Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Double Carboxylation of *o*-Alkynyl Acetophenone with Carbon Dioxide

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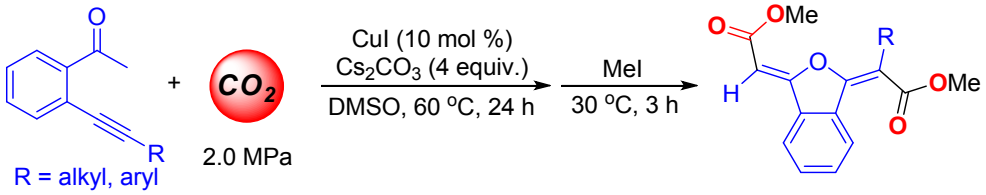
1. General Methods

Unless otherwise stated, all manipulations were performed using standard Schlenk techniques under a dry nitrogen or carbon dioxide atmosphere. DMF, DMAc and DMSO were distilled from CaH_2 at 60 °C under reduced pressure and stored over 4A molecular sieves. Column chromatography was performed on silica gel (200-300 mesh). Thin layer chromatography was performed on 0.20 mm GF254 plates. Visualization was accomplished with UV light (254 nm), cerium ammonium molybdate, and potassium permanganate.

NMR spectra were recorded on Bruker AvanceII 400M or Bruker AvanceIII 500M type (^{1}H NMR, 400 MHz or 500MHz; ^{13}C NMR, 100 MHz or 126 MHz) spectrometer in $CDCl_3$ at ambient temperature and chemical shifts are expressed in parts per million (δ, ppm). Proton chemical shifts are referenced to 7.26 ppm ($CHCl_3$) and carbon chemical shifts are referenced to 77.0 ppm ($CDCl_3$). Data reporting uses the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; hept, heptet, and *J*, coupling constant in Hz. High resolution mass spectra (HRMS) were recorded on a Q-TOF mass spectrometry (Micromass, Wythenshawe, UK) equipped with Z-spray ionization source. Infrared spectra (IR) were measured using a Nicolet NEXUS FT-IR spectrophotometer.

Unless otherwise indicated, commercially available starting materials were purchased from Energy Chemical. *o*-Alkynyl acetophenones[1] were synthesized according to literature procedures.

2. General Procedure for Double Carboxylation reactions



A 20 mL oven dried autoclave containing a stir bar was charged with *o*-alkynyl acetophenone (0.20 mmol), CuI (3.8 mg, 0.02 mmol), cesium carbonate (261 mg, 0.80 mmol) and 2.0 mL dry DMSO in a glove box. After removal from the glove box, the autoclave was purged with carbon dioxide three times and then pressurized to appropriate pressure with carbon dioxide. The reaction mixture was stirred at 60 °C for 24 h. Then the autoclave was cooled to room temperature and the remaining carbon dioxide was vented slowly. MeI (1.0 mmol) was added into the autoclave and the reaction mixture was stirred at 30

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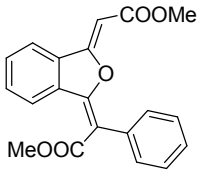
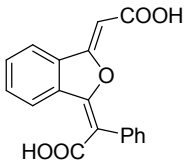
[1] (a) Dell'Acqua, M.; Abbiati, G.; Arcadi. A.; Rossi, E. *Org. Biomol. Chem.* **2011**, *9*, 7836. (b) Chernyak, N.; Gorelsky, S. I.; Gevorgyan, V. *Angew. Chem., Int. Ed.* **2011**, *50*, 2342.

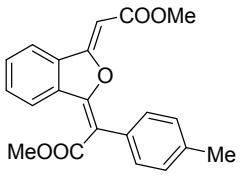
°C for 3 h. The reaction mixture was diluted with water (30 mL) and extracted with ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and brine, dried over Na_2SO_4 and filtered. The solvent was removed under vacuum. The product was isolated by column chromatography on silica gel (ethyl acetate–petroleum ether: 1 : 10).



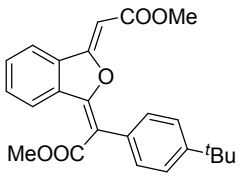
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-phenylacetate (2a). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.71-7.66 (m, 3H), 7.60-7.52 (m, 2H), 7.47-7.44 (m, 2H), 7.38-7.35 (m, 1H), 5.68 (s, 1H), 3.93 (s, 3H), 3.72 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.11, 165.47, 159.98, 154.28, 134.17, 133.49, 132.32, 131.84, 130.80, 129.60, 128.16, 128.01, 124.85, 121.14, 112.79, 90.07, 52.61, 51.40. **IR** (neat, cm^{-1}) ν 2955, 2921, 2851, 1717, 1697, 1659, 1630, 1460, 1434, 1264, 1226, 1156, 1063, 1023, 875, 805, 760, 694. **HRMS** (ESI, *m*/*z*) calcd for $C_{20}H_{17}O_5$ $[M+H]^+$: 337.1076, found: 337.1058.



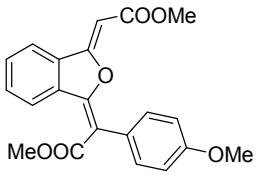
(*E*)-2-[(*Z*)-3-(1-hydroxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-phenylacetic acid (2a'). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.7 Hz, 1H), 7.90 (d, *J* = 7.9 Hz, 3H), 7.74-7.63 (m, 2H), 7.46-7.34 (m, 3H), 6.01 (s, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.65, 170.86, 164.70, 154.86, 138.15, 137.79, 137.39, 136.86, 136.08, 133.95, 133.64, 133.17, 128.16, 127.49, 118.36, 96.11. **IR** (neat, cm^{-1}) ν 2956, 2922, 2852, 2662, 2634, 1462, 1377, 1263, 1190, 1091, 1029, 761, 692. **HRMS** (ESI, *m*/*z*) calcd for $C_{18}H_{11}O_5$ $[M-H]^-$: 307.0606, found: 307.0614.



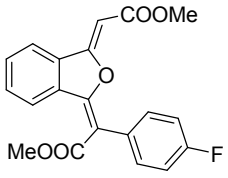
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-(4-methylphenyl)acetate (2b). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.68-7.51 (m, 5H), 7.29-7.27 (m, 2H), 5.69 (s, 1H), 3.94 (s, 3H), 3.76 (s, 3H), 2.41 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.36, 165.54, 160.21, 153.20, 138.09, 133.90, 132.45, 131.81, 130.57, 129.38, 128.98, 124.37, 121.17, 112.85, 89.72, 52.68, 51.45, 21.35. **IR** (neat, cm^{-1}) ν 2956, 1717, 1698, 1659, 1623, 1459, 1434, 1268, 1226, 1155, 1066, 874, 838, 763. **HRMS** (ESI, *m*/*z*) calcd for $C_{21}H_{19}O_5$ $[M+H]^+$: 351.1232, found: 351.1229.



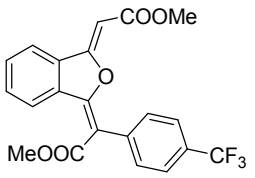
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-(4-*tert*-butylphenyl)acetate (2c). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.8 Hz, 1H), 7.72-7.66 (m, 3H), 7.57-7.48 (m, 4H), 5.69 (s, 1H), 3.96 (s, 3H), 3.77 (s, 3H), 1.36 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.39, 165.64, 160.25, 152.82, 151.16, 133.79, 132.52, 131.81, 130.51, 130.20, 129.11, 125.25, 124.16, 121.20, 112.79, 89.71, 52.69, 51.44, 34.71, 31.28. **IR** (neat, cm^{-1}) ν 2954, 2924, 2854, 1697, 1661, 1625, 1459, 1434, 1266, 1228, 1155, 1067, 873, 818, 761. **HRMS** (ESI, *m*/*z*) calcd for $C_{24}H_{25}O_5$ $[M+H]^+$: 393.1702, found: 393.1700.



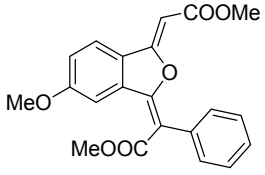
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-(4-methoxyphenyl)acetate (2d). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 7.6 Hz, 1H), 7.58-7.49 (m, 2H), 7.00 (d, *J* = 8.8 Hz, 2H), 5.69 (s, 1H), 3.96 (s, 3H), 3.87 (s, 3H), 3.78 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46, 165.58, 160.39, 159.43, 152.20, 133.65, 132.57, 131.81, 130.84, 130.36, 125.59, 123.98, 121.19, 113.79, 112.61, 89.45, 55.34, 52.71, 51.45. **IR** (neat, cm^{-1}) ν 2924, 2851, 1695, 1658, 1622, 1601, 1512, 1459, 1434, 1258, 1227, 1156, 1066, 873, 834, 801, 762. **HRMS** (ESI, *m*/*z*) calcd for $C_{21}H_{19}O_6$ $[M+H]^+$: 367.1182, found: 367.1177.



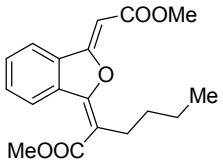
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-(4-fluorophenyl)acetate (2e). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.72-7.68 (m, 3H), 7.64-7.55 (m, 2H), 7.18 (t, *J* = 8.7 Hz, 2H), 5.72 (s, 1H), 3.95 (s, 3H), 3.75 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.94, 165.36, 163.32, 161.34, 159.93, 154.50, 134.18, 132.16, 131.92, 131.54, 130.94, 124.95, 121.17, 115.28, 115.11, 111.74, 90.14, 52.68, 51.46. **IR** (neat, cm^{-1}) ν 2951, 2923, 2852, 1698, 1663, 1624, 1509, 1434, 1266, 1227, 1157, 1067, 873, 837, 814, 761. **HRMS** (ESI, *m*/*z*) calcd for $C_{20}H_{16}O_5F$ $[M+H]^+$: 355.0982, found: 355.0977.



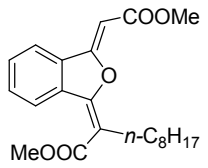
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-(4-trifluoromethylphenyl)acetate (2f). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 2H), 7.72-7.69 (m, 3H), 7.63-7.57 (m, 2H), 5.72 (s, 1H), 3.91 (s, 3H), 3.68 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.44, 165.25, 159.49, 156.21, 137.43, 134.50, 132.03, 131.82, 131.43, 130.10, 129.62, 125.59, 125.02, 124.99, 121.19, 111.28, 90.84, 52.72, 51.47. **IR** (neat, cm^{-1}) ν 2955, 2926, 2854, 1709, 1609, 1434, 1326, 1267, 1234, 1167, 1106, 1068, 836, 817, 762, 718. **HRMS** (ESI, *m*/*z*) calcd for $C_{21}H_{15}O_5F_3Na$ $[M+Na]^+$: 427.0769, found: 427.0758.



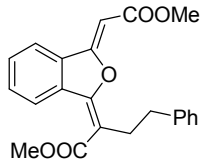
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-6-methoxy-1(3*H*)-isobenzofuranylidene]-2-phenylacetate (2g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69-7.67 (m, 3H), 7.56 (d, *J* = 8.6 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 7.10 (dd, *J* = 8.6, 2.2 Hz, 1H), 5.55 (s, 1H), 3.92 (s, 6H), 3.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.10, 164.68, 161.72, 158.94, 153.43, 133.10, 132.54, 128.59, 127.11, 126.96, 126.04, 121.32, 118.27, 111.80, 107.07, 87.54, 54.72, 51.58, 50.29. **IR** (neat, cm^{-1}) ν 3057, 1950, 2926, 2842, 1715, 1659, 1612, 1488, 1435, 1326, 1266, 1237, 1152, 1084, 1061, 835, 813, 766, 732, 692. **HRMS** (ESI, *m*/*z*) calcd for $C_{21}H_{18}O_6Na$ $[M+Na]^+$: 389.1001, found: 389.1013.



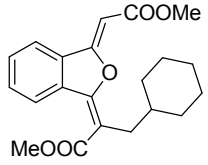
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]caproate (2h). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.5 Hz, 1H), 7.58-7.48 (m, 2H), 5.68 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 2.81 (t, *J* = 7.4 Hz, 2H), 1.62-1.54 (m, 2H), 1.46-1.41 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.18, 164.65, 159.21, 157.14, 133.95, 130.96, 130.77, 129.55, 125.52, 119.75, 112.87, 88.05, 50.86, 50.34, 30.19, 27.61, 21.62, 12.93. **IR** (neat, cm^{-1}) ν 2953, 2860, 1708, 1664, 1614, 1455, 1435, 1251, 1154, 1095, 1058, 815, 764. **HRMS** (ESI, *m*/*z*) calcd for $C_{18}H_{20}O_5Na$ $[M+Na]^+$: 339.1208, found: 339.1216.



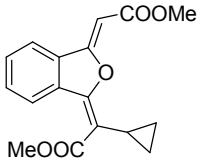
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]caprate (2i). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.9 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.57-7.48 (m, 2H), 5.68 (s, 1H), 3.87 (s, 3H), 3.81 (s, 3H), 2.79 (t, *J* = 7.6 Hz, 2H), 1.33-1.22 (m, 12H), 0.86 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.20, 165.66, 160.23, 158.11, 134.96, 131.98, 131.78, 130.56, 126.53, 120.77, 113.93, 89.05, 51.87, 51.35, 31.89, 30.91, 29.50, 29.07, 28.88, 22.67, 14.09. **IR** (neat, cm^{-1}) ν 2960, 2925, 2852, 1712, 1665, 1614, 1455, 1434, 1261, 1155, 1099, 1066, 1020, 872, 800, 767, 700. **HRMS** (ESI, *m*/*z*) calcd for $C_{22}H_{28}O_5Na$ $[M+Na]^+$: 395.1834, found: 395.1845.



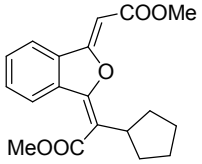
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-4-phenylbutyrate (2j). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 7.6 Hz, 1H), 7.53-7.44 (m, 2H), 7.30-7.18 (m, 4H), 7.12 (t, *J* = 7.3 Hz, 1H), 5.64 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.05-3.01 (m, 2H), 2.88-2.82 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.84, 164.51, 158.92, 158.09, 140.71, 134.05, 130.82, 129.78, 127.68, 127.17, 125.93, 124.86, 119.74, 111.64, 88.47, 50.86, 50.42, 34.43, 30.06. **IR** (neat, cm^{-1}) ν 3026, 2949, 2859, 1711, 1666, 1614, 1454, 1435, 1313, 1250, 1191, 1149, 1084, 1063, 1021, 817, 765, 702, 655. **HRMS** (ESI, *m*/*z*) calcd for $C_{22}H_{20}O_5Na$ $[M+Na]^+$: 387.1208, found: 387.1216.



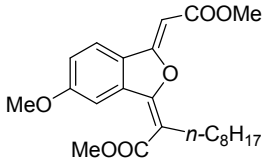
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-3-cyclohexylpropionate (2k). **^{1}H NMR** (400 MHz, $CDCl_3$) δ8.55 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 7.6 Hz, 1H), 7.58-7.46 (m, 2H), 5.67 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 2.73 (d, *J* = 7.0 Hz, 2H), 1.76-1.61 (m, 5H), 1.33-1.06 (m, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.42, 165.70, 160.06, 158.34, 134.98, 131.91, 131.75, 130.55, 126.47, 120.79, 112.75, 89.09, 51.88, 51.36, 38.22, 36.22, 33.12, 26.48, 26.34. **IR** (neat, cm^{-1}) ν 2923, 2850, 1708, 1664, 1612, 1473, 1448, 1305, 1247, 1169, 1156, 1104, 1077, 1060, 815, 762. **HRMS** (ESI, *m*/*z*) calcd for $C_{21}H_{25}O_5$ $[M+H]^+$: 357.1702, found: 357.1682.



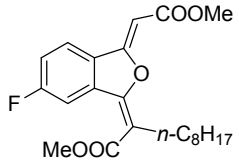
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-cyclopropylacetate (2l). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 1H), 7.66-7.64 (m, 1H), 7.55-7.46 (m, 2H), 5.69 (s, 1H), 3.90 (s, 3H), 3.83 (s, 3H), 2.22-2.18 (m 1H), 1.04-0.91 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.54, 164.70, 159.90, 154.15, 132.80, 131.08, 130.69, 129.01, 123.00, 119.97, 113.65, 87.45, 51.08, 50.27, 9.82, 6.26. **IR** (neat, cm^{-1}) ν 3083, 3005, 2949, 2849, 1715, 1664, 1636, 1434, 1354, 1266, 1154, 1068, 1018, 815, 763, 717. **HRMS** (ESI, *m*/*z*) calcd for $C_{17}H_{16}O_5Na$ $[M+Na]^+$: 323.0895, found: 323.0885.



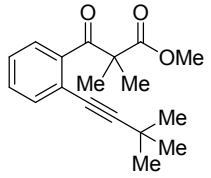
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-2-cyclopentylacetate (2m). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.53-7.44 (m, 2H), 5.65 (s, 1H), 3.90 (s, 3H), 3.80 (s, 3H), 2.03-1.67 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.46, 165.71, 160.87, 153.34, 134.09, 132.19, 131.65, 129.98, 123.71, 120.99, 116.84, 88.25, 51.91, 51.26, 39.33, 31.37, 25.88. **IR** (neat, cm^{-1}) ν 2950, 2870, 1716, 1666, 1639, 1473, 1459, 1434, 1306, 1250, 1154, 1061, 840, 813, 763, 717. **HRMS** (ESI, *m*/*z*) calcd for $C_{19}H_{20}O_5Na$ $[M+Na]^+$: 351.1208, found: 351.1219.



