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SUPPORTING INFORMATION

Chemodivergent synthesis of multi-substituted/fused pyrroles *via* copper-catalyzed carbene cascade reaction of propargyl α-iminodiazoacetates

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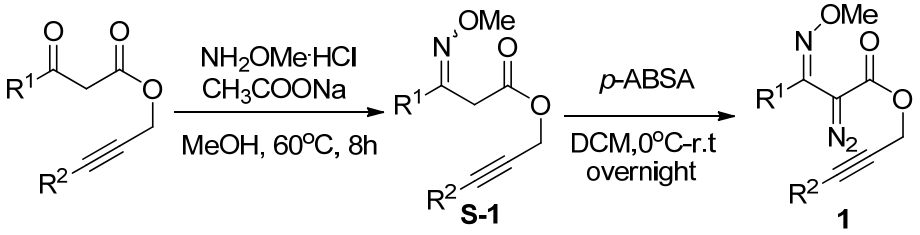
General Information

All reactions were carried out under an atmosphere of argon using oven-dried glassware. Toluene and other solvents were dried and degassed by standard methods. $Cu(hfacac)_2$ was purchased from Sigma Aldrich and used without further treatment. Flash column chromatography was performed using silica gel (300-400 mesh). Analytical thin-layer chromatography was performed using glass plates pre-coated with 200-300 mesh silica gel impregnated with a fluorescent indicator (254 nm). ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ on a 300/400/600 MHz spectrometer; chemical shifts are reported in ppm with the solvent signals as reference, and coupling constants (*J*) are given in Hertz. The peak information is described as: s = singlet, br = broad, d = doublet, t = triplet, q = quartet, m = multiplet, comp = composite. High-resolution mass spectra (HRMS) were recorded on a commercial apparatus (ESI Source).

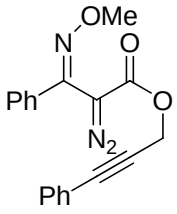
General Procedures for the Preparation of Diazoacetates 1a-1s:[1]



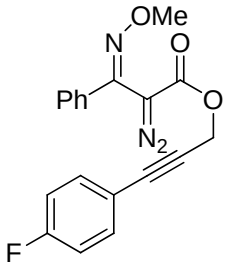
Synthesis of **S-1**: To a solution of *β*-ketoester (2.0 mmol) in MeOH (10 mL) at room temperature was added alkoxyamine hydrochloride (2.2 mmol) and sodium acetate (2.2 mmol) in one portion, and the reaction mixture was stirred at 60 ℃ for 8 h. Upon completion of the reaction (monitored by TLC), the solvent was evaporated under vacuum and the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether /EtOAc = 10:1) to give the **S-1** (> 90% yields based on *β*-ketoester).

Synthesis of **1**: The above obtained **S-1** (2.0 mmol) was dissolved in DCM (5.0 mL), *p*-ABSA (4-acetamidobenzenesulfonyl azide, 576 mg, 2.4 mmol) was added to the solution, and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, 456 mg, 3.0 mmol) in DCM

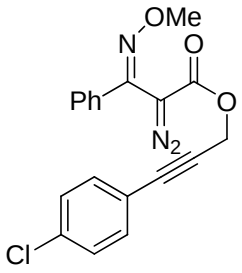
(5.0 mL) was added slowly at 0 ℃. The reaction mixture was stirred overnight from 0 ℃ to room temperature. After filtering through Celite, the solvent was evaporated under vacuum and the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether /EtOAc = 10:1) to give the pure diazo compound **1** as yellow solid (> 90% yields based on **S-1**).



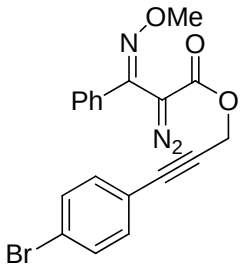
(*Z*)-3-Phenylprop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3-phenyl propanoate. (1a) ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60-7.54 (m, 2H), 7.43-7.41 (m, 2H), 7.40-7.28 (comp, 6H), 4.91 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 143.9, 133.457, 132.0, 129.9, 128.9, 128.5, 128.4, 127.8, 122.2, 86.8, 82.7, 62.9, 53.4 HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{16}N_3O_3$ $[M+H]^+$: 334.1192., found: 334.1184.



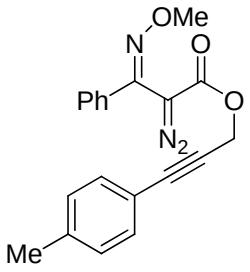
(*Z*)-3-(4-Fluorophenyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino) -3-phenylpropanoate(1b). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59-7.53 (m, 2H), 7.42-7.33 (comp, 5H), 7.06-6.97 (m, 2H), 4.89 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.2, 162.4 (d, J = 150.3 Hz), 143.8, 134.0 (d, J = 8.5 Hz), 133.5, 129.9, 128.5, 127.8, 118.3 (d, J = 3.7 Hz), 115.8 (d, J = 22.1 Hz), 85.8, 82.5, 62.9, 53.3. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}FN_3O_3$ $[M+H]^+$: 352.1097, found: 352.1097.



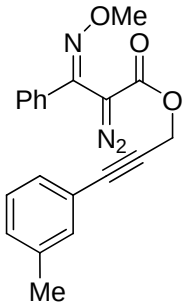
(*Z*)-3-(4-Chlorophenyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino) -3-phenylpropanoate (1c). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.42-7.32 (m, 5H), 7.32-7.27 (m, 2H), 4.89 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 143.8, 135.1, 133.5, 133.3, 129.9, 128.8, 128.5, 127.8, 120.7, 85.7, 83.7, 62.9, 53.3. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}ClN_3O_3$ $[M+H]^+$: 368.0802, found: 368.0802.



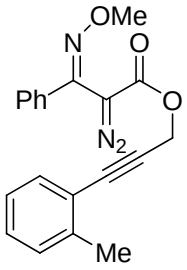
(*Z*)-3-(4-Bromophenyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino) -3-phenylpropanoate (1d) ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58-7.53 (m, 2H), 7.48-7.43 (m, 2H), 7.39-7.33 (comp, 3H), 7.29-7.25 (m, 2H), 4.88 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.1, 143.8, 133.4, 131.8, 130.1, 129.9, 128.5, 127.8, 123.3, 121.2, 85.7, 83.9, 62.9, 53.3. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}BrN_3O_3$ $[M+H]^+$: 412.0297, found: 412.0291.



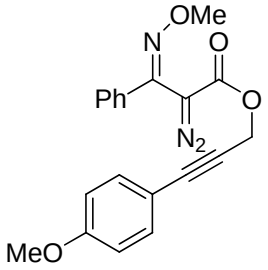
(*Z*)-3-(*p*-Tolyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3 –phenylpropanoate (1e). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61-7.51 (m, 2H), 7.44-7.28 (comp, 5H), 7.17-7.09 (m, 2H), 4.90 (s, 2H), 4.06 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 143.9, 139.1, 133.5, 131.9, 129.9, 129.2, 128.5, 127.8, 119.1, 87.0, 82.0, 62.9, 53.5, 21.6. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}N_3O_3$ $[M+H]^+$: 348.1348, found: 348.1350.



(*Z*)-3-(*m*-Tolyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3-phenyl propanoate (1f). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58-7.54 (m, 2H), 7.40-7.35 (comp, 3H), 7.26-7.13 (comp, 4H), 4.90 (s, 2H), 4.06 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 143.9, 138.1, 133.5, 132.6, 129.9, 129.8, 129.1, 128.5, 128.3, 127.8, 122.0, 87.0, 82.3, 62.9, 53.5, 21.3. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}N_3O_3$ $[M+H]^+$: 348.1348, found: 348.1362.

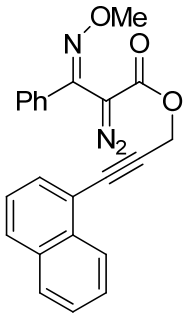


(*Z*)-3-(*o*-Tolyl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3-phenyl propanoate (1g). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59-7.55 (m, 2H), 7.40-7.34 (comp, 4H), 7.26-7.18 (m, 2H), 7.16-7.11 (m, 1H), 4.95 (s, 2H), 4.07 (s, 3H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 143.9, 140.7, 133.5, 132.3, 129.9, 129.6, 128.9, 128.5, 127.8, 125.6, 122.0, 86.5, 85.8, 62.9, 53.6, 20.7. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}N_3O_3$ $[M+H]^+$: 348.1348, found: 348.1361.

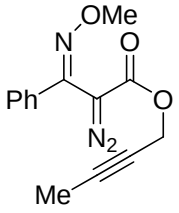


(*Z*)-3-(4-Methoxyphenyl)prop-2-yn-1-yl 2-diazo-3-(methoxy imino)-3-phenylpropanoate (1h). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 (dd, J = 7.6, 1.7 Hz, 2H), 7.42-7.33 (comp, 5H), 6.87-6.82 (m, 2H), 4.90 (s, 2H), 4.06 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.2, 160.1, 143.9, 133.6, 133.5,

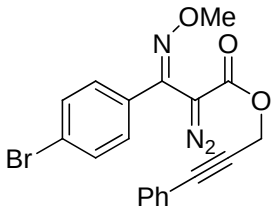
129.9, 128.5, 127.8, 114.2, 114.1, 86.8, 81.4, 62.9, 55.4, 53.6. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}N_3O_4$ $[M+H]^+$: 364.1297, found: 364.1302.



(*Z*)-3-(Naphthalen-1-yl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3 –phenylpropanoate (1i). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.24 (d, *J* = 8.1 Hz, 1H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.64-7.51 (comp, 4H), 7.47-7.41 (m, 1H), 7.40-7.33 (comp, 3H), 5.06 (s, 2H), 4.07 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.3, 143.9, 133.5, 133.5, 133.2, 131.1, 129.9, 129.5, 128.5, 128.4, 127.8, 127.1, 126.6, 126.2, 125.2, 119.8, 87.5, 85.0, 62.9, 53.7. HRMS (TOF MS CI^+) calculated for $C_{23}H_{18}N_3O_3$ $[M+H]^+$: 384.1348, found: 348.1358.

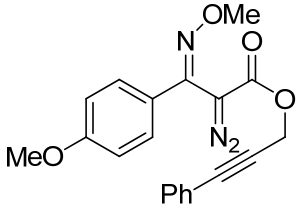


(*Z*)-But-2-yn-1-yl 2-diazo-3-(methoxyimino)-3-phenylpropanoate (1j). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60-7.51 (m, 2H), 7.43-7.33 (comp, 3H), 4.64 (q, *J* = 2.3 Hz, 2H), 4.05 (s, 3H), 1.82 (t, *J* = 2.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.1, 143.9, 133.4, 129.8, 128.4, 127.8, 83.5, 72.9, 62.8, 53.4, 3.7. HRMS (TOF MS CI^+) calculated for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, found: 272.1049.

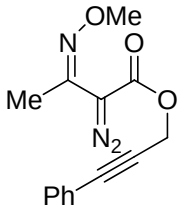


(*Z*)-3-Phenylprop-2-yn-1-yl 3-(4-bromophenyl)-2-diazo-3 -(methoxyimino)propanoate (1k). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52-7.47 (m, 2H), 7.47-7.39 (comp, 4H), 7.38-7.30 (comp, 3H), 4.92 (s, 2H), 4.06 (s, 3H); ^{13}C

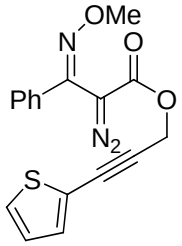
NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.0, 143.0, 132.5, 132.0, 131.7, 129.4, 129.0, 128.5, 124.2, 122.1, 87.0, 82.5, 63.0, 53.5. HRMS (TOF MS CI^+) calculated for $C_{19}H_{15}BrN_3O_3$ $[M+H]^+$: 412.0297, found: 412.0309.



(*Z*)-3-Phenylprop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3-(4-methoxyphenyl)propanoate (1l). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.54-7.48 (m, 2H), 7.45-7.40 (m, 2H), 7.36-7.28 (comp, 3H), 6.92-6.83 (m, 2H), 4.92 (s, 2H), 4.04 (s, 3H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.3, 161.1, 143.4, 132.0, 129.2, 128.9, 128.4, 125.8, 122.2, 114.0, 86.8, 82.8, 62.7, 55.4, 53.4. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}N_3O_4$ $[M+H]^+$: 364.1297, found: 364.1302.

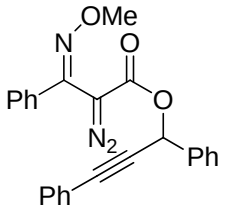


(*Z*)-3-Phenylprop-2-yn-1-yl 2-diazo-3-(methoxyimino)butanoate (1m). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.48-7.43 (m, 2H), 7.35-7.29 (comp, 3H), 5.01 (s, 2H), 3.84 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.3, 141.2, 132.0, 129.0, 128.4, 122.1, 86.9, 82.7, 61.9, 53.3, 19.3. HRMS (TOF MS CI^+) calculated for $C_{14}H_{14}N_3O_3$ $[M+H]^+$: 272.1035, found: 272.1050.

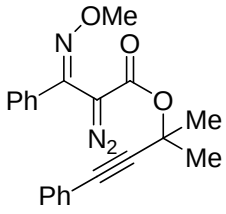


(*Z*)-3-(Thiophen-2-yl)prop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3–phenylpropanoate (1n) ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.60-7.53 (m, 2H), 7.41-7.35 (comp, 3H), 7.29 (dd, J = 5.2, 1.1 Hz, 1H), 7.25-7.21 (m, 1H), 6.98 (dd, J = 5.2, 3.7 Hz, 1H), 4.92 (s, 2H), 4.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.1, 143.8, 133.4, 133.2, 129.9, 128.5, 128.0, 127.8, 127.1, 122.0, 86.7, 80.1, 62.9,

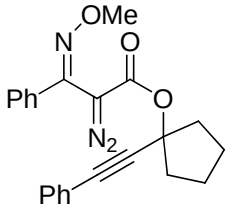
53.4. HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{13}N_3O_3S$ [M+H]$^+$: 340.0756, found: 340.0750.



(*Z*)-1,3-Diphenylprop-2-yn-1-yl 2-diazo-3-(methoxyimino)-3 –phenylpropanoate (1o). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.63 (d, *J* = 6.6 Hz, 2H), 7.55-7.49 (m, 2H), 7.47-7.34 (comp, 11H), 6.75 (s, 1H), 4.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.0, 143.8, 136.7, 133.6, 131.9, 129.7, 128.9, 128.9, 128.6, 128.4, 128.3, 127.8, 127.6, 122.0, 87.4, 85.3, 66.9, 62.7. HRMS (TOF MS CI$^+$) calculated for $C_{25}H_{20}N_3O_3$ [M+H]$^+$: 410.1505, found: 410.1497.

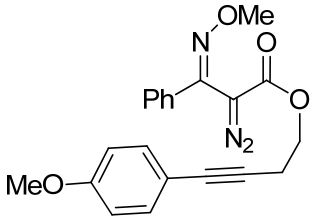


(*Z*)-2-Methyl-4-phenylbut-3-yn-2-yl 2-diazo-3-(methoxyimino) -3-phenylpropanoate (1p). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61-7.53 (m, 2H), 7.45-7.33 (comp, 5H), 7.33-7.27 (comp, 3H), 4.06 (s, 3H), 1.51 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.6, 144.6, 134.2, 131.9, 129.6, 128.5, 128.3, 128.3, 128.0, 122.6, 89.7, 84.1, 74.2, 62.8, 29.0. HRMS (TOF MS CI$^+$) calculated for $C_{21}H_{20}N_3O_3$ [M+H]$^+$:362.1505, found: 362.1510.

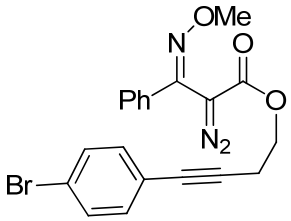


(*Z*)-1-(Phenylethynyl)cyclopentyl 2-diazo-3-(methoxyimino)-3 –phenylpropanoate (1q). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.55 (dd, *J* = 7.9, 1.5 Hz, 2H), 7.43-7.34 (comp, 5H), 7.32-7.27 (comp, 3H), 4.06 (s, 3H), 2.05-2.01 (comp, 4H), 1.65-1.63 (m, 2H), 1.48-1.46 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.8, 144.5, 134.2, 131.9, 129.6, 128.4, 128.4, 128.3, 127.9, 122.8, 89.2, 85.2, 82.7,

62.8, 40.6, 23.4. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{22}N_3O_3$ $[M+H]^+$:388.1661, found: 388.1668.



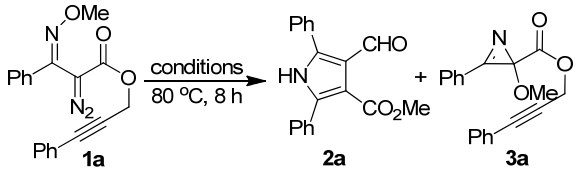
(*Z*)-4-(4-Methoxyphenyl)but-3-yn-1-yl 2-diazo-3-(methoxy imino)-3-phenylpropanoate (1r). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.58-7.51 (m, 2H), 7.40-7.29 (comp, 5H), 6.86-6.79 (m, 2H), 4.23 (t, *J* = 7.0 Hz, 2H), 4.05 (s, 3H), 3.80 (s, 3H), 2.54 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.7, 159.5, 144.1, 133.7, 133.1, 129.8, 128.5, 127.8, 115.6, 114.0, 83.5, 82.1, 63.1, 62.9, 55.4, 20.0. HRMS (TOF MS CI$^+$) calculated for $C_{21}H_{20}N_3O_4$ $[M+H]^+$:378.1454, found: 378.1462.



(*Z*)-4-(4-bromophenyl)but-3-yn-1-yl 2-diazo-3-(methoxy imino)-3-phenylpropanoate (1s). ^{1}H NMR (600 MHz, $CDCl_3$) (δ, ppm) 7.57-7.51 (m, 2H), 7.42 (d, *J* = 8.2 Hz, 2H), 7.40-7.31 (comp, 3H), 7.23 (d, *J* = 8.1 Hz, 2H), 4.24 (t, *J* = 6.8 Hz, 2H), 4.05 (s, 3H), 2.54 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 163.6, 144.0, 133.7, 133.2, 131.6, 129.8, 128.4, 127.8, 122.4, 122.3, 86.4, 81.3, 62.8, 62.8, 20.1. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{17}BrN_3O_3$ $[M+H]^+$:426.0453, found: 426.0444.

Condition Optimization for the Synthesis of Multi-Substituted Pyrroles

Table S1 Optimization of reaction conditions[a]

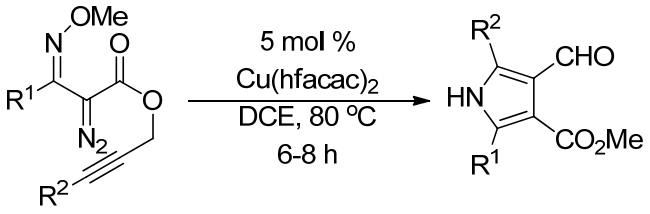


Entry	Cat.	Solvent	Yield **2a** (%)[b]	Yield **3a** (%)[b]
1	$Rh_2(OAc)_4$	DCE	15	60
2	$Rh_2(pfb)_4$	DCE	<10	70
3	Ph_3PAuCl	DCE	ND[c]	80
4	$In(OTf)_3$	DCE	<10	75
5	$Ni(OAc)_2$	DCE	ND[c]	80
6	$Fe(acac)_3$	DCE	<10	75
7	$Cu(OTf)_2$	DCE	30	30
8	$Cu(CH_3CN)_4PF_6$	DCE	45	<10
9	$Cu(hfacac)_2$	DCE	65	<10
10	$Cu(hfacac)_2$	toluene	35	40
11[d]	$Cu(hfacac)_2$	DCE	84	<10

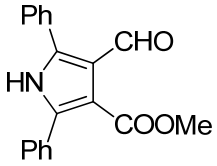
[a] The reaction was carried out in 0.2 mmol scale with catalysts (Rh 1.0 mol% or other catalysts 5.0 mol%) in 1.5 mL of dry solvent at 80 ℃, and **1a** was added as a solution (in 2.0 mL of the same solvent) *via* syringe pump in 0.5 h. [b] Isolated yield. [c] ND = Not detected. [d] Diazo compound **1a** was added in 2 hours under atmosphere of argon.

As could be expected, treatment of this diazo compound with dirhodium catalysts or other Lewis acid catalysts only led to **3a** as the major product instead of giving the pyrrole (Table S1, entries 1-6). However, when copper catalysts were applied, moderate to high yields of 3-formylpyrrole product **2a** was obtained, although the formation of some by-products in low yield, including **3a**, could not be totally excluded (entries 7-9). Solvents and other conditions were investigated to improve the selectivity and yield for the formation of **2a**. We found that the best result was achieved by slow addition of **1a** to the reaction mixture at 80 ℃ in dichloroethane (DCE) under an inert atmosphere (entry 11, 84% isolated yield).

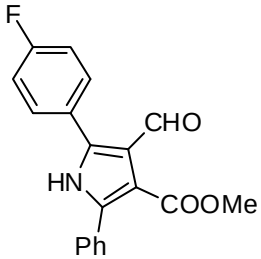
General Procedure for the Synthesis of Multi-Substituted Pyrroles:



To a 10-mL oven-dried vial with a magnetic stirring bar, $Cu(hfacac)_2$ (4.7 mg, 0.01 mmol) in dry DCE(2.0 mL), was added diazo compound **1** (0.2 mmol) in DCE (2.0 mL) *via* syringe pump over 2 h under atmosphere of argon at 80 ℃. The reaction mixture was stirred overnight under this condition. The reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 3:1) to give the pure products **2** in high yields.

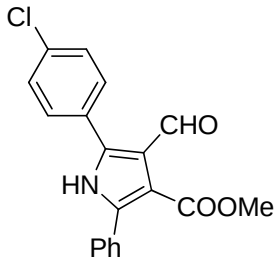


Methyl 4-formyl-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (2a). White solid; m.p. 193.0-195.0 ℃. 51.0 mg, 84 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.12 (s, 1H), 9.01 (s, 1H), 7.60-7.56 (m, 2H), 7.55-7.51 (m, 2H), 7.45-7.38 (comp, 6H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 187.3, 165.9, 139.5, 136.1, 130.8, 130.1, 129.6, 129.1 129.0, 128.9, 128.7, 128.4, 121.1, 113.7, 52.1. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1130, found: 306.1140.

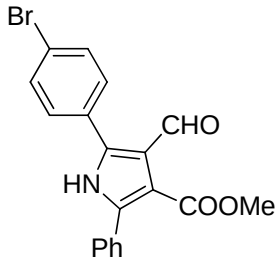


Methyl 5-(4-fluorophenyl)-4-formyl-2-phenyl-1*H*-pyrrole-3 –carboxylate (2b). White solid; m.p. 180.0-184.0 ℃. 49.0 mg, 76 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.12 (s, 1H), 9.16 (s, 1H), 7.58-7.53 (m, 2H), 7.50 (dd, J = 7.5, 2.0 Hz, 2H), 7.43-7.37 (comp, 3H), 7.09 (t, J = 8.6 Hz, 2H), 3.76 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 187.7, 165.6, 164.2, 162.6, 137.9, 136.6, 131.2,

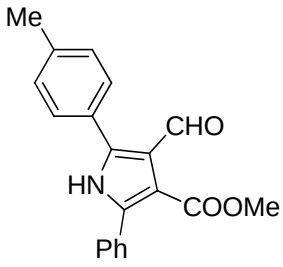
131.1, 130.7, 129.1, 128.7, 128.6, 126.2, 121.0, 115.9, 115.8, 113.7, 52.0. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}FNO_3$ [M+H]$^+$: 324.1036, found: 324.1051.



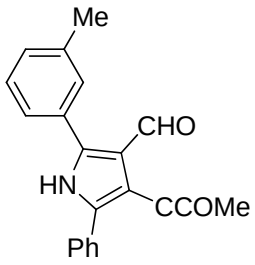
Methyl 5-(4-chlorophenyl)-4-formyl-2-phenyl-1*H*-pyrrole-3-carboxylate (2c). White solid; m.p. 181.0-183.0 ℃. 54.0 mg, 80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 10.09 (s, 1H), 9.36 (s, 1H), 7.51-7.46 (comp, 4H), 7.40-7.32 (comp, 5H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.8, 165.6, 137.7, 136.9, 135. 6, 130.6, 130.4, 129.1, 128.9, 128.6, 128.6, 128.5, 121.1, 113.8, 52.0. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}ClNO_3$ [M+H]$^+$: 340.0740, found: 340.0752.



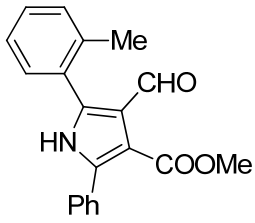
Methyl 5-(4-bromophenyl)-4-formyl-2-phenyl-1*H*-pyrrole-3-carboxylate (2d). White solid; m.p. 178.5-180.0 ℃. 65.0 mg, 85 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.18 (s, 1H), 9.08 (s, 1H), 7.55-7.50 (comp, 4H), 7.47-7.44 (m, 2H), 7.42-7.39 (comp, 3H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.7, 165.4, 137.3, 136.9, 132.0, 130.7, 130.7, 129.2, 129.1 128.7, 128.7, 123.9, 121.3, 114.0, 52.0. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}BrNO_3$ [M+H]$^+$: 384.0235, found: 384.0236.



Methyl 4-formyl-2-phenyl-5-(p-tolyl)-1*H*-pyrrole-3-carbox -ylate. (2e). White solid; m.p. 170.0-172.0 ℃. 50.0 mg, 79 % yield. 1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.02 (s, 1H), 9.35 (s, 1H), 7.49 (dd, *J* = 7.7, 1.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.40-7.34 (comp, 3H), 7.19 (d, *J* = 7.9 Hz, 2H), 3.75 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 187.4, 166.1, 140.2, 139.6, 135.8, 130.7, 129.5, 129.0, 128.8, 128.6, 128.3, 127.0, 120.8, 113.5, 52.0, 21.5. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1297.

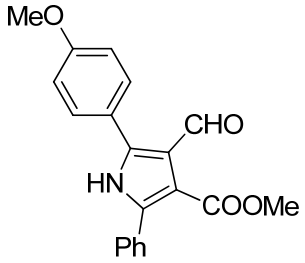


4-(Methoxyethynyl)-5-phenyl-2-(m-tolyl)-1*H*-pyrrole-3-carbal dehyde. (2f). White solid; m.p. 144.5-148.0 ℃. 50.0 mg, 79 % yield. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.08 (s, 1H), 9.08 (s, 1H), 7.54-7.50 (m, 2H), 7.40-7.34 (comp, 5H), 7.33-7.29 (m, 1H), 7.23 (d, *J* = 7.4 Hz, 1H), 3.78 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 187.2, 166.0, 140.0, 138.7, 135.7, 130.7, 130.3, 129.9, 129.7, 128.9, 128.8, 128.7, 128.3, 126.3, 121.1, 113.6, 52.0, 21.5. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1293.

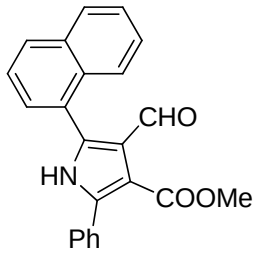


4-(Methoxyethynyl)-5-phenyl-2-(o-tolyl)-1*H*-pyrrole-3-carbald ehyde. (2g). White solid; m.p. 169.0-173.0 ℃. 48.5 mg, 76 % yield. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.03 (s, 1H), 8.78 (s, 1H), 7.53 (d, *J* = 7.1 Hz, 2H), 7.45-7.38 (comp, 3H), 7.36-7.23 (comp, 4H), 3.81 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (150 MHz,

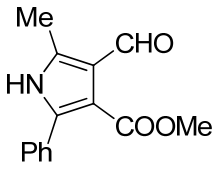
$CDCl_3$) (δ, ppm) 186.4, 164.7, 137.7, 137.0, 135.1, 129.9, 129.6, 129.6, 129.1, 128.7, 128.0, 127.7, 127.5, 124.9, 121.3, 111.6, 50.9, 19.1. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1293.



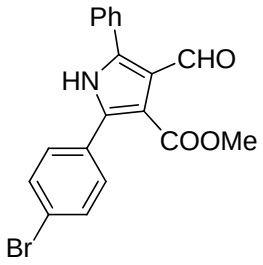
Methyl 4-formyl-5-(4-methoxyphenyl)-2-phenyl-1*H*-pyrrole-3-carboxylate (2h). White solid; m.p. 184.0-186.0 ℃. 60.0 mg, 90 % yield. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.04 (s, 1H), 9.28 (s, 1H), 7.53-7.46 (comp, 4H), 7.41-7.34 (comp, 3H), 6.90 (d, J = 8.7 Hz, 2H), 3.81 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.4, 166.0, 160.6, 139.9, 135.8, 130.8, 130.6, 128.8, 128.6, 128.4, 122.3, 120.5, 114.2, 113.5, 55.5, 52.0. HRMS (TOF MS CI^+) calculated for $C_{20}H_{18}NO_4$ $[M+H]^+$: 336.1236, found: 336.1244.



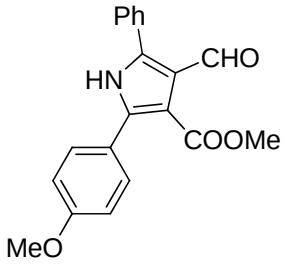
Methyl 4-formyl-5-(naphthalen-1-yl)-2-phenyl-1*H*-pyrrole-3-carboxylate (2i). White solid; m.p. 208.0-211.0 ℃. 53.0 mg, 75 % yield. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.80 (s, 1H), 9.28 (s, 1H), 7.91-7.84 (m, 2H), 7.75 (d, J = 8.0 Hz, 1H), 7.53-7.51 (m, 2H), 7.50-7.43 (comp, 4H), 7.41-7.35 (comp, 3H), 3.79 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 186.9, 165.9, 138.0, 136.1, 133.6, 132.3, 130.7, 130.1, 129.2, 128.9, 128.7, 128.6, 128.3, 127.7, 127.2, 126.5, 125.3, 125.1, 123.0, 112.7, 52.0 HRMS (TOF MS CI^+) calculated for $C_{23}H_{18}NO_3$ $[M+H]^+$: 356.1287, found: 356.1283.



Methyl 4-formyl-5-methyl-2-phenyl-1*H*-pyrrole-3-carboxylate (2j). White solid; m.p. 137.0-141.0 ℃. 26.0 mg, 54 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.40 (s, 1H), 8.67 (s, 1H), 7.51-7.46 (m, 2H), 7.44-7.38 (comp, 3H), 3.75 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 190.0, 165.1, 136.6, 136.3, 131.4, 129.1, 128.9, 128.5, 121.2, 112.4, 51.5, 13.6. HRMS (TOF MS CI$^+$) calculated for $C_{14}H_{14}NO_3$ $[M+H]^+$: 244.0974, found: 244.0968.

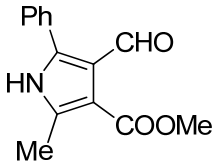


Methyl 2-(4-bromophenyl)-4-formyl-5-phenyl-1*H*-pyrrole-3–carboxylate (2k). White solid; m.p. 196.0-198.0 ℃. 49.0 mg, 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.12 (s, 1H), 9.09 (s, 1H), 7.58-7.52 (comp, 4H), 7.45-7.38 (comp, 5H), 3.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.3, 165.6, 139.7, 134.9, 131.9, 130.0, 129.9, 129.7, 129.7, 129.2, 128.9, 123.3, 121.2, 114.0, 52.1. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{15}BrNO_3$ $[M+H]^+$: 384.0235, found: 384.0242.

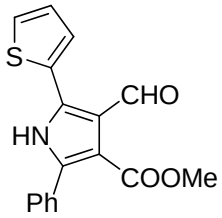


Methyl 4-formyl-2-(4-methoxyphenyl)-5-phenyl-1*H*-pyrrole-3-carboxylate (2l) White solid; m.p. 177.0-180.0 ℃. 57.0 mg, 85 % yield ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.18 (s, 1H), 8.75 (s, 1H), 7.61-7.57 (m, 2H), 7.50-7.43 (comp, 5H), 6.98-6.93 (m, 2H), 3.84 (s, 3H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 186.5, 164.8, 159.3, 137.9, 135.4, 129.2, 128.9, 128.5, 128.1,

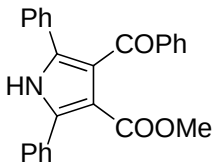
127.9, 122.1, 120.1, 113.2, 112.1, 54.5, 51.0. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}NO_4$ [M+H]$^+$: 336.1236, found: 336.1248.



Methyl 4-formyl-2-methyl-5-phenyl-1*H*-pyrrole-3-carboxylate (2m). White solid; m.p. 209.0-213.0 ℃. 24.0 mg, 50 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.37 (s, 1H), 8.52 (s, 1H), 7.59-7.57 (m, 2H), 7.43 – 7.39 (comp, 3H), 3.89 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 188.5, 165.5, 136.5, 130.7, 129.3, 129.0, 128.7, 128.5, 123.9, 120.4, 51.5, 13.5. HRMS (TOF MS CI$^+$) calculated for $C_{14}H_{14}NO_3$ [M+H]$^+$: 244.0974, found: 244.0980.

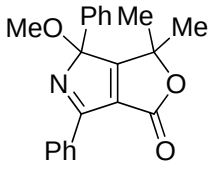


Methyl 4-formyl-2-phenyl-5-(thiophen-2-yl)-1*H*-pyrrole-3-carbo –xylate (2n). White solid; m.p. 174.0-180.0 ℃. 45.0 mg, 72 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.30 (s, 1H), 8.97 (s, 1H), 7.63 (dd, *J* = 3.7, 1.1 Hz, 1H), 7.56-7.47 (m, 2H), 7.47-7.36 (comp, 4H), 7.12 (dd, *J* = 5.1, 3.7 Hz, 1H), 3.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 187.5, 165.3, 136.9, 131.8, 131.1, 130.7, 129.2, 128.8, 128.7, 127.9, 127.7, 121.2, 113.9, 51.9. HRMS (TOF MS CI$^+$) calculated for $C_{17}H_{14}NO_3S$ [M+H]$^+$: 312.0694, found: 312.0695.

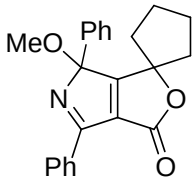


Methyl 4-benzoyl-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (2o). White solid; m.p. 73.5-75.5 ℃. 49.0 mg, 65 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.84 (s, 1H), 7.94-7.87 (m, 2H), 7.70-7.65 (m, 2H), 7.51-7.37 (comp, 9H), 7.31-7.27 (m, 2H), 7.25-7.21 (m, 1H), 3.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 194.3, 164.5, 139.0, 137.0, 132.8, 132.4, 131.0, 130.7, 129.3, 129.2, 129.0,

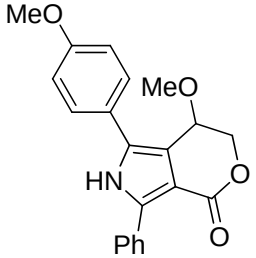
128.5, 128.5, 128.3, 127.3, 122.7, 116.0, 113.6, 51.0. HRMS (TOF MS CI$^+$) calculated for $C_{25}H_{20}NO_3$ $[M+H]^+$: 382.1443, found: 382.1458.



4-Methoxy-3,3-dimethyl-4,6-diphenyl-3,4-dihydro-1*H*-furo[3,4-*c*] pyrrol 1-one (2p). 60.0 mg, 90 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.59 (d, *J* = 7.2 Hz, 2H), 7.61-7.51 (comp, 3H), 7.42-7.35 (comp, 5H), 3.51 (s, 3H), 1.69 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 199.7, 166.6, 163.5, 133.7, 132.6, 131.3, 130.1, 129.2, 129.0, 129.0, 125.8, 101.8, 85.1, 53.3, 25.8, 24.7. HRMS (TOF MS CI$^+$) calculated for $C_{21}H_{20}NO_3$ $[M+H]^+$: 334.1443, found: 334,1435.

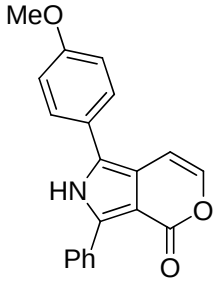


6'-Methoxy-4',6'-diphenylspiro[cyclopentane-1,1'-furo[3,4-*c*]pyrro l]-3'(6'*H*)-one. (2q) White solid; m.p. 136.5-139.0 ℃. 63.0 mg, 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.62-8.56 (m, 2H), 7.60-7.52 (comp, 3H), 7.45-7.40 (m, 2H), 7.38-7.33 (comp, 3H), 3.48 (s, 3H), 2.09-1.96 (m, 2H), 1.92-1.80 (m, 2H), 1.64-1.47 (m, 2H), 1.32-1.21 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 197.2, 166.4, 163.7, 136.3, 134.0, 132.6, 131.3, 130.1, 129.1, 129.0, 129.0, 125.5, 101.8, 94.9, 53.0, 37.2, 36.2, 24.6, 24.5. HRMS (TOF MS CI$^+$) calculated for $C_{23}H_{22}NO_3$ $[M+H]^+$: 360.1600, found: 360.1592.

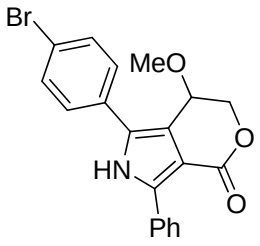


Methyl 5-(4-methoxyphenyl)-4-(oxiran-2-yl)-2-phenyl-1*H* -pyrrole-3-carboxylate. (2r). 24.0 mg, 35 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.20 (s, 1H), 7.82-7.74 (m, 2H), 7.55-7.47 (m, 2H), 7.40-7.28 (comp, 3H), 6.97 (d, *J* = 8.8 Hz, 2H), 4.78 (d, *J* = 12.5 Hz, 1H), 4.43 (s, 1H), 4.34 (dd, *J* = 12.5, 2.0 Hz,

1H), 3.83 (s, 3H), 3.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 163.4, 159.5, 137.4, 130.4, 129.7, 128.8, 128.5, 128.5, 128.1, 123.5, 117.8, 114.7, 107.7, 70.1, 68.2, 55.5, 55.4. HRMS (TOF MS CI$^+$) calculated for $C_{21}H_{20}NO_4$ $[M+H]^+$: 350.1392, found: 350.1400.

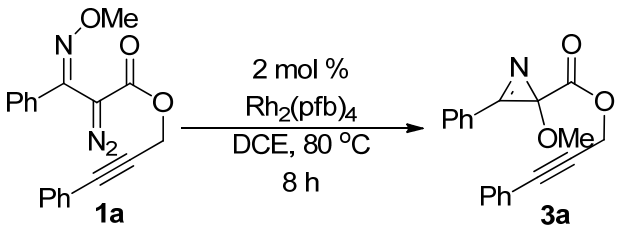


1-(4-Methoxyphenyl)-3-phenylpyrano[3,4-*c*]pyrrol-4(2*H*)-one. (2r'). 25.0 mg, 40 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.33 (s, 1H), 7.88-7.79 (m, 2H), 7.47-7.43 (m, 2H), 7.42-7.33 (comp, 3H), 7.02-6.97 (comp, 3H), 6.58 (d, *J* = 5.7 Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.7, 159.3, 142.1, 135.7, 130.2, 128.8, 128.7, 128.5, 127.8, 124.9, 123.9, 119.3, 114.9, 106.6, 101.3, 55.5. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{16}NO_3$ $[M+H]^+$: 318.1130, found: 318.1137.



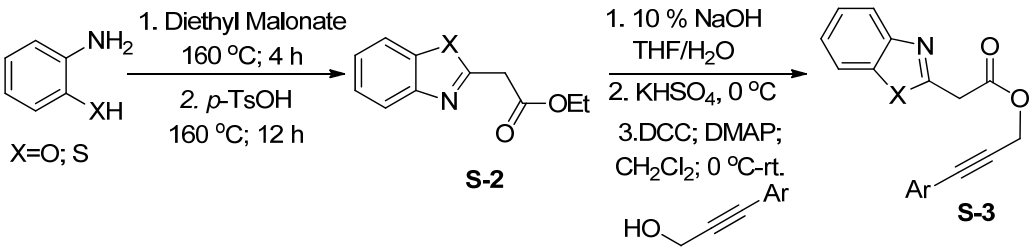
1-(4-Bromophenyl)-7-methoxy-3-phenyl-6,7-dihydropyrano[3, 4-*c*]pyrrol-4(2*H*)-one (2s). 28.0 mg, 35 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 9.02 (s, 1H), 7.79 (dd, *J* = 8.1, 1.3 Hz, 2H), 7.63-7.57 (m, 2H), 7.46-7.36 (comp, 5H), 4.84 (dd, *J* = 12.6, 1.1 Hz, 1H), 4.46-4.42 (m, 1H), 4.38 (dd, *J* = 12.6, 2.2 Hz, 1H), 3.46 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 162.9, 138.1, 132.6, 130.1, 129.7, 129.3, 128.8, 128.5, 128.4, 128.1, 122.2, 119.4, 108.3, 77.5, 69.8, 68.1, 55.5. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{17}BrNO_3$ $[M+H]^+$:398.0392, found: 398.0395.

General Procedures for the Preparation of 3a:



To a 10-mL oven-dried vial with a magnetic stirring bar, $Rh_2(pfb)_4$ (0.002 mmol, 2.1 mg) in dry DCE(2.0 mL), was added diazo compound **1a** (0.2 mmol, 66.6 mg) in DCE (2.0 mL) *via* syringe pump over 2 h under atmosphere of argon at 80 ℃. The reaction mixture was stirred overnight under this condition. The reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 6:1) to give the pure products **3a** with 70 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.93 (d, J = 7.2 Hz, 2H), 7.68-7.62 (m, 1H), 7.57 (t, J = 7.4 Hz, 2H), 7.42-7.27 (comp, 5H), 5.06-4.94 (q, J = 20.8 Hz, 2H), 3.53 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 169.0, 165.4, 134.3, 132.0, 130.5, 129.5, 128.9, 128.4, 122.1, 121.8, 87.0, 82.4, 67.7, 54.7, 54.3. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{16}NO_3$ $[M+H]^+$: 306.1130, found: 306.1142.

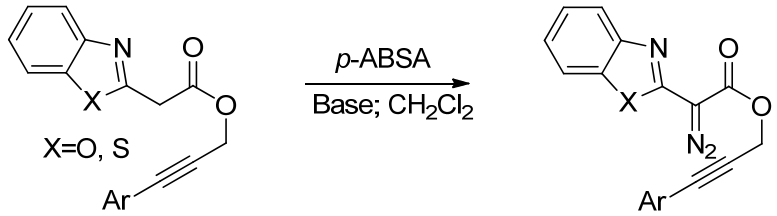
General Procedures for the Preparation of Diazoacetates 4a-4m:[2,3]



Synthesis of **S-2**:[2] To a 50-mL oven-dried flask containing a magnetic stirring bar, diethyl malonate (2.4g, 15.0 mmol) and 2-aminophenol or 2-aminothiophenol (5.0 mmol) were added. The reaction mixture was heated to 160 ℃ and stirred for 4 hours. Then *p*-TsOH (4-Methylbenzenesulfonic acid, 86 mg, 0.5 mmol) was added to the reaction mixture and the solution was stirred at 160 ℃ for another 12 hours. The reaction mixture was cooled to room temperature and directly purified by column

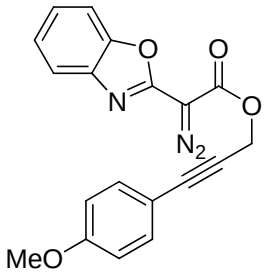
chromatography on silica gel (eluent: petroleum ether /ethyl acetate = 20:1) to provide pure **S-2** (> 75% yield, white solid).

Synthesis of **S-3**: The above obtained white solid **S-2** (2.0 mmol) was dissolved in THF (10 mL) and treated with 10 % NaOH (5 mL). The reaction mixture was stirred at room temperature overnight. Then the reaction mixture was acidified with $KHSO_4$ (1.0 mol/L) at 0 ℃ until pH = 3-4, and extracted with cold DCM (10 mL X 3). The organic phase was combined and dried with anhydrous Na_2SO_4. Then most of the solvent was evaporated under vacuum after filtration (about 10 mL DCM was left), alkynol (2.0 mmol) and DMAP (0.2 mmol) were added in sequence at 0 ℃, and DCC (2.4 mmol) was added partially. The reaction mixture was stirred overnight and the temperature was warmed to room temperature slowly. The crude reaction mixture was filtered through Celite and the filtrate was washed with saturated aqueous $NaHCO_3$ (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4. The solvent was evaporated under vacuum after filtration, the obtained product **S-3** was directly used for the next step without further purification.

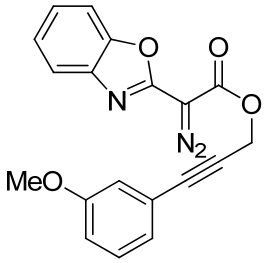


S-3 **4**

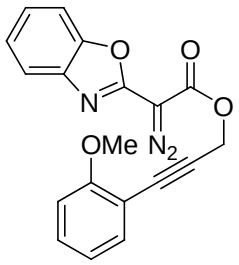
Synthesis of **4**:[3] The above obtained **S-3** was dissolved in DCM (10.0 mL), 4-acetamidobenzenesulfonyl azide (*p*-ABSA, 576 mg, 2.4 mmol) was added to the solution, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 456 mg, 3.0 mmol) in DCM (5.0 mL) was added slowly at 0 ℃. The reaction mixture was stirred overnight from 0 ℃ to room temperature. After filtering through Celite, the solvent was evaporated under vacuum and the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether /EtOAc = 10:1) to give the pure diazo compound **4** as yellow solid (> 90% yields based on **S-3**).



3-(4-Methoxyphenyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4a). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.66 (m, 1H), 7.54-7.52 (m, 1H), 7.44-7.38 (m, 2H), 7.35-7.25 (m, 2H), 6.88-6.80 (m, 2H), 5.17 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.9, 160.3, 154.0, 150.8, 141.9, 133.7, 124.9, 124.4, 119.2, 114.1, 114.0, 110.5, 87.5, 81.1, 55.4, 54.4. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}N_3O_4$ $[M+H]^+$: 348.0984, found: 348.0983.

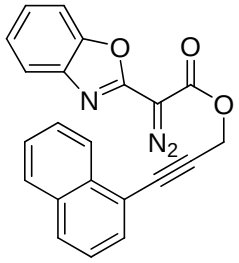


3-(3-Methoxyphenyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4b). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.72-7.65 (m, 1H), 7.56-7.51 (m, 1H), 7.36-7.27 (m, 2H), 7.23 (t, *J* = 8.0 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 7.03-6.97 (m, 1H), 6.92-6.90 (m, 1H), 5.18 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 159.4, 153.9, 150.9, 141.8, 129.6, 124.9, 124.6, 124.5, 123.0, 119.3, 116.8, 115.8, 110.5, 87.4, 82.2, 55.5, 54.2. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}N_3O_4$ $[M+H]^+$: 348.0984, found: 348.0995.

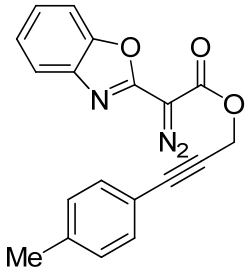


3-(2-Methoxyphenyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4c). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.67 (m, 1H), 7.54 (m, 1H), 7.45 (m, 1H), 7.36-7.27 (comp, 3H), 6.95-6.86 (m, 2H), 5.24 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.8, 160.5, 154.1,

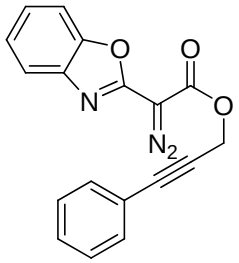
150.9, 141.8, 134.3, 130.7, 124.9, 124.4, 120.6, 119.2, 111.1, 110.8, 110.5, 86.3, 83.9, 55.9, 54.5. HRMS (TOF MS CI^+) calculated for $C_{19}H_{14}N_3O_4$ $[M+H]^+$: 348.0984, found: 348.0988.



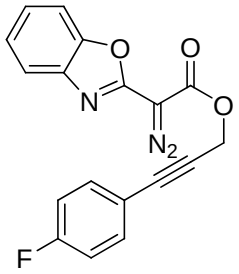
3-(Naphthalen-1-yl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4d). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.33 (d, J = 8.3 Hz, 1H), 7.86 (m, 2H), 7.76-7.65 (m, 2H), 7.63-7.50 (comp, 3H), 7.44-7.42 (m, 1H), 7.37-7.28 (m, 2H), 5.34 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.9, 153.9, 150.9, 141.9, 133.5, 133.2, 131.3 129.7, 128.5, 127.2, 126.7, 126.1, 125.6, 124.9, 124.5, 119.6, 119.3, 110.5, 87.1, 85.7, 54.4. HRMS (TOF MS CI^+) calculated for $C_{22}H_{14}N_3O_3$ $[M+H]^+$: 368.1030, found: 368.1023.



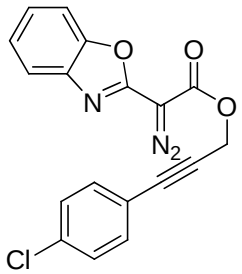
3-(*p*-Tolyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4e). ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.66 (m, 1H), 7.54-7.52 (m, 1H), 7.41-7.27 (comp, 4H), 7.13 (d, J = 7.9 Hz, 2H), 5.18 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.9, 154.0, 150.9, 141.8, 139.3, 132.0, 129.2, 124.9, 124.4, 119.3, 118.9, 110.5, 87.6, 81.7, 54.3, 21.7. HRMS (TOF MS CI^+) calculated for $C_{19}H_{14}N_3O_3$ $[M+H]^+$: 332.1030, found: 332.1027.



3-Phenylprop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4f). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70-7.65 (m, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.49-7.47 (m, 2H), 7.38-7.27 (comp, 5H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.9, 153.9, 150.9, 141.8, 132.1, 129.1, 128.5, 124.9, 124.4, 122.0, 119.3, 110.5, 87.4, 82.4, 54.2. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}N_3O_3$ $[M+H]^+$: 318.0873, found: 318.0866.

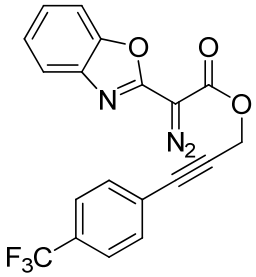


3-(4-Fluorophenyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4g). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.66 (m, 1H), 7.54-7.52 (m, 1H), 7.46-7.44 (m, 2H), 7.36-7.24 (m, 2H), 7.01 (t, *J* = 8.3 Hz, 2H), 5.16 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.2, 161.7, 160.8, 153.8, 150.8, 141.8, 134.1 (d, *J* = 8.5 Hz), 124.6 (d, *J* = 46.3 Hz), 119.2, 118.1 (d, *J* = 3.6 Hz), 115.8 (d, *J* = 22.1 Hz), 110.5, 86.3, 82.1, 54.1. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{11}FN_3O_3$ $[M+H]^+$: 336.0779, found: 336.0780.

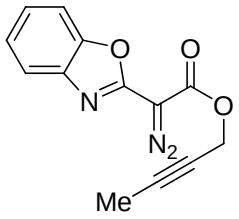


3-(4-Chlorophenyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4h). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70-7.64 (m, 1H), 7.56-7.51 (m, 1H), 7.43-7.37 (m, 2H), 7.35-7.25 (comp, 4H), 5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.8, 153.8, 150.8, 141.8, 135.2,

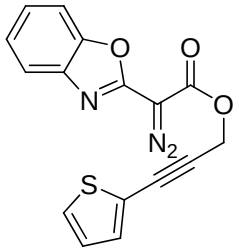
133.3, 128.8, 124.9, 124.5, 120.5, 119.3, 110.5, 86.3, 83.4, 54.1. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{11}ClN_3O_3$ $[M+H]^+$: 352.0483, found: 352.0477.



3-(Trimethylsilyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4i). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68 (d, *J* = 7.9 Hz, 1H), 7.63-7.49 (comp, 5H), 7.35-7.26 (m, 2H), 5.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.8, 153.7, 150.8, 141.8, 132.3, 130.8 (q, *J* = 33.0 Hz), 125.8 (d, *J* = 1.1 Hz), 125.4 (q, *J* = 3.7 Hz), 124.9, 124.5, 123.9 (q, *J* = 272.3 Hz), 119.3, 110.5, 85.9, 84.8, 53.8. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{11}F_3N_3O_3$ $[M+H]^+$: 386.0753, found: 386.0763.

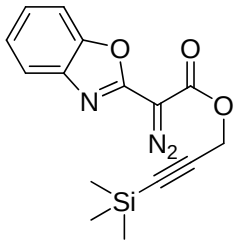


But-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2 –diazoacetate (4j). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.69-7.64 (m, 1H), 7.55-7.51 (m, 1H), 7.35-7.27 (m, 2H), 4.92 (dd, *J* = 4.6, 2.3 Hz, 2H), 1.88 (t, *J* = 2.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.9, 154.0, 150.8, 141.8, 124.8, 124.3, 119.2, 110.5, 84.3, 72.7, 54.2, 3.8. HRMS (TOF MS CI$^+$) calculated for $C_{13}H_{10}N_3O_3$ $[M+H]^+$: 256.0722, found: 256.0720.

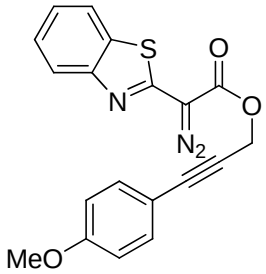


3-(Thiophen-2-yl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4k). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.71-7.63 (m, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.34-7.24 (comp, 4H), 6.96-6.97 (m, 1H),

5.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 160.6, 153.7, 150.7, 141.7, 133.3, 128.2, 127.1, 124.8, 124.3, 121.7, 119.1, 110.44, 86.4, 80.7, 54.0. HRMS (TOF MS CI$^+$) calculated for $C_{16}H_{10}N_3O_3S$ [M+H]$^+$: 324.0443, found: 324.0444.



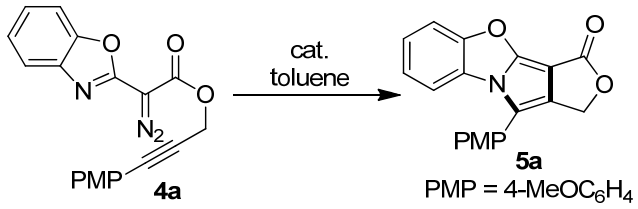
3-(Trimethylsilyl)prop-2-yn-1-yl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (4l). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.70-7.63 (m, 1H), 7.56-7.49 (m, 1H), 7.35-7.24 (m, 2H), 4.95 (s, 2H), 0.20 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 160.6, 153.9, 150.8, 141.8, 124.9, 124.4, 119.2, 110.5, 98.2, 93.3, 54.0, -0.2. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{16}N_3O_3Si$ [M+H]$^+$: 314.0961, found: 314.0962.



3-(4-Methoxyphenyl)prop-2-yn-1-yl 2-(benzo[*d*]thiazol-2-yl)-2-diazoacetate (4m). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.30 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.63-7.56 (m, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 5.25 (s, 2H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) (δ, ppm) 160.1, 159.8, 141.1, 133.6, 131.1, 130.0, 128.0, 127.7, 125.0, 115.1, 114.2, 114.0, 87.2, 81.3, 55.4, 54.0. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}N_3O_3S$[M+H]$^+$: 364.0750, found: 364.0749.

Condition Optimization for the Synthesis of Fused Polycyclic Pyrroles:

Table S2 Optimization of the reaction conditions[a]

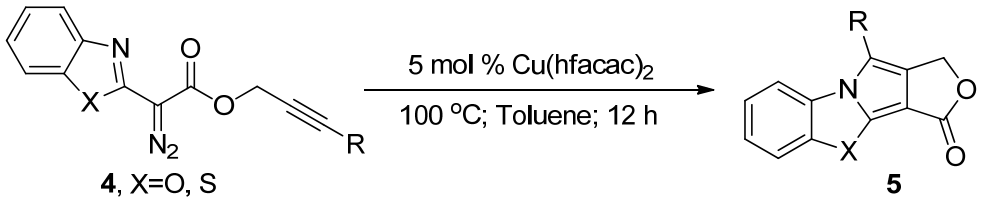


Entry	Catalyst	t (h)	T (^{o}C)	Yield (%)[b]
1	$Rh_2(OAc)_4$	4	100	55
2	$Rh_2(Oct)_4$	4	100	45
3	$Rh_2(pfb)_4$	4	100	44
4	$Cu(OTf)_2$	16	100	21
5	$Cu(CH_3CN)_4PF_6$	16	100	33
6	$Cu(hfacac)_2$	12	100	91
7	-	24	100	10[c]
8	$In(OTf)_3$	12	100	<10[c]
9	$Sc(OTf)_3$	12	100	<10[c]
10	$Cu(hfacac)_2$	24	80	69
11	$Cu(hfacac)_2$	8	110	84

[a] The reaction was carried out in 0.2 mmol scale with corresponding catalysts (Rh 1.0 mol% or Cu 5.0 mol%) in 2.5 mL of dry toluene at indicated temperature. [b] Isolated yields. [c] Most of the material **4a** was recovered.

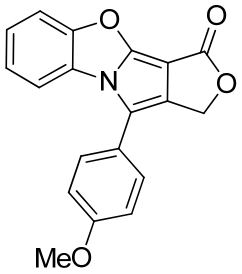
The using of dirhodium catalyst produced **5a** in up to 55% yield (Table S2, entry1-3). Further examination of various Cu(II) complexes gave dramatic outcomes, although **4a** was consumed in these cases, and only $Cu(hfacac)_2$ provided **5a** in high yields (entry 4-6). Control reactions in the absence of the catalyst or with Lewis acids as catalyst, including $In(OTf)_3$ and $Sc(OTf)_3$, were carried out, and less than 10% of the product was obtained (entries 7-9). Other solvents, for examples, DCM or DCE, both gave inferior results. Temperature evaluation turned out that the best result was obtained at 100 ^{o}C with $Cu(hfacac)_2$ (91% yield, entry 6 *vs* entries 10 and 11).

General Procedure for the Synthesis of Fused Polycyclic Pyrroles:

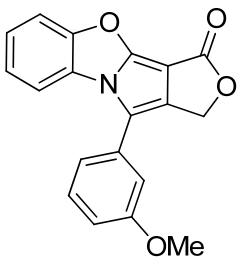


4, X=O, S **5**

To a 10-mL oven-dried vial with a magnetic stirring bar, $Cu(hfacac)_2$ (4.7 mg, 0.01 mmol) in dry toluene (1.0 mL), was added diazo compound **4** (0.2 mmol) in toluene (1.5 mL) *via* syringe pump over 30 min under atmosphere of argon at 100 ℃. The reaction mixture was stirred overnight under this condition. The reaction mixture was purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 5:1) to give the pure products **5** in high yields.

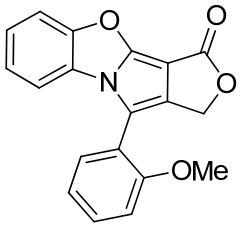


10-(4-Methoxyphenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5a). White solid; m.p. 202.5-203.5 ℃. 58.0 mg, 91 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56-7.54 (m, 1H), 7.51-7.49 (m, 1H), 7.45-7.43 (m, 2H), 7.38-7.32 (m, 1H), 7.28-7.26 (m, 1H), 7.10-7.00 (m, 2H), 5.31 (s, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 159.6, 152.2, 141.3, 131.9, 129.1, 127.1, 125.0, 124.2, 122.2, 114.8, 112.8, 112.8, 112.0, 88.4, 66.3, 55.6. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}NO_4$ $[M+H]^+$: 320.0923, found: 320.0931.

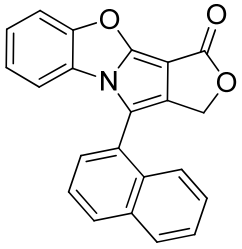


10-(3-Methoxyphenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5b). White solid; m.p. 120.0-124.0 ℃. 58.0mg, 91 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.64-7.62 (m, 1H), 7.57-7.55 (m, 1H), 7.45-7.43 (m, 1H),

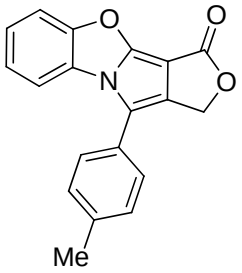
7.38-7.36 (m, 1H), 7.32-7.27 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 7.02 (s, 1H), 6.96-6.94 (m, 1H), 5.33 (s, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.5, 160.2, 152.2, 141.7, 133.1, 131.2, 130.5, 127.1, 125.2, 124.3, 119.6, 113.2, 113.1, 112.8, 112.2, 88.8, 66.3, 55.5. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}NO_4$ $[M+H]^+$: 320.0923, found: 320.0912.



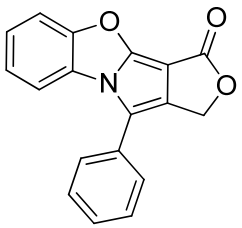
10-(2-Methoxyphenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5c). White solid; m.p. 182.0-183.0 ℃. 56.0mg, 88 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.66 (m, 1H), 7.55-7.53 (m, 1H), 7.45-7.43 (m, 1H), 7.36-7.27 (comp, 3H), 6.95-6.86 (m, 2H), 5.24 (s, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.8, 156.6, 152.1, 141.5, 134.2, 129.9, 129.8, 127.4, 124.7, 124.1, 120.8, 118.4, 113.1, 112.5, 111.3, 108.3, 88.5, 67.1, 55.5. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}NO_4$ $[M+H]^+$: 320.0923, found: 320.0912.



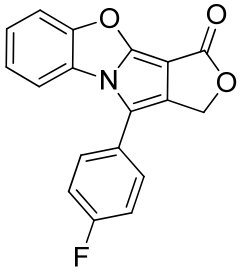
10-(Naphthalen-1-yl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5d). White solid; m.p. 226.0-227.0 ℃. 52.9 mg, 78 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.05-7.97 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.70-7.68 (m, 1H), 7.65-7.54 (comp, 3H), 7.54-7.49 (m, 1H), 7.33-7.28 (m, 1H), 7.12-7.04 (m, 1H), 6.80-6.78 (m, 1H), 5.23 (dd, *J* = 36.4, 14.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 152.2, 141.5, 134.2, 134.1, 131.8, 129.7, 129.0, 128.4, 127.4, 127.0, 126.8, 126.8, 125.5, 125.3, 125.0, 124.3, 112.9, 112.7, 109.6, 88.7, 66.6. HRMS (TOF MS CI$^+$) calculated for $C_{22}H_{14}NO_3$ $[M+H]^+$: 340.0974, found: 340.0959.



10-(*p*-Tolyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5e). White solid; m.p. 248.0-248.5 ℃. 45.0 mg, 75 % yield.^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.57 (d, *J* = 8.1 Hz, 2H), 7.44-7.31 (comp, 5H), 7.30-7.24 (m, 1H), 5.33 (s, 2H), 2.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.6, 152.3, 141.6, 138.1, 132.4, 130.0, 127.4, 127.2, 127.0, 125.1, 124.2, 113.0, 112.8, 112.4, 88.7, 66.3, 21.5. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}NO_3$ $[M+H]^+$: 304.0974, found: 304.0962.

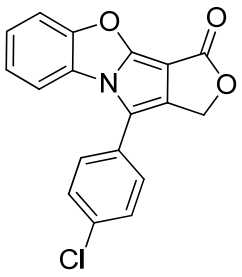


10-Phenylbenzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5f). White solid; m.p. 182.5-183.5 ℃. 49.1 mg, 85 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.61-7.50 (comp, 6H), 7.44-7.34 (m, 2H), 7.31-7.29 (m, 1H), 5.35 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) (δ, ppm) 164.5, 152.3, 141.8, 133.0, 130.0, 129.4, 128.1, 127.3, 127.1, 125.2, 124.3, 113.0, 112.9, 112.3, 88.9, 66.3. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{12}NO_3$ $[M+H]^+$: 290.0817, found: 290.0806.

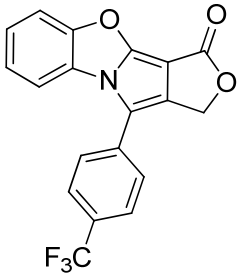


10-(4-Fluorophenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5g). White solid; m.p. 256.0-257.5 ℃. 39.0 mg, 64 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 (d, *J* = 7.9 Hz, 1H), 7.53-7.45 (comp, 3H), 7.41-7.36 (m, 1H), 7.32-7.27 (m, 1H), 7.26-7.20 (m, 2H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.4, 163.7, 161.3, 152.3, 141.7, 133.0, 129.5 (d, *J* = 8.1 Hz),

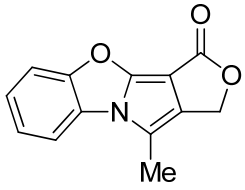
127.0, 126.1 (d, J = 3.4 Hz), 125.3, 124.4, 116.6 (d, J = 21.9 Hz), 112.9 (d, J = 31.8 Hz) , 111.1, 88.9, 66.1. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{11}FNO_3$ [M+H]$^+$: 308.0723, found: 308.0706.



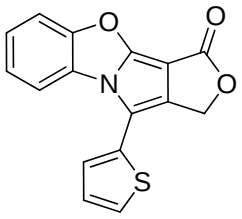
10-(4-Chlorophenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5h). White solid; m.p. 246.5-247.5 ℃. 38.0 mg, 59 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.59 (d, J = 8.2 Hz, 1H), 7.53-7.50 (comp, 3H), 7.45 (d, J = 8.5 Hz, 2H), 7.42-7.36 (m, 1H), 7.30-7.28 (m, 1H), 5.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.3, 152.2, 141.9, 134.0, 133.5, 129.7, 128.6, 128.5, 127.0, 125.4, 124.4, 113.0, 112.8, 111.1, 89.1, 66.2. HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{11}ClNO_3$ [M+H]$^+$: 324.0427, found: 324.0430.



