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# Supplementary Information

## An Efficient Route to Highly Strained Cyclobutenes: Indium-Catalyzed Reactions of Enynals with Alkynes

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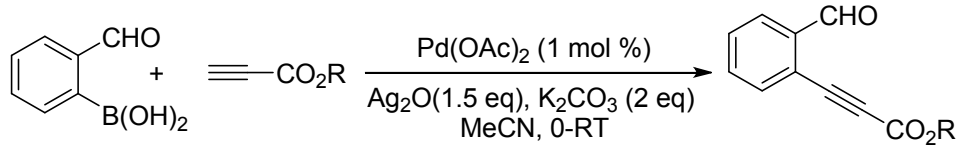
## General information

All reactions were carried out under an inert atmosphere of dry $N_2$ in schlenk tube, solvents were purified by standard method. $^1H$, $^{13}C$, $^{19}F$ NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz for $^1H$; 100 MHz for $^{13}C$; 376 MHz for $^{19}F$), $^1H$ NMR and $^{13}C$ NMR chemical shifts were determined relative to internal standard TMS at δ 0.0. Chemical shifts (δ) are reported in ppm, and coupling constants (*J*) are in Hertz(Hz). The following abbreviations were used to explain the multiplicities: s = singlet, d =doublet, t = triplet, q = quartet, m = multiplet, br = broad. Infrared (IR) spectra are recorded on a Nicolet 210 spectrophotometer and were recorded in potassium bromide (KBr) pellet. Mass spectra (MS) were obtained using EI mass spectrometer. Melting points were determined using a hot stage apparatus.
All reagents were used as received from commercial sources, unless specified otherwise, or prepared as described in the literature.

## General procedure for preparation of enynals

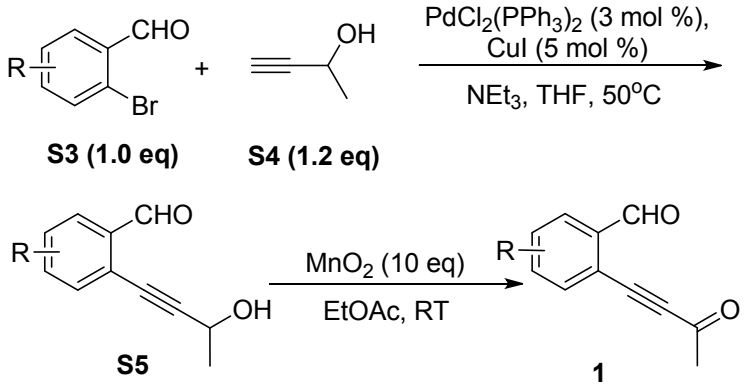
**Method 1:**[1]




**S1 (1.0 eq)** **S2 (2.0 eq)** **1**

To a Schlenk tube with a magnetic bar under $N_2$ atmosphere at 0°C was added $Pd(OAc)_2$ (1.0 mol %), $Ag_2O$ (1.5 eq) and $K_2CO_3$ (2.0 eq), after that, starting materials of **S1** and **S2** in MeCN (0.125 M) was added. The reaction mixture was stirred from 0°C to rt until **S1** was completely consumed monitored by TLC, then the mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel using EtOAc in petroleum ether (5 %) as eluent to afford the product **1**. Characterization data for products was consistent with literature.[2]

**Method 2:**



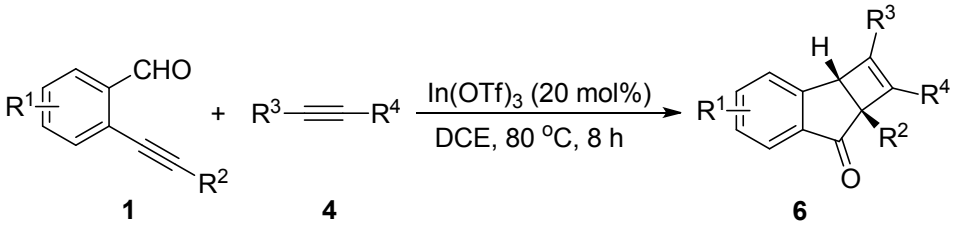

**S3 (1.0 eq)** **S4 (1.2 eq)**

**S5** **1**

To a suspension of $PdCl_2(PPh_3)_2$ (3 mol %) and CuI (5 mol %) in THF (0.125 M) under nitrogen atmosphere was added 2-bromoaldehyde (**S3**, 1.0 eq) and 3-Butyn-2-ol (**S4**, 1.2 eq), and then $NEt_3$ (0.025 M) was added, the mixture was stirred at 50℃ for overnight, after then, the mixture was filtered through short silica gel, and then the solvent was removed under reduced pressure. The crude concentrate was purified by flash column chromatography on silica gel using EtOAc in petroleum ether (25 %) as eluent to afford the product **S5** as yellow oil.[3] The isolated compound was then added to the suspension of $MnO_2$ (10.0 eq) in EtOAc (0.5 M), after

stirred at room temperature for overnight or completion of the reaction (monitored by TLC), the $MnO_2$ was filtered, and the solvent was evaporated under reduced pressure to afford the crude. The crude concentrate was purified by flash column chromatography on silica gel using EtOAc in petroleum ether (20 %) as eluent to afford the product **1**.[4] Characterization data for products was consistent with literature.[2]

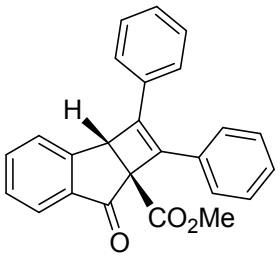
## General procedure for synthesis of 6a-u




**1** **4** **6**

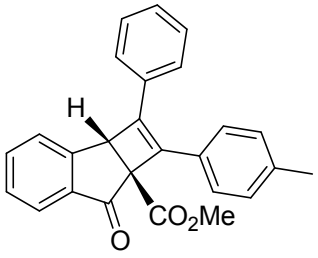
In a Schlenk tube with a magnetic bar under nitrogen atmosphere was added $In(OTf)_3$ (20 mol %) and dichloroethane (DCE, 1 ml), and then the substrates of enynals (**1**, 0.25 mmol) and alkynes (**4**, 1.3 eq, 0.33 mmol) were added respectively. The mixture was stirred at 80°C for 8h. After that, the solvent was evaporated by rotary evaporator, and the residue was purified by flash column chromatography on silica gel using EtOAc/petroleum ether as eluent to afford the product **6**.

**Methyl 7-oxo-1,2-diphenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6a)**




Yield: 87%. White solid, mp 183-184 °C. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 1H), 7.70 (d, *J* = 7.1 Hz, 2H), 7.52 – 7.35 (m, 4H), 7.35 – 7.17 (m, 6H), 4.79 (s, 1H), 3.64 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.2, 169.1, 151.1, 146.3, 137.5, 136.4, 135.0, 133.3, 132.7, 129.0, 128.7, 128.7, 128.5, 128.4, 127.4, 126.7, 126.2, 126.2, 64.2, 52.6, 51.0. IR (KBr, $cm^{-1}$) 2961, 2920, 2851, 1739, 1704, 1600, 1436, 1259, 1511, 1099, 1025, 799, 757, 696; HRMS (DART Postive) Calcd for $C_{25}H_{19}O_3$ $(M+H)^+$ 367.1329, found 367.1326.

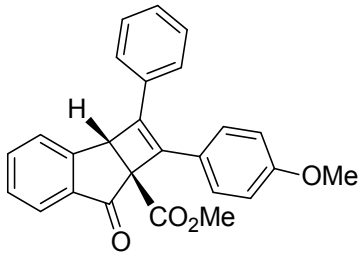
**Methyl 7-oxo-2-phenyl-1-(p-tolyl)-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6b)**




Yield: 73%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.35 (m, 4H), 7.34 – 7.17 (m, 4H), 7.06 (d, *J* = 7.7 Hz, 2H), 4.78 (s, 1H), 3.65 (s, 3H), 2.25 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.2, 169.1, 151.3, 145.3, 138.8, 137.6, 136.4,

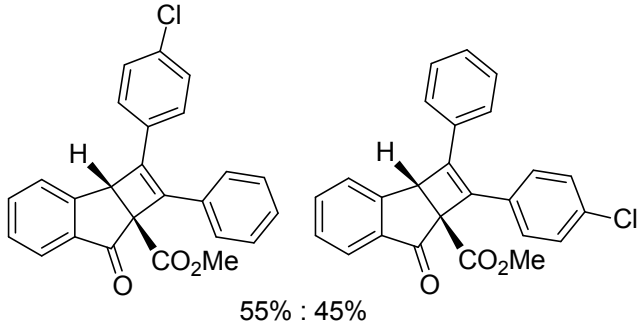
134.9, 133.4, 129.9, 129.2, 128.8, 128.6, 128.5, 127.4, 126.7, 126.2, 126.1, 64.2, 52.5, 50.9, 21.5. IR (KBr, $cm^{-1}$) 3059, 3028, 2954, 2922, 2848, 1752, 1699, 1604, 1513, 1466, 1435, 1374, 1322, 1290, 1240, 1186, 1152, 1097, 1073, 1047, 973, 898, 876, 826, 762, 736, 697, 636, 609, 585, 556, 519, 489, 420; HRMS (DART Postive) Calcd for $C_{26}H_{21}O_3$ $(M+H)^+$ 381.1485, found 381.1480.

**Methyl 1-(4-methoxyphenyl)-7-oxo-2-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6c)**




Yield: 46%. Yellow solid, mp 152-153 °C. $R_f$ 0.2 (EtOAc/petroleum ether = 1/8). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.7 Hz, 1H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.58 – 7.43 (m, 4H), 7.43 – 7.27 (m, 4H), 6.87 (d, *J* = 8.2 Hz, 2H), 4.85 (s, 1H), 3.81 (s, 3H), 3.74 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 197.3, 169.1, 159.9, 151.4, 144.0, 137.5, 136.1, 134.9, 133.6, 129.0, 128.7, 128.6, 128.4, 126.6, 126.2, 126.1, 125.4, 113.9, 64.2, 55.3, 52.5, 50.9. IR (KBr, $cm^{-1}$) 2955, 2839, 1742, 1705, 1604, 1512, 1464, 1439, 1320, 1282, 1252, 1097, 1073, 1030, 972, 898, 839, 813, 784, 761, 735, 698, 657, 588, 557, 522.

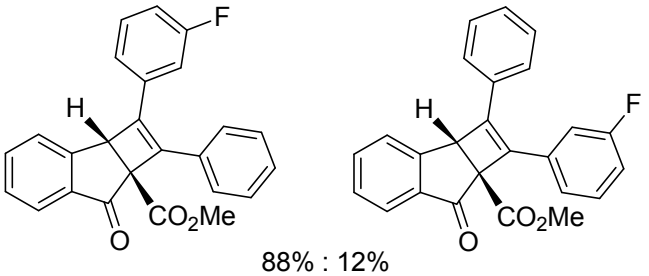
**Methyl 2-(4-chlorophenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6d)**




55% : 45%

Yield: 54%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1H$ NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.8 Hz, 2H), 7.57 – 7.27 (m, 10H), 4.88, 4.85 (s, 1H), 3.74 (s, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) δ 197.1, 196.8, 168.8, 151.0, 150.8, 146.9, 145.0, 137.5, 137.4, 137.1, 135.1, 135.1, 134.8, 134.4, 132.9, 132.4, 131.7, 131.2, 129.2, 129.0, 128.9, 128.8, 128.8, 128.7, 128.7, 128.6, 128.5, 128.0, 127.4, 126.7, 126.3, 126.2, 126.1, 64.3, 64.2, 52.6, 51.1, 50.9. IR (KBr, $cm^{-1}$) 3061, 2958, 2926, 2849, 1911, 1751, 1701, 1603, 1494, 1465, 1433, 1400, 1374, 1321, 1284, 1238, 1207, 1151, 1095, 1047, 1013, 972, 897, 837, 789, 763, 726, 697, 647, 604, 546, 518, 466, 441; HRMS (DART Postive) Calcd for $C_{25}H_{18}ClO_3$ $(M+H)^+$ 401.0939, found 401.0934.

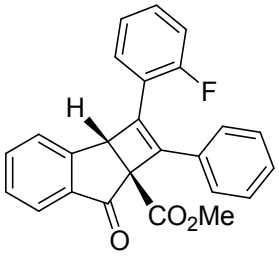
**Methyl 2-(3-fluorophenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6e)**




88% : 12%

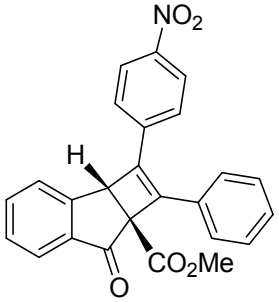
Yield: 62%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.38 – 7.29 (m, 5H), 7.24 (m, 1H), 7.00 (d, *J* = 6.9 Hz, 1H), 4.86 (s, 1H), 3.74 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.01 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.8, 168.8, 164.1, 161.6, 150.8, 144.9, 137.8, 137.5, 135.4, 135.3, 135.1, 132.3, 130.4, 130.3, 129.0, 128.8, 128.7, 128.5, 127.5, 126.8, 126.3, 126.2, 122.5, 122.5, 116.0, 115.8, 113.6, 113.4, 64.3, 52.6, 51.0. IR (KBr, $cm^{-1}$) 2962, 2924, 2850, 1741, 1707, 1606, 1580, 1463, 1377, 1261, 1152, 1102, 1015, 869, 797, 559; HRMS (DART Postive) Calcd for $C_{25}H_{18}FO_3$ $(M+H)^+$ 385.1234, found 385.1229.

**Methyl 2-(2-fluorophenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6f)**




Yield: 60%. Brown oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.53 (t, *J* = 7.3 Hz, 1H), 7.46 (dd, *J* = 12.2, 7.4 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.36 – 7.26 (m, 4H), 7.18 – 7.09 (m, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.99 (s, 1H), 3.74 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.58 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 168.8, 161.4, 158.9, 151.2, 141.2, 138.5, 137.3, 135.2, 132.5, 130.7, 130.7, 128.9, 128.9, 128.9, 128.5, 128.4, 127.6, 126.1, 125.7, 124.2, 124.1, 121.1, 121.0, 116.4, 116.2, 65.3, 52.7, 52.6, 52.5. IR (KBr, $cm^{-1}$) 2957, 1741, 1704, 1597, 1485, 1374, 1290, 1249, 1152, 1106, 1034, 968, 912, 795, 748, 689, 605; HRMS (DART Postive) Calcd for $C_{25}H_{18}FO_3$ $(M+H)^+$ 385.1234, found 385.1229.

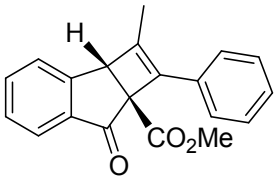
**Methyl 2-(4-nitrophenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6g)**




Yield: 68%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/8). $^1$H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.3 Hz, 2H), 7.82 (d, *J* = 7.6 Hz, 1H), 7.65 (m, 4H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.37 (dd, *J* = 15.7, 7.7 Hz, 2H), 7.29

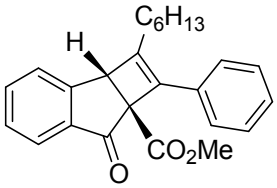
(m, 3H), 4.86 (s, 1H), 3.67 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.2, 168.4, 150.4, 147.5, 143.7, 140.9, 139.5, 137.4, 135.3, 131.9, 129.7, 129.0, 128.7, 127.6, 127.4, 126.4, 126.0, 124.1, 64.6, 52.7, 50.8. IR (KBr, $cm^{-1}$) 2924, 2853, 1743, 1702, 1592, 1524, 1514, 1462, 1380, 1344, 1286, 1245, 1152, 1106, 1042, 968, 911, 856, 806, 745, 728, 686, 608; HRMS (DART Postive) Calcd for $C_{25}H_{18}NO_5$ $(M+H)^+$ 412.1179, found 412.1174.

**Methyl 2-methyl-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6h)**



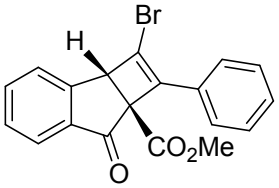

Yield: 73%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 9.3 Hz, 3H), 7.49 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.28 – 7.16 (m, 1H), 4.35 (s, 1H), 3.75 (s, 3H), 2.09 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.4, 169.6, 151.1, 146.8, 137.2, 137.1, 134.9, 132.6, 128.4, 128.4, 127.8, 126.9, 126.3, 125.4, 64.5, 53.1, 52.5, 14.9. IR (KBr, $cm^{-1}$) 3061, 2958, 2922, 2849, 1742, 1705, 1602, 1499, 1464, 1436, 1375, 1285, 1244, 1190, 1154, 1097, 1067, 971, 892, 798, 764, 698, 621, 496; HRMS (DART Postive) Calcd for $C_{20}H_{17}O_3$ $(M+H)^+$ 305.1172, found 305.1169.

**Methyl 2-hexyl-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6i)**




Yield: 61%. Brown oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.7 Hz, 1H), 7.57 – 7.49 (m, 3H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 2H), 7.15 (t, *J* = 7.5 Hz, 1H), 4.36 (s, 1H), 3.67 (s, 3H), 2.60 – 2.43 (m, 1H), 2.33 – 2.13 (m, 1H), 1.55 (dd, *J* = 13.0, 6.8 Hz, 3H), 1.37 – 1.22 (m, 5H), 0.80 (t, *J* = 6.5 Hz, 3H).$^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.4, 169.6, 151.4, 151.4, 137.4, 136.7, 134.8, 132.6, 128.4, 128.3, 127.8, 127.0, 126.2, 125.8, 64.2, 52.5, 51.8, 31.6, 29.3, 29.2, 26.9, 22.5, 14.0. IR (KBr, $cm^{-1}$) 3060, 3026, 2961, 2927, 2852, 1752, 1702, 1603, 1495, 1467, 1433, 1376, 1284, 1241, 1191, 1150, 1095, 1059, 975, 906, 882, 797, 763, 695, 631, 581, 528, 490, 427; HRMS (DART Postive) Calcd for $C_{25}H_{27}O_3$ $(M+H)^+$ 375.1955, found 375.1950.

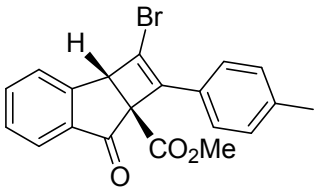
**Methyl 2-bromo-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6j)**




Yield: 63%. Brown oil. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.1 Hz, 2H), 7.77 (d, *J* = 7.7 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.29 (dd, *J* = 16.5, 8.9 Hz, 3H), 4.62 (s, 1H), 3.71 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 195.0, 167.9, 149.1, 142.5, 136.6, 135.4, 130.1, 129.4, 129.2, 128.4, 126.9, 126.4, 125.8, 120.8, 65.9, 56.5, 52.9. IR (KBr, $cm^{-1}$) 3061, 2960, 2926, 2851, 1753, 1073, 1631, 1603, 1492, 1467, 1433, 1374, 1324, 1261, 1188, 1153, 1096, 1023,

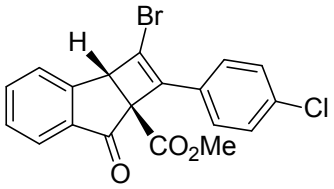
966, 919, 894, 873, 804, 763, 729, 693, 669, 629, 568, 534, 489, 429; HRMS (DART Postive) Calcd for C19H14BrO3 $(M+H)^+$ 369.0121, found 369.0118.

**Methyl 2-bromo-7-oxo-1-(p-tolyl)-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6k)**



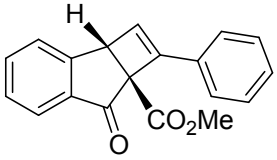

Yield: 70%. White solid, mp 122-123 °C. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 2H), 7.67 (t, *J* = 7.4 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 2H), 4.68 (s, 1H), 3.78 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 194.0, 167.0, 148.2, 141.4, 138.6, 135.5, 134.3, 128.1, 126.3, 125.8, 125.3, 124.8, 118.5, 64.8, 55.4, 51.8, 20.5. IR (KBr, $cm^{-1}$) 2962, 2922, 2856, 1745, 1706, 1598, 1505, 1465, 1370, 1289, 1245, 1194, 1154, 1093, 1051, 970, 910, 812, 730, 683, 634, 562, 471; HRMS (DART Postive) Calcd for $C_{20}H_{16}BrO_3$ $(M+H)^+$ 383.0277, found 383.0271.

**Methyl 2-bromo-1-(4-chlorophenyl)-7-oxo-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6l)**



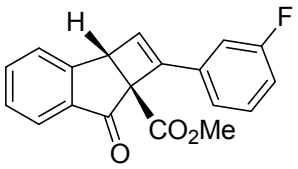

Yield: 72%. Brown oil. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.84 (m, 3H), 7.69 (t, *J* = 7.2 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.35 (d, *J* = 7.3 Hz, 2H), 4.70 (s, 1H), 3.79 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 193.8, 166.6, 148.0, 140.4, 135.4, 134.5, 134.2, 128.3, 127.7, 127.5, 127.2, 125.4, 124.8, 120.5, 64.8, 55.5, 51.9. IR (KBr, $cm^{-1}$) 2996, 2922, 1772, 1753, 1709, 1630, 1488, 1381, 1245, 1151, 1092, 1059, 914, 834, 801, 745, 623, 469; HRMS (DART Postive) Calcd for $C_{19}H_{13}BrClO_3$ $(M+H)^+$ 402.9731, found 402.9731.

**Methyl 7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6m)**



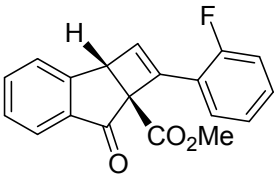

Yield: 54%. Yellow oil. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 7.1 Hz, 3H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.3 Hz, 1H), 7.31 (dt, *J* = 25.8, 7.5 Hz, 3H), 6.89 (s, 1H), 4.57 (s, 1H), 3.77 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 168.9, 152.0, 145.6, 136.6, 135.2, 134.9, 131.3, 128.9, 128.4, 128.4, 126.0, 125.6, 66.7, 52.6, 50.2. IR (KBr, $cm^{-1}$) 3061, 2954, 2848, 1752, 1702, 1603, 1577, 1493, 1467, 1433, 1372, 1288, 1242, 1192, 1153, 1096, 1072, 1000, 951, 897, 852, 810, 779, 755, 694, 666, 613, 523, 479, 429; HRMS (DART Postive) Calcd for $C_{19}H_{15}O_3$ $(M+H)^+$ 296.1016, found 296.1013.

**Methyl 1-(3-fluorophenyl)-7-oxo-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6n)**



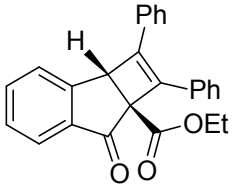

Yield: 50%. Pale yellow solid, mp 75-76 °C. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.42 (dd, *J* = 13.6, 7.3 Hz, 2H), 7.37 – 7.21 (m, 2H), 6.97 (t, *J* = 8.2 Hz, 1H), 6.92 (s, 1H), 4.58 (s, 1H), 3.78 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.82 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.7, 168.7, 164.0, 161.6, 151.7, 144.7, 136.5, 136.4, 135.4, 133.3, 130.1, 130.0, 128.5, 126.1, 125.6, 122.0, 122.0, 115.9, 115.7, 113.0, 112.7, 66.7, 52.7, 50.3. IR (KBr, cm$^{-1}$) 3072, 2956, 2927, 2852, 1746, 1706, 1605, 1581, 1485, 1434, 1374, 1288, 1271, 1246, 1194, 1150, 1098, 1073, 991, 953, 866, 843, 810, 787, 757, 689, 663, 623, 522; HRMS (DART Postive) Calcd for $C_{19}H_{14}FO_3$ $(M+H)^+$ 309.0921, found 309.0918.

**Methyl 1-(2-fluorophenyl)-7-oxo-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6o)**



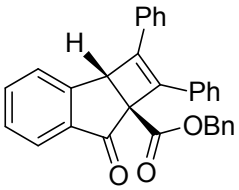

Yield: 54%. Yellow oil. $R_f$ 0.25 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (m, 2H), 7.64 (t, *J* = 7.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.21 (m, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 7.00 (dd, *J* = 11.6, 7.0 Hz, 1H), 4.63 (s, 1H), 3.79 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -112.47 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 168.9, 162.8, 160.3, 151.9, 140.9, 140.8, 140.1, 136.5, 135.3, 130.2, 130.1, 129.4, 128.5, 126.1, 125.6, 124.2, 124.1, 119.5, 115.5, 115.3, 67.0, 52.6, 51.5. IR (KBr, cm$^{-1}$) 2961, 2925, 2853, 1740, 1705, 1602, 1492, 1451, 1432, 1380, 1285, 1260, 1242, 1216, 1190, 1153, 1124, 1096, 1021, 954, 914, 858, 801, 753, 691, 656, 612, 528, 467; HRMS (DART Postive) Calcd for $C_{19}H_{14}FO_3$ $(M+H)^+$ 309.0921, found 309.0918.

**Ethyl 7-oxo-1,2-diphenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6p)**



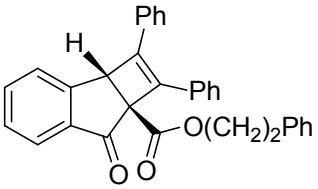

Yield: 65%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.4 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 9.4 Hz, 2H), 7.44 – 7.27 (m, 7H), 4.88 (s, 1H), 4.20 (dd, *J* = 13.7, 6.7 Hz, 2H), 1.17 (t, *J* = 7.0 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.3, 168.5, 151.2, 146.2, 137.6, 136.6, 134.9, 133.3, 132.8, 129.0, 128.7, 128.5, 128.4, 127.5, 126.7, 126.2, 126.1, 64.4, 61.5, 50.9, 14.1. IR (KBr, cm$^{-1}$) 3084, 3058, 3026, 2983, 2920, 2850, 1749, 1694, 1603, 1579, 1498, 1467, 1443, 1392, 1368, 1324, 1278, 1239, 1208, 1185, 1148, 1117, 1096, 1073, 1049, 1010, 959, 904, 858, 817, 785, 760, 733, 695, 644, 560, 537, 519, 496, 465; HRMS (DART Postive) Calcd for $C_{26}H_{21}O_3$ $(M+H)^+$ 381.1485, found 381.1481.

**Benzyl 7-oxo-1,2-diphenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6q)**



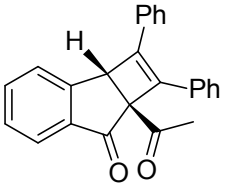

Yield: 74%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 7.1 Hz, 2H), 7.55 (d, *J* = 7.3 Hz, 2H), 7.48 (dd, *J* = 15.5, 7.2 Hz, 2H), 7.33 (ddd, *J* = 33.4, 22.9, 16.1 Hz, 10H), 7.14 (s, 2H), 5.19 (dd, *J* = 27.9, 12.6 Hz, 2H), 4.88 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.1, 168.4, 151.1, 146.3, 137.5, 136.5, 135.6, 134.9, 133.2, 132.9, 129.0, 128.7, 128.5, 128.4, 128.4, 128.0, 127.7, 127.5, 126.7, 126.2, 66.9, 64.4, 50.8. IR (KBr, $cm^{-1}$) 3062, 3030, 2921, 2851, 1743, 1704, 1602, 1497, 1465, 1444, 1374, 1319, 1279, 1236, 1207, 1184, 1152, 1096, 1072, 1048, 1027, 964, 913, 787, 758, 735, 695, 559, 487; HRMS (DART Postive) Calcd for $C_{31}H_{23}O_3$ $(M+H)^+$ 441.1642, found 441.1635.

**Phenethyl 7-oxo-1,2-diphenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6r)**



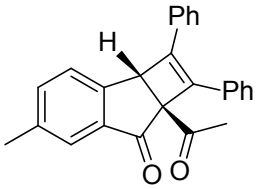

Yield: 77%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.4 Hz, 2H), 7.51 (t, *J* = 8.5 Hz, 3H), 7.47 – 7.24 (m, 9H), 7.17 (s, 2H), 7.05 (s, 2H), 4.70 (s, 1H), 4.39 – 4.32 (m, 2H), 2.84 (t, *J* = 6.7 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.2, 168.5, 151.2, 146.2, 137.6, 136.4, 134.9, 133.3, 132.8, 129.0, 129.0, 128.7, 128.7, 128.5, 128.4, 127.5, 126.7, 126.5, 126.2, 126.1, 65.8, 64.3, 51.0, 35.0. IR (KBr, $cm^{-1}$) 3085, 3061, 3027, 2958, 2920, 2850, 1750, 1695, 1603, 1579, 1497, 1466, 1444, 1375, 1321, 1282, 1235, 1207, 1184, 1150, 1095, 1074, 1049, 1028, 992, 965, 917, 901, 845, 813, 790, 764, 732, 697, 644, 600, 572, 558, 496, 419; MS (DART Postive) Calcd for $C_{32}H_{25}O_3$ $(M+H)^+$ 457.1, found 457.2.

