Supporting Information

Tandem 1,6-addition/cyclization/vinylcyclopropane rearrangement at low temperature under metal-free conditions: an approach to spiro[4.5]cyclohexadienones

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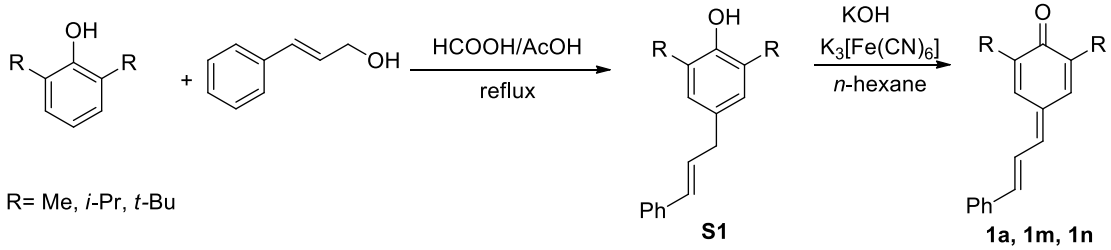
Contents

1. General Information

All reactions were carried out in oven-dried glassware under air with magnetic stirring. All solvents were purified and dried according to standard methods. Malonates **2a**, **2b** were purchased from Sigma-Aldrich Co. and used without further purification. **2c** – **2h** were synthesized according to reported procedures [1]. Flash column chromatography was carried out using commercially available 200 – 300 mesh under pressure and conducted by eluting with PE/EA as volume/volume ratios. ^{1}H and ^{13}C NMR spectra were collected on BRUKER AV - 300 (300 MHz) spectrometer using $CDCl_3$ as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard ($CDCl_3$: δ = 7.26 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz), and integration. Chemical shifts of ^{13}C NMR were reported in ppm with the solvent as the internal standard ($CDCl_3$: δ = 77.0 ppm). Infrared spectra (IR) were recorded on a Thermo Scientific iS10 FT/IR spectrometer. Absorptions are reported in reciprocal centimeters. High Resolution Mass measurement was performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI) as the ion source. Melting point (m.p.) was measured on a microscopic melting point apparatus.

2. Preparation of *p*-QMs

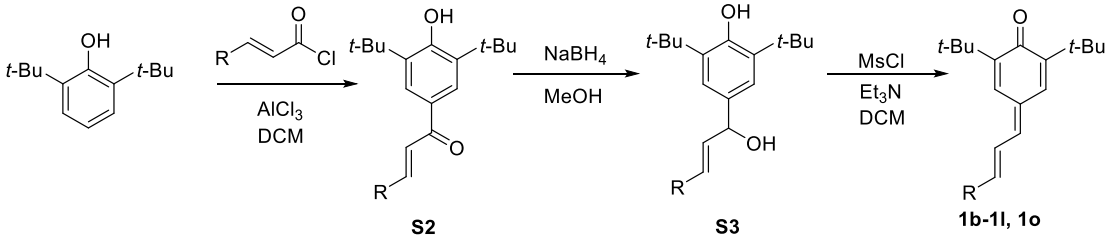
1a, 1m, 1n were synthesized according to the following procedures [2]:



The corresponding phenol (10 mmol, 1.0 equiv) and cinnamic alcohol (11 mmol, 1.1 equiv) were added to a 50 mL round bottom flask. Then HCOOH (8 mL) and AcOH (20 mL) were sequentially added. The solution was heated to reflux for 3 hours. Then the reaction was quenched with saturated solution of $NaHCO_3$, poured into water and extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. The crude product was purified by flash column chromatography. **S1** was obtained as white solid (71% yield).

S1 (7.1 mmol, 1 equiv) was dissolved in n-hexane (200 mL), then the solution of KOH (29.8 mmol, 4.2 equiv), and $K_3[Fe(CN)_6]$ (28.4 mmol, 4.0 equiv) in water (50 mL) were added. The solution was stirred overnight and yellow solid was formed. The reaction was poured into water and extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent were removed under reduced pressure. The crude product was purified by flash column chromatography and recrystallized from PE/EA to obtain the pure product.

1b – **1l, 1o** were synthesized according to following procedures:



To a stirred solution of the corresponding cinnamoyl chloride (2.0 equiv) in DCM was added $AlCl_3$ (1.1 equiv) in portions at room temperature. After stirring for 10 min, 2,6-di-*tert*-butylphenol (1.0 equiv) was added at 0 °C. The mixture was stirred overnight at room temperature. When completed (detected by TLC), the solution was passed through a short pad of celite and extracted with DCM. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Then, the crude product was purified by flash column chromatography to obtain **S2** as white or yellow solids.

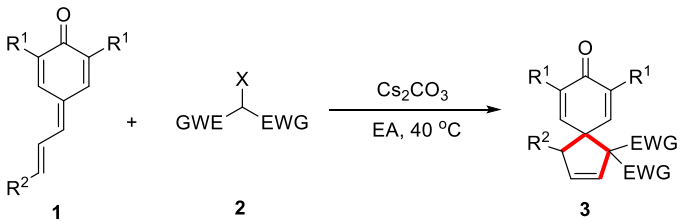
To a stirred solution of **S2** in MeOH at 0 °C was added $NaBH_4$ (4.0 equiv), then the color of solution turned red. After stirring for 2 hours, the mixture was quenched with saturated NH_4Cl, and extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4,

and the solvent was removed under reduced pressure. Then, the crude product **S3** was directly used for the next step without further purification.

To a stirred solution of **S3** in DCM was added Et_3N (2.2 equiv) and MsCl (1.1 equiv) at 0 °C, the reaction was stirred overnight and poured into water. Then the mixture was extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure. Then, the crude product was purified by flash column chromatography to obtain pure product **1** as red or yellow solids.

3. General Procedure for the Synthesis of Spiro-compounds

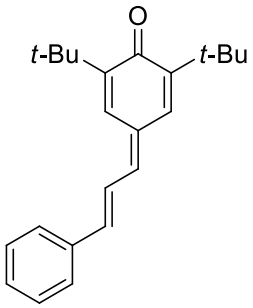
a) General procedure



In a 10 mL test tube was sequentially added *p*-QMs **1** (0.1 mmol, 1.0 equiv), Cs_2CO_3 (0.2 mmol, 2.0 equiv), bromomalonates **2** (0.11 mmol, 1.1 equiv) and EA (1 mL) at 40 °C. Then, the tube was sealed and stirred overnight. After the reaction was completed (detected by TLC), solvent was directly removed under reduced pressure and the crude mixture was purified by flash column chromatography on silica gel to afford the pure product **3**.

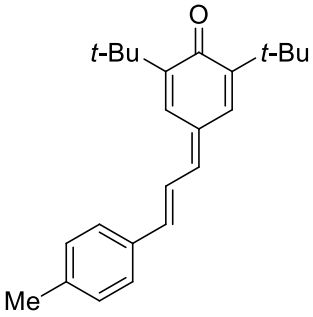
b) Characterization of the substrates

(*E*)-2,6-Di-*tert*-butyl-4-(3-phenylallylidene)cyclohexa-2,5-dienone (1a)



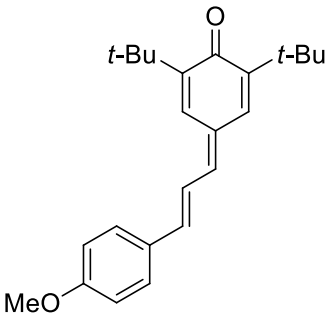
Yellow solid, m.p. 194 – 196 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 4H), 7.43 – 7.34 (m, 3H), 6.99 (d, *J* = 15.3 Hz, 1H), 6.94 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 11.9 Hz, 1H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 148.4, 147.9, 142.0, 140.9, 136.4, 134.6, 131.3, 129.4, 129.0, 127.5, 125.4, 123.6, 35.5, 35.1, 29.6, 29.6 ppm. **IR(KBr):** 2951, 1586, 1538, 1449, 1359, 1255, 1019, 973, 950, 750, 689, 465 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{23}H_{28}O+H]^+$: 321.2213; found: 321.2210.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(p-tolyl)allylidene)cyclohexa-2,5-dienone (1b)



Yellow solid, m.p. 142 – 146 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 1.7 Hz, 1H), 7.46 – 7.38 (m, 3H), 7.20 (d, *J* = 7.9 Hz, 2H), 6.98 – 6.93 (m, 2H), 6.85 (d, *J* = 11.9 Hz, 1H), 2.38 (s, 3H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 148.2, 147.7, 142.5, 141.2, 139.8, 134.7, 133.7, 130.8, 129.7, 127.5, 125.4, 122.7, 35.5, 35.1, 29.6, 29.6, 21.5 ppm. **IR(KBr):** 2944, 1604, 1586, 1561, 1537, 1359, 1249, 965, 949, 802, 446 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{24}H_{30}O+H]^+$: 335.2369; found: 335.2368.

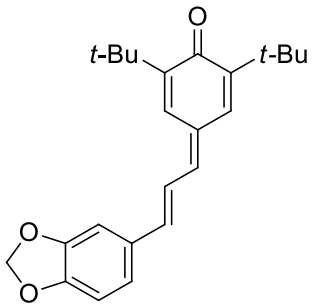
(*E*)-2,6-Di-*tert*-butyl-4-(3-(4-methoxyphenyl)allylidene)cyclohexa-2,5-dienone (1c)



Yellow solid, m.p. 148 – 149 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 – 7.49 (m, 3H), 7.34 (dd, *J* = 15.0, 12.0 Hz, 1H), 6.96 – 6.91 (m, 4H), 6.85 (d, *J* = 11.9 Hz, 1H), 3.84 (s, 3H), 1.37 (s,

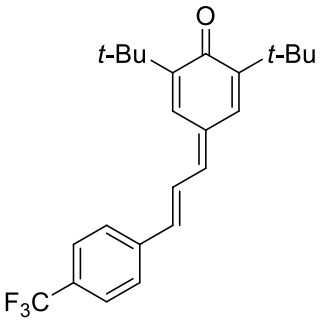
9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 160.8, 148.0, 147.5, 142.8, 140.9, 134.7, 130.3, 129.2, 129.1, 125.4, 121.6, 114.5, 55.4, 35.5, 35.0, 29.6, 29.6 ppm. **IR(KBr):** 2944, 1605, 1586, 1569, 1540, 1384, 1250, 1176, 1169, 952, 813 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{24}H_{30}O_2+H]^+$: 351.2319; found: 351.2321.

(*E*)-4-(3-(Benzo[d][1,3]dioxol-5-yl)allylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (1d)



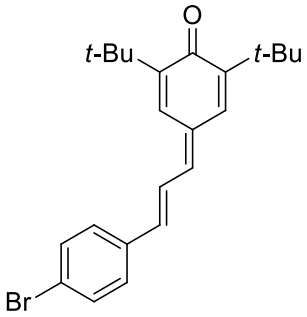
Yellow solid, m.p. 146 – 147 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 1.9 Hz, 1H), 7.34 – 7.25 (m, 1H), 7.09 (d, *J* = 1.1 Hz, 1H), 7.00 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.93 – 6.92 (m, 2H), 6.87 – 6.80 (m, 2H), 6.01 (s, 2H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.8, 148.5, 147.9, 147.6, 147.1, 141.9, 140.3, 134.1, 130.5, 130.1, 124.9, 123.1, 121.4, 108.3, 105.5, 101.1, 35.0, 34.6, 29.1, 29.1 ppm. **IR(KBr):** 2968, 1578, 1540, 1502, 1448, 1359, 1253, 1038, 976, 807 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{24}H_{28}O_3+H]^+$: 365.2111; found: 365.2114.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(4-(trifluoromethyl)phenyl)allylidene)cyclohexa-2,5-dienone (1e)



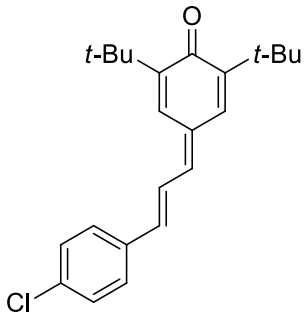
Yellow solid, m.p. 139 – 142 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.57 – 7.49 (m, 2H), 7.00 – 6.94 (m, 2H), 6.85 (d, *J* = 11.9 Hz, 1H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 148.9, 148.5, 140.7, 139.7, 138.5, 134.4, 132.5, 130.8, 127.4, 125.9 (J_{C-F} = 3.8 Hz), 125.7, 125.2, 122.2, 35.6, 35.1, 29.6, 29.5 ppm. **IR(KBr):** 2944, 1605, 1537, 1361, 1323, 1160, 1109, 1065, 972, 819 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{24}H_{27}F_3O+H]^+$: 389.2087; found: 389.2088.

(*E*)-4-(3-(4-Bromophenyl)allylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (1f)



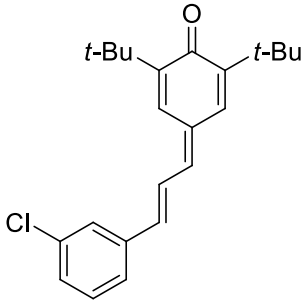
Yellow solid, m.p. 158 – 160 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.52 – 7.47 (m, 3H), 7.44 – 7.38 (m, 3H), 6.93 – 6.87 (m, 2H), 6.82 (d, *J* = 11.9 Hz, 1H), 1.36 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 148.6, 148.2, 141.3, 139.2, 135.3, 134.5, 132.1, 131.7, 128.8, 125.2, 124.1, 123.3, 35.5, 35.1, 29.6, 29.5 ppm. **IR(KBr):** 2952, 1607, 1587, 1542, 1478, 1360, 1252, 1072, 973, 951, 807, 506 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{23}H_{27}BrO+H]^+$: 399.1318; found: 399.1319.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(4-chlorophenyl)allylidene)cyclohexa-2,5-dienone (1g)



Yellow solid, m.p. 149 – 152 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 – 7.34 (m, 6H), 6.94 – 6.89 (m, 2H), 6.82 (d, *J* = 11.9 Hz, 1H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 148.6, 148.1, 141.4, 139.2, 135.1, 134.9, 134.5, 131.6, 129.2, 128.5, 125.2, 124.0, 35.5, 35.1, 29.6, 29.5 ppm. **IR(KBr):** 2950, 1606, 1588, 1561, 1541, 1384, 1356, 1086, 977, 951, 810, 515 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{23}H_{27}ClO+H]^+$: 355.1823; found: 355.1821.

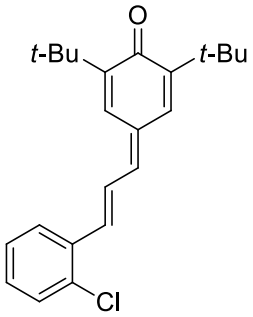
(*E*)-2,6-Di-*tert*-butyl-4-(3-(3-chlorophenyl)allylidene)cyclohexa-2,5-dienone (1h)



Yellow solid, m.p. 152 – 154 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 – 7.41 (m, 4H), 7.32 – 7.28 (m, 2H), 6.94 – 6.82 (m, 2H), 1.38 (s, 9H), 1.33 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 148.7, 148.3, 141.1, 138.9, 138.2, 134.9, 134.5, 132.0, 130.2, 129.1, 127.1, 125.6, 125.2, 124.7, 35.6, 35.1, 29.6, 29.5 ppm. **IR(KBr):** 2949, 1606, 1591, 1538, 1558, 1361 1084, 957, 887,

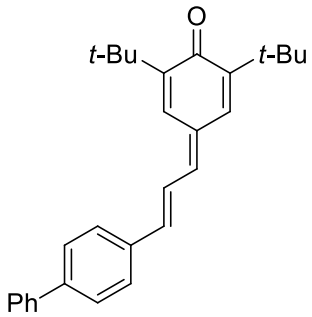
773, 674 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{23}H_{27}ClO+H]^+$: 355.1823; found: 355.1824.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(2-chlorophenyl)allylidene)cyclohexa-2,5-dienone (1i)



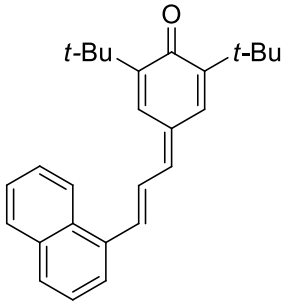
Yellow solid, m.p. 164 – 165 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.50 – 7.37 (m, 4H), 7.34 – 7.22 (m, 2H), 6.95 (d, *J* = 2.3 Hz, 1H), 6.91 (d, *J* = 9.9 Hz, 1H), 1.36 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 148.7, 148.3, 141.5, 136.1, 134.5, 134.3, 134.2, 132.0, 130.2, 130.0, 127.1, 126.9, 125.6, 125.3, 35.5, 35.1, 29.6, 29.5 ppm. **IR(KBr):** 2956, 2855, 1609, 1583, 1541, 1449, 1357, 1253, 967, 953, 880, 758 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{23}H_{27}ClO+H]^+$: 355.1823; found: 355.1826.

(*E*)-4-(3-([1,1'-Biphenyl]-4-yl)allylidene)-2,6-di-*tert*-butylcyclohexa-2,5-dienone (1j)



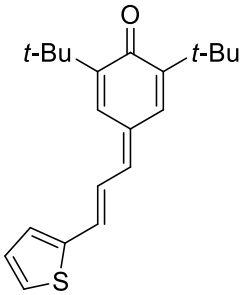
Yellow solid, m.p. 154 – 156 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.63 – 7.61 (m, 6H), 7.53 – 7.44 (m, 4H), 7.40 – 7.35 (d, *J* = 7.3 Hz, 1H), 7.01 (d, *J* = 15.2 Hz, 1H), 6.95 (d, *J* = 2.1 Hz, 1H), 6.88 (d, *J* = 11.9 Hz, 1H), 1.38 (s, 9H), 1.33 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 148.4, 147.9, 142.1, 140.4, 140.2, 135.4, 134.6, 131.3, 129.0, 128.0, 127.8, 127.6, 127.0, 125.4, 123.6, 35.5, 35.1, 29.7, 29.6 ppm. **IR(KBr):** 2955, 1609, 1560, 1575, 1552, 1537, 1453, 1359, 1253, 967, 948, 820, 762, 696, 488 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{29}H_{32}O+H]^+$: 397.2526; found: 397.2526.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(naphthalen-1-yl)allylidene)cyclohexa-2,5-dienone (1k)



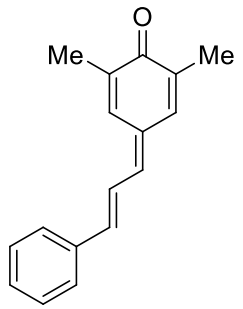
Red solid, m.p. 144 – 146 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.2 Hz, 1H), 7.88–7.77 (m, 4H), 7.61 – 7.49 (m, 5H), 7.01 – 6.98 (m, 2H), 1.38 (s, 9H), 1.35 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 148.0, 147.5, 141.7, 136.7, 134.2, 133.4, 133.0, 130.9, 130.7, 129.4, 128.5, 126.3, 125.7, 125.5, 125.2, 125.0, 123.8, 122.6, 35.1, 34.6, 29.2, 29.1 ppm. **IR(KBr):** 2950, 1589, 1575, 1541, 1566, 1358, 1287, 1253, 1240, 975, 952, 791 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{27}H_{30}O+H]^+$: 371.2369; found: 371.2370.

(*E*)-2,6-Di-*tert*-butyl-4-(3-(thiophen-2-yl)allylidene)cyclohexa-2,5-dienone (1l)



Red solid, m.p. 208 – 210 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 1.7 Hz, 1H), 7.35 (d, *J* = 4.9 Hz, 1H), 7.25 (dd, *J* = 11.2, 3.6 Hz, 1H), 7.20 – 7.12 (m, 2H), 7.07 – 7.05 (m, 1H), 6.92 (d, *J* = 1.9 Hz, 1H), 6.78 (d, *J* = 11.6 Hz, 1H), 1.37 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.3, 148.3, 147.8, 142.1, 141.5, 134.4, 133.2, 131.0, 129.0, 128.3, 127.5, 125.3, 123.3, 35.5, 35.1, 29.6, 29.6 ppm. **IR(KBr):** 2938, 2366, 2324, 1579, 1399, 1534, 1399, 1381, 1172, 704, 639 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{21}H_{26}OS+H]^+$: 327.1777; found: 327.1777.

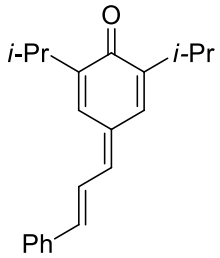
(*E*)-2,6-Dimethyl-4-(3-phenylallylidene)cyclohexa-2,5-dienone (1m)



Red solid, m.p. 100 – 103 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) 7.56 – 7.52 (m, 3H), 7.48 – 7.34 (m, 4H), 7.03 – 6.98 (m, 2H), 6.83 (d, *J* = 11.9 Hz, 1H), 2.12 (d, *J* = 0.9 Hz, 3H), 2.06 (d, *J* = 0.9 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 187.3, 142.1, 141.8, 138.1, 136.4, 136.2, 135.9,

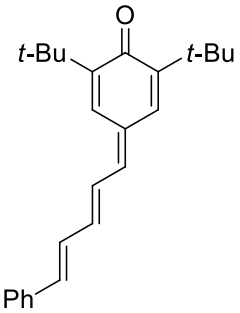
131.2, 129.6, 129.3, 129.0, 127.6, 123.6, 17.0, 16.4 ppm. **IR(KBr):** 1635, 1592, 1538, 1608, 1024, 971, 748, 687 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{17}H_{16}O+H]^+$: 237.1274; found: 237.1275.

(*E*)-2,6-Diisopropyl-4-(3-phenylallylidene)cyclohexa-2,5-dienone (1n)



Yellow solid, m.p. 76 – 78 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.42 – 7.32 (m, 3H), 7.01 (d, *J* = 15.2 Hz, 1H), 6.89 (d, *J* = 11.4 Hz, 2H), 3.31 – 3.13 (m, 2H), 1.21 (s, 3H), 1.19 (s, 3H), 1.16 (s, 3H), 1.14 (s, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.2, 146.4, 145.9, 142.4, 141.5, 136.3, 134.3, 131.4, 129.6, 129.0, 127.6, 125.1, 123.6, 27.1, 26.6, 22.2, 22.1 ppm. **IR(KBr):** 2955, 1586, 1570, 1540, 1448, 1359, 984, 974, 749, 687 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{21}H_{24}O+H]^+$: 293.1900; found: 293.1896.

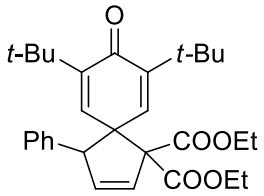
2,6-Di-*tert*-butyl-4-((2*E*,4*E*)-5-phenylpenta-2,4-dien-1-ylidene)cyclohexa-2,5-dienone (1o)



Red solid, m.p. 160–163 ºC. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 – 7.45 (m, 3H), 7.38 – 7.29 (m, 3H), 7.10 – 7.01 (m, 2H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.87 – 6.76 (m, 3H), 1.36 (s, 9H), 1.32 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.8, 147.7, 147.3, 141.2, 140.9, 136.9, 136.2, 133.9, 130.6, 128.4, 128.2, 127.6, 126.6, 126.5, 124.8, 35.0, 34.6, 29.1, 29.1 ppm. **IR(KBr):** 2954, 1610, 1597, 1558, 1570, 1524, 1385, 1359, 984, 944, 754, 690 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{25}H_{30}O+H]^+$: 347.2369; found: 347.2368.

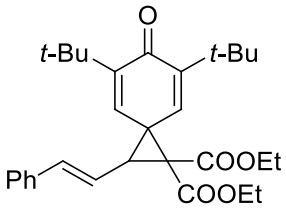
c) Characterization of the products

Diethyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3aa)



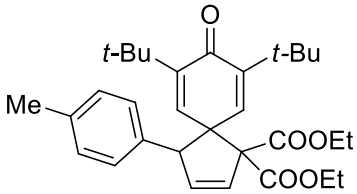
White solid, m.p. 128 – 129 °C. 92% yield (44.0 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 2.9 Hz, 1H), 7.18 – 7.16 (m, 3H), 6.98 – 6.96 (m, 2H), 6.41 (dd, *J* = 5.7, 1.5 Hz, 1H), 6.29 – 6.27 (m, 2H), 4.79 (s, 1H), 4.34 – 4.15 (m, 2H), 4.09 – 3.98 (m, 1H), 3.88 – 3.77 (m, 1H), 1.31 – 1.28 (m, 12H), 1.05 (t, *J* = 7.1 Hz, 3H), 0.82 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.1, 168.7, 168.1, 149.8, 148.0, 139.2, 138.3, 137.4, 137.1, 131.2, 127.2, 127.5, 127.3, 72.8, 61.8, 61.3, 58.7, 56.9, 35.2, 34.6, 29.4, 28.8, 14.1, 13.6 ppm. **IR(KBr):** 2950, 2855, 1753, 1726, 1639, 1366, 1274, 1254, 742, 695 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{38}O_5+H]^+$: 479.2792; found: 479.2785.

(*E*)-Diethyl 5,7-di-*tert*-butyl-6-oxo-2-styrylspiro[2.5]octa-4,7-diene-1,1-dicarboxylate (3aa')



Yellow solid, m.p. 105 – 107 °C. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.37 – 7.24 (m, 5H), 6.91 (d, *J* = 2.7 Hz, 1H), 6.78 (d, *J* = 15.7 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 6.24 (dd, *J* = 15.7, 9.5 Hz, 1H), 4.33 – 4.25 (m, 4H), 3.40 (d, *J* = 9.5 Hz, 1H), 1.33 – 1.24 (m, 24H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.6, 166.8, 165.5, 150.0, 149.9, 136.9, 136.4, 136.3, 134.3, 128.7, 128.1, 126.3, 120.4, 62.6, 62.2, 50.3, 42.4, 39.8, 35.6, 35.3, 29.4, 29.3, 14.2 ppm. **IR(KBr):** 3476, 3414, 2951, 1736, 1724, 1645, 1619, 1302, 1266, 1255, 972, 751 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{38}O_5+Na]^+$: 501.2612; found: 501.2599.

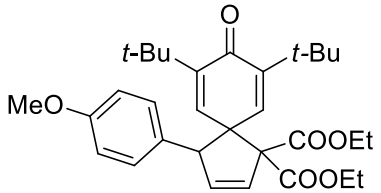
Diethyl 7,9-di-*tert*-butyl-8-oxo-4-(p-tolyl)spiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ba)



White solid, m.p. 136 – 137 °C. 96% yield (47.3 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.8 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 2H), 6.84 (d, *J* = 7.9 Hz, 2H), 6.39 (dd, *J* = 5.7, 1.4 Hz, 1H), 6.28 – 6.25 (m, 2H), 4.75 (s, 1H), 4.33 – 4.15 (m, 2H), 4.08 – 3.97 (m, 1H), 3.88 – 3.77 (m, 1H), 2.24 (s, 3H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.83 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.6, 168.3, 167.7, 149.2, 147.3, 138.8, 138.1, 137.1, 136.4, 133.5, 130.4, 127.9, 126.8, 72.3, 61.3, 60.8, 57.9, 56.5, 34.7, 34.1, 29.0, 28.2, 20.5, 13.6, 13.1 ppm. **IR(KBr):** 2956, 1752, 1725, 1636, 1366, 1273, 1255, 1214, 1104, 721 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for

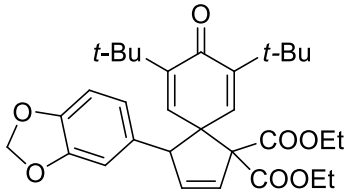
$[C_{31}H_{40}O_5+H]^+$: 493.2949; found: 493.2948.

Diethyl 7,9-di-*tert*-butyl-4-(4-methoxyphenyl)-8-oxospiro[4.5]deca-2,6,9-triene-1,1 -dicarboxylate (3ca)



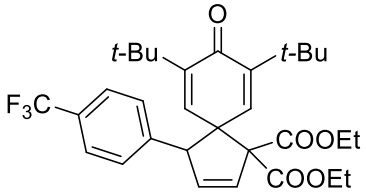
White solid, m.p. 116 – 117 °C. 92% yield (46.7 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.51 (d, *J* = 2.9 Hz, 1H), 6.88 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 6.37 (dd, *J* = 5.8, 1.6 Hz, 1H), 6.29 (d, *J* = 2.9 Hz, 1H), 6.25 (dd, *J* = 5.7, 2.9 Hz, 1H), 4.75 – 4.73(d, *J* = 2.1 Hz, 1H), 4.33 – 4.15 (m, 2H), 4.08 – 3.96 (m, 1H), 3.88 – 3.77 (m, 1H), 3.72 (s, 3H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.1, 168.7, 168.2, 158.9, 149.7, 147.9, 139.3, 138.6, 137.7, 130.9, 129.2, 128.5, 113.3, 72.7, 61.8, 61.3, 58.1, 57.1, 55.3, 35.2, 34.6, 29.5, 28.8, 14.1, 13.6 ppm. **IR(KBr):** 2954, 1730, 1663, 1642, 1516, 1361, 1257, 1206, 1104, 1041, 818 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{31}H_{40}O_6+Na]^+$: 531.2717; found: 531.2703.

Diethyl 4-(benzo[d][1,3]dioxol-5-yl)-7,9-di-*tert*-butyl-8-oxospiro[4.5]deca-2,6,9-triene-1,1 -dicarboxylate (3da)



White solid, m.p. 140 – 141 °C. 88% yield (46.0 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.48 (d, *J* = 2.8 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 1H), 6.44 – 6.41 (m, 2H), 6.34 (dd, *J* = 5.7, 1.3 Hz, 1H), 6.29 – 6.25 (m, 2H), 5.85 (s, 2H), 4.71 (s, 1H), 4.33 – 4.15 (m, 2H), 4.08 – 3.98 (m, 1H), 3.89 – 3.78 (m, 1H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.90 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.1, 168.7, 168.1, 149.9, 148.0, 147.2, 146.7, 139.1, 138.4, 137.4, 131.1, 130.1, 120.7, 108.1, 107.6, 100.9, 72.6, 61.9, 61.4, 58.5, 57.1, 35.2, 34.6, 29.5, 28.9, 14.1, 13.7 ppm. **IR(KBr):** 2968, 2902, 1728, 1639, 1493, 1361, 1256, 1203, 1101, 1036, 736 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{31}H_{38}O_7+Na]^+$: 545.2510; found: 545.2505.

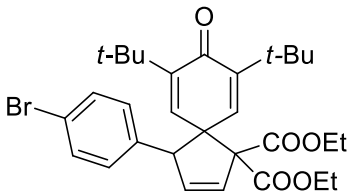
Diethyl 7,9-di-*tert*-butyl-8-oxo-4-(4-(trifluoromethyl)phenyl)spiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ea)



White solid, m.p. 192 – 193 °C. 93% yield (50.9 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.9 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.40 (dd, *J* = 5.8, 1.3 Hz, 1H), 6.34 (dd, *J* = 5.7, 2.7 Hz, 1H), 6.24 (d, *J* = 2.9 Hz, 1H), 4.84 (s, 1H), 4.35 – 4.16 (m, 2H), 4.10 –

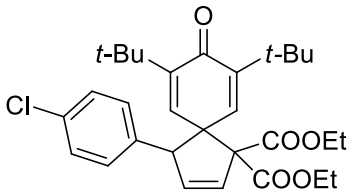
3.99 (m, 1H), 3.88 – 3.77 (m, 1H), 1.32 – 1.27 (m, 12H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.81 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.2, 168.0, 167.3, 149.7, 148.0, 140.9, 138.2, 137.1, 135.7, 131.6, 129.4, 127.2, 124.3 (J_{C-F} = 3.7 Hz), 121.7, 72.3, 61.5, 61.0, 57.8, 56.2, 34.8, 34.1, 28.9, 28.2, 13.6, 13.1 ppm. **IR(KBr):** 2962, 1750, 1722, 1637, 1612, 1367, 1325, 1260, 1163, 1128, 1111, 1068, 1019 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{31}H_{37}F_3O_5+Na]^+$: 569.2485; found: 569.2481.

Diethyl 4-(4-bromophenyl)-7,9-di-*tert*-butyl-8-oxospiro[4.5]deca-2,6,9-triene-1,1 -dicarboxylate (3fa)



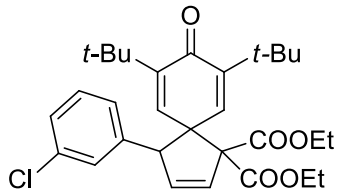
White solid, m.p. 179 – 180 °C. 90% yield (50.9 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.9 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.35 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.29 (dd, *J* = 5.8, 2.7 Hz, 1H), 6.24 (d, *J* = 2.9 Hz, 1H), 4.74 (s, 1H), 4.33 – 4.15 (m, 2H), 4.09 – 3.98 (m, 1H), 3.88 – 3.77 (m, 1H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 168.6, 167.9, 150.1, 148.4, 138.9, 137.9, 136.6, 136.2, 131.7, 130.9, 129.1, 121.2, 72.8, 61.9, 61.4, 58.1, 56.8, 35.3, 34.7, 29.5, 28.8, 14.1, 13.6 ppm. **IR(KBr):** 2944, 2361, 1750, 1724, 1663, 1637, 1401, 1385, 1367, 1101, 617 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{37}BrO_5+Na]^+$: 581.1702; found: 581.1694.

Diethyl 7,9-di-*tert*-butyl-4-(4-chlorophenyl)-8-oxospiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ga)



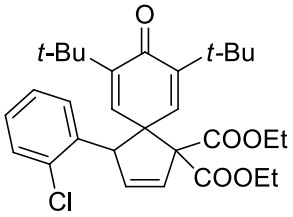
White solid, m.p. 172 – 174 °C. 94% yield (48.2 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.9 Hz, 1H), 7.18 – 7.15 (m, 2H), 6.90 (d, *J* = 8.4 Hz, 2H), 6.36 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.29 (dd, *J* = 5.8, 2.8 Hz, 1H), 6.25 (d, *J* = 3.0 Hz, 1H), 4.75 (s, 1H), 4.33 – 4.13 (m, 2H), 4.11 – 3.98 (m, 1H), 3.87 – 3.77 (m, 1H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 168.6, 167.9, 150.1, 148.3, 138.9, 137.9, 136.7, 135.7, 133.1, 131.6, 128.7, 127.9, 72.8, 61.9, 61.4, 58.0, 56.8, 35.2, 34.7, 29.5, 28.8, 14.1, 13.6 ppm. **IR(KBr):** 2956, 1751, 1724, 1636, 1490, 1372, 1255, 1215, 1134, 1105, 618 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{37}ClO_5+H]^+$: 512.2402; found: 512.2398.

Diethyl 7,9-di-*tert*-butyl-4-(3-chlorophenyl)-8-oxospiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ha)



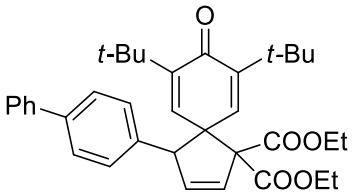
White solid, m.p. 140 – 141 °C. 88% yield (45.1 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.9 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.97 (s, 1H), 6.84 (d, *J* = 7.0 Hz, 1H), 6.37 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.31 (dd, *J* = 5.8, 2.8 Hz, 1H), 6.26 (d, *J* = 2.9 Hz, 1H), 4.76 (s, 1H), 4.34 – 4.15 (m, 2H), 4.09 – 3.98 (m, 1H), 3.89 – 3.78 (m, 1H), 1.31 – 1.26 (m, 12H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.86 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 168.5, 167.9, 150.2, 148.4, 139.2, 138.7, 137.8, 136.5, 133.8, 131.8, 129.1, 127.7, 127.4, 125.6, 72.6, 62.0, 61.4, 58.3, 56.9, 35.3, 34.6, 29.5, 28.8, 14.1, 13.6 ppm. **IR(KBr):** 2997, 2944, 1728, 1641, 1478, 1461, 1367, 1262, 1212, 1105, 1057, 754 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{37}ClO_5+Na]^+$: 535.2222; found: 535.2213.

Diethyl 7,9-di-*tert*-butyl-4-(2-chlorophenyl)-8-oxospiro[4.5]deca-2,6,9-triene-1,1 -dicarboxylate (3ia)



White solid, m.p. 124 – 125 °C. 87% yield (44.6 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 3.0 Hz, 1H), 7.26 – 7.23 (m, 1H), 7.19 – 7.08 (m, 3H), 6.46 (d, *J* = 2.9 Hz, 1H), 6.30 (dd, *J* = 5.7, 2.8 Hz, 1H), 6.24 (dd, *J* = 5.8, 1.6 Hz, 1H), 5.38 – 5.37 (m, 1H), 4.32 – 4.17 (m, 2H), 4.11 – 4.01 (m, 1H), 3.90 – 3.79 (m, 1H), 1.32 – 1.23 (m, 12H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.93 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.7, 168.6, 168.1, 148.2, 147.9, 140.3, 137.9, 137.8, 135.1, 134.1, 131.3, 130.6, 129.8, 128.6, 126.1, 73.1, 61.9, 61.4, 57.2, 55.6, 35.1, 34.8, 29.0, 28.9, 14.1, 13.7 ppm. **IR(KBr):** 2960, 2917, 1869, 1725, 1637, 1474, 1466, 1388, 1367, 1263, 1222, 1109 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{37}ClO_5+Na]^+$: 535.2222; found: 535.2219.

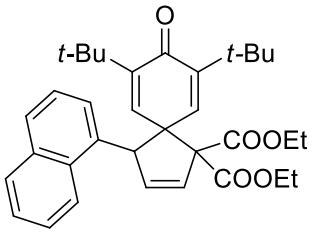
Diethyl 4-([1,1'-biphenyl]-4-yl)-7,9-di-*tert*-butyl-8-oxospiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ja)



White solid, m.p. 130 – 131 °C. 97% yield (53.8 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.55 (d, *J* = 2.8 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.41 – 7.37 (m, 4H), 7.34 – 7.29 (m, 1H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.45 (dd, *J* = 5.8, 1.1 Hz, 1H), 6.32 – 6.29 (m, 2H), 4.83 (s, 1H), 4.35 – 4.16 (m, 2H), 4.09 – 3.98 (m, 1H), 3.91 – 3.78 (m, 1H), 1.32 – 1.27 (m, 12H), 1.06 (t, *J* = 7.1 Hz, 3H), 0.83 (s,

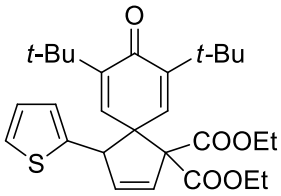
9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.5, 168.2, 167.6, 149.4, 147.5, 140.4, 140.0, 138.7, 137.9, 136.8, 135.7, 130.8, 128.3, 127.3, 126.8, 126.6, 126.1, 72.3, 61.4, 60.9, 57.9, 56.5, 34.8, 34.2, 29.0, 28.3, 13.6, 13.2 ppm. **IR(KBr):** 2953, 1731, 1637, 1484, 1366, 1252, 1211, 1102, 752 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{36}H_{42}O_5+Na]^+$: 577.2924; found: 577.2921 .

Diethyl 7,9-di-*tert*-butyl-4-(naphthalen-1-yl)-8-oxospiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ka)



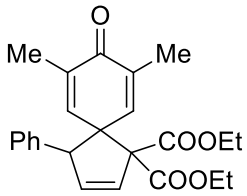
White solid, m.p. 158 – 159 °C. 99% yield (52.4 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.96 (d, *J* = 9.0 Hz, 1H), 7.76 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 2.9 Hz, 1H), 7.44 – 7.34 (m, 3H), 7.28 (s, 1H), 6.47 – 6.44 (m, 2H), 6.36 (dd, *J* = 5.7, 2.7 Hz, 1H), 5.68 (s, 1H), 4.47 – 4.14 (m, 2H), 4.14 – 3.94 (m, 1H), 3.94 – 3.65 (m, 1H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.10 – 1.04 (m, 12H), 0.76 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 184.9, 168.4, 167.6, 147.8, 146.8, 139.4, 138.8, 138.3, 133.3, 133.2, 131.4, 130.4, 128.2, 127.5, 126.0, 125.1, 124.9, 124.3, 124.1, 72.9, 61.4, 60.9, 56.0, 54.1, 34.5, 34.1, 28.4, 28.3, 13.6, 13.2 ppm. **IR(KBr):** 2950, 2855, 1721, 1661, 1638, 1361, 1272, 1219, 1112, 783 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{34}H_{40}O_5+Na]^+$: 551.2768; found: 551.2765.

Diethyl 7,9-di-*tert*-butyl-8-oxo-4-(thiophen-2-yl)spiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3la)



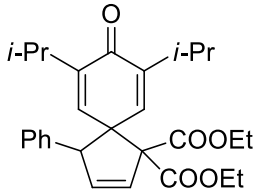
White solid, m.p. 110 – 111 °C. 97% yield (48.5 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.9 Hz, 1H), 7.06 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.85 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.69 (d, *J* = 3.4 Hz, 1H), 6.38 (dd, *J* = 5.7, 1.5 Hz, 1H), 6.30 – 6.27 (m, 2H), 4.99 (s, 1H), 4.33 – 4.14 (m, 2H), 4.10 – 3.99 (m, 1H), 3.88 – 3.77 (m, 1H), 1.30 – 1.26 (m, 12H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.89 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.2, 168.5, 167.8, 150.6, 148.4, 140.2, 138.4, 138.0, 137.0, 131.2, 126.3, 124.5, 123.9, 72.9, 61.9, 61.4, 56.7, 54.1, 35.3, 34.6, 29.4, 28.9, 14.1, 13.6 ppm. **IR(KBr):** 2956, 2855, 1747, 1728, 1638, 1369, 1266, 1223, 1101, 954, 815, 723 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{28}H_{36}O_5S+Na]^+$: 507.2176; found: 507.2173.

Diethyl 7,9-dimethyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ma)



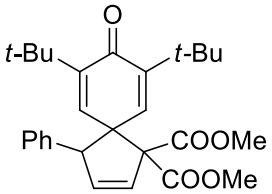
White solid, m.p. 138 – 140 °C. 84% yield (33.4 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ7.60 (dd, J = 2.9, 1.4 Hz, 1H), 7.18 – 7.15 (m, 3H), 6.98 – 6.95 (m, 2H), 6.45 (dd, J = 2.9, 1.4 Hz, 1H), 6.37 (dd, J = 5.8, 1.6 Hz, 1H), 6.27 (dd, J = 5.7, 2.9 Hz, 1H), 4.80 – 4.79 (m, 1H), 4.29 – 4.16 (m, 2H), 4.09 – 3.91 (m, 2H), 1.96 (d, J = 1.3 Hz, 3H), 1.49 (d, J = 1.3 Hz, 3H), 1.28 (t, J = 7.1 Hz, 4H), 1.02 (t, J = 7.1 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.8, 168.5, 168.0, 142.9, 142.4, 138.0, 137.6, 136.9, 136.5, 131.0, 127.9, 127.6, 127.3, 72.5, 62.0, 61.4, 58.5, 58.0, 16.6, 15.6, 14.0, 13.8 ppm. **IR(KBr):** 2979, 2920, 1749, 1728, 1632, 1443, 1361, 1252, 1208, 1103, 939, 727, 699 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{24}H_{26}O_5+Na]^+$: 417.1672; found: 417.1674.

Diethyl 7,9-diisopropyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3na)



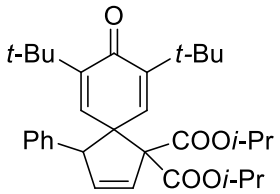
White solid, m.p. 74 – 78 °C. 91% yield (41.2 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 2.9, 0.7 Hz, 1H), 7.18 – 7.14 (m, 3H), 6.99 – 6.95 (m, 2H), 6.41 (dd, *J* = 5.8, 1.6 Hz, 1H), 6.33 (dd, *J* = 2.9, 0.7 Hz, 1H), 6.29 (dd, *J* = 5.8, 2.9 Hz, 1H), 4.85 – 4.83 (m, 1H), 4.34 – 4.15 (m, 2H), 4.05 – 3.80 (m, 2H), 3.13 – 2.99 (m, 1H), 2.73 – 2.59 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.17 – 1.11 (m, 6H), 1.02 (t, *J* = 7.2 Hz, 3H), 0.79 (d, *J* = 6.9 Hz, 3H), 0.48 (d, *J* = 6.9 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 184.9, 168.6, 167.9, 148.1, 146.1, 139.7, 138.7, 137.5, 137.0, 131.1, 127.9, 127.5, 127.3, 72.8, 61.9, 61.3, 58.4, 56.9, 26.7, 26.0, 22.1, 21.5, 21.0, 14.1, 13.6 ppm. **IR(KBr):** 2962, 2855, 1727, 1636, 1455, 1399, 1385, 1252, 1212, 1101, 698 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{28}H_{34}O_5+Na]^+$: 473.2298; found: 473.2286.

Dimethyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ab)



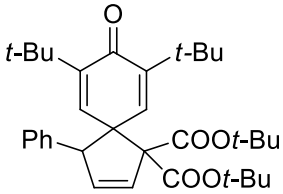
White solid, m.p. 120 – 121 °C. 88% yield (40.0 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 2.9 Hz, 1H), 7.19 – 7.17 (m, 3H), 6.99 – 6.95 (m, 2H), 6.42 (dd, *J* = 5.8, 1.6 Hz, 1H), 6.29 – 6.26 (m, 2H), 4.79 – 4.78 (m, 1H), 3.78 (s, 3H), 3.49 (s, 3H), 1.28 (s, 9H), 0.83 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.0, 169.0, 168.4, 150.1, 148.1, 138.8, 138.1, 137.6, 137.0, 130.9, 127.9, 127.4, 127.3, 73.0, 58.4, 56.9, 52.9, 52.1, 35.2, 34.6, 29.4, 28.1 ppm. **IR(KBr):** 2956, 1750, 1731, 1636, 1366, 1252, 1216, 1104, 751, 698 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{28}H_{34}O_5+Na]^+$: 473.2298; found: 473.2303.

Diisopropyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ac)



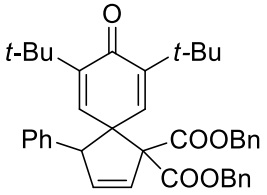
White solid, m.p. 186 – 187 °C. 87% yield (44.1 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.9 Hz, 1H), 7.19 – 7.16 (m, 3H), 6.97 – 6.94 (m, 2H), 6.40 (dd, *J* = 5.7, 1.4 Hz, 1H), 6.32 (d, *J* = 2.9 Hz, 1H), 6.26 (dd, *J* = 5.7, 2.8 Hz, 1H), 5.14 – 5.06 (m, 1H), 4.81 – 4.71 (m, 2H), 1.29 – 1.26 (m, 15H), 1.17 (d, *J* = 6.1 Hz, 3H), 0.96 (d, *J* = 6.3 Hz, 3H), 0.82 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.4, 167.8, 167.1, 149.0, 147.3, 138.9, 138.1, 136.8, 136.6, 131.0, 127.3, 127.1, 126.8, 71.9, 69.0, 68.6, 58.3, 56.5, 34.7, 34.1, 29.0, 28.2, 21.0, 20.9 ppm. **IR(KBr):** 2950, 1722, 1637, 1384, 1361, 1260, 1219, 1108, 951, 704 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{32}H_{42}O_5+Na]^+$: 529.2924; found: 529.2929.

