Supporting Information

Enantioselective Conjugate Addition of Catalytically Generated Zinc Homoenolate

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Contents

Material and Methods

General. All reactions dealing with air- or moisture-sensitive compound were performed by standard Schlenk techniques in oven-dried reaction vessels under nitrogen atmosphere or in the argon-filled glove box. Analytical thin-layer chromatography (TLC) was performed on Merck 60 F254 silica gel plates. Flash chromatography was performed using 40–63 μm silica gel (Si 60, Merck). ^{1}H, ^{13}C and ^{19}F nuclear magnetic resonance (NMR) spectra were recorded on Bruker AV-400 (400 MHz) NMR spectrometers. ^{1}H and ^{13}C NMR spectra are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (0.00 ppm) and $CHCl_3$ (77.0 ppm), respectively. ^{19}F NMR spectra are referenced to external standard (CF_3CO_2H, –76.6 ppm). Gas chromatographic (GC) analysis was performed on a Shimadzu GC-2010 system equipped with an FID detector and a capillary column, DB-5 (Agilent J&W, 0.25 mm i.d. x 30 m, 0.25 μm film thickness). Chiral HPLC analysis was performed on a Shimadzu LC-20AD instrument using Daicel Chiralpak columns at room temperature (25–29 °C). Optical rotations were recorded on an Anton Paar MCP 150 machine. High-resolution mass spectra (HRMS) were obtained with a Q-Tof Premier LC HR mass spectrometer.

Materials. Unless otherwise noted, commercial reagents were purchased from Aldrich, Alfa Aesar, and other commercial suppliers and were used as received. Et_2Zn was purchased from TCI as a hexane solution (1 M) and was used as received. Molecular sieves 4Å was purchased from Aldrich (powder, activated, -325 mesh particle size) and activated under vacuum (<0.06 mbar) at 265 °C for more than 10 h, every time before the reaction. DMPU was distilled over CaH_2 and stored under Ar. Anhydrous DMSO (Aldrich) were used without further purification and stored under Ar. Figure S1 summarizes the substrates and the ligands used in this study. The substrates **1a**,[1] **1b**,[1] **1c**,[2] **1d**,[1] **1e**,[3] **1f**,[1] **1g**,[3] **1h**,[3] **1i**,[4] **1j**,[5] **1k**,[6] **1l**,[1] **1m**,[7] **2b**,[8] **2c**,[8] **2d**,[9] **2e**,[8] **2f**,[10] **2g**,[11] **2h**,[12] **2i**,[13] **2j**,[14] **2k**,[15] **2m**,[16] **2n**,[17] **2o**,[18] and **2q**[19] were prepared according to the literature procedure. The chiral ligands **L5**–**L7**[20] were prepared from (1*S*, 2*R*)-(+)-norephedrine. (1*R*, 2*S*)-**L6** was purchased from Aldrich and used only for preparing racemic and scalemic **L6** for nonlinear effect study. Additional chiral ligands **L8**,[21] **L9**,[22] **L10**,[21] **L11**,[23] **L12**,[24] **L13**,[25], **L14**,[21] **L15**,[21] **L16**,[26] **L17**,[27] **L18**,[28] and **L19**[27] were prepared according to the literature procedure and used during the optimization study.

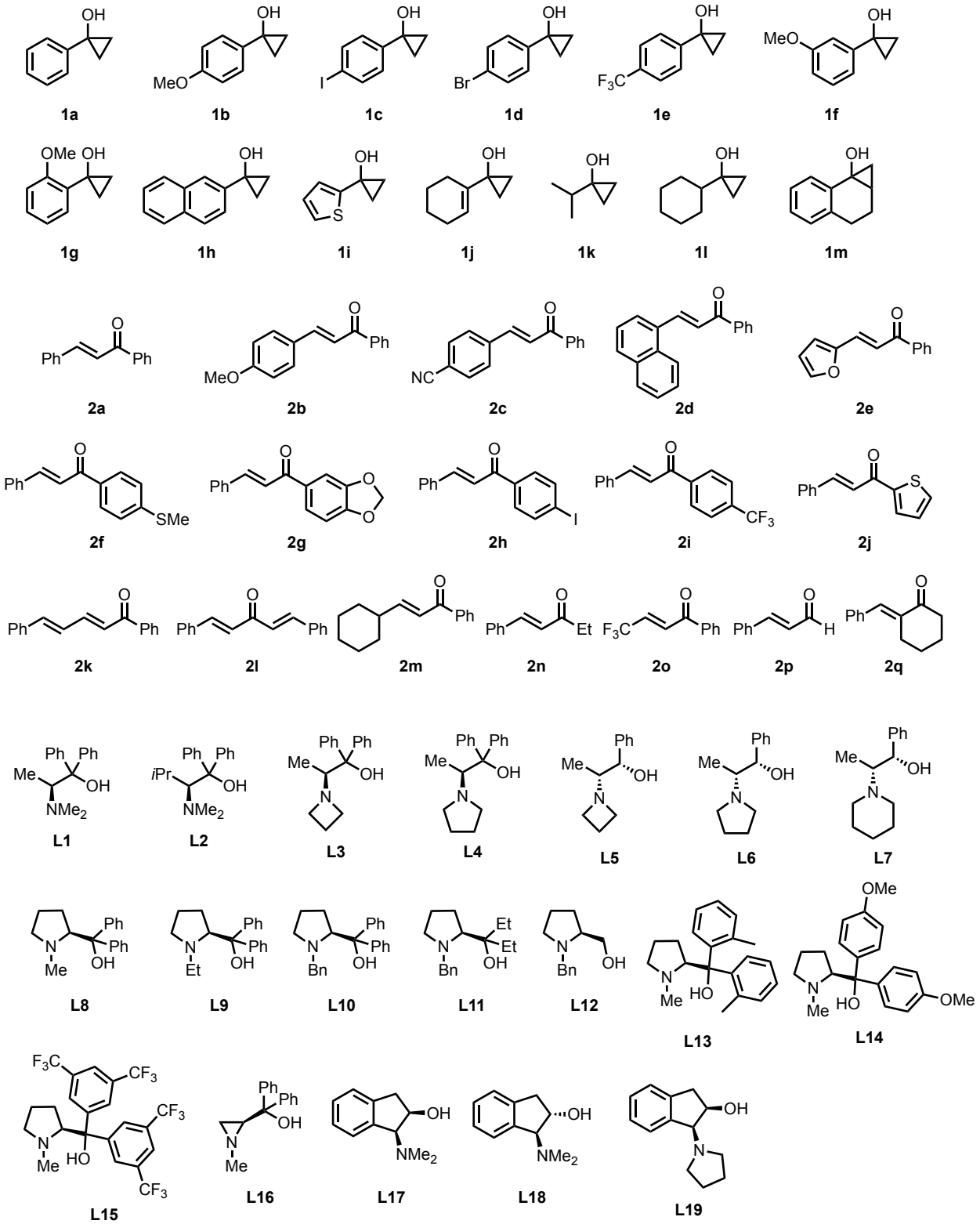
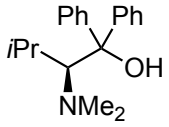
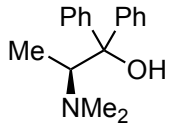


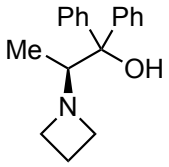
Figure S1. Substrates and ligands used in this study.



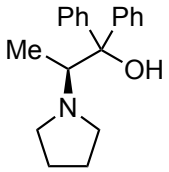
(*S*)-2-(Dimethylamino)-3-methyl-1,1-diphenylbutan-1-ol (L2):[29] Prepared according to the literature procedure.[30] A 25-mL round bottom flask equipped with a magnetic stir bar was charged with (*S*)-2-amino-3-methyl-1,1-diphenylbutan-1-ol[31] (255 mg, 1.00 mmol), paraformaldehyde (300 mg, 10.0 mmol), methanol (6 mL), and acetic acid (0.1 mL), followed by the addition of $NaBH_3CN$ (189 mg, 3.00 mmol). The resultant black suspension was stirred at 23 °C for 48 h and then filtered through a pad of Celite. The organic solution was concentrated under reduced pressure, and to the residue were added Et_2O (5 mL) and H_2O (5 mL). After the aqueous phase was acidified (ca. pH 2) by adding 1 M hydrochloric acid, the layers were separated. The aqueous layer was washed with Et_2O (3 mL), and then 1 M NaOH aq. was added until brown precipitates formed. The aqueous solution was then extracted with CH_2Cl_2 (3 × 2 mL). The organic solution was concentrated under reduced pressure, and the residue was purified by flash chromatography to afford the product as a pale yellow solid (222 mg, 78%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66-7.64 (m, 2H), 7.41-7.37 (m, 4H), 7.33-7.29 (m, 1H), 7.26-7.17 (m, 3H), 6.10 (brs, 1H), 3.04 (d, *J* = 10.4 Hz, 1H), 2.25-2.18 (m, 7H), 0.97 (d, *J* = 6.4 Hz, 3H), 0.61 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.2, 142.8, 128.3 127.7, 127.7, 127.6, 126.9, 126.8, 80.1, 78.6, 43.2, 29.3, 23.4, 23.2; **HRMS** (ESI) Calcd for $C_{19}H_{26}NO$ $[M + H]^+$ 284.2014, found 284.2006; $[\alpha]^{25}_D$ = +129 (*c* = 1.94 in $CHCl_3$).



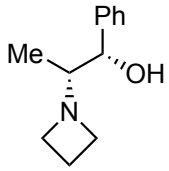
(*S*)-2-(Dimethylamino)-1,1-diphenylpropan-1-ol (L1): Prepared from (*S*)-2-amino-1,1-diphenylpropan-1-ol[31] (227 mg 1.0 mmol), according to the synthetic procedure for **L2**. Pale yellow oil (250 mg, 98%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44-7.42 (m, 4H), 7.30-7.26 (m, 4H), 7.24-7.18 (m, 2H), 6.10 (brs, 1H), 3.52 (q, *J* = 7.1 Hz, 1H), 2.10 (s, 6H), 1.09 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 144.6, 127.9, 127.9, 127.2, 126.9, 126.4, 78.0, 65.7, 42.9, 9.2; **HRMS** (ESI) Calcd for $C_{17}H_{22}NO$ $[M + H]^+$ 256.1701, found 256.1694; $[\alpha]^{25}_D$ = -40.9 (*c* = 2.25 in $CHCl_3$).



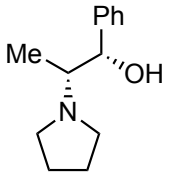
(*S*)-2-(Azetidin-1-yl)-1,1-diphenylpropan-1-ol (L3): Prepared according to the literature procedure.[20] A 25-mL round bottom flask equipped with a magnetic stir bar was charged with (*S*)-2-amino-1,1-diphenylpropan-1-ol[31] (1.00 g, 4.40 mmol), $NaHCO_3$ (0.81 g, 9.68 mmol), and toluene (12 mL), followed by the addition of 1,3-dibromopropane (0.98 g, 4.84 mmol). After 48 h of reflux, the mixture was filtered through a pad of Celite. The organic solution was concentrated under reduced pressure, and the residue was purified by flash chromatography to afford the product as a white solid (859 mg, 73%); m.p. 63-65 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 2H), 7.54-7.52 (m, 2H), 7.26-7.22 (m, 4H), 7.13-7.09 (m, 2H), 4.81 (brs, 1H), 3.54 (q, *J* = 6.4 Hz, 1H), 2.95 (q, *J* = 6.7 Hz, 2H), 2.75 (q, *J* = 6.7 Hz, 2H), 1.74 (quint, *J* = 6.9 Hz, 2H), 0.82 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.1, 145.8, 127.9, 127.7, 126.3, 126.0, 125.7, 125.3, 77.1, 67.5, 54.9, 17.6, 12.3; **HRMS** (ESI) Calcd for $C_{18}H_{22}NO$ $[M + H]^+$ 268.1701, found 268.1692; $[\alpha]^{25}_D$ = +12.5 (*c* = 1.69 in $CHCl_3$).



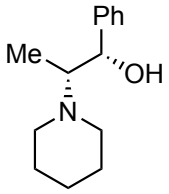
(*S*)-1,1-Diphenyl-2-(pyrrolidin-1-yl)propan-1-ol (L4): Prepared from (*S*)-2-amino-1,1-diphenylpropan-1-ol[31] (227 mg 1.0 mmol) and 1,4-dibromobutane (237 mg, 1.1 mmol), according to the synthetic procedure for **L3**. Pale yellow oil (142 mg, 50%); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.55 (m, 2H), 7.48-7.46 (m, 2H), 7.29-7.24 (m, 4H), 7.20-7.15 (m, 2H), 3.74 (q, *J* = 6.9 Hz, 1H), 2.42-2.39 (m, 4H), 1.62-1.59 (m, 4H), 1.04 (d, *J* = 6.9 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.7, 145.7, 127.9, 127.5, 126.9, 126.6, 126.5, 126.2, 77.9, 63.6, 51.3, 23.5, 12.7; **HRMS** (ESI) Calcd for $C_{19}H_{24}NO$ $[M + H]^+$ 282.1858, found 282.1851; $[\alpha]^{25}_D$ = -51.2 (*c* = 1.64 in $CHCl_3$).



(1*S*,2*R*)-2-(Azetidin-1-yl)-1-phenylpropan-1-ol (L5): Prepared from (1*S*, 2*R*)-(+)-norephedrine (1.89 g 12.5 mmol) and 1,3-dibromopropane (2.78 g, 13.8 mmol), according to the literature procedure.[20] Colorless oil (1.57 g, 65%);[i] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33-7.31 (m, 4H), 7.26-7.20 (m, 1H), 4.71(d, *J* = 2.9 Hz, 1H), 3.41 (brs, 1H), 3.31 (q, *J* = 6.7Hz, 2H), 3.24 (q, *J* = 6.7 Hz, 2H), 2.40 (qd, *J* = 6.5, 3.0 Hz, 1H), 2.05 (quint, *J* = 7.0 Hz, 2H), 0.63 (d, *J* = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.3, 128.0, 126.8, 125.8, 70.9, 68.5, 53.4, 16.8, 8.9; **HRMS** (ESI) Calcd for $C_{12}H_{18}NO$ $[M + H]^+$ 192.1388, found 192.1388; $[\alpha]^{25}_D$ = -32.9 (*c* = 2.07 in $CHCl_3$).



(1*S*,2*R*)-1-Phenyl-2-(pyrrolidin-1-yl)propan-1-ol (L6):[32] Prepared from (1*S*, 2*R*)-(+)-norephedrine (2.27 g 15.0 mmol) and 1,4-dibromobutane (3.56 g, 16.5 mmol) according to the literature procedure.[20] Pale orange solid (2.54 g, 82%); m.p. 44-45 °C, Lit 44-45 °C[20]; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H), 7.25-7.20 (m, 1H), 5.00 (d, *J* = 3.1 Hz, 1H), 3.61 (brs, 1H), 2.81-2.76 (m, 2H), 2.66-2.61 (m, 2H), 2.48 (qd, *J* = 6.6, 3.1 Hz, 1H), 1.83-1.77 (m, 4H), 0.79 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 141.7, 127.9, 126.6, 125.7, 72.6, 65.3, 51.8, 23.5, 12.0; **HRMS** (ESI) Calcd for $C_{13}H_{20}NO$ $[M + H]^+$ 206.1545, found 206.1549; $[\alpha]^{25}_D$ = -12.5 (*c* = 2.15 in $CHCl_3$). Lit $[\alpha]^{24}_D$ = -7.25 (*c* = 2.00 in $CHCl_3$),[32] $[\alpha]^{20}_D$ (**(1*R*, 2*S*)-L6**) = +15.2 (*c* = 2.00 in $CHCl_3$).[20]



(1*S*,2*R*)-1-Phenyl-2-(piperidin-1-yl)propan-1-ol (L7):[33] Prepared from (1*S*, 2*R*)-(+)-norephedrine (756 mg 5.0 mmol) and 1,5-diiodopentane (1.78 g, 5.5 mmol), according to the

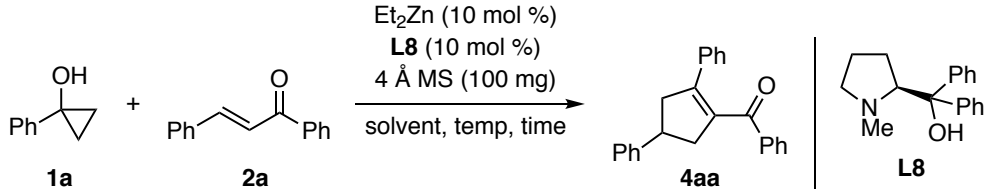
[i] This compound was not stable at room temperature for long-time storage. It should be stored in a fridge, and its purity should be checked by ^{1}H NMR before use.

literature procedure.[20] White solid (883 mg, 81%); m.p. 108-109 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.31-7.30 (m, 4H), 7.25-7.19 (m, 1H), 4.81 (d, *J* = 4.2 Hz, 1H), 4.09 (brs, 1H), 2.69 (qd, *J* = 6.9, 4.3 Hz, 1H), 2.55-2.45 (m, 4H), 1.60-1.54 (m, 4H), 1.46-1.40 (m, 2H), 0.82 (d, *J* = 4.2 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 142.3, 127.8, 126.6, 126.0, 72.2, 64.6, 51.7, 26.6, 24.6, 10.2; **HRMS** (ESI) Calcd for $C_{14}H_{22}NO$ $[M + H]^+$ 220.1701, found 220.1705; $[\alpha]^{25}_D$ = +0.471 (*c* = 2.55 in $CHCl_3$).

Early-Stage Optimization of Reaction Conditions

During initial attempts to render the racemic reaction between **1a** and **2a** (eq 1 in the paper) enantioselective, the proline-derived amino alcohol **L8** was found to induce modest enantioselectivity to afford, after 3 h at 80 °C, the cyclopentene product **4aa** in 68% yield with 67:33 er (Table S1, entry 1). Upon screening of solvents (entries 2–6), we observed improvement of the enantioselectivity up to 77:23 er in solvents such as DMA, NMP, NEt_3, and DMPU, albeit with diminished yields (10–40%). The reaction in DMPU at a lower temperature (60 °C) for a prolonged time (12 h) did not improve the yield and the enantioselectivity (entry 7). Efforts to improve the yield at this stage led us to find a NEt_3/DMPU (6:1) mixed solvent. Though somewhat peculiar, the reaction in this mixed solvent afforded **4aa** in 50% yield with 90:10 er, which was accompanied by uncyclized **3aa** (26%, 69:31 er; entry 8). *The difference between ers of **4aa** and **3aa** indicates that the aldol condensation of **3aa** to **4aa** is promoted by the chiral zinc catalyst and thus involves kinetic resolution.* With this observation, we modified the conditions to ensure full conversion of **3aa** to **4aa** (entries 9 and 10). By performing the conjugate addition at 30 °C and the aldol condensation at 100 °C, **4aa** was obtained in 79% yield with 83:17 er (entry 10).

Table S1. Initial Screening Experiments using **L8** as Ligand[a]

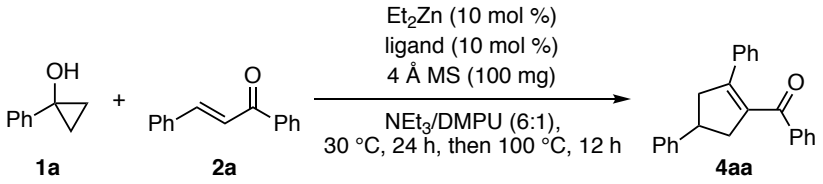


entry	solvent	temp/time	yield(%)[b]	er
1	DMSO	80 °C/3 h	68	67:33
2	DMF	80 °C/3 h	12	65:35
3	DMA	80 °C/3 h	10	74:26
4	NMP	80 °C/3 h	26	75:25
5	NEt_3	80 °C/3 h	16	74:26
6	DMPU	80 °C/3 h	40	77:23
7	DMPU	60 °C/12 h	33	79:21
8	NEt_3/DMPU (6:1)	60 °C/12 h	50	90:10[c]
9	NEt_3/DMPU (6:1)	60 °C/12 h, then 100 °C/12 h	75	81:19
10	NEt_3/DMPU (6:1)	30 °C/24 h, then 100 °C/12 h	79	83:17

[a]The reaction was performed using 0.15 mmol of **1a** and 0.1 mmol of **2a** (0.33 M). [b]Determined by GC using mesitylene as an internal standard. [c]**3aa** was obtained in 26% yield with 69:31 er.

Given the best result using **L8** in Table S1, entry 10, we screened a series of chiral β-amino alcohol ligands using the NEt_3/DMPU solvent system (Table S2). Among the proline-derived ligands **L9**–**L15**, only **L14** bearing *p*-methoxyphenyl groups displayed reaction efficiency and enantioselectivity comparable to that of **L8** (entries 2–8). The aziridine-containing ligand **L16** also gave a comparable result as **L8** (entry 9). The aminoindanol-type ligands **L17**–**L19** induced only modest enantioselectivities (entries 10–12). Finally, the alanine-derived ligands **L1** and **L3** were found to show similar or slightly better enantioselectivity compared with **L8** (entries 13 and 14). With this finding, we decided to revisit the reaction in more convenient single solvent (DMSO or DMPU) using **L1**, **L3** and their structurally related amino alcohols (i.e. **L2** as a valinol analogue of **L1**, **L4** as pyrrolidine analogue of **L3**, and **L5**–**L7** as norephedrine analogues of **L3**; Table 1). As a result, **L6** was found to not only display high enantioselectivity but also promote the reaction smoothly, in contrast to the poor performance of **L8** in DMPU (Table S1, entries 6 and 7).

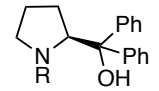
Table S2. Screening of Amino Alcohol Ligands[a]



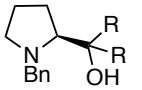
1a **2a** **4aa**

entry	ligand	yield(%)[b]	er (%)
1	**L8**	79	83:17
2	**L9**	86	71:29
3	**L10**	83	55:45
4	**L11**	73	53:47
5	**L12**	25	53:47
6	**L13**	72	54:46
7	**L14**	80	84:16
8	**L15**	53	61:39
9	**L16**	80	82:18
10	**L17**	53	64:36
11	**L18**	40	52:48
12	**L19**	11	58:42
13	**L1**	73	84:16
14	**L3**	79	88:12

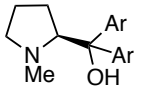
[a]The reaction was performed using 0.15 mmol of **1a** and 0.1 mmol of **2a** (0.33 M). [b]Determined by GC using mesitylene as an internal standard.



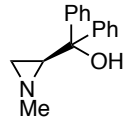
L8: R = Me
L9: R = Et



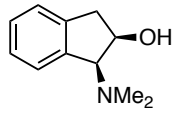
L10: R = Ph
L11: R = Et
L12: R = H



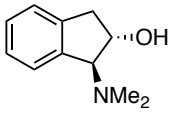
L13: Ar = *o*-MeC_6H_4
L14: Ar = *p*-$OMeC_6H_4$
L15: Ar = 3,5-$(CF_3)_2C_6H_3$



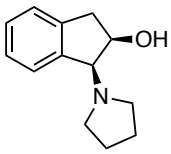
L16



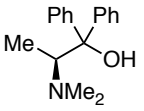
L17



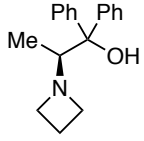
L18



L19



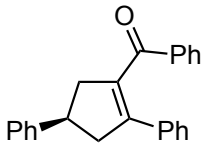
L1



L3

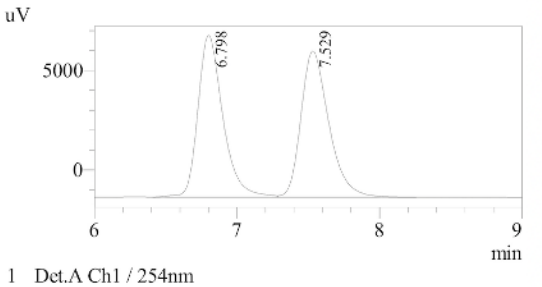
Zn-Catalyzed Enantioselective Ring-Opening Conjugate Addition of Cyclopropanols

General procedure: In an argon-filled glove box, a 4-mL vial equipped with a magnetic stir bar was charged sequentially with **L6** (9.2 mg, 0.045 mmol), molecular sieves 4 Å (300 mg), and DMPU (0.9 mL, stored in –20 °C fridge). To this mixture was added Et_2Zn (1 M in hexane, 45 μL, 0.045 mmol), enone **2** (0.30 mmol), and cyclopropanol **1** (0.45 mmol) sequentially, without a particular break (longer than 15 seconds) between additions. The vial was closed and removed from the glove box, and the mixture was stirred at 0 °C for 48 h. After confirmation of the full conversation of **2** by TLC or GC, the mixture was stirred at 100 °C for 6 h. Upon cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 (3 mL) and filtered through a pad of silica gel with additional CH_2Cl_2 (10 mL) as an eluent. The organic solution was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel or preparative TLC on silica gel to afford the desired product.



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(phenyl)methanone (4aa): Pale yellow solid (78.3 mg, 80%); R_f 0.31 (hexane/EtOAc = 19/1); m.p. 79-80 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.40-7.32 (m, 5H), 7.27-7.21 (m, 3H), 7.19-7.16 (m, 2H), 7.12-7.08 (m, 3H), 3.79 (quint, J = 8.3 Hz, 1H), 3.49-3.33 (m, 2H), 3.23-3.08 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 145.3, 145.0, 136.5, 136.3, 135.6, 132.8, 129.3, 128.6, 128.2, 128.0, 127.9, 127.9, 126.9, 126.3, 45.7, 45.2, 42.4; **HRMS** (ESI) Calcd for $C_{24}H_{21}O$ $[M + H]^+$ 325.1592, found 325.1592; $[\alpha]^{25}_D$ = +14.4 (c = 1.31 in $CHCl_3$, 95:5 er sample).

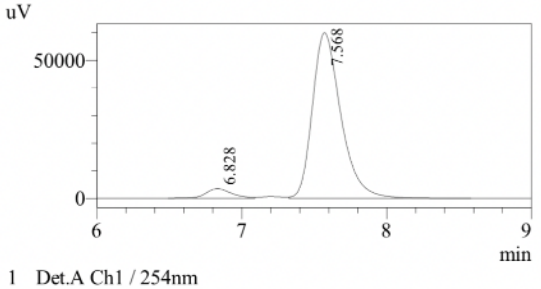
HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 6.8 min (minor) and 7.6 min (major), 95:5 er.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	6.798	49.818
2	7.529	50.182
Total		100.000

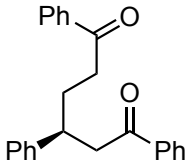


PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	6.828	4.949
2	7.568	95.051
Total		100.000

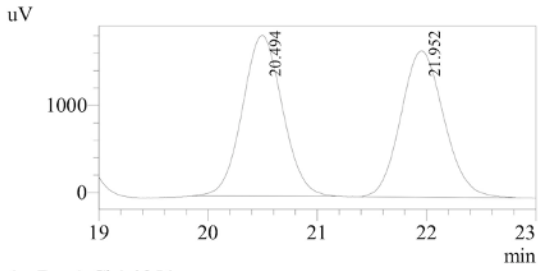
3 mmol-scale reaction: In an argon-filled glove box, a 50-mL Schlenk tube (pre-cooled in –20 °C fridge) equipped with a magnetic stir bar was charged sequentially with **L6** (92.4 mg, 0. 45 mmol), molecular sieves 4 Å (3.0 g), and DMPU (9 mL, stored in –20 °C fridge). To the mixture was added Et_2Zn (1 M in hexane, 450 μL, 0.45 mmol), **2a** (625 mg, 3.0 mmol), and **1a** (604 mg, 4.5 mmol) sequentially. After stirring for 30 seconds, the Schlenk tube was closed and removed from the glove box, and the mixture was stirred at 0 °C for 48 h and then at 100 °C for 6 h. Upon cooling to room temperature, CH_2Cl_2 (30 mL) and H_2O (30 mL) were added to the reaction mixture. The aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the product as a pale yellow solid (683 mg, 70%, 95:5 er).



(*S*)-1,3,6-Triphenylhexane-1,6-dione (3aa): The reaction was performed at 0 °C for 48 h. White solid (88.1 mg, 86%); R_f 0.32 (hexane/EtOAc = 9/1); m.p. 146-148 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90-7.88 (m, 2H), 7.83-7.81 (m, 2H), 7.55-7.48 (m, 2H), 7.44-7.37 (m, 4H), 7.32-7.25 (m, 4H), 7.22-7.18 (m, 1H), 3.48-3.41 (m, 1H), 3.39-3.28 (m, 2H), 2.93 (ddd, *J* = 17.1, 10.2, 5.9 Hz, 1H), 2.75 (ddd, *J* = 17.1, 10.1, 4.9 Hz, 1H), 2.27-2.19 (m, 1H), 2.12-2.02 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.9, 198.6, 143.8, 137.1, 136.8, 133.0, 132.9, 128.7, 128.5, 128.5, 128.0, 127.9, 127.6, 126.6, 46.0, 40.7, 36.7, 30.5; **HRMS** (ESI) Calcd for $C_{24}H_{23}O_2$ $[M + H]^+$ 343.1698,

found 343.1695; $[\alpha]^{25}_{D}$ = -11.7 (*c* = 2.30 in $CHCl_3$, 95:5 er sample).

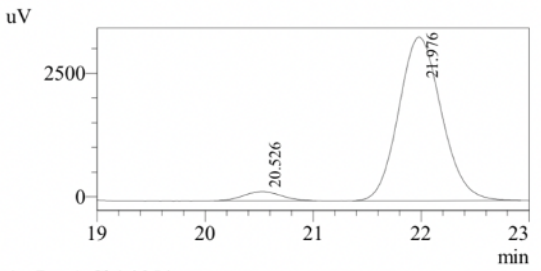
HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 20.5 min (minor) and 22.0 min (major), 95:5 er.



PeakTable

Detector A Ch1 254nm

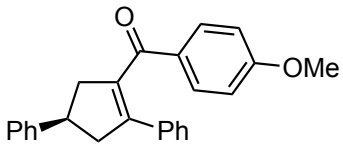
Peak#	Ret. Time	Area %
1	20.494	50.482
2	21.952	49.518
Total		100.000



PeakTable

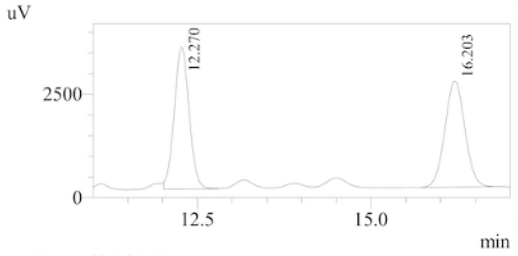
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	20.526	4.687
2	21.976	95.313
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(4-methoxyphenyl)methanone (4ba): Pale yellow oil (71.1 mg, 67%); R_f 0.21 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.78 (m, 2H), 7.39-7.31 (m, 4H), 7.25-7.21 (m, 3H), 7.15-7.08 (m, 3H), 6.78-6.74 (m, 2H), 3.82-3.74 (m, 4H), 3.47-3.30 (m, 2H), 3.21-3.05 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.5, 163.5, 145.4, 142.7, 136.6, 135.6, 131.7, 129.3, 128.5, 128.1, 127.8, 127.7, 126.9, 126.3, 113.6, 55.3, 45.5, 45.3, 42.4; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_2$ $[M + H]^+$ 355.1698, found 355.1699; $[\alpha]^{25}_{D}$ = +13.1 (*c* = 1.12 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 12.3 min (minor) and 16.2 min (major), 95:5 er.

