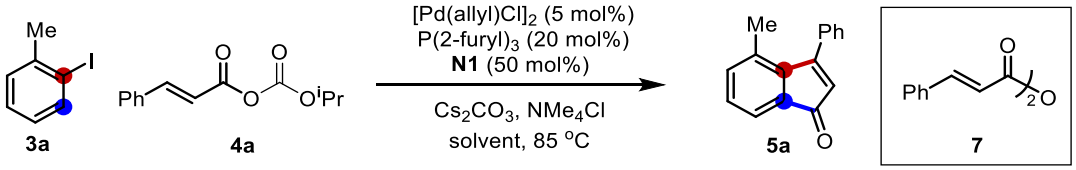
# Table of Content

## 1. General Information

Unless noted otherwise, all solvents were dried by filtration through a Pure-Solv MD-5 Solvent Purification System (Innovative Technology). Tetrahydrofuran and 1,4-dioxane were then vacuum-distilled freshly over sodium. Reaction temperatures were reported as the temperatures of the bather surrounding the flasks or vials. Sensitive reagents and solvents were transferred under nitrogen into a nitrogen-filled glovebox with standard techniques. Cesium carbonate was purchased from Strem, stored and used directly in the glovebox. Analytical thin-layer chromatography (TLC) was carried out using 0.2 mm commercial silica gel plates (silica gel 60, F254, EMD chemical). Vials (15 x 45 mm 1 dram (4 mL) with PTFE lined cap attached) were purchased from Qorpak and flame-dried and cooled in a desiccator prior to usage. High resolution mass spectra (HR-MS) were recorded on an Agilent 6530 LC Q-TOF mass spectrometer using electrospray ionization with fragmentation voltage set at 115 V and processed with an Agilent MassHunter Operating System. Infrared spectra were recorded on a Nicolet 380 FTIR using neat thin film technique. Nuclear magnetic resonance spectra (1H NMR and 13C NMR) were recorded with a Bruker DMX 400 (400 MHz, 1H at 400 MHz, 13C at 101 MHz) or Bruker Model DMX 500 (500 MHz, 1H at 500 MHz, 13C at 126 MHz). Chemical shifts were reported in parts per million (ppm, δ), downfield from tetramethylsilane (TMS, δ=0.00ppm) and were referenced to residual solvent (CDCl3, δ=7.26 ppm (1H) and 77.00 ppm (13C)). All the 19F chemical shifts were not referenced. Coupling constants were reported in Hertz (Hz). Data for $^{1}$H NMR spectra were reported as follows: chemical shift (ppm, referenced to protium, s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, dd = doublet of doublets, td = triplet of doublets, ddd = doublet of doublet of doublets, m = multiplet, coupling constant (Hz), and integration). All other materials were obtained from Sigma-Aldrich, TCI Chemicals or Combi-Blocks and were used as received.

## 2. Optimization of Pd/NBE-Catalyzed Indenone Synthesis

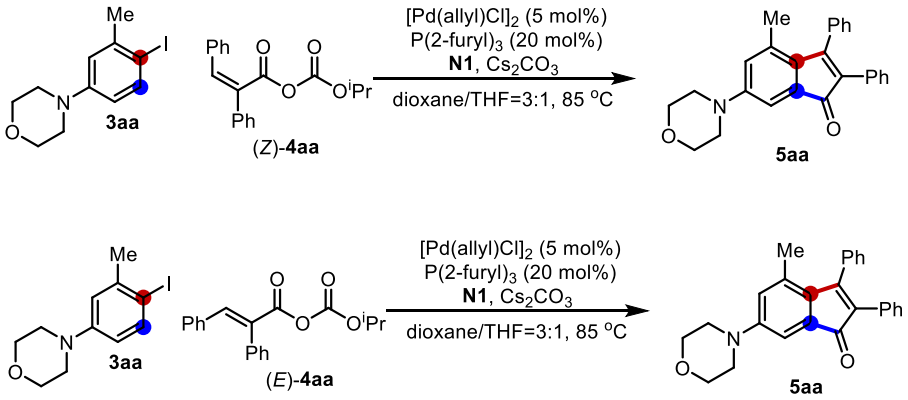
**Table S1** Optimization of Pd/NBE-catalyzed annulation reaction between **3a** and **4a**




| entry | solvent | other changes | yield of **5a** (%) |
|---|---|---|---|
| 1 | THF:MeCN (10:1) | none | 68 |
| 2 | THF:MeCN (10:1) | $PPh_3$ instead of P(2-furyl)$_3$ | 9 |
| 3 | THF:MeCN (10:1) | DPEPhos instead of P(2-furyl)$_3$ | 16 |
| 4 | THF:MeCN (10:1) | $Pd(OAc)_2$ instead of $[Pd(allyl)Cl]_2$ | 5 |
| 5 | THF:MeCN (10:1) | $Pd(MeCN)Cl_2$ instead of $[Pd(allyl)Cl]_2$ | 36 |
| 6 | THF | none | 62 |
| 7 | dioxane | none | 72 |
| 8 | dioxane:THF (3:1) | none | 76 |
| 9 | dioxane:THF (3:1) | no $NMe_4Cl$ | 35 |
| 10 | dioxane:THF (3:1) | **7** instead of **4a** | 54 |
| 11 | dioxane:THF (3:1) | **7** instead of **4a**, no $NMe_4Cl$ | 65 |
| 12 | dioxane:THF (3:1) | norbornene instead of **N1** | 43 |
| 13 | dioxane:THF (3:1) | 30 mol% of **N1** | 66 |

Reaction condition: **3** (0.3 mmol), **4a** or **7** (0.6 mmol), $[Pd(allyl)Cl]_2$ (0.015 mmol), P(2-furyl)$_3$ (0.06 mmol), **N1** (0.15 mmol), $Cs_2CO_3$ (1.2 mmol), $NMe_4Cl$ (1.2 mmol), dioxane (2.25 mL) and THF (0.75 mL) in 85 °C, 14 h.

### 3. Kinetic Monitoring of Reactions of (*Z*)- and (*E*)-4aa with 3aa



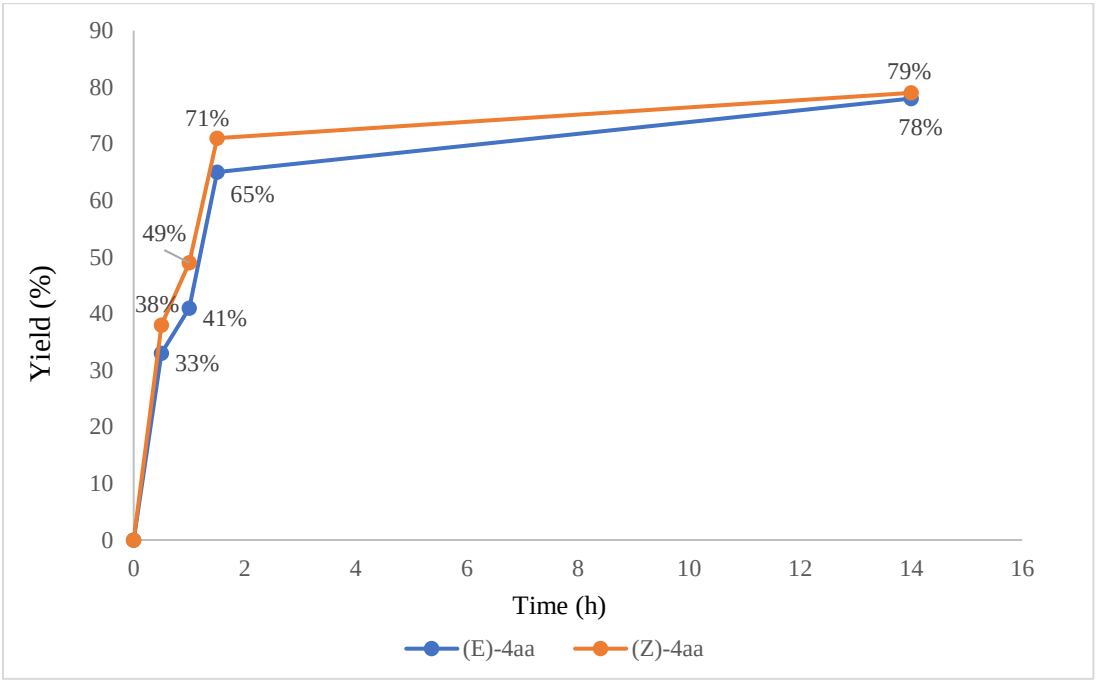




**Figure S1** Reaction profile of annulation reaction with (*E*)- and (*Z*)-**4aa**. Reactions were set up in separate vials and yields were determined by $^{1}$H NMR using tetrachloroethane as internal standard.

The above kinetic studies are inconsistent with ***path a***; however they are consistent with both ***path b*** and ***path c***. ***Path b*** involves a 5-endo-trig cyclization, which was considered as disfavored according to the original Baldwin's rule. Yet, a small number of experimental examples[1] as well as computational studies[2] could support the feasibility of such a process. ***Path c*** involves a Nazarov-type cyclization, followed by β-hydrogen elimination, which cannot be ruled out in the current stage.

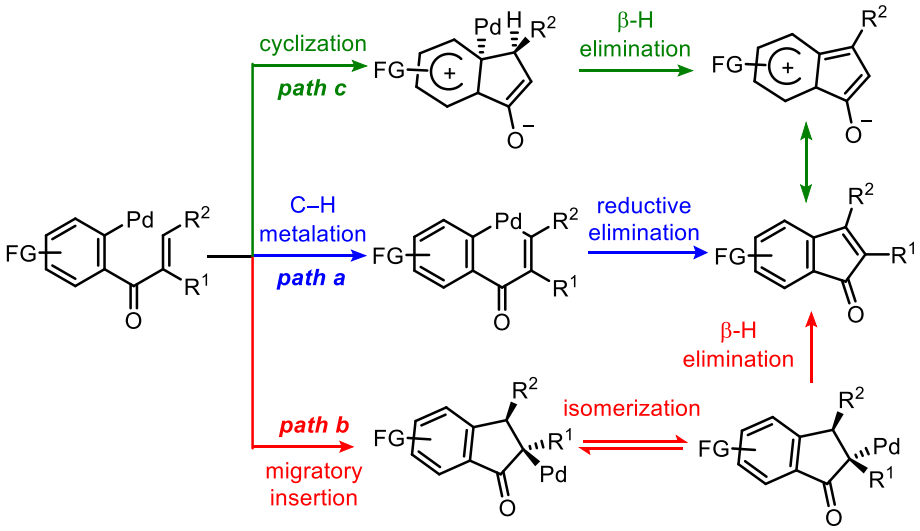



**Figure S2** Possible reaction pathways.

## 4. Experimental Procedures and Characterization Data

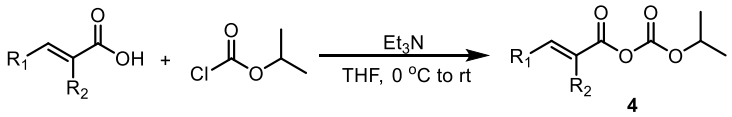
### 4.1. Preparation of aryl iodides (3):

Aryl iodides **3a**, **3b**, **3d**, **3m**, **3p**, and **3s** are commercially available from Combi-Blocks or Sigma-Aldrich, and were used without further purification. Aryl iodides **3c**,[3] **3e**,[4] **3f**,[5] **3g**,[6] **3h**,[7] **3i**,[8] **3j**,[9] **3k**,[10] **3l**,[11] **3n**,[9] **3o**,[12] **3q**,[13] and **3r**[14] were known compounds and were synthesized according to the reported procedures.

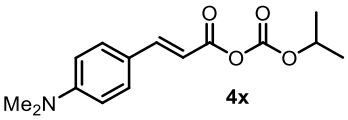
### 4.2 Preparation of substituted acrylic anhydrides (4):

Anhydrides **4a**,[15] **4t**,[15] **4u**,[15] **4v**,[15] **4w**,[15] and symmetrical anhydride **4ac'**[16] were known compounds and synthesized according to the reported procedures. Anhydrides **4x**, **4y**, **4z**, and **4ab** were synthesized according to the following procedure:

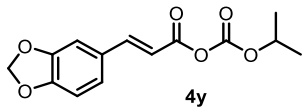
General procedure for preparation of **4**:




In a round-bottom flask, substituted acrylic acids (10.0 mmol, 1.0 equiv) and trimethylamine (1.40 mL, 10.0 mmol, 1.0 equiv) were dissolved in 50 mL anhydrous tetrahydrofuran. The mixture was stirred for 10 min at room temperature. In another round-bottom flask, a 2 M isopropyl choloroformate toluene solution (6.0 mL, 12.0 mmol, 1.2 equiv) was diluted with 50 mL anhydrous tetrahydrofuran. At 0 ℃, the mixture of acrylic acid and triethylamine was added dropwise to the diluted isopropyl choloroformate solution via addition funnel over 40 min. Then, the reaction mixture was stirred at room temperature for additional 1 hour monitored by TLC. When TLC showed full conversion, 10% citric acid (30 mL) was added to the reaction mixture until the system became clear. After extraction with ethyl ether (40 mL×2), the organic layer was washed with saturated sodium bicarbonate solution (40 mL) and brine (40 mL) and dried over $MgSO_4$. The solvents were evaporated under vacuum. The crude products can be directly used in the following Pd/NBE-catalyzed annulation reaction.

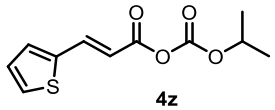


**4x**: Yellow solid (10 mmol scale, 2.66 g, 96%). $R_f$ = 0.30 (hexane/ethyl acetate = 3:1). Melting point: 65-67 ℃. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 15.6 Hz, 1H), 7.42 (d, *J* = 8.9 Hz, 2H), 6.66 (d, *J* = 8.9 Hz, 2H), 6.16 (d, *J* = 15.7 Hz, 1H), 5.03 (hept, *J* = 6.2 Hz, 1H), 3.04 (d, *J* = 1.3 Hz, 6H), 1.38 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 152.4, 149.7, 149.2, 130.5, 121.3, 111.7, 108.9, 73.6, 40.0, 21.5. **IR** (KBr): 2984, 1790, 1724, 1596, 1528, 1487, 1373, 1244, 1147, 1063 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{15}H_{20}NO_4$ ($M+H^+$): 278.1387, found: 278.1390.



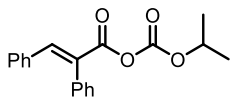
**4y**

**4y**: White solid (10 mmol scale, 2.59 g, 93%). $R_f$ = 0.15 (hexane/ethyl acetate = 10:1). Melting point: 62-64 ℃. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 15.8 Hz, 1H), 6.99 (d, *J* = 8.9 Hz, 1H), 6.98 (s, 1H), 6.78 (d, *J* = 8.3 Hz, 1H), 6.17 (d, *J* = 15.8 Hz, 1H), 5.98 (s, 2H), 5.00 (hept, *J* = 6.3 Hz, 1H), 1.35 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.1, 150.4, 148.7, 148.4, 127.9, 125.4, 113.1, 108.5, 106.5, 101.7, 74.0, 21.3. **IR** (KBr): 2985, 1798, 1731, 1602, 1504, 1450, 1365, 1267,1157, 1070 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{14}H_{15}O_6$ ($M+H^+$): 279.0863, found: 279.0870.



**4z**

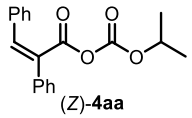
**4z**: Brown oil (10 mmol scale, 2.29 g, 95%). $R_f$ = 0.20 (hexane/ethyl acetate = 10:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 15.6 Hz, 1H), 7.45 (d, *J* = 5.0 Hz, 1H), 7.31 (d, *J* = 3.6 Hz, 1H), 7.07 (ddd, *J* = 4.8, 3.7, 1.0 Hz, 1H), 6.18 (d, *J* = 15.6 Hz, 1H), 5.02 (hept, *J* = 6.4 Hz, 1H), 1.36 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.8, 148.6, 140.9, 138.7, 132.4, 130.1, 128.4, 113.9, 74.1, 21.4. **IR** (KBr): 2984, 1797, 1732, 1620, 1515, 1467, 1361, 1269 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{11}H_{13}O_4S$ ($M+H^+$): 241.0529, found: 241.0530.



(*E*)-**4aa**

The corresponding acid for synthesizing (*E*)-**4aa** was a known compound.[17]

**(*E*)-4aa**: White solid (10 mmol scale, 2.86 g, 92%). $R_f$ = 0.35 (hexane/ethyl acetate = 10:1). Melting point: 69-71 ℃. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.46 – 7.39 (m, 3H), 7.31 – 7.26 (m, 3H), 7.23 – 7.18 (m, 2H), 7.12 – 7.08 (m, 2H), 5.06 (hept, *J* = 6.3 Hz, 1H), 1.40 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.6, 149.0, 144.1, 134.4, 133.9, 131.0, 130.3, 129.9, 129.8, 128.8, 128.3, 74.6, 21.5. **IR** (KBr): 2984, 1797, 1731, 1617, 1493, 1377, 1274, 1195, 1133, 1090, 1032 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{19}H_{19}O_4$ ($M+H^+$): 311.1278, found: 311.1280.

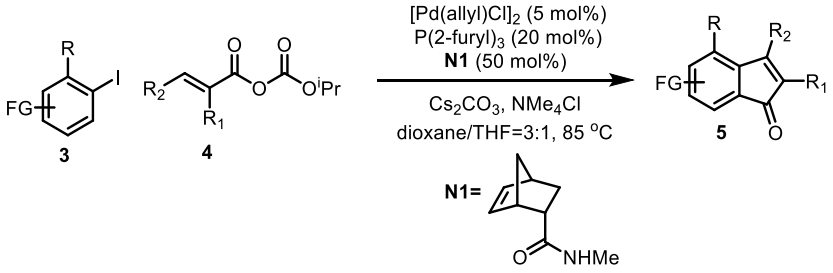


(*Z*)-**4aa**

The corresponding acid for synthesizing (*Z*)-**4aa** was a known compound.[17]

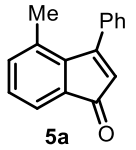
(*Z*)-**4aa**: White solid (2 mmol scale, 0.58 g, 93%). $R_f$ = 0.35 (hexane/ethyl acetate = 10:1). Melting point: 75-77 ℃. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.35 (m, 4H), 7.32 – 7.20 (m, 6H), 7.08 (s, 1H), 4.84 (hept, *J* = 6.3 Hz, 1H), 1.18 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.7, 148.3, 136.2, 135.5, 134.7, 132.3, 128.9, 128.7, 128.6, 128.6, 128.5, 126.8, 74.5, 21.3. **IR** (KBr): 3005, 1803, 1752, 1623, 1496, 1377, 1269, 1203, 1122, 1076, 1032 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{19}H_{19}O_4$ ($M+H^+$): 311.1278, found: 311.1280.

### 4.3 General Procedure of Pd/NBE-Catalyzed Annulation Reaction



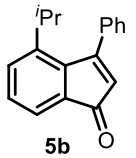

Oven-dried vial A (4 mL) was charged with aryl iodide (0.3 mmol, 1.0 equiv), substituted acrylic anhydride (0.6 mmol, 2.0 equiv), $Cs_2CO_3$ (392.4 mg, 1.20 mmol, 4.0 equiv), and $NMe_4Cl$ (130.4 mg, 1.20 mmol, 4.0 equiv). Oven-dried vial B (2 mL) was charged with **N1** (22.7 mg, 0.15 mmol, 0.5 equiv), allylpalladium(II) chloride dimer (5.1 mg, 0.015 mmol, 0.05 equiv) and tris(2-furyl)phosphine (13.9 mg, 0.06 mmol, 0.20 equiv). After transferred into a nitrogen-filled glovebox, 0.5 mL of degassed 1,4-dioxane was added into vial B and the resulting mixture was stirred at room temperature for 5 minutes until a solution was formed. Degassed 1,4-dioxane (1.75 mL) and tetrahydrofuran (0.75 mL) were added to vial A, and the solution in vial B was transferred to vial A. Vial A was tightly sealed, transferred

out of glovebox and stirred on a pie-block preheated to 85 ℃ for 14 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated under vacuum. The residue was directly purified by flash column chromatography on silica gel to give the desired product. (Note: Carefully dried reagent, freshly distilled anhydrous solvent and vigorous stirring were important to achieve reproducible yields.)



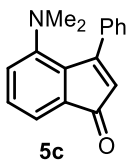
**5a**

**5a**: Yellow oil (0.3 mmol scale, 50.1 mg, 76%). $R_f$ = 0.30 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 5H), 7.39 – 7.32 (m, 1H), 7.17 (t, *J* = 7.4 Hz, 1H), 7.13 – 7.06 (m, 1H), 5.78 (s, 1H), 1.95 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.3, 166.2, 141.5, 137.2, 136.1, 133.0, 132.3, 129.3, 129.2, 128.5, 126.9, 125.8, 120.6, 19.8. **IR** (KBr): υ 3058, 2925, 1703, 1613, 1556, 1443, 1363, 1272, 1249, 1164, 1086 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{16}H_{13}O$ ($M+H^+$): 221.0961, found: 221.0965.



**5b**

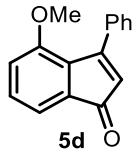
**5b**: Yellow oil (0.3 mmol scale, 49.1 mg, 66%). $R_f$ = 0.30 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.42 (m, 5H), 7.39 (dd, *J* = 6.7, 1.4 Hz, 1H), 7.34 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.32 – 7.27 (m, 1H), 5.80 (s, 1H), (hept, *J* = 6.6 Hz, 1H), 1.03 (d, *J* = 6.8 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.0, 166.3, 144.6, 139.8, 136.8, 132.2, 132.0, 129.8, 129.0, 128.4, 126.6, 126.4, 120.5, 27.3, 23.4. **IR** (KBr): υ 3059, 2965, 1706, 1611, 1560, 1443, 1385, 1283, 1224, 1173 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{17}O$ ($M+H^+$): 249.1274, found: 249.1283.



**5c**

**5c**: Purple oil (0.3 mmol scale, 40.4 mg, 54%). $R_f$ = 0.20 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.75 – 7.58 (m, 2H), 7.49 – 7.34 (m, 3H), 7.24-7.19 (m, 1H), 7.18 – 7.11 (m, 1H), 7.05 (dt, *J* = 8.2, 1.4 Hz, 1H), 5.80

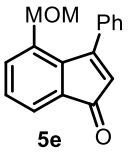
(s, 1H), 2.39 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.1, 166.2, 148.4, 135.2, 134.9, 130.6, 130.3, 129.4, 127.7, 126.9, 124.6, 123.6, 116.0, 43.8. **IR** (KBr): υ 3056, 2923, 1695, 1502, 1443, 1374, 1295, 1114, 1086, 1025 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{16}NO$ ($M+H^+$): 250.1226, found: 250.1230.



**5d**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

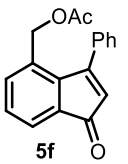
**5d**: Orange solid (0.3 mmol scale, 53.8 mg, 76%). Melting point: 91-93 °C. $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63-7.59 (m, 2H), 7.48 – 7.39 (m, 3H), 7.29 (dd, *J* = 8.4, 7.0 Hz, 1H), 7.18 (dd, *J* = 7.0, 0.9 Hz, 1H), 7.00 (dd, *J* = 8.4, 0.9 Hz, 1H), 5.79 (s, 1H), 3.70 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.9, 165.2, 153.6, 134.9, 134.4, 131.6, 129.6, 128.8, 127.9, 127.6, 123.8, 119.0, 115.7, 55.5. **IR** (KBr): 3061, 2938, 1699, 1607, 1551, 1476, 1368, 1269, 1128, 1096 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{16}H_{13}O_2$ ($M+H^+$): 237.0910, found: 237.0914.



**5e**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

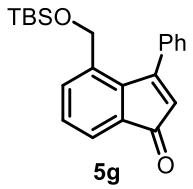
**5e**: Yellow oil (0.3 mmol scale, 47.3 mg, 63%). $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.70 – 7.59 (m, 2H), 7.49 – 7.40 (m, 3H), 7.30 – 7.24 (m, 2H), 7.18 (dt, *J* = 7.9, 1.4 Hz, 1H), 5.85 (s, 1H), 4.95 (s, 2H), 3.31 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.6, 164.8, 151.3, 134.9, 134.4, 131.4, 130.1, 129.6, 127.8, 127.6, 124.3, 122.7, 116.9, 94.8, 56.2. **IR** (KBr): 3060, 2905, 1703, 1606, 1483, 1369, 1269, 1154, 1081, 1008 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{15}O_2$ ($M+H^+$): 251.1067, found: 251.1073.



**5f**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

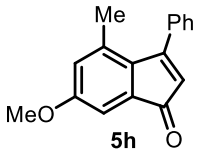
**5f**: Yellow solid (0.3 mmol scale, 56.9 mg, 68%). Melting point: 80-82 ℃. $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 6.0, 2.3 Hz, 1H), 7.49 – 7.40 (m, 5H), 7.38 – 7.27 (m, 2H), 5.86 (s, 1H), 4.70 (s, 2H), 1.94 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.4, 170.1, 165.0, 142.4, 135.5, 135.3, 132.4, 130.5, 129.8, 129.5, 128.6, 126.6, 126.4, 122.7, 62.5, 20.6. **IR** (KBr): 3060, 2910, 1738, 1708, 1613, 1561, 1490, 1443, 1363, 1085, 1020 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{15}O_3$ ($M+H^+$): 279.1016, found: 279.1015.



**5g**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95ºC without $NMe_4Cl$ in dioxane (3 mL).

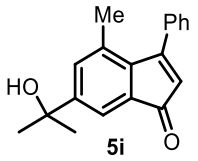
**5g**: Yellow solid (0.3 mmol scale, 82.9 mg, 79%). Melting point: 72-74 ℃. $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.35 (m, 6H), 7.30 (t, *J* = 7.6 Hz, 1H), 5.80 (s, 1H), 4.23 (s, 2H), 0.81 (s, 9H), -0.11 (s, 6H).**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.1, 165.2, 140.0, 136.5, 136.3, 133.0, 131.7, 129.6, 129.3, 128.6, 126.5, 125.8, 121.4, 61.3, 25.8, 18.3, -5.6. **IR** (KBr): 3061, 2929, 1709, 1613, 1471, 1377, 1289, 1270, 1105, 1072, 760 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{22}H_{27}O_2Si$ ($M+H^+$): 351.1775, found: 351.1772.



**5h**

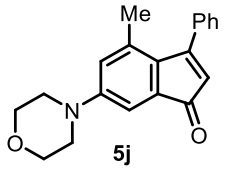
The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95ºC without $NMe_4Cl$ in dioxane (3 mL).

**5h**: Yellow oil (0.3 mmol scale, 52.5 mg, 70%). $R_f$ = 0.2 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 5H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 5.68 (s, 1H), 3.81 (s, 3H), 1.91 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.9, 167.2, 161.0, 136.1, 134.7, 134.4, 133.5, 129.1, 128.4, 126.8, 124.5, 119.3, 108.6, 55.7, 20.0. **IR** (KBr): 3051, 2925, 1698, 1595, 1465, 1438, 1367, 1264, 1083, 1012 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{15}O_2$ ($M+H^+$): 251.1067, found: 251.1070.



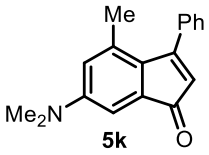

**5i**

**5i**: Orange oil (0.3 mmol scale, 65.8 mg, 79%). $R_f$ = 0.25 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.49 – 7.38 (m, 6H), 7.31 – 7.27 (m, 1H), 5.76 (s, 1H), 1.96 (s, 4H), 1.57 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.3, 166.2, 150.9, 139.8, 135.9, 132.8, 132.7, 132.6, 129.2, 128.5, 126.8, 125.7, 117.6, 72.4, 31.5, 19.9. **IR** (KBr): υ 3058, 2974, 1704, 1621, 1556, 1444, 1399, 1270, 1203, 1029 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{19}H_{19}O_2$ (M+H$^+$): 279.1380, found: 279.1365.



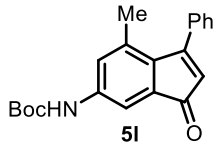

**5j**

**5j**: (CAS: 1808175-82-7) Red oil (0.3 mmol scale, 80.5 mg, 88%). $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.32 (m, 5H), 7.03 (d, *J* = 2.3 Hz, 1H), 6.41 (d, *J* = 2.2 Hz, 1H), 5.63 (s, 1H), 3.92 – 3.78 (m, 4H), 3.26 – 3.16 (m, 4H), 1.91 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.5, 167.6, 152.2, 136.2, 134.5, 134.0, 131.7, 129.1, 128.4, 126.8, 123.8, 119.5, 109.8, 66.6, 48.6, 20.2. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data.[2]



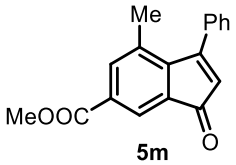

**5k**

**5k**: Purple oil (0.3 mmol scale, 61.8 mg, 78%). $R_f$ = 0.20 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.39 (m, 5H), 6.90 (d, *J* = 2.6 Hz, 1H), 6.16 (d, *J* = 2.5 Hz, 1H), 5.54 (s, 1H), 3.00 (s, 6H), 1.89 (s, 3H).**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 198.1, 168.6, 151.4, 136.7, 134.9, 134.1, 128.9, 128.3, 128.3, 126.8, 122.5, 115.7, 107.4, 40.5, 20.3. **IR** (KBr): υ 3056, 2925, 1707, 1637, 1498, 1373, 1270, 1176, 1108, 760 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{18}NO$ (M+H$^+$): 264.1383, found: 264.1385.




**5l**

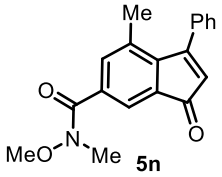
**5l**: Orange oil (0.3 mmol scale, 76.4 mg, 76%). $R_f$ = 0.35 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.37 (m, 5H), 7.32 (s, 1H), 7.21 (d, *J* = 2.1 Hz, 1H), 6.71 (s, 1H), 5.69 (s, 1H), 1.91 (s, 3H), 1.51 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.7, 166.8, 152.4, 139.5, 135.9, 135.4, 134.0, 133.8, 129.1, 128.4, 126.8, 124.8, 124.3, 112.3, 81.0, 28.2, 20.0. **IR** (KBr): 3059, 2929, 1731, 1705, 1621, 1535, 1478, 1368, 1270, 1154 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{22}NO_3$ ($M+H^+$): 336.1594, found: 336.1591.




**5m**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

**5m**: Yellow oil (0.3 mmol scale, 54.2 mg, 65%). $R_f$ = 0.25 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.86 (s, 1H), 7.50 – 7.39 (m, 5H), 5.93 (d, *J* = 1.3 Hz, 1H), 3.91 (s, 3H), 1.99 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.7, 166.0, 165.3, 145.5, 139.0, 135.3, 133.0, 132.5, 131.1, 129.4, 128.6, 127.8, 126.9, 121.0, 52.3, 19.7. **IR** (KBr): 3054, 2952, 1722, 1619, 1592, 1435, 1390, 1293, 1213, 1105 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{15}O_3$ ($M+H^+$): 279.1016, found: 279.1019.

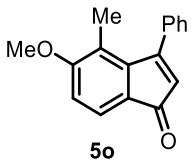



**5n**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

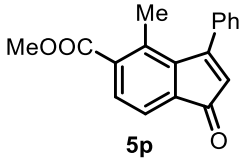
**5n**: Orange oil (0.3 mmol scale, 72.8 mg, 79%). $R_f$ = 0.15 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.48 (s, 1H), 7.46-7.37(m, 5H), 5.86 (s, 1H), 3.58 (s, 3H), 3.34 (s, 3H), 1.96 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.0, 168.5, 165.5, 143.3, 137.6, 135.4, 135.0, 132.8, 131.8, 129.3, 128.5, 127.0, 126.8, 120.0, 61.1,

33.5, 19.7. **IR** (KBr): 3058, 2934, 1708, 1644, 1445, 1385, 1291, 1269, 1181, 1035, 760 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{19}H_{18}NO_3$ ($M+H^+$): 308.1281, found: 308.1288.




**5o**

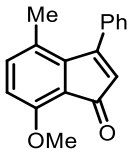
**5o**: Yellow oil (0.3 mmol scale, 59.2 mg, 79%). $R_f$ = 0.2 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.35 (m, 6H), 6.60 (d, *J* = 7.9 Hz, 1H), 5.80 (s, 1H), 3.85 (s, 3H), 1.81 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.0, 164.3, 163.3, 143.2, 136.2, 129.0, 128.4, 127.8, 127.0, 124.8, 124.3, 121.9, 107.6, 55.9, 12.5. **IR** (KBr): 3059, 2925, 1698, 1594, 1437, 1366, 1264, 1223, 1083, 1011 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{15}O_2$ ($M+H^+$): 251.1067, found: 251.1070.




**5p**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

**5p**: Yellow solid (0.3 mmol scale, 68.4 mg, 82%). Melting point: 106-108 °C. $R_f$ = 0.25 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.4 Hz, 1H), 7.59 – 7.32 (m, 6H), 5.87 (s, 1H), 3.87 (s, 3H), 2.09 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.9, 167.8, 166.5, 142.6, 137.5, 135.9, 1345, 133.6, 132.0, 129.4, 128.6, 126.8, 126.7, 119.7, 52.2, 17.9. **IR** (KBr): 3062, 2950, 1707, 1602, 1489, 1442, 1353, 1287, 1208, 1119, 1086 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{15}O_3$ ($M+H^+$): 279.1016, found: 279.1020.

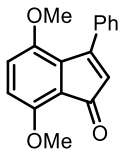



**5q**

The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

**5q**: Yellow solid (0.3 mmol scale, 63.1 mg, 84%). Melting point: 122-124 °C. $R_f$ = 0.2 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.24 (m, 5H), 6.98 (d, *J* = 8.7 Hz, 1H), 6.73 (d, *J* = 8.7 Hz, 1H), 5.64 (s, 1H),

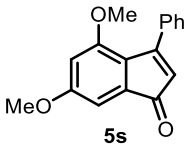
3.87 (s, 3H), 1.76 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.5, 163.2, 155.1, 143.2, 139.3, 136.1, 128.8, 128.4, 126.9, 126.5, 125.9, 116.4, 115.0, 55.9, 19.0. **IR** (KBr): 3061, 2938, 1695, 1607, 1486, 1443, 1228, 1211,1174, 1051 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{15}O_2$ ($M+H^+$): 251.1067, found: 251.1072.



**5r**

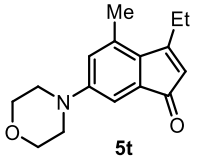
The reaction was run with cinnamic anhydride **7** (0.6 mmol) instead of **4a** at 95°C without $NMe_4Cl$ in dioxane (3 mL).

**5r**: Orange solid (0.3 mmol scale, 51.9 mg, 65%). Melting point: 134-136 °C. $R_f$ = 0.25 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.64 – 7.49 (m, 2H), 7.39 (dd, *J* = 5.2, 2.0 Hz, 3H), 6.98 (d, *J* = 9.2 Hz, 1H), 6.89 (d, *J* = 9.2 Hz, 1H), 5.74 (d, *J* = 1.8 Hz, 1H), 3.93 (s, 3H), 3.59 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.0, 162.3, 151.5, 148.3, 134.9, 130.6, 129.2, 127.8, 127.5, 124.9, 122.1, 118.1, 117.0, 56.3. **IR** (KBr): 3053, 2937, 1694, 1587, 1491, 1289, 1270, 1176, 1057, 743 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{17}H_{15}O_3$ ($M+H^+$): 267.1016, found: 267.1025.



**5s**

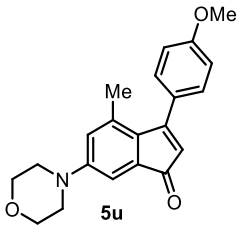
**5s**: (CAS: 885263-46-7) Red solid (0.3 mmol scale, 60.6 mg, 76%). Melting point: 146-148 °C. $R_f$ = 0.3 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.66 – 7.55 (m, 2H), 7.47 – 7.33 (m, 3H), 6.80 (d, J = 2.1 Hz, 1H), 6.44 (d, J = 2.1 Hz, 1H), 5.69 (s, 1H), 3.84 (s, 3H), 3.67 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.5, 166.3, 163.1, 154.6, 136.0, 134.9, 129.7, 127.8, 127.6, 122.1, 121.0, 103.1, 102.6, 55.8, 55.4. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data[3].



**5t**

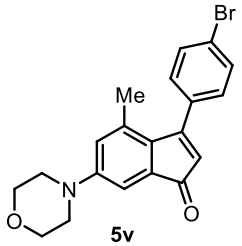
The reaction was run at 85°C for 3 hours.

**5t**: Orange oil (0.3 mmol scale, 44.7 mg, 58%). $R_f$ = 0.30 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.94 (d, *J* = 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.56 (t, *J* = 1.9 Hz, 1H), 3.88 – 3.80 (m, 4H), 3.22 – 3.15 (m, 4H), 2.68 (qd, *J* = 7.2, 1.9 Hz, 2H), 2.39 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 198.1, 172.4, 152.0, 134.7, 132.8, 132.4, 120.2, 119.8, 109.1, 66.6, 48.7, 25.4, 20.1, 11.6. **IR** (KBr): 3058, 2920, 1708, 1609, 1488, 1352, 1291, 1269, 1181, 1035, 763 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{16}H_{20}NO_2$ ($M+H^+$): 258.1489, found: 258.1494.



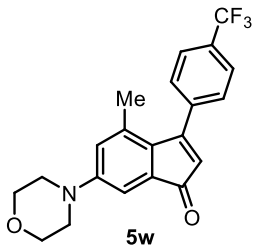
**5u**

**5u**: Red oil (0.3 mmol scale, 87.5 mg, 87%). $R_f$ = 0.20 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 – 7.32 (m, 2H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.98 – 6.93 (m, 2H), 6.41 (d, *J* = 2.4 Hz, 1H), 5.60 (s, 1H), 3.86 (s, 3H), 3.85 – 3.81 (m, 4H), 3.23 – 3.15 (m, 4H), 1.98 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.3, 167.7, 160.5, 152.2, 134.9, 133.9, 131.7, 128.5, 128.3, 123.3, 119.5, 113.8, 109.7, 66.6, 55.3, 48.6, 20.5. **IR** (KBr): 3057, 2931, 1715, 1602, 1510, 1376, 1269, 1244, 1175, 1121, 1029 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{22}NO_3$ ($M+H^+$): 336.1594, found: 336.1600.



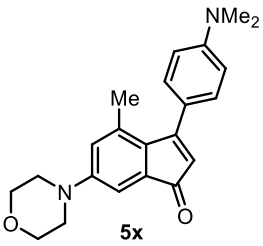
**5v**

**5v**: Red oil (0.3 mmol scale, 93.1 mg, 81%). $R_f$ = 0.25 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.36 – 7.26 (m, 2H), 7.02 (d, *J* = 2.4 Hz, 1H), 6.40 (d, *J* = 2.4 Hz, 1H), 5.62 (s, 1H), 3.90 – 3.78 (m, 4H), 3.26 – 3.12 (m, 4H), 1.91 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.1, 166.2, 152.3, 135.1, 134.4, 133.9, 131.6, 131.2, 128.5, 124.0, 123.2, 119.4, 109.9, 66.5, 48.5, 20.3. **IR** (KBr): 3056, 2962, 1764, 1699, 1483, 1382, 1360, 1257, 1216, 1176, 1070 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{20}H_{19}BrNO_2$ ($M+H^+$): 384.0594, found: 384.0597.



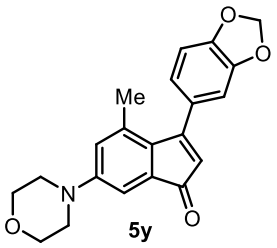

**5w**

**5w**: Red oil (0.3 mmol scale, 75.0 mg, 67%). $R_f$ = 0.30 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.07 (d, *J* = 2.4 Hz, 1H), 6.44 (d, *J* = 2.4 Hz, 1H), 5.68 (s, 1H), 3.87-3.84 (m, 4H), 3.25-3.21 (m, 4H), 1.90 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.9, 165.6, 152.4, 140.1, 134.9, 133.9, 131.2, 131.1 (q, *J* = 32.3 Hz), 127.3, 125.5 (q, *J* = 3.3 Hz), 124.4, 123.8 (q, *J* = 273.4 Hz), 119.4, 110.0, 66.6, 48.5, 20.2. **$^{19}$F NMR** (470 MHz, $CDCl_3$) δ -62.69. **IR** (KBr): 3060, 2981, 1702, 1618, 1482, 1450, 1327, 1269, 1167, 1124, 1067 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{19}F_3NO_2$ ($M+H^+$): 374.1362, found: 374.1367.



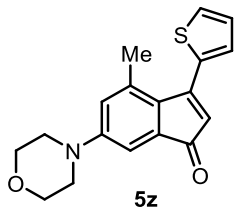

**5x**

**5x**: Red oil (0.3 mmol scale, 88.7 mg, 85%). $R_f$ = 0.20 (hexane/ethyl acetate = 2:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.32 (m, 2H), 7.01 (d, *J* = 2.4 Hz, 1H), 6.78 – 6.70 (m, 2H), 6.43 (d, *J* = 2.4 Hz, 1H), 5.60 (s, 1H), 3.88 – 3.81 (m, 4H), 3.24 – 3.17 (m, 4H), 3.06 – 2.99 (m, 6H), 2.11 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.2, 168.8, 152.0, 151.3, 135.8, 133.9, 131.8, 128.6, 123.1, 122.2, 119.5, 111.3, 109.44, 66.7, 48.7, 40.2, 20.9. **IR** (KBr): 3057, 1961, 1689, 1603, 1509, 1448, 1360, 1303, 1260, 1168, 1094 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{22}H_{25}N_2O_2$ ($M+H^+$): 349.1911, found: 349.1918.




**5y**

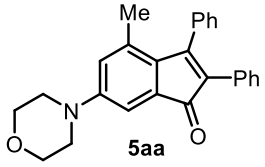
**5y**: Red oil (0.3 mmol scale, 84.8 mg, 81%). $R_f$ = 0.15 (hexane/ethyl acetate = 2:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.01 (d, *J* = 2.4 Hz, 1H), 6.95 – 6.85 (m, 3H), 6.41 (d, *J* = 2.4 Hz, 1H), 6.02 (s, 2H), 5.60 (s, 1H), 3.96 – 3.59 (m, 4H), 3.21 – 3.18 (m, 4H), 2.00 (s, 3H).**$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.2, 167.4, 152.2, 148.5, 147.7, 134.8, 133.9, 131.5, 129.8, 123.5, 120.8, 119.5, 109.7, 108.3, 107.5, 101.36, 66.6, 48.6, 20.4. **IR** (KBr): 3043, 2947, 1695, 1615, 1484, 1445, 1382, 1289, 1269, 1243, 1122, 1038 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{20}NO_4$ ($M+H^+$): 350.1387, found: 350.1394.



**5z**

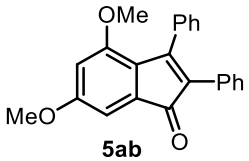
The reaction was run at 85℃ for 4 hours.

**5z**: Purple oil (0.3 mmol scale, 62.5 mg, 67%). $R_f$ = 0.30 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.22 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.05 (dd, *J* = 5.1, 3.6 Hz, 1H), 6.95 (d, *J* = 2.5 Hz, 1H), 6.38 (d, *J* = 2.4 Hz, 1H), 5.69 (s, 1H), 3.81 – 3.74 (m, 4H), 3.17-3.11 (m, 4H), 2.12 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.3, 160.0, 152.2, 136.8, 134.8, 134.1, 130.9, 127.9, 127.6, 127.4, 124.8, 119.6, 109.7, 66.6, 48.5, 20.7. **IR** (KBr): 3074, 2961, 1761, 1615, 1548, 1422, 1381, 1359, 1290, 1178, 1087, 1014 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{18}NO_2S$ ($M+H^+$): 312.1053, found: 312.1060.



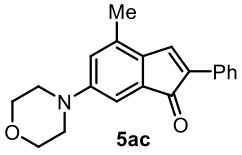
**5aa**

**5aa**: Purple solid (0.3 mmol scale, 90.3 mg, 79%). Melting point: 201-203 ℃. $R_f$ = 0.25 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.35 (m, 3H), 7.34 – 7.27 (m, 2H), 7.23 – 7.13 (m, 5H), 7.12 (d, *J* = 2.4 Hz, 1H), 6.43 (d, *J* = 2.4 Hz, 1H), 3.92 – 3.76 (m, 4H), 3.22 (dd, *J* = 5.8, 3.9 Hz, 4H), 1.76 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.9, 159.7, 151.9, 136.2, 134.0, 132.9, 132.4, 131.9, 131.0, 129.6, 128.7, 128.3, 127.7, 127.0, 120.4, 110.0, 66.6, 48.7, 19.8. **IR** (KBr): 3056, 2985, 1699, 1617, 1432, 1387, 1279, 1258, 1122, 1017 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{26}H_{24}NO_2$ ($M+H^+$): 382.1802, found: 382.1808.




**5ab**

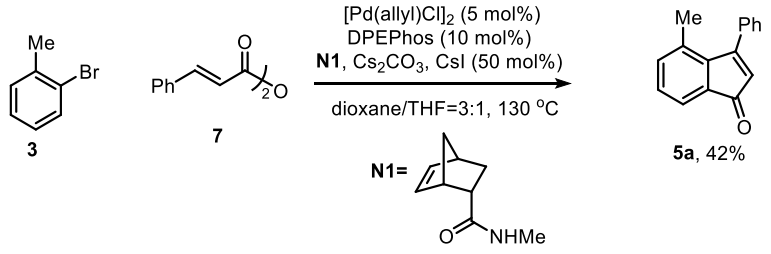
**5ab**: (CAS: 1198193-82-6) Purple solid (0.3 mmol scale, 84.1 mg, 80%). Melting point: 187-189 ℃. $R_f$ = 0.15 (hexane/ethyl acetate = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.25-7.18 (m, 5H), 7.14– 7.06 (m, 3H), 7.04 (dd, *J* = 7.6 Hz, 1.8 Hz, 2H), 6.79 (d, *J* = 2.2 Hz, 1H), 6.34 (d, *J* = 2.2 Hz, 1H), 3.76 (s, 3H), 3.47 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.1, 162.7, 158.3, 154.9, 134.8, 134.2, 131.1, 130.9, 129.9, 128.6, 128.4, 127.8, 127.5, 127.0, 122.4, 103.9, 102.7, 55.9, 55.6. **IR** (KBr): 3055, 2938, 1702, 1615, 1486, 1423, 1348, 1269, 1223, 1103, 1057 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{23}H_{19}O_3$ ($M+H^+$): 343.1329, found: 343.1334. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data[4].




**5ac**

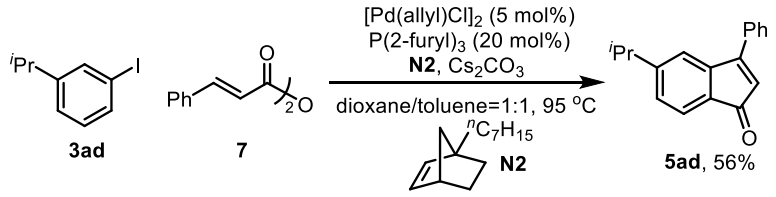
The reaction was run at 85℃ for 2 hours with **4ac**' (0.6 mmol) instead of **4ac**.

**5ac**: Purple solid (0.3 mmol scale, 39.4 mg, 43%). Melting point: 121-123 ℃. $R_f$ = 0.25 (hexane/ethyl acetate = 4:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.74 (d, *J* = 0.9 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.32 – 7.27 (m, 1H), 6.99 (d, *J* = 2.2 Hz, 1H), 6.52 (s, br, 1H), 3.88 – 3.82 (m, 4H), 3.23 – 3.17 (m, 4H), 2.29 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.5, 152.1, 142.6, 133.8, 133.1, 132.4, 132.3, 132.0, 128.5, 127.8, 126.8, 119.1, 110.3, 66.6, 49.0, 17.4. **IR** (KBr): 3054, 2960, 1703, 1618, 1595, 1481, 1379, 1260, 1153, 1122, 1028 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{20}H_{20}NO_2$($M+H^+$): 306.1489, found: 306.1092.

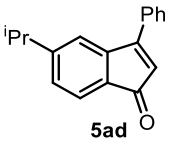



Oven-dried vial A (4 mL) was charged with **3** (51.3 mg, 0.3 mmol, 1.0 equiv), **7** (0.6 mmol, 2.0 equiv), $Cs_2CO_3$ (392.4 mg, 1.20 mmol, 4.0 equiv), and CsI (39.0 mg, 0.15 mmol, 0.5 equiv). Oven-dried vial B (2 mL) was charged with **N1**

(22.7 mg, 0.15 mmol, 0.5 equiv), allylpalladium(II) chloride dimer (5.1 mg, 0.015 mmol, 0.05 equiv) and DPEPhos (16.2 mg, 0.03 mmol, 0.1 equiv). After transferred into a nitrogen-filled glovebox, 0.5 mL of degassed 1,4-dioxane was added into vial B and the resulting mixture was stirred at room temperature for 5 minutes until a solution was formed. Degassed 1,4-dioxane (1.75 mL) and tetrahydrofuran (0.75 mL) were added to vial A, and the solution in vial B was transferred to vial A. Vial A was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 130 ℃ for 14 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated under vacuum. The residue was directly purified by flash column chromatography on silica gel to give the desired product **5a** as a yellow oil (0.3 mmol scale, 27.7 mg, 42%).

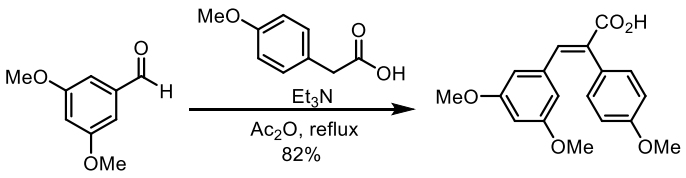



Oven-dried vial A (4 mL) was charged with **3ad** (0.3 mmol, 73.8 mg, 1.5 equiv), **7** (0.20 mmol, 55.6 mg, 1.0 equiv), and $Cs_2CO_3$ (262 mg, 0.80 mmol, 4.0 equiv). Oven-dried vial B (2 mL) was charged with **N2** (38.4 mg, 0.2 mmol, 1.0 equiv), allylpalladium(II) chloride dimer (3.7 mg, 0.01 mmol, 0.05 equiv) and tris(2-furyl)phosphine (9.4 mg, 0.04 mmol, 0.20 equiv). After transferred into a nitrogen-filled glovebox, 0.5 mL of degassed 1,4-dioxane was added into vial B and the resulting mixture was stirred at room temperature for 5 minutes until a solution was formed. Degassed 1,4-dioxane (0.5 mL) and toluene (1.0 mL) were added to vial A, and the solution in vial B was transferred to vial A. Vial A was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 95 ℃ for 14 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel to give the desired product.

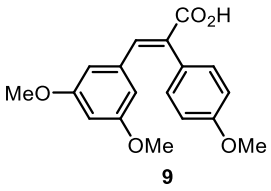


**5ad**: Yellow oil (0.2 mmol scale, 27.8 mg, 56%). $R_f$ = 0.25 (hexane/ethyl acetate = 4:1). δ 7.69 – 7.64 (m, 2H), 7.53 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.46 (d, *J* = 7.4 Hz, 1H), 7.21 (d, *J* = 1.3 Hz, 1H), 7.15 (dd, *J* = 7.3, 1.4 Hz, 1H), 5.98 (s, 1H), 2.94 (hept, *J* = 6.9 Hz, 1H), 1.26 (d, *J* = 6.9 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) 196.9,162.5, 154.8, 144.4, 133.2, 130.3, 130.2, 128.9, 127.4, 126.6, 123.5, 122.9, 120.5, 34.7, 23.7. **IR** (KBr): 2962, 1766, 1703, 1604, 1565, 1491, 1366, 1318, 1268, 1210, 1098, 1028 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{18}H_{17}O$ ($M+H^+$): 249.1274, found: 249.1278.

