Supporting Information

Application of Cu(I)/TEMPO/O_2 Catalytic System for Aerobic Oxidative Dehydrogenative Aromatization of Pyrrolidines

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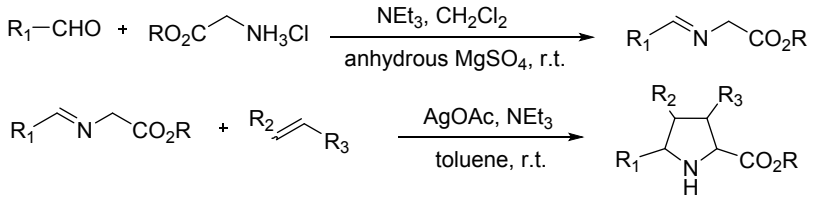
General Information

Unless otherwise noted, all commercial reagents and solvents were obtained from

the commercial provider and used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker 400 MHz spectrometers. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm), $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.49 ppm) for ^{1}H NMR, $CDCl_3$ (δ 77.0 ppm) or DMSO-d_6 (δ 39.5 ppm) for ^{13}C NMR. Flash column chromatography was performed on 300-400 mesh silica gels. Analytical thin layer chromatography was performed with pre-coated glass baked plates (250 μ) and visualized by fluorescence. HRMS were recorded on a Aglient 6540 Q-TOF LC/MS spectrometer. IR spectra were recorded by using a Thermo Scientific Nicolet iS50 FT-IR spectrometer.

Experimental procedure

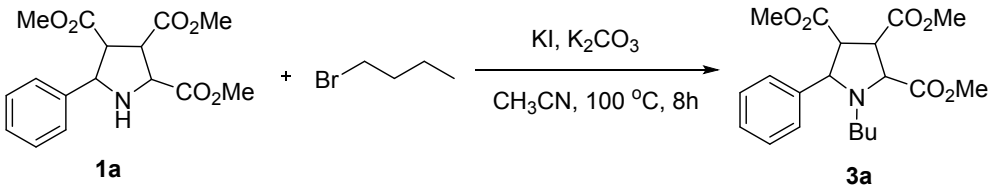
General procedure for synthesis of pyrrolidines 1a-1z.[1-3]



Synthesis of α-Iminoesters. In a 100 mL round-bottomed flask, methyl, ethyl or *tert*-butyl glycinate hydrochloride (12 mmol, 1.2 equiv.), excess magnesium sulfate anhydrous, and Et_3N (12 mmol, 1.2 equiv.) in CH_2Cl_2 (10 mL) was stirred at r.t. for 1 h. Aldehyde (10 mmol, 1.0 equiv.) was added, and the mixture was stirred at r.t. overnight. The reaction was monitored by TLC. The reaction was finished, $MgSO_4$ was removed by filtration and the filtrate was washed with H_2O (30 mL). The aqueous phase was extracted with CH_2Cl_2 (10 mL x 3), and the combined organic layers were washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The crude product was used without any further purification.

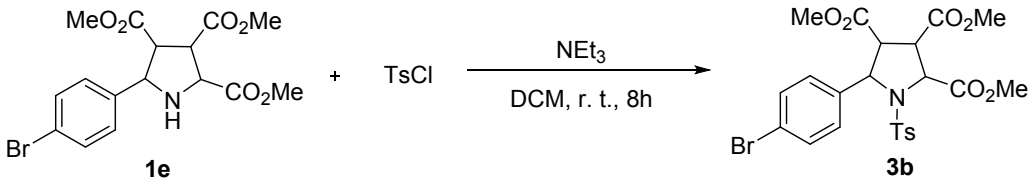
Synthesis of pyrrolidines. Et_3N (1.53 mL, 11 mmol) was added dropwise to the mixture of *α*-Iminoesters, electron-deficient olefin (11 mmol, 1.1 equiv.), AgOAc (0.17g, 1.1 mmol) in toluene (10 mL). The mixture was stirred at r.t. for 12 - 24 h. The reaction was monitored by TLC. After the reaction was finished, toluene was removed by evaporation. The solid residue was suspended in $CHCl_3$ (30 mL), and the precipitate was removed by filtration. The organic phase was washed with 50 mL of water, and 50 mL of brine, dried over Na_2SO_4, and filtered, and volatiles were evaporated. The product was purified by recrystallization or column chromatography on silica gel (petroleum ether/ethyl acetate).

Synthetic procedure for *N*-substituted pyrrolidine 3a, 3b.[4]



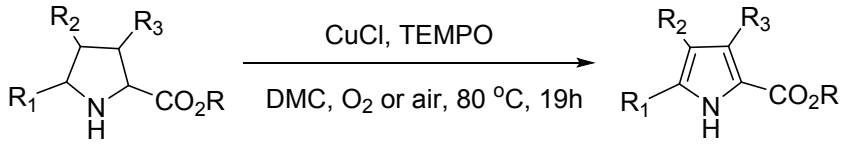
Synthetic Procedure for 3a: A mixture of 1-bromobutane (0.47 mL, 4.4 mmol), pyrrolidine **1a** (0.64 g, 2 mmol), potassium carbonate (0.33 g, 2.4 mmol), and potassium iodide (66.4 mg, 0.40 mmol) in acetonitrile (5.0 mL) was stirred at 100 °C

for 8 h, and to the reaction mixture was added a saturated $NaHCO_3$ aqueous solution. The mixture was then extracted with ethyl acetate (15 mL) for three times. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuum. The residue was purified by flash column chromatography on silica gel (PE/EA = 2/1) to give the title compound **3a** (0.75 g, 73%) as a white solid.



Synthetic Procedure for 3b: The compound **1e** (2.0 mmol) was dissolved in 5.0 mL of methylene chloride. *p*-Toluene-sulfonyl chloride (572.0 mg, 3.0 mmol) and triethyl amine (810 μL, 5.0 mmol) were added subsequently, and the resulting mixture was stirred for 8 h at room temperature. To the reaction mixture was added saturated brine. The mixture was extracted with $CHCl_3$ (15 mL) for three times, dried over Na_2SO_4, and filtered, and volatiles were evaporated. The crude product was purified by column chromatography on silica gel (PE/EA = 3/2) to afford the compound **3b** (84%) as a white solid.

General Procedure for Synthesis of Pyrroles.

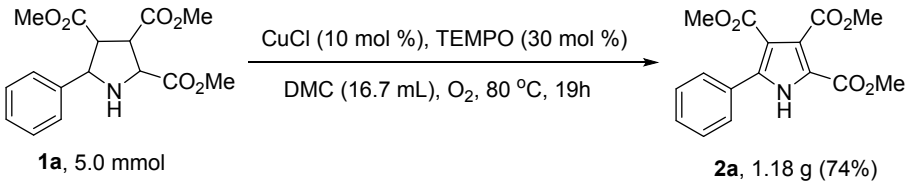


Condition A: Pyrrolidine (0.3 mmol), CuCl (3.0 mg, 0.03 mmol) , TEMPO (14.0 mg, 0.09 mmol) and dimethyl carbonate (1.0 mL) were added into a 15 mL glass test tube, and then the mixture was stirred under O_2 atmosphere (balloon), at 80 °C for 19h. After the reaction was finished, the mixture was cooled down to r.t. Then, the mixture was evaporated under vacuum and the crude mixture was purified by flash chromatography (silica gel, petroleum ether / ethyl acetate).

Condition B: Pyrrolidine (0.3 mmol), CuCl (6.0 mg, 0.06 mmol) , TEMPO (14.0 mg, 0.09 mmol) and dimethyl carbonate (1.0 mL) were added into a 15 mL glass test tube, and then the mixture was stirred under air atmosphere (balloon), at 80 °C for

19h. After the reaction was finished, the mixture was cooled down to r.t. Then, the mixture was evaporated under vacuum and the crude mixture was purified by flash chromatography (silica gel, petroleum ether / ethyl acetate).

Procedure for the Gram-Scale Experiment.

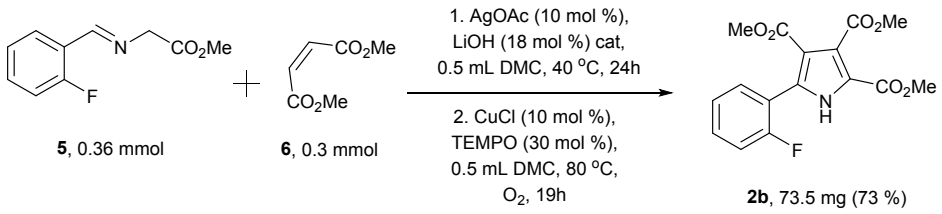


1a, 5.0 mmol

2a, 1.18 g (74%)

Pyrrolidine (**1a**) (1.6067 g, 5.0 mmol), CuCl (49.5 mg, 0.5 mmol) , TEMPO (234.4 mg, 1.5 mmol) and dimethyl carbonate (16.7 mL) were added into a 100 mL glass test tube, and then the mixture was stirred under O_2 atmosphere (balloon), at 80 °C for 19h. When the reaction was finished, the mixture was cooled down to r.t. Then, the mixture was evaporated under vacuum and the crude mixture was purified by flash chromatography (silica gel, petroleum ether / ethyl acetate). The pyrrole (**2a**) was isolated as a white solid in the yield of 74% (1.18 g).

One-pot Reaction for Synthesis of Pyrrole (2b).



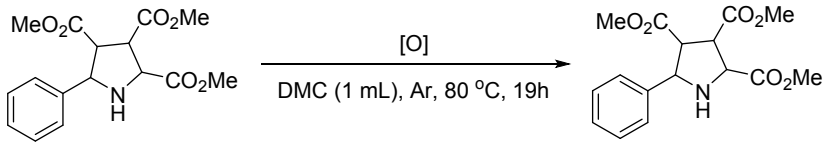
5, 0.36 mmol

6, 0.3 mmol

2b, 73.5 mg (73 %)

α-Iminoester (**5**) (0.36 mmol, 1.2 equiv), dimethyl maleate (**6**) (0.3 mmol, 1.0 equiv), AgOAc (5.0 mg, 10 mol %) , LiOH (1.3 mg, 18 mol %) and 0.5 mL DMC was added into a 15 mL glass test tube stirred at 40 °C for 24 h, The reaction was monitored by TLC. After the reaction was finished, CuCl (3.0 mg, 10 mol %) and TEMPO (14.0 mg, 30 mol %) were added, followed by another 0.5 mL DMC, and then the mixture was stirred under O_2 atmosphere (balloon), at 80 °C for 19h. When the reaction was finished, the mixture was cooled down to r.t. Then, the mixture was evaporated under vacuum and the crude mixture was purified by flash chromatography (silica gel, petroleum ether / ethyl acetate). The pyrrole (**2b**) was isolated as a white solid in the yield of 73% (73.5 mg).

Control experiments.

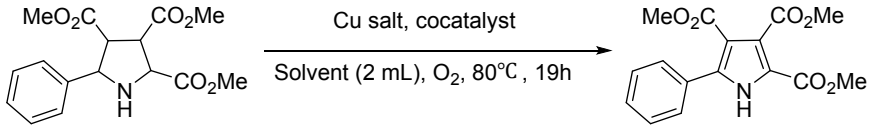


1a, 0.3 mmol **2a**

In three 25-mL Schlenk tubes, pyrrolidine (**1a**) (0.3 mmol, 0.0964g) and $Cu(OAc)_2.H_2O$ (1.5 mmol, 0.2995 g) or TEMPO (1.5 mmol, 0.2334g) or $TEMPO^+BF_4^-$ (0.75 mmol, 0.1824g) were added separately. The air in the Schlenk tube was evacuated and backfilled with Ar three times. DMC (1 mL) was added and the contents were stirred at 80 °C for 19h. After the mixture cooled down to r.t., the mixture was filtered with silica gel and washed the filter cake with CH_2Cl_2 (10 X 3 mL). The combined filtrate was concentrated in vacuo. The NMR yield of the desired product was determined by using CH_2Br_2 as an internal standard.

Table S-1: Optimized reaction conditions.

Table S-1 Optimization of reaction conditions



1a, 0.2 mmol

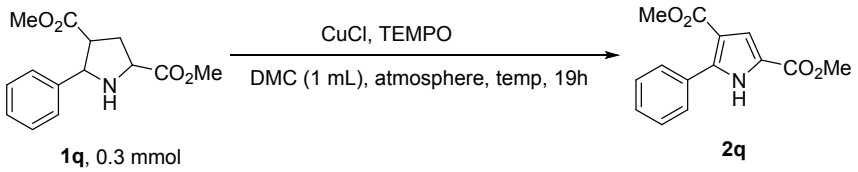
2a

Entry	Cu salt (mol%)	Cocatalyst (mol%)	Solvent	Yield(%)[a]
1	$Cu(NO_3)_2.3H_2O$ (10)	TEMPO (10)	DMC	24
2	$Cu(OTf)_2$ (10)	TEMPO (10)	DMC	31
3	$Cu(OAc)_2.H_2O$ (10)	TEMPO (10)	DMC	25
4	$Cu(CH_3CN)_4PF_6$ (10)	TEMPO (10)	DMC	29
5	CuBr (10)	TEMPO (10)	DMC	37
6	CuCl (10)	TEMPO (10)	DMC	40
7	CuCl (10)	-	DMC	0
8	-	TEMPO (10)	DMC	trace
9	CuCl (10)	4-OH-TEMPO (10)	DMC	17
10	CuCl (10)	4-NHAc-TEMPO (10)	DMC	23
11	CuCl (10)	4-O-TEMPO (10)	DMC	20
12	CuCl (10)	TEMPO (10)	CH_3CH_2OH	27
13	CuCl (10)	TEMPO (10)	CH_3CN	12
14	CuCl (10)	TEMPO (10)	Ethyl acetate	trace
15	CuCl (10)	TEMPO (10)	Toluene	20
16	CuCl (10)	TEMPO (20)	DMC	64
17	CuCl (10)	TEMPO (30)	DMC	68
18	CuCl (10)	TEMPO (50)	DMC	44
19	CuCl (5)	TEMPO (10)	DMC	13
20[b]	CuCl (10)	TEMPO (20)	DMC	37
21[c]	CuCl (10)	TEMPO (20)	DMC	32
22[d]	CuCl (10)	TEMPO (30)	DMC	77
23[e]	CuCl (10)	TEMPO (30)	DMC	81(76[f])
24[e, g]	$FeCl_3$ (10)	TEMPO (30)	DMC	16
25[e, h]	$Co(OAc)_2.4H_2O$ (10)	TEMPO (30)	DMC	16
26[e, i]	$Mn(OAc)_2$ (10)	TEMPO (30)	DMC	12

Reaction conditions: copper salt and TEMPO derivatives as the catalyst, 0.2 mmol **1a**, 2 mL solvent, were stirred under O_2 (balloon) at 80 °C for 19h. [a] Yields were determined by ^1H NMR using CH_2Br_2 as an internal standard. [b] air, 80 °C, 27h. [c] O_2, 60 °C, 44h. [d] 1.0 mL solvent. [e] 0.3 mmol of **1a** in 1.0 mL solvent. [f] Isolated yield. [g] **1a** was recovered in 68%. [h] **1a** was recovered in 44%. [I] **1a** was recovered in 72%.

Table S-2: Re-optimization of reaction conditions.

Table S-2 Re-optimization of reaction condition.



1q, 0.3 mmol

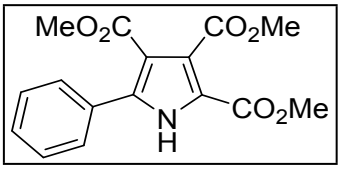
2q

Entry	CuCl (mol %)	TEMPO (mol %)	Atmosphere	Temp (℃)	Yield (%)[a]
1	10	30	air	80	39
2	5	15	O_2	80	27
3	5	30	air	80	33
4	10	50	air	80	60
5	10	30	O_2	60	16
6	10	30	air	60	31
7	20	30	air	80	73 (68[b])

Reaction conditions: CuCl and TEMPO as the catalyst, 0.3 mmol **1q**, 1 mL DMC, were stirred for 19h.[a] Yields were determined by ^{1}H NMR using CH_2Br_2 as an internal standard. [b] Isolated yield.

Characterization data of pyrrole.

Trimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (**2a**).

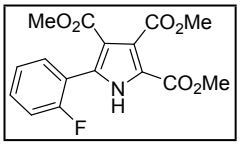


Known compound[4]

Yield: 76% (72.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.34 (br, 1H), 7.58 - 7.52 (m, 2H), 7.48 - 7.42 (m, 3H), 3.97 (s, 3H), 3.86 (s, 3H), 3.73 (s, 3H).

Trimethyl 5-(2-fluorophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2b**).

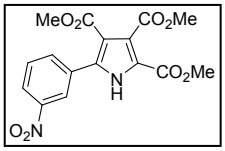


Known compound[4]

Yield: 87% (87.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.31 (br, 1H), 7.47 (dt, J = 7.5, 1.7 Hz, 1H), 7.43 - 7.38 (m, 1H), 7.21 - 7.11 (m, 2H), 3.94 (s, 3H), 3.70 (s, 3H), 3.69 (s, 3H).

Trimethyl 5-(3-nitrophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2c**).



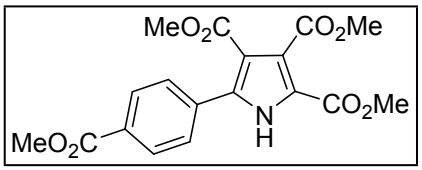
Known compound[4]

Yield: 99% (107.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.54 (br, 1H), 8.45 (s, 1H), 8.25 (d, J = 8.1 Hz, 1H), 7.93 (d, J = 7.5 Hz, 1H), 7.60 (t, J = 7.8 Hz, 1H), 3.94 (s, 3H), 3.73 (s, 3H), 3.72 (s,

3H).

Trimethyl 5-(4-(methoxycarbonyl)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2d**).



Physical state: white solid.

M.P: 172 - 173 °C.

Yield: 74% (82.8 mg).

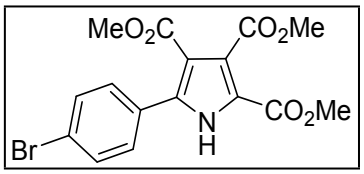
^{1}H NMR (400 MHz, $CDCl_3$): 10.09 (br, 1H), 8.06 (d, J = 8.0 Hz, 2H), 7.63 (d, J = 8.1 Hz, 2H), 3.95 (s, 3H), 3.93 (s, 3H), 3.78 (s, 3H), 3.71 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.5, 165.7, 163.0, 160.1, 138.6, 134.3, 130.8, 129.41, 129.38, 125.0, 120.2, 112.9, 52.8, 52.5, 52.3, 51.7.

IR (KBr) ν: 3289, 3027, 2957, 1721, 1691, 1654, 1615, 1577, 1566, 1530, 1496, 1453, 1438, 1405, 1355 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{18}NO_8$: 376.1027, found 376.1033.

Trimethyl 5-(4-bromophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2e**).



Physical state: white solid.

M.P: 129 - 131 °C.

Yield: 83% (98.9 mg).

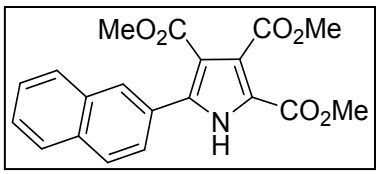
^{1}H NMR (400 MHz, $CDCl_3$): 10.22 (br, 1H), 7.53 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.5 Hz, 2H), 3.94 (s, 3H), 3.712 (s, 3H), 3.708 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.8, 163.0, 160.3, 139.0, 131.4, 131.0, 128.9, 124.9, 123.9, 119.8, 112.4, 52.8, 52.5, 51.7.

IR (KBr) ν: 3295, 2954, 1741, 1719, 1689, 1483, 1452, 1355 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{15}BrNO_6$: 396.0077, found 396.0077.

Trimethyl 5-(naphthalen-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2f**).



Physical state: yellow solid.

M.P: 126 - 128 °C.

Yield: 87% (96.0 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.37 (br, 1H), 7.98 (s, 1H), 7.89 - 7.86 (m, 3H), 7.60

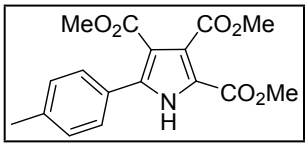
(dd, J = 8.5, 1.6 Hz, 1H), 7.51 - 7.48 (m, 2H), 3.93 (s, 3H), 3.68 (s, 3H), 3.53 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.0, 163.2, 160.4, 140.3, 133.4, 132.7, 128.9, 128.3, 127.7, 127.6, 127.5, 127.1, 126.9, 126.6, 125.1, 119.7, 112.4, 52.8, 52.3, 51.6.

IR (KBr) ν: 3269, 2952, 1697, 1571, 1526, 1499, 1469, 1450, 1365 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}NO_6$: 368.1129, found 368.1133.

Trimethyl 5-(*p*-tolyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2g**).

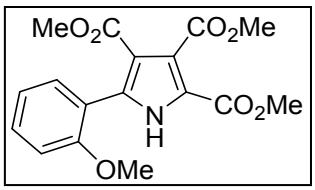


Known compound[4]

Yield: 78% (77.8 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.90 (br, 1H), 7.44 (d, J = 7.8 Hz, 2H), 7.21 (d, J = 7.8 Hz, 2H), 3.94 (s, 3H), 3.74 (s, 3H), 3.71 (s, 3H), 2.38 (s, 3H).

Trimethyl 5-(2-methoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2h**).



Physical state: yellow solid.

M.P: 128 - 130 °C.

Yield: 79% (82.3 mg).