**7a-acetyl-1,2-diphenyl-2aH-cyclobuta[a]inden-7(7aH)-one (6s)**



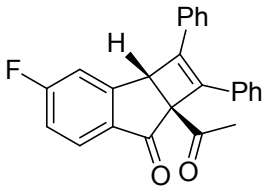

Yield: 32%. Yellow oil. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.51 – 7.39 (m, 4H), 7.37 – 7.19 (m, 7H), 4.81 (s, 1H), 2.21 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.8, 198.6, 150.9, 146.3, 138.0, 137.9, 135.0, 133.1, 133.1, 129.0, 128.8, 128.7, 128.6, 127.5, 126.6, 126.4, 125.9, 72.3, 49.5, 29.0. IR (KBr, $cm^{-1}$) 3059, 3026, 2960, 2926, 2852, 1888, 1743, 1721, 1689, 1602, 1496, 1466, 1444, 1419, 1357, 1318, 1270, 1204, 1147, 1095, 1046, 1025, 958, 918, 874, 831, 800, 773, 764, 738, 692, 611, 555, 513, 483; HRMS (DART Postive) Calcd for $C_{25}H_{19}O_2$ $(M+H)^+$ 351.1380, found 351.1378.

**7a-acetyl-5-methyl-1,2-diphenyl-2aH-cyclobuta[a]inden-7(7aH)-one (6t)**



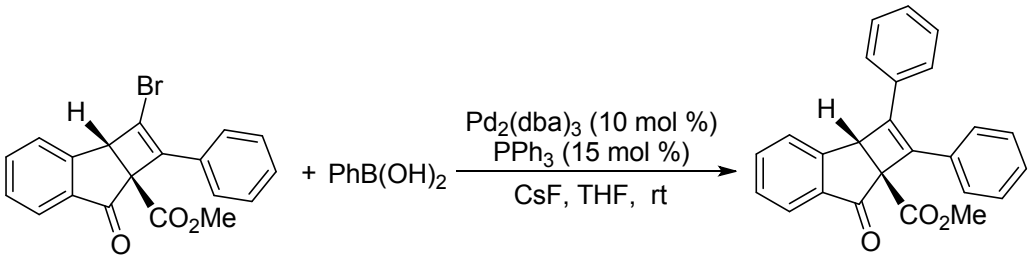

Yield: 34%. Yellow solid, mp 157 °C. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.5 Hz, 2H), 7.66 (s, 1H), 7.54 (d, *J* = 7.5 Hz, 2H), 7.46 – 7.26 (m, 8H), 4.83 (s, 1H), 2.37 (s, 3H), 2.27 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.9, 198.8, 148.3, 146.4, 138.7, 138.0, 137.9, 136.2, 133.2, 133.2, 129.0, 128.8, 128.7, 127.5, 126.6, 126.1, 125.9, 72.7, 49.3, 28.9, 21.2. IR (KBr, $cm^{-1}$) 3057, 2959, 2924, 2852, 1722, 1689, 1613, 1576, 1491, 1445, 1419, 1357, 1208, 1145, 1114, 1081, 1030, 919, 846, 824, 796, 765, 733, 694, 586, 552, 513; HRMS (DART Postive) Calcd for $C_{26}H_{21}O_2$ $(M+H)^+$ 365.1536, found 365.1532.

**7a-acetyl-4-fluoro-1,2-diphenyl-2aH-cyclobuta[a]inden-7(7aH)-one (6u)**




Yield: 33%. Yellow solid, mp 118-121 °C. $R_f$ 0.2 (EtOAc/petroleum ether = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.83 (m, 1H), 7.72 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 13.8, 7.4 Hz, 6H), 7.14 (d, *J* = 8.1 Hz, 1H), 7.09 (t, *J* = 8.6 Hz, 1H), 4.89 (s, 1H), 2.28 (s, 3H). $^{19}$F NMR (376 MHz, $CDCl_3$) δ -100.98 (s). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 202.5, 196.9, 168.3, 165.8, 153.7, 153.6, 145.7, 138.3, 134.2, 132.9, 132.8, 129.3, 129.0, 128.9, 128.8, 128.4, 128.3, 127.5, 126.5, 116.9, 116.6, 113.5, 113.2, 72.6, 48.8, 29.1. IR (KBr, $cm^{-1}$) 3058, 2925, 2852, 1733, 1692, 1615, 1585, 1488, 1474, 1442, 1363, 1321, 1286, 1249, 1208, 1154, 1090, 1040, 922, 877, 841, 796, 762, 730, 695, 646, 606, 551, 522, 482; HRMS (DART Postive) Calcd for $C_{25}H_{18}FO_2$ $(M+H)^+$ 369.1285, found 369.1281.

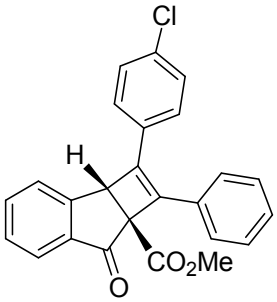
## General procedure of Suzuki coupling between 6j and phenylboronic acid [5]




**6j** **6a**

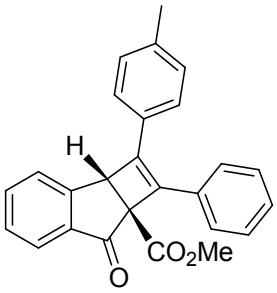
To a suspension of $Pd_2(dba)_3$ (10 mol %) and $PPh_3$ (15 mol %) in deoxygenated THF (1 ml) under $N_2$ atmosphere, was added **6j** (0.15 mmol), phenylboronic acid (2.0 eq, 0.3 mmol) and CsF (5.0 eq, 0.75 mmol). The reaction mixture was stirred at room temperature for overnight. The crude product was purified by column chromatography to obtain **6a** in 87% yield.

**Methyl 2-(4-chlorophenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6d)**



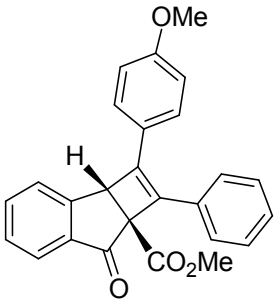

Yield: 74%. Yellow oil. $R_f$ 0.2 (EtOAc/hexanes = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.51 – 7.43 (m, 1H), 7.42 – 7.31 (m, 4H), 7.29 – 7.20 (m, 5H), 4.77 (s, 1H), 3.66 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.0, 169.0, 150.9, 145.1, 137.4, 137.1, 135.1, 134.8, 132.4, 131.7, 129.0, 129.0, 128.7, 128.6, 128.0, 127.4, 126.3, 126.1, 100.0, 64.3, 52.7, 51.0.

**Methyl 7-oxo-1-phenyl-2-(p-tolyl)-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6b')**



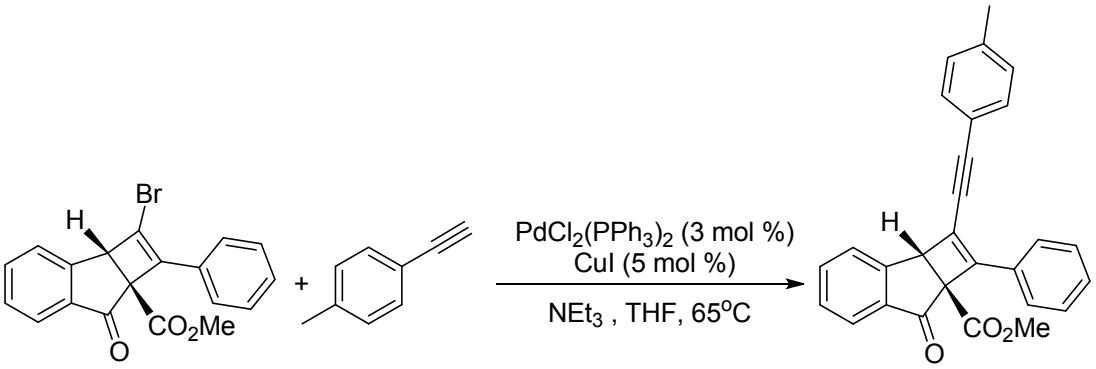

Yield: 85%. Yellow oil. $R_f$ 0.2 (EtOAc/hexanes = 1/15). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.48 – 7.43 (m, 3H), 7.38 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.28 (d, *J* = 7.0 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 4.85 (s, 1H), 3.73 (s, 3H), 2.35 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.3, 169.2, 151.2, 146.5, 139.2, 137.6, 135.4, 134.9, 132.9, 130.0, 129.4, 128.5, 128.5, 128.4, 127.4, 126.7, 126.2, 126.1, 64.2, 52.5, 51.0, 21.5.

**Methyl 2-(4-methoxyphenyl)-7-oxo-1-phenyl-7,7a-dihydro-2aH-cyclobuta[a]indene-7a-carboxylate (6c')**




Yield: 94%. Yellow oil. $R_f$ 0.2 (EtOAc/hexanes = 1/8). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.6 Hz, 1H), 7.69 (d, *J* = 7.5 Hz, 2H), 7.41 (dd, *J* = 15.5, 7.8 Hz, 4H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 10.5 Hz, 1H), 6.80 (d, *J* = 7.8 Hz, 2H), 4.76 (s, 1H), 3.73 (s, 3H), 3.65 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 197.4, 169.3, 160.2, 151.2, 146.2, 137.6, 134.9, 134.1, 133.0, 128.5, 128.4, 128.2, 127.3, 126.2, 116.1, 114.8, 114.1, 64.2, 55.3, 52.5, 51.0.

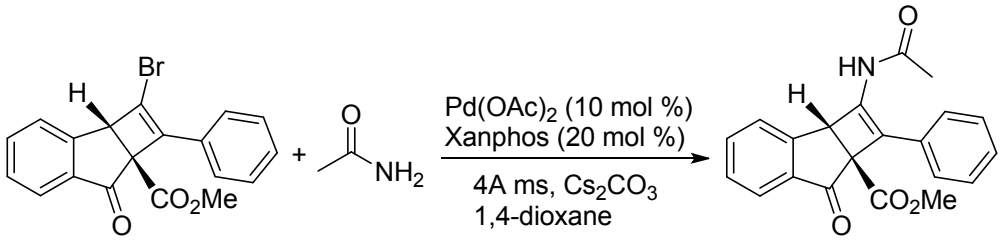
## Sonogashira coupling between 6j and 1-ethynyl-4-methylbenzene [5]




**6j** **7**

A suspension of $PdCl_2(PPh_3)_2$ (3 mol %), CuI (5 mol %) in dry THF (1ml) was prepared in a Schlenk tube with a magnetic bar, and then **6j** (0.15 mmol), 1-ethynyl-4-methylbenzene (1.2 eq, 0.18 mmol) and $NEt_3$ (0.2 ml) were added. The reaction mixture was stirred at 65°C for overnight. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/15) to give **7** in 90% yield. Black oil. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.4 Hz, 2H), 7.75 (d, *J* = 7.6 Hz, 1H), 7.56 (s, 2H), 7.39 – 7.26 (m, 5H), 7.25 – 7.19 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 2H), 4.58 (s, 1H), 3.71 (s, 3H), 2.30 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.0, 168.8, 151.1, 145.5, 139.6, 136.9, 135.3, 132.0, 131.6, 129.3, 129.3, 128.7, 128.4, 127.1, 127.0, 126.1, 125.9, 119.3, 101.4, 83.0, 65.0, 53.0, 52.7, 21.6. IR (KBr, $cm^{-1}$) 3028, 2958, 2923, 2852, 2183, 1743, 1709, 1603, 1510, 1465, 1434, 1375, 1321, 1281, 1243, 1184, 1150, 1097, 1062, 1022, 973, 916, 817, 768, 723, 691, 648, 606, 579, 529, 484, 425; HRMS (DART Postive) Calcd for $C_{28}H_{21}O_3$ $(M+H)^+$ 405.1485, found 405.1480.

## Buchwald-Hartwig amination reaction of 6j with acetamide




**6j** **8**

In a Schlenk tube with a magnetic bar, 4Å ms (20 mg) and $Cs_2CO_3$ (4.0 eq, 0.6 mmol) was added. Under vacuum, the mixture was heated to 300°C using heating gun for 20 min to remove water. After the schlenk tube cooled down, $Pd(OAc)_2$ (10 mol %), Xanphos (20 mol %) and acetamide (4.0 eq, 0.6mmol) were added, then another 10 min heating was conducted under 60°C, after cooling down, **6j** (0.15 mmol) in 1,4-dioxane (1ml) was added at last, and then the reaction mixture was stirred at 110°C for overnight. The crude product was purified by column chromatography (EtOAc/petroleum ether = 1/3) to give white solid **8** in 51% yield. Mp 234-235 °C. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 9.7 Hz, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.24 (s, 1H), 3.76 (s, 3H), 2.16 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ196.8, 169.6, 167.6, 150.3, 138.7, 137.1 , 135.2, 131.7, 128.8, 128.5, 127.7, 127.5, 126.6, 125.8, 116.8, 63.9, 54.1 , 52.6, 24.0. IR (KBr, $cm^{-1}$) 2965, 2923, 2850, 1764, 1700, 1655, 1513, 1474, 1380, 1247, 1155, 1097, 1053, 913, 805, 738, 459; HRMS (DART Postive) Calcd for $C_{21}H_{18}NO_4$ $(M+H)^+$ 348.1230, found 348.1225.

## References

[1] Zhou, M.-B.; Wei, W.-T.; Xie, Y.-X.; Lei, Y.; Li J.-H. *J. Org. Chem.* **2010**, *75*, 5635.

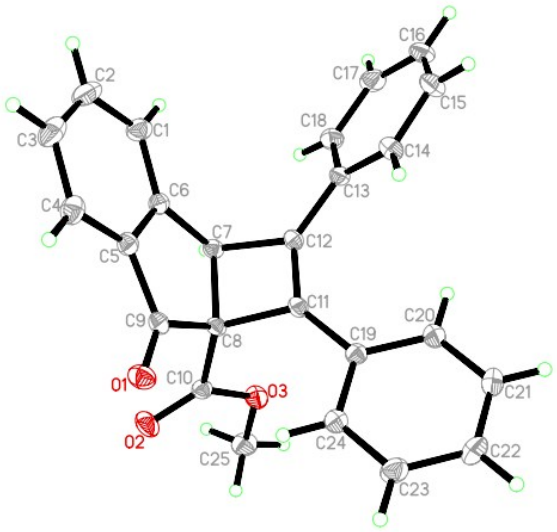
[2] Liang, R.; Ma, T.; Zhu, S. *Org. Lett.* **2014**, *16*, 4412.

[3] Yoshida, K.; Shida, H.; Takahashi, H.; Yanagisawa, A. *Chem. Eur. J.* **2011**, *17*, 344.

[4] Qiu, Y.-F.; Yang, F.; Qiu, Z.-H.; Zhong, M.-J.; Wang, L.-J.; Ye, Y.-Y.; Song, B.; Liang, Y.-M. *J. Org.Chem.* **2013**, *78*, 12018.

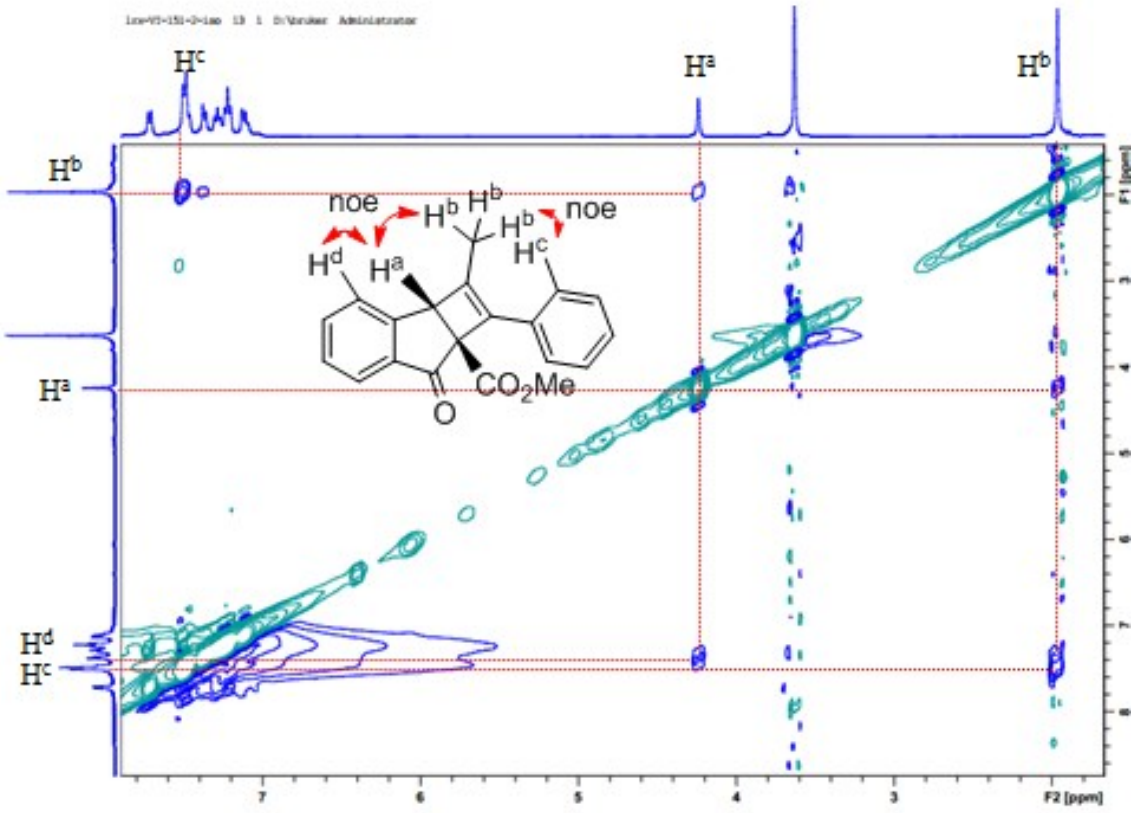
[5] Villeneuve, K.; Riddell, N.; Jordan, R. W.; Tsui, G. C.; Tam, W. *Org. Lett.* **2004**, *6*, 4543.

## Crystal data and structure refinement for 6a

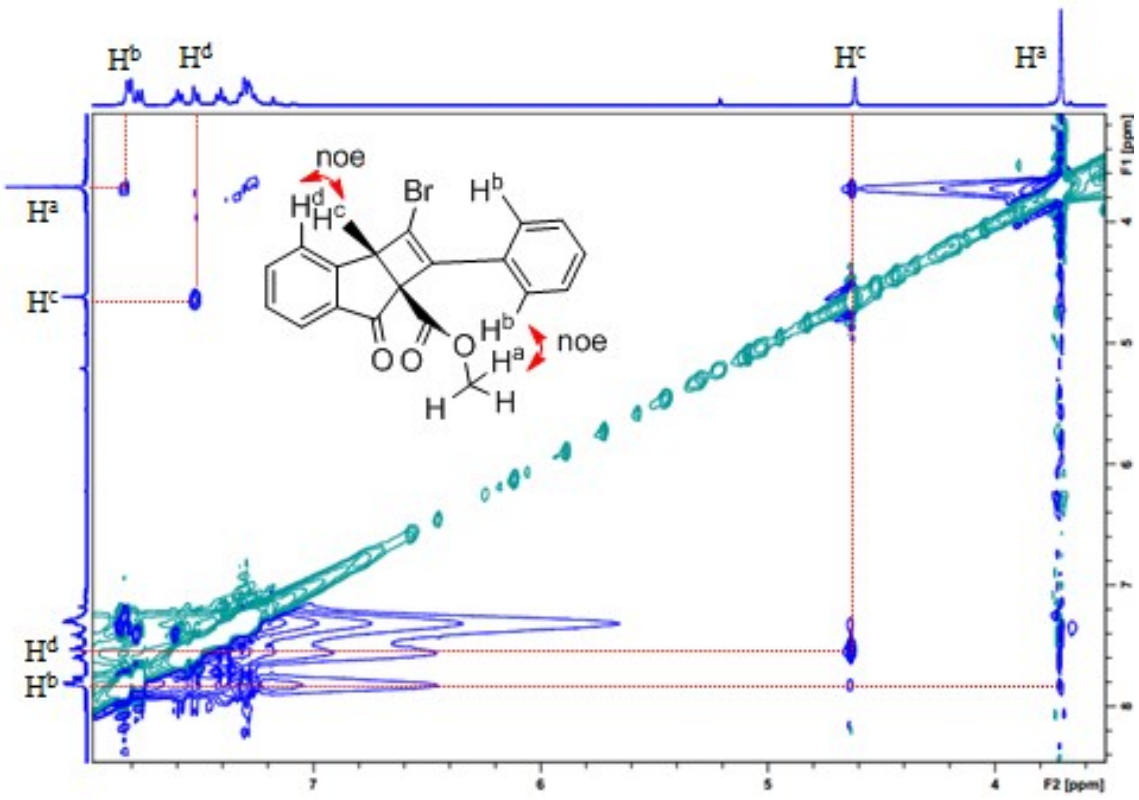



| | |
|---|---|
| CCDC number | 1031051 |
| Identification code | exp_1136 |
| Empirical formula | $C_{25}\ H_{18}\ O_3$ |
| Formula weight | 366.39 |
| Temperature | 293(2) K |
| Wavelength | 1.54178 Å |
| Crystal system, space group | Monoclinic, P 21/c |
| Unit cell dimensions | a = 11.12900(10) Å alpha = 90 deg.<br>b = 10.01500(10) Å beta = 94.2110(10) deg.<br>c = 16.4841(2) Å gamma = 90 deg. |
| Volume | 1832.31(3) $Å^3$ |
| Z, Calculated density | 4, 1.328 $Mg/m^3$ |
| Absorption coefficient | 0.692 $mm^{-1}$ |
| F(000) | 768 |
| Crystal size | 0.2 x 0.1 x 0.2 mm |
| Theta range for data collection | 3.98 to 73.61 deg. |
| Limiting indices | -13⩽h⩽13, -12⩽k⩽12, -20⩽l⩽20 |
| Reflections collected / unique | 20325 / 3686 [R(int) = 0.0269] |
| Completeness to theta = 73.61 | 99.40% |
| Refinement method | Full-matrix least-squares on $F^2$ |
| Data / restraints / parameters | 3686 / 0 / 254 |
| Goodness-of-fit on F^2 | 1.06 |
| Final R indices [I>2sigma(I)] | R1 = 0.0366, wR2 = 0.0960 |
| R indices (all data) | R1 = 0.0400, wR2 = 0.0995 |
| Largest diff. peak and hole | 0.246 and -0.221 e. $Å^{-3}$ |