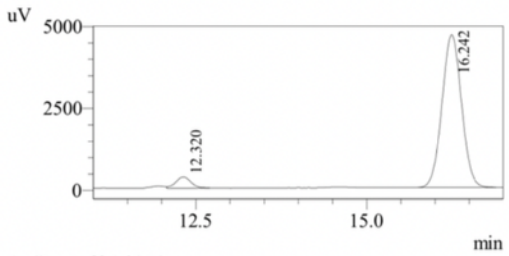


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.270	50.097
2	16.203	49.903
Total		100.000

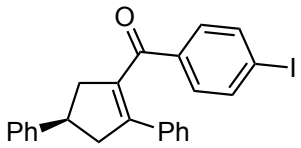


1 Det.A Ch1 / 254nm

PeakTable

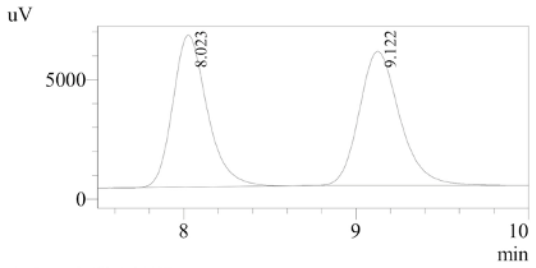
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.320	5.265
2	16.242	94.735
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(4-iodophenyl)methanone (4ca): White solid (115.4 mg, 85%); R_f 0.40 (hexane/EtOAc = 19/1); m.p. 131-133 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.46-7.43 (m, 2H), 7.38-7.32 (m, 4H), 7.26-7.22 (m, 1H), 7.16-7.11 (m, 5H), 3.78 (quint, J = 8.2 Hz, 1H), 3.49-3.42 (m, 1H), 3.38-3.32 (m, 1H), 3.21-3.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 146.0, 145.2, 137.5, 135.9, 135.8, 135.4, 130.7, 128.6, 128.2, 128.2, 127.9, 126.9, 126.4, 100.7, 45.8, 45.0, 42.3; **HRMS** (ESI) Calcd for $C_{24}H_{20}OI$ $[M + H]^+$ 451.0559, found 451.0558; $[\alpha]^{25}_D$ = +14.5 (c = 1.84 in $CHCl_3$, 93:7 er sample).

HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 8.1 min (minor) and 9.1 min (major), 93:7 er.

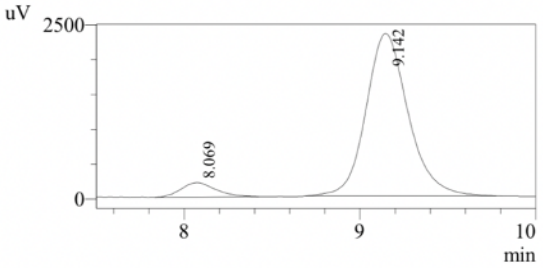


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	8.023	49.028
2	9.122	50.972
Total		100.000

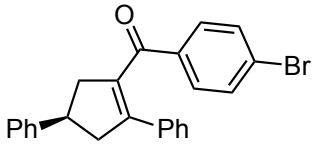


1 Det.A Ch1 / 254nm

PeakTable

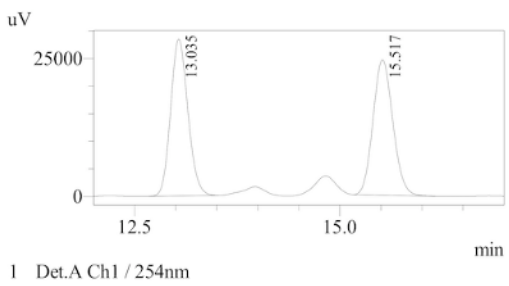
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	8.069	6.837
2	9.142	93.163
Total		100.000



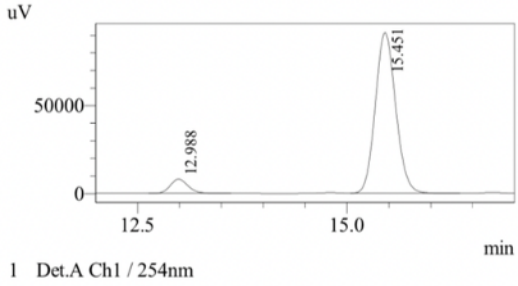
(*R*)-(4-Bromophenyl)(2,4-diphenylcyclopent-1-en-1-yl)methanone (4da): The reaction was performed at 0 °C for 72 h, followed by further heating at 100 °C for 6 h. White solid (109.6 mg, 91%); R_f 0.42 (hexane/EtOAc = 19/1); m.p. 99-101 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.61-7.58 (m, 2H), 7.38-7.32 (m, 6H), 7.26-7.23 (m, 1H), 7.16-7.11 (m, 5H), 3.79 (quint, J = 8.2 Hz, 1H), 3.49-3.43 (m, 1H), 3.39-3.32 (m, 1H), 3.22-3.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.4, 146.1, 145.2, 135.8, 135.4, 135.4, 131.5, 130.8, 128.6, 128.2, 128.2, 127.9, 127.8, 126.9, 126.4, 45.8, 45.0, 42.3; **HRMS** (ESI) Calcd for $C_{24}H_{20}OBr$ $[M + H]^+$ 403.0696, found 403.0698; $[\alpha]^{25}_D$ = +16.2 (c = 1.25 in $CHCl_3$, 93:7 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 13.0 min (minor) and 15.5 min (major), 93:7 er.



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	13.035	50.218
2	15.517	49.782
Total		100.000



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.988	7.159
2	15.451	92.841
Total		100.000

Recrystallization of **4da** (sample of 93:7 er) from THF/pentane afforded single crystals of racemate first. The supernatant of this first recrystallization contained enantiopure **4da** (>99:1 er, confirmed by HPLC). The second recrystallization of this enantiopure sample from THF/pentane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **4da** and its absolute stereochemistry (**Figure S2**).[34]

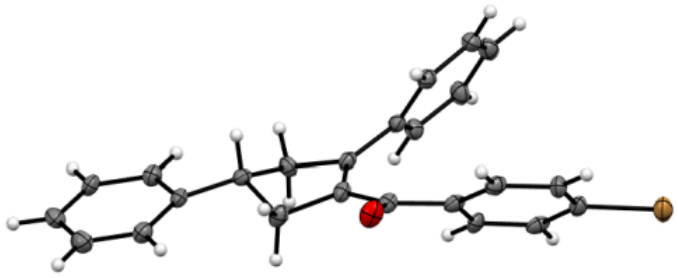
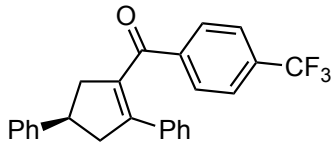


Figure S2. ORTEP drawing of **4da** (thermal ellipsoids set at 50% probability; CCDC 2056575).

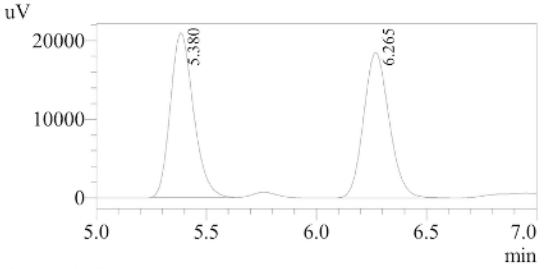
Table S3. Crystal data and structure refinement for **4da**

Identification code	yoshi108m_0m_5	
Chemical formula	$C_{24}H_{19}BrO$	
Formula weight	403.30 g/mol	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal size	0.060 x 0.140 x 0.200 mm	
Crystal habit	colorless plate	
Crystal system	triclinic	
Space group	P 1	
Unit cell dimensions	a = 7.6759(4) Å	α = 87.9511(19)°
	b = 9.4634(5) Å	β = 79.5409(19)°
	c = 13.2999(8) Å	γ = 74.096(2)°
Volume	913.59(9) $Å^3$	
Z	2	
Density (calculated)	1.466 g/cm^3	
Absorption coefficient	2.259 mm^{-1}	
F(000)	412	
Theta range for data collection	2.24 to 33.73°	
Index ranges	-11<=h<=11, -14<=k<=14, -20<=l<=20	
Reflections collected	12460	
Independent reflections	12460 [R(int) = 0.0410]	
Coverage independent reflections	99.7%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.8760 and 0.6610	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2018/2	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	12460 / 3 / 470	
Goodness-of-fit on F^2	1.052	
Final R indices	9274 data; I>2σ(I)	R1 = 0.0525, wR2 = 0.1137
	all data	R1 = 0.0781, wR2 = 0.1268
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0225P)^2+0.1052P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.017(8)	
Largest diff. peak and hole	0.827 and -1.094 $eÅ^{-3}$	
R.M.S. deviation from mean	0.098 $eÅ^{-3}$	



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(4-(trifluoromethyl)phenyl)methanone (4ea): The reaction was performed at 30 °C for 12 h and then at 100 °C for 6 h. White solid (100.2 mg, 85%); R_f 0.43 (hexane/EtOAc = 19/1); m.p. 128-129 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.46-7.44 (m, 2H), 7.39-7.33 (m, 4H), 7.26-7.22 (m, 1H), 7.12-7.06 (m, 5H), 3.79 (quint, J = 8.2 Hz, 1H), 3.51-3.36 (m, 2H), 3.23-3.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.0, 148.2, 145.1, 139.7, 135.8, 135.4, 133.5 (q, $^2J_{C\text{-}F}$ = 32.5 Hz), 129.5, 128.6, 128.4, 128.1, 128.0, 126.9, 126.4, 125.0 (q, $^3J_{C\text{-}F}$ = 3.7 Hz), 123.5 (q, $^1J_{C\text{-}F}$ = 272.6 Hz), 46.2, 44.7, 42.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.1; **HRMS** (ESI) Calcd for $C_{25}H_{20}OF_3$ $[M + H]^+$ 393.1466, found 393.1463; $[\alpha]^{25}_D$ = +15.7 (c = 1.52 in $CHCl_3$, 87:13 er sample).

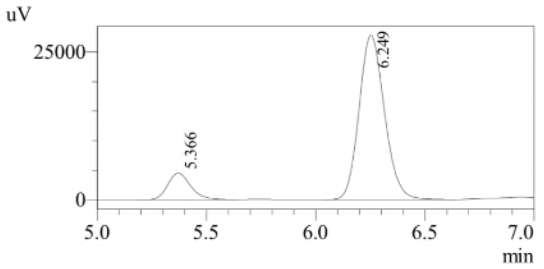
HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 5.4 min (minor) and 6.2 min (major), 87:13 er.



PeakTable

Detector A Ch1 254nm

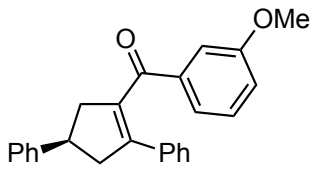
Peak#	Ret. Time	Area %
1	5.380	50.478
2	6.265	49.522
Total		100.000



PeakTable

Detector A Ch1 254nm

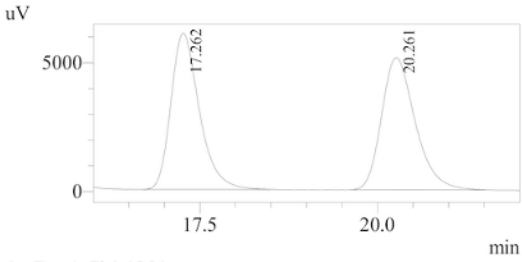
Peak#	Ret. Time	Area %
1	5.366	12.745
2	6.249	87.255
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(3-methoxyphenyl)methanone (4fa): The reaction was performed at 0 °C for 72 h and then at 100 °C for 6 h. Pale yellow oil (82.0 mg, 77%); R_f 0.26 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 6H), 7.25-7.11 (m, 7H),

6.95-6.92 (m, 1H), 3.83-3.72 (m, 4H), 3.48-3.33 (m, 2H), 3.22-3.07 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.4, 159.5, 145.3, 144.7, 137.8, 136.3, 135.6, 129.2, 128.6, 128.0, 127.9, 127.8, 126.9, 126.3, 122.3, 119.7, 113.1, 55.3, 45.6, 45.3, 42.3; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_2$ $[M + H]^+$ 355.1698, found 355.1695; $[\alpha]^{25}_D$ = +6.8 (*c* = 0.38 in $CHCl_3$, 94:6 er sample).

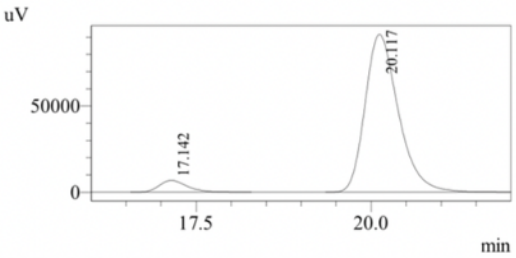
HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 0.5 mL/min. t_R = 17.1 min (minor) and 20.1 min (major), 94:6 er.



PeakTable

Detector A Ch1 254nm

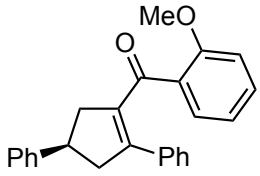
Peak#	Ret. Time	Area %
1	17.262	49.959
2	20.261	50.041
Total		100.000



PeakTable

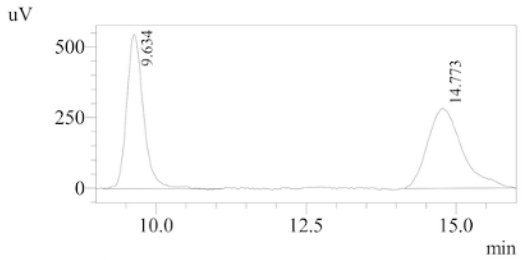
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	17.142	5.822
2	20.117	94.178
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(2-methoxyphenyl)methanone (4ga): The reaction was performed at 30 °C for 48 h and then at 100 °C for 6 h. Pale yellow oil (73.7 mg, 69%); R_f 0.15 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.31 (m, 5H), 7.24-7.20 (m, 1H), 7.18-7.14 (m, 1H), 7.10-7.07 (m, 2H), 7.06-7.02 (m, 3H), 6.78-6.75 (m, 1H), 6.58-6.55 (m, 1H), 3.72-3.64 (m, 4H), 3.42-3.31 (m, 2H), 3.12-3.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.6, 157.4, 149.0, 145.9, 138.1, 136.1, 132.2, 130.1, 129.3, 128.5, 127.8, 127.6, 127.4, 126.8, 126.2, 120.0, 110.7, 55.4, 47.6, 43.5, 41.7; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_2$ $[M + H]^+$ 355.1698, found 355.1697; $[\alpha]^{25}_D$ = -4.3 (*c* = 0.35 in $CHCl_3$, 91:9 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 80:20; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 9.6 min (minor) and 14.7 min (major), 91:9 er.

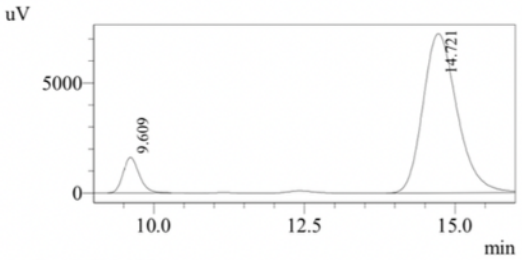


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	9.634	48.120
2	14.773	51.880
Total		100.000

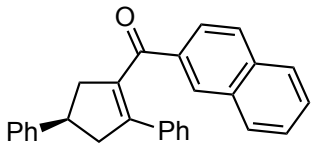


1 Det.A Ch1 / 254nm

PeakTable

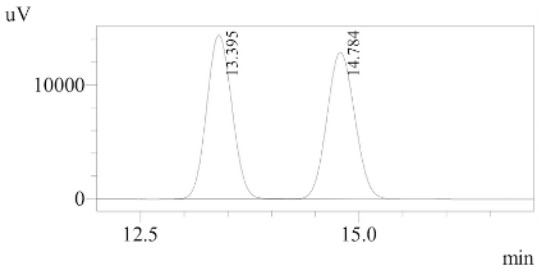
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	9.609	9.459
2	14.721	90.541
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(naphthalen-2-yl)methanone (4ha): The reaction was performed at 0 °C for 72 h and then at 100 °C for 6 h. Colorless oil (105.0 mg, 93%); R_f 0.31 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.93-7.90 (m, 1H), 7.75-7.70 (m, 3H), 7.50-7.46 (m, 1H), 7.43-7.33 (m, 5H), 7.27-7.22 (m, 3H), 7.06-6.96 (m, 3H), 3.82 (quint, J = 8.0 Hz, 1H), 3.52-3.38 (m, 2H), 3.26-3.12 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 145.3, 144.5, 136.5, 135.5, 135.4, 133.7, 132.3, 131.6, 129.4, 128.6, 128.2, 128.2, 128.0, 127.8, 127.7, 127.6, 126.9, 126.4, 126.3, 124.5, 45.5, 45.4, 42.4; **HRMS** (ESI) Calcd for $C_{28}H_{23}O$ $[M + H]^+$ 375.1749, found 375.1747; $[\alpha]^{25}_D$ = +18.7 (c = 3.00 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK AD-H; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 13.5 min (minor) and 14.9 min (major), 95:5 er.

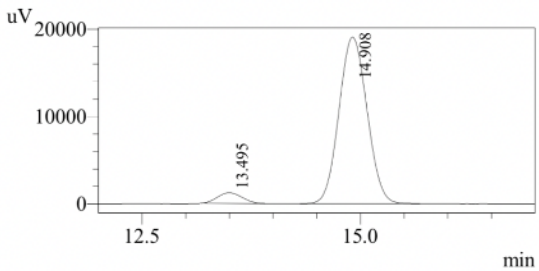


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	13.395	50.403
2	14.784	49.597
Total		100.000

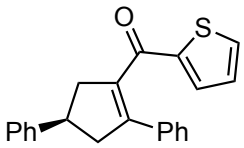


1 Det.A Ch1 / 254nm

PeakTable

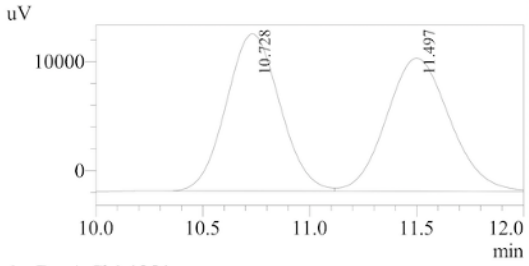
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	13.495	5.295
2	14.908	94.705
Total		100.000



(*R*)-(2,4-Diphenylcyclopent-1-en-1-yl)(thiophen-2-yl)methanone (4ia): Pale yellow oil (81.2 mg, 82%); R_f 0.28 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.49 (m, 1H), 7.41-7.32 (m, 5H), 7.29-7.13 (m, 6H), 6.88-6.86 (m, 1H), 3.77 (quint, J = 8.1 Hz, 1H), 3.47-3.35 (m, 2H), 3.20-3.08 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 189.6, 145.3, 144.1, 143.6, 136.3, 135.6, 134.1, 134.0, 128.6, 128.2, 128.0, 127.9, 127.8, 126.9, 126.3 45.5, 45.3, 42.3; **HRMS** (ESI) Calcd for $C_{22}H_{19}OS$ $[M + H]^+$ 331.1157, found 331.1155; $[\alpha]^{25}_D$ = +9.23 (c = 2.15 in $CHCl_3$, 96:4 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 80:20; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 10.7 min (minor) and 11.5 min (major), 96:4 er.

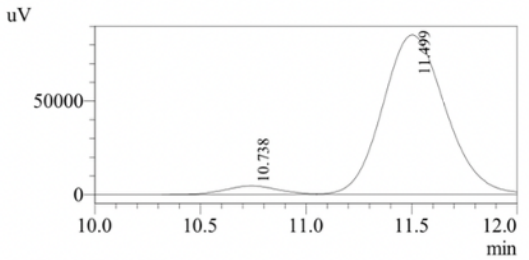


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.728	49.918
2	11.497	50.082
Total		100.000

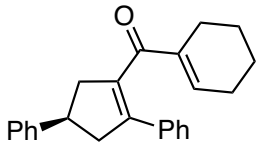


1 Det.A Ch1 / 254nm

PeakTable

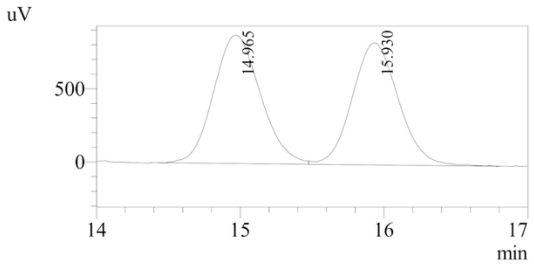
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.738	4.270
2	11.499	95.730
Total		100.000



(*R*)-Cyclohex-1-en-1-yl(2,4-diphenylcyclopent-1-en-1-yl)methanone (4ja): White solid (53.4 mg, 54%); R_f 0.31 (hexane/EtOAc = 19/1); m.p. 73-75 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.17 (m, 10H), 6.65-6.63 (m, 1H), 3.71 (quint, J = 8.2 Hz, 1H), 3.38-3.32 (m, 1H), 3.27-3.21 (m, 1H), 3.12-3.05 (m, 1H), 3.01-2.94 (m, 1H), 2.24-2.21 (m, 2H), 1.94-1.91 (m, 2H), 1.54-1.48 (m, 2H), 1.44-1.38 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.5, 145.5, 143.8, 142.8, 138.4, 136.9, 136.4, 128.5, 128.1, 127.6, 127.5, 126.9, 126.2, 45.3, 45.2, 42.3, 26.0, 23.0, 21.7, 21.4; **HRMS** (ESI) Calcd for $C_{24}H_{25}O$ $[M + H]^+$ 329.1903, found 329.1905; $[\alpha]^{25}_D$ = +10.12 (c = 2.10 in $CHCl_3$, 96:4 er sample).

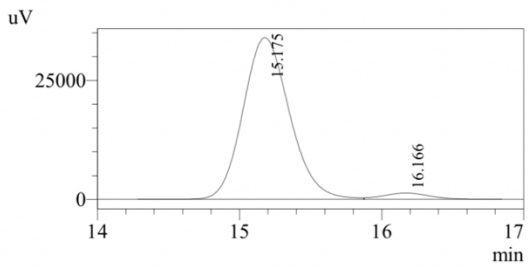
HPLC analysis: Daicel CHIRALPAK OJ-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 0.5 mL/min. t_R = 15.2 min (major) and 16.2 min (minor), 96:4 er.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.965	51.573
2	15.930	48.427
Total		100.000

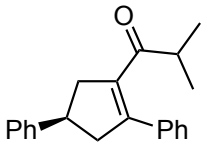


1 Det.A Ch1 / 254nm

PeakTable

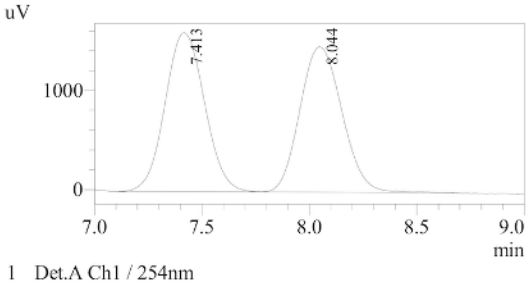
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	15.175	96.277
2	16.166	3.723
Total		100.000



(*R*)-1-(2,4-Diphenylcyclopent-1-en-1-yl)-2-methylpropan-1-one (4ka): The reaction was performed at 30 °C for 48 h and then at 100 °C for 6 h. Pale yellow oil (41.8 mg, 48%); R_f 0.41 (hexane/EtOAc = 39/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.21 (m, 10H), 3.65 (quint, J = 8.2 Hz, 1H), 3.35-3.23 (m, 2H), 3.09-2.94 (m, 2H), 2.63 (sept, J = 6.9 Hz, 1H), 0.98-0.96 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 208.5, 147.1, 145.5, 137.7, 136.9, 128.6, 128.3, 128.3, 127.6, 126.8, 126.3, 47.3, 44.2, 41.9, 38.9, 18.6, 18.3; **HRMS** (ESI) Calcd for $C_{21}H_{23}O$ $[M + H]^+$ 291.1749, found 291.1743; $[\alpha]^{25}_D$ = -9.59 (c = 0.61 in $CHCl_3$, 97:3 er sample).

HPLC analysis: Daicel CHIRALPAK AD-H; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 7.4 min (minor) and 8.0 min (major), 97:3 er.

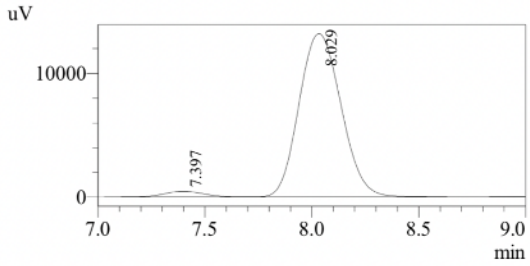


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	7.413	50.667
2	8.044	49.333
Total		100.000

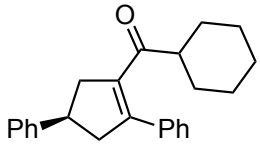


1 Det.A Ch1 / 254nm

PeakTable

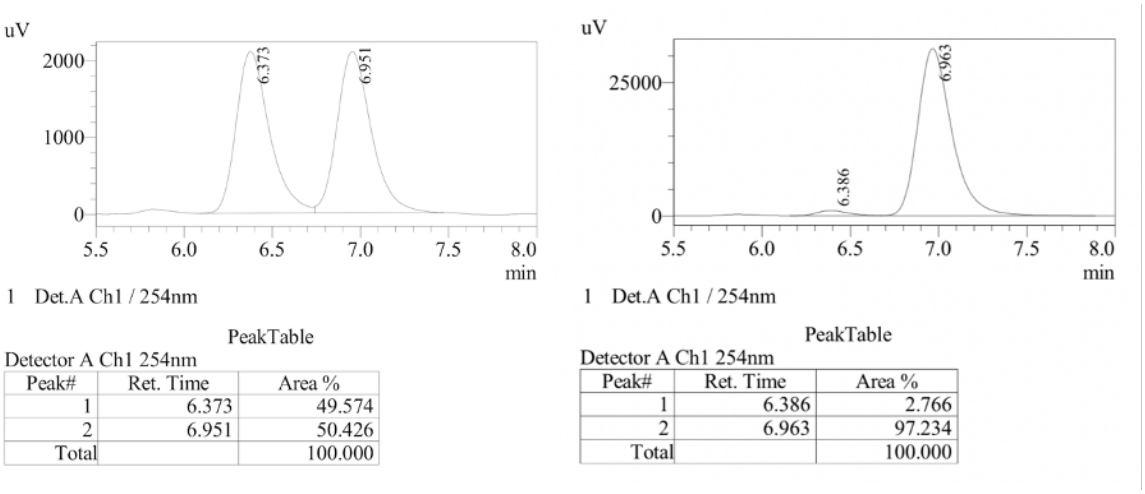
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	7.397	3.140
2	8.029	96.860
Total		100.000



(*R*)-Cyclohexyl(2,4-diphenylcyclopent-1-en-1-yl)methanone (4la): The reaction was performed at 30 °C for 48 h and then at 100 °C for 6 h. Colorless oil (73.3 mg, 74%); R_f 0.19 (hexane/EtOAc = 39/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38-7.19 (m, 10H), 3.63 (quint, *J* = 8.2 Hz, 1H), 3.33-3.21 (m, 2H), 3.08-2.92 (m, 2H), 2.31 (tt, *J* = 11.5, 3.2 Hz, 1H), 1.70-1.61 (m, 4H), 1.54-1.50 (m, 1H), 1.35-1.22 (m, 2H), 1.15-1.04 (m, 1H), 0.97-0.84 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 207.2, 147.5, 145.4, 137.8, 137.0, 128.5, 128.3, 128.1, 127.5, 126.8, 126.2, 48.8, 47.7, 43.8, 41.9, 28.9, 28.6, 25.7, 25.6, 25.5; **HRMS** (ESI) Calcd for $C_{24}H_{27}O$ $[M + H]^+$ 331.2062, found 331.2065; $[\alpha]^{25}_D$ = -5.28 (*c* = 2.35 in $CHCl_3$, 97:3 er sample).

HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 6.4 min (minor) and 7.0 min (major), 97:3 er.

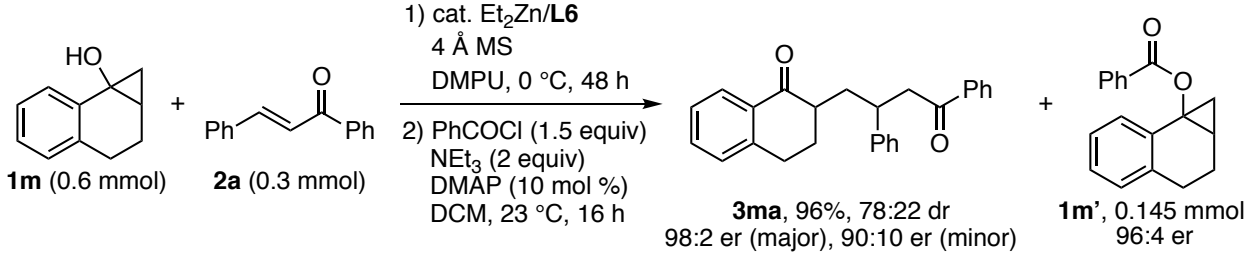


PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	6.373	49.574
2	6.951	50.426
Total		100.000

PeakTable
Detector A Ch1 254nm

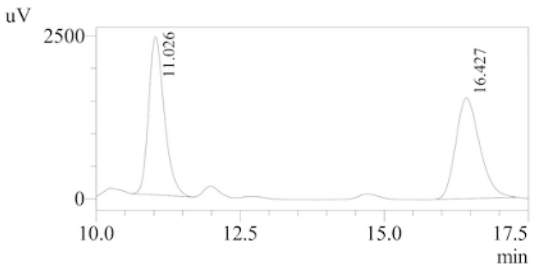
Peak#	Ret. Time	Area %
1	6.386	2.766
2	6.963	97.234
Total		100.000



2-(4-Oxo-2,4-diphenylbutyl)-3,4-dihydronaphthalen-1(2*H*)-one (3ma): The reaction was

conducted using 2 equiv of **1m** at 0 °C for 48 h. A mixture of the unreacted cyclopropanol (**1m**) and the product (**3ma**) was obtained by silica gel chromatography. For the separation of these compounds and detection of **1m** by the UV detector in HPLC, the unreacted **1m** was transformed to the corresponding benzoyl derivative (**1m'**) by the following procedure: To a solution of a mixture of **1m** and **3ma** in CH_2Cl_2 (0.5 mL) was added benzoyl chloride (63.3 mg, 0.45 mmol) and triethylamine (84 μL, 0.6 mmol), and DMAP (3.7 mg, 0.03 mmol). The reaction mixture was stirred at 23 °C for 16 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with CH_2Cl_2 (3 times), and the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified with silica gel chromatography to afford the title compound as a white solid (105.9 mg, 96%, 78:22 dr) along with **1m'** (38.4 mg, 0.145 mmol, 24%). Pure samples of both the diastereomers of **3ma** could be obtained by partial separation of the diastereomer mixture on silica gel using toluene as an eluent; R_f 0.31 (single spot, hexane/EtOAc = 19/1), 0.26 (major diastereomer, toluene), 0.18 (minor diastereomer, toluene); m.p. 152-153 °C (major diastereomer); **^{1}H NMR** (400 MHz, $CDCl_3$) major diastereomer: δ 7.97-7.96 (m, 1H), 7.89-7.87 (m, 2H), 7.54-7.50 (m, 1H), 7.43-7.38 (m, 3H), 7.34-7.14 (m, 7H), 3.61-3.54 (m, 1H), 3.32 (d, *J* = 6.8 Hz, 2H), 3.00 (dt, *J* = 16.8, 4.4 Hz, 1H), 2.87-3.79 (m, 1H), 2.60-2.53 (m, 1H), 2.42-2.35 (m, 1H), 2.21-2.13 (m, 1H), 1.93-1.83 (m, 1H), 1.80-1.73 (m, 1H); minor diastereomer: 8.00-7.98 (m, 1H), 7.89-7.87 (m, 2H), 7.54-7.49 (m, 1H), 7.44-7.38 (m, 3H), 7.30-7.24 (m, 5H), 7.18-7.14 (m, 2H), 3.75-3.67 (m, 1H), 3.38 (dd, *J* = 16.5, 7.7 Hz, 1H), 3.27 (dd, *J* = 16.5, 6.2 Hz, 1H), 2.91-2.87 (m, 2H), 2.52-2.46 (m, 1H), 2.43-2.35 (m, 1H), 2.13-2.06 (m, 1H), 1.88-1.78 (m, 1H), 1.72-1.65 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) major diastereomer: δ 200.1, 198.7, 143.9, 143.4, 137.1, 133.1, 133.0, 132.3, 128.7, 128.6, 128.5, 127.9, 127.7, 127.3, 126.6, 126.4, 46.6, 45.1, 37.8, 34.7, 28.4, 27.4; minor diastereomer: δ 200.1, 198.8, 144.8, 143.7, 137.1, 133.1, 132.9, 132.5, 128.6, 128.5, 128.5, 128.1, 127.7, 127.4, 126.5, 126.4, 46.0, 45.6, 39.4, 37.2, 29.6, 28.4; **HRMS** (ESI) Calcd for $C_{26}H_{25}O_2$ $[M + H]^+$ 369.1855, found 369.1852 (major diastereomer), 369.1857 (minor diastereomer); $[\alpha]^{25}_D$ = +7.48 (*c* = 0.99 in $CHCl_3$, 78:22 dr, 98:2 er (major), 90:10 er (minor) sample of **3ma**); $[\alpha]^{25}_D$ = -151 (*c* = 1.79 in $CHCl_3$, 96:4 er sample of **1m'**).

