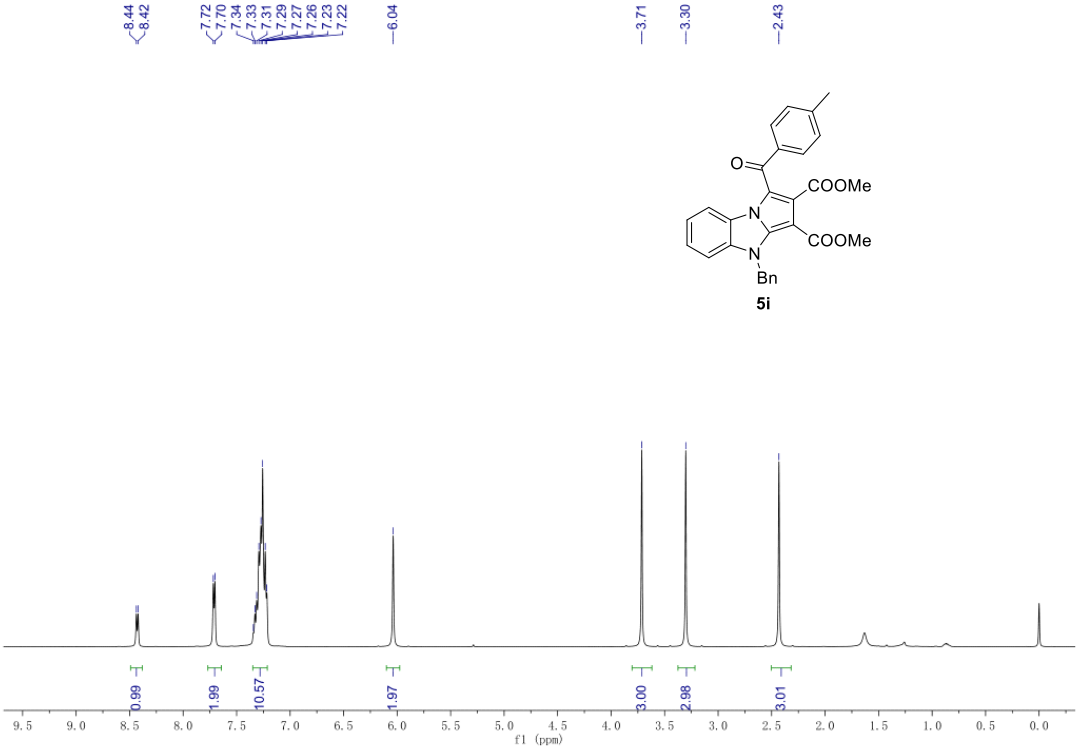
126.60
126.55
125.15
121.94
118.44
116.75
110.55
91.31
77.29
77.03
76.78
52.23
51.69
48.68
Br
O
COOMe
COOMe
N
N
Bn
f1 (ppm)

5h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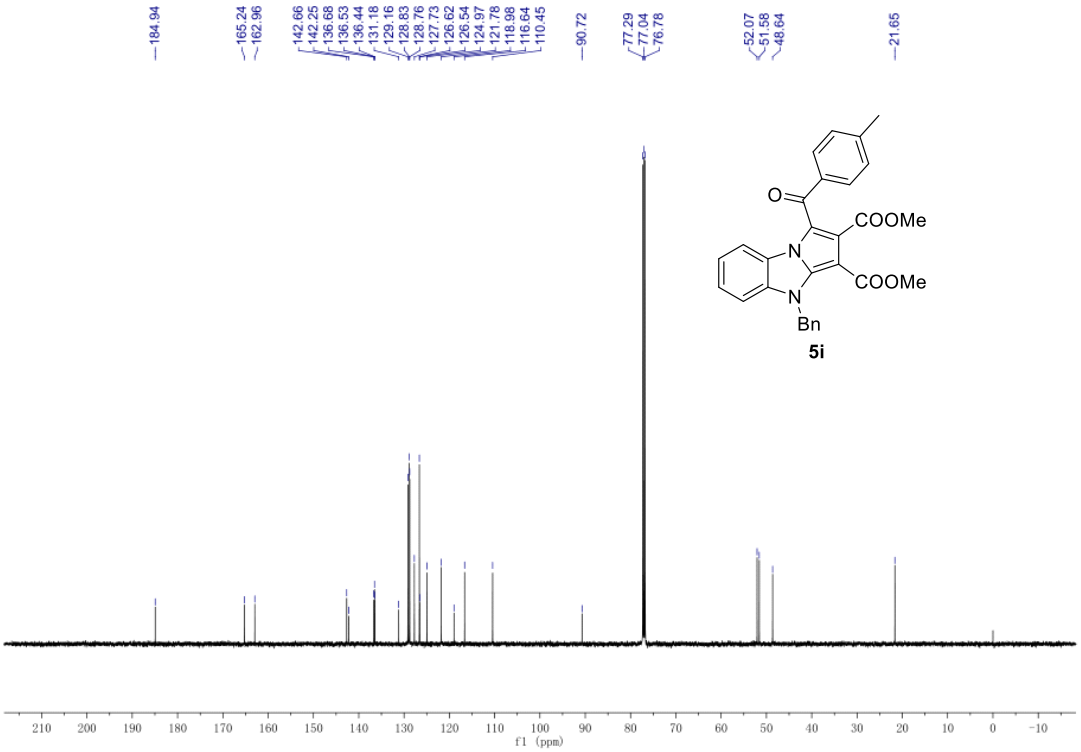
7.31
7.29
7.27
7.26
7.23
7.22
6.04
3.71
3.30
2.43
O
COOMe
COOMe
N
N
Bn
5i
0.99
1.99
10.57
1.97
3.00
2.98
3.01
f1 (ppm)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136.53
136.44
131.18
129.16
128.83
128.76
127.73
126.62
126.54
124.97
121.78
118.98
116.64
110.45
90.72
77.29
77.04
76.78
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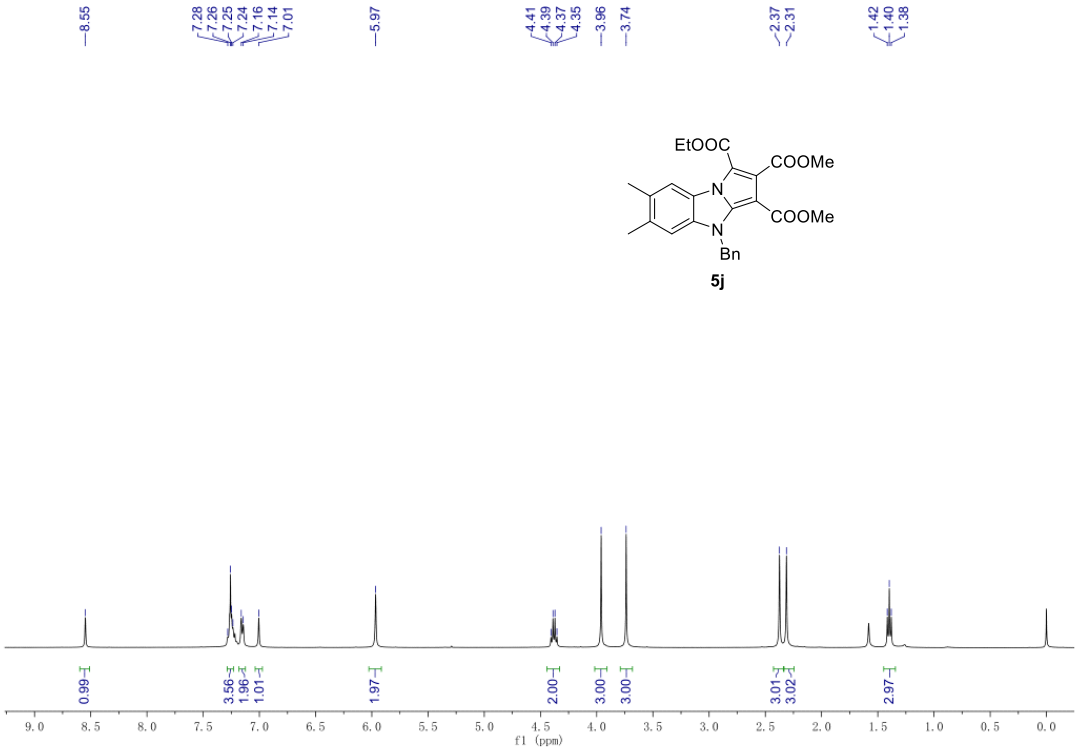
51.58
48.64
21.65
O
COOMe
COOMe
N
N
Bn
5i
f1 (ppm)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7.28
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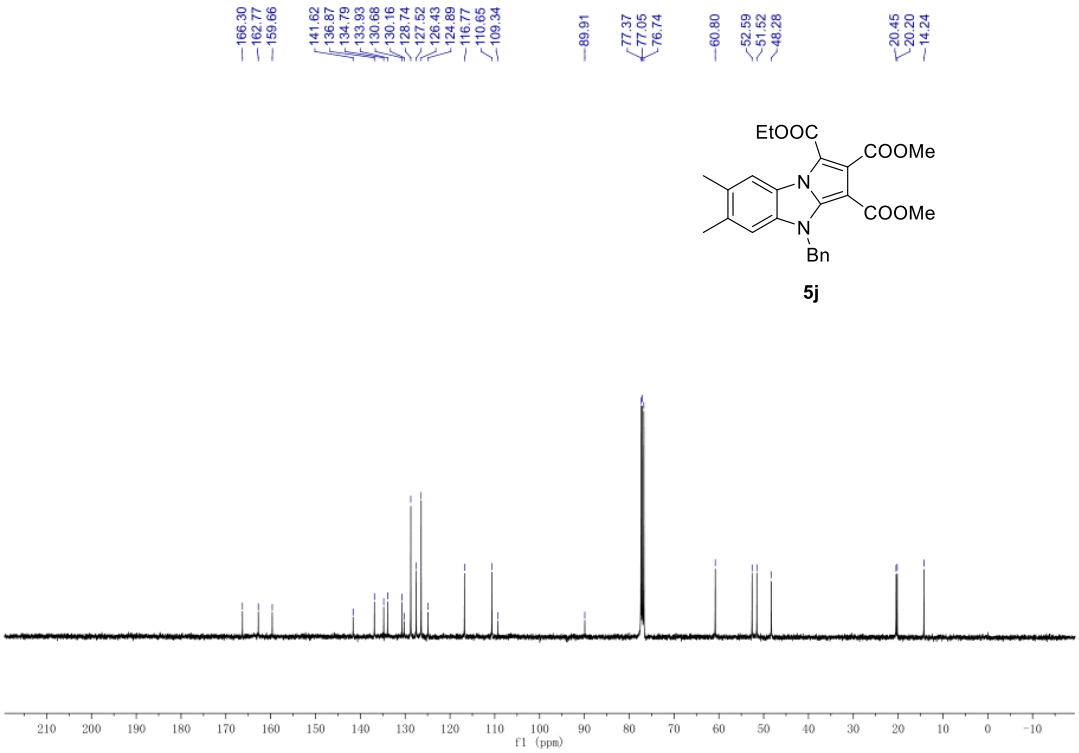
7.24
7.16
7.14
7.01
5.97
4.41
4.39
4.37
4.35
3.96
3.74
2.37
2.31
1.42
1.40
1.38
EtOOC
COOMe
COOMe
N
N
Bn
5j
0.99
3.56
1.96
1.01
1.97
2.00
3.00
3.00
3.01
3.02
2.97
f1 (ppm)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130.68
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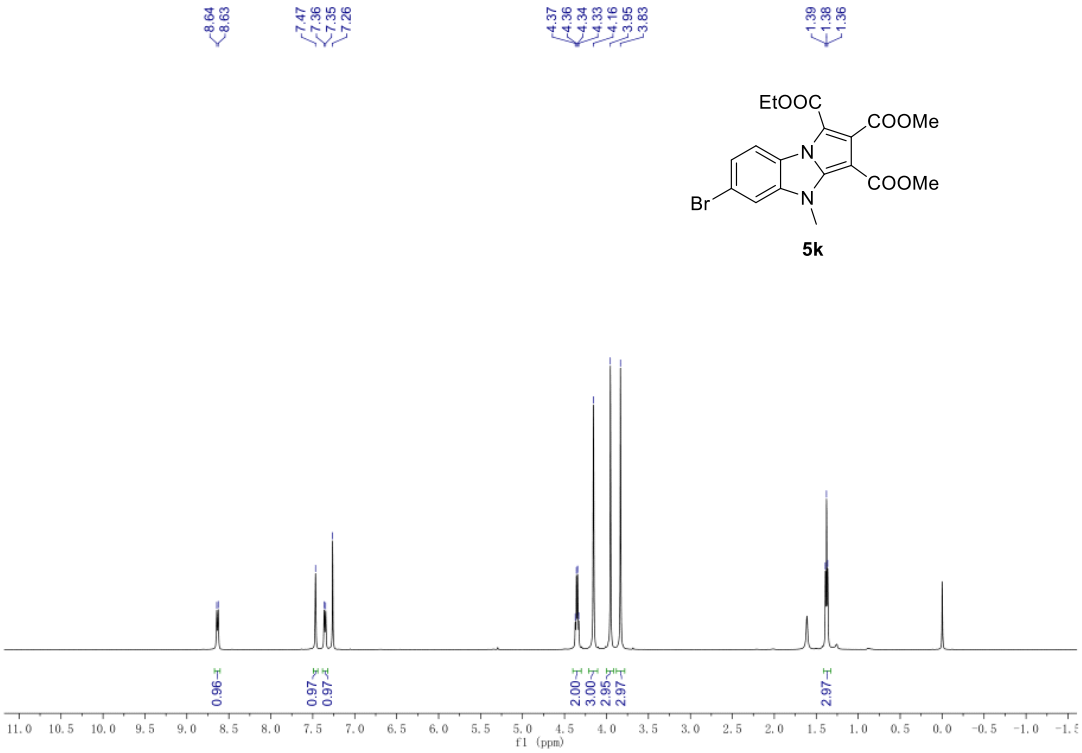
128.74
127.52
126.43
124.89
116.77
110.65
109.34
89.91
77.37
77.05
76.74
60.80
52.59
51.52
48.28
20.45
20.20
14.24
EtOOC
COOMe
COOMe
N
N
Bn
5j
f1 (ppm)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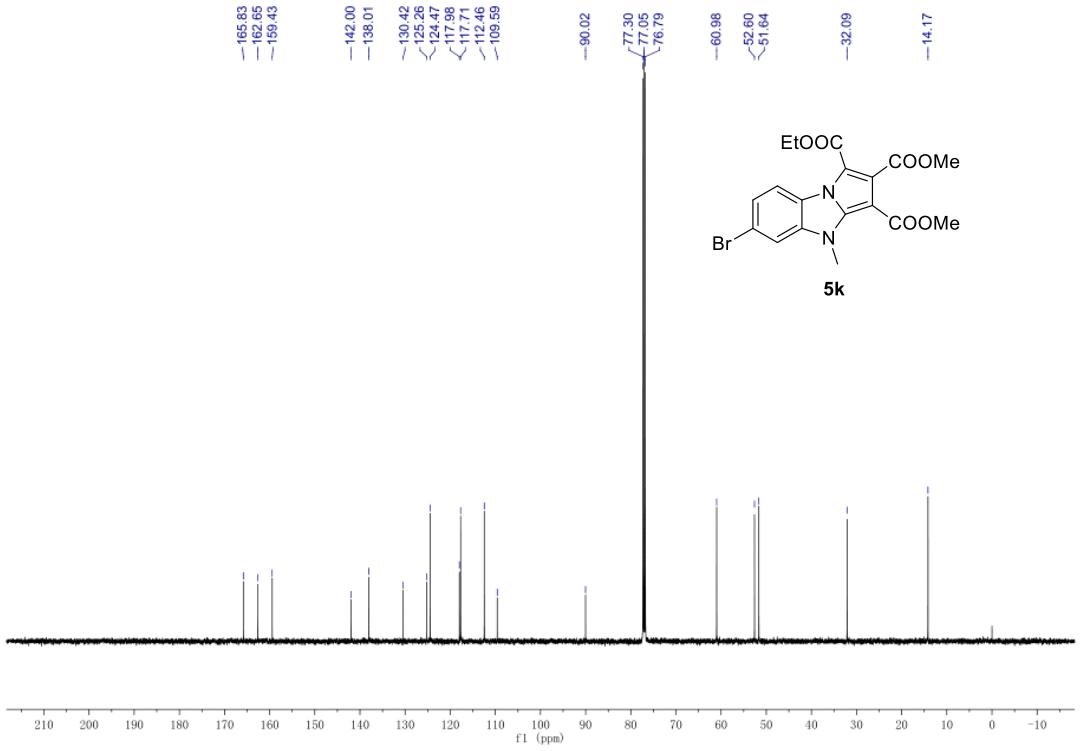
7.35
7.26
4.37
4.36
4.34
4.33
4.16
3.95
3.83
1.39
1.38
1.36
EtOOC
COOMe
COOMe
Br
N
N
5k
0.96
0.97
0.97
2.00
3.00
2.95
2.97
2.97
f1 (ppm)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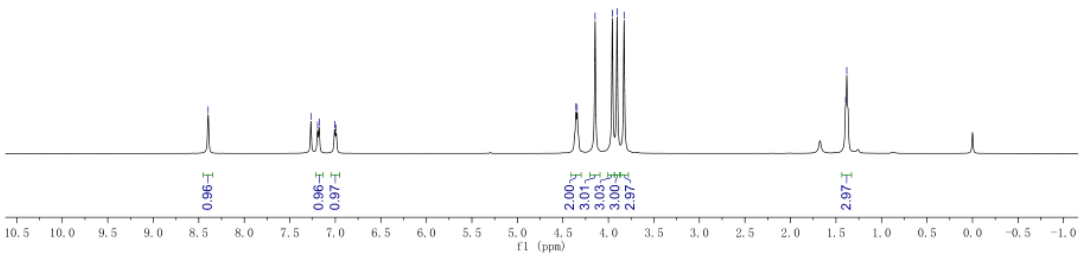
130.42
125.26
124.47
117.98
117.71
112.46
109.59
90.02
77.30
77.05
76.79
60.98
52.60
51.64
32.09
14.17
EtOOC
COOMe
COOMe
Br
N
N
5k
f1 (ppm)