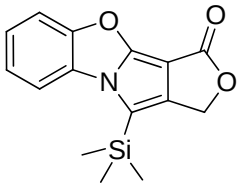
10-(4-(Trifluoromethyl)phenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5i). White solid; m.p. 268.0-270.0 ℃. 39.0 mg, 56 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.79 (d, J = 8.1 Hz, 2H), 7.68-7.56 (comp, 4H), 7.42 (t, J = 7.6 Hz, 1H), 7.34 (t, J = 7.6 Hz, 1H), 5.37 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.1, 152.3, 142.4, 134.9, 133.6, 129.8 (q, J = 32.8 Hz), 127.1, 127.0, 126.5 (q, J = 3.7 Hz), 125.6, 124.6, 124.0 (q, J = 272.1 Hz), 113.2, 112.9, 110.9, 89.7, 66.2. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{11}F_3NO_3$ [M+H]$^+$: 358.0691, found: 358.0681.



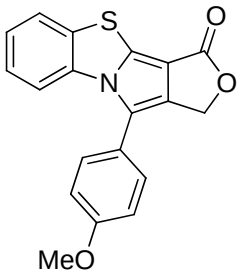
10-Methylbenzo[d]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5j). White solid; m.p. 164.0-168.0 ℃. 22.0 mg, 49 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.66-7.62 (m, 1H), 7.57-7.53 (m, 1H), 7.39-7.34 (m, 2H), 5.22 (s, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.8, 152.1, 140.3, 130.7, 127.4, 124.7, 124.5, 112.9, 111.4, 106.5, 87.0, 65.8, 11.3. HRMS (TOF MS CI$^+$) calculated for $C_{13}H_{10}NO_3$ $[M+H]^+$: 228.0661, found: 228.0652.



10-(Thiophen-2-yl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5k). White solid; m.p. 189.0-191.0 ℃. 53.0 mg, 90 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.69-7.67 (m, 1H), 7.59-7.57 (m, 1H), 7.44-7.31 (comp, 3H), 7.26 (d, J = 2.9 Hz, 1H), 7.20 (dd, J = 5.0, 3.6 Hz, 1H), 5.32 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 164.3, 152.1, 141.4, 134.6, 130.8, 128.0, 126.9, 126.9, 126.4, 125.3, 124.5, 112.9, 112.8, 105.2, 89.0, 66.3. HRMS (TOF MS CI$^+$) calculated for $C_{16}H_{10}NO_3S$ $[M+H]^+$: 296.0381, found: 296.0384.

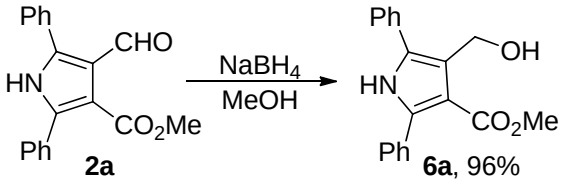


10-(Trimethylsilyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]oxazol-3(1*H*)-one (5l). White solid; m.p. 182.0-183.0 ℃. 37.0 mg, 67 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) δ 7.65-7.61 (m, 1H), 7.61-7.57 (m, 1H), 7.43-7.35 (m, 2H), 5.28 (s, 2H), 0.43 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) δ 164.6, 152.3, 146.4, 144.6, 128.0, 124.8, 124.7, 113.1, 112.2, 109.4, 89.2, 67.3, -0.4. HRMS (TOF MS CI$^+$) calculated for $C_{15}H_{16}NO_3Si$ $[M+H]^+$: 286.0899, found: 286.0891.



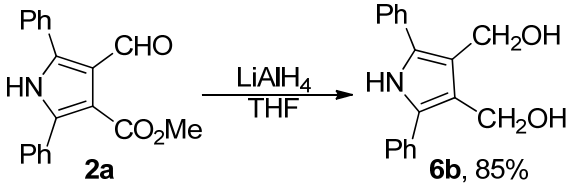
10-(4-Methoxyphenyl)benzo[*d*]furo[3',4':3,4]pyrrolo[2,1-*b*]thiazol-3(1*H*)-one (5m). White solid; m.p. 198.0-200.0 ℃. 62.4 mg, 93 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.72 (d, *J* = 7.9 Hz, 1H), 7.46-7.40 (m, 2H), 7.27 (comp, 3H), 7.09-7.03 (m, 2H), 5.24 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.4, 160.3, 136.7, 134.6, 131.7, 131.3, 126.6, 126.0, 124.9, 124.4, 122.5, 120.1, 114.7, 114.6, 104.7, 66.3, 55.6. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{14}NO_3S$ $[M+H]^+$: 336.0694, found: 336.0677.

The Derivatization:

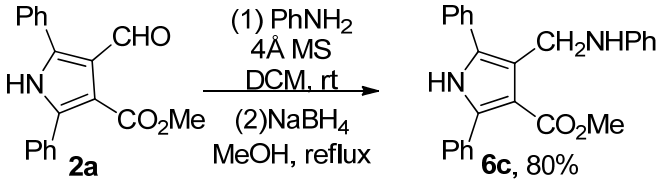


In a 10 mL round bottom flask, compound **2a** (0.20 mmol, 61 mg) was dissolved in dry MeOH (4.0 mL) and cooled to 0 ℃. After 5 min, $NaBH_4$ (0.4 mmol, 15 mg) was added portion-wise to the stirred solution at 0 °C. After completion of addition of $NaBH_4$, the reaction mixture was allowed to warm up to room temperature and stirred for 2 hours. After the consumption of starting material (monitored by TLC analysis), the reaction mixture was quenched by addition of saturated NH_4Cl and extracted with DCM (5.0 mL × 2). Organic layers were combined and dried over Na_2SO_4 followed by evaporation of solvent and resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether / EtOAc = 2:1) to give the pure compound **6a** (59.0 mg, 96% yields). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.52-7.47 (m, 2H), 7.46-7.32 (comp, 8H), 4.66 (s, 2H), 4.07 (t, *J* = 7.1 Hz, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 167.0, 137.9, 132.4, 131.4, 131.3, 129.2, 129.0,

128.5, 128.21, 128.17, 128.0, 122.9, 112.0, 77.5, 56.6, 51.3. HRMS (TOF MS CI$^+$) calculated for $C_{19}H_{18}NO_3$ $[M+H]^+$: 308.1287, found: 308.1294.

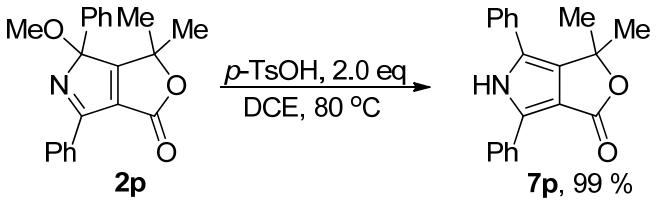


In a 10 mL round bottom flask, compound **2a** (0.20 mmol, 61 mg) was dissolved in dry THF (4.0 mL) and cooled to 0 ℃. After 5 min, $LiAlH_4$ (0.6 mmol, 22.7 mg) was added portion-wise to the stirred solution at 0 °C. After completion of addition of $LiAlH_4$, the reaction mixture was allowed to warm up to room temperature and stirred for 2 hours. After the consumption of starting material, monitored by TLC analysis, the reaction mixture was quenched by addition of $Na_2SO_4{\cdot}10H_2O$, saturated NH_4Cl and extracted with DCM (5.0 mL × 2). Organic layers were combined and dried over Na_2SO_4 followed by evaporation of solvent and resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether / EtOAc = 1:1) to give the pure compound **6b** (47.5 mg, 85% yields based on **2a**). ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 8.25 (s, 1H), 7.53-7.48 (comp, 4H), 7.47-7.42 (comp, 4H), 7.37-7.32 (m, 2H), 4.77 (s, 4H), 2.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 132.3, 131.1, 129.1, 127.6, 127.6, 121.0, 56.5 HRMS (TOF MS CI$^+$) calculated for $C_{18}H_{18}NO_2$ $[M+H]^+$: 280.1338, found: 280.1352.



In a 10 mL round bottom flask, compound **2a** (0.2 mmol, 61 mg) in DCM (3.0 mL) at room temperature was added aniline (0.2 mmol, 18.6 mg) and 4 Å MS (100 mg) in one portion and the reaction mixture was stirred overnight at room temperature. After

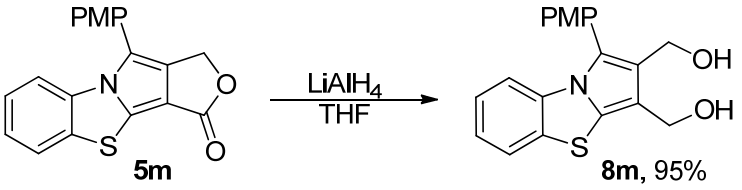
filtering through Celite, the solvent was evaporated under vacuum and the resulting residue was dissolved in dry MeOH (4.0 mL) and cooled to 0 ℃. After 5 min, $NaBH_4$ (0.4 mmol, 15 mg) was added portion-wise to the stirred solution at 0 ℃. After completion of addition of $NaBH_4$, the reaction mixture was allowed to warm up to 60 ℃ and stirred for 2 hours. After the consumption of starting material (monitored by TLC analysis), the reaction mixture was quenched by addition of saturated NH_4Cl and extracted with DCM (5.0 mL × 2). Organic layers were combined and dried over Na_2SO_4 followed by evaporation of solvent and resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether / EtOAc = 5:1) to give the pure compound **6c** (61.0 mg, 80% yields based on **2a**). ^{1}H NMR (400 MHZ, $CDCl_3$) (δ, ppm) 8.48 (s, 1H), 7.55-7.48 (comp, 4H), 7.47-7.35 (comp, 6H), 7.12-7.18 (m, 2H), 6.73-6.62 (comp, 3H), 4.38 (s, 2H), 3.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 166.0, 148.9, 137.6, 132.5, 131.8, 131.7, 129.2, 129.1, 128.5, 128.3, 128.0, 127.9, 120.1, 117.5, 115.3, 113.8, 112.5, 51.2, 39.8. HRMS (TOF MS CI$^+$) calculated for $C_{25}H_{23}N_2O_2$ $[M+H]^+$: 383.1760, found 383.1766.



2p **7p**, 99 %

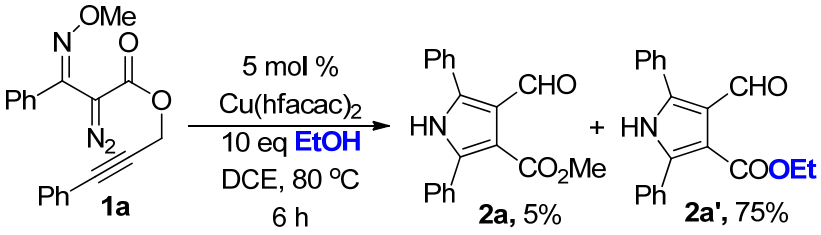
The above obtained product **2p** (0.2 mmol, 66.6 mg) was dissolved in DCM (4.0 mL), *p*-TsOH(0.4 mmol, 68.9 mg) was added to the solution, and the reaction mixture was stirred overnight at 80 ℃. After the consumption of starting material (monitored by TLC analysis), the resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether / EtOAc = 5:1) to give the pure compound **7p** (60.0 mg, 99% yields). White solid; m.p. 148.0-150.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.60 (comp, 4H), 7.57-7.51 (m, 2H), 7.40-7.32 (comp, 4H), 1.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 191.1, 188.0, 168.4, 167.0, 135.8, 135.5, 135.0,

134.5, 129.6, 129.5, 129.2, 129.1, 128.7, 86.5, 25.9. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{18}NO_2$ $[M+H]^+$: 304.1338, found: 304.1342.

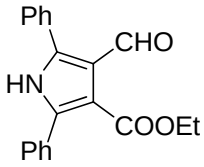


In a 10 mL round bottom flask, compound **5m** (0.2 mmol, 58 mg) was dissolved in dry THF (4.0 mL) and cooled to 0 ℃. After 5 min, $LiAlH_4$ (0.4 mmol, 15.2 mg) was added portion-wise to the stirred solution at 0 °C. After completion of addition of $LiAlH_4$, the reaction mixture was allowed to warm up to room temperature and stirred for 2 hours. After the consumption of starting material (monitored by TLC analysis), the reaction mixture was quenched by addition of $Na_2SO_4{\cdot}10H_2O$, saturated NH_4Cl and extracted with DCM (5.0 mL × 2). Organic layers were combined and dried over Na_2SO_4 followed by evaporation of solvent and resulting residues was purified by column chromatography on silica gel (eluent: petroleum ether / EtOAc = 1:1) to give the pure compound **8m** (64.5 mg, 95% yields based on **5m**). White solid; m.p. 144.0-146.0 ℃. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.56 – 7.34 (comp, 3H), 7.15 – 6.87 (comp, 5H), 4.91 – 4.65 (m, 2H), 4.56 – 4.39 (m, 2H), 3.88 (s, 3H), 3.17 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 156.0, 135.4, 132.4, 131.3, 126.6, 126.39, 126.35, 125.1, 123.9, 123.5, 123.2, 114.1, 113.6, 112.1, 57.1, 56.4, 55.5. HRMS (TOF MS CI$^+$) calculated for $C_{20}H_{22}NO_4S$ $[M+CH_3OH+H]^+$: 372.1270, found: 372.1210.

Control Reactions:

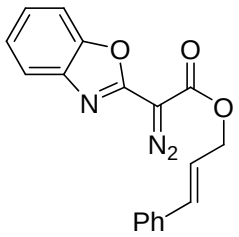


To a 10-mL oven-dried vial with a magnetic stirring bar, $Cu(hfacac)_2$ (4.7 mg, 0.01 mmol) was dissolved in dry DCE(2.0 mL), a solution of diazo compound **1a** (0.2 mmol, 66.6 mg) and EtOH (2.0 mmol, 117 uL) in DCE (2.0 mL) was added slowly *via* syringe pump over 2 h under atmosphere of argon at 80 ℃. After addition, continue stirring at 80 ℃ for 4 h. The reaction mixture was directly purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 3:1) to give the pure products **2a** and **2a'**.[4]



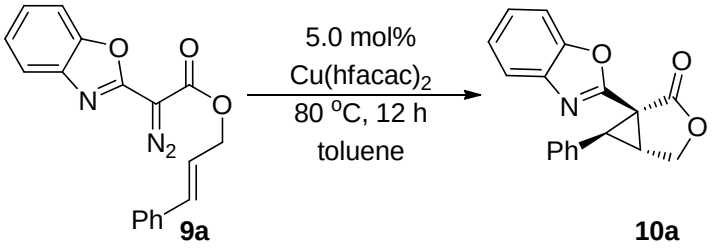
Ethyl 4-formyl-2,5-diphenyl-1*H*-pyrrole-3-carboxylate (2a'). 51.0 mg, 75 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) (δ, ppm) 10.15 (s, 1H), 9.04 (s, 1H), 7.58-7.57 (m, 2H), 7.54-7.52 (m, 2H), 7.45-7.37 (comp, 6H), 4.27 (q, J = 7.1 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) (δ, ppm) 187.4, 165.5, 139.6, 136.0, 130.8, 130.1, 129.4, 129.2, 128.8, 128.7, 128.5, 128.5, 121.0, 114.0, 61.1, 14.1. HRMS (TOF MS CI$^+$) calculated for $C_{10}H_{18}NO_3$ $[M+H]^+$: 320.1287, found: 320.1297.

Control reactions with styryl tethered diazo compounds



Cinnamyl 2-(benzo[*d*]oxazol-2-yl)-2-diazoacetate (9a). Prepared according to the general procedure for the preparation of diazoacetates **1**. ^{1}H NMR

(400 MHz, $CDCl_3$) (δ, ppm) 7.68-7.66 (m, 1H), 7.54-7.52 (m, 1H), 7.41 (d, *J* = 7.3 Hz, 2H), 7.36-7.25 (comp, 5H), 6.76 (d, *J* = 15.9 Hz, 1H), 6.44-6.32 (m, 1H), 5.00 (d, *J* = 6.5 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 161.3, 154.2, 150.8, 141.9, 136.1, 135.5, 128.8, 128.4, 126.9, 124.8, 124.3, 122.4, 119.2, 110.5, 66.6. HRMS (TOF MS CI^+) calculated for $C_{18}H_{14}N_3O_3$ $[M+H]^+$: 320.1035, found: 320.1023.



To a 10-mL oven-dried vial with a magnetic stirring bar, $Cu(hfacac)_2$ (4.7 mg, 0.01 mmol) was dissolved in dry toluene (1.0 mL), diazo compound **9a** (0.2 mmol, 63.8 mg) in toluene (1.5 mL) was added slowly *via* syringe pump over 30 min under atmosphere of argon at 80 ℃. After addition, continue stirring at 80 ℃ for 12 h. The reaction mixture was directly purified by flash column chromatography on silica gel (eluent: petroleum ether:EtOAc = 3:1) to give the pure products **10a** (52 mg, 90 % yield). White solid; m.p. 201.0-203.0 ℃. ^1H NMR (400 MHz, $CDCl_3$) (δ, ppm) 7.62 (s, 1H), 7.42 (s, 1H), 7.28-7.23 (m, 2H), 7.21-7.06 (comp, 5H), 4.72 (dd, *J* = 9.4, 4.6 Hz, 1H), 4.55 (d, *J* = 9.4 Hz, 1H), 3.62-3.61 (m, 1H), 3.05 (d, *J* = 5.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) (δ, ppm) 171.1, 167.7, 131.8, 128.6, 128.2, 128.1, 125.5, 124. 6, 120.2, 111.0, 68.5, 37.4, 29.8, 28.4. HRMS (TOF MS CI^+) calculated for $C_{18}H_{14}NO_3$ $[M+H]^+$: 292.0974, found: 292.0969.

Control reactions in NMR tube:

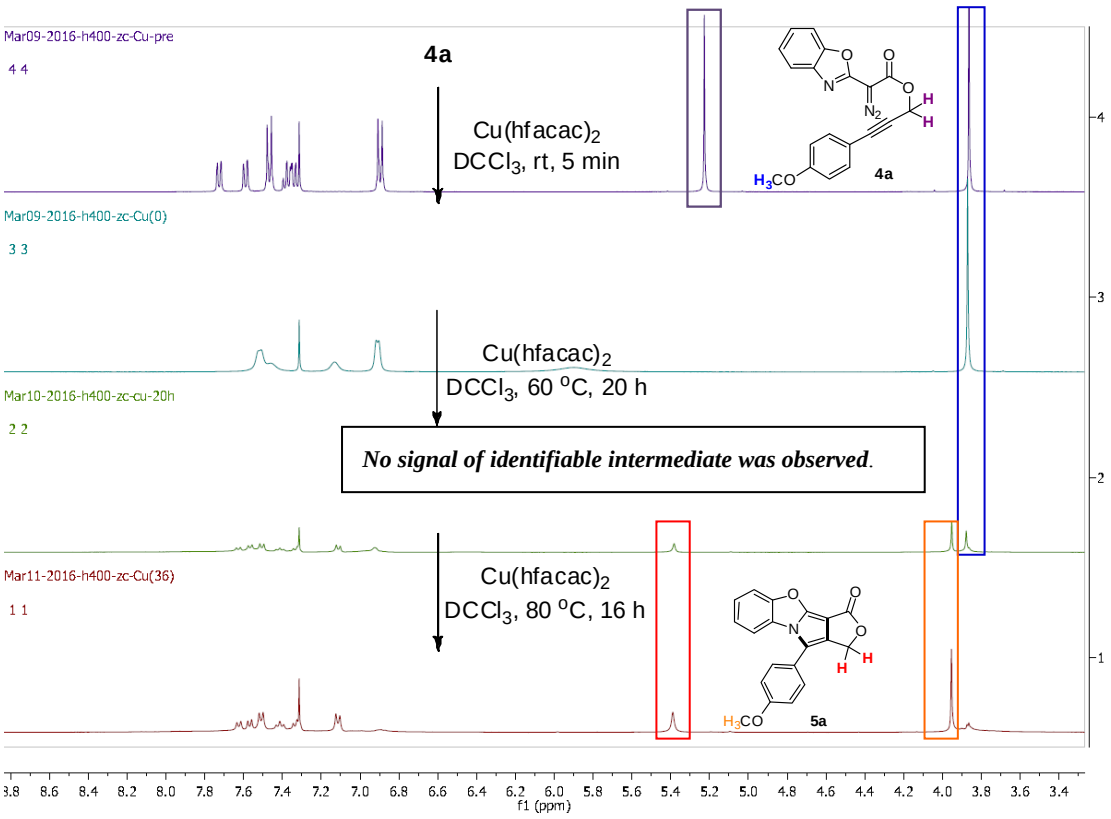


Fig. S1 Control reaction in NMR tube with copper catalyst.

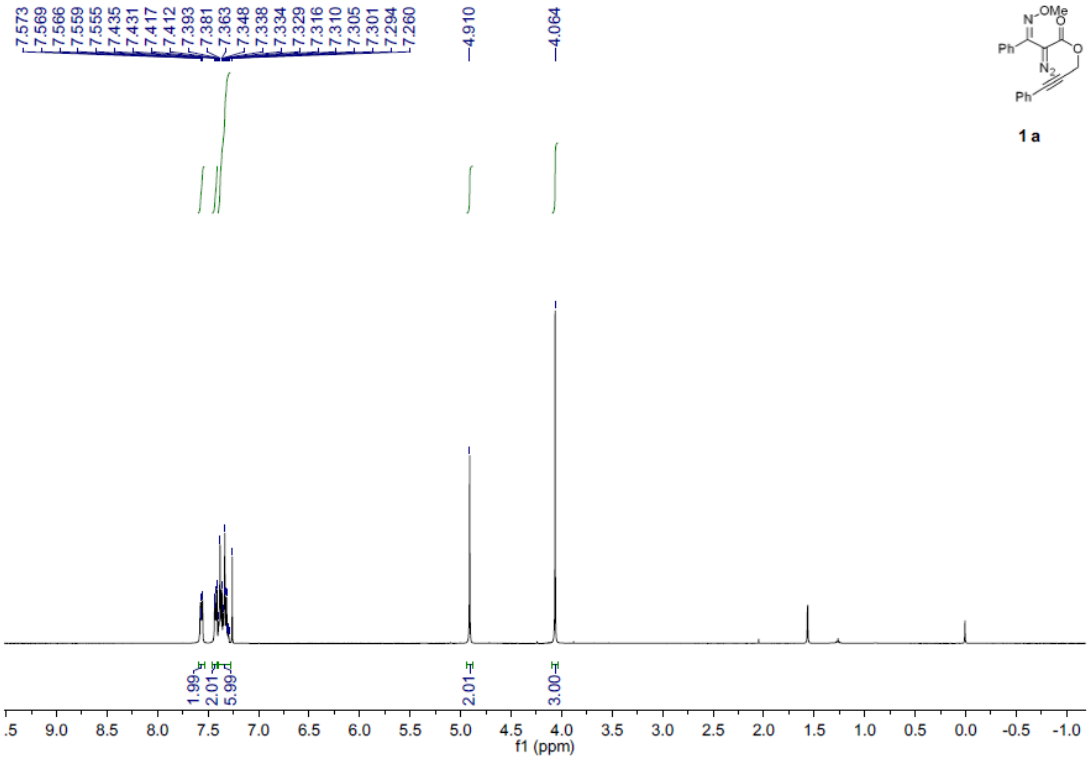
References

(1) E. Lourdusamy, L. Yao and C.-M. Park, *Angew. Chem. Int. Ed.*, 2010, **49**, 7963.

(2) (a) S. R. Waetzig and J. A. Tunge, *J. Am. Chem. Soc.*, 2007, **129**, 4138; (b) R. Shang, Z.-W. Yang, Y. Wang, S.-L. Zhang and L. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 14391.

(3) (a) A. Padwa and M. D. Weingarten, *J. Org. Chem.*, 2000, **65**, 3722; (b) M. C. McMills, R. J. Humes and O. M. Pavlyuk, *Tetrahedron Lett.*, 2012, **53**, 849.

(4) S. Chiba, Y. Wang, G. Lapointe and K. Narasaka, *Org. Lett.*, 2008, **10**, 313.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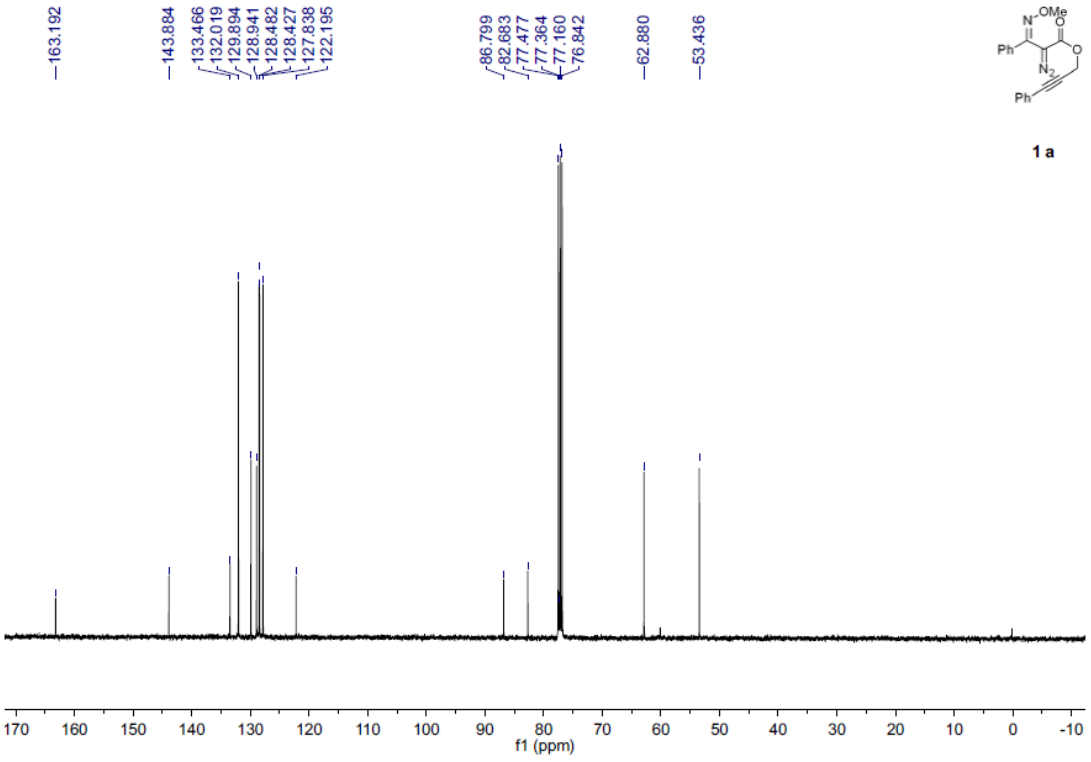
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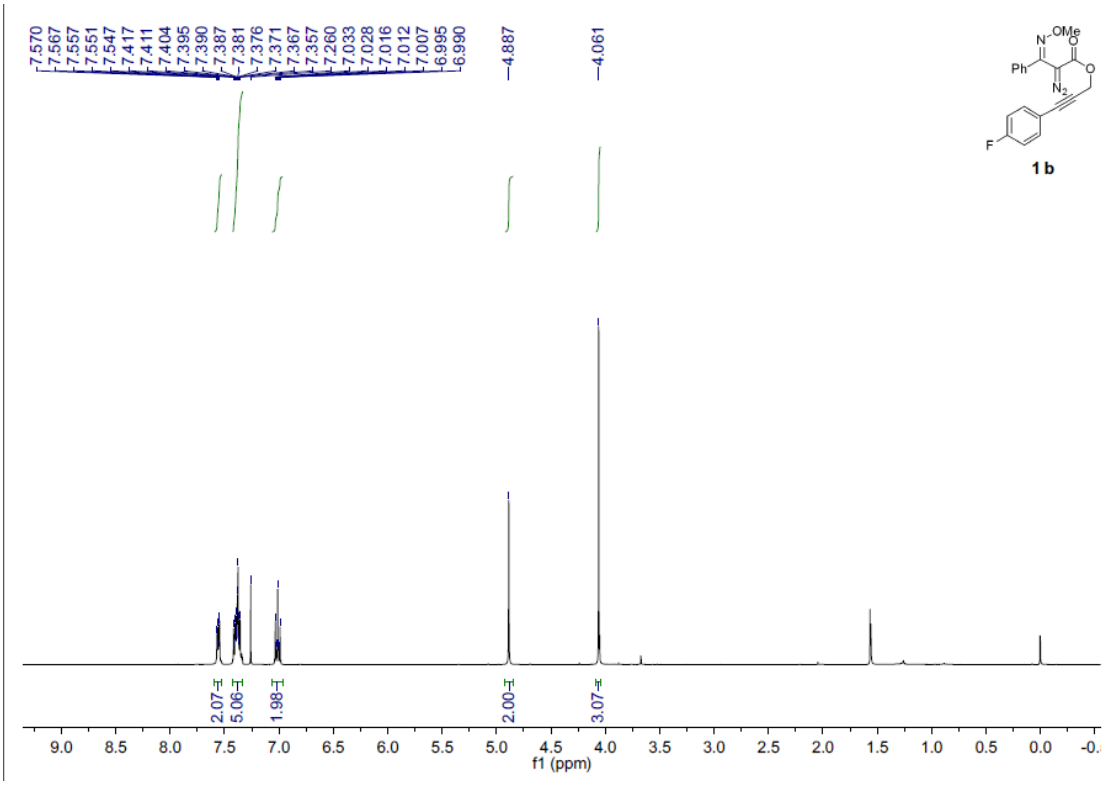
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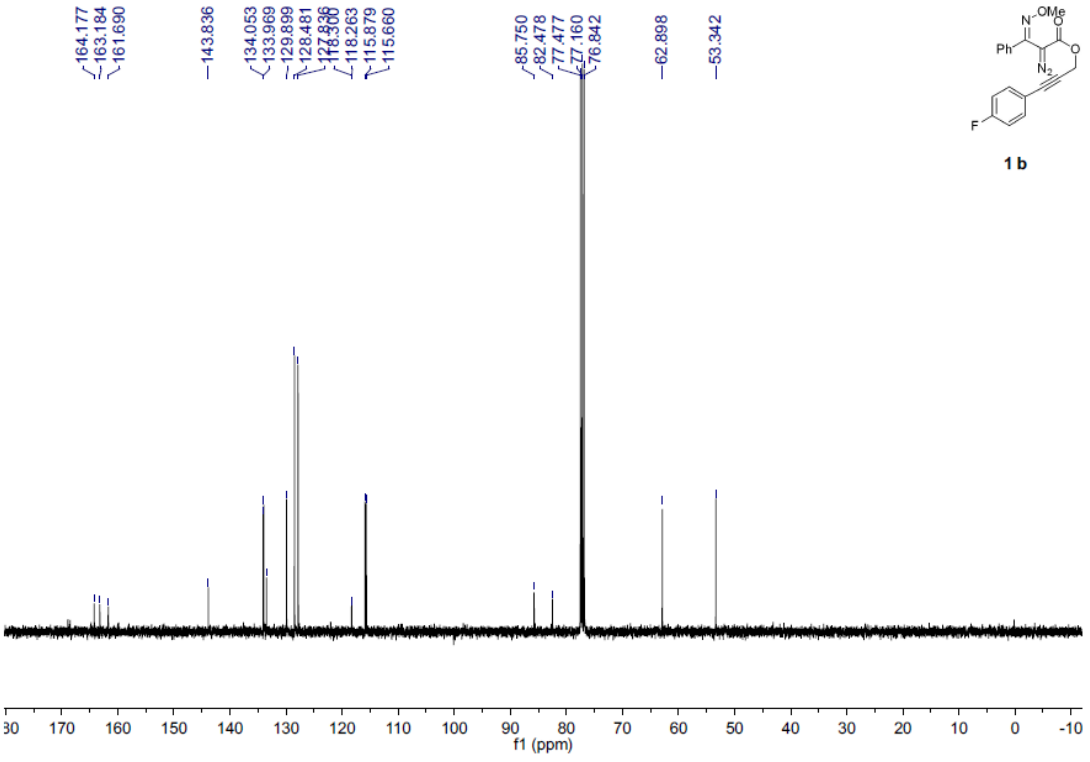
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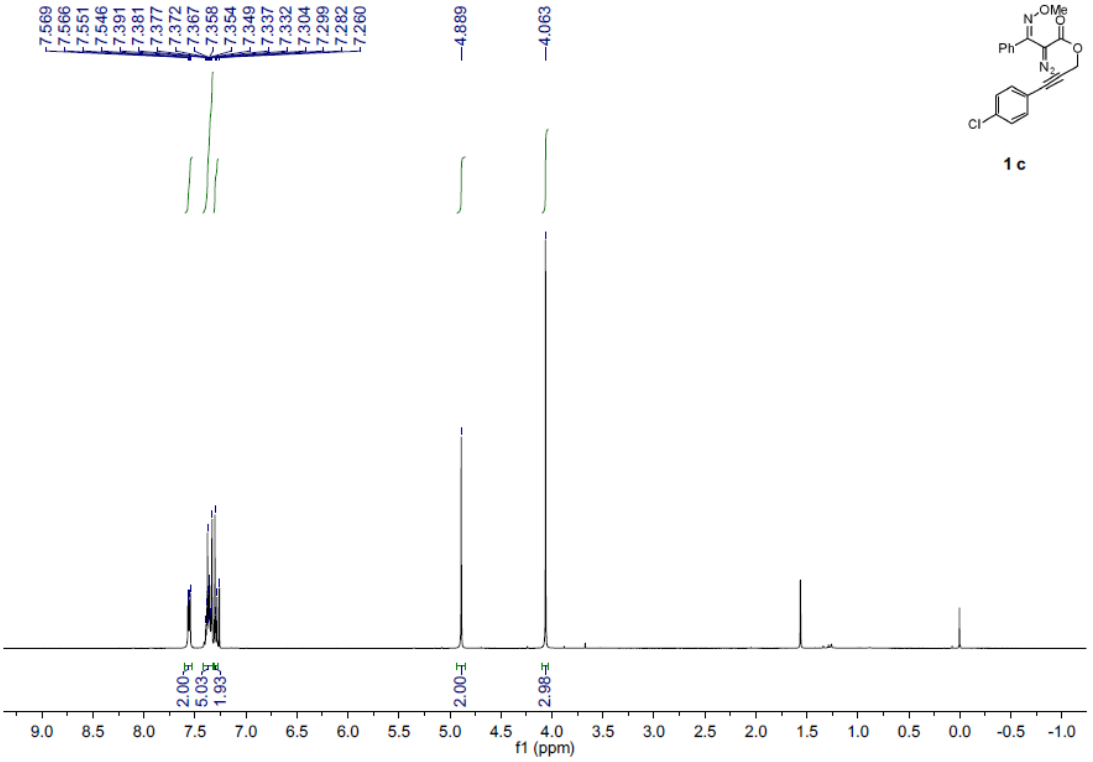
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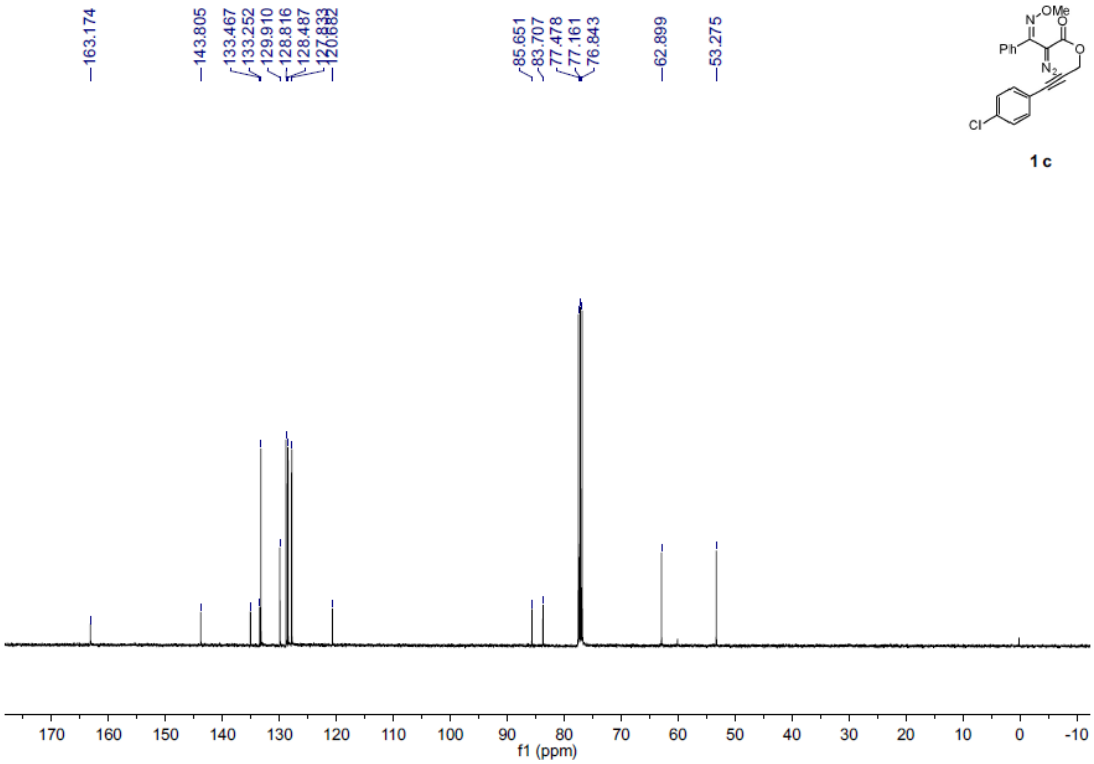
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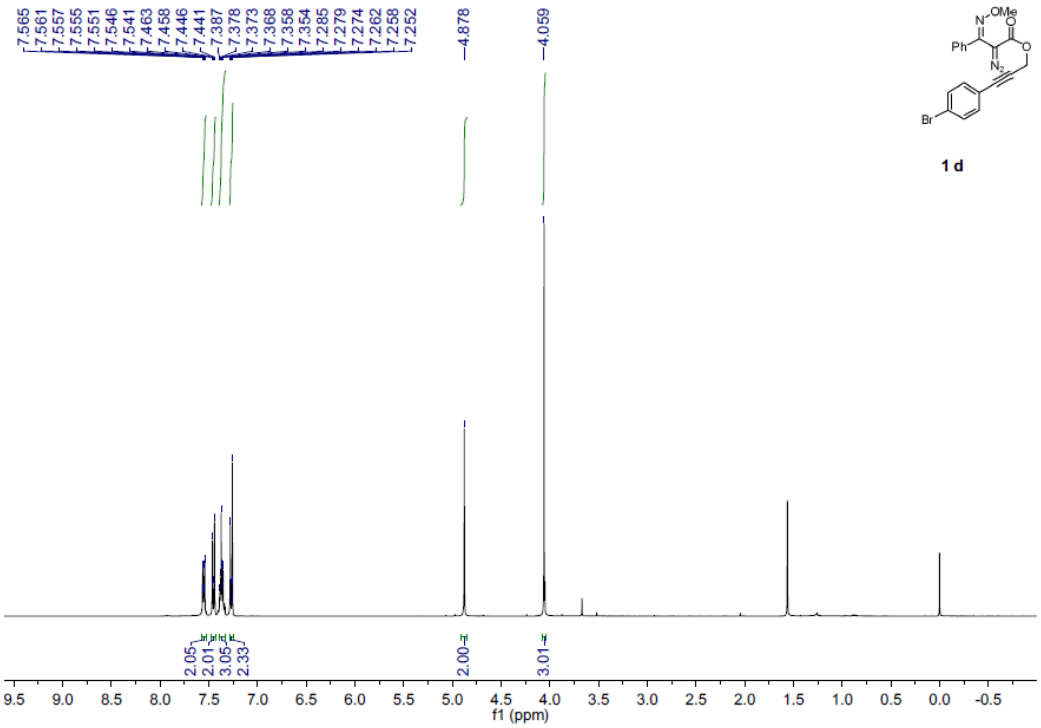
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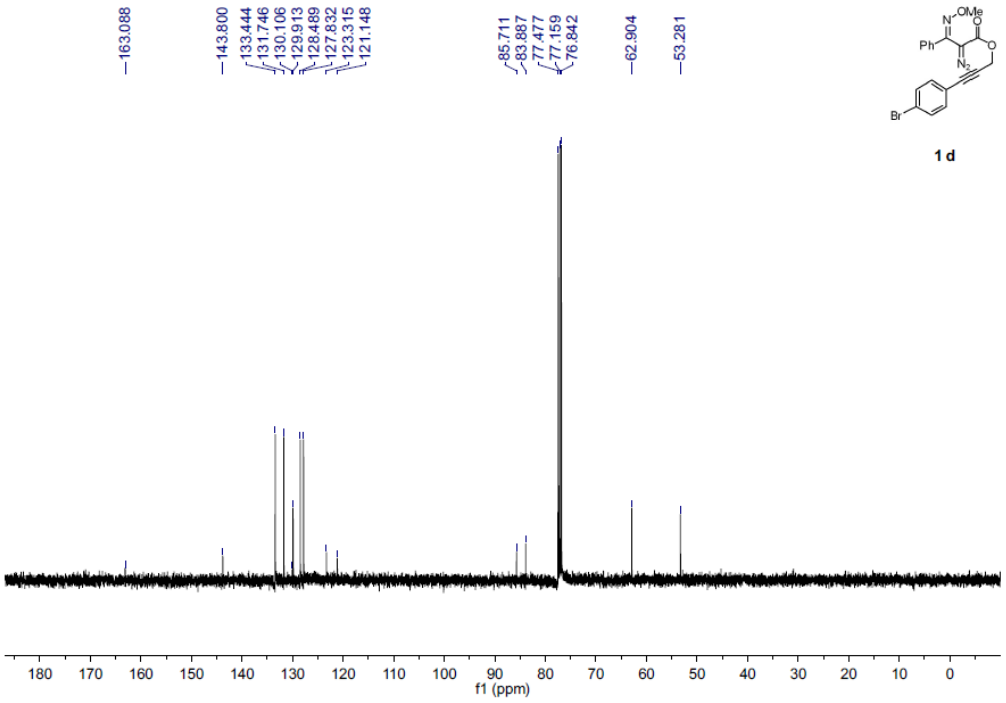
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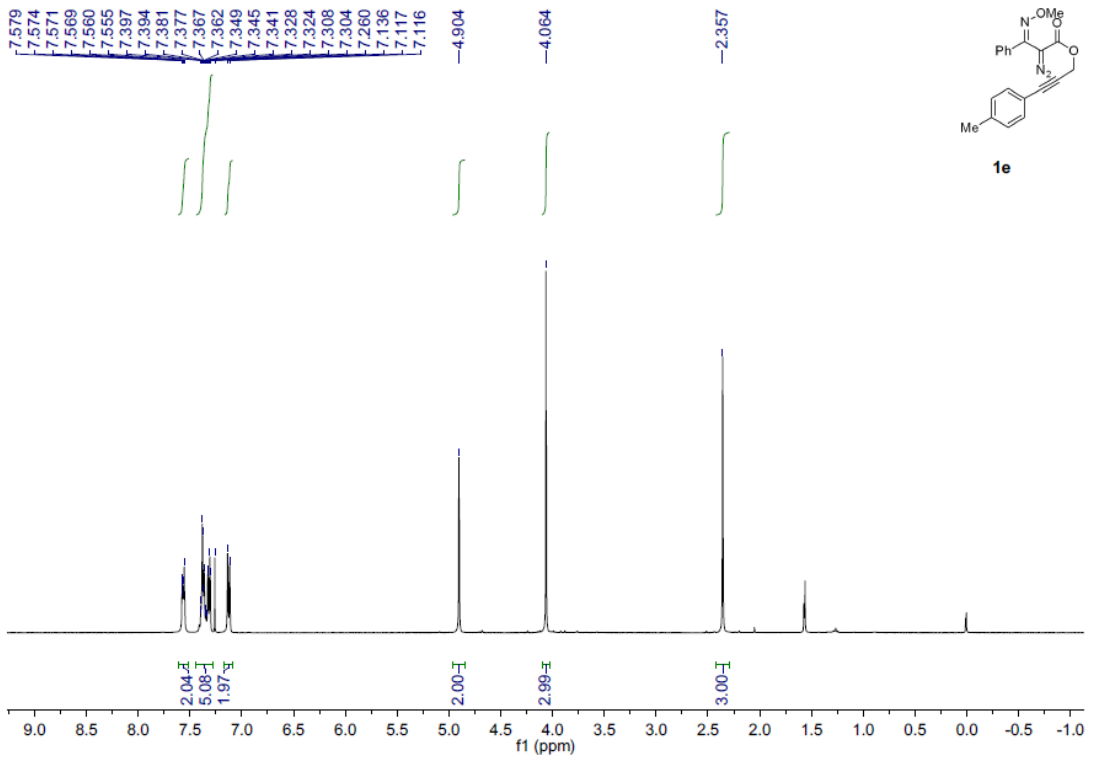
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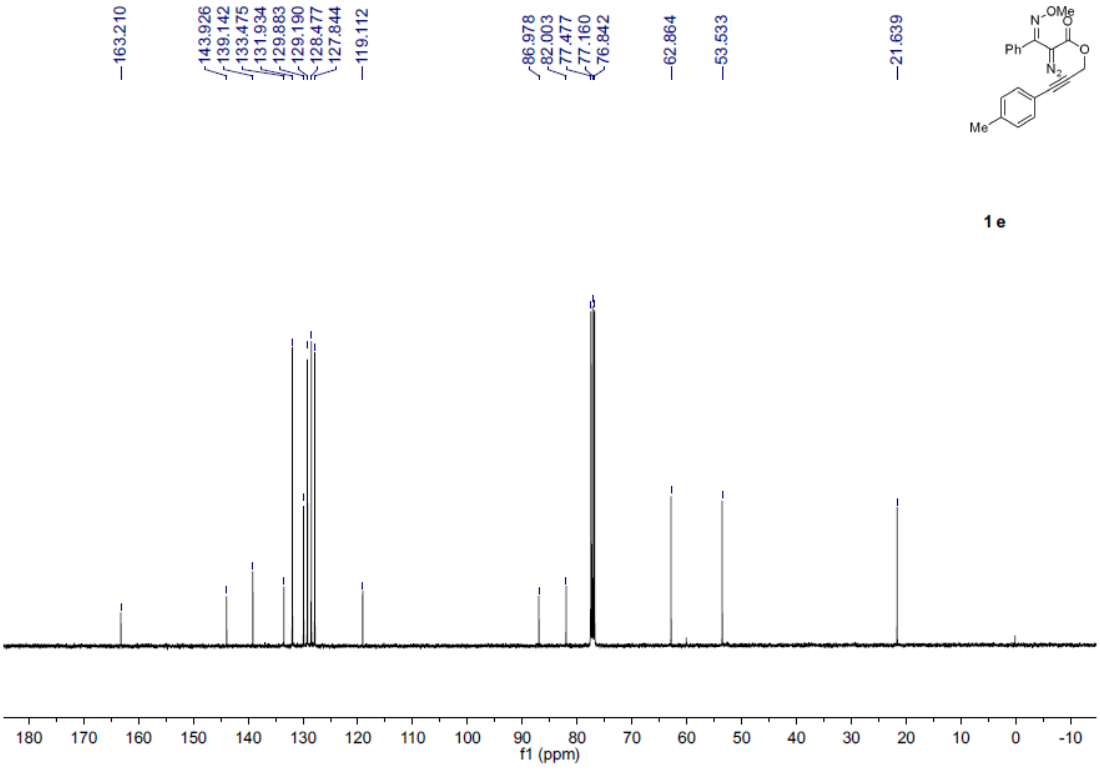
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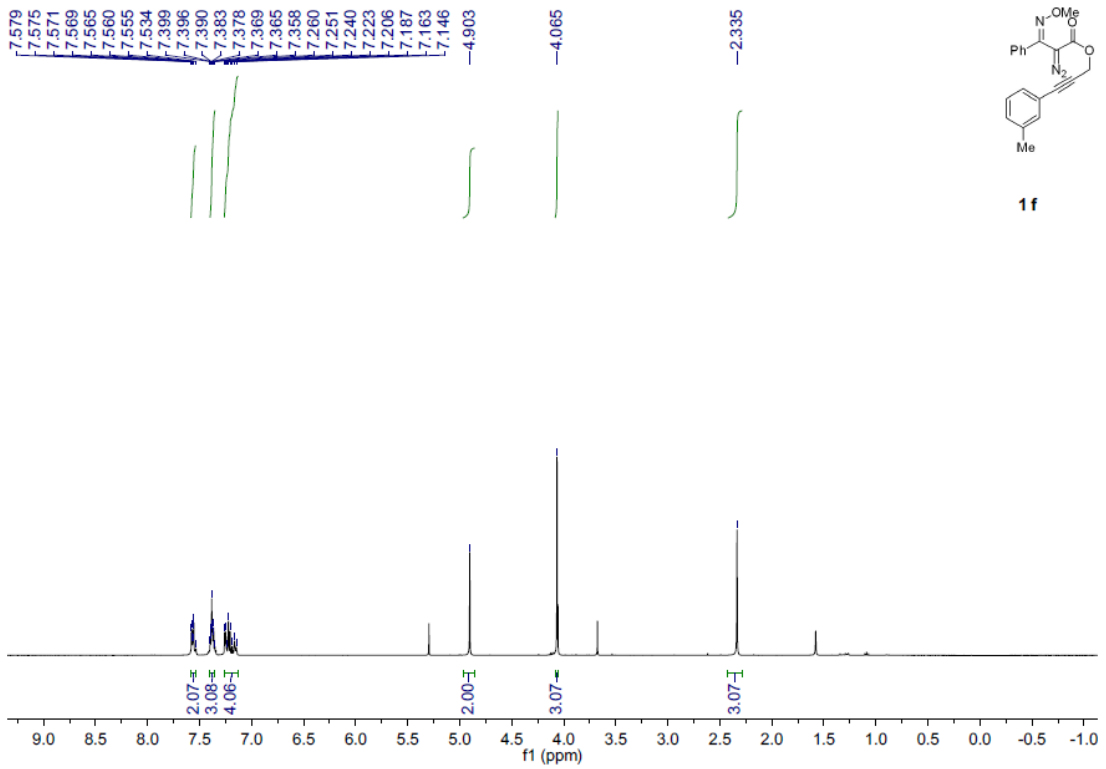
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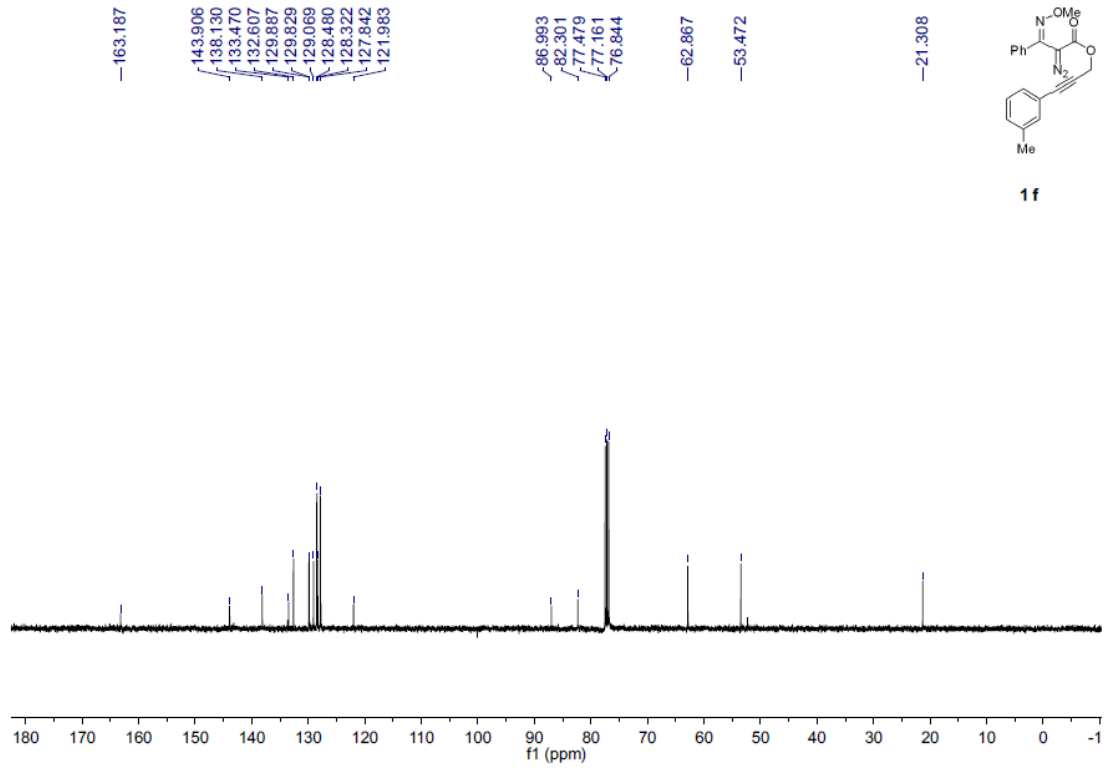
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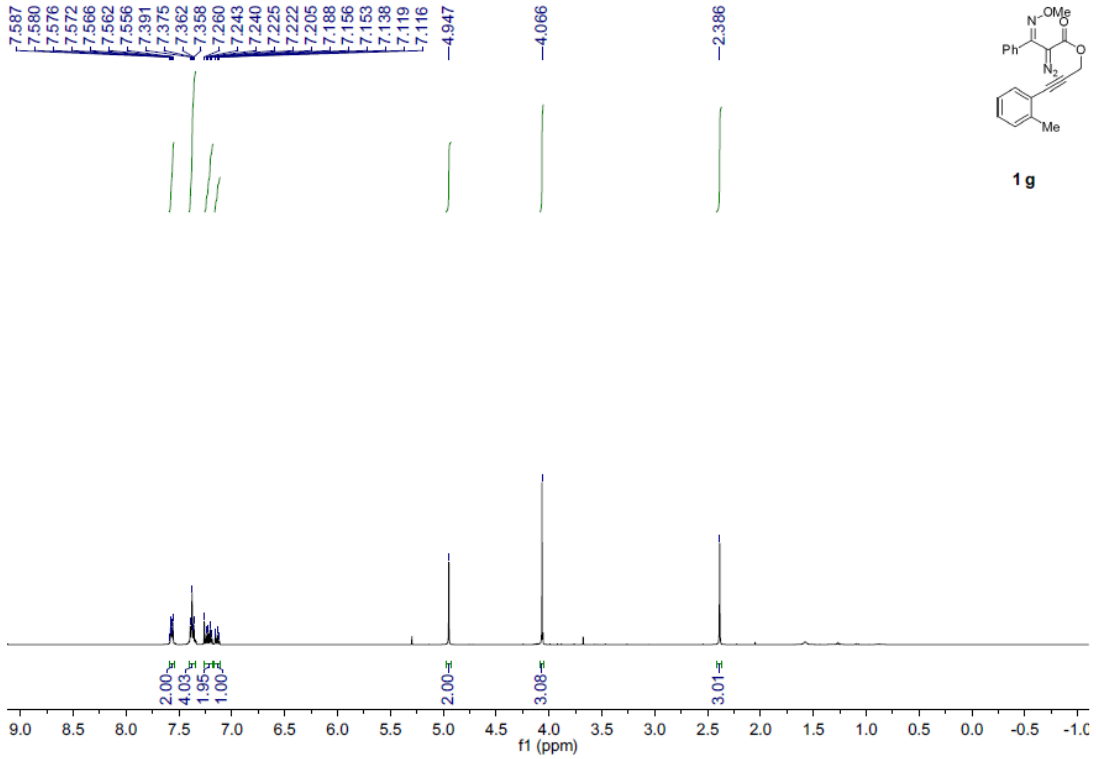
N2
Me
1f
f1 (ppm)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7.556
7.391
7.375
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7.358
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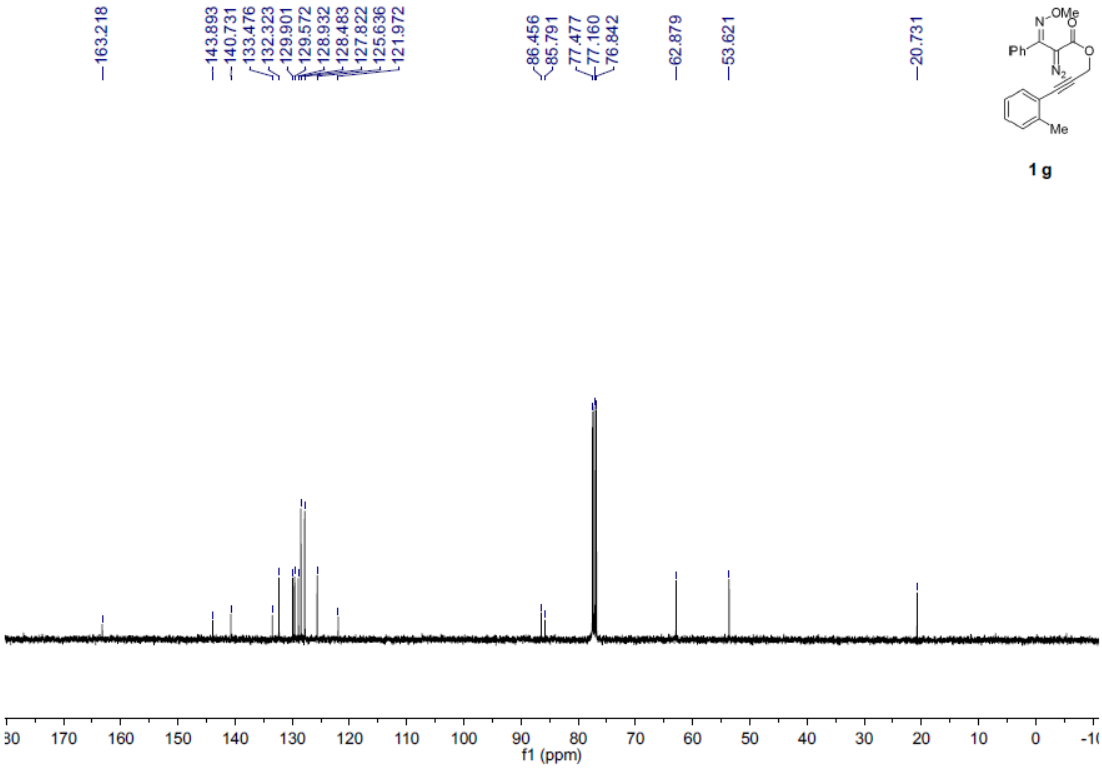
7.240
7.225
7.222
7.205
7.188
7.156
7.153
7.138
7.119
7.116
4.947
4.066
2.386
Ph
N
OMe
O
O
N2
Me
1 g
2.00
4.03
1.95
1.00
2.00
3.08
3.01
f1 (ppm)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133.476
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129.901
129.572
128.932
128.483
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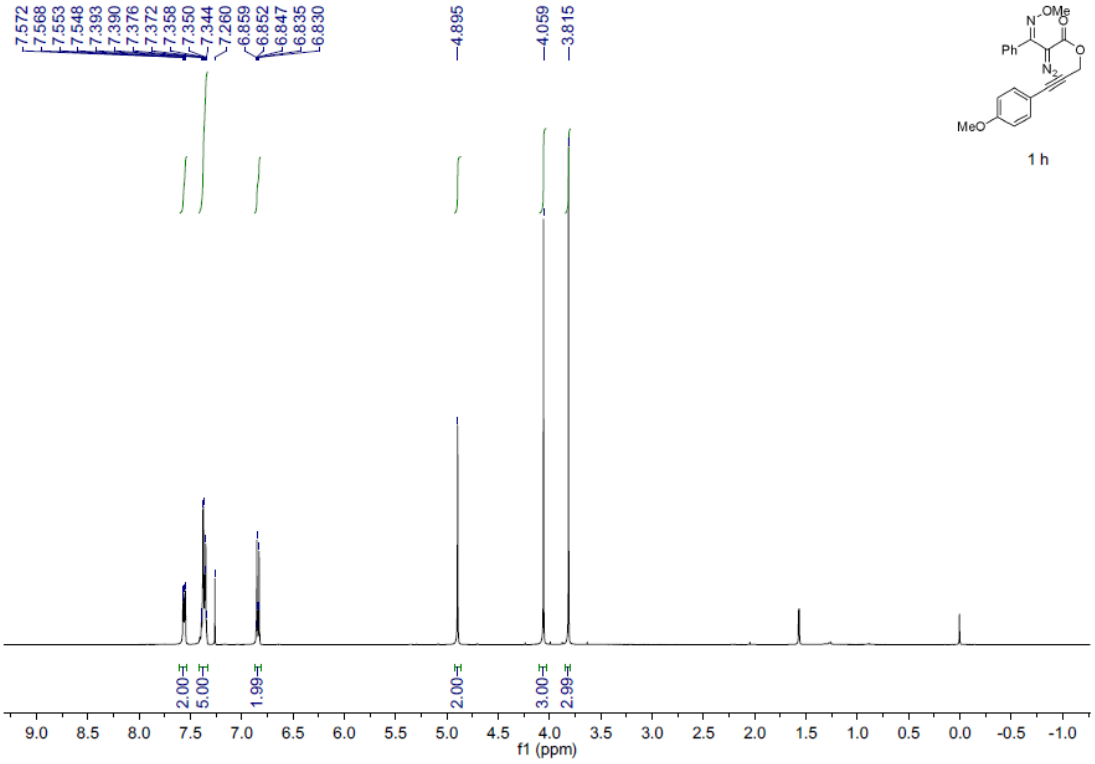
125.636
121.972
86.456
85.791
77.477
77.160
76.842
62.879
53.621
20.731
Ph
N
OMe
O
O
N2
Me
1 g
f1 (ppm)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7.553
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7.390
7.376
7.372
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7.350
7.344
7.260
6.859
6.852
6.847
6.835
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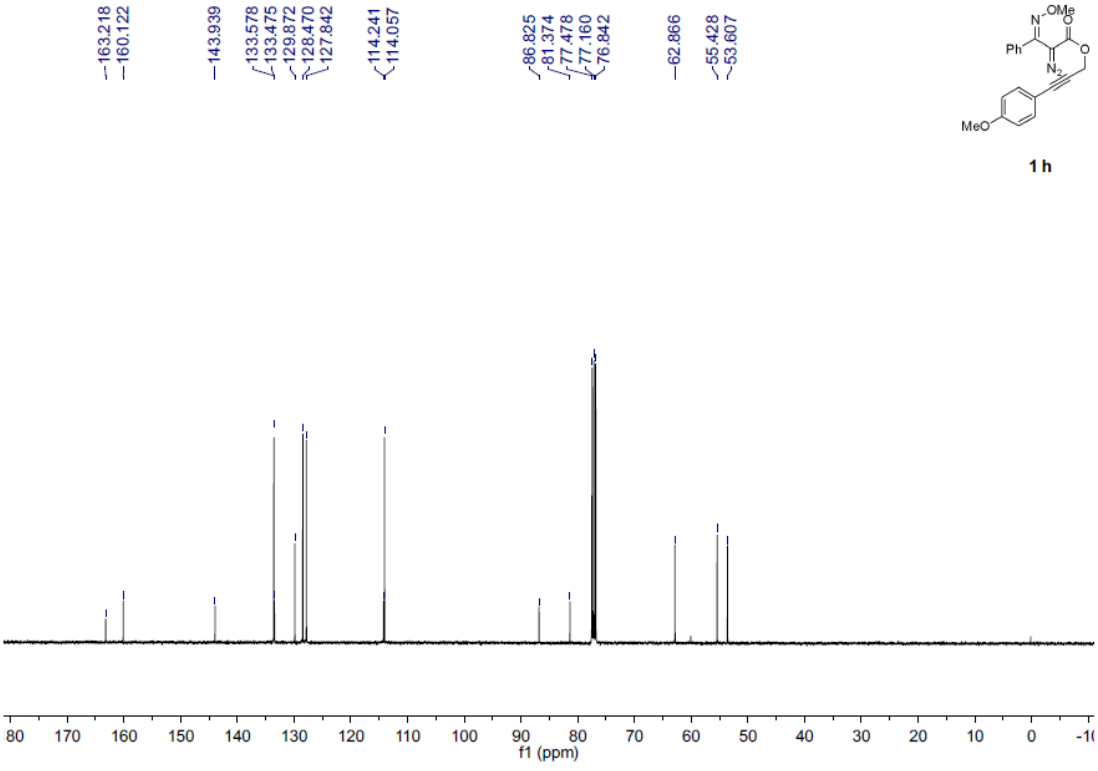
3.815
2.00
5.00
1.99
2.00
3.00
2.99
f1 (ppm)
1 h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77.160
76.842
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55.428
53.607
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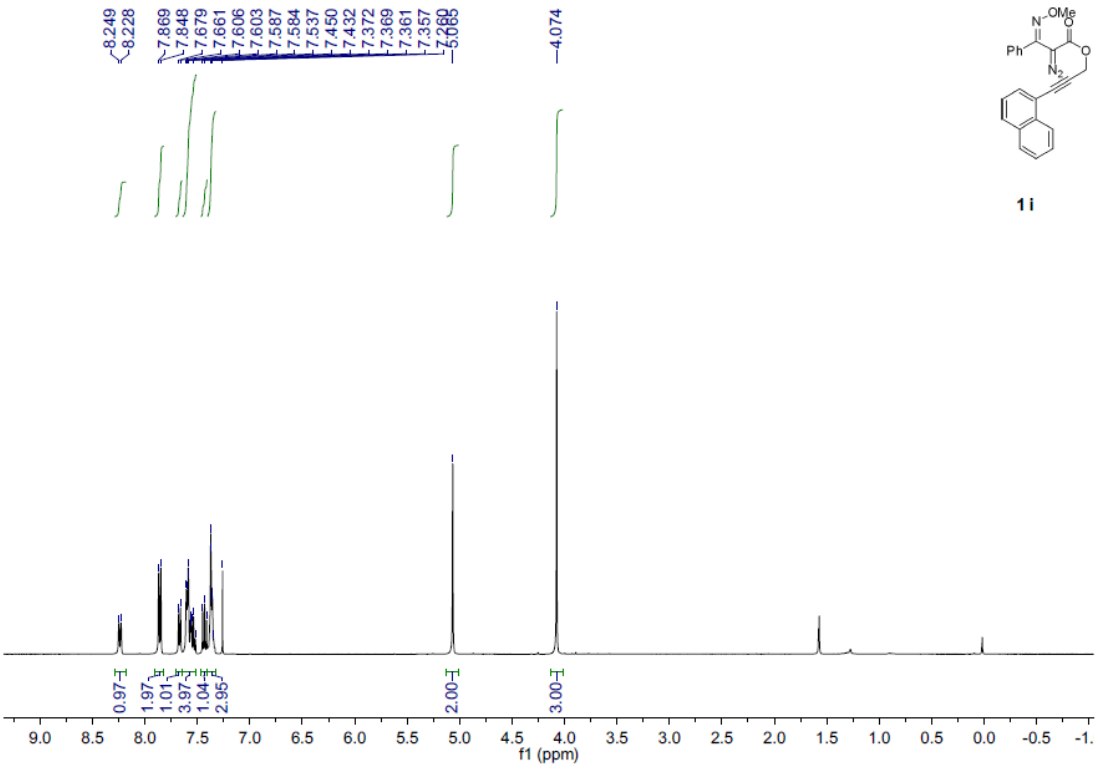
1 h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7.603
7.587
7.584
7.537
7.450
7.432
7.372
7.369
7.361
7.357
4.074
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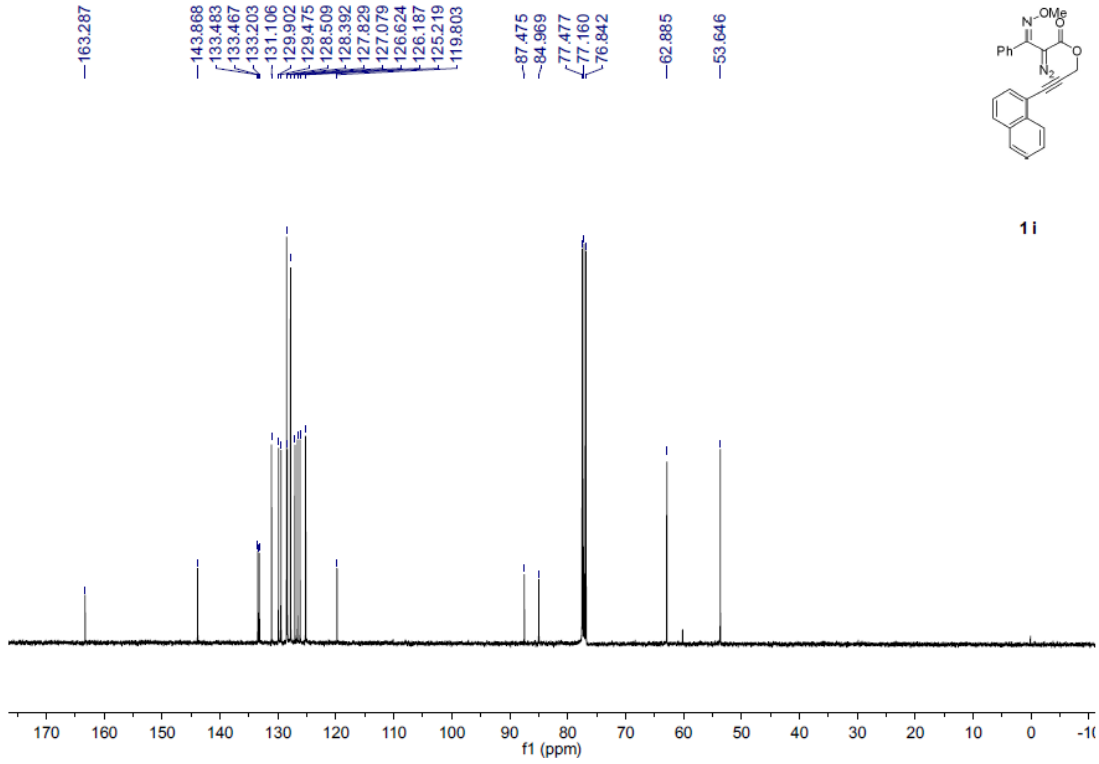
1.97
1.01
3.97
1.04
2.95
2.00
3.00
f1 (ppm)
1i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126.624
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125.219
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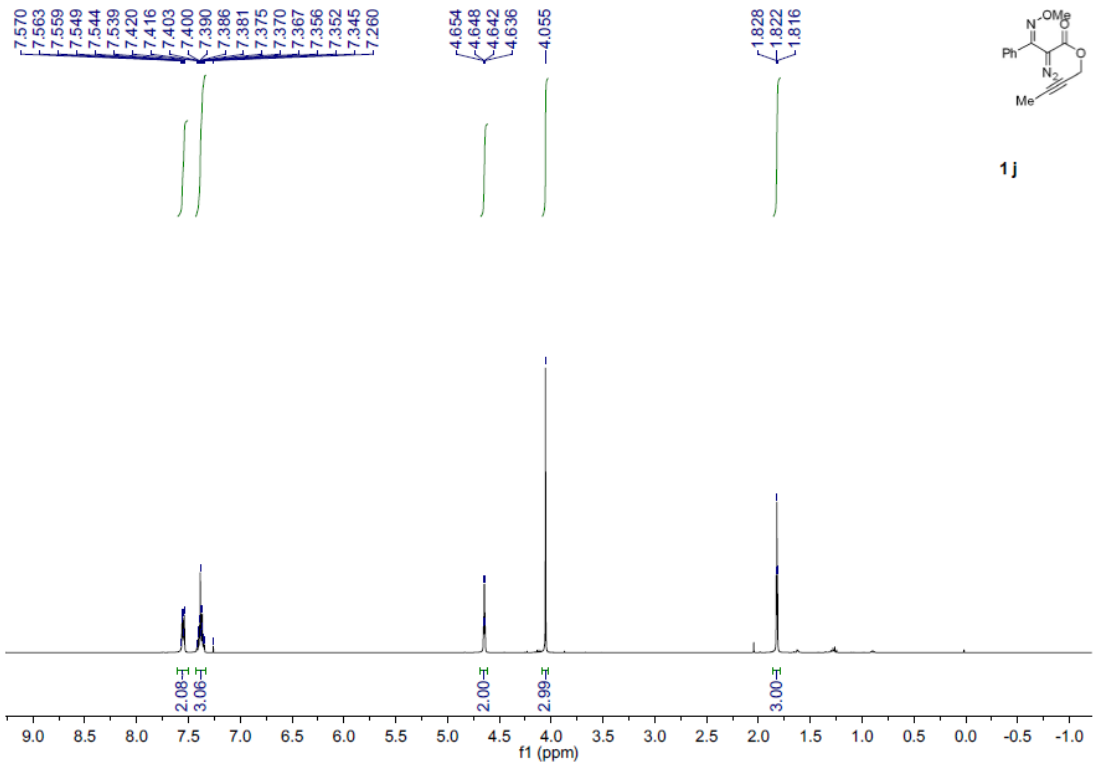
87.475
84.969
77.477
77.160
76.842
62.885
53.646
f1 (ppm)
1i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7.416
7.403
7.400
7.390
7.386
7.381
7.375
7.370
7.367
7.356
7.352
7.345
7.260
4.654
4.648
4.642
4.636
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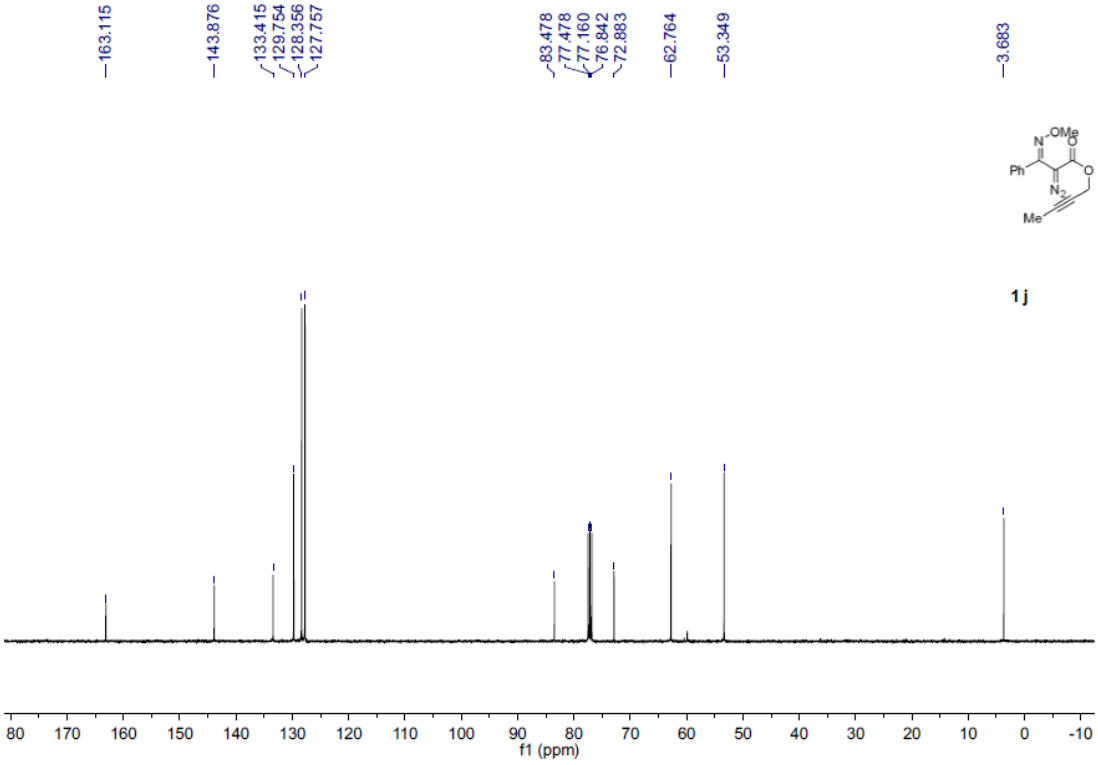
1.822
1.816
2.08
3.06
2.00
2.99
3.00
f1 (ppm)