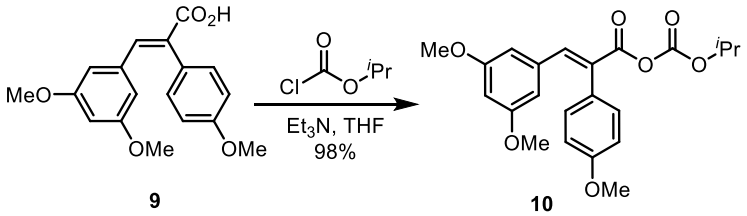
**4.4 Formal total synthesis of pauciflorol F**




Following a known procedure:[18] 4-methoxybenzenacetic acid (8.1 g, 50 mmol), **8** (8.1 g, 50 mmol) and triethylamine (5.1 g, 50 mmol) in acetic anhydride (10.2 g, 100 mmol) were added to a round-bottom flask and heated to 110 ℃ for 6 hours. Aqueous 6% HCl (70 mL) was added to the cooled reaction mixture. The precipitate was filtered, washed with cold water and dissolved in 2% NaOH (120 mL). The aqueous solution was washed with benzene (100 mL) and then acidified to pH ~5. The precipitate was filtered off and washed with cold water to afford crude product. Further recrystallization with ethanol could afford **9** as a white solid (12.9 g, 82%).

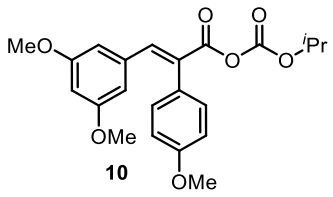



**9**: (CAS: 959961-16-1) White solid (12.7 g, 82%). **$^1$H NMR** (400 MHz, DMSO-d6) δ 7.68 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.38 (s, 1H), 6.29 (s, 2H), 3.77 (s, 3H), 3.53 (s, 6H). **$^{13}$C NMR** (101 MHz, DMSO-d6) δ 169.2, 160.4, 159.2, 138.9, 136.96, 134.3, 131.2, 129.0, 114.3, 108.6, 101.6, 55.5, 55.3. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data[6].



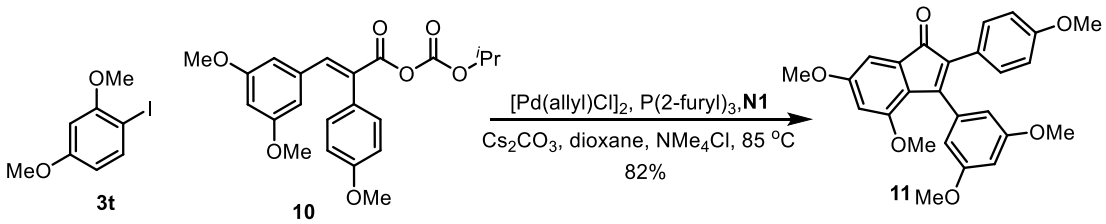

In a round-bottom flask, **9** (5.0 mmol, 1.57 g, 1.0 equiv) and trimethylamine (0.70 mL, 5.0 mmol, 1.0 equiv) were dissolved in 30 mL anhydrous tetrahydrofuran. The mixture was stirred for 10 min at room temperature. In another round-bottom flask, a 2 M isopropyl choloroformate toluene solution (3.0 mL, 6.0 mmol, 1.2 equiv) was diluted with 30 mL anhydrous tetrahydrofuran. At 0 ℃, the solution of **9** and triethylamine was added dropwise to the diluted

isopropyl choloroformate solution via addition funnel over 40 min. Then, the reaction mixture was stirred at room temperature for additional 1 hour monitored by TLC. When TLC shows full conversion, 10% citric acid (15 mL) was added to the reaction mixture until the system became clear. After extraction with ethyl ether (30 mL×2), the organic layer was washed with saturated sodium bicarbonate solution (20 mL) and brine (20 mL), and dried over $MgSO_4$. The solvents were evaporated under vacuum to give the crude product **10** as a white solid (1.96 g, 98%), which can be directly used in the subsequent annulation reaction.

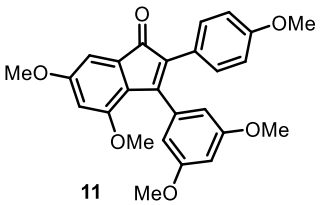


**10**

**10**: White solid (1.96 g, 98%). Melting point: 95-97 °C. **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.68 (s, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 6.96 (d, *J* = 8.3 Hz, 2H), 6.38 (s, 1H), 6.29 (s, 2H), 5.04 (hept, *J* = 6.2 Hz, 1H), 3.77 (s, 3H), 3.53 (s, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.2, 160.4, 159.2, 138.9, 136.96, 134.3, 131.2, 129.0, 114.3, 108.6, 101.6, 55.5, 55.3. **IR** (KBr):2988, 1773,1709, 1598, 1513, 1426, 1291, 1205, 1156, 1092, 1064 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{22}H_{25}O_7$ ($M+H^+$): 401.1595, found: 401.1604.



The reaction was run following the general Pd/NBE-catalyzed annulation procedure (0.3 mmol scale).

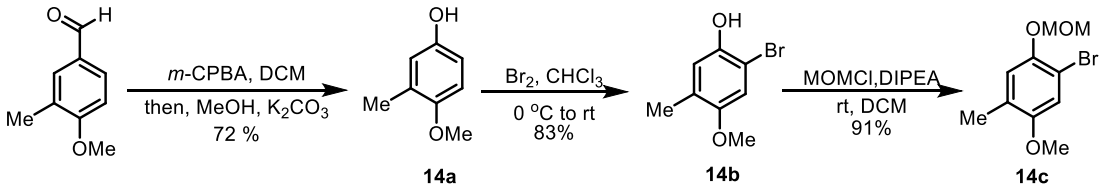


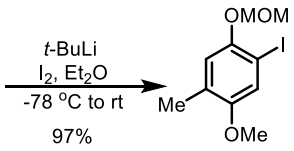
**11:** (CAS: 885263-37-6) Red solid (0.3 mmol scale, 106.3 mg, 82%). Melting point: 154-156 °C. $R_f$ = 0.15 (hexane/ethyl acetate = 2:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.13 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 2.1 Hz, 1H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.50 (d, *J* = 2.3 Hz, 2H), 6.43 (t, *J* = 2.3 Hz, 2H), 3.84 (s, 3H), 3.76 (s, 3H), 3.70 (s, 6H), 3.60 (s,

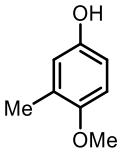
3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.5, 162.4, 160.1, 158.6, 156.5, 154.6, 136.9, 134.0, 130.9, 130.5, 123.5, 122.6, 113.4, 106.5, 104.0, 102.7, 100.9, 55.8, 55.7, 55.3, 55.1. **IR** (KBr): 2956, 1703, 1608, 1516, 1468, 1423, 1307, 1269, 1115, 1061 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{26}H_{25}O_6$ ($M+H^+$):433.1646, found: 433.1650. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data.

### 4.5 Total synthesis of acredinone A

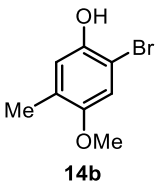
#### 4.5.1 Preparation of 14



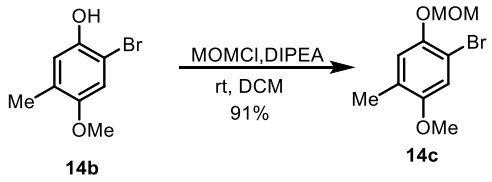




**14a** (CAS: 959961-16-1) was a known compound and prepared according to literature.[19] White solid (60 mmol scale, 5.96 g, 72%). $R_f$ = 0.15 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.77 – 6.60 (m, 3H), 6.25 (s, 1H), 3.80 (s, 3H), 2.20 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 151.8, 148.9, 128.0, 118.0, 112.7, 111.6, 56.1, 16.1. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data[19].

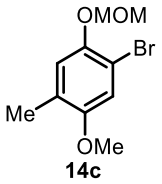



**14b** (CAS: 13523-07-4) was a known compound and prepared according to literature.[20] Off-white solid (35 mmol scale, 6.3 g, 83%). $R_f$ = 0.25 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.82 (d, *J* =

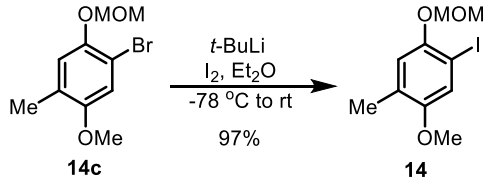
0.9 Hz, 1H), 5.19 (s, 1H), 3.76 (s, 3H), 2.15 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.0, 145.8, 128.0, 117.9, 113.3, 105.8, 55.9, 16.0. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data[20].




Following a known procedure:[21] diisopropylethylamine (6.7 mL, 40 mmol) was added to a solution of **14b** (4.34 g, 20 mmol) in 100 mL dichloromethane; then, MOMCl (2.28 mL, 30 mmol) in 30 mL dichloromethane was added dropwise at 0 °C via addition funnel. The mixture was further stirred at room temperature for 2 hours, diluted with dichloromethane (200 mL), and successively washed with water (50 mL), saturated $NaHCO_3$ (50 mL), and brine. Combined organic layers were dried over $MgSO_4$ and concentrated. The residue was purified by flash column chromatography on silica gel with hexane/ethyl acetate (20:1) to afford **14c** (4.76 g, 91%) as an off-white solid.

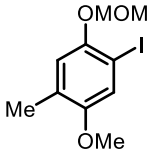



**14c**: Off-white solid (20 mmol scale, 4.76 g, 91%). Melting point: 36-38℃. $R_f$ = 0.35 (hexane/ethyl acetate = 20:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.97 (s, 2H), 5.14 (s, 2H), 3.76 (s, 3H), 3.53 (s, 3H), 2.16 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.2, 147.2, 126.8, 119.6, 114.6, 109.6, 95.9, 56.2, 55.7, 16.1. **IR** (KBr): 2952, 1497, 1440, 1369, 1270, 1203, 1152, 1085, 1013, 786 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{10}H_{14}BrO_3$ ($M+H^+$): 261.0121, found: 261.0126.




Following a known procedure:[21] *tert*-butyl lithium (1.7 M in hexanes, 19.4 mL, 33 mmol) was added to **14c** (3.92 g, 15 mmol) in 100 mL ether at -78 °C under nitrogen. The mixture was stirred at -78 °C for 2 h and a solution of $I_2$ (5.94 g, 23.4 mmol) in 50 mL diethyl ether was added via cannula. After warmed to room temperature and stirred for 12

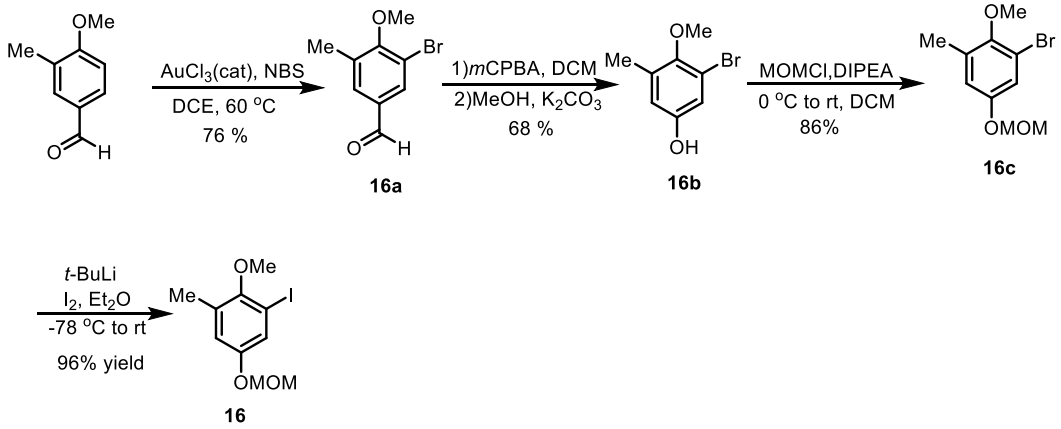
hours, the reaction mixture was quenched with saturated aqueous $NH_4Cl$ (50 mL). The organic layer was washed successively with saturated aqueous $Na_2S_2O_3$ (50 mL), water (50 mL) and brine (50 mL), dried over $MgSO_4$, and concentrated under vacuum. The residue was purified via flash column chromatography on silica gel with hexane/ethyl acetate (20:1) to afford **14** as an off-white solid (5.38 g, 97%).



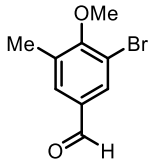

**14**

**14**: Off-white solid (18 mmol scale, 5.38 g, 97%). Melting point: 42-44 ℃. $R_f$ = 0.35 (hexane/ethyl acetate = 20:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.90 (d, *J* = 0.8 Hz, 1H), 5.14 (s, 2H), 3.77 (s, 3H), 3.53 (s, 3H), 2.17 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.5, 149.9, 128.0, 120.4, 118.1, 95.8, 83.1, 56.3, 55.8, 16.3. **IR** (KBr): 2952, 1493, 1439, 1365, 1269, 1202, 1151, 1084, 1012, 765 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{10}H_{14}IO_3$($M+H^+$): 308.9982, found: 308.9987.

**4.5.2 Preparation of 16**

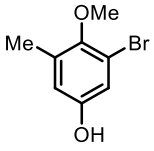



Following a known procedure:[22] 4-methoxy-3-methylbenzaldehyde (3.01 g, 20 mmol), *N*-bromosuccinimide (4.63 g, 26 mmol), $AuCl_3$ (60 mg, 1 mmol%) were dissolved in dichloroethane (30 mL) in a 40 mL vial. The reaction was stirred at 60 ℃ for 6 hours. The solution was then concentrated under vacuum, and the reside was purified by flash column chromatography on silica gel with hexane/ethyl acetate (40:1) to afford product **16a** as a yellow oil (3.48 g, 76%).



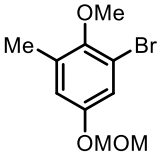

**16a**

**16a** (CAS: 808750-22-3) Yellow oil (20 mmol scale, 3.48 g, 76%). $R_f$ = 0.30 (hexane/ethyl acetate = 10:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.87 (d, *J* = 1.2Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 3.85 (s, 3H), 2.36 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 189.9, 160.4, 134.2, 133.3, 132.6, 131.6, 118.2, 60.2, 16.6. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data.[23]



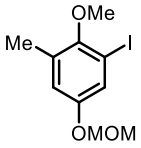

**16b**

**16b** (CAS: 808750-22-3) was a known compound and prepared according to literature.[19] White solid (20 mmol scale, 2.95 g, 68%). $R_f$ = 0.15 (hexane/ethyl acetate = 5:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 6.79 (d, *J* = 2.6 Hz, 1H), 6.52 (d, *J* = 2.7 Hz, 1H), 5.39 (s, 1H), 3.69 (s, 3H), 2.18 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 152.0, 149.0, 133.7, 117.5, 117.1, 117.1, 60.4, 16.7. Both the $^1$H NMR and $^{13}$C NMR match the literature reported data.[23]




**16c**

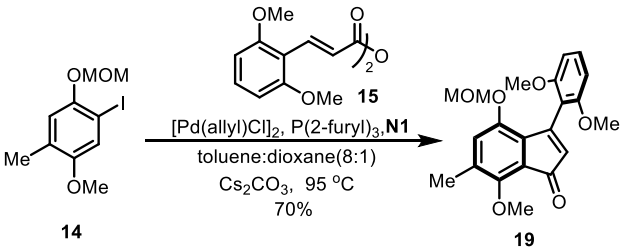
**16c** was prepared following the same procedure as **14c** according to literature.[21] Yellow oil (15 mmol scale, 3.36 g, 86%). $R_f$ = 0.35 (hexane/ethyl acetate = 20:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 2.9 Hz, 1H), 6.80 (d, *J* = 2.7 Hz, 1H), 5.09 (s, 2H), 3.76 (s, 3H), 3.46 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.4, 150.2, 133.5, 118.5, 118.1, 117.1, 94.8, 60.2, 56.0, 16.8. **IR** (KBr): 2954, 1478, 1401, 1254, 1227, 1154, 1084, 1023, 765 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{10}H_{14}BrO_3$ ($M+H^+$): 261.0121, found: 261.0124.



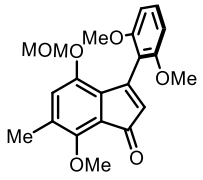

**16**

**16** was prepared following the same procedure as **14** according to literature.[21] Yellow oil (10 mmol scale, 2.96 g, 96%). $R_f$ = 0.35 (hexane/ethyl acetate = 20:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 2.9 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H), 5.09 (s, 2H), 3.73 (s, 3H), 3.46 (s, 3H), 2.31 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 153.7, 152.9, 132.3, 124.3, 119.3, 94.8, 91.5, 60.3, 56.0, 17.3. **IR** (KBr): 2952, 1473, 1421, 1398, 1279, 1218, 1152, 1115, 1081, 1022, 768 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{10}H_{14}IO_3$ ($M+H^+$): 308.9982, found: 308.9985.

**4.5.3 Preparation of indenone 12**

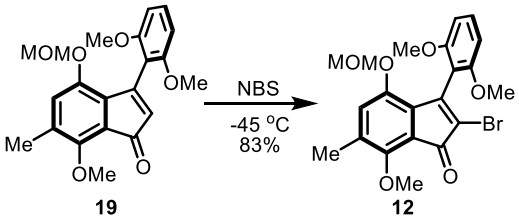



Oven-dried 40 mL vial A was charged with **14** (3.6 mmol, 1.11 g, 1.0 equiv), **15**[24] (4.3 mmol, 1.72 g, 1.2 equiv), and $Cs_2CO_3$ (4.69 g, 14.4 mmol, 4.0 equiv). Oven-dried 20 mL vial B was charged with **N1** (272 mg, 1.8 mmol, 0.5 equiv), allylpalladium(II) chloride dimer (64 mg, 0.18 mmol, 0.05 equiv) and tris(2-furyl)phosphine (167.1mg, 0.72 mmol, 0.20 equiv). After transferred into a nitrogen-filled glovebox, 8 mL of degassed toluene was added into vial B and the resulting mixture was stirred at room temperature for 5 minutes until a solution was formed. Degassed toluene (24 mL) and 1,4-dioxane (4 mL) were added to vial A, and the solution in vial B was transferred to vial A. Vial A was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 95 ℃ for 14 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated. The residue was directly purified by flash column chromatography on silica gel with hexanes/ethyl acetate (5:1) to give the desired product **19** as an orange oil (0.93 g, 70%).



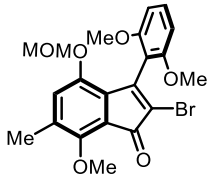

**19**

**19**: Orange oil (3.6 mmol scale, 0.93 g, 70%). $R_f$ = 0.25 (hexane/ethyl acetate = 4:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.29 (t, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 1.0 Hz, 1H), 6.58 (d, *J* = 8.4 Hz, 2H), 5.70 (s, 1H), 4.60 (s, 2H), 3.98 (s, 3H), 3.76 (s, 6H), 3.17 (s, 3H), 2.19 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 195.4, 157.6, 155.2, 151.6, 146.8, 135.9, 131.5, 129.8, 126.4, 125.8, 121.3, 113.5, 103.5, 95.8, 61.5, 55.9, 55.8, 16.3. **IR** (KBr): 3043, 2937, 1693, 1615, 1587, 1473, 1396, 1288, 1251, 1153, 1104, 1065, 1019 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{23}O_6$ ($M+H^+$): 371.1487, found: 371.1490.




**19** **12**

Under a nitrogen atmosphere, **19** (0.74 g, 2.0 mmol, 1.0 equiv) was dissoloved in 30 mL chloroform and then cooled to -45 °C. *N*-Bromosuccinimide (0.36 mg, 2.0 mmol, 1.0 equiv) was subsequently added in one portion. After stirring at -45 °C for 16 hours, the reaction mixture was quenched with water and extracted with dichloromethane (30 mL×2), dried over $MgSO_4$ and concentrated under vacuum. The residue was further purified by flash column chromatography on silica gel with hexanes/ethyl acetate (10:1) to afford **12** as an orange solid (0.75 g, 83%).

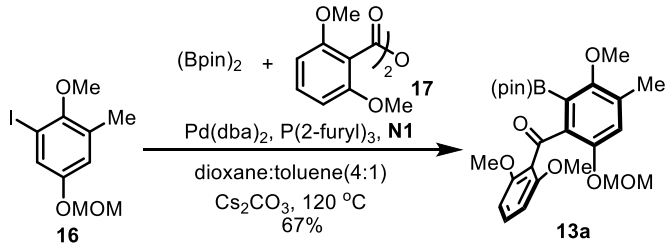



**12**

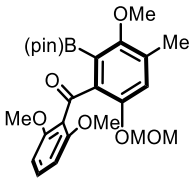
**12**: Orange solid (2 mmol scale, 0.74 g, 83%). Melting point: 127-129 °C. $R_f$ = 0.25 (hexane/ethyl acetate = 4:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.33 (t, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 1.0 Hz, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.59 (s, 2H), 4.02 (s, 3H), 3.78 (s, 6H), 3.18 (s, 3H), 2.16 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 186.5, 156.3, 151.4, 151.3, 145.2, 134.6, 129.5, 129.5, 125.5, 119.3, 118.2, 110.9, 102.6, 94.6, 60.7, 55.0, 54.8, 15.4. **IR** (KBr): 2988, 1708, 1614, 1568,

1431, 1303, 1269, 1152, 1111, 1021 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{21}H_{22}BrO_6$ ($M+H^+$): 449.0594, found: 449.0603.

**4.5.4 Preparation of 13b**

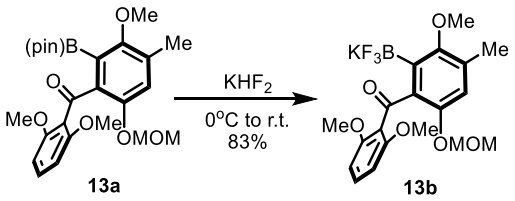



An oven-dried 40 mL vial was charged with bis(dibenzylideneacetone)palladium(0) (188 mg, 0.33 mmol, 0.10 equiv) tris(2-furyl)phosphine (153 mg, 0.66 mmol, 0.20 equiv), **N1** (248 mg, 1.65 mmol, 0.5 equiv), **16** (3.3 mmol, 1.02 g, 1.0 equiv), **17** [25] (4.0 mmol, 1.38 g, 1.2 equiv), bis(pinacolato)diboron (3.47 mmol, 0.89 g, 1.05 equiv) ,$Cs_2CO_3$ (4.30 g, 13.2 mmol, 4.0 equiv). After transferred into a nitrogen-filled glovebox, 26 mL of degassed 1.4-dioxane and 6.5 mL toluene were added to the vial. Then, the vial was tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 120 ℃ for 24 hours. After completion of the reaction, the mixture was filtered through a thin pad of celite. The filter cake was washed with ethyl acetate, and the combined filtrate was concentrated under vacuum. The residue was directly purified by flash column chromatography on silica gel with dichlorometane/ethyl acetate/toluene (30:1:1) to give the desired product **13a** as an off-white solid (1.05 g, 67%).

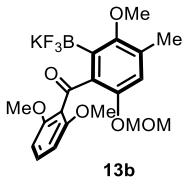



**13a**

**13a:** Off-white solid (3.3 mmol scale, 1.05 g, 67%). Melting point: 102-104 ℃. $R_f$ = 0.25 (hexane/ethyl acetate = 3:2). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 8.4 Hz, 1H), 6.74 (d, *J* = 0.8 Hz, 1H), 6.45 (d, *J* = 8.4 Hz, 2H), 4.54 (s, 2H), 3.72 (s, 3H), 3.60 (s, 6H), 3.05 (s, 3H), 2.21 (s, 3H), 1.39(s, 12H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 193.4, 157.2, 156.4, 154.0, 138.6 130.0, 129.7, 121.7, 119.1, 104.1, 94.7, 83.4, 61.8, 56.0, 55.6, 25.2, 16.5. **IR** (KBr): 2973, 1642, 1594, 1473, 1377, 1295, 1269, 1146, 1112 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{25}H_{34}BO_8$ ($M+H^+$): 473.2341, found: 473.2352.



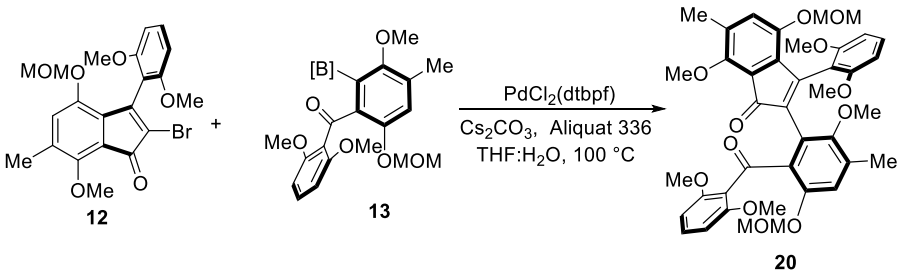

Following a known procedure:[26] At 0 °C, aqueous potassium hydrogen difluoride solution (6 mL, 3.3 M, 20 mmol) was added to a methanol solution (14 mL) of **13a** (2.0 mmol, 0.94 g, 1.0 equiv) in a plastic beaker. Then, the resulting white slurry was stirred at room temperature for 1 hour, monitored by TLC. The reaction mixture was concentrated under vacuum and dissolved in hot acetone (40 mL), filtered and concentrated under vacuum to afford the crude product. The crude product was further purified by recrystallization from a minimal amount of hot acetone (2 mL) and hot diethyl ether (20 mL) to afford the potassium trifluoroborate salt **13b** as a yellow solid (0.75 g, 83%).




**13b**: Yellow solid (2.0 mmol scale, 0.75 g, 83%). Melting point: 124-126 °C. **$^{1}$H NMR** (400 MHz, DMSO-d6) δ 7.56 (t, *J* = 8.5 Hz, 1H), 7.04 (s, 1H), 6.83 (d, *J* = 8.5 Hz, 2H), 5.03 (s, 2H), 3.97 (s, 3H), 3.75 (s, 6H), 3.02 (s, 3H), 2.28 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-d6) δ 193.4, 157.2, 156.4, 154.0, 138.6 130.0, 129.7, 121.7, 119.1, 104.1, 94.7, 83.4, 61.8, 56.0, 55.6, 25.2, 16.5. δ 202.3, 1581, 155.3, 154.0, 146.4, 134.4, 127.0, 118.1, 112.5, 104.7, 94.7, 57.3 (t, *J* = 4.3 Hz), 56.7, 56.3, 18.8. **$^{19}$F NMR** (470 MHz, DMSO-d6) δ -144.4. **IR** (KBr): 2945, 1673, 1601, 1476, 1410, 1301, 1282, 1252, 1154, 1024 cm$^{-1}$. **HRMS** (ESI): Calculated for $C_{19}H_{22}BF_3KO_6$ ($M+H^+$): 453.1093, found: 453.1099.

### 4.5.5 Condition screening for preparation of 20

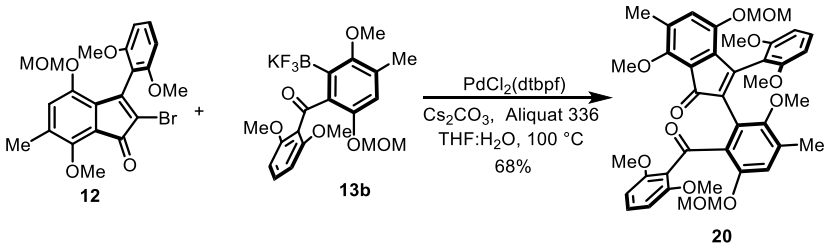
**Table S2** Optimization of the Suzuki−Miyaura reaction between **12** and **13**[a]




| entry | solvent | Pd/ligand | **13** | yield of **20**(%) |
|---|---|---|---|---|
| 1 | DME:$H_2O$ (1:1) | $PdCl_2$(dtbpf) | **13a** | 15 |
| 2 | DME:$H_2O$ (1:1) | $PdCl_2$+$PPh_3$[b] | **13a** | trace |
| 3 | DME:$H_2O$ (1:1) | $PdCl_2$+$P(tBu)_3$[b] | **13a** | trace |
| 4 | DME:$H_2O$ (1:1) | $PdCl_2$+SPhos | **13a** | trace |
| 5 | DME:$H_2O$ (1:1) | $PdCl_2$+Q-Phos | **13a** | trace |
| 6 | DME:$H_2O$ (1:1) | $PdCl_2$+IPr | **13a** | trace |
| 7 | DME:$H_2O$ (1:1) | $PdCl_2$+IMes | **13a** | trace |
| 8 | THF:$H_2O$ (1:1) | $PdCl_2$(dtbpf) | **13a** | 18 |
| 9 | THF:$H_2O$ (1:1) | $PdCl_2$(dtbpf) | **13b** | 56 |
| 10[c] | THF:$H_2O$ (1:1) | $PdCl_2$(dtbpf) | **13b** | 68 |

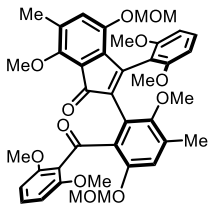
[a]Reaction condition: **12** (0.1 mmol), **13** (0.11 mmol), [Pd] (0.01 mmol), ligands (0.01 mmol), $Cs_2CO_3$ (1.0 mmol), Aliquat 336 (0.8 mg), $H_2O$ (0.25 mL) and THF or DME (0.25 mL) in 85 °C, 14 h. [b]Ligands (0.02 mmol) was used. [c]**13** (0.15 mmol) was used.

### 4.5.6 Syntheses of acredinone A



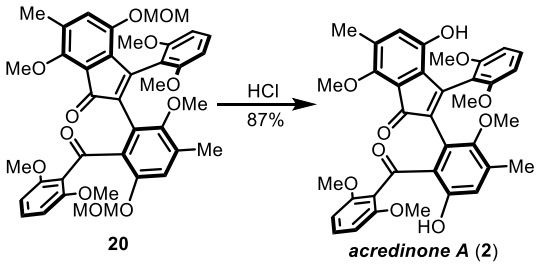

An oven-dried 4 mL vial charged with $PdCl_2$(dtbpf) (6.6 mg, 0.01 mmol, 0.10 equiv), **12** (44.9 mg, 0.1 mmol, 1.0 equiv) and **13b** (68.0 mg, 0.15 mmol, 0.15 equiv) was transferred into a nitrogen filled glovebox. $Cs_2CO_3$ (391.0 mg, 1.0 mmol, 10 equiv), Aliquat 336 (0.8 mg) in water (0.25 mL) and tetrahydrofuran (0.25 mL) were added to the vial. The vial was then tightly sealed, transferred out of glovebox and stirred on a pie-block preheated to 100 ℃ for 16 hours. After completion of the reaction, the mixture was diluted with water (3 mL), extracted with ethyl acetate (10

mL×3), and dried over $MgSO_4$. The mixture was concentrated under vacuum and purified by flash column chromatography on silica gel with hexanes/ethyl acetate (3:1) to give the desired product **20** as an orange oil (48.6 mg, 68%).




**20**

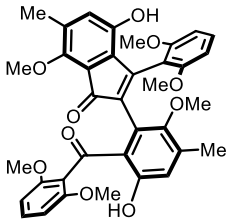
**20:** Orange oil (0.1 mmol scale, 48.6 mg, 68%). $R_f$ = 0.25 (hexane/ethyl acetate = 3:2). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 8.4 Hz, 1H), 7.10 (t, *J* = 8.3 Hz, 1H), 6.79 (d, *J* = 9.4 Hz, 2H), 6.41 (d, *J* = 8.3 Hz, 2H),6.40 (d, *J* = 8.4 Hz, 1H), 6.27 (d, *J* = 8.3 Hz, 1H), 4.75 – 4.63 (m, 2H), 4.53 – 4.45 (m, 2H), 3.97 (s, 3H), 3.66 (s, 3H), 3.61 (s, 3H), 3.45 (s, 6H), 3.36 (s, 3H), 3.21 (s, 3H), 3.18 (s, 3H), 2.21 (s, 3H), 2.18 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 193.4, 190.1, 158.5, 158.4, 158.0, 152.9, 151.9, 151.6, 148.5, 146.8, 134.5, 133.9, 133.8, 132.9, 130.9, 130.6, 128.8, 127.1, 126.0, 121.6, 121.3, 117.9, 113.2, 104.1, 102.7, 102.5, 96.1, 95.7, 61.5, 60.81, 55.8, 55.7, 55.6, 55.2, 54.6, 17.0, 16.1. **IR** (KBr): 2929, 1738, 1703, 1592, 1472, 1431, 1398, 1151, 1113, 1017 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{40}H_{43}O_{12}$ ($M+H^+$): 715.2749, found: 715.2756.




**20** ***acredinone A* (2)**

Following a known procedure:[27] concentrated HCl (0.53 mL, 6.4 mmol, 80 equiv) was added dropwise to **20** (57.2 mg, 0.08 mmol, 1.0 equiv) in tetrahydrofuran (10 mL) at 0 ℃. The reaction mixture was then stirred at room temperature for another 5 hours, monitored by TLC. After completion of the reaction, the mixture was diluted with $H_2O$ (3 mL) and extracted with ethyl acetate (5 mL×3), dried by $MgSO_4$. The mixture was concentrated and purified

by flash column chromatography on silica gel with hexanes/ethyl acetate (3:1) to give acredinone A as an orange-red oil (43.6 mg, 87%).



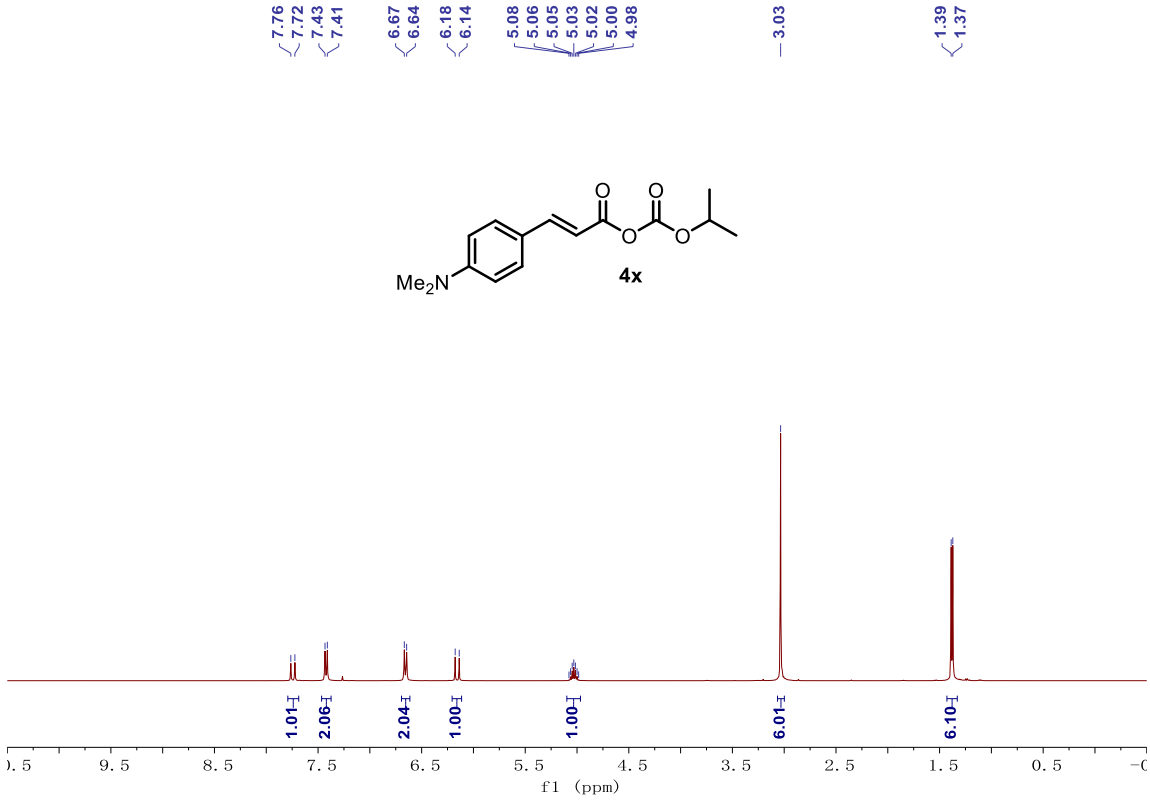
*acredinone A* (2)

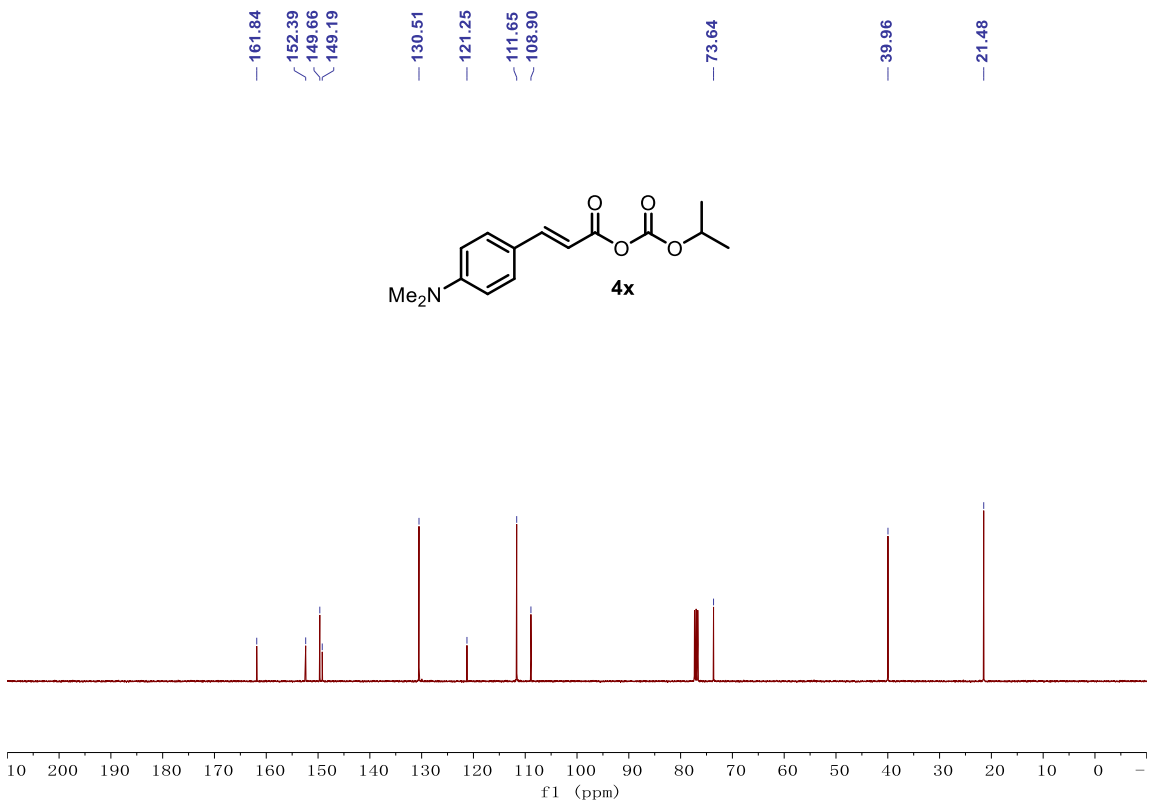
**Acredinone A (2):** (CAS: 1658444-15-5) Orange-red oil (0.08 mmol scale, 43.6 mg, 87%). $R_f$ = 0.30 (hexane/ethyl acetate = 3:2). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.70 (s, 1H), 7.20 (t, *J* = 8.4 Hz, 1H), 7.05 (t, *J* = 8.4 Hz, 1H), 6.68 (s, 1H), 6.56 (s, 1H), 6.47 (d, *J* = 8.3 Hz, 1H), 6.42 (d, *J* = 8.2 Hz, 1H), 6.23 (d, *J* = 8.4 Hz, 2H), 4.87 (s, 1H), 3.84 (s, 3H), 3.68 (s, 3H), 3.59 (s, 3H), 3.49 (s, 6H), 3.35 (s, 3H), 2.14 (s, 3H), 2.12 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 201.4, 190.2, 158.0, 157.9, 157.3, 155.8, 150.4, 150.0, 149.9, 145.4, 138.5, 135.0, 134.5, 131.5, 131.2, 127.0, 126.9, 125.0, 124.7, 120.0, 119.5, 119.2, 110.2, 104.3, 104.3, 103.8, 62.2, 60.9, 56.2, 55.6, 54.7, 17.3, 16.4. **IR** (KBr): 2933, 1694, 1619, 1595, 1473, 1437, 1385, 1252, 1141, 1113, 1032 $cm^{-1}$. **HRMS** (ESI): Calculated for $C_{36}H_{35}O_{10}$ ($M+H^+$): 627.2225, found: 627.2234. $^1$H NMR and $^{13}$C NMR match the literature reported data[14] (*vide infra*).

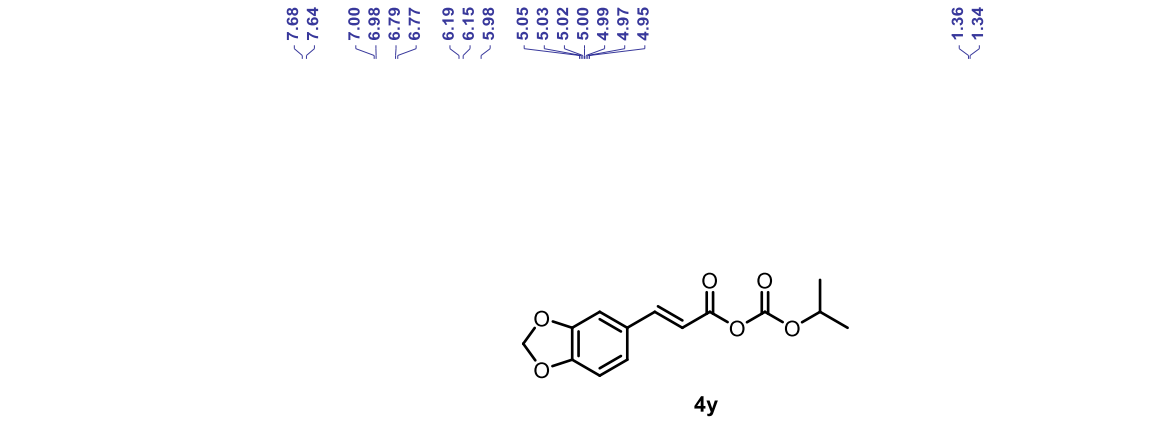
**Table S3** Comparison of $^{13}$C NMR chemical shifts (ppm) between our sample and reference.

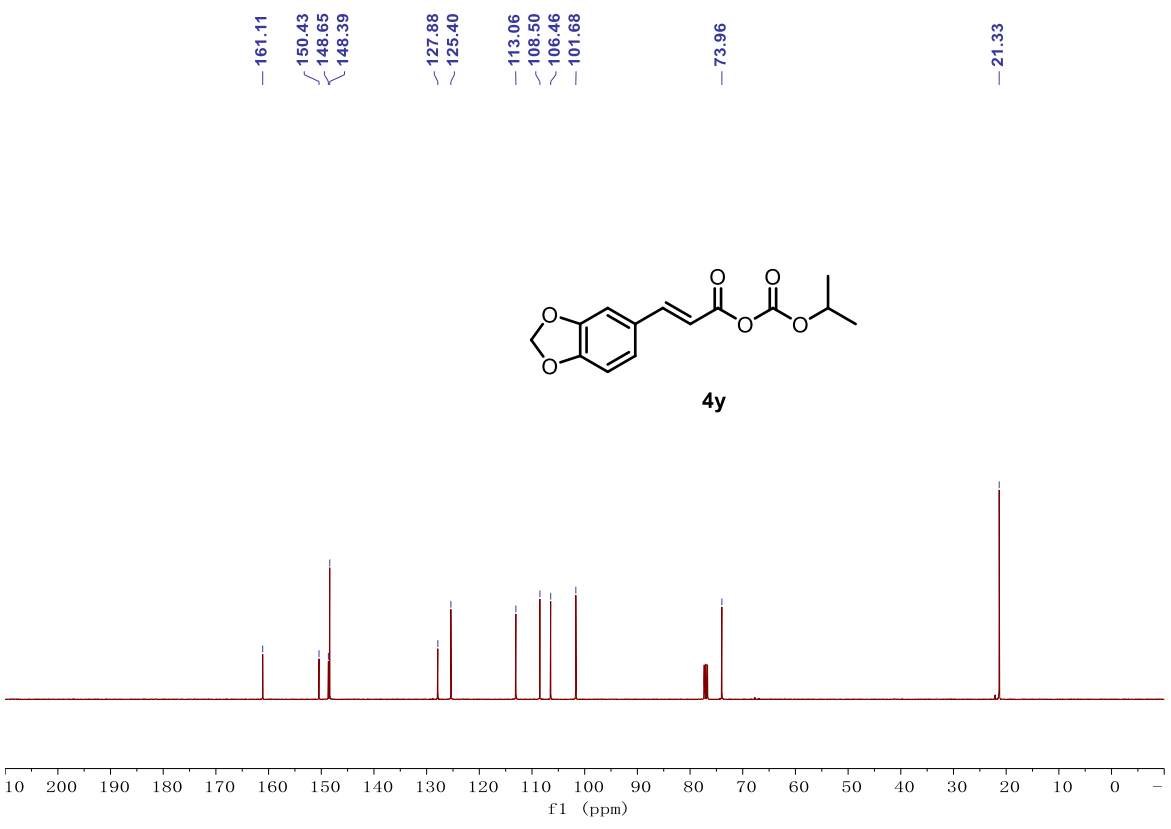
| Reference | Our sample | Reference | Our sample | Reference | Our sample |
|---|---|---|---|---|---|
| 201.38 | 201.36 | 190.15 | 190.15 | 158.05 | 158.00 |
| 157.95 | 157.87 | 157.33 | 157.25 | 155.79 | 155.75 |
| 150.43 | 150.36 | 150.11 | 150.03 | 149.97 | 149.92 |
| 145.44 | 145.40 | 138.47 | 138.46 | 135.03 | 134.98 |
| 134.53 | 134.46 | 131.51 | 131.47 | 131.29 | 131.24 |
| 127.00 | 126.97 | 126.93 | 126.92 | 125.03 | 124.95 |
| 124.68 | 124.65 | 120.00 | 119.97 | 119.55 | 119.45 |
| 119.24 | 119.20 | 110.26 | 110.20 | 104.39 | 104.32 |
| 104.30 | 104.25 | 103.84 | 103.78 | 60.25 | 62.21 |
| 60.95 | 60.90 | 56.26 | 56.22 | 55.63 | 55.58 |
| 54.73 | 54.69 | 17.26 | 17.25 | 16.42 | 16.39 |

## 5. NMR Spectra and X-ray Data

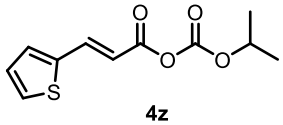


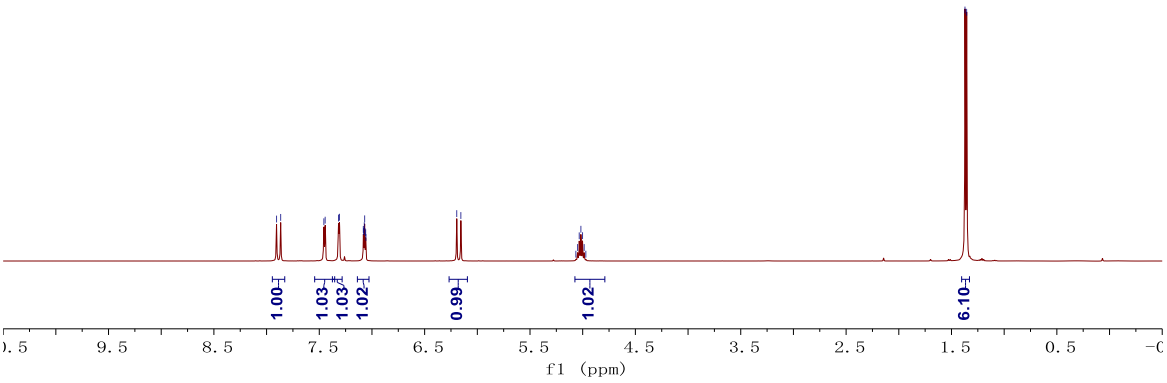

7.68
7.64
7.00
6.98
6.79
6.77
6.19
6.15
5.98
5.05
5.03
5.02
5.00
4.99
4.97
4.95
1.36
1.34
4y
1.00
1.98
1.01
1.02
2.05
1.04
6.10
f1 (ppm)


161.11
150.43
148.65
148.39
127.88
125.40
113.06
108.50
106.46
101.68
73.96
21.33
4y
f1 (ppm)

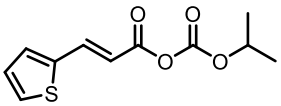

7.91
7.87
7.46
7.44
7.32
7.31
7.08
7.08
7.07
7.07
7.07
7.06
7.06
6.20
6.16
5.06
5.05
5.03
5.02
5.00
4.99
4.97
1.37
1.36


O
O
O
O
S

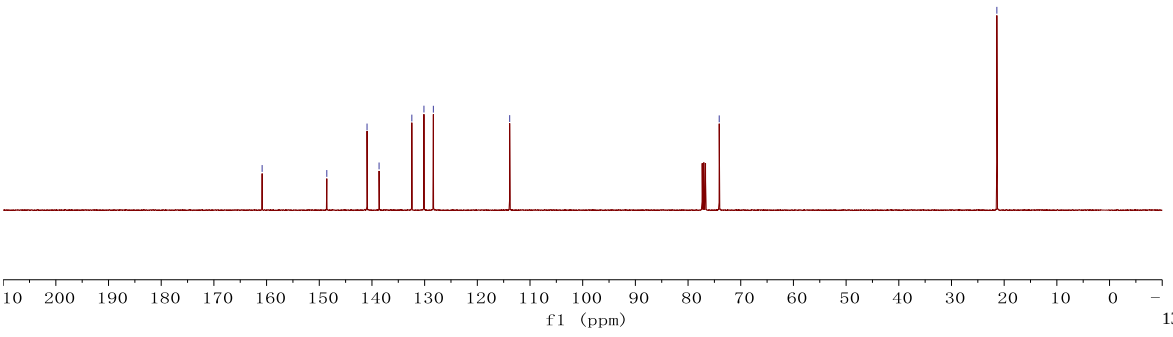
4z


1.00
1.03
1.03
1.02
0.99
1.02
6.10
f1 (ppm)


160.84
148.57
140.93
138.65
132.43
130.13
128.35
113.86
74.09
21.39

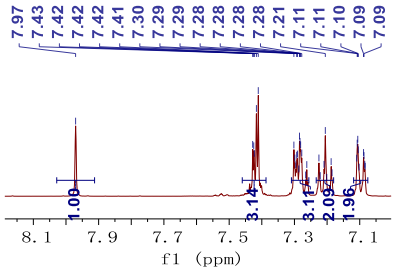

O
O
O
O
S

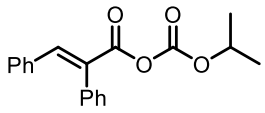
4z


f1 (ppm)

