Electronic Supplementary Material (ESI) for Green Chemistry.

Thermoneutral Synthesis of Spiro-1,4-cyclohexadienes by Visible-Light-Driven Dearomatization of Benzylmalonates

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1. General Information

Commercially available chemical materials were purchased in high quality and used without further purification. All photochemical reactions were carried out in oven-dried glassware applying three consecutive freeze-pump-thaw cycles. Reactions were monitored by thin-layer chromatography (TLC). Anhydrous solvents were prepared by established laboratory procedures.[1] DCM, EtOAc, n-pentane and hexanes (40-60 °C) for chromatography were distilled prior to use. The reported yields are referred to isolated compounds unless otherwise stated.

Chromatography

Thin-layer chromatography (TLC) was performed with TLC precoated aluminum sheets (Merck) Silica gel 60 F254, 0.2 mm layer thickness and visualized by a dual short (λ = 254 nm) / long (λ = 366 nm) wavelength UV lamp. Staining was done with Seebach`s Magic Stain (2.5 g phosphomolybdic acid, 1.0 g cerium(IV) sulfate tetrahydrate, 94.0 mL distilled water and 6.0 mL conc. sulfuric acid), vanillin (6.0 g vanillin, 100.0 mL ethanol (95%) and 1.0 mL conc. sulfuric acid) or potassium permanganate (1.0 g $KMnO_4$, 2.0 g Na_2CO_3 and 100.0 mL distilled water) followed by heating. Column chromatography was performed with silica gel (Merck, 0.063-0.200 mm particle size) and flash silica gel (Merck, 0.040-0.063 mm particle size).

NMR-Spectroscopy

^{1}H NMR spectra were recorded on Bruker Avance 300 (300 MHz), Bruker Avance 400 (400 MHz) or Bruker Avance III 400 “Nanobay” (400 MHz) Chemical shifts for ^{1}H NMR were reported as δ, parts per million (ppm), relative to the signal of $CHCl_3$ at 7.26 ppm. Spectra were evaluated in first order and coupling constants J are reported in Hertz (Hz). Splitting patterns for the spin multiplicity of the signals in the spectra are given as the following: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quartet, p = pentet, sex = sextet, hept = heptet, m = multiplet and combinations thereof. Chemical shifts for ^{1}H NMR were reported as δ, parts per million (ppm), relative to the signal of $CHCl_3$ at 7.26 ppm.
^{13}C NMR spectra were recorded on Bruker Avance 300 (75 MHz), Bruker Avance 400 (101 MHz) or Bruker Avance III 400 “Nanobay” (101 MHz) Spectrometer. Chemical shifts for ^{13}C NMR were reported as δ, parts per million (ppm), relative to the center line signal of the $CDCl_3$ triplet at 77.0 ppm.
^{19}F NMR spectra were recorded on Bruker Avance 300 (282 MHz), Bruker Avance 400 (376 MHz) or Bruker Avance III 400 “Nanobay” (376 MHz) Spectrometer.

Mass Spectrometry

Mass spectra were recorded by the Central Analytic Department of the University of Regensburg using Jeol AccuTOF GCX and Agilent Q-TOF 6540 UHD Spectrometer. High-resolution mass spectra were measured using atmospheric pressure chemical ionization (APCI), electron ionization (EI) or electrospray ionization (ESI) with a quadrupole time-of-flight (Q-TOF) detector

IR-Spectroscopy

FTIR spectroscopy was carried out on a Cary 630 FTIR Spectrometer. Solid and liquid compounds were measured neatly and the wave numbers are reported as cm^{-1}.

Melting Point Apparatus

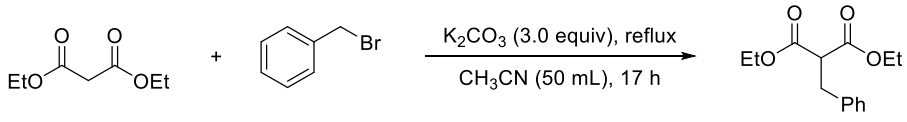
The measurement of melting points was carried out on a MPA100 - Automated melting point system by OptiMelt using a ramp rate of 1K/min.

X-Ray Crystallography

X-ray crystallographic analysis was performed by the Central Analytic Department of the University of Regensburg using an Agilent Technologies SuperNova, an Agilent Technologies Gemini R Ultra, an Agilent GV 50 or a Rigaku GV 50 diffractometer. Suitable crystals were mounted on a Lindemann tube oil and kept at a steady temperature of T = 293 K during data collection. The structures were solved with the SheIXT (Scheldrick 2015) structure solution program using the Intrinsic Phasing solution method and by using Olex2 as the graphical interface. The model was refined with SheIXL using Least Squares minimization

2. Synthesis of Starting Material

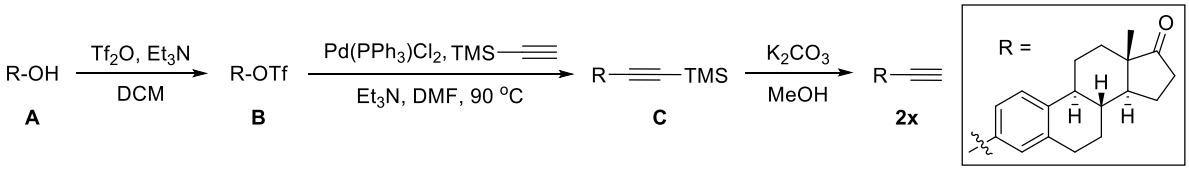
2.1 Synthesis of Benzylmalonates



A **B** **1a**

Compound **1a** was synthesized according to a literature procedure.[2] A mixture of diethyl malonate **A** (3.2 g, 20 mmol), benzylbromide **B** (3.76 g, 22 mmol), and K_2CO_3 (8.29 g, 60 mmol) in CH_3CN (50 mL) was heated to reflux for 17 h. After cooling the solvent was evaporated and the residue was poured into 150 mL of distilled water. The aqueous solution was extracted with dichloromethane and the combined extracts were dried and evaporated. The residue was purified by column chromatography on silica (petroleum ether/ethylacetate 30:1~10:1) directly to give diethyl 2-benzylmalonate **1a** as a colorless liquid (3.2 g, 64% yield). Spectroscopic data are in agreement with those reported in literature.[2] Other benzylmalonates **1a-1f** were synthesized according to above proceduce.

2.2 Synthesis of Alkyne 2x



A **B** **C** **2x**

Compound **2x** was synthesized according to a literature procedure.[3] To a round bottom flask equipped with a magnetic stir bar was added estrone **A** (1.1 g, 4 mmol), Et_3N (1.6 mL, 12 mmol) and CH_2Cl_2 (25 mL) at 0 °C. Trifluoromethanesulfonic anhydride (0.8 mL, 4.4 mmol) was added dropwise. The reaction mixture was stirred at 0 °C for 1 h and quenched with saturated aqueous $NaHCO_3$ (20 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and the volatiles were removed in vacuo. The residue was purified by flash column chromatography on silica to give product **B** (1.19 g, 74% yield).

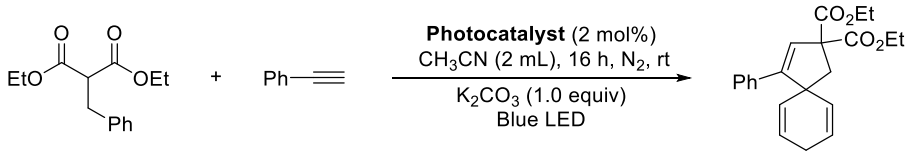
A mixture of **B** (1.35 g, 3.4 mmol), ethynyltrimethylsilane (0.7 mL, 4.8 mmol), triethylamine (2.5 mL), and $Pd(PPh_3)_2Cl_2$ (71 mg, 0.1 mmol) in 15 mL DMF was stirred at 90 °C for 4 h under nitrogen atmosphere. Then, the reaction mixture was diluted with water, extracted with petroleum ether/ether (1:1), washed with water until neutral, dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica to give product **C** (0.57 g, 48% yield).

To product **C** (0.37 g, 1.1 mmol) a solution of K_2CO_3 (0.23 g, 1.65 mmol) in MeOH (10 mL) was added and the mixture was stirred at room temperature until TLC analysis showed that **C** was completely consumed. The reaction mixture was filtered through a short plug of silica gel, concentrated, and purified by flash chromatography on silica to give **2x** (190 mg, 62% yield).

3. Detailed Optimization of Reaction Conditions and Control Experiments

3.1 Optimization of Reaction Conditions

Table S1. Screening of the photocatalyst



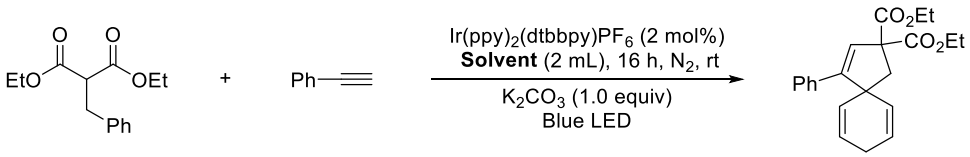
1a **2a** **3a**

Entry[a]	Photocatalyst	Yield[b](%)
1	Eosin	N.D.
2	Mes-Acr-$MeBF_4$	N.D.
3	Riboflavin	N.D.
4	4CzIPN	N.D.
5	$Cu(dmp)_2Cl_2$	N.D.
6	$Ru(bpy)_3Cl{\cdot}6H_2O$	N.D.
7	$Ir(dF(CF_3)ppy_2)dtbbpyPF_6$	N.D.
8	$Ir(ppy)_2bpyPF_6$	14
9	$Ir(ppy)_2(dtbbpy)PF_6$	54

[a] Unless otherwise noted, reactions were carried out with **1a** (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), photocatalyst (2 mol%), K_2CO_3 (13.8 mg, 1.0 equiv.) in CH_3CN (2.0 mL) at rt under blue LED irradiation. [b] NMR yield using 1,3,5-trimethoxylbenzene as internal standard. N.D. implies that no desired product was detected.

As shown in Table *S1*, among all the photocatalysts tested, $Ir(ppy)_2(dtbbpy)PF_6$ gave the best results in terms of yield (54% yield) and thus was selected for further optimization studies.

Table *S2*. Screening of the solvent



1a **2a** **3a**

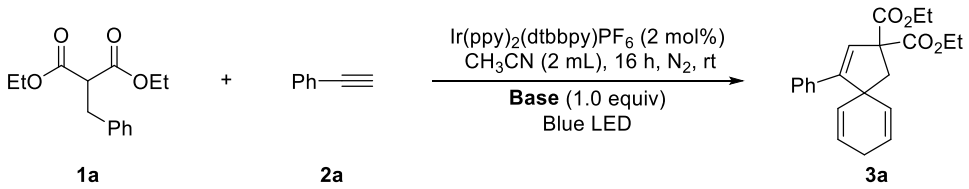
Entry[a]	Solvent	Yield[b](%)
1	$CHCl_3$	N.D.
2	THF	N.D.
3	DCM	N.D.
4	Toluene	N.D.

5	DMF	28
6	DMSO	50
7	CH_3CN	54

[a] Unless otherwise noted, reactions were carried out with **1a** (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), K_2CO_3 (13.8 mg, 1.0 equiv.) in solvent (2.0 mL) at rt under blue LED irradiation. [b] NMR yield using 1,3,5-trimethoxylbenzene as internal standard. N.D. implies that no desired product was detected.

As show in Table S2, among all the solvent tested, CH_3CN gave the best results in terms of yield (54% yield) and thus was selected for further optimization studies.

Table S3. Screening of the base



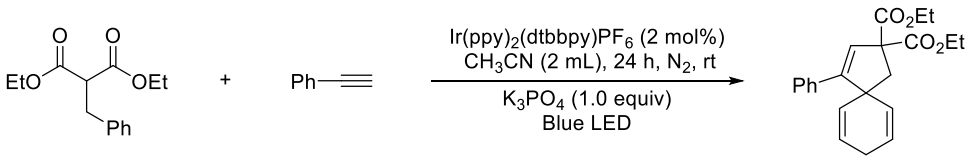
1a **2a** **3a**

Entry[a]	**Base**	**Yield**[b](%)
1	K_2HPO_4	N.D.
2	Na_2CO_3	N.D.
3	K_2CO_3	54
4	Cs_2CO_3	53
5	K_3PO_4	69
6	KOH	14
7	Quinuclidine	15
8[c]	K_3PO_4	89
9[d]	K_3PO_4	99(96[e])
10[d,f]	K_3PO_4	78
11[d,g]	K_3PO_4	74

[a] Unless otherwise noted, reactions were carried out with **1a** (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), Base (1.0 equiv.) in CH_3CN (2.0 mL) at rt under blue LED irradiation. [b] NMR yield using 1,3,5-trimethoxylbenzene as internal standard. N.D. implies that no desired product was detected. [c] 24 h. [d] A flame-dried reactor was used and each component was added under the protection of N_2 gas, 24 h. [e] Isolated yield. [f] K_3PO_4 (0.8 equiv.). [g] K_3PO_4 (0.5 equiv.).

As shown in Table S3, among the base tested, K_3PO_4 gave the best results and the reaction conditions of entry 9 (99% NMR yield and 96% isolated yield) was thus selected for further studies.

3.2 Control Experiments



1a **2a** **3a**

***Table S4*. Control experiments**

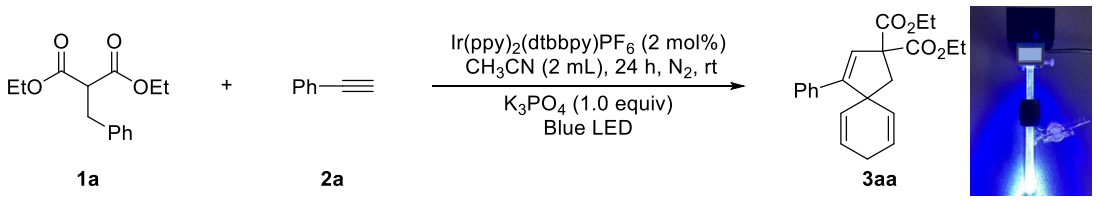
Entry[a]	hv	[Ir]	base	Yield[b] [%]
1[c]	-	+	+	N.D.
2[d]	+	-	+	N.D.
3[e]	+	+	-	N.D.
4	+	+	+	99

[a] Unless otherwise noted, reactions were carried out with **1a** (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2(dtbbpy)PF_6$ (2 mol%), K_3PO_4 (1.0 equiv.) in CH_3CN (2.0 mL) at rt under blue LED irradiation. [b] NMR yield using 1,3,5-trimethoxylbenzene as internal standard. N.D. implies that no desired product was detected. [c] Without hv. [d] Without [Ir]. [e] Without base.

The results of Table S4 revealed that each component of visible light, photocatalyst and base is essential for this protocol.

4. General Procedure and Spectral Data of Products

4.1 General Procedure for Synthesis of 3

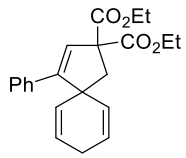


1a **2a** **3aa**

1a (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2dtbbpyPF_6$ (1.8 mg, 2 mol%), K_3PO_4 (21.2 mg, 1.0 equiv) and anhydrous CH_3CN (2 mL) were added to a flame-dried Schlenk tube under nitrogen atmosphere. Then, the reaction mixture was degassed three times via the 'freeze-pump-thaw' procedure under nitrogen atmosphere. The reaction mixture was irradiated (blue LEDs, 455 nm) at room temperature for 24 h upon which the reaction was completed as monitored by TLC analysis. Concentration and purification of the crude by flash chromatography on silica (petroleum ether/ethylacetate 100:1~20:1) gave rise to the desired product **3aa** (33.8 mg, 96% yield) as a yellow liquid.

4.2 Spectral Data of Products

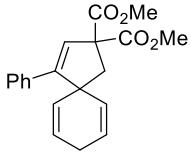
diethyl 4-phenylspiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3aa



3aa

33.8 mg, yellow liquid, yield: 96%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 – 7.45 (m, 2H), 7.19 – 7.18 (m, 1H), 7.17 (d, J = 2.0 Hz, 2H), 6.05 (s, 1H), 5.72 (dt, J = 10.3, 3.2 Hz, 2H), 5.60 (dt, J = 10.3, 1.8 Hz, 2H), 4.20 – 4.12 (m, 4H), 2.65 – 2.60 (m, 2H), 2.55 (s, 2H), 1.20 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.2, 151.4, 135.4, 132.4, 127.9, 127.8, 127.2, 124.7, 123.9, 64.2, 61.7, 51.3, 48.4, 25.8, 14.1. HRMS (EI+, 70 eV): calcd for $C_{22}H_{24}O_4$ [$M^{\cdot+}$] 352.1669, found: 352.1677. IR (neat): 2982, 1726, 1659, 1446, 1372, 1230, 1178, 1088, 1025, 849, 760, 697 cm^{-1}.

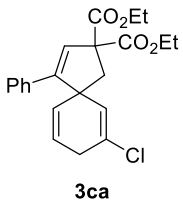
dimethyl 4-phenylspiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ba



3ba

30.8 mg, colorless liquid, yield: 95%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.52 (m, 1H), 7.51 – 7.49 (m, 1H), 7.24 (dd, J = 5.2, 1.9 Hz, 3H), 6.10 (s, 1H), 5.78 (dt, J = 10.3, 3.3 Hz, 2H), 5.64 (dt, J = 10.3, 1.9 Hz, 2H), 3.76 (s, 6H), 2.71 – 2.66 (m, 2H), 2.62 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.6, 151.6, 135.2, 132.2, 127.92, 127.87, 127.2, 124.4, 124.0, 63.9, 52.9, 51.3, 48.5, 25.8. HRMS (EI+, 70 eV): calcd for $C_{20}H_{20}O_4$ [$M^{\cdot+}$] 324.1356, found: 324.1353. IR (neat): 2952, 1730, 1435, 1282, 1230, 1197, 1092, 1028, 850, 768, 731, 697 cm^{-1}.

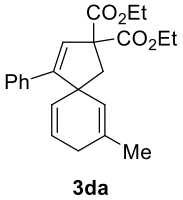
diethyl 7-chloro-4-phenylspiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ca



3ca

37.9 mg, yellow liquid, yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.38 – 7.35 (m, 2H), 7.22 – 7.18 (m, 3H), 6.06 (s, 1H), 5.77 – 5.75 (m, 1H), 5.66 – 5.54 (m, 2H), 4.20 – 4.12 (m, 4H), 2.89 – 2.86 (m, 2H), 2.58 (d, J = 0.8 Hz, 2H), 1.21 (td, J = 7.1, 2.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.9, 170.8, 150.5, 134.9, 131.7, 129.6, 129.5, 128.1, 128.05, 127.1, 125.6, 122.6, 64.2, 61.84, 61.80, 54.7, 47.5, 33.1, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4Cl$ [$M^{\cdot+}$] 386.1279, found: 386.1269. IR (neat): 2982, 1730, 1446, 1282, 1230, 1185, 1137, 1092, 854, 730, 693 cm^{-1}

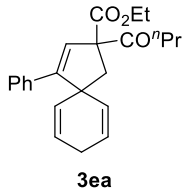
diethyl 7-methyl-4-phenylspiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3da



3da

31.7 mg, colorless liquid, yield: 87%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 – 7.46 (m, 2H), 7.24 (dd, J = 5.1, 1.8 Hz, 3H), 6.10 (s, 1H), 5.77 (dt, J = 9.9, 3.3 Hz, 1H), 5.67 – 5.63 (m, 1H), 5.37 (s, 1H), 4.27 – 4.18 (m, 4H), 2.59 (s, 4H), 1.70 (s, 3H), 1.28 (td, J = 7.1, 2.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.32, 171.30, 151.7, 135.5, 132.2, 131.0, 127.9, 127.7, 127.2, 127.0, 124.5, 123.7, 64.2, 61.6, 52.6, 48.3, 30.7, 23.2, 14.1. HRMS (EI+, 70 eV): calcd for $C_{23}H_{26}O_4$ [$M^{\cdot+}$] 366.1826, found: 366.1819. IR (neat): 2982, 1733, 1446, 1282, 1244, 1185, 1137, 1092, 857, 764, 697 cm^{-1}.

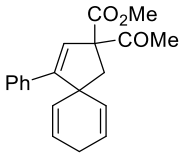
ethyl 2-butyryl-4-phenylspiro[4.5]deca-3,6,9-triene-2-carboxylate 3ea



3ea

23.3 mg, colorless liquid, yield: 66%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.47 – 7.44 (m, 2H), 7.18 (dd, J = 5.0, 2.0 Hz, 3H), 6.10 (s, 1H), 5.74 – 5.68 (m, 2H), 5.58 (dq, J = 9.8, 1.9 Hz, 1H), 5.47 (dq, J = 10.4, 1.9 Hz, 1H), 4.20 – 4.09 (m, 2H), 2.65 – 2.60 (m, 2H), 2.57 – 2.41 (m, 4H), 1.64 – 1.59 (m, 1H), 1.54 – 1.51 (m, 1H), 1.20 (t, J = 7.1 Hz, 3H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 205.8, 171.6, 151.7, 135.4, 132.4, 132.1, 128.0, 127.9, 127.1, 124.7, 124.0, 123.8, 70.8, 61.7, 51.2, 47.2, 41.0, 25.8, 17.2, 14.1, 13.6. HRMS: (EI-MS) m/z calcd for $C_{23}H_{27}O_3$ [M+H]$^{+}$: 351.1955, found: 351.1955. IR (neat): 2981, 1730, 1446, 1282, 1230, 1185, 1136, 1095, 1043, 857, 767, 693 cm^{-1}.

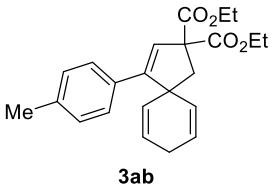
methyl 2-acetyl-4-phenylspiro[4.5]deca-3,6,9-triene-2-carboxylate 3fa



3fa

17.8 mg, colorless liquid, yield: 55%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.53 – 7.50 (m, 2H), 7.27 – 7.24 (m, 3H), 6.16 (s, 1H), 5.81 – 5.76 (m, 2H), 5.64 (dq, J = 9.9, 1.9 Hz, 1H), 5.54 (dq, J = 10.4, 1.9 Hz, 1H), 3.77 (s, 3H), 2.72 – 2.67 (m, 2H), 2.66 – 2.48 (m, 2H), 2.26 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 203.6, 172.0, 152.0, 135.3, 132.2, 132.0, 127.97, 127.95, 127.1, 124.4, 124.2, 124.0, 70.9, 52.9, 51.3, 47.2, 26.7, 25.8. HRMS (EI+, 70 eV): calcd for $C_{20}H_{20}O_3$ [$M^{\cdot+}$] 308.1407, found: 308.1419. IR (neat): 3026, 2952, 1714, 1435, 1357, 1226, 1115, 943, 842, 767, 723, 697 cm^{-1}.

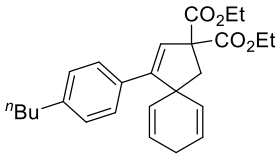
diethyl 4-(p-tolyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ab



3ab

34.5 mg, colorless liquid, yield: 94%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.44 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.08 (s, 1H), 5.78 (dt, J = 10.3, 3.3 Hz, 2H), 5.67 (dt, J = 10.3, 1.9 Hz, 2H), 4.26 – 4.20 (m, 4H), 2.72 – 2.68 (m, 2H), 2.61 (s, 2H), 2.31 (s, 3H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.3, 151.3, 137.7, 132.6, 132.5, 128.7, 127.1, 123.9, 123.8, 64.2, 61.6, 51.3, 48.4, 25.8, 21.2, 14.1. HRMS (EI+, 70 eV): calcd for $C_{23}H_{26}O_4$ [$M^{\cdot+}$] 366.1826, found: 366.1820. IR (neat): 2982, 1726, 1662, 1446, 1366, 1282, 1233, 1178, 1088, 1025, 850, 816, 756 cm^{-1}.

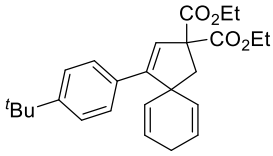
diethyl 4-(4-butylphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ac



3ac

40.8 mg, colorless liquid, yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.49 – 7.45 (m, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.10 (s, 1H), 5.79 (dt, *J* = 10.4, 3.2 Hz, 2H), 5.67 (dt, *J* = 10.3, 1.8 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.73 – 2.70 (m, 2H), 2.61 (s, 2H), 2.59 – 2.54 (m, 2H), 1.60 – 1.52 (m, 2H), 1.40 – 1.33 (m, 2H), 1.28 (t, *J* = 7.1 Hz, 6H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.3, 151.2, 142.7, 132.6, 128.0, 127.0, 123.9, 123.7, 64.1, 61.6, 51.2, 48.5, 35.3, 33.4, 25.8, 22.3, 14.1, 13.9. HRMS (EI+, 70 eV): calcd for $C_{26}H_{32}O_4$ [$M^{\cdot+}$] 408.2295, found: 408.2283. IR (neat): 2960, 2930, 2859, 1730, 1662, 1446, 1369, 1282, 1230, 1178, 1092, 1064, 863, 857, 761 cm^{-1}.

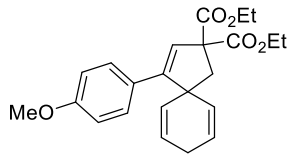
diethyl 4-(4-(tert-butyl)phenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ad



3ad

39.2 mg, white solid, yield: 96%. Melting point: 92 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 – 7.49 (m, 2H), 7.31 – 7.26 (m, 2H), 6.14 (s, 1H), 5.80 (dt, *J* = 10.3, 3.2 Hz, 2H), 5.69 (dt, *J* = 10.2, 1.8 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.76 – 2.72 (m, 2H), 2.62 (s, 2H), 1.30 (s, 9H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.3, 150.84, 150.7, 132.6, 132.3, 126.8, 124.9, 124.0, 123.7, 64.1, 61.6, 51.1, 48.5, 34.5, 31.2, 25.9, 14.0. HRMS (EI+, 70 eV): calcd for $C_{26}H_{32}O_4$ [$M^{\cdot+}$] 408.2295, found: 408.2281. IR (neat): 2960, 2907, 2870, 1722, 1666, 1446, 1367, 1289, 1230, 1178, 1088, 1057, 857, 831, 764, 757 cm^{-1}.

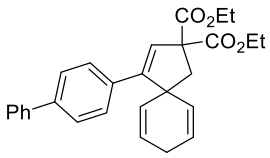
diethyl 4-(4-methoxyphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ae



3ae

34.5 mg, colorless liquid, yield: 90%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.51 – 7.46 (m, 2H), 6.82 – 6.77 (m, 2H), 6.03 (s, 1H), 5.82 – 5.76 (m, 2H), 5.66 (dt, *J* = 10.3, 1.9 Hz, 2H), 4.27 – 4.17 (m, 4H), 3.78 (s, 3H), 2.73 – 2.69 (m, 2H), 2.60 (s, 2H), 1.27 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.4, 159.2, 150.8, 132.6, 128.4, 127.9, 123.7, 122.9, 113.3, 64.1, 61.6, 55.2, 51.2, 48.4, 25.8, 14.1. calcd for $C_{23}H_{26}O_5$ [$M^{\cdot+}$] 382.1775, found: 382.1771. IR (neat): 2982, 1726, 1607, 1513, 1286, 1245, 1178, 1092, 1028, 857, 841, 736 cm^{-1}.

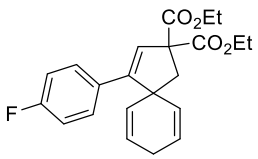
diethyl 4-([1,1'-biphenyl]-4-yl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3af



3af

38 mg, colorless liquid, yield: 89%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.64 – 7.62 (m, 2H), 7.59 – 7.57 (m, 2H), 7.53 – 7.49 (m, 2H), 7.44 – 7.41 (m, 2H), 7.35 – 7.31 (m, 1H), 6.19 (s, 1H), 5.83 (dt, *J* = 10.3, 3.3 Hz, 2H), 5.71 (dt, *J* = 10.3, 1.8 Hz, 2H), 4.28 – 4.22 (m, 4H), 2.77 – 2.72 (m, 2H), 2.65 (s, 2H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.2, 150.9, 140.7, 140.5, 134.4, 132.5, 128.7, 127.6, 127.3, 126.9, 126.6, 124.8, 124.0, 64.2, 61.7, 51.3, 48.5, 25.9, 14.1. HRMS (EI+, 70 eV): calcd for $C_{28}H_{28}O_4$ [$M^{\cdot+}$] 428.1982, found: 428.1964. IR (neat): 2982, 1726, 1487, 1230, 1178, 1043, 941, 838, 767, 730, 697 cm^{-1}.

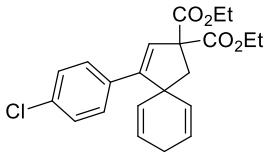
diethyl 4-(4-fluorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ag



3ag

34.7 mg, yellow liquid, yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.54 – 7.47 (m, 2H), 6.97 – 6.91 (m, 2H), 6.06 (s, 1H), 5.82 – 5.76 (m, 2H), 5.64 (dt, *J* = 10.3, 1.9 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.71 – 2.66 (m, 2H), 2.61 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.2, 164.4 (d, *J* = 246 Hz), 150.5, 132.2, 131.5 (d, *J* = 3.3 Hz), 128.9 (d, *J* = 7.9 Hz), 124.5 (d, *J* = 1.7 Hz), 124.1, 114.8 (d, *J* = 21.1 Hz), 64.1, 61.7, 51.4, 48.3, 25.8, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -114.50. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4F$ [$M^{\cdot+}$] 370.1575, found: 370.1598. IR (neat): 2982, 1726, 1662, 1602, 1509, 1282, 1226, 1159, 1088, 857, 843, 812, 759 cm^{-1}.

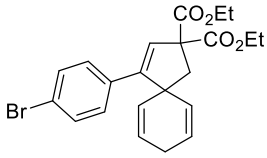
diethyl 4-(4-chlorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ah



3ah

37.5 mg, yellow liquid, yield: 97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.48 – 7.43 (m, 2H), 7.23 – 7.19 (m, 2H), 6.10 (s, 1H), 5.79 (dt, *J* = 10.3, 3.3 Hz, 2H), 5.64 (dt, *J* = 10.3, 1.9 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.71 – 2.66 (m, 2H), 2.61 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.0, 150.4, 133.8, 133.6, 132.1, 128.5, 128.1, 125.2, 124.1, 64.2, 61.7, 51.3, 48.3, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4Cl$ [$M^{\cdot+}$] 386.1301, found: 386.1303. IR (neat): 2982, 1726, 1666, 1491, 1368, 1282, 1230, 1178, 1088, 1013, 857, 827, 734 cm^{-1}.

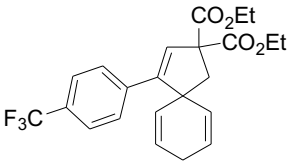
diethyl 4-(4-bromophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ai



3ai

39.6 mg, colorless liquid, yield: 92%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.38 (d, *J* = 1.6 Hz, 4H), 6.11 (s, 1H), 5.79 (dt, *J* = 10.3, 3.3 Hz, 2H), 5.63 (dt, *J* = 10.3, 1.9 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.71 – 2.65 (m, 2H), 2.61 (s, 2H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.0, 150.4, 134.3, 132.1, 131.0, 128.8, 125.3, 124.2, 121.9, 64.2, 61.8, 51.3, 48.3, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4Br$ [$M^{\cdot+}$] 430.0774, found: 430.0763. IR (neat): 2982, 1722, 1659, 1487, 1368, 1282, 1230, 1178, 1092, 1048, 909, 857, 827, 731, 704 cm^{-1}.

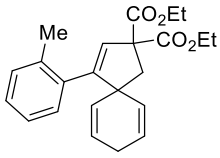
diethyl 4-(4-(trifluoromethyl)phenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3aj



3aj

35.6 mg, colorless liquid, yield: 85%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.59 (d, *J* = 8.1 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 6.15 (s, 1H), 5.80 – 5.74 (m, 2H), 5.60 (dt, *J* = 10.3, 1.9 Hz, 2H), 4.25 – 4.16 (m, 4H), 2.68 – 2.63 (m, 2H), 2.60 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 170.9, 150.3, 139.0 (q, *J* = 1.2 Hz), 131.9, 127.5, 127.0 (q, *J* = 168.6 Hz), 126.8, 124.8 (q, *J* = 3.8 Hz), 124.4, 64.3, 61.8, 51.4, 48.3, 25.8, 14.0. ^{19}F NMR (375 MHz, $CDCl_3$) δ (ppm) -63.16. HRMS (EI+, 70 eV): calcd for $C_{23}H_{23}O_4F_3$ [$M^{\cdot+}$] 420.1543, found: 420.1536. IR (neat): 2986, 1730, 1662, 1323, 1286, 1234, 1162, 1114, 1066, 1014, 842, 741 cm^{-1}.

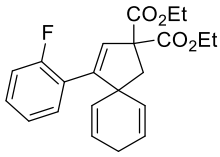
diethyl 4-(o-tolyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ak



3ak

35.9 mg, yellow liquid, yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.18 – 7.13 (m, 3H), 7.07 – 7.02 (m, 1H), 5.72 – 5.61 (m, 4H), 5.70 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 4H), 2.64 (s, 2H), 2.51 – 2.41 (m, 1H), 2.32 (s, 3H), 2.25 – 2.16 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.5, 151.4, 136.5, 135.4, 131.2, 129.8, 128.6, 127.1, 127.0, 124.6, 124.4, 65.1, 61.6, 54.2, 47.1, 25.6, 20.6, 14.1. HRMS (EI+, 70 eV): calcd for $C_{23}H_{26}O_4$ [$M^{\cdot+}$] 366.1826, found: 366.1811. IR (neat): 2982, 1726, 1446, 1368, 1262, 1118, 909, 727 cm^{-1}.

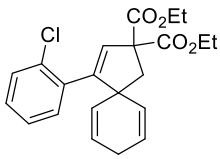
diethyl 4-(2-fluorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3al



3al

36.3 mg, colorless liquid, yield: 98%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.48 (td, *J* = 7.8, 1.8 Hz, 1H), 7.22 – 7.16 (m, 1H), 7.05 – 6.97 (m, 2H), 6.23 (d, *J* = 2.2 Hz, 1H), 5.75 (dt, *J* = 10.3, 3.2 Hz, 2H), 5.67 (dt, *J* = 10.3, 1.8 Hz, 2H), 4.27 – 4.20 (m, 4H), 2.69 – 2.63 (m, 1H), 2.61 (s, 2H), 2.56 – 2.48 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.1, 160.8 (d, *J* = 248.2 Hz), 144.5 (d, *J* = 2.6 Hz), 132.0, 129.6 (d, *J* = 3.0 Hz), 129.2 (d, *J* = 9.4 Hz), 128.9 (d, *J* = 8.9 Hz), 124.1, 123.3, 123.1 (d, *J* = 3.5 Hz), 115.5 (d, *J* = 23.2 Hz), 65.0, 61.7, 52.6, 47.5, 25.7, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -112.29. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4F$ [$M^{\cdot+}$] 370.1575, found: 370.1566. IR (neat): 2982, 1730, 1491, 1446, 1230, 1181, 1115, 1085, 857, 734 cm^{-1}.

diethyl 4-(2-chlorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3am

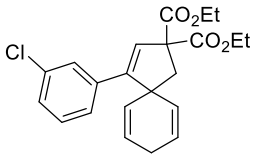


3am

30.5 mg, yellow liquid, yield: 79%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) δ 7.36 – 7.34 (m, 1H), 7.27 – 7.24 (s, 1H), 7.18 – 7.09 (m, 2H), 5.90 (s, 1H), 5.69 (s, 4H), 4.24 (q, *J* = 7.1 Hz, 4H), 2.66

(s, 2H), 2.51 – 2.45 (m, 1H), 2.25 – 2.19 (m, 1H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.2, 148.7, 134.7, 133.8, 131.0, 130.1, 129.4, 128.7, 128.4, 125.5, 124.6, 65.3, 61.7, 54.2, 46.9, 25.6, 14.1. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4Cl$ [$M^{\cdot+}$] 386.1279, found: 386.1267. IR (neat): 2982, 1726, 1472, 1435, 1367, 1260, 1230, 1181, 1055, 909, 857, 730 cm^{-1}.

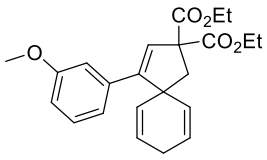
diethyl 4-(3-chlorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3an



3an

36.1 mg, yellow liquid, yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.52 – 7.51 (m, 1H), 7.40 (dt, J = 6.7, 1.9 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.13 (s, 1H), 5.81 (dt, J = 10.3, 3.3 Hz, 2H), 5.63 (dt, J = 10.3, 1.9 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.73 – 2.68 (m, 2H), 2.62 (s, 2H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.0, 150.2, 137.2, 133.8, 132.0, 129.1, 127.8, 127.3, 125.9, 125.3, 124.3, 64.2, 61.8, 51.3, 48.3, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{23}O_4Cl$ [$M^{\cdot+}$] 386.1279, found: 386.1264. IR (neat): 2982, 1726, 1662, 1561, 1476, 1368, 1230, 1178, 1096, 1047, 998, 857, 786, 730 cm^{-1}.

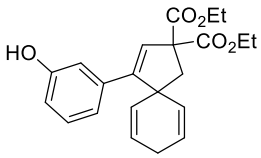
diethyl 4-(4-methoxyphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ao



3ao

35.9 mg, colorless liquid, yield: 94%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.18 – 7.12 (m, 3H), 6.81 – 6.78 (m, 1H), 6.13 (s, 1H), 5.80 (dt, J = 10.3, 3.2 Hz, 2H), 5.68 (dt, J = 10.3, 1.8 Hz, 2H), 4.27 – 4.19 (m, 4H), 3.76 (s, 3H), 2.71 – 2.69 (m, 2H), 2.62 (s, 2H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.2, 159.0, 151.2, 136.7, 132.5, 128.9, 125.0, 123.8, 119.8, 113.6, 112.6, 64.1, 61.7, 55.1, 51.3, 48.4, 25.9, 14.0. HRMS (EI+, 70 eV): calcd for $C_{23}H_{26}O_5$ [$M^{\cdot+}$] 382.1775, found: 382.1760. IR (neat): 2982, 1726, 1599, 1487, 1290, 1248, 1207, 1178, 1040, 849, 782, 697 cm^{-1}.

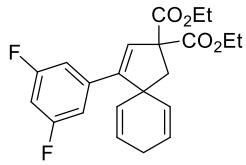
diethyl 4-(3-hydroxyphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ap



3ap

26.3 mg, yellow liquid, yield: 71%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.12 – 7.09 (m, 2H), 7.02 – 7.00 (m, 1H), 6.74 – 6.70 (m, 1H), 6.09 (s, 1H), 5.81 – 5.75 (m, 2H), 5.65 (dt, J = 10.3, 1.9 Hz, 2H), 5.21 (s, 1H), 4.25 – 4.19 (m, 4H), 2.70 – 2.68 (m, 2H), 2.61 (s, 2H), 1.27 (t, J = 7.1 Hz, 6H).^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 171.3, 155.2, 151.2, 137.0, 132.3, 129.1, 125.1, 124.0, 119.8, 114.8, 114.2, 64.1, 61.8, 51.3, 48.4, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{24}O_5$ [$M^{\cdot+}$] 368.1618, found: 368.1615. IR (neat): 2982, 1722, 1580, 1446, 1297, 1260, 1185, 909, 857, 730 cm^{-1}.