HPLC analysis (major diastereomer of **3ma**): Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 70:30; detection wavelength = 254 nm; flow rate = 0.5 mL/min. t_R = 10.9 min (major) and 16.2 min (minor), 98:2 er.

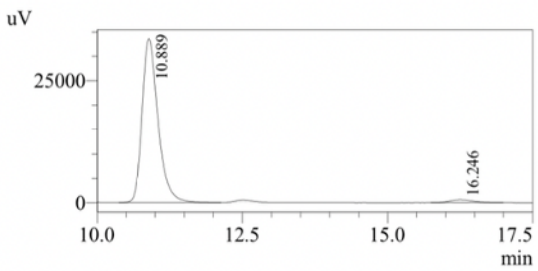


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	11.026	50.849
2	16.427	49.151
Total		100.000



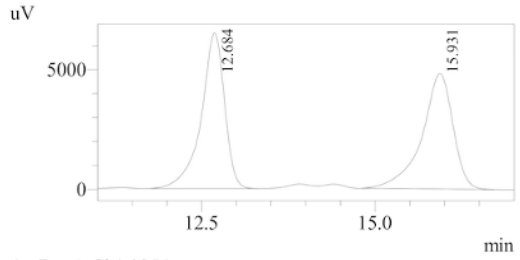
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.889	97.534
2	16.246	2.466
Total		100.000

HPLC analysis (minor diastereomer of **3ma**): Daicel CHIRALPAK OD; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 12.7 min (major) and 15.9 min (minor), 90:10 er.

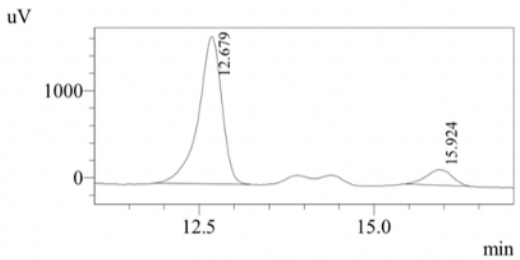


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.684	50.243
2	15.931	49.757
Total		100.000



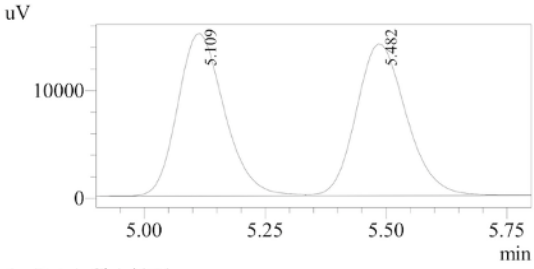
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.679	89.563
2	15.924	10.437
Total		100.000

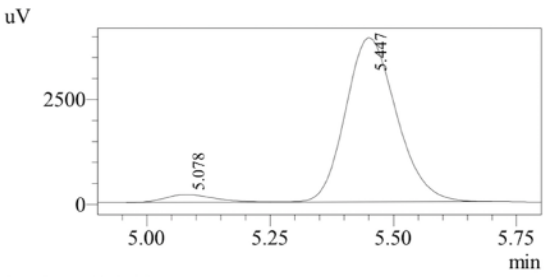
HPLC analysis (**1m'**): Daicel CHIRALPAK ID; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 5.1 min (minor) and 5.4 min (major), 96:4 er.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	5.109	49.918
2	5.482	50.082
Total		100.000



PeakTable

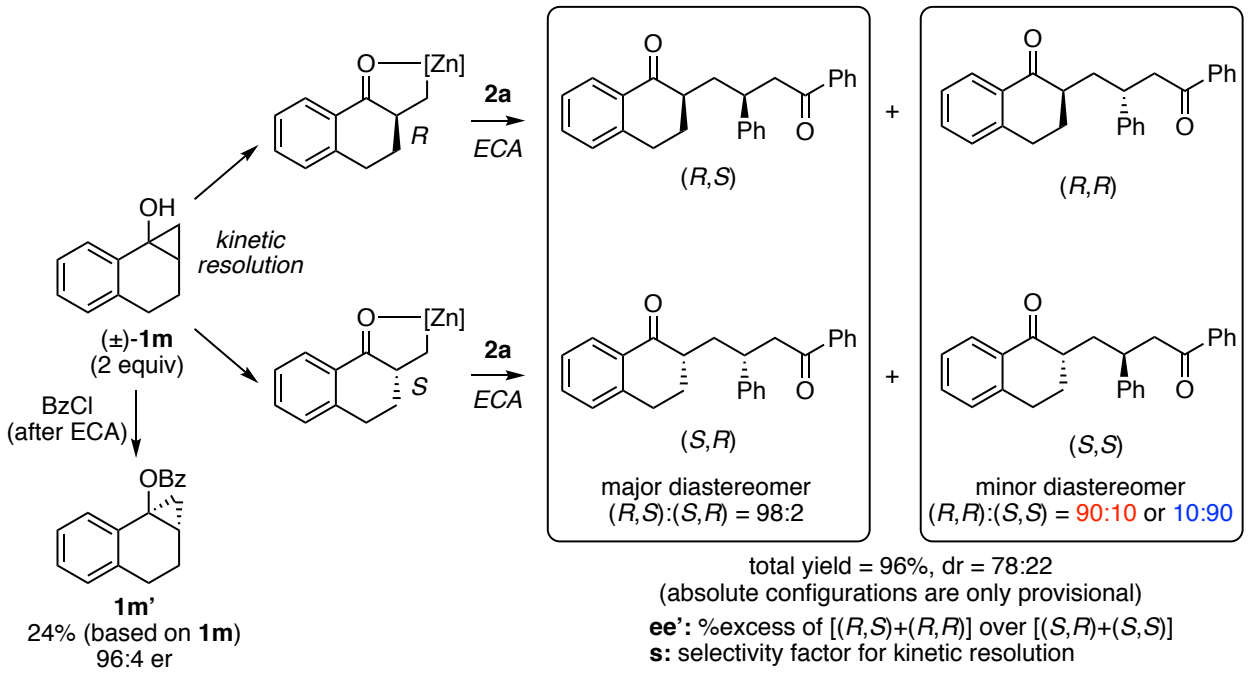
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	5.078	4.333
2	5.447	95.667
Total		100.000

Based on the observed dr and ers of **3ma**, one can formulate the pathways for the formation of the diastereomers/enantiomers as shown in Scheme S1, which involve enantioselective ring-opening (kinetic resolution) of **1m** and enantioselective conjugate addition (ECA) of each of the resulting zinc homoenolate to **2a** (the absolute configurations shown are only provisional, assigning (*R*,*S*) as the dominant enantiomer of the major diastereomer). Here, two possible cases (Cases 1 and 2) can be conceived for the origin of the minor diastereomer, where (*R*,*R*) and (*S*,*S*) are assumed as the dominant enantiomer of the minor diastereomer, respectively. For Cases 1 and 2, %excess of [(*R*,*S*)+(*R*,*R*)] over [(*S*,*R*)+(*S*,*S*)] (**ee'**), which should reflect the kinetic resolution step, is calculated to be 92.5% and 56.9%, respectively. In light of near quantitative yield of **3ma** and these **ee'** values, the selectivity factor (**s**) of the kinetic resolution can be approximated to be 85.6 and 6.3 for Cases 1 and 2, respectively. On the basis of the isolation of benzoyl ester (**1m'**) in a substantial yield (24%)[ii] with high enantiomeric excess (96:4 er; 92% ee), we conclude that Case 1 is the more likely scenario (see the simulated graph in Scheme S1), which corresponds to highly selective kinetic resolution and moderately selective ECA.

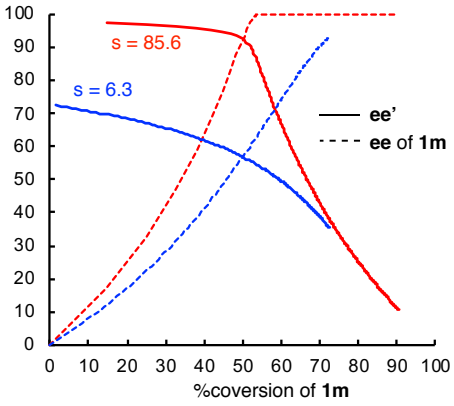
[ii] The isolated yield should be lower than the actual recovery of **1m** because of the loss during the benzoylation step and the purification process.

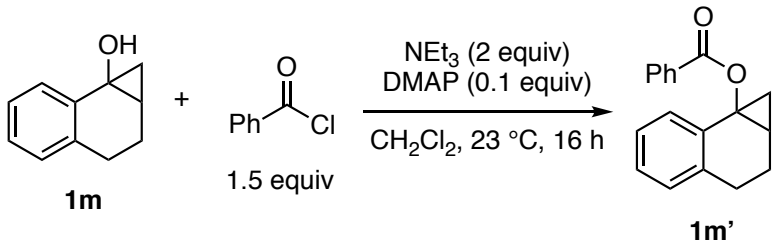
Scheme S1. Kinetic resolution/ECA process in the reaction between **1m** and **2a**



Case 1: (*R*,*R*) is the major enantiomer of the minor diastereomer
ee' = (0.78*0.98+0.22*0.90)–(0.78*0.02+0.22*0.10) = 92.5%
assuming 50% conversion of **1m** and simple first-order kinetics,
s ≒ ln[1–0.5*(1+0.925)]/ln[1–0.5*(1–0.925)] ≒ 85.6

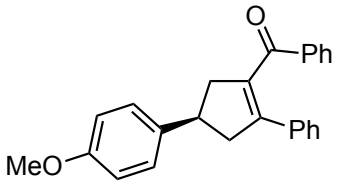
Case 2: (*S*,*S*) is the major enantiomer of the minor diastereomer
ee' = (0.78*0.98+0.22*0.10)–(0.78*0.02+0.22*0.90) = 56.9%
assuming 50% conversion of **1m** and simple first-order kinetics,
s ≒ ln[1–0.5*(1+0.569)]/ln[1–0.5*(1–0.569)] ≒ 6.3





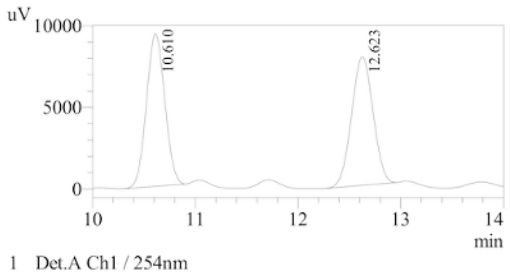
1,1a,2,3-Tetrahydro-7b*H*-cyclopropa[*a*]naphthalen-7b-yl benzoate (1m'): To a solution of **1m** (48.1 mg, 0.30 mmol), benzoyl chloride (63.3 mg, 0.45 mmol) and triethylamine (84 μL, 0.60 mmol) in CH_2Cl_2 (0.3 mL) was added DMAP (3.7 mg, 0.030 mmol), and the reaction mixture was stirred at 23 °C for 16 h. The reaction was quenched with sat. aq. NH_4Cl and extracted with CH_2Cl_2,

and the combined organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified with silica gel chromatography to afford the product as a colorless oil (61.0 mg, 77%); R_f 0.59 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13-8.11 (m, 2H), 7.58-7.55 (m, 1H), 7.47-7.43 (m, 2H), 7.33-7.31 (m, 1H), 7.14-7.07 (m, 3H), 2.73 (dt, J = 16.1, 3.4 Hz, 1H), 2.48-2.39 (m, 1H), 2.10-2.05 (m, 2H), 1.94-1.90 (m, 1H), 1.46 (dd, J = 10.0, 6.4 Hz, 1H), 1.24 (t, J = 6.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.1, 136.8, 133.1, 132.5, 130.1, 129.7, 128.5, 128.4, 126.2, 125.8, 123.5, 58.2, 25.8, 23.5, 18.3, 15.2; **HRMS** (ESI) Calcd for $C_{18}H_{17}O_2$ $[M + H]^+$ 265.1229, found 265.1227.



(*R*)-(4-(4-Methoxyphenyl)-2-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4ab): White solid (72.7 mg, 68%); R_f 0.24 (hexane/EtOAc = 19/1); m.p. 119-120 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2H), 7.40-7.35 (m, 1H), 7.31-7.23 (m, 4H), 7.19-7.15 (m, 2H), 7.11-7.08 (m, 3H), 6.90-6.87 (m, 2H), 3.79-7.70 (m, 4H), 3.46-3.29 (m, 2H), 3.17-3.03 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 158.1, 145.0, 137.4, 136.5, 136.4, 135.6, 132.8, 129.3, 128.2, 128.0, 127.9, 127.8, 113.9, 55.3, 45.9, 45.4, 41.7; **HRMS** (ESI) Calcd for $C_{25}H_{23}O_2$ $[M + H]^+$ 355.1698, found 355.1693; $[\alpha]^{25}_D$ = +12.3 (c = 1.11 in $CHCl_3$, 96:4 er sample).

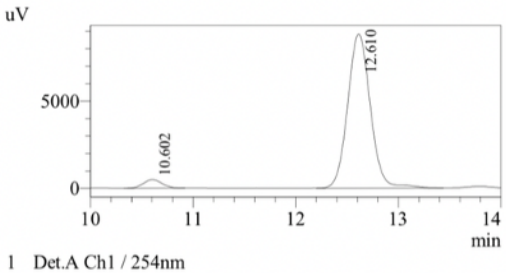
HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 10.6 min (minor) and 12.6 min (major), 96:4 er.



PeakTable

Detector A Ch1 254nm

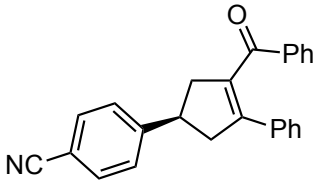
Peak#	Ret. Time	Area %
1	10.610	50.267
2	12.623	49.733
Total		100.000



PeakTable

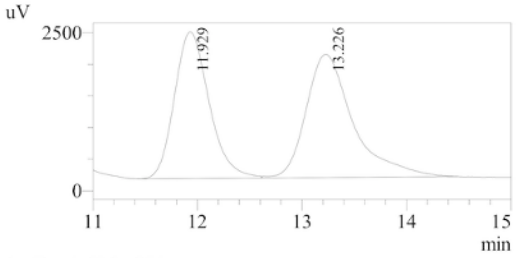
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.602	4.340
2	12.610	95.660
Total		100.000



(*R*)-4-(3-Benzoyl-4-phenylcyclopent-3-en-1-yl)benzonitrile (4ac): Pale yellow oil (73.2 mg, 70%); R_f 0.12 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2H), 7.65-7.62 (m, 2H), 7.49-7.47 (m, 2H), 7.42-7.37 (m, 1H), 7.28-7.24 (m, 2H), 7.18-7.11 (m, 5H), 3.87-3.79 (m, 1H), 3.56-3.48 (m, 1H), 3.44-3.37 (m, 1H), 3.18-3.06 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.2, 151.0, 144.7, 136.3, 135.9, 135.1, 133.0, 132.5, 129.3, 128.3, 128.2, 128.1, 127.9, 127.8, 118.9, 110.3, 45.4, 44.8, 42.3; **HRMS** (ESI) Calcd for $C_{25}H_{20}NO$ $[M + H]^+$ 350.1545, found 350.1545; $[\alpha]^{25}_D$ = +6.4 (*c* = 0.64 in $CHCl_3$, 92:8 er sample).

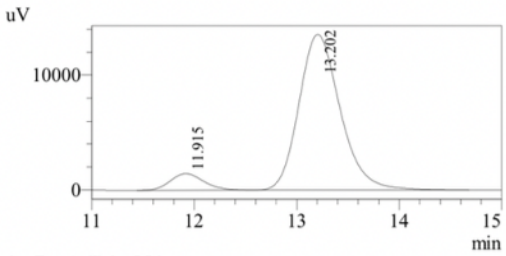
HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 70:30; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 11.9 min (minor) and 13.2 min (major), 92:8 er.



PeakTable

Detector A Ch1 254nm

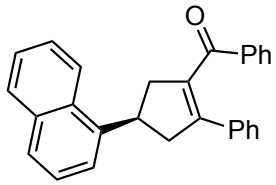
Peak#	Ret. Time	Area %
1	11.929	46.770
2	13.226	53.230
Total		100.000



PeakTable

Detector A Ch1 254nm

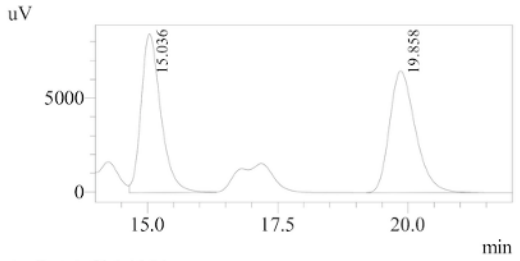
Peak#	Ret. Time	Area %
1	11.915	8.021
2	13.202	91.979
Total		100.000



(*R*)-(4-(Naphthalen-1-yl)-2-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4ad): The reaction was performed at 0 °C for 48 h and then at 50 °C for 16 h. Pale yellow oil (89.7 mg, 80%); R_f 0.29 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.17-8.15 (m, 1H), 7.87-7.85 (m,

1H), 7.79-7.73 (m, 3H), 7.59-7.42 (m, 4H), 7.37-7.32 (m, 1H), 7.24-7.17 (m, 4H), 7.11-7.06 (m, 3H), 4.54-4.46 (m, 1H), 3.63-3.49 (m, 2H), 3.34-3.21 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 145.0, 140.8, 136.5, 136.4, 135.5, 134.1, 132.8, 131.5, 129.3, 129.0, 128.2, 128.0, 127.9, 127.9, 127.0, 125.9, 125.5, 125.5, 123.4, 122.8, 45.0, 44.4, 37.8; **HRMS** (ESI) Calcd for $C_{28}H_{23}O$ $[M + H]^+$ 375.1749, found 375.1751; $[\alpha]^{25}_D$ = -16.7 (*c* = 1.50 in $CHCl_3$, 96:4 er sample).

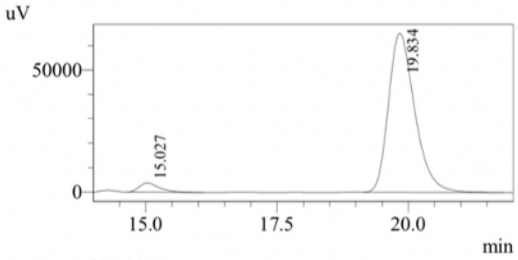
HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 15.0 min (minor) and 19.8 min (major), 96:4 er.



PeakTable

Detector A Ch1 254nm

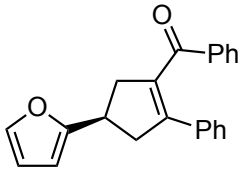
Peak#	Ret. Time	Area %
1	15.036	49.805
2	19.858	50.195
Total		100.000



PeakTable

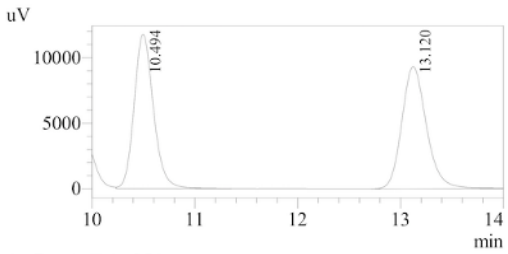
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	15.027	4.154
2	19.834	95.846
Total		100.000



(*R*)-(4-(Furan-2-yl)-2-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4ae): Colorless oil (72.4 mg, 77%); R_f 0.31 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2H), 7.38-7.34 (m, 2H), 7.25-7.21 (m, 2H), 7.17-7.13 (m, 2H), 7.10-7.07 (m, 3H), 6.33-6.31 (m, 1H), 6.14-6.14 (m, 1H), 3.81 (quint, *J* = 7.9 Hz, 1H), 3.39-3.21 (m, 3H), 3.17-3.11 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 158.0, 144.7, 141.3, 136.5, 136.0, 135.4, 132.8, 129.3, 128.2, 128.0, 127.9, 127.9, 110.1, 104.2, 43.0, 42.5, 35.7; **HRMS** (ESI) Calcd for $C_{22}H_{19}O_2$ $[M + H]^+$ 315.1385, found 315.1383; $[\alpha]^{25}_D$ = +23.3 (*c* = 2.63 in $CHCl_3$, 97:3 er).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 10.1 min (minor) and 12.7 min (major), 97:3 er.

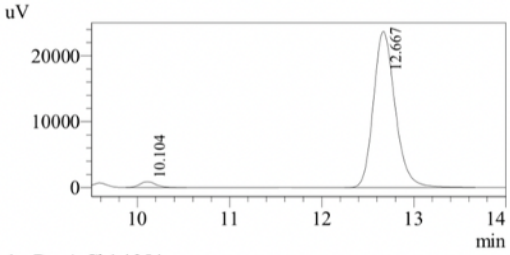


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.494	49.742
2	13.120	50.258
Total		100.000

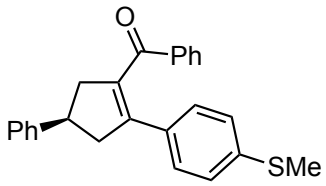


1 Det.A Ch1 / 254nm

PeakTable

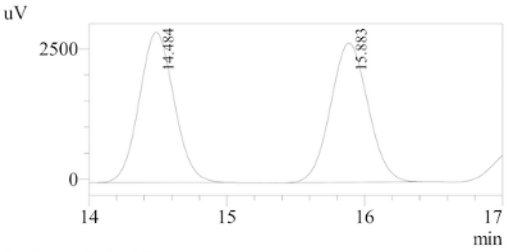
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	10.104	2.740
2	12.667	97.260
Total		100.000



(*R*)-(2-(4-(Methylthio)phenyl)-4-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4af): Pale yellow oil (89.5 mg, 81%); R_f 0.26 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.44-7.22 (m, 8H), 7.12-7.10 (m, 2H), 7.00-6.98 (m, 2H), 3.78 (quint, *J* = 8.2 Hz, 1H), 3.46-3.31 (m, 2H), 3.19-3.06 (m, 2H), 2.38 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.8, 145.3, 144.0, 138.6, 136.5, 136.0, 132.9, 132.2, 129.3, 128.6, 128.4, 128.3, 126.9, 126.4, 125.8, 45.5, 45.3, 42.4, 15.4; **HRMS** (ESI) Calcd for $C_{25}H_{23}OS$ $[M + H]^+$ 371.1470, found 371.1465; $[\alpha]^{25}_D$ = +21.5 (*c* = 0.60 in $CHCl_3$, 97:3 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 14.4 min (minor) and 15.8 min (major), 97:3 er.

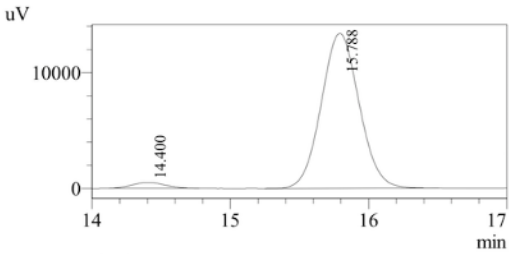


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.484	50.114
2	15.883	49.886
Total		100.000

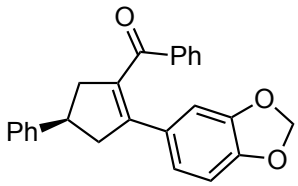


1 Det.A Ch1 / 254nm

PeakTable

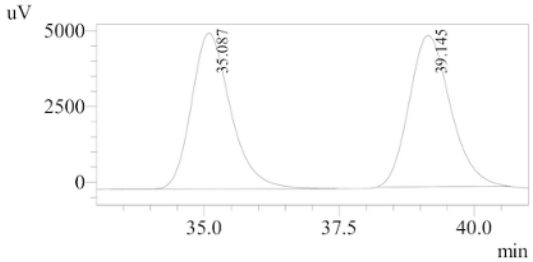
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.400	3.207
2	15.788	96.793
Total		100.000



(*R*)-(2-(Benzo[*d*][1,3]dioxol-5-yl)-4-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4ag): Pale yellow oil (92.7 mg, 84%); R_f 0.33 (hexane/EtOAc = 9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.43-7.21 (m, 8H), 6.69-6.67 (m, 2H), 6.55-6.53 (m, 1H), 5.82 (s, 2H), 3.75 (quint, J = 8.2 Hz, 1H), 3.42-3.29 (m, 2H), 3.15-3.04 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 147.3, 147.3, 145.3, 144.5, 136.6, 135.4, 132.8, 129.7, 129.3, 128.6, 128.3, 126.9, 126.3, 122.1, 108.1, 107.9, 101.0, 45.8, 45.1, 42.3; **HRMS** (ESI) Calcd for $C_{25}H_{21}O_3$ $[M + H]^+$ 369.1491, found 369.1493; $[\alpha]^{25}_D$ = +7.18 (c = 3.39 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 0.5 mL/min. t_R = 32.7 min (minor) and 36.3 min (major), 95:5 er.

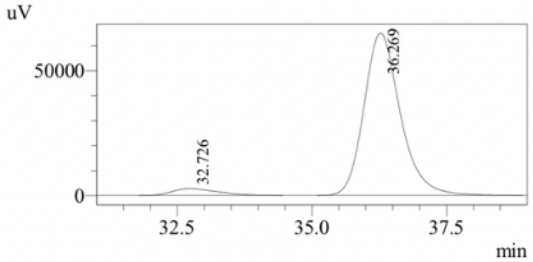


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	35.087	49.416
2	39.145	50.584
Total		100.000

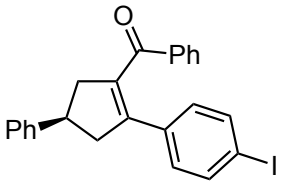


1 Det.A Ch1 / 254nm

PeakTable

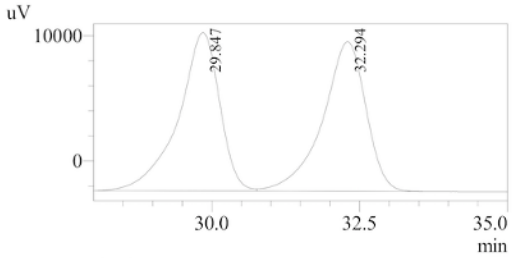
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	32.726	5.092
2	36.269	94.908
Total		100.000



(*R*)-(2-(4-Iodophenyl)-4-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4ah): Pale yellow oil (114.5 mg, 85%); R_f 0.29 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.47-7.43 (m, 3H), 7.37-7.23 (m, 7H), 6.94-6.91 (m, 2H), 3.79 (quint, J = 8.2 Hz, 1H), 3.44-3.30 (m, 2H), 3.19-3.05 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.5, 145.1, 143.2, 137.4, 137.2, 136.2, 135.0, 133.2, 129.5, 129.3, 128.6, 128.5, 126.9, 126.4, 93.7, 45.4, 42.4; **HRMS** (ESI) Calcd for $C_{24}H_{20}OI$ $[M + H]^+$ 451.0559, found 451.0557; $[\alpha]^{25}_D$ = +7.0 (c = 0.46 in $CHCl_3$, 96:4 er sample).

HPLC analysis: Daicel CHIRALPAK OD; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 30.0 min (minor) and 32.4 min (major), 96:4 er.

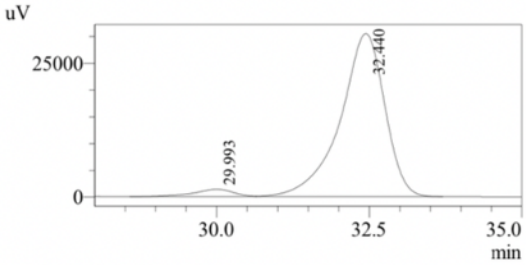


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	29.847	50.257
2	32.294	49.743
Total		100.000

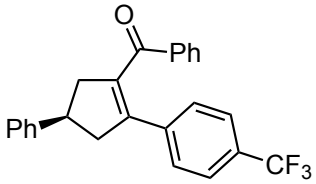


1 Det.A Ch1 / 254nm

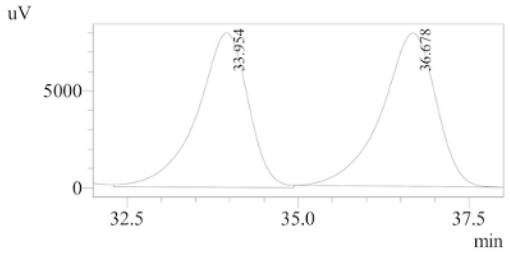
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	29.993	4.081
2	32.440	95.919
Total		100.000



(*R*)-Phenyl(4-phenyl-2-(4-(trifluoromethyl)phenyl)cyclopent-1-en-1-yl)methanone (4ai): The reaction was performed at 0 °C for 48 h and then at 50 °C for 16 h. White solid (109.8 mg, 93%); R_f 0.35 (hexane/toluene = 1/1); m.p. 82-84 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.78-7.76 (m, 2H), 7.46-7.42 (m, 1H), 7.39-7.23 (m, 11H), 3.83 (quint, J = 8.2 Hz, 1H), 3.49-3.35 (m, 2H), 3.24-3.10 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 144.9, 142.8, 139.1, 138.8, 136.2, 133.3, 129.7 (q, $^2J_{C\text{-}F}$ = 32.7 Hz), 129.2, 128.7, 128.5, 128.0, 126.9, 126.5, 125.1 (q, $^3J_{C\text{-}F}$ = 3.8 Hz), 123.9 (q, $^1J_{C\text{-}F}$ = 271.9 Hz), 45.5, 45.4, 42.5; **^{19}F NMR** (376 MHz, $CDCl_3$) δ –63.2; **HRMS** (ESI) Calcd for $C_{25}H_{20}OF_3$ $[M + H]^+$ 393.1466, found 393.1461; $[\alpha]^{25}_D$ = +13 (c = 0.29 in $CHCl_3$, 93:7 er sample). HPLC analysis: Daicel CHIRALPAK OD; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 0.5 mL/min. t_R = 25.7 min (minor) and 27.4 min (major), 93:7 er.

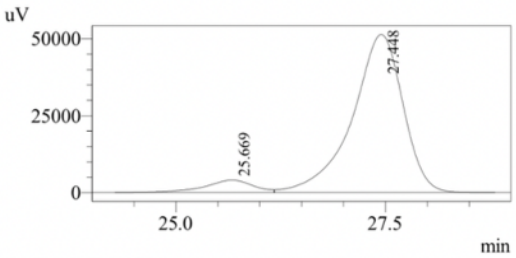


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	33.954	48.674
2	36.678	51.326
Total		100.000

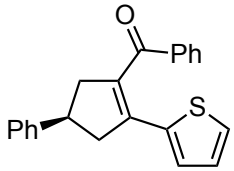


1 Det.A Ch1 / 254nm

PeakTable

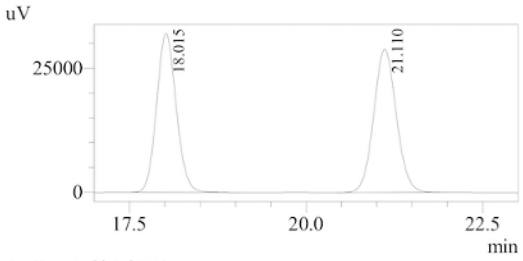
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	25.669	6.963
2	27.448	93.037
Total		100.000



(*S*)-Phenyl(4-phenyl-2-(thiophen-2-yl)cyclopent-1-en-1-yl)methanone (4aj): Pale yellow oil (82.2 mg, 83%); R_f 0.49 (hexane/EtOAc = 9/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88-7.86 (m, 2H), 7.50-7.45 (m, 1H), 7.37-7.31 (m, 6H), 7.25-7.20 (m, 1H), 7.16-7.15 (m, 1H), 7.06-7.04 (m, 1H), 6.90-6.88 (m, 1H), 3.76 (quint, J = 8.2 Hz, 1H), 3.46-3.39 (m, 1H), 3.33-3.27 (m, 1H), 3.18-3.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.9, 145.3, 138.1, 136.4, 136.4, 135.1, 133.2, 129.3, 128.6, 128.5, 127.2, 126.9, 126.3, 125.4, 124.1, 45.4, 45.3, 42.3; **HRMS** (ESI) Calcd for $C_{22}H_{19}OS$ $[M + H]^+$ 331.1157, found 331.1159; $[\alpha]^{25}_D$ = +14 (c = 0.61 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 18.1 min (minor) and 21.3 min (major), 95:5 er.