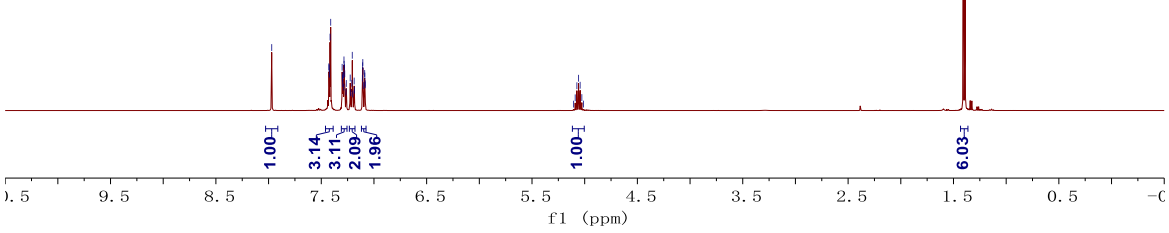
$^{13}C$

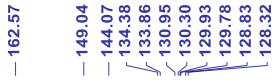

7.97
7.43
7.42
7.42
7.42
7.41
7.30
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.28
7.28
7.27
7.26
7.23
7.22
7.21
7.21
7.20
7.19
7.18
7.11
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
5.11
5.09
5.07
5.06
5.04
5.03
5.01
1.41
1.39

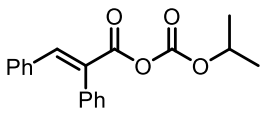

7.97
7.43
7.42
7.42
7.42
7.41
7.30
7.29
7.29
7.28
7.28
7.28
7.28
7.21
7.11
7.11
7.10
7.09
7.09
1.09
3.14
3.11
2.09
1.96
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)


O
O
O
O
Ph
Ph

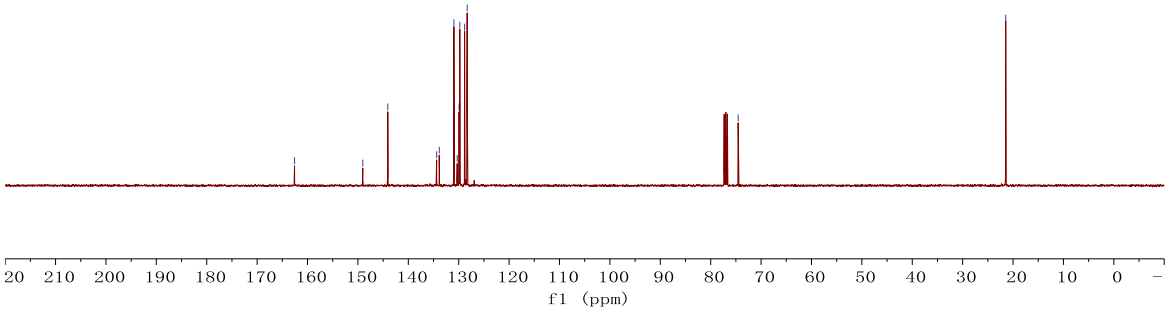
**(*E*)-4aa**

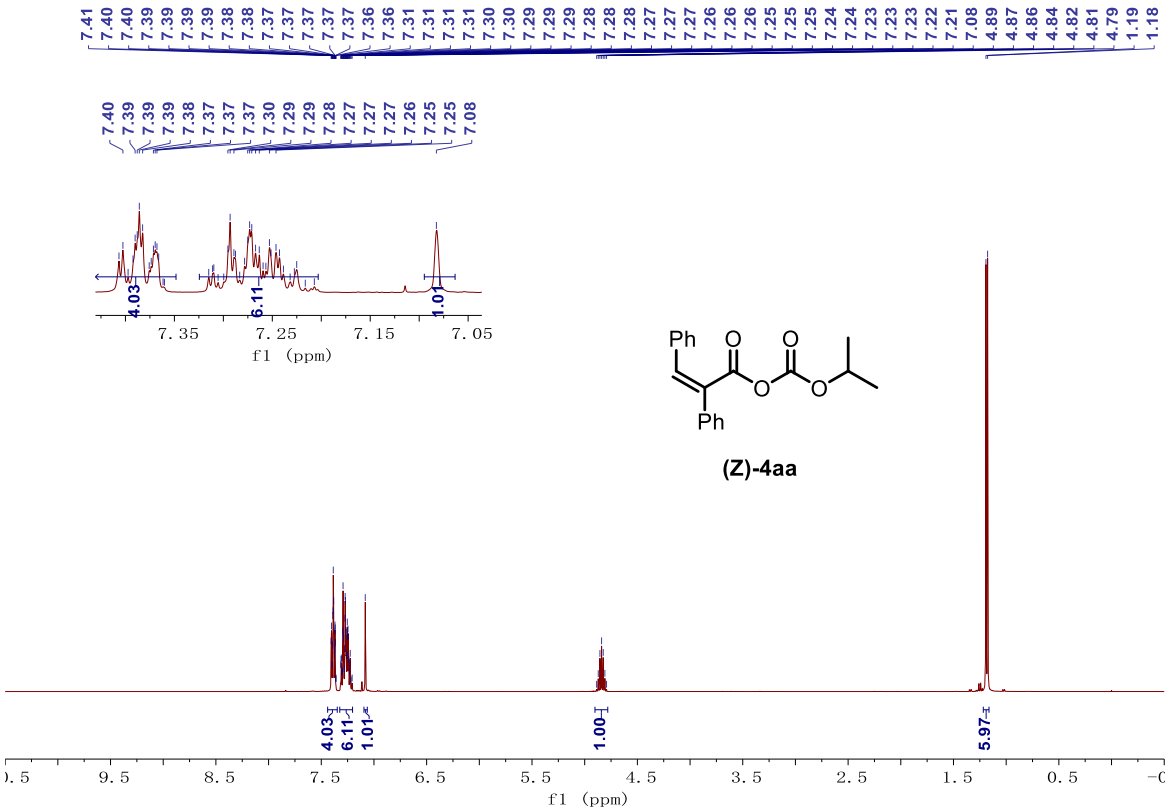

1.00
3.14
3.11
2.09
1.96
1.00
6.03
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

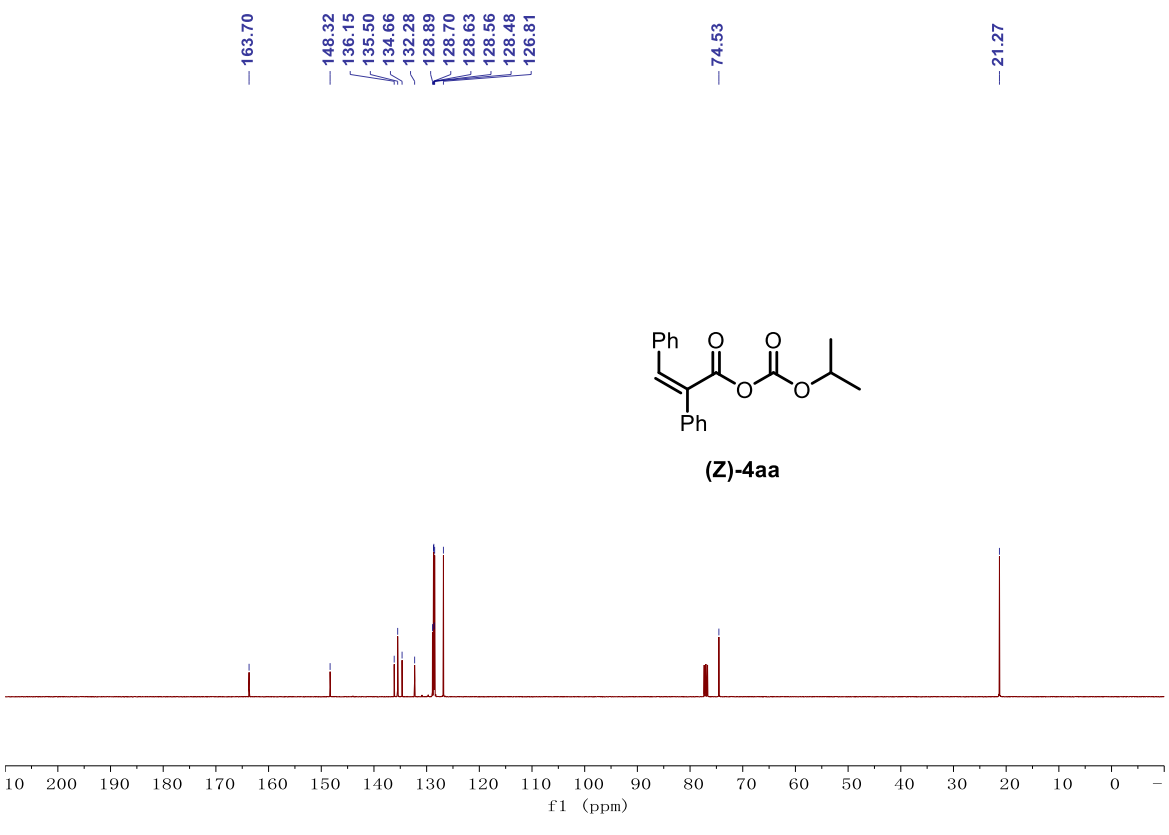

162.57
149.04
144.07
134.38
133.86
130.95
130.30
129.93
129.78
128.83
128.32
74.55
21.45

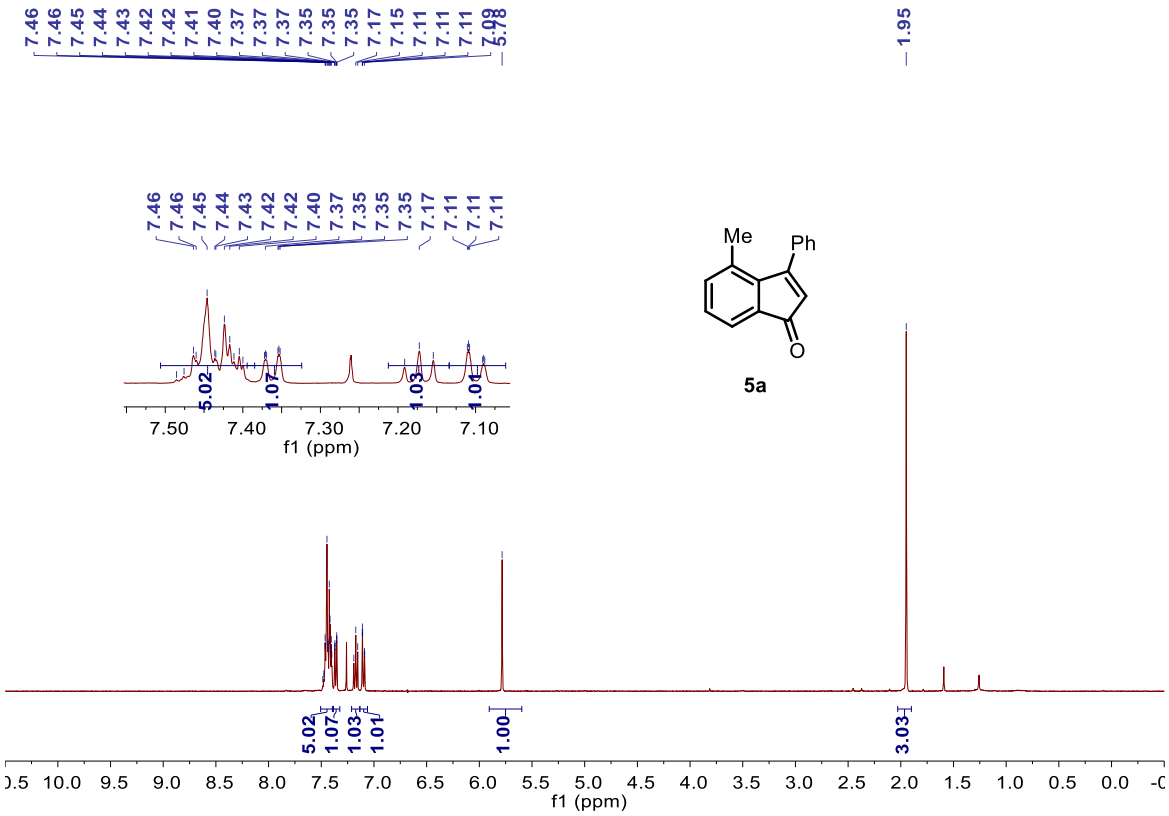

O
O
O
O
Ph
Ph

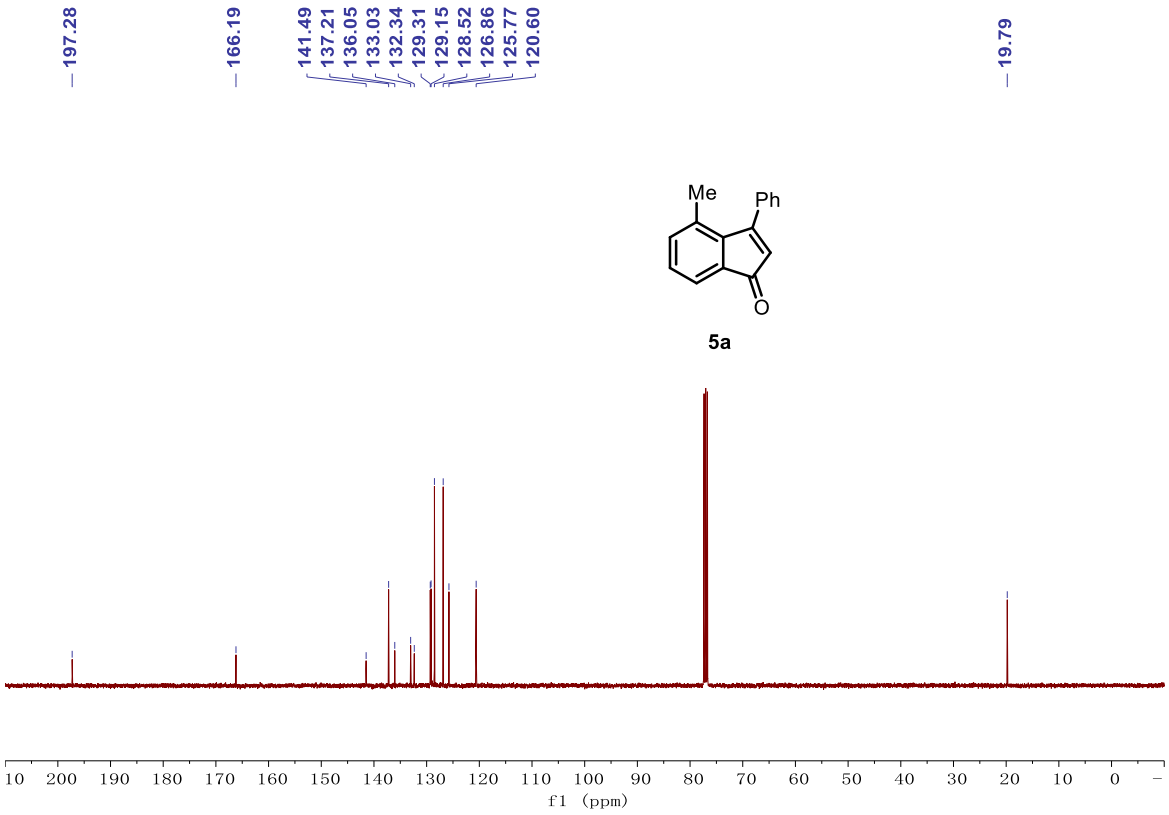
**(*E*)-4aa**

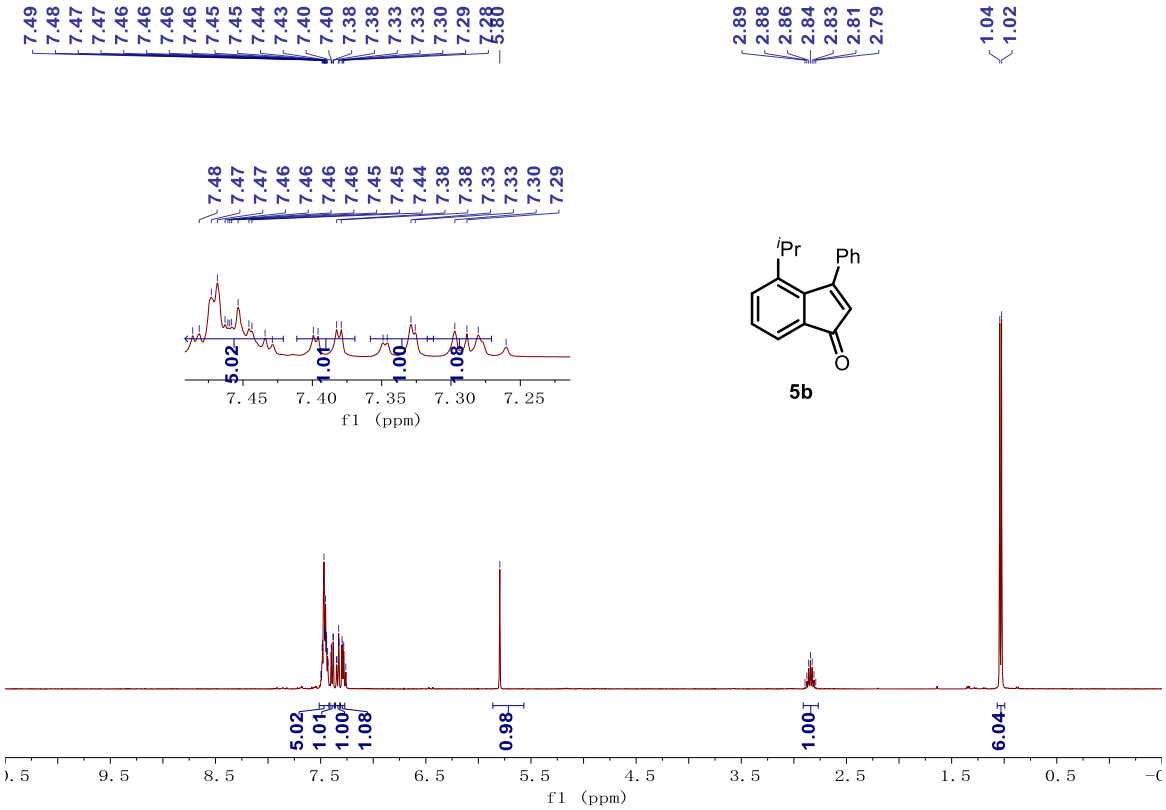

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

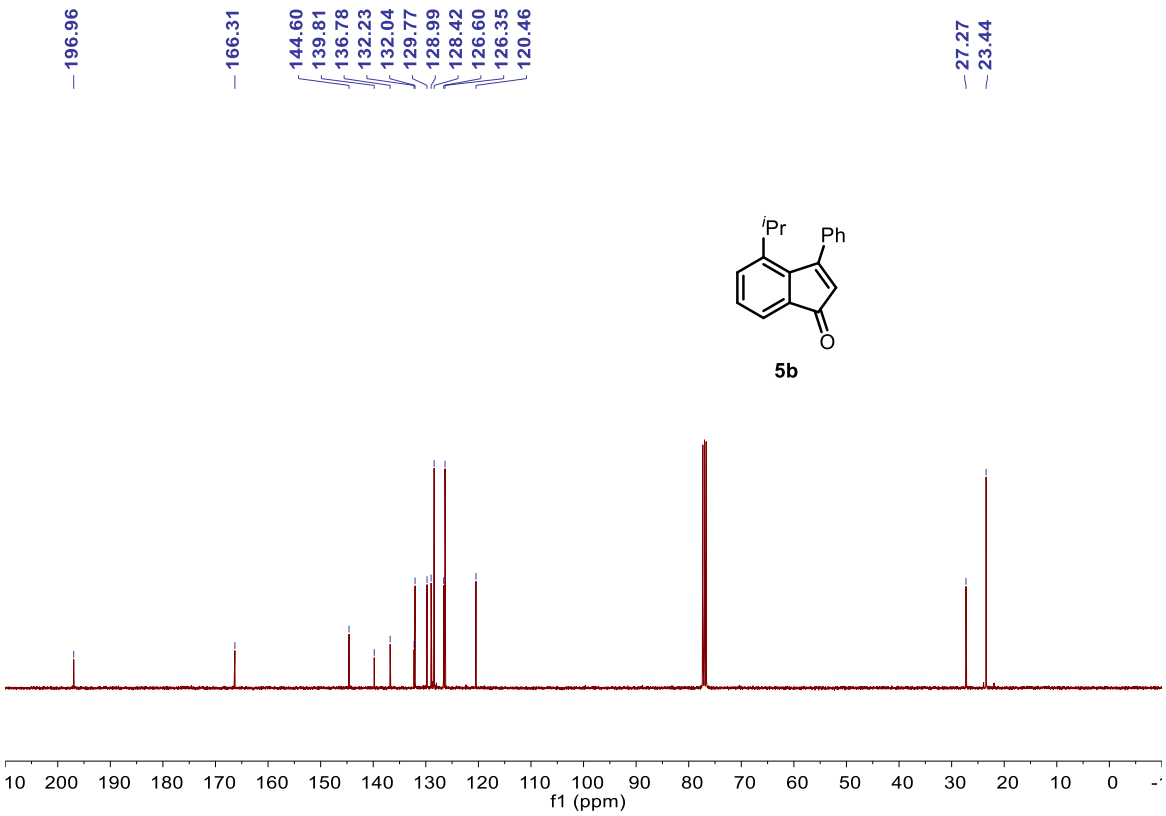

7.41 7.40 7.40 7.39 7.39 7.39 7.39 7.38 7.38 7.37 7.37 7.37 7.37 7.36 7.36 7.31 7.31 7.31 7.30 7.30 7.29 7.29 7.29 7.28 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.25 7.25 7.24 7.24 7.23 7.23 7.23 7.22 7.21 7.08 4.89 4.87 4.86 4.84 4.82 4.81 4.79 1.19 1.18
7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.37 7.30 7.29 7.29 7.28 7.27 7.27 7.27 7.26 7.25 7.25 7.08
4.03 6.11 1.01
7.35 7.25 7.15 7.05
f1 (ppm)
Ph O O O O Ph
(Z)-4aa
4.03 6.11 1.01 1.00 5.97
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

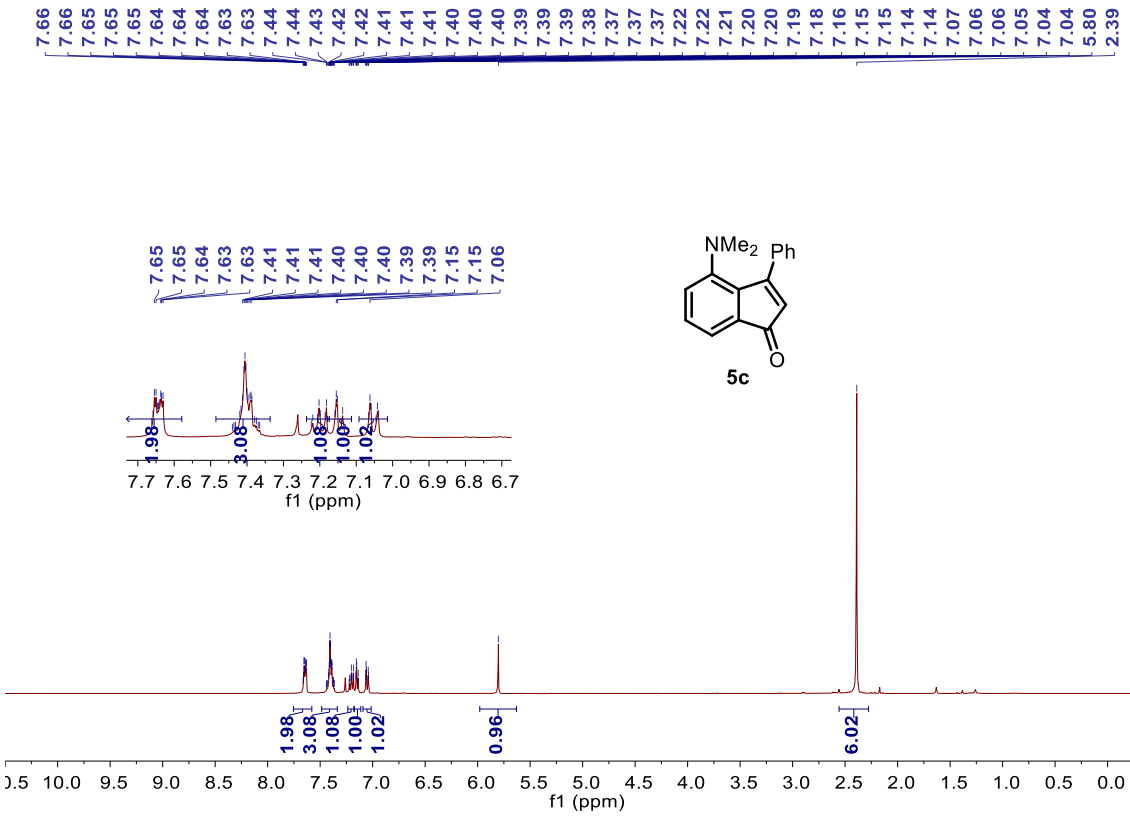

163.70 148.32 136.15 135.50 134.66 132.28 128.89 128.70 128.63 128.56 128.48 126.81 74.53 21.27
Ph O O O O Ph
(Z)-4aa
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

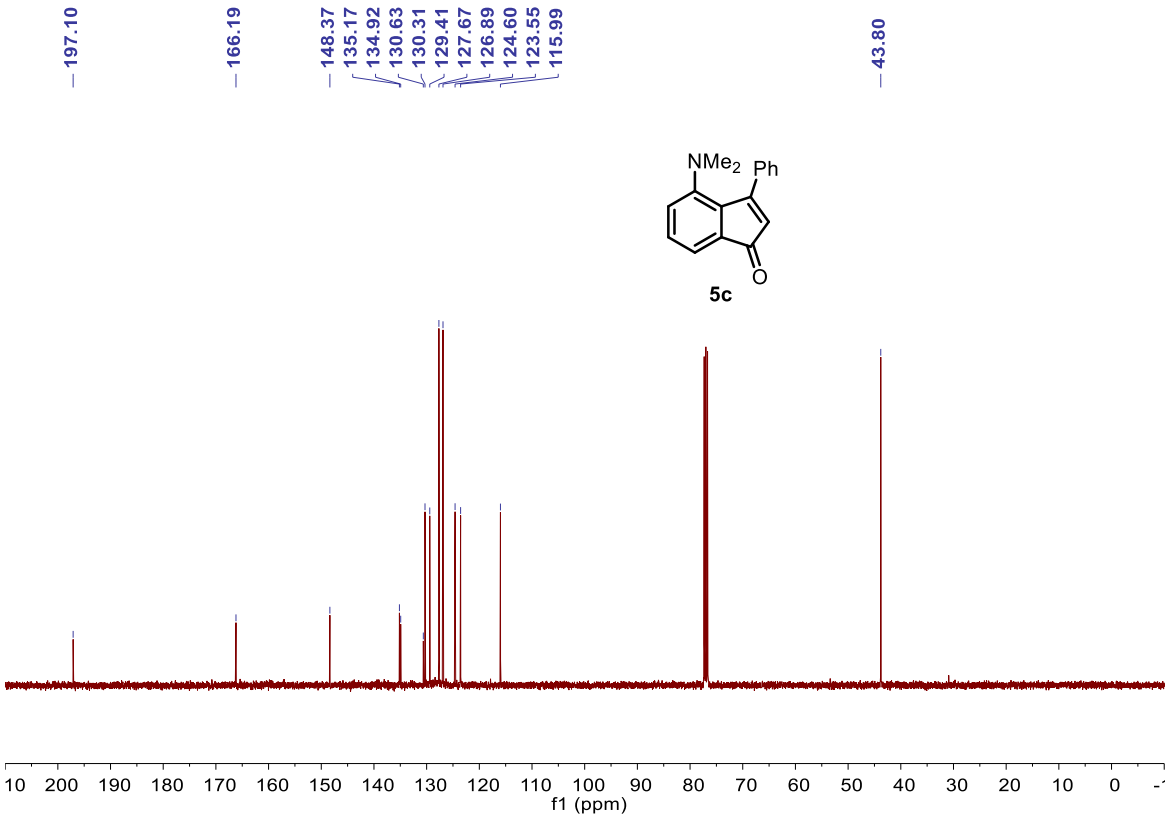

7.46
7.46
7.45
7.44
7.43
7.42
7.42
7.41
7.40
7.37
7.37
7.37
7.35
7.35
7.35
7.17
7.15
7.11
7.11
7.11
7.08
5.78
1.95
7.46
7.46
7.45
7.44
7.43
7.42
7.42
7.40
7.37
7.35
7.35
7.35
7.17
7.11
7.11
7.11
5.02
1.07
1.03
1.01
7.50
7.40
7.30
7.20
7.10
f1 (ppm)
Me
Ph
O
5a
5.02
1.07
1.03
1.01
1.00
3.03
f1 (ppm)


197.28
166.19
141.49
137.21
136.05
133.03
132.34
129.31
129.15
128.52
126.86
125.77
120.60
19.79
Me
Ph
O
5a
f1 (ppm)

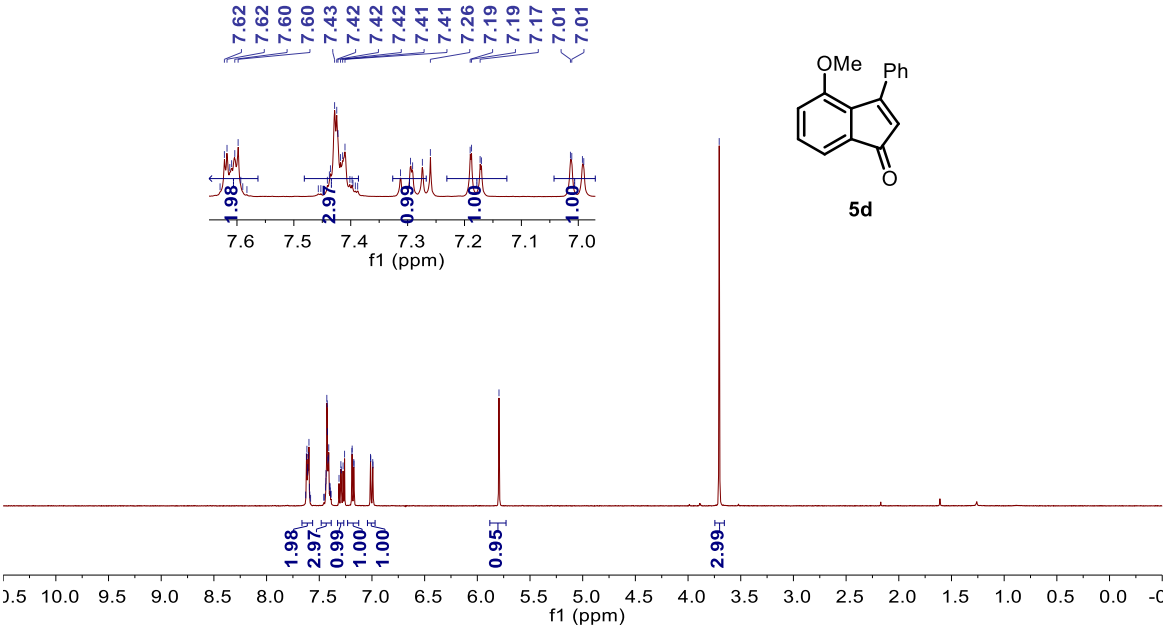

7.49 7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.45 7.44 7.43 7.40 7.40 7.38 7.38 7.33 7.33 7.30 7.29 7.28 5.80
2.89 2.88 2.86 2.84 2.83 2.81 2.79
1.04 1.02
7.48 7.47 7.47 7.46 7.46 7.46 7.46 7.45 7.45 7.44 7.38 7.33 7.33 7.30 7.29
5.02 1.01 1.00 1.08
7.45 7.40 7.35 7.30 7.25
f1 (ppm)
iPr
Ph
O
5b
5.02 1.01 1.00 1.08 0.98 1.00 6.04
f1 (ppm)

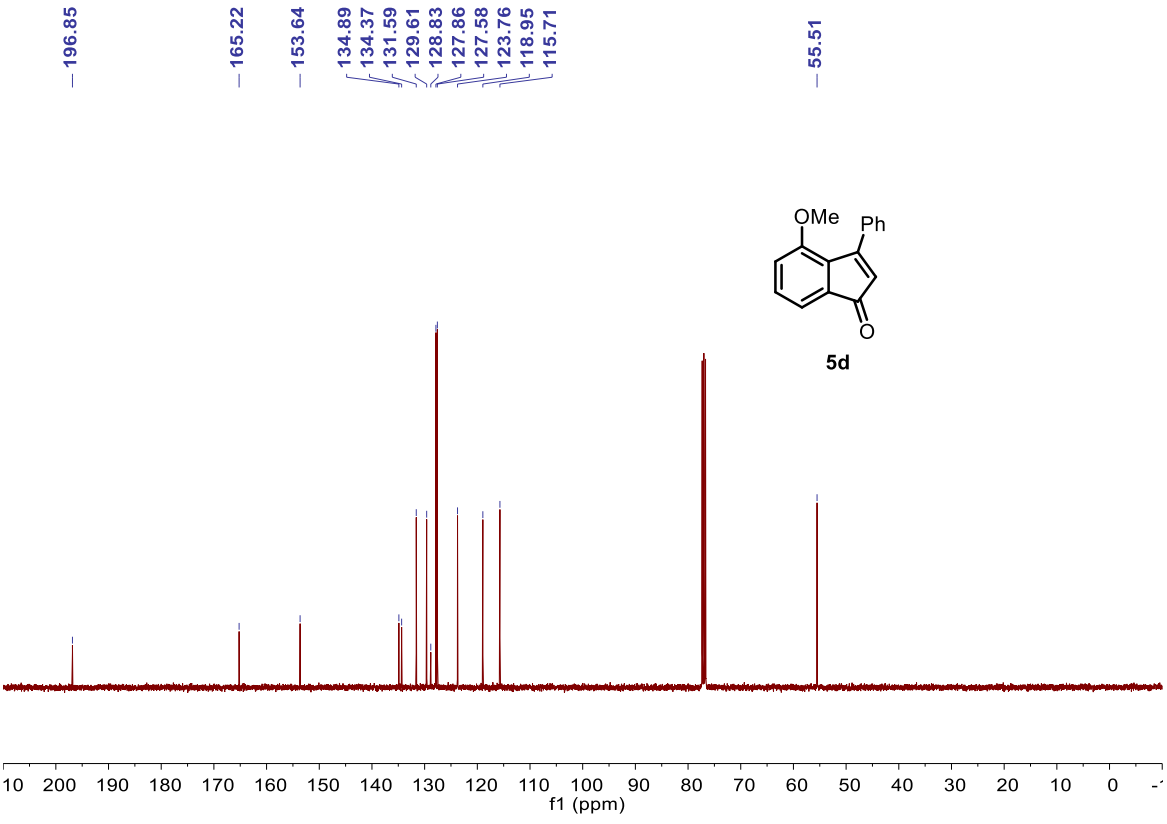

196.96
166.31
144.60 139.81 136.78 132.23 132.04 129.77 128.99 128.42 126.60 126.35 120.46
27.27
23.44
iPr
Ph
O
5b
f1 (ppm)


7.66 7.66 7.65 7.65 7.65 7.64 7.64 7.64 7.63 7.63 7.44 7.44 7.43 7.42 7.42 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.39 7.38 7.37 7.37 7.37 7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.16 7.15 7.15 7.14 7.14 7.07 7.06 7.06 7.05 7.04 7.04 5.80 2.39
7.65 7.65 7.64 7.63 7.63 7.41 7.41 7.41 7.40 7.40 7.40 7.39 7.39 7.15 7.15 7.06
1.98 3.08 1.08 1.00 1.02
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
f1 (ppm)
NMe2 Ph
O
5c
1.98 3.08 1.08 1.00 1.02 0.96 6.02
f1 (ppm)

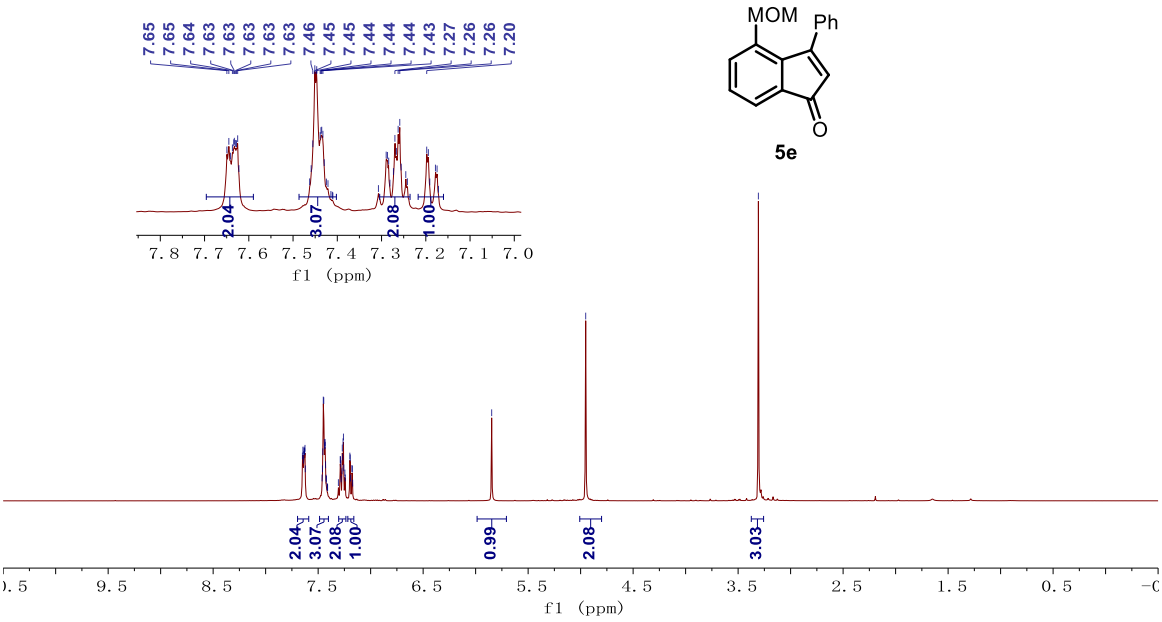

197.10
166.19
148.37 135.17 134.92 130.63 130.31 129.41 127.67 126.89 124.60 123.55 115.99
43.80
NMe2 Ph
O
5c
f1 (ppm)

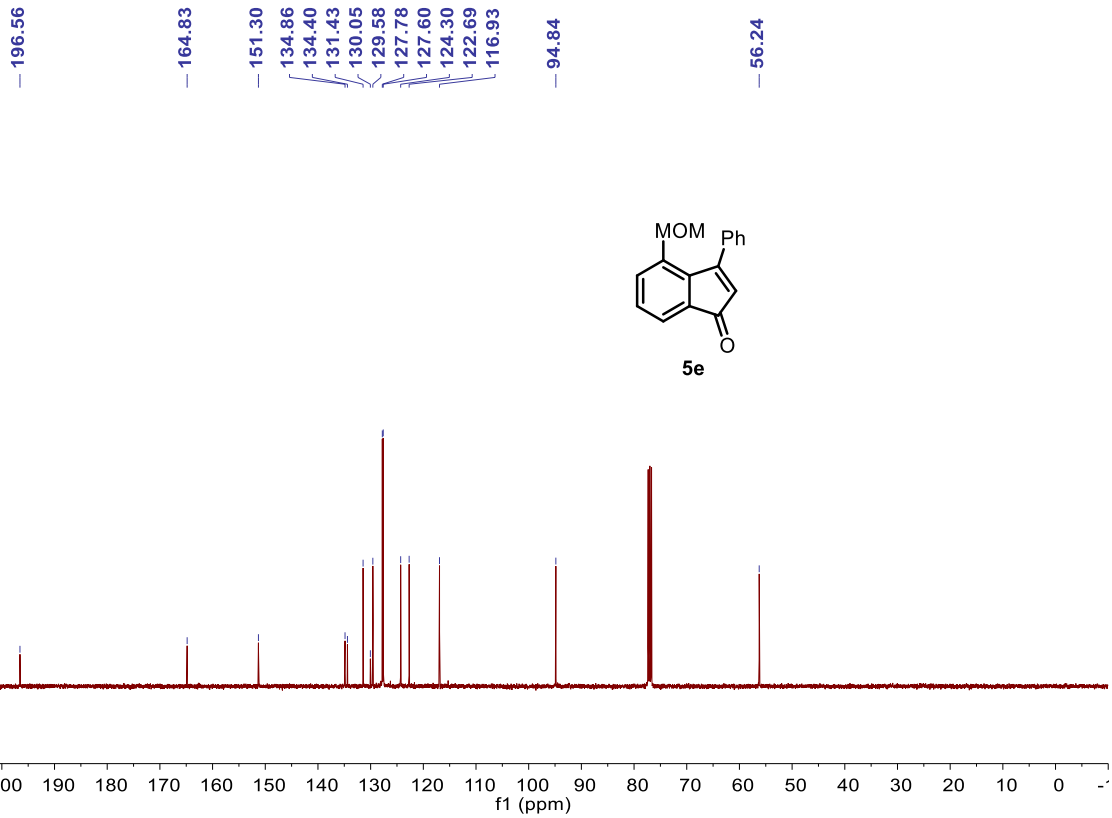

7.63 7.62 7.62 7.61 7.61 7.60 7.60 7.59 7.59 7.58 7.46 7.45 7.44 7.44 7.44 7.43 7.42 7.42 7.42 7.41 7.41 7.40 7.40 7.40 7.39 7.31 7.29 7.29 7.27 7.26 7.19 7.19 7.17 7.17 7.01 7.01 6.99 6.99 5.79 3.70


7.62 7.62 7.60 7.60 7.43 7.42 7.42 7.42 7.41 7.41 7.26 7.19 7.19 7.17 7.01 7.01
1.98 2.97 0.99 1.00 1.00
7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
OMe
Ph
O
5d
1.98 2.97 0.99 1.00 1.00 0.95 2.99
f1 (ppm)

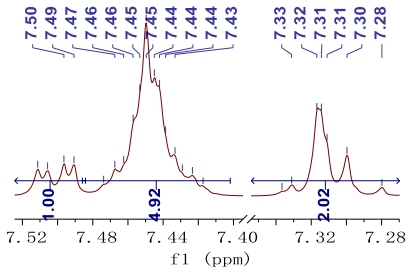

196.85 165.22 153.64 134.89 134.37 131.59 129.61 128.83 127.86 127.58 123.76 118.95 115.71 55.51
OMe
Ph
O
5d
f1 (ppm)

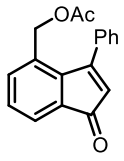

7.65 7.65 7.64 7.64 7.63 7.63 7.63 7.63 7.63 7.62 7.46 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.43 7.42 7.42 7.41 7.41 7.41 7.31 7.29 7.29 7.28 7.28 7.27 7.27 7.27 7.26 7.26 7.26 7.25 7.24 7.20 7.19 7.19 7.18 7.17 7.17 5.85 4.95 3.31


MOM
Ph
O
5e
7.65 7.65 7.64 7.63 7.63 7.63 7.63 7.46 7.45 7.45 7.44 7.44 7.44 7.43 7.27 7.26 7.20
2.04 3.07 2.08 1.00
7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
2.04 3.07 2.08 1.00 0.99 2.08 3.03
f1 (ppm)

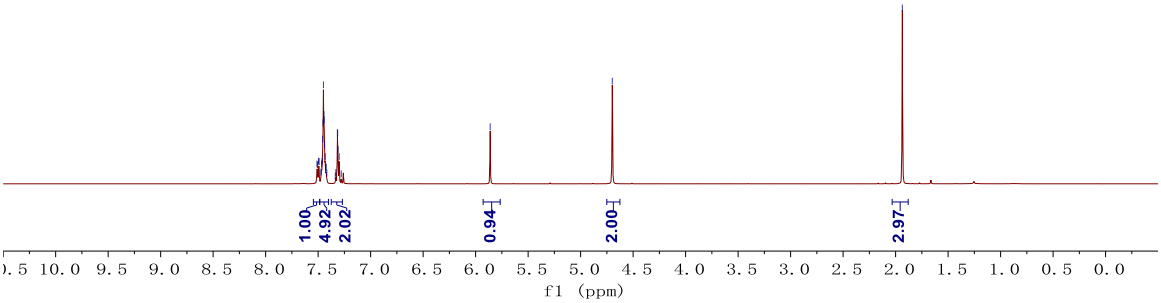

196.56 164.83 151.30 134.86 134.40 131.43 130.05 129.58 127.78 127.60 124.30 122.69 116.93 94.84 56.24
MOM
Ph
O
5e
f1 (ppm)

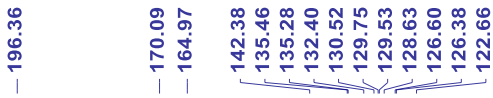

7.51
7.51
7.50
7.49
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.43
7.42
7.42
7.33
7.32
7.31
7.31
7.30
7.28
5.86
4.70
1.94

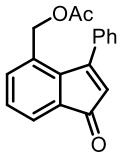

7.50
7.49
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.44
7.43
7.33
7.32
7.31
7.31
7.30
7.28
1.00
4.92
2.02
7.52
7.48
7.44
7.40
7.32
7.28
f1 (ppm)


OAc
Ph
O

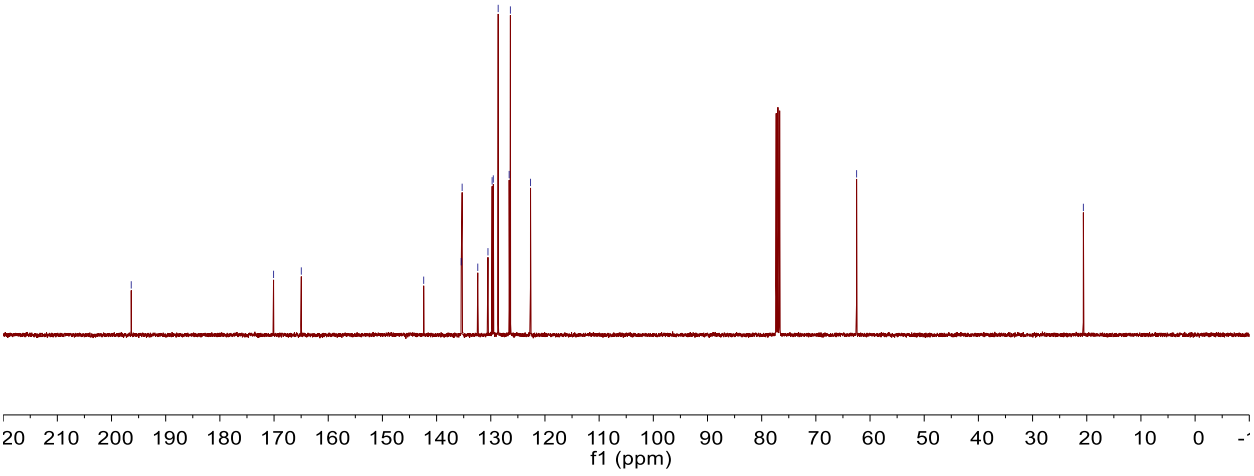
5f

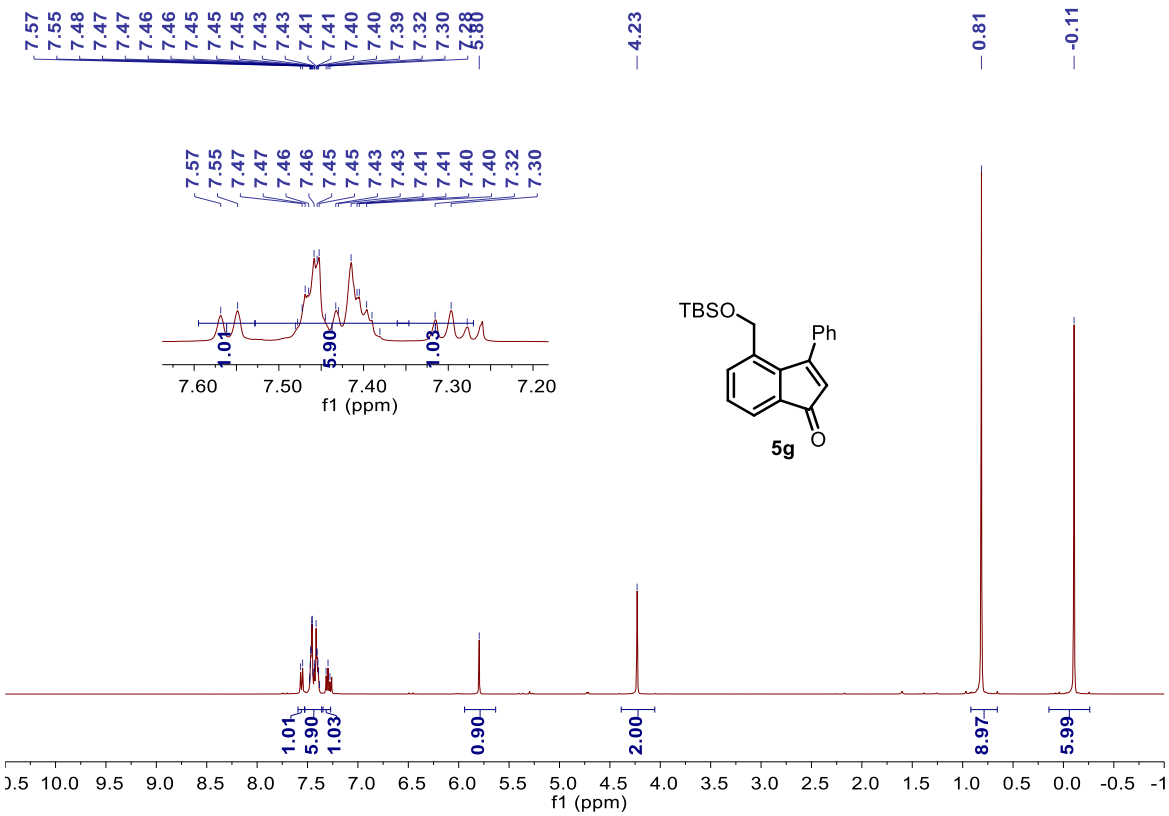

1.00
4.92
2.02
0.94
2.00
2.97
f1 (ppm)

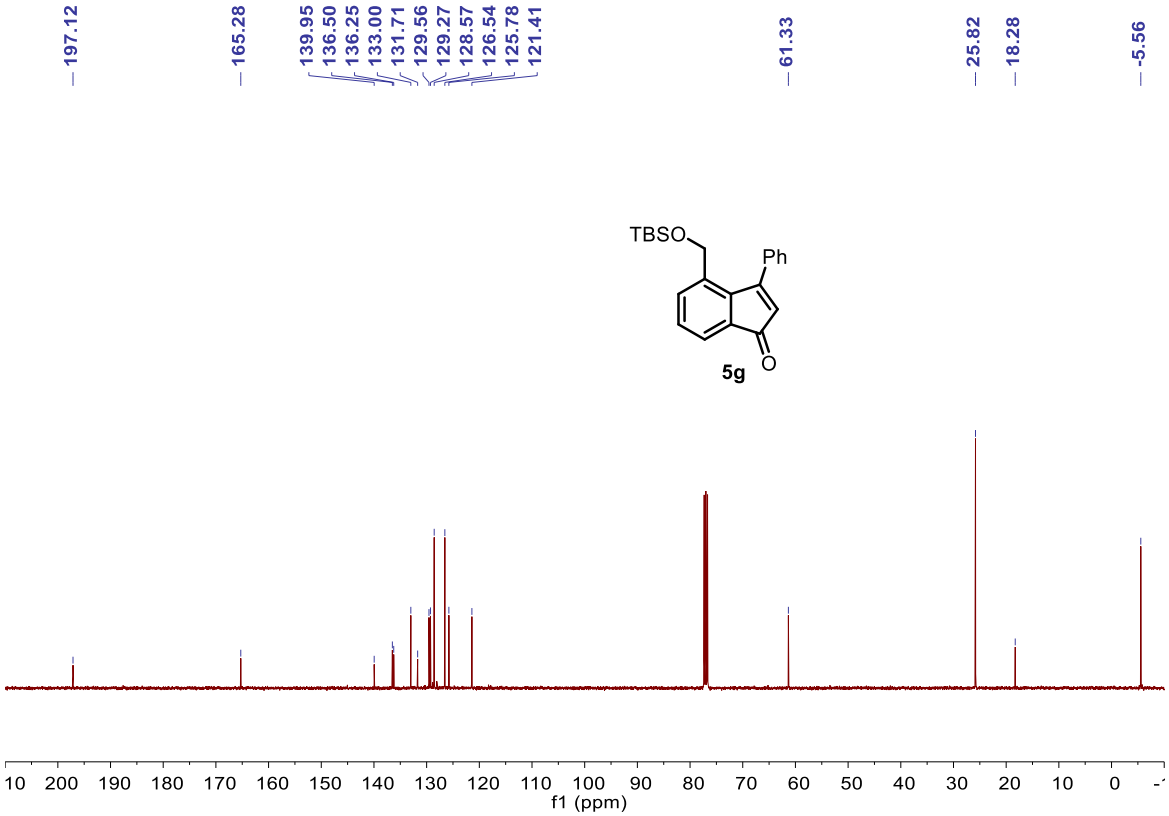

196.36
170.09
164.97
142.38
135.46
135.28
132.40
130.52
129.75
129.53
128.63
126.60
126.38
122.66
62.48
20.62