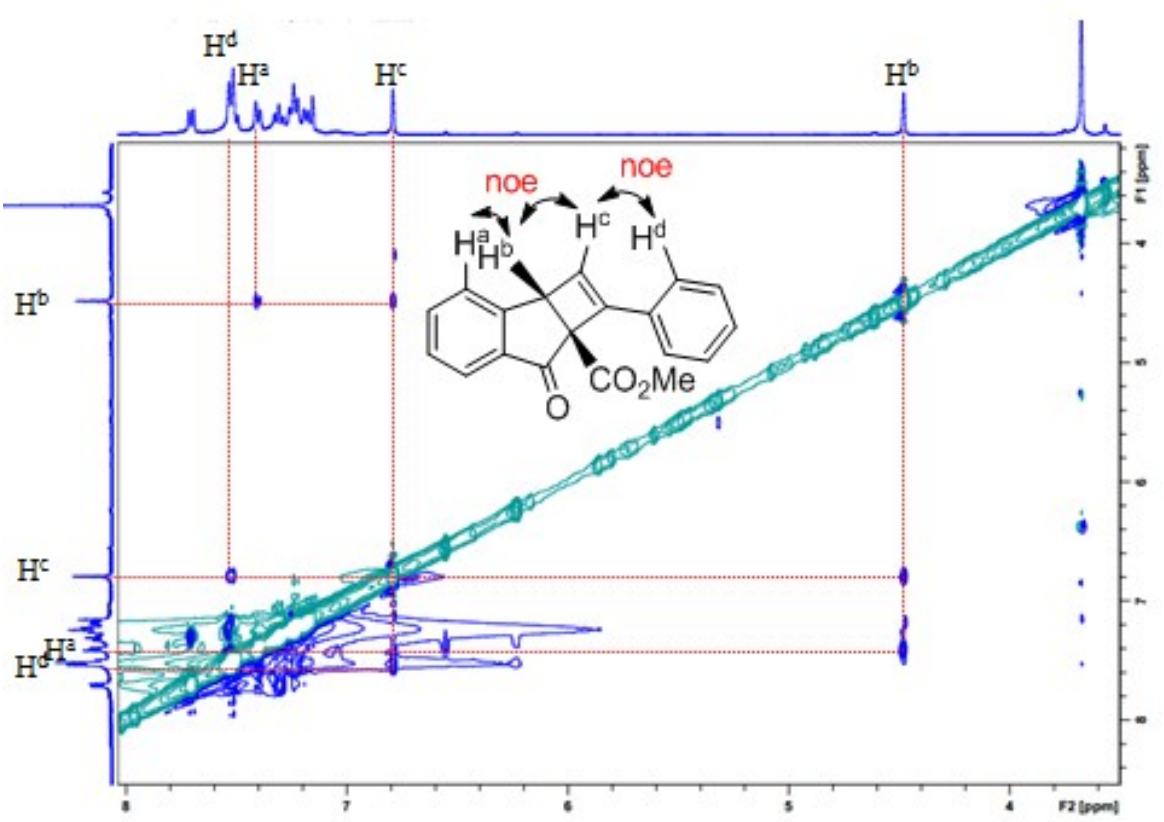
**NOE spectrum of 6h**




**NOE spectrum of 6j**

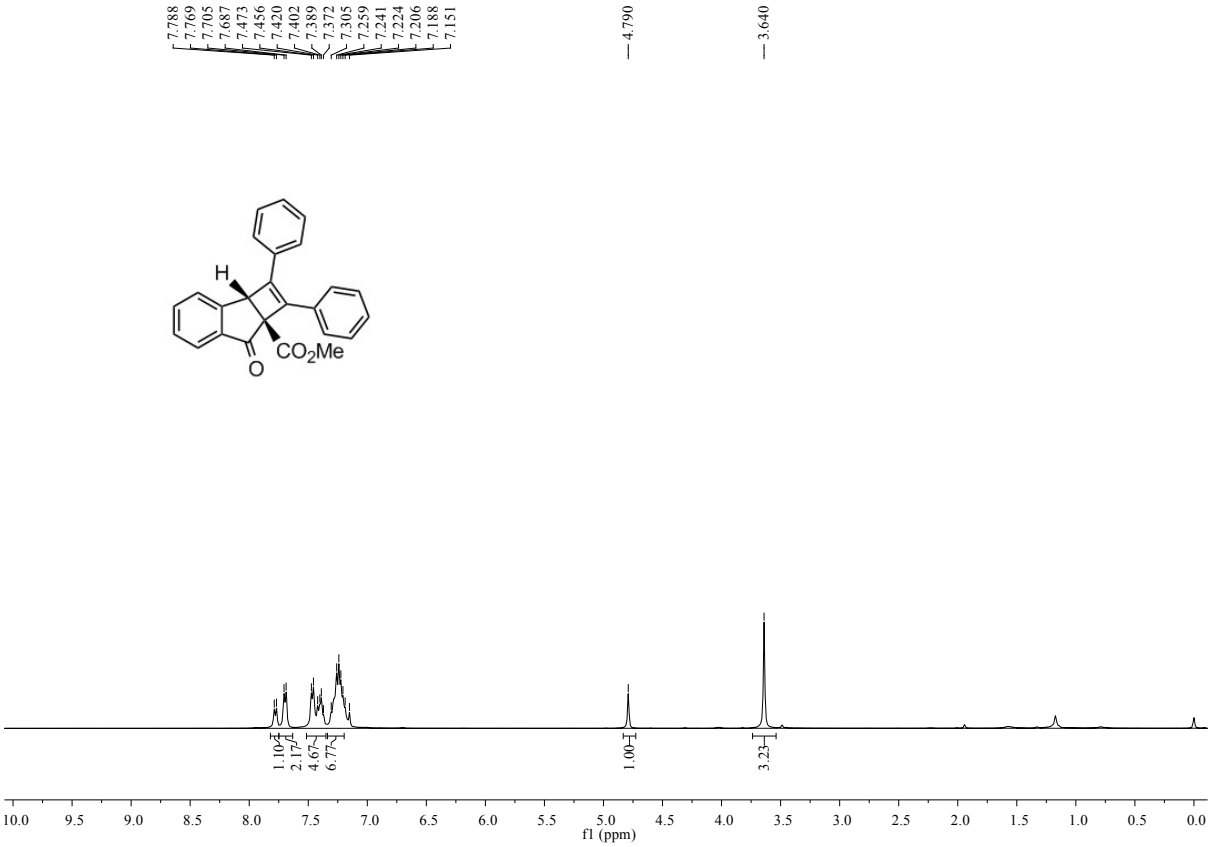


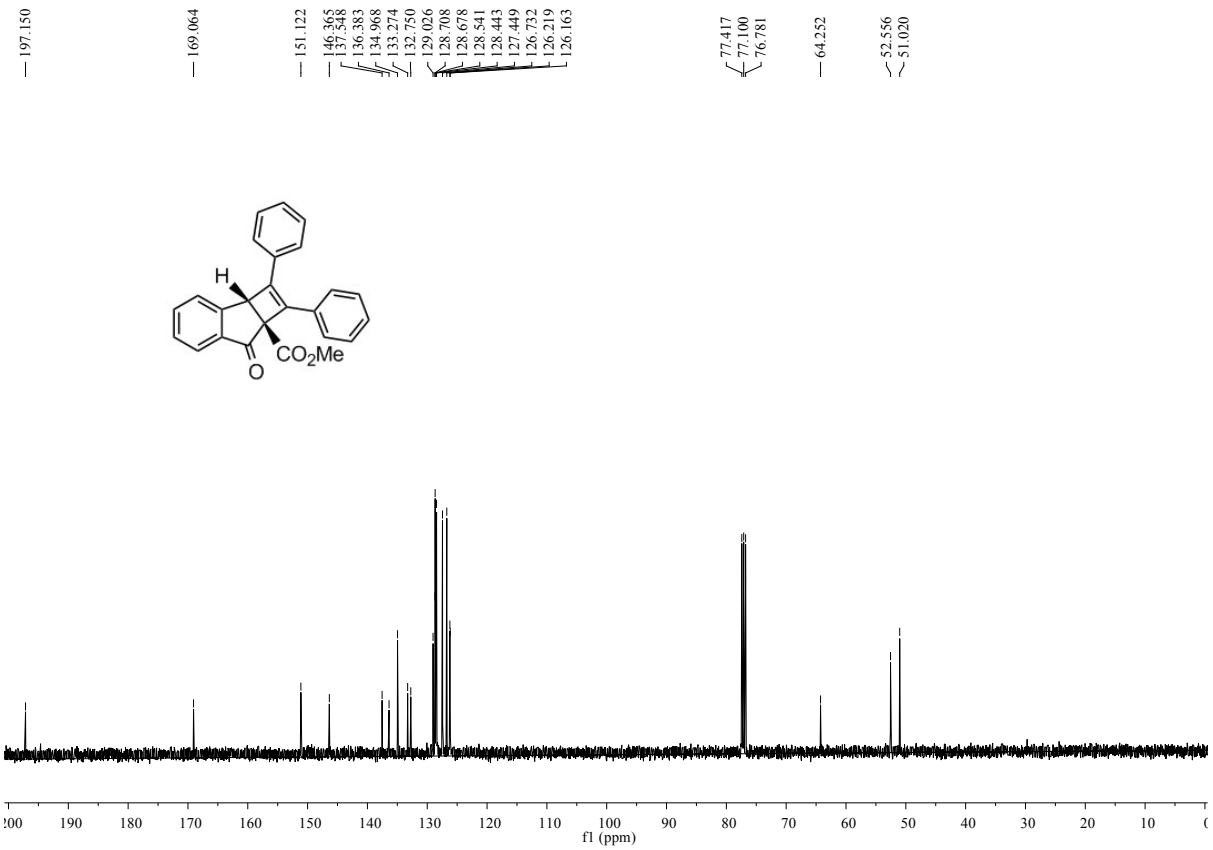

**NOE spectrum of 6m**



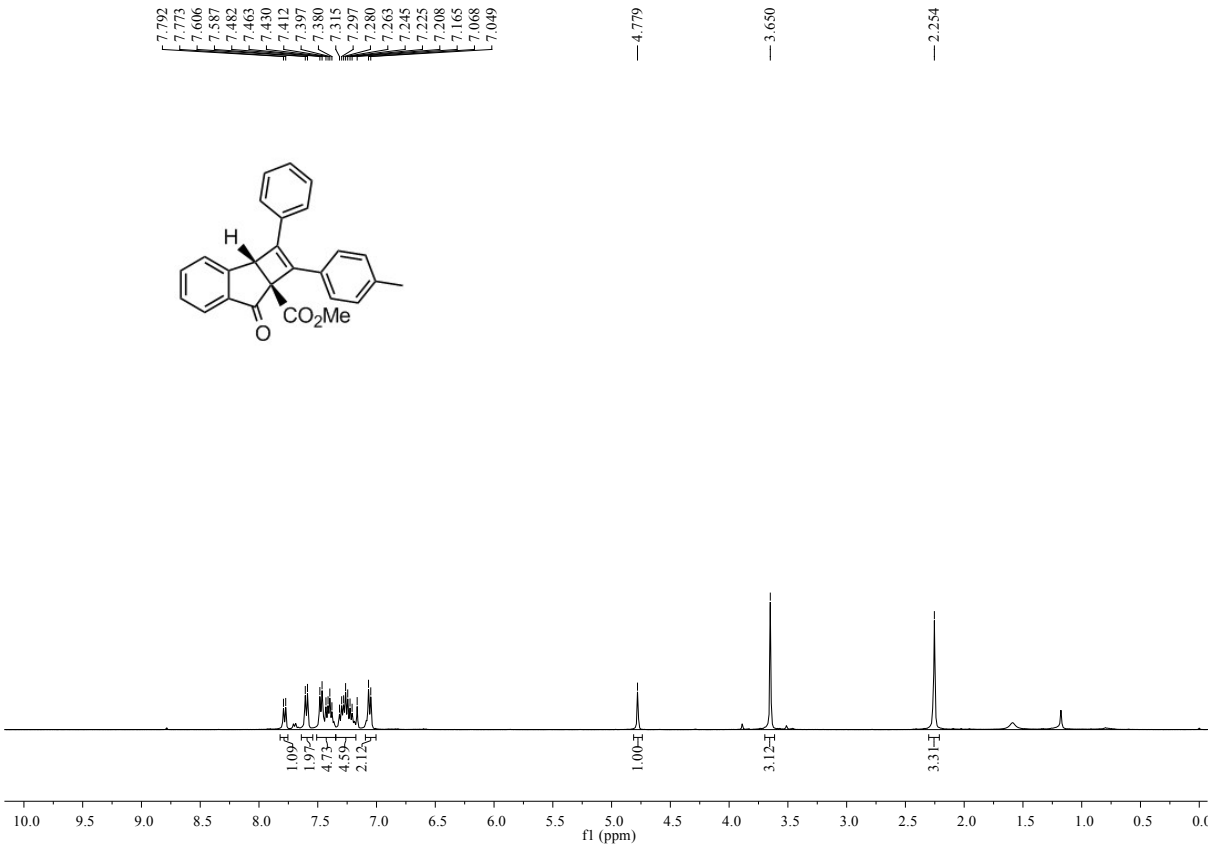

**NMR spectrum**

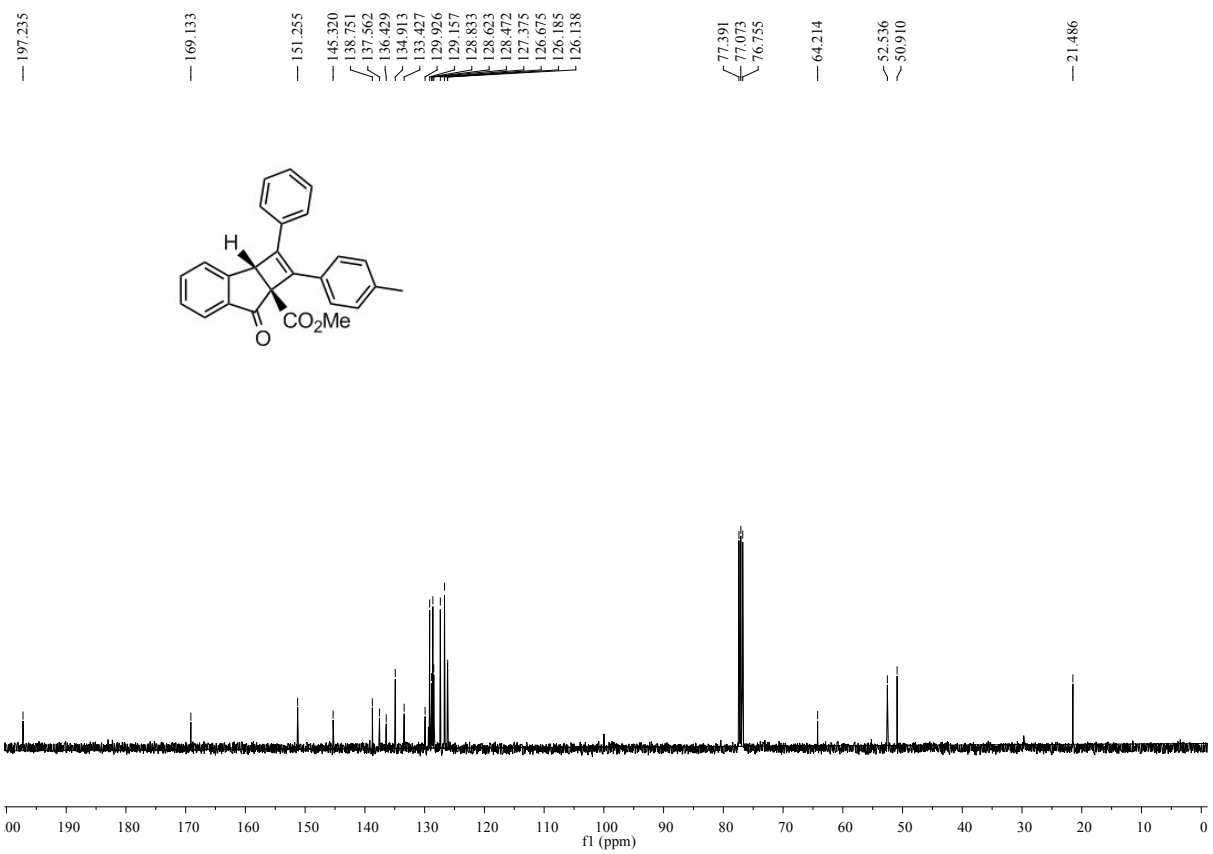
**6a**


7.788
7.769
7.705
7.687
7.473
7.456
7.420
7.402
7.389
7.372
7.305
7.259
7.241
7.224
7.206
7.188
7.151
4.790
3.640
H
CO2Me
O
1.10
2.17
4.67
6.77
1.00
3.23
f1 (ppm)


197.150
169.064
151.122
146.365
137.548
136.383
134.968
133.274
132.750
129.026
128.708
128.678
128.541
128.443
127.449
126.732
126.219
126.163
77.417
77.100
76.781
64.252
52.556
51.020
H
CO2Me
O
f1 (ppm)

**6b**


7.792
7.773
7.606
7.587
7.482
7.463
7.430
7.412
7.397
7.380
7.315
7.297
7.280
7.263
7.245
7.225
7.208
7.165
7.068
7.049
4.779
3.650
2.254
H
CO2Me
O
1.09
1.97
4.73
4.59
2.12
1.00
3.12
3.31
f1 (ppm)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169.133
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145.320
138.751
137.562
136.429
134.913
133.427
129.926
129.157
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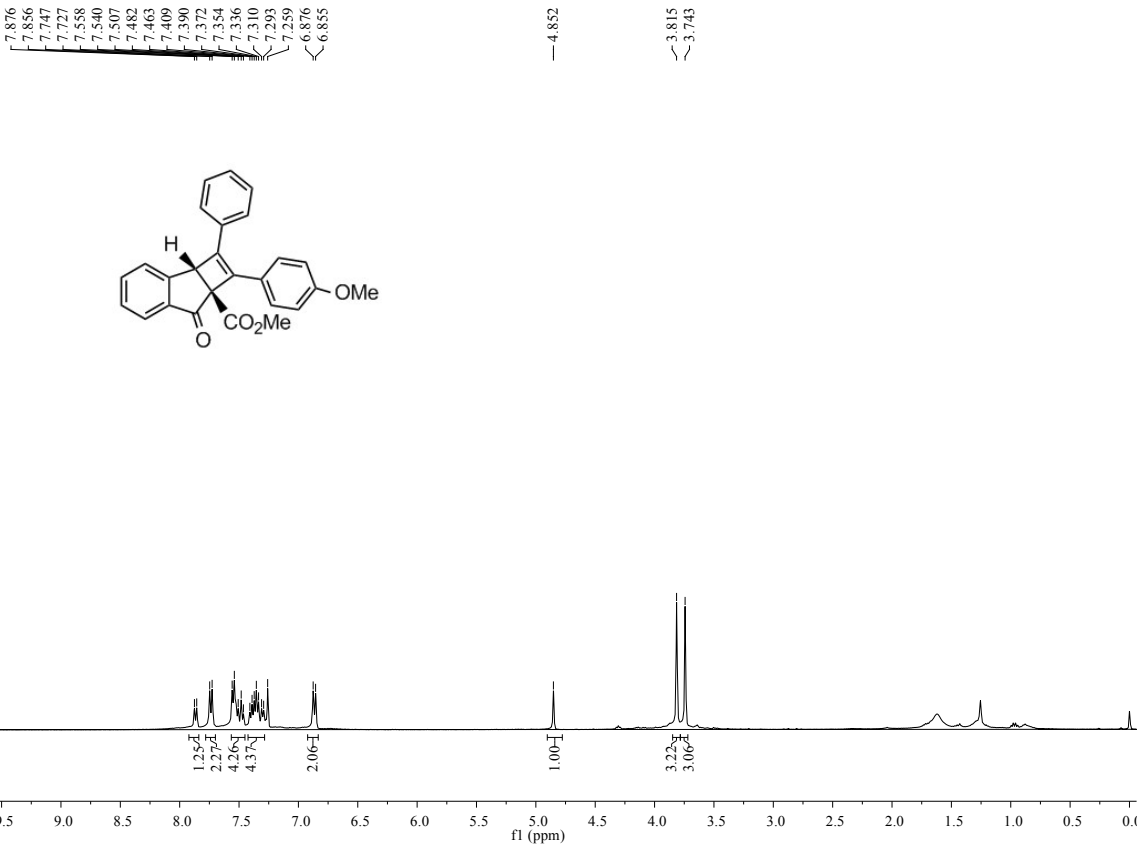
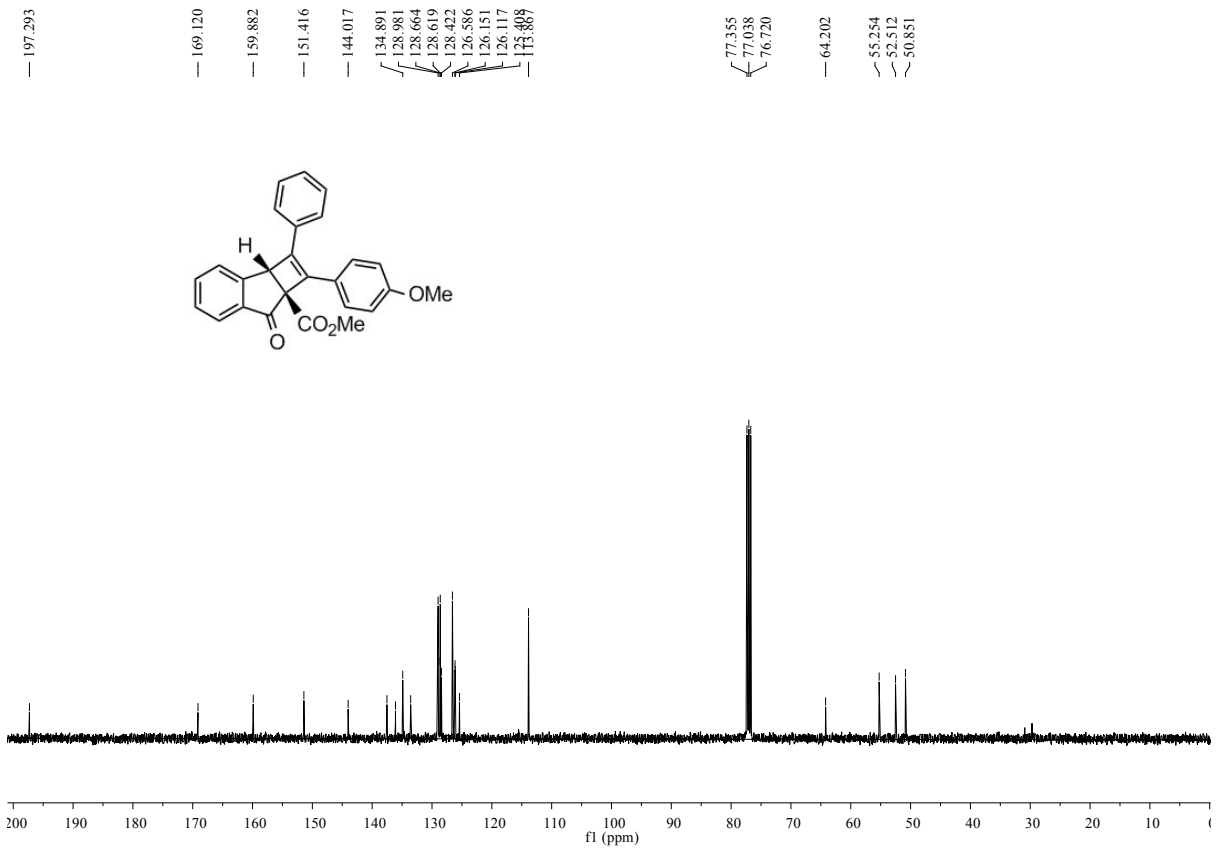
128.623
128.472
127.375
126.675
126.185
126.138
77.391
77.073
76.755
64.214
52.536
50.910
21.486
H
CO2Me
O
f1 (ppm)

**6c**


7.876
7.856
7.747
7.727
7.558
7.540
7.507
7.482
7.463
7.409
7.390
7.372
7.354
7.336
7.310
7.293
7.259
6.876
6.855
4.852
3.815
3.743
H
OMe
CO2Me
O
1.25
2.27
4.26
4.37
2.06
1.00
3.22
3.06
f1 (ppm)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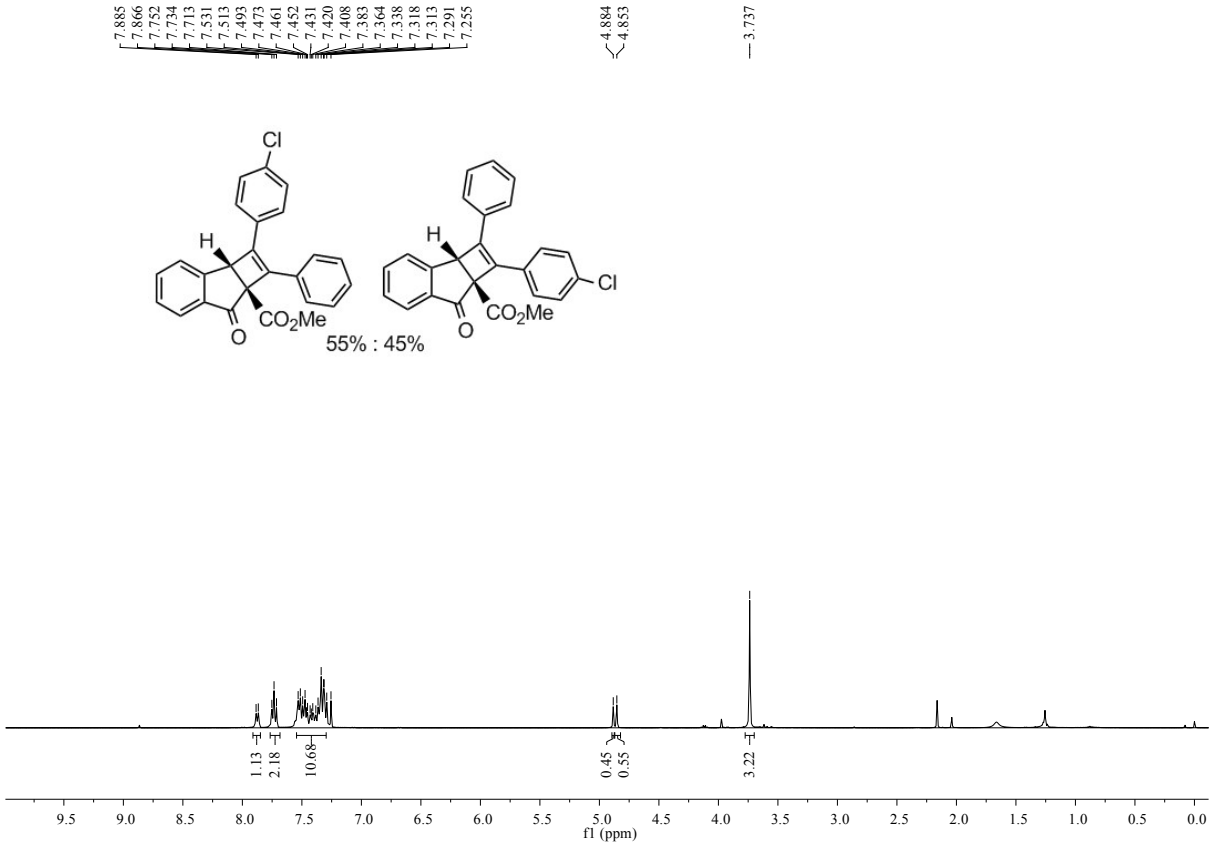
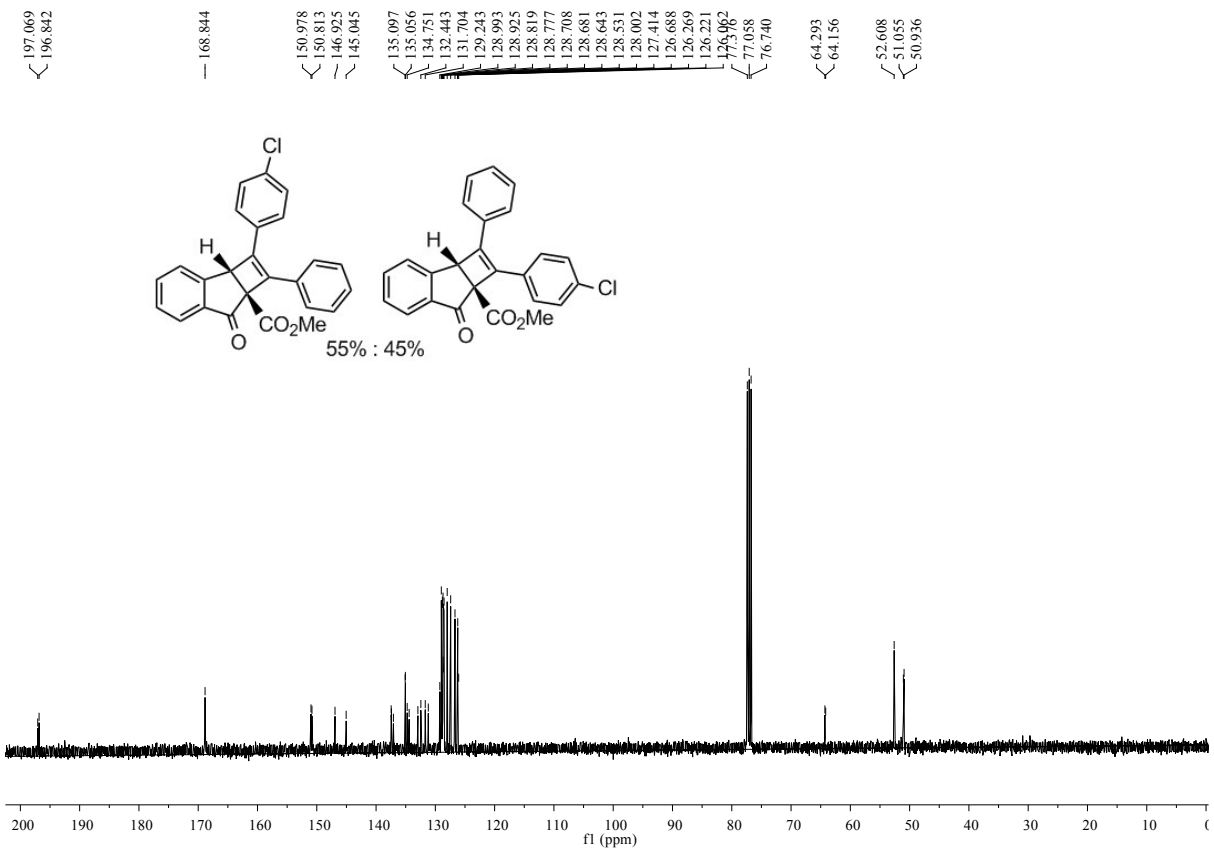
169.120
159.882
151.416
144.017
134.891
128.981
128.664
128.619
128.422
126.586
126.151
126.117
77.355
77.038
76.720
64.202
55.254
52.512
50.851
H
OMe
CO2Me
O
f1 (ppm)

**6d/6d'**


7.885
7.866
7.752
7.734
7.713
7.531
7.513
7.493
7.473
7.461
7.452
7.431
7.420
7.408
7.383
7.364
7.338
7.318
7.313
7.291
7.255
4.884
4.853
3.737
Cl
H
CO2Me
O
55% : 45%
1.13
2.18
10.68
0.45
0.55
3.22
f1 (ppm)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150.813
146.925
145.045
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132.443
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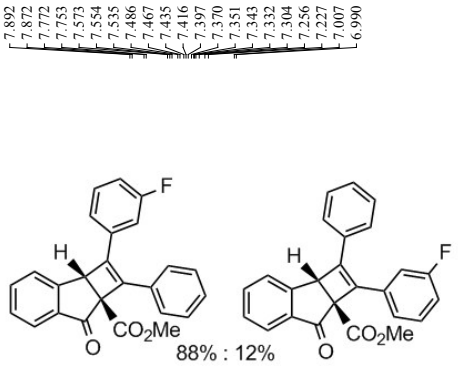
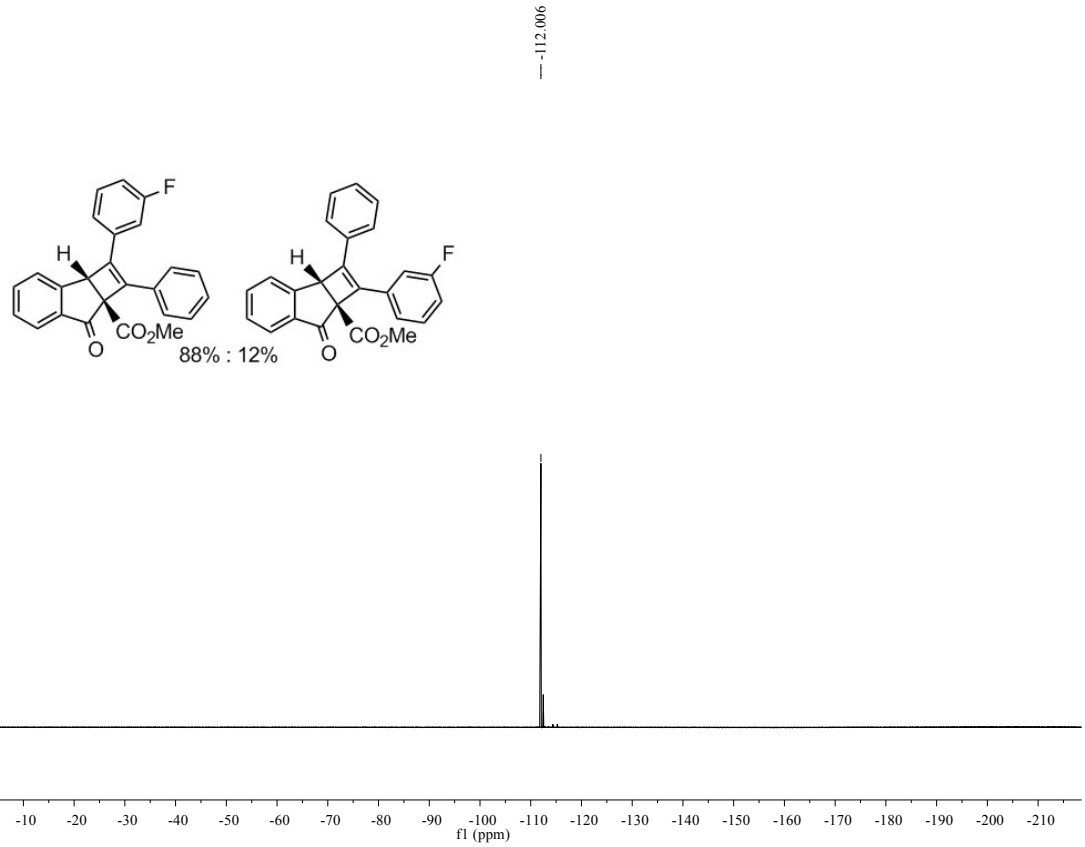
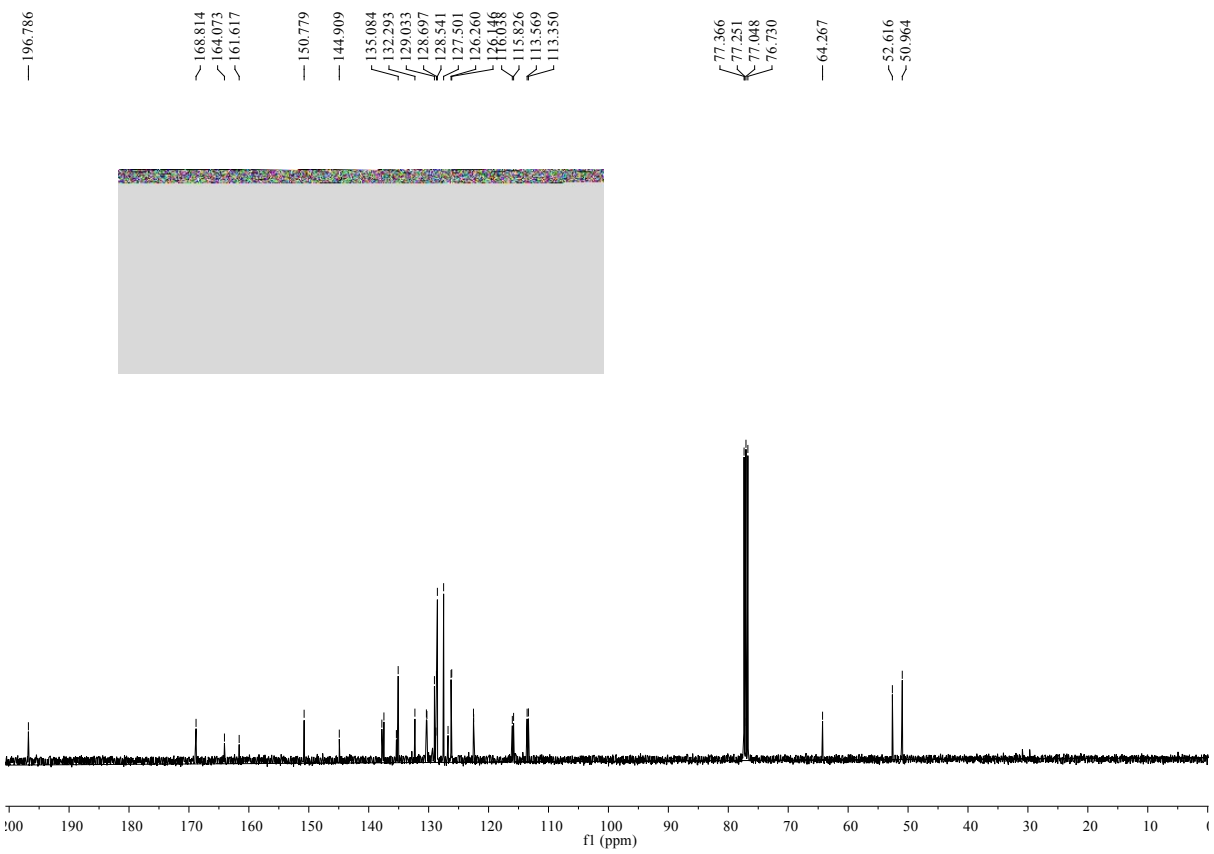
129.243
128.993
128.925
128.819
128.777
128.708
128.681
128.643
128.531
128.002
127.414
126.688
126.269
126.221
126.062
77.376
77.058
76.740
64.293
64.156
52.608
51.055
50.936
Cl
H
CO2Me
O
55% : 45%
f1 (ppm)

