Supporting Information

Rearrangement of a Carboxy-Substituted Spiro[4.4]nonatriene to Annulated Fulvenes Through a Pd(II)-Mediated 1,5-Vinyl Shift

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1. General Information

1.1 Solvents and Reagents

Unless otherwise stated, commercial reagents were purchased and used without purification. Solvents including tetrahydrofuran (THF), diethylether (Et_2O), methanol (MeOH), and benzene (PhH) were dried by passage through activated alumina columns using argon in a Glass Contour solvent purification system. Dichloroethane (DCE, dry and packaged under nitrogen) and dimethylsulfoxide (DMSO, dry and packaged under nitrogen) were used without purification. Dichloromethane (DCM) was freshly distilled over calcium hydride under a N_2 atmosphere. Deuterated solvents were purchased from Cambridge Isotope Laboratories and were used without further purification unless otherwise specified. Deuterated acetic acid was purchased from Sigma Aldrich.

1.2 Experimental Procedures

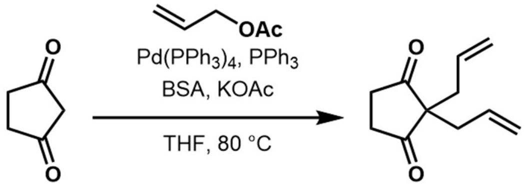
Unless otherwise stated, all reactions were performed in flame-dried or oven-dried glassware under an atmosphere of positive nitrogen pressure using Teflon-coated stir bars. Air and moisture-sensitive liquids were transferred via syringe through rubber septa. Solids were added under inert gas or were dissolved in the appropriate solvent and added via syringe and needle. Reactions ran above room temperature (20–25 °C) were heated in a metal block or oil bath with a thermocouple. Low temperature reactions were carried out in a Dewar flask filled with isopropanol/dry ice (–78 °C) or water/ice (0 °C). Organic solutions were concentrated under reduced pressure on an IKA temperature-controlled rotary evaporator equipped with a dry ice/isopropanol condenser. Reaction progress was monitored by thin layer chromatography (TLC). TLC and preparative TLC were performed on glass-backed Silicycle SiliaPlate 250 μm thickness, 60 Å porosity F-254 precoated plates. Flash column chromatography was performed with either glass columns using Silicycle silica gel (40– 63 μm particle size) or with a Yamazen Smart Flash EPCLC W-Prep 2XY (dual channel) automated flash chromatography system on prefilled, premium, universal columns using ACS grade solvents. Compounds were visualized with UV light (254 nm) and stained with aqueous potassium permanganate ($KMnO_4$) or *p*-anisaldehyde and heat.

1.3 Analytical Instrumentation

NMR spectral data were obtained using deuterated solvents, obtained from Cambridge Isotope Laboratories, Inc. ^1H NMR, proton-decoupled ^{13}C NMR, and ^{19}F NMR data were recorded on Bruker AV-300, AVQ-400, AVB-400, NEO-500, AV-600 and AV-700 spectrometers using $CDCl_3$ as solvent at 20–23 °C. Chemical shifts (δ) are reported in ppm relative to the residual solvent signal (δ 7.26 for ^1H NMR & δ 77.16 for ^{13}C NMR in $CDCl_3$). Data for ^1H, ^{13}C, and ^{19}F spectroscopy are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, app = apparent), coupling constant (Hz), integration. All raw FID files were processed, and the spectra analyzed, using the program MestReNOVA 11.0 from Mestrelab Research S. L. High-resolution mass spectra (HRMS) were obtained from the Mass Spectral Facility at the University of California, Berkeley, on a Finnigan/Thermo LTQ-FT instrument (ESI). Data acquisition and processing were performed using the XcaliburTM software. Chiral HPLC analysis was conducted using a Waters Alliance e2695 Separations Module equipped with ChiralPak® columns. Data was processed and analyzed using Empower®3 software. HPLC grade isopropanol (IPA) and hexanes were used for HPLC analysis.

2. Experimental Procedures and Characterization Data

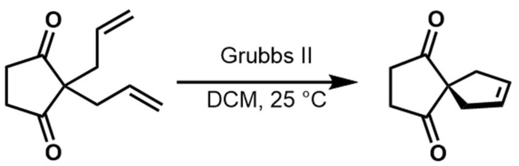
2.1. Preparation of Spiro[4.4]nonatriene Substrate



S1

2,2-Diallylcyclopentane-1,3-dione (S1): This procedure was adapted from Poli et. al.[1] To a flame-dried two-neck flask equipped with a stir bar was added 1,3-cyclopentanedione (10.0 g, 102 mmol, 1.0 equiv) and THF (255 mL, 0.4 M). One neck of the flask was sealed with a septum and the other was fitted with a septum-sealed reflux condenser under a N_2 atmosphere. Allyl acetate (23.1 mL, 214 mmol, 2.1 equiv) and bis-trimethylsilyl acetamide (BSA, 24.9 mL, 102 mmol, 1.0 equiv) were then added by syringe. The septum was removed and the following solid reagents were quickly added before re-capping the flask: oven-dried KOAc (1.00 g, 10.2 mmol, 0.10 equiv), $Pd(PPh_3)_4$ (11.8 g, 10.2 mmol, 0.10 equiv), and then PPh_3 (2.67 g, 10.2 mmol, 0.10 equiv). The reaction mixture was stirred at reflux (heating to 70 °C) for 22 h, then cooled to room temperature, quenched with sat. aq. NH_4Cl (50 mL), and the aqueous phase was extracted with EtOAc (3 x 50 mL). The combined organic layers were dried over Na_2SO_4, filtered, and then concentrated under reduced pressure to afford the crude product as a brown oil. This oil was then purified by silica gel flash column chromatography (5–15% EtOAc/hexanes gradient) to afford **S2** (13.1 g, 72%) as a yellow oil. The ^1H NMR spectrum was consistent with results reported in the literature.[2]

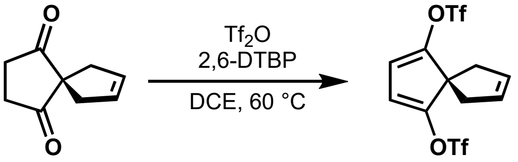
^{1}H NMR: (300 MHz, $CDCl_3$) δ 5.55 (ddt, J = 17.2, 9.7, 7.5 Hz, 2H), 5.12 – 4.99 (m, 4H), 2.62 (s, 4H), 2.37 (dt, J = 7.5, 1.0 Hz, 4H).



S1 **S2**

Spiro[4.4]non-7-ene-1,4-dione (**S2**): This procedure was adapted from a report in the literature.[3] To a flame-dried flask equipped with a stir bar was added diallylated diketone **S1** (13.1 g, 73.4 mmol, 1.0 equiv), DCM (223 mL, 0.33M), and Grubbs' G2 catalyst (312 mg, 0.367 mmol, 0.05 mol % under air. The flask was sealed with a septum and placed under a slow stream of N_2. The resulting solution was stirred at 25 °C until consumption of starting material (4 h). The reaction mixture was then concentrated under reduced pressure to give a brown solid which was used without further purification. The ^1H NMR spectrum was consistent with results reported in the literature.[3]

^{1}H NMR: (300 MHz, $CDCl_3$) δ 5.61 (br s, 2H), 2.83 (br s, 4H), 2.66 (br s, 4H).



S2 **S3**

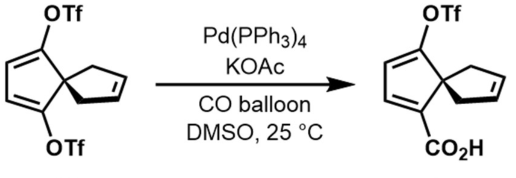
Spiro[4.4]nona-1,3,7-triene-1,4-diyl bis(trifluoromethanesulfonate) (**S3**). This procedure was modified from a report by Stang et. al.[4] To a flame-dried flask equipped with a stir bar was added spiro-diketone **S1** (4.0 g, 27 mmol, 1.0 equiv). The flask was evacuated and refilled with N_2 three times. Under a N_2 atmosphere, DCE (130 mL, 0.20 M) and 2,6-di-*tert*-butyl pyridine (DTBP, 60 mL, 270 mmol, 10 equiv) were added. Then triflic anhydride (45 mL, 270 mmol, 10 equiv) was slowly added. The reaction mixture was heated to 60 °C and stirred for 24 h at this temperature. The reaction mixture was then cooled to 25 °C, transferred to an Erlenmeyer flask, and then further cooled to 0 °C. Water (200 mL) was slowly added until bubbling ceased. Hexanes (400 mL) were then added and a brown solid formed. The resulting biphasic mixture was filtered through a celite pad. The organic layer was separated and washed with 4 M HCl (3 x 200 mL) and then brine (200 mL). The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure to yield a crude, black oil which was then purified by silica gel flash column chromatography (0–8% EtOAc/hexanes gradient) to give 6.6 g (60%) of **S3** as an orange oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.01 (s, 2H), 5.79 (s, 2H), 2.73 (s, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 153.2, 129.0, 118.6 (q, *J* = 320.7 Hz), 111.4, 56.8, 36.1.

^{19}F NMR (470 MHz, $CDCl_3$) δ –73.32 (s).

HRMS (EI): Calcd for ([M], $C_{11}H_8F_6O_6S_2$)$^+$: m/z= 413.9661, found 413.9673



S3 **S4**

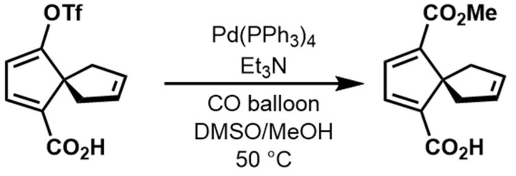
4-(((trifluoromethyl)sulfonyl)oxy)spiro[4.4]nona-1,3,7-triene-1-carboxylic acid (S4). This procedure was adapted from a report in the literature.[5] To a flame-dried flask with a stir bar was added **S3** (2.00 g, 4.83 mmol, 1.0 equiv), which was dissolved in DMSO (28.4 mL, 0.17 M). To this solution was added oven-dried KOAc (497 mg, 5.07 mmol, 1.05 equiv) and $Pd(PPh_3)_4$ (279 mg, 0.241 mmol, 0.05 equiv). The mixture was sparged with CO for 5 min and the reaction mixture was stirred under a CO atmosphere at 25 °C. Reaction progress was monitored by ^{1}HNMR analysis of aliquots of the reaction mixture which were worked up. At the following varying time points, 279 mg (0.05 equiv) of additional $Pd(PPh_3)_4$ was added and the reaction mixture was sparged with CO for 5 mins and allowed to continue stirring: 22 h, 34 h, 46 h, 59 h (0.025 equiv of $PdP(Ph)_3$ added this time). After 66 h of total reaction time, the mixture was diluted with DCM (20 mL), acidified to pH=1 with 1M HCl, and extracted with DCM (3 x 30 mL). The organic layers were combined, washed with brine (3 x 30 mL), dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography (15% EtOAc/2% AcOH/hexanes) to give 541 mg (36%) of **S4** as a pale-yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (d, *J* = 2.9 Hz, 1H), 6.14 (d, *J* = 2.9 Hz, 1H), 5.82 (s, 2H), 3.04 (d, *J* = 14.9 Hz, 2H), 2.53 (d, *J* = 14.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.6, 166.4, 141.3, 138.0, 129.3, 118.60 (q, *J* = 320.7 Hz), 110.9, 57.9, 37.5.

^{19}F NMR (470 MHz, $CDCl_3$) δ –73.28 (s).

HRMS (ESI): Calcd for ([M-H], $C_{11}H_8F_3O_5S$)$^-$: m/z= 309.0050, found 309.0051



S4 **1**

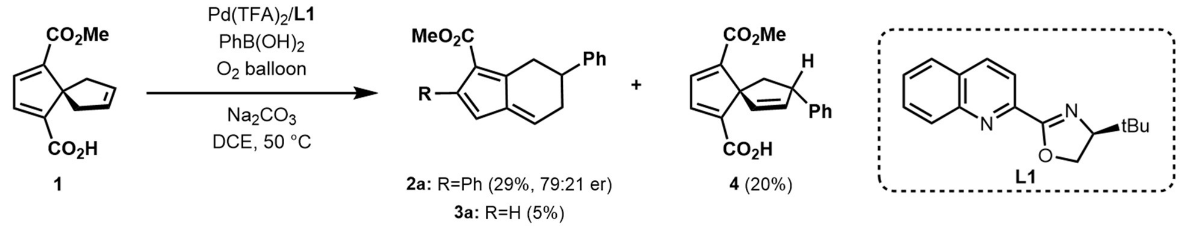
4-(methoxycarbonyl)spiro[4.4]nona-1,3,7-triene-1-carboxylic acid (1): This procedure was adapted from the literature.[6] To a flame-dried flask with a stir bar was added **S4** (720 mg, 2.32 mmol, 1.0 equiv) under air, which was dissolved in DMSO (62.8 mL, 0.037 M) and MeOH (113 mL, 0.021 M). Et_3N (0.97 mL, 3.90 mmol, 3 equiv) was then added, followed by $Pd(PPh_3)_4$ (134 mg, 0.116 mmol, 0.05 equiv). The mixture was sparged with CO for 5 min and then stirred under a CO atmosphere at 50 °C for 4 h. The reaction mixture was cooled to 25 °C and then poured into a separatory funnel with ice. The mixture was acidified to pH=1 with 1M HCl and extracted with Et_2O (3 x 100 mL). The organic layers were combined, washed with brine (3 x 50 mL), dried over Mg_2SO_4, filtered, and concentrated under reduced pressure. The crude mixture was purified by silica gel flash column chromatography (20% EtOAc/2% AcOH/hexanes) to give 419 mg (82%) of **1** as a white to off-white solid. A single crystal of **1** was grown by slow evaporation from a solution in 30% EtOAc/hexanes.

^{1}H NMR ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 2.5 Hz, 1H), 7.19 (d, *J* = 2.5 Hz, 1H), 5.87 (s, 2H), 3.78 (s, 3H), 2.82 – 2.70 (m, 4H).

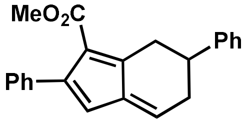
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.8, 163.3, 154.0, 151.8, 140.3, 137.3, 129.5, 59.3, 51.7, 38.7.

HRMS (ESI): Calcd for ([M-H], $C_{12}H_{11}O_4$)$^-$: m/z= 219.0663, found 219.0664

2.2. Discovery and Optimization of Oxidative Heck Reaction Conditions



Initial Reaction Discovery: The rearrangement of spirononatrienes to annulated fulvenes was initially discovered by application of Zhu's conditions to **1**.[7] To a flame-dried vial equipped with a stir bar was added Pd(II) trifluoroacetate ($Pd(TFA)_2$, 0.10 equiv), **L1** (0.10 equiv), and DCE (0.90 mL, 0.05 M). The vial was sealed with a septum cap and the mixture was stirred at 25 °C for 30 min. Sequentially, spirononatriene **1** (10.0 mg, 0.045 mmol, 1.0 equiv), $PhB(OH)_2$ (6.6 mg, 0.054 mmol, 1.2 equiv), and Na_2CO_3 (9.6 mg, 0.091 mmol, 2.0 equiv) were added and, then the mixture was sparged with an O_2 balloon for 2 min. The reaction mixture was stirred under an O_2 atmosphere at 40 °C for 23 h, then cooled to 25 °C and filtered through a celite pad, eluting with DCM. The mixture was concentrated under reduced pressure and purified by preparatory TLC (95% DCM/hexanes) to give 3.3 mg (29%) of diaryl fulvene **2a** as an orange solid (79:21 er) and 0.7 mg of monoaryl fulvene **3a** as a yellow solid (5%). A mixture of starting material **1** and arylated product **4** were isolated from the baseline band and separated through an additional preparatory TLC plate (35% EtOAc/2% AcOH/hexanes). This gave 2.8 mg of **4** (20%) as an off-white powder.



2a

Characterization data for **methyl 2,5-diphenyl-5,6-dihydro-4H-indene-3-carboxylate (2a):**

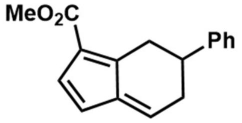
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 – 7.35 (m, 4H), 7.35 – 7.32 (m, 4H), 7.31 – 7.27 (m, 2H), 7.01 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.20 (s, 1H), 3.68 (s, 3H), 3.51 (ddd, *J* = 17.5, 4.3, 1.1 Hz, 1H), 3.29 – 3.19 (m, 1H), 2.90 (dd, *J* = 17.5, 13.0 Hz, 1H), 2.81 (dt, *J* = 19.5, 5.4 Hz, 1H), 2.73 (ddd, *J* = 19.5, 10.9, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 147.1, 144.7, 143.8, 143.7, 142.9, 136.8, 128.8, 128.0, 127.8, 127.4, 127.3, 127.2, 127.0, 118.5, 51.2, 43.4, 35.1, 32.4.

HRMS (EI): Calcd for ([M], $C_{23}H_{20}O_2$)$^+$: m/z= 328.1458, found 328.1460

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t_R(minor)= 11.9 min, t_R(major)=14.1 min, λ= 254 nm

Note: a single crystal of **2a** was grown by slow evaporation from a solution in THF.



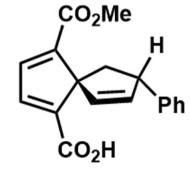
3a

Characterization data for **methyl 5-phenyl-5,6-dihydro-4H-indene-3-carboxylate (3a):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 5H), 7.01 (dd, *J* = 6.0, 2.9 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 6.17 (dd, *J* = 5.3, 1.0 Hz, 1H), 3.78 (s, 3H), 3.60 (ddd, *J* = 17.8, 4.4, 1.0 Hz, 1H), 3.20 (ddt, *J* = 12.9, 10.8, 4.4 Hz, 1H), 2.86 (dd, *J* = 17.8, 12.9 Hz, 1H), 2.79 (dt, *J* = 19.2, 5.3 Hz, 1H), 2.69 (ddd, *J* = 19.4, 10.9, 2.9 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.6, 145.5, 144.7, 143.7, 143.1, 132.5, 128.7, 127.3, 127.2, 126.9, 119.5, 51.3, 43.4, 35.0, 32.2.

HRMS (EI): Calcd for ([M], $C_{17}H_{16}O_2$)$^+$: m/z= 252.1145, found 252.1151



4

Characterization data for **4-(methoxycarbonyl)-8-phenylspiro[4.4]nona-1,3,6-triene-1-carboxylic acid (4)**:

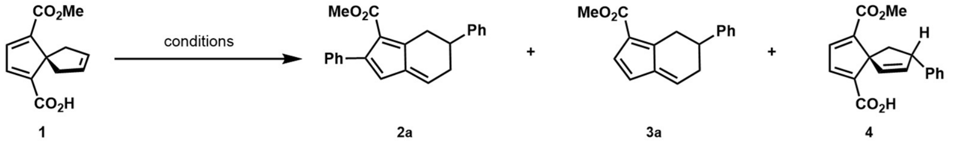
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.44 (d, *J* = 2.5 Hz, 1H), 7.31 (td, *J* = 7.7, 3.0 Hz, 2H), 7.25 (d, *J* = 2.5 Hz, 1H), 7.22 – 7.17 (m, 1H), 6.18 (dt, *J* = 5.4, 2.1 Hz, 1H), 5.22 (ddd, *J* = 4.7, 2.7, 1.8 Hz, 1H), 4.68 (tt, *J* = 8.3, 2.4 Hz, 1H), 3.83 (s, 3H), 2.63 – 2.53 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.1, 163.2, 151.3, 148.5, 148.5, 145.5, 141.7, 141.6, 140.3, 140.3, 138.4, 129.7, 129.7, 128.6, 128.4, 126.5, 69.7, 53.9, 51.7, 38.6.

HRMS (ESI): Calcd for ([M+Na], $C_{18}H_{16}O_2Na$)$^+$: m/z= 319.0941, found 319.0939

Note: a single crystal of **4** was grown by slow evaporation from a solution in DCM.

Table S1. Initial Exploration of Reaction Conditions



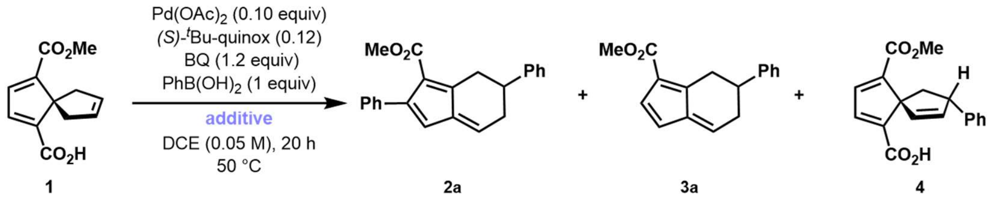
entry	[Pd] (equiv)	ligand (equiv)	ArB(OH)$_2$ (equiv)	oxidant (equiv)	additive (equiv)	temp. (°C)	solvent (M)	results[a]
1	Pd(TFA)$_2$ (0.10)	^{t}Bu-quinox (0.12)	PhB(OH)$_2$ (1.2)	O_2 balloon	Na_2CO_3 (1.2)	50-80	DCE (0.05)	19% **2a+3a**, trace **4**, 40% **1**
2	Pd(TFA)$_2$ (0.10)	^{t}Bu-pyrox (0.12)	PhB(OH)$_2$ (1.2)	O_2 balloon	Na_2CO_3 (1.2)	75	DCE (0.05)	12% **2a+3a**, 21% **4**, 19% **1**
3	Pd(TFA)$_2$ (0.10)	^{t}Bu-pyrox (0.12)	PhB(OH)$_2$ (1.2)	O_2 balloon	Li_2CO_3 (1.2)	75	DCE (0.05)	25% **2a+3a**, 11% **4**, 47% **1**
4[b]	Pd(TFA)$_2$ (0.10)	^{t}Bu-pyrox (0.7)	PhB(OH)$_2$ (1.2)	O_2 balloon	Li_2CO_3 (1.2)	40	DCE (0.05)	23% **2a+3a**, 10% **4**, 47% **1**
5	Pd(TFA)$_2$ (0.10)	^{t}Bu-pyrox (0.12)	PhB(OH)$_2$ (1.2)	BQ (1.2)	Li_2CO_3 (1.2)	50	DCE (0.05)	4% **2a+3a**, 15% **4**,
6	Pd(TFA)$_2$ (0.10)	^{t}Bu-pyrox (0.12)	PhB(OH)$_2$ (1.2)	2,6-di-Me BQ (1.2)	Li_2CO_3 (1.2)	50	DCE (0.05)	14% **2a+3a**, 23% **4**,
7	Pd(OAc)$_2$ (0.10)	^{t}Bu-quinox (0.12)	PhB(OH)$_2$ (1.2)	2,6-di-Me BQ (1.2)	--	50	DCE (0.05)	28% **2a+3a**, 22% **4**, 34% **1**,
8	Pd(OAc)$_2$ (0.10)	^{t}Bu-quinox (0.12)	PhB(OH)$_2$ (1.2)	BQ (1.2)	--	50	DCE (0.05)	28% **2a+3a**, 24% **4**, 19% **1**,

[a]All yields reported are calculated by integration of ^{1}H NMR of crude reaction mixtures relative to pyrazine as an internal standard. All reactions were run for 20 h unless otherwise noted. [b]This reaction was run for three days,

Initial exploration of various reaction parameters indicated the following for further optimization:

- Both Pd(OAc)$_2$ and Pd(TFA)$_2$ showed promise in promoting the reaction.
- Benzoquinones were superior oxidants to molecular O_2.
- 50 °C was an ideal temperature as higher temperatures led to lower conversions.
- 20 h was a sufficient reaction time.

Table S2. Effect of Additives

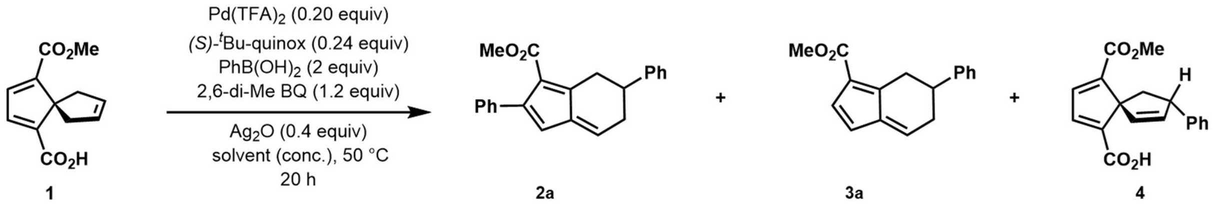


entry	additive (equiv)	results[a]
1	AcOH (9)	14% **2a,** 6% **3a**, 30% **4**, 52% **1**,
2	PivOH (9)	19% **2a,** 11% **3a**, 30% **4**, 45% **1**,
3	$AdCO_2H$ (9)	22% **2a,** 6% **3a**, 32% **4**, 43% **1**,
4	Ag_2CO_3 (0.2)	15% **2a,** 13% **3a**, 31% **4**, 41% **1**,
5	Ag_2O (0.4)	18% **2a,** 1% **3a**, 54% **4**, 16% **1**,
6	CuF_2 (0.2)	14% **2a,** 12% **3a**, 32% **4**, 47% **1**,
7	Cu_2O	16% **2a,** 13% **3a**, 32% **4**, 45% **1**,
8	none	17% **2a,** 12% **3a**, 35% **4**, 41% **1**,
9[b]	Ag_2O (0.4)	30% **2a,** 3% **3a**, 55% **4**

[a]All yields reported are calculated by integration of ^1H NMR of crude reaction mixtures relative to pyrazine as an internal standard. [b]$Pd(TFA)_2$ (0.10 equiv) used instead of $Pd(OAc)_2$.

Exploring various additives indicated that addition of Ag_2O afforded higher overall conversions. Additionally, $Pd(TFA)_2$ resulted in higher yield of desired product **2a**.

Table S3. Effects of Solvents, Concentration, and Ag$_2$O

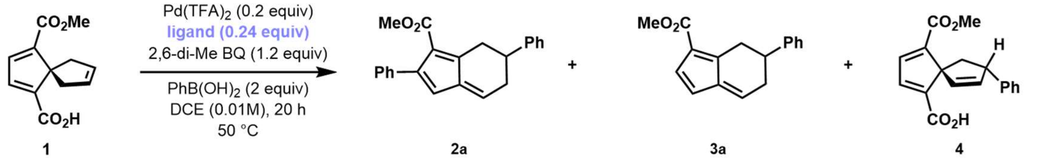


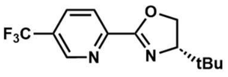
entry	solvent (M)	other variation	results[a]
1	DCE (0.05)		40% **2a,** 7% **3a**, 36 % **4**, 4% **1**,
2	DMSO (0.05)		37% **2a, 4% 3a** 39 % **4**, 2% **1**
3	*o*-DCB (0.05)		14 % **4**
4	PhMe (0.05)		23% **2a,** 63 % **4**
5	THF (0.05)		19% **2a,** 52 % **4**
6	5% AcOH/DCE (0.05)		40% **2a**, 2% **3a**, 31 % **4**
7	5% AcOH/DCE (0.01)		28% **2a**, 4% **3a**, 24 % **4**, 21% SM
8	5% AcOH/DCE (0.05)	no Ag$_2$O	59% (46%)[b] **2a,** 8% **3a**, 12% **4,** 10% **1**
9	5% AcOH/DCE (0.025)	no Ag$_2$O	65% **2a**, 2% **3a**, 14% **4,** 8% **1**
10	5% AcOH/DCE (0.01)	no Ag$_2$O	72% (59%)[b] **2a,** 2% **3a**, 19% **4,** 5% **1**
11	DCE (0.05)	no Ag$_2$O	66% **2a**, 3% **3a**, 10% **4**

[a]All yields reported are calculated by integration of ^{1}H NMR of crude reaction mixtures relative to pyrazine as an internal standard. [b]Isolated yield.

Higher loadings of Pd/L and greater amounts of PhB(OH)$_2$ were shown to give higher yields of **2a** (compare Table S2, entry 9 and Table S3, entry 1). DCE and 5% AcOH/DCE were shown to be optimal solvents for yield of **2a**. Comparing entries 7 and 9, DCE without AcOH seemed to perform slightly better. Additionally, dilute conditions gave higher yields of **2a** (compare entries 8–9). At more dilute conditions, Ag$_2$O showed a detrimental effect on yield of **2a** (compare entries 7 and 10). With these conditions in mind, ligands, benzoquinones, and the effect of acid could be more extensively evaluated (see below).

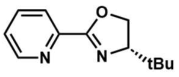
Table S4. Ligand Optimization





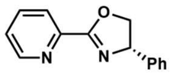
(*S*)-CF$_3$-^{t}Bu-pyrox

25% **2a**, 35% **1**



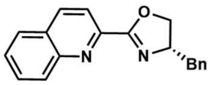
(*S*)-^{t}Bu-pyrox

18% **2a**, 13% B **3a**, 5% **4**, 35% **1**



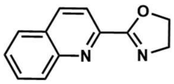
(*S*)-Ph-pyrox

17% **2a**, 23% **3a**, 12% **4**, 23% **1**



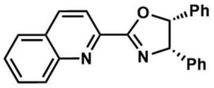
(*S*)-Bn-quinox

64% **2a**, 10% **4**



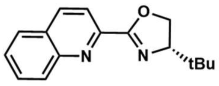
H-quinox

42% **2a**, 19% **4**



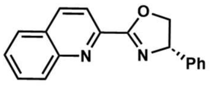
(*S*)-di-Ph-quinox

63% **2a**, 5% **4**, 5% **1**



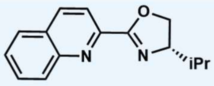
(*S*)-^{t}Bu-quinox

57% **2a**, 10% **4** 9% **1**
er: 76:24



(*S*)-Ph-quinox

68% **2a**
er: 66:34

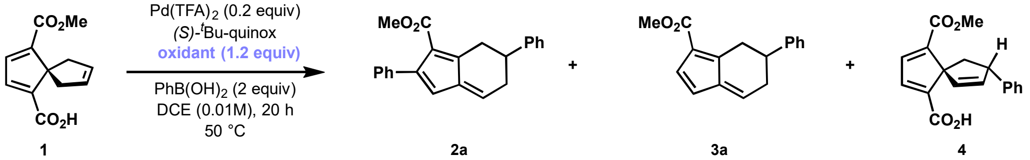


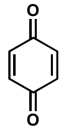
(*S*)-^{i}Pr-quinox

68% **2a**
er: 84:16

All yields reported are calculated by integration of ^{1}H NMR of crude reaction mixtures relative to pyrazine as an internal standard. Yield was the initial consideration for optimization, er's were measured for product **2a** of reactions with ligands that gave a promising yield.

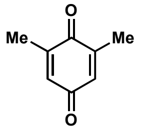
Table S5. Oxidant Optimization





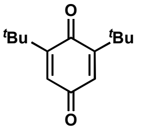
BQ

49% **2a**, 39% **4**



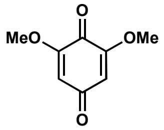
2,6-di-Me BQ

55% **2a**, 6% **1**



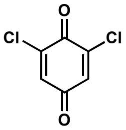
2,6-di-^{t}Bu BQ

37% **2a**, 5% **3a**, 6% **4**, 27% **1**



2,6-di-OMe BQ

60% **2a**, 12% **4**, 13% **1**



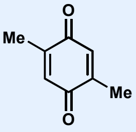
2,6-di-Cl BQ

42% **2a**, 43% **4**

O_2

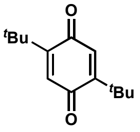
oxygen (1 atm)

8% **2a**, 50% **1**



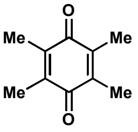
2,5-di-Me BQ

66% **2a**, 10% **4**, 6% **1**



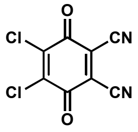
2,5-di-^{t}Bu BQ

29% **2a**, 5% **3a**, 5% **4**, 45% **1**



duroquinone

12% **2a**, 50% **1**



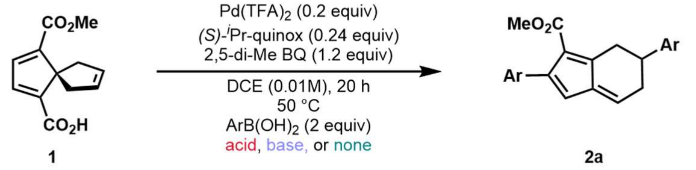
DDQ

no reaction

All yields reported are calculated by integration of ^{1}H NMR of crude reaction mixtures relative to pyrazine as an internal standard. Yields <5% are not shown.

While the role of the benzoquinone (BQ) in this reaction is to oxidize Pd(0) back to Pd(II) to allow for catalyst turnover, as illustrated in the table, there may be other subtle effects which affect the product ratios of **2a** vs. **4**. Interestingly, there is little correlation of product ratio to the oxidation potential of the benzoquinone. We hypothesize that steric effects control the product ratio through the binding of the substituted benzoquinone or the resulting hydroquinone to **Int2** or **Int3**, which may displace the spirononatriene olefin, resulting in the dissociation of **4** as the product. Unsubstituted benzoquinone gives a nearly 1:1 ratio of **2a:4** whereas all of the substituted benzoquinones, except for 2,6-dichlorobenzoquinone, give predominantly **2a**. This may be because the substituents hinder the binding of the BQ to **Int2** or **Int3**. Note that severely hindered quinones (2,6-di-tert-butyl and duroquinone) give the highest ratios of **2a:4.** However, these also give low conversion, likely due to the low binding to the palladium (0) complex, impeding its oxidation and catalytic turnover.

Table S6. Effects of Acidic or Basic Conditions

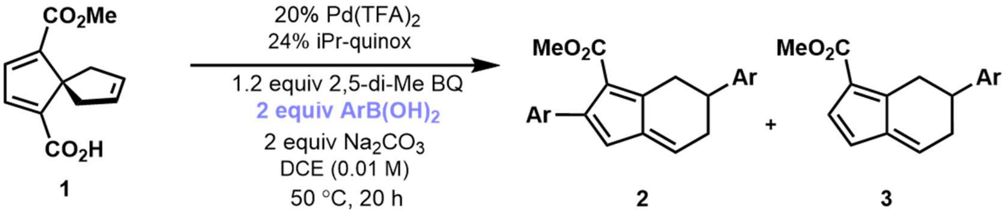


entry	variation	% yield[a]	er
1	$PhB(OH)_2$, no additive	65 (53)	84:16
2	4-OMe-$PhB(OH)_2$, no additive	55 (39)	
3	4-CN-$PhB(OH)_2$, no additive	53 (30)	
4	$PhB(OH)_2$; 5% (v/v) AcOH	88 (46)	84:16
5	4-OMe-$PhB(OH)_2$; 5% (v/v) AcOH	mostly SM	
6	4-CN-$PhB(OH)_2$; 5% (v/v) AcOH	65	
7	$PhB(OH)_2$; 2 equiv Na_2CO_3	76 (59)	87:13
8	4-OMe-$PhB(OH)_2$; 2 equiv Na_2CO_3	74 (26)	
9	4-CN-$PhB(OH)_2$; 2 equiv Na_2CO_3	61 (40)	

[a] Yields reported are calculated by integration of ^1H NMR of crude reaction mixtures relative to pyrazine as an internal standard; isolated yields are reported in parentheses.

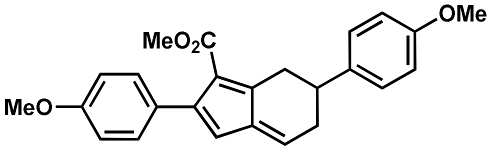
Electron-deficient and -neutral arylboronic acids were shown to tolerate acidic, basic, and neutral conditions. However, electron-rich aryl boronic acids performed poorly under acidic conditions, likely due to protodeboronation.[8] On the basis of the higher yield and enantiomeric ratio, basic conditions were chosen as optimal conditions for a range of substituted arylboronic acids.

2.3 Substrate Scope for Arylboronic Acids



Procedure for 1 mmol reaction with $PhB(OH)_2$: To a flame-dried flask equipped with a stir bar was added $Pd(TFA)_2$ (65.2 mg, 0.196 mmol, 0.2 equiv), *(S)*-^{i}Pr-quinox (56.6 mg, 0.235 mmol, 0.24 equiv), and DCE (98.1 mL, 0.01M) under air. The vial was sealed with a septum and the mixture was stirred at 25 °C for approximately 30 min. Then 2,5-di-Me BQ (160 mg, 1,18 mmol, 1.2 equiv), Na_2CO_3 (208 mg, 1.96 mmol, 2 equiv), spirononatriene **1** (216 mg, 0.981 mmol, 1.0 equiv), and phenylboronic acid (239 mg, 1.96 mmol, 2.0 equiv) were added. The vial was then sealed and stirred at 50 °C for 20 h. The vial was allowed to cool to 25 °C and then filtered through a silica pad, eluting with DCM. The mixture was concentrated under reduced pressure and the resulting residue was purified using silica gel flash column chromatography (70–80% DCM/hexanes) to give 232 mg (72%) of **2a** as an orange solid (86:14 er, see above for characterization data).

General Procedure A: To a 20 mL scintillation vial equipped with a stir bar was added $Pd(TFA)_2$ (3.3 mg, 0.010 mmol, 0.2 equiv), *(S)*-^{i}Pr-quinox (2.9 mg, 0.012 mmol, 0.24 equiv), and DCE (5.0 mL, 0.1) M) under air. The vial was sealed with a PTFE-lined screw cap and the mixture was stirred at r.t. for approximately 30 mins. Then, 2,5-di-Me BQ (8.2 mg, 0.060 mmol, 1.2 equiv), Na_2CO_3 (10.6 mg, 0.10 mmol, 2 equiv), spirononatriene **1** (11.0 mg, 0.050 mmol, 1.0 equiv), and varying arylboronic acids (2 equiv) were added. The vial was then sealed and stirred at 50 °C for 20 h. The vial was allowed to cool to 25 °C and then filtered through a silica pad, eluting with DCM. The mixture was concentrated under reduced pressure and the resulting residue was purified using preparatory TLC. Compounds which were obtained as sticky residues after purification could be reconstituted as solids by addition of 10% ^{i}PrOH/hexanes and concentration under reduced pressure.



2b

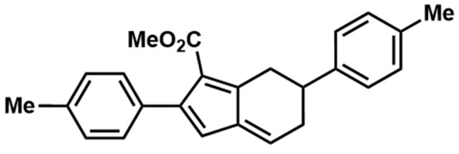
methyl 2,5-bis(4-methoxyphenyl)-5,6-dihydro-4H-indene-3-carboxylate (**2b**) was prepared according to General Procedure A using 15.2 mg (0.10 mmol, 2 equiv) of 4-(methoxy)phenylboronic acid. The crude mixture was purified by preparatory TLC (5% Et_2O/PhMe, run twice) to give 12.4 mg (64%) of a waxy orange solid (87:13 er).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.24 (d, *J* = 2.2 Hz, 2H), 6.96 (dd, *J* = 6.1, 2.9 Hz, 1H), 6.92 – 6.85 (m, 4H), 6.13 (s, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.70 (s, 3H), 3.46 (ddd, *J* = 17.4, 4.3, 1.0 Hz, 1H), 3.18 (ddt, *J* = 12.9, 11.0, 4.3 Hz, 1H), 2.85 (dd, *J* = 17.5, 13.0 Hz, 1H), 2.82 – 2.72 (m, 1H), 2.66 (ddd, *J* = 19.3, 11.1, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 159.2, 158.5, 146.6, 144.0, 143.7, 142.3, 137.0, 129.3, 129.3, 128.1, 127.2, 117.4, 114.1, 114.1, 113.3, 55.5, 55.4, 51.2, 42.6, 35.4, 32.7.

HRMS (ESI): Calcd for ([M+H], $C_{25}H_{25}O_4$)$^+$: m/z= 389.1747, found 389.1751

Chiral HPLC data: AD3 chiral column, 5% IPA/hexanes 1 mL/min, t_R(minor)= 28.6 min, t_R(major)= 33.7 min, λ= 254 nm



2c

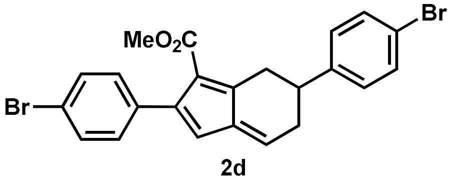
methyl 2,5-di-p-tolyl-5,6-dihydro-4H-indene-3-carboxylate (2c) was prepared according to General Procedure A using 13.6 mg (0.10 mmol, 2 equiv) of *para*-tolylboronic acid. The crude mixture was purified by preparatory TLC (5% Et_2O/PhMe, run twice) to give 9.9 mg (54%) of **2c** as an orange foam (88:12 er).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 7.24 – 7.21 (m, 2H), 7.18 – 7.13 (m, 4H), 6.97 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.16 (s, 1H), 3.69 (s, 3H), 3.47 (ddd, *J* = 17.4, 4.3, 1.0 Hz, 1H), 3.19 (ddt, *J* = 13.1, 10.8, 4.5 Hz, 1H), 2.87 (dd, *J* = 17.5, 13.0 Hz, 1H), 2.78 (dddd, *J* = 19.4, 5.9, 4.7, 1.1 Hz, 1H), 2.69 (ddd, *J* = 19.3, 11.1, 3.0 Hz, 1H), 2.37 (s, 3H), 2.36 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 147.0, 143.8, 143.7, 142.6, 141.8, 137.2, 136.5, 133.8, 129.4, 128.6, 127.9, 127.3, 127.1, 117.9, 51.2, 43.1, 35.2, 32.6, 21.4, 21.2.

HRMS (EI): Calcd for ([M], $C_{25}H_{24}O_2$)$^+$: m/z= 356.1771, found 356.1777

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t_R(minor)= 11.5 min, t_R(major)= 14.7 min, λ= 254 nm



2d

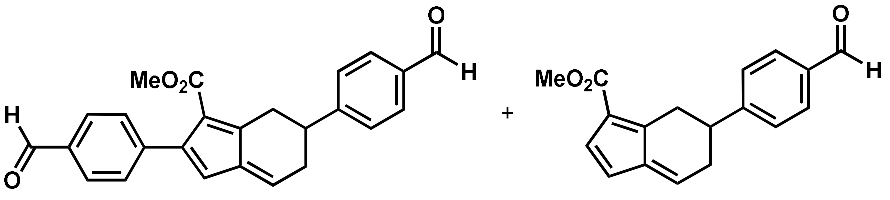
methyl 2,5-bis(4-bromophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2d) was prepared according to General Procedure A using 20.1 mg (0.10 mmol, 2 equiv) of 4-(bromo)phenylboronic acid. The crude mixture was purified by preparatory TLC (80% DCM/hexanes) to give 14.7 mg (61%) of **2d** as a waxy yellow solid (85:15 er).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 4H), 7.22 (app dd, *J* = 19.8, 8.3 Hz, 4H), 7.01 (dd, *J* = 6.1, 2.9 Hz, 1H), 6.18 (s, 1H), 3.69 (s, 3H), 3.52 – 3.45 (m, 1H), 3.20 (ddt, *J* = 15.6, 11.0, 4.4 Hz, 1H), 2.87 (dd, *J* = 17.6, 12.8 Hz, 1H), 2.82 – 2.74 (m, 1H), 2.67 (ddd, *J* = 19.5, 11.0, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 146.0, 143.8, 143.6, 143.5, 143.1, 135.7, 131.8, 130.9, 129.7, 128.9, 127.1, 121.5, 120.7, 118.9, 51.3, 42.7, 34.9, 32.3.

HRMS (ESI): Calcd for ([M+H], $C_{23}H_{19}Br_2O_2$)$^+$: m/z=484.9746, found 484.9746

Chiral HPLC data: AD3 chiral column, 5% IPA/hexanes 1 mL/min, t_R(minor)= 22.0 min, t_R(major)=27.7 min, λ= 254 nm



2e **3e**

methyl 2,5-bis(4-formylphenyl)-5,6-dihydro-4H-indene-3-carboxylate (2e) and **methyl 5-(4-formylphenyl)-5,6-dihydro-4H-indene-3-carboxylate (3e)** were prepared according to General Procedure A using 15.0 mg (0.10 mmol, 2 equiv) of 4-(formyl)phenylboronic acid. The crude mixture was first purified by preparatory TLC (10% Et$_2$O/PhMe) to give 8.6 mg (41%) of **2e** as a waxy orange solid (85:15 er). A yellow band from this preparative TLC plate was isolated and further purified through a second preparative TLC plate (80% DCM/hexanes) to give 1.6 mg (11%) of **3e** as a waxy yellow solid (93:7 er).

Characterization data for **methyl 2,5-bis(4-formylphenyl)-5,6-dihydro-4H-indene-3-carboxylate (2e):**

^{1}H NMR (500 MHz, CDCl$_3$) δ 10.02 (s, 1H), 10.02 (s, 1H), 7.90 – 7.85 (m, 4H), 7.55 – 7.48 (m, 4H), 7.09 (dd, J = 5.9, 3.0 Hz, 1H), 6.31 (s, 1H), 3.69 (s, 3H), 3.56 (ddd, J = 17.6, 4.4, 1.1 Hz, 1H), 3.35 (ddt, J = 12.5, 10.8, 4.4 Hz, 1H), 2.96 (dd, J = 17.5, 12.8 Hz, 1H), 2.87 (dddd, J = 19.3, 5.8, 4.5, 1.1 Hz, 1H), 2.78 (ddd, J = 19.3, 10.8, 3.1 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 192.1, 191.9, 165.4, 151.4, 146.0, 143.8, 143.6, 143.6, 143.1, 135.5, 135.4, 130.3, 129.4, 128.7, 127.9, 127.2, 120.3, 51.3, 43.3, 34.7, 32.0.

HRMS (EI): Calcd for ([M], $C_{25}H_{20}O_4$)$^+$: m/z= 384.1356, found 384.1359

Chiral HPLC data: AD3 chiral column, 30% IPA/hexanes 1 mL/min, t$_R$(minor)= 36.6, t$_R$(major)= 42.3 min, λ= 254 nm

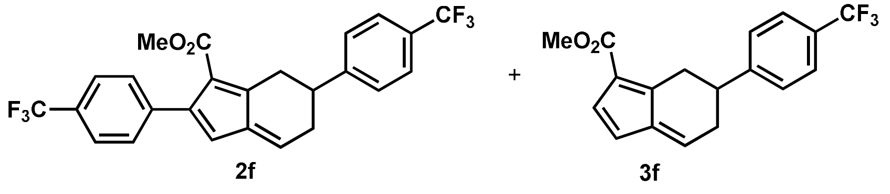
Characterization data for **methyl 5-(4-formylphenyl)-5,6-dihydro-4H-indene-3-carboxylate (3e):**

^{1}H NMR (600 MHz, CDCl$_3$) δ 10.01 (s, 1H), 7.87 – 7.85 (m, 2H), 7.50 – 7.46 (m, 2H), 6.99 (dd, J = 5.9, 2.9 Hz, 1H), 6.80 (d, J = 5.4 Hz, 1H), 6.18 (dd, J = 5.4, 1.0 Hz, 1H), 3.79 (s, 3H), 3.62 (ddd, J = 17.6, 4.4, 1.1 Hz, 1H), 3.30 (ddd, J = 15.5, 11.2, 4.4 Hz, 1H), 2.91 (dd, J = 17.7, 12.7 Hz, 1H), 2.81 (dt, J = 19.2, 5.2 Hz, 1H), 2.72 (ddd, J = 19.3, 10.7, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 192.0, 165.5, 151.7, 145.6, 142.7, 142.2, 135.4, 132.6, 130.3, 127.9, 127.7, 119.7, 51.4, 43.4, 34.5, 31.7.

HRMS (EI): Calcd for ([M], $C_{18}H_{16}O_3$)$^+$: m/z= 280.1094, found 280.1099

Chiral HPLC data: IC3 chiral column, 20% IPA/hexanes 1 mL/min, t$_R$(minor)= 48.1, t$_R$(major)= 36.5 min, λ= 254 nm



2f **3f**

methyl 2,5-bis(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (2f) and **methyl 5-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (3f)** were prepared according to General Procedure A using 19.0 mg (0.10 mmol, 2 equiv) of 4-(trifluoromethyl)phenylboronic acid. The crude mixture was purified by preparatory TLC (80% DCM/hexanes) to give 11.0 mg (47%) of **2f** as a yellow solid (85:15 er) and 2.3 mg (14%) of **3f** as a yellow solid (92:8 er).

Characterization data for **methyl 2,5-bis(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (2f):**

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 (app dd, J = 12.5, 8.0 Hz, 4H), 7.46 (app t, J = 8.6 Hz, 4H), 7.07 (dd, J = 5.9, 3.0 Hz, 1H), 6.25 (s, 1H), 3.70 (s, 3H), 3.54 (ddd, J = 17.5, 4.4, 1.1 Hz, 1H), 3.32 (ddt, J = 12.7, 10.8, 4.4 Hz, 1H), 2.94 (dd, J = 17.5, 12.8 Hz, 1H), 2.85 (dddd, J = 19.4, 5.8, 4.6, 1.1 Hz, 1H), 2.75 (ddd, J = 19.4, 10.8, 3.0 Hz, 1H).

^{13}C NMR (126 MHz, CDCl$_3$) δ 165.4, 148.4, 145.9, 143.6, 143.6, 140.4, 129.4 (q, J = 32.2 Hz), 128.4, 127.6, 127.1, 125.8 (q, J = 3.7 Hz), 125.6, 125.4, 124.7 f(q, J = 3.7 Hz), 123.4, 123.2, 119.9, 51.3, 43.0, 34.8, 32.2.

^{19}F NMR (470 MHz, CDCl$_3$) δ –62.42 (br s), –62.43 (br s).

HRMS (ESI): Calcd for ([M+Na], $C_{25}H_{18}F_6O_2Na)^+$: m/z= 487.1103, found 487.1101

Chiral HPLC data: AD3 chiral column, 3% IPA/hexanes 1 mL/min, t_R(minor)= 9.9 min, t_R(major)=11.9 min, λ= 254 nm

Characterization data for **methyl 5-(4-(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (3f):**

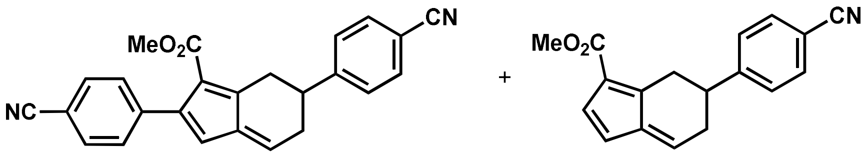
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.99 (dd, *J* = 6.0, 2.9 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 6.17 (dd, *J* = 5.4, 1.0 Hz, 1H), 3.79 (s, 3H), 3.60 (ddd, *J* = 17.6, 4.4, 1.1 Hz, 1H), 3.32 – 3.23 (m, 1H), 2.89 (dd, *J* = 17.7, 12.7 Hz, 1H), 2.80 (dt, *J* = 19.3, 5.2 Hz, 1H), 2.70 (ddd, *J* = 19.2, 10.9, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 148.6, 145.6, 142.8, 142.2, 132.6, 129.3 (d, *J* = 32.6 Hz), 127.6, 127.6, 125.7 (q, *J* = 3.7 Hz), 119.7, 51.4, 43.0, 34.6, 31.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ –62.43 (br s)

HRMS (EI): Calcd for ([M], $C_{18}H_{15}F_3O_2)^+$: m/z= 320.1019, found 320.1031

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 1 mL/min, t_R(minor)= 11.6 min, t_R(major)= 12.5 min, λ= 254 nm



2g **3g**

methyl 2,5-bis(4-cyanophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2g) and **methyl 5-(4-cyanophenyl)-5,6-dihydro-4H-indene-3-carboxylate (3g)** were prepared according to General Procedure A using 14.7 mg (0.10 mmol, 2 equiv) of 4-(cyano)phenylboronic acid. The crude mixture was purified by preparatory TLC (10% Et_2O/hexanes) to give 6.5 mg (34%) of **2g** as an orange solid (80:20 er). A band containing **3g** was isolated and further purified through a second preparatory TLC (10% Et_2O/Hexanes) to give 2.6 mg (19%) of **3g** as an orange solid (87:13 er).

Characterization data for **methyl 2,5-bis(4-cyanophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2g):**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.68 – 7.60 (m, 4H), 7.47 – 7.42 (m, 4H), 7.08 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.26 (d, *J* = 0.8 Hz, 1H), 3.69 (s, 3H), 3.53 (ddd, *J* = 17.5, 4.4, 1.1 Hz, 1H), 3.31 (ddt, *J* = 12.4, 10.8, 4.4 Hz, 1H), 2.92 (ddt, *J* = 17.6, 12.7, 0.9 Hz, 1H), 2.85 (dddd, *J* = 19.4, 5.8, 4.5, 1.1 Hz, 1H), 2.74 (ddd, *J* = 19.2, 10.8, 2.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.2, 149.6, 145.6, 143.9, 143.5, 143.5, 141.5, 132.7, 131.6, 128.8, 128.1, 127.0, 120.5, 119.2, 118.9, 111.1, 110.9, 51.4, 43.1, 34.5, 31.9.

HRMS (EI): Calcd for ([M], $C_{25}H_{18}N_2O_2)^+$: m/z= 378.1363, found 378.1369

Chiral HPLC data: AD3 chiral column, 30% IPA/hexanes 1 mL/min, t_R(minor)= 30.3 min, t_R(major)= 38.4 min, λ= 254 nm

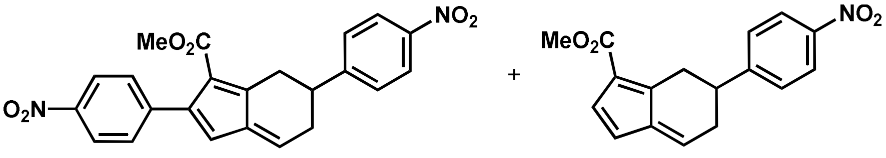
Characterization data for **methyl 5-(4-cyanophenyl)-5,6-dihydro-4H-indene-3-carboxylate (3g):**

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 2H), 7.48 – 7.37 (m, 2H), 6.98 (dd, *J* = 5.9, 2.9 Hz, 1H), 6.79 (d, *J* = 5.4 Hz, 1H), 6.17 (d, *J* = 5.4 Hz, 1H), 3.79 (s, 3H), 3.59 (dd, *J* = 17.9, 4.2 Hz, 1H), 3.32 – 3.22 (m, 1H), 2.87 (dd, *J* = 17.6, 12.5 Hz, 1H), 2.79 (dt, *J* = 19.3, 5.2 Hz, 1H), 2.68 (dd, *J* = 19.2, 10.7 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 150.0, 145.6, 142.4, 141.8, 132.7, 132.6, 128.1, 127.8, 119.8, 119.0, 110.9, 51.4, 43.2, 34.3, 31.6.

HRMS (EI): Calcd for ([M], $C_{18}H_{15}NO_2)^+$: m/z= 277.1097, found 277.1102

Chiral HPLC data: AD3 chiral column, 3% IPA/hexanes 1 mL/min, t_R(minor)= 39.0 min, t_R(major)= 45.1 min, λ= 254 nm



2h **3h**

methyl 2,5-bis(4-nitrophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2h) and **methyl 5-(4-nitrophenyl)-5,6-dihydro-4H-indene-3-carboxylate (3h)** were prepared according to General Procedure A using 16.7 mg (0.10 mmol, 2 equiv) of 4-(nitro)phenylboronic acid. The crude mixture was purified by preparatory TLC (70% DCM/hexanes) to give 8.7 mg (42%) of **2h** as an orange solid (81:19 er) and 3.6 mg (24%) of **3h** as a yellow solid (86:14 er).

Characterization data for **methyl 2,5-bis(4-nitrophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2h):**

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.25 – 8.18 (m, 4H), 7.52 – 7.47 (m, 4H), 7.12 (dd, J = 6.0, 2.9 Hz, 1H), 6.32 (s, 1H), 3.70 (s, 3H), 3.57 (ddd, J = 17.5, 4.3, 1.1 Hz, 1H), 3.39 (ddt, J = 12.4, 10.6, 4.4 Hz, 1H), 2.97 (dd, J = 17.6, 12.6 Hz, 1H), 2.89 (dddd, J = 19.4, 5.8, 4.5, 1.1 Hz, 1H), 2.78 (ddd, J = 19.5, 10.8, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.1, 151.6, 147.1, 147.1, 145.2, 144.2, 143.5, 143.5, 143.5, 128.9, 128.1, 127.1, 124.2, 123.2, 120.9, 51.4, 42.9, 34.6, 31.9.

HRMS (ESI): Calcd for ([M+Na], $C_{23}H_{18}N_2O_6Na)^+$: m/z= 441.1057, found 441.1058

Chiral HPLC data: AD3 chiral column, 20% IPA/hexanes 1 mL/min, t$_R$(minor)= 36.5 min, t$_R$(major)= 41.1 min, λ= 300 nm

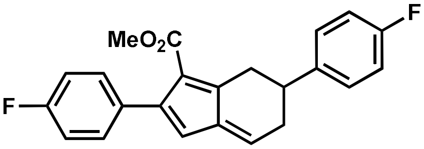
Characterization data for **methyl 5-(4-nitrophenyl)-5,6-dihydro-4H-indene-3-carboxylate (3h):**

^{1}H NMR (600 MHz, CDCl$_3$) δ 8.23 – 8.18 (m, 2H), 7.50 – 7.44 (m, 2H), 6.98 (dd, J = 5.9, 3.0 Hz, 1H), 6.80 (d, J = 5.4 Hz, 1H), 6.18 (dd, J = 5.5, 0.9 Hz, 1H), 3.79 (s, 3H), 3.61 (ddd, J = 17.6, 4.4, 1.1 Hz, 1H), 3.37 – 3.29 (m, 1H), 2.91 (dd, J = 17.6, 12.5 Hz, 1H), 2.82 (dt, J = 19.2, 5.2 Hz, 1H), 2.71 (ddd, J = 19.1, 10.7, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.4, 152.1, 147.0, 145.6, 142.2, 141.7, 132.7, 128.1, 127.9, 124.1, 119.8, 51.4, 43.0, 34.3, 31.6.

HRMS (EI): Calcd for ([M], $C_{17}H_{15}NO_4)^+$: m/z= 297.0996, found 297.0999

Chiral HPLC data: IC3 chiral column, 10% IPA/hexanes 1 mL/min, t$_R$(minor)= 64.6 min, t$_R$(major)= 53.6 min, λ= 300 nm



2i

methyl 2,5-bis(4-fluorophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2i) was prepared according to General Procedure A using 14.0 mg (0.10 mmol, 2 equiv) of 4-(fluoro)phenylboronic acid. The crude mixture was purified by preparatory TLC (35% EtOAc/2% AcOH/hexanes) to give 11.2 mg (61%) of **2i** as an orange solid (87:13 er).

Characterization data for **methyl 2,5-bis(4-fluorophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2i):**

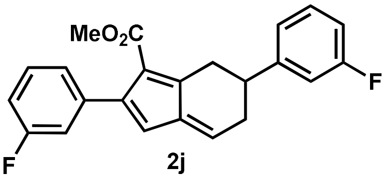
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.36 – 7.31 (m, 2H), 7.30 – 7.27 (m, 2H), 7.06 – 7.01 (m, 4H), 7.00 (dd, J = 6.1, 2.9 Hz, 1H), 6.16 (s, 1H), 3.69 (s, 3H), 3.49 (ddd, J = 17.5, 4.3, 1.1 Hz, 1H), 3.22 (ddt, J = 12.4, 10.8, 4.4 Hz, 1H), 2.86 (dd, J = 17.6, 12.9 Hz, 1H), 2.79 (dddd, J = 19.4, 5.9, 4.5, 1.1 Hz, 1H), 2.68 (ddd, J = 19.4, 10.9, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.7, 162.4 (d, J = 246.1 Hz), 161.8 (d, J = 244.9 Hz), 146.1, 143.9, 143.6, 142.9, 140.3 (d, J = 2.8 Hz), 132.8 (d, J = 3.3 Hz), 129.7 (d, J = 8.0 Hz), 128.6 (d, J = 7.8 Hz), 127.2, 118.5, 115.5 (d, J = 21.1 Hz), 114.7 (d, J = 21.5 Hz), 51.2, 42.6, 35.2, 32.6.

^{19}F NMR (565 MHz, CDCl$_3$) δ –115.08 – –115.20 (m), –116.08 (dt, J = 8.0, 3.8 Hz).

HRMS (EI): Calcd for ([M], $C_{23}H_{18}F_2O_2)^+$: m/z= 364.1269, found 364.1275

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t$_R$(minor)= 14.2 min, t$_R$(major)= 19.3 min, λ= 254 nm



2j

methyl 2,5-bis(3-fluorophenyl)-5,6-dihydro-4H-indene-3-carboxylate (2j) was prepared according to General Procedure A using 14.0 mg (0.10 mmol, 2 equiv) of 3-(fluoro)phenylboronic acid. The crude mixture was purified by preparatory TLC (15% Et_2O/hexanes, run three times) to give 10.0 mg (55%) of **2j** as a yellow solid (86:14 er).

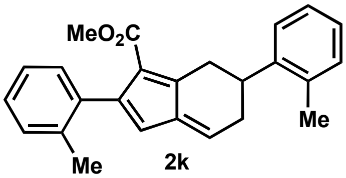
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 7.13 (ddd, *J* = 7.7, 1.6, 1.0 Hz, 1H), 7.10 (ddt, *J* = 7.6, 1.6, 0.7 Hz, 1H), 7.07 (ddd, *J* = 10.1, 2.6, 1.6 Hz, 1H), 7.02–7.04 (m, 2H), 6.95–7.00 (m, 2H), 6.21 (d, *J* = 0.8 Hz, 1H), 3.70 (s, 3H), 3.52 (ddd, *J* = 17.5, 4.3, 1.1 Hz, 1H), 3.24 (ddt, *J* = 15.5, 12.2, 4.4 Hz, 1H), 2.91 – 2.85 (m, 1H), 2.82 (dddd, *J* = 19.4, 5.9, 4.5, 1.1 Hz, 1H), 2.70 (ddd, *J* = 19.4, 11.0, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 163.1 (d, *J* = 246.0 Hz), 162.5 (d, *J* = 244.5 Hz), 147.1 (d, *J* = 6.7 Hz), 146.0 (d, *J* = 2.5 Hz), 143.6 (d, *J* = 8.3 Hz), 143.3, 139.0 (d, *J* = 8.2 Hz), 130.3 (d, *J* = 8.3 Hz), 129.2 (d, *J* = 8.4 Hz), 127.2, 123.8 (d, *J* = 2.8 Hz), 122.9 (d, *J* = 2.8 Hz), 119.3, 115.0 (d, *J* = 22.0 Hz), 114.2, 114.2 (d, *J* = 21.1 Hz), 114.1, 113.9 (d, *J* = 21.0 Hz), 51.3, 43.0, 34.9, 32.2

^{19}F NMR (565 MHz, $CDCl_3$) δ –112.82 (q, *J* = 8.7 Hz), –114.37 (q, *J* = 8.5 Hz).

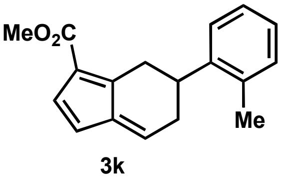
HRMS (EI): Calcd for ([M], $C_{23}H_{18}F_2O_2$)$^+$: m/z= 364.1269, found 364.1270

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 1 mL/min, t_R(minor)= 24.4 min, t_R(major)= 27.0 min, λ= 254 nm



2k

+



3k

methyl 2,5-di-o-tolyl-5,6-dihydro-4H-indene-3-carboxylate (2k) and **methyl 5-(o-tolyl)-5,6-dihydro-4H-indene-3-carboxylate (3k)** were prepared according to General Procedure A using 13.6 mg (0.10 mmol, 2 equiv) of *o*-tolylboronic acid. The crude mixture was purified by preparatory TLC (80% DCM/hexanes) to give 5.1 mg (29%) of **2k** as a yellow solid (74:26 er). A band containing **3k** was isolated and further purified through a second preparatory TLC plate (70% DCM/hexanes) to give 0.9 mg (7%) of **3k** as a yellow solid (83:17 er).

Characterization data for **methyl 2,5-di-o-tolyl-5,6-dihydro-4H-indene-3-carboxylate (2k):**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.25 – 7.19 (m, 4H), 7.19 – 7.15 (m, 3H), 7.02 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.05 (d, *J* = 0.9 Hz, 1H), 3.57 (s, 2H), 3.55 – 3.48 (m, 2H), 2.92 (dd, *J* = 18.4, 13.7 Hz, 1H), 2.74 – 2.71 (m, 2H), 2.39 (s, 3H), 2.22 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.5, 147.2, 143.8, 143.8, 143.1, 142.7, 137.7, 136.3, 135.8, 130.9, 129.4, 128.8, 128.0, 127.3, 126.7, 126.4, 125.8, 125.2, 118.8, 51.1, 39.1, 34.3, 32.0, 20.5, 19.7.

HRMS (ESI): Calcd for ([M+Na], $C_{25}H_{24}O_2Na$)$^+$: m/z= 379.1669, found 379.1667

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t_R(minor)= 4.8 min, t_R(major)= 5.7 min, λ= 254 nm

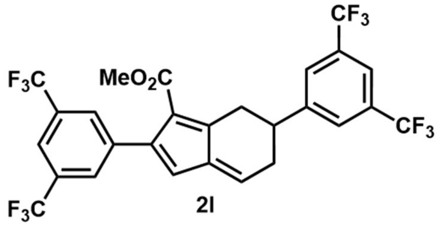
Characterization data for **methyl 5-(o-tolyl)-5,6-dihydro-4H-indene-3-carboxylate (3k):**

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 – 7.35 (m, 1H), 7.23 – 7.18 (m, 2H), 7.15 (td, *J* = 7.3, 1.4 Hz, 1H), 7.03 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 6.18 (dd, *J* = 5.4, 1.0 Hz, 1H), 3.77 (s, 3H), 3.57 – 3.50 (m, 1H), 3.45 (dddd, *J* = 13.5, 9.7, 5.9, 4.2 Hz, 1H), 2.85 (dd, *J* = 17.6, 13.0 Hz, 1H), 2.71 – 2.66 (m, 2H), 2.35 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 145.4, 144.1, 143.3, 142.6, 135.7, 132.5, 130.8, 127.3, 126.6, 126.3, 125.8, 119.5, 51.3, 39.1, 34.2, 31.6, 19.6.