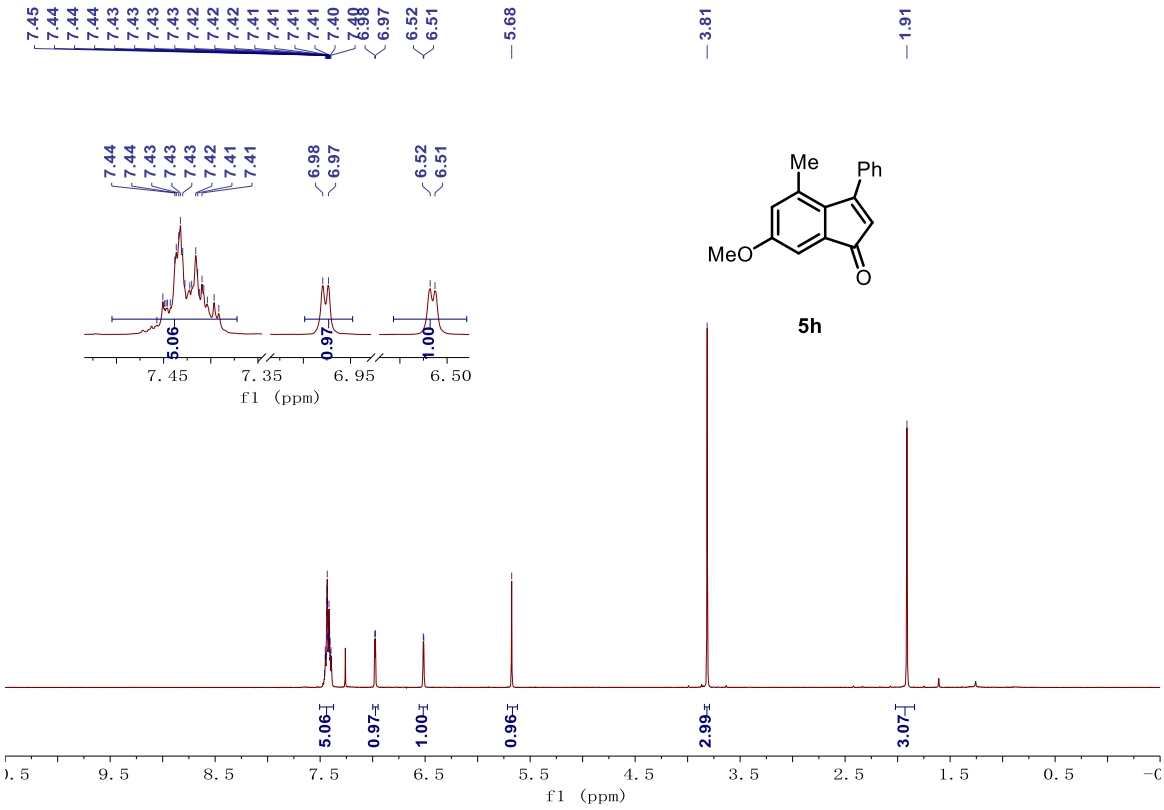

OAc
Ph
O

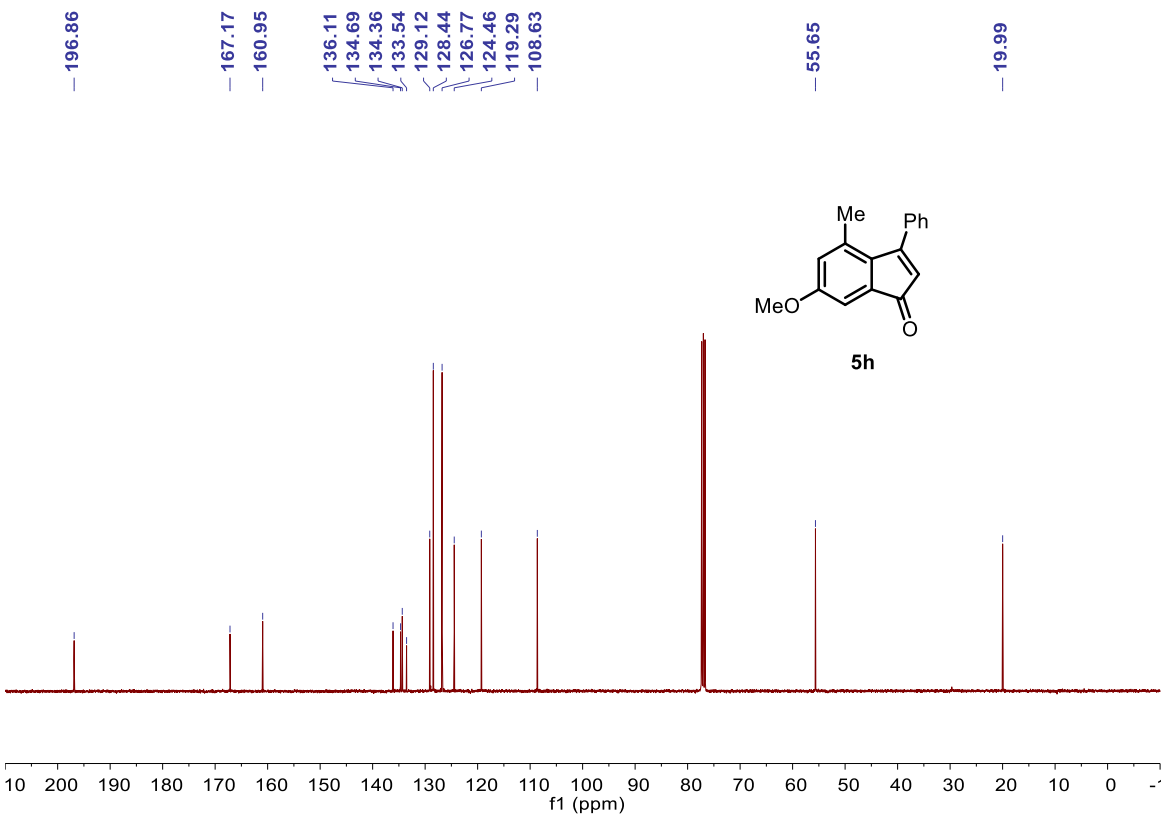
5f

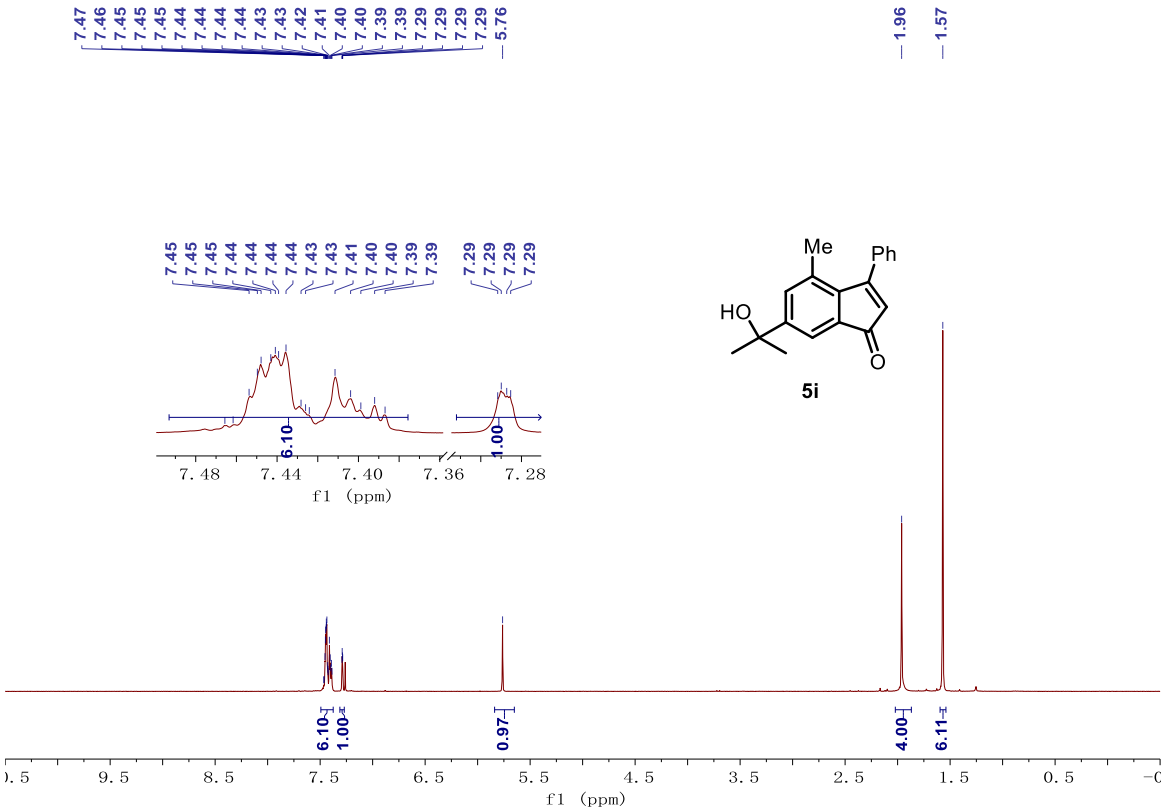

f1 (ppm)

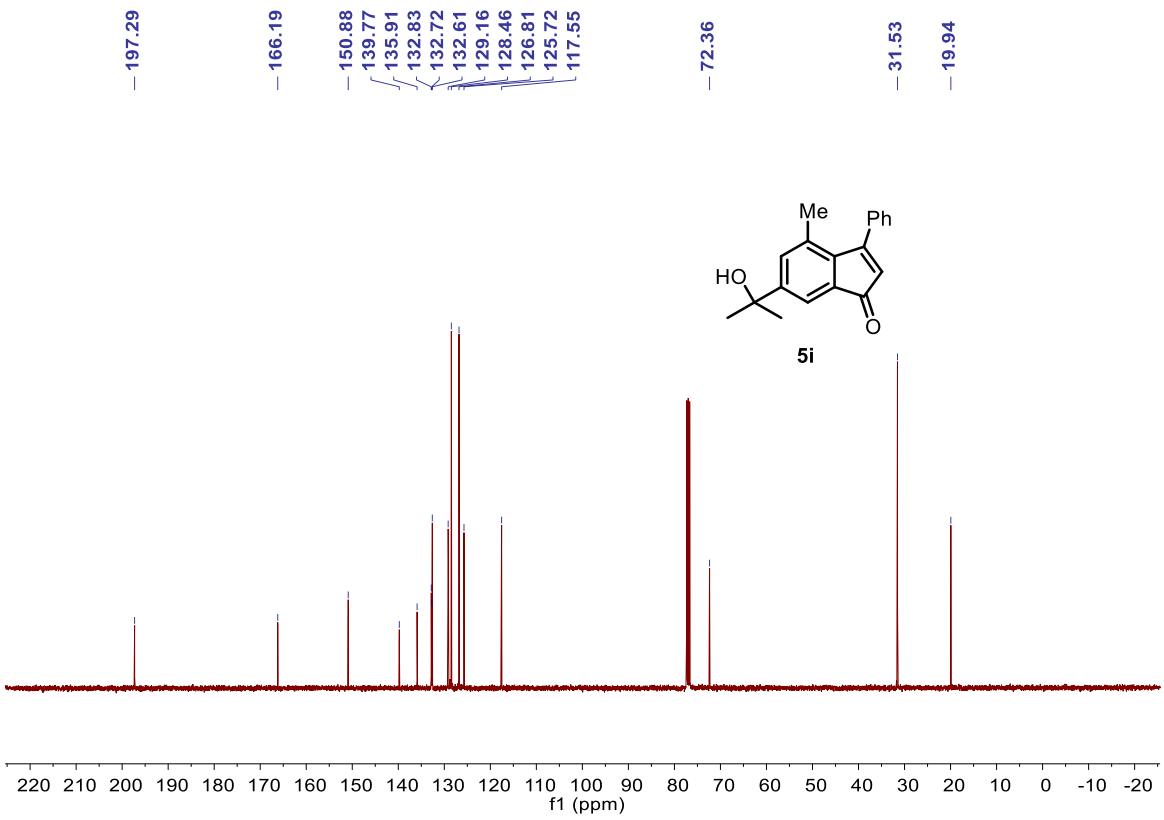

7.57 7.55 7.48 7.47 7.47 7.46 7.46 7.45 7.45 7.45 7.43 7.43 7.41 7.41 7.40 7.40 7.39 7.32 7.30 7.28 5.80
4.23
0.81
-0.11
7.57 7.55 7.47 7.47 7.46 7.46 7.45 7.45 7.43 7.43 7.41 7.41 7.40 7.40 7.32 7.30
1.01 5.90 1.03
7.60 7.50 7.40 7.30 7.20
f1 (ppm)
TBSO
Ph
O
5g
1.01 5.90 1.03 0.90 2.00 8.97 5.99
f1 (ppm)

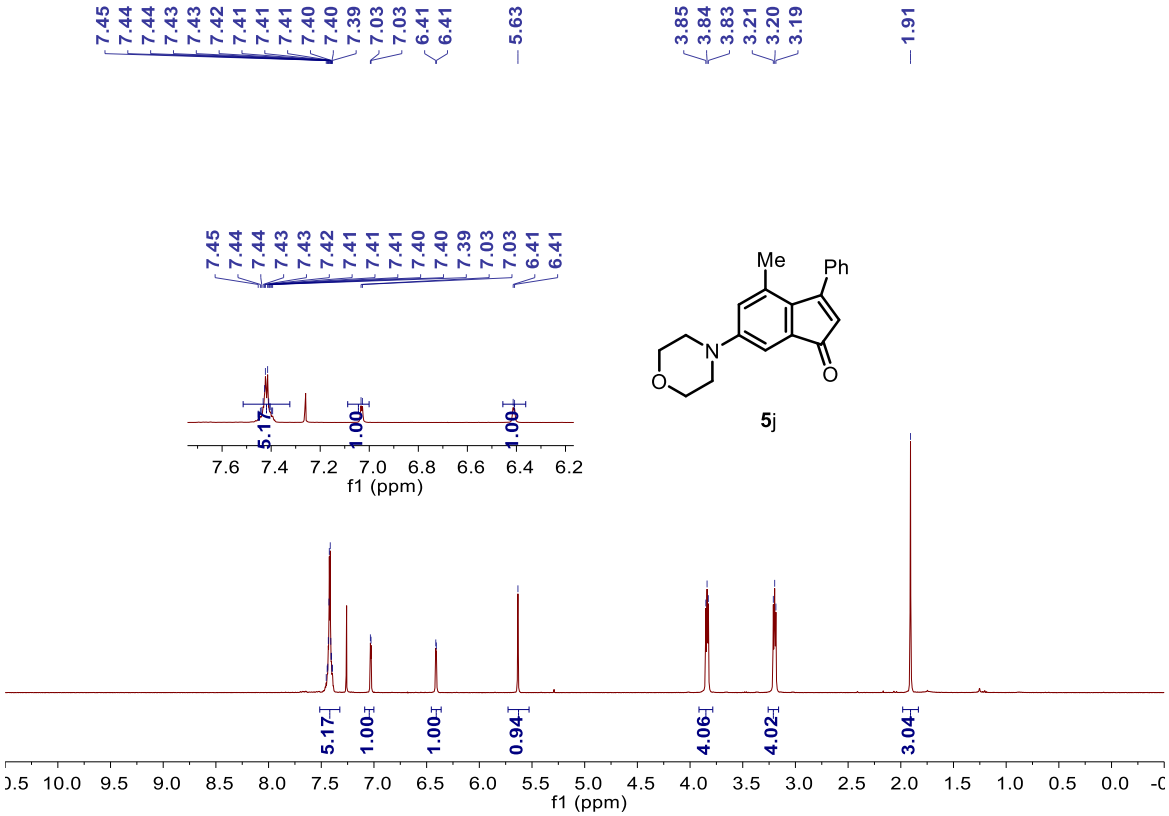

197.12
165.28
139.95 136.50 136.25 133.00 131.71 129.56 129.27 128.57 126.54 125.78 121.41
61.33
25.82
18.28
-5.56
TBSO
Ph
O
5g
f1 (ppm)

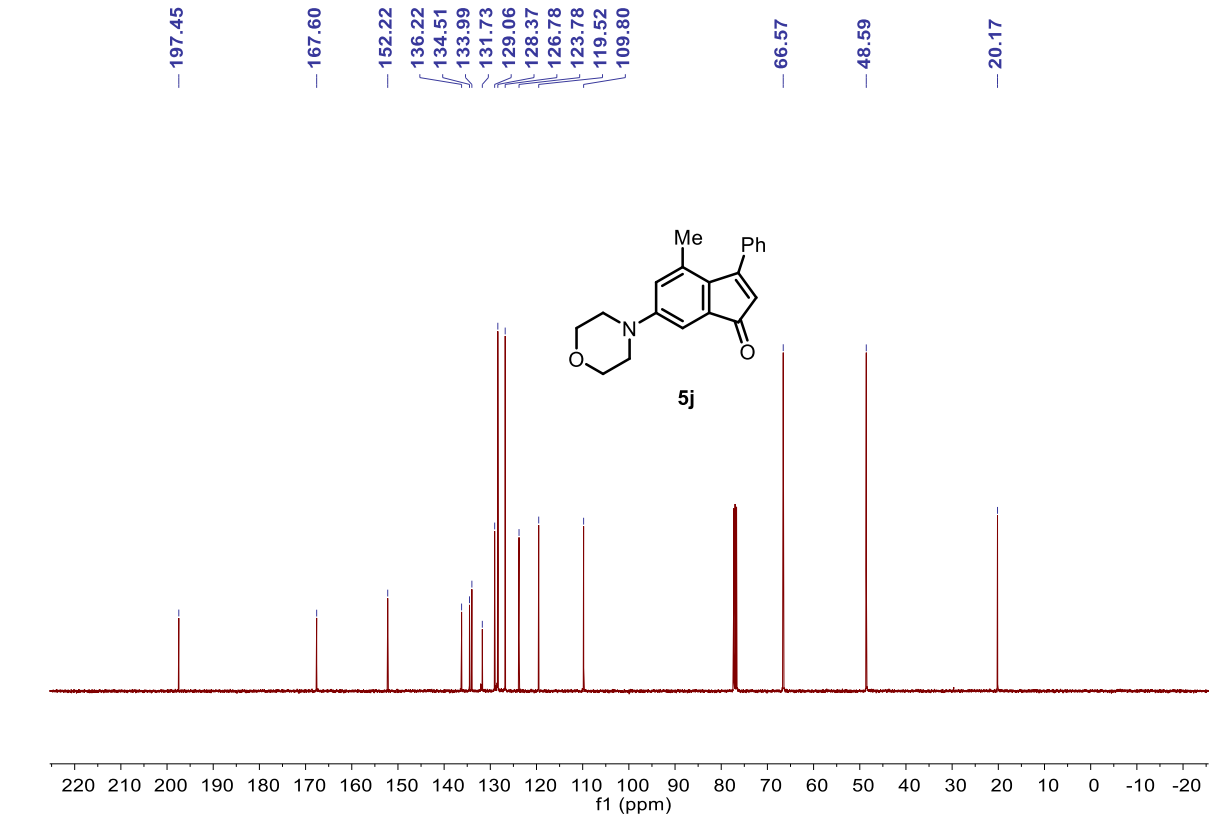

7.45 7.44 7.44 7.44 7.43 7.43 7.43 7.43 7.42 7.42 7.42 7.41 7.41 7.41 7.41 7.40 6.98 6.97 6.52 6.51
5.68
3.81
1.91
7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.41
6.98 6.97
6.52 6.51
5.06
0.97
1.00
7.45 7.35 6.95 6.50
f1 (ppm)
Me
Ph
MeO
O
5h
5.06 0.97 1.00 0.96 2.99 3.07
f1 (ppm)

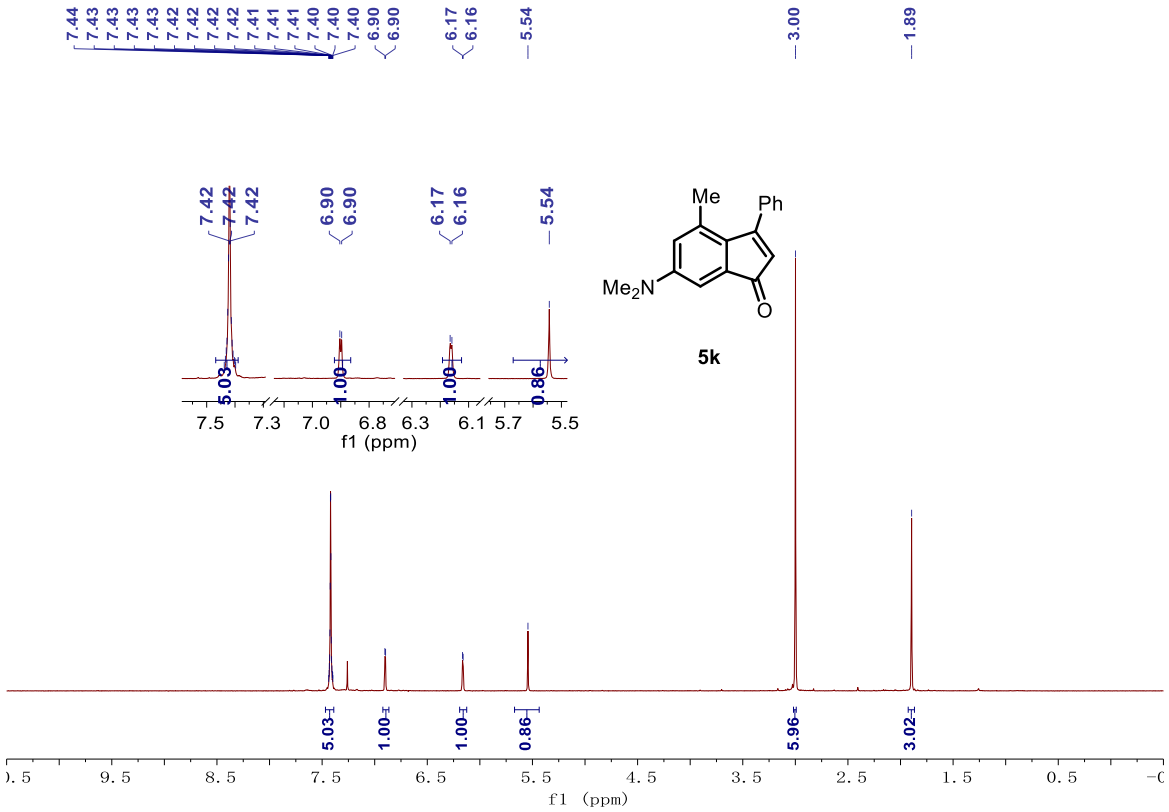

196.86
167.17
160.95
136.11 134.69 134.36 133.54 129.12 128.44 126.77 124.46 119.29
108.63
55.65
19.99
Me
Ph
MeO
O
5h
f1 (ppm)

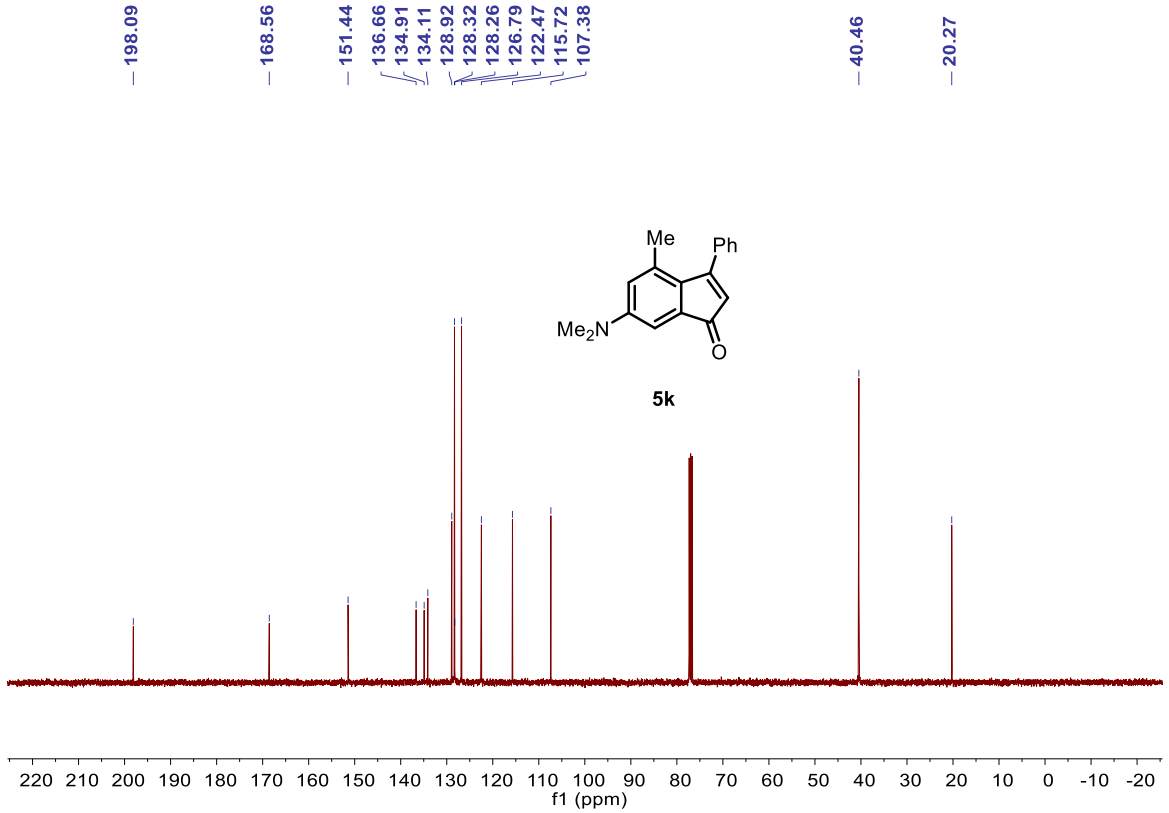

7.47 7.46 7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.42 7.41 7.40 7.40 7.39 7.39 7.29 7.29 7.29 7.29 5.76
1.96
1.57
7.45 7.45 7.45 7.44 7.44 7.44 7.44 7.43 7.43 7.41 7.40 7.40 7.39 7.39
7.29 7.29 7.29 7.29
6.10
1.00
7.48 7.44 7.40 7.36 7.28
f1 (ppm)
Me
Ph
HO
O
5i
6.10
1.00
0.97
4.00
6.11
f1 (ppm)

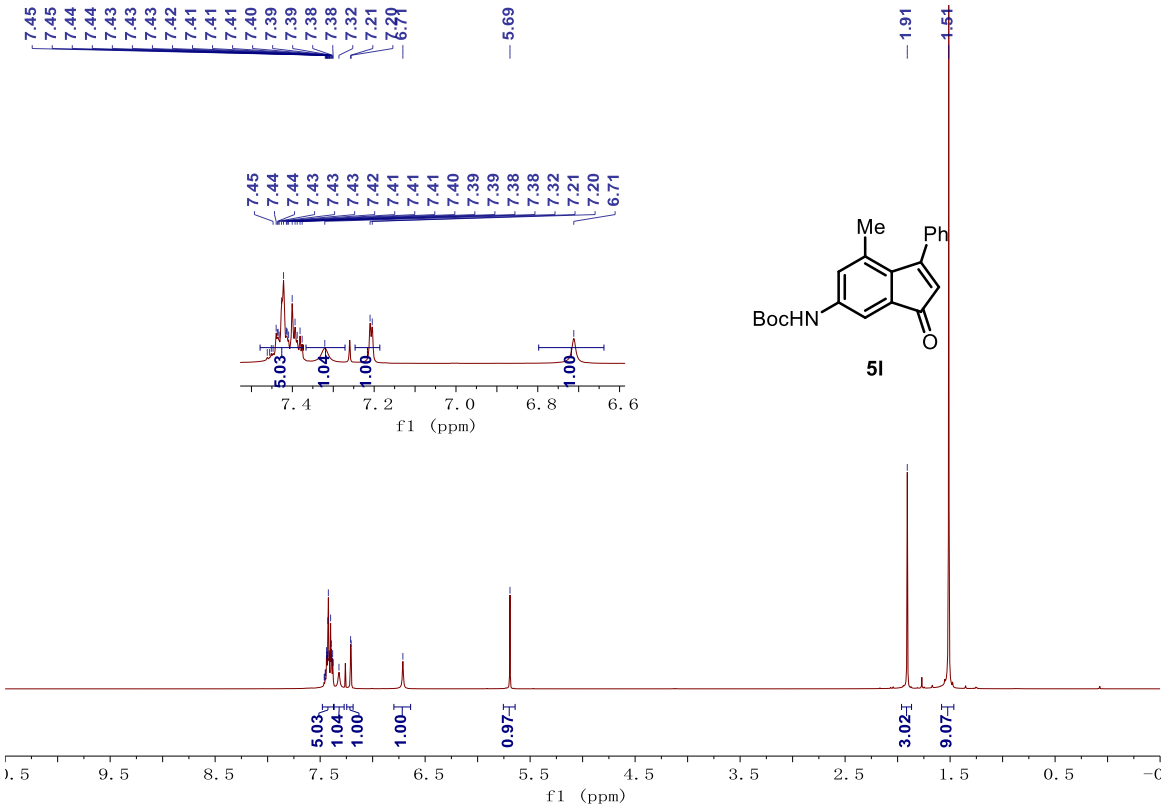

197.29
166.19
150.88
139.77
135.91
132.83
132.72
132.61
129.16
128.46
126.81
125.72
117.55
72.36
31.53
19.94
Me
Ph
HO
O
5i
f1 (ppm)

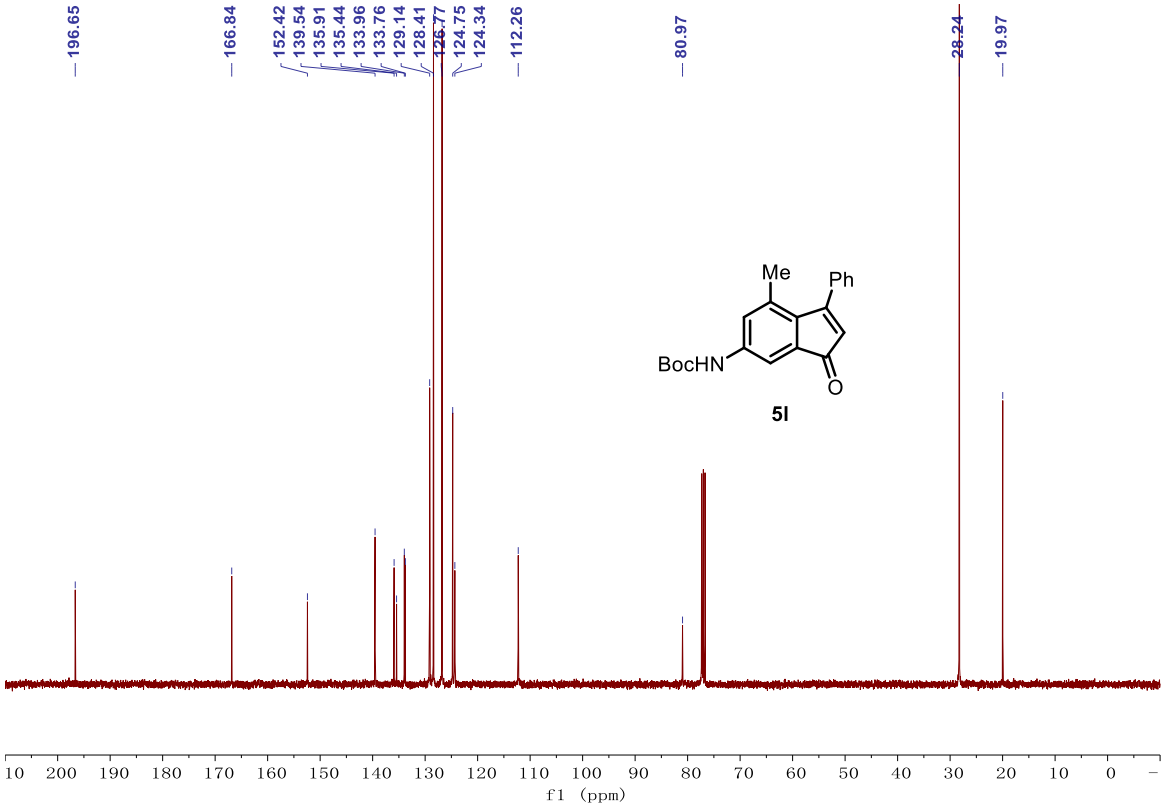

7.45 7.44 7.44 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.40 7.39 7.03 7.03 6.41 6.41
5.63
3.85 3.84 3.83 3.21 3.20 3.19
1.91
Me
Ph
N
O
O
5j
5.17
1.00
1.00
1.00
7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2
f1 (ppm)
5.17
1.00
1.00
0.94
4.06
4.02
3.04
f1 (ppm)


197.45
167.60
152.22
136.22
134.51
133.99
131.73
129.06
128.37
126.78
123.78
119.52
109.80
66.57
48.59
20.17
Me
Ph
N
O
O
5j
f1 (ppm)

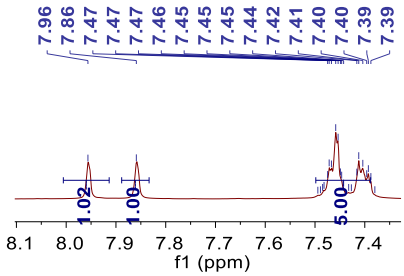

7.44
7.43
7.43
7.43
7.42
7.42
7.42
7.41
7.41
7.40
7.40
6.90
6.90
6.17
6.16
5.54
3.00
1.89
7.42
7.42
7.42
6.90
6.90
6.17
6.16
5.54
5.03
1.00
1.00
0.86
7.5 7.3 7.0 6.8 6.3 6.1 5.7 5.5
f1 (ppm)
Me
Ph
Me2N
O
5k
5.03
1.00
1.00
0.86
5.96
3.02
f1 (ppm)

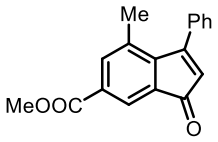

198.09
168.56
151.44
136.66
134.91
134.11
128.92
128.32
128.26
126.79
122.47
115.72
107.38
40.46
20.27
Me
Ph
Me2N
O
5k
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)


7.45 7.45 7.44 7.44 7.43 7.43 7.43 7.42 7.41 7.41 7.41 7.40 7.39 7.39 7.38 7.38 7.32 7.21 7.20 6.71
5.69
1.91
1.51
5.03 1.04 1.00 1.00 0.97 3.02 9.07
f1 (ppm)
Me
Ph
BocHN
O
5l

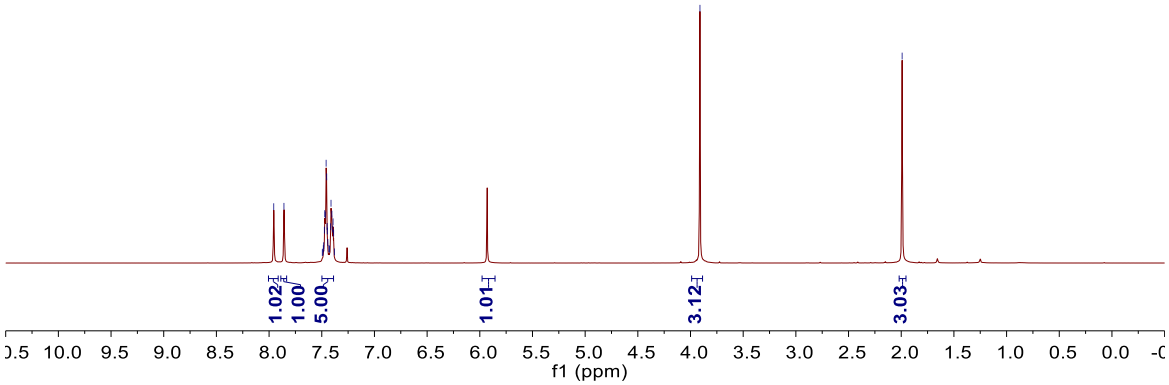

196.65
166.84
152.42 139.54 135.91 135.44 133.96 133.76 129.14 128.41 126.77 124.75 124.34
112.26
80.97
28.24
19.97
f1 (ppm)
Me
Ph
BocHN
O
5l


7.96
7.86
7.49
7.49
7.48
7.48
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.43
7.43
7.42
7.41
7.40
7.40
7.39
7.38
3.91
1.99

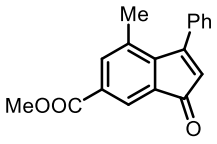

7.96
7.86
7.47
7.47
7.47
7.46
7.45
7.45
7.45
7.44
7.42
7.41
7.40
7.40
7.39
7.39
1.02
1.00
5.00
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
f1 (ppm)


Me
Ph
MeOOC
O

**5m**

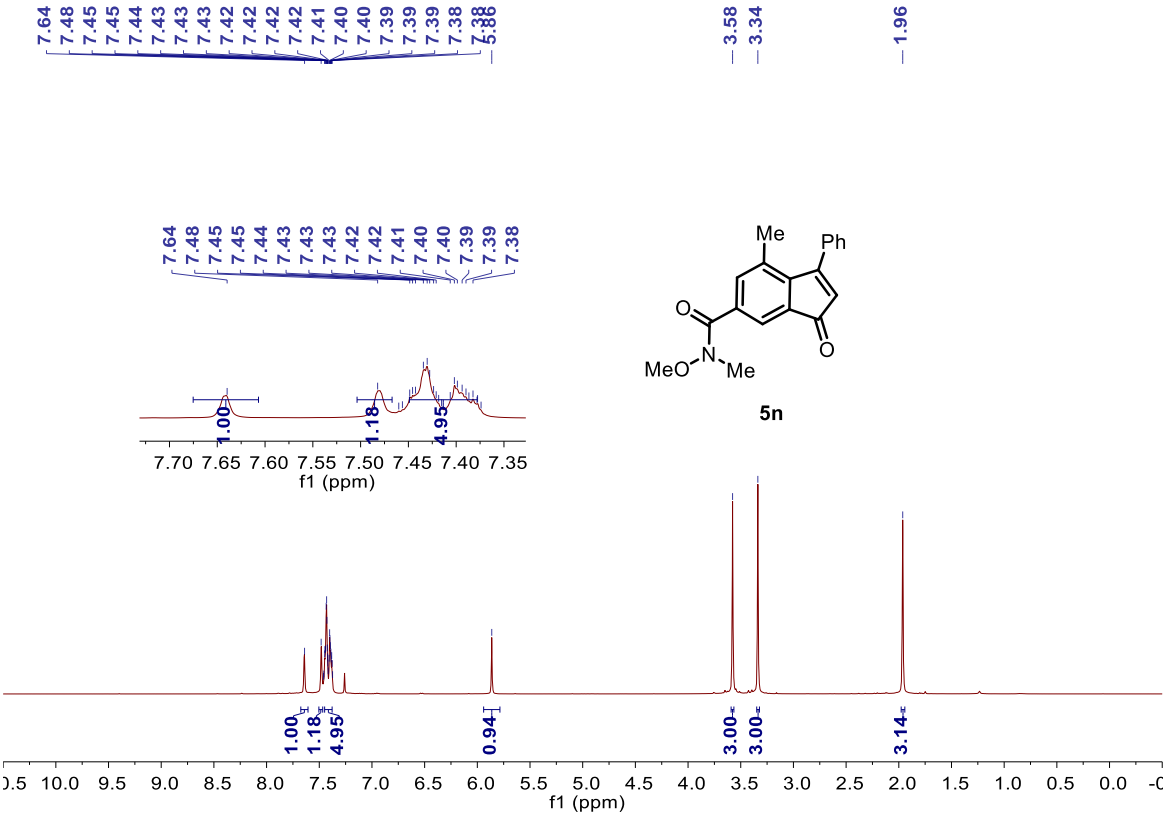

1.02
1.00
5.00
1.01
3.12
3.03
f1 (ppm)

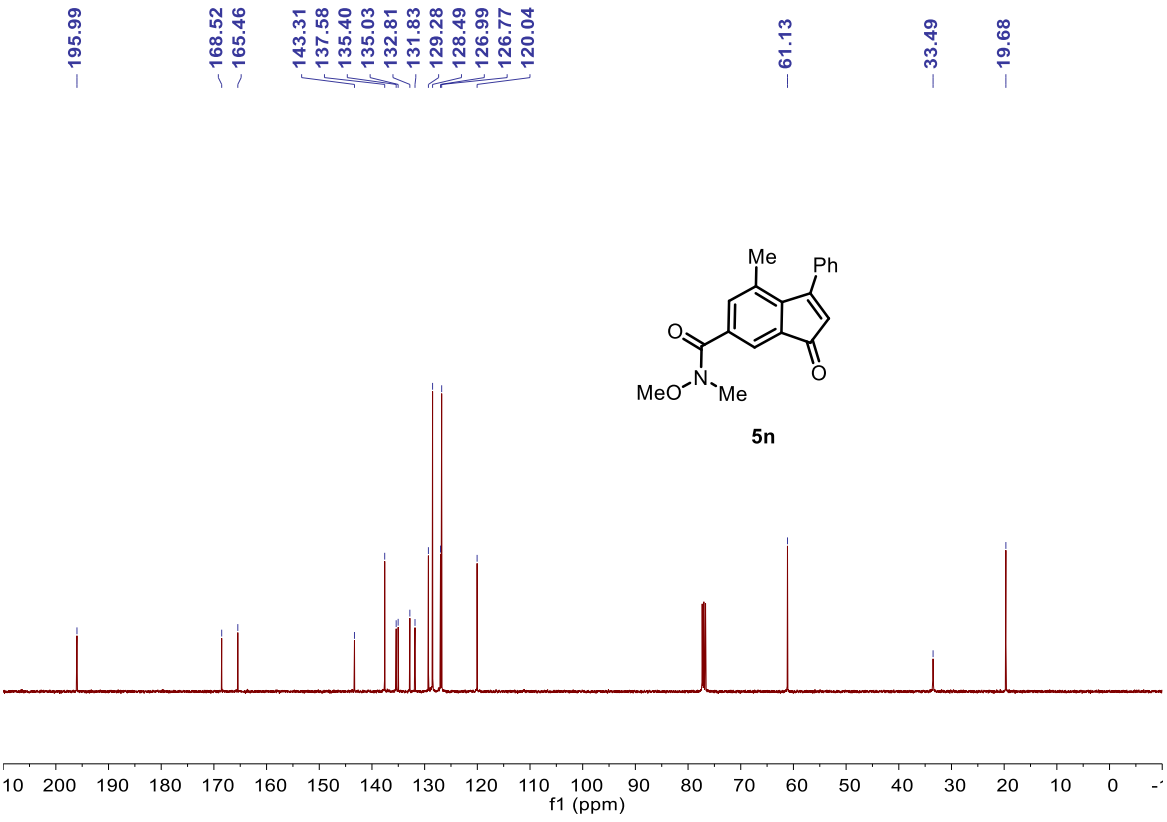

195.69
166.00
165.26
145.53
139.04
135.31
133.00
132.46
131.14
129.40
128.59
127.79
126.85
121.01
52.25
19.72

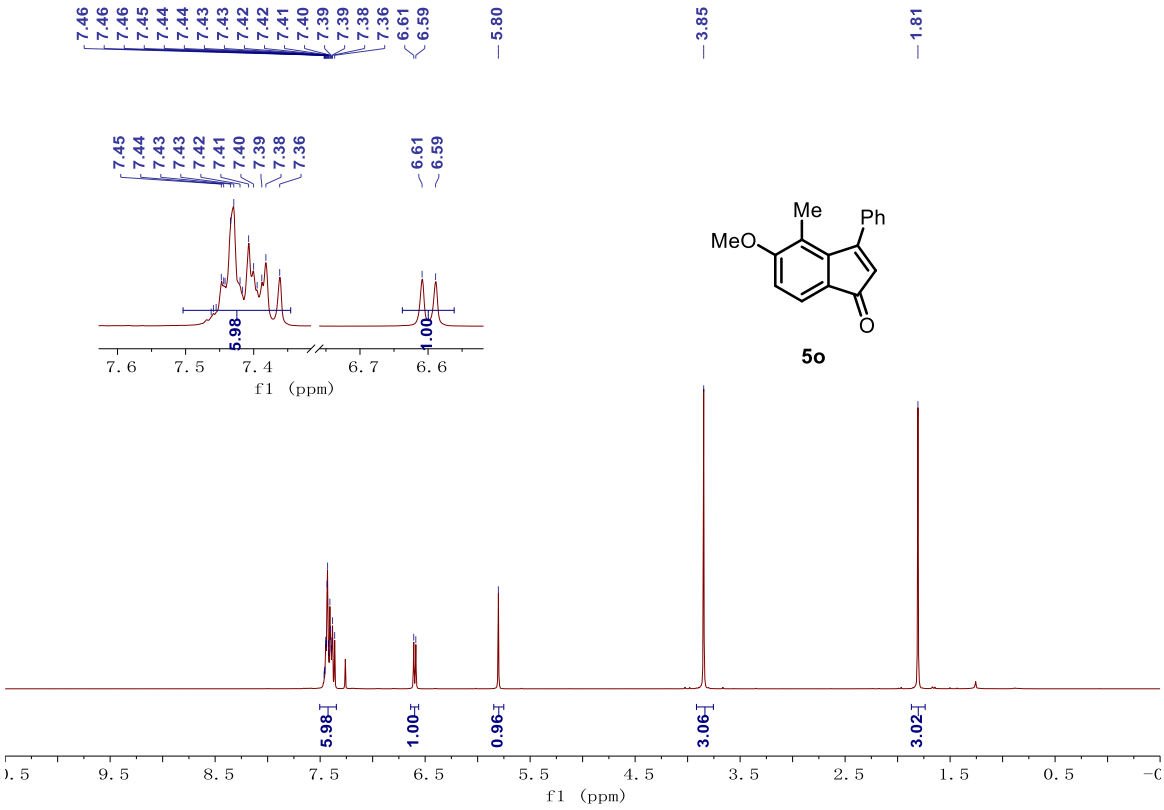

Me
Ph
MeOOC
O

**5m**


f1 (ppm)

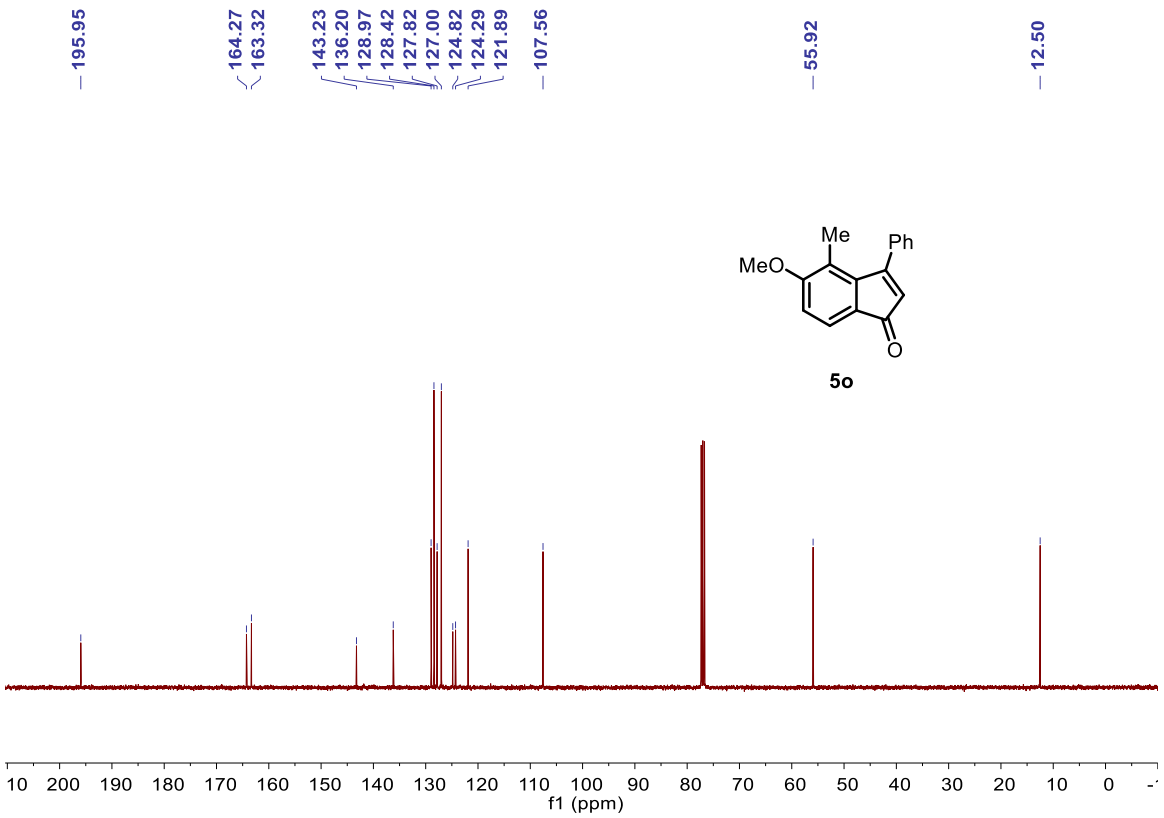

7.64 7.48 7.45 7.45 7.44 7.43 7.43 7.43 7.42 7.42 7.42 7.42 7.41 7.40 7.40 7.39 7.39 7.39 7.38 7.38 7.38
3.58 3.34
1.96
1.00 1.18 4.95
7.70 7.65 7.60 7.55 7.50 7.45 7.40 7.35
f1 (ppm)
Me Ph O O MeO N Me
5n
1.00 1.18 4.95 0.94 3.00 3.00 3.14
f1 (ppm)


195.99
168.52 165.46
143.31 137.58 135.40 135.03 132.81 131.83 129.28 128.49 126.99 126.77 120.04
61.13
33.49
19.68
Me Ph O O MeO N Me
5n
f1 (ppm)


7.46
7.46
7.46
7.45
7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.36
6.61
6.59
5.80
3.85
1.81
5.98
1.00
0.96
3.06
3.02
f1 (ppm)