8.40
7.27
7.19
7.18
7.01
6.99
4.36
4.34
4.15
3.96
3.90
3.83
1.39
1.38
EtOOC
COOMe
MeO
N
COOMe
N

5l


0.96
0.96
0.97
2.00
3.01
3.03
3.00
2.97
2.97
f1 (ppm)


166.19
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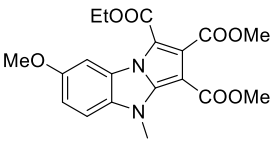
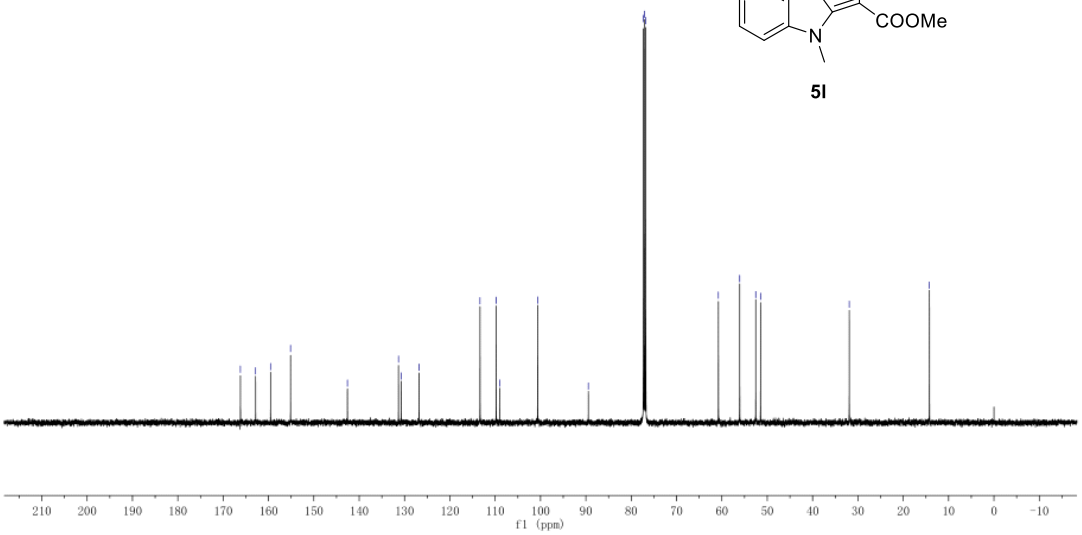
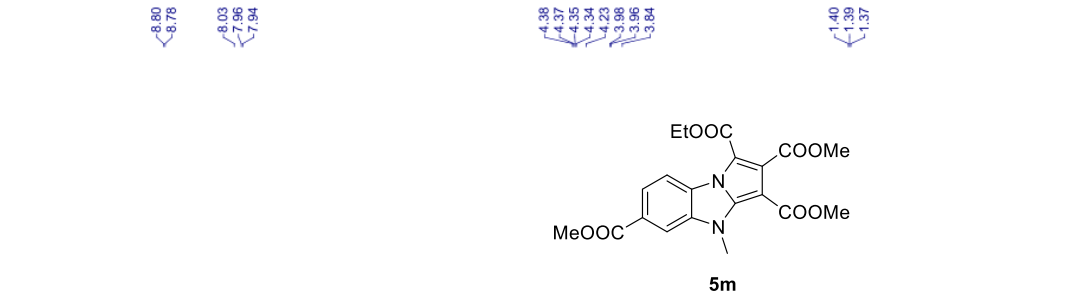
159.56
155.14
142.60
131.34
130.70
126.82
113.35
109.78
109.05
100.66
89.46
77.30
77.05
76.79
60.77
56.07
52.55
51.49
31.91
14.22