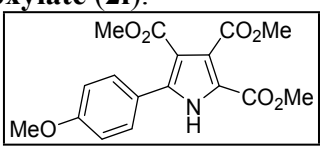
^{1}H NMR (400 MHz, $CDCl_3$): 10.10 (br, 1H), 7.44 (dd, J = 7.6, 1.7 Hz, 1H), 7.36 (dt, J = 7.9, 1.7 Hz, 1H), 7.00 - 6.94 (m, 2H), 3.94 (s, 3H), 3.76 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.1, 163.4, 160.3, 156.9, 136.3, 131.9, 130.9, 124.2, 120.3, 119.1, 118.6, 113.3, 111.0, 55.6, 52.7, 52.2, 51.5.

IR (KBr) ν: 3306, 3002, 2950, 2840, 1733, 1712, 1686, 1608, 1584, 1566, 1523, 1499, 1470, 1447, 1359, 1301 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{18}NO_7$: 348.1078, found 348.1086.

Trimethyl 5-(4-methoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2i**).

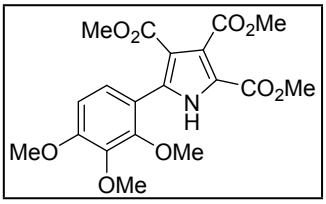


Known compound[4]

Yield: 81% (84.5 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.86 (br, 1H), 7.50 (d, J = 8.2 Hz, 2H), 6.92 (d, J = 8.2 Hz, 2H), 3.94 (s, 3H), 3.83 (s, 3H), 3.76 (s, 3H), 3.71 (s, 3H).

Trimethyl 5-(2,3,4-trimethoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2j**).



Physical state: yellow solid.

M.P: 191 - 193°C.

Yield: 64% (77.5 mg).

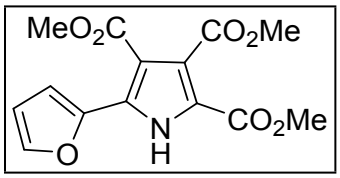
^{1}H NMR (400 MHz, $CDCl_3$): 9.68(br, 1H), 7.32(d, *J* = 8.8 Hz, 1H), 6.74(d, *J* = 8.8 Hz, 1H), 3.97(s, 3H), 3.91(s, 6H), 3.88(s, 3H), 3.74(s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.1, 163.4, 159.8, 154.9, 151.6, 142.1, 135.8, 126.7, 124.2, 119.1, 115.8, 112.7, 107.2, 61.5, 61.1, 56.0, 52.8, 52.3, 51.6.

IR (KBr) ν: 3424, 3294, 2954, 1750, 1735, 1711, 1701, 1686, 1654, 1617, 1603, 1577, 1560, 1493, 1458, 1420, 1383, 1357 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{22}NO_9$: 408.1289, found 408.1296.

Trimethyl 5-(furan-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2k**).



Physical state: yellow solid.

M.P: 122 - 123 °C.

Yield: 59% (53.9 mg).

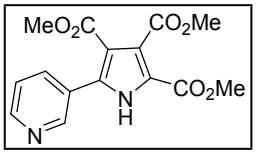
^{1}H NMR (400 MHz, $CDCl_3$): 9.69 (br, 1H), 7.57 (d, *J* = 3.6 Hz, 1H), 7.50 (d, *J* = 1.8 Hz, 1H), 6.54 (dd, *J* = 3.5, 1.8 Hz, 1H), 3.94 (s, 3H), 3.89(s, 3H), 3.84 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.7, 162.7, 159.7, 143.9, 143.1, 129.8, 124.9, 119.2, 113.8, 112.6, 110.2, 52.7, 52.4, 51.8.

IR (KBr) ν: 3375, 3278, 2956, 1706, 1606, 1571, 1541, 1521, 1489, 1441, 1379, 1357 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_7$: 308.0765, found 308.0767.

Trimethyl 5-(pyridin-3-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2l).



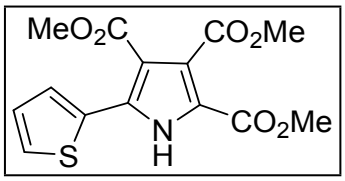
Known compound[4]

Yield: 87% (83.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 11.60 (br, 1H), 8.61 - 8.55 (m, 2H), 7.99 (dt, *J* = 8.0, 1.9 Hz, 1H), 7.36 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.96 (s, 3H), 3.81 (s, 3H), 3.71 (s, 3H).

Trimethyl 5-(thiophen-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2m**).

Physical state: yellow solid.



M.P: 118 - 120 °C.

Yield: 77% (74.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.87 (br, 1H), 7.55 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.44 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.11 - 7.05 (m, 1H), 3.94 (s, 3H), 3.81 (s, 3H), 3.78 (s, 3H).

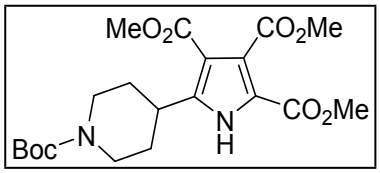
^{13}C NMR (100 MHz, $CDCl_3$): 165.7, 163.0, 160.0, 133.1, 130.4, 129.5, 128.2, 127.2, 125.0, 119.6, 112.2, 52.8, 52.5, 51.7.

IR (KBr) ν: 3278, 2956, 1706, 1571, 1541, 1521, 1489, 1411, 1404 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO_6S$: 324.0536, found 324.0541.

Trimethyl 5-(1-(tert-butoxycarbonyl)piperidin-4-yl)-1*H*-pyrrole-2,3,4-tricarboxyla (2n).

Physical state: yellow solid.



M.P: 147 - 149 °C.

Yield: 77% (97.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.10 (br, 1H), 4.40 - 4.15 (m, 2H), 3.93 (s, 3H), 3.83 (s, 3H), 3.81 (s, 3H), 3.76 - 3.66 (m, 1H), 2.95 - 2.70 (m, 2H), 1.89 (dd, *J* = 12.3, 3.3 Hz, 2H), 1.80 - 1.62 (m, 2H), 1.47 (s, 9H).

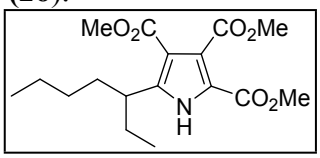
^{13}C NMR (100 MHz, $CDCl_3$): 166.2, 163.5, 160.1, 154.5, 145.9, 124.1, 118.7, 110.9, 79.8, 52.7, 52.4, 51.5, 44.1, 34.2, 30.8, 28.4.

IR (KBr) ν: 3304, 2955, 2856, 1744, 1716, 1686, 1576, 1522, 1458, 1382, 1366, 1313 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{29}N_2O_8$: 425.1918, found 425.1934.

Trimethyl 5-(heptan-3-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2o).

Known compound[4]

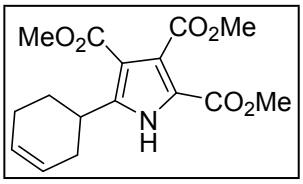


Yield: 84% (85.7 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.70 (br, 1H), 3.94 (s, 3H), 3.86 (s, 3H), 3.80 (s, 3H), 3.65 - 3.55 (m, 1H), 1.80 - 1.55 (m, 4H), 1.33 - 1.16 (m, 4H), 0.85 - 0.78 (m, 6H).

Trimethyl 5-(cyclohex-3-en-1-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2p**).

Physical state: white solid.



M.P: 142 - 144 °C.

Yield: 71% (68.2 mg).

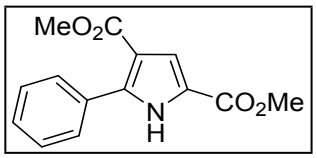
^{1}H NMR (400 MHz, $CDCl_3$): 9.66 (br, 1H), 5.85 - 5.75 (m, 2H), 3,93 (s, 3H), 3.84 (s, 3H), 3.80 (s, 3H), 2.41 (dd, *J* = 16.2, 5.5 Hz, 1H), 2.27 - 2.15 (m, 2H), 2.13 - 1.77 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.3, 163.5, 160.2, 147.1, 127.8, 125.6, 124.1, 118.2, 111.1, 52.7, 52.3, 51.5, 31.1, 30.0, 27.2, 24.4.

IR (KBr) ν: 3298, 2952, 2836, 1748, 1714, 1686, 1654, 1576, 1457, 1420, 1376 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO_6$: 322.1285, found 322.1288.

Dimethyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2q).



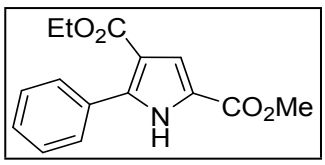
Known compound[5]

Yield: 68% (52.9 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.92 (br, 1H), 7.69 - 7.61 (m, 2H), 7.49 - 7.42 (m, 3H), 7.41 (d, *J* = 2.8 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H).

4-Ethyl 2-methyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2r).

Physical state: white solid.



M.P: 125 - 127 °C.

Yield: 76% (62.3 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 9.89 (br, 1H), 7.62 (dd, *J* = 7.4, 3.2 Hz, 2H), 7.46 - 7.36 (m, 4H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

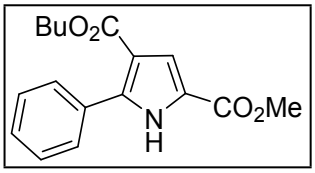
^{13}C NMR (100 MHz, $CDCl_3$): 164.0, 161.5, 140.9, 130.8, 129.3, 129.1, 128.1, 121.9, 118.6, 114.2, 60.0, 51.8, 14.2.

IR (KBr) ν: 3310, 2977, 1720, 1696, 1567, 1473, 1431, 1347 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{16}NO_4$: 274.1074, found 274.1073.

4-Butyl 2-methyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2s).

Physical state: yellow solid.



M.P: 92 - 94 °C.

Yield: 69% (62.4 mg).

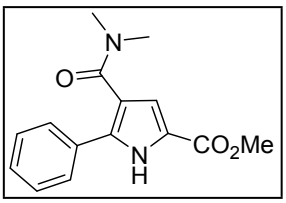
^{1}H NMR (400 MHz, $CDCl_3$): 9.90 (br, 1H), 7.65 - 7.58 (m, 2H), 7.45 - 7.36 (m, 4H), 4.16 (t, *J* = 6.5 Hz, 2H), 3.77 (s, 3H), 1.65 - 1.55 (m, 2H), 1.37-1.26 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 164.1, 161.5, 140.9, 130.9, 129.3, 129.0, 128.1, 121.9, 118.5, 114.3, 64.0, 51.9, 30.7, 19.2, 13.7.

IR (KBr) ν: 3280, 2964, 1713, 1691, 1465, 1446, 1432, 1345 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{20}NO_4$: 302.1387, found 302.1391.

Methyl 4-(dimethylcarbamoyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (2t).



Physical state: white solid.

M.P: 167 - 169 °C.

Yield: 60% (49.0 mg).

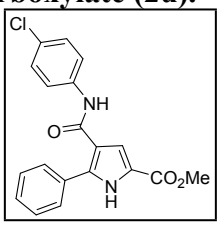
^{1}H NMR (400 MHz, $CDCl_3$): 9.78 (br, 1H), 7.52 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.43 - 7.33 (m, 3H), 7.00 (d, *J* = 2.6 Hz, 1H), 3.84 (s, 3H), 3.03 (s, 3H), 2.72 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 161.5, 134.6, 130.9, 129.0, 128.5, 126.7, 122.4, 118.4, 116.3, 51.8, 38.7, 35.0.

IR (KBr) ν: 3452, 3114, 1712, 1597, 1561, 1512, 1462, 1437 , 1333 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{17}N_2O_3$: 273.1234, found 273.1236.

Methyl 4-((4-chlorophenyl)carbamoyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (2u).



Physical state: yellow solid.

M.P: 226 - 227 °C.

Yield: 59% (62.8 mg).

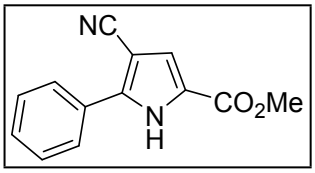
^{1}H NMR (400 MHz, DMSO-d_6): 12.51 (br, 1H), 9.97 (s, 1H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.63 -7.57 (m, 2H), 7.47 (d, *J* = 2.3 Hz, 1H), 7.42 - 7.36 (m, 3H), 7.34 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d_6): 163.2, 161.0, 139.6, 138.9, 131.3, 129.8, 128.8, 128.7, 128.1, 127.0, 121.9, 121.8, 118.1, 116.9, 51.8.

IR (KBr) ν: 3311, 1685, 1655, 1593, 1513, 1494, 1470, 1447, 1395, 1305 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{19}H_{15}ClN_2O_3Na$: 377.0663, found 377.0669.

Methyl 4-cyano-5-phenyl-1*H*-pyrrole-2-carboxylate (2v).



Physical state: white solid.

M.P: 215 - 216 °C.

Yield: 70% (47.5 mg).

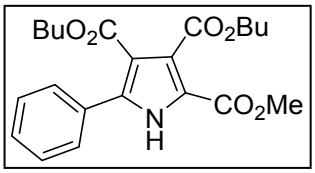
^{1}H NMR (400 MHz, DMSO-d_6): 13.12 (br, 1H), 7.83 (d, *J* = 7.2 Hz, 2H), 7.58 - 7.45 (m, 3H), 7.35 (s, 1H), 3.84 (s, 3H).

^{13}C NMR (100 MH_Z, DMSO-d_6): 160.3, 143.0, 130.0, 129.3, 129.1, 127.8, 124.3, 120.0, 116.9, 91.4, 52.3.

IR (KBr) ν: 3266, 2960, 2224, 1690, 1519, 1472, 1445, 1429, 1416, 1346, 1317 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+Na]^+$ calcd for $C_{13}H_{10}N_2O_2Na$: 249.0634, found 249.0640.

3,4-Dibutyl 2-methyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2w).



Physical state: white solid.

M.P: 56 - 58 °C.

Yield: 75% (90.3 mg).

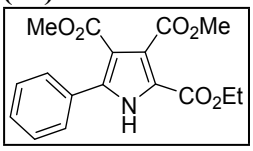
^{1}H NMR (400 MHz, $CDCl_3$): 10.06 (br, 1H), 7.54 (dd, *J* = 6.7, 3.0, 2H), 7.44 - 7.36 (m, 3H), 4.35 (t, *J* = 6.7 Hz, 2H), 4.11 (t, *J* = 6.5 Hz, 2H), 3.70 (s, 3H), 1.80 - 1.70 (m, 2H), 1.57 - 1.40 (m, 4H), 1.28 - 1.17 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H), 0.85 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 165.6, 162.8, 160.5, 140.2, 130.3, 129.5, 129.3, 128.1, 125.2, 119.3, 112.5, 65.7, 64.4, 52.2, 30.6, 30.5, 19.2, 19.0, 13.7, 13.6.

IR (KBr) ν: 3269, 2958, 2874, 1735, 1719, 1701, 1686, 1485, 1459, 1357 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{28}NO_6$: 402.1911, found 402.1919.

2-Ethyl 3,4-dimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2x).



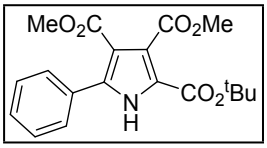
Known compound[6]

Yield: 75% (74.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.40 (br, 1H), 7.55 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 - 7.37 (m, 3H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.92 (s, 3H), 3.69 (s, 3H), 1.23 (t, *J* = 7.1 Hz, 3H).

2-(Tert-butyl) 3,4-dimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2y).

Known compound[6]

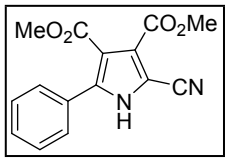


Yield: 76% (82.4 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.02 (br, 1H), 7.53 - 7.51 (m, 2H), 7.41 - 7.40 (m, 3H), 3.92 (s, 3H), 3.69 (s, 3H), 1.39 (s, 9H).

Dimethyl 2-cyano-5-phenyl-1*H*-pyrrole-3,4-dicarboxylate (2z).

Known compound[7]



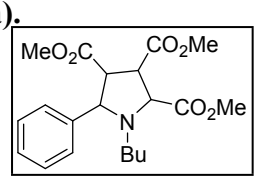
Yield: 30% (25.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 10.41 (br, 1H), 7.49 - 7.43 (m, 2H), 7.43 - 7.37 (m, 3H), 3.89 (s, 3H), 3.82 (s, 3H).

Characterization Data of 3.

Trimethyl 1-butyl-5-phenylpyrrolidine-2,3,4-tricarboxylate (3a).

Physical state: white solid.



M.P: 84 - 85 ^{o}C.

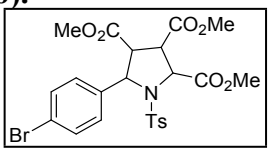
^{1}H NMR (400 MHz, $CDCl_3$): 7.44 (d, *J* = 6.9 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 4.20 (d, *J* = 6.8 Hz, 1H), 3.95 (d, *J* = 9.6 Hz, 1H), 3.80 (s, 3H), 3.72 (s, 3H), 3.53 (dd, *J* = 9.6, 6.7 Hz, 1H), 3.36 (t, *J* = 6.8 Hz, 1H), 3.20 (s, 3H), 2.77 - 2.67 (m, 1H), 2.62 - 2.51 (m, 1H), 1.53 - 1.41 (m, 1H), 1.41 - 1.22 (m, 2H), 1.22 - 1.11 (m, 1H), 0.82 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 172.6, 170.2, 169.9, 138.5, 128.0, 127.8, 127.6, 70.0, 65.3, 53.7, 52.0, 51.9, 51.6, 51.0, 47.9, 29.0, 20.4, 13.9.

IR (KBr) ν: 3456, 2951, 2871, 1760, 1750, 1701, 1494, 1455, 1437, 1384, 1352, 1318 cm $^{-1}$.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{28}NO_6$: 378.1911, found 378.1918.

Trimethyl 5-phenyl-1-tosylpyrrolidine-2,3,4-tricarboxylate (3b).



Physical state: white solid.

M.P: 166 - 167 °C.

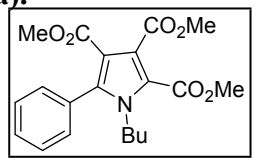
^{1}H NMR (400 MHz, $CDCl_3$): 7.54 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 5.28 (d, *J* = 8.9 Hz, 1H), 5.08 (d, *J* = 7.8 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.49 (dd, *J* = 7.8, 6.5 Hz, 1H), 3.37 (dd, *J* = 8.9, 6.5 Hz, 1H), 3.19 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 169.6, 169.5, 167.9, 144.2, 135.2, 134.7, 130.8, 129.5, 129.2, 128.3, 121.9, 65.2, 61.7, 52.7, 52.3, 51.6, 51.2, 48.3, 21.5.

IR (KBr) ν: 3451, 2995, 2951, 1754, 1742, 1701, 1654, 1617, 1596, 1577, 1560, 1486, 1437, 1408, 1358 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{25}BrNO_8S$: 554.0479, found 554.0478.

Trimethyl 1-butyl-5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (4a).



Physical state: colorless stick oil.

Yield: 25% (27.6 mg).

^{1}H NMR (400 MHz, $CDCl_3$): 7.52 - 7.41 (m, 3H), 7.31 - 7.26 (m, 2H), 4.09 (t, *J* = 7.8 Hz, 2H), 3.96 (s, 3H), 3.85 (s, 3H), 3.58 (s, 3H), 1.57 - 1.48 (m, 2H), 1.17 - 1.06 (m, 2H), 0.73 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 166.9, 163.0, 160.0, 143.0, 130.23, 130.21, 129.3, 128.2, 126.1, 119.2, 112.0, 52.7, 52.0, 51.4, 46.2, 33.4, 19.7, 13.4.

IR (NaCl) ν: 2955, 2874, 1745, 1713, 1547, 1519, 1483, 1446, 1405, 1369, 1314 cm^{-1}.

HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{24}NO_6$: 374.1598, found 374.1603.