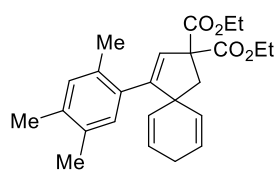
diethyl 4-(3,5-difluorophenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3aq



3aq

33.1mg, colorless liquid, yield: 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.08 – 7.02 (m, 2H), 6.68 (tt, J = 8.8, 2.3 Hz, 1H), 6.15 (s, 1H), 5.82 (dt, J = 10.3, 3.3 Hz, 2H), 5.62 (dt, J = 10.3, 2.0 Hz, 2H), 4.27 – 4.19 (m, 4H), 2.73 – 2.69 (m, 2H), 2.62 (s, 2H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 170.8, 163.8 (d, J = 13.0 Hz), 161.3 (d, J = 13.0 Hz), 149.4 (t, J = 2.6 Hz), 138.5 (t, J = 9.9 Hz), 131.7, 127.0, 124.5, 110.1 (d, J = 25.6 Hz), 110.1 (d, J = 11.7 Hz), 103.1 (t, J = 25.4), 64.1, 61.9, 51.3, 48.3, 25.8, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -110.9 (t, J = 17.6 Hz). HRMS (EI+, 70 eV): calcd for $C_{22}H_{22}O_4F_2$ [$M^{\cdot+}$] 388.1481, found: 388.1479. IR (neat): 2982, 2937, 1730, 1621, 1588, 1435, 1334, 1256, 1193, 988, 845, 730 cm^{-1}.

diethyl 4-(2,4,5-trimethylphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ar

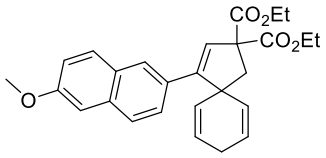


3ar

36.8 mg, colorless liquid, yield: 93%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.98 (s, 1H), 6.93 (s, 1H), 5.70 (dt, J = 10.7, 2.8 Hz, 2H), 5.67 – 5.62 (m, 3H), 4.23 (q, J = 7.1 Hz, 4H), 2.62 (s, 2H), 2.54 – 2.44 (m, 1H), 2.32 – 2.27 (m, 1H), 2.25 (s, 3H), 2.18 (s, 3H), 2.14 (s,

3H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.5, 151.3, 135.3, 133.7, 132.8, 132.4, 131.4, 131.3, 129.6, 126.9, 124.4, 65.0, 61.6, 54.0, 47.3, 25.7, 20.0, 19.4, 19.2, 14.1. HRMS (EI+, 70 eV): calcd for $C_{25}H_{30}O_4$ [$M^{\cdot+}$] 394.2139, found: 394.2152. IR (neat): 2982, 2922, 2866, 1730, 1446, 1249, 1178, 1062, 857, 700 cm^{-1}.

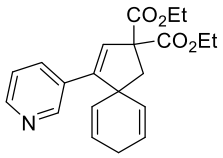
diethyl 4-(6-methoxynaphthalen-2-yl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3as



3as

42.4 mg, yellow liquid, yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.94 (s, 1H), 7.64 – 7.60 (m, 3H), 7.12 – 7.07 (m, 2H), 6.23 (s, 1H), 5.83 (dt, J = 10.4, 3.1 Hz, 2H), 5.73 (dt, J = 10.2, 1.7 Hz, 2H), 4.29 – 4.21 (m, 4H), 3.91 (s, 3H), 2.81 – 2.74 (m, 2H), 2.66 (s, 2H), 1.29 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) δ 171.3, 157.8, 151.3, 134.0, 132.7, 130.5, 129.9, 128.4, 126.22, 126.18, 125.9, 124.3, 123.8, 118.7, 105.5, 64.2, 61.7, 55.3, 51.4, 48.5, 25.9, 14.1. HRMS (EI+, 70 eV): calcd for $C_{27}H_{28}O_5$ [$M^{\cdot+}$] 432.1931, found: 432.1924. IR (neat): 2982, 1726, 1628, 1484, 1390, 1230, 1033, 909, 850, 726 cm^{-1}.

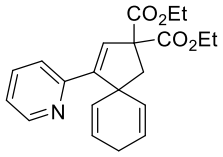
diethyl 4-(pyridin-3-yl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3at



3at

34.7 mg, yellow liquid, yield: 98%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.73 (dd, J = 2.2, 0.7 Hz, 1H), 8.46 (dd, J = 4.8, 1.6 Hz, 1H), 7.79 (dt, J = 8.0, 1.9 Hz, 1H), 7.17 (ddd, J = 8.0, 4.8, 0.7 Hz, 1H), 6.17 (s, 1H), 5.80 (dt, J = 10.3, 3.3 Hz, 2H), 5.63 (dt, J = 10.3, 1.9 Hz, 2H),), 4.29 – 4.19 (m, 4H), 2.71 – 2.66 (m, 2H), 2.63 (s, 2H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 170.9, 148.7, 148.6, 148.4, 134.3, 131.6, 131.2, 126.1, 124.6, 122.8, 64.4, 61.8, 51.4, 48.1, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{21}H_{23}NO_4$ [$M^{\cdot+}$] 353.1621, found: 353.1615. IR (neat): 2982, 1726, 1666, 1286, 1230, 1178, 1088, 1025, 857, 805, 730 cm^{-1}.

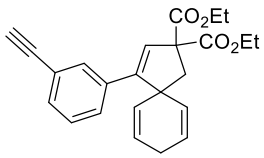
diethyl 4-(pyridin-2-yl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3au



3au

27.3 mg, yellow liquid, yield: 77%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 8.58 – 8.56 (m, 1H), 7.58 – 7.52 (m, 1H), 7.48 – 7.45 (m, 1H), 7.14 – 7.10 (m, 1H), 6.80 (s, 1H), 5.82 (dt, J = 10.3, 3.2 Hz, 2H), 5.69 (dt, J = 10.3, 1.9 Hz, 2H), 4.28 – 4.16 (m, 4H), 2.77 – 2.74 (m, 2H), 2.68 (s, 2H), 1.27 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 170.9, 152.9, 150.3, 149.5, 135.9, 132.3, 129.0, 124.0, 122.5, 121.4, 64.1, 61.8, 50.1, 48.7, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{21}H_{23}NO_4$ [$M^{\cdot+}$] 353.1622, found: 353.1609. IR (neat): 2982, 1726, 1666, 1584, 1469, 1286, 1233, 1148, 1088, 1029, 857, 787 cm^{-1}.

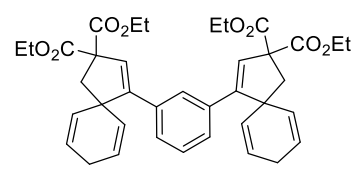
diethyl 4-(3-ethynylphenyl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3av



3av

22.8 mg, colorless liquid, yield: 61%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.66 (t, J = 1.5 Hz, 1H), 7.51 (dt, J = 7.9, 1.4 Hz, 1H), 7.36 (dt, J = 7.5, 1.2 Hz, 1H), 7.20 (t, J = 7.7 Hz, 1H), 6.13 (s, 1H), 5.80 (dt, J = 10.3, 3.3 Hz, 2H), 5.64 (dt, J = 10.3, 1.9 Hz, 2H), 4.27 – 4.19 (m, 4H), 3.04 (s, 1H), 2.71 – 2.68 (m, 2H), 2.62 (s, 2H), 1.28 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.0, 150.6, 135.6, 132.0, 131.3, 131.0, 127.9, 127.6, 125.5, 124.2, 121.7, 83.6, 76.97, 64.2, 61.7, 51.3, 48.3, 25.8, 14.0. HRMS (EI+, 70 eV): calcd for $C_{24}H_{24}O_4$ [$M^{\cdot+}$] 376.1669, found: 376.1660. IR (neat): 3280, 2982, 1722, 1662, 1290, 1238, 1178, 1088, 1054, 857, 797 cm^{-1}.

tetraethyl 4,4'-(1,3-phenylene)bis(spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate) 3av'

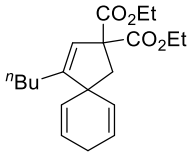


3av'

11.2 mg, colorless liquid, yield: 18%. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.74 (t, J = 1.6 Hz, 1H), 7.42 (dd, J = 7.8, 1.7 Hz, 2H), 7.13 (t, J = 7.8 Hz, 1H), 6.05 (s, 2H), 5.79 (dt, J = 10.3, 3.2 Hz, 4H), 5.64 (dt, J = 10.3, 1.8 Hz, 4H), 4.27 – 4.19 (m, 8H), 2.73 – 2.70 (m, 4H), 2.60 (s, 4H), 1.28 (t, J = 7.1 Hz, 12H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.2, 151.3, 135.0, 132.4, 127.5, 126.6, 126.5, 124.7, 123.9, 64.2, 61.7, 51.3, 48.4, 25.8, 14.1. HRMS (ESI-TOF): m/z calcd for $C_{38}H_{42}O_8Na$ [M + Na]$^+$

649.2772, found: 649.2790. IR (neat): 2982, 2926, 1722, 1662, 1446, 1368, 1230, 1178, 1151, 1092, 1051, 857, 798 731, 700 cm^{-1}.

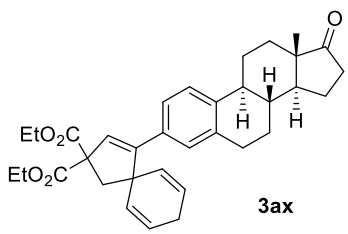
diethyl 4-butylspiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3aw



3aw

24 mg, colorless liquid, yield: 72%. ^1H NMR (300 MHz, , $CDCl_3$) δ (ppm) 5.77 (dt, *J* = 10.1, 3.3 Hz, 2H), 5.43 (m, 3H), 4.19 (q, *J* = 7.2 Hz, 4H), 2.62 (dt, *J* = 5.3, 2.2 Hz, 2H), 2.45 (s, 2H), 1.90 – 1.83 (m, 2H), 1.51 – 1.41 (m, 2H), 1.36 – 1.29 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 6H), 0.88 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 171.9, 155.1, 131.7, 124.1, 120.6, 64.8, 61.4, 52.3, 46.6, 29.8, 27.3, 25.8, 22.6, 14.1, 14.0. HRMS (EI+, 70 eV): calcd for $C_{20}H_{28}O_4$ [$M^{\cdot+}$] 332.1988 found: 332.1988. IR (neat): 2960, 2930, 2870, 1730, 1662, 1446, 1368, 1249, 1178, 1065, 1059, 861, 756 cm^{-1}.

Diethyl4-((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopen-ta[a]phenanthren-3-yl)spiro[4.5]deca-3,6,9-triene-2,2-dicarboxylate 3ax

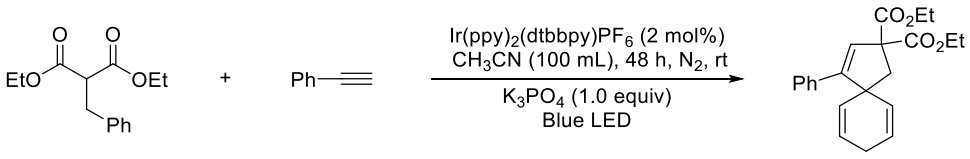


3ax

43 mg, yellow liquid, yield: 81%. ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.36 – 7.30 (m, 2H), 7.20 – 7.17 (m, 1H), 6.10 (s, 1H), 5.82 – 5.77 (m, 2H), 5.67 (dt, *J* = 10.4, 1.9 Hz, 2H), 4.26 – 4.18 (m, 4H), 2.88 – 2.84 (m, 2H), 2.75 – 2.68 (m, 2H), 2.60 (s, 2H), 2.50 (dd, *J* = 18.3, 8.4 Hz, 1H), 2.42 – 2.37 (m, 1H), 2.23 – 2.14 (m, 1H), 2.09 – 1.93 (m, 4H), 1.62 – 1.53 (m, 4H), 1.47 – 1.39 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 6H), 0.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 220.9, 171.3, 151.00, 139.6, 135.9, 132.8, 132.6, 127.8, 124.9, 124.4, 124.2, 123.8, 123.7, 64.1, 61.6, 51.2, 50.5, 48.4, 47.9, 44.4, 38.0, 35.8, 31.5, 29.4, 26.5, 25.9, 25.6, 21.6, 14.1, 13.8. HRMS (EI): m/z [M + H]$^+$ calcd for $C_{34}H_{41}O_5$: 529.2949, found: 529.2958. IR (neat): 2930, 2866, 1454, 1368, 1238, 1178, 1084, 854, 700 cm^{-1}.

5. Preparative Utility of the Methodology

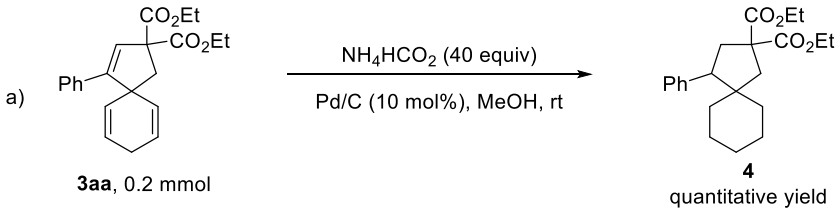
5.1 Gram-Scale Reaction



1a, 5 mmol　　**2a**, 15 mmol　　**3aa**
1.68 g, 95%

1a (1.25 g, 5 mmol), **2a** (1.53 g, 15 mmol), $Ir(ppy)_2dtbbpyPF_6$ (91.3 mg, 2 mol%), K_3PO_4 (1.06 g, 1.0 equiv) and degassed CH_3CN (100 mL) were added to the oven-dried reactor under nitrogen atmosphere. Then, the reaction mixture was degassed three times via 'freeze-pump-thaw' procedure under nitrogen atmosphere. The reaction was irradiated (blue LEDs, 455 nm) at room temperature for 48 h upon which the reaction was completed as monitored by TLC analysis. The resulting mixture was purified by flash chromatography on silica (petroleum ether/ethylacetate 100:1~20:1) to give product **3aa** (1.68 g, 95% yield) as a yellow liquid.

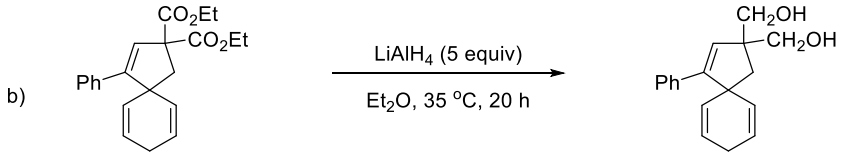
5.2 Synthetic Transformations of 3aa



3aa, 0.2 mmol

4
quantitative yield

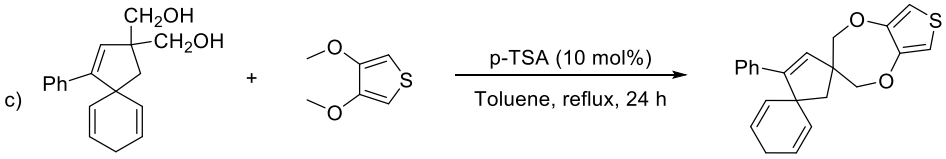
In a flame-dried Schlenk tube, **3aa** (70.5 mg, 0.2 mmol) and ammonium formate (632 mg, 8 mmol) were dissolved in MeOH (2 mL) under nitrogen atmosphere. Then, Pd/C (106.4 mg, 10 w%, 0.02 mmol) was added and the reaction mixture was stirred for 20 h at room temperature. After that, the reaction system was filtered through a plug of silica gel using ethyl acetate and after removal of volatiles under reduced pressure, the desired product **4** was obtained as a colorless liquid (71.4 mg, quantitative yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.33 – 7.28 (m, 2H), 7.26 – 7.23 (m, 1H), 7.18 – 7.15 (m, 2H), 4.27 – 4.17 (m, 4H), 2.86 – 2.70 (m, 2H), 2.66 – 2.51 (m, 2H), 2.14 (dd, J = 14.1, 1.3 Hz, 1H), 1.64 – 1.30 (m, 8H), 1.27 (t, J = 7.1 Hz, 6H), 0.93 – 0.79 (m, 1H), 0.67 – 0.56 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 173.1, 172.9, 138.9, 129.2, 127.7, 126.5, 61.5, 57.5, 56.0, 45.7, 42.5, 37.8, 37.2, 30.4, 25.9, 24.1, 22.1, 14.08, 14.05. HRMS (EI+, 70 eV): calcd for $C_{22}H_{30}O_4$ [$M^{\cdot+}$] 358.2139, found: 358.2133. IR (neat): 2982, 2930, 2855, 1726, 1446, 1245, 1182, 1092, 1058, 861, 764, 700 cm^{-1}.



3aa, 0.2 mmol

5
quantitative yield

To a flame-dried Schlenk tube, $LiAlH_4$ (38 mg, 1 mmol) and Et_2O (2 mL) were added under nitrogen atmosphere. Then, **3aa** (70.5 mg, 0.2 mmol) dissolved in Et_2O (2 mL) was added dropwise to the reaction mixture. After complete addition the mixture was heated at 35 °C for 20 h. After work up, the resulting mixture was purified by flash chromatography on silica gel (petroleum ether/ethylacetate/dichloromethane 3:1:1), the desired product **5** was obtained as a white solid (53.5 mg, quantitative yield). Melting point: 99.5 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.53 (m, 2H), 7.26 – 7.20 (m, 3H), 6.04 (s, 1H), 5.76 (dt, J = 11.1, 2.9 Hz, 2H), 5.70 (dt, J = 10.3, 1.6 Hz, 2H), 3.76 (s, 4H), 2.70 – 2.68 (m, 2H), 2.39 – 2.15 (m, 2H), 1.94 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 149.9, 136.0, 134.0, 128.9, 127.9, 127.4, 126.9, 123.0, 70.0, 54.0, 51.3, 47.9, 25.8. HRMS (ESI-TOF) m/z calcd for $C_{18}H_{24}NO_2$ [M+NH_4]$^+$ 386.1802, found: 286.1805. IR (neat): 3265, 2930, 2870, 1494, 1446, 1371, 1025, 943, 869, 764, 730, 685 cm^{-1}.



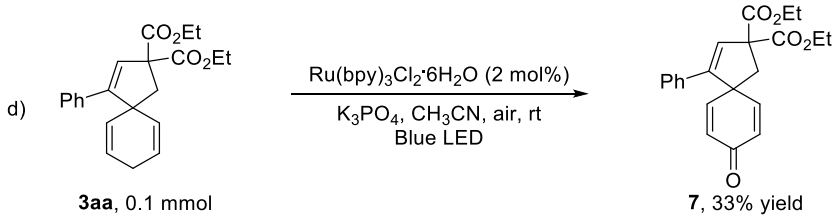
5, 0.56 mmol

0.28 mmol

6, 41% yield

To an oven-dried round flask, **5** (150.3 mg, 0.56 mmol), 3,4-dimethoxythiophene (40.3 mg, 0.28 mmol), *p*-toluenesulfonic acid (*p*-TSA, 10 mol%) and anhydrous toluene (5 mL) were added under nitrogen atmosphere. Then, the reaction mixture was refluxed for 24 h. After cooling the solvent was evaporated and the residue was purified by column chromatography on silica gel eluting with petroleum ether/ethylacetate 50:1 to give the desired product **6** as a yellow liquid (40.1 mg, 41%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.56 – 7.53 (m, 2H), 7.29 – 7.22 (m, 3H), 6.48 (s,

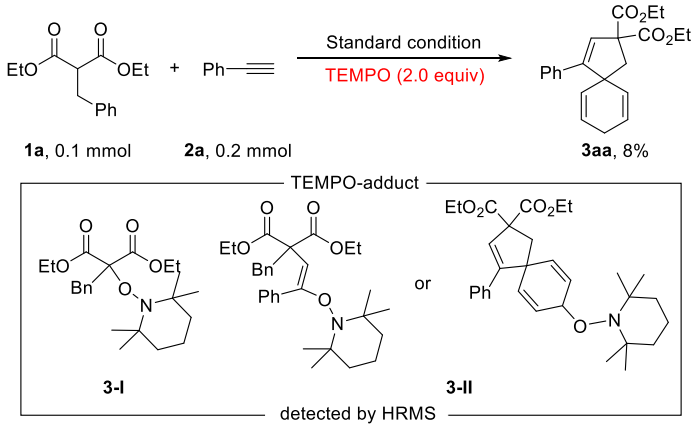
2H), 6.14 (s, 1H), 5.79 (dt, J = 10.3, 3.2 Hz, 2H), 5.68 (dt, J = 10.3, 1.8 Hz, 2H), 4.09 – 4.00 (m, 4H), 2.73 – 2.69 (m, 2H), 2.01 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 145.0, 149.8, 133.6, 128.1, 128.0, 127.6, 127.0, 123.5, 105.1, 78.6, 55.1, 51.2, 48.4, 25.8. HRMS (EI+, 70 eV): calcd for $C_{22}H_{20}O_2S$ [$M^{\cdot+}$] 348.1179, found: 348.1169. IR (neat): 3023, 2922, 2855, 1484, 1446, 1368, 1260, 1189, 1021, 910, 850, 764, 727, 693 cm^{-1}.



In a Schlenk tube, **3aa** (35.2 mg, 0.1 mmol), K_3PO_4 (21.2 mg, 1.0 equiv) and $Ru(bpy)Cl_2·6H_2O$ (1.5 mg, 2 mol%) were dissolved in CH_3CN (2 mL). Then, reaction mixture was stirred for 53 h under the irradiation of blue LED and air atmophere. After that, the reaction system was purified through flash chromatography on silica gel eluting with petroleum ether/ethylacetate 10:1 to give the desired product **7** as a yellow liquid (6.6 mg, 33%, brsm) and 45% of **3aa** was recovered (0.045 mmol, 15.9 mg). In addition, we also found that **3aa** could also be slowly oxidized to give product **7** in the absence of phtotocatalyst. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.33 – 7.30 (m, 2H), 7.27 – 7.20 (m, 3H), 7.02 – 6.96 (m, 2H), 6.40 (s, 1H), 6.37 – 6.31 (m, 2H), 4.32 – 4.22 (m, 4H), 2.81 (s, 2H), 1.30 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 185.4, 170.2, 153.5, 147.9, 133.8, 129.0, 128.8, 128.6, 128.4, 126.4, 64.9, 62.2, 55.3, 43.1, 14.0. HRMS (EI+, 70 eV): calcd for $C_{22}H_{22}O_5$ [$M^{\cdot+}$] 366.1462, found: 366.1448. IR (neat): 2982, 1730, 1662, 1625, 1446, 1282, 1230, 1178, 1085, 1025, 857, 760, 693 cm^{-1}.

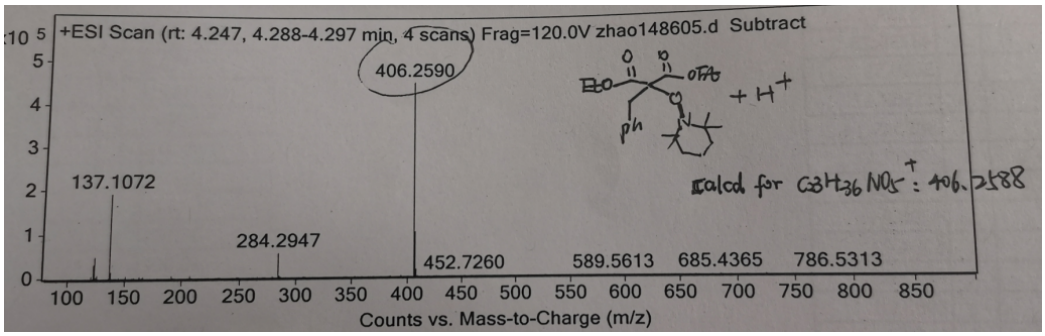
6. Mechanistic Studies

6.1 TEMPO Trapping Experiment

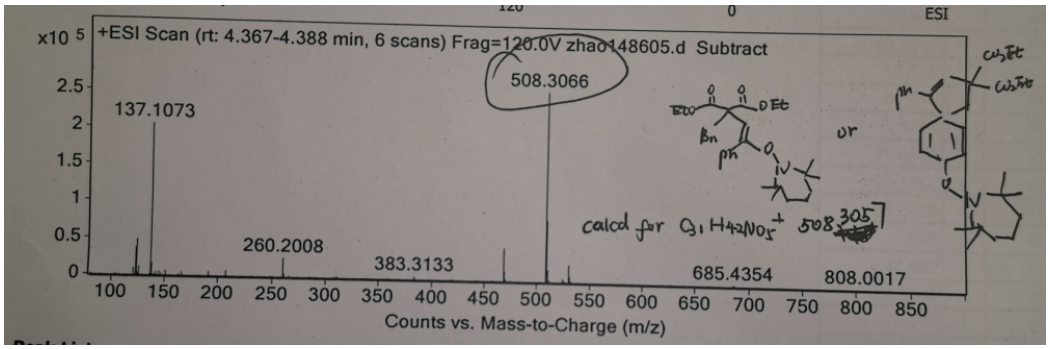


1a (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2dtbbpyPF_6$ (1.8 mg, 2 mol%), K_3PO_4 (21.2 mg, 1.0 equiv), TEMPO (31.3 mg, 2.0 equiv) and anhydrous CH_3CN (2 mL) were added to a flame-dried Schlenk tube under nitrogen protection. Then, the reaction mixture was degassed for three times via the 'freeze-pump-thaw' procedure under a nitrogen atmosphere. The reaction mixture was irradiated (blue LEDs, 455 nm) at room temperature for 24 h. The chemical yield of **3aa** was detected by NMR analysis using 1,3,5-trimethoxylbenzene as internal standard (8% yield) and the key intermediate **3-I** and **3-II** was detected by and HRMS.

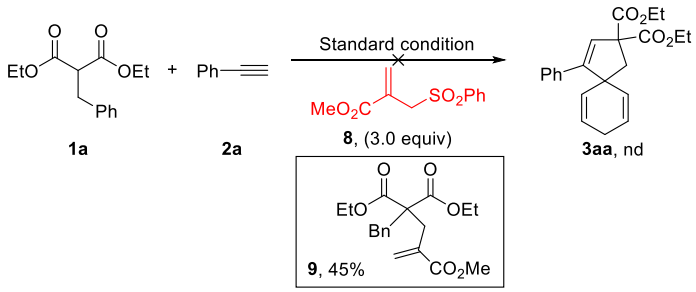
3-I: HRMS (EI): m/z [M + H]$^+$ calcd for $C_{23}H_{36}NO_5$: 406.2588, found: 406.2590.



3-II: HRMS (EI): m/z $[M + H]^+$ calcd for $C_{31}H_{42}NO_5$: 508.3057, found: 406.3066.



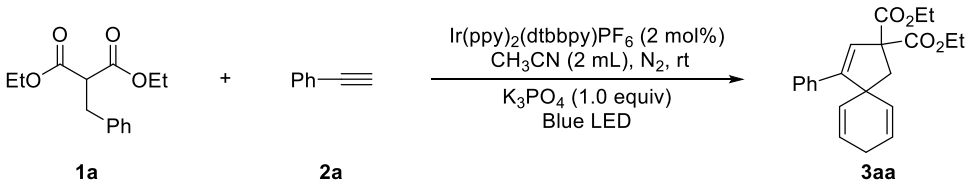
6.2 Allylic Sulfone Trapping Experiment



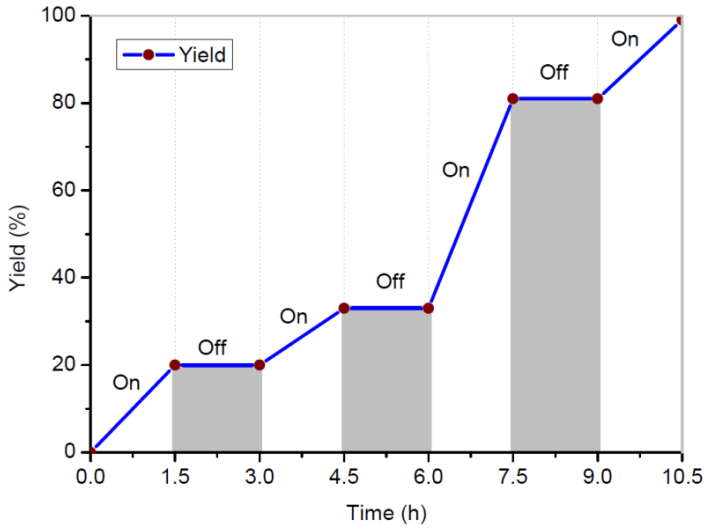
1a (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), **9** (72.1 mg, 0.3 mmol), $Ir(ppy)_2dtbbpyPF_6$ (1.8 mg, 2 mol%), K_3PO_4 (21.2 mg, 1.0 equiv) and anhydrous CH_3CN (2 mL) were added to a flame-dried Schlenk tube under nitrogen atmosphere. Then, the reaction mixture was degassed three times via the 'freeze-pump-thaw' procedure under nitrogen atmosphere. The reaction mixture was irradiated (blue LEDs, 455 nm) at room temperature for 24 h. No desired product **3aa** was generated, but product **9** was isolated as a colorless liquid (15.7 mg, 45% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.26 – 7.02 (m, 3H), 7.15 (dd, J = 7.5, 2.0 Hz, 2H), 6.27 (d, J = 1.4 Hz, 1H), 5.68 (q, J = 1.2 Hz, 1H), 4.15 – 4.05 (m, 4H), 3.73 (s, 3H), 3.26 (s, 2H), 2.93 (d, J = 1.1 Hz, 2H), 1.19 (t, J = 7.1 Hz, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 170.6, 167.6, 136.1, 136.0, 130.1, 129.0, 128.2, 126.9, 61.3, 58.7, 51.9, 39.7, 34.5, 13.9. HRMS (EI+, 70 eV): calcd for $C_{19}H_{24}O_6$ [$M^{\cdot+}$] 348.1567, found: 348.1567. IR (neat): 2982, 2956, 1726, 1443, 1275, 1189, 1152, 1014, 746, 701 cm^{-1}.

Allyl sulfones serves as good radical accepors and the mechanism for the formation of **9** is based on the reported methods.[4] This result together with the TEMPO trapping experiment revealed that the reaction might involve radical pathways and benzylmalonate radical might be the key intermediate.

6.3 Light On-off Experiment



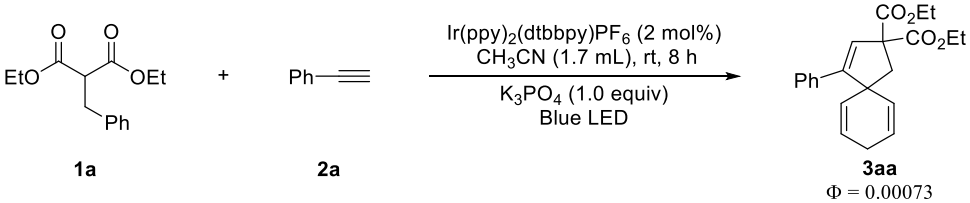
1a **2a** **3aa**



1a (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2dtbbpyPF_6$ (1.8 mg, 2 mol%), K_3PO_4 (21.2 mg, 1.0 equiv) and anhydrous CH_3CN (2 mL) were added to a flame-dried Schlenk tube under nitrogen atmosphere. Then, the reaction mixture was degassed three times via the 'freeze-pump-thaw' procedure under a nitrogen atmosphere. Five parallel experiments were carried out and processed individually after the respective on/off irradiation intervals to ensure reproducibility in the sample collection. The reactions were monitored by NMR analysis using 1,3,5-trimethoxylbenzene as an internal standard. The reaction mixtures were irradiated (blue LEDs, 455 nm) and subsequently left in the dark at room temperature as indicated in the timeline above.

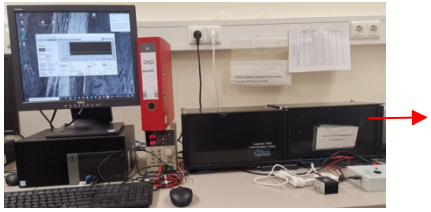
This result showed that the continuous irradiation of visible light is indispensable and it also indicated that the reaction proceeds mainly through a photoredox catalytic pathway. However, the radical chain propagation pathway could not be ruled out completely.[5] Therefore, we further did the quantum yield measurement to gain more insight into the mechanism.

6.4 Quantum Yield Measurement



1a **2a** **3aa**

$\Phi = 0.00073$



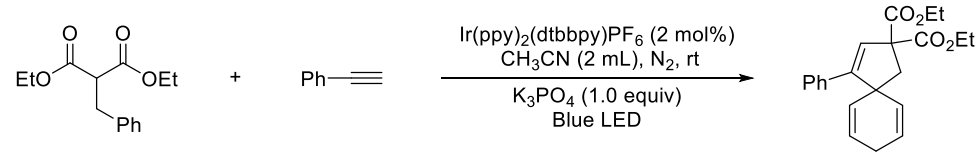
The quantum yield was determined according to the reported method.[6] **1a** (25.0 mg, 0.1 mmol), **2a** (20.4 mg, 0.2 mmol), $Ir(ppy)_2dtbbpyPF_6$ (1.8 mg, 2 mol%), K_3PO_4 (21.2 mg, 1.0 equiv) and anhydrous CH_3CN (1.7 mL) were added to a flame-dried Schlenk tube under nitrogen protection. Then, the reaction mixture was degassed for three times via the 'freeze-pump-thaw' procedure under nitrogen atmosphere. After stirring for 5 minutes, the reaction mixture was transfered to a quartz cuvette to proceed for 8 h under irradiaction of blue LED: $N_A = 6.02214086\times10^{23}$; h = 6.62607004×10^{-34} J·s; $c = 3\times10^8$ m/s; $c_{prod} = 5.9\times10^{-4}$ mol/L; V = 1.7 mL; $\lambda = 4.5\times10^{-7}$ m; t = 28800 s; $P_{ref} = 0.01396$ W; $P_{sample} = 0.00189$ W;

$$\Phi = \frac{N_{prod}}{N_{ph,abs}} = N_A \cdot h \cdot c \frac{c_{prod} \cdot V}{P_{abs} \cdot \Delta t \cdot \lambda_{LED}}$$

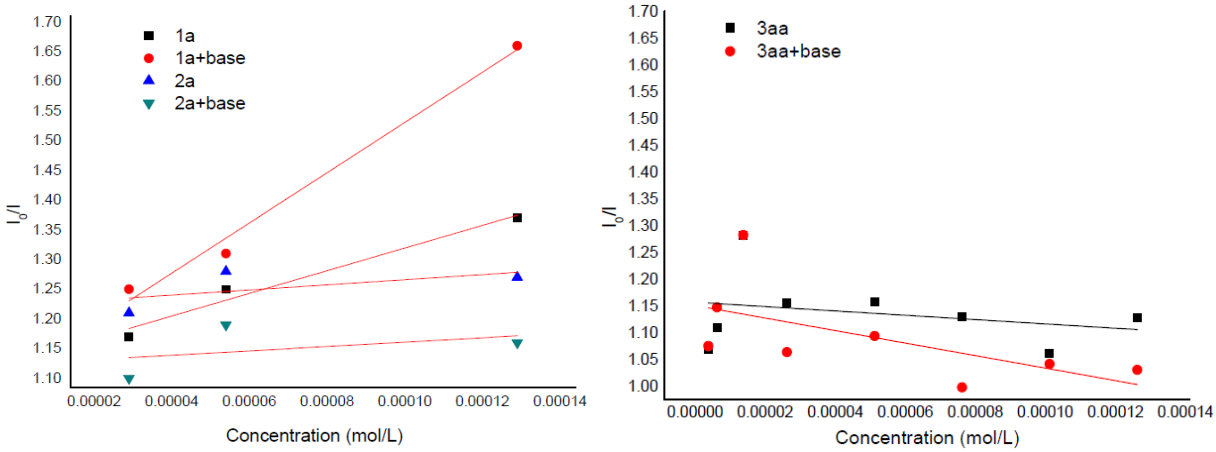
$$f = \frac{1 + R\frac{P_{sample}}{P_{ref}}}{1 - R} \qquad P_{abs} = (P_{ref} - P_{sample})f$$

The value of quantum yield is far less than one (Φ = 0.00073), which showed that this reaction mainly proceed through a photoredox catalytic pathway.

6.5 Luminescence Quenching Experiment



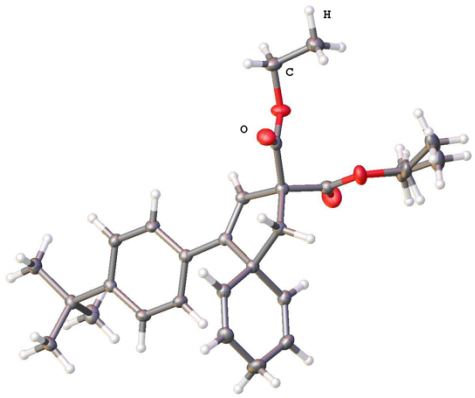
1a **2a** **3aa**



Fluorescence spectra were collected on Cary Eclipse Fluorescence Spectrophotometer. All solutions were excited at 380 nm and the emission intensity at 550 nm was observed. In a typical experiment, the emission spectrum of a 2.5×10^{-7} M solution of $Ir(ppy)_2(dtbbpy)PF_6$ in CH_3CN was collected in the presence and absence of K_3PO_4 (1.0 equiv). Both diethyl benzylmalonate **1a** and phenylacetylene **2a** could quench the excited state of $*[Ir(ppy)_3dtbbpy]^{3+}$. However, the quenching rate constant of **1a** in the presence of K_3PO_4 is much higher than others. Moreover, the luminescence quenching experiment of product **3aa** also was performed, which showed a much smaller quenching rate constant at best. X-axis denotes the concentration of **1a**, **2a** or **3aa**. Y-axis denotes the value of I_0/I (I_0 implies the fluorescence intensity of photocatalyst without addition of quenching agents and I implies the fluorescence intensity of photocatalyst in the presence of quenching agents).

These results suggested that the reaction might undergo an efficient reductive quenching mechanism, in which **1a** might deprotonate first and then be oxidized by the excited state of photocatalyst.

7. X-ray Structure of 3ad



CCDC deposition number 2120296. **Experimental.** Single clear colourless irregular-shaped crystals of **U077** were used as supplied. A suitable crystal with dimensions 0.10 × 0.10 × 0.04 mm³ was selected and mounted on a MITIGEN holder with inert oil on a XtaLAB Synergy R, DW system, HyPix-Arc 150 diffractometer. The crystal was kept at a steady T = 123.00(10) K during data collection. The structure was solved with the **ShelXT** 2018/2 (Sheldrick, 2018) solution program using dual methods and by using **Olex2** 1.3-alpha (Dolomanov et al., 2009) as the graphical interface. The model was refined with **ShelXL** 2018/3 (Sheldrick, 2015) using full matrix least squares minimisation on F^2.