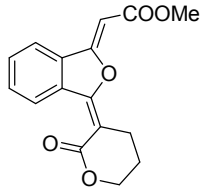
Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-6-methoxy-1(3*H*)-isobenzofuranylidene]caprate (2o). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.3 Hz, 1H), 5.55 (s, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.80 (s, 3H), 2.79 (t, J = 7.4 Hz, 2H), 1.63-0.85 (m, 15H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.21, 165.87, 162.79, 160.27, 158.23, 133.89, 127.82, 121.95, 119.26, 114.06, 109.54, 93.13, 87.54, 55.73, 51.89, 51.24, 31.91, 29.59, 29.44, 29.11, 28.93, 22.68, 14.11. **IR** (neat, cm^{-1}) ν 3138, 2926, 2855, 1707, 1661, 1609, 1485, 1435, 1326, 1264, 1237, 1156, 1122, 1100, 1066, 808, 784, 723. **HRMS** (ESI, *m*/*z*) calcd for $C_{23}H_{30}O_6Na$ $[M+Na]^+$: 425.1940, found: 425.1934.



Methyl (*E*)-2-[(*Z*)-3-(1-methoxycarbonylmethylidene)-6-fluoro-1(3*H*)-isobenzofuranylidene]caprate (2p). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.35 (dd, *J* = 10.0, 2.2 Hz, 1H), 7.57 (dd, *J* = 8.6, 4.9 Hz, 1H), 7.19 (td, *J* = 8.4, 2.3 Hz, 1H), 5.59 (s, 1H), 3.86 (s, 3H), 3.79 (s, 3H), 2.76 (t, *J* = 7.4 Hz, 2H), 1.64-1.48 (m, 2H), 1.42-1.18 (m, 10H), 0.85 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.84, 164.80, 164.44, 162.81, 158.32, 156.37, 132.96, 129.98, 121.44, 117.88, 117.68, 114.02, 112.77, 112.55, 87.97, 50.98, 50.34, 30.86, 28.56, 28.37, 28.28, 27.99, 27.81, 21.64, 13.07. **IR** (neat, cm^{-1}) ν 3123, 2952, 2927, 2855, 1710, 1665, 1615, 1477, 1435, 1358, 1261, 1213, 1153, 1121, 1099, 1066, 809, 635. **HRMS** (ESI, *m*/*z*) calcd for $C_{22}H_{27}O_5FNa$ $[M+Na]^+$: 413.1740, found: 413.1732.

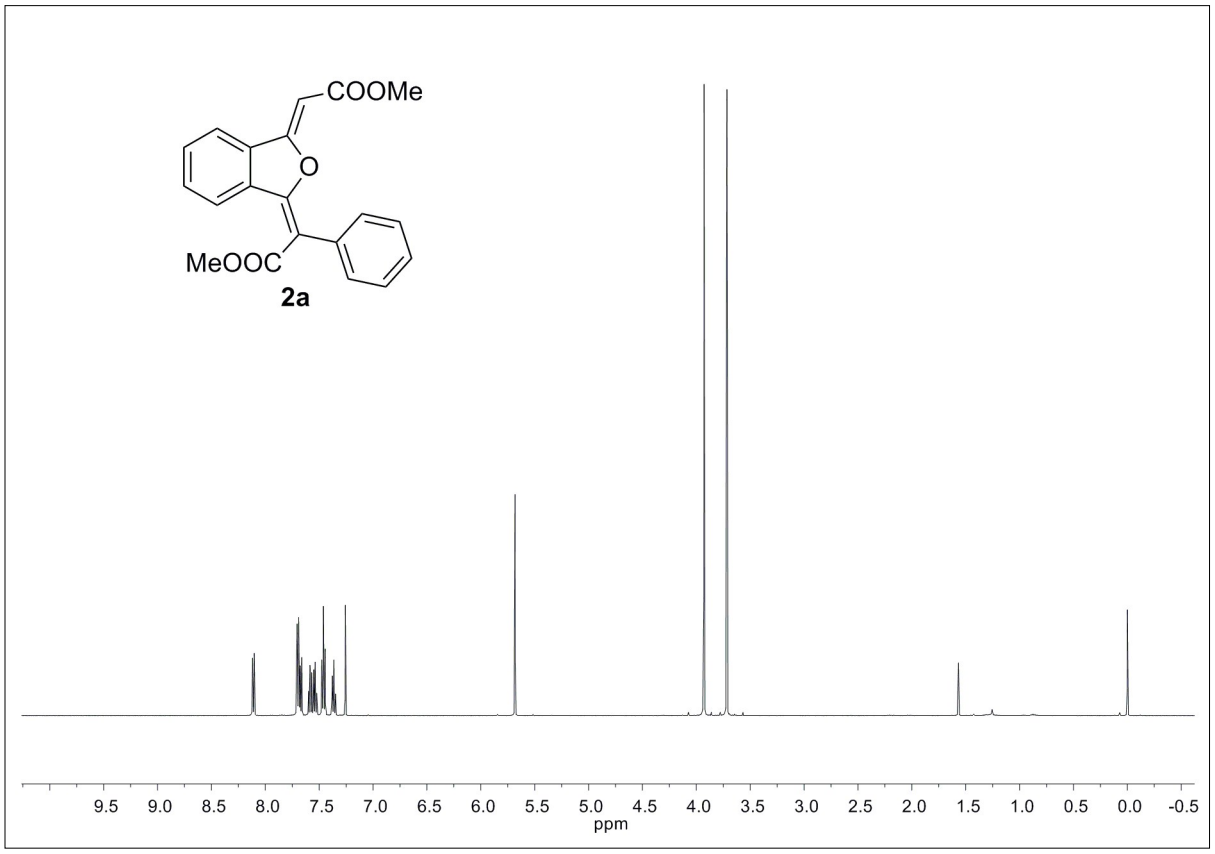


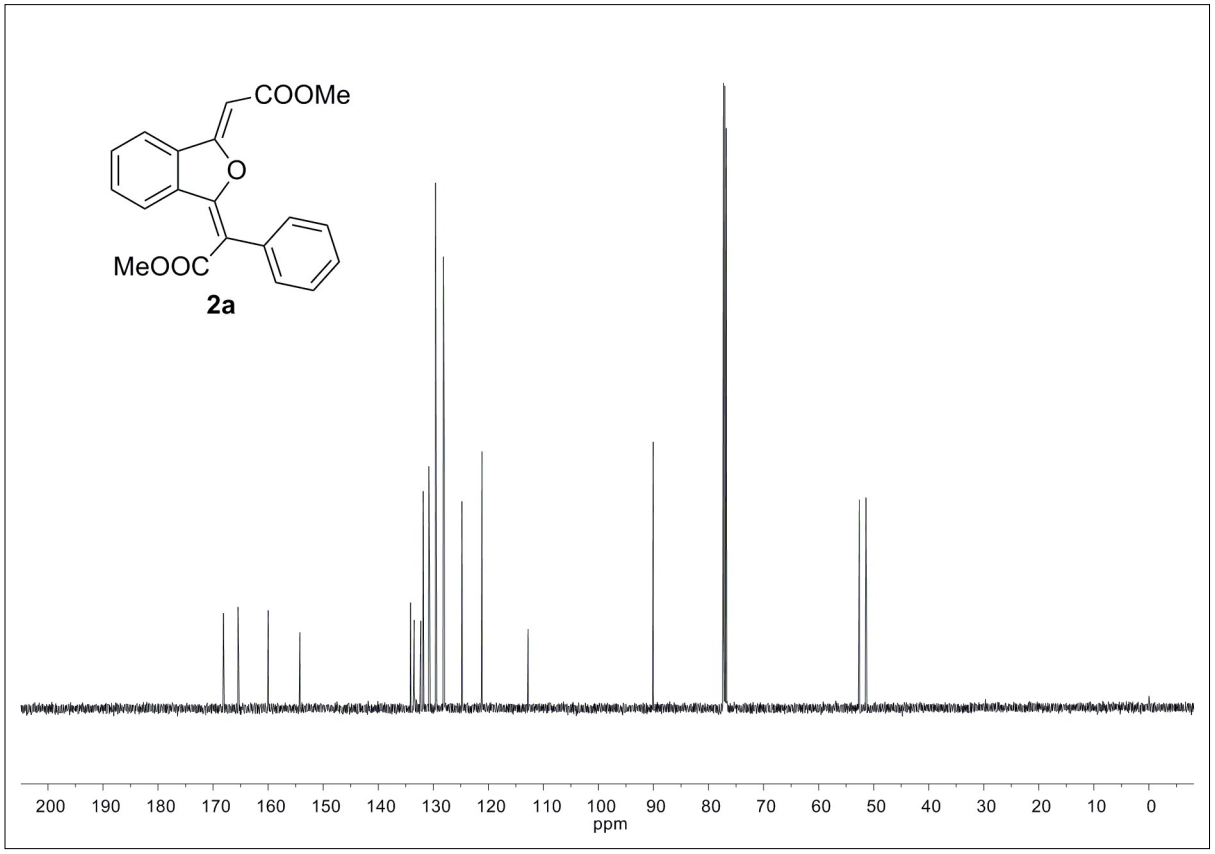
Methyl 2,2-dimethyl-3-oxo-3-[2-(3,3-dimethylbutynyl)phenyl]propionate (4). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.30-7.24 (m, 2H), 7.16 (dd, *J* = 7.7, 1.0 Hz, 1H), 3.70 (s, 3H), 1.51 (s, 6H), 1.29 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 203.69, 173.90, 142.13, 132.88, 129.09, 126.85, 124.66, 121.41, 102.44, 56.07, 52.42, 30.68, 28.05, 23.04. **IR** (neat, cm^{-1}) ν 3063, 2970, 2869, 2239, 1743, 1707, 1473, 1441, 1363, 1274, 1146, 964, 950, 841, 795, 758. **HRMS** (ESI, *m*/*z*) calcd for $C_{18}H_{22}O_3Na$ $[M+Na]^+$: 309.1467, found: 309.1479.

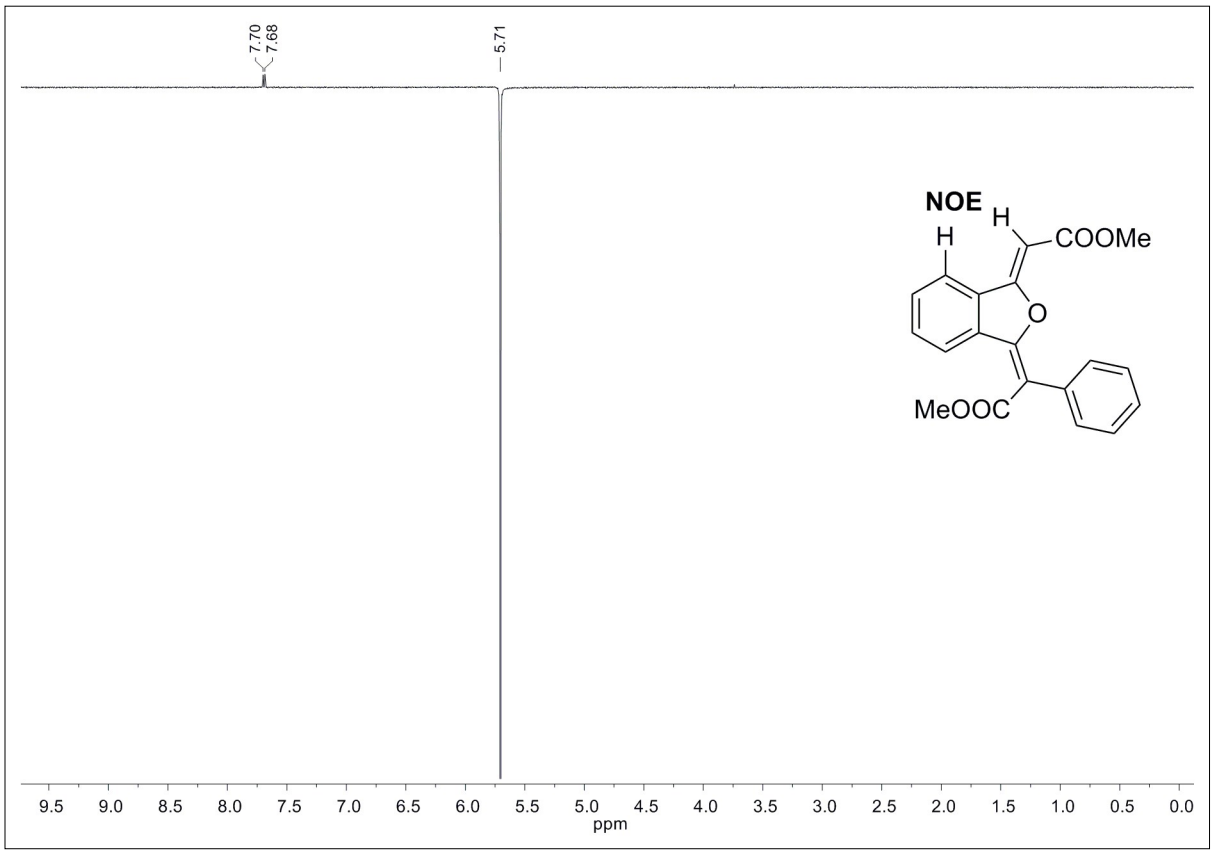


(*E*)-α-[(*Z*)-3-(1-methoxycarbonylmethylidene)-1(3*H*)-isobenzofuranylidene]-δ-valerolactone (5). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.99 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 7.7 Hz, 1H), 7.64-7.54 (m, 2H), 5.78 (s, 1H), 4.37 (t, *J* = 6.8 Hz, 2H), 3.82 (s, 3H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.06-2.03 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.97, 165.36, 160.63, 160.17, 135.06, 132.26, 131.52, 131.33, 128.11, 120.65, 106.20, 90.07, 68.63, 51.42, 24.65, 22.22. **IR** (neat, cm^{-1}) ν 3125, 3080, 2950, 1701, 1664, 1601, 1473, 1325, 1303, 1272, 1252, 1155, 1093, 1060, 976, 816, 770, 747, 730. **HRMS** (ESI, *m*/*z*) calcd for $C_{16}H_{14}O_5Na$ $[M+Na]^+$: 309.0739, found: 309.0742.