Reference

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5. E. E. Galenko, V. A. Bodunov, A. V. Galenko, M. S. Novikov, A. F. Khlebnikov, *J. Org. Chem.*, 2017, **82**, 8568.
6. K. Fukushima, T. Ibata, *Bull. Chem. Soc. Jpn.,* 1995, **68**, 3469.
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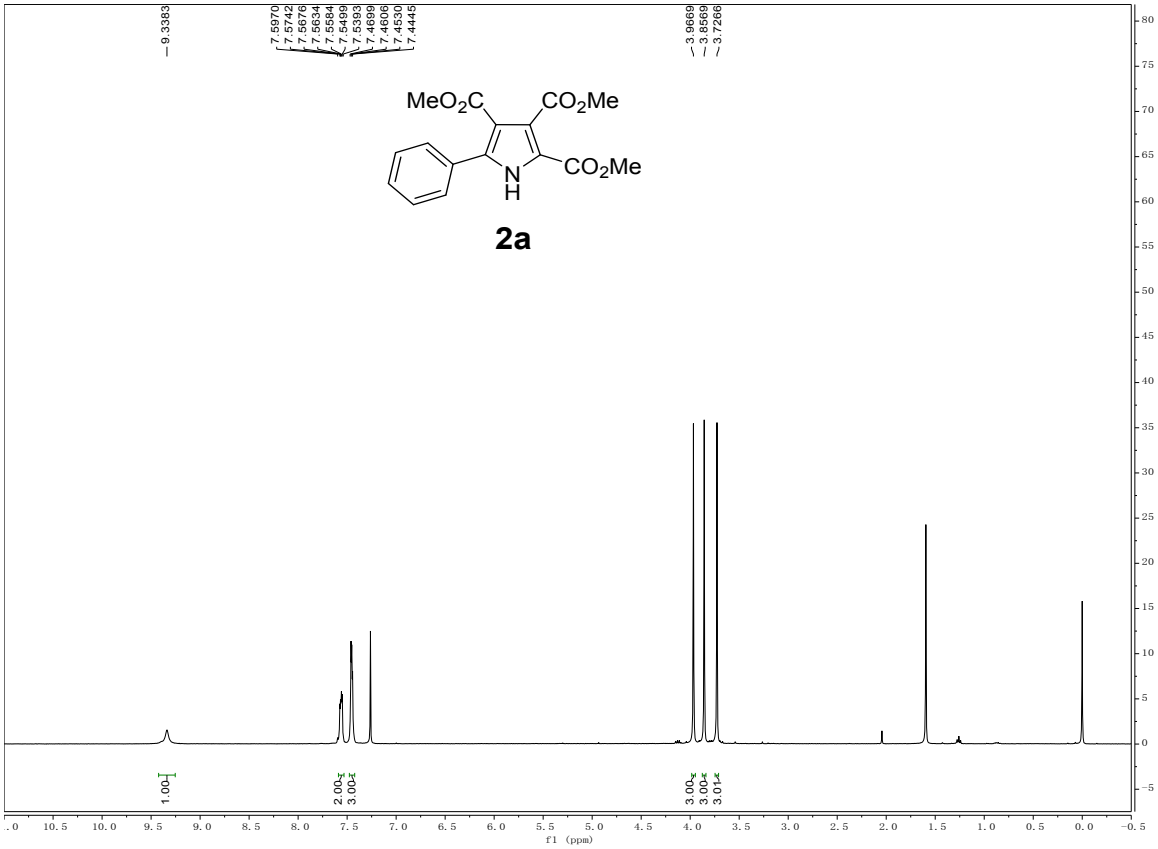
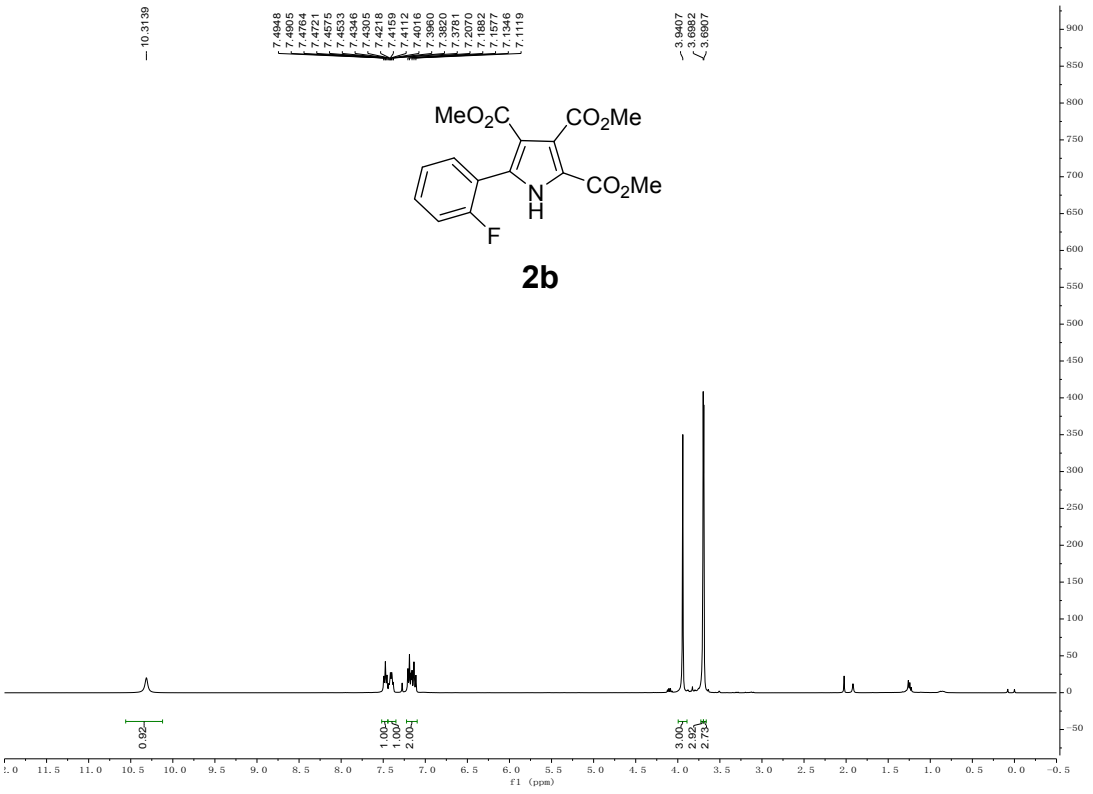
^{1}H and ^{13}C NMR spectra of pyrroles and pyrrolidines.

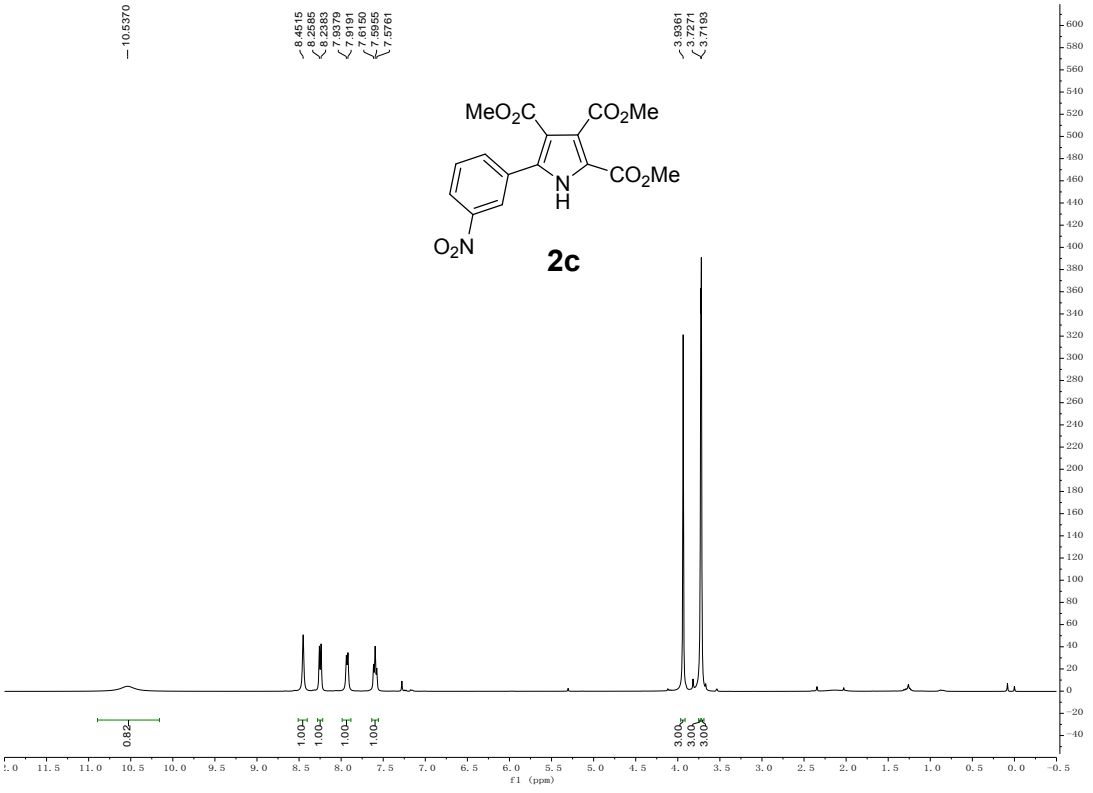
Trimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2a).



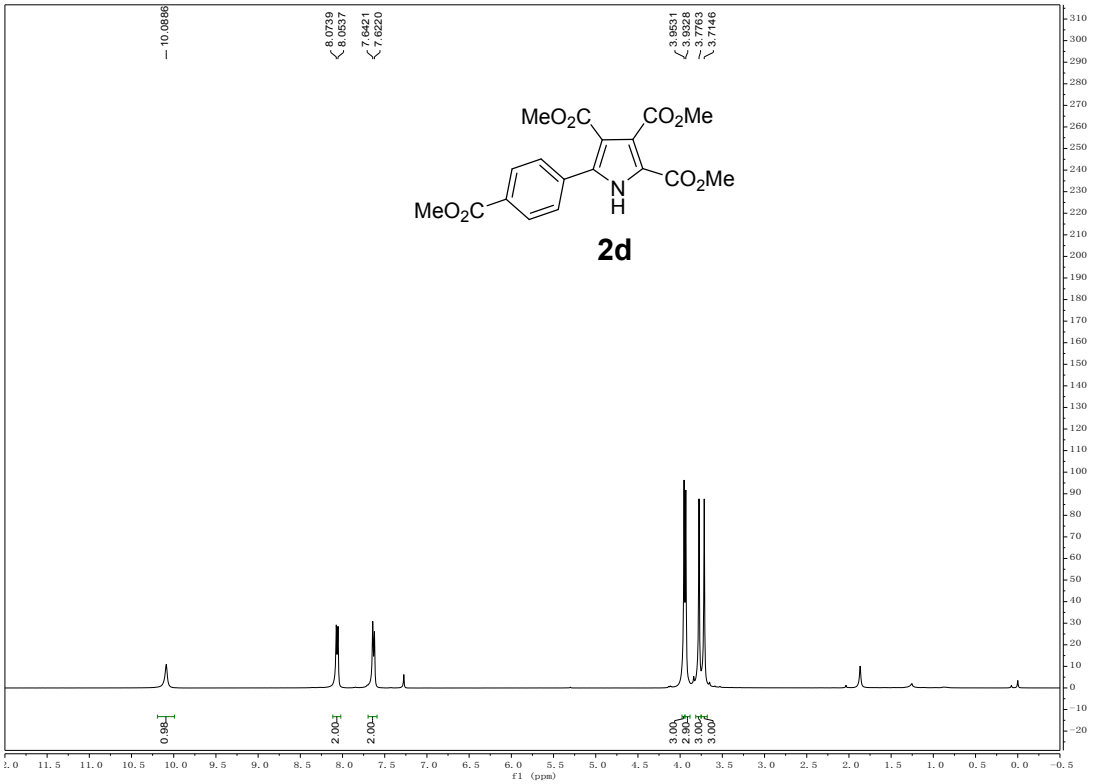
Trimethyl 5-(2-fluorophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2b).

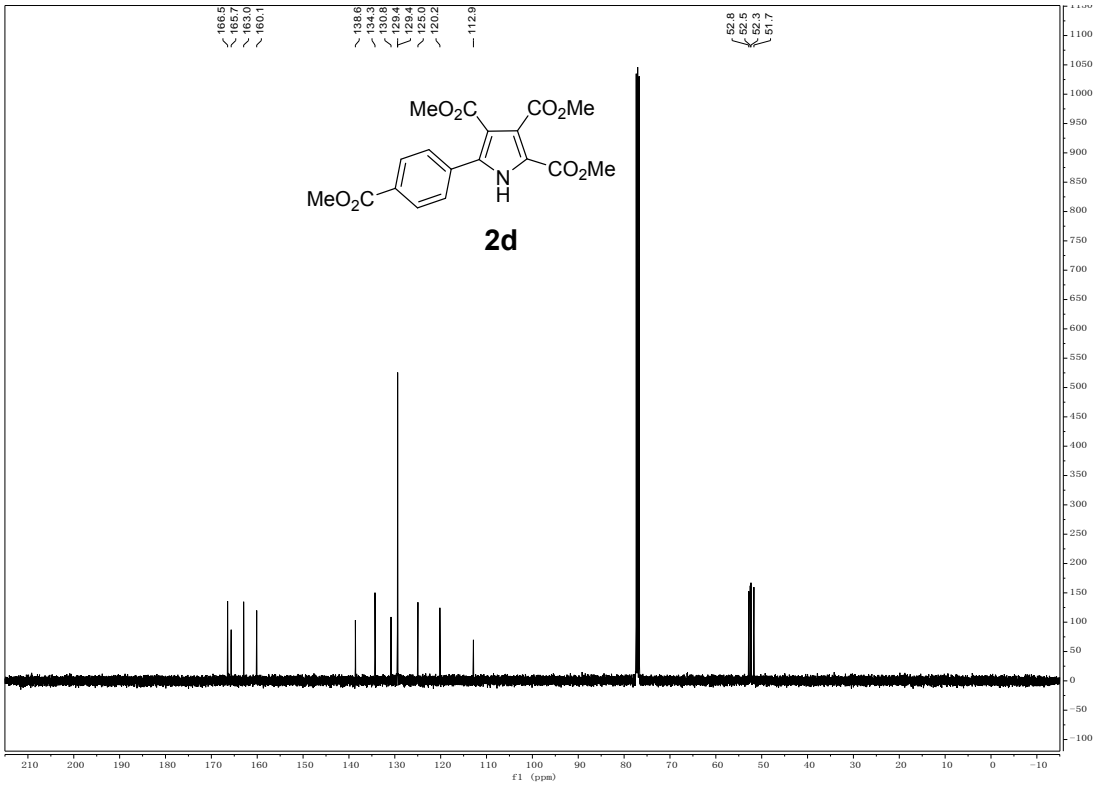


Trimethyl 5-(3-nitrophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2c).

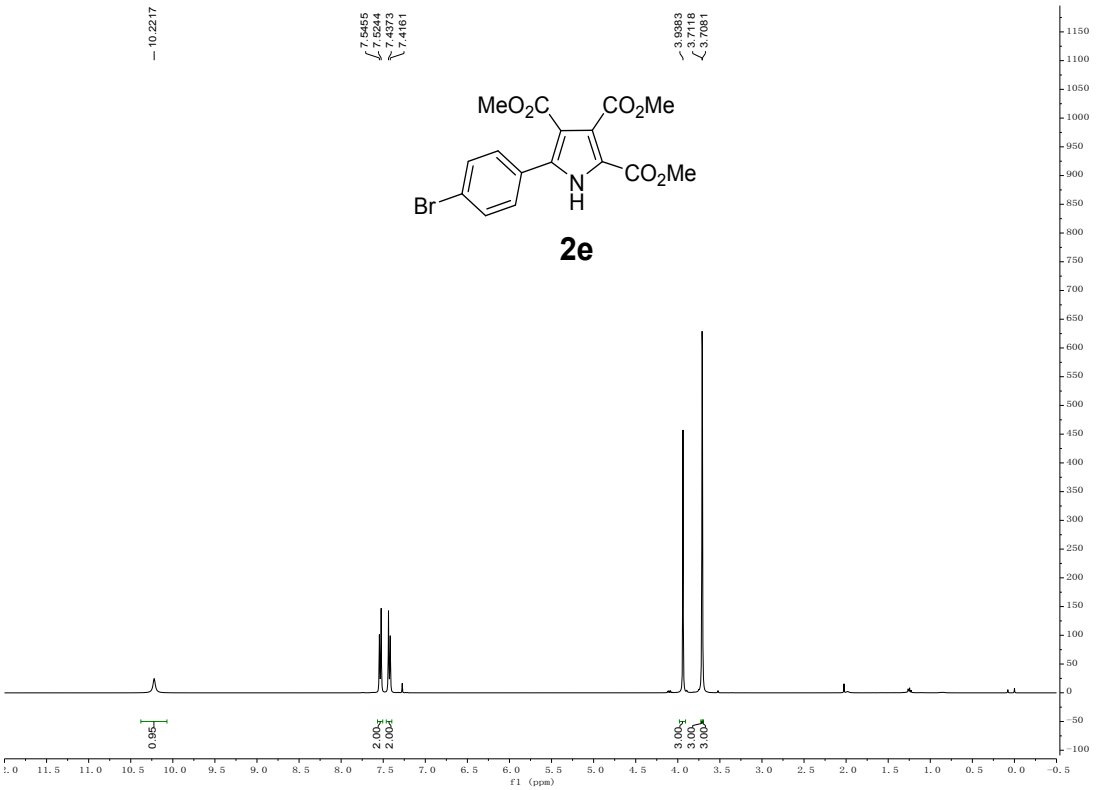


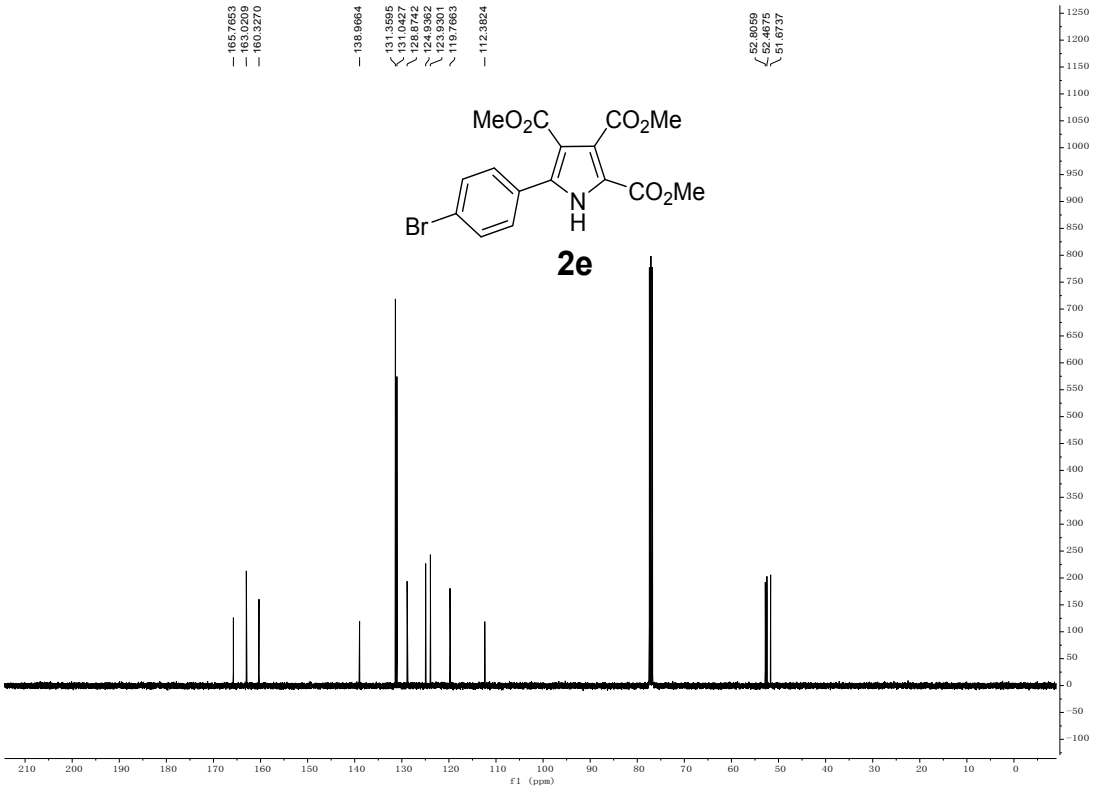
Trimethyl 5-(4-(methoxycarbonyl)phenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2d).