HRMS (EI): Calcd for ([M], $C_{18}H_{18}O_2$)$^+$: m/z= 266.1301, found 266.1308

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t_R(minor)= 4.3 min, t_R(major)= 5.0 min, λ= 254 nm



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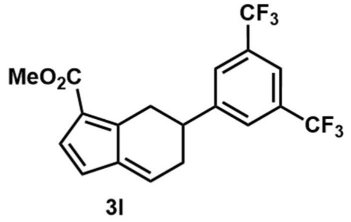


2l

3l

methyl 2,5-bis(3,5-bis(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (2l) and **methyl 5-(3,5-bis(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (3l)** were prepared according to General Procedure A using 25.8 mg (0.10 mmol, 2 equiv) of 3,5-bis(trifluoromethyl)phenylboronic acid. The crude mixture was purified by preparatory TLC (60% DCM/hexanes) to give 7.2 mg (27%) of **2l** as a yellow solid (79:21 er) and 8.2 mg (42%) of **3l** as a yellow solid (84:16 er)

Characterization data for **methyl 2,5-bis(3,5-bis(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (2l):**

^{1}H NMR (600 MHz, CDCl$_3$) δ 7.82 – 7.81 (m, 4H), 7.79 (s, 2H), 7.13 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.33 (s, 1H), 3.68 (s, 3H), 3.65 (ddd, *J* = 17.6, 4.3, 1.0 Hz, 1H), 3.40 (ddt, *J* = 12.7, 11.0, 4.4 Hz, 1H), 2.97 (dd, *J* = 17.6, 13.0 Hz, 1H), 2.91 (dddd, *J* = 19.4, 5.9, 4.5, 1.1 Hz, 1H), 2.80 (ddd, *J* = 19.4, 11.1, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 164.9, 146.6, 144.4, 144.1, 143.9, 143.4, 138.7, 132.2 (q, *J* = 33.3 Hz, 2CF$_3$), 131.0 (q, *J* = 33.1 Hz, 2CF$_3$), 128.5 (app d, *J* = 4.1 Hz), 127.5 (app d, *J* = 4.0 Hz), 126.9, 124.4 (app d, *J* = 24.0 Hz), 122.61 (app d, *J* = 24.3 Hz), 121.3 (app dt, *J* = 7.2, 3.5 Hz), 121.0 (app dt, *J* = 7.3, 3.1 Hz),120.9, 51.3, 42.9, 34.7, 32.0.

^{19}F NMR (565 MHz, CDCl$_3$) δ –62.79 (br s), –62.83 (br s).

HRMS (ESI): Calcd for ([M+Na], $C_{27}H_{16}F_{12}O_2Na)^+$: m/z= 623.0847, found 623.0847

Chiral HPLC data: AD3 chiral column, 0.1% IPA/hexanes 2 mL/min, t_R(minor)= 8.2 min, t_R(major)= 10.0 min, λ= 254 nm

Characterization data for **methyl 5-(3,5-bis(trifluoromethyl)phenyl)-5,6-dihydro-4H-indene-3-carboxylate (3l):**

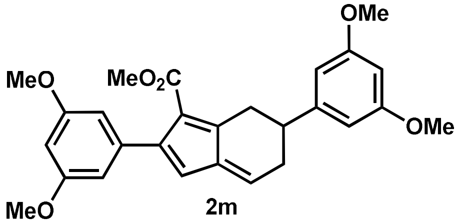
^{1}H NMR (600 MHz, CDCl$_3$) δ 7.79 (s, 1H), 7.76 (s, 1H), 6.98 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.80 (d, *J* = 5.4 Hz, 1H), 6.19 (dd, *J* = 5.4, 1.0 Hz, 1H), 3.80 (s, 3H), 3.65 (ddd, *J* = 17.4, 4.3, 1.1 Hz, 1H), 3.35 (ddt, *J* = 12.3, 10.9, 4.4 Hz, 1H), 2.89 (dd, *J* = 17.6, 12.9 Hz, 1H), 2.83 (dt, *J* = 19.1, 5.3 Hz, 1H), 2.72 (ddd, *J* = 19.2, 11.0, 2.8 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.4, 147.0, 145.6, 142.0, 141.4, 132.7, δ 132.1 (q, *J* = 33.2 Hz), 128.0, 127.5 (d, *J* = 3.8 Hz), 124.4, 122.6, 121.09 (p, *J* = 3.9 Hz), 119.8, 51.4, 43.0, 34.4, 31.7.

^{19}F NMR (565 MHz, CDCl$_3$) δ -62.80 (br s).

HRMS (ESI): Calcd for ([M+Na], $C_{27}H_{16}F_{12}O_2Na)^+$: m/z= 623.0847, found 623.0847

Chiral HPLC data: AD3 chiral column, 1% IPA/hexanes 2 mL/min, t_R(minor)= 4.9 min, t_R(major)= 5.5 min, λ= 254 nm



2m

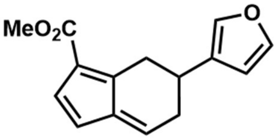
methyl 2,5-bis(3,5-dimethoxyphenyl)-5,6-dihydro-4H-indene-3-carboxylate (2m) was prepared according to General Procedure A using 18.2 mg (0.10 mmol, 2 equiv) of 3,5-(dimethoxy)phenylboronic acid. The crude mixture was purified by preparatory TLC (5% Et$_2$O/PhMe) to give 10.9 mg (49%) of **2m** as a waxy yellow solid (88:12 er).

^{1}H NMR (500 MHz, CDCl$_3$) δ 6.99 (dd, *J* = 6.0, 2.9 Hz, 1H), 6.53 (d, *J* = 2.3 Hz, 2H), 6.48 (d, *J* = 2.3 Hz, 2H), 6.42 (t, *J* = 2.3 Hz, 1H), 6.37 (t, *J* = 2.2 Hz, 1H), 6.20 (s, 1H), 3.81 (s, 6H), 3.79 (s, 6H), 3.70 (s, 3H), 3.47 (dd, *J* = 17.4, 4.2 Hz, 1H), 3.22 – 3.10 (m, 1H), 2.86 (dd, *J* = 17.5, 13.0 Hz, 1H), 2.79 (dt, *J* = 19.4, 5.3 Hz, 1H), 2.70 (ddd, *J* = 19.4, 10.9, 3.0 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 165.8, 161.1, 160.3, 147.2, 146.9, 143.5, 143.4, 143.0, 138.7, 127.5, 118.6, 106.2, 105.5, 99.9, 98.5, 55.5, 55.5, 51.3, 43.8, 35.1, 32.2

HRMS (ESI): Calcd for ([M+Na], $C_{27}H_{28}O_6Na)^+$: m/z= 471.1778, found 471.1772

Chiral HPLC data: AD3 chiral column, 10% IPA/hexanes 0.5 mL/min, t_R(minor)= 52.3 min, t_R(major)= 47.9 min, λ= 254 nm



3n

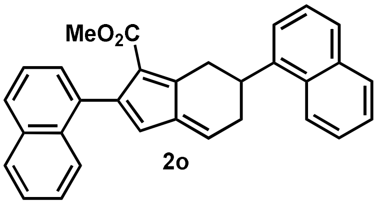
methyl 5-(furan-3-yl)-5,6-dihydro-4H-indene-3-carboxylate (3n) was prepared according to General Procedure A using 11.2 mg (0.10 mmol, 2 equiv) of 3-furanylboronic acid. The crude mixture was purified by preparatory TLC (30% DCM/PhMe) to give 1.8 mg (15%) of **3n** as a waxy yellow solid (83:17 er).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.38 (t, *J* = 1.7 Hz, 1H), 7.30 (dt, *J* = 1.7, 0.9 Hz, 1H), 6.97 (dd, *J* = 5.8, 3.1 Hz, 1H), 6.78 (d, *J* = 5.4 Hz, 1H), 6.36 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.15 (dd, *J* = 5.3, 0.9 Hz, 1H), 3.80 (s, 3H), 3.59 (ddd, *J* = 17.6, 4.4, 1.1 Hz, 1H), 3.12 (tt, *J* = 9.9, 4.4 Hz, 1H), 2.86 – 2.73 (m, 2H), 2.55 (ddd, *J* = 19.2, 10.1, 2.8 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 145.6, 143.3, 143.1, 142.8, 138.6, 132.3, 128.7, 127.4, 119.6, 109.7, 51.3, 34.2, 33.5, 31.5.

HRMS (EI): Calcd for ([M], $C_{15}H_{14}O_3$)$^+$: m/z= 242.0937, found 242.0942

Chiral HPLC data: AD3 chiral column, 3% IPA/hexanes 1 mL/min, t_R(minor)= 10.7 min, t_R(major)= 11.2 min, λ= 254 nm



2o

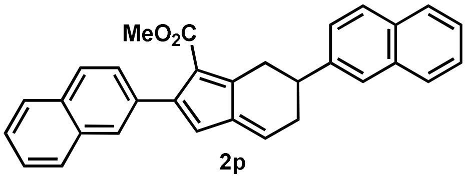
methyl 2,5-di(naphthalen-1-yl)-5,6-dihydro-4H-indene-3-carboxylate (2o) was prepared according to General Procedure A using 17.2 mg (0.10 mmol, 2 equiv) of 1-naphthylboronic acid. The crude mixture was purified by preparatory TLC (70% DCM/hexanes) to give 11.7 mg (55%) of **2o** as a waxy yellow solid (75:25 er).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 1H), 7.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.88 – 7.85 (m, 2H), 7.84 – 7.77 (m, 2H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.56 (ddd, *J* = 8.4, 6.7, 1.5 Hz, 1H), 7.53 – 7.49 (m, 2H), 7.49 – 7.40 (m, 4H), 7.15 (dd, *J* = 6.0, 2.8 Hz, 1H), 6.30 (d, *J* = 0.8 Hz, 1H), 4.25 – 4.15 (m, 1H), 3.77 (dd, *J* = 17.4, 3.9 Hz, 1H), 3.30 (s, 3H), 3.17 (dd, *J* = 17.5, 12.8 Hz, 1H), 3.02 (dddd, *J* = 19.4, 5.8, 4.3, 1.2 Hz, 1H), 2.91 (ddd, *J* = 19.2, 11.0, 2.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 146.0, 144.0, 143.9, 143.5, 140.5, 136.0, 134.2, 133.4, 132.6, 131.5, 129.3, 128.9, 128.3, 127.7, 127.5, 126.4, 126.3, 125.8 (2C), 125.8, 125.6, 125.6, 125.3, 123.3, 123.0, 120.1, 50.9, 38.4, 35.0, 32.2

HRMS (EI): Calcd for ([M], $C_{31}H_{24}O_2$)$^+$: m/z= 428.1771, found 428.1778

Chiral HPLC data: IC3 chiral column, 5% IPA/hexanes 1 mL/min, t_R(minor)= 14.7 min, t_R(major)= 9.8 min, λ= 254 nm



2p

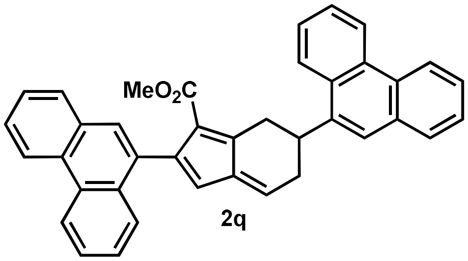
methyl 2,5-di(naphthalen-2-yl)-5,6-dihydro-4H-indene-3-carboxylate (2p) was prepared according to General Procedure A using 17.2 mg (0.10 mmol, 2 equiv) of 2-naphthylboronic acid. The crude mixture was purified by preparatory TLC (70% DCM/hexanes) to give 11.8 mg (55%) of **2p** as an orange solid (84:16 er).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.83 (m, 6H), 7.82 – 7.77 (m, 2H), 7.53 – 7.49 (m, 2H), 7.48 – 7.45 (m, 4H), 7.08 (dd, *J* = 5.8, 3.1 Hz, 1H), 6.33 (s, 1H), 3.67 (s, 3H), 3.67 – 3.62 (m, 1H), 3.44 (ddt, *J* = 17.6, 9.4, 4.5 Hz, 1H), 3.05 (dd, *J* = 17.5, 13.0 Hz, 1H), 2.92 (dt, *J* = 19.3, 5.3 Hz, 1H), 2.85 (ddd, *J* = 19.5, 10.7, 3.2 Hz, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 165.9, 147.1, 144.1, 143.8, 143.0, 142.1, 134.5, 133.7, 133.3, 132.9, 132.6, 128.4, 128.2, 127.9, 127.8, 127.8, 127.4, 127.0, 126.8, 126.4, 126.3, 126.1, 125.9, 125.8, 125.8, 125.5, 118.9, 51.2, 43.5, 35.2, 32.4.

HRMS (EI): Calcd for ([M], $C_{31}H_{24}O_2$)$^+$: m/z= 428.1771, found 428.1775

Chiral HPLC data: IC3 chiral column, 10% IPA/hexanes 0.5 mL/min, t_R(minor)= 37.4 min, t_R(major)= 35.2 min, λ= 254 nm



2q

methyl 2,5-di(phenanthren-9-yl)-5,6-dihydro-4H-indene-3-carboxylate (2q) was prepared according to General Procedure A using 22.2 mg (0.10 mmol, 2 equiv) of 9-phenanthracenylboronic acid. The crude mixture was purified by preparatory TLC (70% DCM/hexanes) to give 13.7 mg (52%) of **2q** a yellow solid (65:35 er).

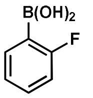
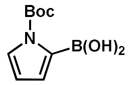
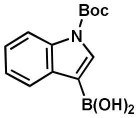
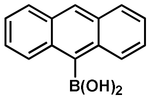
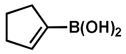
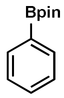
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.84 – 8.78 (m, 1H), 8.75 – 8.72 (m, 1H), 8.71 (dd, *J* = 8.2, 3.4 Hz, 2H), 8.27 – 8.22 (m, 1H), 7.94 – 7.88 (m, 3H), 7.87 (s, 1H), 7.73 (s, 1H), 7.73 – 7.58 (m, 7H), 7.55 (ddd, *J* = 8.1, 6.9, 1.2 Hz, 1H), 7.20 (dd, *J* = 6.1, 2.8 Hz, 1H), 6.40 (s, 1H), 4.27 – 4.17 (m, 1H), 3.90 (d, *J* = 17.4 Hz, 1H), 3.29 (dd, *J* = 17.5, 12.6 Hz, 1H), 3.24 (s, 3H), 3.17 – 3.08 (m, 1H), 2.96 (dd, *J* = 19.3, 10.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 146.3, 144.3, 144.1, 143.6, 138.6, 135.0, 132.1, 131.9, 131.7, 131.1, 130.6, 130.4, 130.1, 129.9, 129.0, 128.8, 128.7, 127.0, 127.0 (2C), 126.7, 126.7, 126.5, 126.5, 126.5, 126.3, 126.2, 124.1, 123.7, 123.7, 122.9, 122.7, 122.6, 120.1, 50.9, 38.5, 35.0, 31.9.

HRMS (ESI): Calcd for ([M+H], $C_{39}H_{29}O_2$)$^+$: m/z= 529.2162, found 529.2161

Chiral HPLC data: AD3 chiral column, 10% IPA/hexanes 1.0 mL/min, t_R(minor)= 42.9 min, t_R(major)= 23.2 min, λ= 254 nm

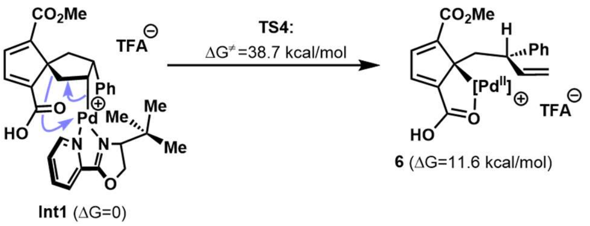
Table S7. Substrate Scope of Arylboronic Acids- Unsuccessful Substrates

					
30% SM[a], 15% Heck product[b]	mostly SM	only SM	only SM	only SM	only SM

[a]Determined by integration of ^{1}H NMR of crude reaction mixture relative to pyrazine internal standard. [b]The likely Heck product was determined by analogy to known diagnostic peaks of **4**, NMR yield was determined with pyrazine as internal standard.

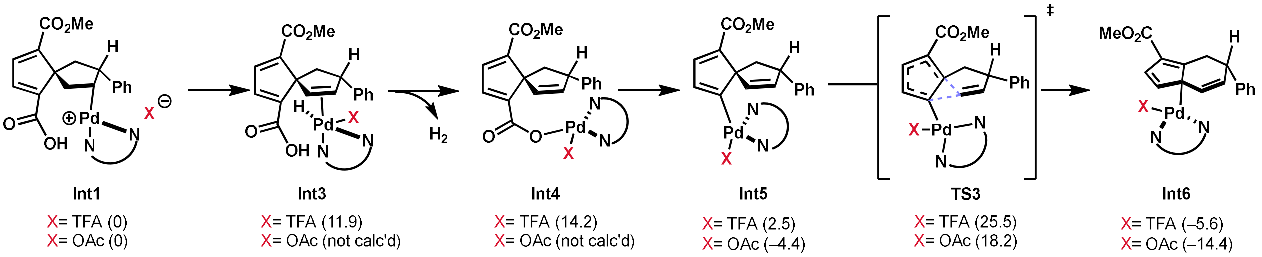
3. Additional Mechanistic Insight and Discussion

3.1 Beta-Carbon Elimination

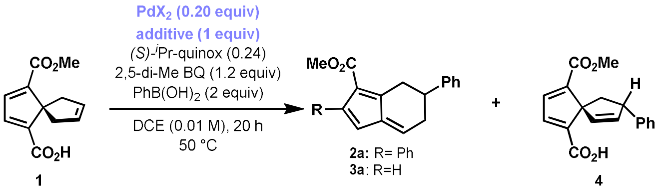


Scheme S1. Calculated thermodynamic and TS energies (in units of kcal/mol) are shown for the proposed β-carbon elimination pathway.

3.2 Effects of Acetate vs. Trifluoroacetate Coordination



Scheme S2. Calculated energies for TFA and OAc as X-type ligands are shown in parentheses in units of kcal/mol. For cationic structure **Int1**, the energy of the respective anion (OAc or TFA) at infinite distance was added. The acetate bound versions of **Int5**, **TS3**, and **Int6** are labeled as **Int5-OAc, TS3-OAc,** and **Int6-OAc** in the SI.



entry	PdX_2	additive	ratio of fulvenes (2a+3a) to 4[a]
1	$Pd(TFA)_2$	KTFA	11.9 : 1
2	$Pd(TFA)_2$	KOAc	1 : 1
3	$Pd(OAc)_2$	KTFA	1 : 1.1
4	$Pd(OAc)_2$	KOAc	1 : 2

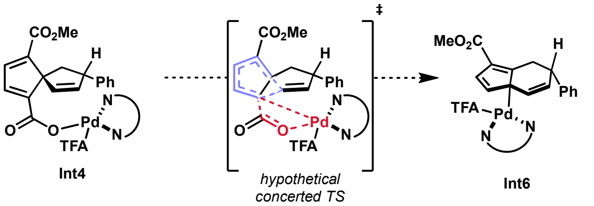
[a]Ratios are calculated by integration of peaks in the ^{1}HNMR of the crude reaction mixtures.

Table S8. Effects of Acetate and Trifluoroacetate on product ratio

DFT calculations indicate that OAc as an X-type ligand gives lower energies for key vinyl palladium intermediate **Int5**, key transition state **TS3**, and product **Int6**, as opposed to having TFA as an X-type ligand (Figure SX.) However, empirical observations suggest that the presence of OAc results in lower amounts of fulvene products **2a**/**3a** versus Heck product **4** (Table S5). We hypothesize this is because OAc can more strongly bind the palladium center, as opposed to TFA. This may result in OAc displacing the spirononene in **Int3** or the pendant carboxylate in **Int4**, hindering the formation of key intermediate **Int5**.

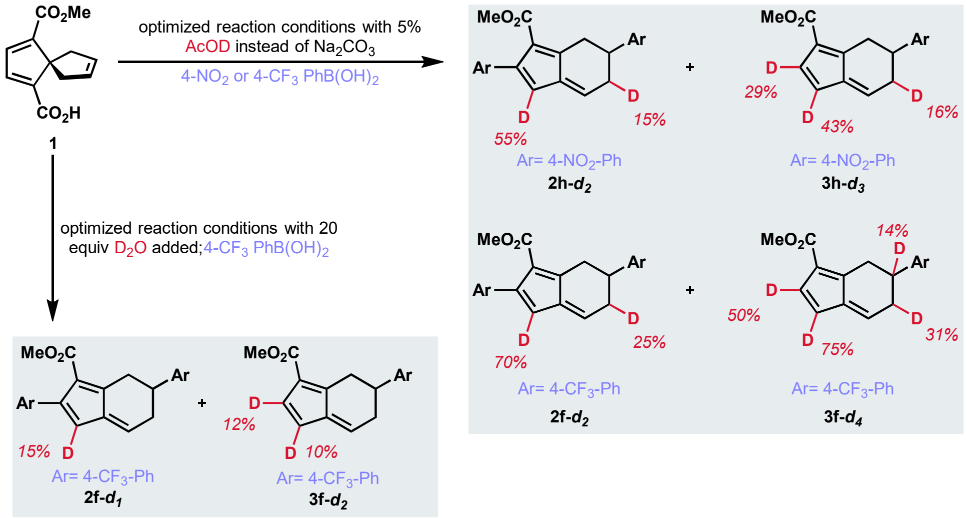
3.3 Discussion of Decarboxylation Step

Palladium-mediated decarboxylations of aryl, vinyl, and alkynyl carboxylic acids are well-documented in the literature.[9] While many of these reports employ high temperatures (100 – 200 °C), there are indeed reports of lower temperature decarboxylations (room temperature or 70 °C).[10–12] DFT calculations to identify a feasible TS for the decarboxylation of **Int4** to form **Int5** were conducted but were not successful. However, the existing precedents referenced above suggest a decarboxylation at 50 °C is, indeed, a feasible mechanistic step. It may be that this decarboxylation is slower than the 1,5-vinyl shift of **Int5**. We have observed that upon the addition of acetate to the reaction mixture (see Table S8), a reduced amount of fulvene (**2a**) is formed. This is likely because **Int3** and **Int4** persist long enough such that acetate anion can displace the spirononatriene carboxylate, releasing product **4**. If the 1,5-vinyl shift (see TS3) was slower than the decarboxylation, we might expect **Int5** to persist for enough time for other pathways to become competitive (e.g. protodemetalation). However, no such products from **Int5** were observed. Additionally, there is a possibility that the proposed decarboxylation and 1,5-vinyl shift are concerted (see Scheme S3).



Scheme S3. A hypothetical TS for a concerted Pd-mediated decarboxylation and 1,5-vinyl shift step is shown above.

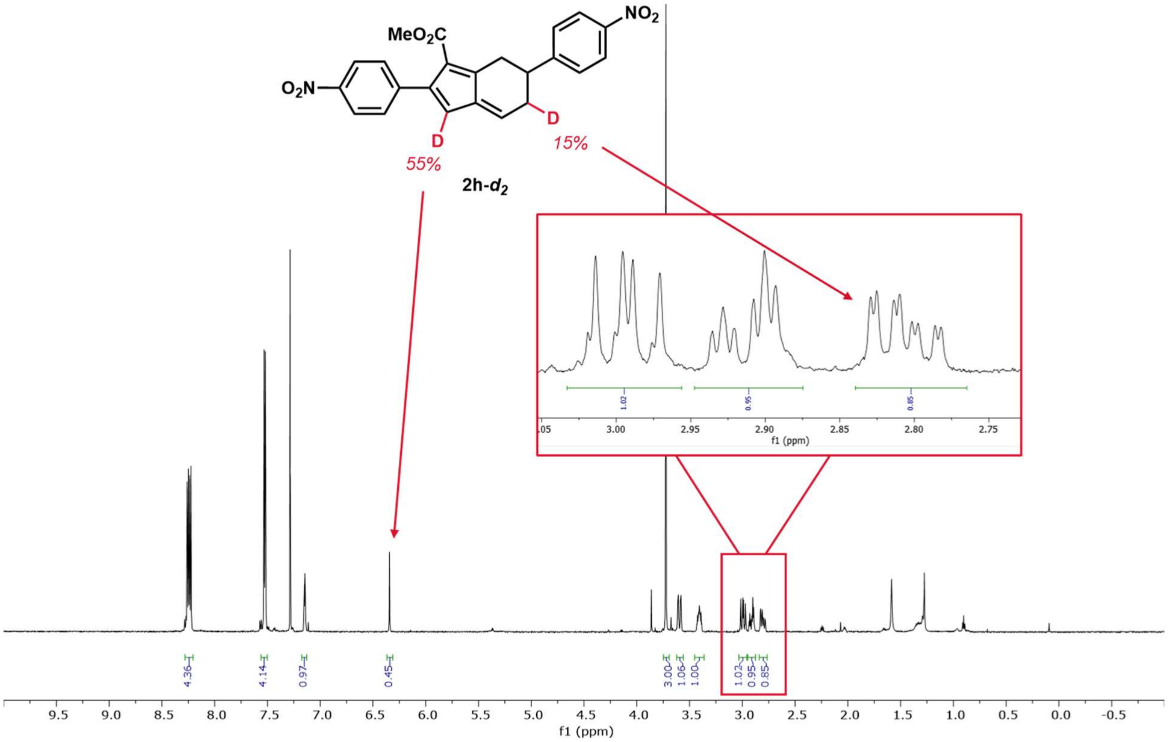
3.4 Protodemetalation Studies and ^{1}H NMR Spectra for Deuterated Compounds:



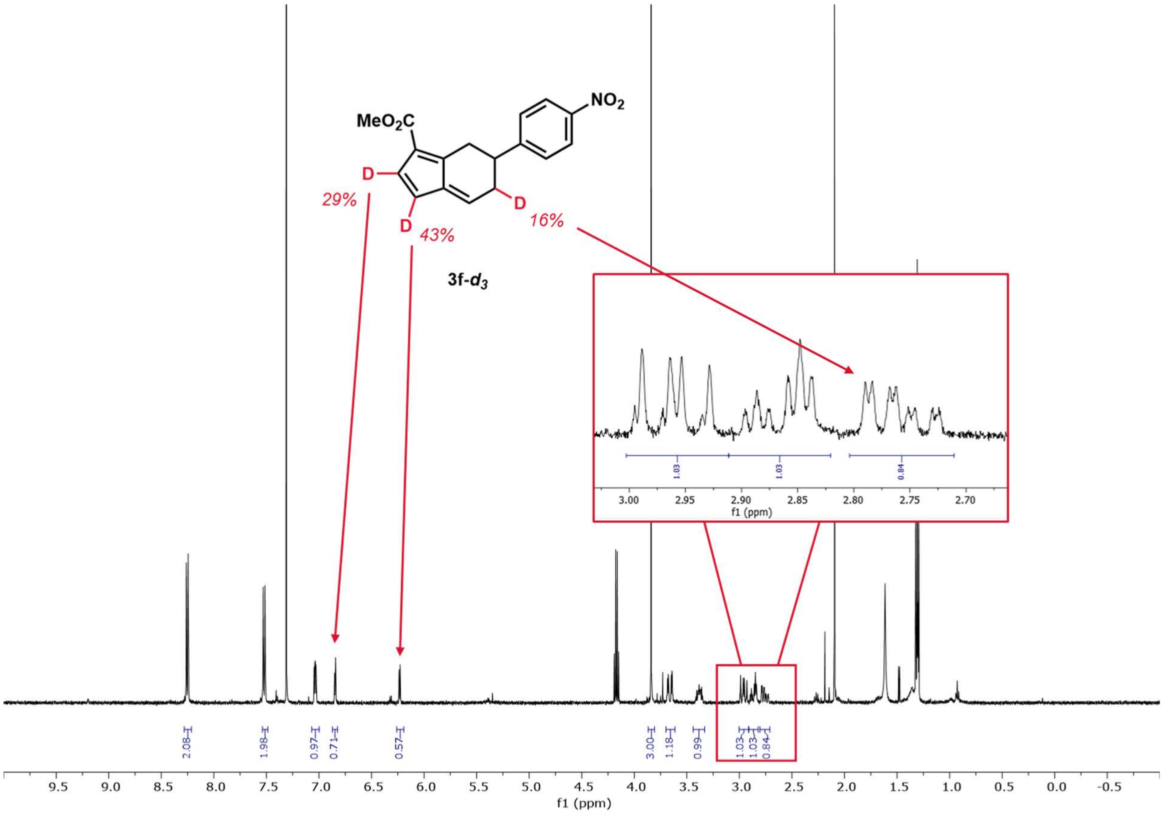
Scheme S4. The results of protodemetalation investigations are shown above.

Percent deuteration for the above compounds was determined by ^{1}H NMR integration with the methyl of the methyl ester group standardized to 3H. The spectra for these compounds are shown below. The ^{1}H identity was determined by analogy to those of **3a**, for which COESY and NOESY spectra are reported in the NMR spectra section.

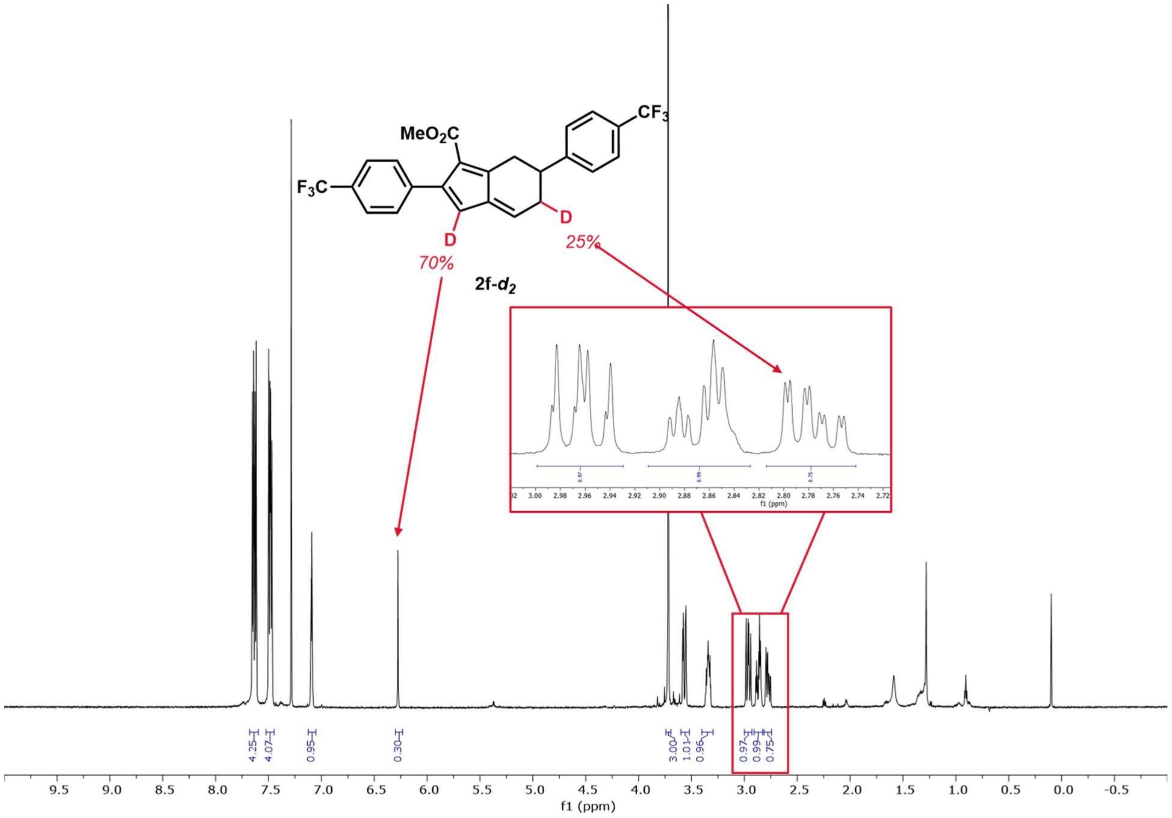
^1H NMR (700 MHz, $CDCl_3$)



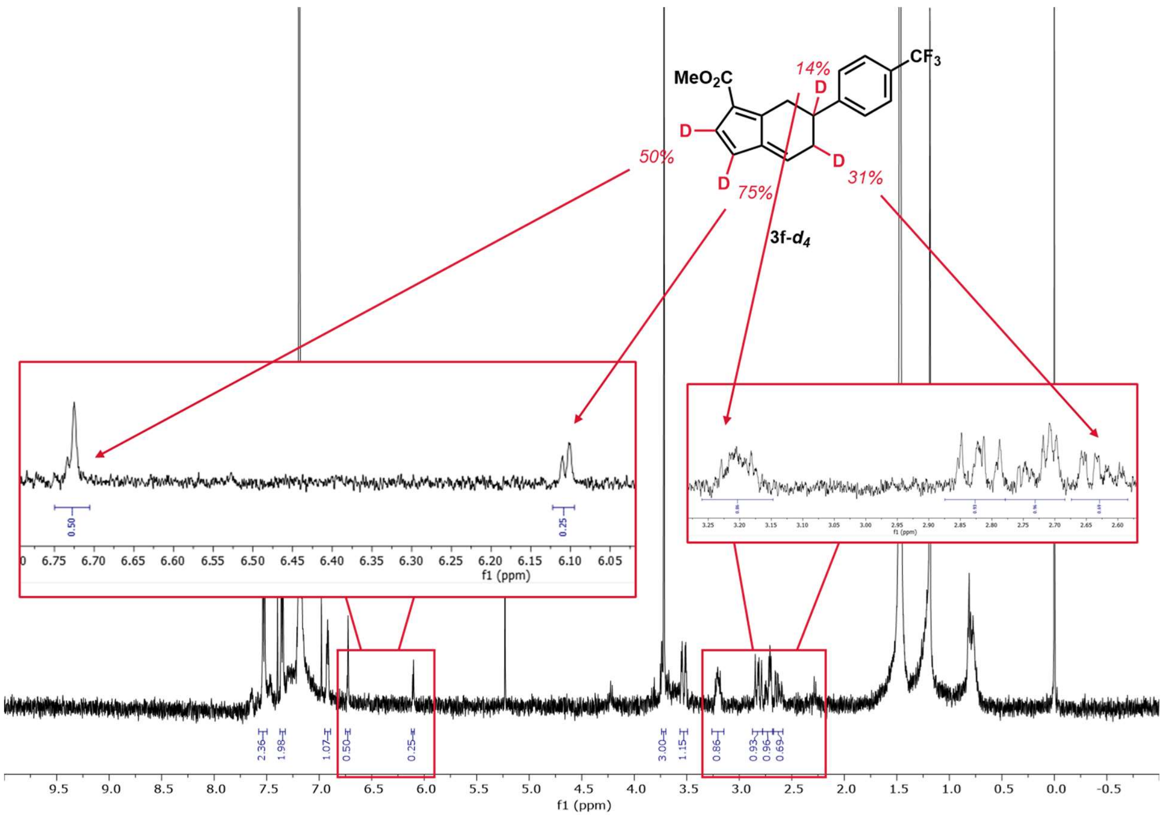
^1H NMR (500 MHz, $CDCl_3$)



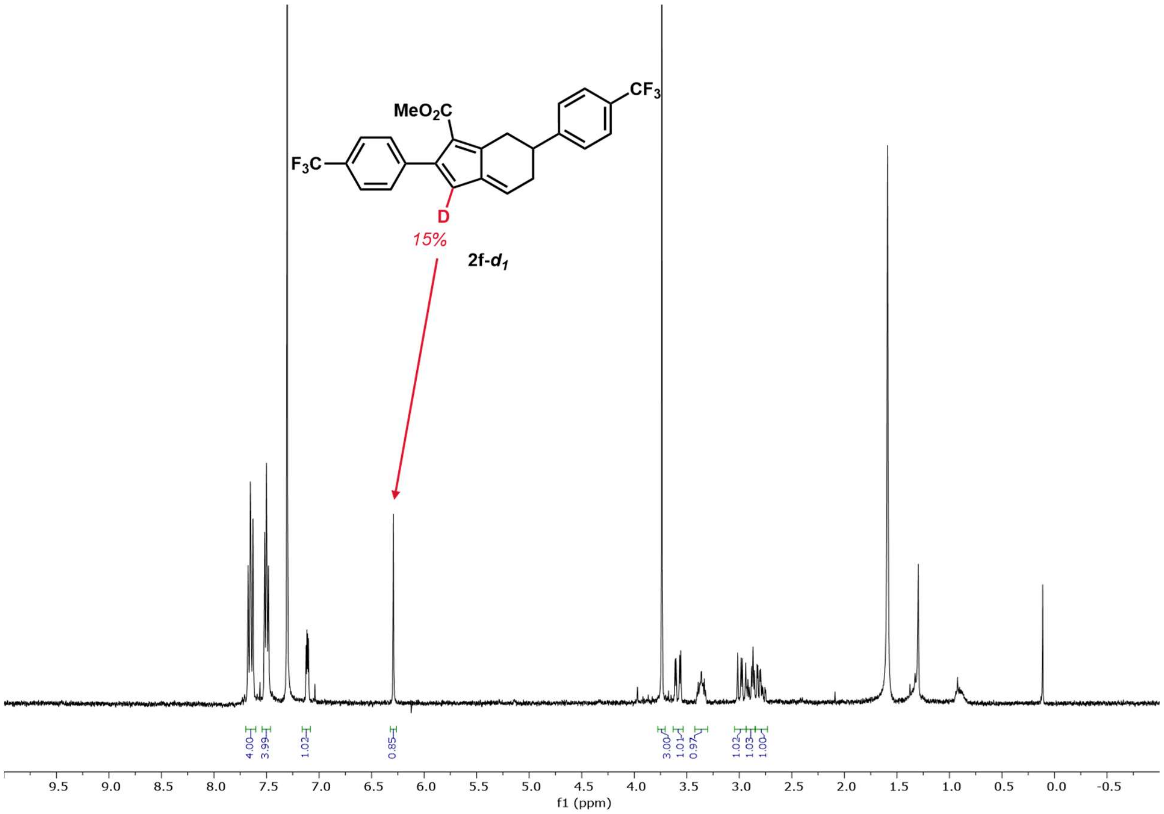
^{1}H NMR (500 MHz, $CDCl_3$)



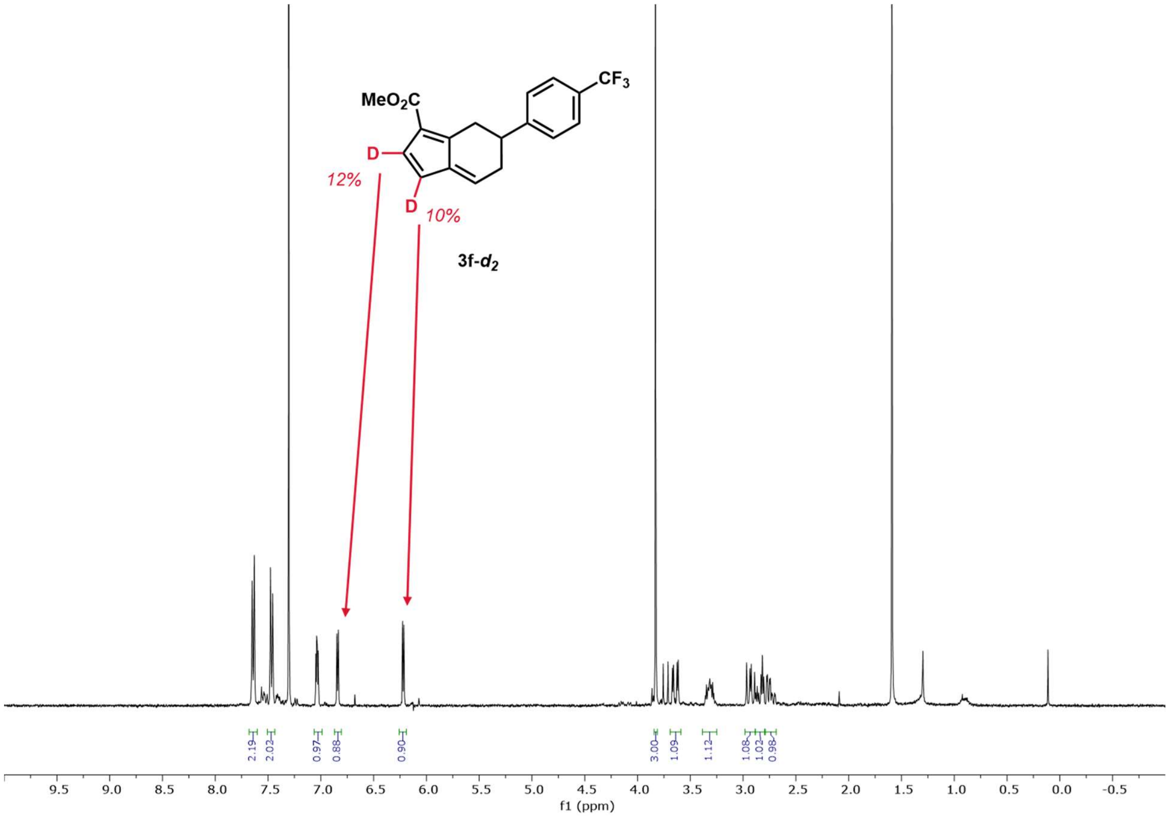
^{1}H NMR (500 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



3.5 Monitoring Product Distribution of 2h vs. 3h Over Time

Procedure for Reaction Monitoring:

General Procedure A was followed for the reaction of **1** with 4-NO_2-phenylboronic acid to give diaryl fulvene **2h** and monoaryl fulvene **3h**. Na_2CO_3 was omitted from this reaction in order to maintain homogeneity of aliquots removed for ^1H NMR analysis. For each time point taken, the reaction mixture was allowed to cool for 10 minutes. Then, a 450 microliter aliquot of the reaction mixture was removed and filtered through a silica plug (approximately 1 inch of silica in a glass pipette) with 7 mL of EtOAc as the eluent. The resulting solution was then concentrated under reduced pressure. The crude residue was analyzed by ^1H NMR analysis with pyrazine as an internal standard (δ 8.64 ppm (s, 4H) for pyrazine, δ 6.32 ppm (s, 1H) for **2h**, and δ 6.19 (d, 1H) for **3h**).

Results:

time (h)	% **2h**	% **3h**	ratio **2h**:**3h**
1	0	4	--
2	0	14	--
3	1	20	1:20
4	3	27	1:9
5	4	32	1:8
6	4	33	1:8.3
7	7	43	1:6.1
8	9	43	1:4.8
9	11	47	1:4.3
10	15	51	1:3.4
11	17	51	1:3
23	40	42	1:1
49	46	33	1.4:1

Table S9. % Yields of **2h** and **3h** determined by ^1H NMR analysis are shown above, along with the ratio of **2h**:**3h**.

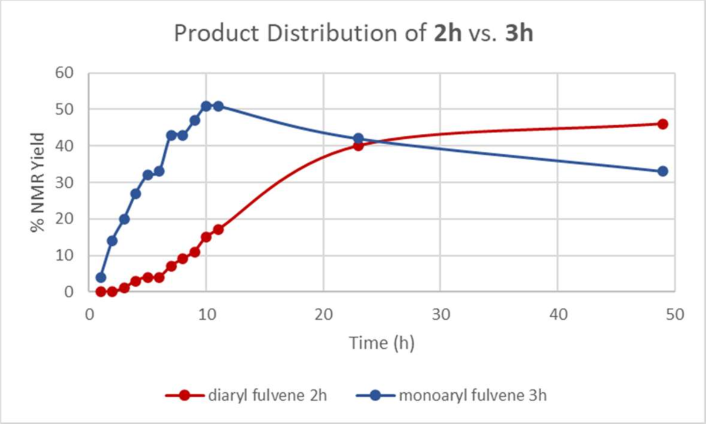


Figure S1. % Yields of **2h** (red) and **3h** (blue) determined by ^1H NMR analysis are graphed above.

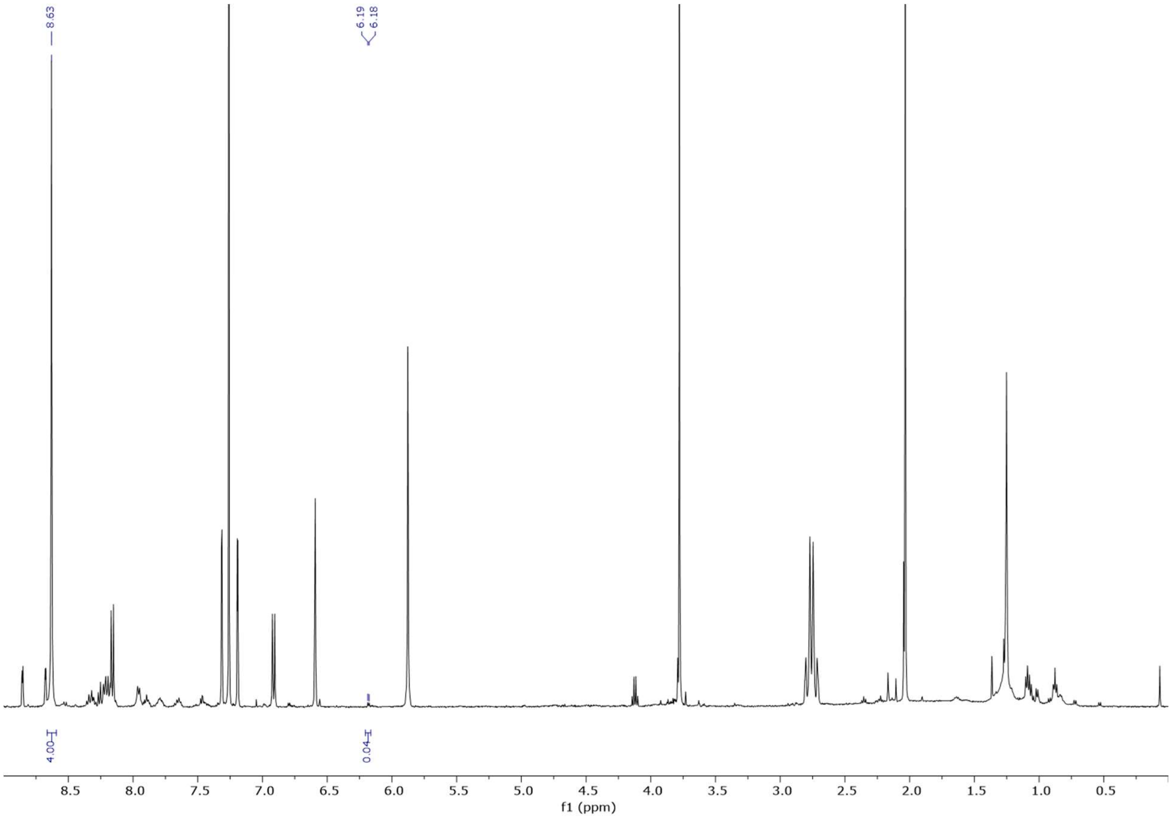
Discussion:

The oxidative Heck reaction of **1** with 4-NO_2-phenylboronic acid was monitored over a 49 hour period in order to test the hypothesis that 4-NO_2-Ph monoaryl fulvene (**3h**) forms initially and is then converted to 4-NO_2-Ph diaryl fulvene (**2h**). After two hours of reaction, only monoaryl fulvene **3h** is detected and no diaryl fulvene **2h** is observed, indicating that the monoarylfulvene is, indeed formed first. Trace amounts of **2h** (1%) are first detected after three hours of reaction time. The NMR yield of **3h** continues to increase faster than that of **2h** with the mixture containing 51% **3h** and 17% **2h** (a ratio of 3:1, **3h**:**2h**) at 11 hours of reaction time. After 23 hours of total reaction time, the amount of **3h** is reduced to 42% while the amount of **2h** is increased 40% (approximately 1:1 ratio). Extended reaction time to 49 hours results in a further increase in the amount of diaryl fulvene **2h** (46%), accompanied by a further decrease in the amount of monoaryl fulvene **3h** (33%). The initial increase in monoaryl fulvene **3h**, followed by a decrease in **3h** and concurrent increase in **2h** supports the initial hypothesis that monoaryl fulvene is formed first and then converted to diaryl fulvene. For electron deficient arylboronic acids, the second oxidative Heck to give diaryl fulvene is likely slow enough such that monoaryl fulvenes are present in isolable quantities after 20 hours of reaction time. For electron-rich or -neutral arylboronic, the second oxidative Heck reaction is likely fast such that little monoaryl fulvene remains after the standard reaction time of 20 hours.

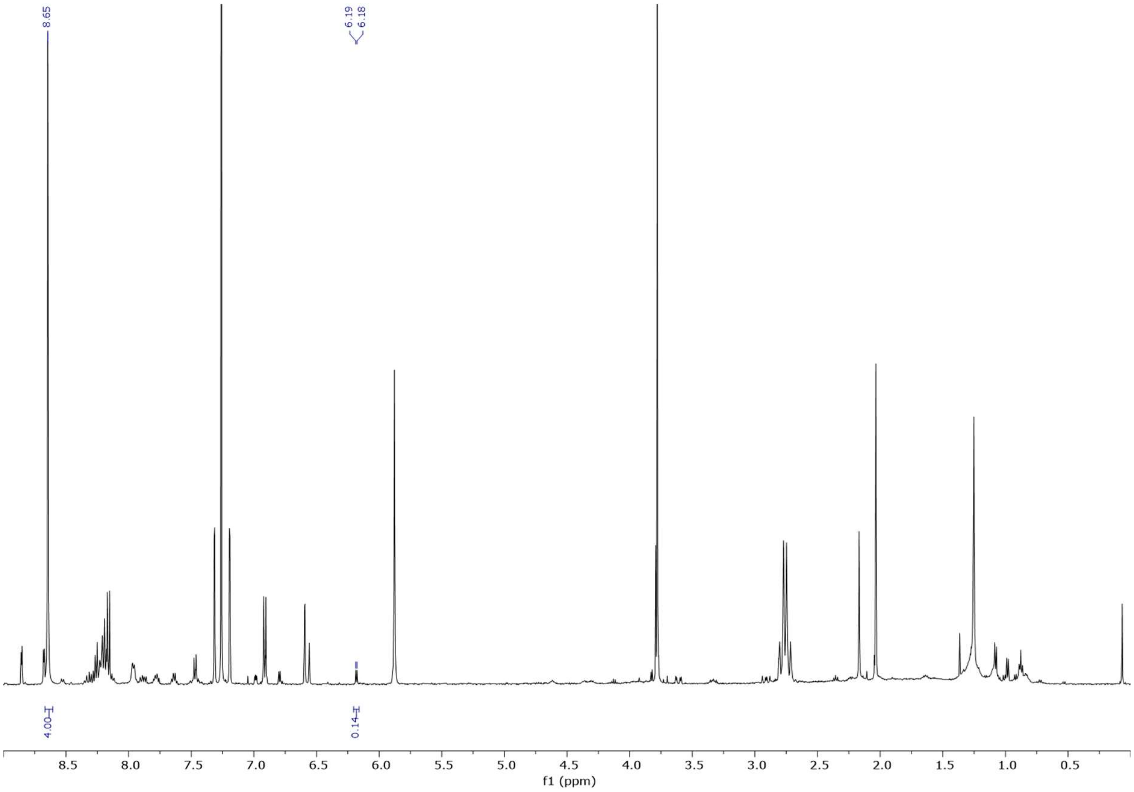
^{1}H NMR Spectra Used to Determine Product Distribution

All spectra shown in this section are ^{1}H NMRs (500 MHz, $CDCl_3$). Insets around diagnostic peaks for **2h** and **3h** for t=3h, t=11h, t=23h, and t=49h are shown for clarity.

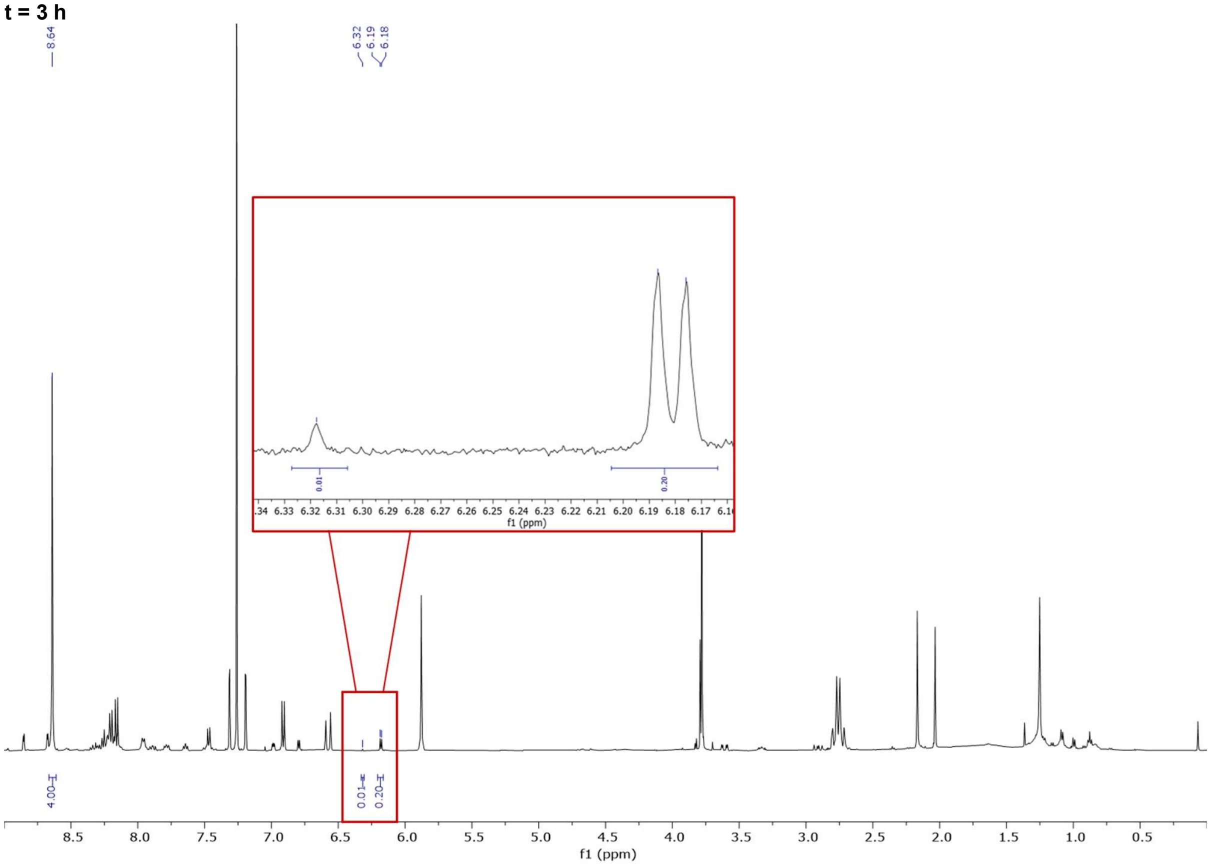
t = 1 h



t = 2 h

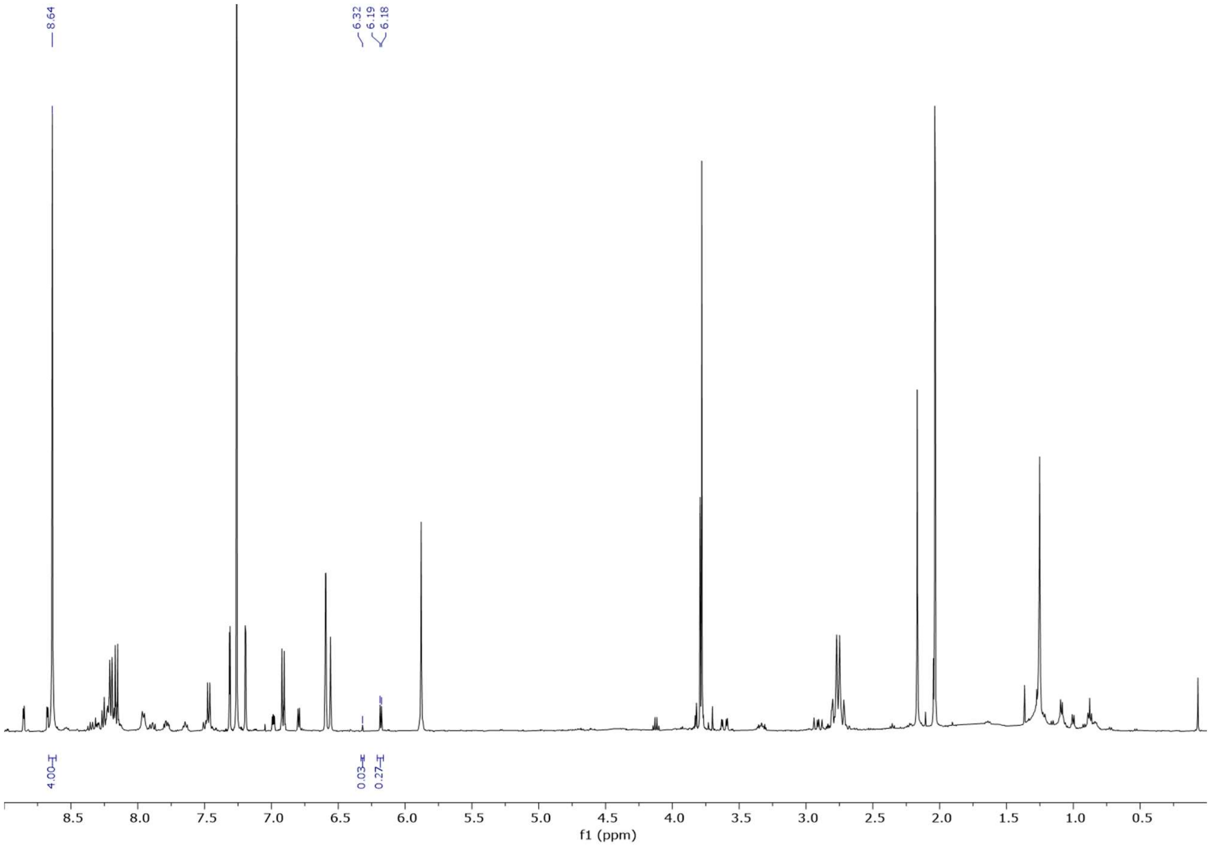


t = 3 h



8.64
6.32
6.19
6.18
0.01
0.20
.34 6.33 6.32 6.31 6.30 6.29 6.28 6.27 6.26 6.25 6.24 6.23 6.22 6.21 6.20 6.19 6.18 6.17 6.16
f1 (ppm)
4.00
0.01
0.20
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

t = 4 h



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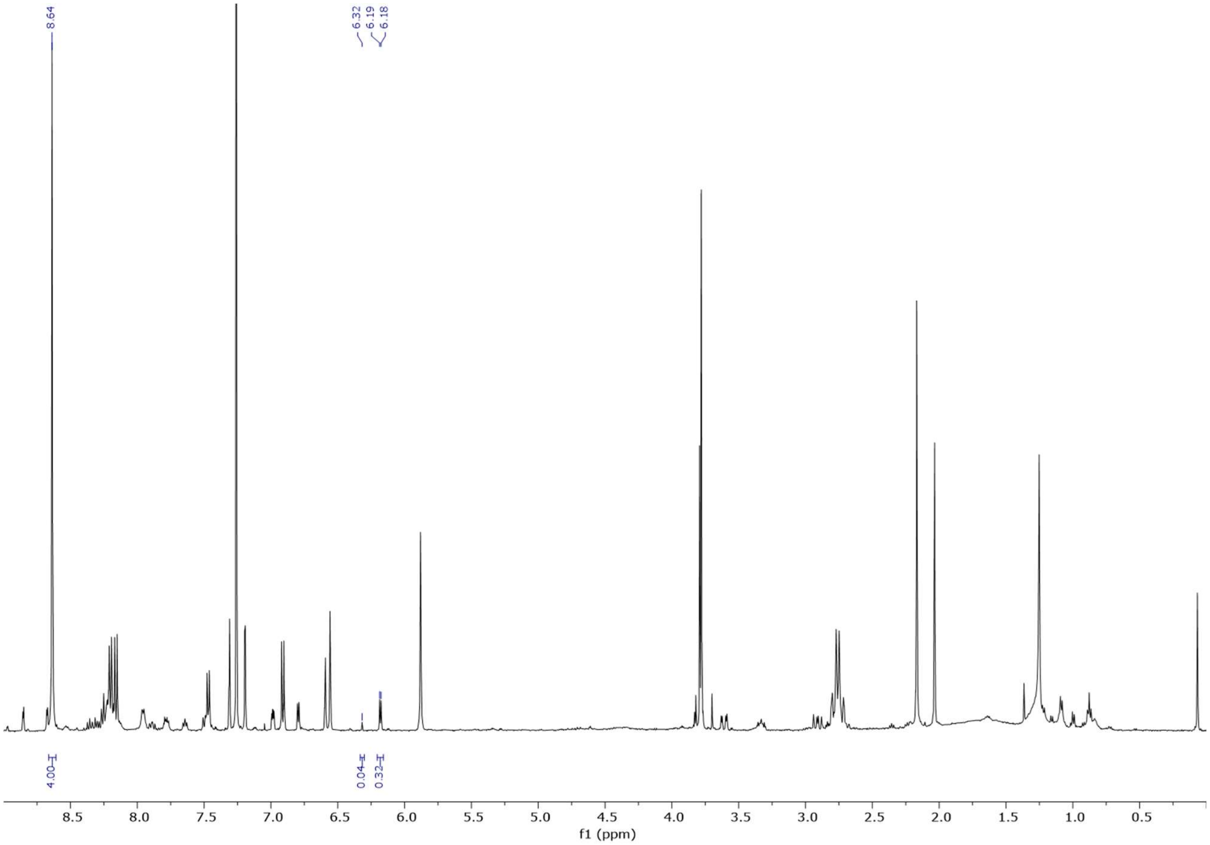
6.32
6.19
6.18
4.00
0.03
0.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

t = 5 h



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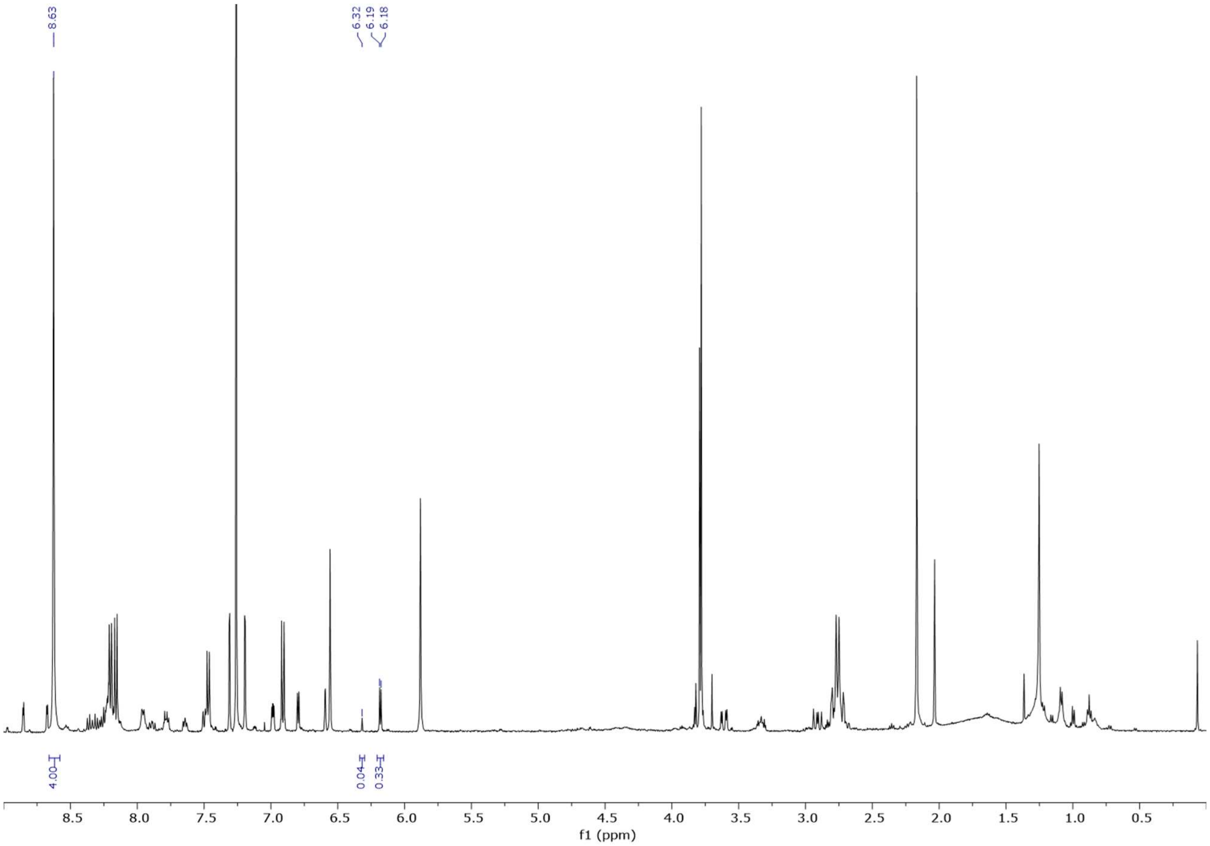
6.32
6.19
6.18
4.00
0.04
0.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 6 h



