Supporting Information

Catalyst-free reaction of 2-(4H-benzo[d][1,3]oxazin-4-yl)acrylates: synthesis of 1,2-dihydroquinolines and 2,3-dihydropyrroles

Tao Wang,‡ Zhongyue Lu,‡ and Pengfei Li*

Department of Chemistry, Guangdong Provincial Key Laboratory of Catalysis, College of Science, Southern University of Science and Technology Guangming Advanced Research Institute, Southern University of Science and Technology, Shenzhen 518055, China

E-mail: lipf@sustech.edu.cn; flyli1980@gmail.com

Table of contents

General information

The 2-(2-aryl-4*H*-benzo[*d*][1,3]oxazin-4-yl)acrylates **1** were synthesized following the general procedure reported by our group earlier. [1,2] The sulfur ylides **2** were synthesized following the general procedure reported earlier.[3,4] The α,β-unsaturated *N*-arylaldimine **4** were synthesized following the general procedure. [5,6]

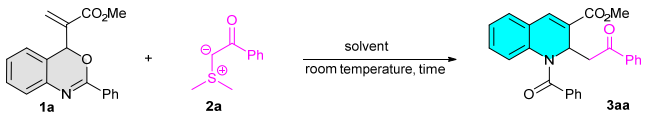
Starting material and solvents were used without further purification as commercially available unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel plates (60GF254) using UV-light (254 and 365nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR spectra were recorded on a Bruker-400 MHz, 500 MHz and 600 MHz spectrometer. Chemical shifts (δ) are reported in ppm and coupling constants (*J*) are given in Hertz (Hz). Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet, coupling constant (Hz), integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High resolution mass spectral (HRMS) analyses were measured on a Thermo Scientific Orbitrap Fusion mass spectrometer using ESI and quadrupole technology.

General procedure for the reaction between 1 and 2

A mixture of **1** (0.1 mmol, 1.0 equiv), **2** (0.2 mmol, 2.0 equiv) in the DMF (0.5 mL) was stirred at room temperature (rt) for 0.5 h. After removing the solvent under atmospheric-vacuum condition, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **3**.

Optimization of reaction conditions

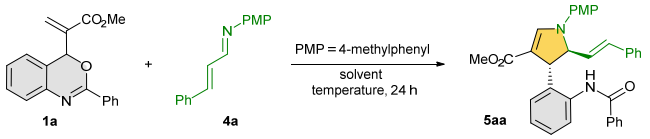
Table S1 Optimization of reaction between **1a** and **2a**.



Entry[a]	**2a** [equiv.]	Solvent	Time [h]	Isolated yield [%][b]
1	2.0	CH_2Cl_2	24	54
2	2.0	$ClCH_2CH_2Cl$	24	39
3	2.0	$CHCl_3$	24	37
4	2.0	toluene	24	0
5	2.0	EtOAc	24	0
6	2.0	acetone	24	0
7	2.0	THF	24	0
8	2.0	MeCN	24	66
9	2.0	DMF	24	98
10	2.0	DMF	12	98
11	2.0	DMF	6	95
12	2.0	DMF	3	95
13	2.0	DMF	1	95
14	2.0	DMF	0.5	95
15	2.0	DMF	0.3	78
16	1.8	DMF	0.5	93
17	1.5	DMF	0.5	93
18	1.2	DMF	0.5	51

a Unless noted, a mixture of **1a** (0.1 mmol) and **2a** in the solvent (0.5 mL) was stirred at room temperature (rt) for the time given.

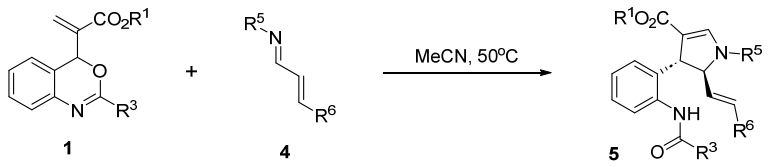
Table S2 Optimization of reaction between **1a** and **4a**.



Entry[a]	**4a** [equiv.]	Solvent	Temp. [°C]	Isolated yield [%][b]
1	1.5	DMF	rt	31
2	1.5	CH_2Cl_2	rt	47
3	1.5	$ClCH_2CH_2Cl$	rt	12
4	1.5	$CHCl_3$	rt	45
5	1.5	toluene	rt	37
6	1.5	THF	rt	31
7	1.5	MeCN	rt	53
8	1.5	MeCN	30	53
9	1.5	MeCN	40	68
10	1.5	MeCN	50	79
11	1.5	MeCN	55	79
12	2.0	MeCN	50	91
13	3.0	MeCN	50	91

[a] Unless noted, a mixture of **1a** (0.1 mmol) and **4a** in the solvent (1.0 mL) was stirred at the indicated temperature for 24 h. [b] Exclusive product.

General procedure for the reaction between 1 and 4

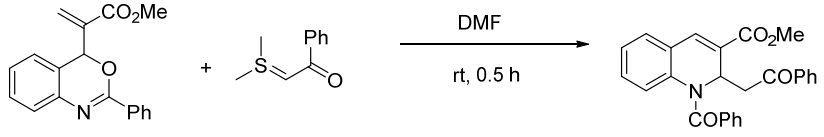


A mixture of α,ß-unsaturated *N*-arylaldimine **4** (0.20 mmol), **1** (0.10 mmol) in CH_3CN (1.0 mL) was stirred at 50 °C for 24 hours. After removing the solvent under atmospheric-vacuum condition, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **5**.

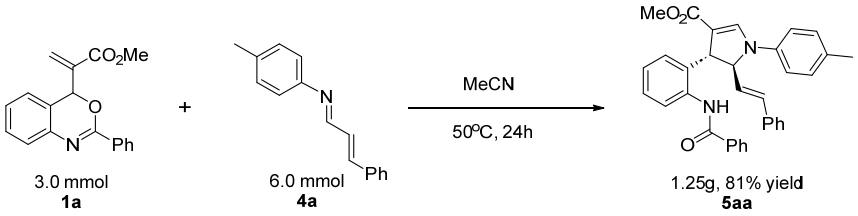
General procedure for the synthesis of compound 6l

A mixture of aniline (0.20 mmol), MBH adduct **1l** (0.10 mmol) in CH_3CN (1.0 mL) was stirred at 50 °C for 24 hours. After removing the solvent under atmospheric-vacuum condition, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **6l**.

General procedure for the gram-scale synthesis of 3aa and 5aa



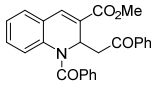
A mixture of **1a** (2 mmol, 1.0 equiv), **2a** (4 mmol, 2.0 equiv) in the DMF (10 mL) was stirred at rt for 0.5 h. After removing the solvent under atmospheric-vacuum condition, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) to afford the desired product **3aa** (0.71 g, 86% yield).



A mixture of **1a** (3.0 mmol) and **4a** (6.0 mmol), in CH_3CN (30.0 mL) was stirred at 50 °C for 24 hours. After removing the solvent under atmospheric-vacuum condition, the residue was purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford the desired product **5aa** (1.25 g, 81% yield).

Characterization Data of the Compounds 3

Methyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3aa):

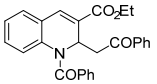


3aa

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point, 39.0 mg, 95% yield, 104.1-104.6 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.7 Hz, 2H), 7.68 (s, 1H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 8.2 Hz, 2H), 7.25 (s, 2H), 7.21 (t, *J* = 7.5 Hz, 2H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (t, *J* = 7.7 Hz, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.19 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.79 (s, 3H), 3.22 (dd, *J* = 12.7, 5.6 Hz, 1H), 3.00 (dd, *J* = 12.8, 8.5 Hz, 1H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 197.13, 169.77, 165.22,

137.02, 136.61, 134.99, 134.19, 133.19, 130.78, 130.05, 129.84, 129.12, 128.73, 128.68, 128.67, 128.23, 126.28, 125.67, 125.23, 52.21, 50.34, 40.81 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{22}NO_4$ 412.1543; Found 412.1543.

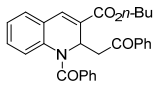
Ethyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ba):



3ba

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 40.0 mg, 94% yield, melting point 104.7-104.9 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 – 7.94 (m, 2H), 7.69 (s, 1H), 7.62 – 7.54 (m, 1H), 7.53 – 7.44 (m, 2H), 7.40 – 7.30 (m, 2H), 7.25 (d, *J* = 1.7 Hz, 2H), 7.24 – 7.19 (m, 2H), 7.12 – 7.05 (m, 1H), 7.04 – 6.89 (m, 1H), 6.62 (s, 1H), 6.25 – 6.12 (m, 1H), 4.35 – 4.21 (m, 2H), 3.24 (dd, *J* = 12.6, 5.6 Hz, 1H), 2.96 (dd, *J* = 12.5, 8.8 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 169.79, 164.79, 136.99, 136.55, 134.95, 134.04, 133.23, 130.79, 130.31, 129.81, 129.16, 128.75, 128.70, 128.66, 128.22, 126.28, 125.68, 125.23, 61.37, 50.40, 40.86, 14.25 ppm. HRMS (ESI) m/z: [M+H]+ Calcd for $C_{27}H_{24}NO_4$ 426.1700; Found 426.1700.

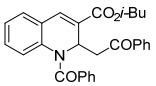
Butyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ca):



3ca

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 39.9 mg, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 8.05 (m, 2H), 7.68 (s, 1H), 7.60 – 7.52 (m, 1H), 7.52 – 7.46 (m, 2H), 7.38 – 7.33 (m, 2H), 7.25 – 7.19 (m, 3H), 7.14 – 7.06 (m, 1H), 7.05 – 6.93 (m, 1H), 6.68 – 6.49 (m, 1H), 6.18 (dd, *J* = 8.7, 5.4 Hz, 1H), 4.41 – 4.13 (m, 2H), 3.24 (dd, *J* = 12.6, 5.5 Hz, 1H), 2.95 (dd, *J* = 12.6, 8.7 Hz, 1H), 1.71 – 1.57 (m, 3H), 1.49 – 1.33 (m, 2H), 0.95 (t, J = 7.4 Hz, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$)δ 197.15, 169.79, 164.87, 137.00, 136.54, 134.95, 134.00, 133.22, 130.77, 130.34, 129.81, 129.14, 128.75, 128.69, 128.66, 128.22, 126.31, 125.70, 125.23, 65.27, 50.41, 40.82, 30.70, 19.33, 13.90 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}NO_4$ 454.2013; Found 454.2014.

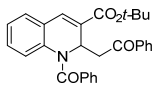
Isobutyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3da):



3da

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 39.4 mg, 87% yield, melting point 107.6 - 108.0 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 7.99 (m, 2H), 7.67 (s, 1H), 7.63 – 7.53 (m, 1H), 7.53 – 7.44 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.17 (m, 4H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.04 – 6.95 (m, 1H), 6.64 (s, 1H), 6.19 (dd, *J* = 8.9, 5.2 Hz, 1H), 4.10 – 3.95 (m, 2H), 3.26 (dd, *J* = 12.7, 5.2 Hz, 1H), 2.95 (dd, *J* = 12.7, 8.9 Hz, 1H), 2.03 – 1.92 (m, 1H), 0.98 (dd, *J* = 6.7, 1.8 Hz, 6H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ197.15, 169.78, 164.84, 137.00, 136.54, 134.94, 133.97, 133.21, 130.74, 130.35, 129.83, 129.10, 128.73, 128.68, 128.64, 128.21, 126.36, 125.71, 125.24, 71.41, 50.42, 40.72, 27.89, 19.35, 19.31 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}NO_4$ 454.2013; Found 454.2014.

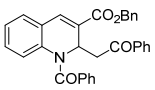
Tert-butyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ea):



3ea

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 36.7 mg, 81% yield, melting point 110.4 - 110.6 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 – 8.04 (m, 2H), 7.65 – 7.55 (m, 2H), 7.53 – 7.42 (m, 2H), 7.39 – 7.30 (m, 2H), 7.27 (d, *J* = 6.9 Hz, 2H), 7.24 – 7.18 (m, 2H), 7.14 – 7.03 (m, 1H), 7.03 – 6.92 (m, 1H), 6.63 (s, 1H), 6.13 (dd, *J* = 8.4, 5.9 Hz, 1H), 3.17 (dd, *J* = 12.4, 6.0 Hz, 1H), 2.99 (dd, *J* = 12.4, 8.5 Hz, 1H), 1.49 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 13C NMR (126 MHz, CDCl3) δ 197.18, 169.79, 163.87, 137.08, 136.41, 135.03, 133.26, 133.21, 131.88, 130.77, 129.53, 129.19, 128.78, 128.73, 128.56, 128.21, 126.17, 125.87, 125.17, 81.98, 50.44, 41.02, 28.13 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{29}H_{28}NO_4$ 454.2013; Found 454.2015.

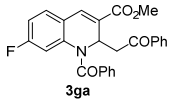
Benzyl 1-benzoyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3fa):



3fa

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 42.9 mg, 88% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.10 – 7.88 (m, 2H), 7.72 (s, 1H), 7.63 – 7.47 (m, 1H), 7.47 – 7.29 (m, 9H), 7.26 – 7.17 (m, 4H), 7.16 – 7.07 (m, 1H), 7.06 – 6.95 (m, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.20 (dd, *J* = 9.0, 5.1 Hz, 1H), 5.38 – 5.22 (m, 2H), 3.28 (dd, *J* = 12.7, 5.2 Hz, 1H), 2.91 (dd, *J* = 12.6, 9.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.14, 169.76, 164.63, 136.88, 136.61, 135.64, 134.90, 134.57, 133.17, 130.75, 129.96, 129.94, 129.10, 128.83, 128.72, 128.69, 128.64, 128.62, 128.58, 128.20, 126.36, 125.58, 125.23, 67.13, 50.39, 40.70 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{26}NO_4$ 488.1856; Found 488.1862.

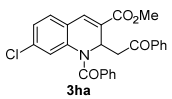
Methyl 1-benzoyl-7-fluoro-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ga):



3ga

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 35.6 mg, 83% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ8.11 – 7.94 (m, 2H), 7.64 (s, 1H), 7.59 – 7.53 (m, 1H), 7.50 – 7.44 (m, 2H), 7.40 – 7.34 (m, 1H), 7.32 – 7.26 (m, 2H), 7.26 – 7.20 (m, 3H), 6.88 – 6.72 (m, 1H), 6.39 (d, *J* = 10.2 Hz, 1H), 6.11 (dd, *J* = 8.6, 5.4 Hz, 1H), 3.79 (s, 3H), 3.23 (dd, *J* = 12.9, 5.4 Hz, 1H), 2.95 (dd, *J* = 12.9, 8.7 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.00, 169.97, 165.10, 162.93 (J_{CF} = 251.5 Hz), 138.40 (J_{CF} = 10.1 Hz), 136.86, 134.40, 133.43, 133.33, 131.20, 130.12 (J_{CF} = 10.1 Hz), 128.92, 128.86, 128.77, 128.60, 128.48, 122.02 (J_{CF} = 2.6 Hz), 113.67 (J_{CF} = 26.3 Hz), 112.65 (J_{CF} = 22.2 Hz), 52.29, 50.46, 40.77 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -107.29 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}FNO_4$ 430.1449; Found 430.1452.

Methyl 1-benzoyl-7-chloro-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ha):

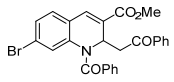


3ha

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 35.6 mg, 80% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.99 (m, 2H), 7.64 (s, 1H), 7.61 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.43 – 7.35 (m, 1H), 7.31 – 7.26 (m, 3H), 7.24 (s, 2H), 7.06 (dd, J = 8.2, 2.0 Hz, 1H), 6.61 (s, 1H), 6.14 (dd, J = 8.5, 5.4 Hz,

1H), 3.81 (s, 3H), 3.25 (dd, J = 12.9, 5.4 Hz, 1H), 2.96 (dd, J = 12.9, 8.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.95, 169.90, 165.00, 137.59, 136.86, 135.52, 134.33, 133.36, 133.28, 131.19, 129.97, 129.43, 128.91, 128.78, 128.60, 128.46, 126.26, 125.49, 124.06, 52.36, 50.46, 40.74 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}ClNO_4$ 446.1154; Found 446.1157.

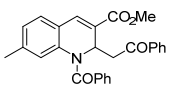
Methyl 1-benzoyl-7-bromo-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ia):



3ia

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, melting point 132.1 – 132.7 ºC 38.6 mg, 79% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 8.00 (m, 2H), 7.62 (s, 1H), 7.58 – 7.55 (m, 1H), 7.50 – 7.46 (m, 2H), 7.40 – 7.38 (m, 1H), 7.29 – 7.26 (m, 4H), 7.24 – 7.16 (m, 2H), 6.74 (s, 1H), 6.15-6.11 (m, 1H), 3.81 (s, 3H), 3.27 – 3.23 (m, 1H), 2.99 – 2.94 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.95, 169.88, 165.00, 137.59, 136.86, 134.31, 133.37, 133.34, 131.19, 130.13, 129.57, 129.15, 128.90, 128.79, 128.60, 128.46, 128.38, 124.43, 123.55, 52.38, 50.46, 40.72 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}BrNO_4$ 490.0648; Found 490.0651.

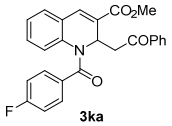
Methyl 1-benzoyl-7-methyl-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3ja):



3ja

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 36.1 mg, 85% yield, melting point 139.4 – 139.6 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 – 7.97 (m, 2H), 7.66 (s, 1H), 7.61 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 7.37 – 7.30 (m, 1H), 7.26 – 7.18 (m, 5H), 6.95 – 6.84 (m, 1H), 6.39 (s, 1H), 6.16 (dd, J = 8.7, 5.3 Hz, 1H), 3.79 (s, 3H), 3.24 (dd, *J* = 12.7, 5.4 Hz, 1H), 2.95 (dd, J = 12.7, 8.7 Hz, 1H), 2.02 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.25, 169.86, 165.36, 140.54, 137.00, 136.41, 135.09, 134.34, 133.15, 130.64, 128.97, 128.70, 128.66, 128.63, 128.47, 128.12, 127.01, 126.15, 123.09, 52.16, 50.40, 40.76, 21.61 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_4$ 426.1700, Found 426.1703.

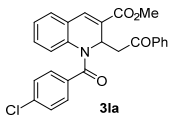
Methyl 1-(4-fluorobenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



3ka

(3ka): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 39.9 mg, 93% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H), 7.68 (s, 1H), 7.59 – 7.55 (m, 1H), 7.51 – 7.46 (m, 2H), 7.35 – 7.33 (m, 1H), 7.19 (s, 4H), 7.14 – 7.10 (m, 1H), 7.05 – 7.01 (m, 1H), 6.62 – 6.60 (m, 1H), 6.17 – 6.14 (m, 1H), 3.81 (s, 3H), 3.26 – 3.21 (m, 1H), 2.97 – 2.92 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.09, 168.60, 165.16, 136.97, 136.88, 136.27, 134.15, 133.33, 133.30, 130.62, 130.11, 130.07, 128.81, 128.78, 128.65, 128.56, 126.26, 125.67, 125.54, 52.32, 50.42, 40.59 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.24 ppm. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{26}H_{21}FNO_4Na$ 452.1269; Found 452.1270.

Methyl 1-(4-chlorobenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate (3la):

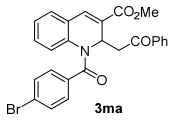


3la

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 41.4 mg, 93% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 – 8.01

(m, 2H), 7.68 (s, 1H), 7.60 – 7.55 (m, 1H), 7.52 – 7.46 (m, 2H), 7.36 – 7.33 (m, 1H), 7.19 (s, 4H), 7.15 – 7.10 (m, 1H), 7.06 – 7.00 (m, 1H), 6.62 (s, 1H), 6.16 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.81 (s, 3H), 3.24 (dd, *J* = 12.8, 5.3 Hz, 1H), 2.94 (dd, *J* = 12.8, 8.9 Hz, 1H).ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.08, 168.59, 165.15, 136.96, 136.87, 136.26, 134.14, 133.32, 133.29, 130.61, 130.11, 130.07, 128.81, 128.77, 128.64, 128.55, 126.26, 125.67, 125.53, 52.31, 50.41, 40.58 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}ClNO_4$ 446.1154; Found 446.1154.

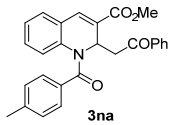
Methyl 1-(4-bromobenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



3ma

(3ma): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 42.5 mg, 87% yield, melting point 144.1 – 144.7 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.67 (s, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.45 (m, 2H), 7.39 – 7.32 (m, 3H), 7.16 – 7.09 (m, 3H), 7.07 – 7.01 (m, 1H), 6.62 (s, 1H), 6.15 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.81 (s, 3H), 3.23 (dd, *J* = 12.8, 5.2 Hz, 1H), 2.94 (dd, *J* = 12.8, 9.0 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.06, 168.65, 165.14, 136.85, 136.20, 134.13, 133.79, 133.29, 131.50, 130.76, 130.09, 128.80, 128.76, 128.68, 128.63, 126.25, 125.66, 125.55, 125.39, 52.31, 50.40, 40.55 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}BrNO_4$ 490.0648; Found 490.0651.

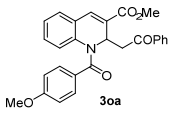
Methyl 1-(4-methylbenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



3na

(3na): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 35.7 mg, 84% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.04 (m, 2H), 7.68 (s, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.45 (m, 2H), 7.35 – 7.30 (m, 1H), 7.19 – 7.12 (m, 2H), 7.11 – 7.05 (m, 1H), 7.04 – 6.91 (m, 3H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.17 (dd, *J* = 8.3, 5.9 Hz, 1H), 3.78 (s, 3H), 3.20 (dd, *J* = 12.5, 5.9 Hz, 1H), 3.02 (dd, *J* = 12.6, 8.3 Hz, 1H), 2.30 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.25, 169.82, 165.27, 141.29, 137.01, 136.86, 134.25, 133.18, 131.96, 129.93, 129.86, 129.32, 128.91, 128.74, 128.69, 128.67, 126.21, 125.53, 125.05, 52.21, 50.41, 40.96, 21.61 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_4$ 426.1700; Found 426.1700.

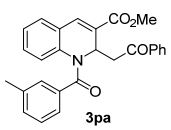
Methyl 1-(4-methoxybenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



3oa

(3oa): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 36.5 mg, 82% yield, melting point 126.4 – 126.9 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 – 8.05 (m, 2H), 7.68 (s, 1H), 7.59 – 7.53 (m, 1H), 7.52 – 7.46 (m, 2H), 7.35 – 7.29 (m, 1H), 7.23 (d, J = 8.4 Hz, 2H), 7.11 – 7.05 (m, 1H), 7.03 – 6.96 (m, 1H), 6.74 – 6.68 (m, 2H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.15 (dd, *J* = 8.1, 6.1 Hz, 1H), 3.77 (s, 3H), 3.77 (s, 3H), 3.19 (dd, *J* = 12.4, 6.1 Hz, 1H), 3.03 (dd, *J* = 12.4, 8.2 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.30, 169.34, 165.28, 161.72, 137.14, 137.04, 134.20, 133.17, 131.44, 129.93, 129.88, 128.74, 128.70, 126.90, 126.13, 125.44, 125.31, 124.93, 113.49, 55.41, 52.19, 50.54, 41.08 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_5$ 442.1649; Found 442.1653.

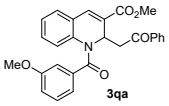
Methyl 1-(3-methylbenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



3pa

(3pa): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 34.4 mg, 81% yield, melting point 87.3 – 88.1 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 8.03 (m, 2H), 7.68 (s, 1H), 7.65 – 7.54 (m, 1H), 7.54 – 7.46 (m, 2H), 7.38 – 7.31 (m, 1H), 7.21 – 6.92 (m, 6H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.18 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.79 (s, 3H), 3.21 (dd, *J* = 12.6, 5.6 Hz, 1H), 2.98 (dd, *J* = 12.6, 8.6 Hz, 1H), 2.25 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.22, 169.99, 165.27, 138.26, 136.98, 136.65, 134.85, 134.30, 133.22, 131.56, 129.92, 129.87, 129.84, 128.75, 128.68, 128.66, 127.93, 126.27, 126.05, 125.57, 125.18, 52.24, 50.33, 40.86, 21.34 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_4$ 426.1700; Found 426.1701.

Methyl 1-(3-methoxybenzoyl)-2-(2-oxo-2-phenylethyl)-1,2-dihydroquinoline-3-carboxylate



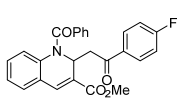
3qa

(3qa): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 36.2 mg, 82% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 – 8.00 (m, 2H), 7.68 (s, 1H), 7.60 – 7.53 (m, 1H), 7.53 – 7.44 (m, 2H), 7.32 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.14 – 7.04 (m, 2H), 7.04 – 6.96 (m, 1H), 6.91 – 6.81 (m, 2H), 6.74 (d, *J* = 7.5 Hz, 1H), 6.64 (d, *J* = 8.1 Hz, 1H), 6.19 (dd, *J* = 8.6, 5.5 Hz, 1H), 3.79 (s, 3H), 3.68 (s, 3H), 3.21 (dd, *J* = 12.7, 5.5 Hz, 1H), 2.99 (dd, *J* = 12.7, 8.6 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.16, 169.56, 165.23, 159.42, 136.96, 136.55, 136.15, 134.23, 133.23, 129.98, 129.91, 129.21, 128.75, 128.67, 128.65, 126.18, 125.55, 125.29, 121.42, 117.32, 113.88, 55.41, 52.25, 50.34, 40.76 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_5$ 442.1649; Found 442.1652.

Methyl 2-(2-oxo-2-phenylethyl)-1-(thiophene-2-carbonyl)-1,2-dihydroquinoline-3-carboxylate (3ra): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 33.4 mg, 80% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.17 – 7.97 (m, 2H), 7.67 (s, 1H), 7.59 – 7.53 (m, 1H), 7.55 – 7.44 (m, 2H), 7.43 – 7.33 (m, 2H), 7.22 – 7.15 (m, 1H), 7.14 – 7.04 (m, 1H), 6.99 – 6.91 (m, 2H), 6.87 – 6.76 (m, 1H), 6.14 (dd, *J* = 8.2, 6.0 Hz, 1H), 3.76 (s, 3H), 3.19 (dd, *J* = 12.7, 6.0 Hz, 1H), 3.03 (dd, *J* = 12.6, 8.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.12, 165.18, 163.00, 137.29, 136.91, 136.50, 134.06, 133.26, 132.27, 130.88, 130.32, 129.87, 128.79, 128.71, 128.65, 126.90, 126.34, 126.01, 125.74, 52.23, 50.87, 40.83 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_4S$ 418.1108, Found 418.1107.

3ra

Methyl 1-benzoyl-2-(2-(4-fluorophenyl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate

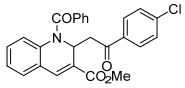


3ab

(3ab): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 23.6 mg, 55% yield, melting point 154.1 – 154.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.19 – 8.10 (m, 2H), 7.68 (s, 1H), 7.39 – 7.30 (m, 2H), 7.27 – 7.19 (m, 5H), 7.20 – 7.13 (m, 2H), 7.12 – 7.05 (m, 1H), 7.02 – 6.94 (m, 1H), 6.59 (d, *J* = 8.1

Hz, 1H), 6.16 (dd, *J* = 8.7, 5.5 Hz, 1H), 3.81 (s, 3H), 3.21 (dd, *J* = 12.6, 5.6 Hz, 1H), 2.94 (dd, *J* = 12.6, 8.7 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.67, 169.88, 166.0 (J_{CF} = 254.5 Hz), 165.33, 136.62, 134.87, 134.33, 133.47 (J_{CF} = 2.5 Hz), 131.40 (J_{CF} = 8.8 Hz), 130.99, 130.01, 129.85, 129.26, 128.34, 128.3, 126.28, 125.59, 125.35, 115.95 (J_{CF} = 22.7 Hz), 52.37, 50.47, 41.00 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -105.41ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}FNO_4$ 430.1449; Found 430.1453.

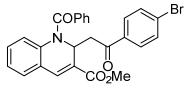
Methyl 1-benzoyl-2-(2-(4-chlorophenyl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate



3ac

(3ac): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 31.2 mg, 70% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 – 8.02 (m, 2H), 7.68 (s, 1H), 7.50 – 7.43 (m, 2H), 7.38 – 7.31 (m, 2H), 7.26 – 7.20 (m, 4H), 7.12 – 7.06 (m, 1H), 7.02 – 6.93 (m, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.15 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.82 (s, 3H), 3.21 (dd, *J* = 12.5, 5.5 Hz, 1H), 2.93 (dd, *J* = 12.6, 8.8 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.98, 169.81, 165.24, 139.66, 136.54, 135.29, 134.76, 134.30, 130.95, 130.13, 129.97, 129.71, 129.21, 129.11, 128.76, 128.28, 126.21, 125.49, 125.29, 52.32, 50.39, 40.96 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}ClNO_4$ 446.1154; Found 446.1157.

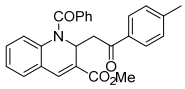
Methyl 1-benzoyl-2-(2-(4-bromophenyl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate



3ad

(3ad): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 38.1 mg, 78% yield, melting point 127.3 – 127.5 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.68 (s, 1H), 7.67 – 7.60 (m, 2H), 7.38 – 7.30 (m, 2H), 7.26 – 7.20 (m, 4H), 7.12 – 7.06 (m, 1H), 7.03 – 6.95 (m, 1H), 6.58 (d, *J* = 8.1 Hz, 1H), 6.14 (dd, *J* = 8.7, 5.4 Hz, 1H), 3.82 (s, 3H), 3.21 (dd, *J* = 12.5, 5.5 Hz, 1H), 2.92 (dd, *J* = 12.5, 8.7 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.19, 169.81, 165.23, 136.54, 135.68, 134.75, 134.31, 132.11, 130.96, 130.25, 129.98, 129.70, 129.22, 128.76, 128.48, 128.29, 126.21, 125.49, 125.29, 52.33, 50.39, 40.95 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{21}BrNO_4$ 490.0648; Found 490.0654.

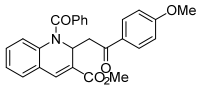
Methyl 1-benzoyl-2-(2-oxo-2-(p-tolyl)ethyl)-1,2-dihydroquinoline-3-carboxylate (3ae):



3ae

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white solid, 35.3 mg, 83% yield, melting point 125.7 – 126.4 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.68 (s, 1H), 7.37 – 7.31 (m, 2H), 7.28 (d, J = 8.1 Hz, 2H), 7.26 – 7.24 (m, 2H), 7.24 – 7.19 (m, 2H), 7.12 – 7.06 (m, 1H), 7.02 – 6.95 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 6.18 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.80 (s, 3H), 3.18 (dd, *J* = 12.7, 5.7 Hz, 1H), 2.96 (dd, *J* = 12.7, 8.5 Hz, 1H), 2.41 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.80, 169.74, 165.26, 143.97, 136.62, 134.99, 134.53, 134.16, 130.76, 130.13, 129.83, 129.47, 129.15, 128.80, 128.68, 128.22, 126.31, 125.67, 125.22, 52.24, 50.36, 40.77, 21.85 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_4$ 426.1700; Found 426.1701.

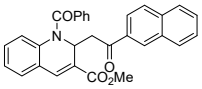
Methyl 1-benzoyl-2-(2-(4-methoxyphenyl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate



3af

(3af): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 36.2 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 – 8.01 (m, 2H), 7.67 (s, 1H), 7.36 – 7.31 (m, 2H), 7.26 – 7.24 (m, 2H), 7.23 – 7.18 (m, 2H), 7.12 – 7.05 (m, 1H), 7.01 – 6.93 (m, 3H), 6.72 – 6.47 (m, 1H), 6.16 (dd, *J* = 8.4, 5.8 Hz, 1H), 3.87 (s, 3H), 3.79 (s, 3H), 3.15 (dd, *J* = 12.6, 5.8 Hz, 1H), 2.94 (dd, *J* = 12.6, 8.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.66, 169.74, 165.27, 163.59, 136.61, 134.96, 134.11, 130.96, 130.75, 130.16, 130.11, 129.82, 129.13, 128.67, 128.21, 126.27, 125.65, 125.21, 113.92, 55.56, 52.23, 50.47, 40.71 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_5$ 442.1648; Found 442.1652.

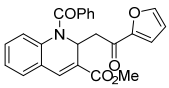
Methyl 1-benzoyl-2-(2-(naphthalen-1-yl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate



3ag

(3ag): Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 30.9 mg, 67% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.66 (s, 1H), 8.12 – 8.06 (m, 1H), 8.04 – 7.98 (m, 1H), 7.94 – 7.85 (m, 2H), 7.71 (s, 1H), 7.63 – 7.57 (m, 1H), 7.57 – 7.53 (m, 1H), 7.38 – 7.28 (m, 2H), 7.26 – 7.22 (m, 2H), 7.19 (dd, *J* = 8.1, 7.0 Hz, 2H), 7.12 – 7.06 (m, 1H), 7.00 – 6.91 (m, 1H), 6.57 (d, *J* = 8.4 Hz, 1H), 6.27 (dd, *J* = 8.5, 5.6 Hz, 1H), 3.82 (s, 3H), 3.34 (dd, *J* = 12.7, 5.6 Hz, 1H), 3.14 (dd, *J* = 12.7, 8.5 Hz, 1H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.12, 169.82, 165.24, 136.62, 135.77, 134.91, 134.32, 134.27, 132.76, 130.78, 130.75, 130.04, 129.95, 129.85, 129.12, 128.73, 128.56, 128.55, 128.22, 127.87, 126.72, 126.28, 125.64, 125.24, 124.23, 52.29, 50.63, 40.99 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{30}H_{24}NO_4$ 462.1700; Found 462.1704.

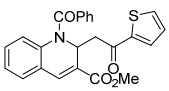
Methyl 1-benzoyl-2-(2-(furan-2-yl)-2-oxoethyl)-1,2-dihydroquinoline-3-carboxylate (3ah):



3ah

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 34.5 mg, 75% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.60 (dd, *J* = 1.7, 0.7 Hz, 1H), 7.39 – 7.30 (m, 3H), 7.28 (s, 2H), 7.22 (dd, *J* = 8.1, 6.8 Hz, 2H), 7.11 – 7.05 (m, 1H), 7.01 – 6.94 (m, 1H), 6.61 (d, *J* = 8.1 Hz, 1H), 6.57 – 6.53 (m, 1H), 6.15 (dd, *J* = 8.4, 5.5 Hz, 1H), 3.84 (s, 3H), 3.08 (dd, *J* = 12.6, 5.5 Hz, 1H), 2.83 (dd, *J* = 12.6, 8.5 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.40, 169.78, 165.18, 152.62, 146.81, 136.59, 134.90, 134.29, 130.82, 129.89, 129.78, 129.14, 128.67, 128.25, 126.16, 125.56, 125.26, 118.33, 112.51, 52.33, 50.47, 41.26 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_5$ 402.1336; Found 402.1337.

Methyl 1-benzoyl-2-(2-oxo-2-(thiophen-2-yl)ethyl)-1,2-dihydroquinoline-3-carboxylate (3ai):

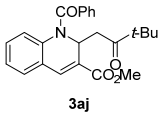


3ai

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 29.2 mg, 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 1H), 7.69 (s, 1H), 7.67 – 7.61 (m, 1H), 7.37 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H),

7.25 – 7.19 (m, 2H), 7.19 – 7.13 (m, 1H), 7.12 – 7.05 (m, 1H), 7.01 – 6.93 (m, 1H), 6.60 (d, *J* = 8.1 Hz, 1H), 6.18 (dd, *J* = 8.3, 5.6 Hz, 1H), 3.83 (s, 3H), 3.15 (dd, *J* = 12.4, 5.7 Hz, 1H), 2.92 (dd, *J* = 12.5, 8.3 Hz, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 189.88, 169.78, 165.21, 144.71, 136.57, 134.88, 134.35, 134.21, 133.20, 130.85, 129.91, 129.80, 129.15, 128.72, 128.41, 128.26, 126.24, 125.59, 125.26, 52.34, 50.69, 41.88 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{20}NO_4S$ 418.1108; Found 418.1108.

Methyl 1-benzoyl-2-(3,3-dimethyl-2-oxobutyl)-1,2-dihydroquinoline-3-carboxylate (3aj):

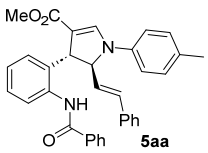


3aj

Purified by flash chromatography (petroleum ether/ethyl acetate = 4/1) and obtained as white oil, 32.1 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.31 – 7.26 (m, 1H), 7.25 – 7.20 (m, 3H), 7.20 – 7.14 (m, 2H), 7.07 – 6.99 (m, 1H), 7.00 – 6.90 (m, 1H), 6.73 (s, 1H), 5.93 (dd, *J* = 9.8, 4.7 Hz, 1H), 3.80 (s, 3H), 2.70 (dd, *J* = 13.2, 4.7 Hz, 1H), 2.29 (dd, *J* = 13.2, 9.8 Hz, 1H), 1.11 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 212.02, 169.82, 165.32, 136.66, 135.30, 133.80, 130.70, 130.63, 129.75, 129.07, 128.47, 128.20, 126.52, 125.85, 125.19, 52.29, 49.48, 45.06, 37.64, 26.02 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{26}NO_4$ 392.1856; Found 392.1862.

Characterization Data of the Compounds 5

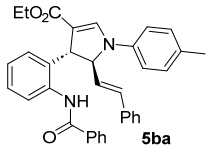
Methyl (*E*)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3 carboxylate



5aa

(5aa): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 46.7 mg, 91% yield, melting point 197.6-197.9 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.31 – 10.14 (m, 1H), 8.05 – 8.02 (m, 2H), 7.74 (s, 1H), 7.71 (d, *J* = 8.1 Hz, 1H), 7.43 – 7.37 (m, 3H), 7.23 – 7.04 (m, 10H), 6.94 – 6.91 (m, 2H), 6.39 (d, *J* = 15.9 Hz, 1H), 6.16 – 6.13 (m, 1H), 5.00 – 4.98 (m, 1H), 4.15 (d, *J* = 2.2 Hz, 1H), 3.65 (s, 3H), 2.22 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.72, 166.11, 141.33, 138.03, 137.57, 135.97, 134.74, 134.70, 132.08, 131.76, 131.73, 130.39, 128.67, 128.65, 128.13, 127.81, 127.67, 126.82, 126.80, 126.68, 126.29, 126.17, 115.71, 109.51, 72.43, 51.47, 47.78, 20.71 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{31}N_2O_3$ 515.2329; Found 515.2329.

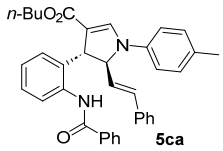
Ethyl (*E*)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate



5ba

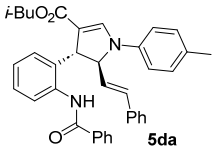
(5ba): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 47.0 mg, 89% yield, melting point 184.7 – 185.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.39 (s, 1H), 8.14 (d, *J* = 7.6 Hz, 2H), 7.82 (s, 1H), 7.80 (d, *J* = 8.1 Hz, 1H), 7.51 (t, *J* = 7.2 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.25 – 7.13 (m, 7H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.26 – 6.22 (m, 1H), 5.07 (d, *J* = 6.9 Hz, 1H), 4.26 – 4.25 (m, 1H), 4.21 (d, *J* = 2.2 Hz, 1H), 4.16 – 4.13 (m, 1H), 2.31 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ167.45, 166.06, 140.98, 138.08, 137.59, 135.98, 134.76, 134.73, 131.95, 131.71, 131.68, 130.37, 128.67, 128.65, 128.13, 127.84, 127.64, 126.80, 126.74, 126.72, 126.31, 126.07, 115.64, 109.94, 72.42, 60.32, 47.75, 20.73, 14.63ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{33}N_2O_3$ 529.2486; Found 529.2485.

Butyl (E)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1H-pyrrole-3-carboxylate

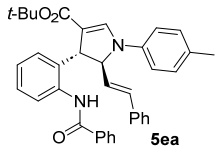


(5ca): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 46.1 mg, 83% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.11 (d, *J* = 7.6 Hz, 2H), 7.78 (d, *J* = 6.7 Hz, 2H), 7.49 – 7.43 (m, 3H), 7.30 – 7.27 (m, 3H), 7.25 – 7.14 (m, 4H), 7.12 – 7.10 (m, 3H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.24 – 6.20 (m, 1H), 5.05 (d, *J* = 6.9 Hz, 1H), 4.21 – 4.17 (m, 2H), 4.06 – 4.02 (m, 1H), 2.29 (s, 3H), 1.66 – 1.61 (m, 2H), 1.42 – 1.35 (m, 2H), 0.94 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ δ 167.52, 166.04, 140.91, 138.08, 137.54, 135.97, 134.77, 134.72, 131.95, 131.70, 131.15, 130.36, 128.66, 128.64, 128.12, 127.82, 127.63, 126.79, 126.77, 126.71, 126.34, 126.05, 115.64, 109.91, 72.44, 64.24, 47.82, 31.08, 20.73, 19.41, 13.95 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{37}N_2O_3$ 557.2799; Found 557.2798.

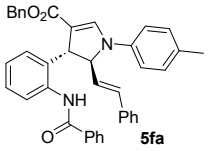
Isobutyl (*E*)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5da): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 45.5 mg, 82% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 7.81 – 7.79 (m, 2H), 7.51 – 7.45 (m, 3H), 7.32 – 7.27 (m, 3H), 7.26 – 7.20 (m, 4H), 7.16 – 7.13 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.48 (d, *J* = 15.9 Hz, 1H), 6.27 – 6.23 (m, 1H), 5.07 (d, *J* = 6.9 Hz, 1H), 4.22 (d, *J* = 2.4 Hz, 1H), 4.01 – 3.98 (m, 1H), 3.85 – 3.82 (m, 1H), 2.31 (s, 3H), 1.99 – 1.95 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 6H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.17, 166.04, 140.89, 138.09, 137.55, 135.98, 134.79, 134.71, 131.99, 131.74, 131.70, 130.39, 130.36, 128.84, 128.67, 128.14, 127.81, 127.64, 127.08, 126.80, 126.72, 126.37, 126.07, 115.67, 72.47, 70.50, 28.08, 20.74, 19.47, 19.41 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{37}H_{37}N_2O_3$ 557.2799; Found 557.2799.



Tert-butyl (*E*)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ea): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 45.1 mg, 81% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.59 (s, 1H), 8.16 (d, *J* = 7.5 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.68 (s, 1H), 7.52 – 7.44 (m, 3H), 7.31 – 7.27 (m, 4H), 7.25 – 7.18 (m, 3H), 7.13 (t, *J* = 8.7 Hz, 3H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.26 – 6.22 (m, 1H), 5.03 (d, *J* = 6.9 Hz, 1H), 4.16 (d, *J* = 2.3 Hz, 1H), 2.31 (s, 3H), 1.50 (s, 9H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.25, 166.05, 140.57, 140.20, 138.28, 136.06, 135.29, 134.87, 133.31, 131.64, 131.60, 131.55, 130.31, 128.65, 128.62, 128.54, 128.08, 127.94, 127.50, 127.05, 126.80, 126.47, 125.67, 115.47, 80.54, 72.58, 36.35, 28.65, 20.72 ppm. HRMS (ESI) m/z: [M+H]+ Calcd for $C_{37}H_{37}N_2O_3$ 557.2799; Found 557.2797.

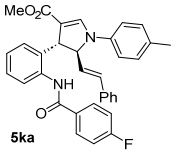


Benzyl (*E*)-4-(2-benzamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate



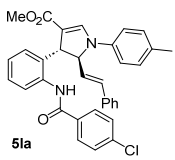
(5fa): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 51.4 mg, 87% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.24 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.29 (m, 6H), 7.29 – 7.27 (m, 1H), 7.26 – 7.20 (m, 4H), 7.19 – 7.10 (m, 4H), 6.99 (d, *J* = 8.1 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.24 – 6.21 (m, 1H), 5.27 (d, *J* = 12.3 Hz, 1H), 5.07 – 5.03 (m, 2H), 4.23 (d, *J* = 2.3 Hz, 1H), 2.29 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.21, 166.07, 141.61, 137.93, 137.57, 136.50, 135.94, 134.77, 134.68, 132.16, 131.79, 131.73, 130.45, 130.36, 129.83, 128.68, 128.66, 128.35, 128.14, 127.81, 127.71, 126.83, 126.81, 126.72, 126.42, 126.11, 115.77, 109.32, 72.54, 66.27, 47.40, 20.73 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{40}H_{35}N_2O_3$ 591.2642; Found 591.2644.

Methyl (*E*)-4-(2-(4-fluorobenzamido)phenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-

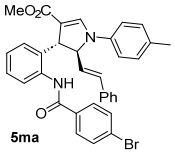


carboxylate (5ka): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 46.1 mg, 85% yield, melting point 200.3-201.9 ^{o}C ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.07 (d, *J* = 8.3 Hz, 2H), 7.81 (s, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.43 – 7.41 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.18 (m, 3H), 7.18 – 7.11 (m, 3H), 7.00 (d, *J* = 8.5 Hz, 2H), 6.46 (d, *J* = 15.9 Hz, 1H), 6.23 – 6.20 (m, 1H), 5.07 – 5.05 (m, 1H), 4.17 (d, *J* = 2.1 Hz, 1H), 3.72 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.91, 165.04, 141.43, 137.98, 137.95, 137.49, 135.93, 134.56, 133.15, 132.21, 131.83, 130.41, 129.30, 128.91, 128.70, 128.21, 127.72, 126.92, 126.78, 126.60, 126.30, 126.03, 115.74, 109.35, 72.41, 51.54, 47.78, 20.72 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -108.44 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}FN_2O_3$ 533.2235; Found 533.2238.

Methyl (*E*)-4-(2-(4-chlorobenzamido)phenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-

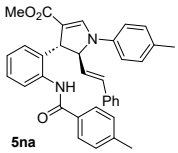


carboxylate (5la): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 46.7 mg, 85% yield, melting point 208.7-210.0 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.38 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 2H), 7.82 – 7.76 (m, 2H), 7.44 – 7.43 (m, 2H), 7.31 – 7.26 (m, 3H), 7.25 – 7.13 (m, 7H),7.01 (d, *J* = 8.5 Hz, 2H), 6.47 (d, *J* = 15.9 Hz, 1H), 6.25 – 6.21 (m, 1H), 5.07 (d, *J* = 6.6 Hz, 1H), 4.18 (d, *J* = 2.1 Hz, 1H), 3.73 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.94, 165.05, 141.39, 137.98, 137.92, 137.49, 135.90, 134.50, 133.12, 132.21, 131.79, 130.41, 129.31, 128.93, 128.71, 128.23, 127.73, 126.93, 126.78, 126.53, 126.29, 126.02, 115.71, 109.36, 72.38, 51.57, 47.70, 20.74 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}ClN_2O_3$ 549.1939; Found 549.1942.

Methyl (*E*)-4-(2-(4-chlorobenzamido)phenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ma): 

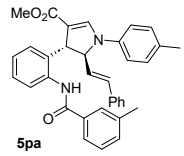
5ma

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 50.4 mg, 87% yield, melting point 216.1-218.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.3 (s, 1H), 7.98 (d, *J* = 8.2 Hz, 2H), 7.80 (s, 1H), 7.75 – 7.74 (m, 1H), 7.58 – 7.56 (m, 2H), 7.29 – 7.26 (m, 4H), 7.25 – 7.10 (m, 6H), 6.99 – 6.98 (m, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.22 – 6.18 (m, 1H), 5.05 – 5.04 (m, 1H), 4.15 (d, *J* = 2.1 Hz, 1H), 3.71 (s, 3H), 2.28 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.91, 165.13, 141.42, 137.95, 137.47, 135.92, 134.54, 133.62, 132.21, 131.89, 131.83, 130.41, 129.49, 128.70, 128.22, 127.72, 126.92, 126.78, 126.59, 126.51, 126.31, 126.01, 115.74, 109.34, 72.40, 51.54, 47.79, 20.72 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{30}BrN_2O_3$ 593.1434; Found 593.1434.

Methyl (*E*)-4-(2-(4-methylbenzamido)phenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5na): 

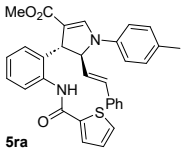
5na

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 46.1 mg, 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.20 (s, 1H), 8.01 (d, *J* = 7.9 Hz, 2H), 7.81 – 7.77 (m, 2H), 7.30 – 7.26 (m, 4H), 7.25 – 7.16 (m, 5H), 7.15 – 7.11 (m, 3H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.45 (d, *J* = 15.9 Hz, 1H), 6.23 – 6.19 (m, 1H), 5.05 – 5.04 (m, 1H), 4.21 (d, *J* = 2.2 Hz, 1H), 3.72 (s, 3H), 2.38 (s, 3H), 2.29 (s, 3H) ppm. ^{13}C NMR (151 MHz, $CDCl_3$) δ 167.67, 166.08, 142.11, 141.29, 138.05, 137.47, 135.98, 134.85, 132.04, 131.96, 131.73, 130.37, 128.63, 128.10, 127.80, 127.64, 126.80, 126.67, 126.27, 126.14, 115.69, 109.52, 72.44, 51.45, 47.79, 21.60, 20.71 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{33}N_2O_3$ 529.2486; Found 529.2486.