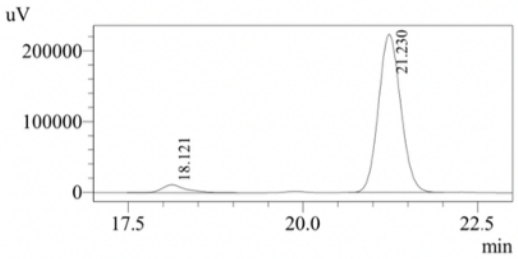


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	18.015	49.026
2	21.110	50.974
Total		100.000

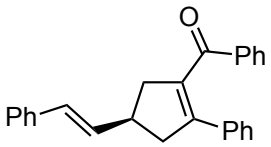


1 Det.A Ch1 / 254nm

PeakTable

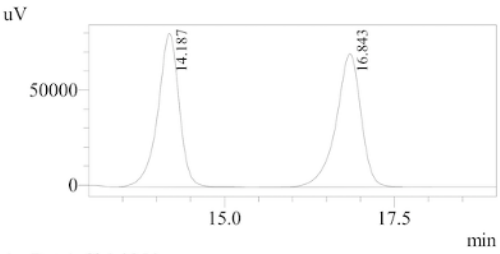
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	18.121	4.941
2	21.230	95.059
Total		100.000



(*R*,*E*)-Phenyl(2-phenyl-4-styrylcyclopent-1-en-1-yl)methanone (4ak): Yellow oil (79.0 mg, 75%); R_f 0.32 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77-7.75 (m, 2H), 7.39-7.07 (m, 13H), 6.52-6.38 (m, 2H), 3.41-3.31 (m, 1H), 3.27-3.12 (m, 2H), 3.01-2.87 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 145.0, 137.3, 136.5, 136.3, 135.6, 133.3, 132.7, 129.4, 129.3, 128.5, 128.2, 128.0, 127.8, 127.8, 127.1, 126.0, 44.1, 43.7, 40.7; **HRMS** (ESI) Calcd for $C_{26}H_{23}O$ $[M + H]^+$ 351.1749, found 351.1744; $[\alpha]^{25}_D$ = +14.7 (*c* = 0.985 in $CHCl_3$, 97:3 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 14.3 min (major) and 17.0 min (minor), 97:3 er.

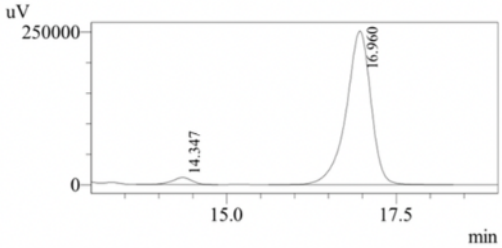


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.187	49.548
2	16.843	50.452
Total		100.000

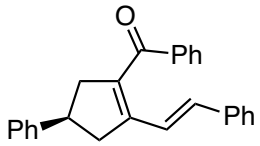


1 Det.A Ch1 / 254nm

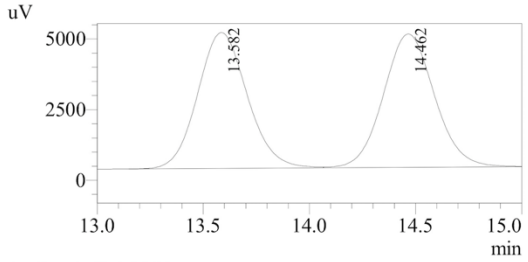
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.347	3.486
2	16.960	96.514
Total		100.000

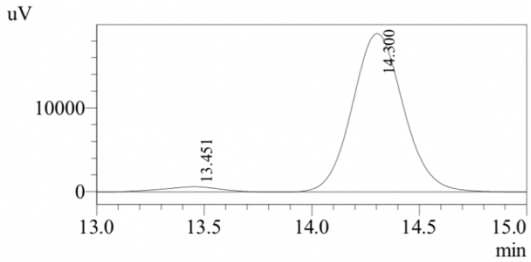


(*R*,*E*)-Phenyl(4-phenyl-2-styrylcyclopent-1-en-1-yl)methanone (4al): Pale yellow oil (63.1 mg, 60%); R_f 0.28 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.57-7.54 (m, 1H), 7.47-7.44 (m, 2H), 7.34-7.33 (m, 4H), 7.25-7.18 (m, 6H), 7.02 (d, *J* = 16.1 Hz, 1H), 6.66 (d, *J* = 16.1 Hz, 1H), 3.65 (quint, *J* = 8.2 Hz, 1H), 3.38-3.23 (m, 2H), 3.11-2.96 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.9, 147.3, 145.3, 139.3, 138.1, 136.7, 134.1, 132.6, 129.1, 128.7, 128.7, 128.6, 128.4, 127.0, 126.9, 126.4, 123.3, 44.3, 42.1, 42.0; **HRMS** (ESI) Calcd for $C_{26}H_{23}O$ $[M + H]^+$ 351.1749, found 351.1748; $[\alpha]^{25}_D$ = +79.9 (*c* = 2.10 in $CHCl_3$, 96:4 er sample).
HPLC analysis: Daicel CHIRALPAK IA; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 13.5 min (minor) and 14.3 min (major), 96:4 er.



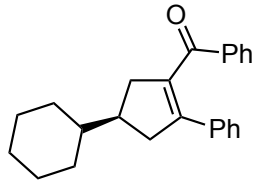
PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	13.582	49.718
2	14.462	50.282
Total		100.000



PeakTable
Detector A Ch1 254nm

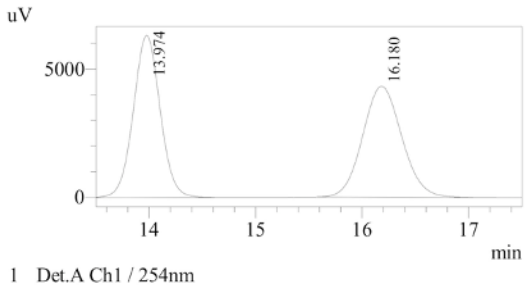
Peak#	Ret. Time	Area %
1	13.451	3.734
2	14.300	96.266
Total		100.000



(*R*)-(4-Cyclohexyl-2-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4am): The reaction was performed using **L3** as the ligand in DMSO at 40 °C for 48 h and then at 100 °C for 6 h. Colorless oil (82.4 mg, 83%); R_f 0.39 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.71 (m, 2H), 7.37-7.33 (m, 1H), 7.24-7.20 (m, 2H), 7.14-7.05 (m, 5H), 3.07-2.91 (m, 2H), 2.79-2.65 (m, 2H), 2.29 (sext, *J* = 8.7 Hz, 1H), 1.84-1.66 (m, 5H), 1.41-1.13 (m, 4H), 1.07-0.96 (m, 2H); **^{13}C**

NMR (100 MHz, $CDCl_3$) δ 198.1, 145.7, 136.9, 136.6, 136.1, 132.6, 129.3, 128.1, 127.9, 127.8, 127.6, 43.6, 43.2, 42.0, 41.6, 31.5, 31.3, 26.5, 26.3, 26.2; **HRMS** (ESI) Calcd for $C_{24}H_{27}O$ $[M + H]^+$ 331.2062, found 331.2066; $[\alpha]^{25}_D$ = +13.2 (*c* = 2.17 in $CHCl_3$, 78:22 er sample). The absolute configuration was deduced as (*R*) based on the result that **L3** gave (*R*)-**4aa** as the major enantiomer in the reaction between **1a** and **2a**.

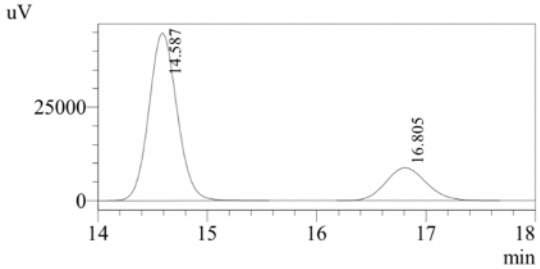
HPLC analysis: Daicel CHIRALPAK IA; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 14.6 min (major) and 16.8 min (minor), 78:22 er.



PeakTable

Detector A Ch1 254nm

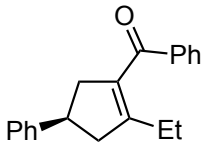
Peak#	Ret. Time	Area %
1	13.974	50.111
2	16.180	49.889
Total		100.000



PeakTable

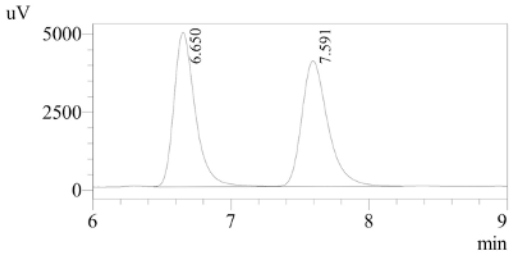
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.587	77.924
2	16.805	22.076
Total		100.000



(*R*)-(2-Ethyl-4-phenylcyclopent-1-en-1-yl)(phenyl)methanone (4an): The reaction was performed using **L3** as the ligand at 30 °C for 48 h and then at 100 °C for 6 h. Colorless oil (47.9 mg, 58%); R_f 0.40 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.82-7.79 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.43 (m, 2H), 7.35-7.29 (m, 4H), 7.24-7.19 (m, 1H), 3.58 (quint, *J* = 8.2 Hz, 1H), 3.19-3.13 (m, 1H), 3.04-2.91 (m, 2H), 2.76-2.69 (m, 1H), 2.15 (q, *J* = 7.5 Hz, 2H), 0.99 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.8, 153.3, 145.6, 139.0, 134.5, 132.5, 128.8, 128.5, 128.4, 126.9, 126.2, 44.6, 43.6, 42.2, 23.5, 12.4; **HRMS** (ESI) Calcd for $C_{20}H_{21}O$ $[M + H]^+$ 277.1592, found 277.1590; $[\alpha]^{25}_D$ = -7.17 (*c* = 0.600 in $CHCl_3$, 79:21 er sample).

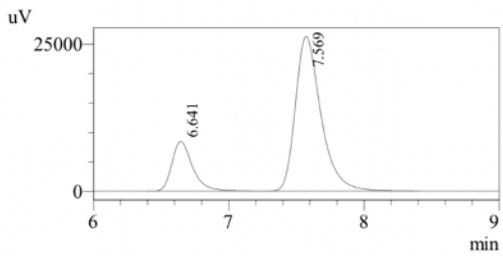
HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 99:1; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 6.6 min (minor) and 7.6 min (major), 79:21 er.



PeakTable

Detector A Ch1 254nm

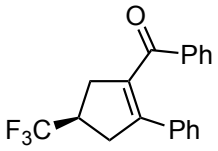
Peak#	Ret. Time	Area %
1	6.650	50.079
2	7.591	49.921
Total		100.000



PeakTable

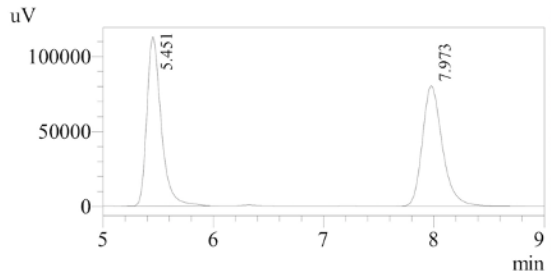
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	6.641	20.669
2	7.569	79.331
Total		100.000



Phenyl(2-phenyl-4-(trifluoromethyl)cyclopent-1-en-1-yl)methanone (4ao): The reaction was performed using **L3** as the ligand at 30 °C for 24 h and then at 100 °C for 6 h. Pale yellow oil (36.8 mg, 39%); R_f 0.27 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 2H), 7.40-7.37 (m, 1H), 7.27-7.23 (m, 2H), 7.14-7.09 (m, 5H), 3.28-3.08 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 143.7, 136.1, 134.8, 134.6, 133.0, 129.3, 128.4, 128.3, 128.1, 127.9 (q, $^1J_{C\text{-}F}$ = 277.1 Hz), 127.9, 39.5 (q, $^2J_{C\text{-}F}$ = 28.3 Hz), 37.7 (q, $^3J_{C\text{-}F}$ = 2.7 Hz), 37.1 (q, $^3J_{C\text{-}F}$ = 2.6 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ –73.2; **HRMS** (ESI) Calcd for $C_{19}H_{16}OF_3$ $[M + H]^+$ 317.1153, found 317.1154; $[\alpha]^{25}_D$ = +2.2 (*c* = 0.49 in $CHCl_3$, 77:23 er sample).

HPLC analysis: Daicel CHIRALPAK AS-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 5.4 min (minor) and 8.0 min (major), 77:23 er.

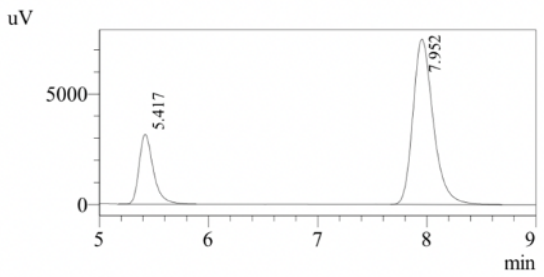


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	5.451	50.299
2	7.973	49.701
Total		100.000

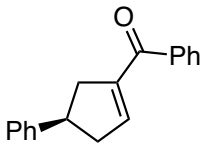


1 Det.A Ch1 / 254nm

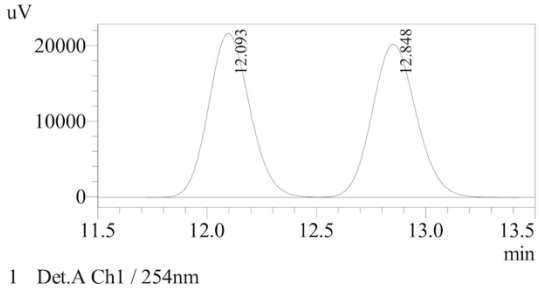
PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	5.417	22.781
2	7.952	77.219
Total		100.000



(*R*)-Phenyl(4-phenylcyclopent-1-en-1-yl)methanone (4ap): The reaction was performed at 60 °C for 12 h. Pale yellow oil (25.5 mg, 34%); R_f 0.16 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79-7.76 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.34-7.28 (m, 4H), 7.25-7.20 (m, 1H), 6.58-6.56 (m, 1H), 3.66 (quint, *J* = 8.3 Hz, 1H), 3.27-3.20 (m, 1H), 3.15-3.07 (m, 1H), 2.96-2.88 (m, 1H), 2.78-2.70 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8, 145.5, 145.1, 143.5 138.7, 131.9, 128.9, 128.5, 128.2, 126.9, 126.2, 42.9, 42.5, 39.8; **HRMS** (ESI) Calcd for $C_{18}H_{17}O$ $[M + H]^+$ 249.1279, found 249.1278; $[\alpha]^{25}_D$ = -3.07 (*c* = 1.76 in $CHCl_3$, 62:38 er sample). HPLC analysis: Daicel CHIRALPAK OJ-H; hexane:*i*-PrOH = 95:5; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 12.1 min (major) and 12.8 min (minor), 62:38 er.

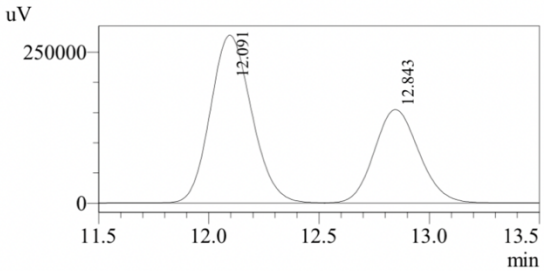


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.093	50.056
2	12.848	49.944
Total		100.000



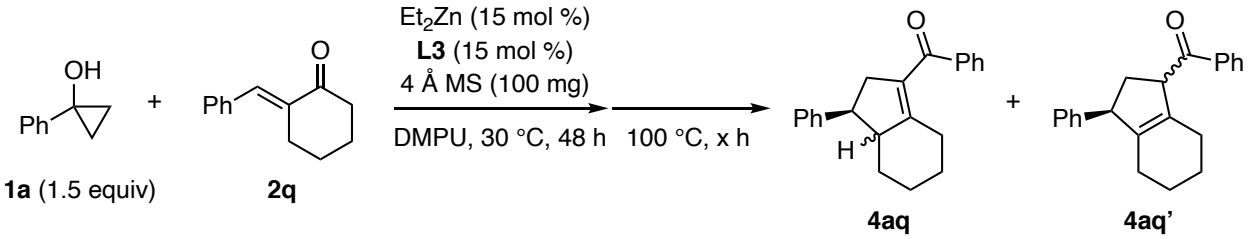
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	12.091	62.305
2	12.843	37.695
Total		100.000

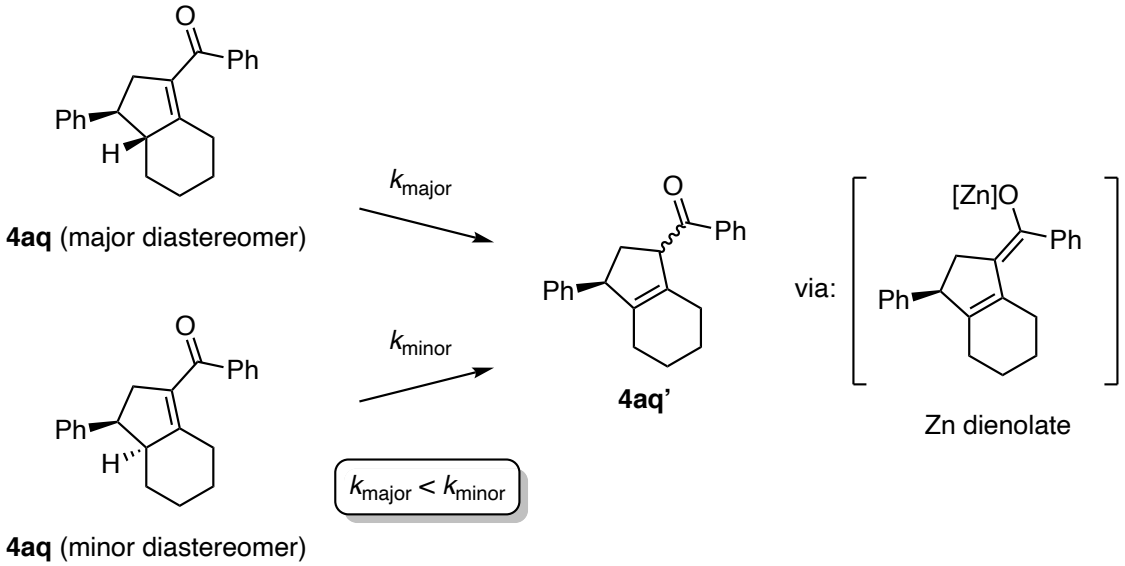
The reaction between 1a and 2q



1a (1.5 equiv) **2q** **4aq** **4aq'**

The reaction was performed using **L3** as the ligand at 30 °C for 48 h and then at 100 °C. The time profile of the aldol condensation step showed that **4aq** gradually transformed to **4aq'**, presumably via zinc dienolate intermediate (Scheme S2 and Figure S3). As the minor diastereomer of **4aq** had a higher rate of conversion than the major diastereomer, the de of **4aq** increased as the reaction proceeded. When the reaction was quenched after 3 h at 100 °C, **4aq** was obtained as a colorless oil (57.0 mg, 63%, 80:20 dr; The relative stereochemistry of the major diastereomer was determined by X-ray crystallographic analysis of its anilide derivative **5aq** (vide infra)). When the reaction was quenched after 6 h at 100 °C, **4aq** was obtained in 51% yield (46.6 mg, as a single diastereomer). When the reaction was quenched after 144 h at 100 °C, **4aq'** was obtained as a colorless oil (0.6 mmol scale, 120.5 mg, 66%, 50:50 dr).

Scheme S2. Conversion of **4aq** to **4aq'**



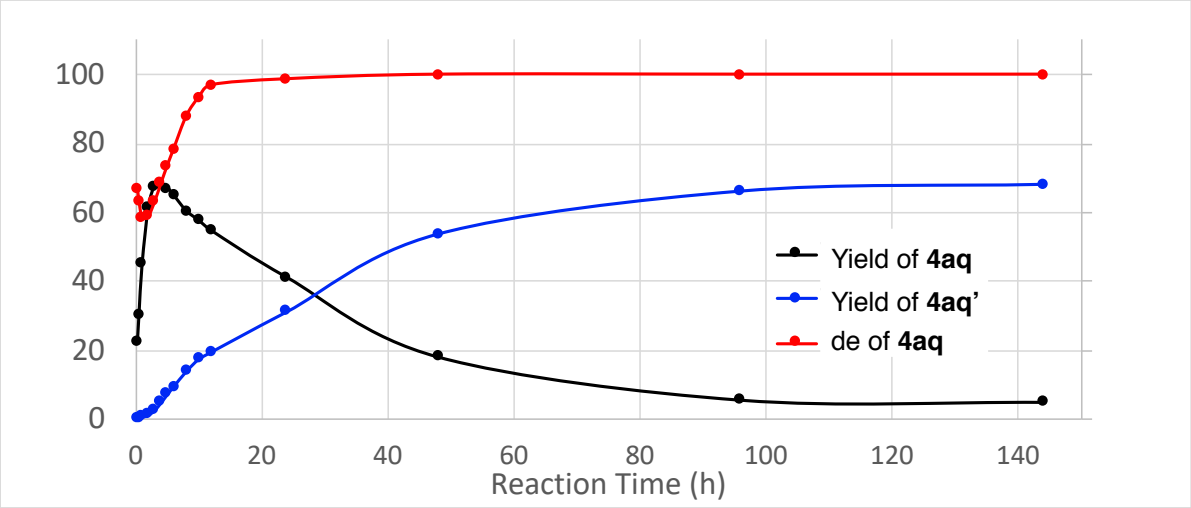
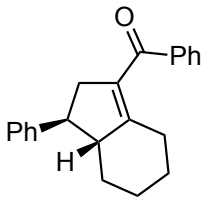
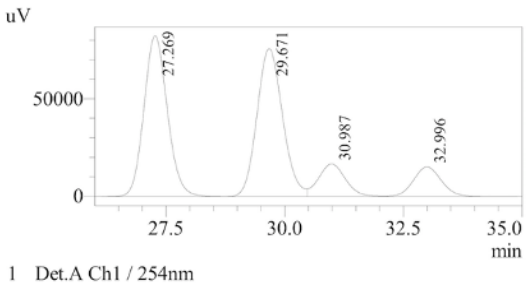


Figure S3. Time profile of the aldol condensation–isomerization step at 100 °C.



Phenyl(1-phenyl-2,4,5,6,7,7a-hexahydro-1*H*-inden-3-yl)methanone (4aq): R_f 0.34 (hexane/EtOAc = 19/1); **^{1}H NMR** (major diastereomer, 500 MHz, $CDCl_3$) δ 7.83-7.81 (m, 2H), 7.55-7.52 (m, 1H), 7.47-7.44 (m, 2H), 7.34-7.29 (m, 4H), 7.24-7.20 (m, 1H), 3.17-3.12 (m, 1H), 3.07 (q, J = 8.4 Hz, 1H), 2.99-2.93 (m, 1H), 2.73-2.68 (m, 1H), 2.47-2.44 (m, 1H), 2.13-2.10 (m, 1H), 1.84-1.77 (m, 2H), 1.72-1.69 (m, 1H), 1.36-1.19 (m, 3H); **^{13}C NMR** (major diastereomer, 126 MHz, $CDCl_3$) δ 196.5, 153.5, 144.7, 139.2, 132.4, 131.8, 128.8, 128.5, 128.4, 127.3, 126.2, 56.3, 50.6, 42.6, 34.4, 28.6, 26.1, 25.2; **HRMS** (ESI) Calcd for $C_{22}H_{23}O$ $[M + H]^+$ 303.1749, found 303.1746; $[\alpha]^{25}_D$ = -14.0 (c = 2.36 in $CHCl_3$, 80:20 dr, 84:16 er (major), 70:30 er (minor) sample). HPLC analysis (the sample obtained after 3 h at 100 °C, 80:20 dr): Daicel CHIRALPAK ID; hexane:*i*-PrOH = 80:20; detection wavelength = 254 nm; flow rate = 0.2 mL/min. Major diastereomer t_R = 25.6 min (minor) and 27.7 min (major), 84:16 er. Minor diastereomer t_R = 29.0 min (minor) and 30.8 min (major), 70:30 er.

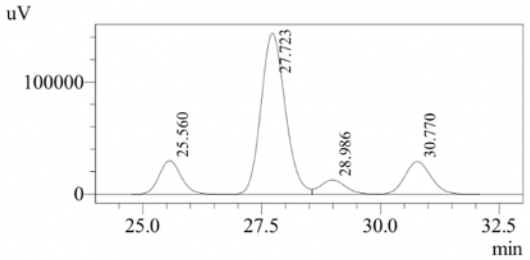


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	27.269	40.587
2	29.671	40.811
3	30.987	9.573
4	32.996	9.029
Total		100.000



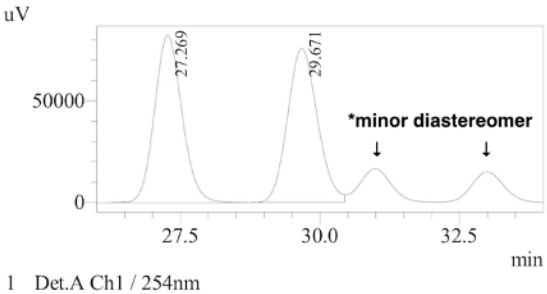
1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	25.560	12.588
2	27.723	66.789
3	28.986	6.131
4	30.770	14.492
Total		100.000

HPLC analysis (the sample obtained after 6 h at 100 °C, single diastereomer): Daicel CHIRALPAK ID; hexane:*i*-PrOH = 80:20; detection wavelength = 254 nm; flow rate = 0.2 mL/min. t_R = 27.3 min (minor) and 29.7 min (major), 82:18 er.

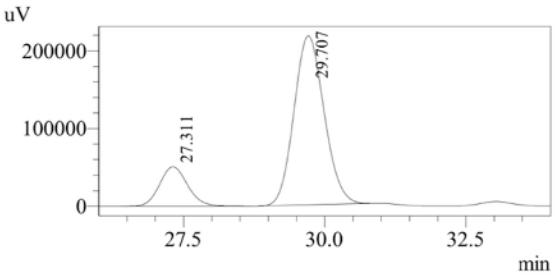


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	27.269	50.000
2	29.671	50.000
Total		100.000

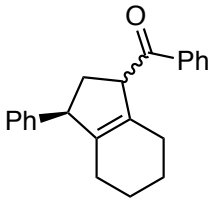


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

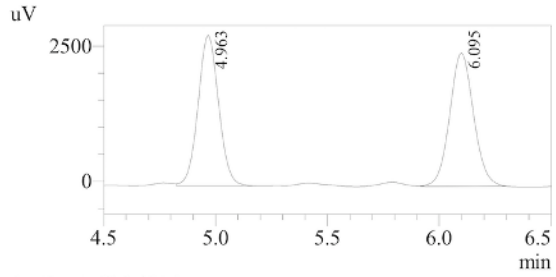
Peak#	Ret. Time	Area %
1	27.311	17.733
2	29.707	82.267
Total		100.000



Phenyl(3-phenyl-2,3,4,5,6,7-hexahydro-1*H*-inden-1-yl)methanone (4aq'): Colorless oil (120.5 mg, 66%, 50:50 dr); R_f 0.49, 0.44 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) the diastereomer of R_f 0.49: δ 8.02-8.00 (m, 2H), 7.57-7.52 (m, 1H), 7.48-7.44 (m, 2H), 7.30-7.22 (m, 4H), 7.19-7.14 (m, 1H), 4.51-4.47 (m, 1H), 3.76 (brs, 1H), 2.80 (dt, *J* = 13.4, 9.2 Hz, 1H), 2.17-

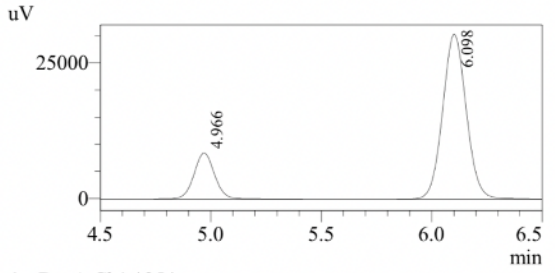
2.13 (m, 1H), 1.98 (dt, J = 13.6, 6.8 Hz, 1H), 1.89-1.85 (m, 1H), 1.75 (brs, 2H), 1.72-1.54 (m, 4H); the diastereomer of R_f 0.44: δ 8.02-7.99 (m, 2H), 7.58-7.54 (m, 1H), 7.48-7.44 (m, 2H), 7.33-7.29 (m, 2H), 7.23-7.19 (m, 1H), 7.17-7.15 (m, 2H), 4.61-4.58 (m, 1H), 3.89 (brs, 1H), 2.60 (ddd, J = 13.3, 8.8, 5.1 Hz, 1H), 2.15 (ddd, J = 13.3, 9.2, 5.3 Hz, 1H), 2.00 (brs, 2H), 1.89-1.85 (m, 1H), 1.77-1.55 (m, 5H); **^{13}C NMR** (100 MHz, $CDCl_3$) the diastereomer of R_f 0.49: δ 202.3, 145.0, 140.7, 137.3, 134.9, 132.9, 128.5, 128.5, 128.4, 128.0, 126.1, 55.0, 54.3, 38.0, 25.2, 24.5, 22.8, 22.6; the diastereomer of R_f 0.44: δ 202.5, 145.3, 141.2, 137.3, 135.0, 132.9, 128.6, 128.5, 127.6, 126.2, 55.1, 53.9, 38.5, 25.4, 24.5, 22.9, 22.6; **HRMS** (ESI) Calcd for $C_{22}H_{23}O$ $[M + H]^+$ 303.1749, found 303.1739; $[\alpha]^{25}_D$ = -56.9 (c = 1.80 in $CHCl_3$, 80:20 er sample of the diastereomer of R_f 0.49), -111 (c = 1.52 in $CHCl_3$, 80:20 er sample of the diastereomer of R_f 0.44).

HPLC analysis (the diastereomer of R_f 0.49): Daicel CHIRALPAK IA; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 5.0 min (minor) and 6.1 min (major), 80:20 er.



PeakTable
Detector A Ch1 254nm

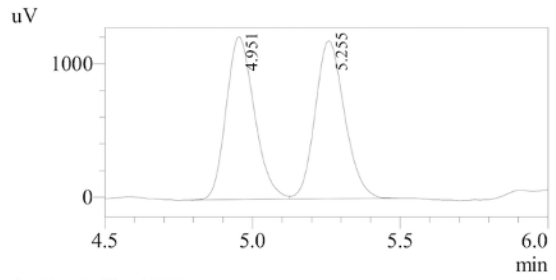
Peak#	Ret. Time	Area %
1	4.963	49.289
2	6.095	50.711
Total		100.000



PeakTable
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	4.966	19.560
2	6.098	80.440
Total		100.000

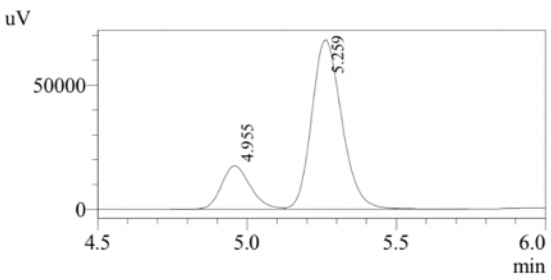
HPLC analysis (the diastereomer of R_f 0.44): Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 5.0 min (minor) and 5.3 min (major), 80:20 er.