**6e/6e'**


7.892
7.872
7.772
7.753
7.573
7.554
7.535
7.486
7.467
7.435
7.416
7.397
7.370
7.351
7.343
7.332
7.304
7.256
7.227
7.007
6.990
4.856
3.740
F
H
CO2Me
O
88% : 12%
1.13
2.00
1.53
1.28
1.23
5.25
1.01
1.19
0.97
3.22
f1 (ppm)


-112.006
F
H
CO2Me
O
88% : 12%
f1 (ppm)

**6e/6e'**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168.814
164.073
161.617
150.779
144.909
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132.293
129.033
128.697
128.541
127.501
126.260
116.038
115.826
113.569
113.350
77.366
77.251
77.048
76.730
64.267
52.616
50.964
f1 (ppm)

**6f**


7.879
7.860
7.732
7.714
7.546
7.527
7.509
7.489
7.469
7.458
7.440
7.412
7.393
7.375
7.347
7.331
7.312
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7.255
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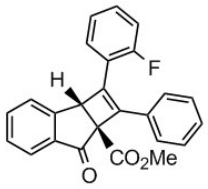
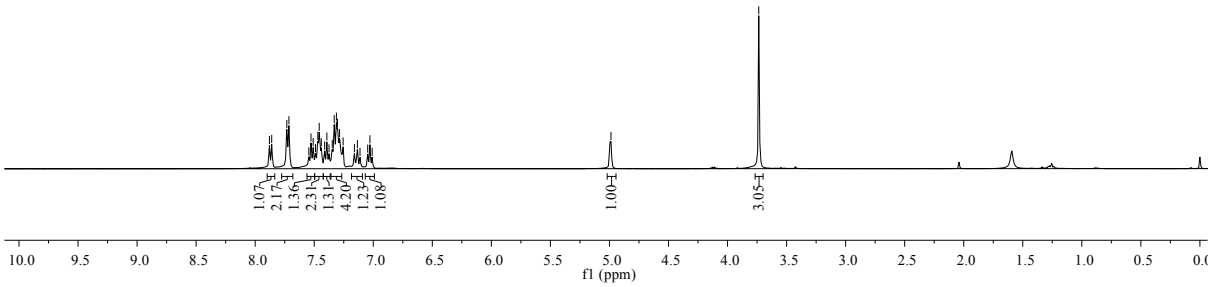
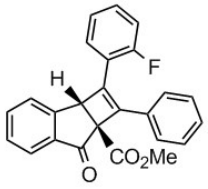
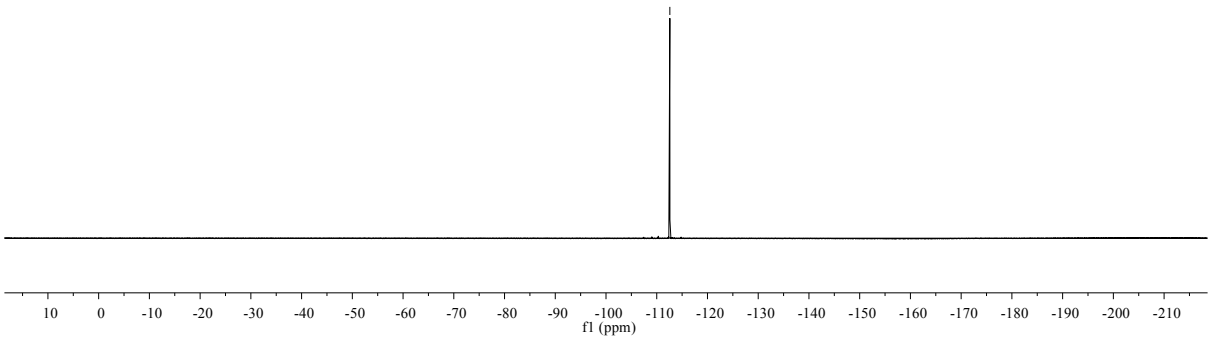
3.736


H
F
CO2Me
O

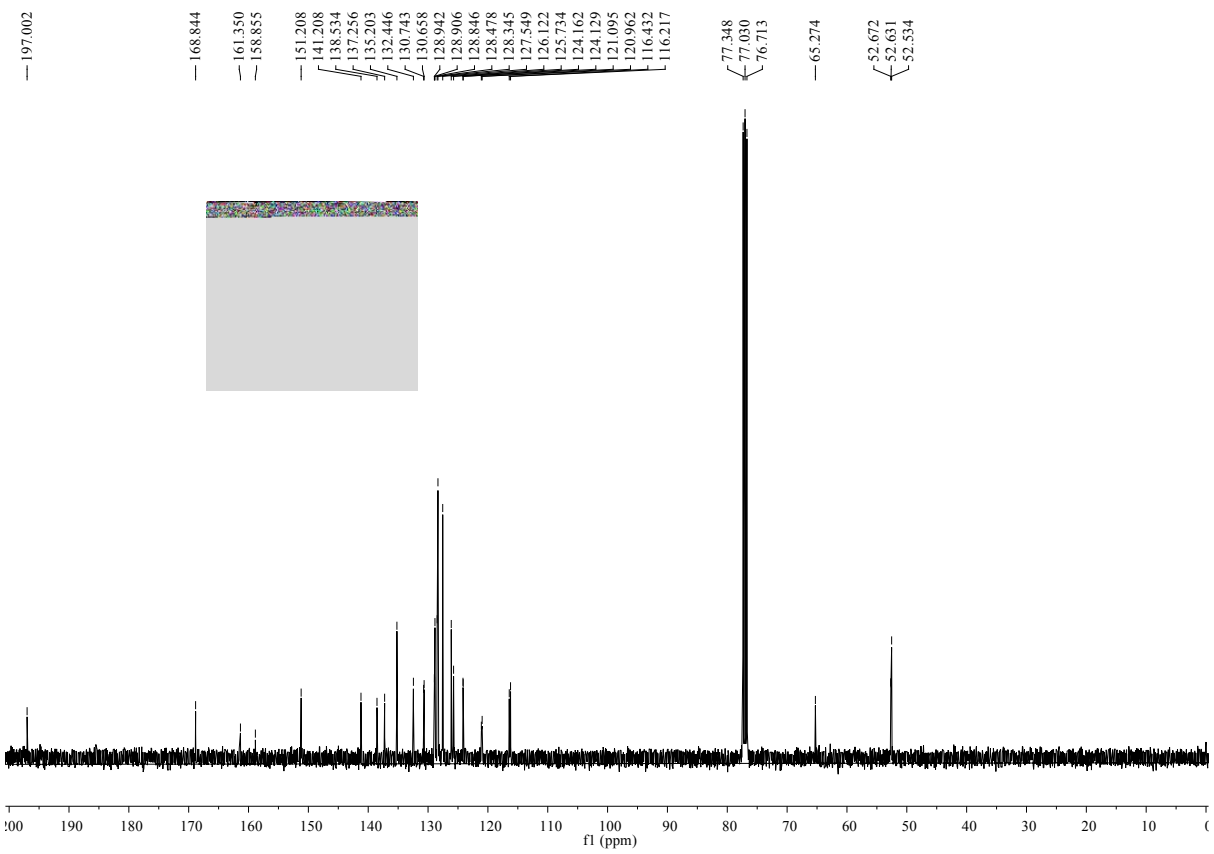

1.07
2.17
1.36
2.31
1.31
4.20
1.23
1.08
1.00
3.05
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


-112.584


H
F
CO2Me
O


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

**6f**


197.002
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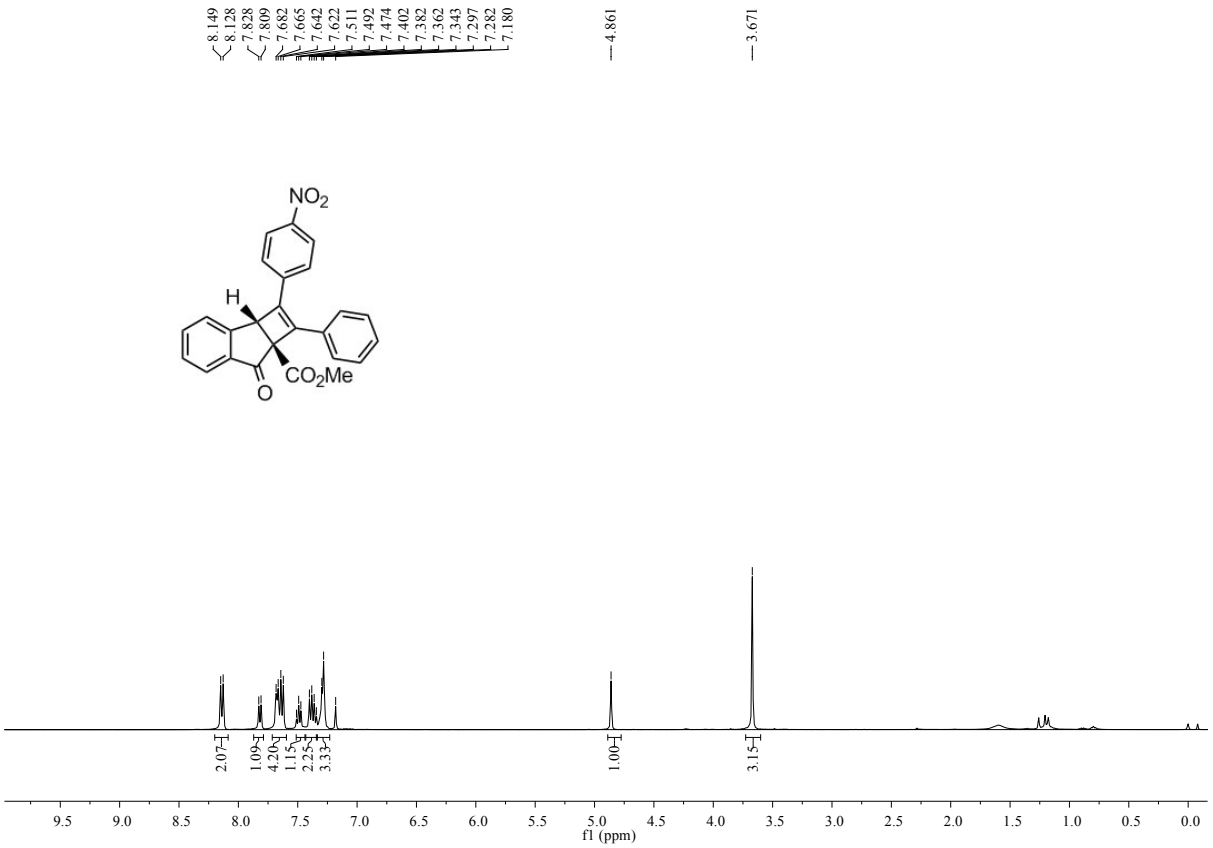
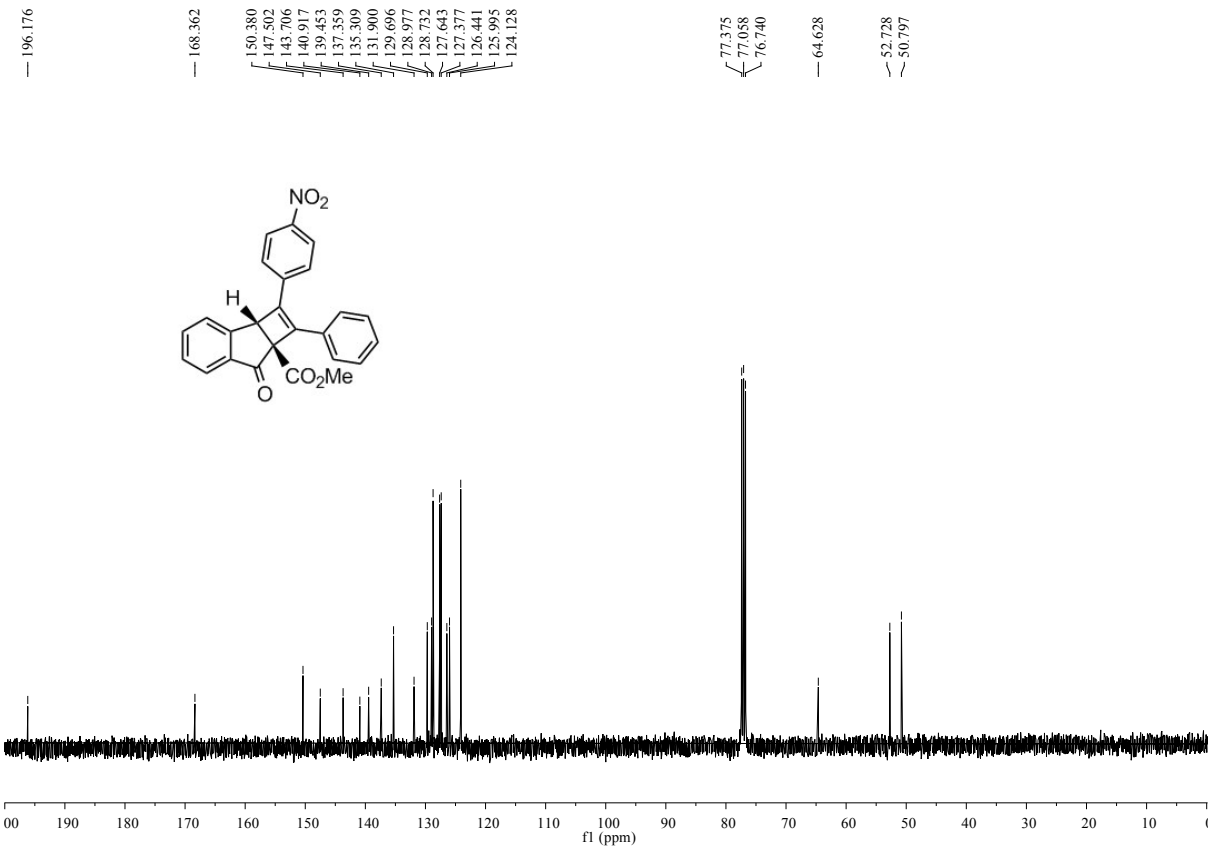
161.350
158.855
151.208
141.208
138.534
137.256
135.203
132.446
130.743
130.658
128.942
128.906
128.846
128.478
128.345
127.549
126.122
125.734
124.162
124.129
121.095
120.962
116.432
116.217
77.348
77.030
76.713
65.274
52.672
52.631
52.534
f1 (ppm)

**6g**


8.149
8.128
7.828
7.809
7.682
7.665
7.642
7.622
7.511
7.492
7.474
7.402
7.382
7.362
7.343
7.297
7.282
7.180
4.861
3.671
NO2
H
CO2Me
O
2.07
1.09
4.20
1.15
2.25
3.33
1.00
3.15
f1 (ppm)


196.176
168.362
150.380
147.502
143.706
140.917
139.453
137.359
135.309
131.900
129.696
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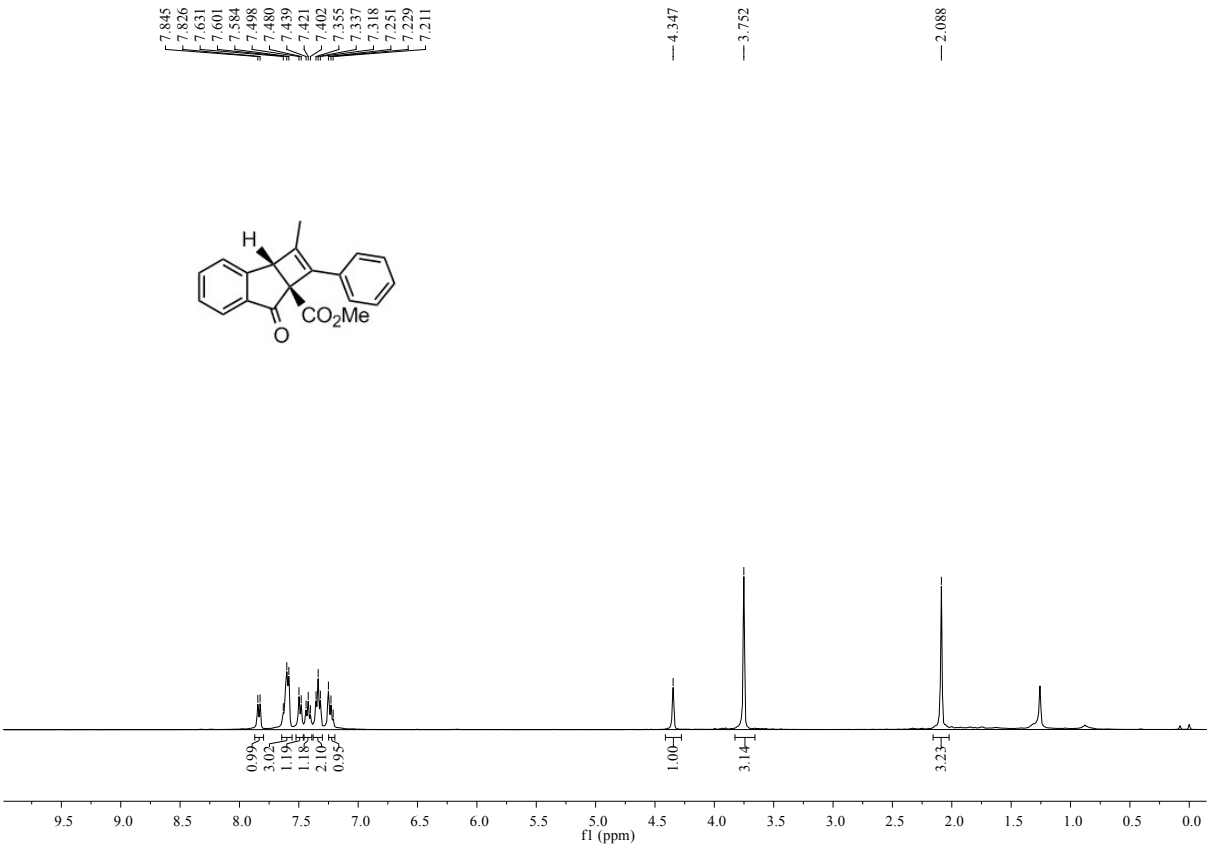
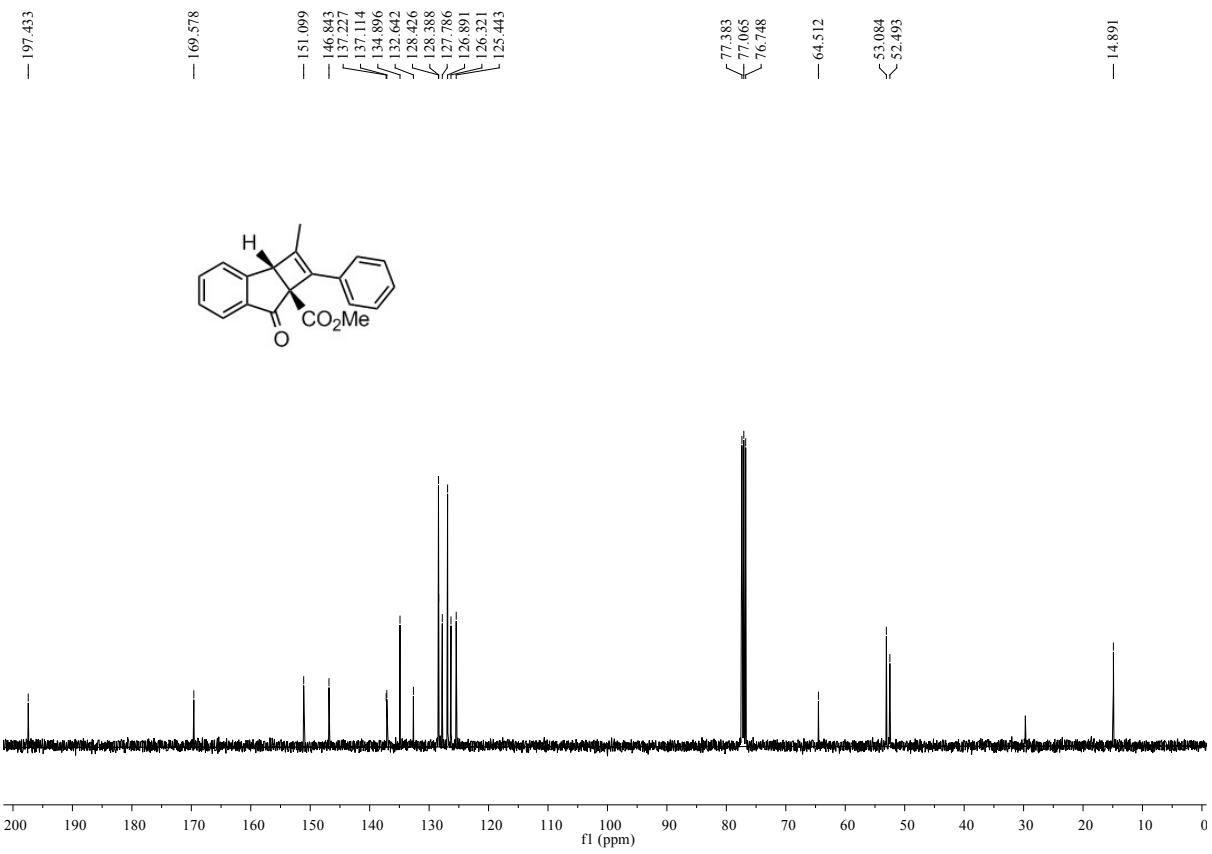
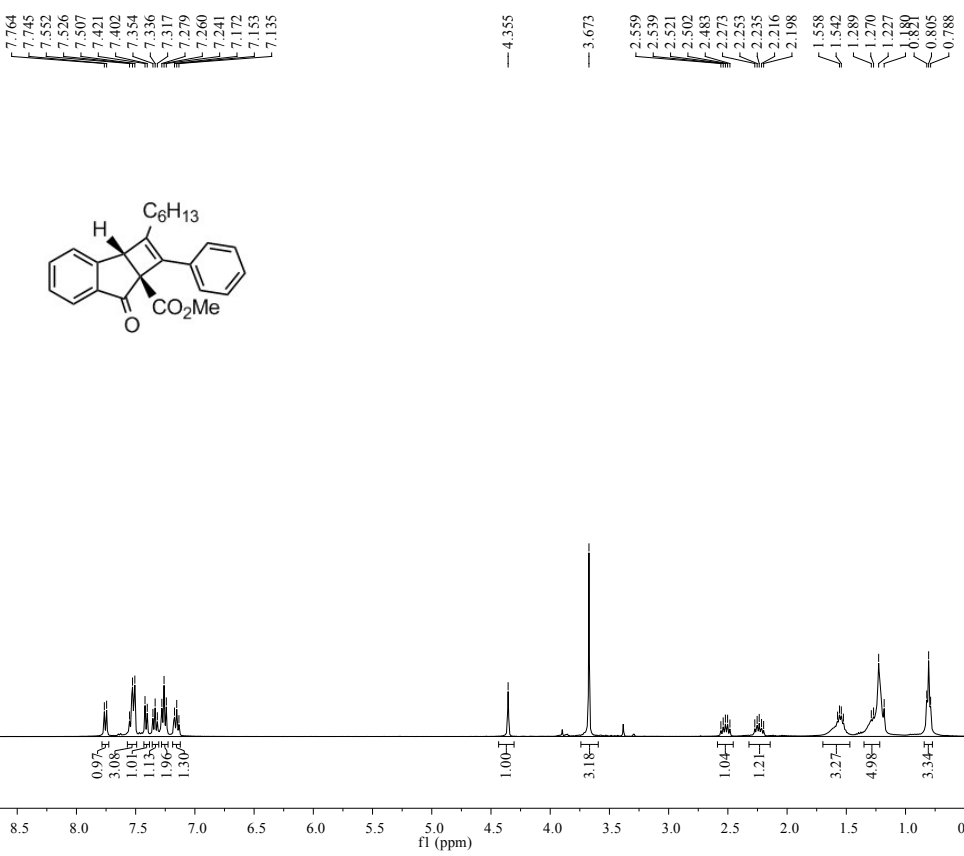
128.732
127.643
127.377
126.441
125.995
124.128
77.375
77.058
76.740
64.628
52.728
50.797
NO2
H
CO2Me
O
f1 (ppm)

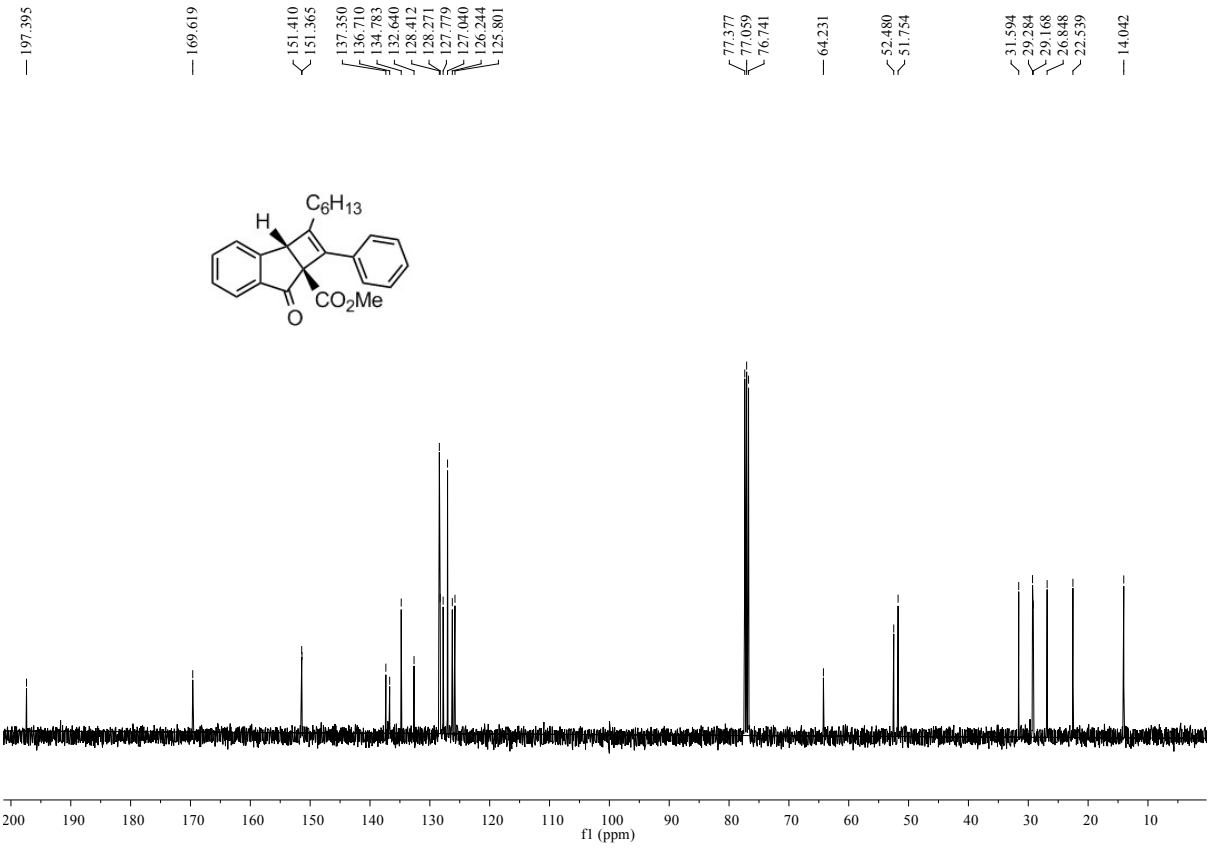
**6h**


7.845
7.826
7.631
7.601
7.584
7.498
7.480
7.439
7.421
7.402
7.355
7.337
7.318
7.251
7.229
7.211
4.347
3.752
2.088
H
CO2Me
O
0.99
3.02
1.19
1.18
2.10
0.95
1.00
3.14
3.23
f1 (ppm)