5pa

Methyl (*E*)-4-(2-(3-methylbenzamido)phenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5pa): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 43.9 mg, 83% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.64 (s, 1H), 7.84 – 7.80 (m, 2H), 7.68 – 7.66 (m, 1H), 7.34 – 7.27 (m, 6H), 7.24 – 7.12 (m, 7H), 7.02 – 6.99 (m, 2H), 6.52 (d, *J* = 16.0 Hz, 1H), 6.29 – 6.24 (m, 1H), 5.08 – 5.06 (m, 1H), 4.24 (d, *J* = 2.5 Hz, 1H), 3.64 (s, 3H), 2.54 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.91, 167.29, 141.25, 138.02, 137.37, 137.15, 136.21, 135.97, 134.57, 131.99, 131.80, 131.38, 130.36, 130.31, 130.23, 128.70, 128.17, 127.71, 127.41, 126.94, 126.76, 126.54, 125.94, 125.87, 115.62, 109.35, 72.37, 51.34, 48.02, 20.72, 20.40 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{33}N_2O_3$ 529.2486; Found 529.2486.

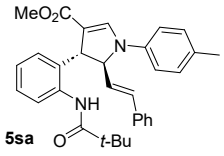
Methyl (*E*)-5-styryl-4-(2-(thiophene-2-carboxamido)phenyl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ra): 

5ra

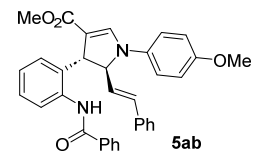
Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 37.5 mg, 72% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.41 (s, 1H), 7.94 – 7.93 (m, 1H), 7.83 (s, 1H), 7.78 – 7.77 (m,

1H), 7.52 – 7.51 (m, 1H), 7.31 – 7.26 (m, 4H), 7.25 (d, *J* = 6.0 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.15 – 7.11 (m, 4H), 7.03 (d, *J* = 2.2 Hz, 2H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.23 (m, 1H), 5.09 – 5.07 (m, 1H), 4.22 (d, *J* = 2.3 Hz, 1H), 3.75 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.97, 160.82, 141.36, 140.48, 137.94, 137.34, 135.93, 134.35, 132.15, 131.73, 130.83, 130.41, 129.89, 128.69, 128.63, 128.18, 127.98, 127.71, 126.81, 126.53, 126.22, 125.86, 115.69, 109.44, 72.43, 51.58, 47.61, 20.74 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{29}N_2O_3$ 521.1893; Found 521.1894.

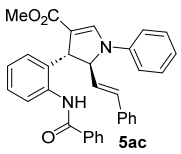
Methyl (*E*)-4-(2-pivalamidophenyl)-5-styryl-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5sa): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 46.1 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.44 (s, 1H), 7.84 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.36 – 7.30 (m, 4H), 7.25 – 7.22 (m, 2H), 7.20 – 7.11 (m, 4H), 7.05 – 7.02 (m, 2H), 6.53 (d, *J* = 16.0 Hz, 1H), 6.31 – 6.27 (m, 1H), 5.06 – 5.05 (m, 1H), 4.16 (d, *J* = 2.3 Hz, 1H), 3.71 (s, 3H), 2.34 (s, 3H), 1.38 (s, 9H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 178.22, 167.53, 141.21, 138.31, 137.99, 136.35, 134.87, 132.17, 131.88, 130.61, 128.96, 128.37, 127.69, 127.21, 126.98, 126.92, 126.65, 126.32, 115.83, 110.06, 72.53, 51.56, 47.88, 39.86, 28.06, 20.95 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{32}H_{35}N_2O_3$ 495.2624; Found 495.2629.



Methyl (*E*)-4-(2-benzamidophenyl)-1-(4-methoxyphenyl)-5-styryl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ab): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 48.9 mg, 92% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.35 (s, 1H), 8.15 – 8.14 (m, 2H), 7.81 – 7.76 (m, 1H), 7.76 (s, 1H), 7.52 – 7.46 (m, 3H), 7.32 – 7.26 (m, 4H), 7.25 – 7.17 (m, 4H), 7.07 – 7.05 (m, 2H), 6.89 – 6.87 (m, 2H), 6.48 (d, *J* = 15.8 Hz, 1H), 6.27 – 6.22 (m, 1H), 5.05 – 5.03 (m, 1H), 4.23 (d, *J* = 2.2 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.75, 166.06, 155.47, 141.82, 137.61, 135.90, 134.70, 134.66, 134.63, 134.11, 131.81, 131.72, 129.11, 128.66, 128.16, 127.80, 127.65, 126.78, 126.70, 126.26, 126.13, 117.30, 115.15, 108.84, 72.91, 55.71, 51.44, 47.76 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{31}N_2O_4$ 531.2278; Found 531.2280.



Methyl (*E*)-4-(2-benzamidophenyl)-1-phenyl-5-styryl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ac): Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow liquid, 43.8 mg, 82% yield. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.15 (dd, *J* = 8.3, 1.5 Hz, 2H), 7.87 (s, 1H), 7.83-7.79 (m, 1H), 7.56 – 7.45 (m, 3H), 7.37 – 7.26 (m, 6H), 7.25 – 7.14 (m, 4H), 7.14 – 7.09 (m, 2H), 7.06 – 6.98 (m, 1H), 6.50 (d, *J* = 15.9 Hz, 1H), 6.25 (dd, *J* = 16.0, 6.8 Hz, 1H), 5.11 (d, *J* = 6.1 Hz, 1H), 4.25 (d, *J* = 2.2 Hz, 1H), 3.75 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.67, 166.09, 140.93, 140.32, 137.41, 135.86, 134.69, 134.63, 131.77, 131.75, 129.87, 128.68, 128.66, 128.17, 127.78, 127.73, 126.84, 126.78, 126.46, 126.26, 126.17,

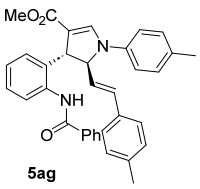


122.33, 115.54, 110.25, 72.26, 51.57, 47.73 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{33}H_{29}N_2O_3$ 501.2173; Found 501.2170.

Methyl (*E*)-4-(2-benzamidophenyl)-1-(naphthalen-1-yl)-5-styryl-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ad)： Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 39.6 mg, 72% yield, melting point 189.3-191.0 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.22 (s, 1H), 8.17 – 8.07 (m, 3H), 7.92 – 7.84 (m, 2H), 7.72 (t, *J* = 6.8 Hz, 2H), 7.63 (s, 1H), 7.62 – 7.58 (m, 1H), 7.56 – 7.49 (m, 2H), 7.48 – 7.40 (m, 4H), 7.39 – 7.35 (m, 1H), 7.33 – 7.29 (m, 1H), 7.20 – 7.11 (m, 5H), 6.40 – 6.21 (m, 2H), 5.22 (dd, *J* = 8.2, 3.1 Hz, 1H), 4.45 (d, *J* = 3.1 Hz, 1H), 3.73 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.77, 165.95, 148.61, 137.89, 137.55, 135.92, 135.15, 134.95, 134.73, 132.97, 131.71, 129.47, 129.02, 128.98, 128.67, 128.55, 128.09, 127.76, 127.68, 126.96, 126.93, 126.88, 126.76, 126.68, 126.55, 126.16, 125.60, 122.69, 121.51, 107.96, 76.99, 51.40, 47.82 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{37}H_{31}N_2O_3$ 551.2329; Found 551.2326.

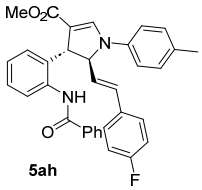
Methyl (*E*)-4-(2-benzamidophenyl)-1-benzyl-5-styryl-4,5-dihydro-1*H*-pyrrole-3-carboxylat (5ae)： Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 42.0 mg, 82% yield, melting point 170.9-172.3 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.55 – 7.36 (m, 6H), 7.35 – 7.27 (m, 6H), 7.26 – 7.21 (m, 3H), 7.08 – 7.01 (m, 2H), 6.41 (d, *J* = 15.7 Hz, 1H), 6.17 (dd, *J* = 15.8, 8.7 Hz, 1H), 4.48 – 4.37 (m, 2H), 4.28 (d, *J* = 14.5 Hz, 1H), 4.21 (d, *J* = 3.5 Hz, 1H), 3.66 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.69, 165.82, 149.20, 135.92, 135.87, 134.95, 134.81, 133.60, 133.55, 131.61, 129.16, 128.74, 128.71, 128.61, 128.46, 128.32, 128.00, 127.77, 127.26, 126.85, 126.65, 126.25, 126.05, 125.78, 73.26, 60.54, 51.85, 51.05 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{34}H_{31}N_2O_3$ 515.2329; Found 515.2333.

Methyl (*E*)-4-(2-benzamidophenyl)-5-(4-methoxystyryl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5af)： Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 45.0 mg, 82% yield, melting point 146.0-147.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.14 (d, *J* = 6.9 Hz, 2H), 7.83 – 7.77 (m, 2H), 7.54 – 7.45 (m, 3H), 7.33 – 7.28 (m, 1H), 7.24 – 7.19 (m, 3H), 7.17 – 7.11 (m, 3H), 7.05 – 6.97 (m, 2H), 6.82 – 6.75 (m, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.08 (dd, *J* = 15.9, 7.0 Hz, 1H), 5.09 – 5.01 (m, 1H), 4.20 (d, *J* = 2.1 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.78, 166.05, 159.63, 141.25, 138.04, 137.61, 134.71, 132.00, 131.72, 131.21, 130.36, 128.69, 128.67, 128.03, 127.81, 127.62, 126.77, 126.27, 126.08, 124.42, 115.69, 114.06, 110.43, 109.47, 72.60, 55.43, 51.49, 47.82, 20.73 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{35}H_{33}N_2O_4$ 545.2435; Found 545.2438.

Methyl (*E*)-4-(2-benzamidophenyl)-5-(4-methylstyryl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ag)： 

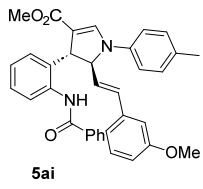
5ag

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 41.2 mg, 78% yield, melting point 148.6-149.1 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.33 (s, 1H), 8.14 (d, *J* = 7.9 Hz, 2H), 7.86 – 7.75 (m, 2H), 7.55 – 7.43 (m, 3H), 7.33 – 7.28 (m, 1H), 7.24 – 7.20 (m, 1H), 7.19 – 7.10 (m, 5H), 7.05 (d, *J* = 7.9 Hz, 2H), 7.03 – 6.99 (m, 2H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.17 (dd, *J* = 15.9, 6.9 Hz, 1H), 5.10 – 5.02 (m, 1H), 4.21 (d, *J* = 2.1 Hz, 1H), 3.73 (s, 3H), 2.31 (s, 3H), 2.28 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.77, 166.07, 141.26, 138.08, 138.02, 137.58, 134.70, 133.14, 132.03, 131.72, 131.64, 130.36, 129.94, 129.35, 128.67, 127.81, 127.64, 126.78, 126.70, 126.27, 126.09, 125.58, 115.70, 109.51, 72.54, 51.50, 47.74, 21.30, 20.73 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{35}H_{33}N_2O_3$ 529.2486; Found 529.2488;

Methyl (*E*)-4-(2-benzamidophenyl)-5-(4-fluorostyryl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ah)： 

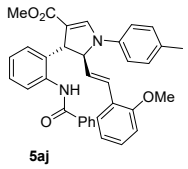
5ah

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 25.5 mg, 48% yield, melting point 143.0-144.8 °C. ^{1}H NMR (600 MHz, $CDCl_3$) δ 10.30 (s, 1H), 8.14 (d, *J* = 7.2 Hz, 2H), 7.82 (s, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.54 – 7.45 (m, 3H), 7.32 – 7.28 (m, 1H), 7.25 – 7.20 (m, 3H), 7.17 – 7.11 (m, 3H), 7.03 – 6.97 (m, 2H), 6.96 – 6.88 (m, 2H), 6.43 (d, *J* = 15.9 Hz, 1H), 6.13 (dd, *J* = 15.9, 6.9 Hz, 1H), 5.07 – 5.04 (m, 1H), 4.20 (d, *J* = 2.2 Hz, 1H), 3.73 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.73, 166.09, 162.63 (d, *J* = 247.8 Hz), 141.24, 137.95, 137.54, 134.69, 134.67, 132.11, 132.08, 131.79, 130.58, 130.42, 128.70, 128.39 (d, *J* = 8.0 Hz), 127.81, 127.72, 126.87, 126.36 (d, *J* = 3.0 Hz), 126.25, 126.21, 115.58 (d, *J* = 22.6 Hz), 115.63, 109.51, 72.31, 51.53, 47.70, 20.74 ppm. ^{19}F NMR (565 MHz, $CDCl_3$) δ -113.67 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{34}H_{30}FN_2O_3$ 533.2235; Found 533.2230;

Methyl (*E*)-4-(2-benzamidophenyl)-5-(3-methoxystyryl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ai)： 

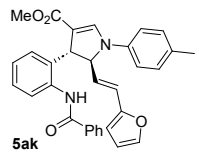
5ai

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 44.9 mg, 82% yield, melting point 133.6-134.5 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.19 – 8.07 (m, 2H), 7.85 – 7.76 (m, 2H), 7.54 – 7.45 (m, 3H), 7.33 – 7.28 (m, 1H), 7.23 – 7.19 (m, 1H), 7.18 – 7.11 (m, 4H), 7.03 – 6.97 (m, 2H), 6.89 – 6.85 (m, 1H), 6.83 – 6.78 (m, 1H), 6.78 – 6.71 (m, 1H), 6.44 (d, *J* = 15.9 Hz, 1H), 6.22 (dd, *J* = 15.9, 6.8 Hz, 1H), 5.10 – 5.02 (m, 1H), 4.21 (d, *J* = 2.2 Hz, 1H), 3.75 (s, 3H), 3.73 (s, 3H), 2.31 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.75, 166.10, 159.87, 141.25, 137.99, 137.53, 137.35, 134.70, 134.68, 132.09, 131.76, 131.64, 130.40, 129.66, 128.69, 127.82, 127.69, 126.89, 126.82, 126.26, 126.14, 119.48, 115.67, 114.15, 111.74, 109.56, 72.38, 55.36, 51.52, 47.68, 20.74 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{35}H_{33}N_2O_4$ 545.2435; Found 545.2433.

Methyl (*E*)-4-(2-benzamidophenyl)-5-(2-methoxystyryl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5aj)： 

5aj

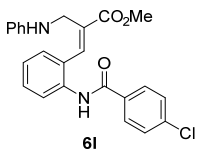
Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 43.6 mg, 80% yield, melting point 150.6-152.3 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.34 (s, 1H), 8.13 (d, *J* = 7.0 Hz, 2H), 7.83 – 7.78 (m, 2H), 7.52 – 7.43 (m, 3H), 7.32 – 7.28 (m, 2H), 7.24 – 7.21 (m, 1H), 7.19 – 7.10 (m, 4H), 7.05 – 7.01 (m, 2H), 6.86 – 6.77 (m, 3H), 6.28 (dd, *J* = 16.1, 7.4 Hz, 1H), 5.08 (dd, *J* = 7.1, 2.8 Hz, 1H), 4.23 (d, *J* = 2.1 Hz, 1H), 3.74 (s, 3H), 3.73 (s, 3H), 2.30 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.80, 166.01, 157.06, 141.37, 138.12, 137.58, 134.79, 134.72, 131.96, 131.68, 130.32, 129.19, 128.64, 127.82, 127.59, 127.31, 127.18, 126.69, 126.37, 126.34, 125.94, 124.88, 120.58, 115.83, 111.06, 109.83, 73.20, 55.50, 51.47, 47.06, 20.74 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{35}H_{33}N_2O_4$ 545.2435; Found 545.2438.

Methyl (*E*)-4-(2-benzamidophenyl)-5-(2-(furan-2-yl)vinyl)-1-(p-tolyl)-4,5-dihydro-1*H*-pyrrole-3-carboxylate (5ak)： 

5ak

Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 37.3 mg, 74% yield, melting point 179.0-180.6 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.32 (s, 1H), 8.15 (d, *J* = 6.8 Hz, 2H), 7.84 – 7.72 (m, 2H), 7.56 – 7.46 (m, 3H), 7.33 – 7.27 (m, 2H), 7.22 – 7.18 (m, 1H), 7.17 – 7.11 (m, 3H), 7.02 – 6.94 (m, 2H), 6.32 – 6.23 (m, 2H), 6.20 – 6.11 (m, 2H), 5.03 (dd, *J* = 6.6, 2.2 Hz, 1H), 4.21 (d, *J* = 2.3 Hz, 1H), 3.73 (s, 3H), 2.32 (s, 3H) ppm. ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.71, 166.04, 151.64, 142.40, 141.09, 137.91, 137.48, 134.68, 132.04, 131.74, 130.41, 128.68, 127.83, 127.67, 126.79, 126.18, 126.14, 125.09, 124.96, 119.77, 115.58, 111.50, 109.62, 109.25, 71.93, 51.51, 47.72, 20.73 ppm. HRMS (ESI) m/z: $[M+H]^+$Calcd for $C_{32}H_{29}N_2O_4$ 505.2122; Found 505.2127;

Methyl (E)-3-(2-(4-chlorobenzamido)phenyl)-2-((phenylamino)methyl)acrylate (6l):



6l

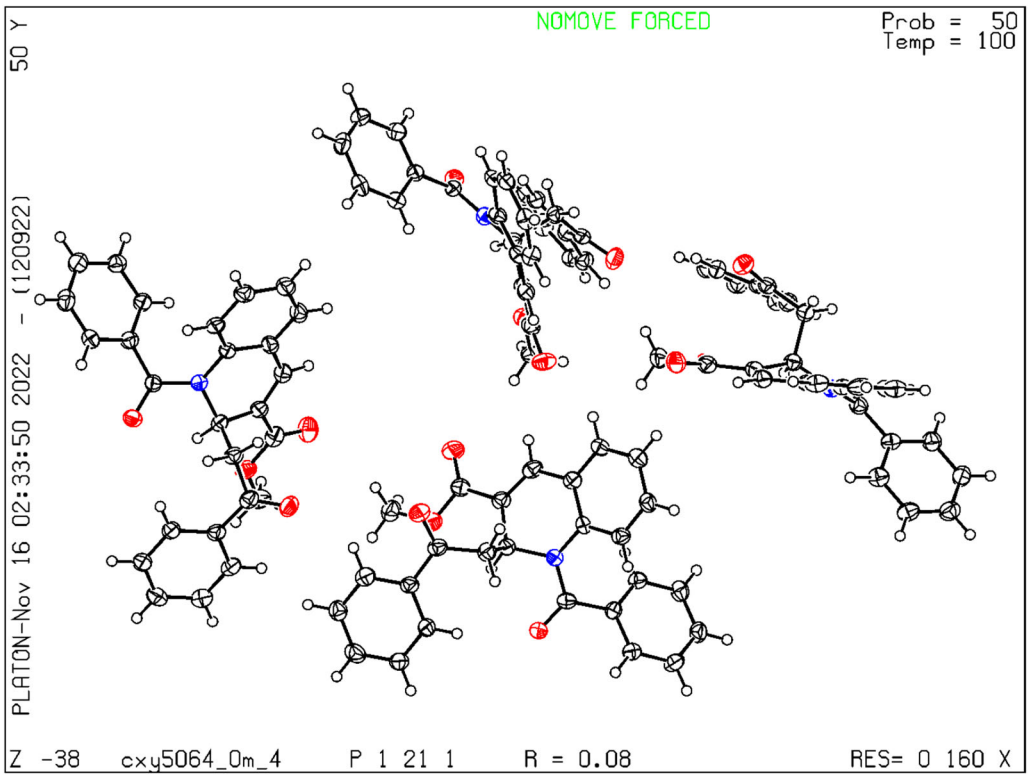
Purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) and obtained as yellow solid, 40.0 mg, 95% yield, melting point 155.4-156.6 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.2 Hz, 1H), 7.90 (s, 1H), 7.79 (s, 1H), 7.68 – 7.59 (m, 2H), 7.56 – 7.44 (m, 2H), 7.44 – 7.36 (m, 2H), 7.26 – 7.24 (m, 1H), 7.19 – 7.02 (m, 2H), 6.73 – 6.64 (m, 1H), 6.47 – 6.33 (m, 2H), 4.18 (s, 1H), 4.06 (s, 2H), 3.84 (s, 3H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.59, 166.19, 146.52, 138.83, 135.91, 134.73, 132.68, 132.39, 132.30, 130.38, 129.46, 129.17, 127.76, 127.58, 125.59, 124.31, 115.87, 110.64, 52.84, 41.57 ppm. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{22}ClN_2O_3$ 421.1313; Found 421.1315.

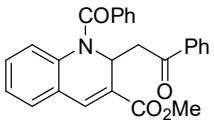
X-ray crystallographic data for 3aa, 5aa and 6l

Crystal Structure and data for compound **3aa**

Table 1 Crystal data and structure refinement for cxy5064_0m _4.

Identification code	cxy5064_0m _4
Empirical formula	$C_{26}H_{21}NO_4$
Formula weight	411.44
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	6.9055(4)
b/Å	21.4299(11)
c/Å	27.6189(15)
α/°	90
β/°	92.031(2)
γ/°	90
Volume/Å3	4084.6(4)
Z	8
ρcalcg/cm3	1.338
μ/mm-1	0.466
F(000)	1728.0
Crystal size/mm3	0.3 × 0.22 × 0.18
Radiation	CuKα (λ = 1.34139)
2Θ range for data collection/°	8.418 to 144.37
Index ranges	? ≤ h ≤ ?, ? ≤ k ≤ ?, ? ≤ l ≤ ?
Reflections collected	15953
Independent reflections	15953 [R_{int} = 0.0498, R_{sigma} = 0.0640]
Data/restraints/parameters	5978/22/442
Goodness-of-fit on F2	1.043
Final R indexes [I>=2σ (I)]	R1 = 0.0753, wR2 = 0.2086
Final R indexes [all data]	R1 = 0.0899, wR2 = 0.2168
Largest diff. peak/hole / e Å-3	0.47/-0.35
Flack parameter	0.01 (13)


NOMOVE FORCED
Prob = 50
Temp = 100
50 Y
PLATON-Nov 16 02:33:50 2022 - (120922)
Z -38 cxy5064_0m_4 P 1 21 1 R = 0.08 RES= 0 160 X

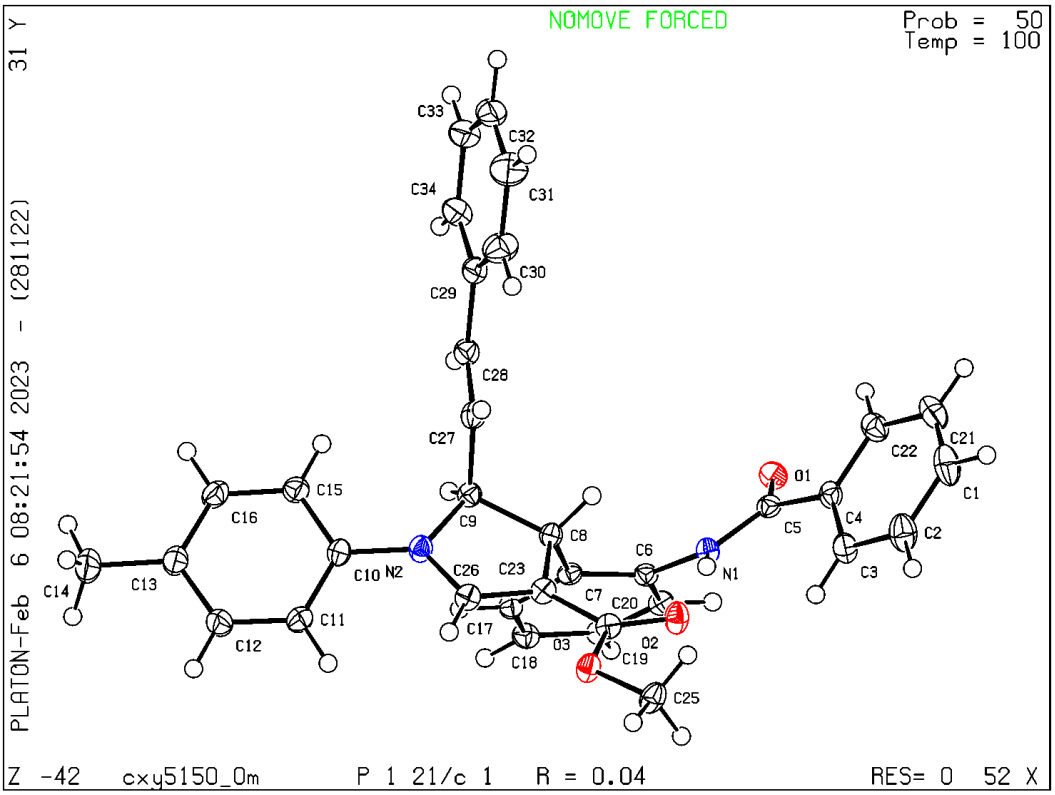

COPh
N
Ph
O
CO2Me

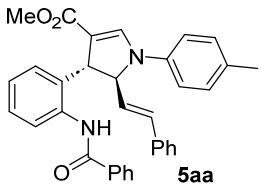
3aa

Crystal Structure and data for compound **5aa**

Table 2 Crystal data and structure refinement for cxy5150_0m.

Identification code	cxy5150_0m
Empirical formula	C34H30N2O3
Formula weight	514.60
Temperature/K	100.0(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	11.8470(7)
b/Å	18.1061(10)
c/Å	13.0266(7)
α/°	90
β/°	95.964(2)
γ/°	90
Volume/Å3	2779.1(3)
Z	4
ρcalcg/cm3	1.230
μ/mm-1	0.397
F(000)	1088.0
Crystal size/mm3	0.31 × 0.26 × 0.18
Radiation	GaKα (λ = 1.34138)
2Θ range for data collection/°	7.3 to 113.948
Index ranges	-14 ≤ h ≤ 14, -21 ≤ k ≤ 22, -16 ≤ l ≤ 16
Reflections collected	33411
Independent reflections	5641 [Rint = 0.0573, Rsigma = 0.0378]
Data/restraints/parameters	5641/0/355
Goodness-of-fit on F2	1.040
Final R indexes [I>=2σ (I)]	R1 = 0.0368, wR2 = 0.0953
Final R indexes [all data]	R1 = 0.0400, wR2 = 0.0969
Largest diff. peak/hole / e Å-3	0.26/-0.19


NOMOVE FORCED
Prob = 50
Temp = 100
PLATON-Feb 6 08:21:54 2023 - (281122)
31 Y
C33
C32
C34
C31
C30
C29
C28
C27
C15
C16
C9
C8
C6
O1
C5
C22
C21
C1
C4
C2
C3
C14
C13
C10
N2
C26
C23
C7
C20
N1
C11
C12
C17
O3
O2
C18
C19
C25
Z -42
cxy5150_0m
P 1 21/c 1
R = 0.04
RES= 0 52 X

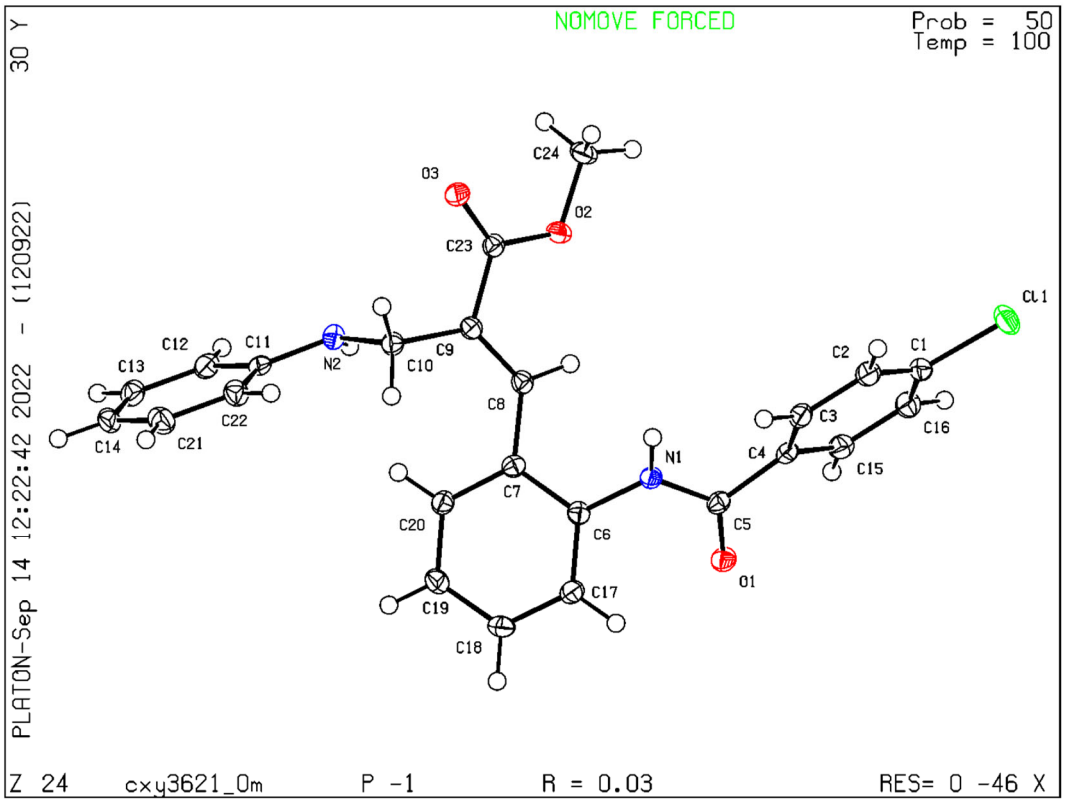

MeO2C
N
NH
Ph
O
Ph

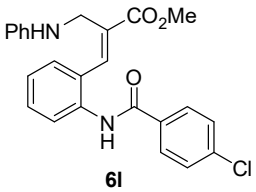
5aa

Crystal Structure and data for compound **6l**

Table 3 Crystal data and structure refinement for cxy3621_0m.

Identification code	cxy3621_0m
Empirical formula	C24H21N2O3Cl
Formula weight	420.88
Temperature/K	100.0(2)
Crystal system	triclinic
Space group	P-1
a/Å	9.6896(5)
b/Å	10.1998(5)
c/Å	10.8323(6)
α/°	89.990(2)
β/°	71.675(2)
γ/°	84.875(2)
Volume/Å3	1011.78(9)
Z	2
ρcalcg/cm3	1.381
μ/mm-1	1.911
F(000)	440.0
Crystal size/mm3	0.28 × 0.22 × 0.15
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.602 to 144.272
Index ranges	-11 ≤ h ≤ 11, -12 ≤ k ≤ 12, -13 ≤ l ≤ 13
Reflections collected	22984
Independent reflections	3990 [Rint = 0.0272, Rsigma = 0.0177]
Data/restraints/parameters	3990/1/275
Goodness-of-fit on F2	1.042
Final R indexes [I>=2σ (I)]	R1 = 0.0291, wR2 = 0.0740
Final R indexes [all data]	R1 = 0.0295, wR2 = 0.0743
Largest diff. peak/hole / e Å-3	0.28/-0.26


NOMOVE FORCED
Prob = 50
Temp = 100
30 Y
PLATON-Sep 14 12:22:42 2022 - (120922)
C24
O3
O2
C23
Cl1
C12
C11
C13
N2
C10
C9
C2
C1
C8
C3
C16
C14
C21
C22
N1
C4
C15
C7
C20
C6
C5
O1
C19
C17
C18
Z 24
cxy3621_0m
P -1
R = 0.03
RES= 0 -46 X


PhHN
CO2Me
O
N
H
Cl

6l

Reference

1. Cai, W.; Zhou, Y.; He, Y.; Chen, K.; Yu, C.; Huang, Y. Designing and Accurately Developing a [6+2] Dipolar Cycloaddition for the Synthesis of Benzodiazocines. *Org. Lett.* **2021**, *23*, 5430−5434.

2. Wang, T.; Chen, X; Li, P. One-pot Divergent Synthesis of Benzoxazines and Dihydroquinolines from Morita-Baylis-Hillm an Alcohols. *Eur. J. Org. Chem*. **2022.** e202200767(5 of 5).

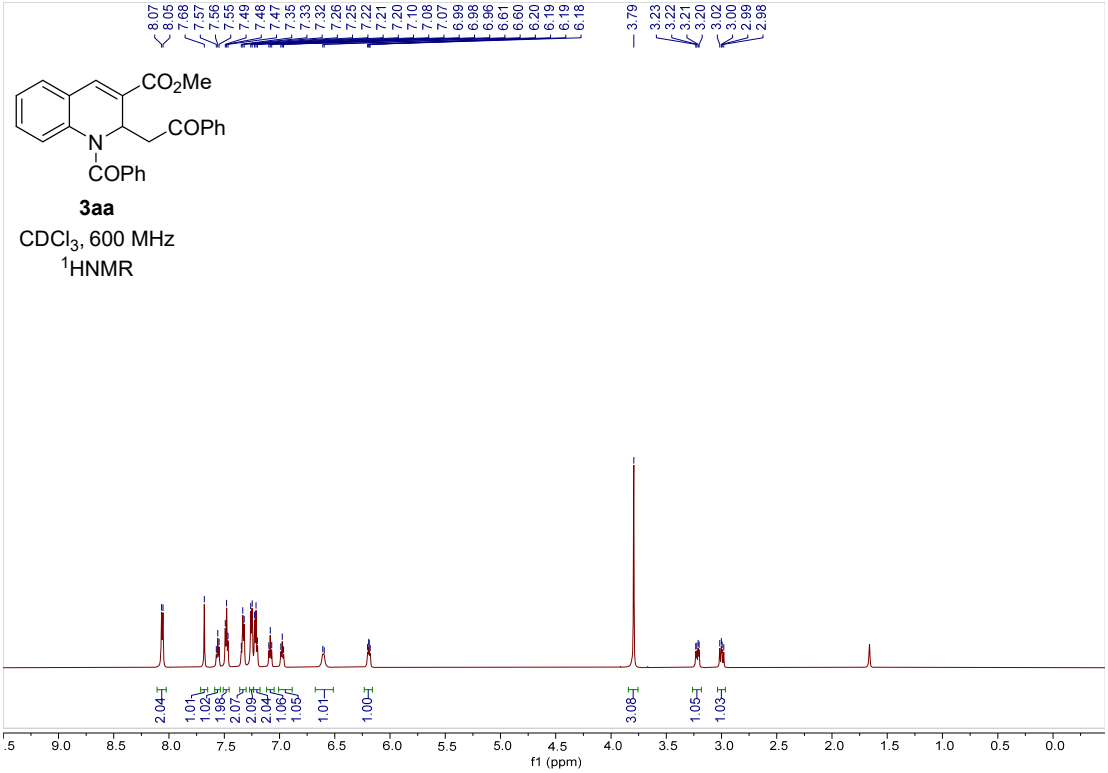
3. Li, Q.; Jia, Z.; Chen, L.; Zhnag, X.; Leng, H.; Zeng, R.; Liu, Y.; Zou, W.; Li, J. Construction of a Benzo[b]azepine Skeleton through Decarboxylative Ylide [6+1] Annulations with Modified Vinyl Benzoxazinanones. *Org. Lett*. **2021**, *23*, 814−818.

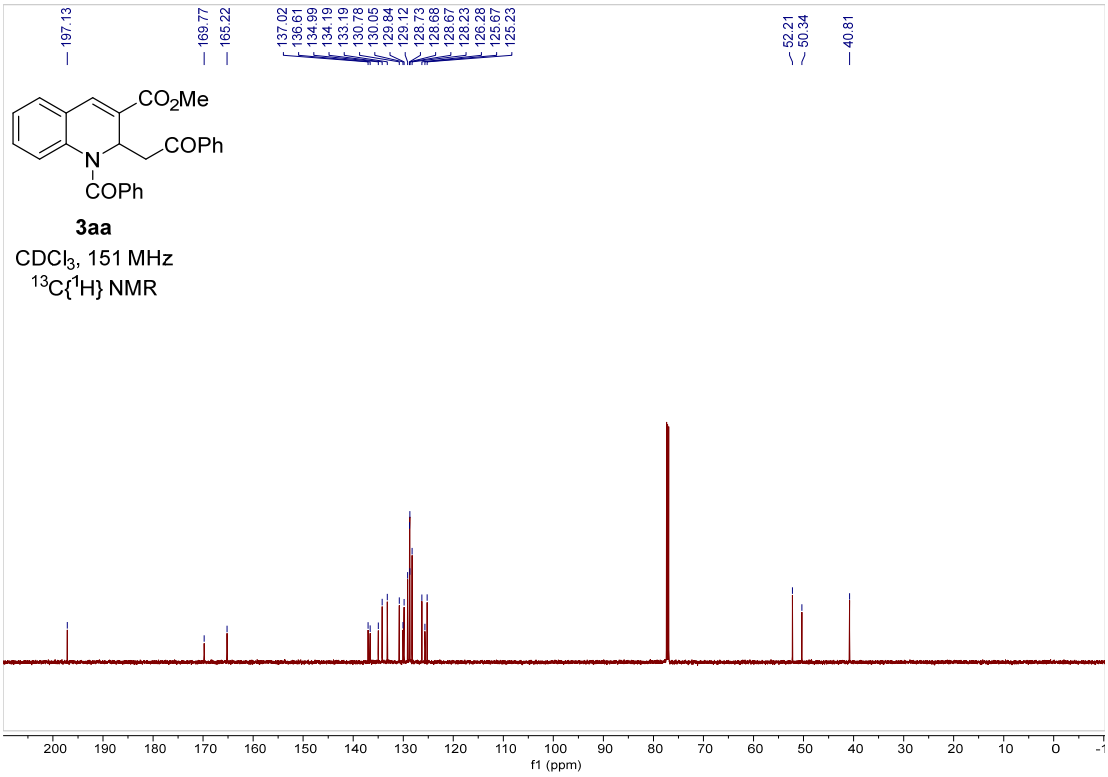
4. Yu, W.; Tung, C.; Xu, Z. Synthesis of Benzofurans from Sulfur Ylides andortho-Hydroxy-Functionalized Alkynes. *Adv. Synth.Catal*. **2022**, 364−374.

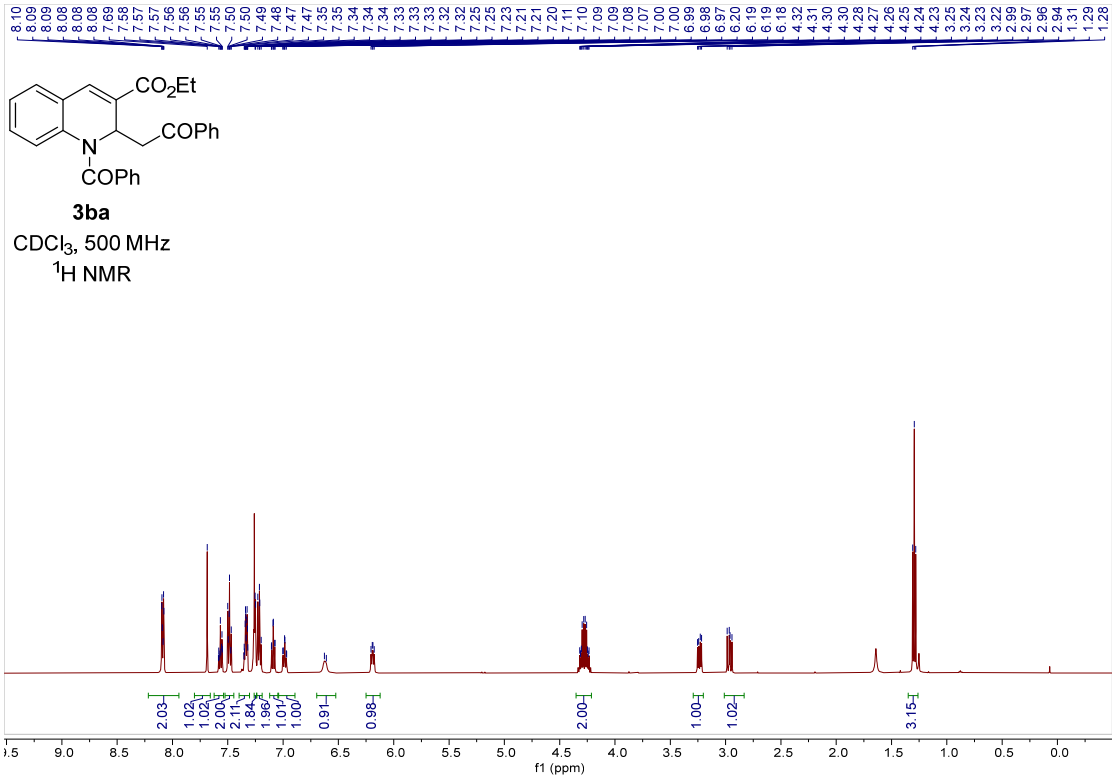
5. Yu, S.; Xiong, M.; Xie, X.; Liu, Y. Insertion of Nitriles into Zirconocene 1-aza-1,3-diene Complexes: Chemoselective Synthesis of N–H and N-Substituted Pyrroles. *Angew. Chem. Int. Ed.* **2014**, *53*, 11596-11599.

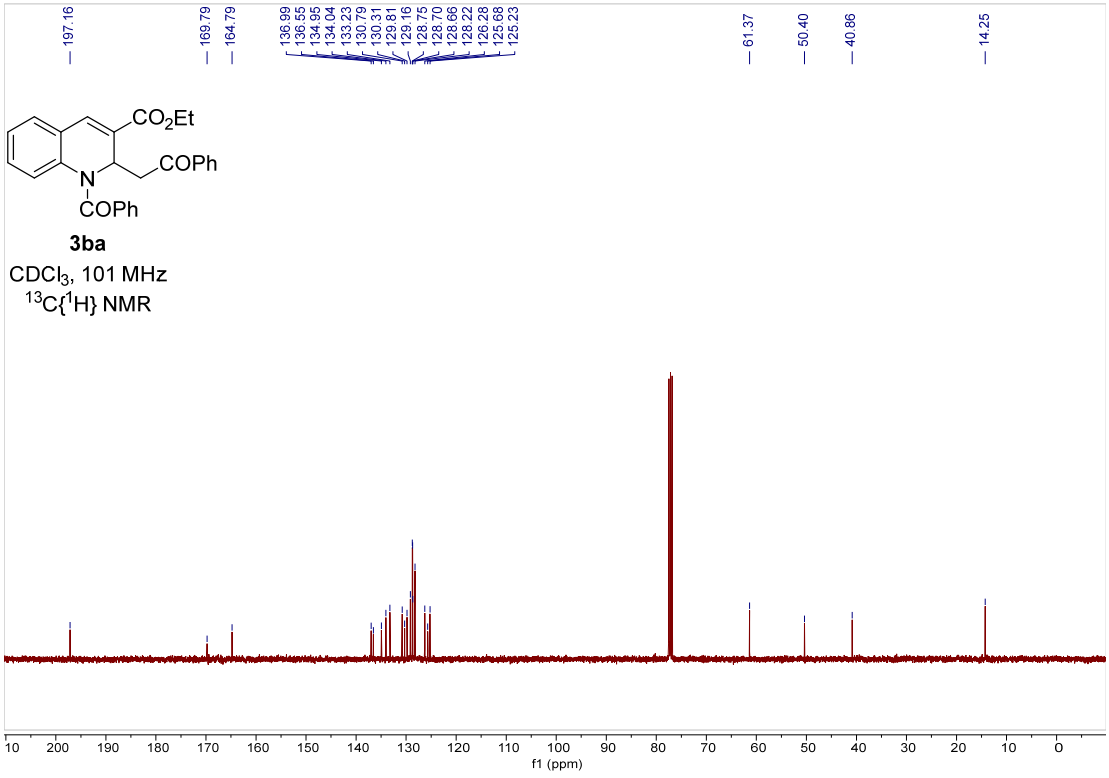
6. Chu, J. C. K.; Dalton, D. M.; Rovis T. Zn-Catalyzed Enantio- and Diastereoselective Formal [4 + 2] Cycloaddition Involving Two Electron-Deficient Partners: Asymmetric Synthesis of Piperidines from 1-Azadienes and Nitro-Alkenes. *J. Am. Chem. Soc.* **2015**, *137*, 4445-4452.