Di-*tert*-butyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ad)



White solid, m.p. 182 – 183 °C. 90% yield (43.0 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.67 (d, *J* = 2.8 Hz, 1H), 7.17 – 7.14 (m, 3H), 6.93 – 6.91 (m, 2H), 6.38 – 6.34 (m, 2H), 6.26 (dd, *J* = 5.7, 2.8 Hz, 1H), 4.80 (s, 1H), 1.51 (s, 9H), 1.30 – 1.29 (m, 18H), 0.81 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.0, 168.3, 167.2, 149.2, 147.8, 139.7, 138.9, 137.1 137.0, 132.0, 127.8, 127.8, 127.2, 82.8, 81.5, 73.3, 59.0, 57.8, 35.2, 34.6, 29.6, 28.7, 28.0, 27.9 ppm. **IR(KBr):** 2950, 1719, 1637, 1396, 1368, 1284, 1152, 1136, 1103, 839, 695, 618 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{34}H_{46}O_5+Na]^+$: 557.3237; found: 557.3237.

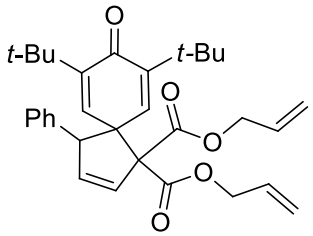
Dibenzyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ae)



White solid, m.p. 100 – 101 °C. 90% yield (54.3 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.9 Hz, 1H), 7.31 – 7.15 (m, 11H), 7.03 (dd, *J* = 7.4, 1.8 Hz, 2H), 6.94 (dd, *J* = 6.5, 2.8 Hz, 2H), 6.43 (dd, *J* = 5.8, 1.5 Hz, 1H), 6.34 – 6.31 (m, 2H), 5.22 (d, *J* = 12.3 Hz, 1H), 5.08 (dd, *J* = 12.3, 1.8 Hz, 2H), 4.79 (s, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 1.10 (s, 9H), 0.83 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 168.5, 168.0, 149.9, 148.2, 138.9, 138.1, 137.7, 136.9, 135.1, 134.5, 131.0, 128.6, 128.4, 128.3, 128.0, 127.9, 127.5, 127.4, 72.9, 67.6, 67.5, 58.9, 57.2, 35.1, 34.6, 29.3, 28.9 ppm. **IR(KBr):** 2950, 1753, 1731, 1636, 1449, 1369, 1250, 1212, 1092, 957, 736,

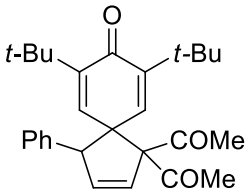
698 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{40}H_{42}O_5+Na]^+$: 625.2924; found: 625.2927.

Diallyl 7,9-di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3af)



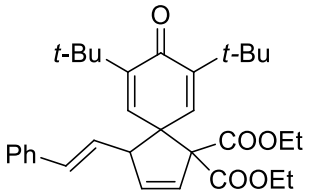
White solid, m.p. 97 – 98 °C. 94% yield (47.3 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ7.51 (d, J = 2.9 Hz, 1H), 7.20 – 7.16 (m, 3H), 6.96 (dd, J = 6.5, 2.7 Hz, 2H), 6.44 (dd, J = 5.8, 1.5 Hz, 1H), 6.30 (dd, J = 5.4, 2.9 Hz, 2H), 5.95 – 5.82 (m, 1H), 5.74 – 5.61 (m, 1H), 5.35 – 5.24 (m, 2H), 5.21 – 5.11 (m, 2H), 4.80 – 4.79 (m, 1H), 4.73 (dd, J = 13.3, 5.4 Hz, 1H), 4.62 (dd, J = 13.3, 5.5 Hz, 1H), 4.50 (dd, J = 13.0, 6.0 Hz, 1H), 4.23 (dd, J = 13.0, 5.8 Hz, 1H), 1.26 (s, 9H), 0.82 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 185.9, 168.2, 167.7, 150.0, 148.1, 138.8, 138.1, 137.7, 136.9, 130.9, 127.8, 127.5, 127.3, 119.1, 118.7, 72.9, 66.2, 58.7, 57.1, 35.2, 34.6, 29.4, 28.8 ppm. **IR(KBr):** 2954, 2861, 1750, 1728, 1661, 1639, 1452, 1367, 1253, 1215, 1101, 940, 734, 699 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{32}H_{38}O_5+Na]^+$: 525.2611; found: 525.2612.

1,1'-(7,9-Di-*tert*-butyl-8-oxo-4-phenylspiro[4.5]deca-2,6,9-triene-1,1-diyl)diethanone (3ag)



Yellow solid, m.p. 136 – 137 °C. 45% yield (18.9 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.61 (d, *J* = 2.9 Hz, 1H), 7.18 –7.15 (m, 3H), 6.94 – 6.91 (m, 2H), 6.47 (dd, *J* = 5.9, 2.8 Hz, 1H), 6.41 (dd, *J* = 5.9, 1.5 Hz, 1H), 6.17 (d, *J* = 2.9 Hz, 1H), 4.56 (s, 1H), 2.21 (s, 3H), 1.86 (s, 3H), 1.30 (s, 9H), 0.82 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 203.2, 202.3, 185.3, 150.1, 148.3, 139.3, 138.9, 137.2, 136.4, 131.5, 127.9, 127.6, 127.5, 86.4, 59.4, 56.6, 35.4, 34.7, 29.4, 29.3, 28.5, 28.1 ppm. **IR(KBr):** 2944, 2873, 1698, 1658,1638, 1366, 1357, 1255, 1184, 757, 701 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{28}H_{34}O_3+Na]^+$: 441.2400; found: 441.2406.

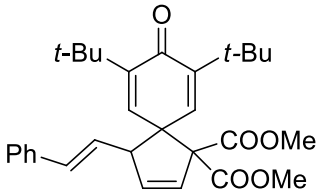
(*E*)-Diethyl 7,9-di-*tert*-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3oa)



White solid, m.p. 122 – 126 °C. 86% yield (43.4 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 2.8 Hz, 1H), 7.28 – 7.18 (m, 5H), 6.58 (d, *J* = 2.8 Hz, 1H), 6.33 (d, *J* = 15.8 Hz, 1H), 6.21 – 6.15 (m, 2H), 5.84 (dd, *J* = 15.8, 8.0 Hz, 1H), 4.25 – 4.13 (m, 3H), 4.10 – 4.04 (m, 1H), 3.95 – 3.86 (m, 1H), 1.25 (s, 12H), 1.10 (s, 12H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.6, 168.5, 168.1, 150.0, 149.0, 139.3, 138.3, 137.2, 136.6, 132.1, 130.4, 128.5, 127.5, 126.1, 125.6, 72.7, 61.8, 61.4,

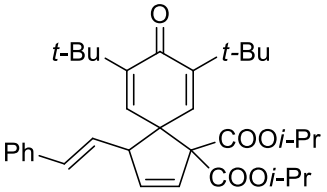
56.8, 56.4, 35.1, 35.0, 29.5, 29.4, 14.0, 13.7 ppm. **IR(KBr):** 2957, 1727, 1638, 1367, 1255, 1210, 1119, 751, 692 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{32}H_{40}O_5+Na]^+$: 527.2768; found: 527.2768.

(*E*)-Dimethyl 7,9-di-*tert*-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3ob)



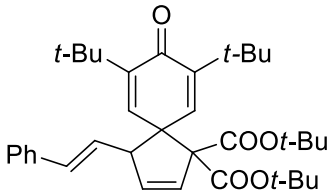
White solid, m.p. 98 – 102 °C. 81% yield (38.6 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 6H), 6.57 (d, *J* = 2.8 Hz, 1H), 6.34 (d, *J* = 15.8 Hz, 1H), 6.21 (dd, *J* = 5.7, 1.4 Hz, 1H), 6.16 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.85 (dd, *J* = 15.8, 8.1 Hz, 1H), 4.21 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.54 (s, 3H), 1.25 (s, 9H), 1.11 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 168.9, 168.3, 150.3, 149.2, 139.0, 138.1, 137.4, 136.6, 132.2, 130.1, 128.6, 127.6, 126.1, 125.4, 72.8, 56.5, 56.4, 52.8, 52.3, 35.2, 35.0, 29.5, 29.4 ppm. **IR(KBr):** 2957, 2861, 1735, 1637, 1364, 1269, 1218, 1060, 969, 750, 689 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{36}O_5+Na]^+$: 499.2455; found: 499.2450.

(*E*)-Diisopropyl 7,9-di-*tert*-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3oc)



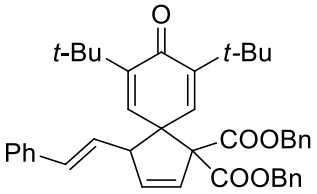
White solid, m.p. 146 – 148 °C. 79% yield (42.1 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.43 (d, *J* = 2.8 Hz, 1H), 7.27 – 7.18 (m, 5H), 6.59 (d, *J* = 2.8 Hz, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 5.7, 1.4 Hz, 1H), 6.15 (dd, *J* = 5.7, 2.5 Hz, 1H), 5.79 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.11 – 4.99 (m, 1H), 4.85 – 4.75 (m, 1H), 4.21 (d, *J* = 8.1 Hz, 1H), 1.26 – 1.22 (m, 15H), 1.18 (d, *J* = 6.1 Hz, 3H), 1.10 (s, 9H), 1.02 (d, *J* = 6.3 Hz, 3H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 168.2, 167.6, 149.6, 148.8, 139.6, 138.6, 137.1, 136.6, 132.1, 130.7, 128.5, 127.5, 126.1, 125.5, 72.1, 69.5, 69.2, 57.0, 56.6, 35.2, 35.0, 29.6, 29.4, 21.6, 21.5, 21.4 ppm. **IR(KBr):** 2991, 2956, 1722, 1664, 1637, 1364, 1259, 1107, 692 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{34}H_{44}O_5+Na]^+$: 555.3081; found: 555.3075.

(*E*)-Di-*tert*-butyl 7,9-di-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3od)



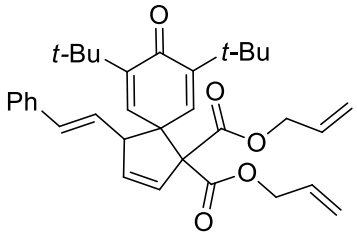
White solid, m.p. 138 – 139 °C. 93% yield (52.2 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 2.8 Hz, 1H), 7.27 – 7.16 (m, 5H), 6.56 (d, *J* = 2.8 Hz, 1H), 6.21 (d, *J* = 15.6 Hz, 1H), 6.18 – 6.14 (m, 2H), 5.70 (dd, *J* = 15.8, 8.4 Hz, 1H), 4.22 (d, *J* = 8.3 Hz, 1H), 1.49 (s, 9H), 1.33 (s, 9H), 1.26 (s, 9H), 1.10 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.5, 168.1, 167.2, 149.5, 148.9, 139.7, 138.8, 136.9, 136.5, 132.2, 131.2, 128.5, 127.4, 126.1, 125.4, 82.7, 81.5, 72.8, 57.7, 57.3, 35.1, 35.0, 29.7, 29.4, 28.0, 27.9 ppm. **IR(KBr):** 2955, 1722, 1635, 1455, 1367, 1282, 1231, 1165, 1113, 948, 848, 695 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{36}H_{48}O_5+Na]^+$: 583.3394; found: 583.3394.

(*E*)-Dibenzyl 7,9-di-*tert*-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3oe)



White solid, m.p. 102 – 103 °C. 83% yield (52.2 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 – 7.16 (m, 14H), 7.07 (dd, *J* = 7.3, 1.9 Hz, 2H), 6.60 (d, *J* = 2.8 Hz, 1H), 6.29 (d, *J* = 15.8 Hz, 1H), 6.25 – 6.20 (m, 2H), 5.81 (dd, *J* = 15.8, 8.2 Hz, 1H), 5.16 – 5.04 (m, 3H), 4.70 (d, *J* = 12.2 Hz, 1H), 4.21 (d, *J* = 8.0 Hz, 1H), 1.10 (s, 18H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 168.3, 167.9, 150.2, 149.3, 139.0, 138.1, 137.6, 136.5, 135.0, 134.6, 132.3, 130.2, 128.6, 128.6, 128.5, 128.4, 128.3, 128.0, 127.6, 126.1, 125.3, 72.8, 67.5, 67.5, 57.1, 56.7, 35.1, 35.0, 29.5, 29.4 ppm. **IR(KBr):** 2962, 2861, 1745, 1726, 1639, 1267, 1248, 1215, 957, 755, 739, 694 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{42}H_{44}O_5+Na]^+$: 651.3081; found: 651.3085.

(*E*)-Diallyl 7,9-di-*tert*-butyl-8-oxo-4-styrylspiro[4.5]deca-2,6,9-triene-1,1-dicarboxylate (3of)



White solid, m.p. 80 – 82 °C. 85% yield (45.0 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.30 (d, *J* = 2.8 Hz, 1H), 7.28 – 7.18 (m, 5H), 6.58 (d, *J* = 2.8 Hz, 1H), 6.32 (d, *J* = 15.8 Hz, 1H), 6.24 – 6.17 (m, 2H), 5.92 – 5.78 (m, 2H), 5.76 – 5.65 (m, 1H), 5.33 – 5.13 (m, 4H), 4.70 – 4.50 (m, 3H), 4.31 (dd, *J* = 13.1, 5.8 Hz, 1H), 4.21 (d, *J* = 8.1 Hz, 1H), 1.24 (s, 9H), 1.10 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.4, 168.1, 167.7, 150.2, 149.2, 139.0, 138.1, 137.5, 136.6, 132.3, 131.1,

131.1, 130.2, 128.6, 127.6, 126.1, 125.4, 119.1, 118.8, 72.7, 66.2, 56.8, 56.6, 35.2, 35.0, 30.0, 29.4 ppm. **IR(KBr):** 2953, 1753, 1730, 1655, 1637, 1618, 1385, 1366, 1340, 1250, 1120, 689, 612 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{34}H_{40}O_5+Na]^+$: 551.2768; found: 551.2763.

4. General Procedure for the Further Transformation of 3aa

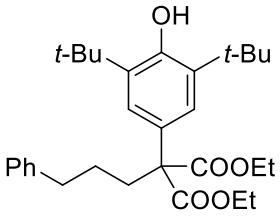
4.1 Treating 3aa with Pd/C under ambient pressure of H_2

a) General procedure

Into a 25 mL round bottom flask were placed Pd/C (0.01 mmol, 10% equiv) and **3aa** (0.1 mmol, 1 equiv) in EA (1 mL). The reactants were degassed and filled with hydrogen gas while stirring magnetically. After refluxing for 12 h, the solution was filtered, concentrated in *vacuo* and purified by chromatography on silica gel to afford the desired product **4aa**.

b) Characterization of the product

diethyl 2-(3,5-di-tert-butyl-4-hydroxyphenyl)-2-(3-phenylpropyl)malonate (4aa)



Colorless oil. 88% yield (42.5 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.21 (d, J = 7.5 Hz, 2H), 7.15 – 7.09 (m, 5H), 5.13 (s, 1H), 4.16 (q, J = 7.1 Hz, 4H), 2.62 (t, J = 7.6 Hz, 2H), 2.31 – 2.25 (m, 2H), 1.63 – 1.52 (m, 2H), 1.39 (s, 18H), 1.19 (t, J = 7.1 Hz, 6H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 171.2, 152.9, 141.8, 135.0, 128.3, 128.2, 127.2, 125.7, 124.9, 62.4, 61.1, 36.0, 35.2, 34.4, 30.3, 26.4, 14.0 ppm. **IR(KBr):** 2959, 2867, 1730, 1439, 1390, 1364, 1239, 1175, 1161, 1123, 1093, 1025, 886, 748, 701 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{30}H_{42}O_5+Na]^+$: 505.2924; found: 505.2923.

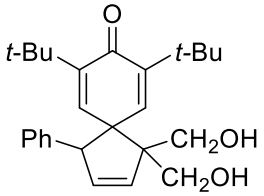
4.2 Reduction of 3aa with LAH

a) General procedure

A sealed tube was charged with **3aa** (0.1 mmol, 1 equiv), lithium aluminum hydride (0.3 mmol, 3 equiv), and tetrahydrofuran (1.0 mL). The reaction mixture was stirred at ambient temperature until the reaction was judged to be completed by TLC analysis. 1N Hydrochloric acid was added, and the mixture was extracted by ethyl acetate. Then the solution was concentrated in *vacuo* and purified by chromatography on silica gel to afford the desired product **5aa**.

b) Characterization of the product

7,9-di-tert-butyl-1,1-bis(hydroxymethyl)-4-phenylspiro[4.5]deca-2,6,9-trien-8-one (5aa)



Colorless oil. 62% yield (24.5 mg). **^{1}H NMR** (300 MHz, $CDCl_3$) δ 7.18 – 7.16 (m, 3H), 7.07 (d, *J* = 3.0 Hz, 1H), 6.94 (dd, *J* = 6.7, 2.4 Hz, 2H), 6.41 (d, *J* = 3.0 Hz, 1H), 6.27 (dd, *J* = 5.9, 1.4 Hz, 1H), 5.99 (dd, *J* = 5.9, 2.8 Hz, 1H), 4.40 (s, 1H), 3.99 – 3.88 (m, 2H), 3.67 – 3.52 (m, 2H), 2.23 (s,

1H), 1.57 (s, 1H), 1.29 (s, 9H), 0.87 (s, 9H) ppm. **^{13}C NMR** (75 MHz, $CDCl_3$) δ 186.0, 148.7, 146.5, 141.6, 140.6, 137.9, 134.0, 133.6, 127.9, 127.2, 127.1, 65.4, 65.3, 63.2, 59.2, 55.1, 35.1, 34.7, 29.5, 28.9 ppm. **IR(KBr):** 2956, 2924, 2868, 1708, 1657, 1635, 1455, 1366, 1313, 1251, 1199, 1031, 963, 930, 907, 883, 759, 744, 700 cm^{-1}. **HRMS (ESI)**: *m/z* calculated for $[C_{26}H_{34}O_3+Na]^+$: 417.2400; found: 417.2402.

5. Crystallographic Data

Procedure for recrystallization of compounds **3ga**, **3oa**: the hexane was slowly added into the solution of target products in dichloromethane (with different concentration), then the dichloromethane was evaporated from the mixed solvent system at room temperature under dark and the crystals were obtained after a few days.

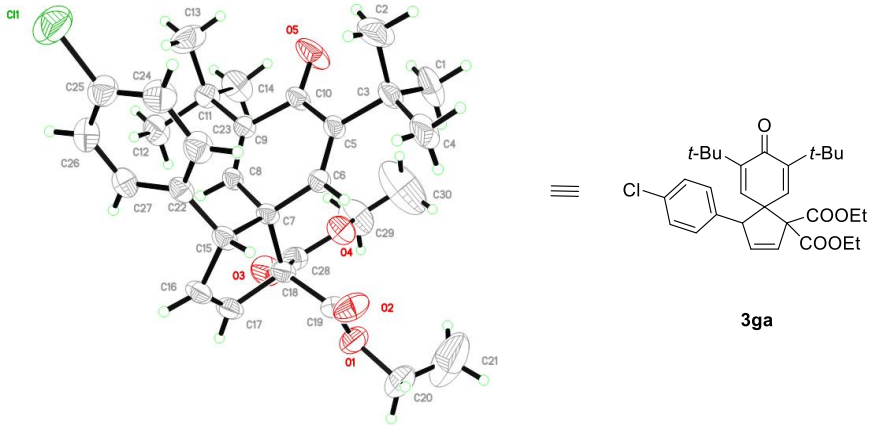
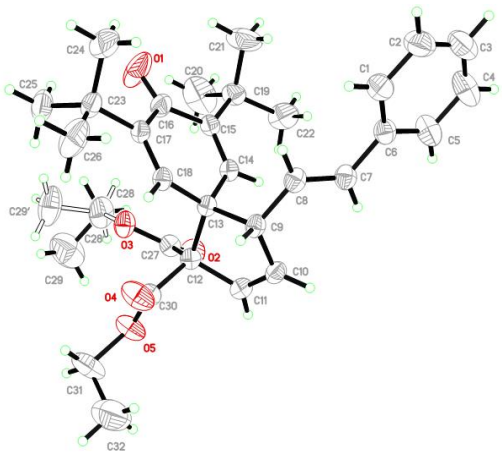
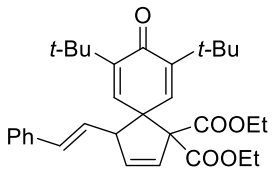


Table S1 Crystallographic Data of 3ga

Bond precision	C - C = 0.0044 A Wavelength = 0.71073
Cell	a = 9.7421 (6) b = 16.0093 (9) c = 19.0370 (11) alpha = 90 beta = 94.910 (2) gamma = 90
Temperature	296 K
Volume	2958.2 (3)
Space group	P2 (1) /n
Sum formula	$C_{30}H_{37}ClO_5$
Mr	512.04
Dx,g cm^{-3}	1.150
Z	4
Mu (mm^{-1})	0.163
F000	1092.0
h,k,lmax	11,19,22
Nref	5212
Tmin,Tmax	0.956,0.965
Correction method	# Reported T Limits:Tmin=0.956 Tmax=0.965
AbsCorr	MULTI-SCAN
Data completeness	0.999
Theta(max)	25.010
R(reflections)	0.0638(3468)
wR2(reflections)	0.1870(5212)
S	1.028
Npar	333



≡



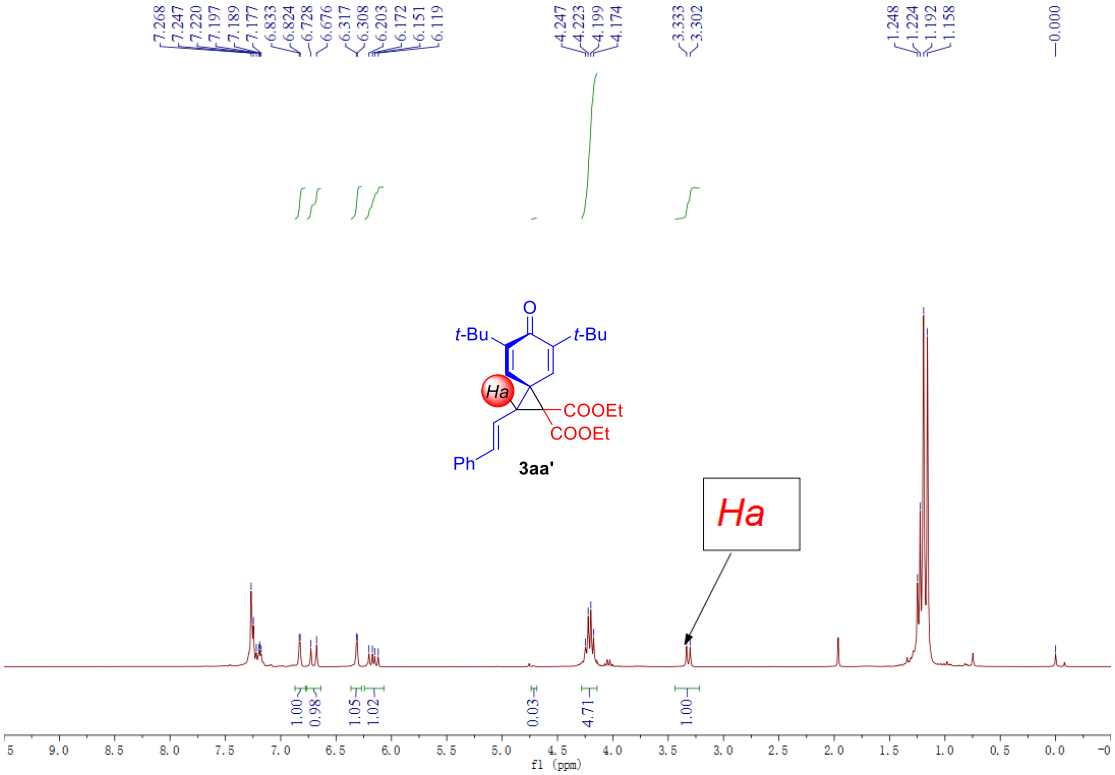
3oa

Table S2 Crystallographic Data of 3oa

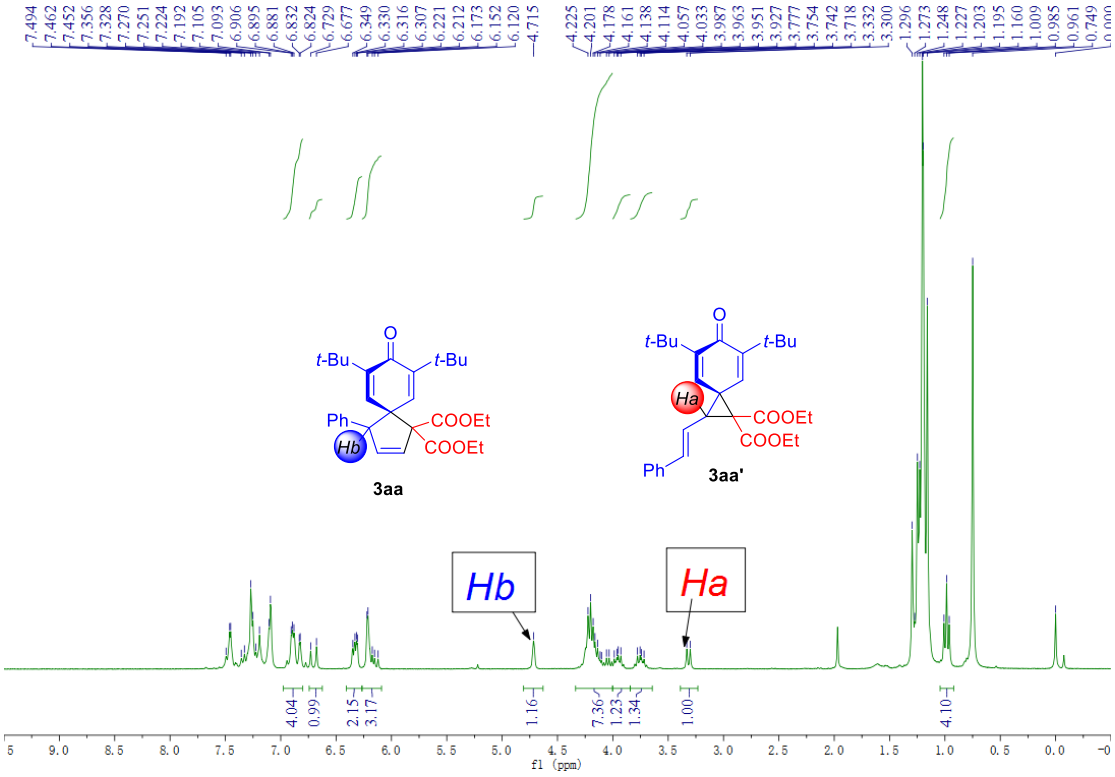
Bond precision	C - C = 0.0040 A Wavelength = 0.71073
Cell	a = 12.654 (3) b = 21.405 (5) c = 11.307 (3) alpha = 90 beta = 97.659 (4) gamma = 90
Temperature	296 K
Volume	3035.4(12)
Space group	P 21/c
Hall group	-P 2ybc
Sum formula	$C_{30}H_{40}O_5$
Mr	504.64
Dx,g cm^{-3}	1.104
Z	4
Mu (mm-1)	0.073
F000	1088.0
h,k,l max	14, 25, 13
N_{ref}	5351
Data completeness	1.000
Theta(max)	25.010
R(reflections)	0.0622(3588)
wR2(reflections)	0.2143(5351)
S	1.005
Npar	345

6. Full Spectrum of Control Experiments

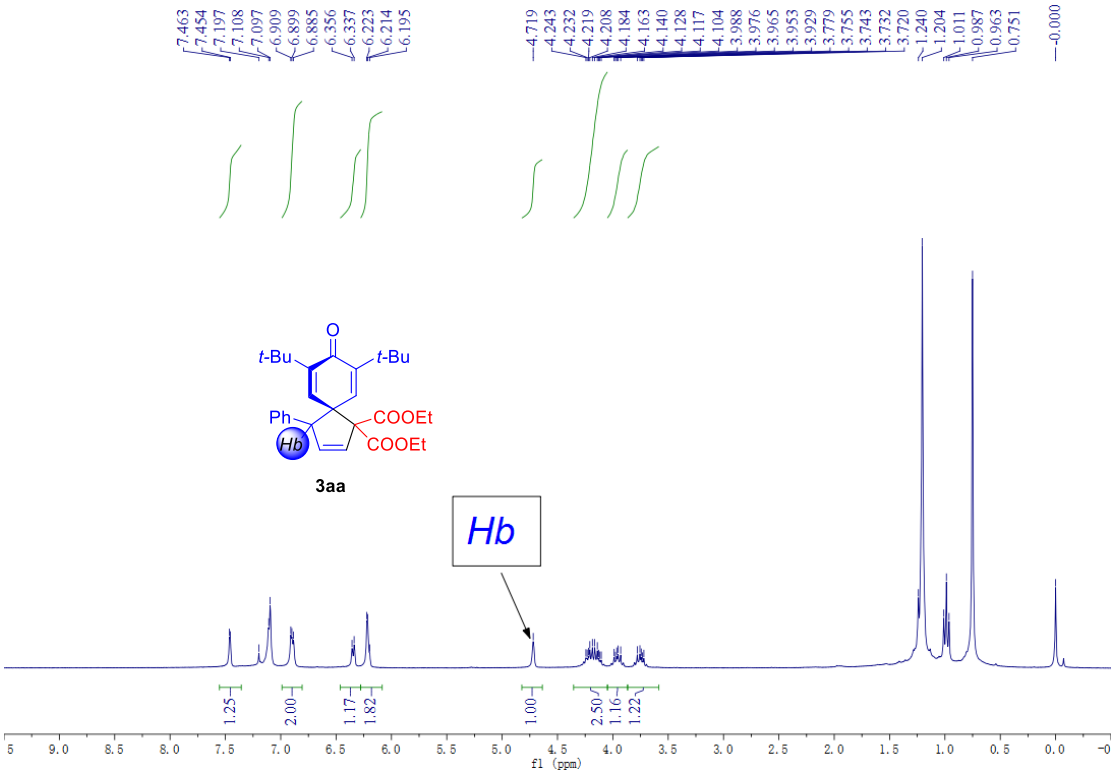
The ^{1}H NMR crude mixture spectrum (300 MHz). Reaction was performed at -10 ^{o}C for 12 h.



The ^{1}H NMR crude mixture spectrum (300 MHz). Reaction was performed at -10 ^{o}C for 12 h, then at 40 ^{o}C for 1 h.



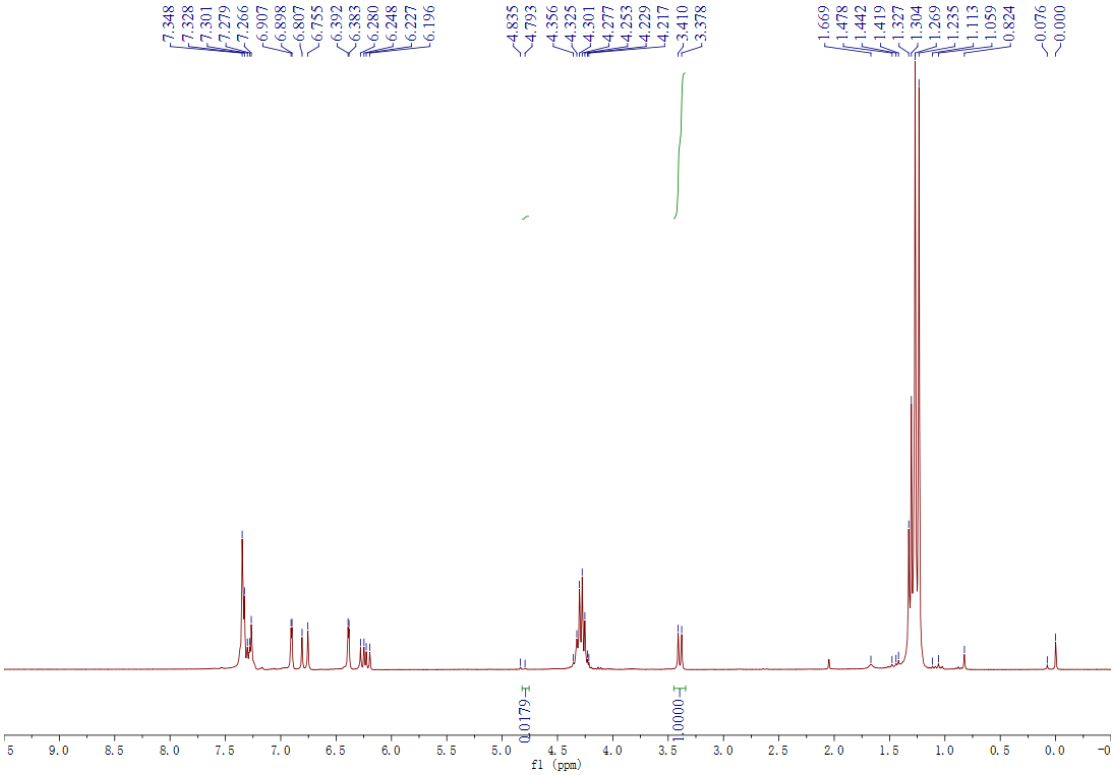
The ^{1}H NMR crude mixture spectrum (300 MHz). Reaction was performed at 40 ^{o}C for 12 h.



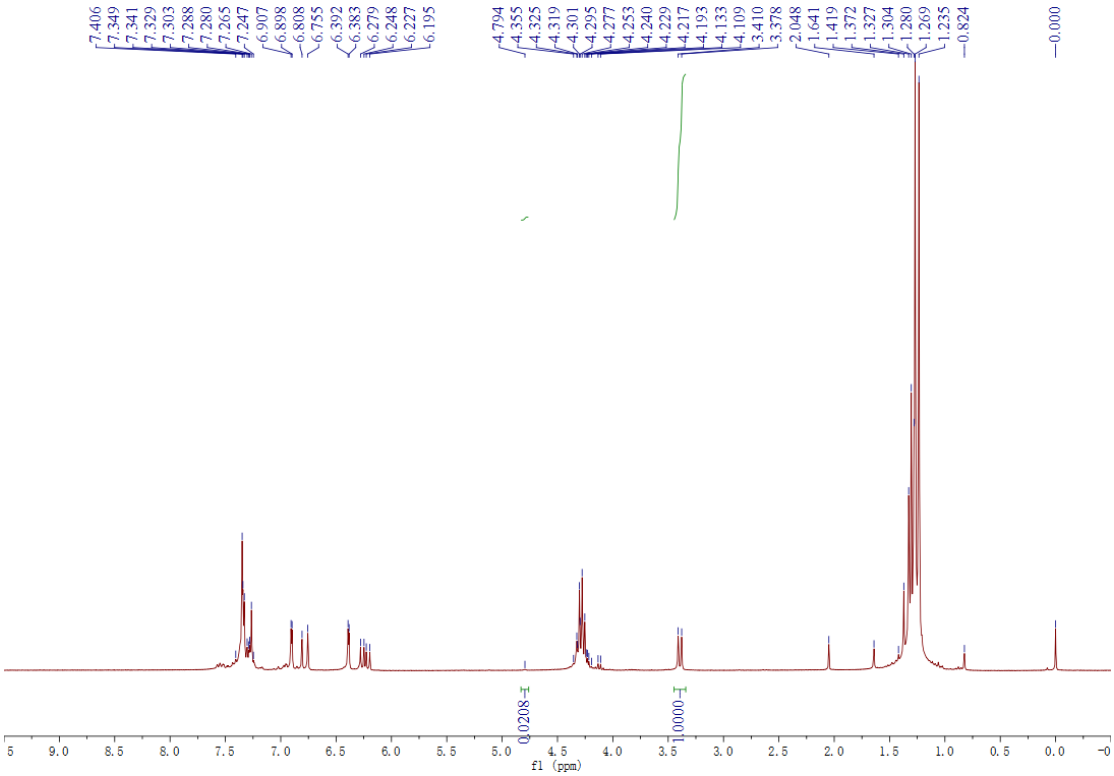
7. Kinetic Experiments

7.1 ^{1}H NMR (300 MHz) copies of rearrangement from 3aa'to 3aa at 25 ^{o}C

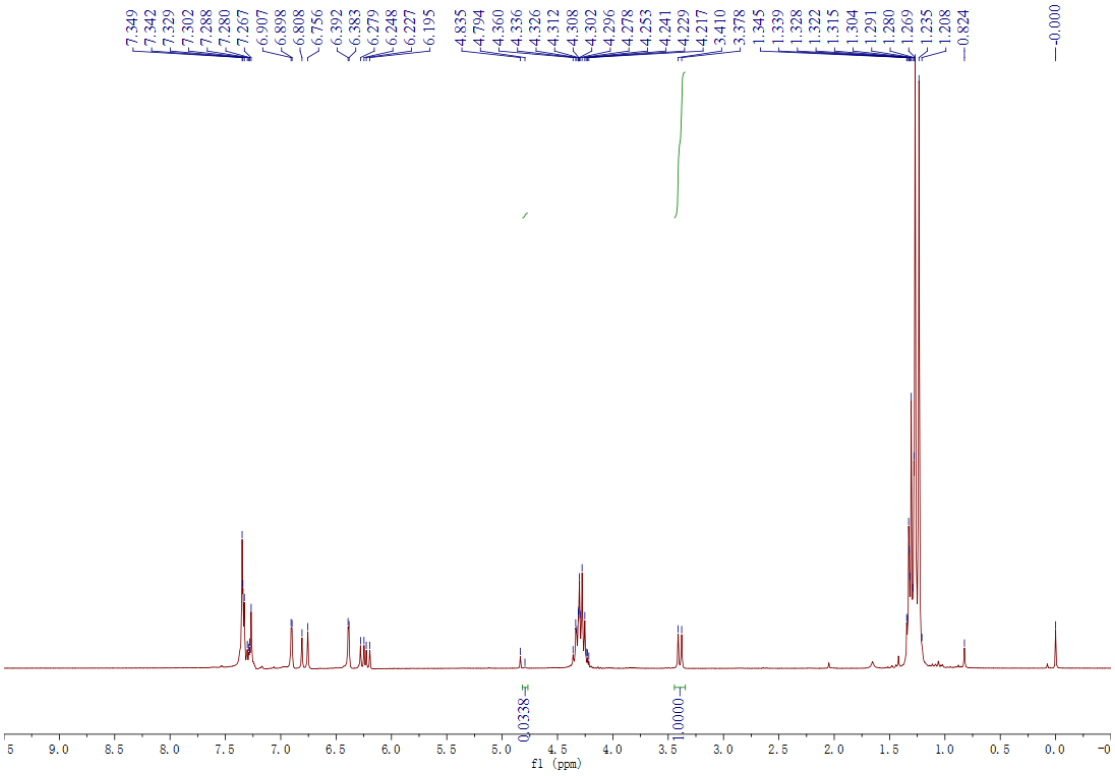
After heating 15 min:



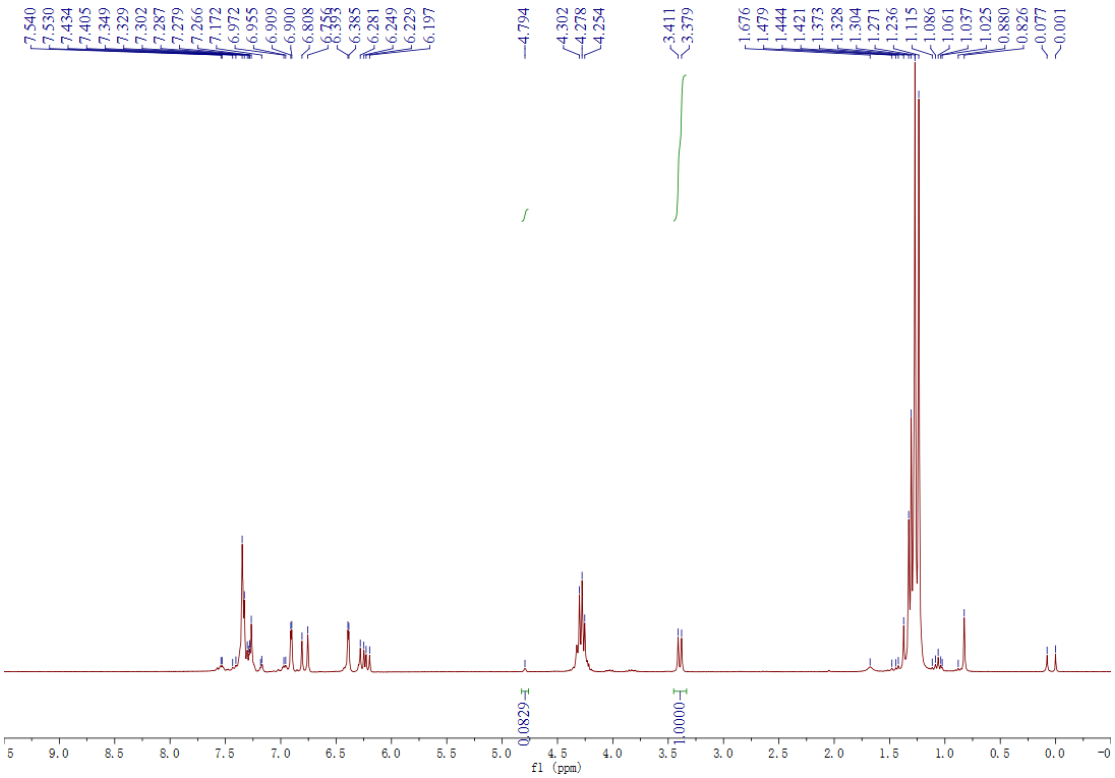
After heating 30 min:



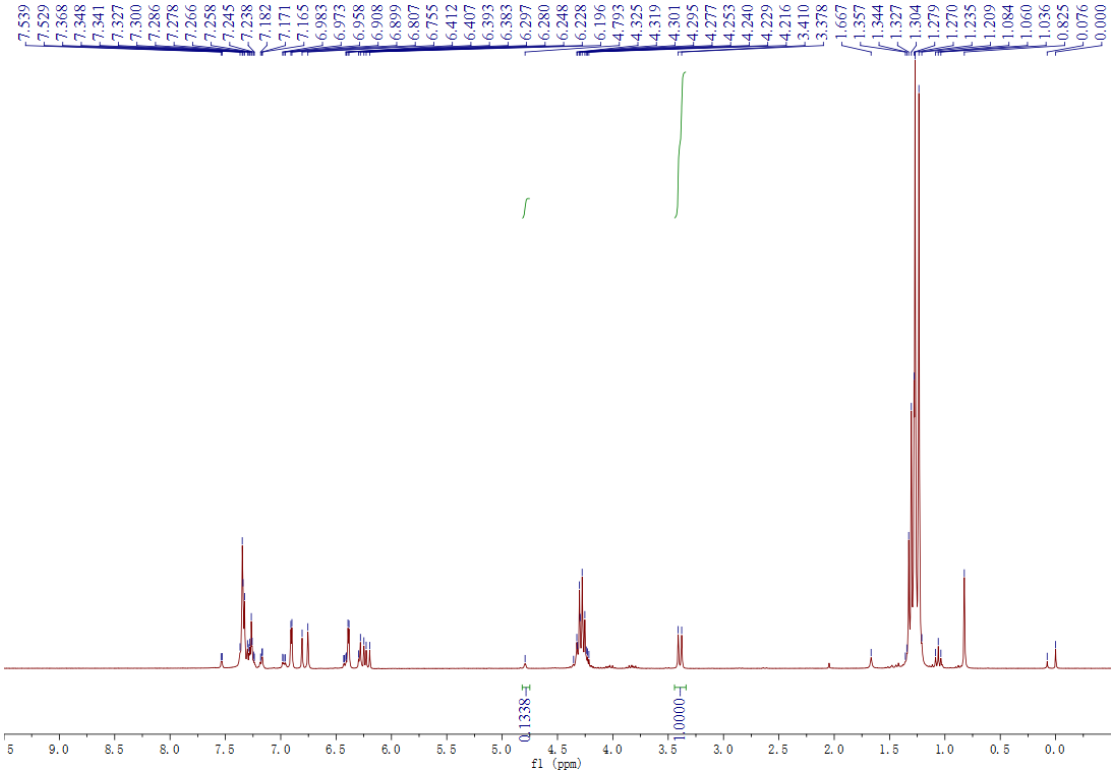
After heating for 45 min:



After heating for 120 min:

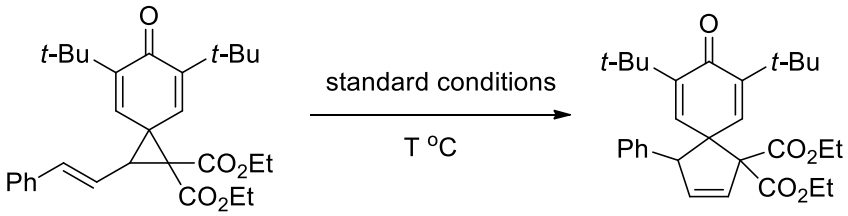


After heating for 240 min:



7.2 Kinetic data

The parallel reactions were run for indicated time, then quickly subjected to ^{1}H NMR (300 MHz) analysis at four different temperatures: 25 °C, 40 °C, 50 °C, and 60 °C [3].