1j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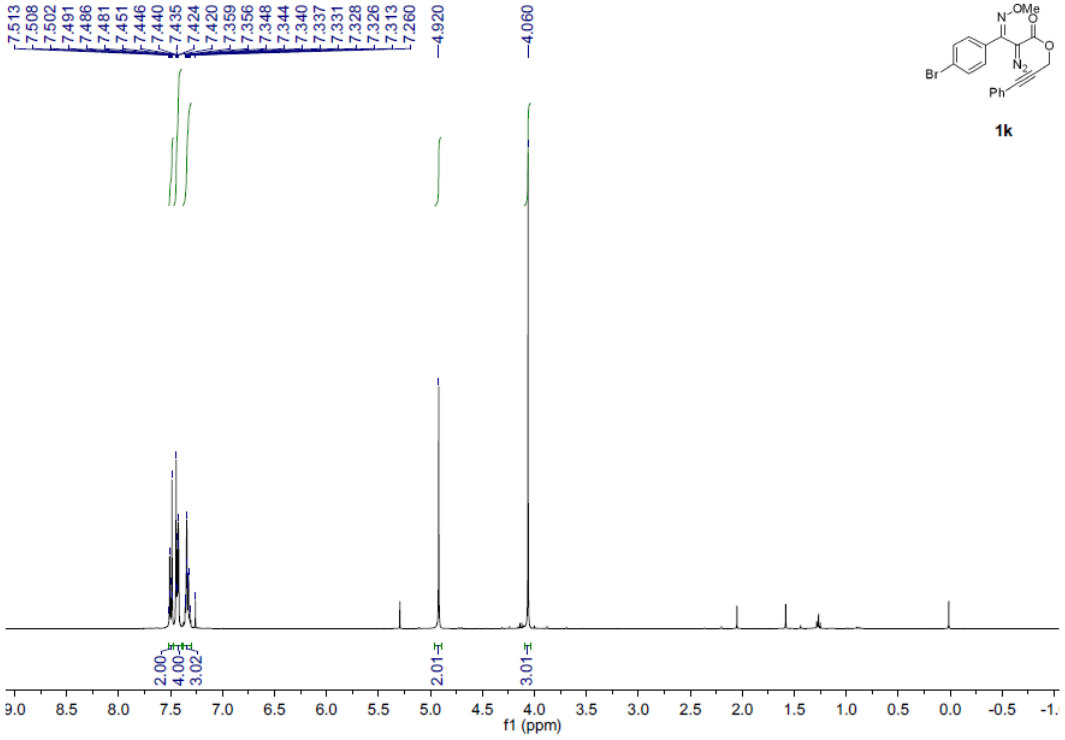
133.415
129.754
128.356
127.757
83.478
77.478
77.160
76.842
72.883
62.764
53.349
3.683
f1 (ppm)

1j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7.508
7.502
7.491
7.486
7.481
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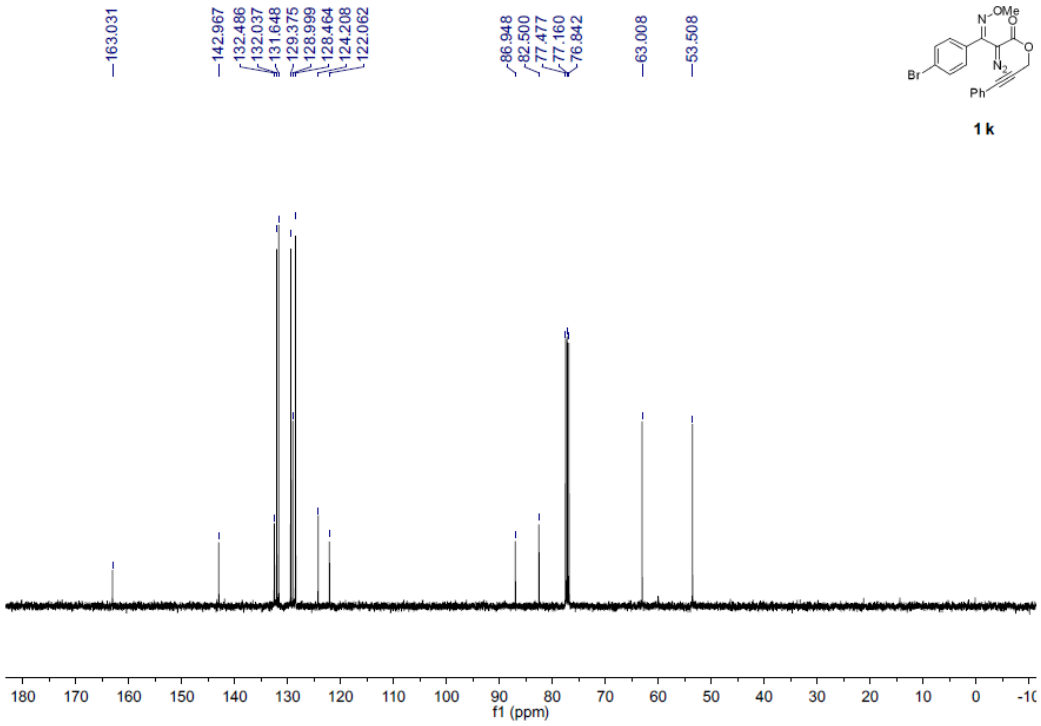
7.446
7.440
7.435
7.424
7.420
7.359
7.356
7.348
7.344
7.340
7.337
7.331
7.328
7.326
7.313
7.260
4.920
4.060
2.00
4.00
3.02
2.01
3.01
f1 (ppm)
1k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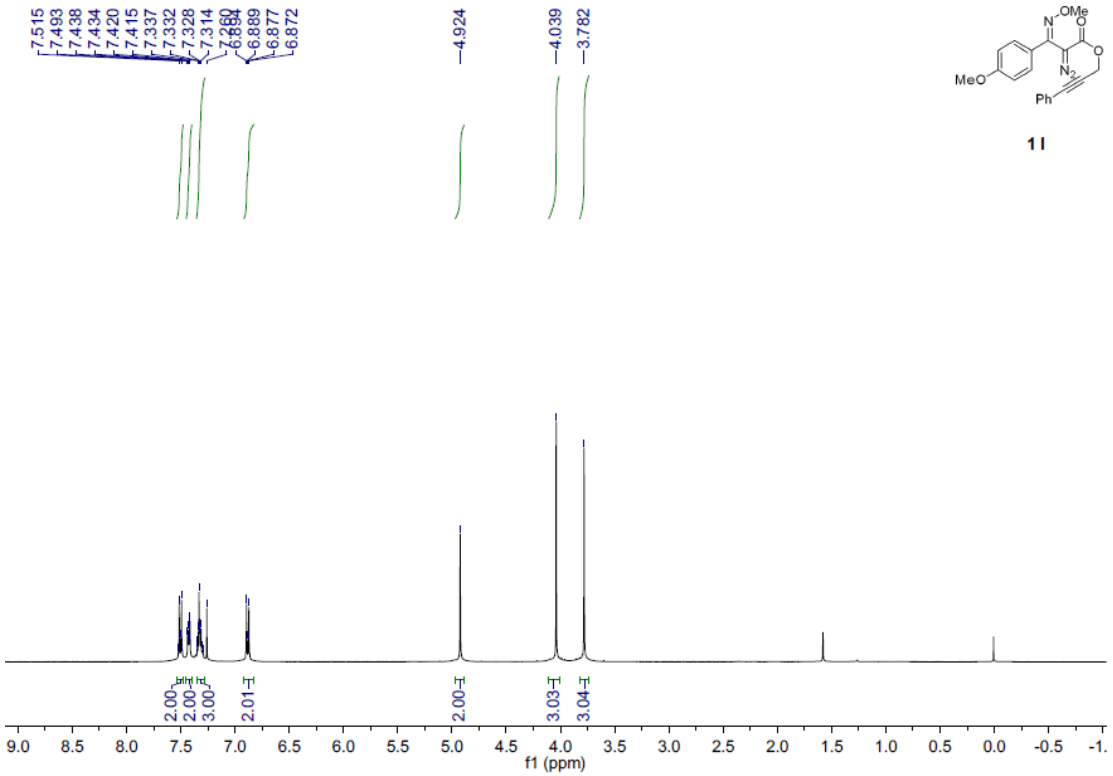
142.967
132.486
132.037
131.648
129.375
128.999
128.464
124.208
122.062
86.948
82.500
77.477
77.160
76.842
63.008
53.508
f1 (ppm)
1 k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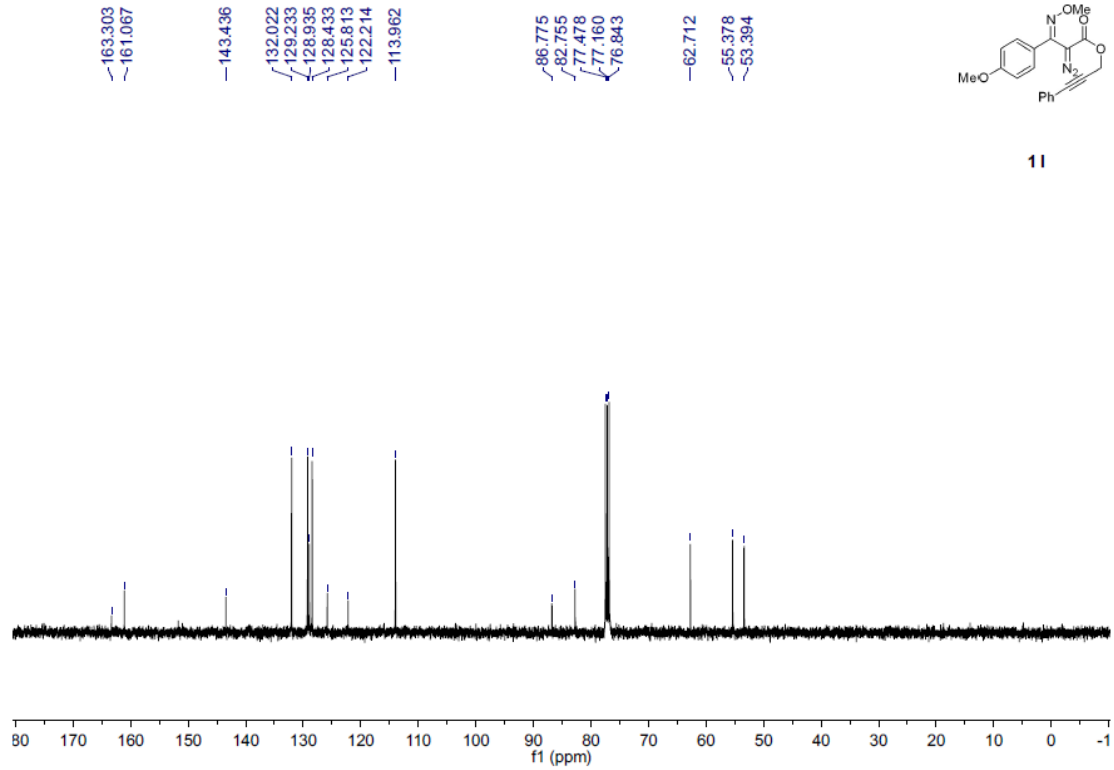
7.493
7.438
7.434
7.420
7.415
7.337
7.332
7.328
7.314
7.260
6.889
6.877
6.872
4.924
4.039
3.782
MeO
N
OMe
O
O
N2
Ph
1l
2.00
2.00
3.00
2.01
2.00
3.03
3.04
f1 (ppm)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143.436
132.022
129.233
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128.433
125.813
122.214
113.962
86.775
82.755
77.478
77.160
76.843
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55.378
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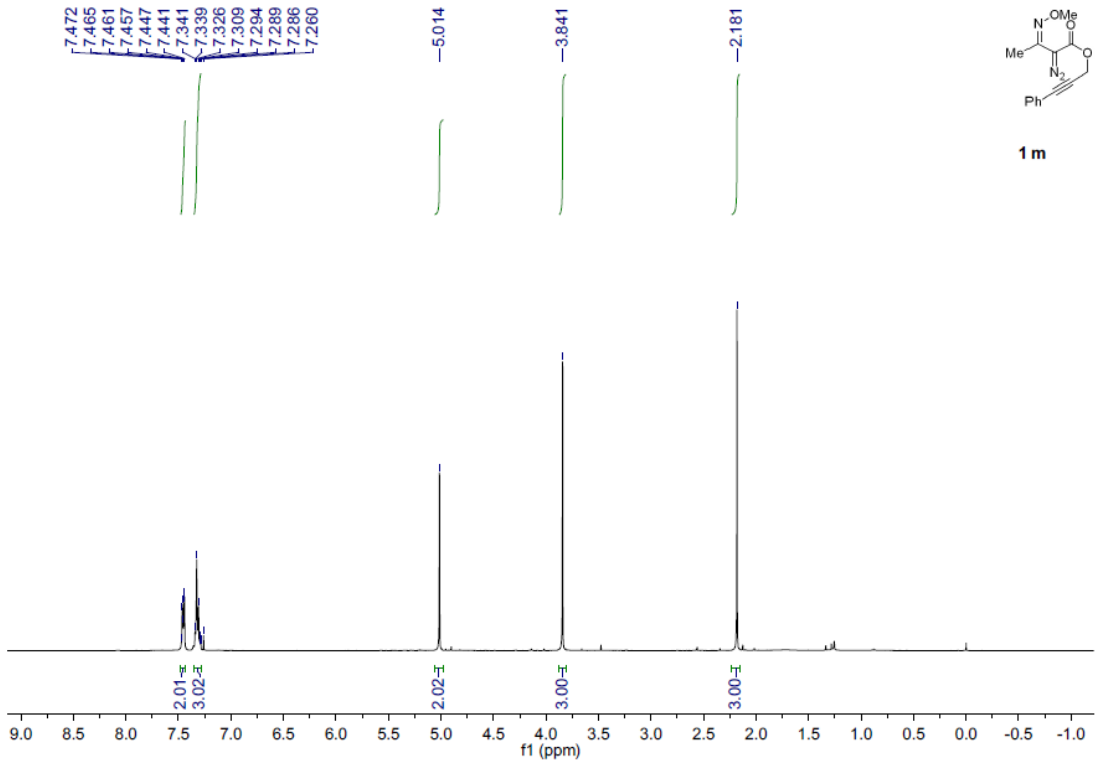
MeO
N
OMe
O
O
N2
Ph
1l
f1 (ppm)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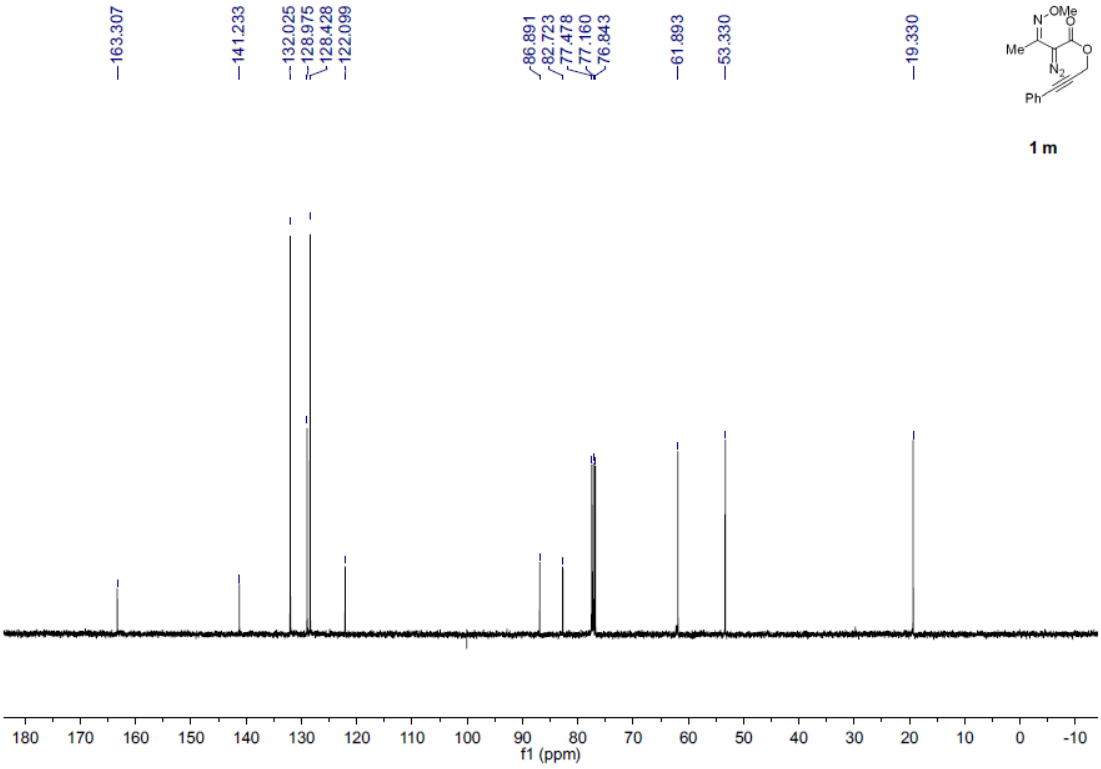
7.339
7.326
7.309
7.294
7.289
7.286
7.260
5.014
3.841
2.181
2.01
3.02
2.02
3.00
3.00
f1 (ppm)
1 m


163.307
141.233
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128.428
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82.723
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77.160
76.843
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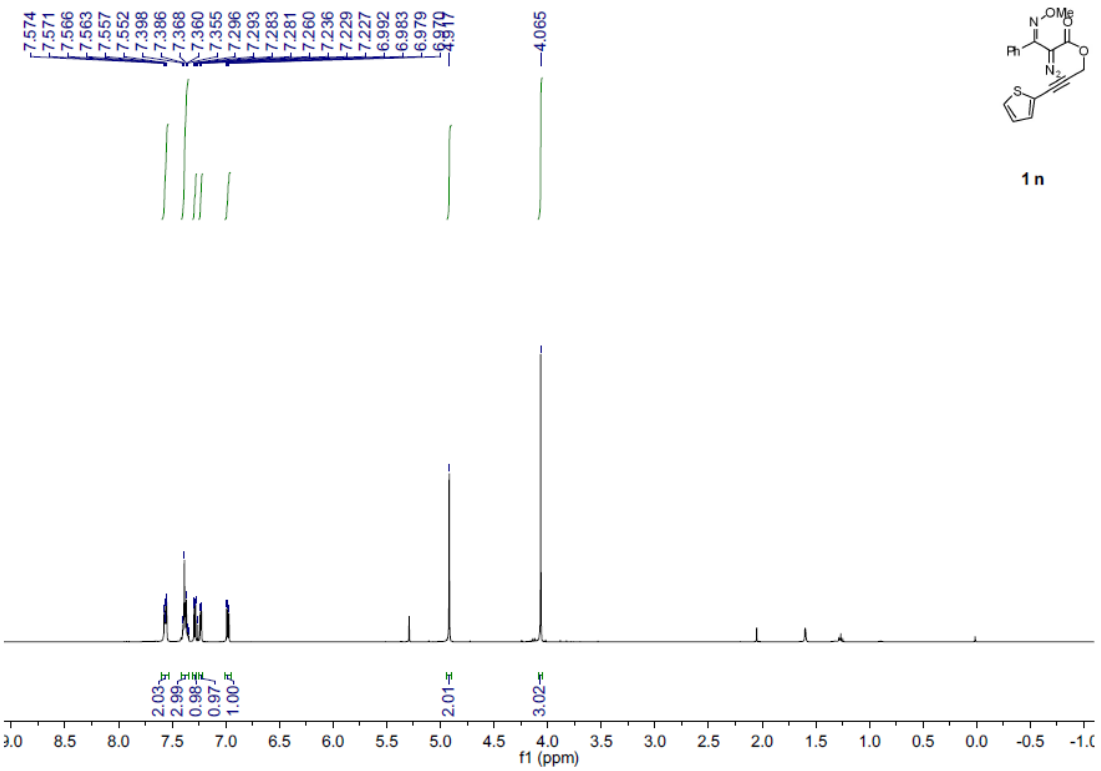
19.330
f1 (ppm)
1 m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7.557
7.552
7.398
7.386
7.368
7.360
7.355
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7.293
7.283
7.281
7.260
7.236
7.229
7.227
6.992
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0.98
0.97
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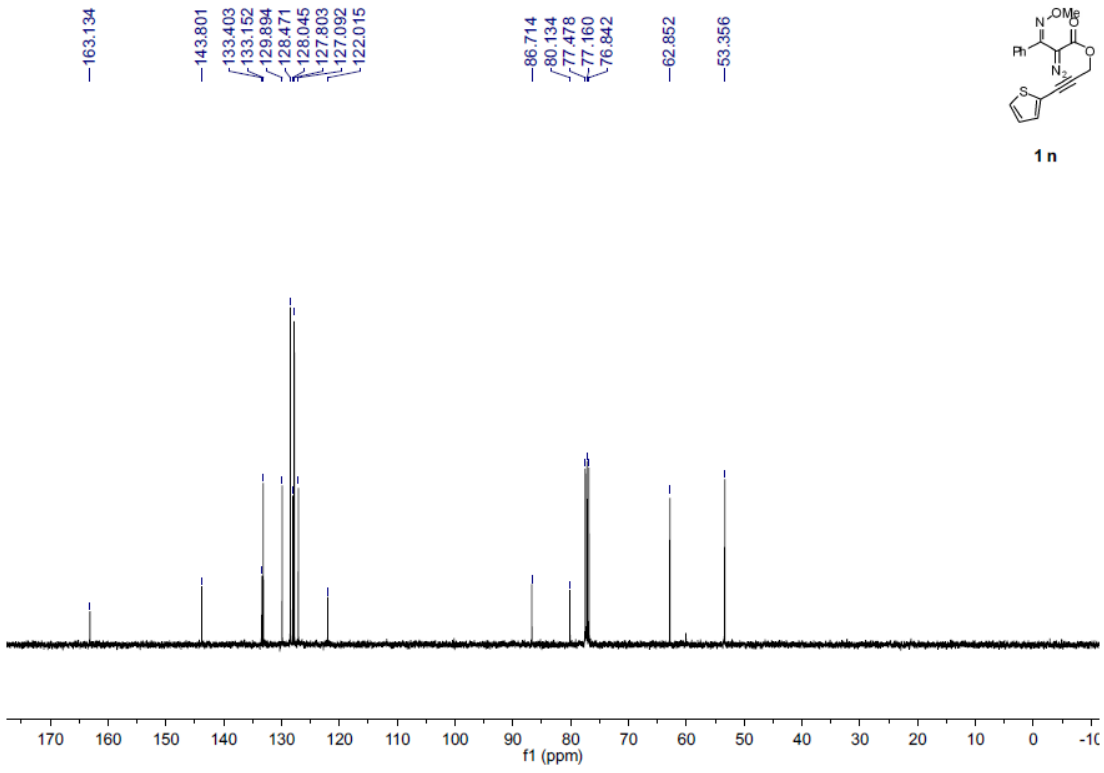
2.01
3.02
f1 (ppm)
1 n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129.894
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128.045
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77.160
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f1 (ppm)
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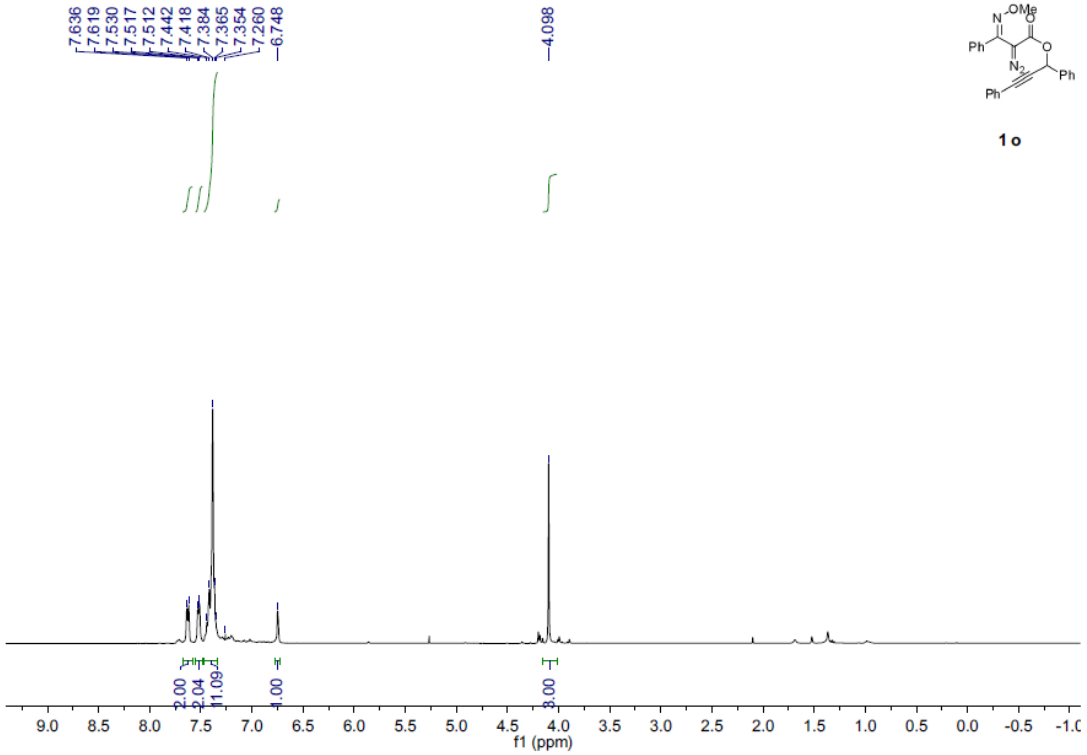
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7.418
7.384
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6.748
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2.00
2.04
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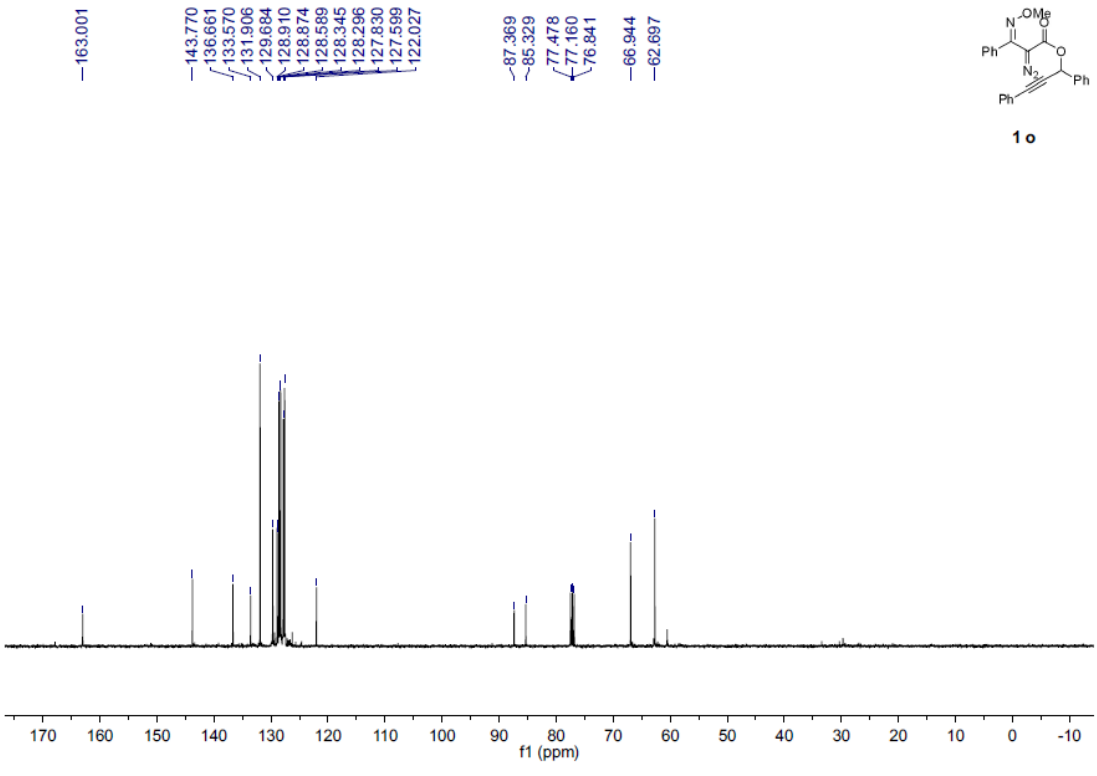
3.00
f1 (ppm)