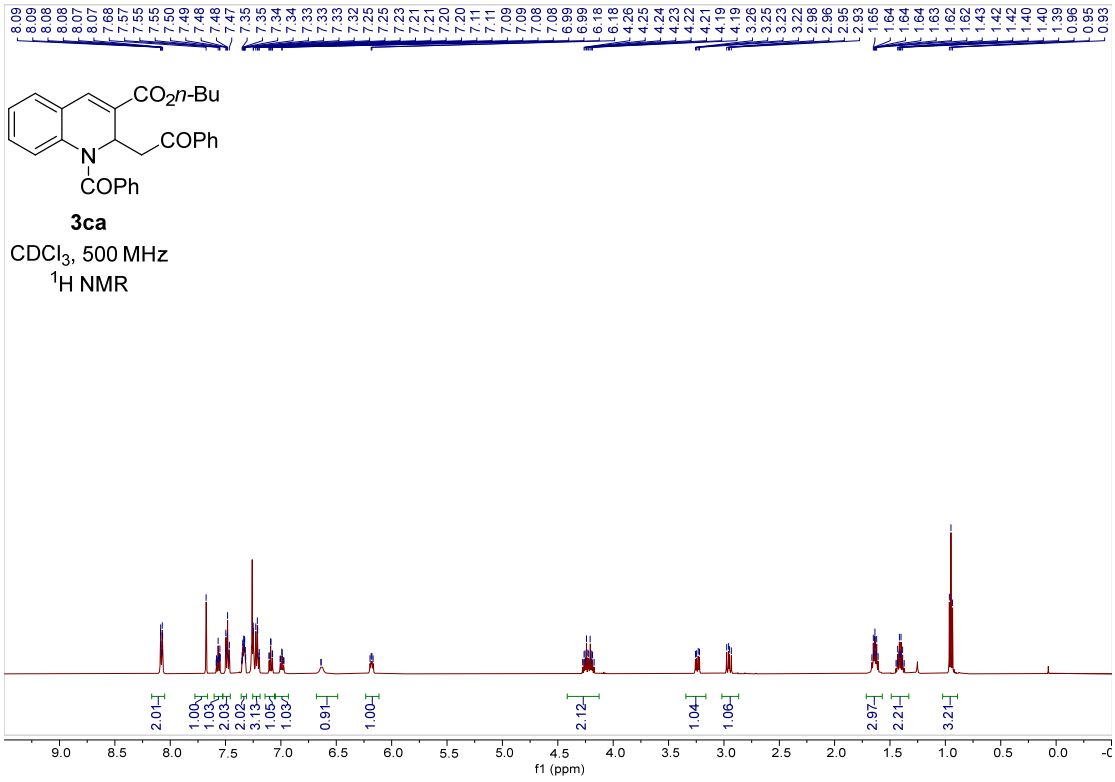
NMR spectra of compounds 3

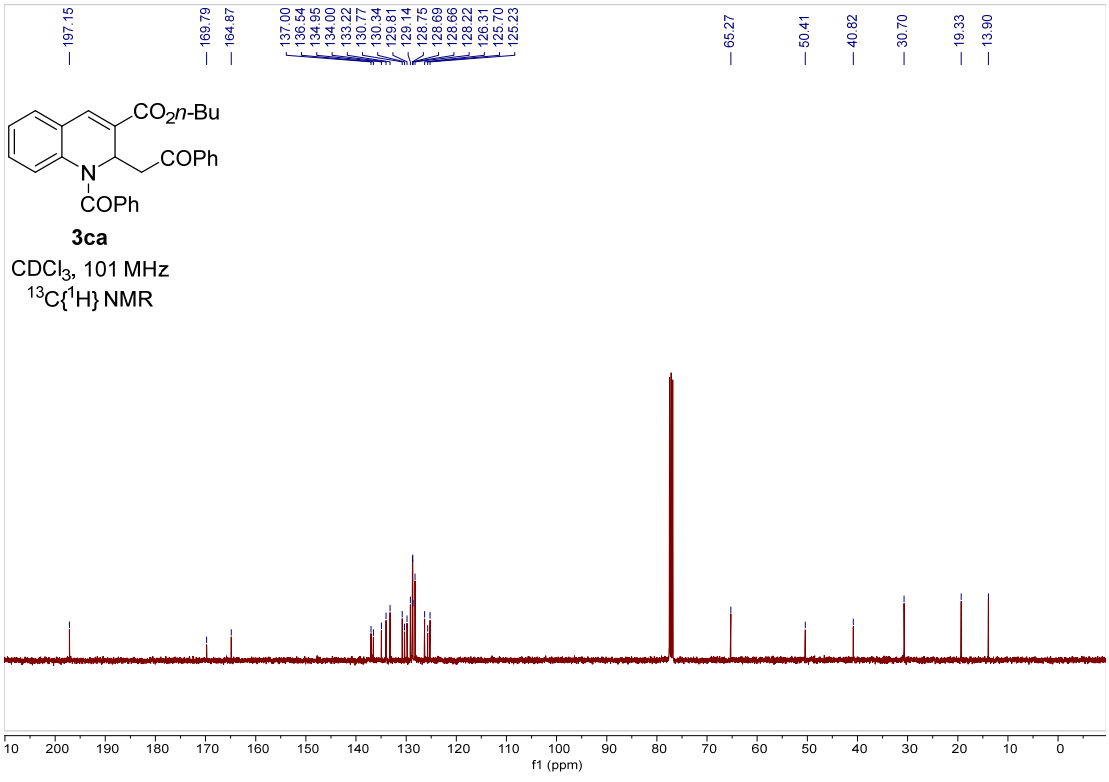


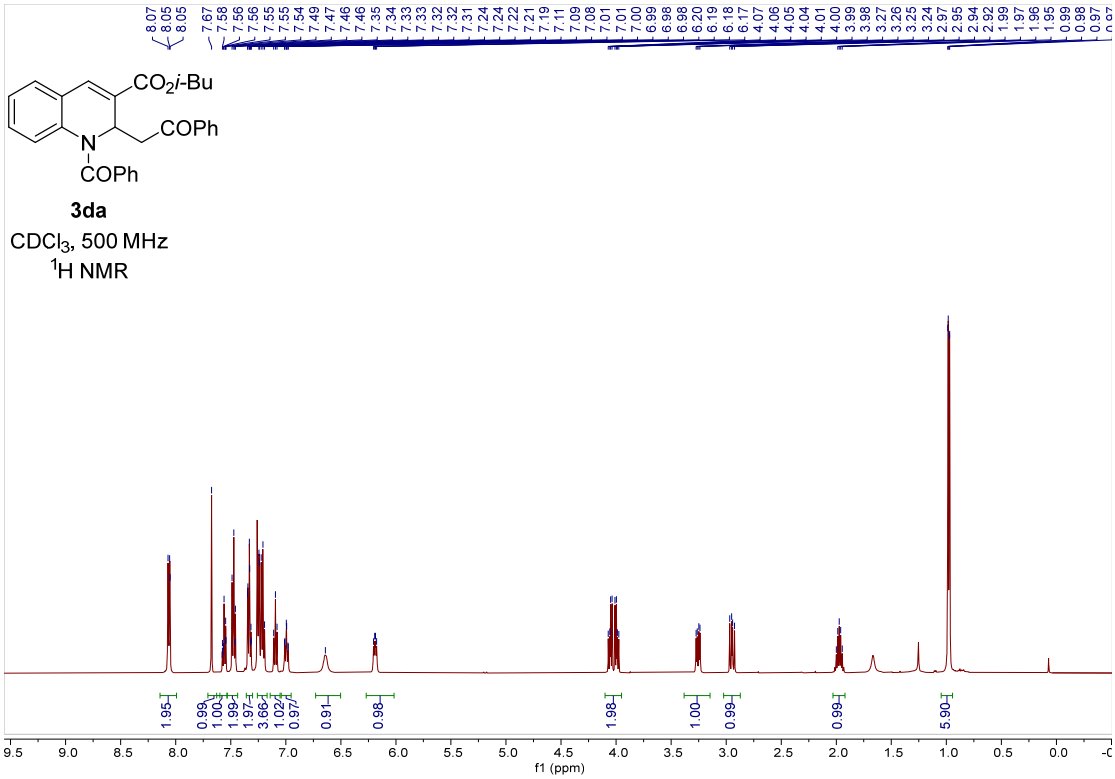


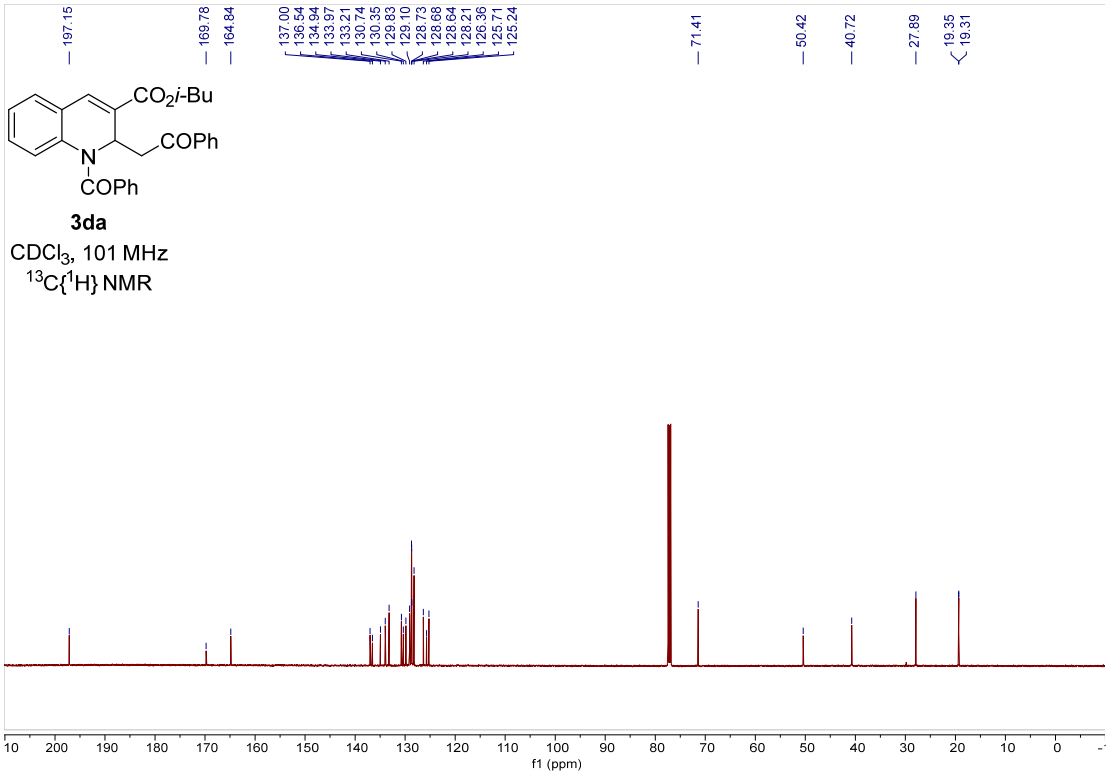

CO2Et
COPh
N
COPh
3ba
CDCl3, 500 MHz
1H NMR
f1 (ppm)

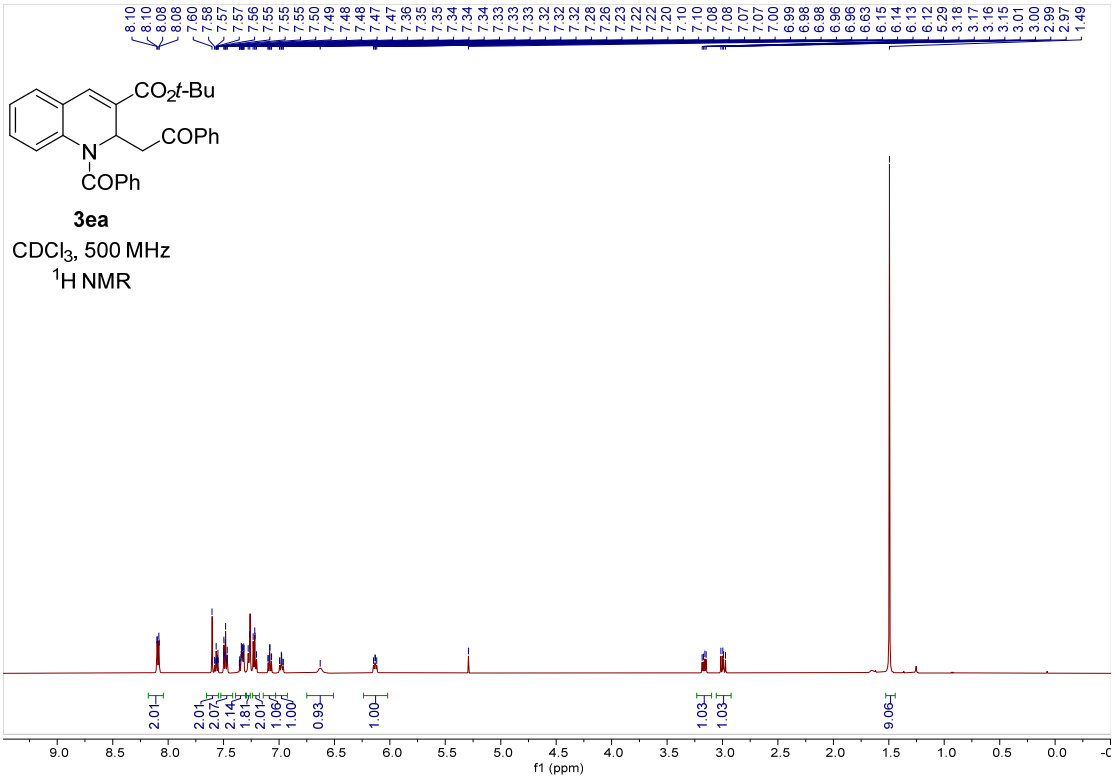

CO2Et
COPh
N
COPh
3ba
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

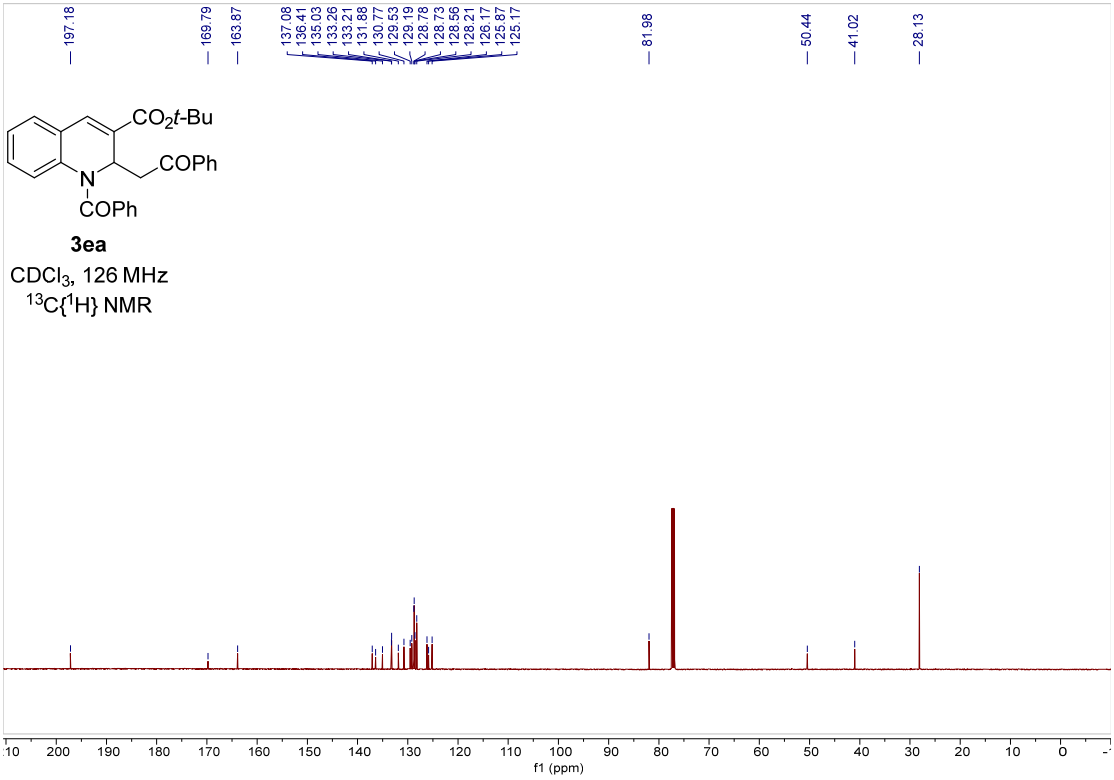

CO2n-Bu
COPh
N
COPh
3ca
CDCl3, 500 MHz
1H NMR
f1 (ppm)

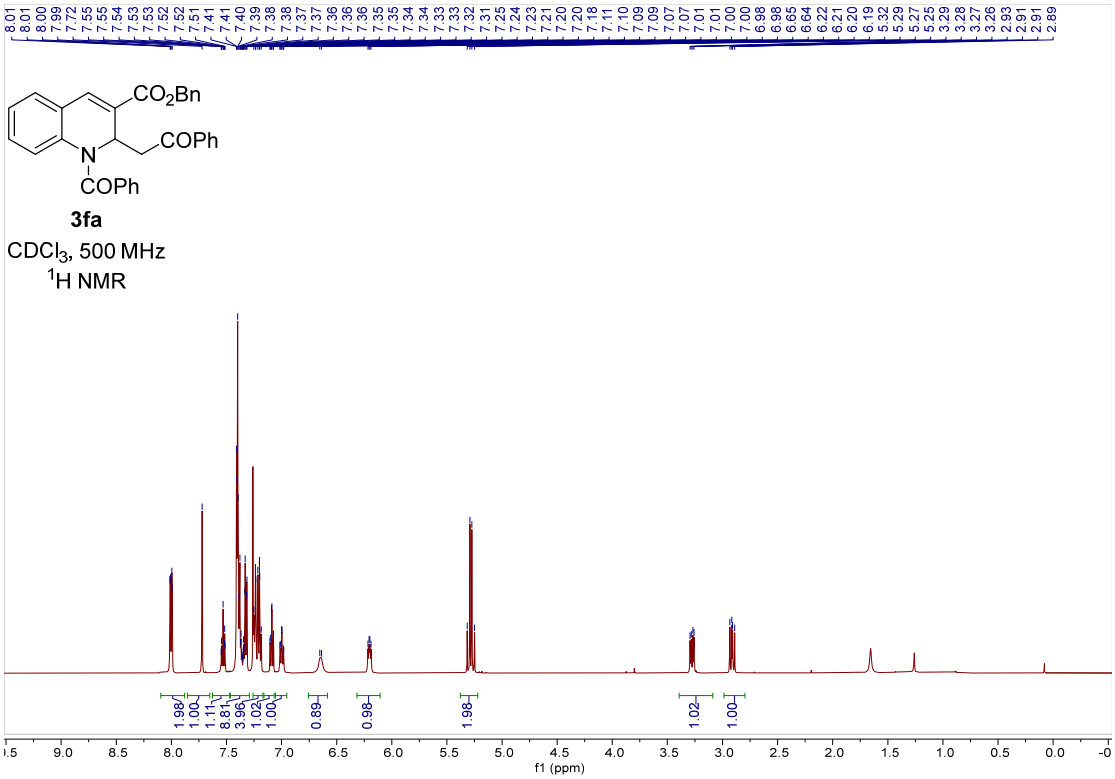

CO2n-Bu
COPh
N
COPh
3ca
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

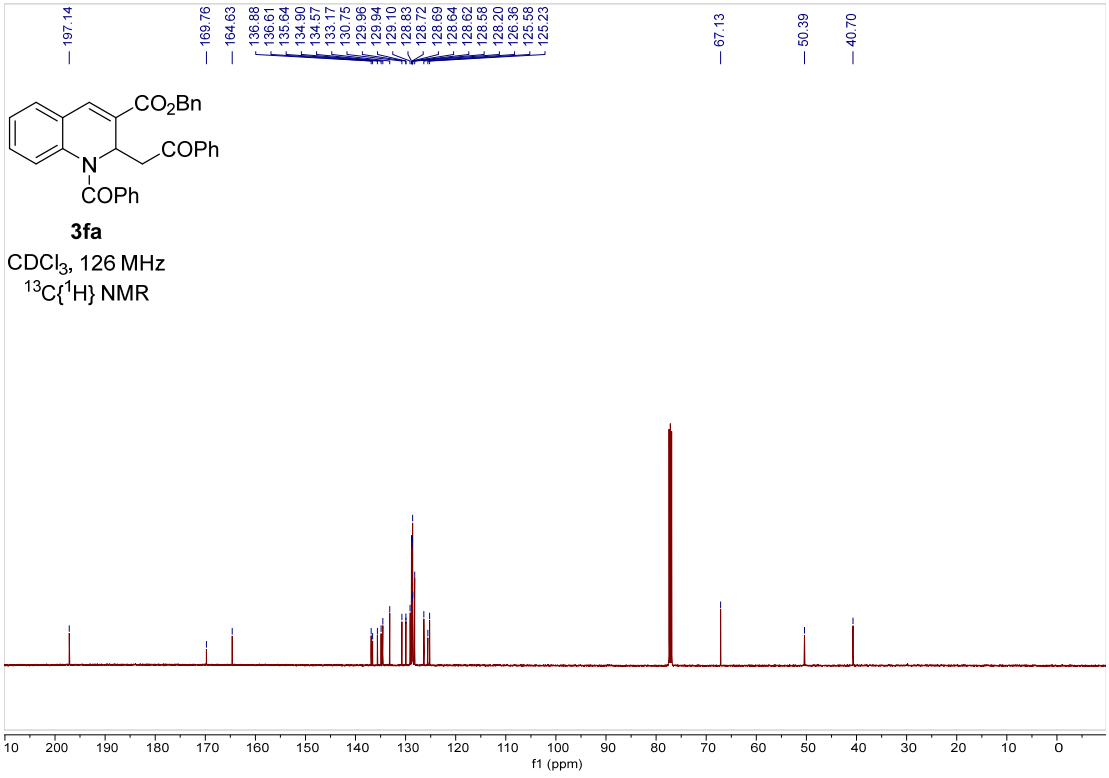

CO2i-Bu
COPh
N
COPh
3da
CDCl3, 500 MHz
1H NMR
f1 (ppm)

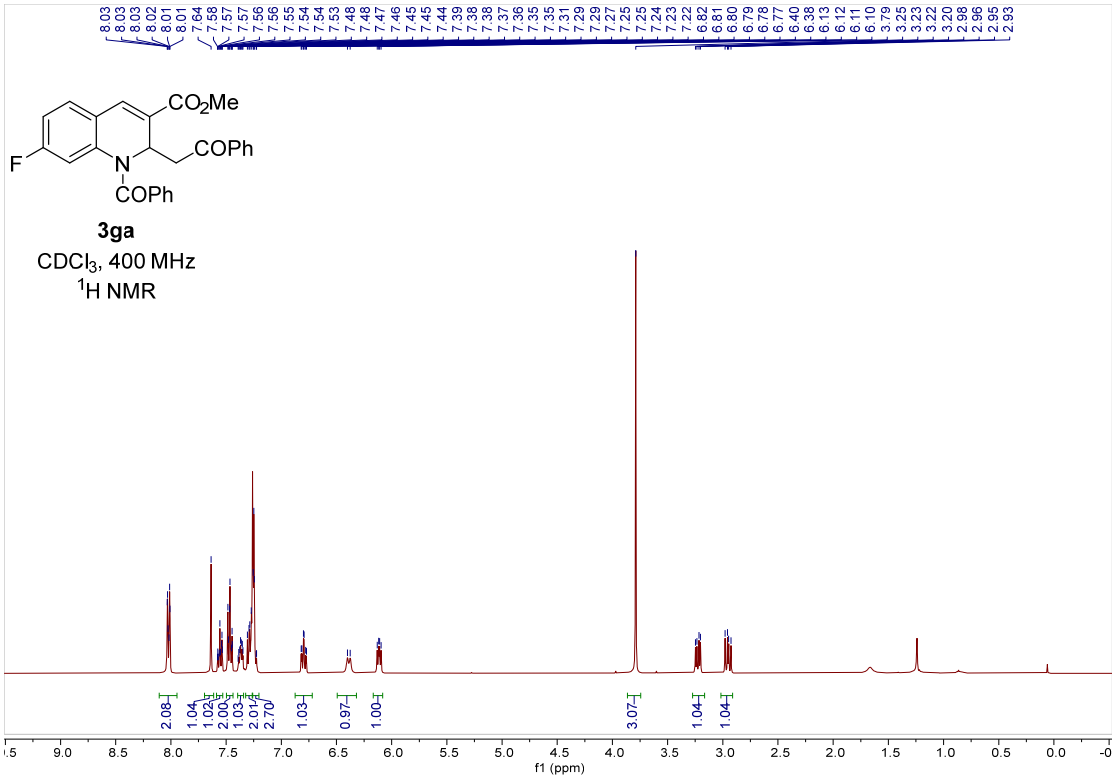

CO2i-Bu
COPh
N
COPh
3da
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

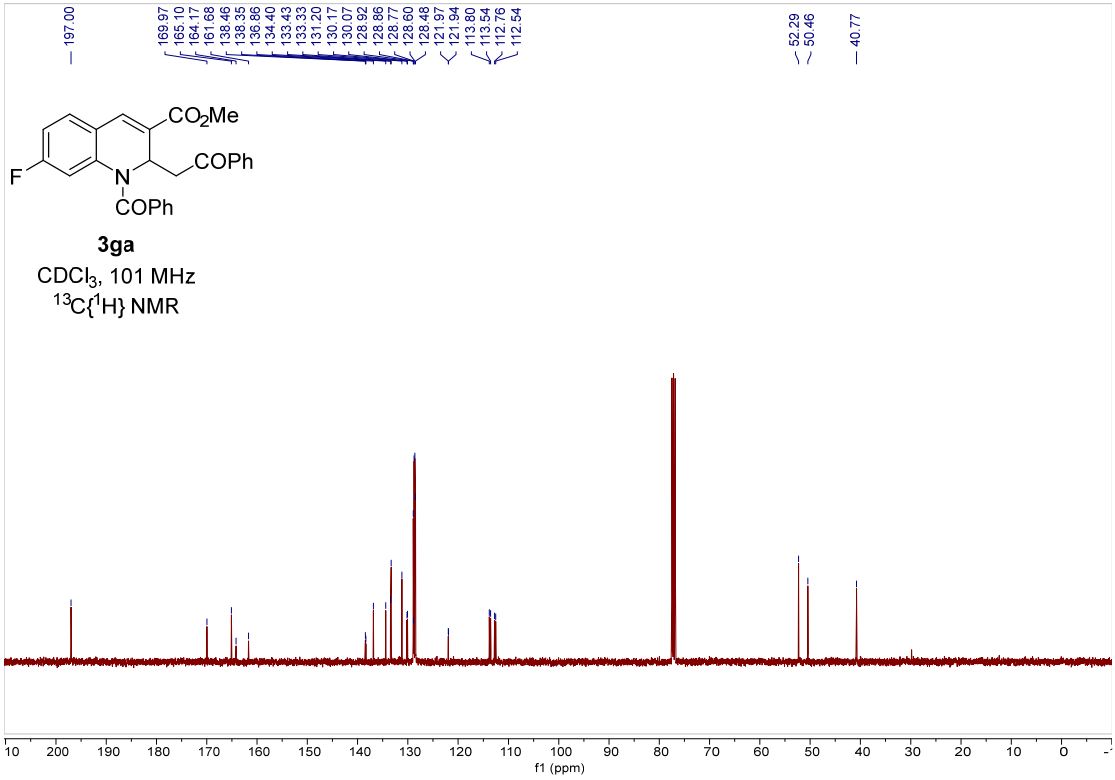

CO2t-Bu
COPh
N
COPh
3ea
CDCl3, 500 MHz
1H NMR
f1 (ppm)

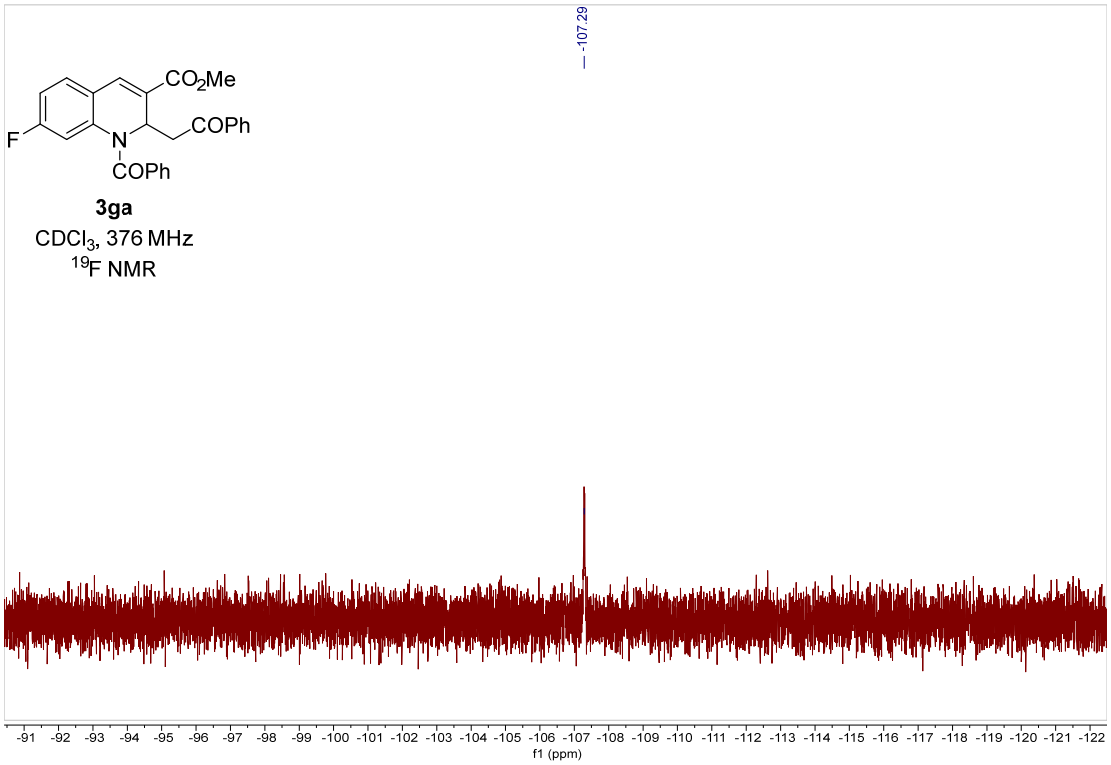

CO2t-Bu
COPh
N
COPh
3ea
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)


CO2Bn
COPh
N
COPh
3fa
CDCl3, 500 MHz
1H NMR
f1 (ppm)


CO2Bn
COPh
N
COPh
3fa
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)


8.03 8.03 8.03 8.02 8.01 8.01 7.64 7.58 7.57 7.57 7.56 7.56 7.55 7.54 7.54 7.53 7.48 7.48 7.47 7.46 7.45 7.45 7.44 7.39 7.38 7.38 7.37 7.36 7.35 7.35 7.31 7.29 7.29 7.27 7.25 7.25 7.24 7.23 7.22 6.82 6.81 6.80 6.79 6.78 6.77 6.40 6.38 6.13 6.12 6.11 6.10 3.79 3.25 3.23 3.22 3.20 2.98 2.96 2.95 2.93
CO2Me
COPh
F
N
COPh
3ga
CDCl3, 400 MHz
1H NMR
2.08 1.04 1.02 2.00 1.03 2.01 2.70 1.03 0.97 1.00 3.07 1.04 1.04
f1 (ppm)

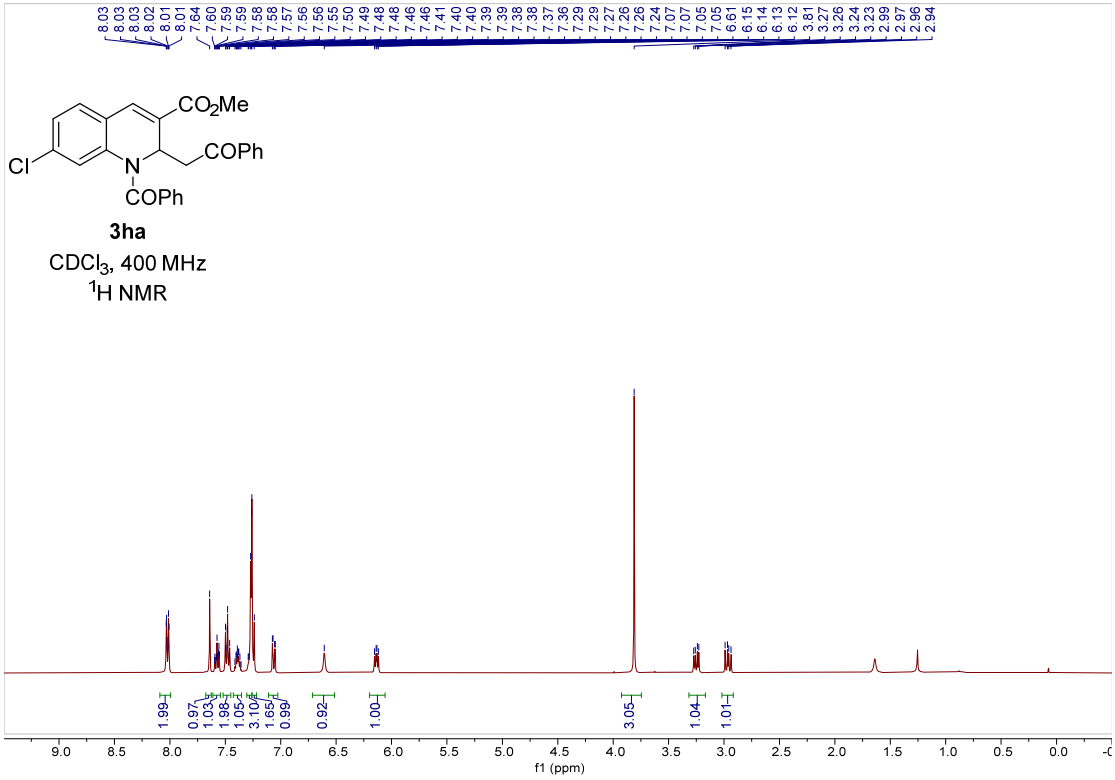

197.00
169.97 165.10 164.17 161.68 138.46 138.35 136.86 134.40 133.43 133.33 131.20 130.17 130.07 128.92 128.86 128.77 128.60 128.48 121.97 121.94 113.80 113.54 112.76 112.54
52.29 50.46 40.77
CO2Me
COPh
F
N
COPh
3ga
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)



3ga

$CDCl_3$, 376 MHz

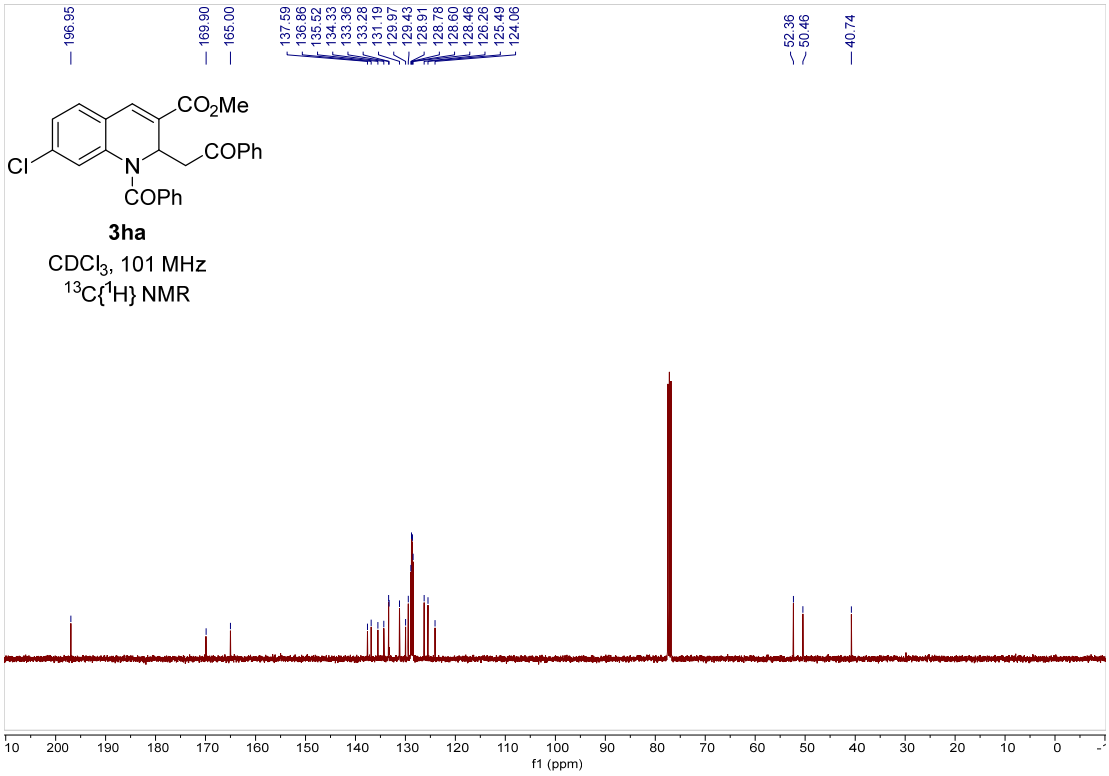
^{19}F NMR

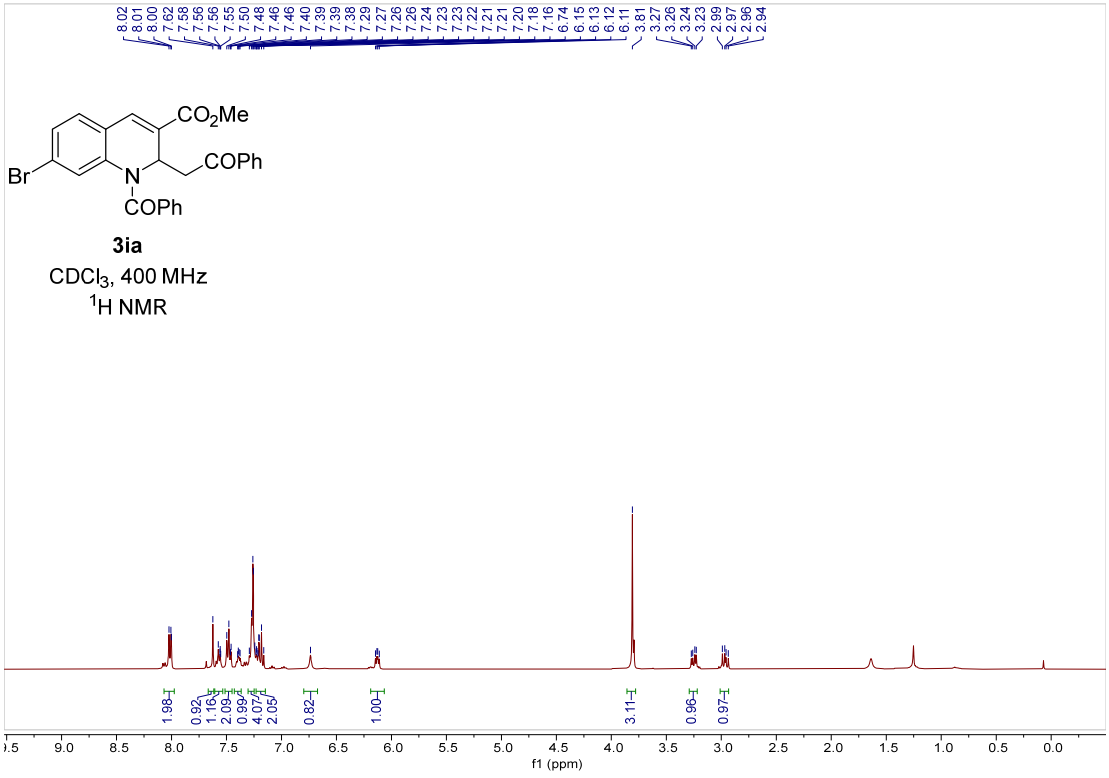


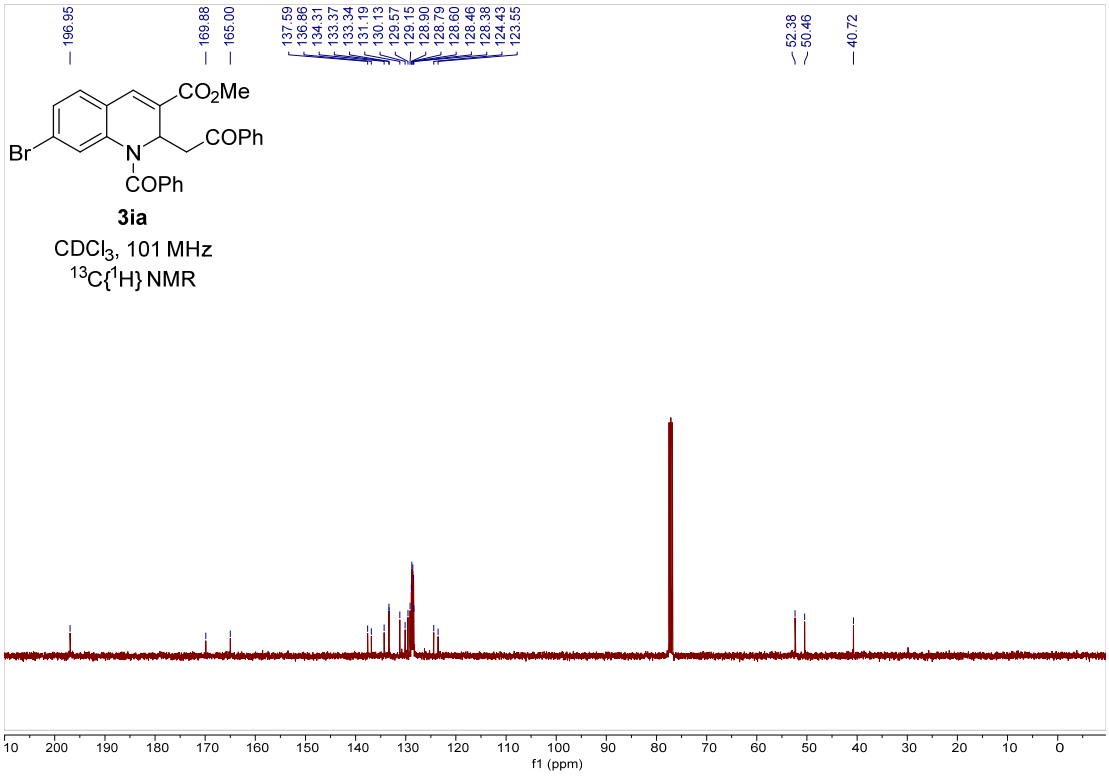
3ha

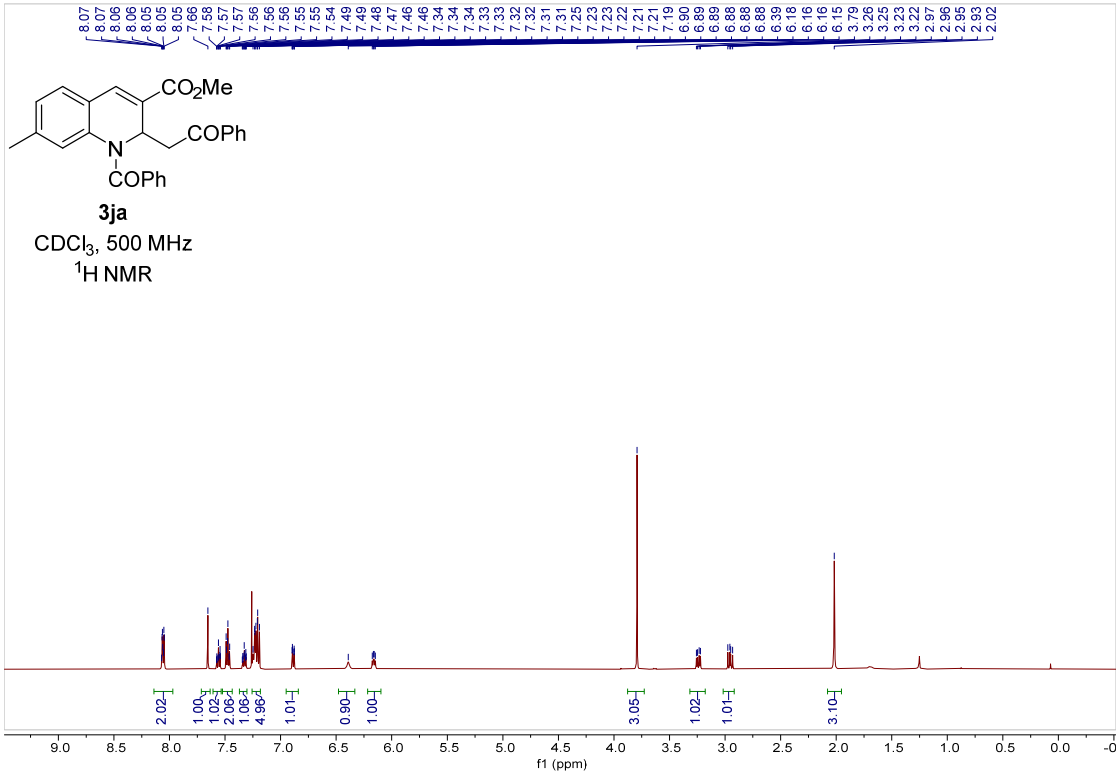
$CDCl_3$, 400 MHz

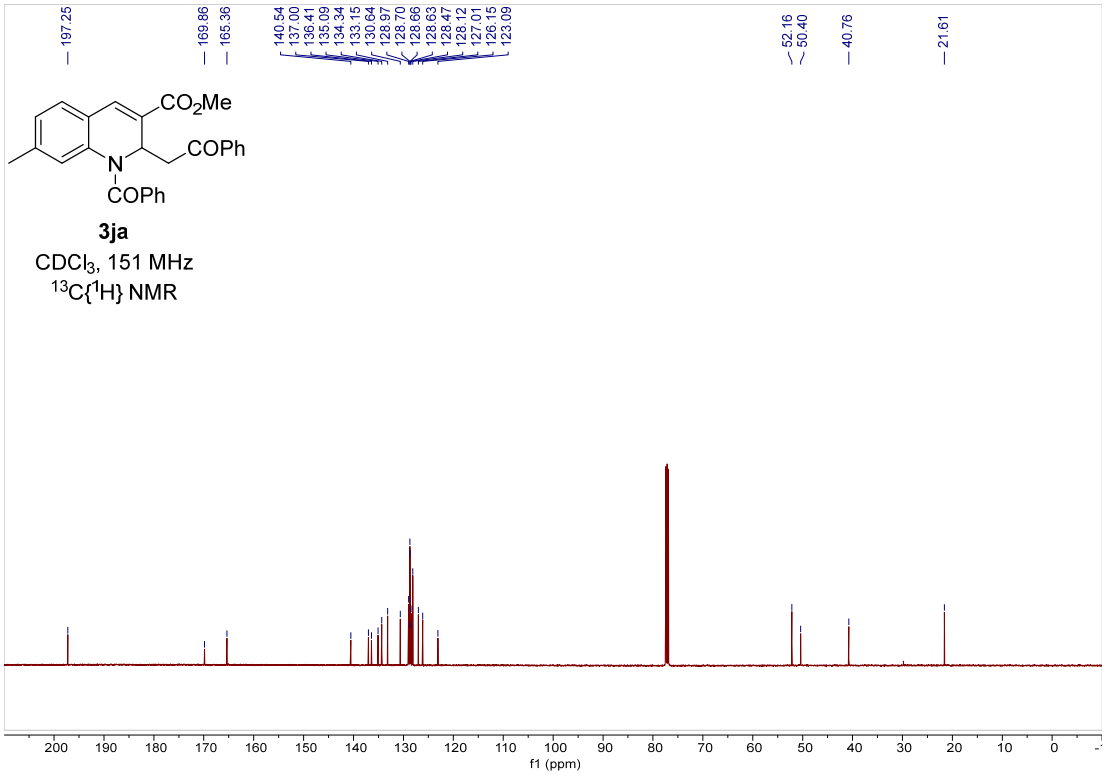
^{1}H NMR


196.95
169.90
165.00
137.59
136.86
135.52
134.33
133.36
133.28
131.19
129.97
129.43
128.91
128.78
128.60
128.46
126.26
125.49
124.06
52.36
50.46
40.74
CO2Me
COPh
Cl
N
COPh
3ha
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)


8.02
8.01
8.00
7.62
7.58
7.56
7.56
7.55
7.50
7.48
7.46
7.46
7.40
7.39
7.39
7.38
7.29
7.27
7.26
7.26
7.24
7.23
7.23
7.22
7.21
7.21
7.20
7.18
7.16
6.74
6.15
6.13
6.12
6.11
3.81
3.27
3.26
3.24
3.23
2.99
2.97
2.96
2.94
CO2Me
COPh
Br
N
COPh
3ia
CDCl3, 400 MHz
1H NMR
1.98
0.92
1.16
2.09
0.99
4.07
2.05
0.82
1.00
3.11
0.96
0.97
f1 (ppm)


196.95
169.88
165.00
137.59
136.86
134.31
133.37
133.34
131.19
130.13
129.57
129.15
128.90
128.79
128.60
128.46
128.38
124.43
123.55
52.38
50.46
40.72
CO2Me
COPh
Br
N
COPh
3ia
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

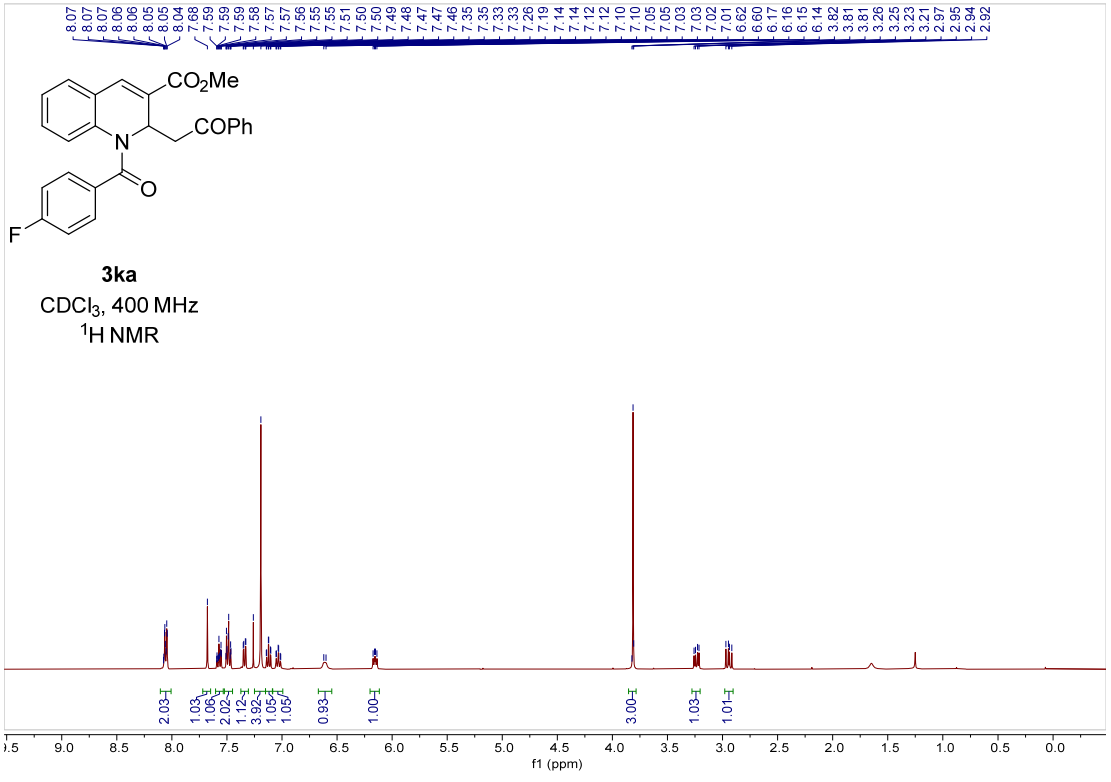

CO2Me
COPh
N
COPh
3ja
CDCl3, 500 MHz
1H NMR
2.02
1.00
1.02
2.06
1.06
4.96
1.01
0.90
1.00
3.05
1.02
1.01
3.10
f1 (ppm)