PeakTable

Detector A Ch1 254nm

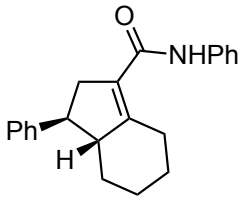
Peak#	Ret. Time	Area %
1	4.951	49.777
2	5.255	50.223
Total		100.000



PeakTable

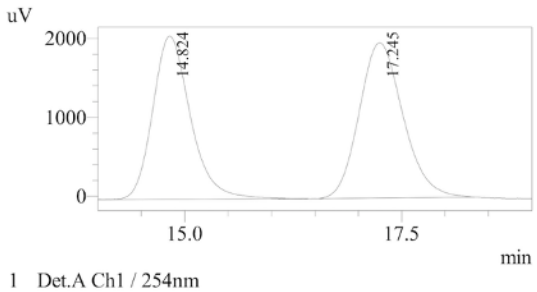
Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	4.955	19.626
2	5.259	80.374
Total		100.000



(1*S*,7a*R*)-*N*,1-Diphenyl-2,4,5,6,7,7a-hexahydro-1*H*-indene-3-carboxamide (5aq): Prepared according to the synthetic procedure for **5** (vide infra). Pale yellow solid (59.2 mg, 62%); R_f 0.18 (hexane/EtOAc = 19/1); m.p. 148-150 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56-7.54 (m, 2H), 7.33-7.20 (m, 8H), 7.10-7.06 (m, 1H), 3.63-3.60 (m, 1H), 3.09-2.97 (m, 2H), 2.83-2.76 (m, 1H), 2.67-2.61 (m, 1H), 2.07-1.97 (m, 2H), 1.88-1.76 (m, 2H), 1.38-1.13 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.6, 155.5, 144.5, 137.9, 128.9, 128.5, 127.3, 126.3, 125.5, 124.1, 120.0, 55.9, 50.4, 41.3, 34.1, 27.6, 26.0, 25.2; **HRMS** (ESI) Calcd for $C_{22}H_{24}NO$ $[M + H]^+$ 318.1858, found 318.1857; $[\alpha]^{25}_D$ = -20.8 (*c* = 2.86 in $CHCl_3$, 84:16 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 80:20; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 14.8 min (minor) and 17.2min (major), 84:16 er.

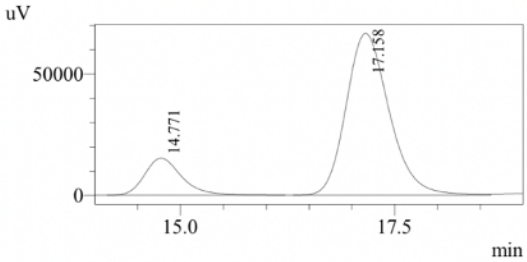


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.824	47.583
2	17.245	52.417
Total		100.000



1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	14.771	16.495
2	17.158	83.505
Total		100.000

Recrystallization of **5aq** from THF/pentane afforded single crystals suitable for X-ray diffraction analysis, which unambiguously confirmed the molecular structure of **5aq** (major diastereomer) and its relative configuration (Figure S4).[31]

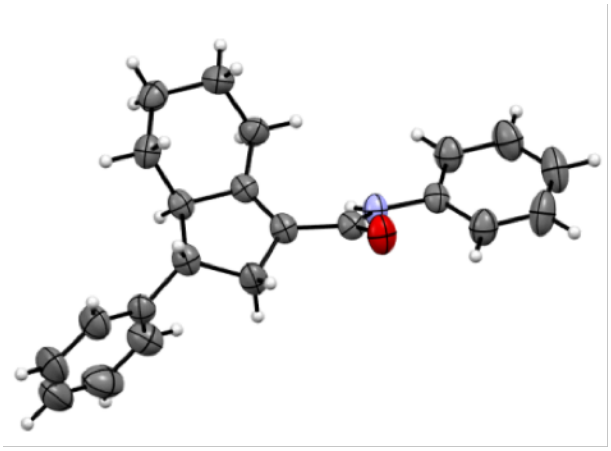
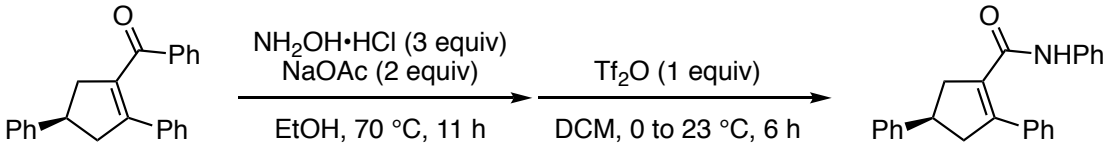


Figure S4. ORTEP drawing of **5aq** (thermal ellipsoids set at 50% probability; CCDC 2056576).

Table S4. Crystal data and structure refinement for **5aq**

Identification code	yoshi107s	
Chemical formula	$C_{22}H_{23}NO$	
Formula weight	317.41 g/mol	
Temperature	296(2) K	
Wavelength	1.54178 Å	
Crystal size	0.010 x 0.040 x 0.240 mm	
Crystal habit	colorless needle	
Crystal system	monoclinic	
Space group	C 1 2 1	
Unit cell dimensions	a = 24.6438(8) Å	α = 90°
	b = 5.1210(2) Å	β = 123.8273(17)°
	c = 16.5702(6) Å	γ = 90°
Volume	1737.18(11) $Å^3$	
Z	4	
Density (calculated)	1.214 g/cm^3	
Absorption coefficient	0.569 mm^{-1}	
F(000)	680	
Theta range for data collection	3.21 to 68.04°	
Index ranges	-29<=h<=29, -5<=k<=5, -19<=l<=19	
Reflections collected	24610	
Independent reflections	3078 [R(int) = 0.0648]	
Coverage independent reflections	98.8%	
Absorption correction	Multi-Scan	
Max. and min. transmission	0.9940 and 0.8760	
Structure solution technique	direct methods	
Structure solution program	XT, VERSION 2014/5	
Refinement method	Full-matrix least-squares on F^2	
Refinement program	SHELXL-2018/3 (Sheldrick, 2018)	
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	3078 / 1 / 193	
Goodness-of-fit on F^2	1.045	
Final R indices	2832 data; I>2σ(I)	R1 = 0.0429, wR2 = 0.1154
	all data	R1 = 0.0470, wR2 = 0.1203
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0783P)^2+0.3359P]$ where $P=(F_o^2+2F_c^2)/3$	
Absolute structure parameter	0.0(2)	
Largest diff. peak and hole	0.183 and -0.165 $eÅ^{-3}$	
R.M.S. deviation from mean	0.036 $eÅ^{-3}$	

Product Transformations

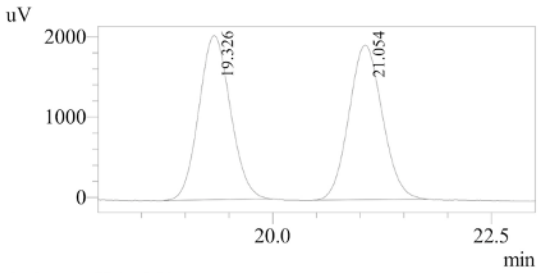


4aa
0.3 mmol, 95:5 er

5
86%, 95:5 er

(*R*)-*N*,2,4-Triphenylcyclopent-1-ene-1-carboxamide (5): A 4-mL vial equipped with a magnetic stir bar was charged with **4aa** (97.3 mg, 0.30 mmol, 95:5 er), hydroxylammonium chloride (62.6 mg, 0.90 mmol, 3 equiv) and sodium acetate (49.2 mg, 0.6 mmol, 2 equiv), followed by the addition of ethanol (0.9 mL). The mixture was stirred at 70 °C for 11 h. After the reaction mixture was concentrated under the reduced pressure, the residue was diluted with H_2O (1.5 mL) and CH_2Cl_2 (2 mL). The layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 2 mL). The combined organic layers were dried Na_2SO_4, filtered, and concentrated to give the crude oxime intermediate as a colorless oil. The crude oxime product was dissolved in anhydrous CH_2Cl_2 (4 mL) and the solution was stirred at 0 °C. To the mixture was added triflic anhydride solution (84.3 mg in CH_2Cl_2 (2 mL)) dropwise over 15 min, and the resulting mixture was stirred and allowed to warm to room temperature. After 6 h, the reaction mixture was washed with sat. $NaHCO_3$ aq (2 mL) and the organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography to afford the product as a pale yellow solid (88.0 mg, 86%); R_f 0.23 (hexane/EtOAc = 9/1); m.p. 126-127 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41-7.32 (m, 9H), 7.24-7.15 (m, 6H), 7.04-7.00 (m, 1H), 3.66 (quint, J = 8.2 Hz, 1H), 3.43-3.28 (m, 2H), 3.12-3.02 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.3, 145.3, 145.2, 137.7, 135.9, 133.3, 128.9, 128.8, 128.6, 128.5, 127.8, 126.8, 126.3, 124.0, 119.4, 47.8, 43.0, 41.6; **HRMS** (ESI) Calcd for $C_{24}H_{22}NO$ $[M + H]^+$ 340.1701, found 340.1703; $[\alpha]^{25}_D$ = +8.18 (c = 2.29 in $CHCl_3$, 95:5 er sample).

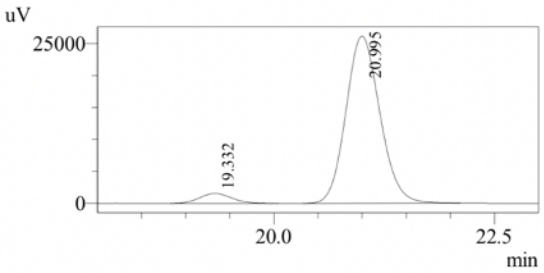
HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 90:10; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 19.3 min (minor) and 21.0 min (major), 95:5 er.



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	19.326	50.037
2	21.054	49.963
Total		100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
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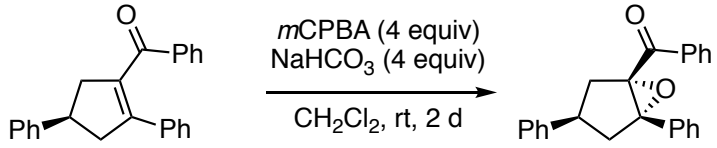
2	20.995	94.752
Total		100.000



4aa

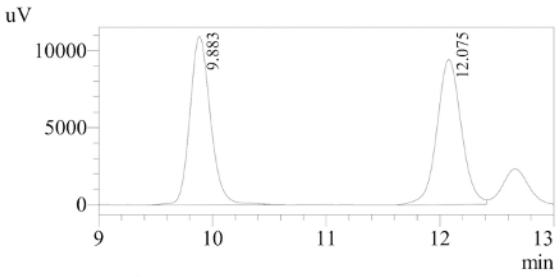
0.3 mmol, 95:5 er

6

36%, 95:5 er

((1*S*,3*R*,5*S*)-3,5-Diphenyl-6-oxabicyclo[3.1.0]hexan-1-yl)(phenyl)methanone (6): A 25 mL round bottom flask equipped with a magnetic stir bar was charged with **4aa** (97.3 mg, 0.30 mmol, 95:5 er), *m*-chloroperoxybenzoic acid (50-55 wt%, 414 mg, ca. 1.2 mmol, 4 equiv) and sodium bicarbonate (100.8 mg, 1.20 mmol, 4 equiv), followed by the addition of CH_2Cl_2 (9 mL). The mixture was stirred at rt for 48 h. The reaction progress was monitored by GC-MS as R_f of the product was very close to that of the starting material. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and washed with sat. $NaHCO_3$ aq (2 × 10 mL) and brine (10 mL). The organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash column chromatography to afford the product as a colorless oil (36.9 mg, 36%); R_f 0.31 (hexane/EtOAc = 19/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 2H), 7.53-7.49 (m, 1H), 7.41-7.31 (m, 8H), 7.27-7.17 (m, 4H), 3.41-3.32 (m, 1H), 2.80-2.64 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.8, 142.2, 135.8, 134.5, 133.3, 129.0, 128.6, 128.4, 128.2, 128.1, 127.4, 126.7, 126.0, 75.9, 72.5, 39.5, 38.9, 38.7; **HRMS** (ESI) Calcd for $C_{24}H_{21}O_2$ $[M + H]^+$ 341.1542, found 341.1544; $[\alpha]^{25}_D$ = -7.80 (*c* = 1.30 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK ID; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 9.9 min (minor) and 12.0 min (major), 95:5 er.



1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
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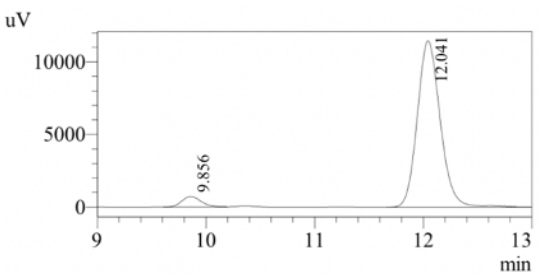
2	12.075	50.536
Total		100.000



1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

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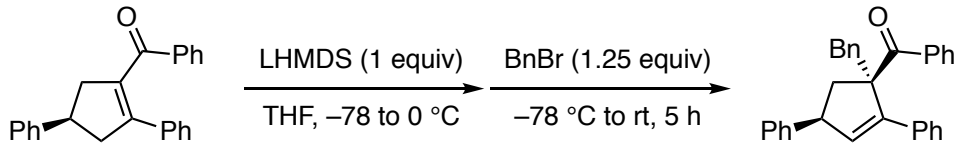
2	12.041	94.878
Total		100.000



4aa

0.3 mmol, 95:5 er

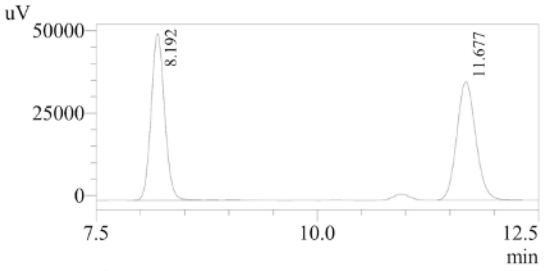
7

75%, 95:5 er

((1*S*,4*S*)-1-Benzyl-2,4-diphenylcyclopent-2-en-1-yl)(phenyl)methanone (7): A 10 mL schlenk flask equipped with a magnetic stir bar was charged with **4aa** (97.3 mg, 0.30 mmol, 95:5 er) and anhydrous THF (3 mL) under nitrogen atmosphere. The mixture was cooled to –78 °C, and lithium bis(trimethylsilyl)amide (1.3 M in THF, 0.23 mL, 0.30 mmol) was added slowly. The resulting pale yellow mixture was stirred at 0 °C for 1 h. The mixture was cooled again to –78 °C, followed by dropwise addition of benzyl bromide (1.25 equiv, 64.4 mg, 0.375 mmol). The reaction mixture was gradually warmed to room temperature. After 5 h, the reaction mixture was concentrated in vacuo. The crude product was purified by flash column chromatography to afford the product as a colorless oil (93.5 mg, 75%); R_f 0.15 (hexane/EtOAc = 39/1); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08-8.06 (m, 2H), 7.53-7.51 (m, 2H), 7.42-7.38 (m, 1H), 7.33-7.28 (m, 4H), 7.27-7.10 (m, 9H), 6.97-6.95 (m, 2H), 6.44 (d, *J* = 2.2 Hz, 1H), 3.56 (d, *J* = 13.8 Hz, 1H), 3.38 (d, *J* = 13.8 Hz, 1H), 2.89-2.84 (m, 1H), 2.64 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.48 (ddd, *J* = 13.5, 9.5, 0.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$; peaks showing positive and negative DEPT 135 signals are indicated with + and –, respectively) δ 204.2, 145.0, 144.2, 138.0, 137.5, 135.2 (+), 134.6, 131.9 (+), 131.0 (+), 129.5 (+), 128.9 (+), 128.5 (+), 128.1 (+), 127.8 (+), 127.6 (+), 127.2 (+), 126.7 (+), 126.4 (+), 126.4 (+), 66.7, 49.9 (+), 45.2 (–), 40.7 (–); **HRMS** (ESI) Calcd for $C_{31}H_{27}O$ $[M + H]^+$ 415.2062, found

415.2067; $[\alpha]^{25}_{D}$ = -62.7 (*c* = 1.10 in $CHCl_3$, 95:5 er sample).

HPLC analysis: Daicel CHIRALPAK IA; hexane:*i*-PrOH = 98:2; detection wavelength = 254 nm; flow rate = 1.0 mL/min. t_R = 8.2 min (minor) and 11.4 min (major), 95:5 er.

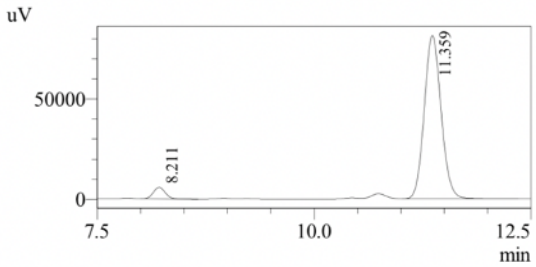


1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	8.192	50.007
2	11.677	49.993
Total		100.000



1 Det.A Ch1 / 254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area %
1	8.211	4.874
2	11.359	95.126
Total		100.000

Mechanistic Experiments

Nonlinear effect (Figures 1a and S5-S7). The model reaction between **1a** and **2a** was performed using ligand **L6** of different ees (25%, 50%, 75%, and 100%) with variation of other reaction parameters including the catalyst loading (10% (33 mM), 15% (50 mM), or 20% (67 mM); Figure 1a), the order of reagent addition (Figure S5), the temperature for the ECA step (0 °C or 30 °C; Figure S6), and the solvent composition (DMPU or DMPU/THF (1:1); Figure S7), and the ee of the product determined by chiral HPLC.

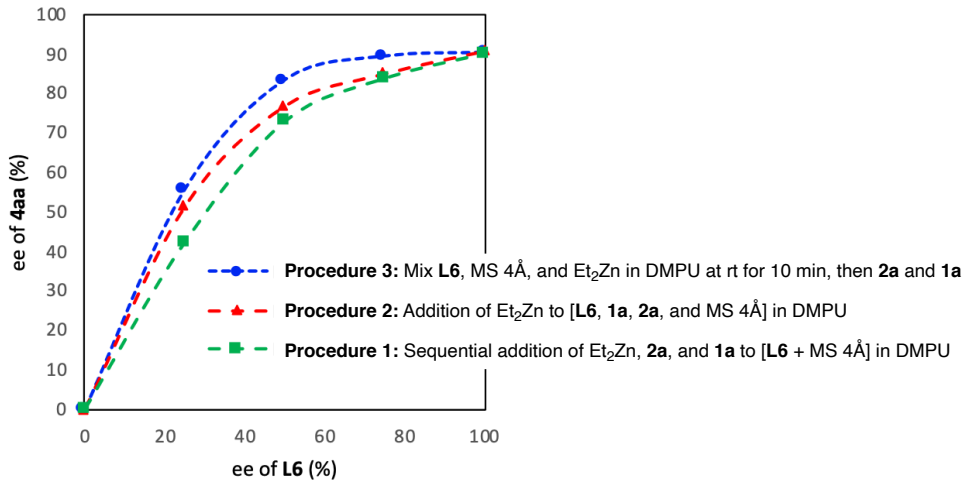


Figure S5. Nonlinear effects depending on the procedure for the reaction setup: Procedure 1, sequential addition of Et_2Zn, **2a**, and **1a** (in this order) to a mixture of **L6** and 4 Å MS in DMPU (standard procedure); Procedure 2, addition of Et_2Zn to a mixture of **L6**, **1a**, **2a**, and 4 Å MS in DMPU; Procedure 3, a mixture of **L6**, 4 Å MS, and Et_2Zn stirred at room temperature for 10 min, followed by addition of **2a** and **1a**. The reactions were conducted with 20 mol % catalyst loading at 30 °C for 30 h, then 100 °C for 6 h.

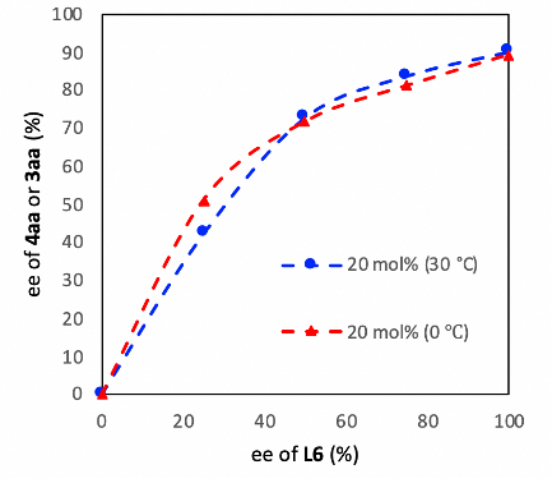


Figure S6. Nonlinear effects with the different reaction temperature (30 °C and 0 °C). The reactions were conducted with 20 mol % catalyst loading. Ee of **3aa** was determined for the reaction conducted at 0 °C.

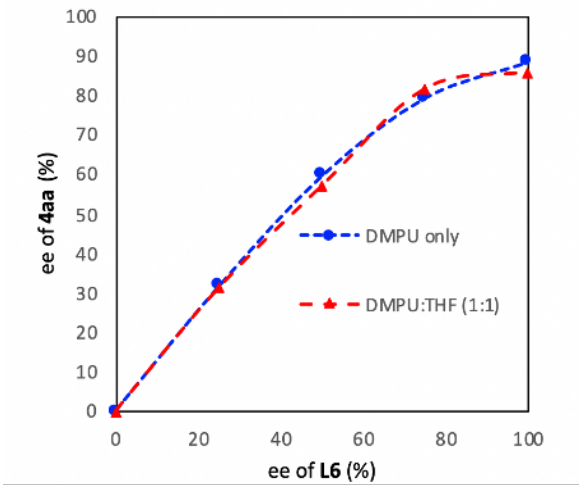


Figure S7. Nonlinear effects with different solvent composition (DMPU and DMPU/THF (1:1)). The reactions were conducted with 15 mol % catalyst loading at 30 °C for 30 h, then 100 °C for 6 h.

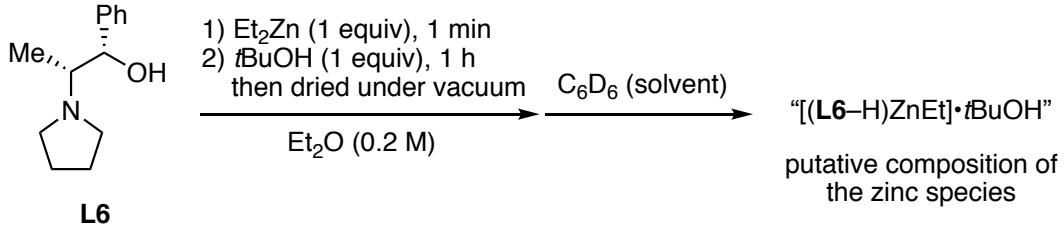
Initial rate study (Figure 1b). The model reaction between **1a** and **2a** was performed according to the standard procedure (15 mol % catalyst loading, 0 °C) using racemic, scalemic (50% ee), or enantiopure **L6**. Each reaction was tracked by GC analysis of periodically taken aliquots using mesitylene as an internal standard.

Control reaction of 1a (Figure 1c). The cyclopropanol **1a** was subjected to the standard conditions in the absence of an enone reaction partner. The conversion of **1a** to propiophenone was tracked by GC analysis of periodically taken aliquots using mesitylene as an internal standard. Full and clean conversion was observed after 48 h. Analogous experiments were also performed using DABCO instead of **L6** or simply omitting **L6**.

Solvent effect (Figure 1d). The model reaction between **1a** and **2a** was performed according to the standard procedure (15% catalyst, 0 °C for 48 h; without aldol condensation step) using THF/DMPU mixed solvents with different ratios (%THF = 0, 25%, 50%, 75%, and 100%). The crude reaction mixture was analyzed by GC to determine the yield of **3aa**. The ee of **3aa** was determined using a pure sample obtained by preparative TLC of the crude mixture. When the reaction was performed in pure THF, we observed the formation of a substantial amount of 2-methyl-1,3,5-triphenylpentane-1,5-dione (21% GC yield) as a result of Michael addition of propiophenone enolate to **2a**.[35]

^{1}H NMR analysis of zinc species.

Typical procedure for sample preparation: To a solution of **L6** (205 mg, 1.0 mmol) in Et_2O (5 mL) was added Et_2Zn (1 M in hexane, 1.0 mL, 1.0 mmol) at room temperature. After stirring for 1 min, *t*BuOH (95 μL, 1.0 mmol) was added, and the resulting solution was stirred for 1 h. The solution was then concentrated into dryness under vacuum. Inside a glove box, the resulting solid material was dissolved in benzene-d_6 and the solution was transferred to a J. Young NMR tube. ^{1}H NMR spectrum of the solution was recorded at room temperature.



As shown in Figures S8 and S9, the samples prepared using *t*BuOH or *i*PrOH displayed well-resolved quartet (~0.6 ppm) and triplet (~1.6 ppm) that could be assigned to an ethyl group on zinc. In accordance with this signal, we observed gas evolution when adding Et_2Zn to **L6** but did not do

so upon the following addition of the alcohol. The former spectrum was particularly clean and allowed assignment of other signals to the respective protons with reasonable integrations, while the latter spectrum was more complex and suggested the generation of multiple aggregate species. Note that the reaction using *i*PrOH was also conducted in DMSO, which gave a spectrum identical to the one shown in Figure S9. The sample prepared using MeOH gave a much more complicated spectrum with no sign of a Zn–Et bond (Figure S10), which implied that both the ethyl groups of Et_2Zn had been mostly lost by protonation and a mixture of zinc alkoxide aggregates had formed. In addition, ^{1}H NMR spectrum of the sample prepared by swapping **L6** and *t*BuOH in the above procedure (Figure S11) turned out to be close to the one shown in Figure S8, suggesting the formation of the same zinc species. Similar to the observation made in the standard sample preparation, we observed gas evolution when adding Et_2Zn to *t*BuOH but did not do so upon the following addition of **L6**.

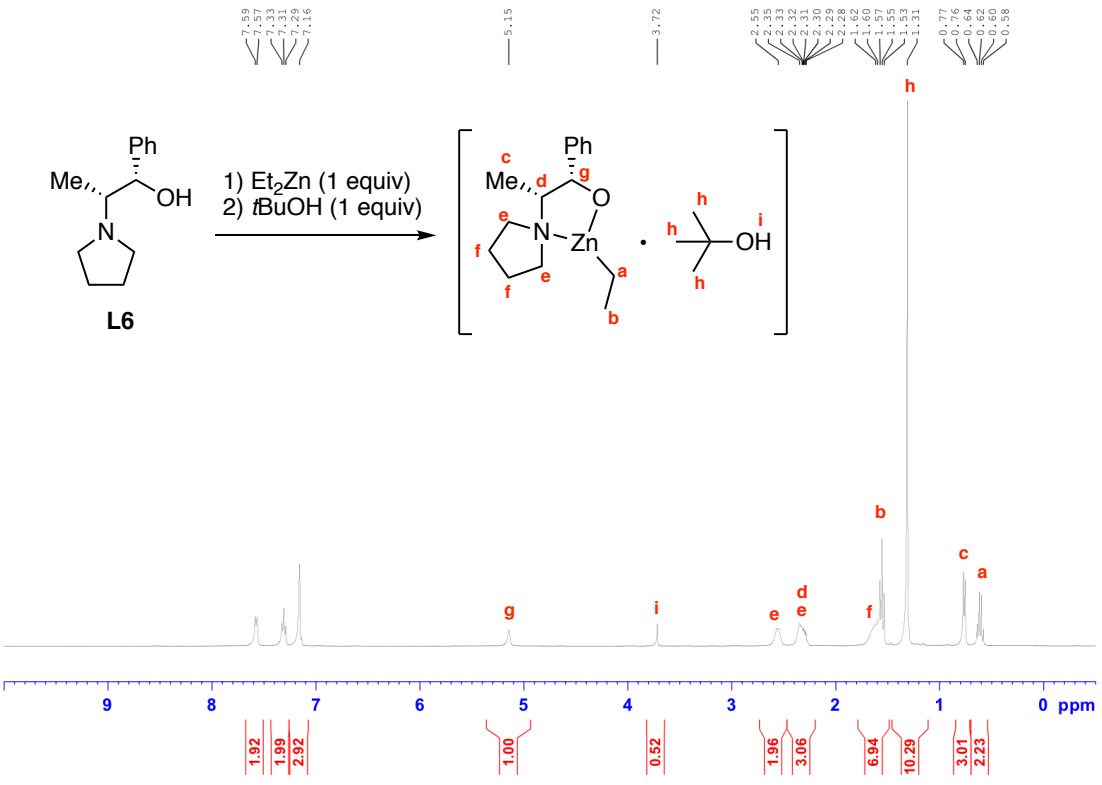


Figure S8. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of zinc species prepared from **L6**, Et_2Zn, and *t*BuOH.

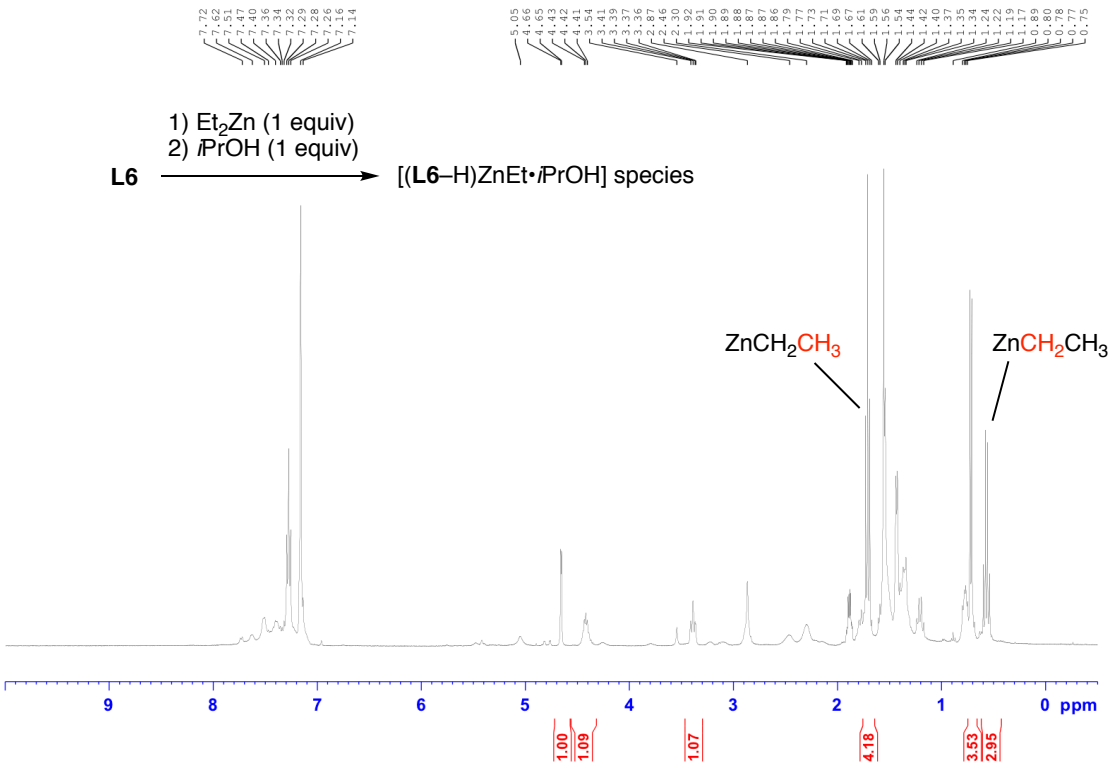


Figure S9. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of zinc species prepared from **L6**, Et_2Zn, and *i*PrOH.