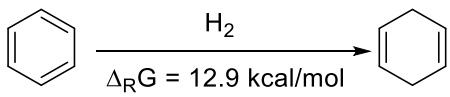
Crystal Data. $C_{26}H_{32}O_4$, M_r = 408.51, monoclinic, $P2_1/c$ (No. 14), a = 10.56390(10) Å, b = 21.9239(2) Å, c = 10.47960(10) Å, β = 111.9890(10)°, $\alpha = \gamma = 90°$, V = 2250.54(4) Å³, T = 123.00(10) K, Z = 4, Z' = 1, μ(Cu K_α) = 0.635, 45358 reflections measured, 4621 unique (R_{int} = 0.0264) which were used in all calculations. The final wR_2 was 0.1059 (all data) and R_1 was 0.0403 (I≥2 σ(I)).

8. Computational Studies

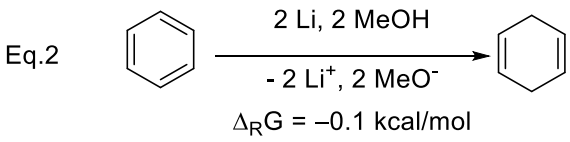
The calculations have been run with the Gaussian16 software package employing the M06-2X functional by Truhlar and co-worker and the 6-311+G** basis set to ensure reliable predictions of relative energies.

All structures have been fully optimized using the standard Berny algorithm and the default integrations grid. The obtained structures were then verified to be minimum energy structures by a subsequent frequency analysis using the harmonic oscillator approximation. The calculated values of ΔG and ΔH remained unscaled but include ZPE corrections and are reported for 298.15K in kcal/mol. To avoid issues arising from calculating separate ions in gasphase the Birch reduction was mimicked by calculating the LiOMe and Lewis-acid base complex of [Li●MeOH].

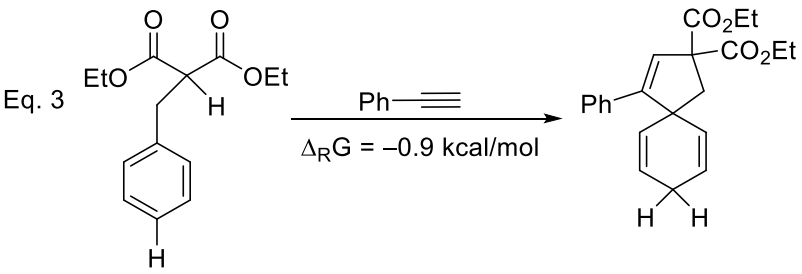
The inherent thermodynamic penalty for reducing benzene to 1,4-cyclohexen was estimated by eq. 1.

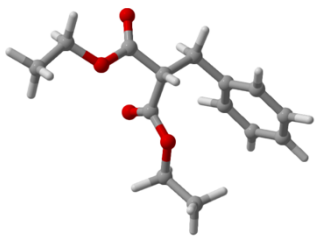
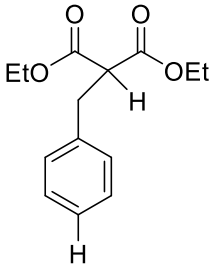
Eq.1 

This formal process of course can only be realized by certain reaction conditions like the Birch reduction (Eq. 2), that not only change the pathway and hence overcome the presumably high barriers, but also renders the process from a significantly endergonic to a thermodynamically allowed process ($\Delta_R G \leq 0$, eq. 2).



Similarly, the title reaction (Eq.3) is a process that is thermodynamically allowed but lacks a significant driving force. To still obtain the product in high yields the reaction design requires the inclusion of irreversible steps. In this specific case both, the reduction of the radical **2a-II** (see main text) by the reduced PC and the protonation of the resulting anion **2a-III** can be in principle considered as irreversible. Confirmation of these irreversible steps was sought in two ways: a) by subjecting product **3aa** to the catalysis conditions. Here no reaction of the **3aa** was observed. b) Addressing the interaction of product, PC* a Stern-Vollmer-plot was recorded, indicating insignificant quenching of the PC excited state by **3aa** (see part 6.5).



	**1a**	

xyz matrix

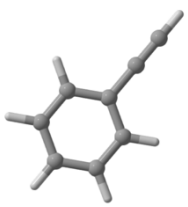
C	-0.40726200	0.65178900	0.43285100
C	-0.76359900	-0.64907900	-0.26354500
O	-0.70160300	0.90754600	1.56965200
C	-2.21420100	-1.00341200	0.00527300
O	-2.59345200	-2.03292700	0.49006000
C	0.18247700	-1.75105800	0.25448600
H	-0.63502000	-0.50713000	-1.33948500
C	1.62833300	-1.34930800	0.09508600
C	2.28520100	-1.51712700	-1.12395200
C	3.59163900	-1.07280100	-1.29512900
C	4.25997200	-0.44989400	-0.24501200
C	3.61549800	-0.28068000	0.97641700
C	2.30885200	-0.72947700	1.14432500
H	5.27853800	-0.10431300	-0.37641000

O	0.35784000	1.41930400	-0.34155200
C	2.08648400	3.01265000	-0.63260200
C	0.99279600	2.54054600	0.29741400
O	-3.02417600	-0.01732800	-0.39153500
C	-5.14806500	1.02082000	-0.62692600
C	-4.42777000	-0.21847200	-0.14844000
H	-0.05346500	-1.93153600	1.30500800
H	-0.03232700	-2.67261300	-0.28957300
H	1.76681900	-1.99996800	-1.94673400
H	4.08924400	-1.21377100	-2.24747400
H	4.13152100	0.19632900	1.80178700
H	1.80511800	-0.59283900	2.09652100
H	2.61400800	3.85823100	-0.18753600
H	2.79934600	2.20378400	-0.80537200
H	1.67162800	3.32681200	-1.59141100
H	0.23887900	3.30769900	0.48675600
H	1.39112700	2.20696100	1.25784300
H	-6.22096500	0.91201400	-0.45944100
H	-4.79882900	1.89980300	-0.08383900
H	-4.97754600	1.17849600	-1.69277400
H	-4.74837900	-1.11556400	-0.68213100
H	-4.57069400	-0.39213400	0.91977500

Thermodynamic data

Zero-point correction=	0.302416 (Hartree/Particle)
Thermal correction to Energy=	0.320751
Thermal correction to Enthalpy=	0.321695
Thermal correction to Gibbs Free Energy=	0.253732
Sum of electronic and zero-point Energies=	-844.841232
Sum of electronic and thermal Energies=	-844.822897
Sum of electronic and thermal Enthalpies=	-844.821952
Sum of electronic and thermal Free Energies=	-844.889916

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	201.274	66.358	143.041

	**2a**	Ph—≡

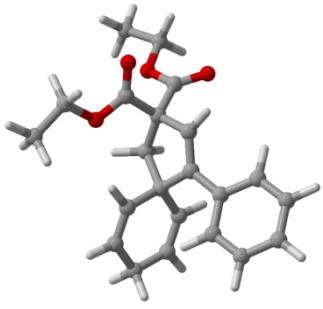
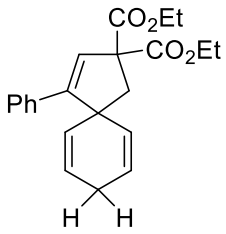
xyz matrix

C	2.02017900	0.00033600	-0.00001200
C	3.22199400	-0.00012100	-0.00000100
C	0.58609700	0.00014100	-0.00000500
C	-0.11896800	1.20882600	-0.00000300
C	-1.50739300	1.20473400	0.00000200
C	-2.20412600	-0.00016700	0.00000500
C	-1.50713500	-1.20491700	0.00000200
C	-0.11870800	-1.20869900	-0.00000200
H	4.28580900	-0.00045200	0.00007600
H	0.43136800	2.14157800	-0.00000400
H	-2.04680000	2.14424700	0.00000400
H	-3.28750900	-0.00028500	0.00000900
H	-2.04634000	-2.14454700	0.00000400
H	0.43182600	-2.14133200	-0.00000500

Thermodynamic data

Zero-point correction=	0.110396 (Hartree/Particle)
Thermal correction to Energy=	0.116770
Thermal correction to Enthalpy=	0.117714
Thermal correction to Gibbs Free Energy=	0.080000
Sum of electronic and zero-point Energies=	-308.227101
Sum of electronic and thermal Energies=	-308.220728
Sum of electronic and thermal Enthalpies=	-308.219784
Sum of electronic and thermal Free Energies=	-308.257497

	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	73.274	24.879	79.375

	**3aa**	

xyz matrix

C	-1.49359900	0.15145400	-2.19939200
C	-2.25780500	0.99599700	-2.88341300
C	-2.52978300	2.40526800	-2.44780700
C	-1.83070800	2.76056900	-1.16877500
C	-1.07886400	1.90855400	-0.47845200

C	-0.77921300	0.49010600	-0.91436000
C	0.76184200	0.29202200	-1.07827500
C	1.26472400	-0.44528600	0.18651200
C	-0.00875900	-0.98727400	0.78786400
C	-1.10952600	-0.52107400	0.19370000
H	-2.23681100	3.10440300	-3.24076000
H	-3.61255400	2.54989800	-2.32947000
C	-2.48553600	-0.94294200	0.52912500
C	-3.58291700	-0.09256400	0.35606700
C	-4.86430600	-0.51380900	0.69349200
C	-5.07497000	-1.79261600	1.19720400
C	-3.99331700	-2.65399700	1.35616200
C	-2.71320000	-2.23492300	1.02015900
C	1.97432200	0.40965800	1.23611900
O	2.68946300	-0.05205800	2.08392400
O	1.66659200	1.70567600	1.14944100
C	1.72360300	3.95521100	1.90904500
C	2.23498900	2.55554100	2.16256000
C	2.22716400	-1.57091200	-0.17799300
O	2.00896900	-2.74145500	-0.04046000
O	3.34649700	-1.07256400	-0.71503500
C	5.54059700	-1.26494100	-1.60618500
C	4.35571400	-2.03397700	-1.06899500
H	-1.34863400	-0.86380000	-2.56106000
H	-2.72843900	0.66305000	-3.80342100
H	-1.96970900	3.77038400	-0.79366200
H	-0.60390600	2.22182800	0.44503400
H	0.94006200	-0.34730800	-1.94629800
H	1.27833000	1.23543200	-1.24751900
H	0.02326000	-1.67682200	1.62202800
H	-3.43120900	0.90705600	-0.02999100
H	-5.70174900	0.16116400	0.56078100
H	-6.07513600	-2.11967700	1.45553200
H	-4.14852300	-3.65870500	1.73125300
H	-1.87939700	-2.92129200	1.11367900
H	2.14914900	4.64238700	2.64226200
H	2.00596800	4.29299100	0.91088900
H	0.63634400	3.99098500	1.99430600
H	1.93707600	2.17605700	3.14177300
H	3.32280500	2.49364500	2.09456700
H	6.33464700	-1.95892000	-1.88717500
H	5.25796200	-0.68645900	-2.48687000
H	5.92812400	-0.58195700	-0.84921800
H	4.60855100	-2.61067900	-0.17722300

H	3.93890200	-2.72084300	-1.80858000

Thermodynamic data

Zero-point correction=	0.417560 (Hartree/Particle)
Thermal correction to Energy=	0.442303
Thermal correction to Enthalpy=	0.443247
Thermal correction to Gibbs Free Energy=	0.360048
Sum of electronic and zero-point Energies=	-1153.091336
Sum of electronic and thermal Energies=	-1153.066593
Sum of electronic and thermal Enthalpies=	-1153.065649
Sum of electronic and thermal Free Energies=	-1153.148848

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	277.549	93.050	175.107

	benzene	

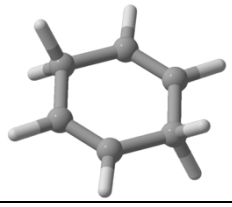
xyz matrix

C	0.00000000	1.39166700	0.00000000
C	1.20521900	0.69583400	0.00000000
C	1.20521900	-0.69583400	0.00000000
C	0.00000000	-1.39166700	0.00000000
C	-1.20521900	-0.69583400	0.00000000
C	-1.20521900	0.69583400	0.00000000
H	0.00000000	2.47537700	0.00000000
H	2.14374000	1.23768900	0.00000000
H	2.14374000	-1.23768900	0.00000000
H	0.00000000	-2.47537700	0.00000000
H	-2.14374000	-1.23768900	0.00000000
H	-2.14374000	1.23768900	0.00000000

Thermodynamic data

Zero-point correction=	0.101092 (Hartree/Particle)
Thermal correction to Energy=	0.105478
Thermal correction to Enthalpy=	0.106422
Thermal correction to Gibbs Free Energy=	0.075980
Sum of electronic and zero-point Energies=	-232.097257
Sum of electronic and thermal Energies=	-232.092870
Sum of electronic and thermal Enthalpies=	-232.091926
Sum of electronic and thermal Free Energies=	-232.122368

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	66.189	17.070	64.071

	1,4-cyclohexadiene	

xyz matrix

C	0.66460400	-1.25146000	-0.00003600
C	-0.66460700	-1.25145900	-0.00003600
C	-1.49670300	0.00000100	0.00006300
C	-0.66460400	1.25146000	-0.00003600
C	0.66460700	1.25145900	-0.00003600
C	1.49670300	-0.00000100	0.00006300
H	1.19853200	-2.19701400	-0.00022000
H	-1.19853700	-2.19701200	-0.00021800
H	-2.16477700	0.00000200	-0.87046700
H	-2.16432800	0.00000200	0.87095800
H	-1.19853300	2.19701400	-0.00021900
H	1.19853700	2.19701200	-0.00022000
H	2.16477900	-0.00000200	-0.87046500
H	2.16432600	-0.00000200	0.87096000

Thermodynamic data

Zero-point correction=	0.122947 (Hartree/Particle)
Thermal correction to Energy=	0.128238
Thermal correction to Enthalpy=	0.129182
Thermal correction to Gibbs Free Energy=	0.094339
Sum of electronic and zero-point Energies=	-233.242826
Sum of electronic and thermal Energies=	-233.237536
Sum of electronic and thermal Enthalpies=	-233.236591
Sum of electronic and thermal Free Energies=	-233.271434

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	80.470	19.997	73.332

	H_2	

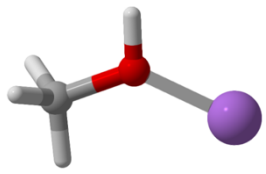
xyz matrix

H	0.00000000	0.00000000	0.36774000
H	0.00000000	0.00000000	-0.36774000

Thermodynamic data

Zero-point correction=	0.010467 (Hartree/Particle)
Thermal correction to Energy=	0.012827
Thermal correction to Enthalpy=	0.013771
Thermal correction to Gibbs Free Energy=	-0.001002
Sum of electronic and zero-point Energies=	-1.122024
Sum of electronic and thermal Energies=	-1.119664
Sum of electronic and thermal Enthalpies=	-1.118720
Sum of electronic and thermal Free Energies=	-1.133493

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	8.049	4.968	31.093

	[MeOH ● Li]	

xyz matrix

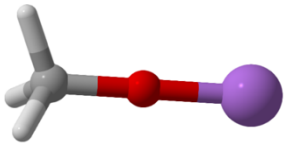
C	-0.95584500	0.19543500	0.00002900
H	-0.87481600	1.28047100	0.00027900
H	-1.48785700	-0.12700700	0.89586000
H	-1.48790200	-0.12662200	-0.89591400
O	0.38304400	-0.31747200	-0.00013600
H	0.37937100	-1.28286000	0.00042500
Li	2.04730600	0.54106300	0.00008900

Thermodynamic data

Zero-point correction=	0.053236 (Hartree/Particle)
Thermal correction to Energy=	0.058241
Thermal correction to Enthalpy=	0.059185
Thermal correction to Gibbs Free Energy=	0.026492
Sum of electronic and zero-point Energies=	-123.152289
Sum of electronic and thermal Energies=	-123.147285
Sum of electronic and thermal Enthalpies=	-123.146340
Sum of electronic and thermal Free Energies=	-123.179034

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin

Total	36.547	13.998	68.809

	[MeOLi]	

xyz matrix

C	0.93106400	-0.00002400	0.00005000
H	1.34945400	0.67958200	0.76104800
H	1.35008600	0.31925500	-0.96873900
H	1.34963700	-0.99875600	0.20817800
O	-0.44256600	0.00001100	-0.00015500
Li	-2.03167700	-0.00000800	0.00015000

Thermodynamic data

Zero-point correction=	0.041644 (Hartree/Particle)
Thermal correction to Energy=	0.045790
Thermal correction to Enthalpy=	0.046735
Thermal correction to Gibbs Free Energy=	0.017151
Sum of electronic and zero-point Energies=	-122.615529
Sum of electronic and thermal Energies=	-122.611383
Sum of electronic and thermal Enthalpies=	-122.610439
Sum of electronic and thermal Free Energies=	-122.640022

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	28.734	11.093	62.264

9. References

[1] W. L. F. Armarego, Purification of laboratory chemicals, Eighth edition; Butterworth-Heinemann: Kidlington, Oxford, United Kingdom, Cambridge, MA, 2017.

[2] A. S. Sarac, S. E. Ozgul, H. Faltz, A. Gencturk, H. D. Gilsing, B. Schulz, *J. Nanosci. Nanotechnol.* **2010**, *10*, 8043-8053.

[3] a) N. Wurzer, U. Klimczak, T. Babl, S. Fischer, R. A. Angnes, D. Kreutzer, A. Pattanaik, J. Rehbein, O. Reiser, *ACS Catal.* **2021**, *11*, 12019-12028; b) C. Song, X. Dong, Z. Wang, K. Liu, C. W. Chiang, A. Lei, *Angew. Chem. Int. Ed.* **2019**, *58*, 12206-12210. c) Z. F. Xu, H. Dai, L. Shan, C. Y. Li, *Org. Lett.* **2018**, *20*, 1054-1057.

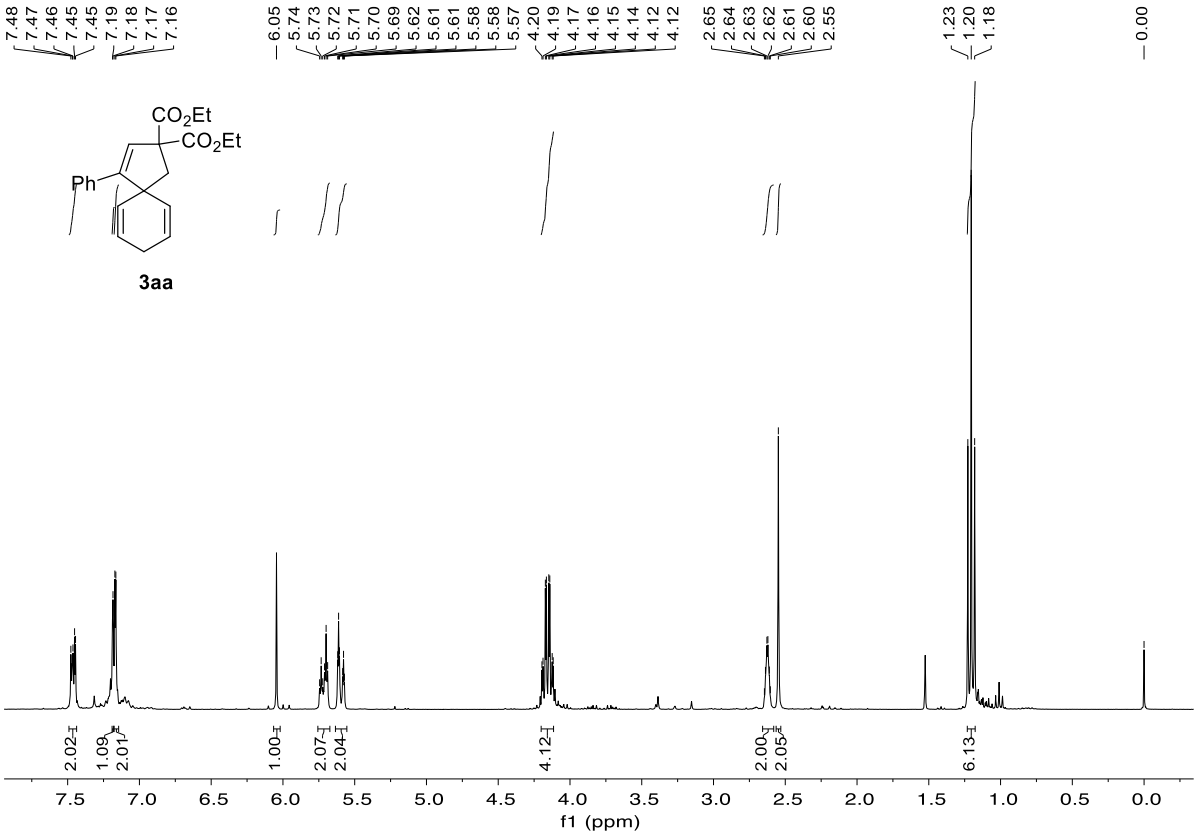
[4] a) L. Qi, Y. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 13312-13315; b) J. Zhang, Y. Li, F. Zhang, C. Hu, Y. Chen, *Angew. Chem. Int. Ed.* **2016**, *55*, 1872-1875; c) Q. Q. Zhao, J. Chen, D. M. Yan, J. R. Chen, W. J. Xiao, *Org. Lett.* **2017**, *19*, 3620-3623;

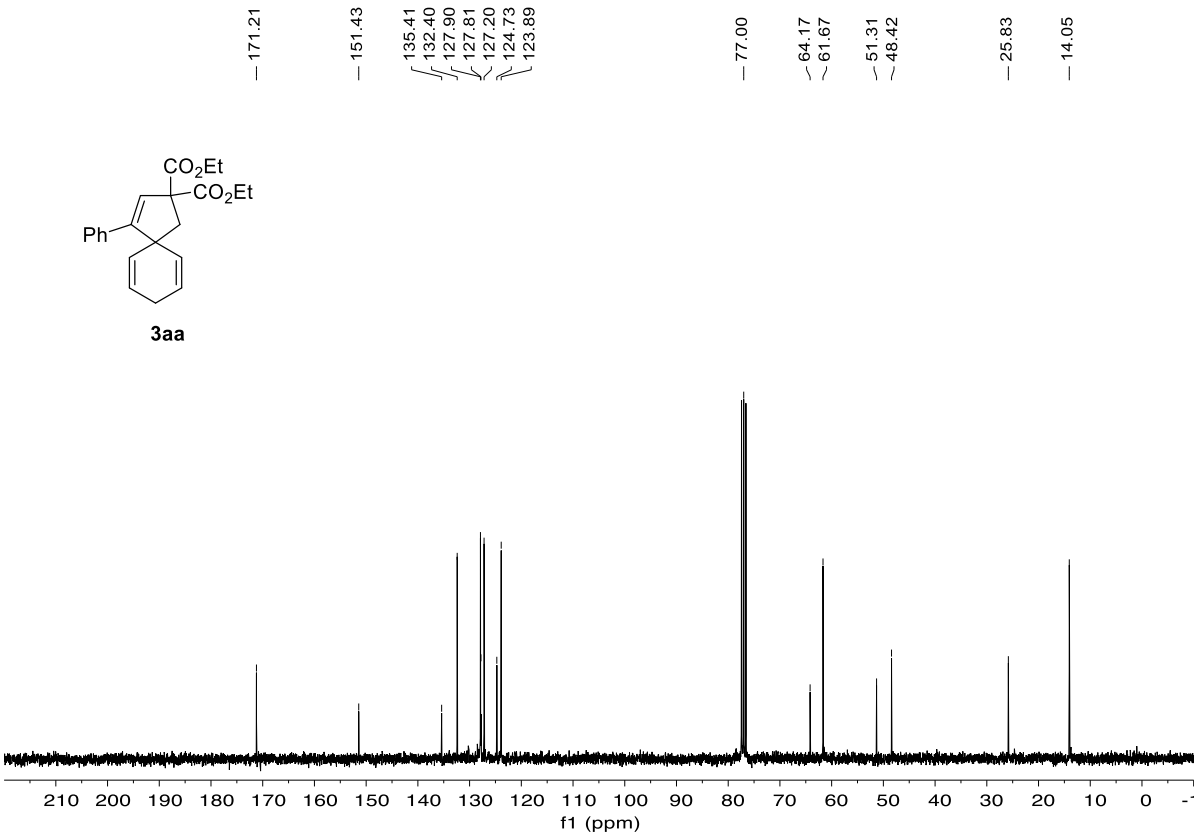
[5] M. A. Cismesia, T. P. Yoon, *Chem. Sci*. **2015**, *6*, 5426-5434.

[6] U. Megerle, R. Lechner, B. König, E. Riedle, *Photochem. Photobiol. Sci.* **2010**, *9*, 1400-1406.

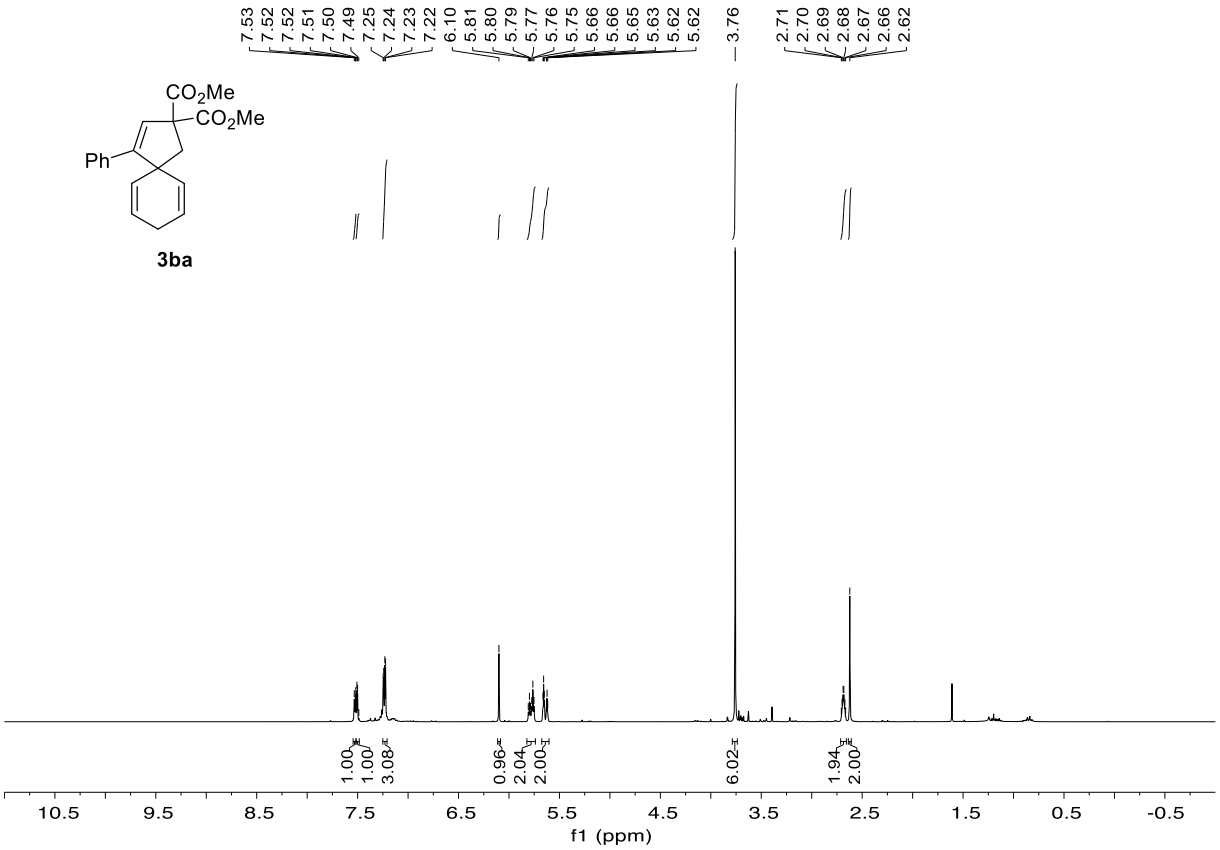
10. NMR Spectra

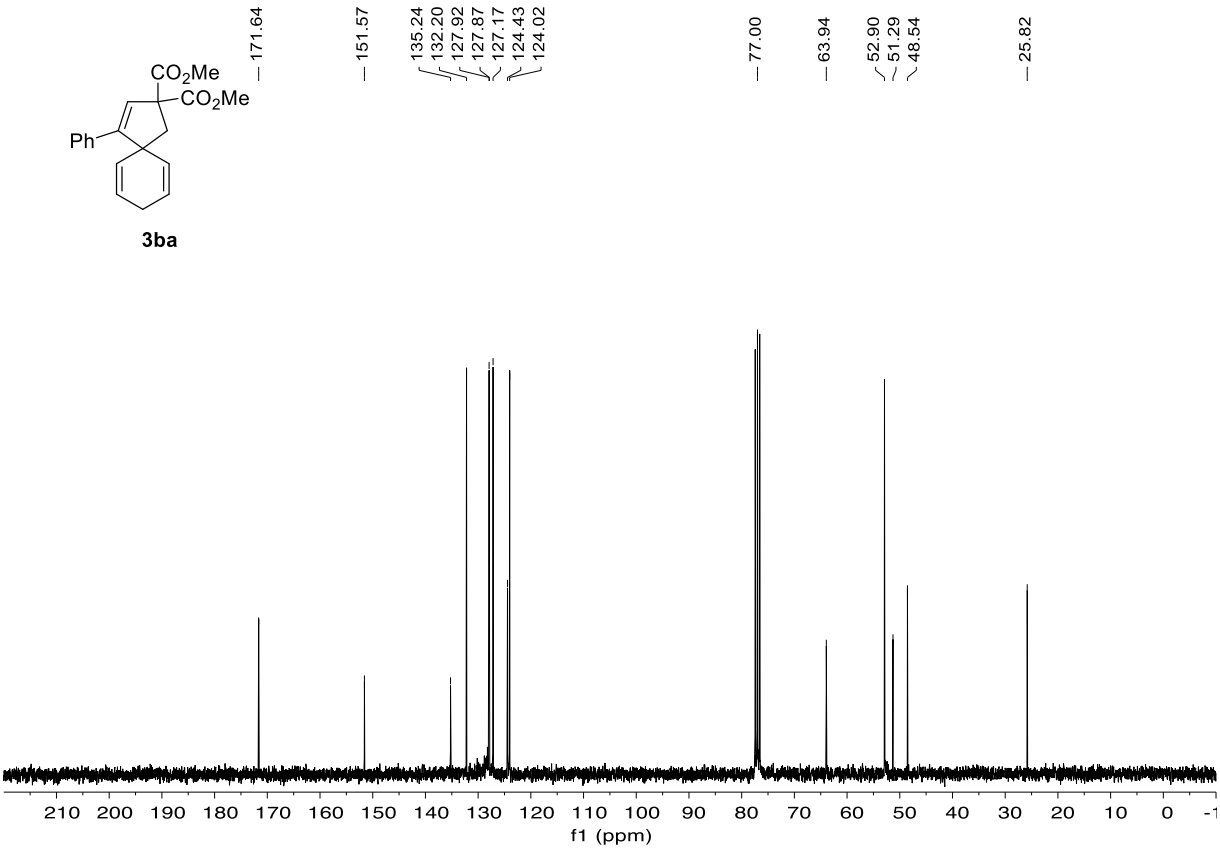
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3aa



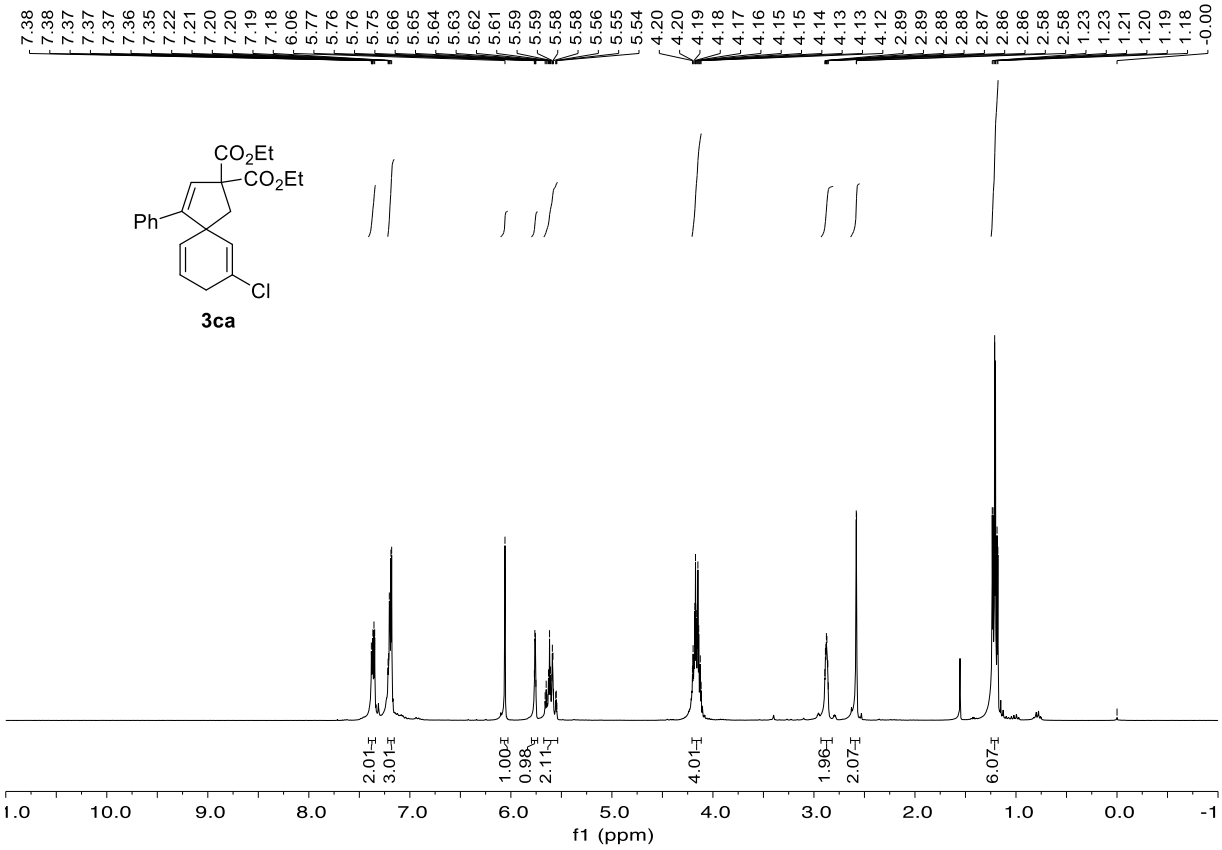


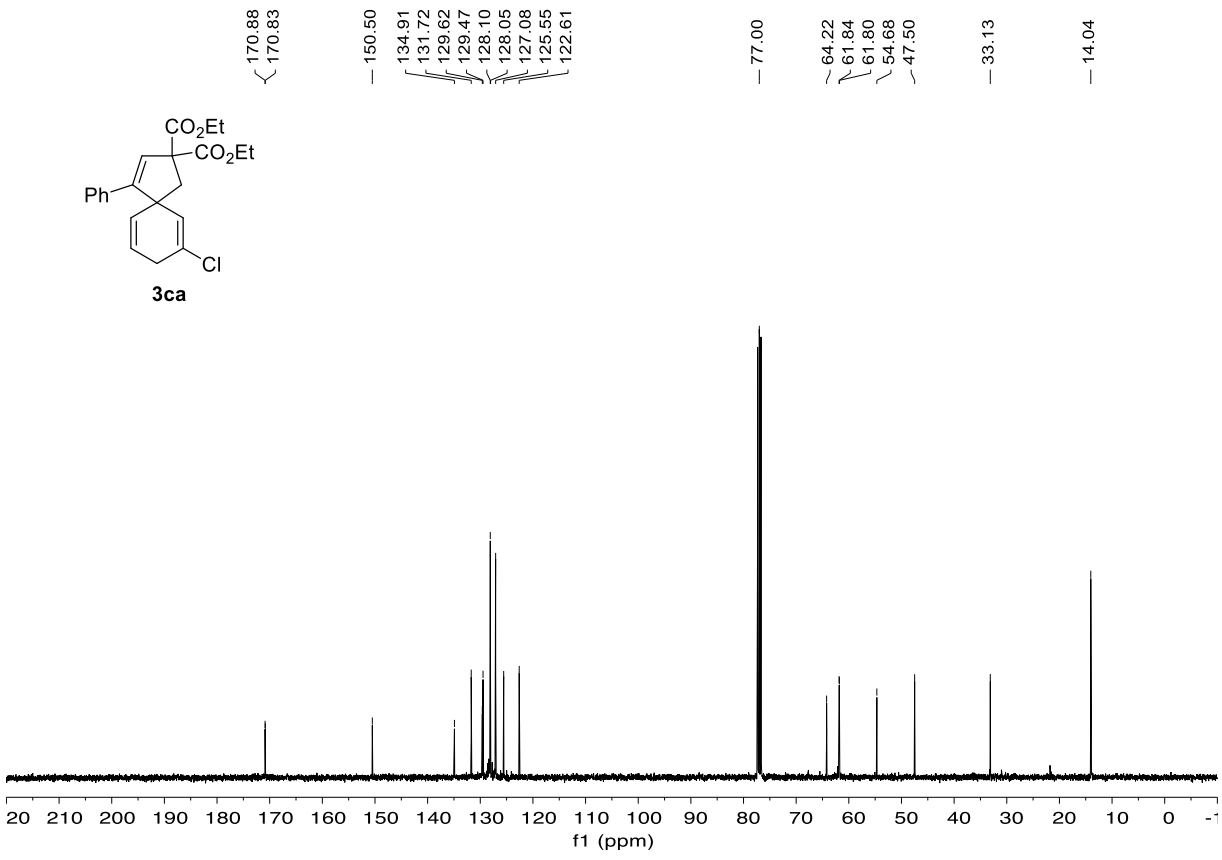
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ba