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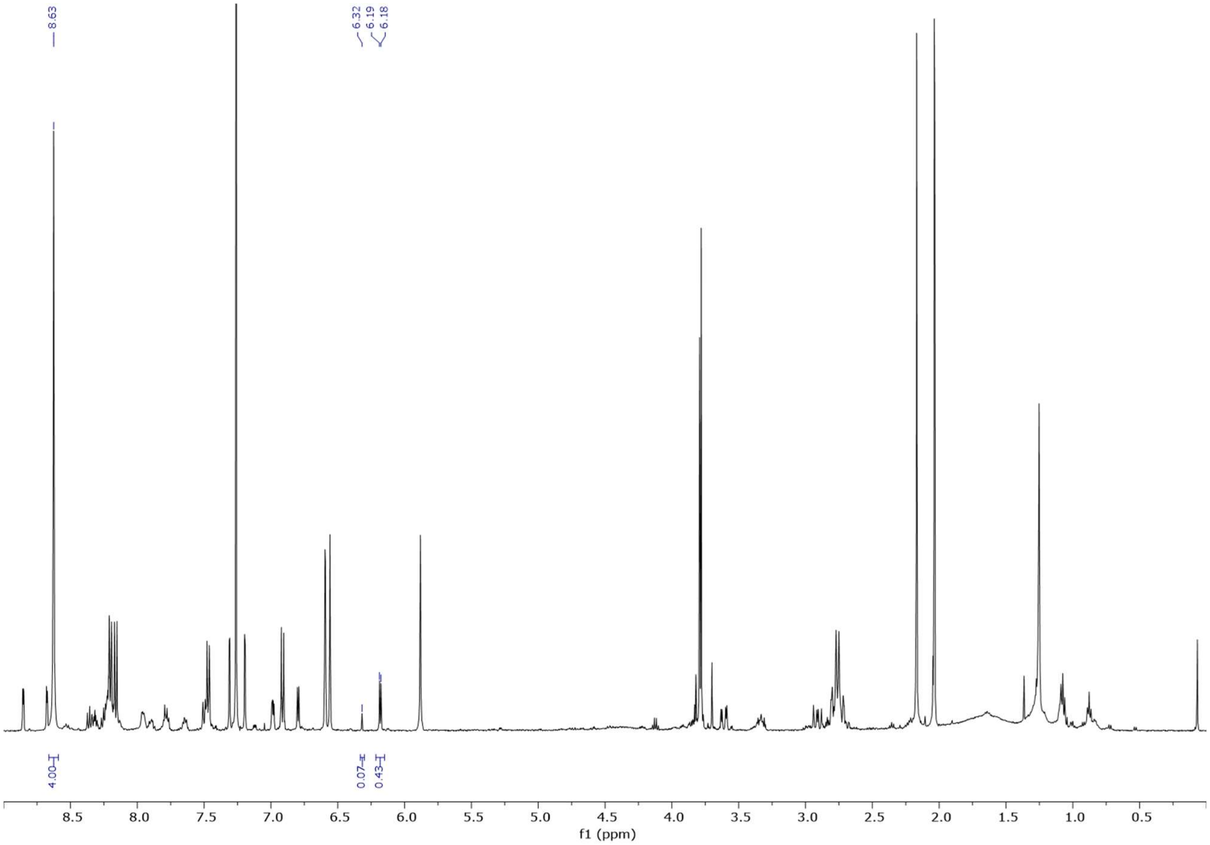
6.19
6.18
4.00
0.04
0.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 7 h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6.0
5.5
5.0
4.5
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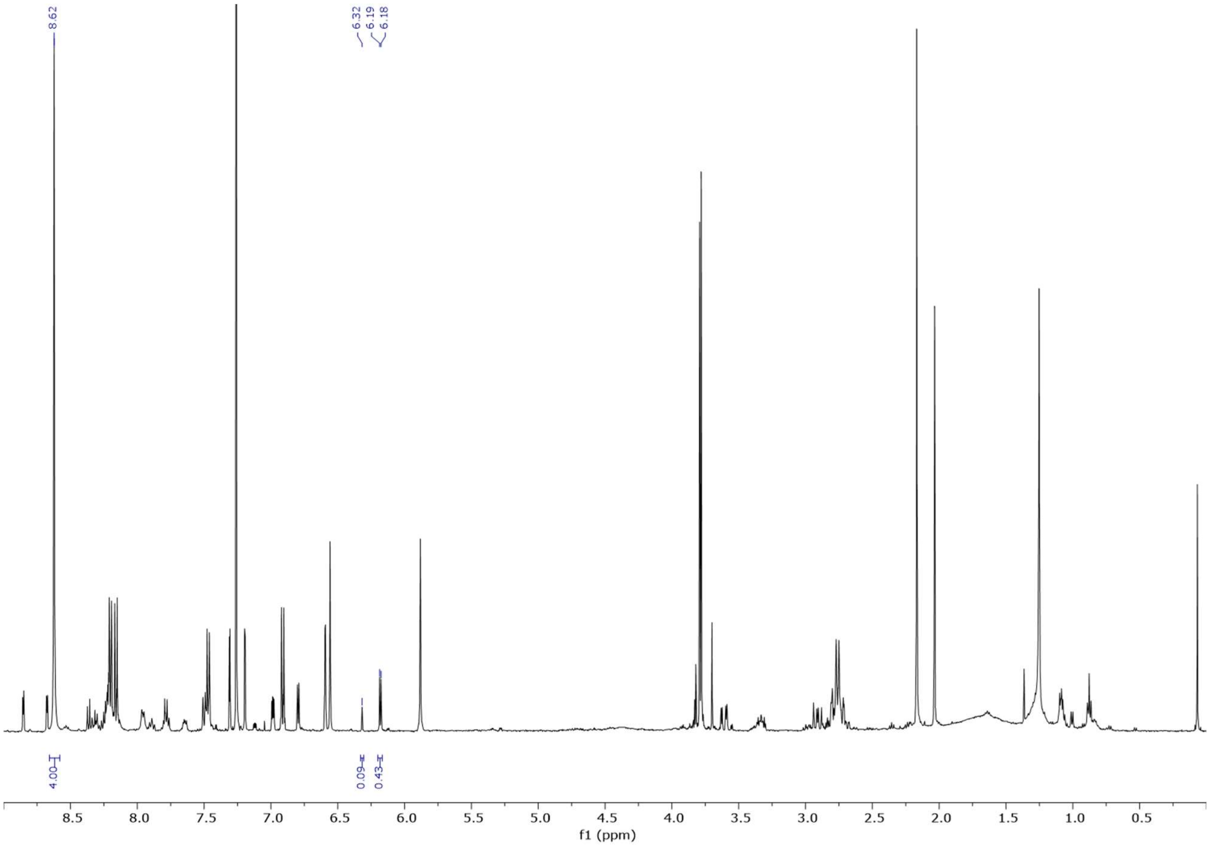
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 8 h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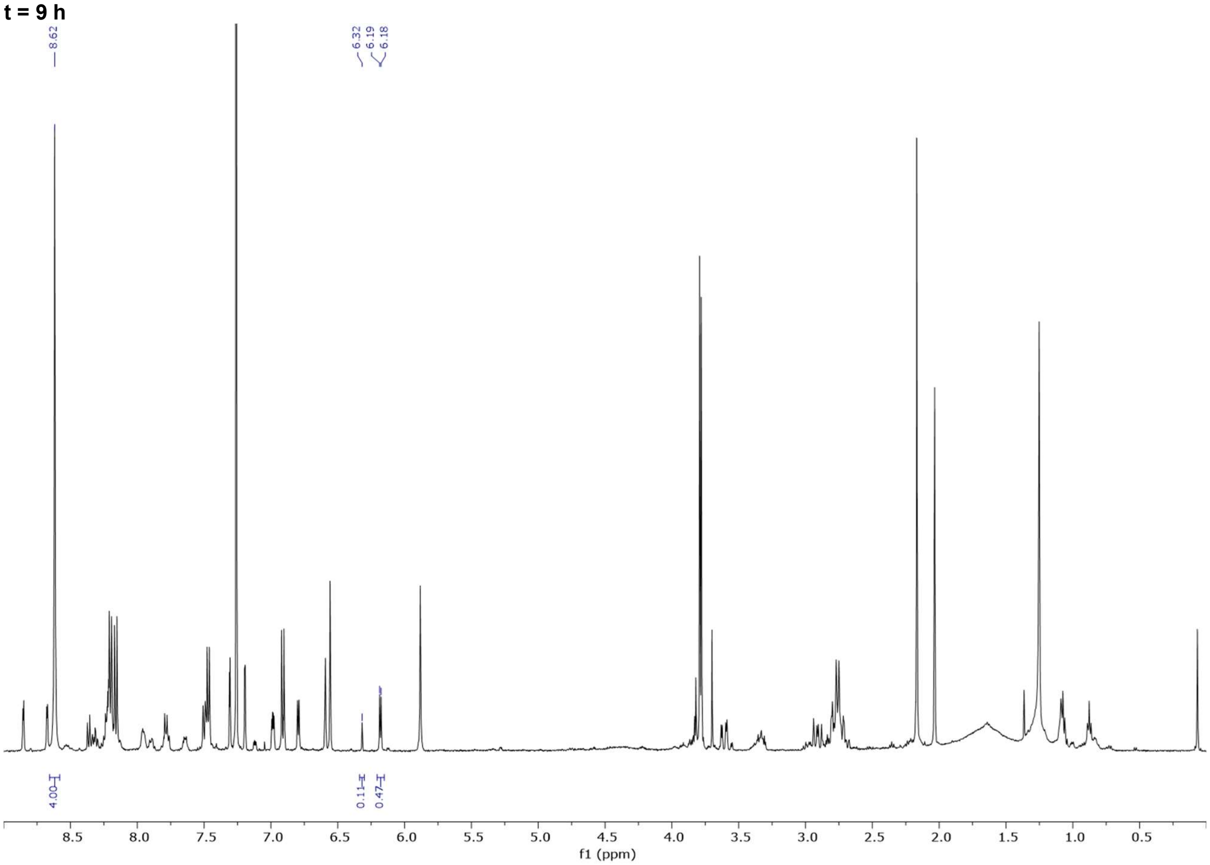
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 9 h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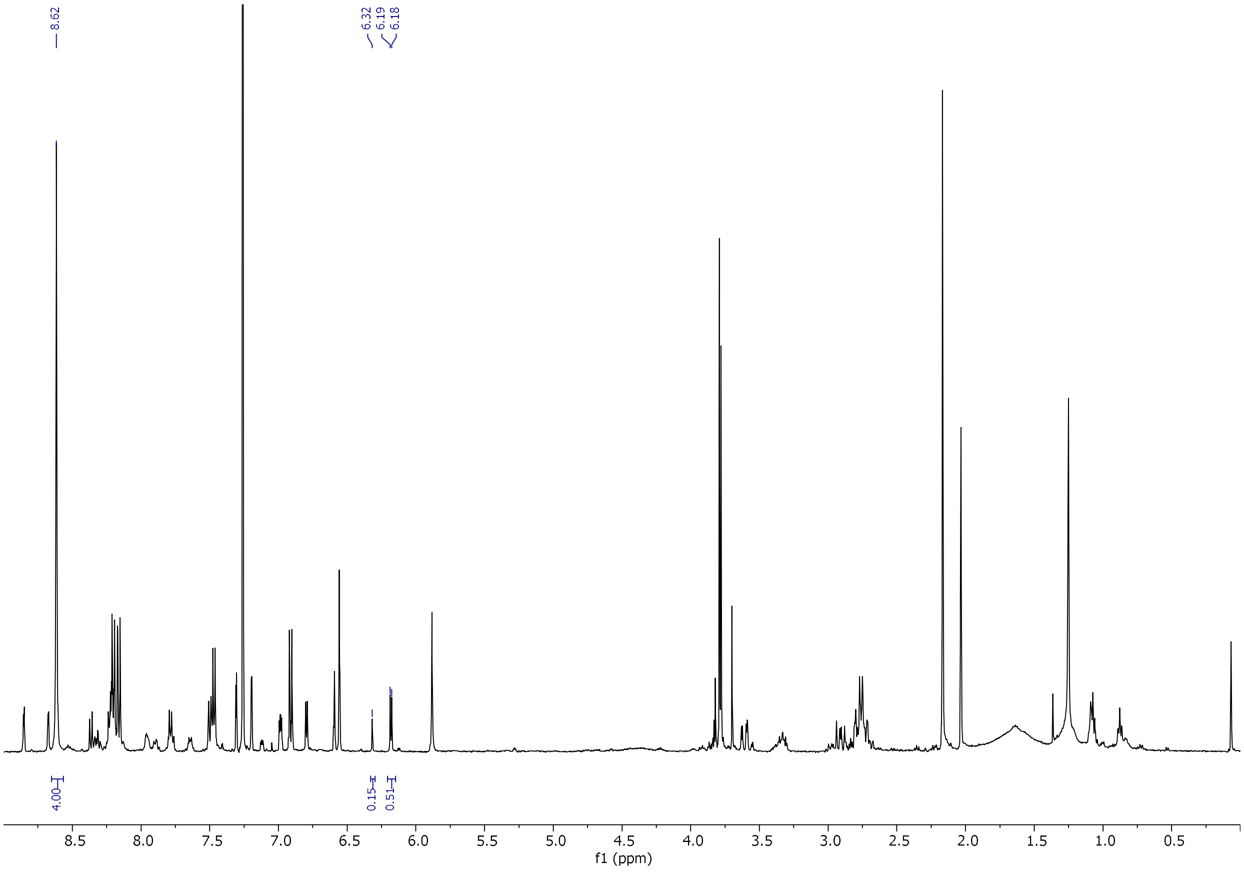
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 10 h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7.0
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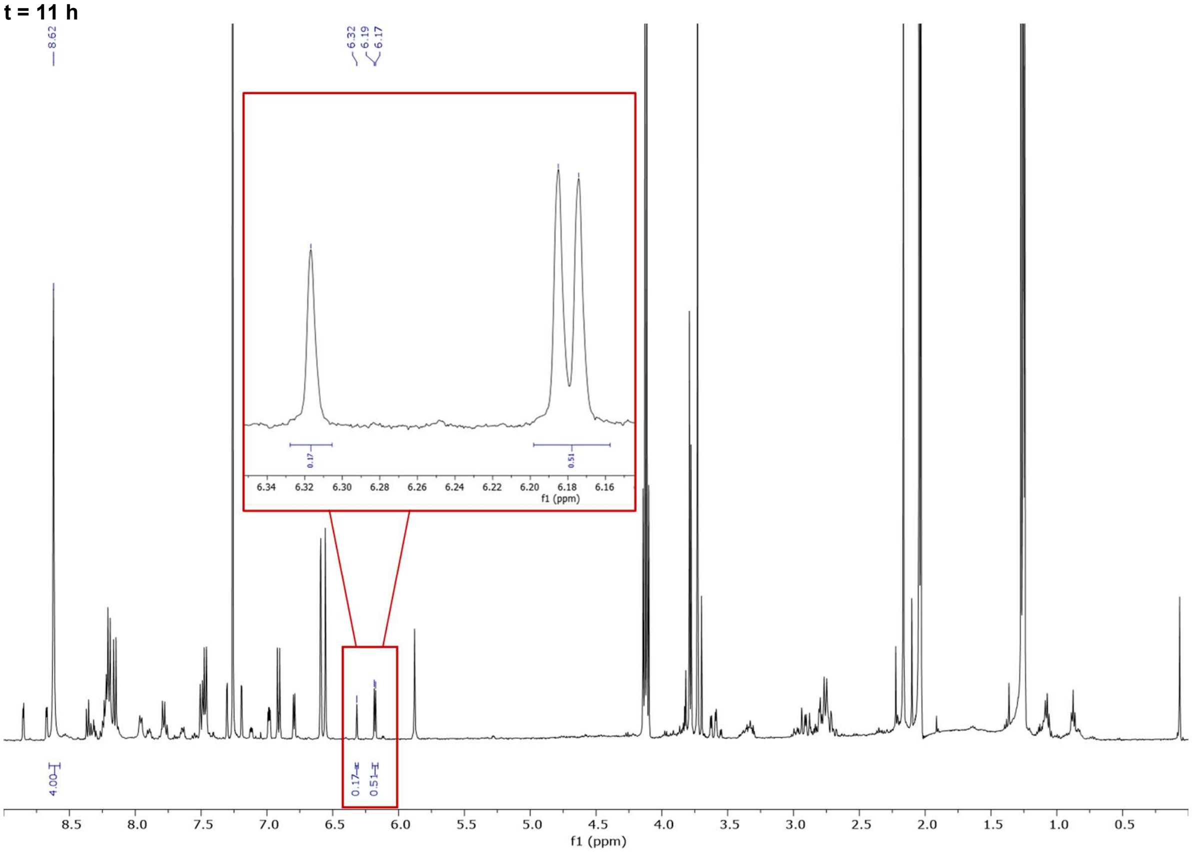
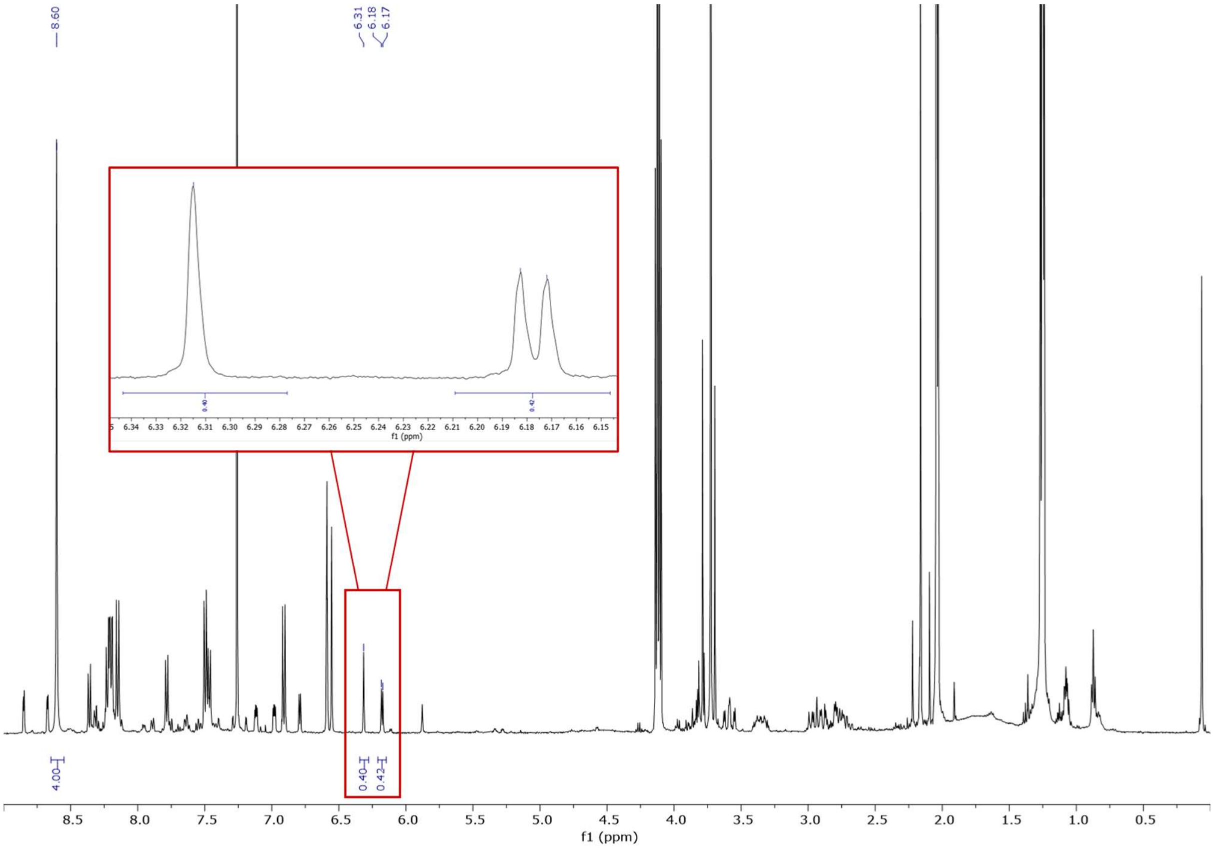
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

t = 11 h


8.62
6.32
6.19
6.17
0.17
0.51
6.34 6.32 6.30 6.28 6.26 6.24 6.22 6.20 6.18 6.16
f1 (ppm)
4.00
0.17
0.51
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

t = 23 h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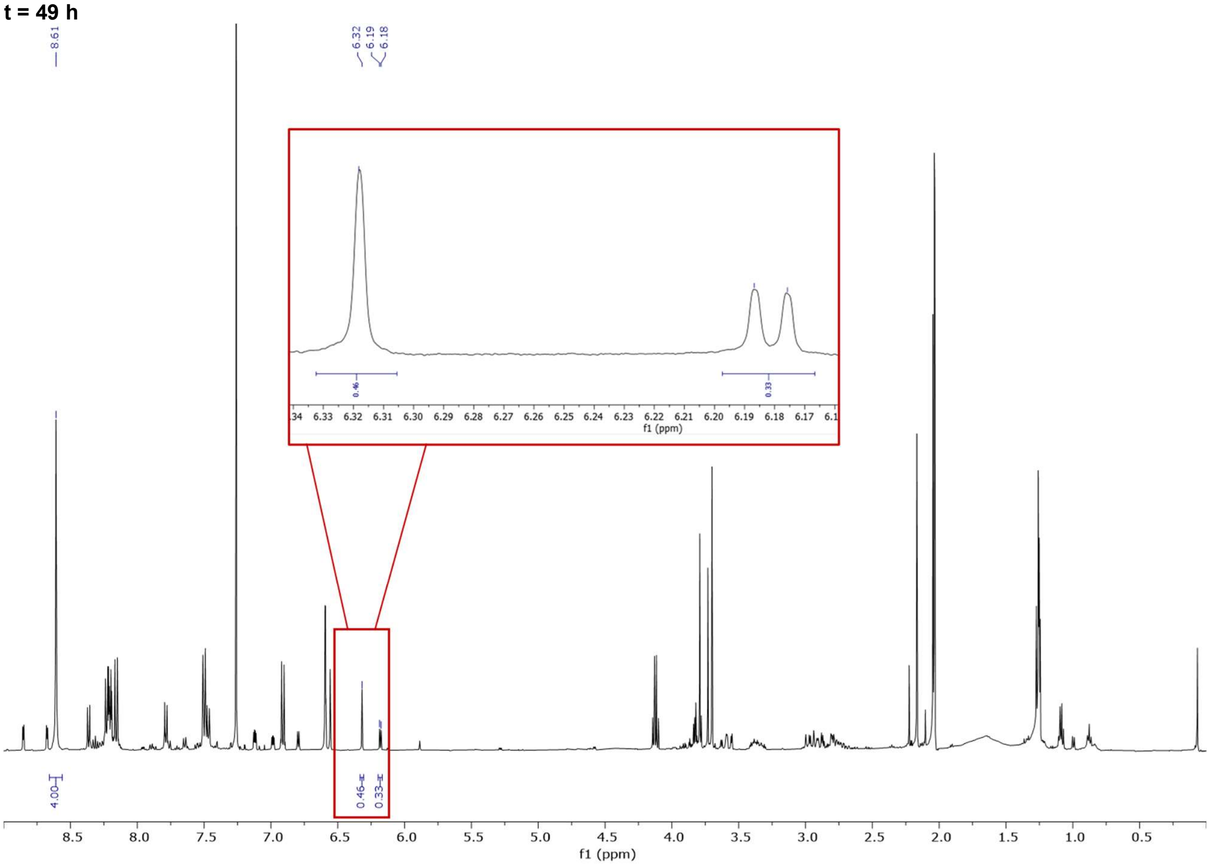
6.18
6.17
0.40
0.42
6.34 6.33 6.32 6.31 6.30 6.29 6.28 6.27 6.26 6.25 6.24 6.23 6.22 6.21 6.20 6.19 6.18 6.17 6.16 6.15
f1 (ppm)
4.00
0.40
0.42
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

t = 49 h


8.61
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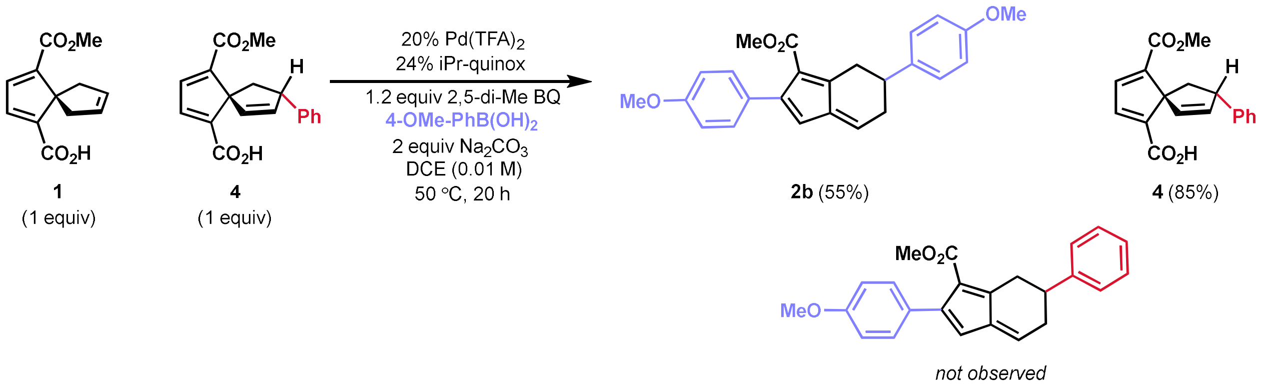
6.19
6.18
4.00
0.46
0.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
6.33
6.32
6.31
6.30
6.29
6.28
6.27
6.26
6.25
6.24
6.23
6.22
6.21
6.20
6.19
6.18
6.17
f1 (ppm)

3.6 Resubjecting Heck Product (4) to Reaction Conditions with Starting Material (1)

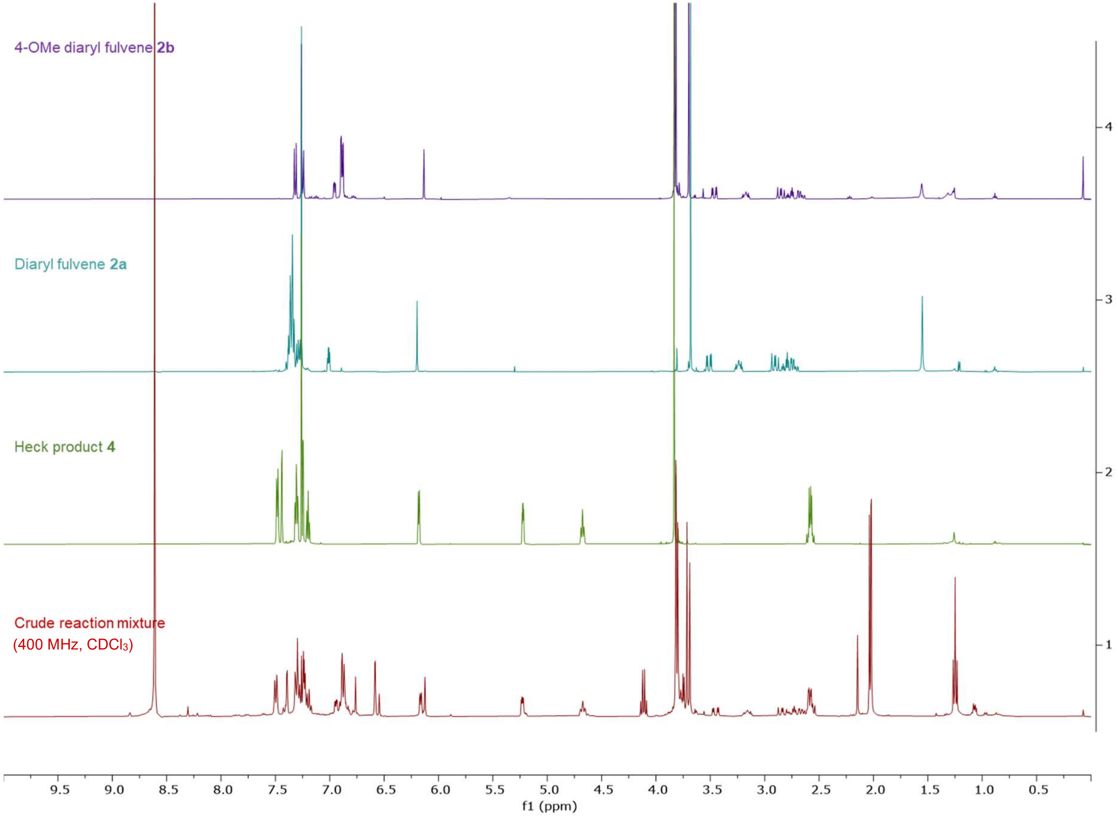


Scheme S5. Heck product (**4**) was subjected to the reaction conditions, along with starting material (**1**).

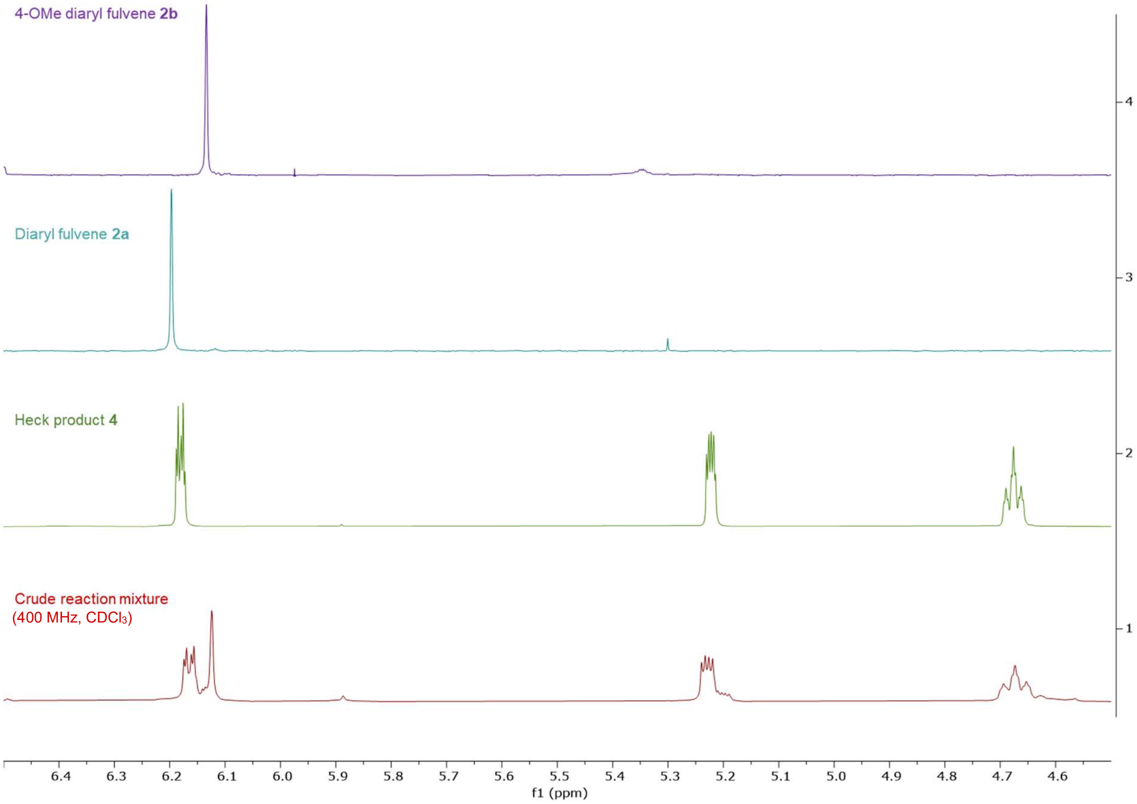
The reaction shown in Scheme S5 was conducted according to General Procedure A, with the addition of a solution of **4** in DCE prior to the addition of arylboronic acid.

This experiment offers additional support for the Heck product (**4**) not being transformed to fulvene products under the reaction conditions. While the results presented in Table 3 indicate that **4** does not rearrange to fulvene products when subjected to the reaction conditions, those experiments do not account for any transient species that may be formed from the reaction of **1**. It could be that such a transient species may react intermolecularly with **4** to facilitate its rearrangement to a fulvene product. We tested this hypothesis by subjecting a mixture of both **4** and **1** to the reaction conditions with 4-OMe-PhB(OH)$_2$. If **4** is, in fact, transformed to a fulvene product by reaction with some transient species formed due to the presence of **1**, we would expect significant consumption of **4**, along with the observation of a new diaryl fulvene bearing an unsubstituted phenyl group conserved from **4** and a newly installed 4-OMe-phenyl group. ^{1}H analysis of the crude reaction mixture with an internal standard indicates that diaryl fulvene **2b** was obtained and in 55% yield and **4** was recovered in 85% yield. Moreover, no new diaryl fulvene bearing both a phenyl group and 4-OMe-phenyl group was observed (by comparison to diagnostic regions of **2a** and **2b**; see stacked spectra below). This experiment provides additional support that Heck product (**4**) is not converted to fulvene products.

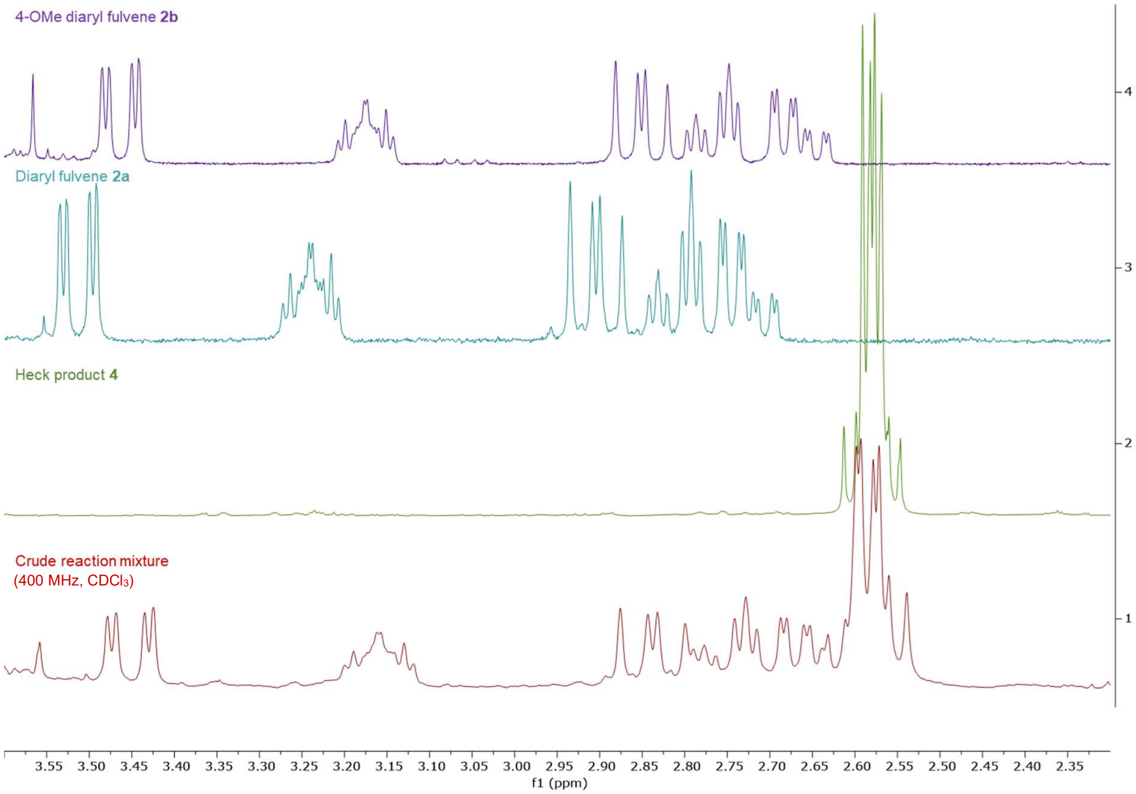
Stacked ^{1}H NMR Spectra for Comparison and Analysis of Crude Reaction Mixture



Stacked ^{1}H NMR Spectra for Comparison and Analysis of Crude Reaction Mixture (4.5–6.5 ppm)

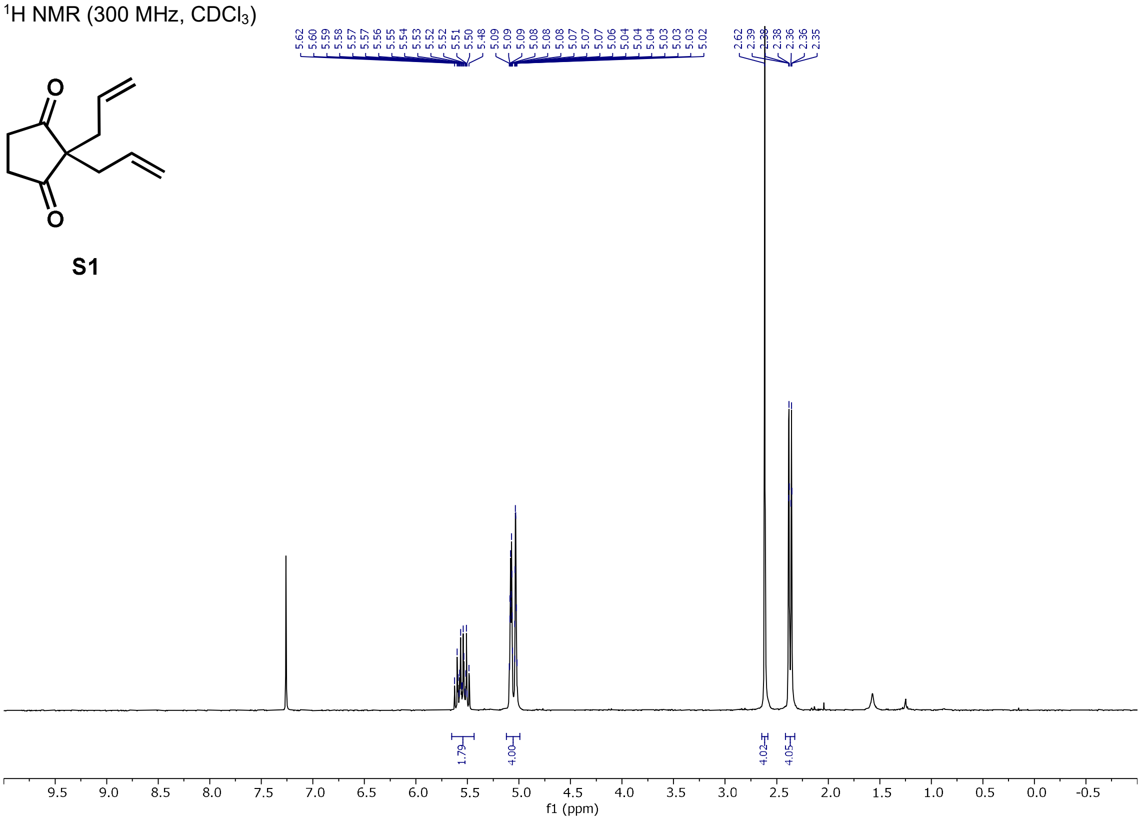


Stacked ^{1}H NMR Spectra for Comparison and Analysis of Crude Reaction Mixture (2.3–3.6 ppm)



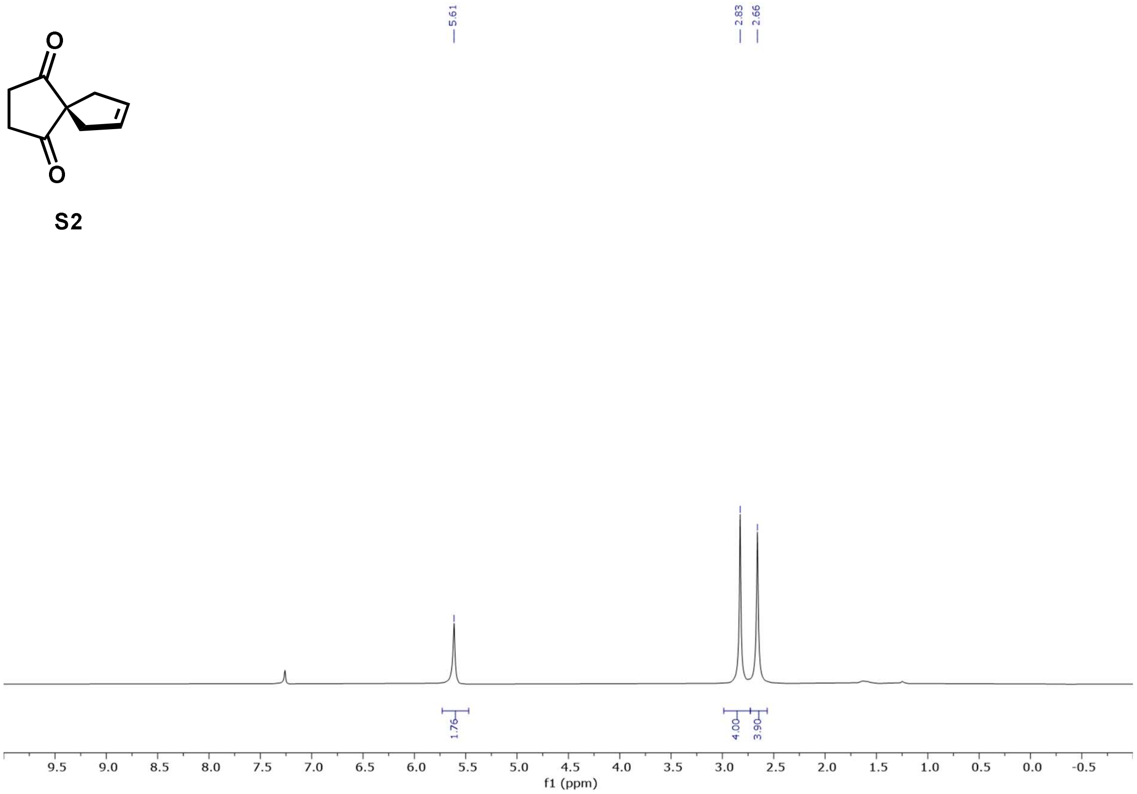
4. ¹H and ¹³C NMR Spectra

¹H NMR (300 MHz, CDCl₃)



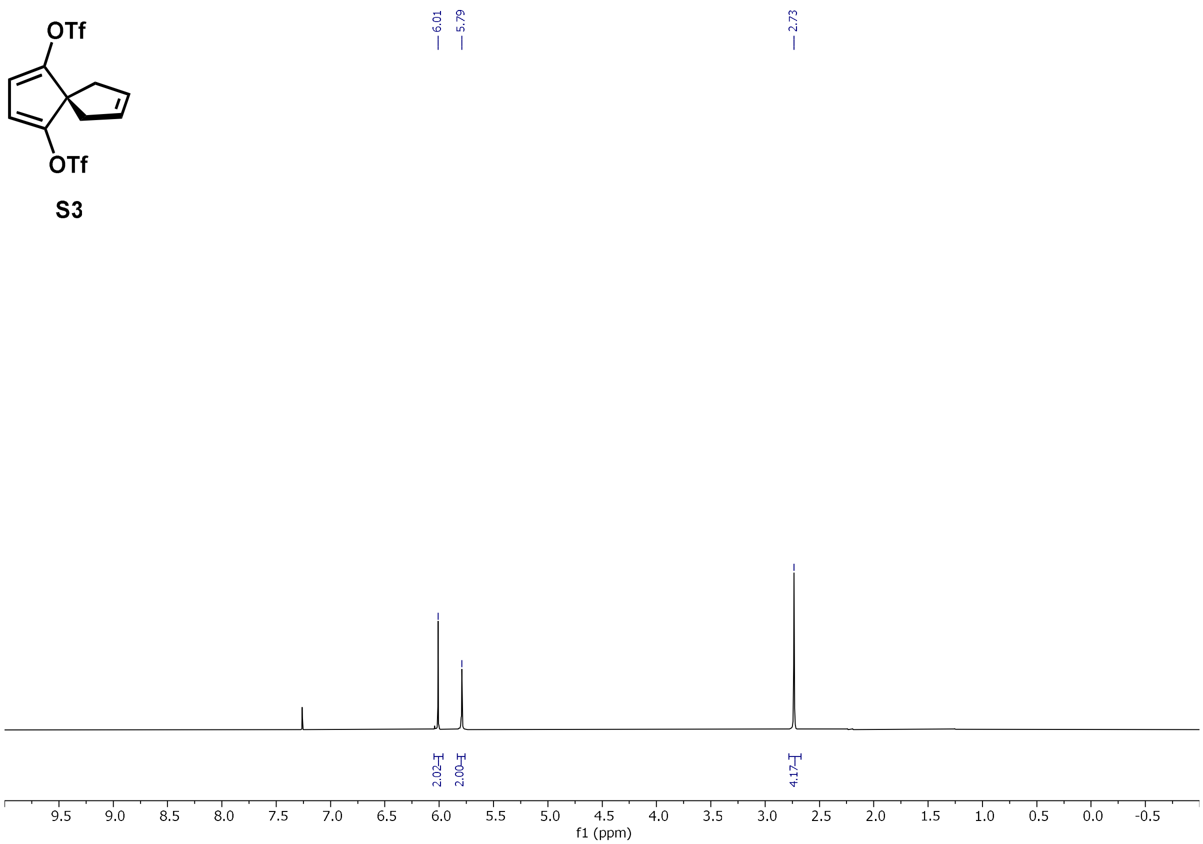
S1

¹H NMR (300 MHz, CDCl₃)

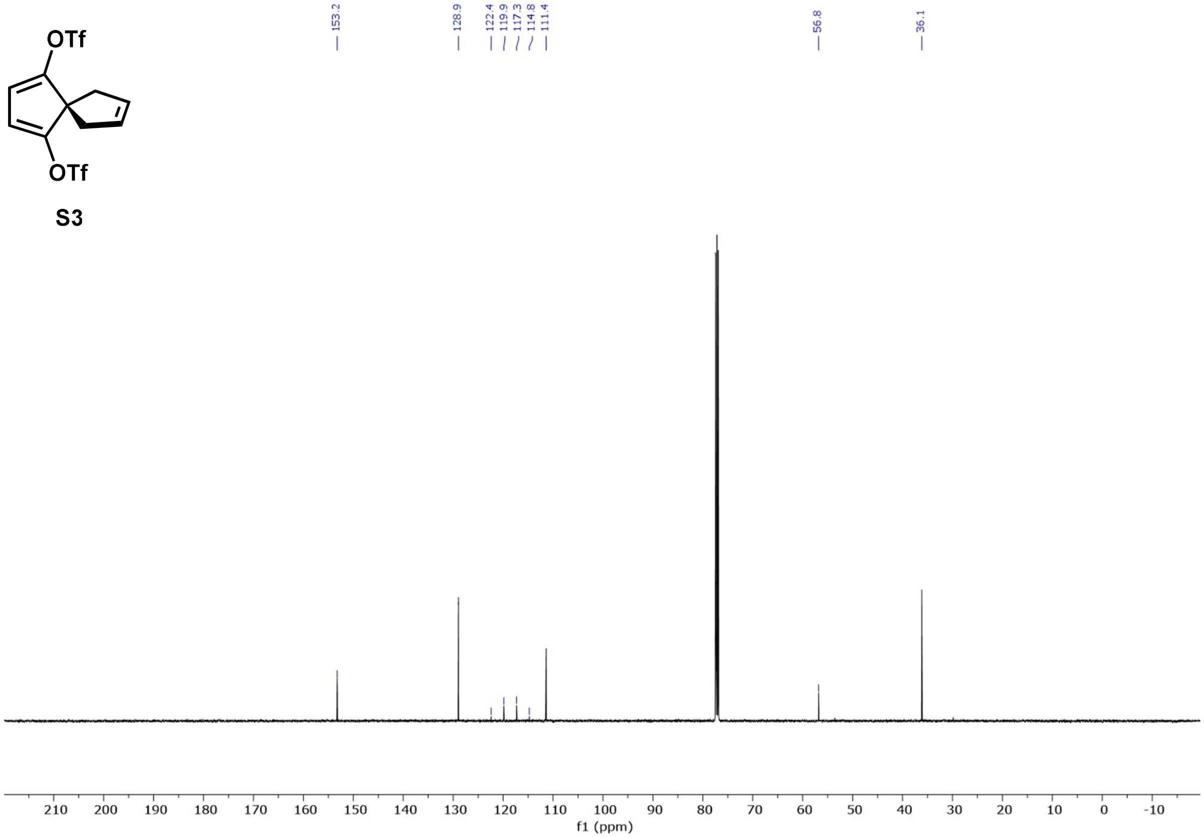


S2

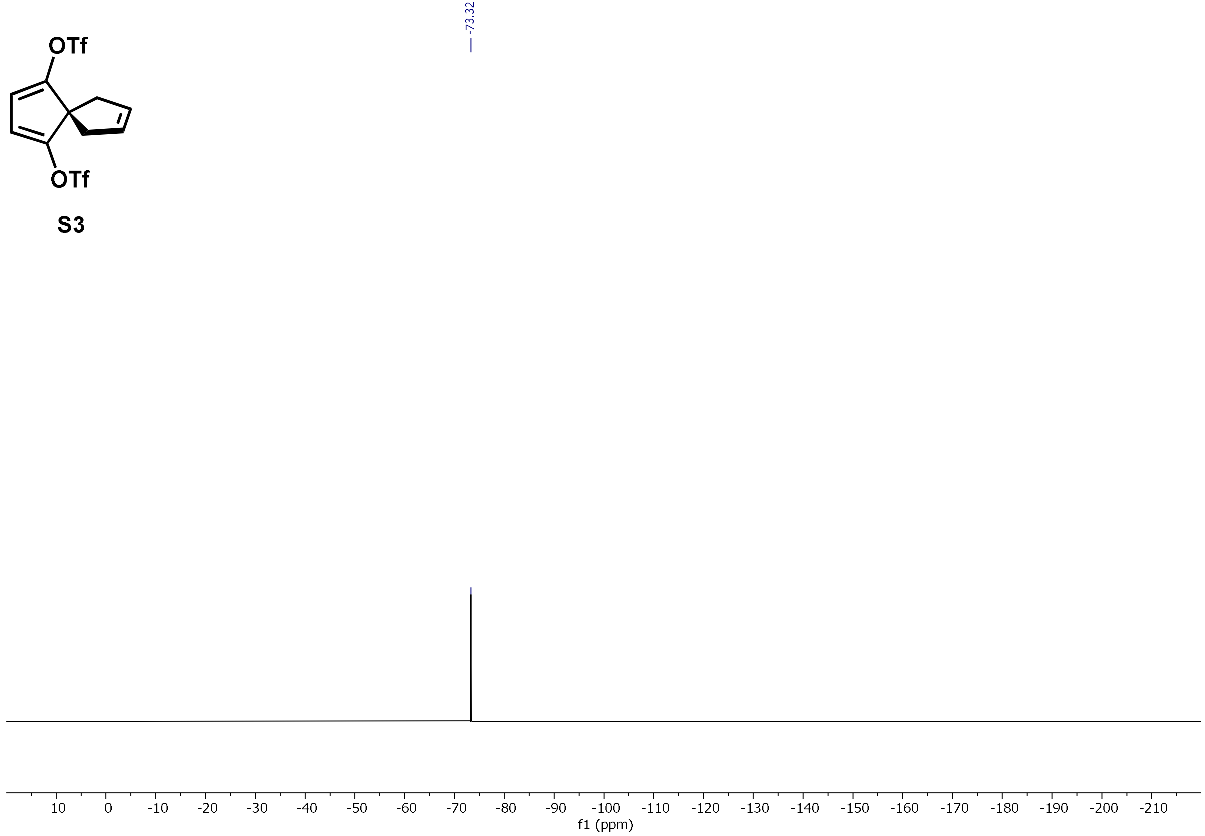
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (126 MHz, $CDCl_3$)

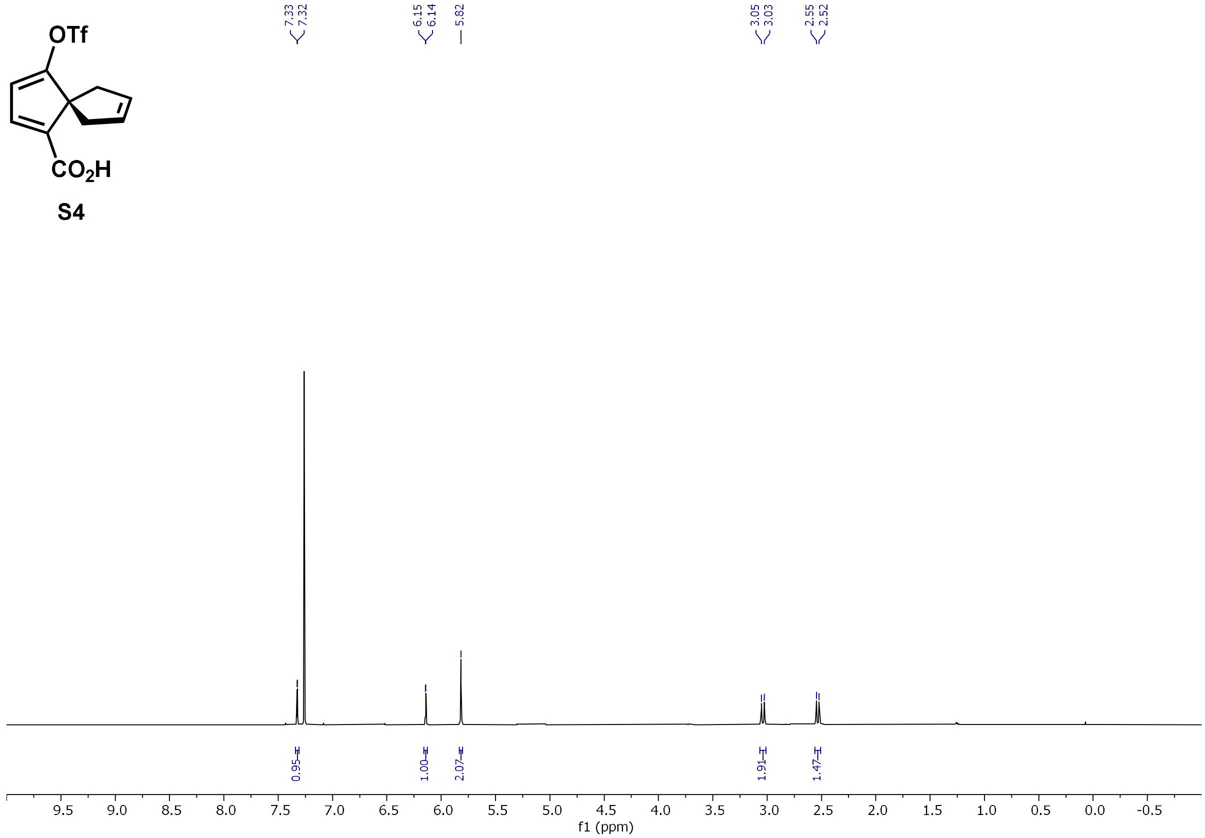


^{19}F NMR (470 MHz, $CDCl_3$)



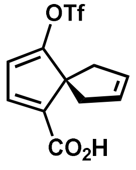
S3

^{1}H NMR (600 MHz, $CDCl_3$)

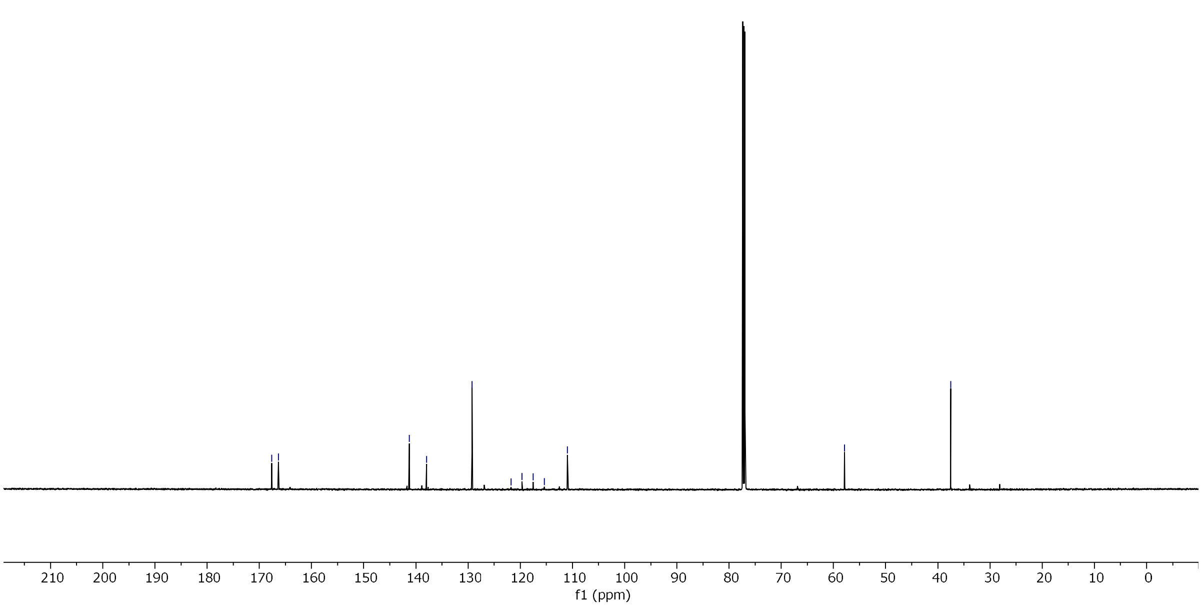


S4

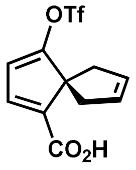
^{13}C NMR (151 MHz, $CDCl_3$)



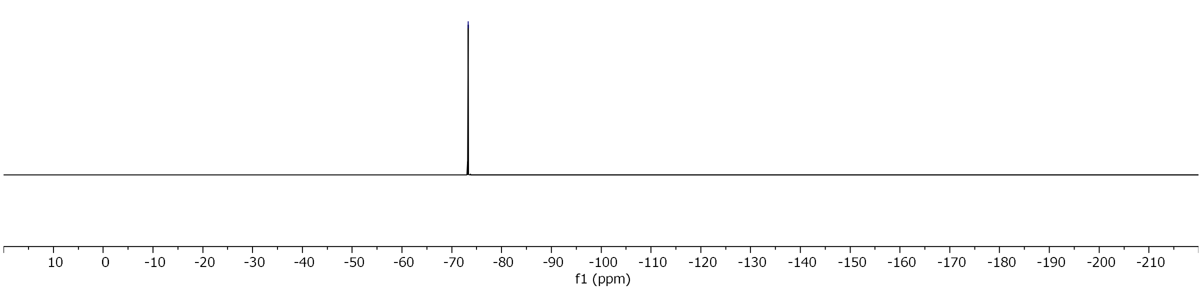
S4



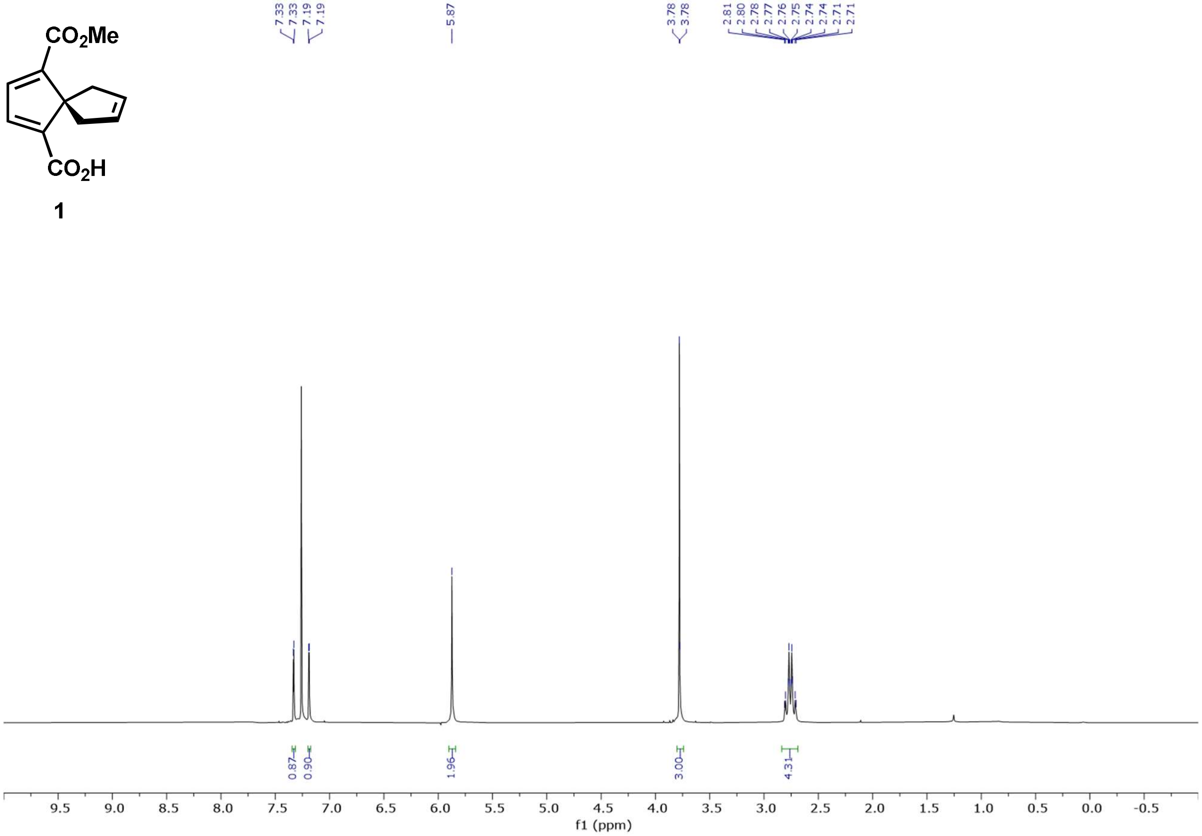
^{19}F NMR (470 MHz, $CDCl_3$)



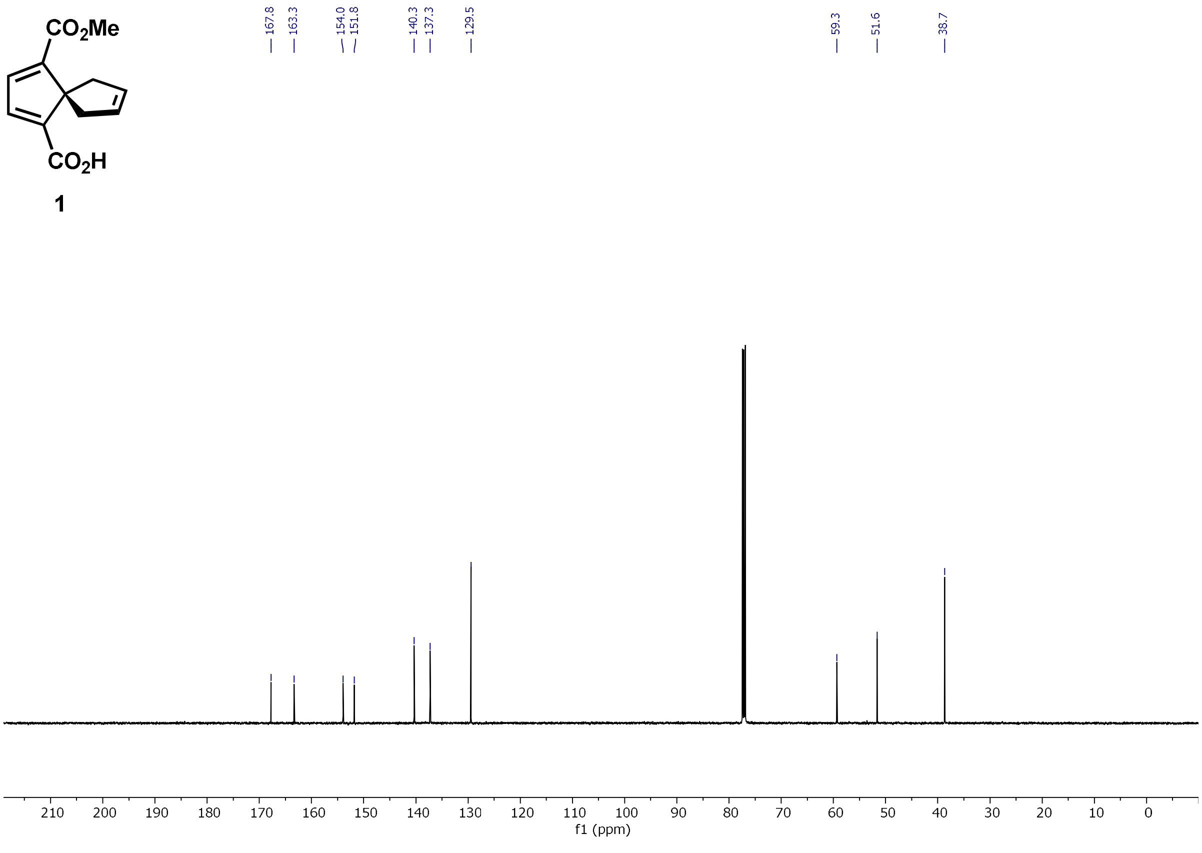
S4



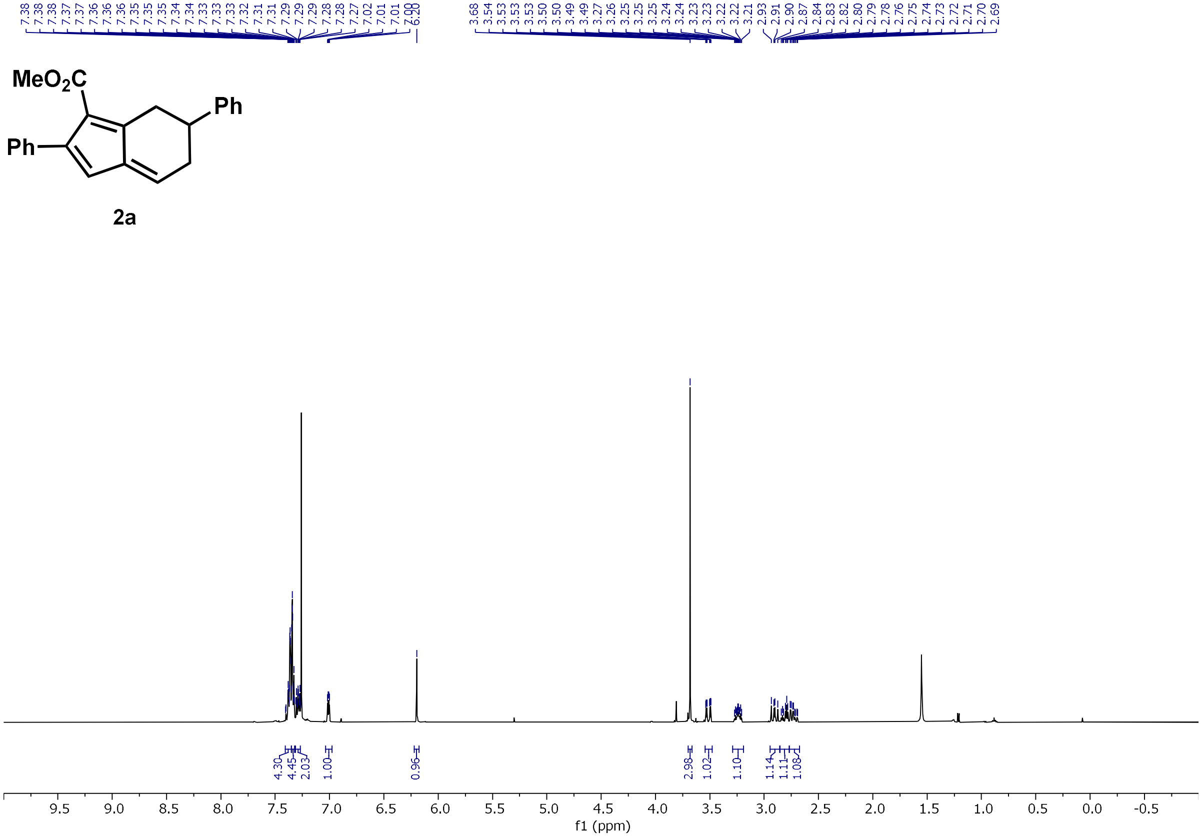
^{1}H NMR (500 MHz, CDCl$_3$)