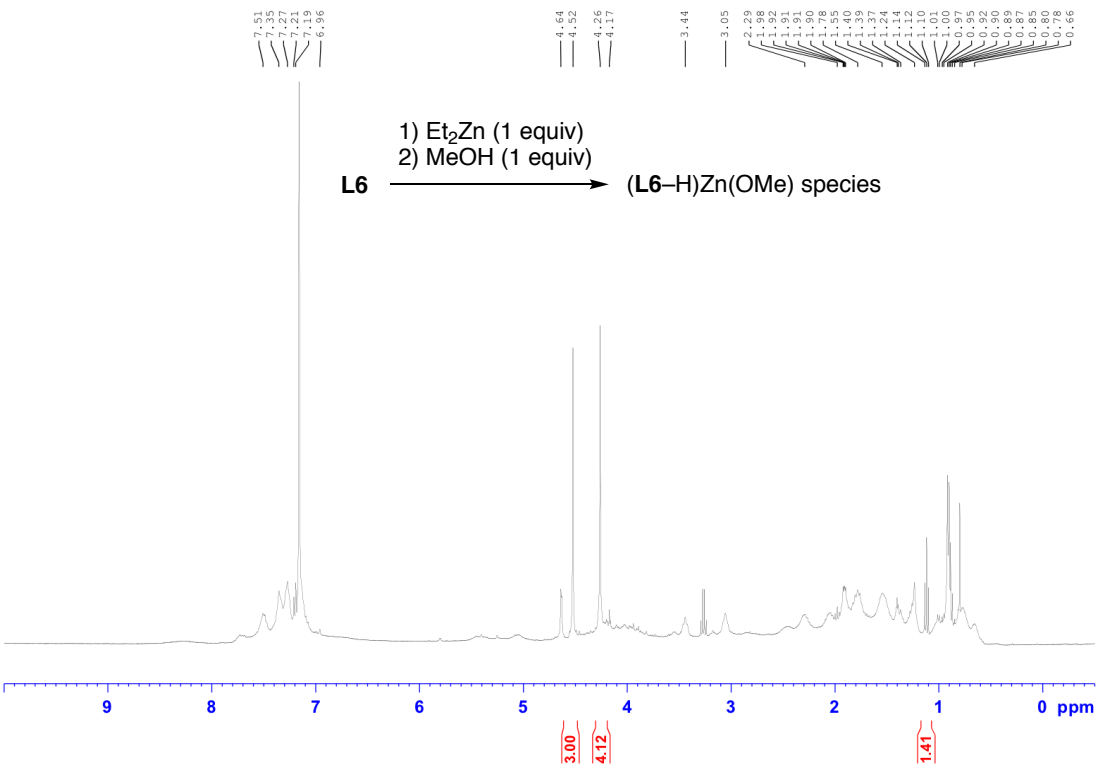


Figure S10. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of zinc species prepared from **L6**, Et_2Zn, and MeOH.

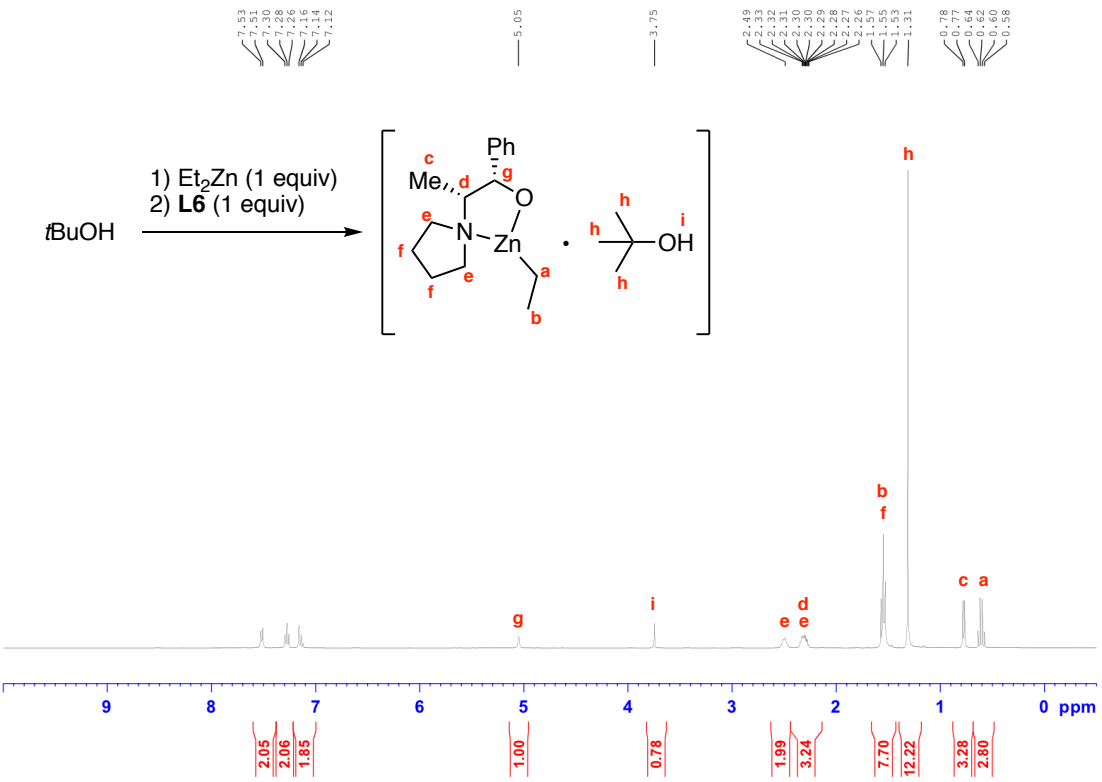


Figure S11. ^{1}H NMR spectrum (C_6D_6, 400 MHz) of zinc species prepared from *t*BuOH, Et_2Zn, and **L6** (the order of reagent addition: *t*BuOH, Et_2Zn, and then **L6**).

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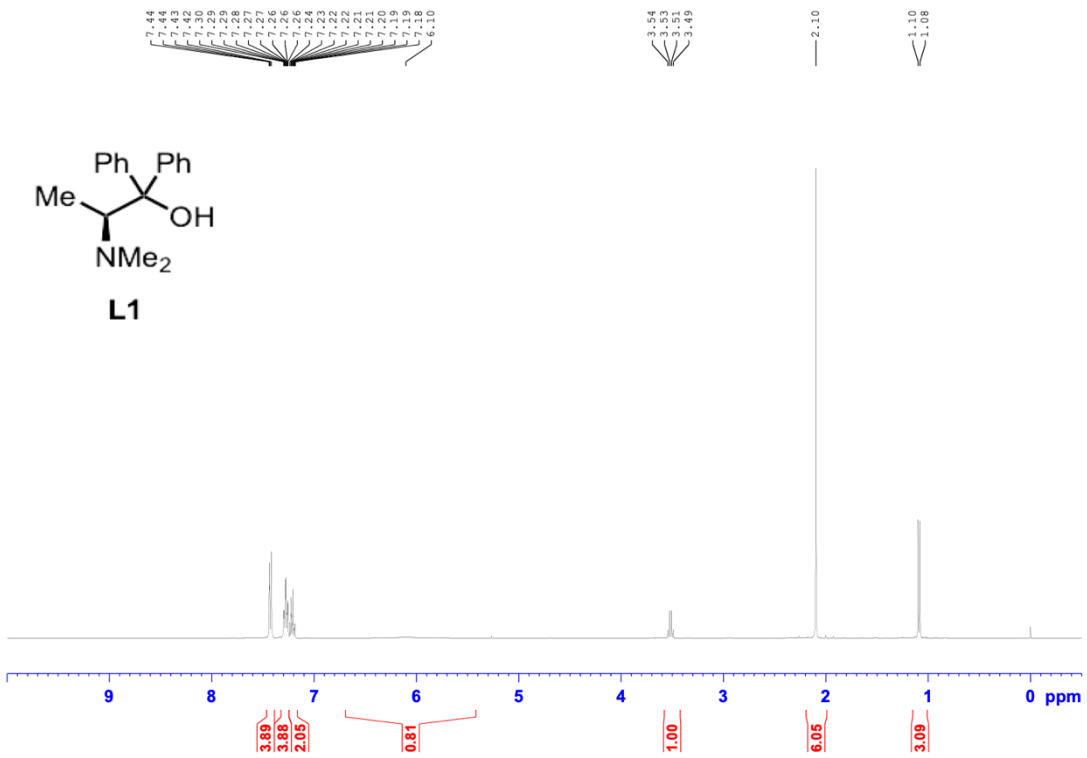
NMR Spectra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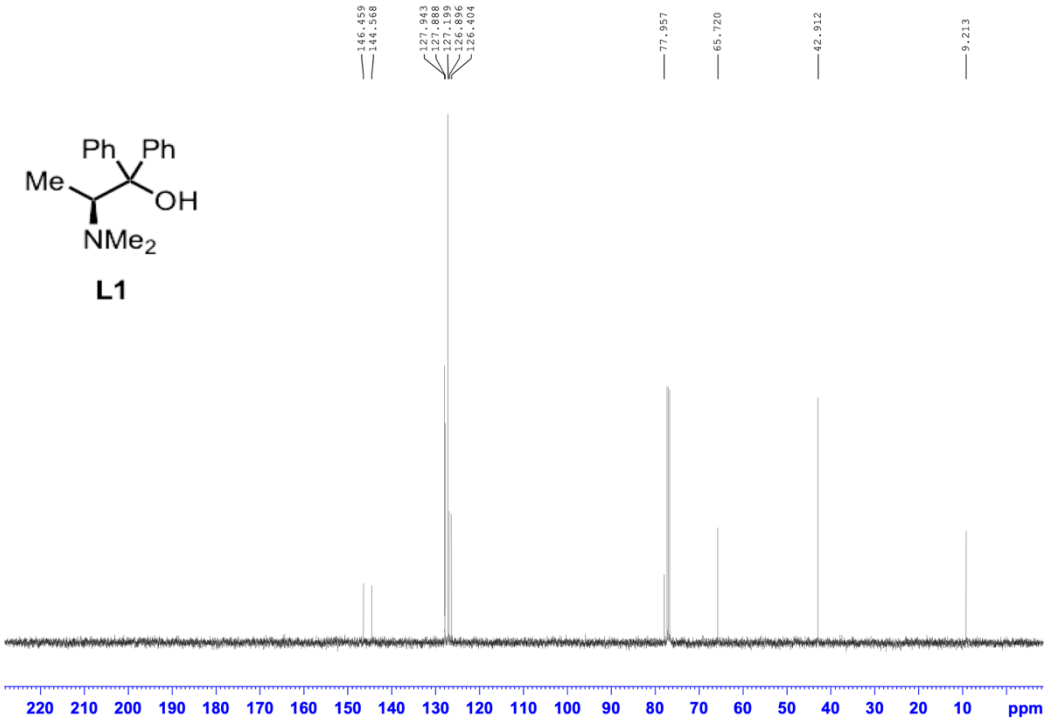
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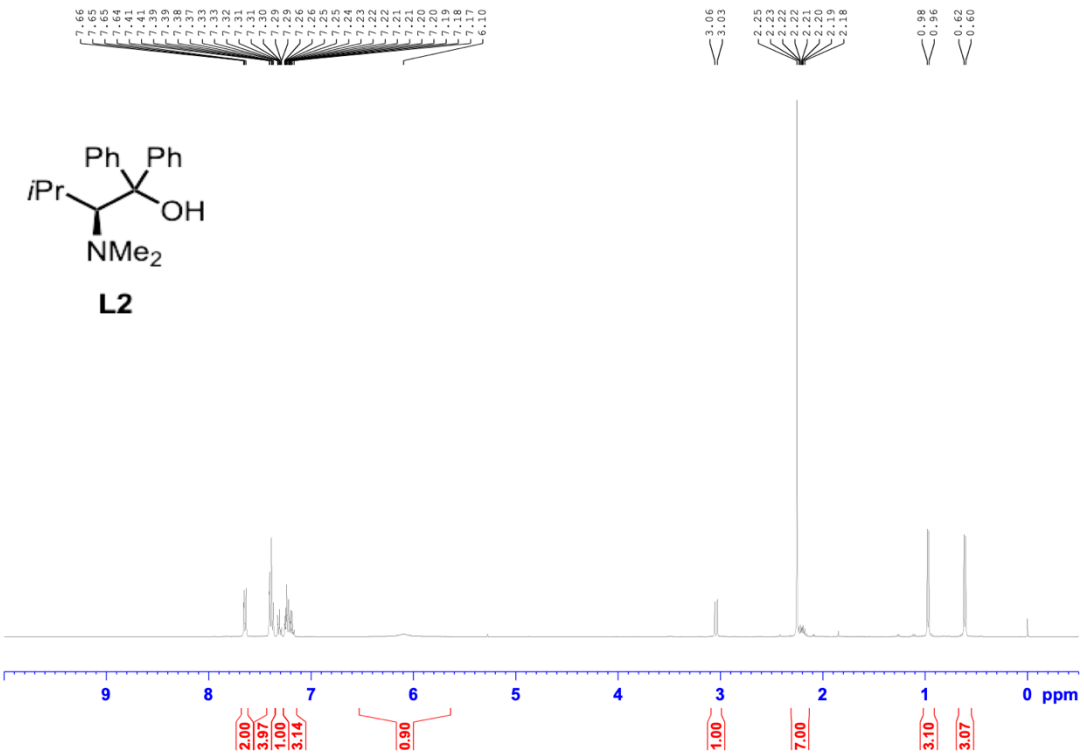
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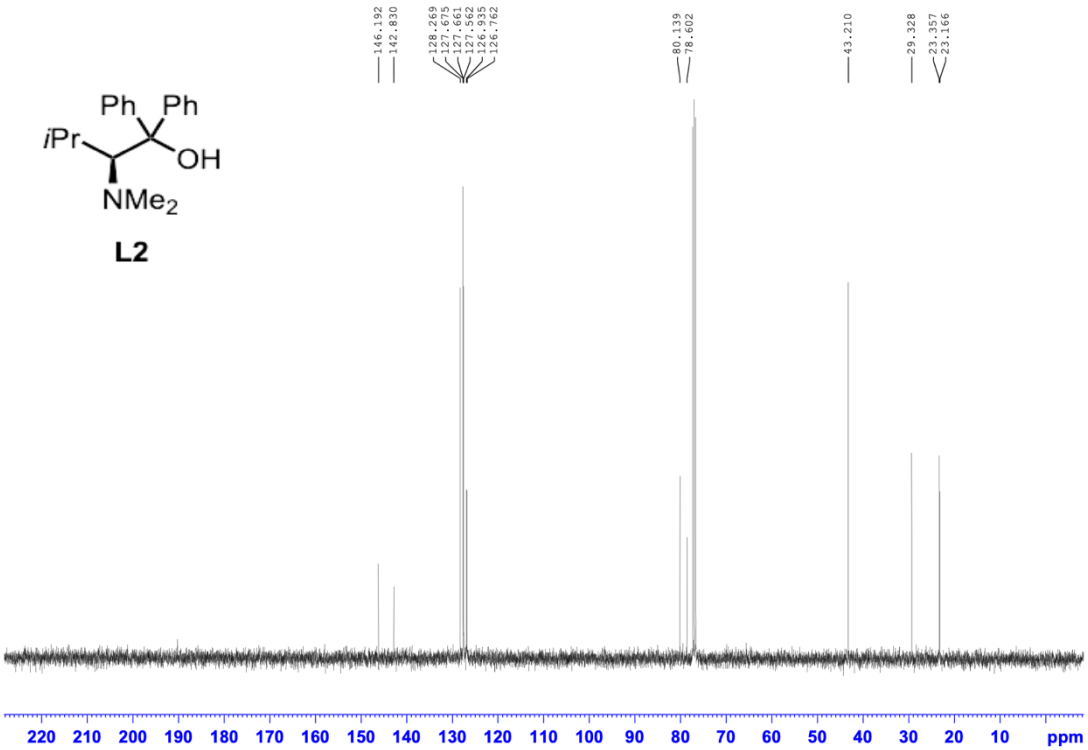
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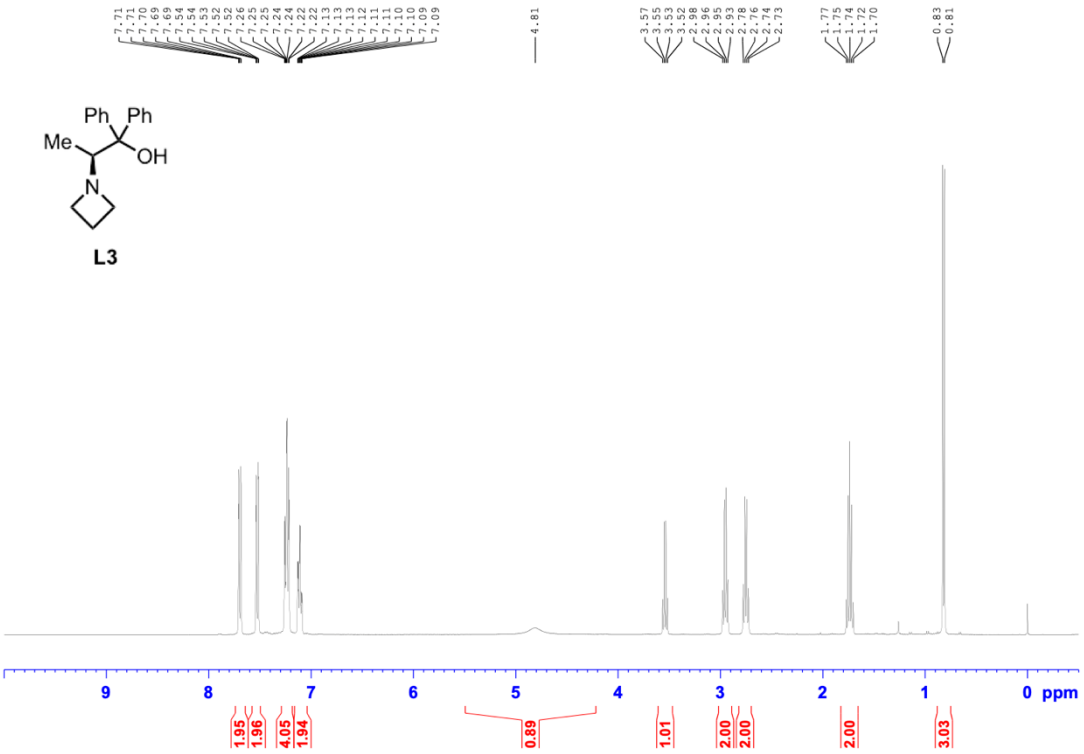
ppm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7.69
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7.53
7.52
7.52
7.26
7.25
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7.24
7.22
7.22
7.13
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.09
4.81
3.57
3.55
3.53
3.52
2.98
2.96
2.95
2.93
2.78
2.76
2.74
2.73
1.77
1.75
1.74
1.72
1.70
0.83
0.81
Ph
Ph
Me
OH
N
L3
9
8
7
6
5
4
3
2
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1.96
4.05
1.94
0.89
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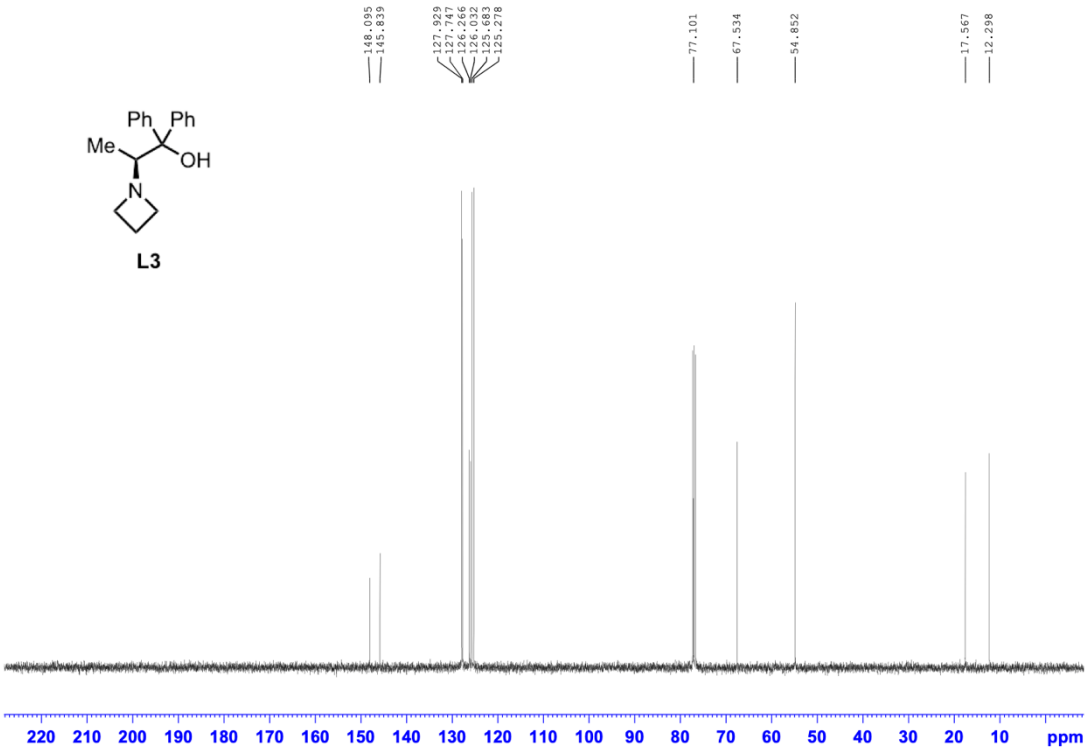
2.00
2.00
2.00
3.03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125.683
125.278
77.101
67.534
54.852
17.567
12.298
Ph
Ph
Me
OH
N
L3
220
210
200
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180
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150
140
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90
80
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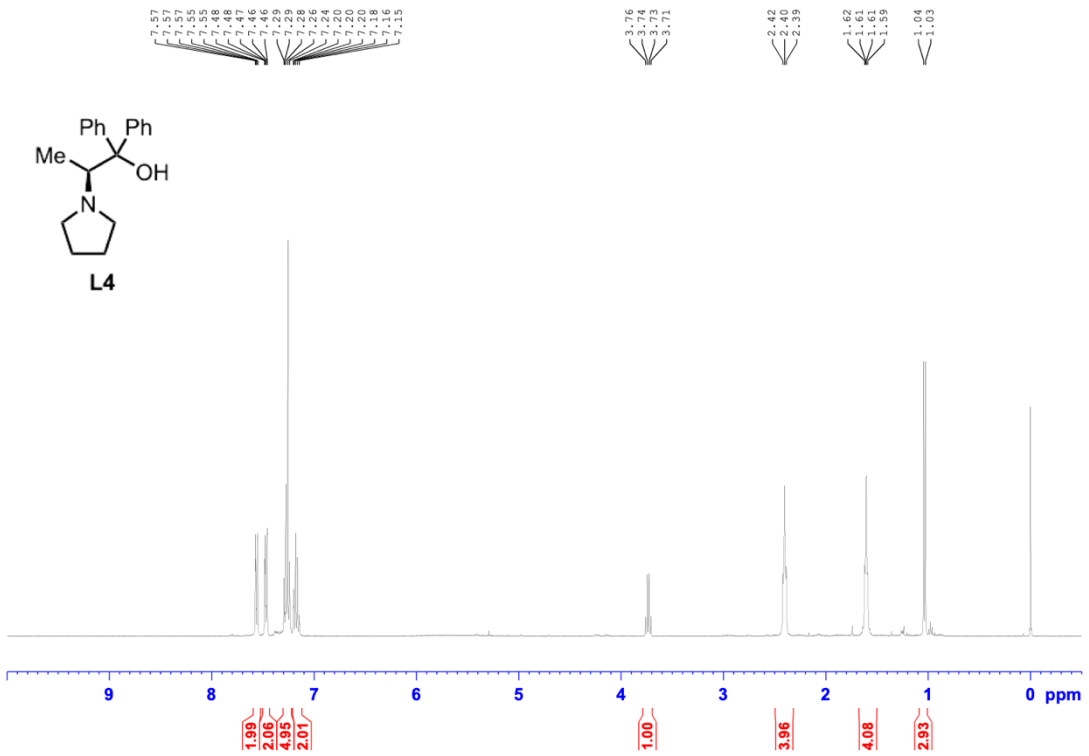
20
10
ppm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7.57
7.55
7.55
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7.48
7.47
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7.46
7.29
7.29
7.28
7.26
7.24
7.20
7.20
7.18
7.16
7.15
3.76
3.74
3.73
3.71
2.42
2.40
2.39
1.62
1.61
1.61
1.59
1.04
1.03
Ph
Ph
Me
OH
N
L4
9
8
7
6
5
4
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2
1
0 ppm
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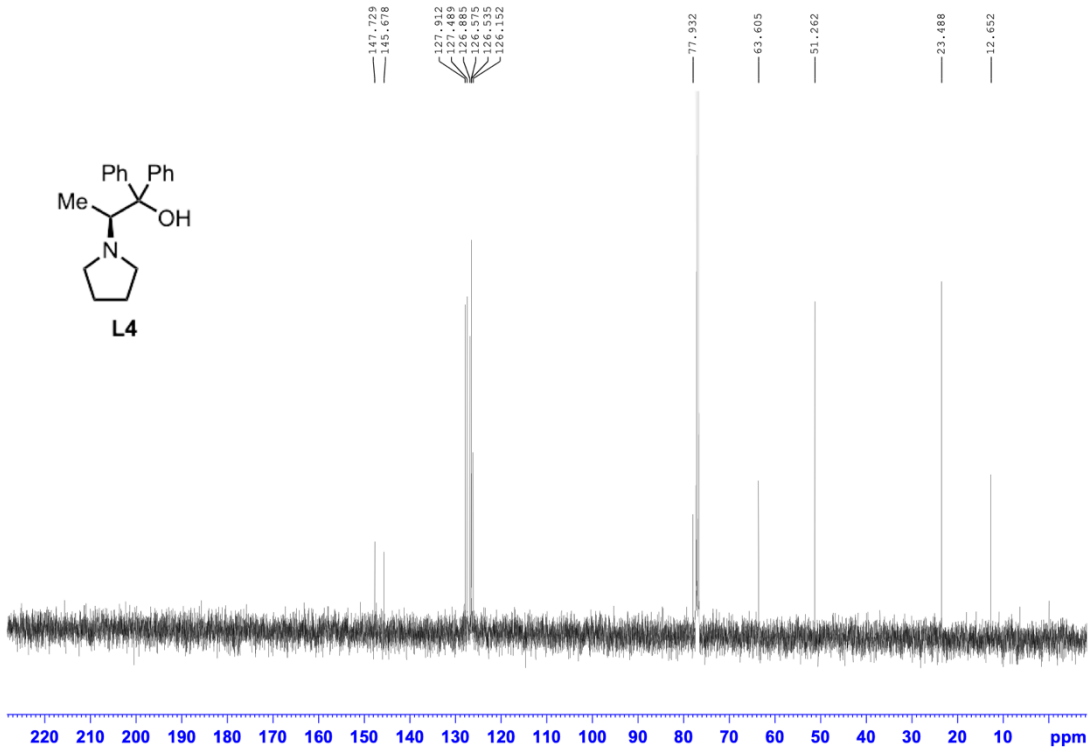
2.06
4.95
2.01
1.00
3.96
4.08
2.93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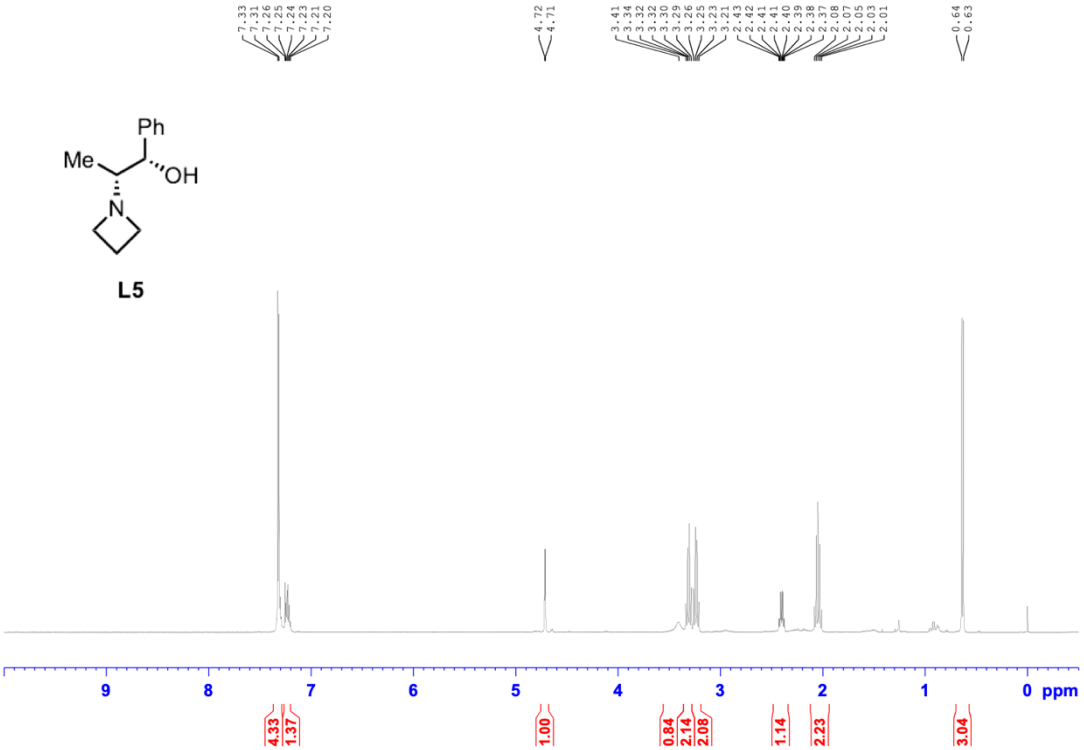
145.678
127.912
127.489
126.885
126.575
126.535
126.152
77.932
63.605
51.262
23.488
12.652
Ph
Ph
Me
OH
N
L4
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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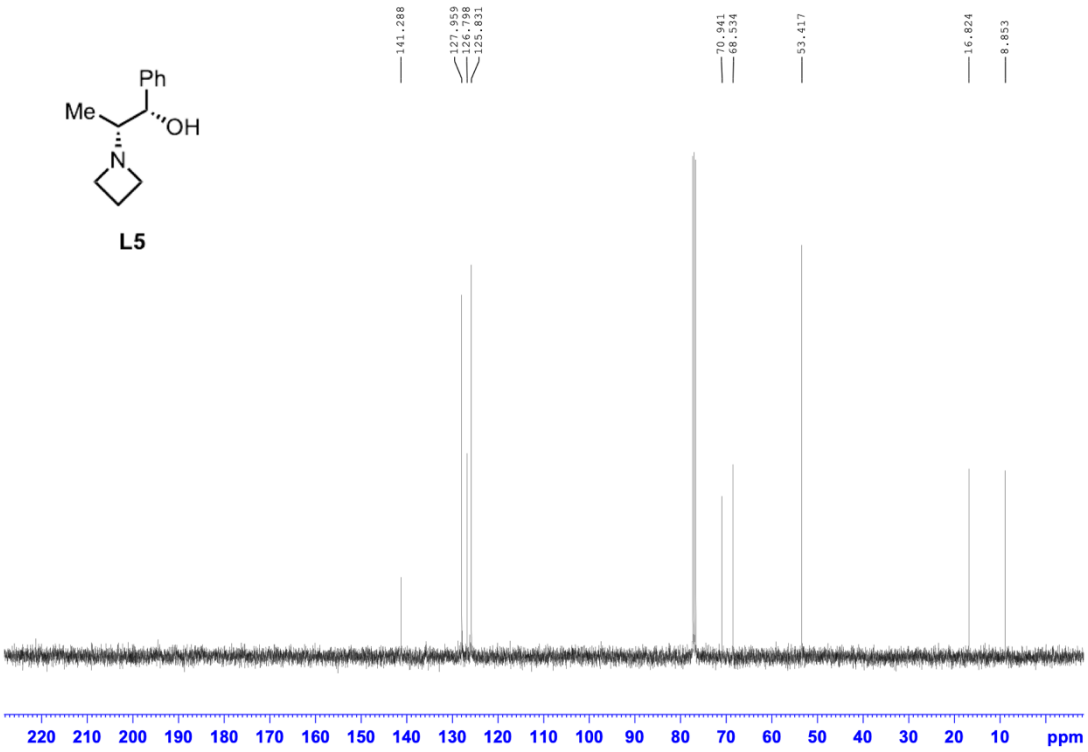
7.26
7.25
7.24
7.23
7.21
7.20
4.72
4.71
3.41
3.34
3.32
3.32
3.30
3.28
3.26
3.25
3.23
3.21
2.43
2.42
2.41
2.41
2.40
2.39
2.38
2.37
2.08
2.07
2.05
2.03
2.01
0.64
0.63
Ph
Me
OH
N
L5
9
8
7
6
5
4
3
2
1
0 ppm
4.33
1.37
1.00
0.84
2.14
2.08
1.14
2.23
3.04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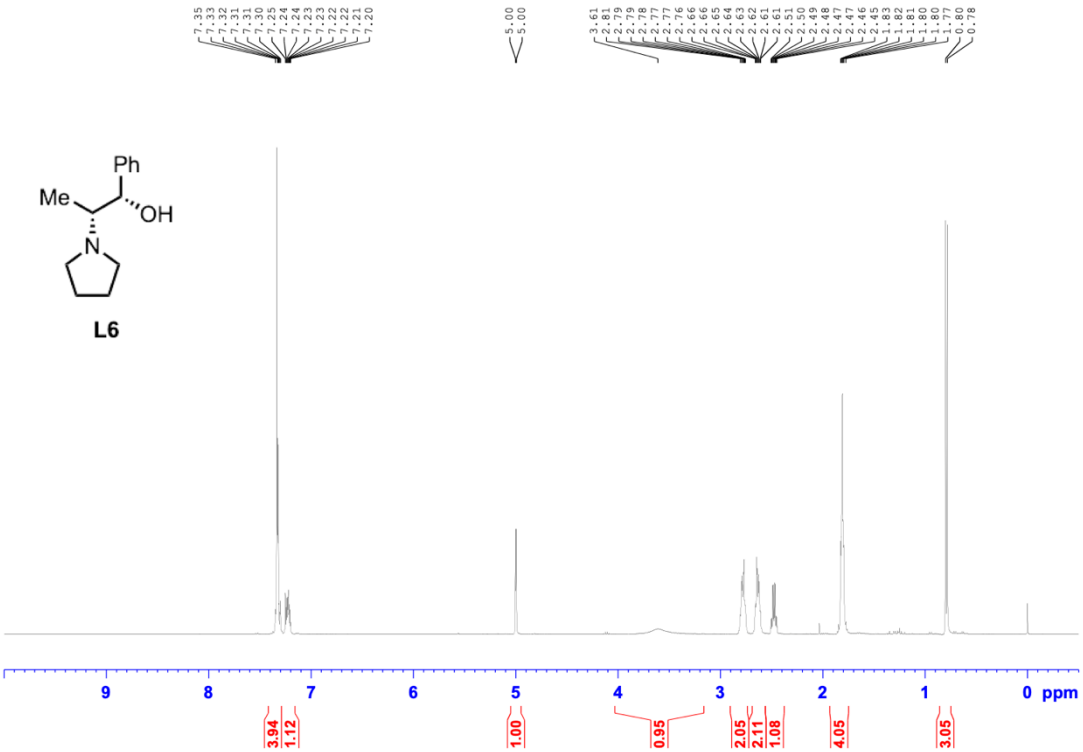
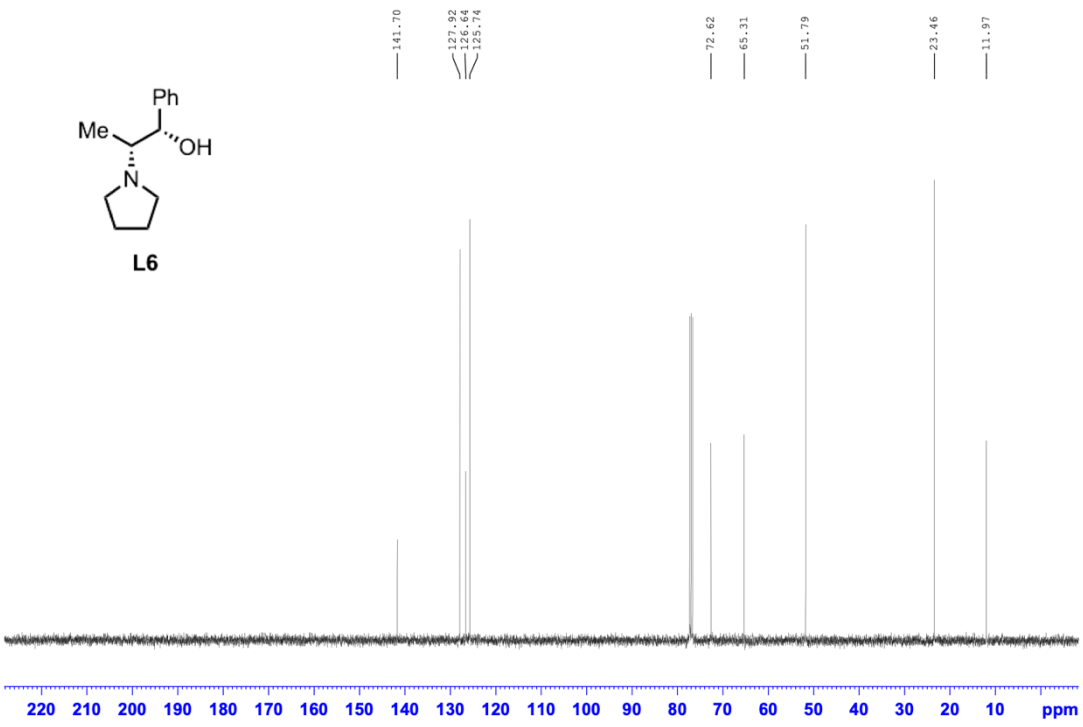
127.798
125.831
70.941
68.534
53.417
16.824
8.853
Ph
Me
OH
N
L5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
Me
OH
N
L6
9
8
7
6
5
4
3
2
1
0 ppm
3.94
1.12
1.00
0.95
2.05
2.11
1.08
4.05
3.05