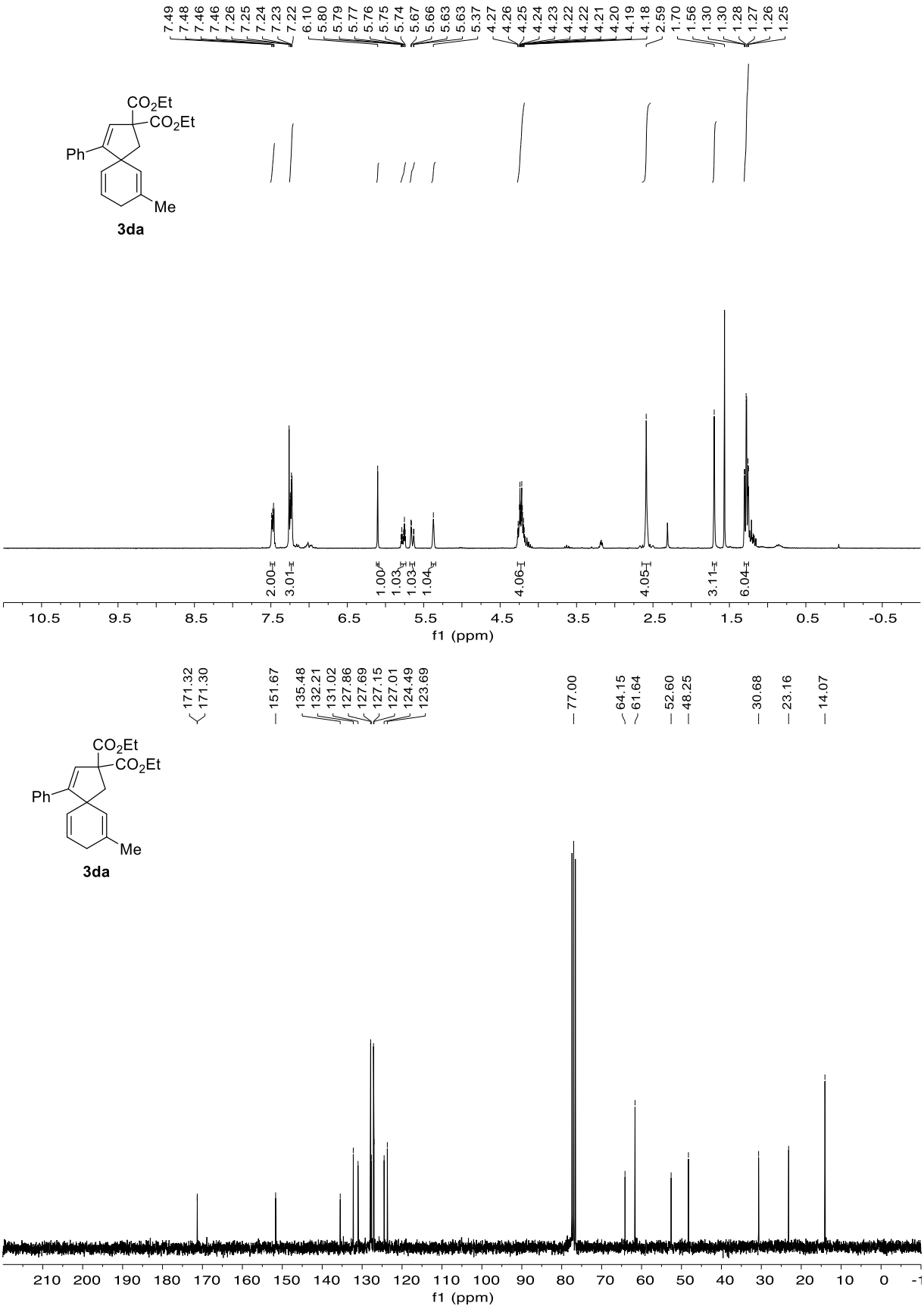


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ca

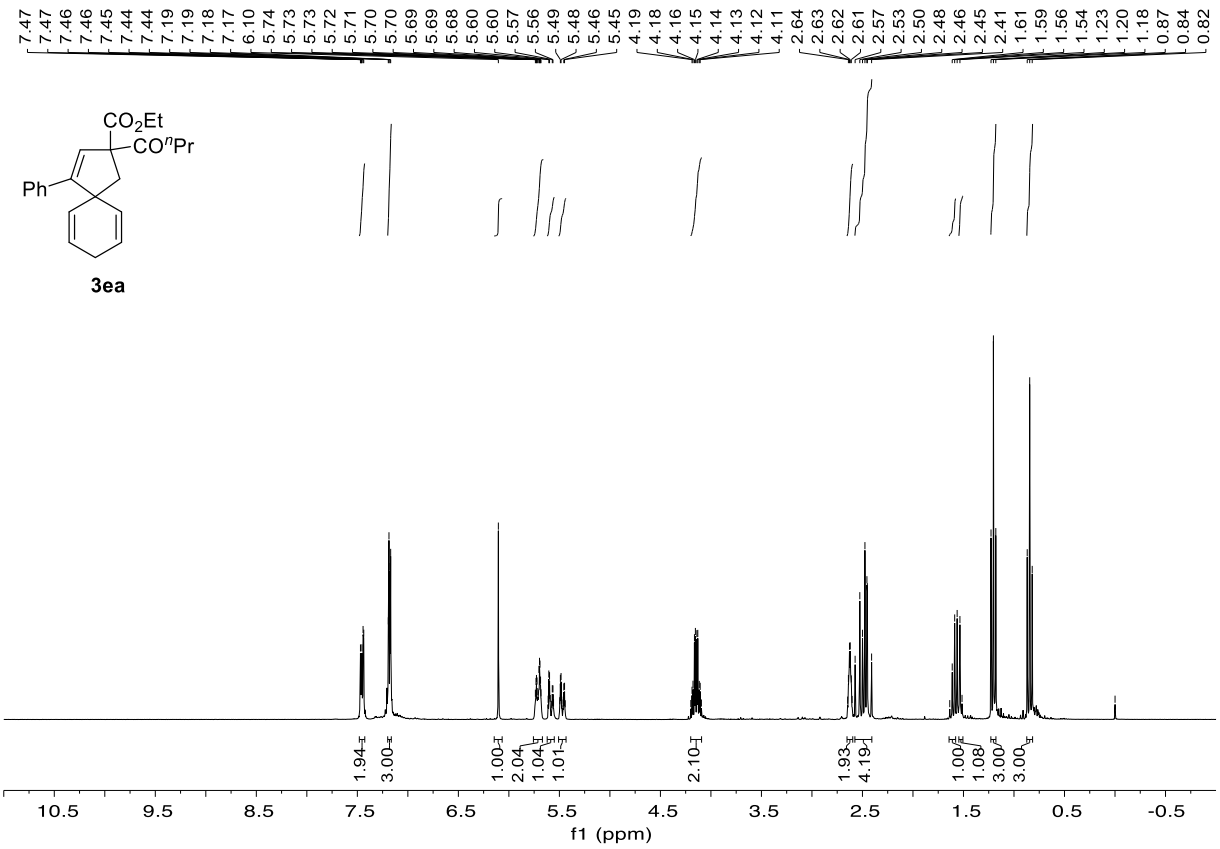


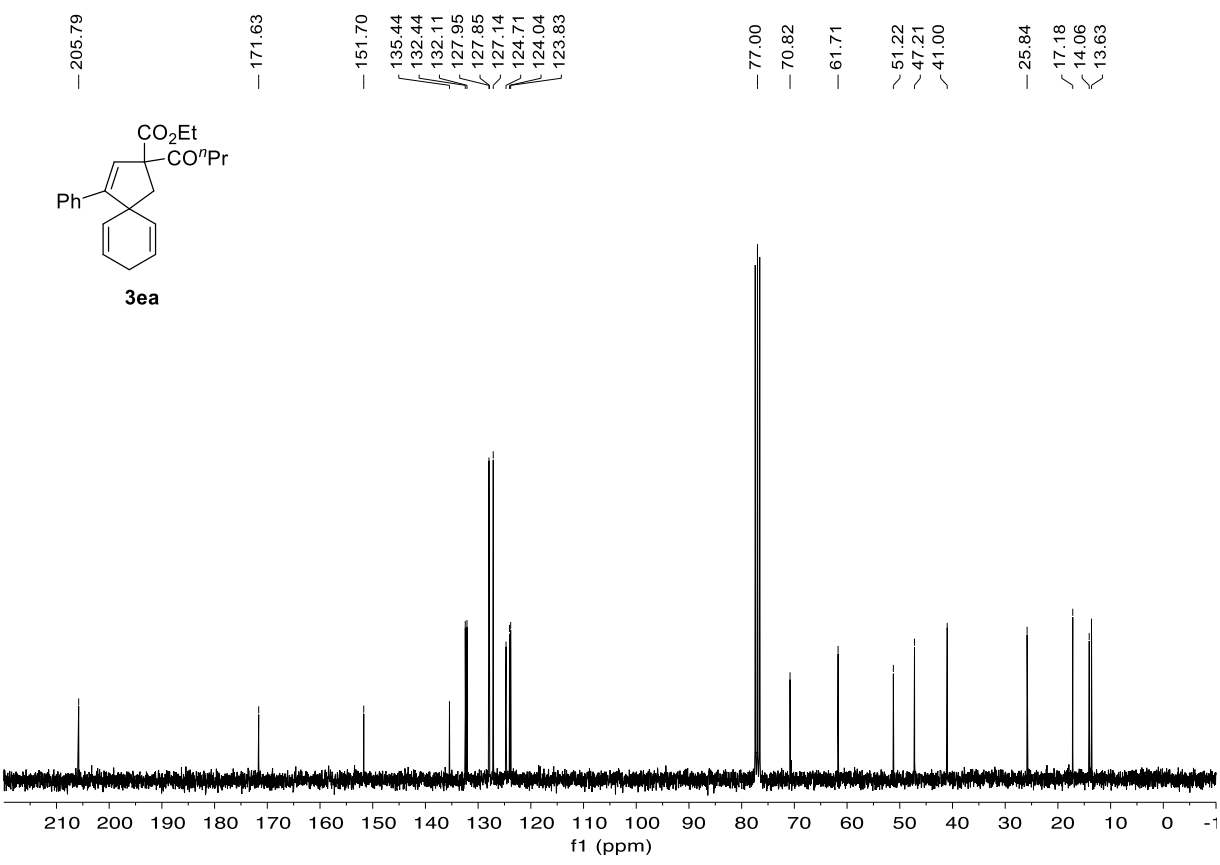


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3da

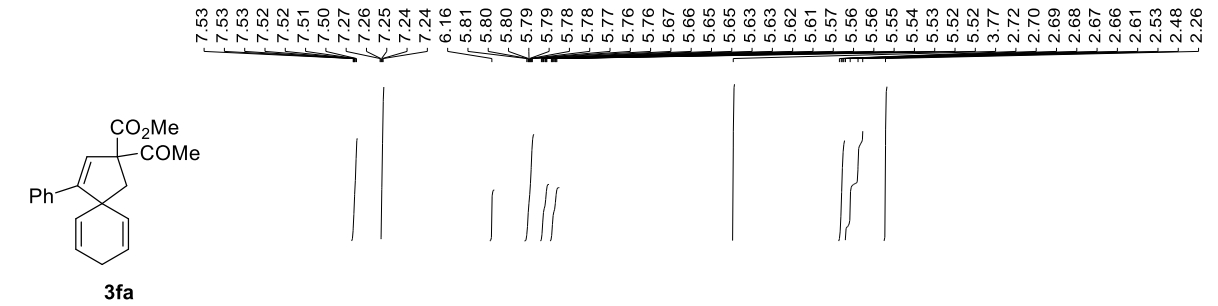


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ea

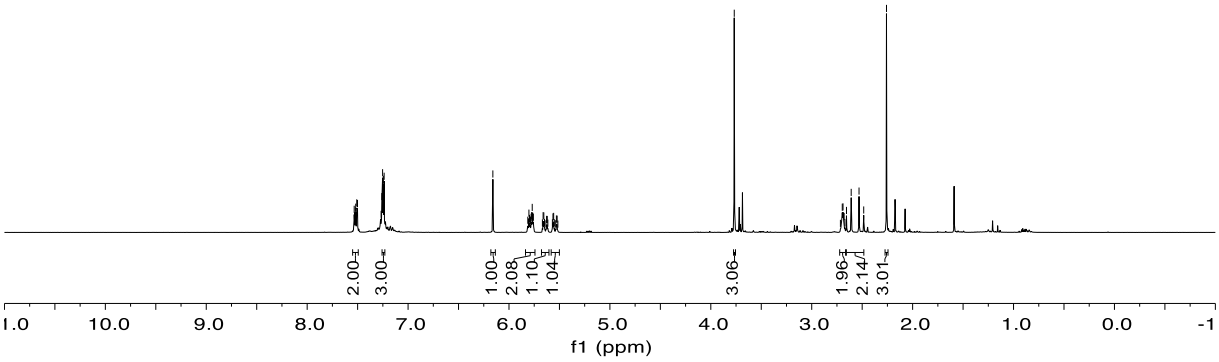


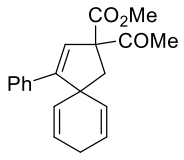


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3fa

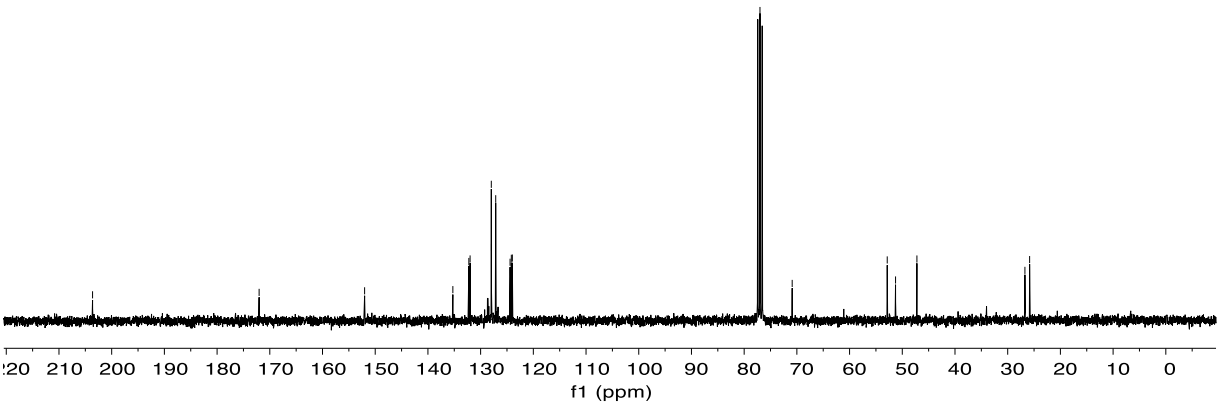


3fa

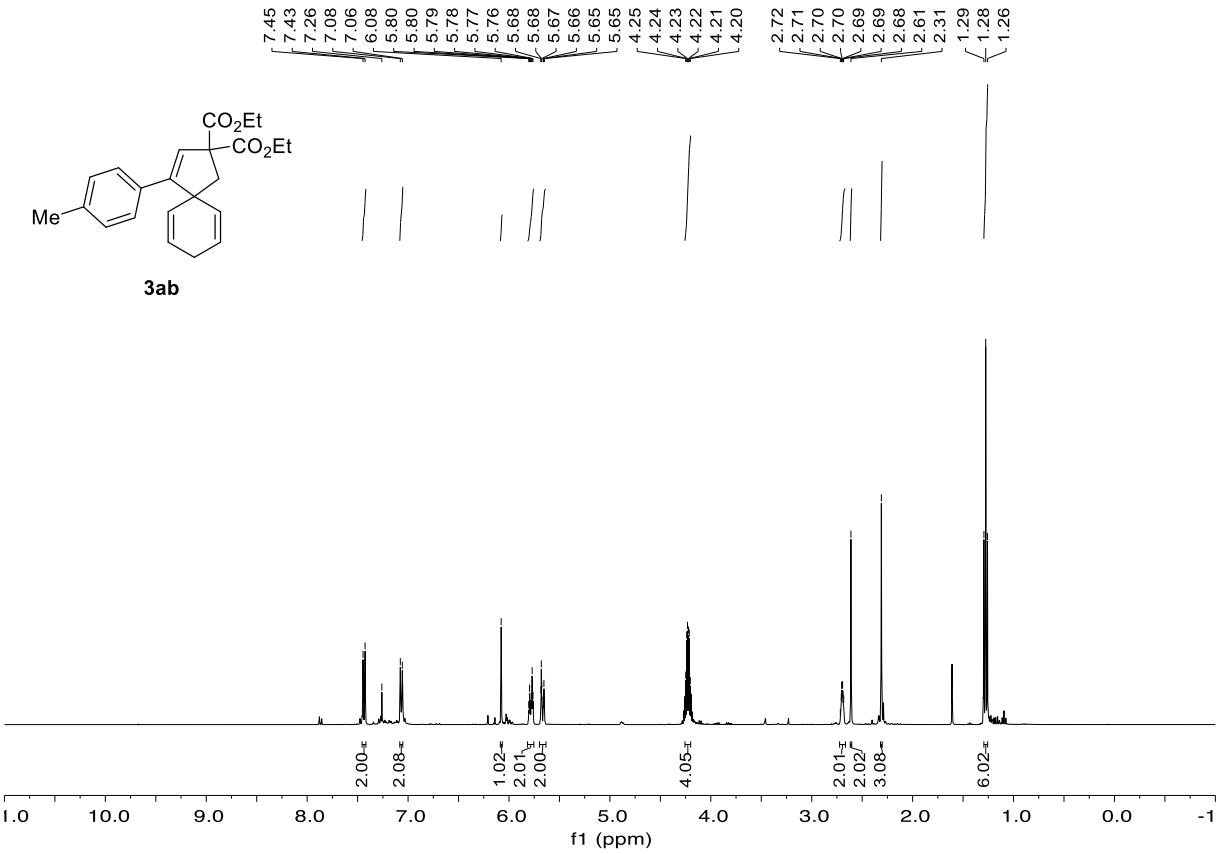


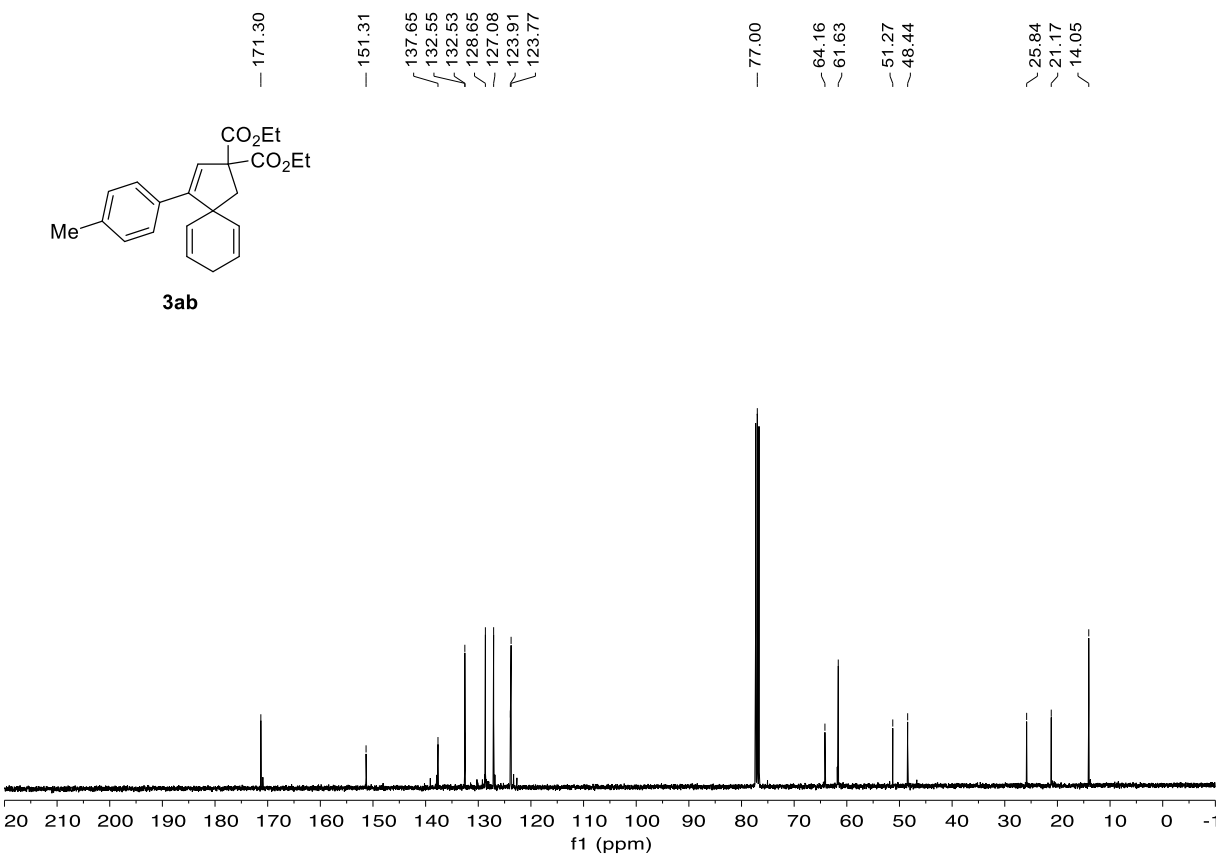


3fa

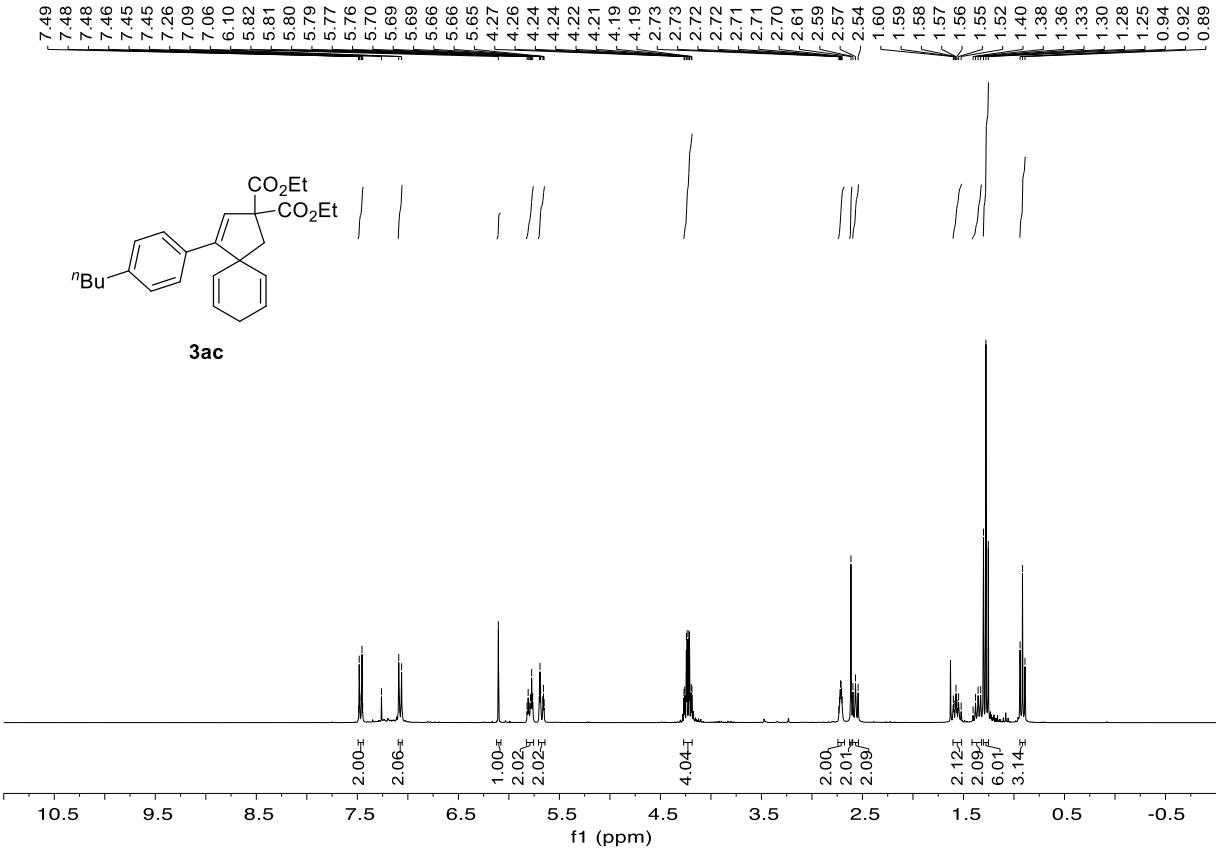


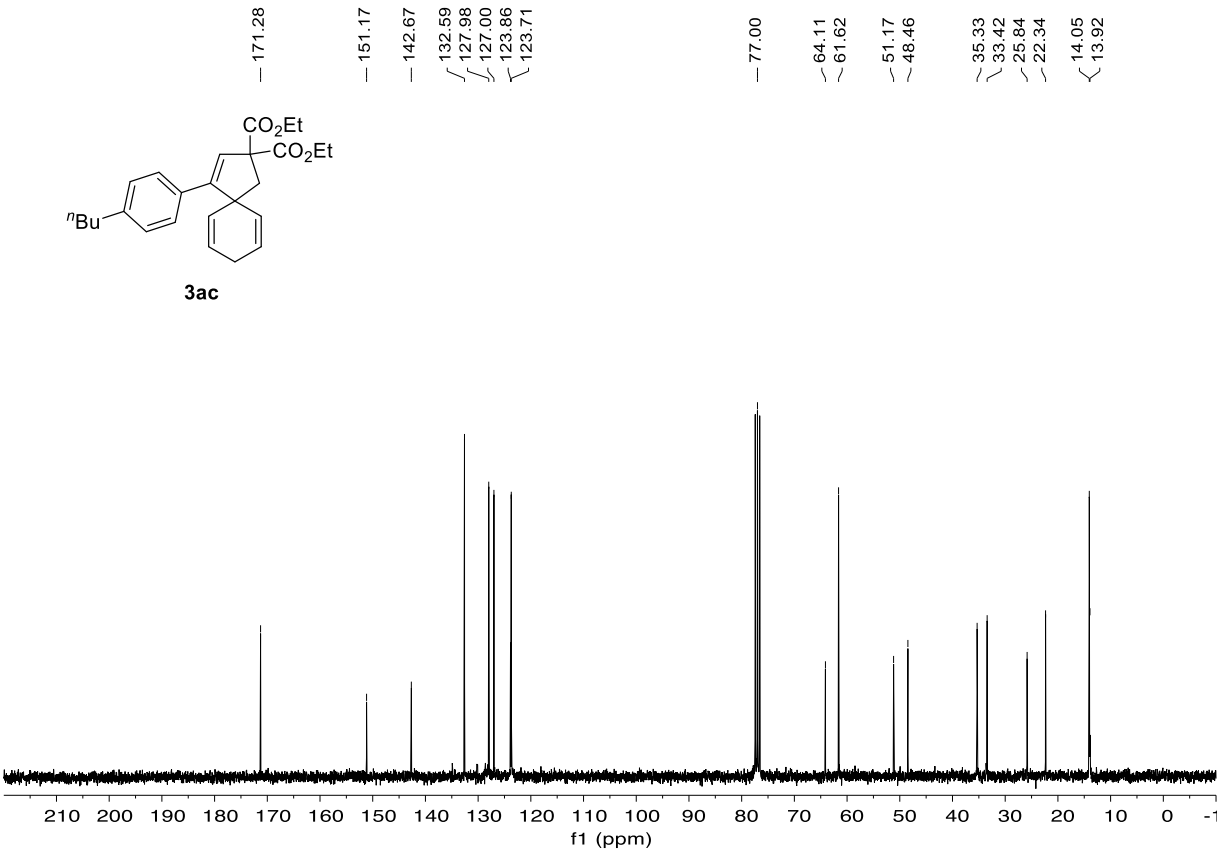
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ab



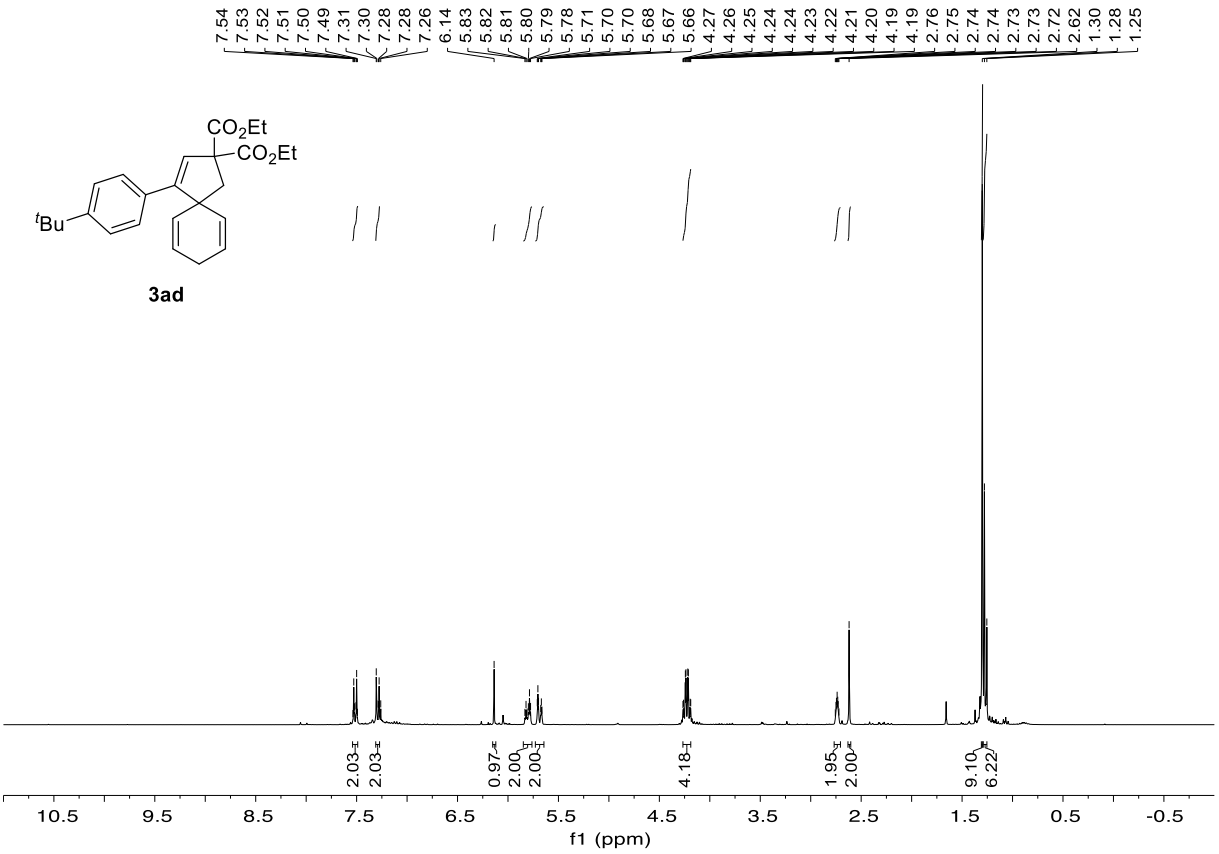


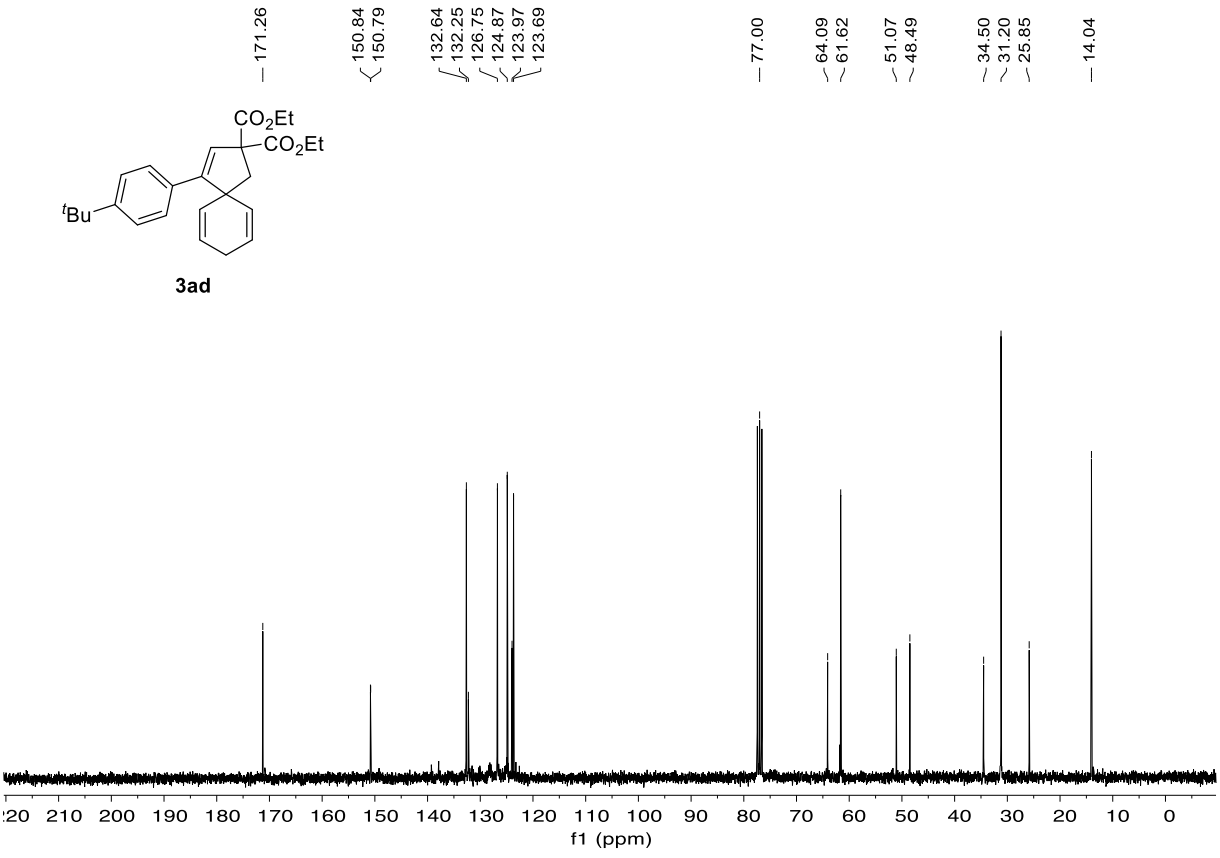
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ac



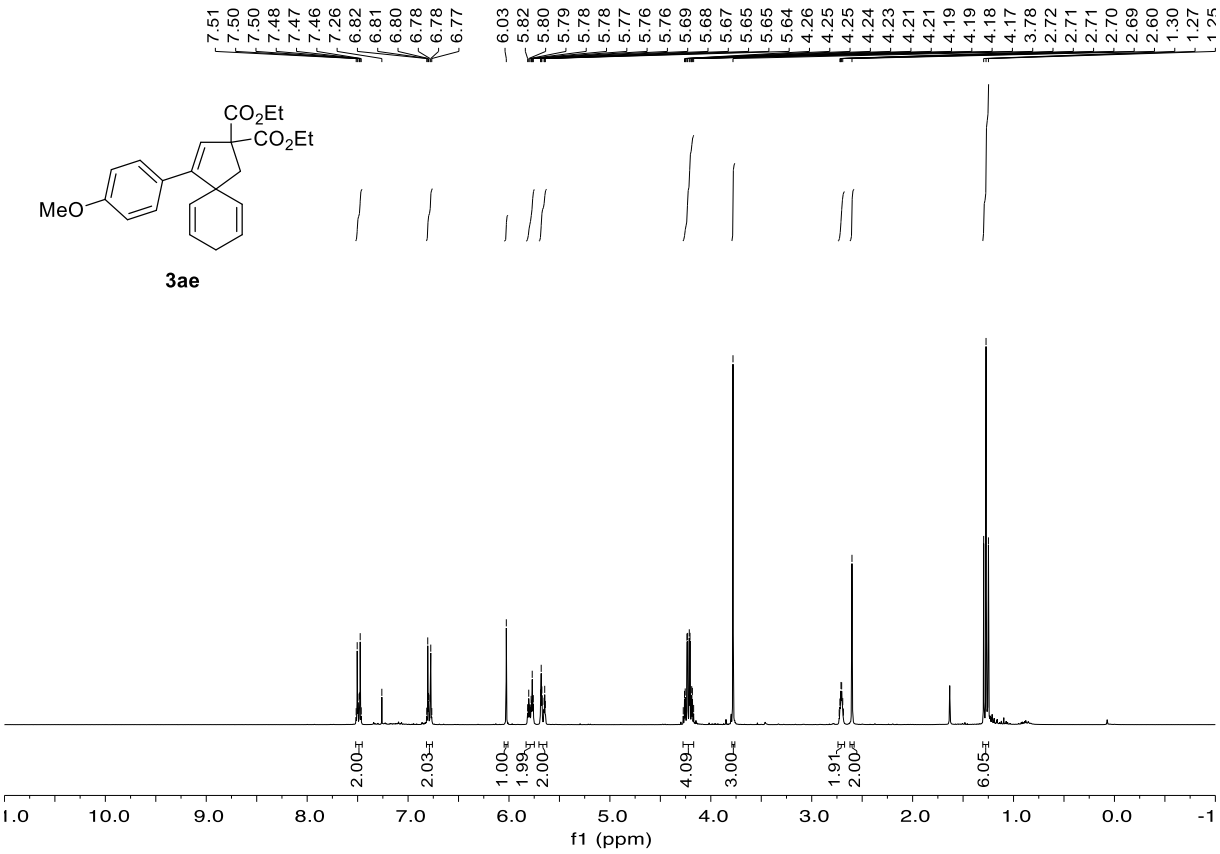


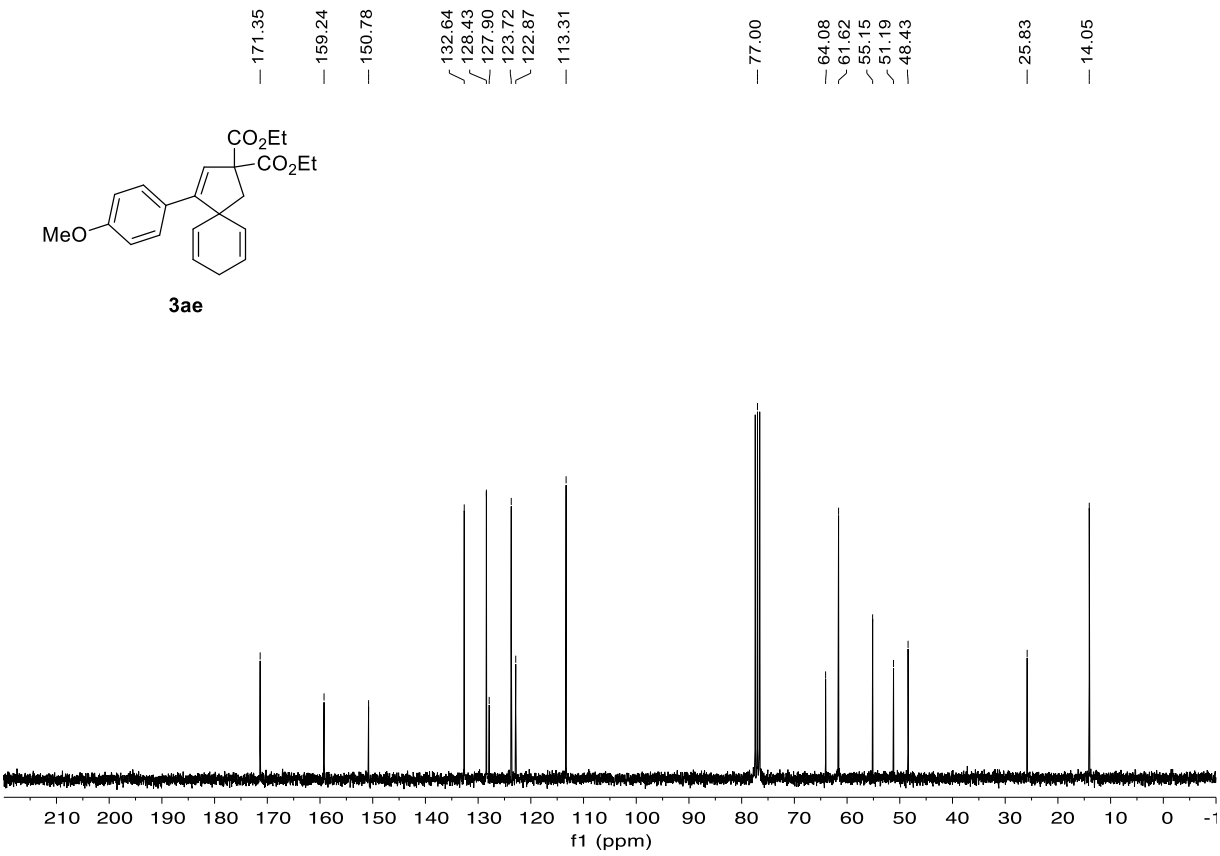
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ad