EtOOC
COOMe
MeO
N
COOMe
N

5l


f1 (ppm)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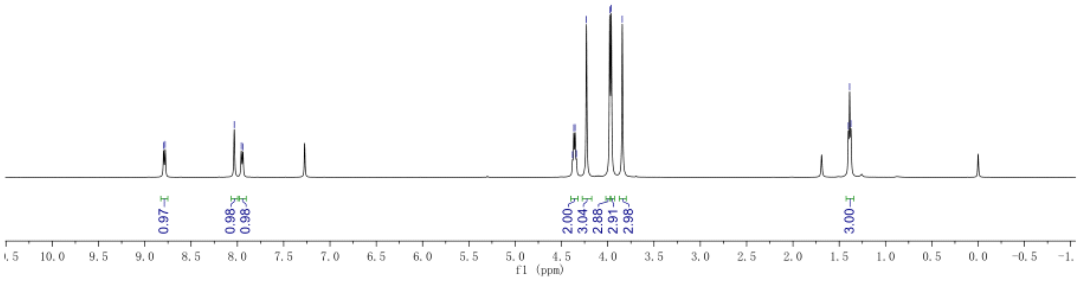
8.03
7.96
7.94
4.38
4.37
4.35
4.34
4.23
3.98
3.96
3.84
1.40
1.39
1.37
EtOOC
COOMe
COOMe
MeOOC
N
N

5m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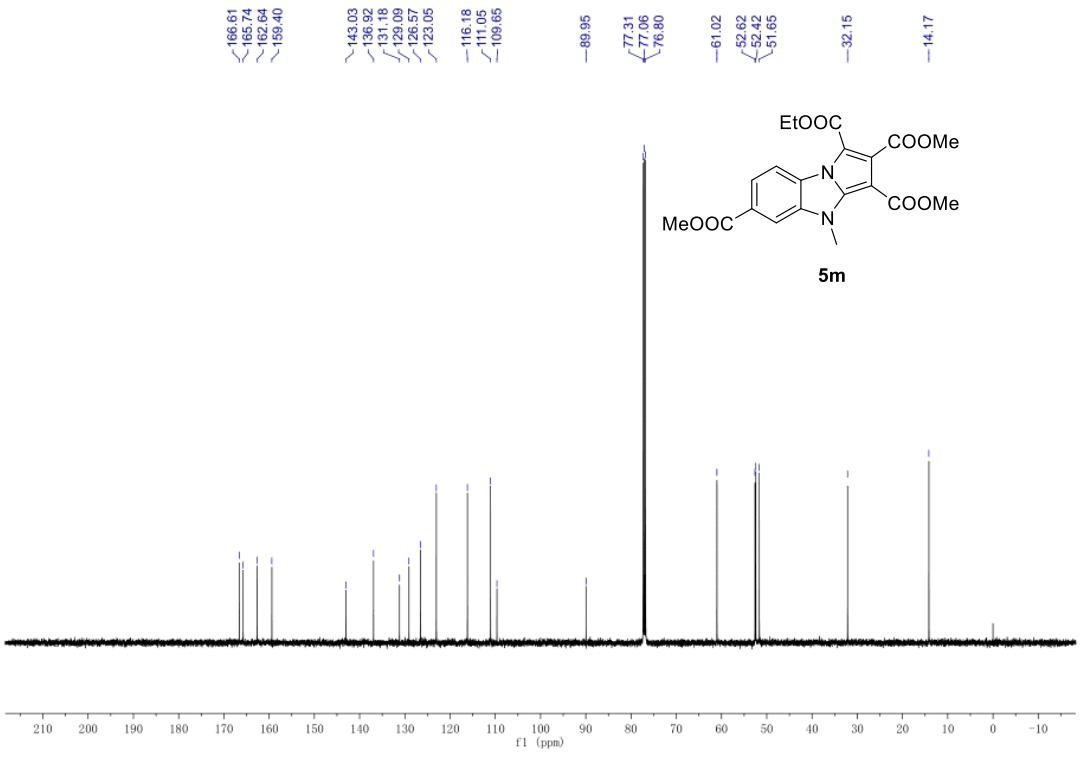
0.98
0.98
2.00
3.04
2.88
2.91
2.98
3.00
f1 (ppm)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165.74
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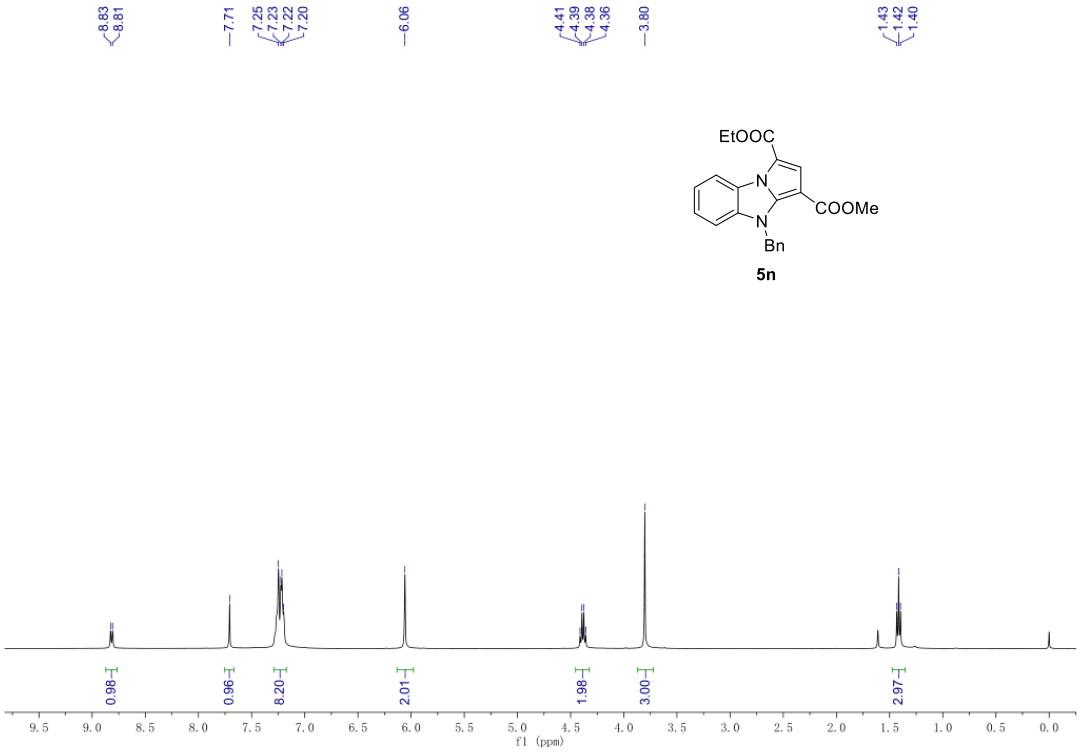
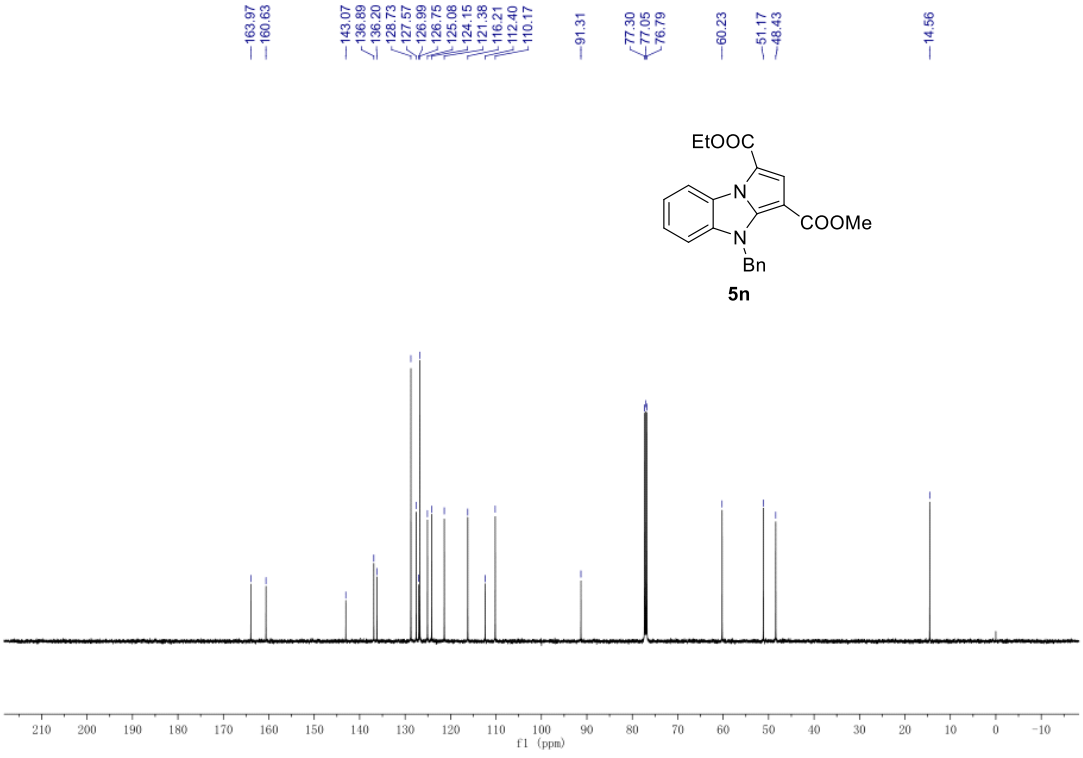
143.03
136.92
131.18
129.09
126.57
123.05
116.18
111.05
109.65
89.95
77.31
77.06
76.80
61.02
52.62
52.42
51.65
32.15
14.17
EtOOC
COOMe
COOMe
MeOOC
N
N
f1 (ppm)