Ph
Me
OH
N
L6
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127.92
126.64
125.74
72.62
65.31
51.79
23.46
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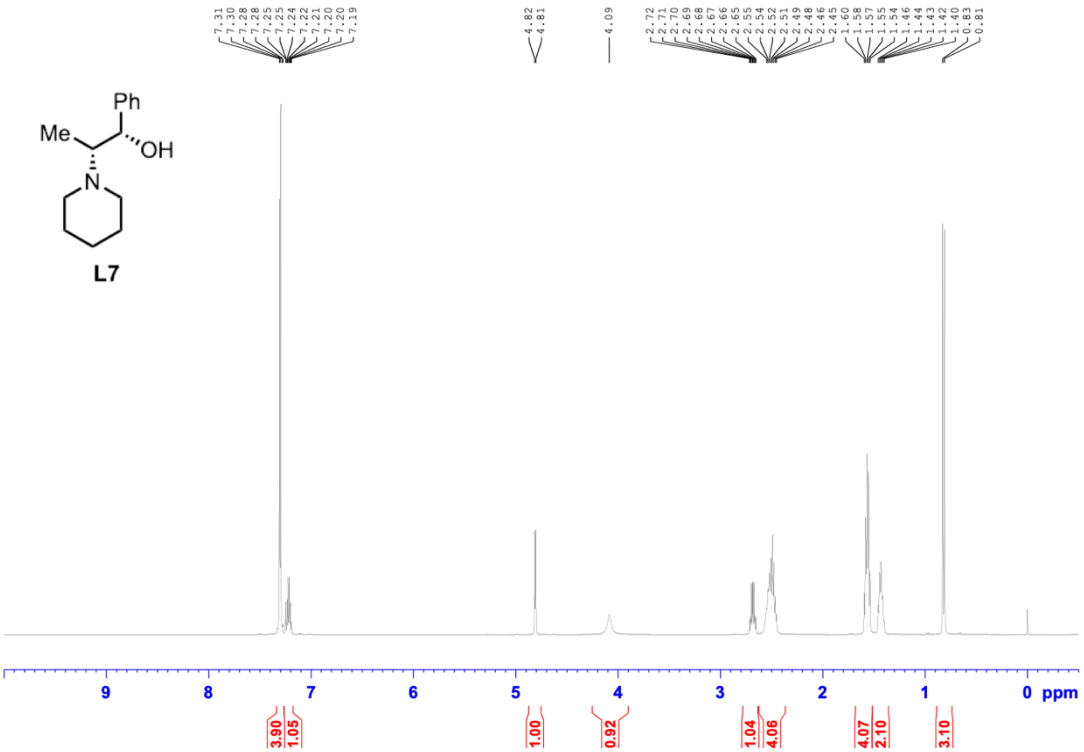
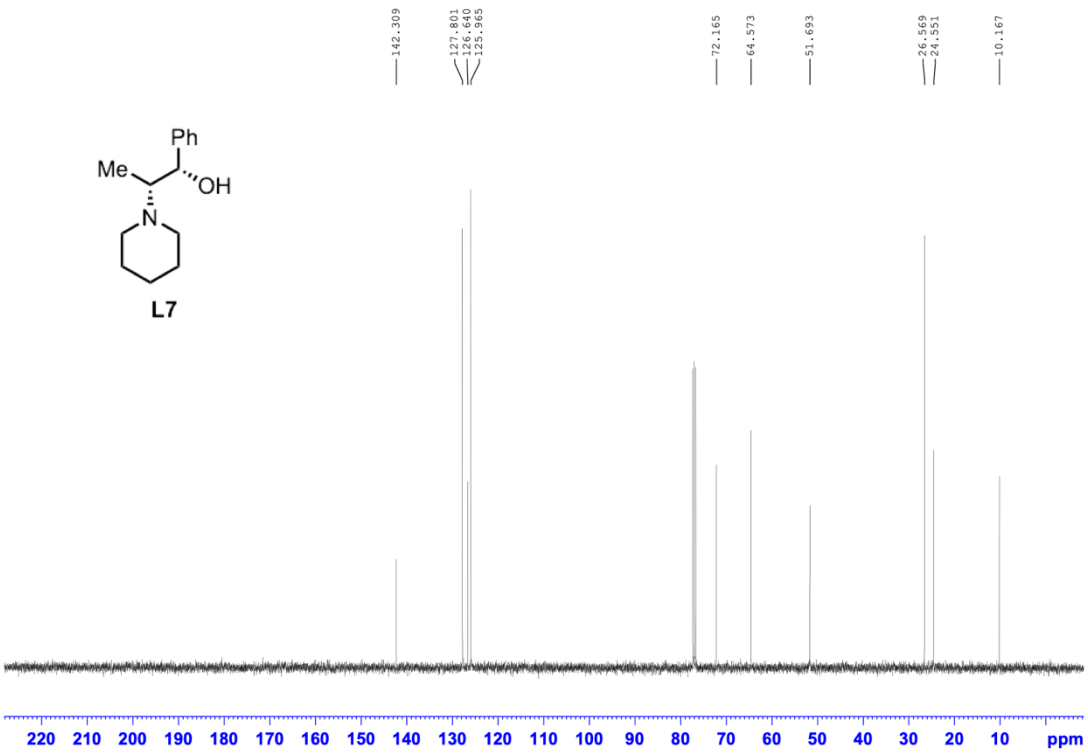
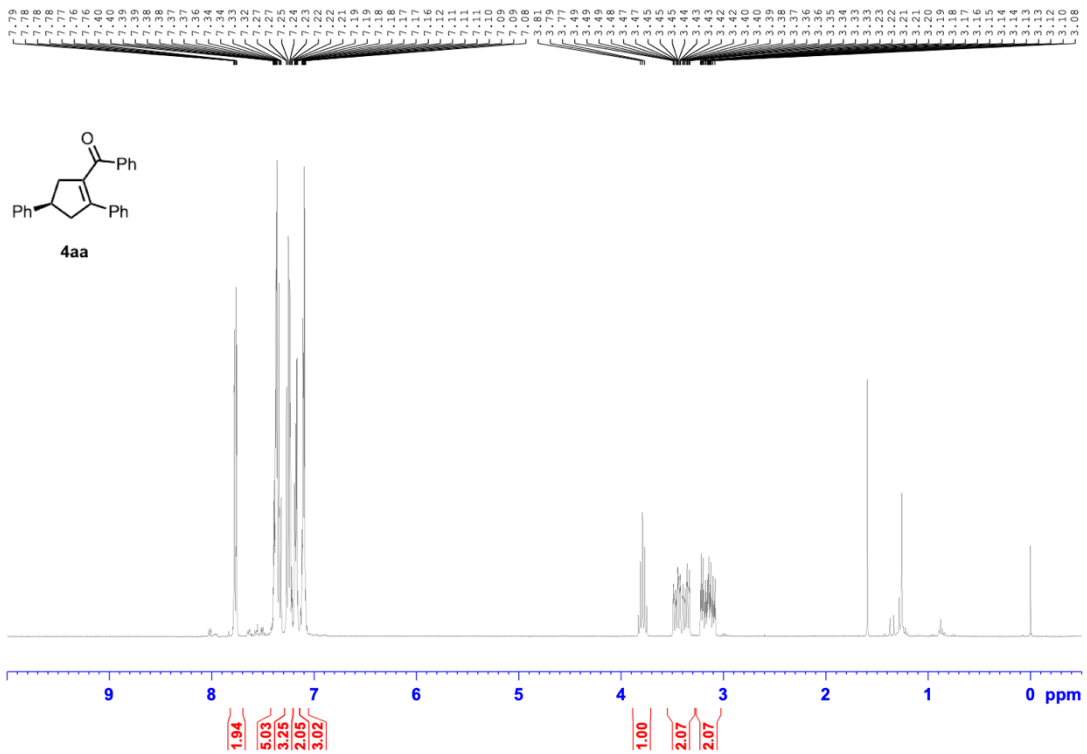
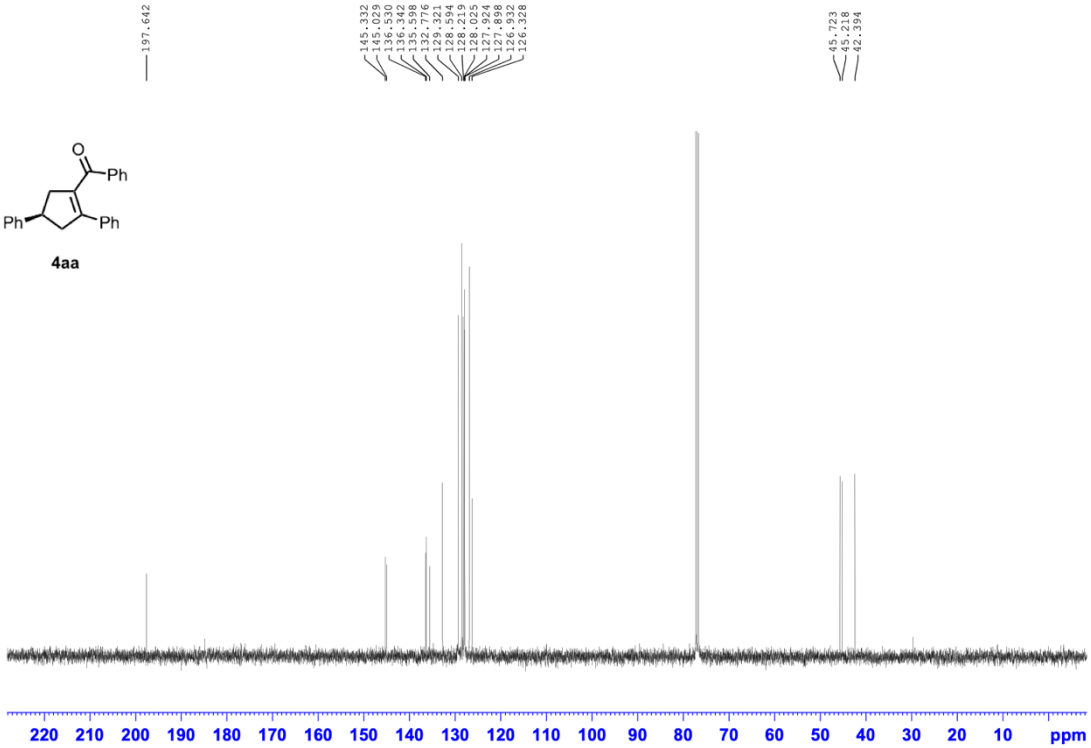
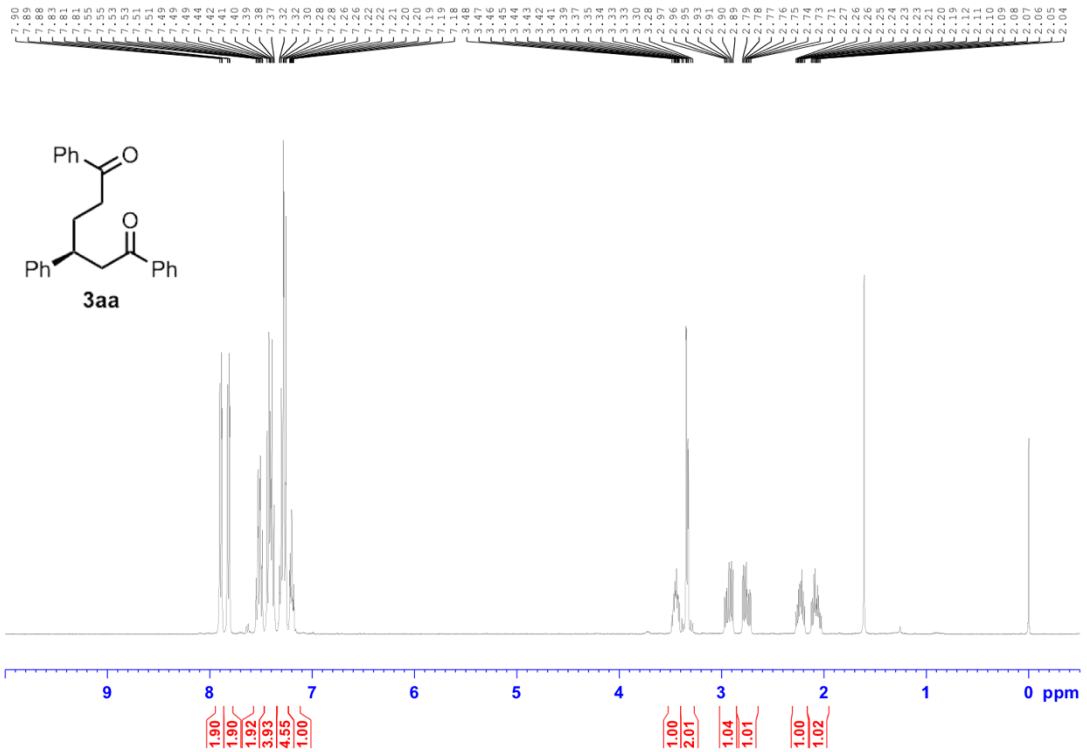
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

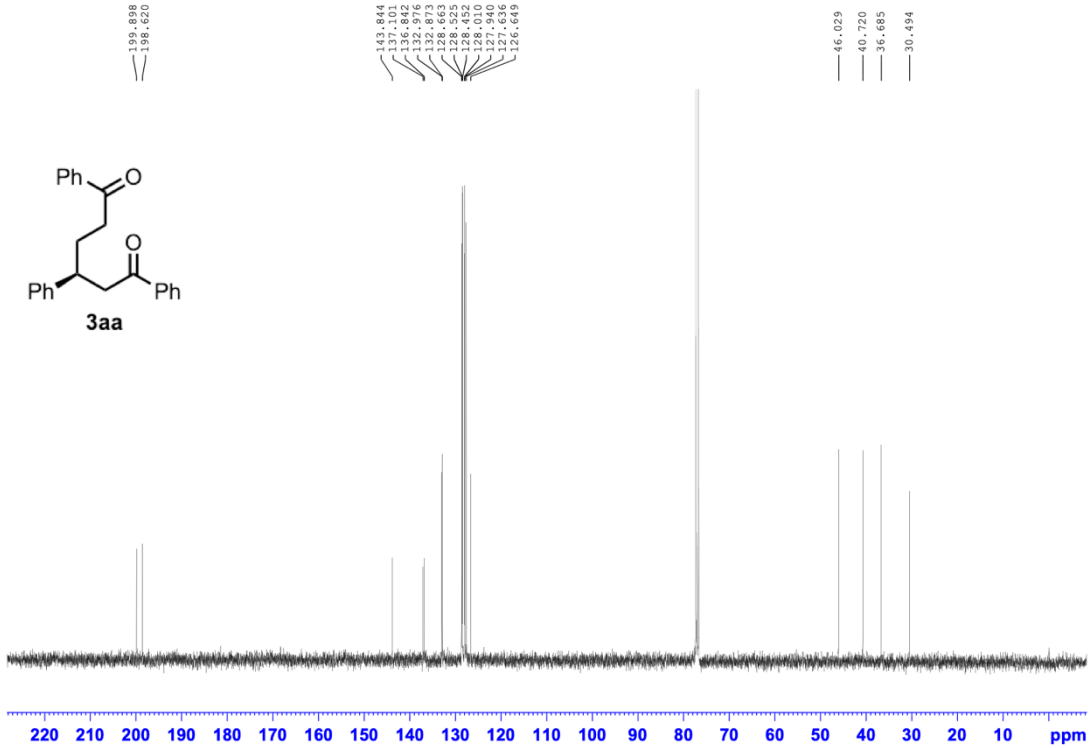

7.31
7.30
7.28
7.28
7.25
7.25
7.24
7.22
7.21
7.20
7.20
7.19
4.82
4.81
4.09
2.72
2.71
2.70
2.69
2.68
2.67
2.66
2.65
2.55
2.54
2.52
2.51
2.49
2.48
2.46
2.45
1.60
1.58
1.57
1.55
1.54
1.46
1.44
1.43
1.42
1.40
0.83
0.81
Ph
Me
OH
N
L7
9
8
7
6
5
4
3
2
1
0 ppm
3.90
1.05
1.00
0.92
1.04
4.06
4.07
2.10
3.10


142.309
127.801
126.440
125.965
72.165
64.573
51.693
26.569
24.551
10.167
Ph
Me
OH
N
L7
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4aa
9
8
7
6
5
4
3
2
1
0 ppm
1.94
5.03
3.25
2.05
3.02
1.00
2.07
2.07


4aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
O
O
Ph
Ph
3aa
9
8
7
6
5
4
3
2
1
0 ppm
1.90
1.90
1.92
3.93
4.55
1.00
1.00
2.01
1.04
1.01
1.00
1.02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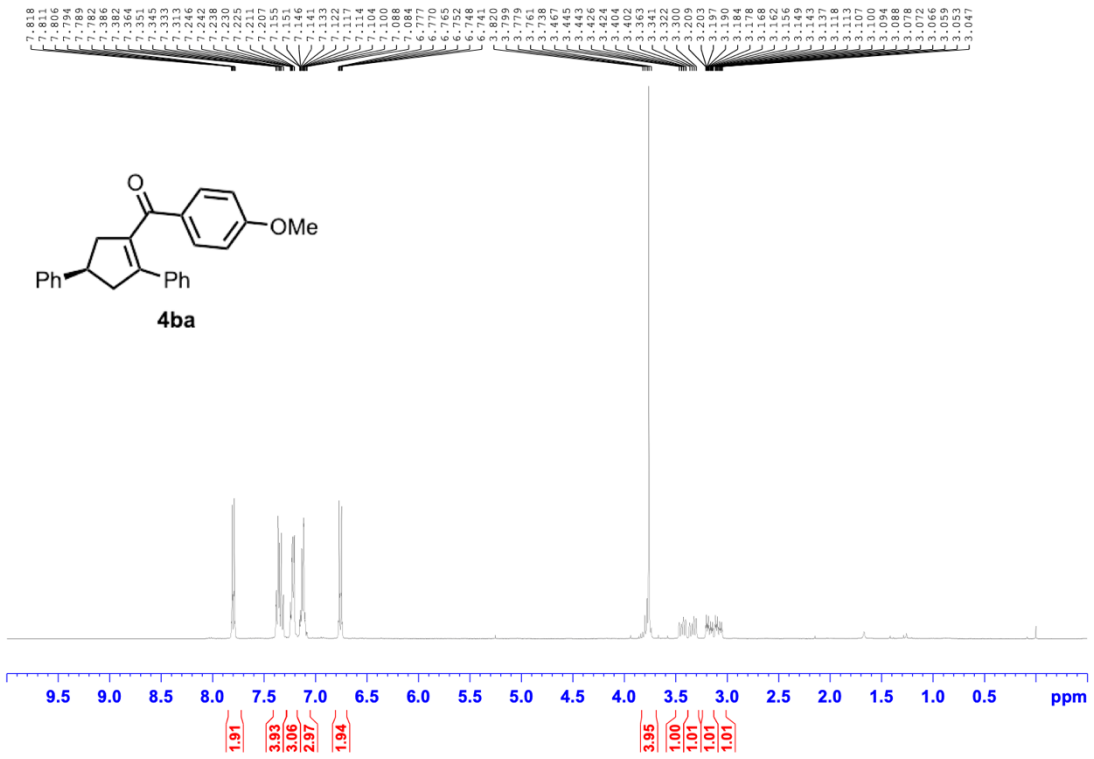
143.844
137.101
136.842
132.976
132.873
128.663
128.525
128.452
128.010
127.940
127.636
126.649
46.029
40.720
36.685
30.494
Ph
O
O
Ph
Ph
3aa
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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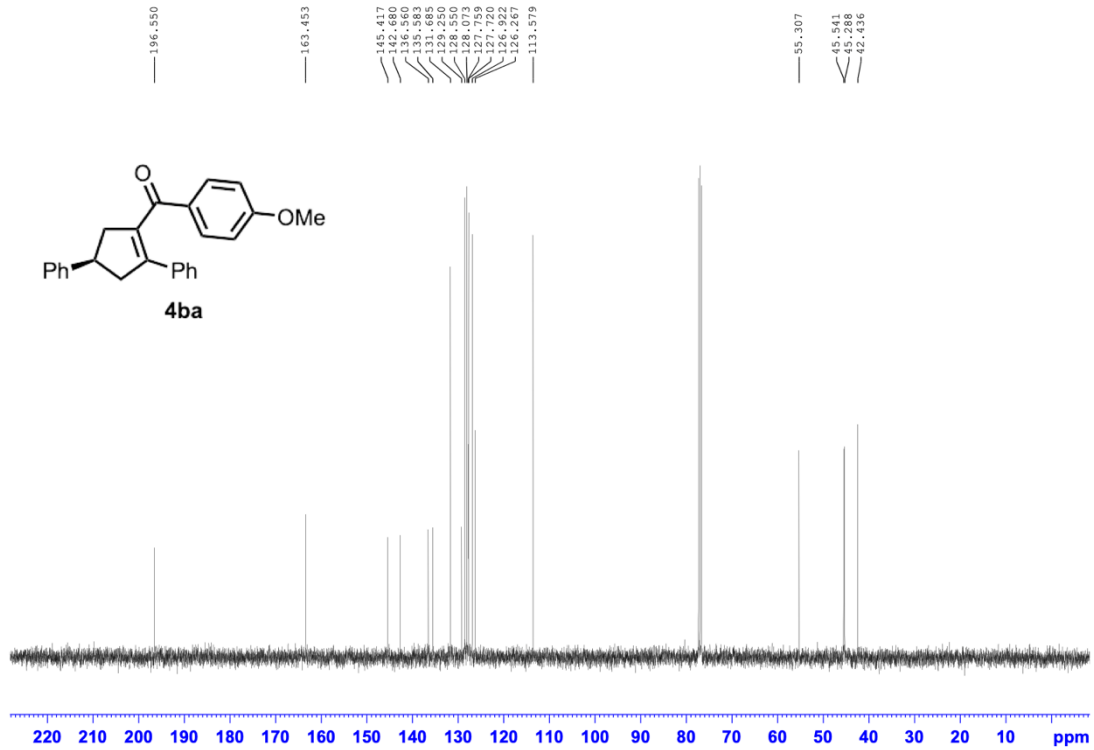
7.811
7.806
7.794
7.789
7.782
7.386
7.382
7.364
7.351
7.345
7.333
7.313
7.246
7.242
7.238
7.230
7.225
7.211
7.207
7.155
7.151
7.146
7.141
7.133
7.122
7.117
7.114
7.104
7.100
7.088
7.084
6.777
6.770
6.755
6.752
6.748
6.741
3.820
3.799
3.779
3.761
3.738
3.467
3.445
3.443
3.426
3.424
3.404
3.402
3.363
3.341
3.322
3.300
3.209
3.203
3.197
3.190
3.184
3.178
3.168
3.162
3.156
3.149
3.143
3.137
3.118
3.113
3.107
3.100
3.094
3.088
3.078
3.072
3.066
3.059
3.053
3.047
O
OMe
Ph
Ph
4ba
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91
3.93
3.06
2.97
1.94
3.95
1.00
1.01
1.01
1.01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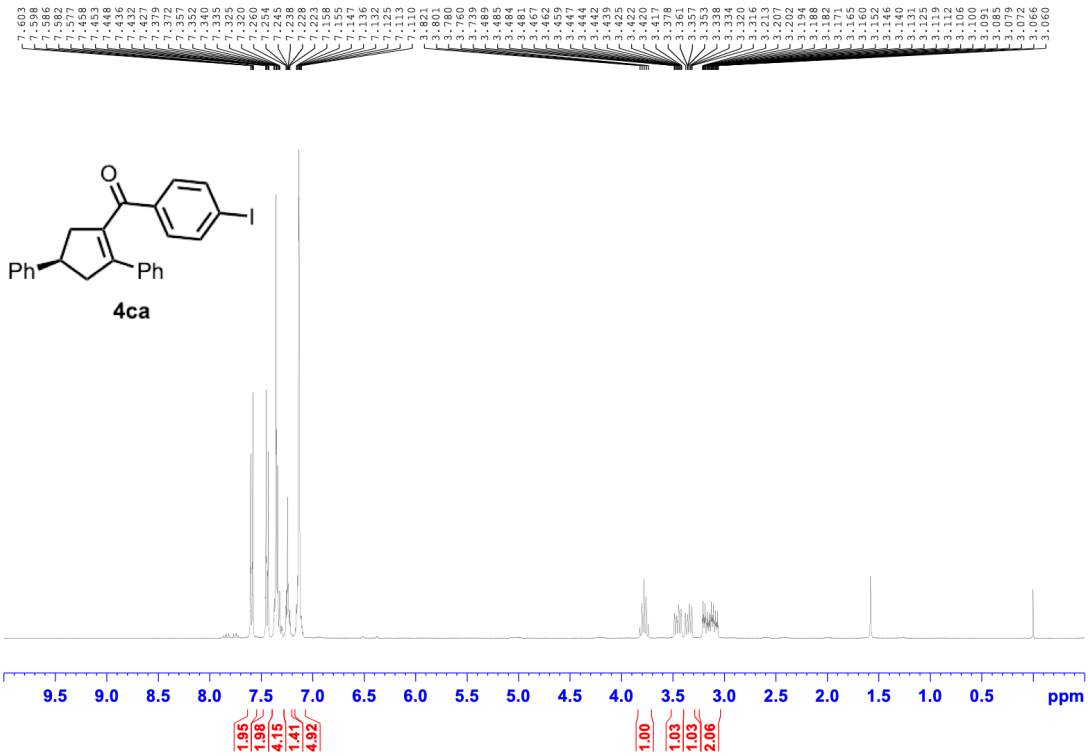
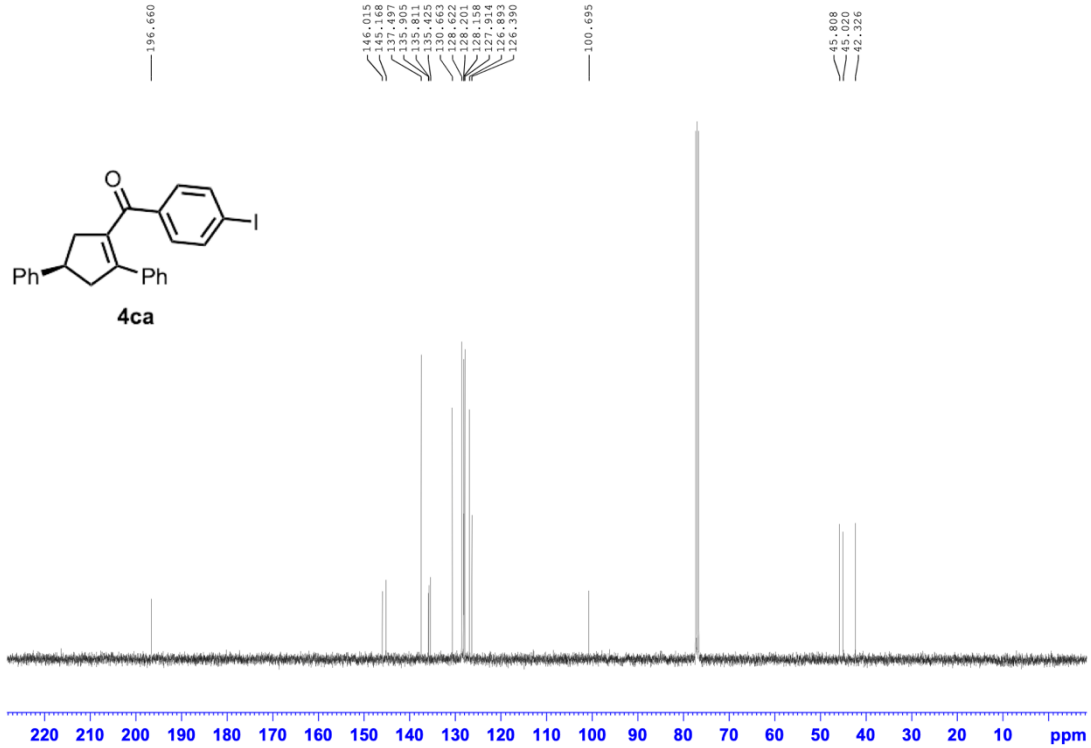
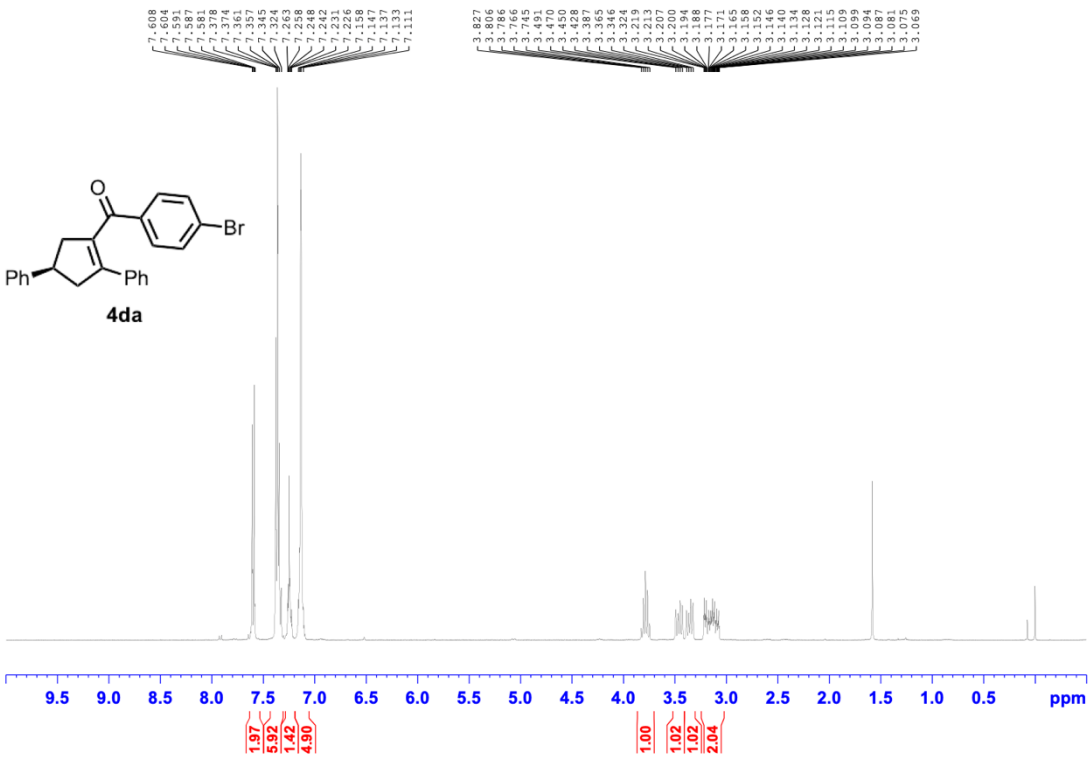
145.417
142.680
136.560
135.283
131.685
129.250
128.550
128.073
127.759
127.720
126.922
126.267
113.579
55.307
45.541
45.288
42.436
O
OMe
Ph
Ph
4ba
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