3ja

$CDCl_3$, 151 MHz

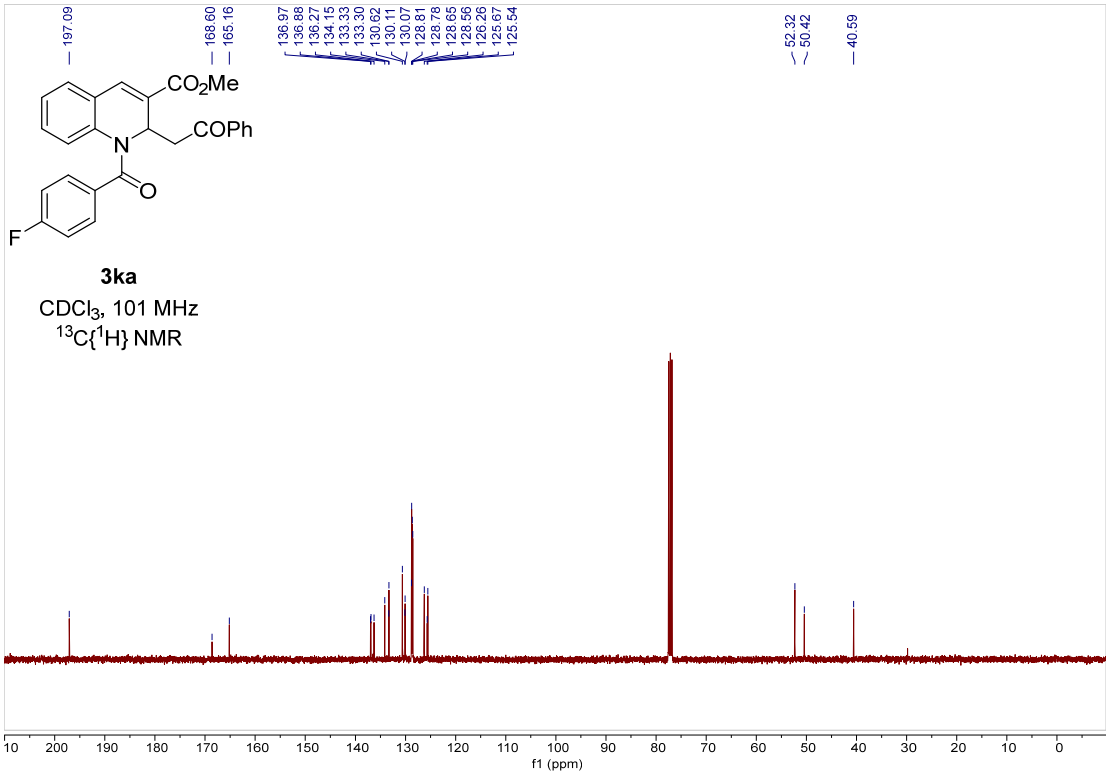
$^{13}C\{^1H\}$ NMR

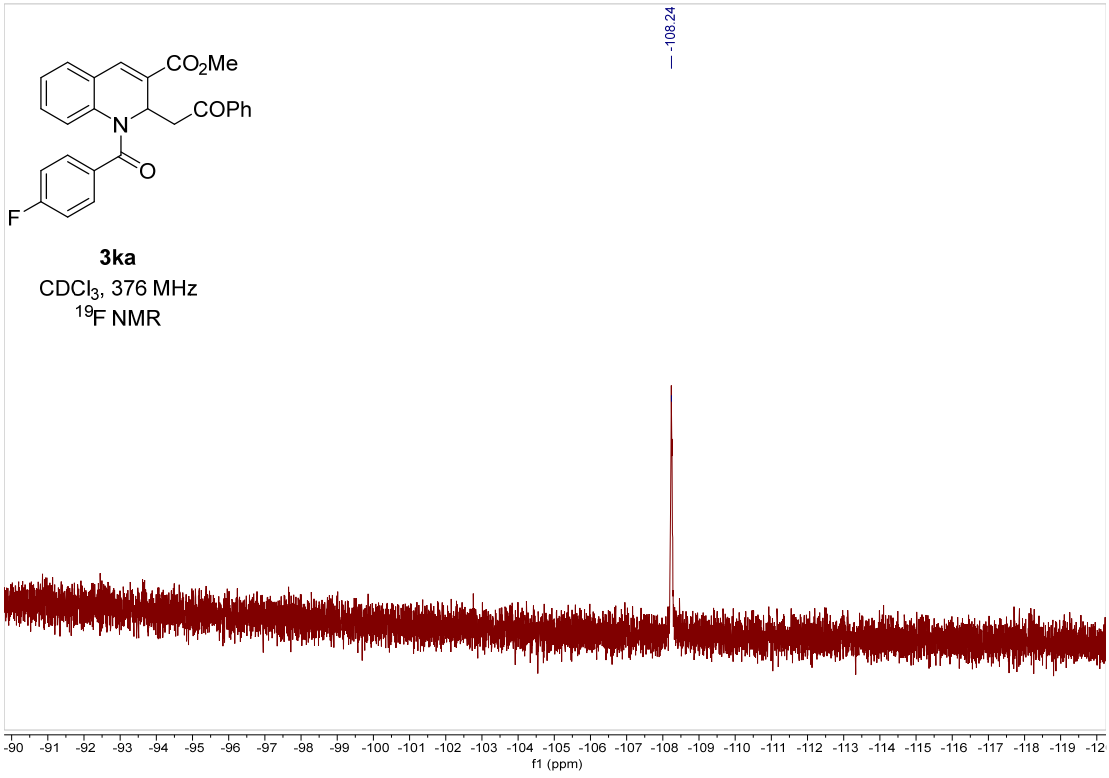


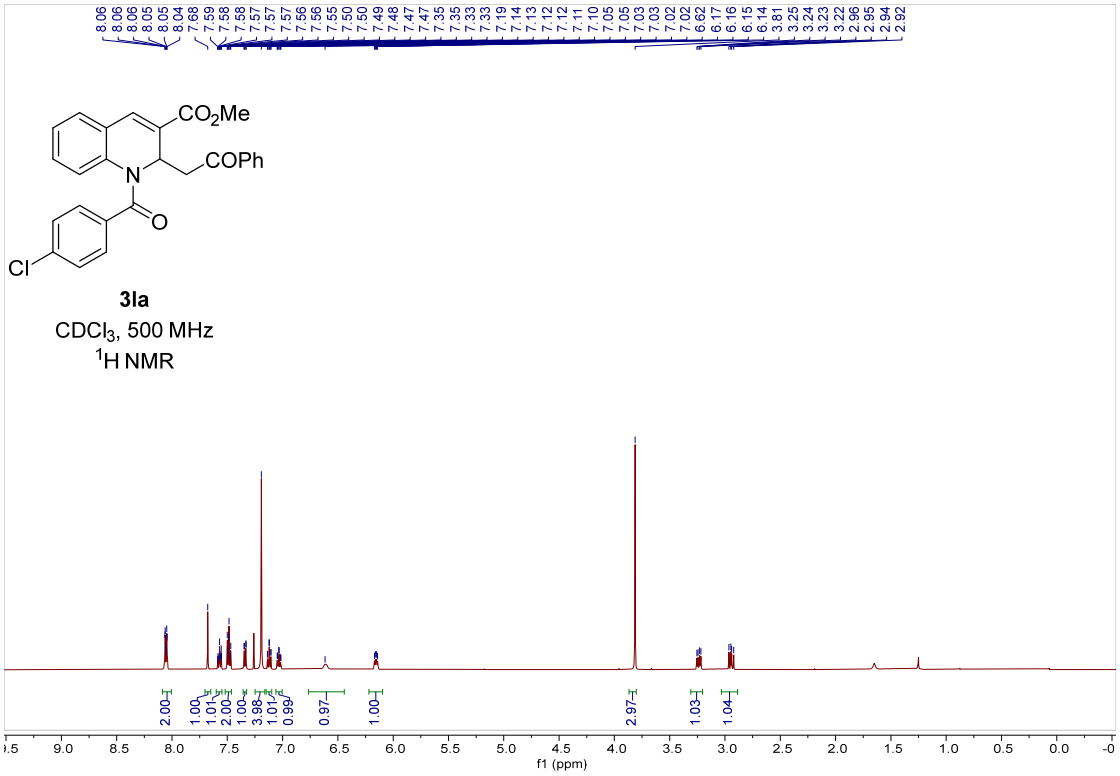
3ka

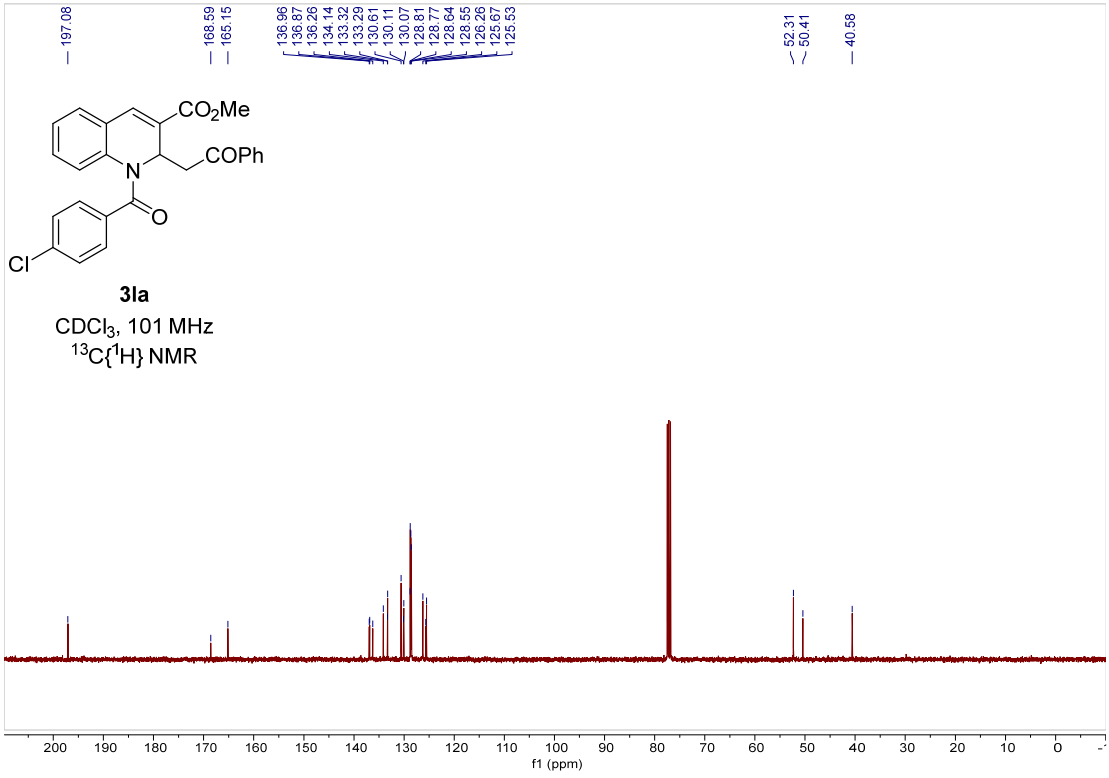
$CDCl_3$, 400 MHz

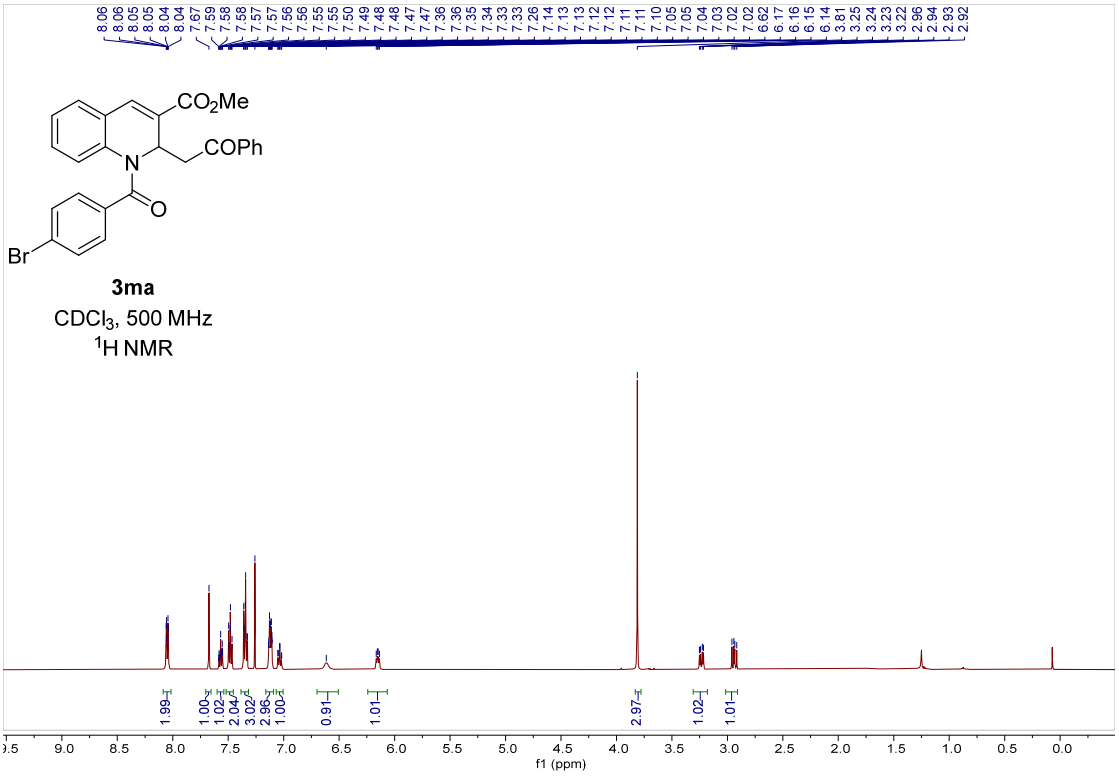
^1H NMR

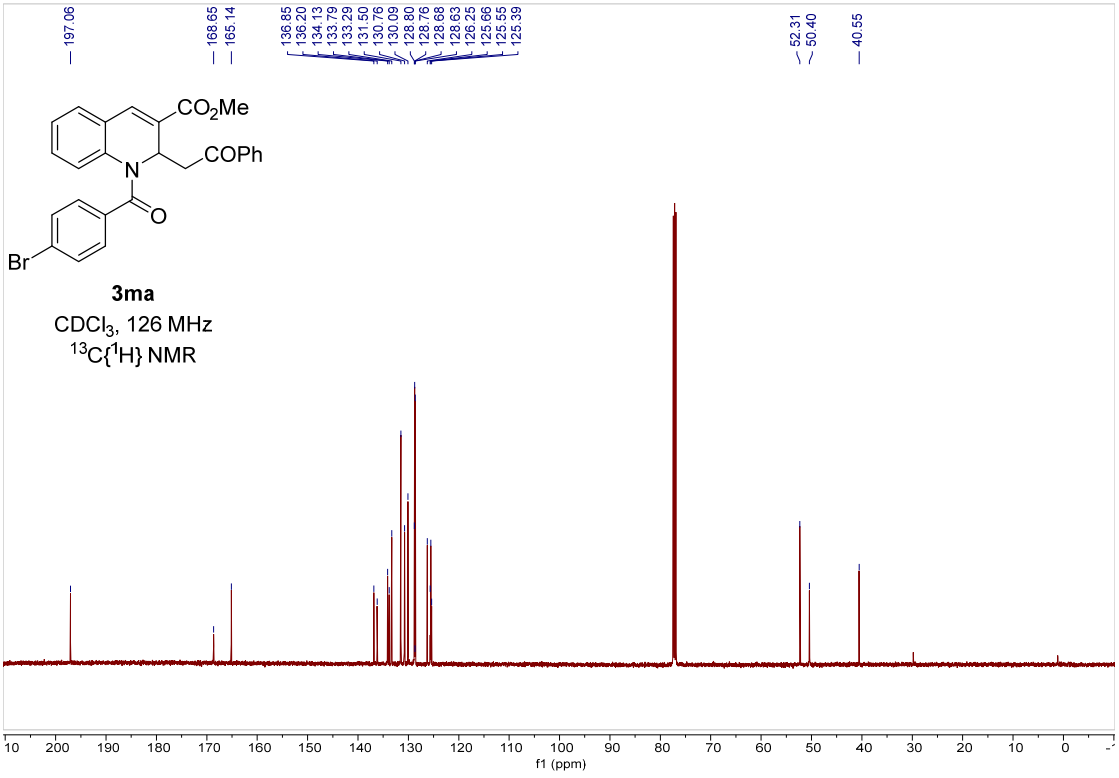

197.09
168.60
165.16
136.97
136.88
136.27
134.15
133.33
133.30
130.62
130.11
130.07
128.81
128.78
128.65
128.56
126.26
125.67
125.54
52.32
50.42
40.59
CO2Me
COPh
N
O
F
3ka
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

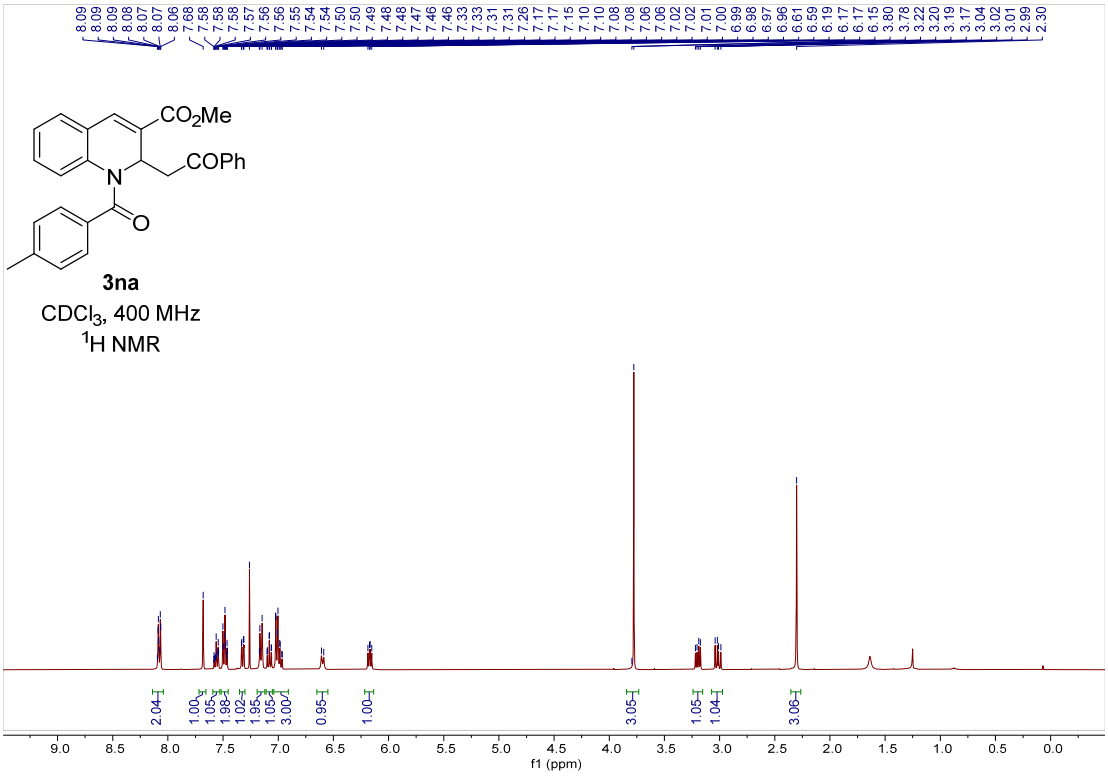

-108.24
CO2Me
COPh
N
O
F
3ka
CDCl3, 376 MHz
19F NMR
f1 (ppm)

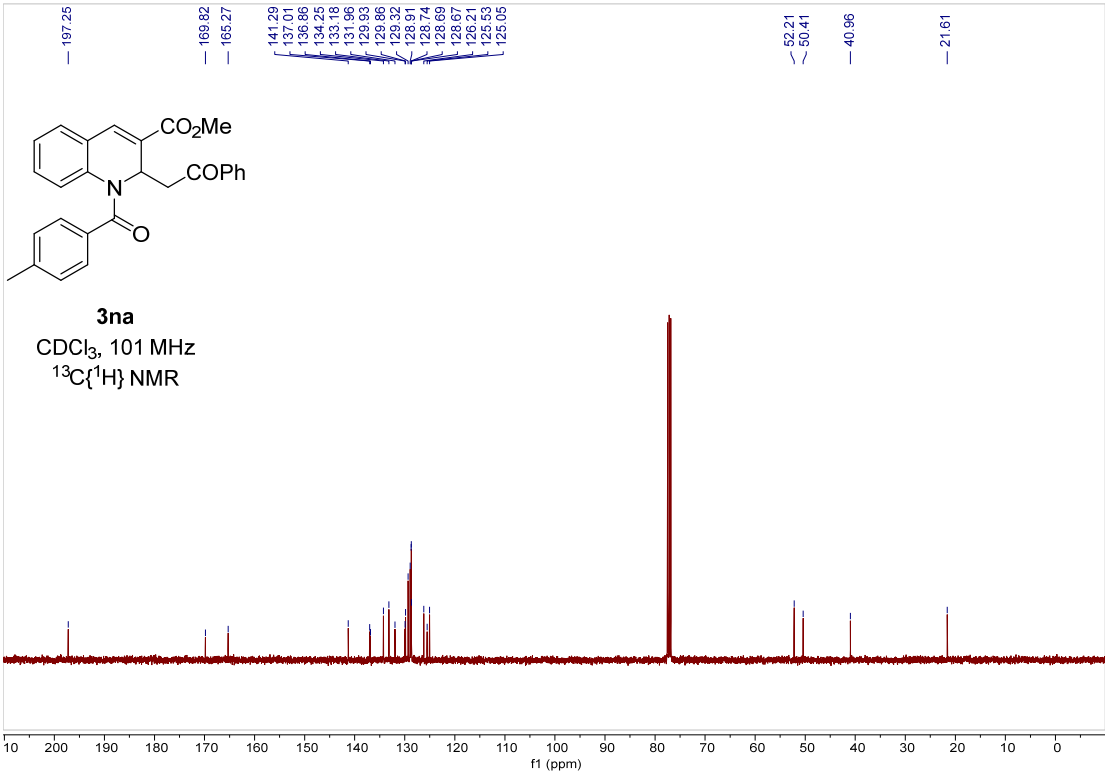

8.06 8.06 8.06 8.05 8.05 8.04 7.68 7.59 7.58 7.58 7.57 7.57 7.57 7.56 7.56 7.55 7.50 7.50 7.49 7.48 7.47 7.47 7.35 7.35 7.33 7.33 7.19 7.14 7.13 7.12 7.12 7.11 7.10 7.05 7.05 7.03 7.03 7.02 7.02 6.62 6.17 6.16 6.15 6.14 3.81 3.25 3.24 3.23 3.22 2.96 2.95 2.94 2.92
CO2Me
COPh
N
O
Cl
3la
CDCl3, 500 MHz
1H NMR
2.00 1.00 1.01 2.00 1.00 3.98 1.01 0.99 0.97 1.00 2.97 1.03 1.04
f1 (ppm)

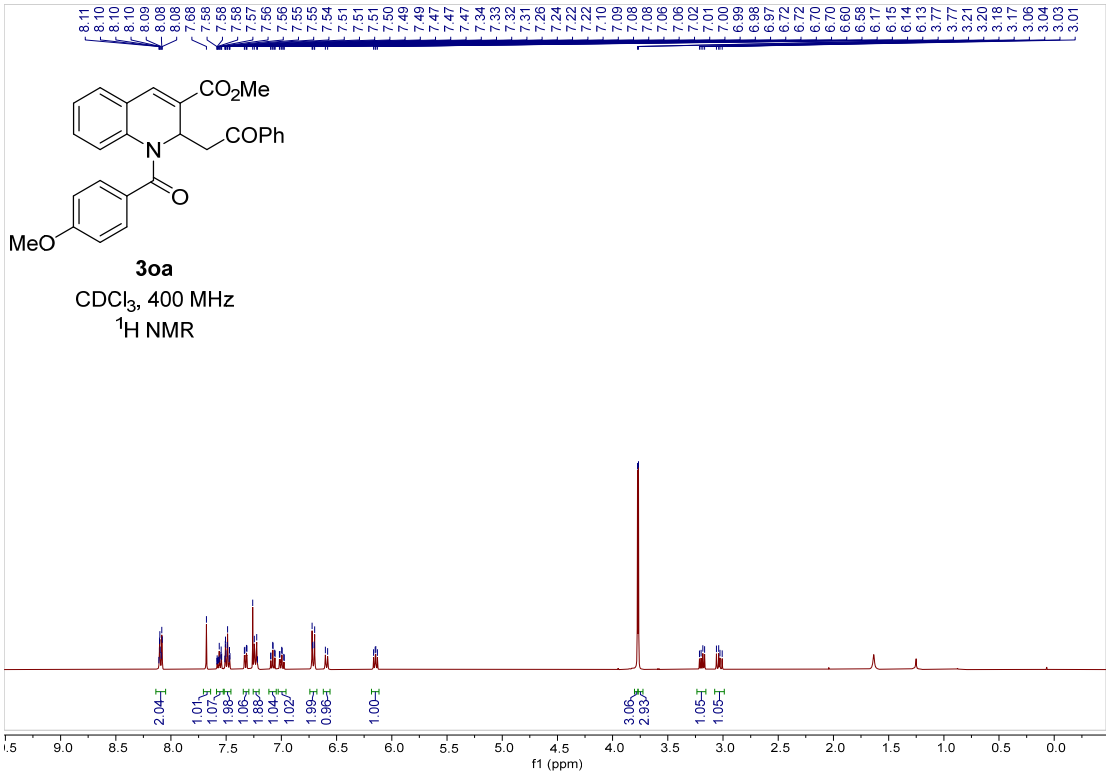

197.08
168.59 165.15
136.96 136.87 136.26 134.14 133.32 133.29 130.61 130.11 130.07 128.81 128.77 128.64 128.55 126.26 125.67 125.53
52.31 50.41
40.58
CO2Me
COPh
N
O
Cl
3la
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

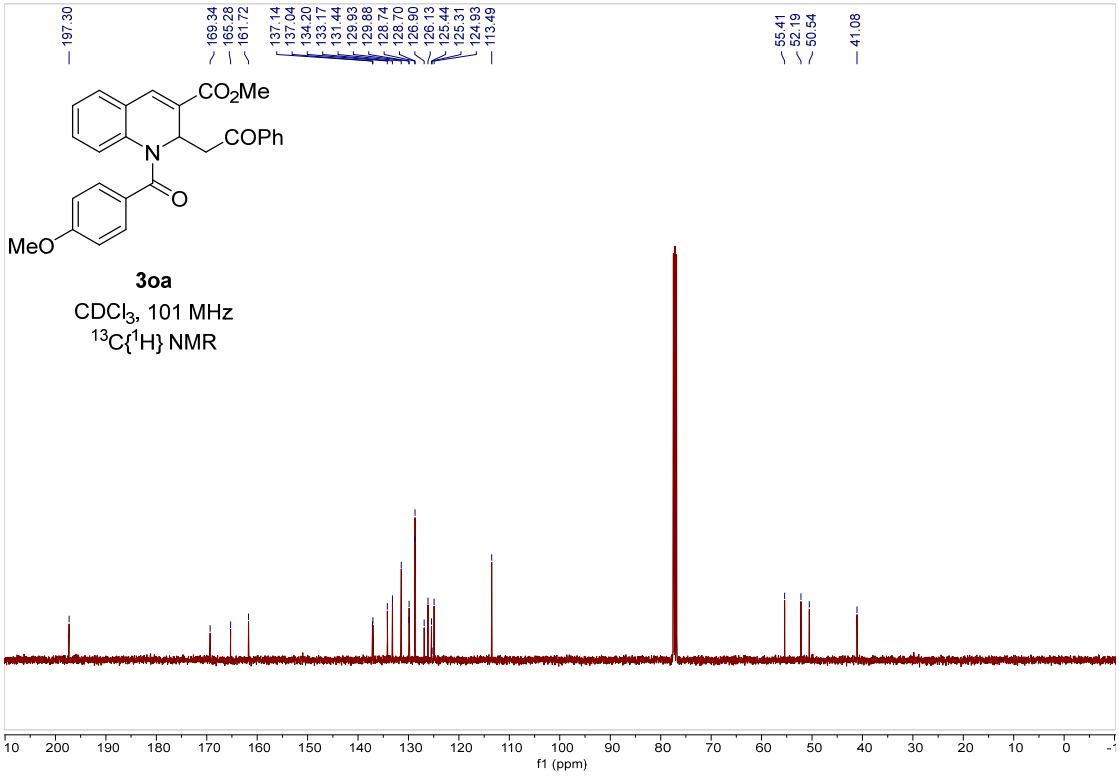

CO2Me
COPh
N
O
Br
3ma
CDCl3, 500 MHz
1H NMR
f1 (ppm)

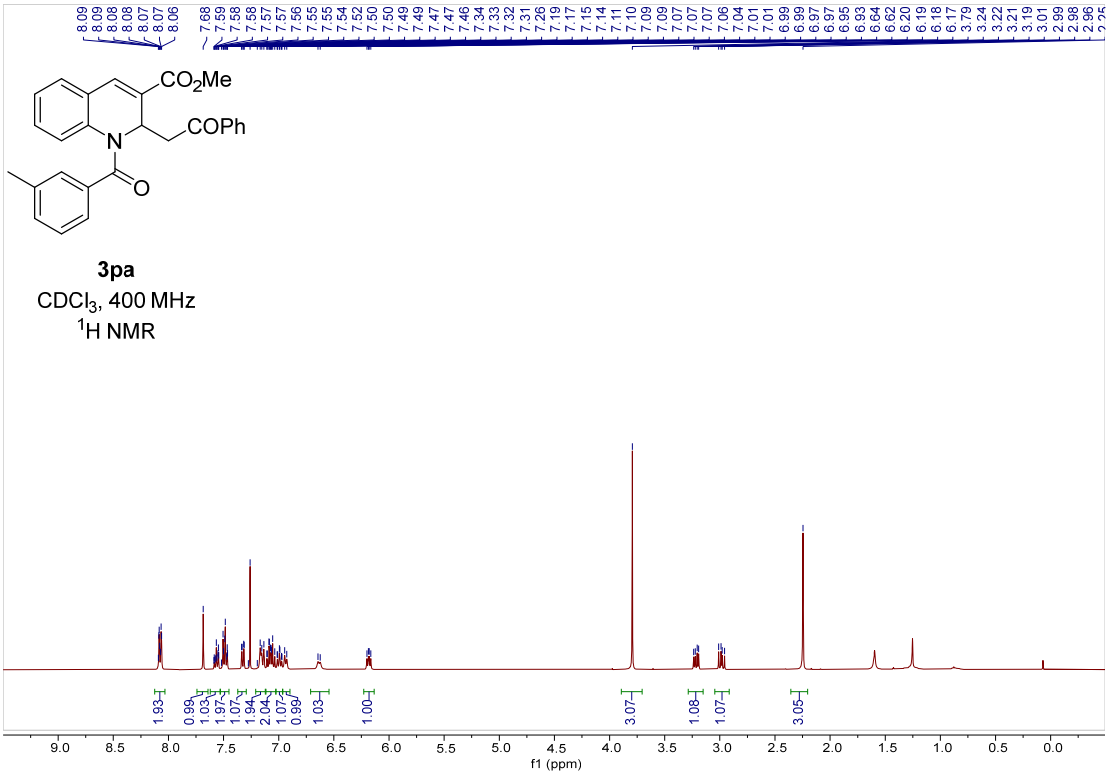

CO2Me
COPh
N
O
Br
3ma
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

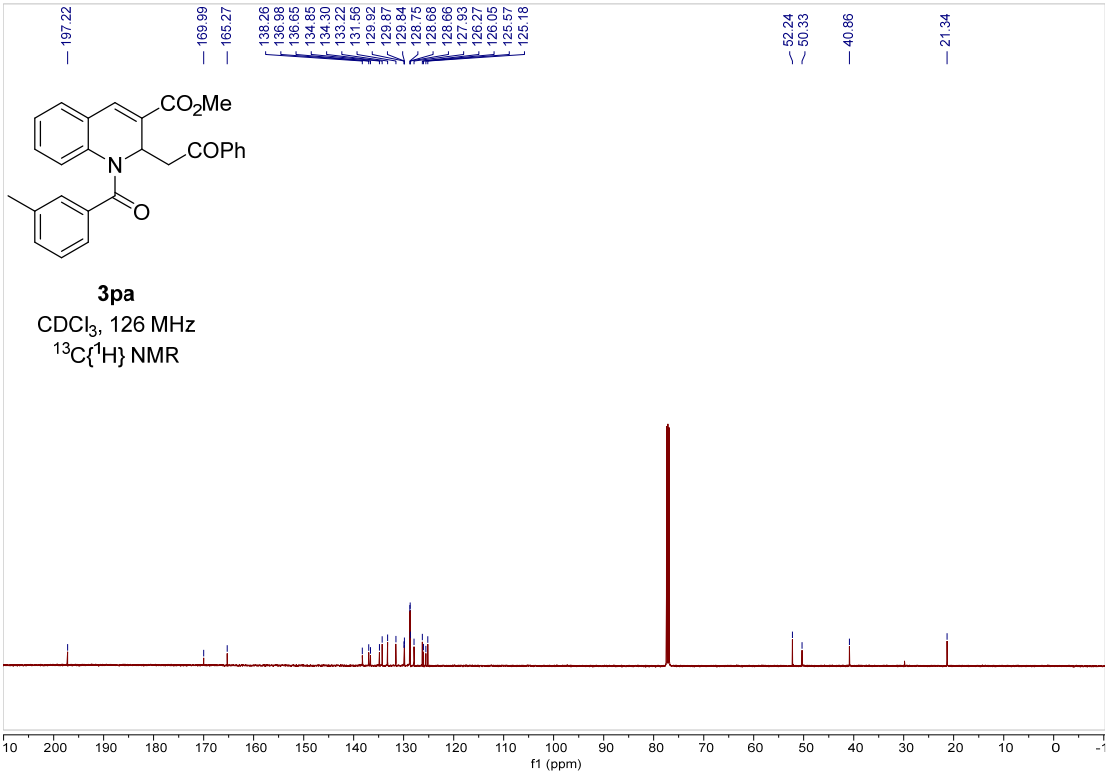

CO2Me
COPh
N
O
3na
CDCl3, 400 MHz
1H NMR
f1 (ppm)

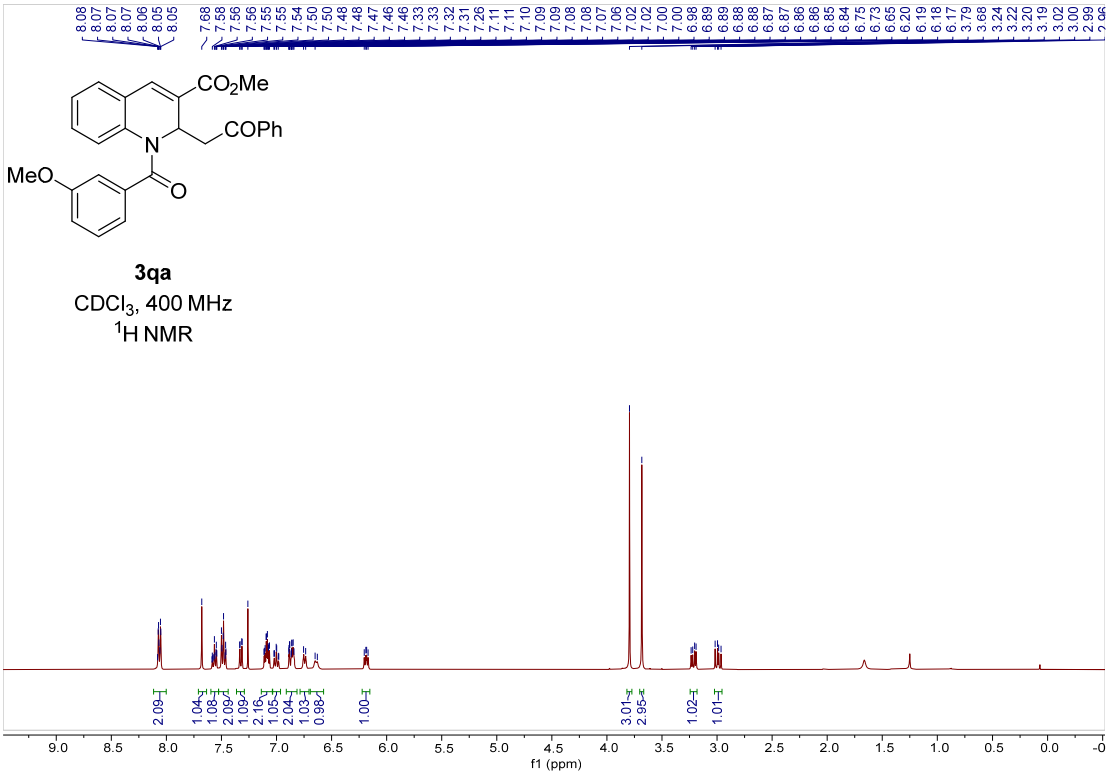

CO2Me
COPh
N
O
3na
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

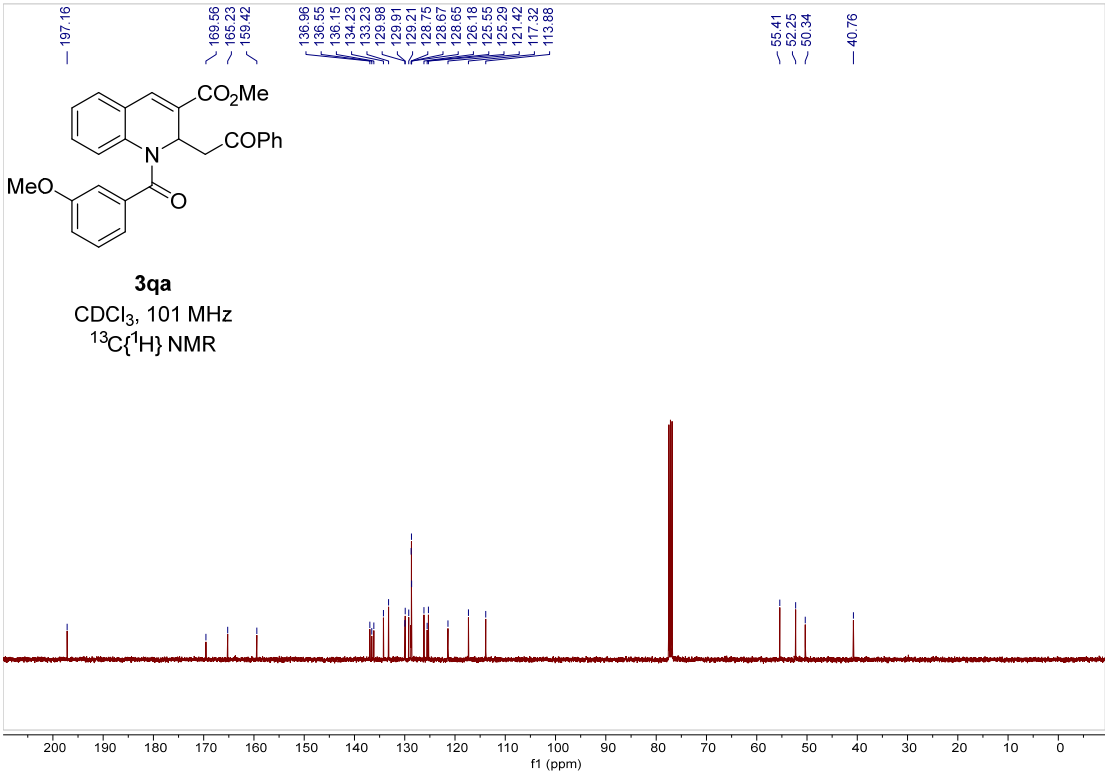

CO2Me
COPh
N
O
MeO
3oa
CDCl3, 400 MHz
1H NMR
f1 (ppm)

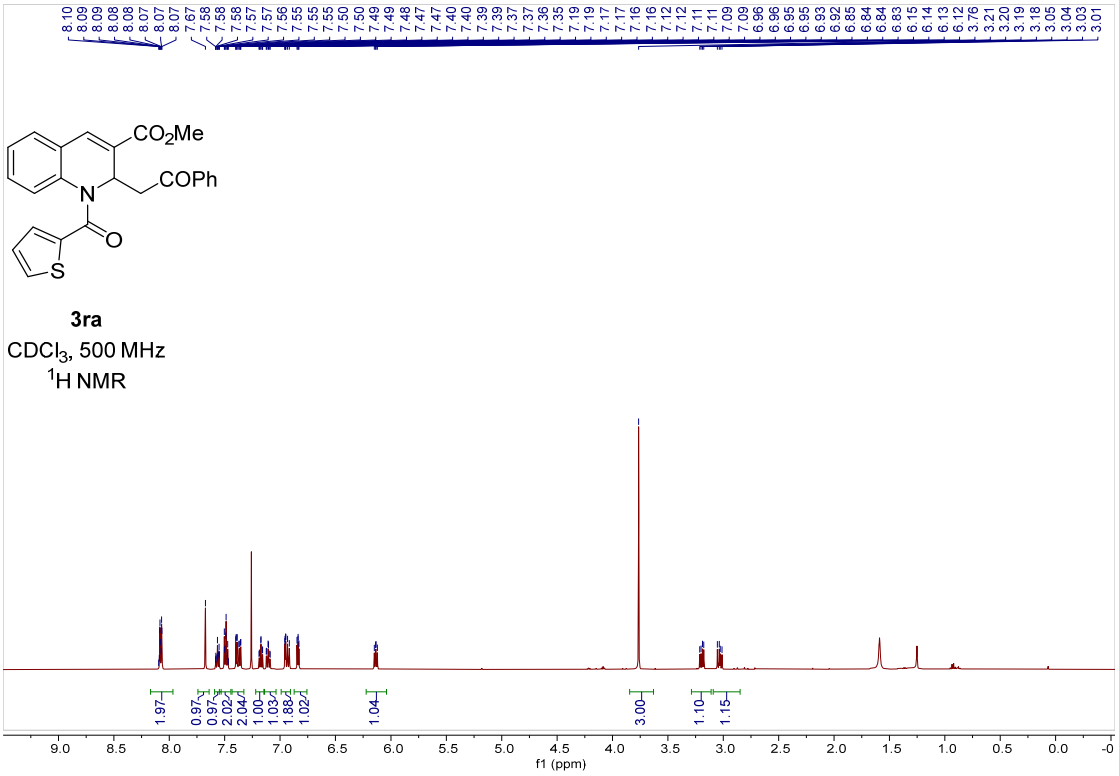

CO2Me
COPh
N
O
MeO
3oa
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

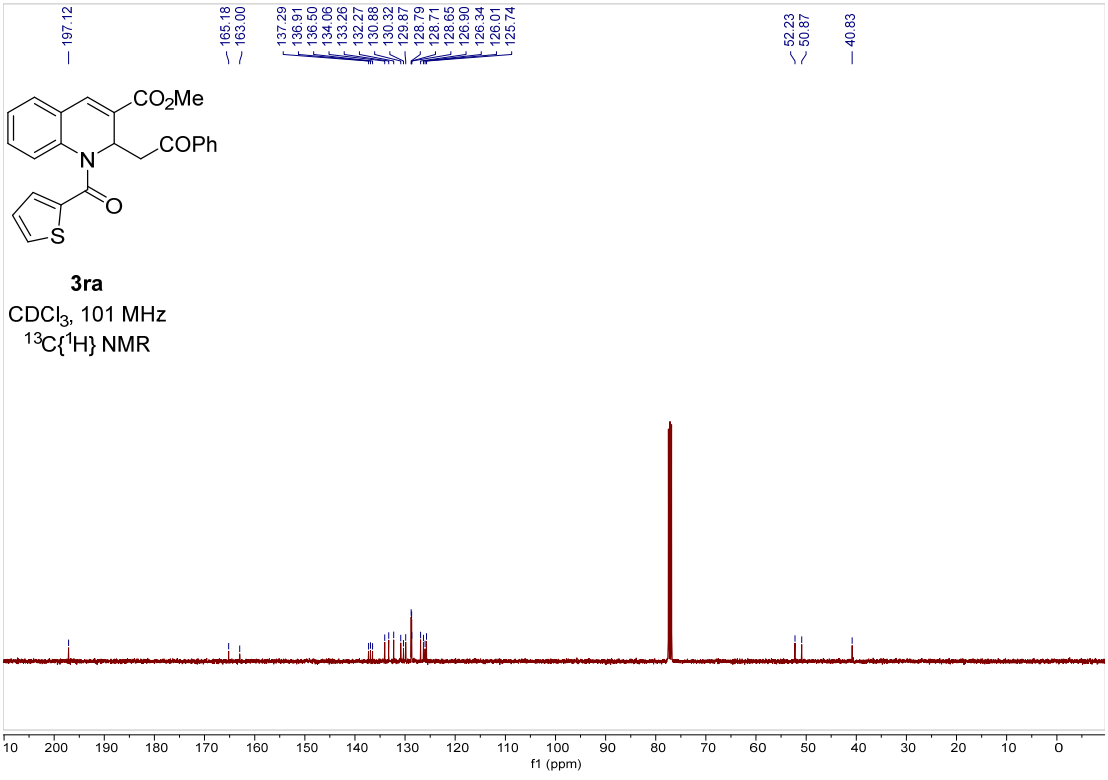

CO2Me
COPh
N
O
3pa
CDCl3, 400 MHz
1H NMR
f1 (ppm)

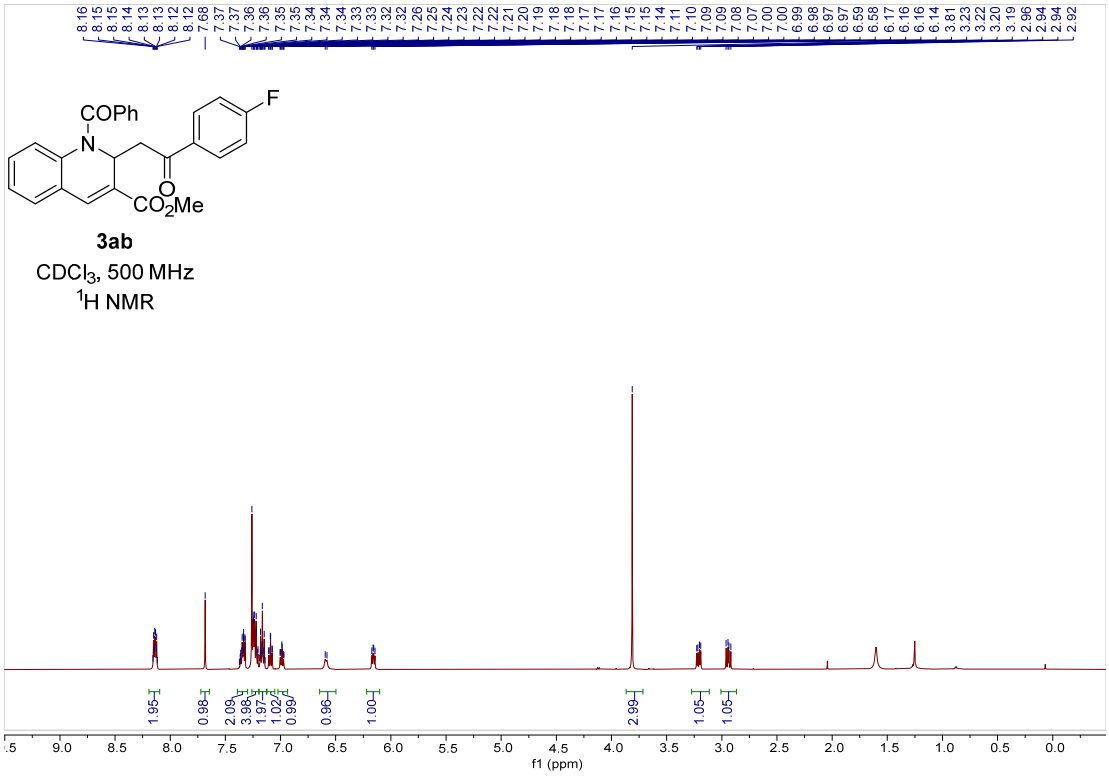

CO2Me
COPh
N
O
3pa
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

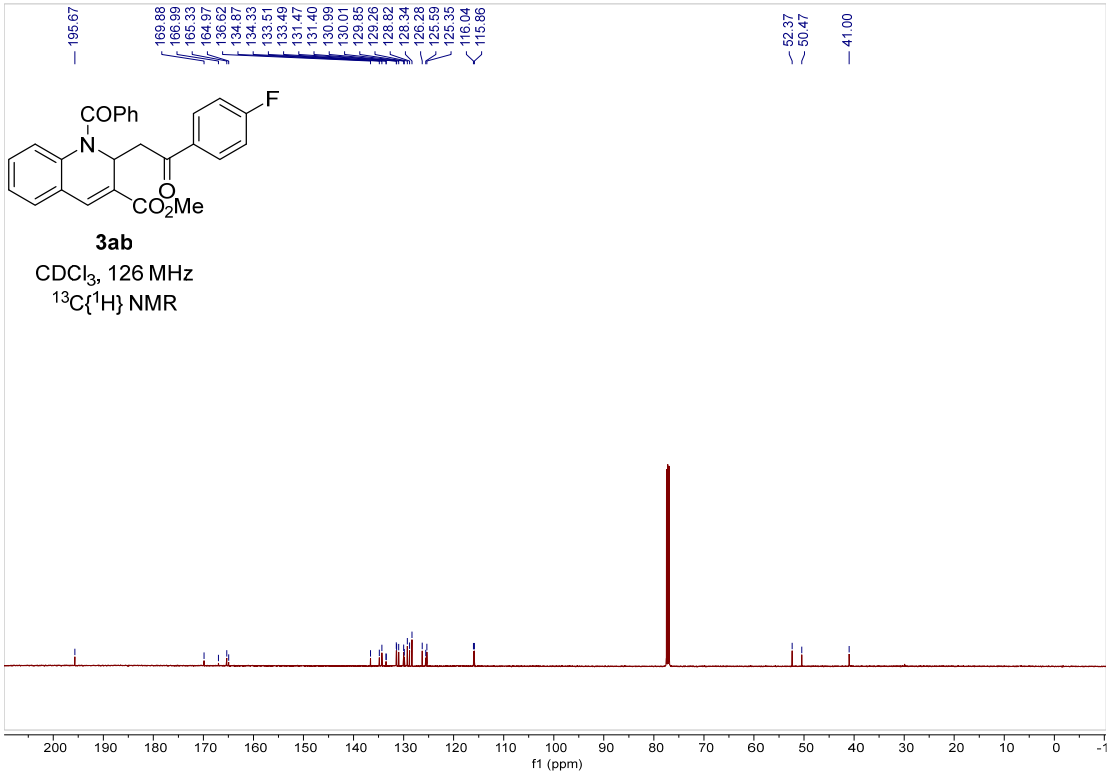

CO2Me
COPh
N
MeO
O
3qa
CDCl3, 400 MHz
1H NMR
f1 (ppm)