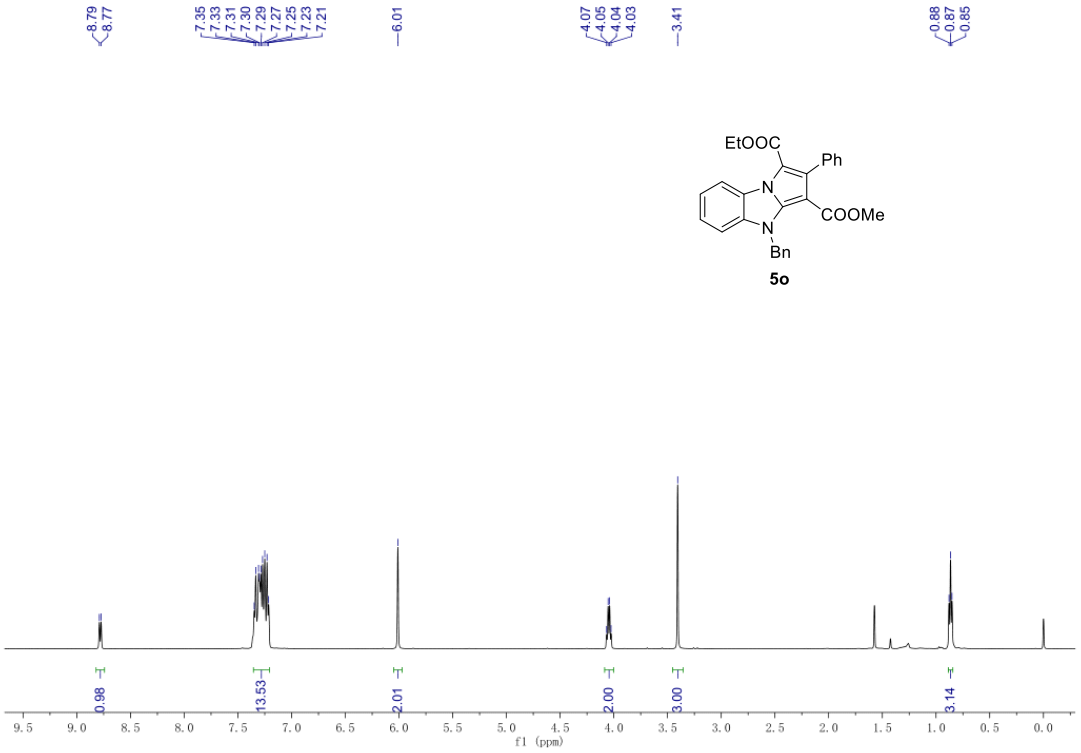
5m

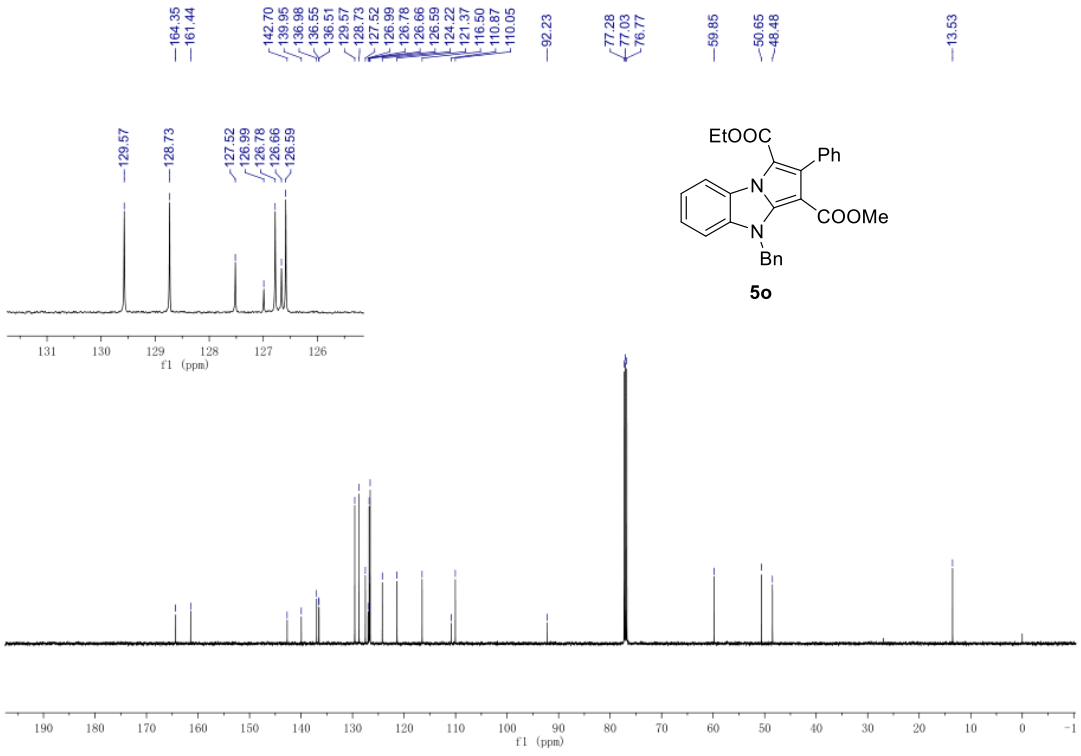

8.83
8.81
7.71
7.25
7.23
7.22
7.20
6.06
4.41
4.39
4.38
4.36
3.80
1.43
1.42
1.40
EtOOC
COOMe
N
N
Bn
0.98
0.96
8.20
2.01
1.98
3.00
2.97
f1 (ppm)

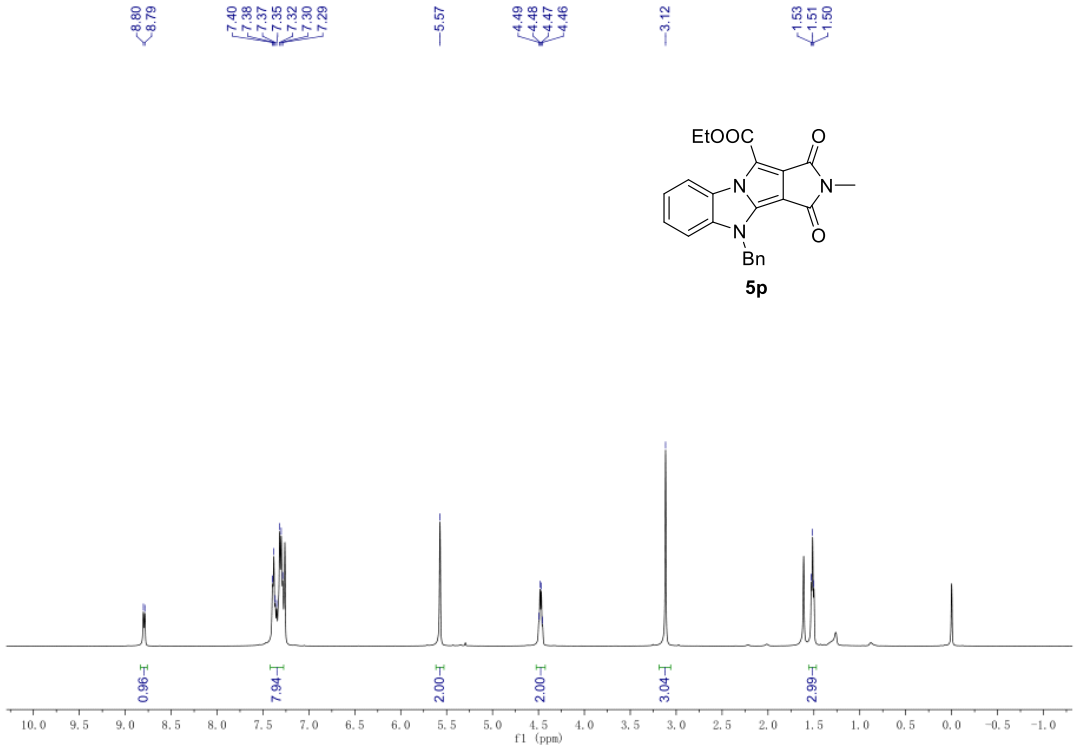
5n

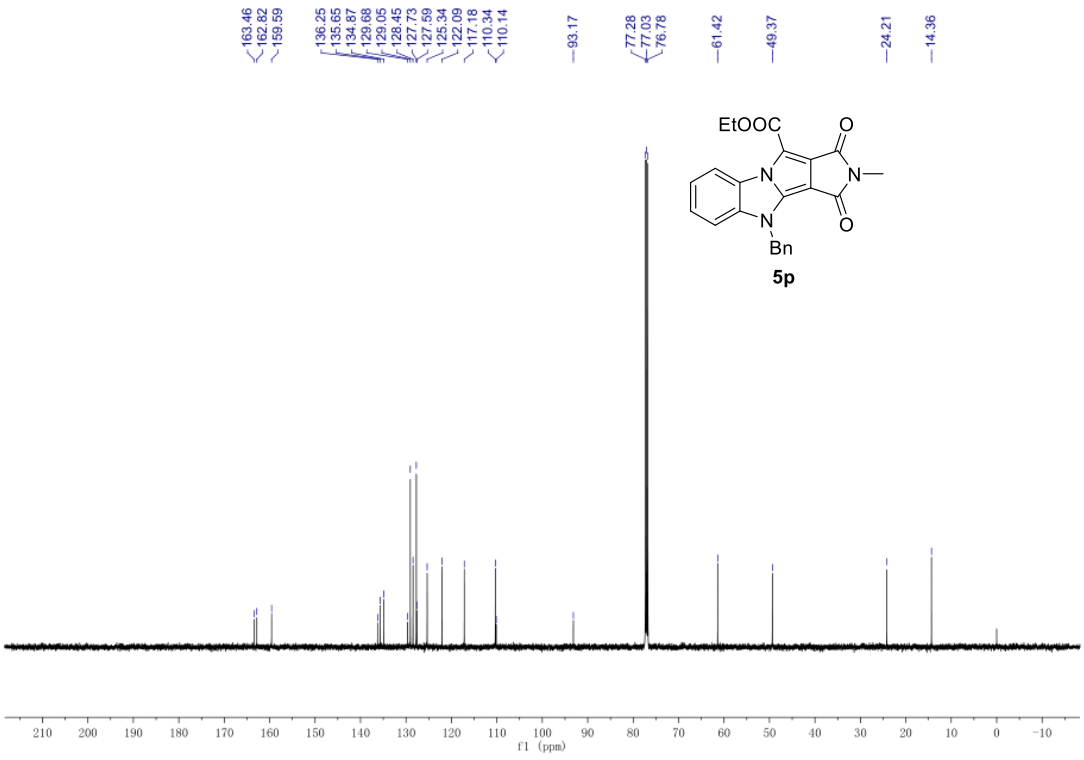

163.97
160.63
143.07
136.89
136.20
128.73
127.57
126.99
126.75
125.08
124.15
121.38
116.21
112.40
110.17
91.31
77.30
77.05
76.79
60.23
51.17
48.43
14.56
EtOOC
COOMe
N
N
Bn
f1 (ppm)

5n

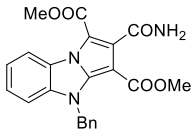

8.79
8.77
7.35
7.33
7.31
7.30
7.29
7.27
7.25
7.23
7.21
6.01
4.07
4.05
4.04
4.03
3.41
0.88
0.87
0.85
EtOOC
Ph
N
COOMe
N
Bn
5o
0.98
13.53
2.01
2.00
3.00
3.14
f1 (ppm)


164.35
161.44
142.70
139.95
136.98
136.55
136.51
129.57
128.73
127.52
126.99
126.78
126.66
126.59
124.22
121.37
116.50
110.87
110.05
92.23
77.28
77.03
76.77
59.85
50.65
48.48
13.53
129.57
128.73
127.52
126.99
126.78
126.66
126.59
EtOOC
Ph
N
COOMe
N
Bn
5o
f1 (ppm)

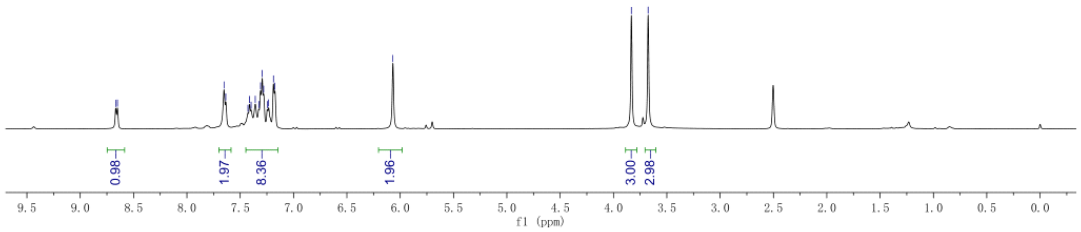

8.80
8.79
7.40
7.38
7.37
7.35
7.32
7.30
7.29
5.57
4.49
4.48
4.47
4.46
3.12
1.53
1.51
1.50
EtOOC
O
N
N
O
N
Bn
5p
0.96
7.94
2.00
2.00
3.04
2.99
f1 (ppm)