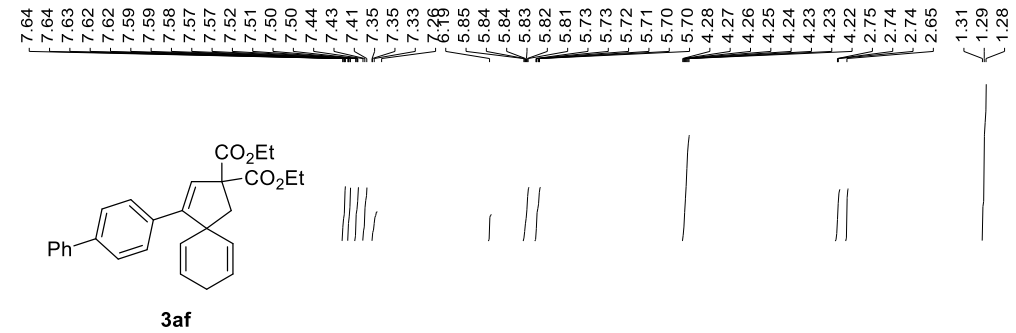


^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ae

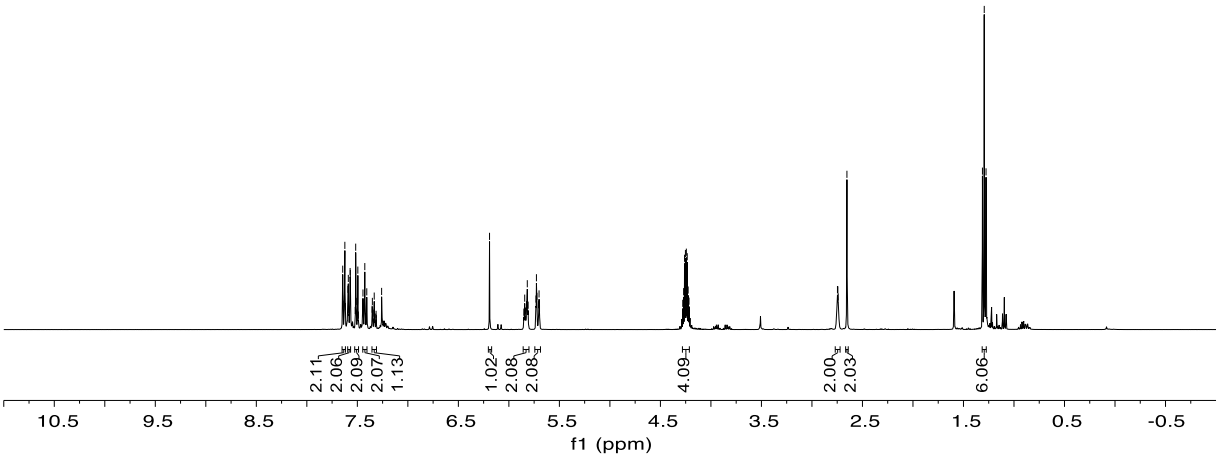


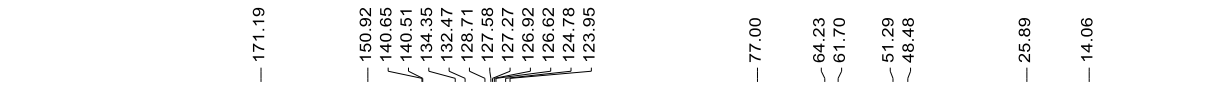


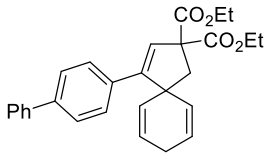
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3af



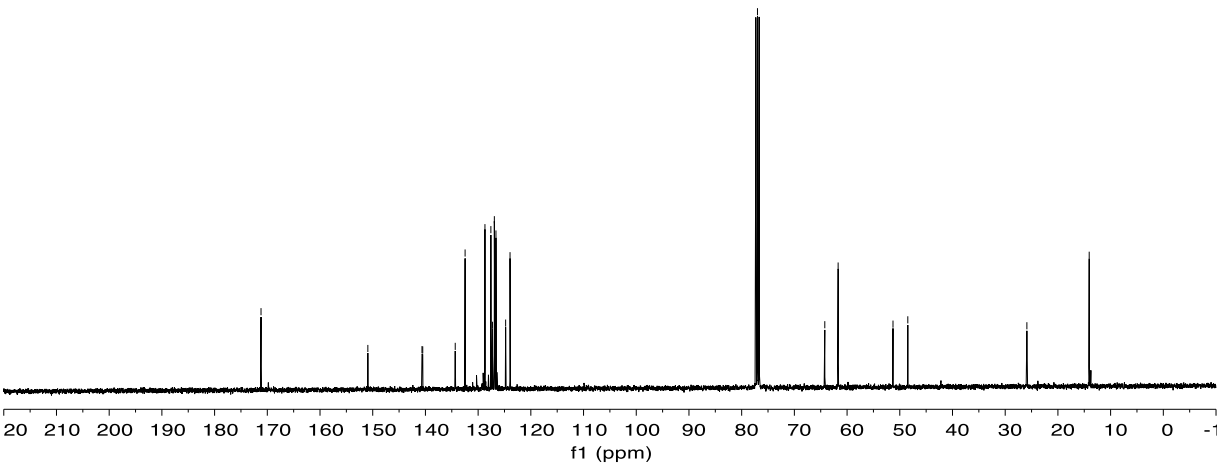
3af



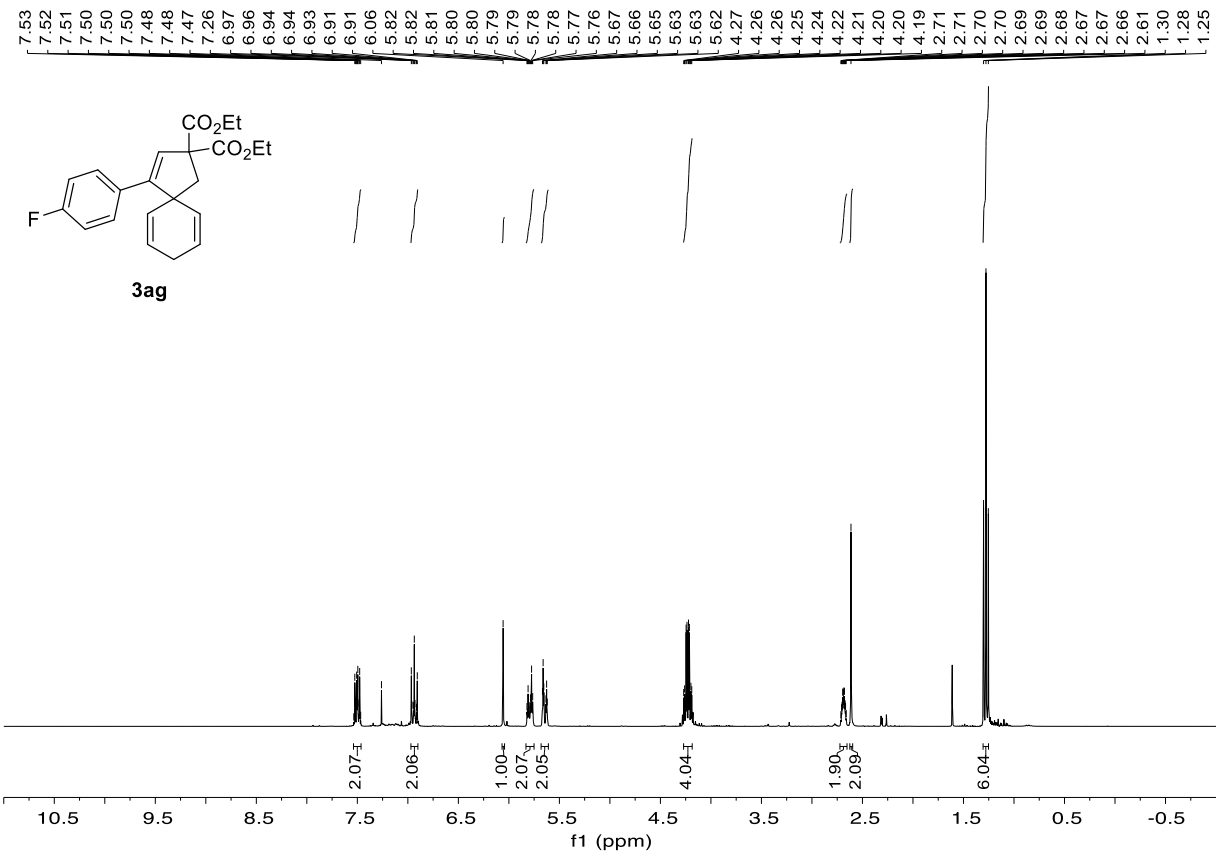


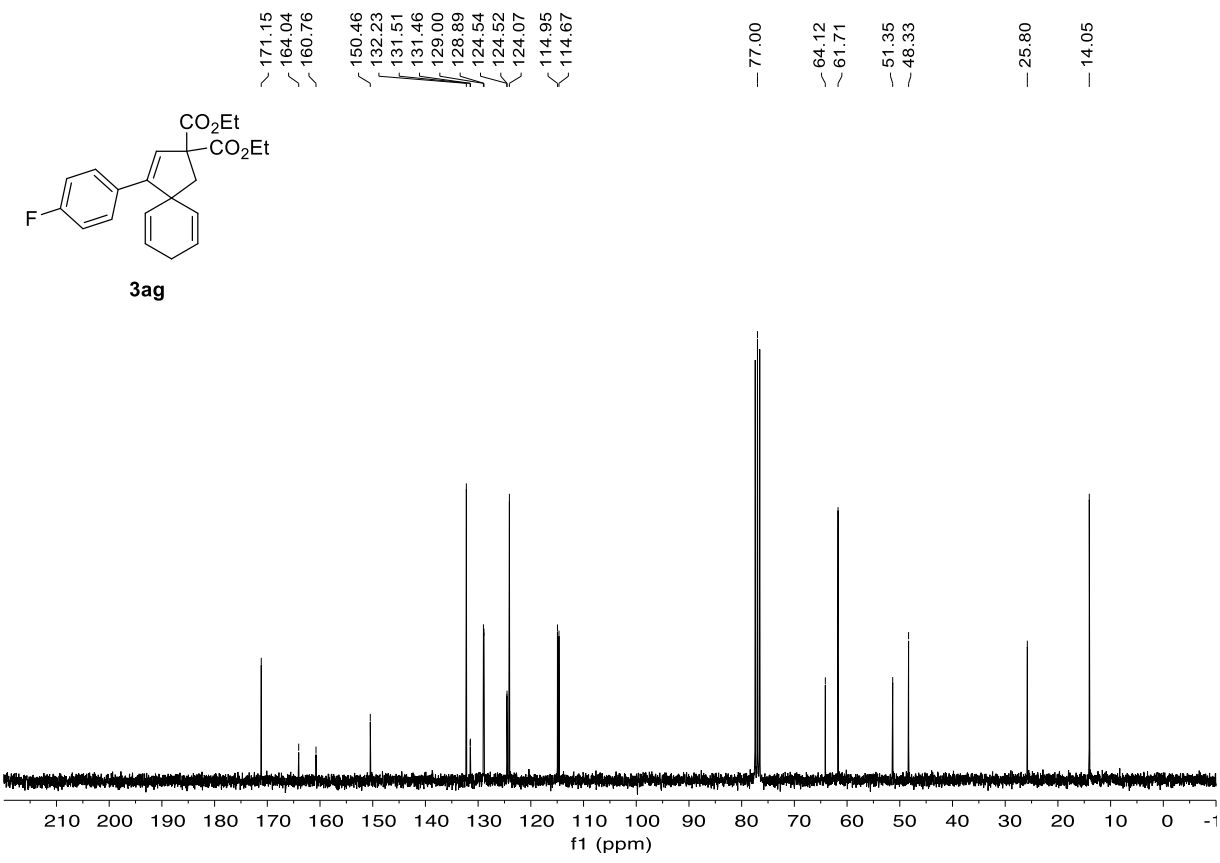


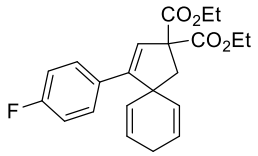
3af



^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3ag



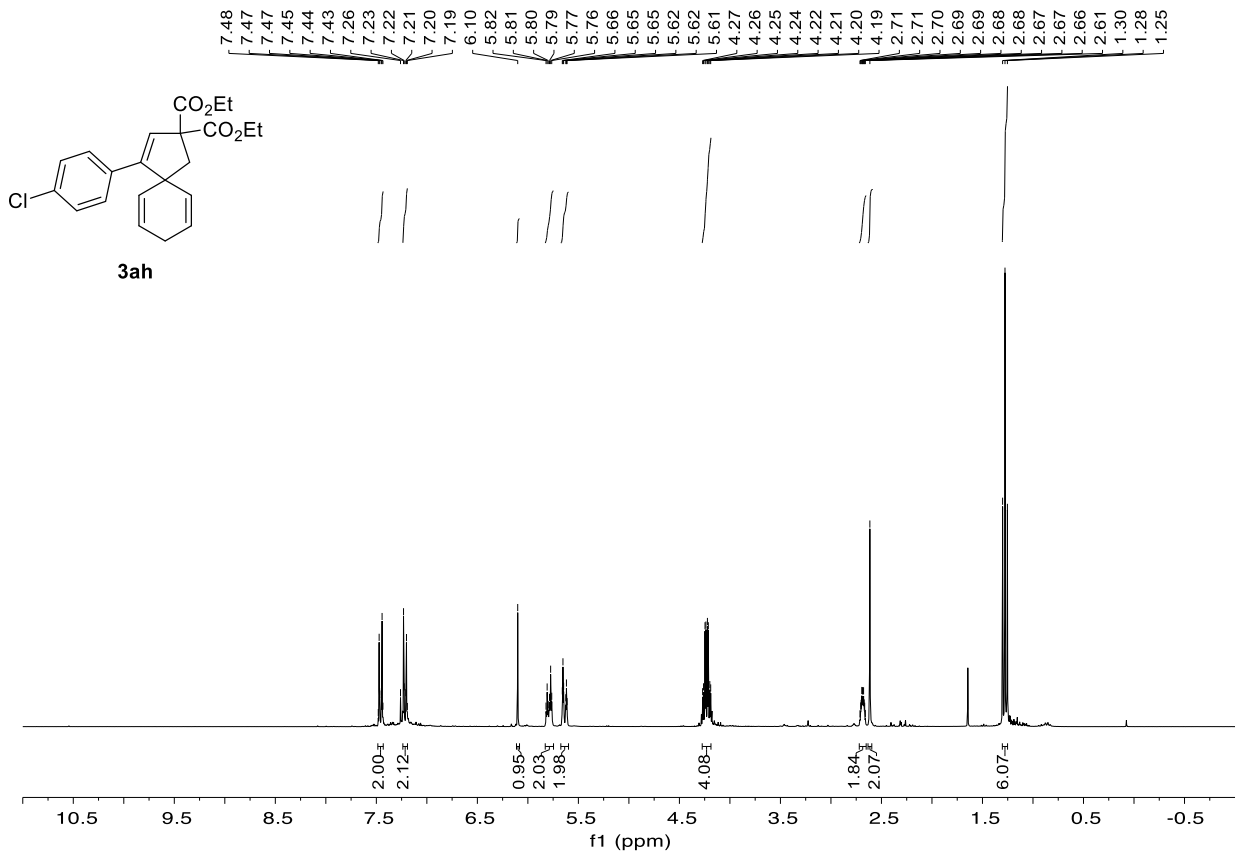


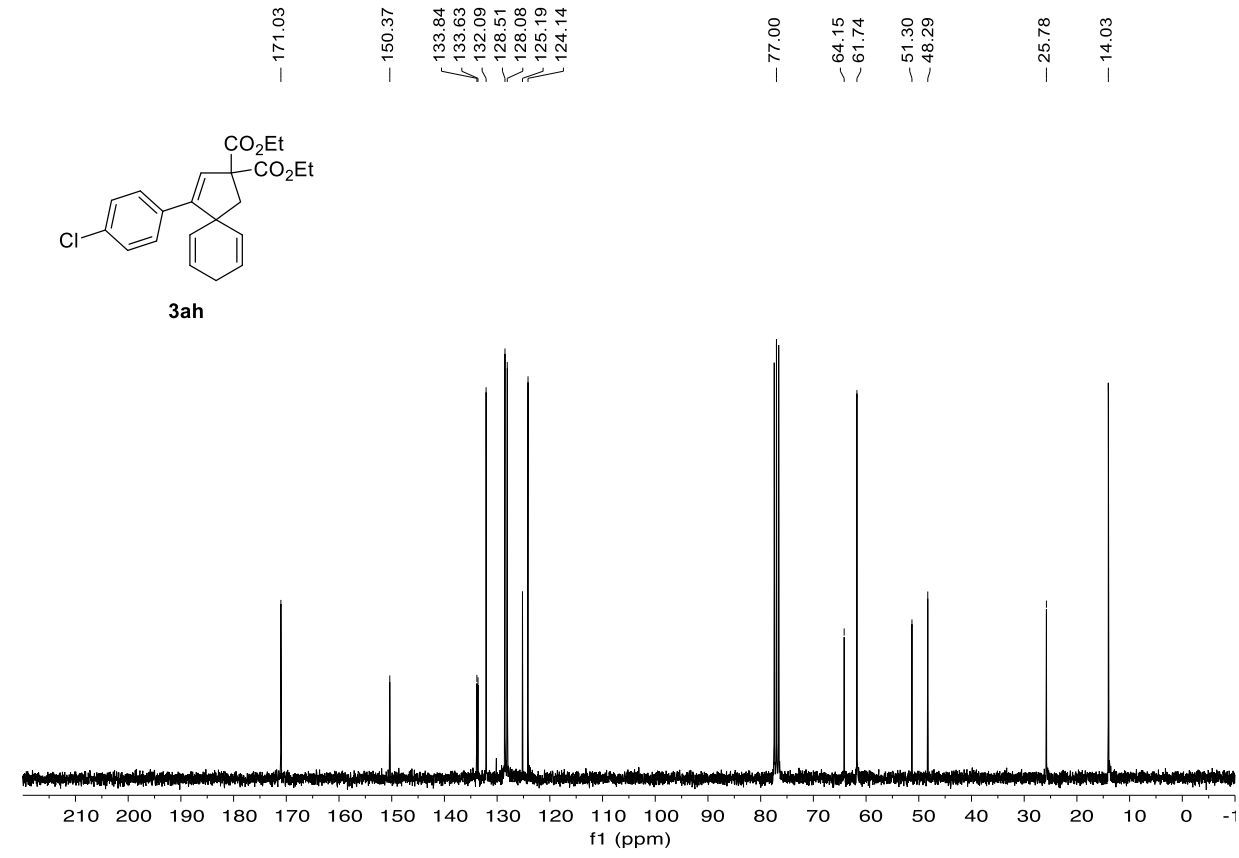

CO2Et
CO2Et
F

3ag

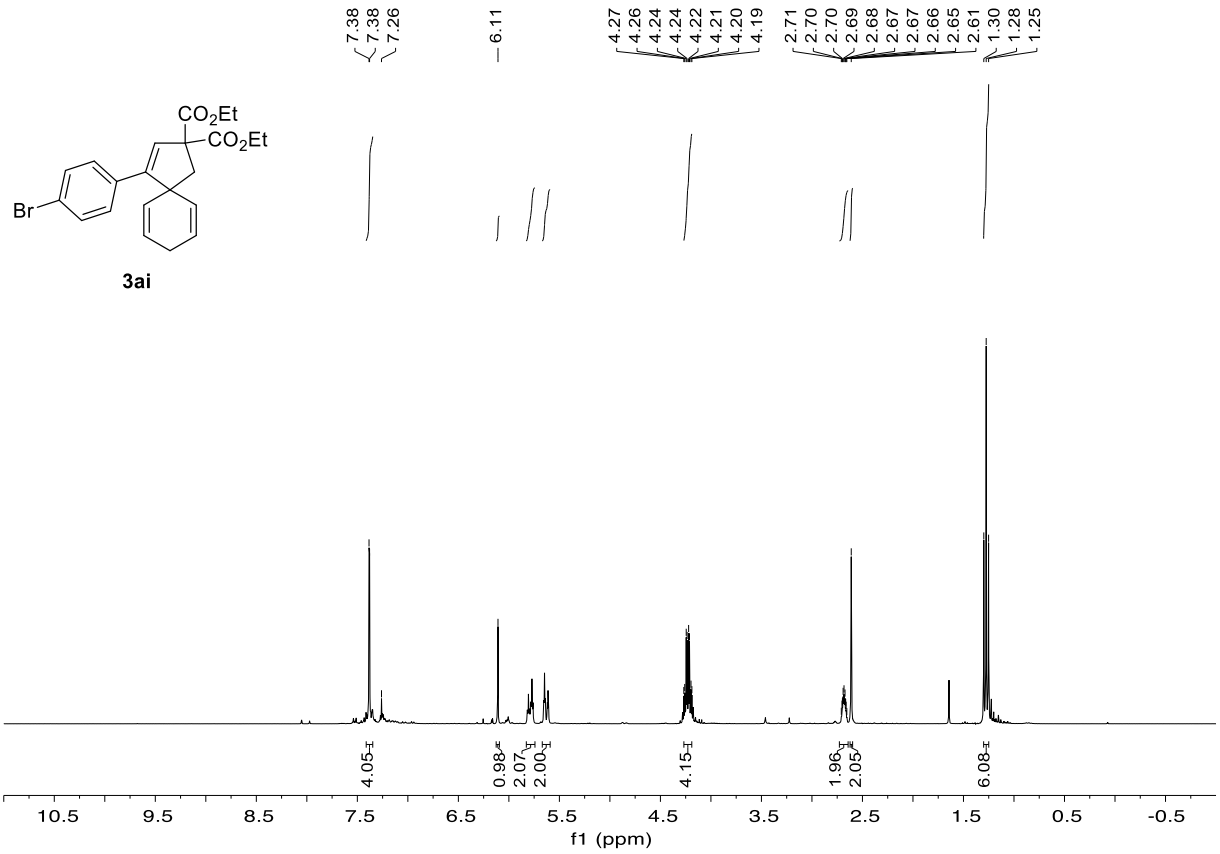
-114.50
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

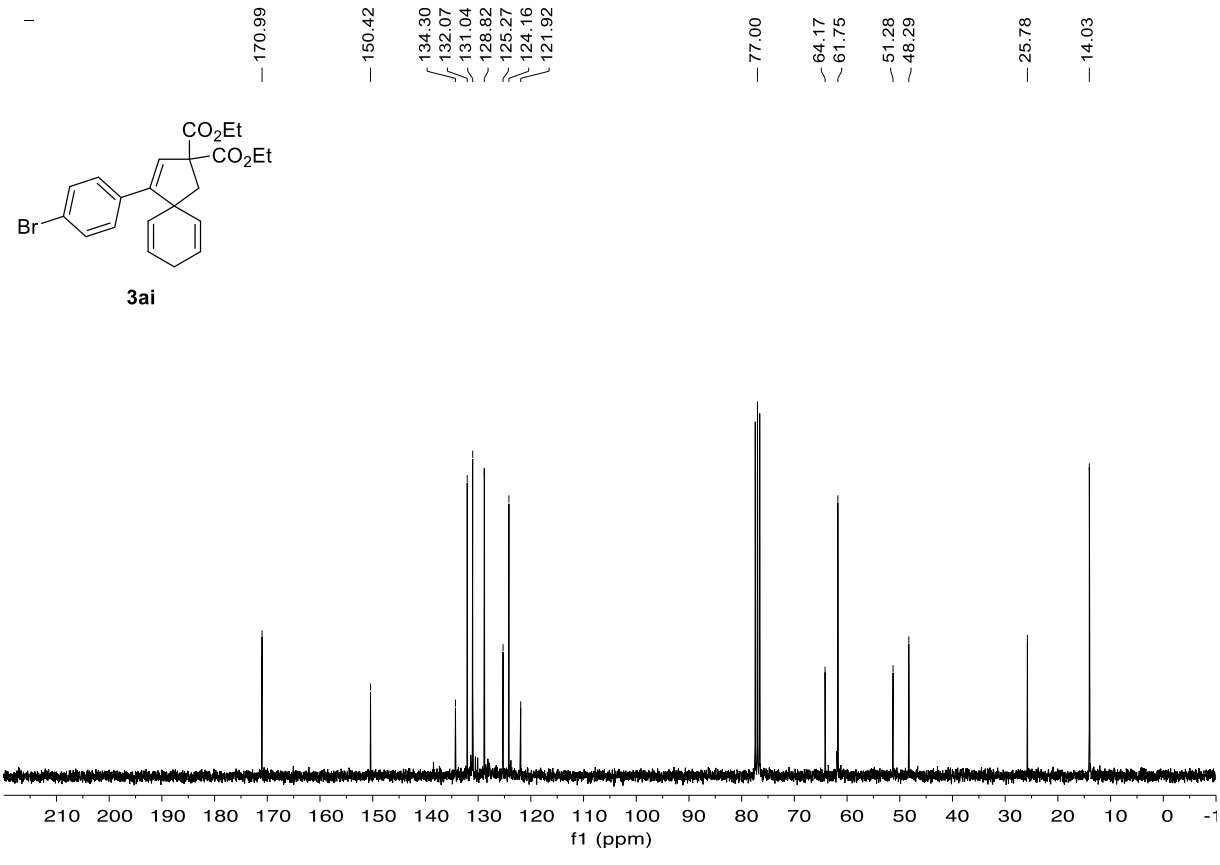
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ah



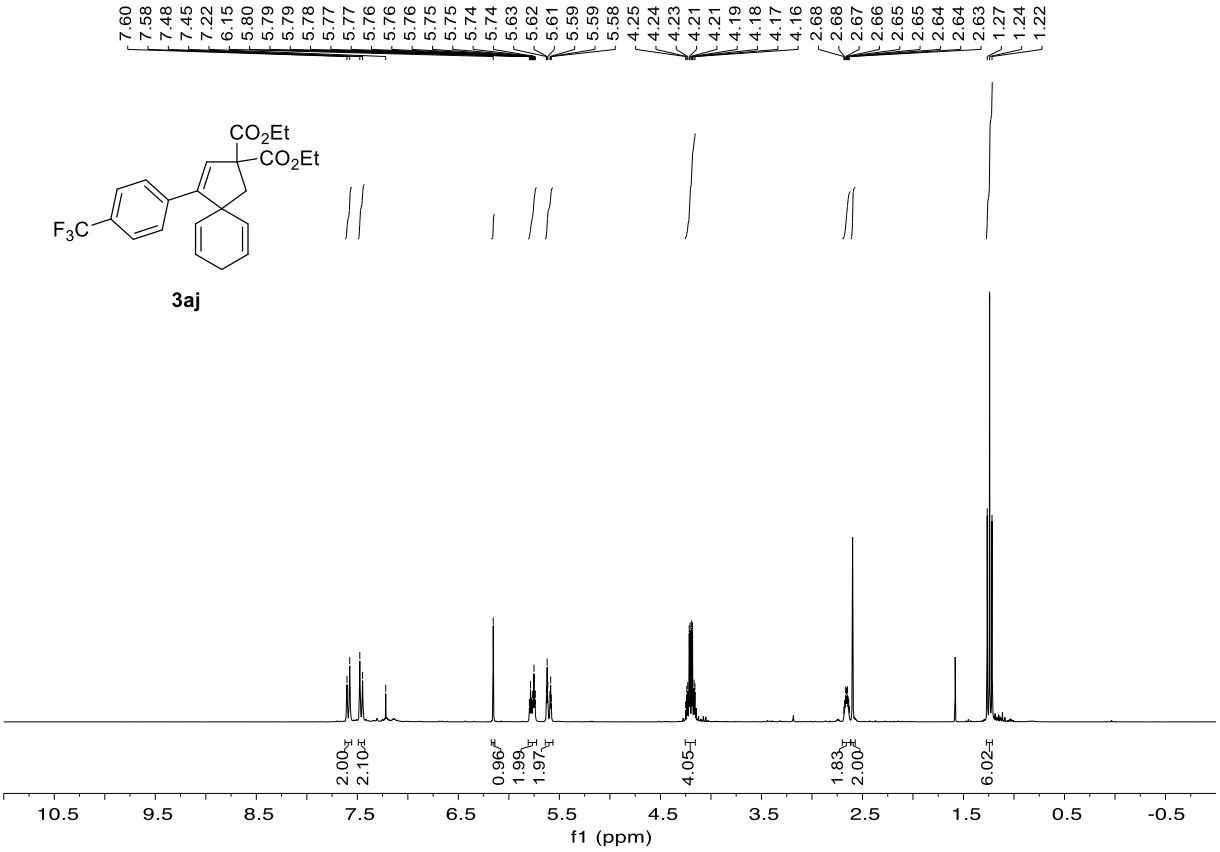


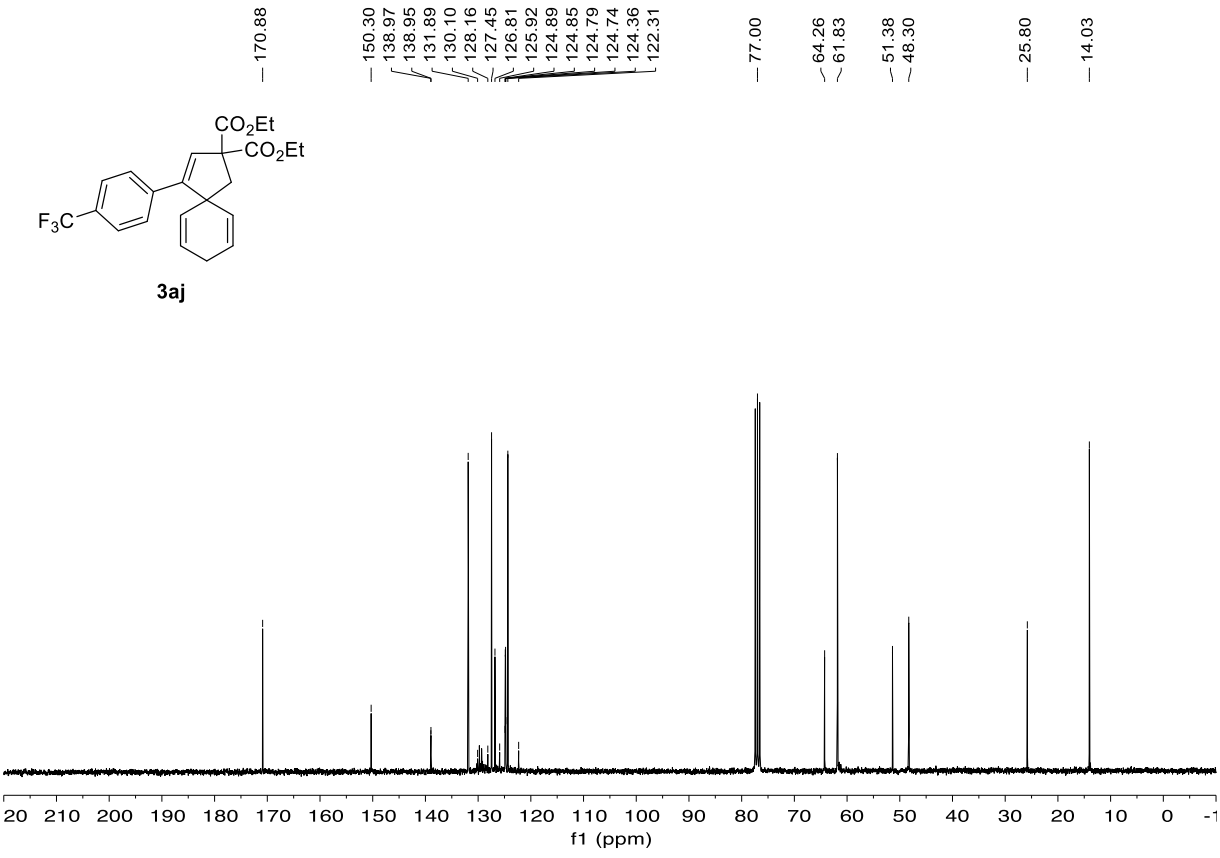
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ai

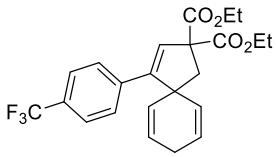




^{1}H NMR (300 MHz, $CDCl_3$), ^{13}C NMR (75 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3aj



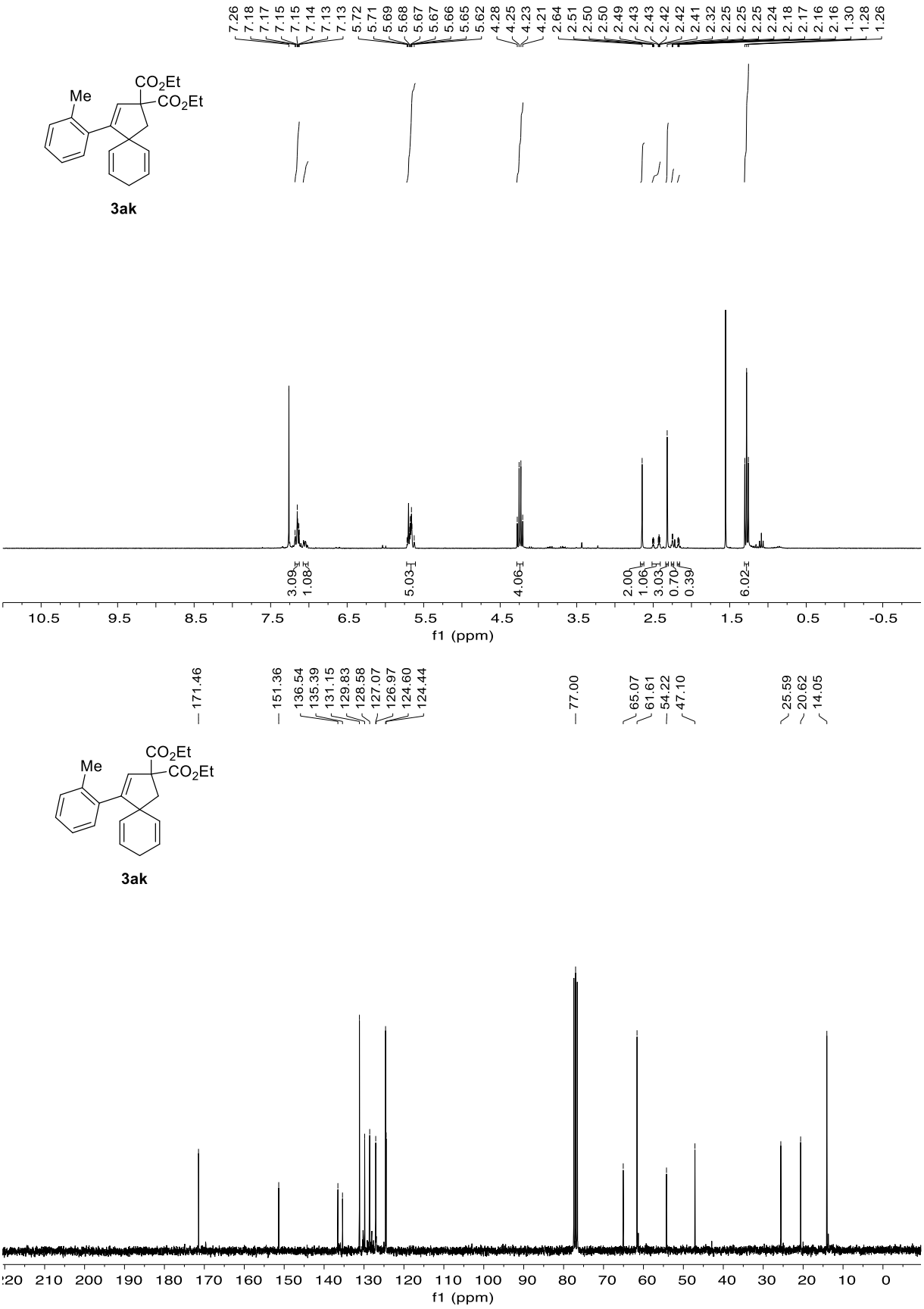



CO2Et
CO2Et
F3C

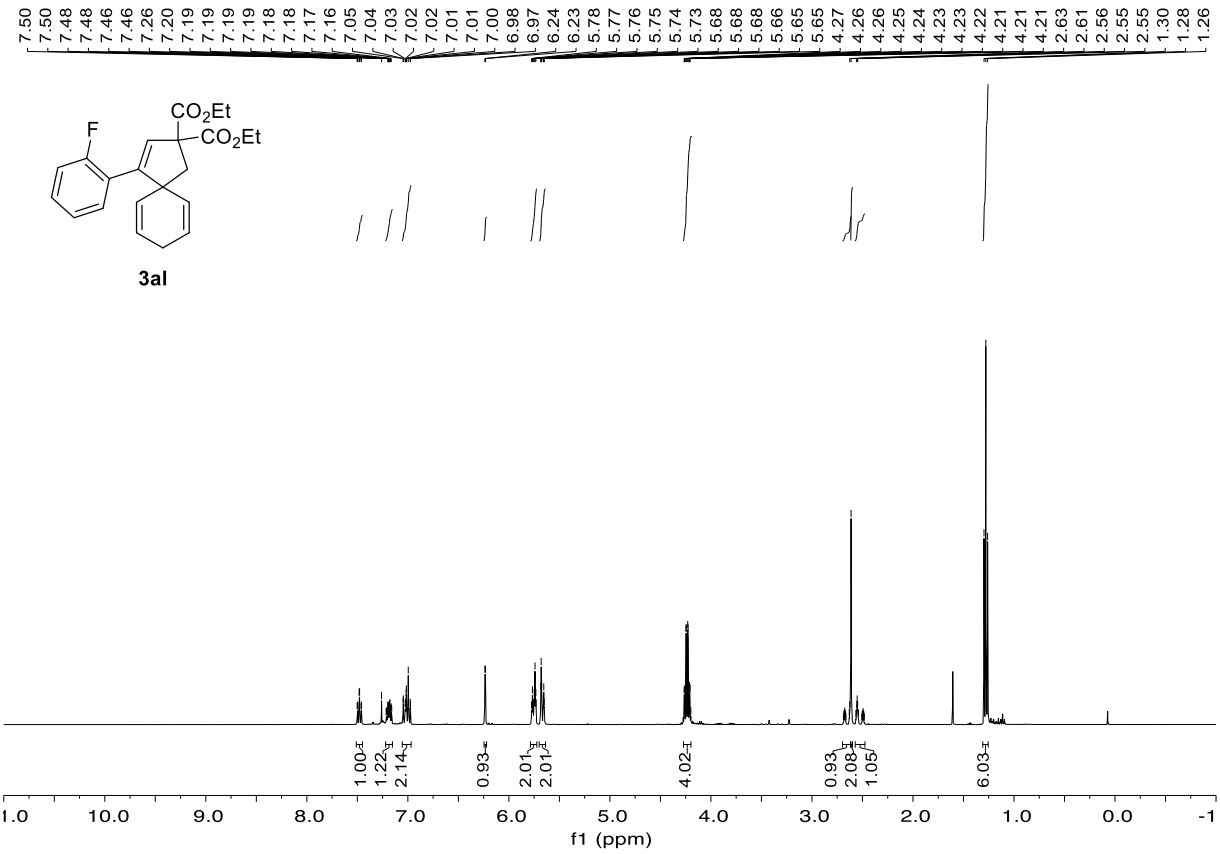
3aj

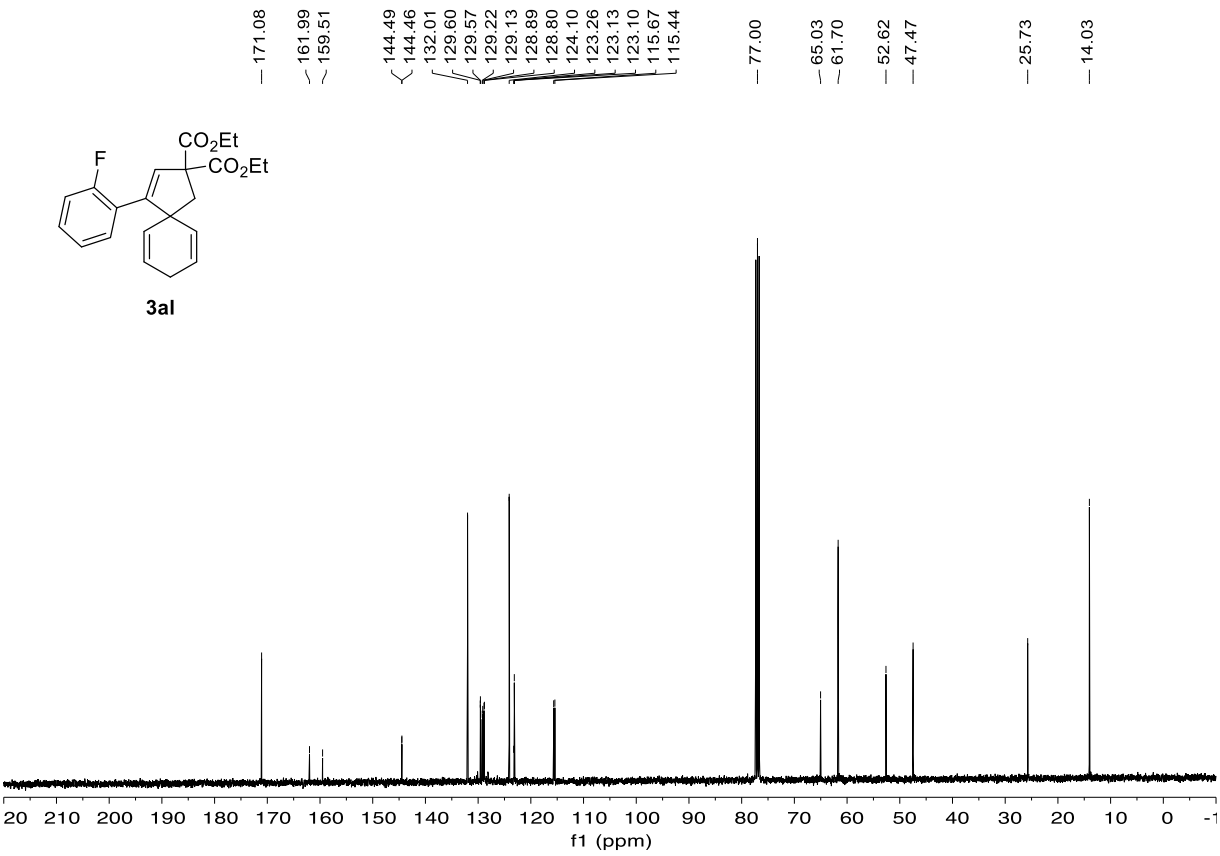
-63.16
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