3. ^{1}H NMR and ^{13}C NMR Spectra of New Compounds



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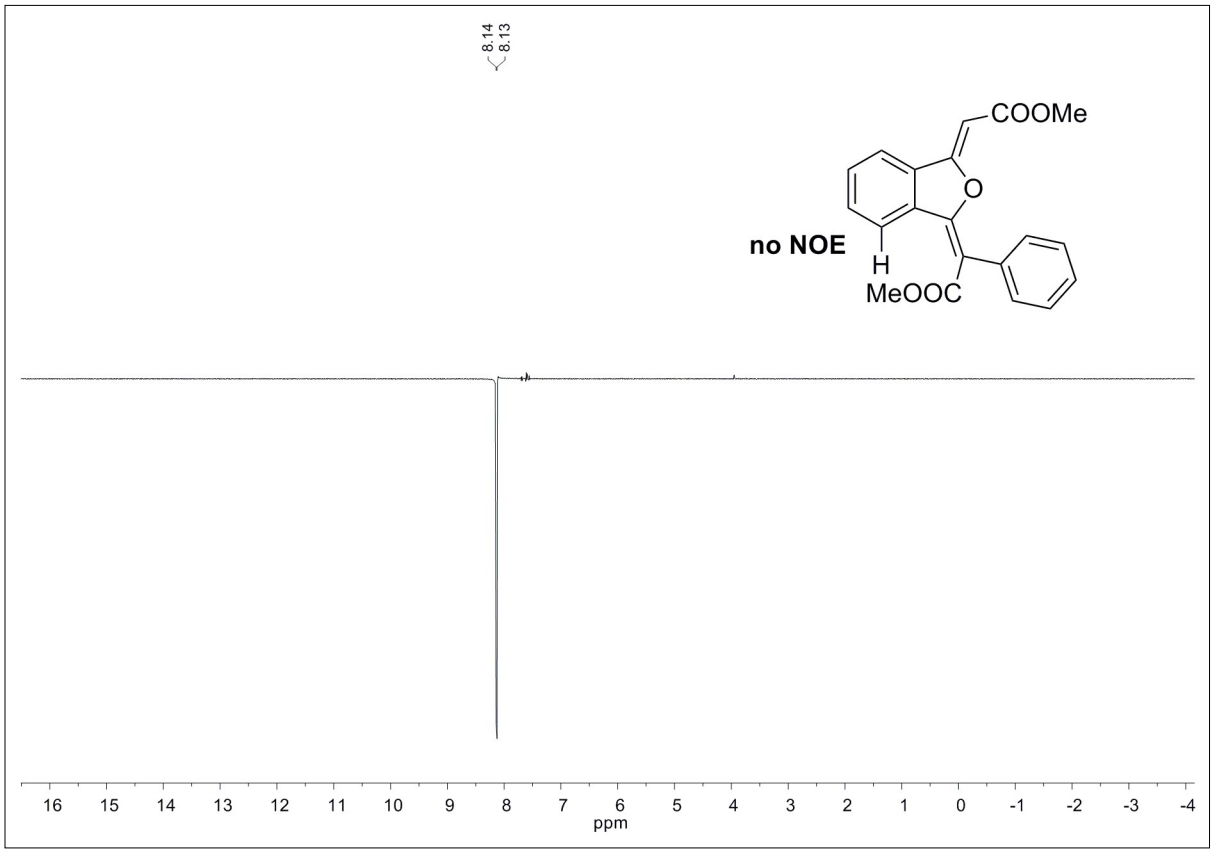
ppm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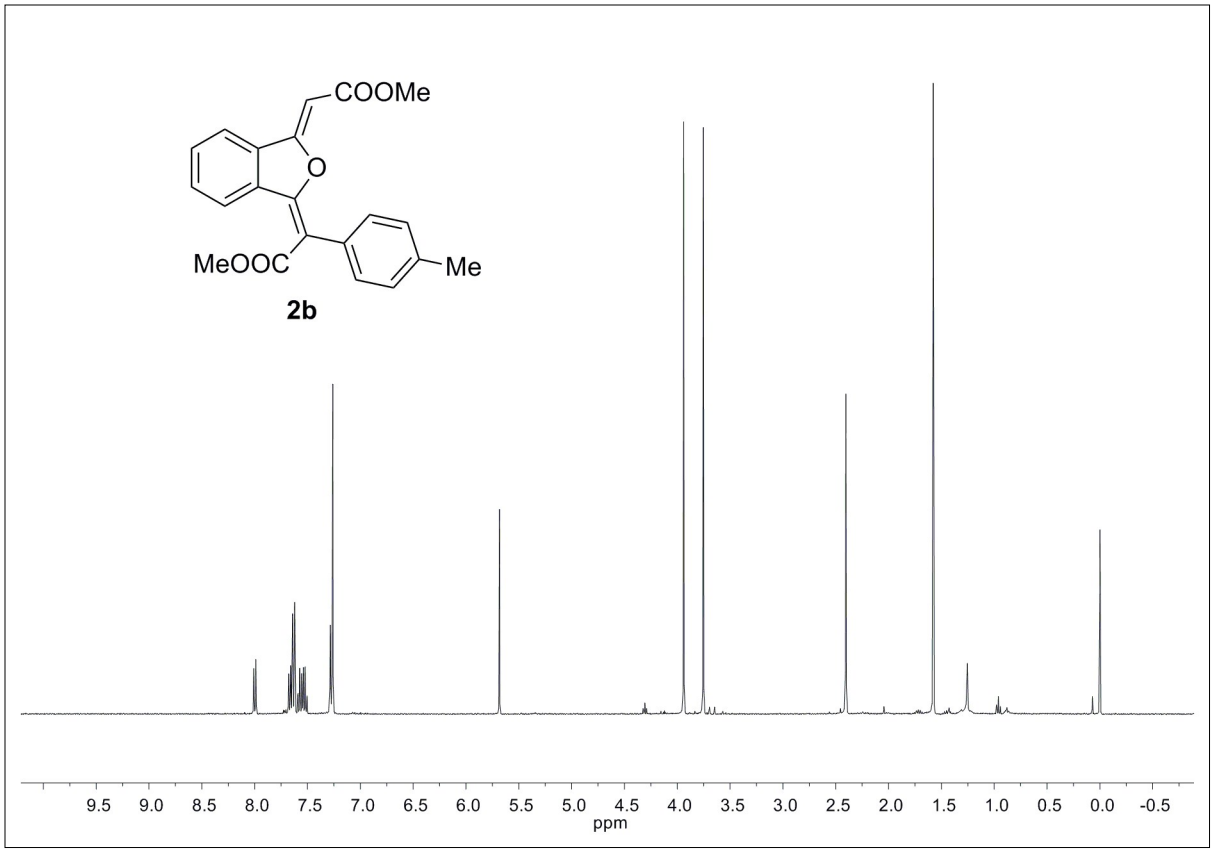
ppm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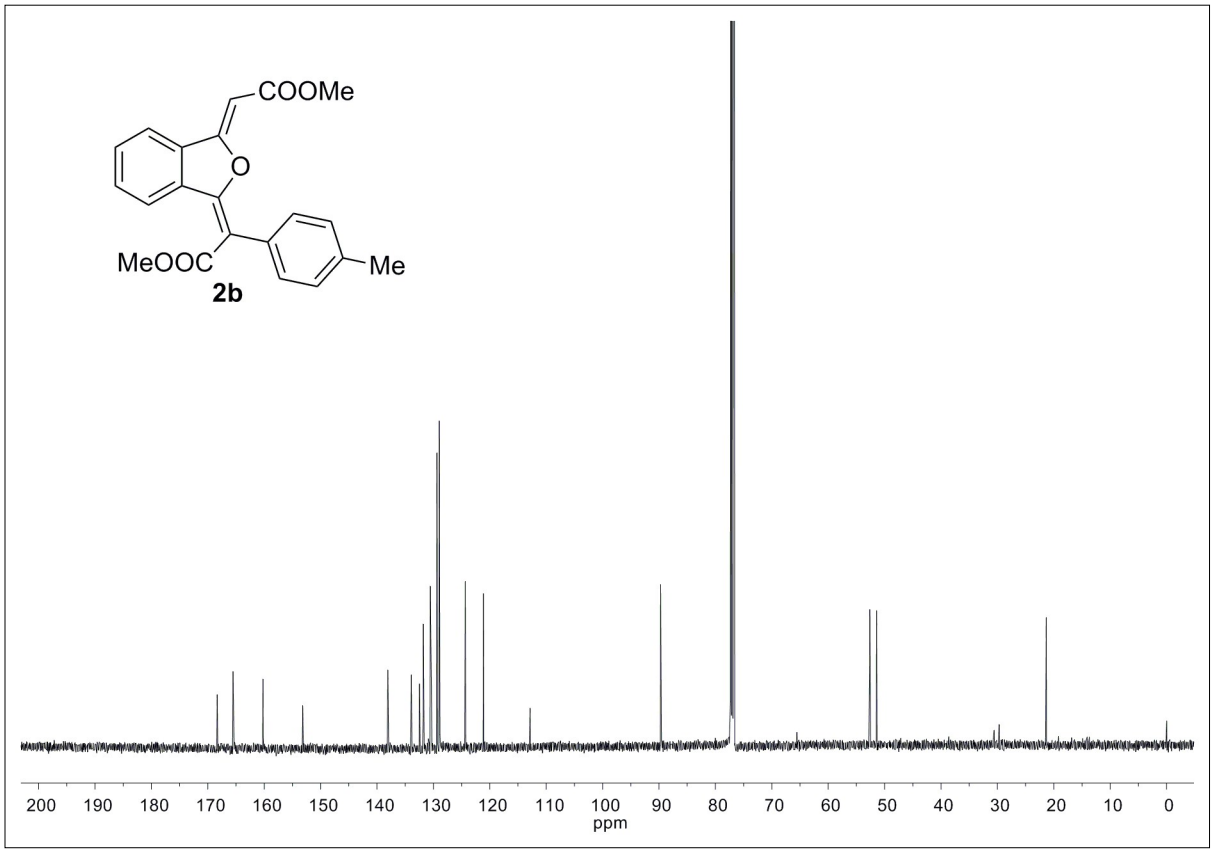
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Me
2b
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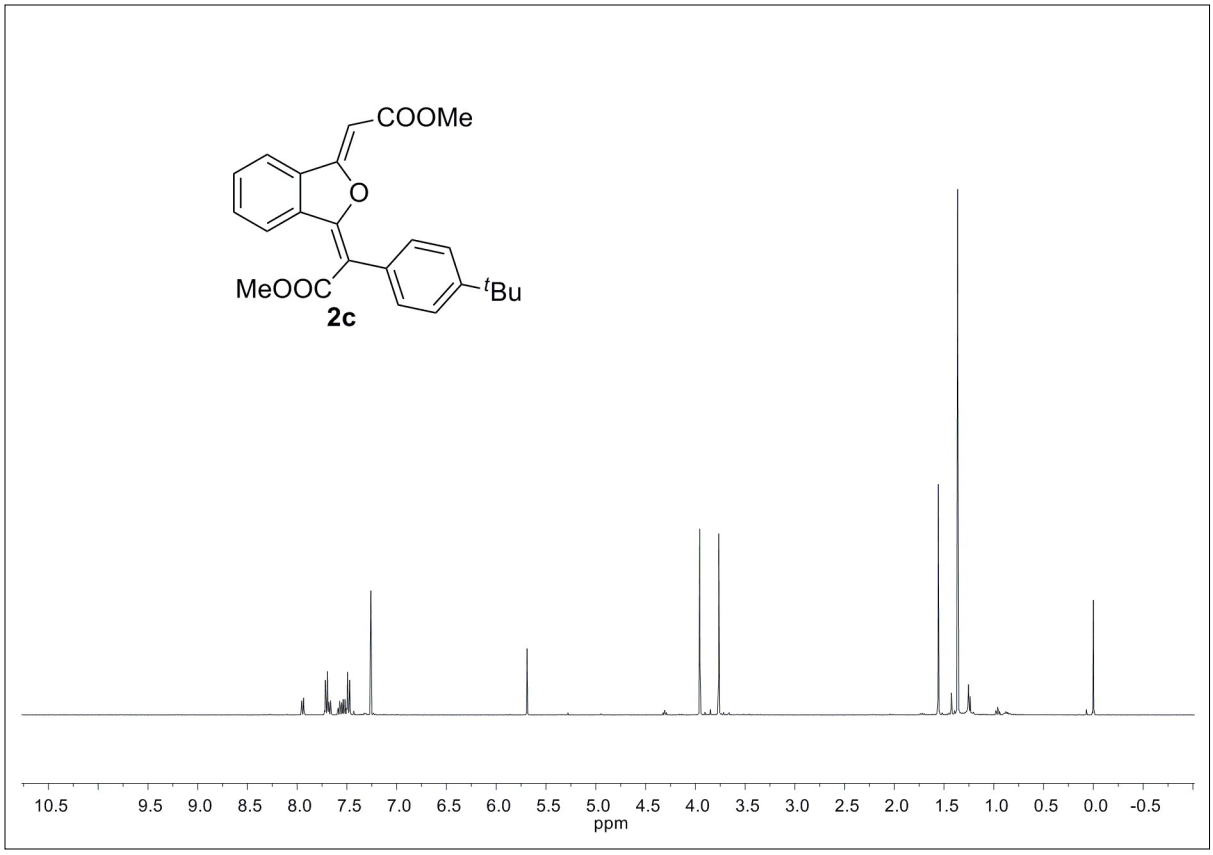
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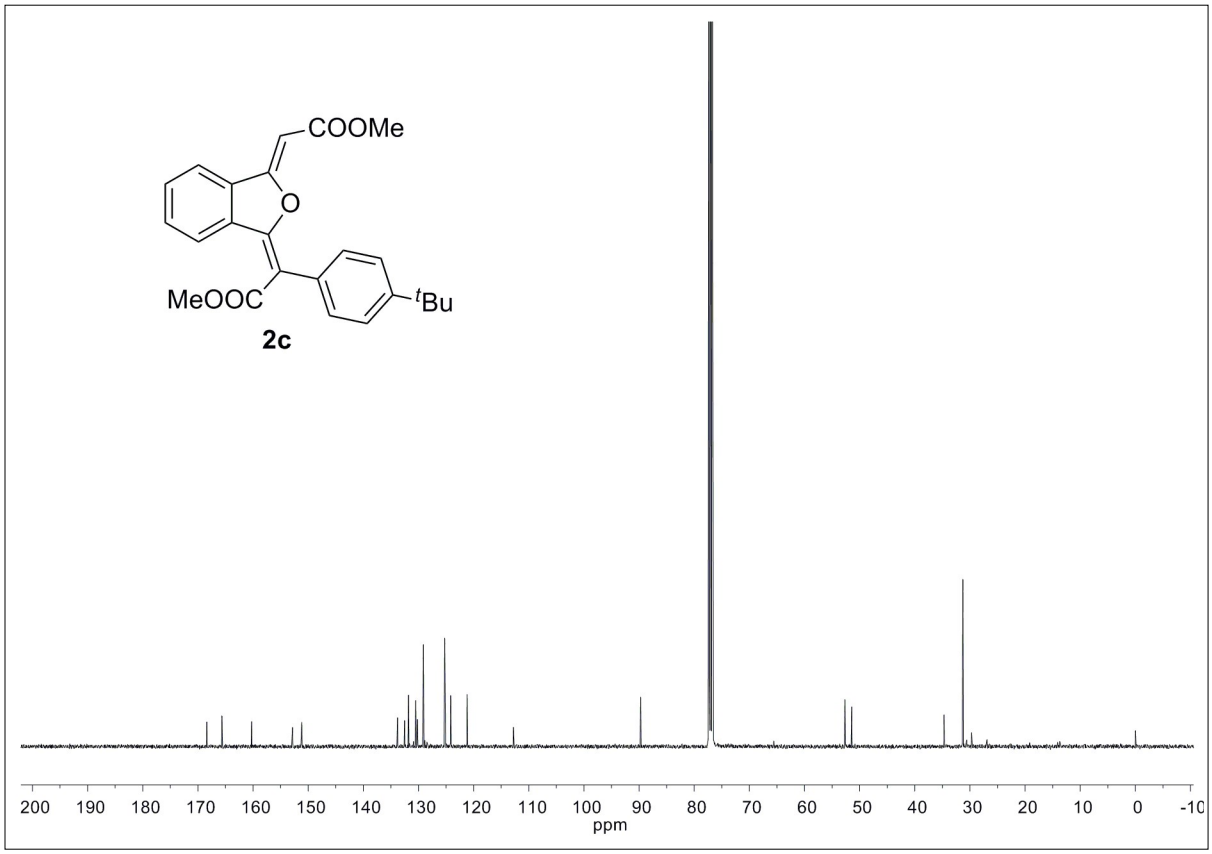