163.46
162.82
159.59
136.25
135.65
134.67
129.68
129.05
128.45
127.73
127.59
125.34
122.09
117.18
110.34
110.14
93.17
77.28
77.03
76.78
61.42
49.37
24.21
14.36
EtOOC
O
N
N
O
N
Bn
5p
f1 (ppm)

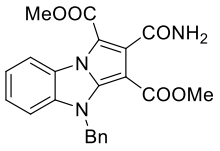

8.67
8.65
7.65
7.64
7.43
7.41
7.40
7.36
7.33
7.31
7.29
7.28
7.25
7.23
7.19
7.18
6.07
3.83
3.68


MeOOC
CONH2
N
N
COOMe
Bn

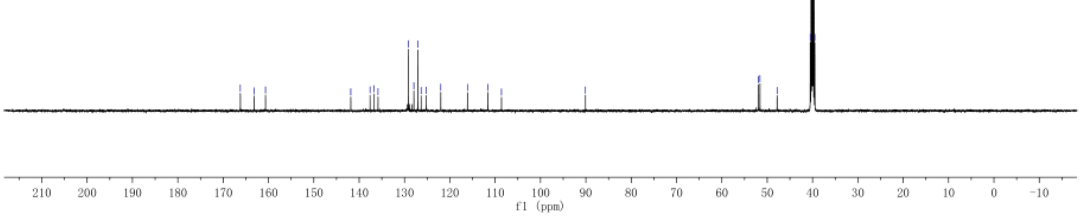
5q

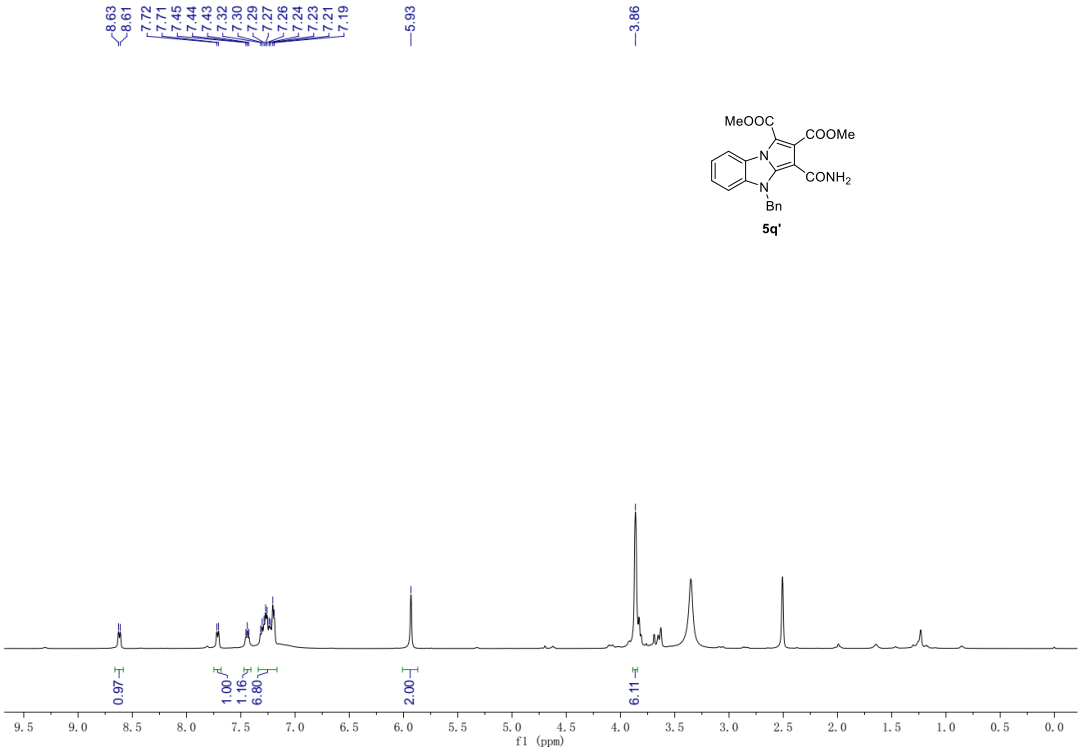

0.98
1.97
8.36
1.96
3.00
2.98
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

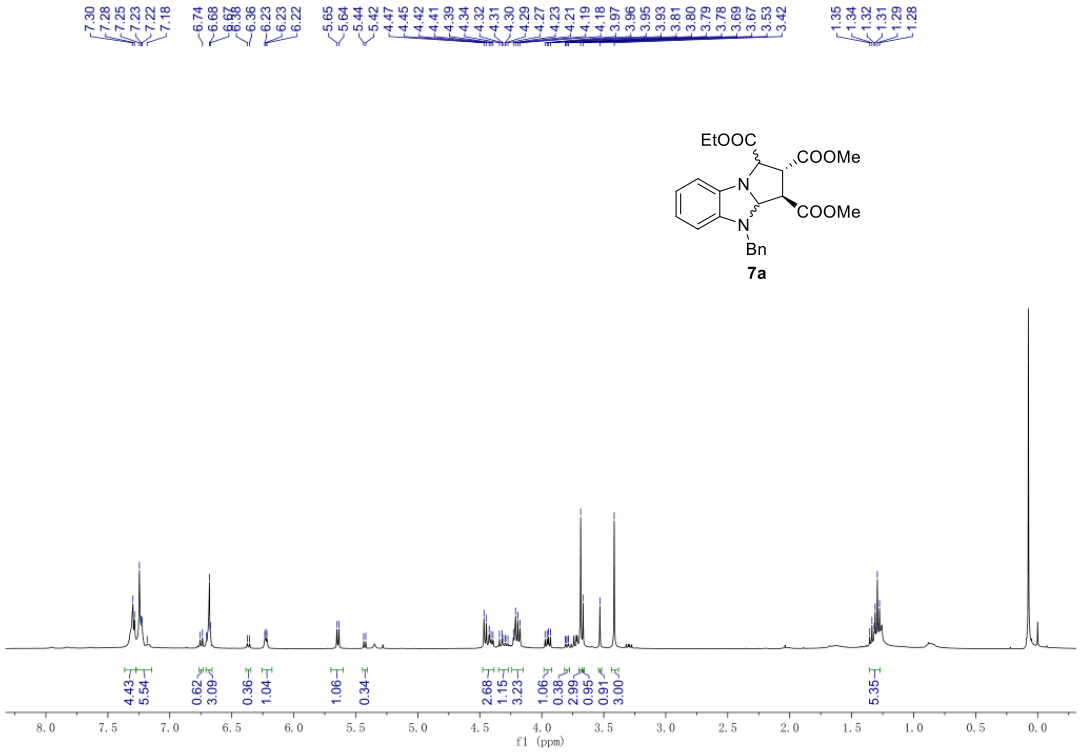

166.20
163.17
160.66
141.85
137.61
136.68
135.84
129.13
127.93
127.04
126.34
125.20
122.00
116.12
111.61
108.62
90.09
52.00
51.60
47.82
40.50
40.33
40.17
40.00
39.83
39.67
39.50

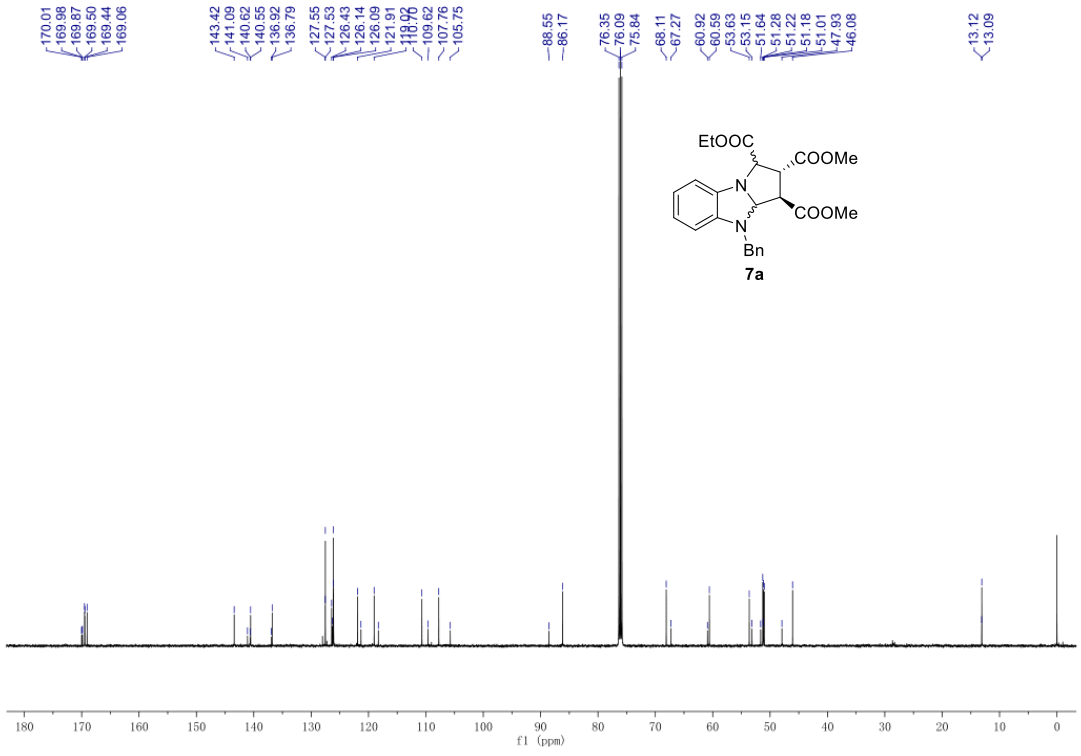

MeOOC
CONH2
N
N
COOMe
Bn

5q

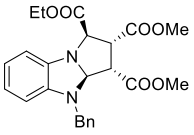

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


8.63
8.61
7.72
7.71
7.45
7.44
7.43
7.32
7.30
7.29
7.27
7.26
7.24
7.23
7.21
7.19
5.93
3.86
MeOOC
COOMe
CONH2
N
N
Bn
5q'
0.97
1.00
1.16
6.80
2.00
6.11
f1 (ppm)
166.32
164.29
160.08
140.30
137.28
136.80
129.15
128.21
128.06
127.53
126.16
125.46
121.65
116.01
111.52
107.75
95.58
53.30
52.36
47.34
40.49
40.33
39.99
39.83
39.66
39.49
MeOOC
COOMe
CONH2
N
N
Bn
5q'
f1 (ppm)