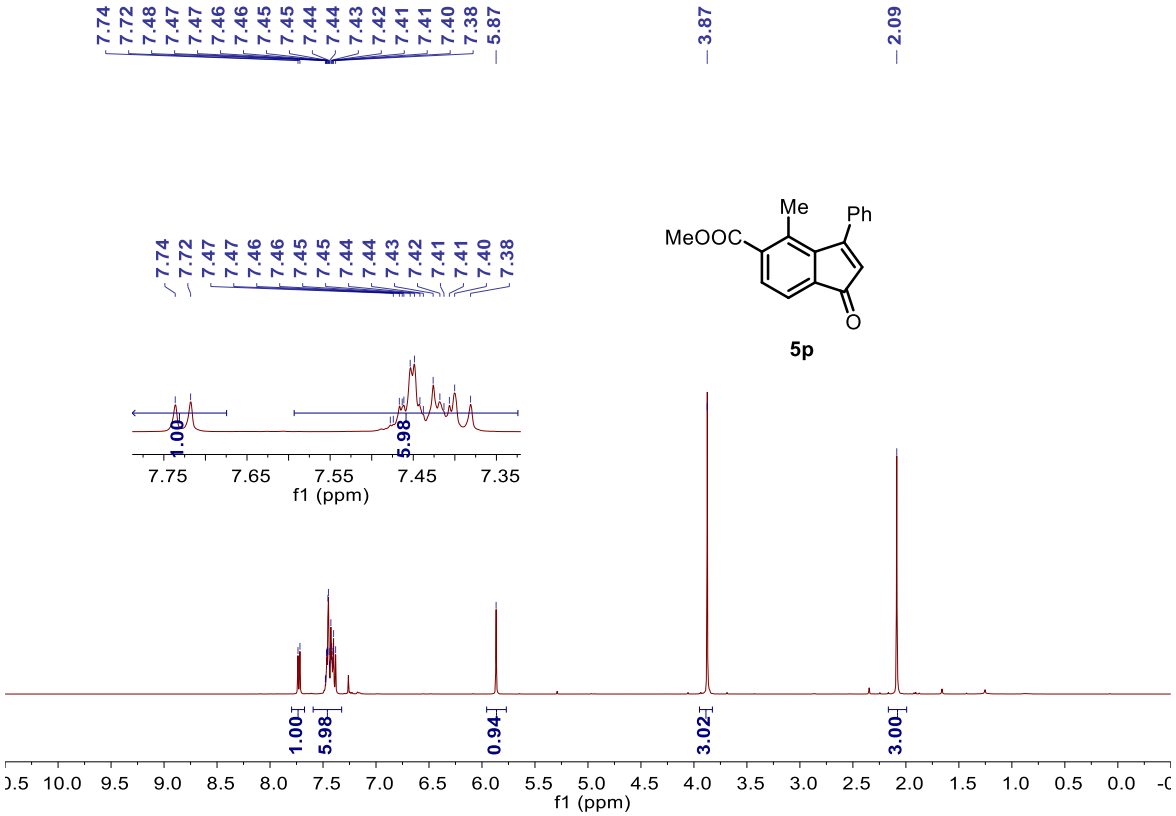

Me
Ph
MeO
O

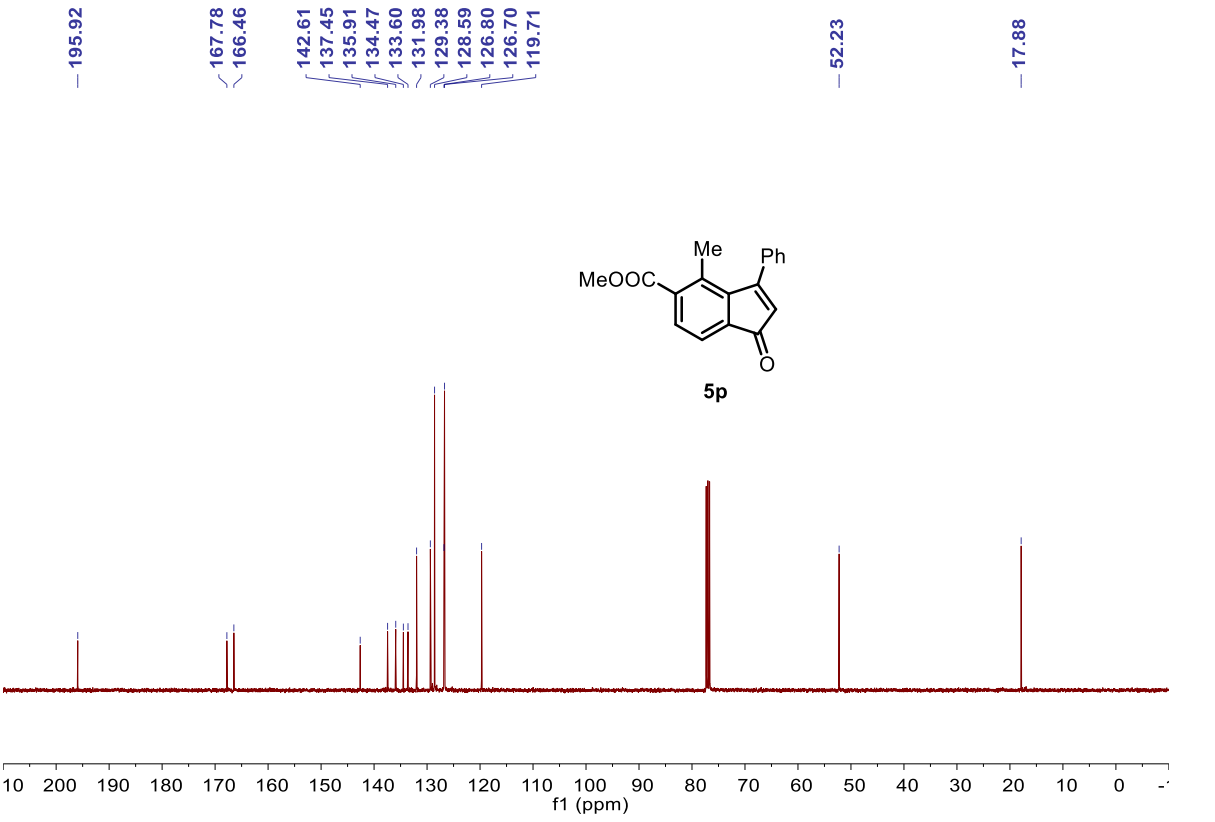
**5o**

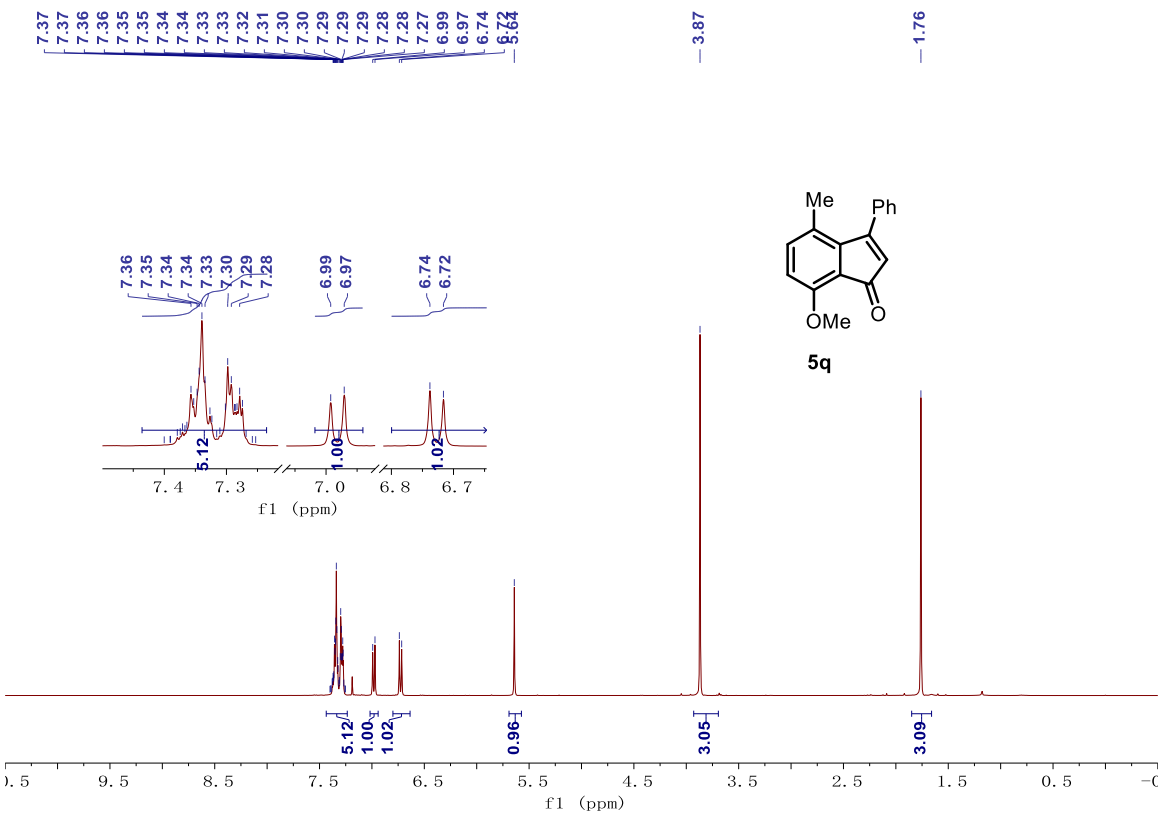

195.95
164.27
163.32
143.23
136.20
128.97
128.42
127.82
127.00
124.82
124.29
121.89
107.56
55.92
12.50
f1 (ppm)

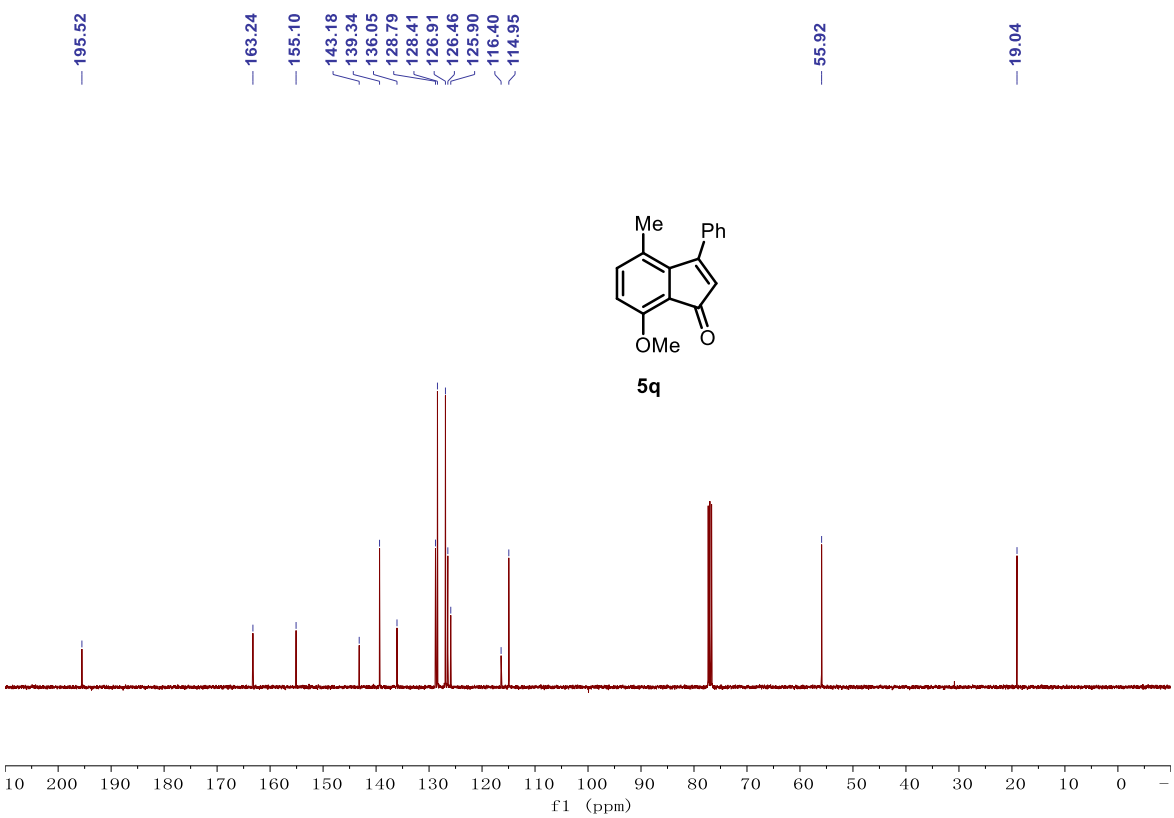

Me
Ph
MeO
O

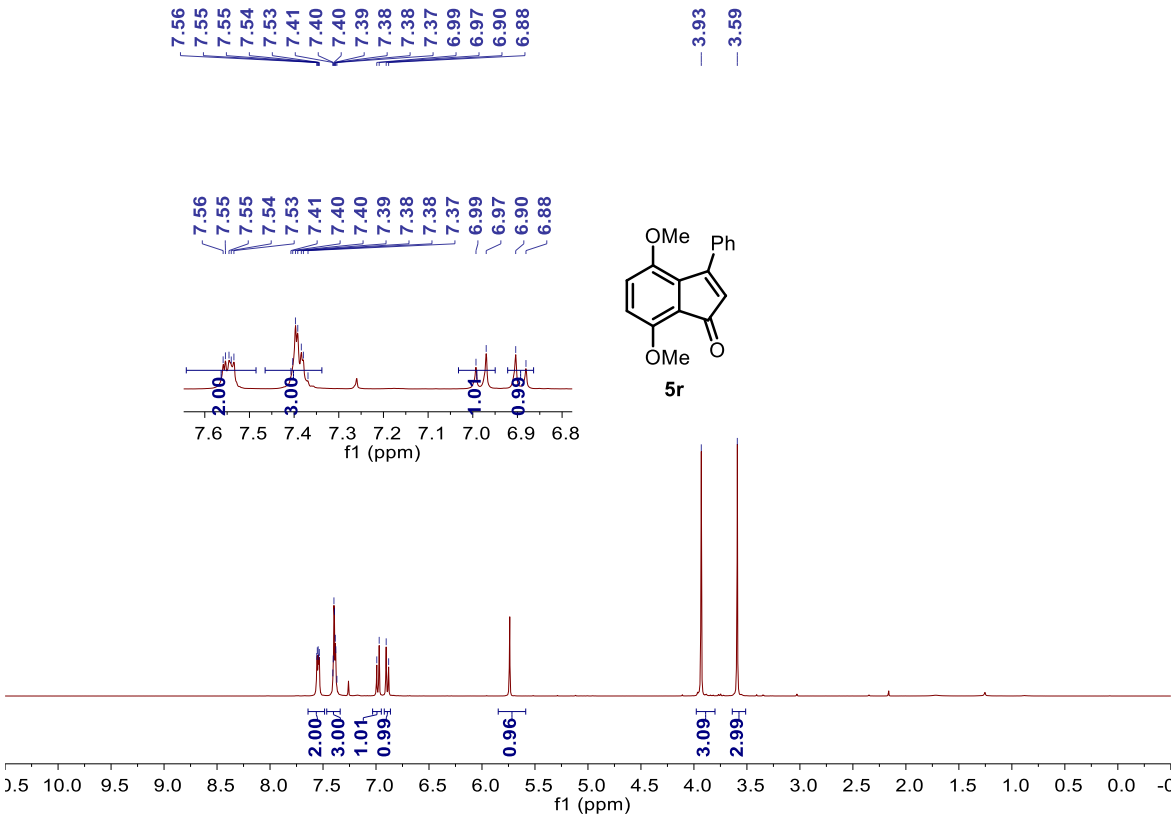
**5o**

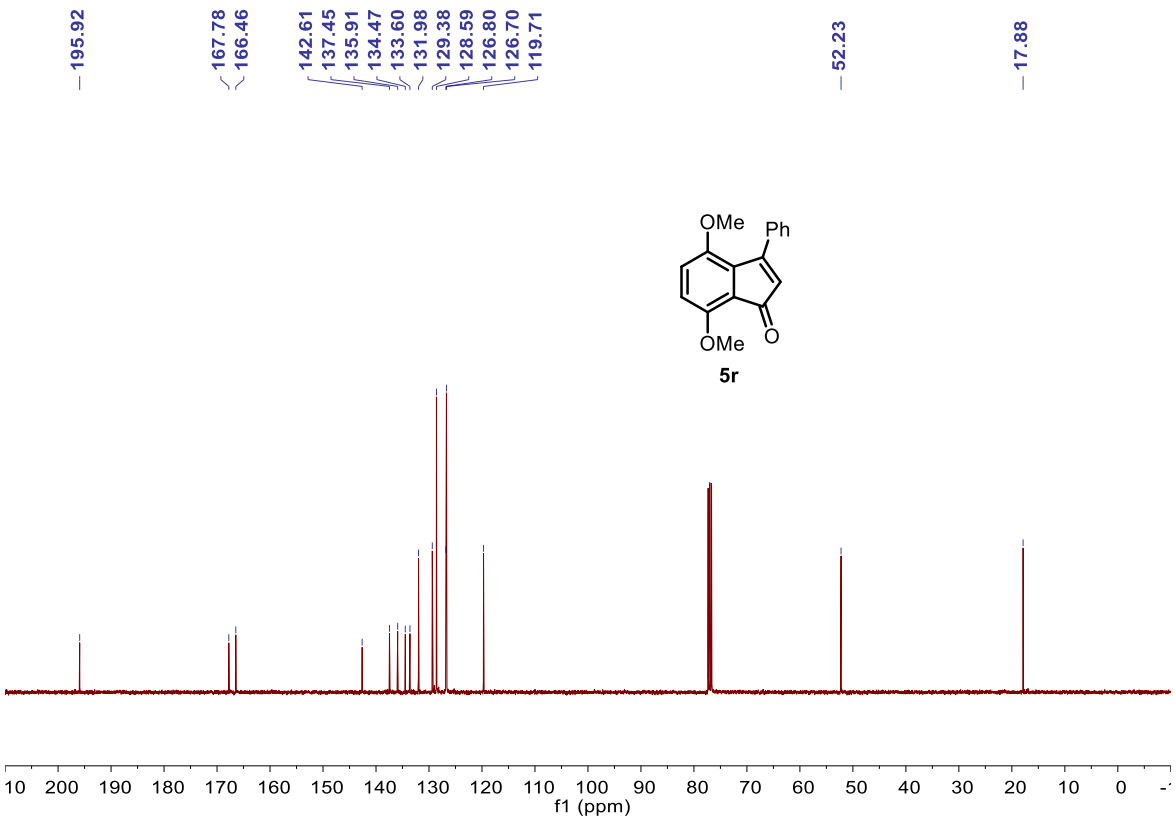

7.74
7.72
7.48
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.40
7.38
5.87
3.87
2.09
Me
Ph
MeOOC
O
5p
1.00
5.98
7.75
7.65
7.55
7.45
7.35
f1 (ppm)
1.00
5.98
0.94
3.02
3.00
f1 (ppm)

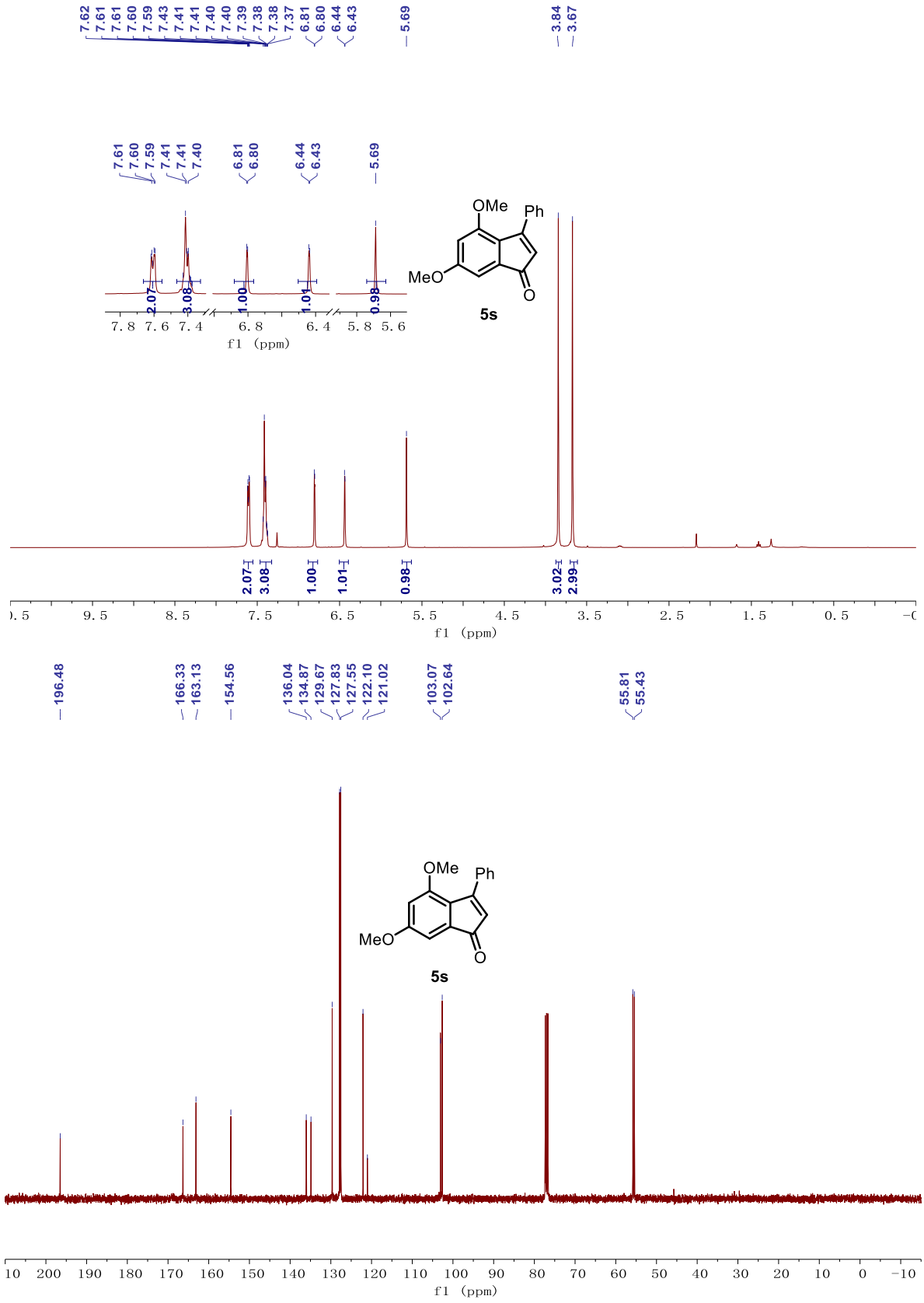

195.92
167.78
166.46
142.61
137.45
135.91
134.47
133.60
131.98
129.38
128.59
126.80
126.70
119.71
52.23
17.88
Me
Ph
MeOOC
O
5p
f1 (ppm)


7.37
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.31
7.30
7.30
7.29
7.29
7.29
7.28
7.28
7.27
6.99
6.97
6.74
6.72
5.64
3.87
1.76
Me
Ph
OMe
O
5q
5.12
1.00
1.02
0.96
3.05
3.09
f1 (ppm)

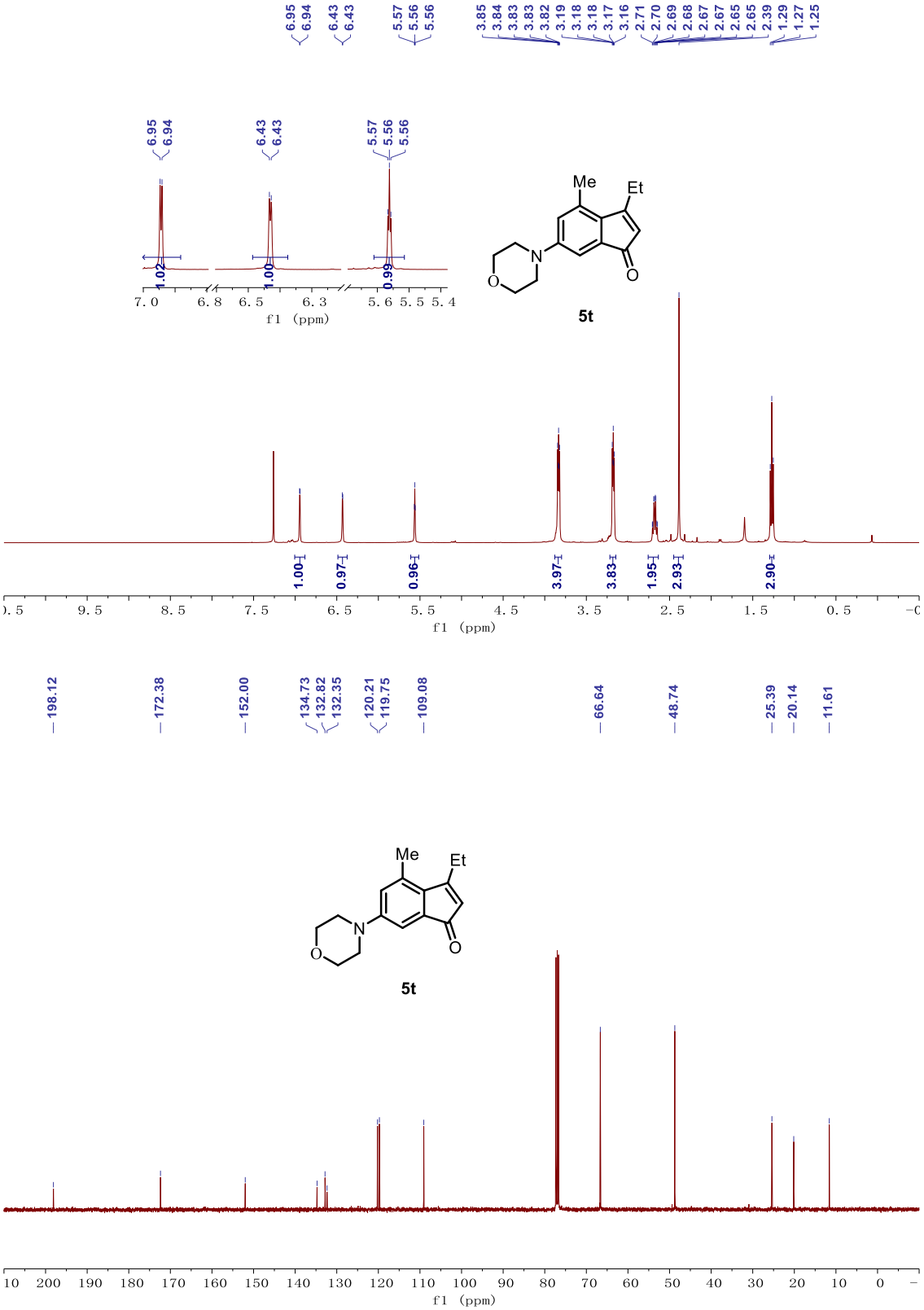

195.52
163.24
155.10
143.18
139.34
136.05
128.79
128.41
126.91
126.46
125.90
116.40
114.95
55.92
19.04
Me
Ph
OMe
O
5q
f1 (ppm)

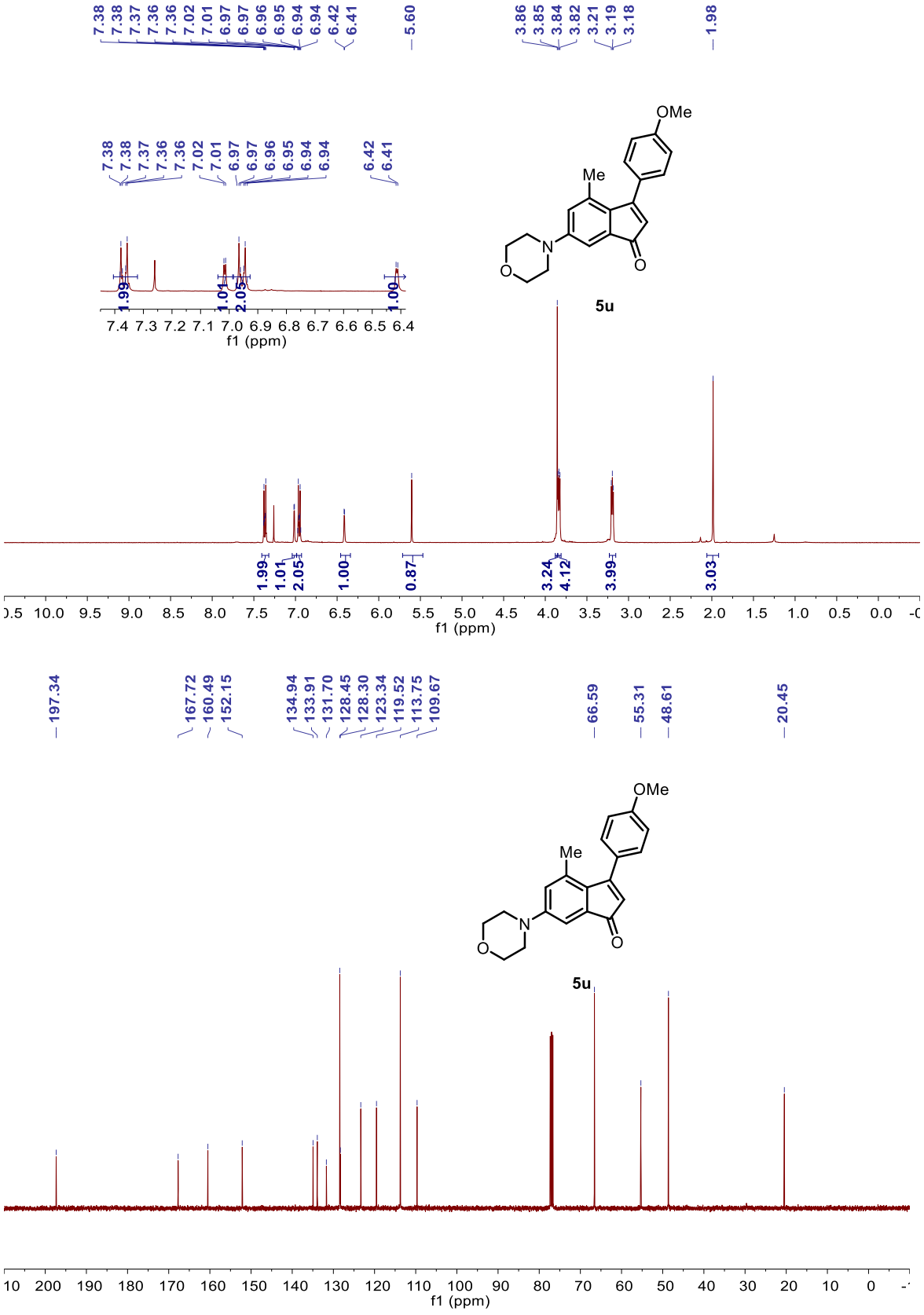

7.56
7.55
7.55
7.54
7.53
7.41
7.40
7.40
7.39
7.38
7.38
7.37
6.99
6.97
6.90
6.88
3.93
3.59
OMe
Ph
OMe
O
5r
2.00
3.00
1.01
0.99
0.96
3.09
2.99
f1 (ppm)

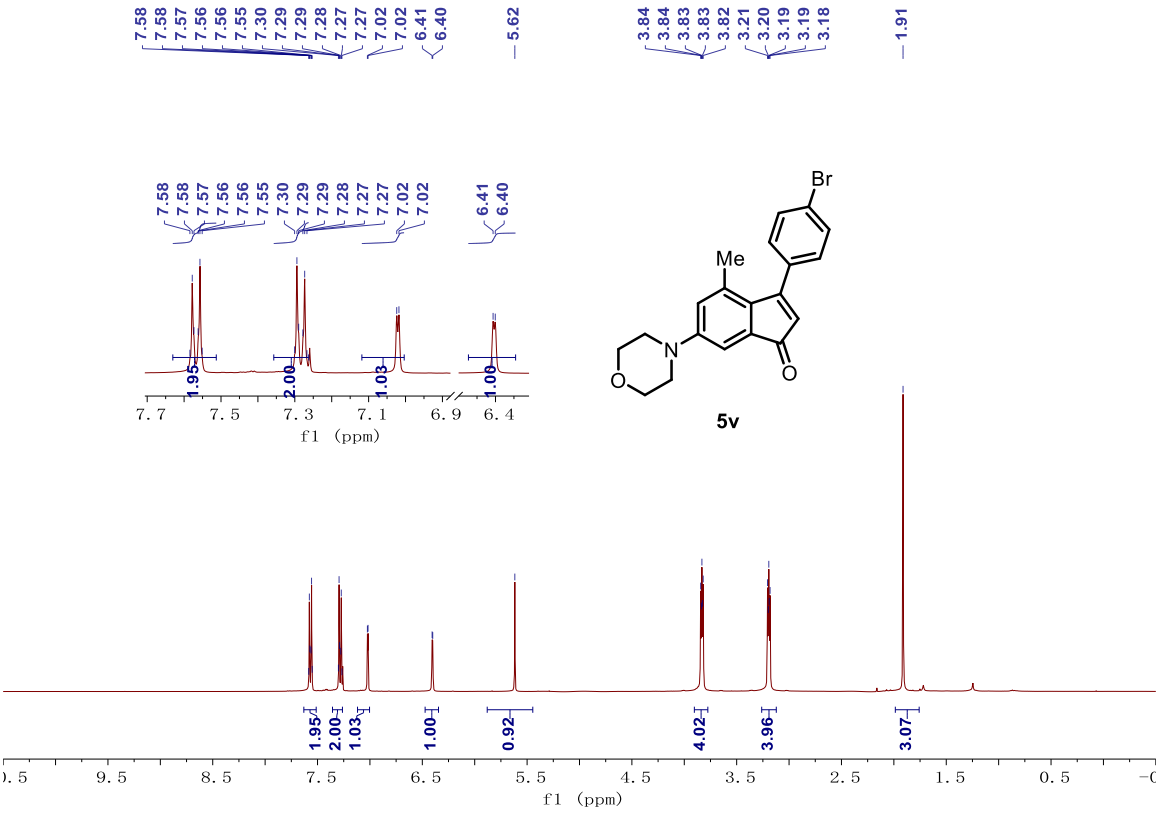

195.92
167.78
166.46
142.61
137.45
135.91
134.47
133.60
131.98
129.38
128.59
126.80
126.70
119.71
52.23
17.88
OMe
Ph
OMe
O
5r
f1 (ppm)

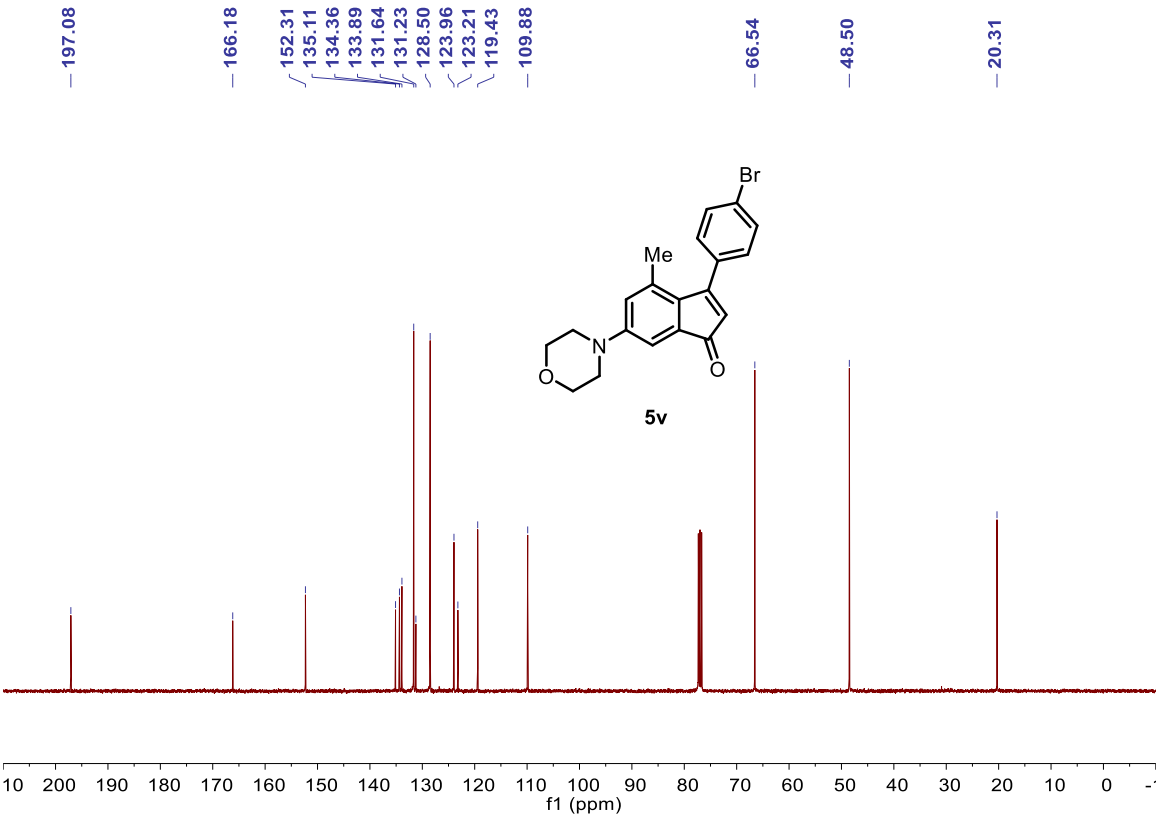

7.62
7.61
7.61
7.60
7.59
7.43
7.41
7.41
7.40
7.40
7.39
7.38
7.38
7.37
6.81
6.80
6.44
6.43
5.69
3.84
3.67
OMe
Ph
MeO
O
5s
2.07
3.08
1.00
1.01
0.98
3.02
2.99
f1 (ppm)
196.48
166.33
163.13
154.56
136.04
134.87
129.67
127.83
127.55
122.10
121.02
103.07
102.64
55.81
55.43
OMe
Ph
MeO
O
5s
f1 (ppm)

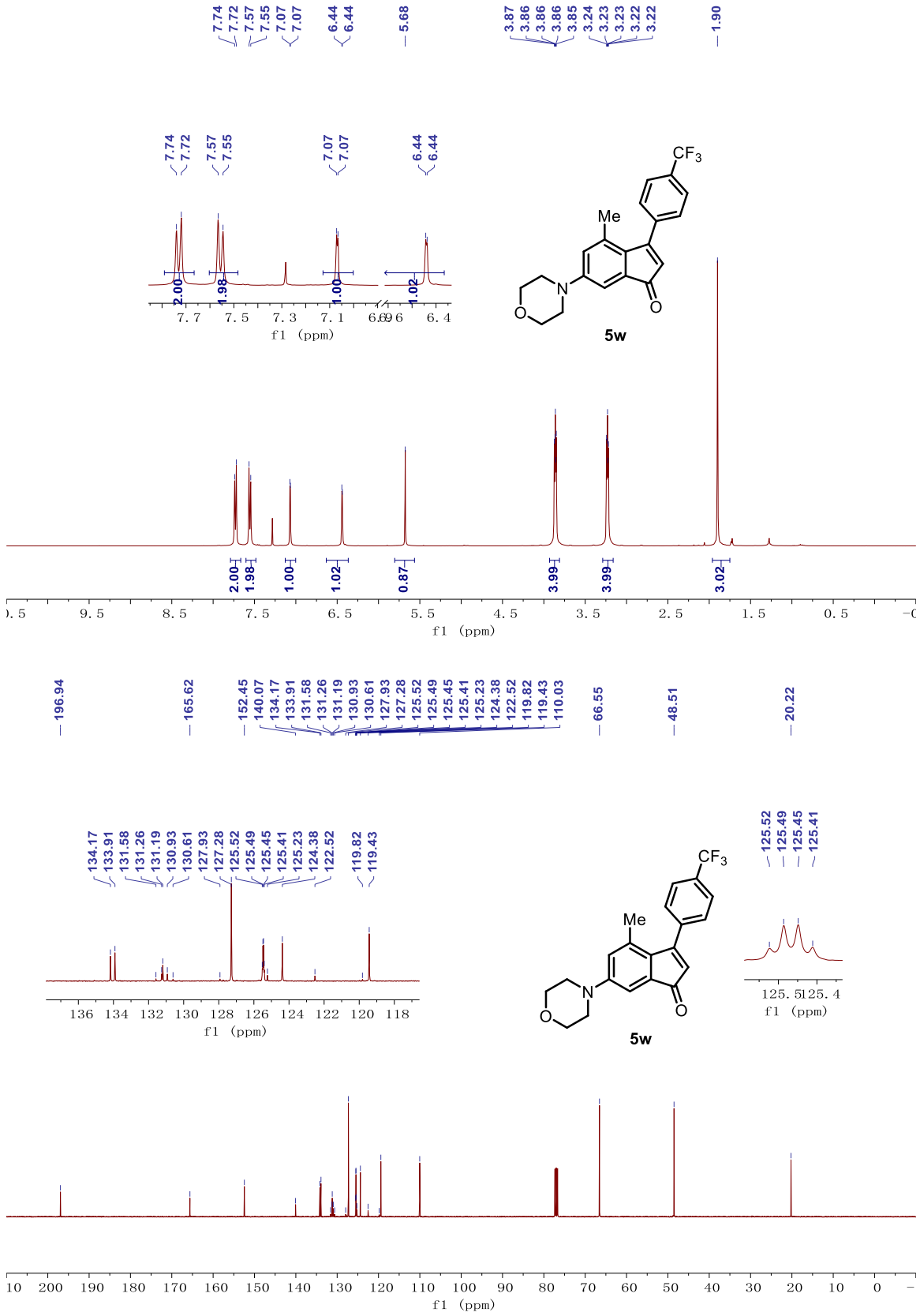
Purity 92%

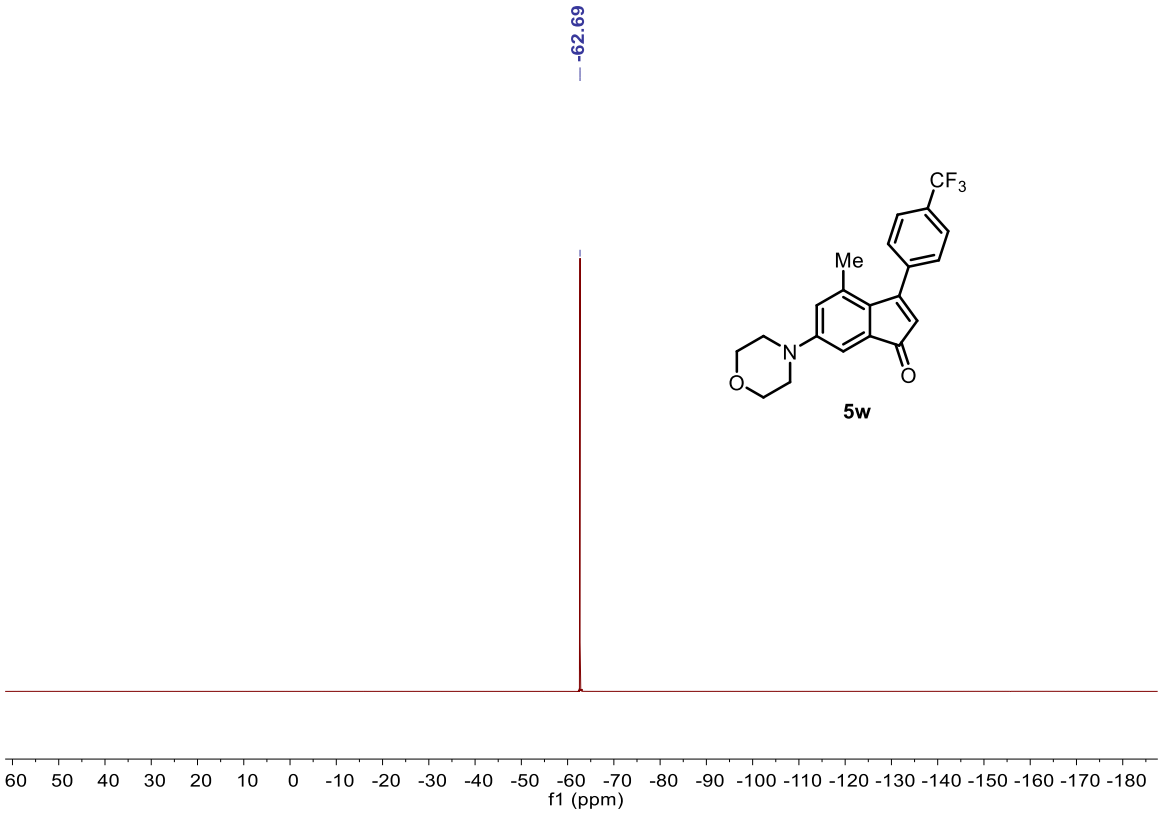

6.95
6.94
6.43
6.43
5.57
5.56
5.56
3.85
3.84
3.83
3.83
3.82
3.19
3.18
3.18
3.17
3.16
2.71
2.70
2.69
2.68
2.67
2.67
2.65
2.65
2.39
1.29
1.27
1.25
1.02
1.00
0.99
f1 (ppm)
Me
Et
N
O
O
5t
1.00
0.97
0.96
3.97
3.83
1.95
2.93
2.90
f1 (ppm)
198.12
172.38
152.00
134.73
132.82
132.35
120.21
119.75
109.08
66.64
48.74
25.39
20.14
11.61
Me
Et
N
O
O
5t
f1 (ppm)

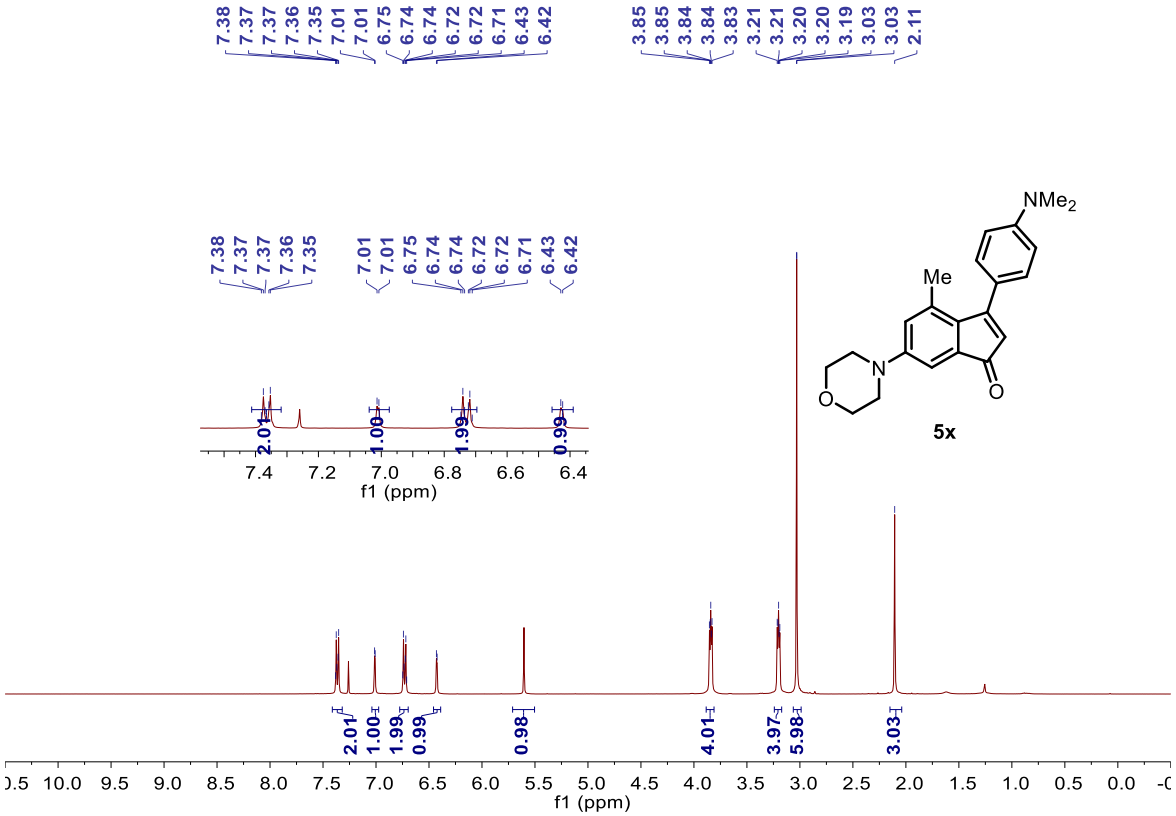

7.38
7.38
7.37
7.36
7.36
7.02
7.01
6.97
6.97
6.96
6.95
6.94
6.94
6.42
6.41
5.60
3.86
3.85
3.84
3.82
3.21
3.19
3.18
1.98
OMe
Me
N
O
O
5u
1.99
1.01
2.05
1.00
0.87
3.24
4.12
3.99
3.03
f1 (ppm)
197.34
167.72
160.49
152.15
134.94
133.91
131.70
128.45
128.30
123.34
119.52
113.75
109.67
66.59
55.31
48.61
20.45
f1 (ppm)

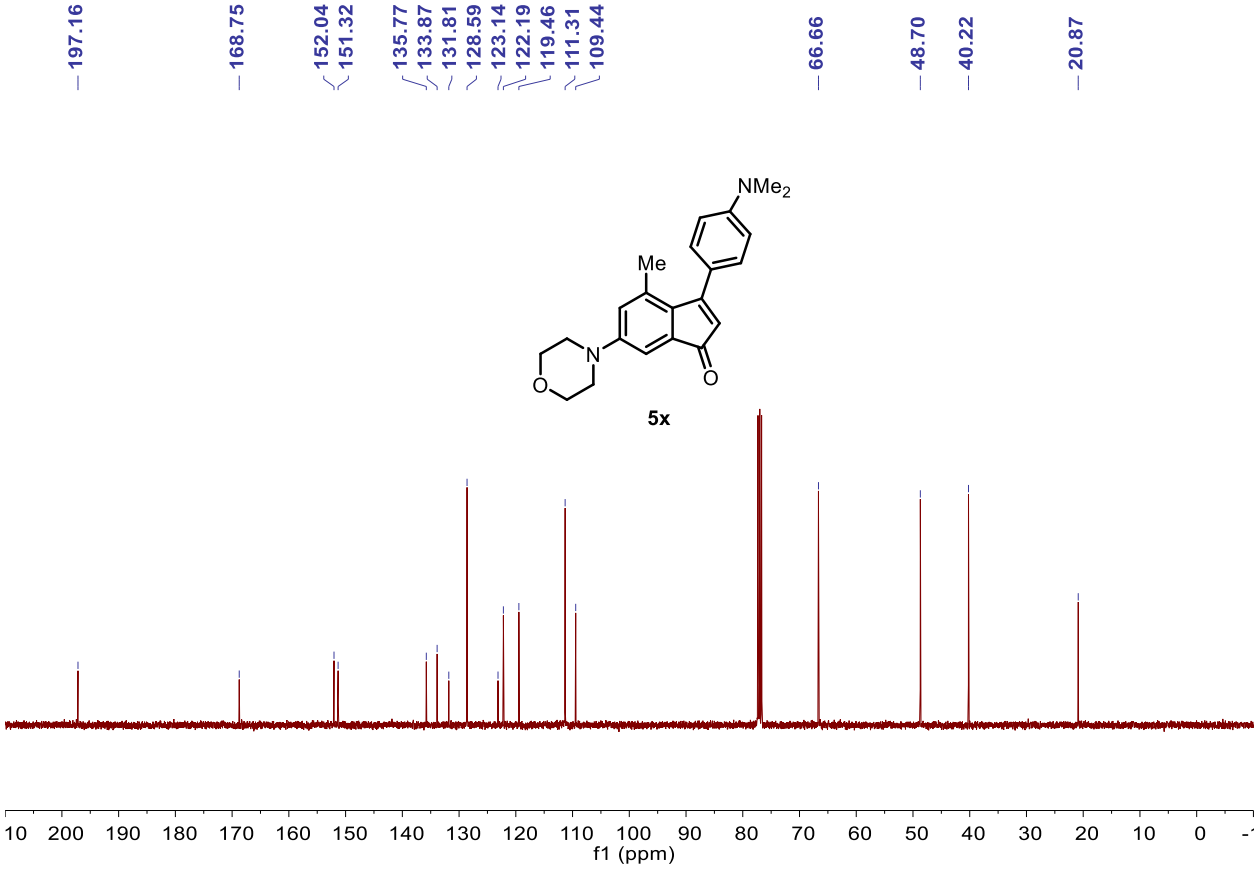

7.58
7.58
7.57
7.56
7.56
7.55
7.30
7.29
7.29
7.28
7.27
7.27
7.02
7.02
6.41
6.40
5.62
3.84
3.84
3.83
3.83
3.82
3.21
3.20
3.19
3.19
3.18
1.91
1.95
2.00
1.03
1.00
7.7
7.5
7.3
7.1
6.9
6.4
f1 (ppm)
Br
Me
N
O
O
5v
1.95
2.00
1.03
1.00
0.92
4.02
3.96
3.07
f1 (ppm)