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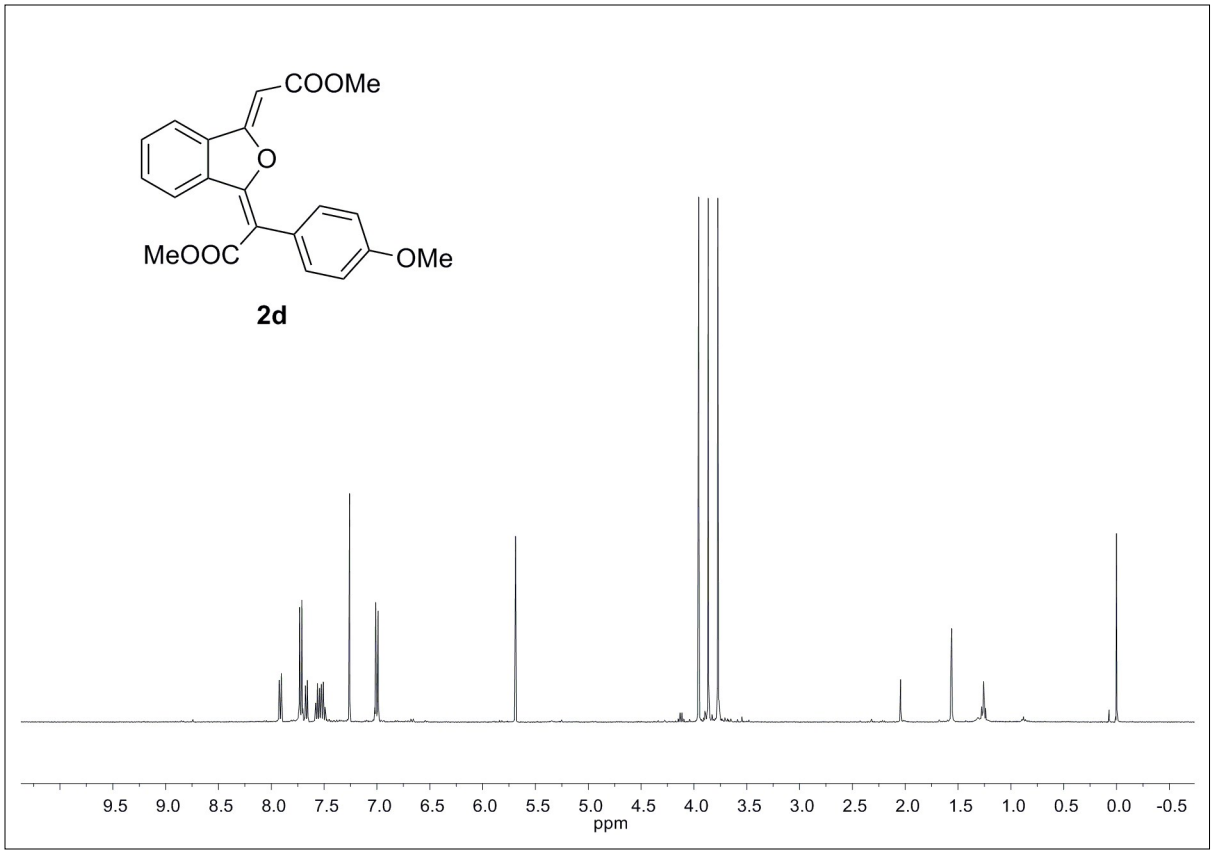
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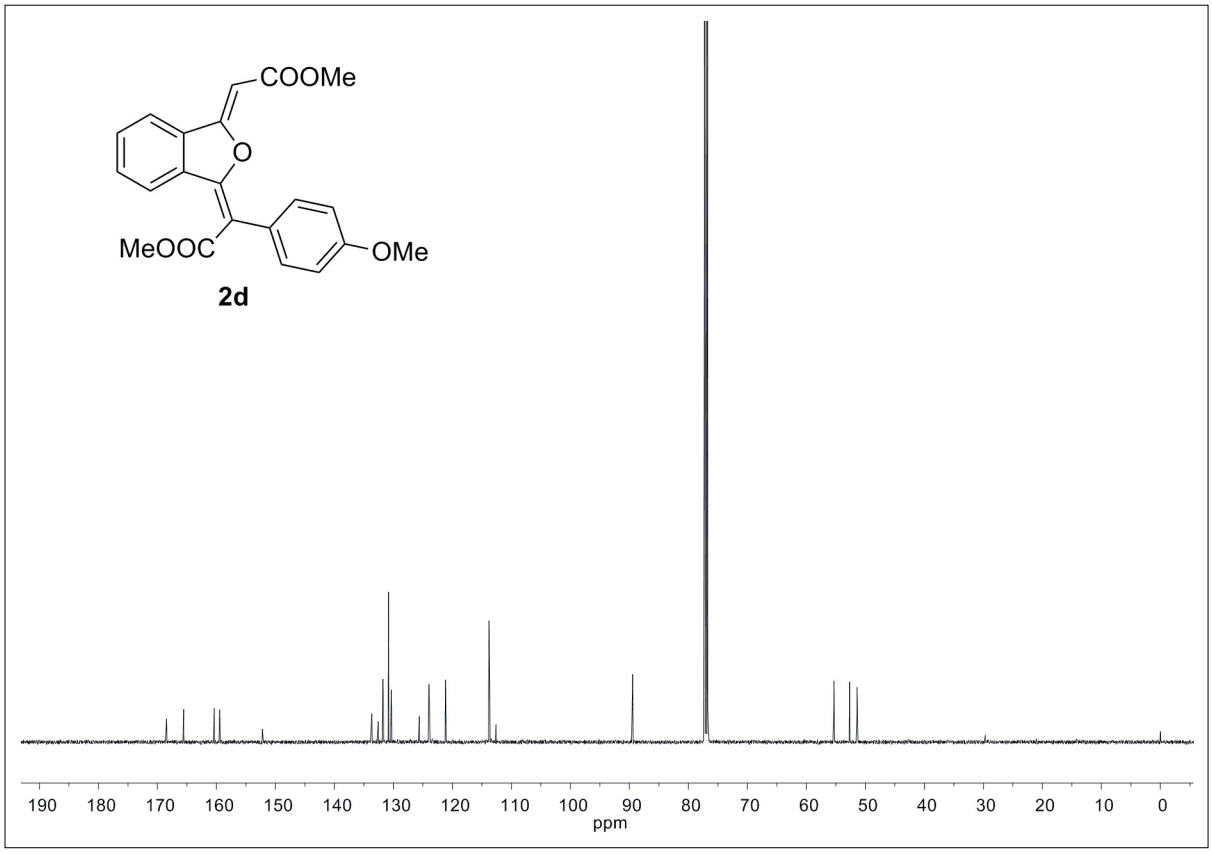
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OMe
2d
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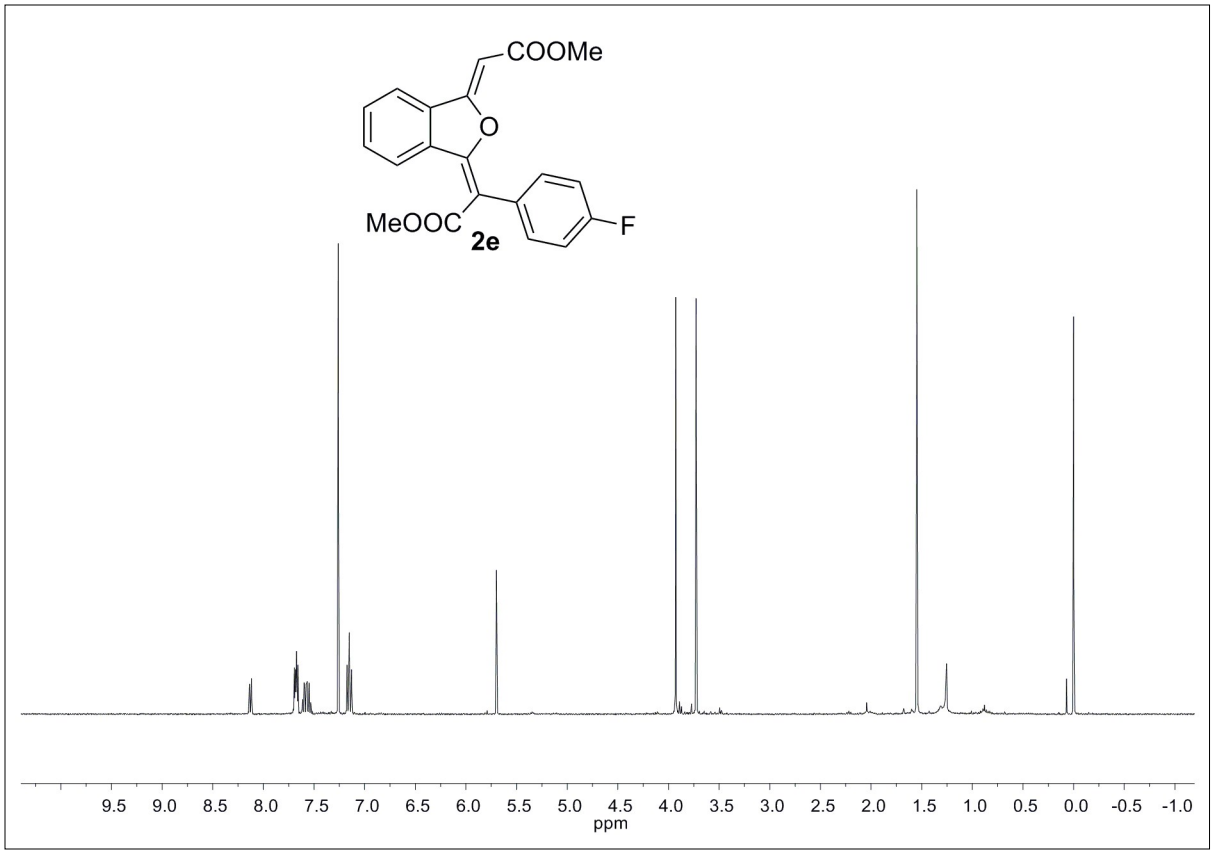
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F
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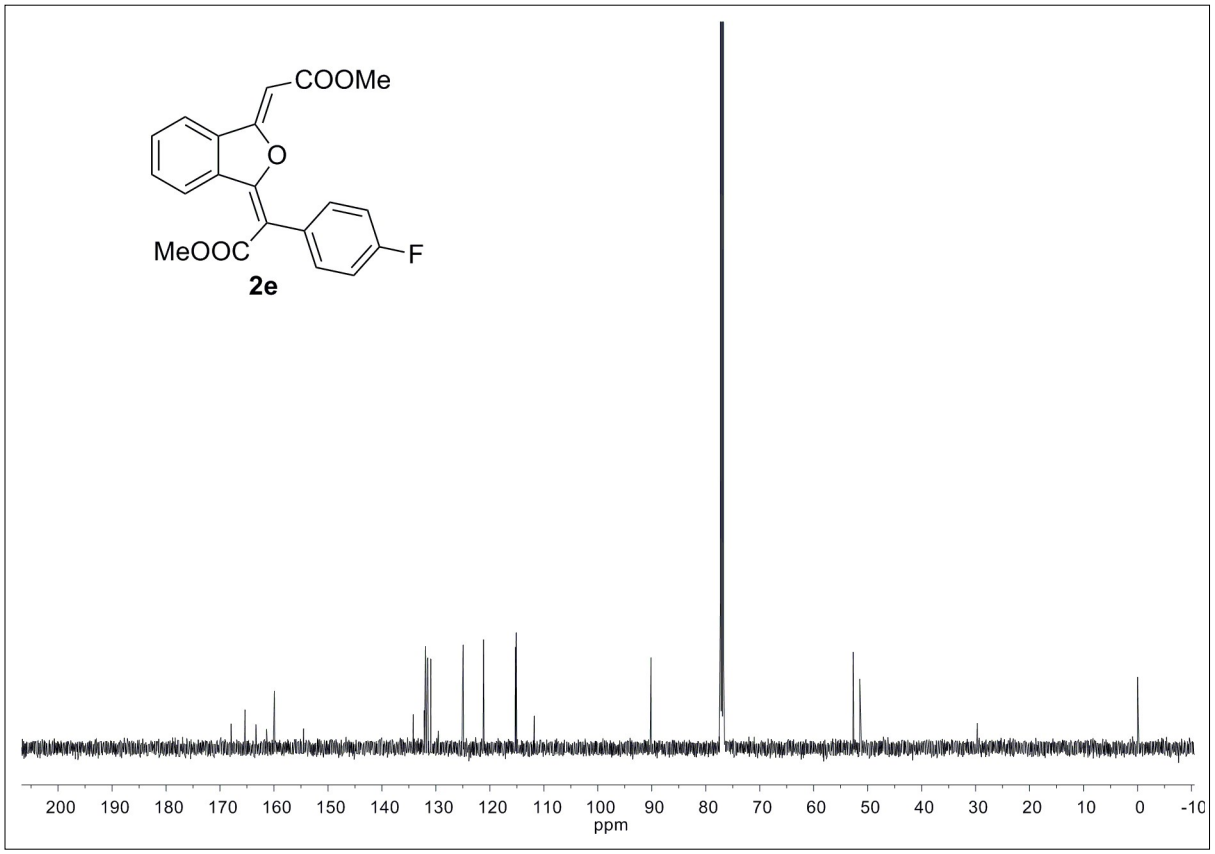
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F