^{13}C NMR (126 MHz, CDCl$_3$)

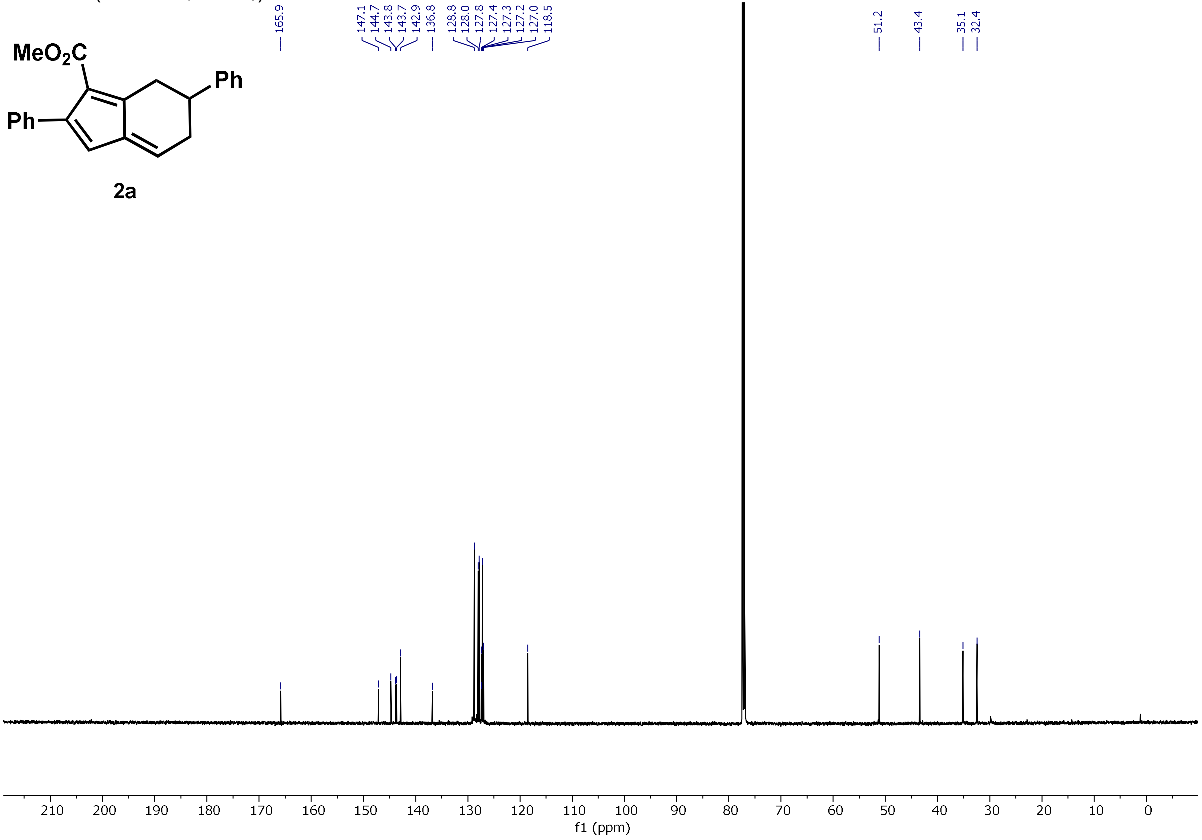


^1H NMR (500 MHz, $CDCl_3$)



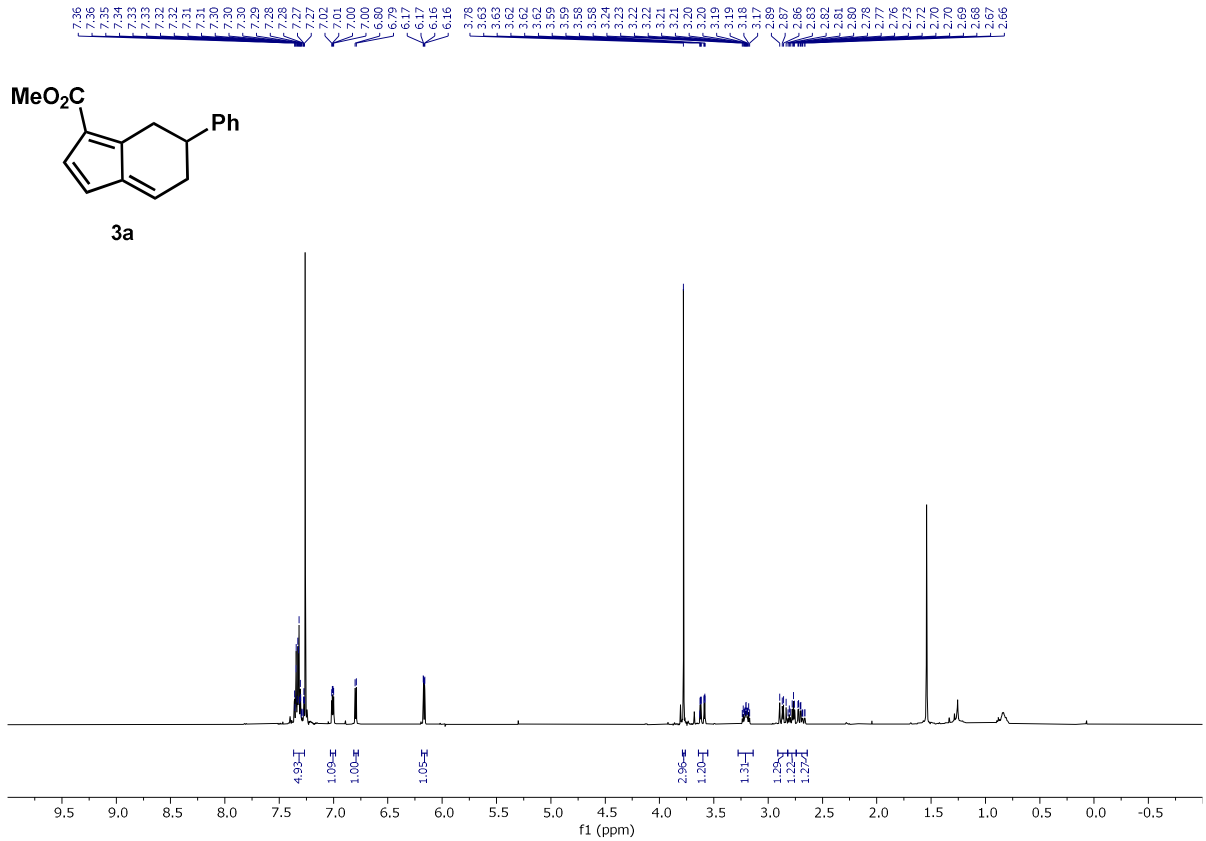
2a

^{13}C NMR (126 MHz, $CDCl_3$)

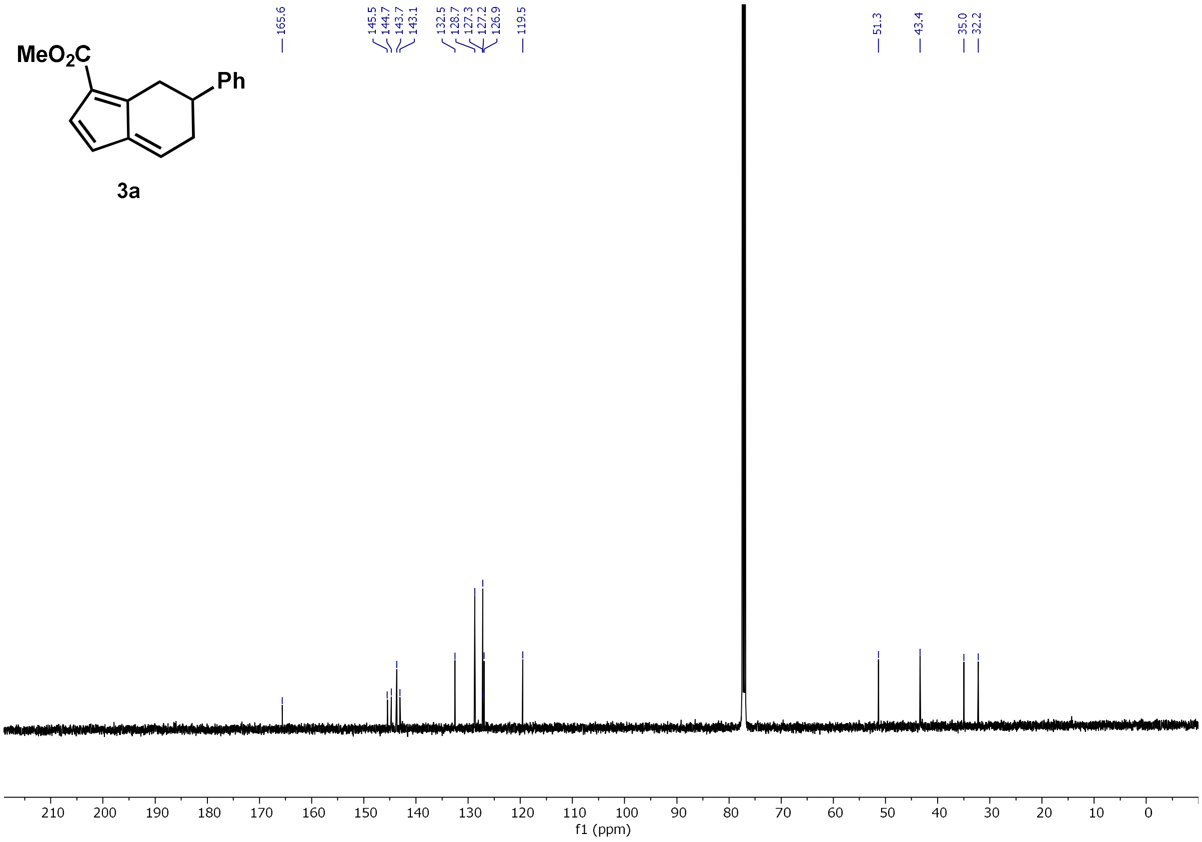


2a

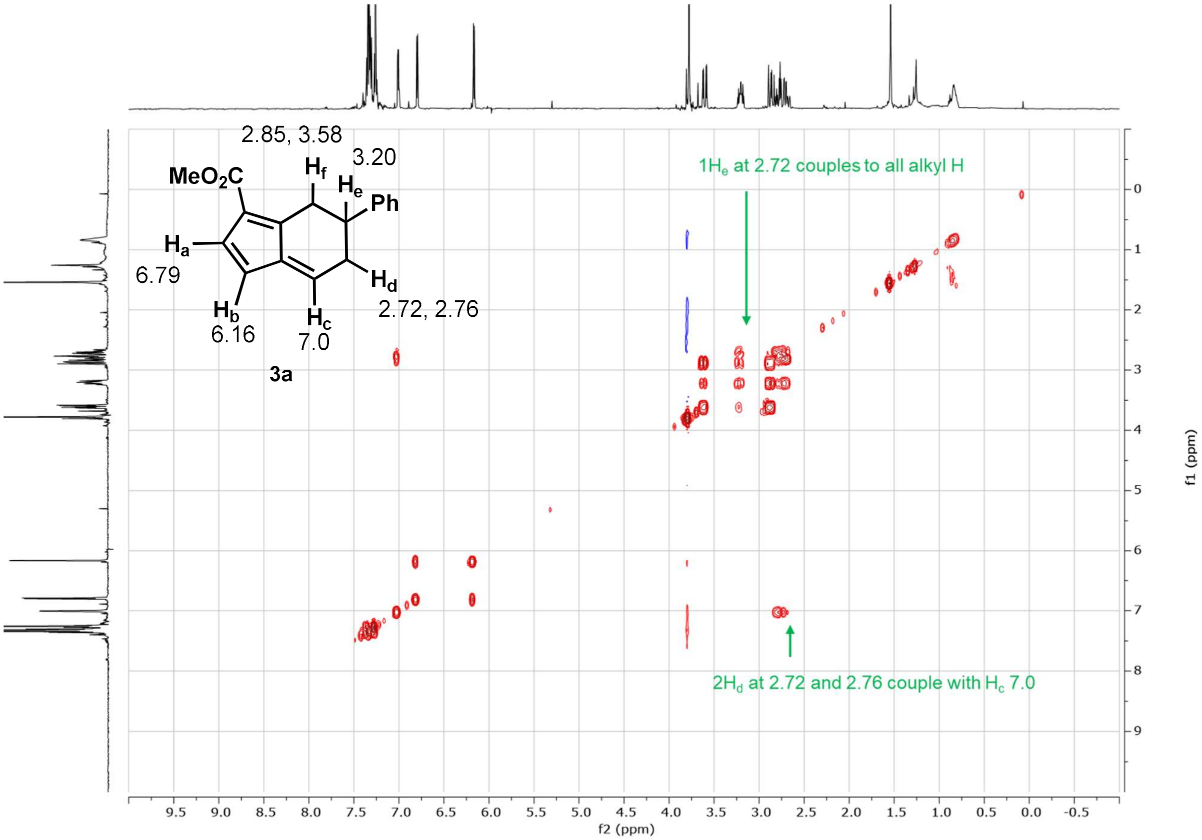
^{1}H NMR (500 MHz, CDCl$_3$)



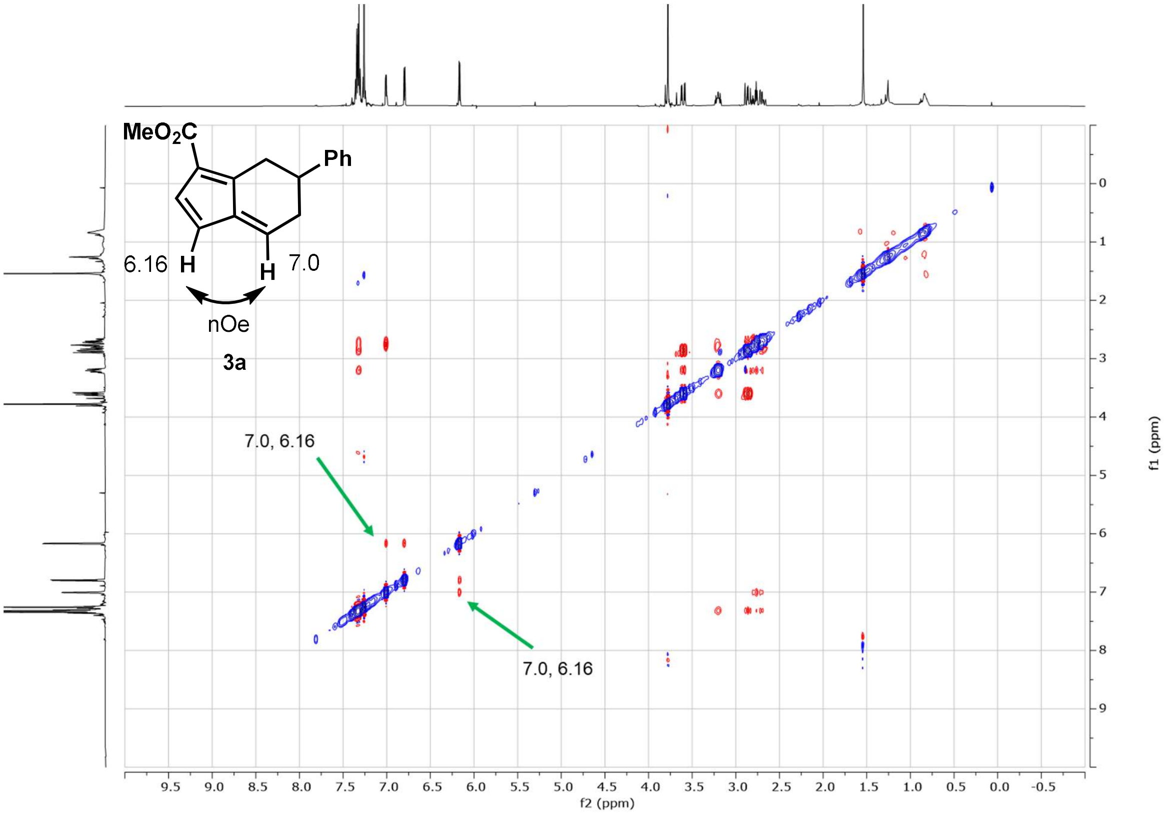
^{13}C NMR (126 MHz, CDCl$_3$)



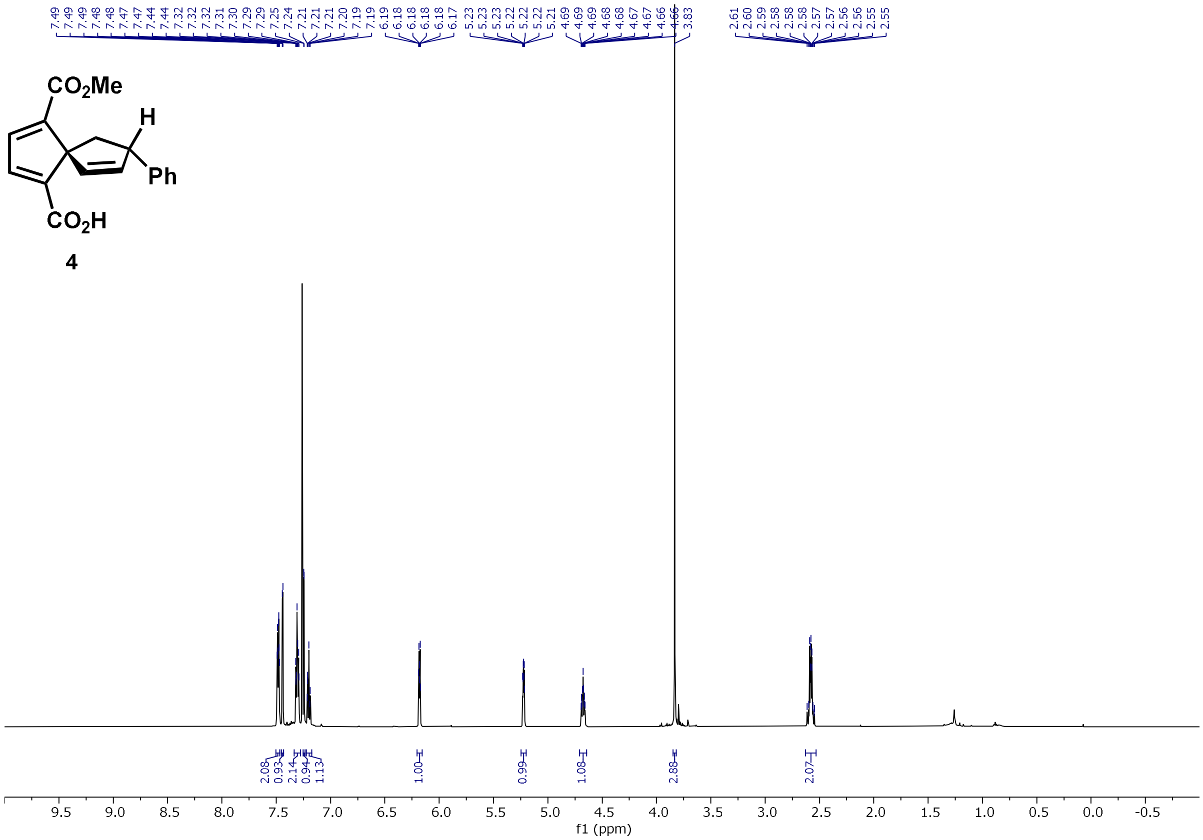
^{1}H-^{1}H COSY (500 MHz, CDCl$_3$)



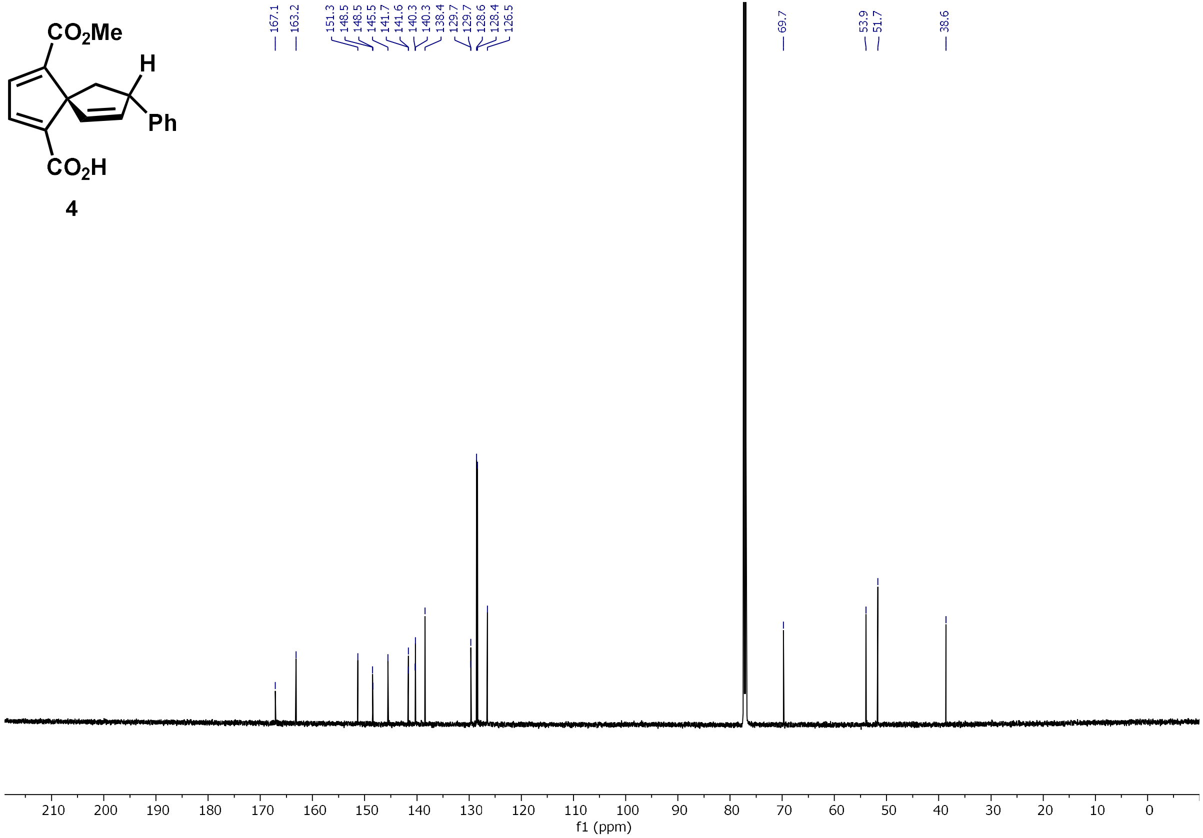
^{1}H-^{1}H NOESY (500 MHz, CDCl$_3$)



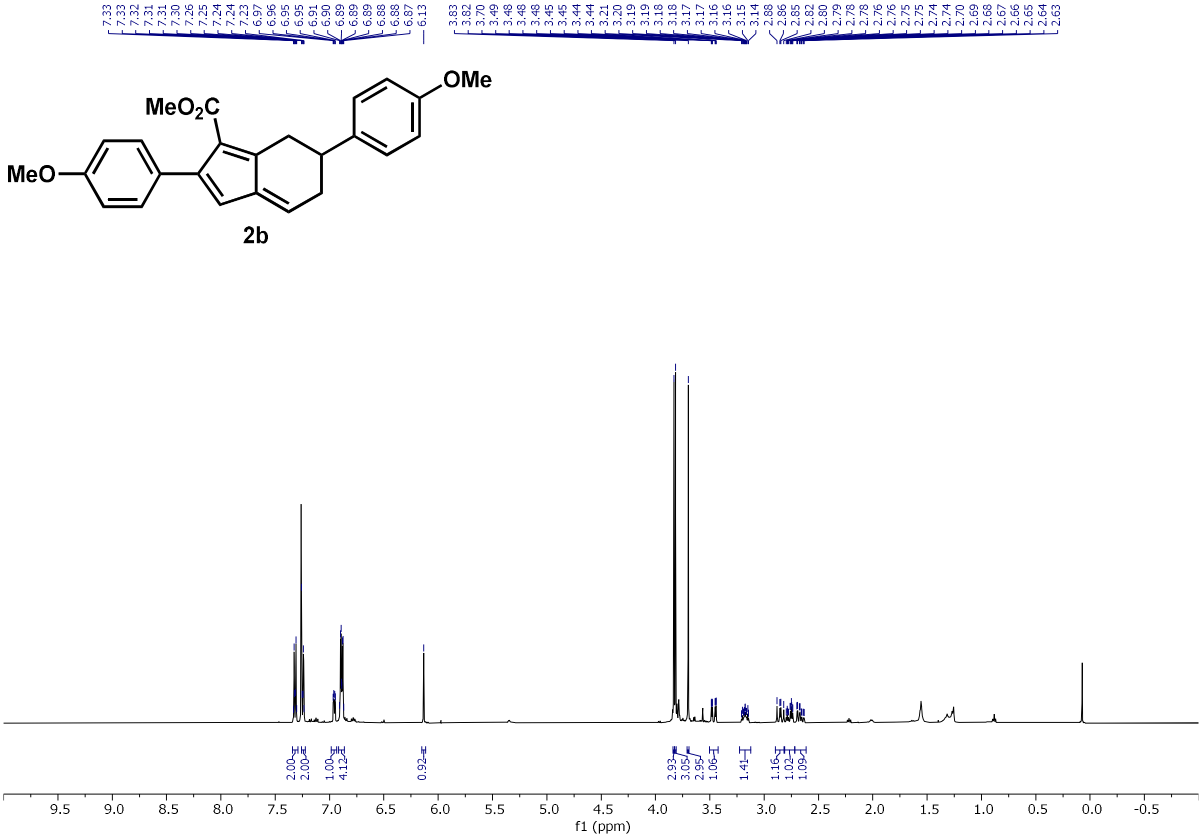
^{1}H NMR (600 MHz, CDCl$_3$)



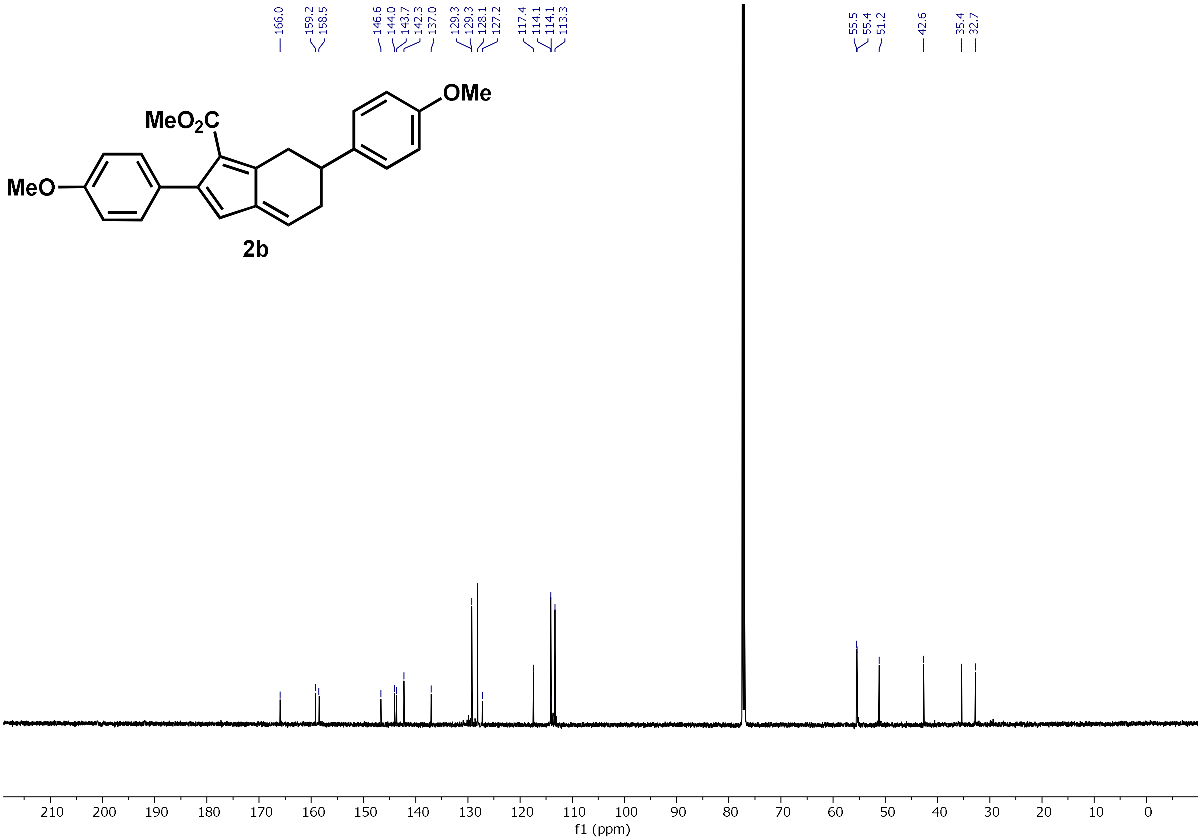
^{13}C NMR (151 MHz, CDCl$_3$)



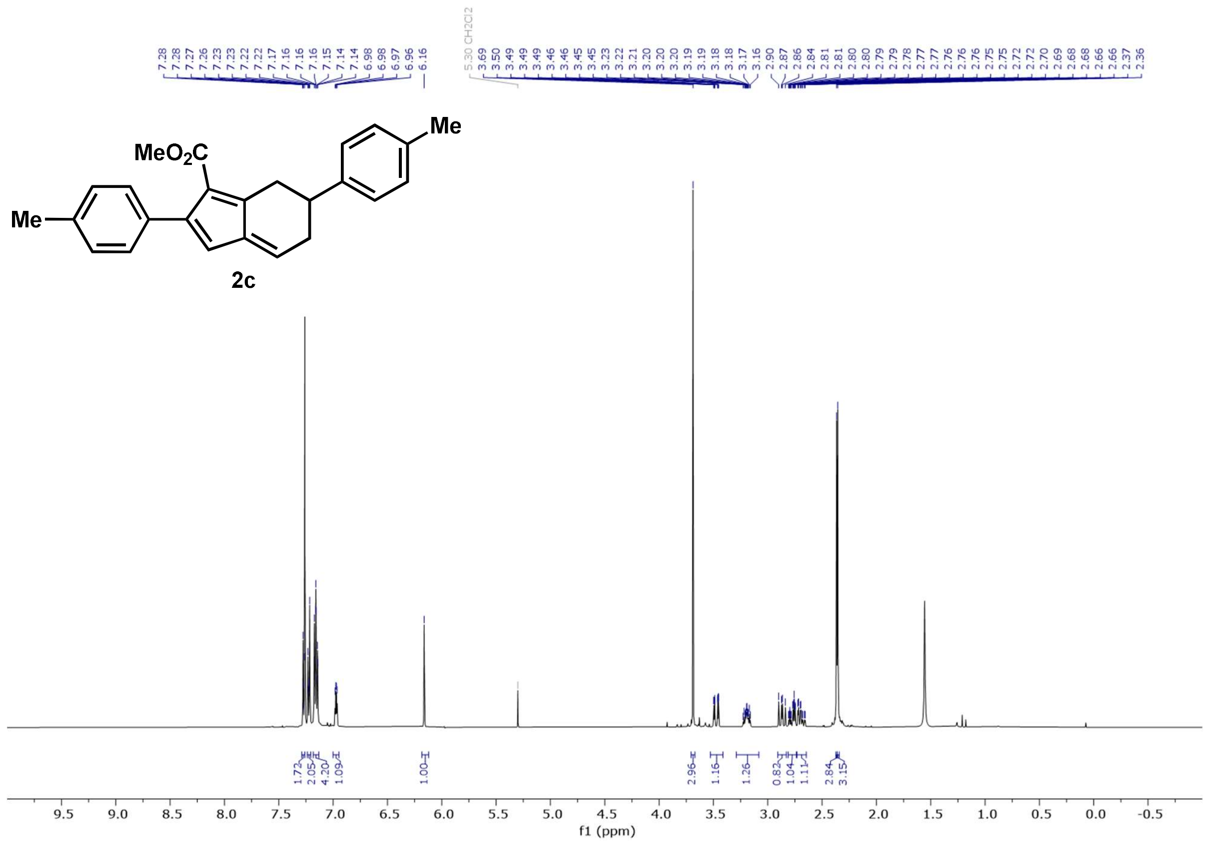
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (151 MHz, $CDCl_3$)

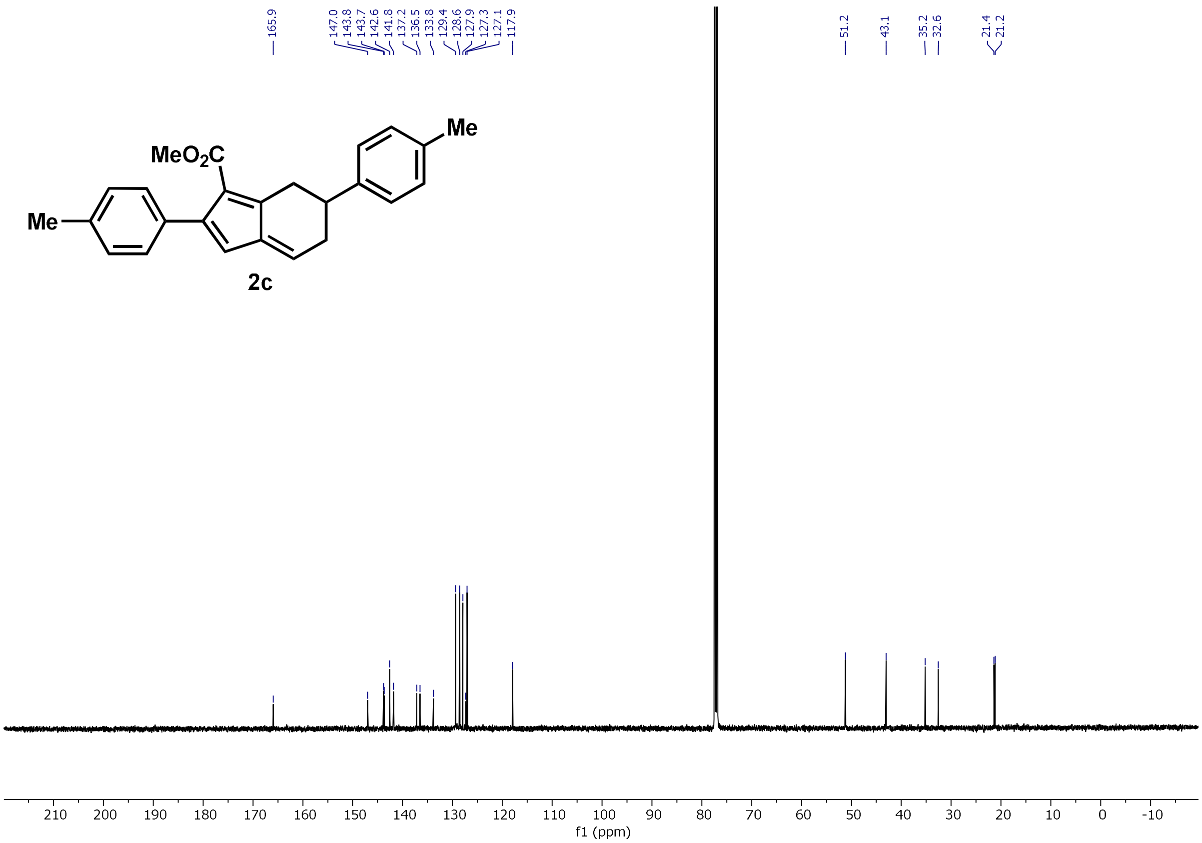


^{1}H NMR (500 MHz, CDCl$_3$)



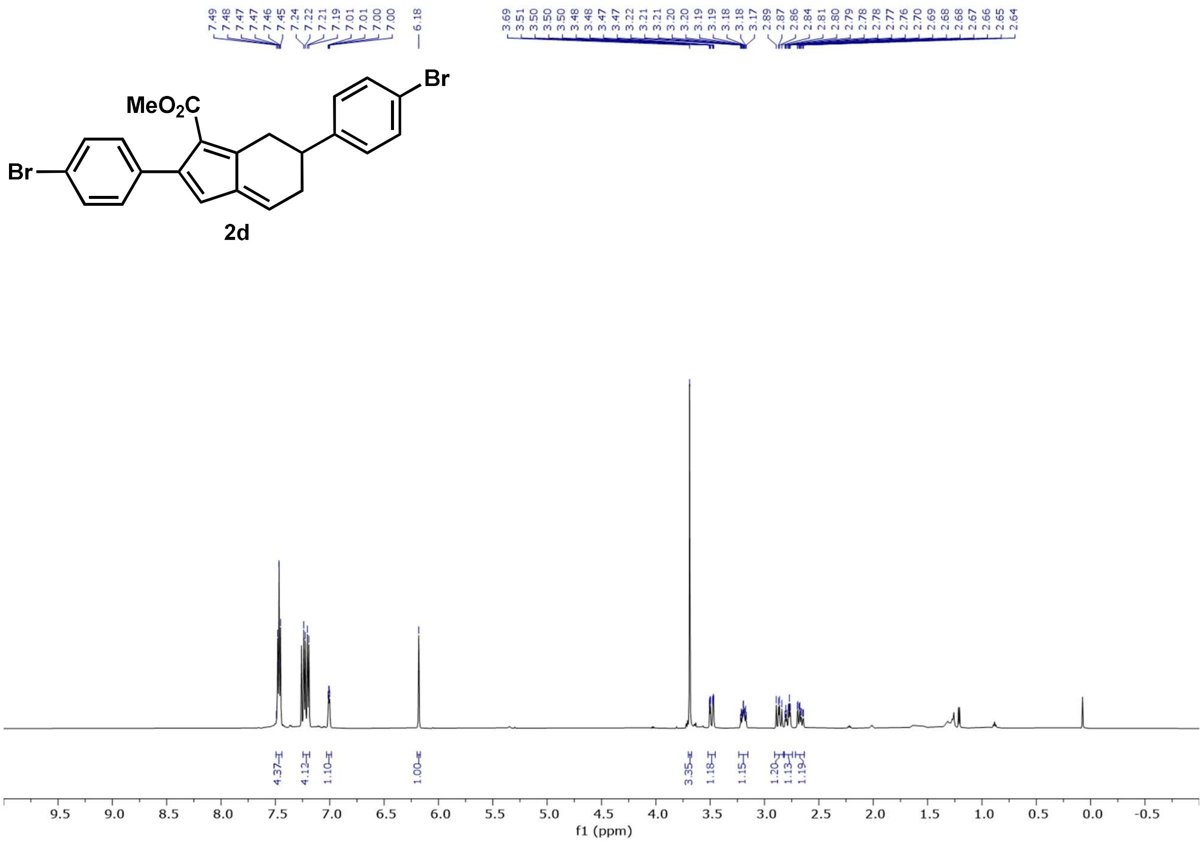
2c

^{13}C NMR (126 MHz, CDCl$_3$)



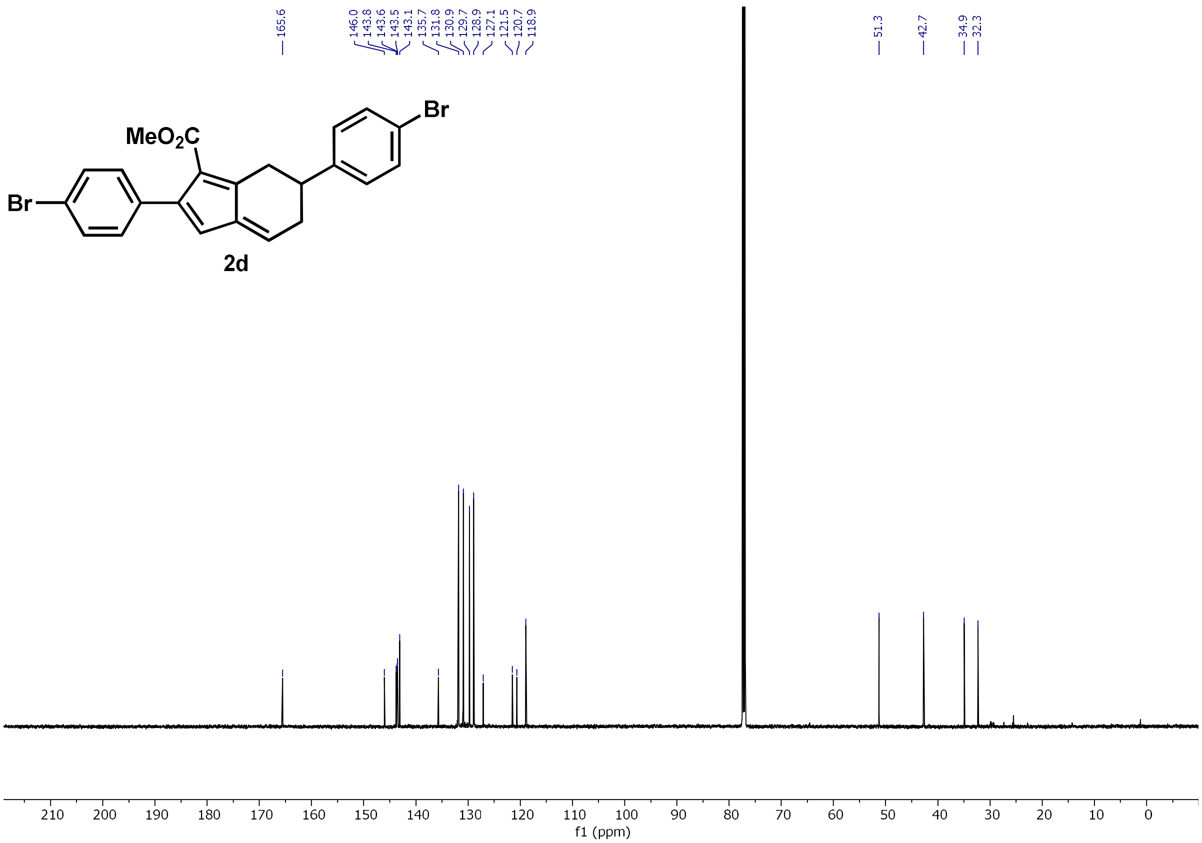
2c

^{1}H NMR (600 MHz, CDCl$_3$)



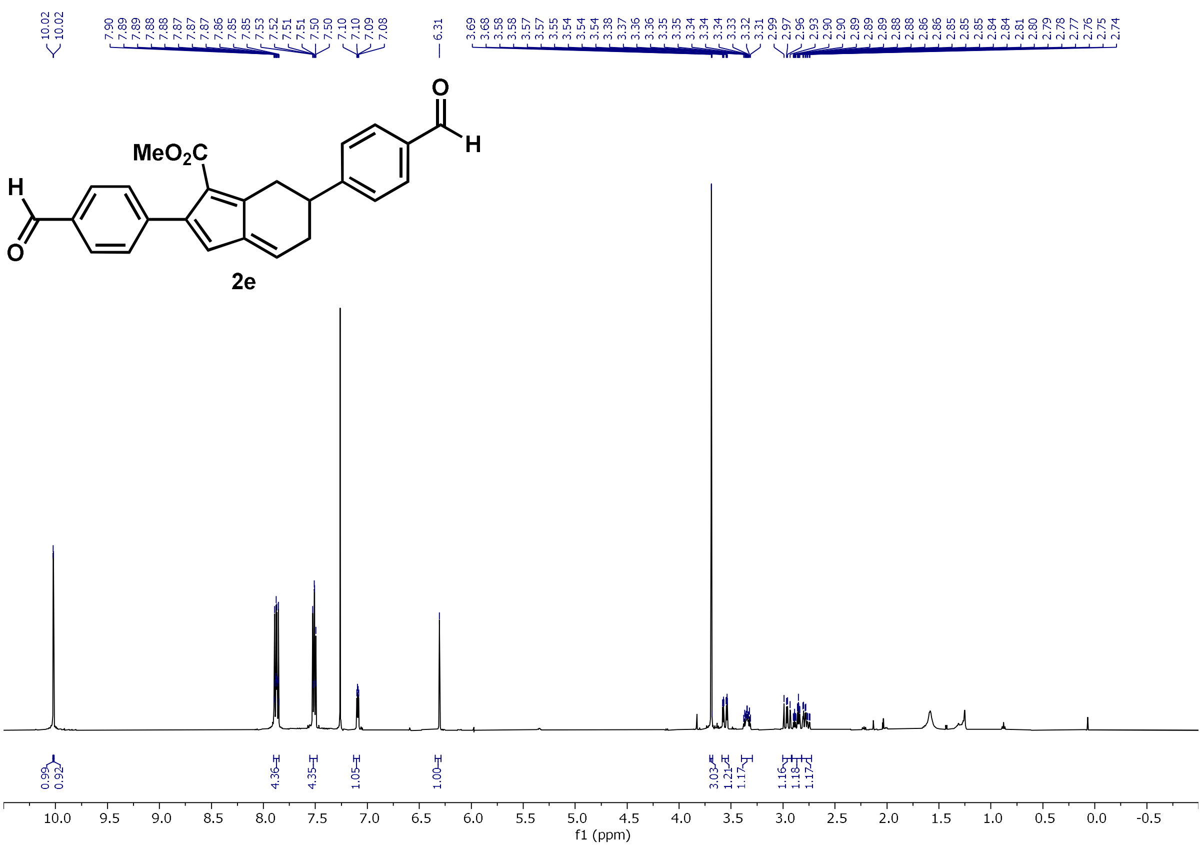
2d

^{13}C NMR (126 MHz, CDCl$_3$)

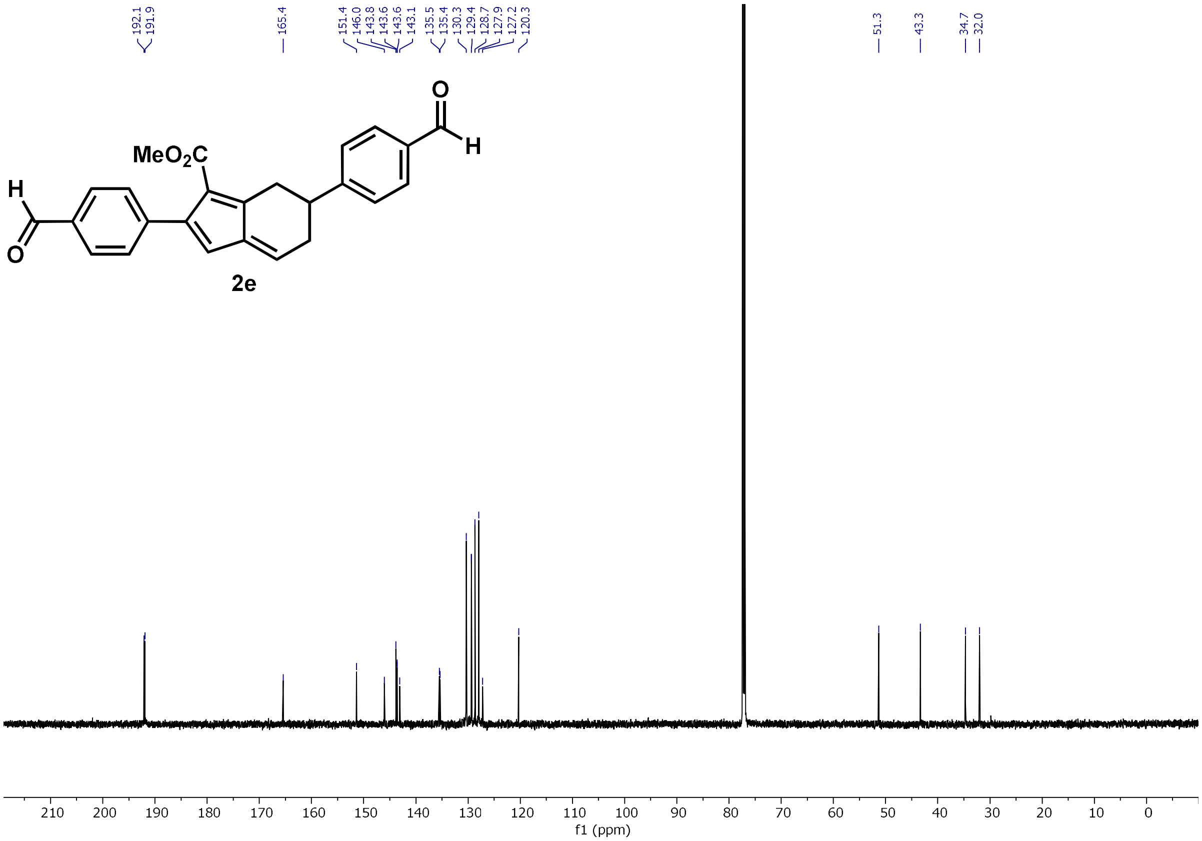


2d

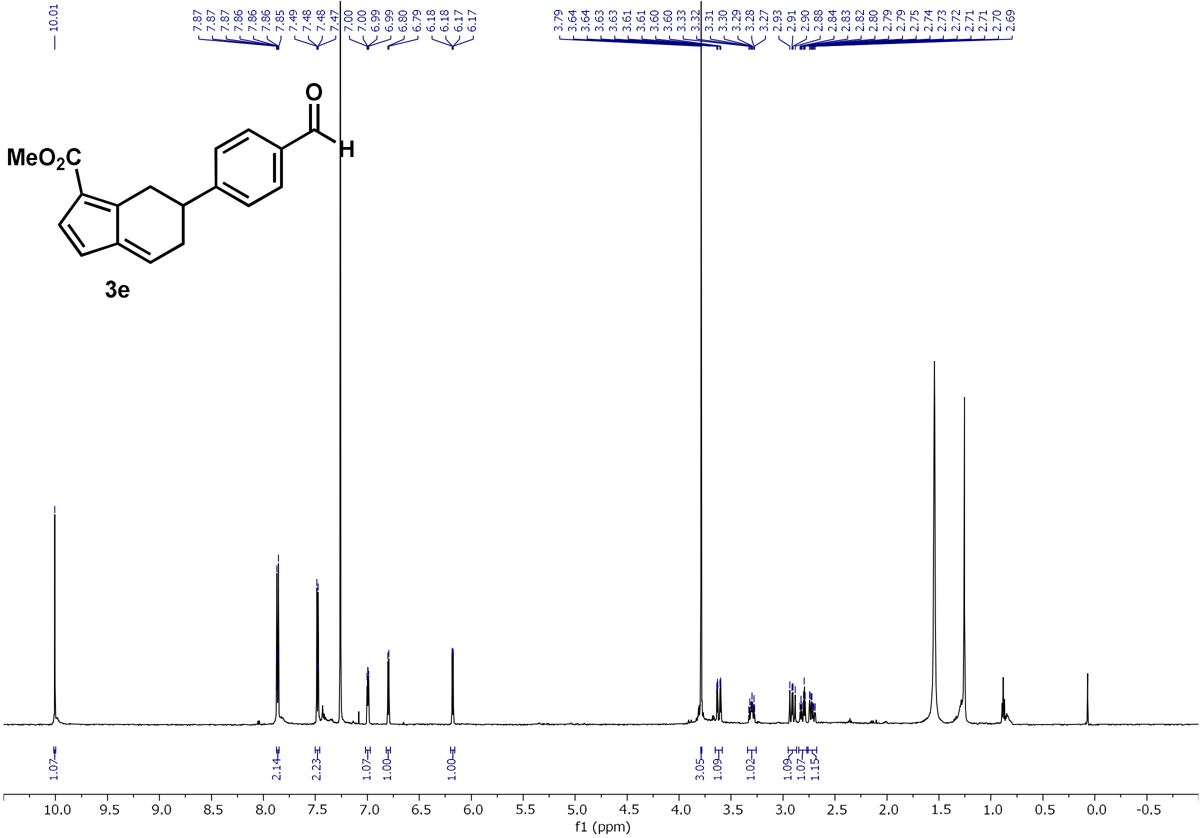
^{1}H NMR (500 MHz, $CDCl_3$)



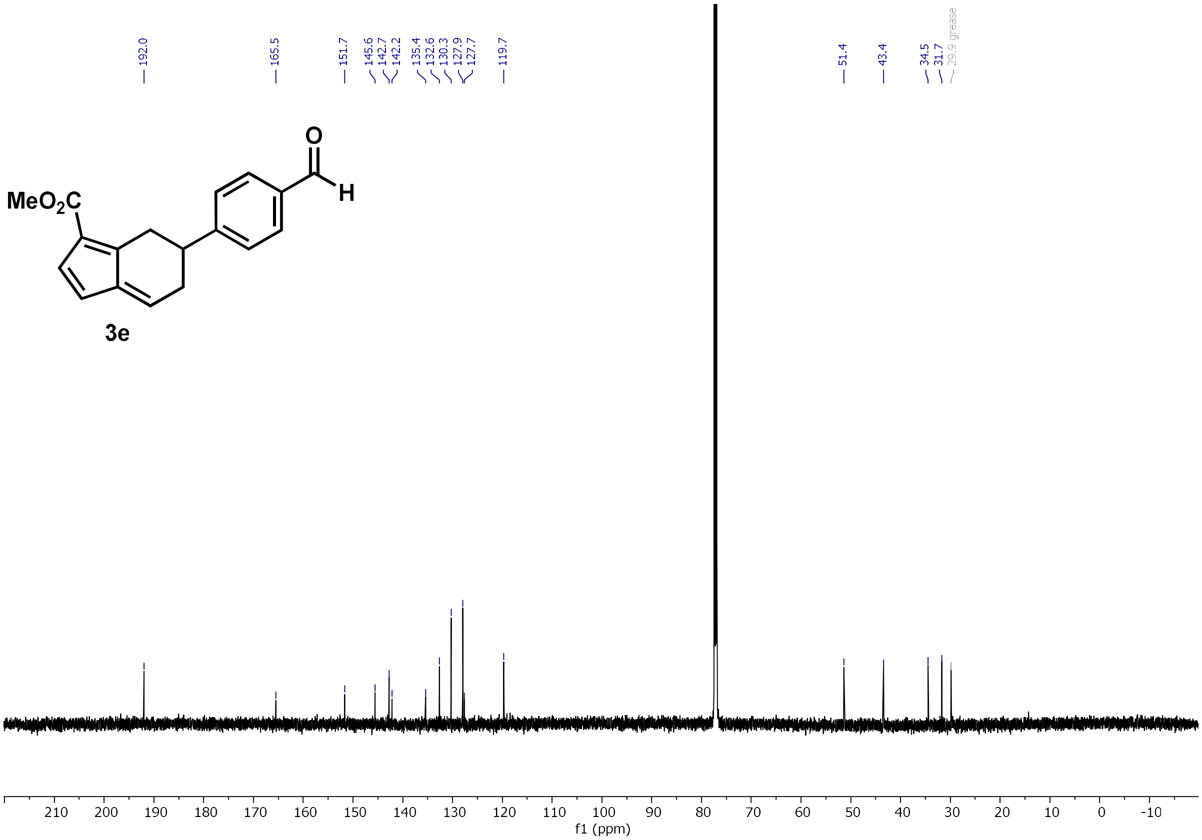
^{13}C NMR (151 MHz, $CDCl_3$)



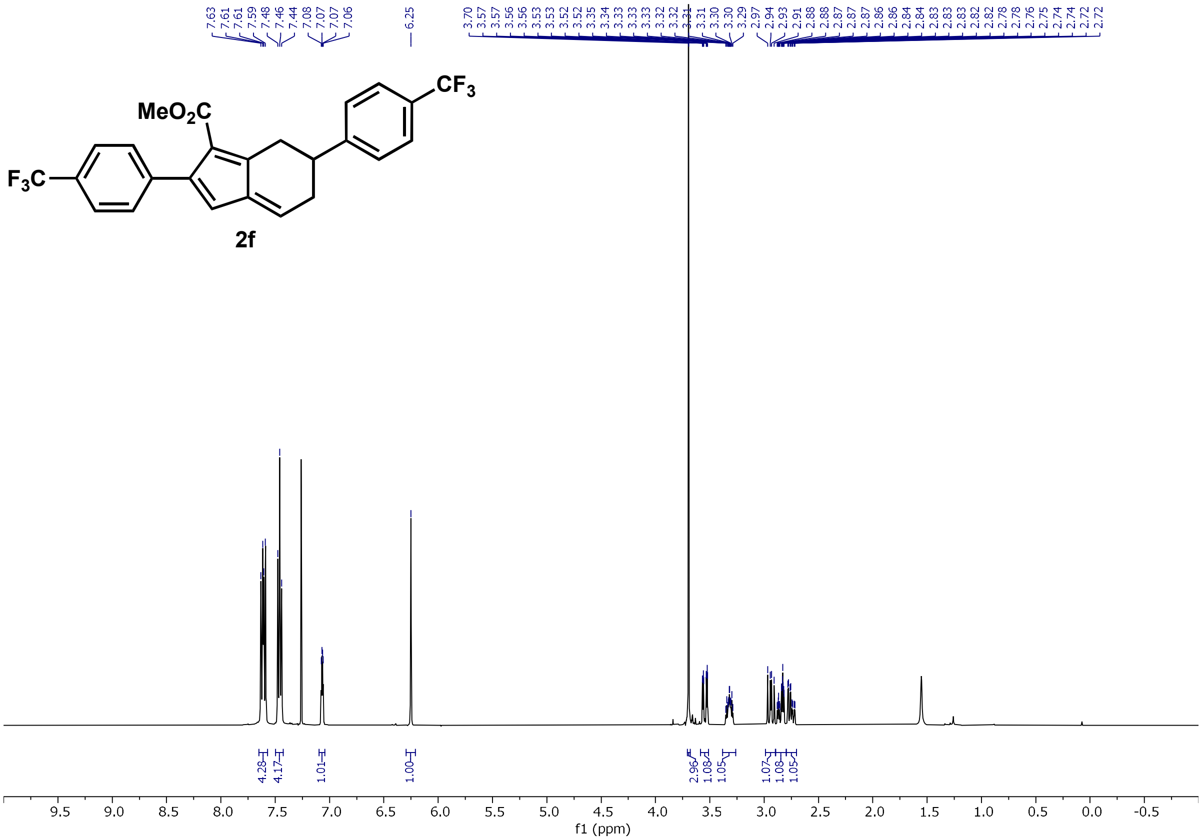
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

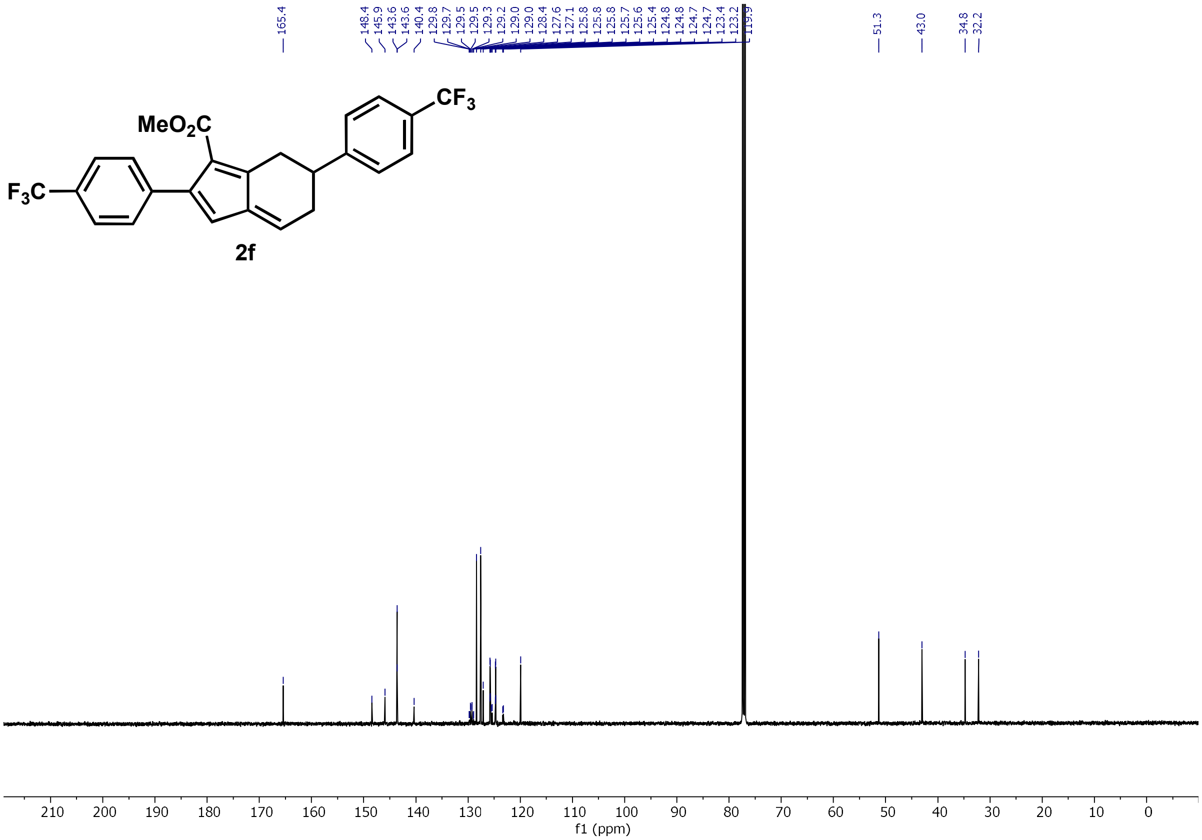


^{1}H NMR (600 MHz, $CDCl_3$)