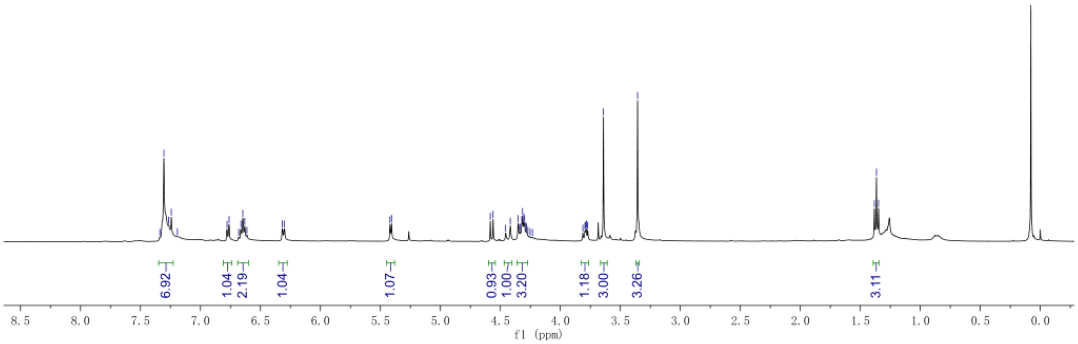

7.30
7.28
7.25
7.23
7.22
7.18
6.74
6.68
6.67
6.38
6.36
6.23
6.22
5.65
5.64
5.44
5.42
4.47
4.45
4.42
4.41
4.39
4.34
4.32
4.31
4.30
4.29
4.27
4.23
4.21
4.19
4.18
3.97
3.96
3.95
3.93
3.81
3.80
3.79
3.78
3.69
3.67
3.53
3.42
1.35
1.34
1.32
1.31
1.29
1.28
EtOOC
COOMe
COOMe
N
N
Bn
7a
4.43
5.54
0.62
3.09
0.36
1.04
1.06
0.34
2.68
1.15
3.23
1.06
0.38
2.99
0.95
0.91
3.00
5.35
f1 (ppm)


170.01
169.98
169.87
169.50
169.44
169.06
143.42
141.09
140.62
140.55
136.92
136.79
127.55
127.53
126.43
126.14
126.09
121.91
109.62
107.76
105.75
88.55
86.17
76.35
76.09
75.84
68.11
67.27
60.92
60.59
53.63
53.15
51.64
51.28
51.22
51.18
51.01
47.93
46.08
13.12
13.09
EtOOC
COOMe
COOMe
N
N
Bn
7a
f1 (ppm)

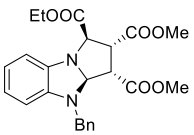

7.34
7.30
7.26
7.24
7.19
6.76
6.66
6.65
6.63
6.32
6.30
5.42
5.41
4.58
4.56
4.42
4.35
4.33
4.32
4.31
4.30
4.30
4.29
3.79
3.78
3.77
3.64
3.56
1.38
1.37
1.35


EtOOC
COOMe
COOMe
N
N
Bn

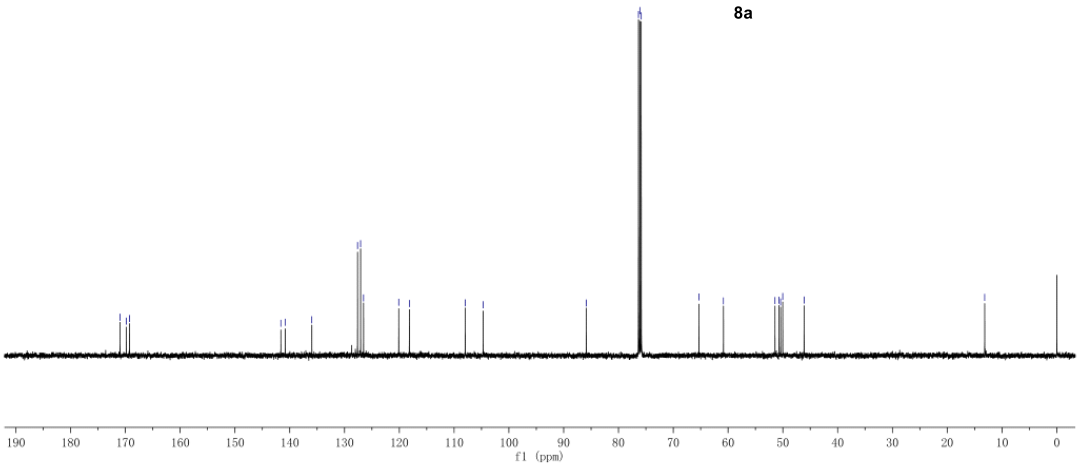
8a

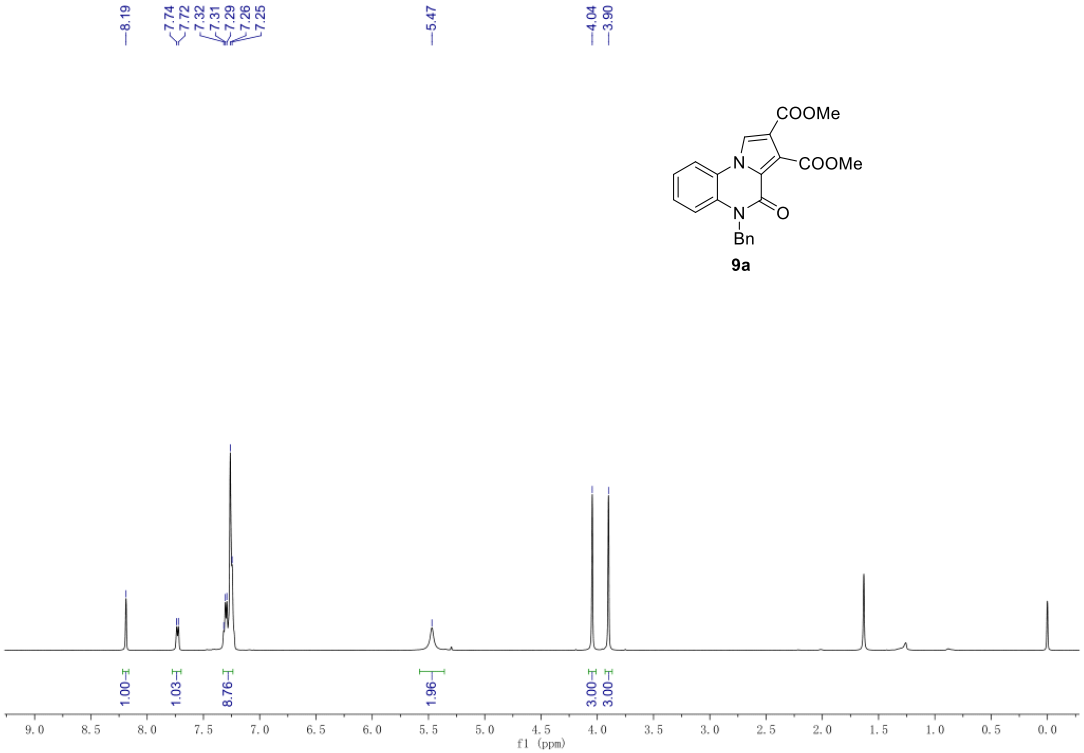

6.92
1.04
2.19
1.04
1.07
0.93
1.00
3.20
1.18
3.00
3.26
3.11
f1 (ppm)

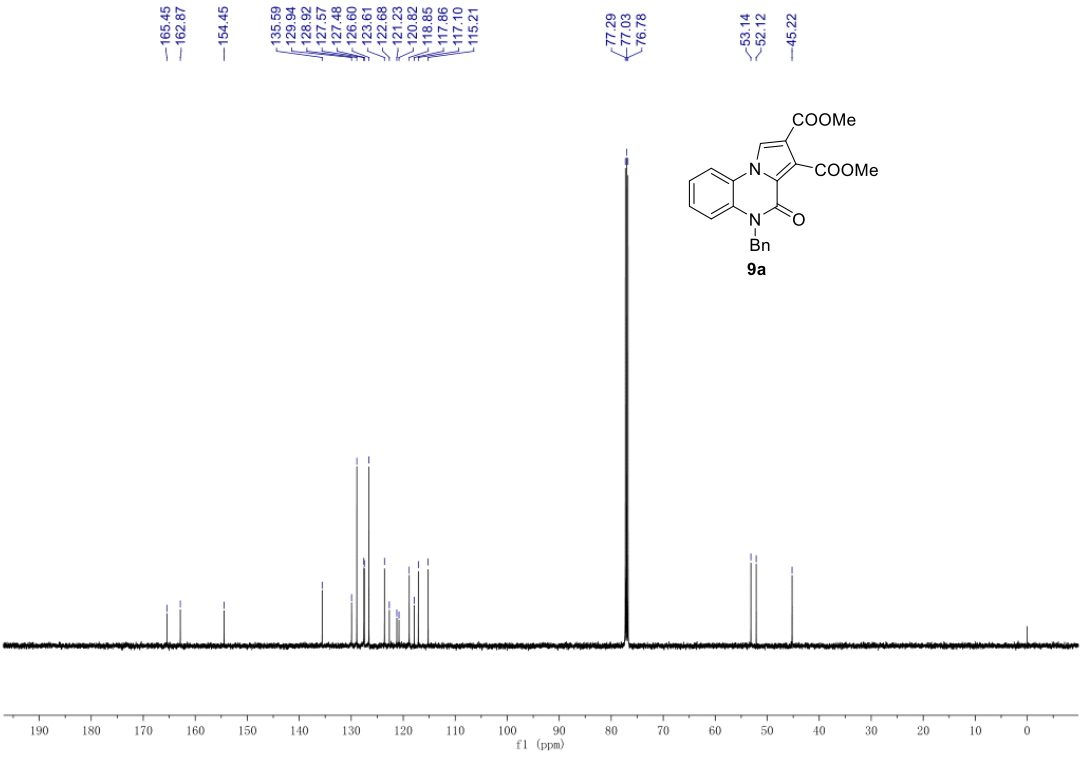

170.99
169.81
169.24
141.63
140.82
135.97
127.63
127.07
126.53
120.11
118.17
107.97
104.70
85.86
76.35
76.10
75.85
65.31
60.84
51.43
50.69
50.41
50.02
46.12
13.16