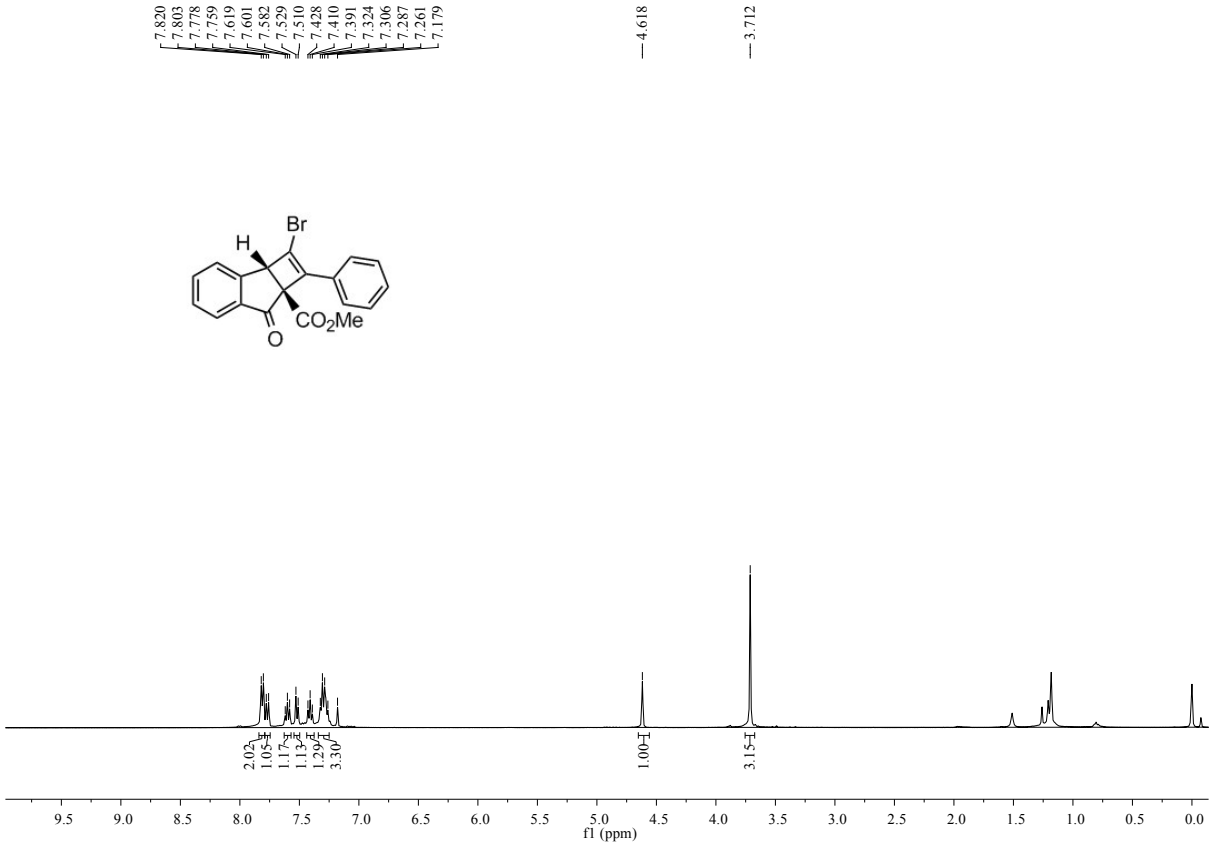

197.433
169.578
151.099
146.843
137.227
137.114
134.896
132.642
128.426
128.388
127.786
126.891
126.321
125.443
77.383
77.065
76.748
64.512
53.084
52.493
14.891
H
CO2Me
O
f1 (ppm)

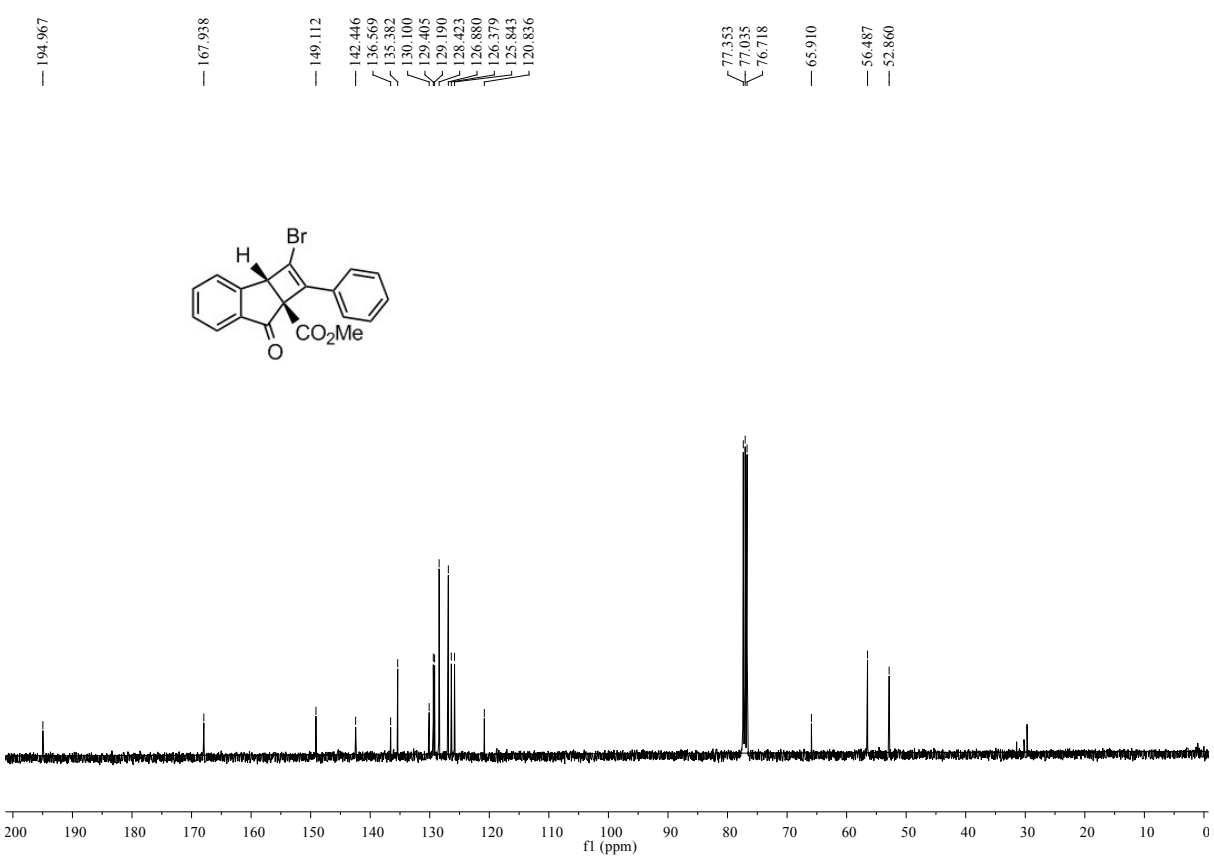
**6i**


7.764
7.745
7.552
7.526
7.507
7.421
7.402
7.354
7.336
7.317
7.279
7.260
7.241
7.172
7.153
7.135
4.355
3.673
2.559
2.539
2.521
2.502
2.483
2.273
2.253
2.235
2.216
2.198
1.558
1.542
1.289
1.270
1.227
1.180
0.821
0.805
0.788
C6H13
H
CO2Me
O
0.97
3.08
1.01
1.13
1.96
1.30
1.00
3.18
1.04
1.21
3.27
4.98
3.34
f1 (ppm)

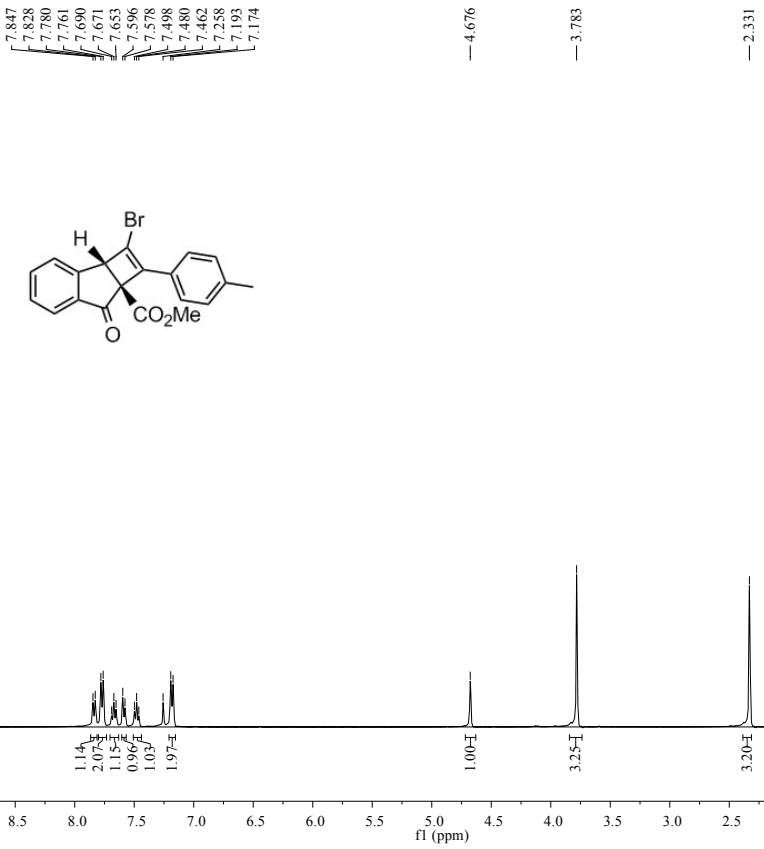

197.395
169.619
151.410
151.365
137.350
136.710
134.783
132.640
128.412
128.271
127.779
127.040
126.244
125.801
77.377
77.059
76.741
64.231
52.480
51.754
31.594
29.284
29.168
26.848
22.539
14.042
C6H13
H
CO2Me
O
f1 (ppm)

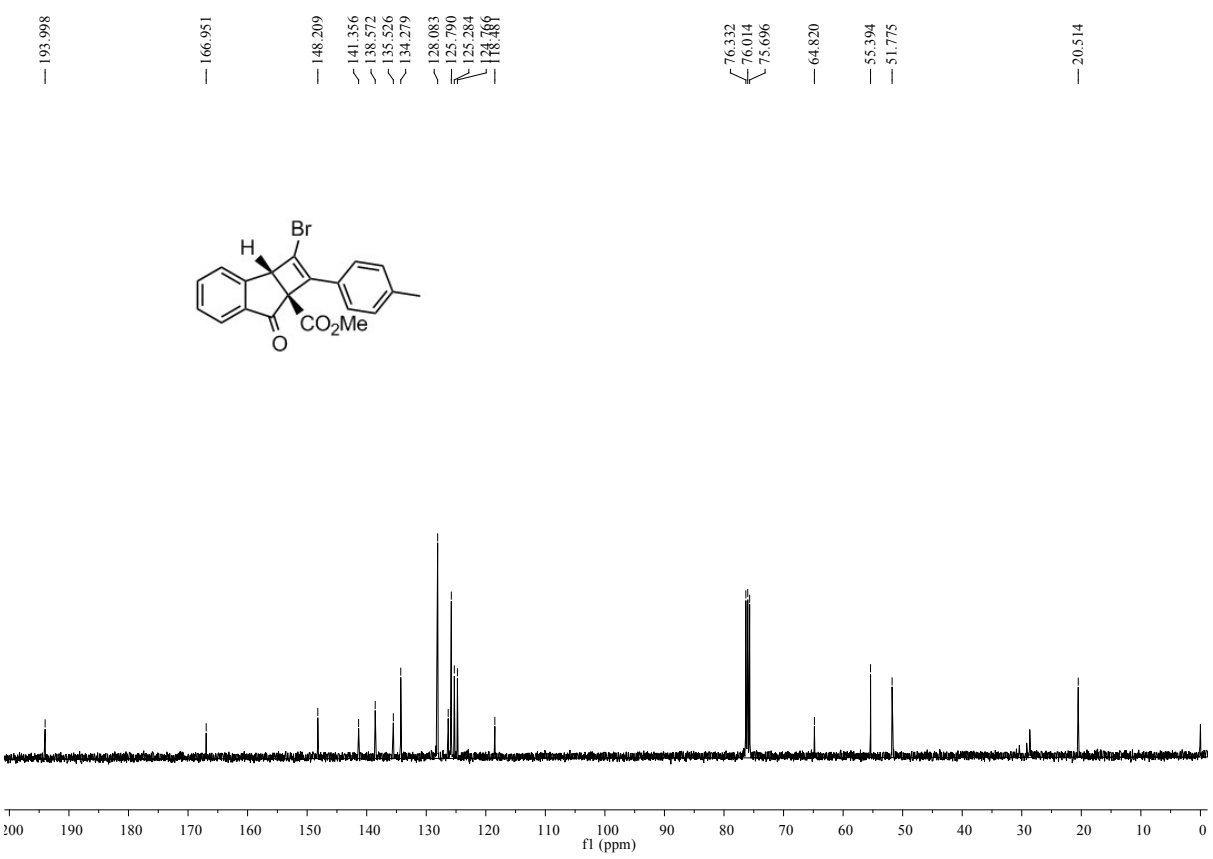
**6j**


7.820
7.803
7.778
7.759
7.619
7.601
7.582
7.529
7.510
7.428
7.410
7.391
7.324
7.306
7.287
7.261
7.179
4.618
3.712
Br
H
CO2Me
O
2.02
1.05
1.17
1.13
1.29
3.30
1.00
3.15
f1 (ppm)

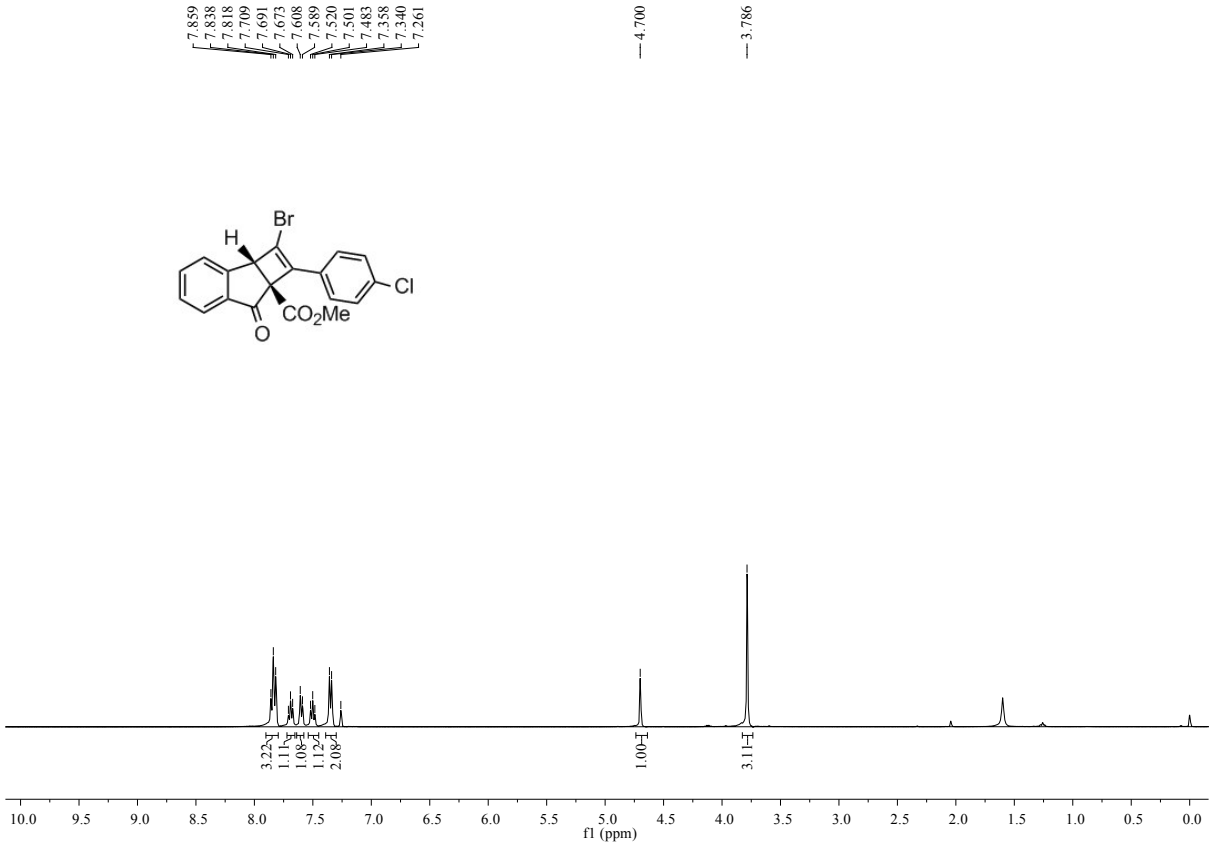

194.967
167.938
149.112
142.446
136.569
135.382
130.100
129.405
129.190
128.423
126.880
126.379
125.843
120.836
77.353
77.035
76.718
65.910
56.487
52.860
Br
H
CO2Me
O
f1 (ppm)

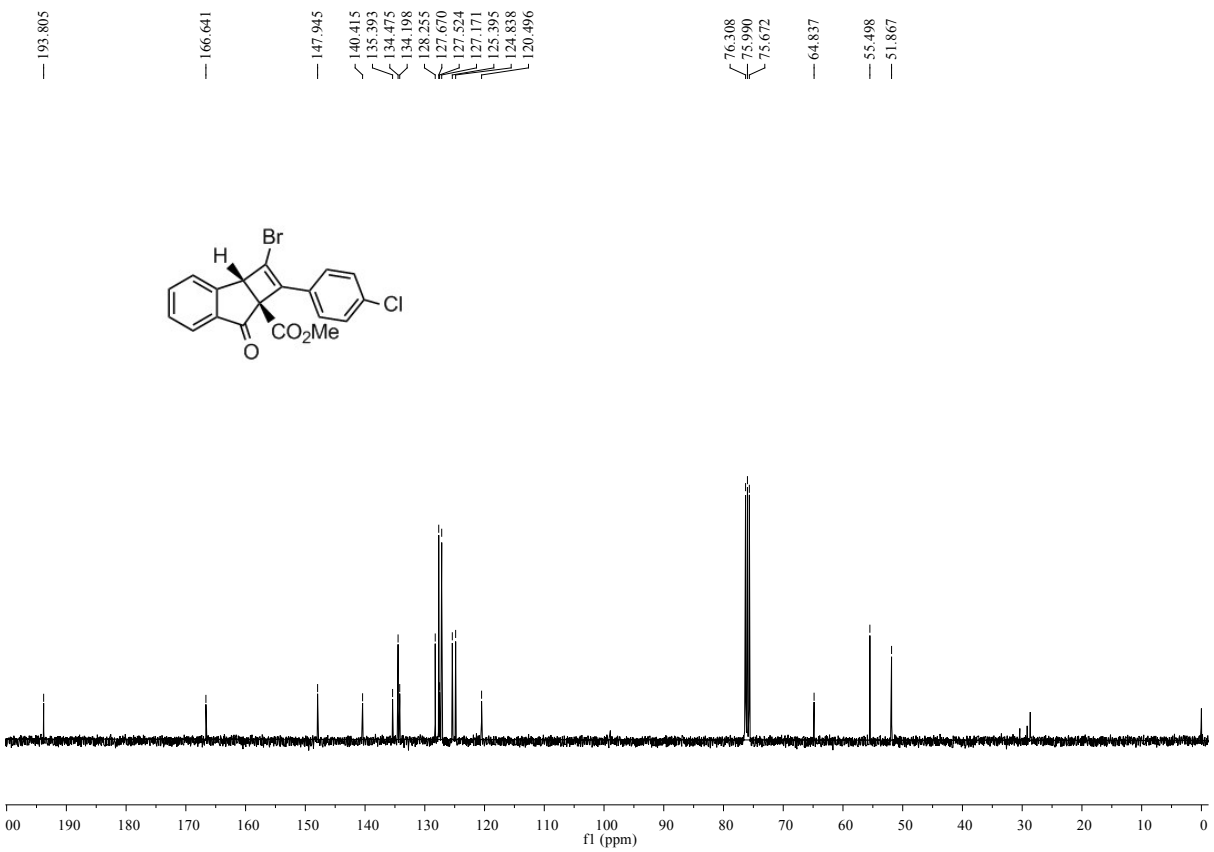
**6k**


7.847
7.828
7.780
7.761
7.690
7.671
7.653
7.596
7.578
7.498
7.480
7.462
7.258
7.193
7.174
4.676
3.783
2.331
Br
H
CO2Me
O
1.14
2.07
1.15
0.96
1.03
1.97
1.00
3.25
3.20
f1 (ppm)


193.998
166.951
148.209
141.356
138.572
135.526
134.279
128.083
125.790
125.284
124.486
118.481
76.332
76.014
75.696
64.820
55.394
51.775
20.514
Br
H
CO2Me
O
f1 (ppm)

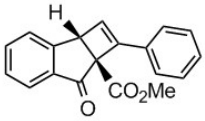
**6l**

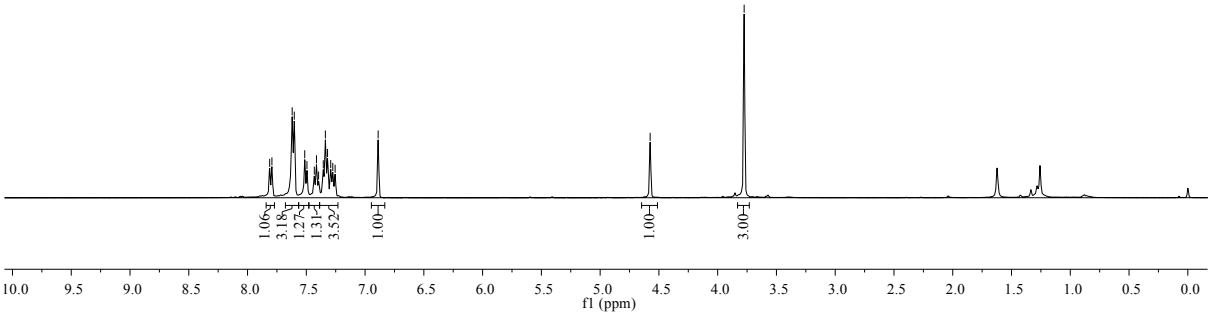

7.859
7.838
7.818
7.709
7.691
7.673
7.608
7.589
7.520
7.501
7.483
7.358
7.340
7.261
4.700
3.786
Br
H
Cl
CO2Me
O
3.22
1.11
1.08
1.12
2.08
1.00
3.11
f1 (ppm)

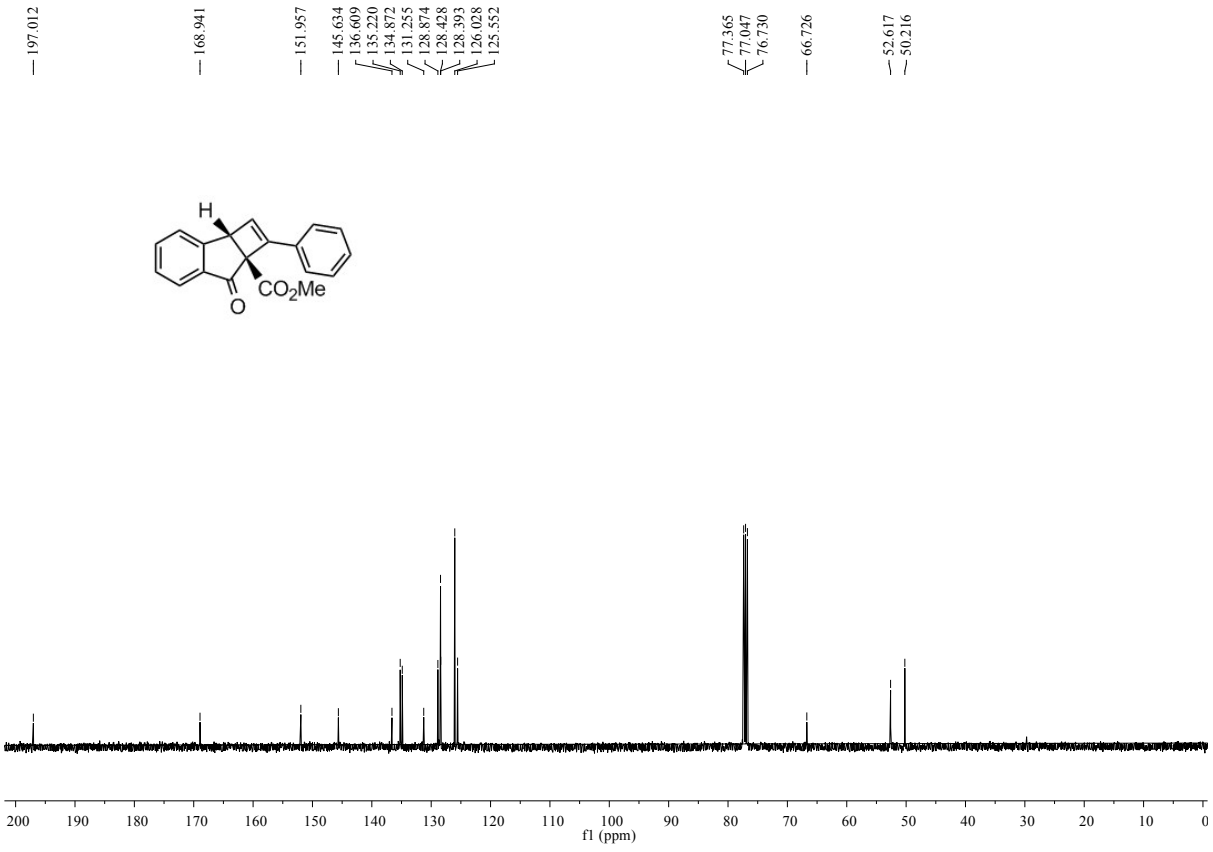

193.805
166.641
147.945
140.415
135.393
134.475
134.198
128.255
127.670
127.524
127.171
125.395
124.838
120.496
76.308
75.990
75.672
64.837
55.498
51.867
Br
H
Cl
CO2Me
O
f1 (ppm)

**6m**


7.812
7.793
7.620
7.603
7.513
7.495
7.432
7.413
7.396
7.356
7.338
7.319
7.292
7.275
7.255
6.889
4.575
3.775