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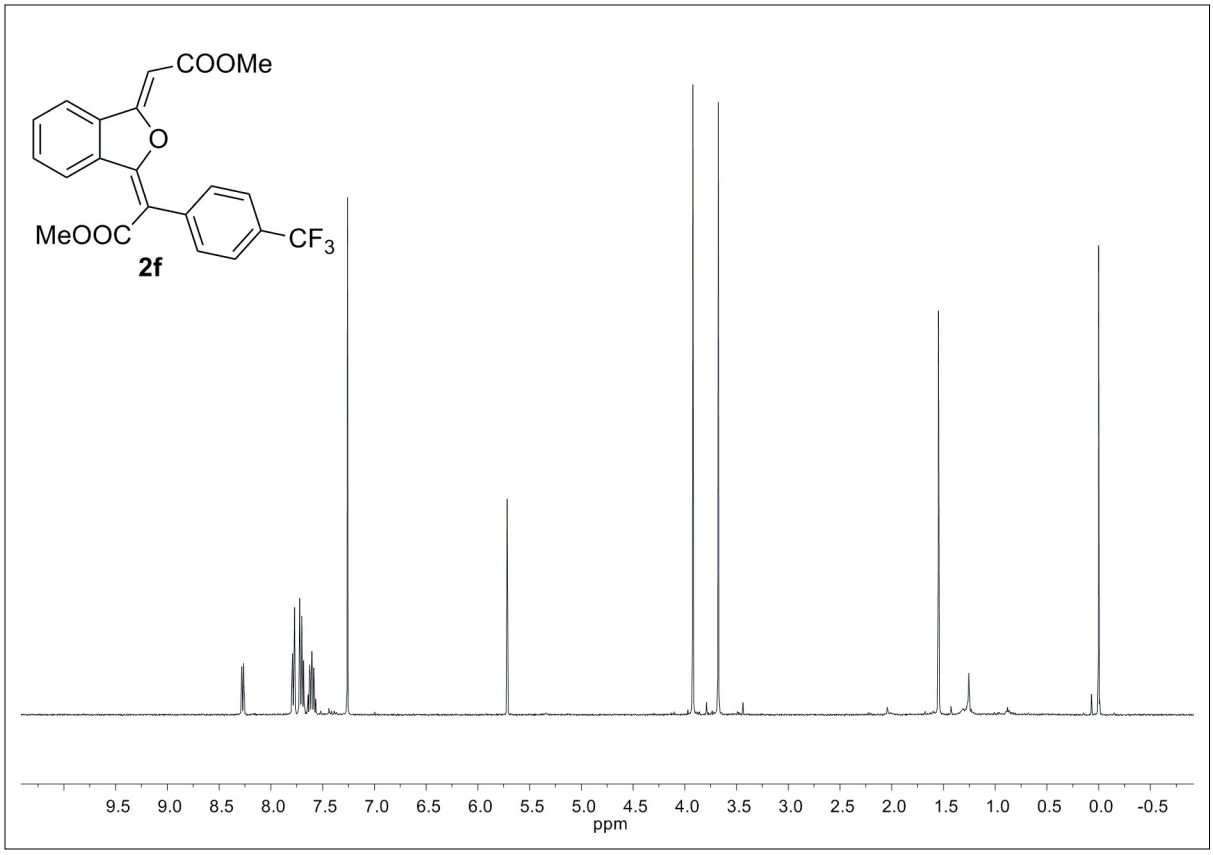
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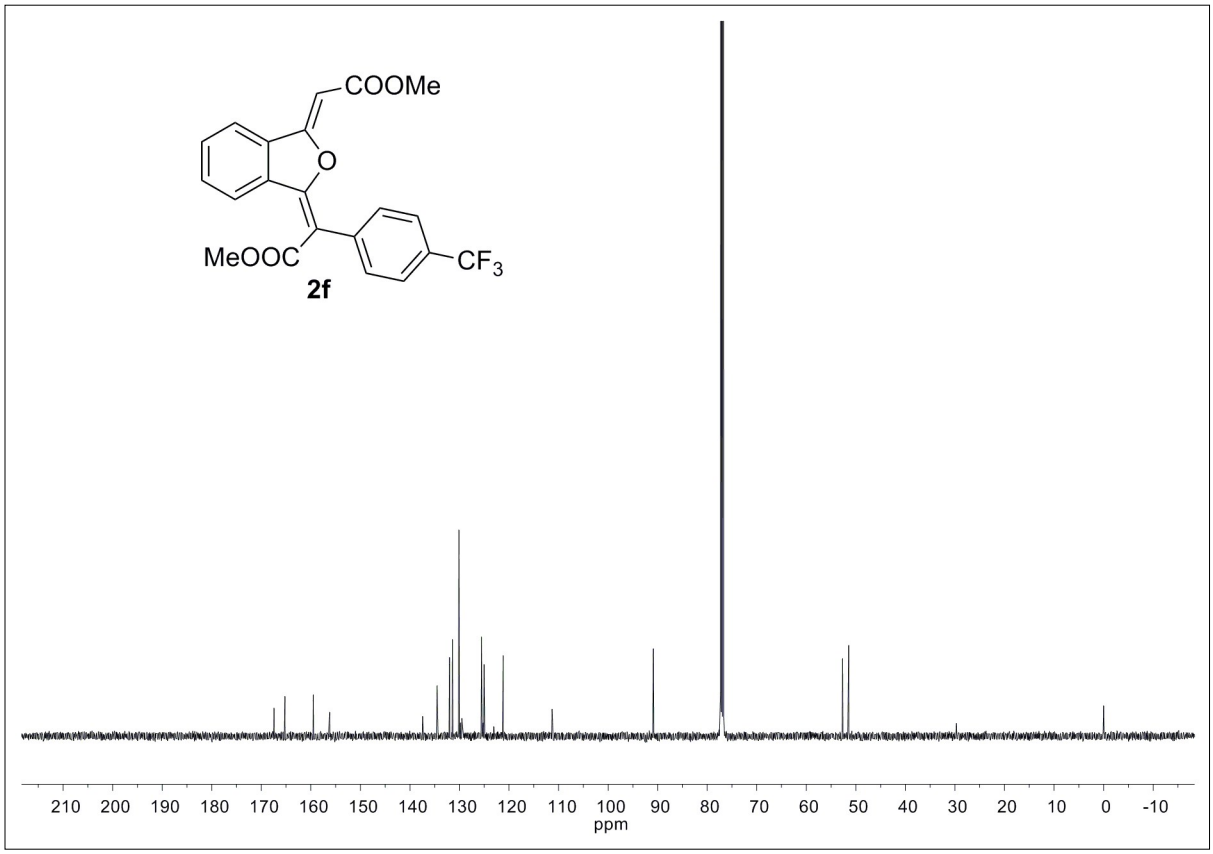
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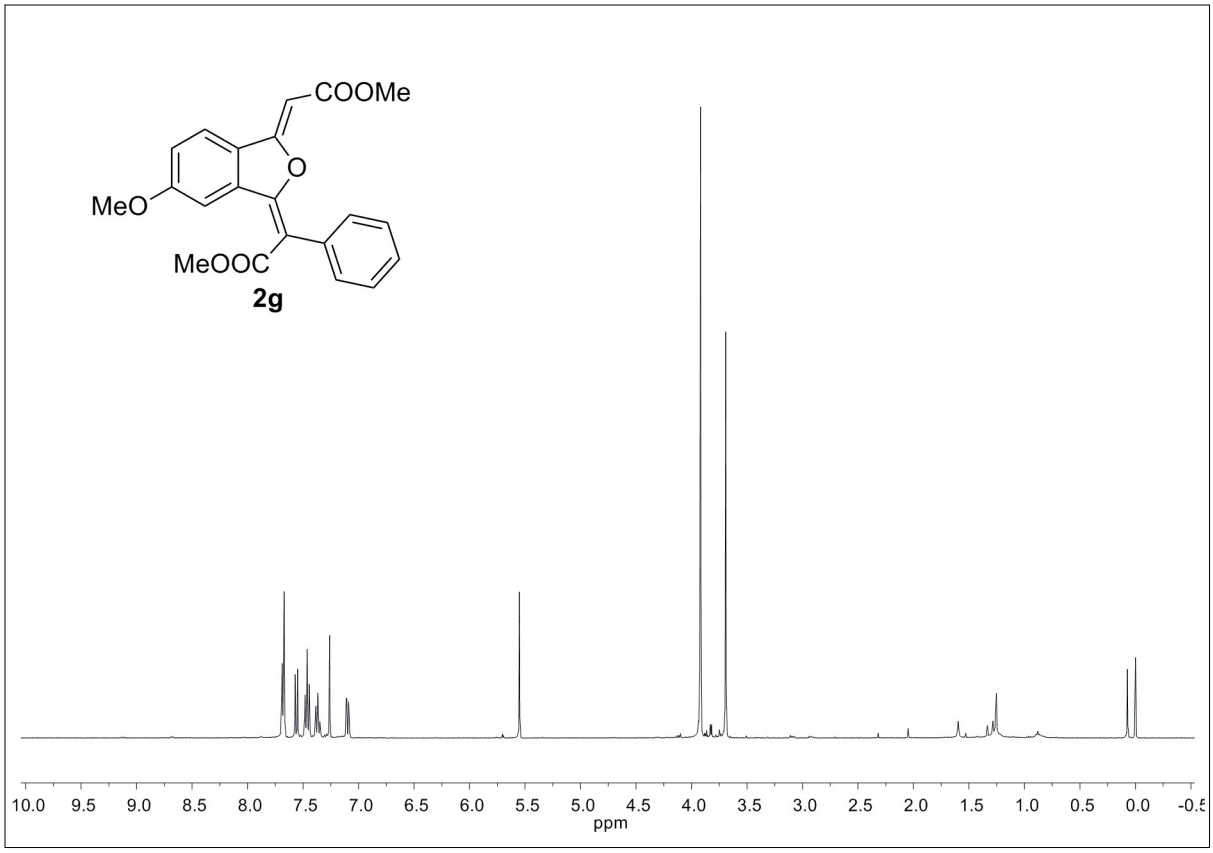
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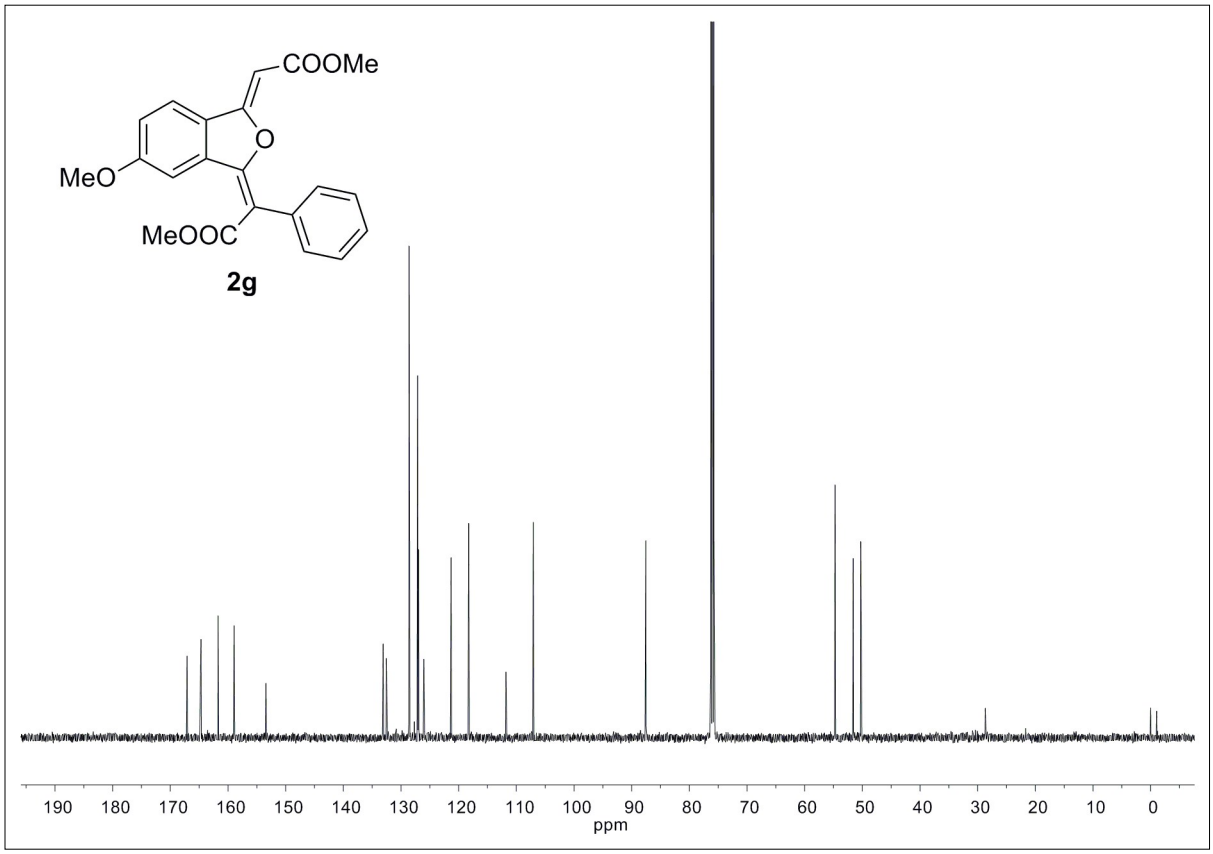
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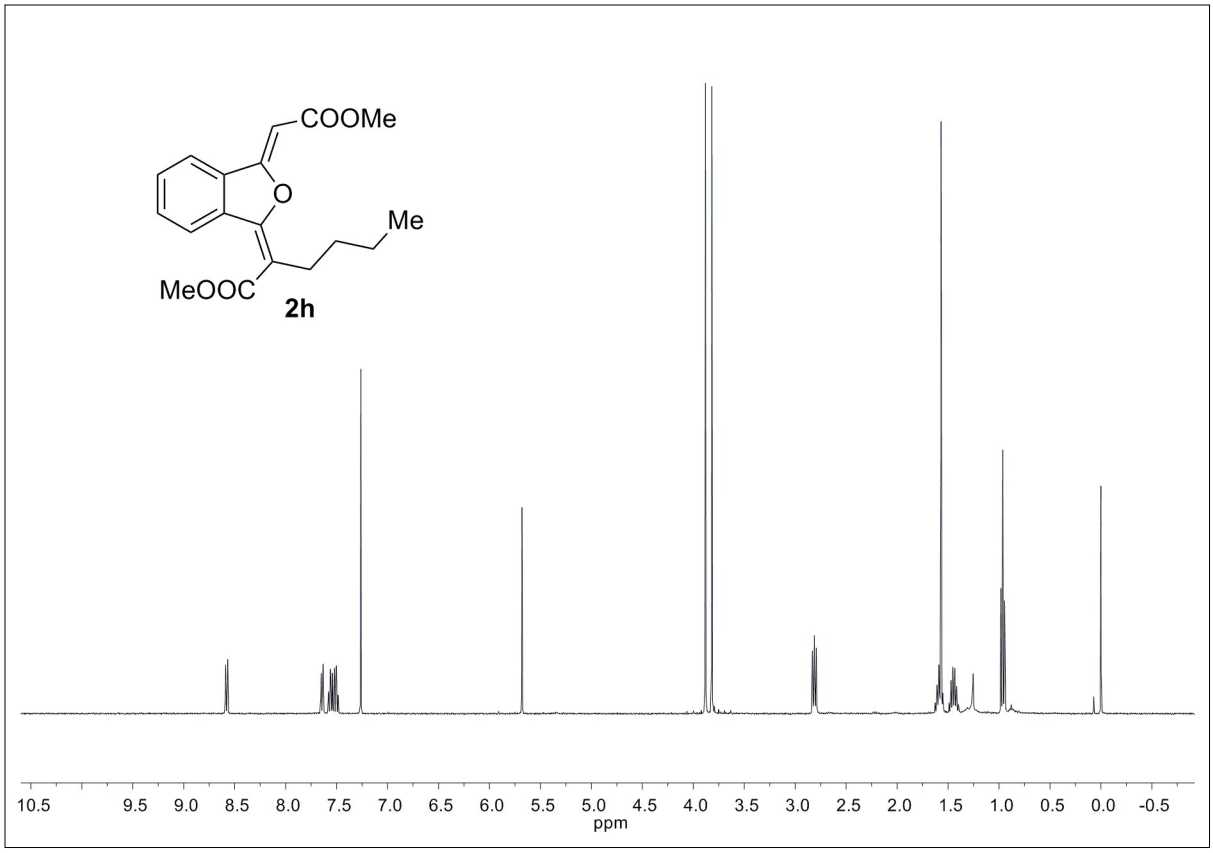
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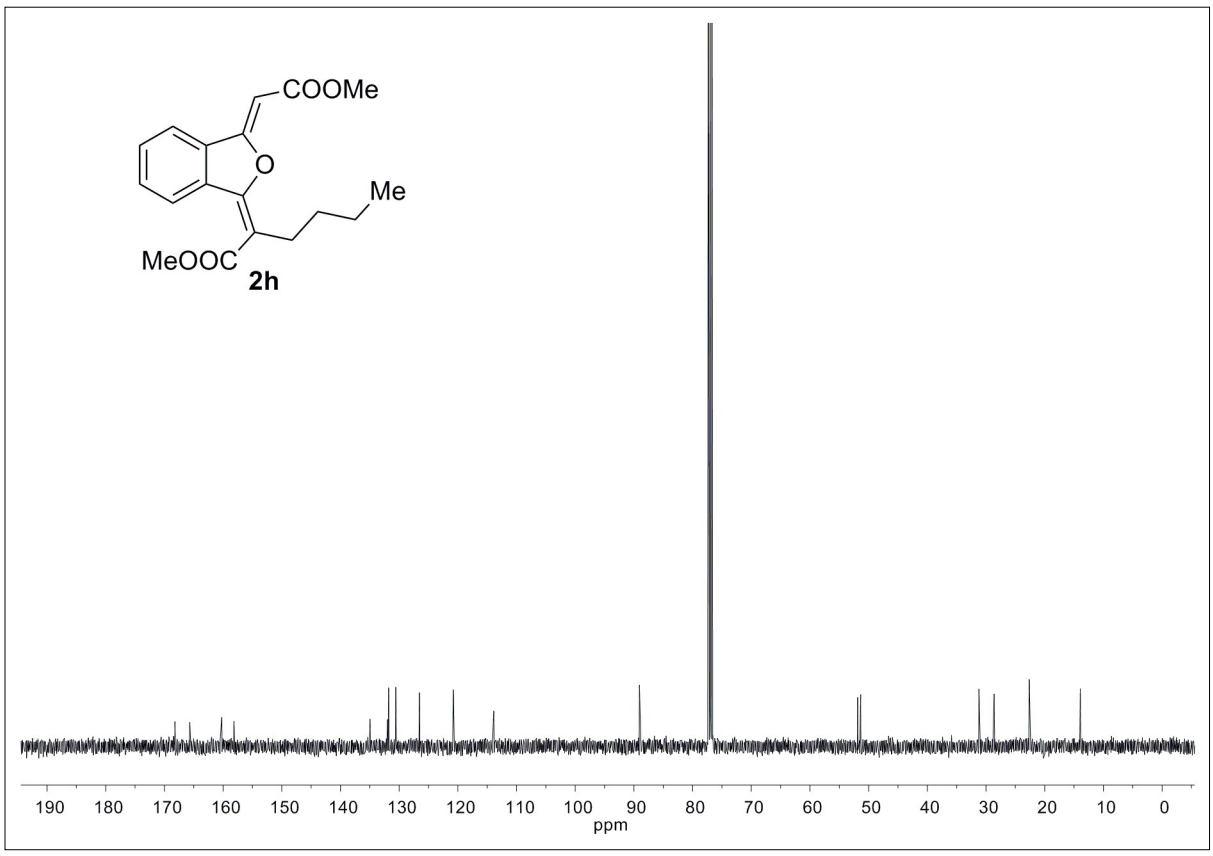