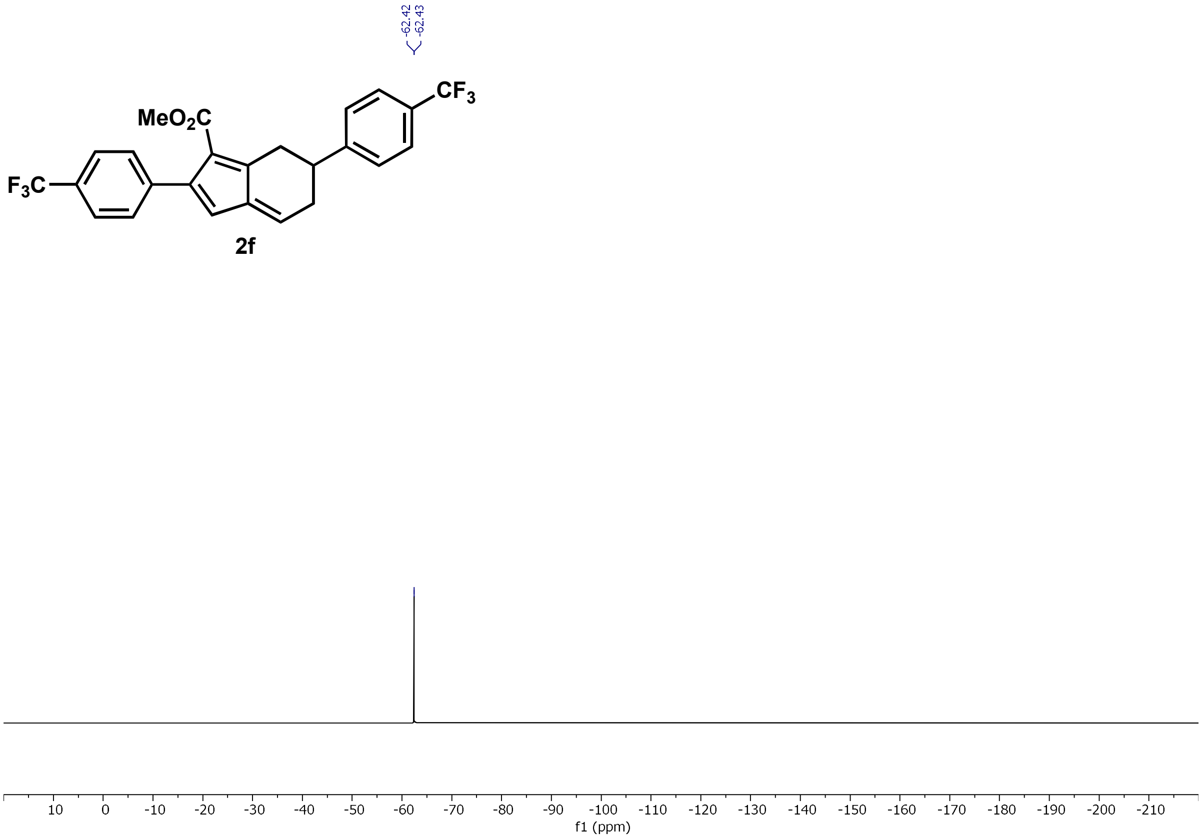
2f

^{13}C NMR (126 MHz, $CDCl_3$)



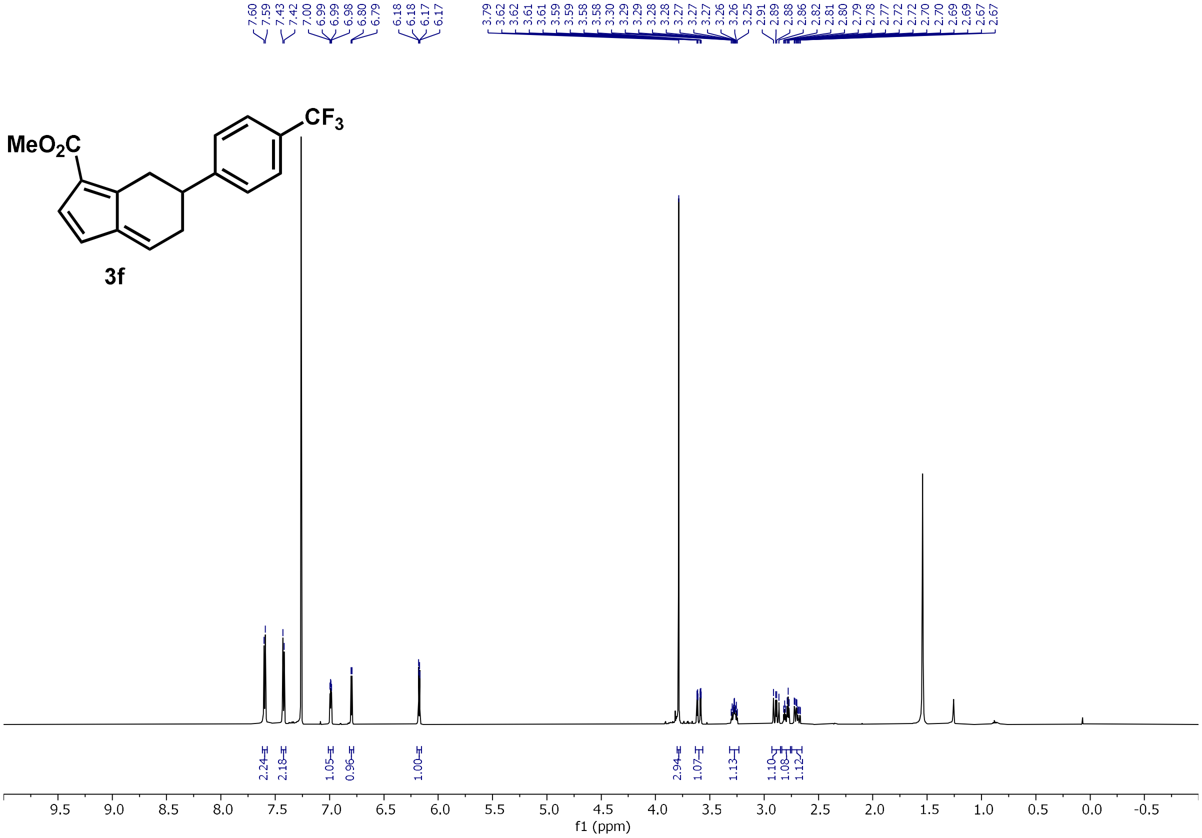
2f

^{19}F NMR (470 MHz, CDCl$_3$)



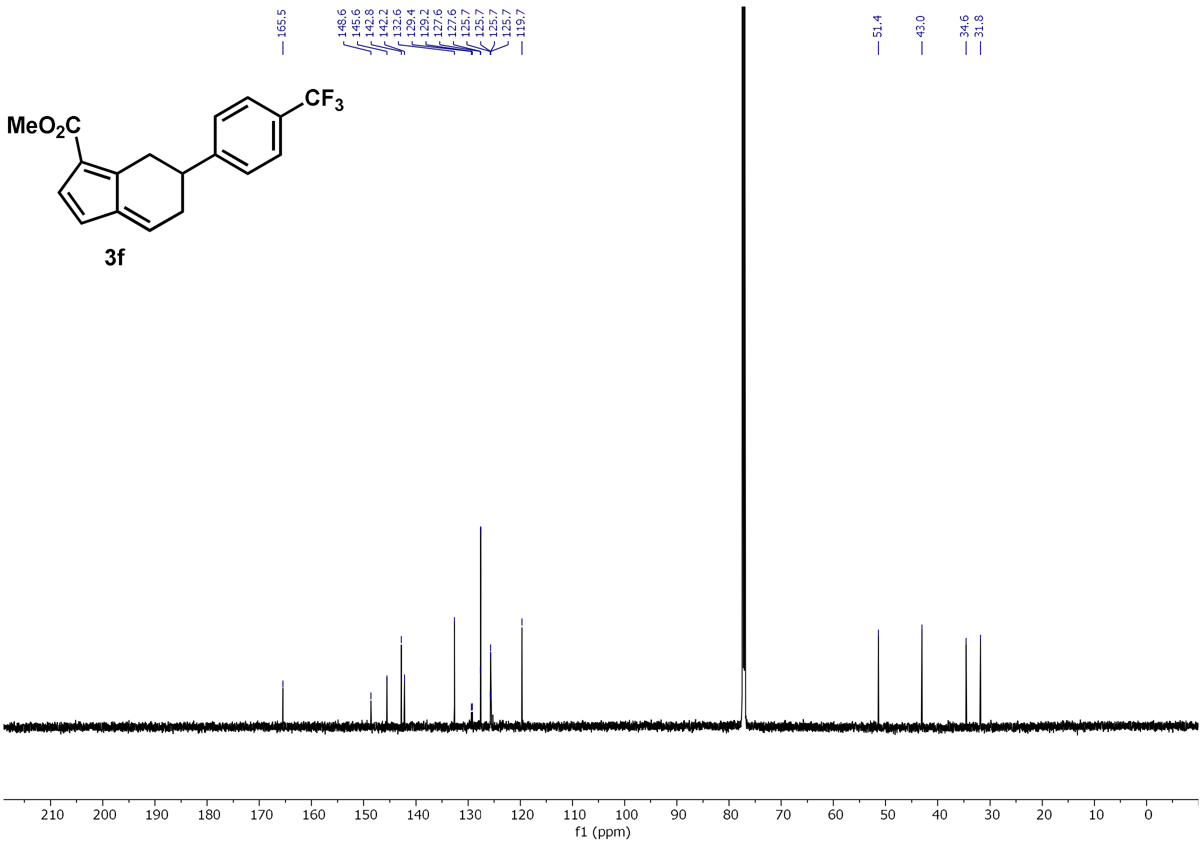
2f

^{1}H NMR (600 MHz, CDCl$_3$)

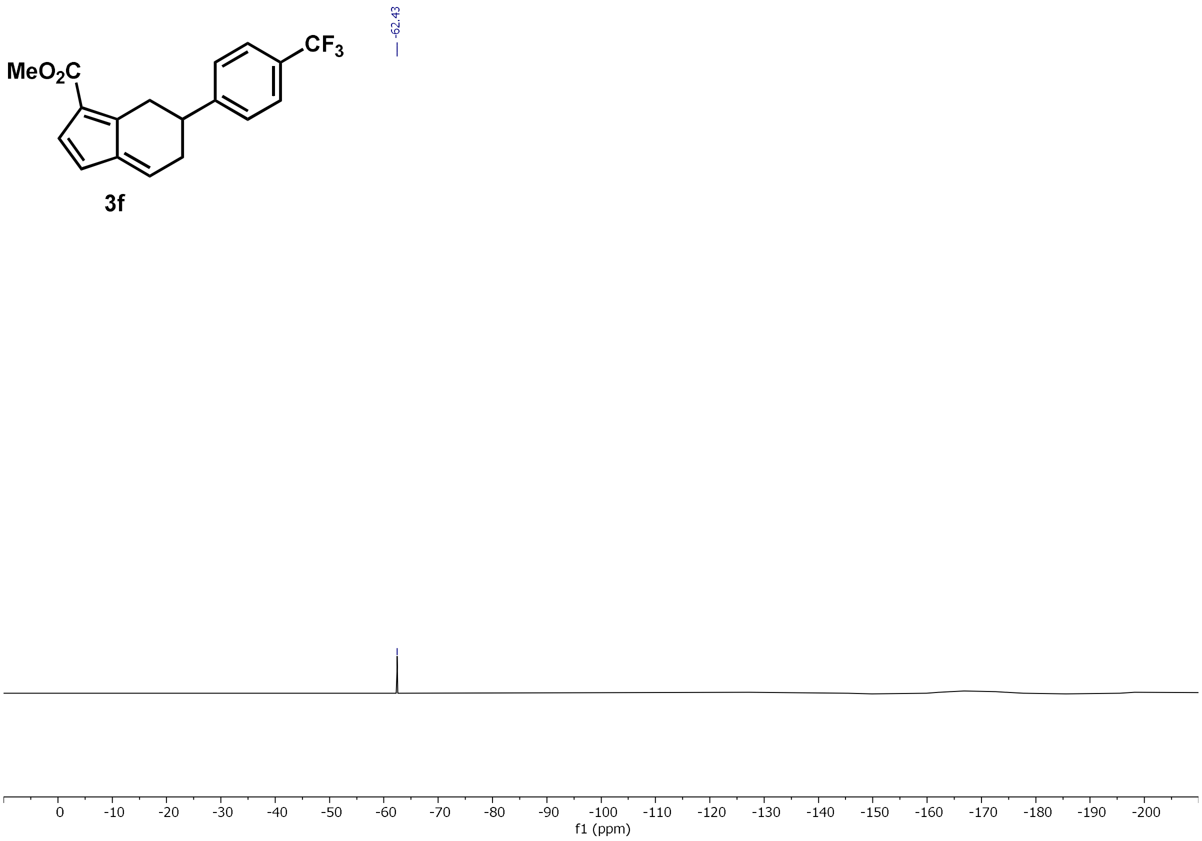


3f

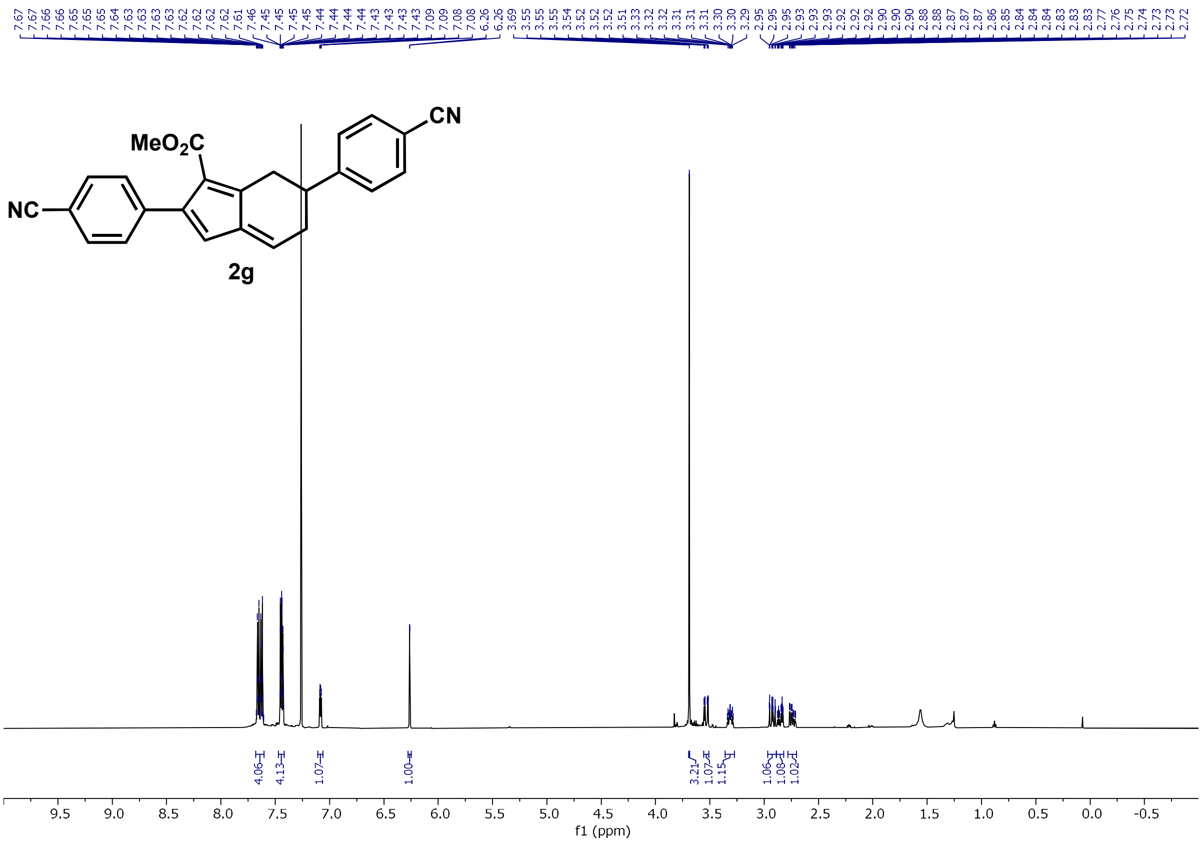
^{13}C NMR (151 MHz, $CDCl_3$)



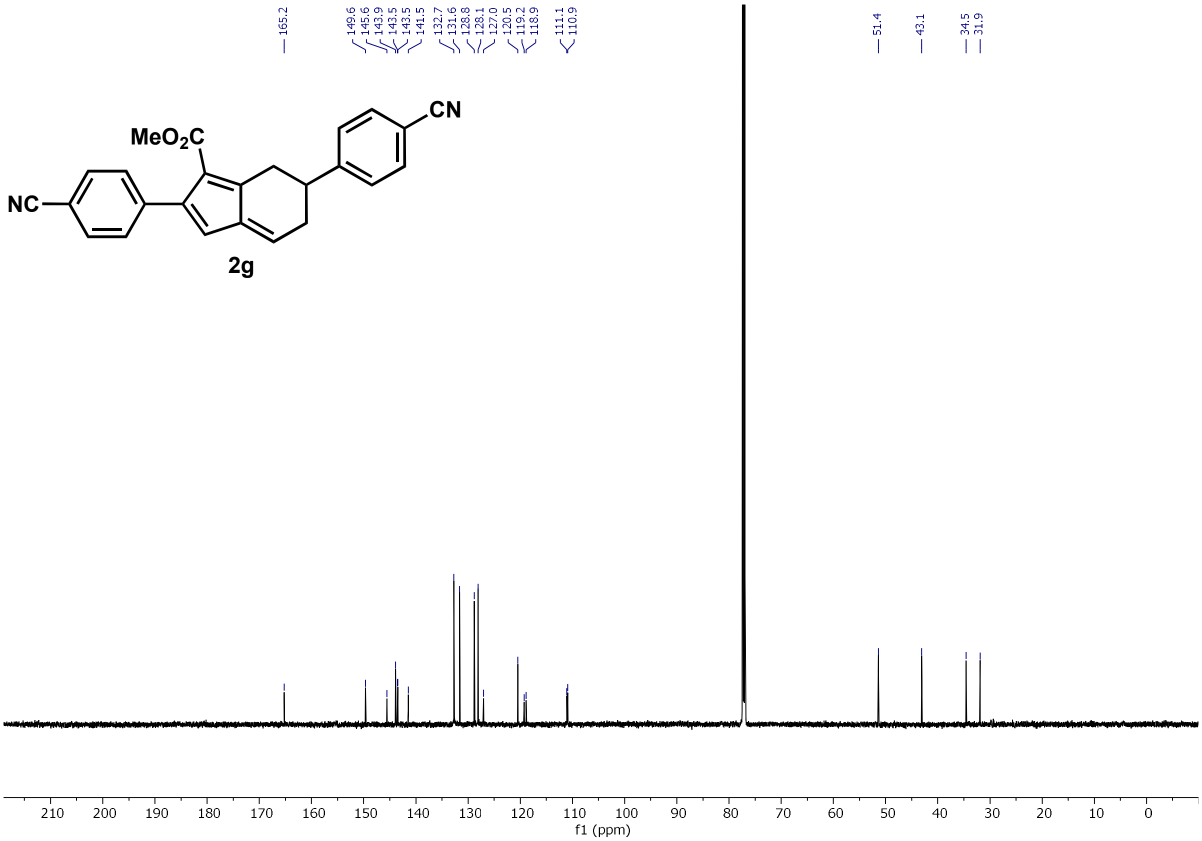
^{19}F NMR (565 MHz, $CDCl_3$)



^1H NMR (600 MHz, $CDCl_3$)

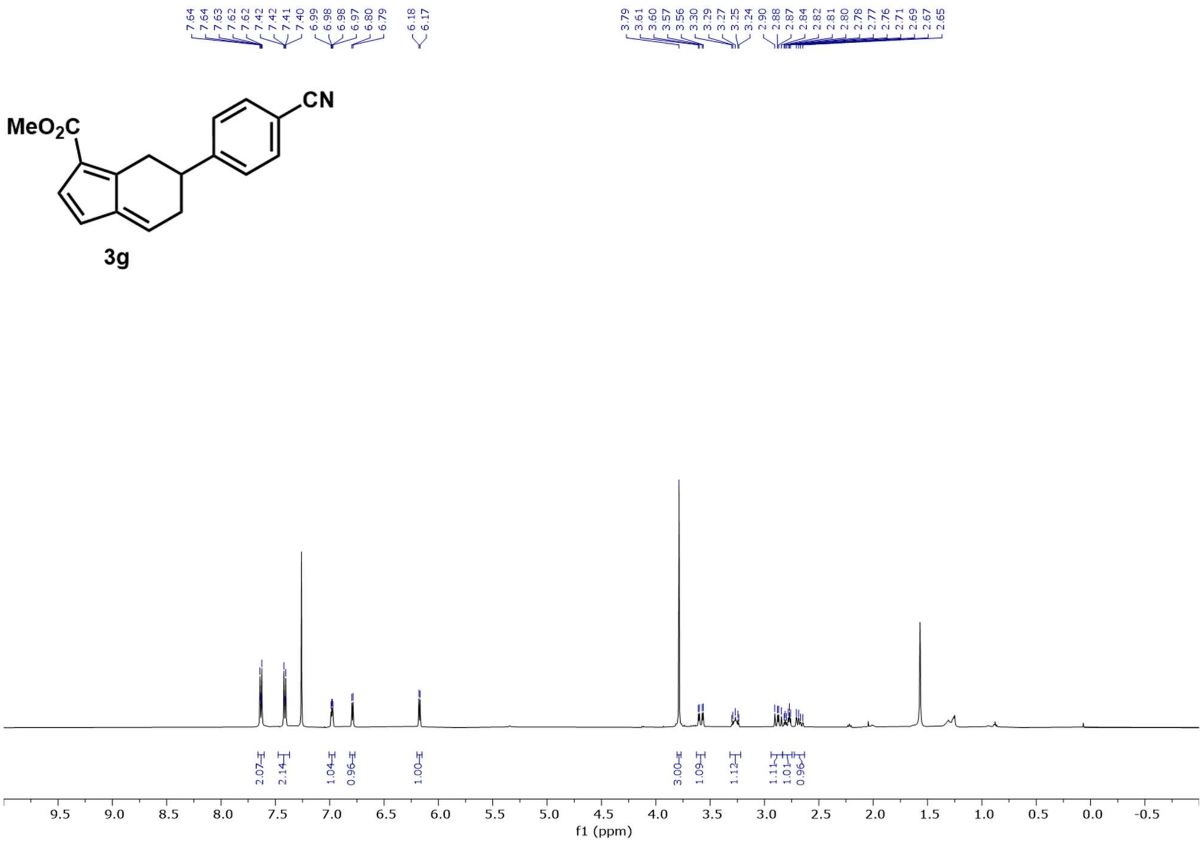


^{13}C NMR (151 MHz, $CDCl_3$)



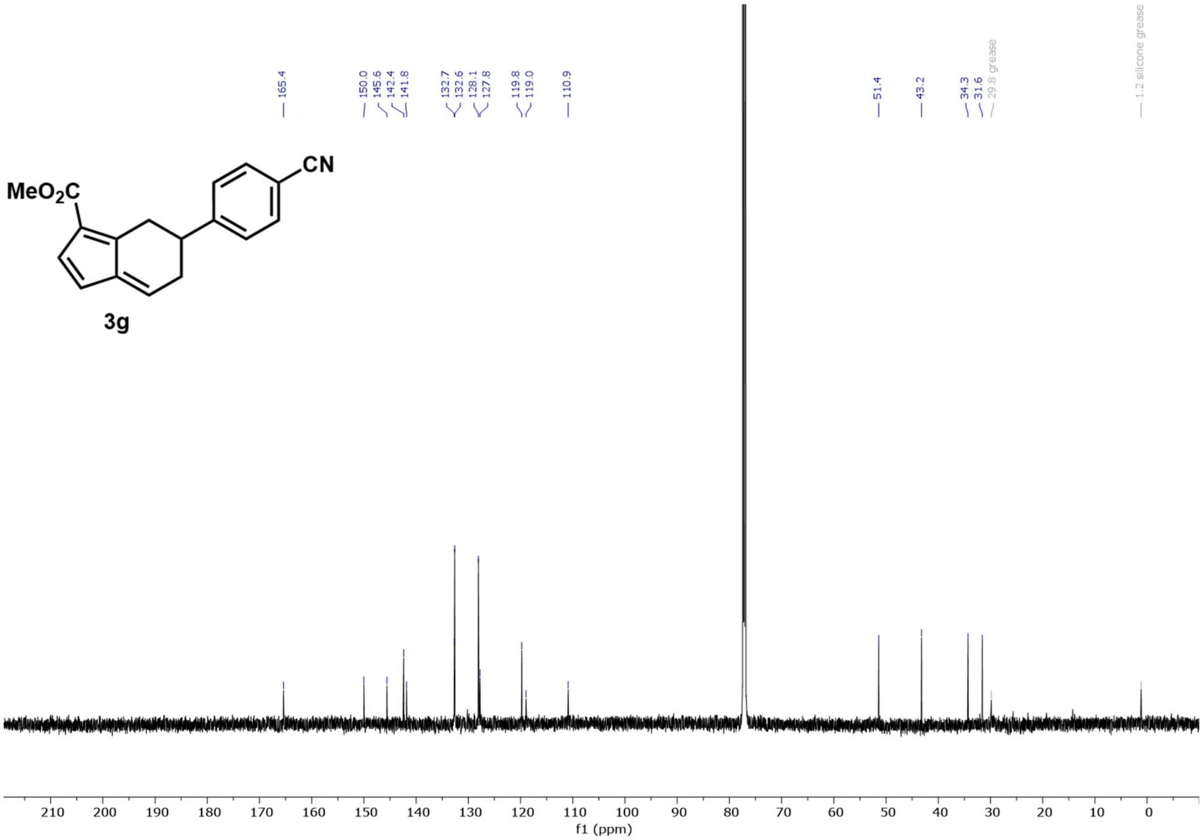
^1H NMR (500 MHz, $CDCl_3$)

3g

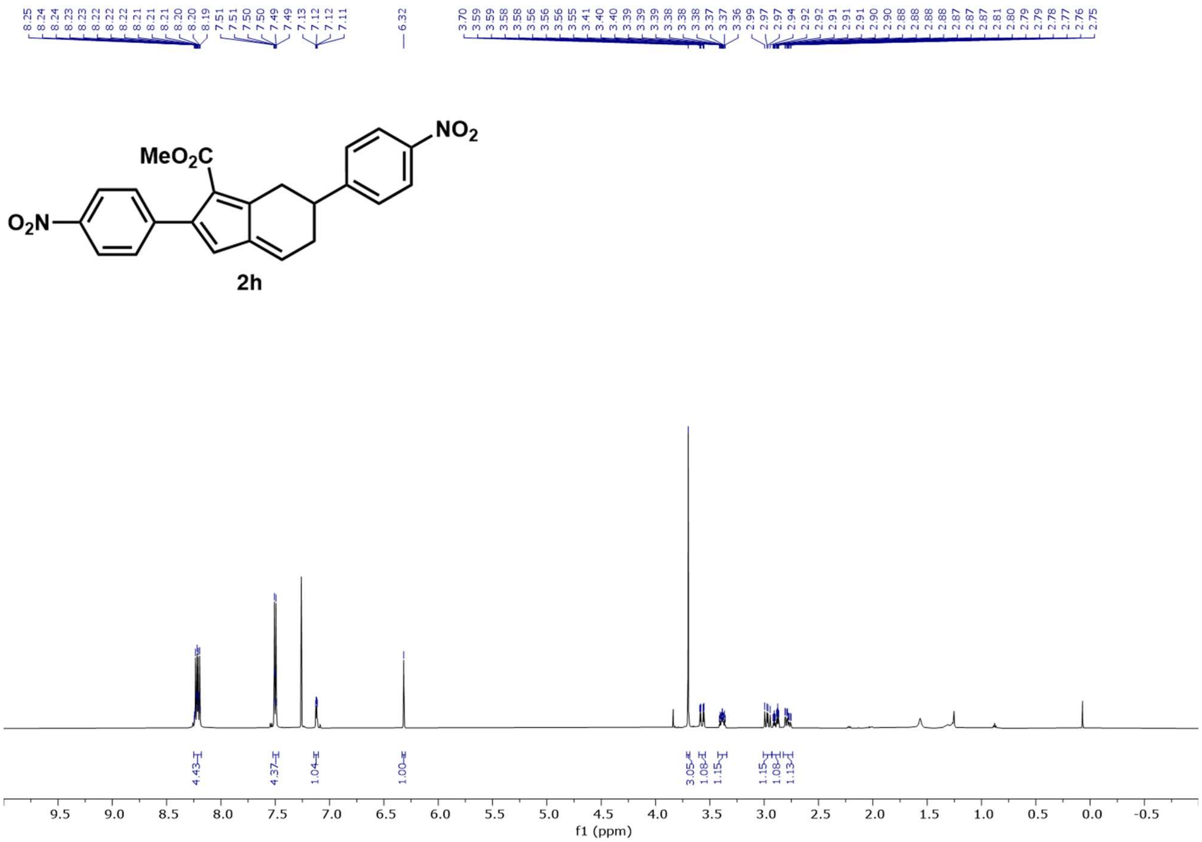


^{13}C NMR (151 MHz, $CDCl_3$)

3g

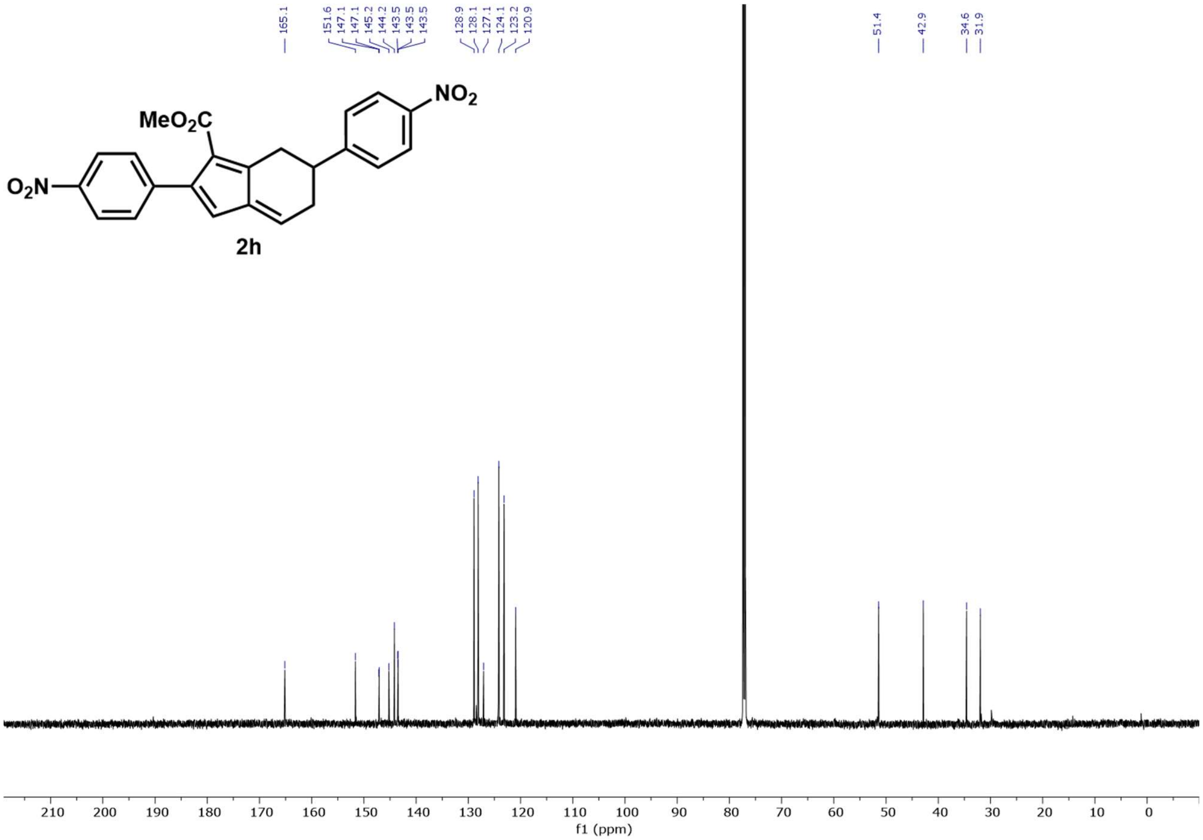


^1H NMR (600 MHz, $CDCl_3$)



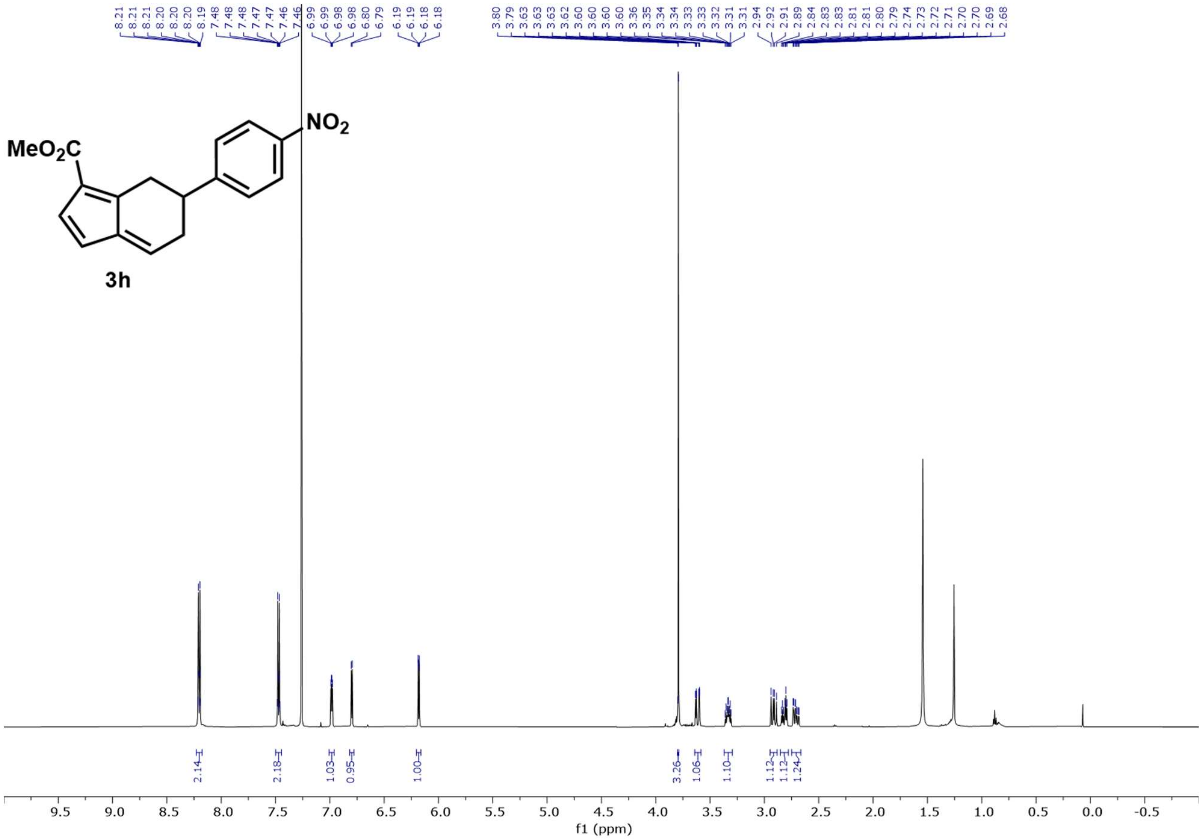
2h

^{13}C NMR (151 MHz, $CDCl_3$)

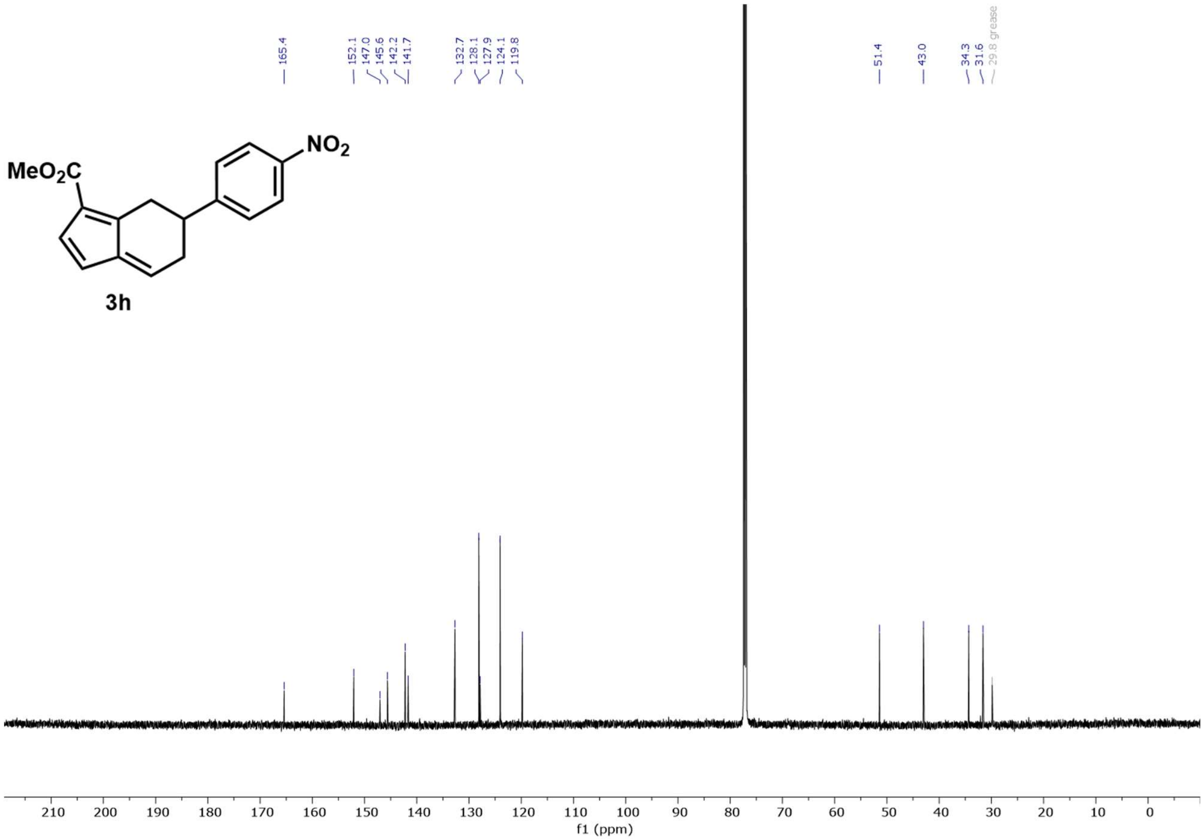


2h

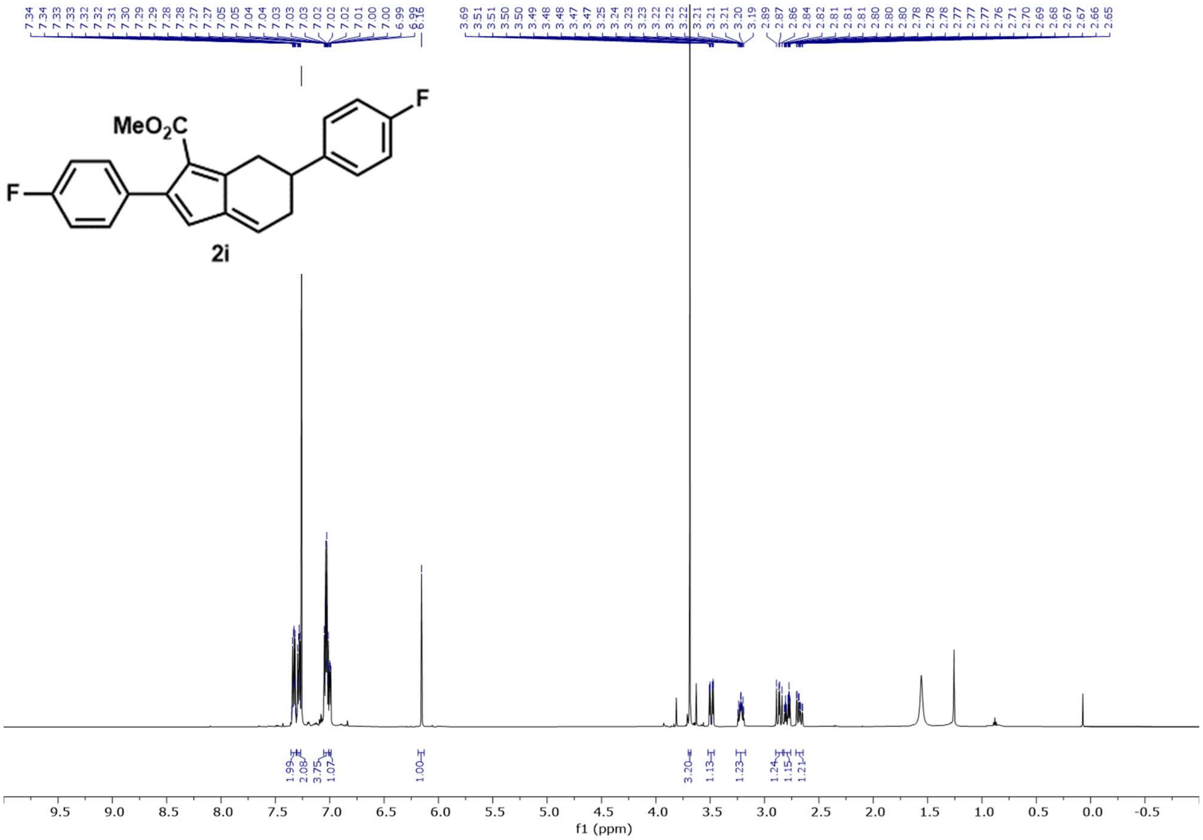
^{1}H NMR (600 MHz, CDCl$_3$)



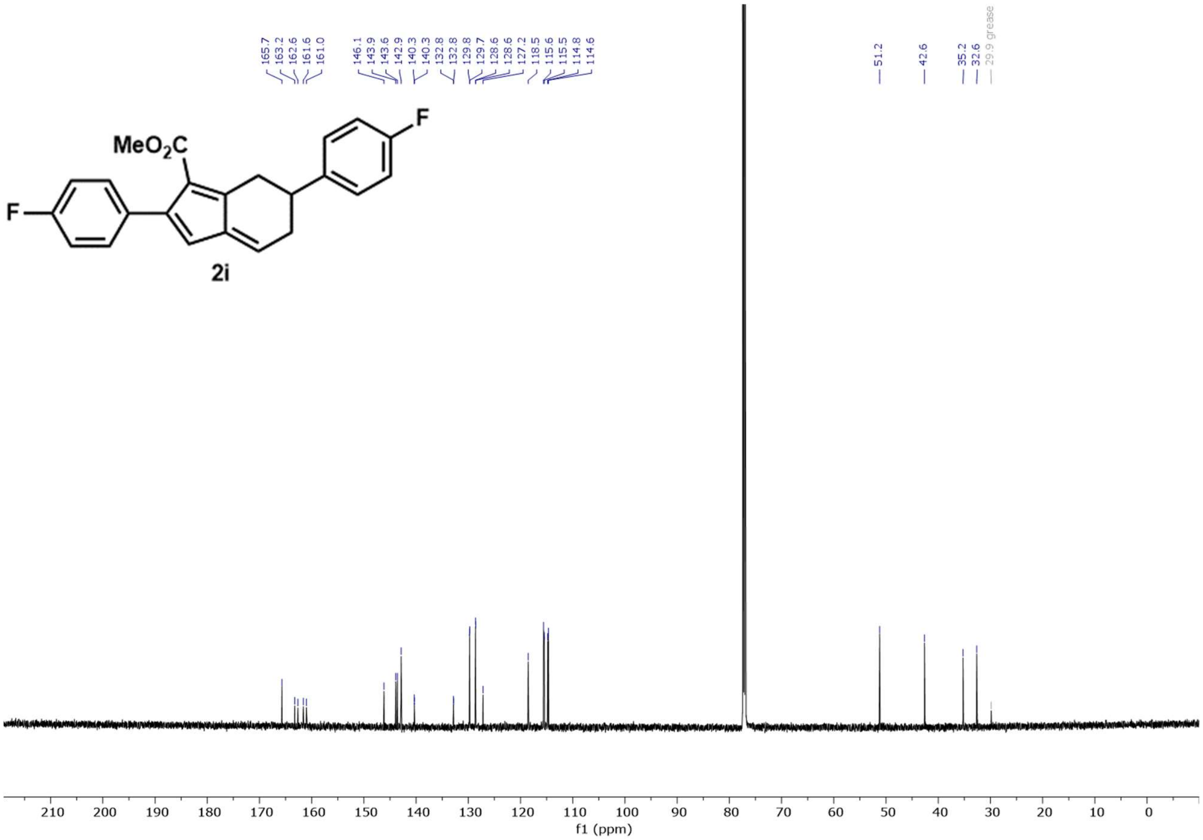
^{13}C NMR (151 MHz, CDCl$_3$)



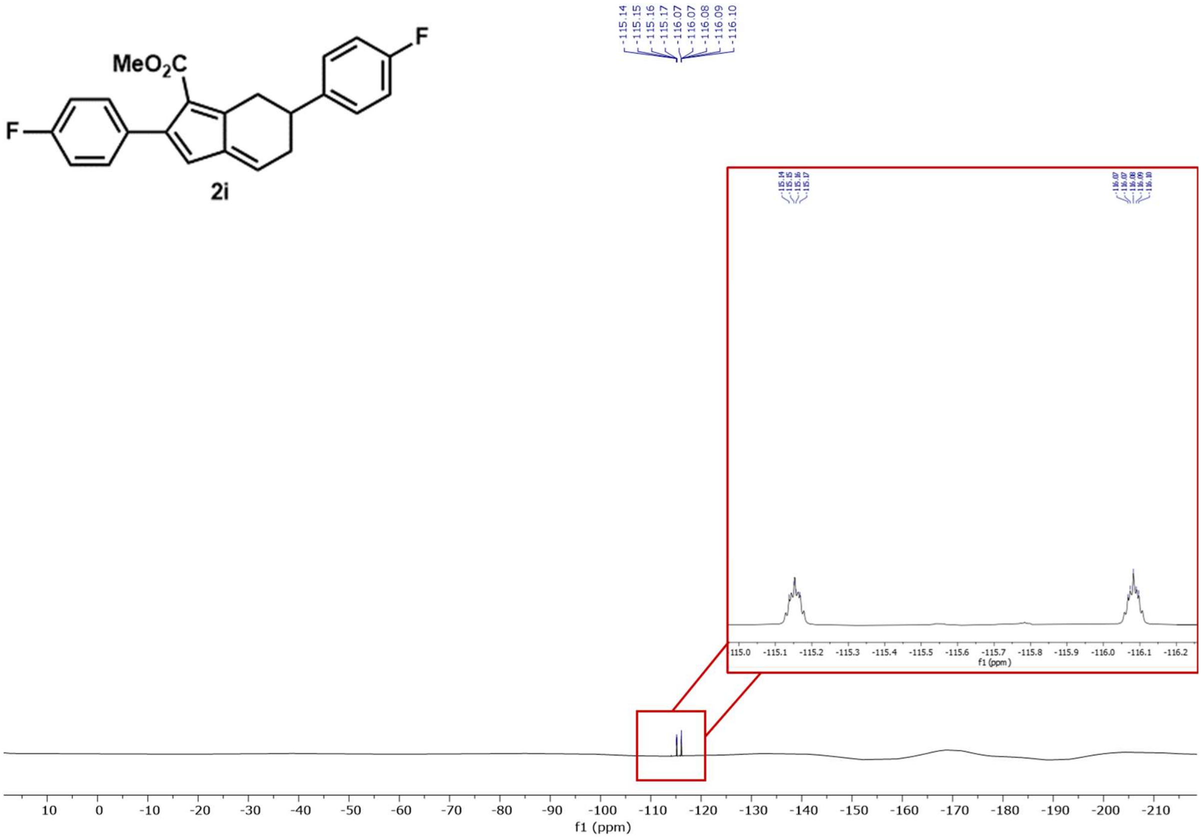
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

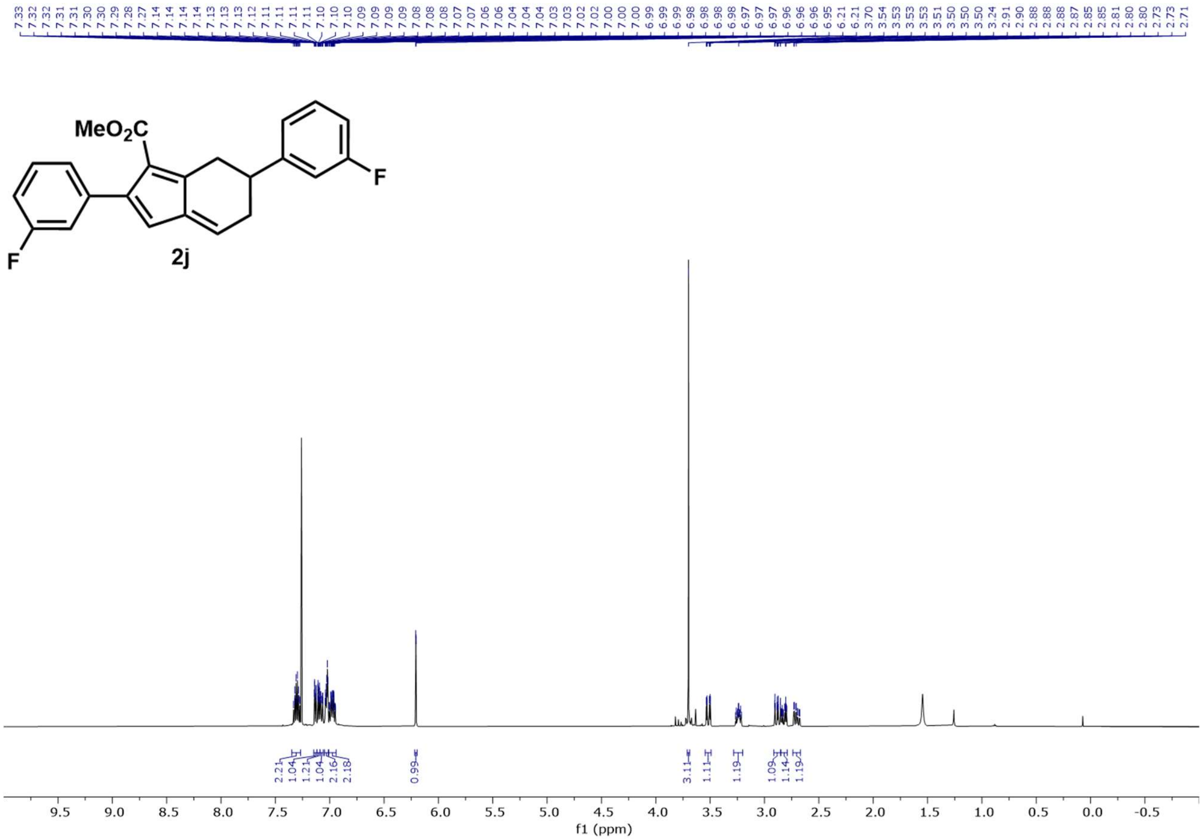


^{19}F NMR (565 MHz, CDCl$_3$)



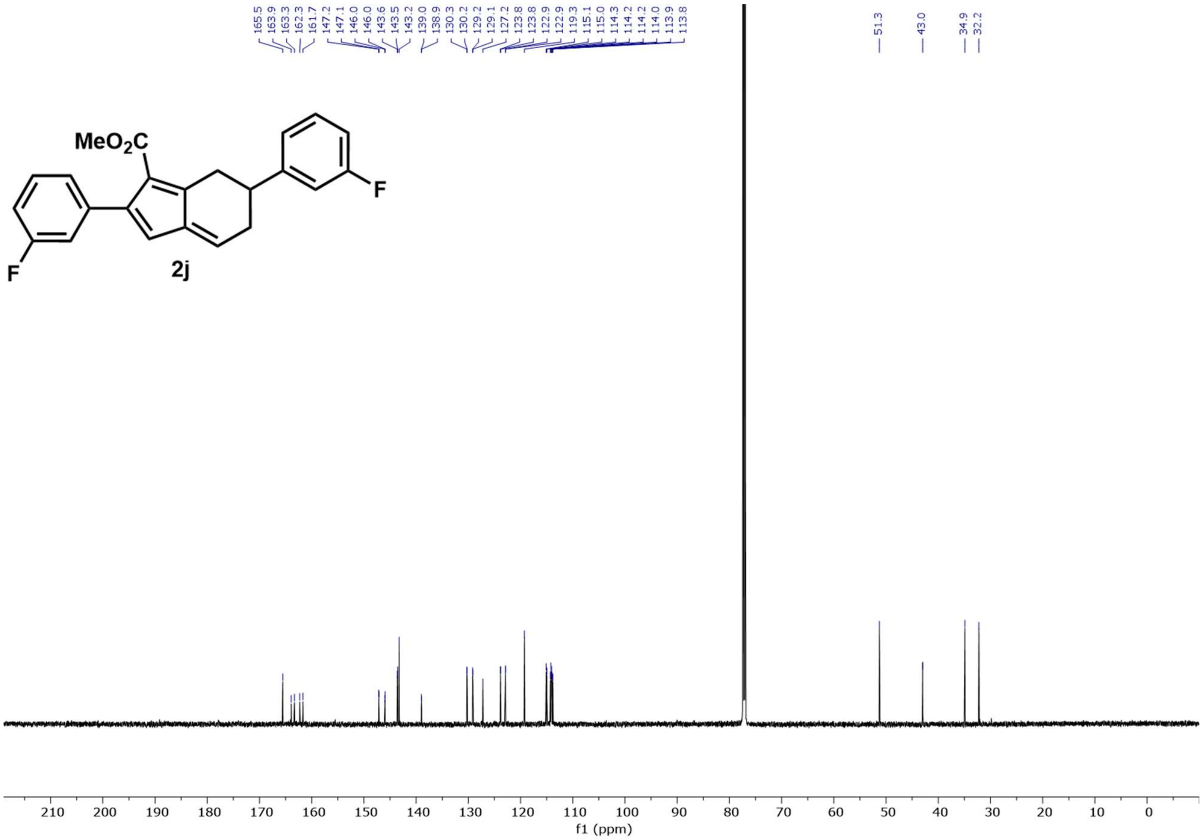
2i

^{1}H NMR (600 MHz, CDCl$_3$)

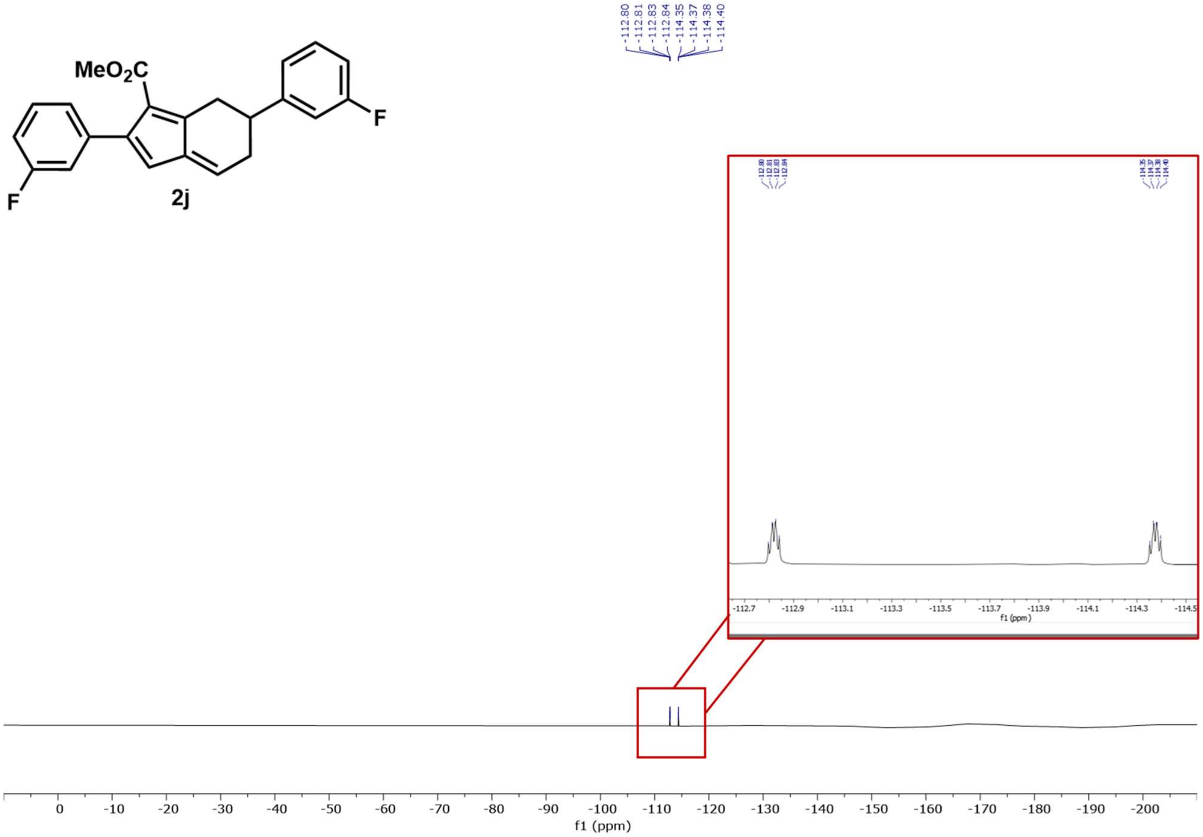


2j

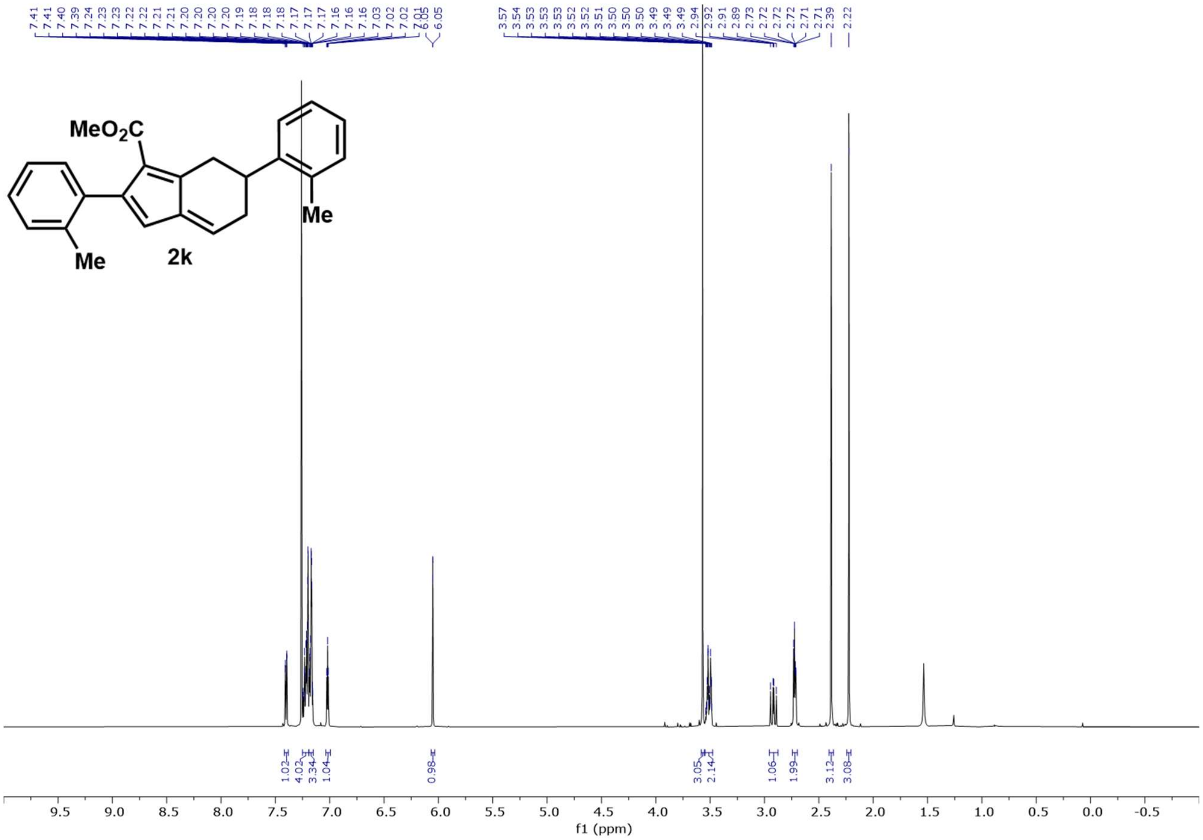
^{13}C NMR (151 MHz, CDCl$_3$)



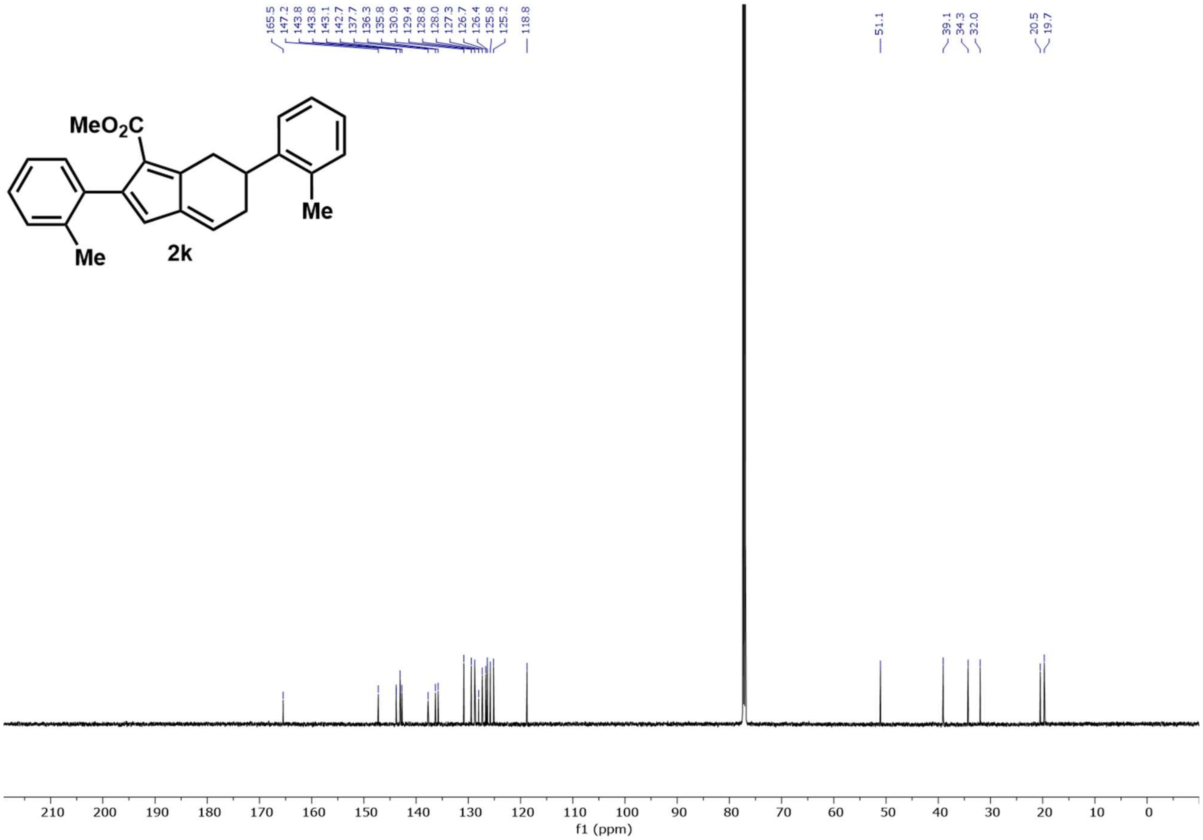
^{19}F NMR (565 MHz, CDCl$_3$)



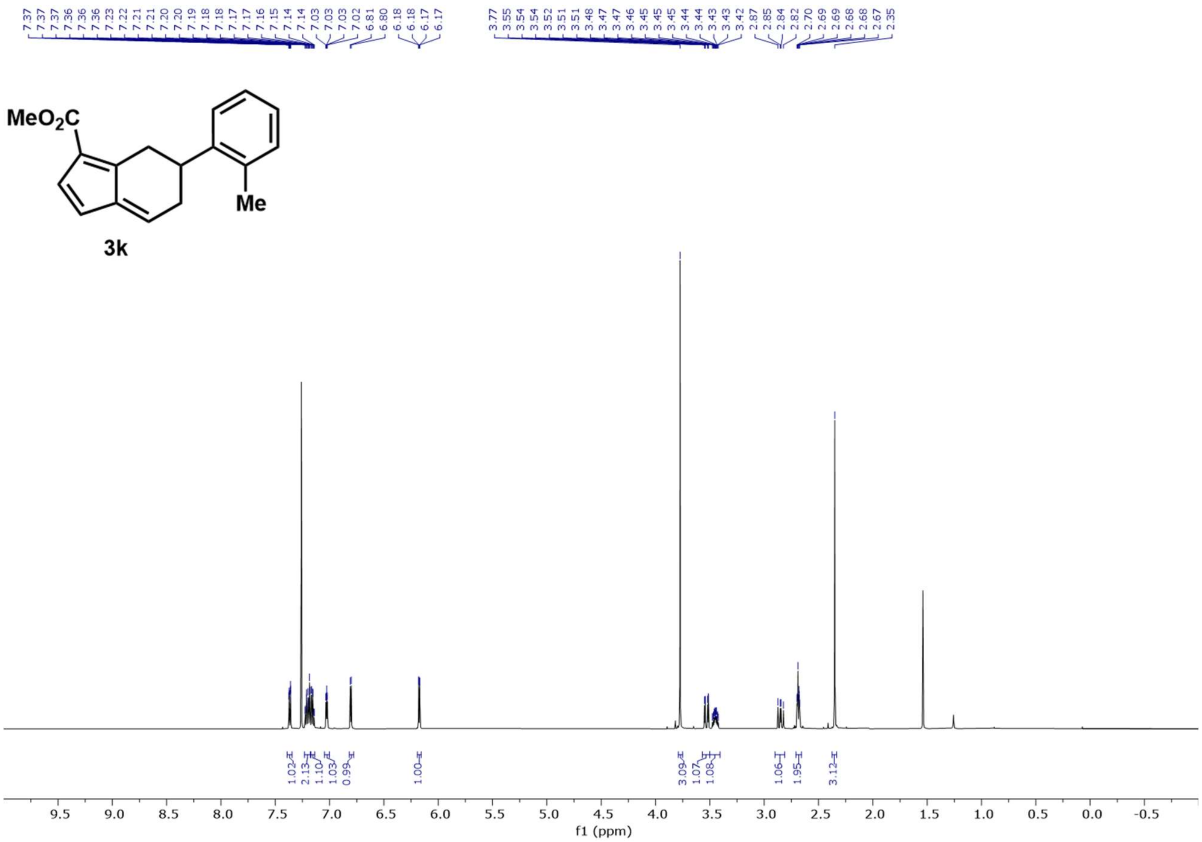
^{1}H NMR (600 MHz, CDCl$_3$)