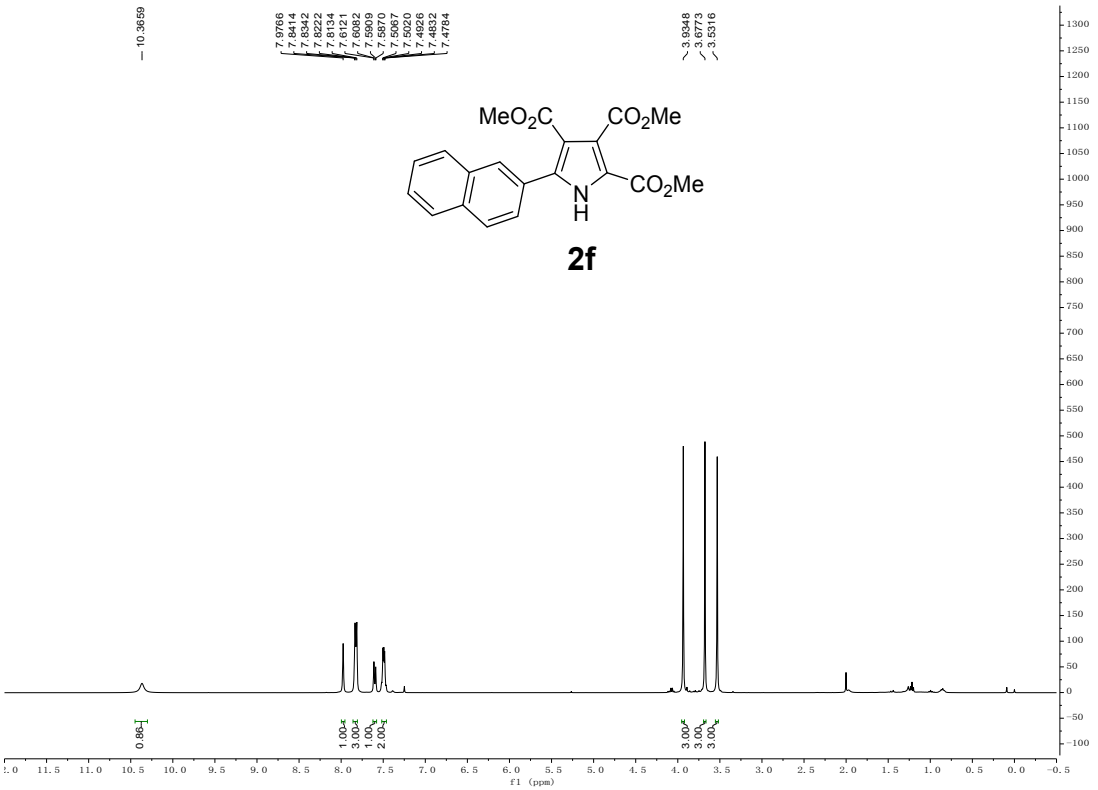


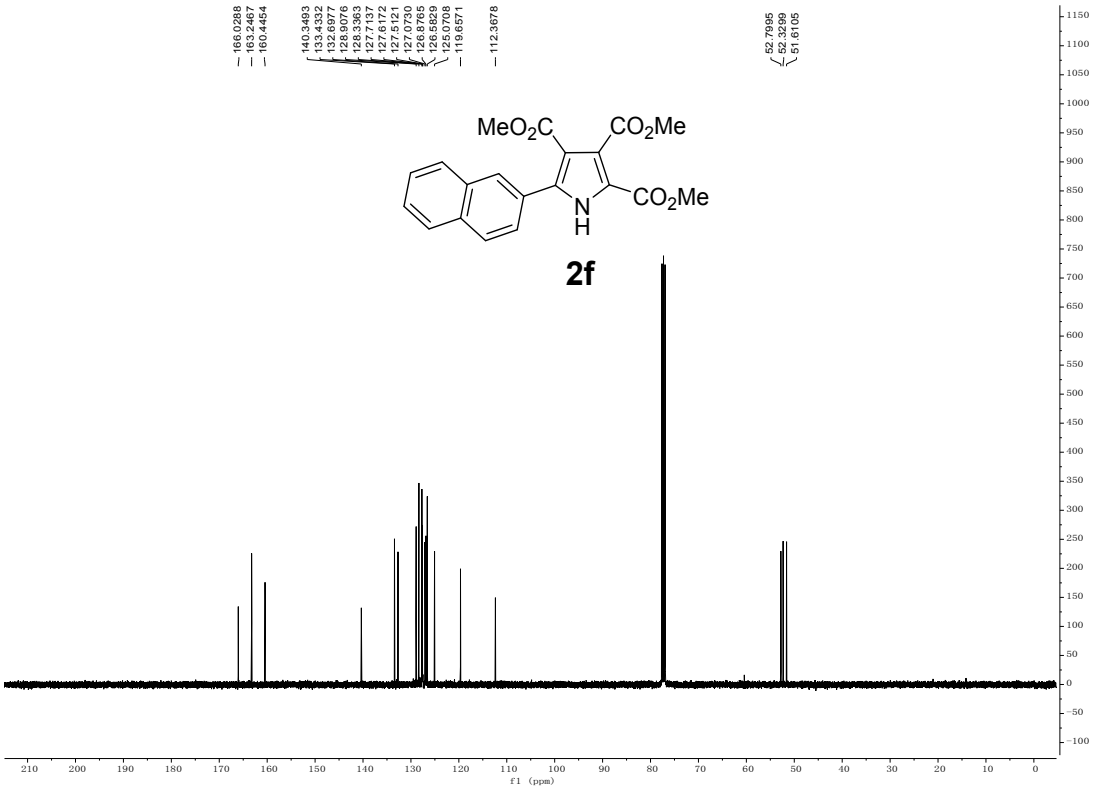
Trimethyl 5-(4-bromophenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2e).



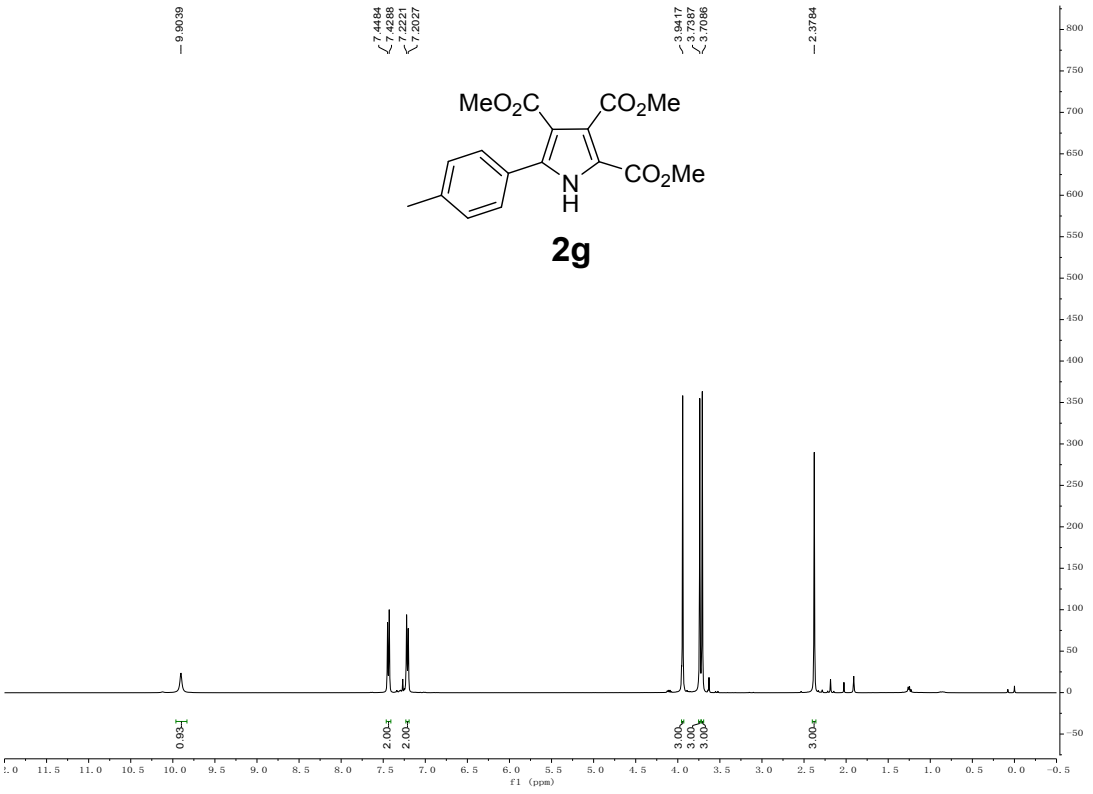


Trimethyl 5-(naphthalen-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2f).



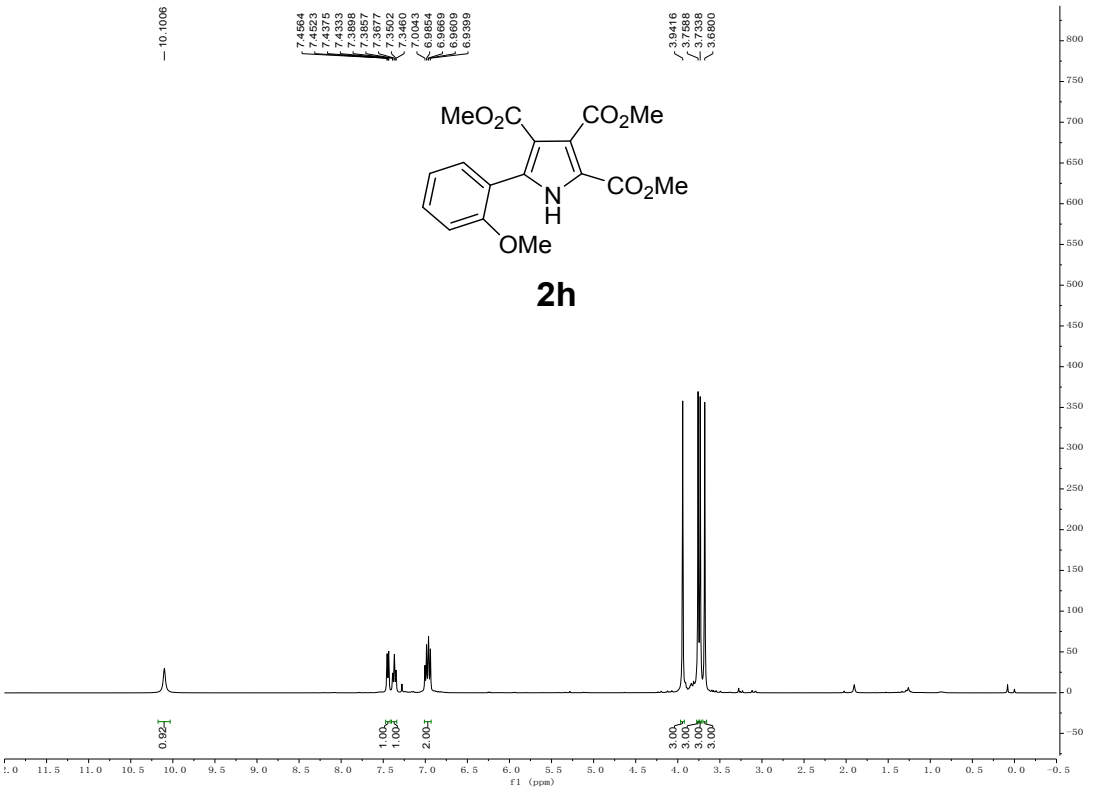


Trimethyl 5-(*p*-tolyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2g).

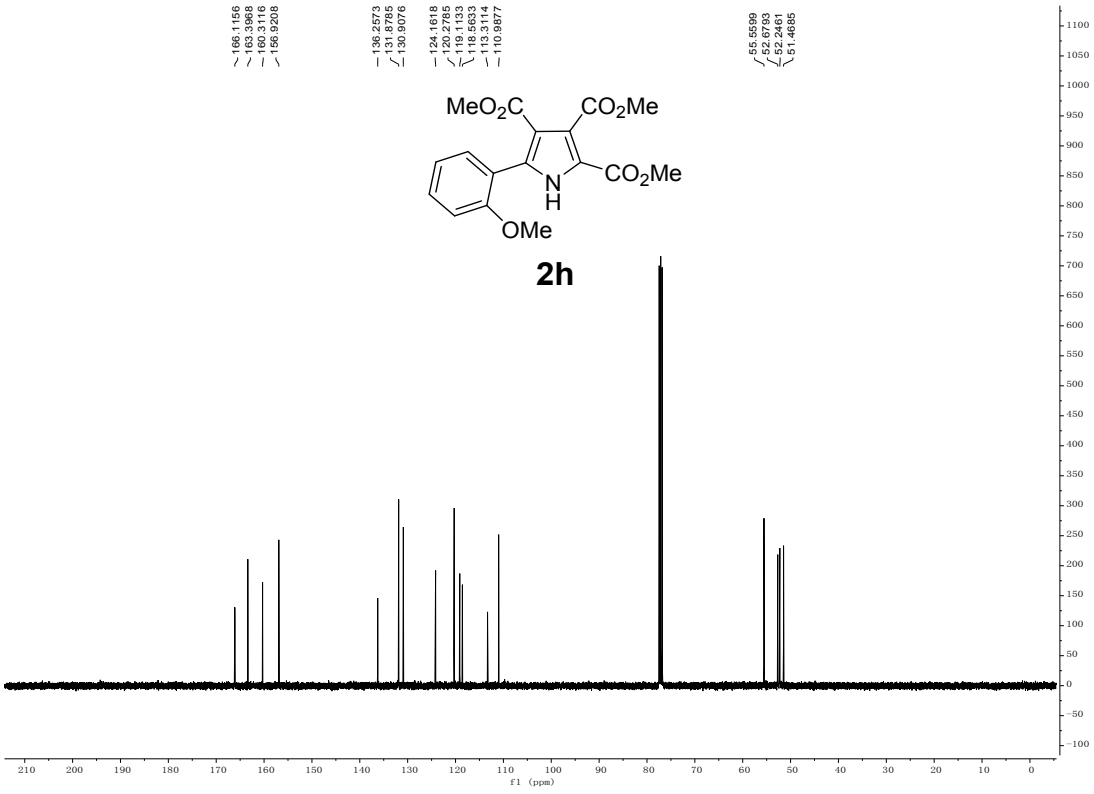


2g

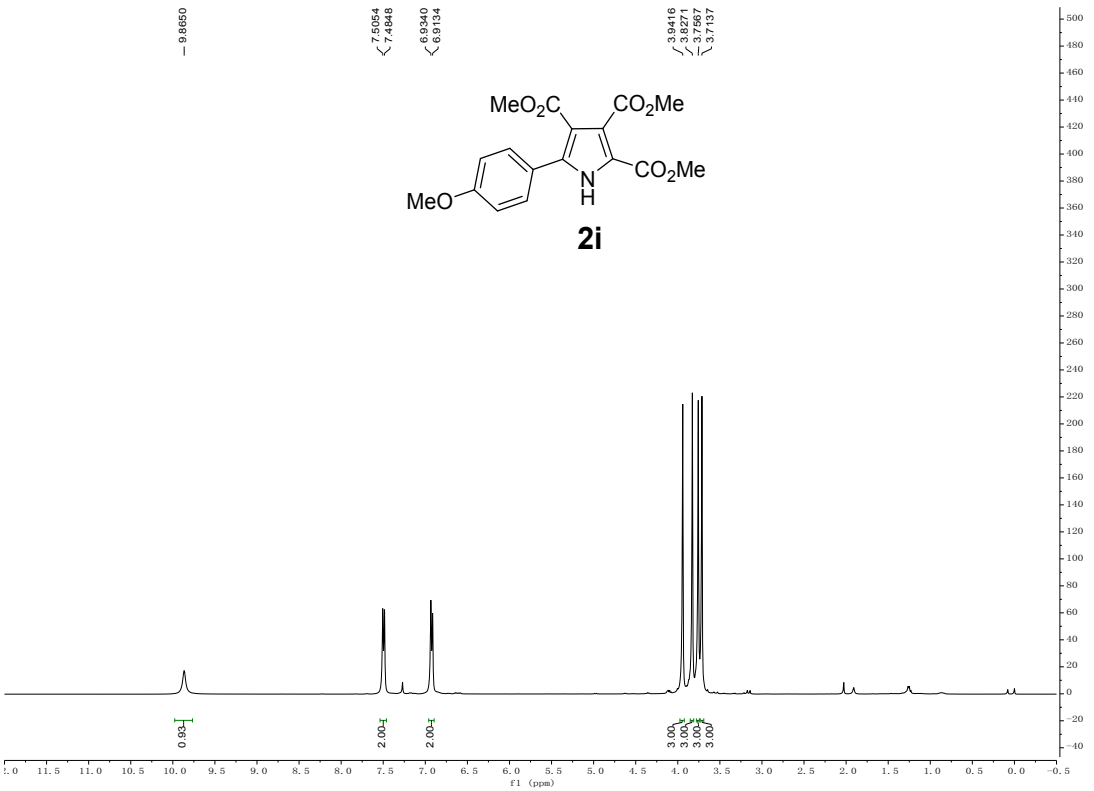
Trimethyl 5-(2-methoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2h).



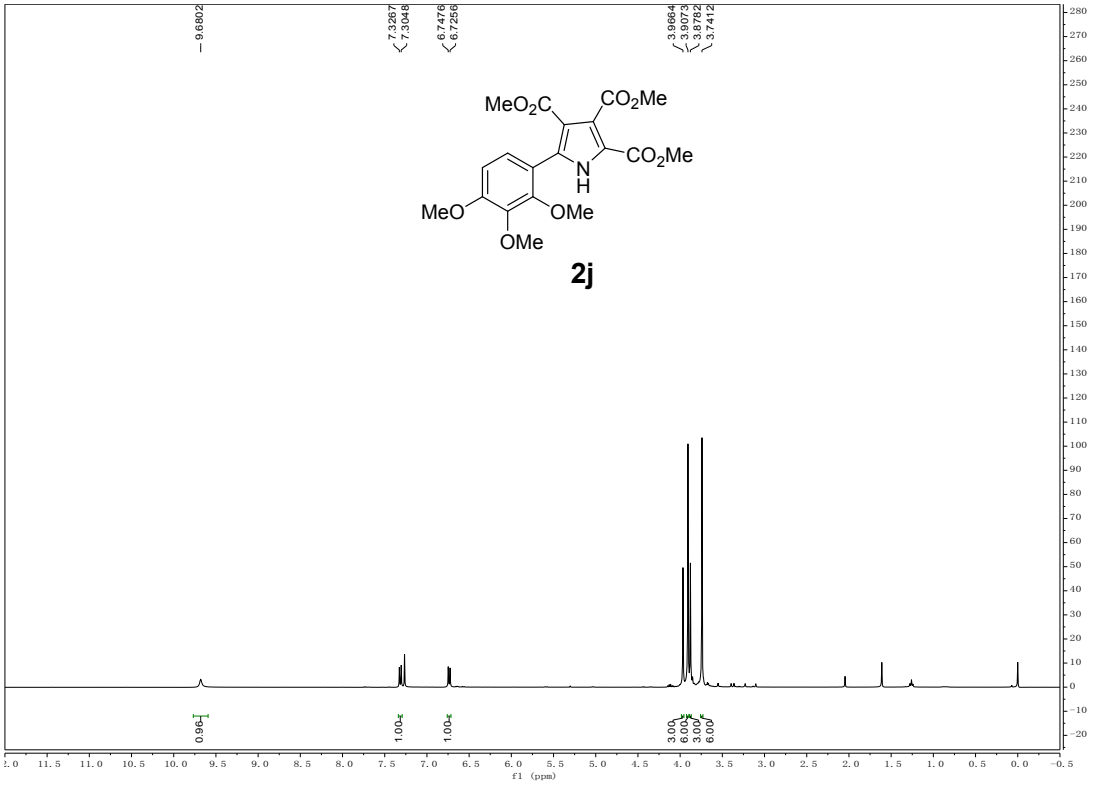
2h

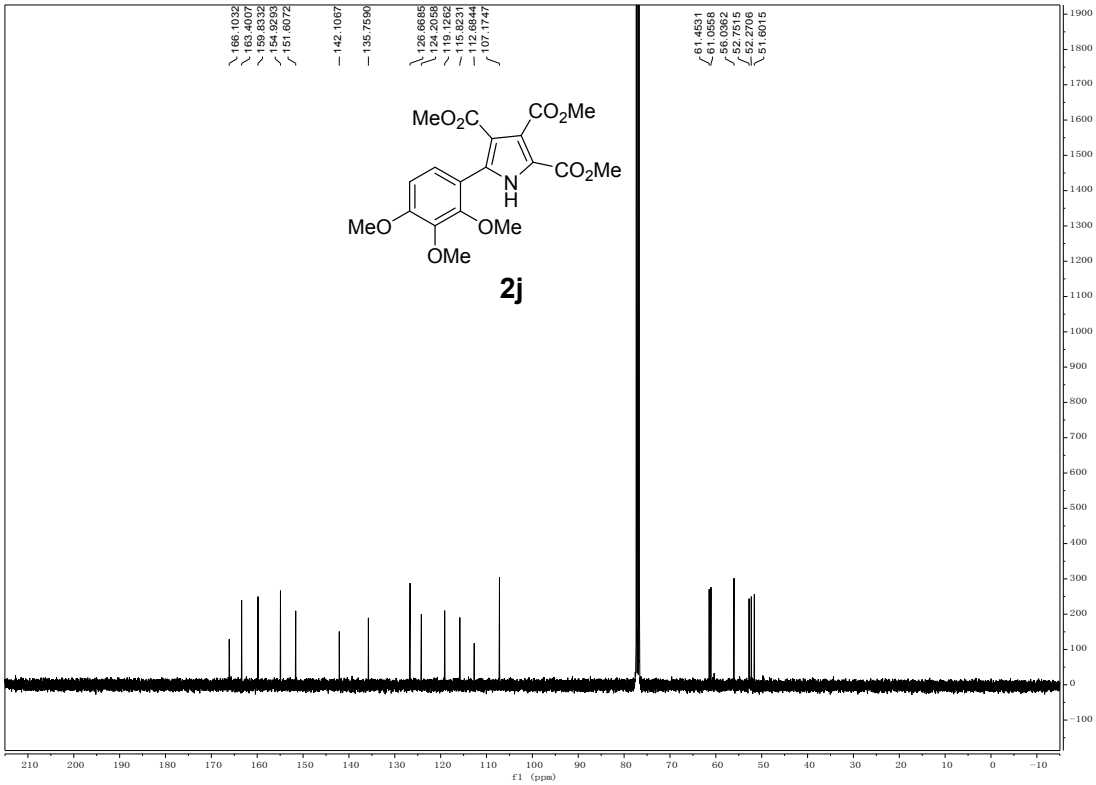


Trimethyl 5-(4-methoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2i).