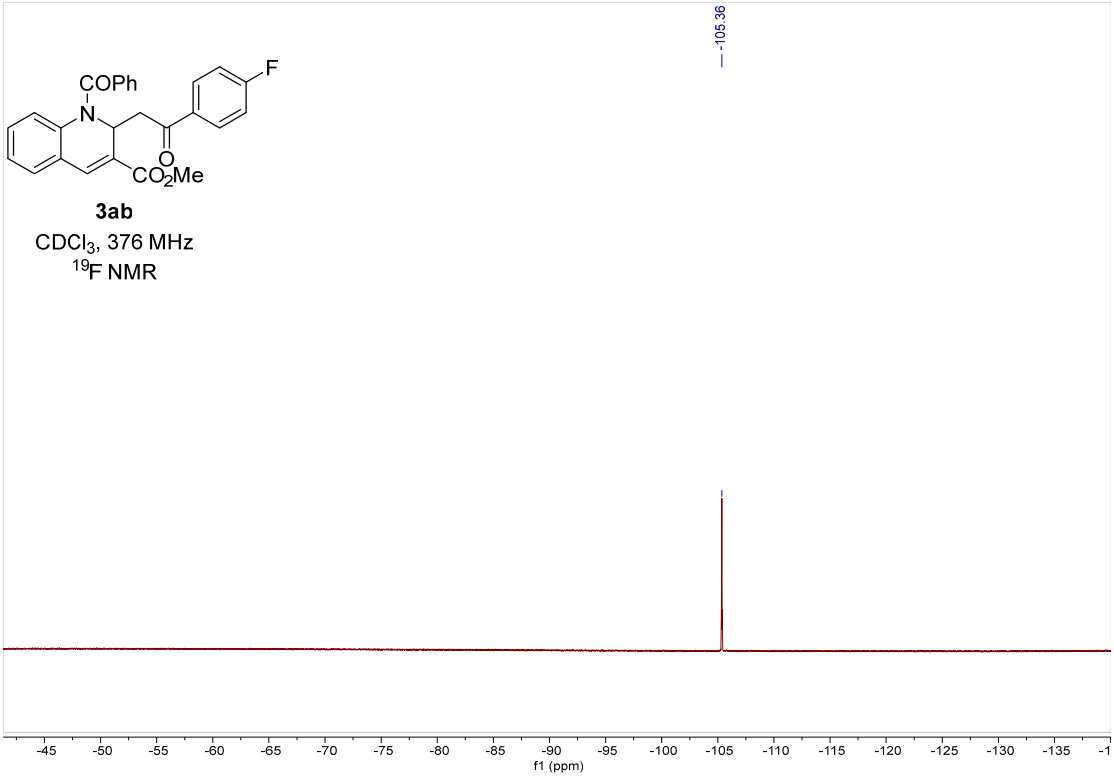

CO2Me
COPh
N
MeO
O
3qa
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)


CO2Me
COPh
N
O
S
3ra
CDCl3, 500 MHz
1H NMR
f1 (ppm)


CO2Me
COPh
N
O
S
3ra
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)


COPh
N
F
O
CO2Me
3ab
CDCl3, 500 MHz
1H NMR
f1 (ppm)

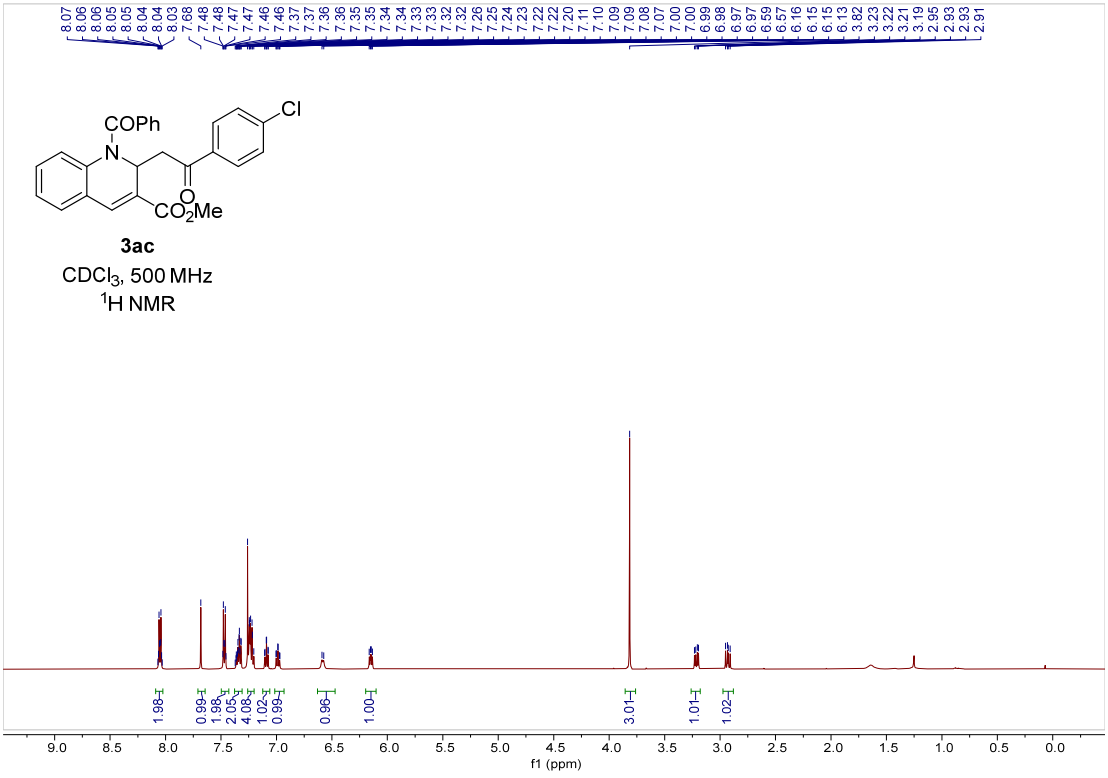

COPh
N
F
O
CO2Me
3ab
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)



3ab

$CDCl_3$, 376 MHz

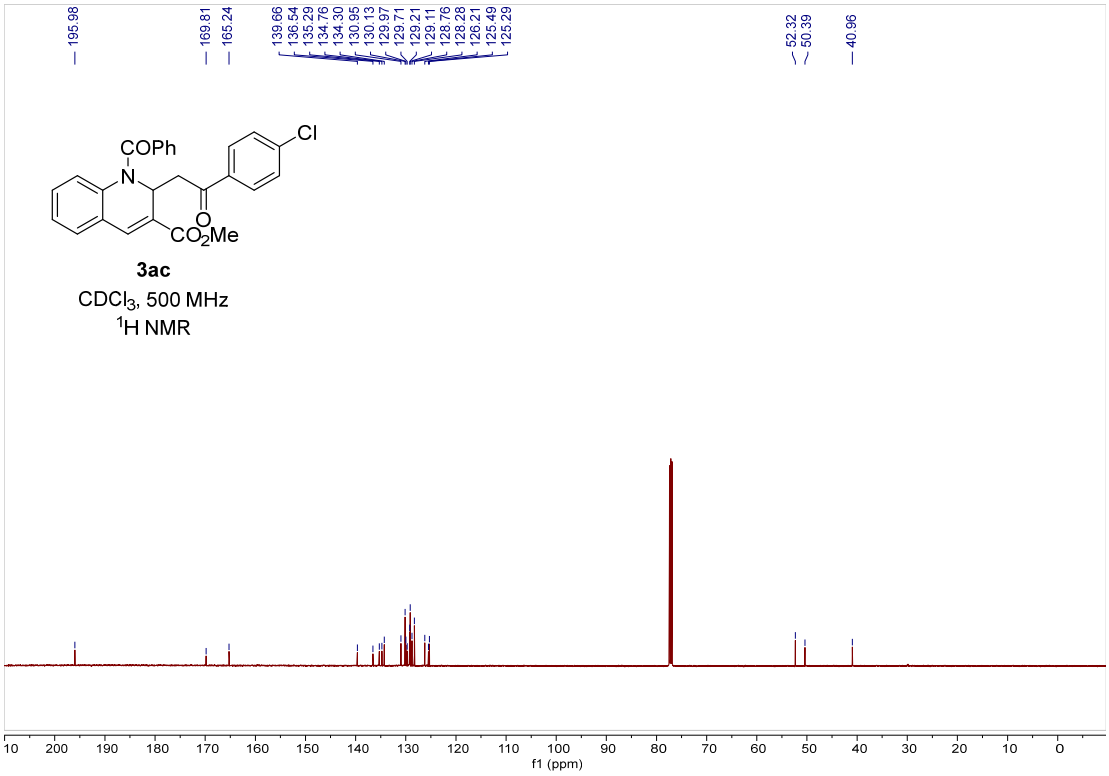
^{19}F NMR



3ac

$CDCl_3$, 500 MHz

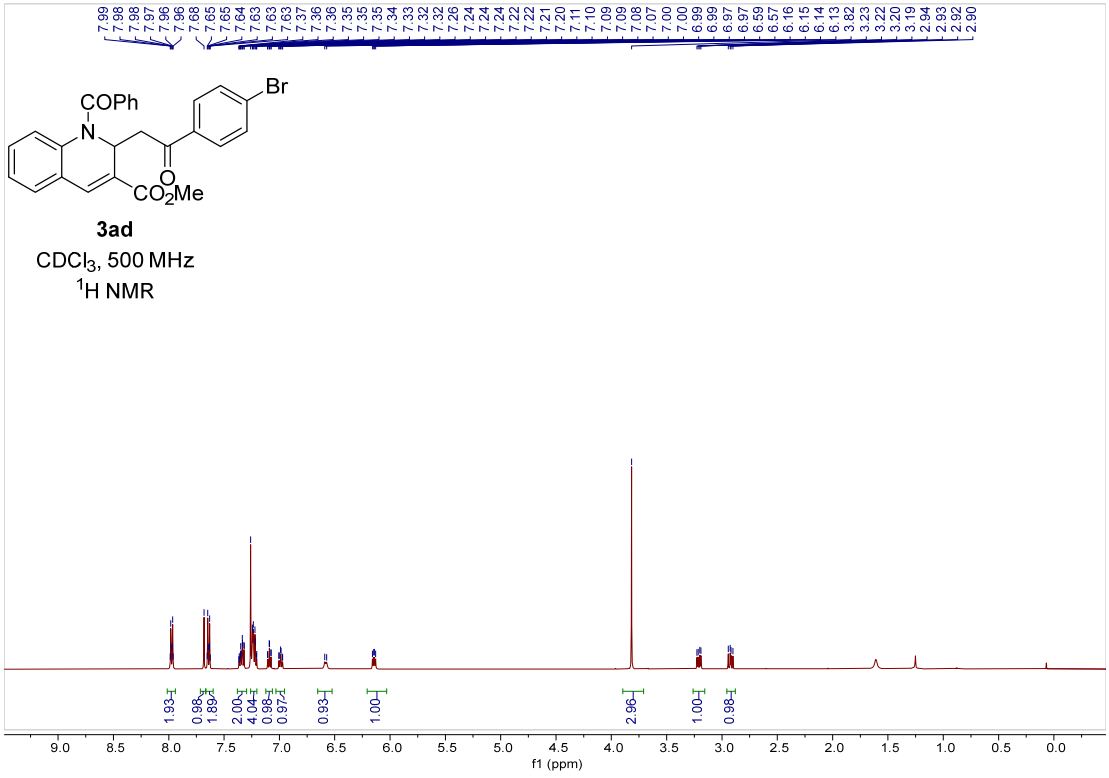
^{1}H NMR



3ac

$CDCl_3$, 500 MHz

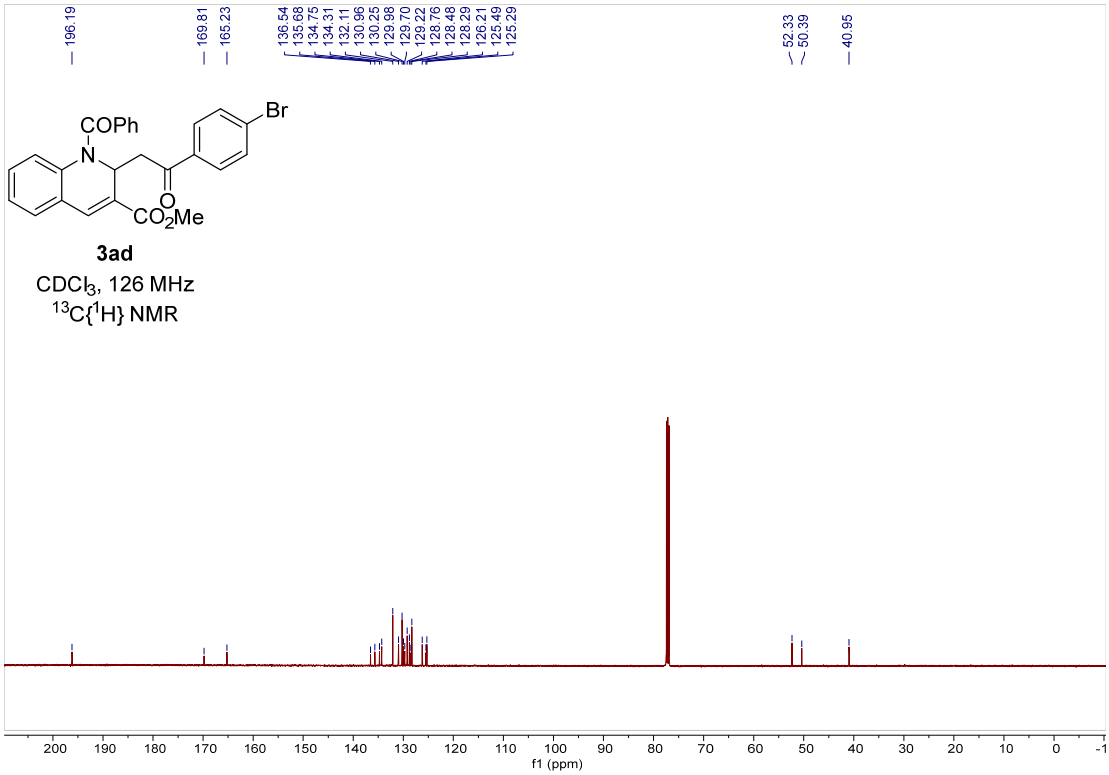
^1H NMR

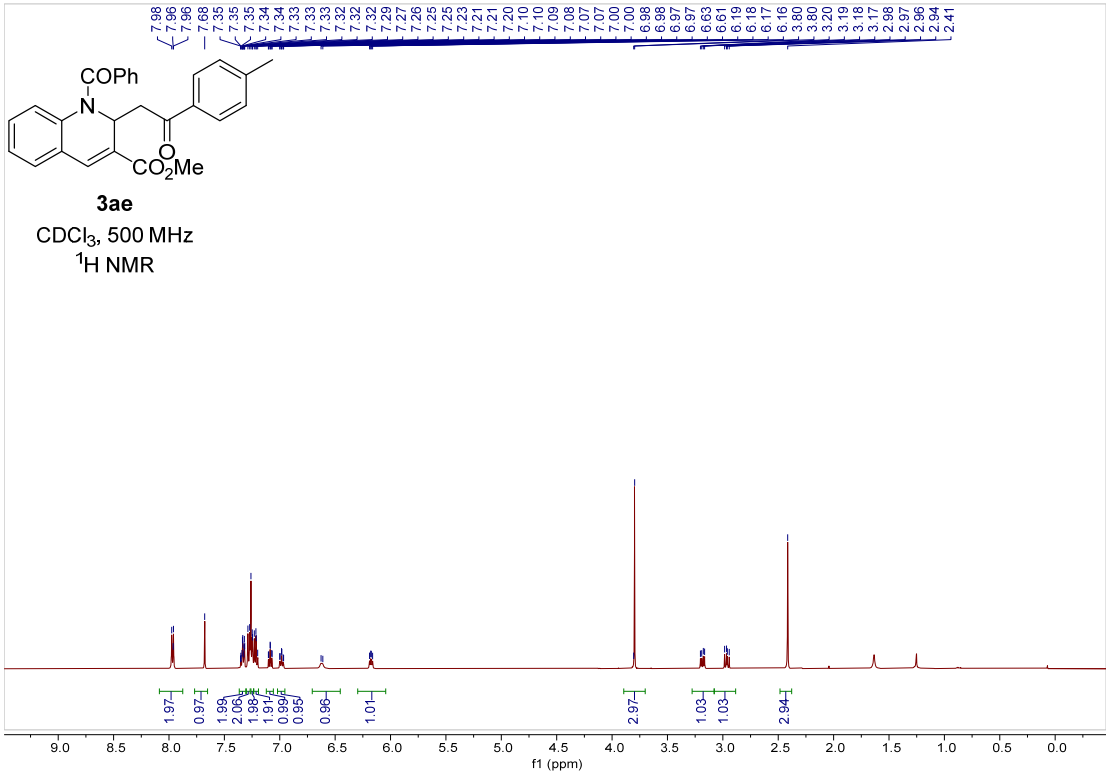


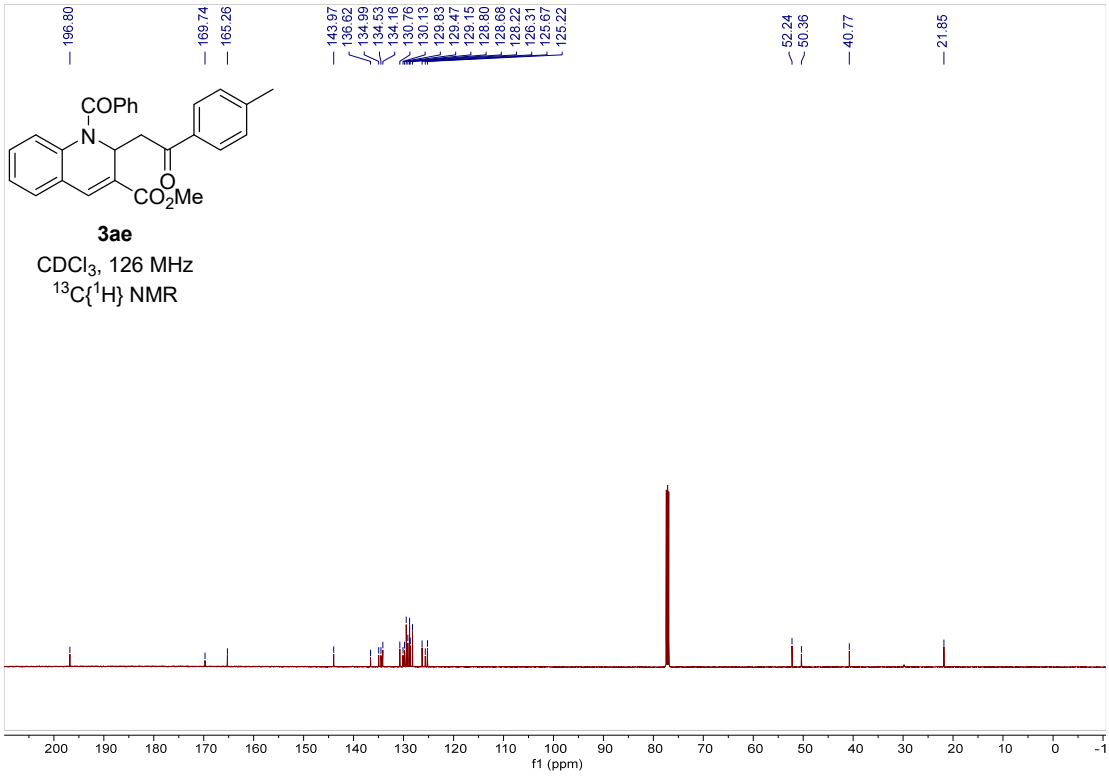
3ad

$CDCl_3$, 500 MHz

^1H NMR


196.19
169.81
165.23
136.54
135.68
134.75
134.31
132.11
130.96
130.25
129.98
129.70
129.22
128.76
128.48
128.29
126.21
125.49
125.29
52.33
50.39
40.95
COPh
N
Br
O
CO2Me
3ad
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

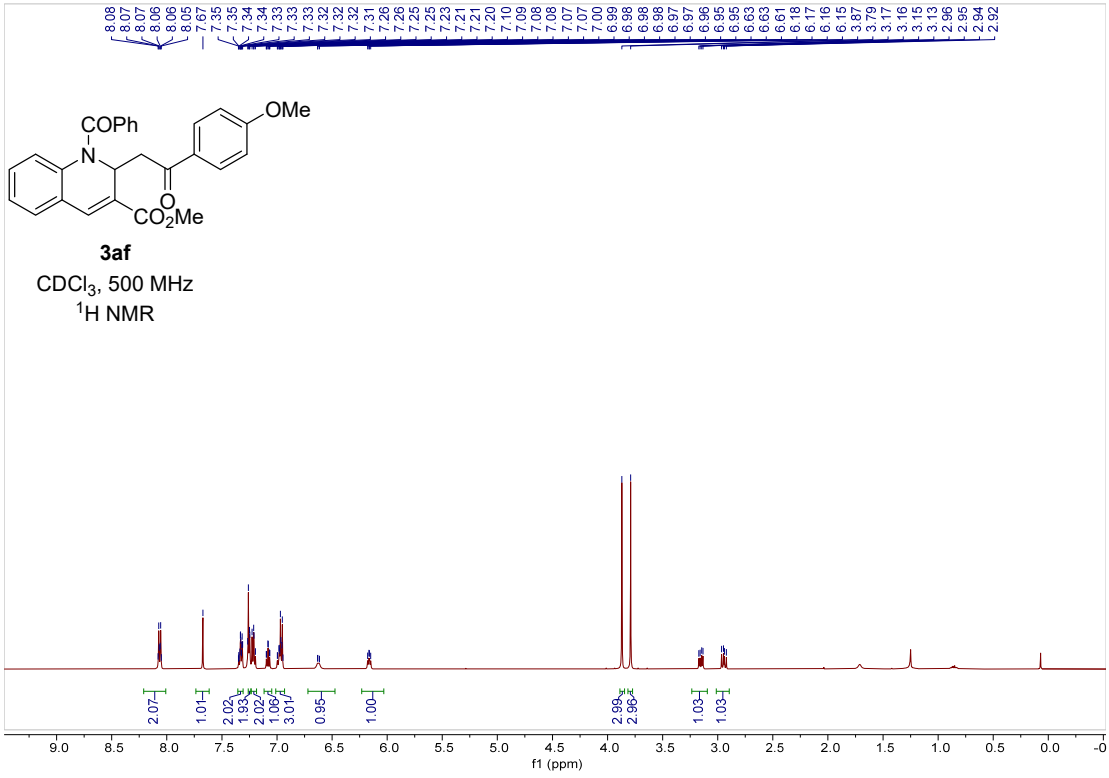

7.98
7.96
7.96
7.68
7.35
7.35
7.35
7.34
7.34
7.33
7.33
7.33
7.32
7.32
7.32
7.29
7.27
7.26
7.25
7.25
7.23
7.21
7.21
7.20
7.10
7.10
7.09
7.08
7.07
7.07
7.00
7.00
6.98
6.98
6.97
6.97
6.63
6.61
6.19
6.18
6.17
6.16
3.80
3.80
3.20
3.19
3.18
3.17
2.98
2.97
2.96
2.94
2.41
COPh
N
O
CO2Me
3ae
CDCl3, 500 MHz
1H NMR
1.97
0.97
1.99
2.06
1.98
1.91
0.99
0.95
0.96
1.01
2.97
1.03
1.03
2.94
f1 (ppm)



3ae

$CDCl_3$, 126 MHz

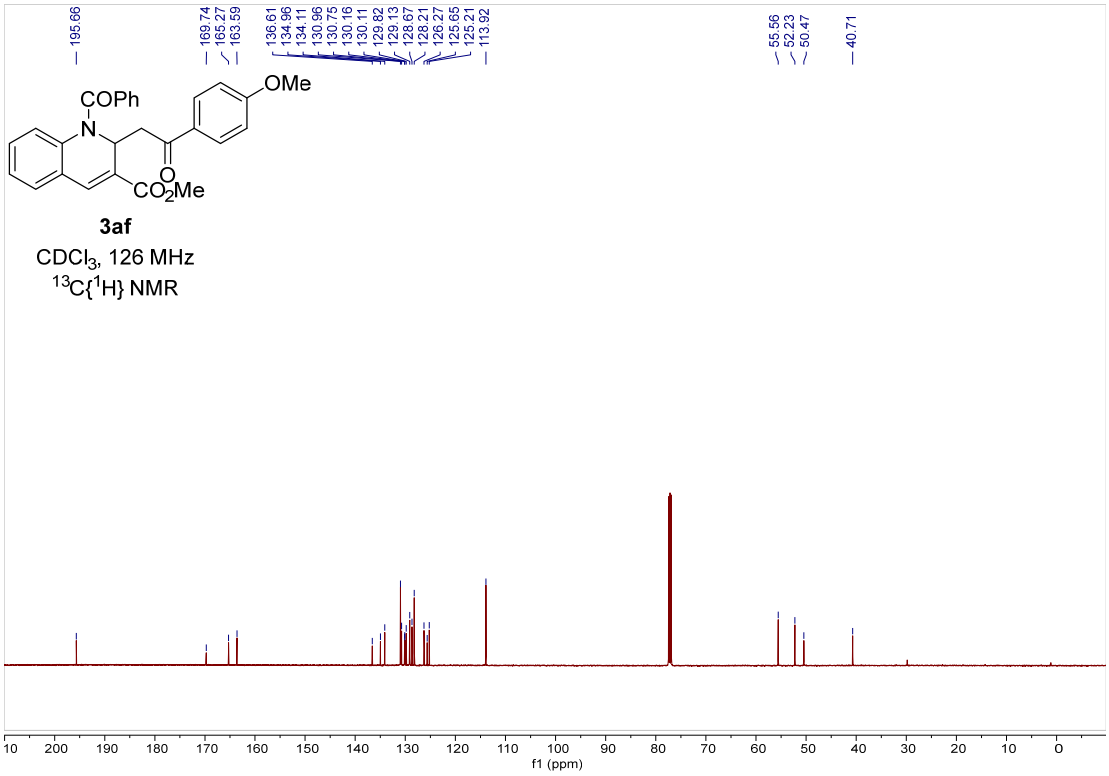
$^{13}C\{^1H\}$ NMR

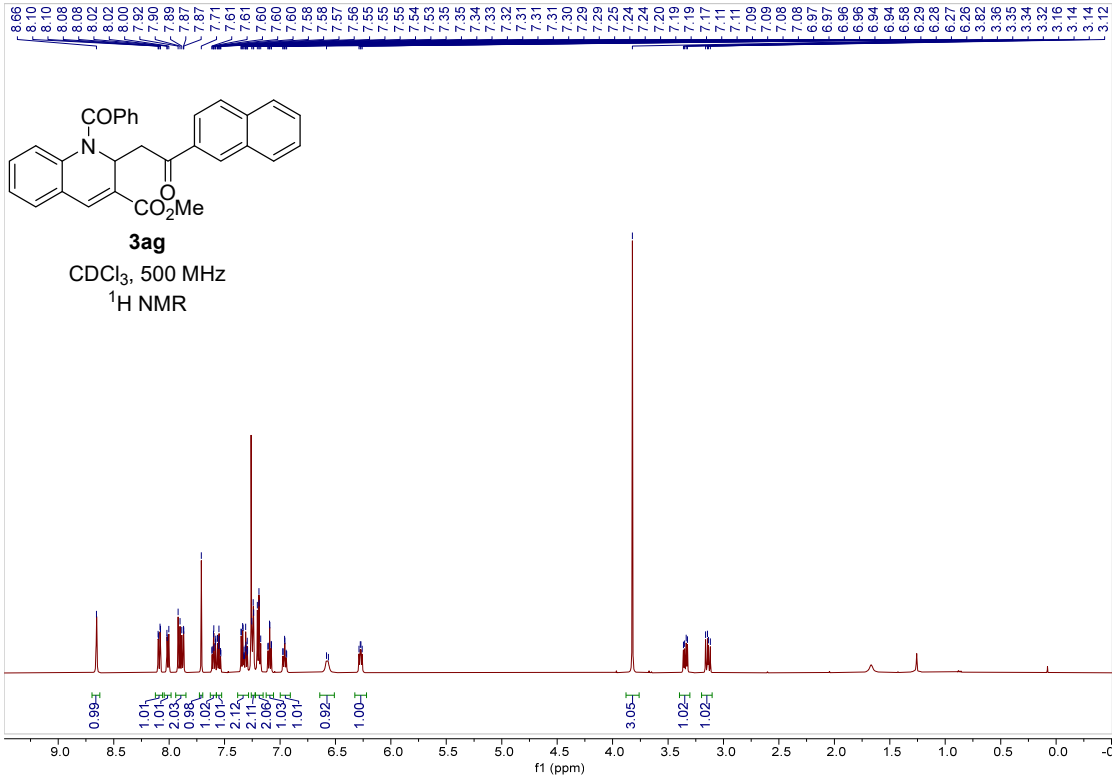


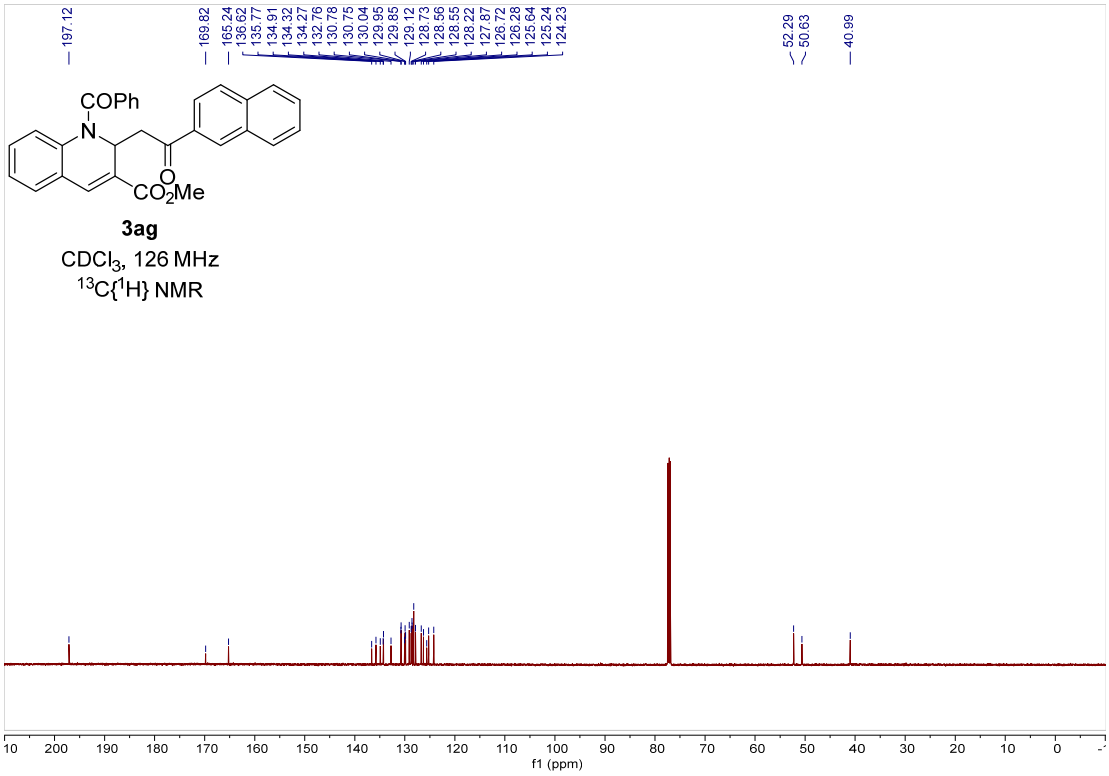
3af

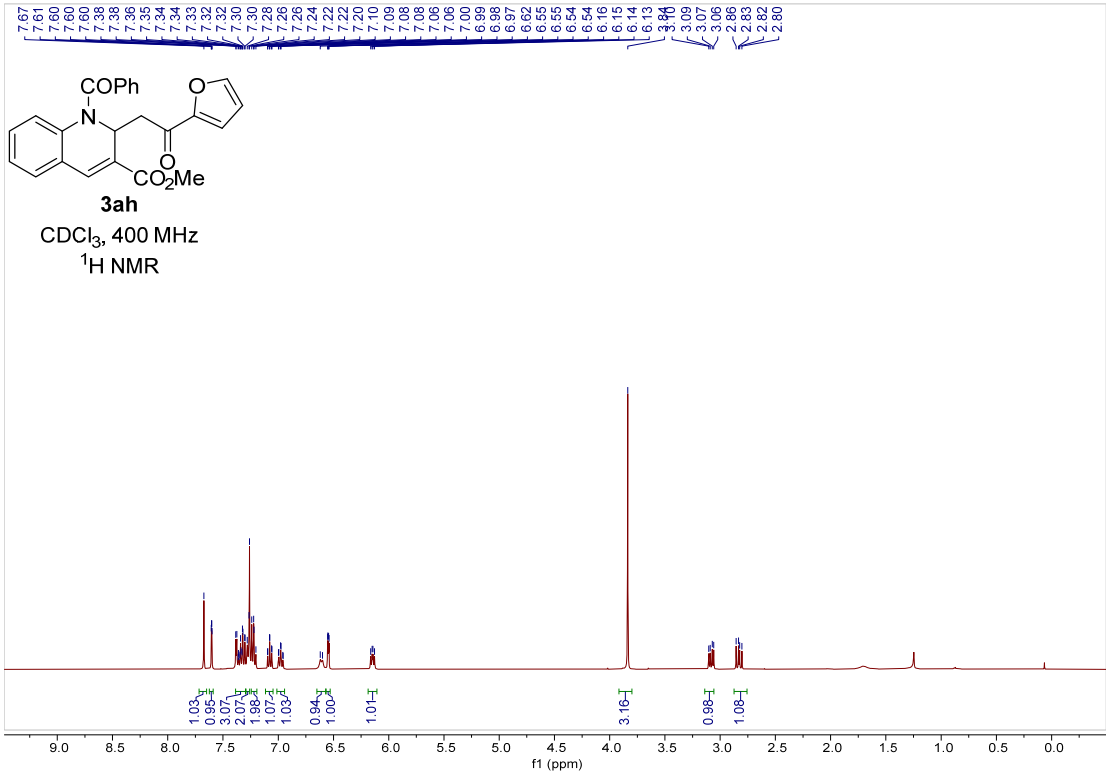
$CDCl_3$, 500 MHz

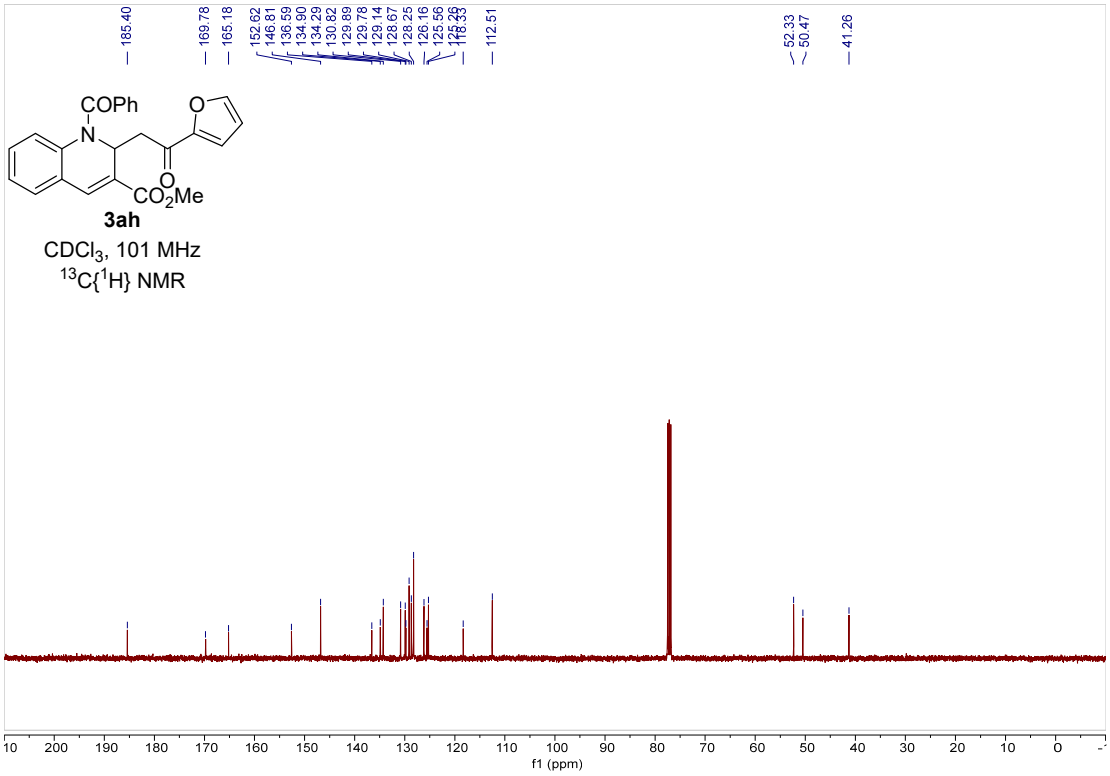
^1H NMR

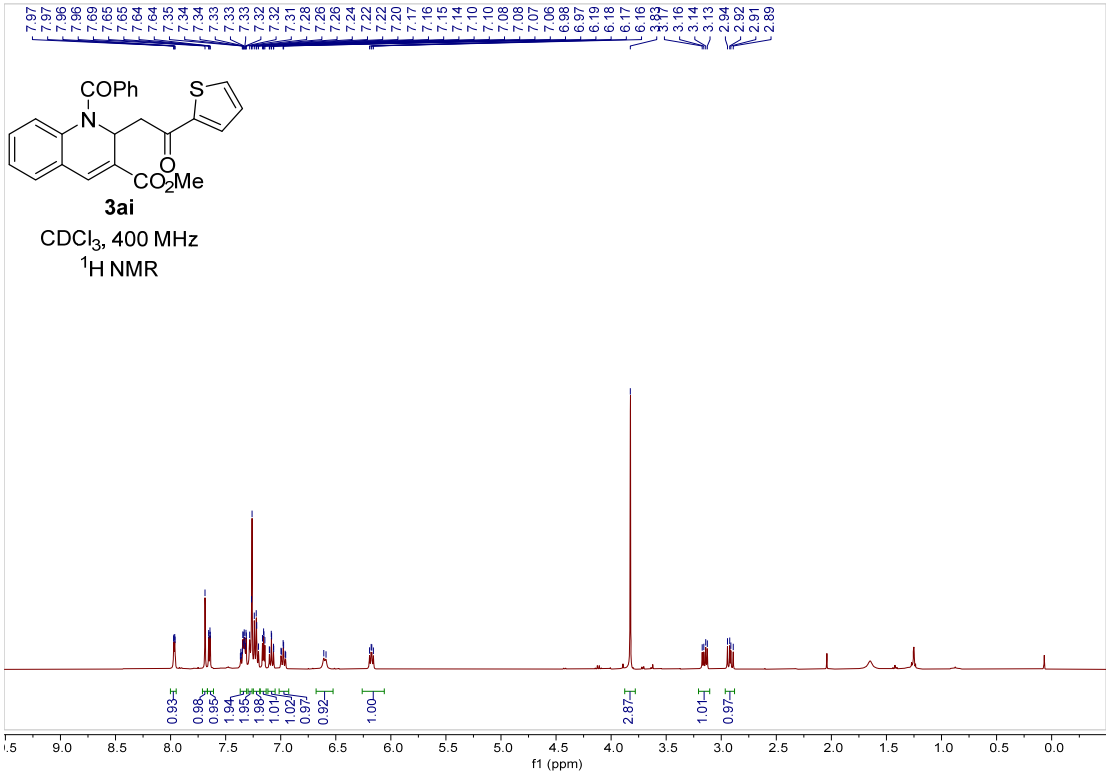

195.66
169.74
165.27
163.59
136.61
134.96
134.11
130.96
130.75
130.16
130.11
129.82
129.13
128.67
128.21
126.27
125.65
125.21
113.92
55.56
52.23
50.47
40.71
COPh
N
OMe
O
CO2Me
3af
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

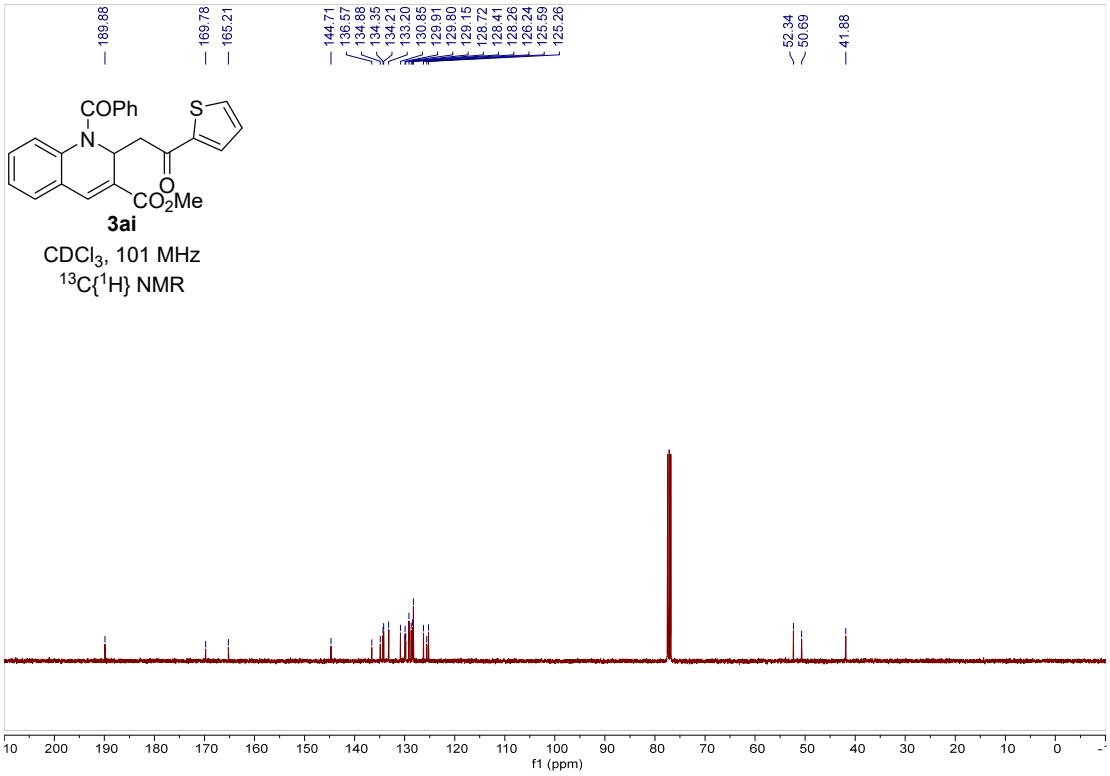

COPh
N
O
CO2Me
3ag
CDCl3, 500 MHz
1H NMR
0.99
1.01
1.01
2.03
0.98
1.02
1.01
2.12
2.11
2.06
1.03
1.01
0.92
1.00
3.05
1.02
1.02
f1 (ppm)


COPh
N
O
CO2Me
3ag
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)


COPh
N
O
O
CO2Me
3ah
CDCl3, 400 MHz
1H NMR
f1 (ppm)


185.40
169.78
165.18
152.62
146.81
136.59
134.90
134.29
130.82
129.89
129.78
129.14
128.67
128.25
126.16
125.56
112.51
52.33
50.47
41.26
COPh
N
O
O
CO2Me
3ah
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)

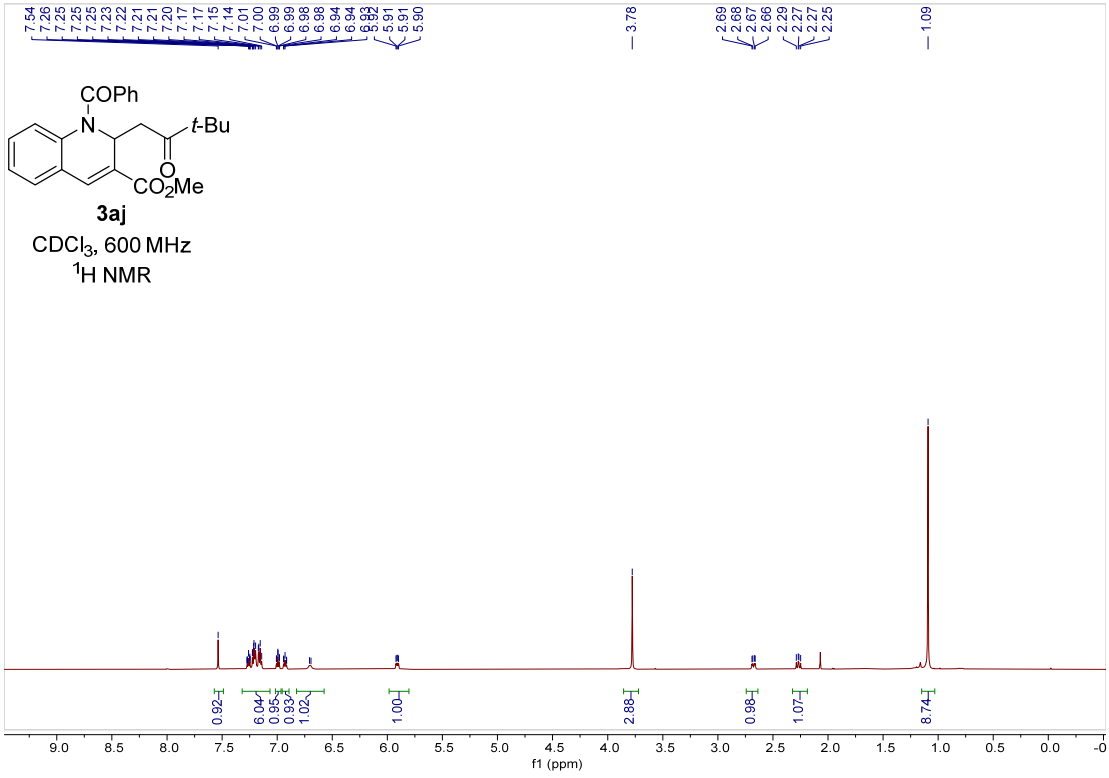

7.97
7.96
7.69
7.65
7.64
7.35
7.34
7.33
7.32
7.31
7.28
7.26
7.24
7.22
7.20
7.17
7.16
7.15
7.14
7.10
7.08
7.07
7.06
6.98
6.97
6.19
6.18
6.17
6.16
3.83
3.17
3.16
3.14
3.13
2.94
2.92
2.91
2.89
COPh
N
S
O
CO2Me
3ai
CDCl3, 400 MHz
1H NMR
0.93
0.98
0.95
1.94
1.95
1.98
1.01
1.02
0.97
0.92
1.00
2.87
1.01
0.97
f1 (ppm)