1 o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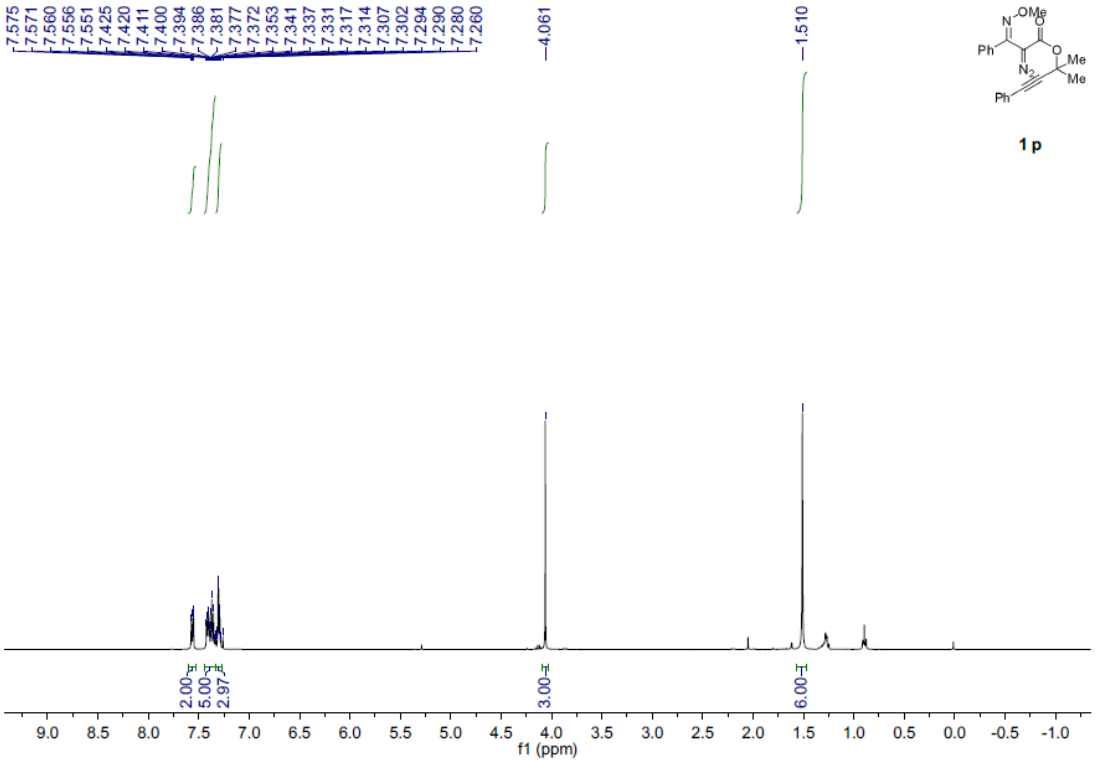
1 o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7.400
7.394
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7.381
7.377
7.372
7.353
7.341
7.337
7.331
7.317
7.314
7.307
7.302
7.294
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2.00
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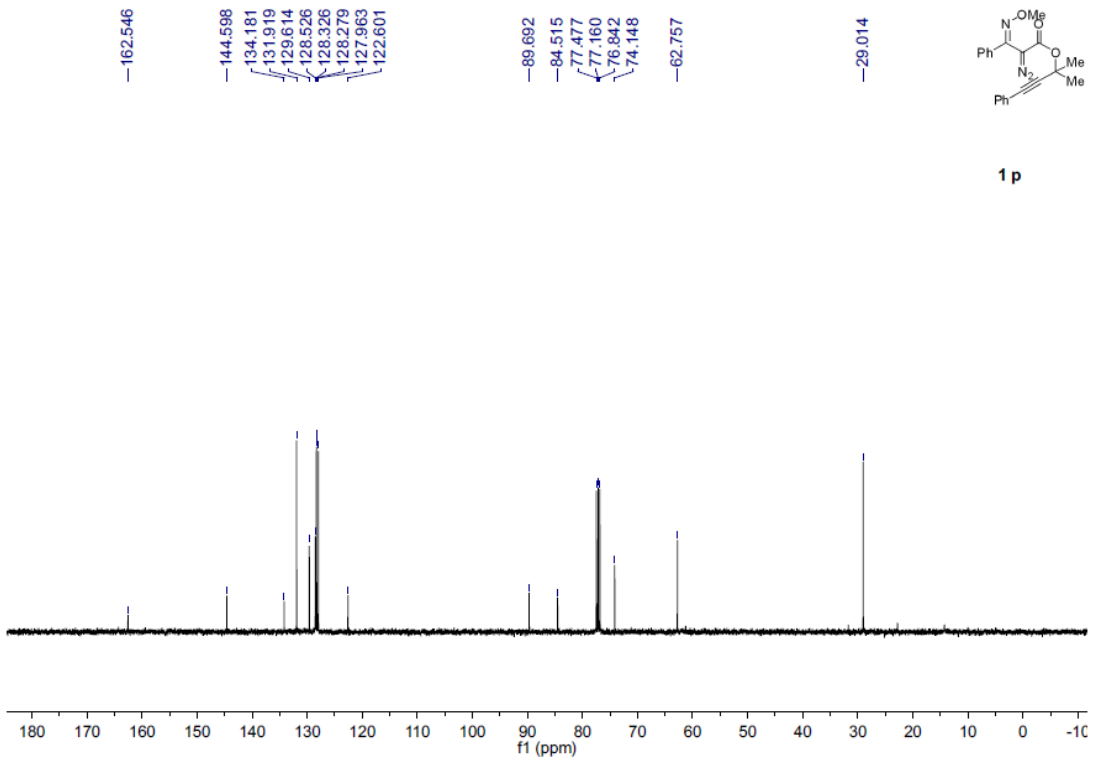
6.00
f1 (ppm)
1 p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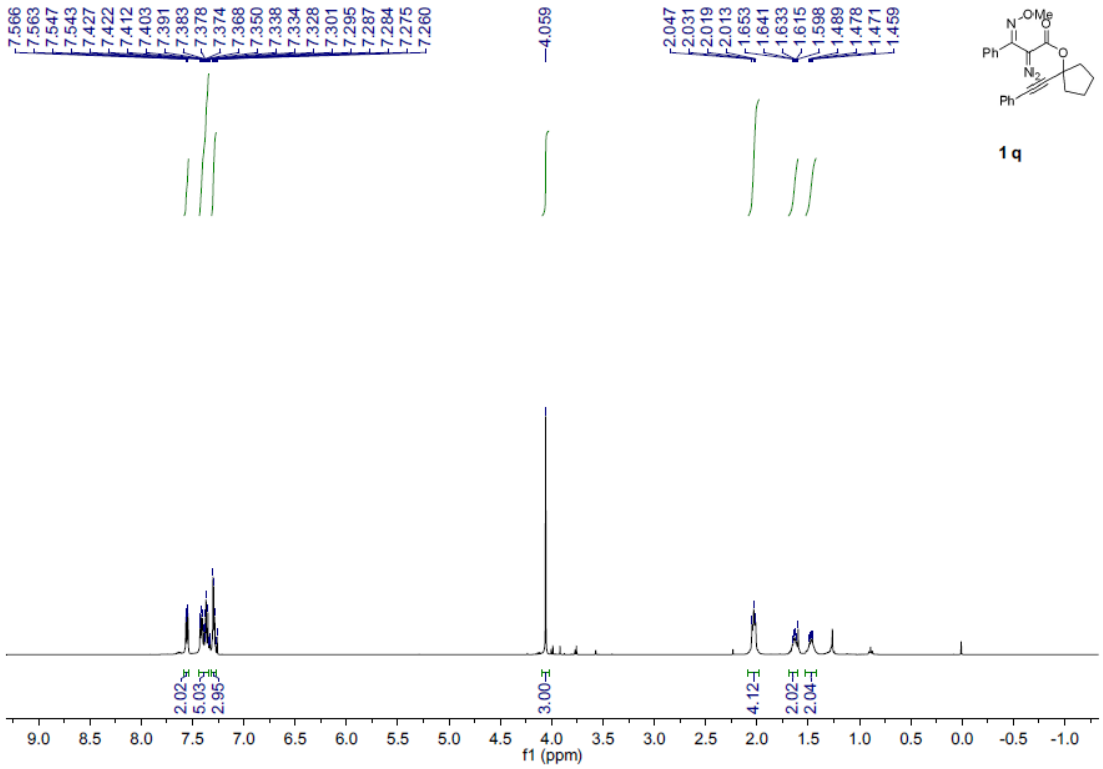
77.160
76.842
74.148
62.757
29.014
f1 (ppm)
1 p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7.368
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7.328
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7.275
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2.013
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1.615
1.598
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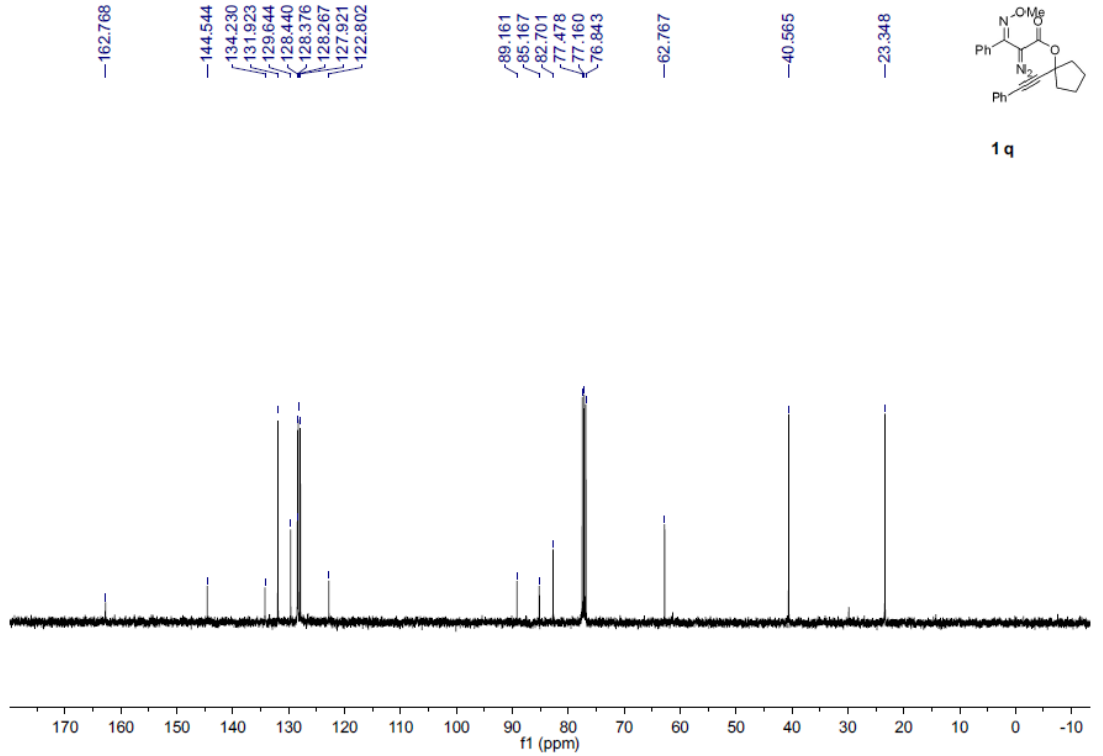
1.478
1.471
1.459
Ph
N
OMe
O
O
N2
Ph
1 q
2.02
5.03
2.95
3.00
4.12
2.02
2.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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85.167
82.701
77.478
77.160
76.843
62.767
40.565
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Ph
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OMe
O
O
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Ph
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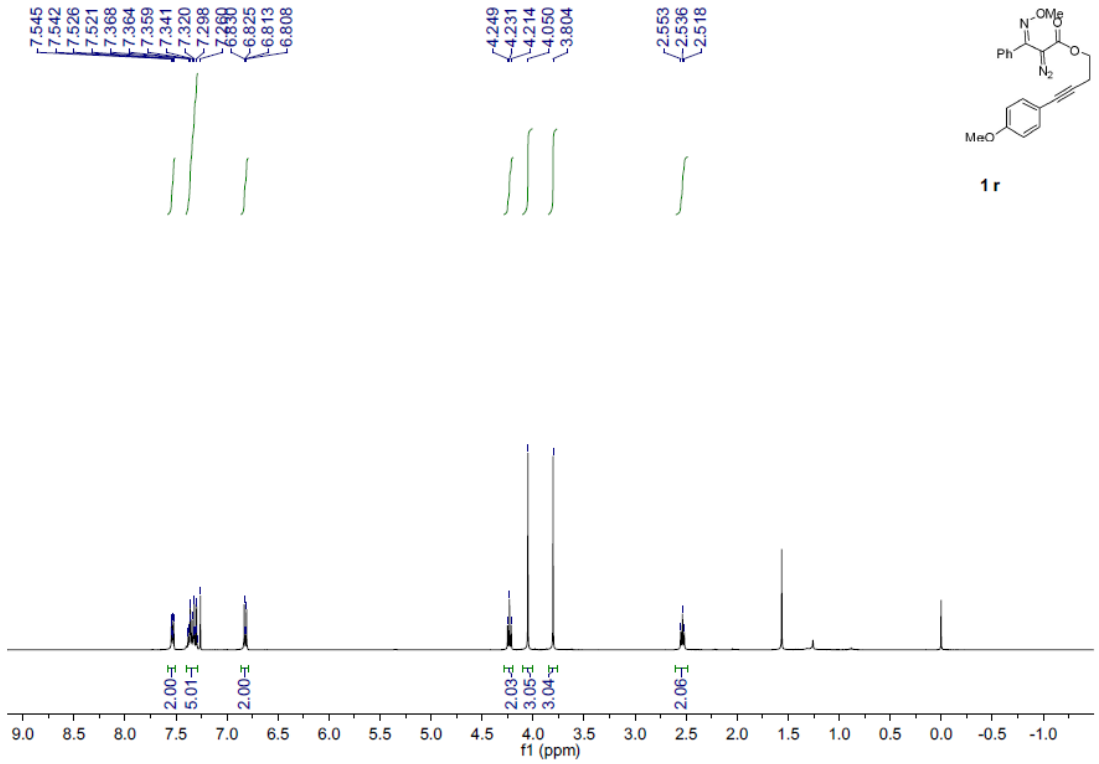
f1 (ppm)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7.298
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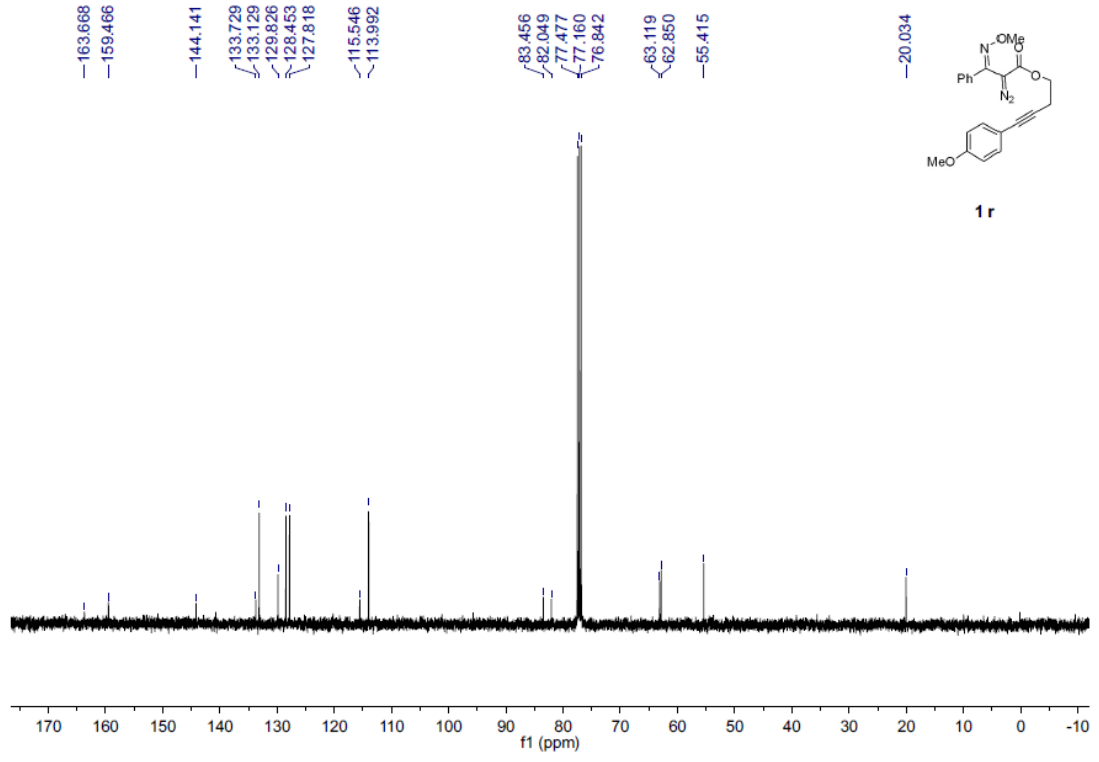
6.813
6.808
4.249
4.231
4.214
4.050
3.804
2.553
2.536
2.518
OMe
N
O
Ph
O
N2
MeO
1 r
2.00
5.01
2.00
2.03
3.05
3.04
2.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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77.477
77.160
76.842
63.119
62.850
55.415
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OMe
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Ph
O
N2
MeO
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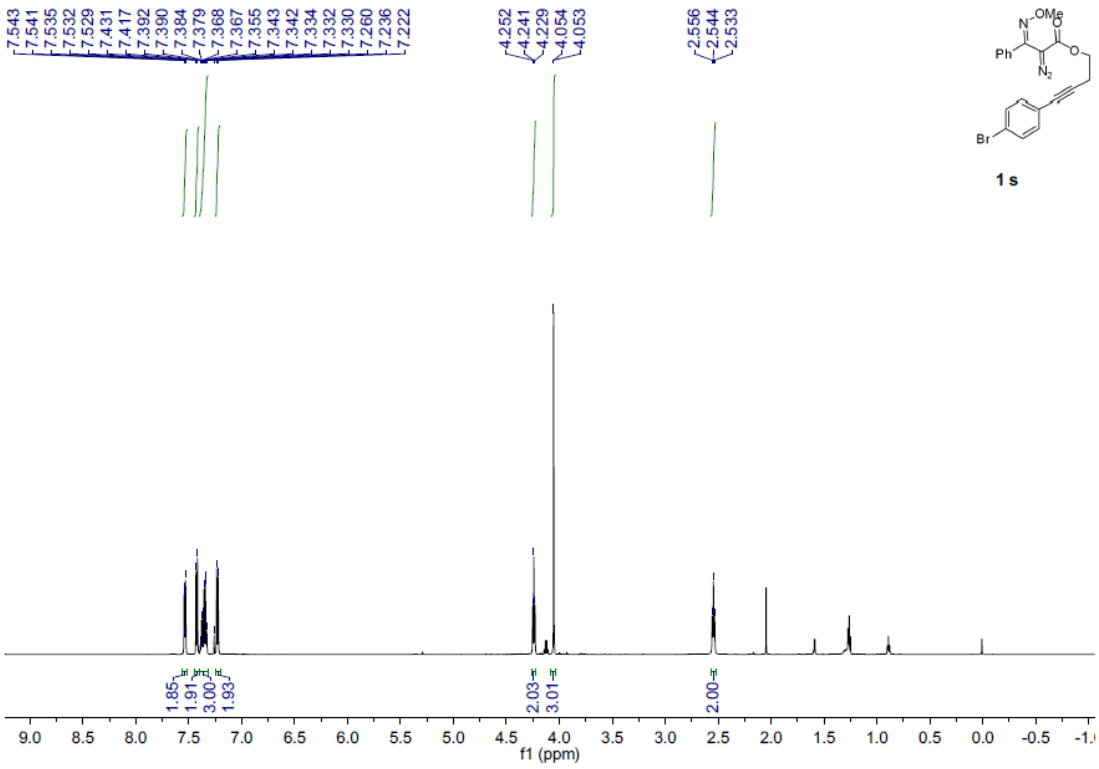
f1 (ppm)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7.367
7.355
7.343
7.342
7.334
7.332
7.330
7.260
7.236
7.222
4.252
4.241
4.229
4.054
4.053
2.556
2.544
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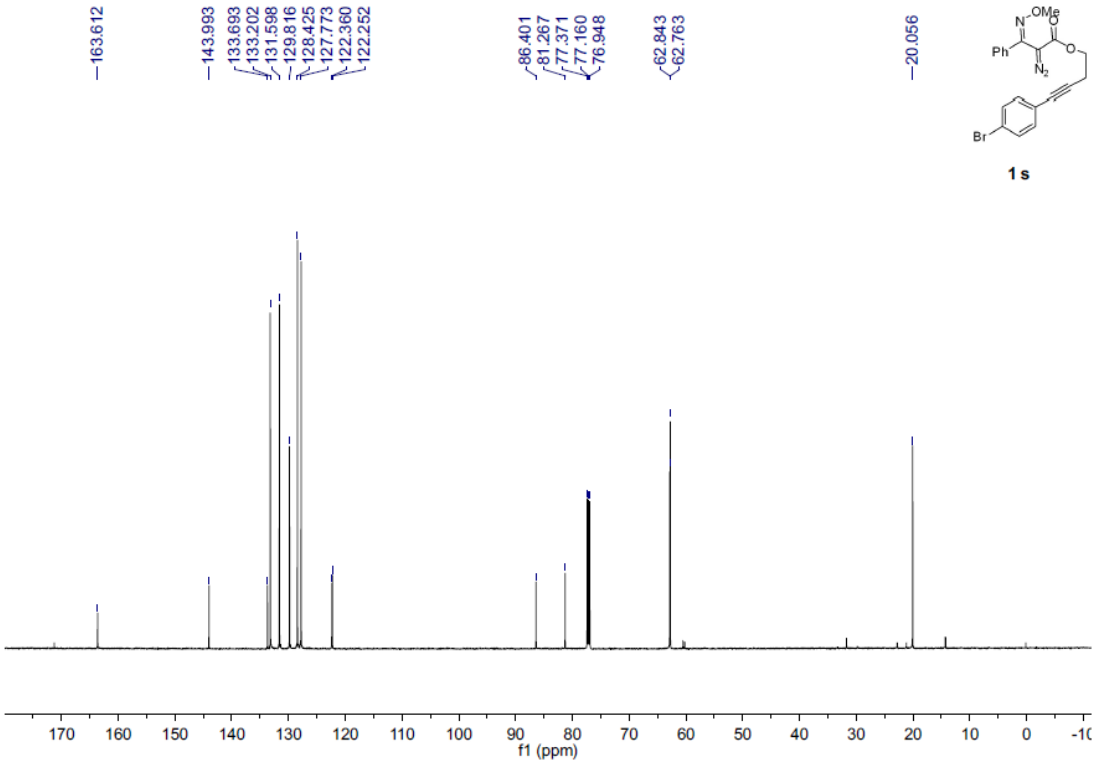
1.85
1.91
3.00
1.93
2.03
3.01
2.00
f1 (ppm)
1 s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127.773
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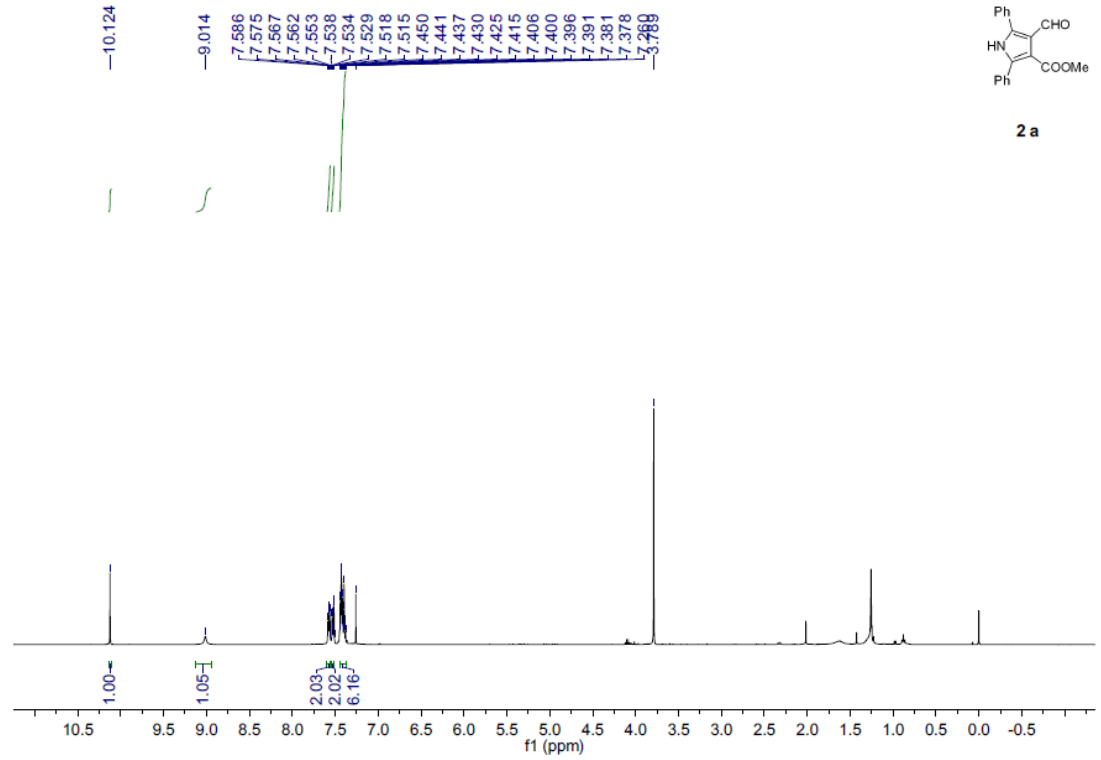
20.056
f1 (ppm)
1 s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7.518
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7.450
7.441
7.437
7.430
7.425
7.415
7.406
7.400
7.396
7.391
7.381
7.378
7.260
3.789
Ph
CHO
HN
COOMe
Ph
2 a
1.00
1.05
2.03
2.02
6.16
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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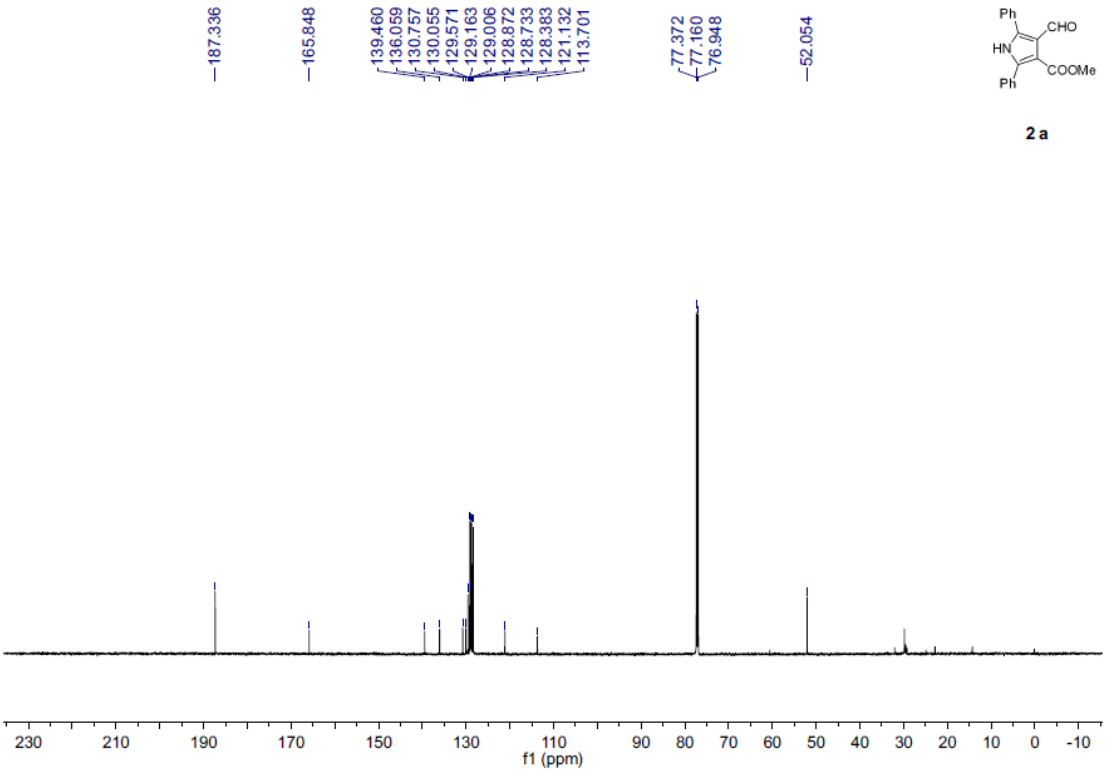
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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128.733
128.383
121.132
113.701
77.372
77.160
76.948
52.054
Ph
CHO
HN
COOMe
Ph
2 a
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190
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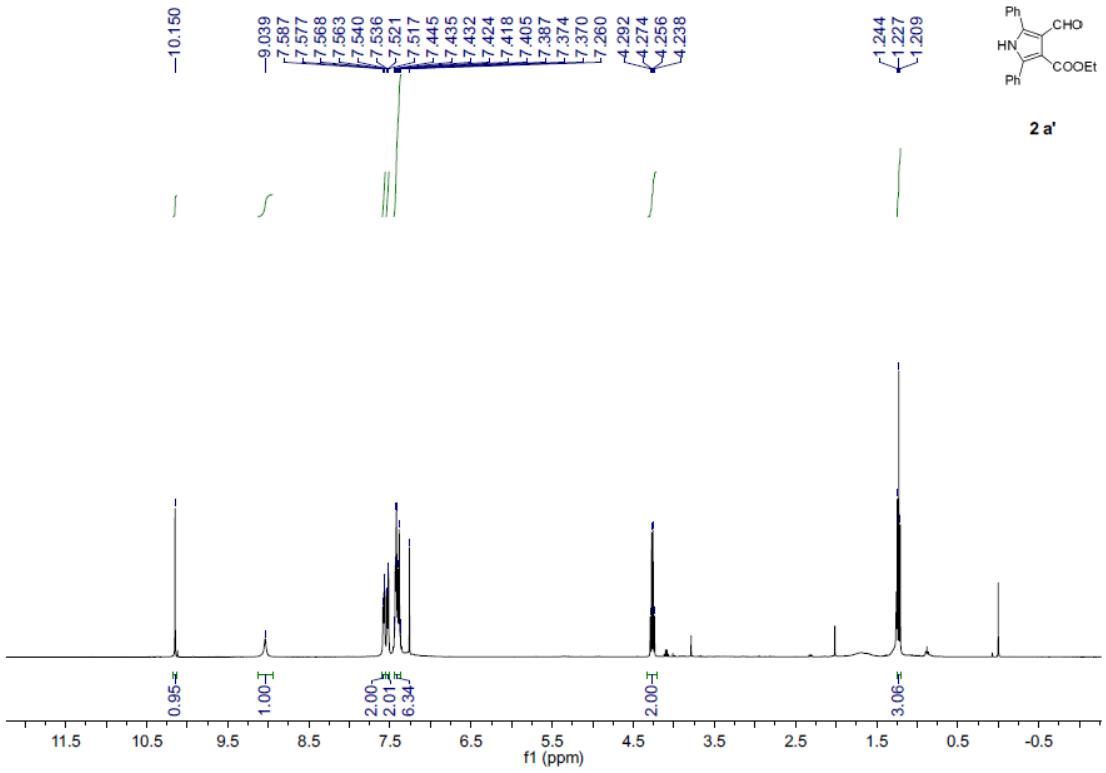
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.418
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7.374
7.370
7.260
4.292
4.274
4.256
4.238
1.244
1.227
1.209
Ph
CHO
HN
COOEt
Ph
2 a'
0.95
1.00
2.00
2.01
6.34
2.00
3.06
11.5
10.5
9.5
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6.5
5.5
4.5
3.5
2.5
1.5
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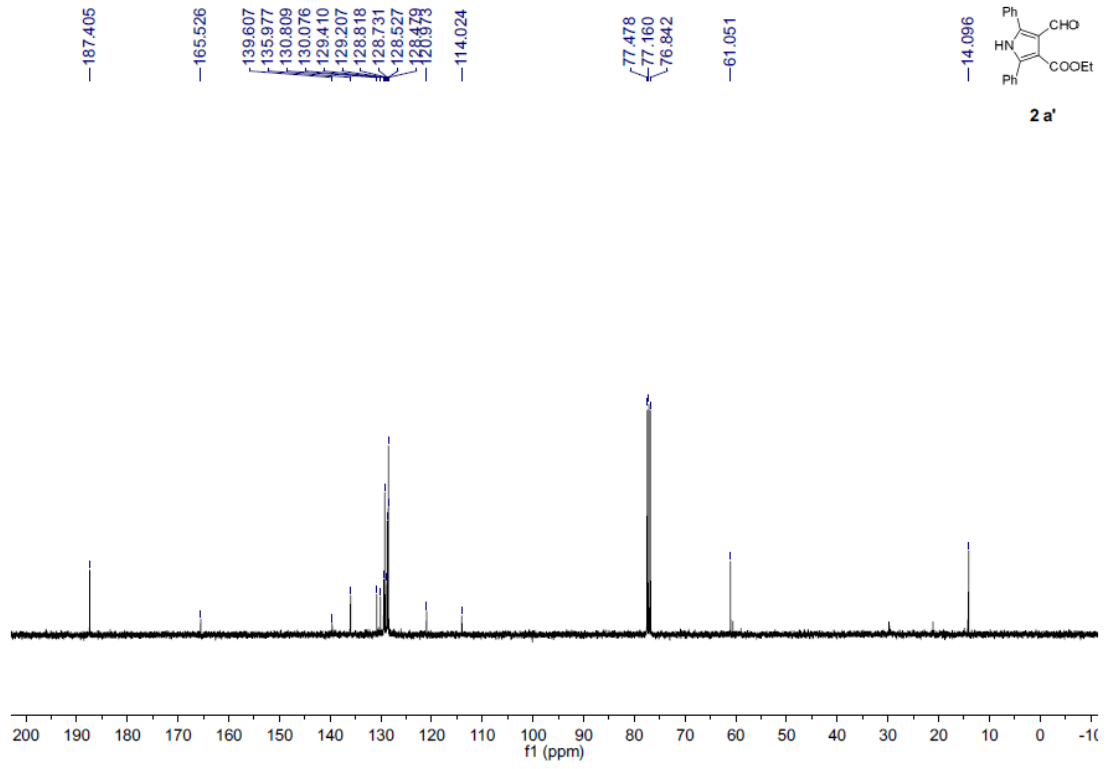
f1 (ppm)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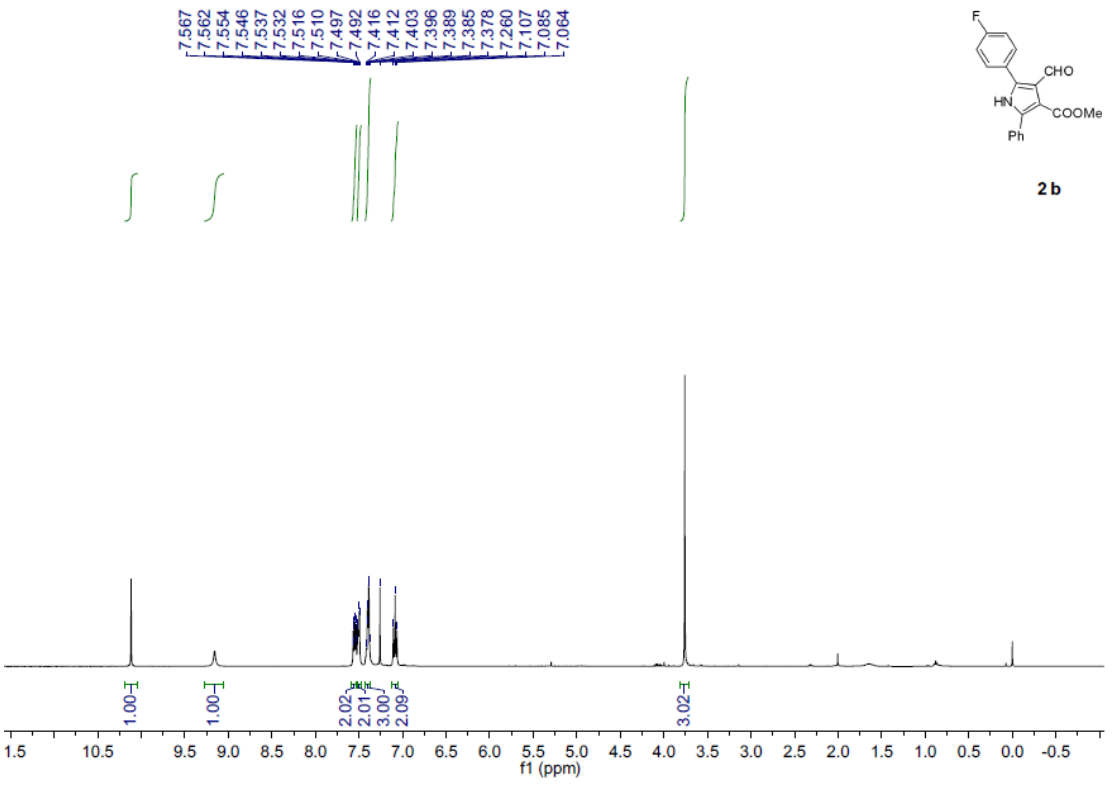
139.607
135.977
130.809
130.076
129.410
129.207
128.818
128.731
128.527
114.024
77.478
77.160
76.842
61.051
14.096
Ph
CHO
HN
COOEt
Ph
2 a'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.510
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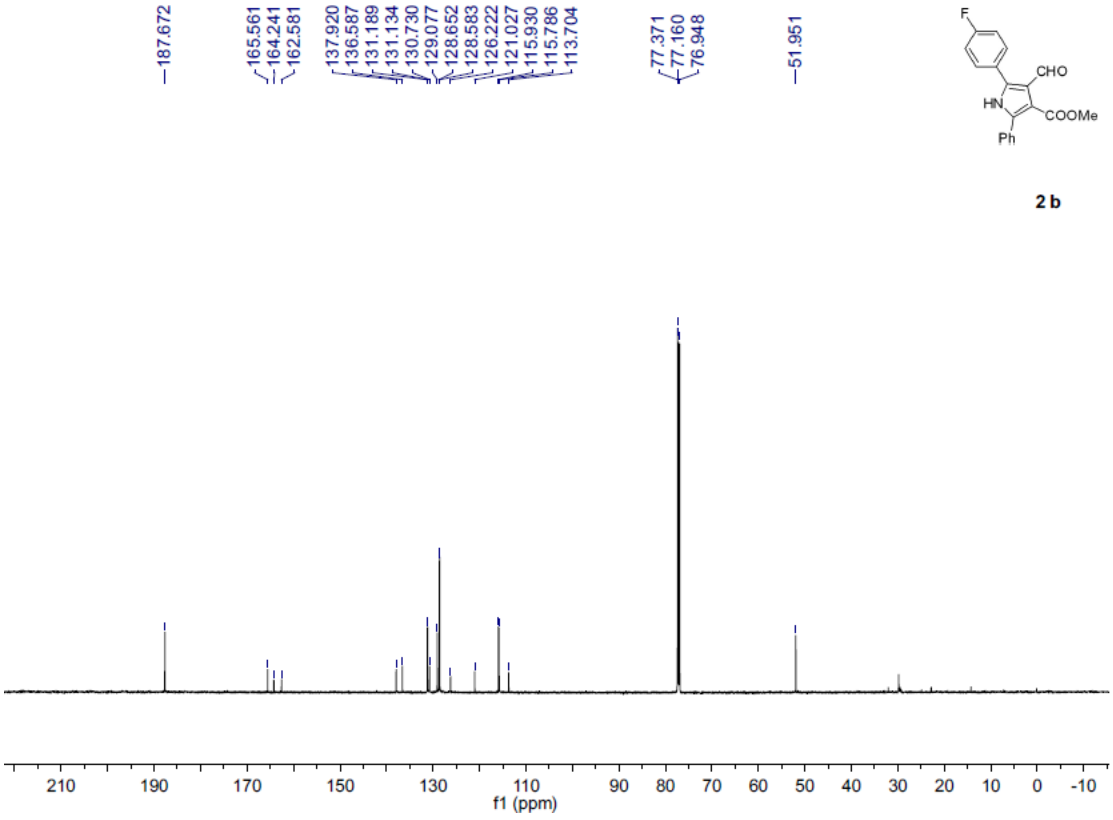
7.492
7.416
7.412
7.403
7.396
7.389
7.385
7.378
7.260
7.107
7.085
7.064
F
CHO
HN
COOMe
Ph
2b
1.00
1.00
2.02
2.01
3.00
2.09
3.02
f1 (ppm)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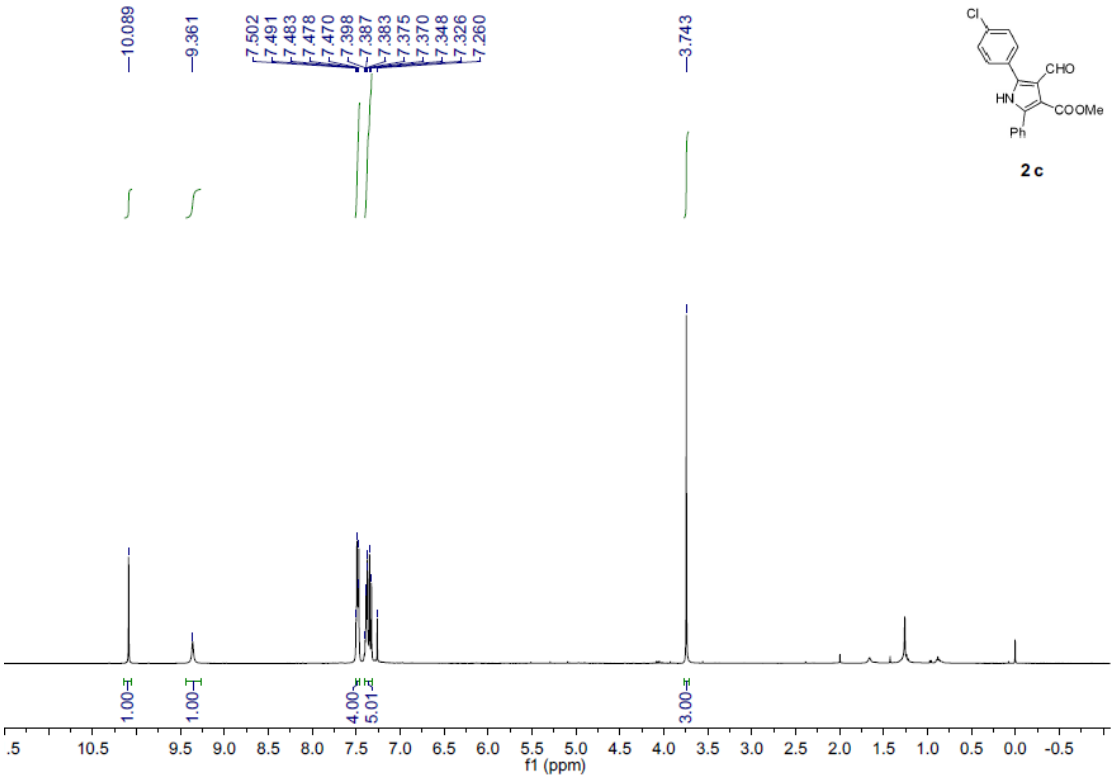
131.134
130.730
129.077
128.652
128.583
126.222
121.027
115.930
115.786
113.704
77.371
77.160
76.948
51.951
F
CHO
HN
COOMe
Ph
2b
f1 (ppm)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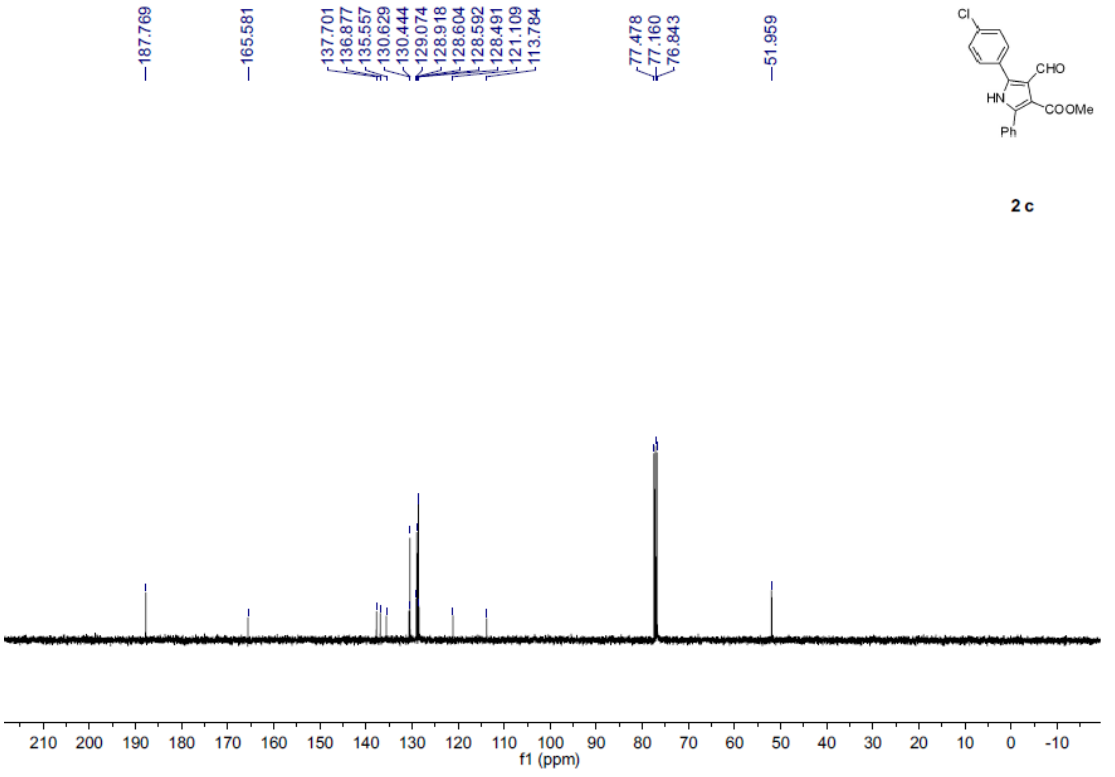
9.361
7.502
7.491
7.483
7.478
7.470
7.398
7.387
7.383
7.375
7.370
7.348
7.326
7.260
3.743
Cl
CHO
HN
COOMe
Ph
2c
1.00
1.00
4.00
5.01
3.00
f1 (ppm)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137.701
136.877
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130.444
129.074
128.918
128.604
128.592
128.491
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77.478
77.160
76.843
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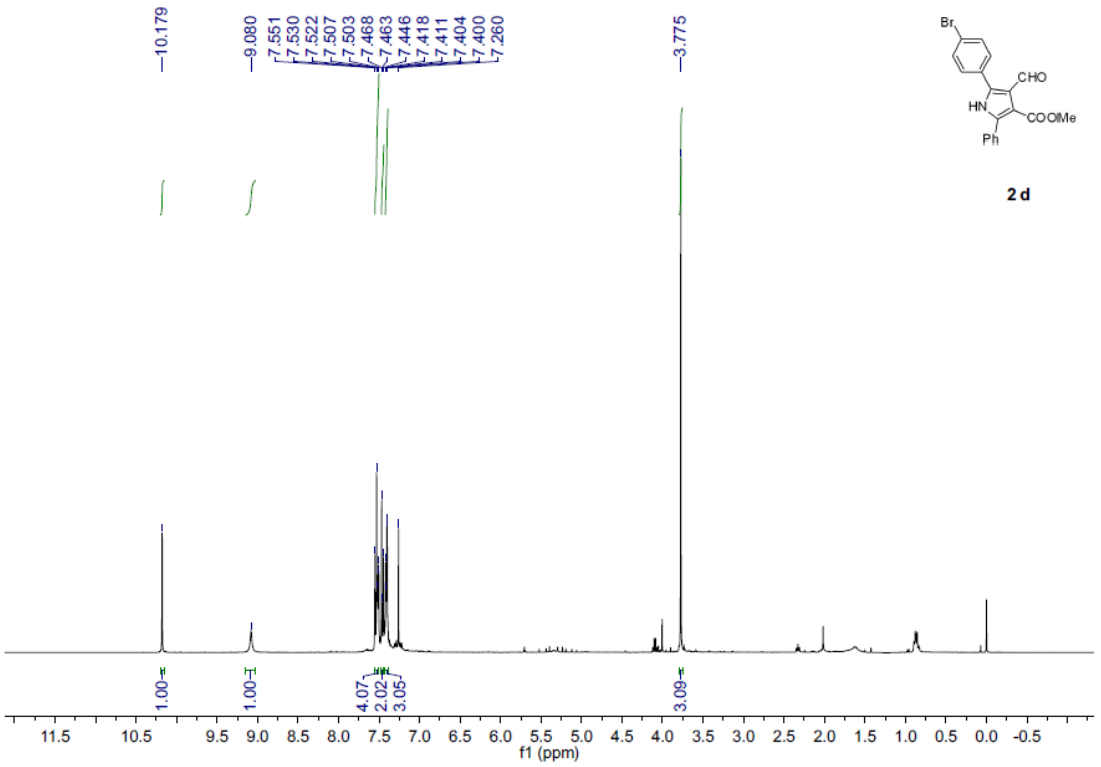
Cl
CHO
HN
COOMe
Ph
2c
f1 (ppm)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7.551
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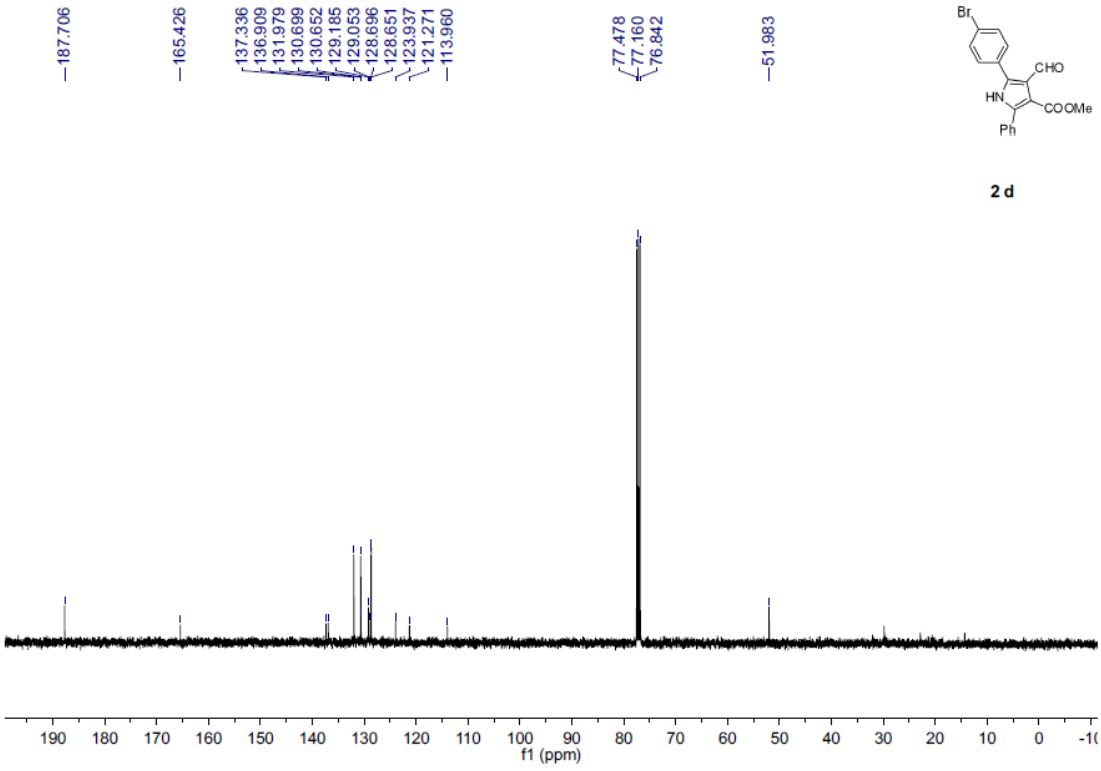
7.507
7.503
7.468
7.463
7.446
7.418
7.411
7.404
7.400
7.260
3.775
Br
CHO
HN
COOMe
Ph
2 d
1.00
1.00
4.07
2.02
3.05
3.09
f1 (ppm)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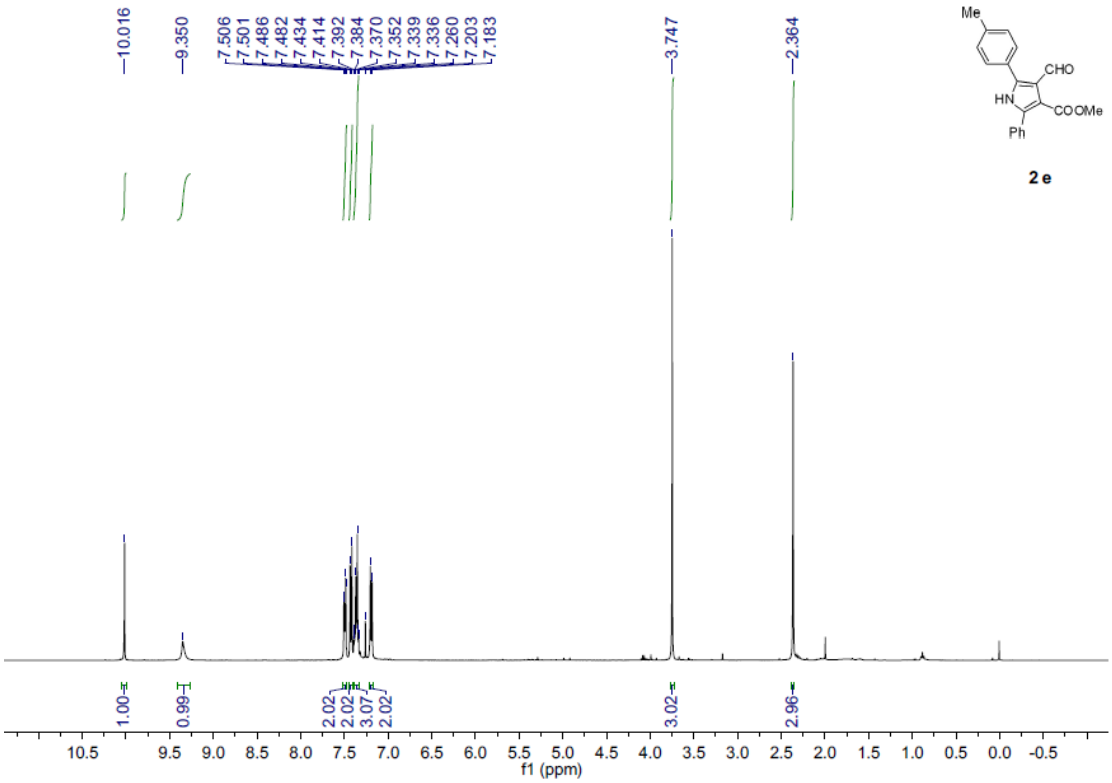
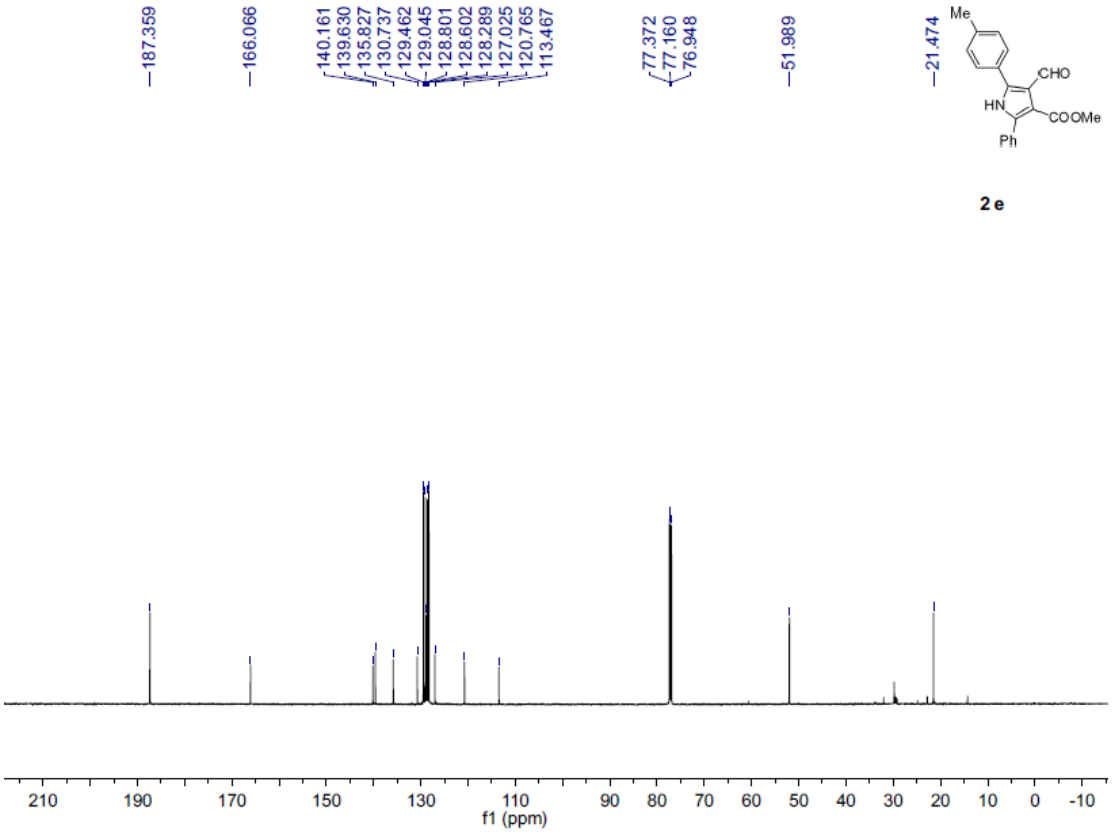
130.699
130.652
129.185
129.053
128.696
128.651
123.937
121.271
113.960
77.478
77.160
76.842
51.983
Br
CHO
HN
COOMe
Ph
2 d
f1 (ppm)


10.016
9.350
7.506
7.501
7.486
7.482
7.434
7.414
7.392
7.384
7.370
7.352
7.339
7.336
7.260
7.203
7.183
3.747
2.364
Me
CHO
HN
COOMe
Ph
2e
1.00
0.99
2.02
2.02
3.07
2.02
3.02
2.96
f1 (ppm)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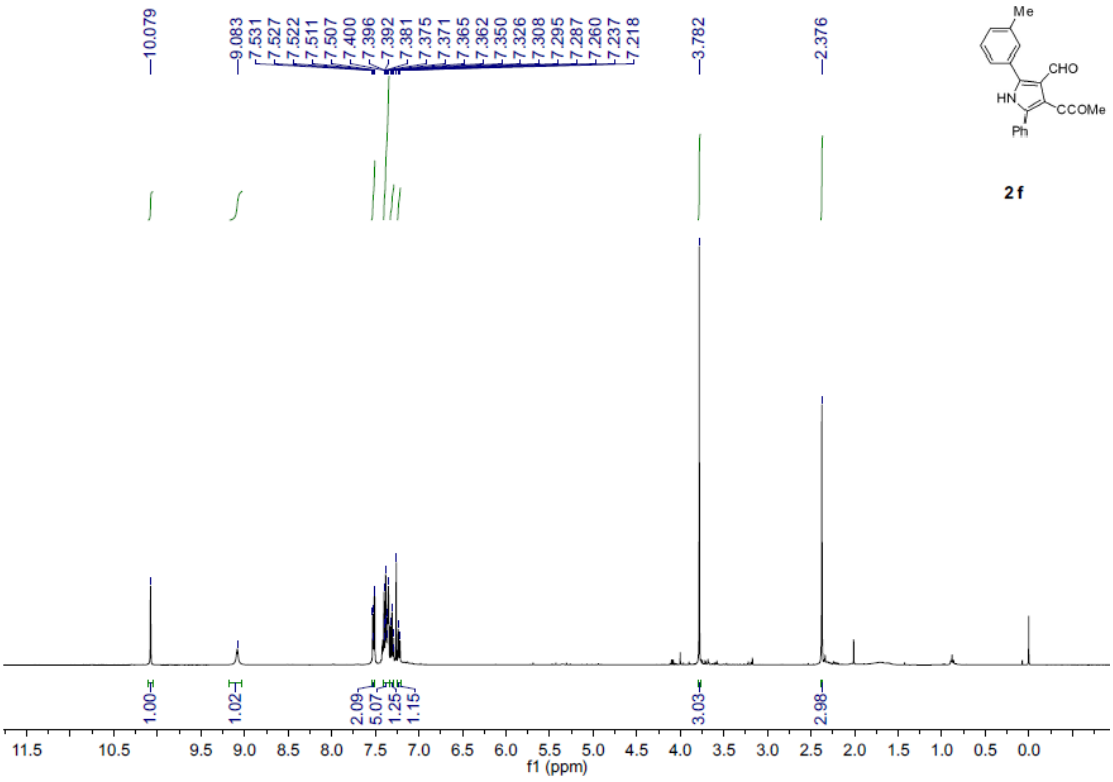
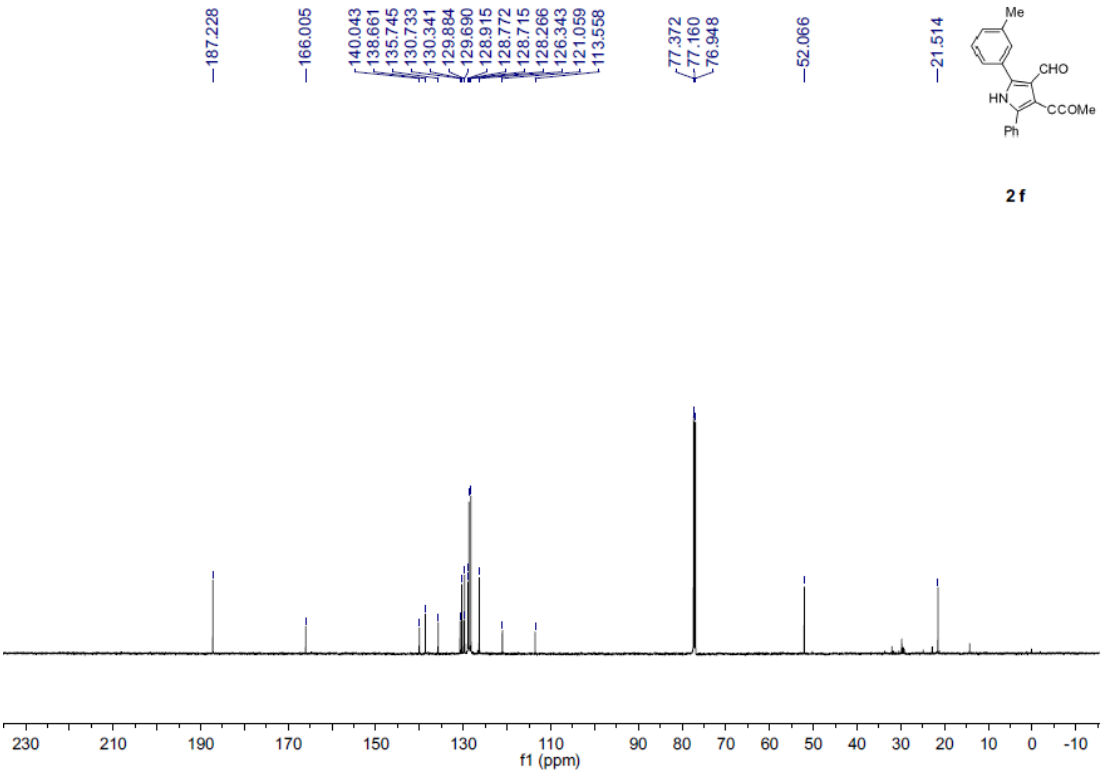
166.066
140.161
139.630
135.827
130.737
129.462
129.045
128.801
128.602
128.289
127.025
120.765
113.467
77.372
77.160
76.948
51.989
21.474
Me
CHO
HN
COOMe
Ph
2e
f1 (ppm)


10.079
9.083
7.531
7.527
7.522
7.511
7.507
7.400
7.396
7.392
7.381
7.375
7.371
7.365
7.362
7.350
7.326
7.308
7.295
7.287
7.260
7.237
7.218
3.782
2.376
Me
CHO
HN
CCOMe
Ph
2f
1.00
1.02
2.09
5.07
1.25
1.15
3.03
2.98
f1 (ppm)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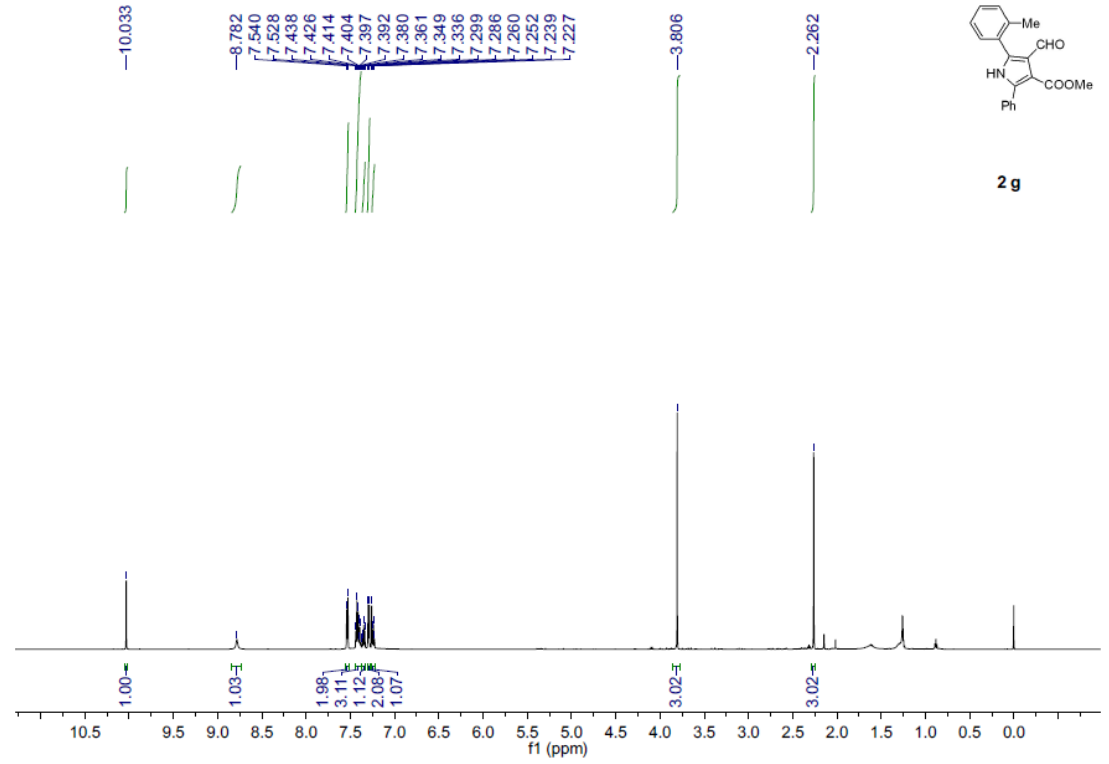
138.661
135.745
130.733
130.341
129.884
129.690
128.915
128.772
128.715
128.266
126.343
121.059
113.558
77.372
77.160
76.948
52.066
21.514
Me
CHO
HN
CCOMe
Ph
2f
f1 (ppm)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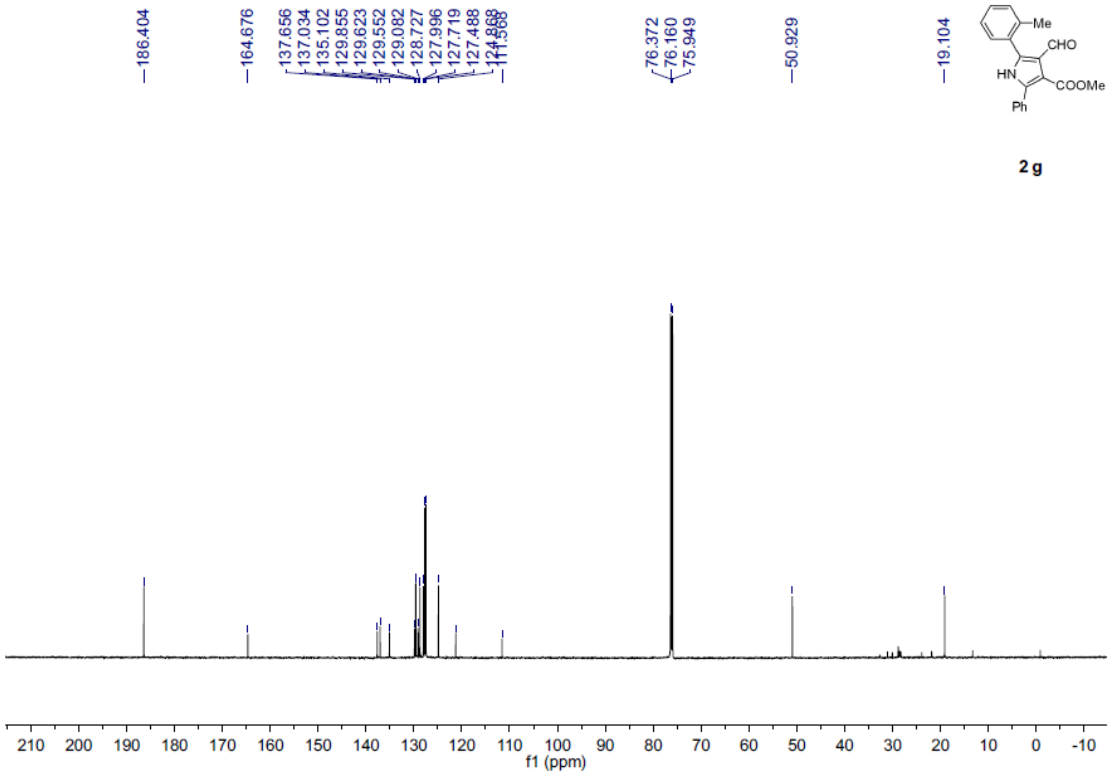
8.782
7.540
7.528
7.438
7.426
7.414
7.404
7.397
7.392
7.380
7.361
7.349
7.336
7.299
7.286
7.260
7.252
7.239
7.227
3.806
2.262
Me
CHO
HN
COOMe
Ph
2g
1.00
1.03
1.98
3.11
1.12
2.08
1.07
3.02
3.02
f1 (ppm)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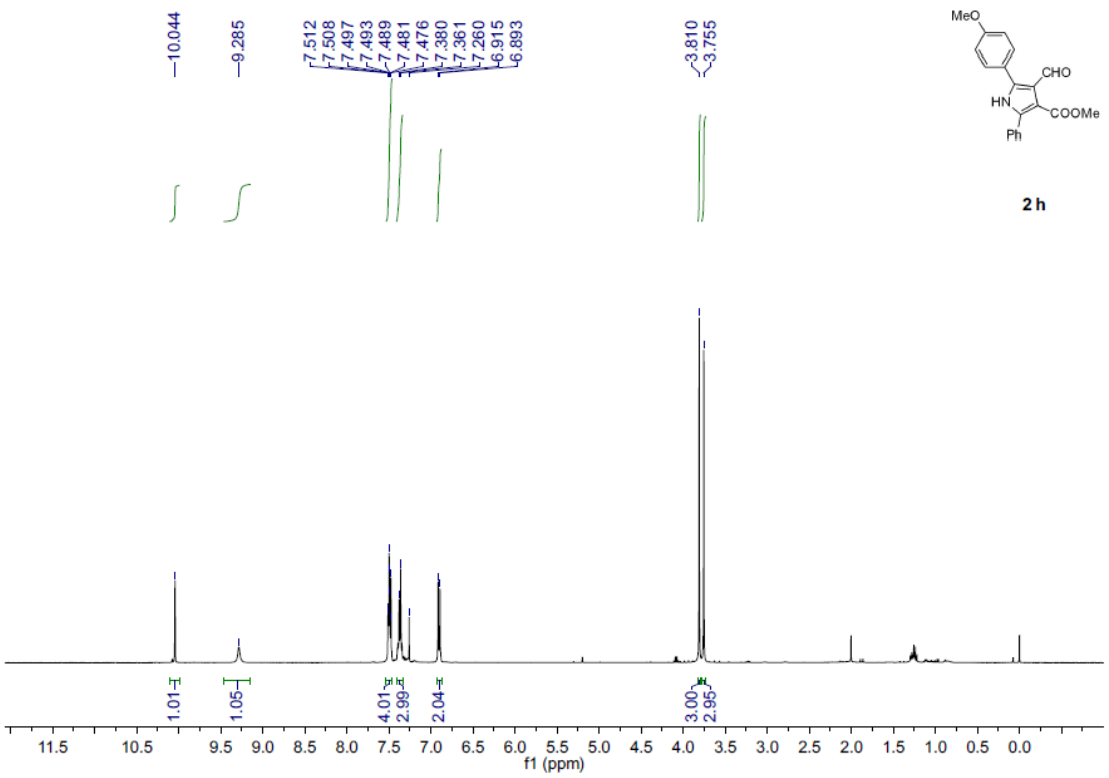
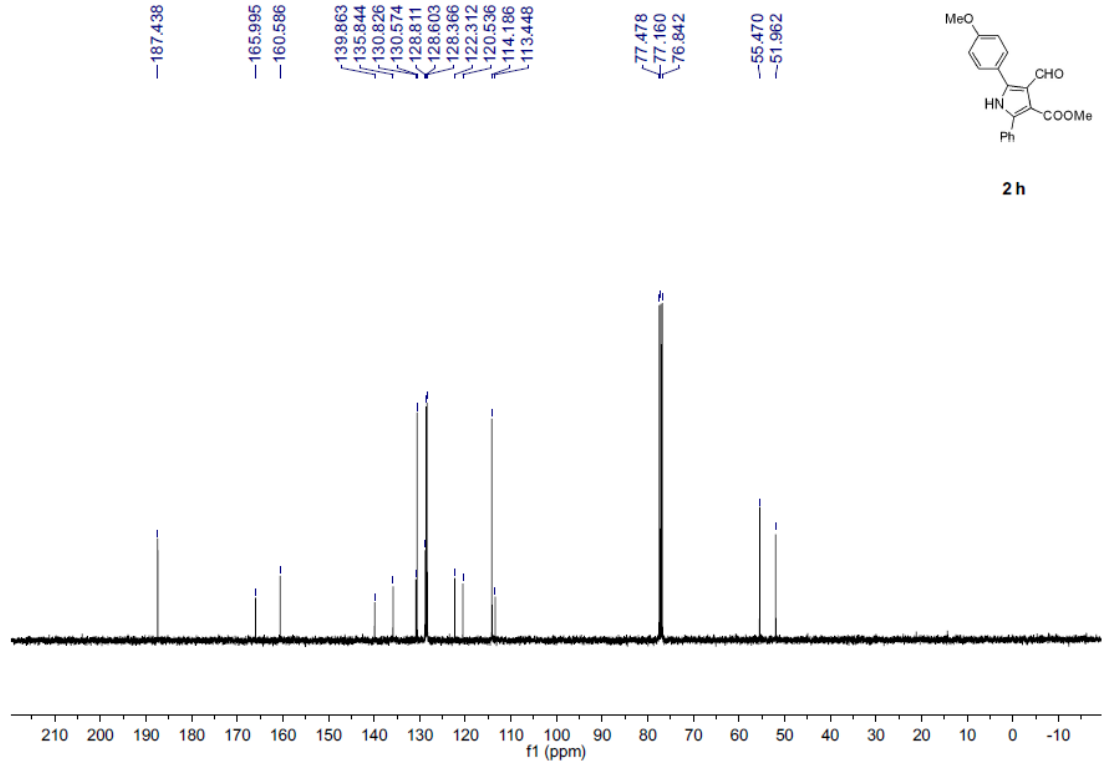
137.656
137.034
135.102
129.855
129.623
129.552
129.082
128.727
127.996
127.719
127.488
76.372
76.160
75.949
50.929
19.104
Me
CHO
HN
COOMe
Ph
2g
f1 (ppm)


10.044
9.285
7.512
7.508
7.497
7.493
7.489
7.481
7.476
7.380
7.361
7.260
6.915
6.893
3.810
3.755
MeO
CHO
HN
COOMe
Ph
2 h
1.01
1.05
4.01
2.99
2.04
3.00
2.95
f1 (ppm)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139.863
135.844
130.826
130.574
128.811
128.603
128.366
122.312
120.536
114.186
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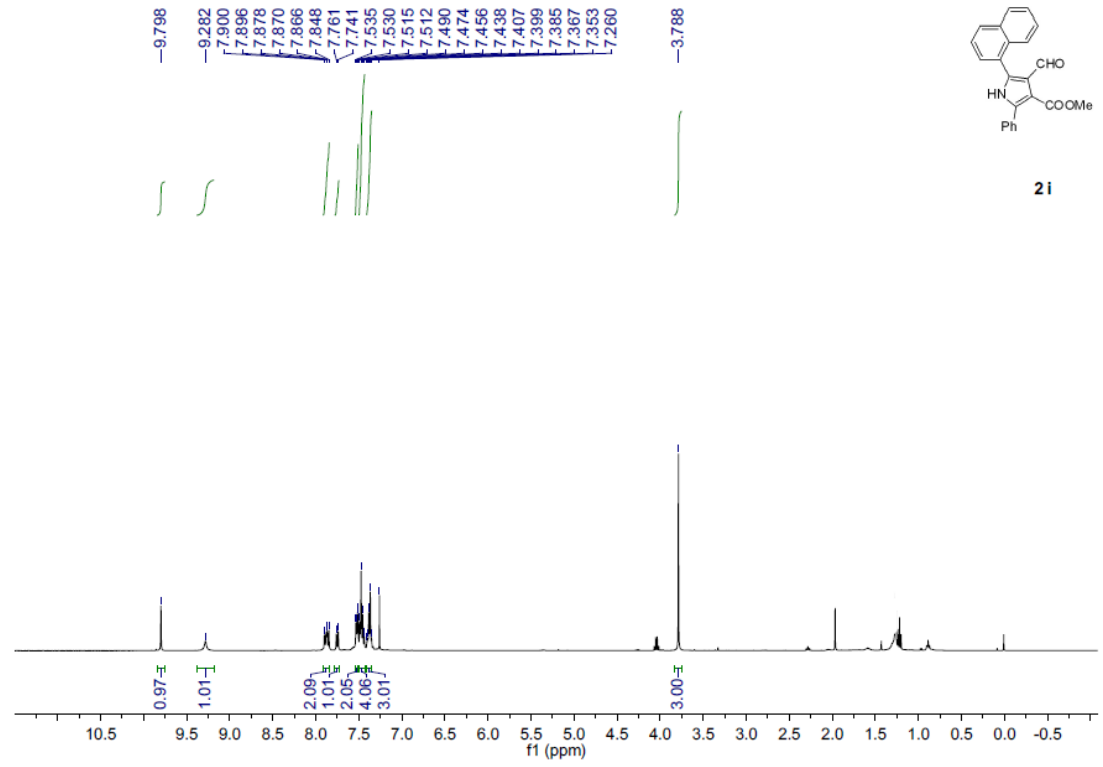
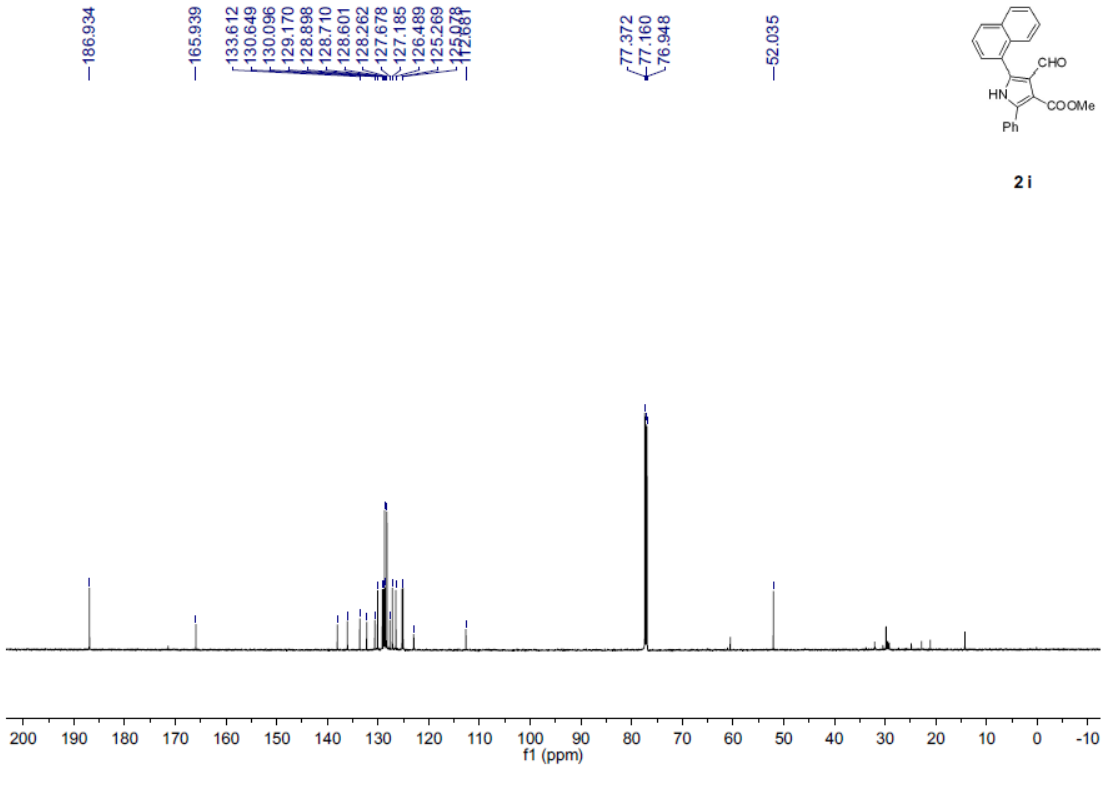
77.478
77.160
76.842
55.470
51.962
MeO
CHO
HN
COOMe
Ph
2 h
f1 (ppm)