197.08
166.18
152.31
135.11
134.36
133.89
131.64
131.23
128.50
123.96
123.21
119.43
109.88
66.54
48.50
20.31
Br
Me
N
O
O
5v
f1 (ppm)

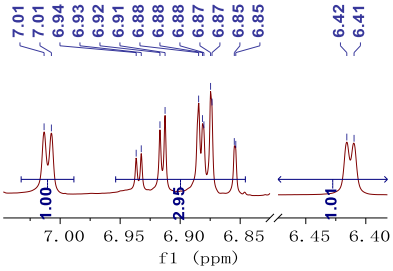

7.74
7.72
7.57
7.55
7.07
7.07
6.44
6.44
5.68
3.87
3.86
3.86
3.86
3.85
3.24
3.23
3.23
3.22
3.22
1.90
2.00
1.98
1.00
1.02
f1 (ppm)
CF3
Me
N
O
O
5w
2.00
1.98
1.00
1.02
0.87
3.99
3.99
3.02
f1 (ppm)
196.94
165.62
152.45
140.07
134.17
133.91
131.58
131.26
131.19
130.93
130.61
127.93
127.28
125.52
125.49
125.45
125.41
125.23
124.38
122.52
119.82
119.43
110.03
66.55
48.51
20.22
f1 (ppm)
CF3
Me
N
O
O
5w
125.52
125.49
125.45
125.41
f1 (ppm)
f1 (ppm)

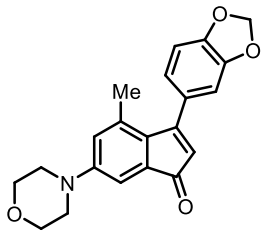

-62.69
CF3
Me
N
O
O
5w
60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180
f1 (ppm)


7.38
7.37
7.37
7.36
7.35
7.01
7.01
6.75
6.74
6.74
6.72
6.72
6.71
6.43
6.42
3.85
3.85
3.84
3.84
3.83
3.21
3.21
3.20
3.20
3.19
3.03
3.03
2.11
NMe2
Me
N
O
O
5x
2.01
1.00
1.99
0.99
7.4
7.2
7.0
6.8
6.6
6.4
f1 (ppm)
0.98
4.01
3.97
5.98
3.03
f1 (ppm)

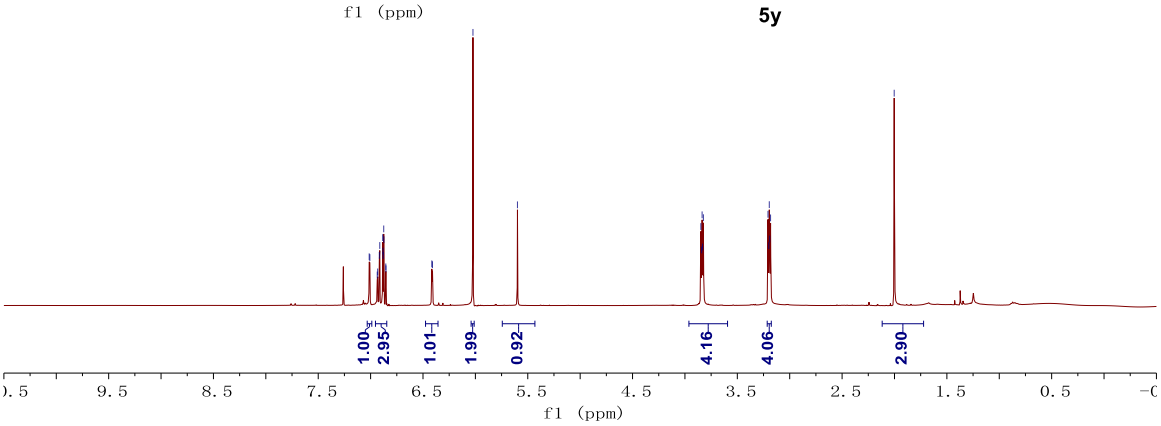

197.16
168.75
152.04
151.32
135.77
133.87
131.81
128.59
123.14
122.19
119.46
111.31
109.44
66.66
48.70
40.22
20.87
NMe2
Me
N
O
O
5x
f1 (ppm)


7.01
7.01
6.94
6.93
6.92
6.91
6.88
6.88
6.88
6.87
6.87
6.85
6.85
6.42
6.41
6.02
5.60
3.85
3.84
3.84
3.83
3.82
3.21
3.20
3.19
3.19
3.18
2.00

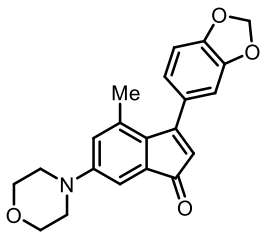

7.01
7.01
6.94
6.93
6.92
6.91
6.88
6.88
6.88
6.87
6.87
6.85
6.85
6.42
6.41
1.00
2.95
1.01
7.00
6.95
6.90
6.85
6.45
6.40
f1 (ppm)


Me
O
O
N
O
O

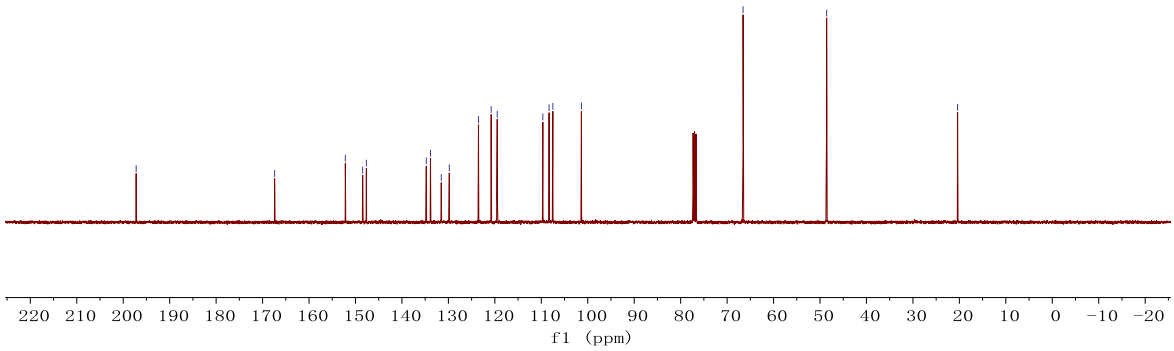
5y

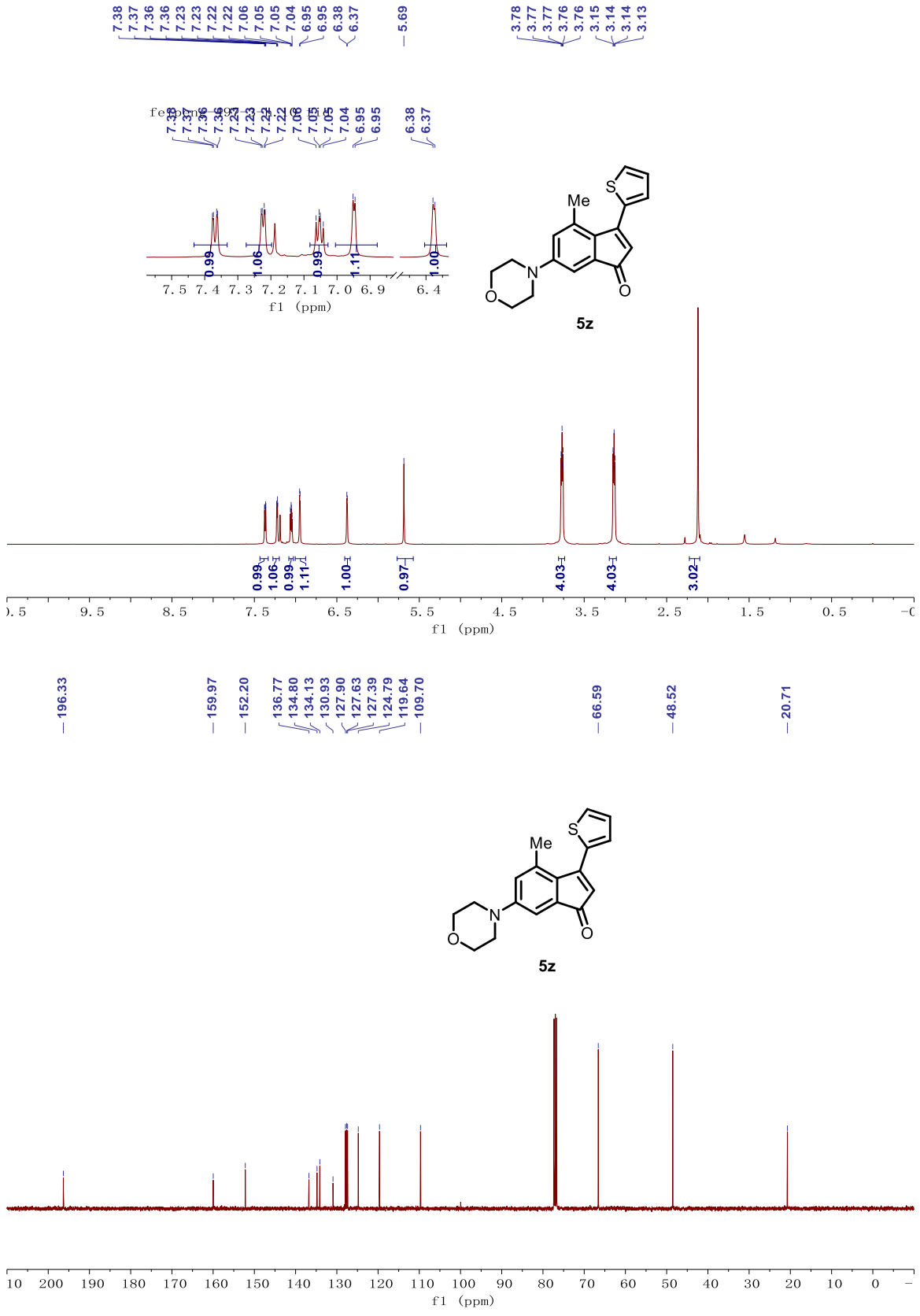

1.00
2.95
1.01
1.99
0.92
4.16
4.06
2.90
f1 (ppm)


197.21
167.41
152.18
148.45
147.65
134.76
133.86
131.53
129.81
123.52
120.79
119.49
109.67
108.32
107.52
101.36
66.56
48.57
20.38

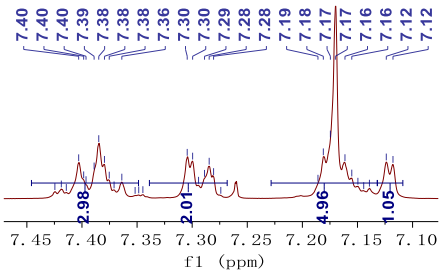

Me
O
O
N
O
O

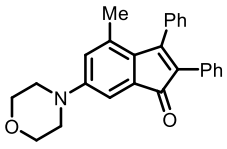
5y


f1 (ppm)

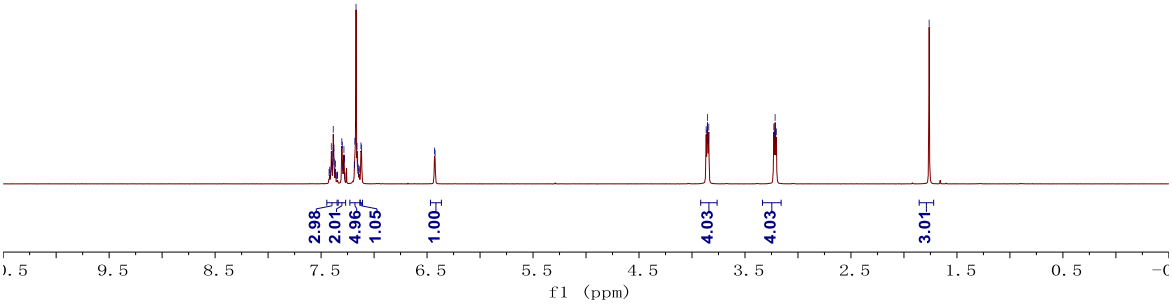

7.38
7.37
7.36
7.36
7.23
7.23
7.22
7.22
7.06
7.05
7.05
7.04
6.95
6.95
6.38
6.37
5.69
3.78
3.77
3.77
3.76
3.76
3.15
3.14
3.14
3.13
0.99
1.06
0.99
1.11
1.00
7.5 7.4 7.3 7.2 7.1 7.0 6.9
6.4
f1 (ppm)
Me
S
N
O
O
5z
0.99
1.06
0.99
1.11
1.00
0.97
4.03
4.03
3.02
f1 (ppm)
196.33
159.97
152.20
136.77
134.80
134.13
130.93
127.90
127.63
127.39
124.79
119.64
109.70
66.59
48.52
20.71
Me
S
N
O
O
5z
f1 (ppm)

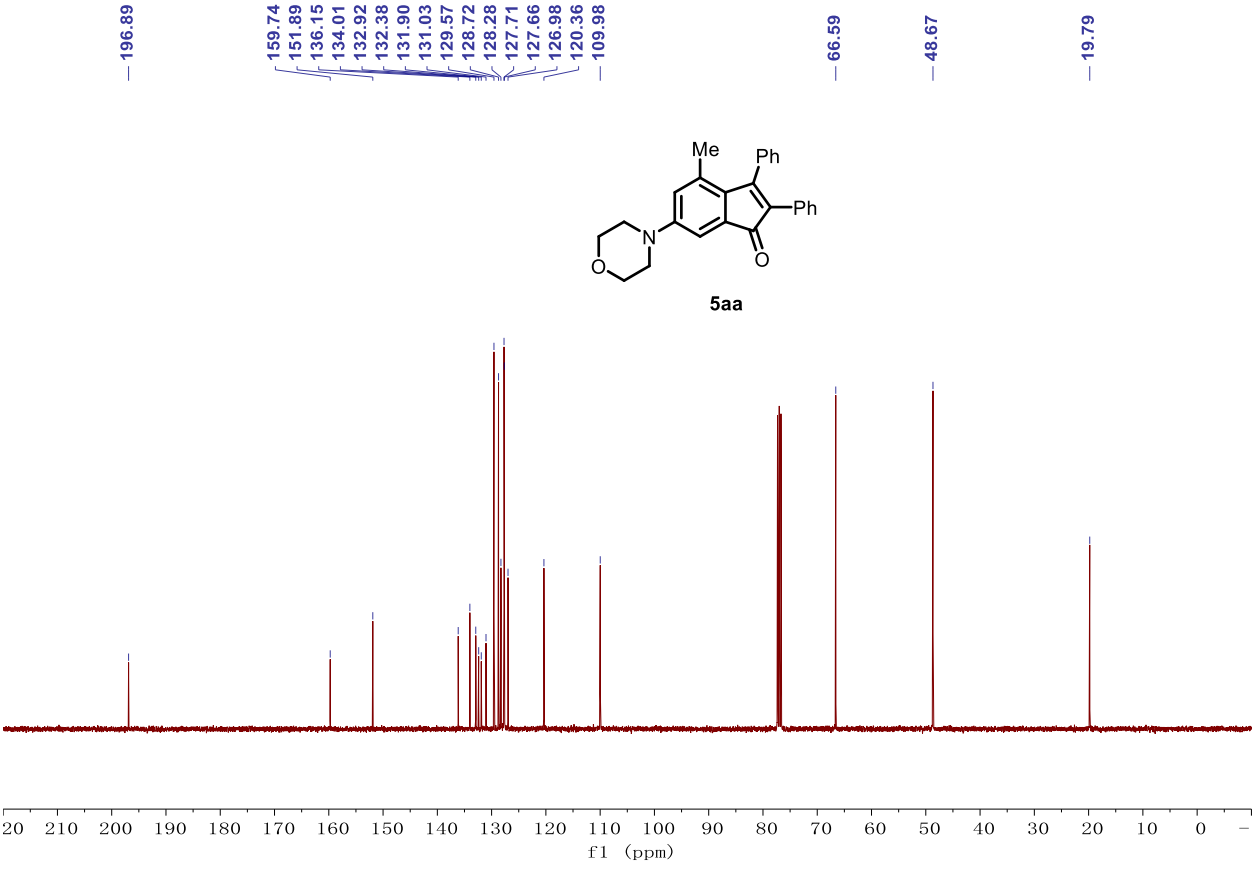

7.40
7.40
7.39
7.38
7.38
7.38
7.36
7.30
7.30
7.29
7.28
7.28
7.19
7.18
7.17
7.17
7.16
7.16
7.12
6.43
6.42
3.87
3.86
3.85
3.85
3.84
3.23
3.22
3.22
3.21
3.20
1.76


7.40
7.40
7.40
7.39
7.38
7.38
7.38
7.36
7.30
7.30
7.29
7.28
7.28
7.19
7.18
7.17
7.17
7.16
7.16
7.12
7.12
2.98
2.01
4.96
1.05
7.45 7.40 7.35 7.30 7.25 7.20 7.15 7.10
f1 (ppm)


Me
Ph
Ph
N
O
O

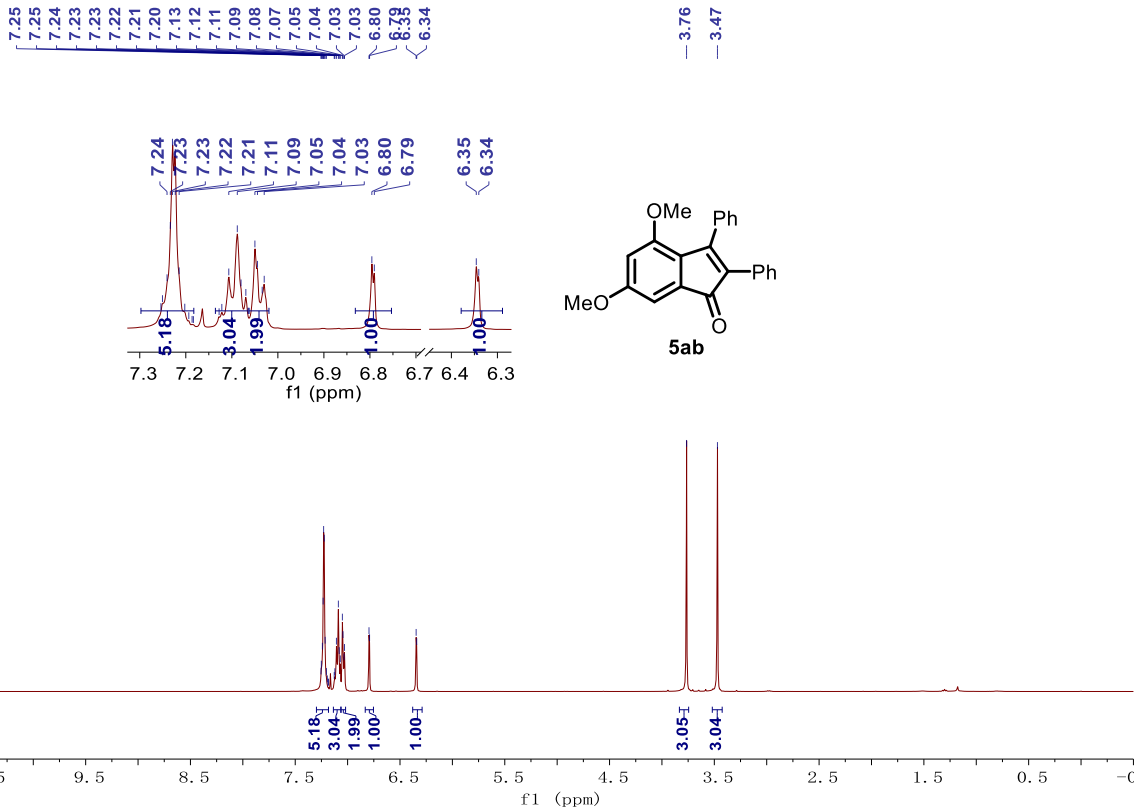
**5aa**

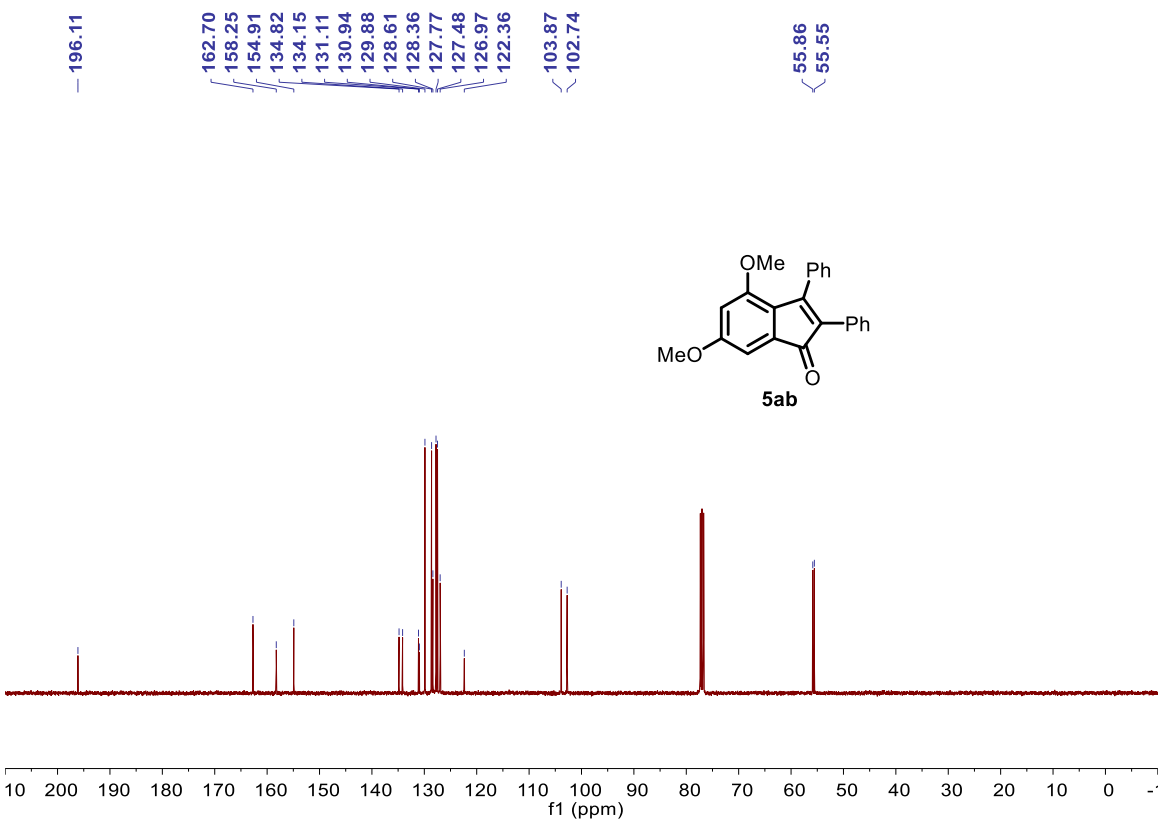

2.98
2.01
4.96
1.05
1.00
4.03
4.03
3.01
f1 (ppm)

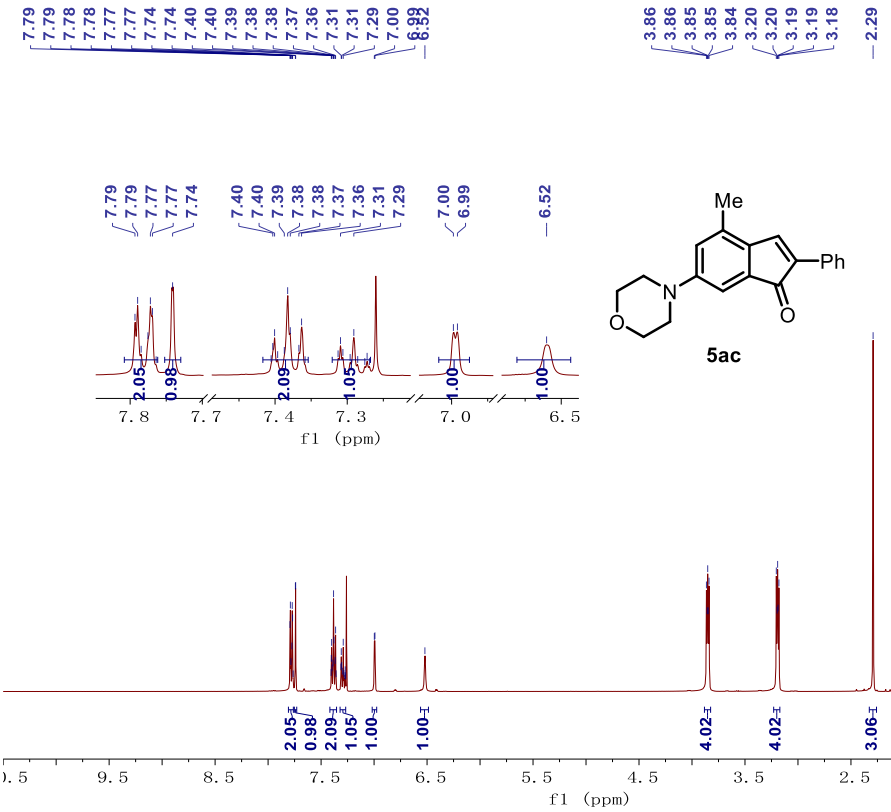

196.89
159.74
151.89
136.15
134.01
132.92
132.38
131.90
131.03
129.57
128.72
128.28
127.71
127.66
126.98
120.36
109.98
66.59
48.67
19.79
f1 (ppm)

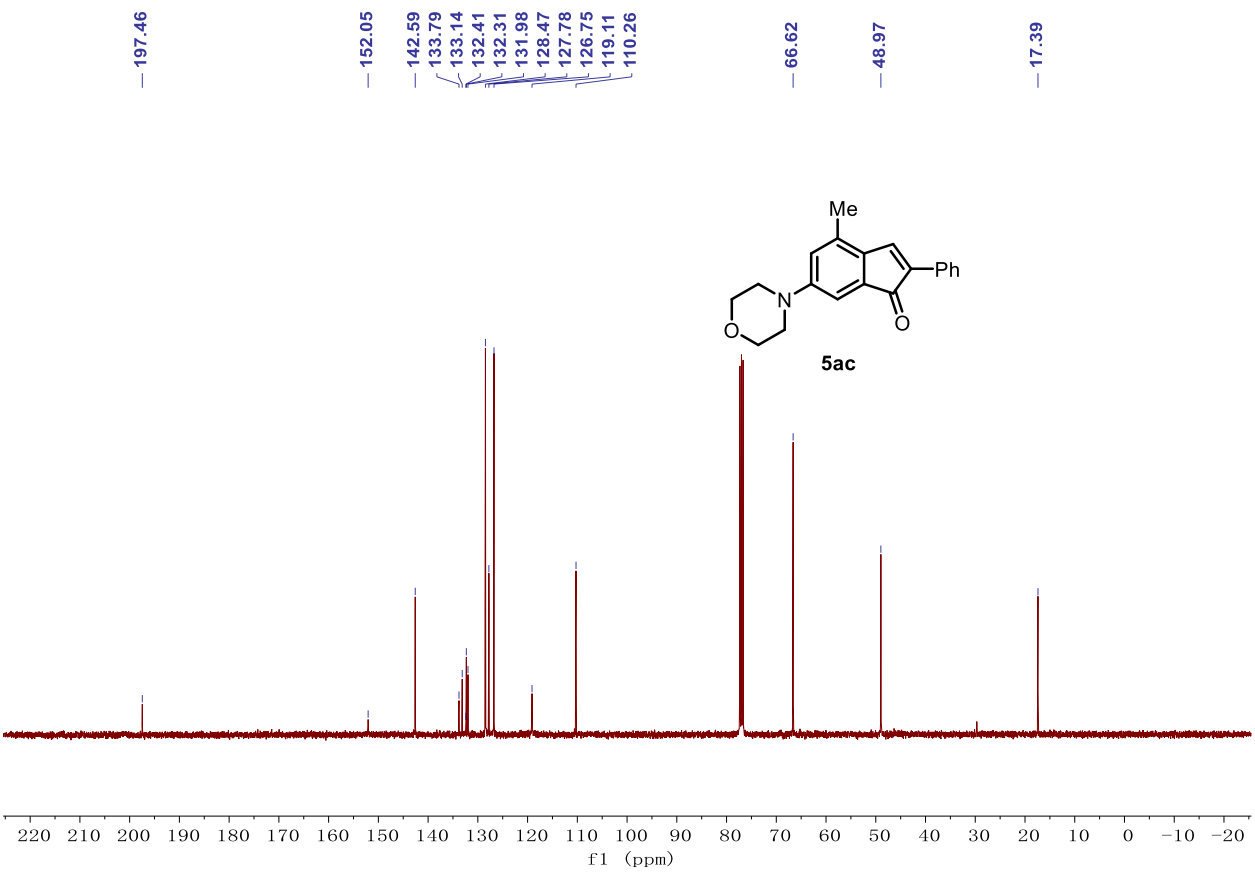

Me
Ph
Ph
N
O
O

**5aa**

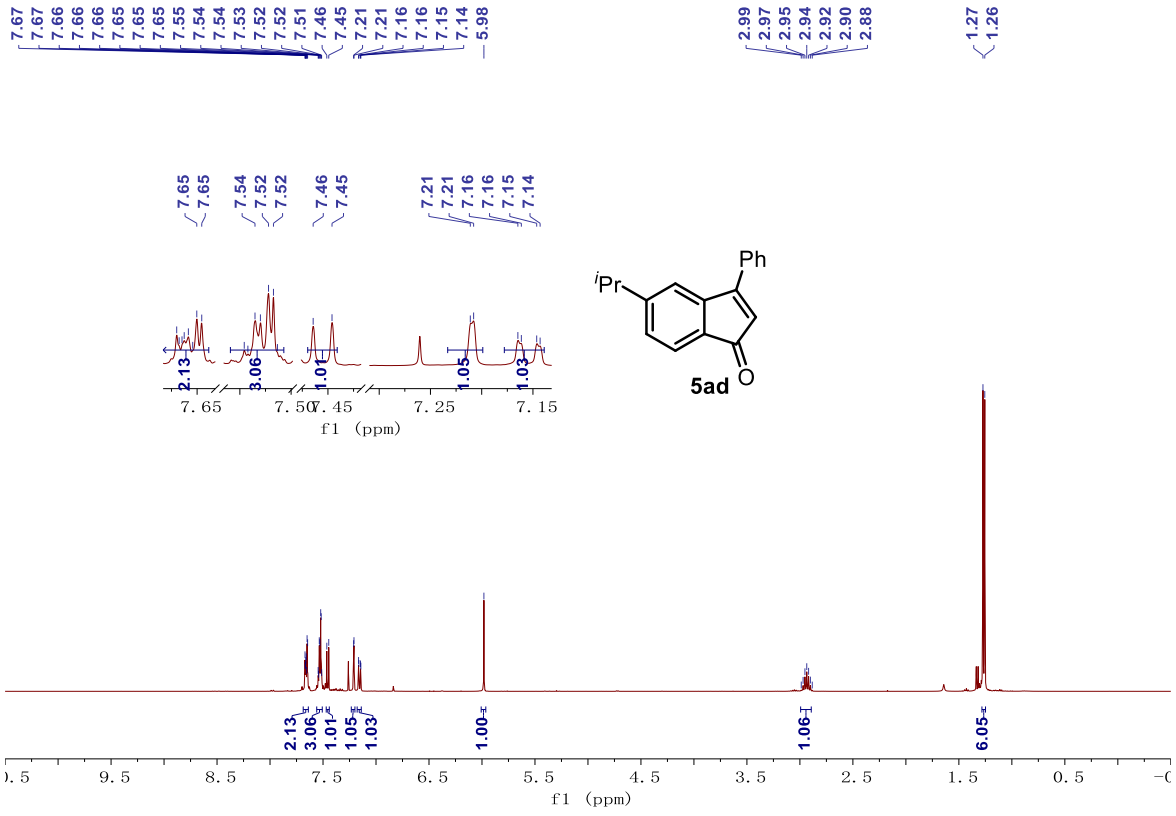

7.25 7.25 7.24 7.23 7.23 7.22 7.21 7.20 7.13 7.12 7.11 7.09 7.08 7.07 7.05 7.04 7.03 7.03 6.80 6.79 6.35 6.34
3.76
3.47
7.24 7.23 7.23 7.22 7.21 7.11 7.09 7.05 7.04 7.03 6.80 6.79 6.35 6.34
5.18 3.04 1.99 1.00 1.00
7.3 7.2 7.1 7.0 6.9 6.8 6.7 6.4 6.3
f1 (ppm)
OMe
Ph
Ph
MeO
O
5ab
5.18 3.04 1.99 1.00 1.00 3.05 3.04
f1 (ppm)

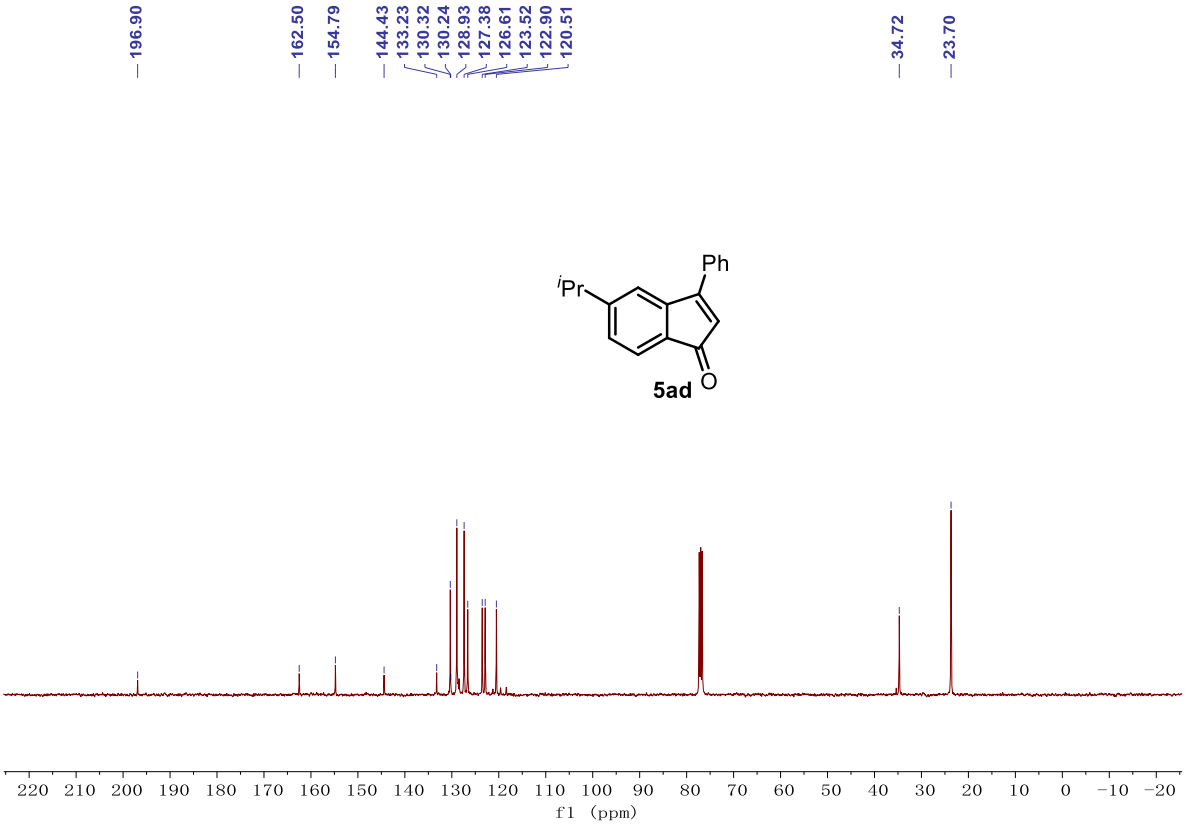

196.11
162.70 158.25 154.91 134.82 134.15 131.11 130.94 129.88 128.61 128.36 127.77 127.48 126.97 122.36
103.87 102.74
55.86 55.55
OMe
Ph
Ph
MeO
O
5ab
f1 (ppm)

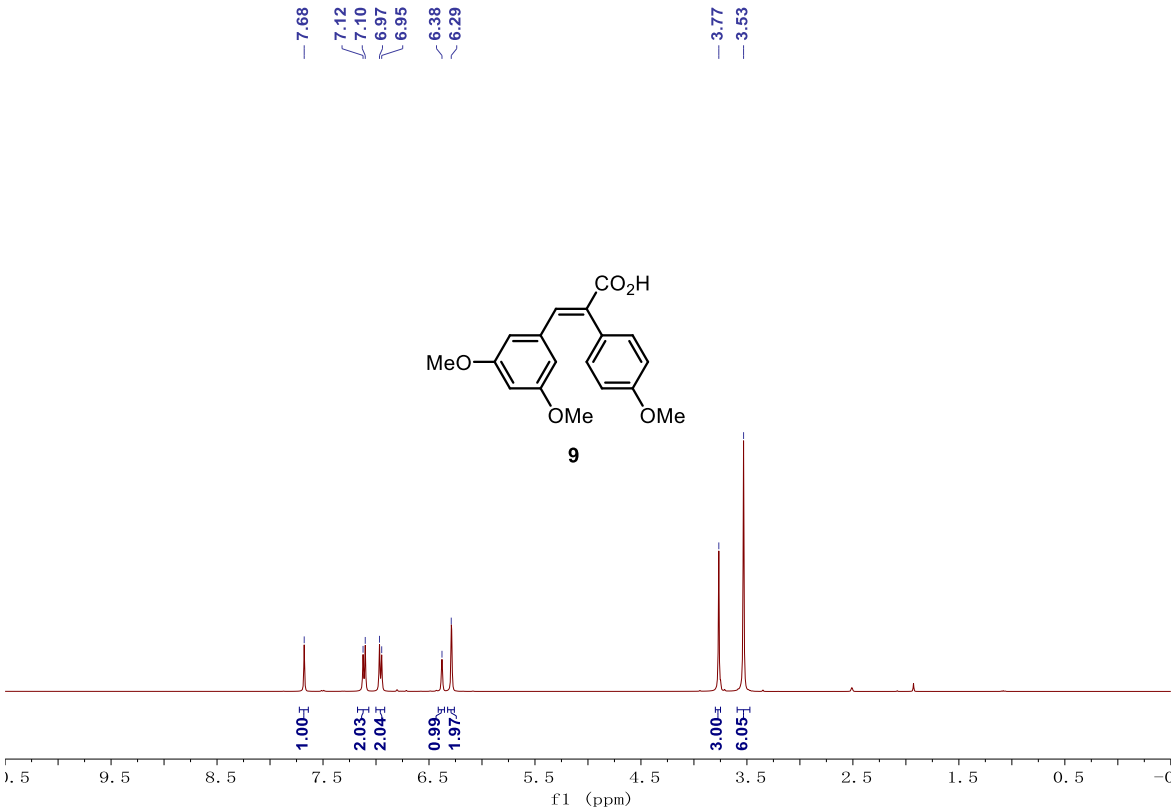

7.79
7.79
7.78
7.78
7.77
7.77
7.74
7.74
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.31
7.31
7.29
7.00
6.99
6.52
3.86
3.86
3.85
3.85
3.84
3.20
3.20
3.19
3.19
3.18
2.29
2.05
0.98
2.09
1.05
1.00
1.00
7.8
7.7
7.4
7.3
7.0
6.5
f1 (ppm)
Me
Ph
N
O
O
5ac
4.02
4.02
3.06
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

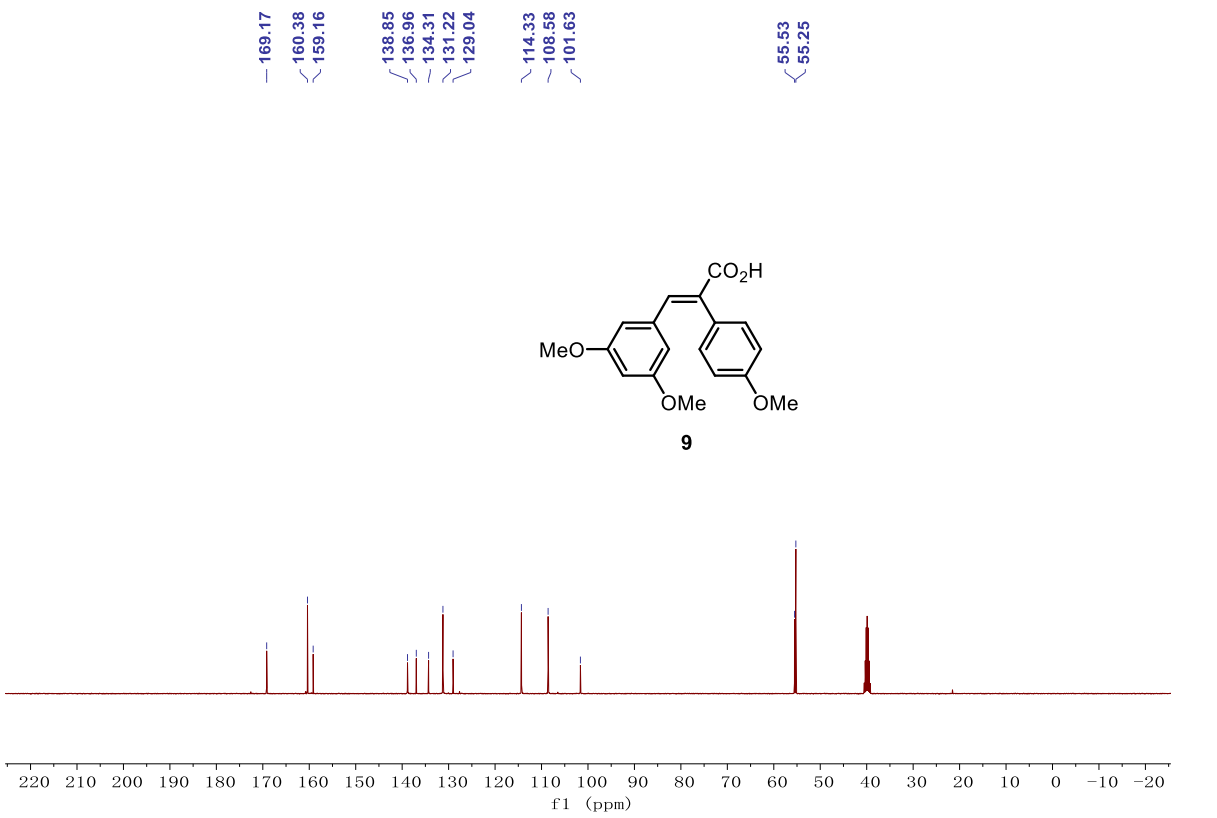

197.46
152.05
142.59
133.79
133.14
132.41
132.31
131.98
128.47
127.78
126.75
119.11
110.26
66.62
48.97
17.39
Me
Ph
N
O
O
5ac
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
−20
f1 (ppm)

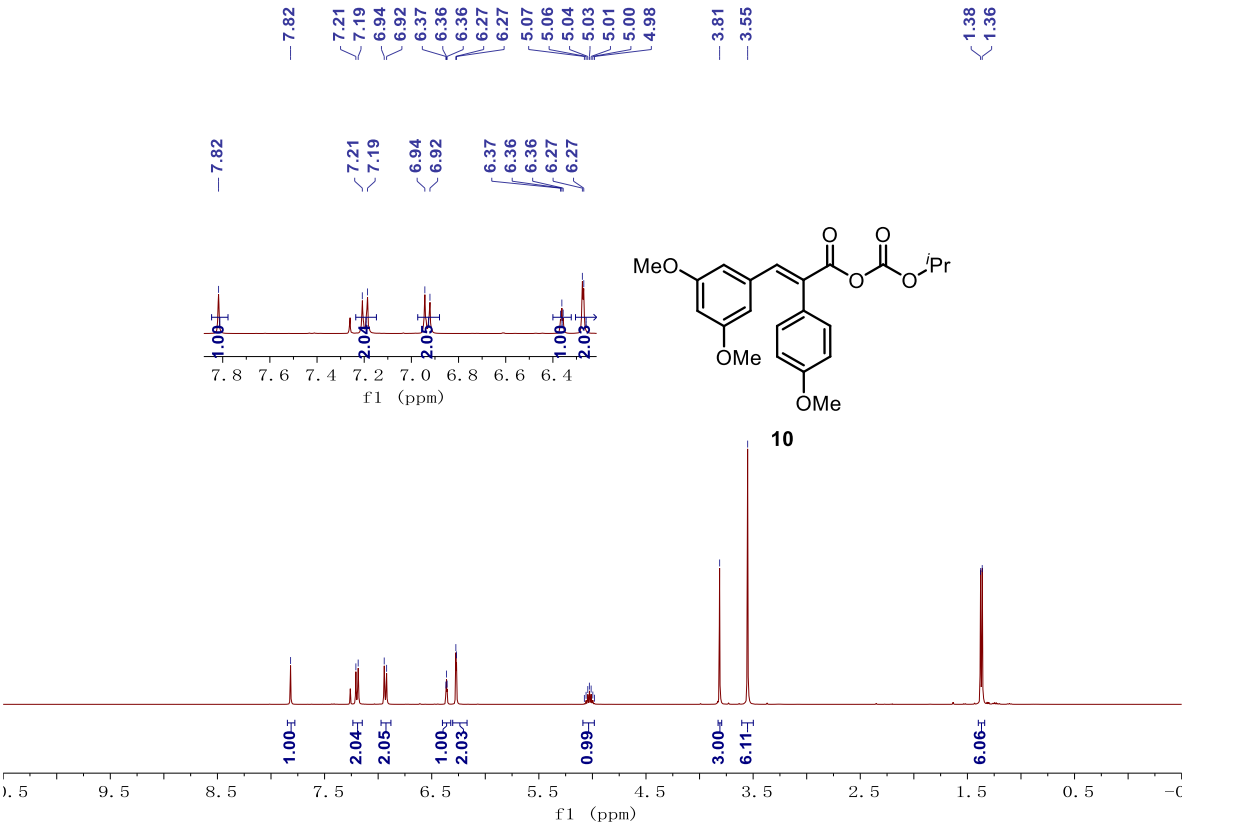
93% purity

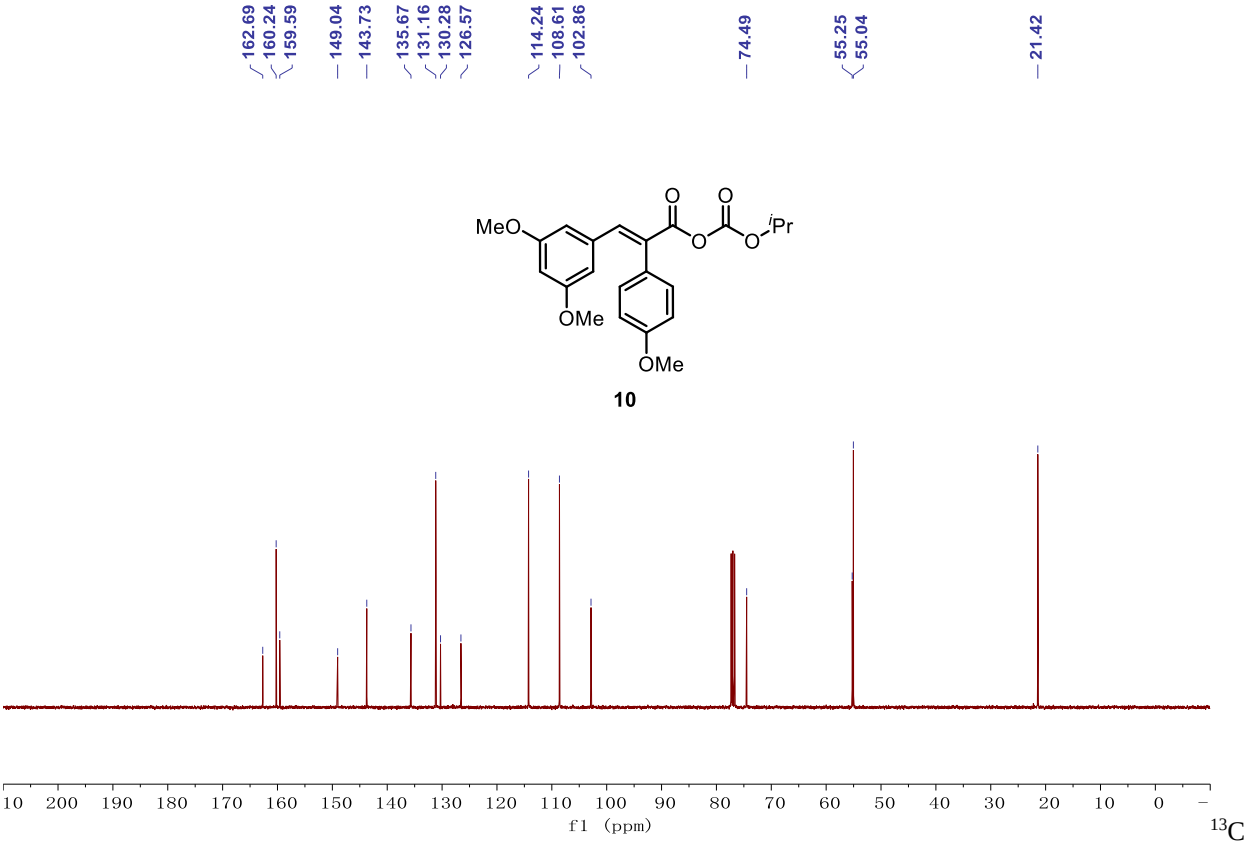

7.67 7.67 7.66 7.66 7.66 7.65 7.65 7.65 7.55 7.54 7.54 7.53 7.52 7.52 7.51 7.46 7.45 7.21 7.21 7.16 7.16 7.15 7.14 5.98
2.99 2.97 2.95 2.94 2.92 2.90 2.88
1.27 1.26
7.65 7.65 7.54 7.52 7.52 7.46 7.45 7.21 7.21 7.16 7.16 7.15 7.14
2.13 3.06 1.01 1.05 1.03
7.65 7.50 7.45 7.25 7.15
f1 (ppm)
iPr
Ph
O
5ad
2.13 3.06 1.01 1.05 1.03 1.00 1.06 6.05
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)


196.90
162.50 154.79 144.43 133.23 130.32 130.24 128.93 127.38 126.61 123.52 122.90 120.51
34.72 23.70
iPr
Ph
O
5ad
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20
f1 (ppm)