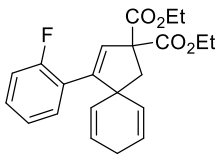
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ak



^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (375 MHz, $CDCl_3$) spectra of product 3al



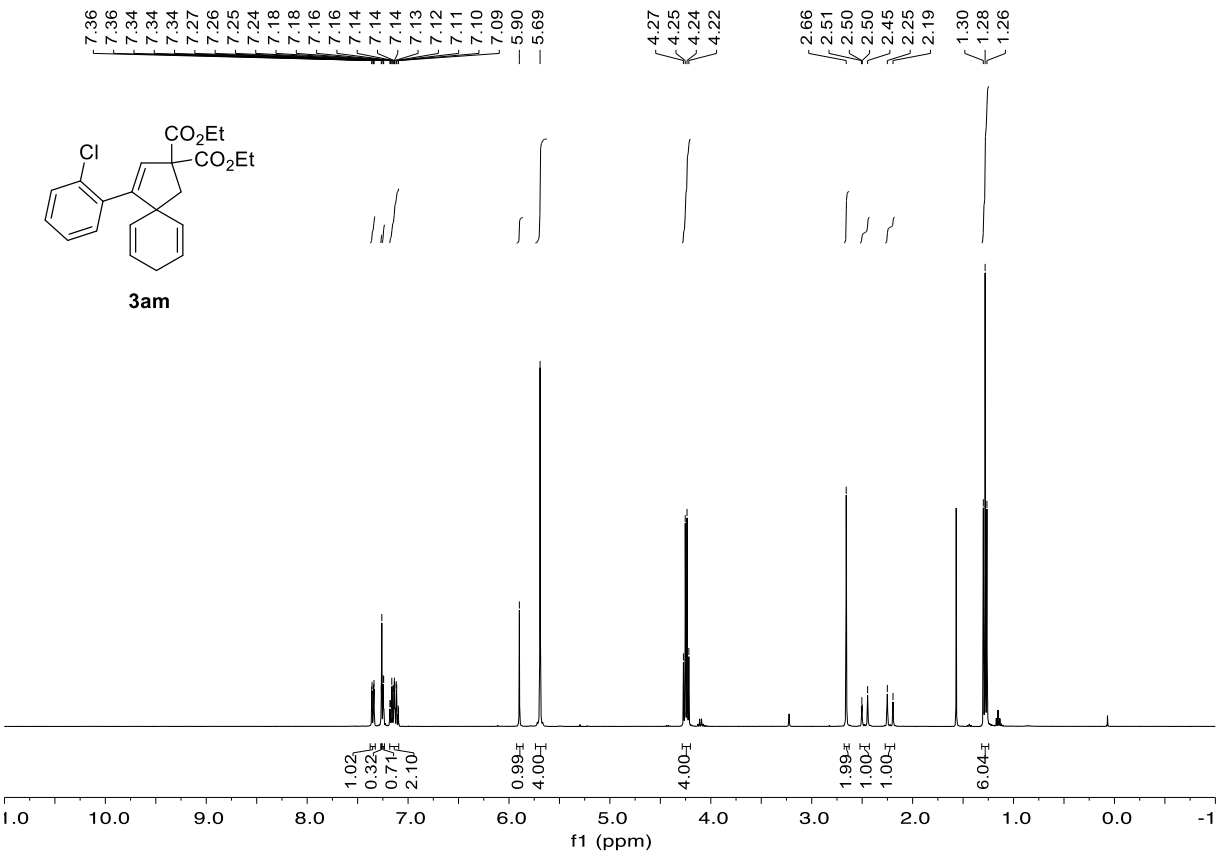


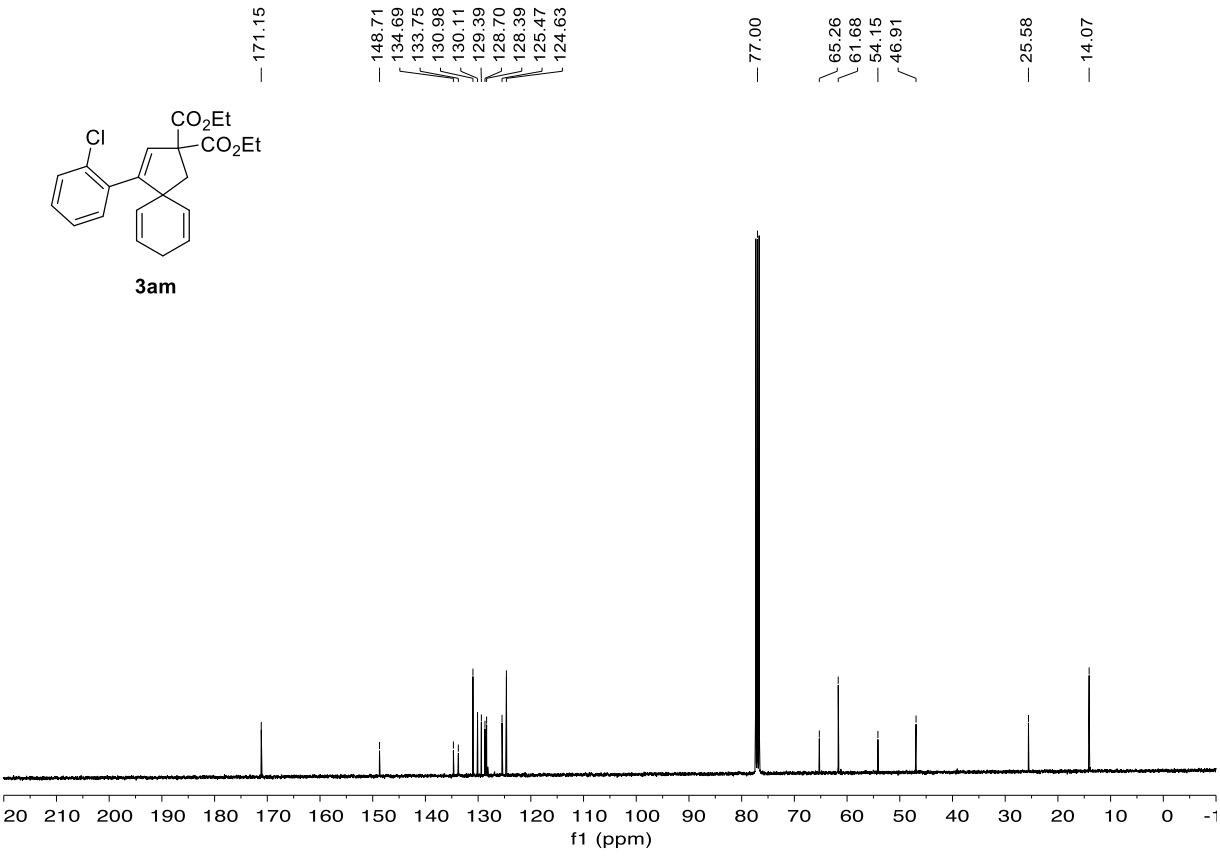

F
CO2Et
CO2Et

3al

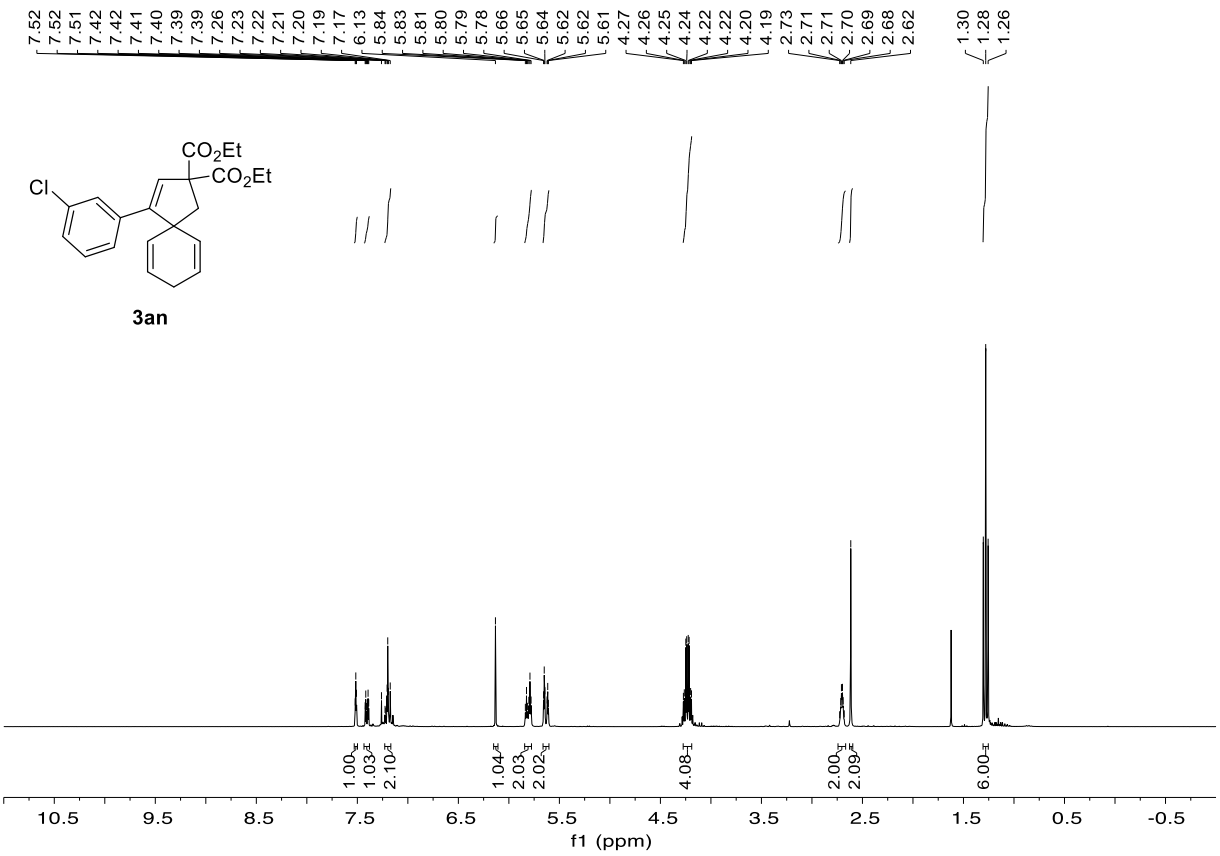
-112.29
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

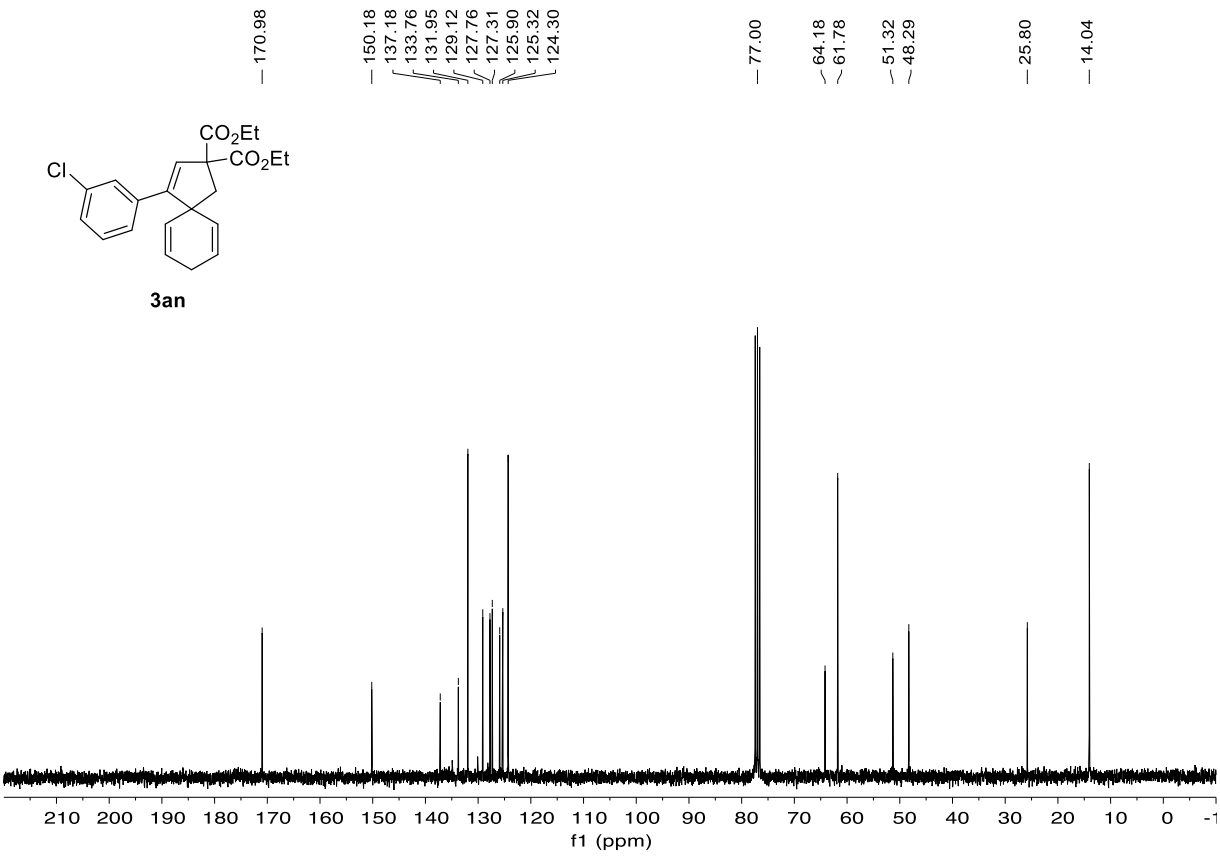
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3am



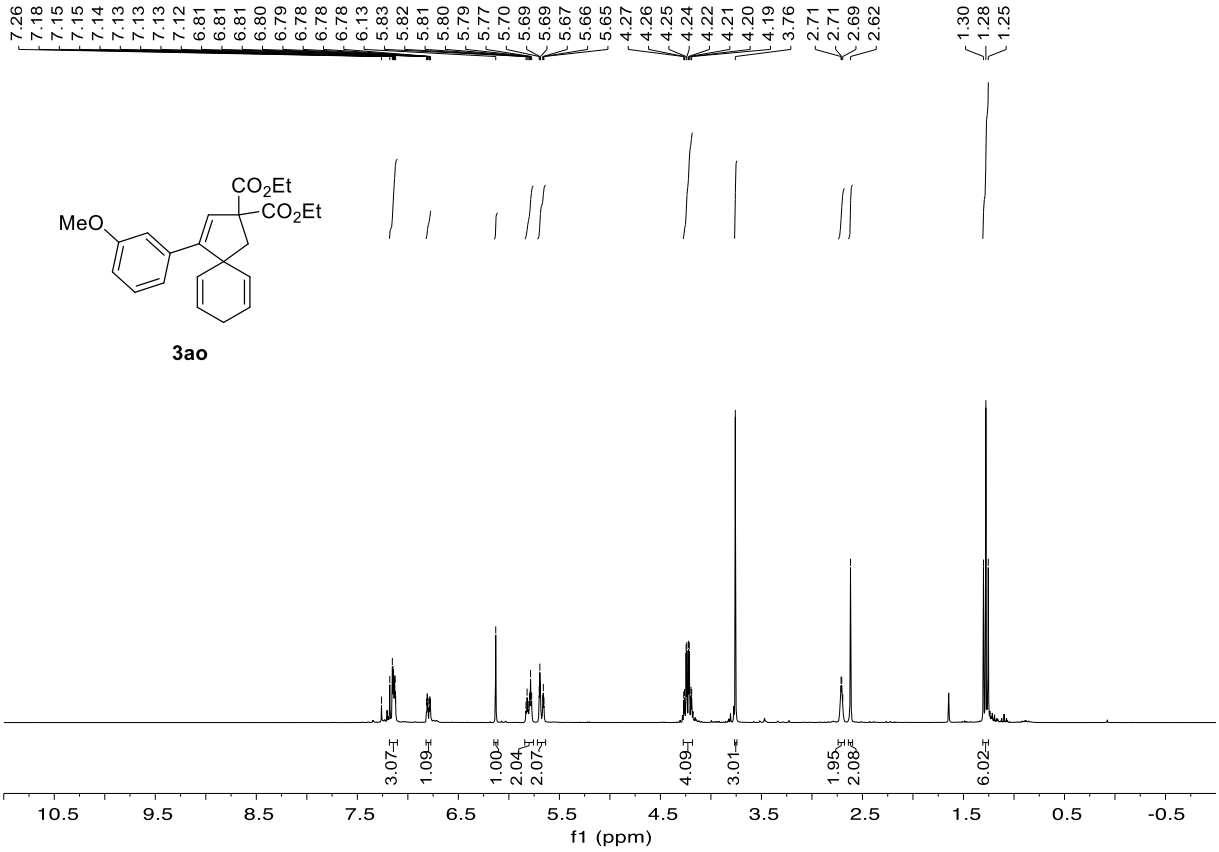


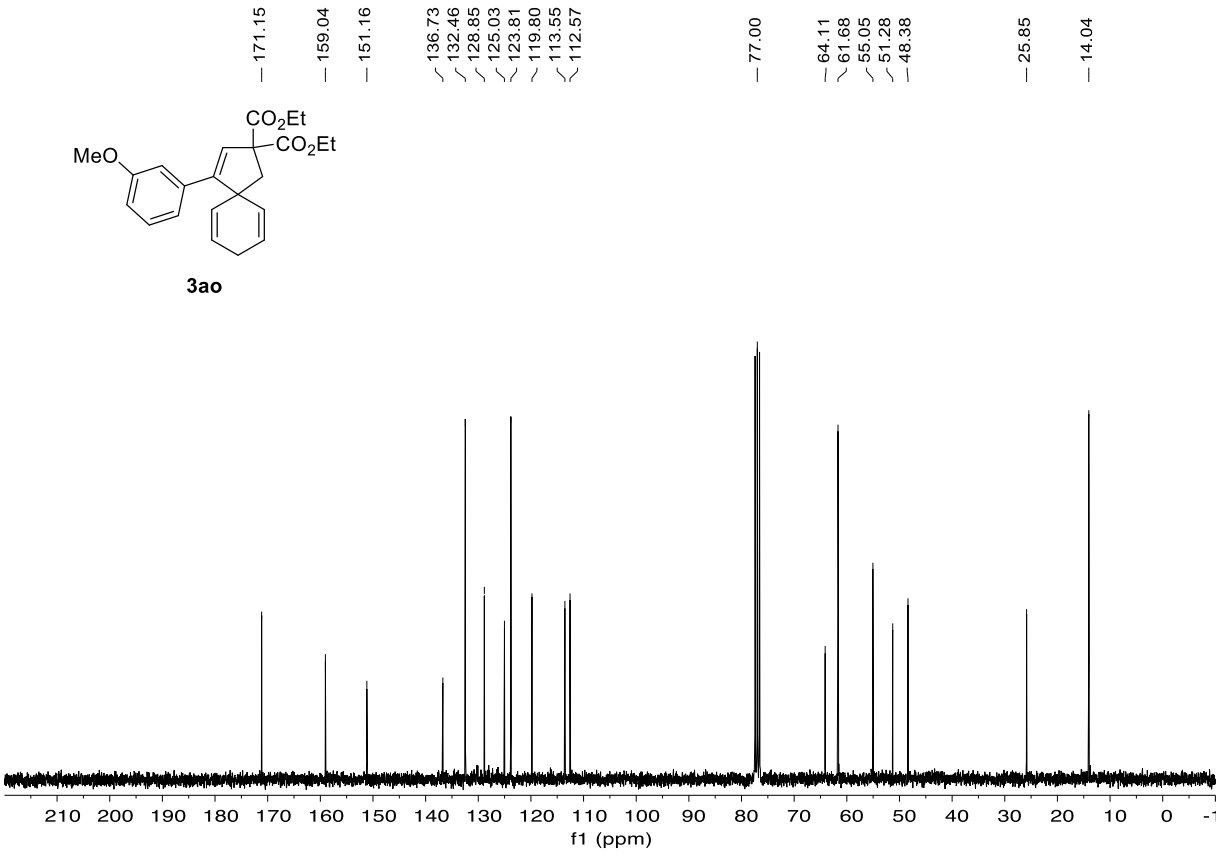
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3an



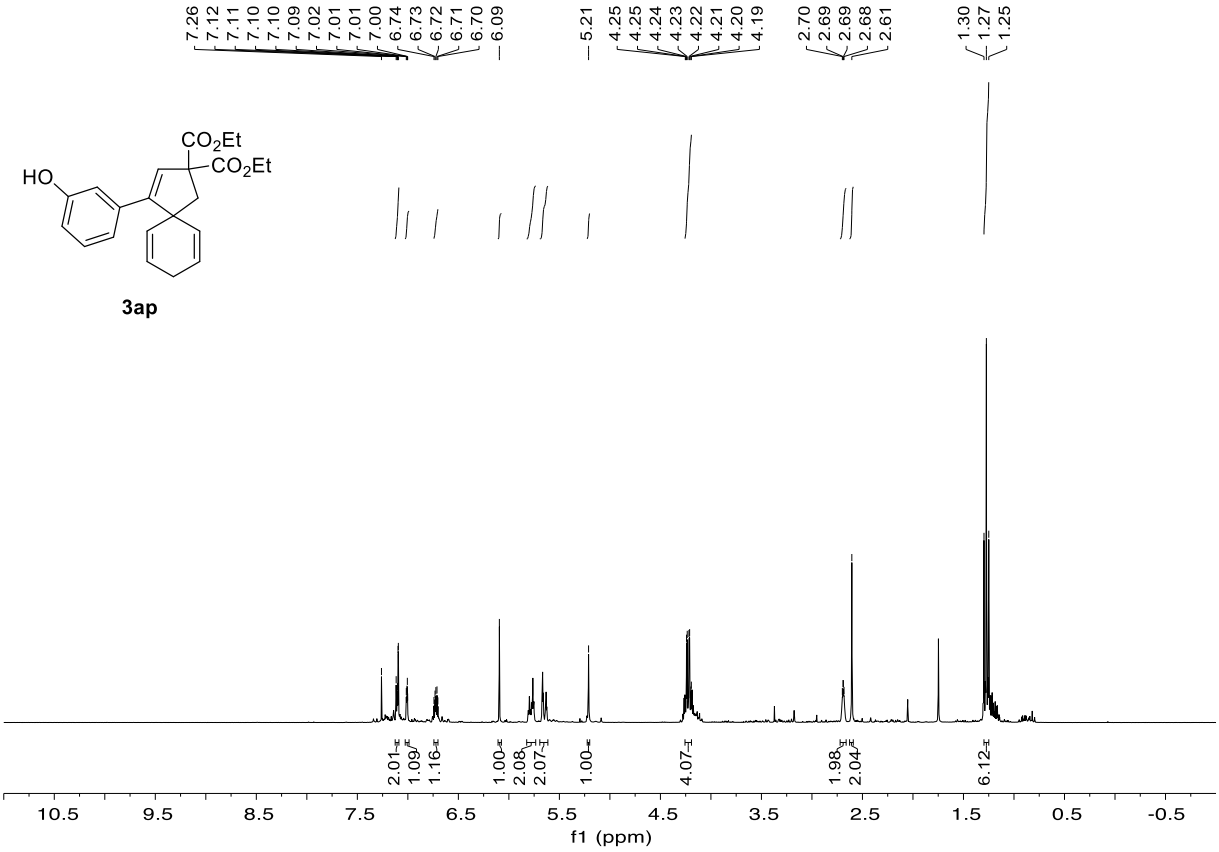


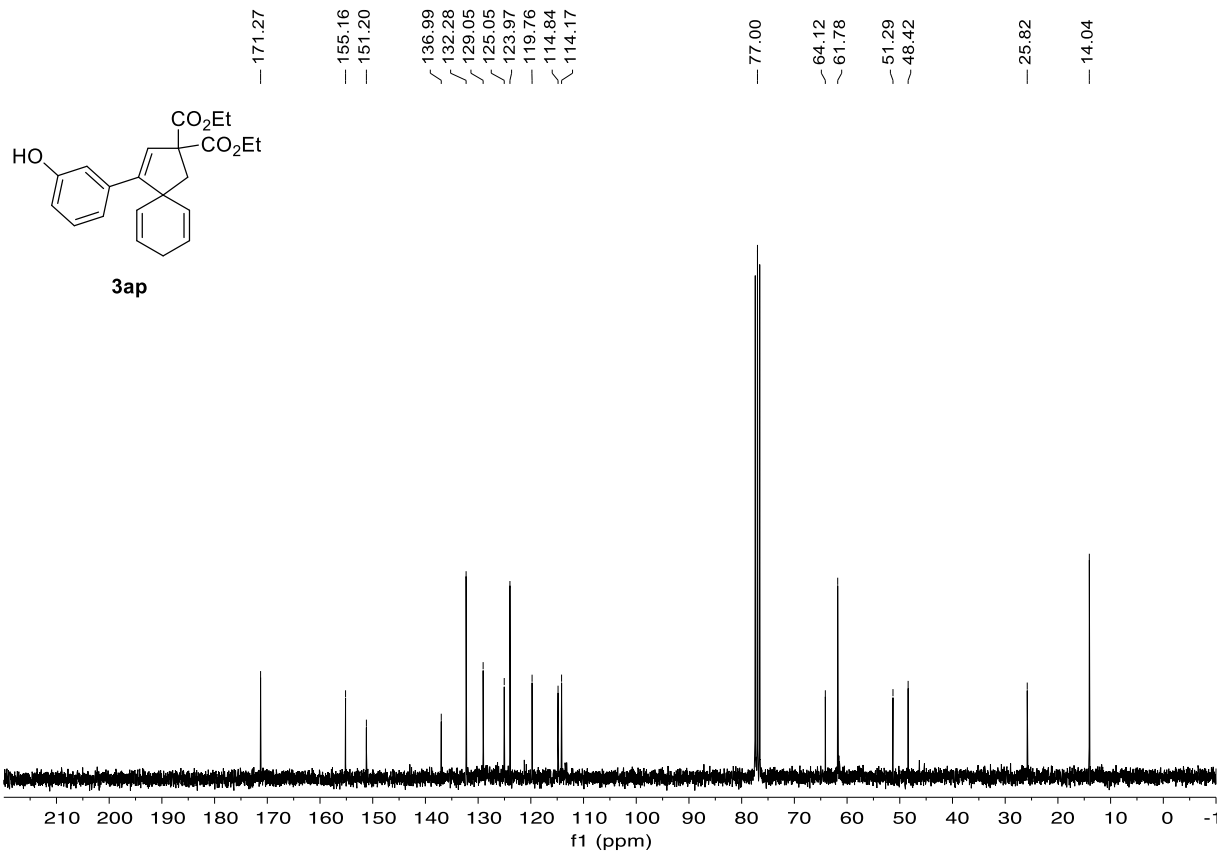
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ao



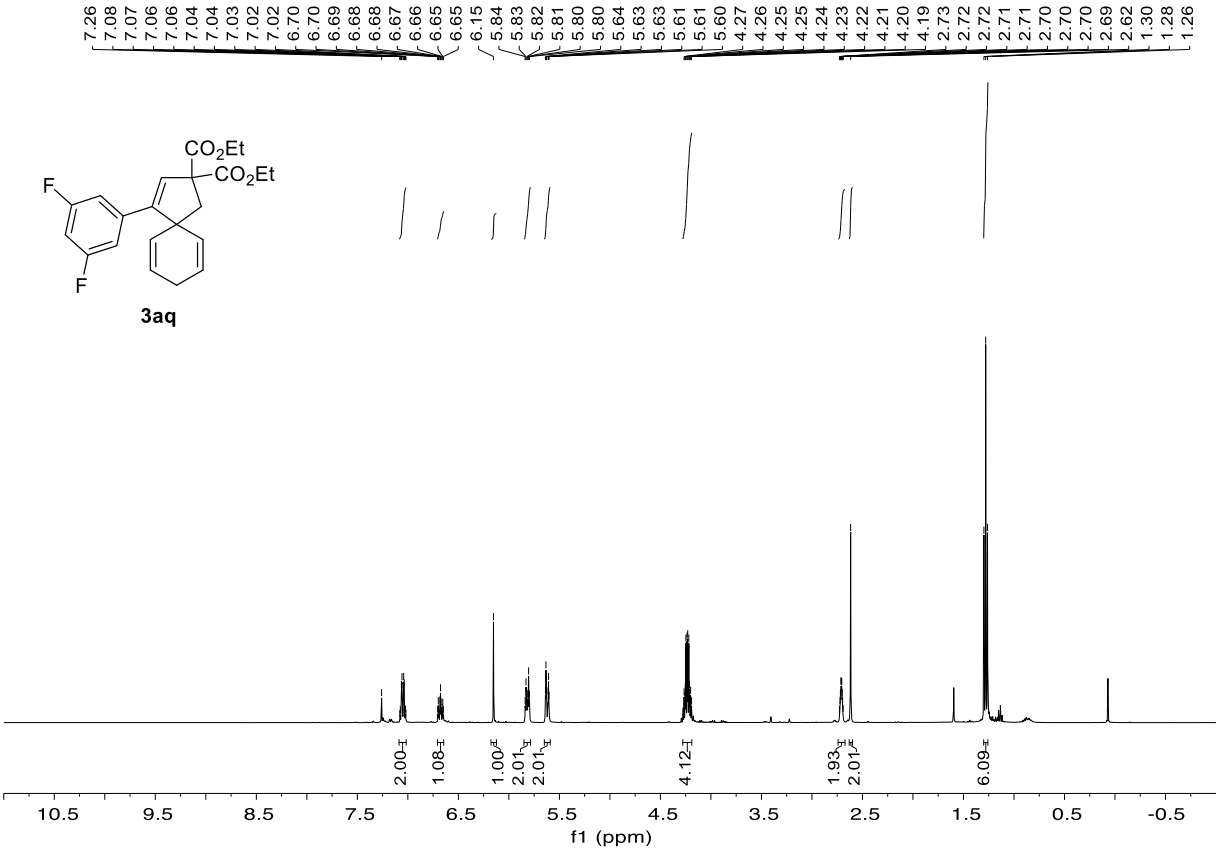


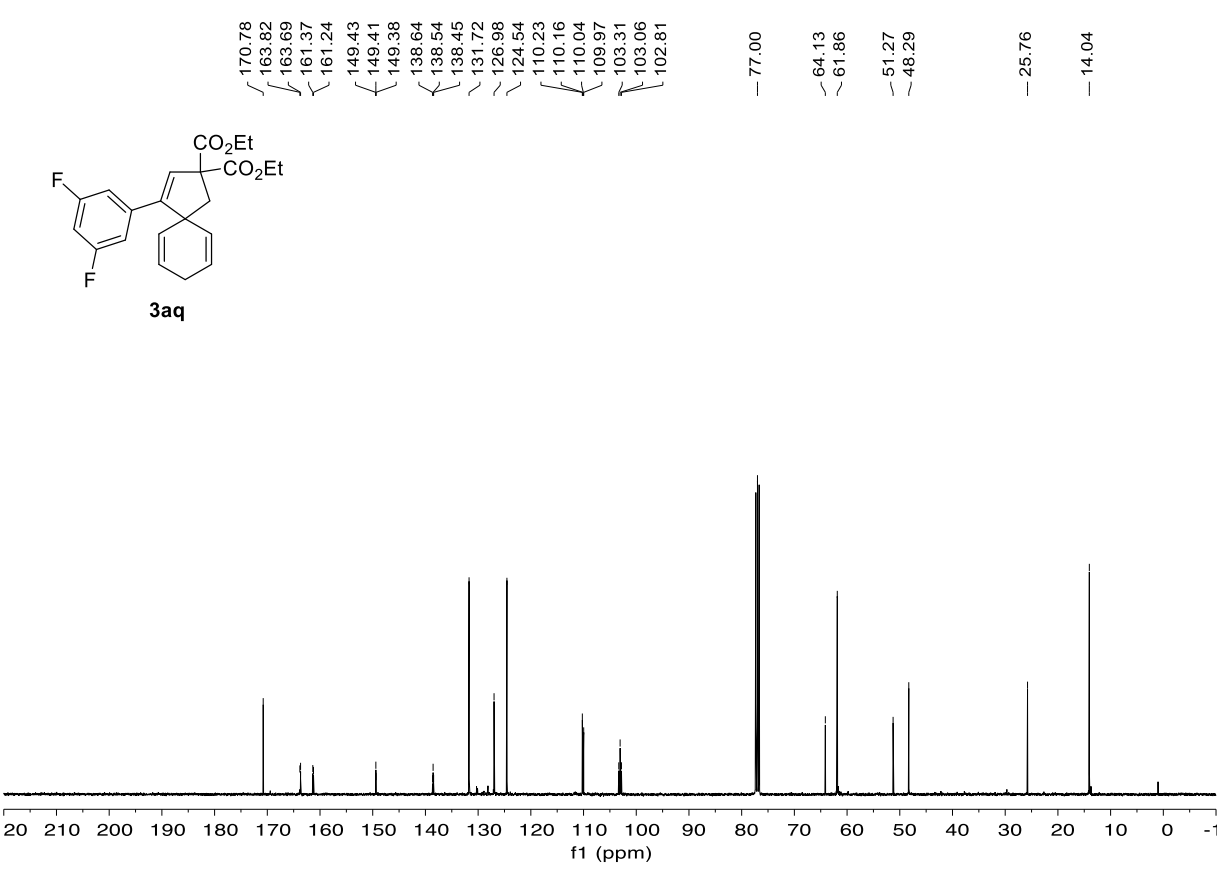
^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3ap

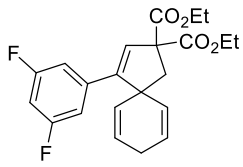




^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) and ^{19}F NMR (376 MHz, $CDCl_3$) spectra of product 3aq