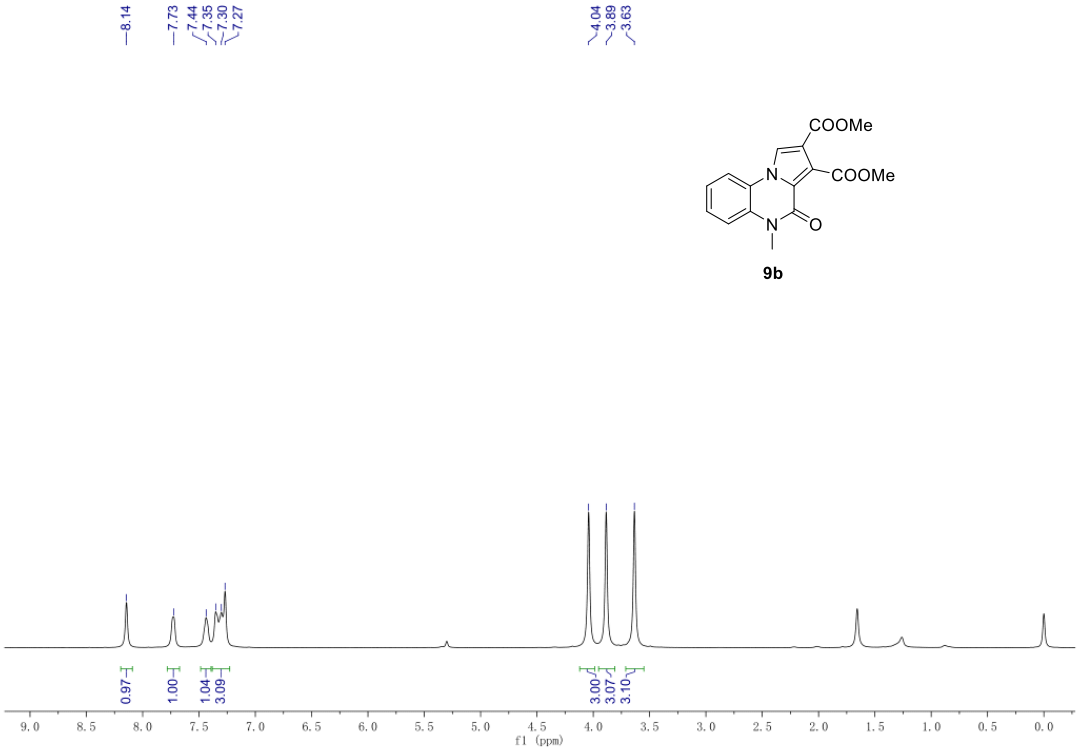

EtOOC
COOMe
COOMe
N
N
Bn

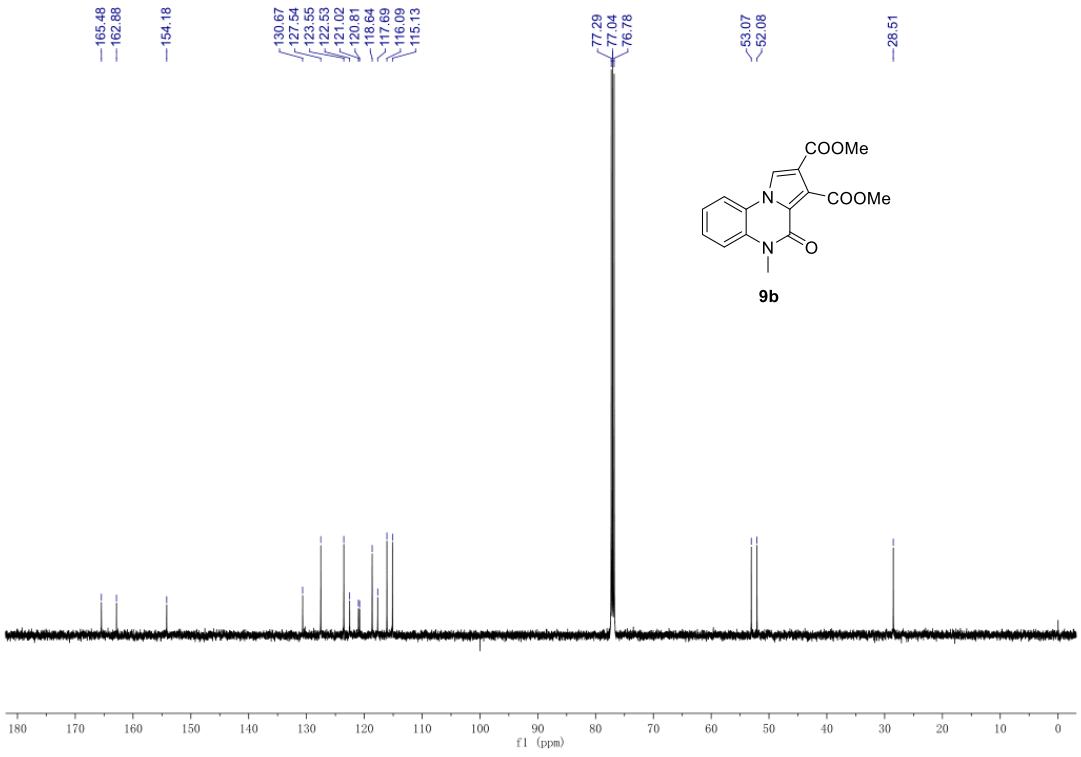
8a

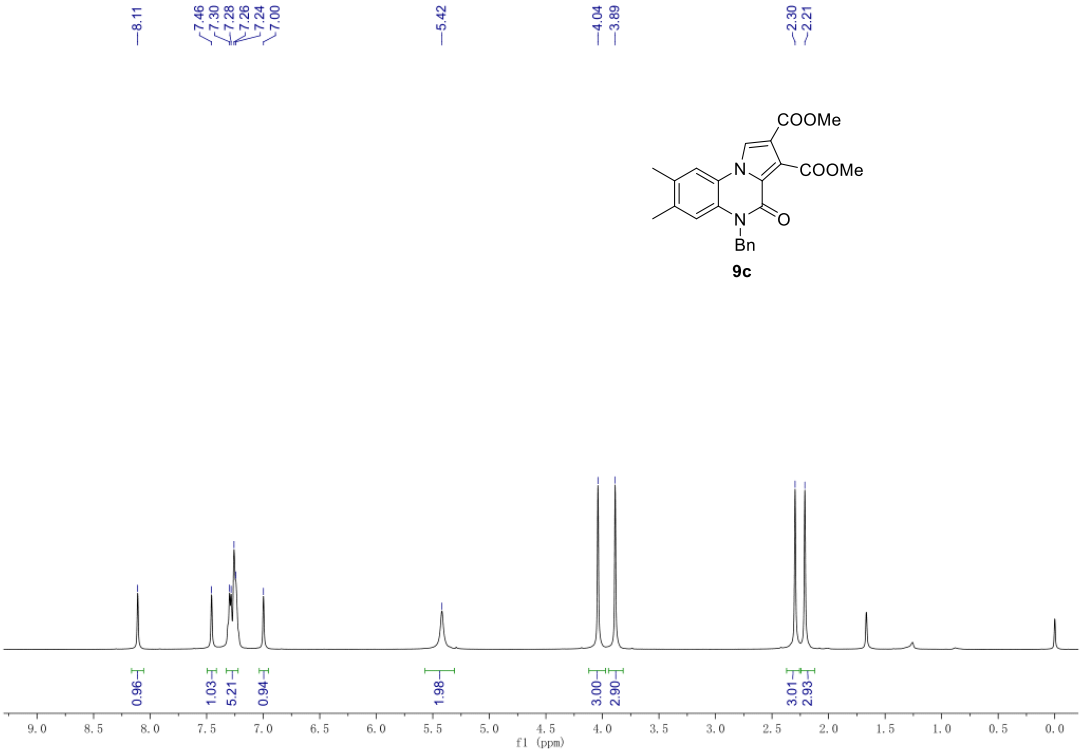

f1 (ppm)


8.19
7.74
7.72
7.32
7.31
7.29
7.26
7.25
5.47
4.04
3.90
COOMe
COOMe
N
N
O
Bn
9a
1.00
1.03
8.76
1.96
3.00
3.00
f1 (ppm)

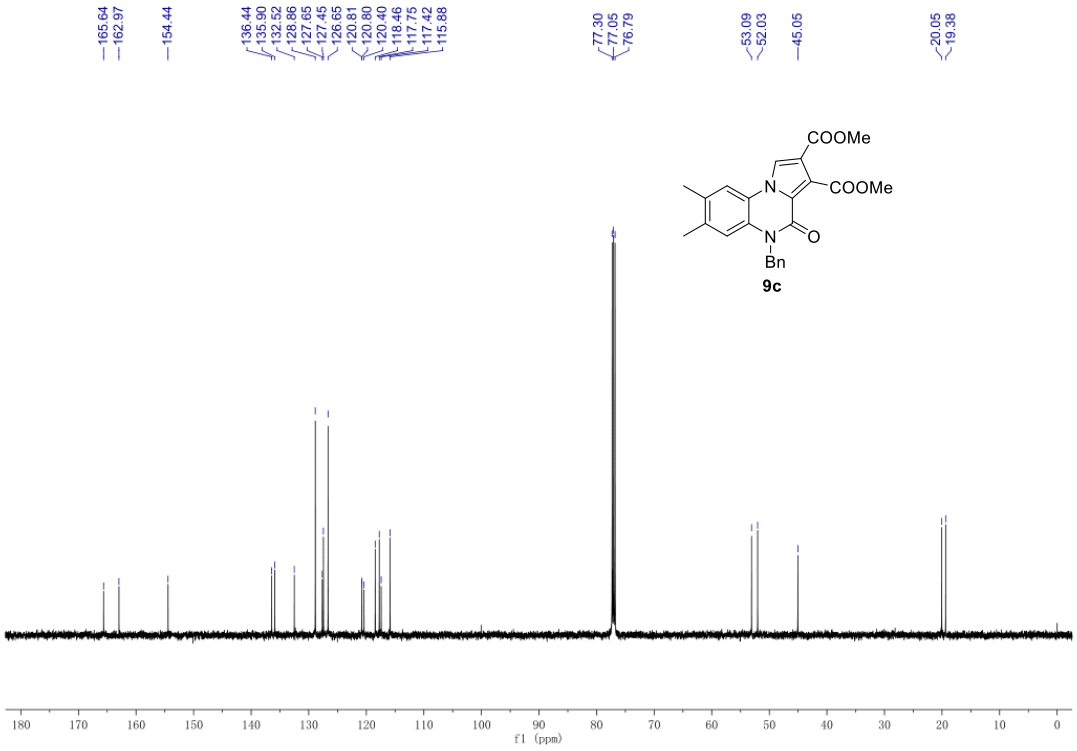

165.45
162.87
154.45
135.59
129.94
128.92
127.57
127.48
126.60
123.61
122.68
121.23
120.82
118.85
117.86
117.10
115.21
77.29
77.03
76.78
53.14
52.12
45.22
COOMe
COOMe
N
N
O
Bn
9a
f1 (ppm)


8.14
7.73
7.44
7.35
7.30
7.27
4.04
3.89
3.63
COOMe
COOMe
N
N
O
9b
0.97
1.00
1.04
3.09
3.00
3.07
3.10
f1 (ppm)

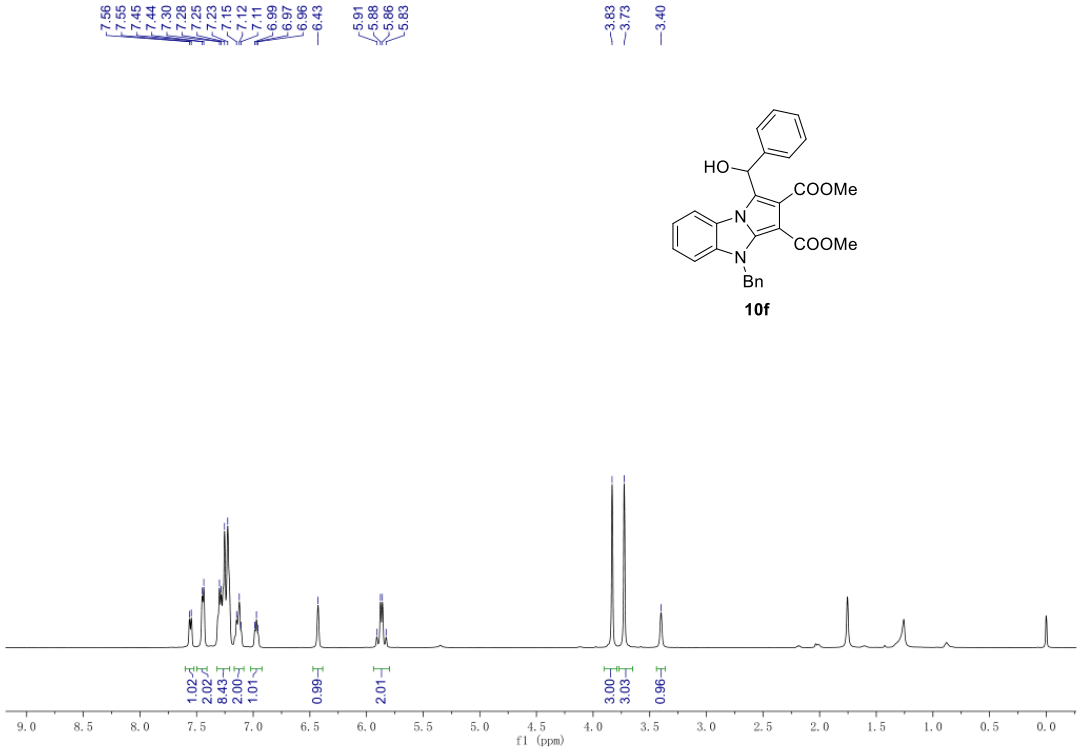

165.48
162.88
154.18
130.67
127.54
123.55
122.53
121.02
120.81
118.64
117.69
116.09
115.13
77.29
77.04
76.78
53.07
52.08
28.51
COOMe
COOMe
N
N
O
9b
f1 (ppm)


8.11
7.46
7.30
7.28
7.26
7.24
7.00
5.42
4.04
3.89
2.30
2.21
COOMe
COOMe
N
N
O
Bn
0.96
1.03
5.21
0.94
1.98
3.00
2.90
3.01
2.93
f1 (ppm)

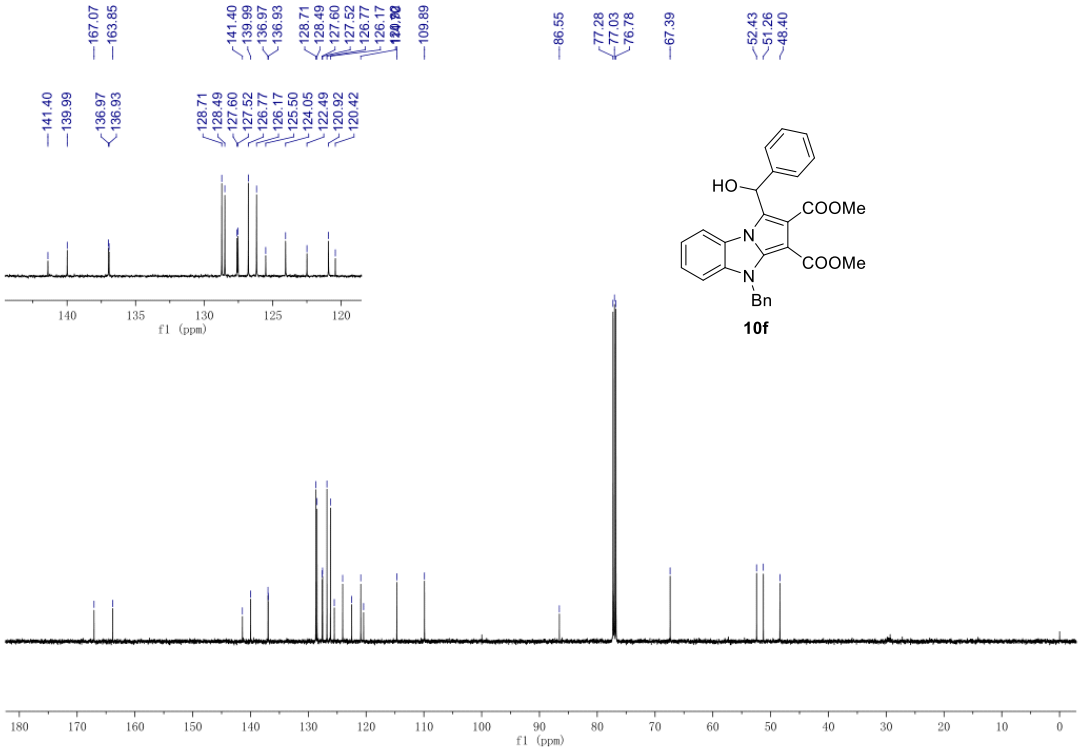
9c


165.64
162.97
154.44
136.44
135.90
132.52
128.86
127.65
127.45
126.65
120.81
120.80
120.40
118.46
117.75
117.42
115.88
77.30
77.05
76.79
53.09
52.03
45.05
20.05
19.38
COOMe
COOMe
N
N
O
Bn
f1 (ppm)

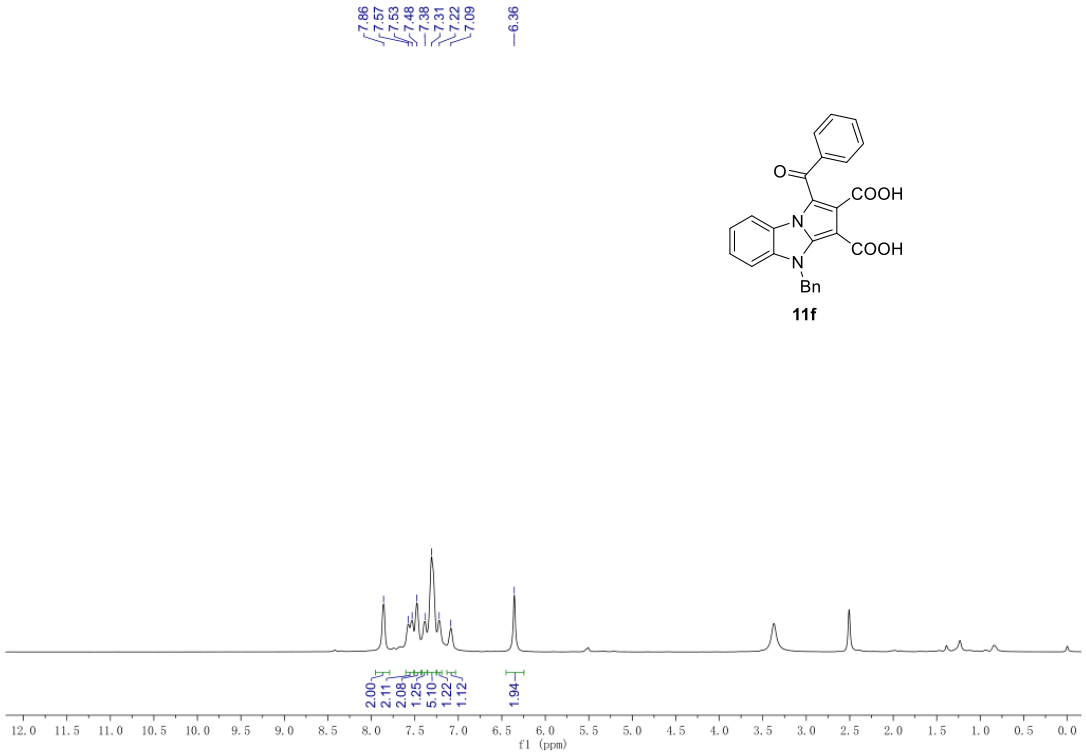
9c

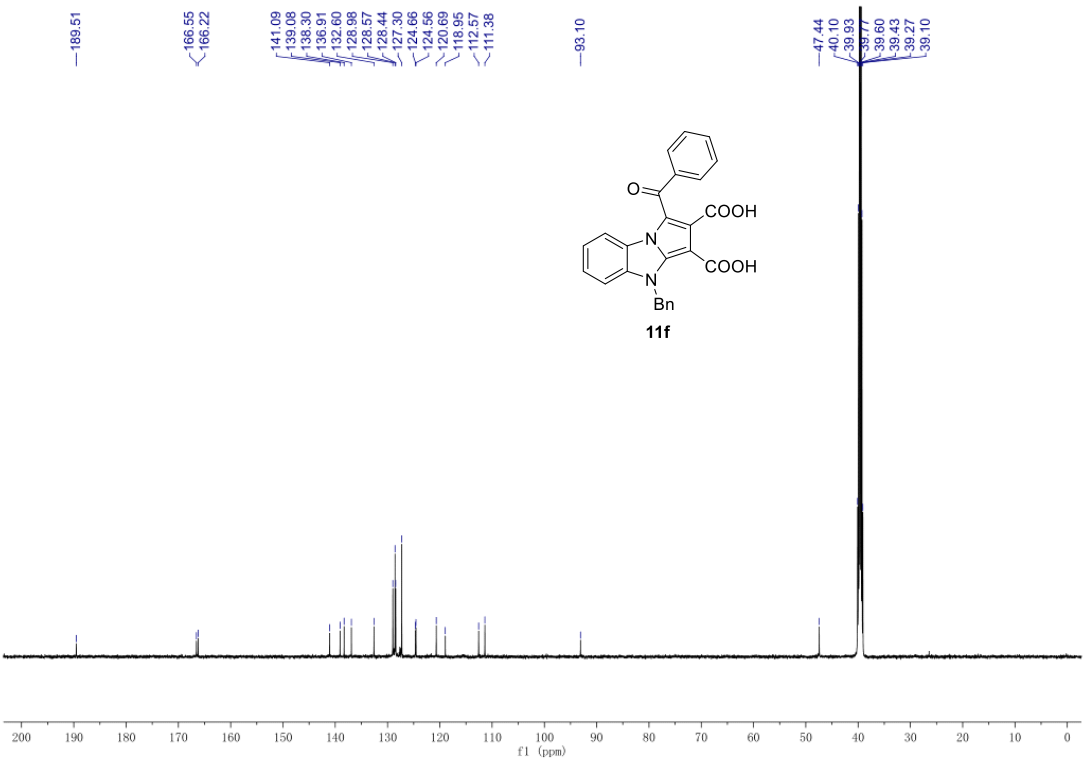

7.56
7.55
7.45
7.44
7.30
7.28
7.25
7.23
7.15
7.12
7.11
6.99
6.97
6.96
6.43
5.91
5.88
5.86
5.83
3.83
3.73
3.40
HO
COOMe
COOMe
N
N
Bn
1.02
2.02
8.43
2.00
1.01
0.99
2.01
3.00
3.03
0.96
f1 (ppm)

10f


167.07
163.85
141.40
139.99
136.97
136.93
128.71
128.49
127.60
127.52
126.77
126.17
109.89
86.55
77.28
77.03
76.78
67.39
52.43
51.26
48.40
HO
COOMe
COOMe
N
N
Bn
f1 (ppm)

10f


7.86
7.57
7.53
7.48
7.38
7.31
7.22
7.09
6.36
O
COOH
COOH
N
N
Bn
11f
2.00
2.11
2.08
1.25
5.10
1.22
1.12
1.94
f1 (ppm)


189.51
166.55
166.22
141.09
139.08
138.30
136.91
132.60
128.98
128.57
128.44
127.30
124.66
124.56
120.69
118.95
112.57
111.38
93.10
47.44
40.10
39.93
39.77
39.60
39.43
39.27
39.10
O
COOH
COOH
N
N
Bn
11f
f1 (ppm)