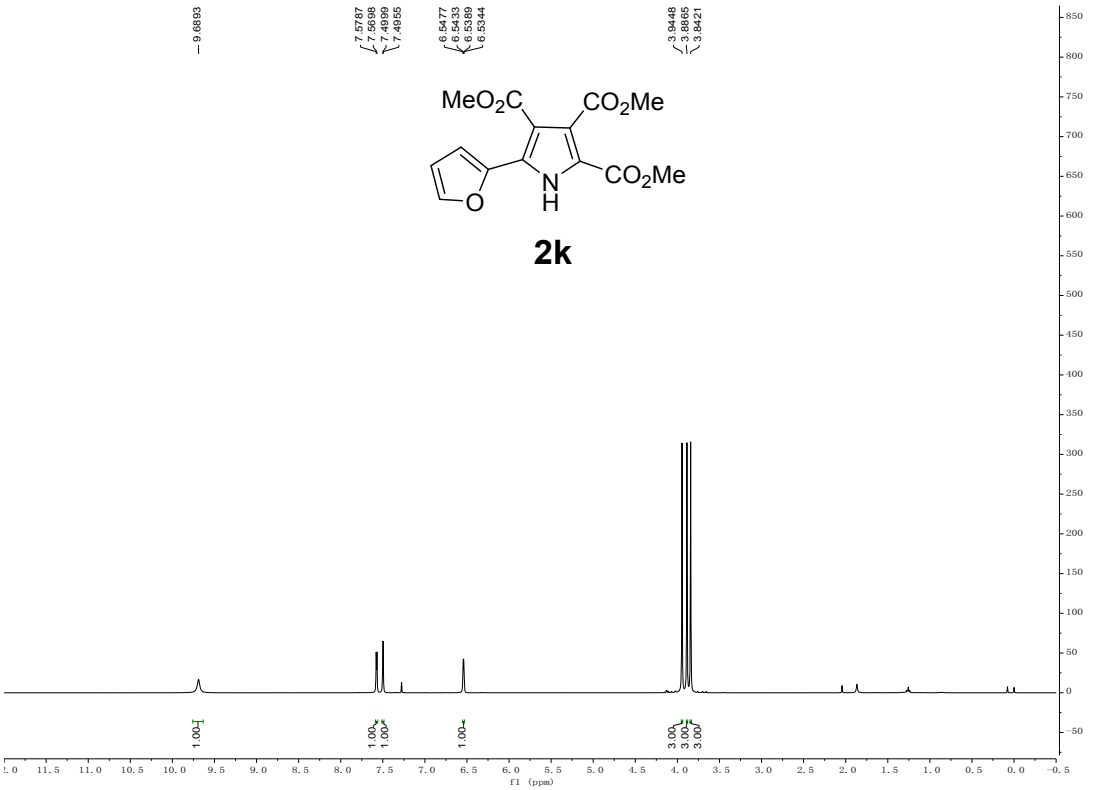


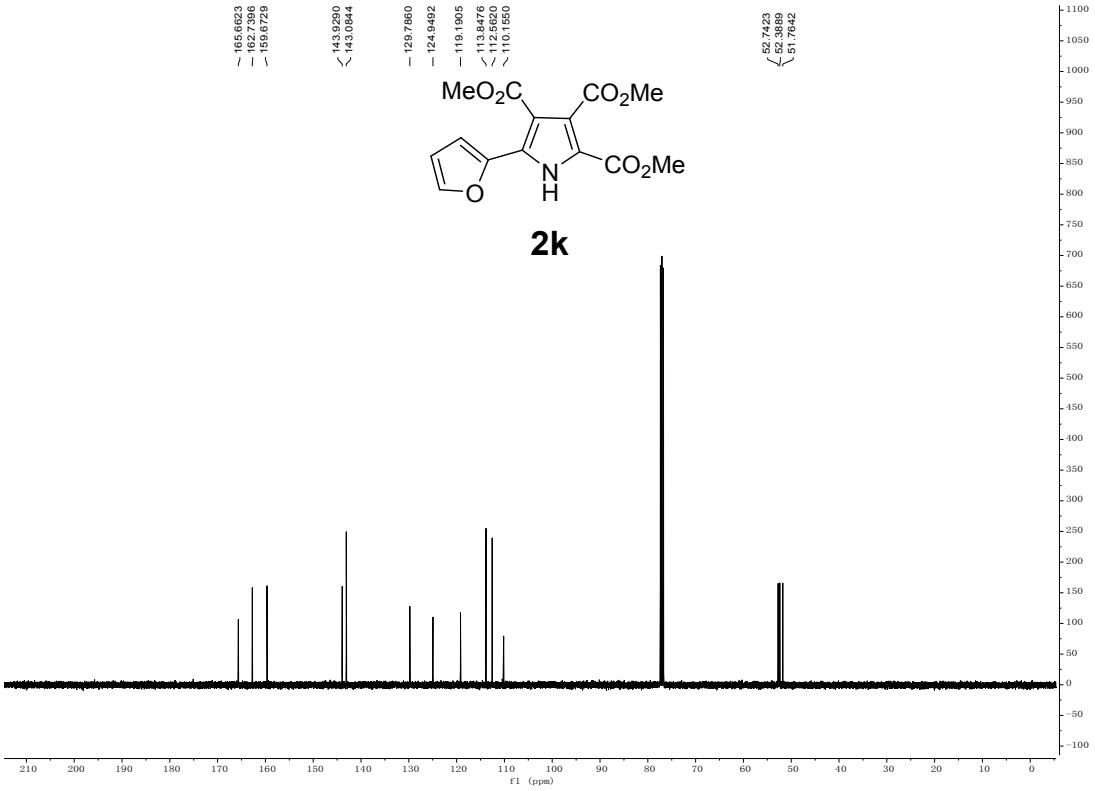
Trimethyl 5-(2,3,4-trimethoxyphenyl)-1*H*-pyrrole-2,3,4-tricarboxylate (2j).



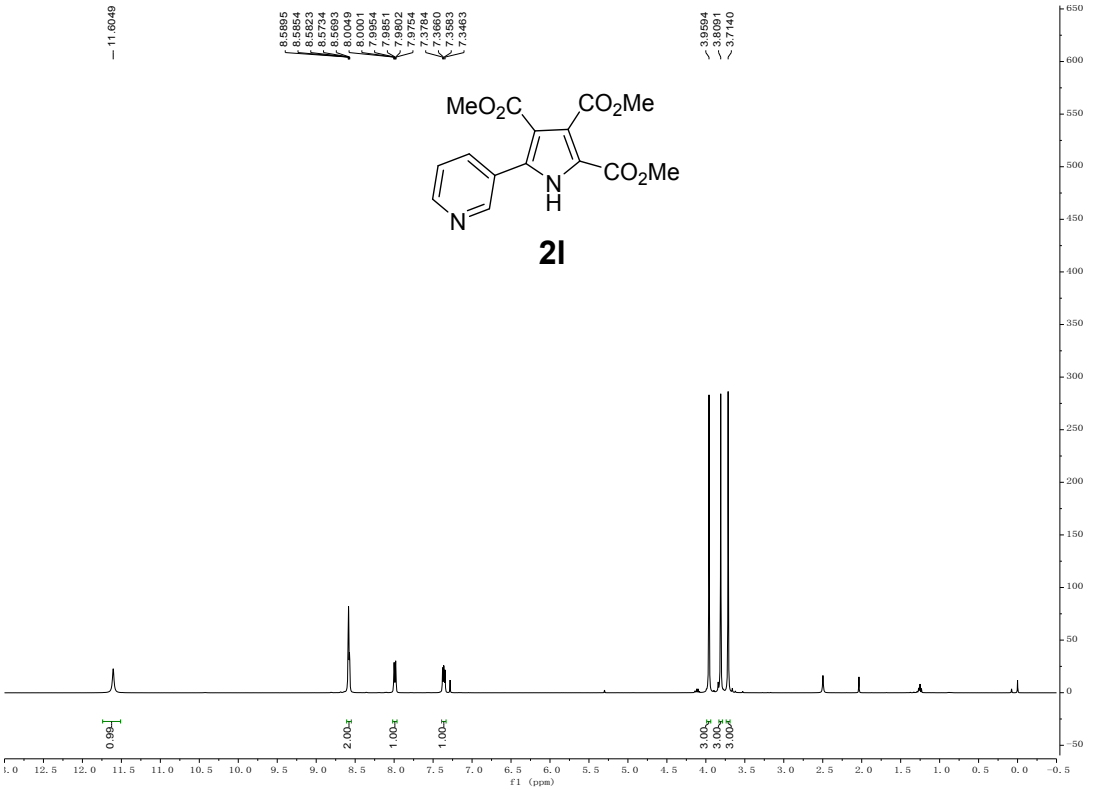


Trimethyl 5-(furan-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2k).

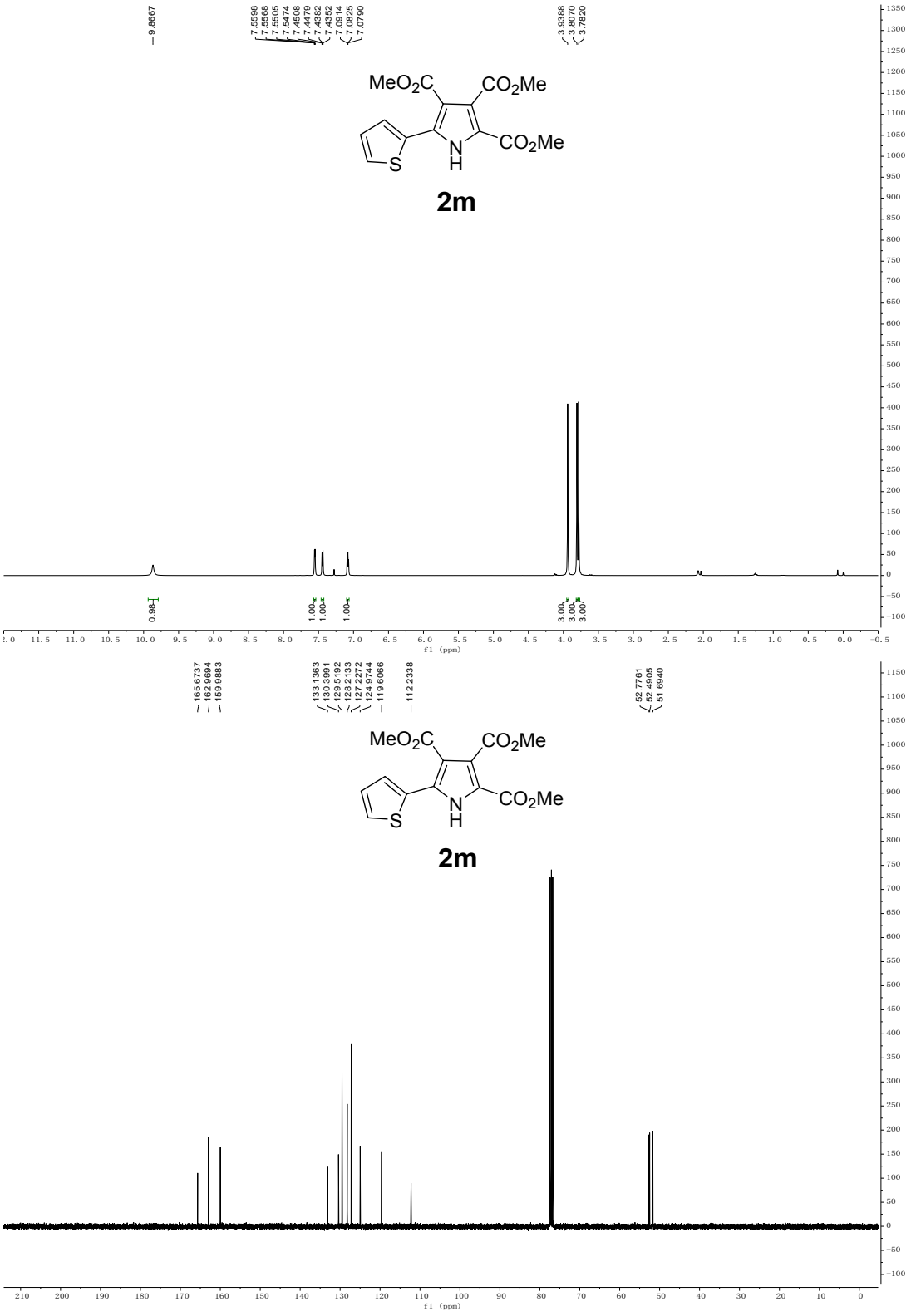




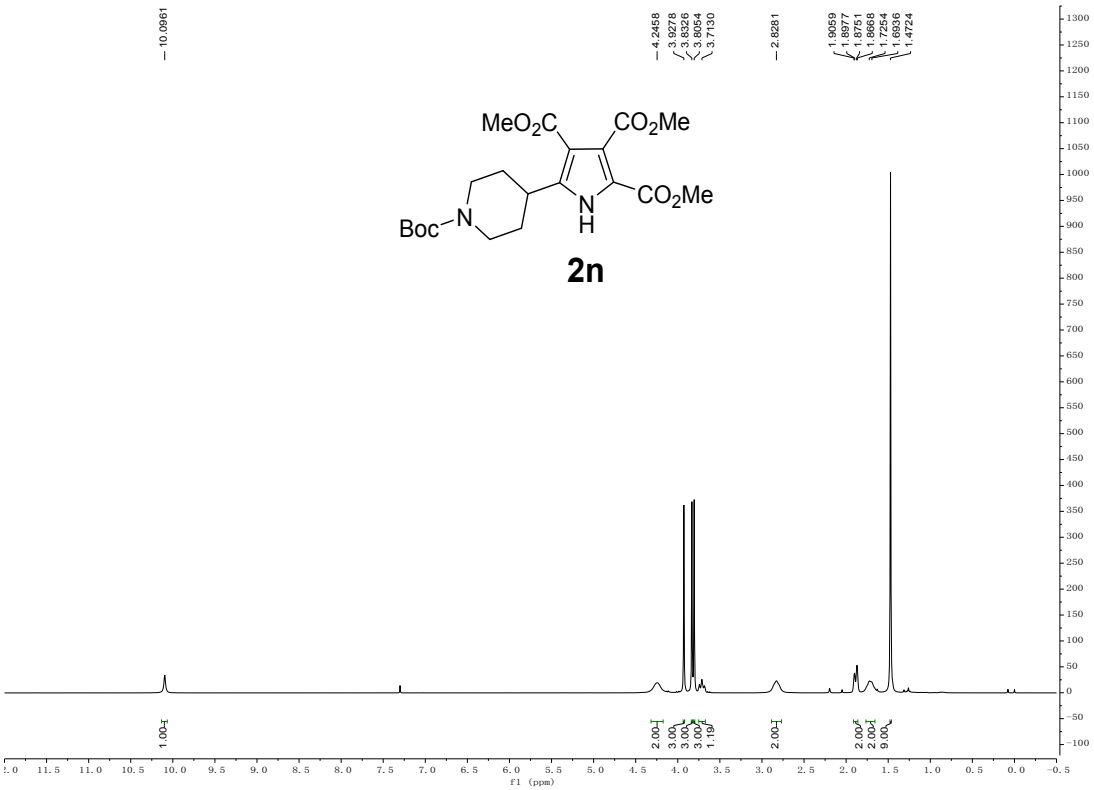
Trimethyl 5-(pyridin-3-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2l).

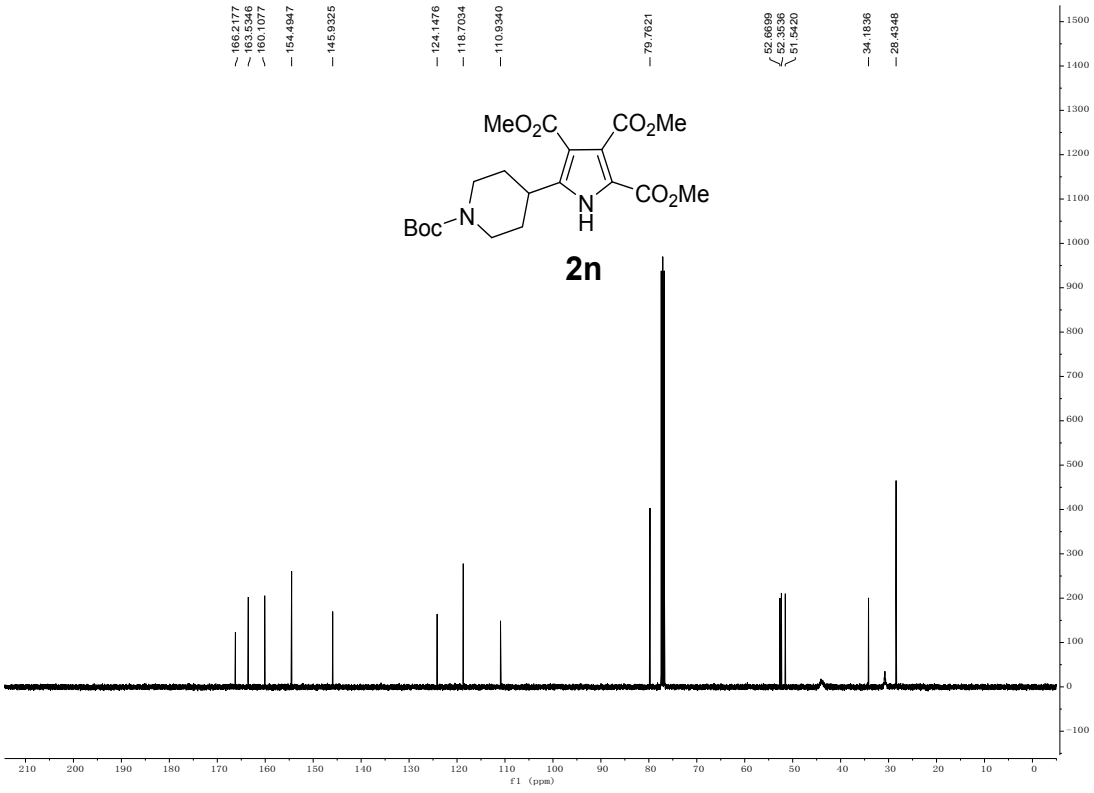


Trimethyl 5-(thiophen-2-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (**2m**).

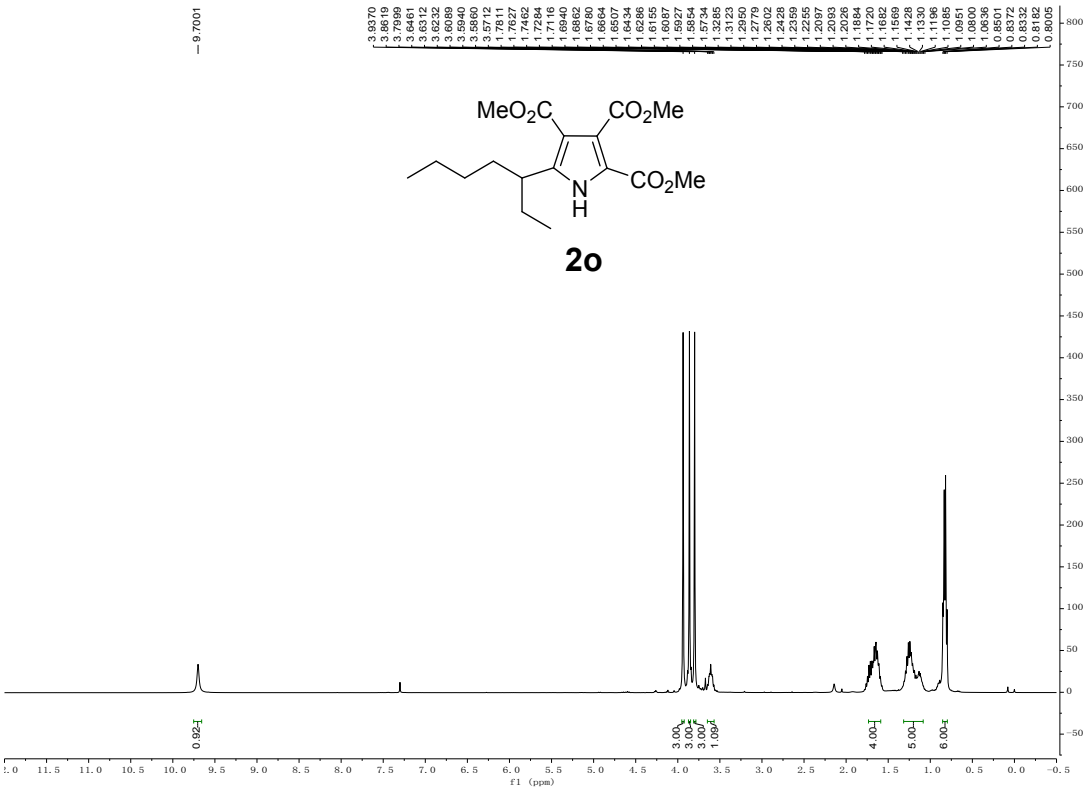


Trimethyl 5-(1-(tert-butoxycarbonyl)piperidin-4-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2n).