3ai

$CDCl_3$, 101 MHz

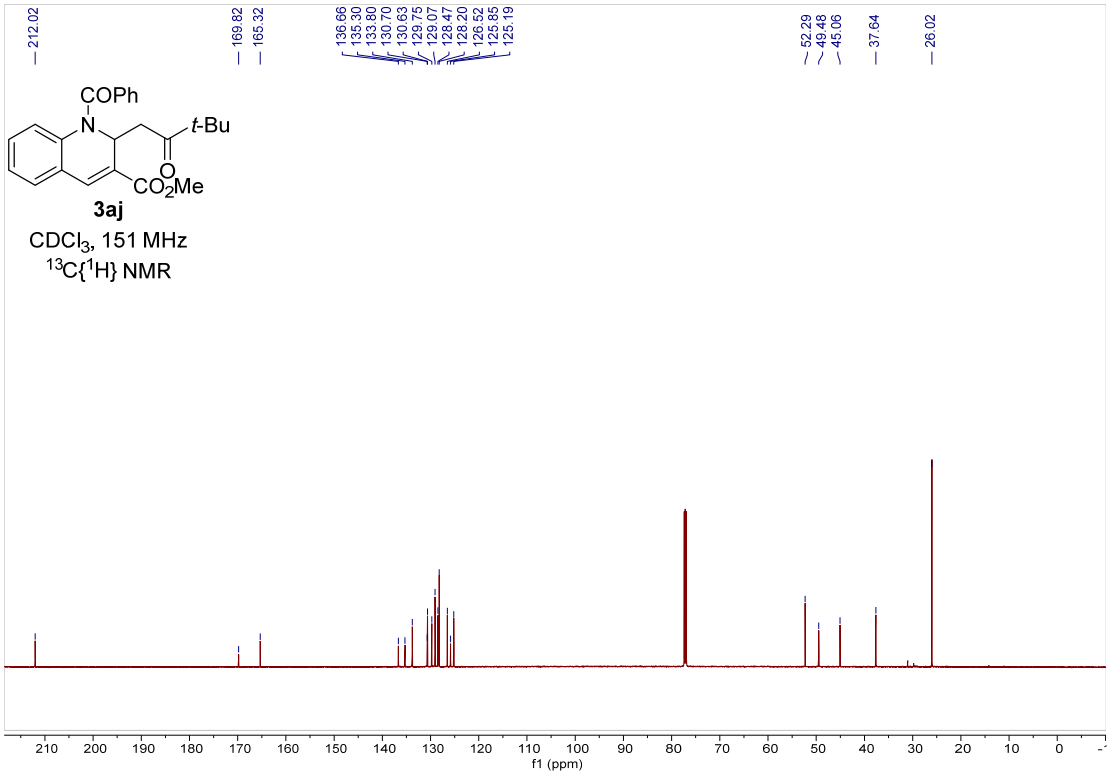
$^{13}C\{^1H\}$ NMR



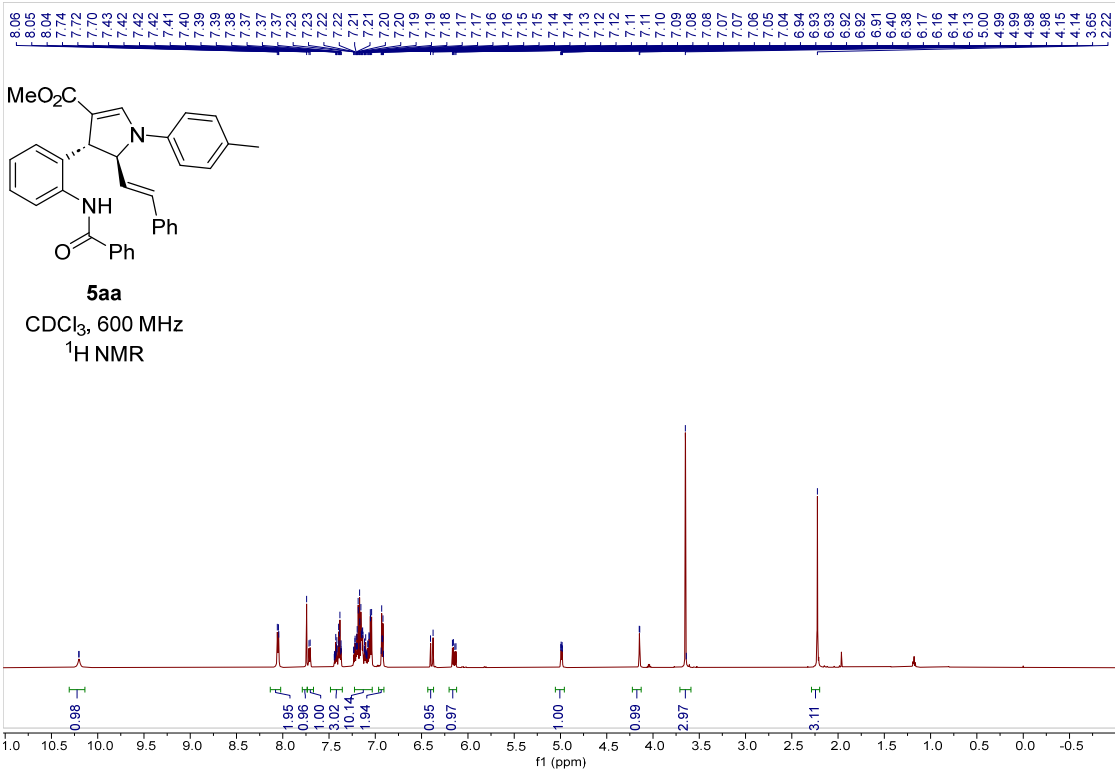
3aj

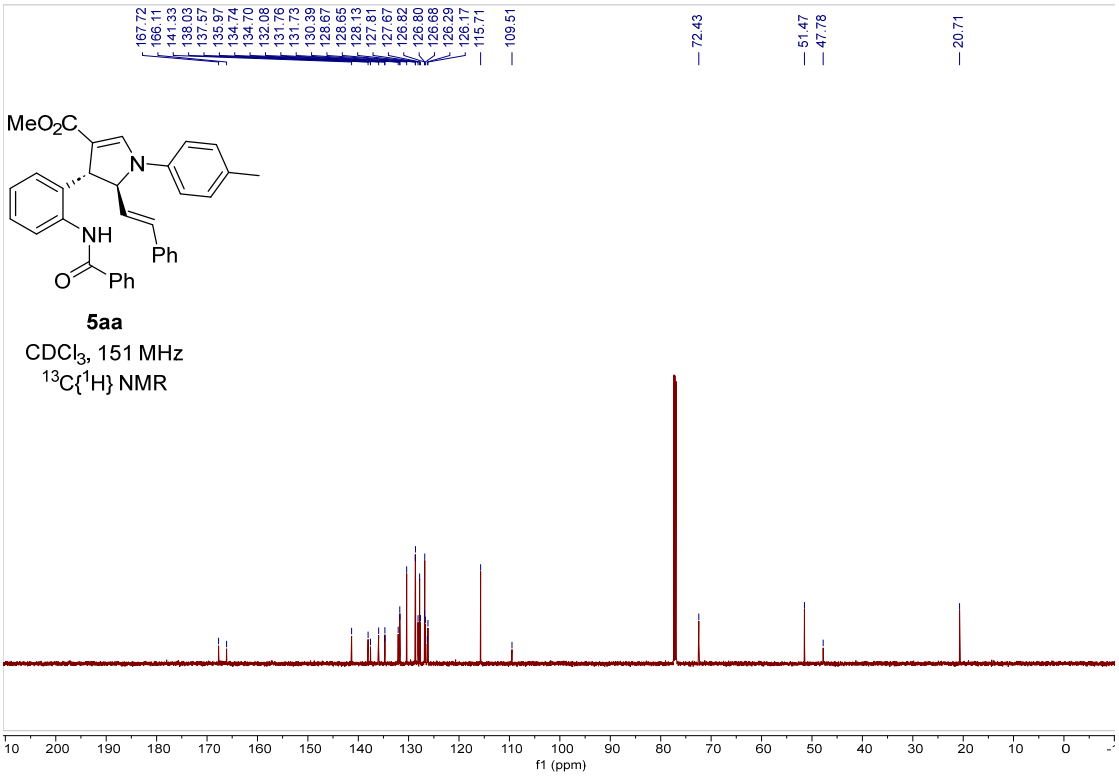
$CDCl_3$, 600 MHz

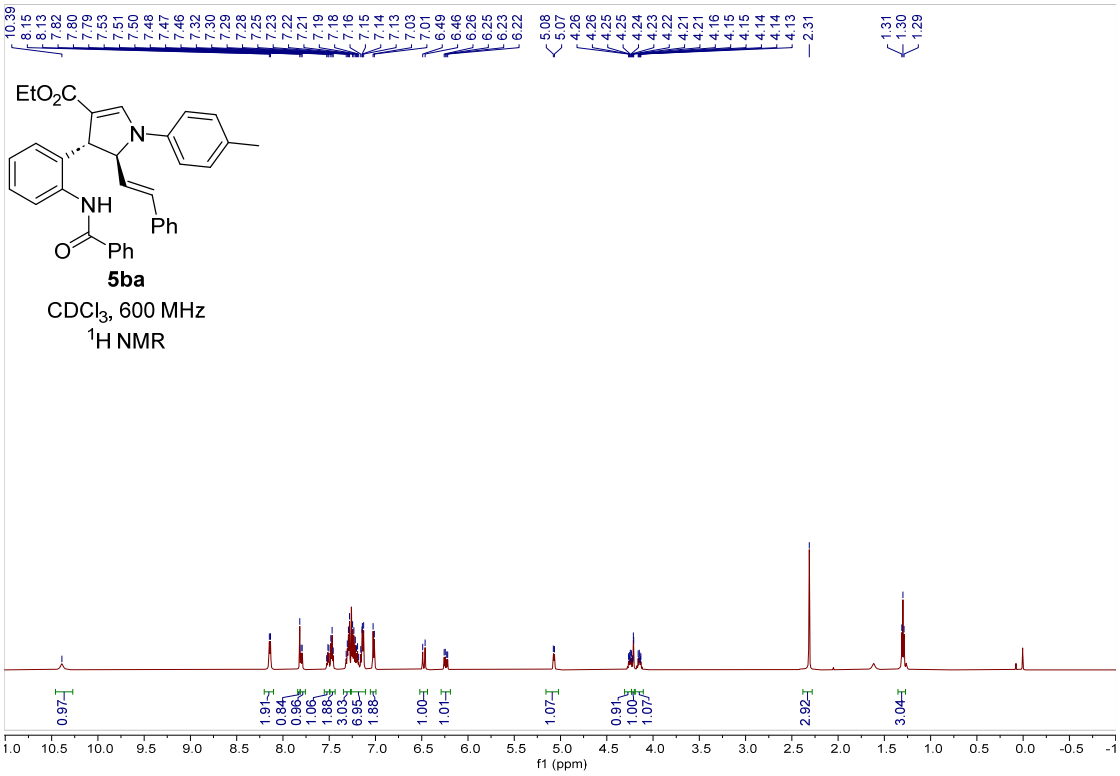
^1H NMR

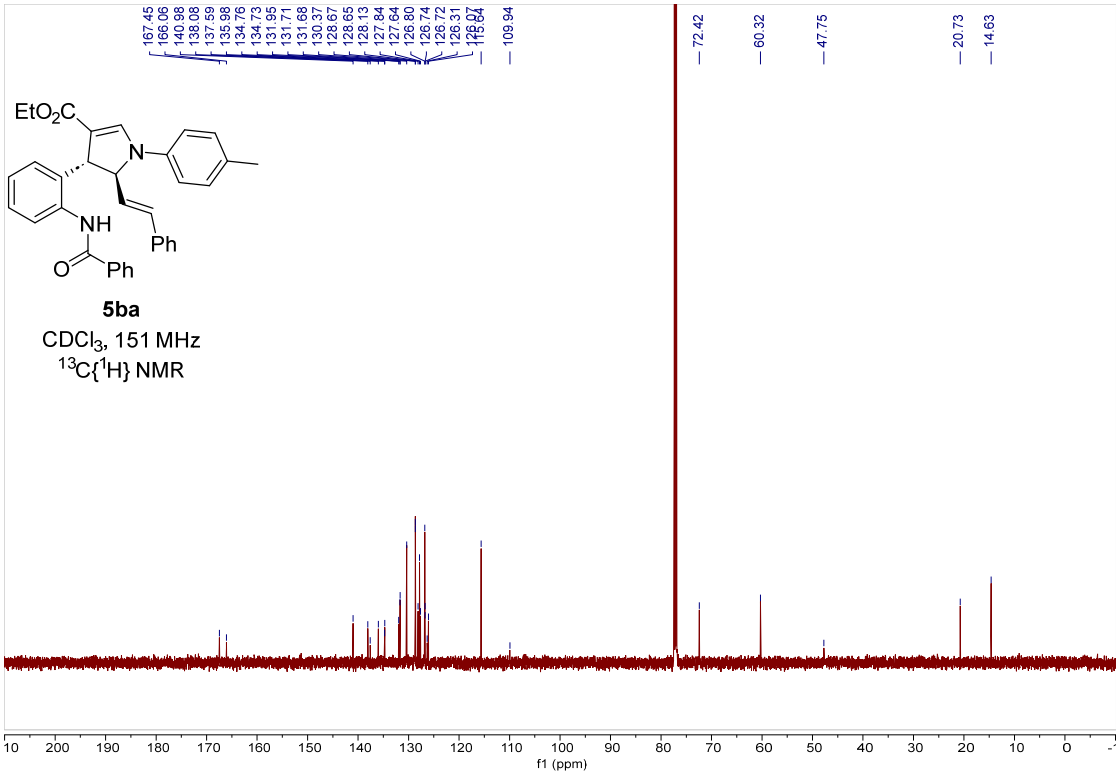

212.02
169.82
165.32
136.66
135.30
133.80
130.70
130.63
129.75
129.07
128.47
128.20
126.52
125.85
125.19
52.29
49.48
45.06
37.64
26.02
COPh
N
t-Bu
O
CO2Me
3aj
CDCl3, 151 MHz
13C{1H} NMR
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

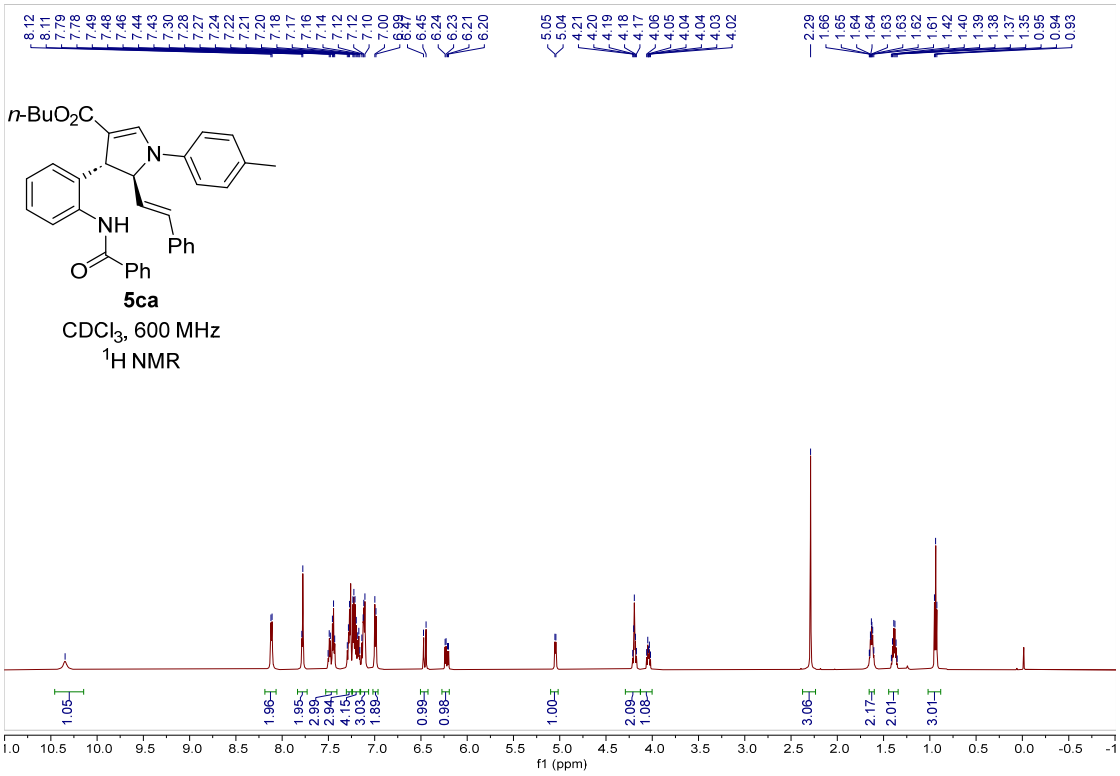
NMR spectra of compounds 5

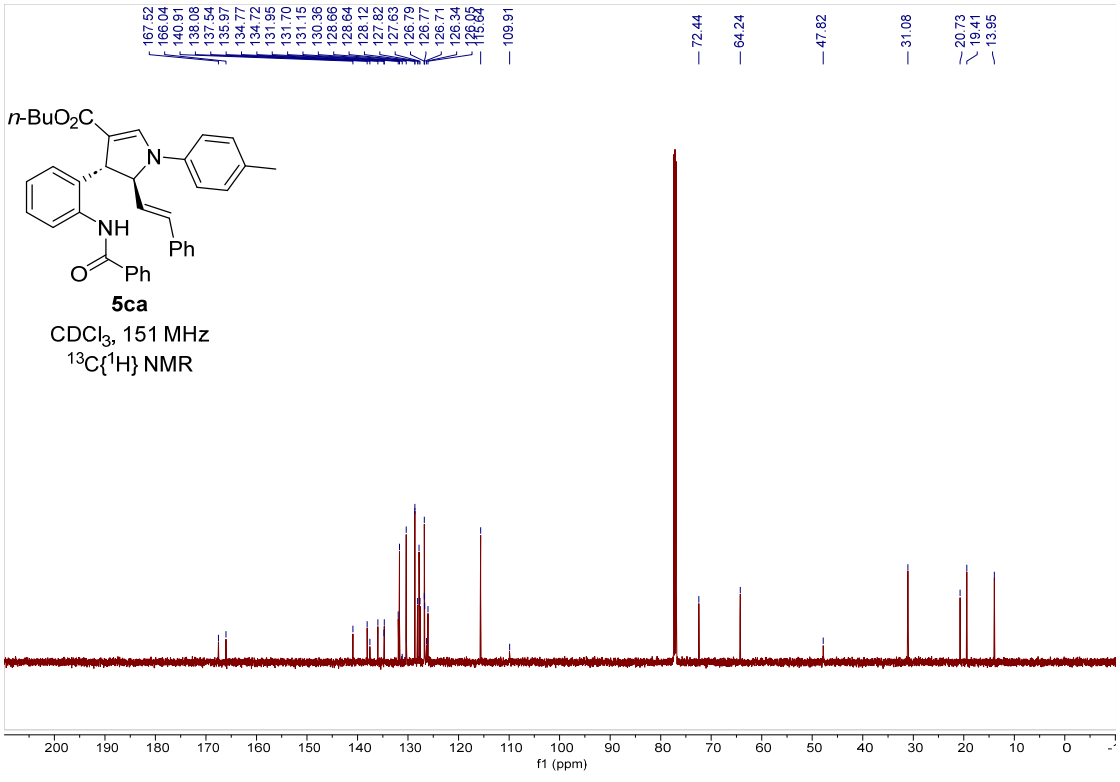


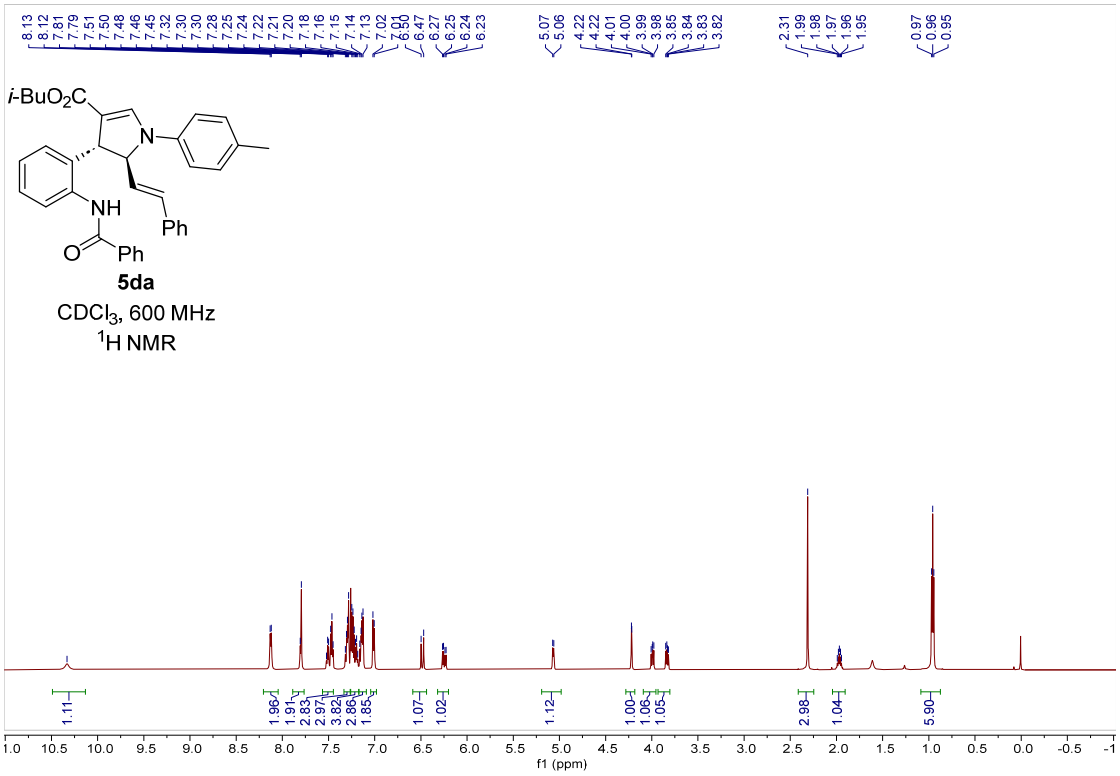


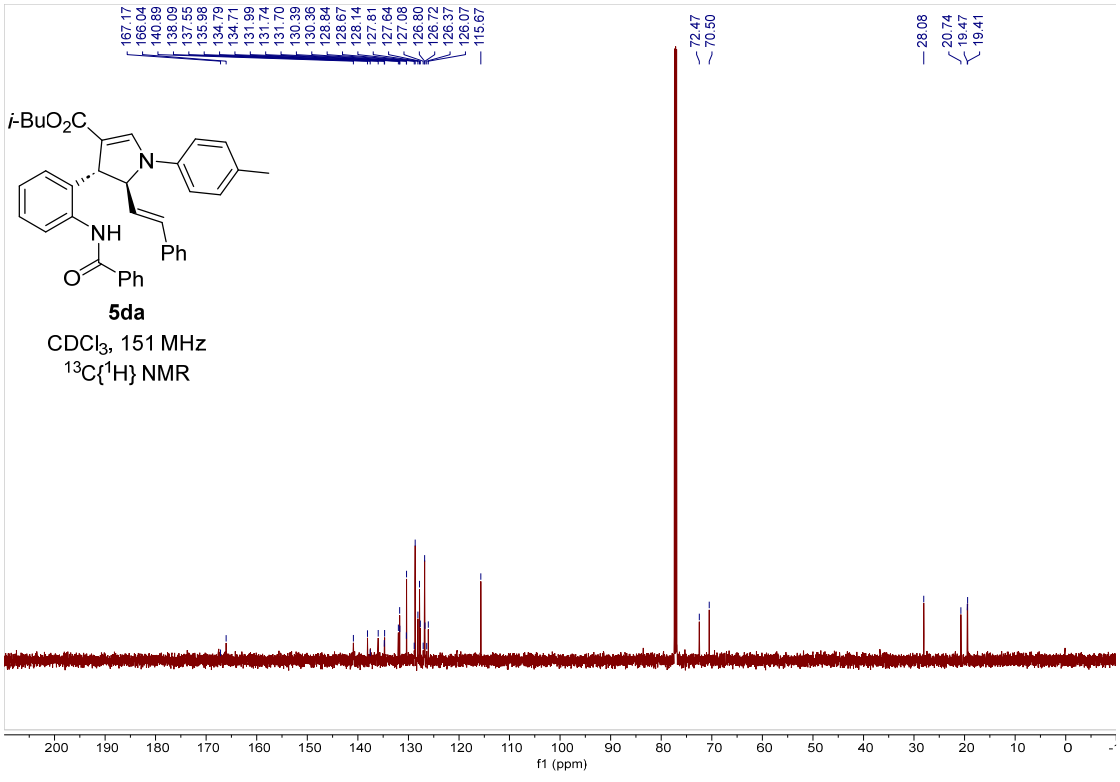

EtO2C
N
NH
Ph
O
Ph
5ba
CDCl3, 600 MHz
1H NMR
f1 (ppm)

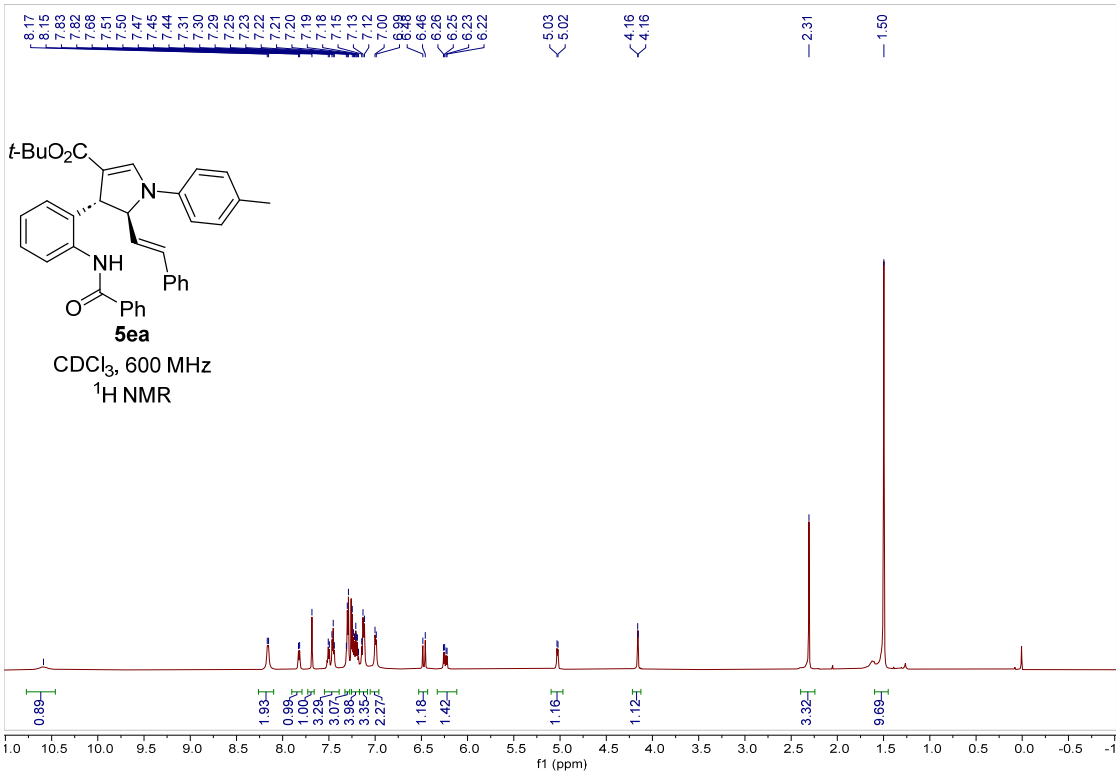

EtO2C
N
NH
Ph
O
Ph
5ba
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

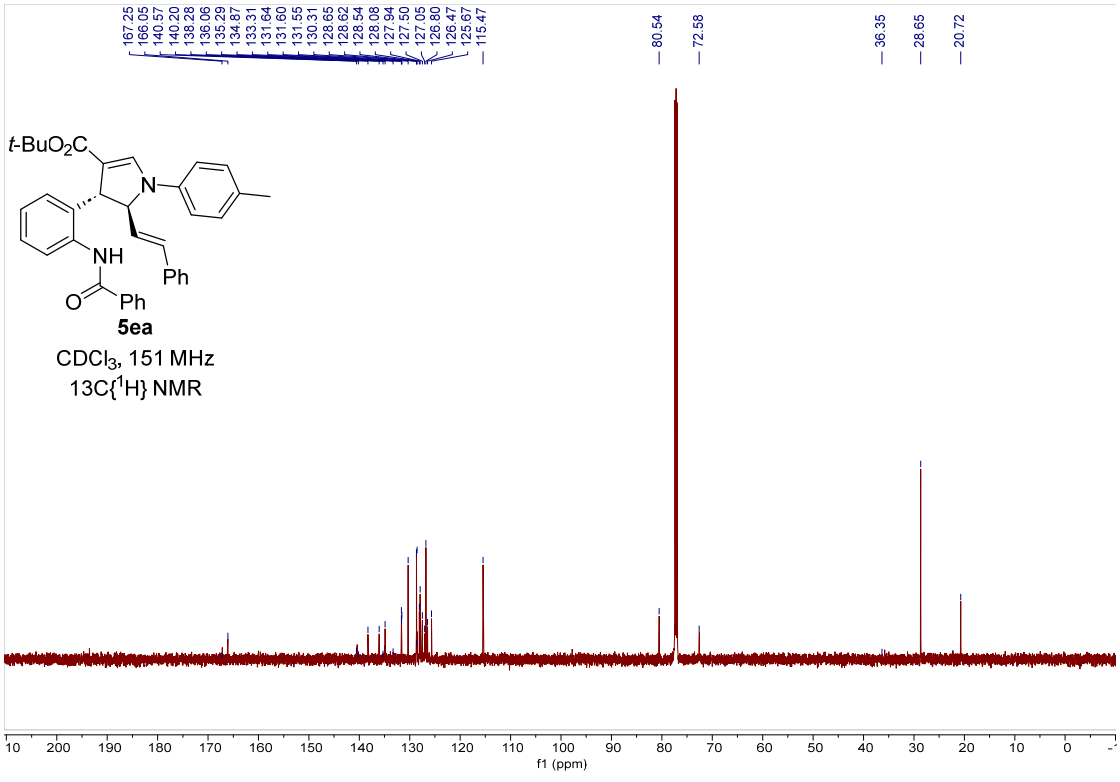

8.12
8.11
7.79
7.78
7.49
7.48
7.46
7.44
7.43
7.30
7.28
7.27
7.24
7.22
7.21
7.20
7.18
7.17
7.16
7.14
7.12
7.12
7.10
7.00
6.99
6.97
6.45
6.24
6.23
6.21
6.20
5.05
5.04
4.21
4.20
4.19
4.18
4.17
4.06
4.05
4.04
4.04
4.03
4.02
2.29
1.66
1.65
1.64
1.64
1.63
1.63
1.62
1.61
1.42
1.40
1.39
1.38
1.37
1.35
0.95
0.94
0.93
n-BuO2C
N
NH
Ph
O
Ph
5ca
CDCl3, 600 MHz
1H NMR
1.05
1.96
1.95
2.99
2.94
4.15
3.03
1.89
0.99
0.98
1.00
2.09
1.08
3.06
2.17
2.01
3.01
f1 (ppm)

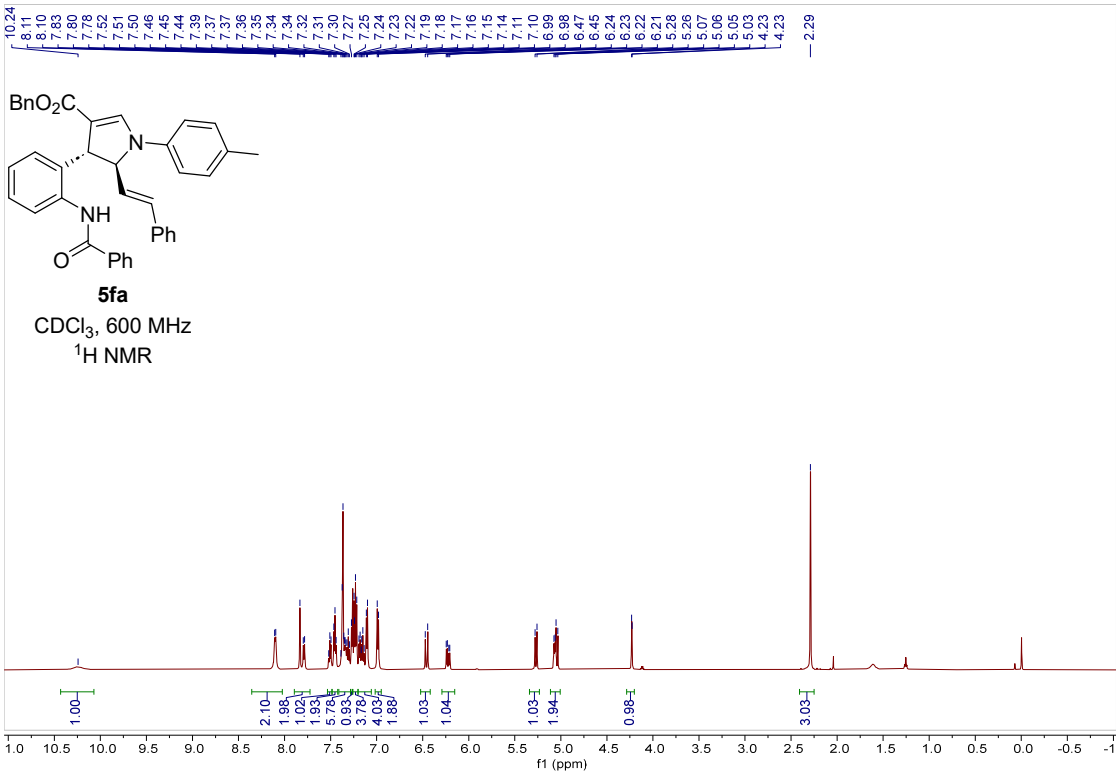

167.52
166.04
140.91
138.08
137.54
135.97
134.77
134.72
131.95
131.70
131.15
130.36
128.66
128.64
128.12
127.82
127.63
126.79
126.77
126.71
126.34
109.91
72.44
64.24
47.82
31.08
20.73
19.41
13.95
n-BuO2C
N
NH
Ph
O
Ph
5ca
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

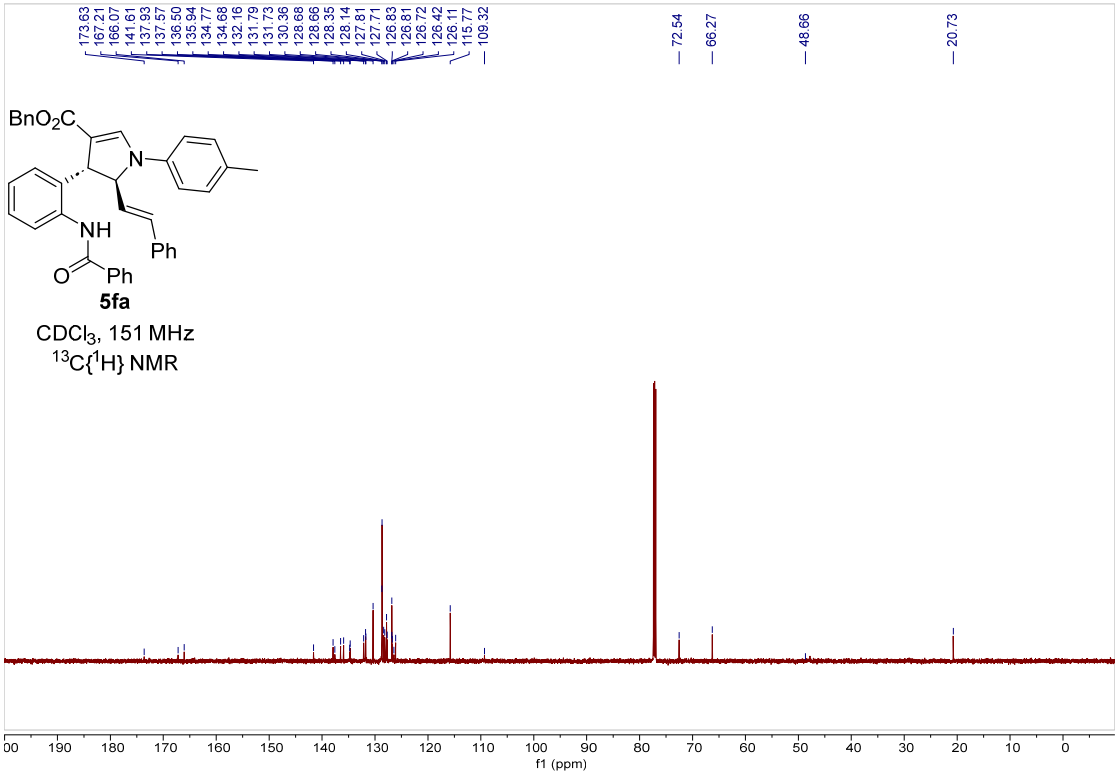

i-BuO2C
N
NH
Ph
O
Ph
5da
CDCl3, 600 MHz
1H NMR
f1 (ppm)

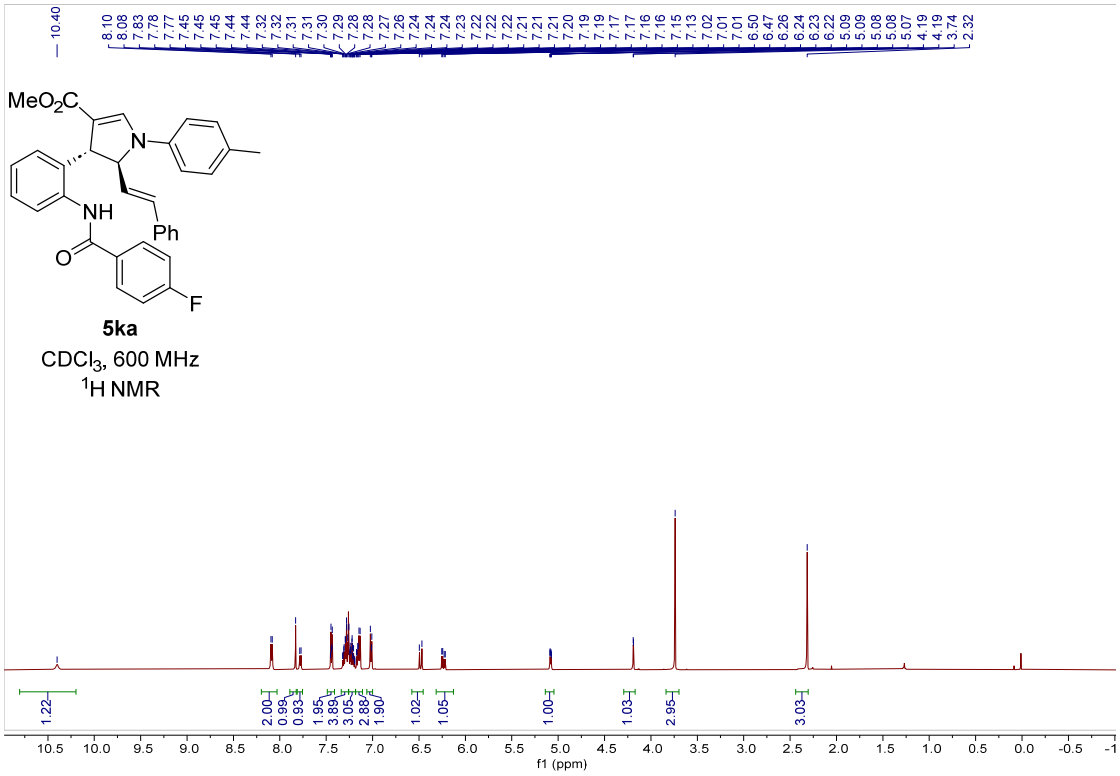

i-BuO2C
N
NH
Ph
O
Ph
5da
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

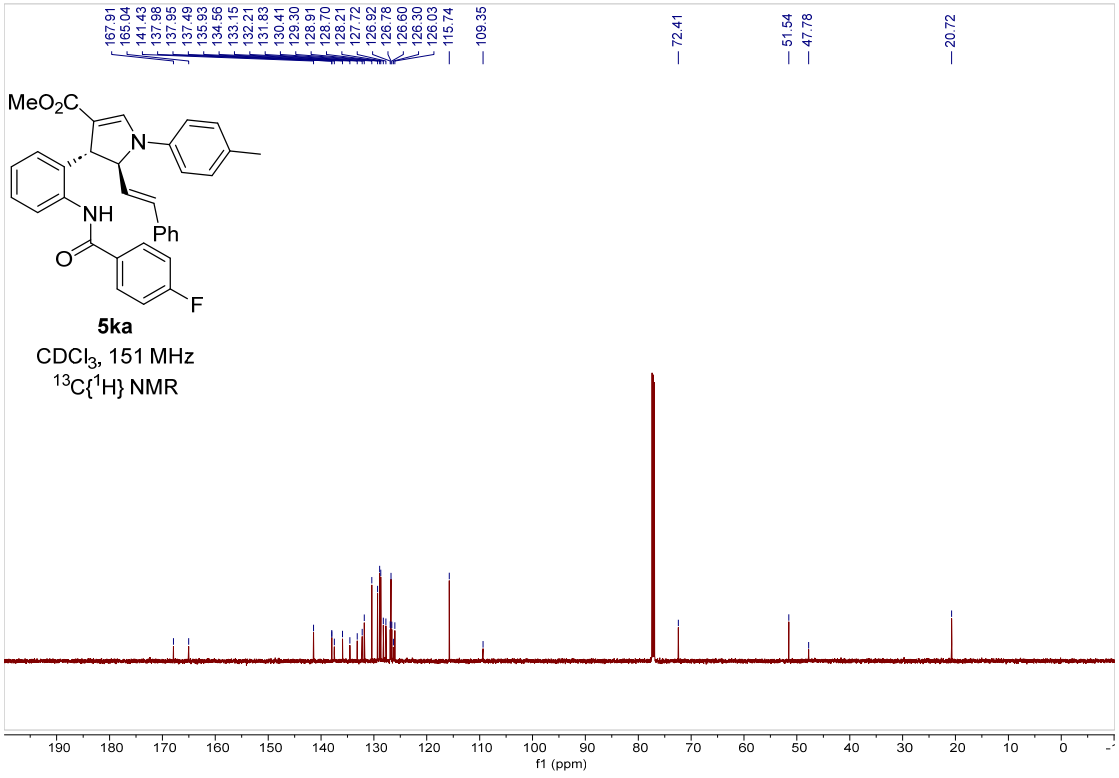

8.17
8.15
7.83
7.82
7.68
7.51
7.50
7.47
7.45
7.44
7.31
7.30
7.29
7.25
7.23
7.22
7.21
7.20
7.19
7.18
7.15
7.13
7.12
7.00
6.98
6.46
6.26
6.25
6.23
6.22
5.03
5.02
4.16
4.16
2.31
1.50
t-BuO2C
N
NH
Ph
O
Ph
5ea
CDCl3, 600 MHz
1H NMR
0.89
1.93
0.99
1.00
3.29
3.07
3.98
3.35
2.27
1.18
1.42
1.16
1.12
3.32
9.69
f1 (ppm)

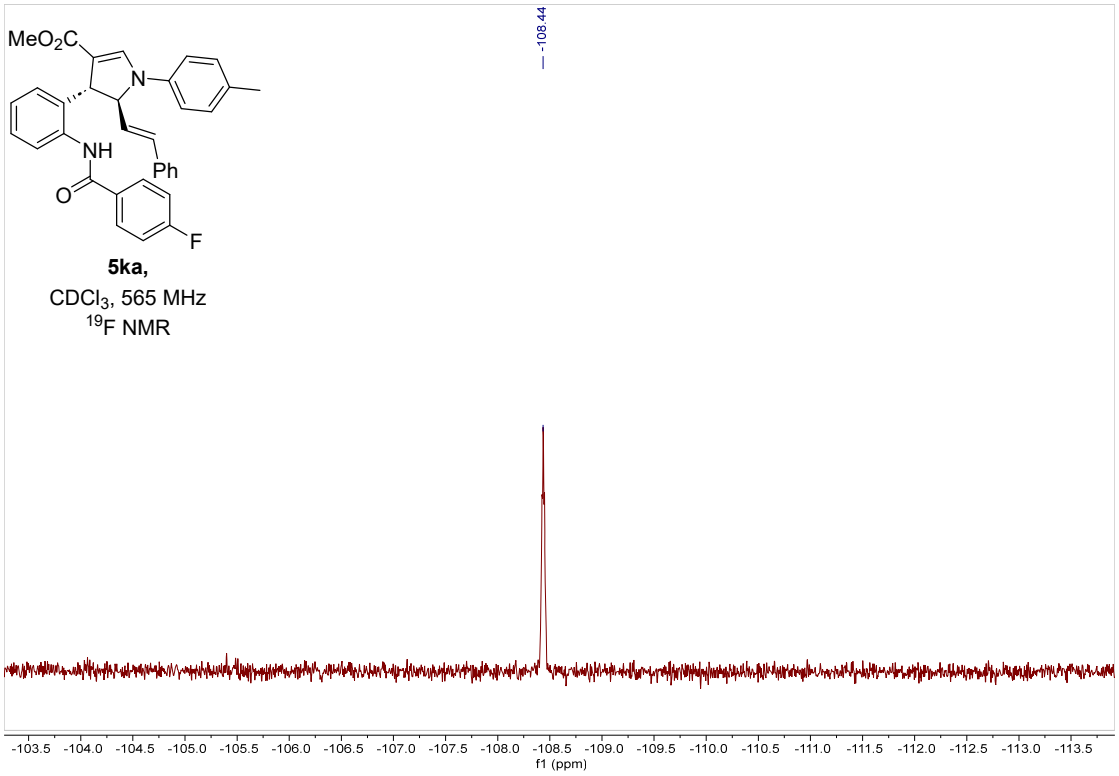

167.25
166.05
140.57
140.20
138.28
136.06
135.29
134.87
133.31
131.64
131.60
131.55
130.31
128.65
128.62
128.54
128.08
127.94
127.50
127.05
126.80
128.47
125.67
115.47
80.54
72.58
36.35
28.65
20.72
t-BuO2C
N
NH
Ph
O
Ph
5ea
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)


BnO2C
N
NH
Ph
O
Ph
5fa
CDCl3, 600 MHz
1H NMR
f1 (ppm)


BnO2C
N
NH
Ph
O
Ph
5fa
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)


MeO2C
N
NH
Ph
O
F
5ka
CDCl3, 600 MHz
1H NMR
f1 (ppm)

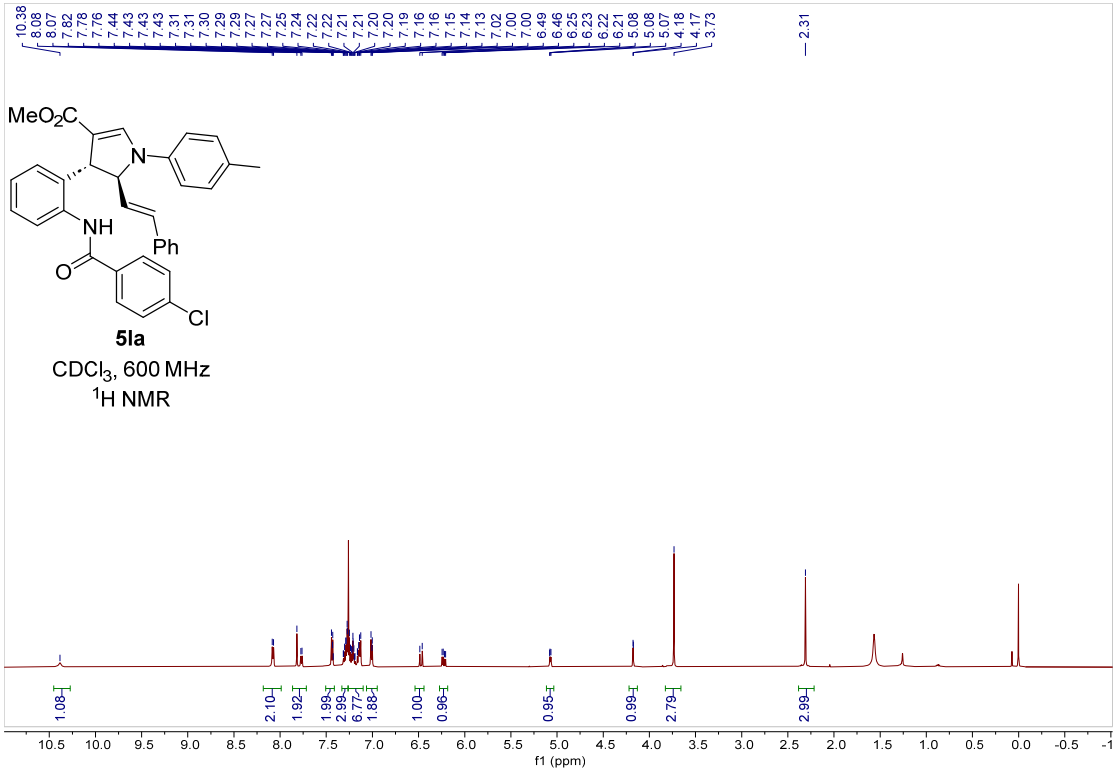

MeO2C
N
NH
Ph
O
F
5ka
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)