9.798
9.282
7.900
7.896
7.878
7.870
7.866
7.848
7.761
7.741
7.535
7.530
7.515
7.512
7.490
7.474
7.456
7.438
7.407
7.399
7.385
7.367
7.353
7.260
3.788
CHO
HN
COOMe
Ph
2i
0.97
1.01
2.09
1.01
2.05
4.06
3.01
3.00
f1 (ppm)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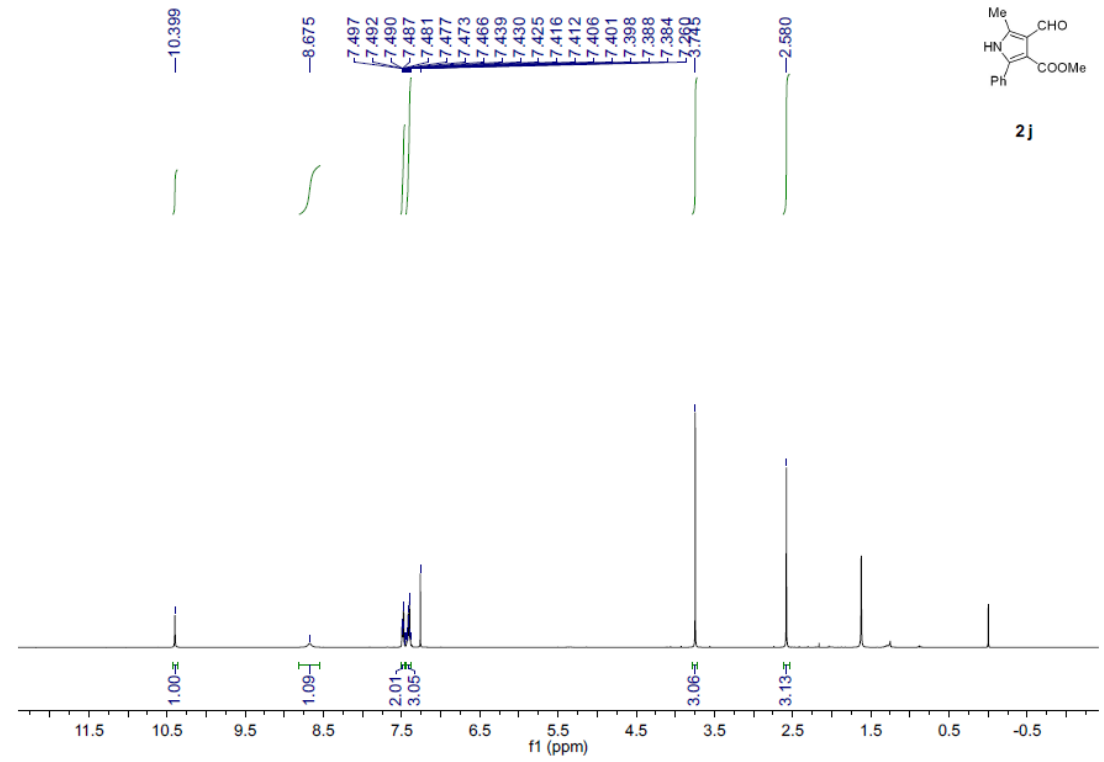
129.170
128.898
128.710
128.601
128.262
127.678
127.185
126.489
125.269
77.372
77.160
76.948
52.035
CHO
HN
COOMe
Ph
2i
f1 (ppm)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7.490
7.487
7.481
7.477
7.473
7.466
7.439
7.430
7.425
7.416
7.412
7.406
7.401
7.398
7.388
7.384
7.260
3.745
2.580
Me
CHO
HN
COOMe
Ph
2j
1.00
1.09
2.01
3.05
3.06
3.13
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
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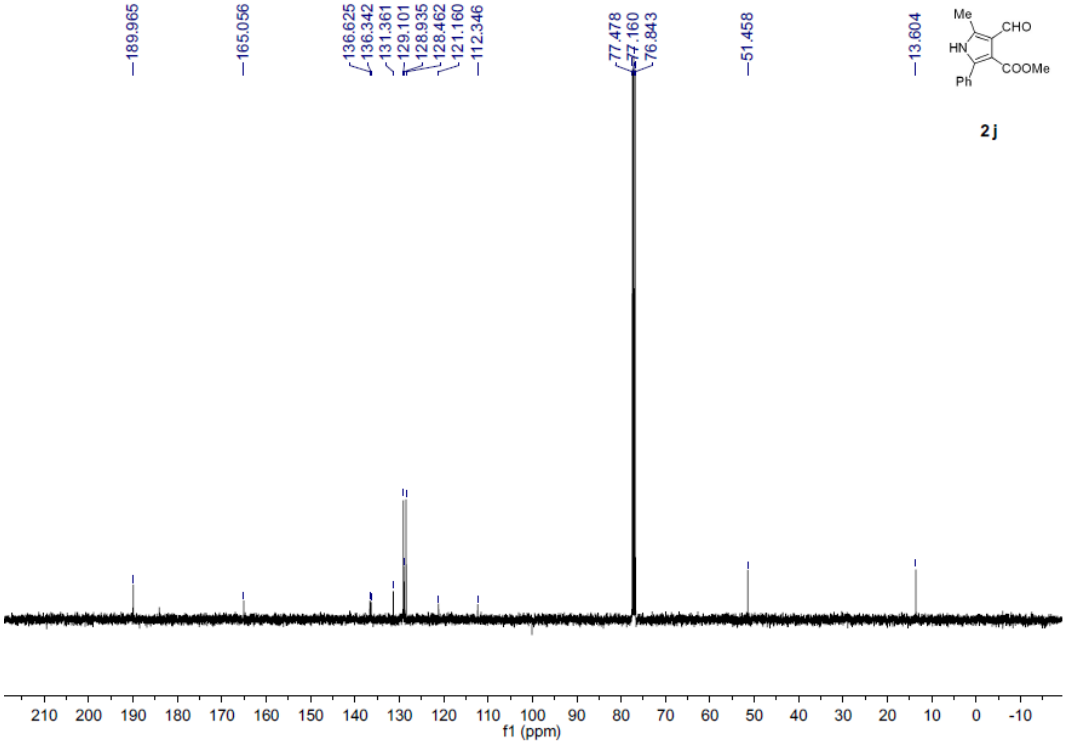
-0.5
f1 (ppm)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136.342
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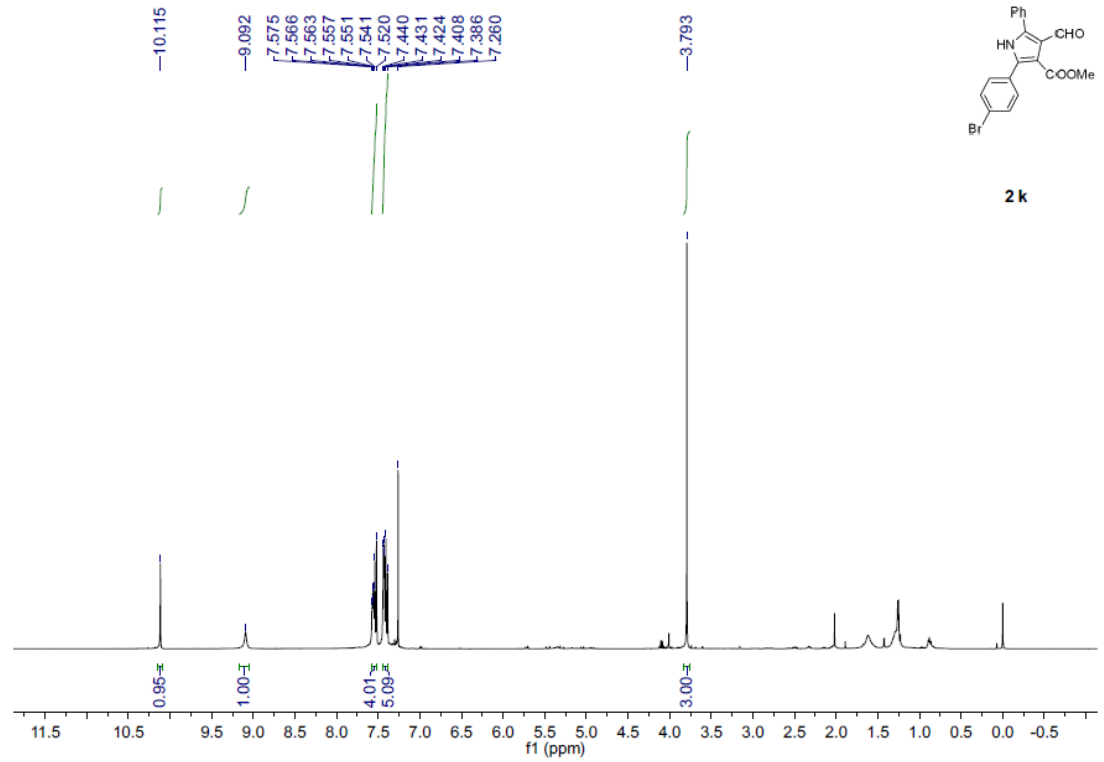
128.935
128.462
121.160
112.346
77.478
77.160
76.843
51.458
13.604
Me
CHO
HN
COOMe
Ph
2j
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.557
7.551
7.541
7.520
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7.431
7.424
7.408
7.386
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Ph
HN
CHO
COOMe
Br
2k
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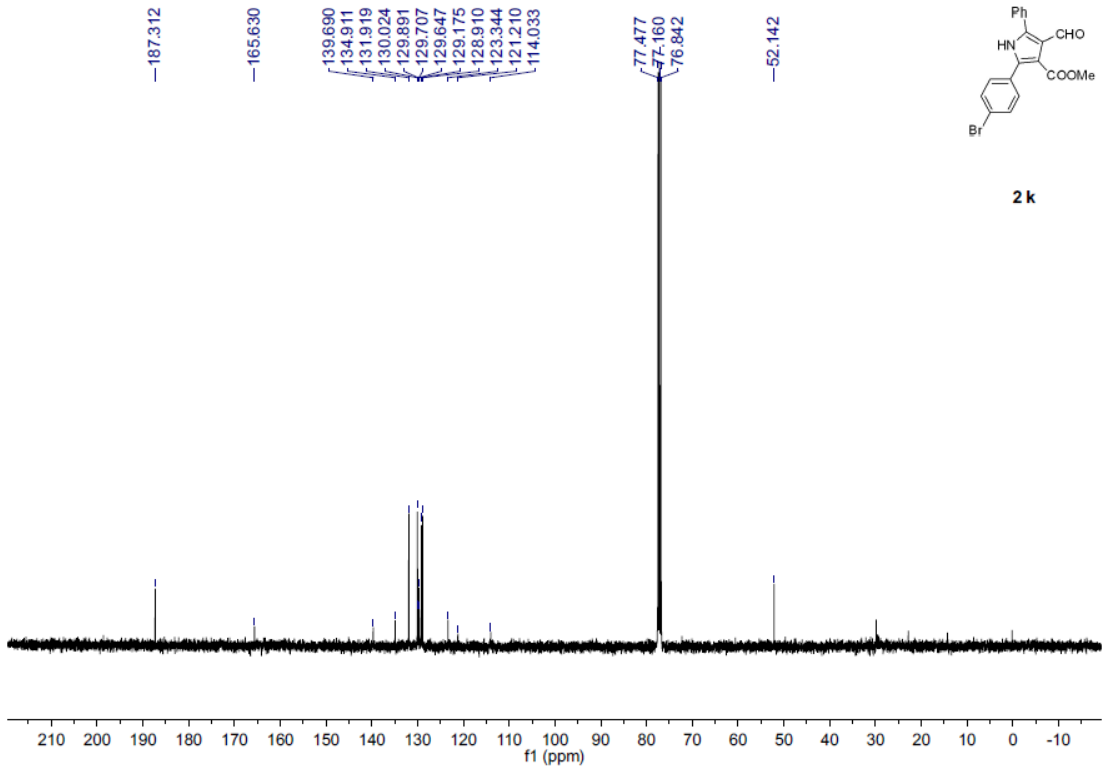
1.00
4.01
5.09
3.00
f1 (ppm)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131.919
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129.891
129.707
129.647
129.175
128.910
123.344
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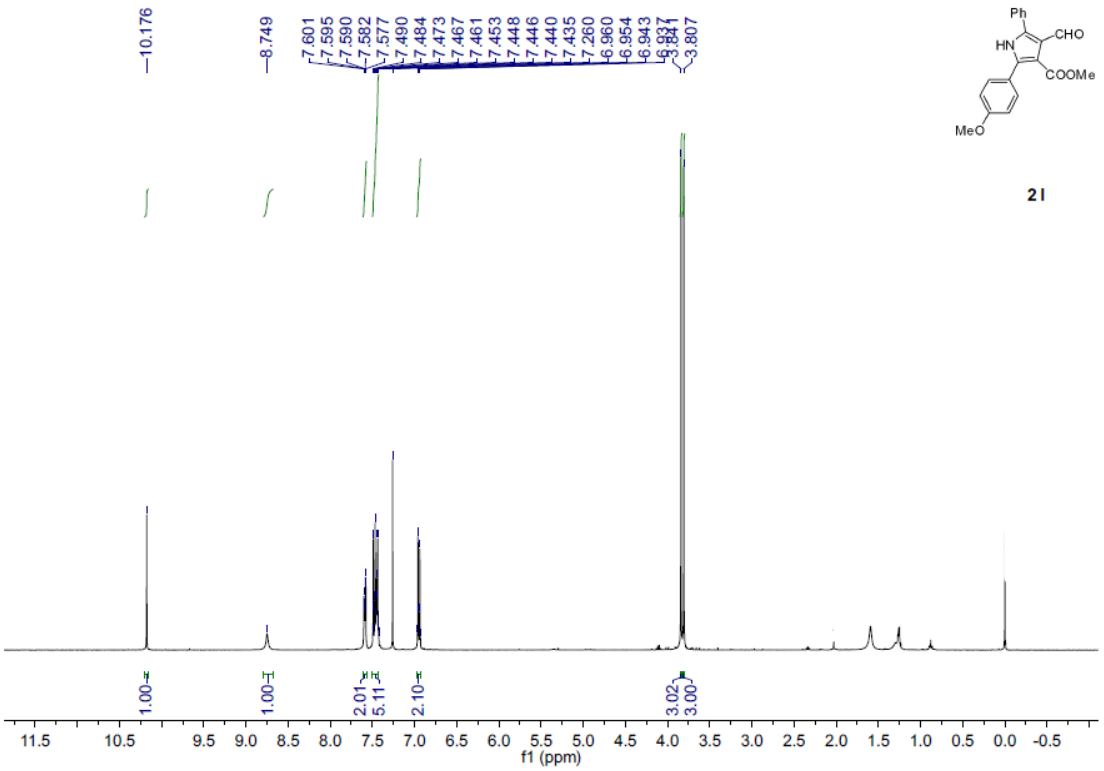
77.477
77.160
76.842
52.142
Ph
HN
CHO
COOMe
Br
2k
f1 (ppm)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7.484
7.473
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7.461
7.453
7.448
7.446
7.440
7.435
7.260
6.960
6.954
6.943
6.937
3.841
3.807
Ph
HN
CHO
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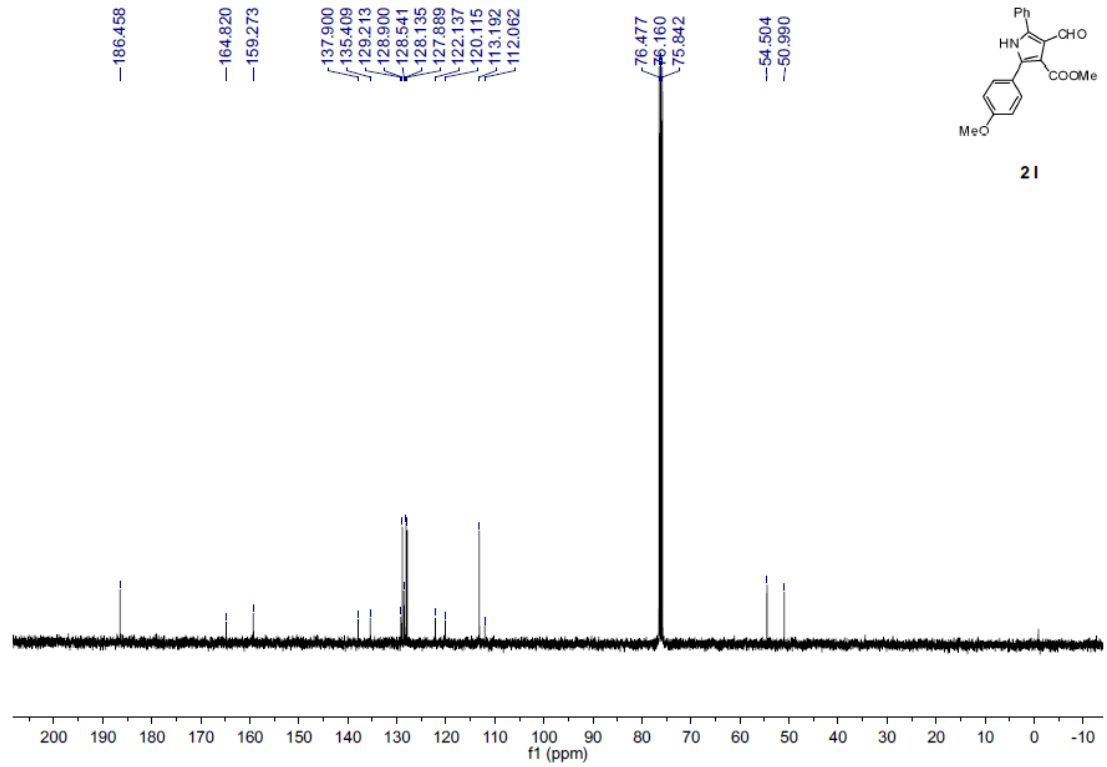
MeO
2l
1.00
1.00
2.01
5.11
2.10
3.02
3.00
f1 (ppm)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129.213
128.900
128.541
128.135
127.889
122.137
120.115
113.192
112.062
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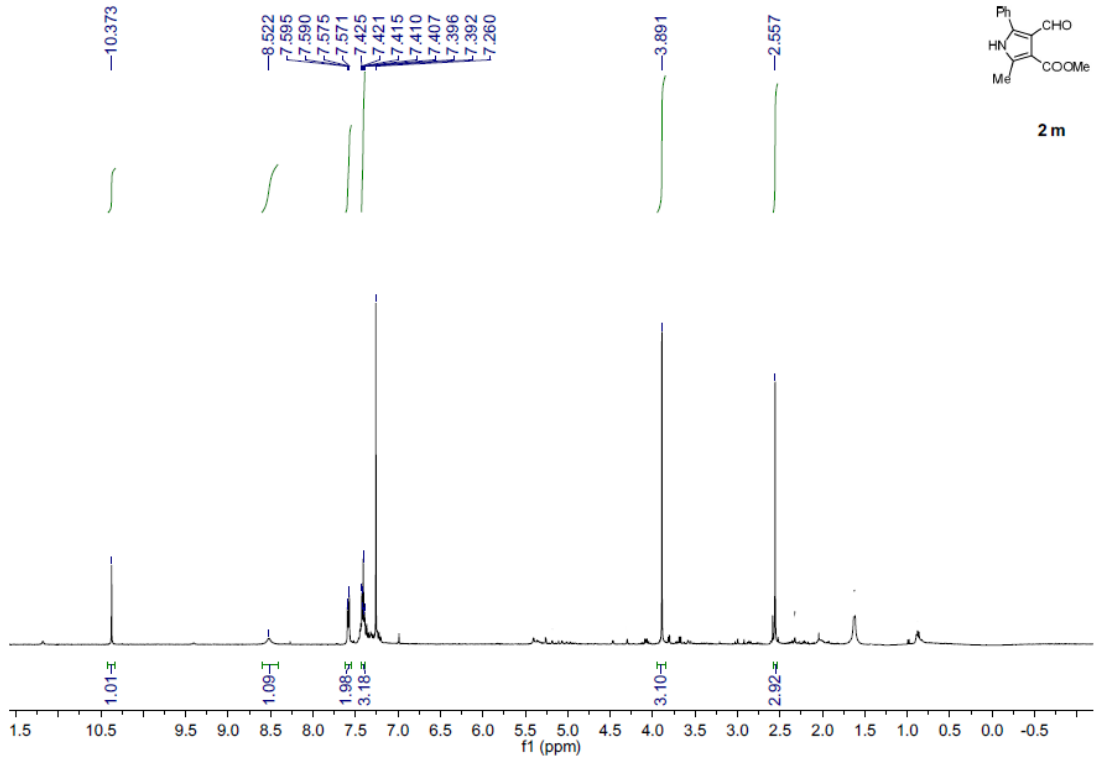
76.160
75.842
54.504
50.990
Ph
HN
CHO
COOMe
MeO
2l
f1 (ppm)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7.590
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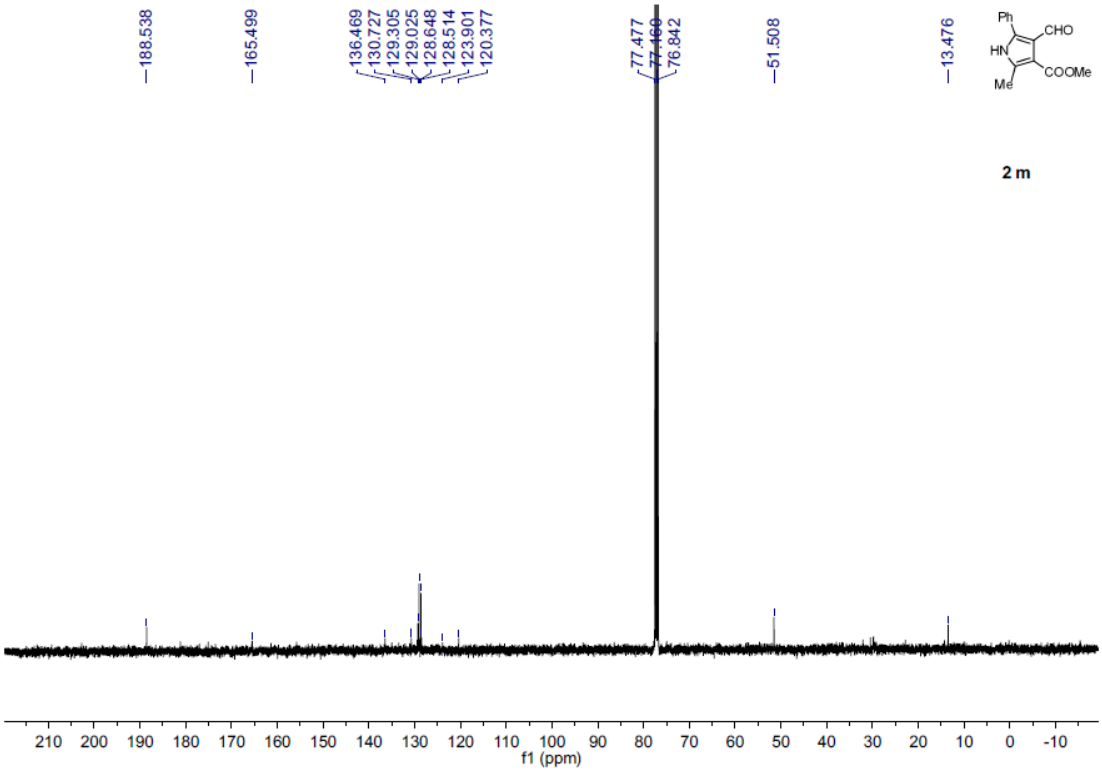
7.425
7.421
7.415
7.410
7.407
7.396
7.392
7.260
3.891
2.557
Ph
CHO
HN
Me
COOMe
2 m
1.01
1.09
1.98
3.18
3.10
2.92
f1 (ppm)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129.025
128.648
128.514
123.901
120.377
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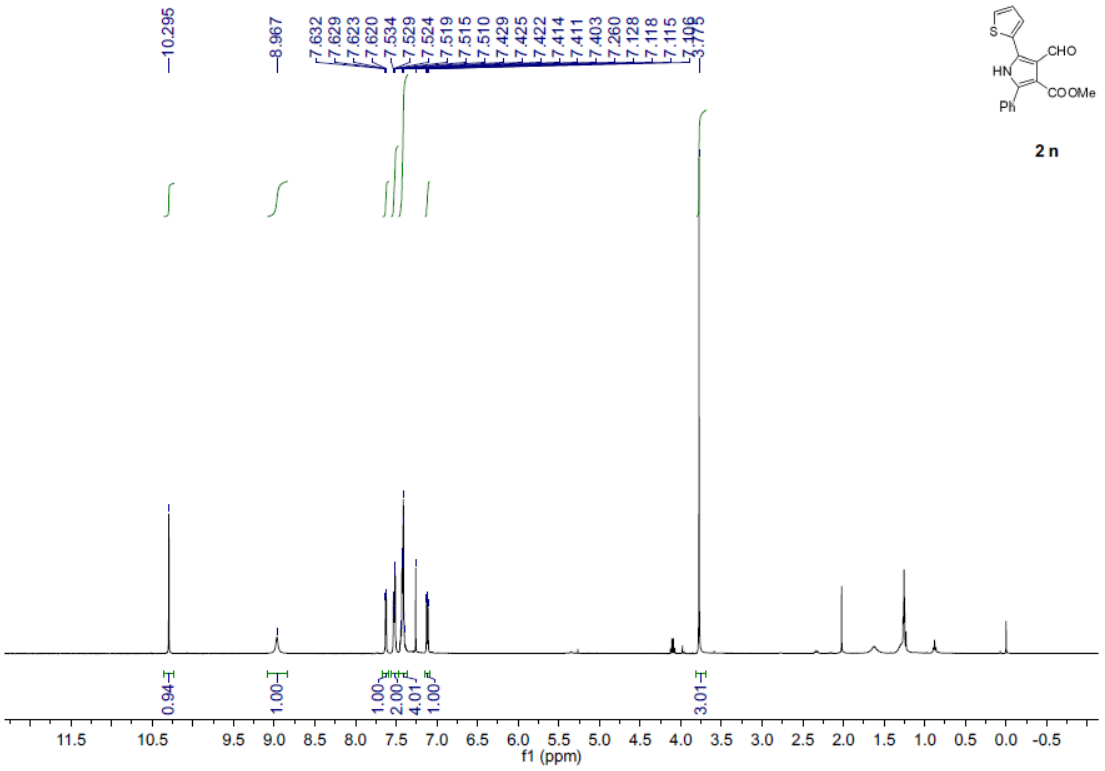
77.160
76.842
51.508
13.476
Ph
CHO
HN
Me
COOMe
2 m
f1 (ppm)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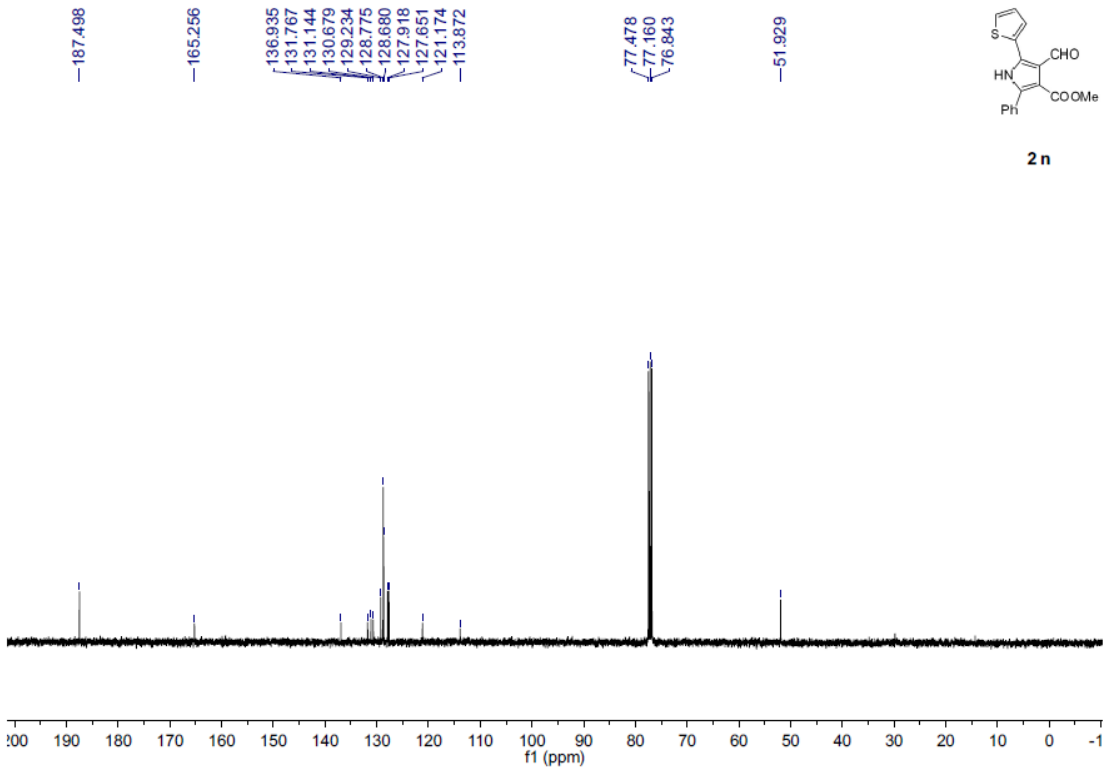
7.510
7.429
7.425
7.422
7.414
7.411
7.403
7.260
7.128
7.118
7.115
3.775
0.94
1.00
1.00
2.00
4.01
1.00
3.01
f1 (ppm)
CHO
HN
COOMe
Ph
2n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131.767
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130.679
129.234
128.775
128.680
127.918
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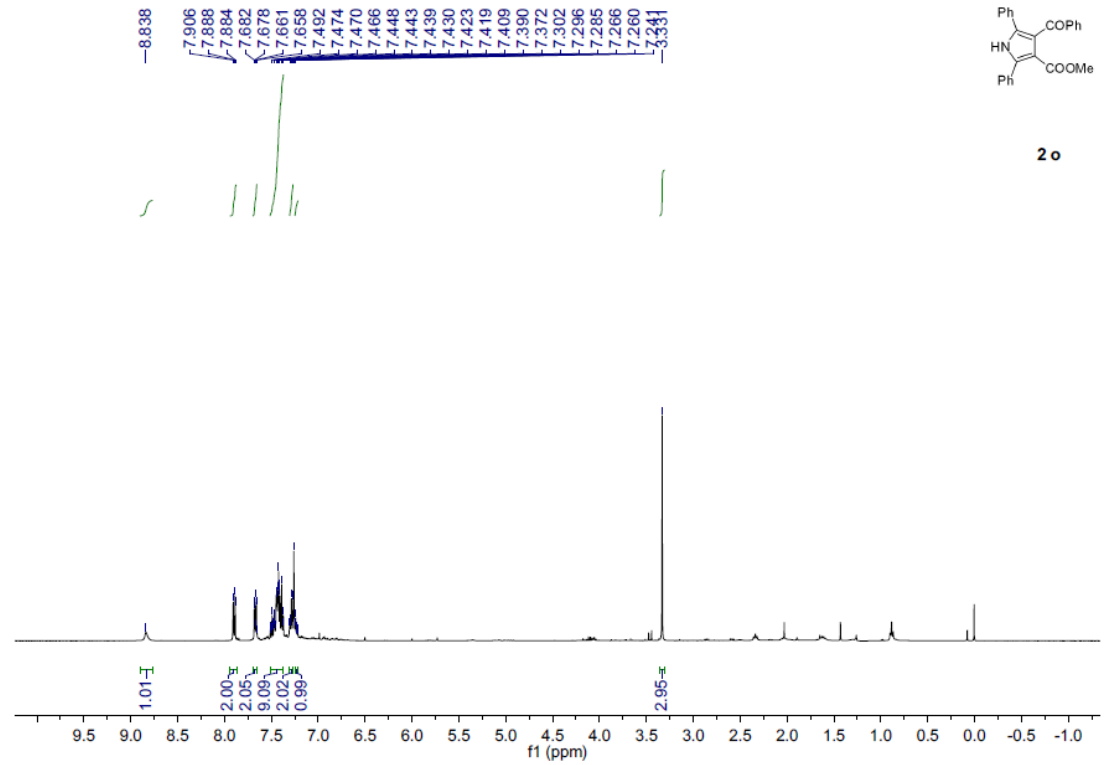
121.174
113.872
77.478
77.160
76.843
51.929
f1 (ppm)
CHO
HN
COOMe
Ph
2n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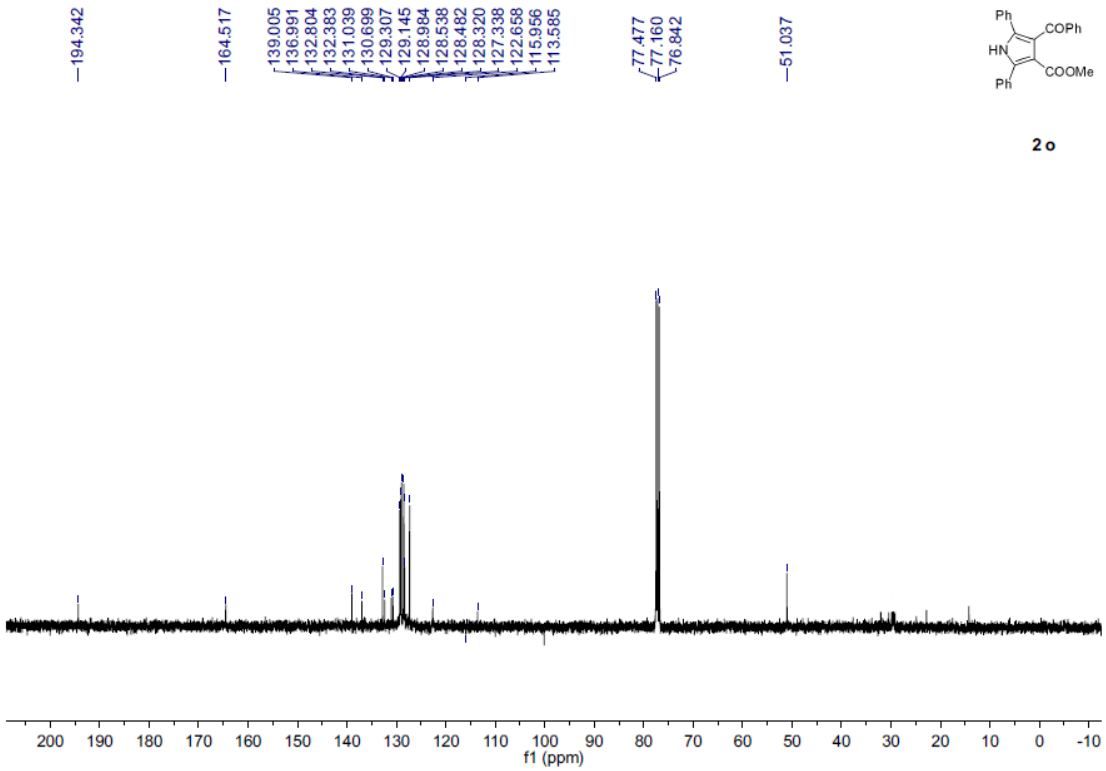
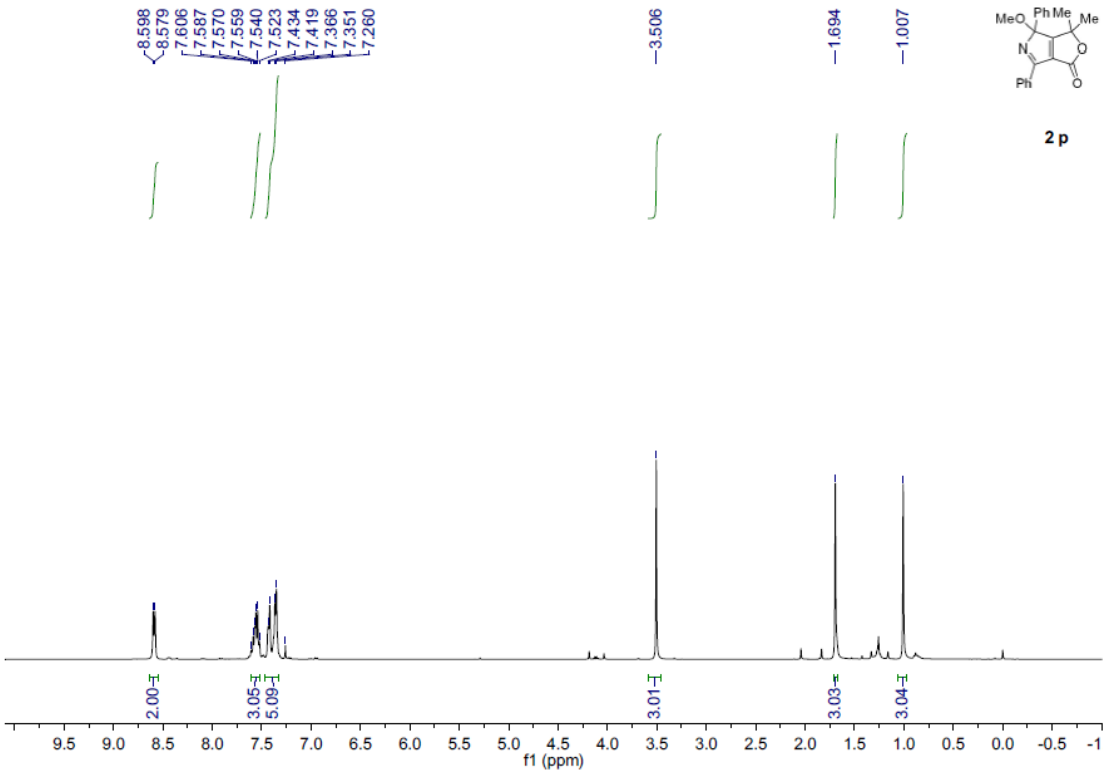
7.448
7.443
7.439
7.430
7.423
7.419
7.409
7.390
7.372
7.302
7.296
7.285
7.266
7.260
7.241
3.331
Ph
COPh
HN
COOMe
Ph
2o
1.01
2.00
2.05
9.09
2.02
0.99
2.95
f1 (ppm)


194.342
164.517
139.005
136.991
132.804
132.383
131.039
130.699
129.307
129.145
128.984
128.538
128.482
128.320
127.338
122.658
115.956
113.585
77.477
77.160
76.842
51.037
Ph
COPh
HN
COOMe
Ph
2o
f1 (ppm)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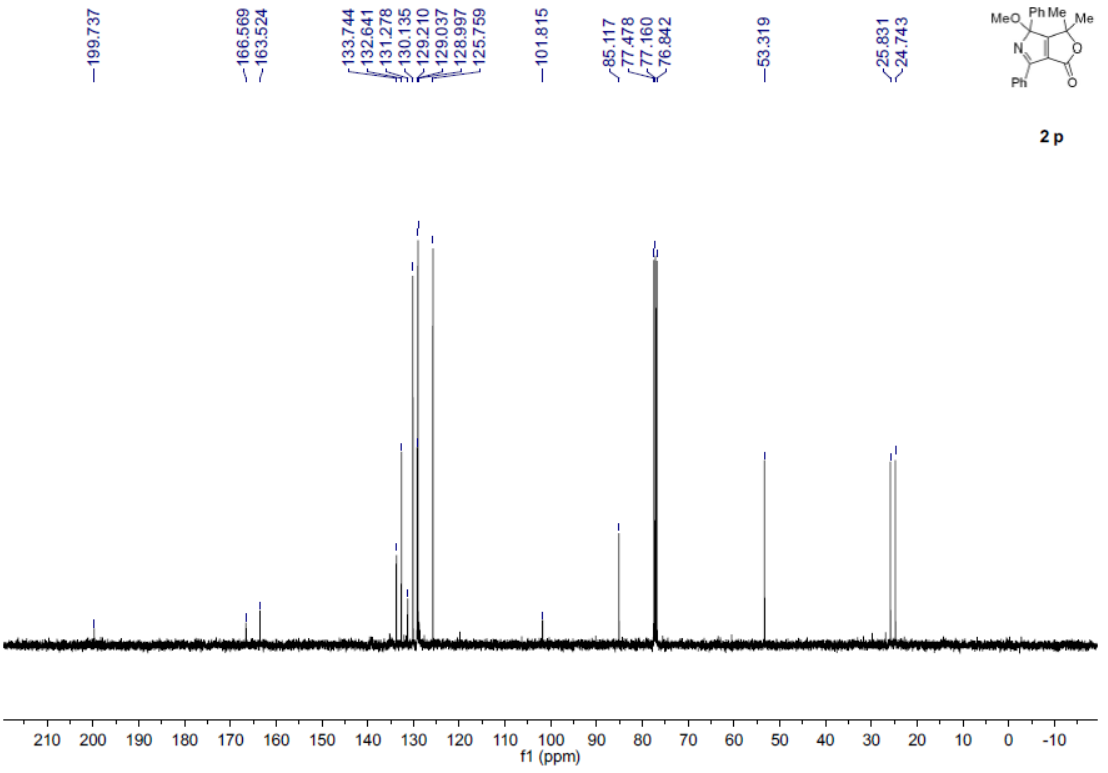
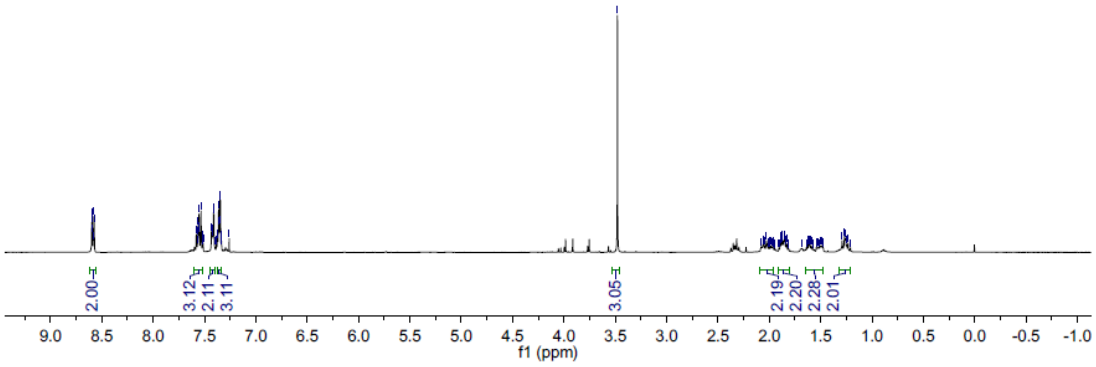
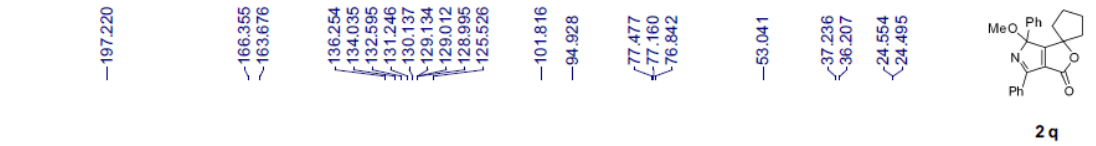
8.579
7.606
7.587
7.570
7.559
7.540
7.523
7.434
7.419
7.366
7.351
7.260
3.506
1.694
1.007
MeO
Ph
Me
Me
N
O
Ph
O
2 p
2.00
3.05
5.09
3.01
3.03
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1
f1 (ppm)


199.737
166.569
163.524
133.744
132.641
131.278
130.135
129.210
129.037
128.997
125.759
101.815
85.117
77.478
77.160
76.842
53.319
25.831
24.743
MeO
Ph
Me
Me
N
O
Ph
O
2 p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

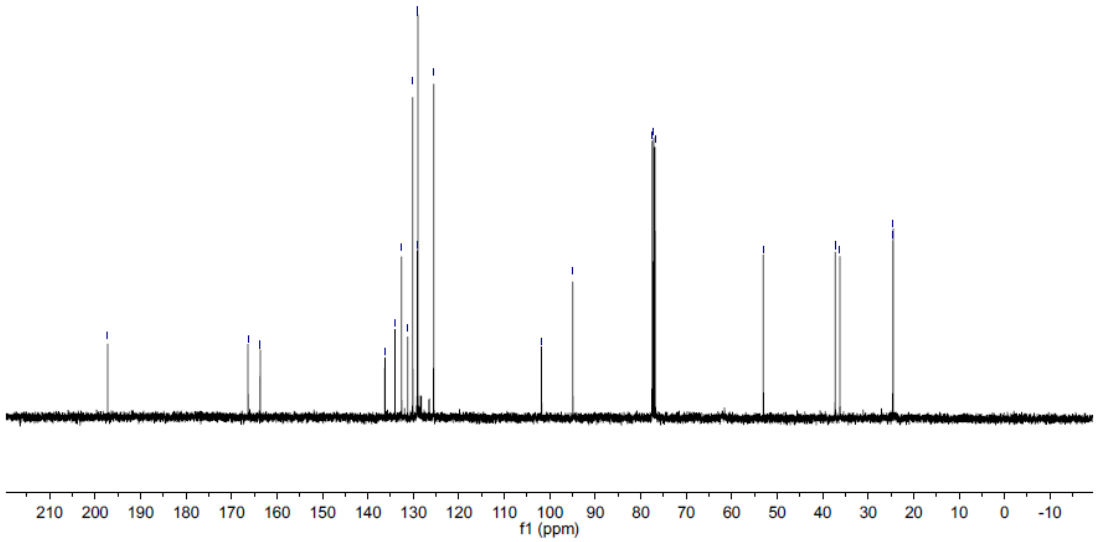

8.598
8.595
8.591
8.583
8.578
8.574
7.580
7.573
7.567
7.563
7.559
7.553
7.550
7.535
7.522
7.518
7.513
7.433
7.427
7.422
7.418
7.413
7.408
7.401
7.385
7.375
7.370
7.362
7.358
7.355
7.348
7.344
7.337
7.332
7.260
3.479
2.058
2.052
2.042
2.028
1.965
1.893
1.884
1.878
1.872
1.855
1.851
1.839
1.831
1.628
1.615
1.604
1.507
1.291
1.268
1.260
1.246
1.233
MeO
Ph
N
O
Ph
O

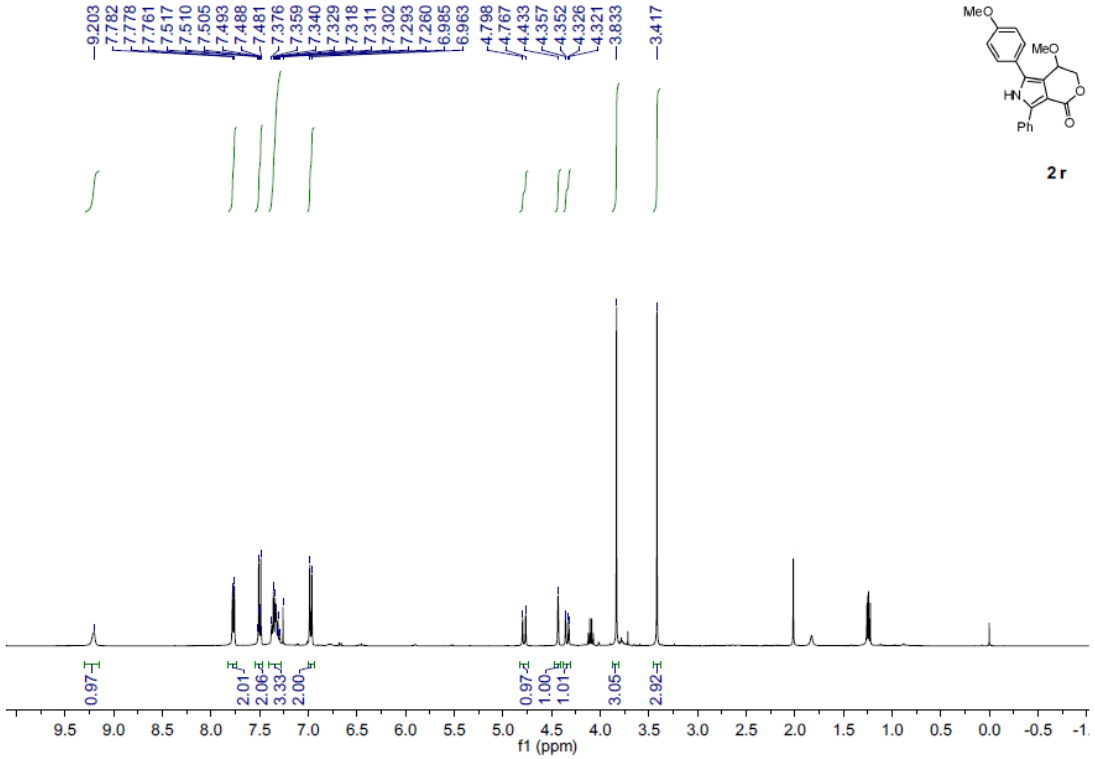
2q

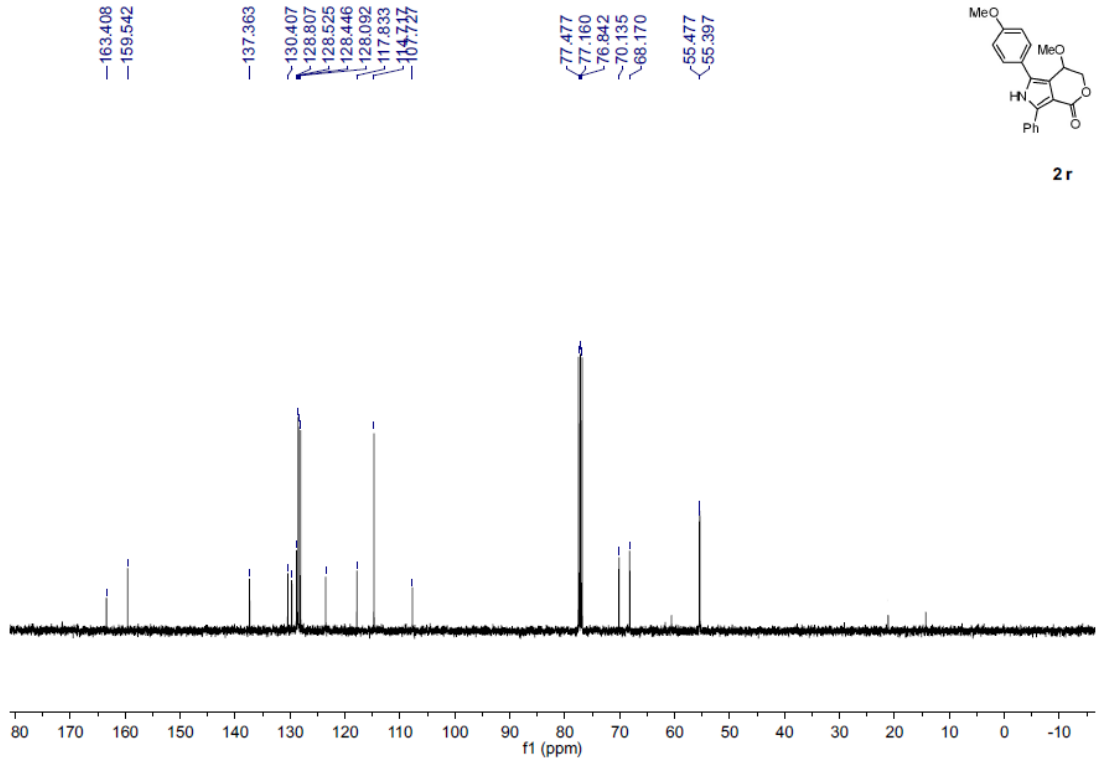

2.00
3.12
2.11
3.11
3.05
2.19
2.20
2.28
2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

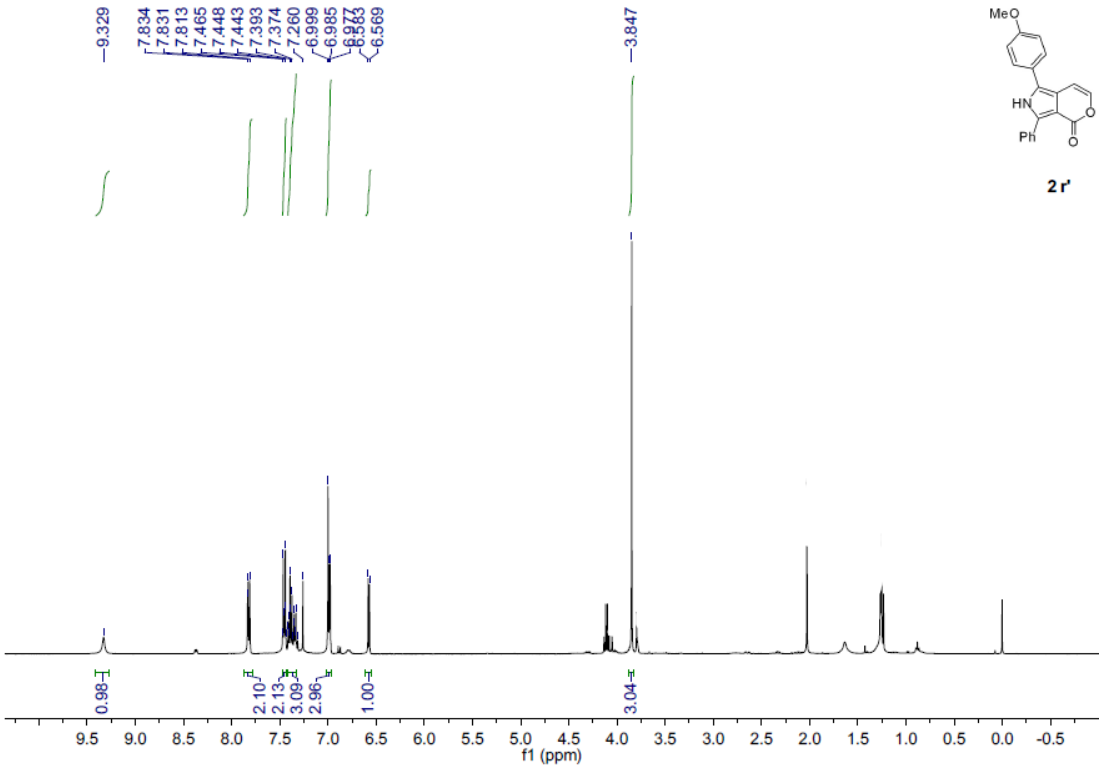

197.220
166.355
163.676
136.254
134.035
132.595
131.246
130.137
129.134
129.012
128.995
125.526
101.816
94.928
77.477
77.160
76.842
53.041
37.236
36.207
24.554
24.495
MeO
Ph
N
O
Ph
O

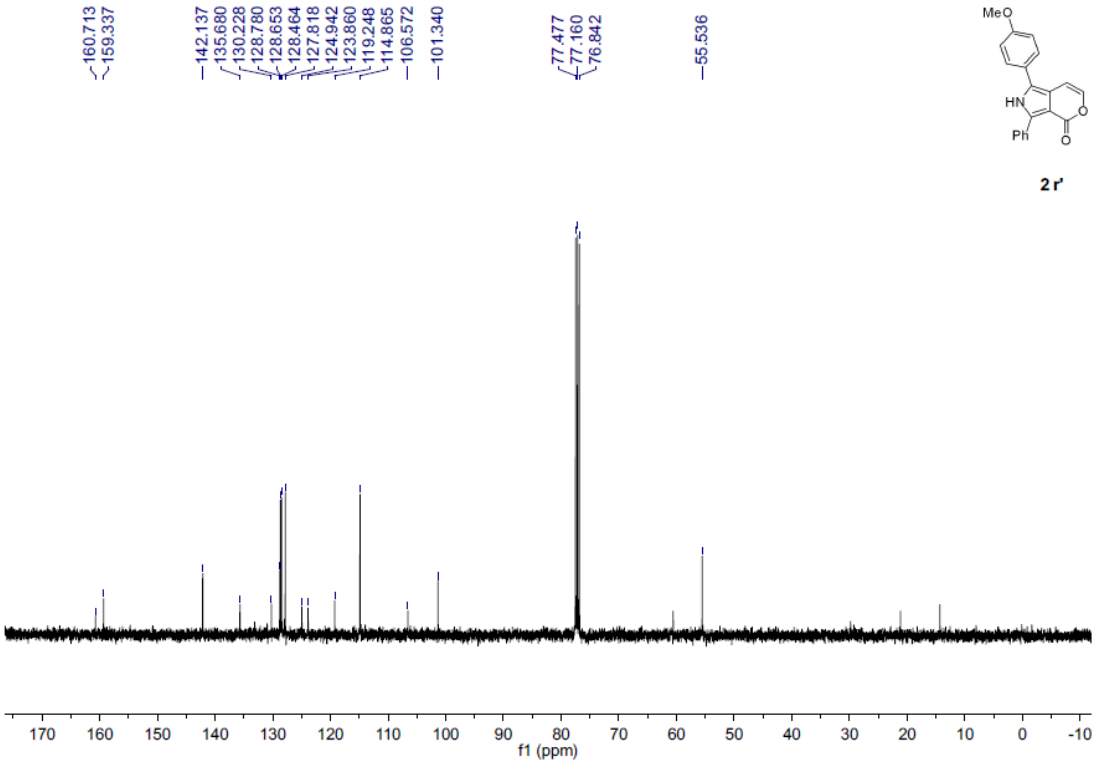
2q

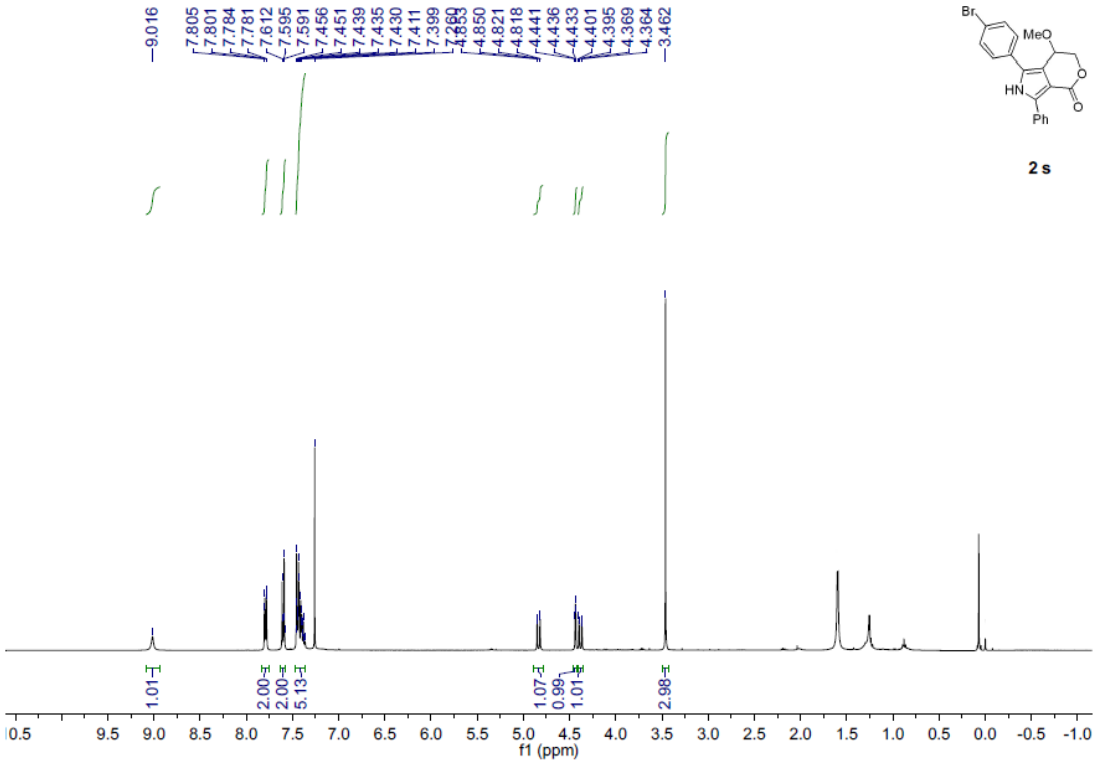

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

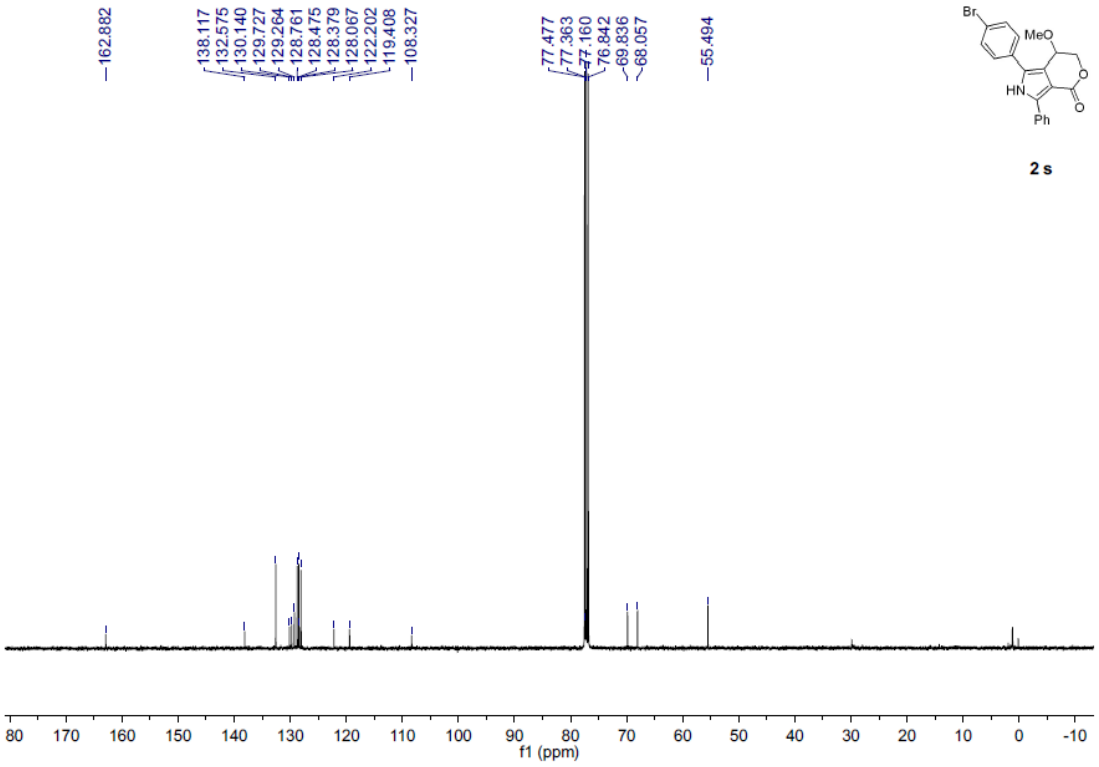

9.203
7.782
7.778
7.761
7.517
7.510
7.505
7.493
7.488
7.481
7.376
7.359
7.340
7.329
7.318
7.311
7.302
7.293
7.260
6.985
6.963
4.798
4.767
4.433
4.357
4.352
4.326
4.321
3.833
3.417
MeO
MeO
HN
O
O
Ph
2r
0.97
2.01
2.06
3.33
2.00
0.97
1.00
1.01
3.05
2.92
f1 (ppm)

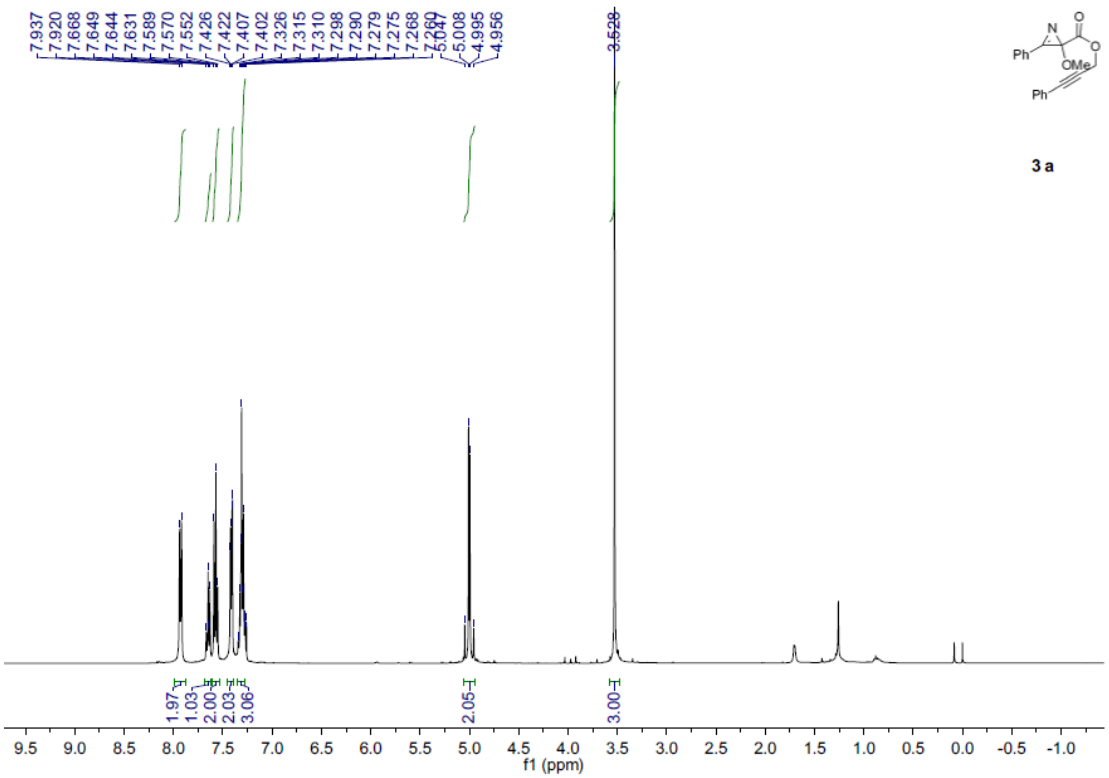

163.408
159.542
137.363
130.407
128.807
128.525
128.446
128.092
117.833
77.477
77.160
76.842
70.135
68.170
55.477
55.397
MeO
MeO
HN
O
O
Ph
2r
f1 (ppm)

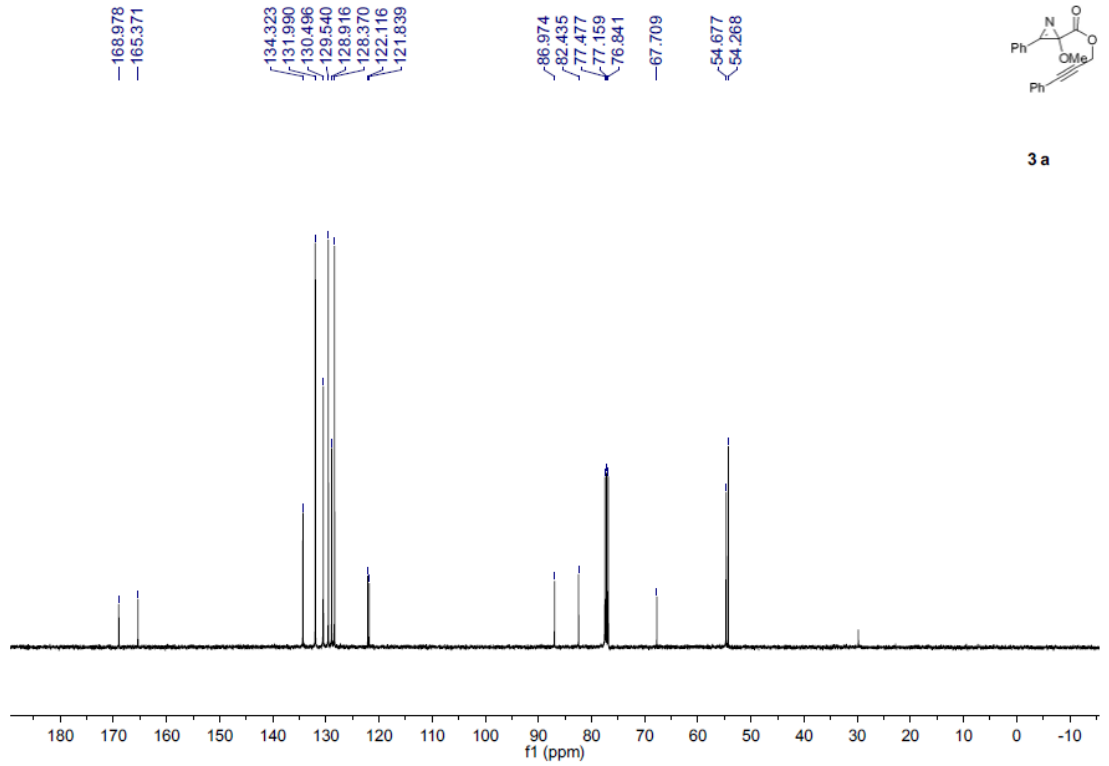

9.329
7.834
7.831
7.813
7.465
7.448
7.443
7.393
7.374
7.260
6.999
6.985
6.877
6.583
6.569
3.847
MeO
HN
Ph
O
2 r'
0.98
2.10
2.13
3.09
2.96
1.00
3.04
f1 (ppm)

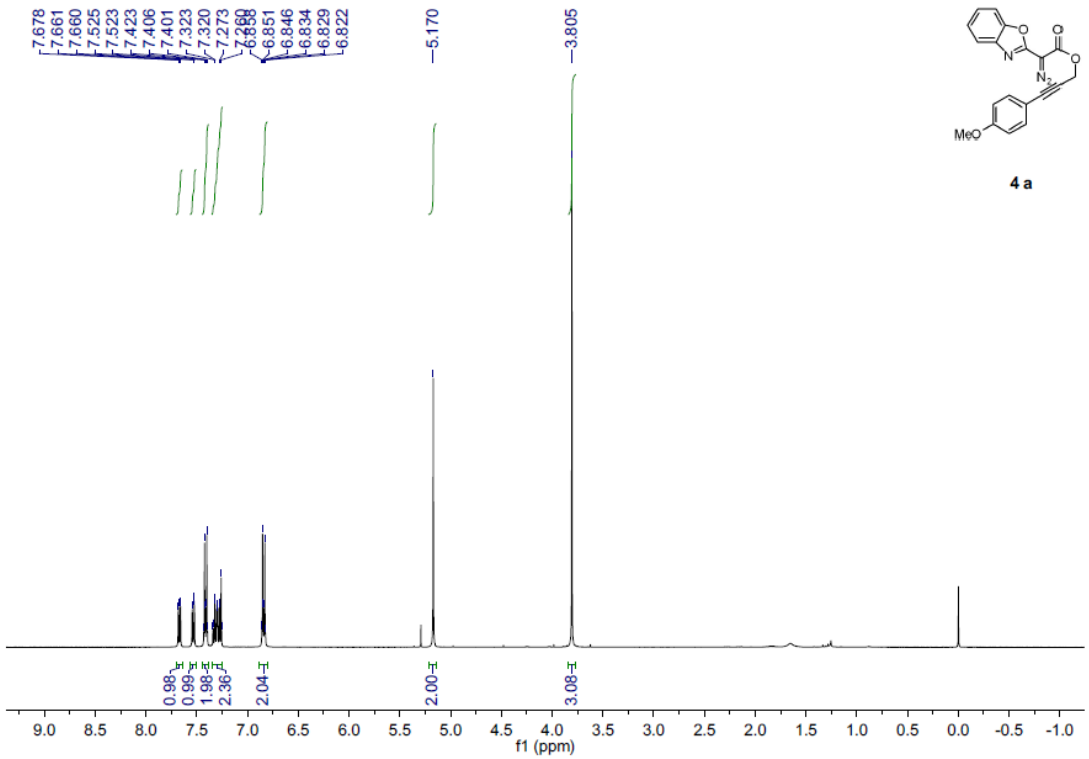

160.713
159.337
142.137
135.680
130.228
128.780
128.653
128.464
127.818
124.942
123.860
119.248
114.865
106.572
101.340
77.477
77.160
76.842
55.536
MeO
HN
Ph
O
2 r'
f1 (ppm)

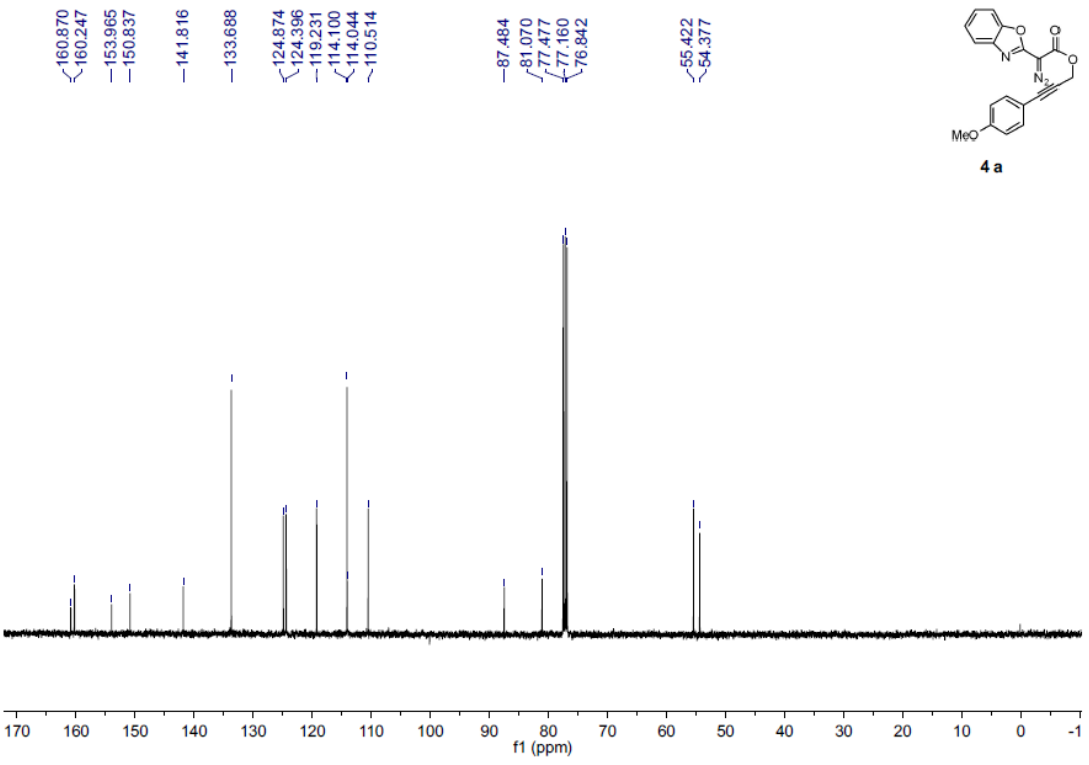

9.016
7.805
7.801
7.784
7.781
7.612
7.595
7.591
7.456
7.451
7.439
7.435
7.430
7.411
7.399
4.850
4.821
4.818
4.441
4.436
4.433
4.401
4.395
4.369
4.364
3.462
Br
MeO
HN
Ph
O
2 s
1.01
2.00
2.00
5.13
1.07
0.99
1.01
2.98
f1 (ppm)


162.882
138.117
132.575
130.140
129.727
129.264
128.761
128.475
128.379
128.067
122.202
119.408
108.327
77.477
77.363
77.160
76.842
69.836
68.057
55.494
Br
MeO
HN
Ph
O
2 s
f1 (ppm)


7.937
7.920
7.668
7.649
7.644
7.631
7.589
7.570
7.552
7.426
7.422
7.407
7.402
7.326
7.315
7.310
7.298
7.290
7.279
7.275
7.268
7.260
5.047
5.008
4.995
4.956
3.528
1.97
1.03
2.00
2.03
3.06
2.05
3.00
f1 (ppm)
Ph
N
O
O
OMe
Ph
3 a


168.978
165.371
134.323
131.990
130.496
129.540
128.916
128.370
122.116
121.839
86.974
82.435
77.477
77.159
76.841
67.709
54.677
54.268
f1 (ppm)
Ph
N
O
O
OMe
Ph
3 a