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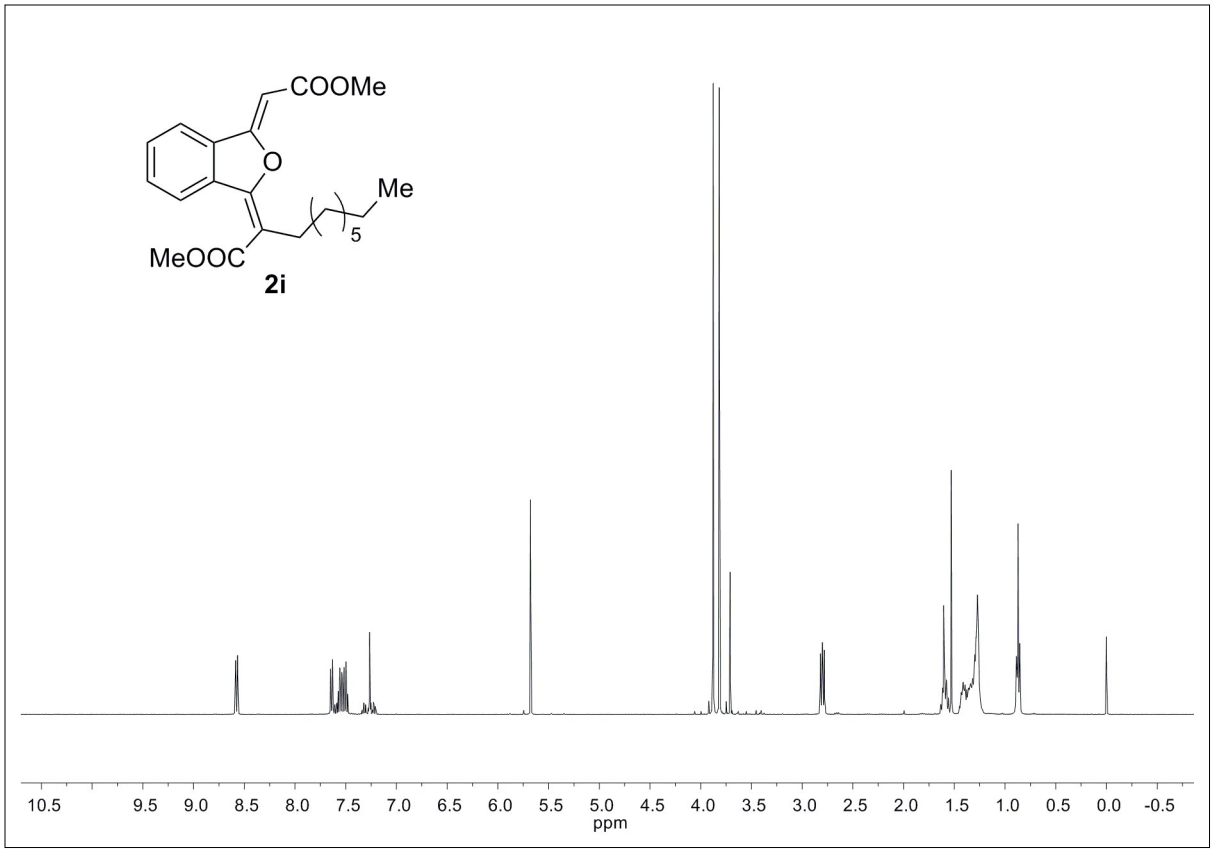
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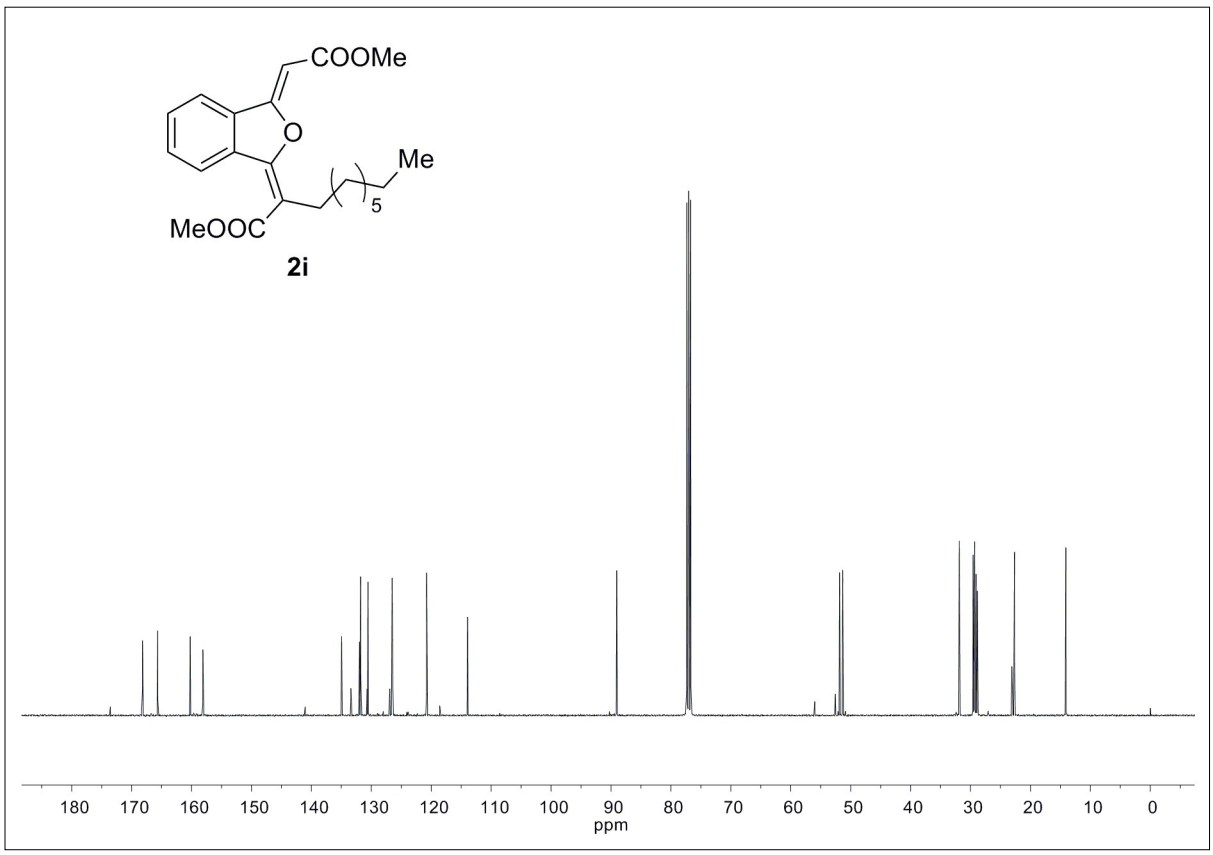
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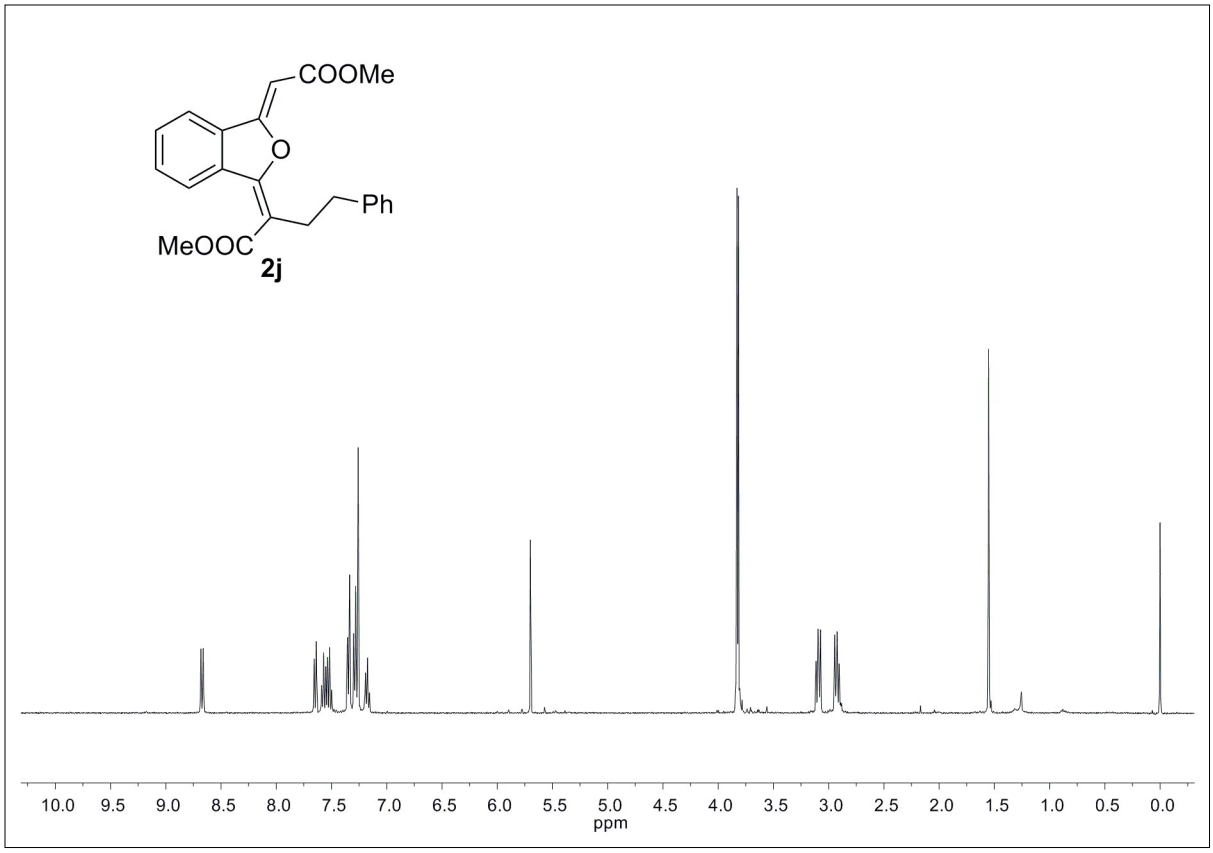
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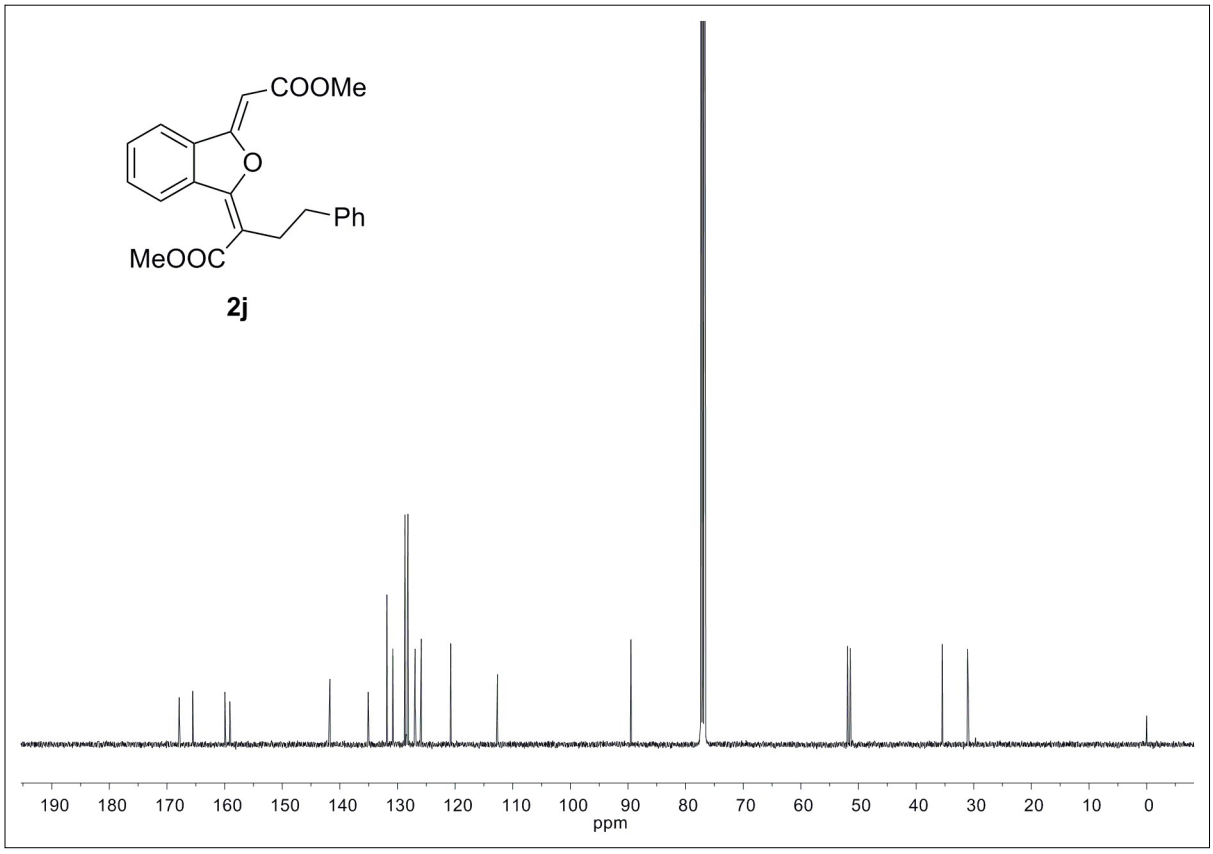
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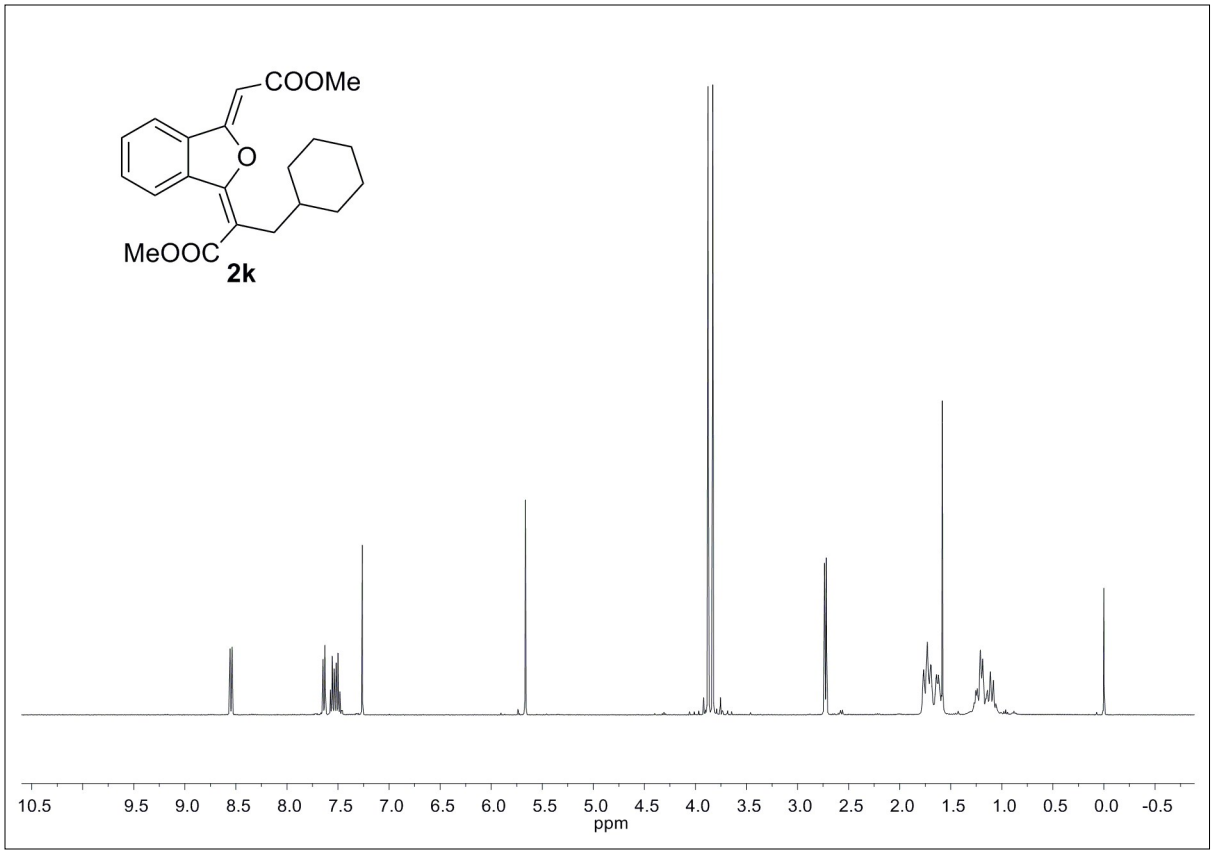
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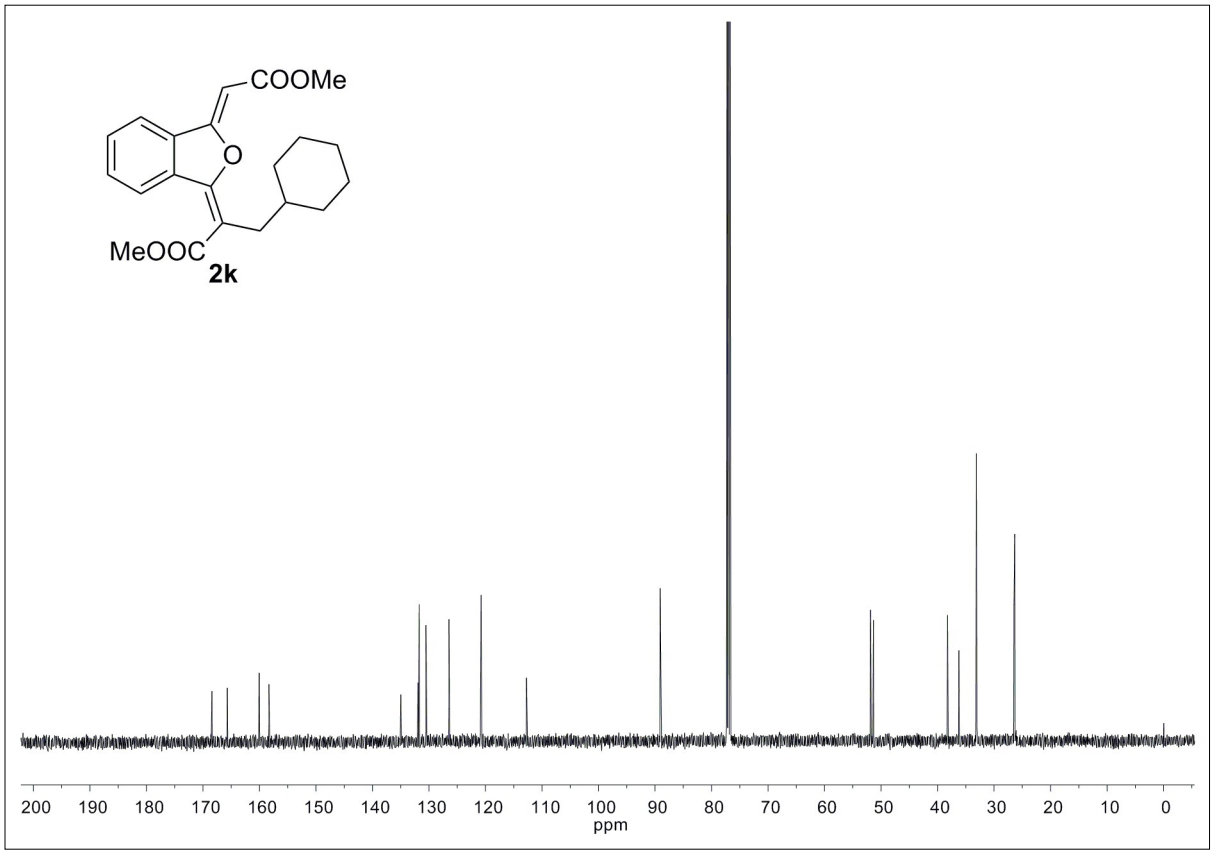