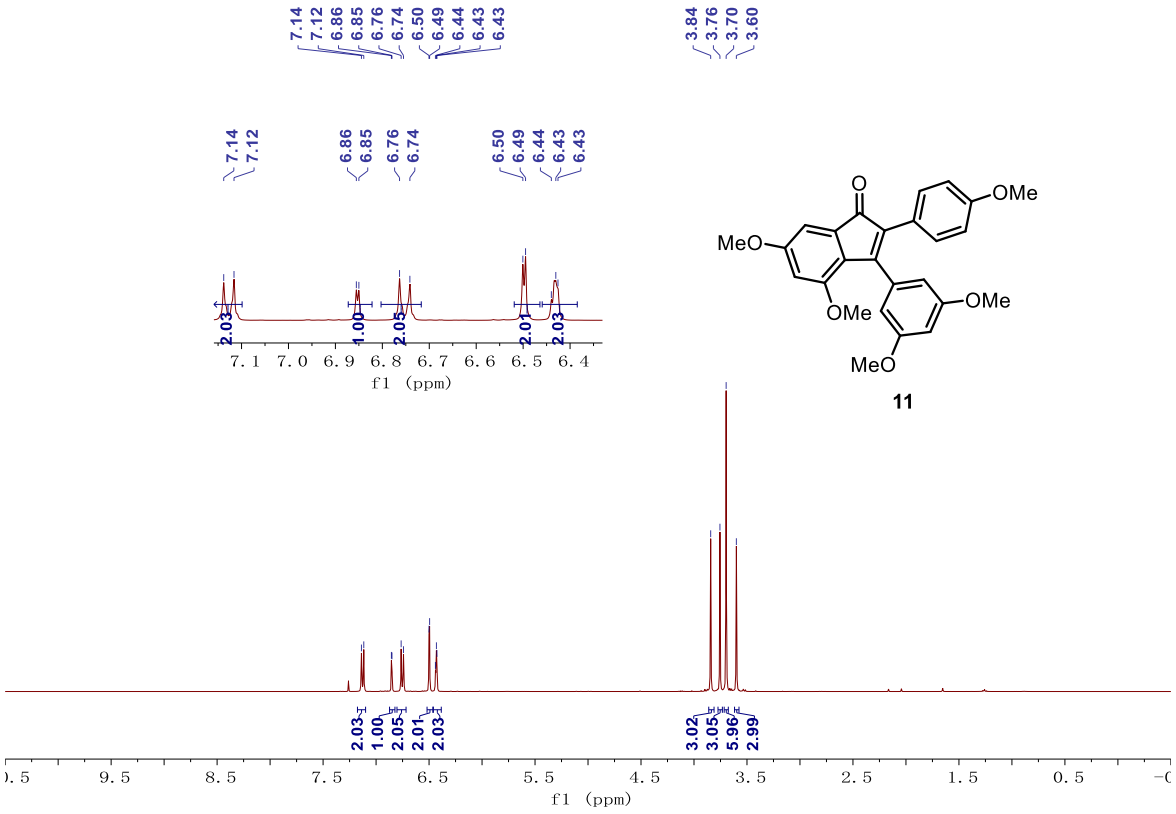

7.68
7.12
7.10
6.97
6.95
6.38
6.29
3.77
3.53
CO2H
MeO
OMe
OMe
9
1.00
2.03
2.04
0.99
1.97
3.00
6.05
f1 (ppm)

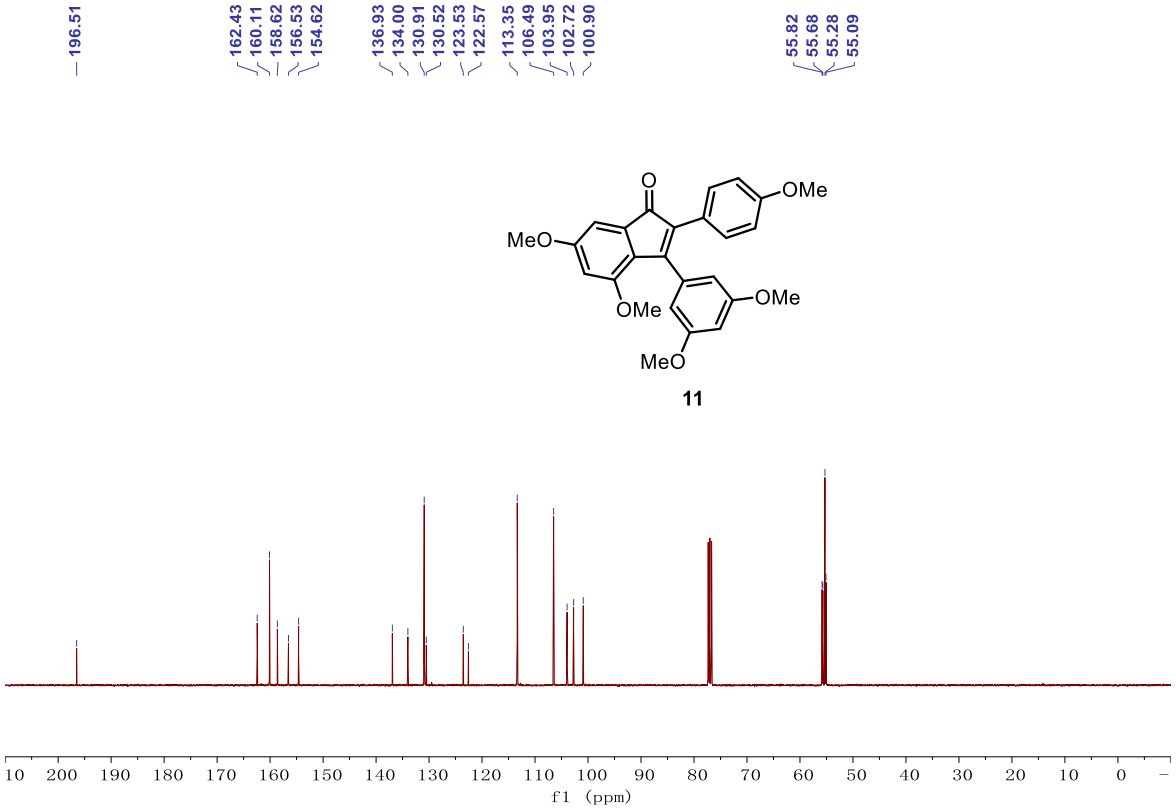

169.17
160.38
159.16
138.85
136.96
134.31
131.22
129.04
114.33
108.58
101.63
55.53
55.25
CO2H
MeO
OMe
OMe
9
f1 (ppm)

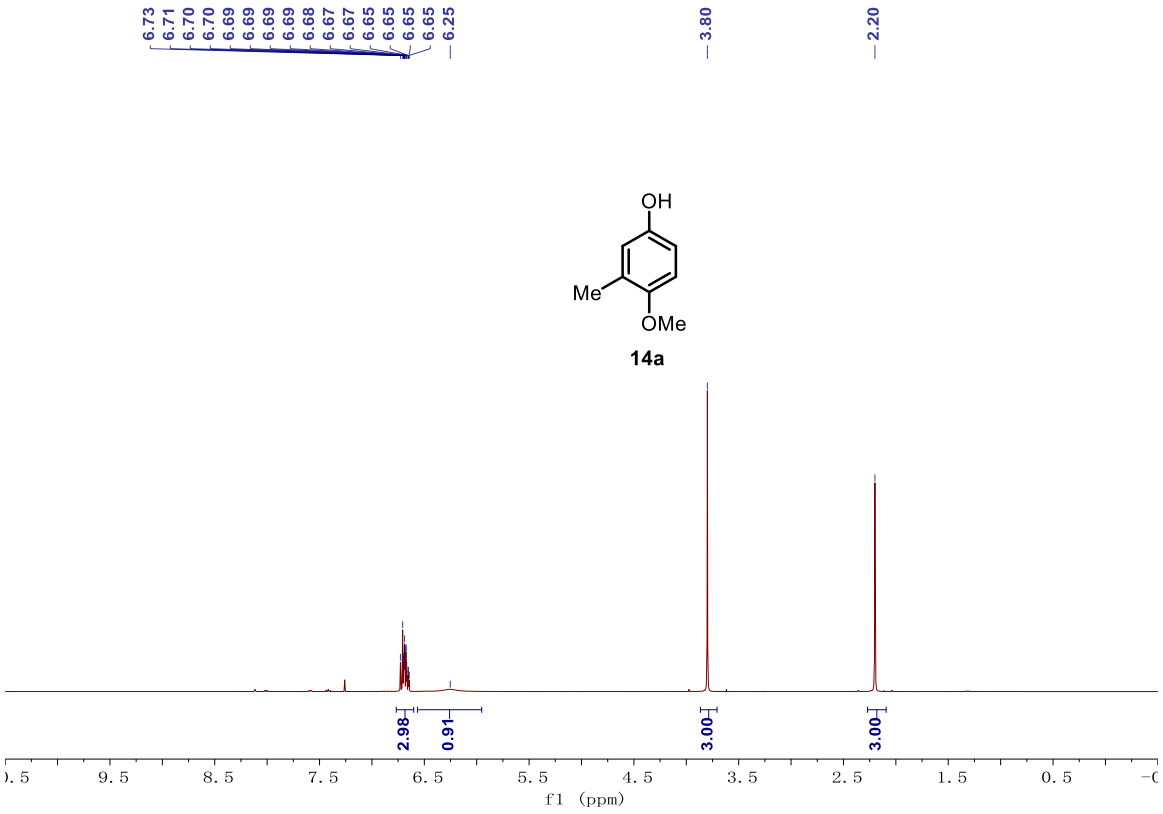

7.82
7.21
7.19
6.94
6.92
6.37
6.36
6.36
6.27
6.27
5.07
5.06
5.04
5.03
5.01
5.00
4.98
3.81
3.55
1.38
1.36
1.00
2.04
2.05
1.00
2.03
7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4
f1 (ppm)
MeO
OMe
OMe
O
O
O
O
iPr
10
1.00
2.04
2.05
1.00
2.03
0.99
3.00
6.11
6.06
f1 (ppm)

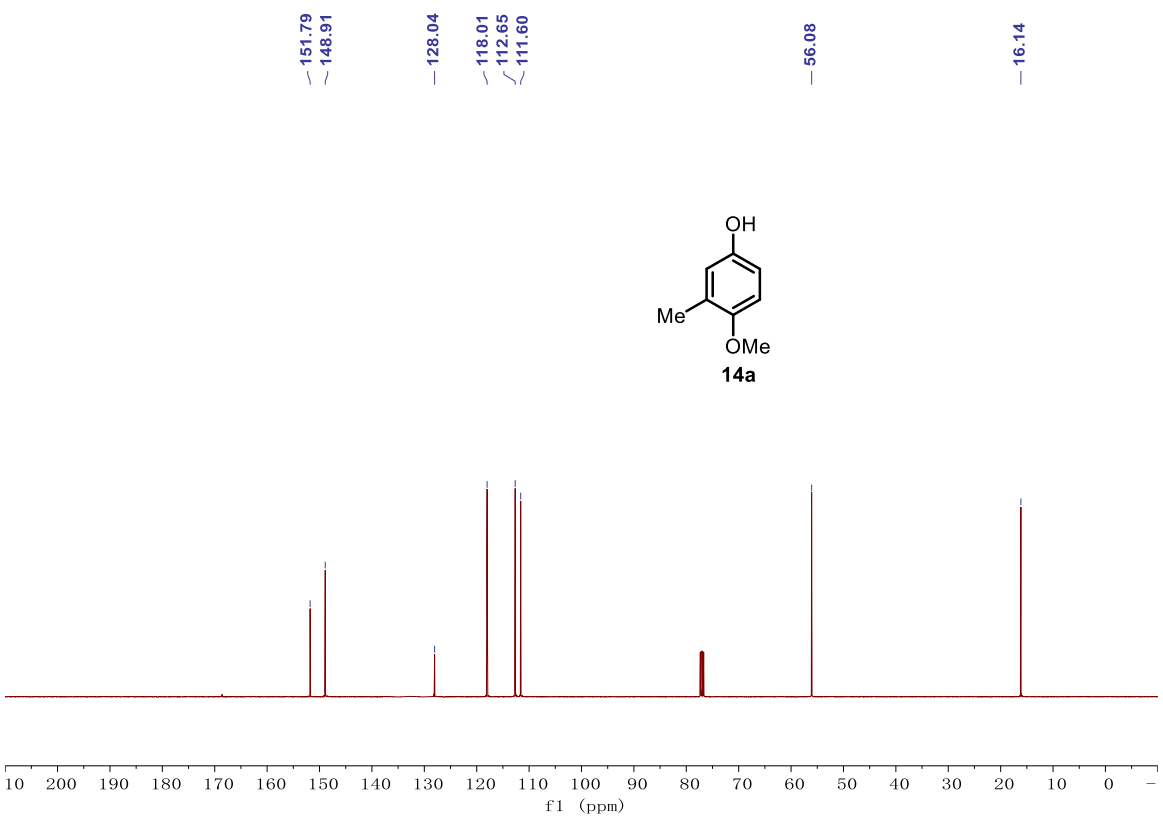

162.69
160.24
159.59
149.04
143.73
135.67
131.16
130.28
126.57
114.24
108.61
102.86
74.49
55.25
55.04
21.42
MeO
OMe
OMe
O
O
O
O
iPr
10
f1 (ppm)

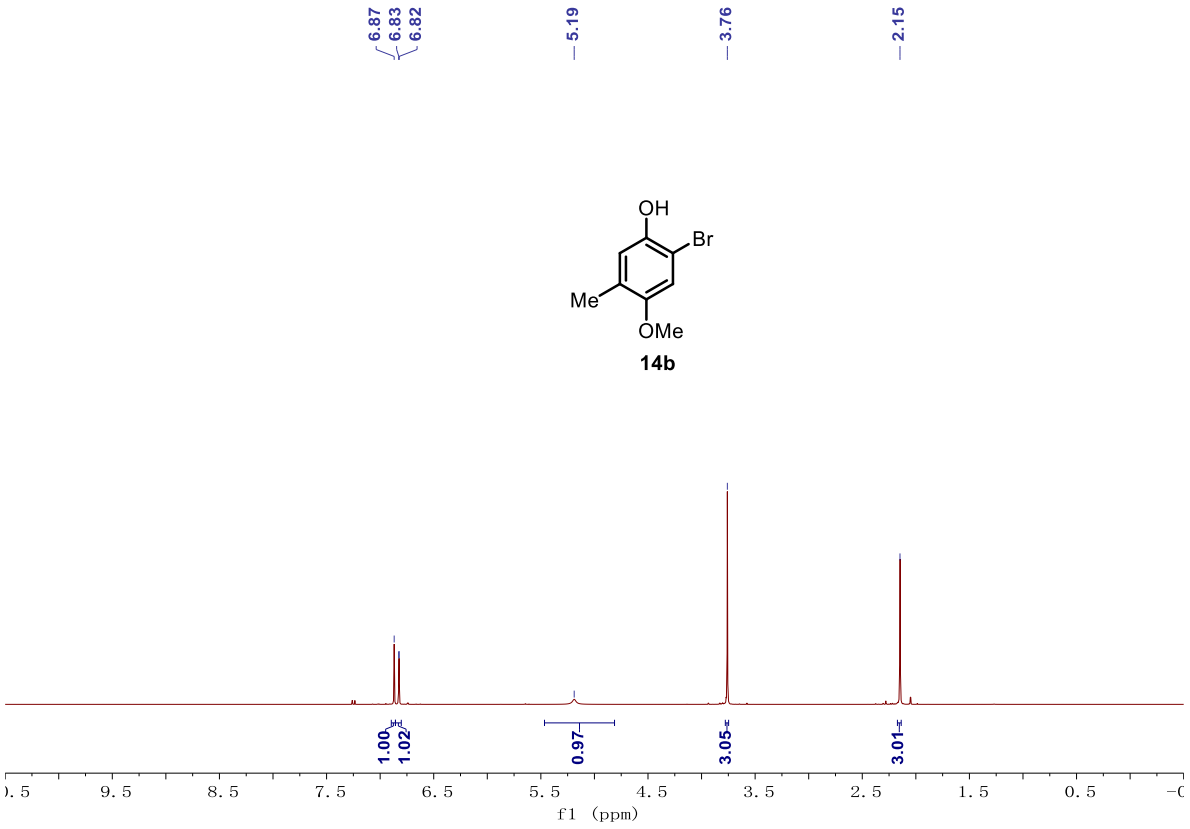
$^{13}C$

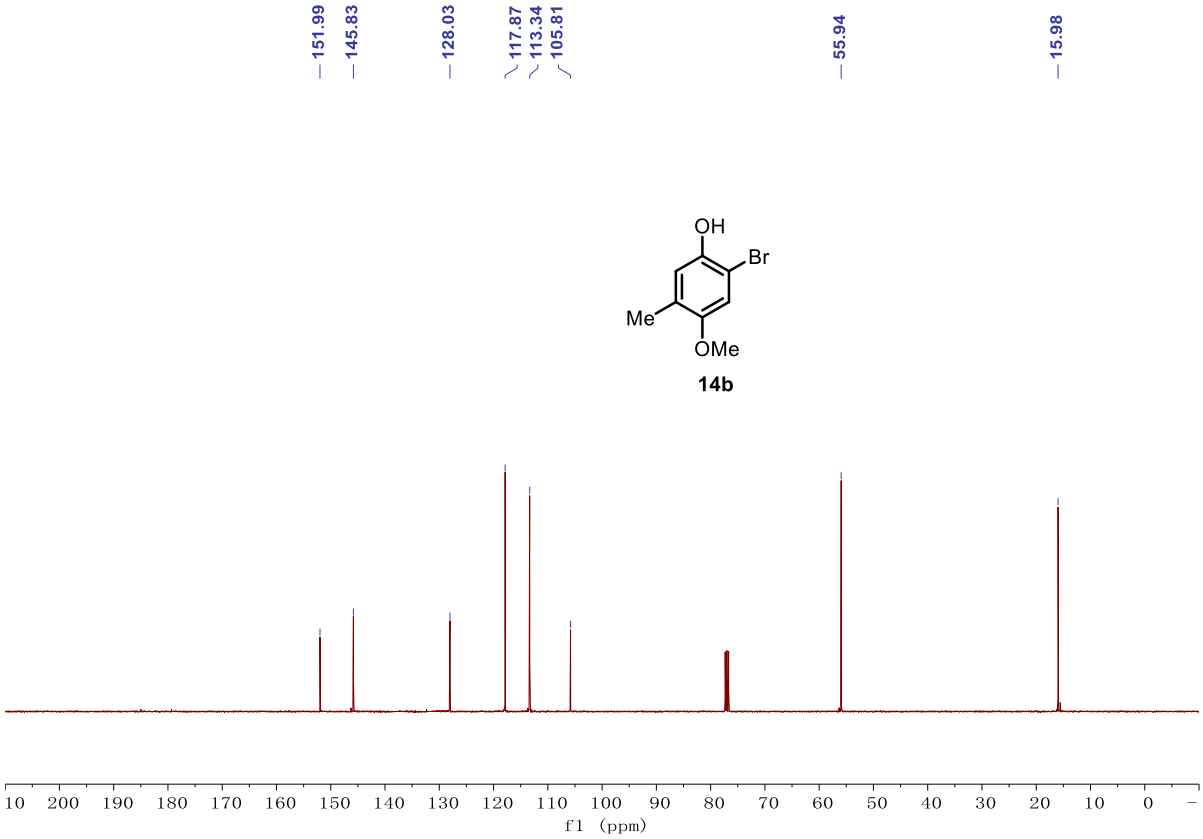

7.14
7.12
6.86
6.85
6.76
6.74
6.50
6.49
6.44
6.43
6.43
3.84
3.76
3.70
3.60
2.03
1.00
2.05
2.01
2.03
7.1 7.0 6.9 6.8 6.7 6.6 6.5 6.4
f1 (ppm)
O
OMe
MeO
OMe
OMe
MeO
11
2.03
1.00
2.05
2.01
2.03
3.02
3.05
5.96
2.99
9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5
f1 (ppm)

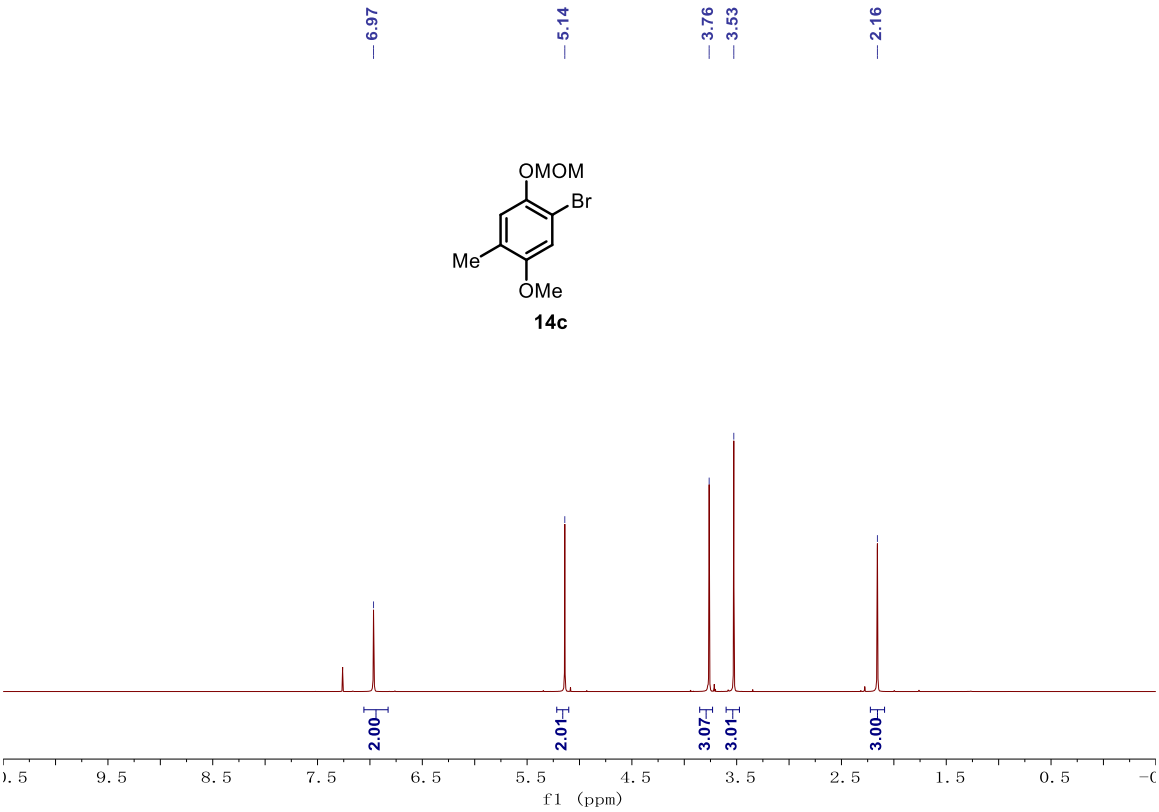

196.51
162.43
160.11
158.62
156.53
154.62
136.93
134.00
130.91
130.52
123.53
122.57
113.35
106.49
103.95
102.72
100.90
55.82
55.68
55.28
55.09
O
OMe
MeO
OMe
OMe
MeO
11
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

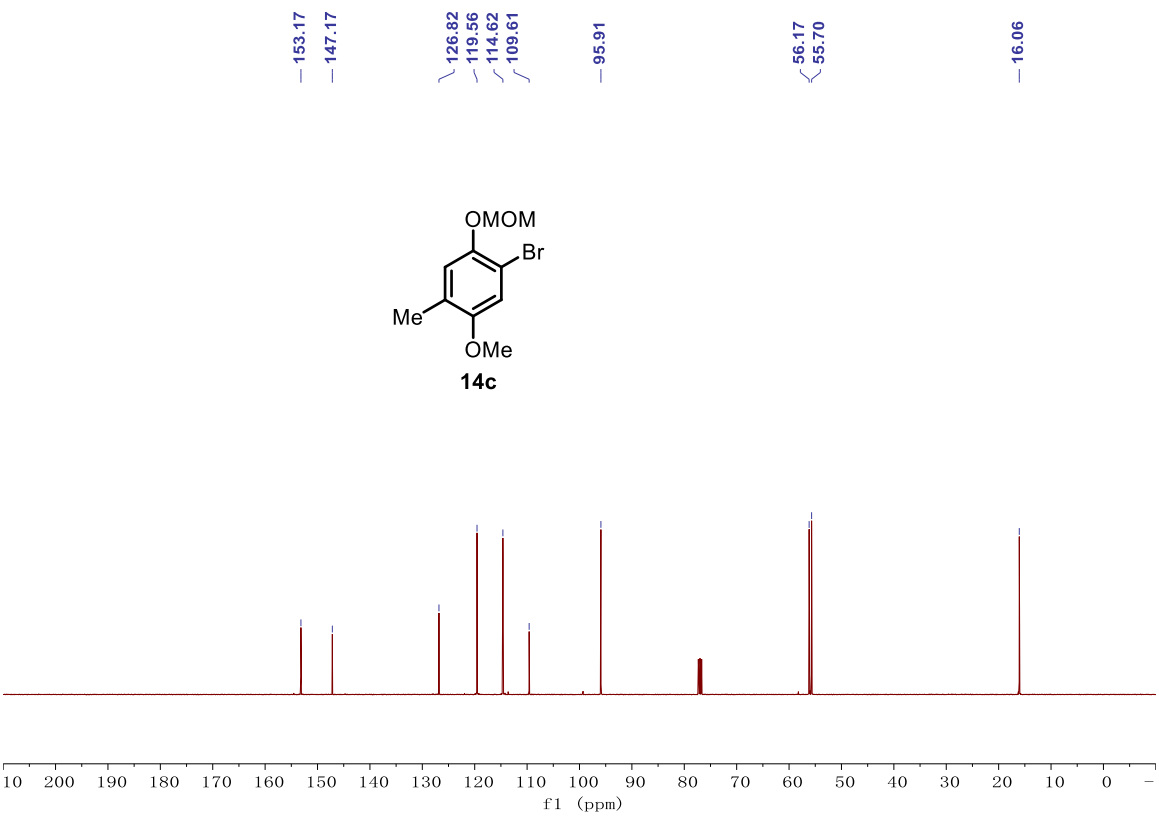

6.73
6.71
6.70
6.70
6.69
6.69
6.69
6.69
6.68
6.67
6.67
6.65
6.65
6.65
6.65
6.25
3.80
2.20
OH
Me
OMe
14a
2.98
0.91
3.00
3.00
f1 (ppm)

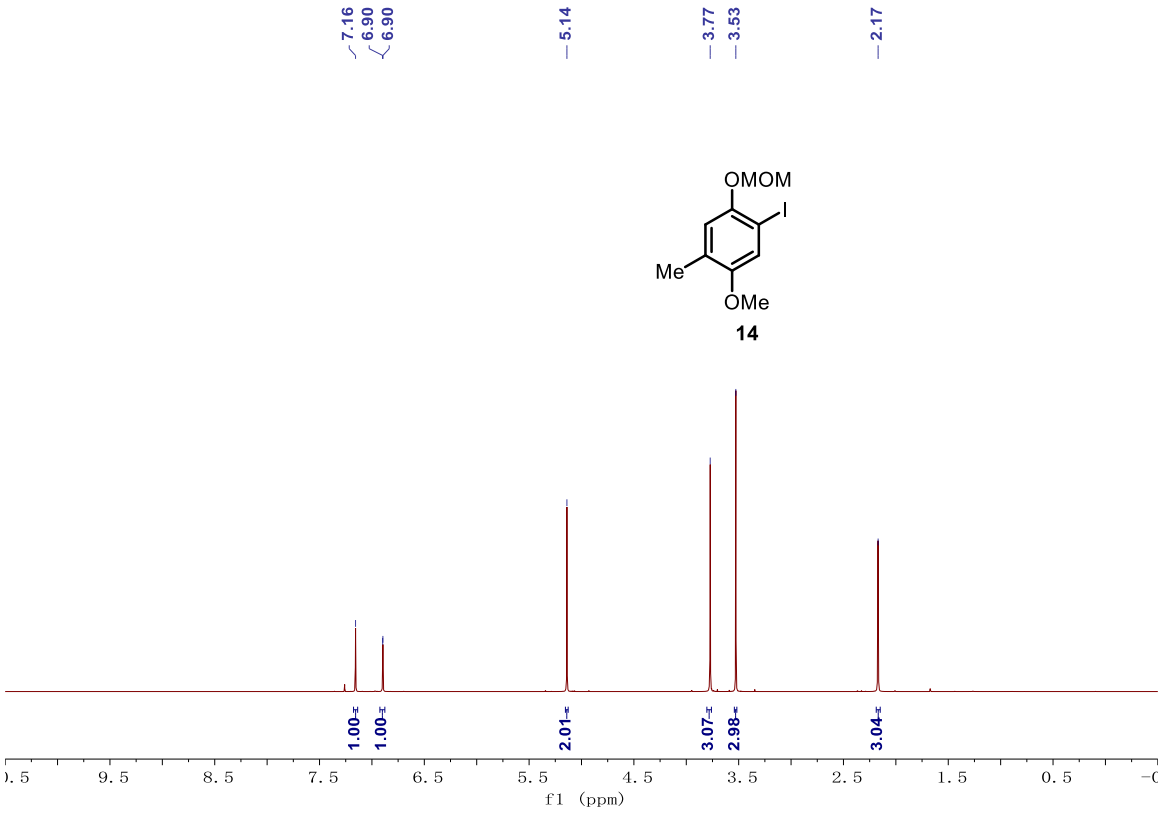

151.79
148.91
128.04
118.01
112.65
111.60
56.08
16.14
OH
Me
OMe
14a
f1 (ppm)

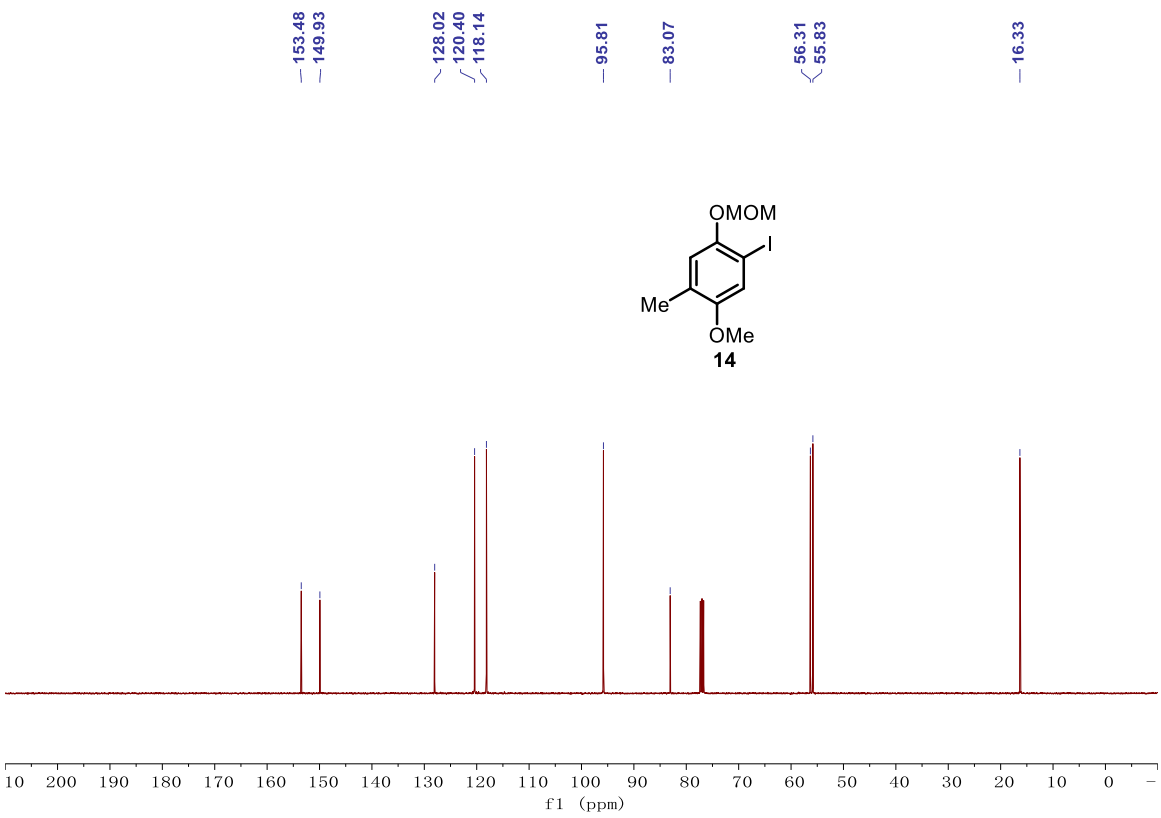

6.87
6.83
6.82
5.19
3.76
2.15
OH
Br
Me
OMe
14b
1.00
1.02
0.97
3.05
3.01
f1 (ppm)

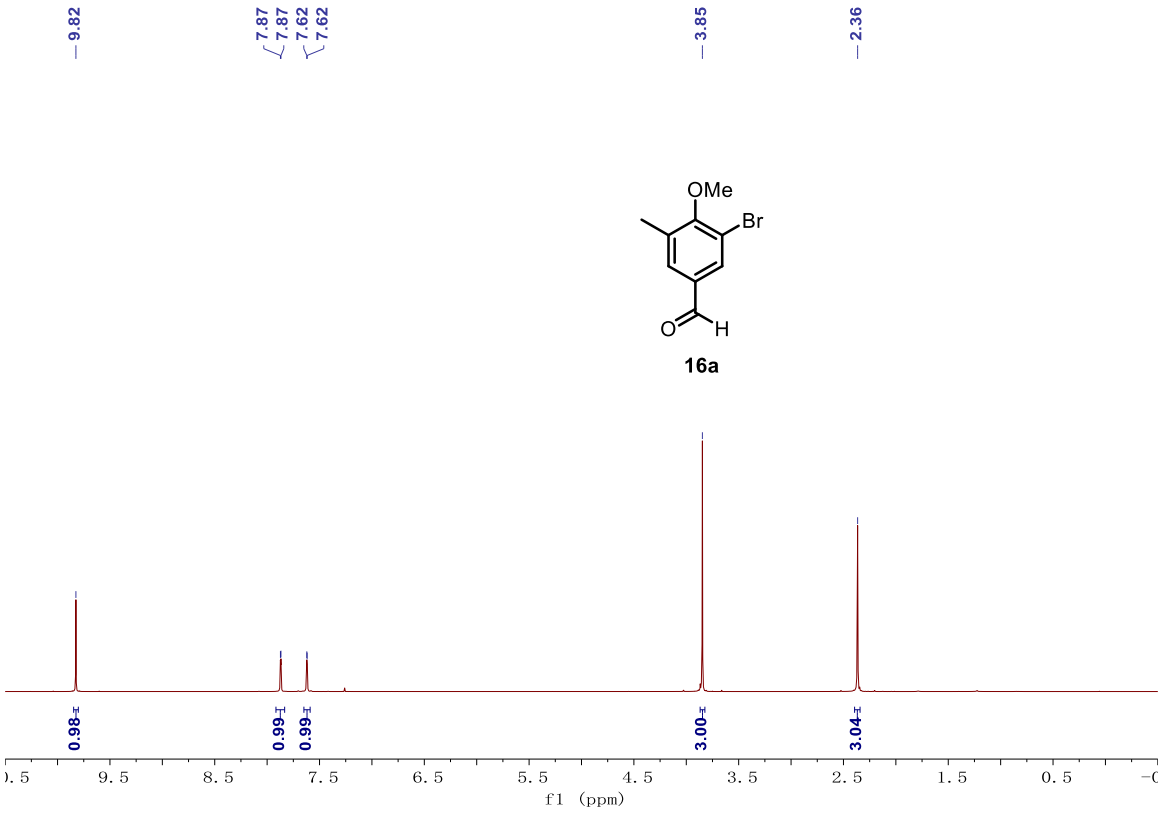

151.99
145.83
128.03
117.87
113.34
105.81
55.94
15.98
OH
Br
Me
OMe
14b
f1 (ppm)

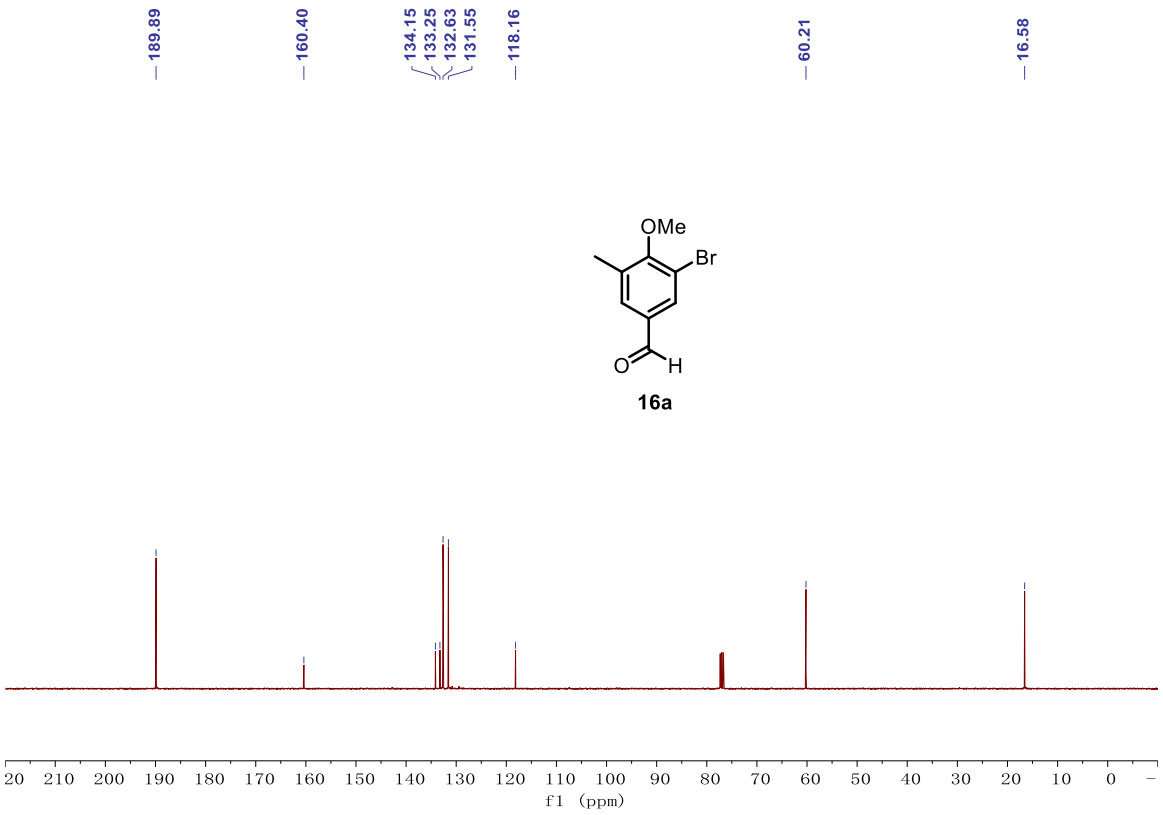

6.97
5.14
3.76
3.53
2.16
OMOM
Br
Me
OMe
14c
2.00
2.01
3.07
3.01
3.00
f1 (ppm)

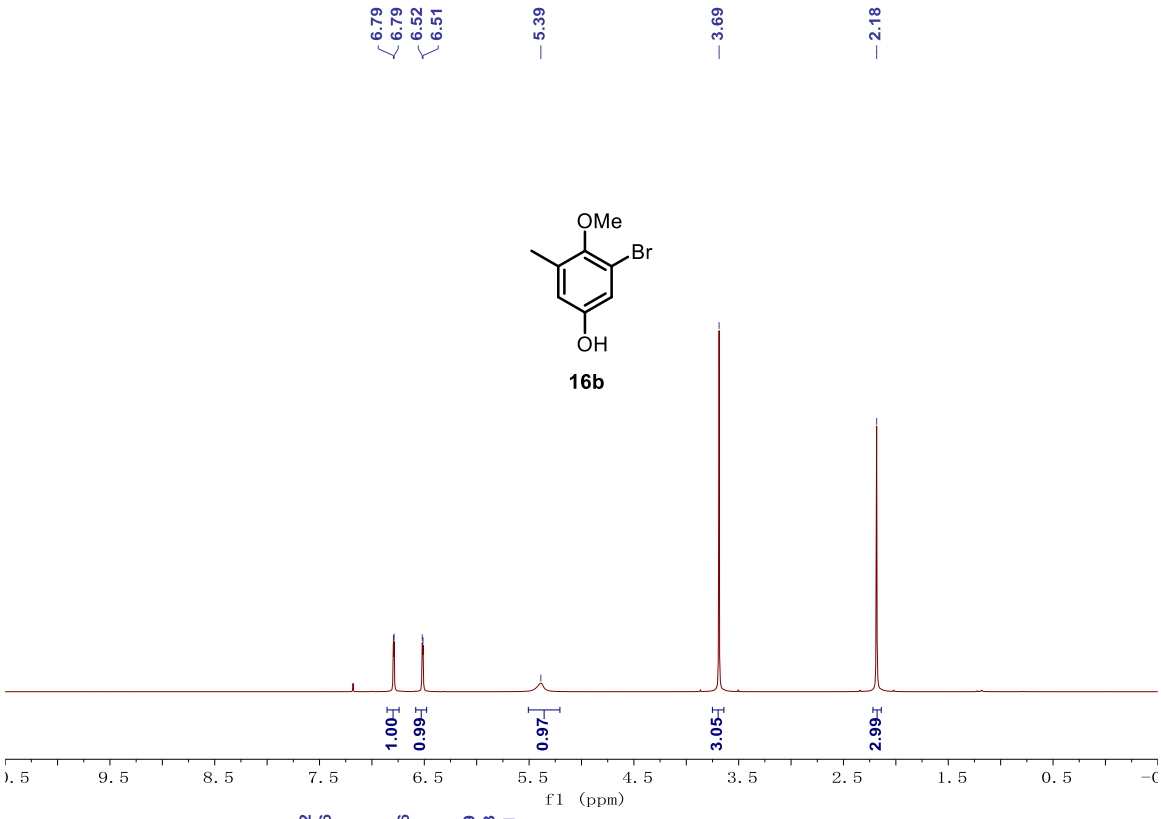

153.17
147.17
126.82
119.56
114.62
109.61
95.91
56.17
55.70
16.06
OMOM
Br
Me
OMe
14c
f1 (ppm)

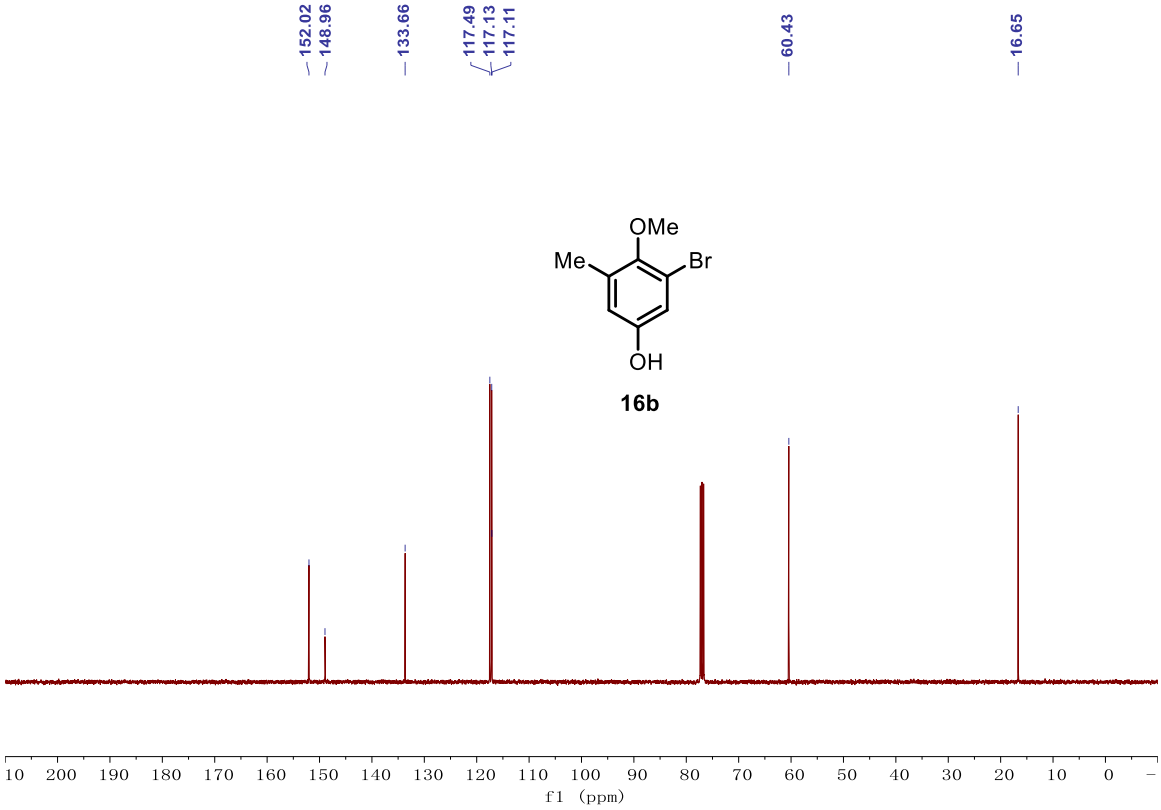

7.16
6.90
6.90
5.14
3.77
3.53
2.17
OMOM
I
Me
OMe
14
1.00
1.00
2.01
3.07
2.98
3.04
f1 (ppm)

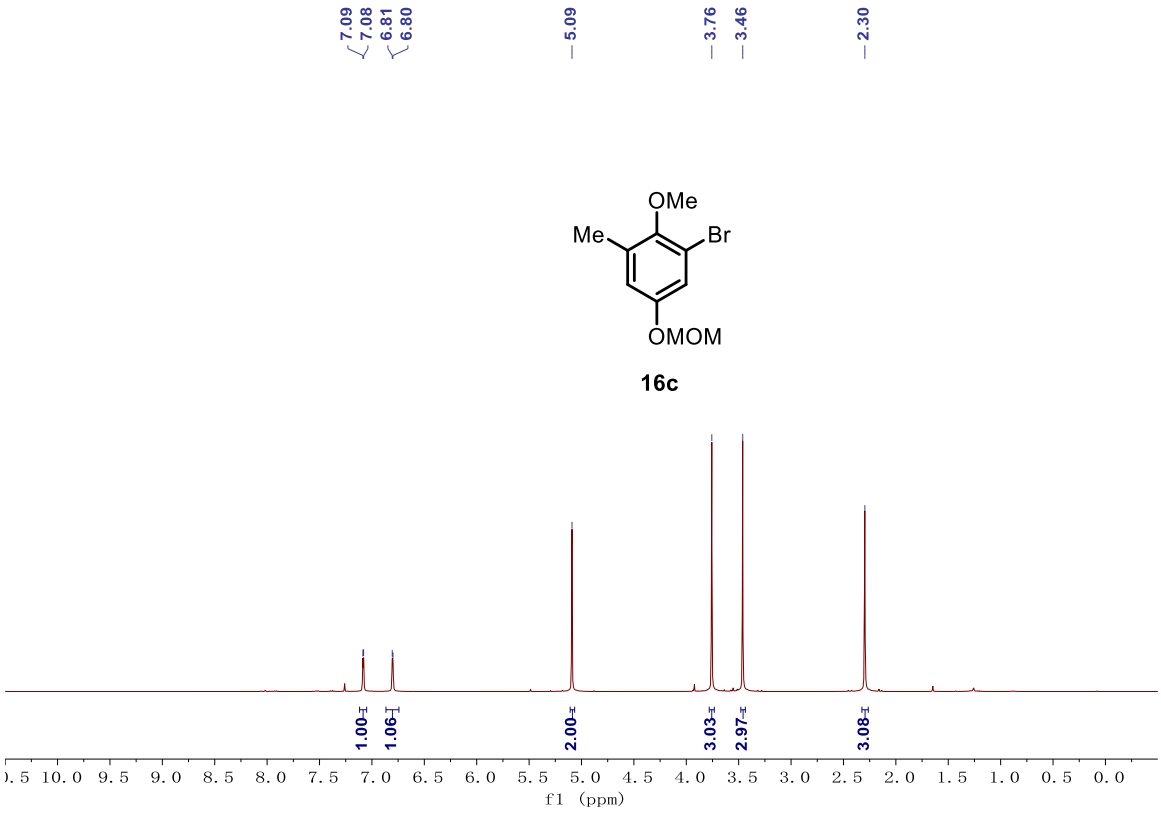

153.48
149.93
128.02
120.40
118.14
95.81
83.07
56.31
55.83
16.33
OMOM
I
Me
OMe
14
f1 (ppm)


9.82
7.87
7.87
7.62
7.62
3.85
2.36
OMe
Br
O
H
16a
0.98
0.99
0.99
3.00
3.04
f1 (ppm)

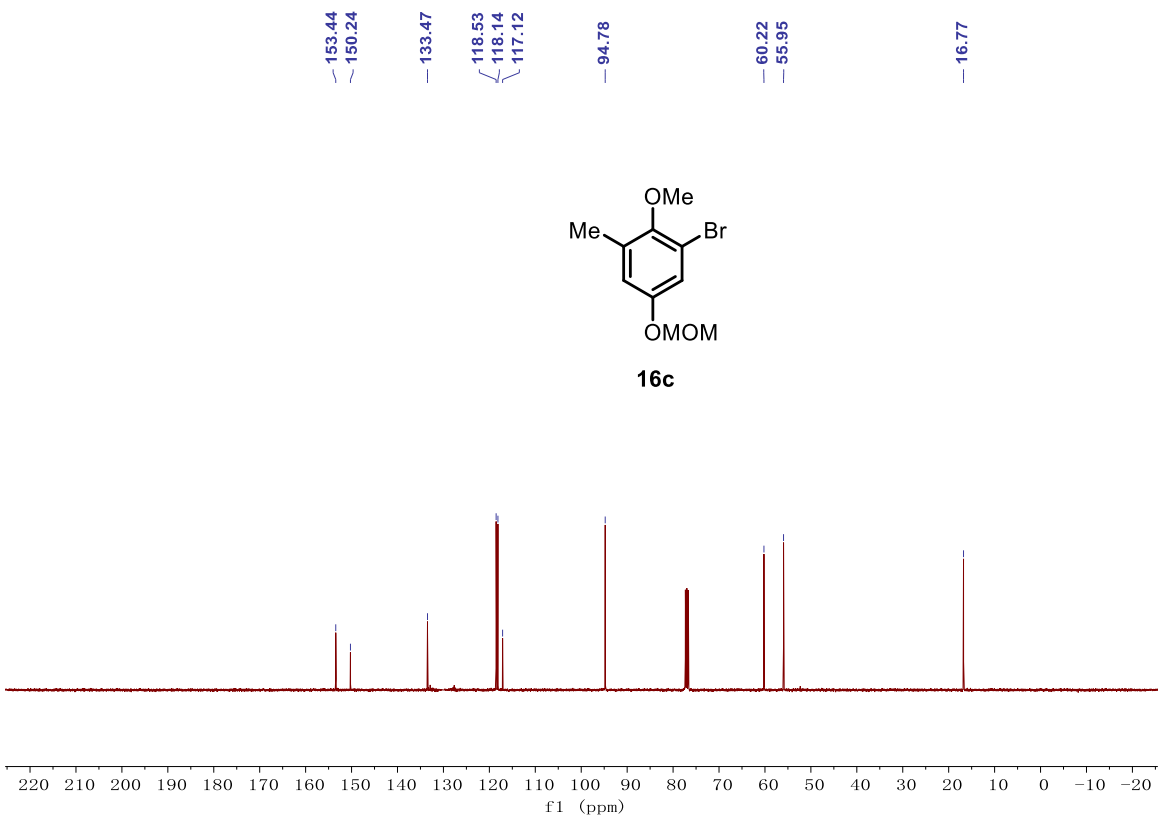

189.89
160.40
134.15
133.25
132.63
131.55
118.16
60.21
16.58
OMe
Br
O
H
16a
f1 (ppm)


6.79
6.79
6.52
6.51
5.39
3.69
2.18
OMe
Br
OH
16b
1.00
0.99
0.97
3.05
2.99
f1 (ppm)