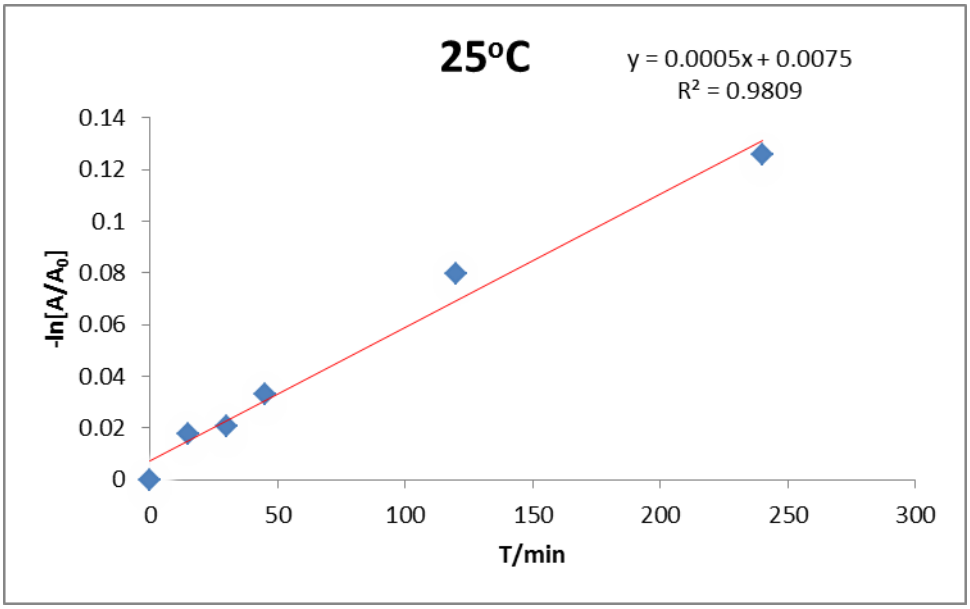


3aa' **3aa**

25 °C data:

Time(min)	Average Integrals		Relative Percentage	
	3aa'	**3aa**	**3aa'**	**3aa**
15	1.0000	0.0179	98.24	1.76
30	1.0000	0.0208	97.96	2.04
45	1.0000	0.0338	96.73	3.27
120	1.0000	0.0829	92.34	7.66
240	1.0000	0.1338	88.20	11.8

Time/min	-ln[A/A$_0$]
0	0
15	0.01776
30	0.02061
45	0.03325
120	0.07969
240	0.12556

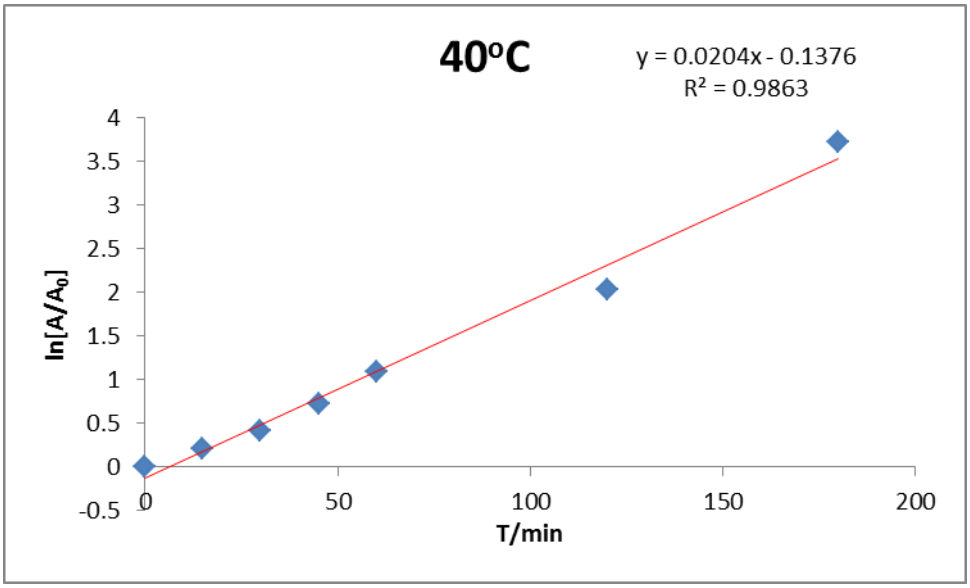


40 °C Data:

The 6 parallel reactions were run at 40 °C for indicated time, then quickly subjected to ^{1}H NMR (300 MHz) analysis.

Time(min)	Average Integrals		Relative Percentage	
	3aa'	**3aa**	**3aa'**	**3aa**
15	4.4408	1.0000	81.62	18.38
30	1.9193	1.0000	65.74	34.26
45	0.9349	1.0000	48.32	51.68
60	0.5034	1.0000	33.48	66.52
120	0.1510	1.0000	13.12	86.88
180	0.0246	1.0000	2.40	97.60

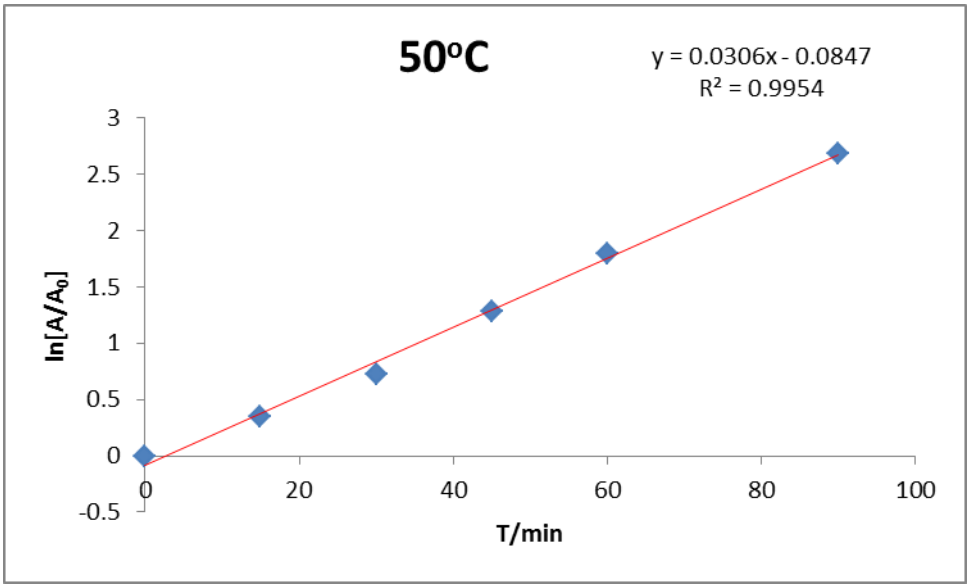
Time/min	$-\ln[A/A_0]$
0	0
15	0.20310
30	0.41946
45	0.72732
60	1.09422
120	2.03103
180	3.72970



50 °C data:

Time(min)	Average Integrals		Relative Percentage	
	3aa'	**3aa**	**3aa'**	**3aa**
15	1.0000	0.4220	70.32	29.68
30	1.0000	1.0545	48.67	51.33
45	1.0000	2.6019	27.76	72.24
60	1.0000	5.0112	16.64	83.36
90	1.0000	13.6880	6.81	93.19

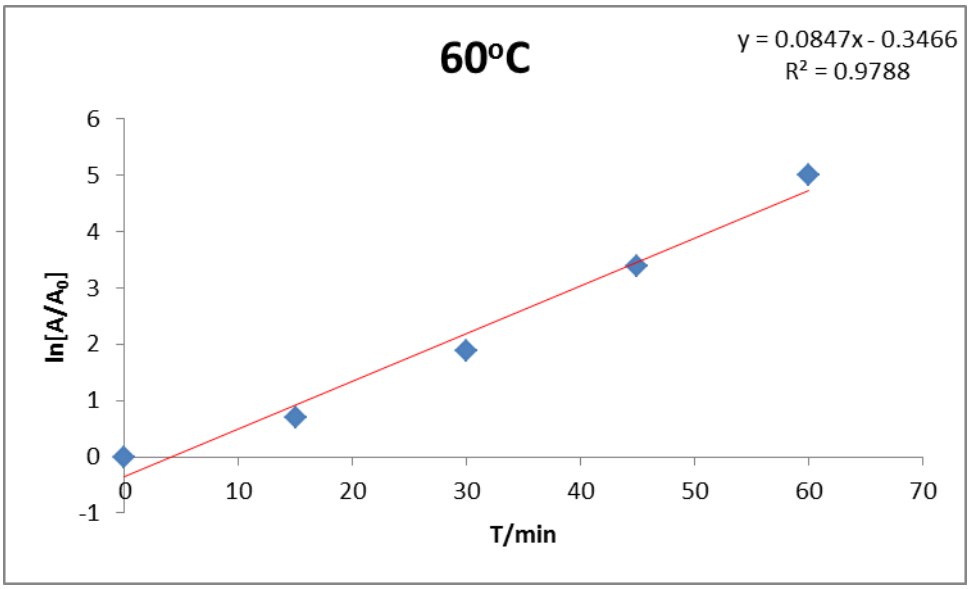
Time/min	$-\ln[A/A_0]$
0	0
15	0.35211
30	0.72011
45	1.28157
60	1.79336
90	2.68678



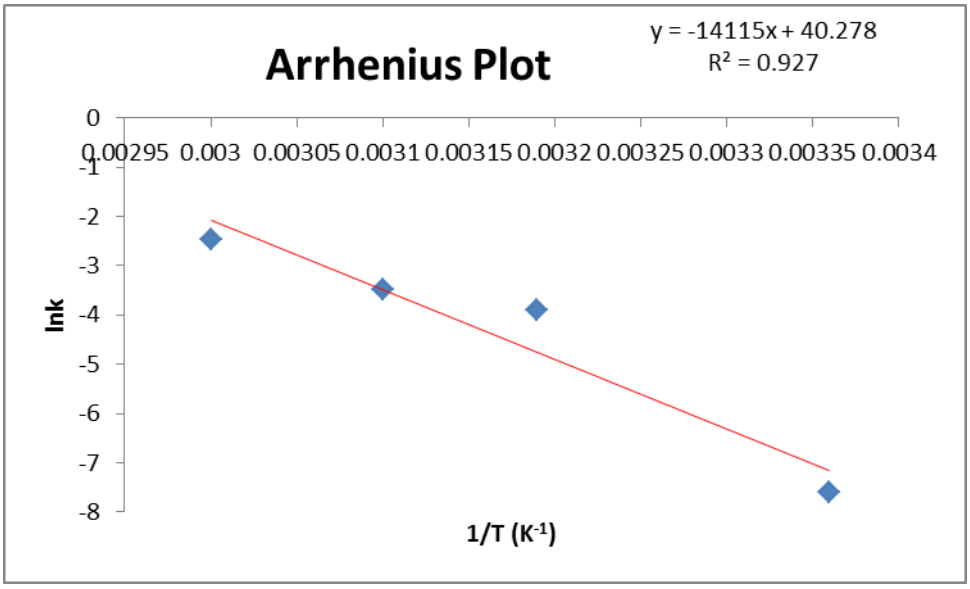
60 °C

Time(min)	Average Integrals		Relative Percentage	
	3aa'	**3aa**	**3aa'**	**3aa**
15	1.0000	1.0070	49.82	50.17
30	1.0000	5.5499	15.27	84.73
45	1.0000	24.7114	3.88	96.11
60	1.0000	148.1014	0.67	99.33

Time/min	$-\ln[A/A_0]$
0	0
15	0.69675
30	1.87928
45	3.38729
60	5.00565



T(°C)	k(min^{-1})	T(K)	1/T(K^{-1})	lnk
25	0.0006	298	0.00336	-7.6009
40	0.0192	313	0.00319	-3.8922
50	0.0292	323	0.00310	-3.4868
60	0.0770	333	0.00300	-2.4686



E_a = -R*K_a = -8.314 * (-14115) = 1.17*10^5 J/mol = 27.99 kcal/mol

A = 3.11*10^{17} min^{-1}

Error Plots 1

T	1/T(K^{-1})	lnk	Error
298	0.00336	-7.6009	-7.9809
333	0.00300	-2.4686	-2.3452

Error Plots 2

T	1/T(K^{-1})	lnk	Error
298	0.00336	-7.6009	-7.2209
333	0.00300	-2.4686	-2.5920

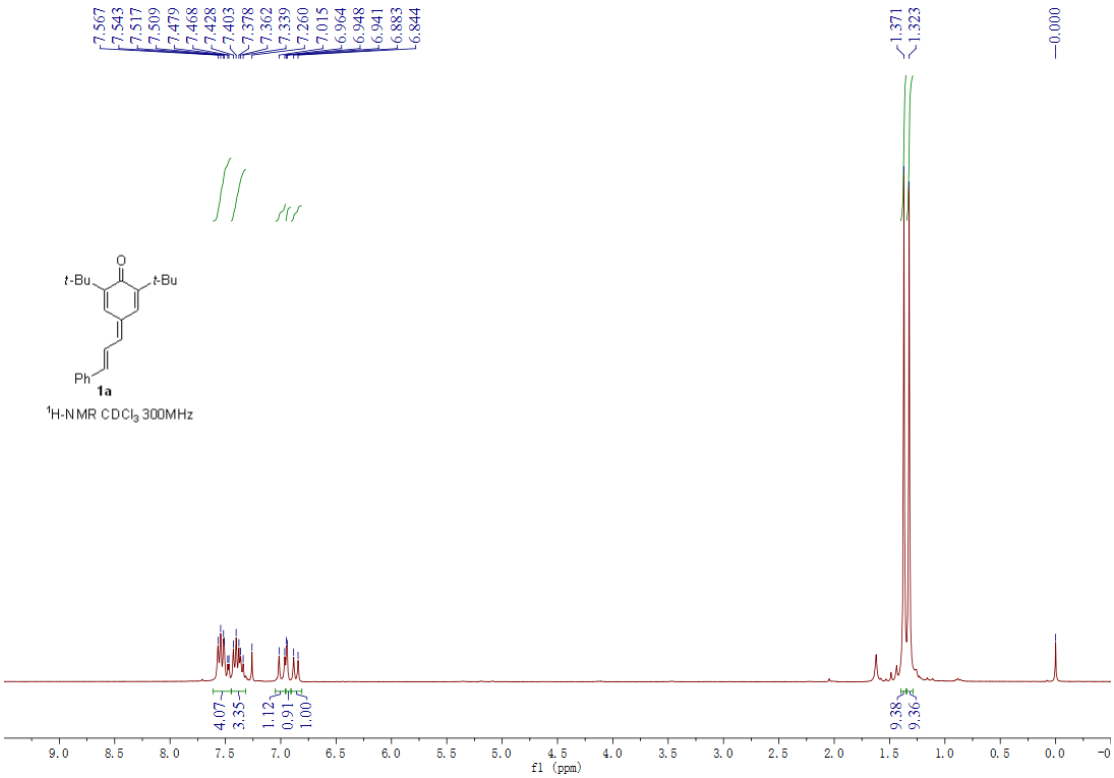
Error = -1.40 * 10^3 E_a'= -R* Error = -8.314 * (-1.40 * 10^3) J/mol = 1.16 * 10^4 J/mol = 2.78 kcal/mol

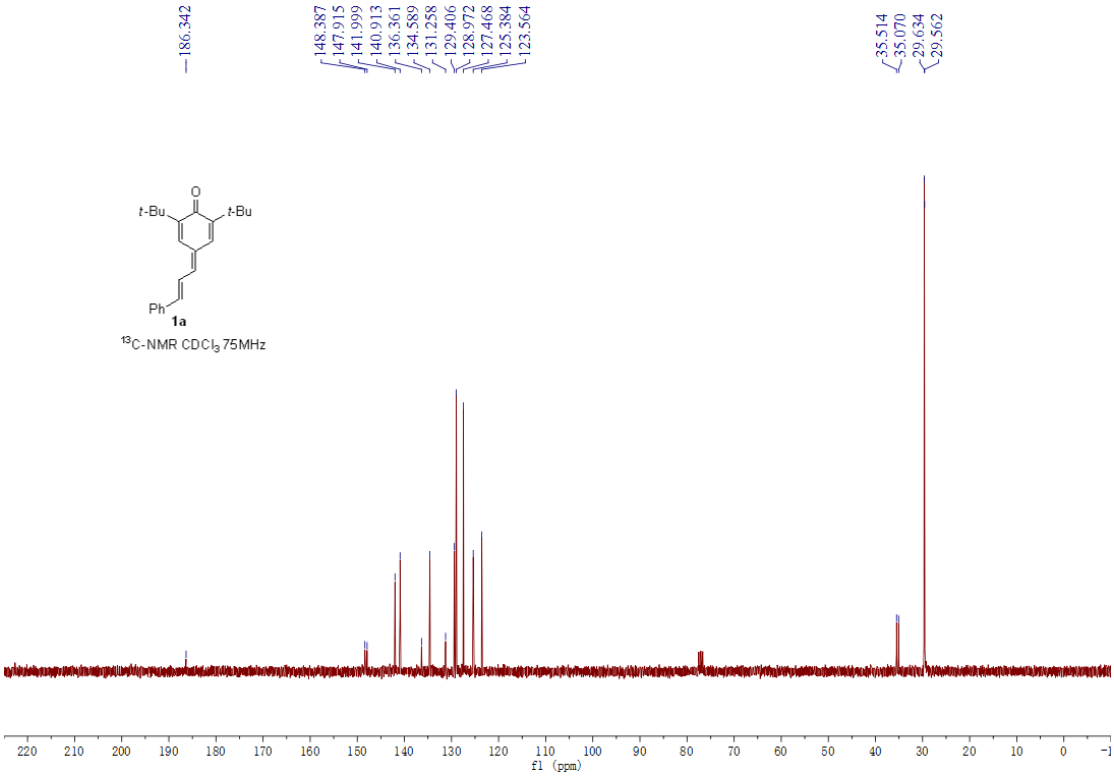
E_a= 27.99 ± 2.78 kcal/mol

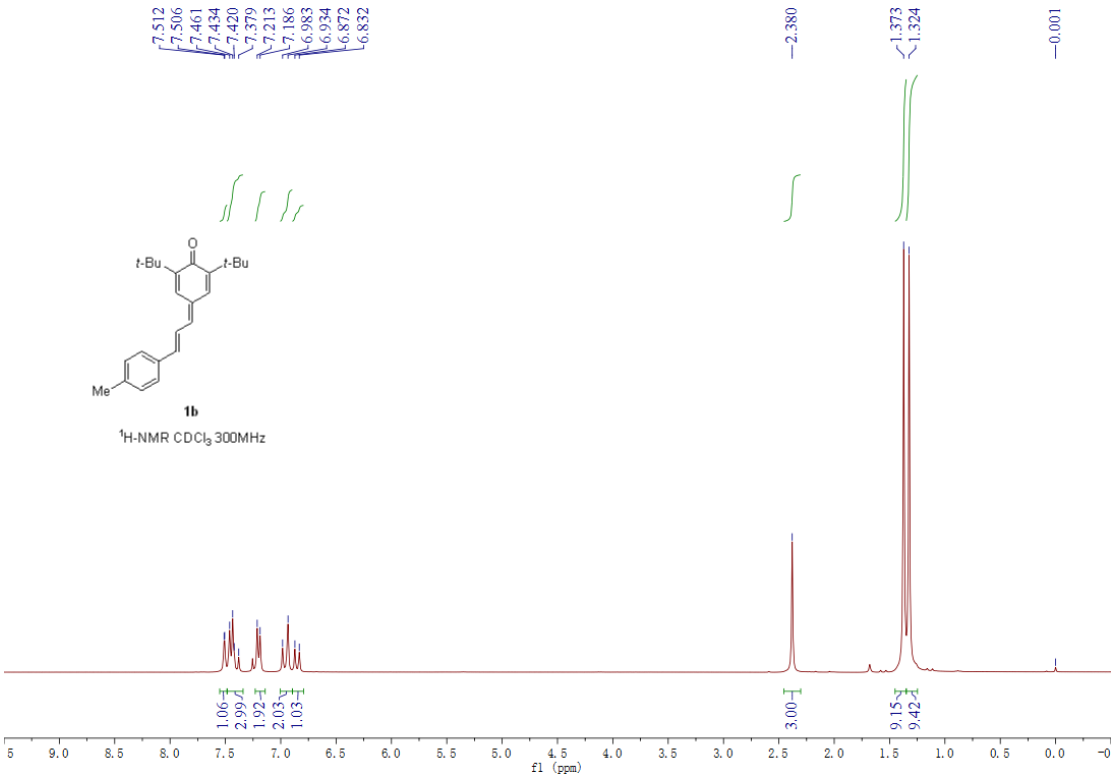
8. References

[1] Gai K.; Fang X.; Li X.; Xu J.; Wu X.; Lin A.; Yao H. *Chem. Commun.* **2015**, *51*, 15831.
[2] Jurd L.; Fye R. L.; Morgan J. *J. Agric. Food Chem.* **1979**, *27*, 1007.
[3] Chen Y.; Ye S.; Jiao L.; Liang Y.; Sinha-Mahapatra D. K.; Herndon J. W.; Yu Z.-X. *J. Am. Chem. Soc.*, **2007**, *129*, 10773.

9. NMR Copies of Substrates and Products



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1.373
1.324
0.001
t-Bu
t-Bu
Me
1b
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1.03
3.00
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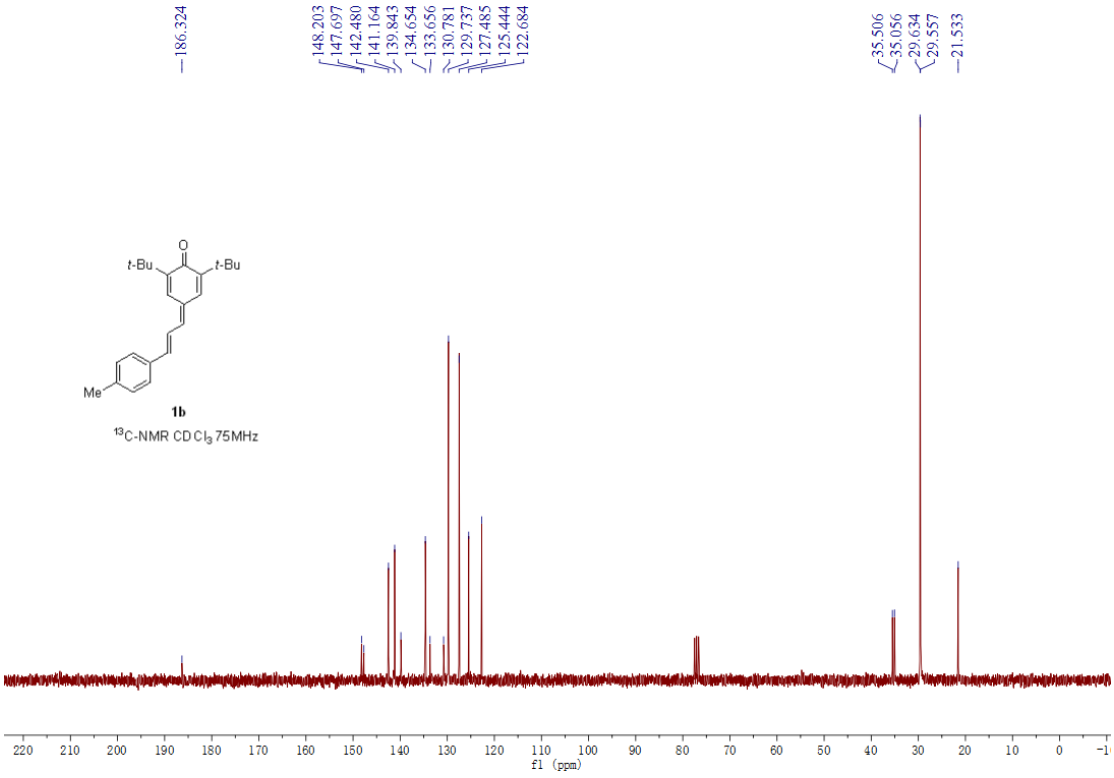
9.42
f1 (ppm)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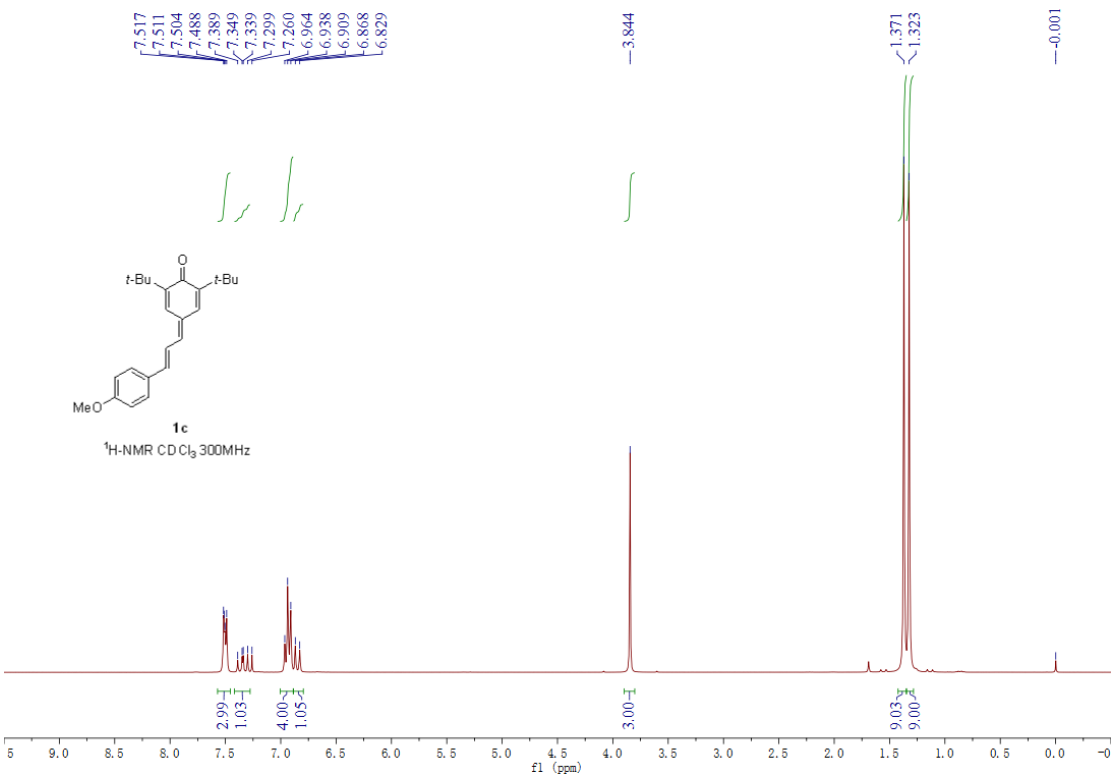
t-Bu
t-Bu
Me
1b
13C-NMR CDCl3 75MHz
f1 (ppm)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6.829
3.844
1.371
1.323
0.001
t-Bu
t-Bu
MeO
1c
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1.03
4.00
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3.00
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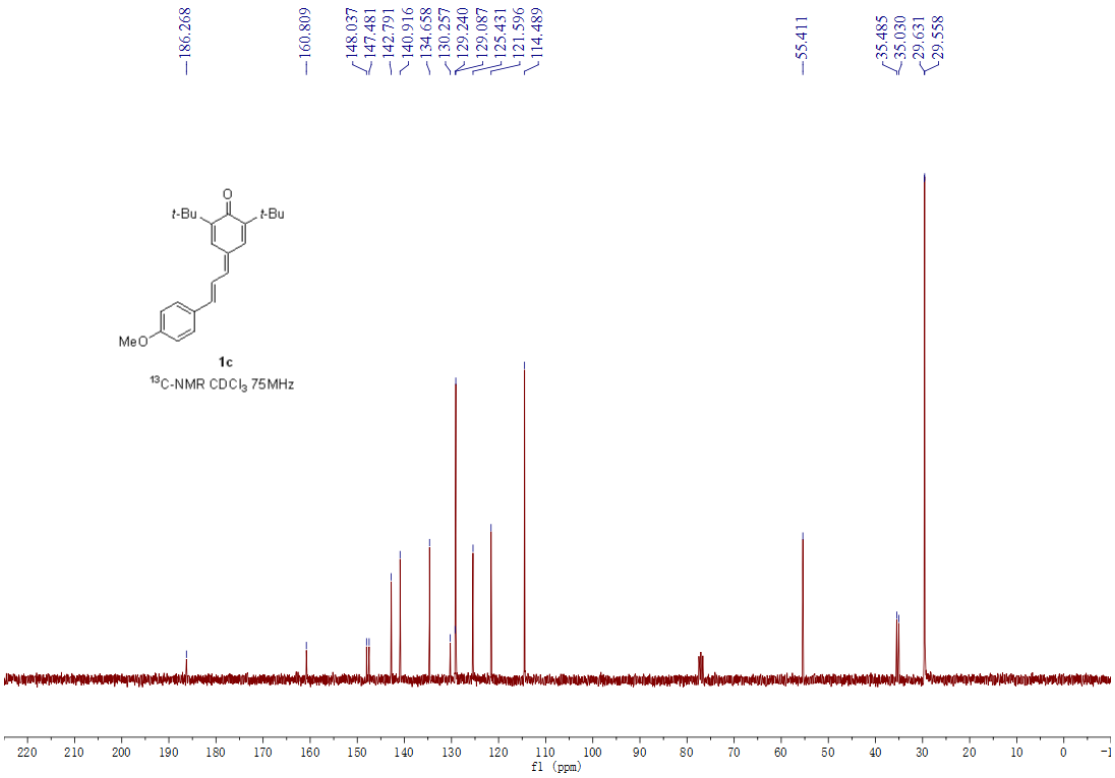
f1 (ppm)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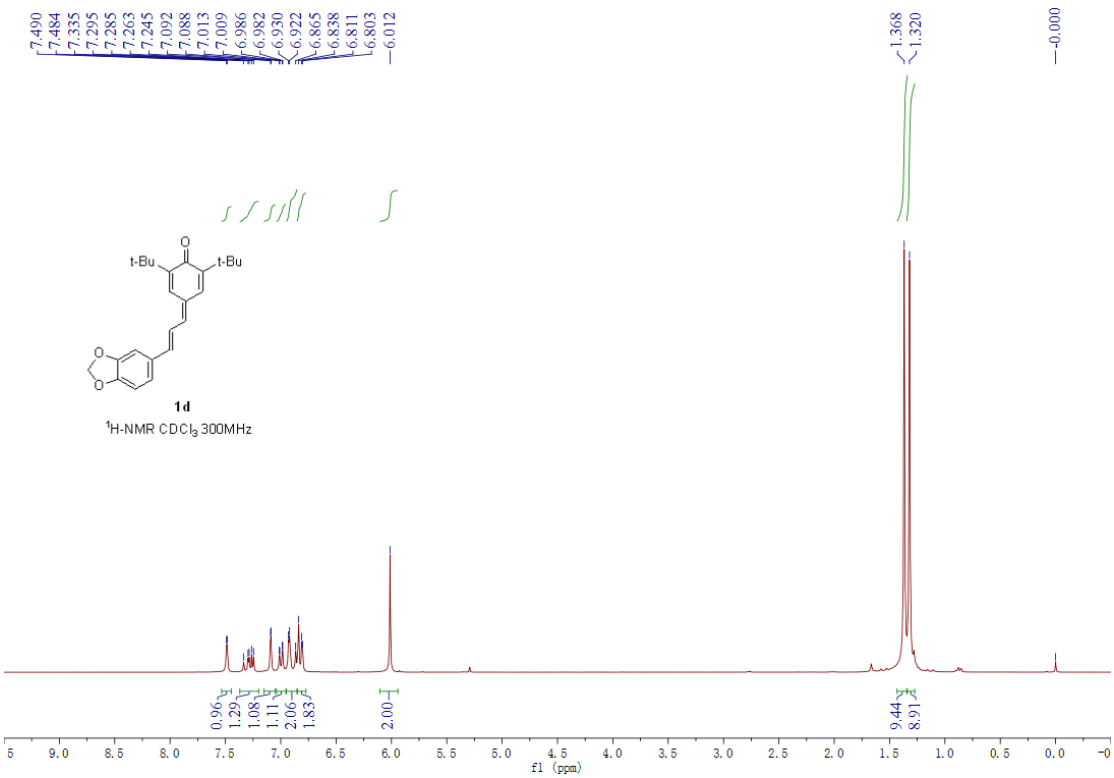
1c
13C-NMR CDCl3 75MHz
f1 (ppm)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6.930
6.922
6.865
6.838
6.811
6.803
6.012
1.368
1.320
0.000
t-Bu
t-Bu
O
O
O
1d
1H-NMR CDCl3 300MHz
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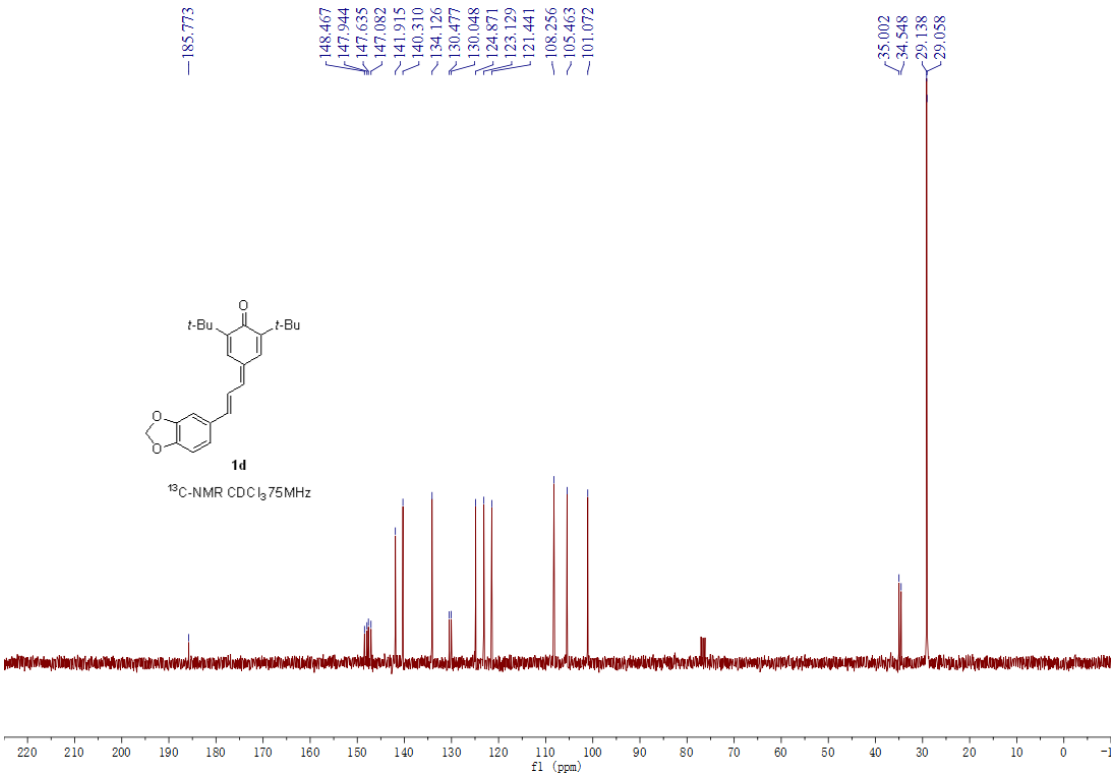
f1 (ppm)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t-Bu
t-Bu
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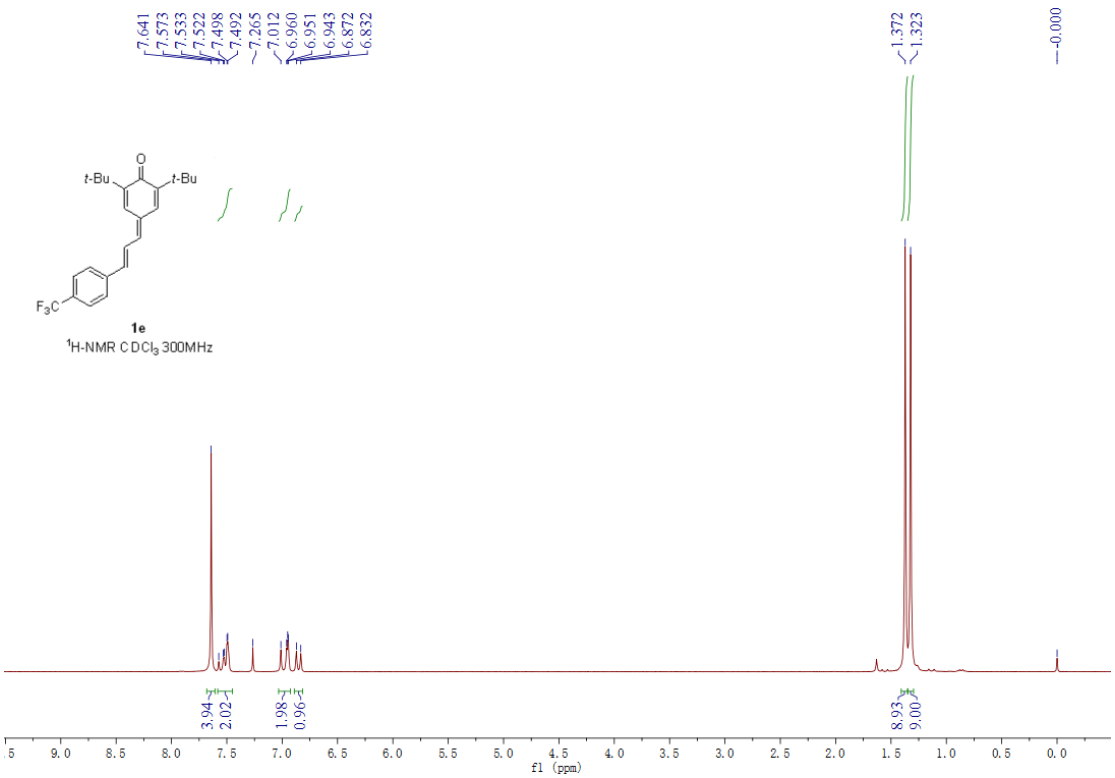
O
O
1d
13C-NMR CDCl3 75MHz
f1 (ppm)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1.372
1.323
0.000
t-Bu
t-Bu
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F3C
1e
1H-NMR CDCl3 300MHz
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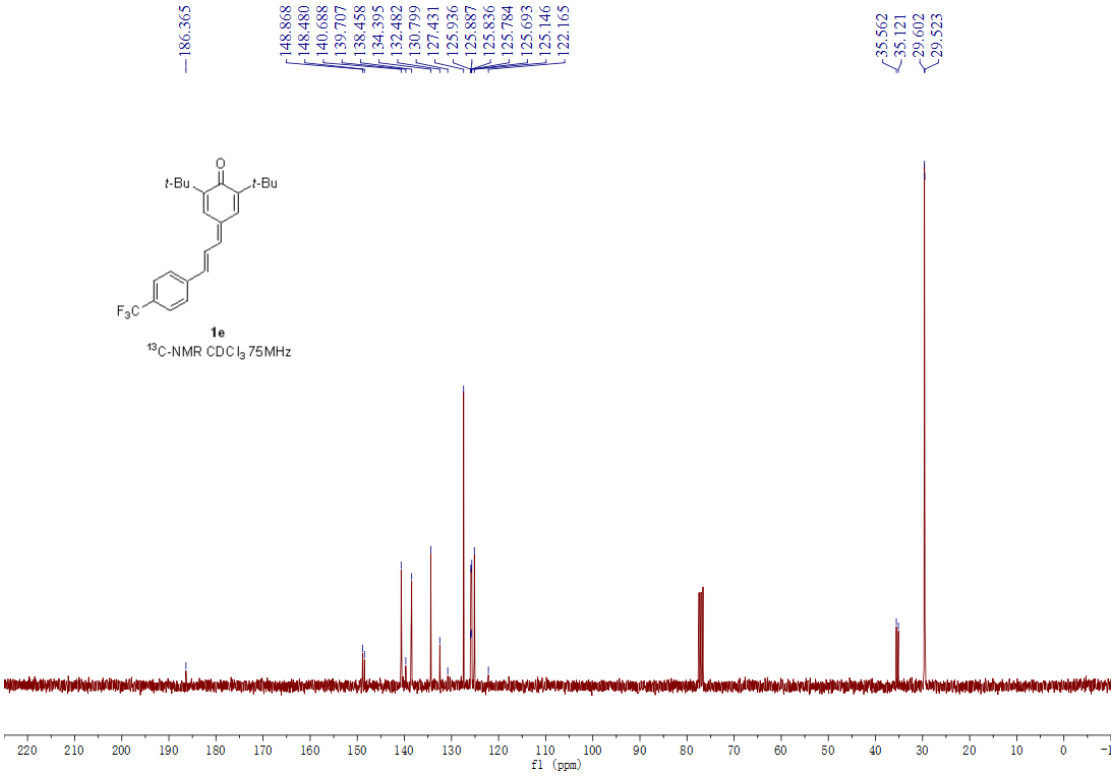
8.93
9.00
f1 (ppm)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122.165
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1e
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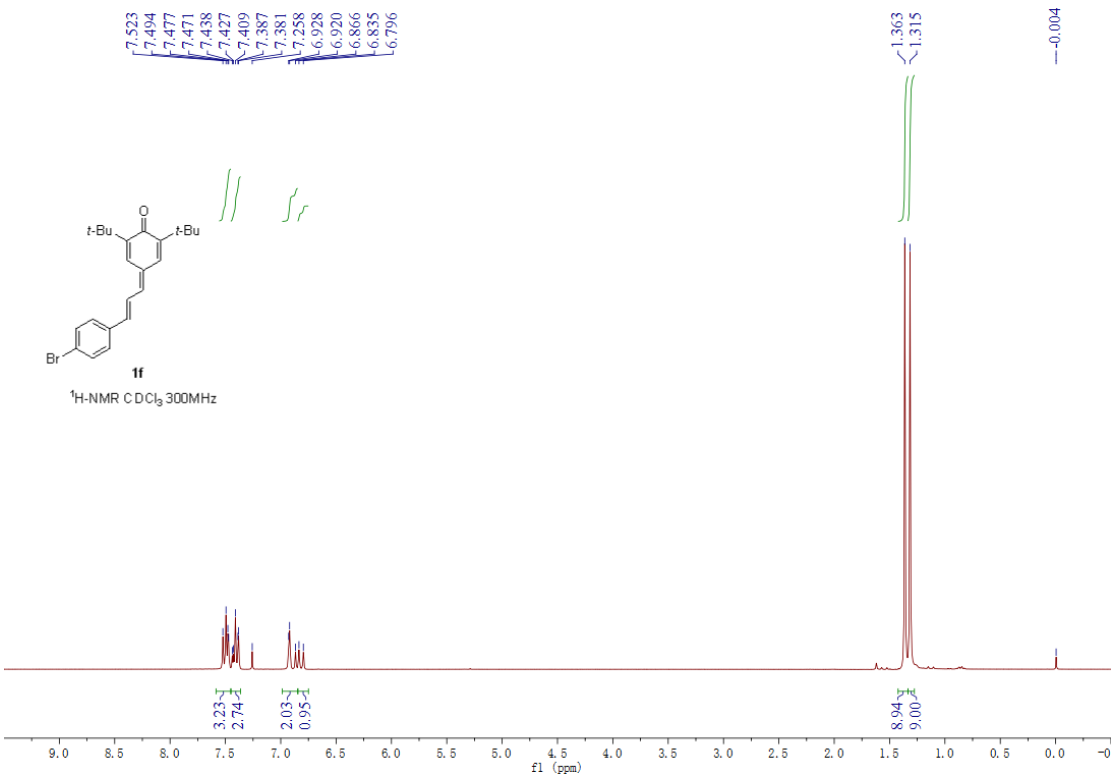
f1 (ppm)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1.315
0.004
t-Bu
t-Bu
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1f
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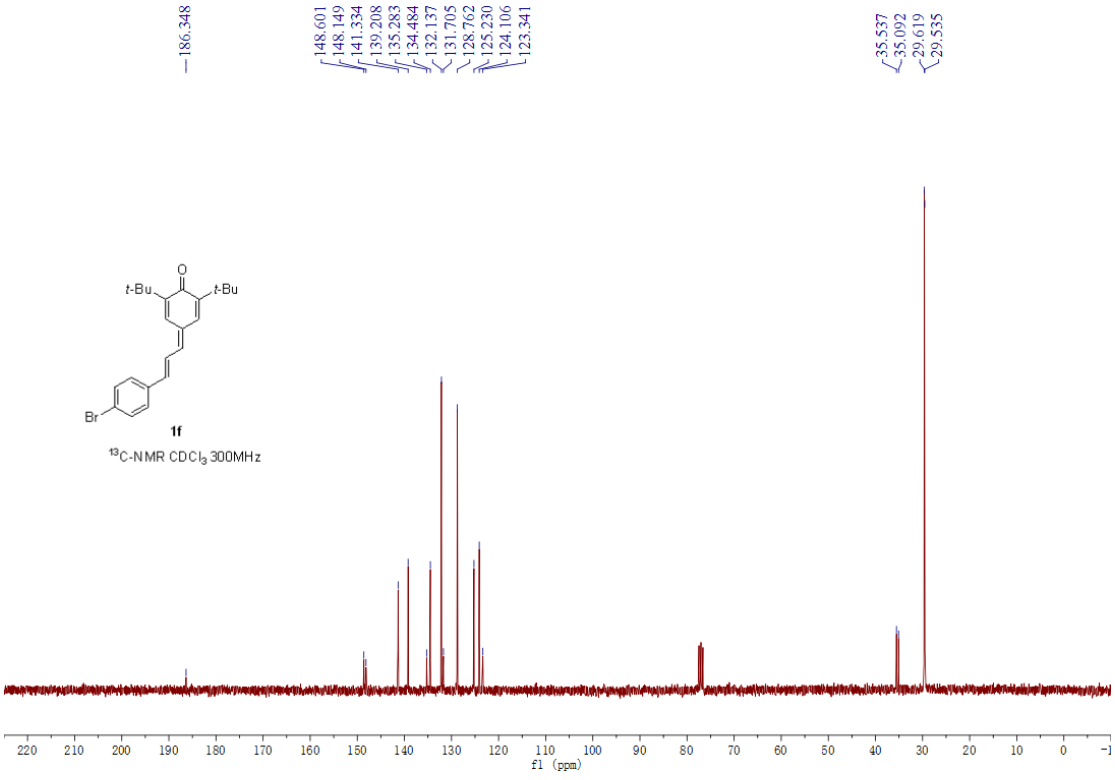
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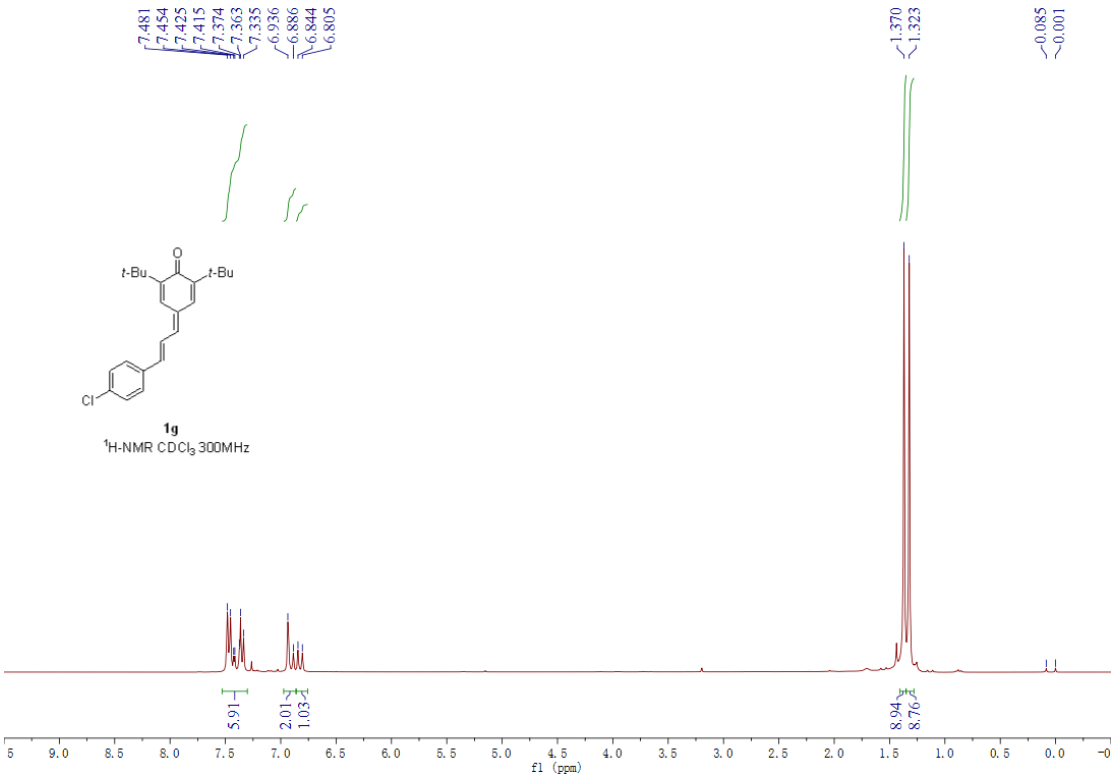
Br
1f
^{13}C-NMR CDCl$_3$ 300MHz
f1 (ppm)



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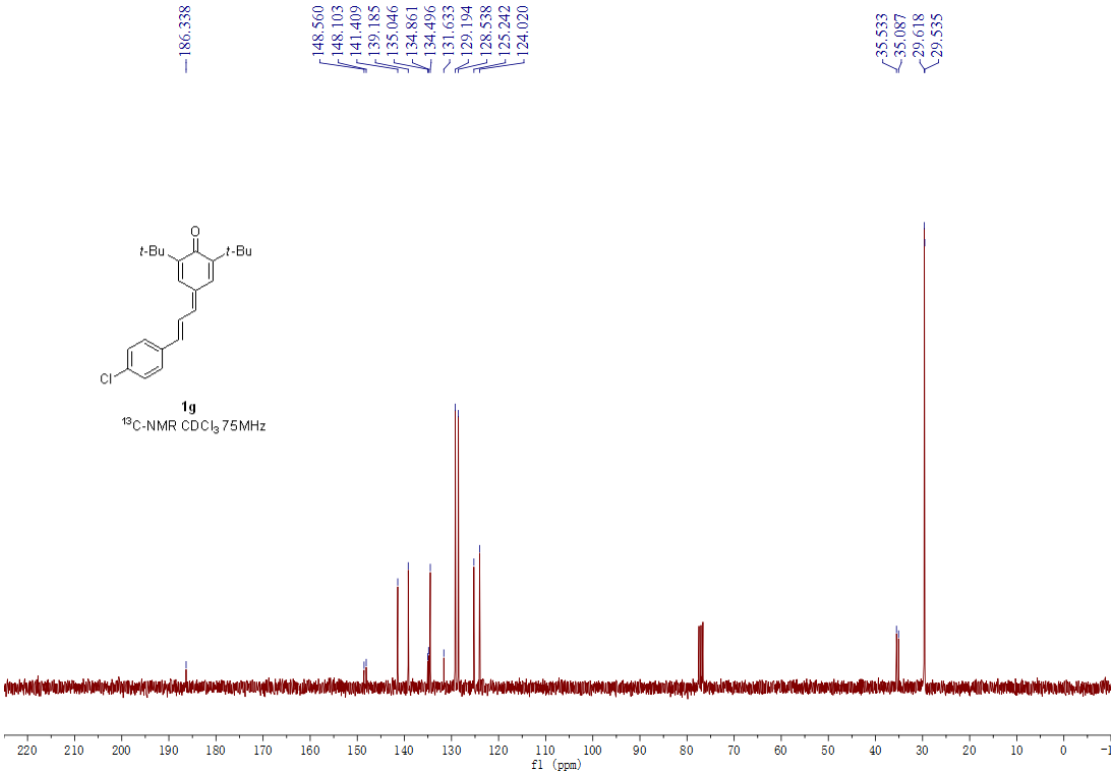

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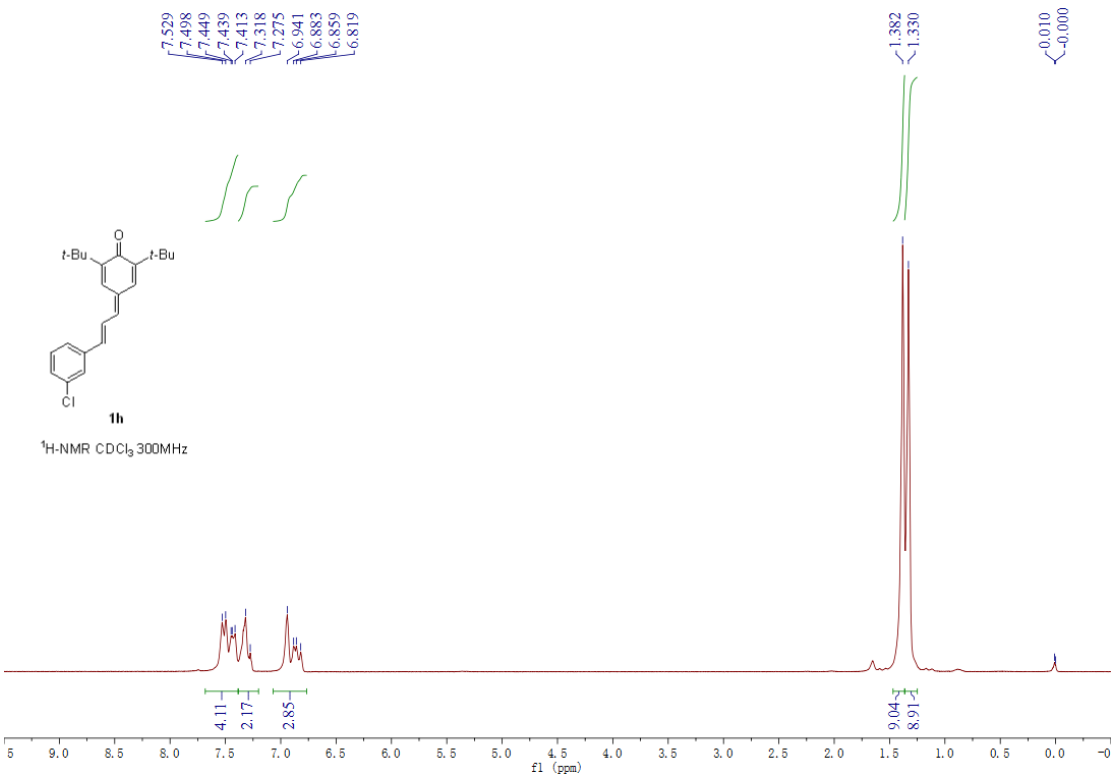
^{13}C-NMR $CDCl_3$ 75MHz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-0.000
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Cl
1h
1H-NMR CDCl3 300MHz
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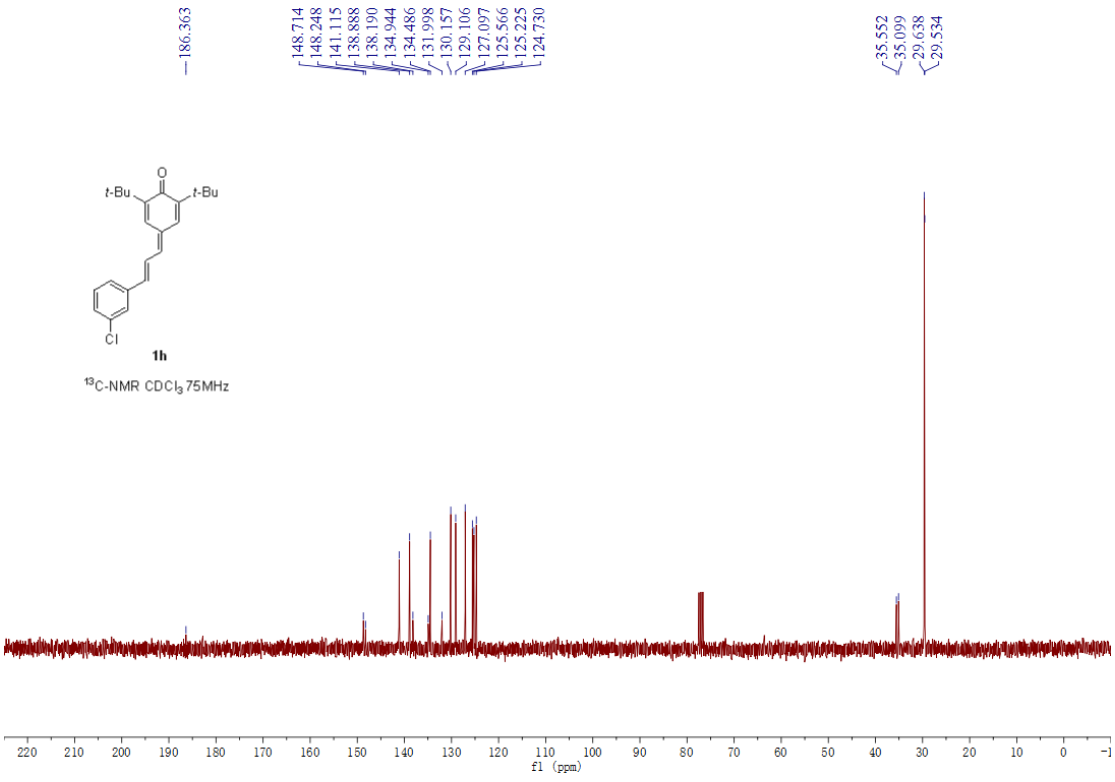
f1 (ppm)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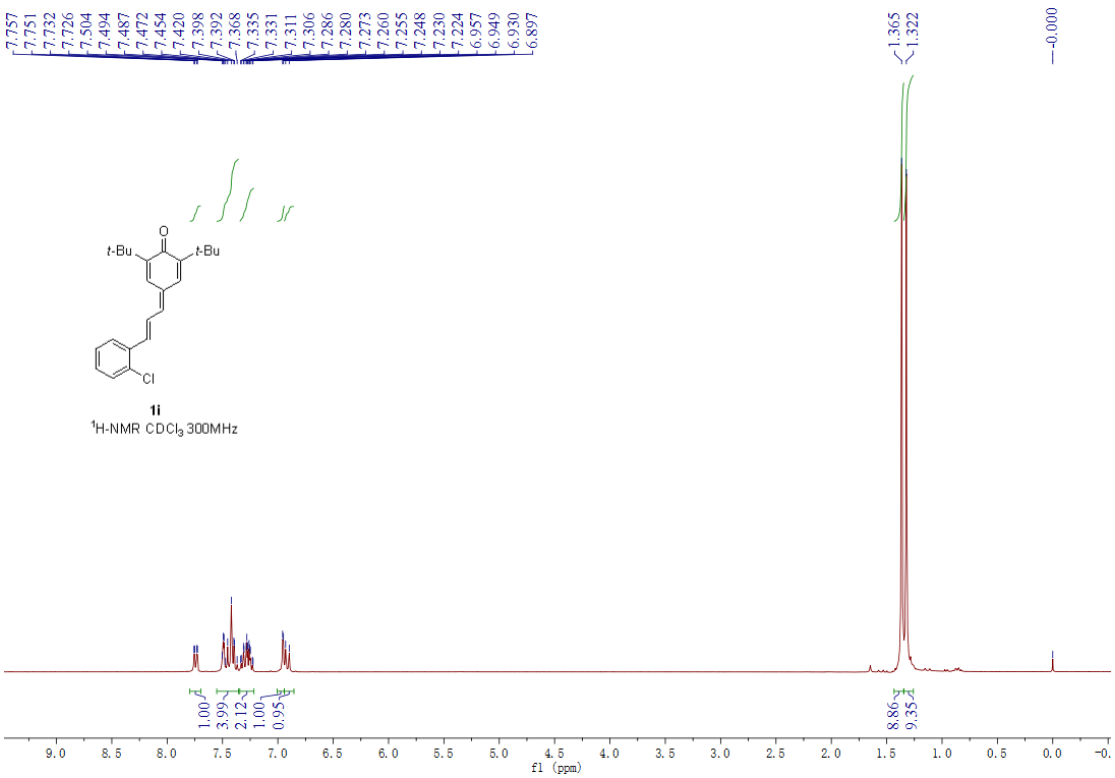
Cl
1h
13C-NMR CDCl3 75MHz
f1 (ppm)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6.949
6.930
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t-Bu
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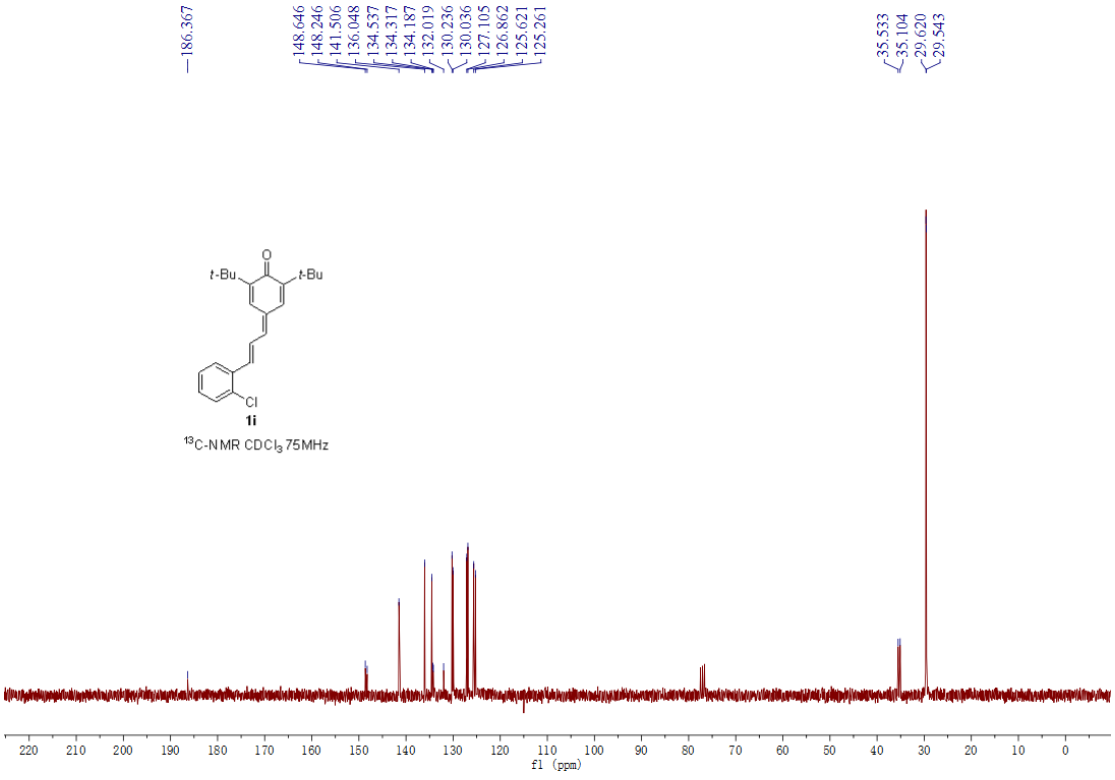
f1 (ppm)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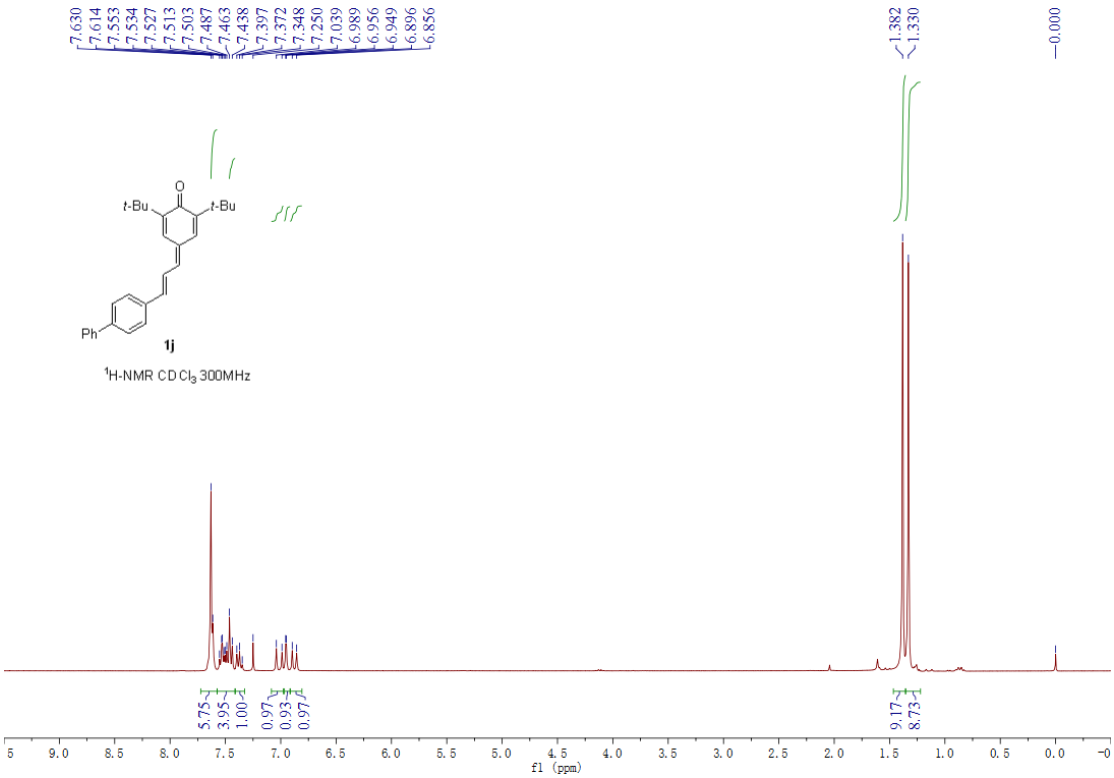
t-Bu
Cl
1i
13C-NMR CDCl3 75MHz
f1 (ppm)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7.250
7.039
6.989
6.956
6.949
6.896
6.856
1.382
1.330
0.000
t-Bu
t-Bu
Ph
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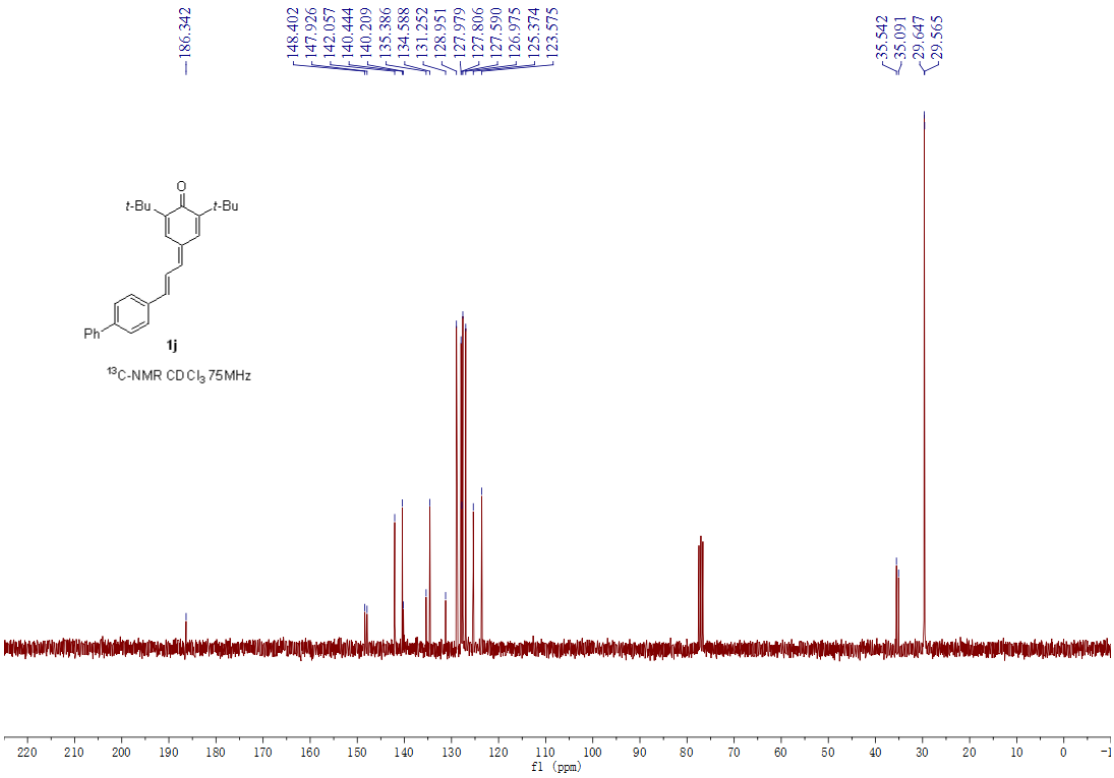
8.73
f1 (ppm)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Ph
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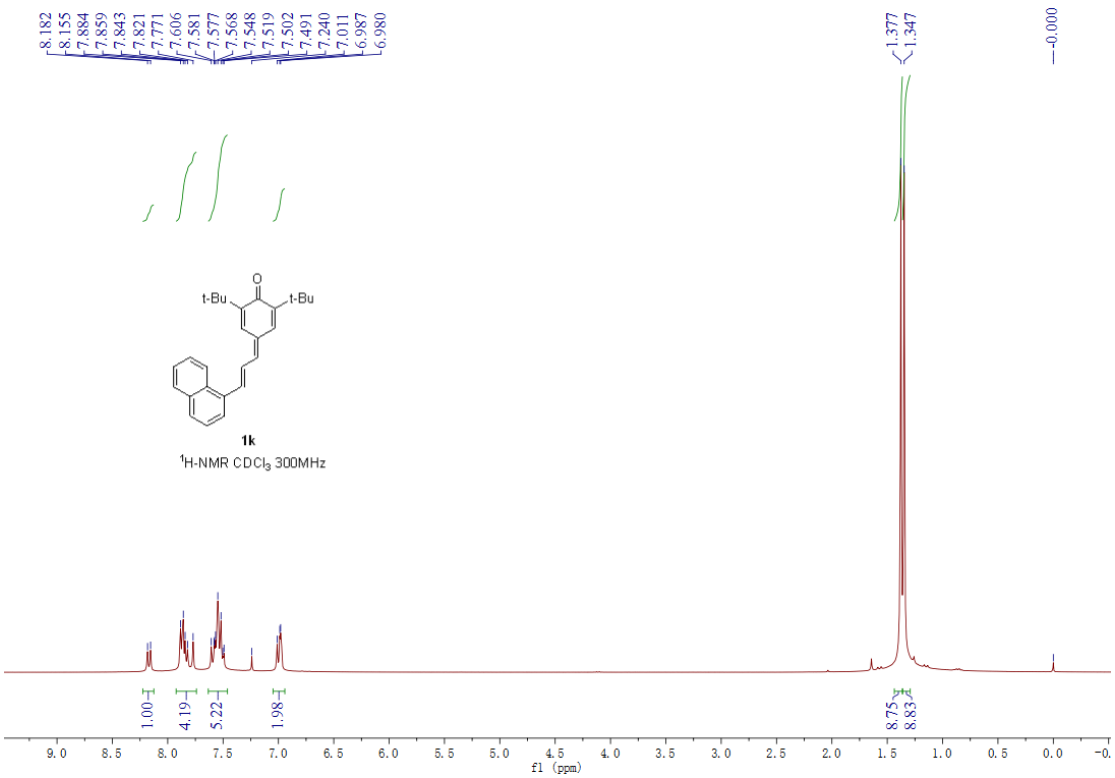
13C-NMR CDCl3 75MHz
f1 (ppm)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7.011
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6.980
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0.000
t-Bu
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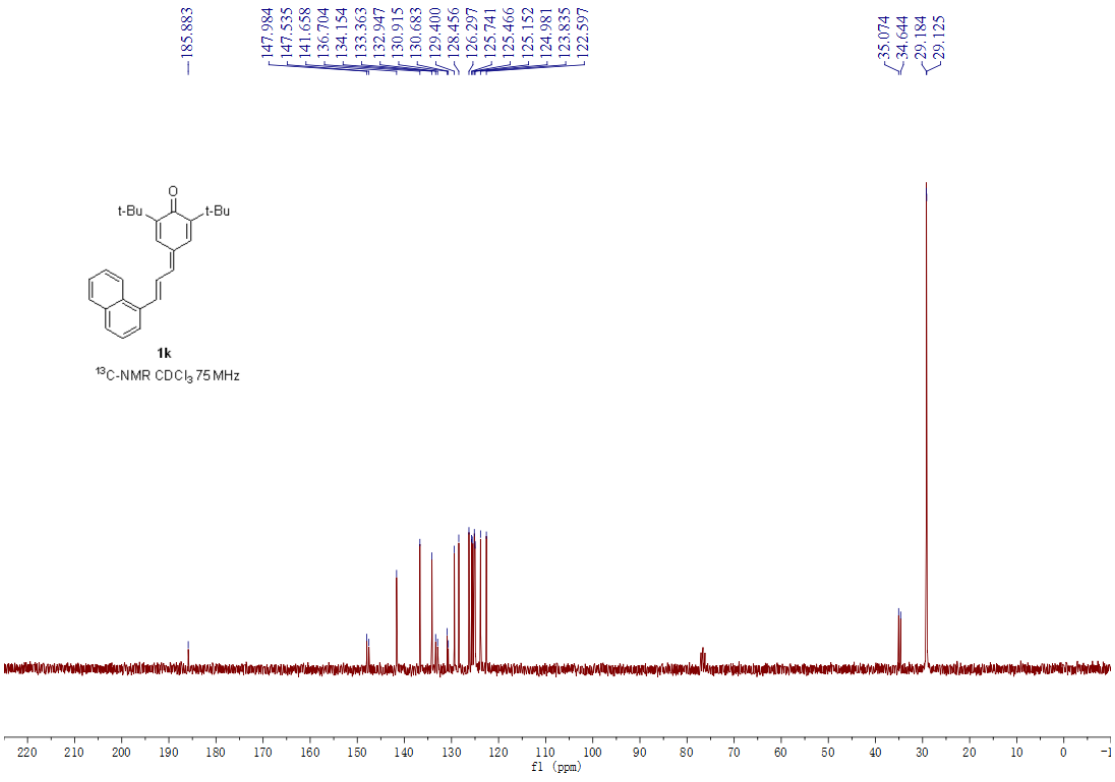
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123.835
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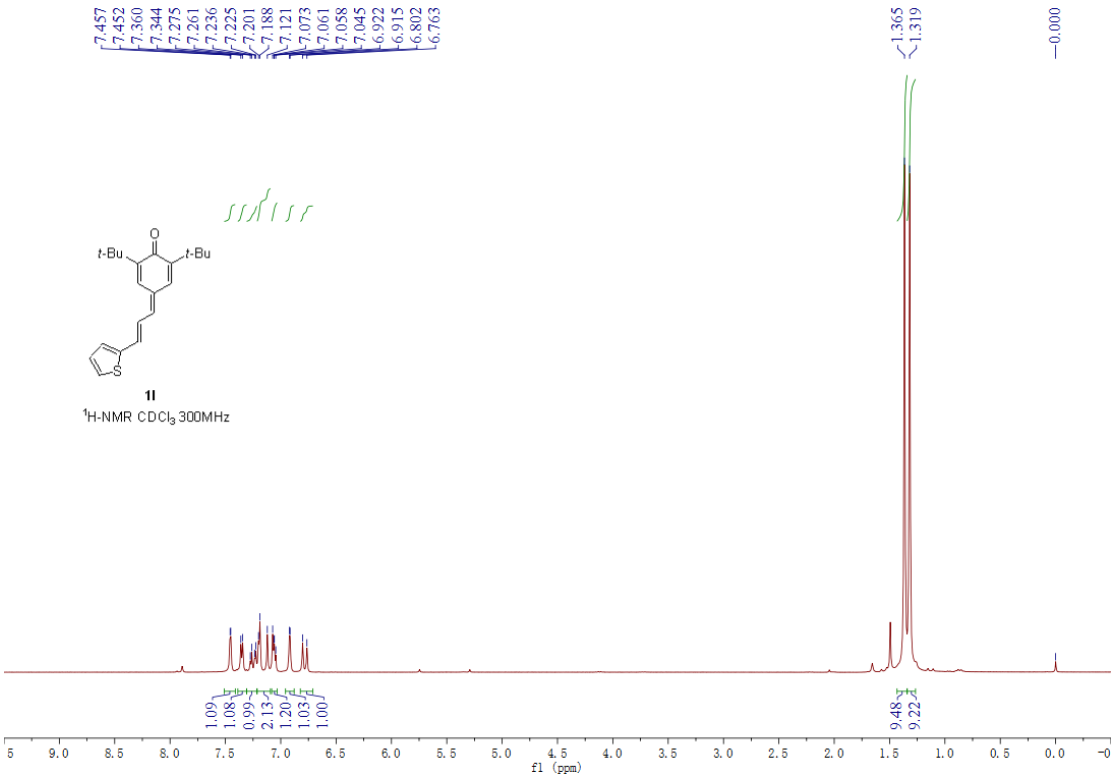
O
1k
13C-NMR CDCl3 75MHz
f1 (ppm)



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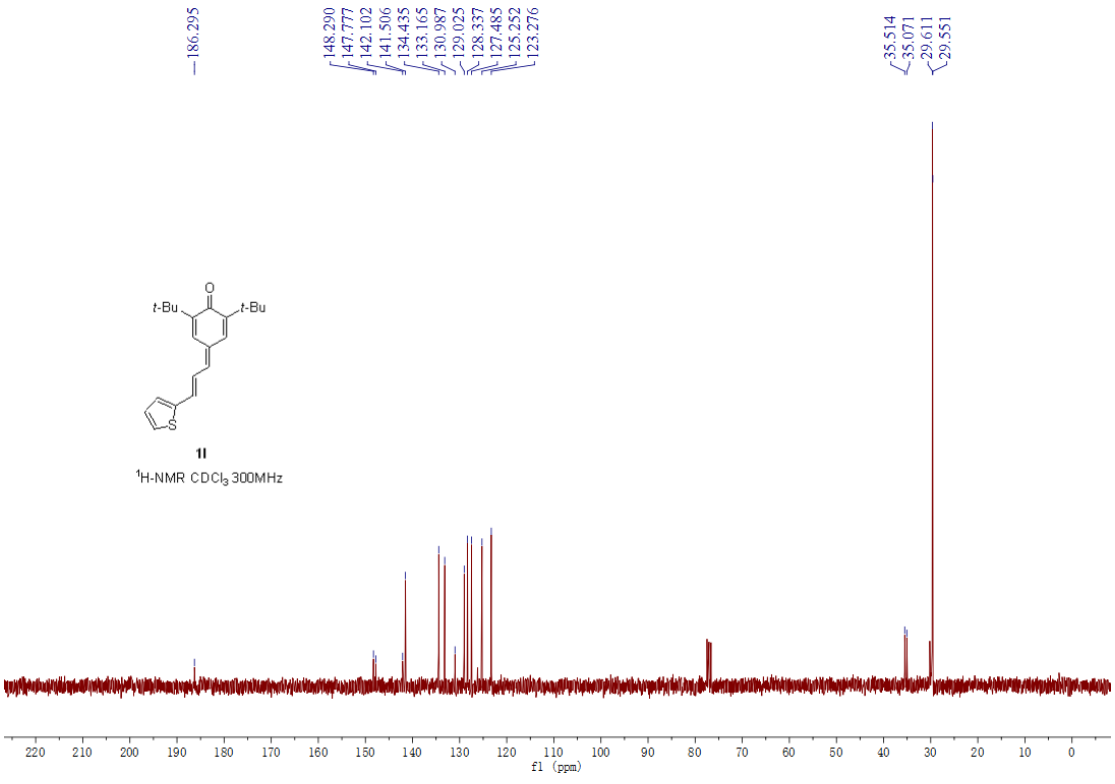

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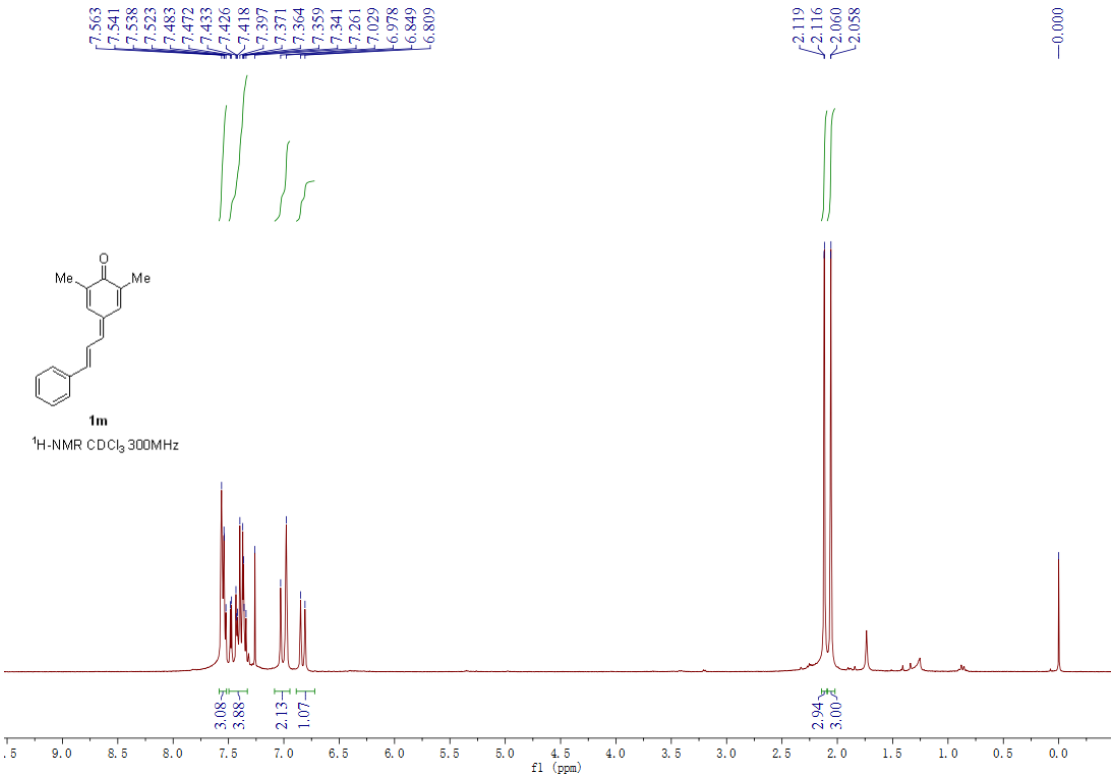
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7.341
7.261
7.029
6.978
6.849
6.809
2.119
2.116
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2.058
0.000
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1H-NMR CDCl3 300MHz
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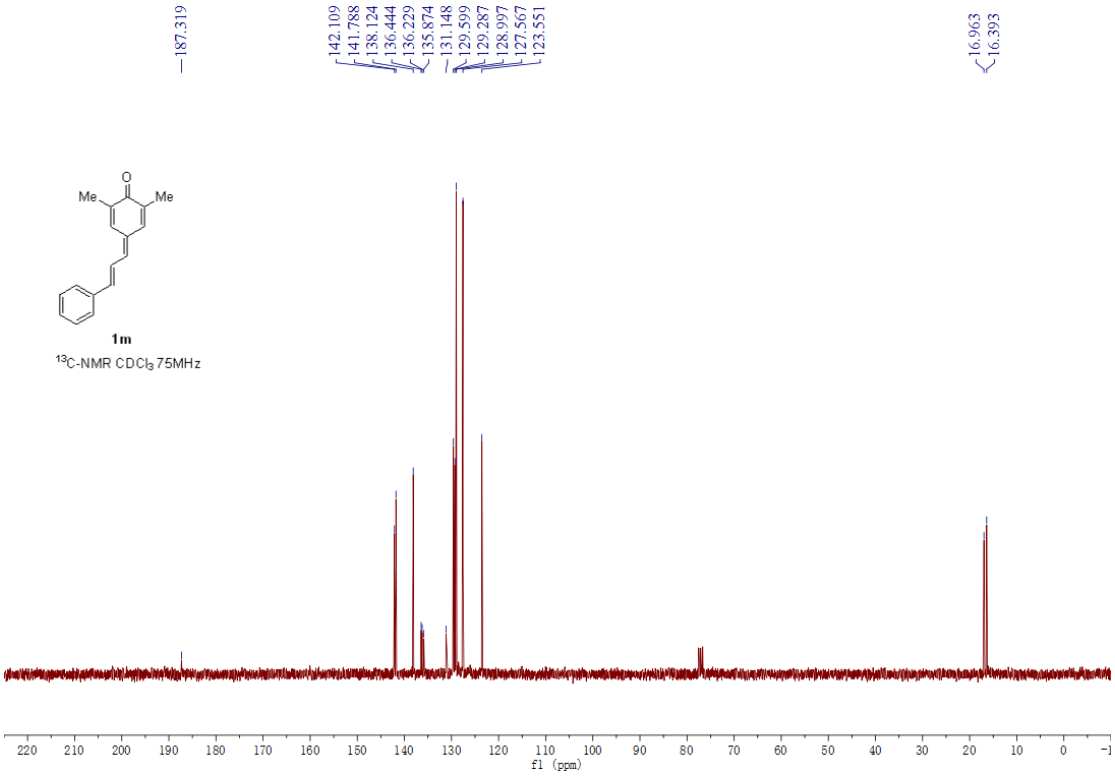
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O
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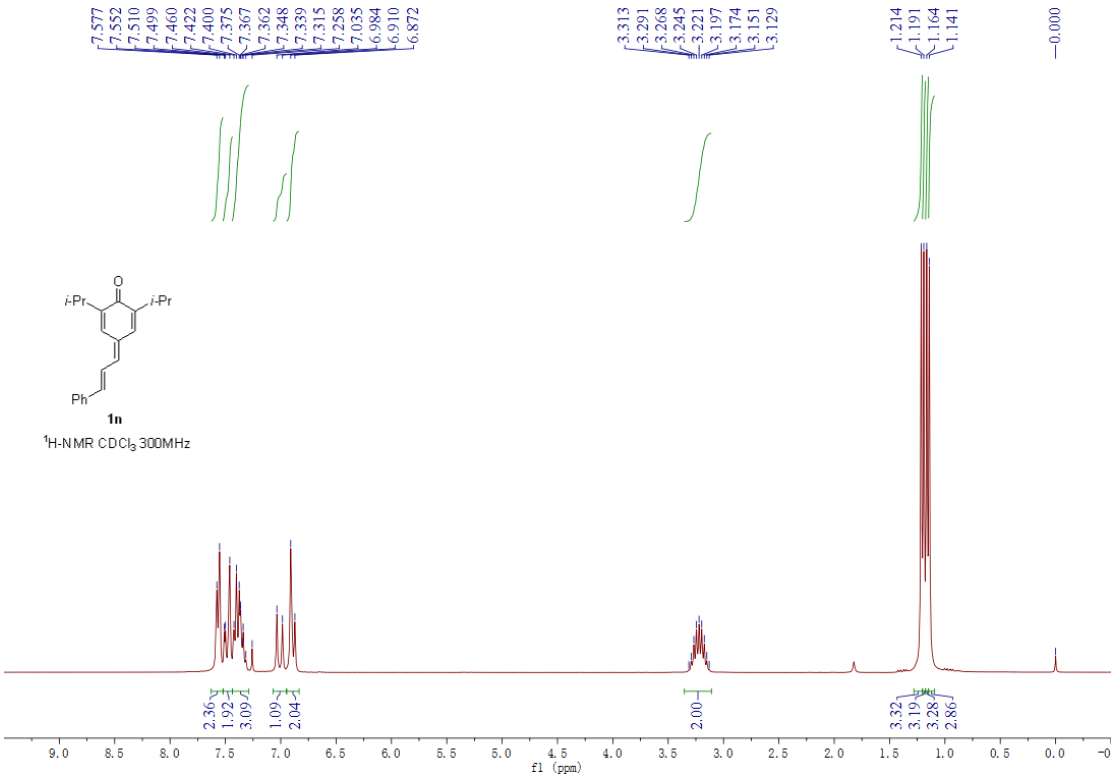
f1 (ppm)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3.291
3.268
3.245
3.221
3.197
3.174
3.151
3.129
1.214
1.191
1.164
1.141
0.000
i-Pr
i-Pr
Ph
O
1n
1H-NMR CDCl3 300MHz
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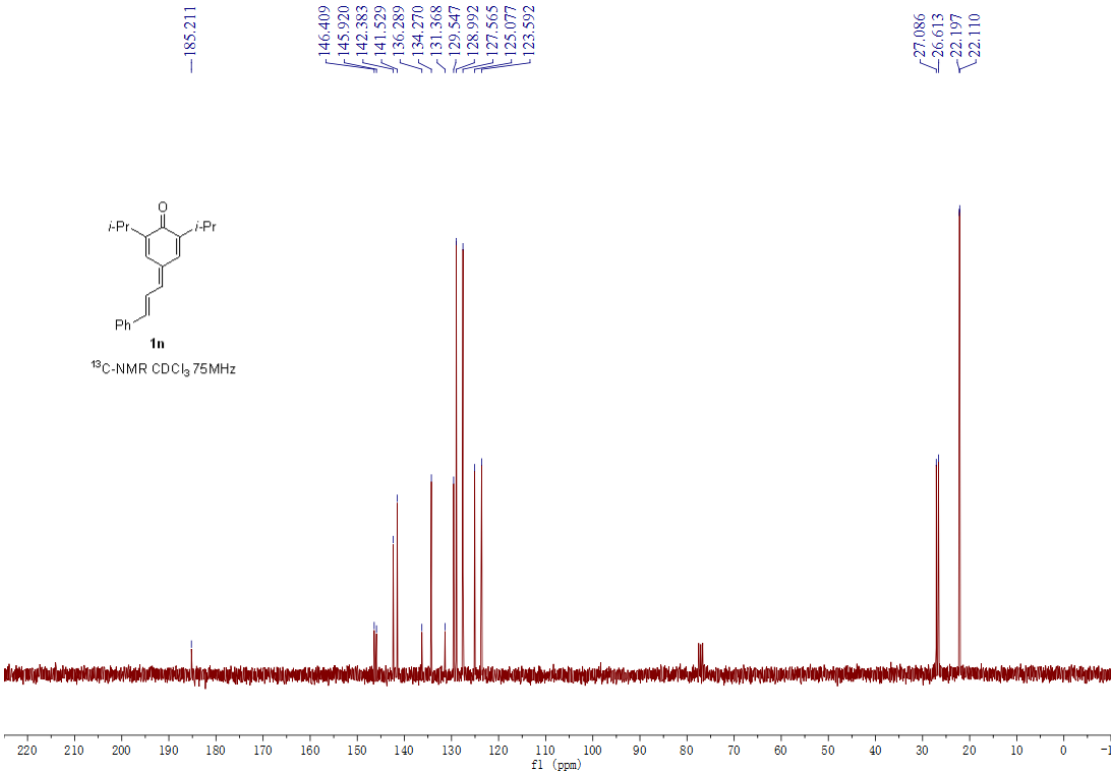
f1 (ppm)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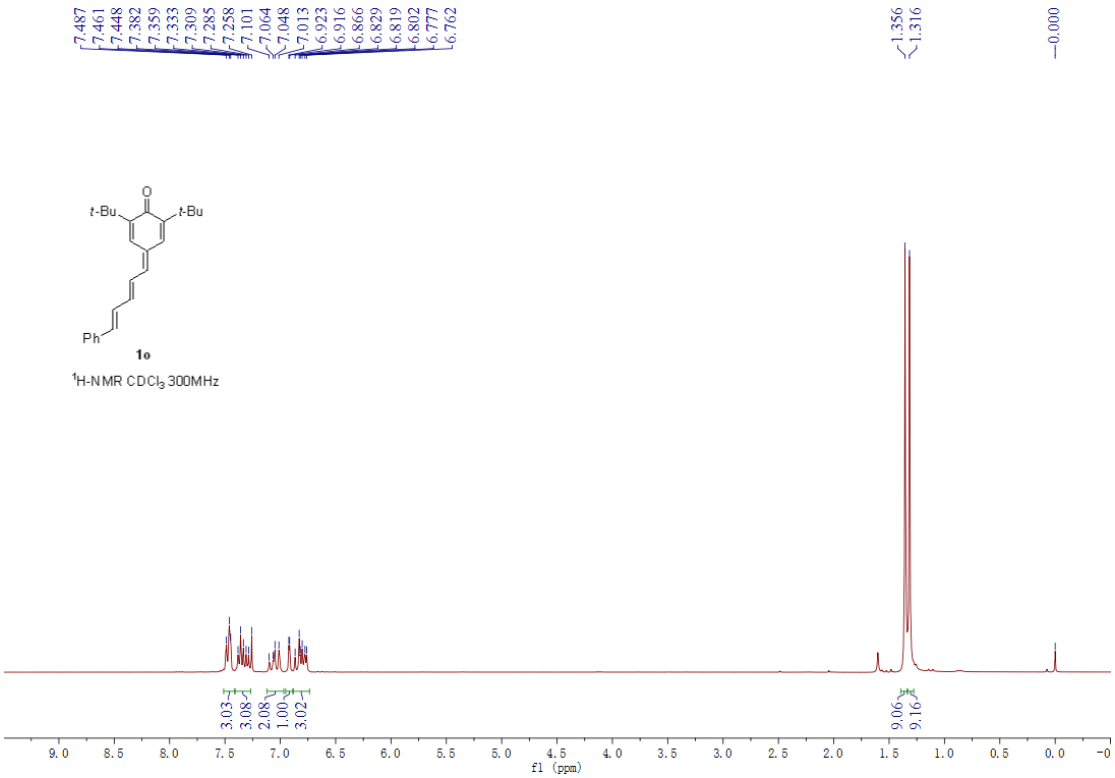
i-Pr
Ph
O
1n
13C-NMR CDCl3 75MHz
f1 (ppm)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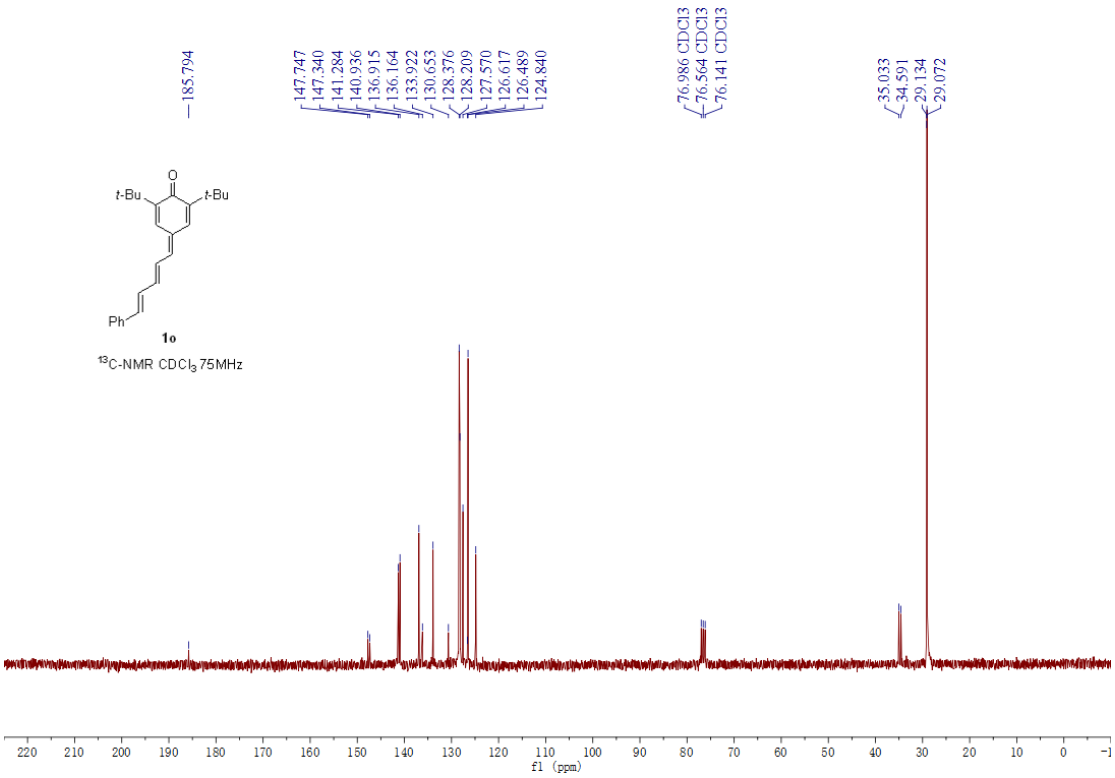
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76.564 CDCl3
76.141 CDCl3
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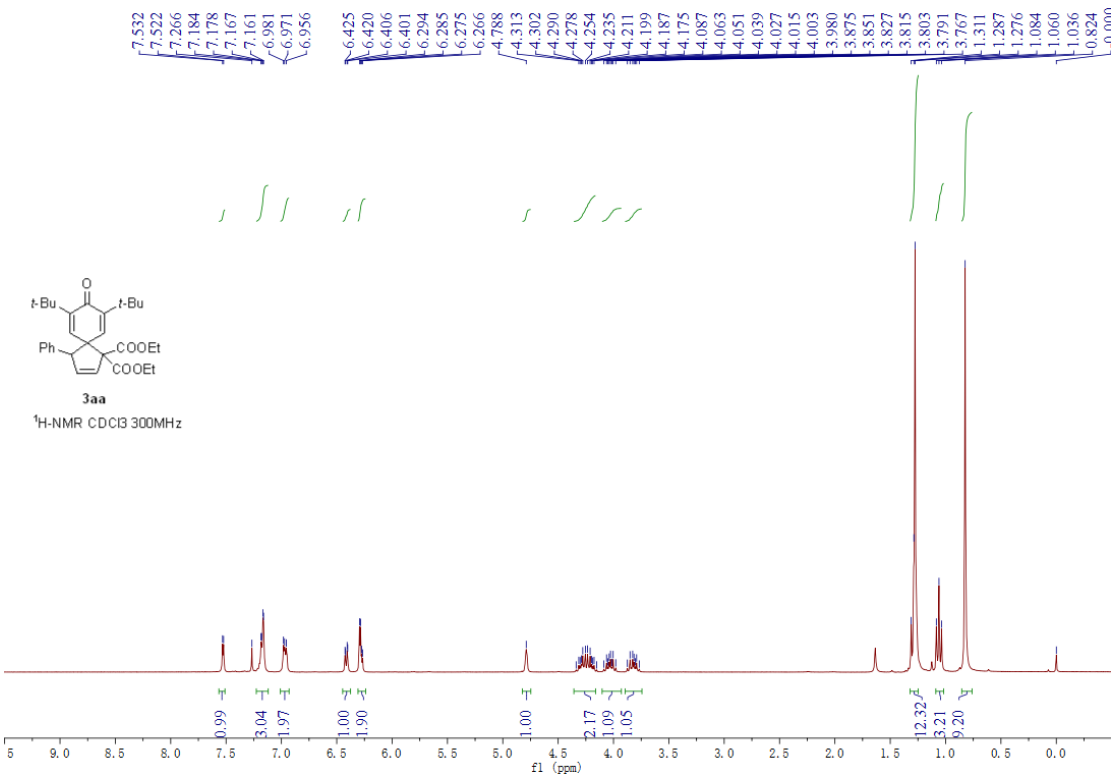
34.591
29.134
29.072
t-Bu
t-Bu
Ph
1o
13C-NMR CDCl3 75MHz
f1 (ppm)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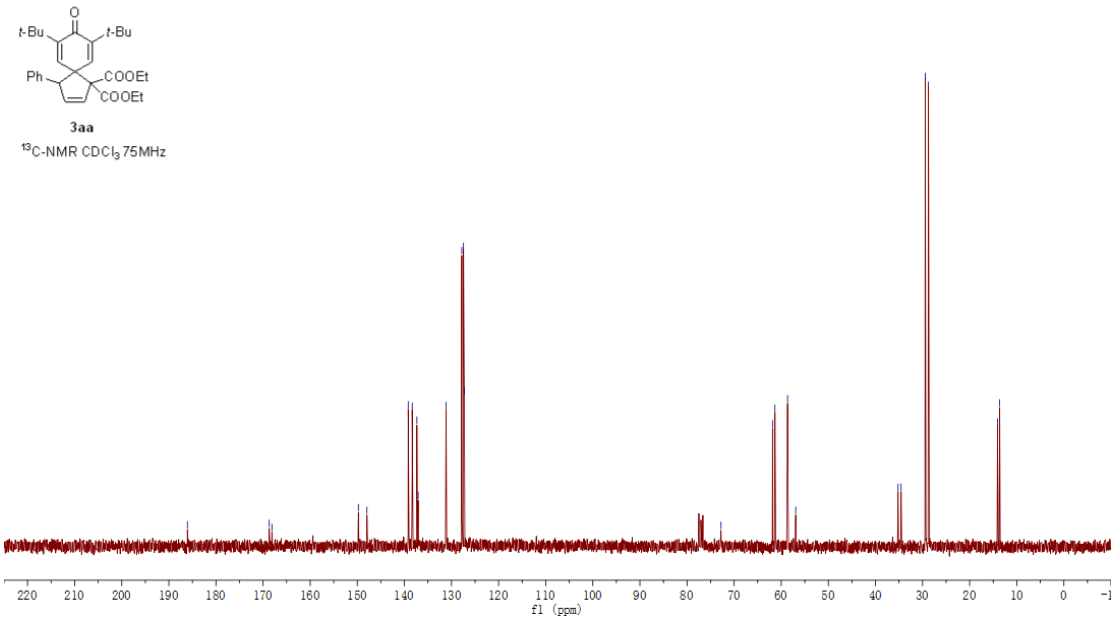
7.266
7.184
7.178
7.167
7.161
6.981
6.971
6.956
6.425
6.420
6.406
6.401
6.294
6.285
6.275
6.266
4.788
4.313
4.302
4.290
4.278
4.254
4.235
4.211
4.199
4.187
4.175
4.087
4.063
4.051
4.039
4.027
4.015
4.003
3.980
3.875
3.851
3.827
3.815
3.803
3.791
3.767
1.311
1.287
1.276
1.084
1.060
1.036
0.824
t-Bu
t-Bu
Ph
COOEt
COOEt
3aa
1H-NMR CDCl3 300MHz
0.99
3.04
1.97
1.00
1.90
1.00
2.17
1.09
1.05
12.32
3.21
9.20
f1 (ppm)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131.152
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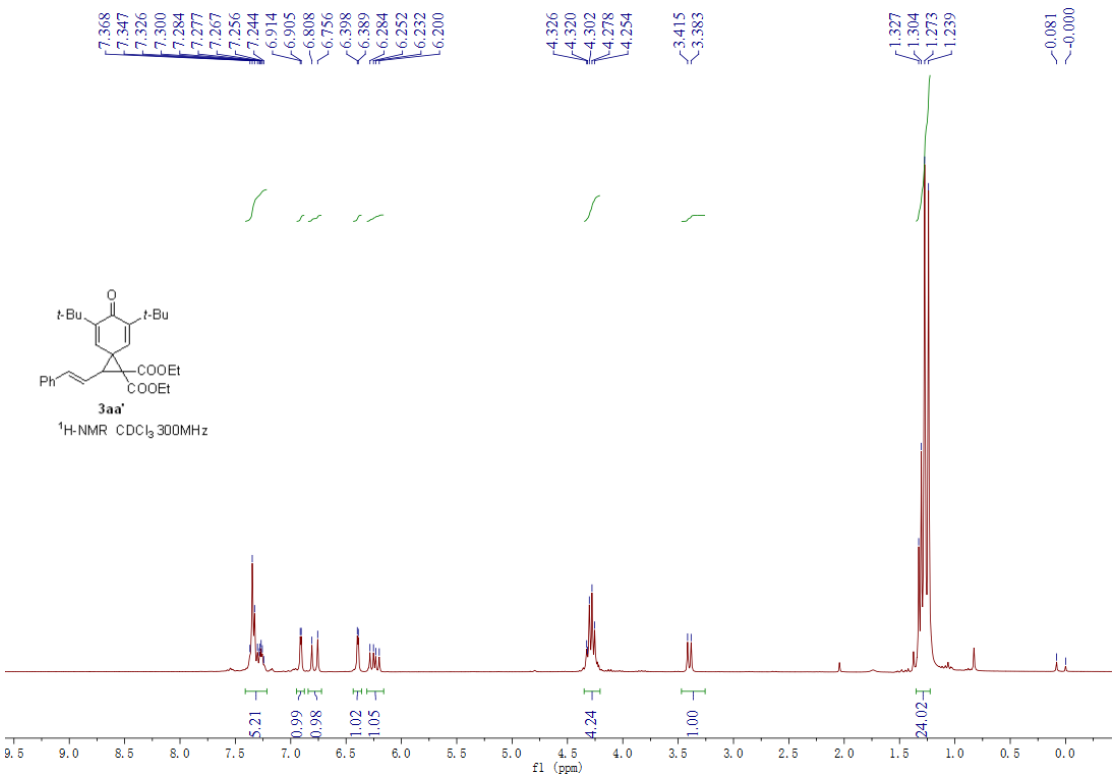
127.446
127.281
72.793
61.844
61.338
58.654
56.927
35.208
34.560
29.436
28.752
14.091
13.631
t-Bu
t-Bu
Ph
COOEt
COOEt
3aa
13C-NMR CDCl3 75MHz
f1 (ppm)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7.347
7.326
7.300
7.284
7.277
7.267
7.256
7.244
6.914
6.905
6.808
6.756
6.398
6.389
6.284
6.252
6.232
6.200
4.326
4.320
4.302
4.278
4.254
3.415
3.383
1.327
1.304
1.273
1.239
0.081
-0.000
t-Bu
t-Bu
COOEt
COOEt
Ph
3aa'
1H-NMR CDCl3 300MHz
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0.99
0.98
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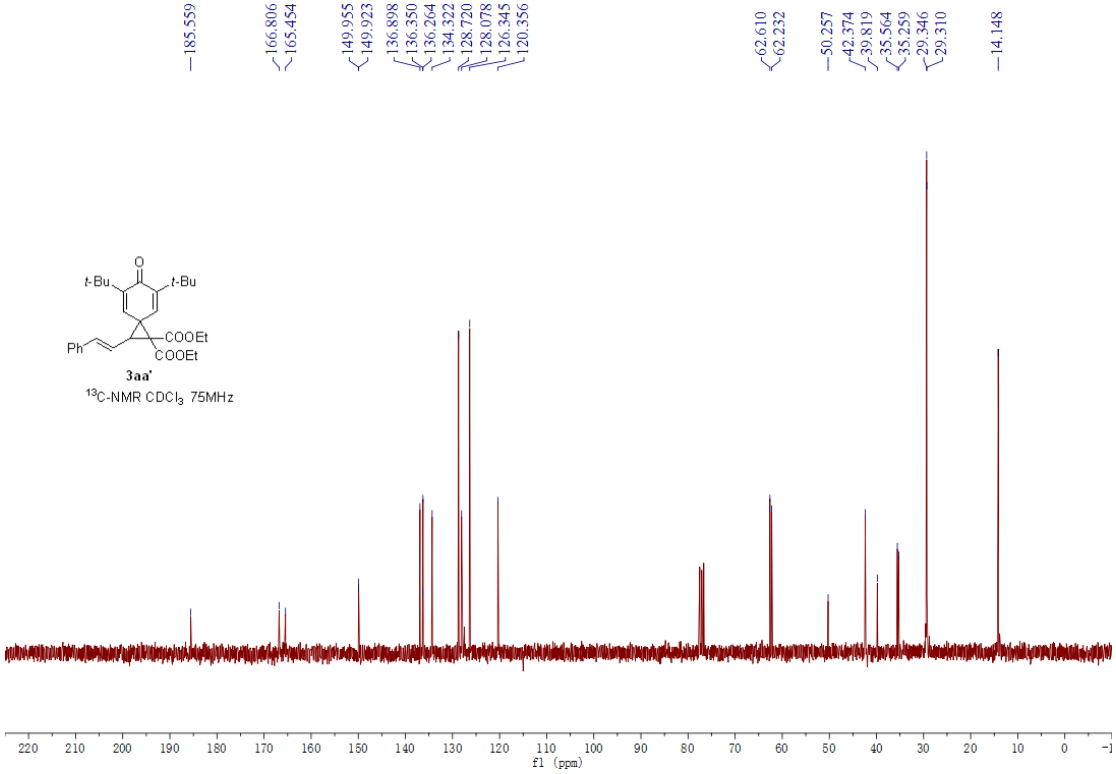
1.05
4.24
1.00
24.02
f1 (ppm)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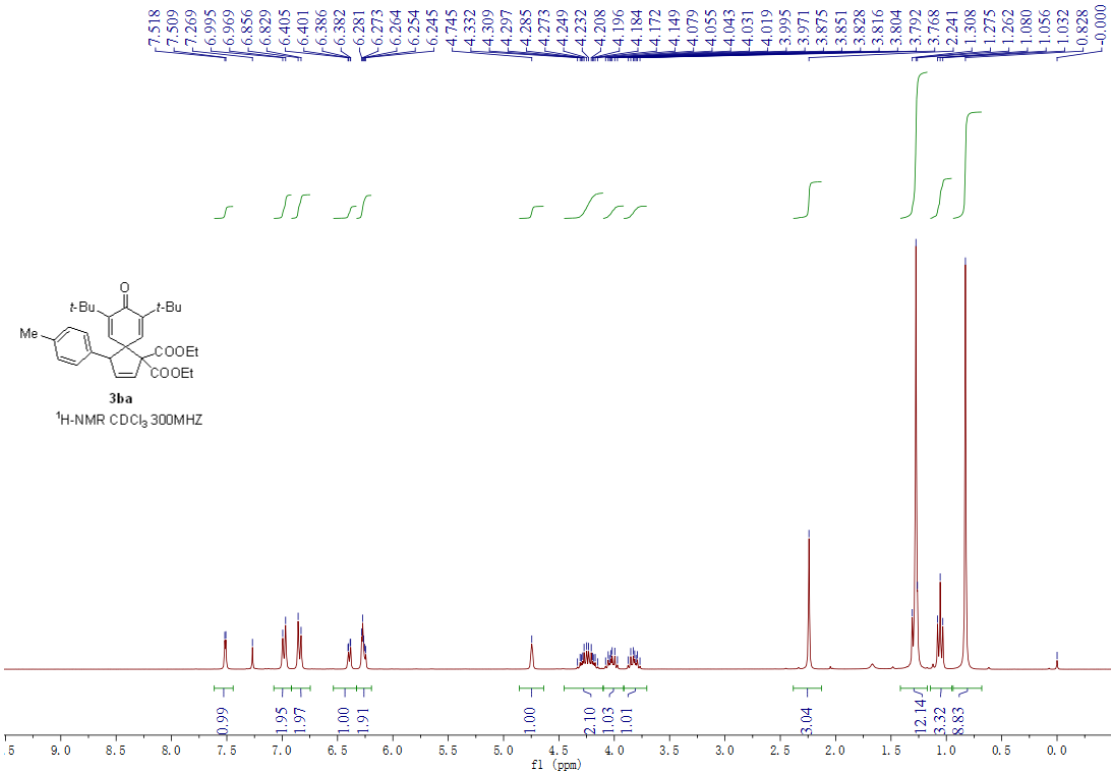
166.806
165.454
149.955
149.923
136.898
136.350
136.264
134.322
128.720
128.078
126.345
120.356
62.610
62.232
50.257
42.374
39.819
35.564
35.259
29.346
29.310
14.148
t-Bu
t-Bu
COOEt
COOEt
Ph
3aa'
13C-NMR CDCl3 75MHz
f1 (ppm)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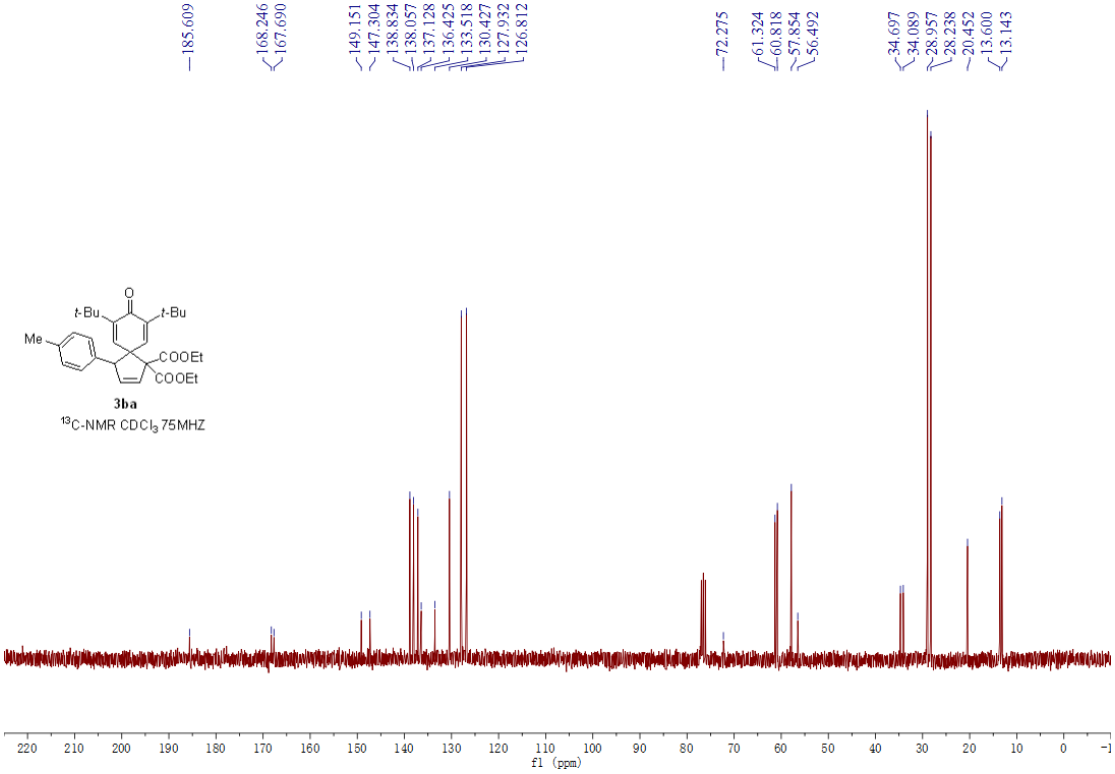
7.509
7.269
6.995
6.969
6.856
6.829
6.405
6.401
6.386
6.382
6.281
6.273
6.264
6.254
6.245
4.745
4.332
4.309
4.297
4.285
4.273
4.249
4.232
4.208
4.196
4.184
4.172
4.149
4.079
4.055
4.043
4.031
4.019
3.995
3.971
3.875
3.851
3.828
3.816
3.804
3.792
3.768
2.241
1.308
1.275
1.262
1.080
1.056
1.032
0.828
-0.000
t-Bu
t-Bu
Me
COOEt
COOEt
3ba
1H-NMR CDCl3 300MHZ
0.99
1.95
1.97
1.00
1.91
1.00
2.10
1.03
1.01
3.04
12.14
3.32
8.83
f1 (ppm)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167.690
149.151
147.304
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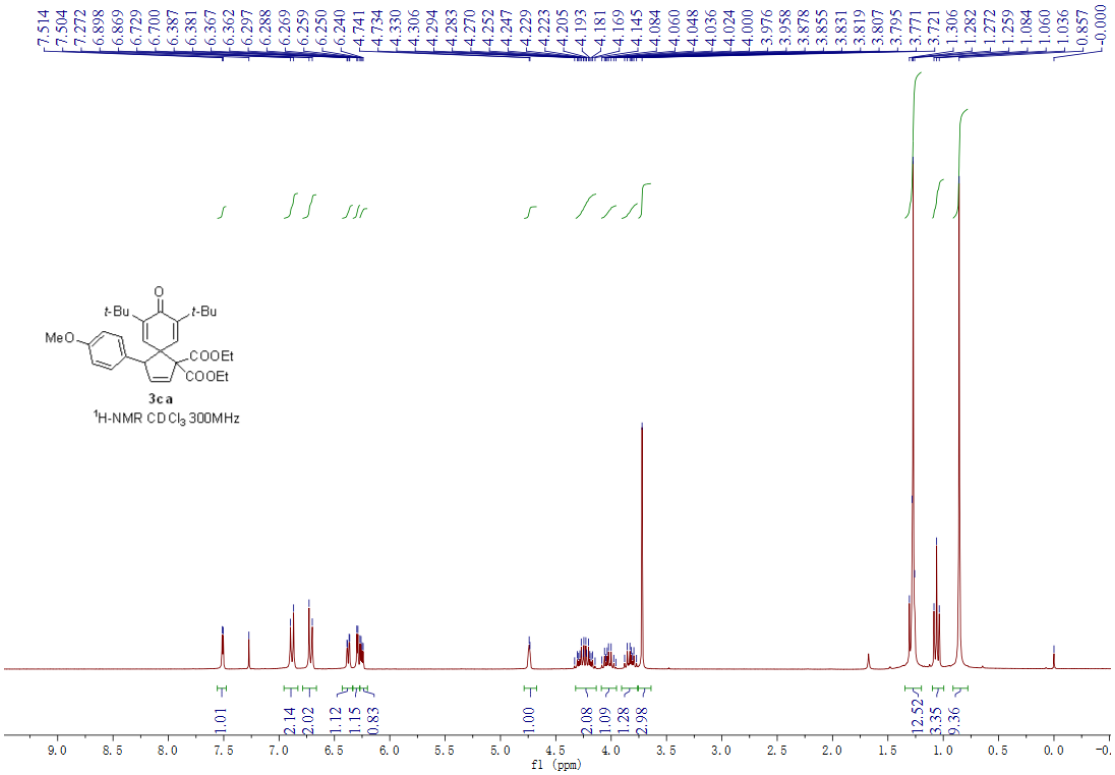
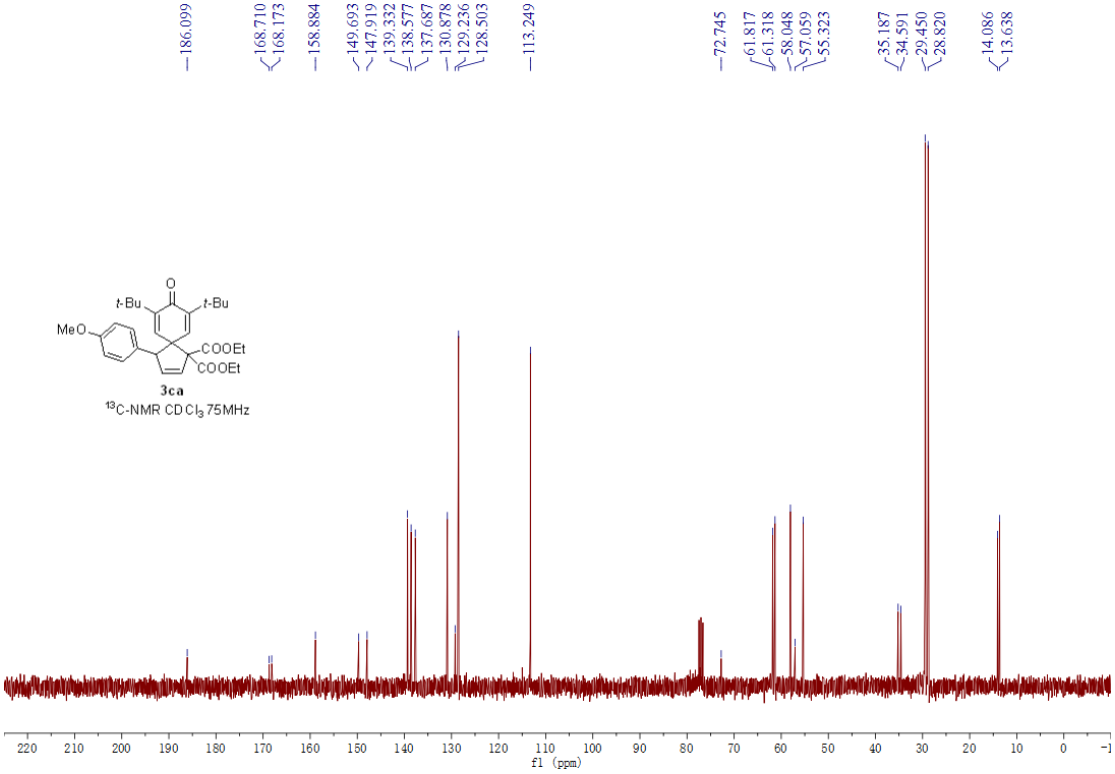
138.057
137.128
136.425
133.518
130.427
127.932
126.812
72.275
61.324
60.818
57.854
56.492
34.697
34.089
28.957
28.238
20.452
13.600
13.143
t-Bu
t-Bu
Me
COOEt
COOEt
3ba
13C-NMR CDCl3 75MHZ
f1 (ppm)


7.514
7.504
7.272
6.898
6.869
6.729
6.700
6.387
6.381
6.367
6.362
6.297
6.288
6.269
6.259
6.250
6.240
4.741
4.734
4.330
4.306
4.294
4.283
4.270
4.252
4.247
4.229
4.223
4.205
4.193
4.181
4.169
4.145
4.084
4.060
4.048
4.036
4.024
4.000
3.976
3.958
3.878
3.855
3.831
3.819
3.807
3.795
3.771
3.721
1.306
1.282
1.272
1.259
1.084
1.060
1.036
0.857
-0.000
t-Bu
t-Bu
MeO
COOEt
COOEt
3ca
1H-NMR CDCl3 300MHz
1.01
2.14
2.02
1.12
1.15
0.83
1.00
2.08
1.09
1.28
2.98
12.52
3.35
9.36
f1 (ppm)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168.173
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149.693
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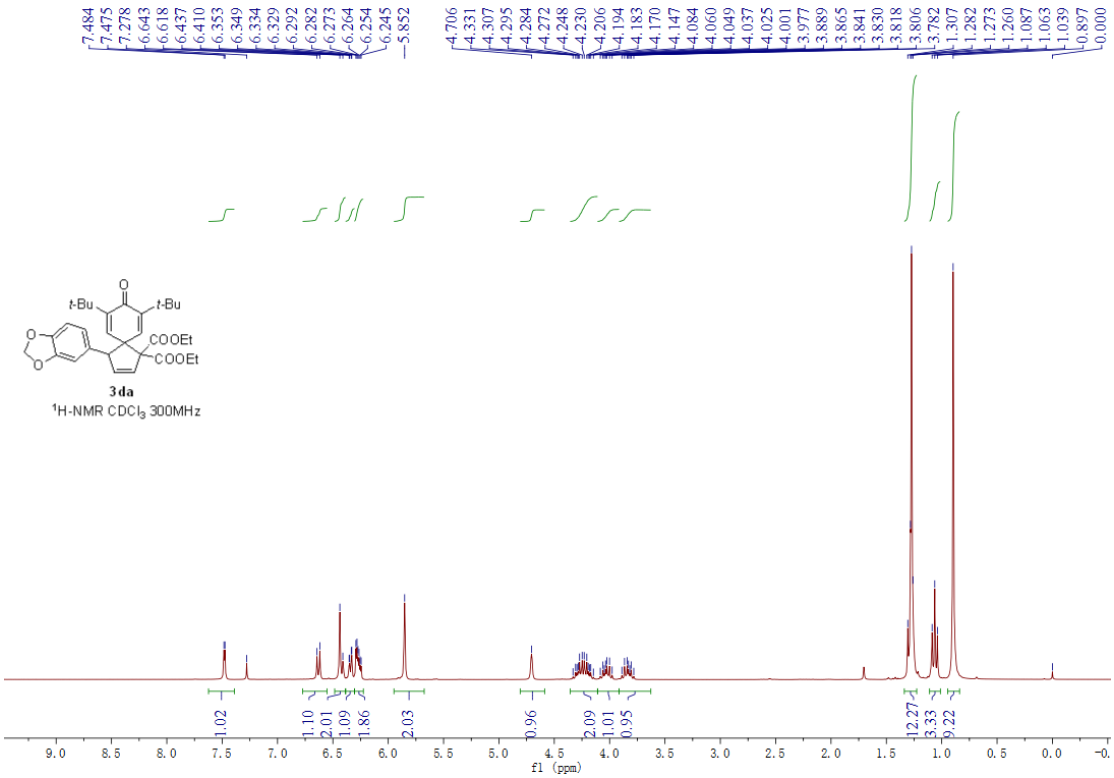
139.332
138.577
137.687
130.878
129.236
128.503
113.249
72.745
61.817
61.318
58.048
57.059
55.323
35.187
34.591
29.450
28.820
14.086
13.638
t-Bu
t-Bu
MeO
COOEt
COOEt
3ca
13C-NMR CDCl3 75MHz
f1 (ppm)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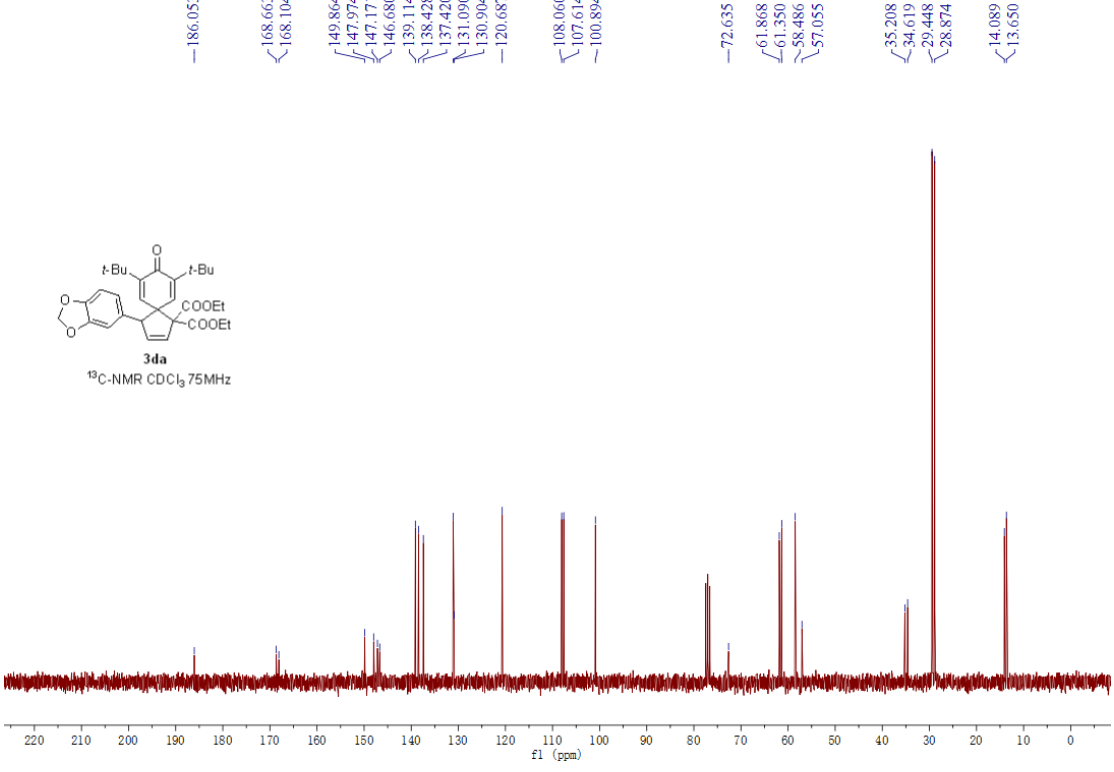
7.278
6.643
6.618
6.437
6.410
6.353
6.349
6.334
6.329
6.292
6.282
6.273
6.264
6.254
6.245
5.852
4.706
4.331
4.307
4.295
4.284
4.272
4.248
4.230
4.206
4.194
4.183
4.170
4.147
4.084
4.060
4.049
4.037
4.025
4.001
3.977
3.889
3.865
3.841
3.830
3.818
3.806
3.782
1.307
1.282
1.273
1.260
1.087
1.063
1.039
0.897
0.000
t-Bu
t-Bu
COOEt
COOEt
3da
1H-NMR CDCl3 300MHz
1.02
1.10
2.01
1.09
1.86
2.03
0.96
2.09
1.01
0.95
12.27
3.33
9.22
f1 (ppm)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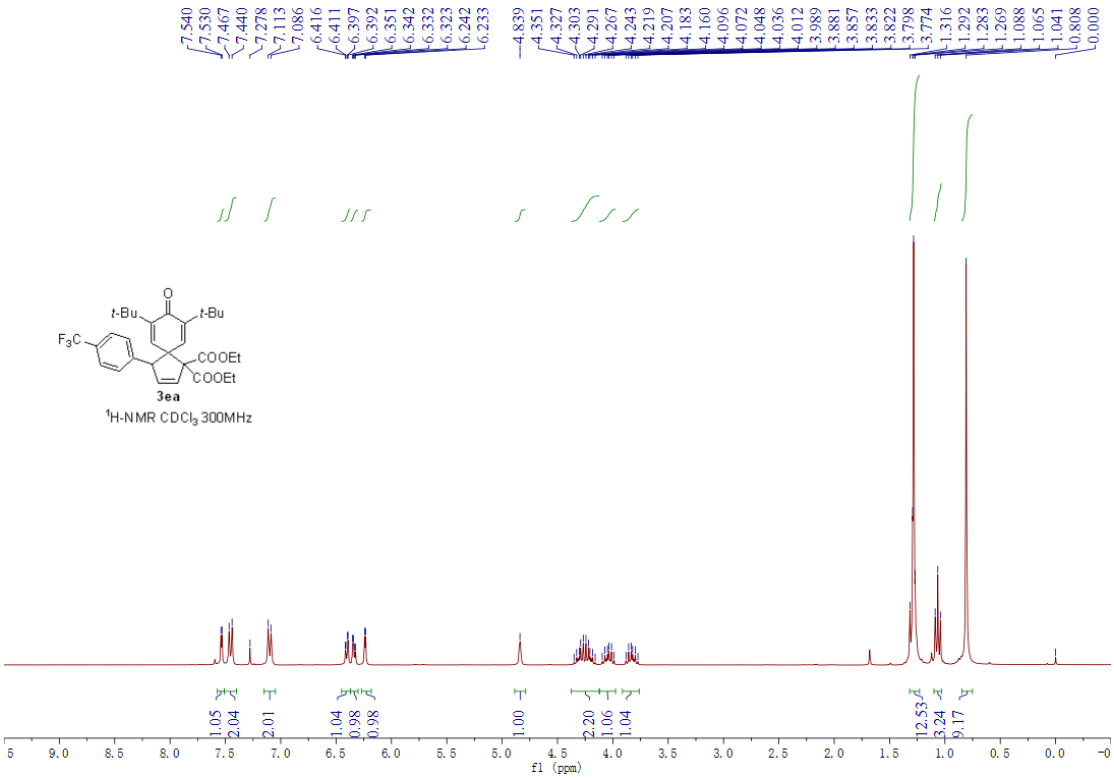
168.104
149.864
147.974
147.171
146.680
139.114
138.428
137.420
131.090
130.904
120.687
108.060
107.614
100.894
72.635
61.868
61.350
58.486
57.055
35.208
34.619
29.448
28.874
14.089
13.650
t-Bu
t-Bu
COOEt
COOEt
3da
13C-NMR CDCl3 75MHz
f1 (ppm)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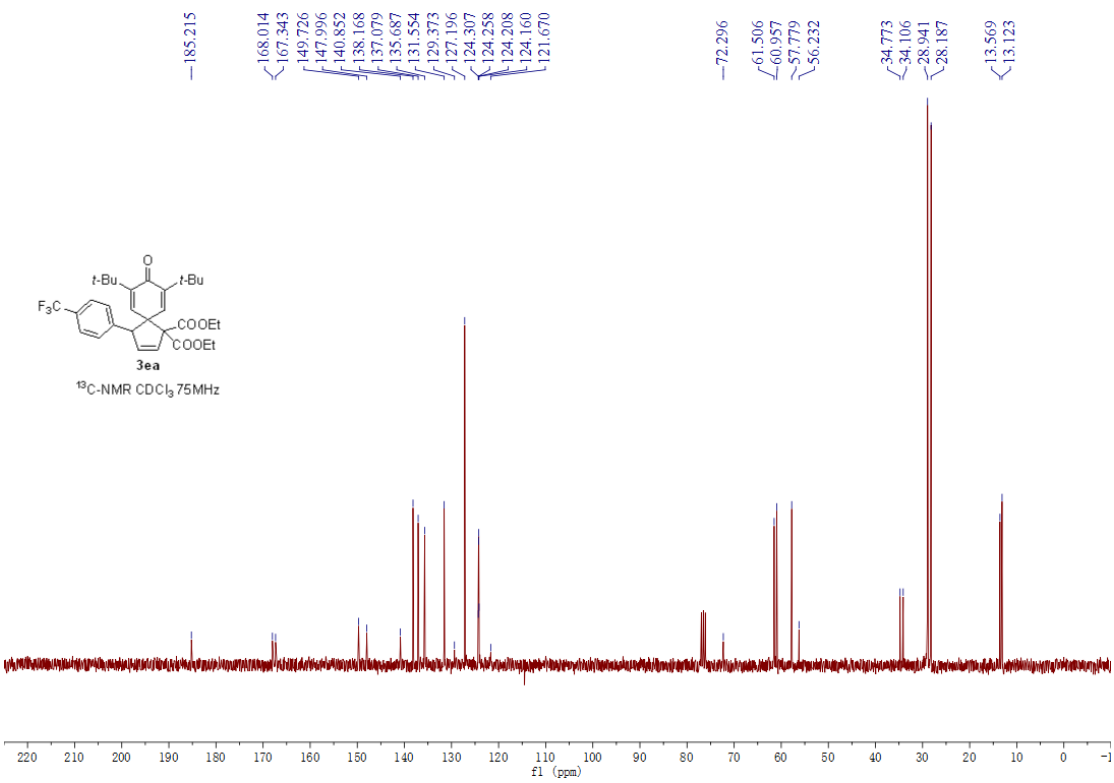
7.530
7.467
7.440
7.278
7.113
7.086
6.416
6.411
6.397
6.392
6.351
6.342
6.332
6.323
6.242
6.233
4.839
4.351
4.327
4.303
4.291
4.267
4.243
4.219
4.207
4.183
4.160
4.096
4.072
4.048
4.036
4.012
3.989
3.881
3.857
3.833
3.822
3.798
3.774
1.316
1.292
1.283
1.269
1.088
1.065
1.041
0.808
0.000
t-Bu
t-Bu
F3C
COOEt
COOEt
3ea
1H-NMR CDCl3 300MHz
1.05
2.04
2.01
1.04
0.98
0.98
1.00
2.20
1.06
1.04
12.53
3.24
9.17
f1 (ppm)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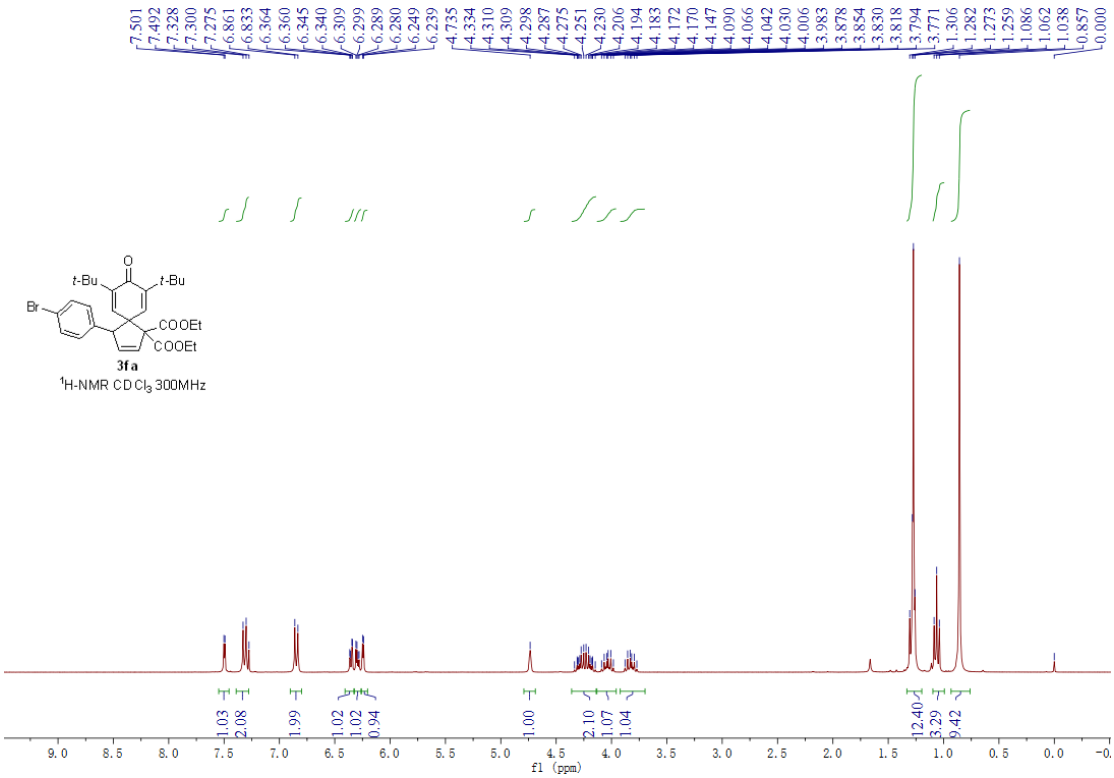
140.852
138.168
137.079
135.687
131.554
129.373
127.196
124.307
124.258
124.208
124.160
121.670
72.296
61.506
60.957
57.779
56.232
34.773
34.106
28.941
28.187
13.569
13.123
t-Bu
t-Bu
F3C
COOEt
COOEt
3ea
13C-NMR CDCl3 75MHz
f1 (ppm)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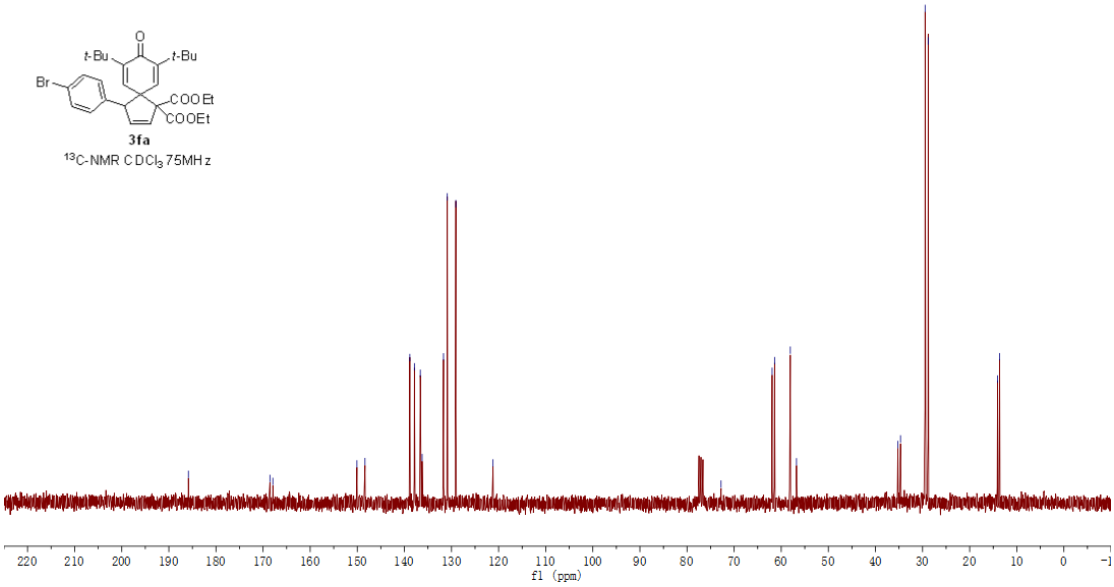
7.328
7.300
7.275
6.861
6.833
6.364
6.360
6.345
6.340
6.309
6.299
6.289
6.280
6.249
6.239
4.735
4.334
4.310
4.309
4.298
4.287
4.275
4.251
4.230
4.206
4.194
4.183
4.172
4.170
4.147
4.090
4.066
4.042
4.030
4.006
3.983
3.878
3.854
3.830
3.818
3.794
3.771
1.306
1.282
1.273
1.259
1.086
1.062
1.038
0.857
0.000
t-Bu
t-Bu
Br
COOEt
COOEt
3fa
1H-NMR CDCl3 300MHz
1.03
2.08
1.99
1.02
1.02
0.94
1.00
2.10
1.07
1.04
12.40
3.29
9.42
f1 (ppm)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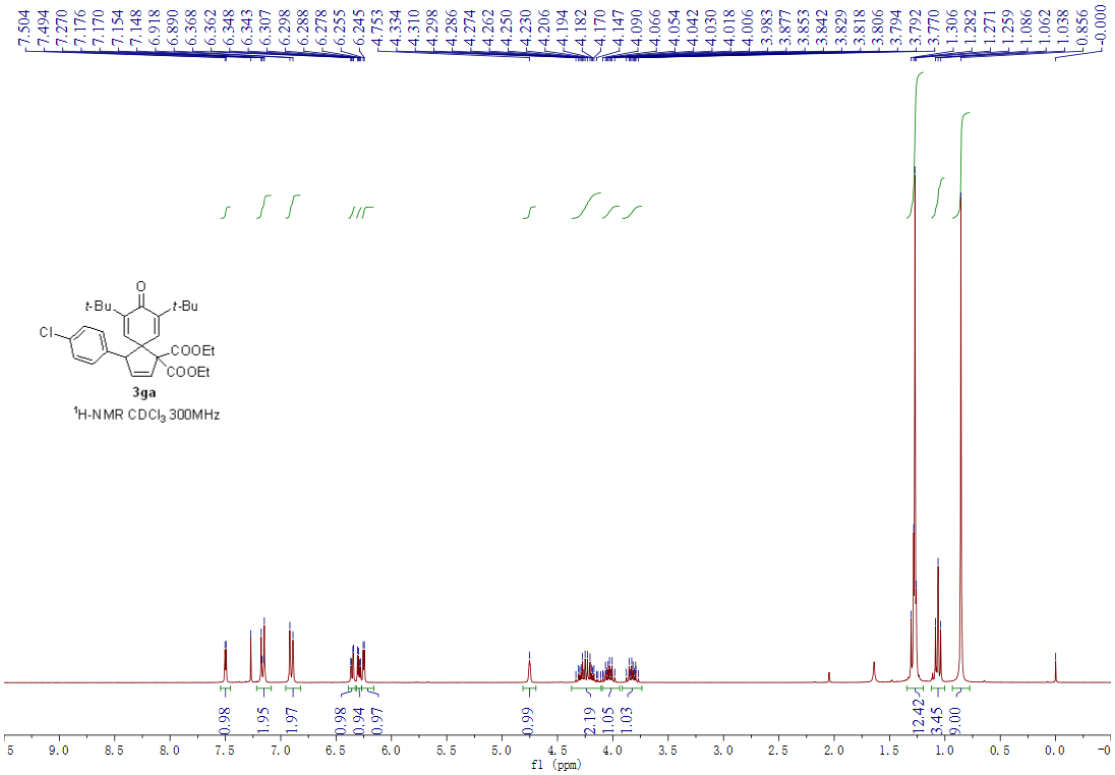
130.895
129.079
121.185
72.776
61.936
61.411
58.070
56.762
35.246
34.677
29.460
28.803
14.080
13.637
t-Bu
t-Bu
Br
COOEt
COOEt
3fa
13C-NMR CDCl3 75MHz
f1 (ppm)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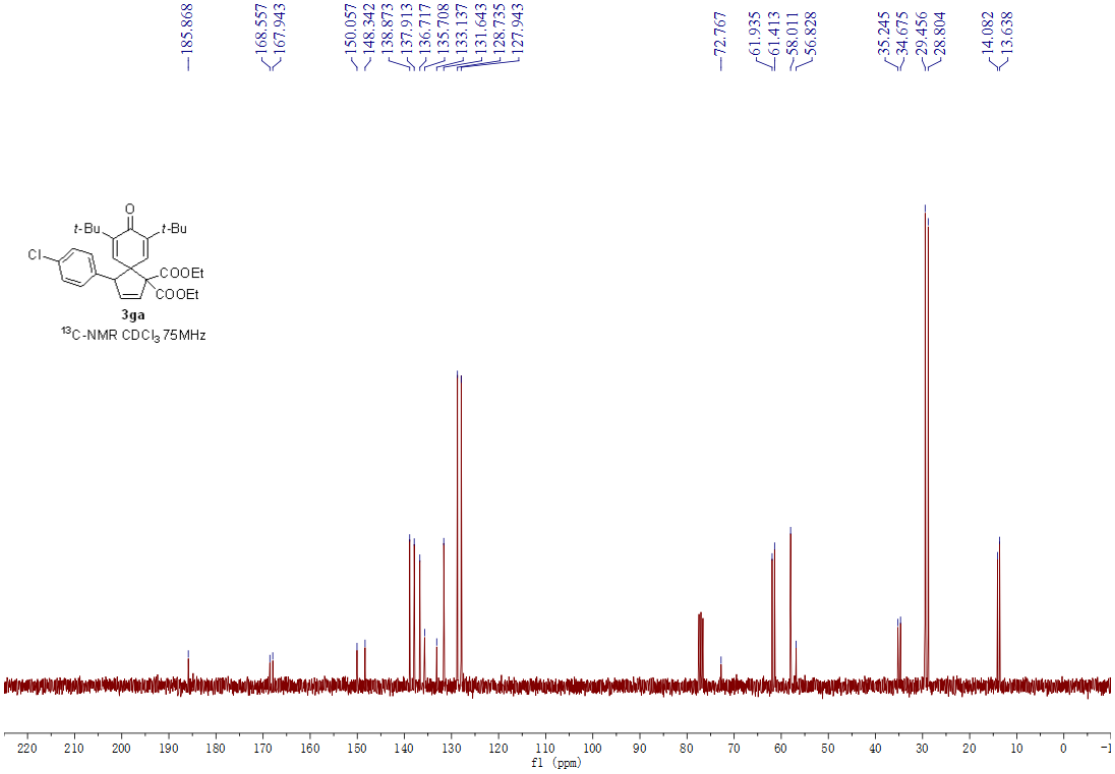
7.494
7.270
7.176
7.170
7.154
7.148
6.918
6.890
6.368
6.362
6.348
6.343
6.307
6.298
6.288
6.278
6.255
6.245
4.753
4.334
4.310
4.298
4.286
4.274
4.262
4.250
4.230
4.206
4.194
4.182
4.170
4.147
4.090
4.066
4.054
4.042
4.030
4.018
4.006
3.983
3.877
3.853
3.842
3.829
3.818
3.806
3.794
3.792
3.770
1.306
1.282
1.271
1.259
1.086
1.062
1.038
0.856
-0.000
t-Bu
t-Bu
Cl
COOEt
COOEt
O
3ga
1H-NMR CDCl3 300MHz
0.98
1.95
1.97
0.98
0.94
0.97
0.99
2.19
1.05
1.03
12.42
3.45
9.00
f1 (ppm)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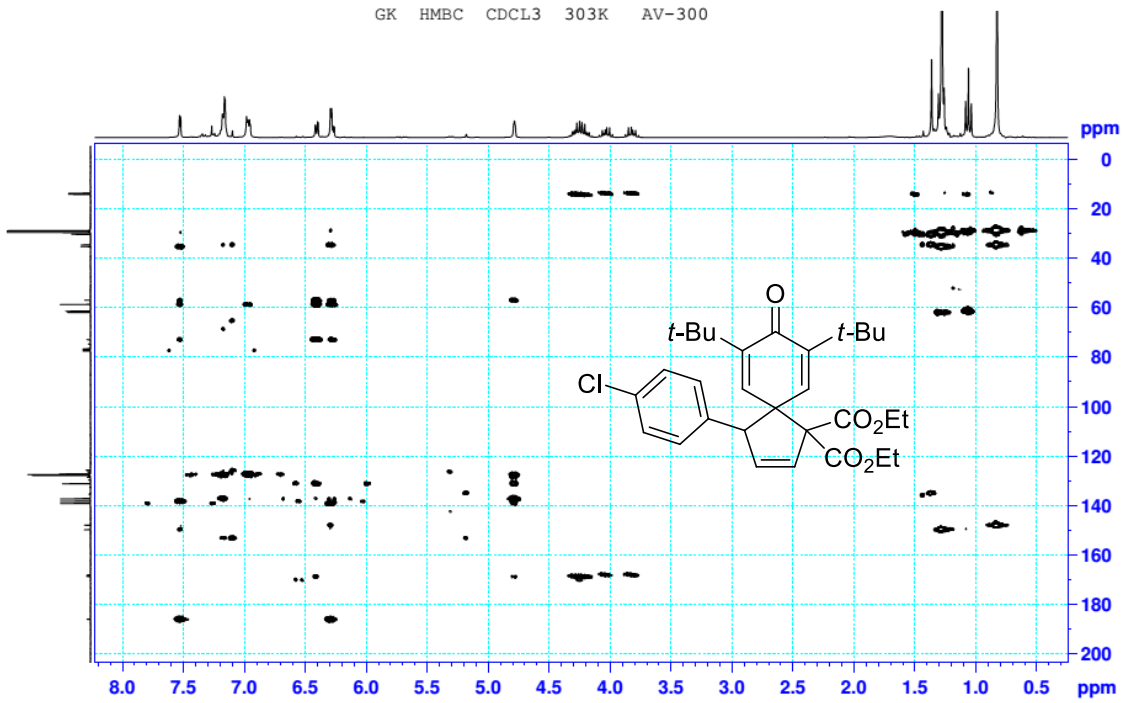
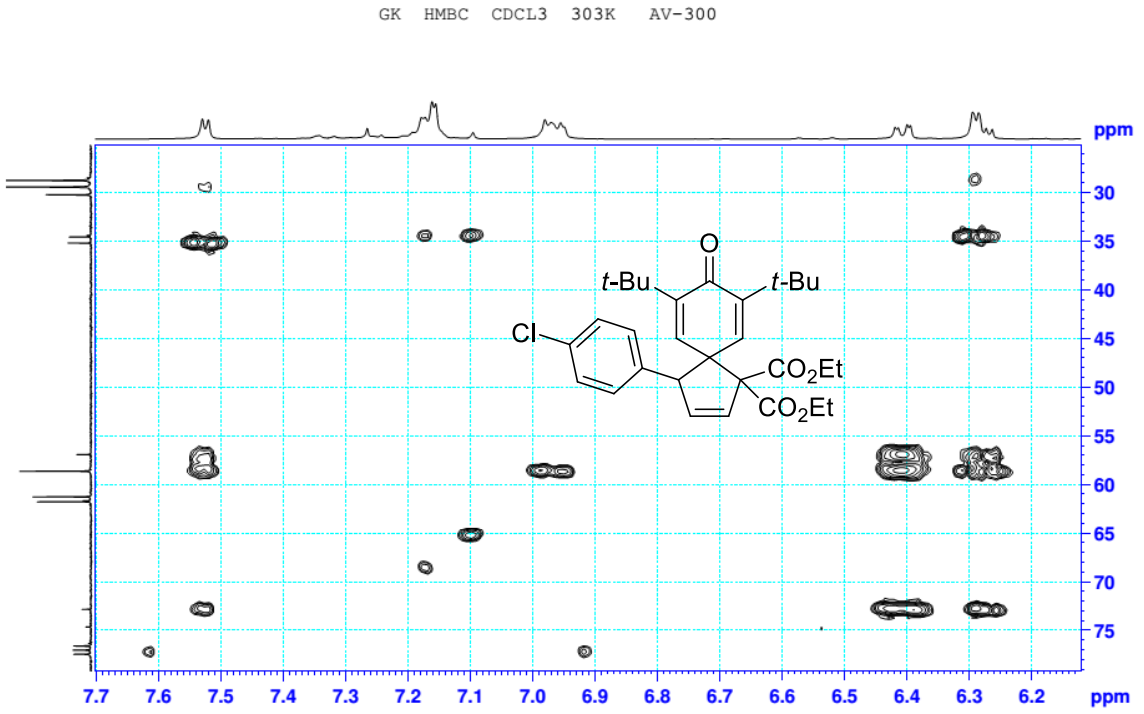
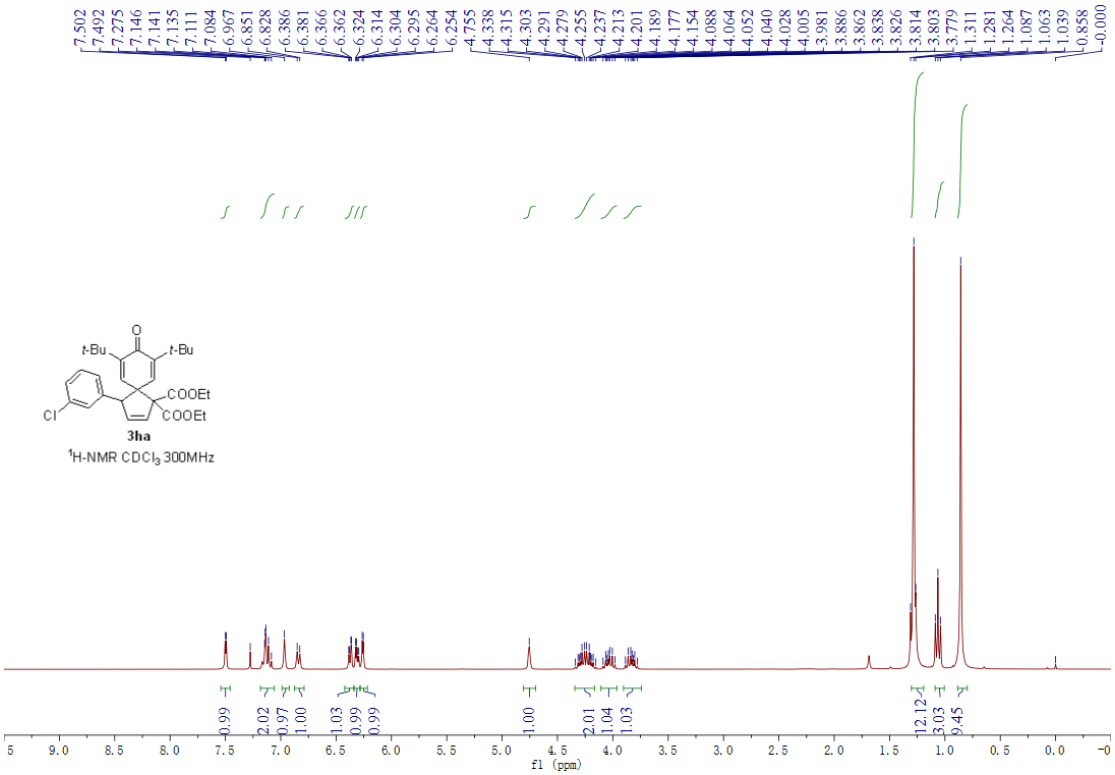
150.057
148.342
138.873
137.913
136.717
135.708
133.137
131.643
128.735
127.943
72.767
61.935
61.413
58.011
56.828
35.245
34.675
29.456
28.804
14.082
13.638
t-Bu
t-Bu
Cl
COOEt
COOEt
O
3ga
13C-NMR CDCl3 75MHz
f1 (ppm)



HMBC spectrum of **3ga**



Zoom-in HMBC spectrum of **3ga**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7.492
7.275
7.146
7.141
7.135
7.111
7.084
6.967
6.851
6.828
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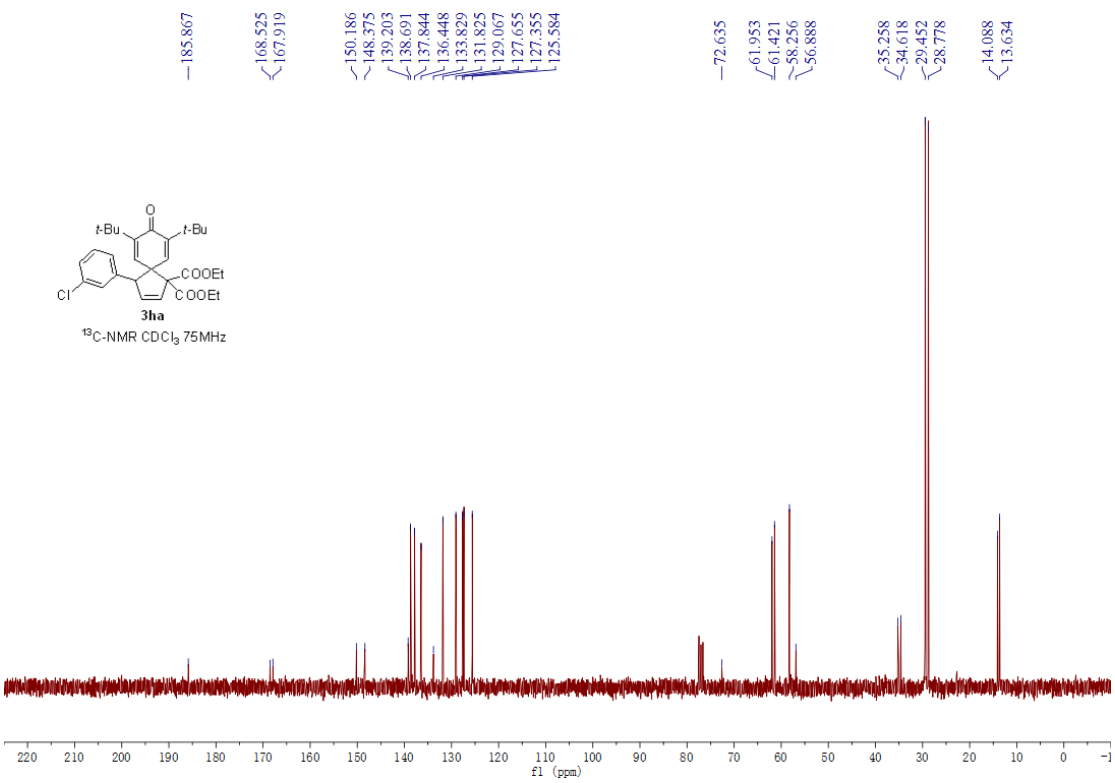
6.381
6.366
6.362
6.324
6.314
6.304
6.295
6.264
6.254
4.755
4.338
4.315
4.303
4.291
4.279
4.255
4.237
4.213
4.201
4.189
4.177
4.154
4.088
4.064
4.052
4.040
4.028
4.005
3.981
3.886
3.862
3.838
3.826
3.814
3.803
3.779
1.311
1.281
1.264
1.087
1.063
1.039
0.858
-0.000
t-Bu
t-Bu
COOEt
COOEt
Cl
O
3ha
1H-NMR CDCl3 300MHz
0.99
2.02
0.97
1.00
1.03
0.99
0.99
1.00
2.01
1.04
1.03
12.12
3.03
9.45
f1 (ppm)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150.186
148.375
139.203
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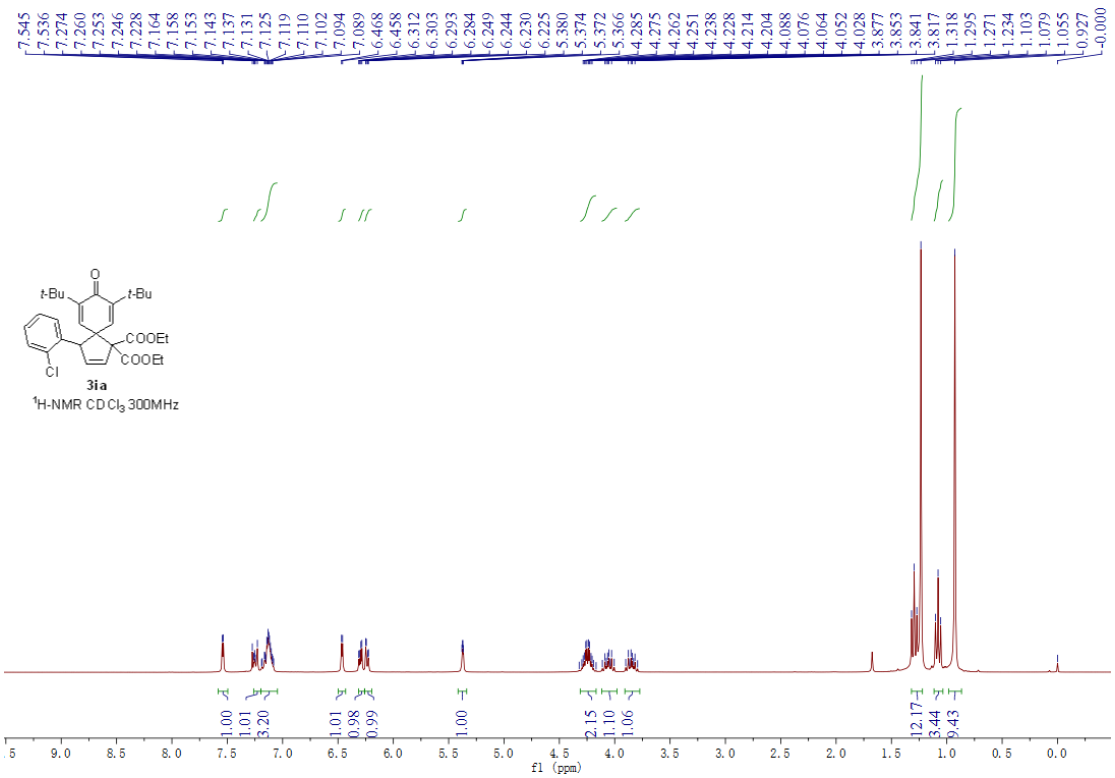
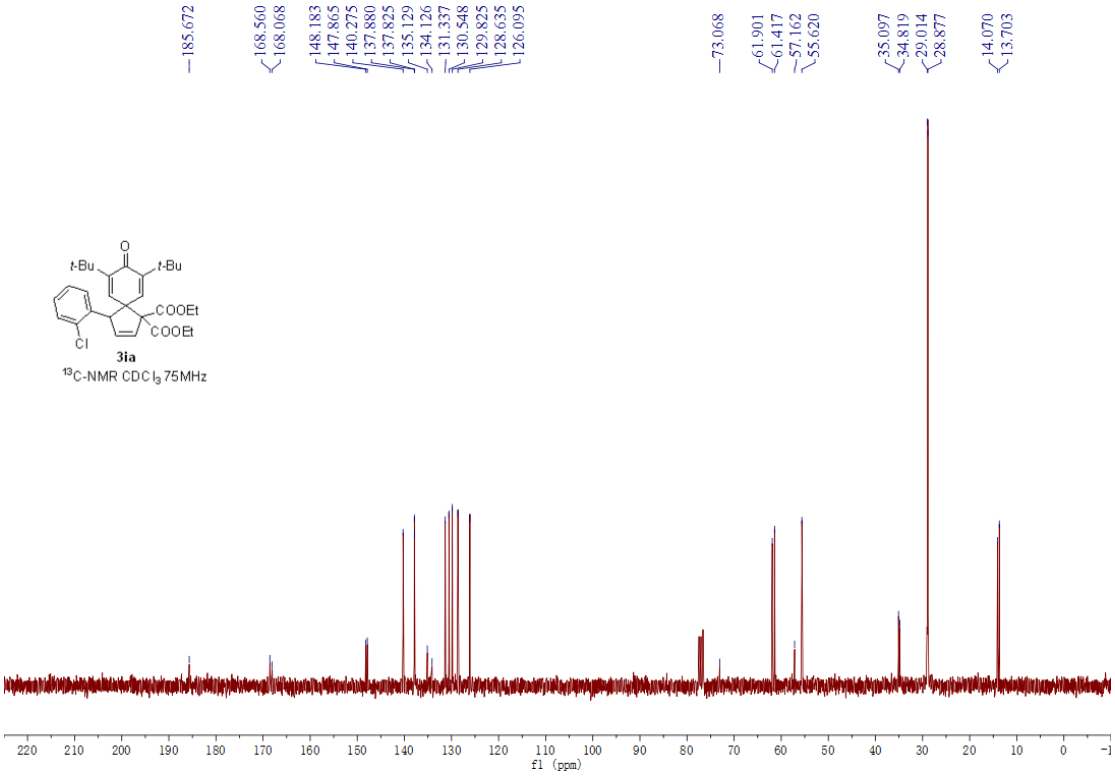
137.844
136.448
133.829
131.825
129.067
127.655
127.355
125.584
72.635
61.953
61.421
58.256
56.888
35.258
34.618
29.452
28.778
14.088
13.634
t-Bu
t-Bu
COOEt
COOEt
Cl
O
3ha
13C-NMR CDCl3 75MHz
f1 (ppm)