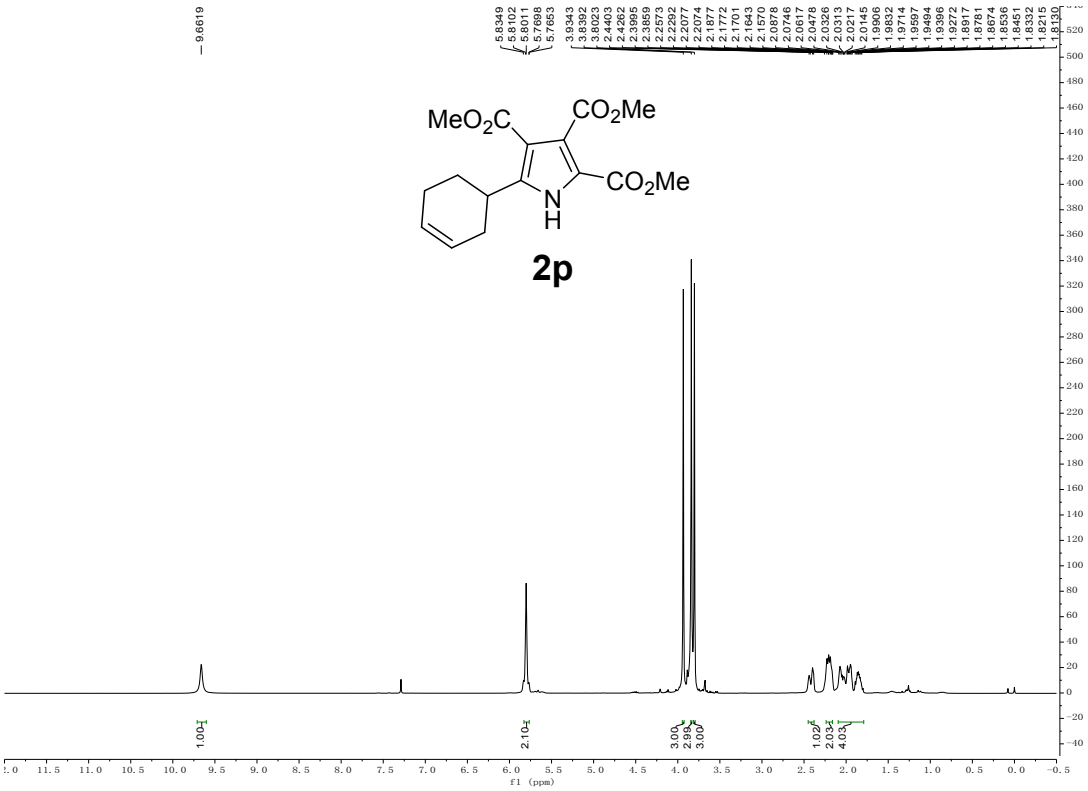


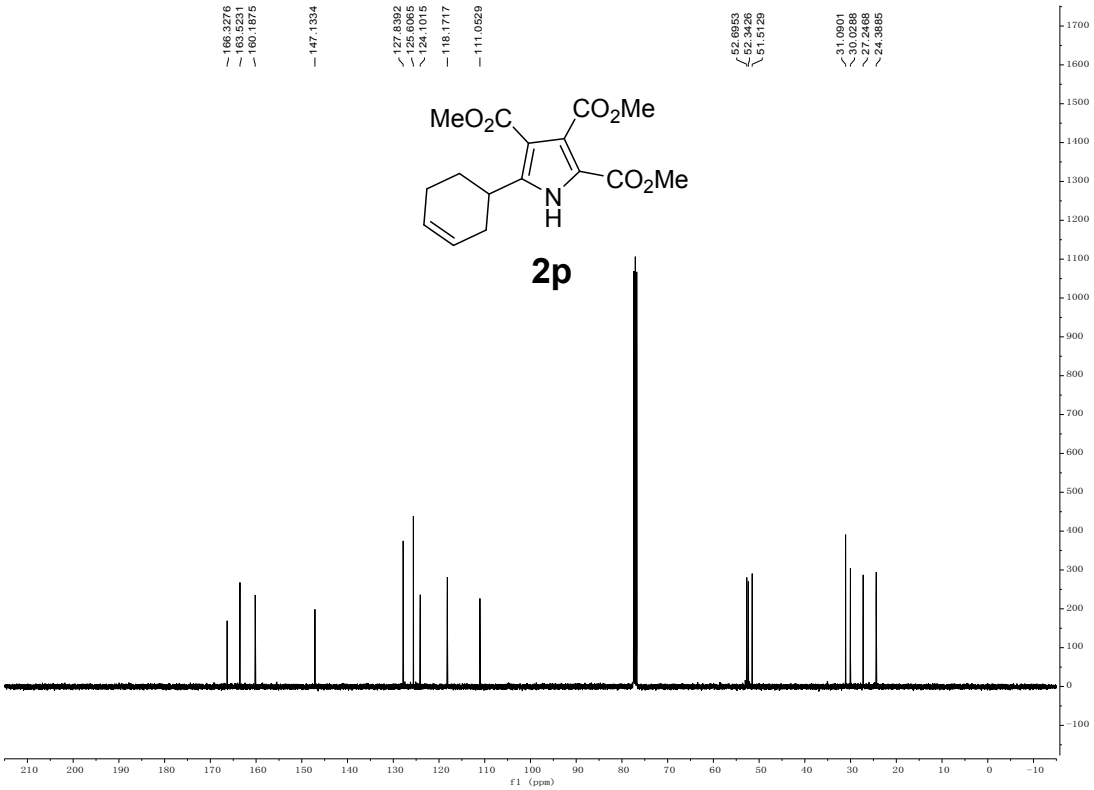


Trimethyl 5-(heptan-3-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2o).

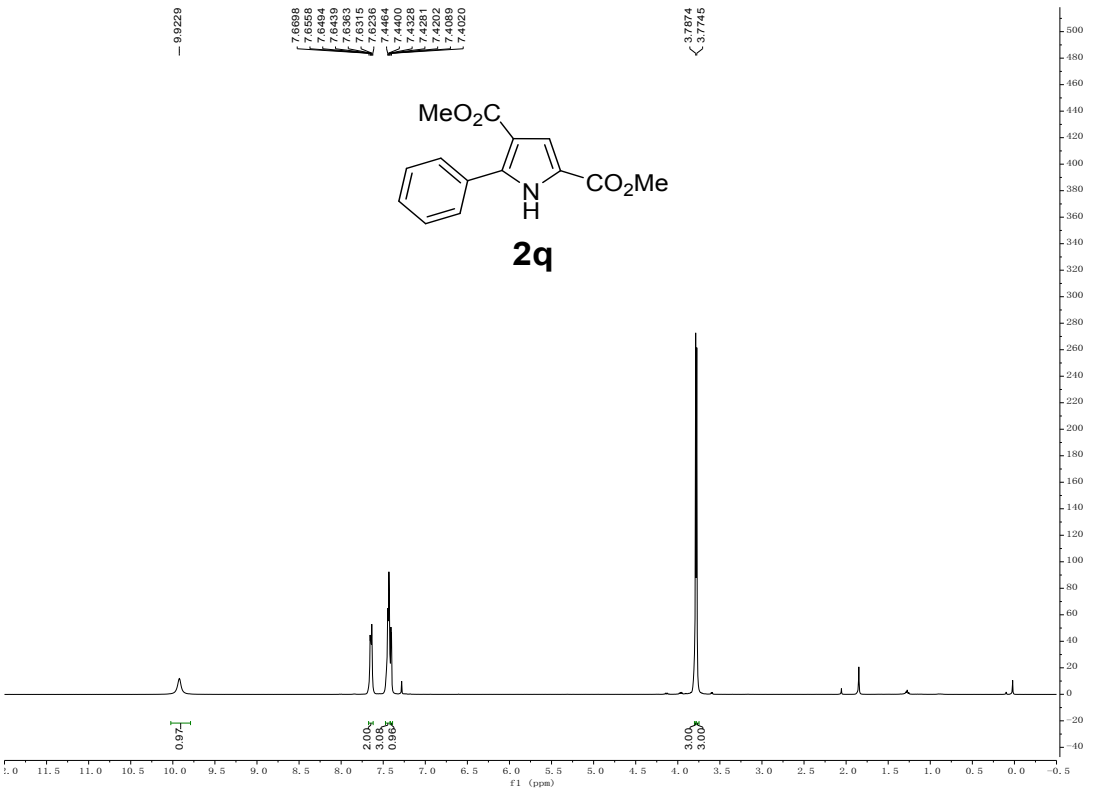


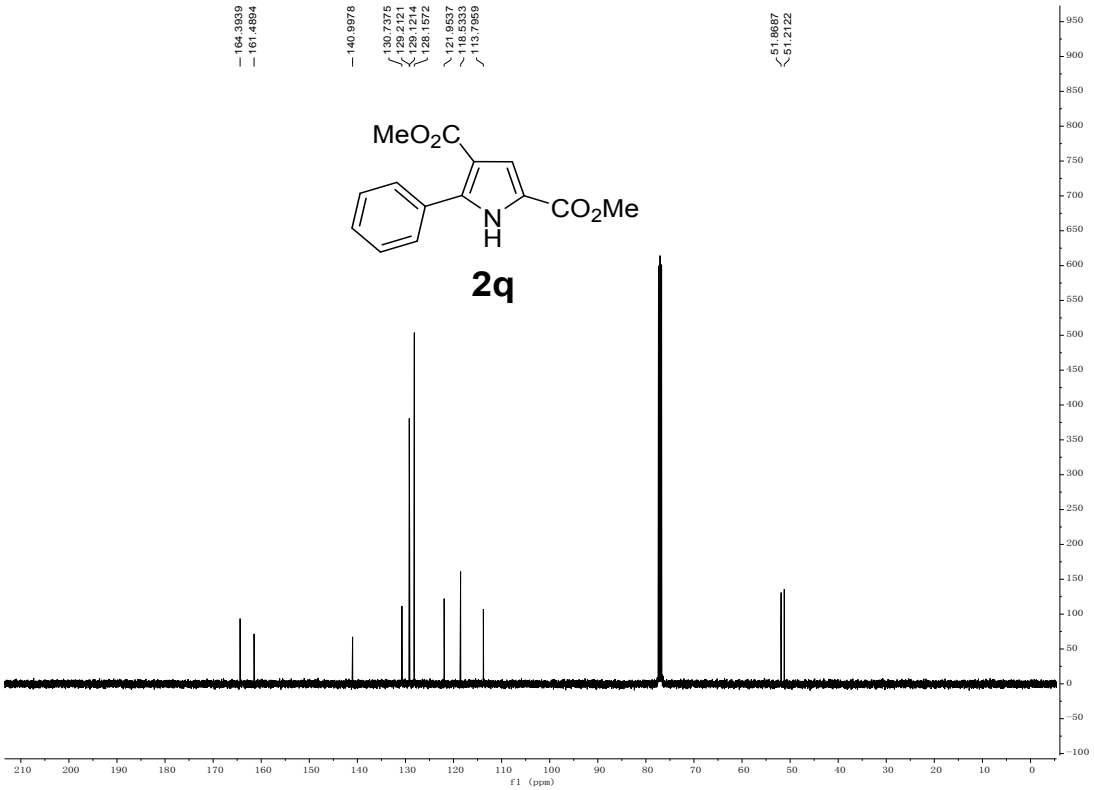
Trimethyl 5-(cyclohex-3-en-1-yl)-1*H*-pyrrole-2,3,4-tricarboxylate (2p).



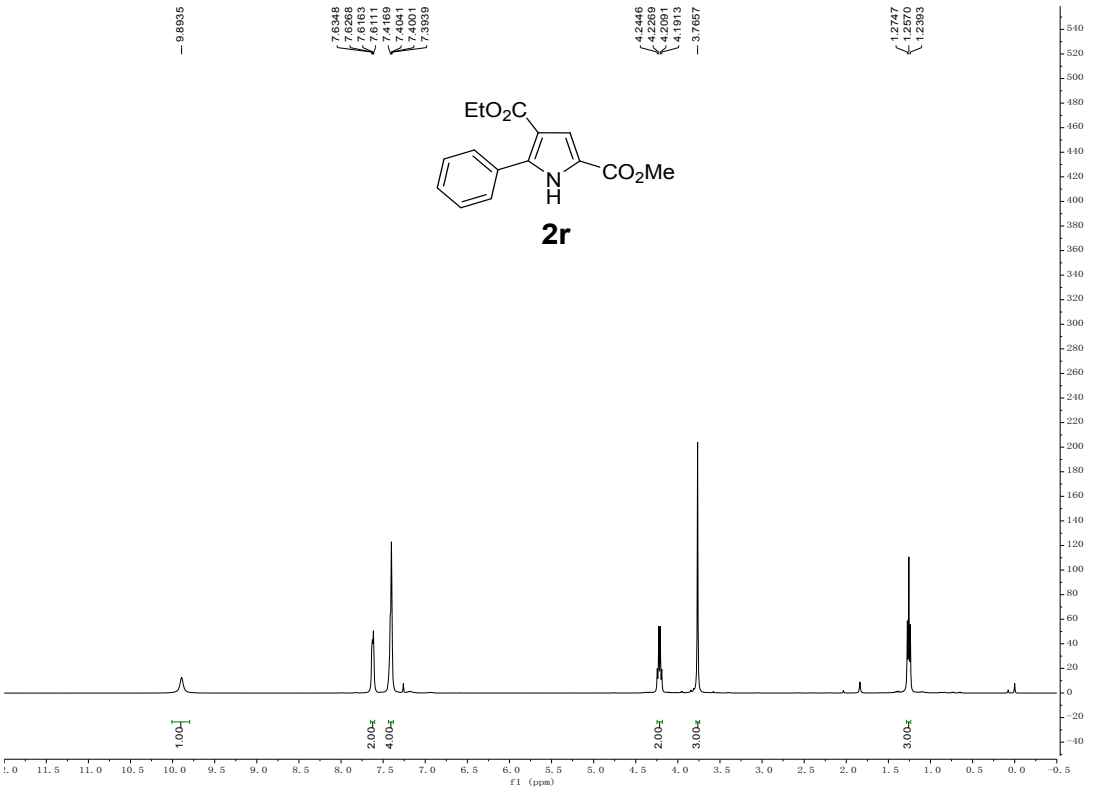


Dimethyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2q).

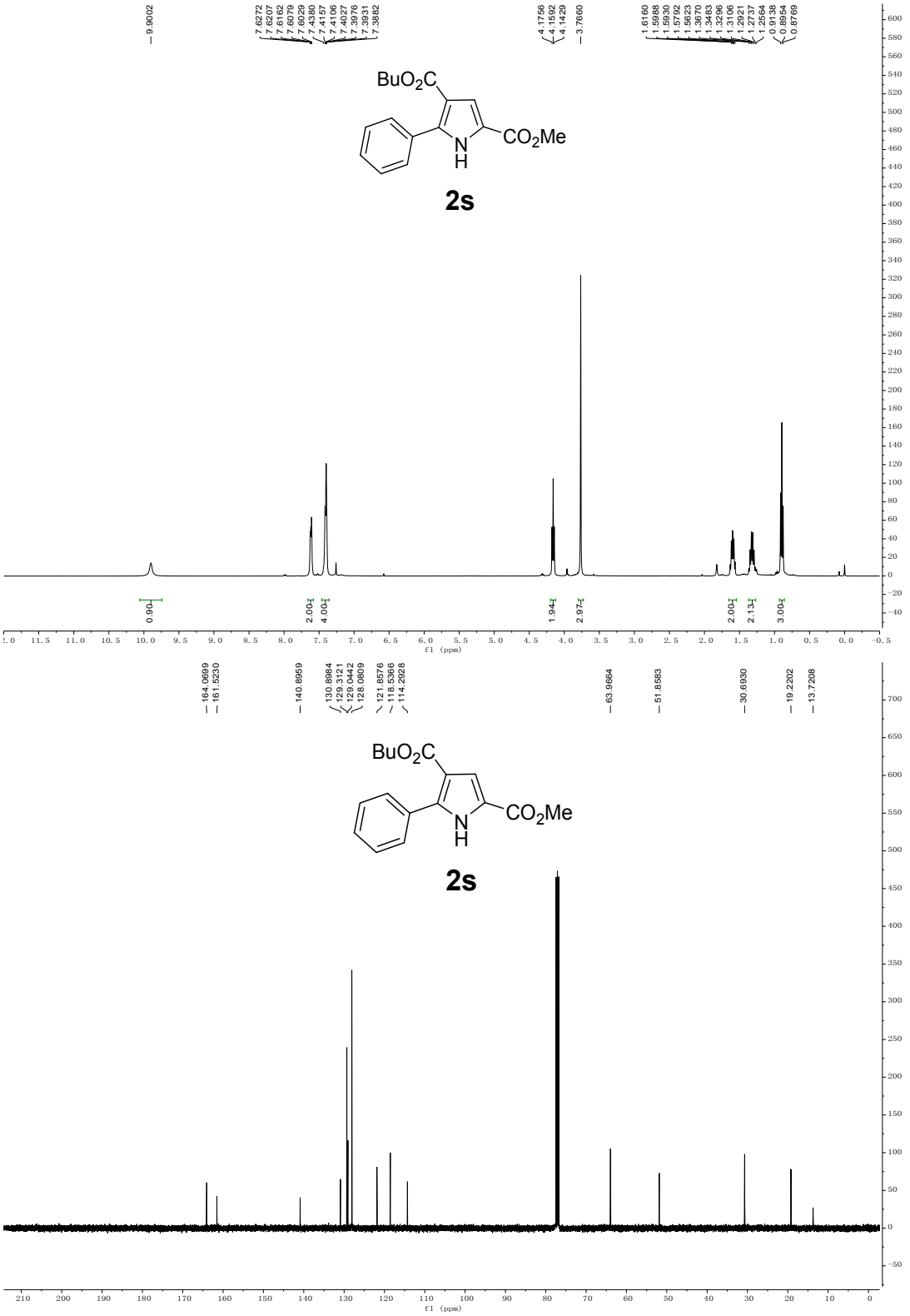




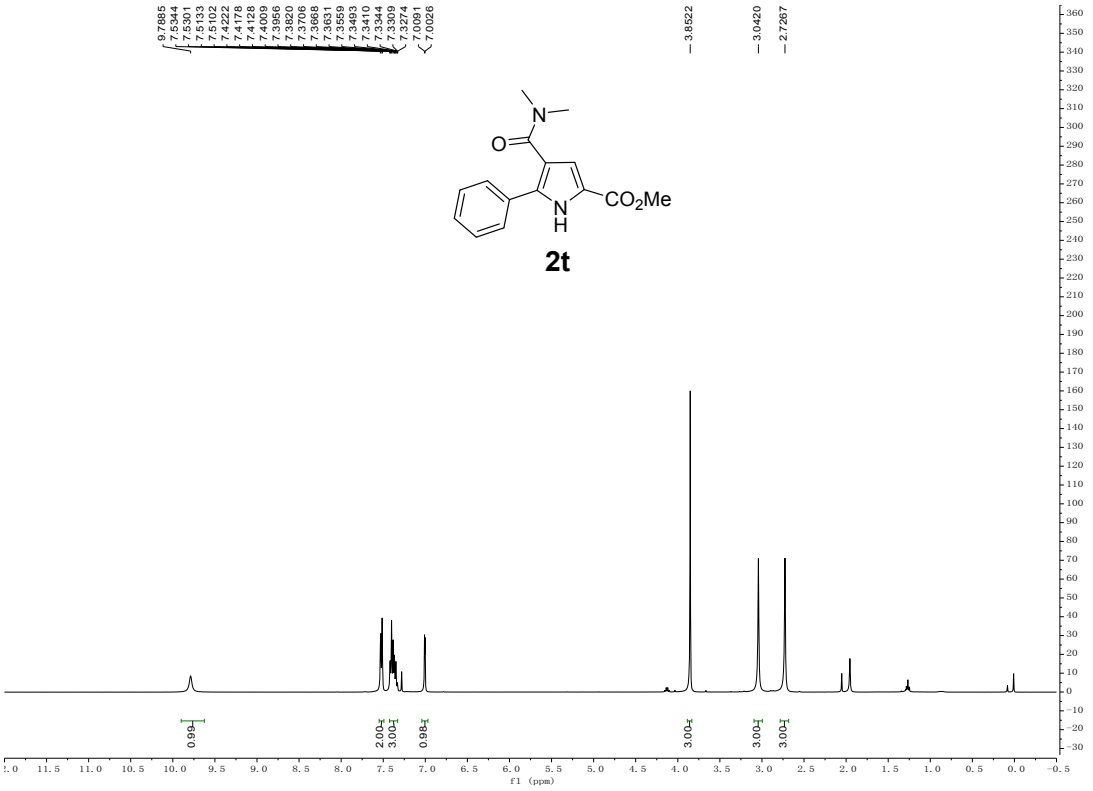
4-Ethyl 2-methyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2r).

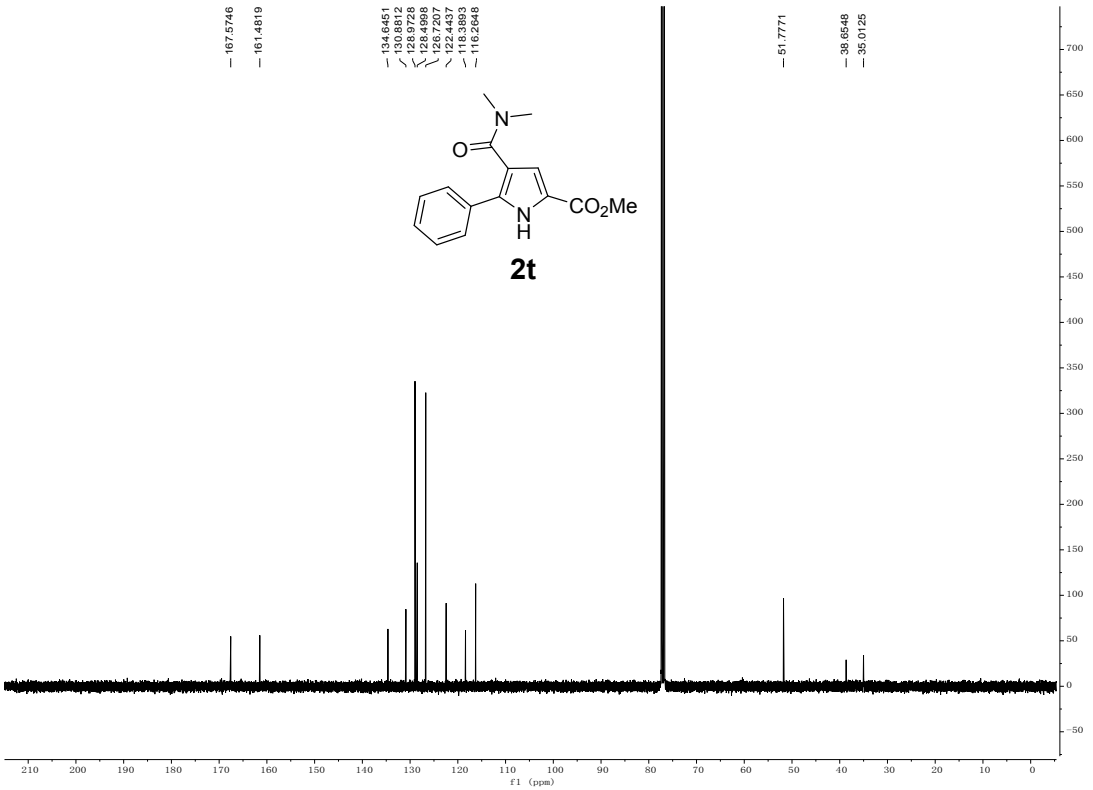


4-Butyl 2-methyl 5-phenyl-1*H*-pyrrole-2,4-dicarboxylate (2s).