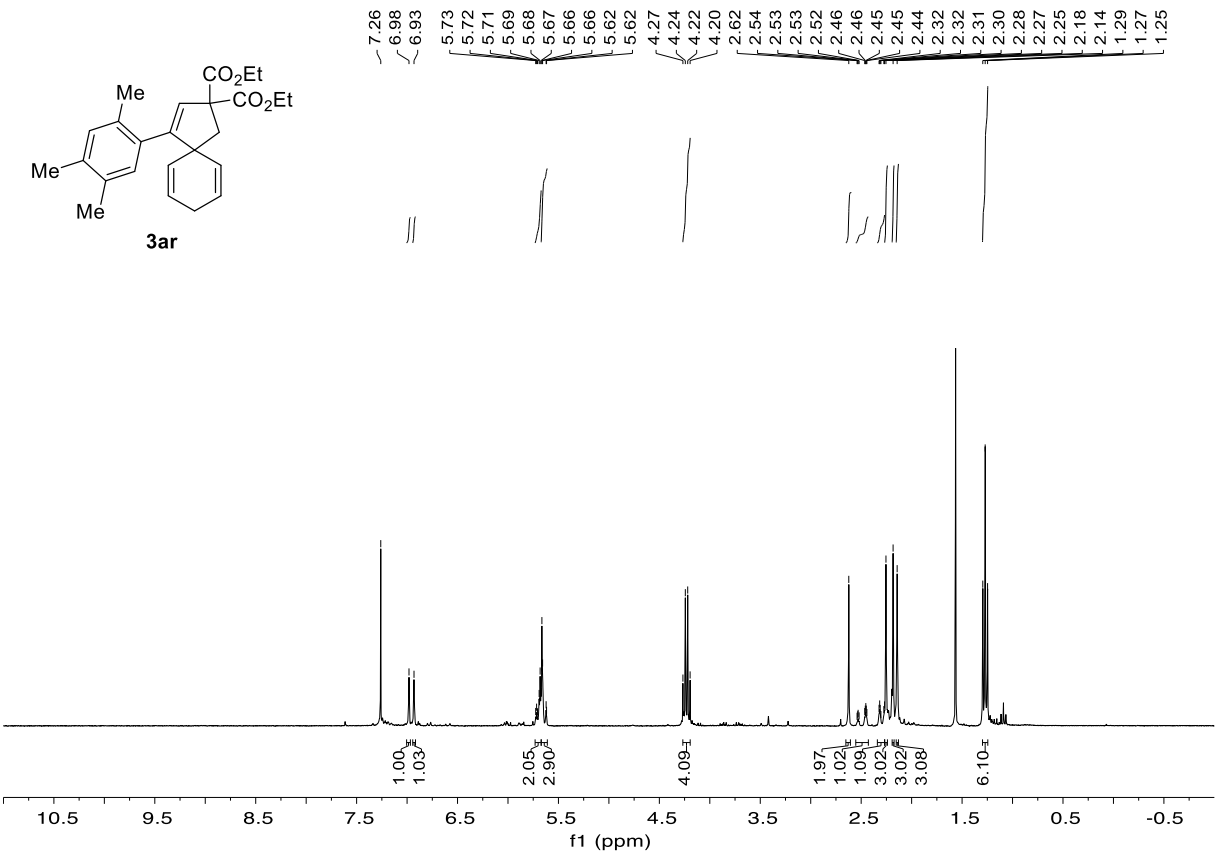


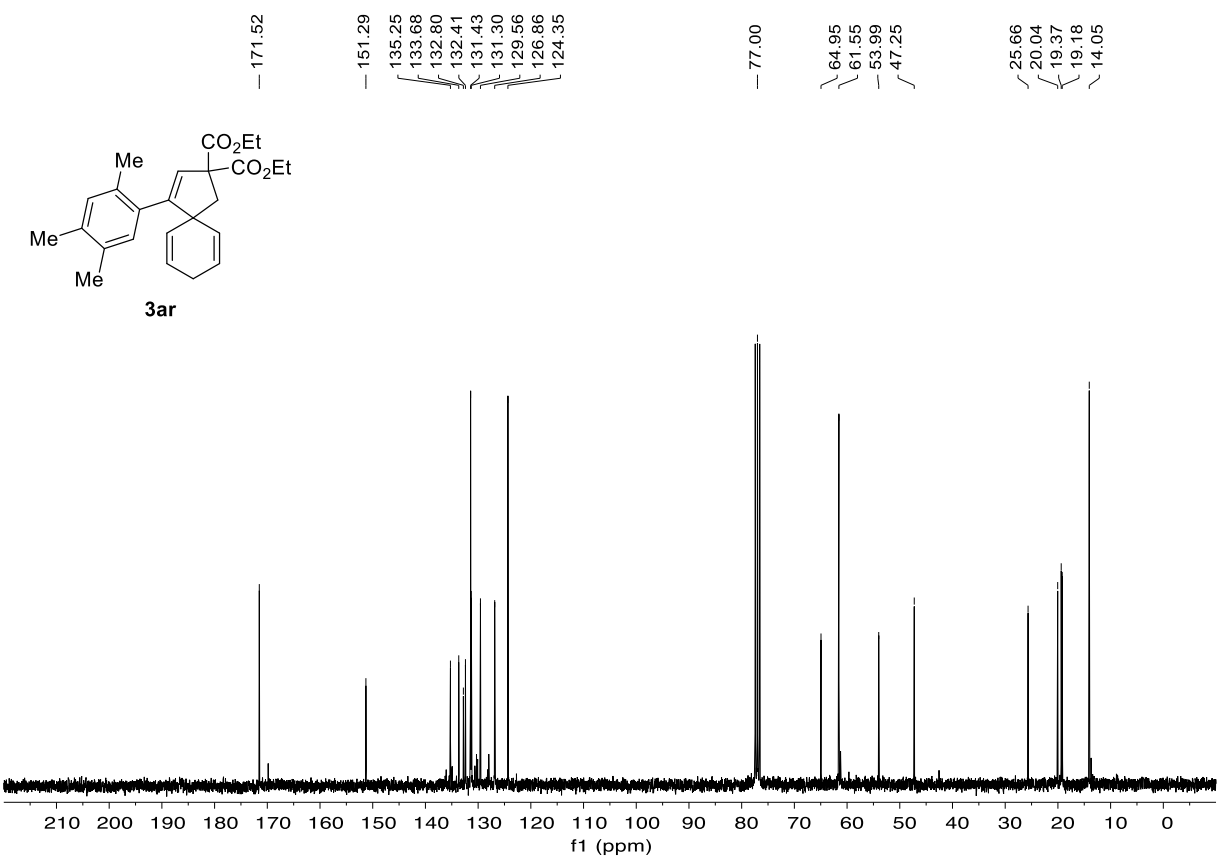

CO2Et
CO2Et
F
F

3aq

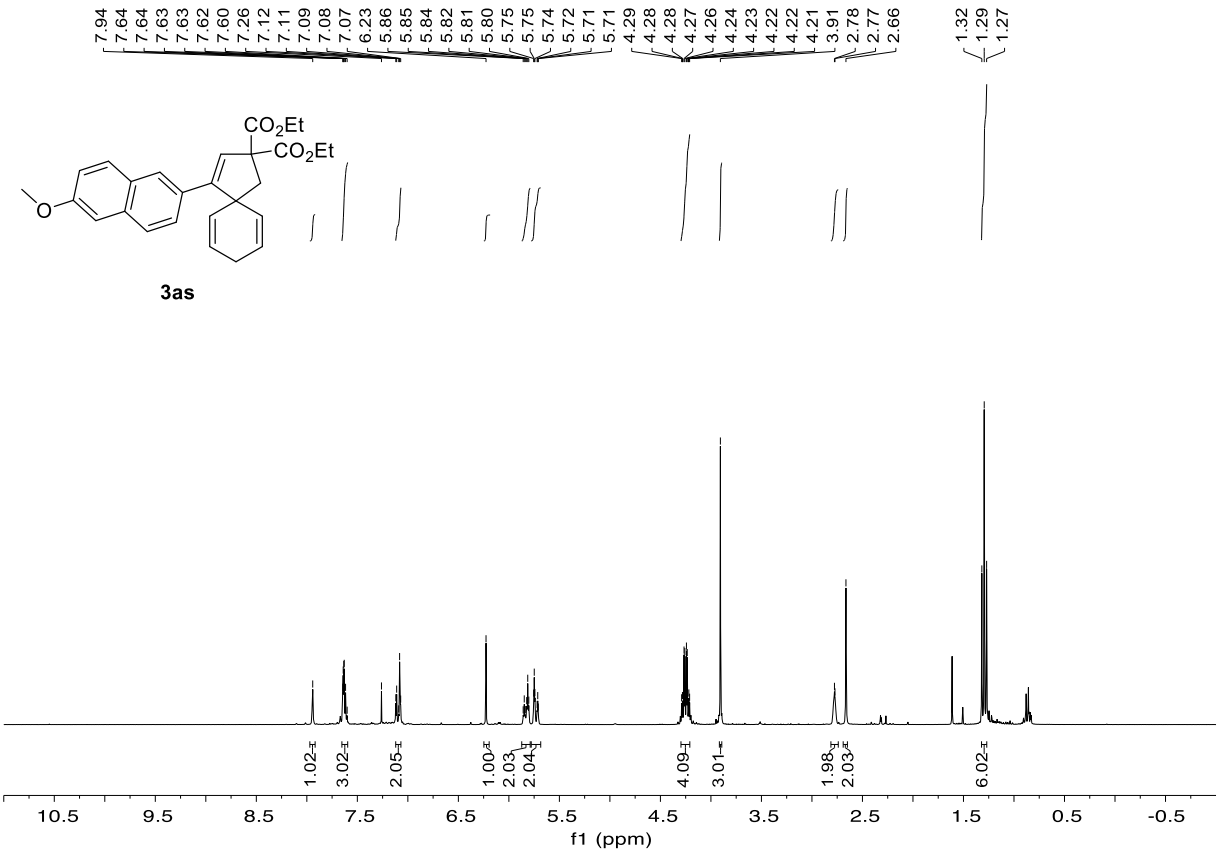
-110.92
-110.94
-110.97
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
f1 (ppm)

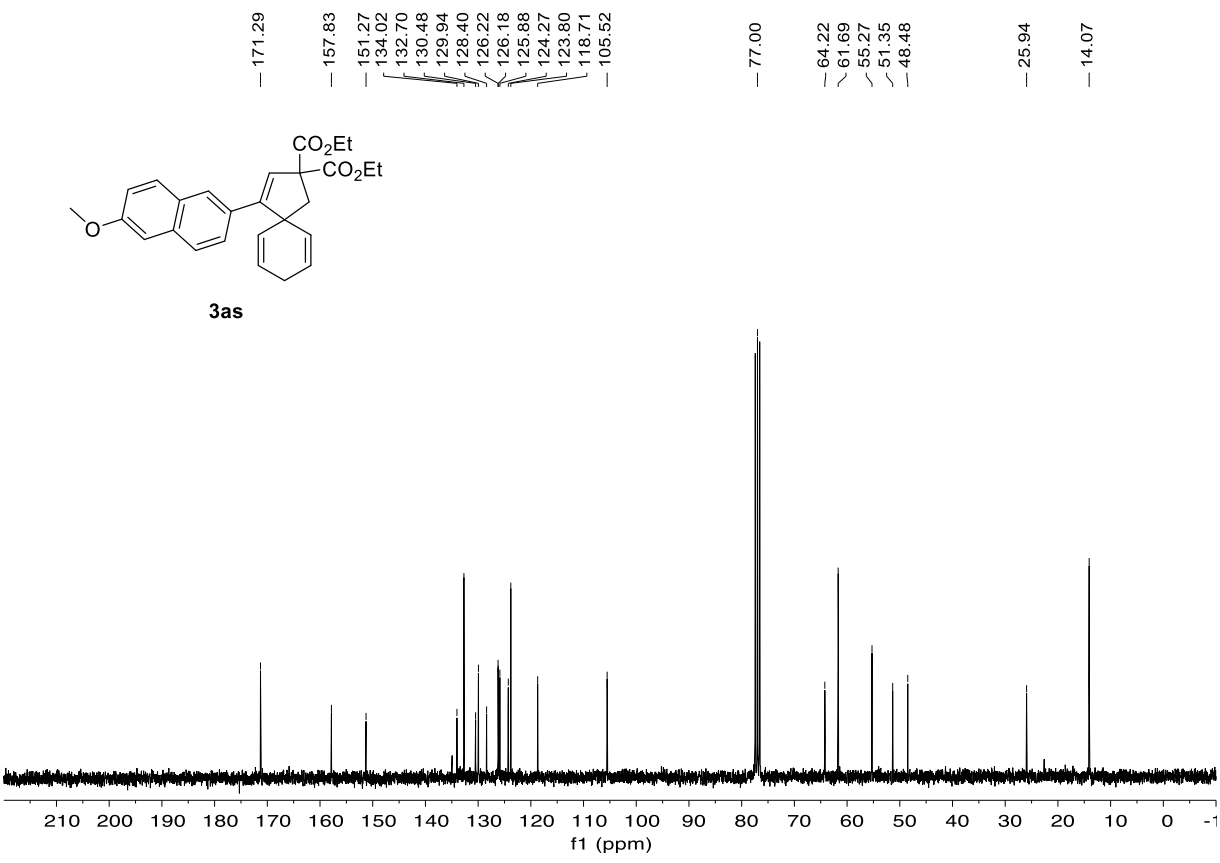
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ar



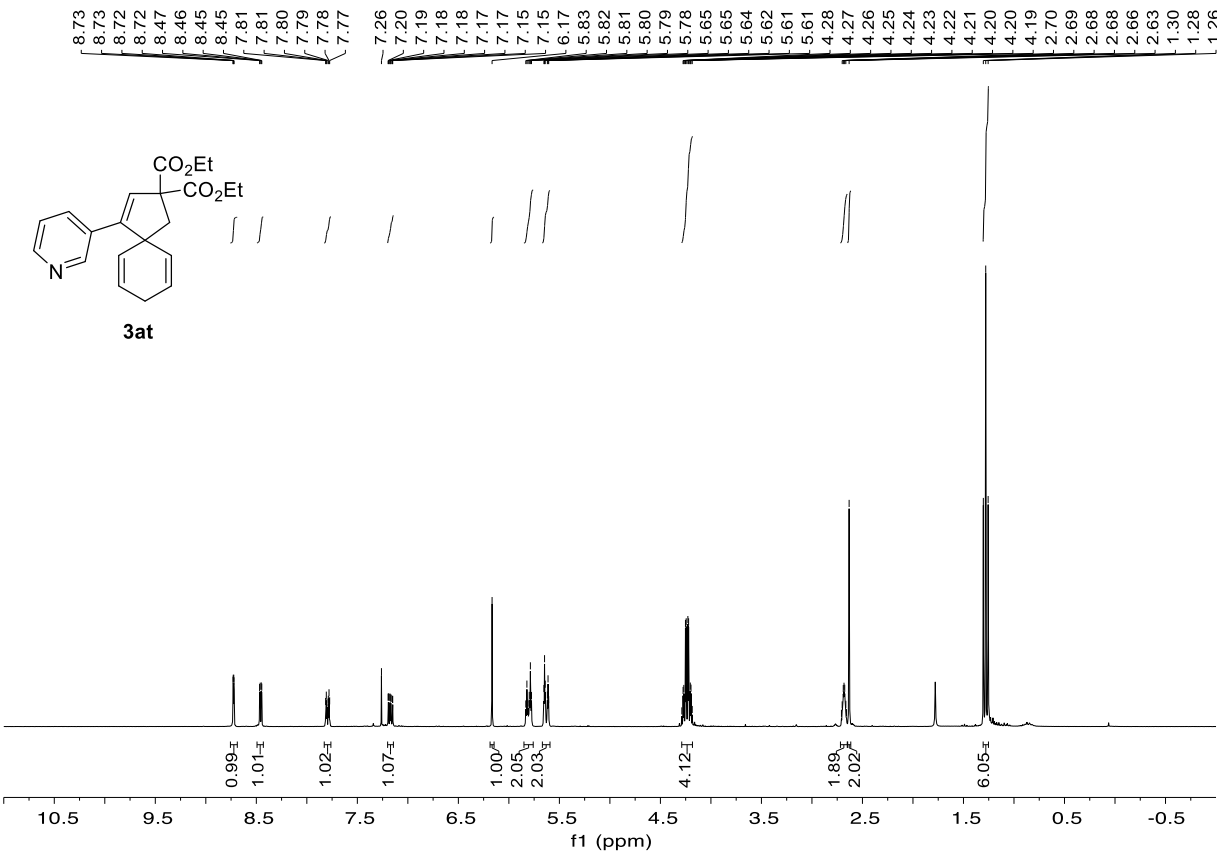


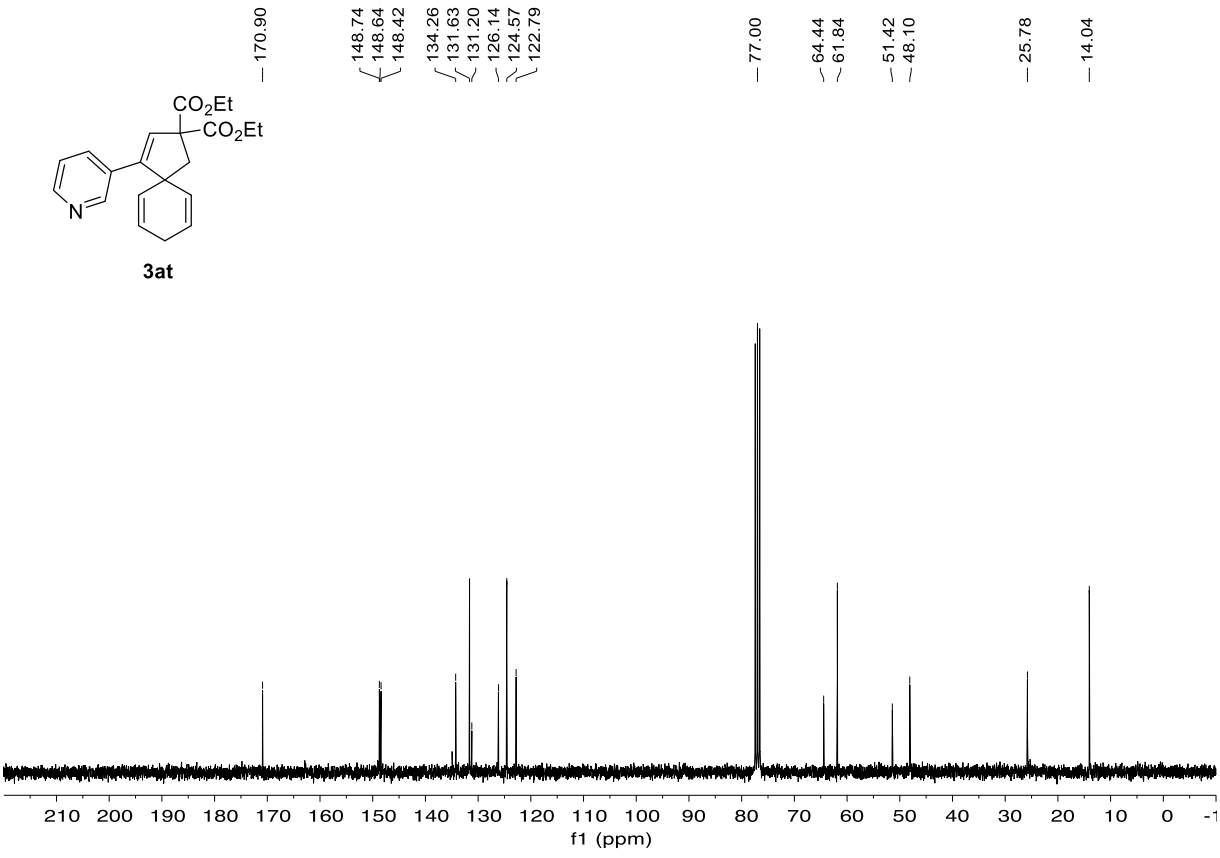
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3as



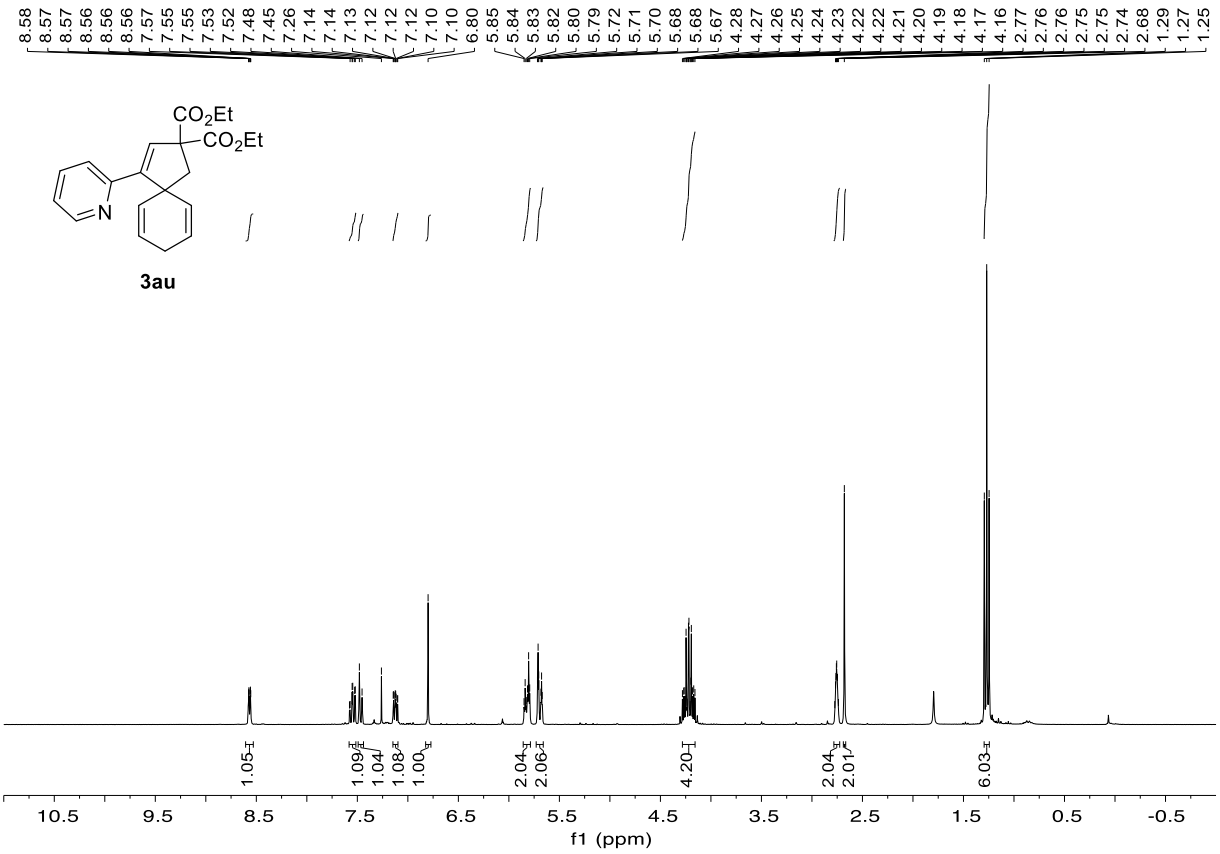


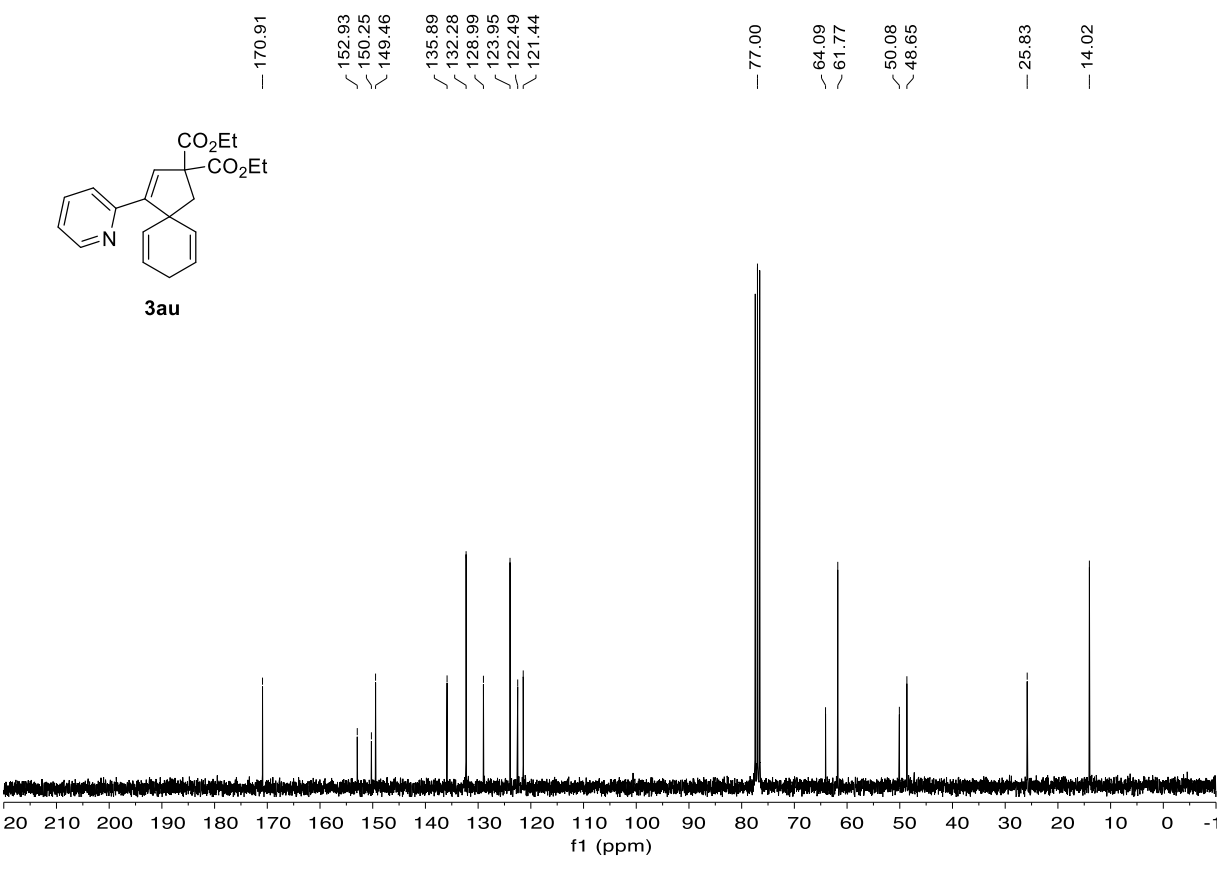
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3at



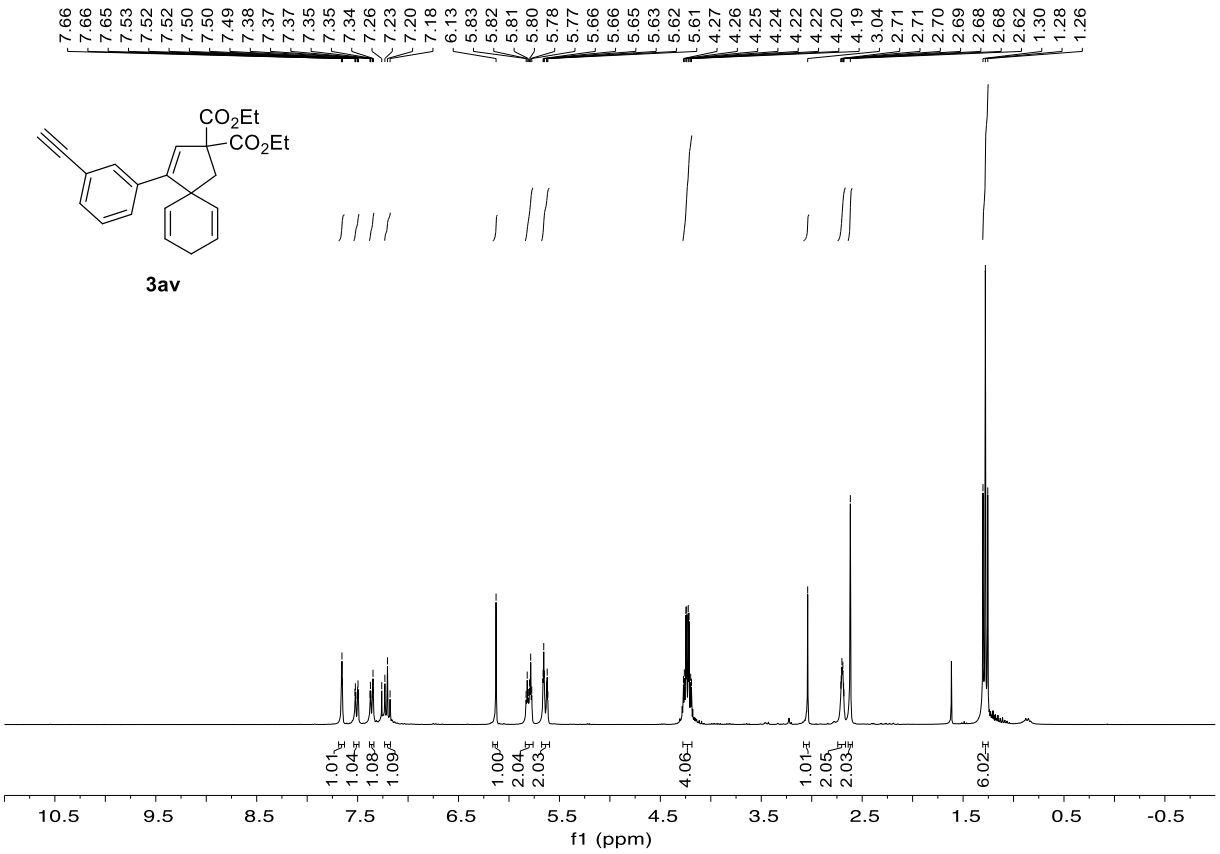


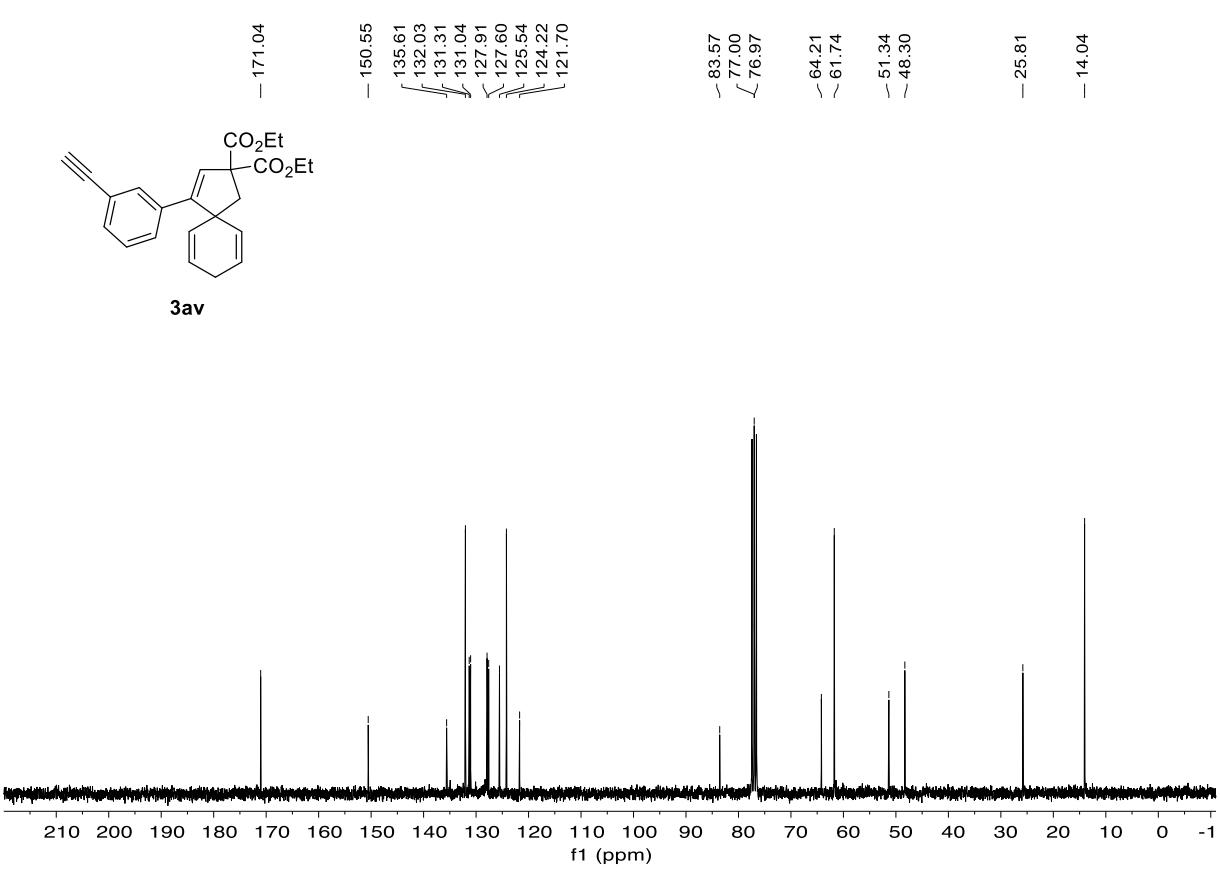
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3au



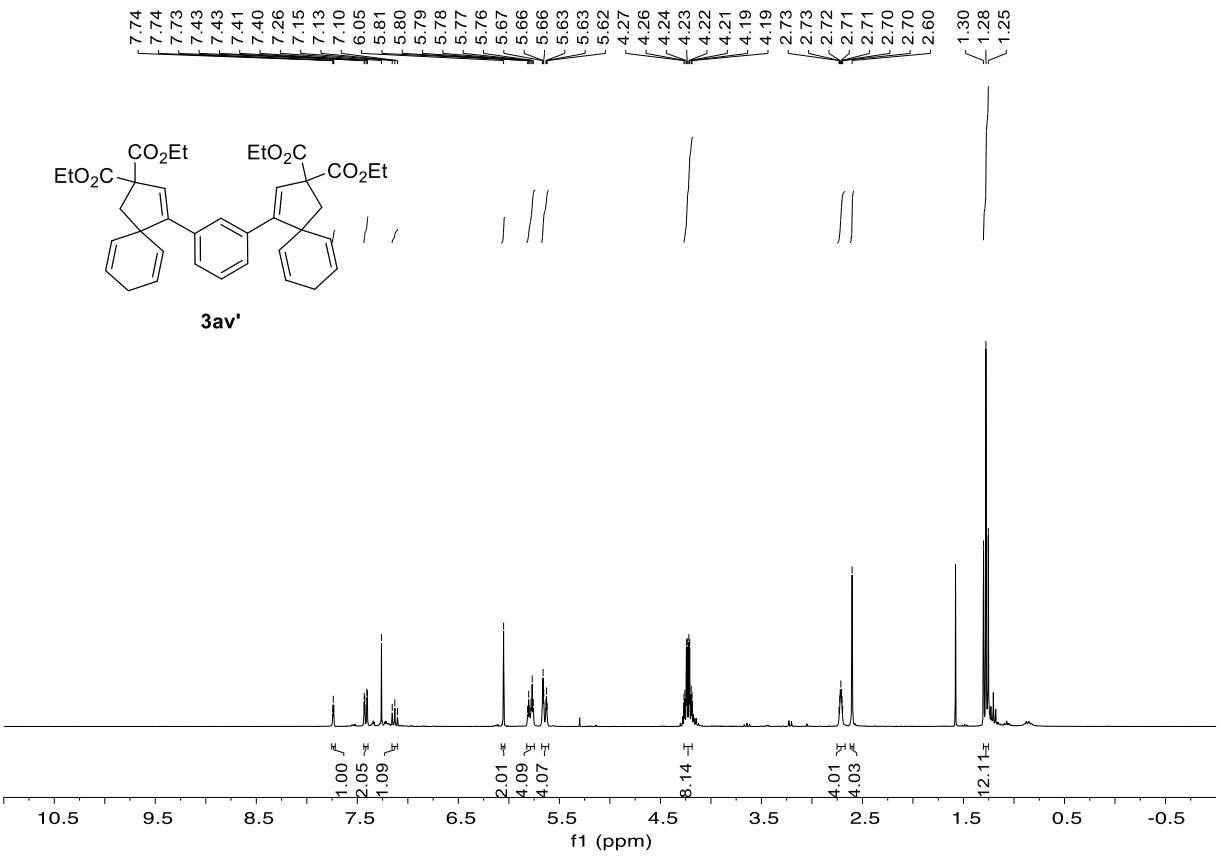


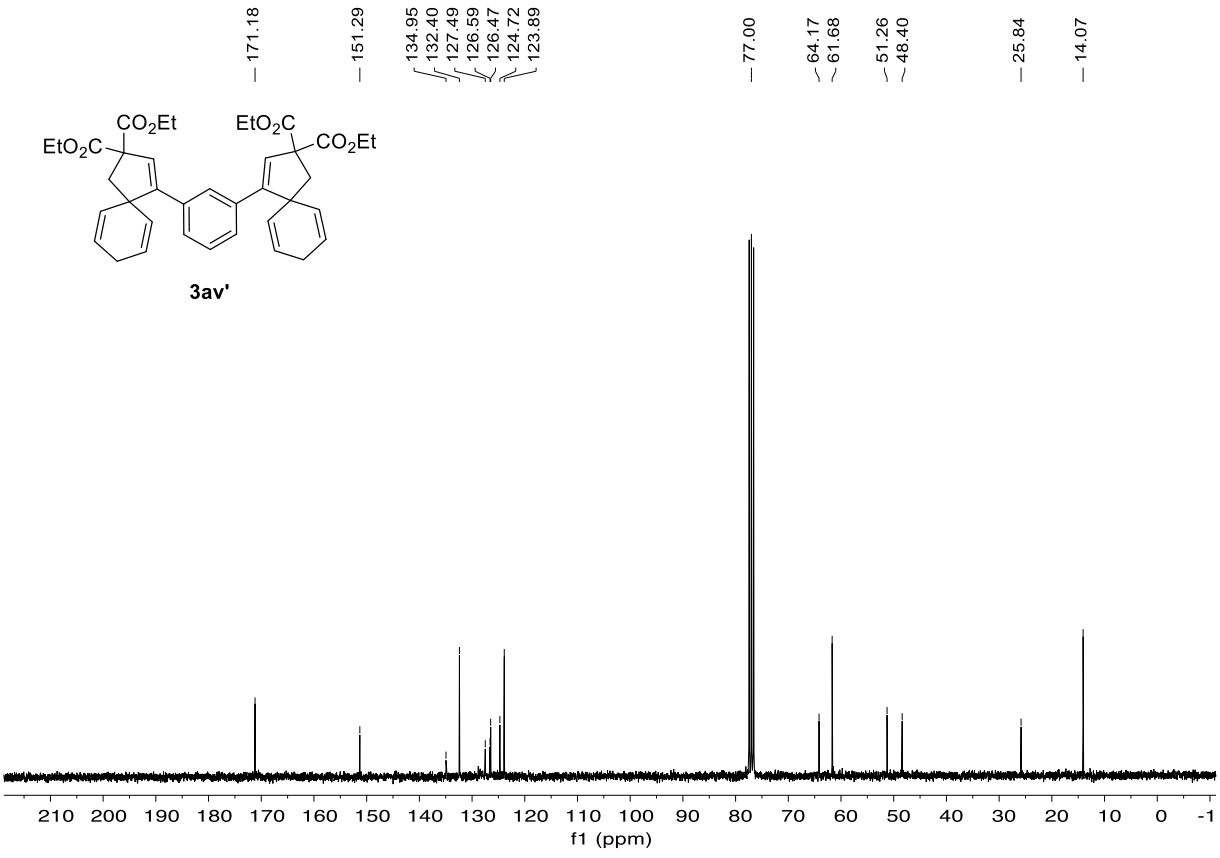
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3av