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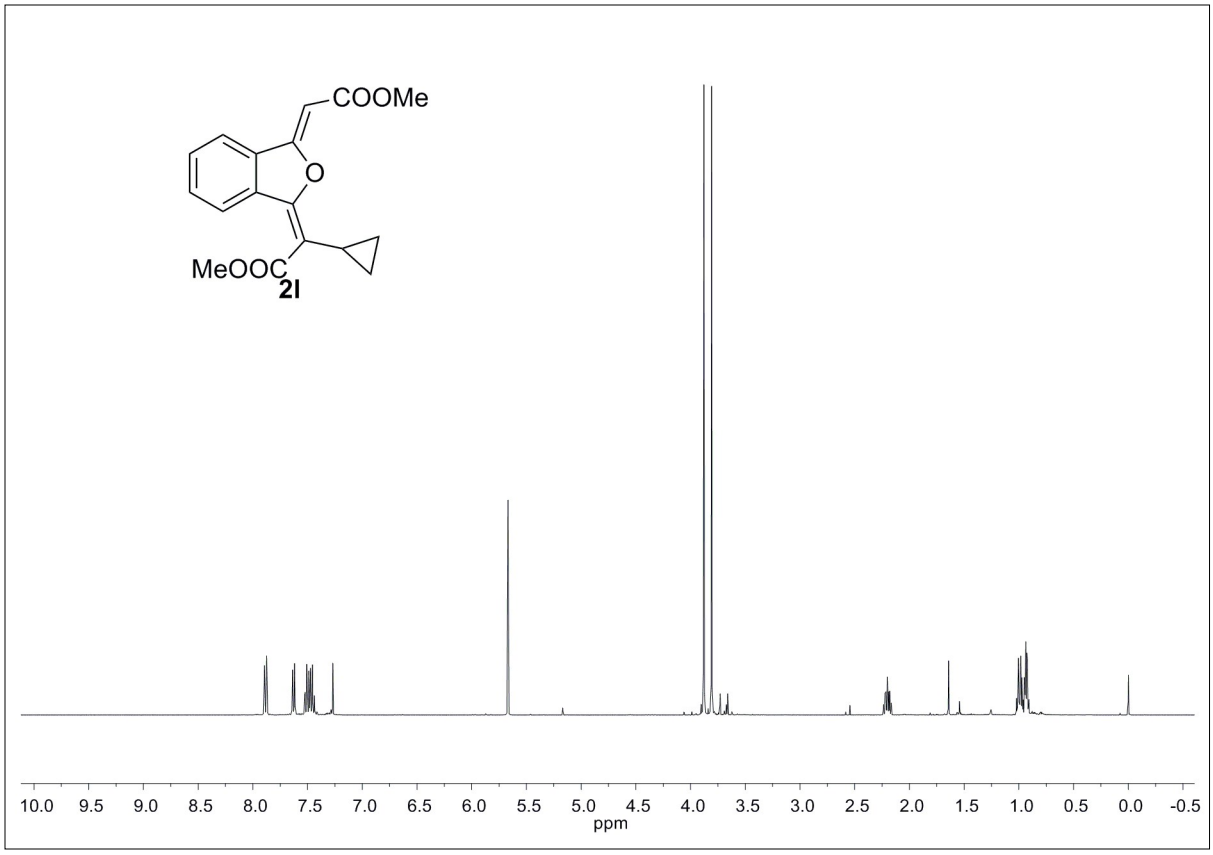
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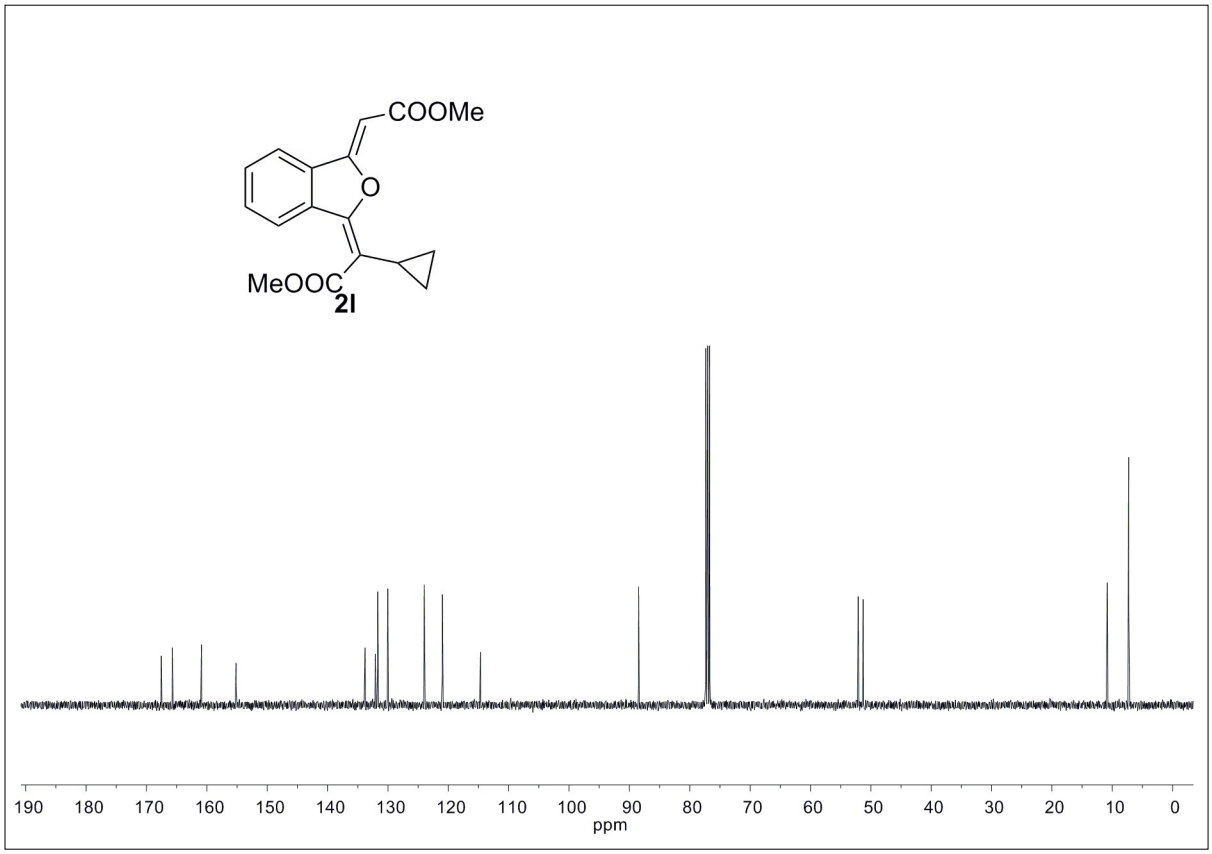
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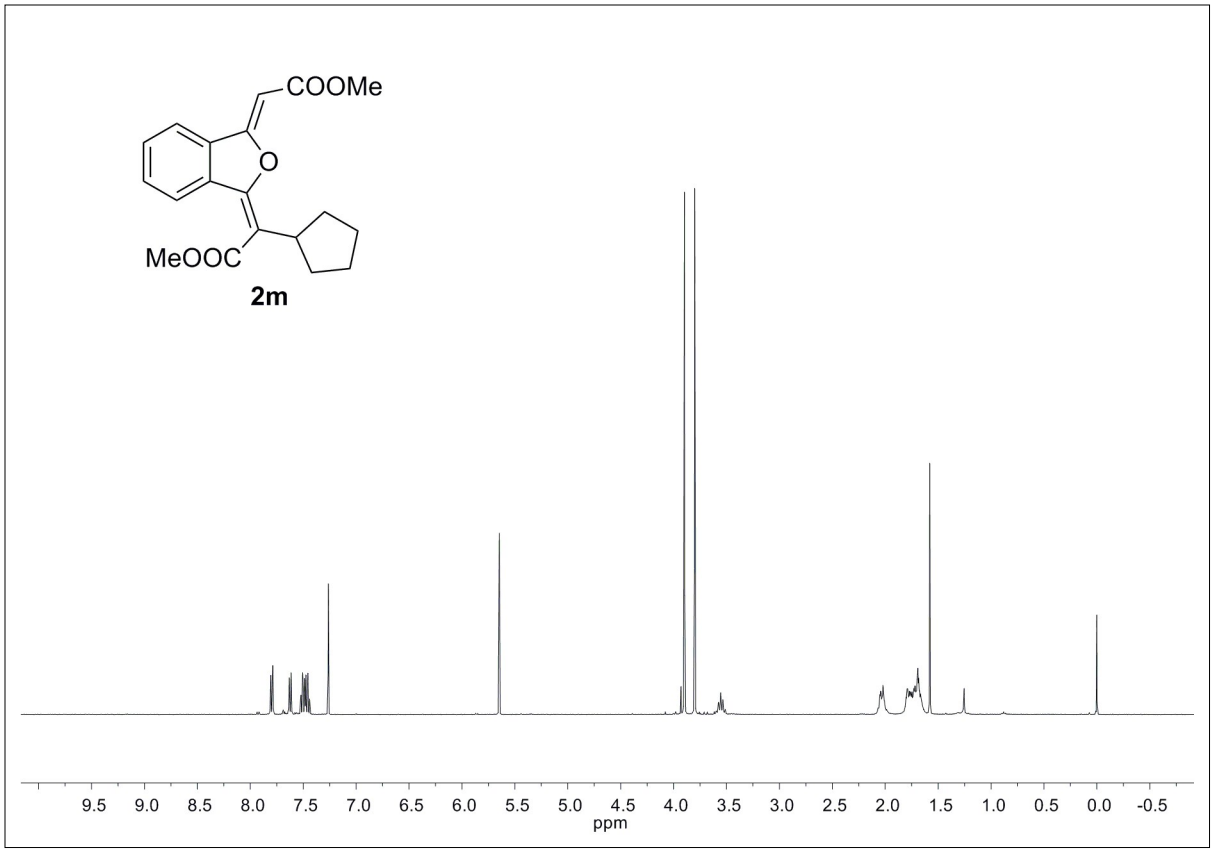
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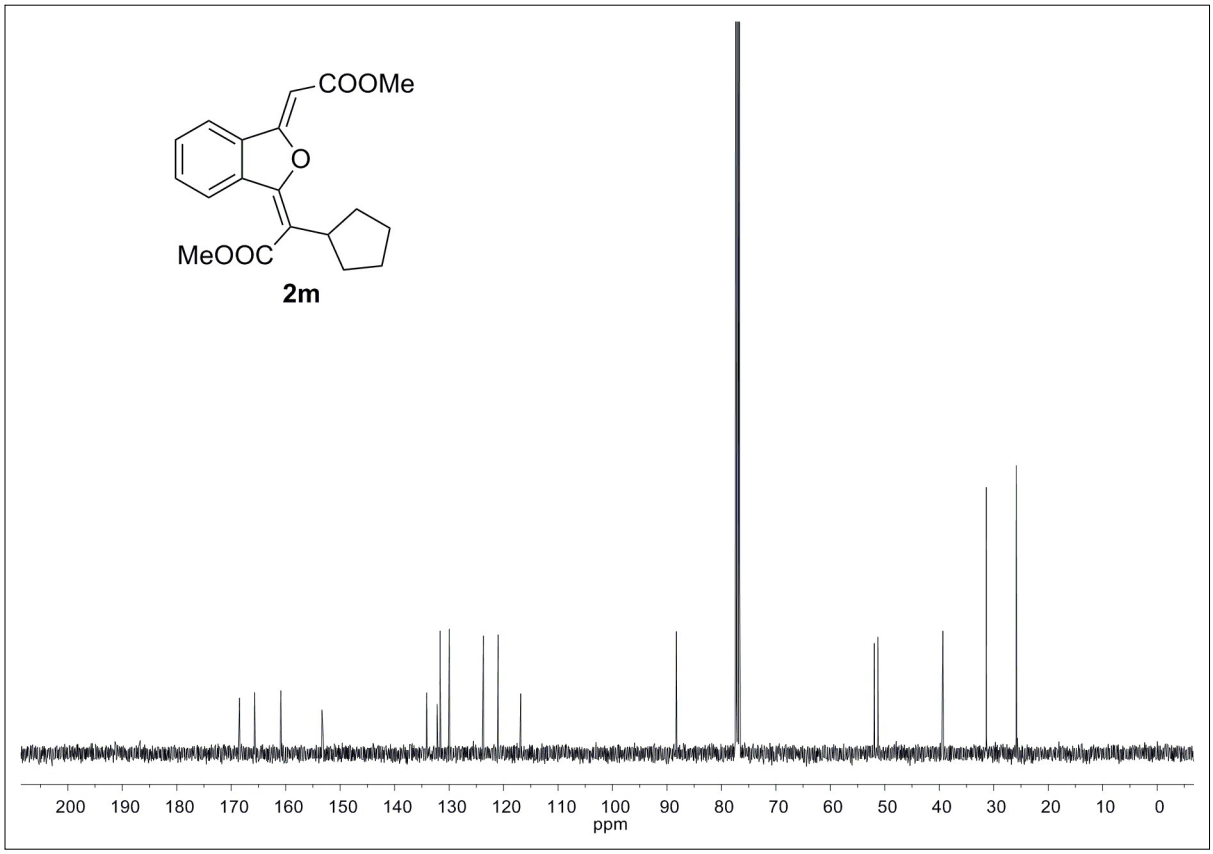
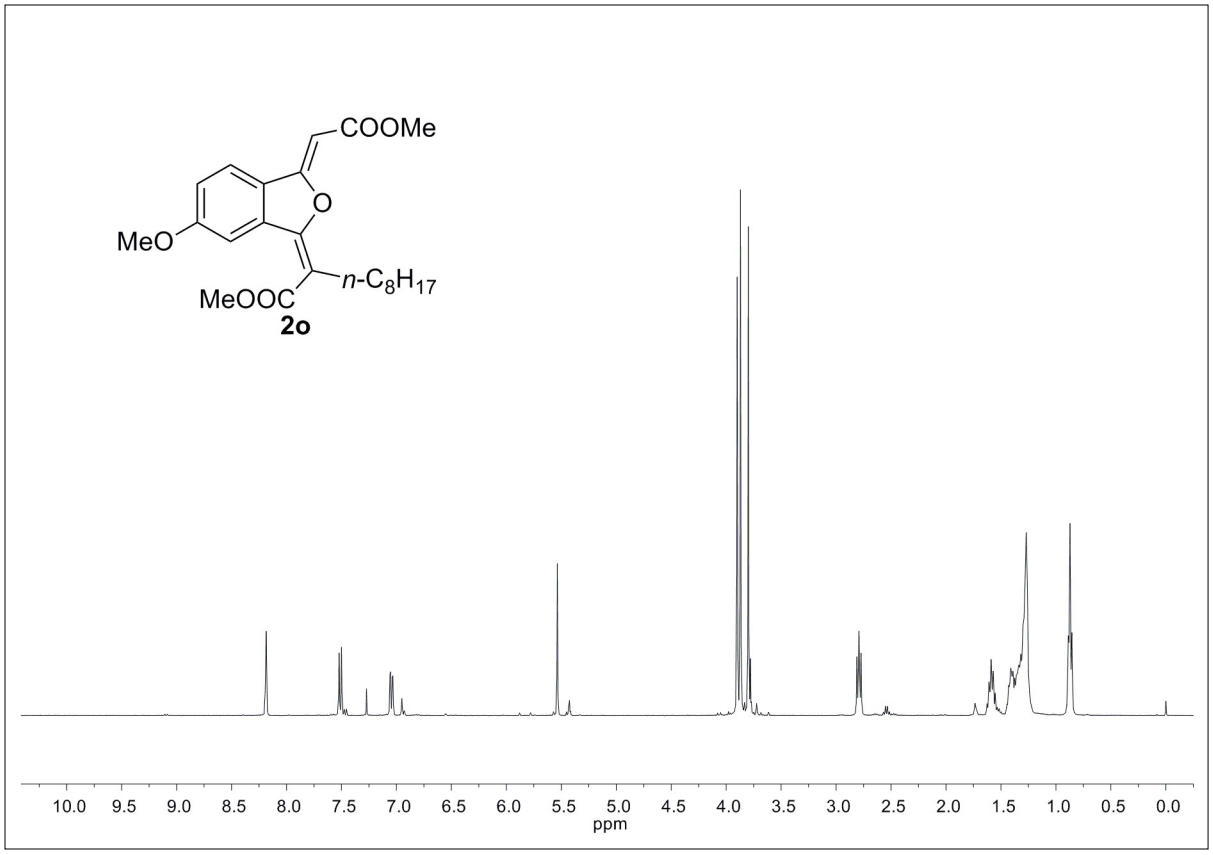
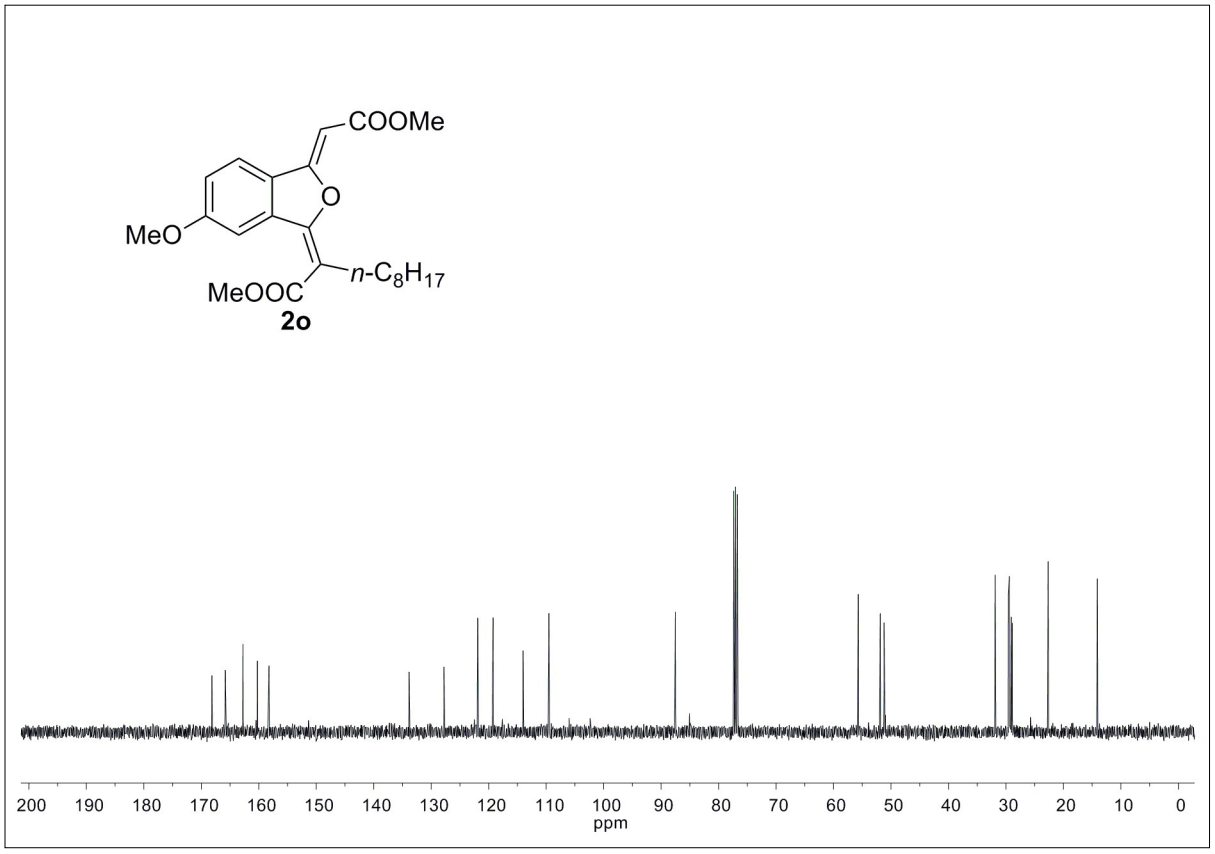
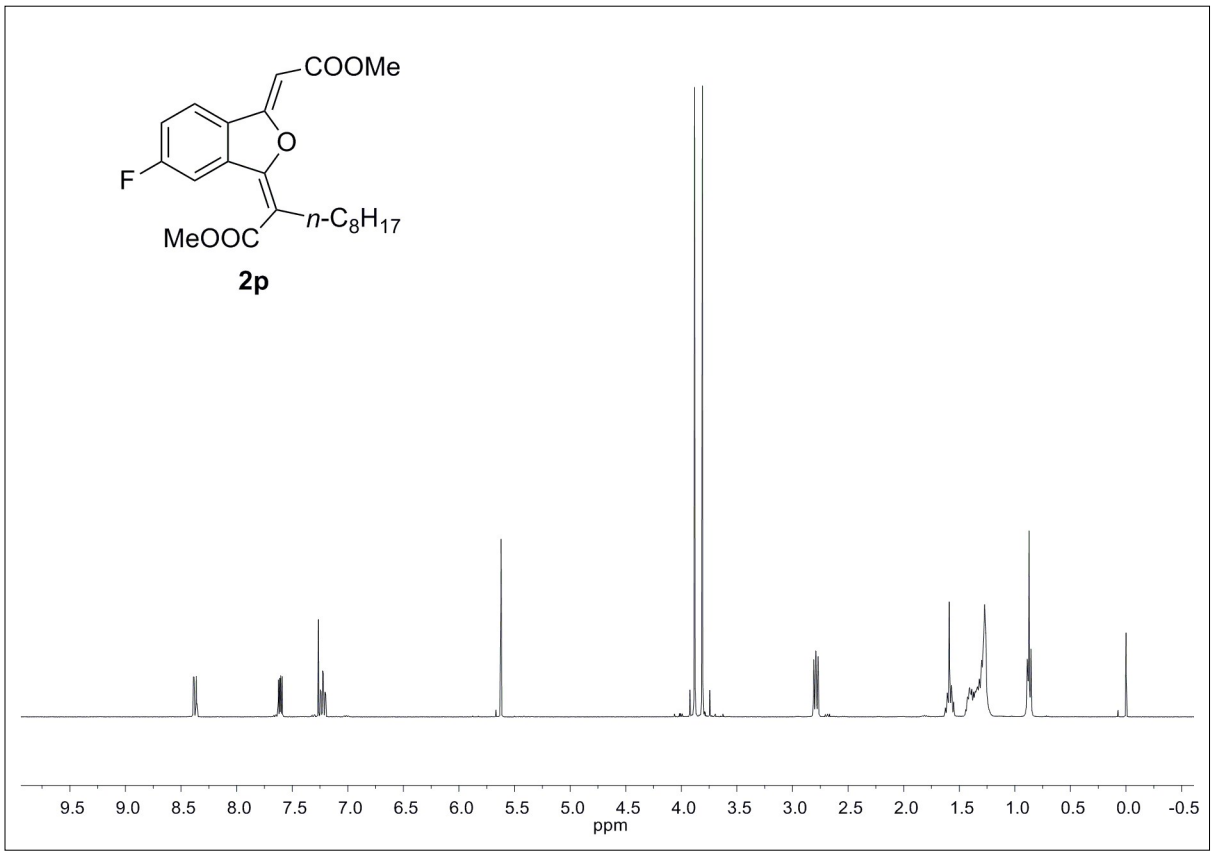
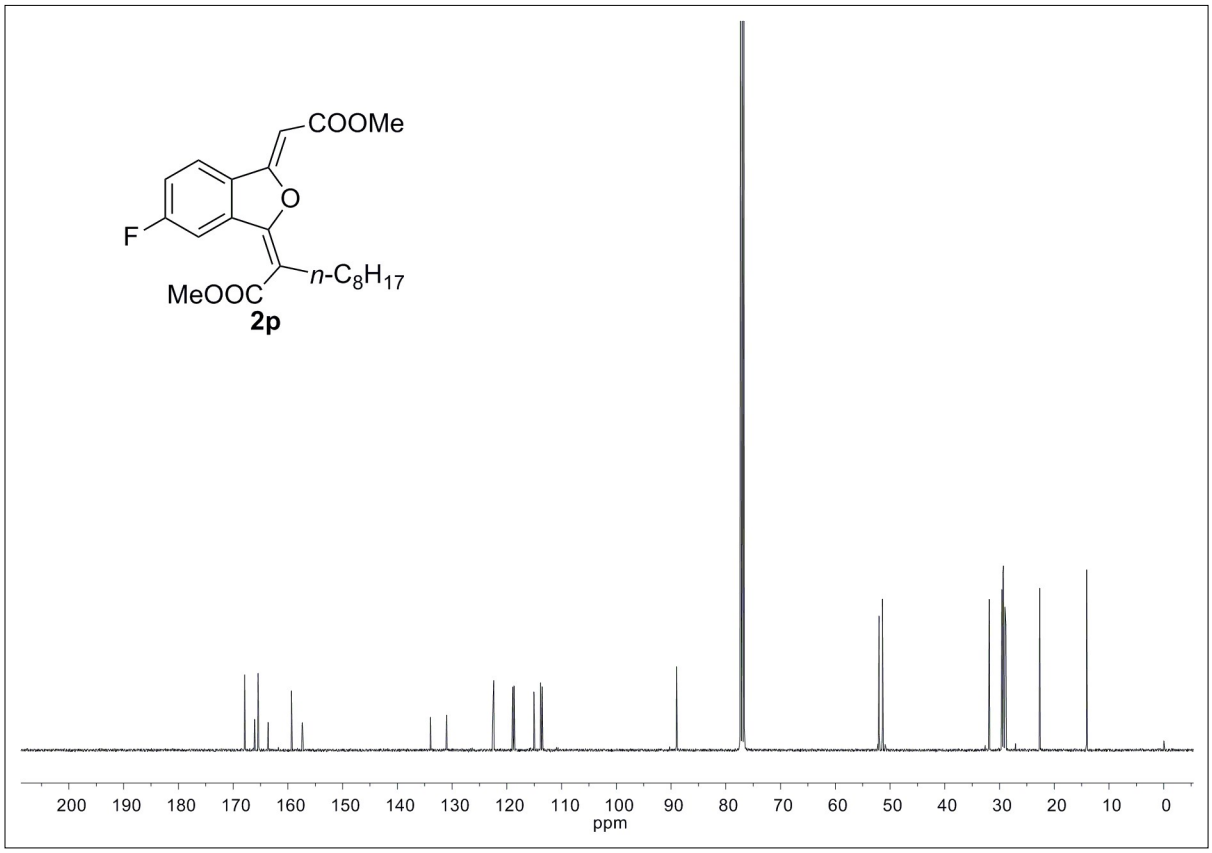
MeOOC
2m
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm

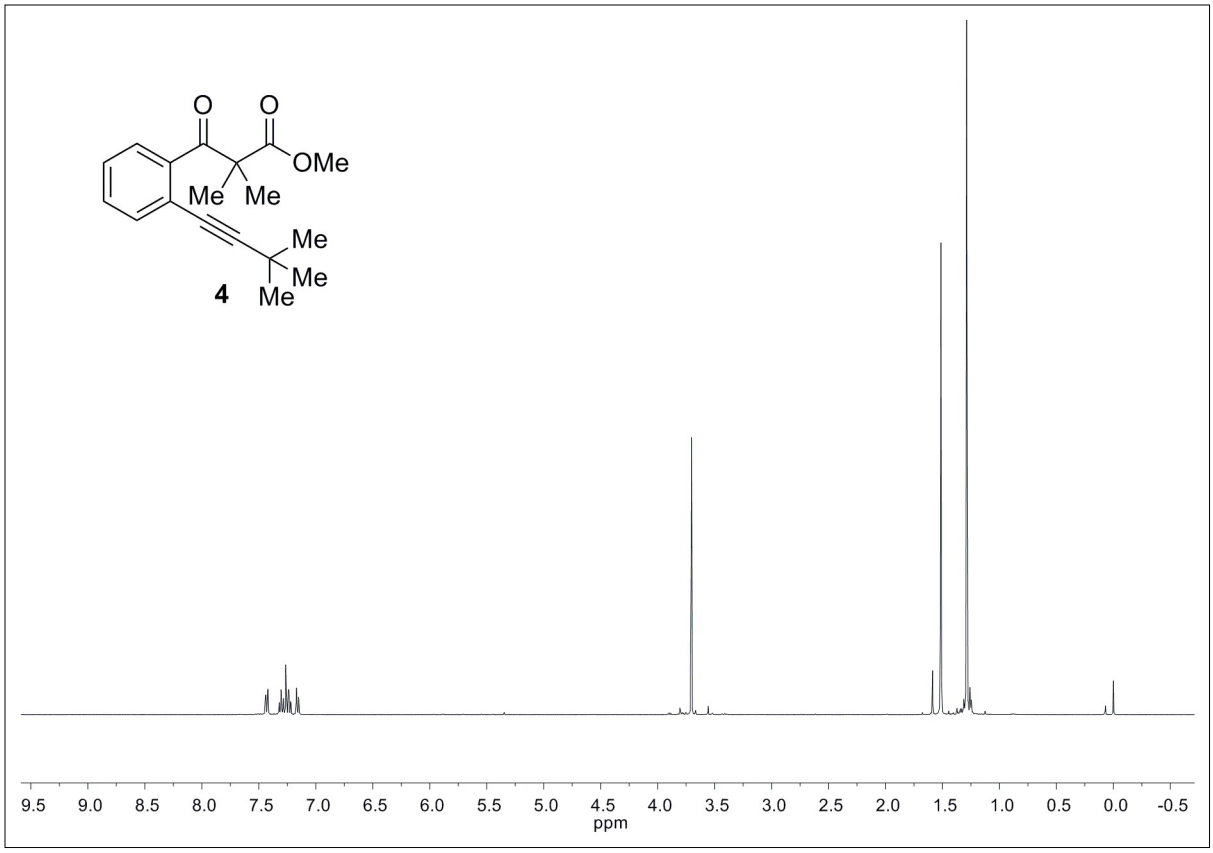

COOMe
O
MeOOC
2m
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

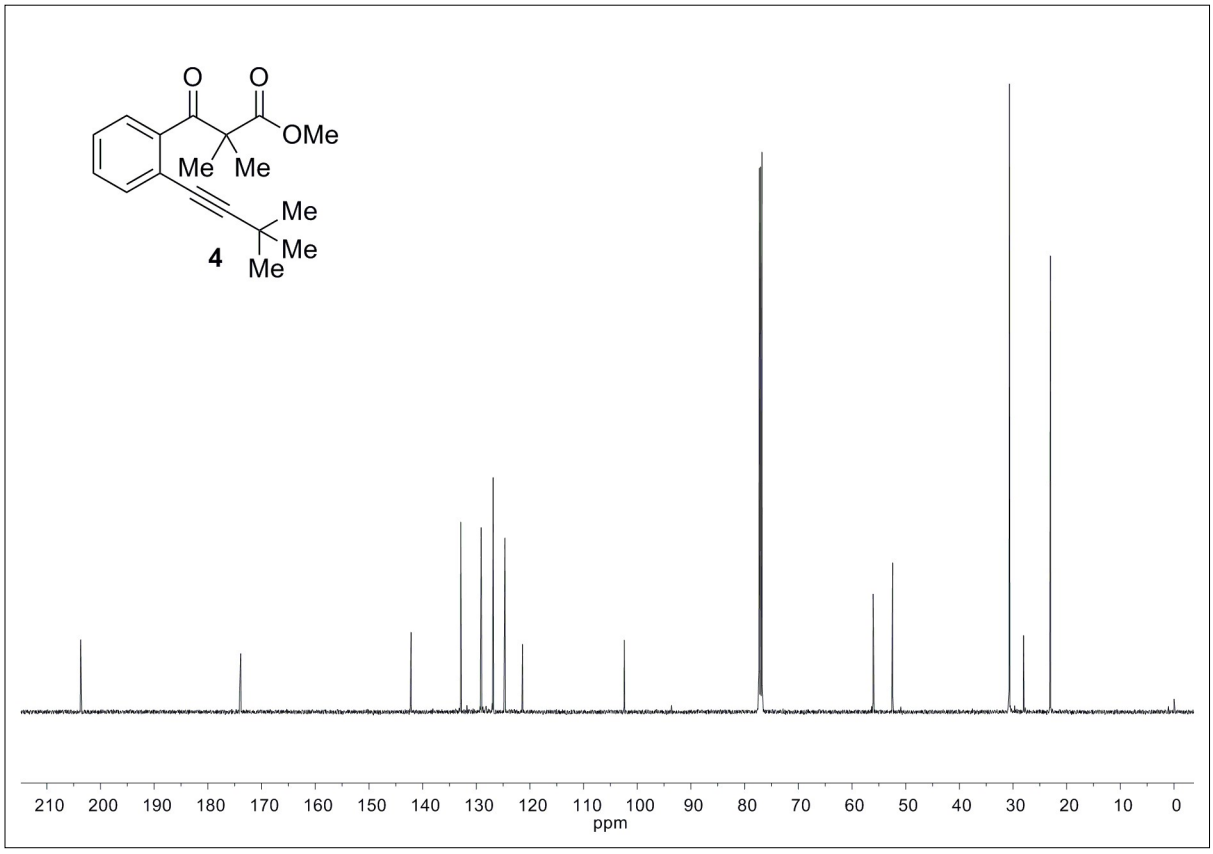

COOMe
O
MeO
n-C8H17
MeOOC
2o
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm

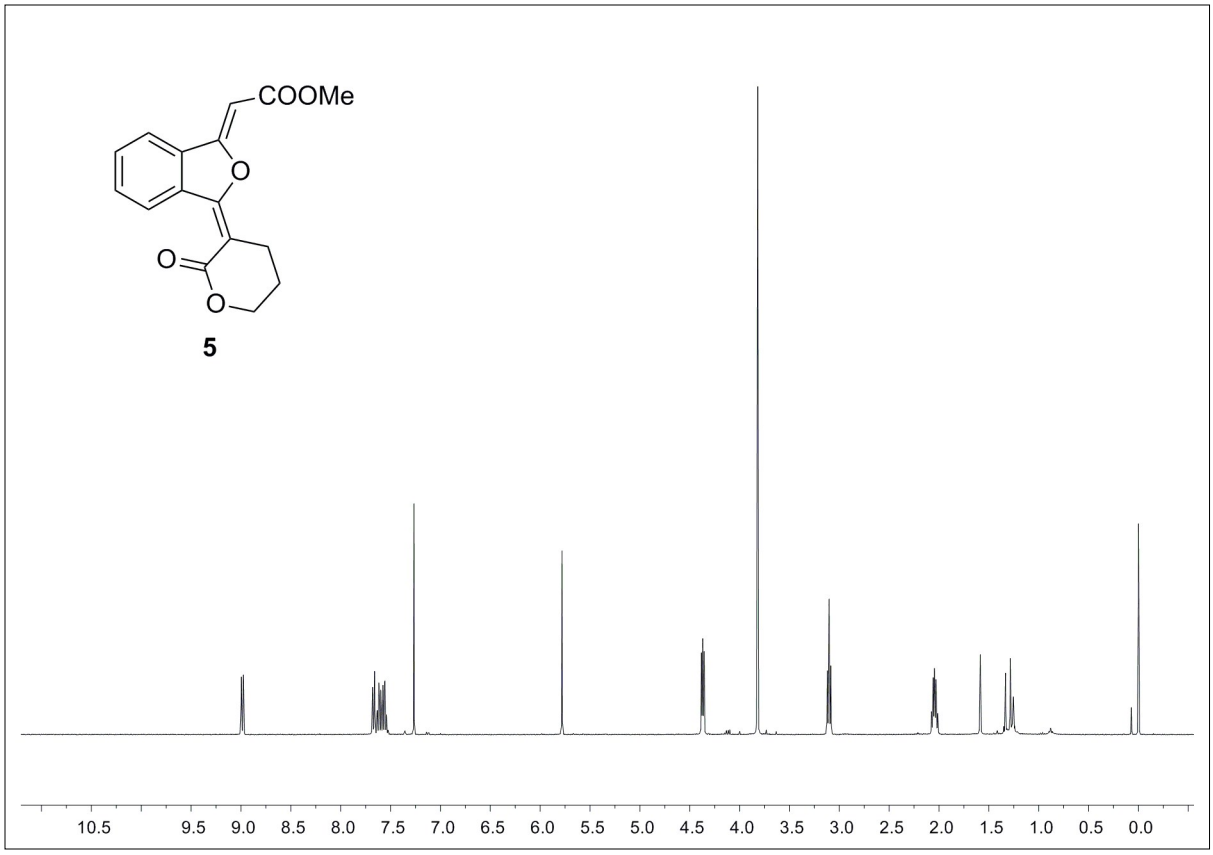

COOMe
O
MeO
n-C8H17
MeOOC
2o
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm

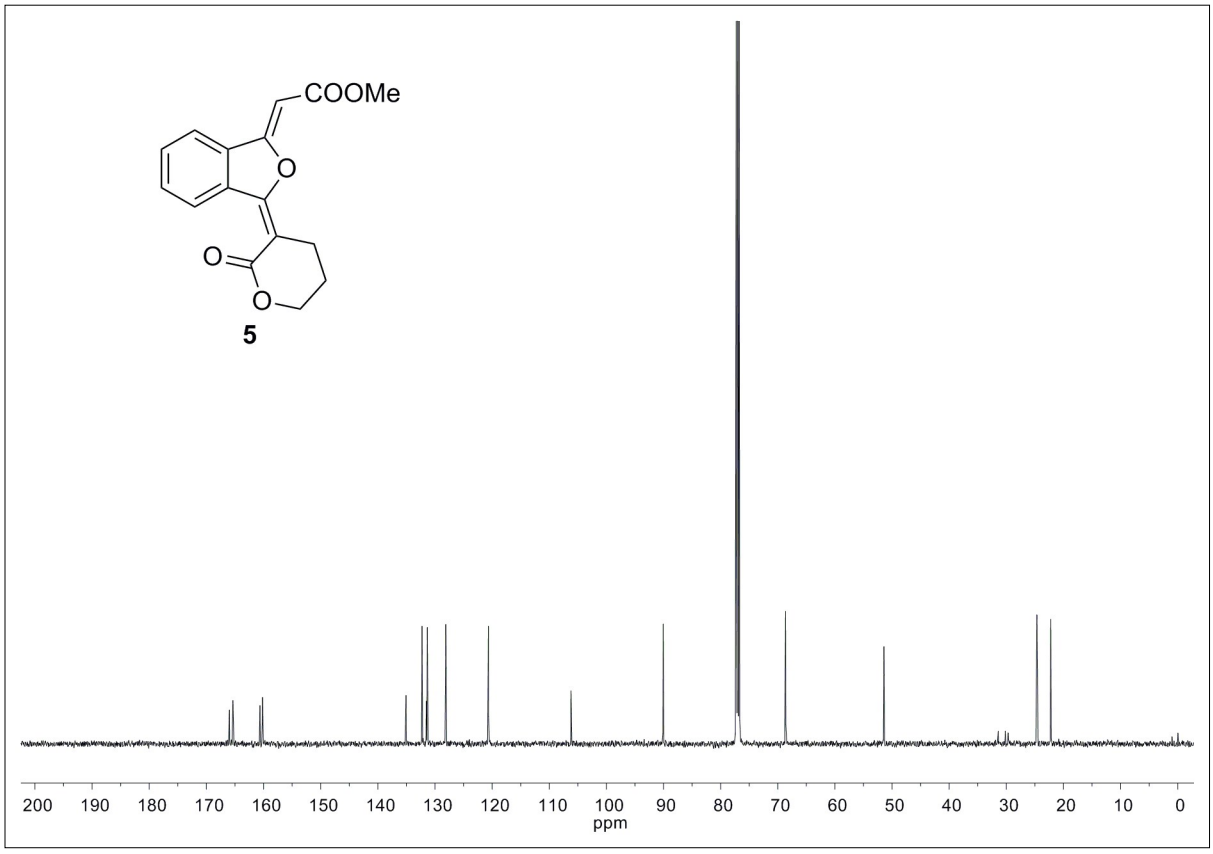

COOMe
O
F
n-C8H17
MeOOC
2p
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


COOMe
O
F
n-C8H17
MeOOC
2p
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


O
O
OMe
Me
Me
Me
Me
Me
4
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
ppm


O
O
OMe
Me
Me
Me
Me
Me
4
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm


COOMe
O
O
O
5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0


COOMe
O
O
O
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm