A Cooperative Photo-/Lewis Acids-catalysed Tandem Intramolecular [3+2] Cross-Cycloadditions of Cyclopropane 1,1-diesters with α,β-Unsaturated Carbonyls for Medium-sized Carbocycles

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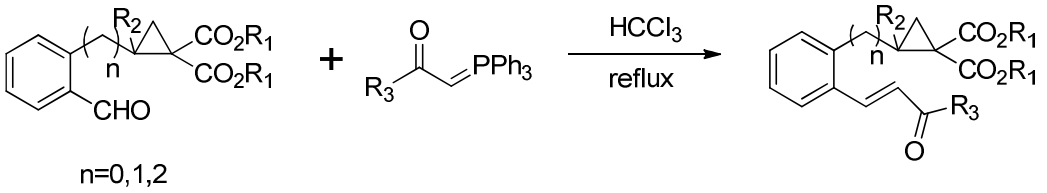
Generational Information:

The ^{1}H NMR and ^{13}C NMR spectra were recorded with Bruker 400 MHz spectrometer instruments in $CDCl_3$. The chemical shifts (δ) were measured in ppm and with the solvents as references (For $CDCl_3$, ^{1}H: δ= 7.26 ppm, ^{13}C δ = 77.16 ppm). The multiplicities of the signals are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. All solvents were obtained from commercial sources and were purified according to standard procedures. Purification of products was accomplished by flash chromatography using silica gel (200~300 or 300~400 mesh or neutral Al_2O_3). Thin layer chromatography (TLC) was performed on Merck silica gel GF254 plates and visualized by UV-light (254+365 nm). Melting points were obtained on a Yanaco-241 apparatus and are uncorrected. IR spectra were recorded on a MAGNA-560 spectrometer made by Nicolet Company. HRMS were recorded on VG ZAB-HS mass spectrometer with ESI resource. IBX (*o*-Iodoxybenzoic acid); THF (Tetrahydrofuran); Et_3N (Triethylamine); DMF (*N,N*-Dimethylformamide); DMSO (Dimethylsulfoxide); DCM (Dichloromethane); DCE (1,2-Dichloroethane).

Preparation of Starting Materials

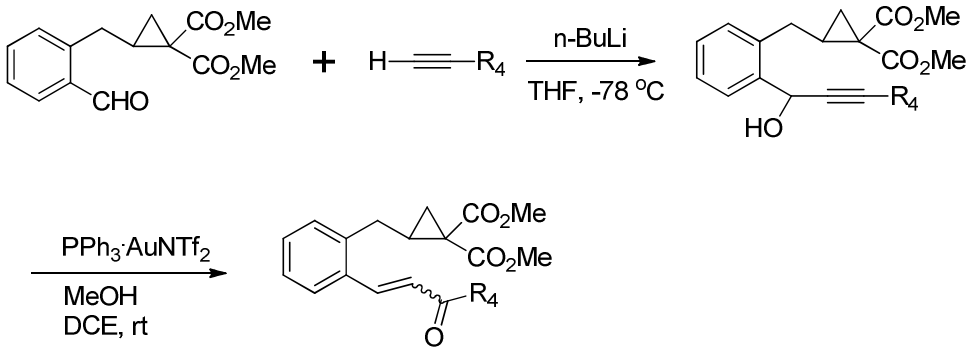
General procedure for the synthesis of substrates 1a, 1e, 1g, 1i, 1j, 1k, 1l (GP1)



n=0,1,2

The aldehyde (1.0 equiv., 1.0 mmol) and the wittig reagent (2.0 equiv., 2.0 mmol) were added to a 50 mL round-bottom flask and 15 mL $CHCl_3$ was added at room temperature. Then the mixture was warmed to reflux for 24 h. The mixture was concentrated under reduced pressure. Then the residue was purified by flash chromatography.

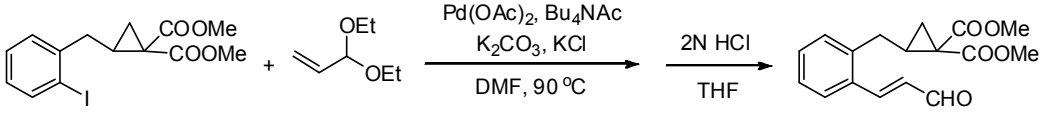
General procedure for the synthesis of substrates 1b, 1c, 1d (GP2)[1]



The alkyne (1.2 equiv., 2.4 mmol) and 4 mL THF were added to a 15 mL schlenk and the mixture was cooled to -78 °C, then n-BuLi (1.5 equiv., 3 mmol) was dropped to the mixture and reacted for 1 h. Next, the substrate (1 equiv., 2 mmol) was added to the Schlenk and made the mixture at -60 °C for another 3.5 h. Then added the water to quench the reaction. The whole mixture was extracted with ethyl ether (10 mL×3) and the extract was washed with water (10 mL×2) and brine (10 mL×1), and then dried over $MgSO_4$. The filtrate was concentrated under reduced pressure followed by purification by column chromatography over silica gel.

To a stirred solution of the alkynol product (1.0 equiv., 0.2 mmol) in DCE (1 mL) was added MeOH (1.0 equiv., 0.2 mmol) and the PPh_3·$AuNTf_2$ catalyst (0.02 equiv., 0.004 mmol) under argon atmosphere at room temperature and the mixture reacted at room temperature for 5 h. After stirring for 5 h, the mixture was separated by the pre-TLC.

General procedure for the synthesis of substrate 1h (GP3)[2]

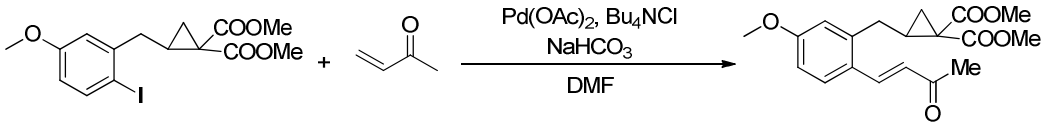


At the argon atmosphere, the substrate cycloprapane 1,1-diesters (1.0 equiv., 1.6 mmol), acrolein acetal (3.0 equiv., 4.8 mmol), $Bu_4N^+AcO^-$ (3.0 equiv., 4.8 mmol), K_2CO_3 (1.5 equiv., 2.4 mmol), KCl (1.0 equiv., 1.6 mmol) were added to 2 mL DMF, then $Pd(OAc)_2$ (0.05 equiv., 0.08 mmol) was added. The mixture was warmed to 90 °C for 4 h.

After cooled to the room temperature, water was added to quench the reaction. The mixture was extracted with ethyl ether (10 mL×3). The combined organic phase

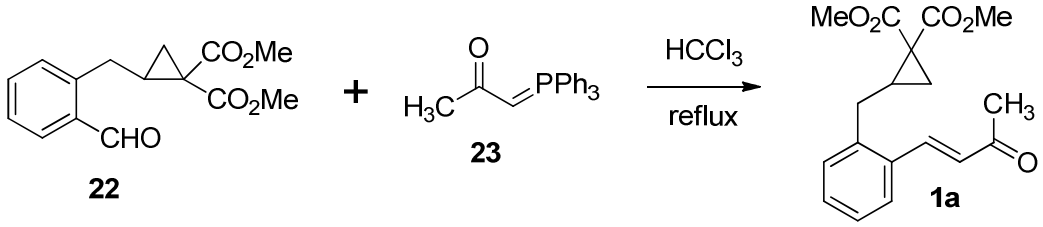
was concentrated and 7 mL THF and 7 mL 2N HCl (aq) were added. The mixture reacted at room temperature for 12 h, then was concentrated under reduced pressure and next extracted with ethyl ether (10 mL×3), then dried over $MgSO_4$. The filtrate was concentrated under reduced pressure followed by purification by column chromatography over silica gel.

General procedure for the synthesis of substrate 1f (GP4)[3]



At the argon atmosphere, the substrate cycloprapane 1,1-diesters (1.0 equiv., 0.5 mmol), methyl vinyl ketone (3.0 equiv., 1.5 mmol), $Bu_4N^+AcO^-$ (2.0 equiv., 1.0 mmol)，$NaHCO_3$ (2.5 equiv., 1.25 mmol) were added to 2 mL DMF, then $Pd(OAc)_2$ (0.1 equiv., 0.05 mmol) was added. The mixture was warmed to 70 ^oC for 24 h. After cooled to the room temperature, water was added to quench the reaction. The mixture was extracted with ethyl ether (10 mL×3) and the extract was washed with water (10 mL×2) and brine (10 mL×1), and then dried over $MgSO_4$. The filtrate was concentrated under reduced pressure followed by purification by column chromatography over silica gel.

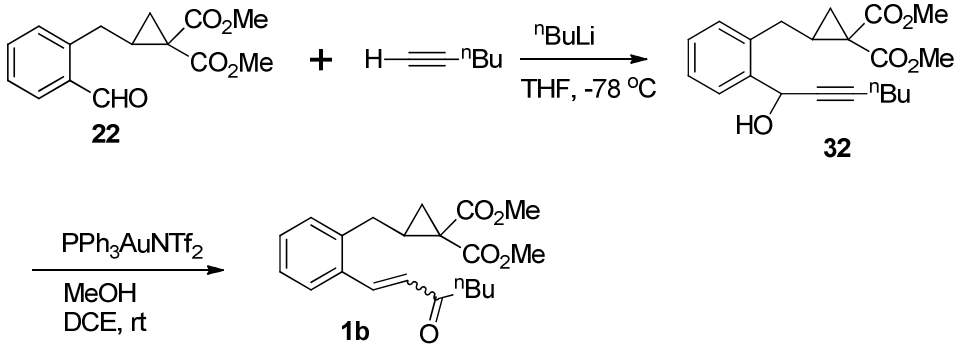
(E)-dimethyl 2-(2-(3-oxobut-1-en-1-yl)benzyl)cyclopropane-1,1-dicarboxylate(1a)



The aldehyde **22**[4] (260 mg, 1 equiv.) was reacted with Wittig reagent **23** (637 mg, 2 equiv.) according to **GP1**. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) yielded **1a** as a yellow oil (0.81 mmol, 255 mg, 85%); ^1H NMR (400 MHz, $CDCl_3$): δ= 7.81 (d, *J* = 16.0 Hz, 1H), 7.59 (m, 1H), 7.40-7.32 (m, 1H), 7.27 (m, 2H), 6.65 (d, *J* = 16.0 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.04 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.66 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.41 (s, 3H), 2.22-2.12 (m, 1H), 1.65-1.57 (m, 1H), 1.48 (dd, *J* = 9.0, 4.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 198.35, 170.40, 168.66, 140.39, 139.39, 133.31, 130.58, 129.74, 129.05, 127.31, 126.90, 52.90, 52.82,

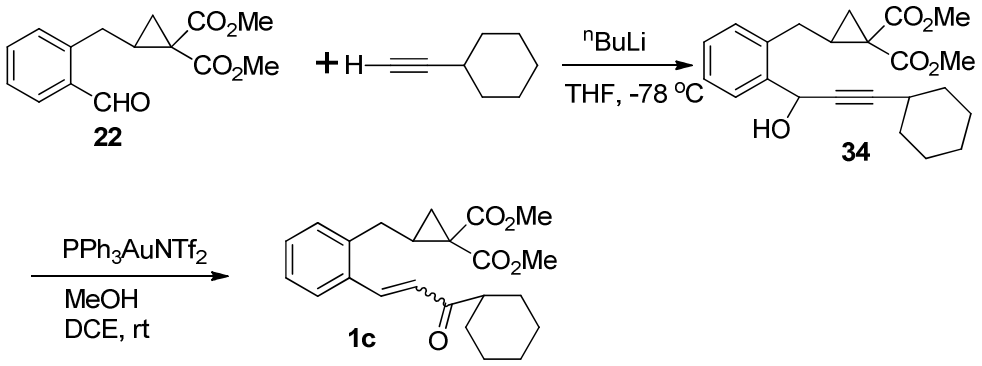
34.43, 31.37, 28.54, 27.98, 21.50; IR (KBr): v = 3276, 2954, 1727, 1671, 1437, 757 cm^{-1}; HRMS (ESI) Calcd. for: $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384; Found: 317.1388.

Dimethyl 2-(2-(3-oxohept-1-en-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1b)



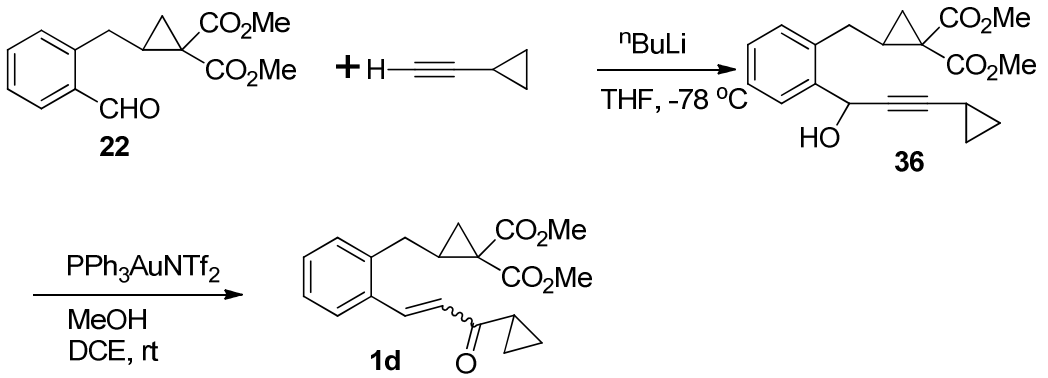
The aldehyde **22** (553 mg, 2 mmol, 1.0 equiv.) reacted with hexyne (197 mg, 2.4 mmol, 1.2 equiv.) to give the intermediate **32** (1.67 mmol, 600 mg, 83.7%) as a yellow oil (Petroleum/ ethyl acetate = 10/1 then 3/1), **1b** was prepared from **32** according to GP**2.** Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) as a yellow oil (0.18 mmol, 63 mg, 88%), Z:E = 1.6:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.84 (d, J = 15.9 Hz, 0.37H), 7.59 (d, J = 7.7 Hz, 0.38H), 7.37 -7.16 (m, 4H), 7.07 (d, J = 12.3 Hz, 0.63H), 6.67 (d, J = 15.9 Hz, 0.37H), 6.25 (d, J = 12.3 Hz, 0.6H), 3.78- 3.70 (m, 6H), 3.04-2.90 (m, 1H), 2.71 -2.48 (m, 2H), 2.30 - 2.22 (m, 1.5H), 1.72- 1.55 (m, 2H), 1.51 -1.34 (m, 3H), 1.17 (m, 1.4H), 0.95 (t, J = 7.3 Hz, 1.2H), 0.79 (t, J = 7.3 Hz, 1.8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.48, 200.56, 170.50, 170.40, 168.63, 168.60, 139.44, 139.29, 138.76, 137.40, 135.35, 133.51, 130.92, 130.40, 129.67, 129.52, 129.01, 128.79, 128.16, 127.21, 126.81, 126.54, 52.83, 52.81, 52.75, 52.69, 42.82, 41.11, 34.40, 34.21, 32.04, 31.43, 28.52, 28.07, 26.58, 26.18, 22.57, 22.28, 21.63, 21.49, 14.02, 13.85; IR (KBr): v = 3300, 2986, 1752, 1375, 1243, 1049 cm^{-1}; HRMS (ESI) Calcd. for: $C_{21}H_{26}O_5$ $[M+H]^+$: 359.1853; Found: 359.1860.

Dimethyl2-(2-(3-cyclohexyl-3-oxoprop-1-en-1-yl)benzyl)cyclopropane-1,1-dicarb oxylate (1c)



The aldehyde **22** (7.0 mmol, 1.93 g, 1.0 equiv.) reacted with cyclohexyl alkyne (9.24 mmol, 1.3 equiv., 1.0 g) to give the intermediate **34** (5.76 mmol, 2.21 g, 82.1%) as a colorless oil (Petroleum/ ethyl acetate = 10/1 then 3/1), **1c** was prepared from **34** according to GP2. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) as a yellow oil (0.15 mmol, 57 mg, 79%), E:Z = 2:1; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 15.7 Hz, 0.66H), 7.53 (d, *J* = 7.5 Hz, 0.66H), 7.31-7.09 (m, 4.3H), 6.98 (d, *J* = 12.3 Hz, 0.36H), 6.68 (d, *J* = 15.7 Hz, 0.66H), 6.23 (d, *J* = 12.3 Hz, 0.33H), 3.72 - 3.62 (m, 6H), 2.91 (m, 1H), 2.57 (m, 1H), 2.35- 2.03 (m, 2H), 1.81 (dd, *J* = 32.1, 12.5 Hz, 3H), 1.72 - 1.58 (m, 2H), 1.58 - 1.48 (m, 2H), 1.40 - 1.10 (m, 5H), 1.02 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 203.03, 170.46, 168.60, 139.54, 139.28, 133.68, 130.35, 129.68, 127.16, 126.80, 126.64, 52.86, 52.79, 49.81, 34.39, 31.53, 28.81, 28.78, 28.56, 26.04, 25.87, 21.55; IR (KBr): *v* = 2933, 1734, 1439, 1244, 550 cm^{-1}; HRMS (ESI) Calcd. for: $C_{23}H_{29}O_5$ $[M+H]^+$: 385.2010; Found: 385.2016.

Dimethyl2-(2-(3-cyclopropyl-3-oxoprop-1-en-1-yl)benzyl)cyclopropane-1,1-dicar boxylate(1d)

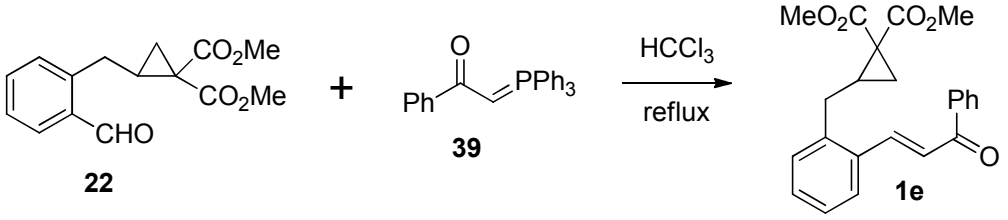


The aldehyde **22** (2 mmol, 553mg, 1 equiv.) reacted with cyclopropyl acetylene (2.4 mmol, 160 mg) to give the intermediate **36** (1.26 mmol, 430 mg, 63%) as a

colorless oil (Petroleum/ ethyl acetate = 10/1 then 3/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.67 (d, *J* = 6.5 Hz, 1H), 7.38- 7.20 (m, 3H), 5.59 (d, J = 5.2 Hz, 1H), 3.82 -3.69 (m, 6H), 3.09 (m, 1H), 2.65 (m, 1H), 2.40 - 2.11 (m, 2H), 1.72-1.62 (m, 1H), 1.53 (m 1H), 1.38-1.22 (m, 1H), 0.85-0.77 (m, 2H), 0.76 - 0.68 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 170.97, 169.17, 169.09, 139.12,139.04, 137.73, 129.58, 129.51, 128.98, 127.46, 127.43, 127.27, 91.19, 75.40, 75.38, 62.73, 62.66, 53.15, 53.08, 34.73, 34.70, 30.82, 30.74, 28.86, 28.80, 22.17, 22.04, 8.71.

1d was prepared from **36** according to GP2. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) as a yellow oil (0.15 mmol, 56 mg, 82%); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.91 (d, *J* = 15.8 Hz, 1H), 7.63 -7.29 (m, 4H), 6.82 (d, *J* = 15.8 Hz, 1H), 3.77 (s, 3H), 3.75(s, 3H) 3.06 (dd, *J* = 15.2, 6.1 Hz, 1H), 2.68 (dd, *J* = 15.3, 8.4 Hz, 1H), 2.33-2.12 (m, 2H), 1.63 (m, 1H), 1.49 (m, 1H), 1.23-1.16 (m, 2H), 1.02 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 199.91, 170.32, 168.51, 139.41, 138.88, 133.49, 130.27, 129.57, 128.23, 127.10, 126.71, 52.74, 52.66, 34.30, 31.34, 28.47, 21.40, 19.93, 11.50; IR (KBr): *ν* = 3279, 3183, 1725, 1596, 1437, 1389, 1123, 1094 cm^{-1}; HRMS (ESI) Calcd. for: $C_{20}H_{22}O_5Na$ $[M+Na]^+$: 365.1359; Found: 365.1364.

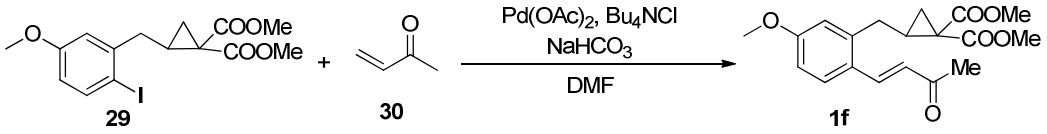
Dimethyl2-(2-(1-hydroxy-3-phenylprop-2-yn-1-yl)benzyl)cyclopropane-1,1-dicar boxylate (1e)



The aldehyde **22** (4.0 mmol, 1.1 g, 1.0 equiv.) reacted with Wittig reagent **39** (5.0 mmol, 1.9 g, 1.3 equiv.) to give the substrate **1e** (3.33 mmol, 1.26 g, 83%) as a brown oil according to the GP1. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.11 (d, *J* = 15.4 Hz, 1H), 8.04 (m, 2H), 7.72 (m, 1H), 7.60 (m, 1H), 7.50 (m, 3H), 7.40-7.35 (m, 1H), 7.31 (m, 2H), 3.76 (s, 3H), 3.72 (s, 3H), 3.08 (dd, *J* = 15.3, 6.0 Hz, 1H), 2.68 (dd, *J* = 15.3, 8.4 Hz, 1H), 2.23-2.13 (m, 1H), 1.61 (m, 1H), 1.51-1.45 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=

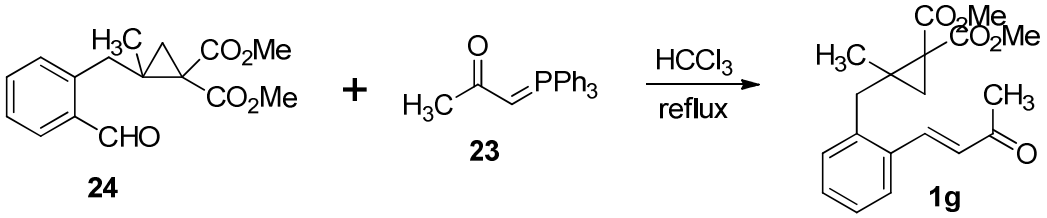
190.36, 170.47, 168.59, 141.95, 139.83, 138.25, 133.92, 133.01, 130.60, 129.77, 128.81, 128.68, 127.23, 126.94, 124.14, 52.84, 52.77, 34.42, 31.66, 28.59, 21.56; IR (KBr): v = 3298, 2988, 1735, 1438, 1243, 1048, 753 cm^{-1}; HRMS (ESI) Calcd. for: $C_{23}H_{23}O_5$ $[M+H]^+$: 379.1540; Found: 379.1541.

(E)-dimethyl2-(5-methoxy-2-(3-oxobut-1-en-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1f)



The substrate **1f** was prepared by **29** (0.5 mmol, 202 mg, 1.0 equiv.) according to **GP4** and silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) yielded **1f** as a yellow oil (0.28 mmol, 105 mg, 56%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.68 (d, J = 15.9 Hz, 1H), 7.51 (d, J = 8.4 Hz, 1H), 6.74 (m, 2H), 6.51 (d, J = 15.9 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.67 (s, 3H), 2.95 (dd, J = 15.2, 6.2 Hz, 1H), 2.58 (dd, J = 15.2, 8.4 Hz, 1H), 2.31 (s, 3H), 2.15-2.03 (m, 1H), 1.54 (dd, J = 7.7, 4.9 Hz, 1H), 1.42 (dd, J = 9.0, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.42, 170.34, 168.65, 161.56, 141.53, 139.95, 128.45, 126.69, 125.61, 115.00, 112.97, 55.48, 52.90, 52.84, 34.39, 31.35, 28.47, 27.84, 21.37; IR (KBr): v = 3294, 2970, 1725, 1433, 1240, 745 cm^{-1}; HRMS (ESI) Calcd. for: $C_{19}H_{23}O_6$ $[M+H]^+$: 347.1489; Found: 347.1495.

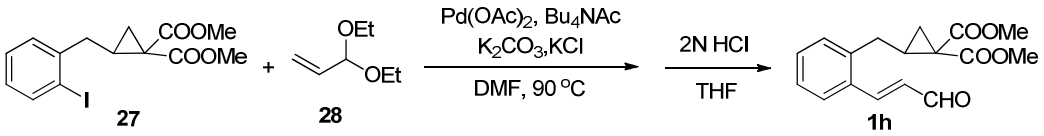
(E)-dimethyl2-methyl-2-(2-(3-oxobut-1-en-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1g)



The aldehyde **24**[4] (0.09 mmol, 27 mg, 1.0 equiv.) was reacted with Wittig reagent **23** (0.18 mmol, 59 mg, 2.0 equiv.) according to **GP1**. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 4/1) yielded **1b** as a yellow oil (0.06 mmol, 20 mg, 66%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (d, J = 15.9 Hz, 1H), 7.52 (m, 1H), 7.35-7.25 (m, 2H), 7.23-7.14 (m, 1H), 6.56 (d, J = 15.9 Hz, 1H), 3.72 (s, 3H), 3.68(s,3H), 3.05 (s, 2H), 2.35 (s, 3H), 1.70 (d, J = 5.2 Hz, 1H), 1.40 (d, J = 5.2 Hz,

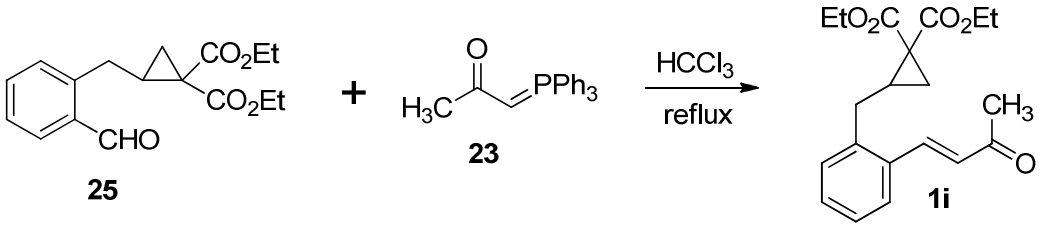
1H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.54, 169.58, 168.88, 141.33, 138.82, 134.11, 130.32, 130.22, 129.01, 127.08, 127.00, 52.90, 52.75, 39.43, 35.46, 32.92, 27.77, 27.11, 20.37; IR (KBr): ν = 3293, 2986, 1736, 1435, 1241, 749 cm^{-1} ; HRMS (ESI) Calcd. for: $C_{19}H_{22}O_5$ $[M+H]^+$: 331.1540; Found: 331.1538.

(E)-dimethyl2-(2-(3-oxoprop-1-en-1-yl)benzyl)cyclopropane-1,1-dicarb-oxylate (1h)



The substrate **1h** was prepared by **27** (1.6 mmol, 600 mg, 1.0 equiv.) according to **GP3**, and silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) yielded **1h** as a yellow oil (0.86 mmol, 260 mg, 54%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.69 (d, *J* = 7.7 Hz, 1H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.55 (m, 1H), 7.36 - 7.30 (m, 1H), 7.28 - 7.21 (m, 2H), 6.61 (dd, *J* = 15.7, 7.7 Hz, 1H), 3.69 (s, 3H), 3.67(s,3H), 3.01 (dd, *J* = 15.3, 6.0 Hz, 1H), 2.59 (dd, *J* = 15.2, 8.5 Hz, 1H), 2.11 (m, 1H), 1.54 (m, 1H), 1.43 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.81, 170.33, 168.63, 149.55, 139.43, 132.69, 131.38, 130.46, 129.91, 127.46, 127.21, 52.95, 52.86, 34.43, 31.32, 28.41, 21.49; IR (KBr): *v* = 3299, 3193, 2995, 1756, 1679, 1244, 1049 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{19}O_5$ $[M+H]^+$: 303.1227; Found: 303.1230.

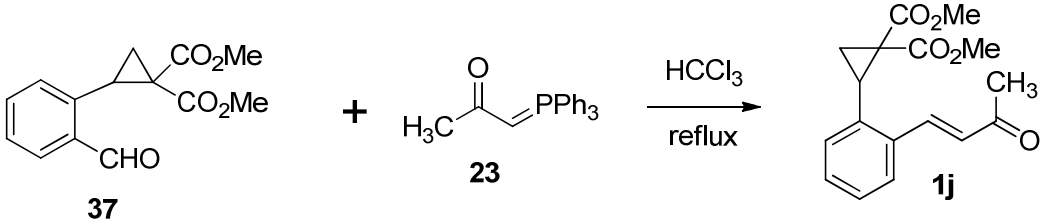
(E)-diethyl 2-(2-(3-oxobut-1-en-1-yl)benzyl)cyclopropane-1,1-dicarboxylate (1i)



The aldehyde **25**[4] (2 mmol, 628 mg, 1.0 equiv.) was reacted with Wittig reagent **23** (4 mmol, 1.52 g, 2.0 equiv.) according to **GP1**. Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 3/1) yielded **1i** as a yellow oil (1.88 mmol, 650 mg, 94%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.81 (d, *J* = 15.9 Hz, 1H), 7.58 (m, 1H), 7.43 - 7.21 (m, 3H), 6.64 (d, *J* = 15.9 Hz, 1H), 4.21 (m, 4H), 3.04 (dd, *J* = 15.4, 6.1 Hz, 1H), 2.66 (dd, *J* = 15.4, 8.6 Hz, 1H), 2.40 (s, 3H), 2.22 - 2.11 (m, 1H), 1.57 (m, 1H), 1.44 (dd, *J* = 8.9, 4.8 Hz, 1H), 1.25 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.36, 170.02,

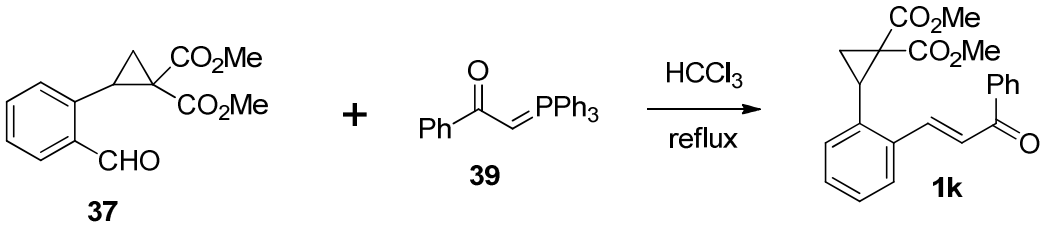
168.25, 140.44, 139.48, 133.30, 130.53, 129.64, 129.04, 127.21, 126.82, 61.71, 61.69, 34.70, 31.33, 27.87, 27.84, 21.10, 14.23, 14.17; IR (KBr): ν = 3297, 2984, 1728, 1671, 1370, 1250, 1210, 755, 565 cm^{-1}; HRMS (ESI) Calcd. for: $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1697; Found: 345.1698.

(E)-dimethyl 2-(2-(3-oxobut-1-en-1-yl)phenyl)cyclopropane-1,1-dicarboxylate(1j)



The substrate **1j** was prepared by **37**[4] (3 mmol, 787 mg, 1.0 equiv.) according to **GP1** and silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 3/1) yielded **1j** as a yellow oil (2.36 mmol, 712 mg, 79%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, J = 16.4 Hz, 1H), 7.63 - 7.54 (m, 1H), 7.32 (m, 2H), 7.25 - 7.17 (m, 1H), 6.59 (d, J = 16.4 Hz, 1H), 3.85 (s, 3H), 3.34 - 3.27 (m, 4H), 2.41 (s, 3H), 2.30 (dd, J = 8.1, 5.2 Hz, 1H), 1.81 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (100MHz, $CDCl_3$): δ = 199.20, 169.96, 167.00, 141.12, 135.24, 134.19, 130.18, 129.37,129.20, 128.32, 126.21, 53.20, 52.39, 36.81, 30.45, 26.39, 18.89; IR (KBr): ν = 2954, 1730, 1670, 1599, 1437, 1284, 1132, 978, 756 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{19}O_5$ $[M+H]^+$: 303.1227; Found: 303.1229.

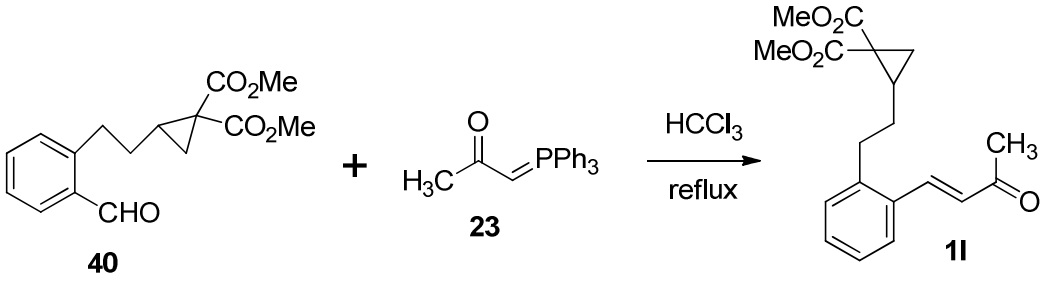
(E)-dimethyl2-(2-(3-oxo-3-phenylprop-1-en-1-yl)phenyl)cyclopropane-1,1-dicarb oxylate (1k)



1k was prepared by **37** (3.0 mmol, 787 mg, 1.0 equiv.) according to **GP1** Silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) yielded **1k** as a yellow oil (2.41 mmol, 881 mg, 81%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.06 (d, J = 15.8 Hz, 1H), 7.96 - 7.89 (m, 2H), 7.62 (m, 1H), 7.55 - 7.48 (m, 1H), 7.43 (m, 2H), 7.32 - 7.18 (m, 4H), 7.14 - 7.08 (m, 1H), 3.67 (s, 3H), 3.29 - 3.21 (m, 4H), 2.21 (dd, J = 8.0, 5.3 Hz, 1H), 1.72 (dd, J = 9.2, 5.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =191.34,

169.68, 167.08, 142.20, 138.18, 136.00, 134.38, 132.71, 130.00, 128.92, 128.82, 128.72, 128.15, 126.80, 125.02, 53.09, 52.34, 36.90, 30.63, 19.19; IR (KBr): ν = 2953, 1732, 1664, 1598, 1438, 1331, 1281, 755, 697 cm^{-1}; HRMS (ESI) Calcd. for: $C_{22}H_{21}O_5$ $[M+H]^+$: 365.1384; Found: 365.1387.

(E)-dimethyl2-(2-(3-oxobut-1-en-1-yl)phenethyl)cyclopropane-1,1-dicarboxylate (1l)



1l was prepared by **40**[4] (2.0 mmol, 581 mg, 1.0 equiv.) according to **GP1** and silica gel chromatography (Petroleum/ ethyl acetate = 10/1 then 5/1) yielded **1l** as a brown oil (1.54 mmol, 510 mg, 77%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, J = 16.1 Hz, 1H), 7.57 (m, 1H), 7.39 - 7.28 (m, 2H), 7.20 (m, 1H), 6.64 (d, J = 16.1 Hz, 1H), 3.75 (s, 3H), 3.71(s,3H) 2.89 (m, 2H), 2.41 (s, 3H), 1.97 - 1.85 (m, 1H), 1.71 (m, 1H), 1.53 (m, 1H), 1.39 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 198.46, 170.74, 168.67, 141.22, 140.48, 133.15, 130.49, 130.36, 128.81, 127.01, 126.83, 52.81, 52.75, 34.14, 32.36, 30.83, 28.06, 27.96, 21.19; IR (KBr): ν = 3297, 1733, 1670, 1437, 1245, 1133, 1048, 757 cm^{-1}; HRMS (ESI) Calcd. for: $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540; Found: 331.1542.

Synthesis of bridged oxa-[n.2.1] skeletons

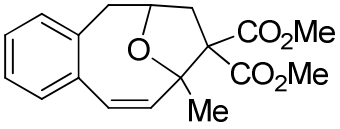
General procedure for the synthesis of 2

General Procedure A: The substrate **1** (0.04 mmol, 1 equiv.) was dissolved in the 2 mL solvent ($CDCl_3$ or DCE) in an NMR tube at room temperature and then catalyst (0.2 equiv., 0.008 mmol) was added. The solution was irradiated by UV (the most common one for detection of TLC in laboratory) and warmed to 50 ^{o}C. After it finished then filtered on silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by the pre-TLC or by flash chromatography using silica gel (200~300 or 300~400 mesh or neutral Al_2O_3) (petroleum / ethyl

acetate = 10/1~3/1) to afford product **2**.

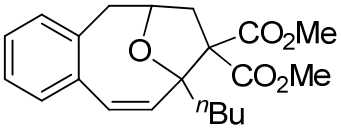
General Procedure B : The substrate **1** (0.1 mmol, 1 equiv.) was dissolved in the solvent (5 mL) in a 25 mL quartz glass bottle at room temperature and then catalyst (0.2 equiv., 0.02 mmol) was added. The solution was irradiated by UV (Ultraviolet disinfection lamp) and warmed to 50 ^{o}C. After it finished then filtered on silica gel. The filtrate was concentrated under reduced pressure and the residue was purified by the pre-TLC or by flash chromatography using silica gel (200~300 or 300~400 mesh or neutral Al_2O_3) (petroleum / ethyl acetate =10/1) to afford product **2**.

(Z)-dimethyl9-methyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2a)



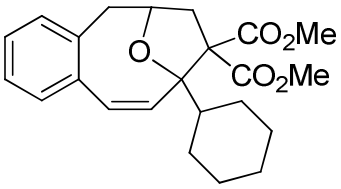
2a was prepared according to **GPA** yielded **2a** as a white solid (0.038 mmol, 12 mg, 92%), according to **GPB** (0.088 mmol, 28 mg, 88%); Mp: 75-77 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.21 - 7.09 (m, 4H), 6.37 (d, *J* = 12.2 Hz, 1H), 6.04 (d, *J* = 12.5 Hz, 1H), 4.45 - 4.36 (m, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 3.05 - 2.92 (m, 3H), 2.53 (dd, *J* = 13.4, 4.6 Hz, 1H), 1.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 170.45, 169.60, 139.63, 136.35, 136.03, 129.49, 128.25, 127.80, 126.98, 126.17, 87.43, 73.81, 70.14, 52.76, 44.24, 42.40, 24.73; IR (KBr): *v* = 2952, 1737, 1435, 1246, 1087 cm^{-1}; HRMS (ESI) Calcd. for: $C_{18}H_{21}O_5$ $[M+H]^+$: 317.1384; Found: 317.1382.

(Z)-dimethyl9-butyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2b)



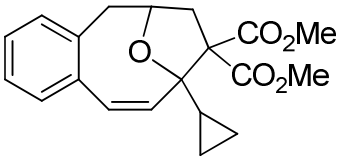
2b was prepared according to GPA as a yellow oil (0.03 mmol, 10.2 mg, 73%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.13 -7.00 (m, 4H), 6.47 (d, *J* = 12.3 Hz, 1H), 5.81 (d, *J* = 12.3 Hz, 1H), 4.39 - 4.33 (m, 1H), 3.75 (s, 3H), 3.64 (s, 3H), 2.97 (dd, *J* = 13.0, 7.9 Hz, 1H), 2.92 - 2.83 (m, 2H), 2.43 (dd, *J* = 13.4, 5.2 Hz, 1H), 1.92 (dt, *J* = 19.2, 9.5 Hz, 1H), 1.36-1.17 (m, 4H), 1.09 (dq, *J* = 13.7, 7.0 Hz, 2H), 0.71 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.57, 169.69, 140.22, 136.29, 133.41, 132.40, 128.19, 127.61, 126.69, 126.07, 90.35, 73.46, 71.00, 52.74, 52.72, 44.61, 42.48, 36.28, 26.59, 23.07, 14.09; IR (KBr): *v* = 3445, 1737, 1434, 1246, 1090 cm^{-1}; HRMS (ESI) Calcd. for: $C_{21}H_{27}O_5$ $[M+H]^+$: 359.1853; Found: 359.1855.

(Z)-dimethyl9-cyclohexyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2c)



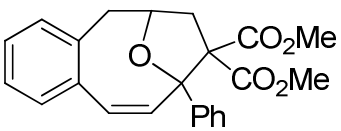
2c was prepared according to **GPA** and yielded **2c** as a yellow oil (0.023 mmol, 9 mg, 55%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 - 7.06 (m, 4H), 6.55 (d, *J* = 12.5 Hz, 1H), 6.33 (d, *J* = 12.5 Hz, 1H), 4.35 (m, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.06 - 2.88 (m, 3H), 2.45 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.09 (m, 1H), 1.75 (m, 1H), 1.58 (m, 2H), 1.36 (m, 2H), 1.09 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 169.80, 168.87, 139.43, 136.09, 126.92, 126.68, 125.34, 124.81, 91.62, 71.70, 69.36, 51.41, 46.68, 43.29, 43.16, 27.79, 27.32, 26.01, 25.48, 25.31; IR (KBr): *v* = 3524, 3437, 1629, 553, 449 cm^{-1}; HRMS (ESI) Calcd. for: $C_{23}H_{29}O_5$ $[M+H]^+$: 385.2010; Found: 385.2011.

(Z)-dimethyl9-cyclopropyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2d)



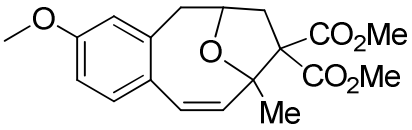
2d was prepared according to **GPB** and silica gel chromatography (petroleum/ ethyl acetate = 10/1) yielded **2d** as a yellow oil (0.09 mmol, 30 mg, 76%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.20 -7.04 (m, 4H), 6.43 (d, *J* = 12.3 Hz, 1H), 6.17 (d, *J* = 12.3 Hz, 1H), 4.35 (m, 1H), 3.83 (s, 3H), 3.71 (s, 3H), 2.99 (m, 3H), 2.41 (m, 4.9 Hz, 1H), 1.41 (m, 1H), 0.53 - 0.42 (m, 1H), 0.33 - 0.18 (m, 2H), 0.09 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 168.56, 168.30, 138.67, 134.87, 133.58, 128.50, 126.71, 126.41, 125.18, 124.56, 86.19, 72.11, 69.03, 51.32, 51.23, 43.06, 40.84, 16.32; IR (KBr): *v*= 3011, 2952, 1736, 1433, 1264, 785 cm^{-1}; HRMS (ESI) Calcd. for: $C_{20}H_{22}O_5Na$ $[M+Na]^+$: 365.1359; Found: 365.1363.

(Z)-dimethyl 9-phenyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2e)



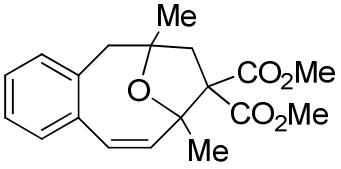
2e was prepared by **1e** (0.05 mmol, 0.02 M) according to **GPA** and separated by neutral Al_2O_3 flash column chromatography as a yellow oil (0.04 mmol, 14 mg, 74%).^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.51 (d, *J* = 7.4 Hz, 2H), 7.20 - 7.13 (m, 2H), 7.13 - 7.03 (m, 4H), 6.97 - 6.92 (d, *J* = 6.3 Hz, 1H), 6.49 (d, *J* = 12.4 Hz, 1H), 6.18 (d, *J* = 12.4 Hz, 1H), 4.61 - 4.50 (m, 1H), 3.84 (s, 3H), 3.10 (dd, *J* = 13.1, 10.7 Hz, 1H), 3.01 (s, 3H), 2.96 (dd, *J* = 13.1, 7.8 Hz, 1H), 2.87 (dd, *J* = 13.2, 6.7 Hz, 1H), 2.76 (dd, *J* = 13.1, 2.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.35, 169.92, 142.61, 139.47, 136.07, 135.61, 128.43, 128.19, 127.83, 127.60, 127.06, 127.00, 126.22, 125.63, 90.93, 76.10, 72.91, 52.99, 52.30, 43.01, 42.93; IR (KBr): *v* = 2957, 1630, 700, 570 cm^{-1}; HRMS (ESI) Calcd. for: $C_{23}H_{23}O_5$ $[M+H]^+$: 379.1540; Found: 379.1544.

(Z)-dimethyl3-methoxy-9-methyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2f)



2f was prepared according to GPA and yielded **2f** (0.035 mmol, 13 mg, 83%) as a yellow oil; ^{1}H NMR (400 MHz, CDCl3)**:** δ = 6.98 (d, *J* = 8.4 Hz, 1H), 6.71-6.57 (m, 2H), 6.25 (d, *J* = 12.3 Hz, 1H), 5.89 (d, *J* = 12.3 Hz, 1H), 4.35 (m, 1H), 3.79- 3.61 (m, 9H), 2.96-2.80 (m, 3H), 2.47 (m, 1H), 1.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ=170.51, 169.65, 158.51, 137.87, 135.13, 132.10, 129.09, 129.02, 114.17, 111.28, 87.53, 73.83, 70.09, 55.33, 52.75, 44.46, 42.43, 24.89; IR (KBr): *v* = 2954, 1736, 1500, 1249, 767 cm^{-1}; HRMS (ESI) Calcd. for: $C_{19}H_{23}O_6$ $[M+H]^+$: 347.1489; Found: 347.1495.

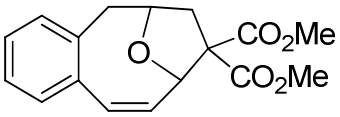
(Z)-dimethyl6,9-dimethyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2g)



2g was prepared by **1g** (0.08 mmol, 0.02 M) according to **GPA** and yielded **2g** as a yellow oil (0.07 mmol, 24 mg, 89%); ^{1}H NMR (400 MHz, $CDCl_3$): δ=7.23 - 7.12 (m,

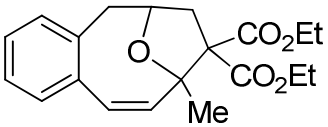
3H), 7.12 -7.05 (m, 1H), 6.28 (d, *J* = 12.4 Hz, 1H), 6.03 (d, *J* = 12.4 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.29 (d, *J* = 12.8 Hz, 1H), 2.90 (d, *J* = 13.6 Hz, 1H), 2.66 (dd, *J* = 13.6, 12.8 Hz, 2H), 1.44 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.99, 169.94, 139.38,136.34, 136.06, 128.91, 128.28, 127.68, 126.71, 126.36, 88.24, 80.19, 70.50, 52.78, 52.67, 48.63, 48.02, 26.41,26.27; IR (KBr): *v* = 2950, 1733, 1429, 1236, 1082, 752 cm^{-1}; HRMS (ESI) Calcd. for: $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540; Found: 331.1543.

(Z)-dimethyl 6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2h)



2h was prepared according to **GPA** and yielded **2h** as a yellow oil (0.03 mmol, 9 mg, 75%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16 - 6.99 (m, 4H), 6.24 (dd, *J* = 12.5, 1.9 Hz, 1H), 5.63 - 5.56 (m, 1H), 5.48 (dd, *J* = 12.5, 3.2 Hz, 1H), 4.31 - 4.22 (m, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 3.28 - 3.16 (m, 1H), 2.98 (d, *J* = 13.2 Hz, 1H), 2.61 (dd, *J* = 13.5, 5.7 Hz, 1H), 2.37 (dd, *J* = 13.2, 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =171.25, 169.93, 138.48, 136.42, 129.94, 129.11, 128.95, 128.71, 127.42, 126.42, 82.63, 79.06, 67.66, 53.37, 53.13, 42.25, 40.30; IR (KBr): *v*= 3443, 2829, 1737, 1627,1249 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{19}O_5$ $[M+H]^+$: 303.1227; Found: 303.1230.

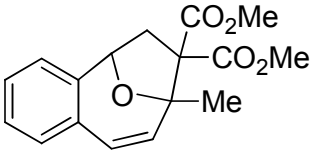
(Z)-diethyl9-methyl-6,7-dihydro-5H-6,9-epoxybenzo[9]annulene-8,8(9H)-dicarboxylate (2i)



2i was prepared according to **GPA** and yielded **2i** as a yellow oil (0.03 mmol, 11.4 mg, 87%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.22-7.05 (m, 4H), 6.36 (d, *J* = 12.3 Hz, 1H), 6.08 (d, *J* = 12.3 Hz, 1H), 4.45 - 4.34 (m, 1H), 4.29 (q, *J* = 7.1 Hz, 2H), 4.22- 4.12 (m, 2H), 3.04-2.90 (m, 3H), 2.51 (dd, *J* = 13.4, 4.8 Hz, 1H), 1.43 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =170.01, 169.18, 139.74, 136.45, 136.33, 129.28, 128.28, 127.83, 126.96, 126.17,

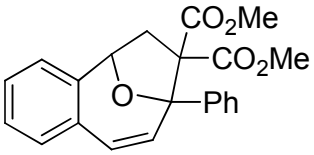
87.31, 73.75, 70.10, 61.80, 61.65, 44.33, 42.57, 29.85, 24.72, 14.18, 14.15; IR (KBr): ν = 3524, 3479, 3437, 1629, 554 cm^{-1}; HRMS (ESI) Calcd. for: $C_{20}H_{25}O_5$ $[M+H]^+$: 345.1697; Found: 345.1700.

dimethyl 8-methyl-5,6-dihydro-5,8-epoxybenzo[8]annulene-7,7(8H)-dicarboxylate (2j)



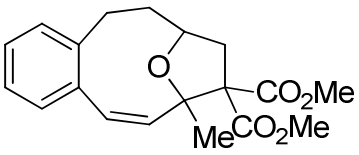
2j was prepared by **1j** (0.02 mmol, 0.02 M) according to **GPA** and yielded **2j** as a yellow oil (0.016 mmol, 5 mg, 80%); ^{1}H NMR (400 MHz, $CDCl_3$)： δ= 7.24 -7.07 (m, 4H), 6.37 (d, *J* = 12.2 Hz, 1H), 6.02 (d, *J* = 12.2 Hz, 1H), 5.22 (m, 1H), 3.81 (s, 3H), 3.75 (s, 3H), 2.94 (dd, *J* = 13.6, 8.5 Hz, 1H), 2.55 (dd, *J* = 13.4, 6.7 Hz, 1H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 169.66, 168.52, 143.33, 136.56, 132.83, 132.81, 129.89, 127.91, 127.88, 126.54, 86.86, 80.32, 74.79, 52.92, 52.65, 40.28, 21.40; IR (KBr): ν = 3272, 2954, 1736, 1545, 1451, 1261, 1070, 766 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{19}O_5$ $[M+H]^+$: 303.1227; Found: 303.1226.

dimethyl8-phenyl-5,6-dihydro-5,8-epoxybenzo[8]annulene-7,7(8H)-dicarboxylate (2k)



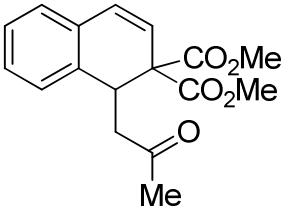
2k was prepared according to **GPA** and yielded **2k** as a yellow oil (0.01 mmol, 3 mg, 20%); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.91 (d, *J* = 7.6 Hz, 2H), 7.34 -7.14 (m, 7H), 6.75 (d, *J* = 12.2 Hz, 1H), 6.46 (d, *J* = 12.2 Hz, 1H), 5.48 (dd, *J* = 8.6, 6.8 Hz, 1H), 3.72 (s, 3H), 3.23-3.10 (m, 4H), 2.66 (dd, J = 13.2, 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =168.84, 168.60, 143.27, 138.15, 136.28, 133.04, 129.67, 128.04, 127.94, 127.85, 126.60, 126.49, 89.27, 80.07, 78.26, 52.61, 52.40, 41.48; IR (KBr): ν = 2954, 2923, 2853, 1735, 1468, 745 cm^{-1}; HRMS (ESI) Calcd. for: $C_{22}H_{21}O_5$ $[M+H]^+$: 365.1384; Found: 365.1390.

(Z)-dimethyl7-methyl-9,10,11,12-tetrahydro-7,10-epoxybenzo[10]annulene-8,8(7 H)-dicarboxylate (2l)



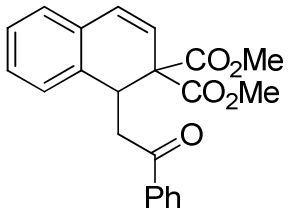
2l was prepared according to **GPA** and yielded **2l** as a yellow oil (0.015 mmol, 5 mg, 34%); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.22 -7.06 (m, 3H), 6.92 (d, *J* = 7.3 Hz, 1H), 6.55 (d, *J* = 12.3 Hz, 1H), 5.80 (d, *J* = 12.3 Hz, 1H), 4.69 (m, 1H), 3.85 (s, 3H), 3.71 (s, 3H), 2.99 (t, *J* = 13.1 Hz, 1H), 2.73- 2.63 (m, 1H), 2.54 (dd, *J* = 13.0, 6.1 Hz, 1H), 2.30 -2.16 (m, 2H), 1.80 (dd, *J* = 14.7, 6.2 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ =169.89, 169.38, 142.07, 137.65, 135.72, 131.19, 128.54, 126.93, 126.57, 125.33, 86.80, 86.11, 52.82, 52.65, 37.24, 33.87, 27.50, 24.09; IR (KBr): *v* = 3271, 2952, 1733, 1261, 1073, 761 cm^{-1}; HRMS (ESI) Calcd. for: $C_{19}H_{23}O_5$ $[M+H]^+$: 331.1540; Found: 331.1535.

Dimethyl 1-(2-oxopropyl)naphthalene-2,2(1H)-dicarboxylate (3j)



3j was prepared by **1j** (0.02 mmol, 0.02 M) according to **GPA** and yielded **3j** as a white solid (0.0196 mmol, 5.9 mg , 98%); Mp: 100-102 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.17 (m, 3H), 7.04 (dd, *J* = 5.6, 3.0 Hz, 1H), 6.59 (d, *J* = 9.5 Hz, 1H), 6.14 (dd, *J* = 9.5, 0.9 Hz, 1H), 4.27 (t, *J* = 6.7 Hz, 1H), 3.76 (s, 3H), 3.60 (s, 3H), 2.69 -2.56 (m, 2H), 1.94 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 206.35, 170.79,168.93, 136.79, 130.27, 129.40, 128.82, 128.31, 127.48, 127.12, 123.94, 58.69, 53.22, 53.01, 44.95, 38.24, 30.94; IR (KBr): *v*= 3271, 3056, 2955, 1734, 1434, 1268, 1241, 744 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{19}O_5$ $[M+H]^+$: 303.1227; Found: 303.1233.

Dimethyl 1-(2-oxo-2-phenylethyl)naphthalene-2,2(1H)-dicarboxylate (3k)



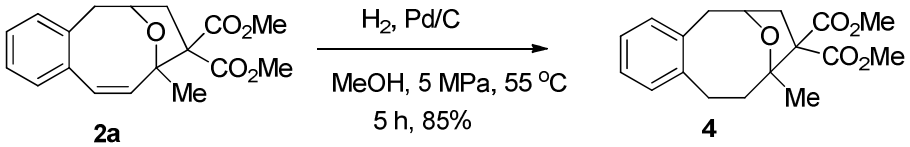
3k was prepared by **1k** (0.02 mmol, 0.02 M) according to **GPA** and yielded **3k** as a yellow oil (0.0184 mmol, 6.8 mg , 92%); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.78 (d, *J* = 7.8 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.22-7.01 (m, 4H), 6.64 (d, *J* = 9.5 Hz, 1H), 6.22 (d, *J* = 9.5 Hz, 1H), 4.51 (dd, *J* = 7.9, 5.0 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.22 (dd, *J* = 16.8, 8.4 Hz, 1H), 3.10 (dd, *J* = 16.6, 4.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 197.79, 170.69, 168.98, 137.07, 136.76, 133.16, 130.31, 129.55, 128.70, 128.62, 128.60, 128.17, 127.45, 127.08, 123.98, 58.99, 53.25, 53.05, 40.18, 38.54; IR (KBr): *v* = 3127, 2359, 1733, 1540, 950 cm^{-1}; HRMS (ESI) Calcd. for: $C_{22}H_{21}O_5$ $[M+H]^+$: 365.1384; Found: 365.1383.

The procedure of the one-pot tandem reaction

To a stirred solution of the alkynol product (0.1 mmol, 1.0 equiv.) in DCE (5 mL) in a 25 mL quartz glass bottle was added MeOH (1.0 equiv., 0.1 mmol) and the PPh_3·$AuNTf_2$ catalyst (0.02 equiv., 0.002 mmol) at room temperature and the mixture was stirred at room temperature for 5 h. After the reaction finished totally, $Sc(OTf)_3$ (0.02 mmol, 0.2 equiv.) was then added and under the irradiation of an UV disinfection lamp. The reaction was further stirred for 30 min. at 50 °C in a water bath for. The product was separated with the pre-TLC.

2b (52%), **2c** (50%), **2d** (50%), **2e** (48%)

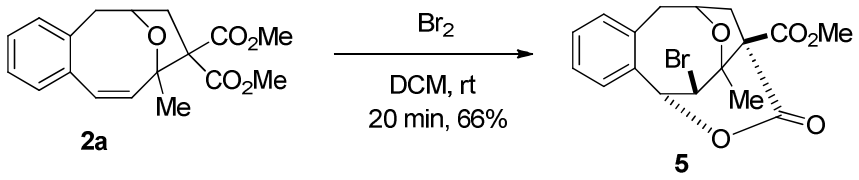
Application



2a **4**

In the room temperature, added **2a** (0.1mmol, 32 mg, 1 equiv), Pd/C (3.2 mg, 10 w%), MeOH (10 mL) to a 25 mL round flask and reacted in the atmosphere of H_2 at the 5 MPa pressure at 55 °C for 5 h. After it finished totally, filtered the Pd/C, and the mixture was purified by pre-TLC and yielded the **4** as a yellow oil (0.84 mmol, 27 mg, 85%); ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.20 -7.07 (m, 3H), 7.03 (d, *J* = 7.0 Hz, 1H), 4.89- 4.78 (m, 1H), 3.77 (s, 3H), 3.67 (s, 3H), 3.45 (dd, *J* = 15.7, 1.6 Hz, 1H), 3.11 (dd, *J* = 13.9, 9.3 Hz, 1H), 2.83 (dd, *J* = 15.7, 5.2 Hz, 1H), 2.60 (dd, *J* = 13.8, 9.7 Hz, 1H), 2.40 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.28 (dd, *J* = 15.3, 9.7 Hz, 1H), 1.83 (dd, *J* =

13.6, 8.6 Hz, 1H), 1.45 (s, 3H), 1.32 - 1.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 170.56, 169.43, 143.69, 135.81, 132.05, 130.23, 127.22, 126.16, 83.02, 75.23, 69.49, 52.53, 52.30, 43.38, 41.64, 35.13, 29.08, 25.58; IR (KBr): *v*= 3272, 2952, 1737, 1258, 899, 760 cm^{-1}; HRMS (ESI) Calcd. for: $C_{18}H_{22}O_5Na$ $[M+Na]^+$: 341.1359; Found: 341.1362.



Added the **2a** (0.1 mmol, 32 mg, 1 equiv), DCM (5 mL) to a 25 mL round flask and then dropped the Br_2 (0.12 mmol, 1.2 equiv.) to the mixture. After it finished, added the $Na_2S_2O_5$ to the mixture until the color faded. The organic layer was washed by the brine (10 mL×3) and water (10 mL×3) and dried by the $MgSO_4$. Then the mixture was concentrated under reduced pressure. Then the residue was purified by flash chromatography and yielded the **5** as a white solid (0.78 mmol, 25 mg, 66%); Mp: 181-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.20 (m, 4H), 7.03 (d, *J* = 7.2 Hz, 1H), 5.73 (d, *J* = 5.7 Hz, 1H), 4.87 (d, *J* = 5.7 Hz, 1H), 4.53 (m, 1H), 3.77 (s, 3H), 3.12-2.82 (m, 3H), 2.53 (d, J = 13.0 Hz, 1H), 1.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 169.51, 167.38, 135.44, 133.59, 132.93, 132.20, 129.38, 125.74, 85.64, 82.76, 74.08, 64.61, 53.54, 53.42, 42.47, 39.92, 25.30; IR (KBr): *v* = 3271, 1754, 1732, 1543, 1260, 745 cm^{-1}; HRMS (ESI) Calcd. for: $C_{17}H_{17}BrO_5Na$ $[M+Na]^+$: 403.0152; Found: 403.0155.

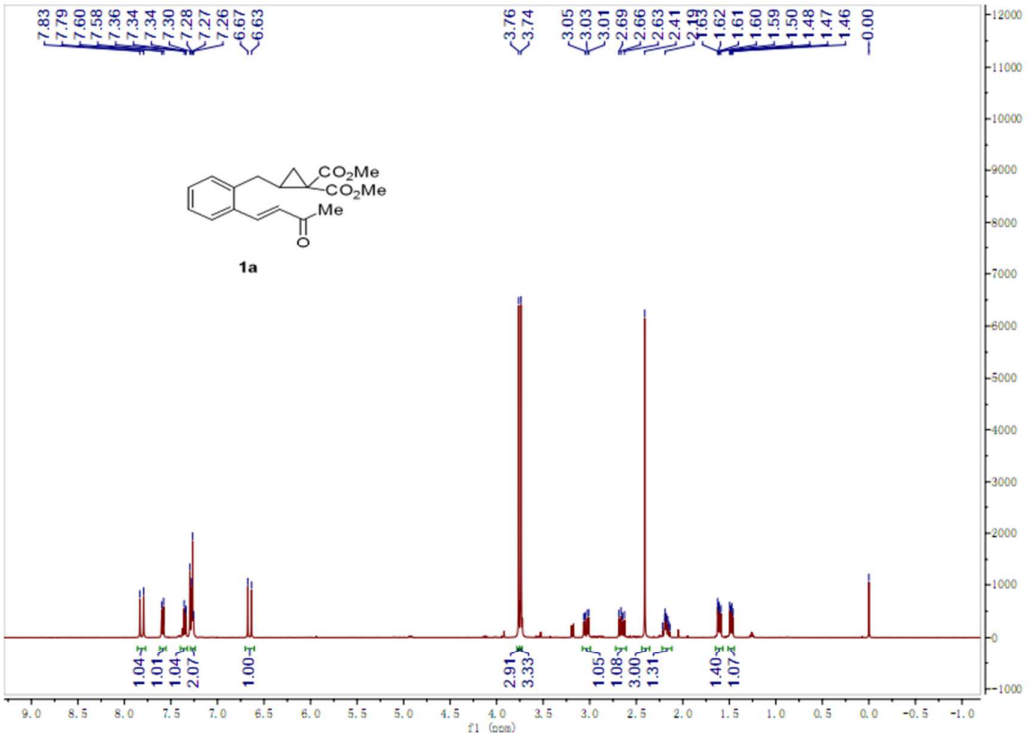
References

[1] M. N. Pennell, P. G. Turner, T. D. Sheppard, *Chem. Eur. J.* **2012,** *18,* 4748.

[2] G. Battistuzzi, S. Cacchi, G. Fabrizi, *Org. Lett.* **2003**, *5*, 777.

[3] T. Jeffery, *J. Chem. Soc. Chem. Commun*. **1984**, 1287.

[4] S. Xing, W. Pan, C. Liu, J. Ren, Z. Wang, *Angew. Chem. Int. Ed*., **2010**, *49*, 3215.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6.63
3.76
3.74
3.05
3.03
3.01
2.69
2.66
2.63
2.41
2.19
1.63
1.62
1.61
1.60
1.59
1.50
1.48
1.47
1.46
0.00
CO2Me
CO2Me
Me
O
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1.04
1.01
1.04
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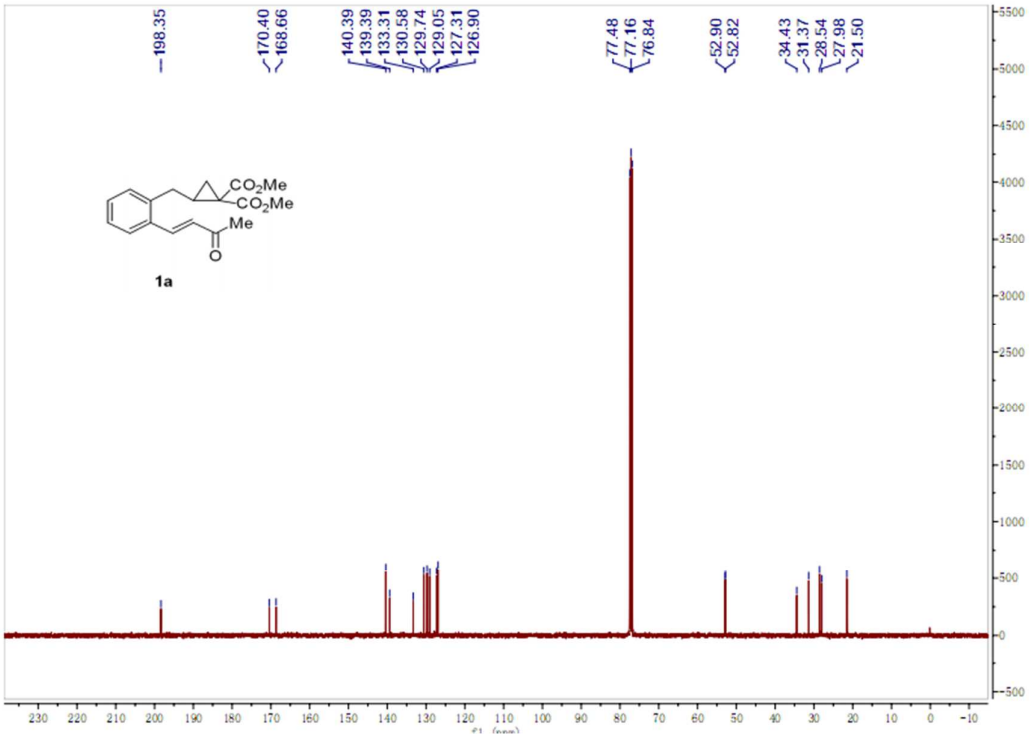
1.00
2.91
3.33
1.05
1.08
3.00
1.31
1.40
1.07
f1 (ppm)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127.31
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77.16
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52.82
34.43
31.37
28.54
27.98
21.50
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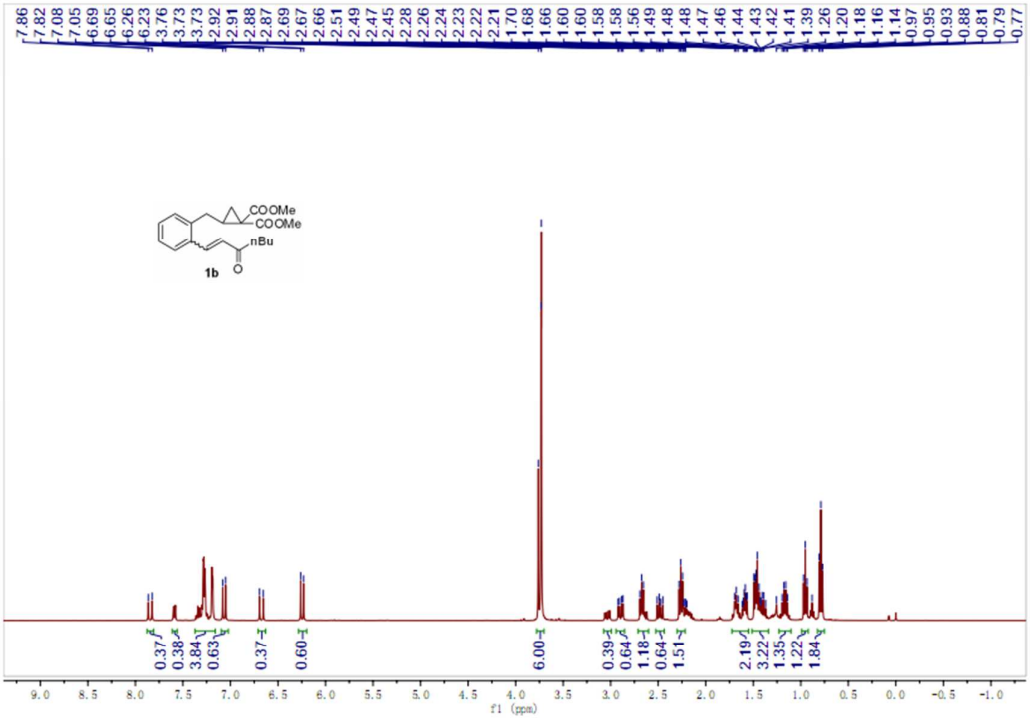
CO2Me
Me
O
1a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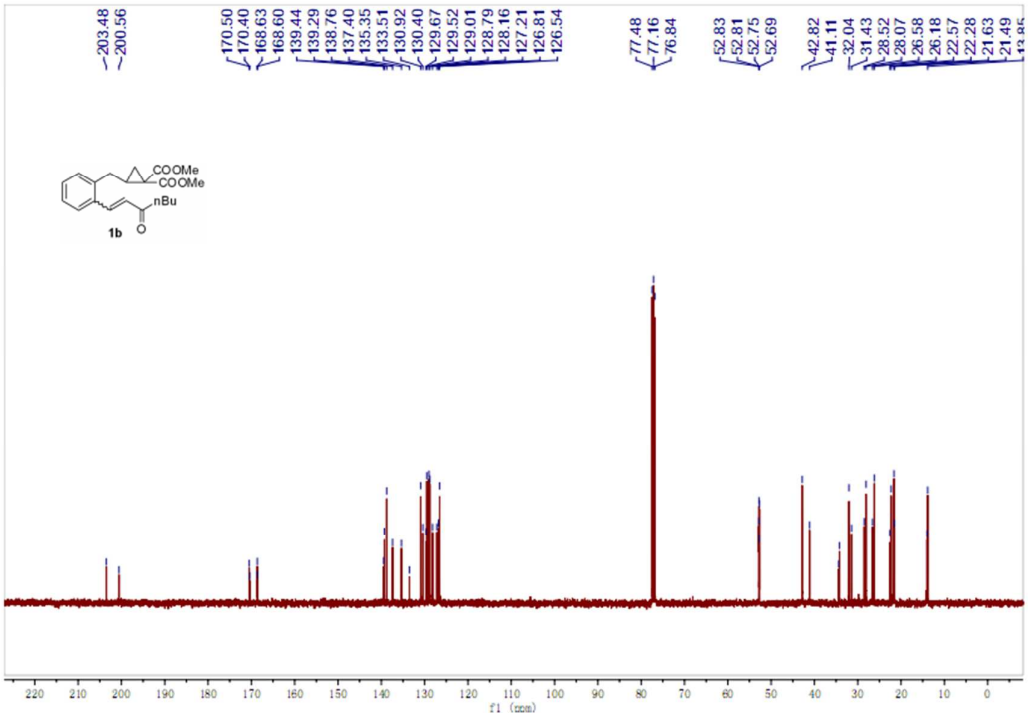
f1 (ppm)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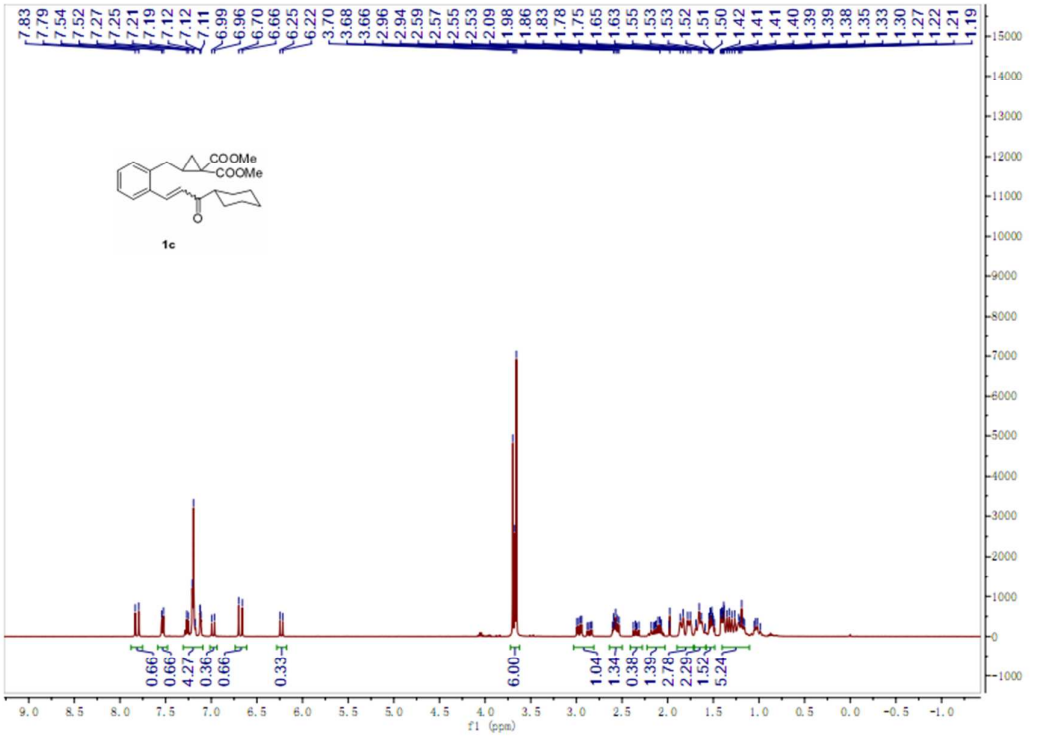
COOMe
nBu
O
1b
f1 (ppm)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1.22
1.21
1.19
COOMe
COOMe
1c
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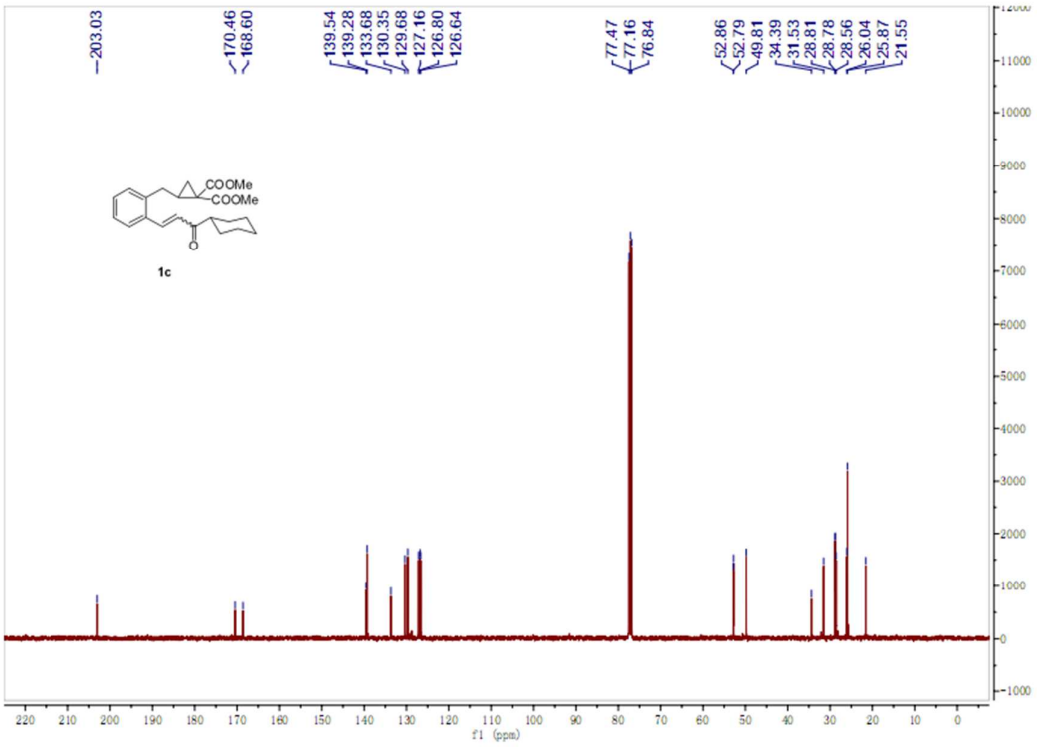
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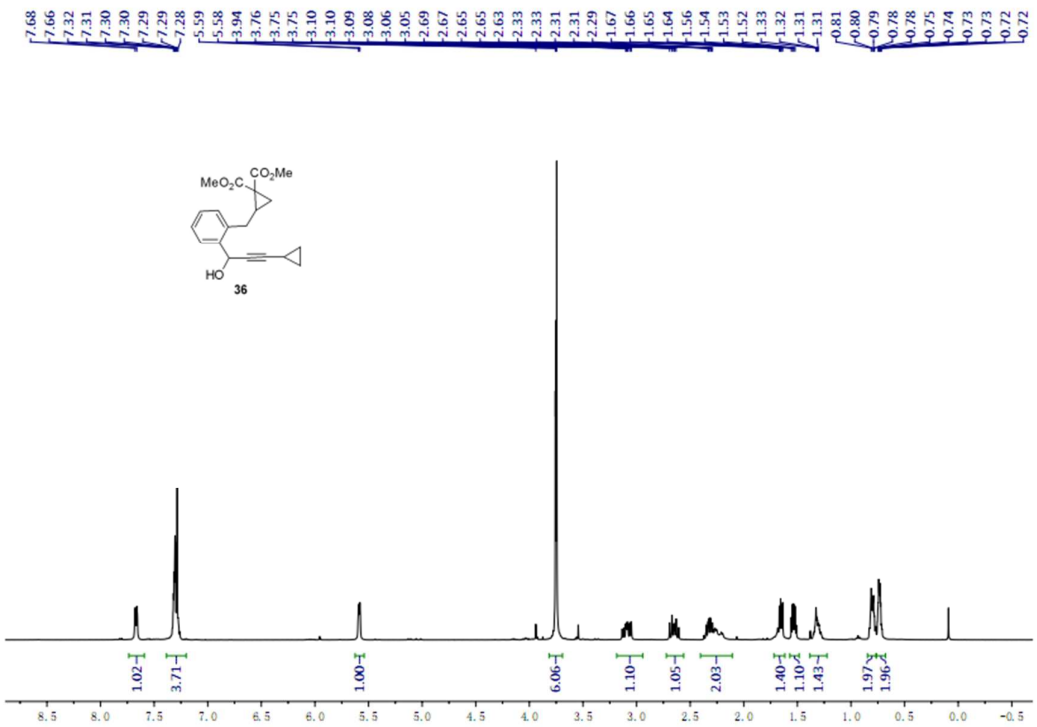
COOMe
COOMe
1c
f1 (ppm)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0.81 0.80 0.79 0.78 0.78 0.75 0.74 0.73 0.73 0.72 0.72
MeO2C
CO2Me
HO
36
1.02 3.71 1.00 6.06 1.10 1.05 2.03 1.40 1.10 1.43 1.97 1.96
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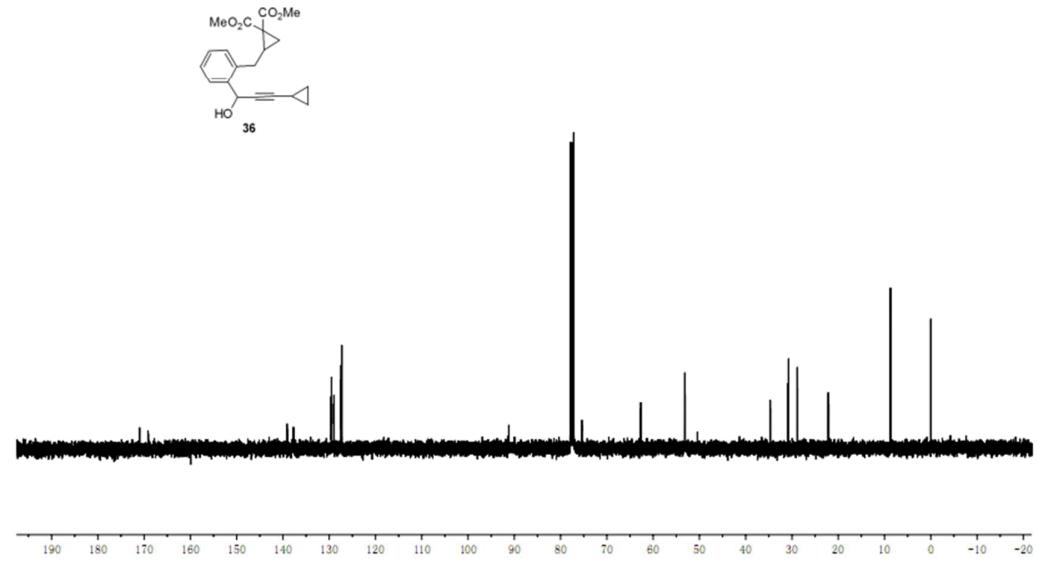
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91.19
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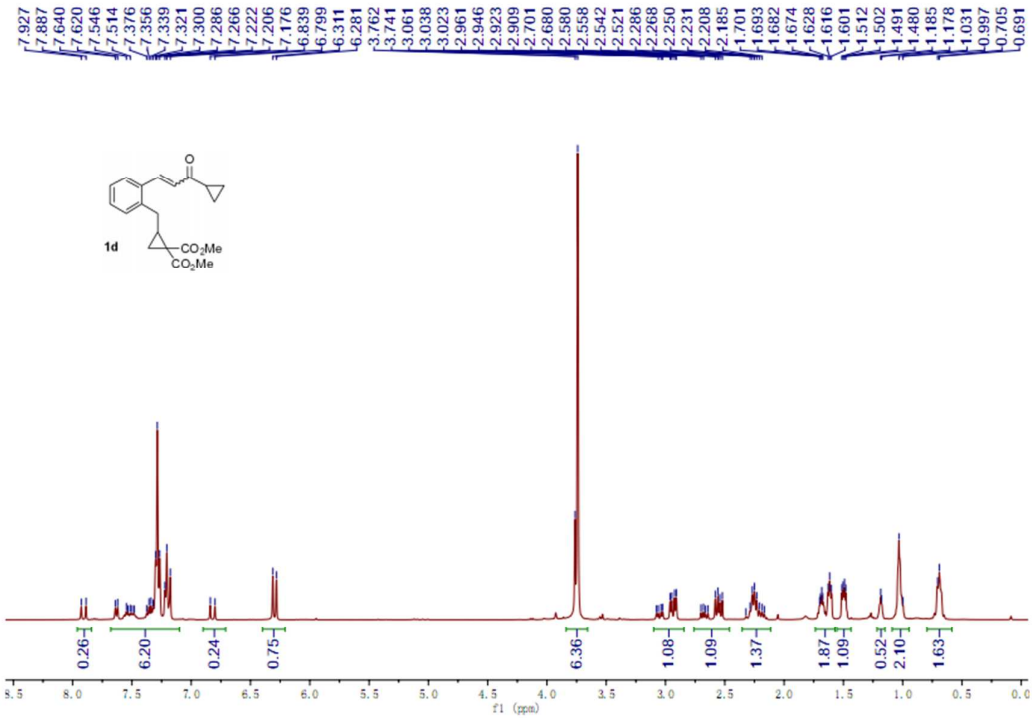
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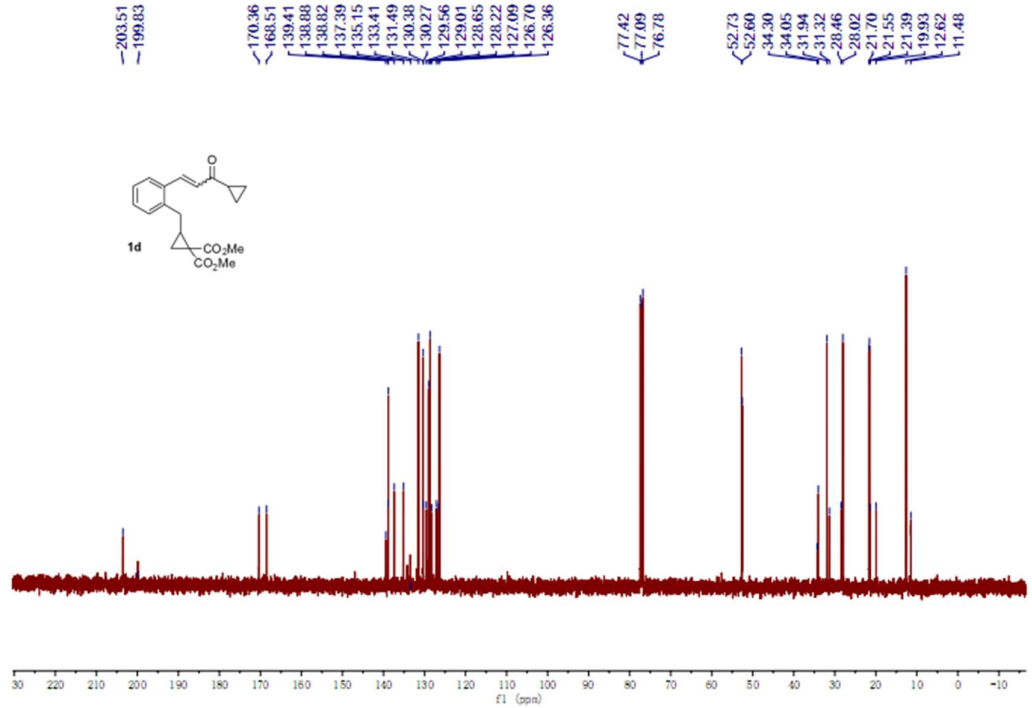
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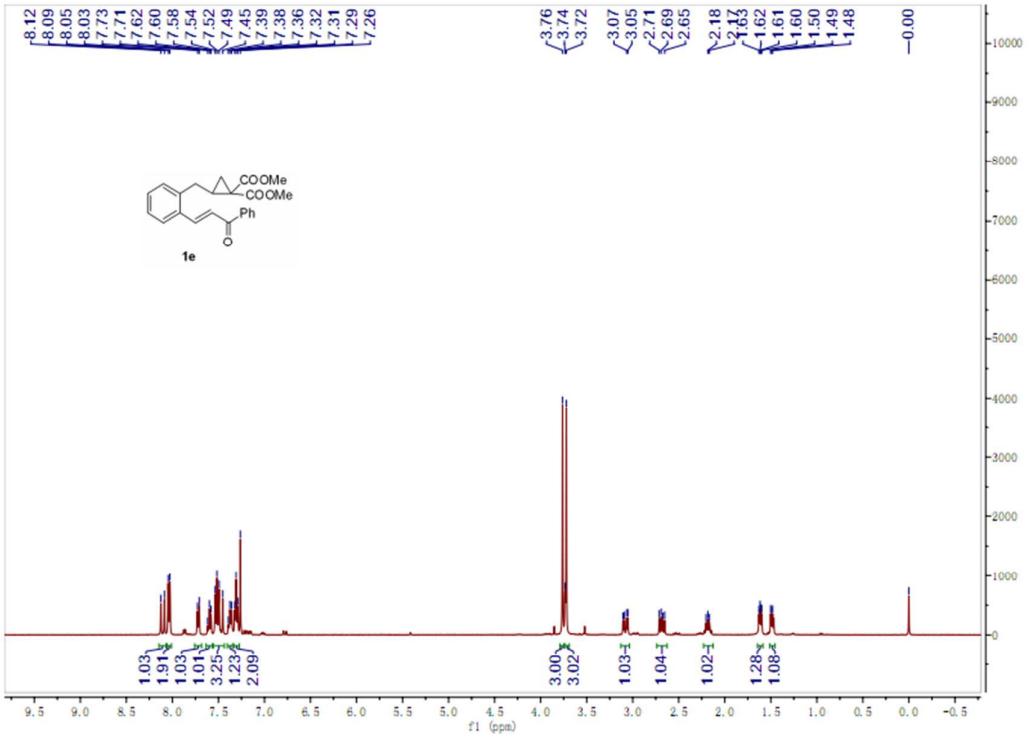
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2.69
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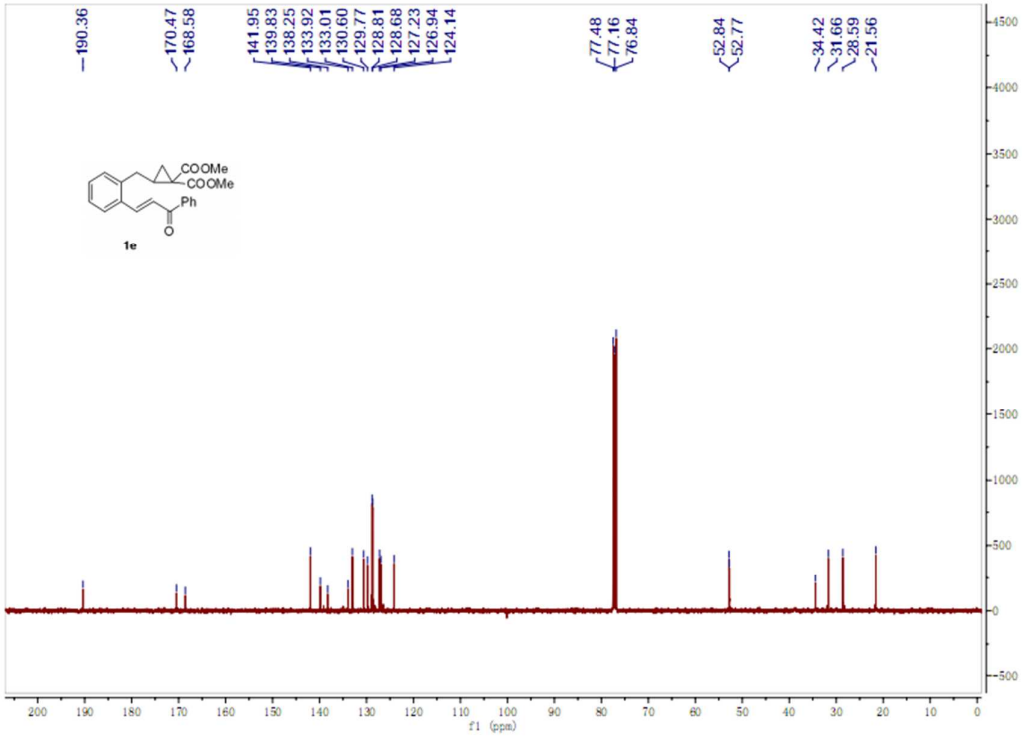
1.28
1.08
f1 (ppm)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127.23
126.94
124.14
77.48
77.16
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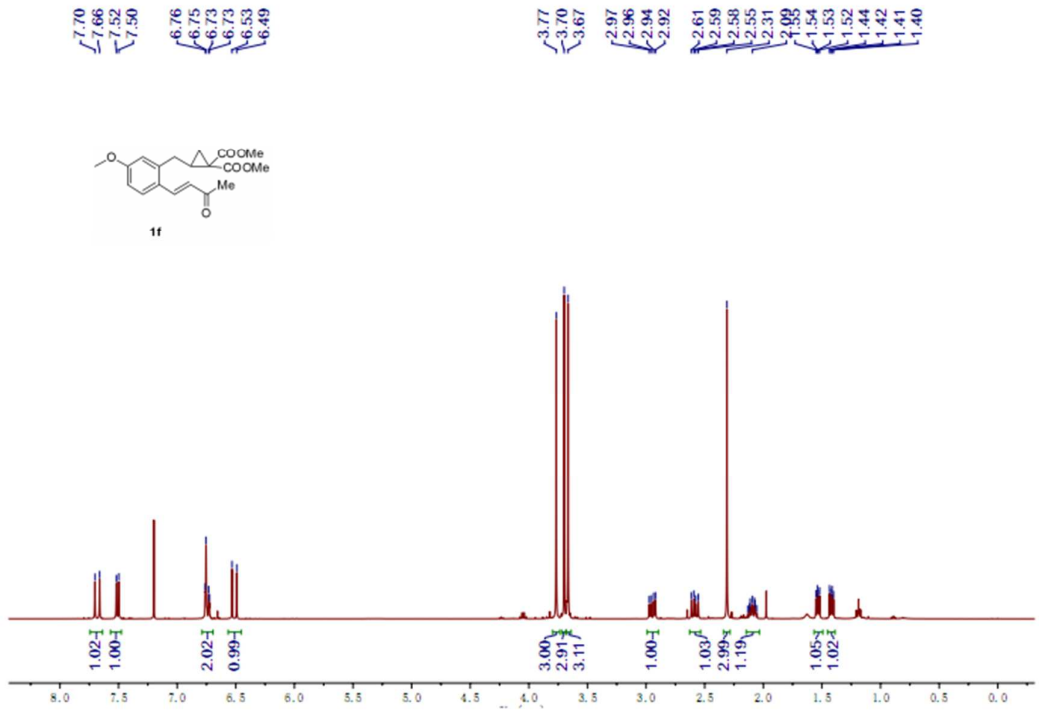
31.66
28.59
21.56
COOMe
COOMe
Ph
O
1e
f1 (ppm)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6.49
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3.70
3.67
2.97
2.96
2.94
2.92
2.61
2.59
2.58
2.55
2.31
1.55
1.54
1.53
1.52
1.44
1.42
1.41
1.40
COOMe
COOMe
Me
O
1f
1.02
1.00
2.02
0.99
3.00
2.91
3.11
1.00
1.03
2.99
1.19
1.05
1.02
8.0
7.5
7.0
6.5
6.0
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4.0
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1.0
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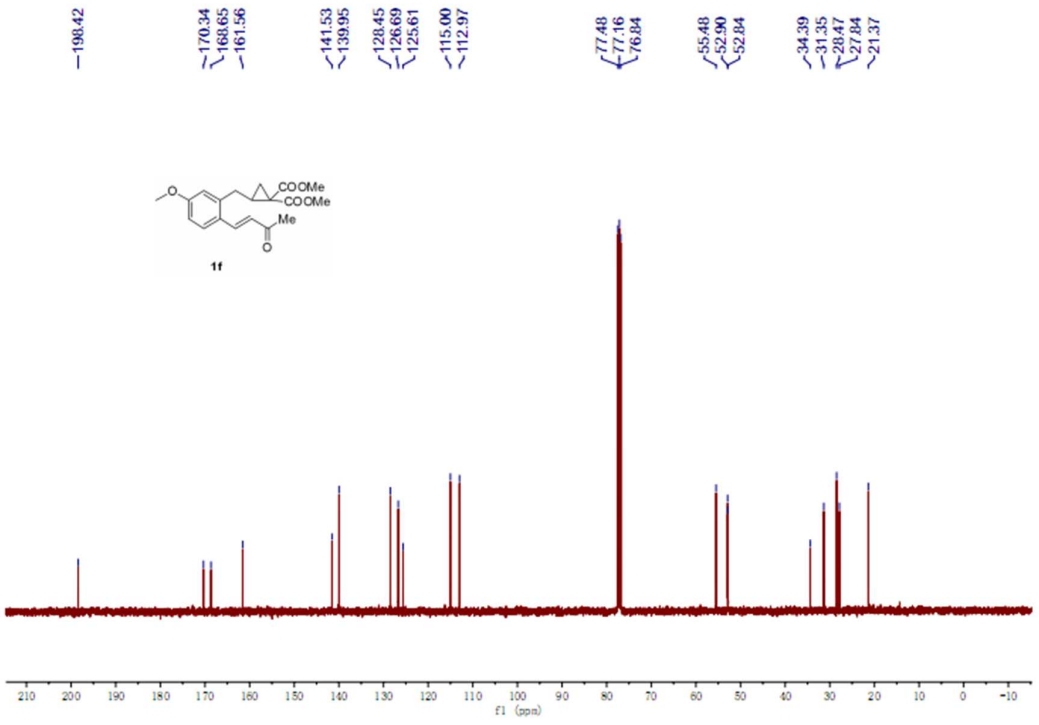
0.0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55.48
52.90
52.84
34.39
31.35
28.47
27.84
21.37
COOMe
COOMe
Me
O
1f
210
200
190
180
170
160
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140
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120
110
100
90
80
70
60
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40
30
20
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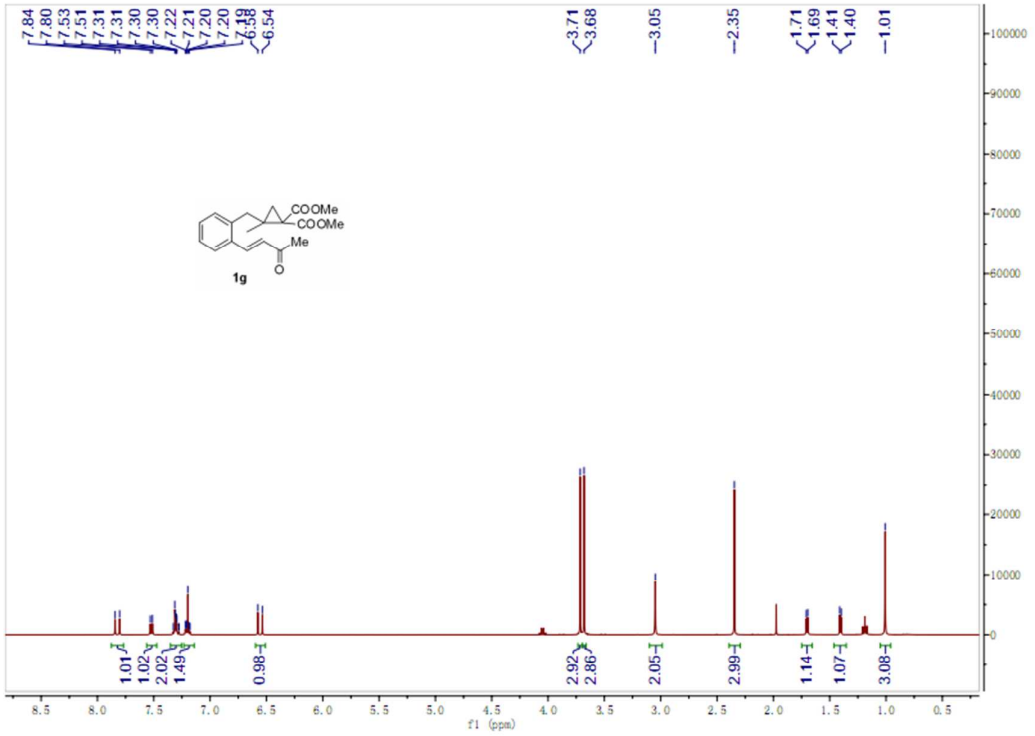
-10
f1 (ppm)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7.30
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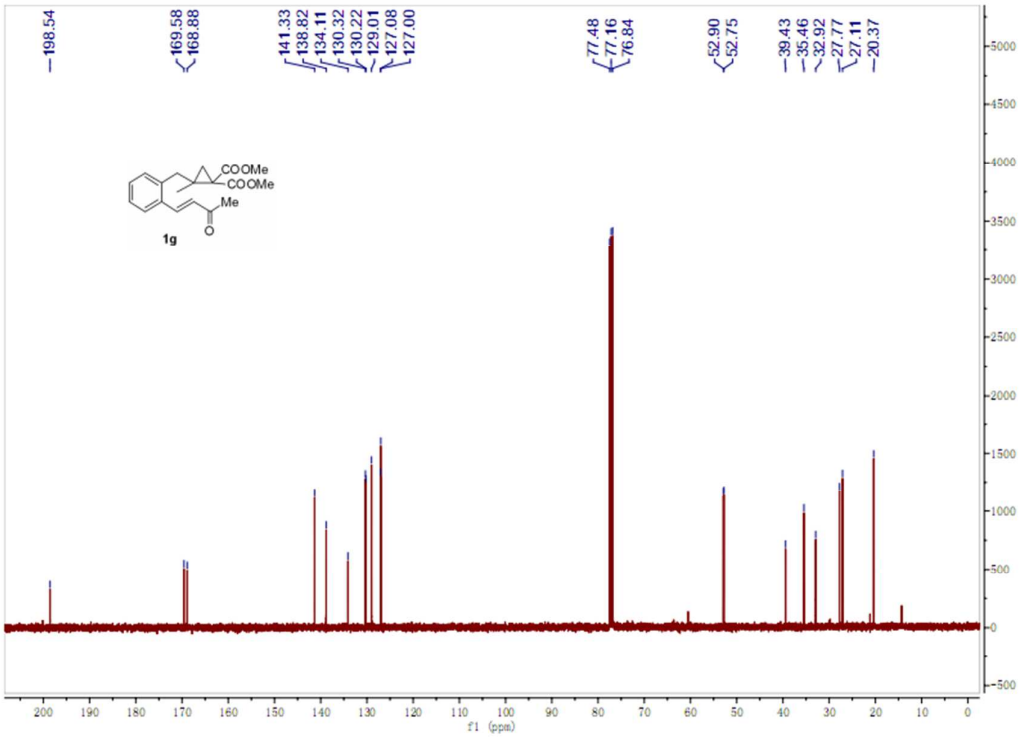
7.21
7.20
7.20
6.58
6.54
3.71
3.68
3.05
2.35
1.71
1.69
1.41
1.40
1.01
COOMe
COOMe
Me
O
1g
1.01
1.02
2.02
1.49
0.98
2.92
2.86
2.05
2.99
1.14
1.07
3.08
f1 (ppm)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77.16
76.84
52.90
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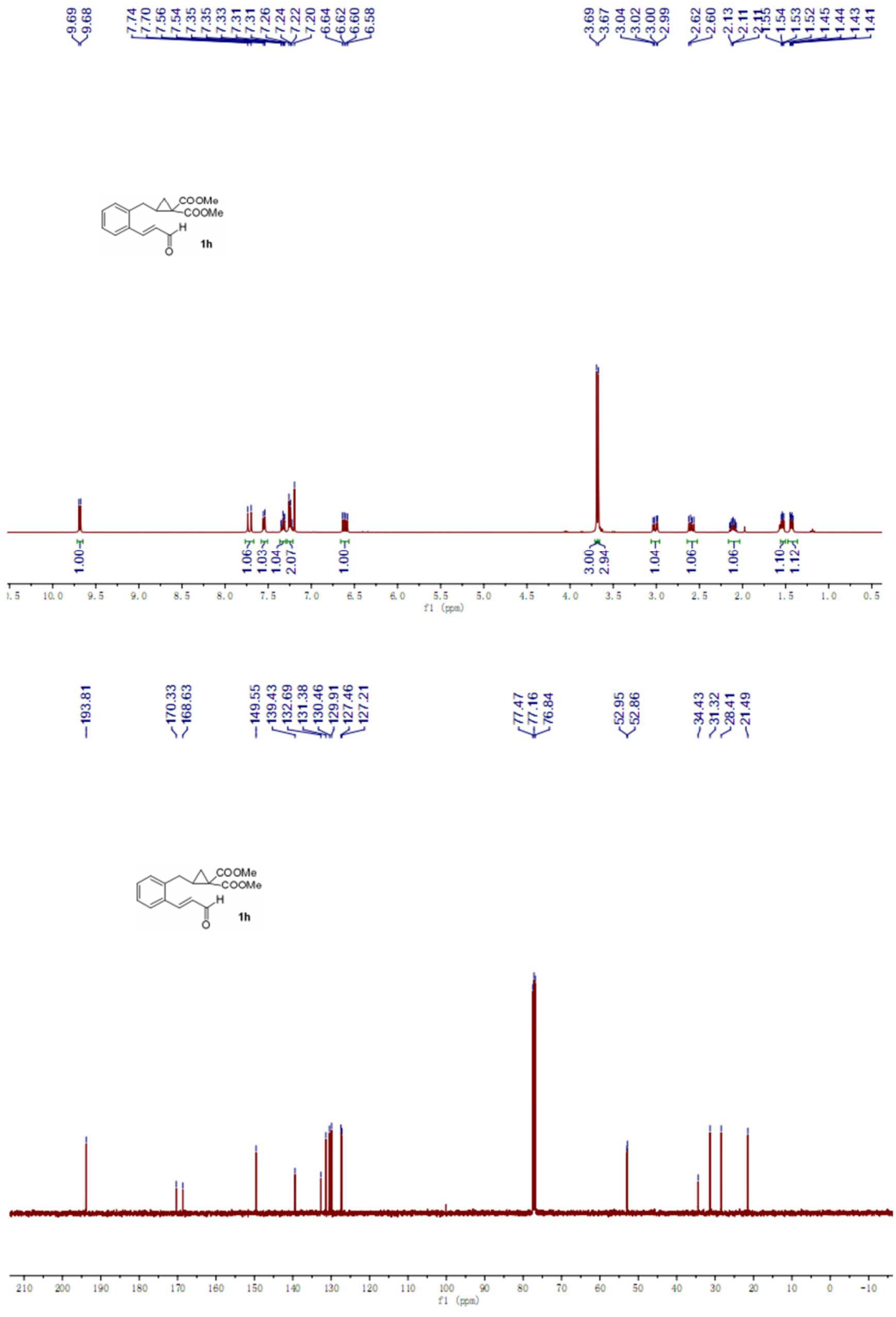
32.92
27.77
27.11
20.37
COOMe
COOMe
Me
O
1g
f1 (ppm)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7.26
7.24
7.22
7.20
6.64
6.62
6.60
6.58
3.69
3.67
3.04
3.02
3.00
2.99
2.62
2.60
2.13
2.11
1.55
1.54
1.53
1.52
1.45
1.44
1.43
1.41
COOMe
COOMe
H
O
1h
1.00
1.06
1.03
1.04
2.07
1.00
3.00
2.94
1.04
1.06
1.06
1.10
1.12
f1 (ppm)
193.81
170.33
168.63
149.55
139.43
132.69
131.38
130.46
129.91
127.46
127.21
77.47
77.16
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31.32
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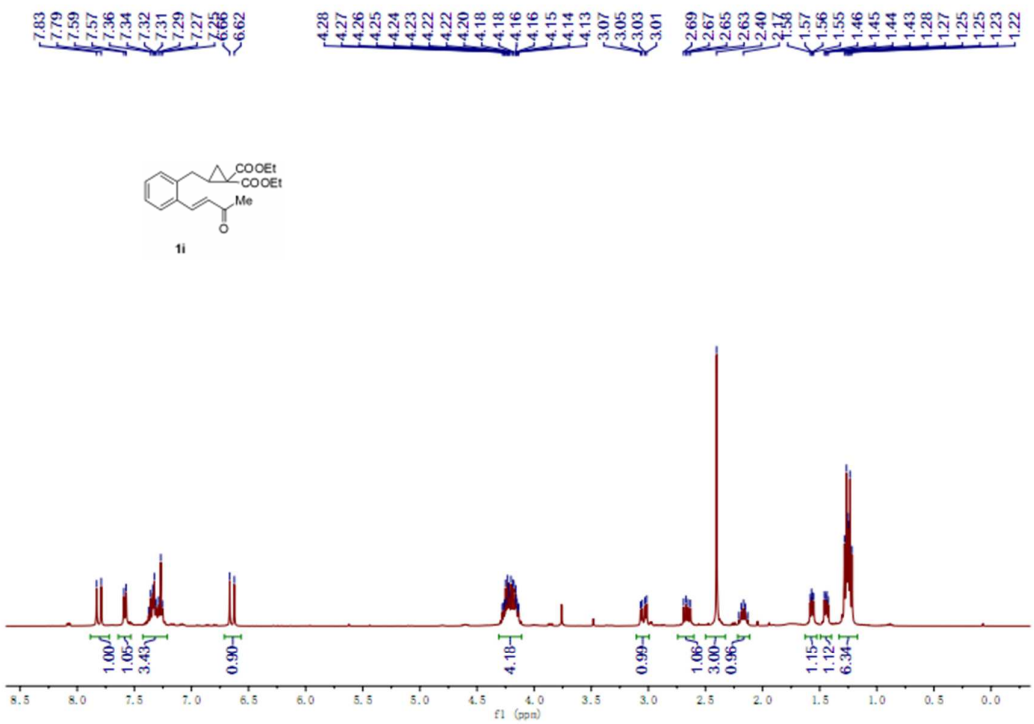
COOMe
COOMe
H
O
1h
f1 (ppm)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7.25
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6.62
4.28
4.27
4.26
4.25
4.24
4.23
4.22
4.22
4.20
4.18
4.18
4.16
4.16
4.15
4.14
4.13
3.07
3.05
3.03
3.01
2.69
2.67
2.65
2.63
2.40
2.17
1.58
1.57
1.56
1.55
1.46
1.45
1.44
1.43
1.28
1.27
1.25
1.25
1.23
1.22
COOEt
COOEt
Me
O
1i
1.00
1.05
3.43
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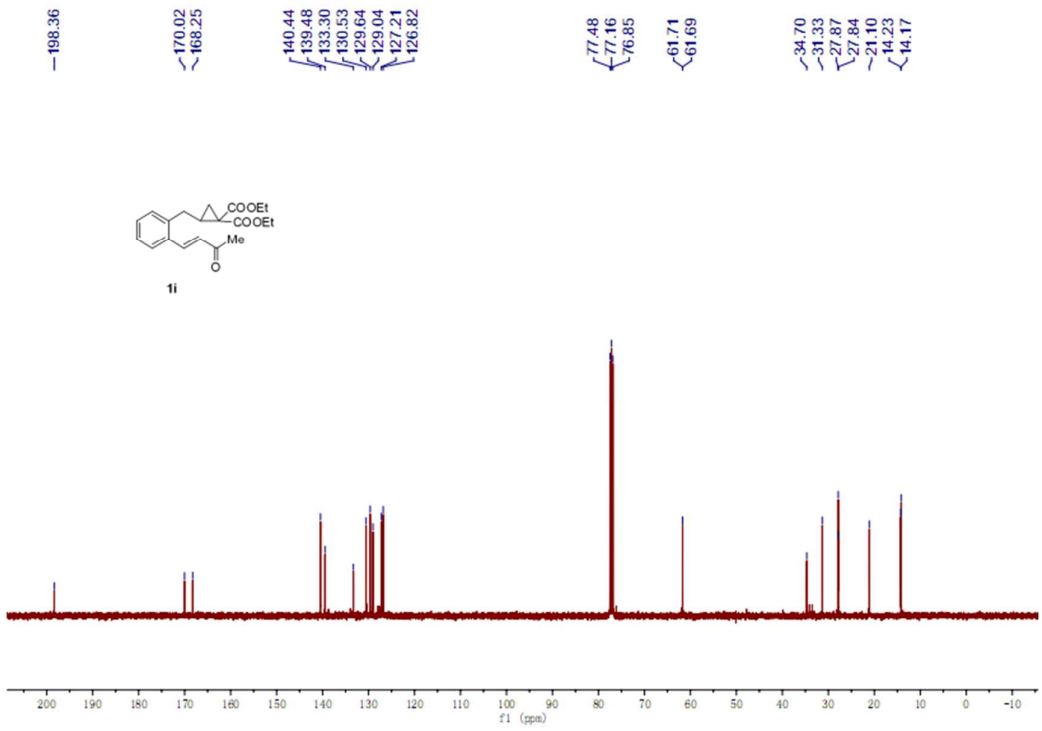
4.18
0.99
1.06
3.00
0.96
1.15
1.12
6.34
f1 (ppm)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129.64
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127.21
126.82
77.48
77.16
76.85
61.71
61.69
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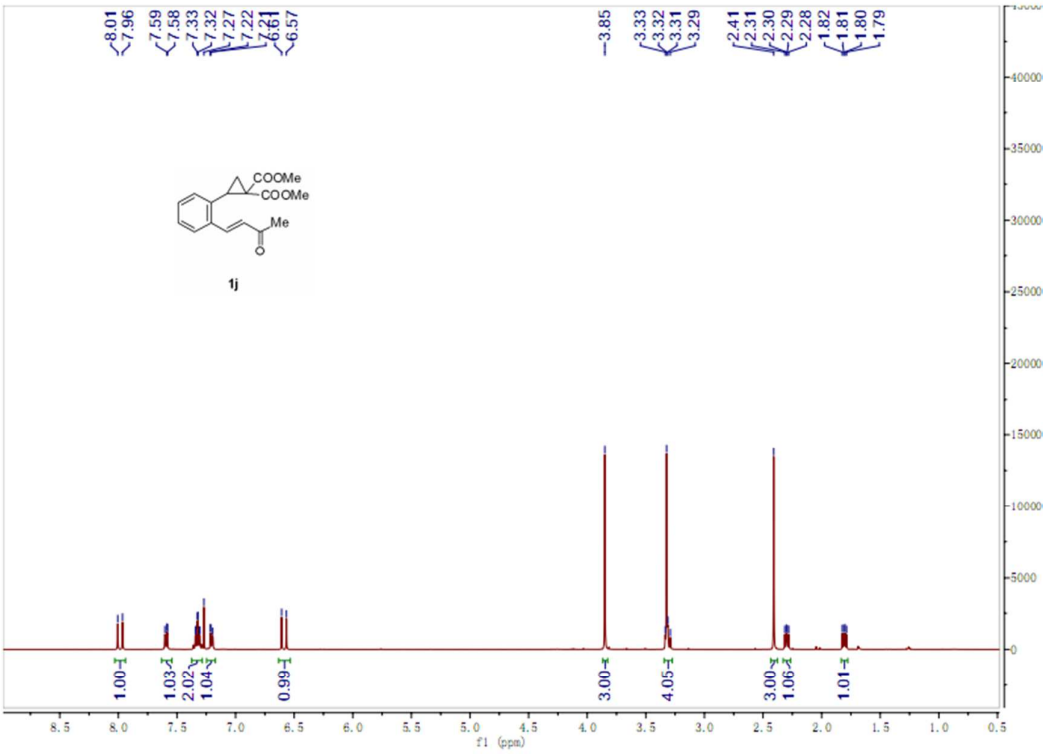
27.84
21.10
14.23
14.17
COOEt
COOEt
Me
O
1i
f1 (ppm)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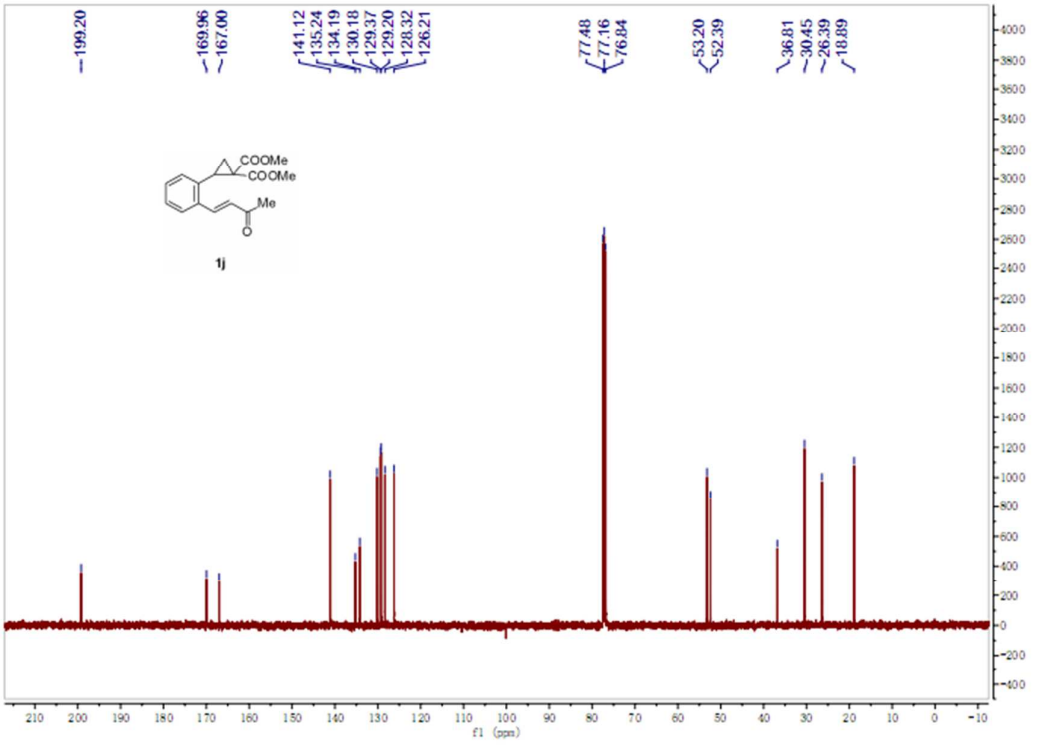
7.59
7.58
7.33
7.32
7.27
7.22
6.61
6.57
3.85
3.33
3.32
3.31
3.29
2.41
2.31
2.30
2.29
2.28
1.82
1.81
1.80
1.79
COOMe
COOMe
Me
1j
1.00
1.03
2.02
1.04
0.99
3.00
4.05
3.00
1.06
1.01
f1 (ppm)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129.37
129.20
128.32
126.21
77.48
77.16
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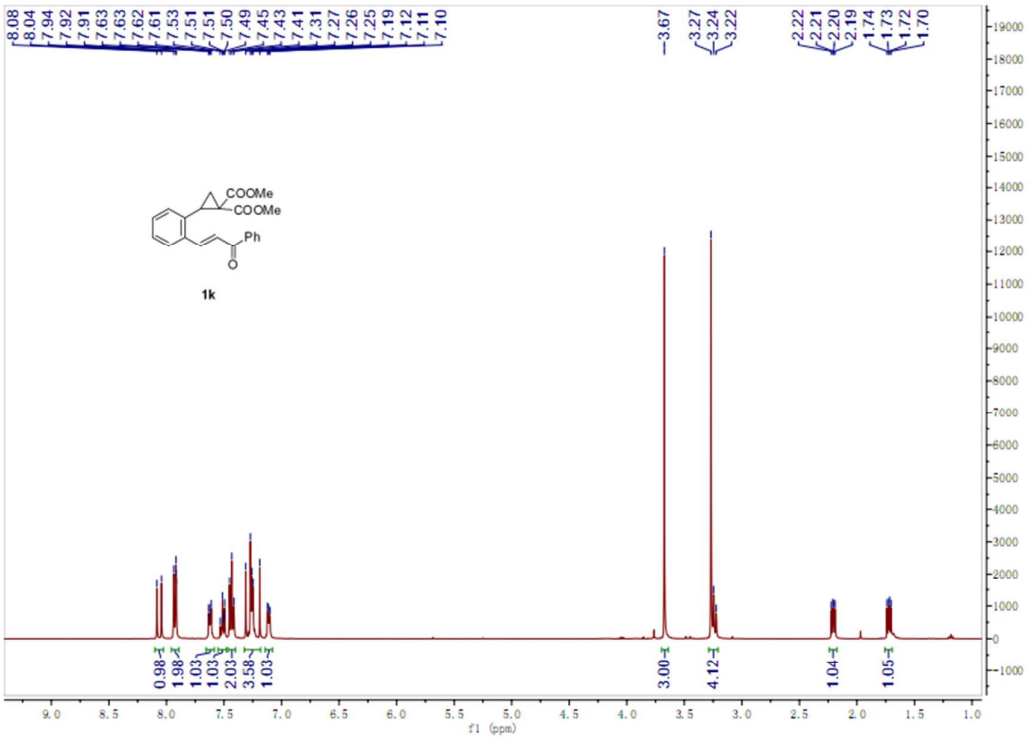
53.20
52.39
36.81
30.45
26.39
18.89
COOMe
COOMe
Me
1j
f1 (ppm)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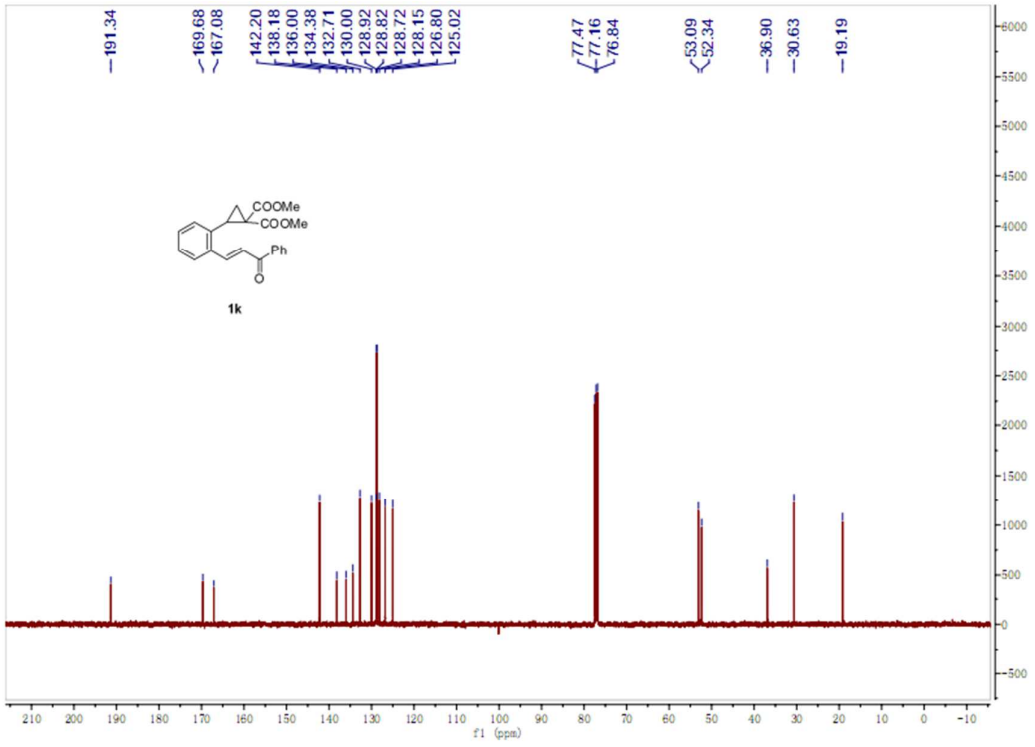
7.63
7.62
7.61
7.53
7.51
7.51
7.50
7.49
7.45
7.43
7.41
7.31
7.27
7.26
7.25
7.19
7.12
7.11
7.10
3.67
3.27
3.24
3.22
2.22
2.21
2.20
2.19
1.74
1.73
1.72
1.70
COOMe
COOMe
Ph
O
1k
0.98
1.98
1.03
1.03
2.03
3.58
1.03
3.00
4.12
1.04
1.05
f1 (ppm)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128.82
128.72
128.15
126.80
125.02
77.47
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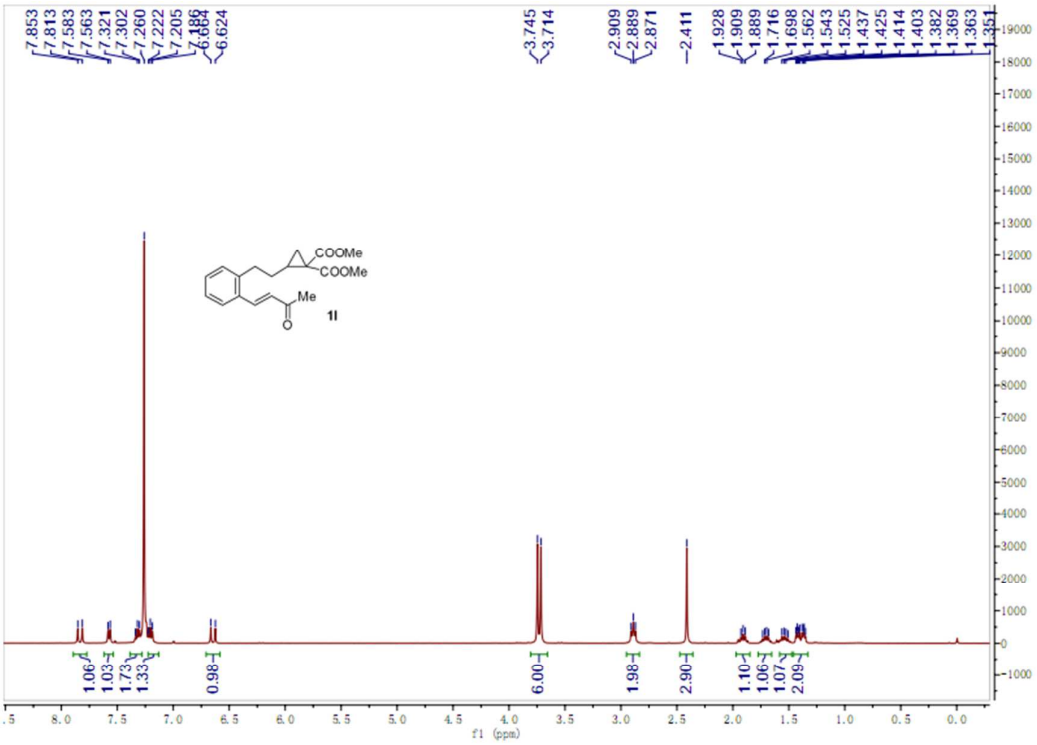
52.34
36.90
30.63
19.19
COOMe
COOMe
Ph
O
1k
f1 (ppm)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2.889
2.871
2.411
1.928
1.909
1.889
1.716
1.698
1.562
1.543
1.525
1.437
1.425
1.414
1.403
1.382
1.369
1.363
1.351
COOMe
COOMe
Me
1l
1.06
1.03
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1.98
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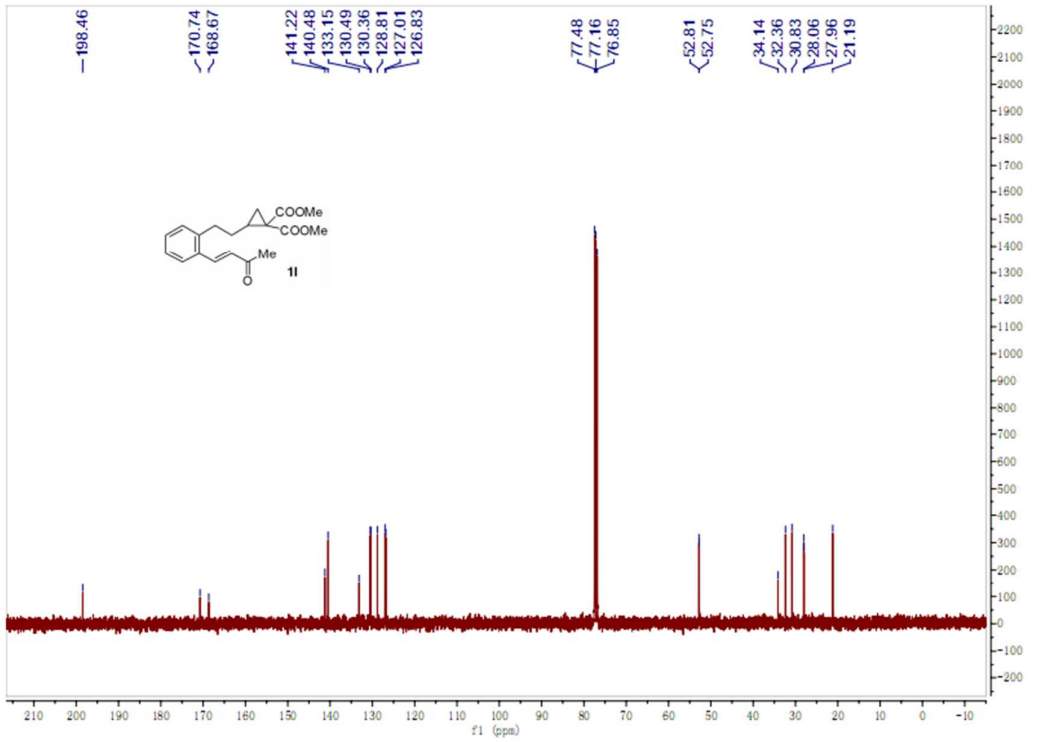
1.10
1.06
1.07
2.09
f1 (ppm)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77.16
76.85
52.81
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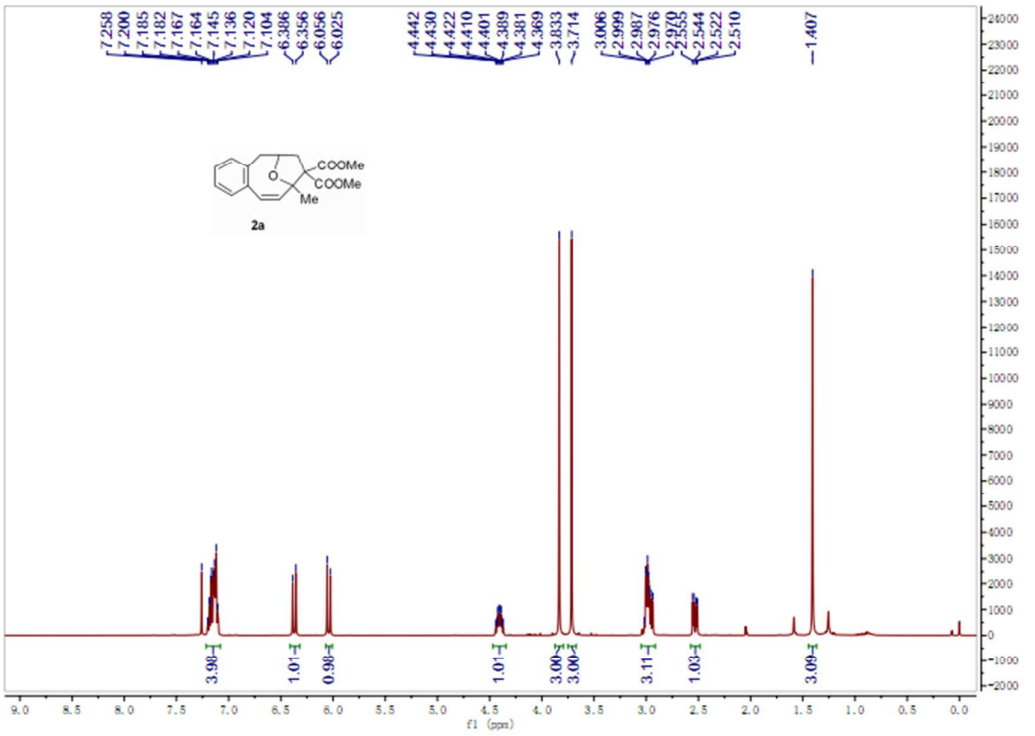
30.83
28.06
27.96
21.19
COOMe
COOMe
Me
1l
f1 (ppm)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6.056
6.025
4.442
4.430
4.422
4.410
4.401
4.389
4.381
4.369
3.833
3.714
3.006
2.999
2.987
2.976
2.970
2.555
2.544
2.522
2.510
1.407
COOMe
COOMe
Me
2a
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3.00
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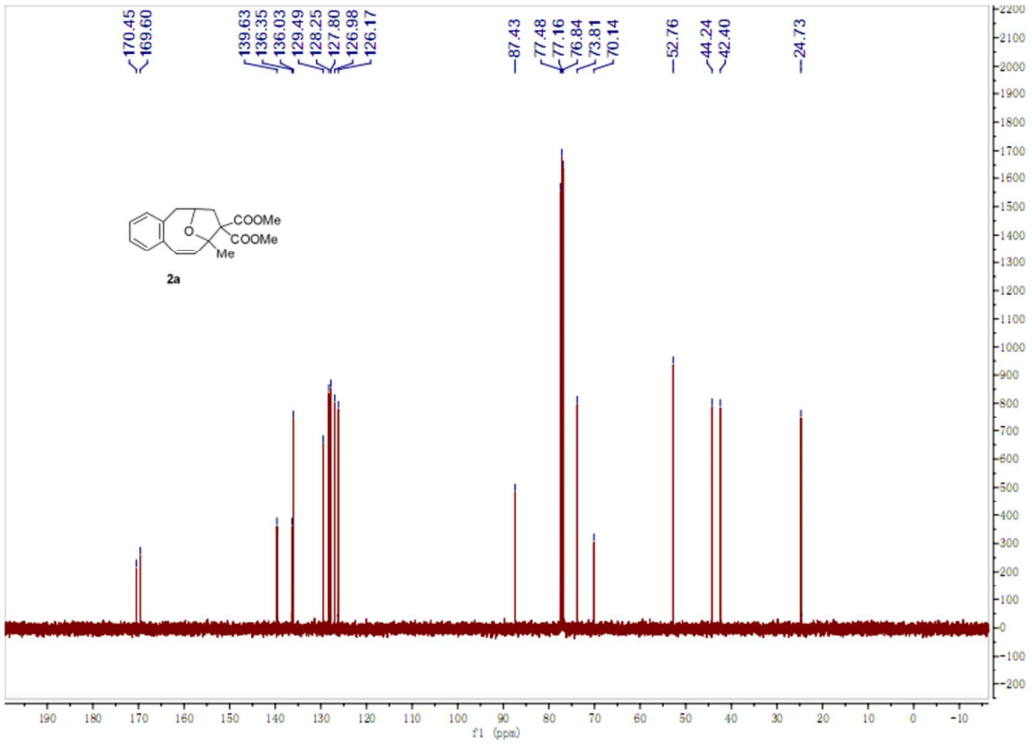
1.03
3.09
f1 (ppm)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77.16
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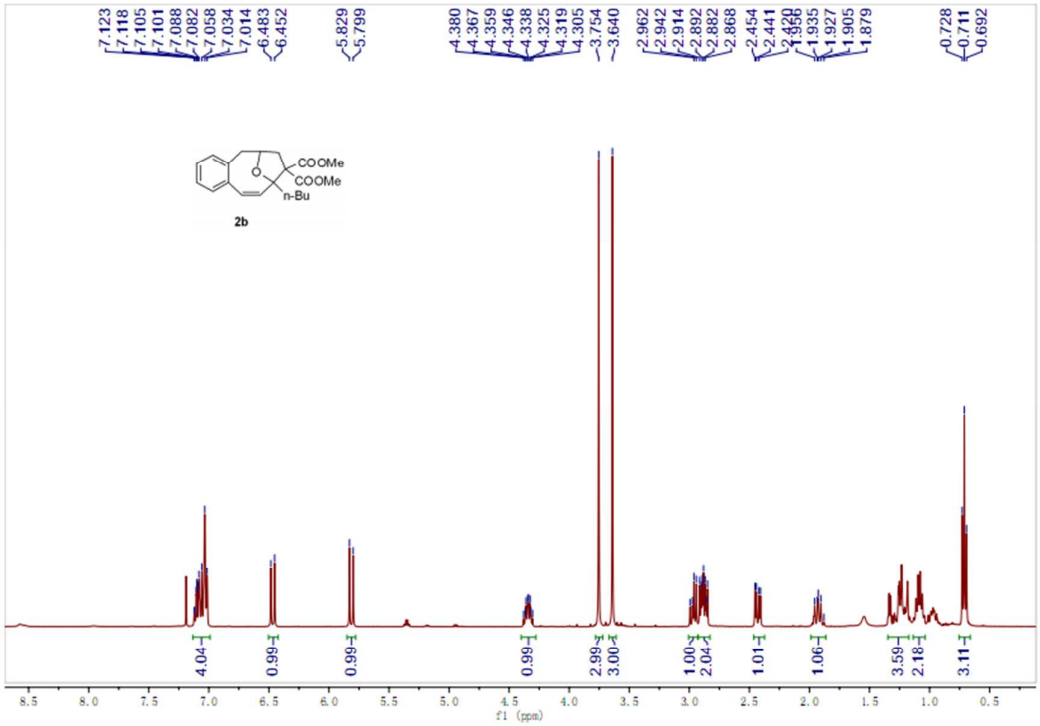
52.76
44.24
42.40
24.73
COOMe
COOMe
Me
2a
f1 (ppm)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5.799
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4.346
4.338
4.325
4.319
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3.640
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2.942
2.914
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2.868
2.454
2.441
1.935
1.927
1.905
1.879
0.728
0.711
0.692
COOMe
COOMe
n-Bu
2b
4.04
0.99
0.99
0.99
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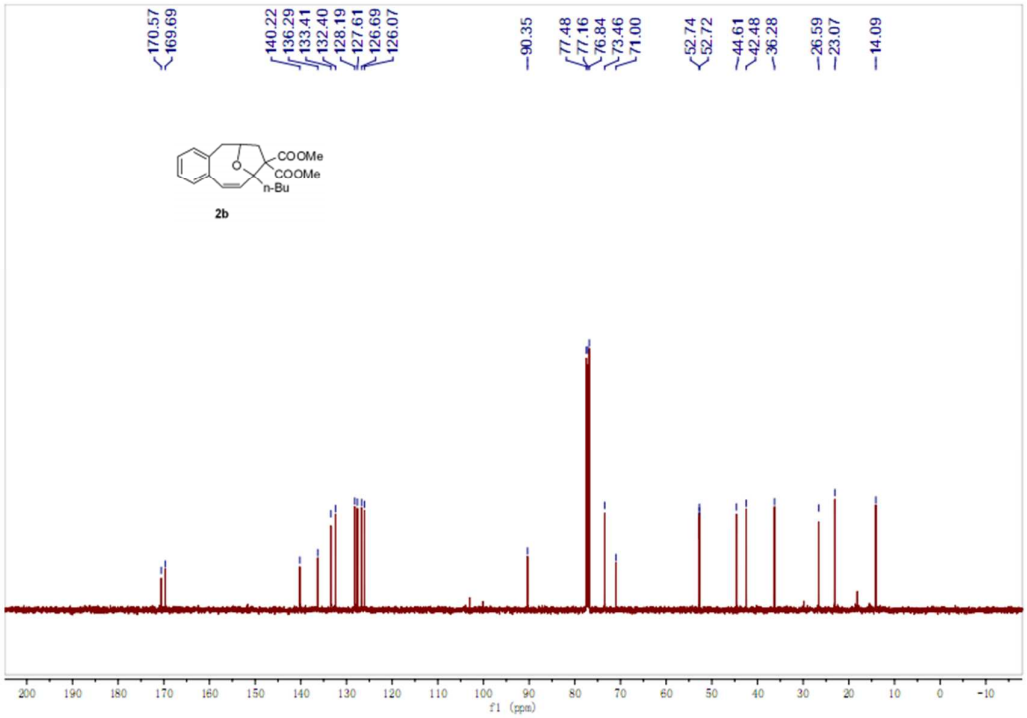
3.00
1.00
2.04
1.01
1.06
3.59
2.18
3.11
f1 (ppm)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127.61
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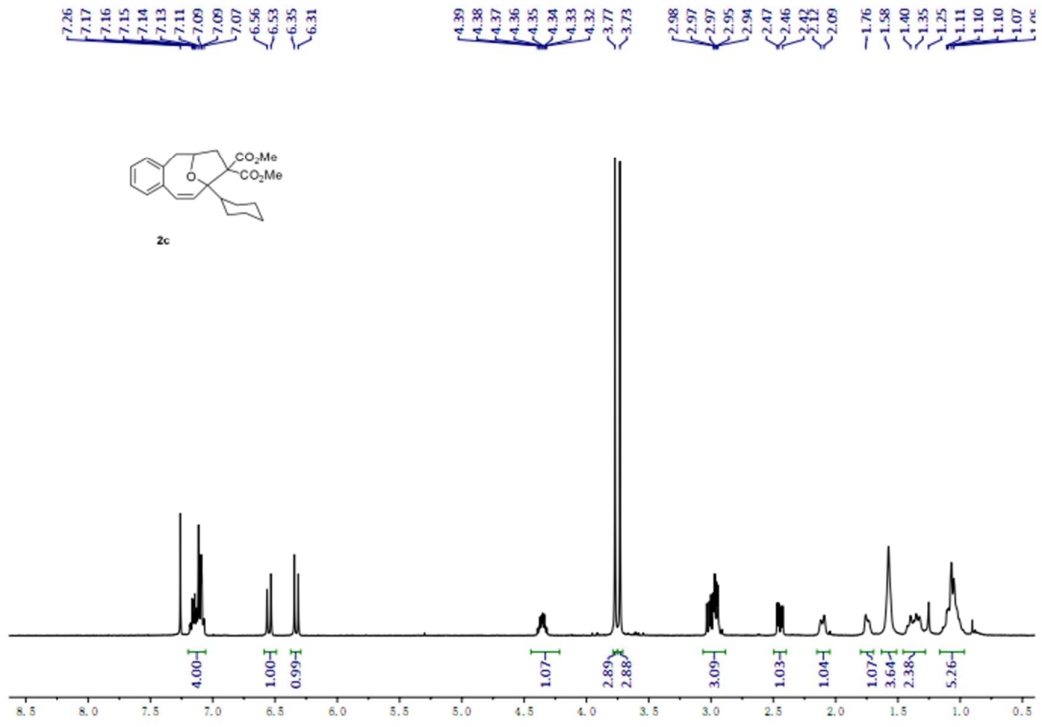
77.16
76.84
73.46
71.00
52.74
52.72
44.61
42.48
36.28
26.59
23.07
14.09
COOMe
COOMe
n-Bu
2b
f1 (ppm)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6.31
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4.38
4.37
4.36
4.35
4.34
4.33
4.32
3.77
3.73
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2.97
2.97
2.95
2.94
2.47
2.46
2.12
2.09
1.76
1.58
1.40
1.35
1.25
1.11
1.10
1.07
CO2Me
CO2Me
O
2c
4.00
1.00
0.99
1.07
2.89
2.88
3.09
1.03
1.04
1.07
3.64
2.38
5.26
8.5
8.0
7.5
7.0
6.5
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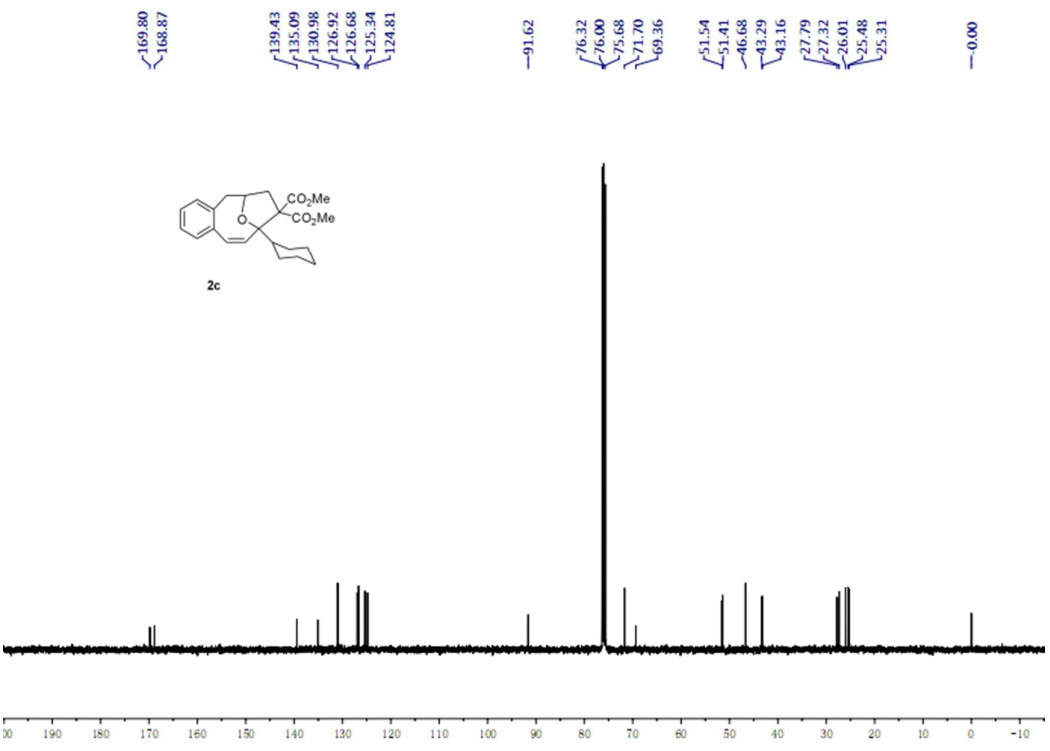
1.0
0.5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76.00
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71.70
69.36
51.54
51.41
46.68
43.29
43.16
27.79
27.32
26.01
25.48
25.31
0.00
CO2Me
CO2Me
O
2c
190
180
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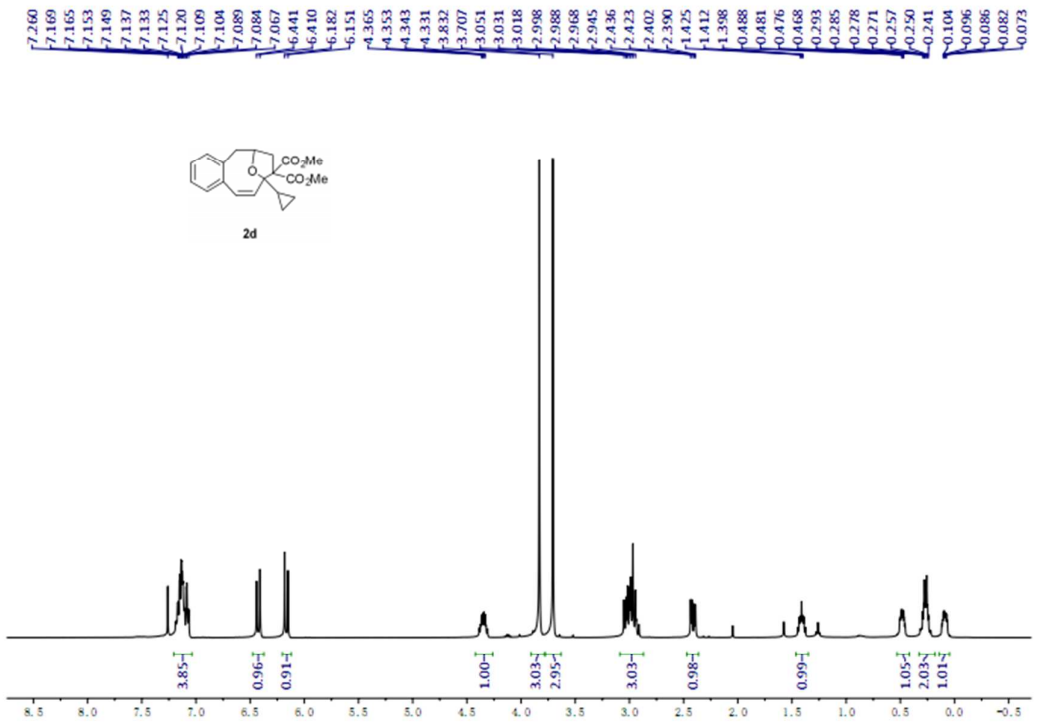
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10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7.125
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7.104
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7.084
7.067
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6.410
6.182
6.151
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4.353
4.343
4.331
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3.707
3.051
3.031
3.018
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2.988
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1.412
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0.285
0.278
0.271
0.257
0.250
0.241
0.104
0.096
0.086
0.082
0.073
CO2Me
CO2Me
2d
3.85
0.96
0.91
1.00
3.03
2.95
3.03
0.98
0.99
1.05
2.03
1.01
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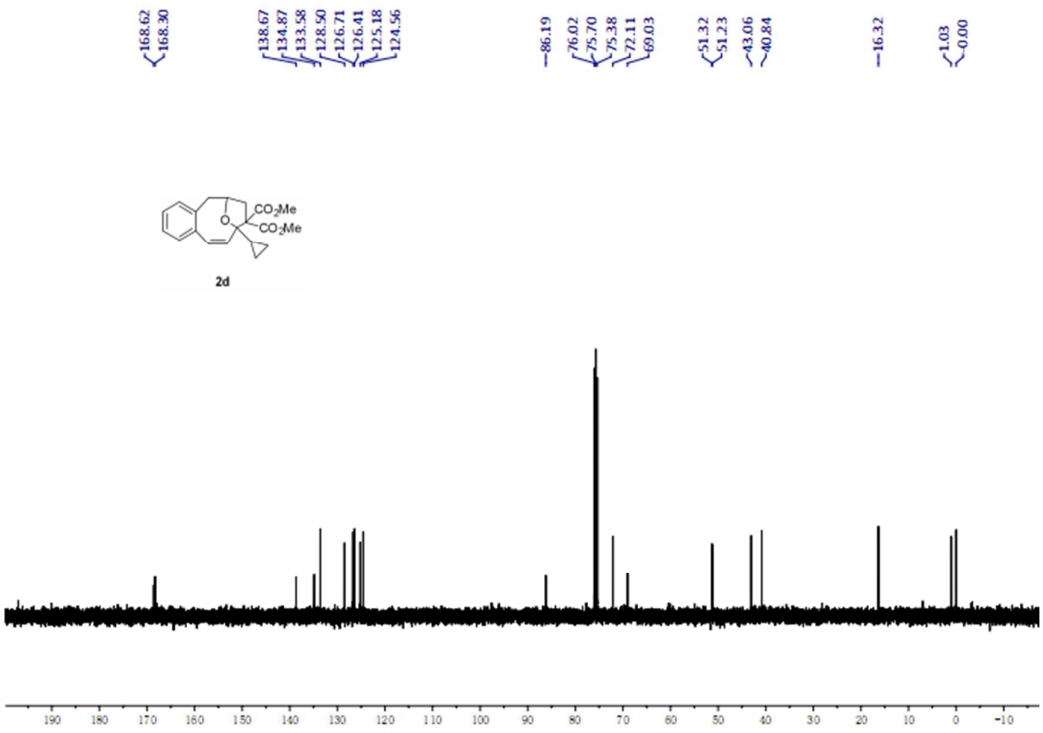
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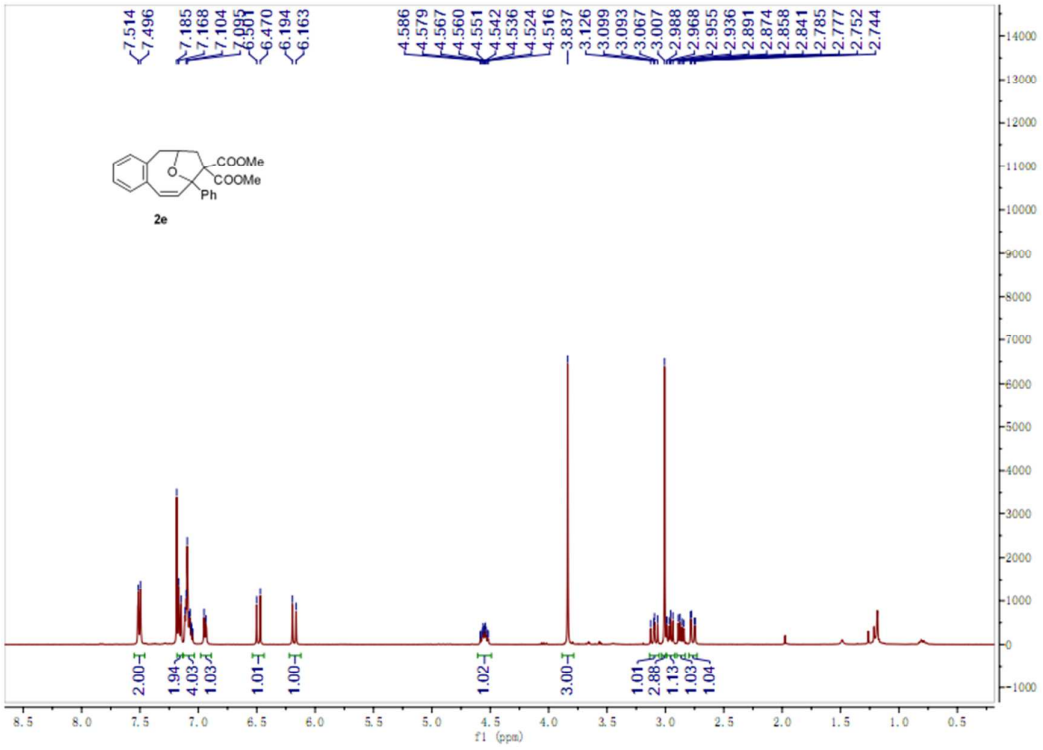
75.70
75.38
72.11
69.03
51.32
51.23
43.06
40.84
16.32
1.03
0.00
CO2Me
CO2Me
2d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10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6.163
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4.542
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4.524
4.516
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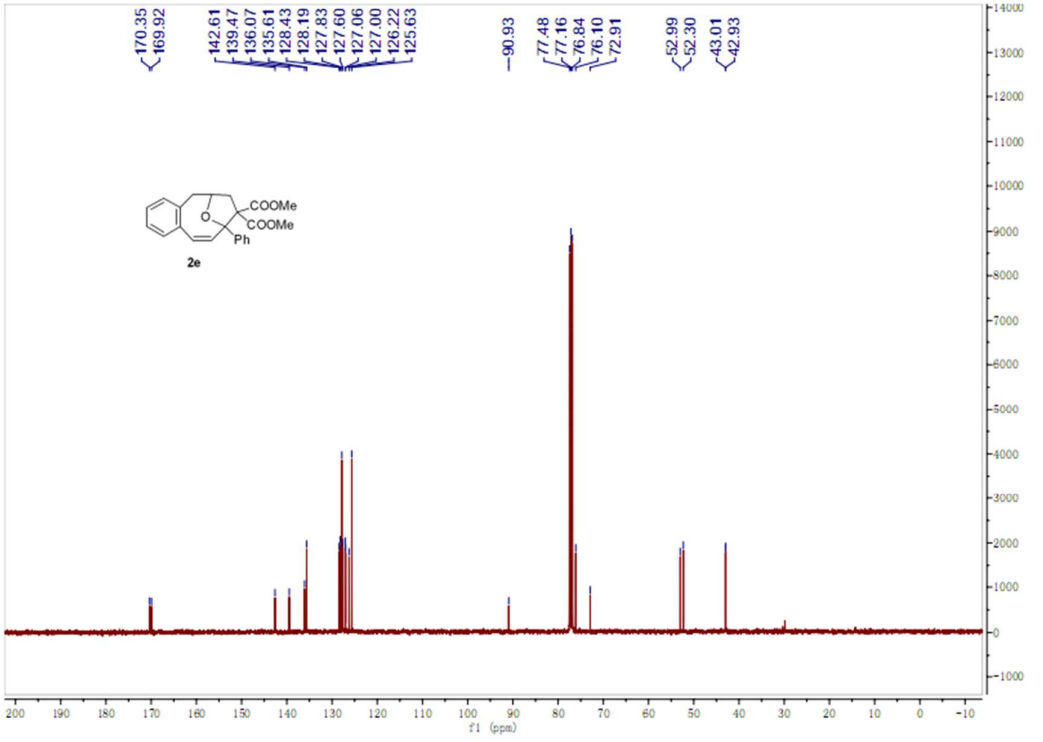
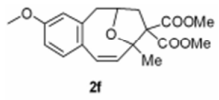
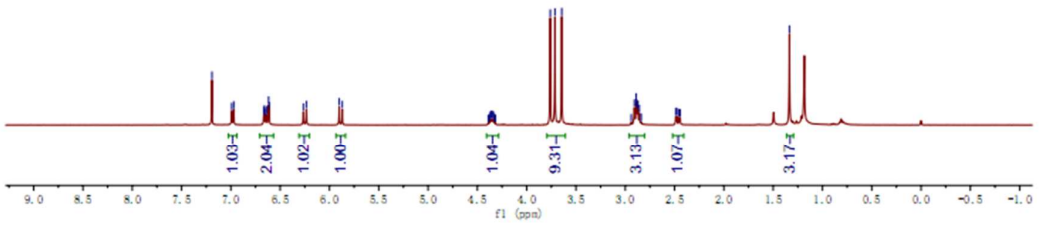
2.858
2.841
2.785
2.777
2.752
2.744
COOMe
COOMe
Ph
2e
2.00
1.94
4.03
1.03
1.01
1.00
1.02
3.00
1.01
2.88
1.13
1.03
1.04
f1 (ppm)


170.35
169.92
142.61
139.47
136.07
135.61
128.43
128.19
127.83
127.60
127.06
127.00
126.22
125.63
90.93
77.48
77.16
76.84
76.10
72.91
52.99
52.30
43.01
42.93
COOMe
COOMe
Ph
2e
f1 (ppm)

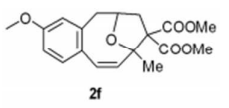

7.192
6.991
6.970
6.667
6.660
6.646
6.640
6.617
6.611
6.264
6.234
5.901
5.870
4.378
4.370
4.358
4.348
4.336
4.328
3.713
3.644
2.908
2.890
2.884
2.876
2.871
2.857
2.839
2.488
2.477
2.455


COOMe
COOMe
Me

2f

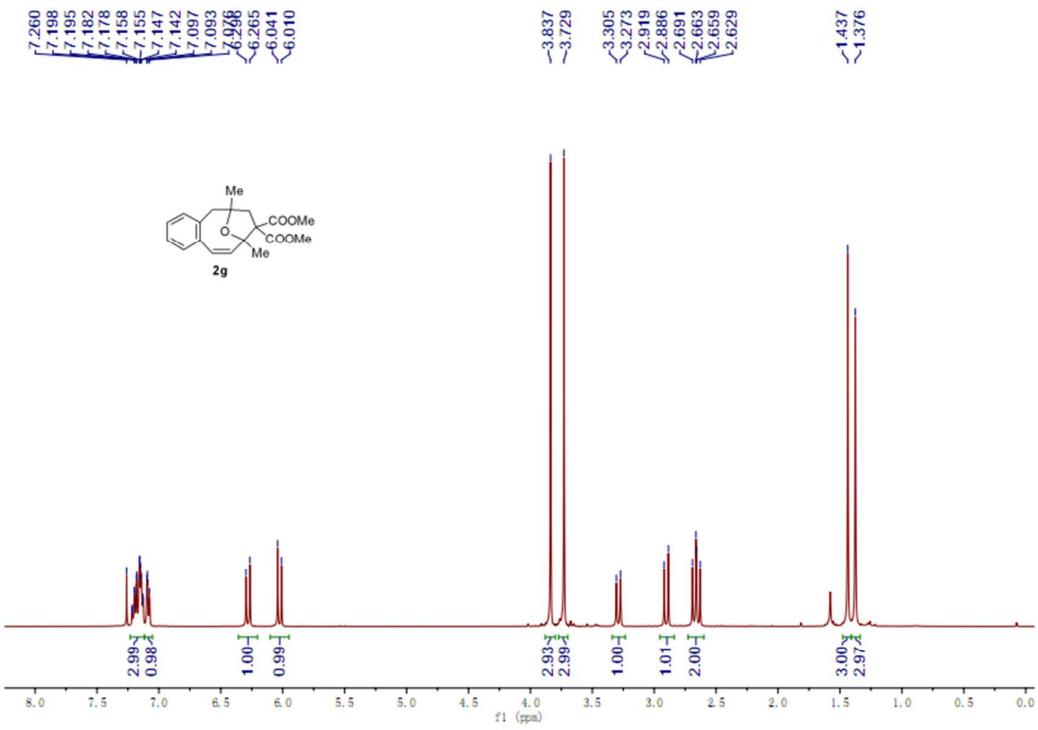

1.03
2.04
1.02
1.00
1.04
9.31
3.13
1.07
3.17
f1 (ppm)


170.513
169.646
158.507
137.870
135.126
132.102
129.087
129.024
114.174
111.276
87.534
77.478
77.162
76.846
73.831
70.093
55.334
52.752
44.456
42.425
24.894


COOMe
COOMe
Me

2f

f1 (ppm)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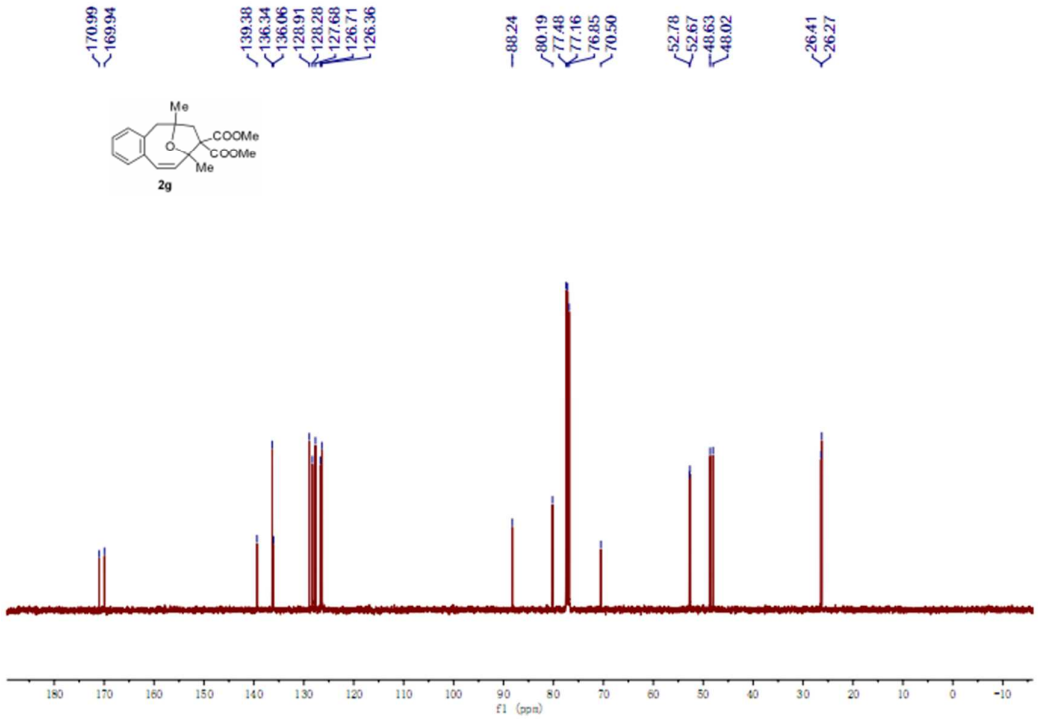
7.198
7.195
7.182
7.178
7.158
7.155
7.147
7.142
7.097
7.093
6.265
6.041
6.010
3.837
3.729
3.305
3.273
2.919
2.886
2.691
2.663
2.659
2.629
1.437
1.376
Me
COOMe
COOMe
Me
2g
2.99
0.98
1.00
0.99
2.93
2.99
1.00
1.01
2.00
3.00
2.97
f1 (ppm)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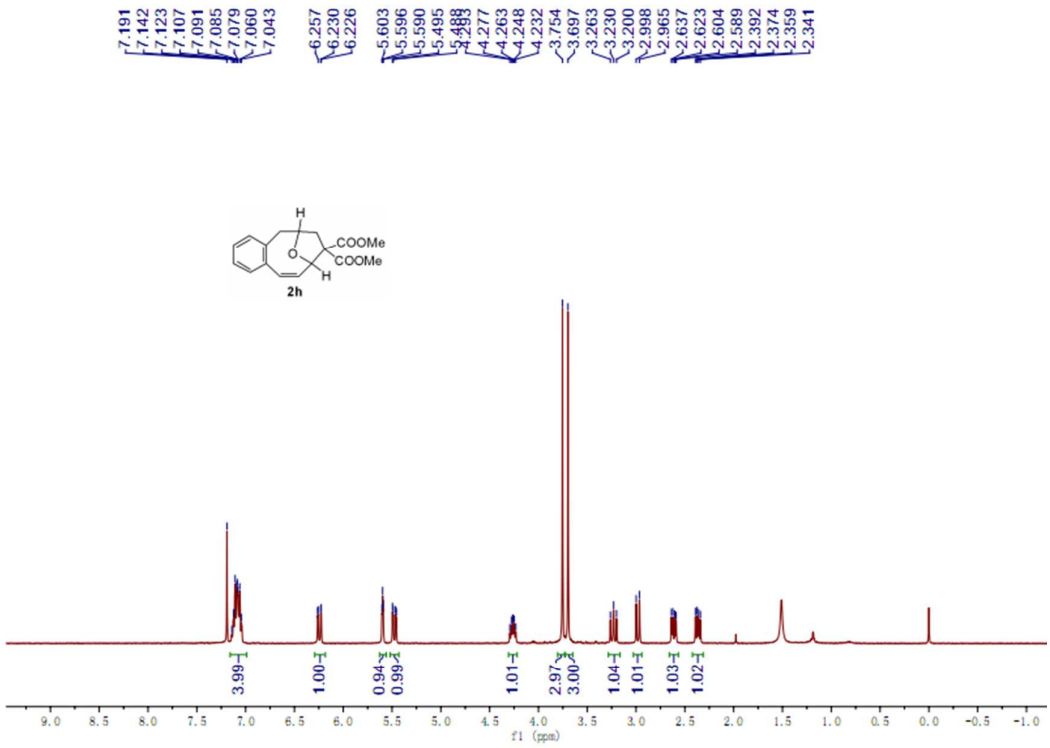
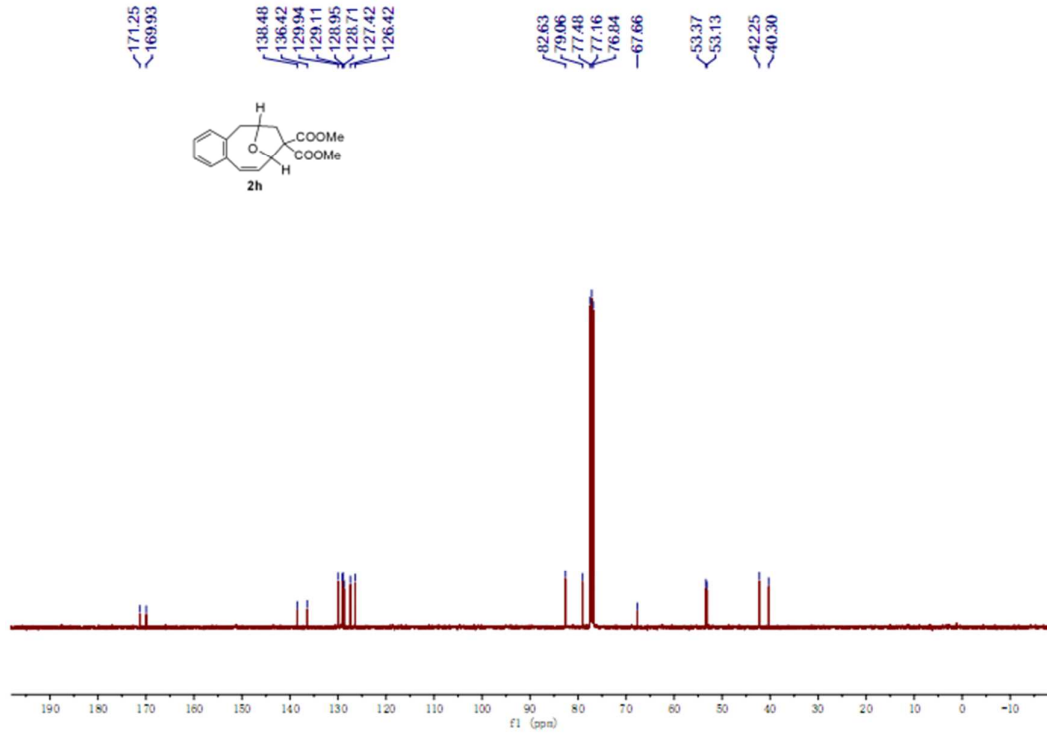
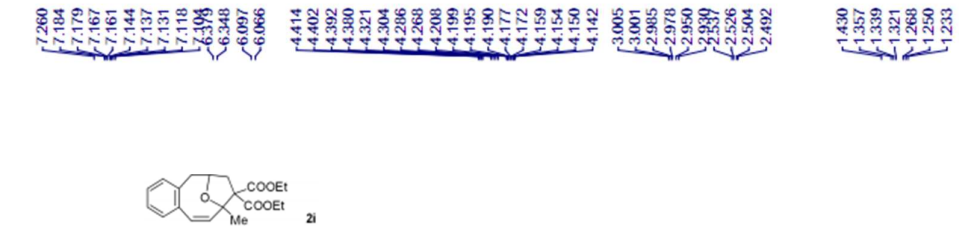
169.94
139.38
136.34
136.06
128.91
128.28
127.68
126.71
126.36
88.24
80.19
77.48
77.16
76.85
70.50
52.78
52.67
48.63
48.02
26.41
26.27
Me
COOMe
COOMe
Me
2g
f1 (ppm)

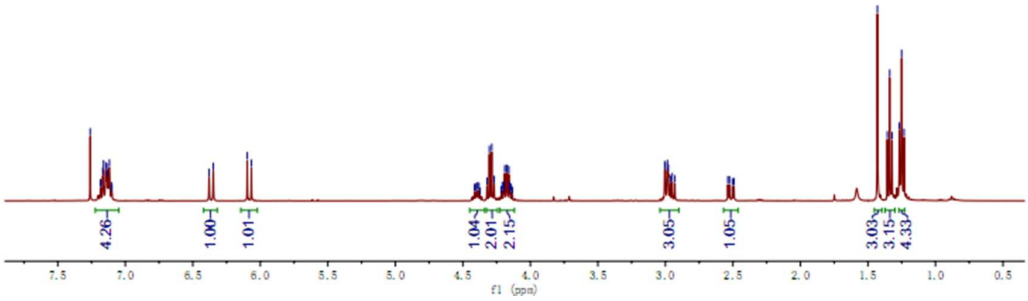

7.191
7.142
7.123
7.107
7.091
7.085
7.079
7.060
7.043
6.257
6.230
6.226
5.603
5.596
5.590
5.495
4.277
4.263
4.248
4.232
3.754
3.697
3.263
3.230
3.200
2.998
2.965
2.637
2.623
2.604
2.589
2.392
2.374
2.359
2.341
COOMe
COOMe
2h
3.99
1.00
0.94
0.99
1.01
2.97
3.00
1.04
1.01
1.03
1.02
f1 (ppm)

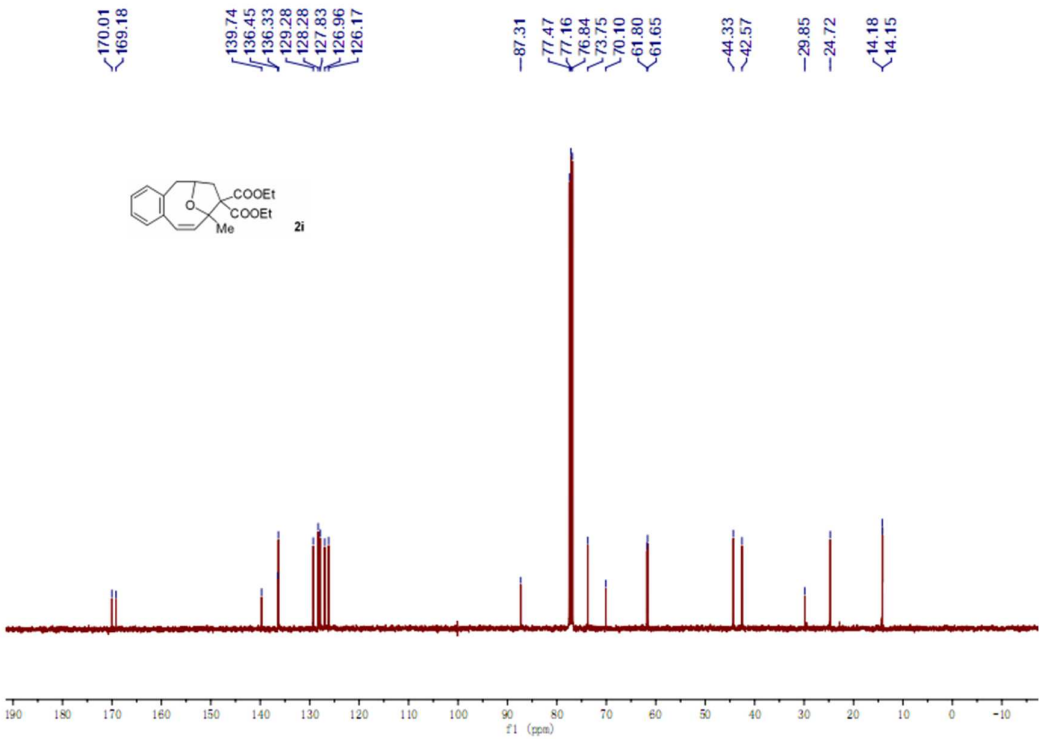

171.25
169.93
138.48
136.42
129.94
129.11
128.95
128.71
127.42
126.42
82.63
79.06
77.48
77.16
76.84
67.66
53.37
53.13
42.25
40.30
COOMe
COOMe
2h
f1 (ppm)


7.260
7.184
7.179
7.167
7.161
7.144
7.137
7.131
7.118
6.348
6.097
6.066
4.414
4.402
4.392
4.380
4.321
4.304
4.286
4.268
4.208
4.199
4.195
4.190
4.177
4.172
4.159
4.154
4.150
4.142
3.005
3.001
2.985
2.978
2.950
2.930
2.526
2.504
2.492
1.430
1.357
1.339
1.321
1.268
1.250
1.233

COOEt
COOEt
Me

2i


4.26
1.00
1.01
1.04
2.01
2.15
3.05
1.05
3.03
3.15
4.33
f1 (ppm)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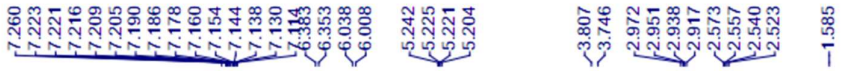
169.18
139.74
136.45
136.33
129.28
128.28
127.83
126.96
126.17
87.31
77.47
77.16
76.84
73.75
70.10
61.80
61.65
44.33
42.57
29.85
24.72
14.18
14.15
f1 (ppm)

COOEt
COOEt
Me

2i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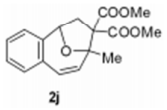
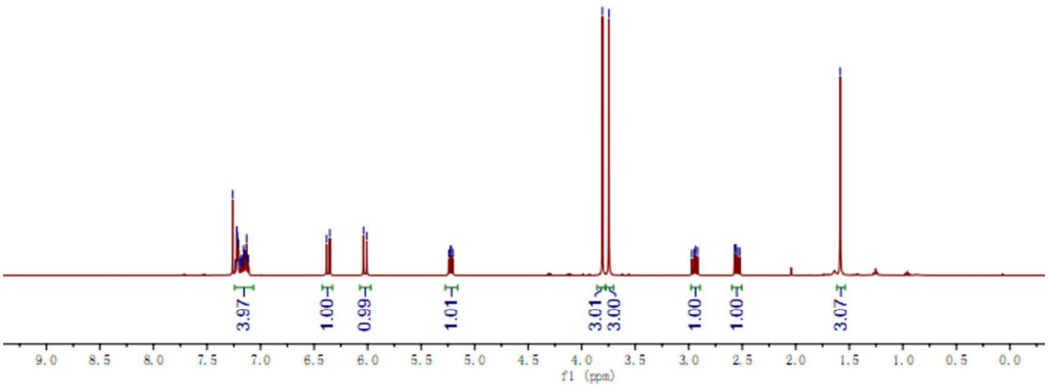
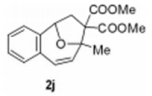
7.223
7.221
7.216
7.209
7.205
7.190
7.186
7.178
7.160
7.154
7.144
7.138
7.130
6.383
6.353
6.038
6.008
5.242
5.225
5.221
5.204
3.807
3.746
2.972
2.951
2.938
2.917
2.573
2.557
2.540
2.523
1.585


COOMe
COOMe
Me

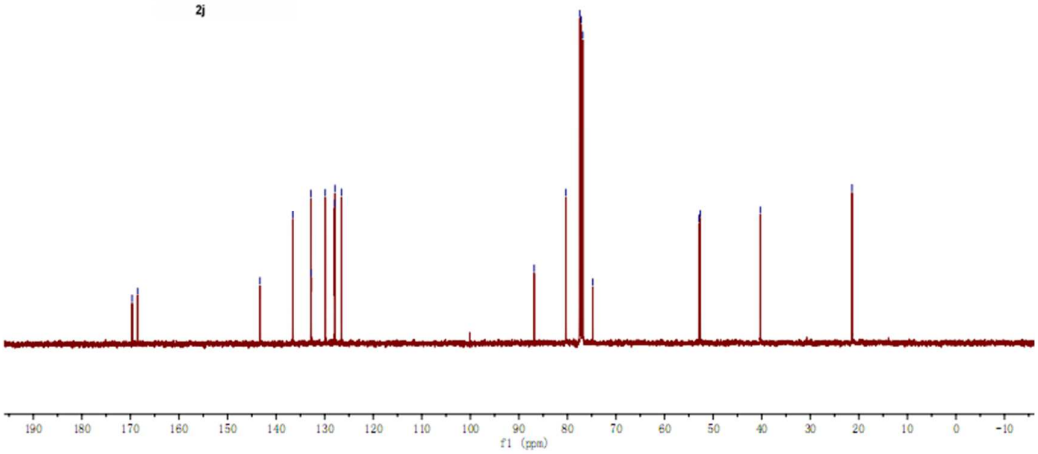
2j

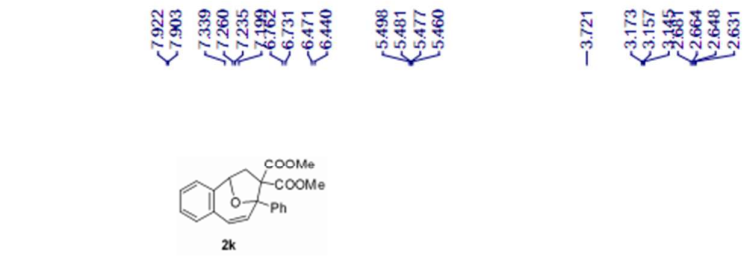

3.97
1.00
0.99
1.01
3.01
3.00
1.00
1.00
3.07
f1 (ppm)


169.66
168.52
143.33
136.56
132.83
132.81
129.89
127.91
127.88
126.54
86.86
80.32
77.48
77.16
76.84
74.79
52.92
52.65
40.28
21.40


COOMe
COOMe
Me

2j


f1 (ppm)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7.903
7.339
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7.235
6.731
6.471
6.440
5.498
5.481
5.477
5.460
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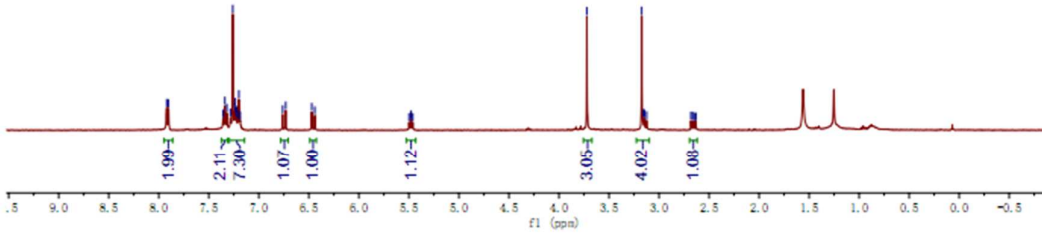
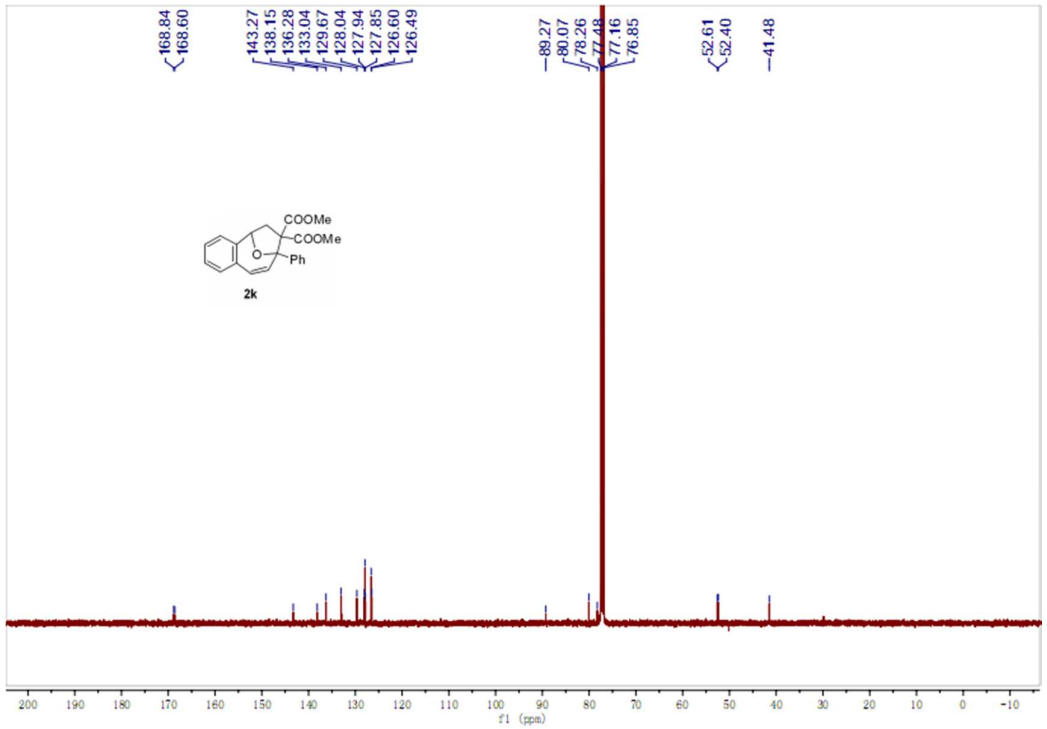
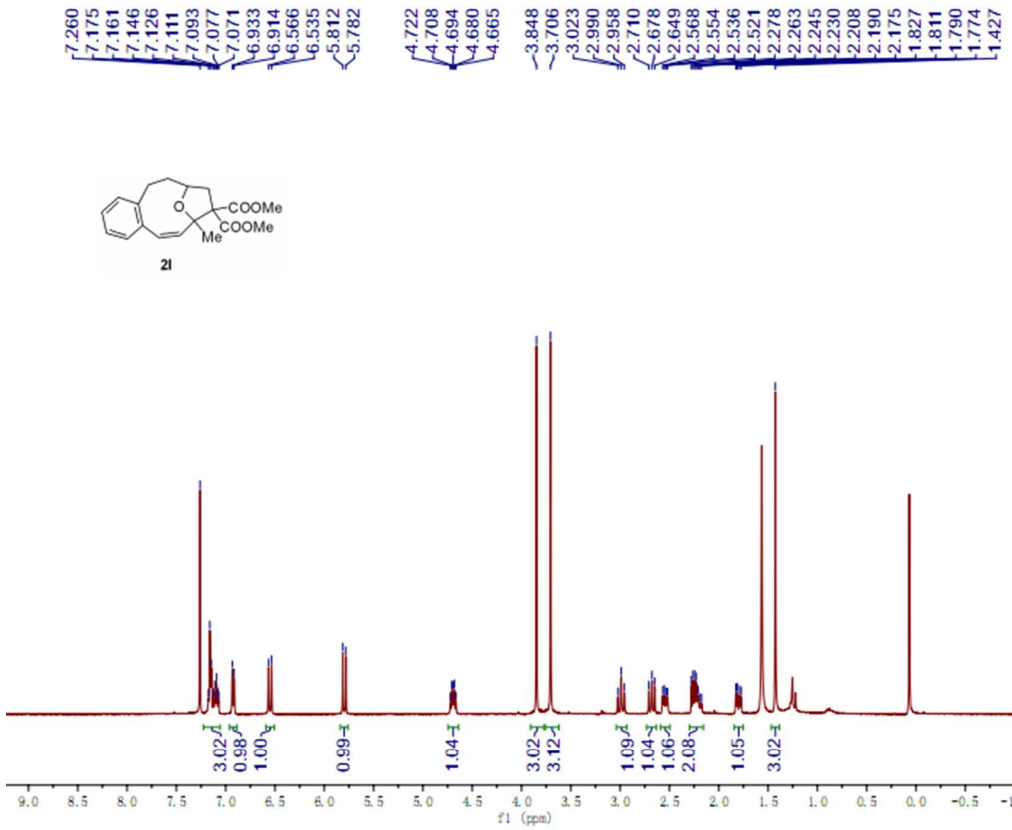
3.173
3.157
2.664
2.648
2.631
COOMe
COOMe
Ph
O
2k


1.99
2.11
7.30
1.07
1.00
1.12
3.05
4.02
1.08
f1 (ppm)


168.84
168.60
143.27
138.15
136.28
133.04
129.67
128.04
127.94
127.85
126.60
126.49
89.27
80.07
78.26
77.48
77.16
76.85
52.61
52.40
41.48
COOMe
COOMe
Ph
O
2k
f1 (ppm)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7.175
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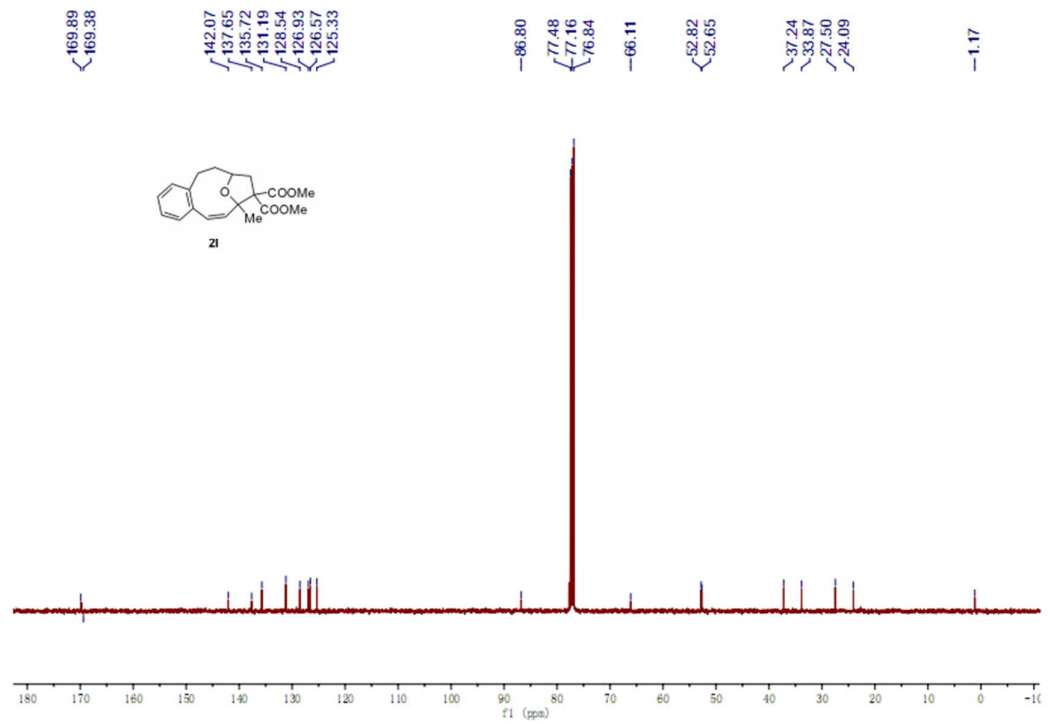
7.126
7.111
7.093
7.077
7.071
6.933
6.914
6.566
6.535
5.812
5.782
4.722
4.708
4.694
4.680
4.665
3.848
3.706
3.023
2.990
2.958
2.710
2.678
2.649
2.568
2.554
2.536
2.521
2.278
2.263
2.245
2.230
2.208
2.190
2.175
1.827
1.811
1.790
1.774
1.427
COOMe
COOMe
Me
2l
3.02
0.98
1.00
0.99
1.04
3.02
3.12
1.09
1.04
1.06
2.08
1.05
3.02
f1 (ppm)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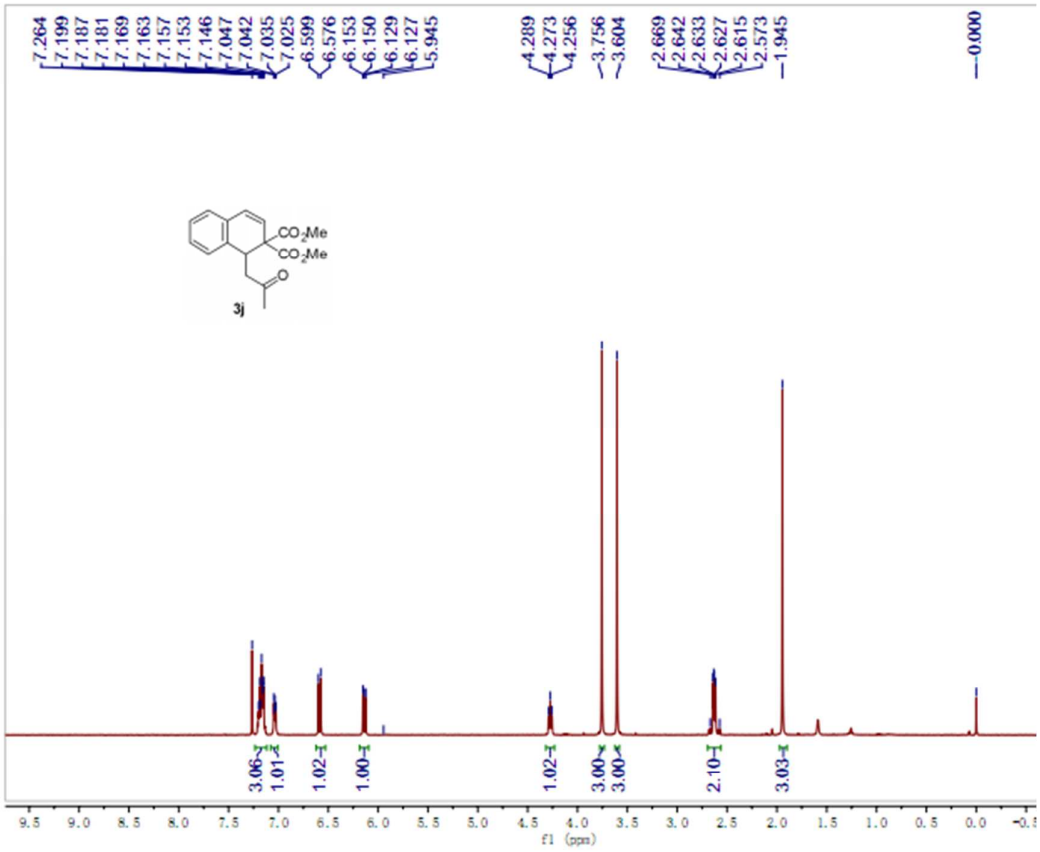
128.54
126.93
126.57
125.33
86.80
77.48
77.16
76.84
66.11
52.82
52.65
37.24
33.87
27.50
24.09
1.17
COOMe
COOMe
Me
2l
f1 (ppm)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7.163
7.157
7.153
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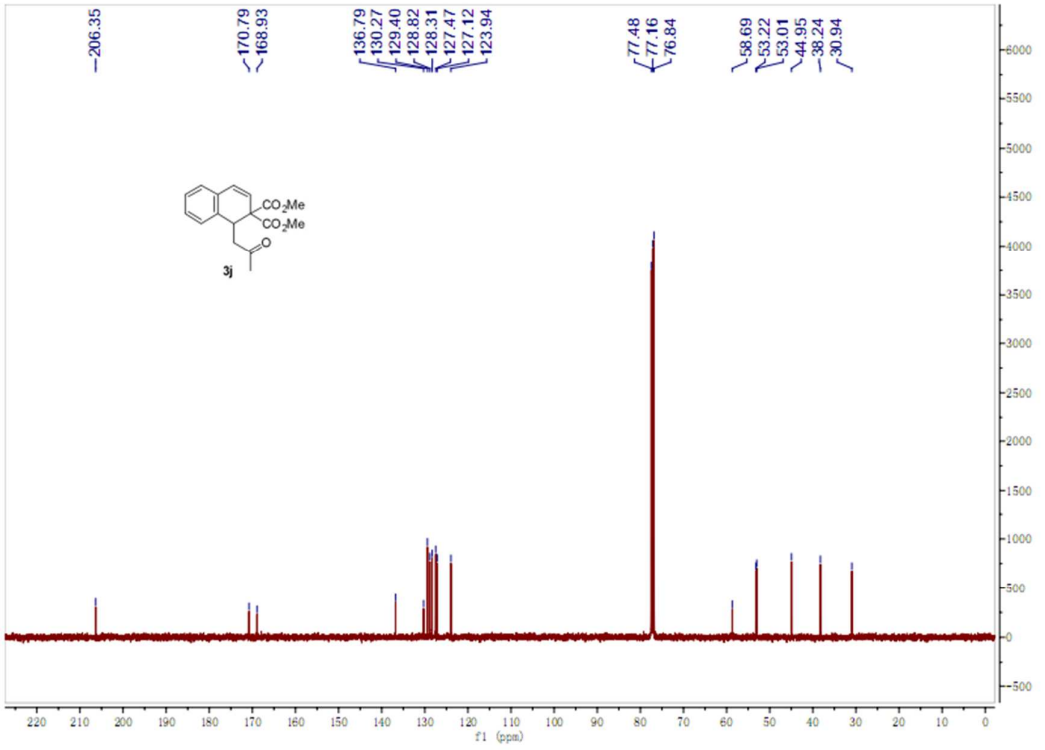
7.047
7.042
7.035
7.025
6.599
6.576
6.153
6.150
6.129
6.127
5.945
4.289
4.273
4.256
3.756
3.604
2.669
2.642
2.633
2.627
2.615
2.573
1.945
0.000
CO2Me
CO2Me
O
3j
3.06
1.01
1.02
1.00
1.02
3.00
3.00
2.10
3.03
f1 (ppm)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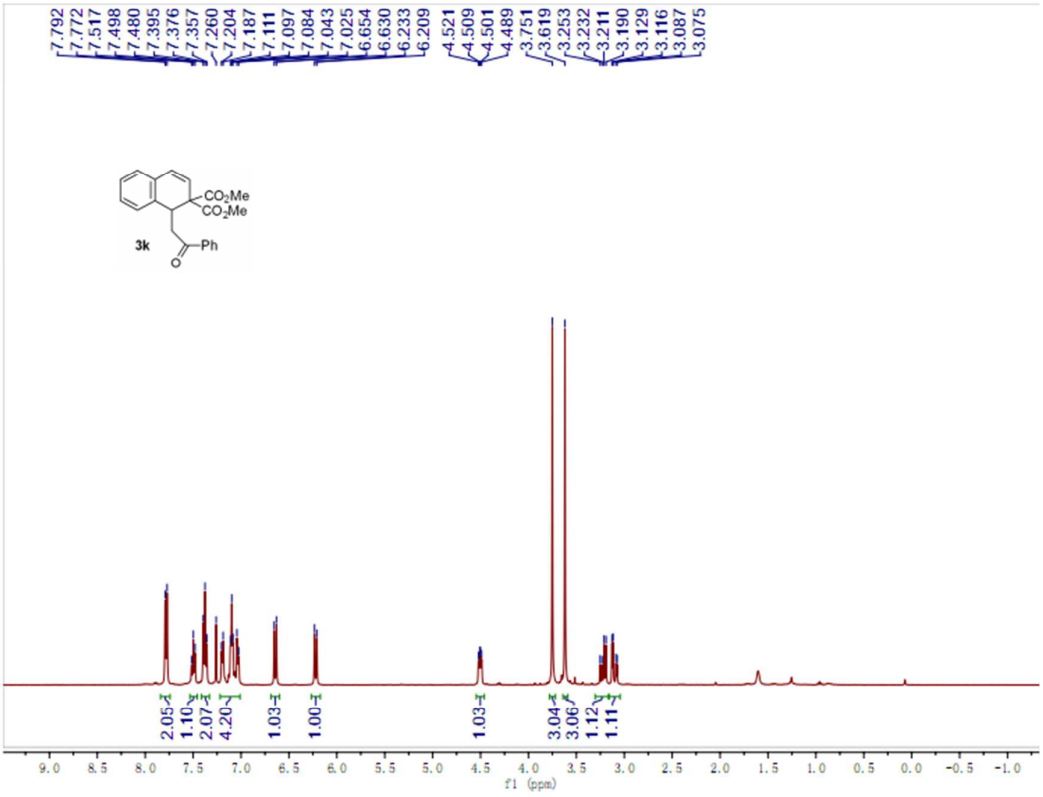
129.40
128.82
128.31
127.47
127.12
123.94
77.48
77.16
76.84
58.69
53.22
53.01
44.95
38.24
30.94
CO2Me
CO2Me
O
3j
f1 (ppm)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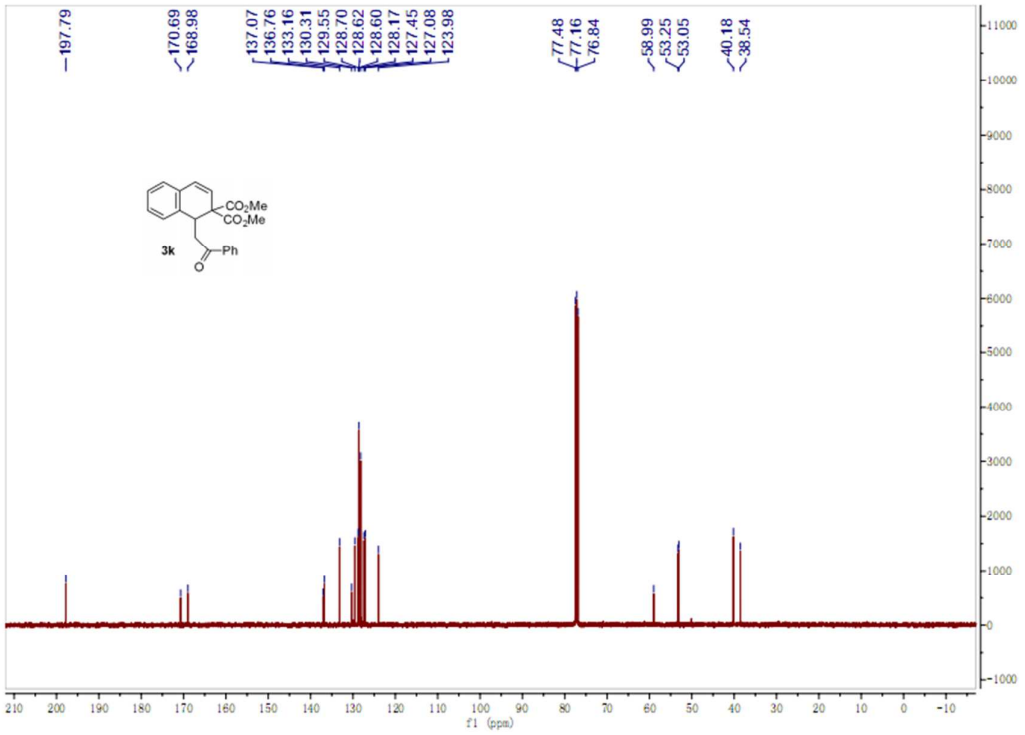
7.772
7.517
7.498
7.480
7.395
7.376
7.357
7.260
7.204
7.187
7.111
7.097
7.084
7.043
7.025
6.654
6.630
6.233
6.209
4.521
4.509
4.501
4.489
3.751
3.619
3.253
3.232
3.211
3.190
3.129
3.116
3.087
3.075
CO2Me
CO2Me
3k
Ph
O
2.05
1.10
2.07
4.20
1.03
1.00
1.03
3.04
3.06
1.12
1.11
f1 (ppm)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129.55
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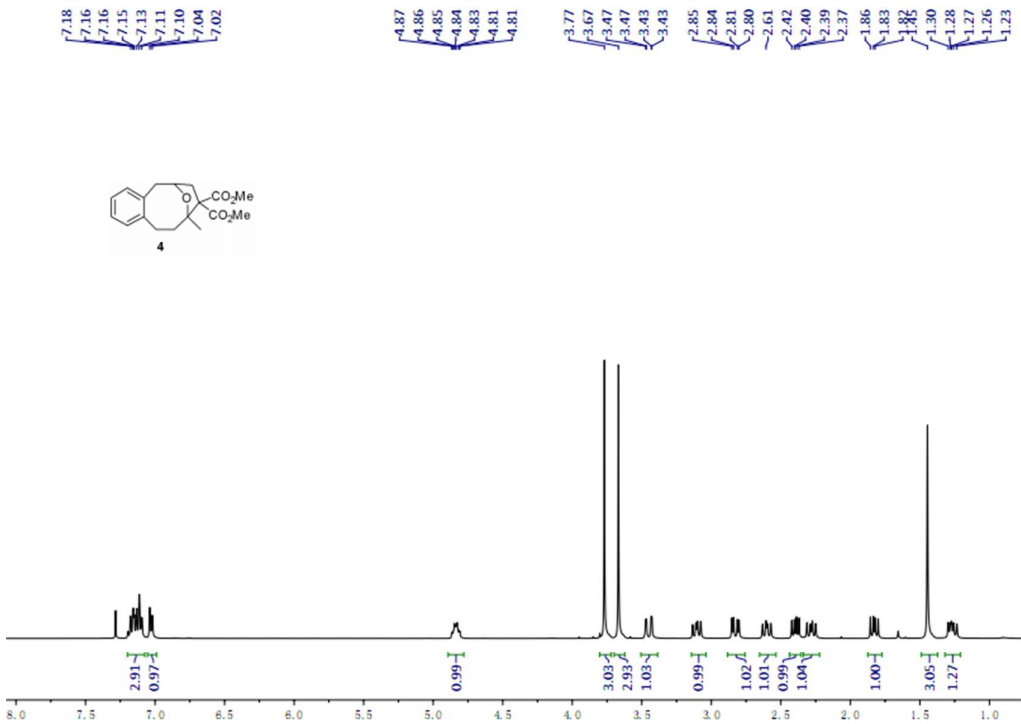
128.62
128.60
128.17
127.45
127.08
123.98
77.48
77.16
76.84
58.99
53.25
53.05
40.18
38.54
CO2Me
CO2Me
3k
Ph
O
f1 (ppm)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7.15
7.13
7.11
7.10
7.04
7.02
4.87
4.86
4.85
4.84
4.83
4.81
4.81
3.77
3.67
3.47
3.47
3.43
3.43
2.85
2.84
2.81
2.80
2.61
2.42
2.40
2.39
2.37
1.86
1.83
1.30
1.28
1.27
1.26
1.23
CO2Me
CO2Me
4
2.91
0.97
0.99
3.03
2.93
1.03
0.99
1.02
1.01
0.99
1.04
1.00
3.05
1.27
8.0
7.5
7.0
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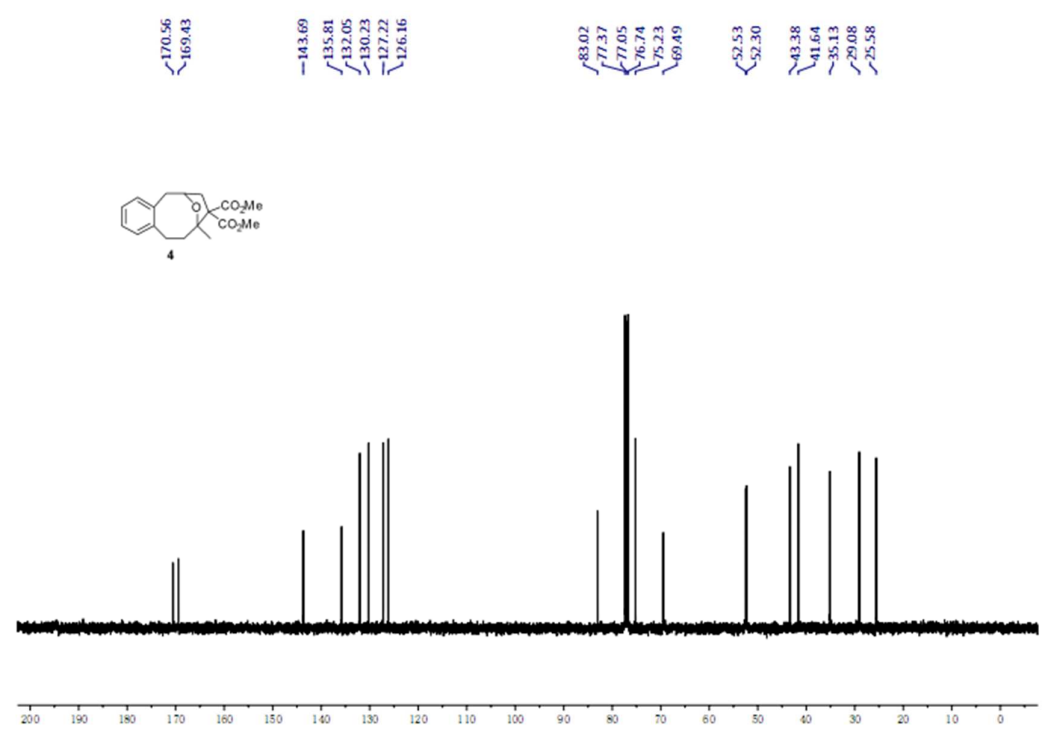
1.5
1.0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130.23
127.22
126.16
83.02
77.37
77.05
76.74
75.23
69.49
52.53
52.30
43.38
41.64
35.13
29.08
25.58
CO2Me
CO2Me
4
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.23
7.21
7.19
7.18
7.04
7.02
5.73
5.72
4.87
4.86
3.77
3.09
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3.04
3.03
2.99
2.97
2.94
2.91
2.90
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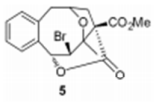
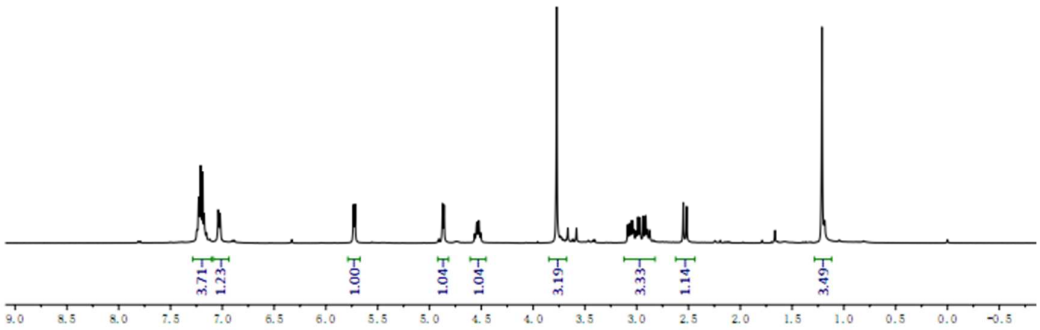
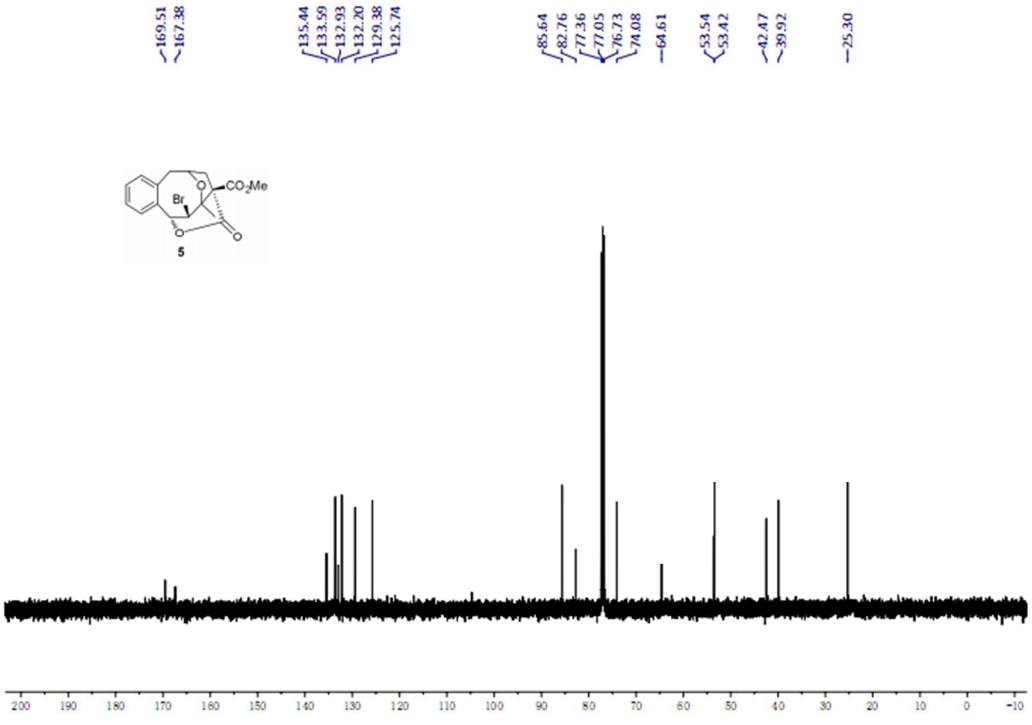
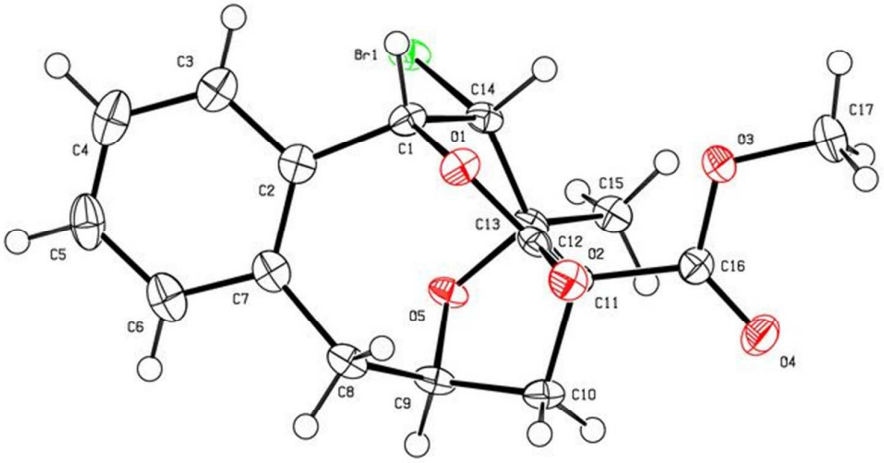
1.21

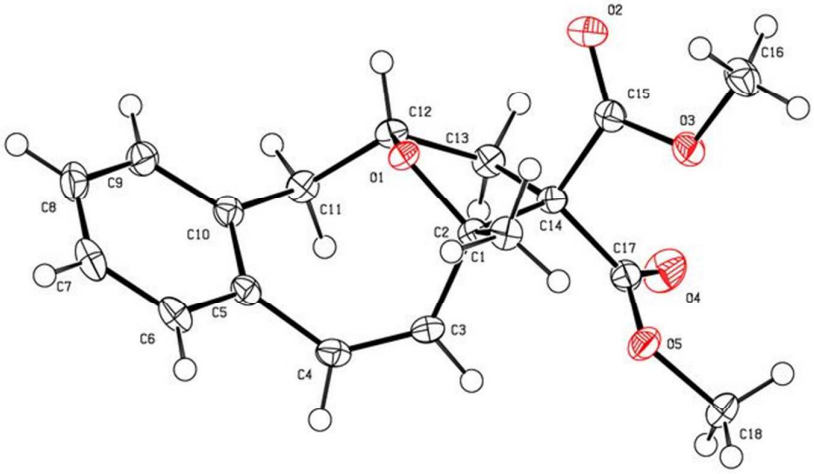

CO2Me
Br
O
O
O
5


3.71
1.23
1.00
1.04
1.04
3.19
3.33
1.14
3.49
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5


169.51
167.38
135.44
133.59
132.93
132.20
129.38
125.74
85.64
82.76
77.36
77.05
76.73
74.08
64.61
53.54
53.42
42.47
39.92
25.30
CO2Me
Br
O
O
O
5
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10



X-ray spectra of **5**



X-ray spectra of **2a**