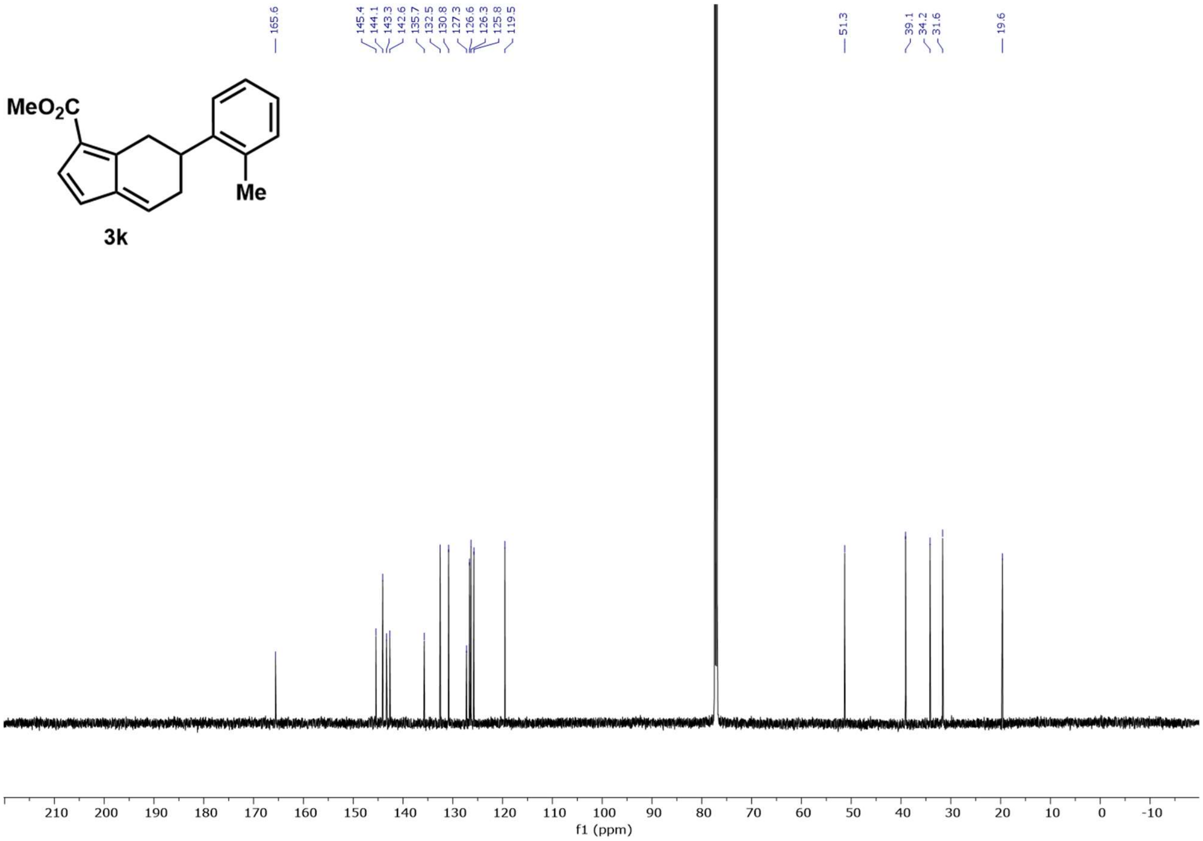
^{13}C NMR (151 MHz, CDCl$_3$)



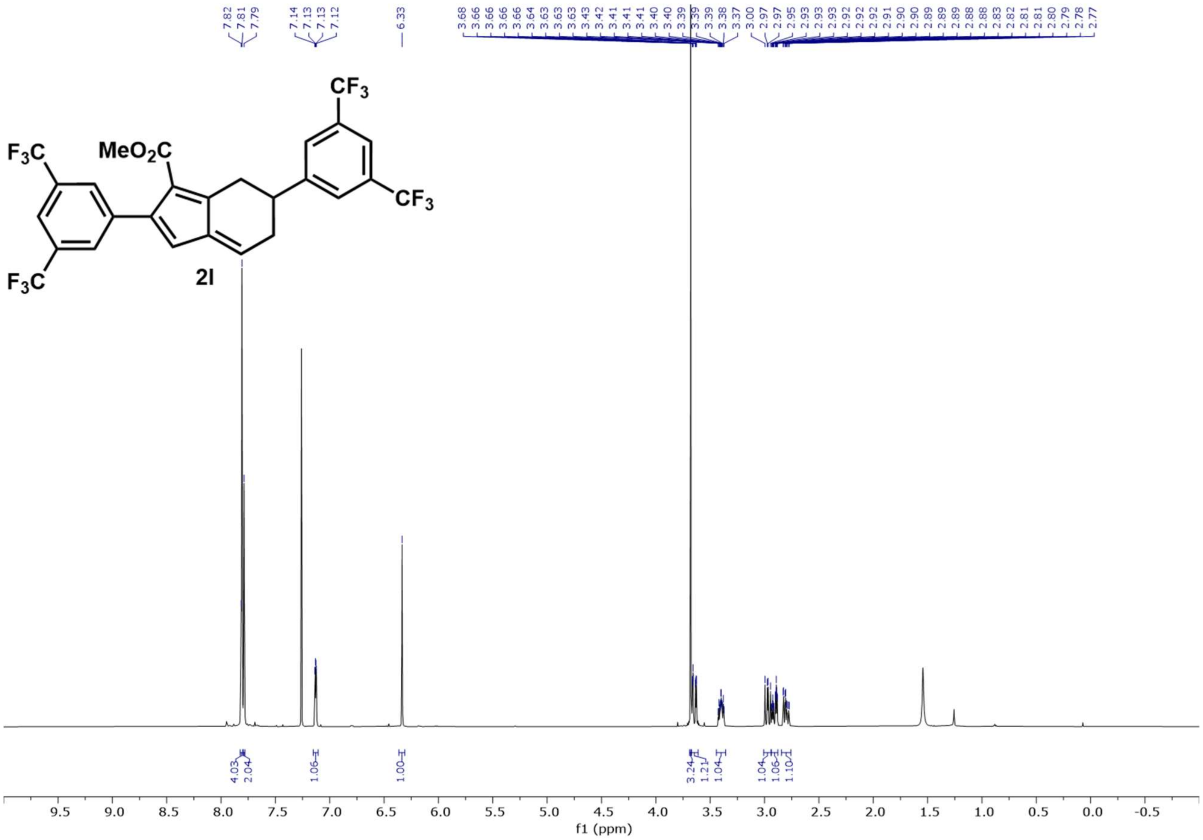
^{1}H NMR (600 MHz, $CDCl_3$)



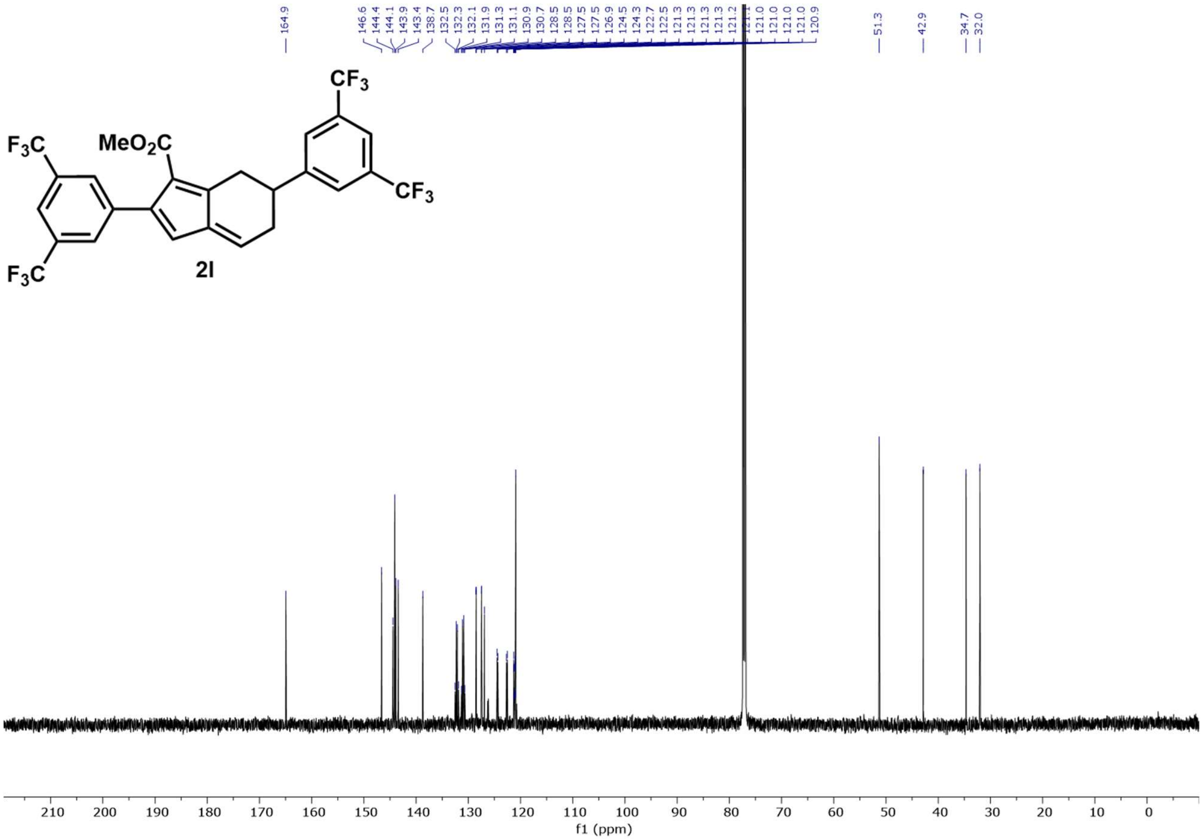
^{13}C NMR (151 MHz, $CDCl_3$)



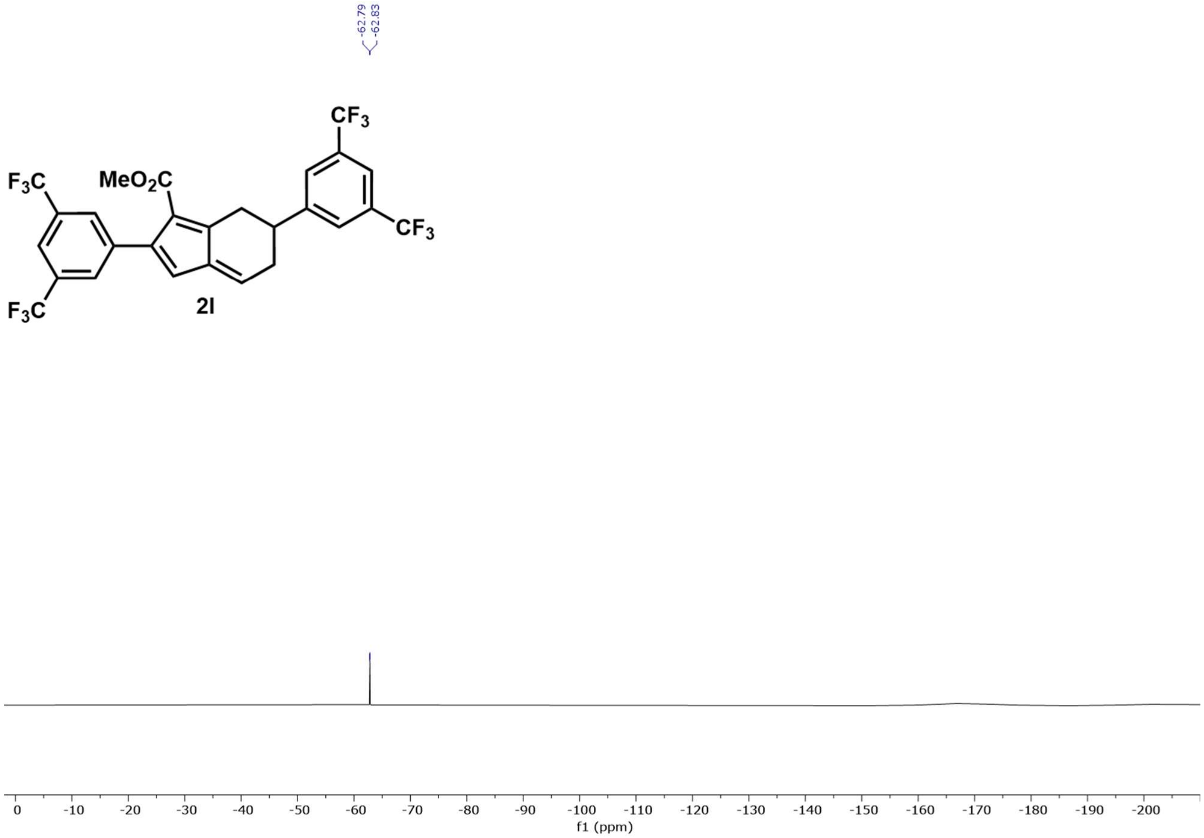
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)

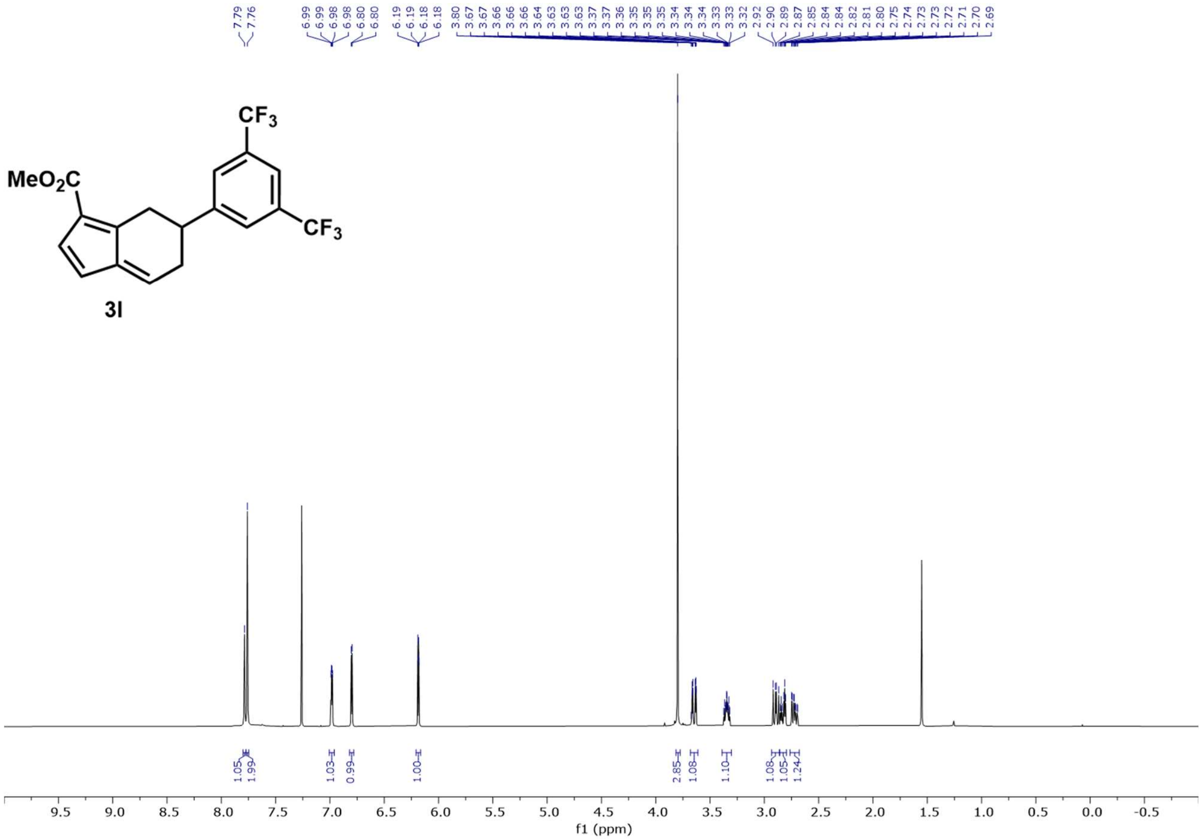


^{19}F NMR (565 MHz, CDCl$_3$)



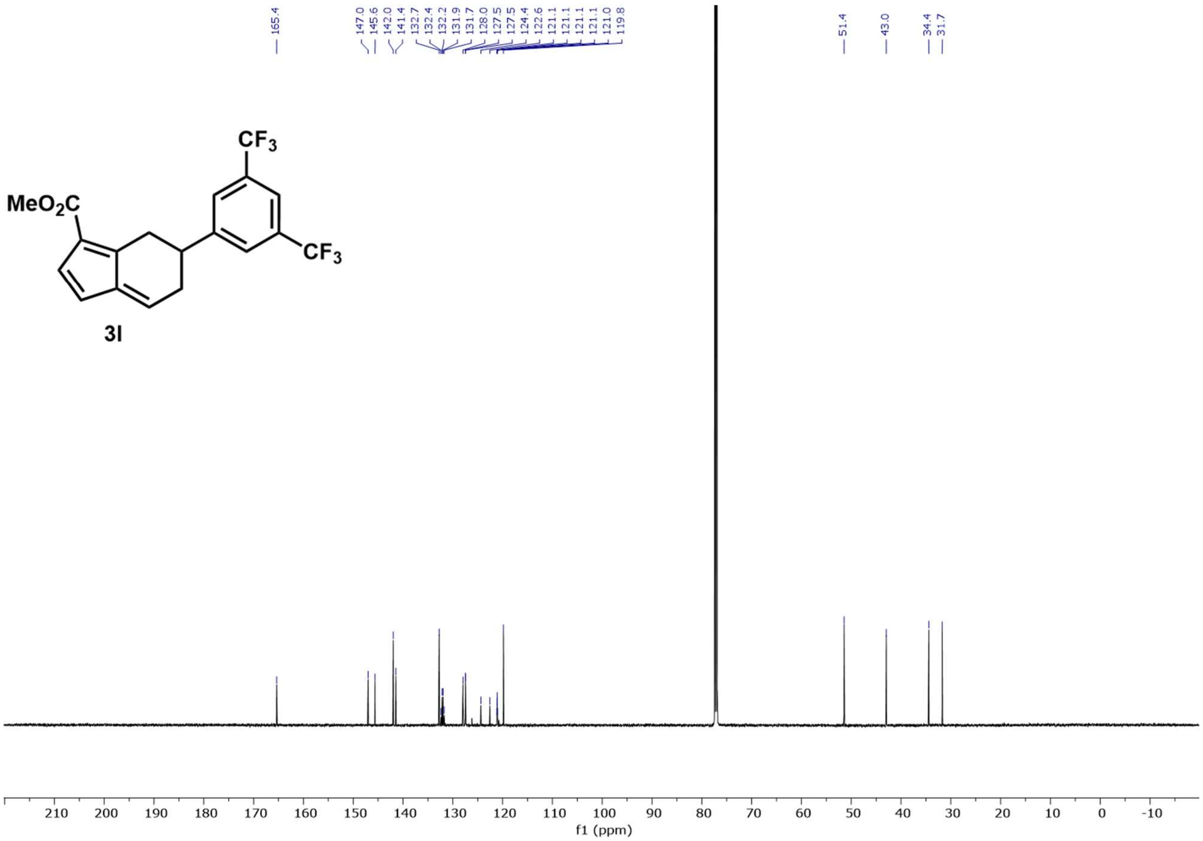
2l

^{1}H NMR (600 MHz, CDCl$_3$)

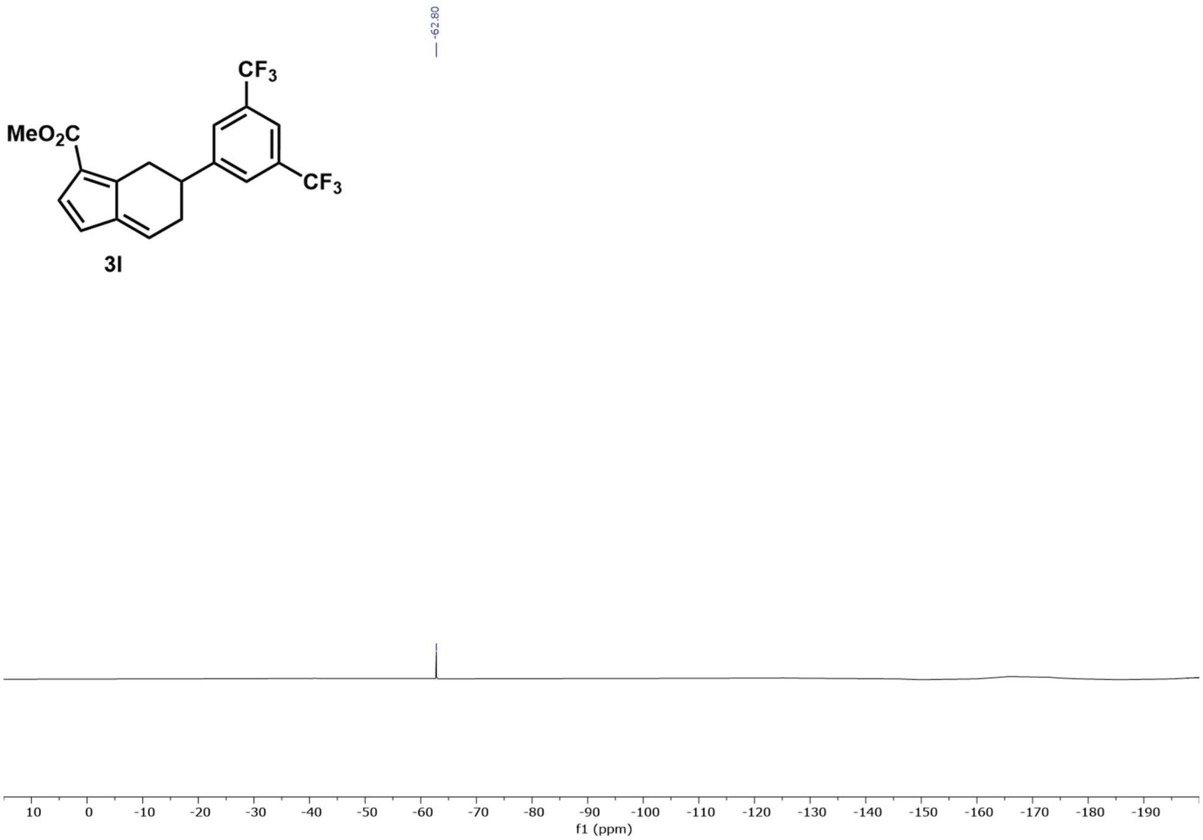


3l

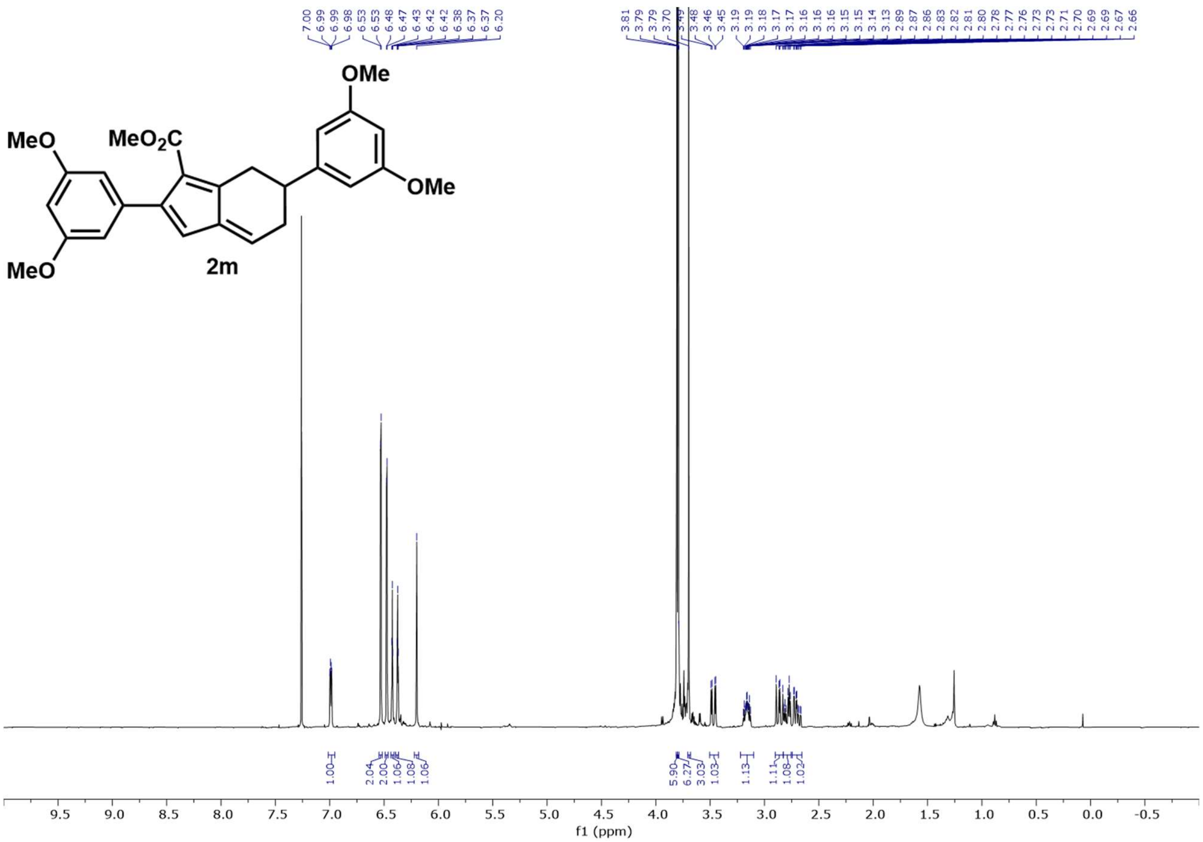
^{13}C NMR (151 MHz, CDCl$_3$)



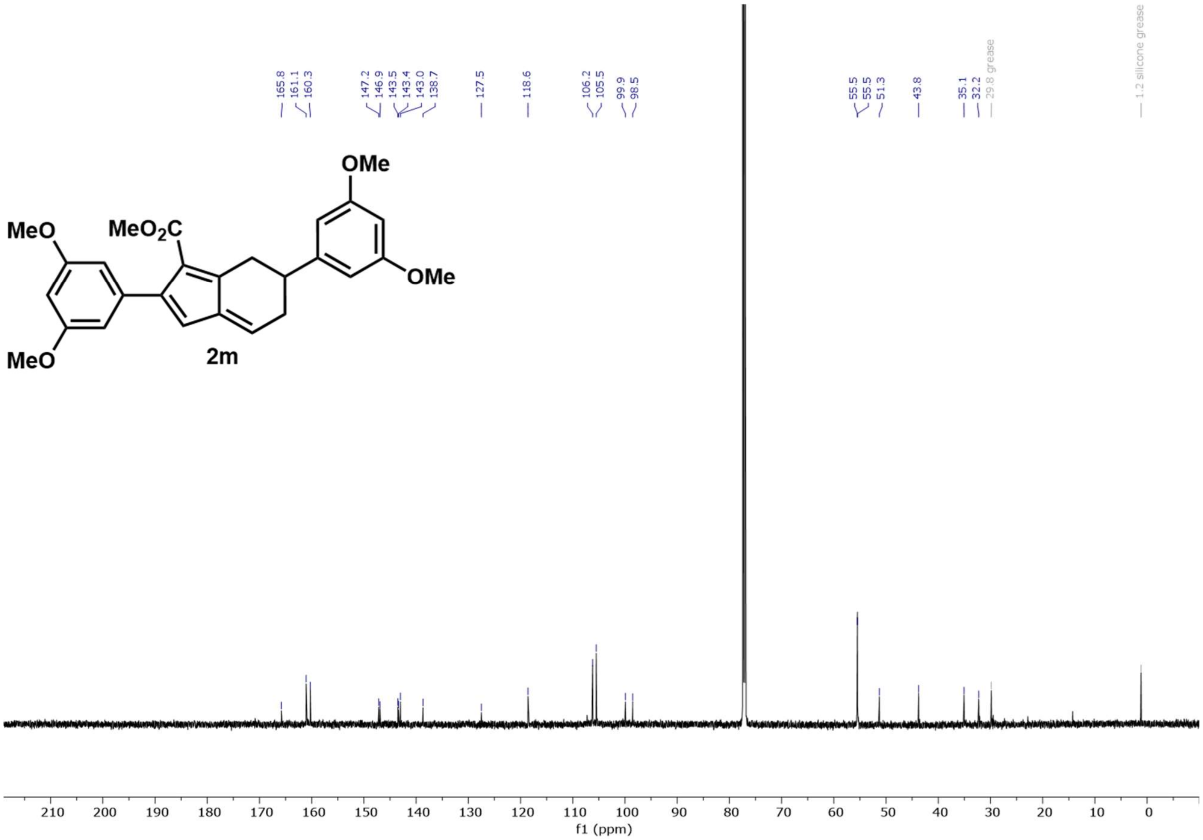
^{19}F NMR (565 MHz, CDCl$_3$)



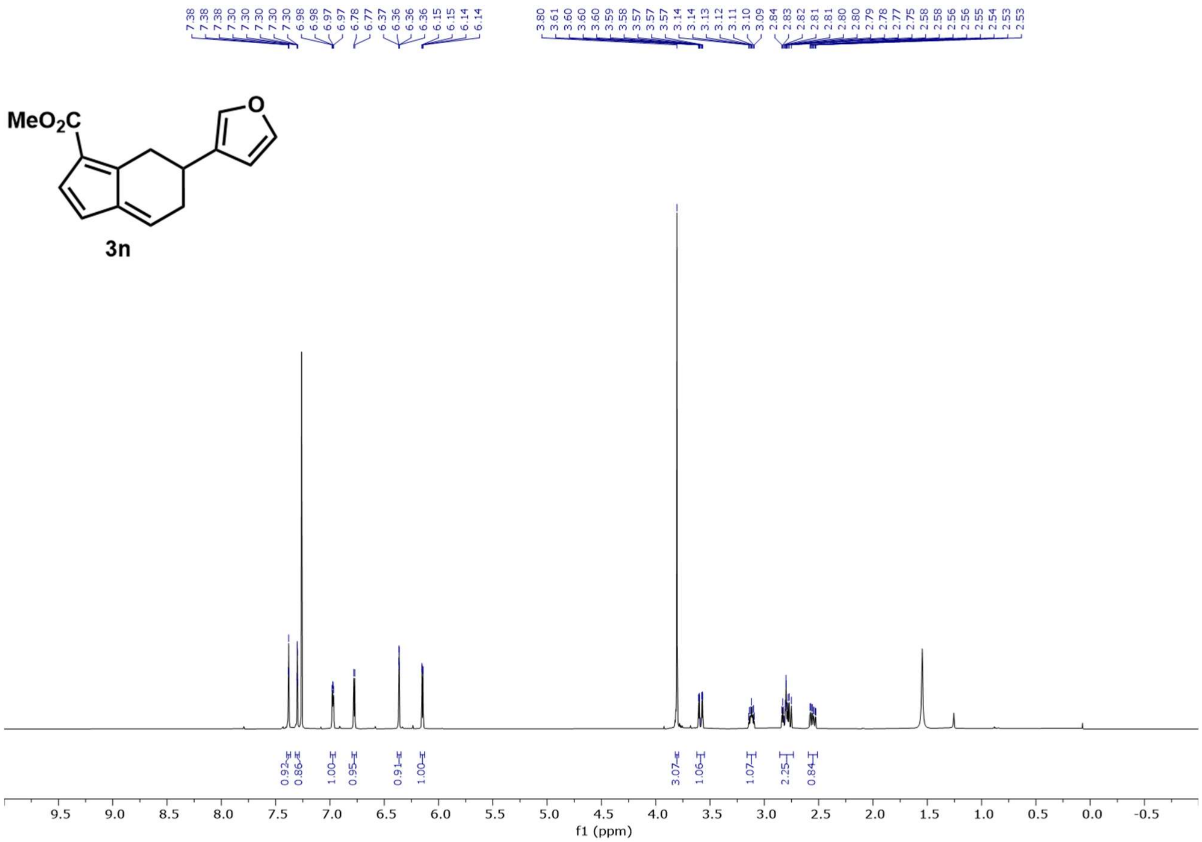
^{1}H NMR (500 MHz, CDCl$_3$)



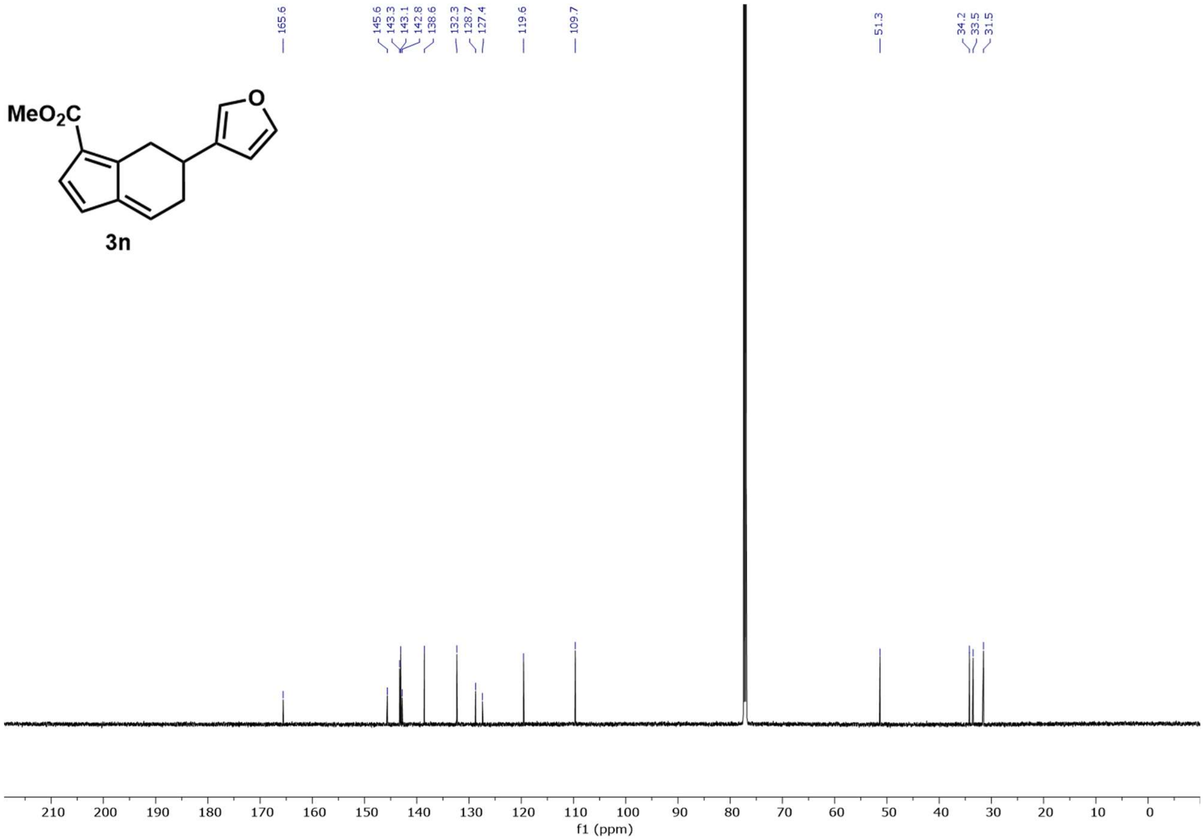
^{13}C NMR (151 MHz, CDCl$_3$)



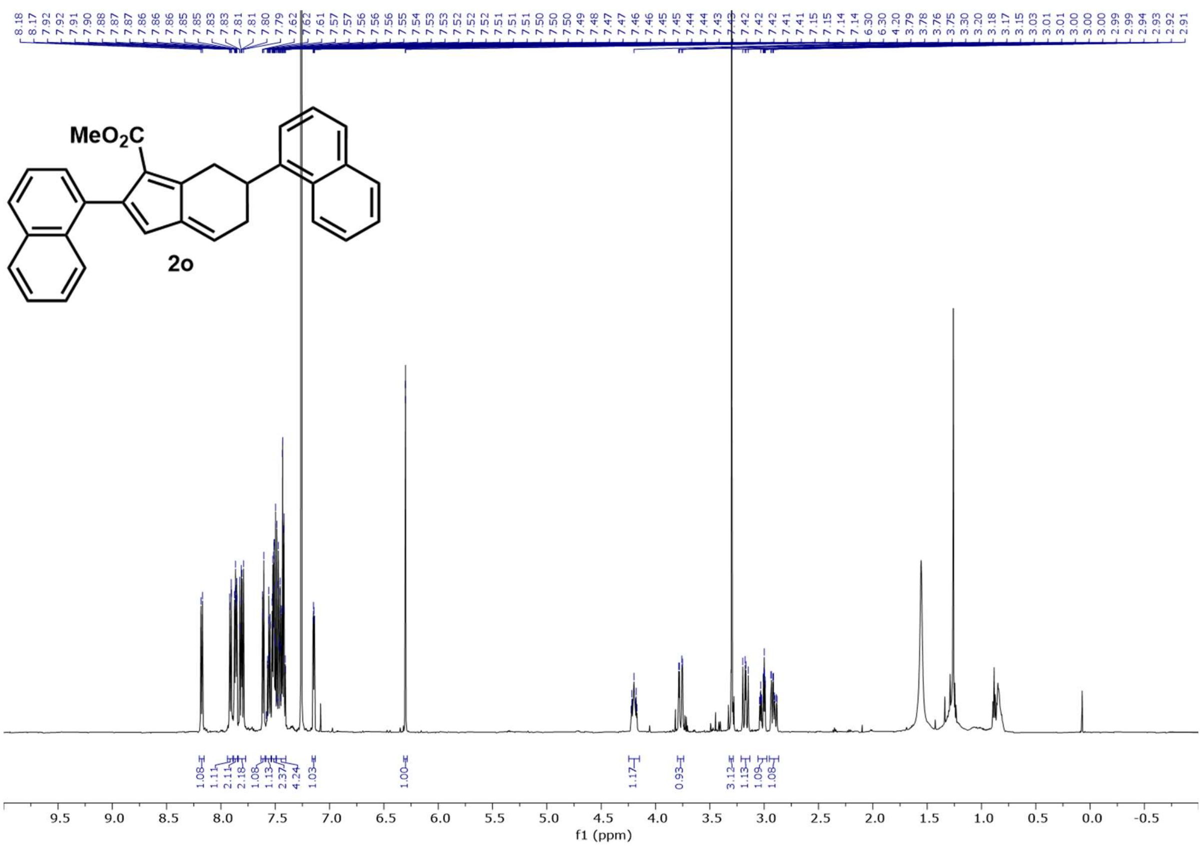
^{1}H NMR (600 MHz, $CDCl_3$)



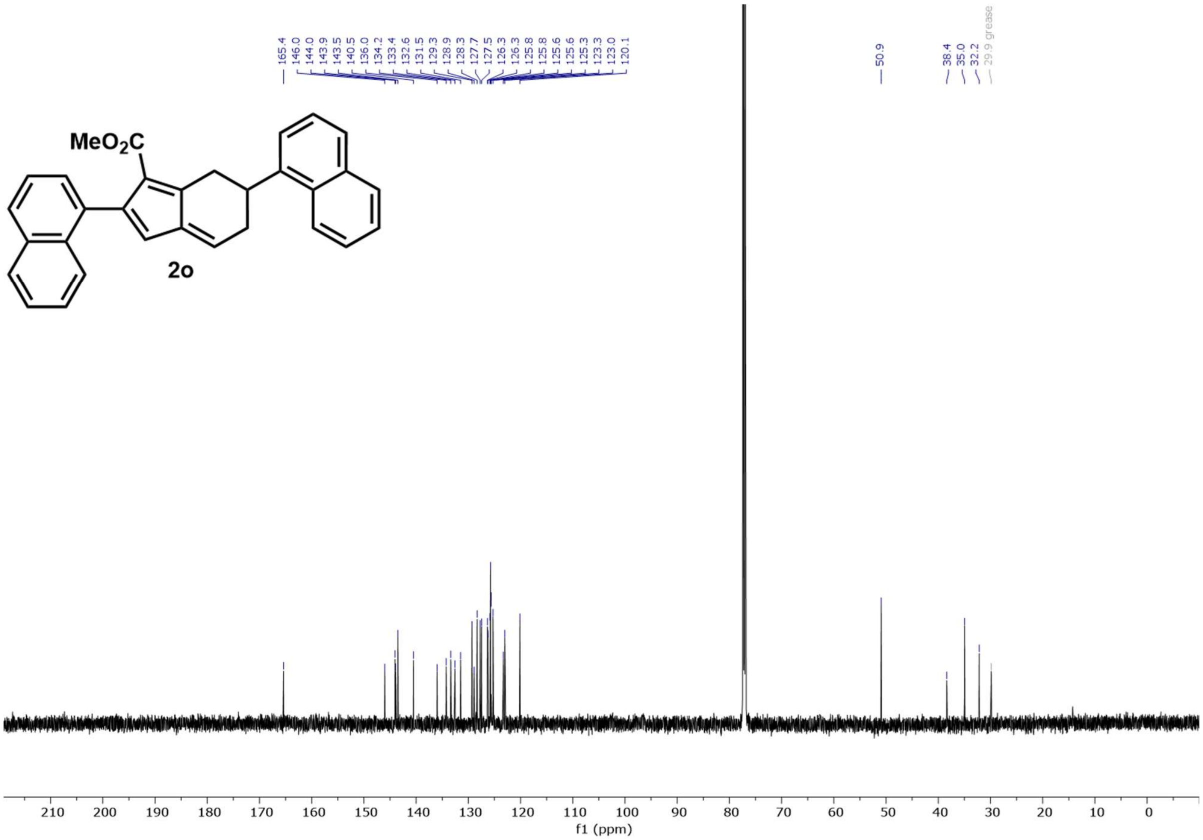
^{13}C NMR (151 MHz, $CDCl_3$)



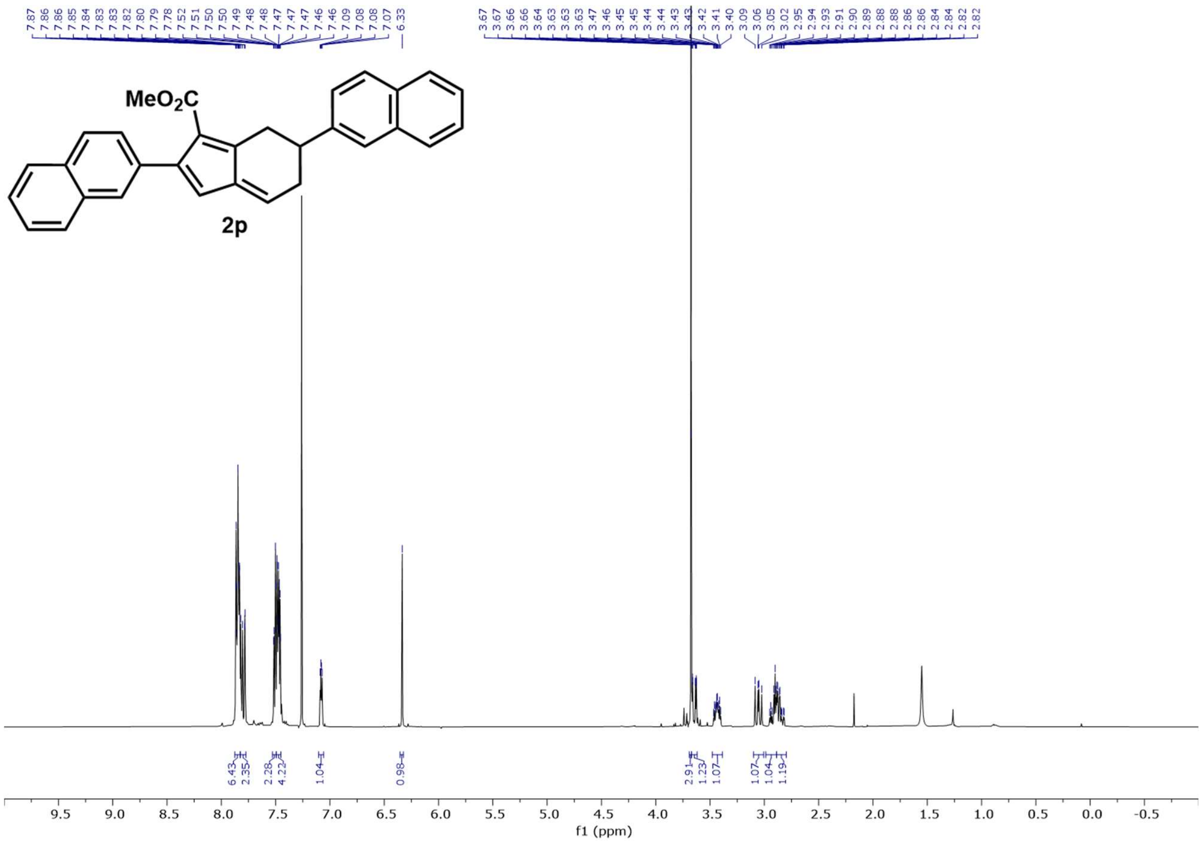
^{1}H NMR (600 MHz, CDCl$_3$)



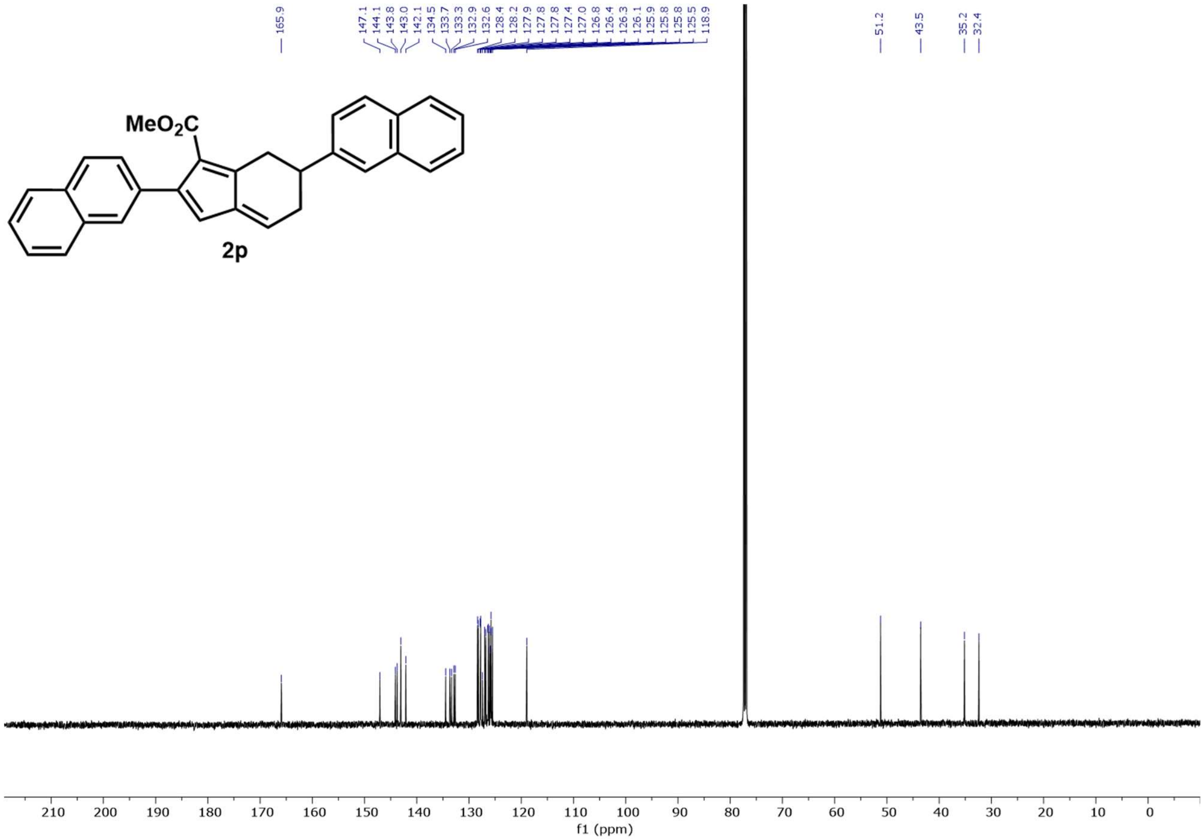
^{13}C NMR (151 MHz, CDCl$_3$)



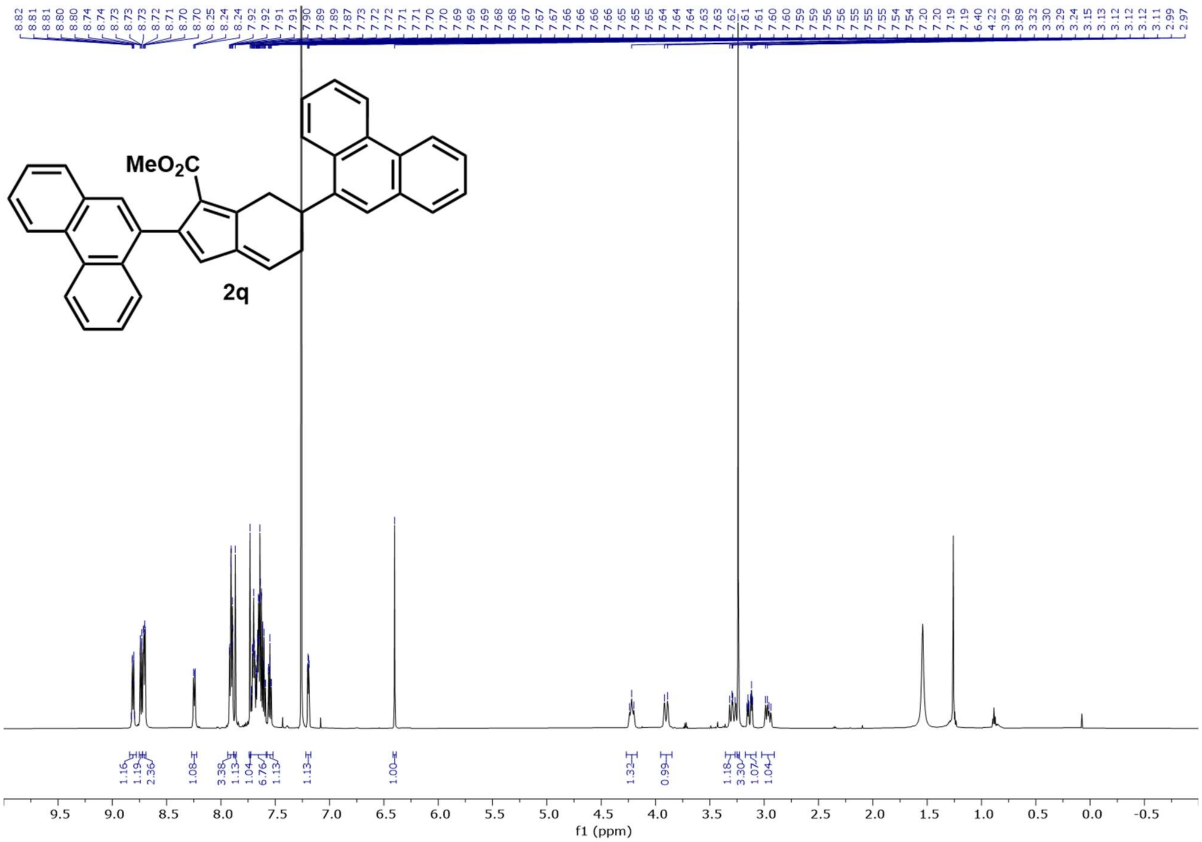
^{1}H NMR (500 MHz, CDCl$_3$)



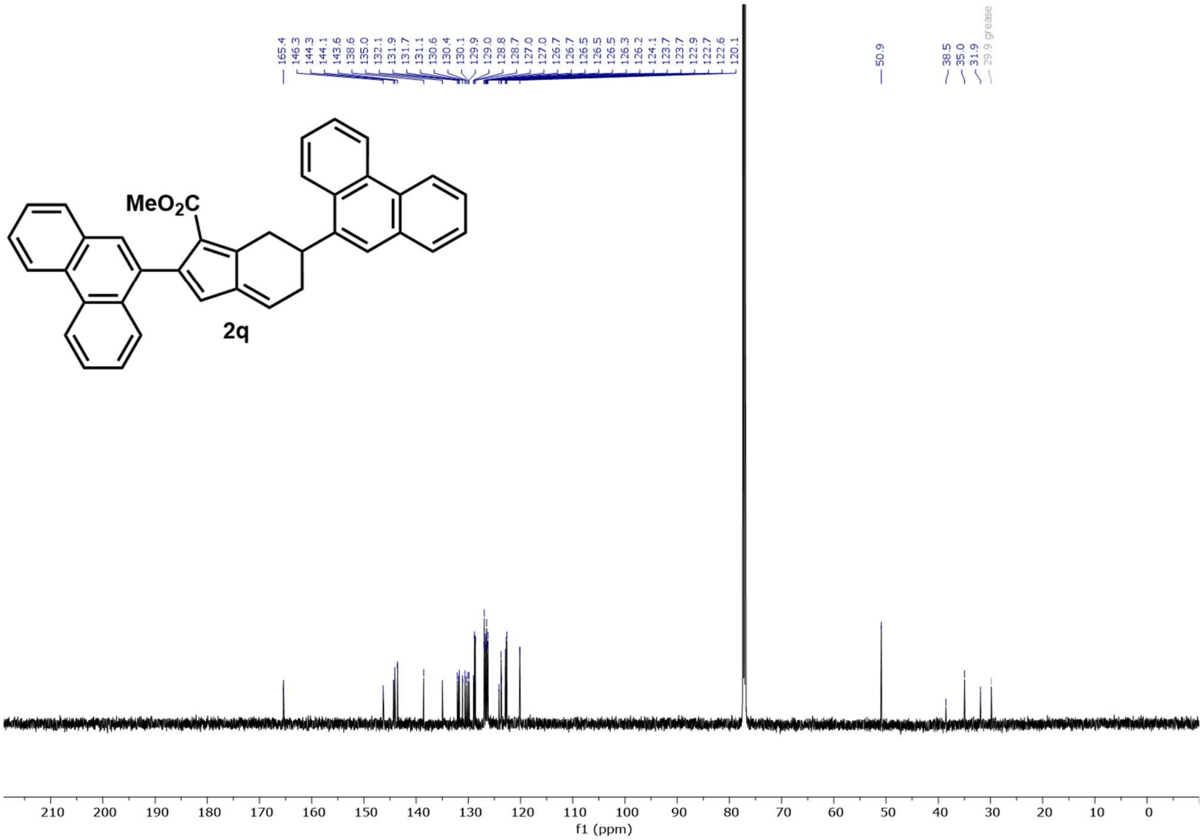
^{13}C NMR (126 MHz, CDCl$_3$)



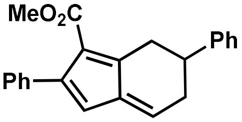
^{1}H NMR (600 MHz, CDCl$_3$)



^{13}C NMR (151 MHz, CDCl$_3$)



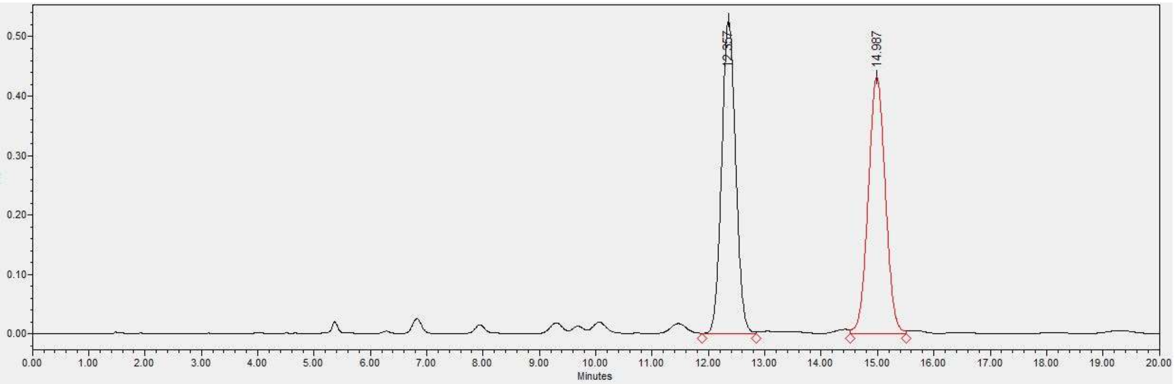
5. Chiral HPLC Traces



2a

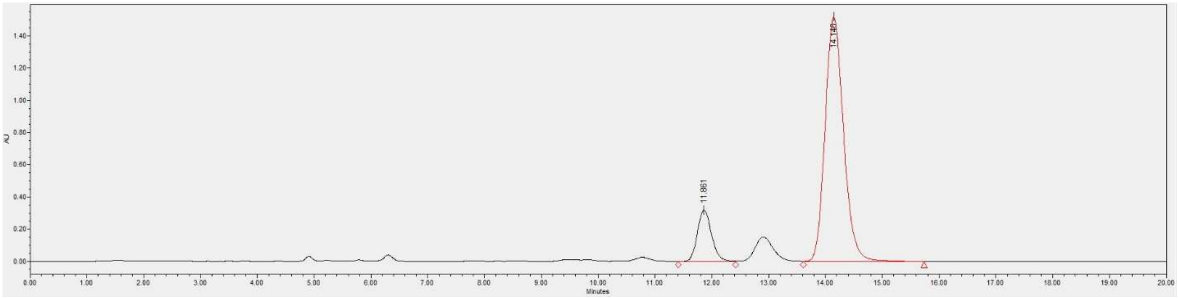
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

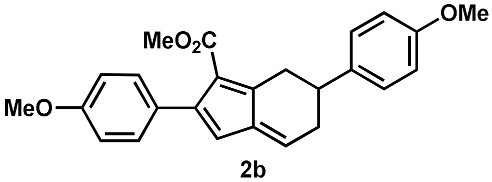


retention time (min)	area (µV*sec)	% area
12.357	9093061	49.93
14.987	9118099	50.07

Enantioenriched (1 mmol scale):



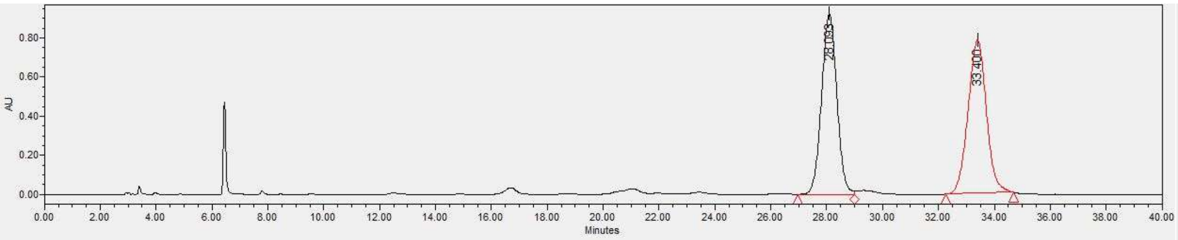
retention time (min)	area (µV*sec)	% area
11.861	5528729	13.84
14.146	34423325	86.16



2b

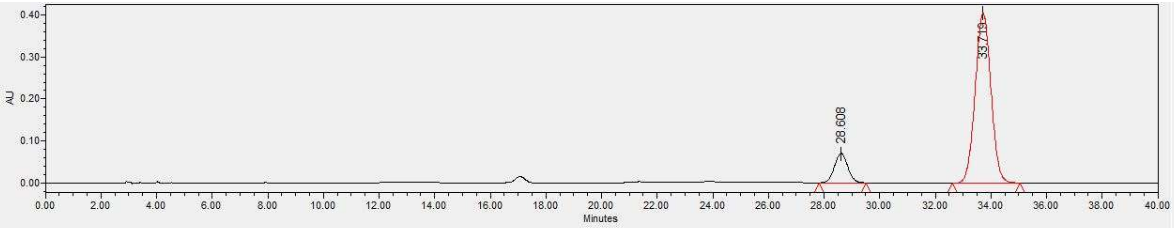
Method: AD3 chiral column, 5% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

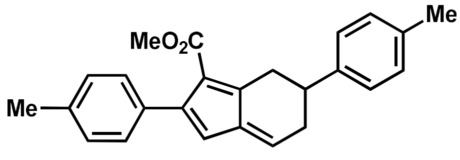


retention time (min)	area (μV*sec)	% area
28.093	34869206	49.41
33.400	35708050	50.59

Enantioenriched:



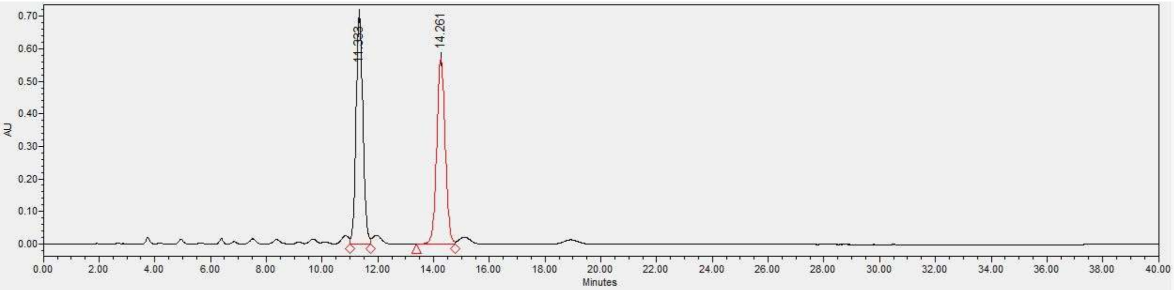
retention time (min)	area (μV*sec)	% area
28.608	2301910	12.61
33.719	15949113	87.39



2c

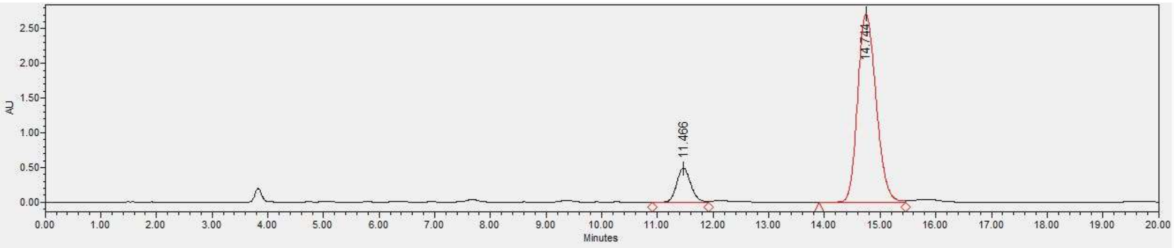
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

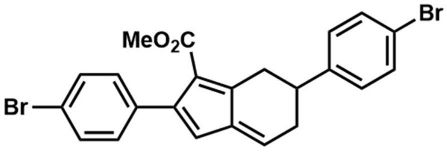


retention time (min)	area (µV*sec)	% area
11.333	12021951	49.88
14.261	12080718	50.12

Enantioenriched:



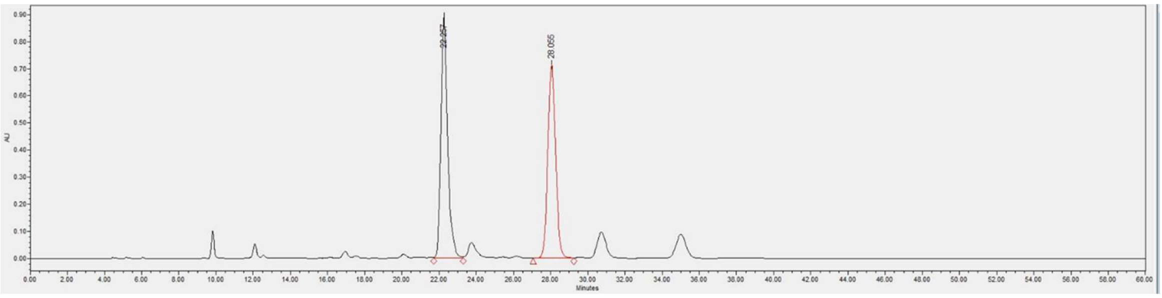
retention time (min)	area (µV*sec)	% area
11.466	8515477	12.02
14.744	62326780	87.98



2d

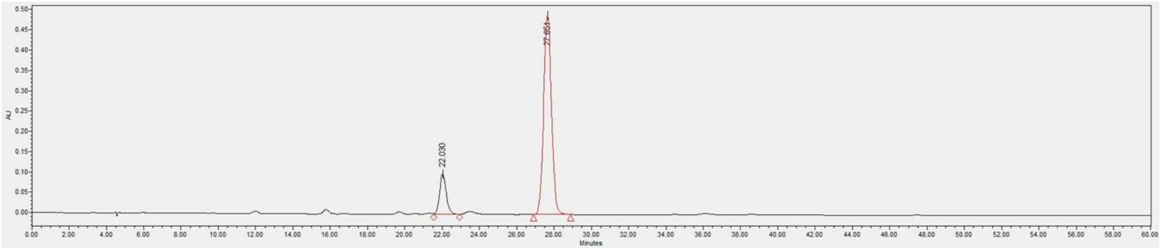
Method: AD3 chiral column, 5% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

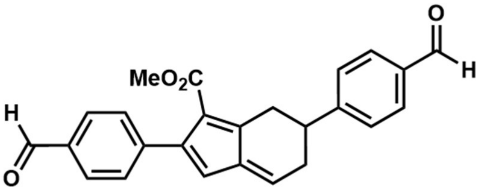


retention time (min)	area (μV*sec)	% area
22.257	22193296	51.48
28.055	20918567	48.52

Enantioenriched:



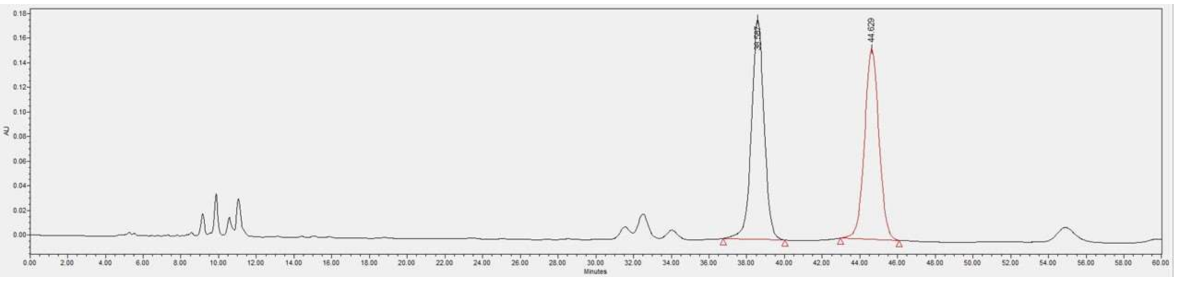
retention time (min)	area (μV*sec)	% area
22.030	2437316	14.57
27.651	14291891	85.43



2e

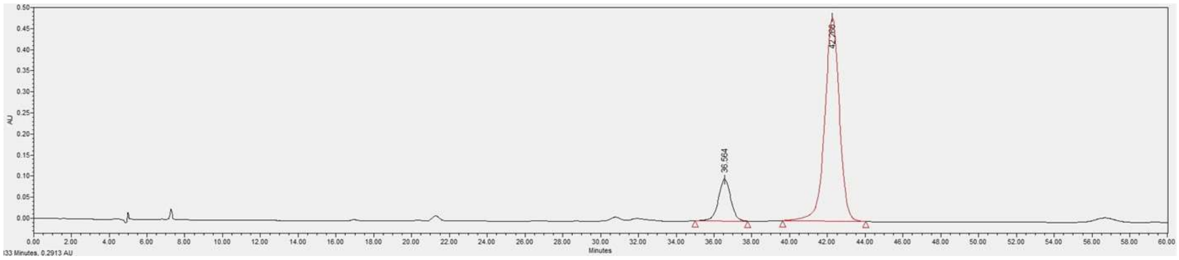
Method: AD3 chiral column, 30% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

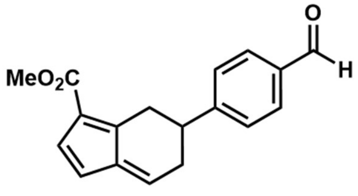


retention time (min)	area (µV*sec)	% area
38.587	8322196	50.33
44.629	8214296	49.67

Enantioenriched:



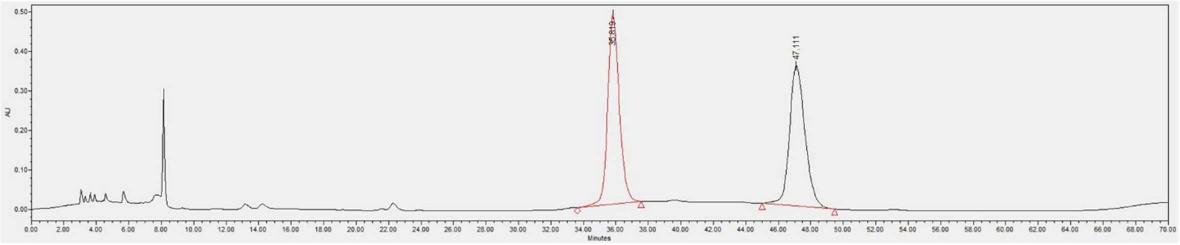
retention time (min)	area (µV*sec)	% area
36.564	4520051	14.79
42.266	26041114	85.21



3e

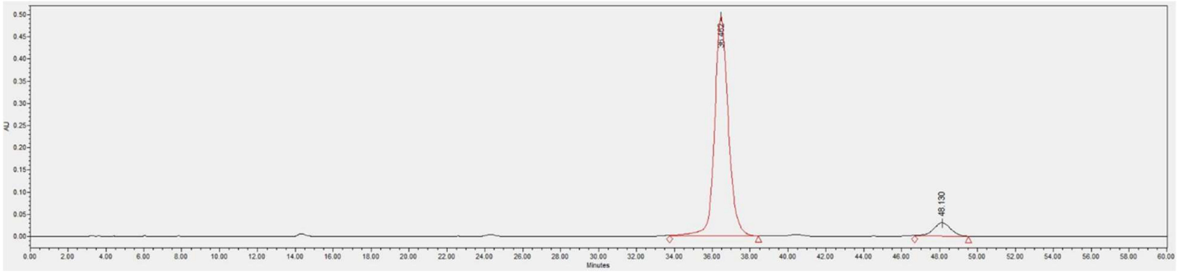
Method: IC3 chiral column, 20% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

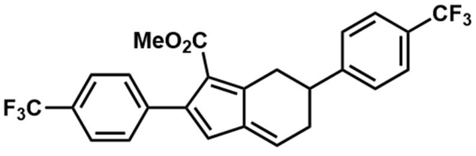


retention time (min)	area (µV*sec)	% area
35.819	23869218	50.37
47.111	23514074	49.63

Enantioenriched:



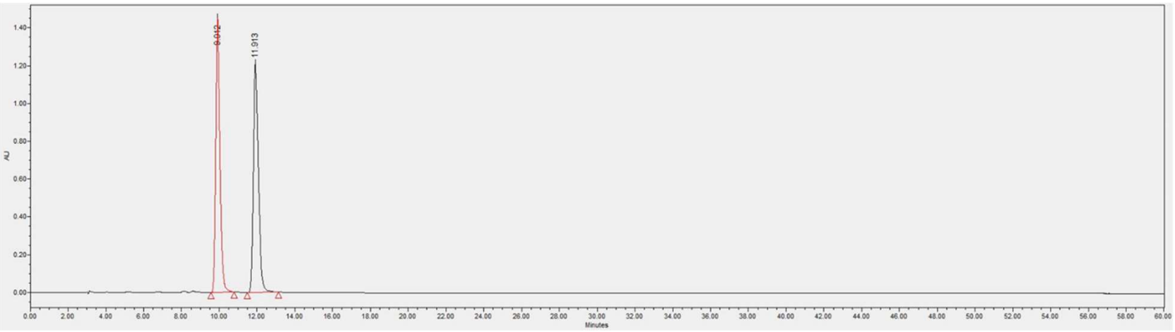
retention time (min)	area (µV*sec)	% area
36.462	25041887	92.76
48.130	1954341	7.24



2f

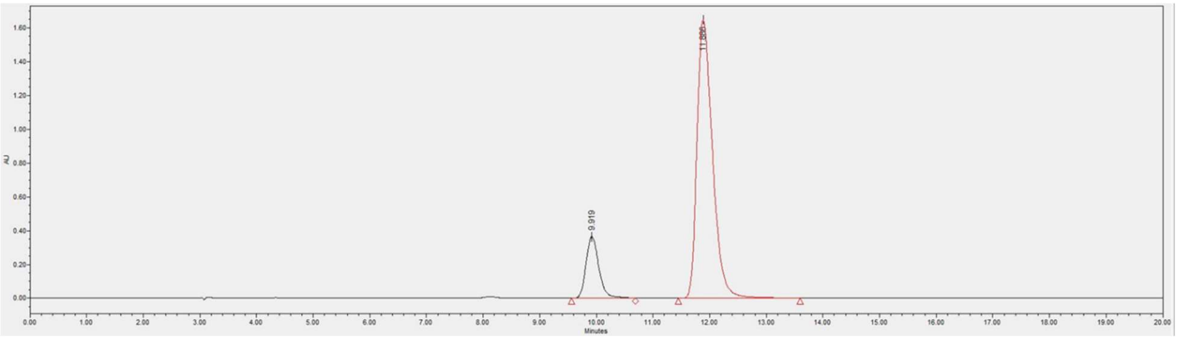
Method: AD3 chiral column, 3% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

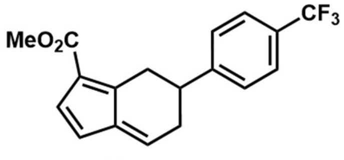


retention time (min)	area (µV*sec)	% area
9.912	22549545	49.85
11.913	22681739	50.15

Enantioenriched:



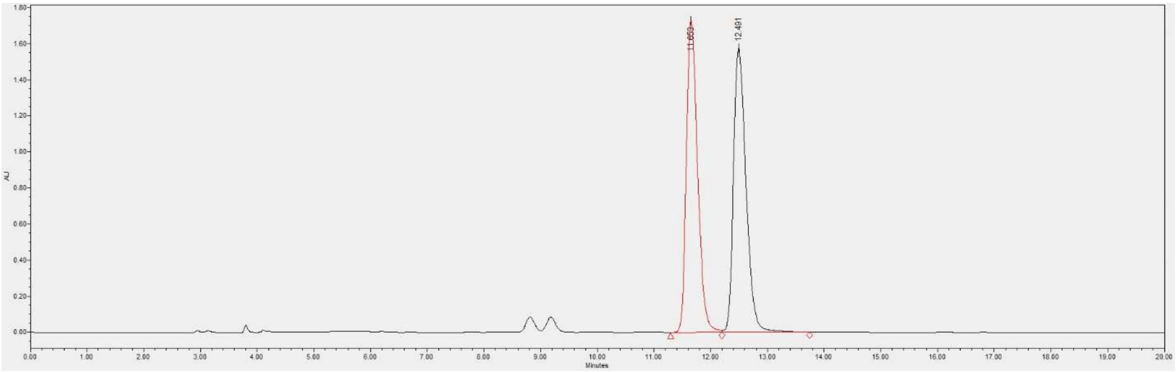
retention time (min)	area (µV*sec)	% area
9.919	5696403	15.42
11.886	31240884	84.58



3f

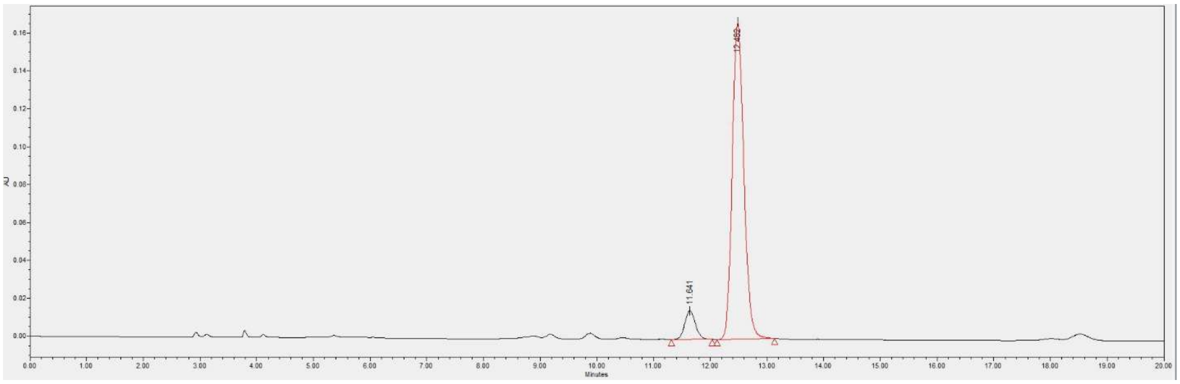
Method: AD3 chiral column, 1% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

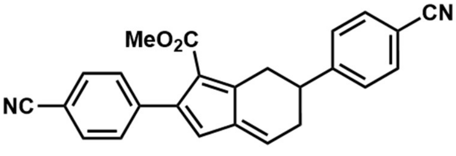


retention time (min)	area (µV*sec)	% area
11.653	23846934	49.70
12.491	24132775	50.30

Enantioenriched:



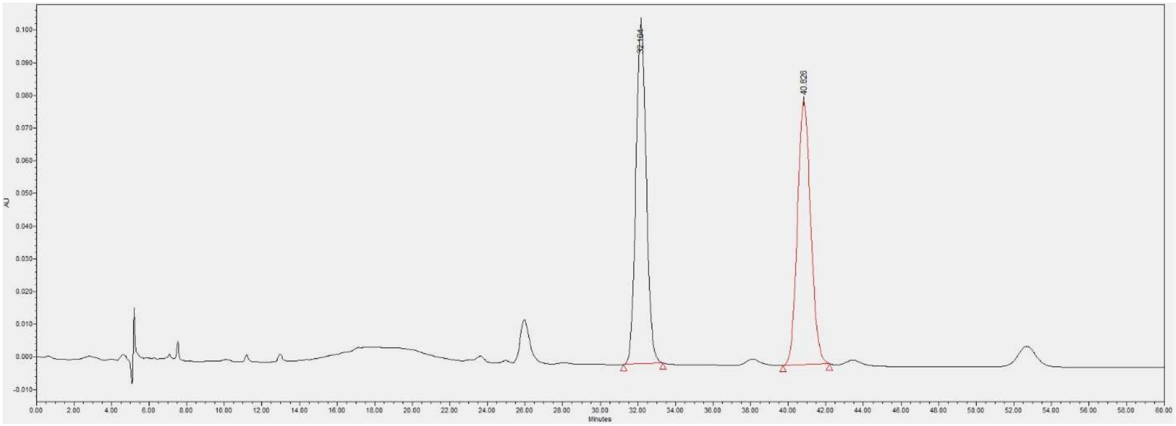
retention time (min)	area (µV*sec)	% area
11.641	197838	7.69
12.482	2374692	92.31



2g

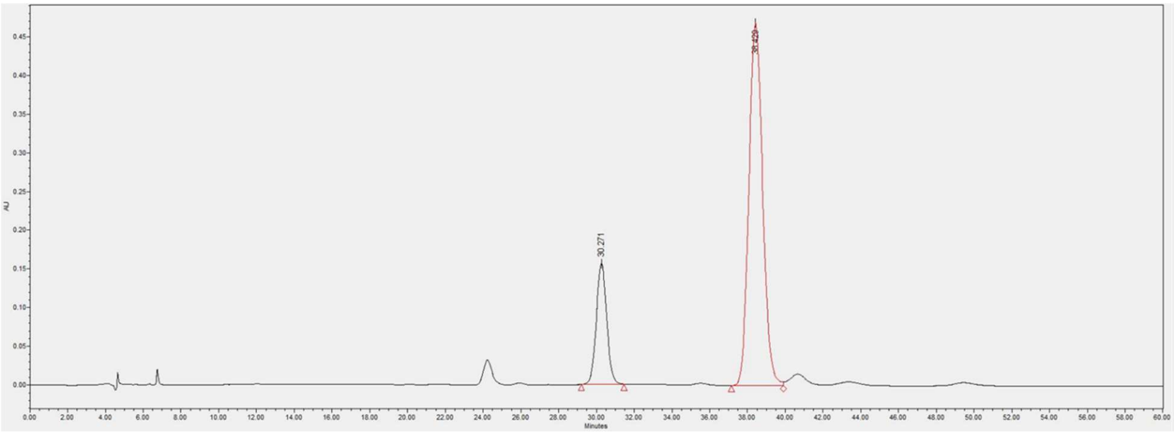
Method: AD3 chiral column, 30% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

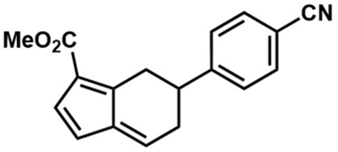


retention time (min)	area (μV*sec)	% area
32.164	3981262	50.15
40.826	3957668	49.85

Enantioenriched:



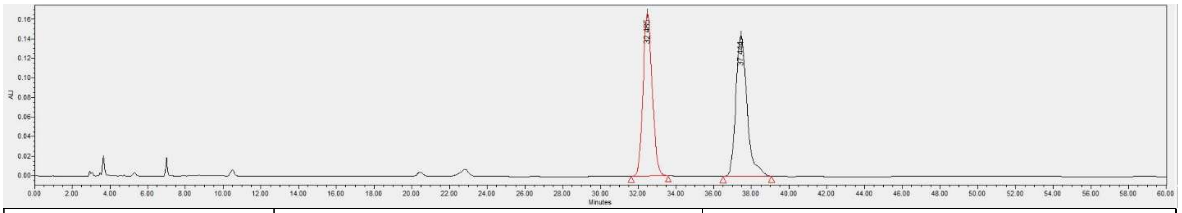
retention time (min)	area (μV*sec)	% area
30.271	5978424	20.14
38.429	23710119	79.86



3g

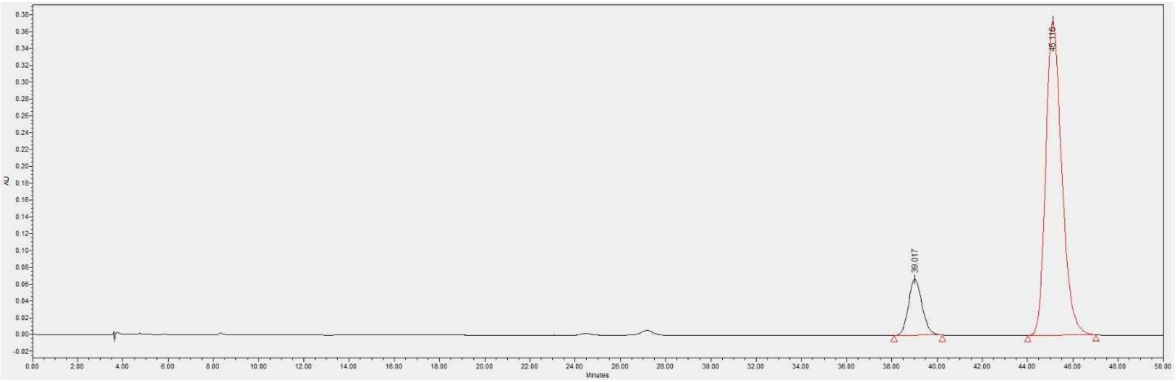
Method: AD3 chiral column, 3% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

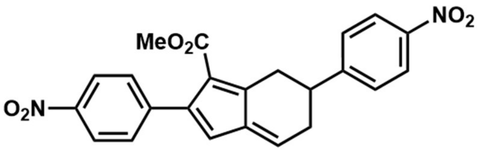


retention time (min)	area (µV*sec)	% area
32.485	5649874	48.67
37.444	5957878	51.33

Enantioenriched:



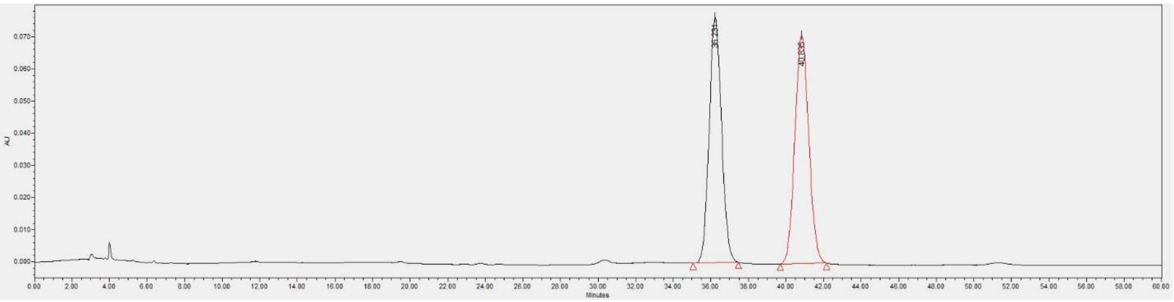
retention time (min)	area (µV*sec)	% area
39.017	2782198	13.14
45.116	18385501	86.86



2h

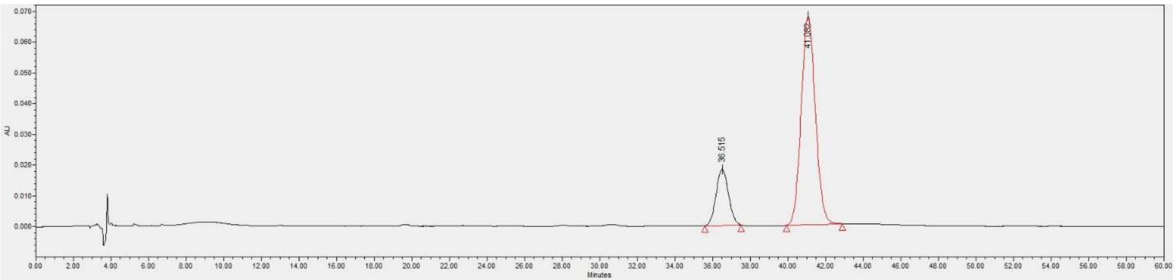
Method: AD3 chiral column, 20% IPA/hexanes 1 mL/min, λ= 300 nm

Racemic:

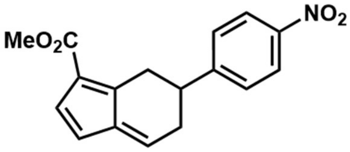


retention time (min)	area (μV*sec)	% area
36.231	3497024	48.93
40.835	3650375	51.07

Enantioenriched:



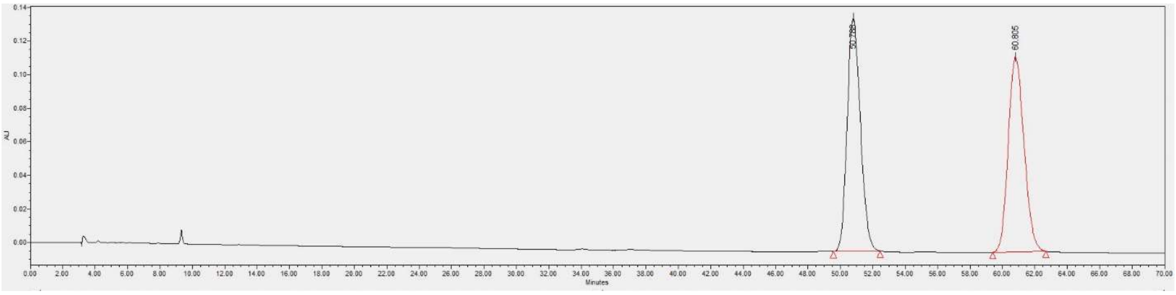
retention time (min)	area (μV*sec)	% area
36.515	833811	19.03
41.082	3548646	80.97



3h

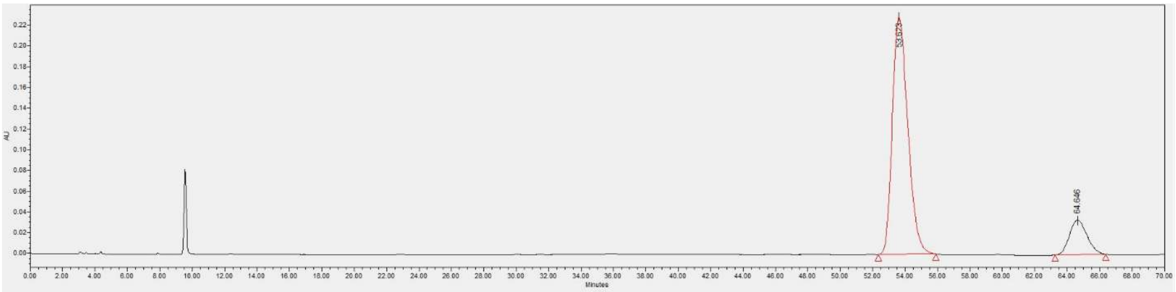
Method: IC3 chiral column, 10% IPA/hexanes 1 mL/min, λ= 300 nm

Racemic:

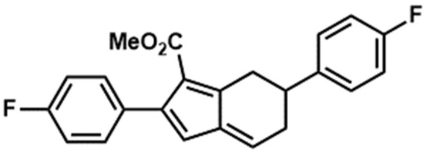


retention time (min)	area (µV*sec)	% area
50.788	7884483	50.05
60.805	7867752	49.95

Enantioenriched:



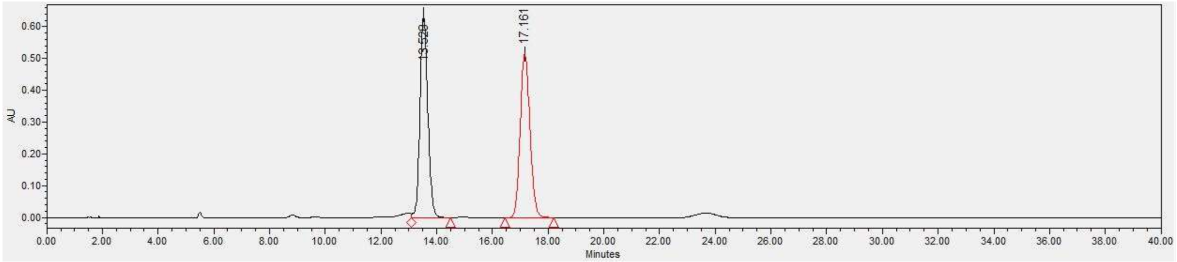
retention time (min)	area (µV*sec)	% area
53.623	15204151	85.79
64.646	2517547	14.21



2i

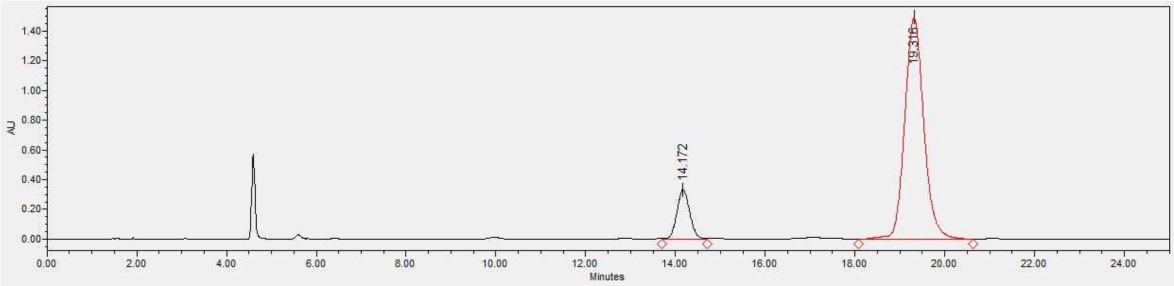
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

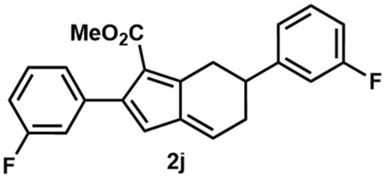


retention time (min)	area (μV*sec)	% area
13.528	12514684	49.92
17.161	12553489	50.08

Enantioenriched:



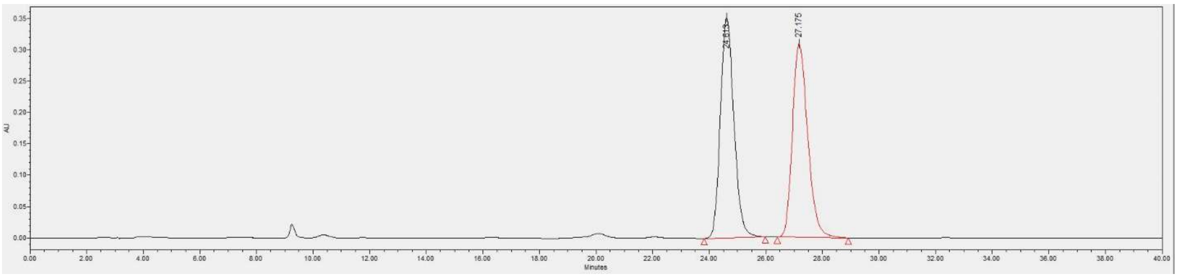
retention time (min)	area (μV*sec)	% area
14.172	6559553	13.01
19.316	43870177	86.99



2j

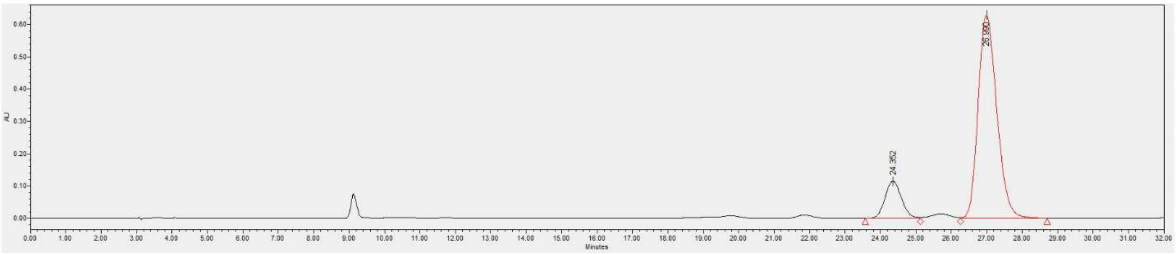
Method: AD3 chiral column, 1% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

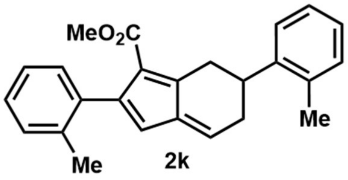


retention time (min)	area (µV*sec)	% area
24.613	11663305	50.16
27.175	11587976	49.84

Enantioenriched:



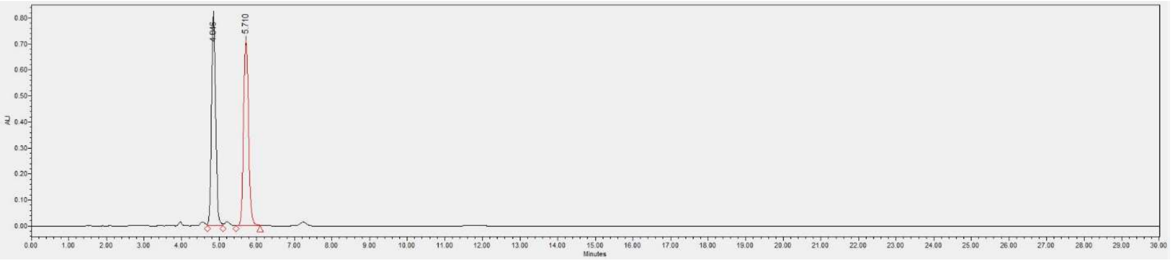
retention time (min)	area (µV*sec)	% area
24.352	3728105	13.91
26.990	23065599	86.09



2k

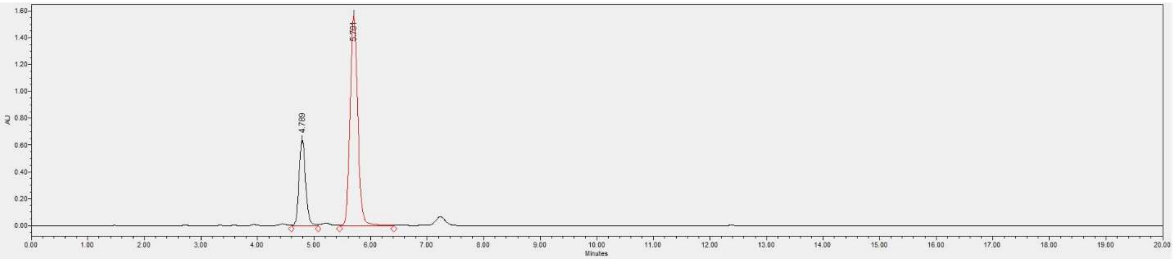
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

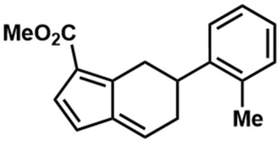


retention time (min)	area (µV*sec)	% area
4.846	6268940	49.23
5.710	6466074	50.77

Enantioenriched:



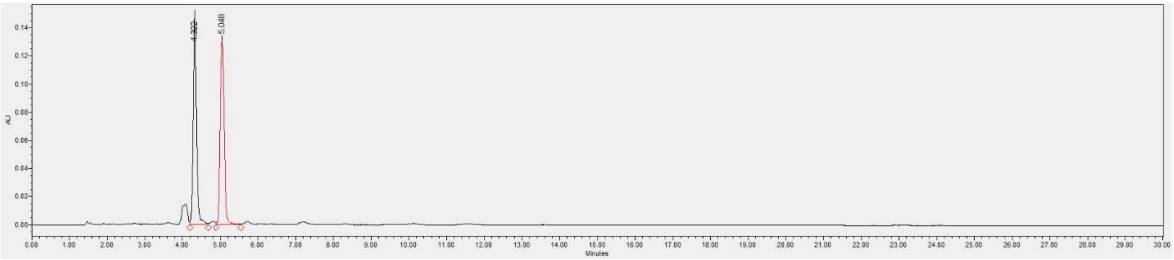
retention time (min)	area (µV*sec)	% area
4.789	5091885	25.77
5.701	14666872	74.23



3k

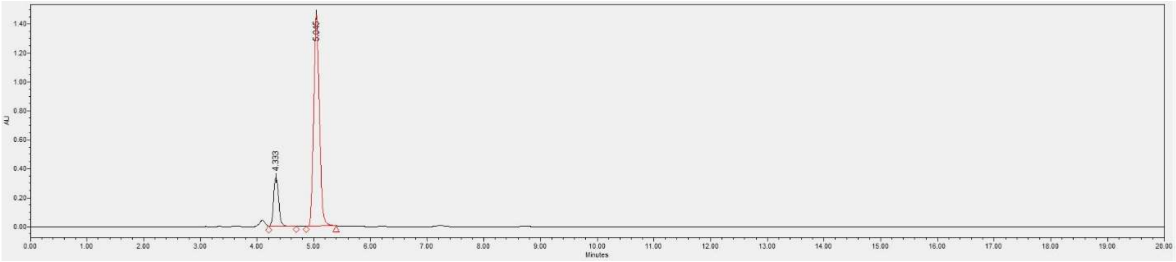
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

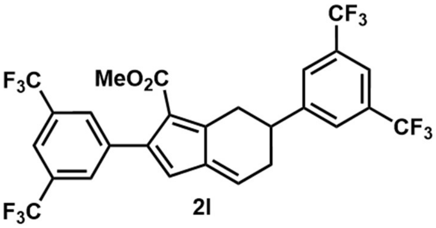


retention time (min)	area (µV*sec)	% area
4.322	933441	50.29
5.048	922497	49.71

Enantioenriched:



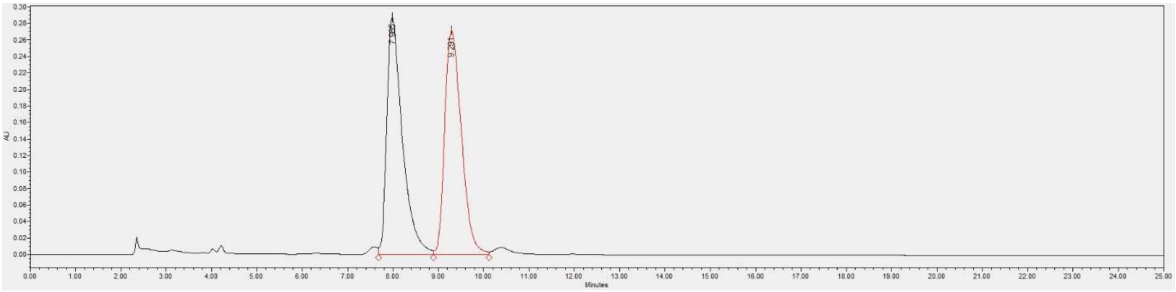
retention time (min)	area (µV*sec)	% area
4.333	2074475	16.88
5.045	10217293	83.12



2l

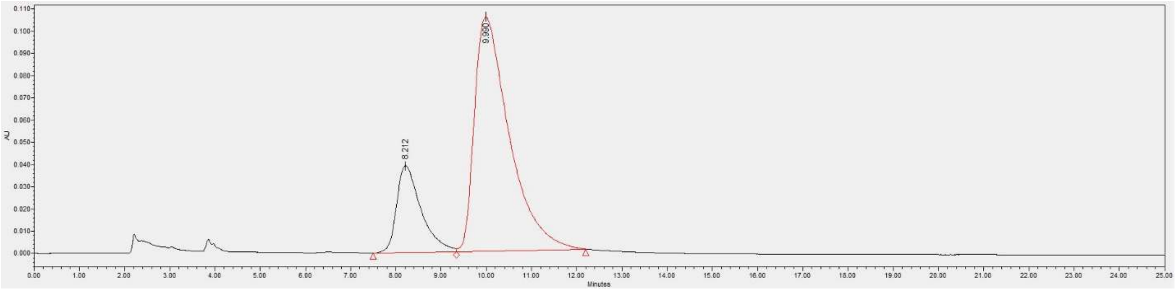
Method: AD3 chiral column, 0.1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

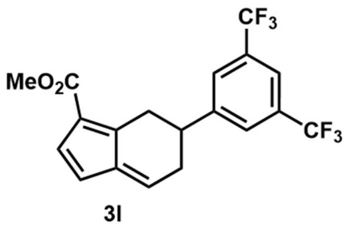


retention time (min)	area (µV*sec)	% area
7.985	6870120	49.88
9.291	6903733	50.12

Enantioenriched:



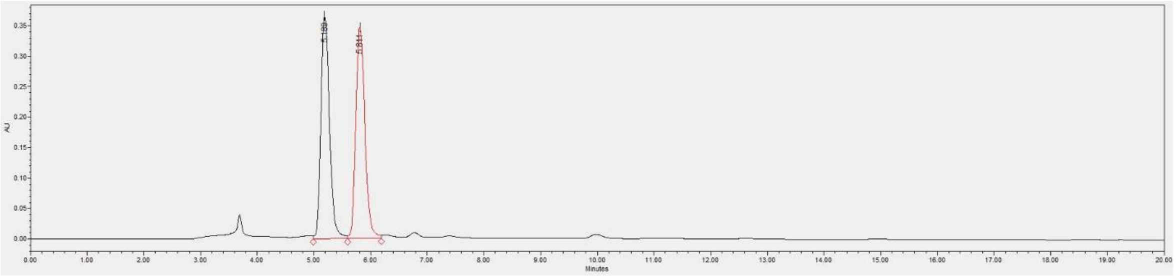
retention time (min)	area (µV*sec)	% area
8.212	1471906	20.70
9.990	5638367	79.30



3l

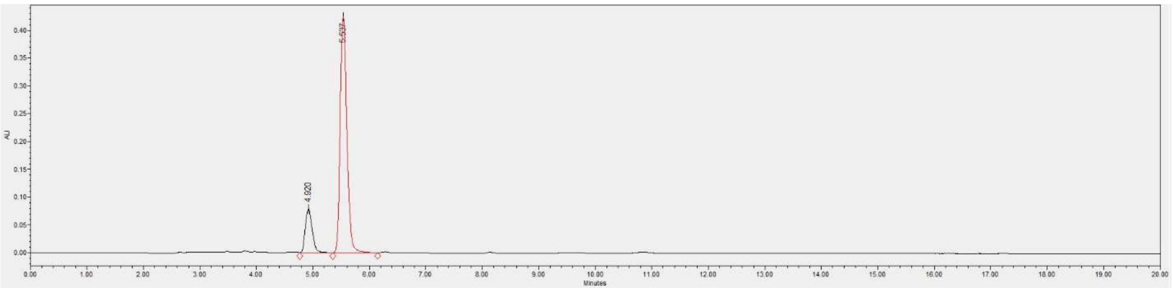
Method: AD3 chiral column, 1% IPA/hexanes 2 mL/min, λ= 254 nm

Racemic:

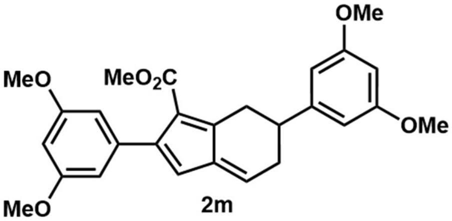


retention time (min)	area (µV*sec)	% area
5.189	3860051	49.89
5.811	3877174	50.11

Enantioenriched:



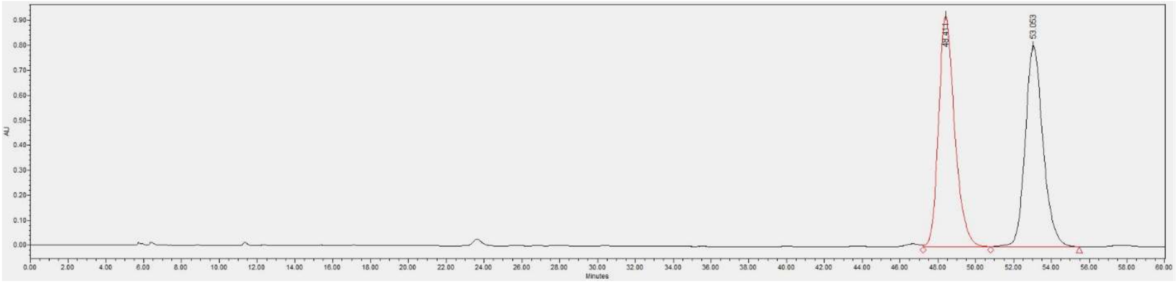
retention time (min)	area (µV*sec)	% area
4.920	683361	16.23
5.537	3527634	83.77



2m

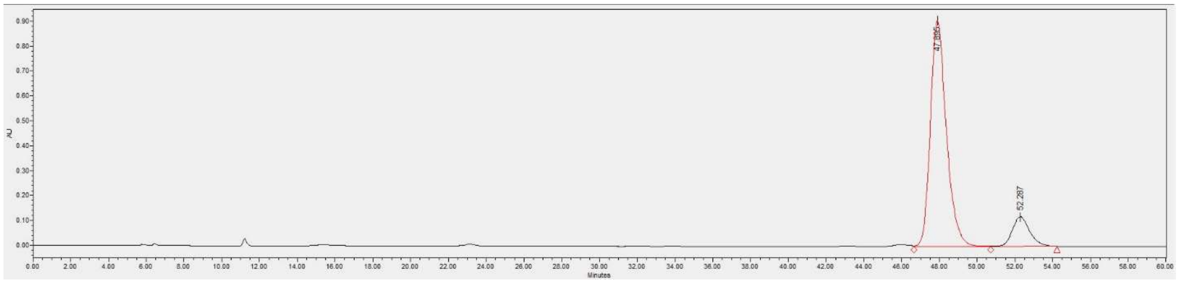
Method: AD3 chiral column, 10% IPA/hexanes 0.5 mL/min, λ= 254 nm

Racemic:

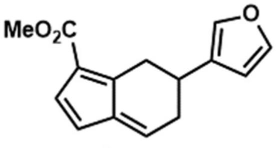


retention time (min)	area (µV*sec)	% area
48.411	54608707	51.00
53.053	52468745	49.00

Enantioenriched:



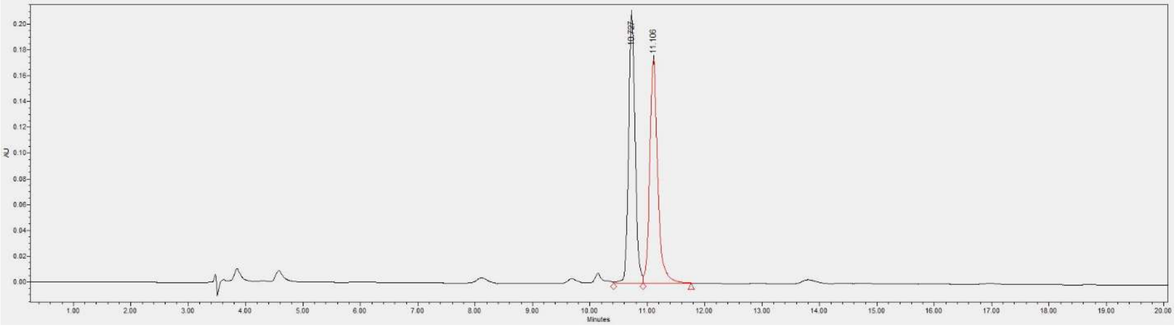
retention time (min)	area (µV*sec)	% area
47.895	53172216	87.62
52.287	7509946	12.38



3n

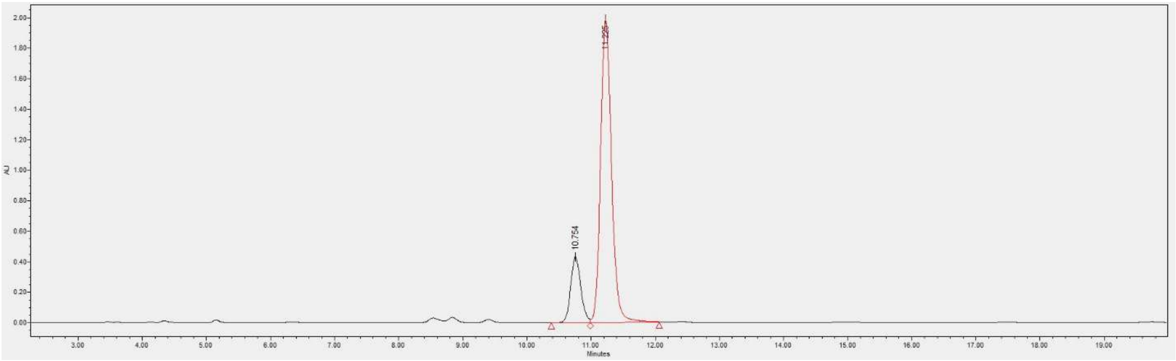
Method: AD3 chiral column, 3% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

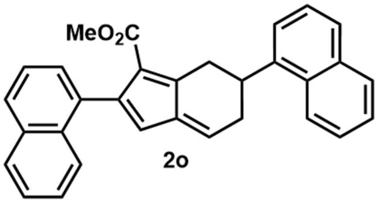


retention time (min)	area (µV*sec)	% area
10.727	1650568	49.48
11.106	1684933	50.52

Enantioenriched:



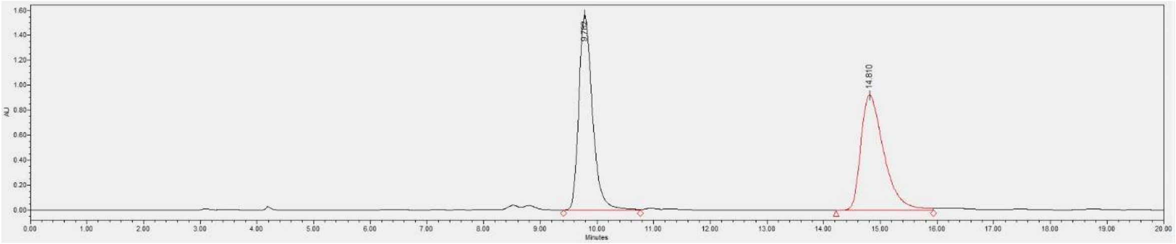
retention time (min)	area (µV*sec)	% area
10.754	4760779	16.89
11.225	23426907	83.11



2o

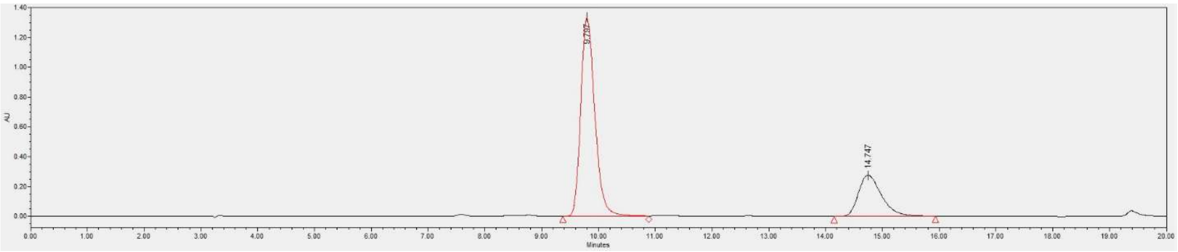
Method: IC3 chiral column, 5% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:

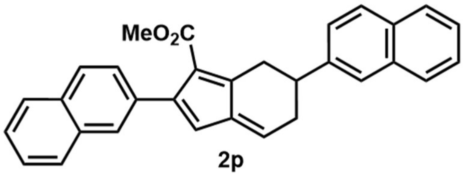


retention time (min)	area (µV*sec)	% area
9.782	26232252	50.35
14.810	25867050	49.65

Enantioenriched:



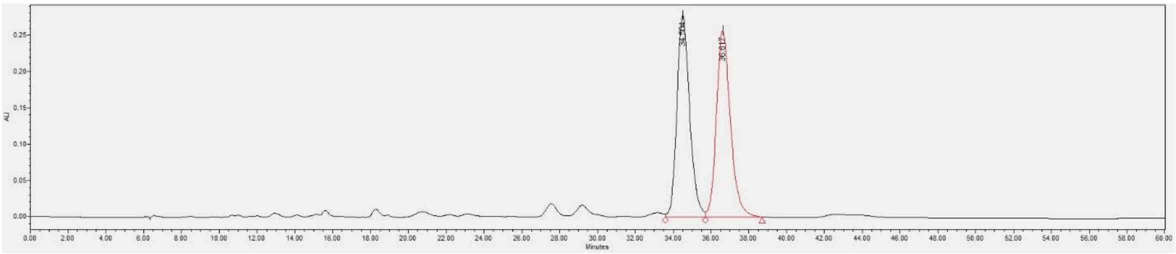
retention time (min)	area (µV*sec)	% area
9.797	23099233	74.81
14.747	7779830	25.19



2p

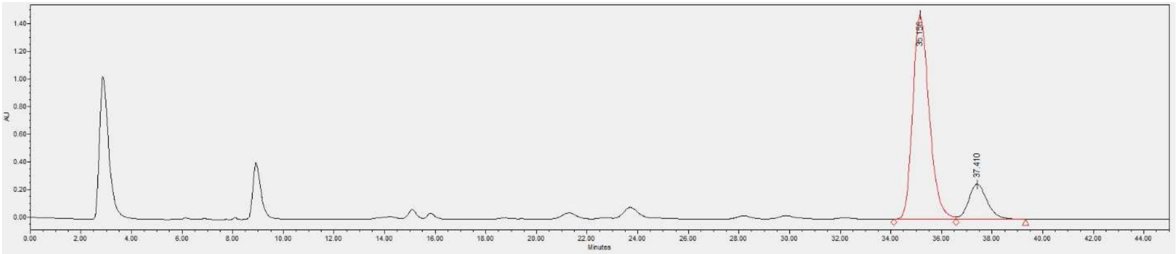
Method: IC3 chiral column, 10% IPA/hexanes 0.5 mL/min, λ= 254 nm

Racemic:

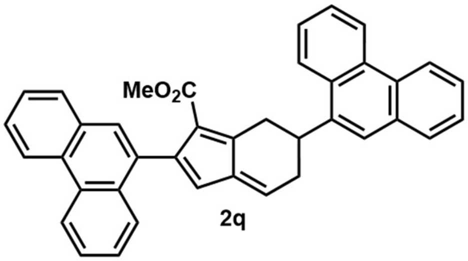


retention time (min)	area (µV*sec)	% area
34.504	12983708	49.55
36.617	13218519	50.45

Enantioenriched:



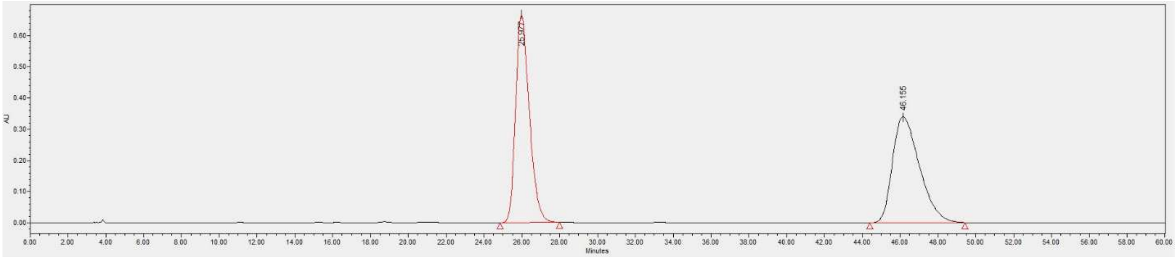
retention time (min)	area (µV*sec)	% area
35.156	66720938	83.90
37.410	12800823	16.10



2q

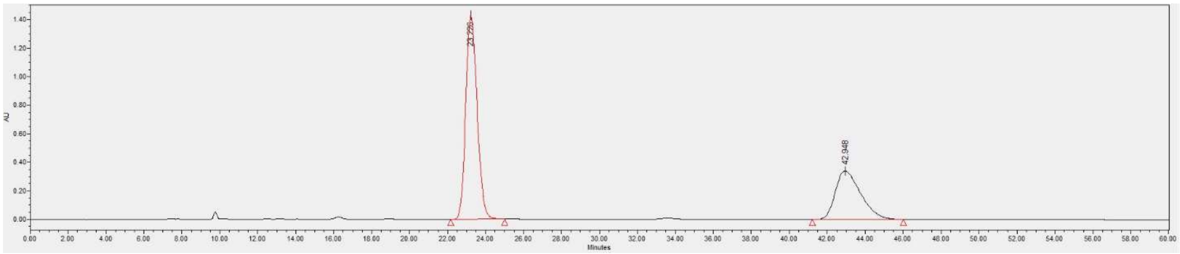
Method: AD3 chiral column, 10% IPA/hexanes 1 mL/min, λ= 254 nm

Racemic:



retention time (min)	area (µV*sec)	% area
25.977	33538266	49.96
46.155	33596746	50.04

Enantioenriched:



retention time (min)	area (µV*sec)	% area
23.226	59220409	65.21
42.948	31598331	34.79

6. X-Ray Crystallographic Information

6.1 X-ray Analysis of 1

A colorless block 0.37 x 0.24 x 0.12 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 40 mm and exposure time was 0.50 seconds per frame at low angles and 2.50 seconds at high angles, using a scan width of 0.5°. Data collection was 99% complete to 74.000° in θ. A total of 26165 reflections were collected covering the indices -21<=h<=21, -9<=k<=10, -39<=l<=39. 4271 reflections were founded to be symmetry independent, with an R_{int} of 0.0410. Indexing and unit cell refinement indicated a centered, monoclinic lattice. The space group was found to be C 2/c (No. 15). The data were integrated using the CrysAlis^{Pro} 1.171.40.84a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

[Note: The instruments are supported by an NIH Shared Instrument Grant S10-RR027172.]

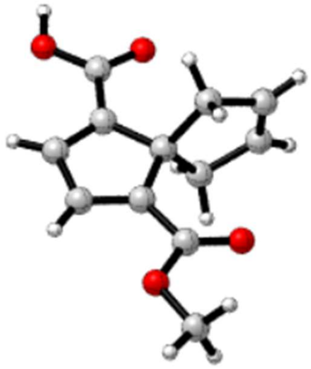


Figure S2. CYLview representation of **1**.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under CCDC 2245692.

Table S10. Crystal data and structure refinement for KGoyal001_Sarpong.

Identification code	KGoyal001_Sarpong	
Empirical formula	C12 H12 O4	
Formula weight	220.22	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 17.1400(2) Å	a= 90°.
	b = 8.09620(10) Å	b= 105.1660(10)°.
	c = 31.5007(4) Å	g = 90°.
Volume	4219.07(9) Å^3	

Z	16
Density (calculated)	1.387 Mg/m^3
Absorption coefficient	0.873 mm^{-1}
F(000)	1856
Crystal size	0.370 x 0.240 x 0.120 mm^3
Theta range for data collection	5.348 to 74.480°.
Index ranges	-21<=h<=21, -9<=k<=10, -39<=l<=39
Reflections collected	26165
Independent reflections	4271 [R(int) = 0.0410]
Completeness to theta = 74.000°	99.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89090
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4271 / 0 / 299
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0423, wR2 = 0.1139
R indices (all data)	R1 = 0.0451, wR2 = 0.1168
Extinction coefficient	n/a
Largest diff. peak and hole	0.277 and -0.240 e.Å^{-3}

6.2 X-Ray Analysis of 2a

An orange block 0.33 x 0.19 x 0.12 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame using a scan width of 0.5°. Data collection was 100% complete to 74.000° in θ. A total of 31264 reflections were collected covering the indices -16<=h<=16, -10<=k<=10, -20<=l<=20. 6878 reflections were found to be symmetry independent, with an R_{int} of 0.0434. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21 (No. 4). The data were integrated using the CrysAlis^{Pro} 1.172.42.72a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014. Although a solution was found in P21/n, the presence of an ordered molecule alongside a disordered molecule in the P21 solution likely indicates that P21 is the correct space group, as we would expect both molecules to have the same disorder in the P21 solution if it was meant to be P21/n. However, the Flack parameter is ill-determined due to a lack of noticeable difference in the Friedel pairs, and thus the presence of a single enantiomer cannot be definitively stated.

[Note: The instruments are supported by an NIH Shared Instrument Grant S10-RR027172.]

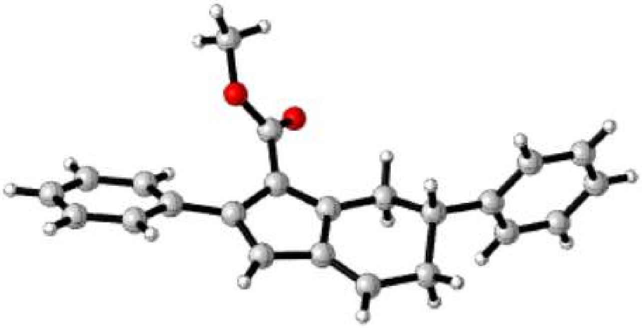


Figure S3. CYLview representation of **2a**.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under CCDC 2245684.

Table S11. Crystal data and structure refinement for KGoyal06_Sarpong.

Identification code	KGoyal06_Sarpong	
Empirical formula	C23 H20 O2	
Formula weight	328.39	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 12.9522(3) Å	a= 90°.
	b = 8.0449(2) Å	b= 98.837(2)°.
	c = 16.5583(4) Å	g = 90°.

Volume	1704.88(7) Å^3
Z	4
Density (calculated)	1.279 Mg/m^3
Absorption coefficient	0.631 mm^{-1}
F(000)	696
Crystal size	0.330 x 0.190 x 0.120 mm^3
Theta range for data collection	3.453 to 74.502°.
Index ranges	-16<=h<=16, -10<=k<=10, -20<=l<=20
Reflections collected	31264
Independent reflections	6878 [R(int) = 0.0434]
Completeness to theta = 74.000°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89267
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6878 / 79 / 527
Goodness-of-fit on F^2	1.049
Final R indices [I>2sigma(I)]	R1 = 0.0513, wR2 = 0.1356
R indices (all data)	R1 = 0.0533, wR2 = 0.1372
Absolute structure parameter	-0.12(17)
Extinction coefficient	0.0036(6)
Largest diff. peak and hole	0.287 and -0.258 e.Å^{-3}

6.3 X-ray Analysis of 4

A colorless block 0.20 x 0.11 x 0.08 mm in size was mounted on a Cryoloop with Paratone oil. Data were collected in a nitrogen gas stream at 100(2) K using omega scans. Crystal-to-detector distance was 33.00 mm and exposure time was 0.50 seconds per frame at low and high angles, using a scan width of 0.5°. Data collection was 98% complete to 74.000° in θ. A total of 33501 reflections were collected covering the indices -12<=h<=12, -13<=k<=17, -25<=l<=26. 6110 reflections were founded to be symmetry independent, with an R_{int} of 0.0295. Indexing and unit cell refinement indicated a primitive, monoclinic lattice. The space group was found to be P 21/n (No. 14). The data were integrated using the CrysAlis^{Pro} 1.171.41.112a software program and scaled using the SCALE3 ABSPACK scaling algorithm. Solution by intrinsic phasing (SHELXT-2015) produced a heavy-atom phasing model consistent with the proposed structure. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares (SHELXL-2014). All hydrogen atoms were placed using a riding model. Their positions were constrained relative to their parent atom using the appropriate HFIX command in SHELXL-2014.

[Note: The instruments are supported by an NIH Shared Instrument Grant S10-RR027172.]

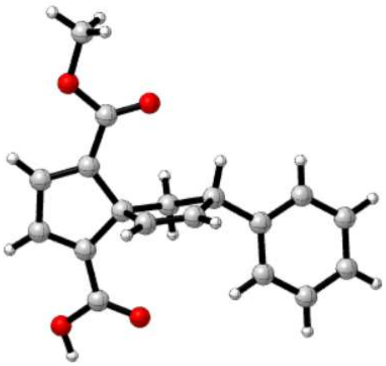


Figure S4. CYLview representation of **4**.

This crystal structure has been deposited at the Cambridge Crystallographic Data Center under CCDC 2245677.

Table S12. Crystal data and structure refinement for KGoyal03_Sarpong.

Identification code	KGoyal03_Sarpong	
Empirical formula	C18 H16 O4	
Formula weight	296.31	
Temperature	100(2) K	
Wavelength	1.54184 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.18740(10) Å	a= 90°.
	b = 13.9611(2) Å	b= 93.5000(10)°.
	c = 21.4180(3) Å	g = 90°.
Volume	3040.54(7) Å^3	
Z	8	
Density (calculated)	1.295 Mg/m^3	

Absorption coefficient	0.748 mm^{-1}
F(000)	1248
Crystal size	0.200 x 0.110 x 0.080 mm^3
Theta range for data collection	3.781 to 74.502°.
Index ranges	-12<=h<=12, -13<=k<=17, -25<=l<=26
Reflections collected	33501
Independent reflections	6110 [R(int) = 0.0295]
Completeness to theta = 74.000°	98.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.85005
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6110 / 0 / 407
Goodness-of-fit on F^2	1.031
Final R indices [I>2sigma(I)]	R1 = 0.0351, wR2 = 0.0884
R indices (all data)	R1 = 0.0405, wR2 = 0.0936
Extinction coefficient	n/a
Largest diff. peak and hole	0.240 and -0.222 e.Å^{-3}

7. Computational Results

7.1 Methods

All DFT calculations were performed with the Gaussian 16 package.[13] Geometry optimizations were performed in the gas phase using the B3LYP functional, 6-31G(d) basis set[14] for all nonmetal atoms and the LANL2DZ[15,16] basis set with effective core potential (ECP) for Pd. Frequency analyses were carried out at the same level of theory as that used for geometry optimizations to characterize the stationary points as either minima (no imaginary frequencies) or saddle points (one imaginary frequency) on the potential energy surface, and to obtain thermal corrections for Gibbs free energies and enthalpies. All transition states were confirmed to connect reactants and products by intrinsic reaction coordinate (IRC) calculations. Single point energies were calculated with the PBE1PBE[17,18] functional, the 6-311++G(d,p) basis set for all nonmetal atoms and the SDD[18,19] for Pd. All calculations used Grimme's dispersion correction, GD3BJ,[21] and intrinsic dichloroethane solvent via the SMD[22,23] solvation model (solvent = dichloroethane). Conformational searches were carried out using the CREST conformer-rotamer ensemble sampling tool, version 2.7.1[24,25] with XTB version 6.2 RC2 (SAW190805)[26–28]. Molecular structures were visualized using PyMOL.[29]

7.2 Optimized TS Structures

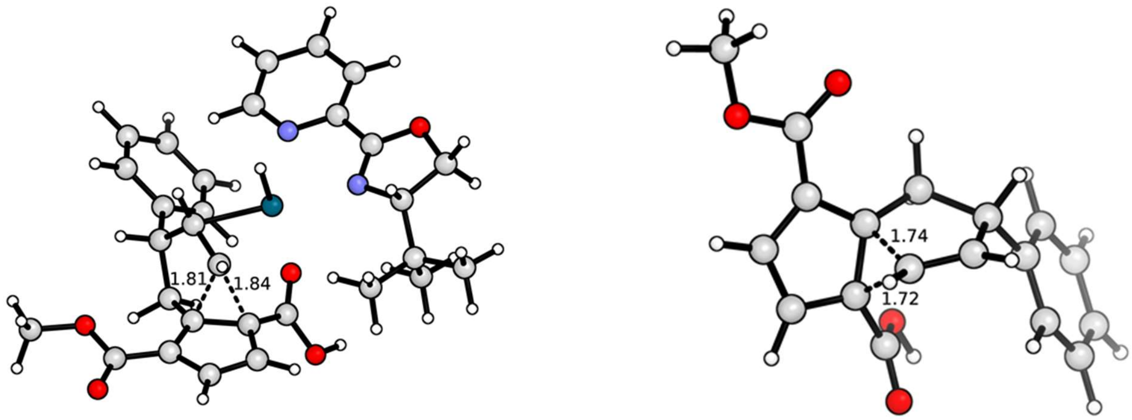


Figure S5. Optimized structure for TS1 (left) and TS2 (right) are shown above.

7.3 Coordinates and Energies:

Table S13. Calculated thermochemical data is shown below (in units of a.u.).