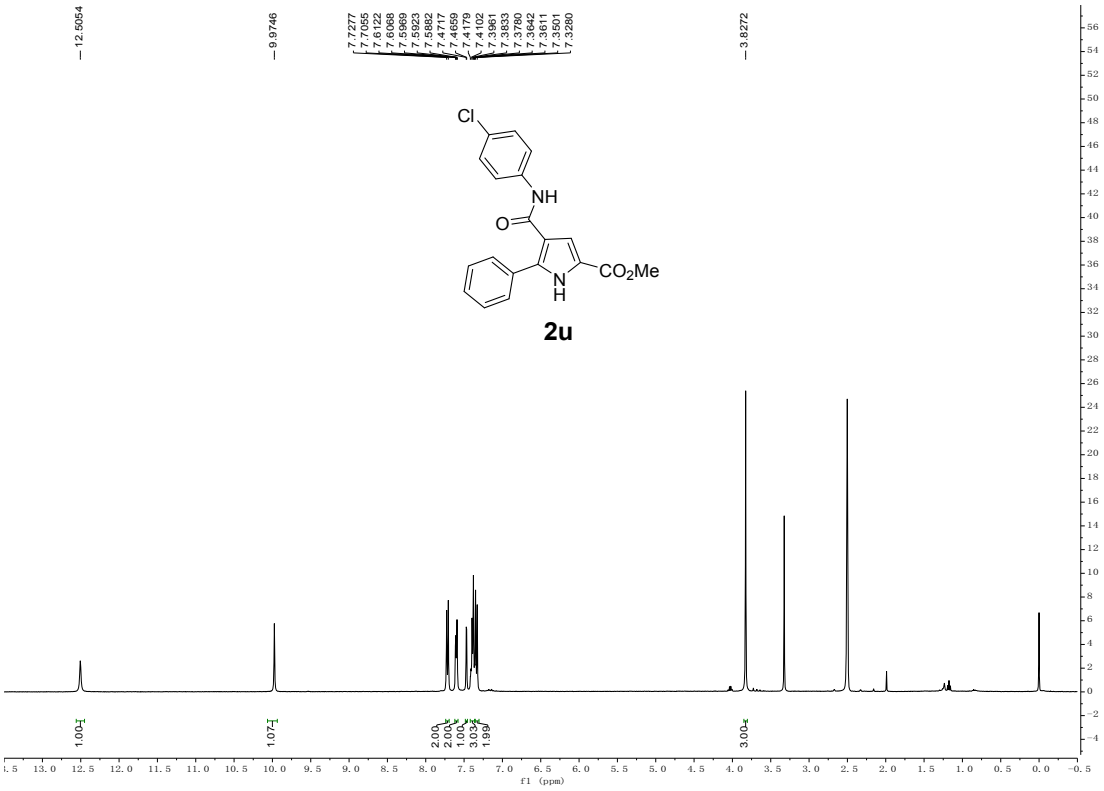


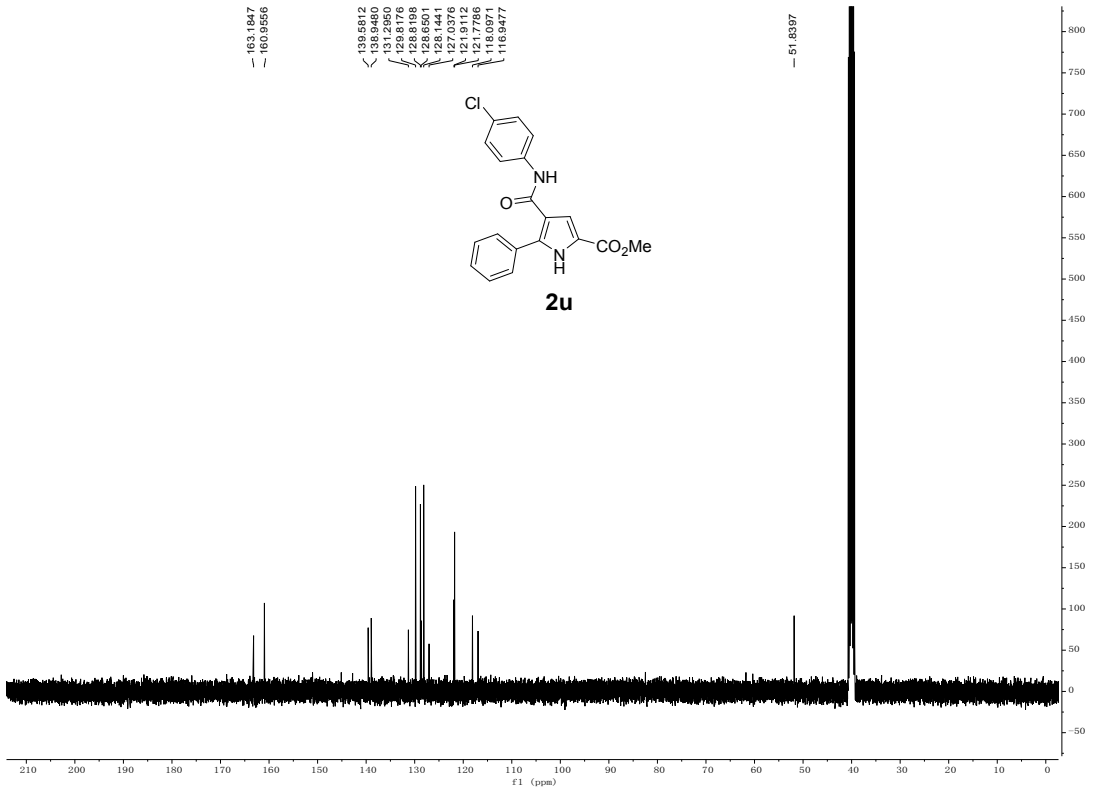
Methyl 4-(dimethylcarbamoyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (2t).



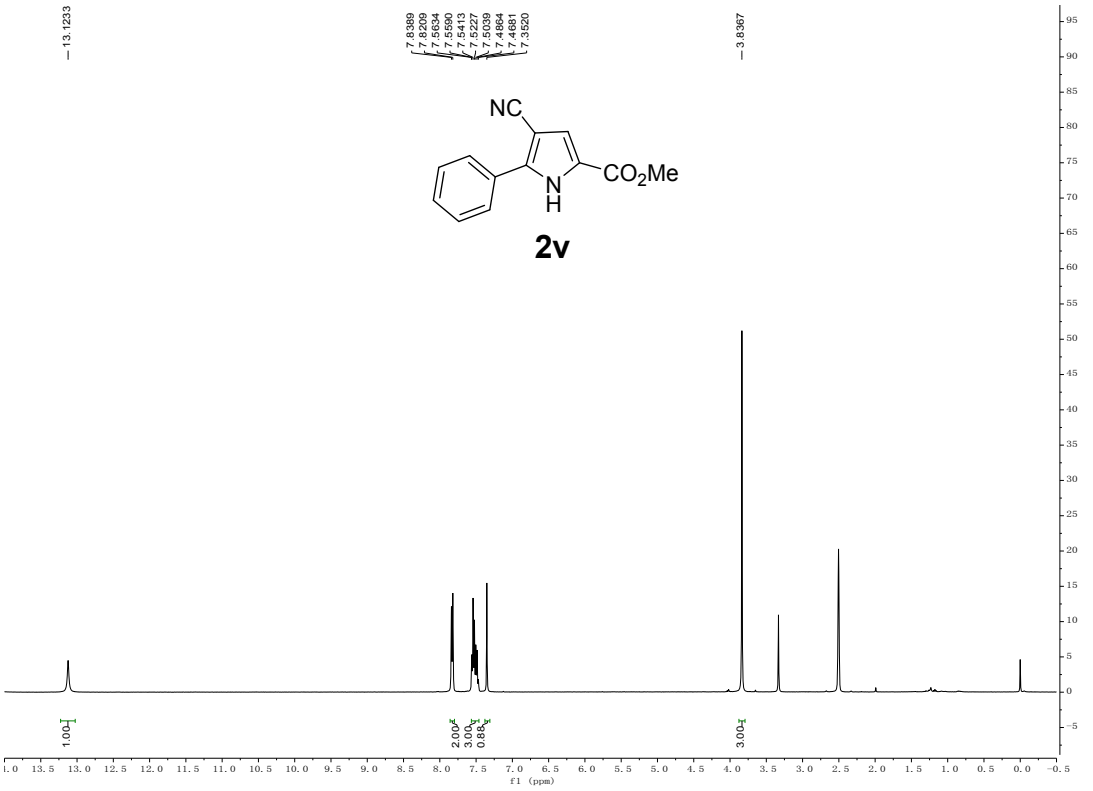


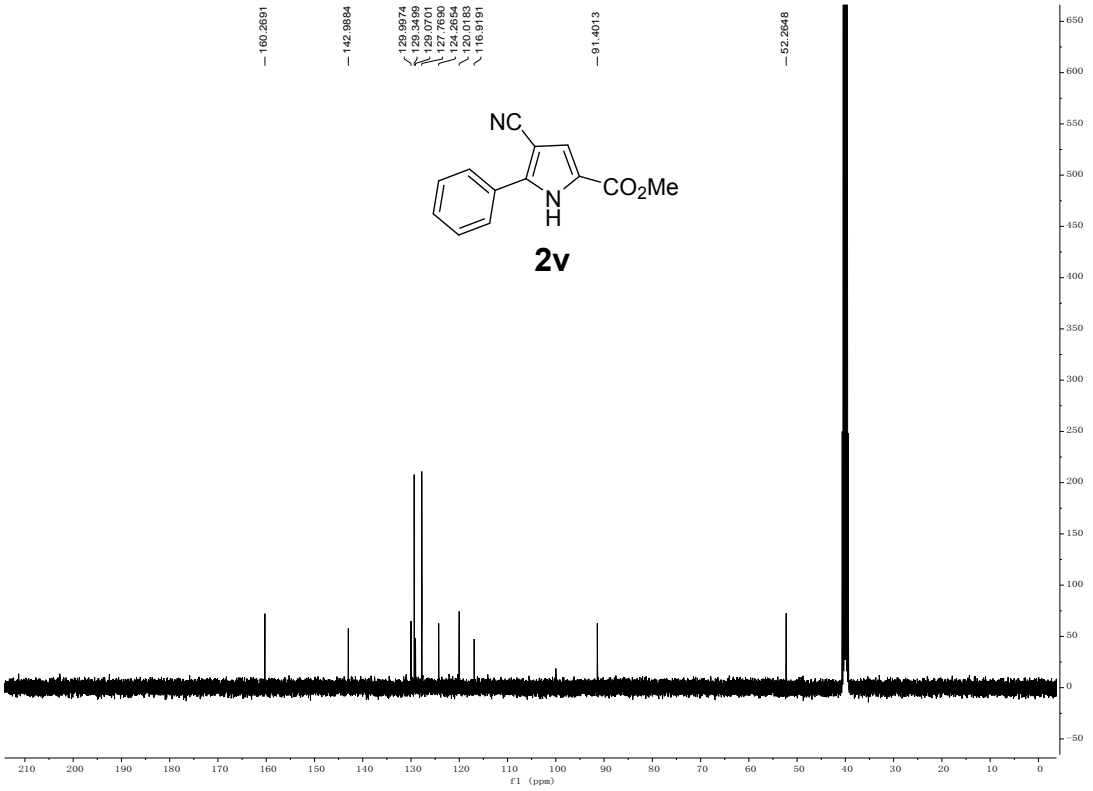
Methyl 4-((4-chlorophenyl)carbamoyl)-5-phenyl-1*H*-pyrrole-2-carboxylate (2u).



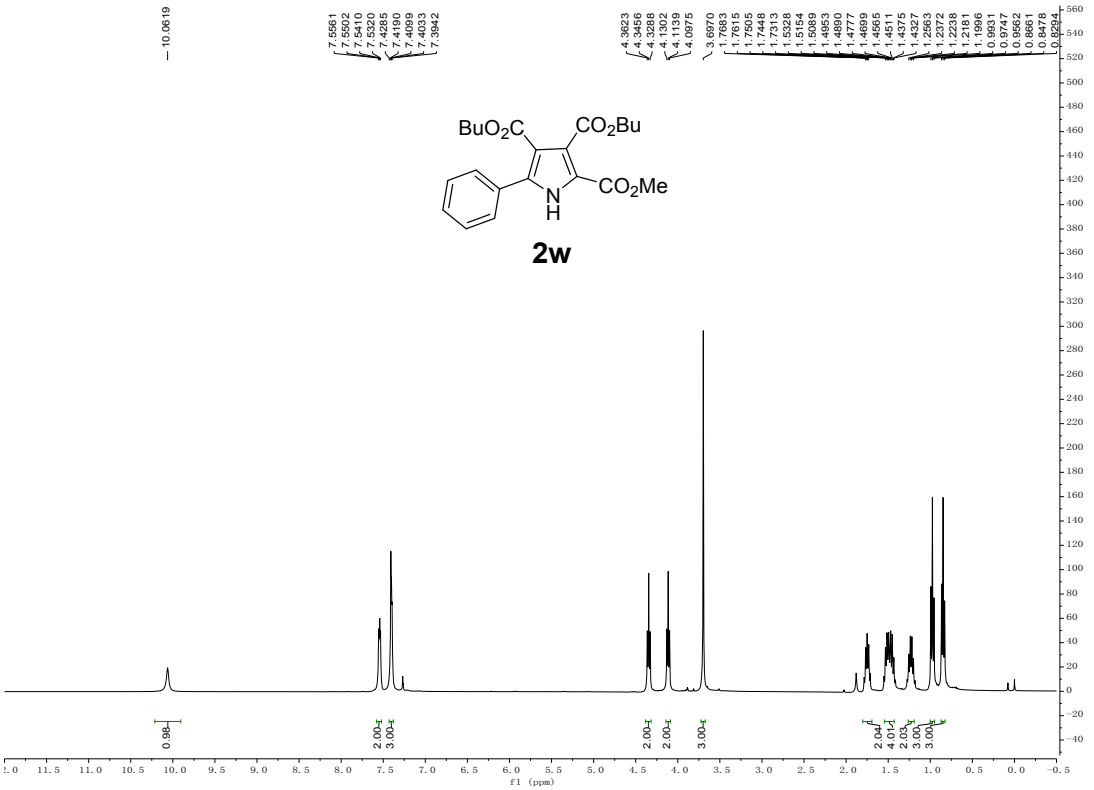


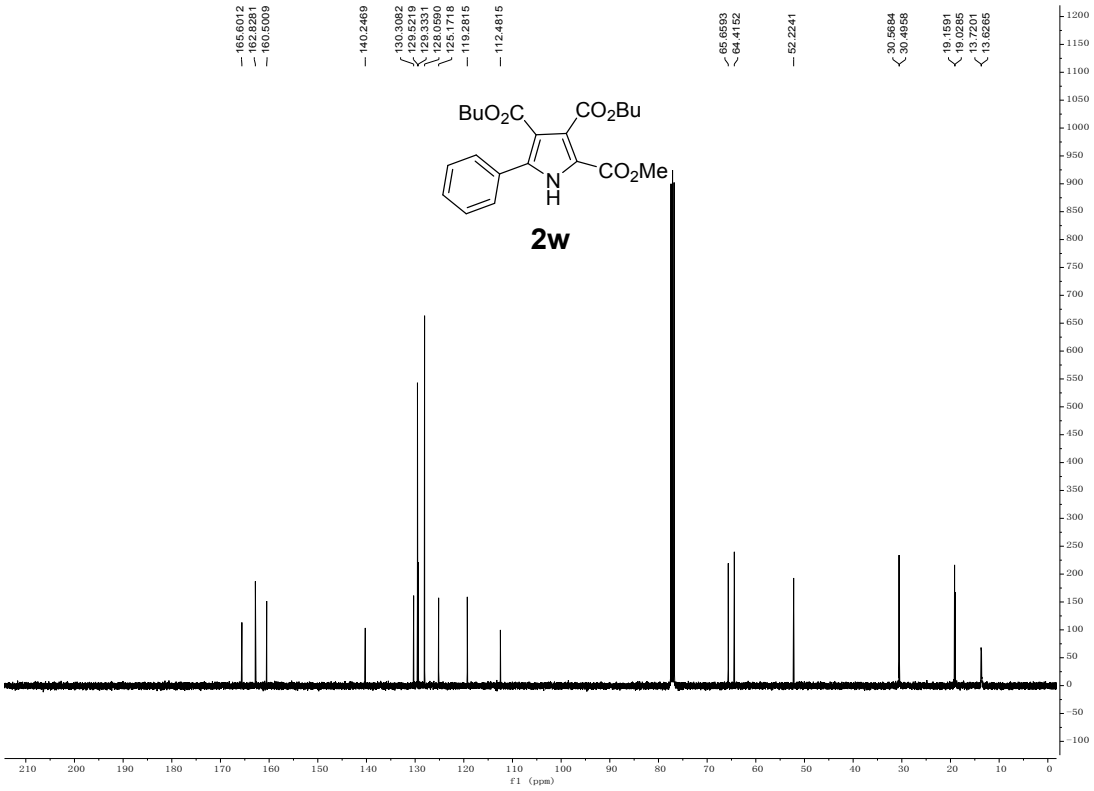
Methyl 4-cyano-5-phenyl-1*H*-pyrrole-2-carboxylate (2v).



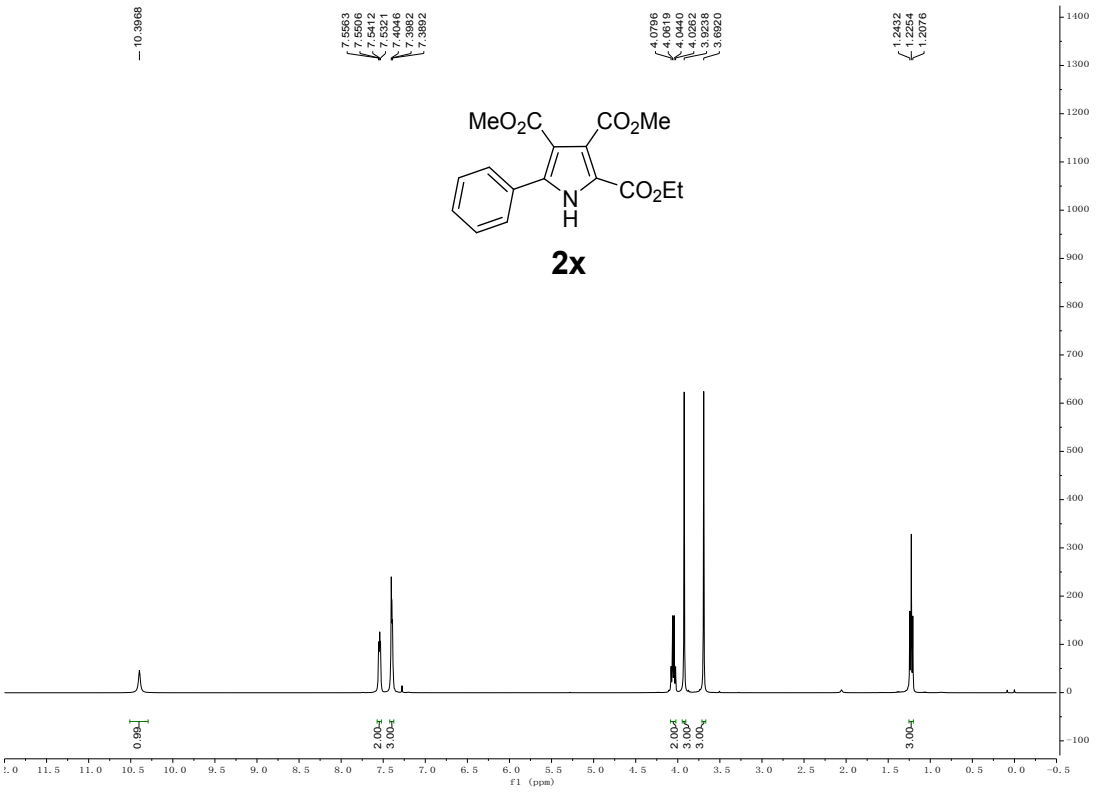


3,4-Dibutyl 2-methyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2w).