7.678
7.661
7.660
7.525
7.523
7.423
7.406
7.401
7.323
7.320
7.273
6.851
6.846
6.834
6.829
6.822
5.170
3.805
0.98
0.99
1.98
2.36
2.04
2.00
3.08
f1 (ppm)
MeO
4 a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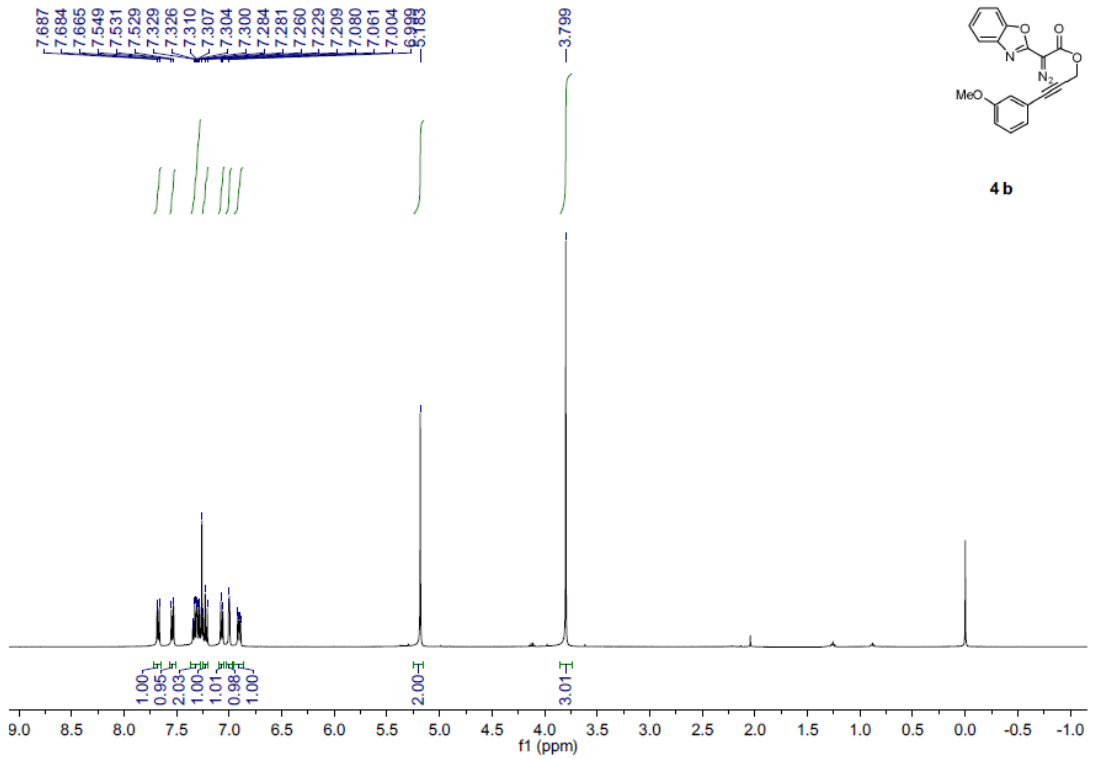
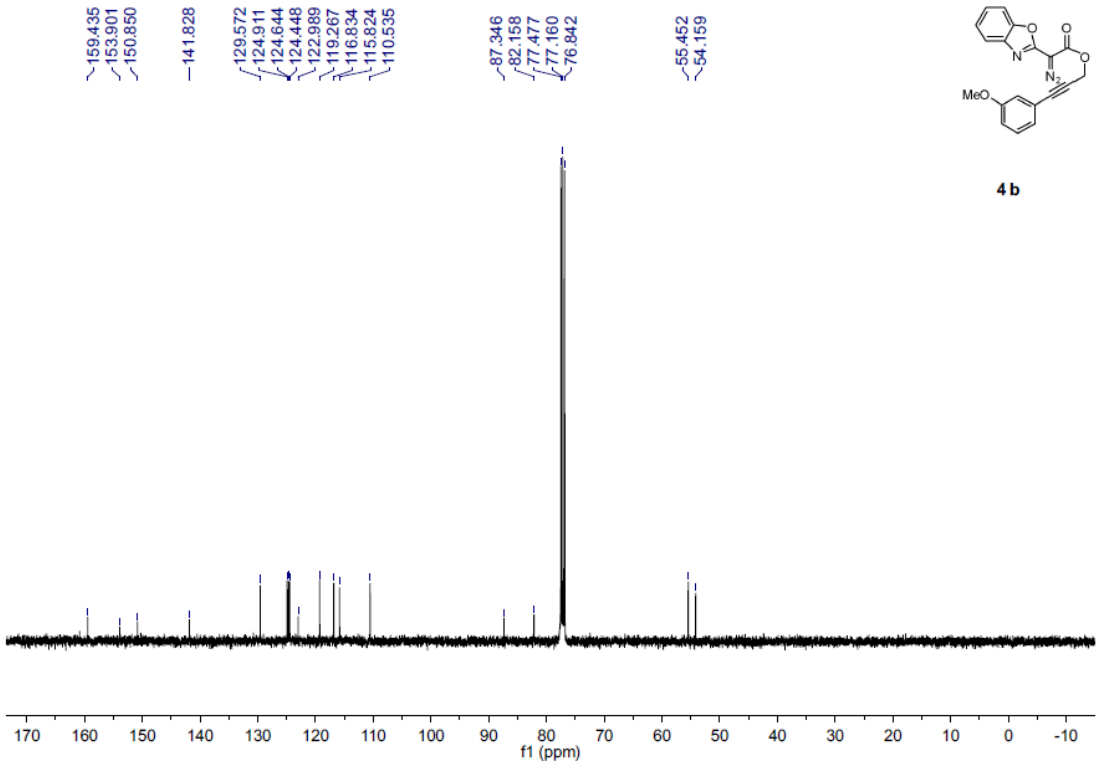
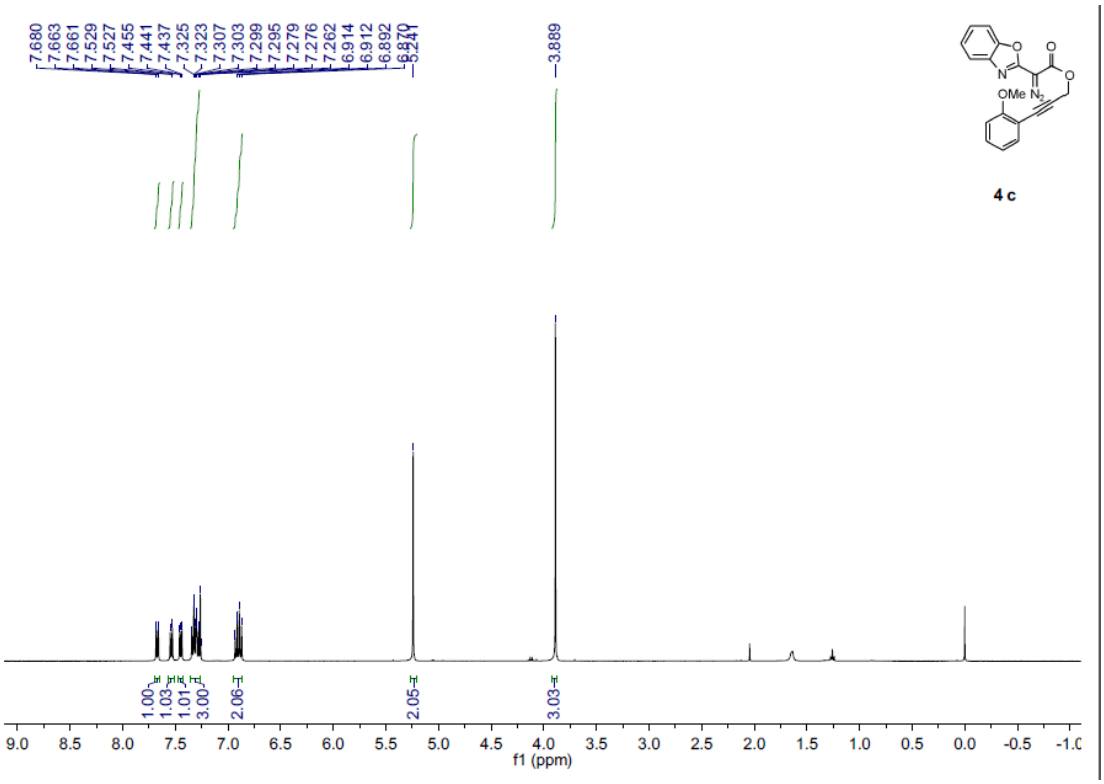
160.247
153.965
150.837
141.816
133.688
124.874
124.396
119.231
114.100
114.044
110.514
87.484
81.070
77.477
77.160
76.842
55.422
54.377
f1 (ppm)
MeO
4 a


7.687
7.684
7.665
7.549
7.531
7.529
7.329
7.326
7.310
7.307
7.304
7.300
7.284
7.281
7.260
7.229
7.209
7.080
7.061
7.004
6.988
5.183
3.799
1.00
0.95
2.03
1.00
1.01
0.98
1.00
2.00
3.01
f1 (ppm)
MeO
4b


159.435
153.901
150.850
141.828
129.572
124.911
124.644
124.448
122.989
119.267
116.834
115.824
110.535
87.346
82.158
77.477
77.160
76.842
55.452
54.159
f1 (ppm)
MeO
4b


7.680
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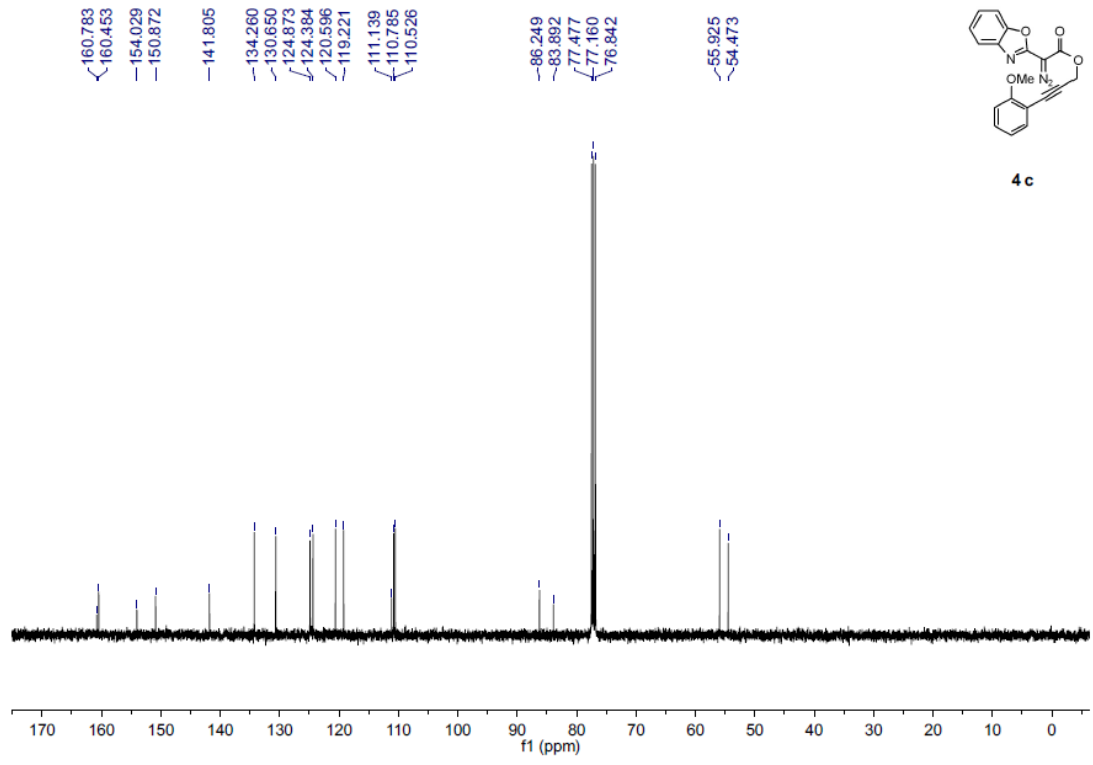
7.661
7.529
7.527
7.455
7.441
7.437
7.325
7.323
7.307
7.303
7.299
7.295
7.279
7.276
7.262
6.914
6.912
6.892
6.870
5.241
3.889
OMe
N2
4c
1.00
1.03
1.01
3.00
2.06
2.05
3.03
f1 (ppm)


160.783
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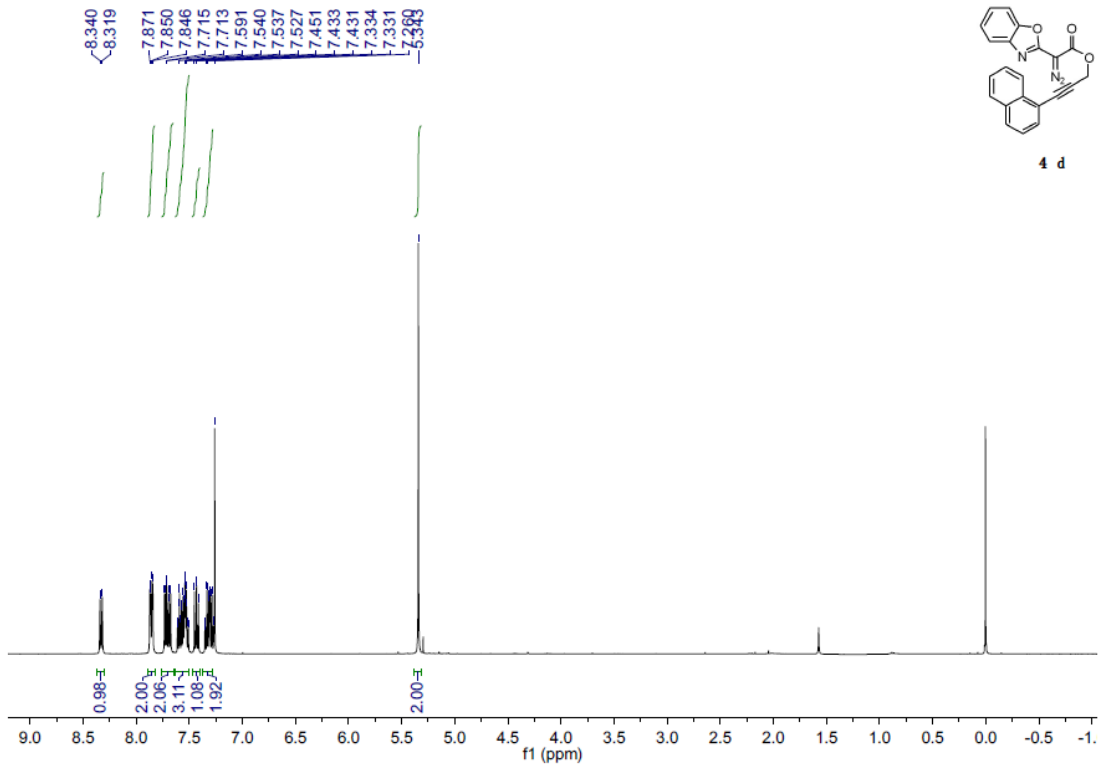
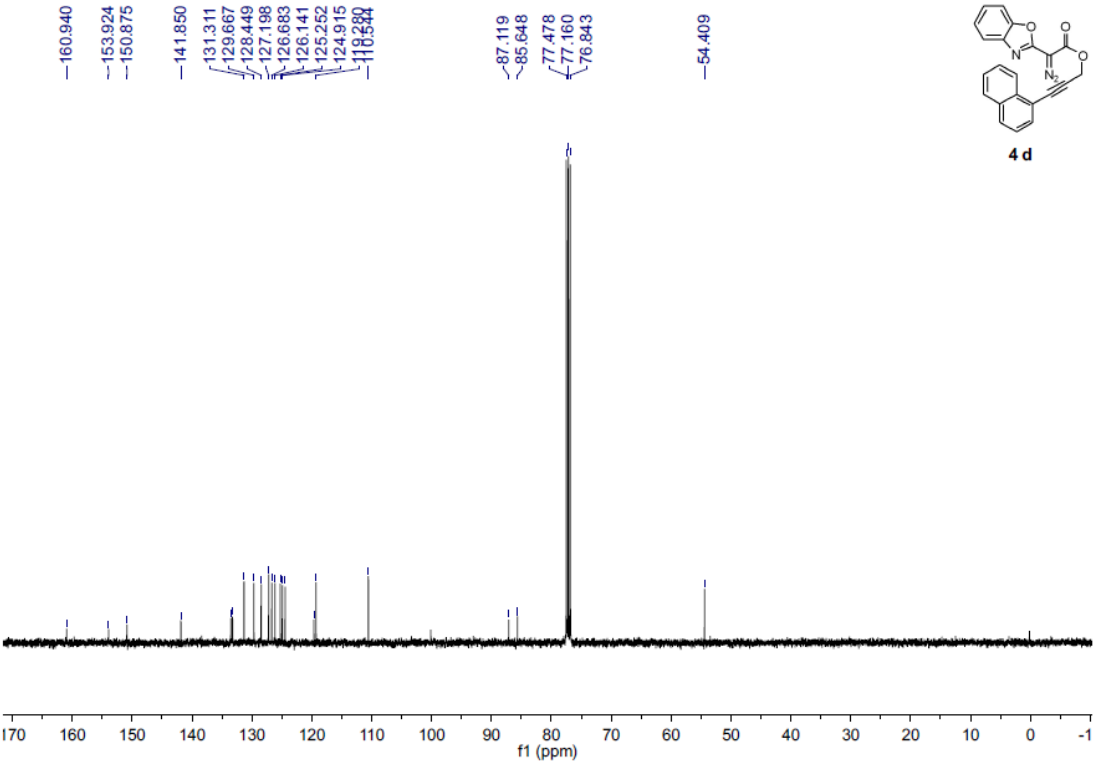
134.260
130.650
124.873
124.384
120.596
119.221
111.139
110.785
110.526
86.249
83.892
77.477
77.160
76.842
55.925
54.473
OMe
N2
4c
f1 (ppm)


8.340
8.319
7.871
7.850
7.846
7.715
7.713
7.591
7.540
7.537
7.527
7.451
7.433
7.431
7.334
7.331
7.260
5.343
0.98
2.00
2.06
3.11
1.08
1.92
2.00
f1 (ppm)
4 d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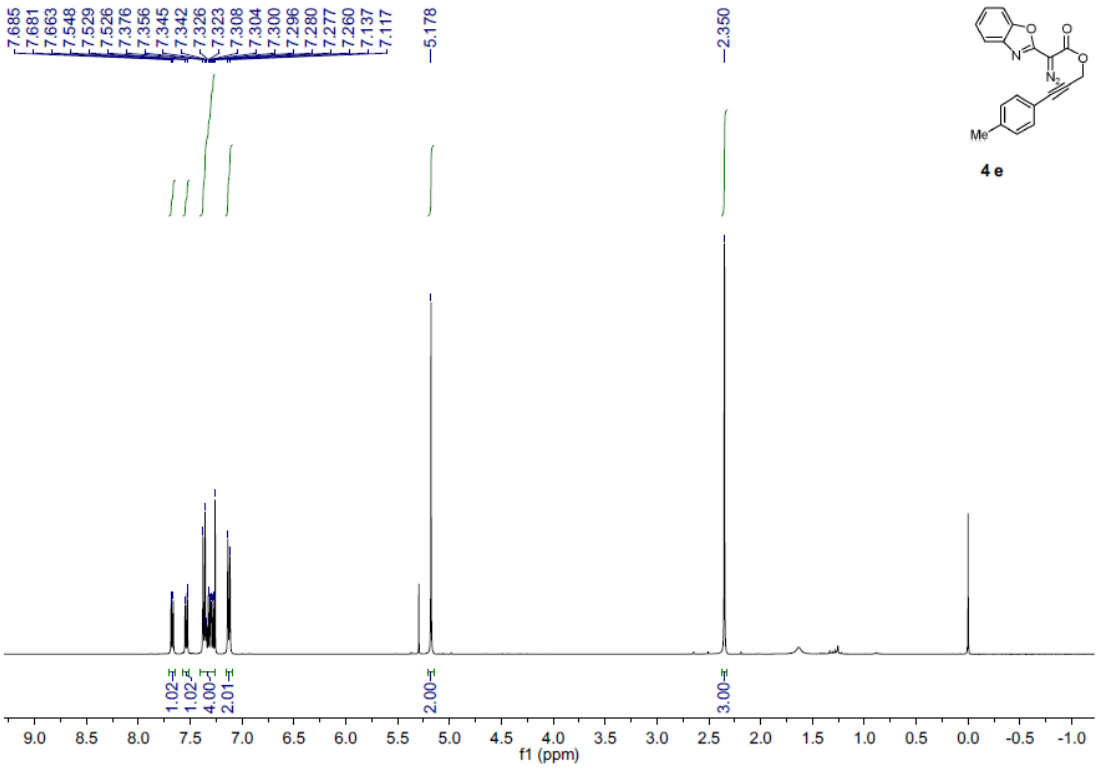
153.924
150.875
141.850
131.311
129.667
128.449
127.198
126.683
126.141
125.252
124.915
87.119
85.648
77.478
77.160
76.843
54.409
f1 (ppm)
4 d


7.685
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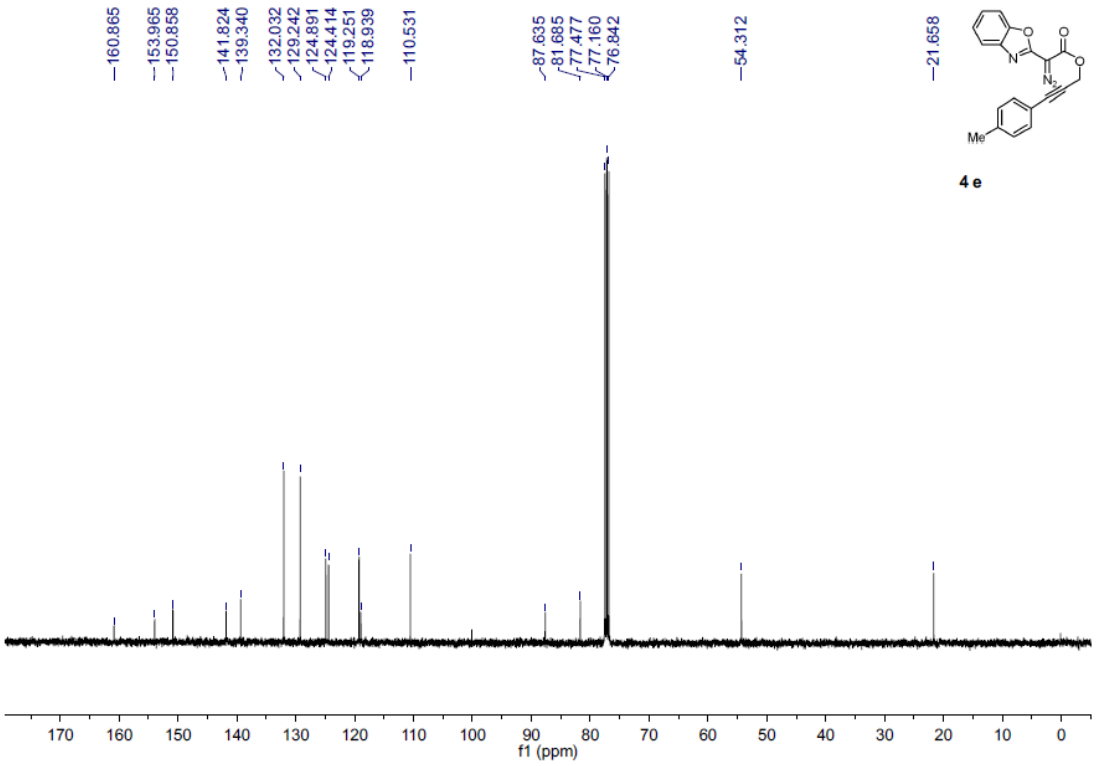
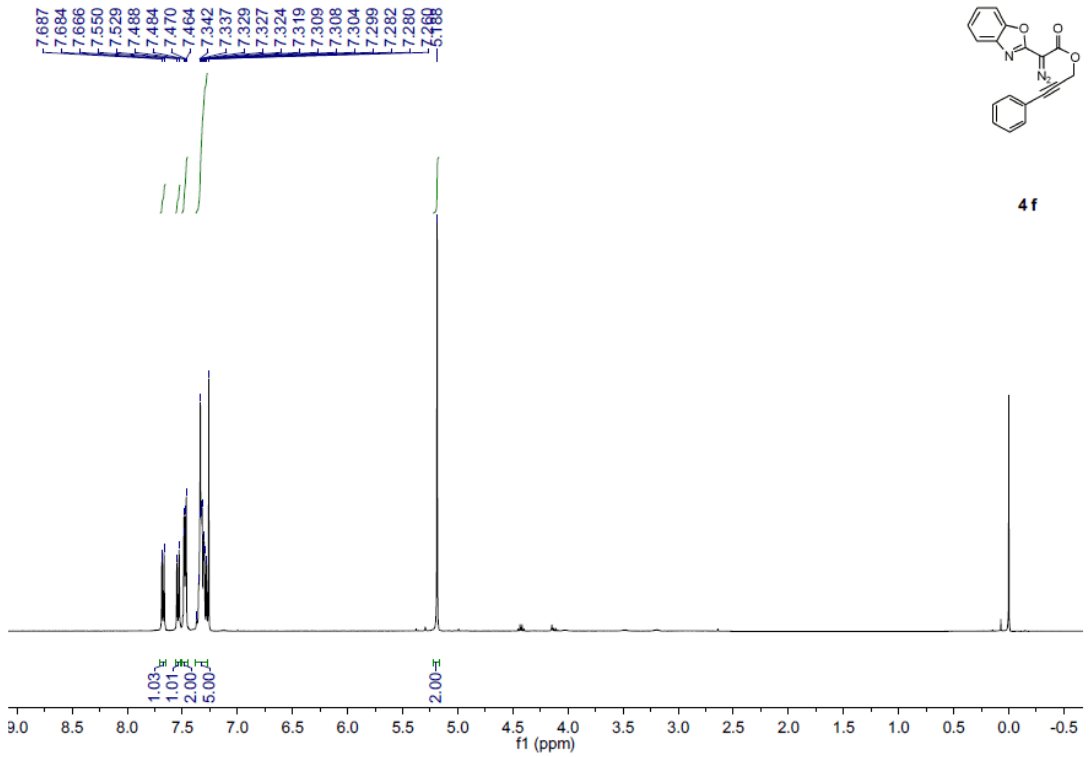
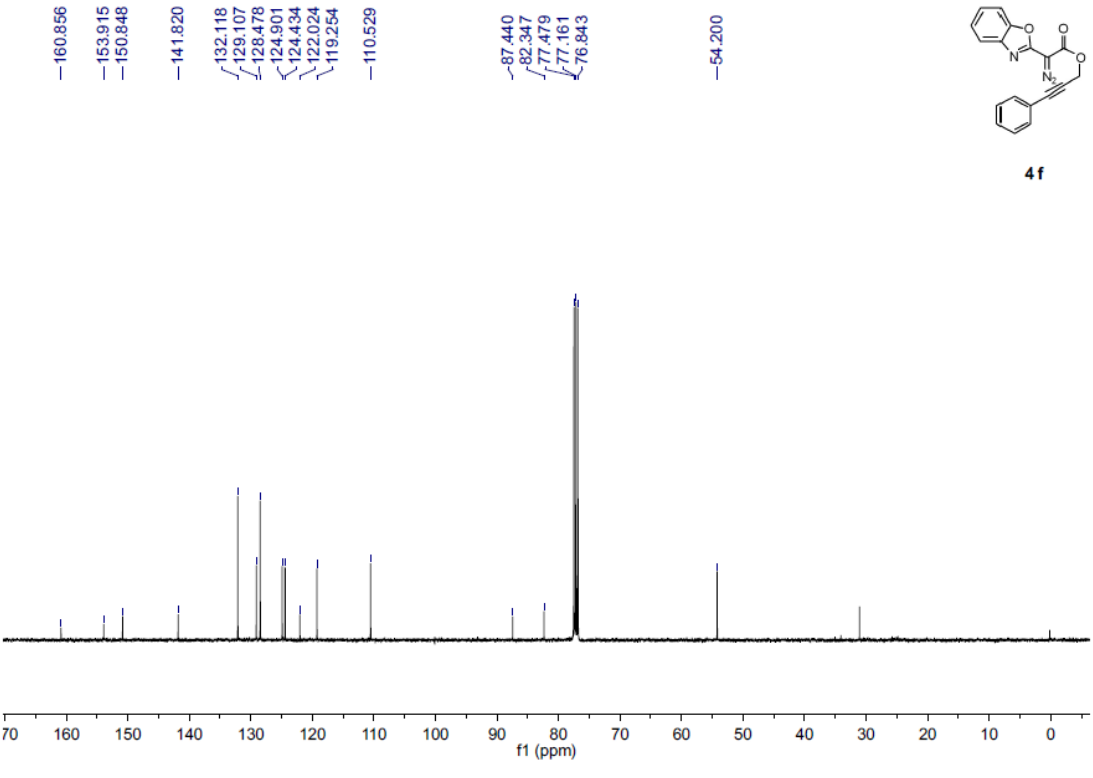
7.526
7.376
7.356
7.345
7.342
7.326
7.323
7.308
7.304
7.300
7.296
7.280
7.277
7.260
7.137
7.117
5.178
2.350
1.02
1.02
4.00
2.01
2.00
3.00
f1 (ppm)
Me
4 e


160.865
153.965
150.858
141.824
139.340
132.032
129.242
124.891
124.414
119.251
118.939
110.531
87.635
81.685
77.477
77.160
76.842
54.312
21.658
f1 (ppm)
Me
4 e


7.687
7.684
7.666
7.550
7.529
7.488
7.484
7.470
7.464
7.342
7.337
7.329
7.327
7.324
7.319
7.309
7.308
7.304
7.299
7.282
7.280
5.188
1.03
1.01
2.00
5.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

4f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141.820
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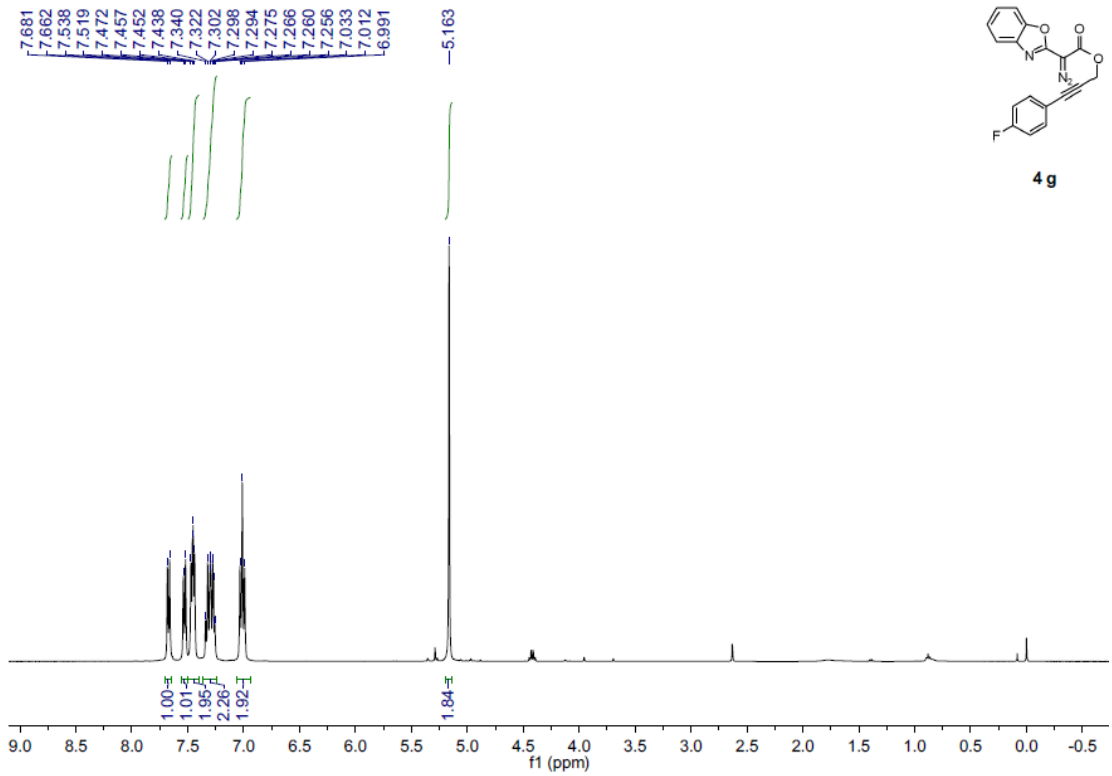
129.107
128.478
124.901
124.434
122.024
119.254
110.529
87.440
82.347
77.479
77.161
76.843
54.200
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

4f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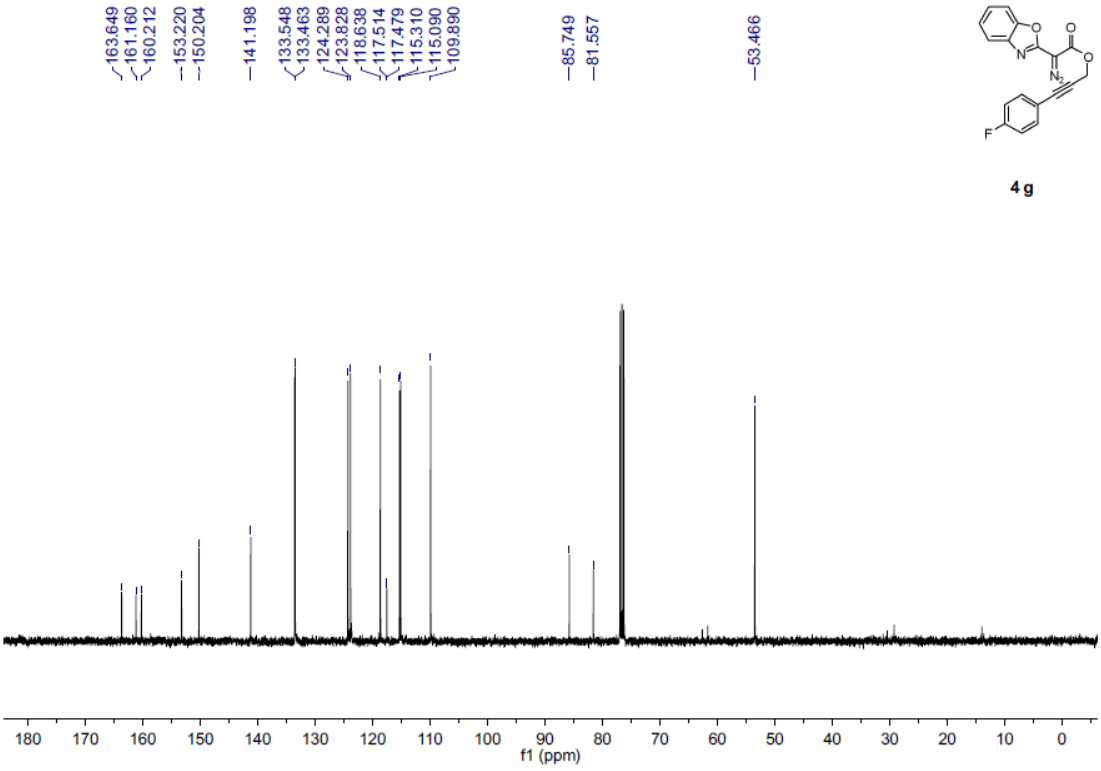
7.662
7.538
7.519
7.472
7.457
7.452
7.438
7.340
7.322
7.302
7.298
7.294
7.275
7.266
7.260
7.256
7.033
7.012
6.991
5.163
1.00
1.01
1.95
2.26
1.92
1.84
f1 (ppm)

4 g


163.649
161.160
160.212
153.220
150.204
141.198
133.548
133.463
124.289
123.828
118.638
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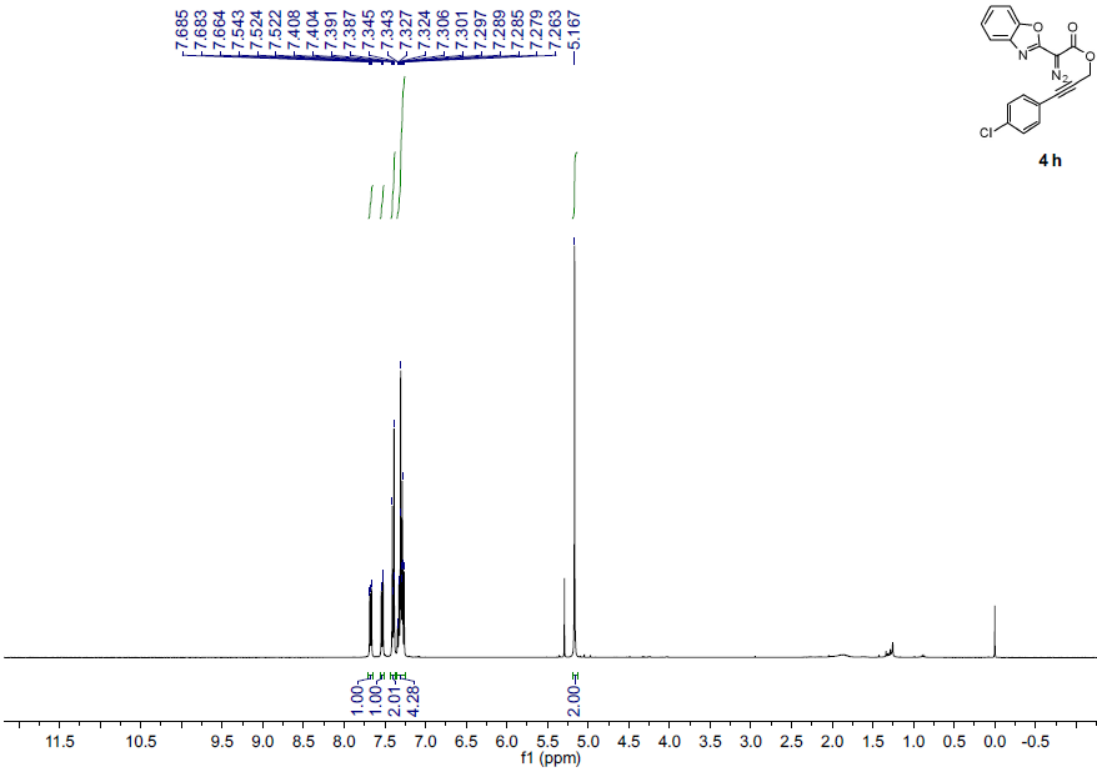
117.479
115.310
115.090
109.890
85.749
81.557
53.466
f1 (ppm)

4 g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7.683
7.664
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7.524
7.522
7.408
7.404
7.391
7.387
7.345
7.343
7.327
7.324
7.306
7.301
7.297
7.289
7.285
7.279
7.263
5.167
1.00
1.00
2.01
4.28
2.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
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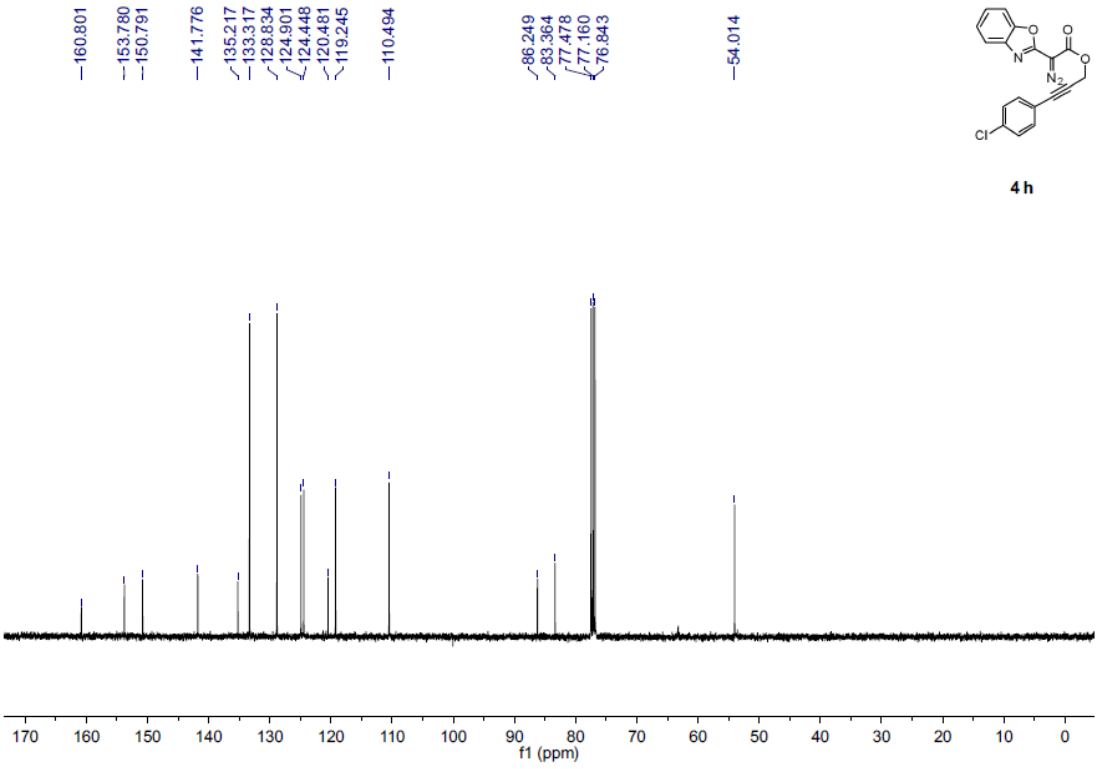
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
4 h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150.791
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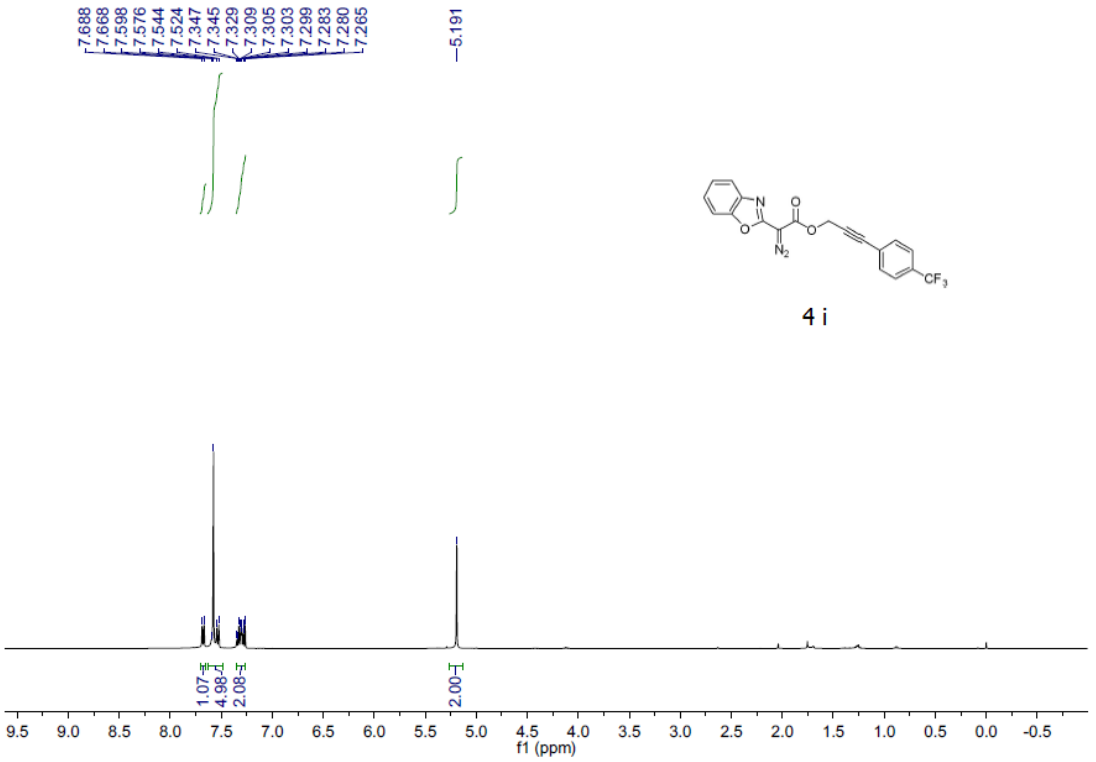
133.317
128.834
124.901
124.448
120.481
119.245
110.494
86.249
83.364
77.478
77.160
76.843
54.014
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
4 h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7.598
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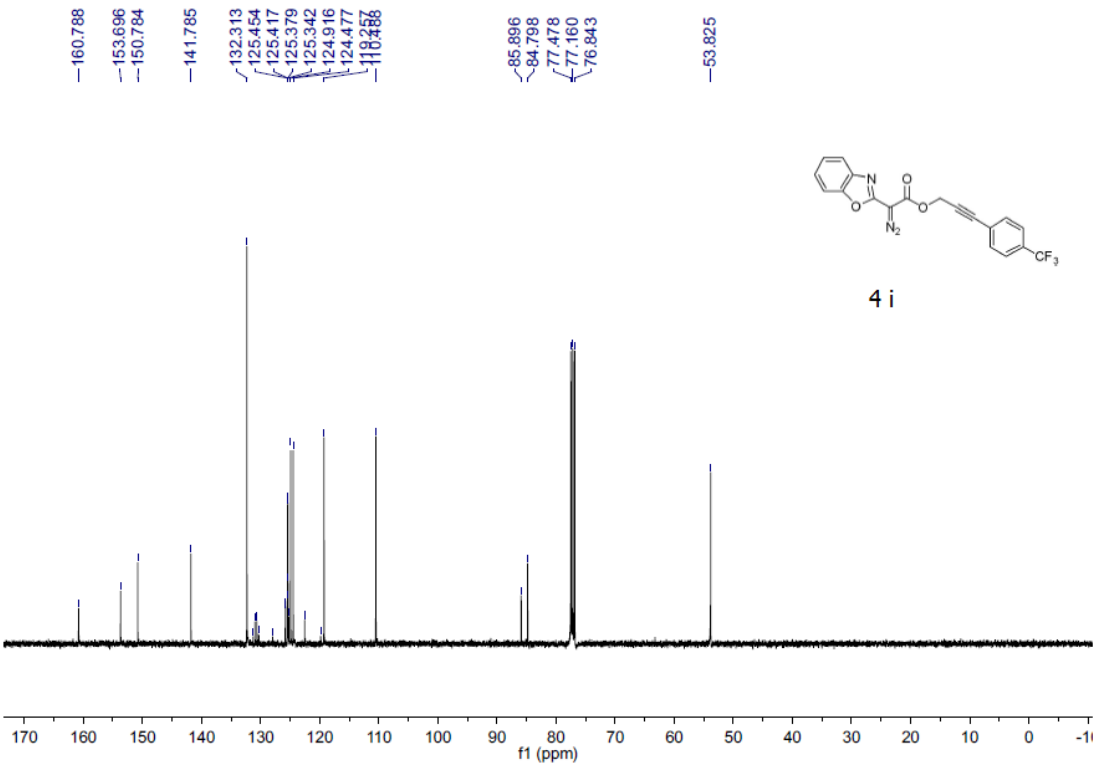
7.544
7.524
7.347
7.345
7.329
7.309
7.305
7.303
7.299
7.283
7.280
7.265
5.191
1.07
4.98
2.08
2.00
f1 (ppm)

4 i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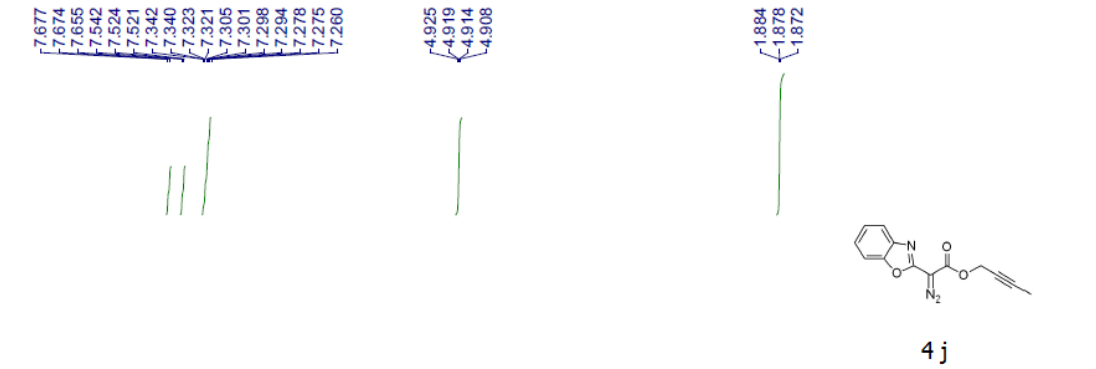
153.696
150.784
141.785
132.313
125.454
125.417
125.379
125.342
124.916
124.477
85.896
84.798
77.478
77.160
76.843
53.825
f1 (ppm)

4 i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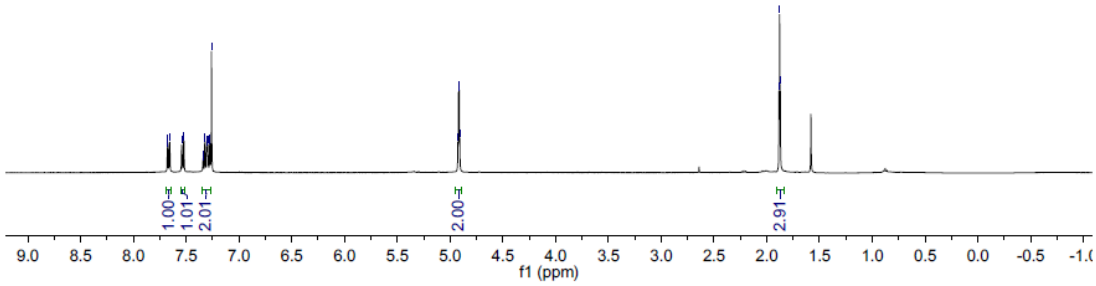
7.524
7.521
7.342
7.340
7.323
7.321
7.305
7.301
7.298
7.294
7.278
7.275
7.260
4.925
4.919
4.914
4.908
1.884
1.878
1.872
N
O
O
O
N2

4j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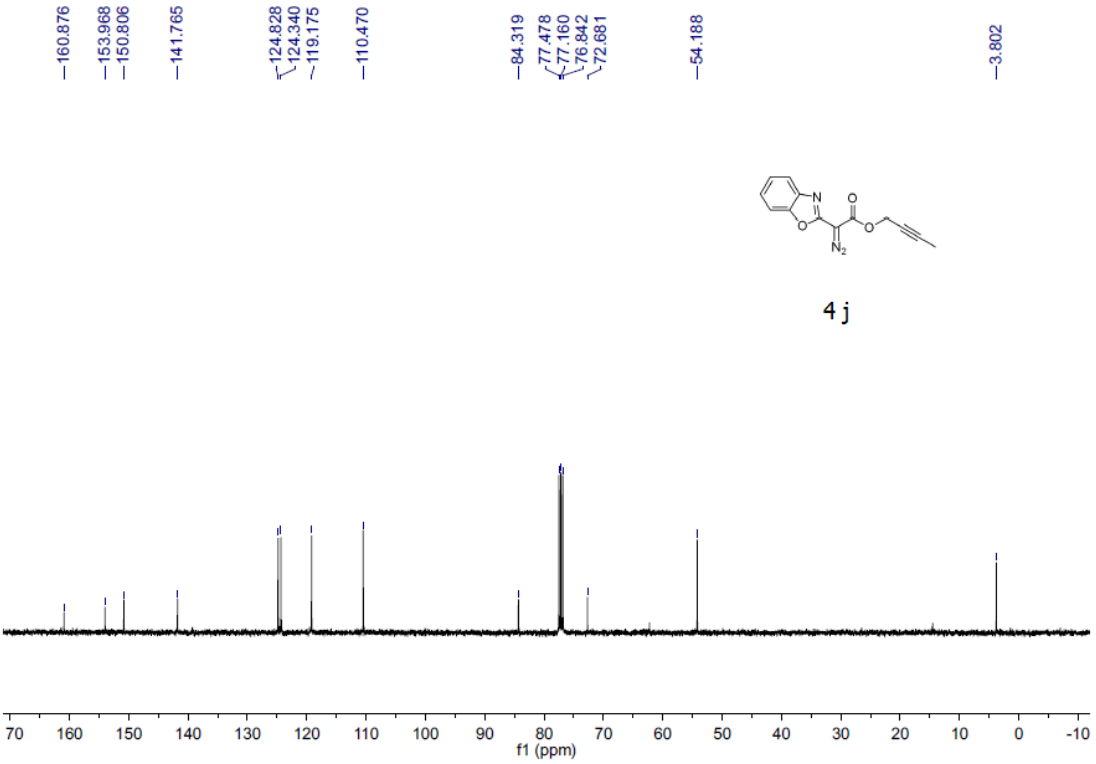
1.01
2.01
2.00
2.91
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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153.968
150.806
141.765
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124.340
119.175
110.470
84.319
77.478
77.160
76.842
72.681
54.188
3.802
N
O
O
O
N2
70
160
150
140
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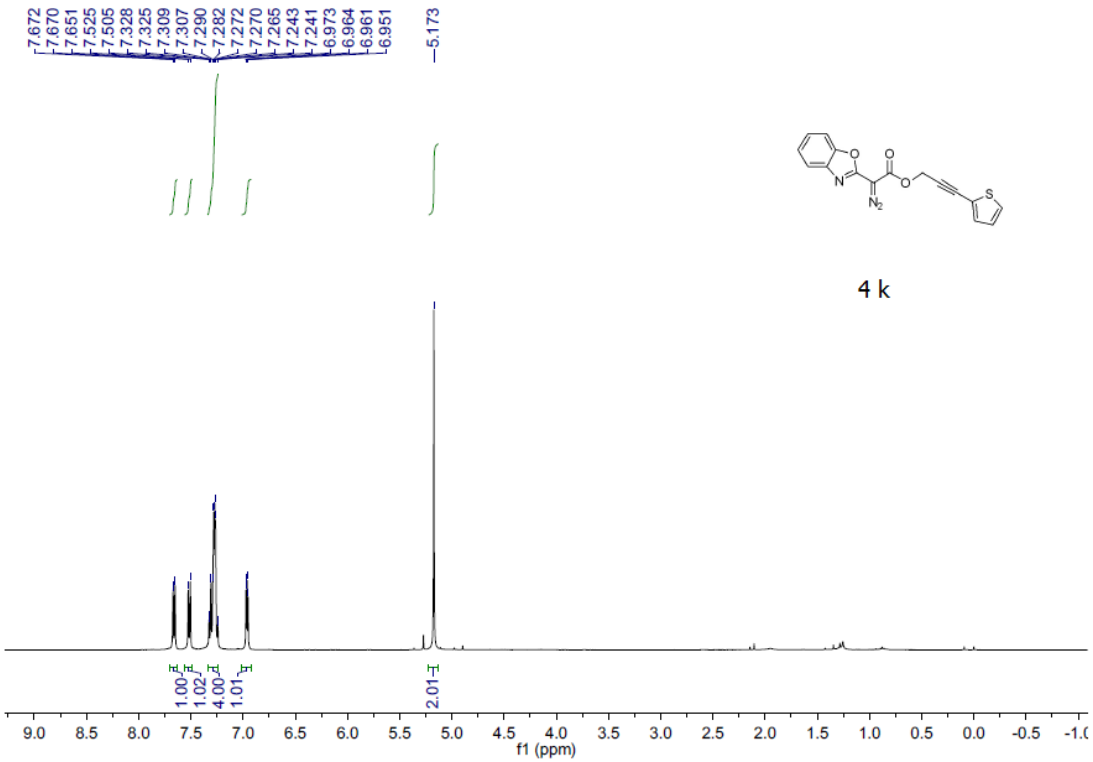
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4j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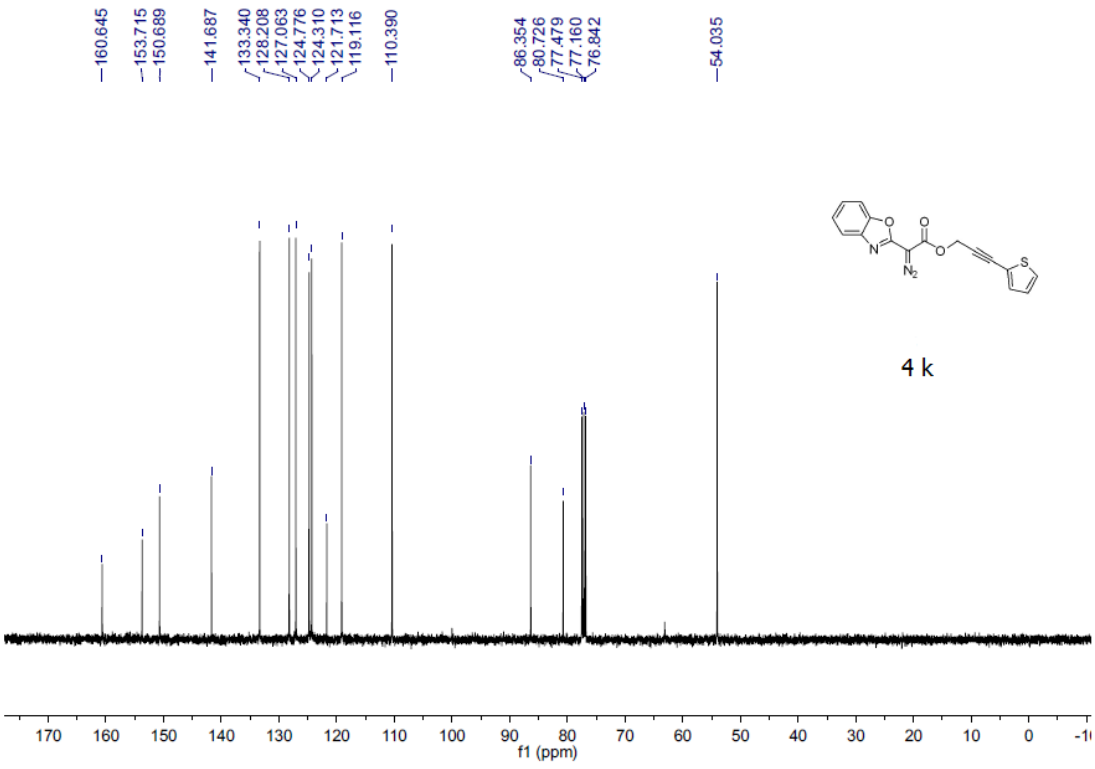
7.670
7.651
7.525
7.505
7.328
7.325
7.309
7.307
7.290
7.282
7.272
7.270
7.265
7.243
7.241
6.973
6.964
6.961
6.951
5.173
4 k
1.00
1.02
4.00
1.01
2.01
f1 (ppm)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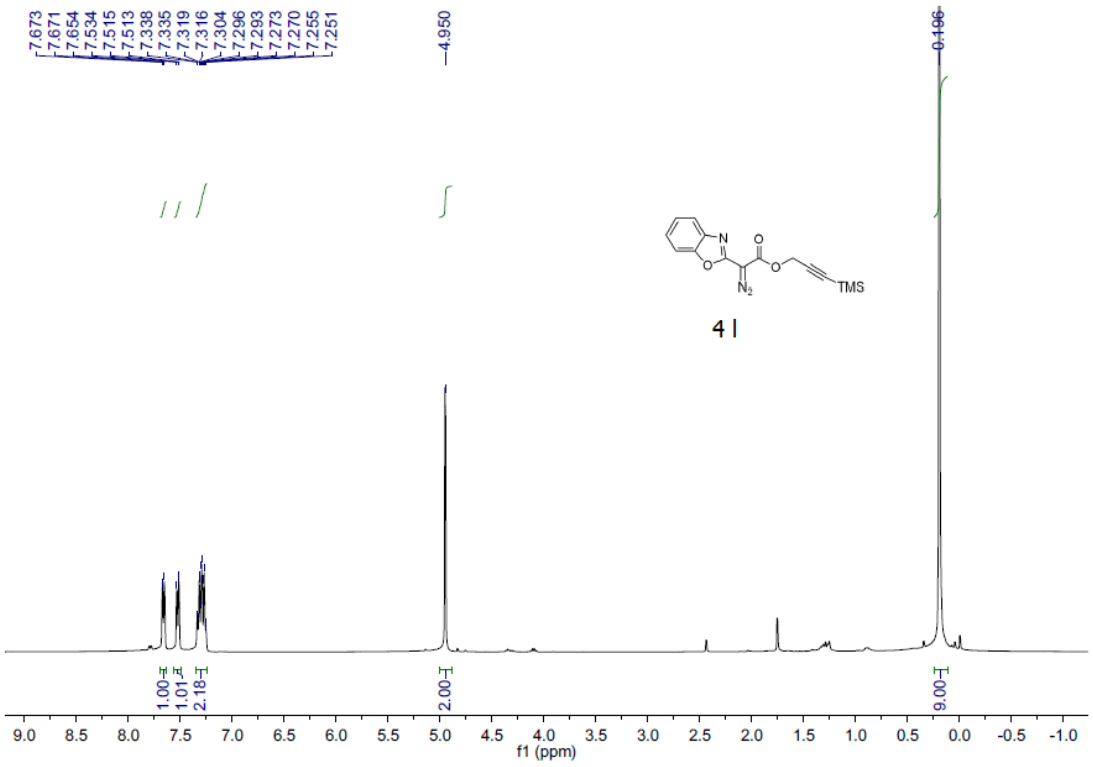
153.715
150.689
141.687
133.340
128.208
127.063
124.776
124.310
121.713
119.116
110.390
86.354
80.726
77.479
77.160
76.842
54.035
4 k
f1 (ppm)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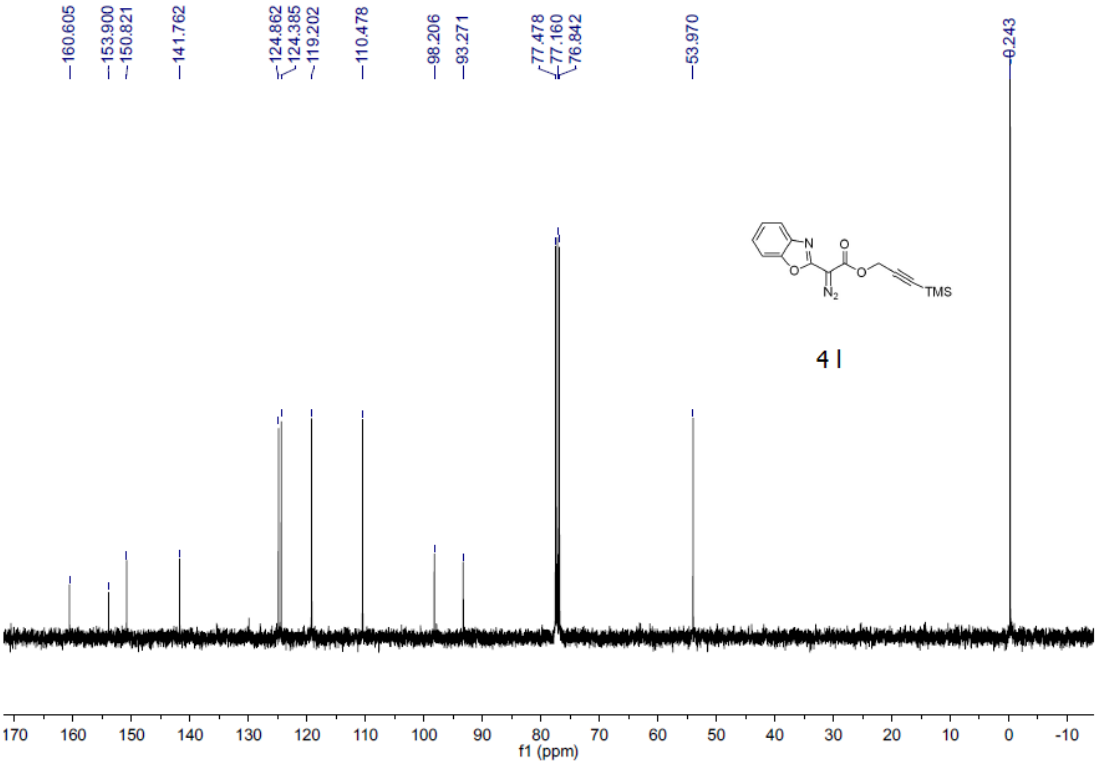
7.671
7.654
7.534
7.515
7.513
7.338
7.335
7.319
7.316
7.304
7.296
7.293
7.273
7.270
7.255
7.251
4.950
0.196
TMS
4 l
1.00
1.01
2.18
2.00
9.00
f1 (ppm)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153.900
150.821
141.762
124.862
124.385
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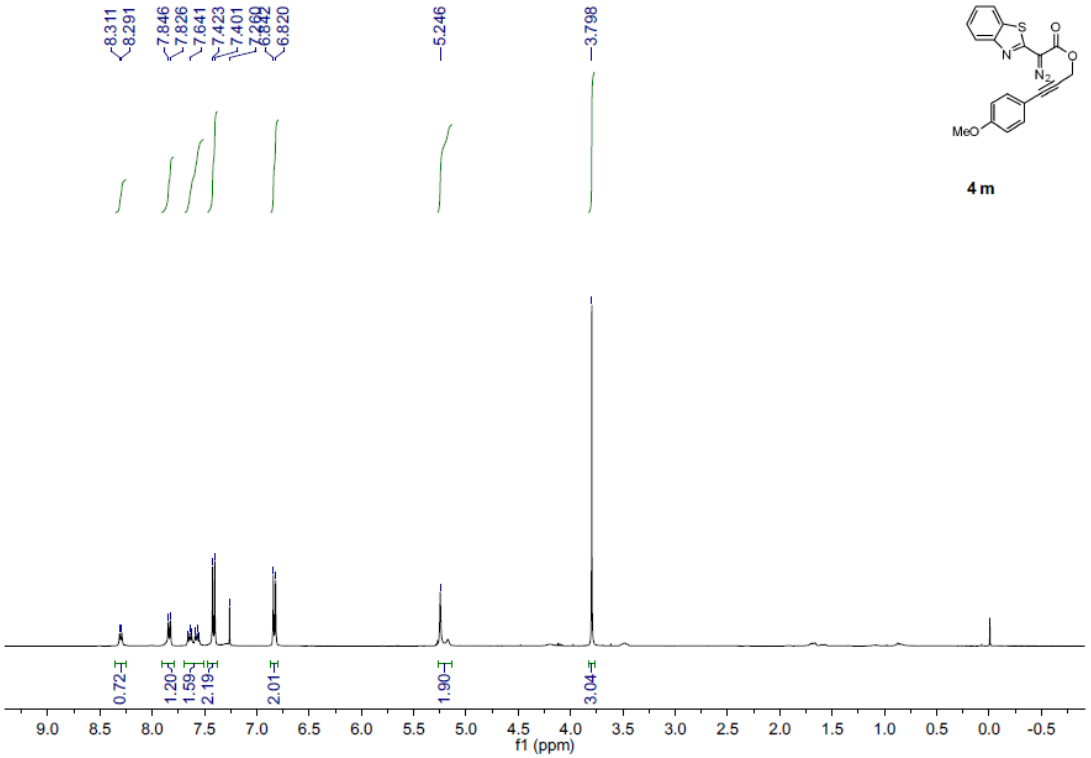
110.478
98.206
93.271
77.478
77.160
76.842
53.970
9.243
TMS
4 l
f1 (ppm)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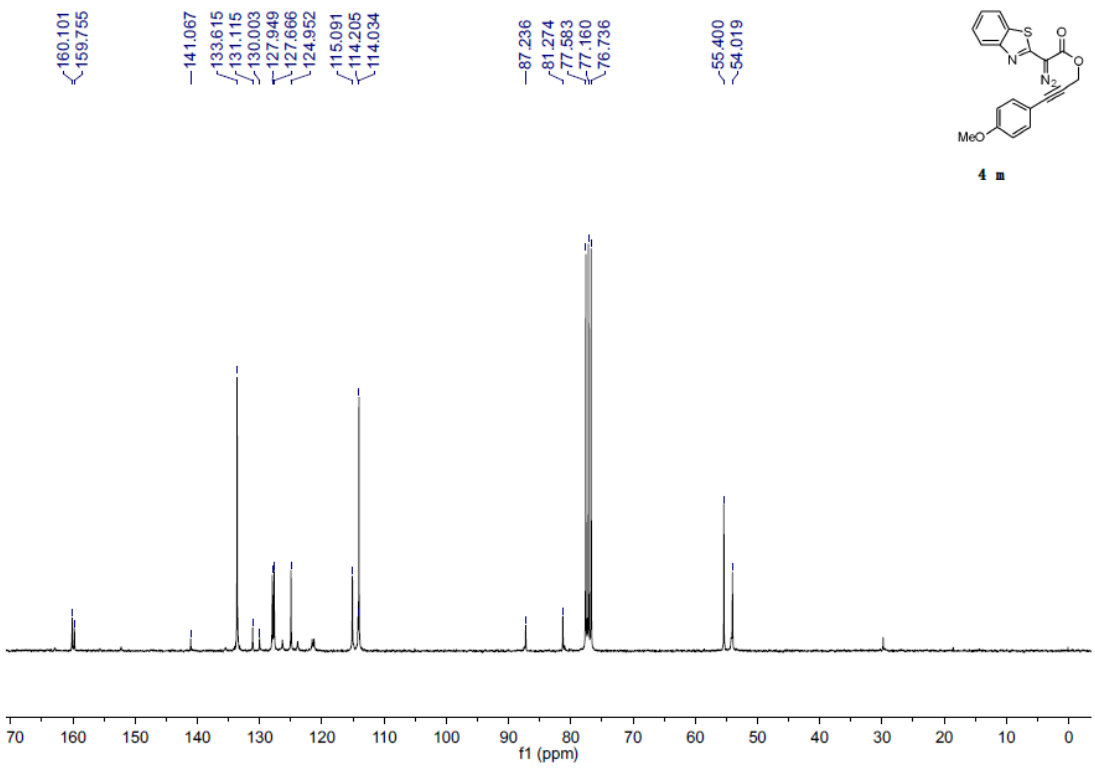
8.291
7.846
7.826
7.641
7.423
7.401
7.260
6.842
6.820
5.246
3.798
MeO
4 m
0.72
1.20
1.59
2.19
2.01
1.90
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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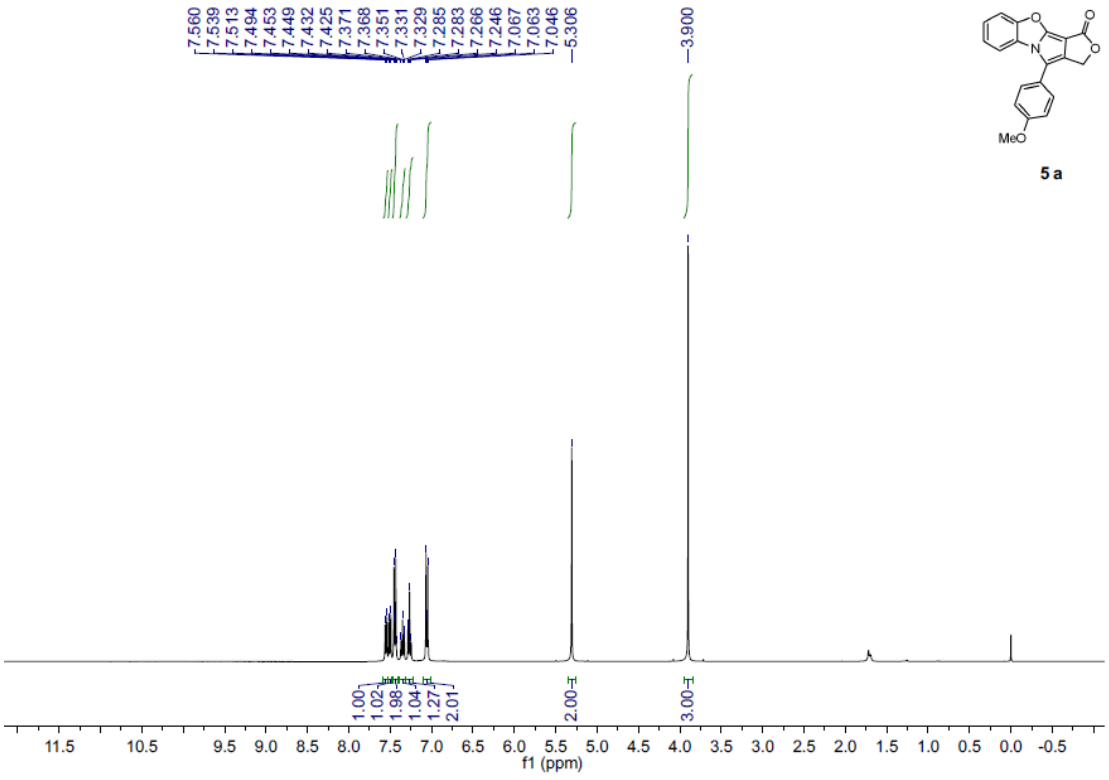
130.003
127.949
127.666
124.952
115.091
114.205
114.034
87.236
81.274
77.583
77.160
76.736
55.400
54.019
MeO
4 m
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.494
7.453
7.449
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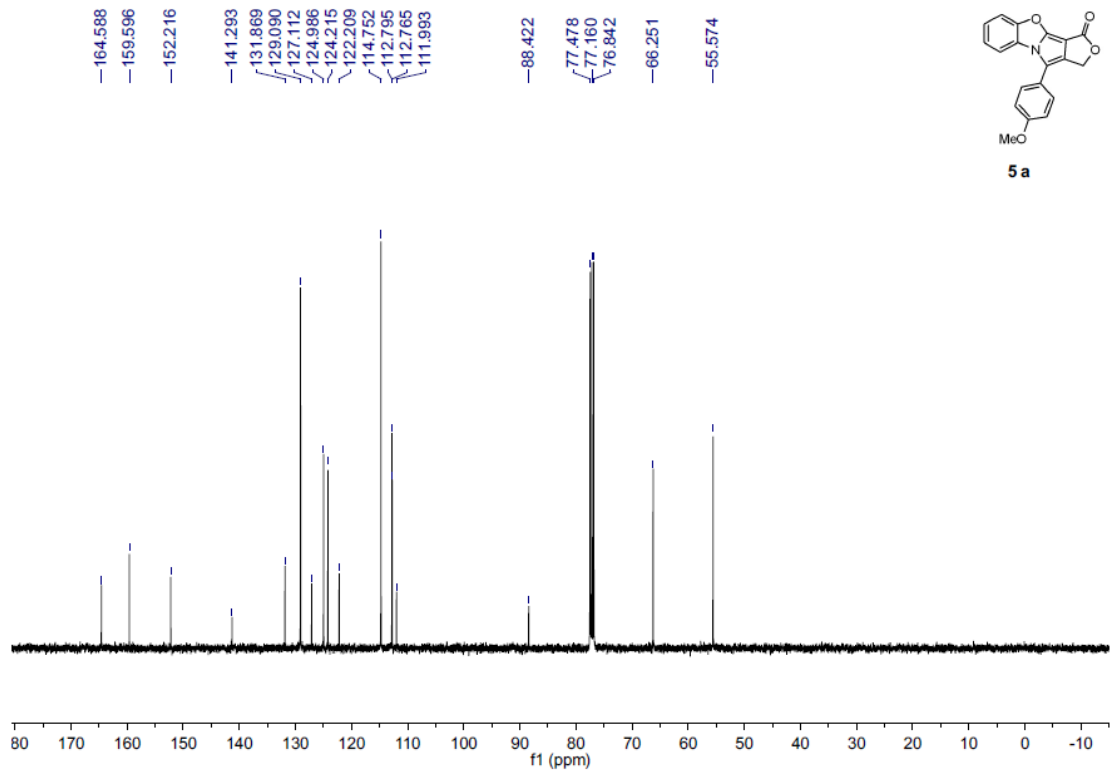
7.425
7.371
7.368
7.351
7.331
7.329
7.285
7.283
7.266
7.246
7.067
7.063
7.046
5.306
3.900
MeO
5a
1.00
1.02
1.98
1.04
1.27
2.01
2.00
3.00
f1 (ppm)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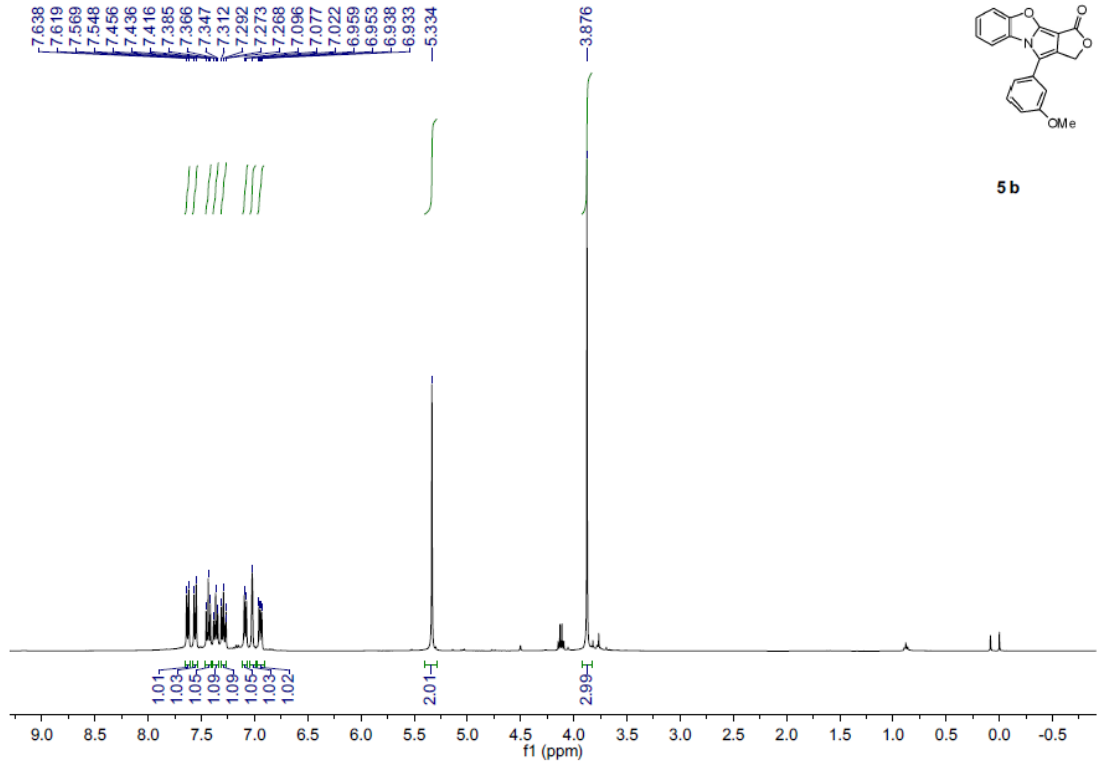
152.216
141.293
131.869
129.090
127.112
124.986
124.215
122.209
114.752
112.795
112.765
111.993
88.422
77.478
77.160
76.842
66.251
55.574
MeO
5a
f1 (ppm)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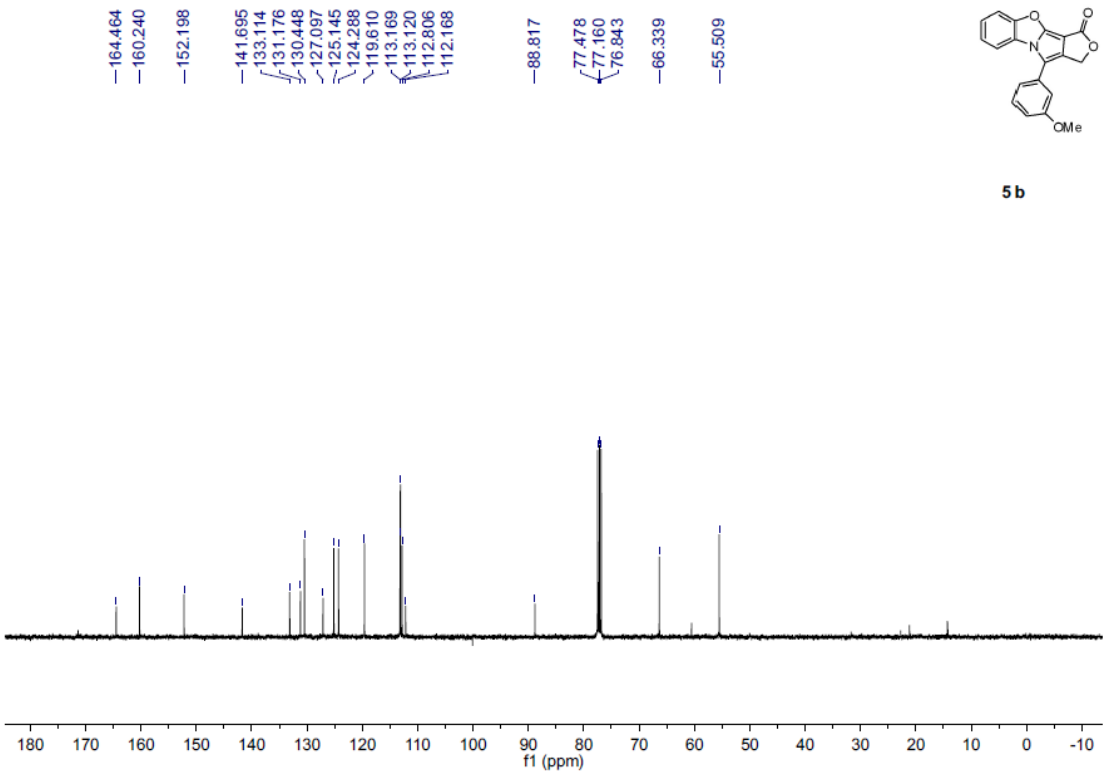
7.569
7.548
7.456
7.436
7.416
7.385
7.366
7.347
7.312
7.292
7.273
7.268
7.096
7.077
7.022
6.959
6.953
6.938
6.933
5.334
3.876
1.01
1.03
1.05
1.09
1.09
1.05
1.03
1.02
2.01
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)
OMe
5b