5ka,

$CDCl_3$, 565 MHz

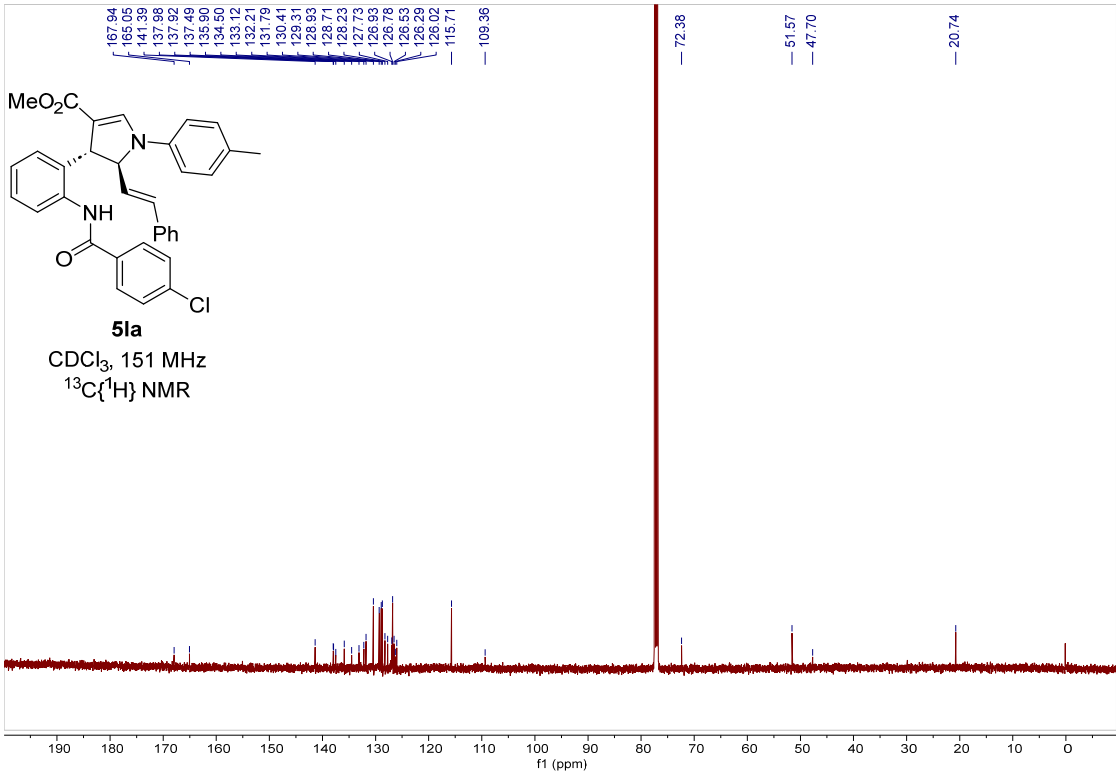
^{19}F NMR

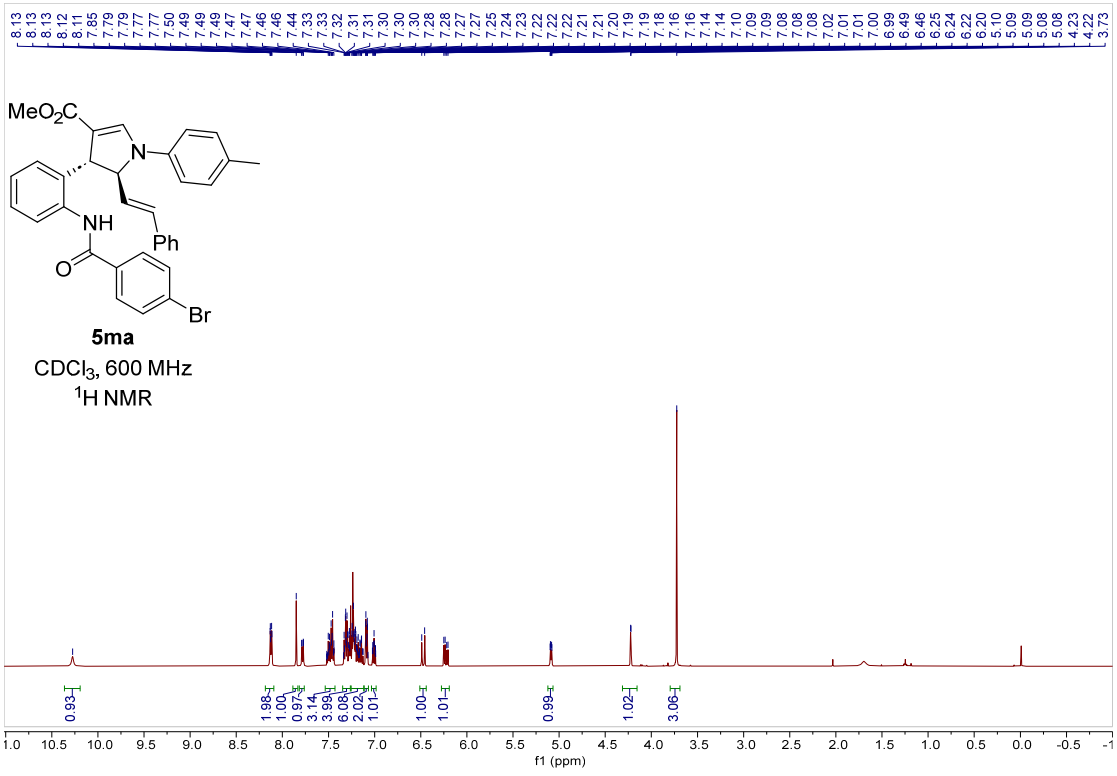


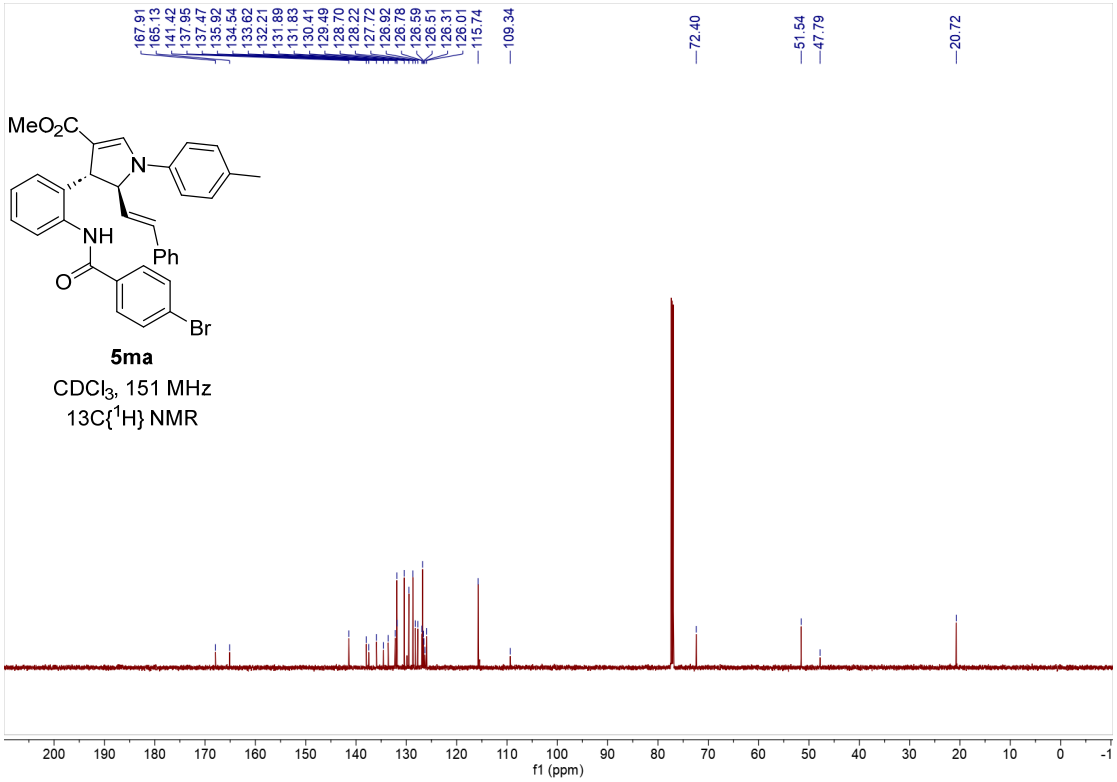
5la

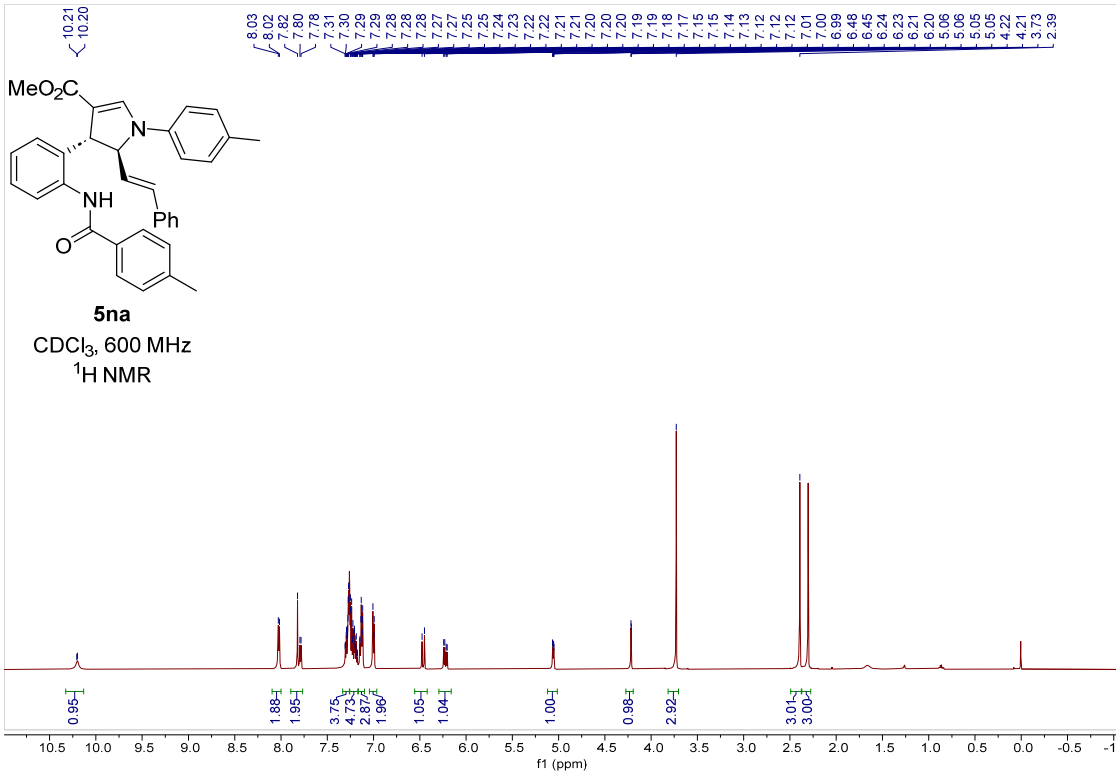
$CDCl_3$, 600 MHz

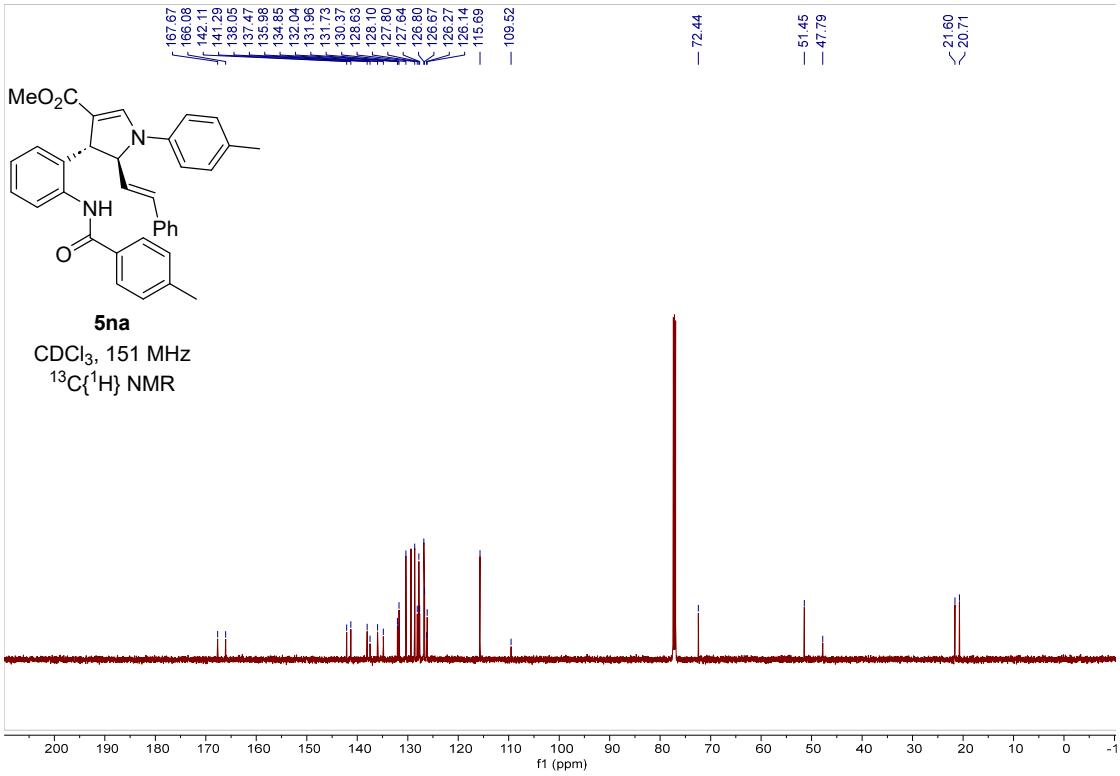
^{1}H NMR

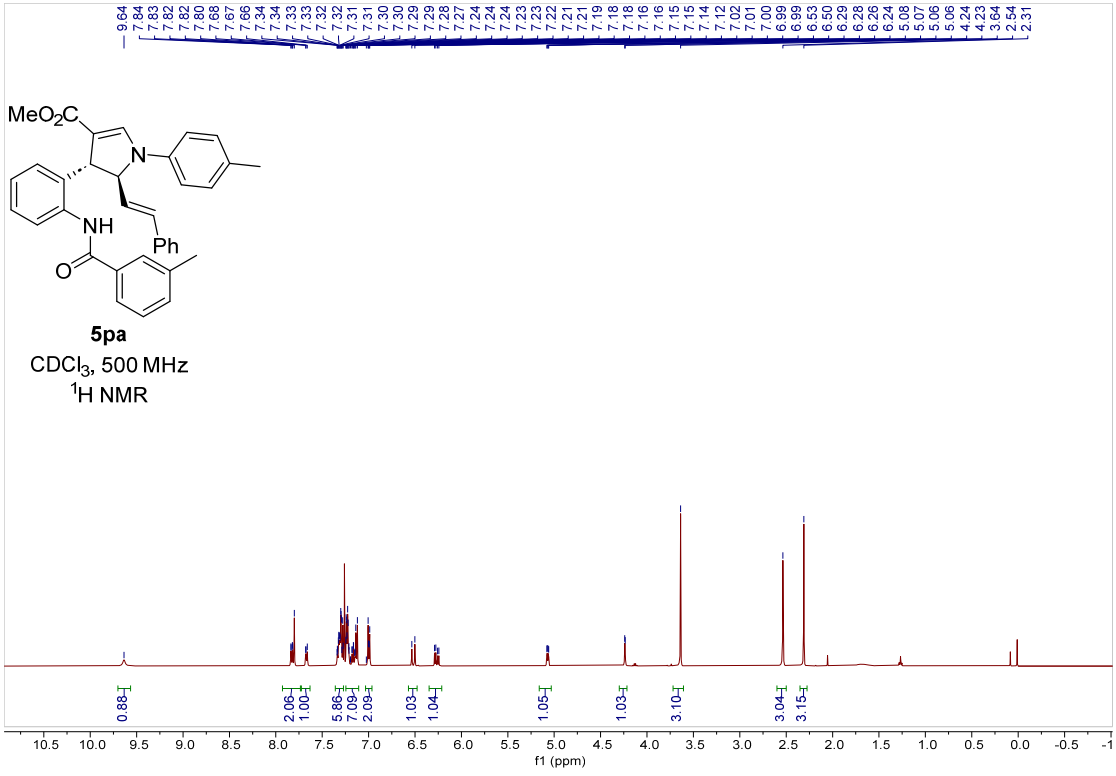

MeO2C
N
NH
Ph
O
Cl
5la
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

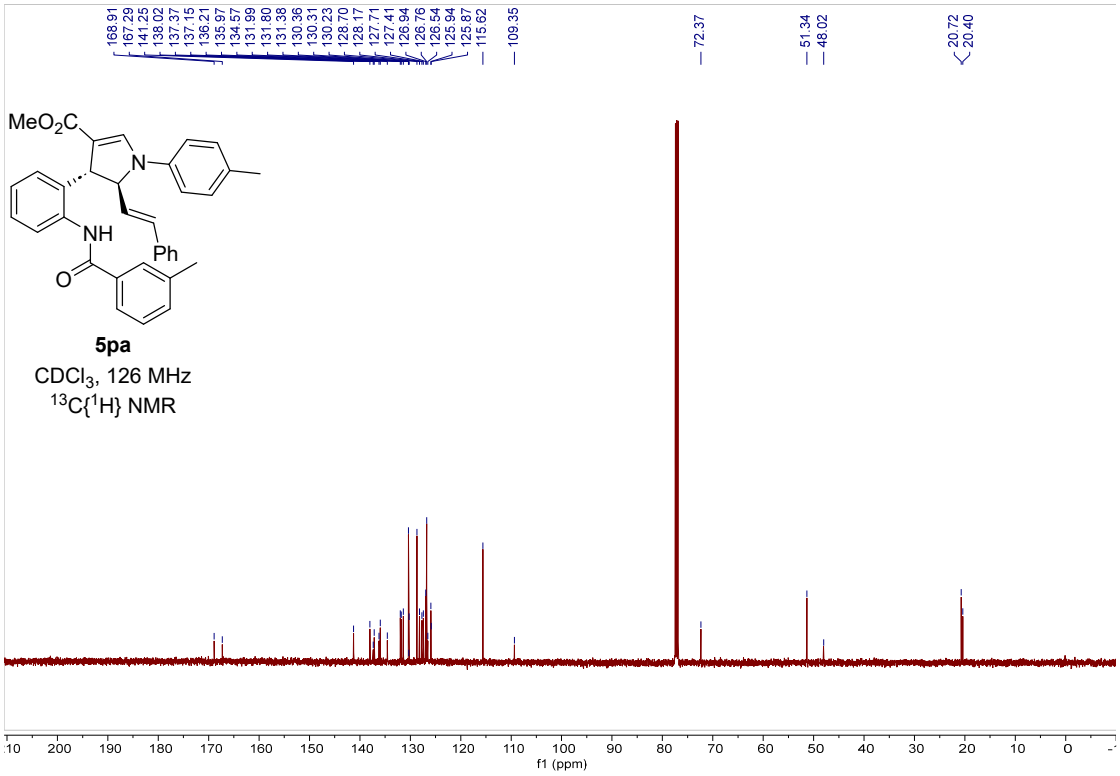

MeO2C
N
NH
Ph
O
Br
5ma
CDCl3, 600 MHz
1H NMR
f1 (ppm)

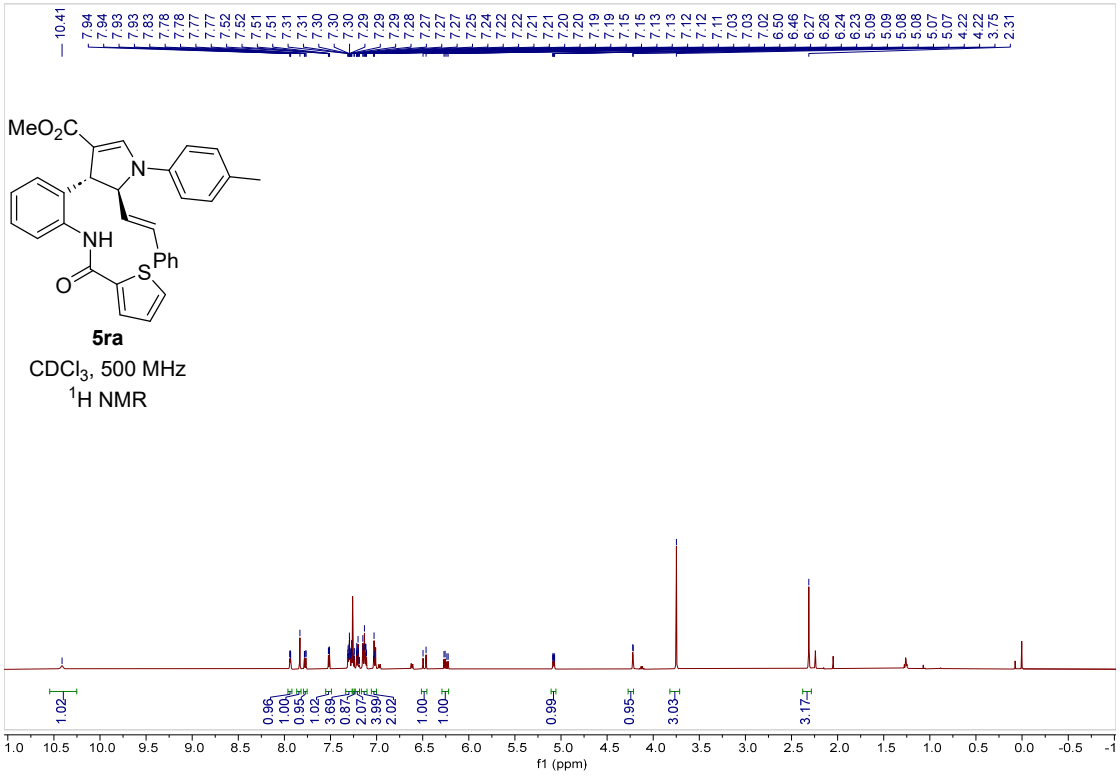

MeO2C
N
NH
Ph
O
Br
5ma
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

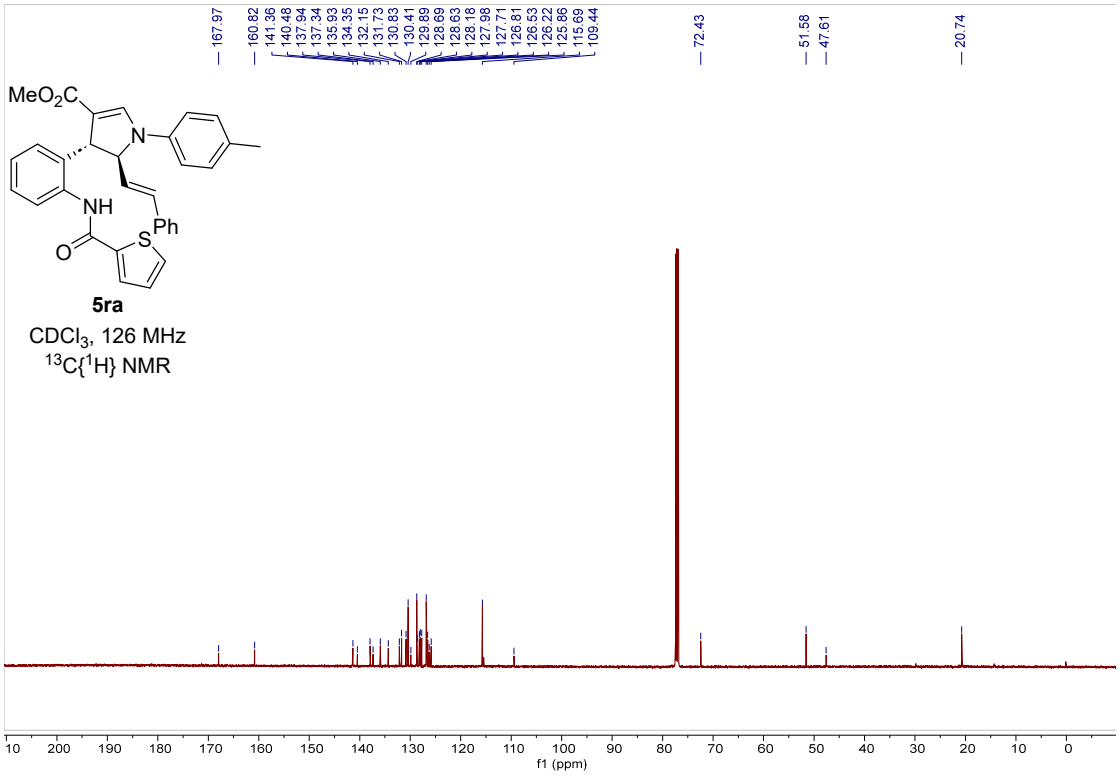

MeO2C
N
NH
Ph
O
5na
CDCl3, 600 MHz
1H NMR
f1 (ppm)

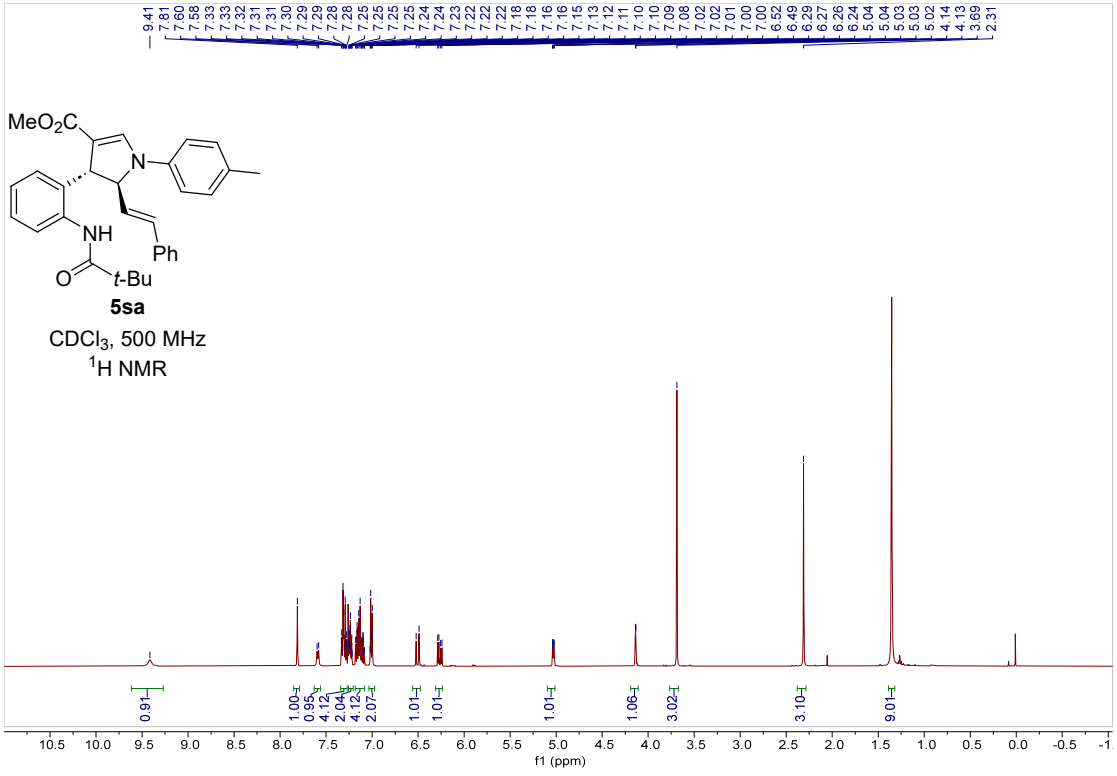

MeO2C
N
NH
Ph
O
5na
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

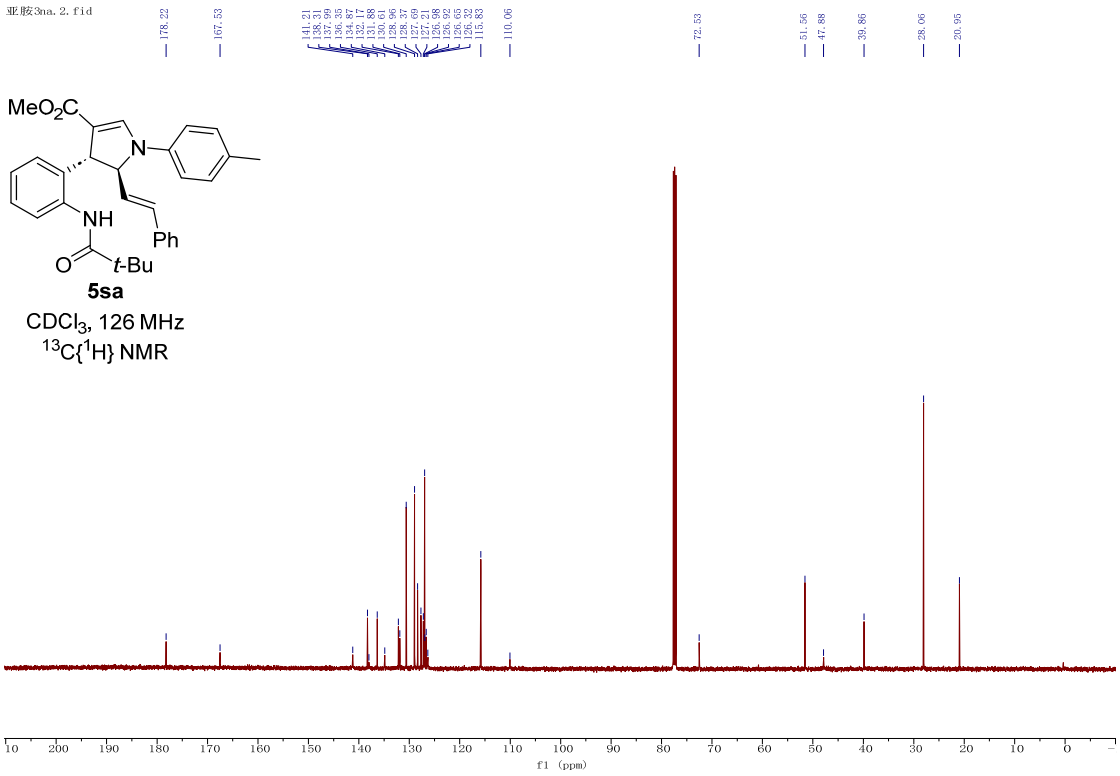

MeO2C
N
NH
Ph
O
5pa
CDCl3, 500 MHz
1H NMR
f1 (ppm)

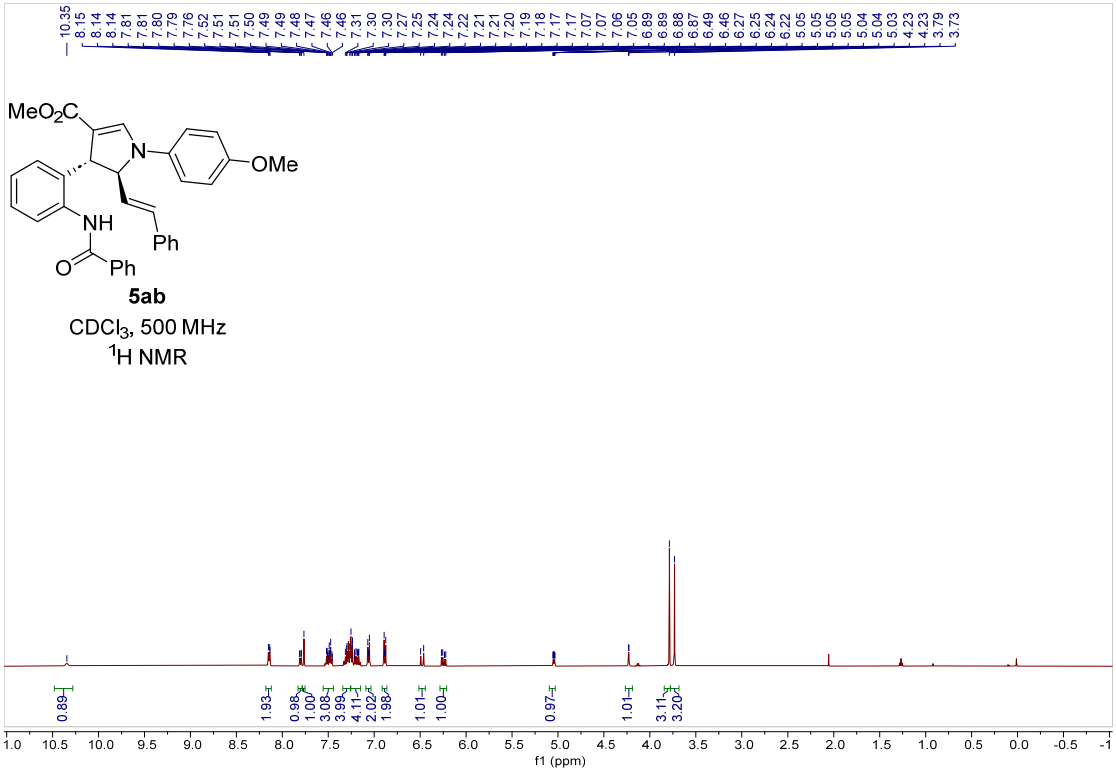

MeO2C
N
NH
Ph
O
5pa
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

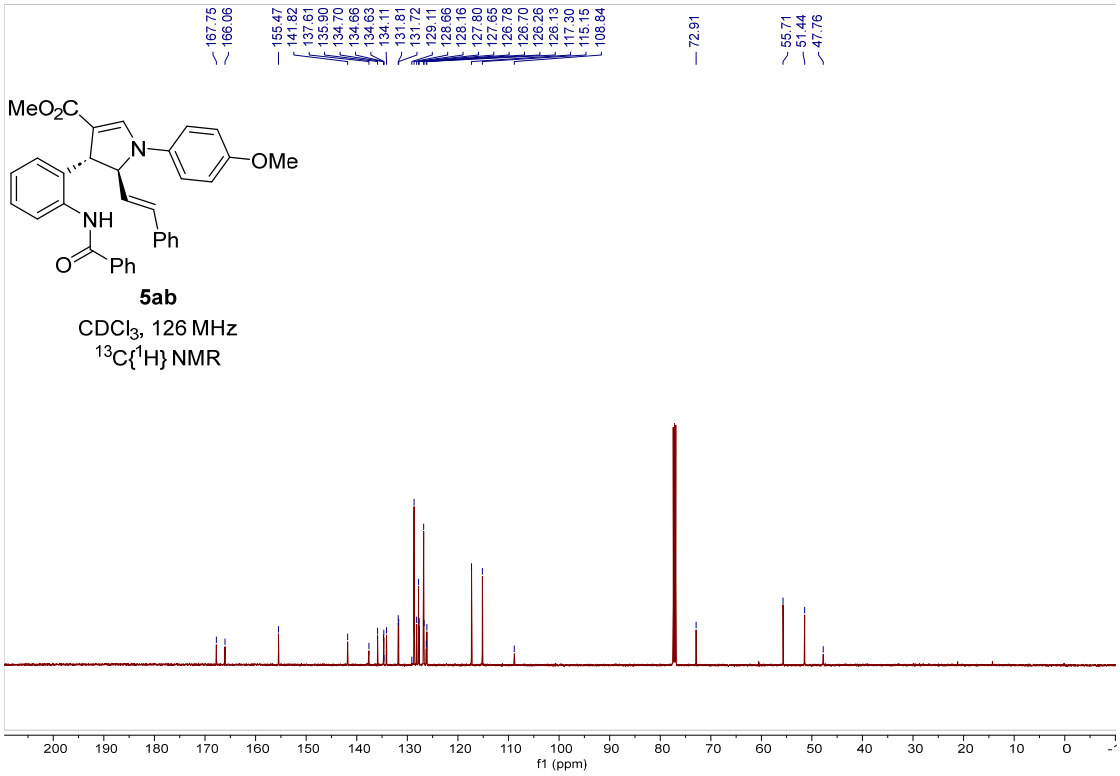

MeO2C
N
NH
Ph
S
O
5ra
CDCl3, 500 MHz
1H NMR
f1 (ppm)

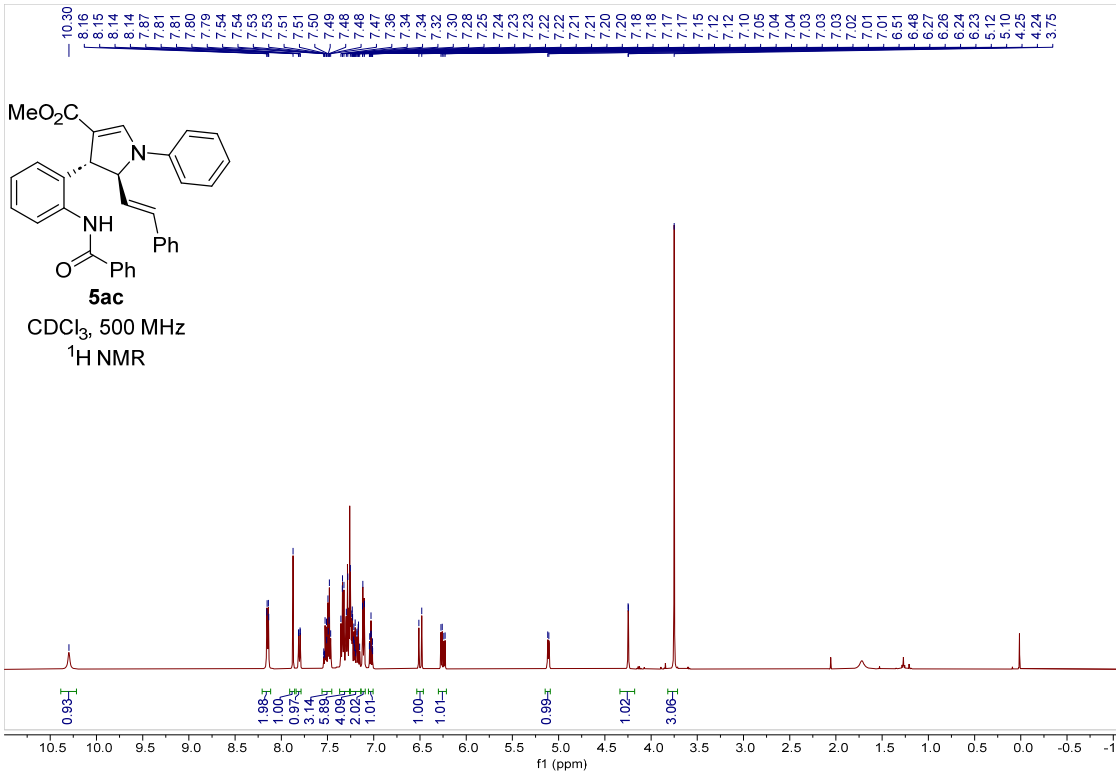

MeO2C
N
NH
Ph
O
S
5ra
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

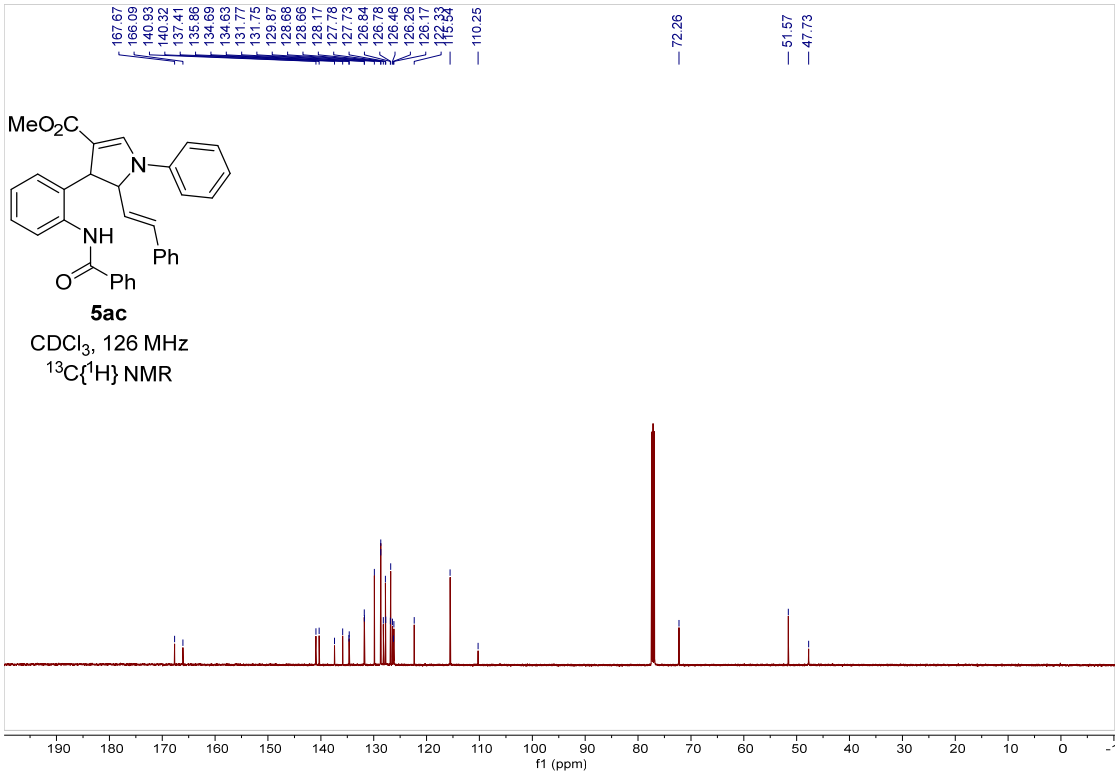

MeO2C
N
NH
Ph
O
t-Bu
5sa
CDCl3, 500 MHz
1H NMR
f1 (ppm)

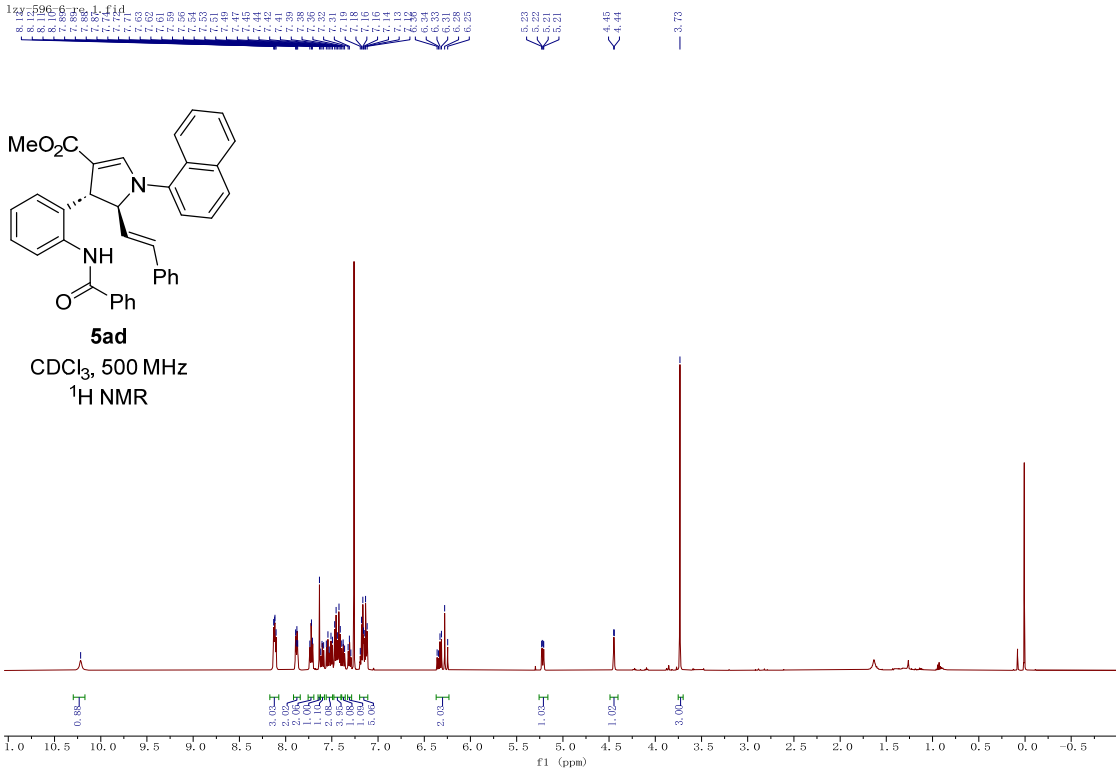

亚胺3na. 2. fid
MeO2C
N
NH
Ph
O
t-Bu
5sa
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

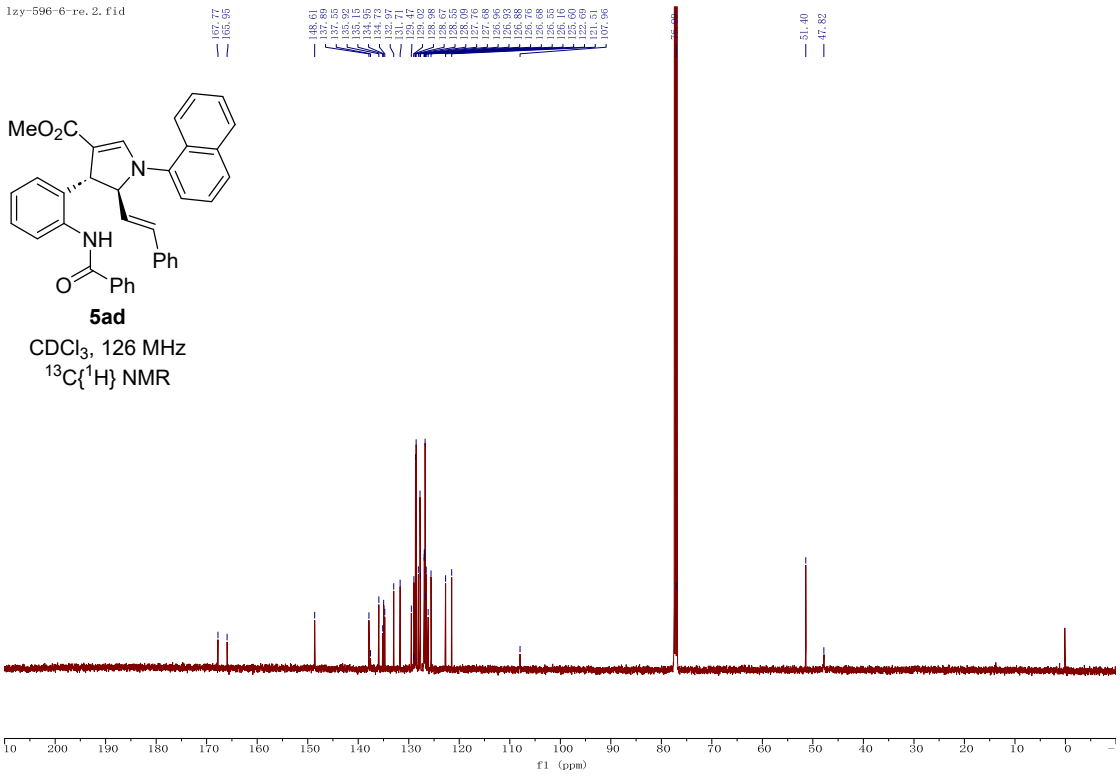

MeO2C
N
OMe
NH
Ph
O
Ph
5ab
CDCl3, 500 MHz
1H NMR
f1 (ppm)