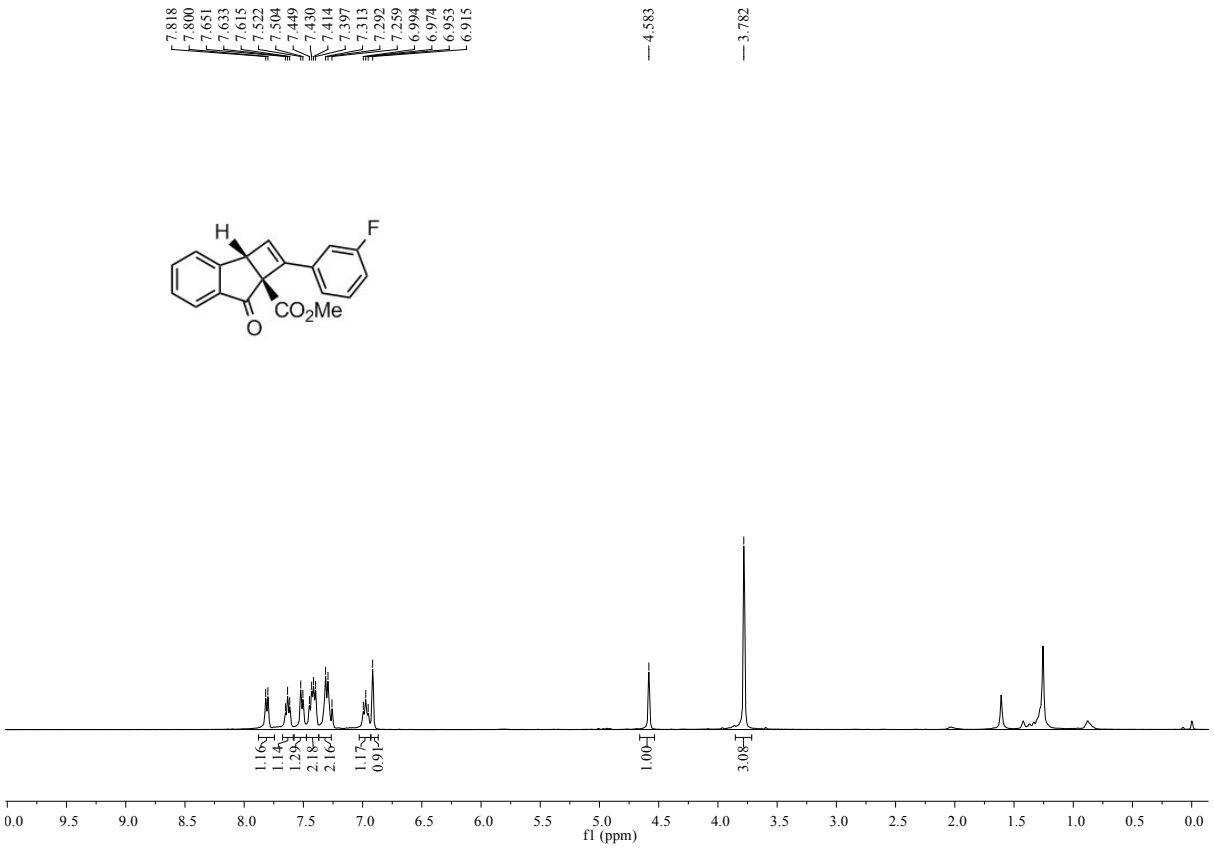

H
CO2Me
O

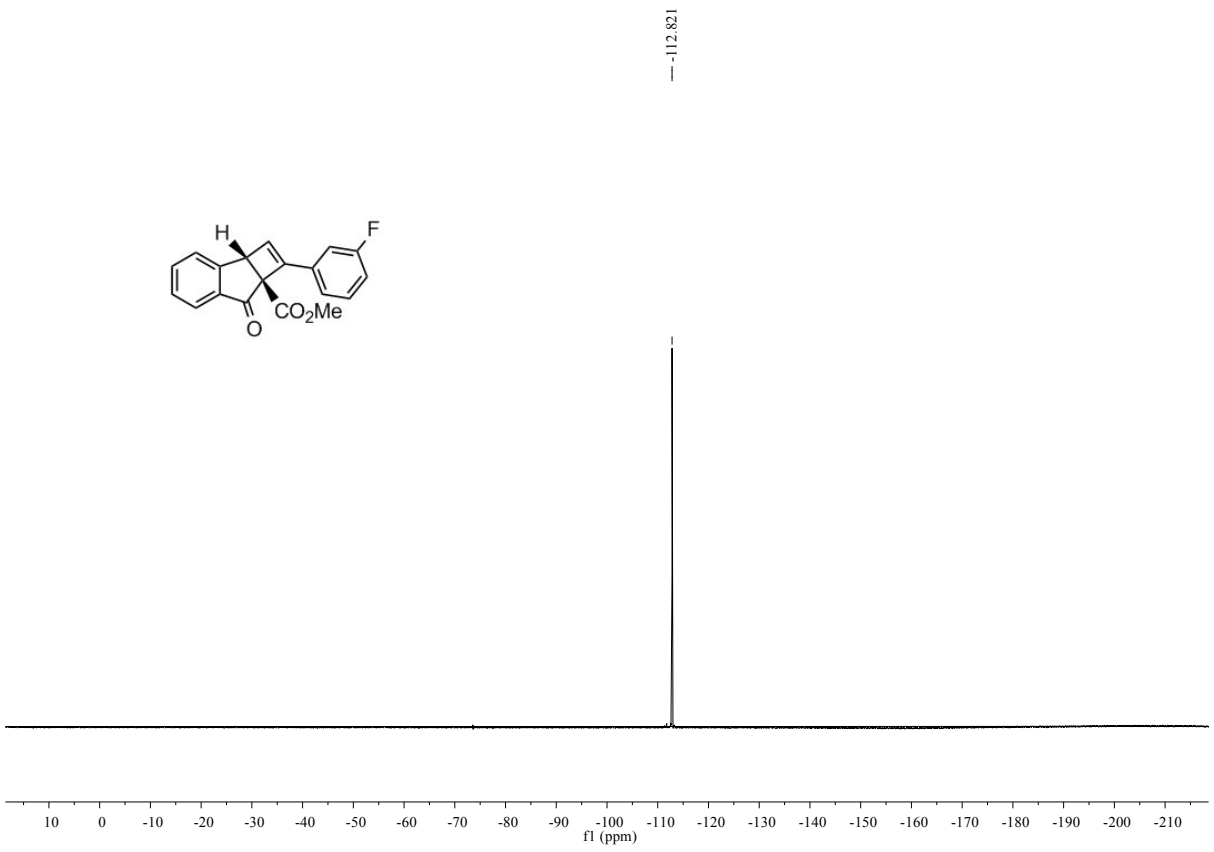

1.06
3.18
1.27
1.31
3.52
1.00
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.012
168.941
151.957
145.634
136.609
135.220
134.872
131.255
128.874
128.428
128.393
126.028
125.552
77.365
77.047
76.730
66.726
52.617
50.216
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

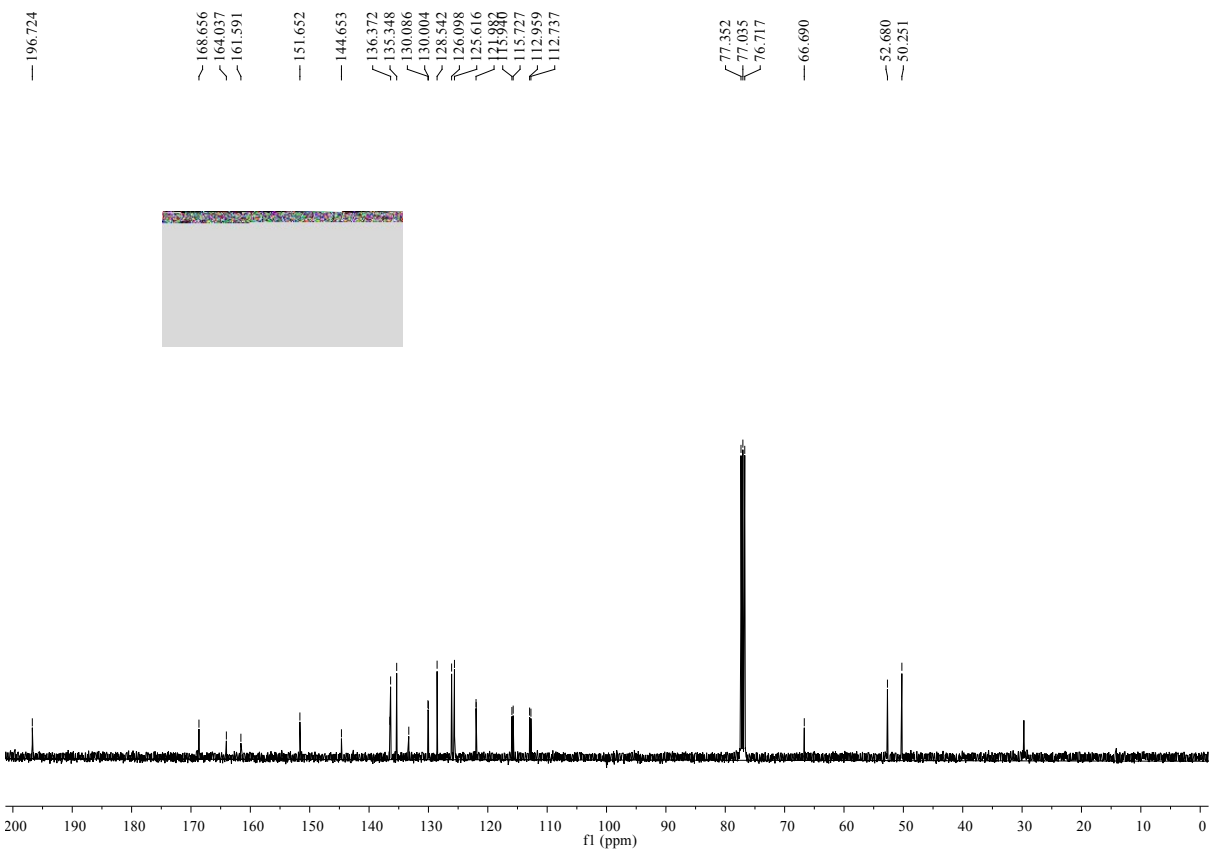

H
CO2Me
O

**6n**

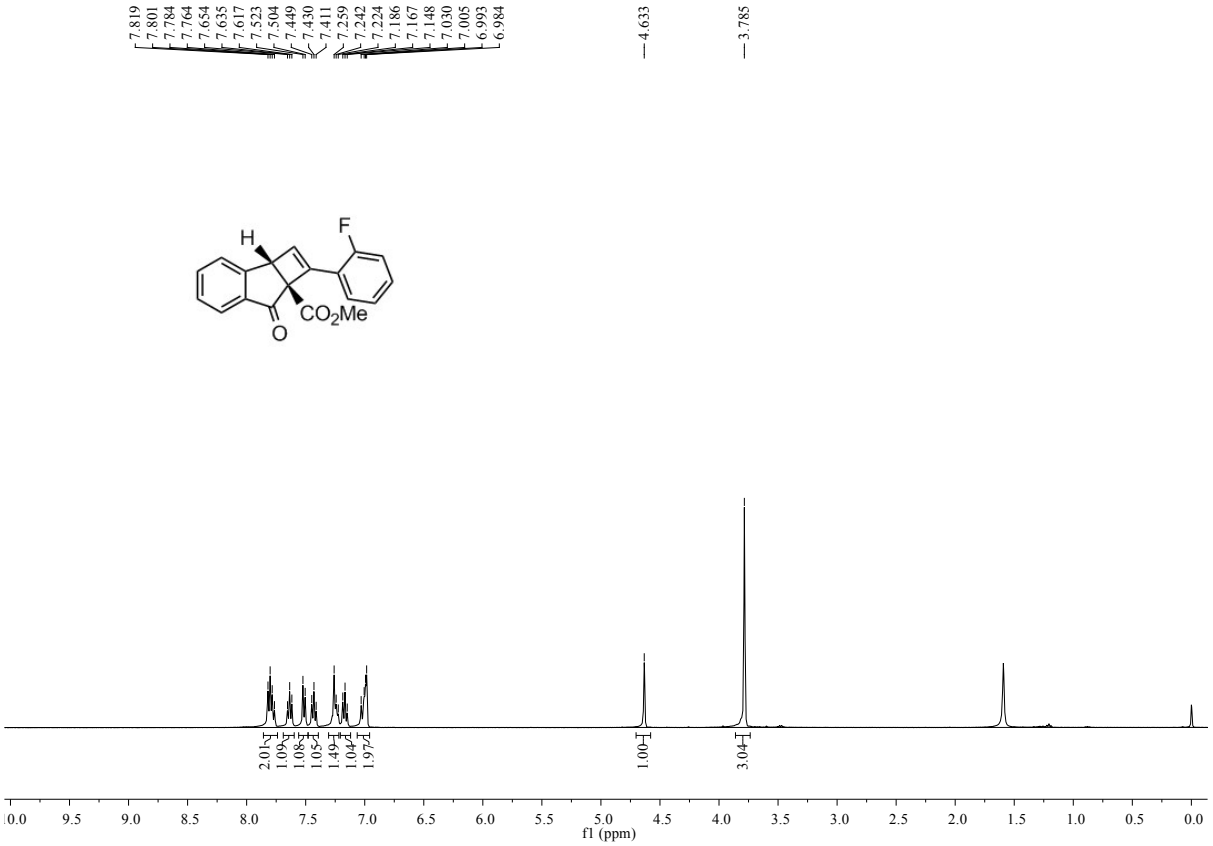

7.818
7.800
7.651
7.633
7.615
7.522
7.504
7.449
7.430
7.414
7.397
7.313
7.292
7.259
6.994
6.974
6.953
6.915
4.583
3.782
H
F
CO2Me
O
1.16
1.14
1.29
2.18
2.16
1.17
0.91
1.00
3.08
f1 (ppm)

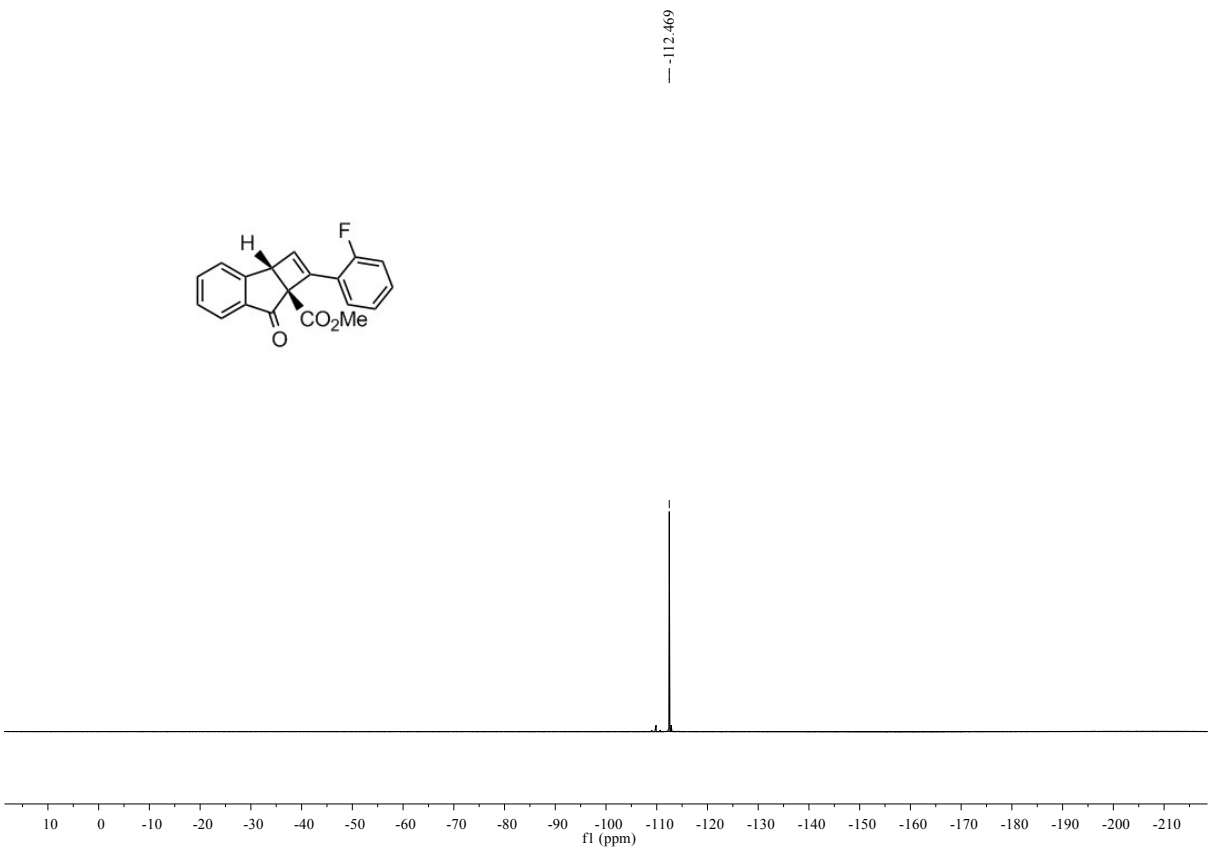

-112.821
H
F
CO2Me
O
f1 (ppm)

**6n**

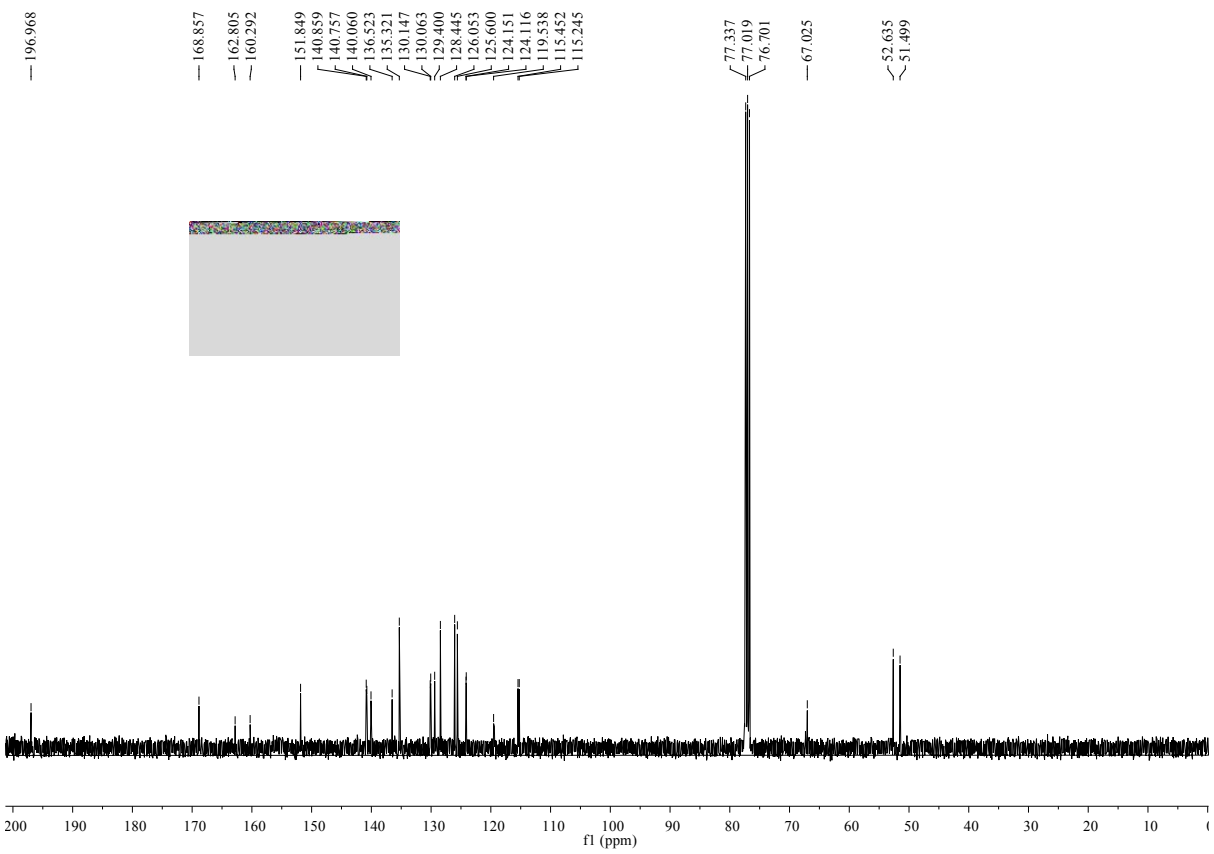

196.724
168.656
164.037
161.591
151.652
144.653
136.372
135.348
130.086
130.004
128.542
126.098
125.616
121.982
115.940
115.727
112.959
112.737
77.352
77.035
76.717
66.690
52.680
50.251
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**6o**


7.819
7.801
7.784
7.764
7.654
7.635
7.617
7.523
7.504
7.449
7.430
7.411
7.259
7.242
7.224
7.186
7.167
7.148
7.030
7.005
6.993
6.984
4.633
3.785
H
F
CO2Me
O
2.01
1.09
1.08
1.05
1.49
1.04
1.97
1.00
3.04
f1 (ppm)

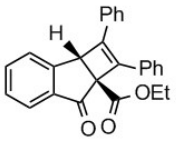

-112.469
H
F
CO2Me
O
f1 (ppm)

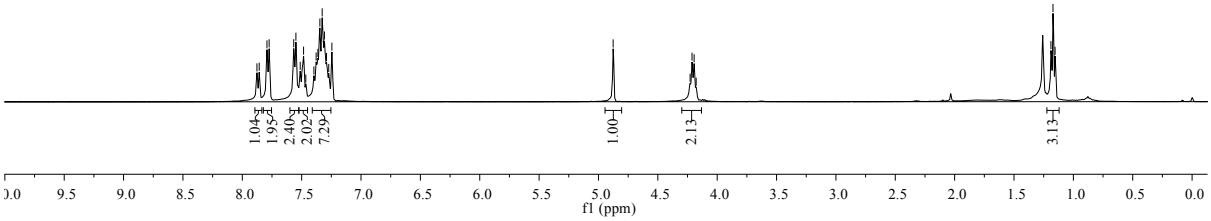
**6o**


196.968
168.857
162.805
160.292
151.849
140.859
140.757
140.060
136.523
135.321
130.147
130.063
129.400
128.445
126.053
125.600
124.151
124.116
119.538
115.452
115.245
77.337
77.019
76.701
67.025
52.635
51.499
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

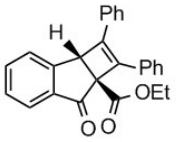
**6p**

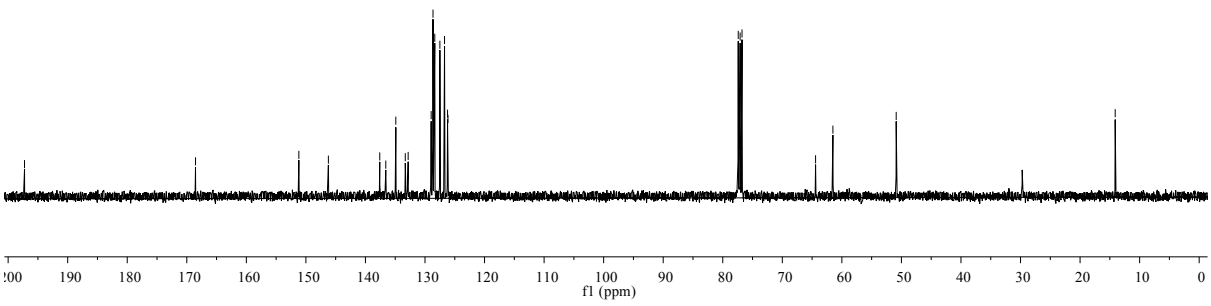

7.877
7.858
7.792
7.774
7.567
7.548
7.512
7.484
7.465
7.397
7.378
7.363
7.347
7.327
7.308
7.291
7.272
7.245
4.876
4.228
4.212
4.194
4.177
1.189
1.172
1.154


Ph
H
Ph
OEt
O
O


1.04
1.95
2.40
2.02
7.29
1.00
2.13
3.13
f1 (ppm)

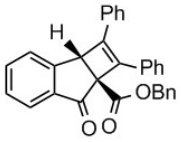

197.249
168.534
151.183
146.225
137.596
136.585
134.899
133.313
132.828
128.965
128.656
128.480
128.357
127.501
126.719
126.213
126.139
77.401
77.285
77.083
76.765
64.413
61.503
50.876
14.101

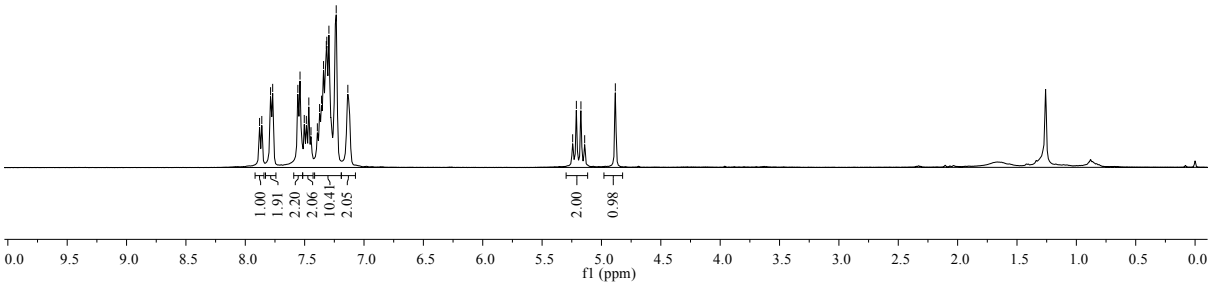

Ph
H
Ph
OEt
O
O

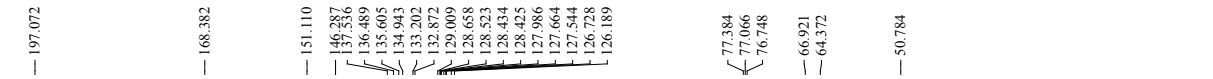

f1 (ppm)

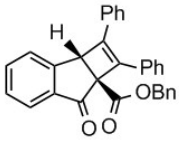
**6q**

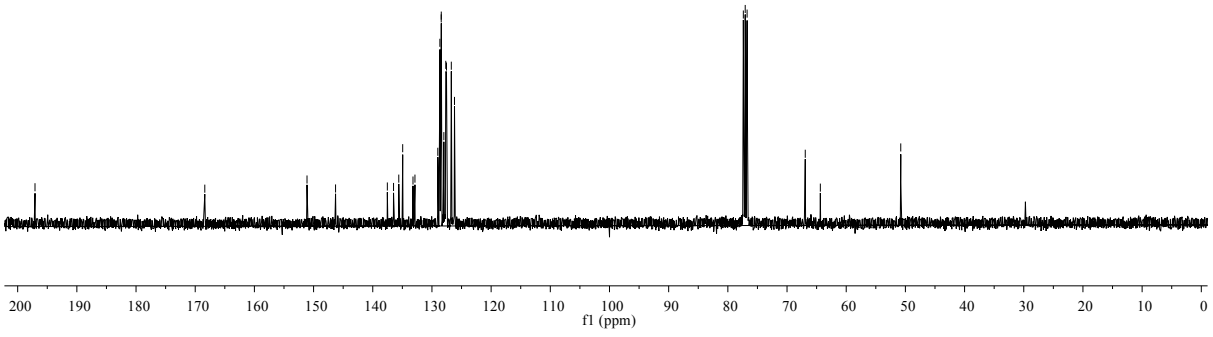

7.880
7.861
7.787
7.769
7.557
7.539
7.503
7.486
7.465
7.447
7.393
7.374
7.358
7.341
7.318
7.313
7.296
7.234
7.136
5.243
5.211
5.173
5.141
4.883


Ph
H
Ph
OBn
O
O


1.00
1.91
2.20
2.06
10.41
2.05
2.00
0.98
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

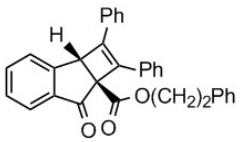

197.072
168.382
151.110
146.287
137.536
136.489
135.605
134.943
133.202
132.872
129.009
128.658
128.523
128.434
128.425
127.986
127.664
127.544
126.728
126.189
77.384
77.066
76.748
66.921
64.372
50.784

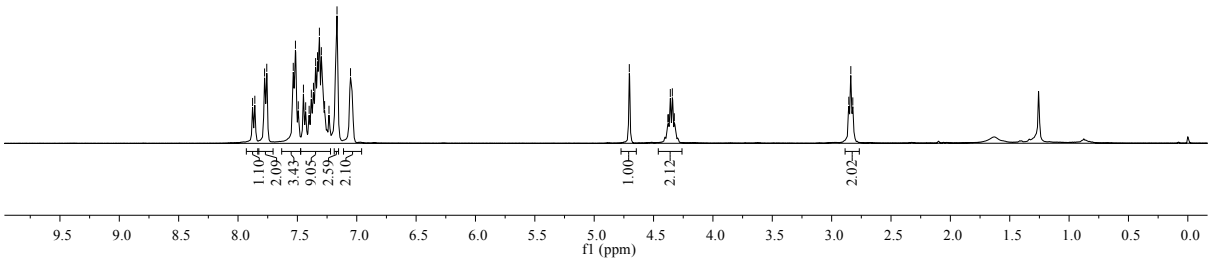

Ph
H
Ph
OBn
O
O

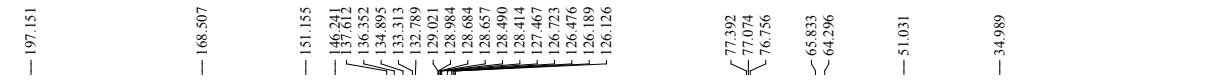

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

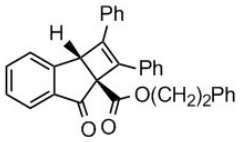
**6r**

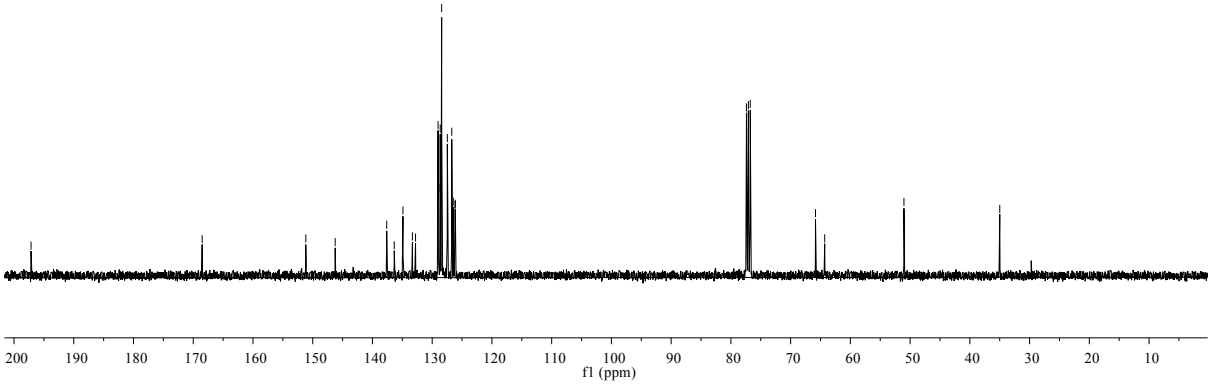

7.877
7.858
7.776
7.758
7.535
7.516
7.492
7.449
7.430
7.401
7.382
7.365
7.347
7.331
7.315
7.298
7.271
7.234
7.166
7.052
4.704
4.380
4.375
4.359
4.342
4.325
2.855
2.839
2.822