164.464
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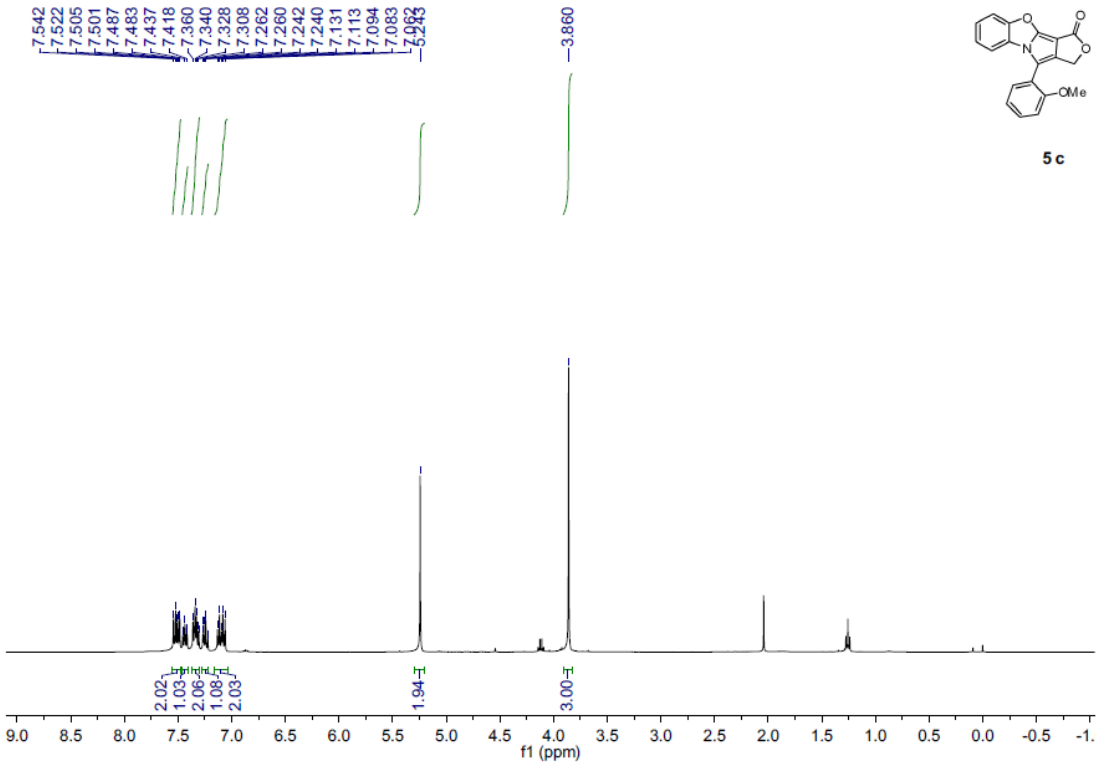
152.198
141.695
133.114
131.176
130.448
127.097
125.145
124.288
119.610
113.169
113.120
112.806
112.168
88.817
77.478
77.160
76.843
66.339
55.509
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
OMe
5b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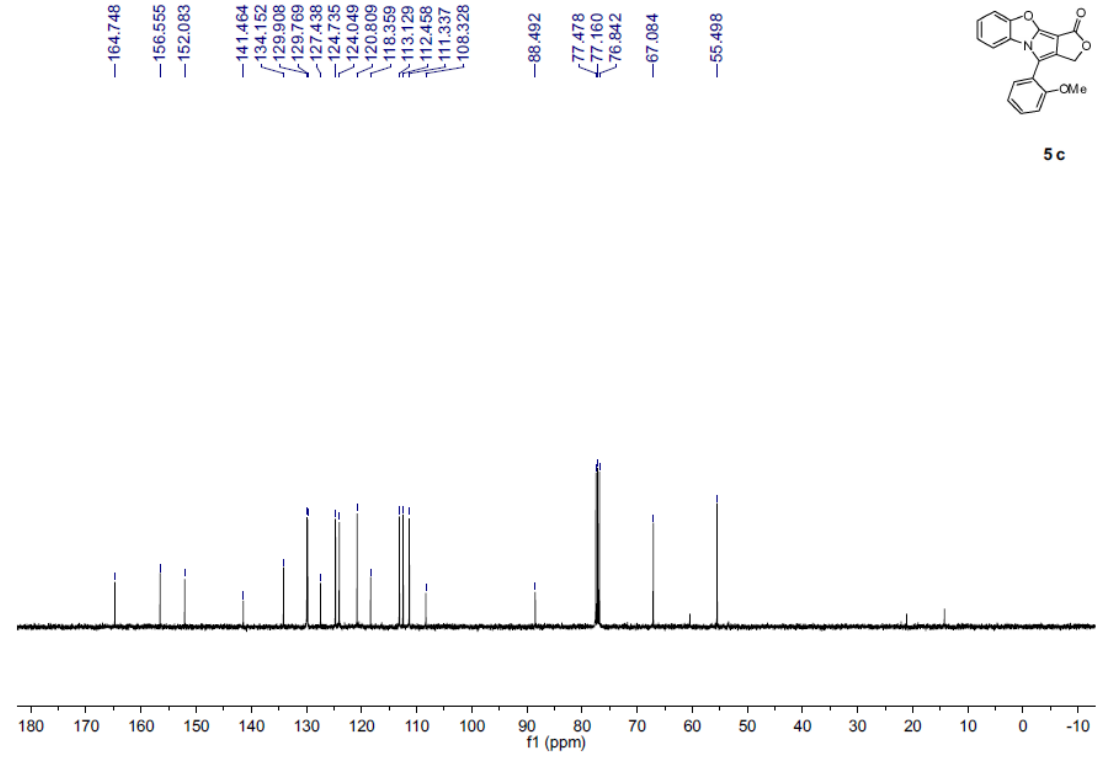
7.501
7.487
7.483
7.437
7.418
7.360
7.340
7.328
7.308
7.262
7.260
7.242
7.240
7.131
7.113
7.094
7.083
5.243
3.860
OMe
5c
2.02
1.03
2.06
1.08
2.03
1.94
3.00
f1 (ppm)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129.908
129.769
127.438
124.735
124.049
120.809
118.359
113.129
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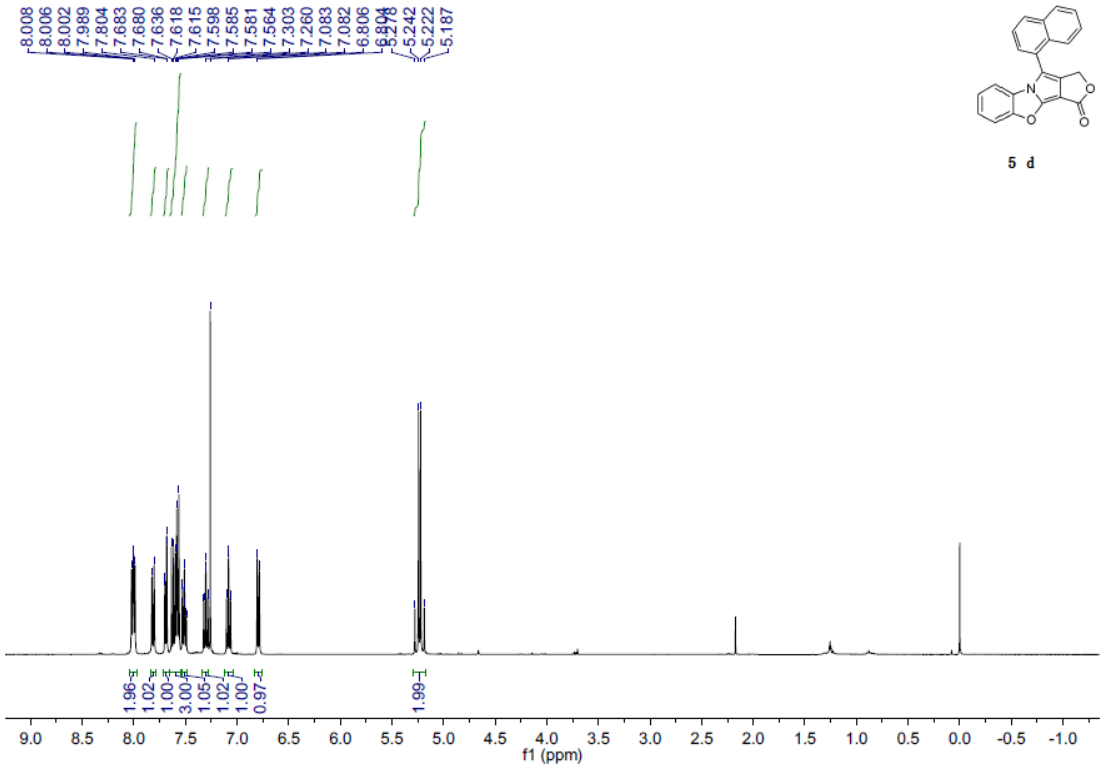
108.328
88.492
77.478
77.160
76.842
67.084
55.498
OMe
5c
f1 (ppm)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7.804
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7.636
7.618
7.615
7.598
7.585
7.581
7.564
7.303
7.260
7.083
7.082
6.806
5.242
5.222
5.187
1.96
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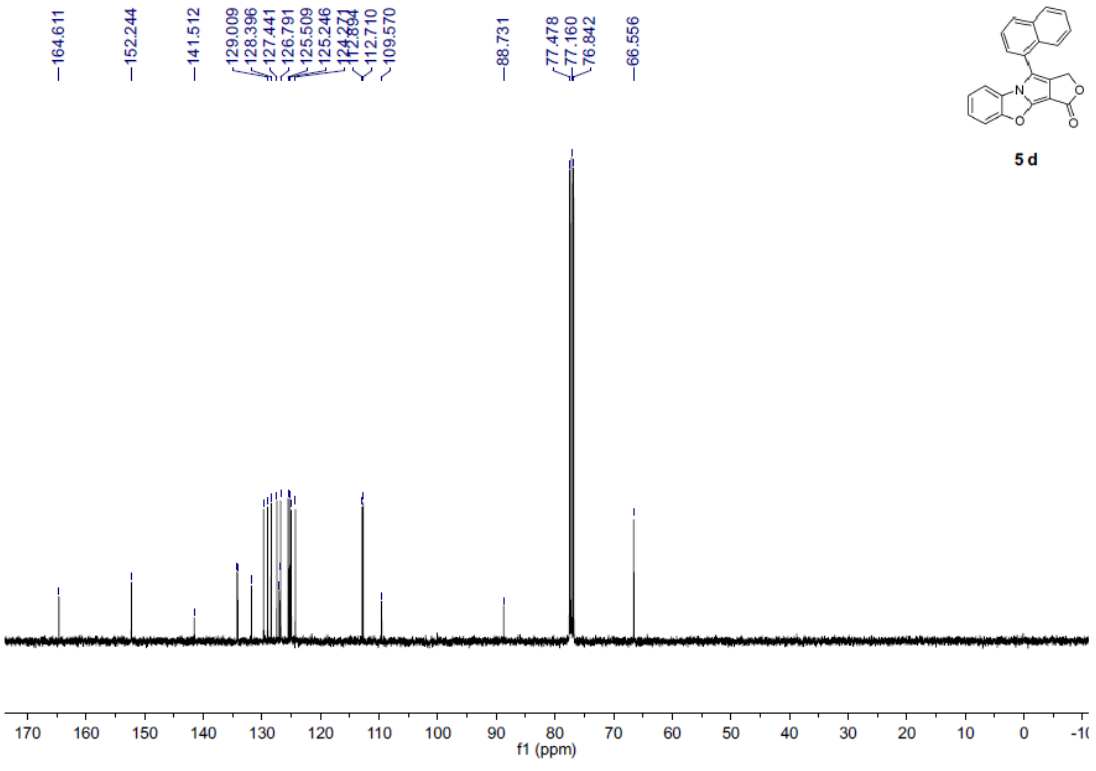
1.00
3.00
1.05
1.02
1.00
0.97
1.99
f1 (ppm)

5 d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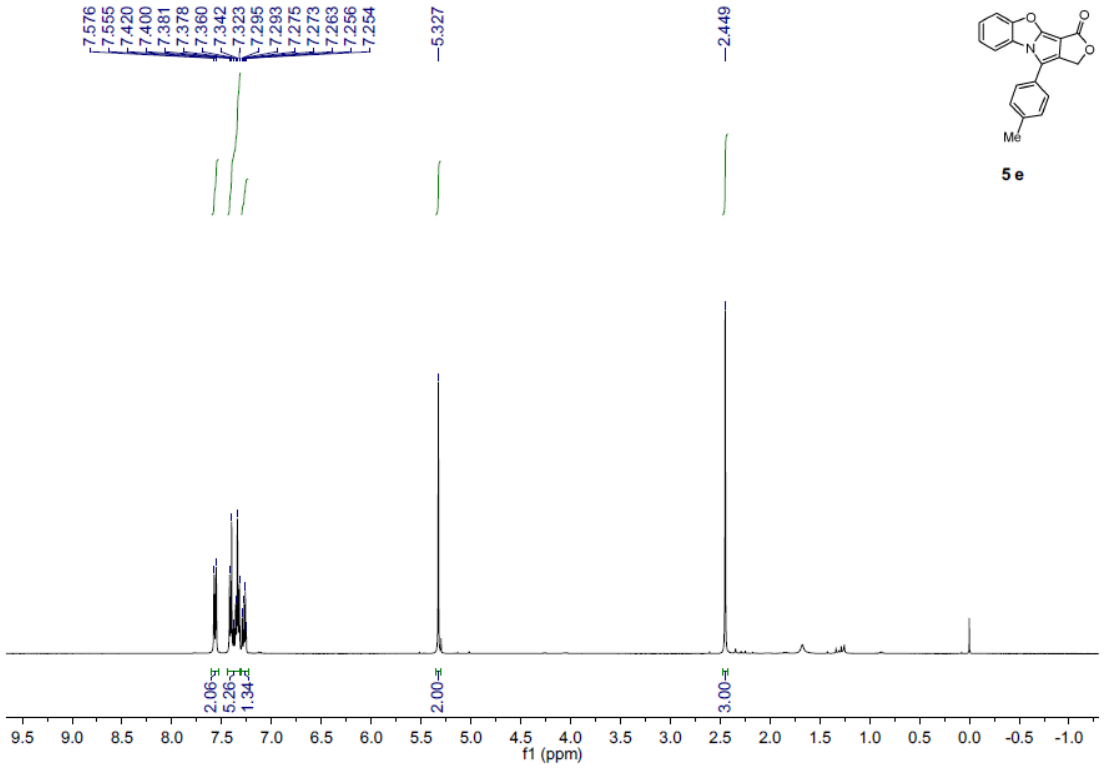
129.009
128.396
127.441
126.791
125.509
125.246
112.710
109.570
88.731
77.478
77.160
76.842
66.556
f1 (ppm)

5 d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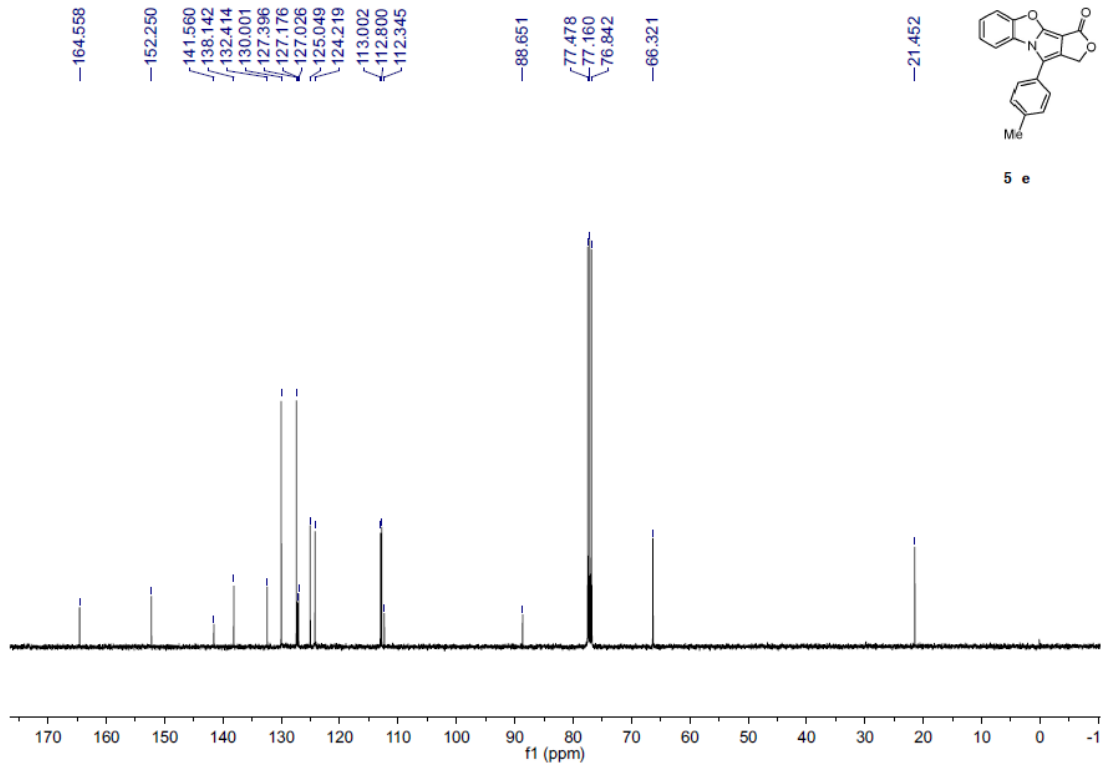
7.400
7.381
7.378
7.360
7.342
7.323
7.295
7.293
7.275
7.273
7.263
7.256
7.254
5.327
2.449
Me
5 e
2.06
5.26
1.34
2.00
3.00
f1 (ppm)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130.001
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127.176
127.026
125.049
124.219
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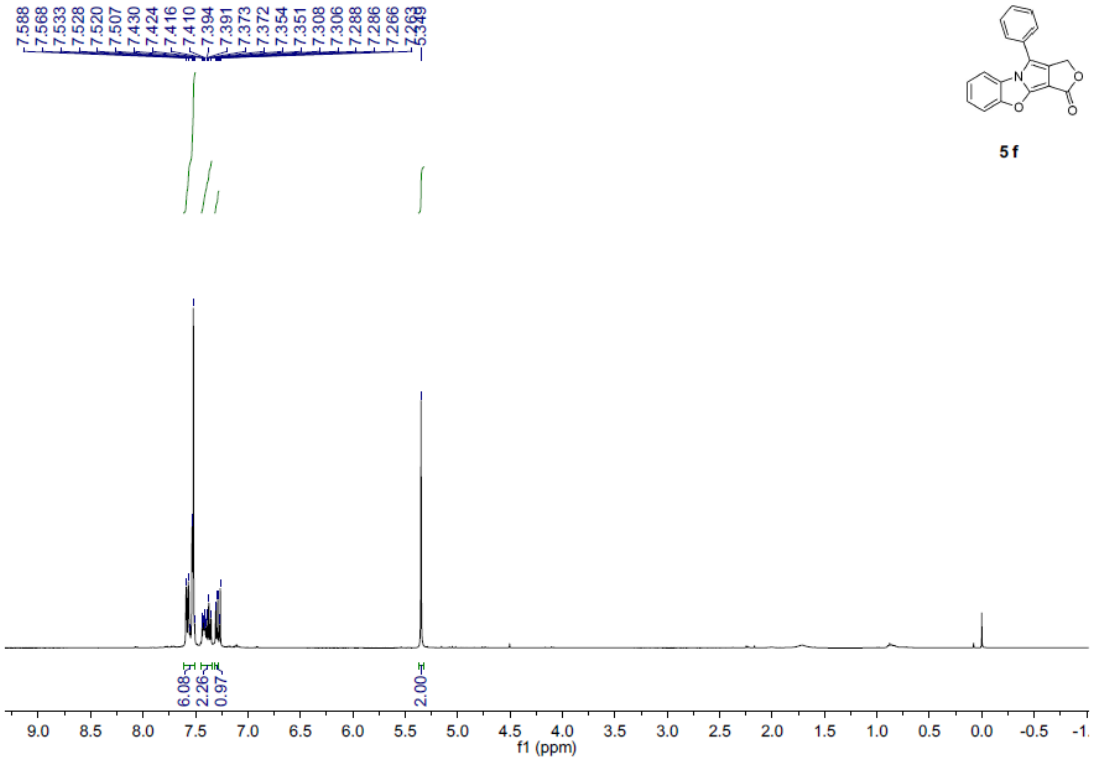
112.345
88.651
77.478
77.160
76.842
66.321
21.452
Me
5 e
f1 (ppm)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7.528
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7.507
7.430
7.424
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7.410
7.394
7.391
7.373
7.372
7.354
7.351
7.308
7.306
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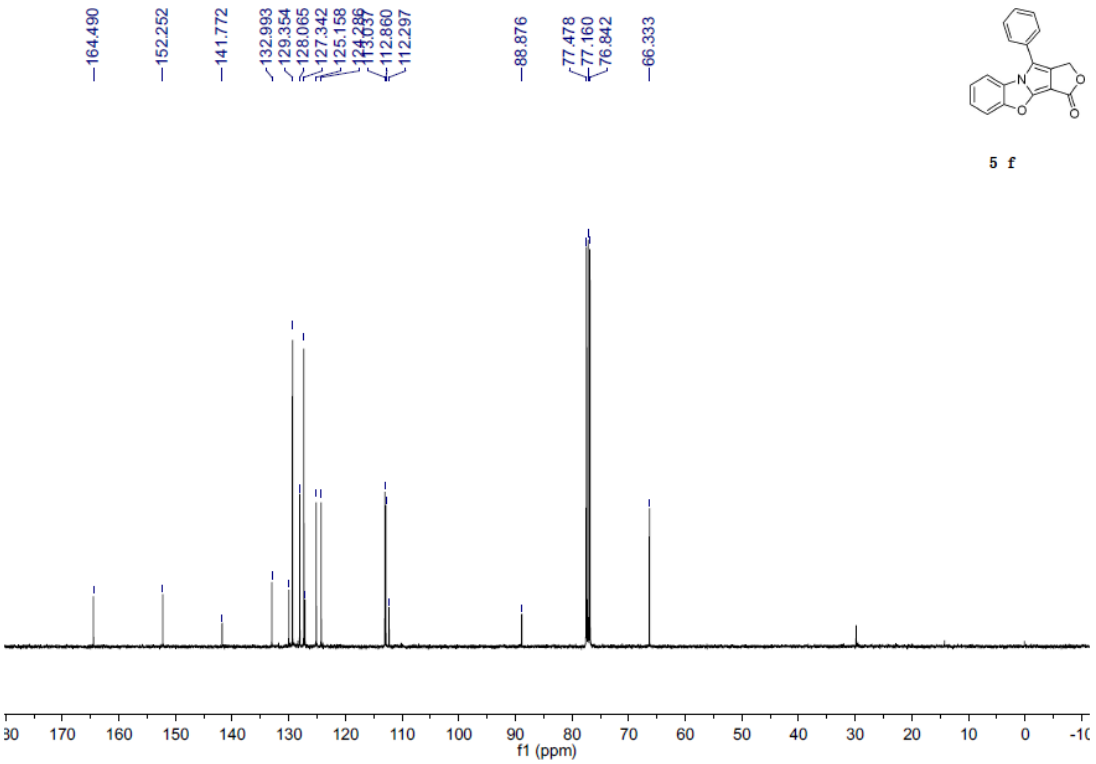
7.286
7.266
5.349
6.08
2.26
0.97
2.00
f1 (ppm)
5f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132.993
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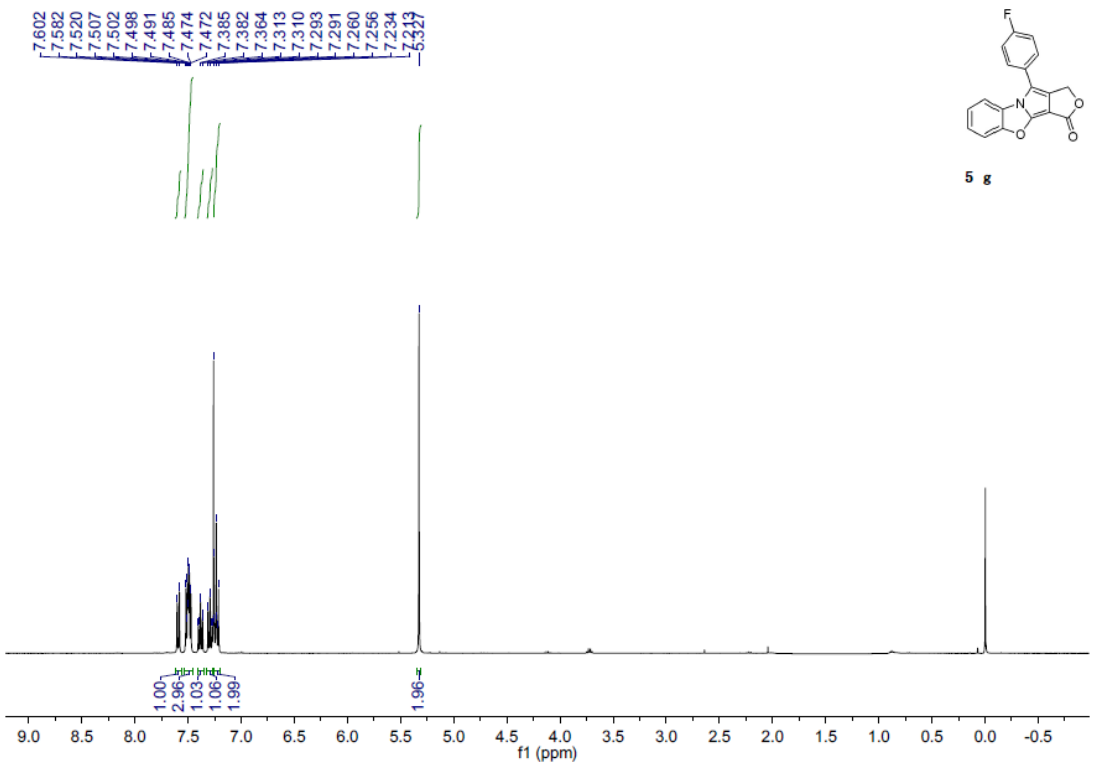
88.876
77.478
77.160
76.842
66.333
f1 (ppm)
5 f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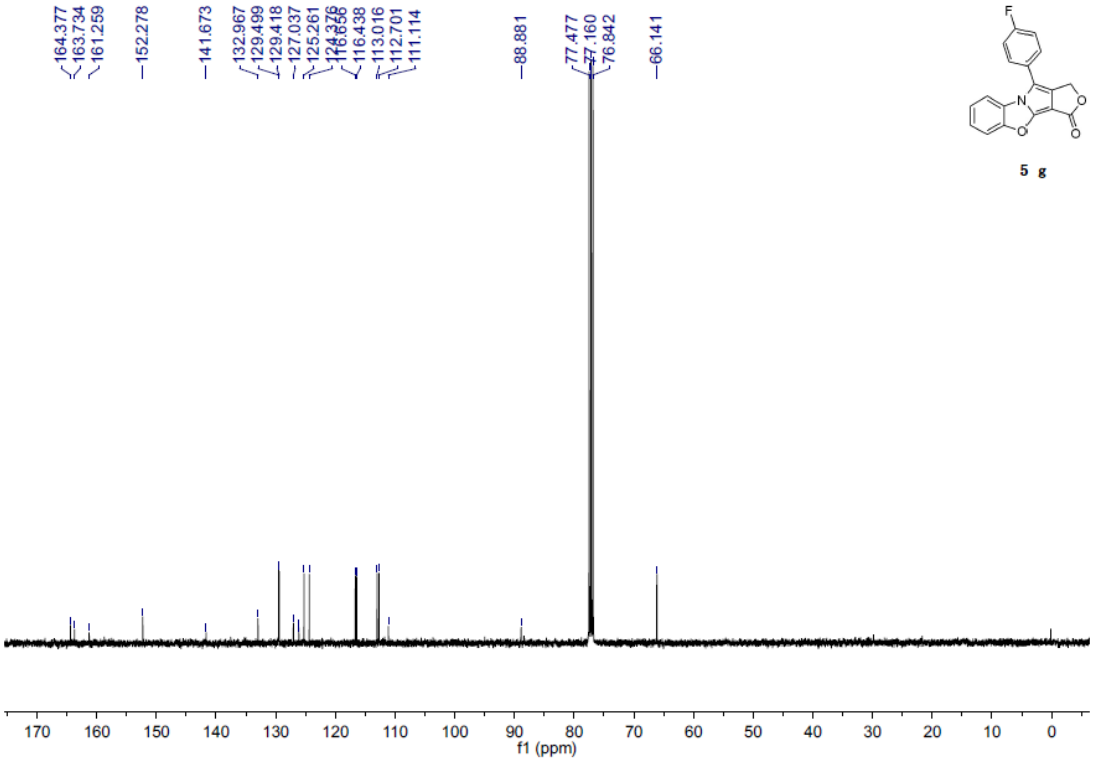
7.485
7.474
7.472
7.385
7.382
7.364
7.313
7.310
7.293
7.291
7.260
7.256
7.234
7.213
5.327
F
5 g
1.00
2.96
1.03
1.06
1.99
1.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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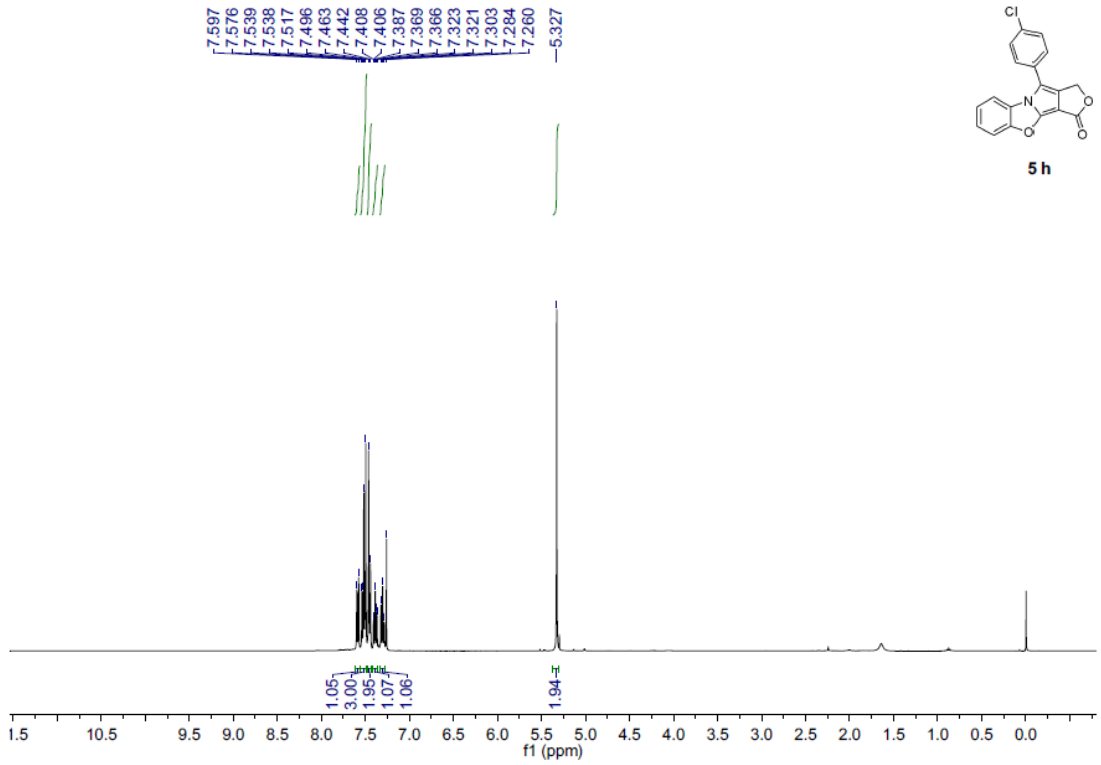
129.499
129.418
127.037
125.261
116.438
113.016
112.701
111.114
88.881
77.477
77.160
76.842
66.141
F
5 g
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.576
7.539
7.538
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7.496
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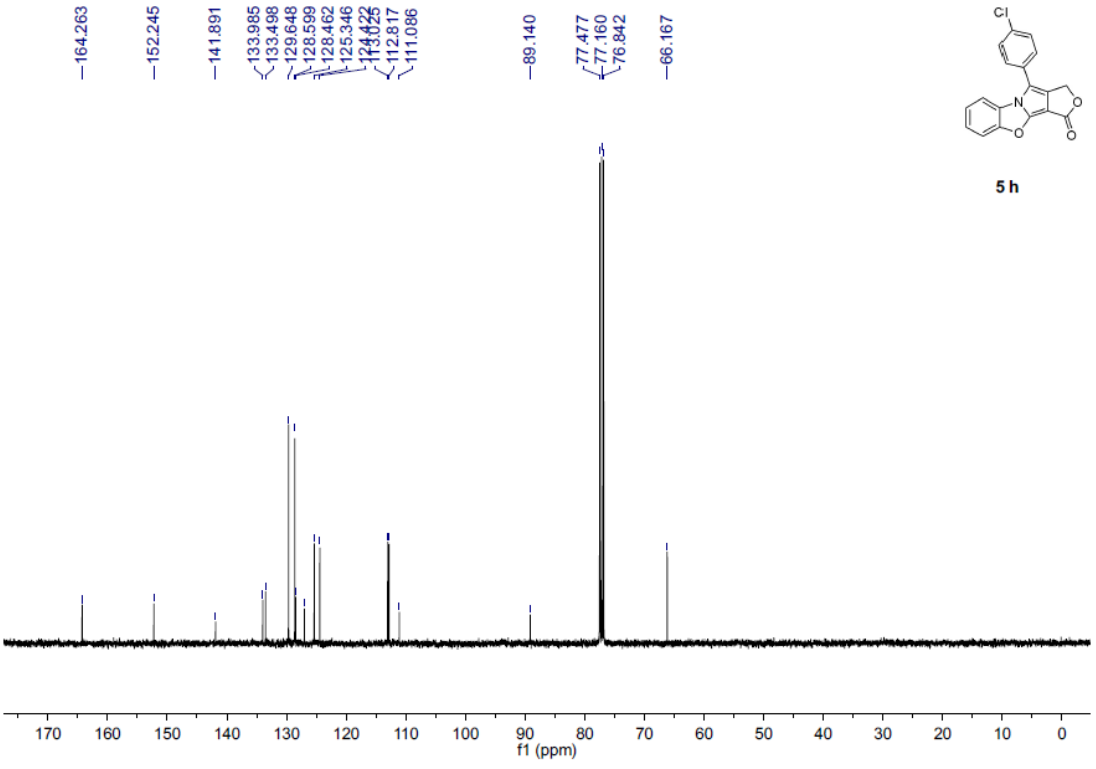
7.442
7.408
7.406
7.387
7.369
7.366
7.323
7.321
7.303
7.284
7.260
5.327
Cl
O
N
O
O
1.05
3.00
1.95
1.07
1.06
1.94
1.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

5 h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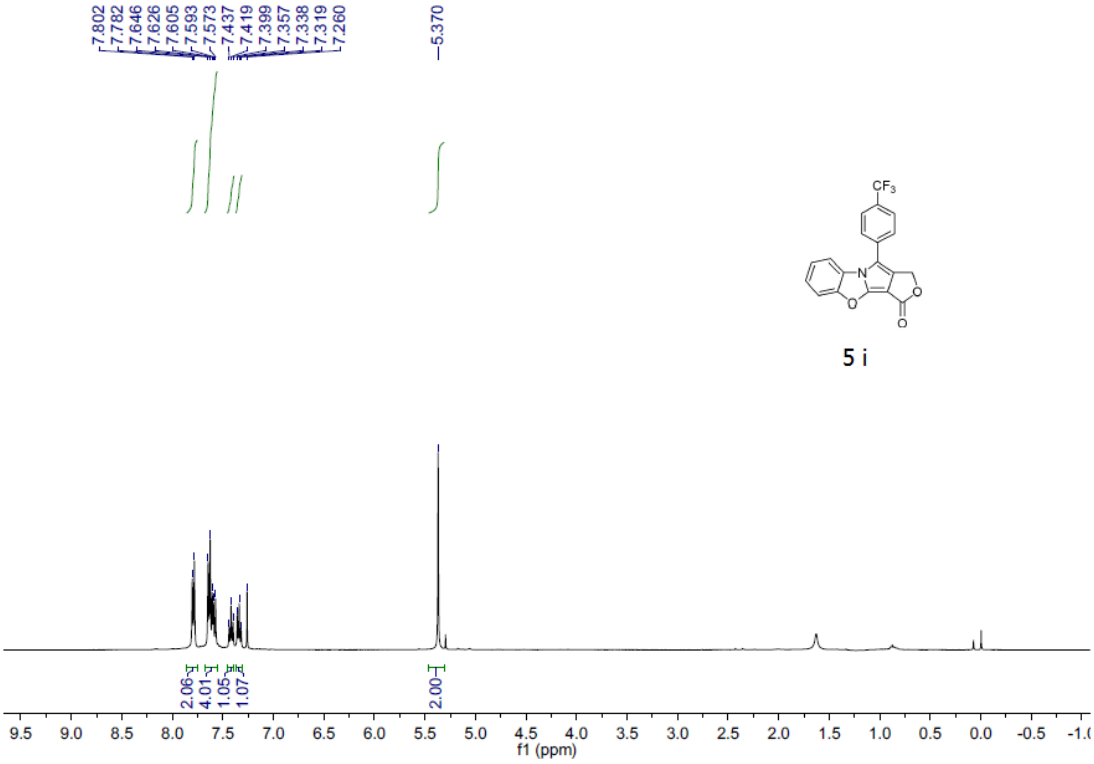
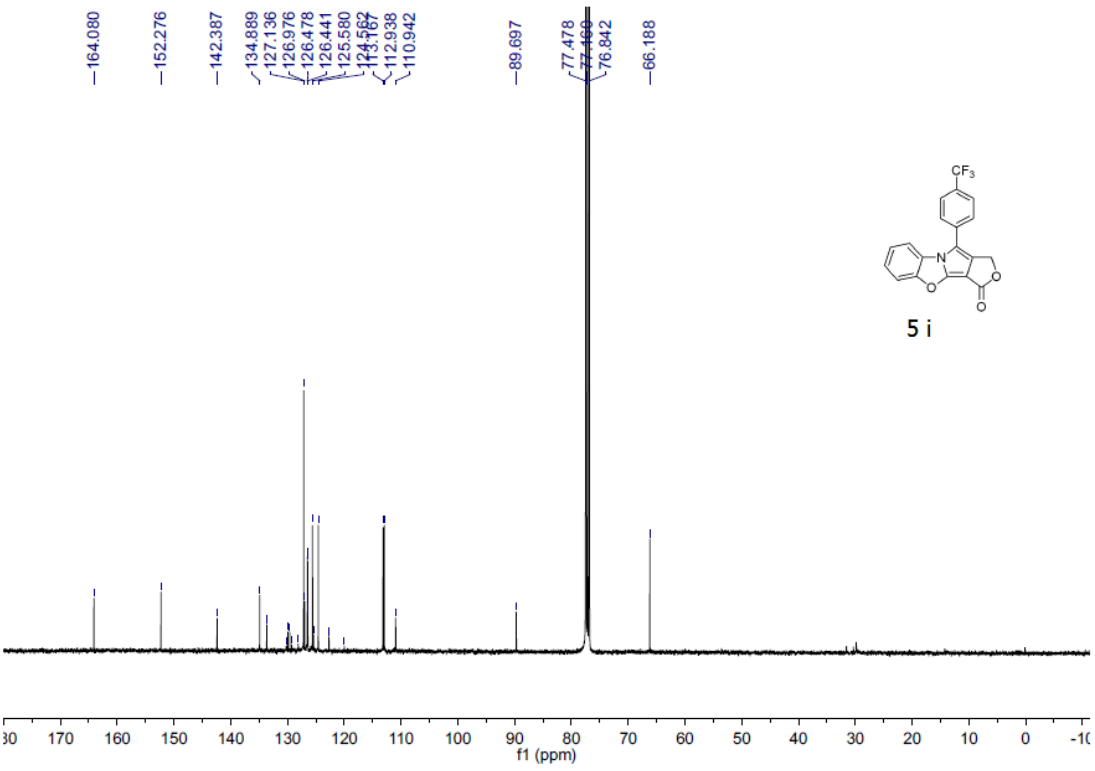
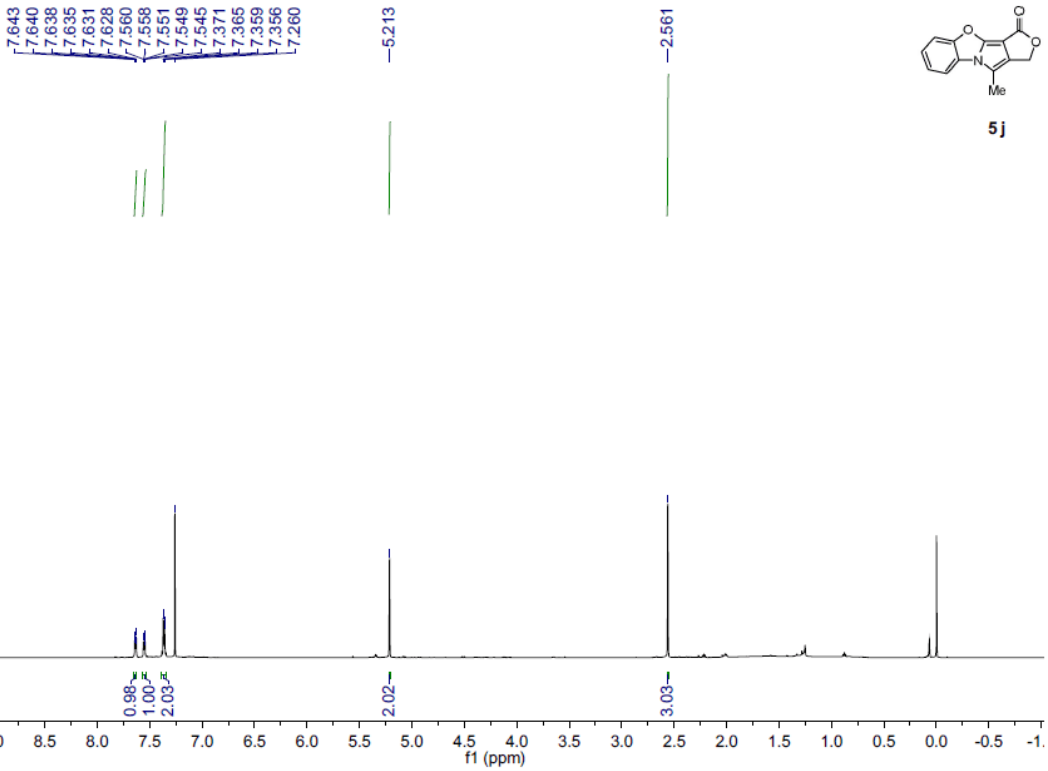
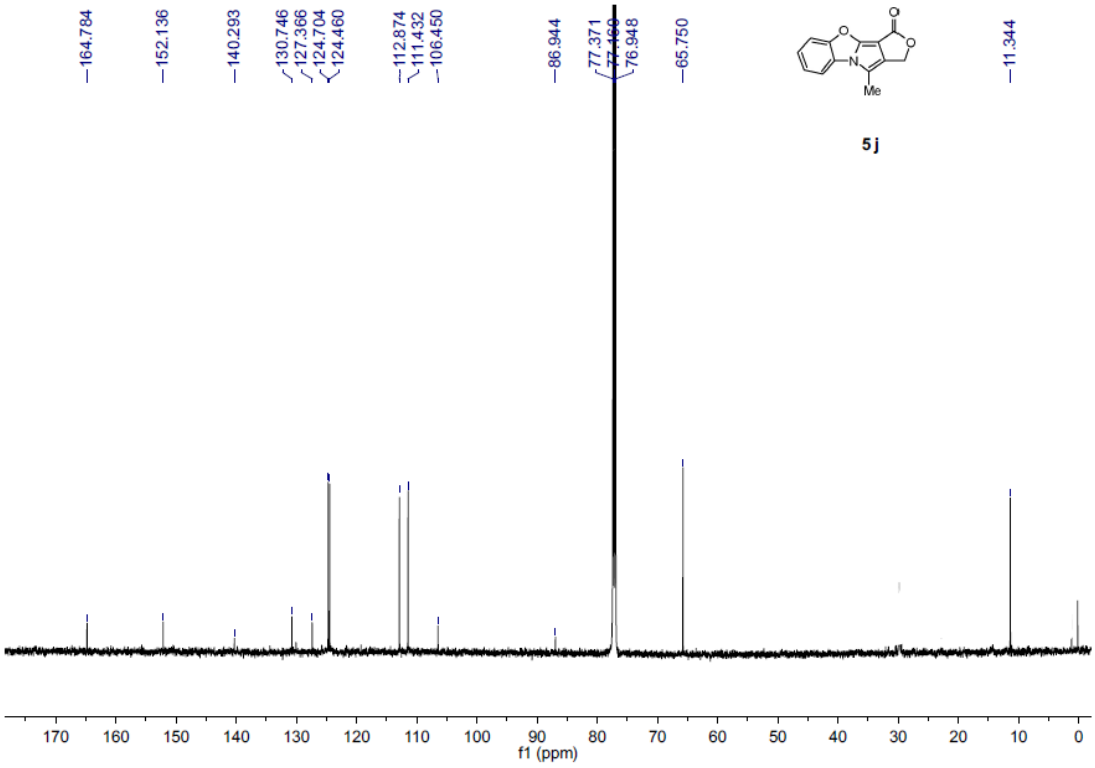
133.498
129.648
128.599
128.462
125.346
124.422
113.025
112.817
111.086
89.140
77.477
77.160
76.842
66.167
Cl
O
N
O
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

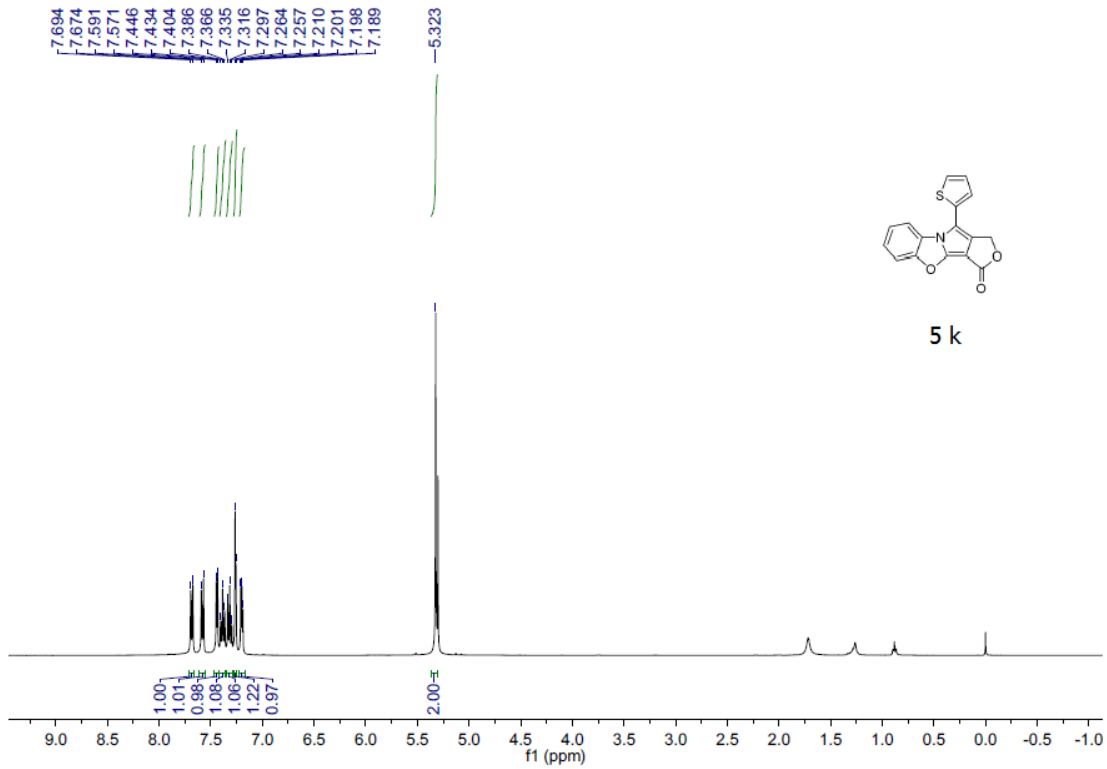
5 h


7.802
7.782
7.646
7.626
7.605
7.593
7.573
7.437
7.419
7.399
7.357
7.338
7.319
7.260
5.370
CF3
N
O
O
O
5 i
2.06
4.01
1.05
1.07
2.00
f1 (ppm)

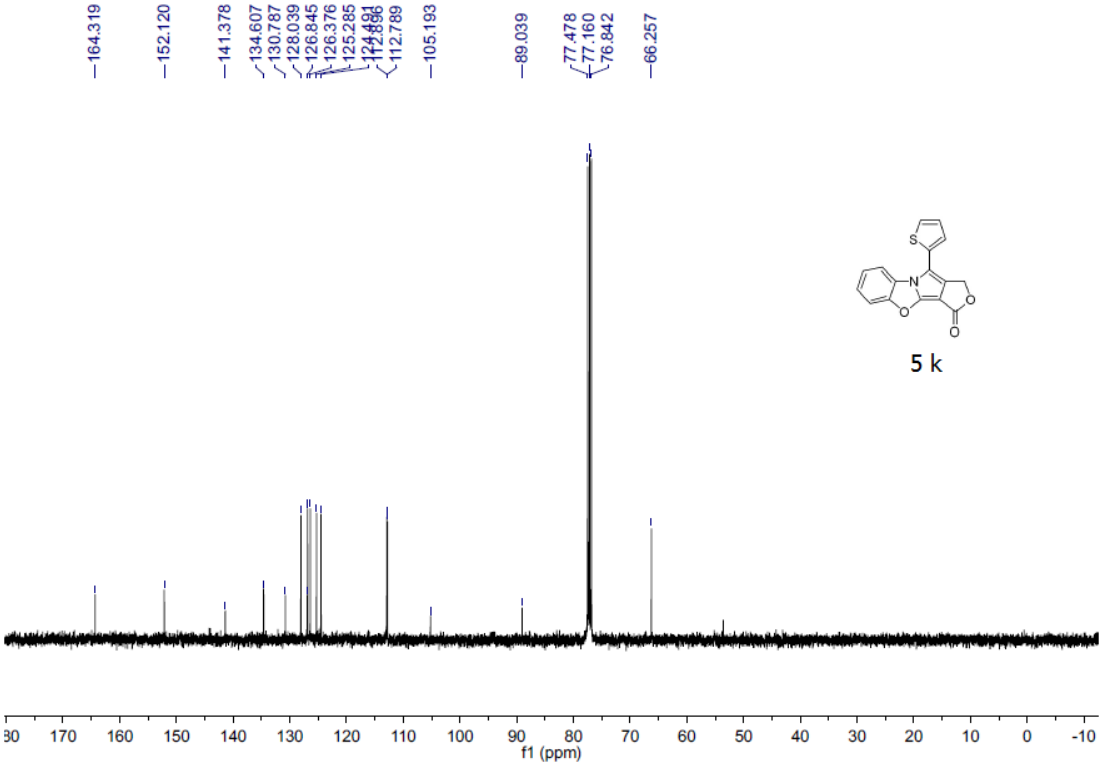

164.080
152.276
142.387
134.889
127.136
126.976
126.478
126.441
125.580
112.938
110.942
89.697
77.478
76.842
66.188
CF3
N
O
O
O
5 i
f1 (ppm)