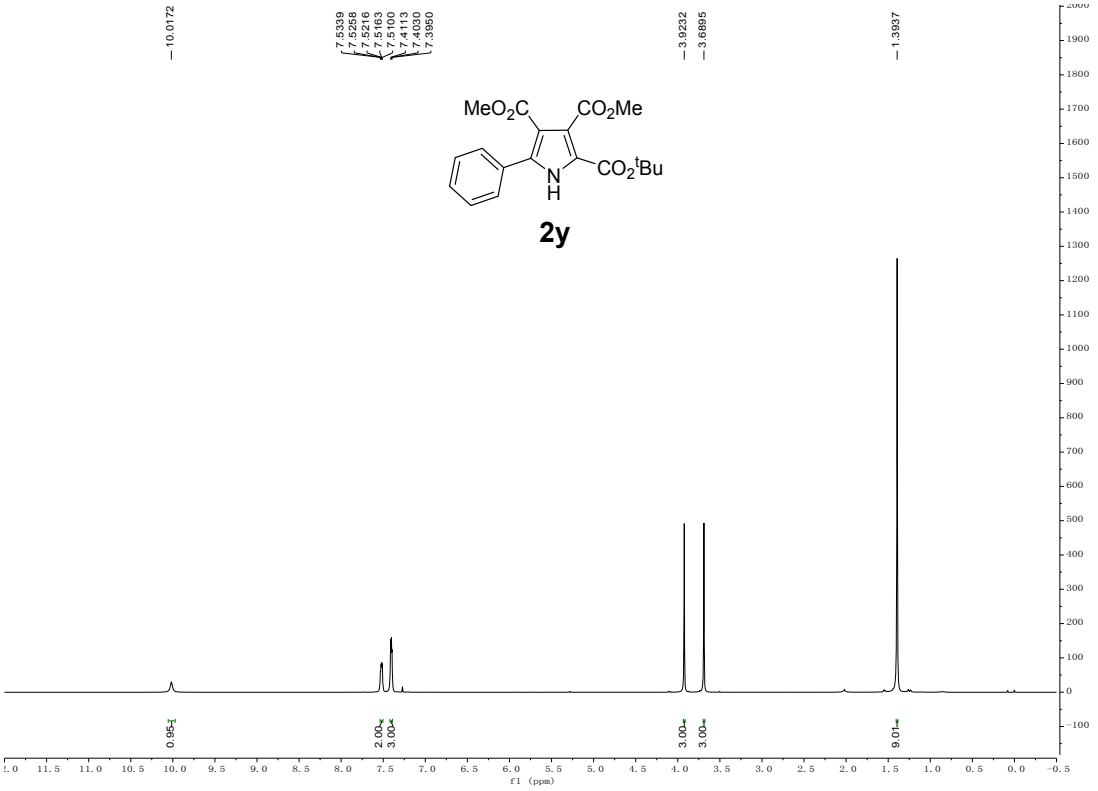




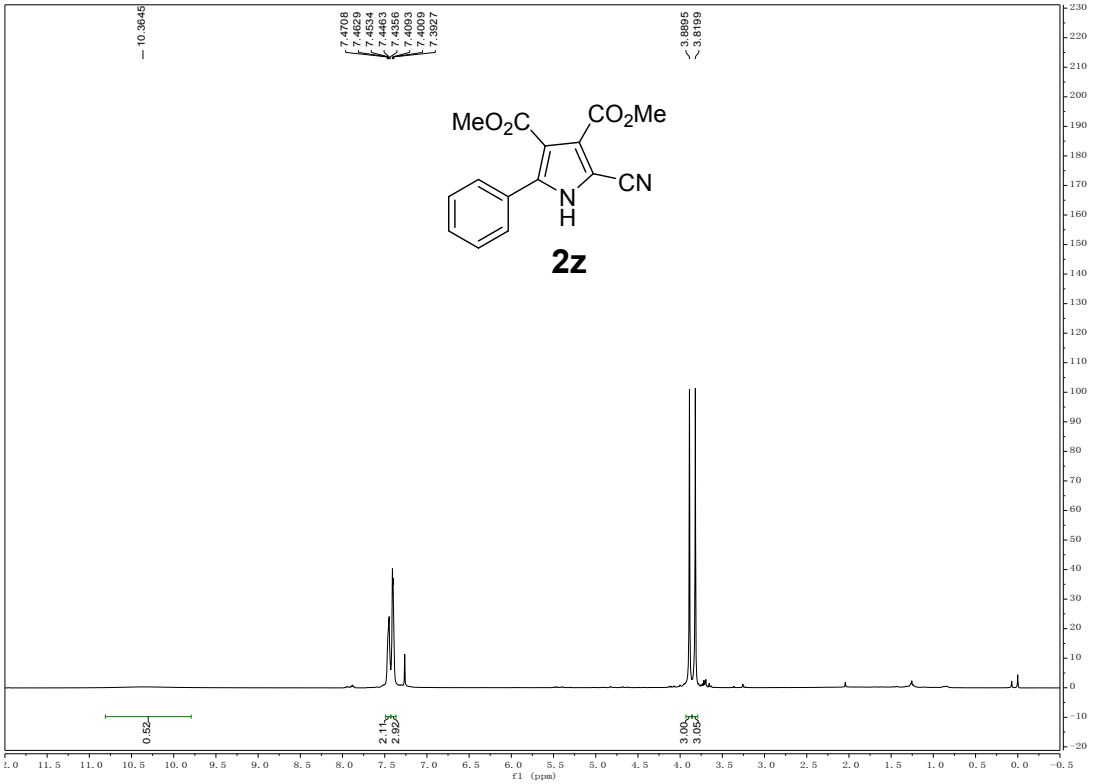
2-Ethyl 3,4-dimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2x).



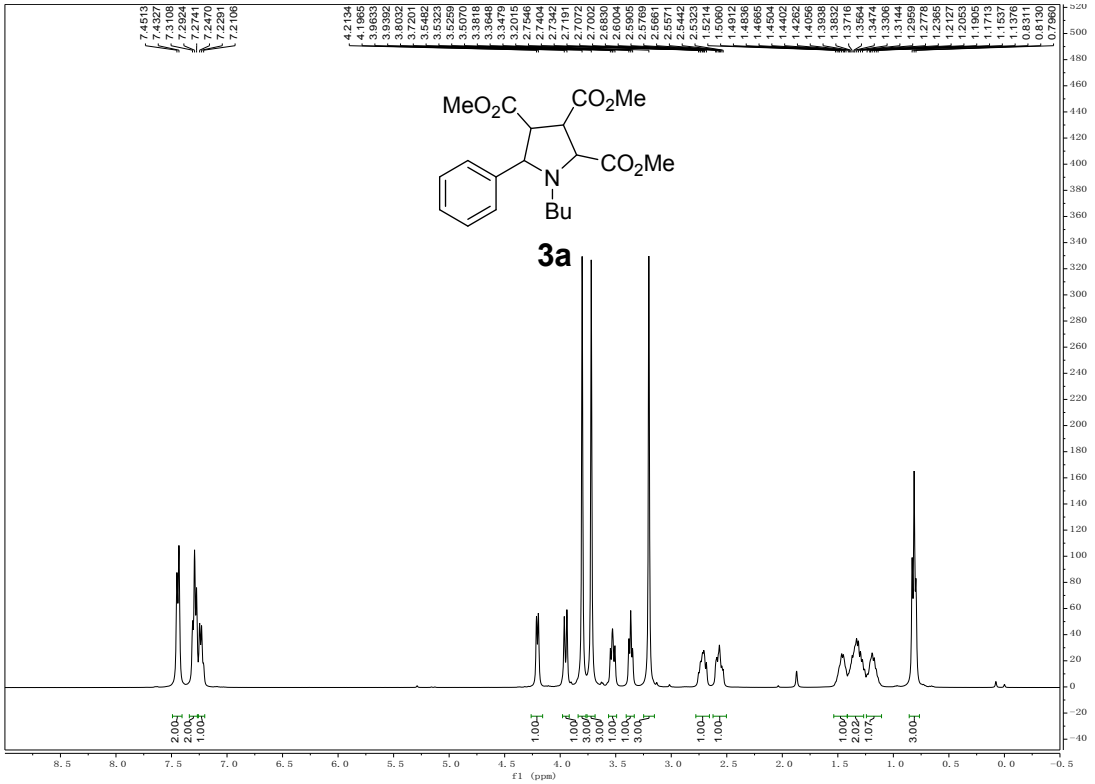
2-(Tert-butyl) 3,4-dimethyl 5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (2y).

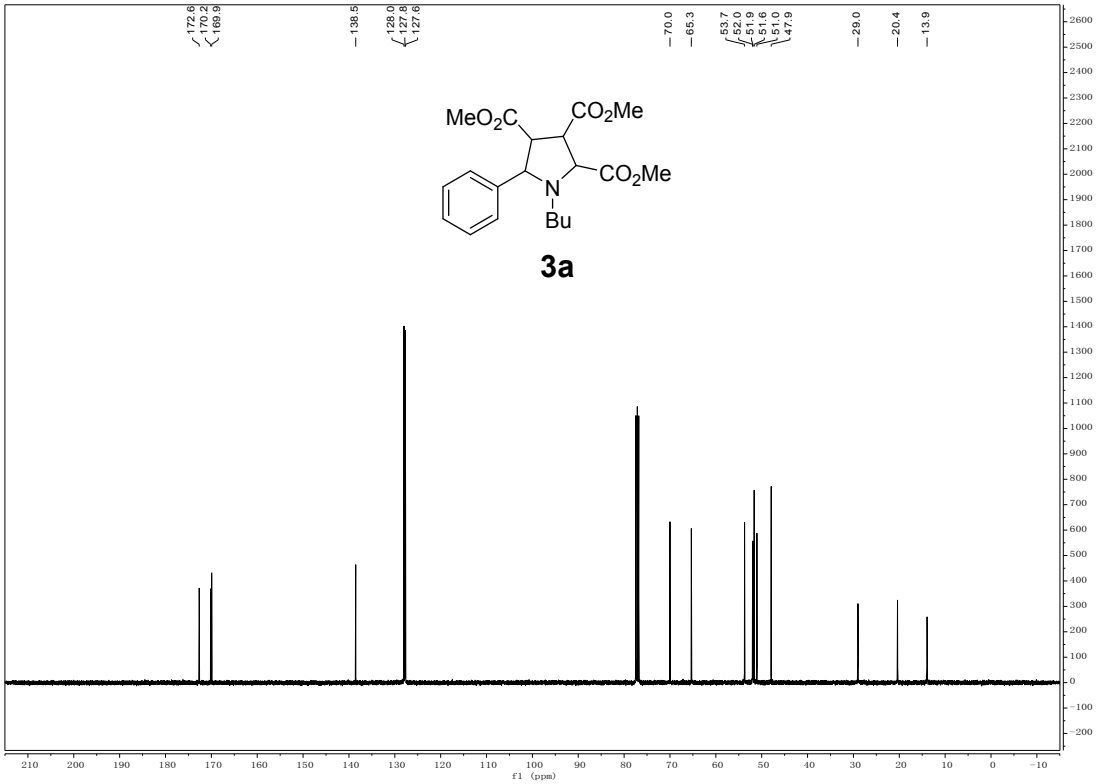


Dimethyl 2-cyano-5-phenyl-1*H*-pyrrole-3,4-dicarboxylate (2z).

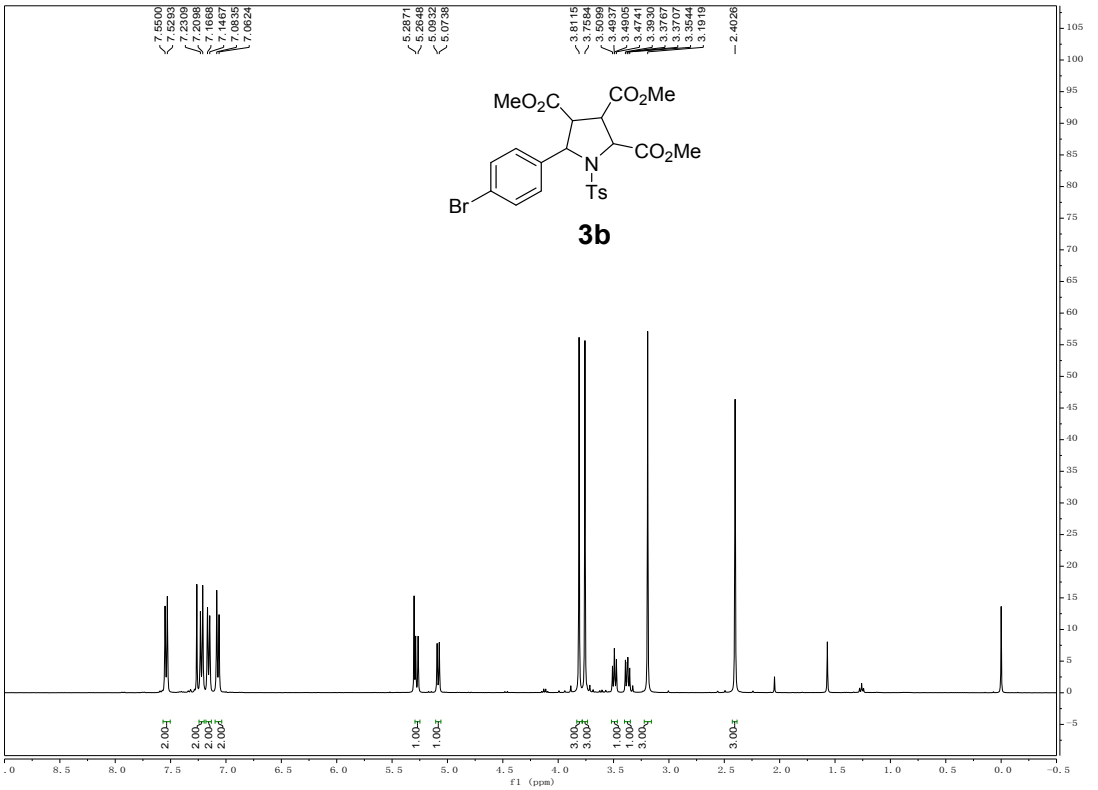


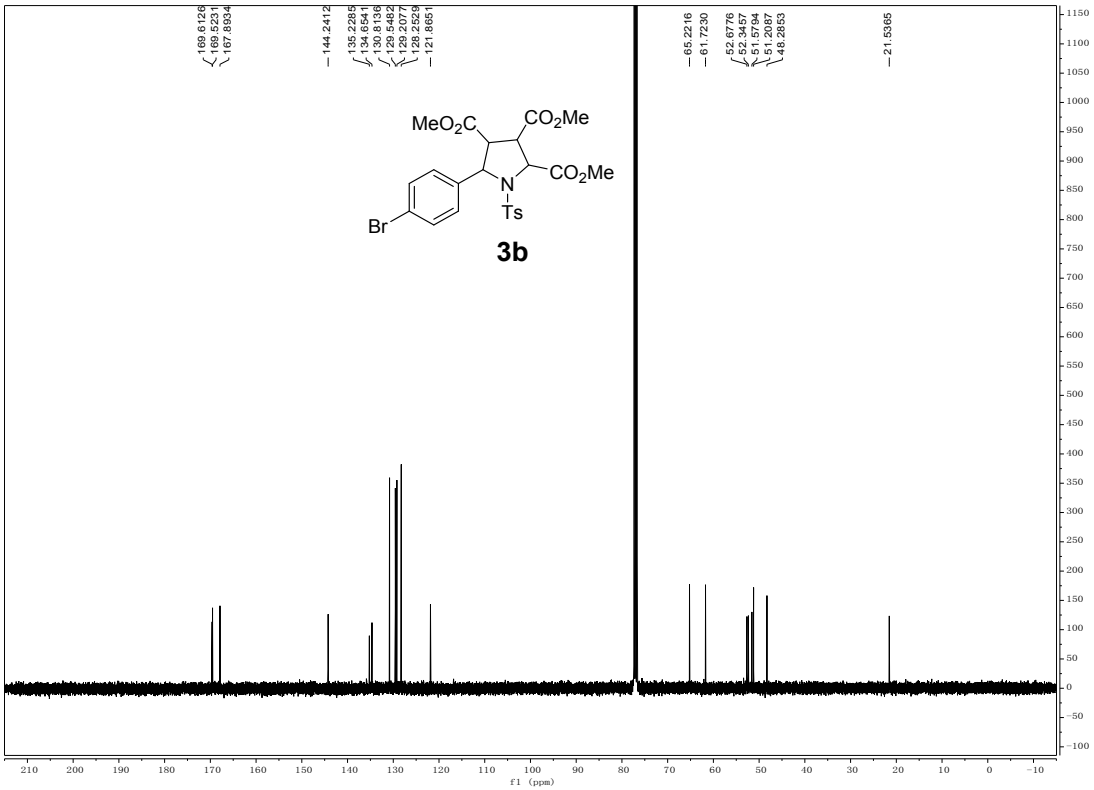
Trimethyl 1-butyl-5-phenylpyrrolidine-2,3,4-tricarboxylate (3a).



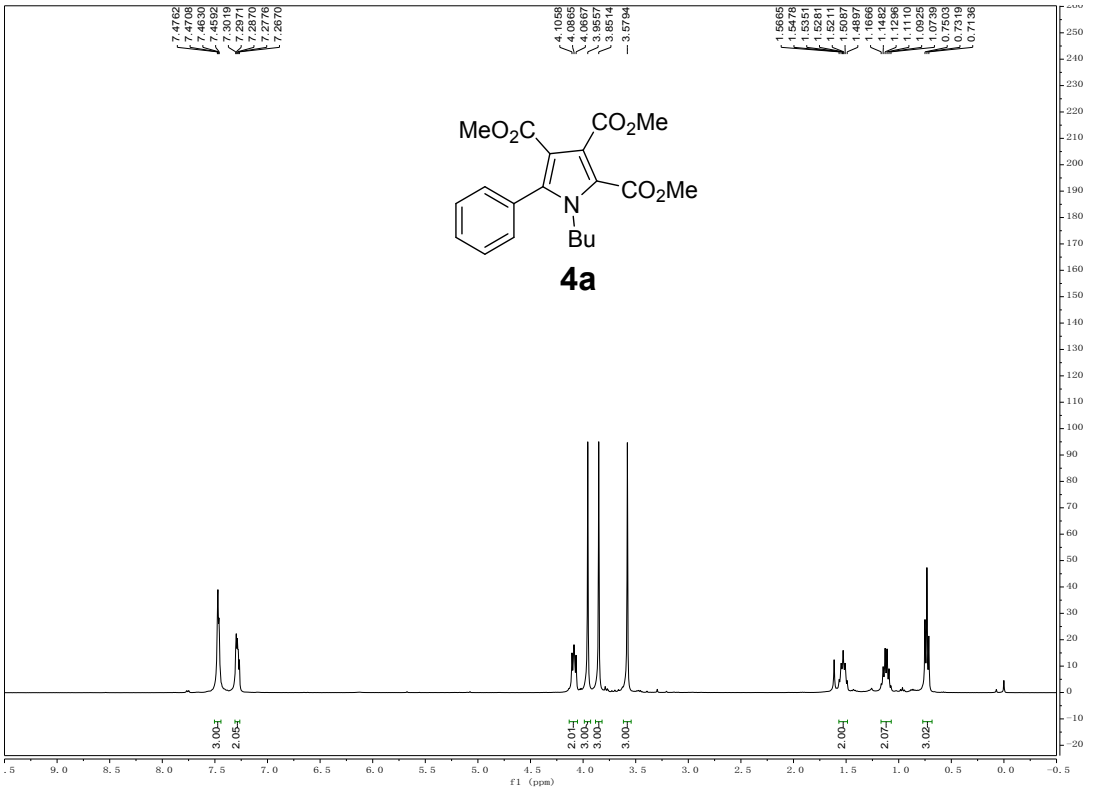


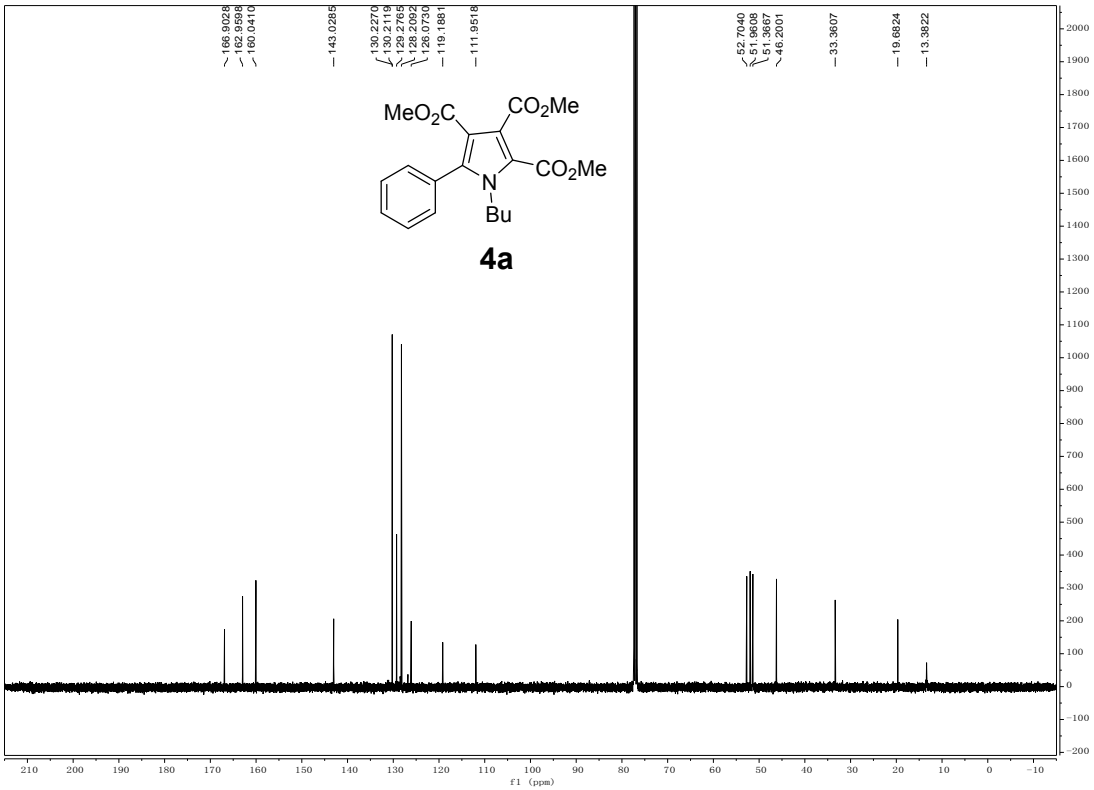
Trimethyl 5-phenyl-1-tosylpyrrolidine-2,3,4-tricarboxylate (3b).





Trimethyl 1-butyl-5-phenyl-1*H*-pyrrole-2,3,4-tricarboxylate (4a).

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4a
f1 (ppm)