Ph
H
Ph
O(CH2)2Ph
O
O

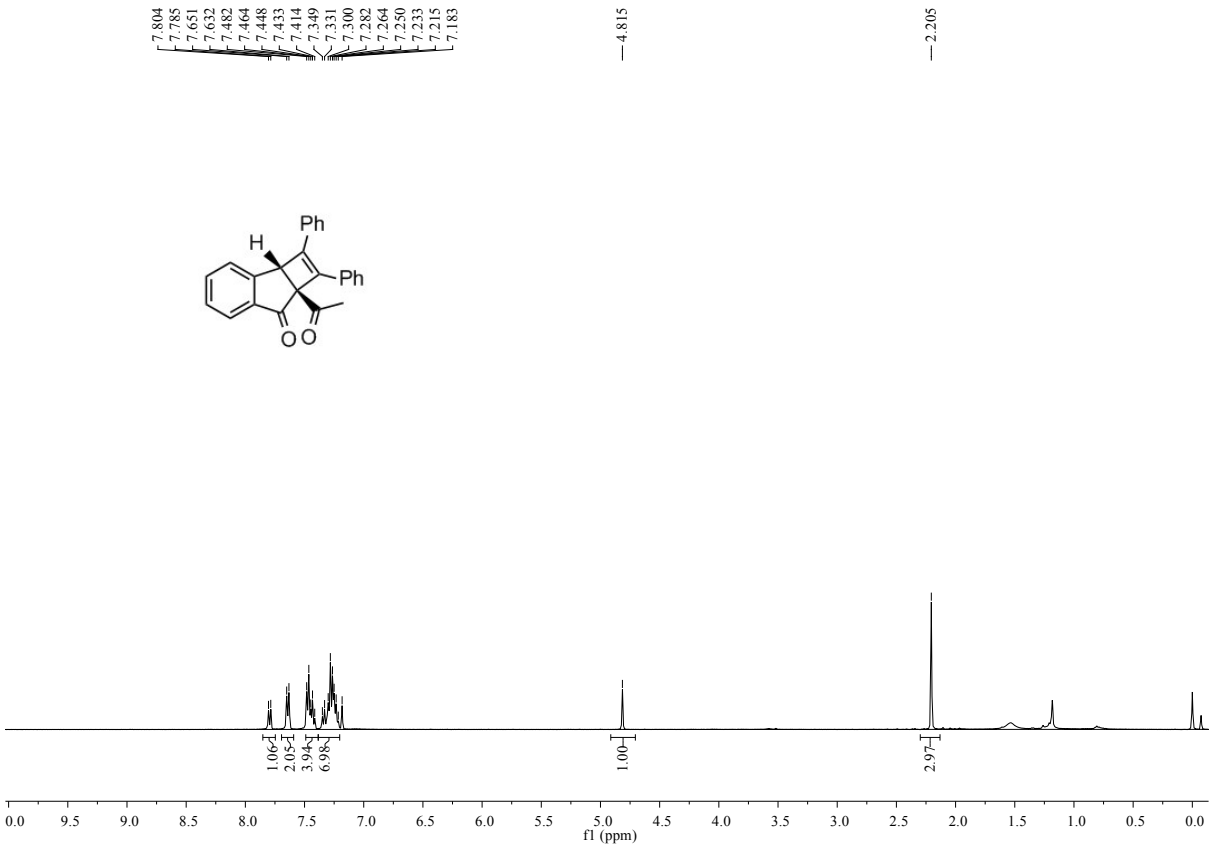

1.10
2.09
3.43
9.05
2.59
2.10
1.00
2.12
2.02
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

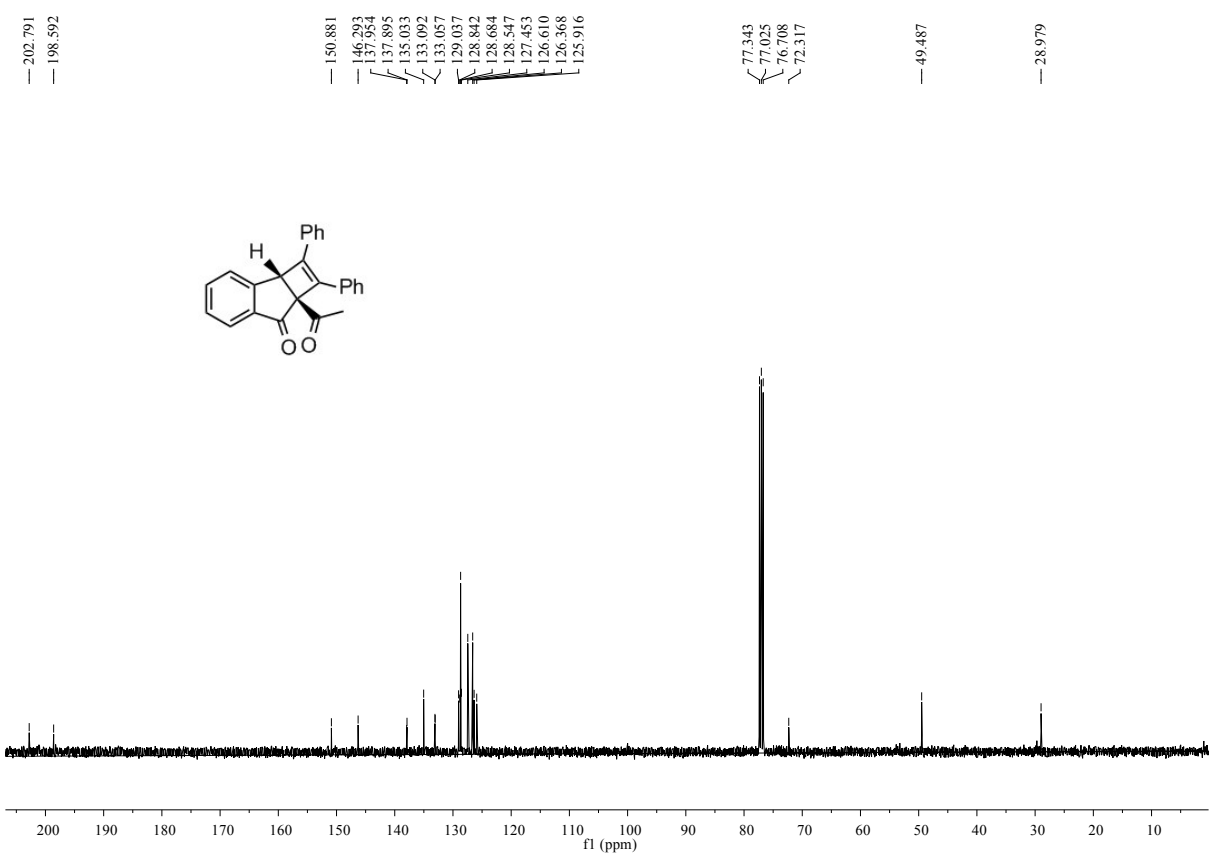

197.151
168.507
151.155
146.241
137.612
136.352
134.895
133.313
132.789
129.021
128.984
128.684
128.657
128.490
128.414
127.467
126.723
126.476
126.189
126.126
77.392
77.074
76.756
65.833
64.296
51.031
34.989


Ph
H
Ph
O(CH2)2Ph
O
O

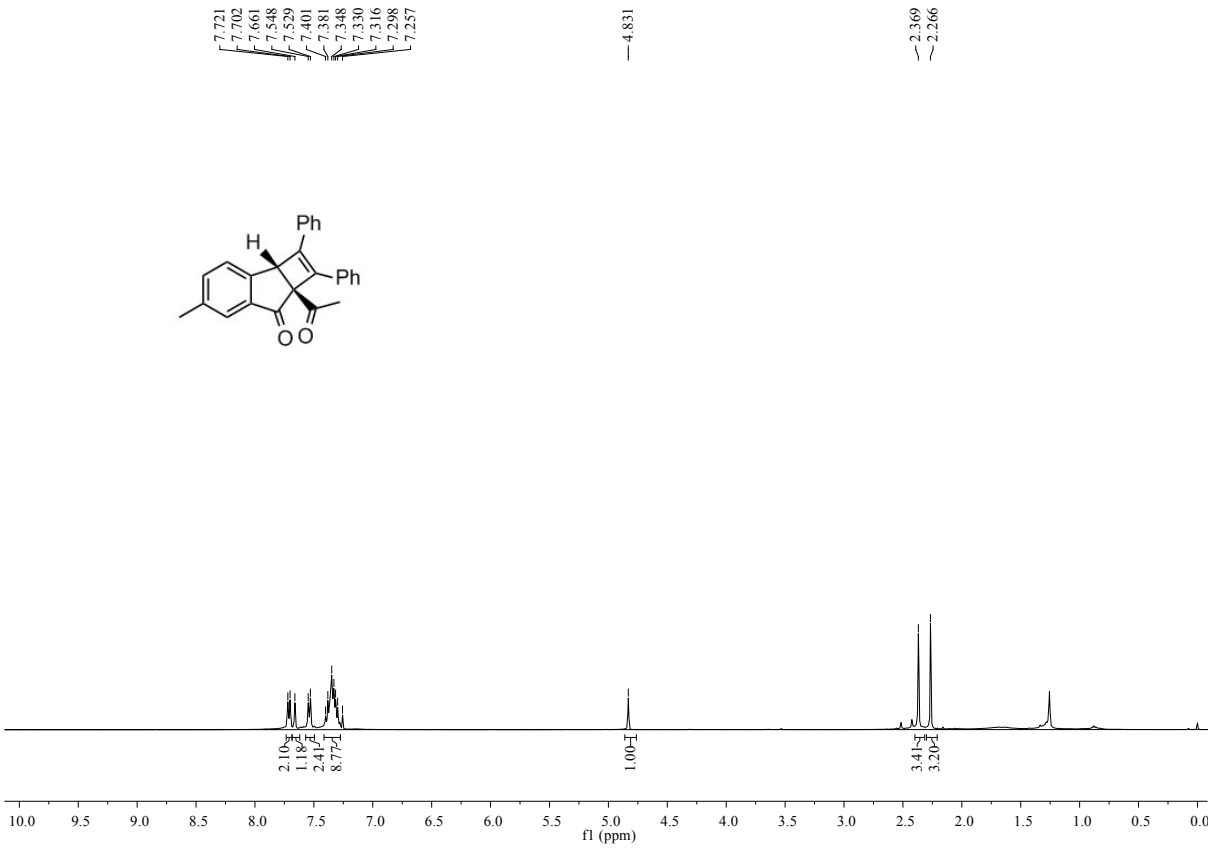

200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

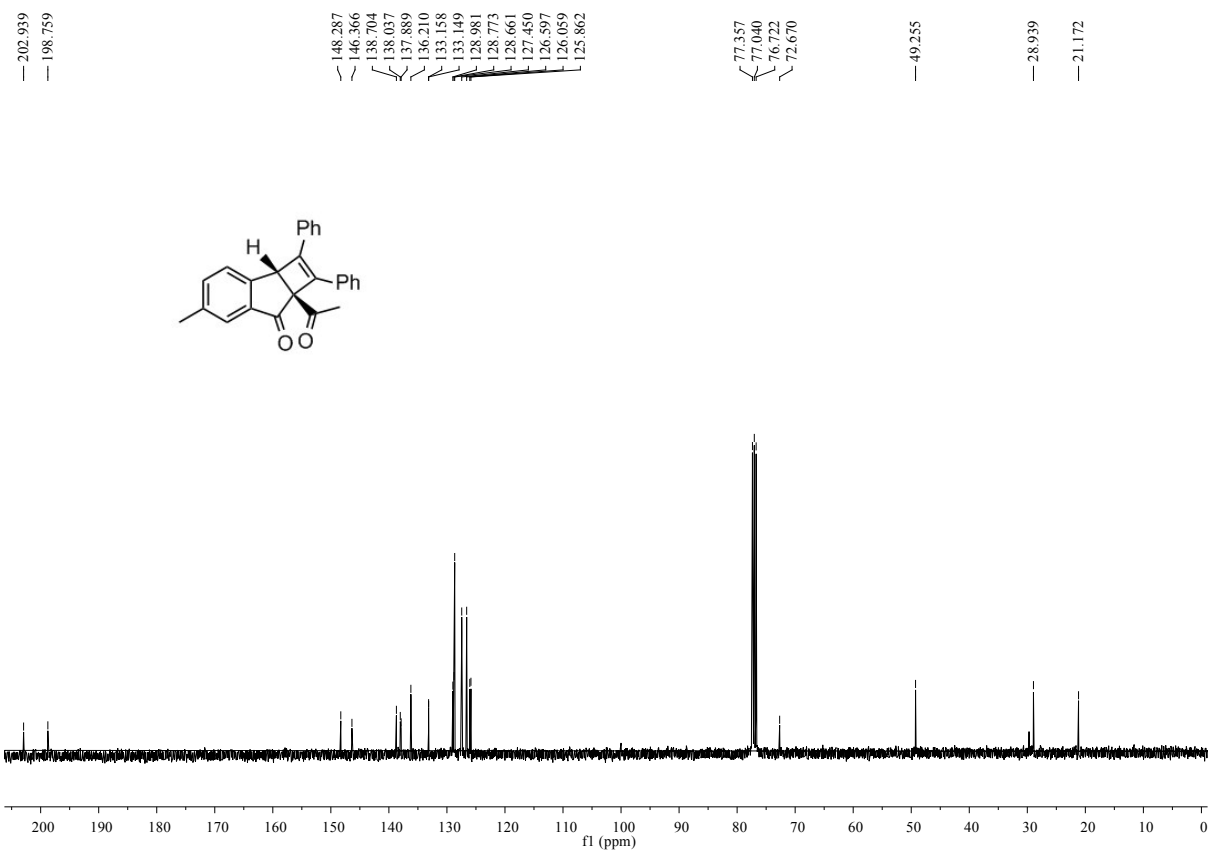
**6s**


7.804
7.785
7.651
7.632
7.482
7.464
7.448
7.433
7.414
7.349
7.331
7.300
7.282
7.264
7.250
7.233
7.215
7.183
4.815
2.205
Ph
H
Ph
O
O
1.06
2.05
3.94
6.98
1.00
2.97
f1 (ppm)

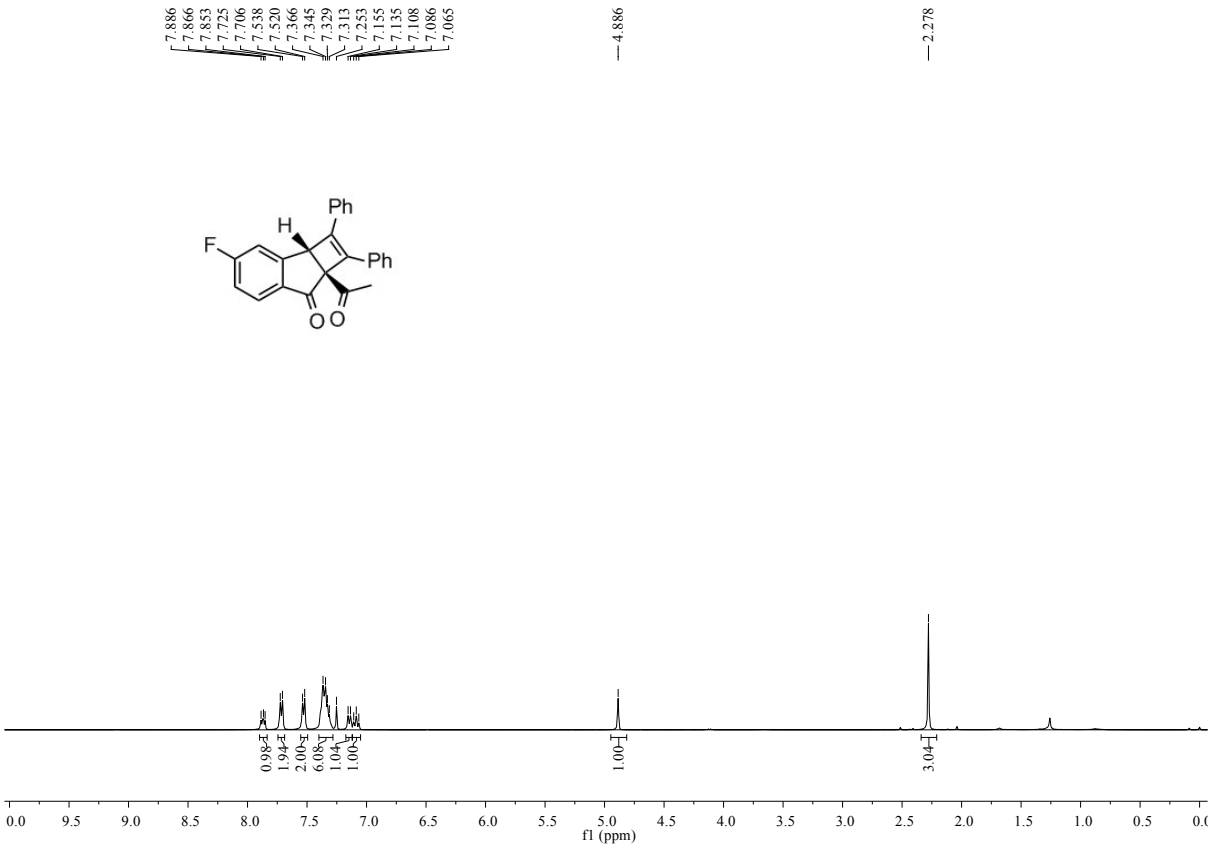

202.791
198.592
150.881
146.293
137.954
137.895
135.033
133.092
133.057
129.037
128.842
128.684
128.547
127.453
126.610
126.368
125.916
77.343
77.025
76.708
72.317
49.487
28.979
Ph
H
Ph
O
O
f1 (ppm)

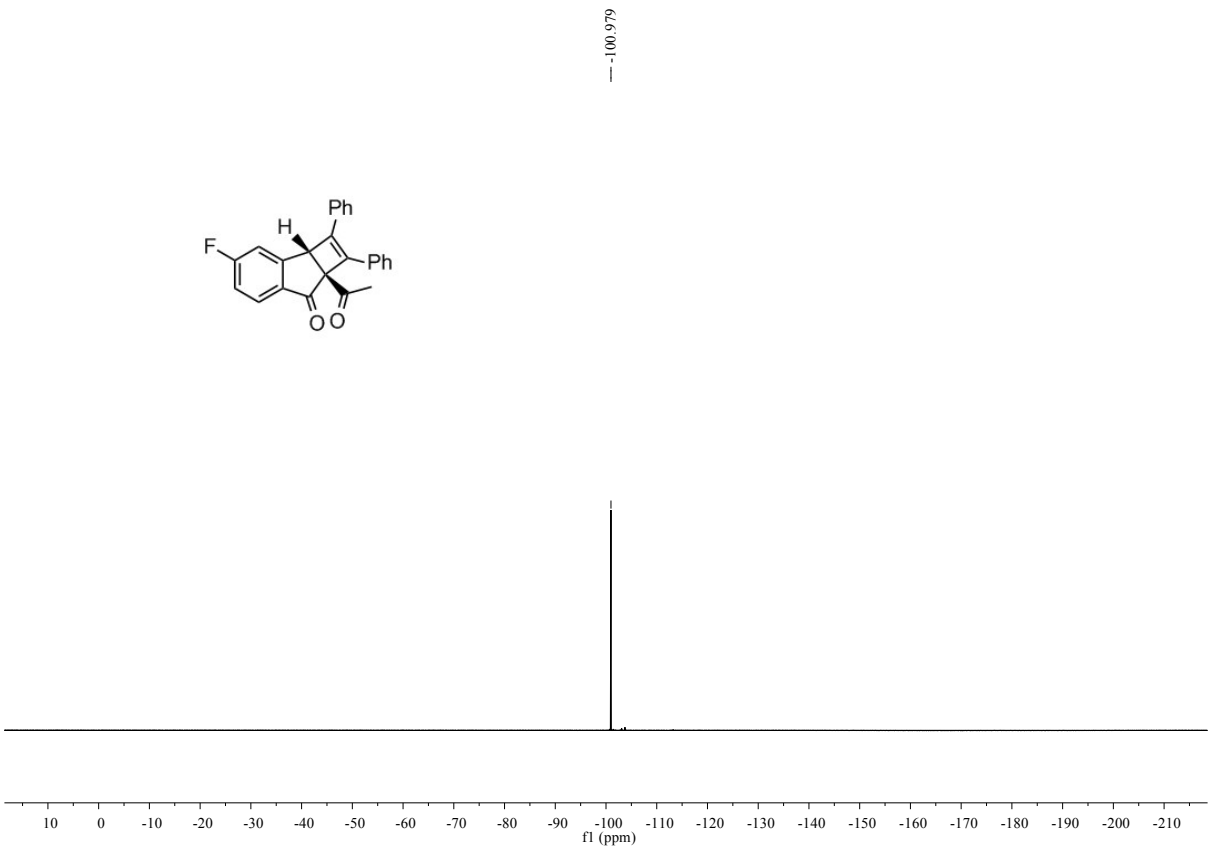
**6t**


7.721
7.702
7.661
7.548
7.529
7.401
7.381
7.348
7.330
7.316
7.298
7.257
4.831
2.369
2.266
Ph
H
Ph
O
O
2.10
1.18
2.41
8.77
1.00
3.41
3.20
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

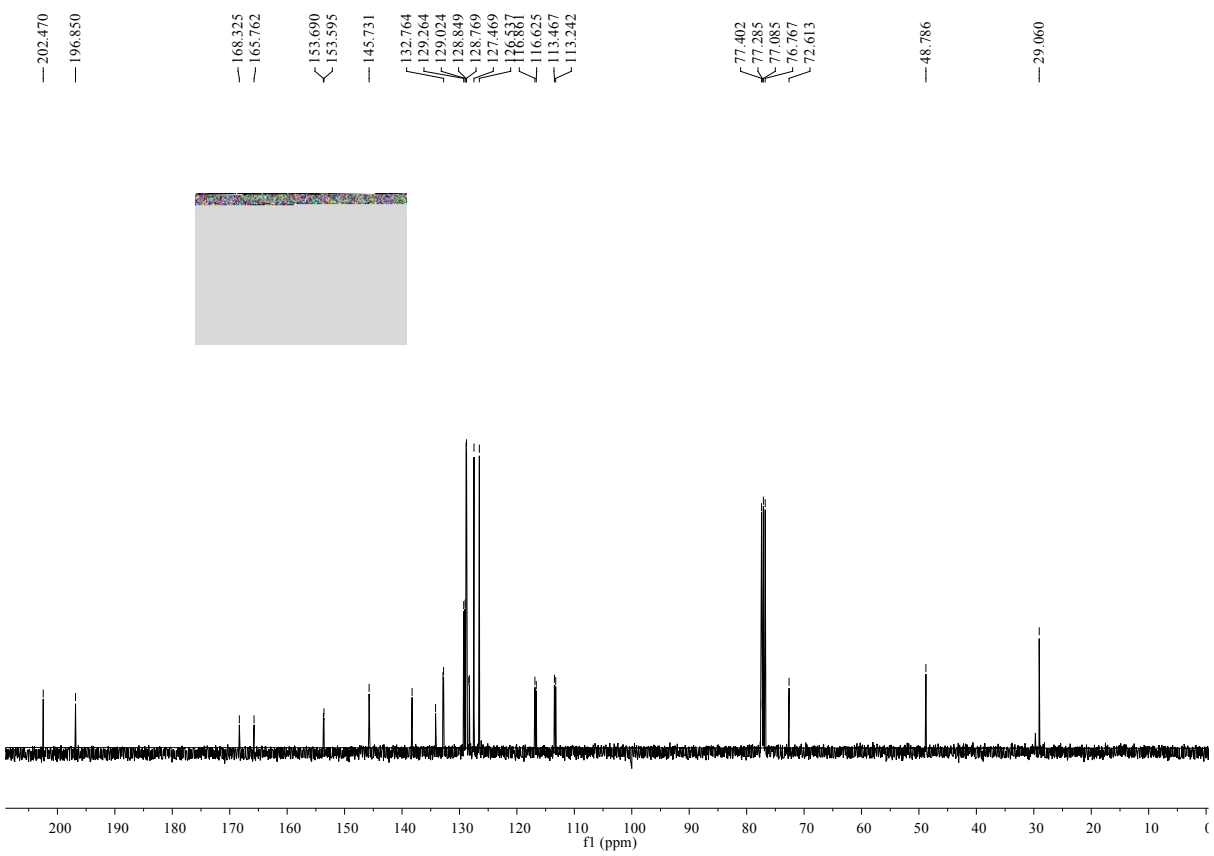

202.939
198.759
148.287
146.366
138.704
138.037
137.889
136.210
133.158
133.149
128.981
128.773
128.661
127.450
126.597
126.059
125.862
77.357
77.040
76.722
72.670
49.255
28.939
21.172
Ph
H
Ph
O
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

**6u**

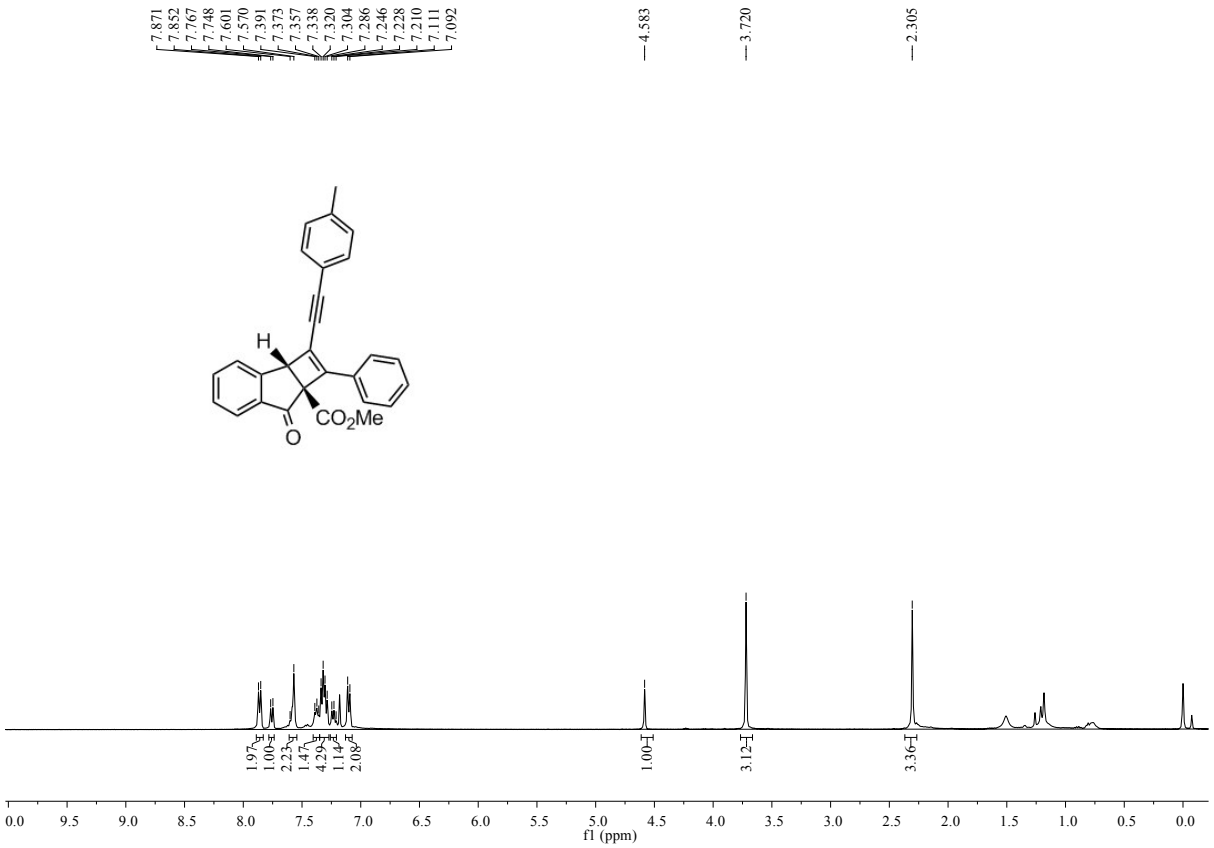

7.886
7.866
7.853
7.725
7.706
7.538
7.520
7.366
7.345
7.329
7.313
7.253
7.155
7.135
7.108
7.086
7.065
4.886
2.278
Ph
H
F
Ph
O
O
0.98
1.94
2.00
6.08
1.04
1.00
1.00
3.04
f1 (ppm)