7.643
7.640
7.638
7.635
7.631
7.628
7.560
7.558
7.551
7.549
7.545
7.371
7.365
7.359
7.356
7.260
5.213
2.561
Me
5j
0.98
1.00
2.03
2.02
3.03
f1 (ppm)

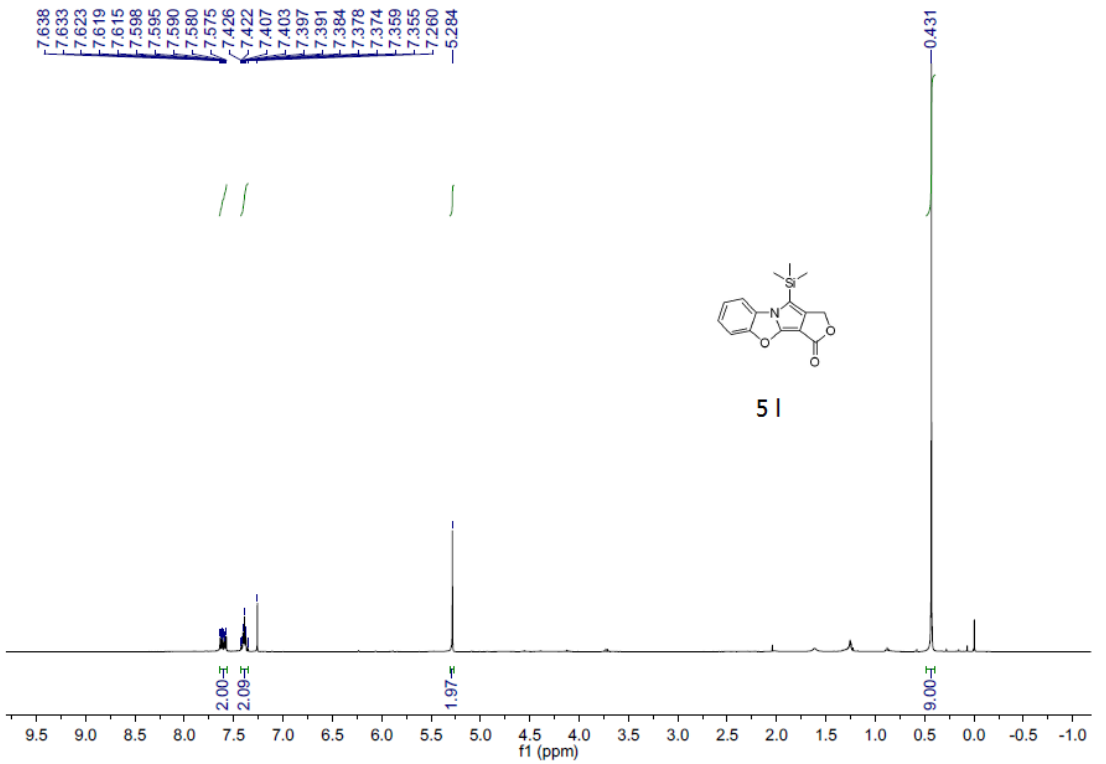

164.784
152.136
140.293
130.746
127.366
124.704
124.460
112.874
111.432
106.450
86.944
77.371
77.160
76.948
65.750
11.344
Me
5j
f1 (ppm)

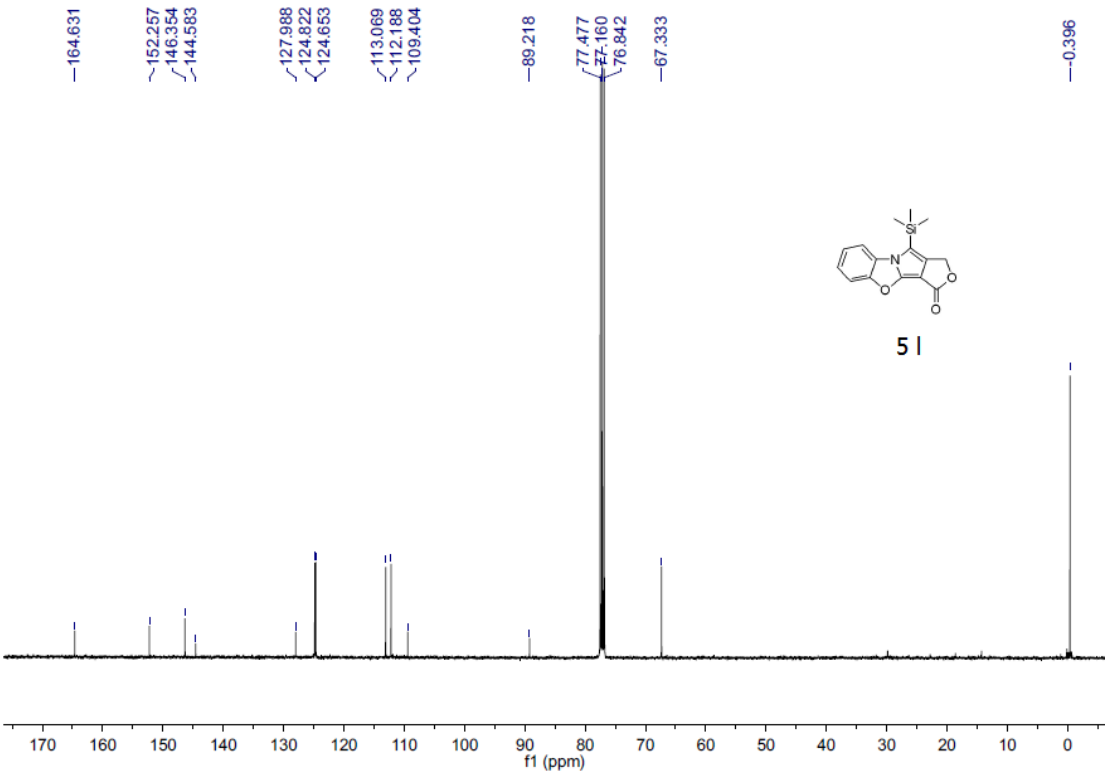

7.694
7.674
7.591
7.571
7.446
7.434
7.404
7.386
7.366
7.335
7.316
7.297
7.264
7.257
7.210
7.201
7.198
7.189
5.323
1.00
1.01
0.98
1.08
1.06
1.22
0.97
2.00
f1 (ppm)

5 k


164.319
152.120
141.378
134.607
130.787
128.039
126.845
126.376
125.285
112.789
105.193
89.039
77.478
77.160
76.842
66.257
f1 (ppm)

5 k


7.638
7.633
7.623
7.619
7.615
7.598
7.595
7.590
7.580
7.575
7.426
7.422
7.407
7.403
7.397
7.391
7.384
7.378
7.374
7.359
7.355
7.260
5.284
0.431
Si
N
O
O
O
5 l
2.00
2.09
1.97
9.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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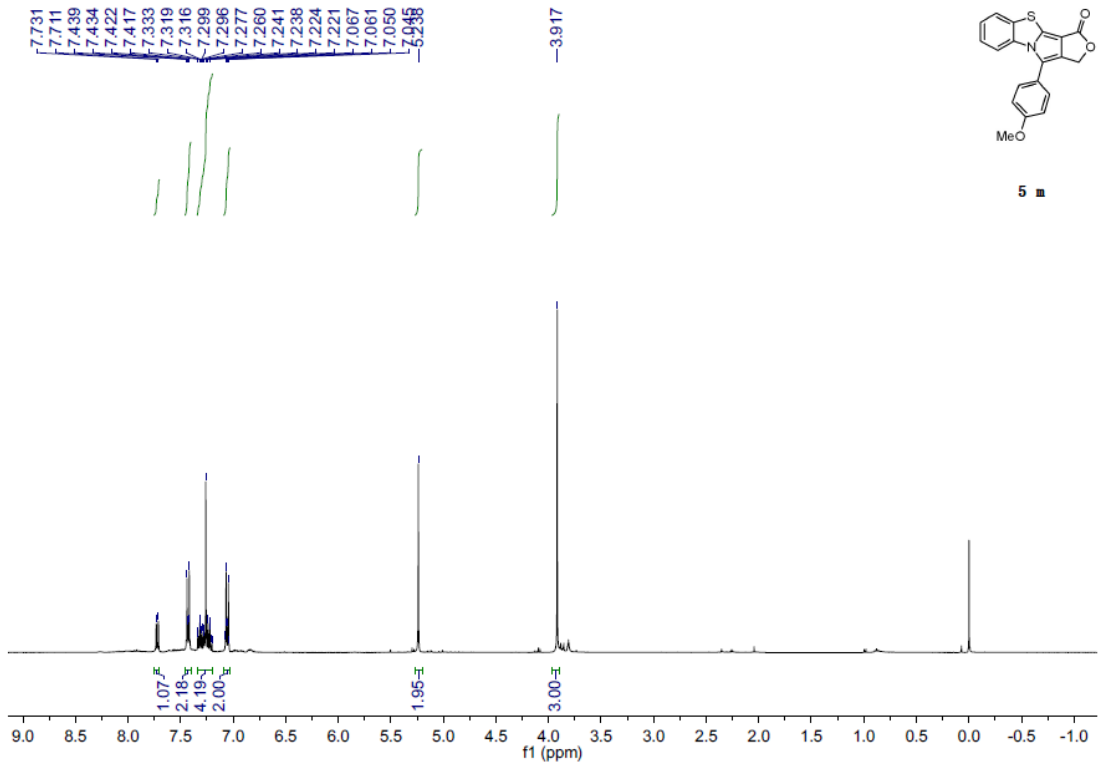
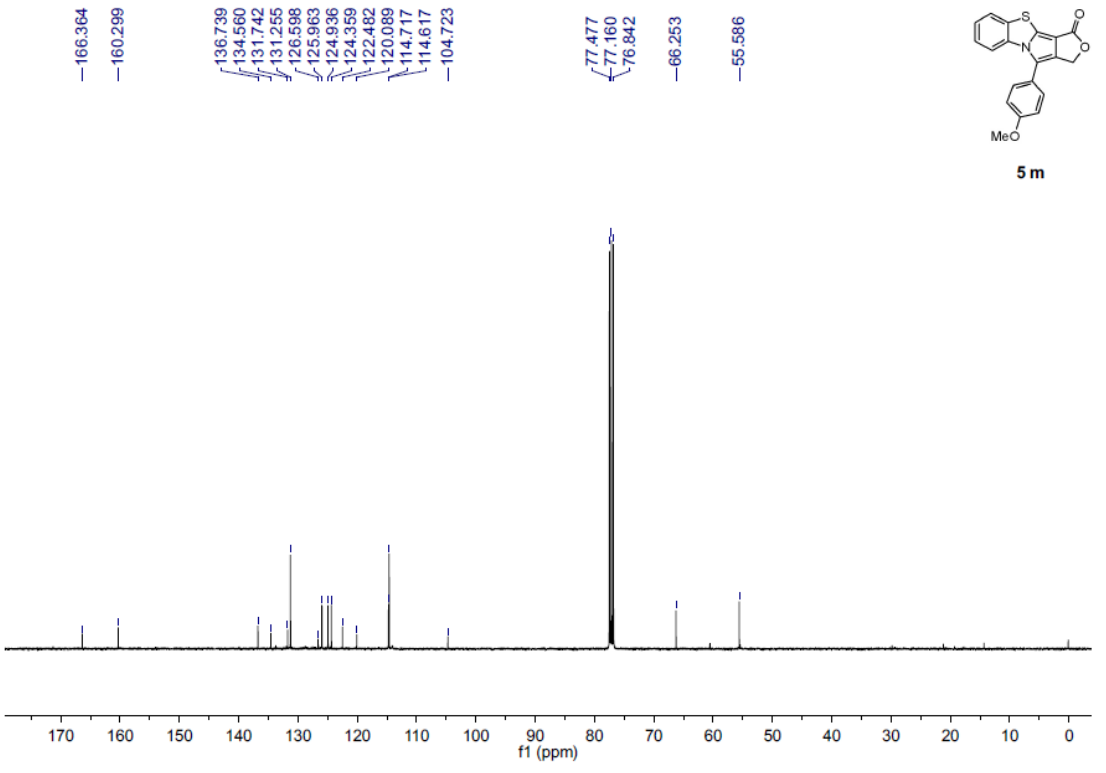
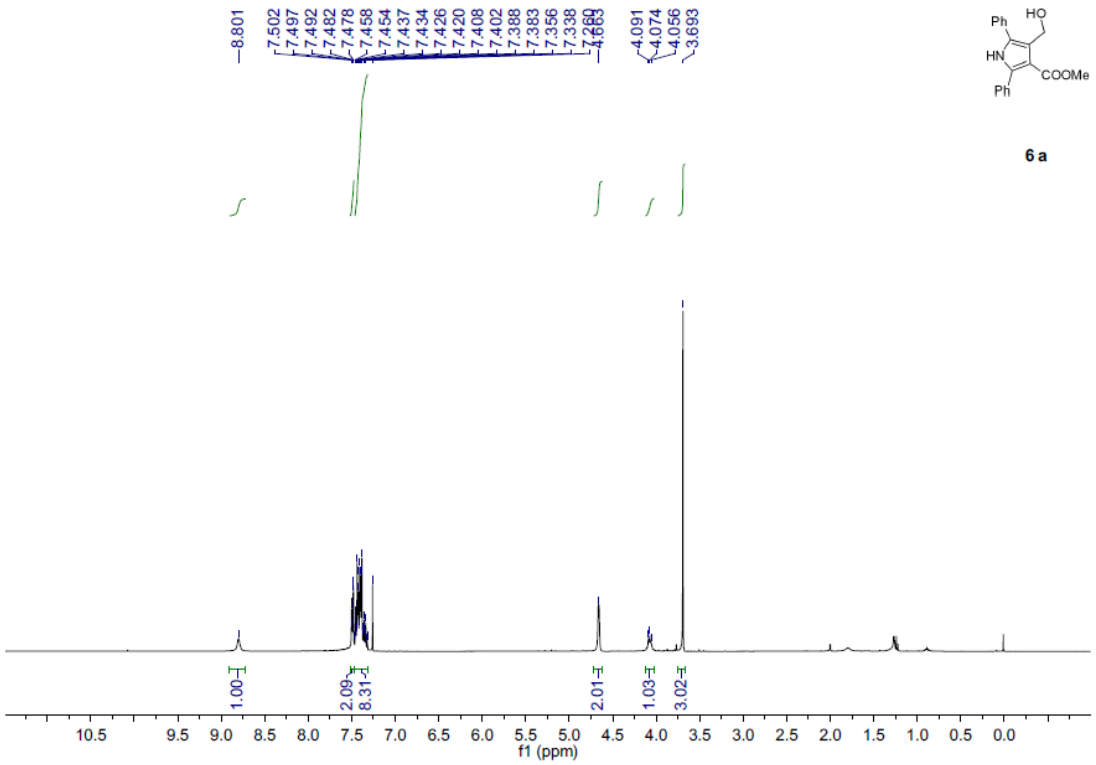
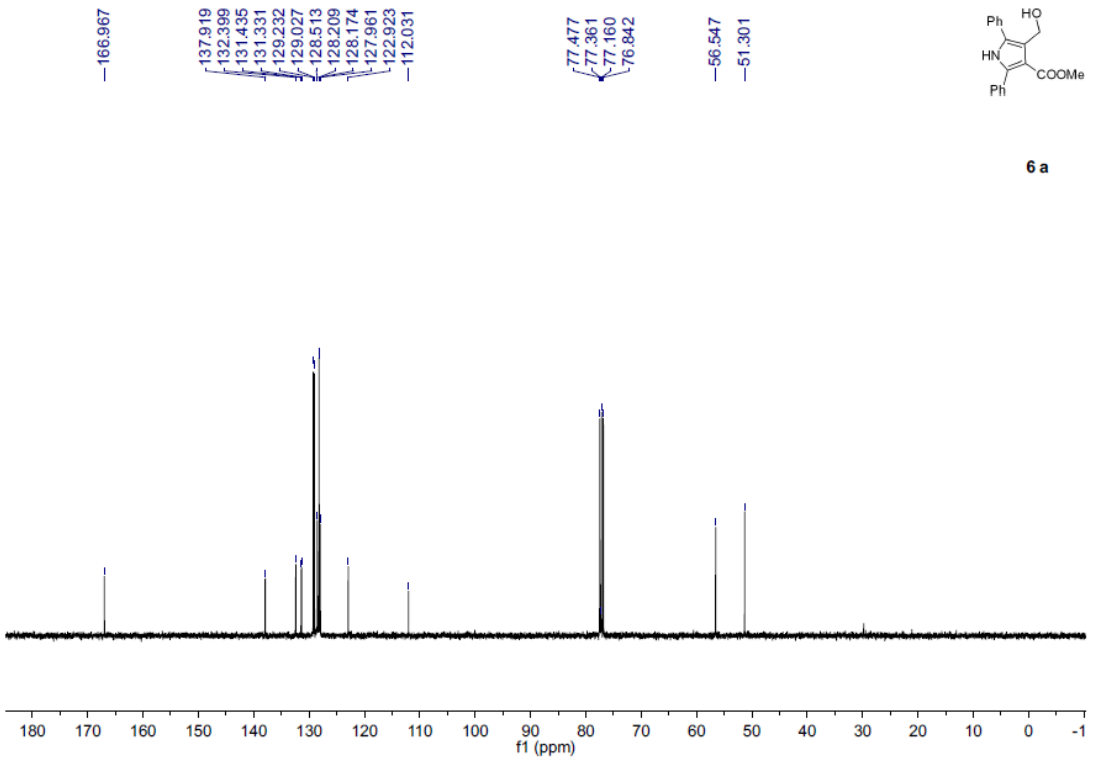
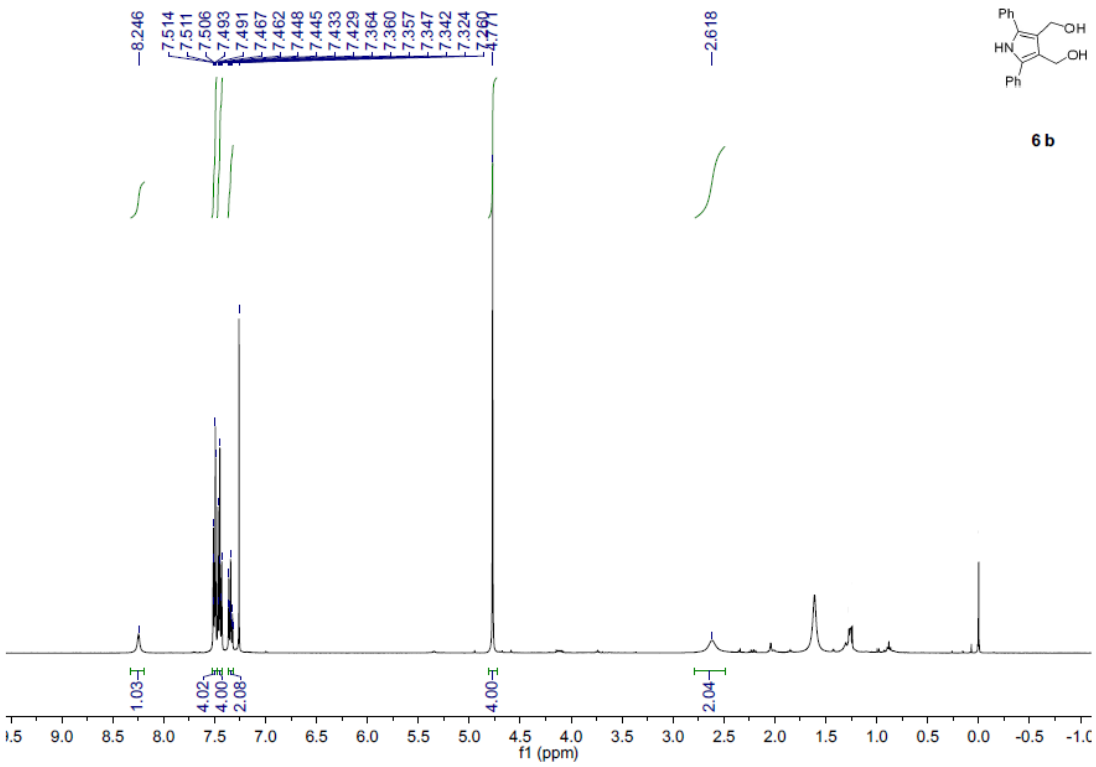
152.257
146.354
144.583
127.988
124.822
124.653
113.069
112.188
109.404
89.218
77.477
77.160
76.842
67.333
-0.396
Si
N
O
O
O
5 l
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

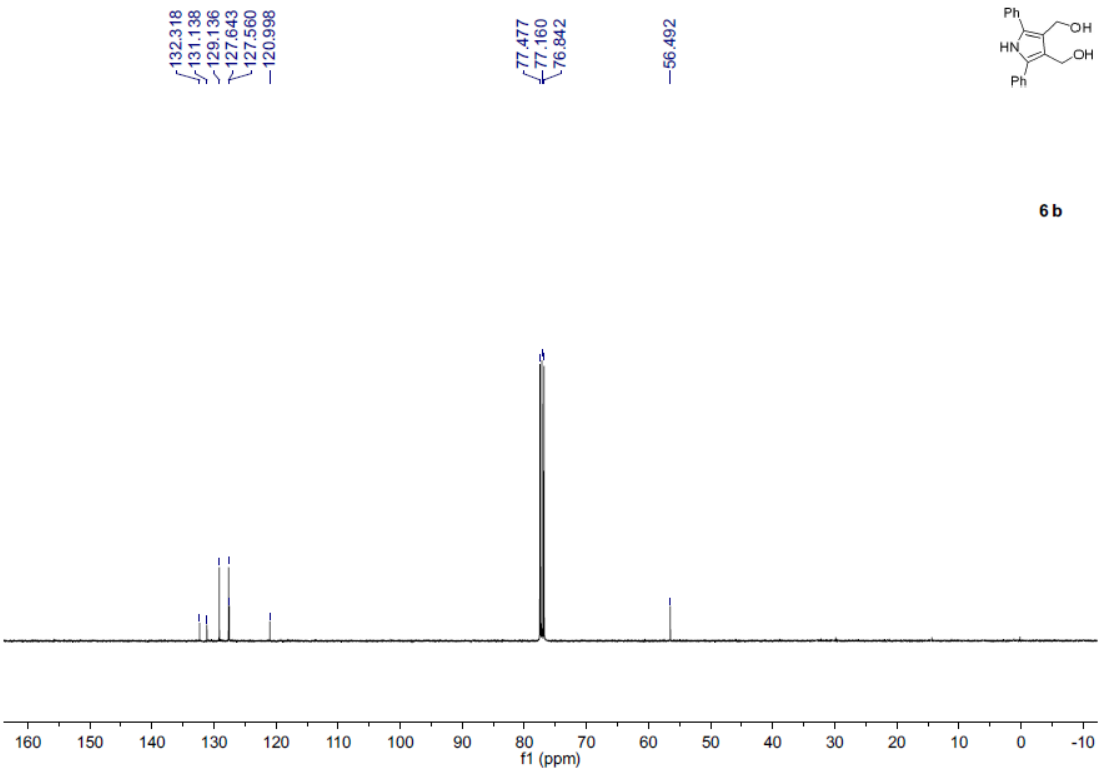

7.731
7.711
7.439
7.434
7.422
7.417
7.333
7.319
7.316
7.299
7.296
7.277
7.260
7.241
7.238
7.224
7.221
7.067
7.061
7.050
5.238
3.917
MeO
5 m
1.07
2.18
4.19
2.00
1.95
3.00
f1 (ppm)

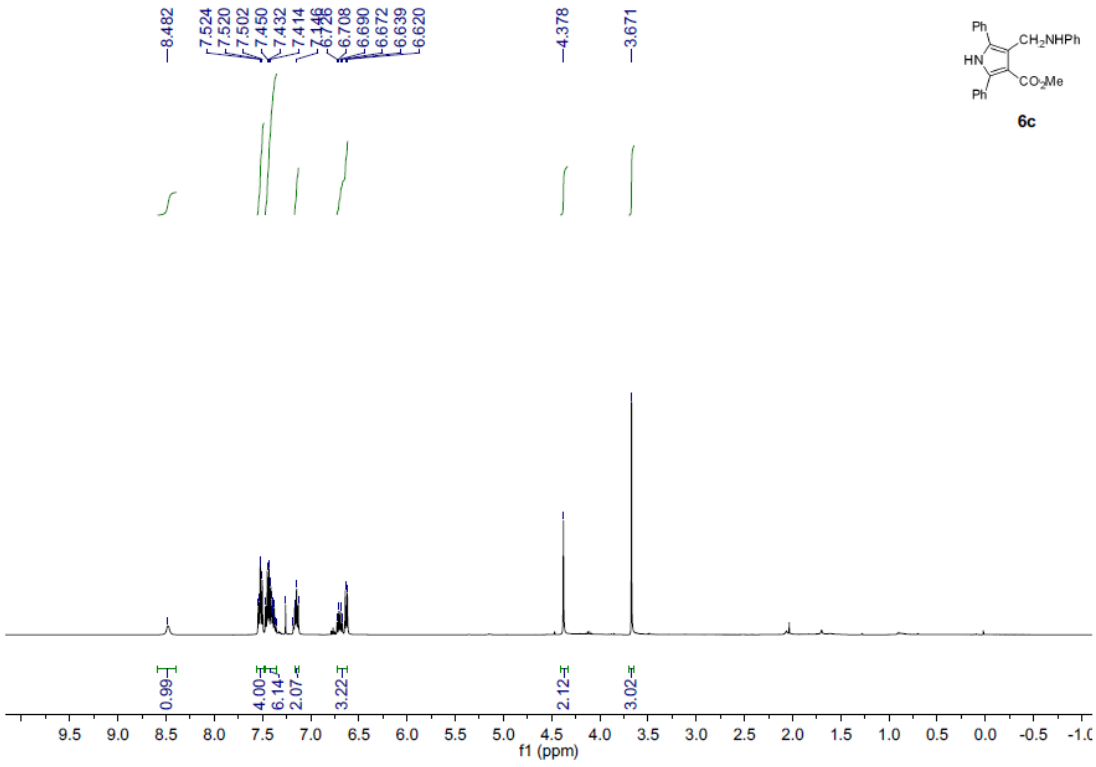

166.364
160.299
136.739
134.560
131.742
131.255
126.598
125.963
124.936
124.359
122.482
120.089
114.717
114.617
104.723
77.477
77.160
76.842
66.253
55.586
MeO
5 m
f1 (ppm)

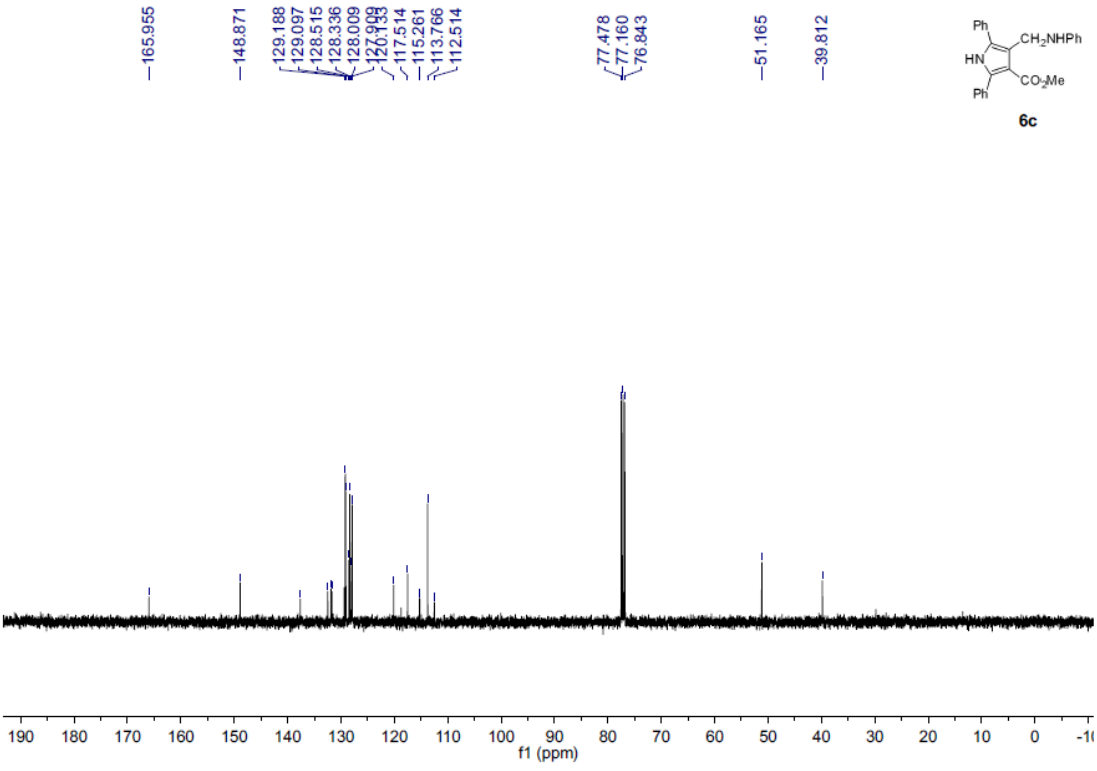

8.801
7.502
7.497
7.492
7.482
7.478
7.458
7.454
7.437
7.434
7.426
7.420
7.408
7.402
7.388
7.383
7.356
7.338
7.260
4.663
4.091
4.074
4.056
3.693
Ph
HO
HN
COOMe
Ph
6 a
1.00
2.09
8.31
2.01
1.03
3.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

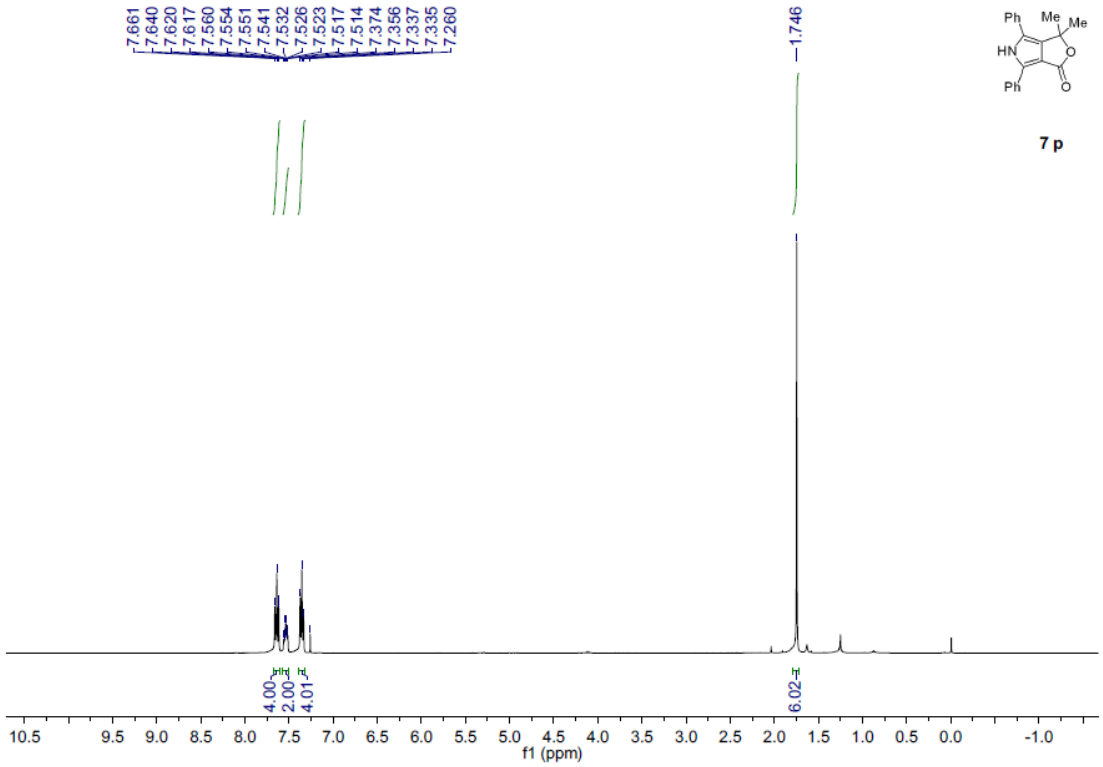

166.967
137.919
132.399
131.435
131.331
129.232
129.027
128.513
128.209
128.174
127.961
122.923
112.031
77.477
77.361
77.160
76.842
56.547
51.301
Ph
HO
HN
COOMe
Ph
6 a
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)

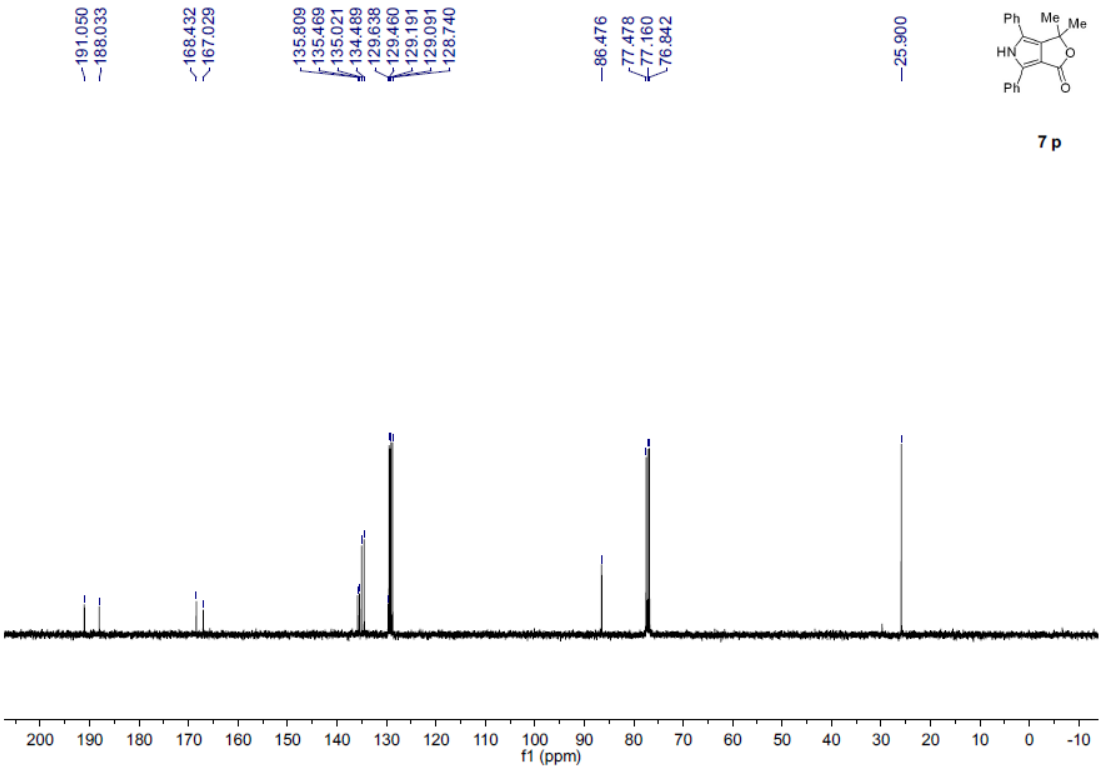

8.246
7.514
7.511
7.506
7.493
7.491
7.467
7.462
7.448
7.445
7.433
7.429
7.364
7.360
7.357
7.347
7.342
7.324
7.260
4.771
2.618
Ph
HN
Ph
OH
OH
6 b
1.03
4.02
4.00
2.08
4.00
2.04
f1 (ppm)

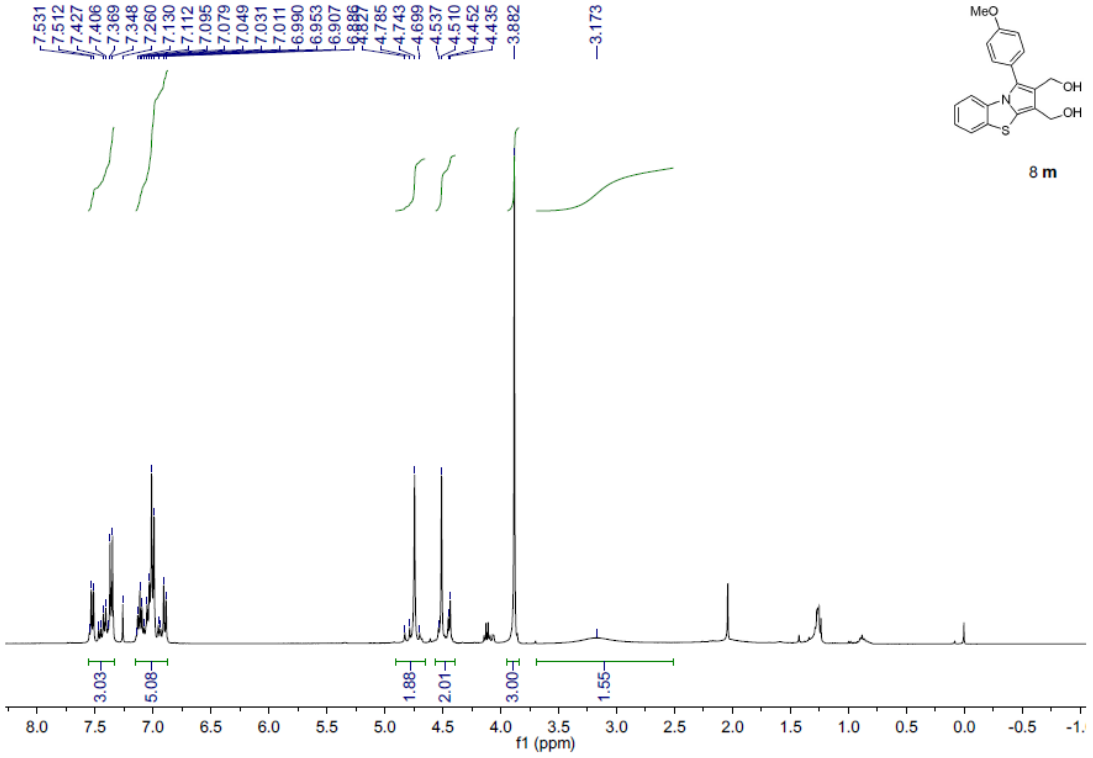

132.318
131.138
129.136
127.643
127.560
120.998
77.477
77.160
76.842
56.492
Ph
HN
Ph
OH
OH
6 b
f1 (ppm)

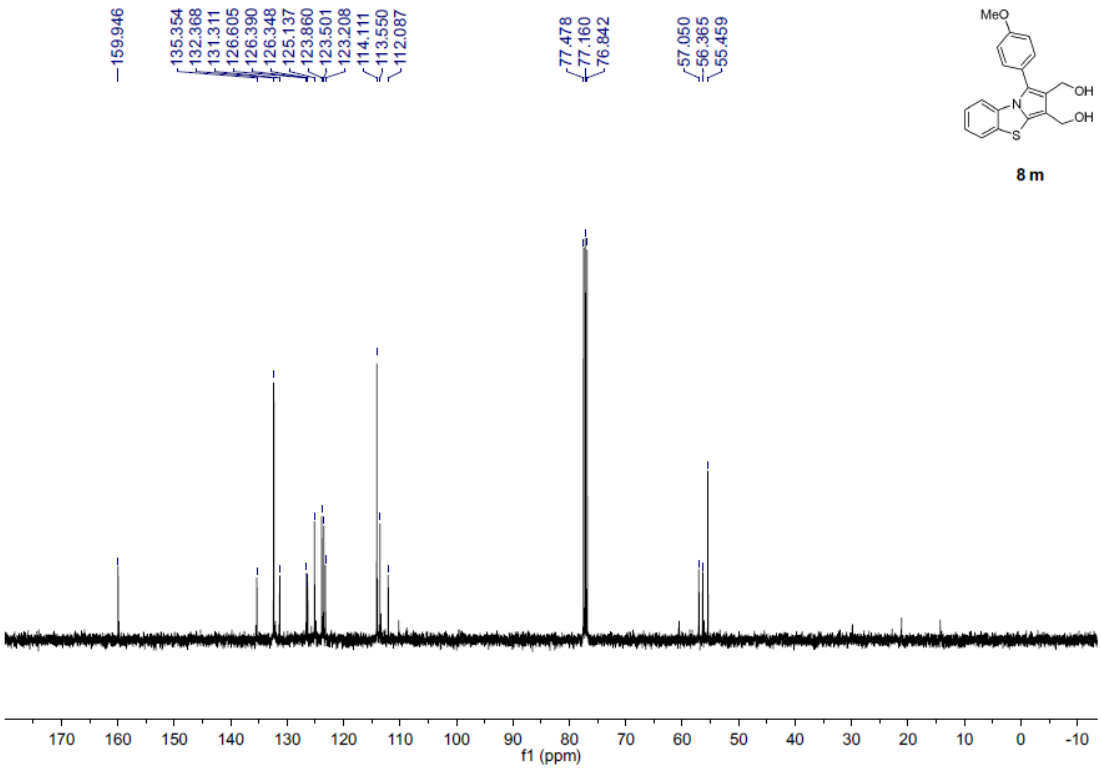

8.482
7.524
7.520
7.502
7.450
7.432
7.414
7.146
6.728
6.708
6.690
6.672
6.639
6.620
4.378
3.671
Ph
CH2NHPh
HN
CO2Me
Ph
6c
0.99
4.00
6.14
2.07
3.22
2.12
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

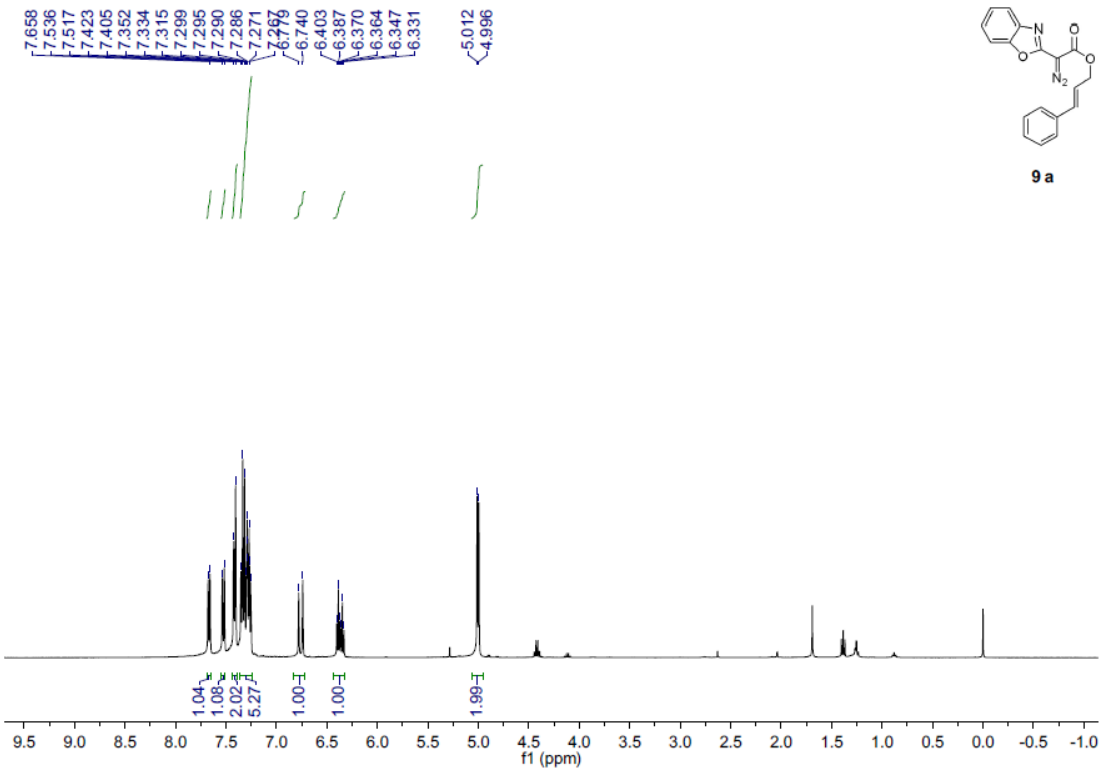

165.955
148.871
129.188
129.097
128.515
128.336
128.009
120.133
117.514
115.261
113.766
112.514
77.478
77.160
76.843
51.165
39.812
Ph
CH2NHPh
HN
CO2Me
Ph
6c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.661
7.640
7.620
7.617
7.560
7.554
7.551
7.541
7.532
7.526
7.523
7.517
7.514
7.374
7.356
7.337
7.335
7.260
1.746
Ph
Me
Me
HN
O
Ph
O
7 p
4.00
2.00
4.01
6.02
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-1.0
f1 (ppm)


191.050
188.033
168.432
167.029
135.809
135.469
135.021
134.489
129.638
129.460
129.191
129.091
128.740
86.476
77.478
77.160
76.842
25.900
Ph
Me
Me
HN
O
Ph
O
7 p
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


7.531
7.512
7.427
7.406
7.369
7.348
7.260
7.130
7.112
7.095
7.079
7.049
7.031
7.011
6.990
6.953
6.907
4.785
4.743
4.699
4.537
4.510
4.452
4.435
3.882
3.173
MeO
OH
OH
N
S
8 m
3.03
5.08
1.88
2.01
3.00
1.55
f1 (ppm)


159.946
135.354
132.368
131.311
126.605
126.390
126.348
125.137
123.860
123.501
123.208
114.111
113.550
112.087
77.478
77.160
76.842
57.050
56.365
55.459
MeO
OH
OH
N
S
8 m
f1 (ppm)


7.658
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7.517
7.423
7.405
7.352
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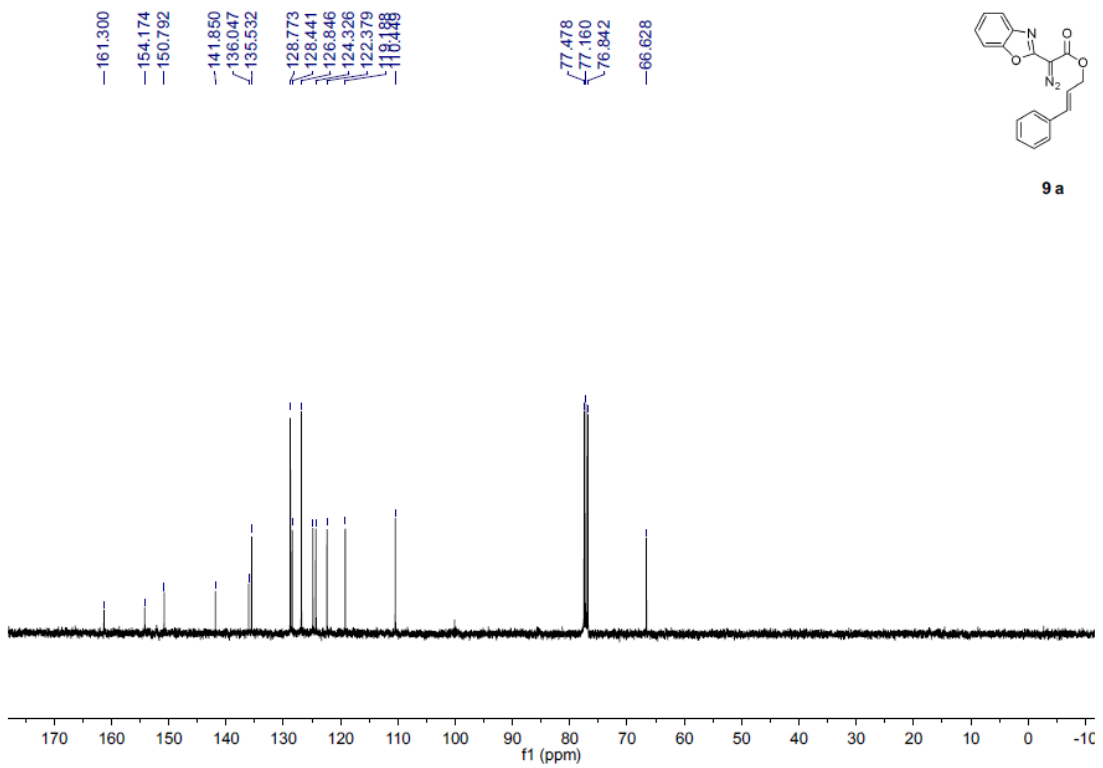
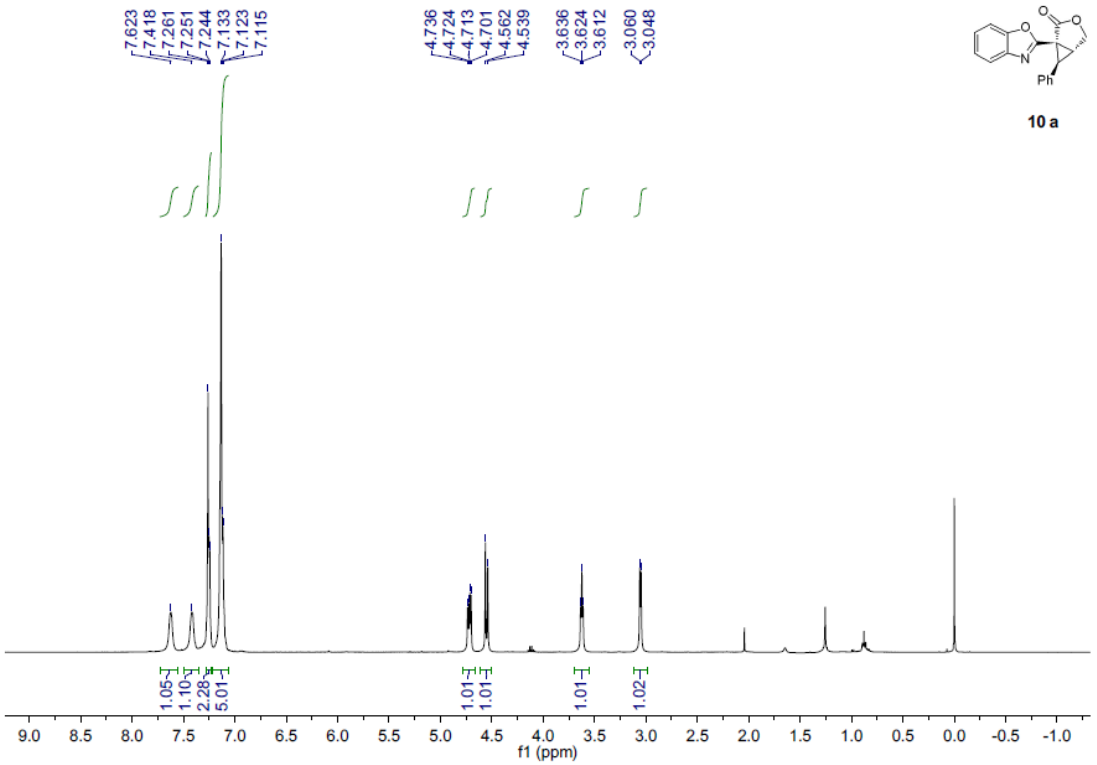
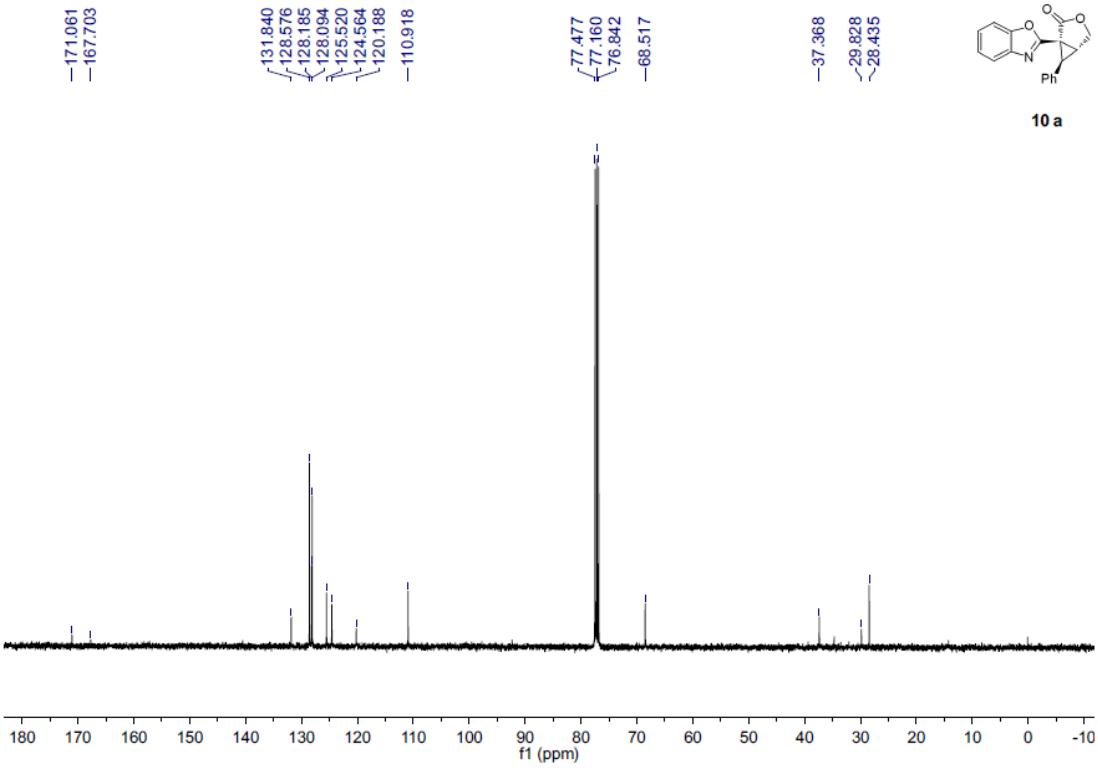
7.315
7.299
7.295
7.290
7.286
7.271
6.779
6.740
6.403
6.387
6.370
6.364
6.347
6.331
5.012
4.996
1.04
1.08
2.02
5.27
1.00
1.00
1.99
f1 (ppm)

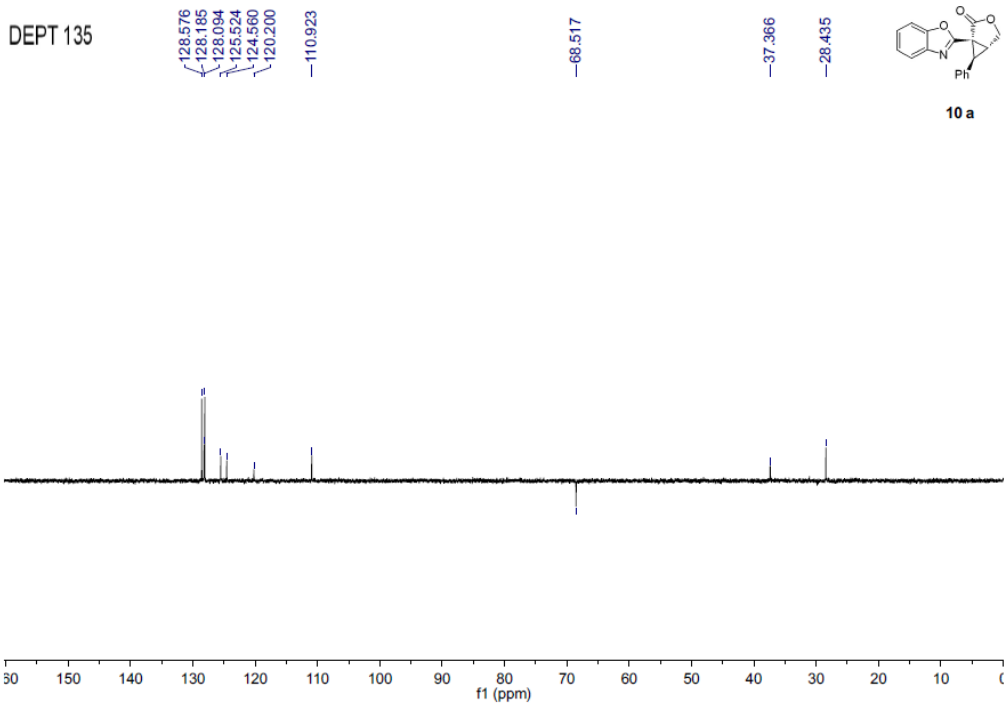
9 a


161.300
154.174
150.792
141.850
136.047
135.532
128.773
128.441
126.846
124.326
122.379
77.478
77.160
76.842
66.628
f1 (ppm)

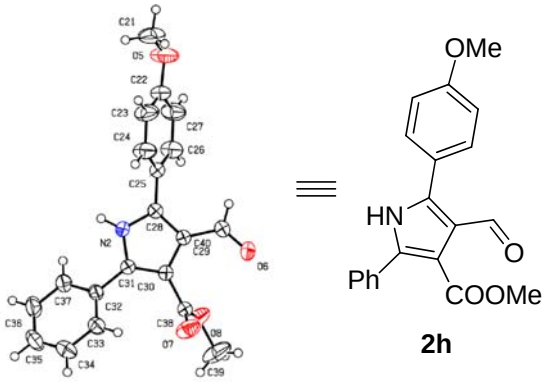
9 a


7.623
7.418
7.261
7.251
7.244
7.133
7.123
7.115
4.736
4.724
4.713
4.701
4.562
4.539
3.636
3.624
3.612
3.060
3.048
Ph
10 a
1.05
1.10
2.28
5.01
1.01
1.01
1.01
1.02
f1 (ppm)


171.061
167.703
131.840
128.576
128.185
128.094
125.520
124.564
120.188
110.918
77.477
77.160
76.842
68.517
37.368
29.828
28.435
Ph
10 a
f1 (ppm)


DEPT 135
128.576
128.185
128.094
125.524
124.560
120.200
110.923
68.517
37.366
28.435
Ph
10 a
50
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

X-ray crystal structures of 2h

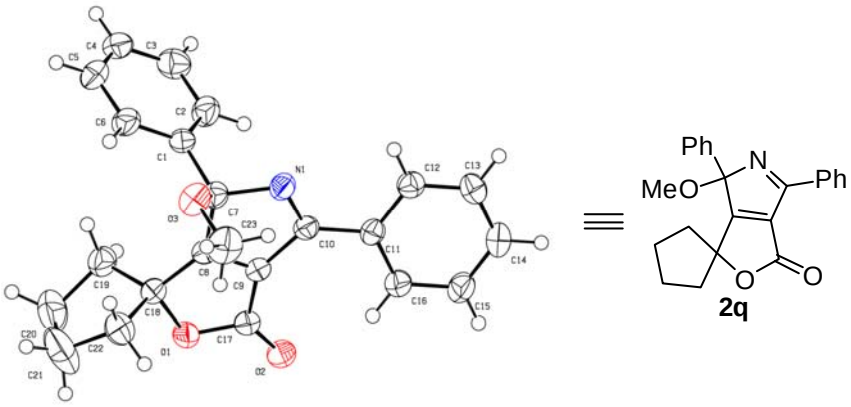


2h

Datablock: zccuno_0m

```
Bond precision:      C-C = 0.0025 A              Wavelength=0.71073
Cell:         a=11.1811(4)   b=11.6175(5)   c=14.5096(6)
              alpha=70.505   beta=78.122(2) gamma=74.189(2)
              (2)
Temperature: 273 K
                    Calculated                    Reported
Volume              1695.70(12)                   1695.70(12)
Space group         P -1                          ?
Hall group          -P 1                          ?
Moiety formula      C20 H17 N O4                  ?
Sum formula         C20 H17 N O4                  C13 H39 N24 O13
Mr                  335.35                        739.68
Dx,g cm-3           1.314                         1.449
Z                   4                             2
Mu (mm-1)           0.092                         0.126
F000                704.0                         778.0
F000'               704.36
h,k,lmax            14,15,18                      14,15,18
Nref                7820                          7780
Tmin,Tmax           0.001,0.002
Tmin'               0.000
Correction method= Not given
Data completeness= 0.995        Theta(max)= 27.550
R(reflections)= 0.0562( 5902)      wR2(reflections)= 0.1938( 7780)
S = 1.399              Npar= 451
```

X-ray crystal structures of 2q



CCDC 1483111

Datablock: t

Bond precision: C-C = 0.0027 A Wavelength=0.71073

Cell: a=8.6755(7) b=10.6916(10) c=11.4390(9)
alpha=69.968(8) beta=73.363(7) gamma=72.428(7)

Temperature: 223 K

	Calculated	Reported
Volume	930.30(15)	930.30(14)
Space group	P -1	P -1
Hall group	-P 1	-P 1
Moiety formula	C23 H21 N O3	C23 H21 N O3
Sum formula	C23 H21 N O3	C23 H21 N O3
Mr	359.41	359.41
Dx,g cm-3	1.283	1.283
Z	2	2
Mu (mm-1)	0.085	0.085
F000	380.0	380.0
F000'	380.17	
h,k,lmax	10,12,13	10,12,13
Nref	3448	3444
Tmin,Tmax	0.975,0.983	0.975,0.983
Tmin'	0.975	

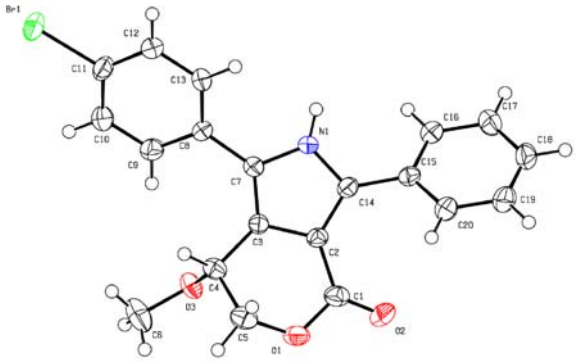
Correction method= # Reported T Limits: Tmin=0.975 Tmax=0.983 AbsCorr = MULTI-SCAN

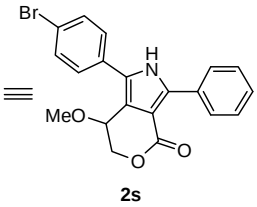
Data completeness= 0.999 Theta(max)= 25.490

R(reflections)= 0.0444(2740) wR2(reflections)= 0.1281(3444)

S = 1.049 Npar= 245

X-ray crystal structures of 2s





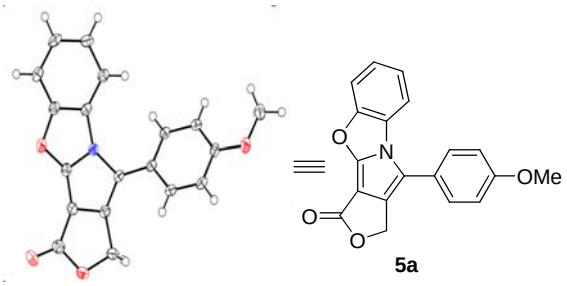
2s

CCDC: 1485648

Datablock: g160613c

```
Bond precision:      C-C = 0.0042 A              Wavelength=0.71073
Cell:         a=4.2880(5)     b=27.2739(16)  c=14.6976(9)
              alpha=90        beta=90.213(8) gamma=90
Temperature: 223 K
                     Calculated                      Reported
Volume               1718.9(2)                       1718.9(2)
Space group          P 21/c                          P 1 21/c 1
Hall group           -P 2ybc                         -P 2ybc
Moiety formula       C20 H16 Br N O3                 C20 H16 Br N O3
Sum formula          C20 H16 Br N O3                 C20 H16 Br N O3
Mr                   398.24                          398.25
Dx,g cm-3            1.539                           1.539
Z                    4                               4
Mu (mm-1)            2.410                           2.410
F000                 808.0                           808.0
F000'                807.19
h,k,lmax             5,34,18                         5,34,18
Nref                 3530                            3104
Tmin,Tmax            0.566,0.697                     0.427,1.000
Tmin'                0.207
Correction method= # Reported T Limits: Tmin=0.427
Tmax=1.000 AbsCorr = MULTI-SCAN
Data completeness= 0.879        Theta(max)= 26.370
R(reflections)= 0.0432( 2200)      wR2(reflections)= 0.0883( 3104)
S = 1.001              Npar= 227
```

X-ray crystal structures of 5a



5a

Datablock: b151009a_1_0m_a

Bond precision: C-C = 0.0020 A Wavelength=0.71073

Cell: a=10.7549(6) b=7.0492(4) c=19.1664(12)
alpha=90 beta=102.500(2) gamma=90

Temperature: 293 K

	Calculated	Reported
Volume	1418.63(14)	1418.63(14)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C19 H13 N O4	C19 H13 N O4
Sum formula	C19 H13 N O4	C19 H13 N O4
Mr	319.30	319.30
Dx,g cm-3	1.495	1.495
Z	4	4
Mu (mm-1)	0.106	0.106
F000	664.0	664.0
F000'	664.35	
h,k,lmax	13,9,24	13,9,24
Nref	3268	3257
Tmin,Tmax	0.950,0.984	0.920,0.984
Tmin'	0.919	

Correction method= # Reported T Limits: Tmin=0.920 Tmax=0.984
AbsCorr = MULTI-SCAN

Data completeness= 0.997 Theta(max)= 27.540

R(reflections)= 0.0492(2574) wR2(reflections)= 0.1298(3257)

S = 1.049 Npar= 218