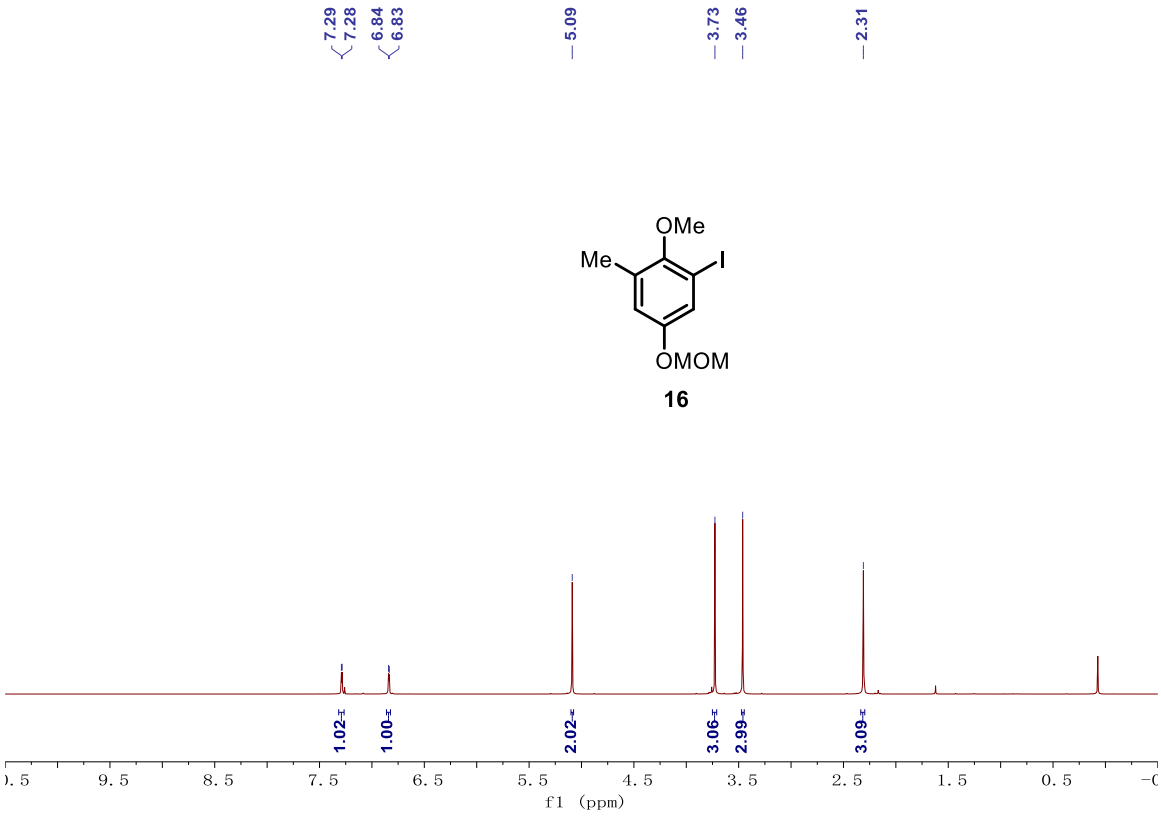

152.02
148.96
133.66
117.49
117.13
117.11
60.43
16.65
OMe
Me
Br
OH
16b
f1 (ppm)

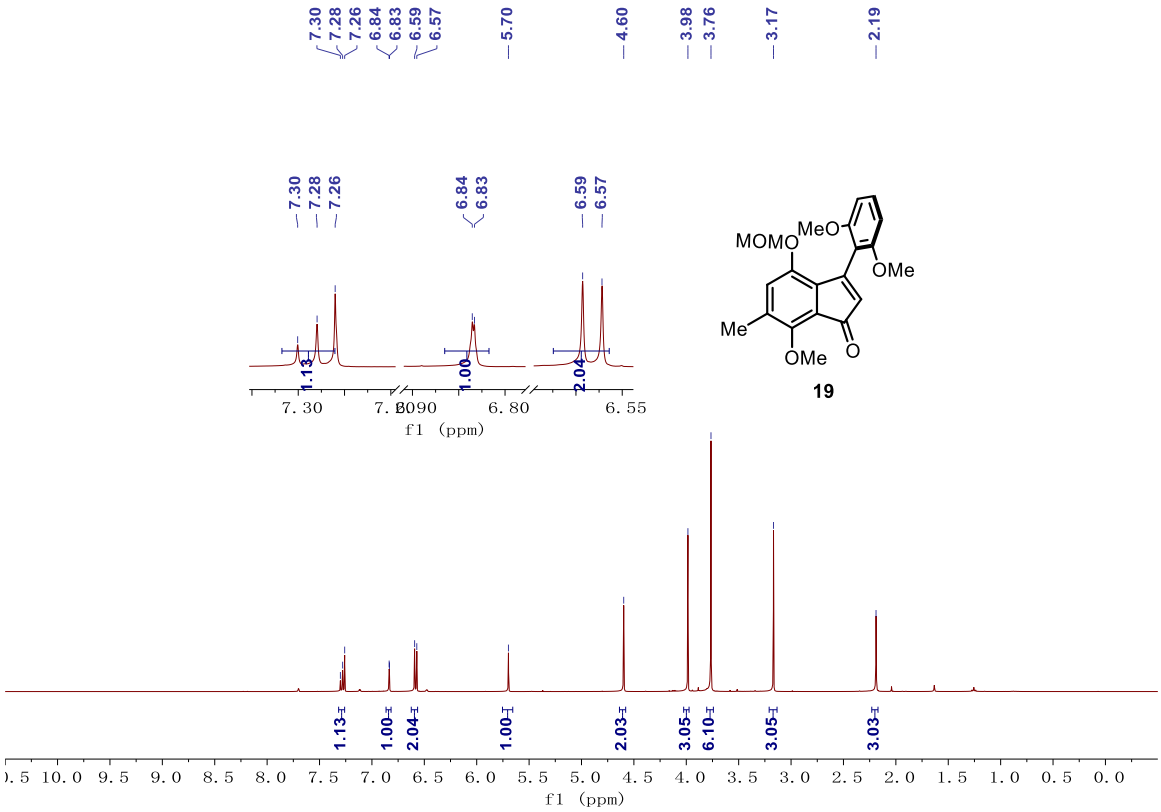

7.09
7.08
6.81
6.80
5.09
3.76
3.46
2.30
OMe
Me
Br
OMOM
1.00
1.06
2.00
3.03
2.97
3.08
f1 (ppm)

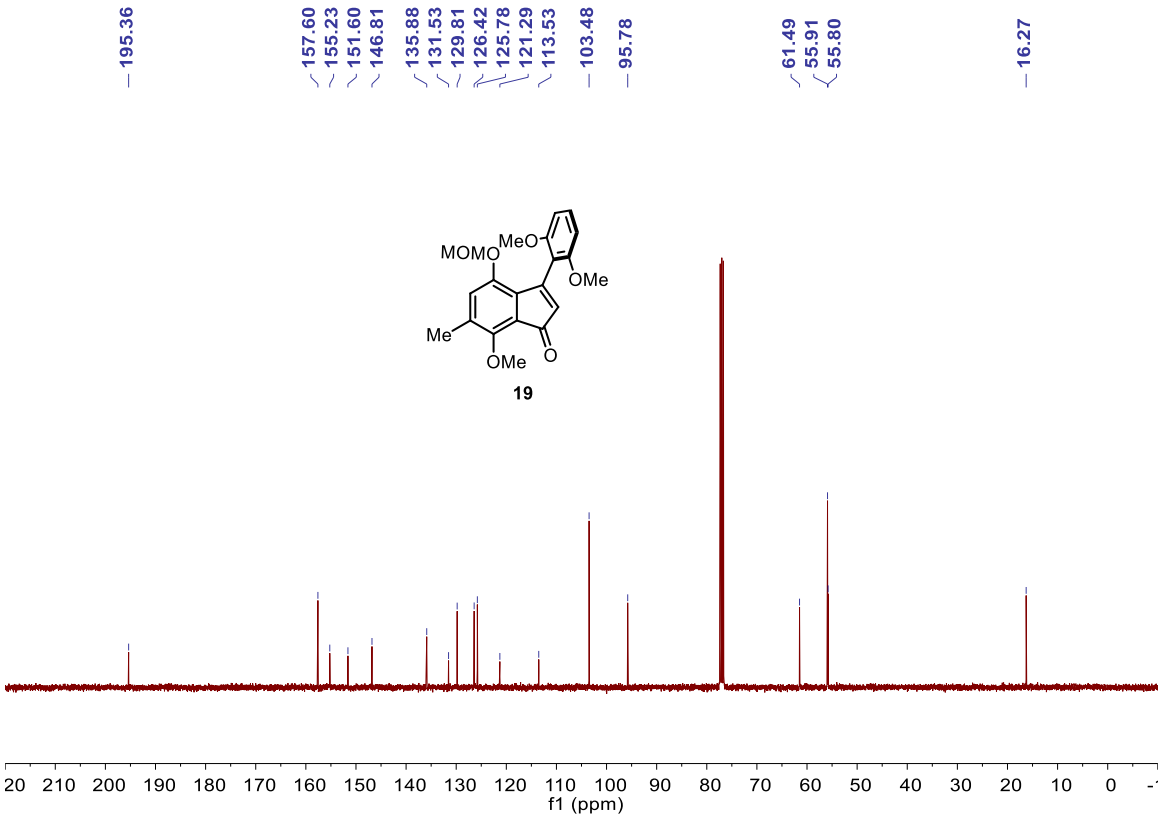
**16c**

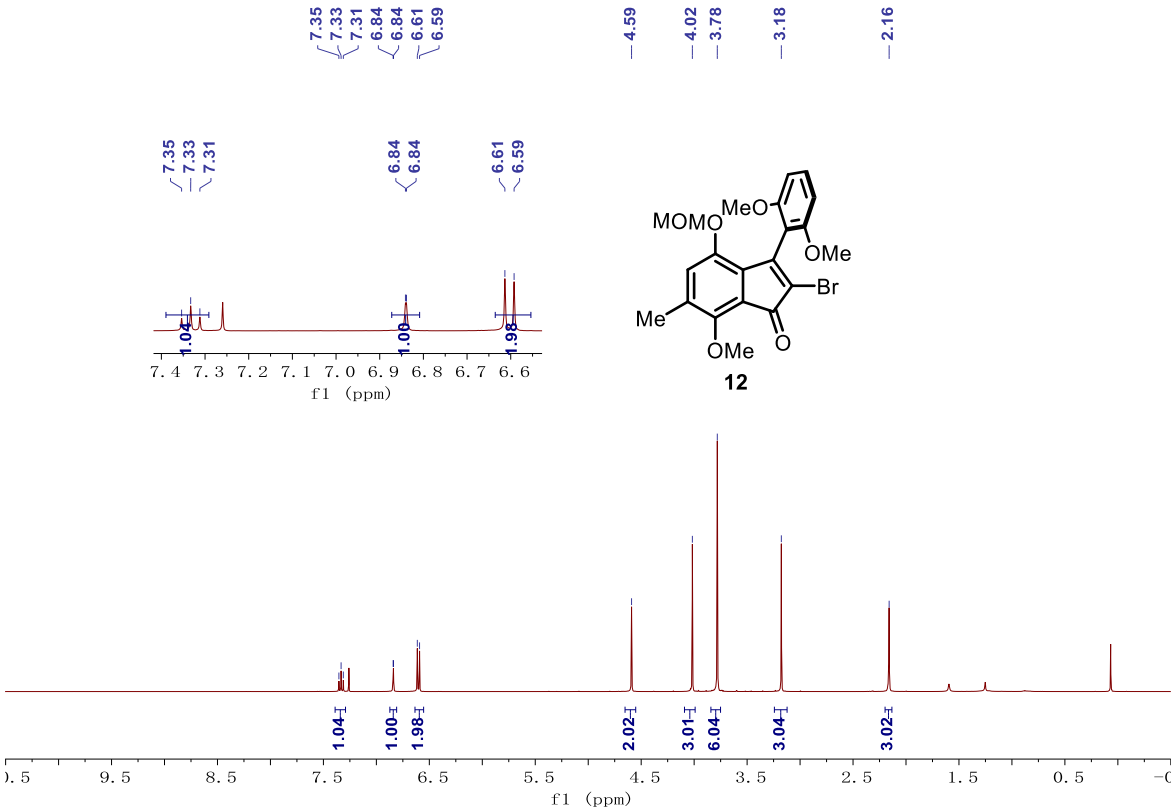

153.44
150.24
133.47
118.53
118.14
117.12
94.78
60.22
55.95
16.77
OMe
Me
Br
OMOM
f1 (ppm)

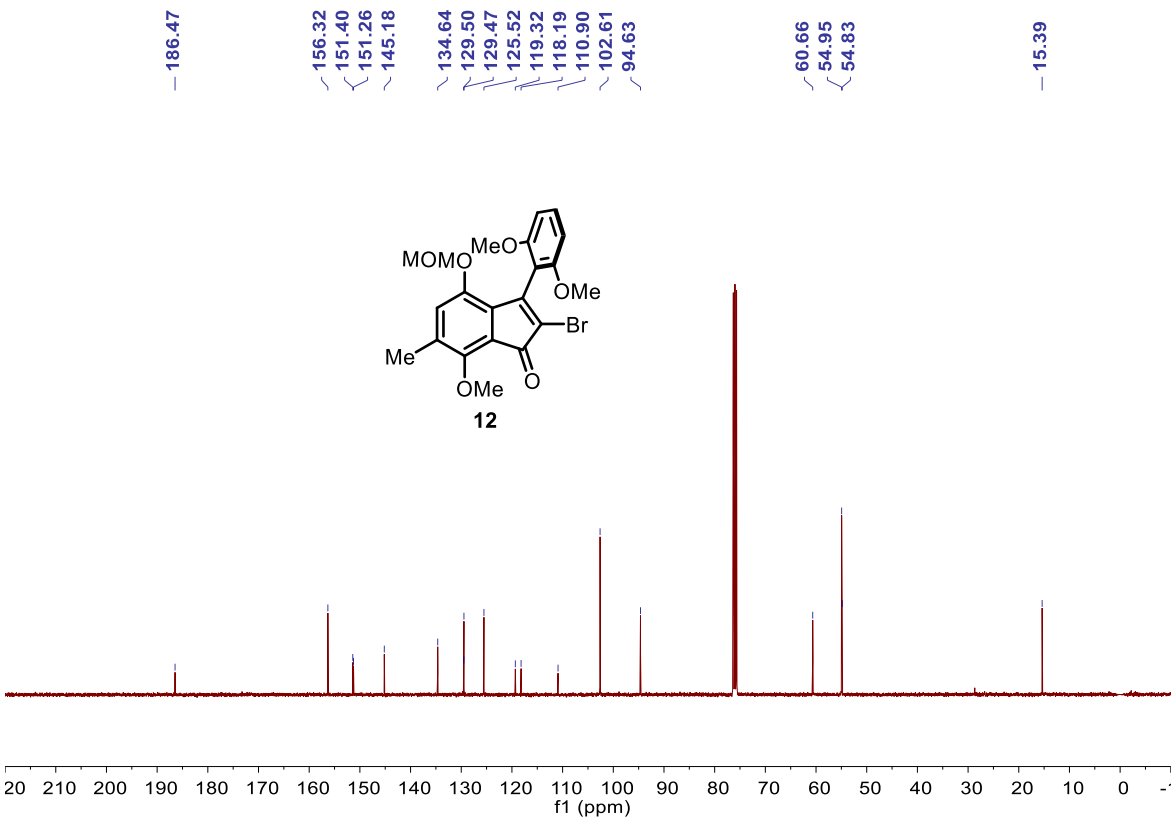
**16c**

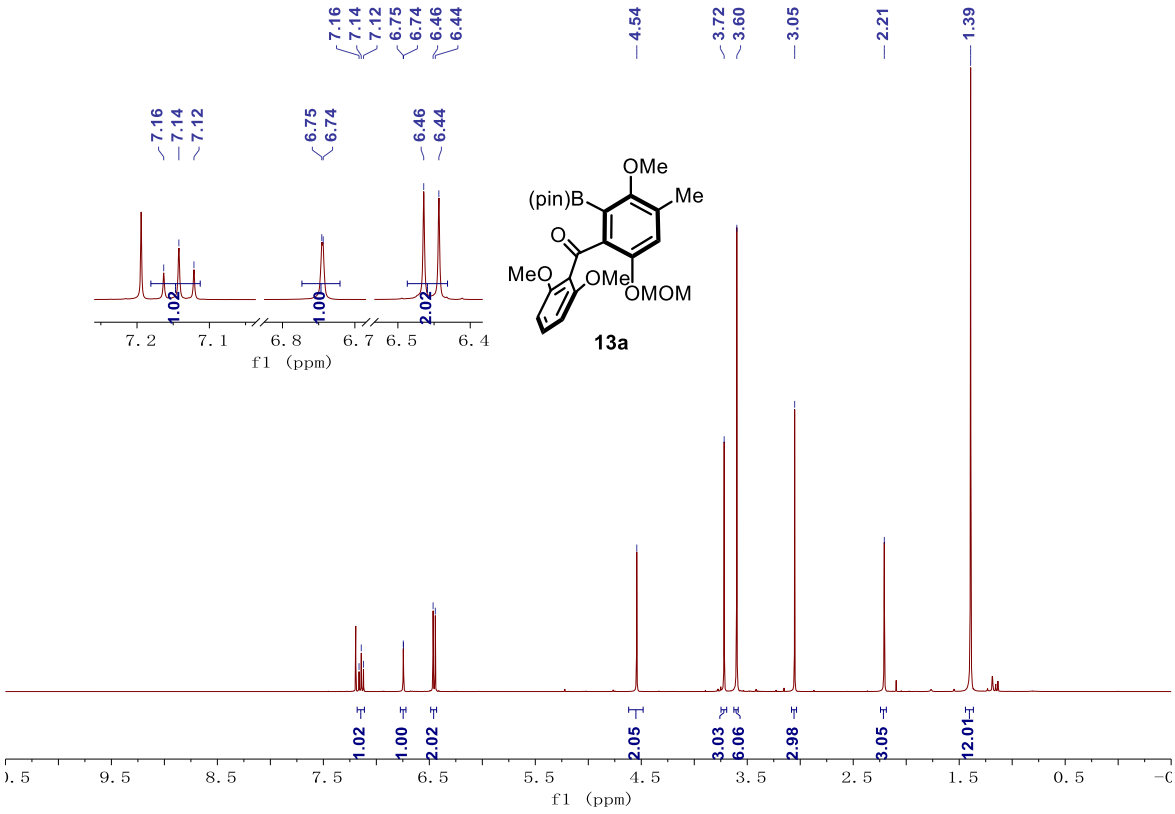

7.29
7.28
6.84
6.83
5.09
3.73
3.46
2.31
OMe
Me
I
OMOM
16
1.02
1.00
2.02
3.06
2.99
3.09
f1 (ppm)
153.74
152.93
132.34
124.29
119.28
94.75
91.52
60.31
55.99
17.25
OMe
Me
I
OMOM
16
f1 (ppm)

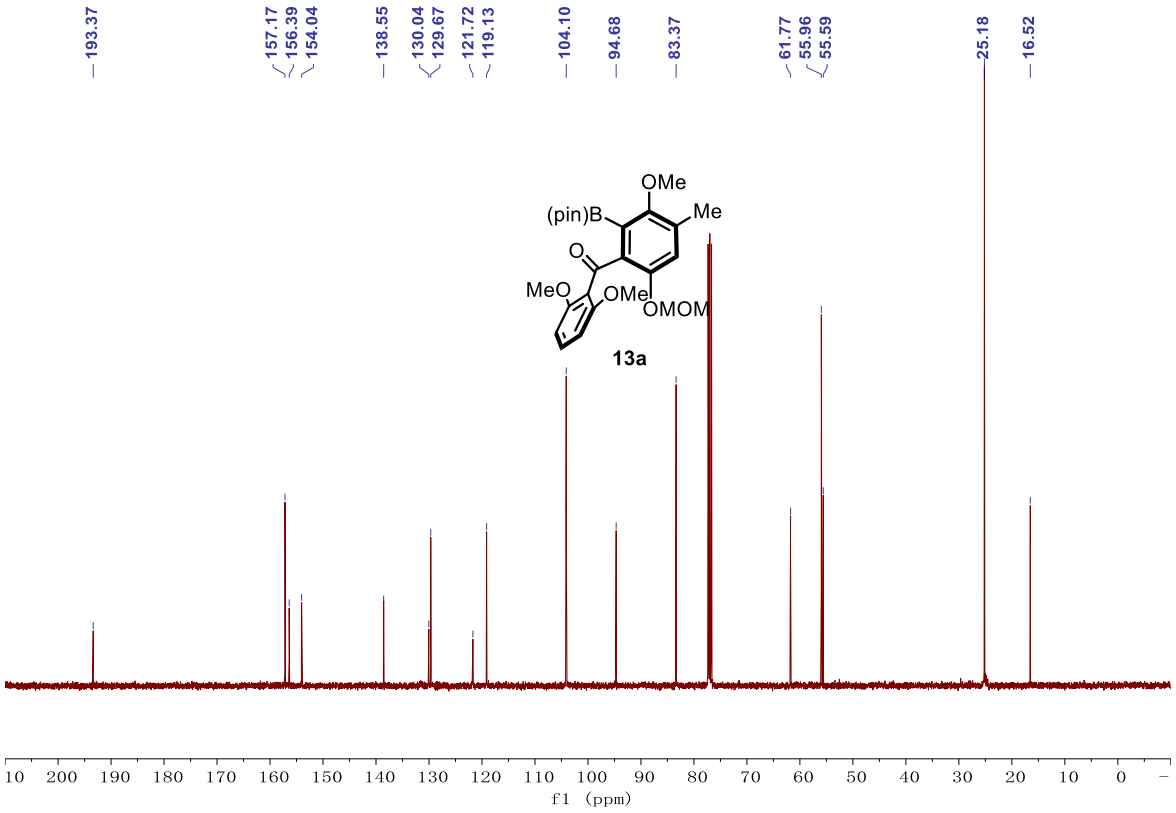

7.30
7.28
7.26
6.84
6.83
6.59
6.57
5.70
4.60
3.98
3.76
3.17
2.19
MOMO
MeO
OMe
Me
OMe
O
19
1.13
1.00
2.04
1.00
2.03
3.05
6.10
3.05
3.03
f1 (ppm)


195.36
157.60
155.23
151.60
146.81
135.88
131.53
129.81
126.42
125.78
121.29
113.53
103.48
95.78
61.49
55.91
55.80
16.27
MOMO
MeO
OMe
Me
OMe
O
19
f1 (ppm)

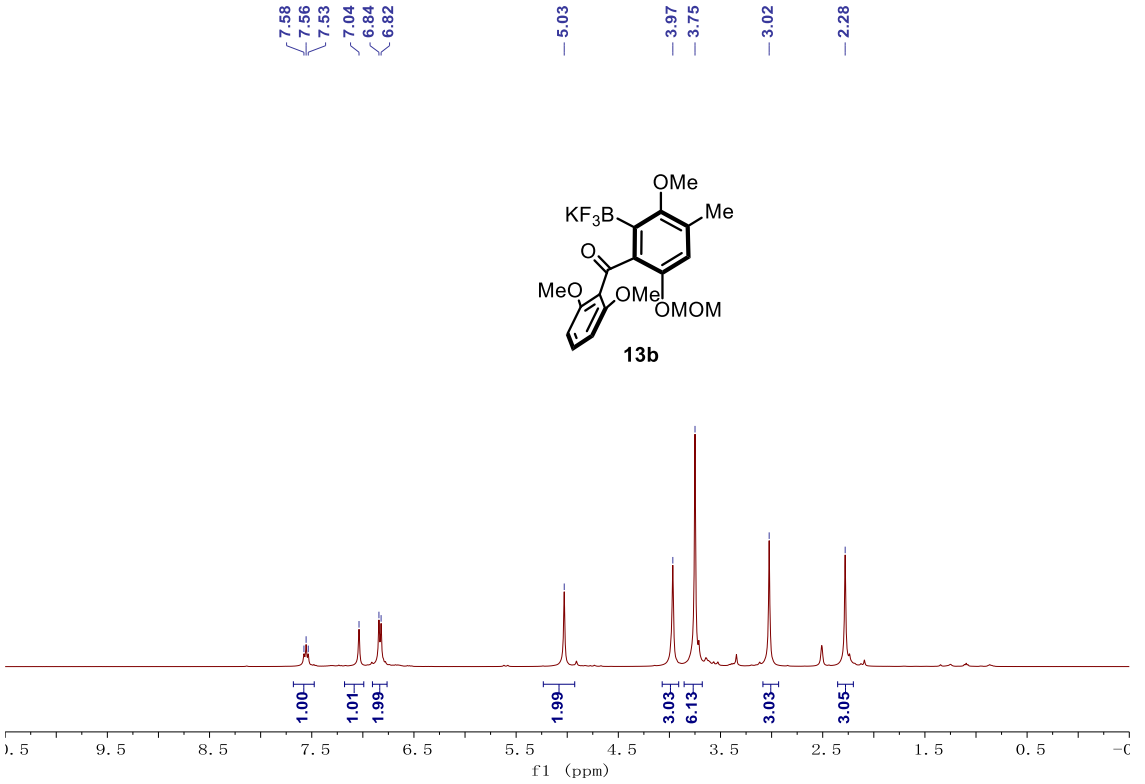

7.35
7.33
7.31
6.84
6.84
6.61
6.59
4.59
4.02
3.78
3.18
2.16
1.04
1.00
1.98
2.02
3.01
6.04
3.04
3.02
f1 (ppm)
MOMO
MeO
OMe
Br
Me
OMe
O
12

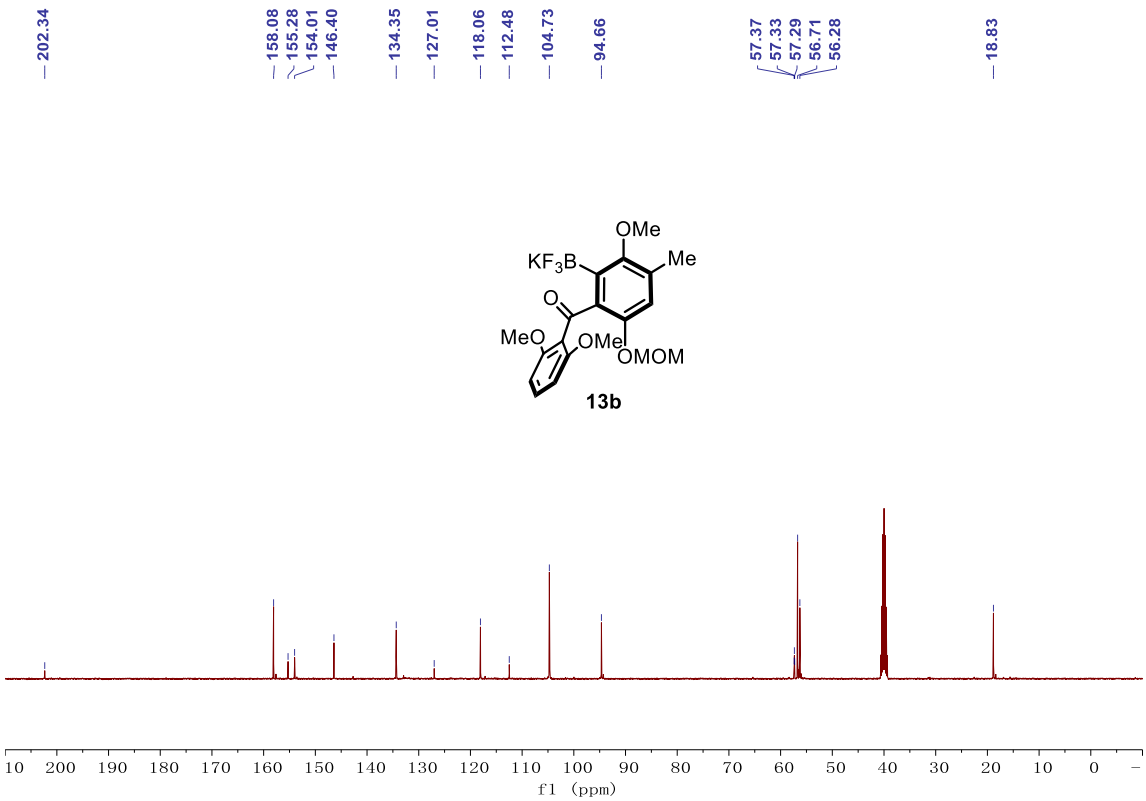

186.47
156.32
151.40
151.26
145.18
134.64
129.50
129.47
125.52
119.32
118.19
110.90
102.61
94.63
60.66
54.95
54.83
15.39
f1 (ppm)
MOMO
MeO
OMe
Br
Me
OMe
O
12

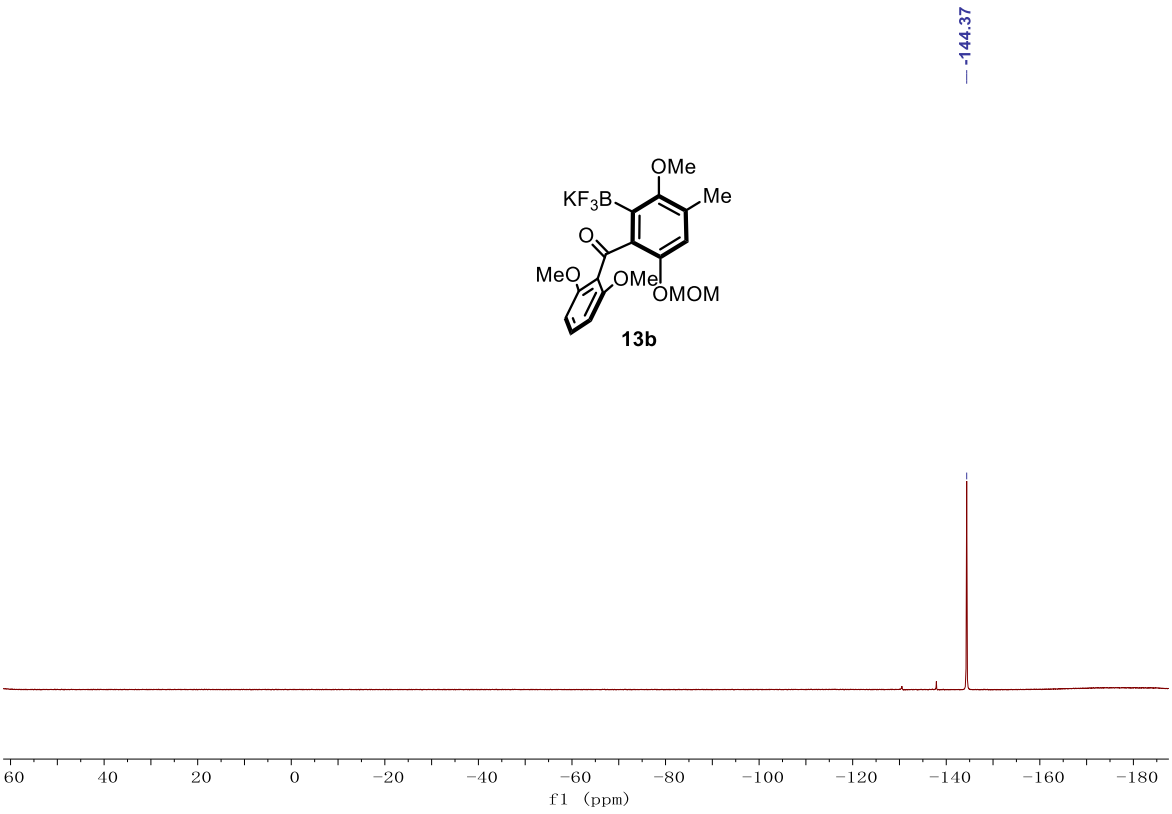

7.16
7.14
7.12
6.75
6.74
6.46
6.44
4.54
3.72
3.60
3.05
2.21
1.39
1.02
1.00
2.02
2.05
3.03
6.06
2.98
3.05
12.01
f1 (ppm)
OMe
(pin)B
Me
O
MeO
OMe
OMOM
13a

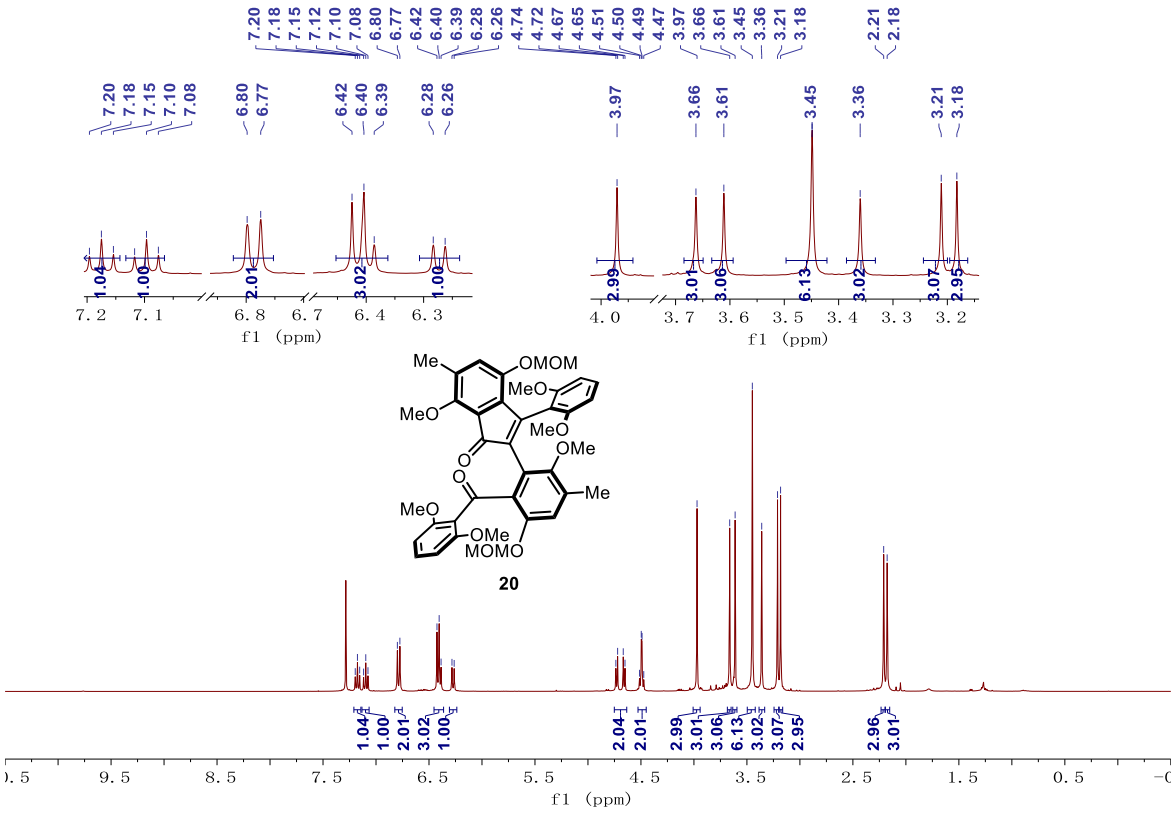

193.37
157.17
156.39
154.04
138.55
130.04
129.67
121.72
119.13
104.10
94.68
83.37
61.77
55.96
55.59
25.18
16.52
f1 (ppm)
OMe
(pin)B
Me
O
MeO
OMe
OMOM
13a

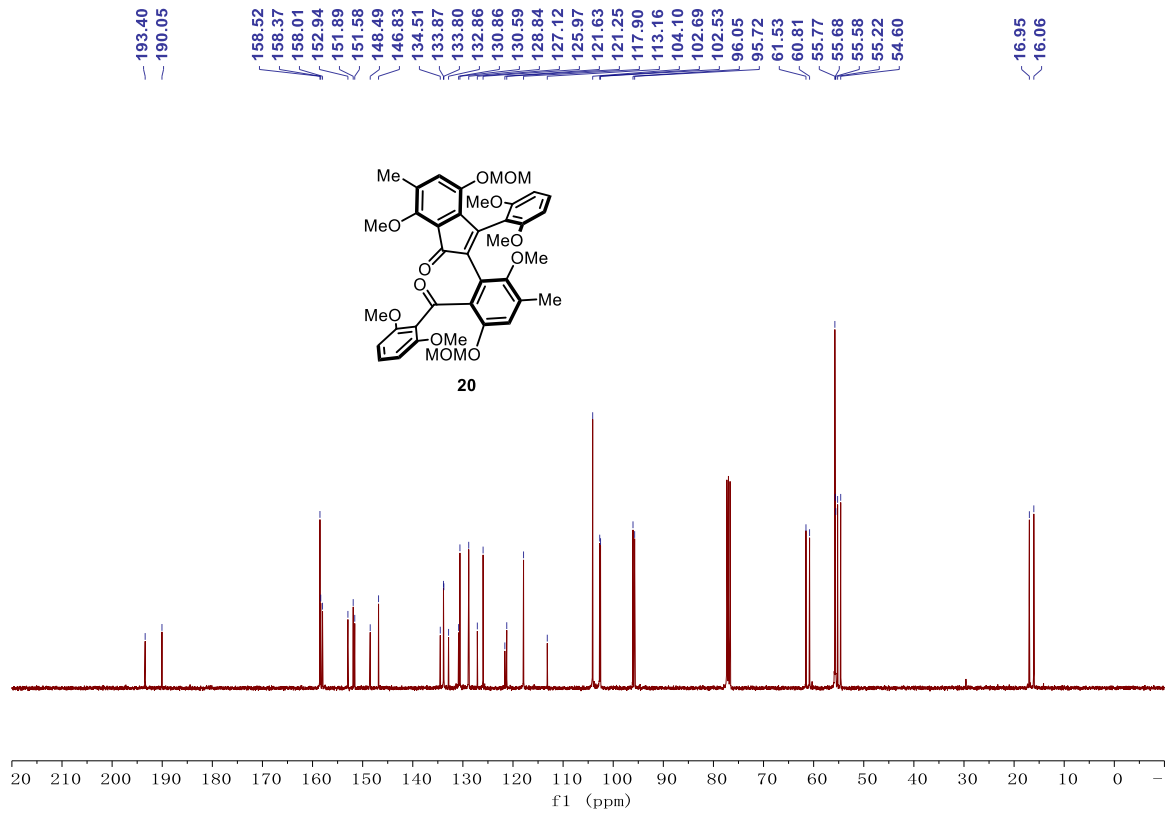
90% purity

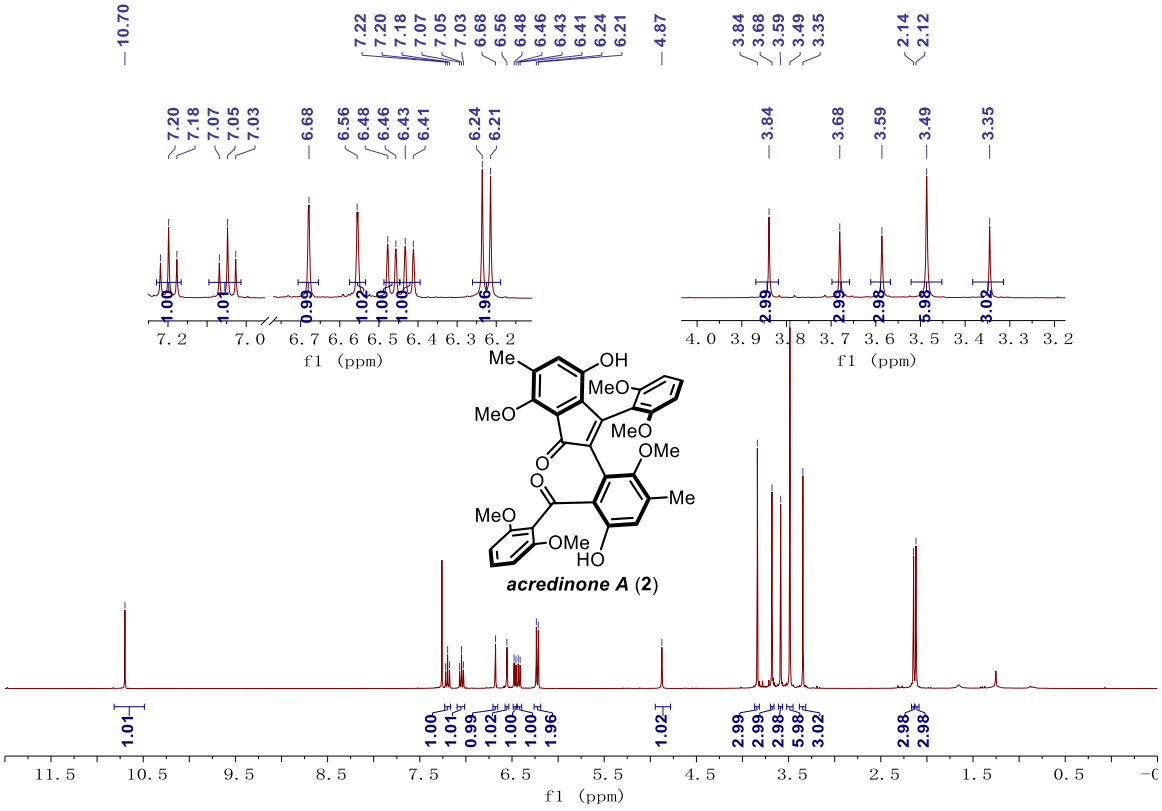

7.58
7.56
7.53
7.04
6.84
6.82
5.03
3.97
3.75
3.02
2.28
OMe
KF3B
Me
O
MeO
OMe
OMOM
13b
1.00
1.01
1.99
1.99
3.03
6.13
3.03
3.05
f1 (ppm)

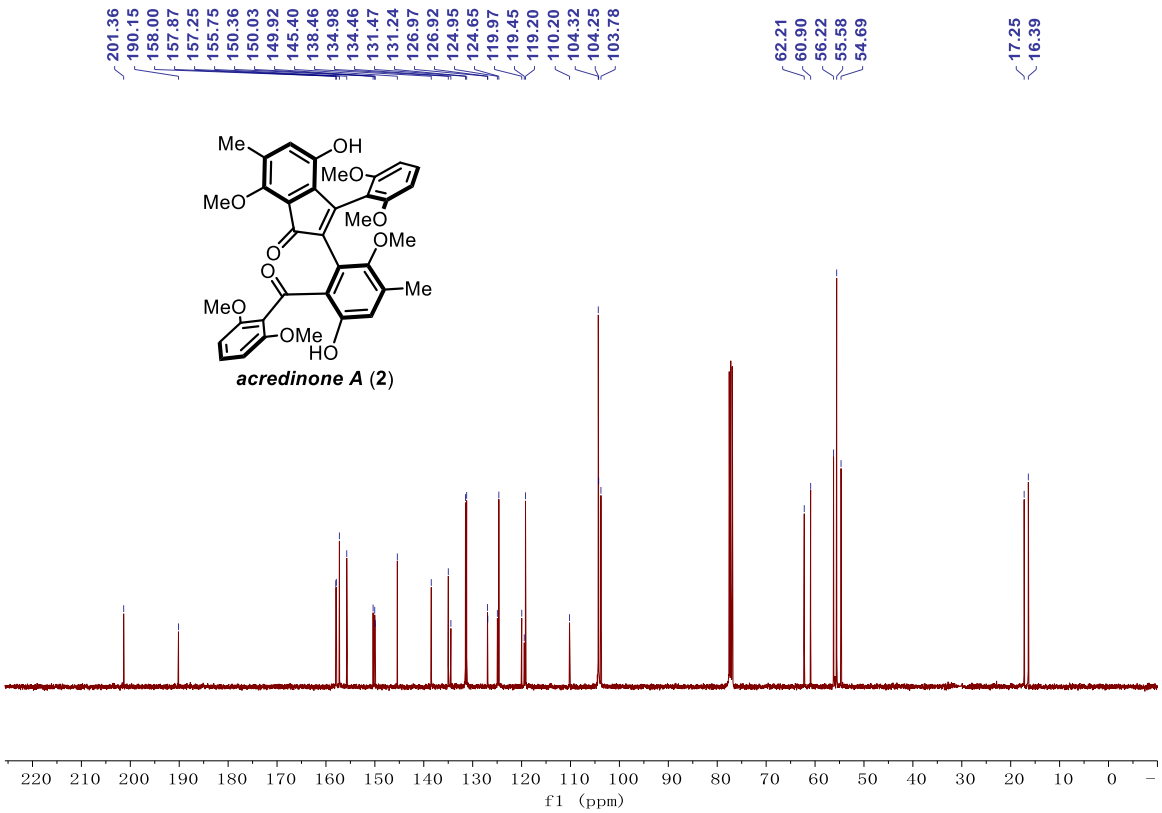

202.34
158.08
155.28
154.01
146.40
134.35
127.01
118.06
112.48
104.73
94.66
57.37
57.33
57.29
56.71
56.28
18.83
OMe
KF3B
Me
O
MeO
OMe
OMOM
13b
f1 (ppm)

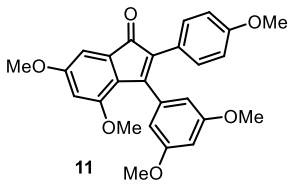

-144.37
OMe
KF3B
Me
O
MeO
OMe
OMOM
13b
60
40
20
0
−20
−40
−60
−80
−100
−120
−140
−160
−180
f1 (ppm)


7.20 7.18 7.15 7.12 7.10 7.08 6.80 6.77 6.42 6.40 6.39 6.28 6.26 4.74 4.72 4.67 4.65 4.51 4.50 4.49 4.47 3.97 3.66 3.61 3.45 3.36 3.21 3.18 2.21 2.18
1.04 1.00 2.01 3.02 1.00
2.99 3.01 3.06 6.13 3.02 3.07 2.95
f1 (ppm)
Me OMOM MeO MeO MeO OMe Me MeO OMe MOMO
20

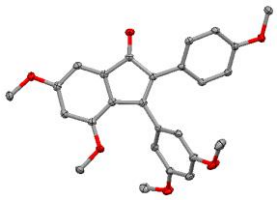

193.40 190.05 158.52 158.37 158.01 152.94 151.89 151.58 148.49 146.83 134.51 133.87 133.80 132.86 130.86 130.59 128.84 127.12 125.97 121.63 121.25 117.90 113.16 104.10 102.69 102.53 96.05 95.72 61.53 60.81 55.77 55.68 55.58 55.22 54.60 16.95 16.06
f1 (ppm)
Me OMOM MeO MeO MeO OMe Me MeO OMe MOMO
20


acredinone A (2)
f1 (ppm)


acredinone A (2)
f1 (ppm)



11



| | | |
|---|---|---|
| CCDC Number | 1881705 | |
| Empirical formula | $C_{26}H_{24}O_6$ | |
| Formula weight | 432.45 | |
| Temperature/K | Temperature/K | |
| Crystal system | triclinic | |
| Space group | P-1 | |
| Unit cell dimensions | a= 7.2326(4) Å | α= 105.6° |
| | b= 11.2053(7) Å | β = 98.5° |
| | c= 14.6268(9) Å | γ = 108.5° |
| Volume | 1047.15(11) $Å^3$ | |
| Z | 2 | |
| Density (calculated) | 1.372 $g/cm^3$ | |
| Absorption coefficient | 0.097 | |
| F(000) | 456.0 | |
| Crystal Size | 0.1 × 0.05 × 0.05 $mm^3$ | |
| Theta range for data collection | 4.07 to 56.65° | |
| Index ranges | $-9 \le h \le 9$, $-14 \le k \le 14$, $-19 \le l \le 19$ | |
| Reflections collected | 36863 | |
| Independent reflections | 5198 [$R_{int}$ = 0.0395, $R_{sigma}$ = 0.0322] | |
| Data/restraints/parameters | 5198/0/294 | |
| Goodness-of-fit on $F^2$ | 1.028 | |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0420, $wR_2$ = 0.0955 | |
| Final R indexes [all data] | $R_1$ = 0.0654, $wR_2$ = 0.1053\ | |
| Largest diff. peak and hole | 0.35/-0.22 $e.Å^{-3}$ | |

**References**


[1] a) D. Ray, S. Paul, S. Brahma, J. K. Ray, *Tetrahedron Lett.* **2007**, *48*, 8005-8008; b) A. M. Zawisza, B. Ganchegui, I. Gonzalez, S. Bouquillon, A. Roglans, F. Henin, J. Muzart, *J. Mol. Catal. A: Chem.* **2008**, *283*, 140-145.

[2] a) B. Fiser, J. M. Cuerva, E. Gomez-Bengoa, *Organometallics* **2018**, *37*, 390-395; b) K. Gilmore, M. Manoharan, J. I. C. Wu, P. V. Schleyer, I. V. Alabugin, *J. Am. Chem. Soc.* **2012**, *134*, 10584-10594.

[3] P. S. Volvoikar, S. G. Tilve, *Org. Lett.* **2016**, *18*, 892-895.

[4] T. Obata, S. Suzuki, A. Nakagawa, R. Kajihara, K. Noguchi, A. Saito, *Org. Lett.* **2016**, *18*, 4136-4139.

[5] Y. Liu, S. M. Ma, *Org. Lett.* **2012**, *14*, 720-723.

[6] M. Lautens, J. F. Paquin, S. Piguel, M. Dahlmann, *J. Org. Chem.* **2001**, *66*, 8127-8134.

[7] R. C. Samanta, H. Yamamoto, *Chem. Eur. J.* **2015**, *21*, 11976-11979.

[8] H. Shi, D. J. Babinski, T. Ritter, *J. Am. Chem. Soc.* **2015**, *137*, 3775-3778.

[9] Z. Dong, J. Wang, Z. Ren, G. Dong, *Angew. Chem. Int. Ed.* **2015**, *54*, 12664-12668.

[10] D. W. Slocum, K. C. Tekin, N. Quang, P. E. Whitley, T. K. Reinscheld, B. Fouzia, *Tetrahedron Lett.* **2011**, *52*, 7141-7145.

[11] S. W. Youn, Y. H. Kim, *Org. Lett.* **2016**, *18*, 6140-6143.

[12] H. R. Khatri, J. L. Zhu, *Chem. Eur. J.* **2012**, *18*, 12232-12236.

[13] F. Teply, I. G. Stara, I. Stary, A. Kollarovic, D. Lustinec, Z. Krausova, D. Saman, P. Fiedler, *Eur. J. Org. Chem.* **2007**, 4244-4250.

[14] R. R. Kadiyala, D. Tilly, E. Nagaradja, T. Roisnel, V. E. Matulis, O. A. Ivashkevich, Y. S. Halauko, F. Chevallier, P. C. Gros, F. Mongin, *Chem. Eur. J.* **2013**, *19*, 7944-7960.

[15] Y. Fukata, K. Asano, S. Matsubara, *J. Am. Chem. Soc.* **2015**, *137*, 5320-5323.

[16] R. Kocz, J. Roestamadji, S. Mobashery, *J. Org. Chem.* **1994**, *59*, 2913-2914.

[17] A. S. Pankova, A. Y. Stukalov, M. A. Kuznetsov, *Org. Lett.* **2015**, *17*, 1826-1829.

[18] C.-F. Xiao, Y. Zou, J.-L. Du, H.-Y. Sun, X.-K. Liu, *Synth. Commun.* **2012**, *42*, 1243-1258.

[19] T.-Z. Li, C.-A. Geng, X.-J. Yin, T.-H. Yang, X.-L. Chen, X.-Y. Huang, Y.-B. Ma, X.-M. Zhang, J.-J. Chen, *Org. Lett.* **2017**, *19*, 429-431.

[20] K. V. Chuang, R. Navarro, S. E. Reisman, *Chem. Sci.* **2011**, *2*, 1086-1089.

[21] M. W. Carson, M. W. Giese, M. J. Coghlan, *Org. Lett.* **2008**, *10*, 2701-2704.

[22] D. Qiu, F. Y. Mo, Z. T. Zheng, Y. Zhang, J. B. Wang, *Org. Lett.* **2010**, *12*, 5474-5477.

[23] L. F. Tietze, S. G. Stewart, M. E. Polomska, A. Modi, A. Zeeck, *Chem. Eur. J.* **2004**, *10*, 5233-5242.

[24] D. L. Terrian, T. Mohammad, H. Morrison, *J. Org. Chem.* **1995**, *60*, 1981-1984.

[25] J. Cabrecastellvi, A. Palomocoll, A. L. Palomocoll, *Synthesis* **1981**, 616-620.

[26] D. K. Scrafton, J. E. Taylor, M. F. Mahon, J. S. Fossey, T. D. James, *J. Org. Chem.* **2008**, *73*, 2871-2874.

[27] S. A. Snyder, T. C. Sherwood, A. G. Ross, *Angew. Chem. Int. Ed.* **2010**, *49*, 5146-5150.