7.545
7.536
7.274
7.260
7.253
7.246
7.228
7.164
7.158
7.153
7.143
7.137
7.131
7.125
7.119
7.110
7.102
7.094
7.089
6.468
6.458
6.312
6.303
6.293
6.284
6.249
6.244
6.230
6.225
5.380
5.374
5.372
5.366
4.285
4.275
4.262
4.251
4.238
4.228
4.214
4.204
4.088
4.076
4.064
4.052
4.028
3.877
3.853
3.841
3.817
1.318
1.295
1.271
1.234
1.103
1.079
1.055
0.927
-0.000
t-Bu
t-Bu
COOEt
COOEt
Cl
3ia
1H-NMR CDCl3 300MHz
1.00
1.01
3.20
1.01
0.98
0.99
1.00
2.15
1.10
1.06
12.17
3.44
9.43
f1 (ppm)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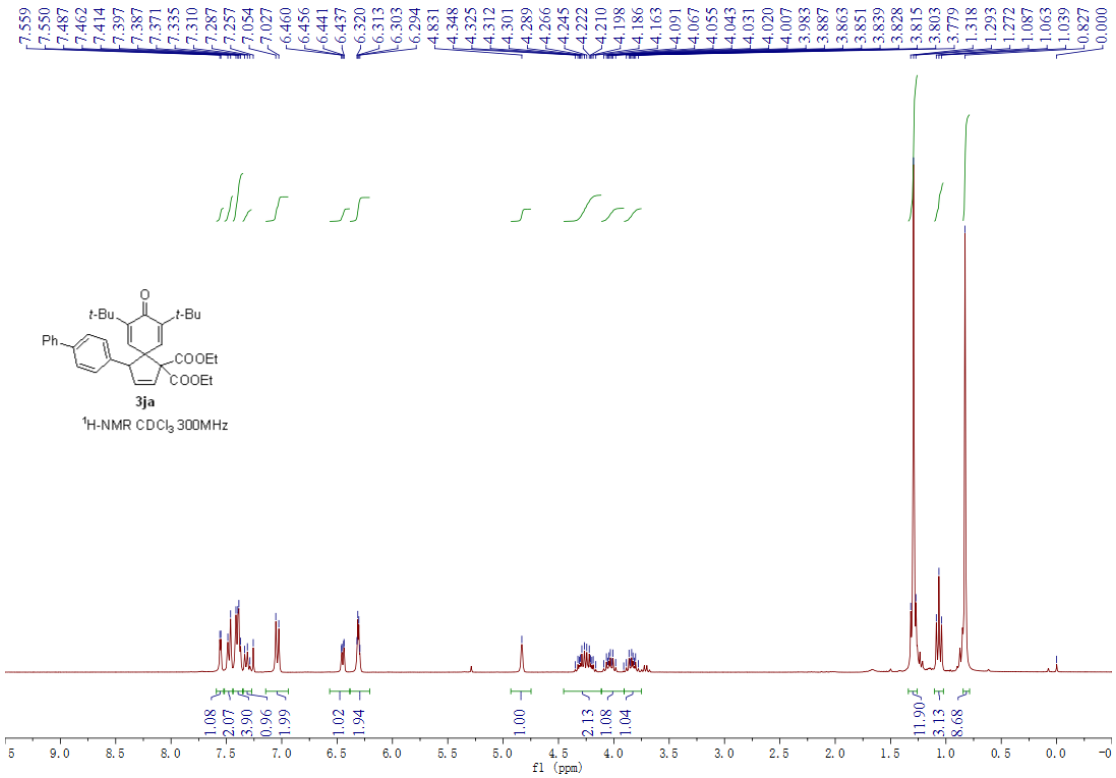
129.825
128.635
126.095
73.068
61.901
61.417
57.162
55.620
35.097
34.819
29.014
28.877
14.070
13.703
t-Bu
t-Bu
COOEt
COOEt
Cl
3ia
13C-NMR CDCl3 75MHz
f1 (ppm)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7.027
6.460
6.456
6.441
6.437
6.320
6.313
6.303
6.294
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4.348
4.325
4.312
4.301
4.289
4.266
4.245
4.222
4.210
4.198
4.186
4.163
4.091
4.067
4.055
4.043
4.031
4.020
4.007
3.983
3.887
3.863
3.851
3.839
3.828
3.815
3.803
3.779
1.318
1.293
1.272
1.087
1.063
1.039
0.827
0.000
t-Bu
t-Bu
Ph
COOEt
COOEt
3ja
1H-NMR CDCl3 300MHz
1.08
2.07
3.90
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1.94
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11.90
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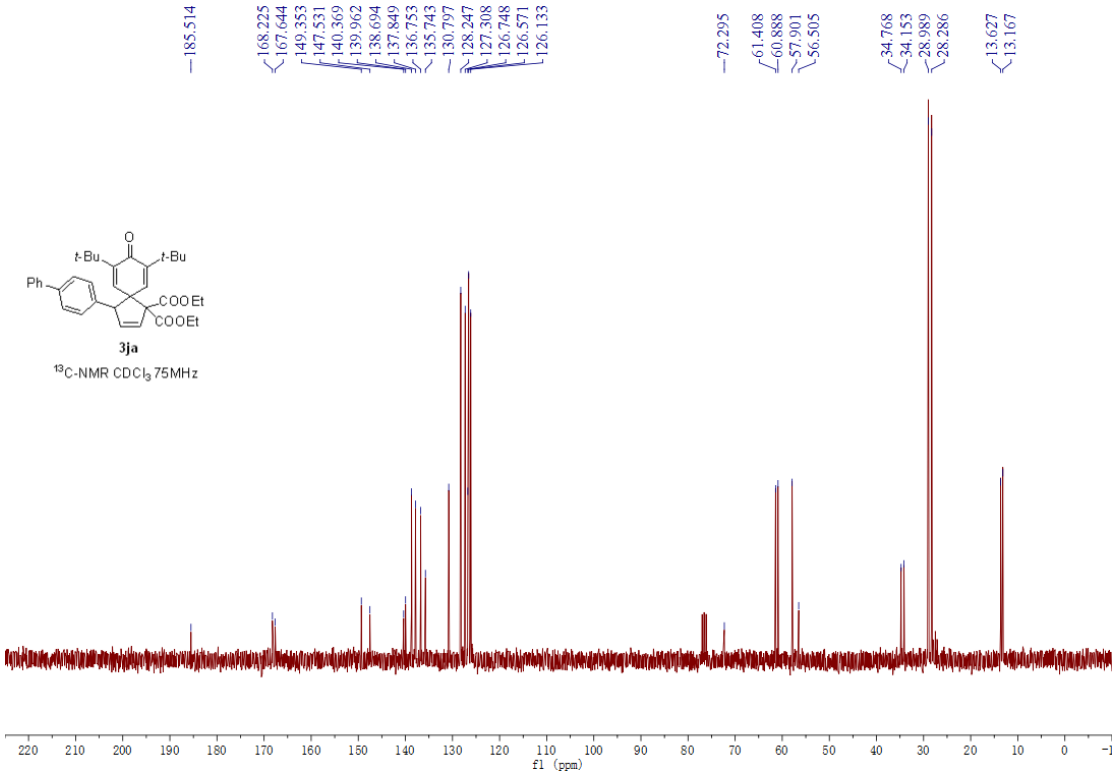
8.68
f1 (ppm)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127.308
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126.571
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72.295
61.408
60.888
57.901
56.505
34.768
34.153
28.989
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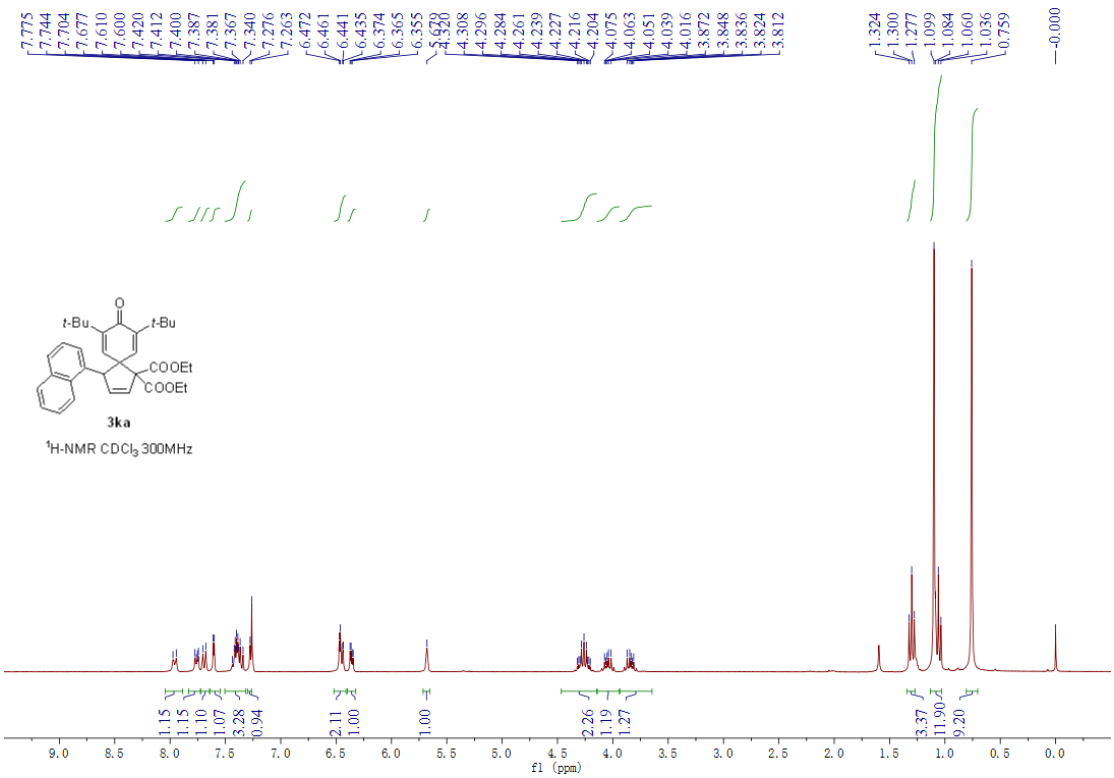
13.167
t-Bu
t-Bu
Ph
COOEt
COOEt
3ja
13C-NMR CDCl3 75MHz
f1 (ppm)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7.276
7.263
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6.441
6.435
6.374
6.365
6.355
5.679
4.420
4.308
4.296
4.284
4.261
4.239
4.227
4.216
4.204
4.075
4.063
4.051
4.039
4.016
3.872
3.848
3.836
3.824
3.812
1.324
1.300
1.277
1.099
1.084
1.060
1.036
0.759
-0.000
t-Bu
t-Bu
COOEt
COOEt
3ka
1H-NMR CDCl3 300MHz
1.15
1.15
1.10
1.07
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1.00
1.00
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1.27
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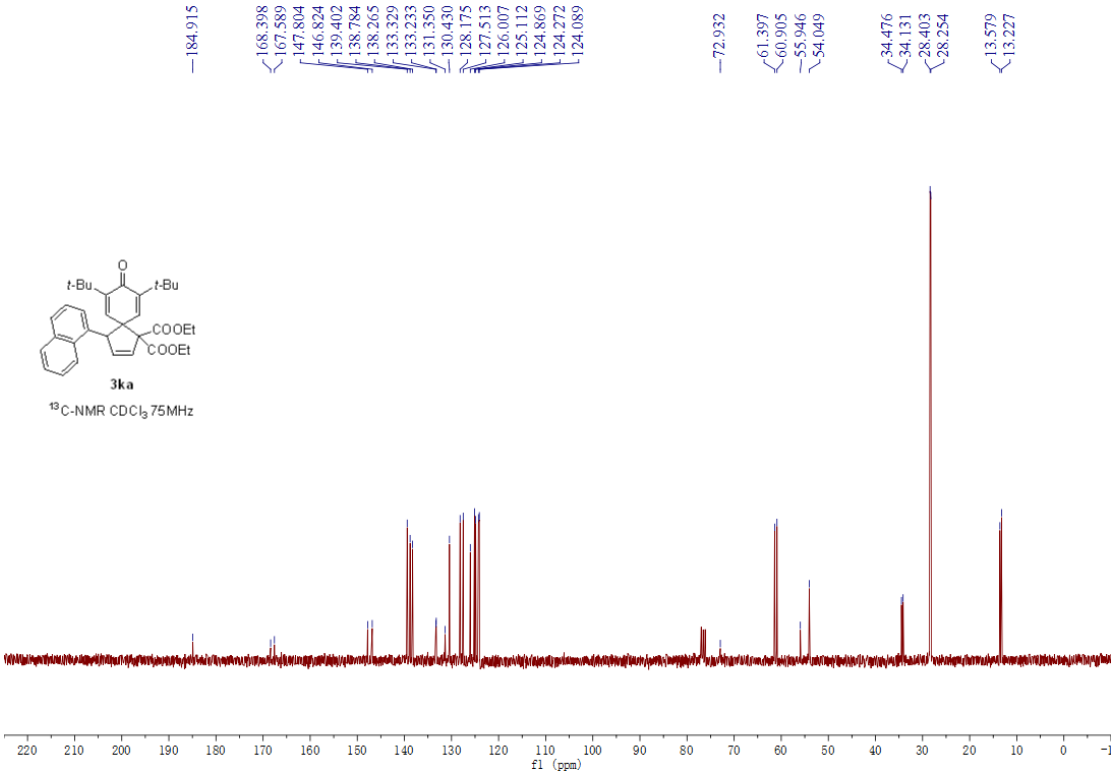
9.20
f1 (ppm)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126.007
125.112
124.869
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61.397
60.905
55.946
54.049
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t-Bu
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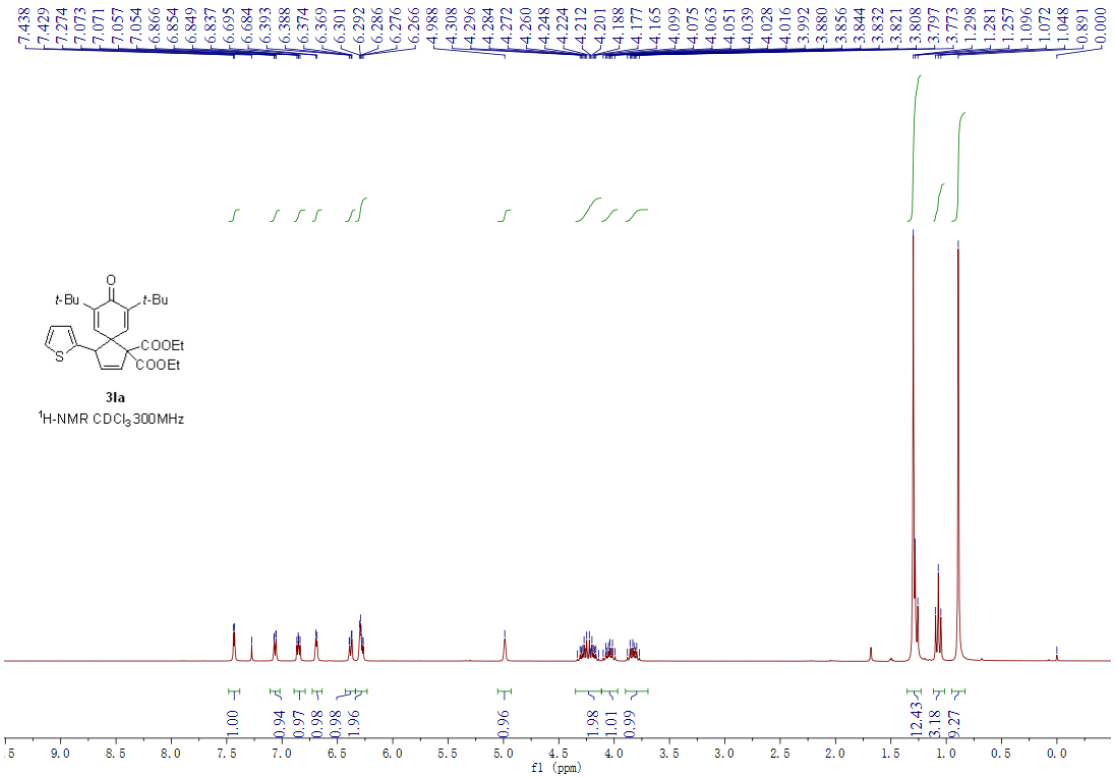
COOEt
3ka
13C-NMR CDCl3 75MHz
f1 (ppm)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6.684
6.393
6.388
6.374
6.369
6.301
6.292
6.286
6.276
6.266
4.988
4.308
4.296
4.284
4.272
4.260
4.248
4.224
4.212
4.201
4.188
4.177
4.165
4.099
4.075
4.063
4.051
4.039
4.028
4.016
3.992
3.880
3.856
3.844
3.832
3.821
3.808
3.797
3.773
1.298
1.281
1.257
1.096
1.072
1.048
0.891
0.000
t-Bu
t-Bu
COOEt
COOEt
3la
1H-NMR CDCl3 300MHz
1.00
0.94
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0.96
1.98
1.01
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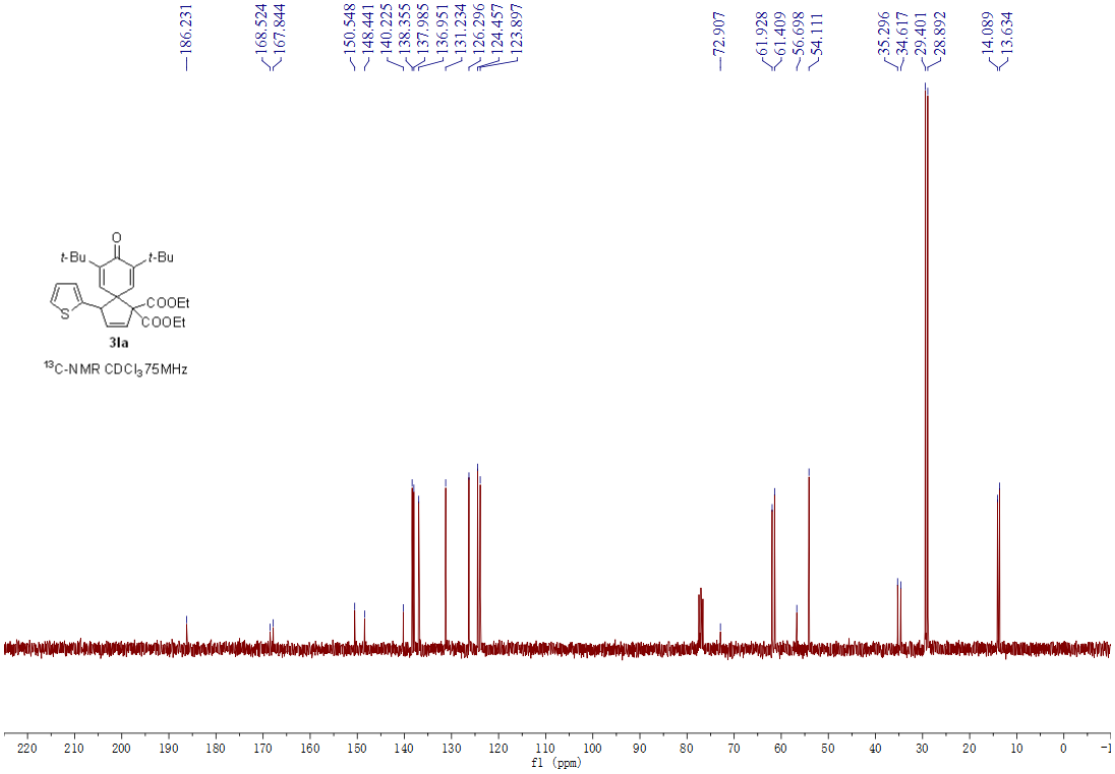
3.18
9.27
f1 (ppm)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72.907
61.928
61.409
56.698
54.111
35.296
34.617
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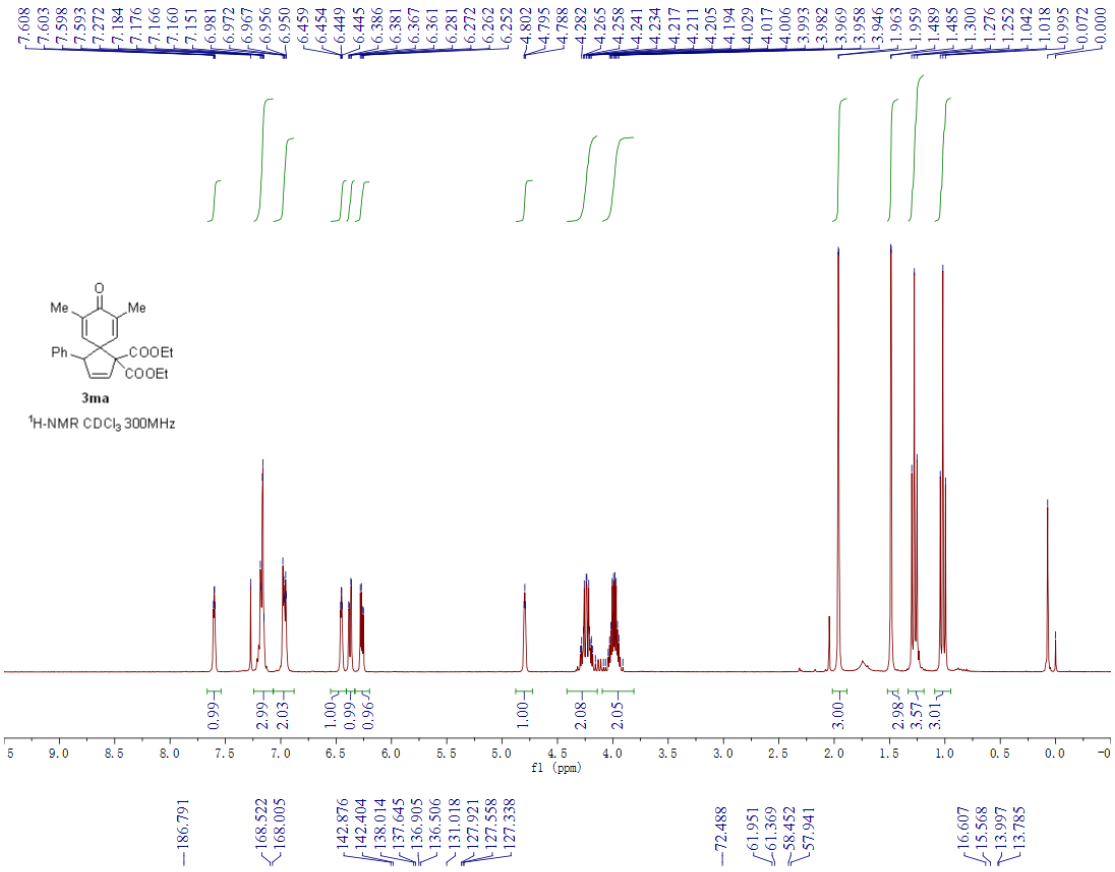
13.634
t-Bu
t-Bu
COOEt
COOEt
3la
13C-NMR CDCl3 75MHz
f1 (ppm)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7.166
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7.151
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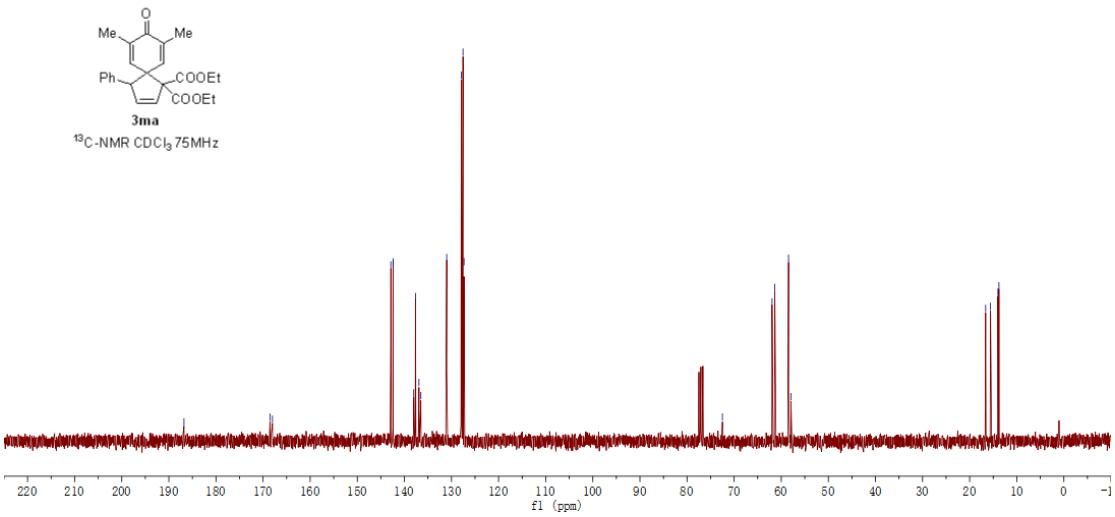
6.967
6.956
6.950
6.459
6.454
6.449
6.445
6.386
6.381
6.367
6.361
6.281
6.272
6.262
6.252
4.802
4.795
4.788
4.282
4.265
4.258
4.241
4.234
4.217
4.211
4.205
4.194
4.029
4.017
4.006
3.993
3.982
3.969
3.958
3.946
1.963
1.959
1.489
1.485
1.300
1.276
1.252
1.042
1.018
0.995
0.072
0.000
Me
Me
Ph
COOEt
COOEt
3ma
1H-NMR CDCl3 300MHz
0.99
2.99
2.03
1.00
0.99
0.96
1.00
2.08
2.05
3.00
2.98
3.57
3.01
f1 (ppm)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127.921
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127.338
72.488
61.951
61.369
58.452
57.941
16.607
15.568
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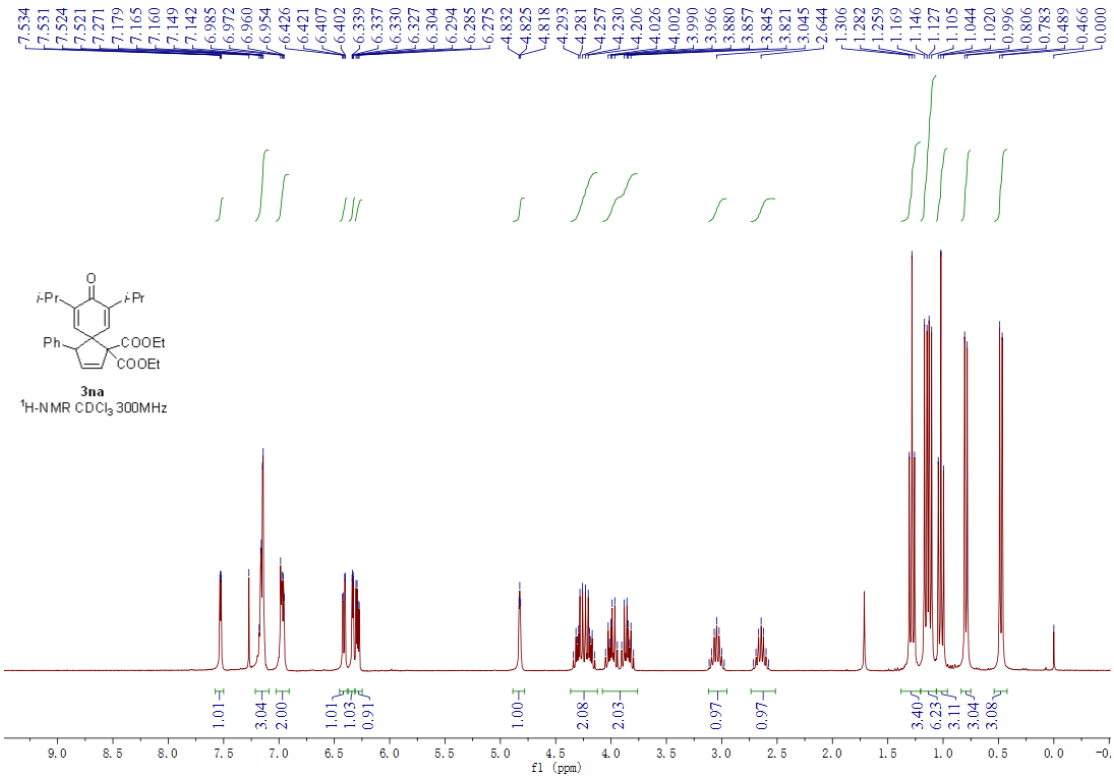
13.785
Me
Me
Ph
COOEt
COOEt
3ma
13C-NMR CDCl3 75MHz
f1 (ppm)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i-Pr
i-Pr
Ph
COOEt
COOEt
3na
1H-NMR CDCl3 300MHz
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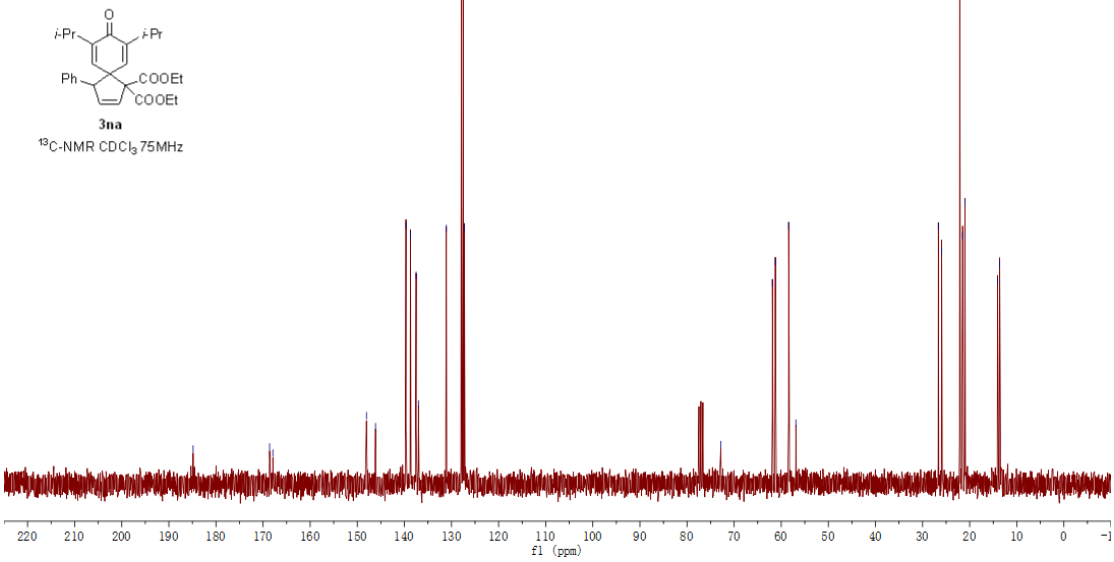
f1 (ppm)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i-Pr
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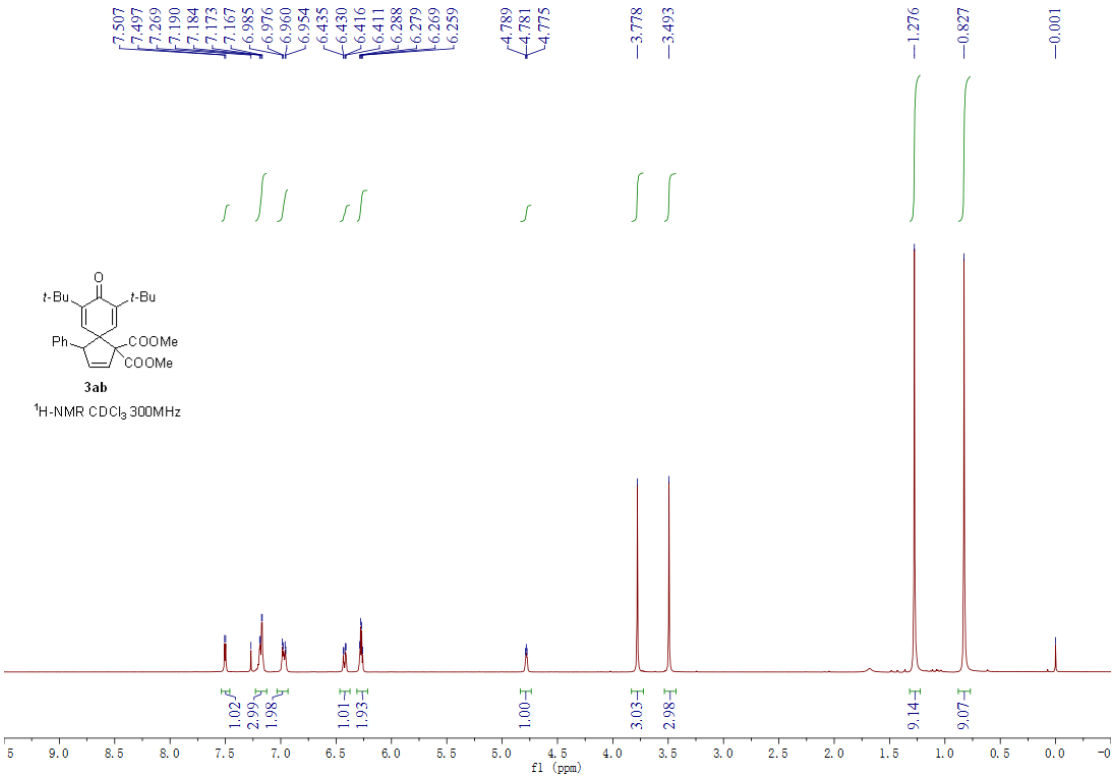
Ph
COOEt
COOEt
3na
13C-NMR CDCl3 75MHz
f1 (ppm)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6.976
6.960
6.954
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6.430
6.416
6.411
6.288
6.279
6.269
6.259
4.789
4.781
4.775
3.778
3.493
1.276
0.827
0.001
t-Bu
t-Bu
Ph
COOMe
COOMe
3ab
1H-NMR CDCl3 300MHz
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1.98
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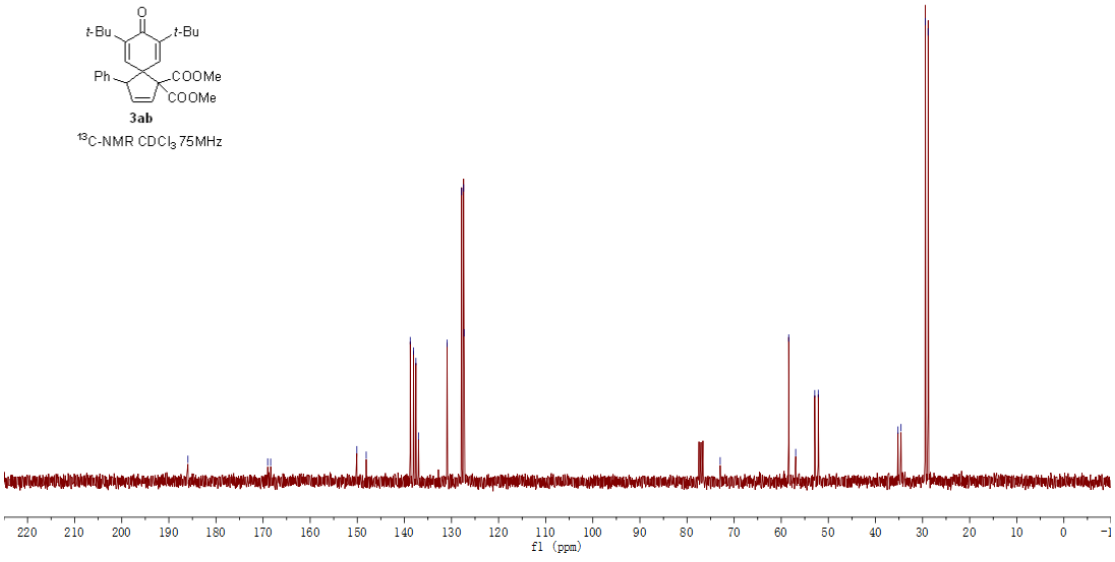
3.03
2.98
9.14
9.07
f1 (ppm)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127.330
72.958
58.412
56.935
52.886
52.142
35.211
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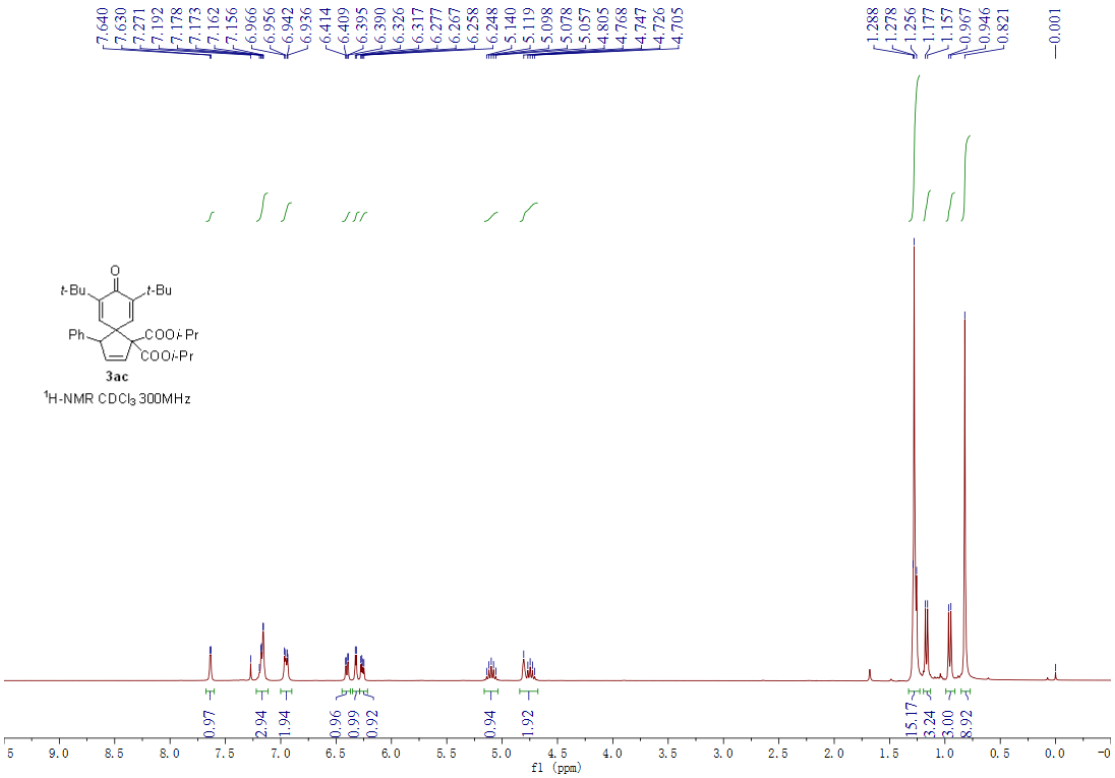
28.814
t-Bu
t-Bu
Ph
COOMe
COOMe
3ab
13C-NMR CDCl3 75MHz
f1 (ppm)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6.956
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6.936
6.414
6.409
6.395
6.390
6.326
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6.277
6.267
6.258
6.248
5.140
5.119
5.098
5.078
5.057
4.805
4.768
4.747
4.726
4.705
1.288
1.278
1.256
1.177
1.157
0.967
0.946
0.821
0.001
t-Bu
t-Bu
Ph
COOi-Pr
COOi-Pr
3ac
1H-NMR CDCl3 300MHz
0.97
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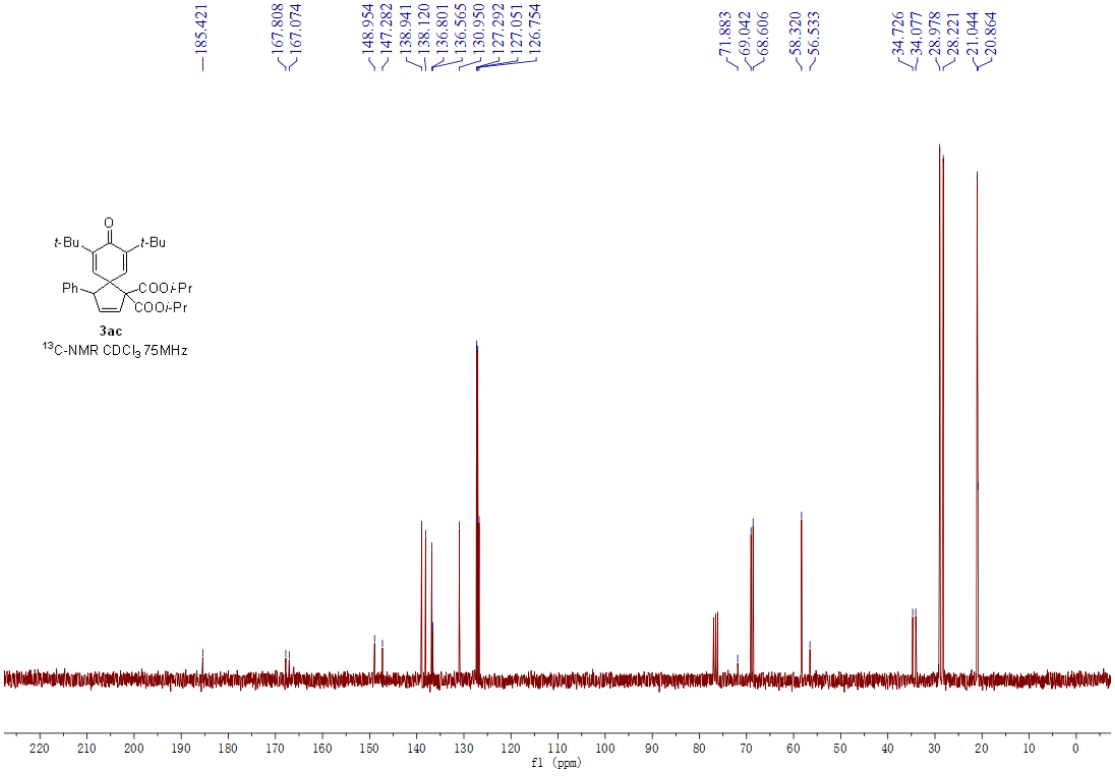
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126.754
71.883
69.042
68.606
58.320
56.533
34.726
34.077
28.978
28.221
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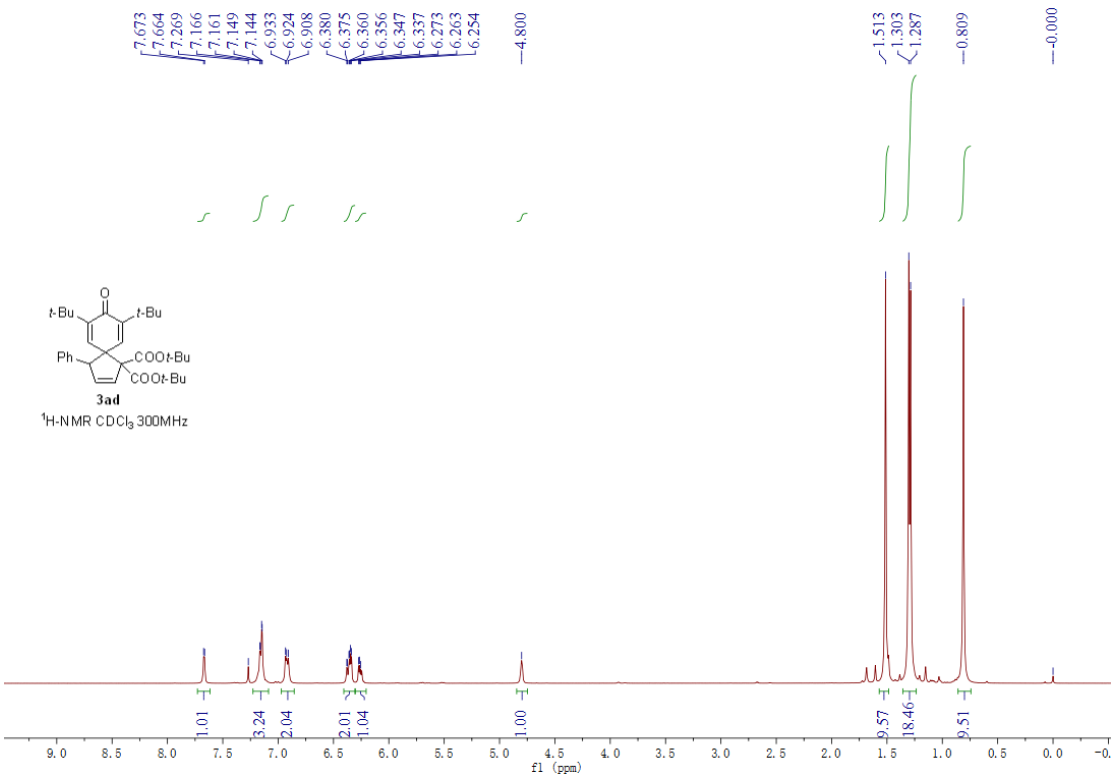
20.864
t-Bu
t-Bu
Ph
COOi-Pr
COOi-Pr
3ac
13C-NMR CDCl3 75MHz
f1 (ppm)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6.360
6.356
6.347
6.337
6.273
6.263
6.254
4.800
1.513
1.303
1.287
0.809
0.000
t-Bu
t-Bu
Ph
COOt-Bu
COOt-Bu
3ad
1H-NMR CDCl3 300MHz
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3.24
2.04
2.01
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1.00
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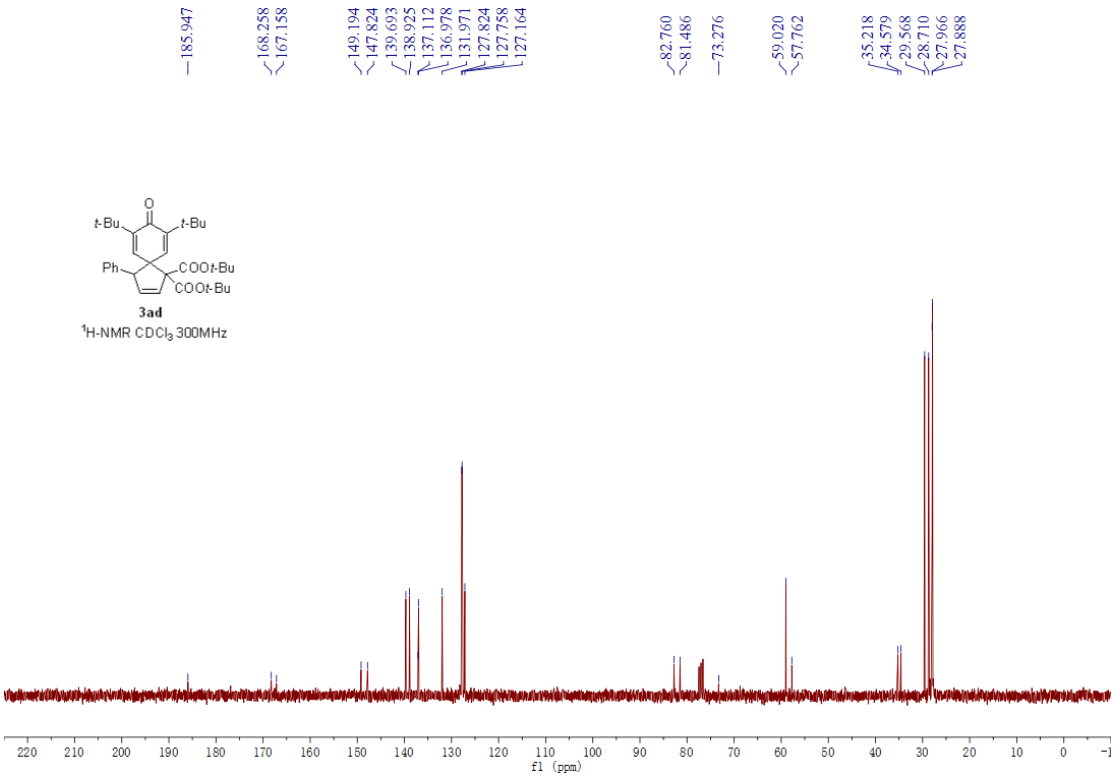
18.46
9.51
f1 (ppm)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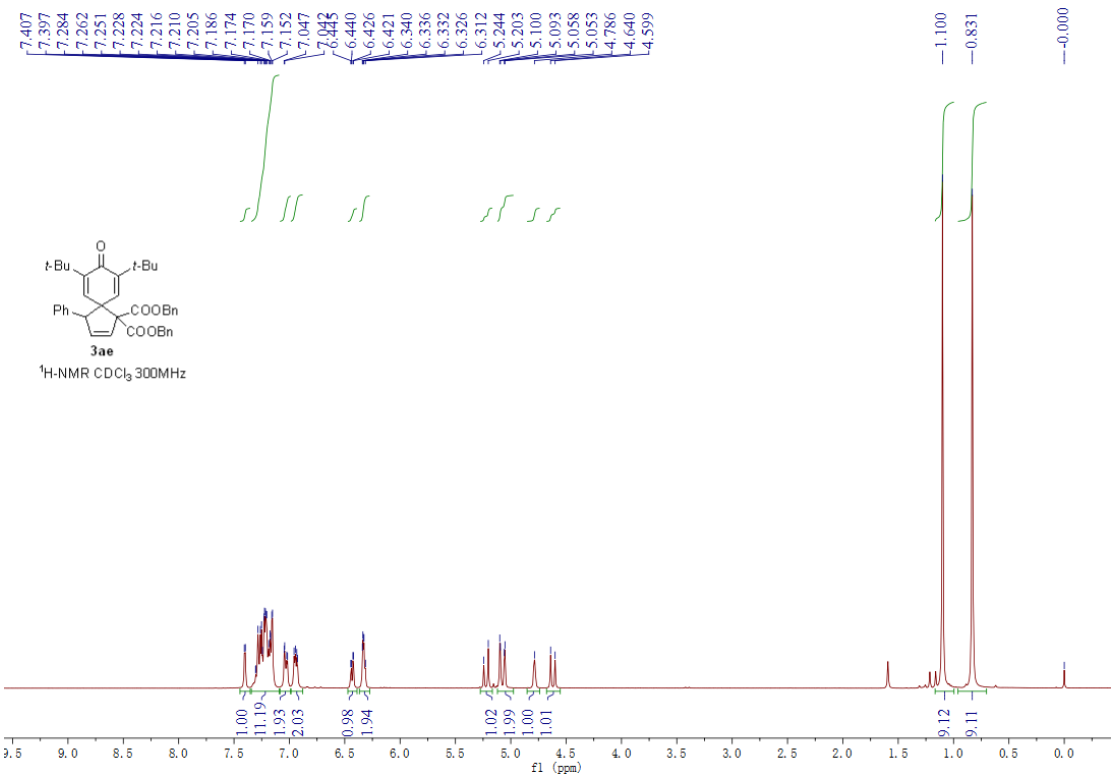
127.758
127.164
82.760
81.486
73.276
59.020
57.762
35.218
34.579
29.568
28.710
27.966
27.888
t-Bu
t-Bu
Ph
COOt-Bu
COOt-Bu
3ad
1H-NMR CDCl3 300MHz
f1 (ppm)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7.186
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7.170
7.159
7.152
7.047
6.440
6.426
6.421
6.340
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6.326
6.312
5.244
5.203
5.100
5.093
5.058
5.053
4.786
4.640
4.599
1.100
0.831
0.000
t-Bu
t-Bu
Ph
COOBn
COOBn
3ae
1H-NMR CDCl3 300MHz
1.00
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0.98
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1.02
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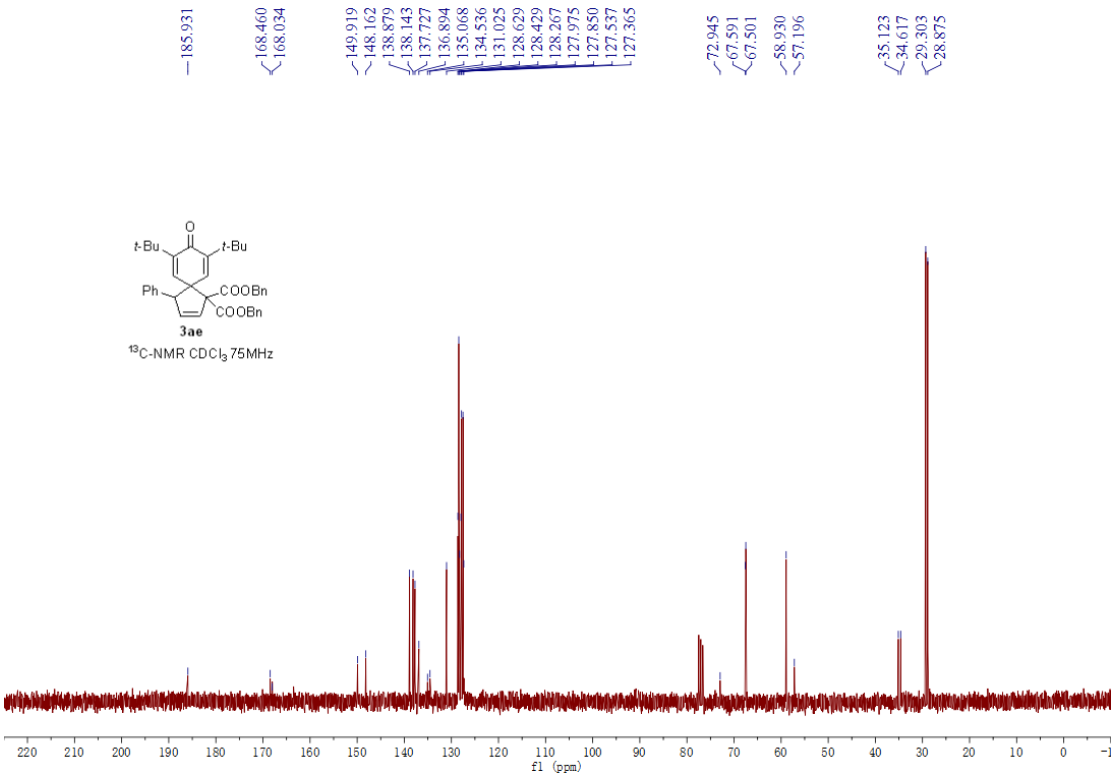
1.00
1.01
9.12
9.11
f1 (ppm)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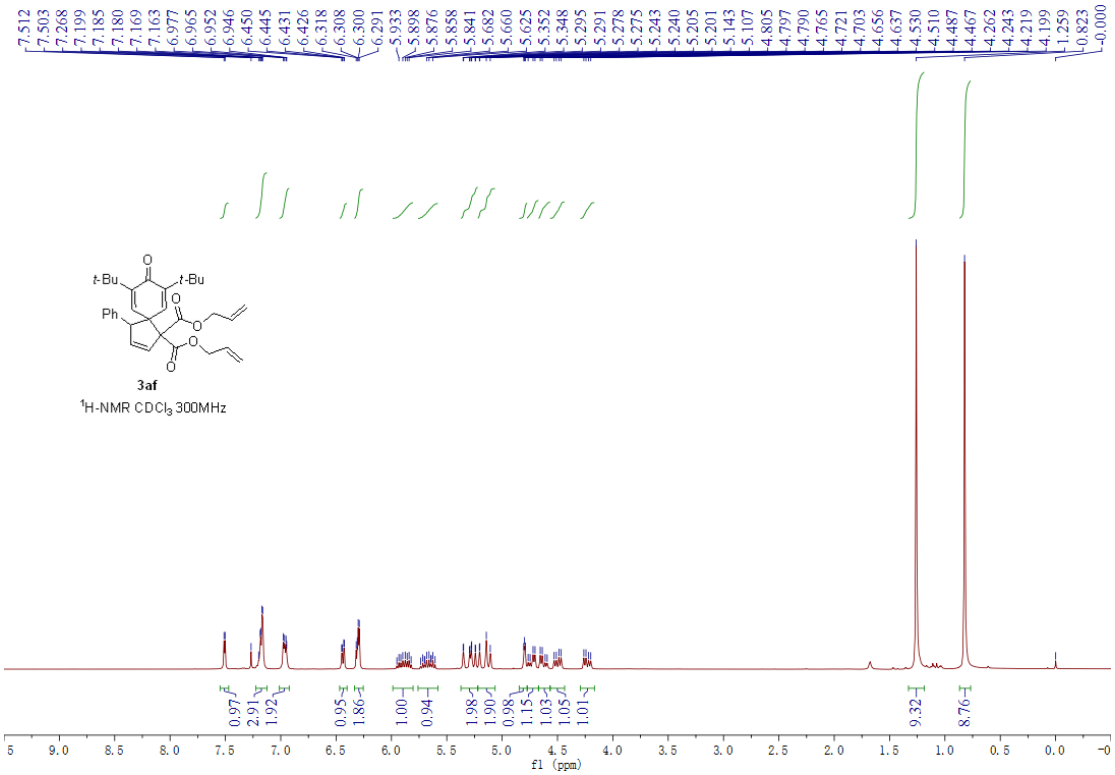
131.025
128.629
128.429
128.267
127.975
127.850
127.537
127.365
72.945
67.591
67.501
58.930
57.196
35.123
34.617
29.303
28.875
t-Bu
t-Bu
Ph
COOBn
COOBn
3ae
13C-NMR CDCl3 75MHz
f1 (ppm)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6.450
6.445
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5.143
5.107
4.805
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4.510
4.487
4.467
4.262
4.243
4.219
4.199
1.259
0.823
0.000
t-Bu
t-Bu
Ph
O
O
O
O
O
3af
1H-NMR CDCl3 300MHz
0.97
2.91
1.92
0.95
1.86
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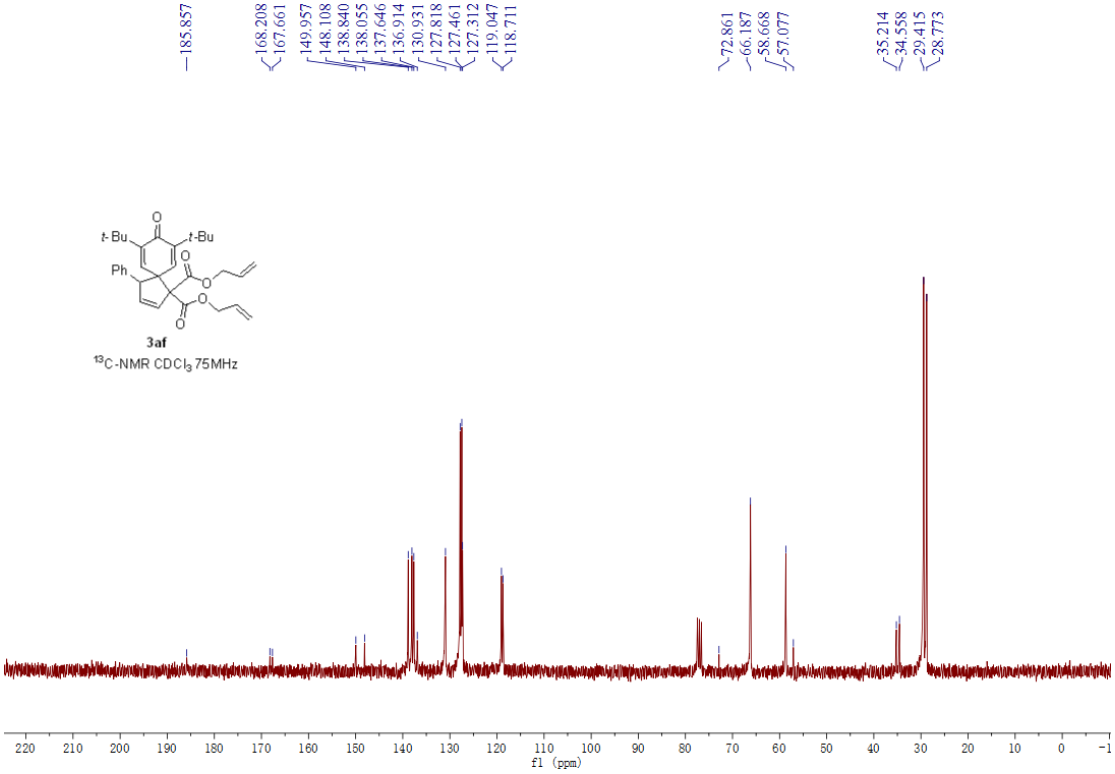
1.90
0.98
1.15
1.03
1.05
1.01
9.32
8.76
f1 (ppm)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127.312
119.047
118.711
72.861
66.187
58.668
57.077
35.214
34.558
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t-Bu
t-Bu
Ph
O
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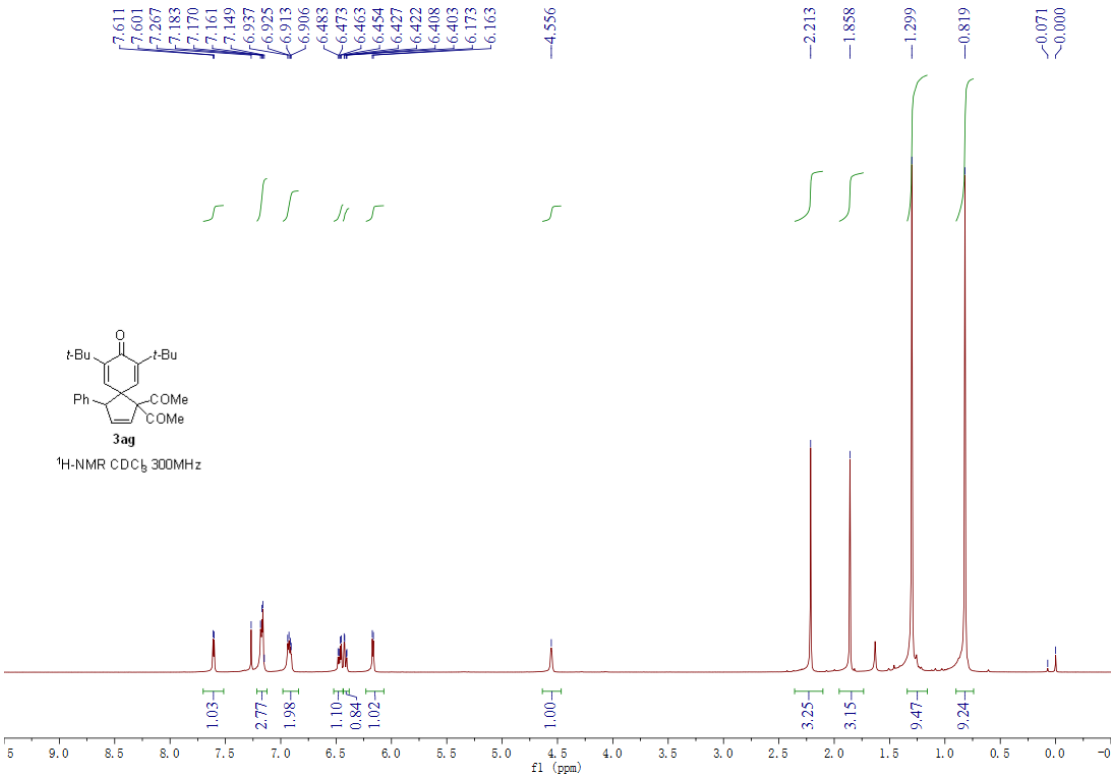
O
O
O
3af
13C-NMR CDCl3 75MHz
f1 (ppm)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7.601
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7.170
7.161
7.149
6.937
6.925
6.913
6.906
6.483
6.473
6.463
6.454
6.427
6.422
6.408
6.403
6.173
6.163
4.556
2.213
1.858
1.299
0.819
0.071
0.000
t-Bu
t-Bu
Ph
COMe
COMe
3ag
1H-NMR CDCl3 300MHz
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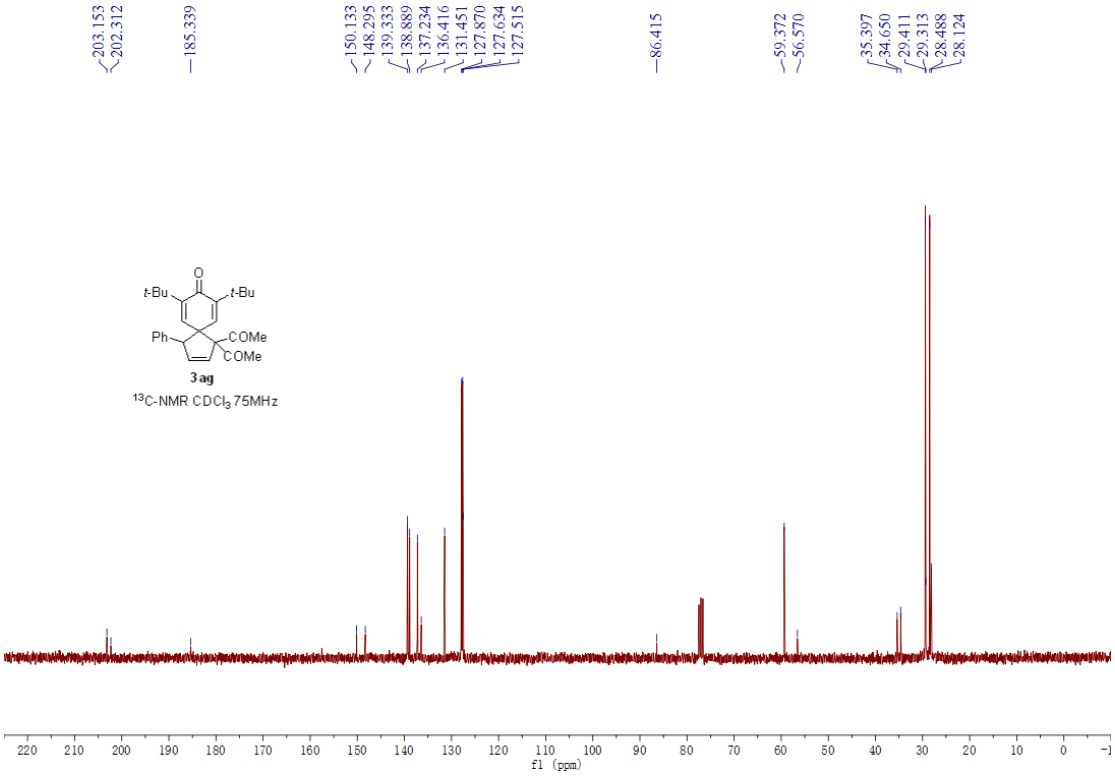
2.77
1.98
1.10
0.84
1.02
1.00
3.25
3.15
9.47
9.24
f1 (ppm)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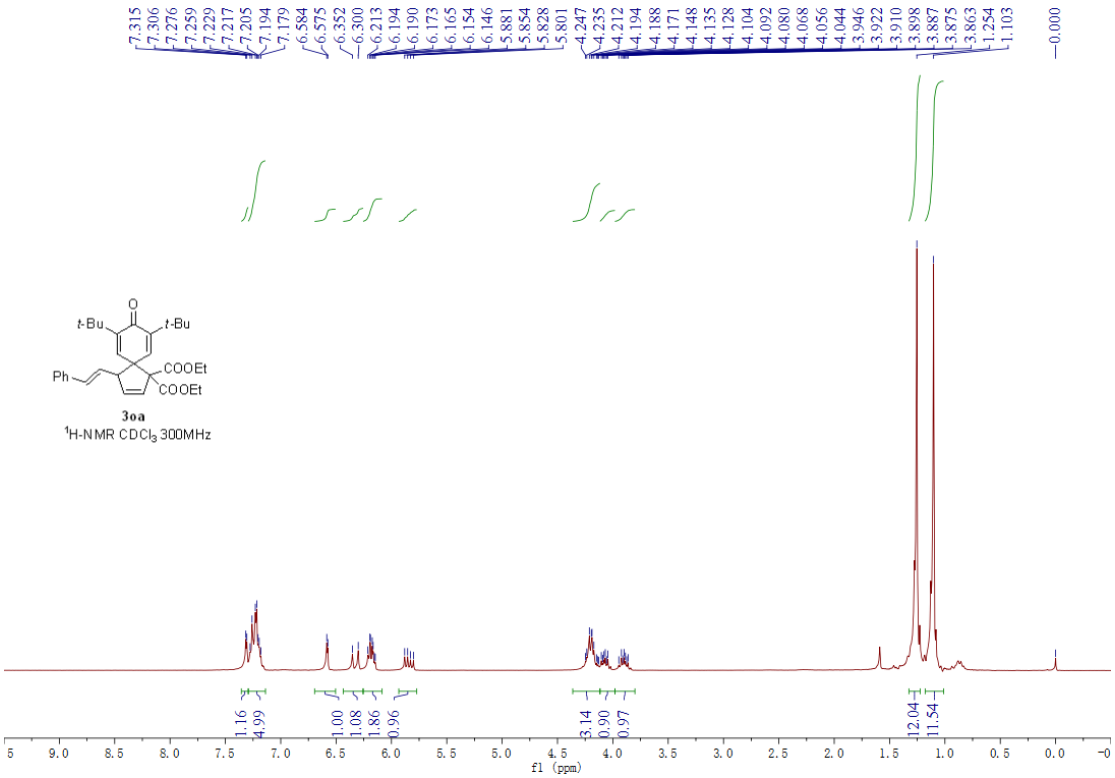
202.312
185.339
150.133
148.295
139.333
138.889
137.234
136.416
131.451
127.870
127.634
127.515
86.415
59.372
56.570
35.397
34.650
29.411
29.313
28.488
28.124
t-Bu
t-Bu
Ph
COMe
COMe
3ag
13C-NMR CDCl3 75MHz
f1 (ppm)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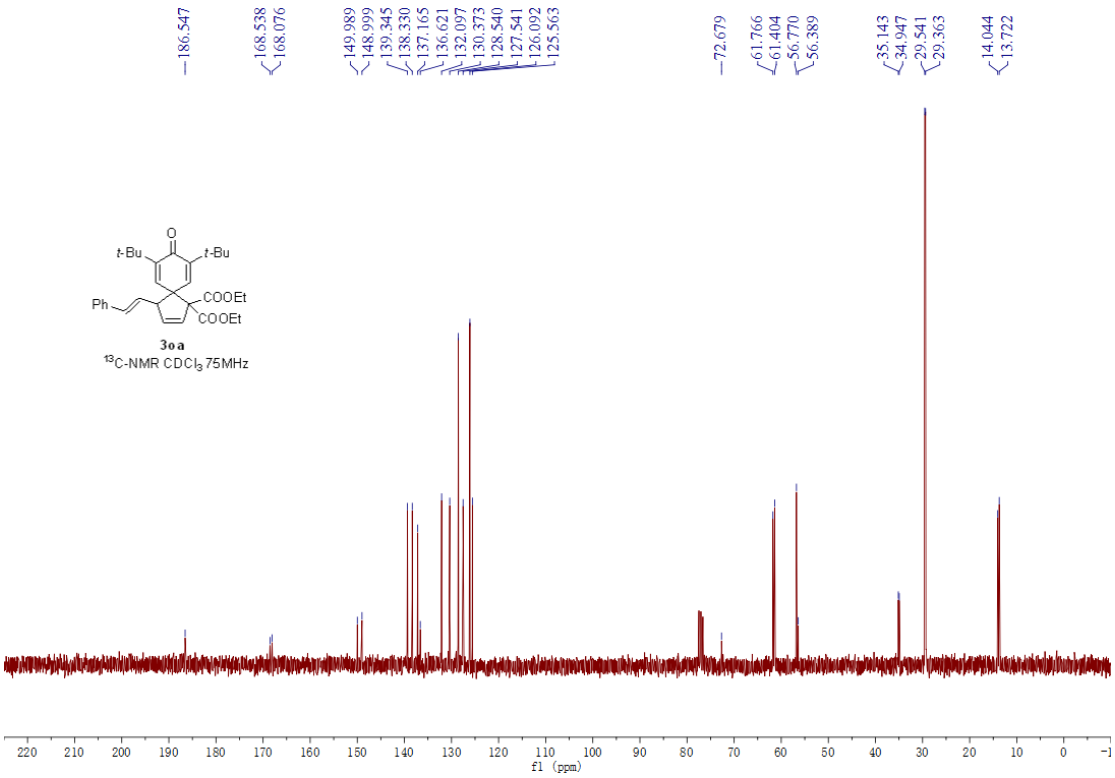
7.306
7.276
7.259
7.229
7.217
7.205
7.194
7.179
6.584
6.575
6.352
6.300
6.213
6.194
6.190
6.173
6.165
6.154
6.146
5.881
5.854
5.828
5.801
4.247
4.235
4.212
4.194
4.188
4.171
4.148
4.135
4.128
4.104
4.092
4.080
4.068
4.056
4.044
3.946
3.922
3.910
3.898
3.887
3.875
3.863
1.254
1.103
0.000
t-Bu
t-Bu
COOEt
COOEt
Ph
3oa
1H-NMR CDCl3 300MHz
1.16
4.99
1.00
1.08
1.86
0.96
3.14
0.90
0.97
12.04
11.54
f1 (ppm)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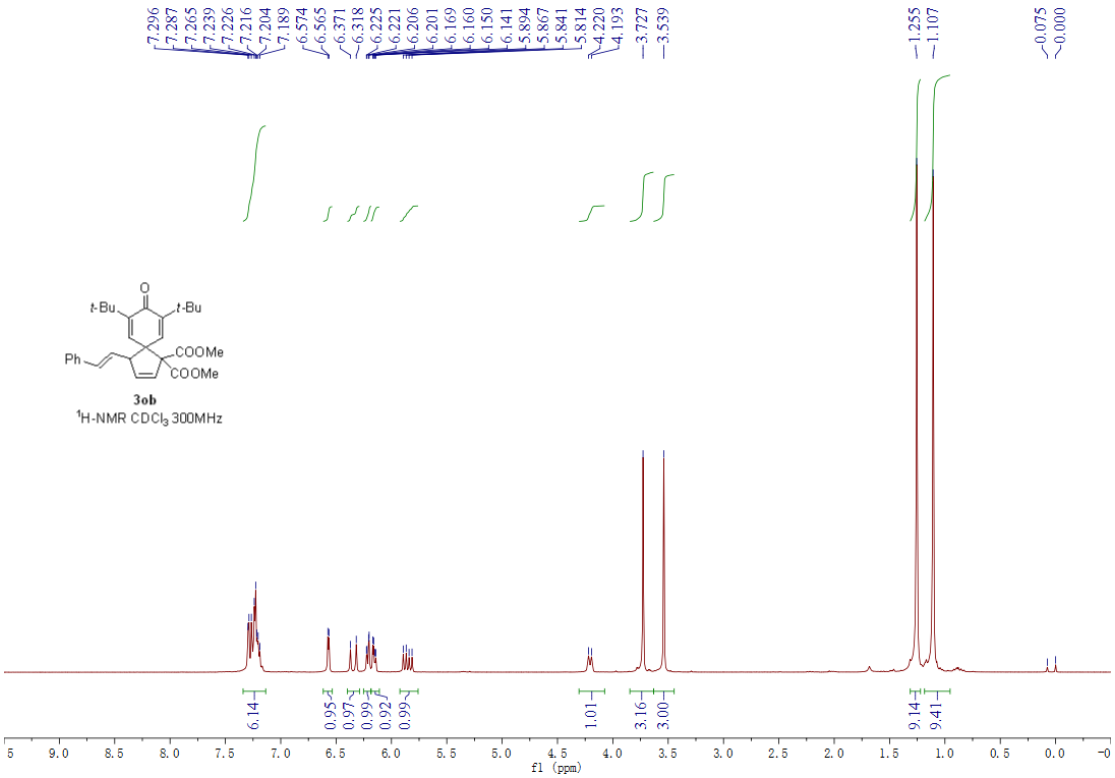
168.076
149.989
148.999
139.345
138.330
137.165
136.621
132.097
130.373
128.540
127.541
126.092
125.563
72.679
61.766
61.404
56.770
56.389
35.143
34.947
29.541
29.363
14.044
13.722
t-Bu
t-Bu
COOEt
COOEt
Ph
3oa
13C-NMR CDCl3 75MHz
f1 (ppm)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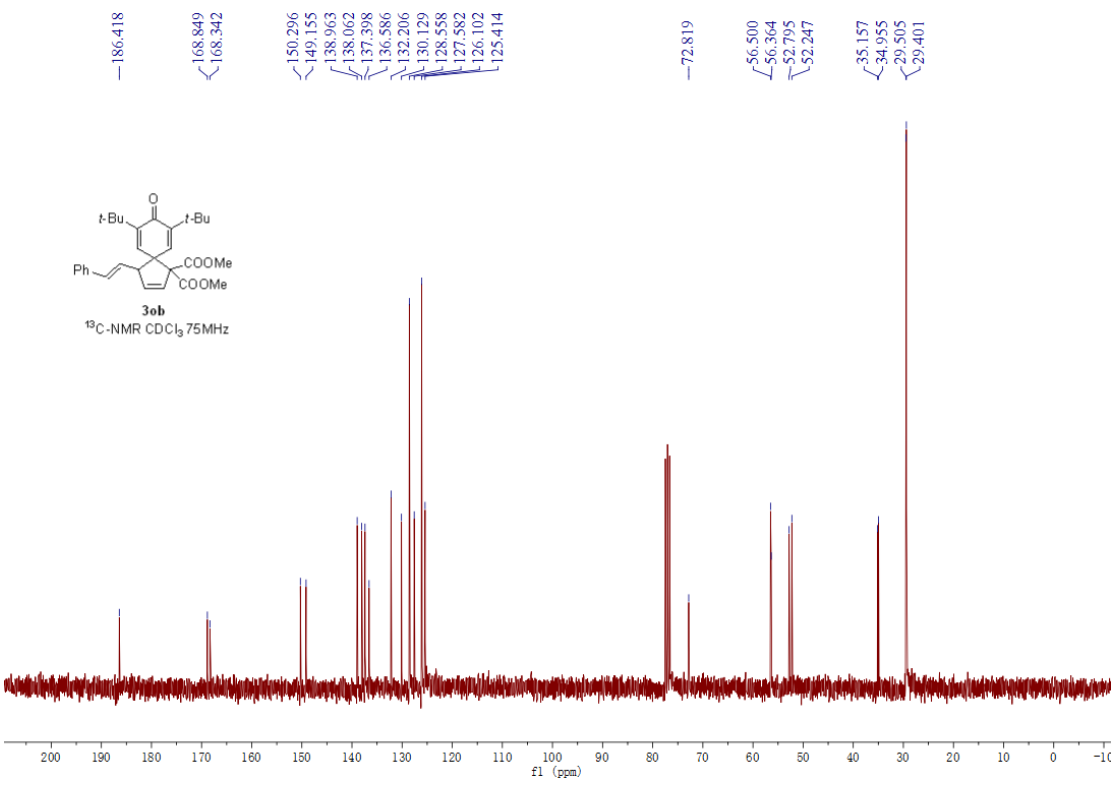
7.287
7.265
7.239
7.226
7.216
7.204
7.189
6.574
6.565
6.371
6.318
6.225
6.221
6.206
6.201
6.169
6.160
6.150
6.141
5.894
5.867
5.841
5.814
4.220
4.193
3.727
3.539
1.255
1.107
0.075
0.000
t-Bu
t-Bu
Ph
COOMe
COOMe
3ob
1H-NMR CDCl3 300MHz
6.14
0.95
0.97
0.99
0.92
0.99
1.01
3.16
3.00
9.14
9.41
f1 (ppm)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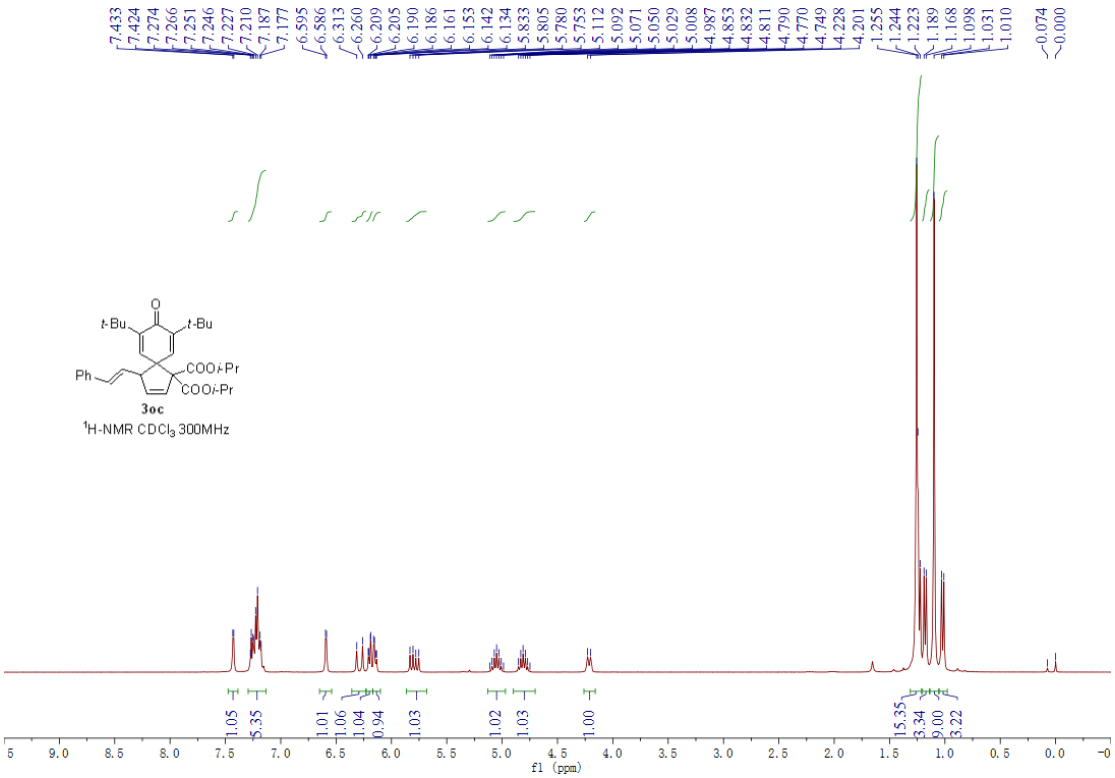
168.342
150.296
149.155
138.963
138.062
137.398
136.586
132.206
130.129
128.558
127.582
126.102
125.414
72.819
56.500
56.364
52.795
52.247
35.157
34.955
29.505
29.401
t-Bu
t-Bu
Ph
COOMe
COOMe
3ob
13C-NMR CDCl3 75MHz
f1 (ppm)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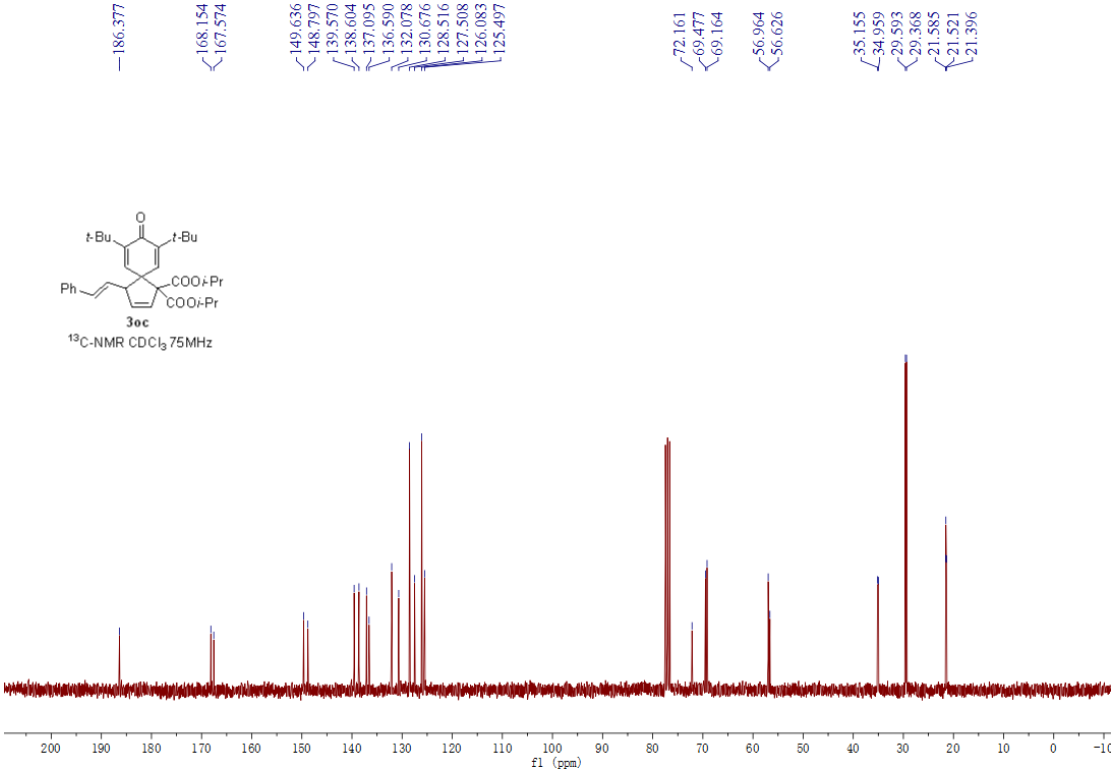
7.424
7.274
7.266
7.251
7.246
7.227
7.210
7.187
7.177
6.595
6.586
6.313
6.260
6.209
6.205
6.190
6.186
6.161
6.153
6.142
6.134
5.833
5.805
5.780
5.753
5.112
5.092
5.071
5.050
5.029
5.008
4.987
4.853
4.832
4.811
4.790
4.770
4.749
4.228
4.201
1.255
1.244
1.223
1.189
1.168
1.098
1.031
1.010
0.074
0.000
t-Bu
t-Bu
Ph
COOi-Pr
COOi-Pr
3oc
1H-NMR CDCl3 300MHz
1.05
5.35
1.01
1.06
1.04
0.94
1.03
1.02
1.03
1.00
15.35
3.34
9.00
3.22
f1 (ppm)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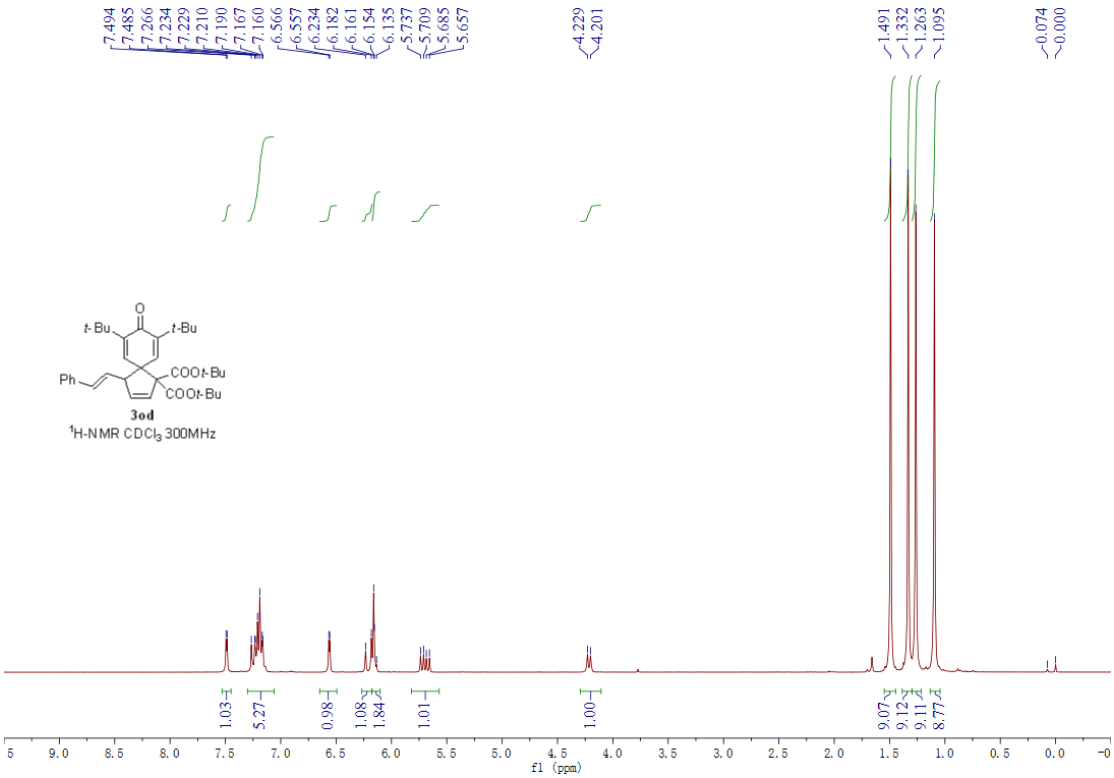
167.574
149.636
148.797
139.570
138.604
137.095
136.590
132.078
130.676
128.516
127.508
126.083
125.497
72.161
69.477
69.164
56.964
56.626
35.155
34.959
29.593
29.368
21.585
21.521
21.396
t-Bu
t-Bu
Ph
COOi-Pr
COOi-Pr
3oc
13C-NMR CDCl3 75MHz
f1 (ppm)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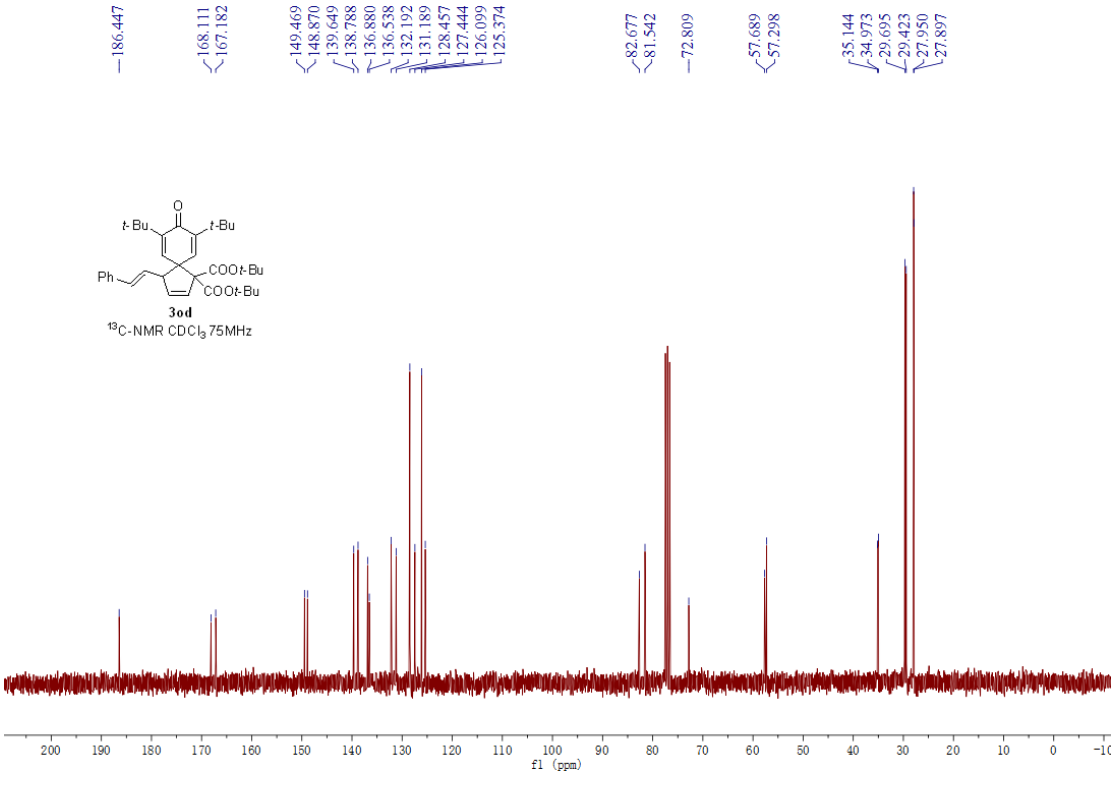
7.485
7.266
7.234
7.229
7.210
7.190
7.167
7.160
6.566
6.557
6.234
6.182
6.161
6.154
6.135
5.737
5.709
5.685
5.657
4.229
4.201
1.491
1.332
1.263
1.095
0.074
0.000
t-Bu
t-Bu
Ph
COOt-Bu
COOt-Bu
3od
1H-NMR CDCl3 300MHz
1.03
5.27
0.98
1.08
1.84
1.01
1.00
9.07
9.12
9.11
8.77
f1 (ppm)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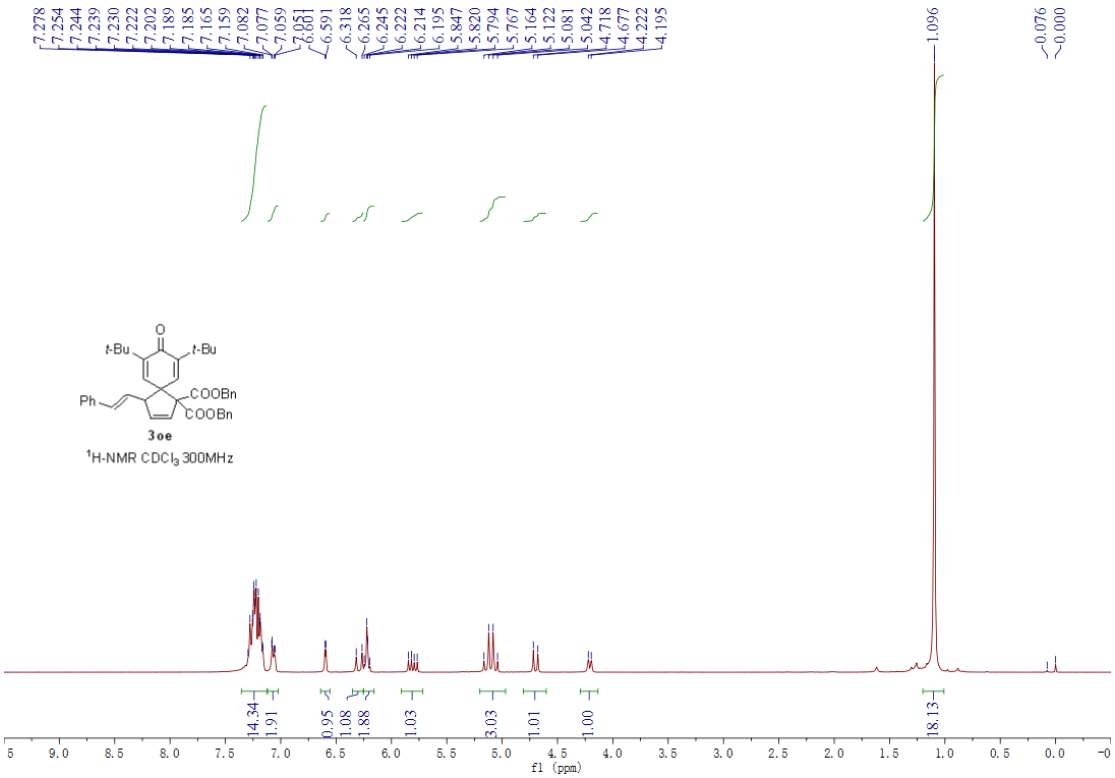
168.111
167.182
149.469
148.870
139.649
138.788
136.880
136.538
132.192
131.189
128.457
127.444
126.099
125.374
82.677
81.542
72.809
57.689
57.298
35.144
34.973
29.695
29.423
27.950
27.897
t-Bu
t-Bu
Ph
COOt-Bu
COOt-Bu
3od
13C-NMR CDCl3 75MHz
f1 (ppm)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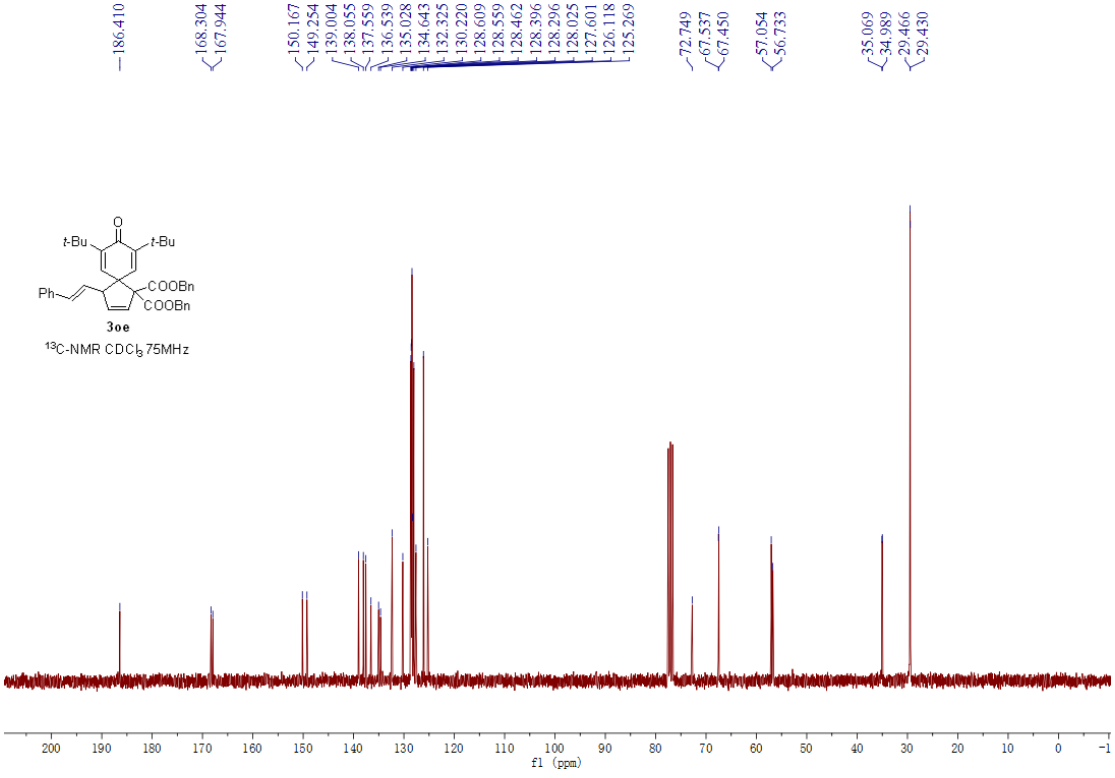
7.254
7.244
7.239
7.230
7.222
7.202
7.189
7.185
7.165
7.159
7.082
7.077
7.059
6.591
6.318
6.265
6.245
6.222
6.214
6.195
5.847
5.820
5.794
5.767
5.164
5.122
5.081
5.042
4.718
4.677
4.222
4.195
1.096
0.076
0.000
t-Bu
t-Bu
Ph
COOBn
COOBn
3oe
1H-NMR CDCl3 300MHz
14.34
1.91
0.95
1.08
1.88
1.03
3.03
1.01
1.00
18.13
f1 (ppm)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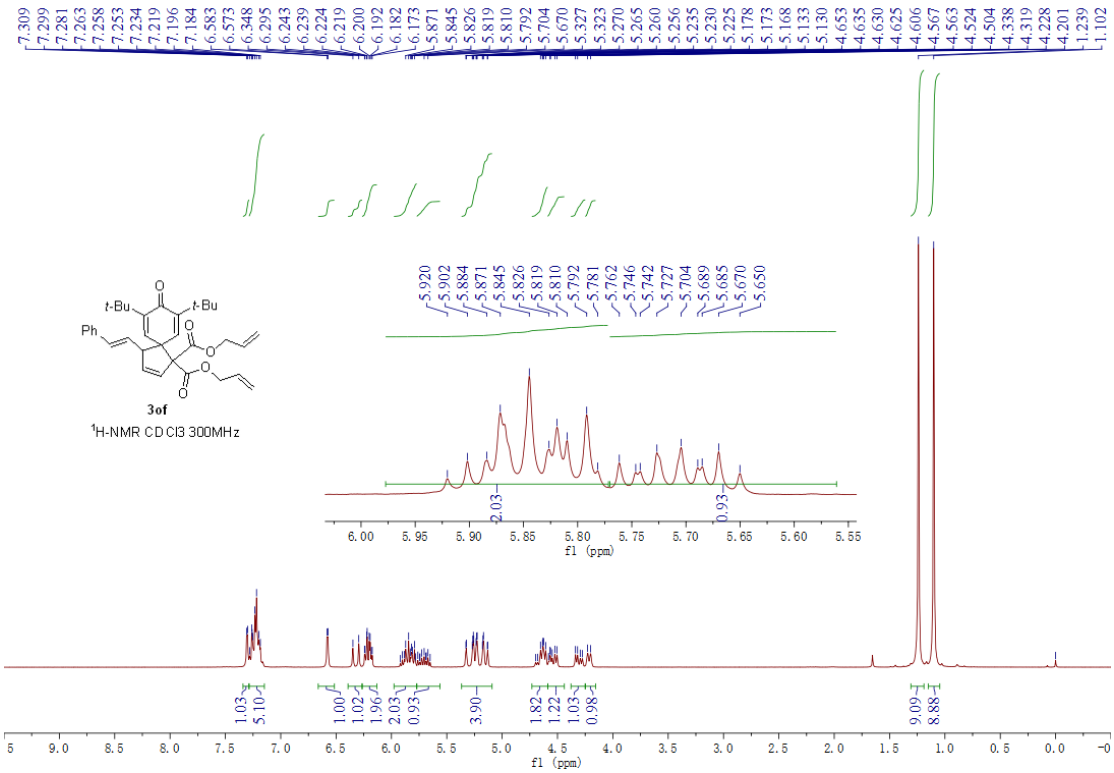
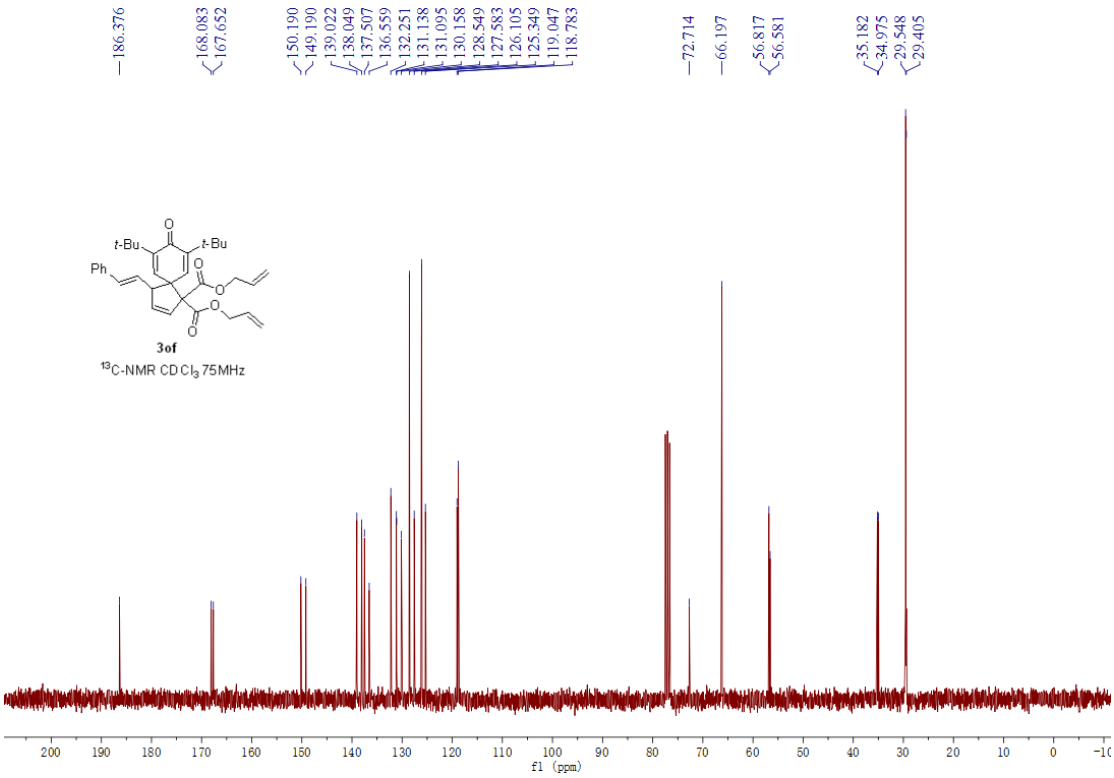
167.944
150.167
149.254
139.004
138.055
137.559
136.539
135.028
134.643
132.325
130.220
128.609
128.559
128.462
128.396
128.296
128.025
127.601
126.118
125.269
72.749
67.537
67.450
57.054
56.733
35.069
34.989
29.466
29.430
t-Bu
t-Bu
Ph
COOBn
COOBn
3oe
13C-NMR CDCl3 75MHz
f1 (ppm)