Structure	E_SPC	E	ZPE	H_SPC	qh-H_SPC	T.S	T.qh-S	G(T)_SPC	qh-G(T)_SPC
Acetate anion	-228.432394	-228.592382	0.048679	-228.3784	-228.37883	0.03251	0.032046	-228.41091	-228.410876
TFA anion	-525.99598	-526.322888	0.026019	-525.962994	-525.963503	0.038203	0.037386	-526.001197	-526.000889
H_2	-1.167744	-1.174961	0.010116	-1.154323	-1.154323	0.014793	0.014793	-1.169116	-1.169116
CO_2	-188.442296	-188.58139	0.01153	-188.427168	-188.427169	0.024319	0.024319	-188.451487	-188.451489
Int1	-1775.124914	-1775.518231	0.585589	-1774.50317	-1774.509205	0.102981	0.096727	-1774.606151	-1774.605932
Int2	-1775.102047	-1775.487989	0.580655	-1774.484353	-1774.491208	0.106298	0.098708	-1774.590651	-1774.589916
TS1	-1775.04595	-1775.427529	0.578519	-1774.4309	-1774.437214	0.103667	0.09732	-1774.534566	-1774.534534
9	-1775.093381	-1775.477135	0.580139	-1774.476263	-1774.483065	0.10658	0.098753	-1774.582843	-1774.581818
4	-995.624092	-995.368171	0.304582	-995.299329	-995.302776	0.069376	0.065851	-995.368705	-995.368627
TS2	-995.576104	-995.319086	0.302491	-995.253922	-995.257129	0.067901	0.064613	-995.321823	-995.321742
5	-995.622326	-995.364755	0.304722	-995.297494	-995.300928	0.070498	0.066057	-995.367993	-995.366985
Int5	-2111.482933	-2112.079202	0.573915	-2110.868036	-2110.876114	0.116126	0.106845	-2110.984162	-2110.98296
TS3	-2111.445356	-2112.033814	0.572035	-2110.83285	-2110.84049	0.114492	0.105675	-2110.947342	-2110.946166
Int6	-2111.497317	-2112.095019	0.574469	-2110.882149	-2110.889869	0.114527	0.105901	-2110.996676	-2110.995771
Int3	-2301.118371	-2301.845578	0.608258	-2300.465457	-2300.474614	0.124405	0.113967	-2300.589862	-2300.588581
Int4	-2299.92657	-2300.660108	0.58882	-2299.293969	-2299.302659	0.124002	0.113112	-2299.417971	-2299.415771
Int7	-2111.506653	-2112.105067	0.574919	-2110.891353	-2110.898897	0.113096	0.104989	-2111.00445	-2111.003886
Int8	-2111.495801	-2112.095385	0.574486	-2110.880436	-2110.88857	0.116377	0.106647	-2110.996813	-2110.995217
TS4	-1775.058231	-1775.45177	0.58128	-1774.44055	-1774.446735	0.104458	0.097474	-1774.545008	-1774.544209
6	-1775.104094	-1775.495859	0.583762	-1774.483532	-1774.489912	0.104126	0.09752	-1774.587658	-1774.587432
Int5-Oac	-1813.930732	-1814.364017	0.597087	-1813.294739	-1813.302008	0.109834	0.102287	-1813.404574	-1813.404296
TS3-Oac	-1813.893178	-1814.31909	0.594923	-1813.259663	-1813.266898	0.108727	0.101427	-1813.368389	-1813.368326
Int6-Oac	-1813.946733	-1814.380312	0.597003	-1813.310784	-1813.31812	0.109669	0.102156	-1813.420453	-1813.420276
IntS1	-2111.477422	-2112.070395	0.574396	-2110.862044	-2110.870112	0.117751	0.107531	-2110.979795	-2110.977643

Table S14. The cartesian coordinates of optimized geometries (in units of Å) are given below in the standard XYZ format. Electronic energy values (in units of Hartrees) for singlepoint calculations are also provided. For cationic structures, the energy of a trifluoroacetate (TFA) anion (or acetate anion for **Int1-OAc**) was calculated separately (not shown).

Counteranions and By-products

Acetate (AcO) (E = –228.432394)

C	0.205511	0.000173	-0.013226
O	0.745335	1.138710	0.002891
O	0.767022	-1.127550	0.002976
C	-1.350921	-0.010561	-0.003704
H	-1.712251	0.068827	1.032160
H	-1.761103	0.844657	-0.554617
H	-1.753048	-0.940444	-0.422901

Trifluoroacetate (TFA) (E= –525.995980)

C	-1.049417	0.005478	-0.025839
O	-1.571297	1.138377	-0.010421
O	-1.539867	-1.142872	-0.011076
C	0.517245	0.007504	-0.008573
F	1.057953	-0.951444	-0.805950
F	0.990787	-0.235064	1.248908
F	1.071521	1.181850	-0.400907

Dihydrogen (H_2) (E= –1.167744)

H	0.000000	0.000000	0.371619
H	0.000000	0.000000	-0.371619

Carbon dioxide (CO_2) (E= –188.442296)

C	0.000000	0.000000	0.000000
O	0.000000	0.000000	1.168936
O	0.000000	0.000000	-1.168936

For Figure 3A: Int1, Int2, TS1, and 9

Structure **Int1** (E= –1775.124914)

Pd	-0.522196	-0.135053	-0.817799
N	-1.708499	1.609685	-1.127293
C	-3.047608	1.369932	-1.148325
C	-3.985250	2.376482	-1.344659

C	-3.539677	3.687773	-1.515293
C	-2.172782	3.934150	-1.487187
C	-1.291355	2.868642	-1.297334
H	-0.225564	3.039813	-1.272282
H	-1.773510	4.934588	-1.609521
H	-4.250062	4.493945	-1.664133
H	-5.039801	2.128658	-1.354947
C	-3.448762	-0.020141	-0.906945
N	-2.607874	-0.951177	-0.633399
C	-3.378646	-2.162545	-0.275130
C	-3.270798	-2.493576	1.242755
C	-3.781445	-1.324028	2.099637
H	-4.833095	-1.090558	1.898106
H	-3.700287	-1.578240	3.162478
H	-3.190133	-0.418235	1.928401
C	-4.103203	-3.757644	1.518232
H	-5.170588	-3.606841	1.323039
H	-4.000086	-4.050010	2.569287
H	-3.760812	-4.597031	0.900434
C	-1.807494	-2.782294	1.608729
H	-1.406602	-3.613629	1.018044
H	-1.172416	-1.909897	1.438996
H	-1.735735	-3.057378	2.667391
H	-2.988894	-3.012196	-0.842023
C	-4.802668	-1.786955	-0.755378
H	-5.049878	-2.220281	-1.727289
H	-5.599270	-1.993471	-0.043436
O	-4.749637	-0.331467	-0.931753
C	1.261993	0.855662	-0.919888
C	2.421037	0.008847	-1.432924
H	3.200117	0.682892	-1.806352
H	2.156722	-0.665324	-2.251824
C	2.975363	-0.766165	-0.184467
C	4.485655	-0.803612	-0.097383
C	4.933403	-2.087584	-0.071118
C	3.798652	-2.982523	-0.162268
C	2.657721	-2.241271	-0.237031
C	1.328077	-2.765636	-0.448464
O	0.309675	-2.096675	-0.681962
O	1.232962	-4.098114	-0.405029
H	0.298100	-4.337133	-0.577898
H	3.861765	-4.063552	-0.190140
H	5.966170	-2.403253	0.002989
C	5.315198	0.409409	-0.022533
O	4.873171	1.549035	-0.029478
O	6.627768	0.126687	0.047574
C	7.509185	1.263731	0.115433
H	8.515504	0.847747	0.165673
H	7.297362	1.859447	1.007162
H	7.397774	1.887408	-0.775433
C	2.317266	-0.043986	1.054598
H	3.046247	0.147282	1.844544
H	1.541503	-0.688480	1.472569
C	1.707828	1.255971	0.498228
C	0.650505	1.931229	1.346648
C	0.595681	3.330591	1.379476
C	-0.431543	3.998994	2.049904
C	-1.421300	3.272193	2.714489
C	-1.363766	1.876141	2.713953
C	-0.337072	1.214218	2.038425
H	-0.316508	0.129338	2.045581
H	-2.119843	1.298174	3.238398
H	-2.222816	3.787260	3.236537
H	-0.457073	5.085382	2.052125
H	1.360543	3.901348	0.857947
H	2.534513	1.965392	0.366490
H	1.075578	1.707956	-1.577200

Structure **Int2** (E= –1775.102047)

Pd	-0.420181	0.264897	-0.549415
H	-0.596996	0.536072	-2.029507
N	-2.233126	1.524944	-0.221237
C	-2.122434	2.817886	0.102729

C	-3.235799	3.610308	0.385965
C	-4.502661	3.036732	0.324575
C	-4.619639	1.687634	-0.013184
C	-3.458613	0.964446	-0.276043
C	-3.488990	-0.466204	-0.623380
N	-2.444156	-1.188849	-0.767508
C	-2.887353	-2.552290	-1.125303
H	-2.541329	-2.759483	-2.144801
C	-2.275187	-3.631449	-0.196295
C	-0.751739	-3.630725	-0.396521
H	-0.325650	-2.650107	-0.175229
H	-0.276168	-4.368417	0.259700
H	-0.492819	-3.881459	-1.432896
C	-2.609406	-3.334936	1.273549
H	-2.293610	-2.323838	1.547069
H	-2.097421	-4.046551	1.930635
H	-3.684171	-3.416815	1.472716
C	-2.834741	-5.004936	-0.599975
H	-3.919041	-5.065897	-0.451157
H	-2.373911	-5.793294	0.006399
H	-2.622806	-5.223773	-1.653767
C	-4.437166	-2.442634	-1.096319
H	-4.911835	-3.032417	-0.310552
H	-4.906004	-2.665914	-2.055360
O	-4.696125	-1.034886	-0.795545
H	-5.584535	1.198766	-0.069299
H	-5.389601	3.624930	0.536605
H	-3.096707	4.654339	0.643569
H	-1.119607	3.221999	0.130744
C	1.582717	-0.493388	-0.848280
C	1.602684	0.851339	-1.219841
C	2.312461	1.725073	-0.208462
C	1.636469	3.064009	0.045422
C	1.265604	3.857786	-1.053068
C	0.640959	5.091032	-0.872490
C	0.376862	5.562898	0.417133

C	0.751753	4.790503	1.516243
C	1.377587	3.553096	1.331426
H	1.665249	2.977831	2.204819
H	0.559864	5.146607	2.524654
H	-0.110798	6.522851	0.560870
H	0.359300	5.683143	-1.738870
H	1.467450	3.506530	-2.061206
H	3.298938	1.920705	-0.648895
C	2.497731	0.793732	1.010256
H	3.463991	0.929792	1.498998
H	1.720515	0.985423	1.749298
C	2.321418	-0.677746	0.487071
C	1.632478	-1.564811	1.502878
C	2.414022	-2.630982	1.817293
C	3.643779	-2.554766	1.051151
C	3.624527	-1.435618	0.280802
C	4.686362	-0.990708	-0.635833
O	4.636451	0.026821	-1.309331
O	5.729649	-1.838423	-0.649464
C	6.819549	-1.473229	-1.518047
H	6.480732	-1.422773	-2.556132
H	7.236592	-0.507041	-1.222045
H	7.562463	-2.261826	-1.397764
H	4.448630	-3.276908	1.102091
H	2.171330	-3.415376	2.523719
C	0.338291	-1.234871	2.072768
O	-0.396835	-0.327208	1.658151
O	-0.014532	-1.977514	3.123860
H	-0.913097	-1.702425	3.403932
H	1.503573	1.176563	-2.248441
H	1.508762	-1.322598	-1.544281

Transition State **TS1** (E= –1775.045950)

Pd	-0.525560	0.004173	-0.624335
H	-0.679099	0.092112	-2.128288
N	-2.651287	-0.914388	-0.590618
C	-3.581881	-0.031153	-0.537012

C	-3.342271	1.418770	-0.483133
N	-2.049370	1.783887	-0.579270
C	-1.747562	3.083507	-0.613334
C	-2.726253	4.077320	-0.525886
C	-4.059821	3.700176	-0.401648
C	-4.380916	2.341245	-0.386028
H	-5.406392	2.001264	-0.305716
H	-4.843544	4.446993	-0.326115
H	-2.432540	5.120569	-0.553985
H	-0.699839	3.333438	-0.716592
O	-4.853919	-0.444395	-0.584421
C	-4.805696	-1.905423	-0.596575
H	-5.427450	-2.249507	-1.422648
H	-5.227717	-2.245524	0.350705
C	-3.301818	-2.237214	-0.766883
C	-2.762388	-3.333179	0.182041
C	-2.796544	-2.859252	1.643068
H	-2.361232	-3.623924	2.296258
H	-3.820822	-2.677968	1.988517
H	-2.234542	-1.929343	1.769590
C	-1.324825	-3.669713	-0.239378
H	-0.876977	-4.384407	0.459189
H	-1.306994	-4.117479	-1.240526
H	-0.698199	-2.775525	-0.272515
C	-3.628816	-4.594111	0.018080
H	-4.658765	-4.435345	0.357224
H	-3.209854	-5.414618	0.611775
H	-3.659735	-4.919640	-1.028911
H	-3.102217	-2.559939	-1.795797
C	1.460562	0.577057	-1.031419
C	1.535877	-0.823051	-0.837541
C	2.815700	-0.919074	0.443868
C	1.671972	-1.821714	0.704146
C	2.094664	-3.155858	0.395464
C	3.389179	-3.090310	-0.085214
C	3.853603	-1.751240	-0.060979
C	5.159739	-1.338366	-0.574742
O	6.051932	-2.110482	-0.888497
O	5.273377	0.006221	-0.682500
C	6.538898	0.487537	-1.169103
H	7.351460	0.168843	-0.510966
H	6.725328	0.119669	-2.181636
H	6.455105	1.574653	-1.169815
H	3.967733	-3.921152	-0.470692
H	1.467730	-4.032769	0.467826
C	0.597359	-1.487819	1.666966
O	-0.138898	-0.499428	1.600084
O	0.509967	-2.360814	2.659864
H	-0.238549	-2.097517	3.240090
C	2.870407	0.490085	0.980941
H	3.901054	0.763667	1.203410
H	2.307663	0.543621	1.914810
C	2.281390	1.447342	-0.087867
C	1.614856	2.700028	0.446315
C	1.860995	3.928408	-0.181985
C	1.255266	5.102885	0.271572
C	0.396985	5.066086	1.372349
C	0.144715	3.847096	2.006408
C	0.744425	2.674384	1.545666
H	0.518837	1.736568	2.039552
H	-0.527071	3.806098	2.859312
H	-0.071053	5.977617	1.732823
H	1.461748	6.044305	-0.229894
H	2.538650	3.963573	-1.031631
H	3.119886	1.772529	-0.715892
H	1.614578	-1.546189	-1.639598
H	1.426721	0.911385	-2.066440

Structure **9** (E= –1775.093381)

Pd	-0.752959	0.282405	-0.635997
H	-1.167419	0.832933	-1.986861
C	1.229393	0.681055	-1.521294
C	1.029257	-0.694971	-1.346419

C	1.726265	-1.444037	-0.195067
C	2.379805	-2.740101	-0.610772
C	3.705995	-2.651593	-0.408670
C	4.042153	-1.317680	0.126274
C	2.908591	-0.588118	0.276170
C	2.643249	0.836166	0.598805
H	3.538015	1.325965	0.981216
H	1.861766	0.891977	1.365117
C	2.153544	1.550386	-0.686338
C	1.574548	2.942133	-0.446915
C	1.114544	3.695613	-1.539496
C	0.573965	4.967660	-1.358800
C	0.492873	5.522250	-0.077645
C	0.962686	4.791634	1.013014
C	1.497265	3.511769	0.829752
H	1.854516	2.968363	1.696873
H	0.912959	5.210618	2.014111
H	0.074343	6.514423	0.064558
H	0.221758	5.528772	-2.219848
H	1.185562	3.287936	-2.543965
H	3.043102	1.676927	-1.323890
C	5.409060	-0.827511	0.401459
O	5.693046	0.293113	0.791564
O	6.325011	-1.785047	0.166833
C	7.695313	-1.411473	0.406333
H	8.284546	-2.295350	0.161497
H	7.837989	-1.135537	1.454442
H	7.980132	-0.572597	-0.234029
H	4.441715	-3.421252	-0.604835
H	1.818334	-3.590001	-0.977093
C	0.809749	-1.582440	1.014344
O	-0.075372	-0.764263	1.274645
O	1.075454	-2.606971	1.806448
H	0.468912	-2.570588	2.578864
H	0.715852	-1.303099	-2.189582
H	1.000659	1.081746	-2.503245
N	-2.331927	1.588537	0.156269
C	-2.072088	2.864061	0.467291
C	-3.038689	3.703679	1.020898
C	-4.315419	3.199595	1.250827
C	-4.588331	1.871087	0.922214
C	-3.568829	1.094973	0.376081
C	-3.777782	-0.314470	0.002516
N	-2.864468	-1.079928	-0.461602
C	-3.481742	-2.397401	-0.730009
H	-3.475514	-2.551390	-1.815652
C	-2.693577	-3.569206	-0.090991
C	-2.500311	-3.344007	1.416487
H	-3.457596	-3.313128	1.950028
H	-1.912043	-4.162988	1.846229
H	-1.977809	-2.402894	1.611235
C	-3.468505	-4.874718	-0.334521
H	-2.890576	-5.729570	0.035242
H	-3.653645	-5.031866	-1.404252
H	-4.434359	-4.881880	0.183462
C	-1.326741	-3.665100	-0.787397
H	-0.709502	-4.441399	-0.321896
H	-1.443774	-3.913865	-1.849308
H	-0.793025	-2.714685	-0.729691
C	-4.939197	-2.218230	-0.224342
H	-5.691444	-2.391494	-0.994344
H	-5.177839	-2.808573	0.661885
O	-5.017898	-0.810698	0.162688
H	-5.567779	1.437557	1.083322
H	-5.091508	3.826284	1.677884
H	-2.781330	4.730003	1.257297
H	-1.068306	3.212675	0.268264

For Figure 3B: 4, TS2, and 5

Structure **4** (E= –995.624092)

C	-0.535330	-0.540639	1.590138
C	0.508779	0.282310	1.540186
H	1.032426	0.716584	2.386857

C	0.973222	0.536941	0.114765
C	1.238733	1.998066	-0.155687
C	2.545080	2.192131	-0.464108
C	3.229999	0.918668	-0.445134
C	2.343688	-0.056837	-0.126144
C	2.636485	-1.492783	-0.044186
O	1.803037	-2.367626	0.090835
O	3.949908	-1.742343	-0.151490
C	4.311228	-3.122947	-0.117070
H	5.396173	-3.145720	-0.223638
H	4.015562	-3.576462	0.833067
H	3.838931	-3.667259	-0.939628
H	4.282100	0.777084	-0.663621
H	3.013561	3.144131	-0.686399
C	0.218650	3.041392	-0.044214
O	-0.941568	2.857464	0.273739
O	0.693387	4.264686	-0.337349
H	-0.052669	4.884588	-0.231445
C	-0.177647	-0.094238	-0.726251
H	0.203023	-0.636921	-1.594556
H	-0.823334	0.710323	-1.085081
C	-0.982827	-1.008207	0.231214
C	-2.477140	-0.946686	0.018112
C	-3.188038	-2.076648	-0.391074
C	-4.567630	-2.022050	-0.584875
C	-5.255735	-0.831166	-0.367535
C	-4.555020	0.303668	0.041827
C	-3.178055	0.246229	0.233209
H	-2.629710	1.133267	0.542965
H	-5.085152	1.237449	0.213321
H	-6.331498	-0.785748	-0.516699
H	-5.104215	-2.912017	-0.904439
H	-2.653244	-3.009322	-0.559520
H	-0.657808	-2.047342	0.099451
H	-1.012905	-0.883312	2.504458

Transition State **TS2** (E= –995.576104)

C	-0.438520	-0.165531	1.883853
H	-0.697343	-0.261388	2.934821
C	-0.905802	-1.164668	0.869911
C	0.478522	0.730734	1.469095
H	-0.836415	-2.154830	1.342259
C	0.167665	-1.106780	-0.263580
H	1.107443	1.327338	2.119525
C	1.007768	0.130504	-0.072707
H	-0.296993	-1.092143	-1.252948
H	0.824909	-1.974945	-0.203691
C	2.424574	0.302863	-0.195759
C	0.439772	1.479754	-0.075405
C	2.699646	1.686673	-0.272944
C	1.525095	2.409531	-0.216112
H	1.410281	3.486148	-0.209433
H	3.698118	2.107319	-0.312682
C	-2.345122	-1.019591	0.410060
C	-3.181552	-0.016564	0.902261
C	-2.861638	-1.922916	-0.525281
C	-4.498335	0.096069	0.457489
H	-2.794889	0.697696	1.625142
C	-4.173991	-1.812708	-0.972522
H	-2.225438	-2.716954	-0.910829
C	-4.998470	-0.798922	-0.483970
H	-5.131025	0.889442	0.847372
H	-4.555790	-2.520472	-1.704023
H	-6.023624	-0.711001	-0.833917
C	-0.932209	1.910406	-0.474484
O	-1.525464	2.832024	0.036583
O	-1.397600	1.208078	-1.510372
C	3.400881	-0.772436	-0.120582
O	3.152326	-1.951607	0.075491
O	4.657608	-0.319206	-0.296009
C	5.675342	-1.314898	-0.238694
H	6.615740	-0.785199	-0.397221
H	5.682957	-1.810248	0.736547

H	5.531177	-2.065940	-1.020935
H	-2.305816	1.521751	-1.689314

Structure **5** (E= –995.622326)

C	1.060654	0.854904	-1.576017
C	0.106581	1.780399	-1.446457
C	-0.981868	1.678948	-0.399869
C	-2.385544	1.863007	-0.937183
C	-3.088531	0.740025	-0.714905
C	-2.229252	-0.261209	-0.071366
C	-0.997742	0.271624	0.133268
C	0.297606	-0.319974	0.531918
H	0.179222	-1.315431	0.960713
H	0.785546	0.326567	1.272821
C	1.202939	-0.382759	-0.730153
C	2.639553	-0.643406	-0.335722
C	3.173417	-1.931780	-0.405317
C	4.484661	-2.180927	-0.005398
C	5.279945	-1.140313	0.469044
C	4.755614	0.149508	0.543207
C	3.444653	0.394411	0.144995
H	3.038311	1.402330	0.203338
H	5.370065	0.967336	0.911072
H	6.303988	-1.332221	0.778457
H	4.885795	-3.189286	-0.068030
H	2.554210	-2.745476	-0.777298
H	0.861019	-1.238407	-1.329794
C	-2.622424	-1.643397	0.241947
O	-1.899024	-2.497178	0.718792
O	-3.908528	-1.863903	-0.067769
C	-4.384748	-3.182888	0.199905
H	-5.430052	-3.187173	-0.110454
H	-3.817195	-3.922024	-0.372202
H	-4.305913	-3.412818	1.266023
H	-4.126065	0.566791	-0.976952
H	-2.728615	2.788287	-1.385416
C	-0.767865	2.751703	0.666345
O	-0.320620	3.851081	0.437940
O	-1.165834	2.354720	1.878976
H	-1.033150	3.109409	2.485836
H	0.079671	2.651910	-2.094856
H	1.809311	0.985181	-2.356215

For Figure 3C: Int1 (see above), Int5, TS3, Int6

Structure **Int5** (E= -2111.482933)

Pd	-0.274528	0.041639	-0.720692
N	-2.478998	-0.174852	-0.340475
C	-2.780650	-1.422427	-0.345382
C	-1.846588	-2.454858	-0.809377
N	-0.607114	-2.002487	-1.128250
C	0.296439	-2.873428	-1.598652
C	0.008066	-4.228967	-1.750974
C	-1.256109	-4.698238	-1.406729
C	-2.203098	-3.792664	-0.929186
H	-3.201604	-4.106259	-0.649899
H	-1.505983	-5.748984	-1.508933
H	0.773535	-4.894240	-2.134392
H	1.263631	-2.462753	-1.856465
O	-3.992747	-1.782905	0.086387
C	-4.615281	-0.549580	0.582528
H	-4.686066	-0.641326	1.667719
H	-5.613503	-0.501797	0.150608
C	-3.653976	0.583851	0.133107
C	-4.222187	1.531839	-0.960349
C	-4.571145	0.750656	-2.236285
H	-3.677581	0.292964	-2.675382
H	-5.003243	1.425792	-2.983617
H	-5.304063	-0.043074	-2.048252
C	-3.180231	2.611891	-1.289374
H	-2.937944	3.206743	-0.402928
H	-2.252148	2.176787	-1.668751
H	-3.575583	3.292545	-2.052810
C	-5.478645	2.218031	-0.396945
H	-6.290013	1.508132	-0.200412

H	-5.855375	2.955646	-1.114754
H	-5.253191	2.744512	0.538636
H	-3.335847	1.190263	0.983891
C	2.194998	0.354123	2.224294
C	2.557438	0.908301	1.066671
C	2.750133	-0.117661	-0.038835
C	1.659174	-0.000871	-1.106216
C	2.233917	0.179861	-2.325665
C	3.680496	0.217259	-2.175378
C	4.016023	0.060074	-0.866205
C	5.358320	0.030015	-0.300692
O	5.624181	-0.159378	0.879984
O	6.321016	0.234611	-1.237047
C	7.669711	0.218603	-0.748750
H	7.911327	-0.749760	-0.300548
H	8.299579	0.396598	-1.621710
H	7.824726	1.006278	-0.005570
H	4.382145	0.354465	-2.991385
H	1.717716	0.300319	-3.272487
C	2.729402	-1.463904	0.762354
H	3.760797	-1.783127	0.914599
H	2.201306	-2.254062	0.228032
C	2.088336	-1.151088	2.148444
C	0.677904	-1.706186	2.309778
C	0.476148	-3.094393	2.233194
C	-0.796357	-3.645434	2.373592
C	-1.898097	-2.815756	2.610445
C	-1.707836	-1.437393	2.693286
C	-0.432311	-0.885831	2.535701
H	-0.318270	0.191533	2.558986
H	-2.554888	-0.779091	2.866263
H	-2.891851	-3.241100	2.718277
H	-0.930427	-4.721429	2.299781
H	1.327741	-3.747915	2.058171
H	2.700949	-1.617633	2.932971
H	2.657093	1.970579	0.872169
H	1.973484	0.909112	3.131442
C	-0.426657	2.652448	0.642077
O	0.032955	2.097779	-0.414728
O	-1.091782	2.198288	1.569013
C	-0.052093	4.156675	0.663229
F	-0.421812	4.757977	1.806547
F	-0.656819	4.814020	-0.354827
F	1.281313	4.336826	0.522561

Transition State **TS3** (E= –2111.445356)

Pd	-0.196956	0.115728	-0.503257
N	-2.204823	-0.736381	-0.480813
C	-2.119175	-2.018796	-0.475390
C	-0.869995	-2.707903	-0.810824
N	0.190431	-1.879531	-0.989034
C	1.353868	-2.399166	-1.401167
C	1.517413	-3.768986	-1.607708
C	0.443047	-4.625053	-1.382466
C	-0.779249	-4.083023	-0.984025
H	-1.651055	-4.703289	-0.813722
H	0.547111	-5.695446	-1.525053
H	2.479341	-4.143882	-1.938519
H	2.163537	-1.701278	-1.565880
O	-3.213340	-2.723780	-0.183083
C	-4.221998	-1.731370	0.211340
H	-4.360156	-1.828461	1.289486
H	-5.142713	-1.993582	-0.306558
C	-3.607713	-0.366638	-0.197668
C	-4.291352	0.315893	-1.416694
C	-4.237585	-0.590739	-2.656159
H	-3.202571	-0.780817	-2.961883
H	-4.750159	-0.107634	-3.495676
H	-4.726924	-1.556959	-2.485826
C	-3.583458	1.643449	-1.727677
H	-3.650954	2.334282	-0.881378
H	-2.526380	1.493370	-1.962264
H	-4.059700	2.125168	-2.590006

C	-5.752304	0.617707	-1.040086
H	-6.335846	-0.292850	-0.862707
H	-6.241542	1.167681	-1.852090
H	-5.804404	1.236269	-0.135729
H	-3.605214	0.333667	0.639881
C	1.875087	1.022805	2.157038
C	2.151804	1.511561	0.929663
C	2.940242	0.189054	0.093024
C	1.718680	0.697282	-0.551693
C	2.150634	1.465133	-1.692117
C	3.531367	1.413169	-1.775682
C	4.054168	0.643564	-0.703565
C	5.455291	0.438982	-0.394793
O	5.915722	-0.129369	0.592649
O	6.267809	0.961231	-1.357924
C	7.673086	0.805678	-1.129415
H	7.947782	-0.252193	-1.073571
H	8.163384	1.274889	-1.984233
H	7.978043	1.302130	-0.203127
H	4.142718	1.927849	-2.508788
H	1.487779	2.037785	-2.328891
C	2.963815	-0.888483	1.154986
H	3.989920	-0.983069	1.510356
H	2.670096	-1.851807	0.732642
C	2.026365	-0.466819	2.330511
C	0.734729	-1.271462	2.442589
C	0.779273	-2.673975	2.411839
C	-0.384297	-3.430955	2.544356
C	-1.617916	-2.798392	2.729573
C	-1.669745	-1.405671	2.775621
C	-0.504098	-0.649022	2.628627
H	-0.576072	0.431988	2.628290
H	-2.620085	-0.896821	2.908951
H	-2.525275	-3.386958	2.830576
H	-0.328419	-4.515567	2.504644
H	1.731704	-3.180261	2.279644
H	2.568518	-0.637559	3.271557
H	2.329413	2.555801	0.706173
H	1.689724	1.676877	3.004013
C	-1.376170	2.574611	0.629184
O	-0.609105	2.146223	-0.294052
O	-1.974696	1.979544	1.524709
C	-1.568995	4.112867	0.592345
F	-2.885596	4.418972	0.517590
F	-0.957668	4.719904	-0.440939
F	-1.092389	4.669567	1.728752

Structure **Int6** (E= –2111.497317)

Pd	0.173773	-0.291802	-0.330176
N	1.649932	1.243649	-0.601101
C	1.132596	2.409880	-0.444977
C	-0.311591	2.618236	-0.525397
N	-1.040834	1.473888	-0.601538
C	-2.361143	1.588456	-0.784983
C	-3.006239	2.822993	-0.865882
C	-2.261058	3.990820	-0.749465
C	-0.881039	3.884294	-0.580741
H	-0.246194	4.758368	-0.498634
H	-2.736077	4.965033	-0.795091
H	-4.080143	2.844372	-1.013306
H	-2.912017	0.665846	-0.866874
O	1.957464	3.438359	-0.244978
C	3.291909	2.838714	-0.093078
H	3.543504	2.890008	0.968191
H	3.983301	3.449327	-0.670199
C	3.122258	1.384092	-0.598876
C	3.736633	1.102922	-1.999336
C	3.172943	2.066330	-3.056083
H	2.088904	1.946274	-3.163917
H	3.628043	1.857387	-4.030777
H	3.380324	3.115779	-2.816971
C	3.427188	-0.342019	-2.419546
H	3.837527	-1.064593	-1.707974

H	2.350348	-0.518671	-2.492147
H	3.874596	-0.545032	-3.399947
C	5.261866	1.269337	-1.888899
H	5.551399	2.294004	-1.629454
H	5.735768	1.026061	-2.846668
H	5.675942	0.596694	-1.127841
H	3.532468	0.672682	0.119157
C	-1.068124	-1.874642	2.661037
C	-0.680795	-2.396118	1.484218
C	-2.590595	-1.338223	0.333790
C	-1.236664	-1.881134	0.215787
C	-1.193532	-2.576598	-1.092118
C	-2.387910	-2.389540	-1.720568
C	-3.269907	-1.630724	-0.834316
C	-4.645003	-1.227556	-1.115624
O	-5.327367	-0.493911	-0.408474
O	-5.104283	-1.746965	-2.279508
C	-6.445412	-1.379728	-2.636161
H	-6.534725	-0.295011	-2.746244
H	-6.640868	-1.872817	-3.589347
H	-7.156461	-1.724478	-1.879924
H	-2.657820	-2.714346	-2.717964
H	-0.323473	-3.098274	-1.469107
C	-3.096411	-0.771339	1.621947
H	-3.917788	-1.409125	1.974932
H	-3.549892	0.211690	1.462867
C	-2.010622	-0.695061	2.735361
C	-1.267664	0.650191	2.743253
C	-1.999433	1.845114	2.835746
C	-1.358503	3.083281	2.861350
C	0.037353	3.154155	2.808532
C	0.775097	1.974129	2.732032
C	0.128711	0.734599	2.696645
H	0.726513	-0.164914	2.615026
H	1.860410	2.008431	2.687767
H	0.539142	4.117679	2.822886
H	-1.948900	3.993674	2.922136
H	-3.084569	1.809133	2.889020
H	-2.546974	-0.743523	3.691657
H	0.042792	-3.203362	1.439825
H	-0.648462	-2.252184	3.590108
C	2.428320	-1.889998	0.672944
O	1.537158	-1.863562	-0.243891
O	2.698492	-1.082374	1.557200
C	3.240942	-3.208428	0.595122
F	4.251108	-3.235319	1.479024
F	3.770713	-3.396037	-0.634788
F	2.442558	-4.271638	0.854910

For Scheme 2: Int1 (see above), Int2 (see above), Int3, Int4, Int5 (see above), TS3 (see above), Int6 (see above), Int7, Int8

<u>Structure **Int3** (E= –2301.118371)</u>

Pd	-0.516190	0.171820	-0.262961
N	-2.545322	1.424762	-0.598393
N	-2.278573	-1.211629	0.176244
C	-2.660306	2.711010	-0.931341
C	-3.663433	0.717990	-0.348488
C	-4.940126	1.273003	-0.411353
H	-5.811606	0.664617	-0.199979
C	-5.054486	2.621927	-0.753361
C	-3.899760	3.351271	-1.023465
H	-3.944312	4.399081	-1.299557
H	-6.032200	3.089648	-0.810672
C	1.278676	1.234062	-0.701853
H	1.172678	1.361997	-1.774958
C	1.709555	2.409199	0.161867
C	1.638400	0.005017	-0.125612
H	2.559840	2.846892	-0.369954
C	2.233128	1.757188	1.467183
H	1.842174	-0.896462	-0.692509
C	2.446956	0.239011	1.167600
H	1.506065	1.845395	2.270296
H	-0.437870	0.619953	1.179169

H	3.159845	2.226772	1.804781
C	3.883124	-0.164819	0.839568
C	2.149645	-0.686386	2.337536
C	4.275549	-1.189986	1.639800
C	3.211781	-1.504420	2.569177
H	3.274830	-2.255143	3.346911
H	5.234956	-1.690330	1.605725
C	0.670613	3.504073	0.333976
C	0.646413	4.564606	-0.583308
C	-0.285869	3.493593	1.359187
C	-0.300418	5.586787	-0.483129
H	1.383363	4.588606	-1.382789
C	-1.227910	4.518201	1.469015
H	-0.310323	2.678448	2.074120
C	-1.239465	5.570398	0.550651
H	-0.296982	6.398085	-1.206190
H	-1.958621	4.489070	2.272964
H	-1.973058	6.367064	0.638446
C	0.963656	-0.633276	3.195627
O	0.105721	0.241472	3.188209
O	0.908289	-1.662131	4.071576
H	0.097484	-1.534102	4.604319
C	4.693348	0.437080	-0.231349
O	4.356553	1.386958	-0.919899
O	5.884085	-0.180945	-0.366733
C	6.747442	0.352021	-1.386843
H	6.274499	0.272015	-2.369346
H	6.985201	1.399347	-1.181538
H	7.650961	-0.257153	-1.349905
H	-1.736038	3.239946	-1.131321
C	-3.434084	-0.703418	-0.043497
C	-2.441714	-2.678746	0.269875
C	-3.981802	-2.851703	0.280688
O	-4.496762	-1.525133	-0.055079
H	-4.348374	-3.548030	-0.473422
H	-4.390899	-3.117904	1.257590
H	-2.021626	-3.100972	-0.649614
C	-1.693296	-3.316824	1.463145
C	-0.183263	-3.189659	1.211722
H	0.105426	-3.715097	0.294849
H	0.109588	-2.143290	1.096680
H	0.383669	-3.614661	2.046672
C	-2.062448	-4.809007	1.522715
H	-1.844751	-5.307640	0.570104
H	-1.478938	-5.309402	2.304224
H	-3.122976	-4.963566	1.753730
C	-2.070930	-2.624738	2.781168
H	-3.146158	-2.691021	2.984990
H	-1.550486	-3.104468	3.617709
H	-1.795316	-1.566048	2.763252
O	1.272746	-0.434751	-3.518975
C	0.335996	-1.029939	-2.979336
O	-0.697849	-0.580403	-2.396400
C	0.461273	-2.582450	-2.945181
F	1.039760	-3.083894	-4.054174
F	1.244419	-2.952767	-1.889797
F	-0.720596	-3.220477	-2.789299

Structure **Int4** (E= –2299.926570)

C	-4.105948	0.736883	2.066144
H	-4.245481	1.129234	3.069697
C	-4.101866	1.638667	0.855707
C	-3.906769	-0.546550	1.772843
H	-5.090746	2.096555	0.729945
C	-3.834877	0.651664	-0.325609
H	-3.864140	-1.368014	2.480485
C	-3.757689	-0.796856	0.280913
H	-2.896555	0.901477	-0.821039
H	-4.627030	0.713088	-1.072066
C	-4.813129	-1.751746	-0.254121
C	-2.476647	-1.538999	-0.076570
C	-4.215646	-2.845449	-0.794557
C	-2.769444	-2.705670	-0.699576

H	-2.051149	-3.431118	-1.064316
H	-4.725887	-3.686355	-1.249428
C	-3.074767	2.757017	0.934935
C	-3.397857	4.056862	0.527438
C	-1.771690	2.501060	1.391058
C	-2.447825	5.081206	0.576851
H	-4.403809	4.269155	0.172360
C	-0.823807	3.522944	1.447552
H	-1.501449	1.493857	1.692268
C	-1.157642	4.818128	1.041827
H	-2.718808	6.084391	0.257963
H	0.179229	3.305002	1.805355
H	-0.418708	5.613581	1.084940
C	-1.126754	-1.014283	0.269763
O	-0.866399	-0.646711	1.418113
O	-0.311553	-0.960722	-0.750767
C	-6.244426	-1.453301	-0.207052
O	-6.722706	-0.386312	0.150887
O	-7.002006	-2.494889	-0.622236
C	-8.419763	-2.264172	-0.631629
H	-8.674041	-1.438889	-1.302972
H	-8.864562	-3.193313	-0.990118
H	-8.781383	-2.035111	0.374828
Pd	1.481758	-0.129277	-0.284319
N	0.891131	1.677545	-1.052001
N	3.222688	1.016162	0.086680
C	-0.275649	1.911348	-1.658788
C	1.798096	2.674660	-0.929238
C	1.552503	3.958313	-1.394686
H	2.302561	4.730943	-1.274406
C	0.324911	4.212739	-2.012143
C	-0.593252	3.176987	-2.152808
H	-1.555005	3.334949	-2.626600
H	0.096269	5.207295	-2.379208
H	-0.941075	1.063294	-1.744760
C	3.034937	2.242702	-0.282036
C	4.538786	0.962918	0.797231
C	5.145221	2.330105	0.409174
O	4.001654	3.122562	-0.055639
H	5.601278	2.864582	1.240023
H	5.837237	2.271519	-0.433079
C	2.275780	-2.844488	-0.437759
O	1.999586	-1.963692	0.458294
O	2.431339	-2.714538	-1.645395
C	2.412541	-4.250224	0.198033
F	2.803061	-5.168566	-0.700387
F	1.228778	-4.654415	0.710223
F	3.312664	-4.256240	1.205440
H	4.312408	0.946751	1.869837
C	5.447875	-0.252036	0.471205
C	6.899873	0.100225	0.855986
H	7.342913	0.854957	0.197504
H	6.962408	0.463661	1.889123
H	7.520958	-0.799472	0.783326
C	5.017578	-1.447907	1.334679
H	5.566252	-2.348569	1.035634
H	5.240334	-1.255421	2.391797
H	3.951929	-1.652977	1.245597
C	5.375764	-0.602941	-1.021793
H	6.111031	-1.381563	-1.255303
H	4.387037	-0.979820	-1.299589
H	5.600021	0.265668	-1.653290

Structure **Int7** (E= –2111.506653)

C	3.533751	-2.108174	-2.851897
C	2.263784	-2.557664	-2.830460
C	1.508501	-2.559520	-1.591927
C	0.165003	-2.711589	-1.345654
C	-0.086154	-2.487964	0.087287
C	1.260314	-2.320020	0.683688
C	2.191627	-2.319272	-0.325448
C	3.678040	-2.154765	-0.306268
H	4.130546	-3.150477	-0.182894

C	4.226609	-1.545144	-1.630217
C	4.168668	-0.017748	-1.594026
C	5.255788	0.694513	-1.068537
C	5.218588	2.084988	-0.956442
C	4.087331	2.789444	-1.375390
C	3.002252	2.090691	-1.907927
C	3.042564	0.699130	-2.016141
H	2.191235	0.167814	-2.427816
Pd	-1.176136	-0.676240	0.035355
N	-2.517921	1.023075	0.009245
C	-3.739033	0.625876	-0.037916
O	-4.702088	1.527794	0.165242
C	-4.000489	2.758384	0.561350
H	-4.460482	3.577288	0.012244
H	-4.166791	2.887831	1.633007
C	-2.514407	2.487056	0.213601
H	-1.866351	2.706754	1.064064
C	-1.982755	3.252047	-1.030862
C	-2.827382	2.939289	-2.276125
H	-2.786098	1.872698	-2.524874
H	-3.878902	3.221577	-2.147673
H	-2.442253	3.496276	-3.137711
C	-0.523322	2.852980	-1.295969
H	-0.139010	3.419262	-2.152544
H	0.115695	3.069737	-0.434589
H	-0.429242	1.787388	-1.520152
C	-2.031708	4.758032	-0.719979
H	-1.600463	5.325129	-1.552809
H	-3.054757	5.121628	-0.570699
H	-1.452659	4.991938	0.181723
C	-4.085538	-0.771185	-0.312600
N	-3.018471	-1.610173	-0.398008
C	-3.243245	-2.899409	-0.677944
C	-4.527823	-3.405336	-0.881247
C	-5.619659	-2.549465	-0.781265
C	-5.393758	-1.203666	-0.489067
H	-6.209152	-0.495418	-0.400731
H	-6.629993	-2.916595	-0.926986
H	-4.652290	-4.457970	-1.109154
H	-2.377691	-3.545674	-0.737584
O	0.547691	0.351339	0.509670
C	0.555715	1.007292	1.606077
O	-0.341578	1.220358	2.418916
C	1.943408	1.641637	1.885246
F	2.968592	0.922499	1.400227
F	2.009922	2.877247	1.323464
F	2.148738	1.796198	3.209732
H	2.118934	2.628257	-2.238782
H	4.052198	3.872006	-1.288542
H	6.072102	2.616840	-0.544023
H	6.137154	0.149333	-0.737979
H	5.288052	-1.813298	-1.683440
H	3.993928	-1.560529	0.553059
C	1.541528	-2.045789	2.085508
O	2.651842	-1.908386	2.585509
O	0.404662	-1.931406	2.821064
C	0.589742	-1.515226	4.180502
H	1.094520	-0.547042	4.220261
H	1.172322	-2.253203	4.740015
H	-0.413600	-1.430873	4.600034
H	-0.793595	-3.121641	0.623963
H	-0.598665	-2.923376	-2.085936
H	1.780265	-2.900656	-3.743073
H	4.084910	-2.075910	-3.789082

Structure **Int8** (E= –2111.495801)

C	0.704985	1.796393	0.571068
C	1.496415	2.302608	-0.523244
C	3.431148	0.942407	0.178148
C	2.802546	1.925041	-0.697849
C	3.760295	2.264378	-1.741786
C	4.892288	1.536683	-1.514418
C	4.692087	0.696907	-0.326664

C	5.632416	-0.284283	0.207233
O	5.422032	-1.035260	1.151438
O	6.803145	-0.289775	-0.478241
C	7.781615	-1.236240	-0.024256
H	7.395446	-2.257537	-0.091925
H	8.639203	-1.112661	-0.687120
H	8.071238	-1.029988	1.010226
H	5.804824	1.553952	-2.097093
H	3.587425	2.981902	-2.535057
C	2.667648	0.296061	1.289293
H	3.318990	0.071872	2.138146
H	2.306253	-0.676696	0.931703
C	1.484050	1.172616	1.743165
C	0.537852	0.479265	2.712245
C	0.232193	-0.886506	2.621717
C	-0.716694	-1.467100	3.465951
C	-1.378307	-0.691514	4.420600
C	-1.073116	0.667158	4.530012
C	-0.122263	1.241560	3.684468
H	0.105105	2.301638	3.770213
H	-1.574598	1.280813	5.273529
H	-2.118043	-1.141888	5.076710
H	-0.935956	-2.528032	3.375375
H	0.727564	-1.509176	1.885252
H	1.917904	2.033228	2.276413
H	1.024193	2.986478	-1.224282
H	-0.047980	2.504331	0.914388
N	-1.999077	-1.418031	-0.379013
C	-1.225775	-2.444527	-0.408736
C	0.139304	-2.361665	-0.940179
N	0.611925	-1.094654	-1.093811
C	1.770555	-0.921712	-1.736755
C	2.542919	-1.995723	-2.184254
C	2.098047	-3.292807	-1.956801
C	0.862661	-3.480151	-1.332305
H	0.452413	-4.469505	-1.167215
H	2.686085	-4.147518	-2.274143
H	3.480697	-1.796723	-2.690115
H	2.095787	0.098665	-1.882270
O	-1.701247	-3.610785	0.035137
C	-3.036531	-3.312726	0.573037
H	-2.981871	-3.449124	1.654321
H	-3.722198	-4.040286	0.141692
C	-3.306538	-1.839445	0.160813
C	-4.452422	-1.640668	-0.868153
C	-4.166117	-2.412596	-2.165548
H	-4.989266	-2.270484	-2.874881
H	-4.063658	-3.490961	-1.995329
H	-3.247630	-2.053075	-2.643020
C	-4.591632	-0.144419	-1.186927
H	-5.424999	0.013117	-1.882007
H	-4.793534	0.438393	-0.282479
H	-3.686193	0.252492	-1.652668
C	-5.761452	-2.135231	-0.229842
H	-5.738549	-3.209413	-0.012645
H	-6.601653	-1.955222	-0.910112
H	-5.967061	-1.603236	0.707053
H	-3.523863	-1.226277	1.040022
C	-2.917011	2.460166	0.167200
O	-2.182041	1.541668	0.674299
O	-3.948153	2.920898	0.645863
C	-2.421599	3.091838	-1.166622
F	-1.279712	3.799506	-0.961881
F	-3.325074	3.934199	-1.687150
F	-2.144470	2.167840	-2.122626
Pd	-0.675000	0.386027	-0.221513

Scheme S1 (β-Carbon Elimination Pathway): Int1 (see above), TS4, and 6

Transition State **TS4** (E= –1775.058231)

Pd	0.132354	-0.383947	0.305560
N	1.188626	-1.845267	1.574859
N	1.964956	-0.820034	-0.845473

C	0.815016	-2.333842	2.762074
C	2.174657	-2.486747	0.898354
C	2.809434	-3.621913	1.390143
H	3.589894	-4.097390	0.808052
C	2.418680	-4.118773	2.634419
C	1.408316	-3.462953	3.330056
H	1.071947	-3.809611	4.300734
H	2.896535	-5.000910	3.047002
C	-1.407100	0.053637	1.687791
H	-0.837007	-0.225267	2.577228
C	-1.920554	1.489576	1.631871
C	-2.425227	-0.871795	1.308201
H	-2.581595	1.630176	2.499953
C	-2.846888	1.564123	0.351706
H	-3.478565	-0.646985	1.461687
C	-2.539240	0.396308	-0.538061
H	-2.650880	2.484354	-0.200055
H	-2.184738	-1.926567	1.188898
H	-3.896195	1.536670	0.642485
C	-3.351695	-0.651702	-1.048206
C	-1.219111	0.284205	-1.246203
C	-2.593498	-1.430575	-1.971931
C	-1.332285	-0.890992	-2.092442
H	-0.553366	-1.234970	-2.758948
H	-2.962337	-2.319641	-2.466451
C	-0.853050	2.568099	1.726229
C	0.473669	2.285980	2.076631
C	-1.209426	3.909070	1.519627
C	1.423626	3.307948	2.181476
H	0.785253	1.265702	2.273753
C	-0.268052	4.929952	1.626002
H	-2.236026	4.156858	1.264144
C	1.059645	4.632793	1.950915
H	2.449026	3.058981	2.441085
H	-0.569250	5.959670	1.453323
H	1.796386	5.427344	2.029293

C	-0.611226	1.513048	-1.827945
O	-0.744612	2.656474	-1.435255
O	0.110247	1.228059	-2.943310
H	0.477599	2.077595	-3.261367
C	-4.747191	-0.916500	-0.658045
O	-5.307030	-0.430306	0.316009
O	-5.345778	-1.767167	-1.506393
C	-6.721424	-2.082114	-1.212513
H	-6.802639	-2.561258	-0.233433
H	-7.331542	-1.175499	-1.228551
H	-7.035435	-2.766922	-2.000112
H	0.019847	-1.812493	3.281360
C	2.552784	-1.864631	-0.374331
C	2.804641	-0.313204	-1.958623
C	3.650188	-1.560019	-2.288722
O	3.593552	-2.354714	-1.052925
H	3.211024	-2.169962	-3.082417
H	4.700273	-1.370521	-2.500118
H	2.163145	-0.033337	-2.794004
C	3.636710	0.931376	-1.515849
C	2.698792	2.063586	-1.071784
H	2.117281	2.454313	-1.910345
H	2.002186	1.733459	-0.296875
H	3.284285	2.895190	-0.664103
C	4.455019	1.409722	-2.726916
H	3.802273	1.627581	-3.581144
H	4.994459	2.329260	-2.472998
H	5.198073	0.670932	-3.047328
C	4.578092	0.590654	-0.347842
H	5.278721	-0.214637	-0.593190
H	5.171757	1.473579	-0.086709
H	4.015407	0.298270	0.546180

Structure **6** (E= –1775.104094)

Pd	0.044397	0.654219	-0.438346
N	-1.021070	2.571563	-0.315120
N	-1.929641	0.106377	0.443762

C	-0.537346	3.800808	-0.512776
C	-2.358852	2.399363	-0.219525
C	-3.260085	3.450592	-0.341378
H	-4.325077	3.264247	-0.268943
C	-2.751488	4.735336	-0.544457
C	-1.373188	4.914498	-0.621675
H	-0.939263	5.896966	-0.770146
H	-3.425708	5.580234	-0.636902
C	1.765395	1.303299	-1.703009
H	2.038244	2.301293	-1.373021
C	2.828619	0.223218	-1.655024
C	0.617911	1.176070	-2.480888
H	3.381778	0.290575	-2.605053
C	2.103806	-1.131004	-1.657139
H	0.402023	0.288589	-3.065198
C	0.963547	-1.209954	-0.604117
H	2.796593	-1.960956	-1.488200
H	0.031015	2.058198	-2.719599
H	1.663404	-1.290972	-2.641345
C	0.039080	-2.347658	-0.913307
C	1.433254	-1.548286	0.785413
C	0.089802	-3.267920	0.094415
C	0.964865	-2.778325	1.140940
H	1.132988	-3.273063	2.090005
H	-0.450641	-4.205783	0.129126
C	3.874004	0.370386	-0.550745
C	3.947511	1.474836	0.305513
C	4.845713	-0.633933	-0.411012
C	4.938901	1.561537	1.286147
H	3.213955	2.268876	0.242988
C	5.838646	-0.551758	0.563683
H	4.832310	-1.491436	-1.077773
C	5.886342	0.547133	1.424502
H	4.963585	2.425811	1.944508
H	6.574108	-1.346876	0.650454
H	6.655988	0.614039	2.188429
C	1.983553	-0.577336	1.737427
O	1.580378	0.579683	1.806409
O	2.892450	-1.080361	2.581453
H	3.160855	-0.360337	3.189811
C	-0.751780	-2.461667	-2.144538
O	-0.658256	-1.727590	-3.119467
O	-1.642434	-3.471845	-2.076891
C	-2.472513	-3.654834	-3.238278
H	-3.072649	-2.760213	-3.425591
H	-1.861427	-3.874234	-4.117715
H	-3.117106	-4.501989	-3.002787
H	0.540267	3.890889	-0.591319
C	-2.767013	1.022583	0.084070
C	-2.739238	-1.052619	0.902573
C	-4.092804	-0.757332	0.232458
O	-4.059866	0.700218	0.031581
H	-4.182972	-1.212390	-0.757669
H	-4.972218	-0.982258	0.831548
H	-2.299499	-1.973345	0.518392
C	-2.805456	-1.126095	2.459670
C	-1.389574	-1.219700	3.043111
H	-0.883250	-2.123831	2.697799
H	-0.777523	-0.357458	2.763823
H	-1.441637	-1.260680	4.137300
C	-3.579423	-2.402435	2.832746
H	-3.095895	-3.292107	2.411138
H	-3.606505	-2.518376	3.922064
H	-4.616066	-2.379664	2.478417
C	-3.504341	0.106024	3.060376
H	-4.535307	0.219667	2.709000
H	-3.539245	0.008683	4.151073
H	-2.957649	1.028444	2.833032

Scheme S2 (Acetate as X-type Ligand): Int1-OAc (see Int1 above), Int5-OAc, TS3-OAc, and Int6-OAc

Structure **Int5-OAc** (E= –1813.930732)

Pd	0.272482	-0.539773	-0.604667

N	2.480189	-0.195766	-0.276145
C	2.738492	1.047877	-0.457429
C	1.778271	1.969773	-1.074628
N	0.558710	1.434184	-1.331612
C	-0.360992	2.192748	-1.943787
C	-0.112340	3.518018	-2.298666
C	1.129540	4.076918	-2.011185
C	2.095750	3.285784	-1.390401
H	3.079449	3.670865	-1.150698
H	1.347894	5.108220	-2.267608
H	-0.890740	4.090868	-2.790135
H	-1.310434	1.715821	-2.149158
O	3.931997	1.511950	-0.070719
C	4.590021	0.387227	0.603123
H	4.648875	0.639217	1.663518
H	5.593059	0.310871	0.186645
C	3.671657	-0.832457	0.319775
C	4.289529	-1.913402	-0.610660
C	4.642009	-1.321084	-1.983601
H	3.745600	-0.956245	-2.497498
H	5.102859	-2.087780	-2.616839
H	5.353081	-0.489820	-1.905603
C	3.286282	-3.063350	-0.789086
H	3.055166	-3.530000	0.174358
H	2.346208	-2.718183	-1.226645
H	3.711542	-3.832367	-1.445225
C	5.553505	-2.468917	0.068454
H	6.341663	-1.713965	0.168254
H	5.964415	-3.294577	-0.523904
H	5.324189	-2.854935	1.069341
H	3.354326	-1.314972	1.246355
C	-2.223938	-0.318324	2.362744
C	-2.570726	-1.075649	1.321523
C	-2.756112	-0.272379	0.045125
C	-1.663546	-0.596104	-0.978793
C	-2.244917	-1.011754	-2.137747
C	-3.690612	-1.015133	-1.982758
C	-4.024529	-0.602698	-0.729529
C	-5.363007	-0.460647	-0.175081
O	-5.622465	-0.052082	0.950647
O	-6.332473	-0.832103	-1.052434
C	-7.678046	-0.713434	-0.570627
H	-7.911790	0.324744	-0.316151
H	-8.314071	-1.051403	-1.390306
H	-7.834368	-1.342003	0.311045
H	-4.393876	-1.308598	-2.755211
H	-1.731159	-1.317692	-3.043418
C	-2.735302	1.199434	0.581726
H	-3.764637	1.553049	0.646425
H	-2.184616	1.871375	-0.076090
C	-2.126811	1.148700	2.016852
C	-0.728093	1.745887	2.106673
C	-0.556551	3.118487	1.862376
C	0.704224	3.709512	1.927503
C	1.823704	2.937268	2.256811
C	1.663024	1.574767	2.503621
C	0.399956	0.980260	2.418782
H	0.313028	-0.090916	2.563264
H	2.524226	0.960058	2.751005
H	2.808434	3.393070	2.309320
H	0.814636	4.771663	1.724855
H	-1.423719	3.727490	1.616138
H	-2.763861	1.740219	2.689646
H	-2.679451	-2.154946	1.324204
H	-2.011860	-0.696245	3.358968
C	0.533969	-2.891804	1.130688
O	0.027386	-2.516302	-0.004456
O	1.154869	-2.183316	1.933146
C	0.282375	-4.367290	1.424409
H	0.587033	-4.984511	0.572600
H	-0.790012	-4.533913	1.581843
H	0.827233	-4.678410	2.318977

Transition State **TS3-OAc** (E= –1813.893178)

Pd	0.288684	-0.603071	-0.376541
N	2.385357	0.015371	-0.433118
C	2.447560	1.280649	-0.648142
C	1.294807	2.035495	-1.147255
N	0.148478	1.313145	-1.219077
C	-0.934971	1.876935	-1.768144
C	-0.931991	3.196459	-2.220664
C	0.229706	3.954287	-2.101263
C	1.370440	3.359334	-1.561667
H	2.305049	3.898868	-1.466031
H	0.255387	4.986799	-2.433025
H	-1.835008	3.610790	-2.654581
H	-1.816289	1.254120	-1.841576
O	3.607831	1.904279	-0.430615
C	4.490370	0.891251	0.160791
H	4.634405	1.164617	1.207444
H	5.438445	0.948320	-0.370743
C	3.724611	-0.447617	-0.013255
C	4.356030	-1.430061	-1.039526
C	4.406908	-0.802534	-2.440972
H	3.398935	-0.594329	-2.816700
H	4.890498	-1.490880	-3.143443
H	4.976923	0.134202	-2.455161
C	3.525588	-2.721648	-1.085064
H	3.520000	-3.214293	-0.106580
H	2.487895	-2.528534	-1.367079
H	3.959009	-3.419114	-1.811979
C	5.776570	-1.780251	-0.562609
H	6.450280	-0.916321	-0.583061
H	6.210004	-2.548156	-1.213638
H	5.761713	-2.176209	0.460321
H	3.608872	-0.965507	0.941022
C	-1.906052	-0.652548	2.365473
C	-2.204370	-1.378461	1.268373
C	-2.852027	-0.209935	0.125125
C	-1.683507	-0.970088	-0.350316
C	-2.190792	-1.937817	-1.291589
C	-3.557428	-1.771474	-1.425385
C	-4.004077	-0.725711	-0.574344
C	-5.378483	-0.322558	-0.359536
O	-5.787925	0.500201	0.457003
O	-6.234833	-0.974338	-1.199517
C	-7.618367	-0.637301	-1.051520
H	-7.788020	0.425973	-1.247588
H	-8.148921	-1.242399	-1.788946
H	-7.975954	-0.874791	-0.044838
H	-4.215249	-2.378776	-2.037567
H	-1.585560	-2.704791	-1.758368
C	-2.780776	1.077530	0.917376
H	-3.798761	1.357216	1.188340
H	-2.366207	1.884642	0.310084
C	-1.927391	0.844741	2.205689
C	-0.579731	1.558282	2.209969
C	-0.532442	2.940219	1.966637
C	0.678456	3.631166	1.985653
C	1.868969	2.952730	2.266606
C	1.828983	1.582233	2.520429
C	0.615876	0.887870	2.486389
H	0.621772	-0.186082	2.637233
H	2.746292	1.039019	2.730149
H	2.814241	3.487877	2.279999
H	0.693448	4.698907	1.783242
H	-1.452539	3.480500	1.757671
H	-2.486719	1.258464	3.057014
H	-2.472875	-2.427062	1.278715
H	-1.794974	-1.114775	3.342213
C	1.121361	-2.892469	1.265553
O	0.462399	-2.574695	0.195764
O	1.693820	-2.113371	2.039282
C	1.125958	-4.395139	1.528437
H	0.117218	-4.718560	1.813163

H	1.401554	-4.943976	0.621964
H	1.819714	-4.642143	2.335753

Structure **Int6-OAc** (E= –1813.946733)

Pd	0.295361	-0.724661	-0.117260
N	2.107597	0.318752	-0.611609
C	1.885860	1.575242	-0.766934
C	0.540563	2.089442	-1.013305
N	-0.445151	1.163194	-0.888195
C	-1.692542	1.538790	-1.193775
C	-2.012305	2.835243	-1.598600
C	-1.004863	3.789044	-1.689335
C	0.302519	3.404321	-1.394759
H	1.131150	4.099294	-1.459901
H	-1.224134	4.808862	-1.987547
H	-3.044995	3.073397	-1.827546
H	-2.452517	0.779476	-1.106815
O	2.929951	2.405663	-0.729679
C	4.071773	1.571218	-0.329598
H	4.295980	1.817368	0.710535
H	4.909158	1.850084	-0.966373
C	3.569300	0.116121	-0.505109
C	4.146022	-0.628663	-1.741686
C	3.856016	0.143880	-3.038200
H	2.777886	0.232138	-3.213713
H	4.290161	-0.385055	-3.894167
H	4.284685	1.152700	-3.024611
C	3.522113	-2.029383	-1.836164
H	3.736876	-2.619078	-0.938911
H	2.436077	-1.980336	-1.950072
H	3.937456	-2.562705	-2.699713
C	5.664002	-0.779280	-1.541903
H	6.179906	0.187221	-1.514917
H	6.094651	-1.358394	-2.366776
H	5.886356	-1.308201	-0.606997
H	3.763002	-0.473415	0.391542
C	-1.388616	-1.173758	3.060142
C	-1.100215	-2.041553	2.075529
C	-2.660336	-0.900474	0.540640
C	-1.482614	-1.752610	0.678284
C	-1.566484	-2.738046	-0.423550
C	-2.656037	-2.441146	-1.189177
C	-3.351794	-1.306256	-0.589290
C	-4.571097	-0.676267	-1.084576
O	-5.077461	0.345991	-0.633183
O	-5.102928	-1.342486	-2.139251
C	-6.292856	-0.767987	-2.698727
H	-6.101215	0.245855	-3.062540
H	-6.571288	-1.419306	-3.528413
H	-7.096324	-0.737323	-1.957092
H	-2.958486	-2.926681	-2.109010
H	-0.835709	-3.518969	-0.587864
C	-3.061726	0.061758	1.613698
H	-4.023266	-0.271834	2.027057
H	-3.262572	1.052510	1.194573
C	-2.029371	0.165653	2.775427
C	-0.994305	1.276888	2.542836
C	-1.433968	2.593601	2.331035
C	-0.527386	3.634052	2.129467
C	0.847904	3.380474	2.147865
C	1.295904	2.079354	2.369981
C	0.384538	1.036134	2.563071
H	0.765211	0.031696	2.704315
H	2.360615	1.861574	2.382279
H	1.557288	4.187563	1.986277
H	-0.894308	4.642830	1.958990
H	-2.499571	2.809553	2.324566
H	-2.597353	0.471450	3.663523
H	-0.585063	-2.973599	2.284391
H	-1.093366	-1.390132	4.083931
C	2.085639	-2.463546	1.394393
O	1.218681	-2.480452	0.428485
O	2.428177	-1.476258	2.056811

C	2.663247	-3.840581	1.700967
H	2.042684	-4.319364	2.469425
H	2.665340	-4.485445	0.818450
H	3.677293	-3.742633	2.098351

IntS1 (initial vinyl palladium species furnished from decarboxylation of **Int4**) (E= –2111.477422)

Pd	0.457116	0.904026	0.569567
N	2.632639	0.903554	-0.045247
C	2.926970	2.070811	-0.493743
C	1.922745	3.117477	-0.721765
N	0.666002	2.816695	-0.303139
C	-0.293014	3.742796	-0.437425
C	-0.047559	4.988963	-1.013920
C	1.235443	5.292732	-1.456601
C	2.243009	4.340391	-1.299383
H	3.262078	4.533334	-1.612206
H	1.455919	6.253738	-1.909174
H	-0.860983	5.700293	-1.103044
H	-1.270832	3.477282	-0.061013
O	4.209540	2.358188	-0.730916
C	4.968845	1.182722	-0.296881
H	5.580879	1.489669	0.552895
H	5.610042	0.897502	-1.129379
C	3.889716	0.128720	0.078090
C	3.909089	-1.154908	-0.797504
C	3.587074	-0.820641	-2.261364
H	3.654054	-1.724321	-2.877346
H	4.287998	-0.088123	-2.680141
H	2.573845	-0.417005	-2.361822
C	2.887977	-2.161849	-0.249487
H	2.909003	-3.082040	-0.843849
H	3.132097	-2.429958	0.784514
H	1.869701	-1.771165	-0.271119
C	5.308543	-1.788521	-0.692481
H	6.089675	-1.163306	-1.138665
H	5.319566	-2.749987	-1.218298
H	5.577975	-1.975809	0.354263
H	3.988128	-0.172338	1.124317
C	-2.666262	0.120456	-2.117523
C	-2.576217	1.092349	-1.210368
C	-2.595905	0.572285	0.220795
C	-1.441906	1.149984	1.041776
C	-1.933679	1.871897	2.083398
C	-3.387571	1.827594	2.050330
C	-3.810605	1.082191	0.994342
C	-5.220657	0.834444	0.705853
O	-6.161283	1.313851	1.326287
O	-5.396414	-0.009959	-0.339349
C	-6.757958	-0.306635	-0.678569
H	-7.300174	0.605599	-0.943444
H	-6.706863	-0.977383	-1.537297
H	-7.267604	-0.798469	0.155033
H	-4.042334	2.310556	2.768703
H	-1.356454	2.408199	2.829034
C	-2.536487	-0.981097	0.014742
H	-3.274654	-1.490389	0.637391
H	-1.551316	-1.343179	0.304774
C	-2.780950	-1.253763	-1.501794
C	-1.829295	-2.272952	-2.096659
C	-2.289820	-3.532313	-2.498192
C	-1.417143	-4.475706	-3.046854
C	-0.065845	-4.165835	-3.208789
C	0.405686	-2.910841	-2.811995
C	-0.467482	-1.975537	-2.256990
H	-0.093884	-1.003414	-1.942708
H	1.454355	-2.660837	-2.935863
H	0.615618	-4.894103	-3.640102
H	-1.794545	-5.448666	-3.350644
H	-3.343566	-3.774145	-2.379471
H	-3.803718	-1.622022	-1.649032
H	-2.533632	2.155660	-1.423043
H	-2.692045	0.272282	-3.193409

C	1.157231	-1.237551	2.390070	F	0.715740	-3.553550	1.870544
O	0.319296	-0.981047	1.455467	F	0.064717	-2.807844	3.810887
O	1.978736	-0.510766	2.939967	F	2.181479	-3.142690	3.419787
C	1.032261	-2.705961	2.869916				

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