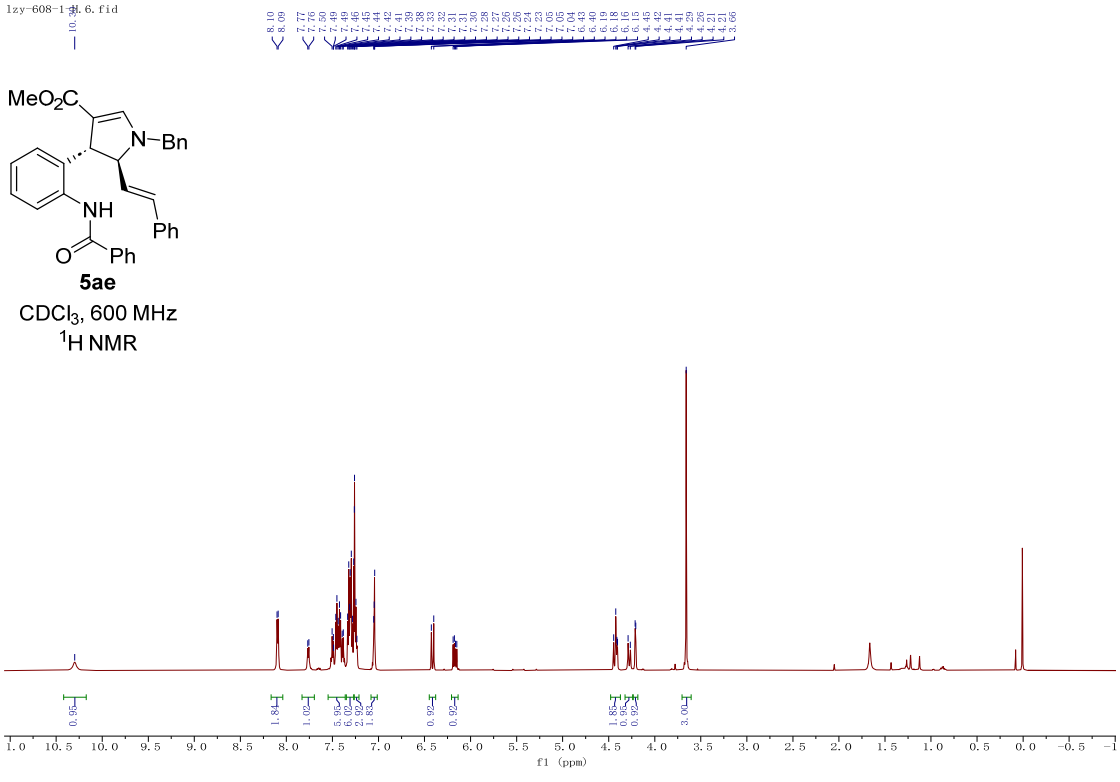

MeO2C
N
OMe
NH
Ph
O
Ph
5ab
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

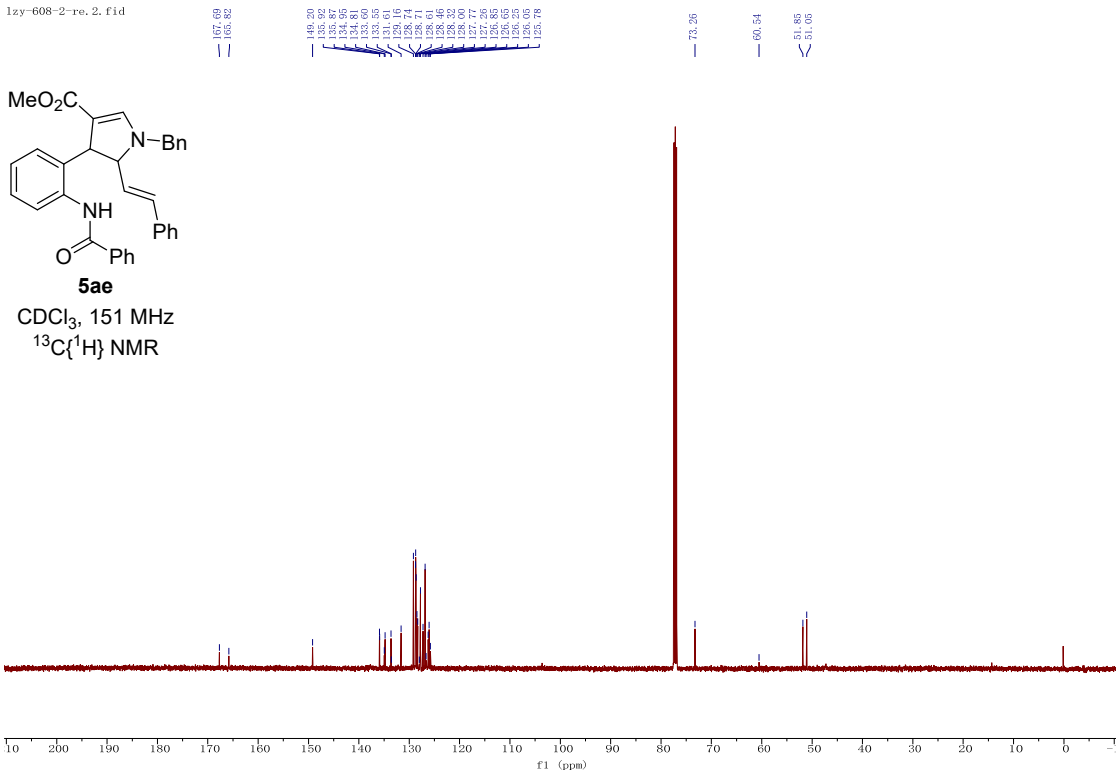

MeO2C
N
NH
Ph
O
Ph
5ac
CDCl3, 500 MHz
1H NMR
f1 (ppm)

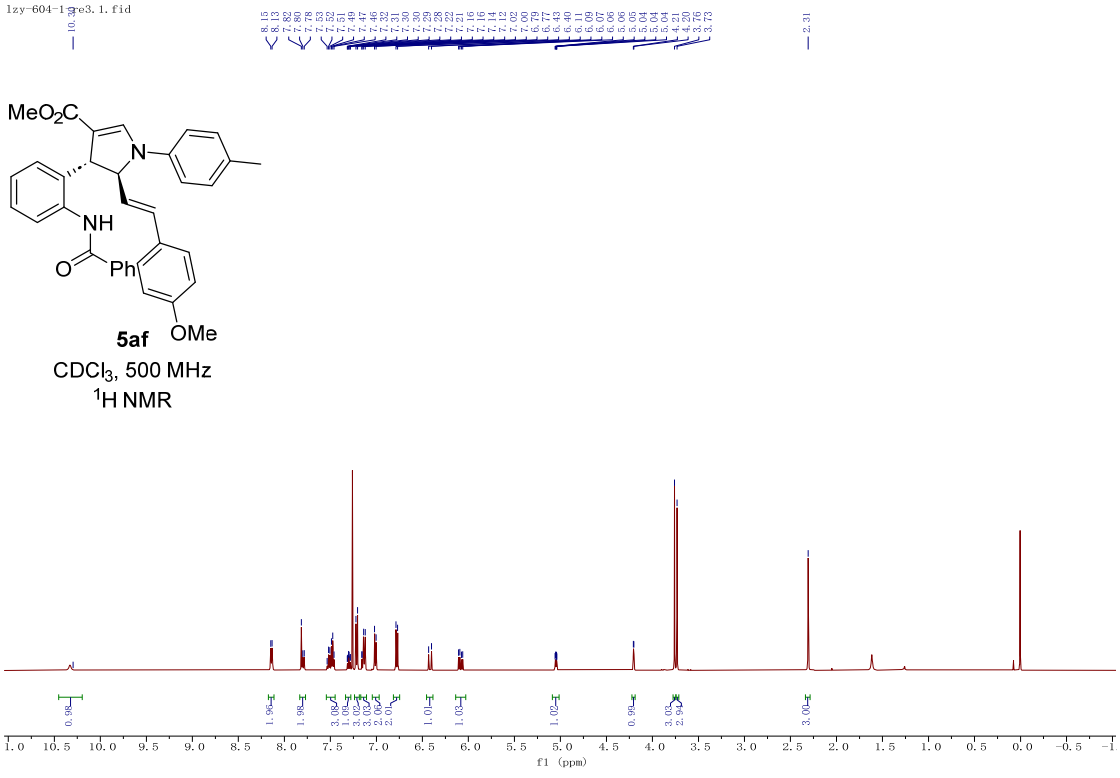

MeO2C
N
NH
Ph
O
Ph
5ac
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

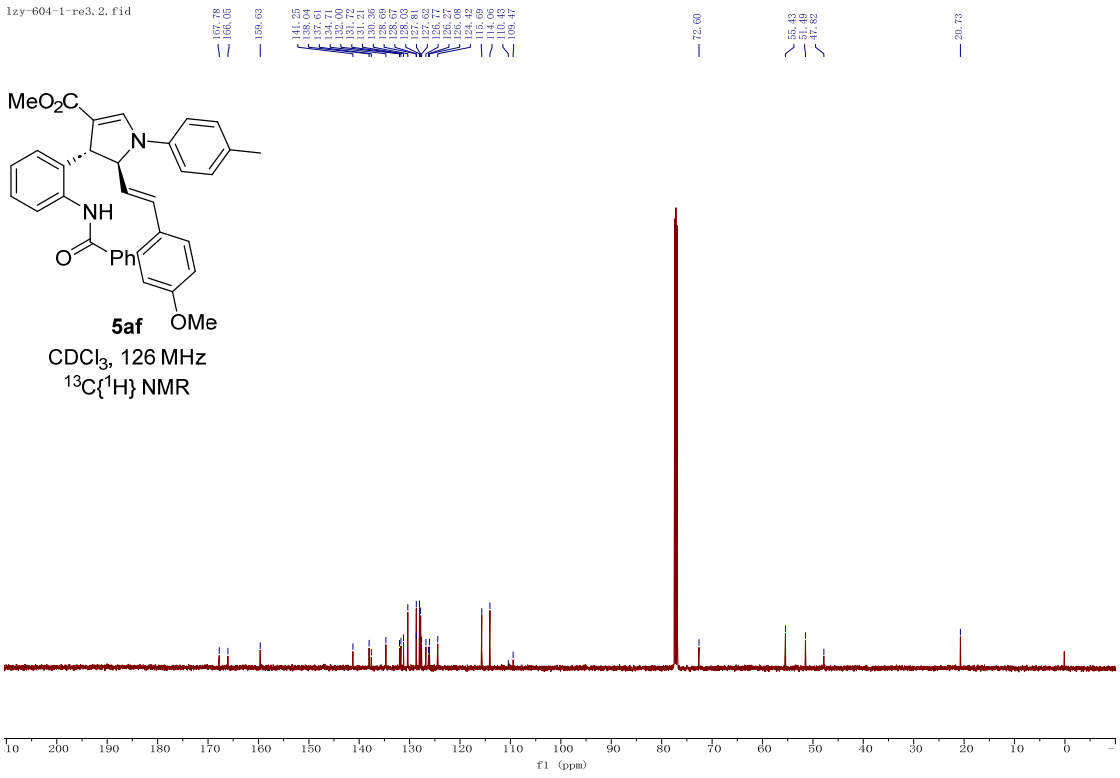

MeO2C
N
NH
Ph
O
Ph
5ad
CDCl3, 500 MHz
1H NMR
f1 (ppm)

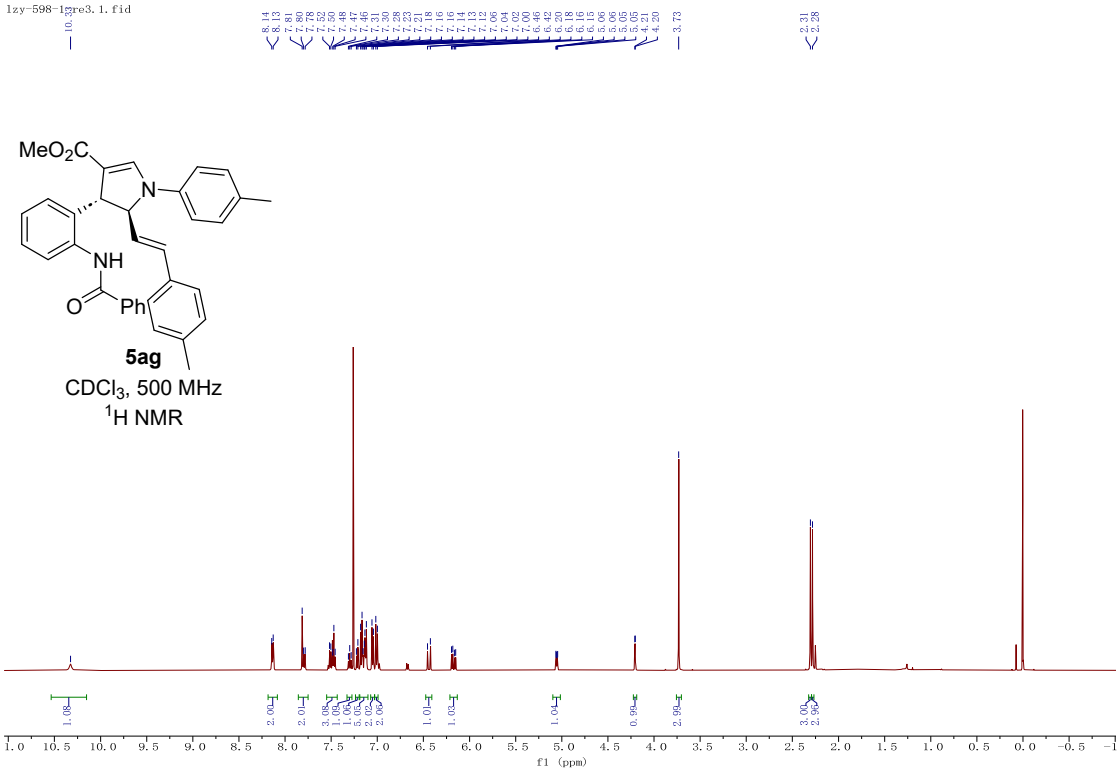

lzy-596-6-re.2.fid
MeO2C
N
NH
Ph
O
Ph
5ad
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

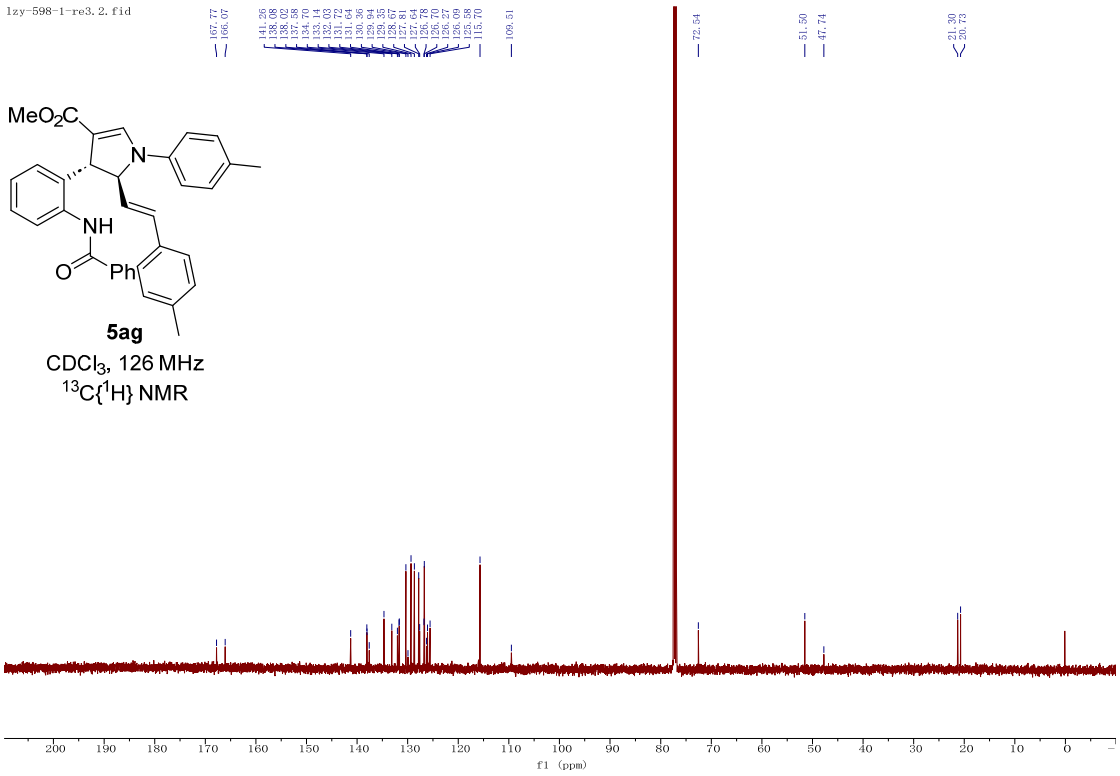

lzy-608-1-H.6.fid
MeO2C
N–Bn
NH
Ph
O
Ph
5ae
CDCl3, 600 MHz
1H NMR
f1 (ppm)

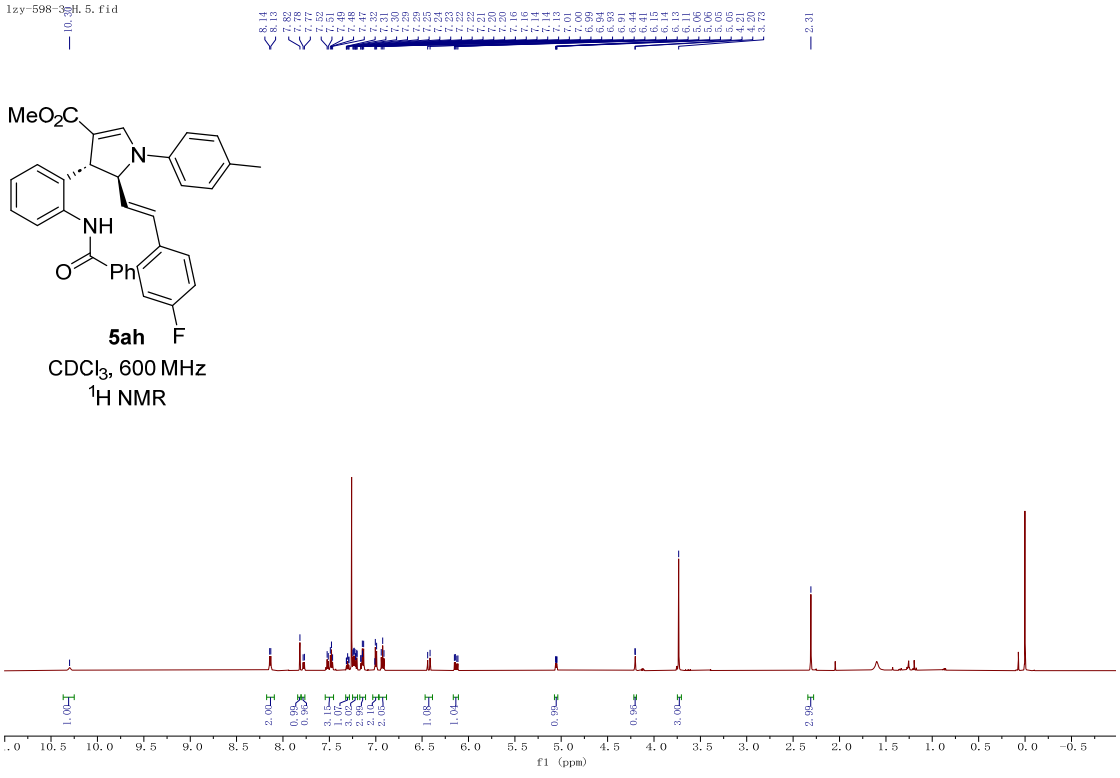

lzy-608-2-re.2.fid
MeO2C
N–Bn
NH
Ph
O
Ph
5ae
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

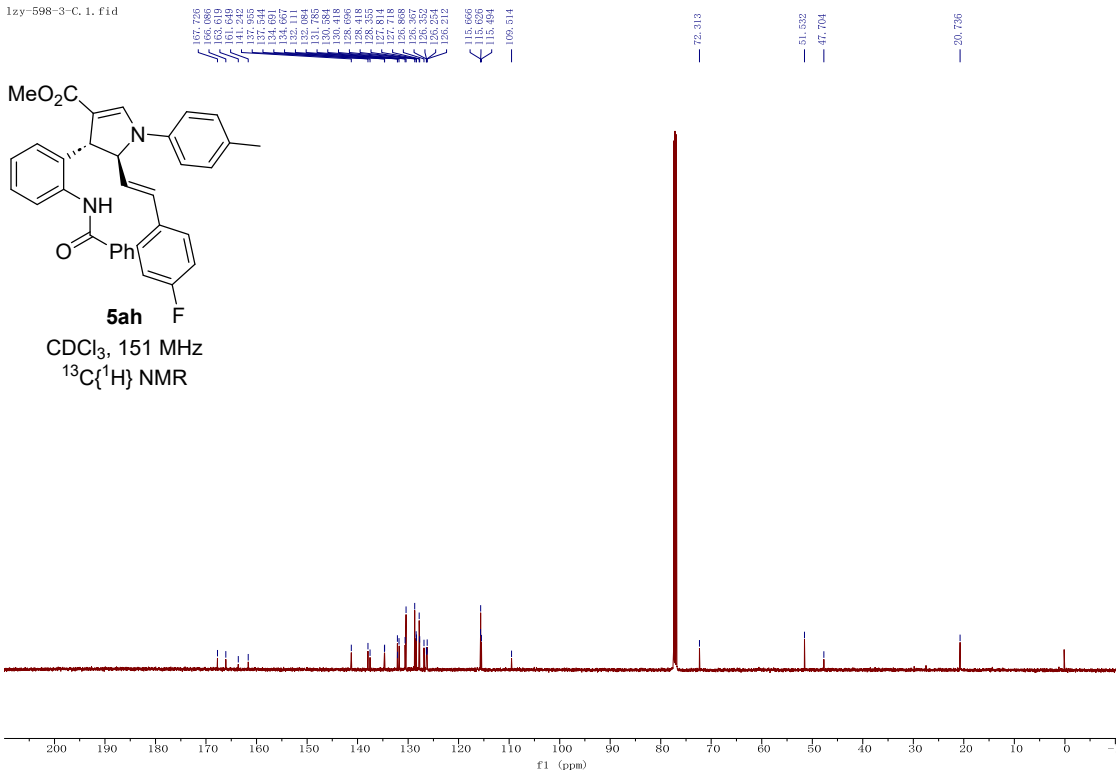

lzy-604-1-re3.1.fid
MeO2C
N
NH
O
Ph
OMe
5af
CDCl3, 500 MHz
1H NMR
f1 (ppm)

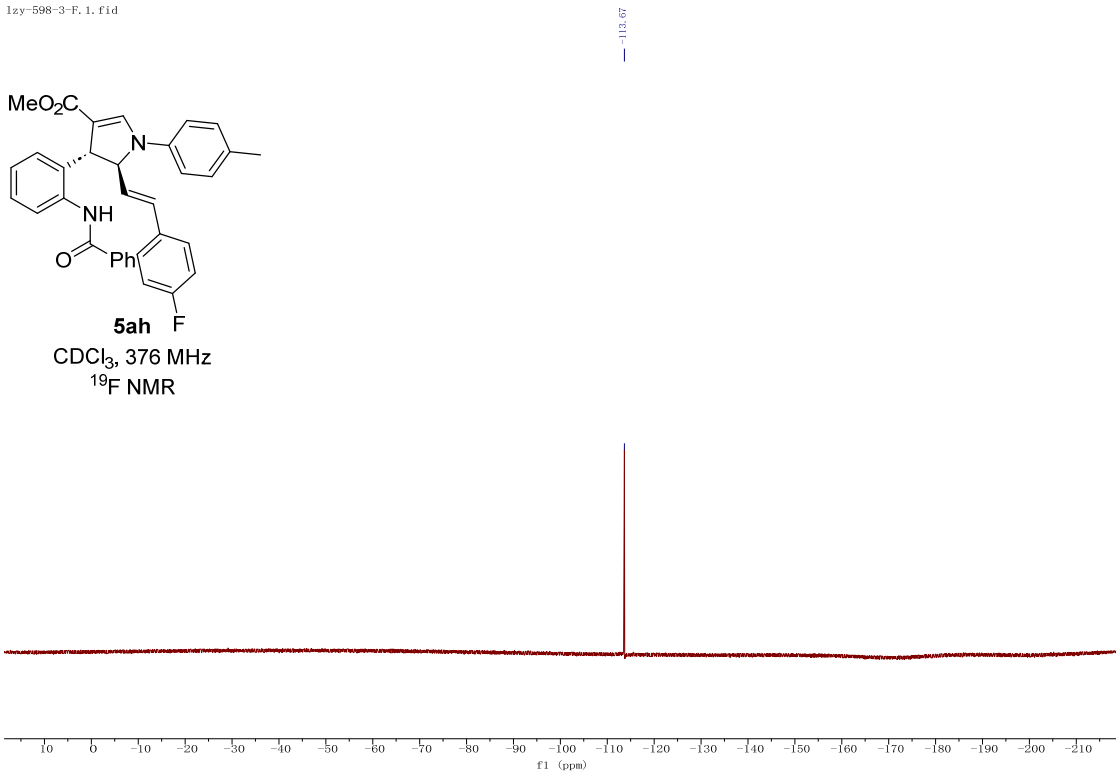

lzy-604-1-re3.2.fid
MeO2C
N
NH
O
Ph
OMe
5af
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

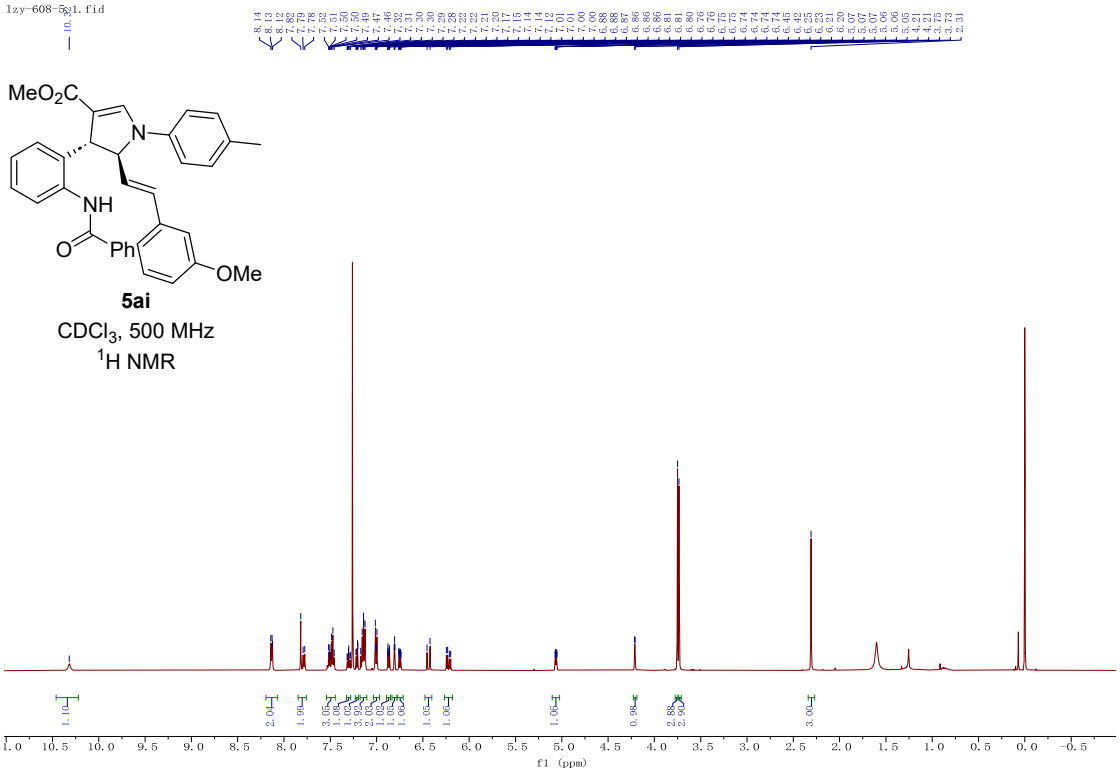

lzy-598-1-re3.1.fid
MeO2C
N
NH
O
Ph
5ag
CDCl3, 500 MHz
1H NMR
f1 (ppm)

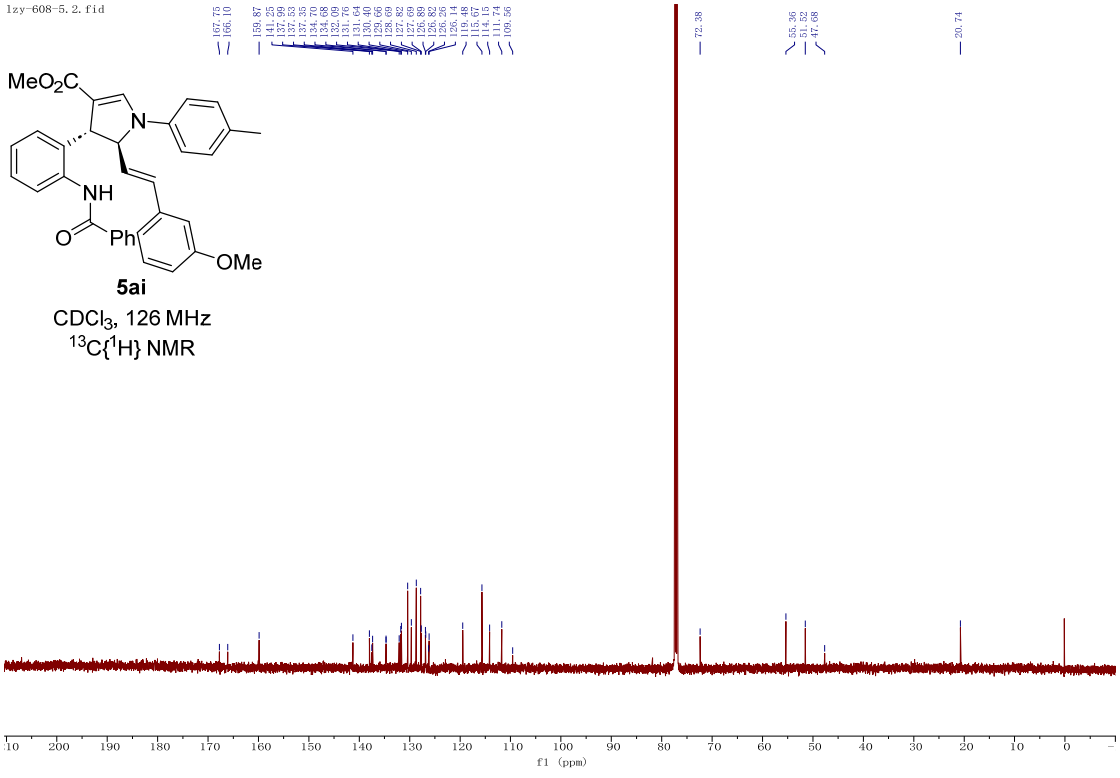

lzy-598-1-re3.2.fid
MeO2C
N
NH
O
Ph
5ag
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

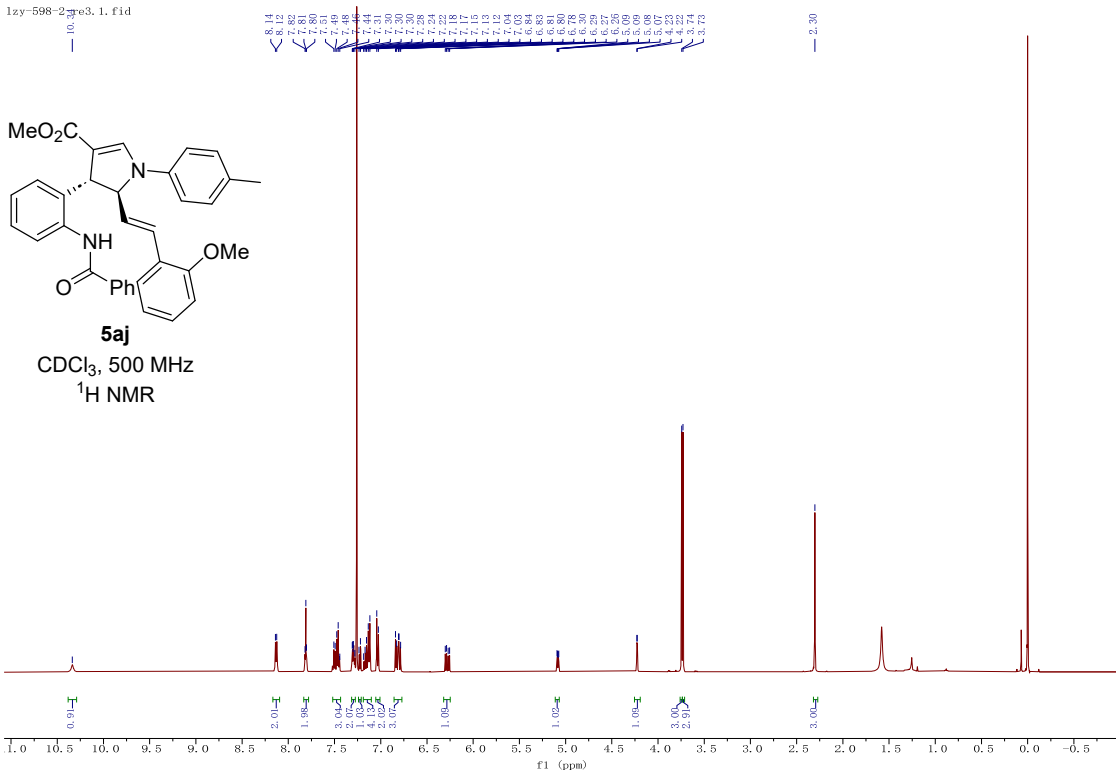

lzy-598-3-H.5.fid
MeO2C
N
NH
O
Ph
F
5ah
CDCl3, 600 MHz
1H NMR
f1 (ppm)

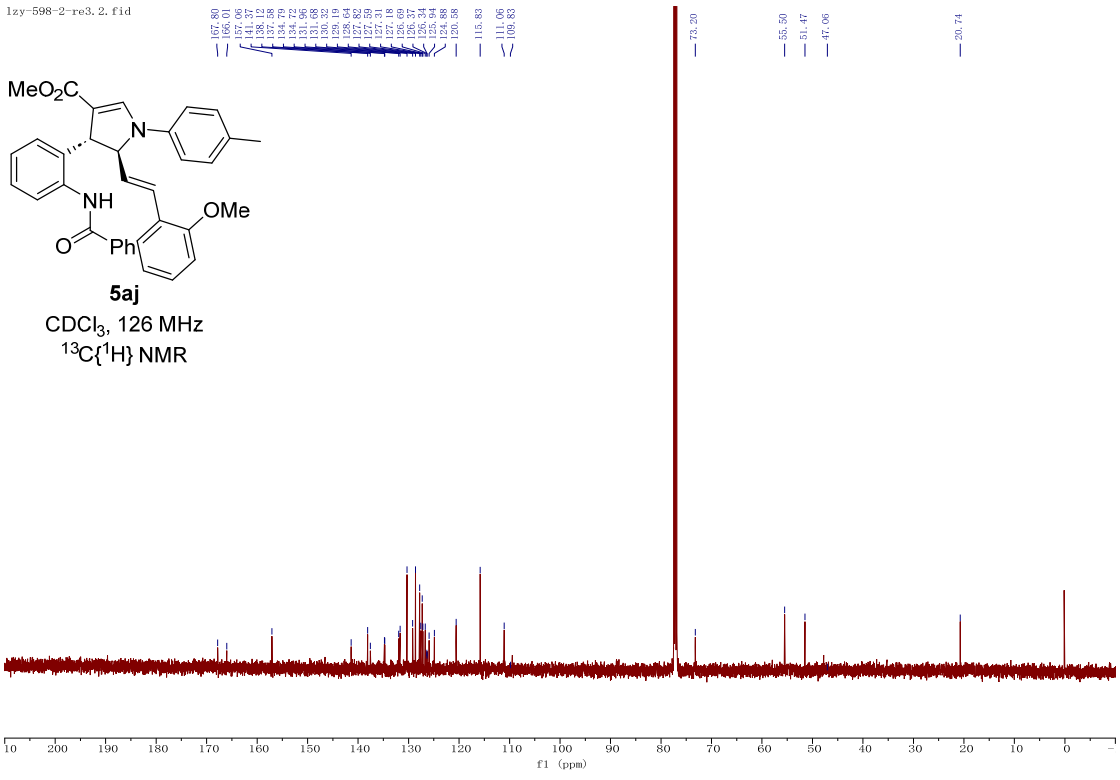

lzy-598-3-C.1.fid
MeO2C
N
NH
O
Ph
F
5ah
CDCl3, 151 MHz
13C{1H} NMR
f1 (ppm)

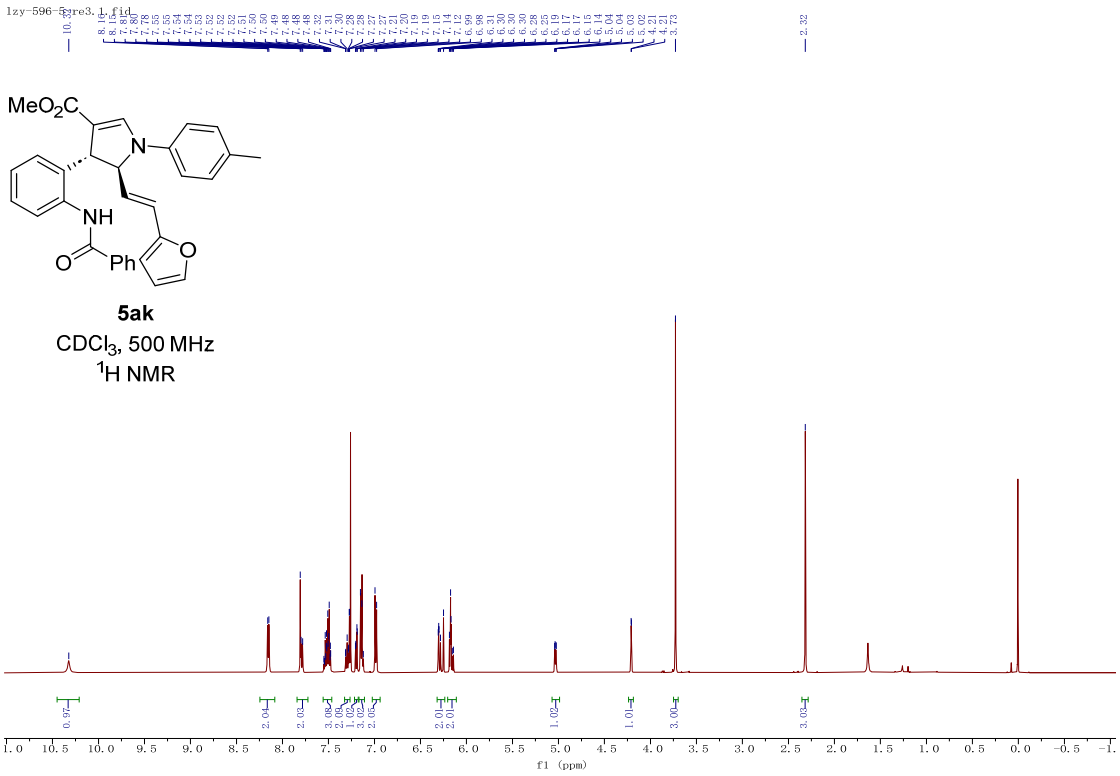

lzy-598-3-F.1.fid
-113.67
MeO2C
N
NH
O
Ph
F
5ah
CDCl3, 376 MHz
19F NMR
f1 (ppm)

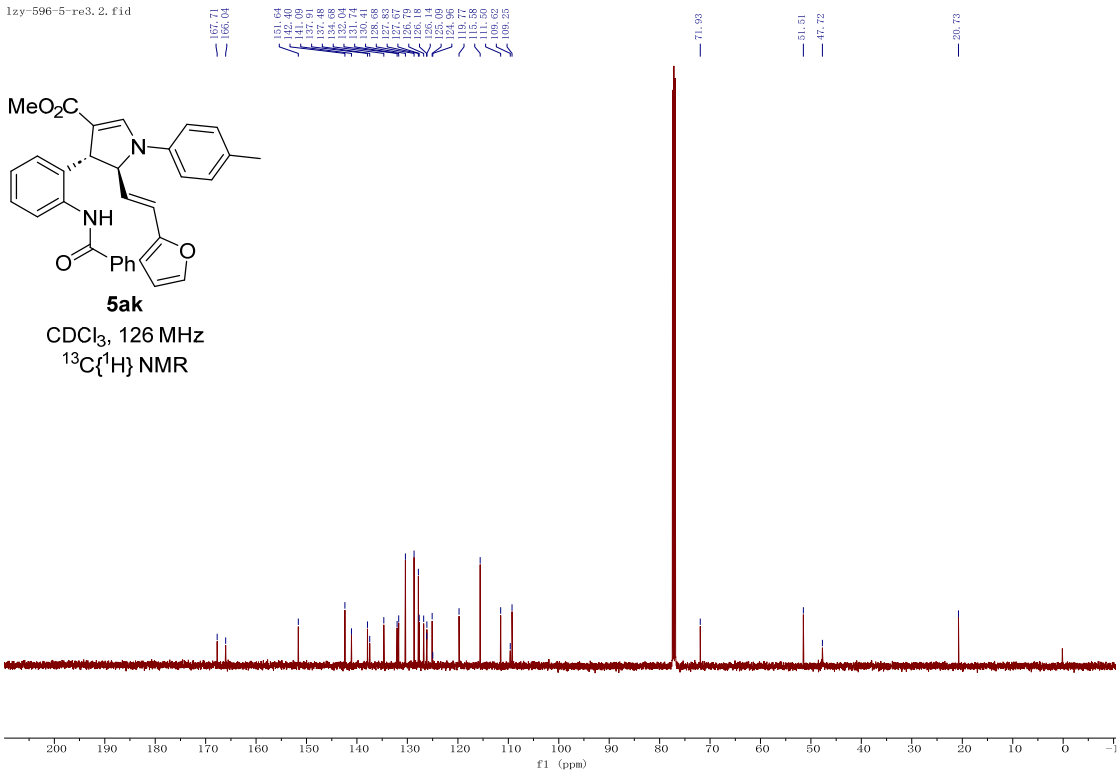

lzy-608-5.1.fid
MeO2C
N
NH
O
Ph
OMe
5ai
CDCl3, 500 MHz
1H NMR
f1 (ppm)

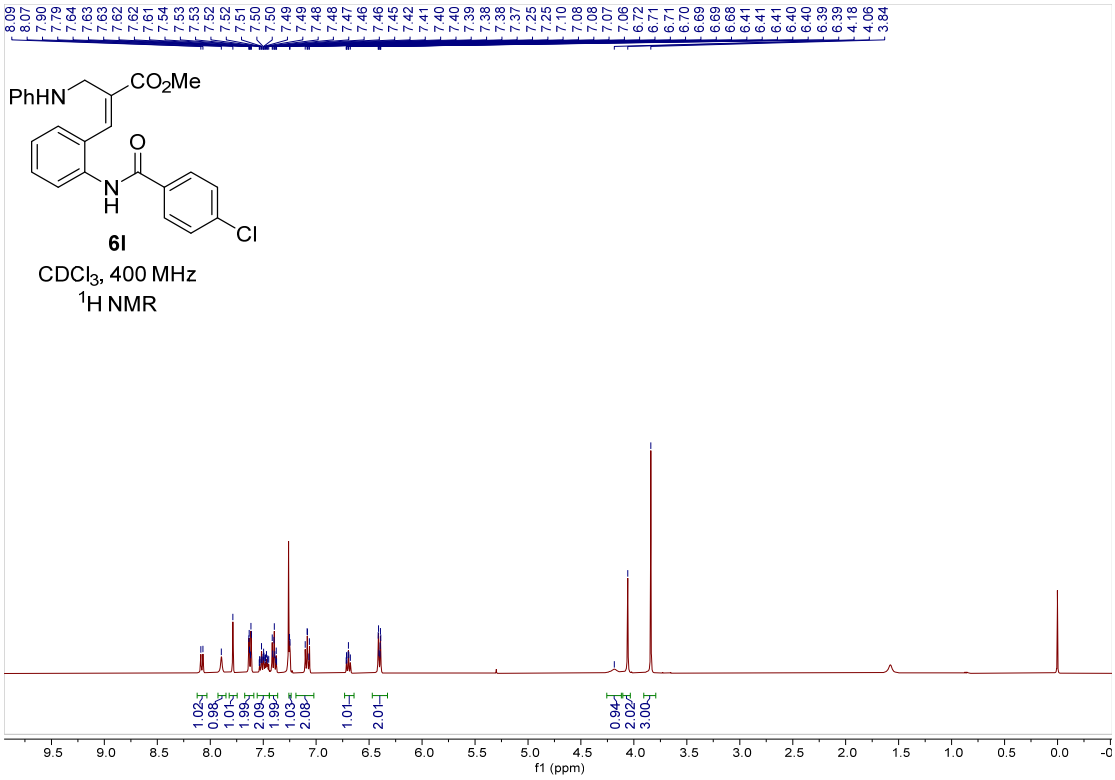

lzy-608-5.2.fid
MeO2C
N
NH
O
Ph
OMe
5ai
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)

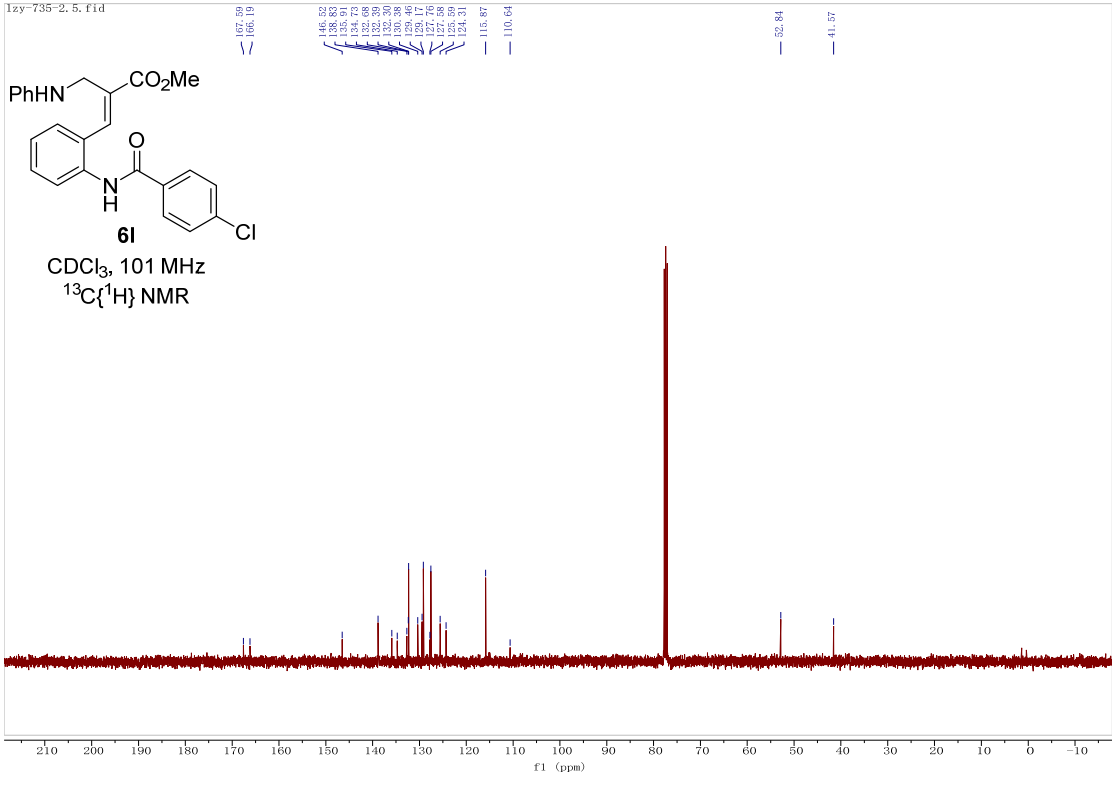

lzy-598-2-re3.1.fid
MeO2C
N
NH
OMe
O
Ph
5aj
CDCl3, 500 MHz
1H NMR
f1 (ppm)


lzy-598-2-re3.2.fid
MeO2C
N
NH
OMe
O
Ph
5aj
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)


lzy-596-5-re3.1.fid
MeO2C
N
NH
O
Ph
O
5ak
CDCl3, 500 MHz
1H NMR
f1 (ppm)


lzy-596-5-re3.2.fid
MeO2C
N
NH
O
Ph
O
5ak
CDCl3, 126 MHz
13C{1H} NMR
f1 (ppm)


PhHN
CO2Me
O
N
H
Cl
6l
CDCl3, 400 MHz
1H NMR
f1 (ppm)


lzy-735-2.5.fid
PhHN
CO2Me
O
N
H
Cl
6l
CDCl3, 101 MHz
13C{1H} NMR
f1 (ppm)