3of
1H-NMR CDCl3 300MHz
f1 (ppm)


3of
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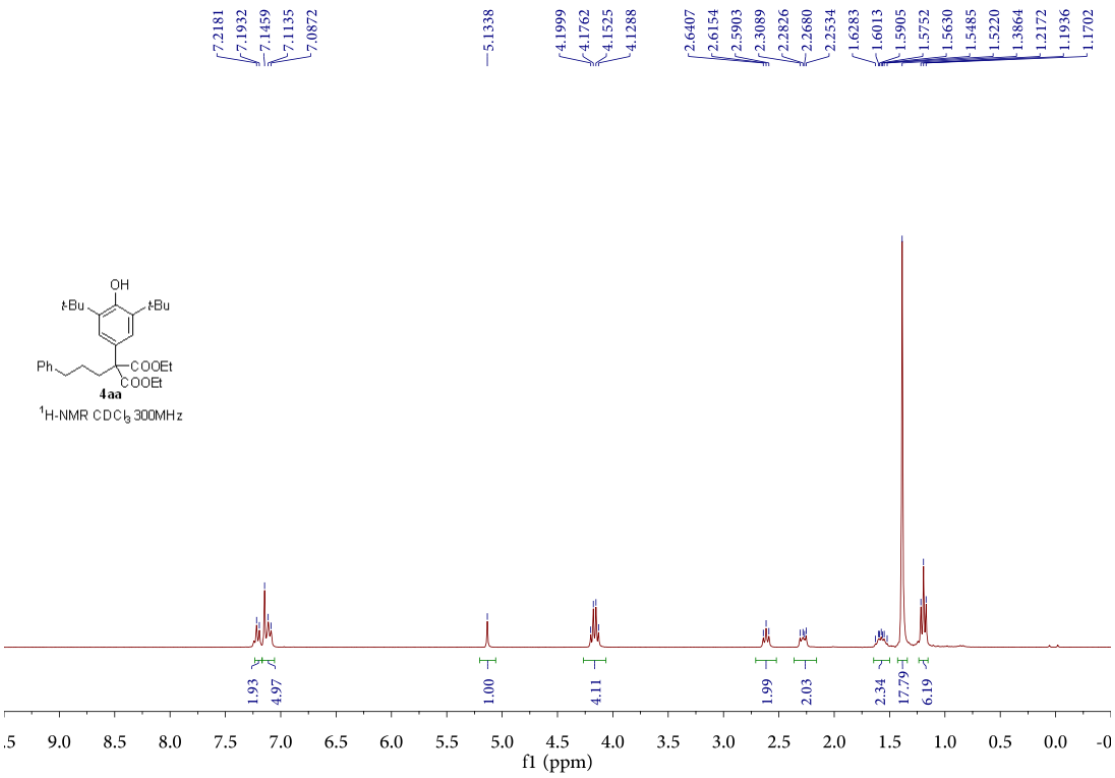
f1 (ppm)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7.1135
7.0872
5.1338
4.1999
4.1762
4.1525
4.1288
2.6407
2.6154
2.5903
2.3089
2.2826
2.2680
2.2534
1.6283
1.6013
1.5905
1.5752
1.5630
1.5485
1.5220
1.3864
1.2172
1.1936
1.1702
OH
t-Bu
t-Bu
Ph
COOEt
COOEt
4aa
1H-NMR CDCl3 300MHz
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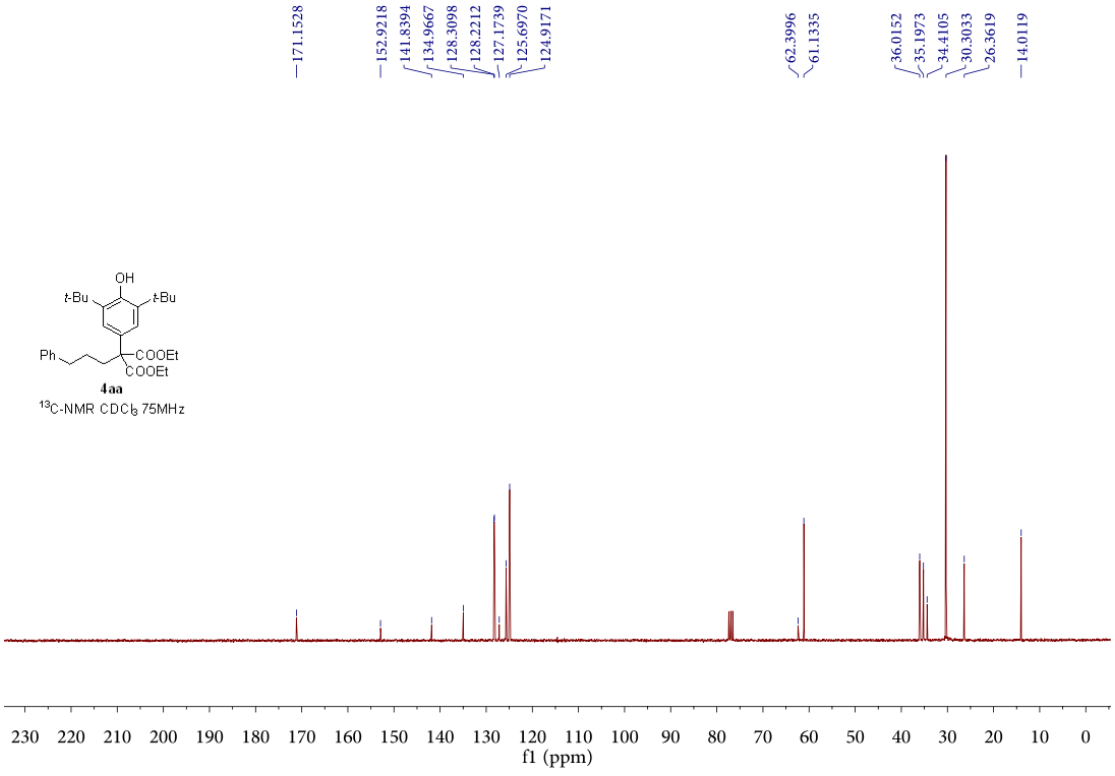
4.97
1.00
4.11
1.99
2.03
2.34
17.79
6.19
f1 (ppm)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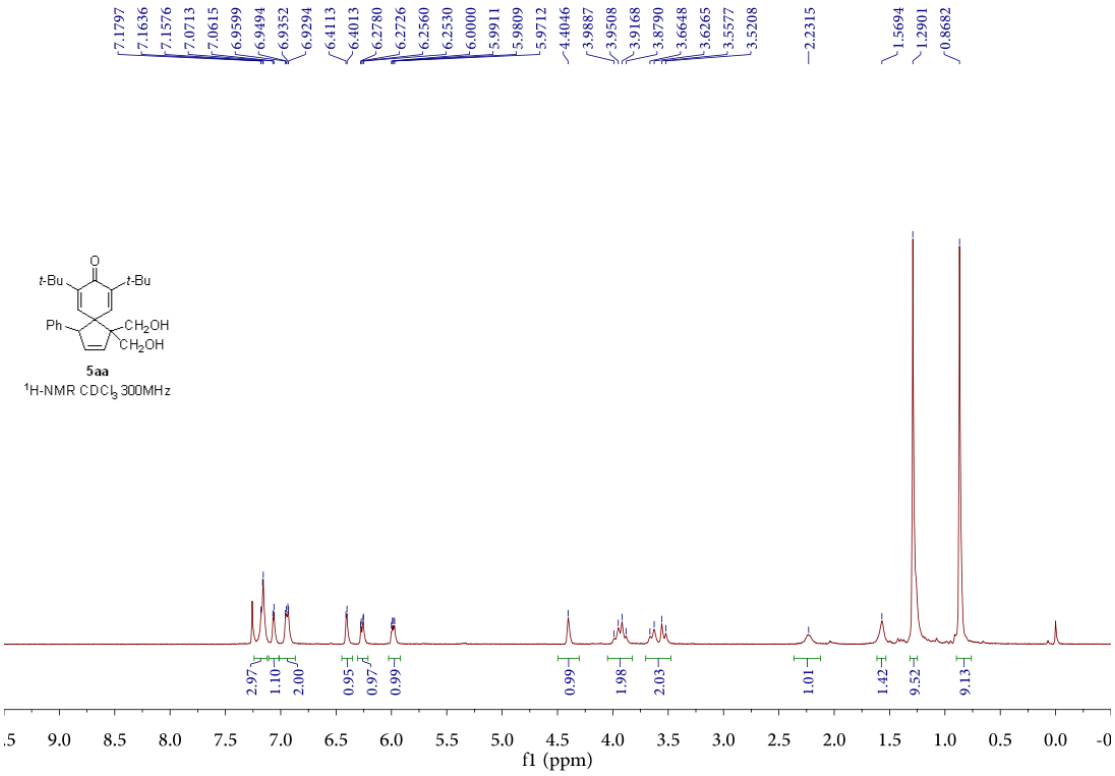
127.1739
125.6970
124.9171
62.3996
61.1335
36.0152
35.1973
34.4105
30.3033
26.3619
14.0119
OH
t-Bu
t-Bu
Ph
COOEt
COOEt
4aa
13C-NMR CDCl3 75MHz
f1 (ppm)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7.0615
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6.9494
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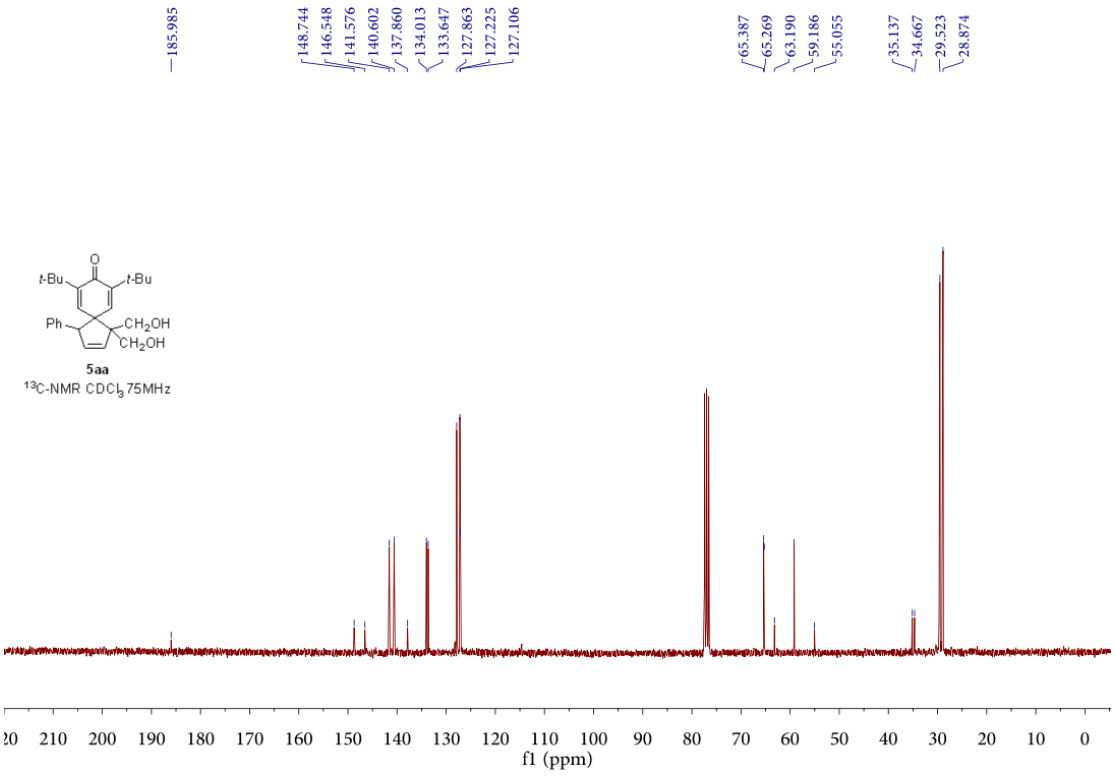
6.9294
6.4113
6.4013
6.2780
6.2726
6.2560
6.2530
6.0000
5.9911
5.9809
5.9712
4.4046
3.9887
3.9508
3.9168
3.8790
3.6648
3.6265
3.5577
3.5208
2.2315
1.5694
1.2901
0.8682
t-Bu
t-Bu
Ph
CH2OH
CH2OH
5aa
1H-NMR CDCl3 300MHz
2.97
1.10
2.00
0.95
0.97
0.99
0.99
1.98
2.03
1.01
1.42
9.52
9.13
f1 (ppm)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146.548
141.576
140.602
137.860
134.013
133.647
127.863
127.225
127.106
65.387
65.269
63.190
59.186
55.055
35.137
34.667
29.523
28.874
t-Bu
t-Bu
Ph
CH2OH
CH2OH
5aa
13C-NMR CDCl3 75MHz
f1 (ppm)