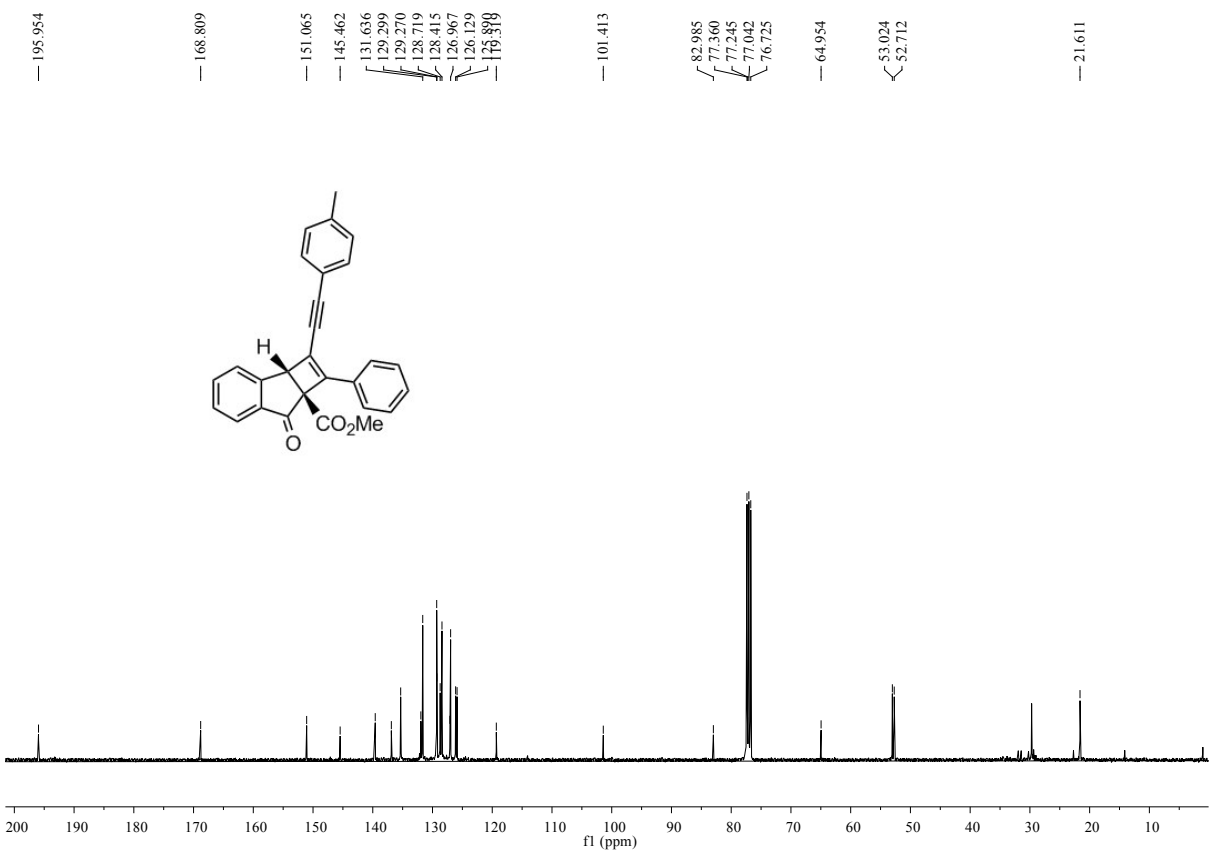

-100.979
Ph
H
F
Ph
O
O
f1 (ppm)

**6u**

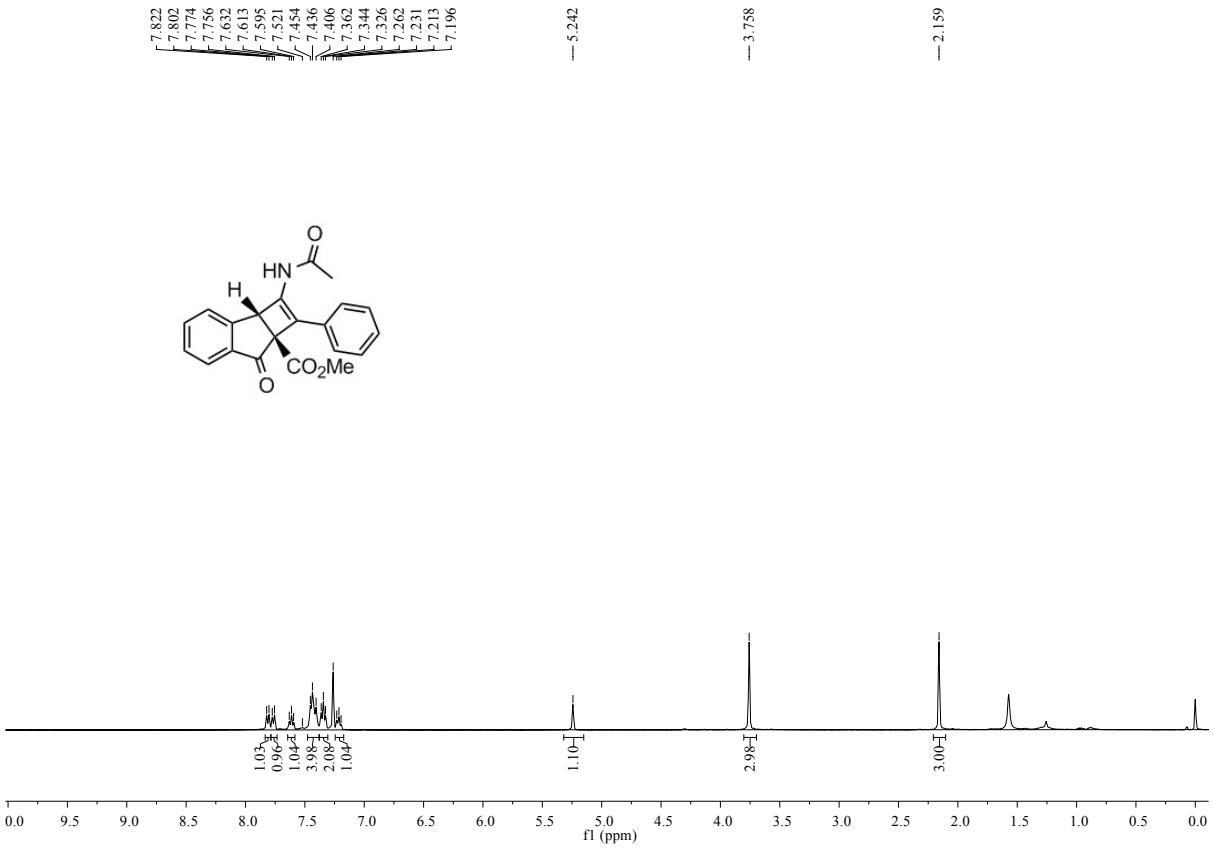

202.470
196.850
168.325
165.762
153.690
153.595
145.731
132.764
129.264
129.024
128.849
128.769
127.469
126.537
116.861
116.625
113.467
113.242
77.402
77.285
77.085
76.767
72.613
48.786
29.060
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

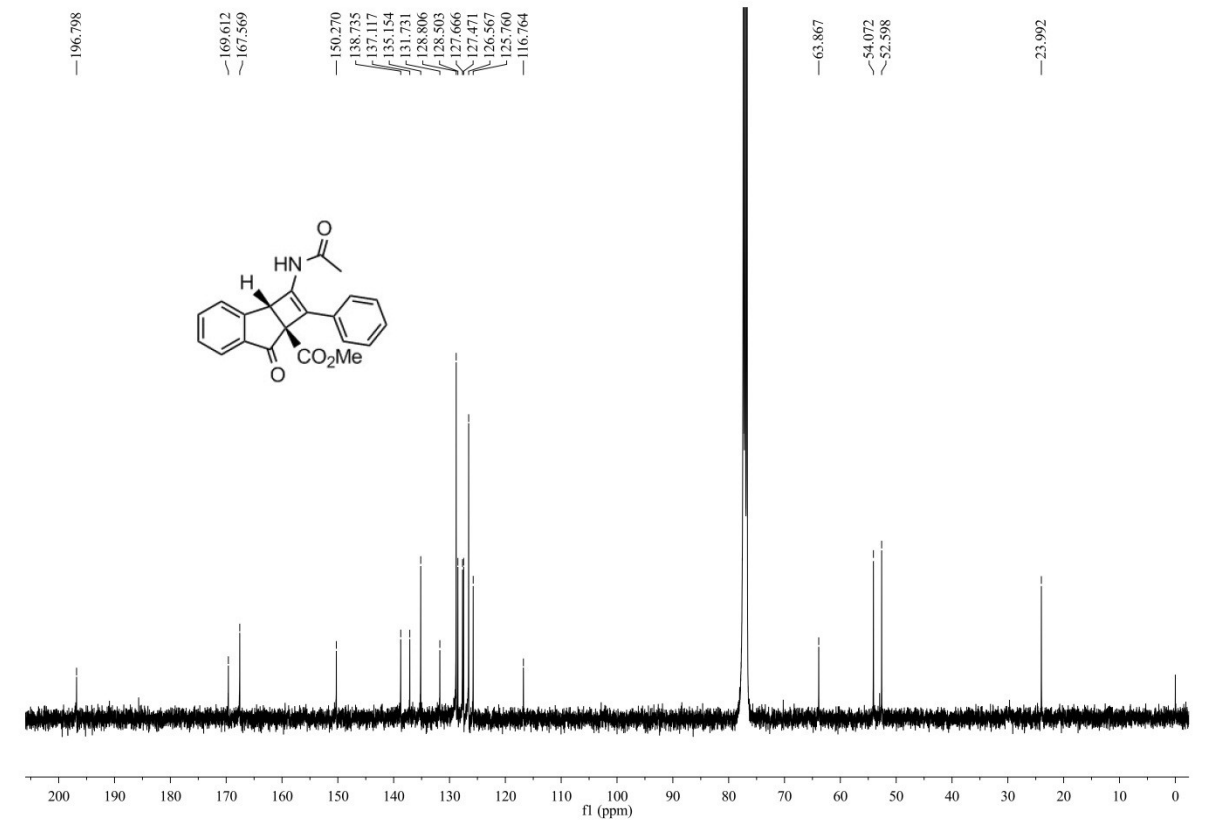
7


7.871
7.852
7.767
7.748
7.601
7.570
7.391
7.373
7.357
7.338
7.320
7.304
7.286
7.246
7.228
7.210
7.111
7.092
4.583
3.720
2.305
H
CO2Me
O
1.97
1.00
2.23
1.47
4.29
1.14
2.08
1.00
3.12
3.36
f1 (ppm)

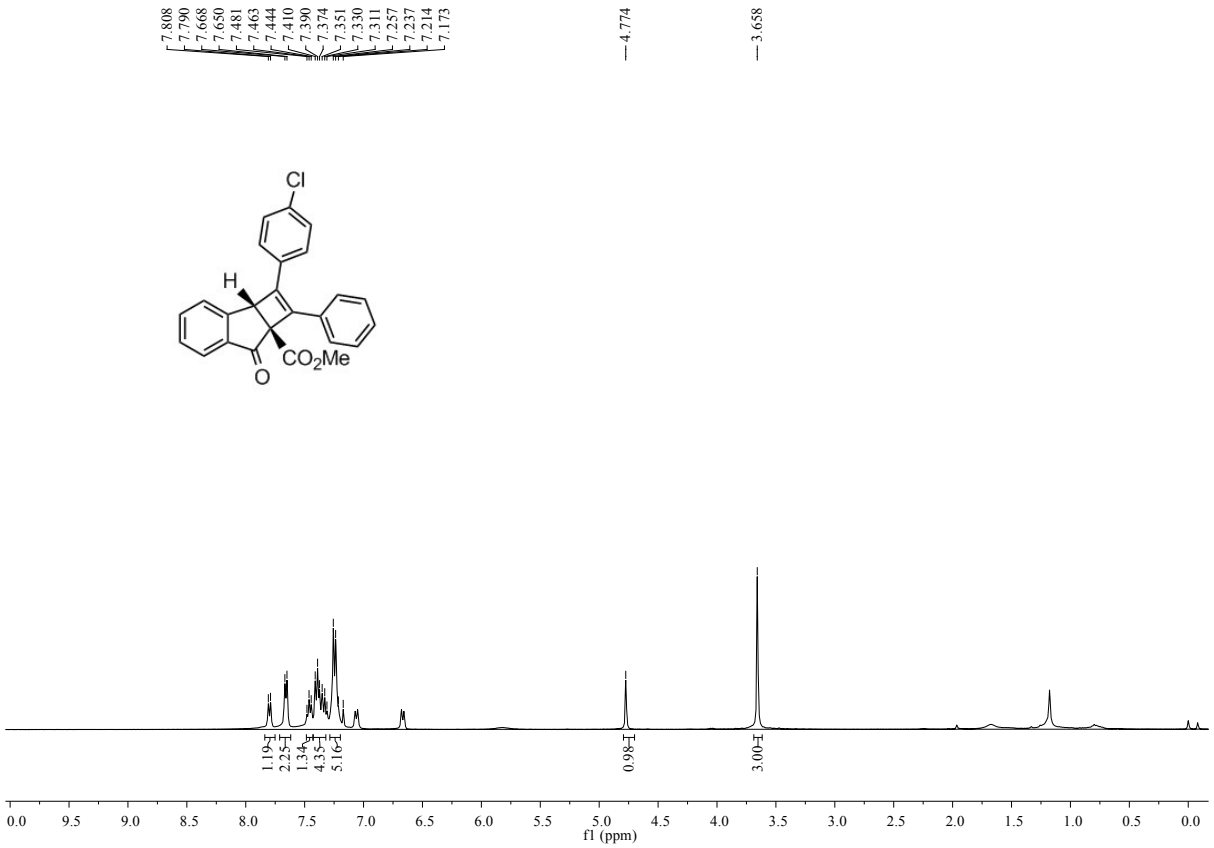

195.954
168.809
151.065
145.462
131.636
129.299
129.270
128.719
128.415
126.967
126.129
101.413
82.985
77.360
77.245
77.042
76.725
64.954
53.024
52.712
21.611
H
CO2Me
O
f1 (ppm)

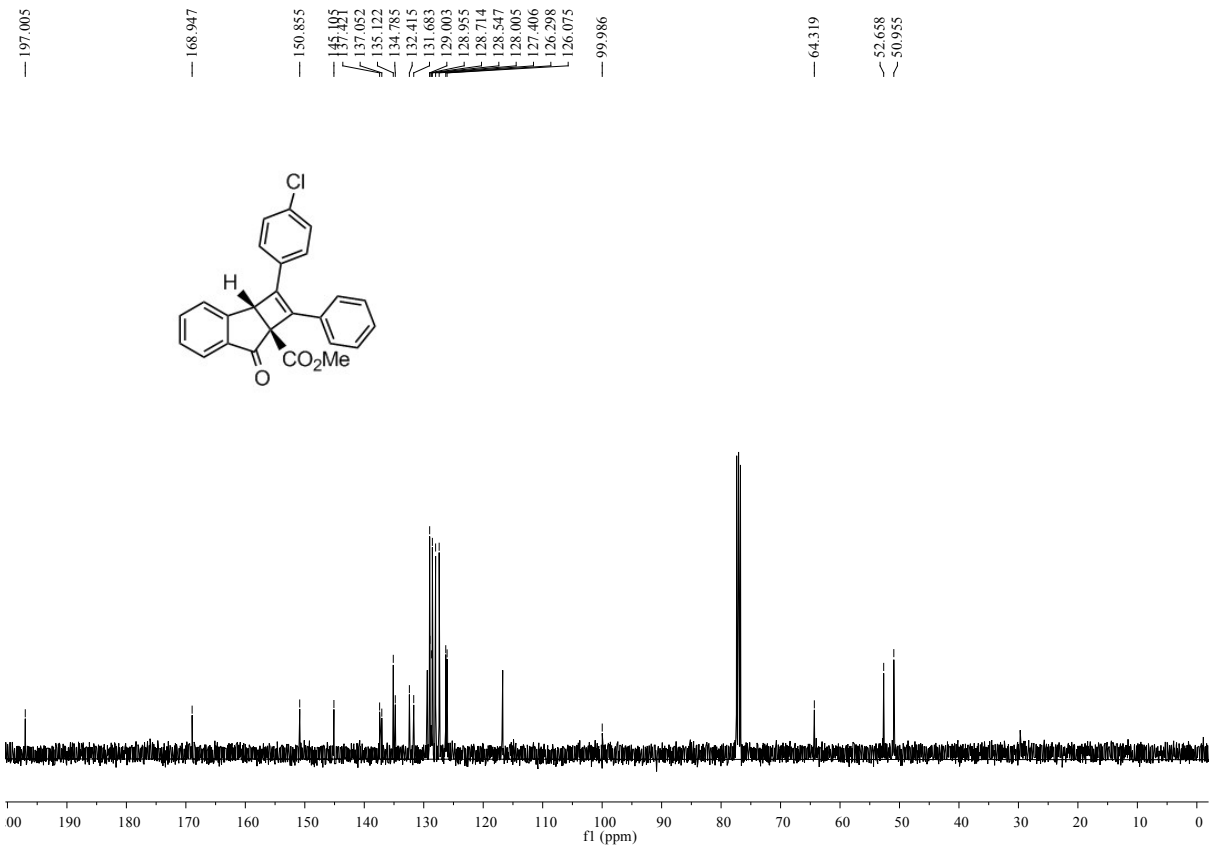
**8**


7.822
7.802
7.774
7.756
7.632
7.613
7.595
7.521
7.454
7.436
7.406
7.362
7.344
7.326
7.262
7.231
7.213
7.196
5.242
3.758
2.159
HN
H
CO2Me
O
1.03
0.96
1.04
3.98
2.08
1.04
1.10
2.98
3.00
f1 (ppm)


196.798
169.612
167.569
150.270
138.735
137.117
135.154
131.731
128.806
128.503
127.666
127.471
126.567
125.760
116.764
63.867
54.072
52.598
23.992
HN
H
CO2Me
O
f1 (ppm)

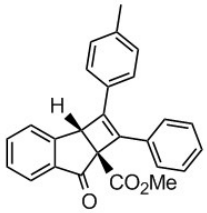
**6d**

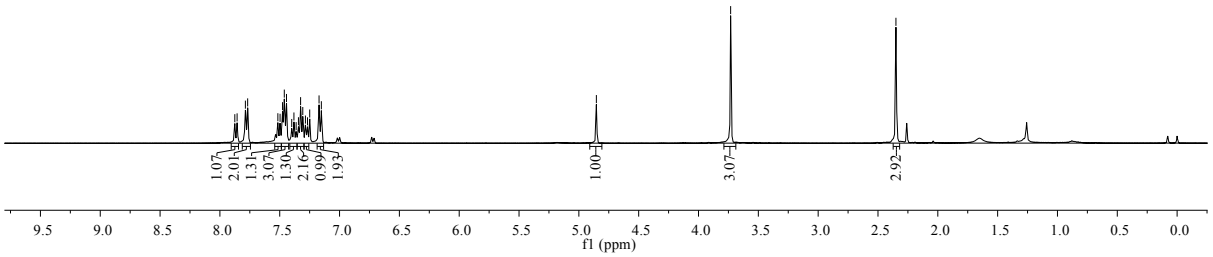

7.808
7.790
7.668
7.650
7.481
7.463
7.444
7.410
7.390
7.374
7.351
7.330
7.311
7.257
7.237
7.214
7.173
4.774
3.658
Cl
H
CO2Me
O
1.19
2.25
1.34
4.35
5.16
0.98
3.00
f1 (ppm)


197.005
168.947
150.855
145.105
137.052
135.122
134.785
132.415
131.683
129.003
128.955
128.714
128.547
128.005
127.406
126.298
126.075
99.986
64.319
52.658
50.955
Cl
H
CO2Me
O
f1 (ppm)

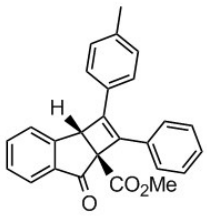
**6b'**

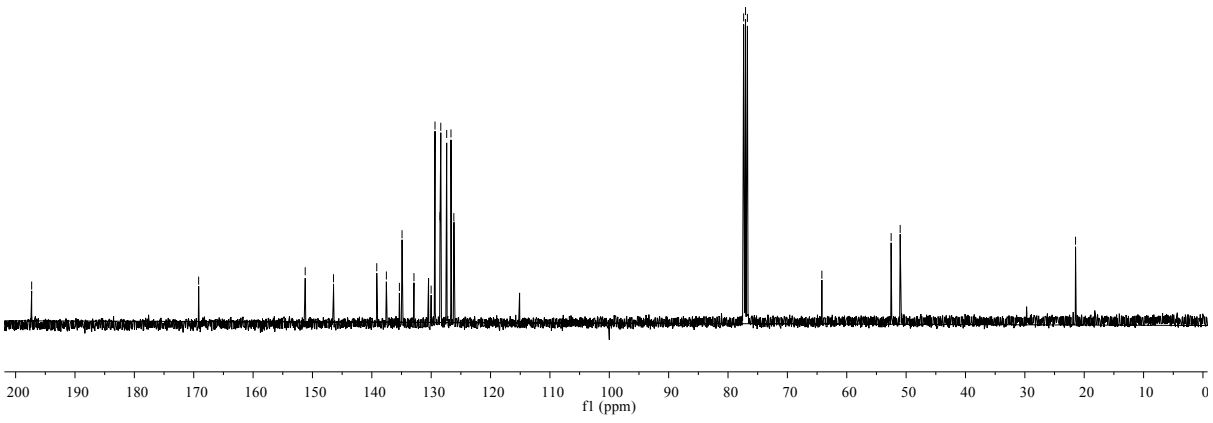

7.875
7.856
7.787
7.768
7.516
7.497
7.476
7.462
7.443
7.400
7.381
7.363
7.344
7.326
7.307
7.285
7.268
7.249
7.171
7.152
4.854
3.731
2.350


H
CO2Me
O

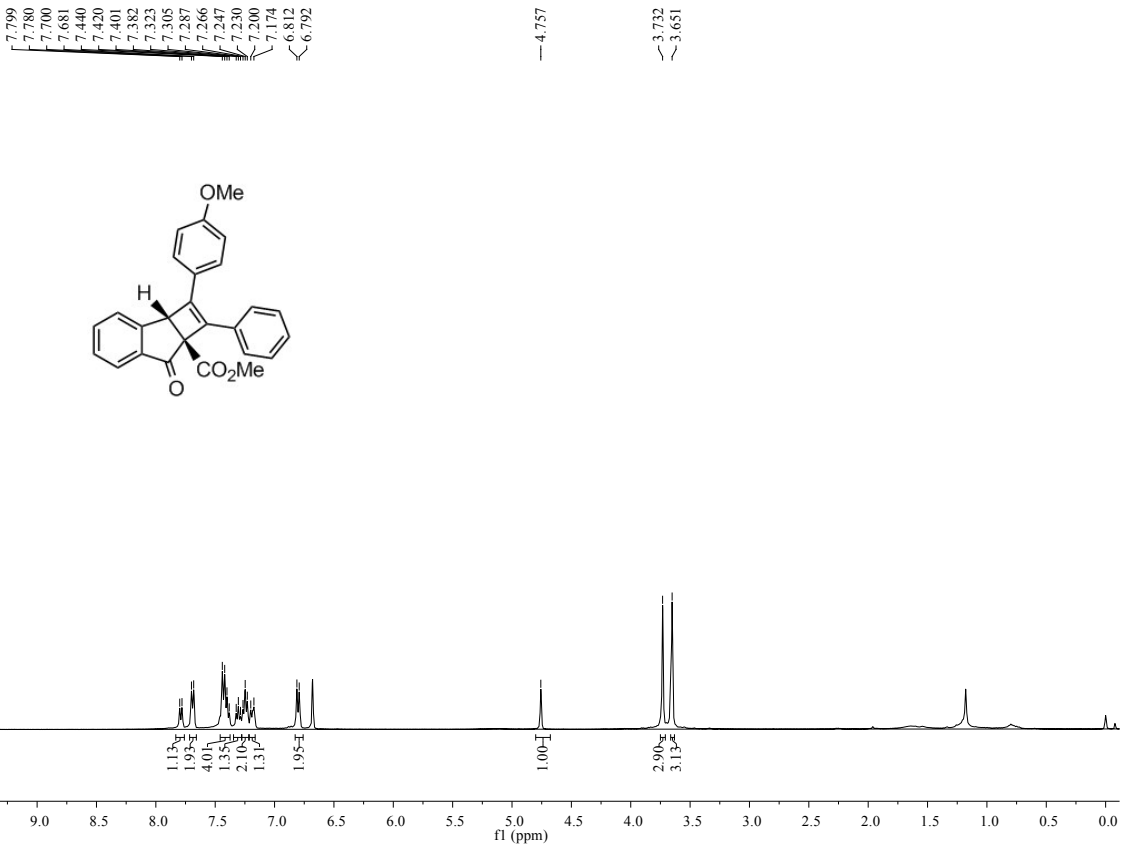

1.07
2.01
1.31
3.07
1.30
2.16
0.99
1.93
1.00
3.07
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

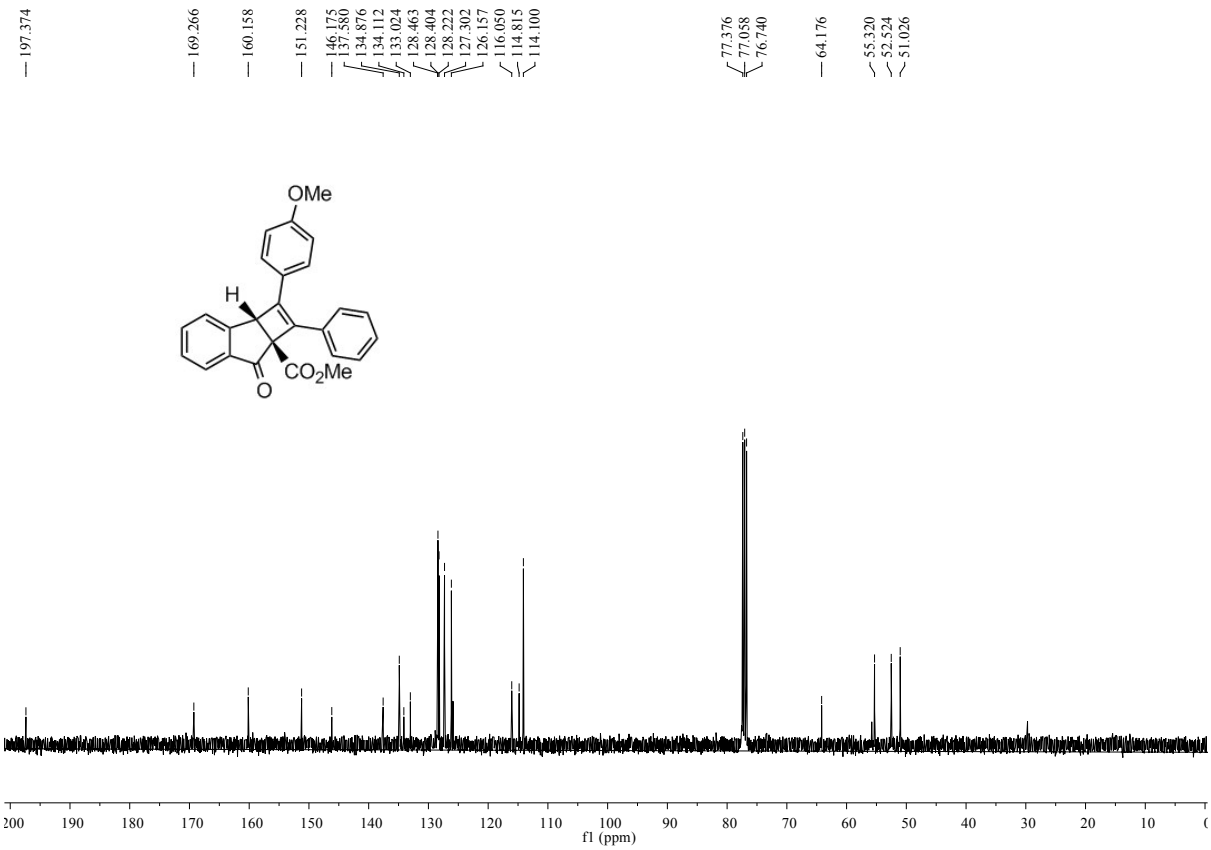

197.300
169.171
151.221
146.453
139.169
137.550
135.355
134.909
132.903
130.008
129.357
128.510
128.459
128.383
127.390
126.667
126.185
126.139
77.368
77.051
76.733
64.191
52.523
51.001
21.461


H
CO2Me
O


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

**6c'**


7.799
7.780
7.700
7.681
7.440
7.420
7.401
7.382
7.323
7.305
7.287
7.266
7.247
7.230
7.200
7.174
6.812
6.792
4.757
3.732
3.651
OMe
H
CO2Me
O
1.13
1.93
4.01
1.35
2.10
1.31
1.95
1.00
2.90
3.13
f1 (ppm)


197.374
169.266
160.158
151.228
146.175
137.580
134.876
134.112
133.024
128.463
128.404
128.222
127.302
126.157
116.050
114.815
114.100
77.376
77.058
76.740
64.176
55.320
52.524
51.026
OMe
H
CO2Me
O
f1 (ppm)