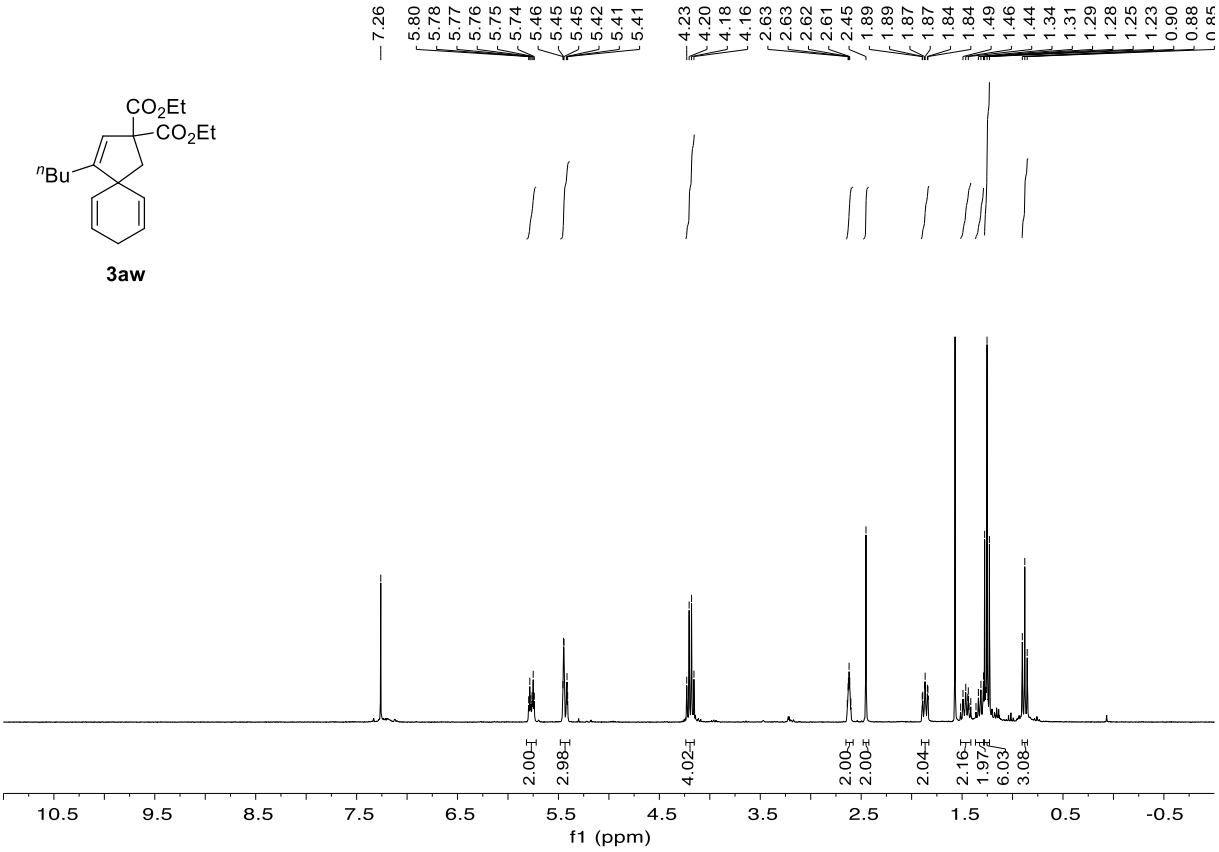


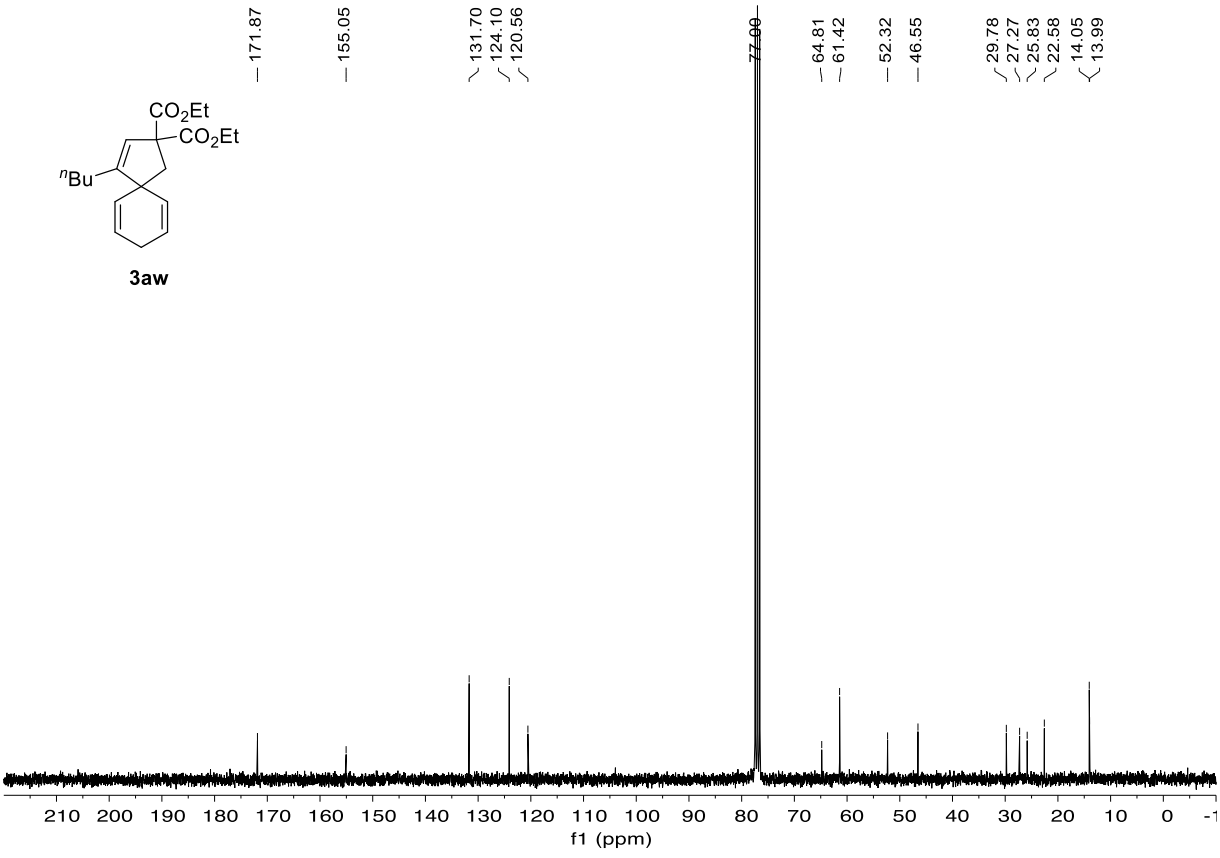
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3av'



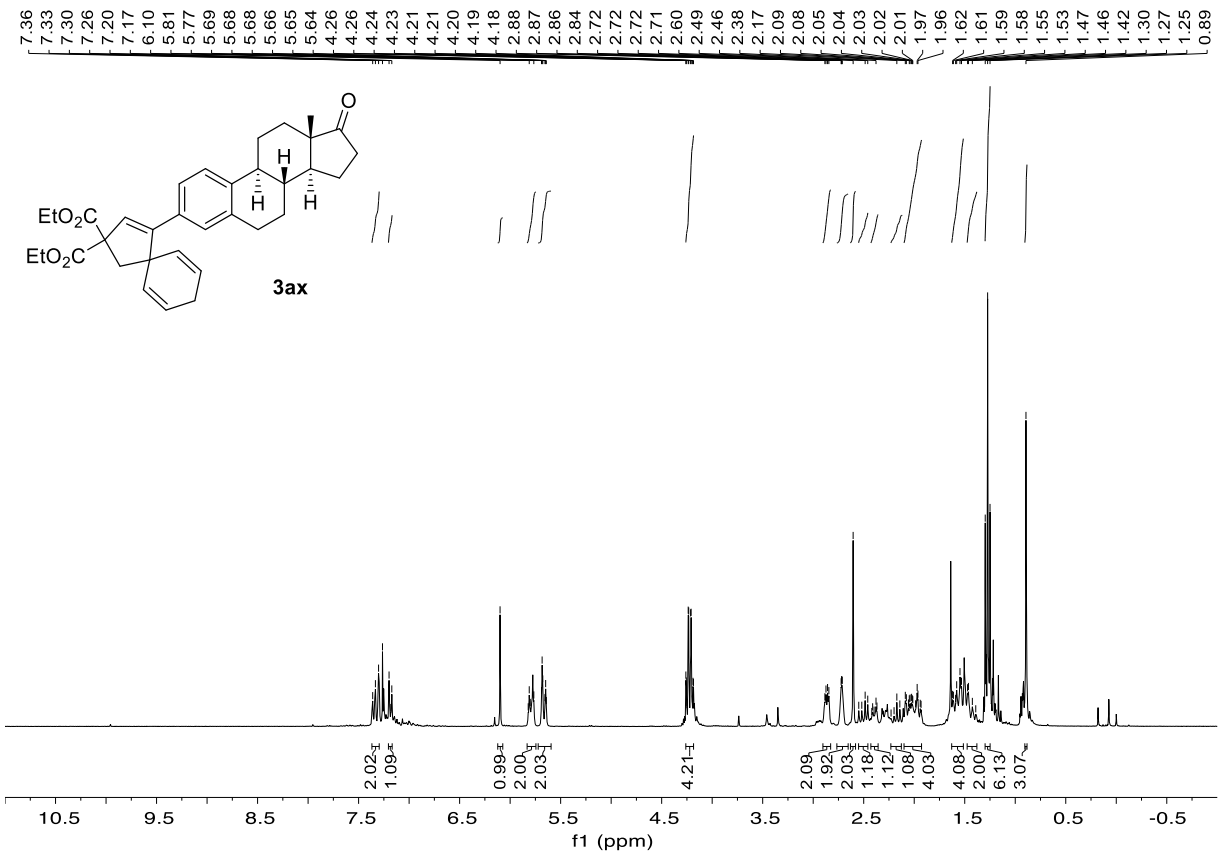


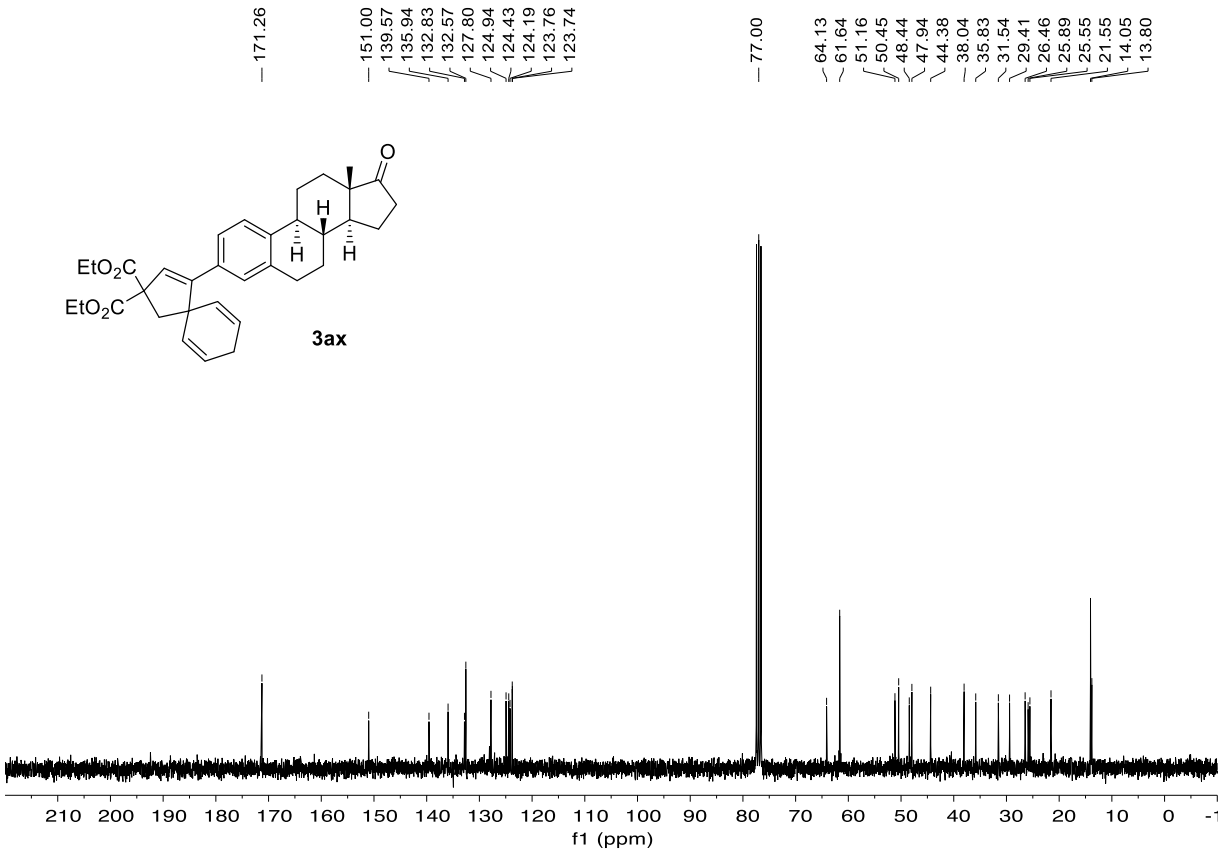
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3aw



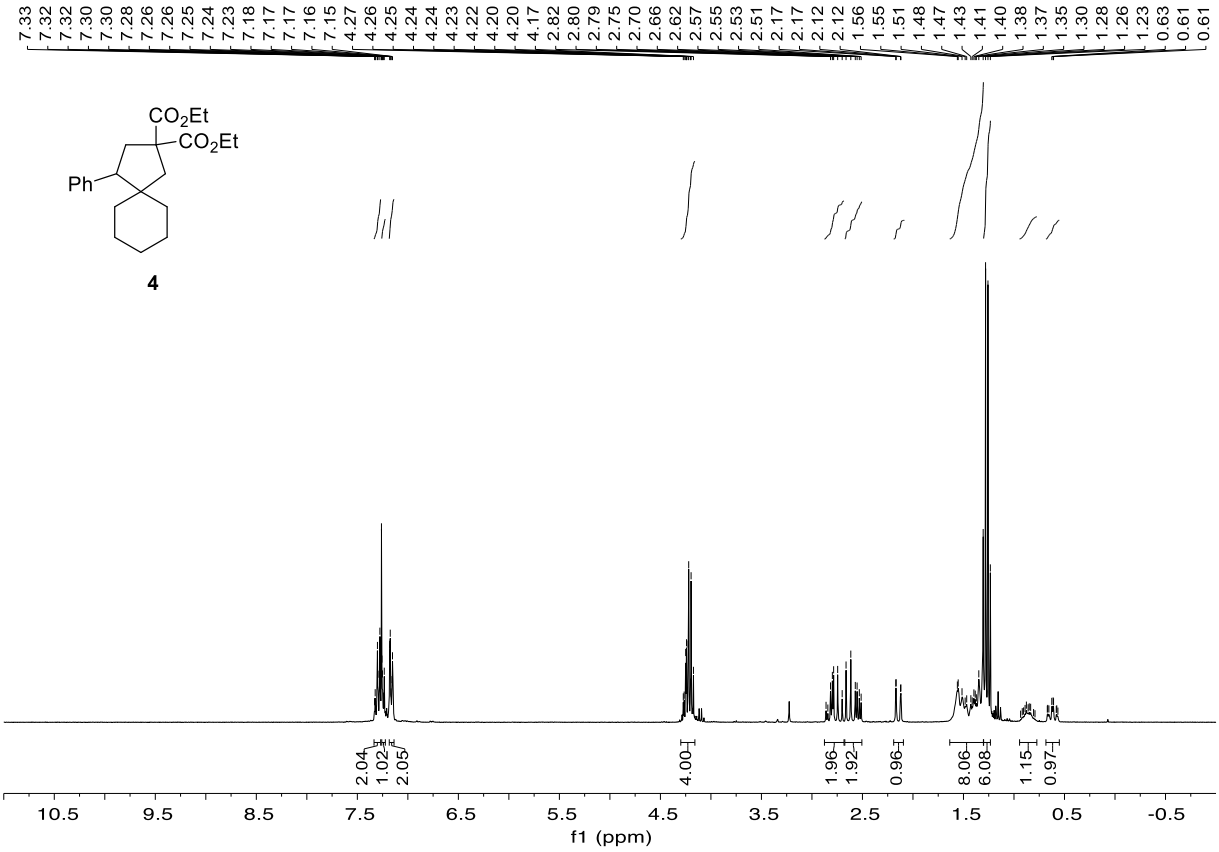


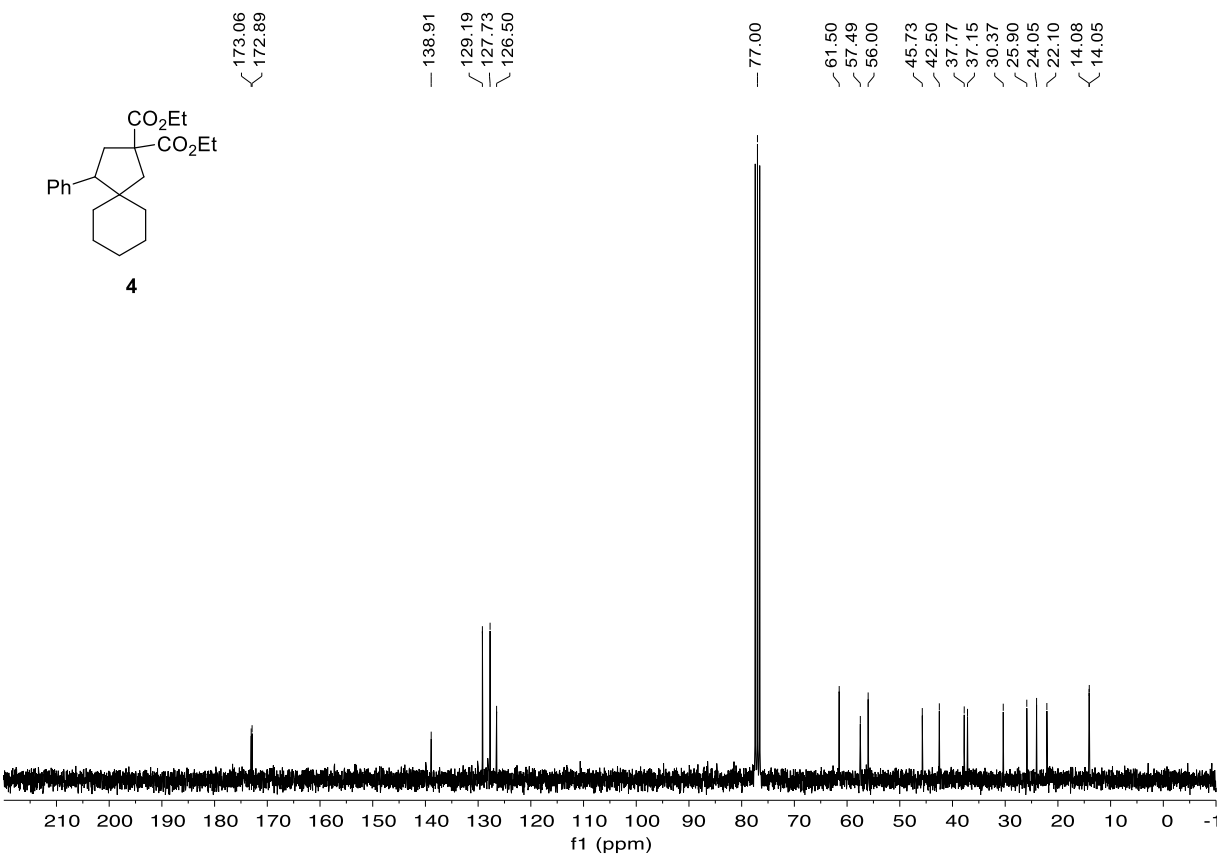
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 3ax



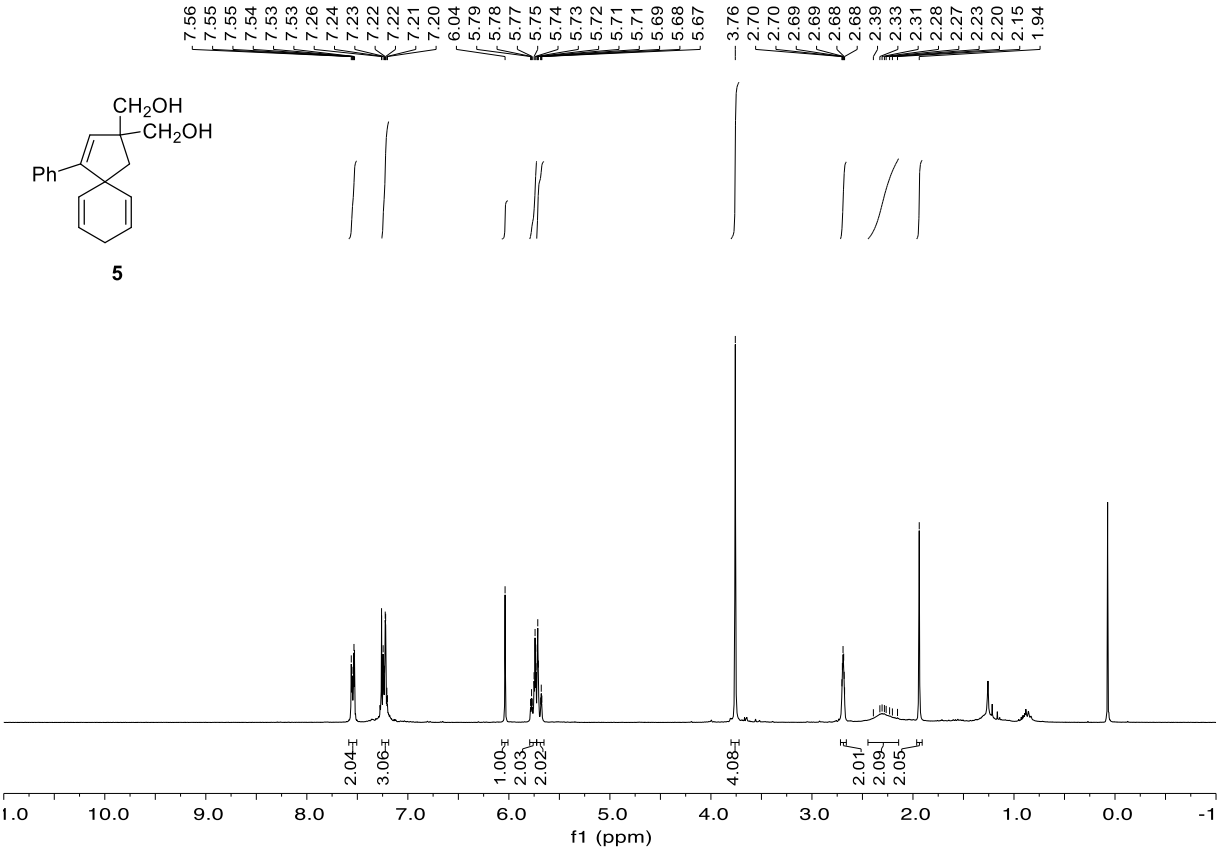


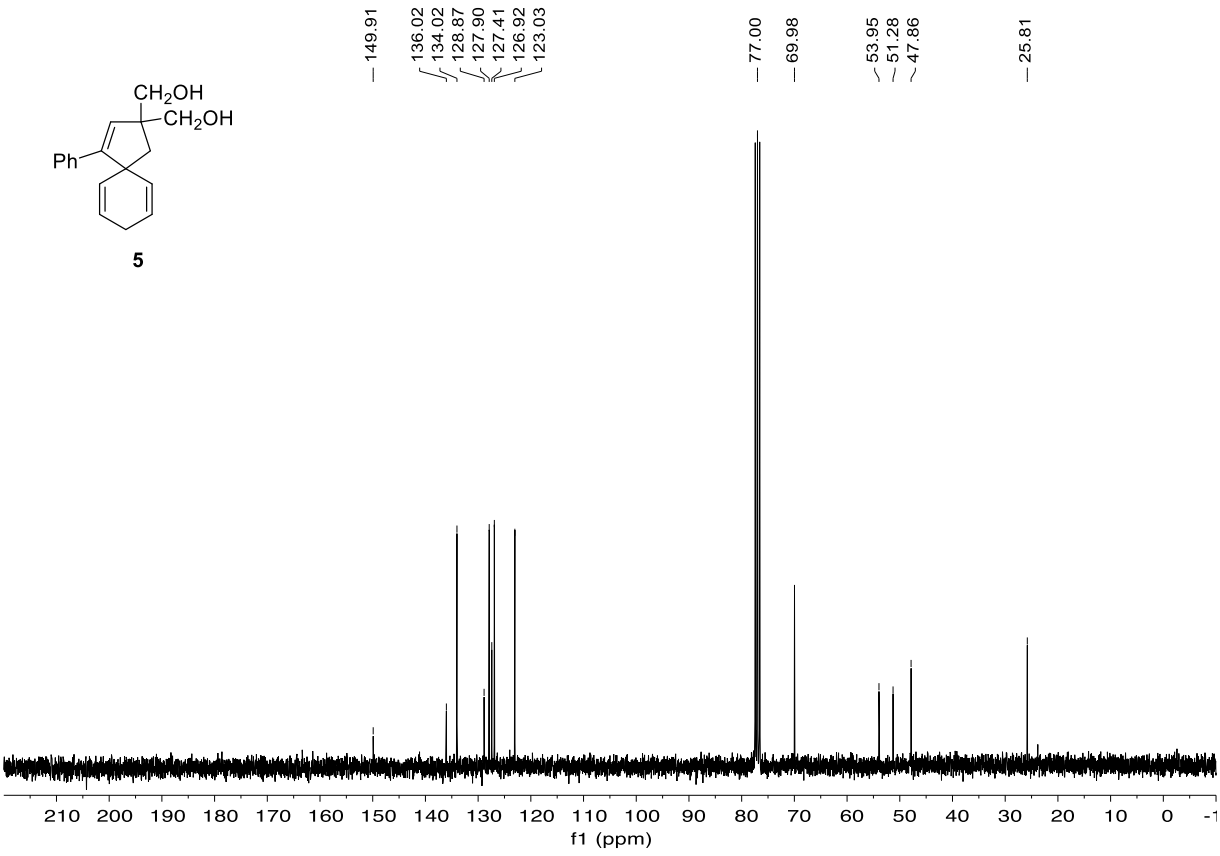
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 4



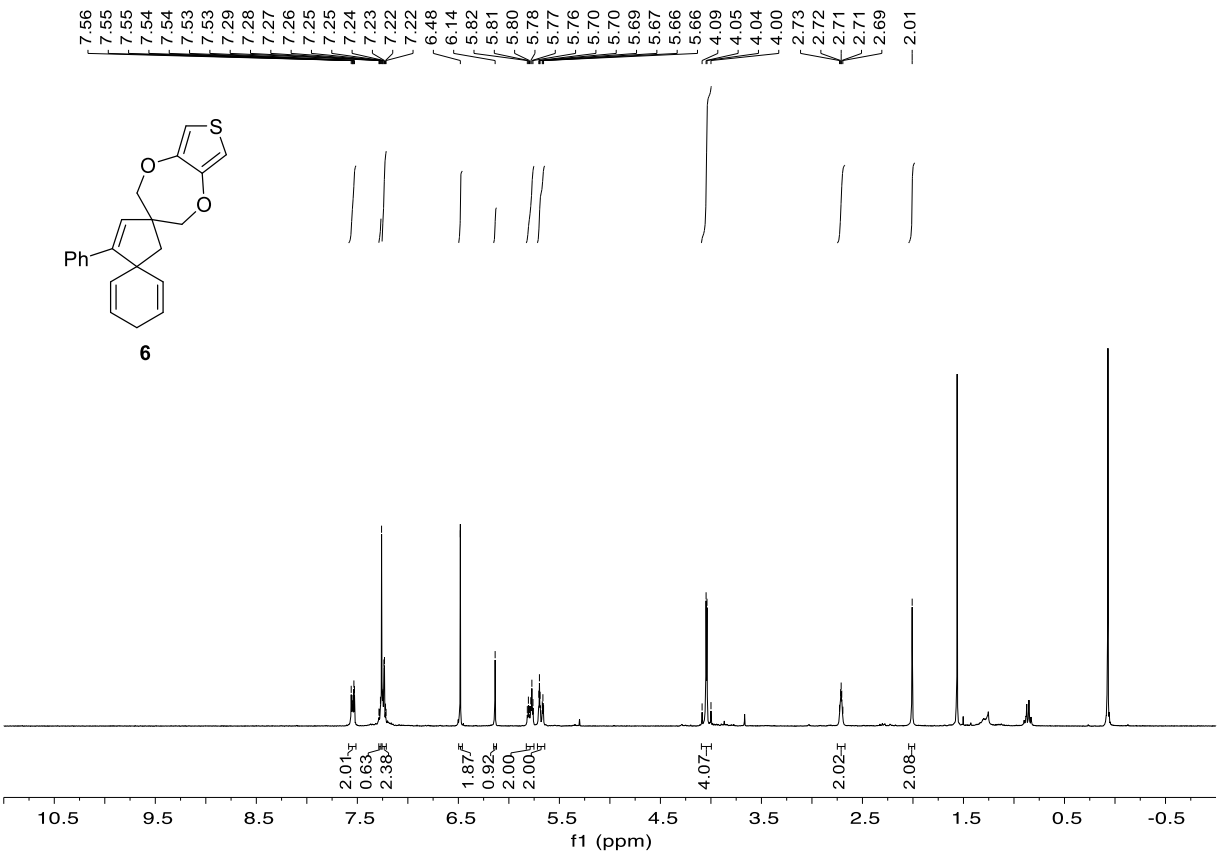


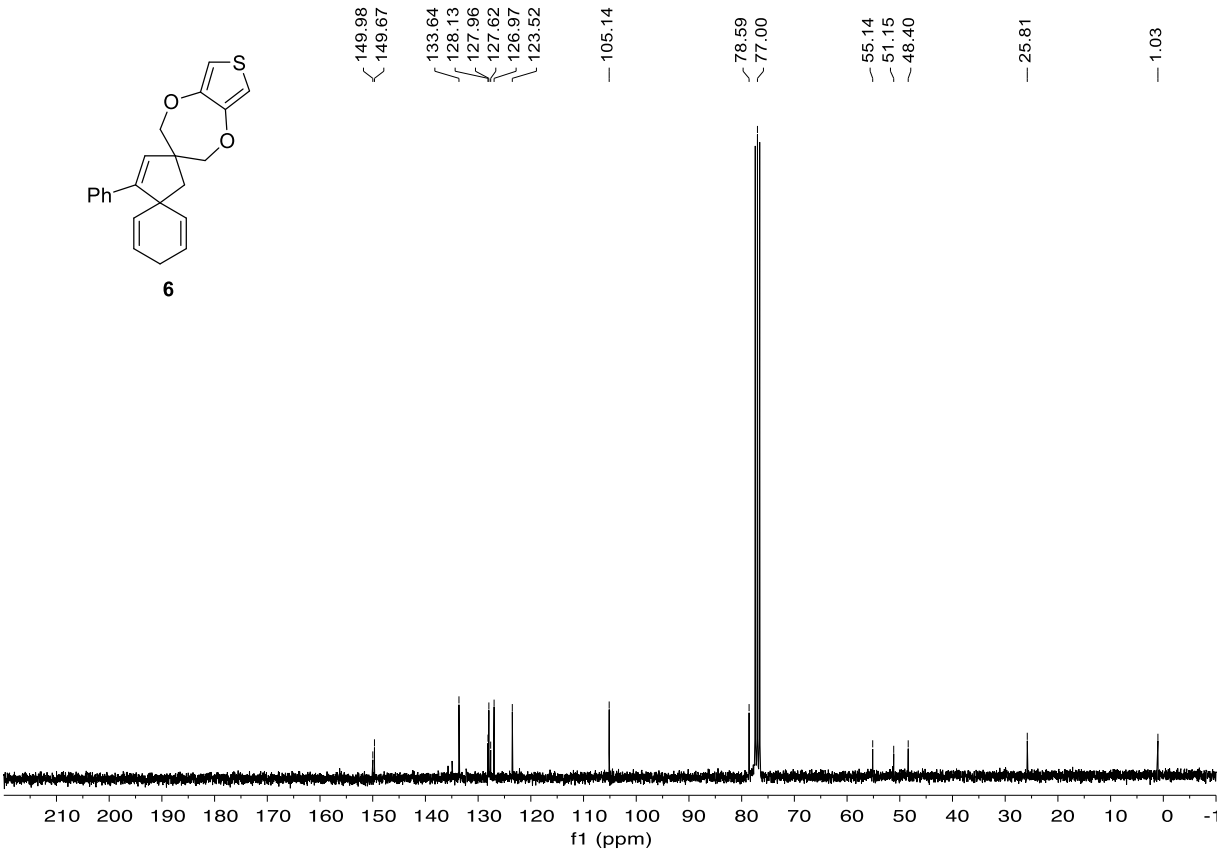
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 5



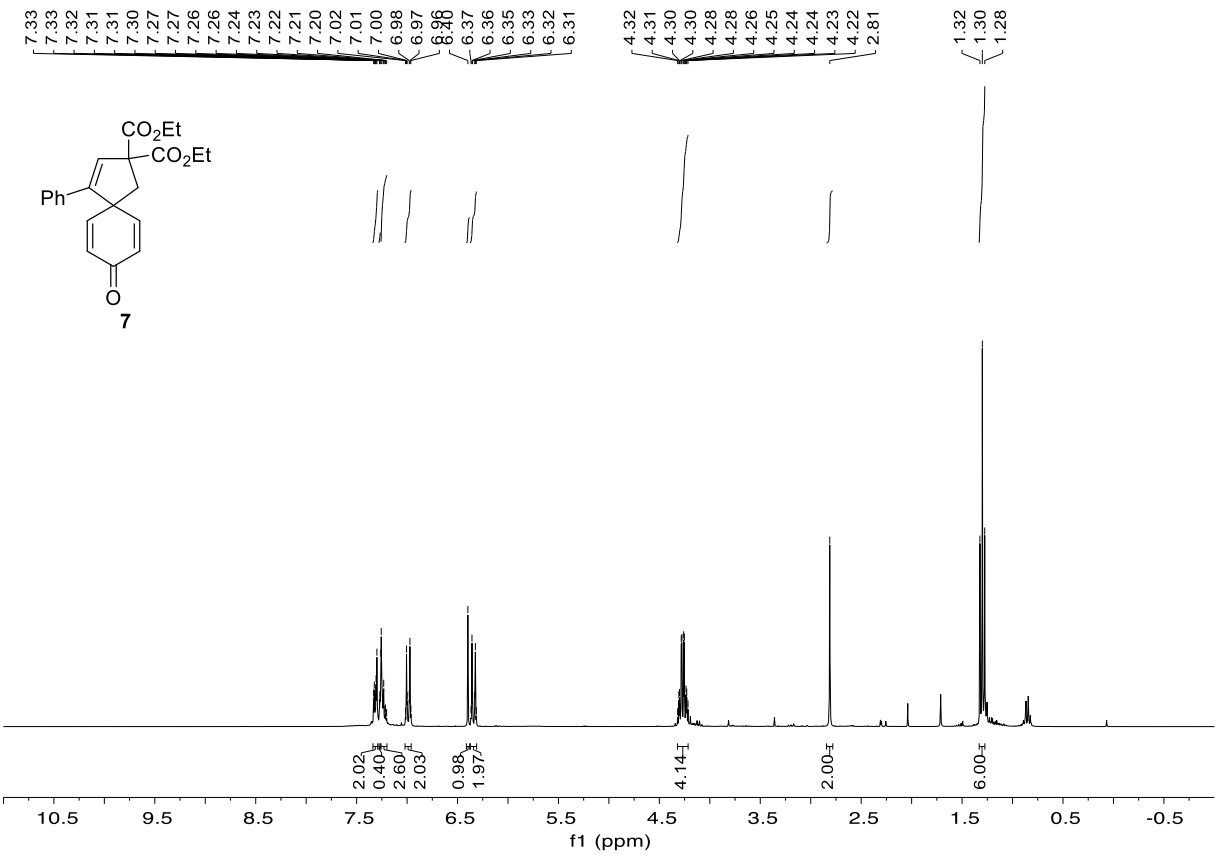


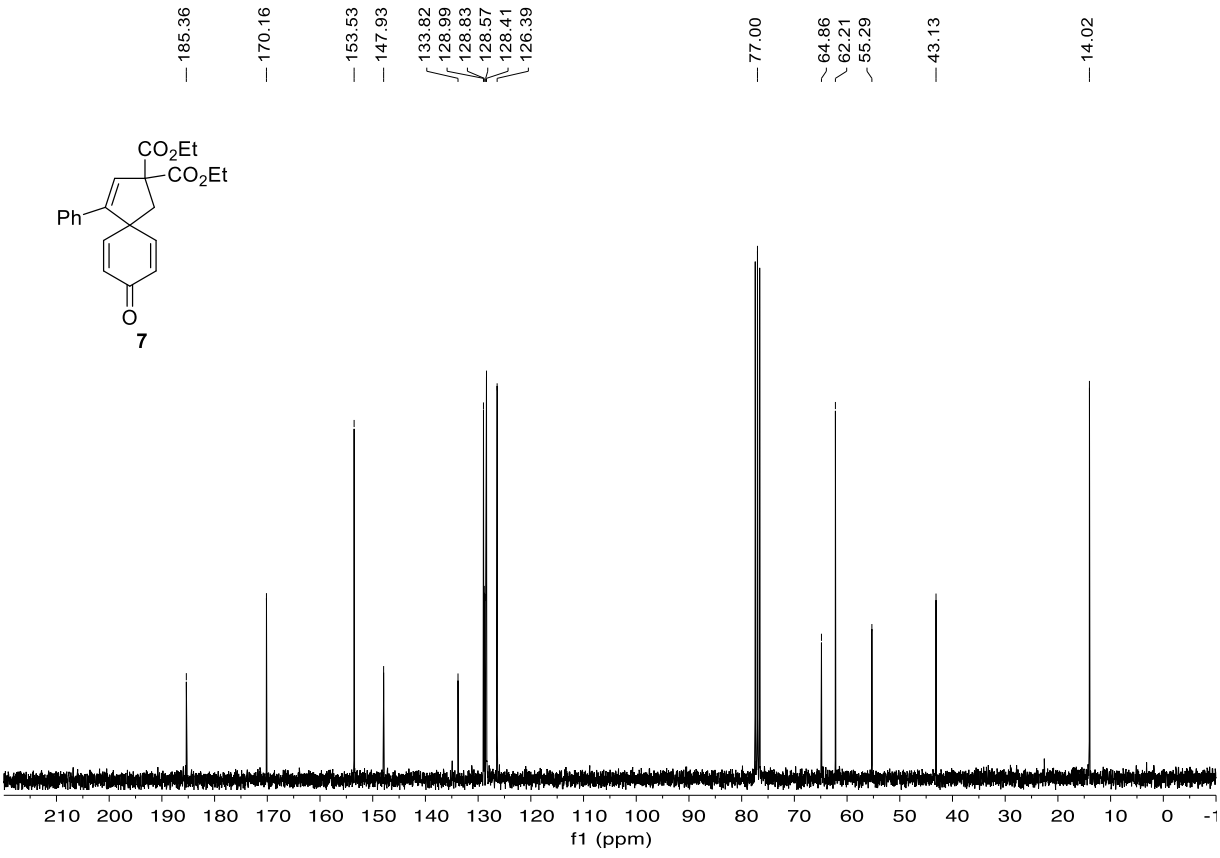
^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 6





^{1}H NMR (400 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 7





^{1}H NMR (300 MHz, $CDCl_3$), and ^{13}C NMR (75 MHz, $CDCl_3$) spectra of product 9