4ca
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.95 1.98 4.15 1.41 4.92
1.00 1.03 1.03 2.06


4ca
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.587
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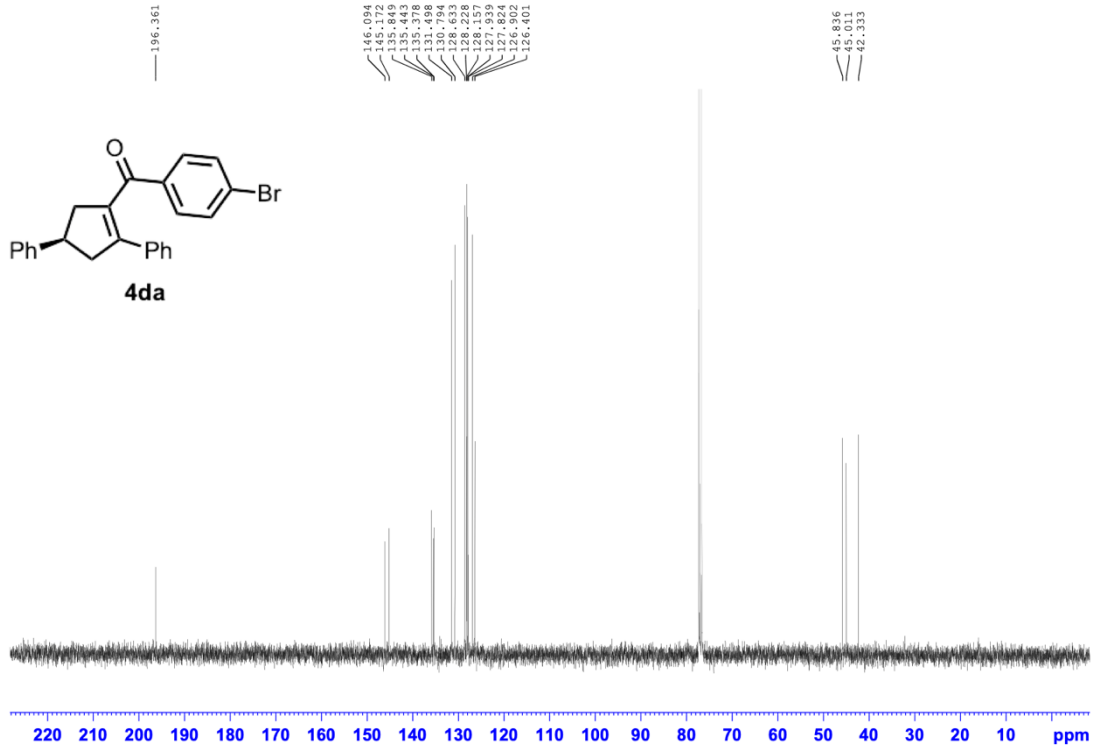
7.374
7.361
7.357
7.345
7.324
7.263
7.258
7.248
7.242
7.231
7.226
7.158
7.147
7.137
7.133
7.111
3.827
3.806
3.786
3.766
3.745
3.491
3.470
3.450
3.428
3.387
3.365
3.346
3.324
3.219
3.213
3.207
3.200
3.194
3.188
3.177
3.171
3.165
3.158
3.152
3.146
3.140
3.134
3.128
3.121
3.115
3.109
3.099
3.094
3.087
3.081
3.075
3.069
O
Br
Ph
Ph
4da
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.97
5.92
1.42
4.90
1.00
1.02
1.02
2.04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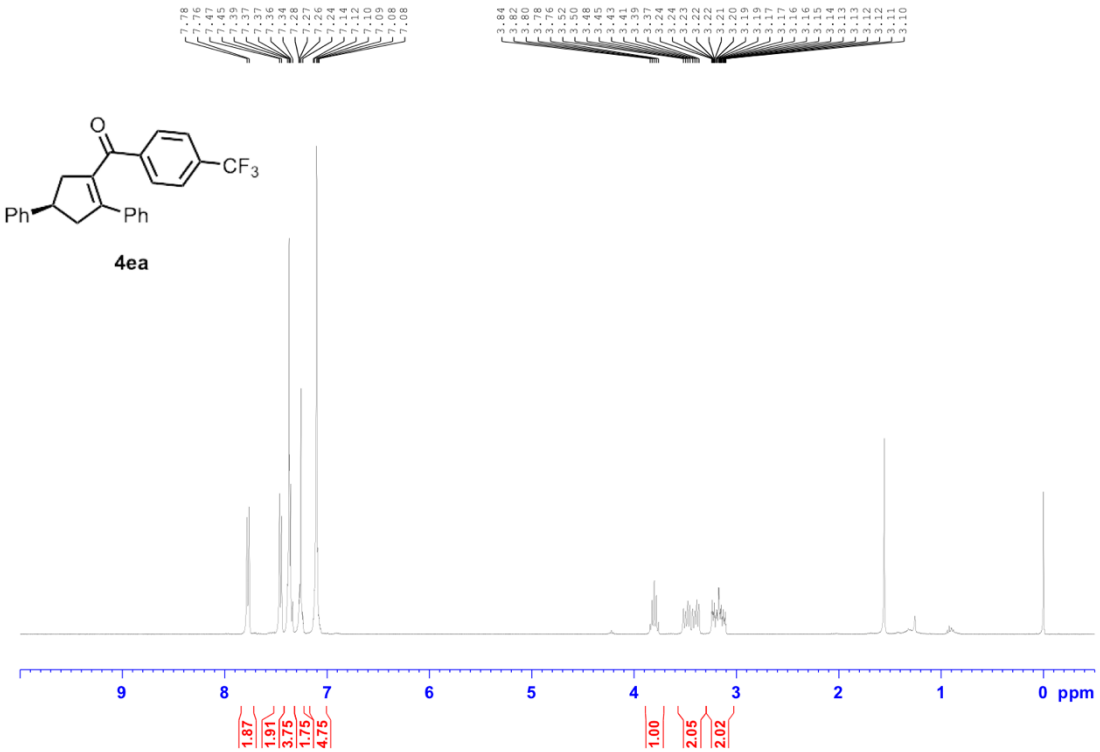
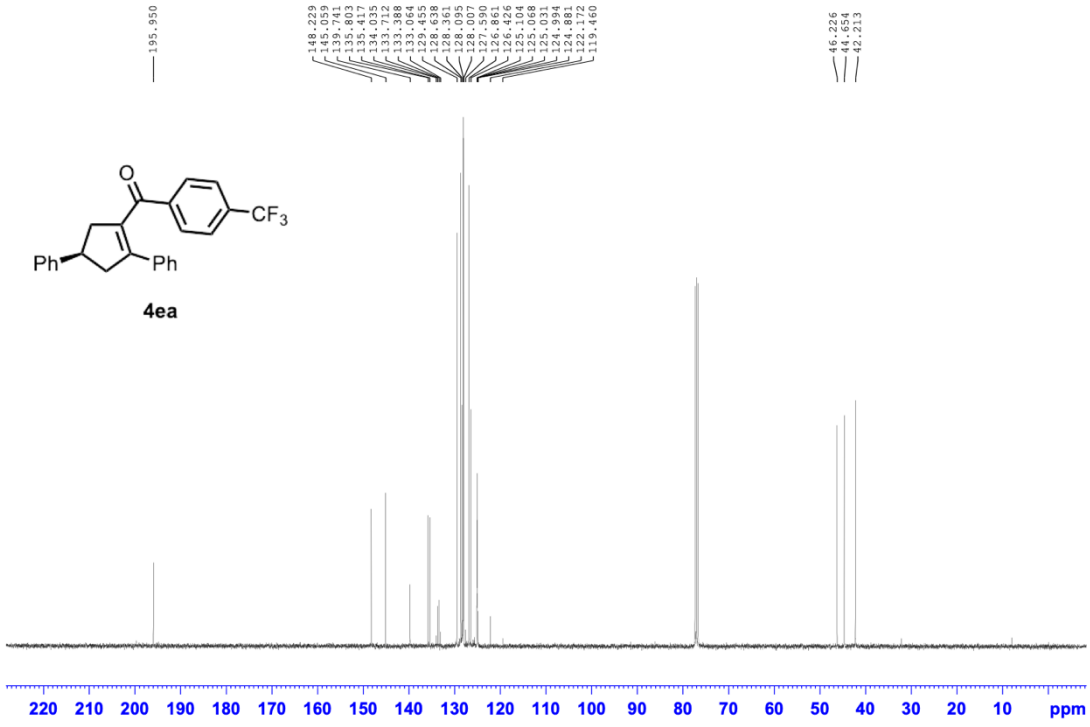
145.172
135.849
135.443
135.178
131.498
130.794
128.633
128.228
128.157
127.939
127.824
126.602
126.401
45.836
45.011
42.333
O
Br
Ph
Ph
4da
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


7.78
7.76
7.47
7.45
7.39
7.37
7.37
7.36
7.34
7.28
7.27
7.26
7.24
7.14
7.12
7.10
7.09
7.08
7.08
3.84
3.82
3.80
3.78
3.76
3.52
3.50
3.48
3.45
3.43
3.41
3.39
3.37
3.24
3.24
3.23
3.22
3.21
3.20
3.19
3.17
3.17
3.16
3.15
3.14
3.13
3.13
3.12
3.11
3.10
O
CF3
Ph
Ph
4ea
9
8
7
6
5
4
3
2
1
0 ppm
1.87
1.91
3.75
1.75
4.75
1.00
2.05
2.02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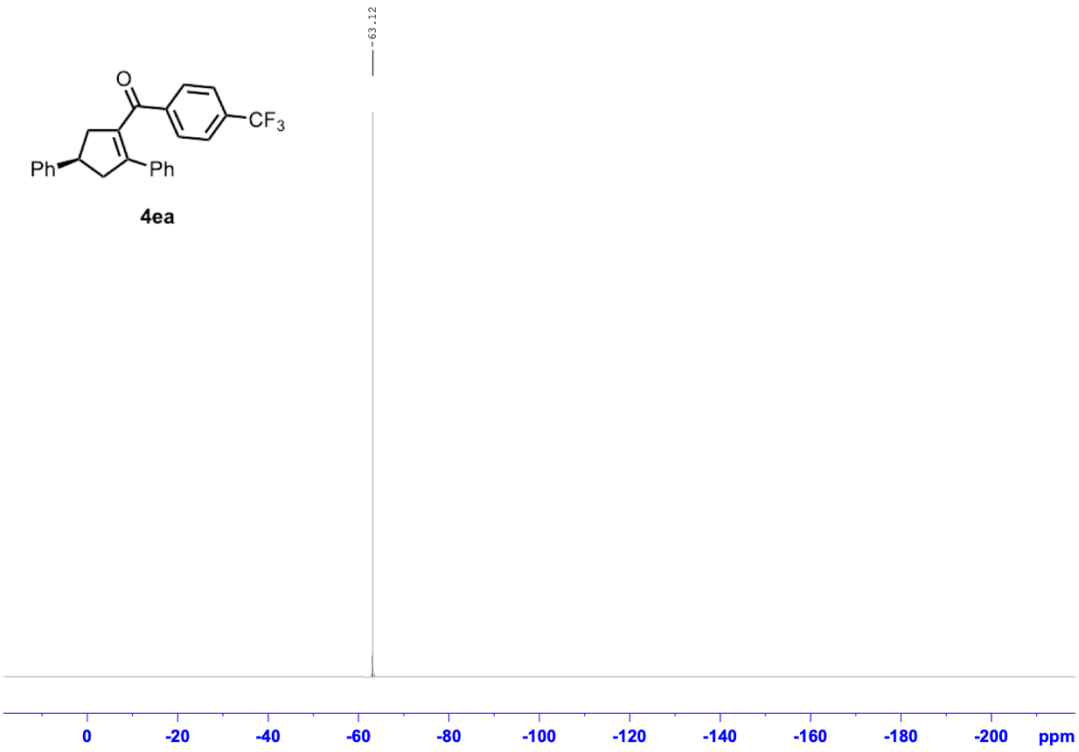
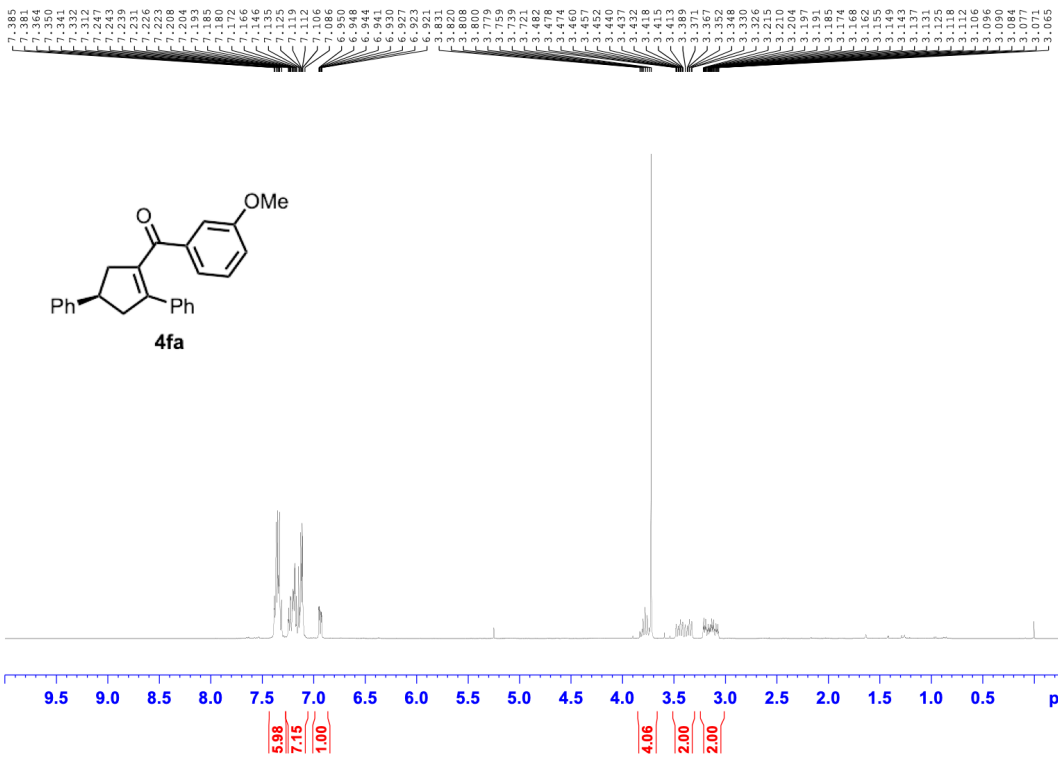
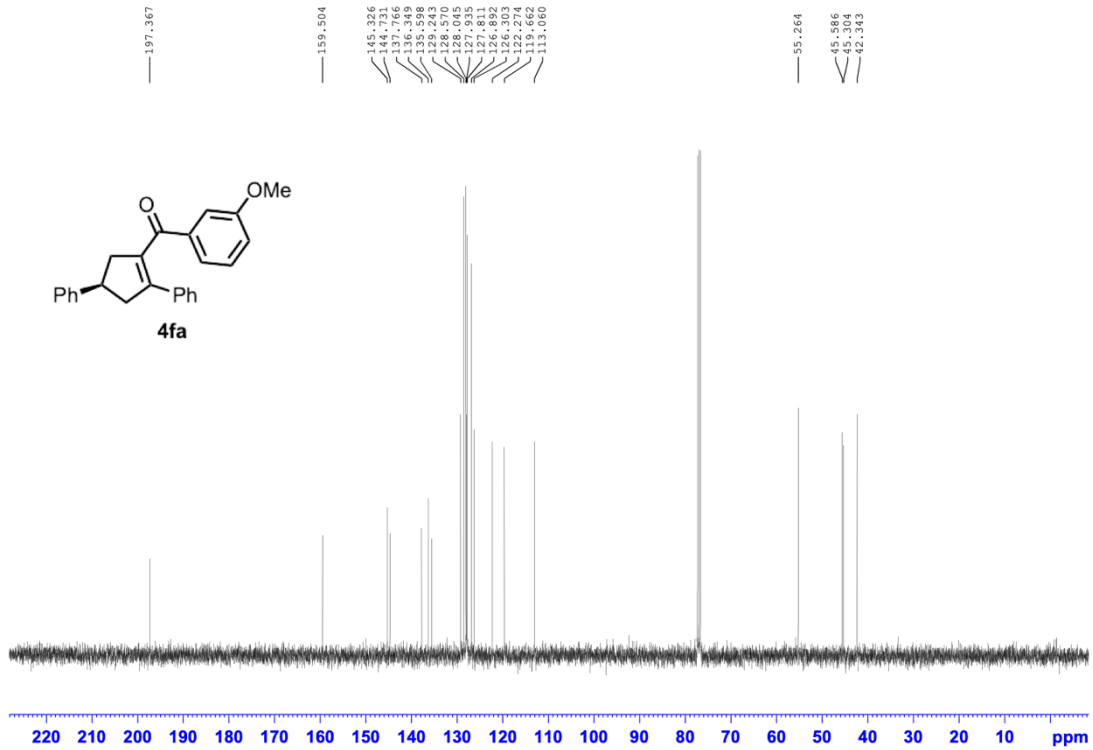
148.229
145.059
139.741
135.803
135.437
134.035
133.712
133.388
133.064
129.455
128.638
128.361
128.055
128.007
127.590
126.861
126.426
125.104
125.068
125.031
124.994
124.881
122.172
119.460
46.226
44.654
42.213
O
CF3
Ph
Ph
4ea
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



4ea


OMe
O
Ph
Ph
4fa
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.98
7.15
1.00
4.06
2.00
2.00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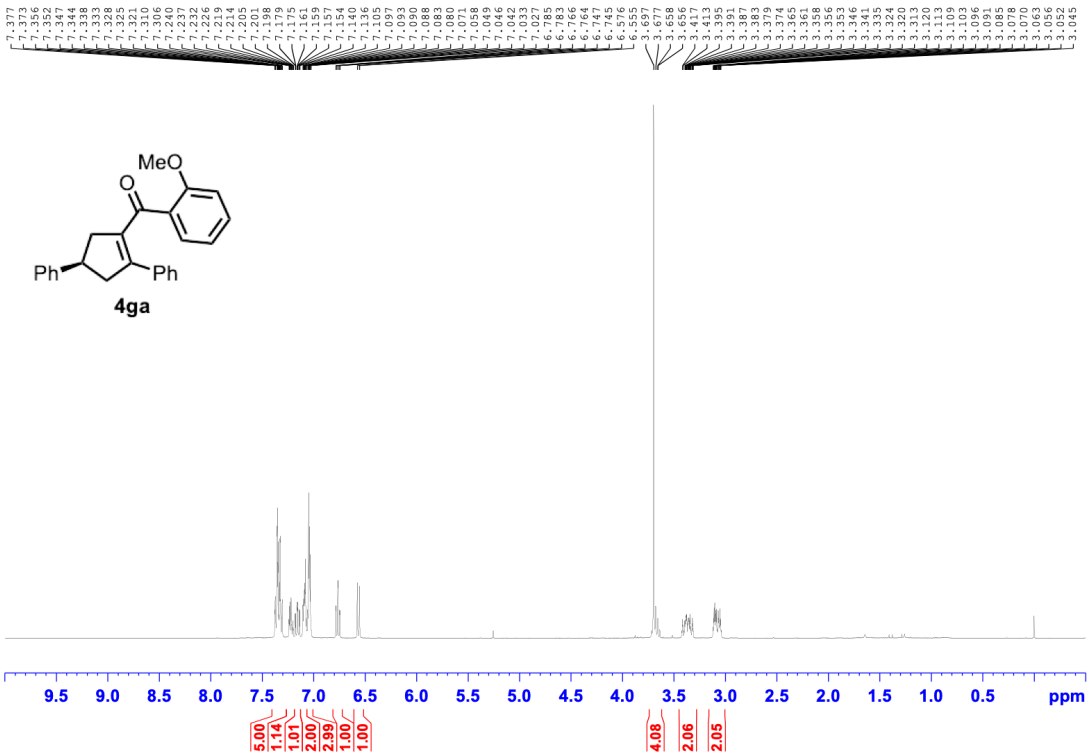
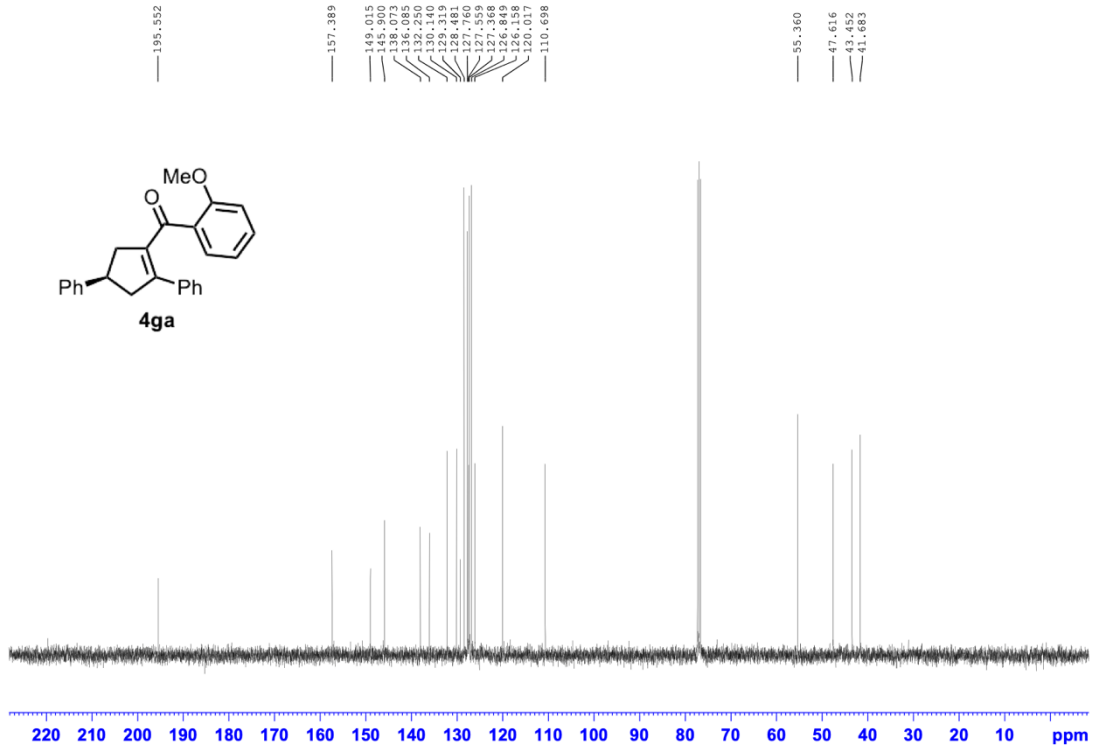
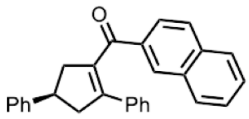
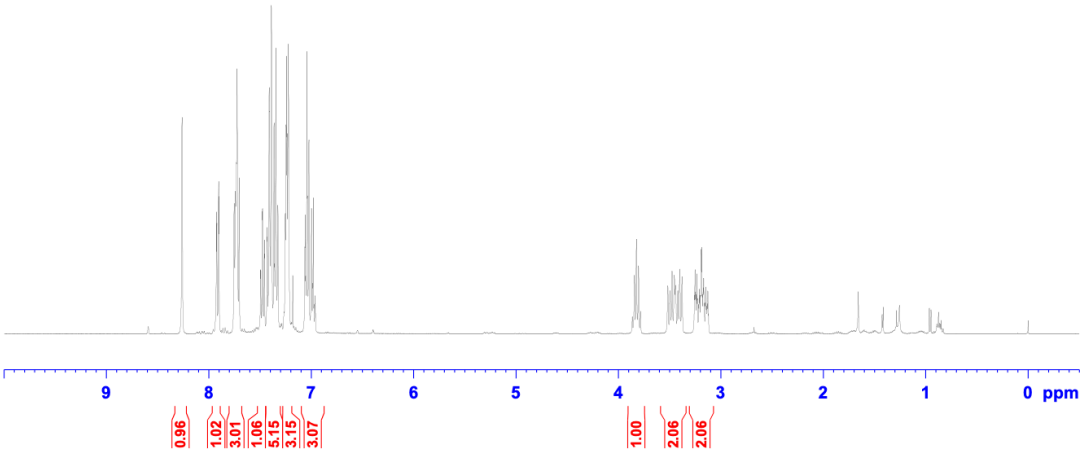
145.326
144.731
137.766
136.349
135.598
129.243
128.570
128.465
127.935
127.811
126.892
126.303
122.274
119.662
113.060
55.264
45.586
45.304
42.343
OMe
O
Ph
Ph
4fa
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

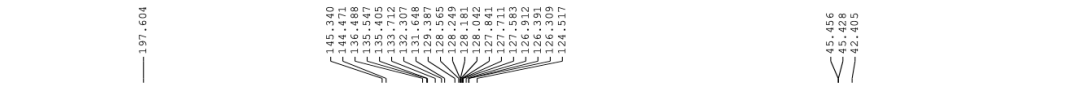

MeO
O
Ph
Ph
4ga
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.00 1.14 1.01 2.00 2.99 1.00 1.00
4.08 2.06 2.05

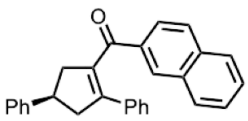

195.552
157.389
149.015
145.900
138.073
136.085
132.250
130.110
129.319
128.481
127.760
127.559
127.368
126.849
126.158
120.017
110.698
55.360
47.616
43.452
41.683
MeO
O
Ph
Ph
4ga
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



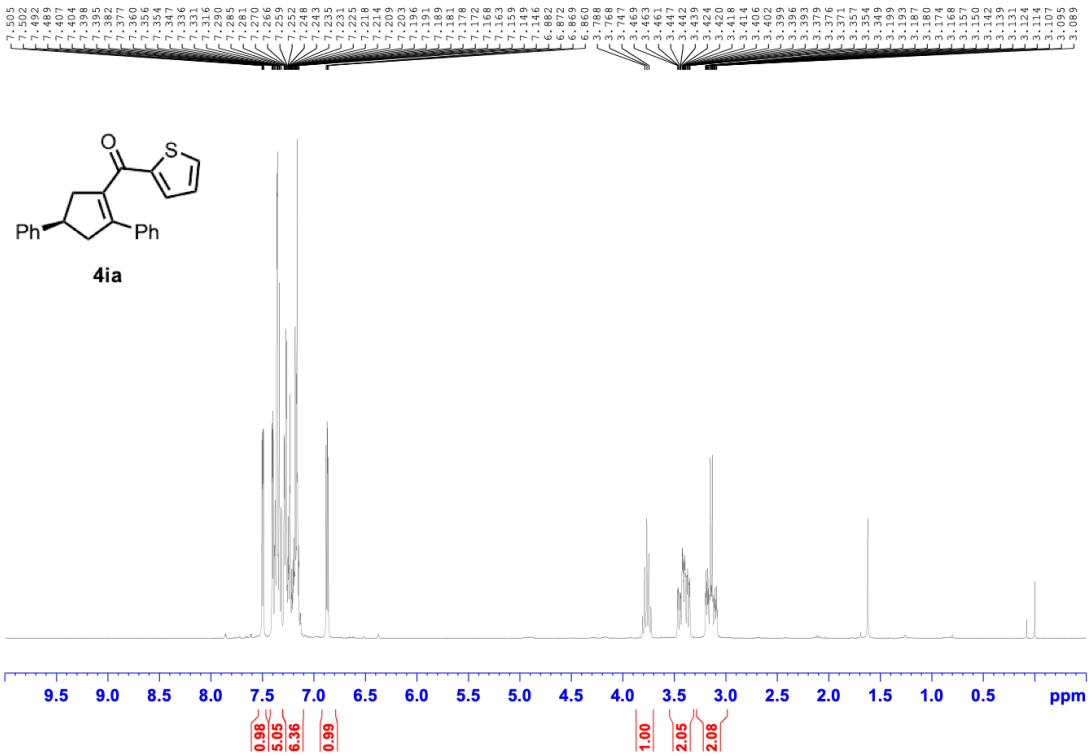
4ha

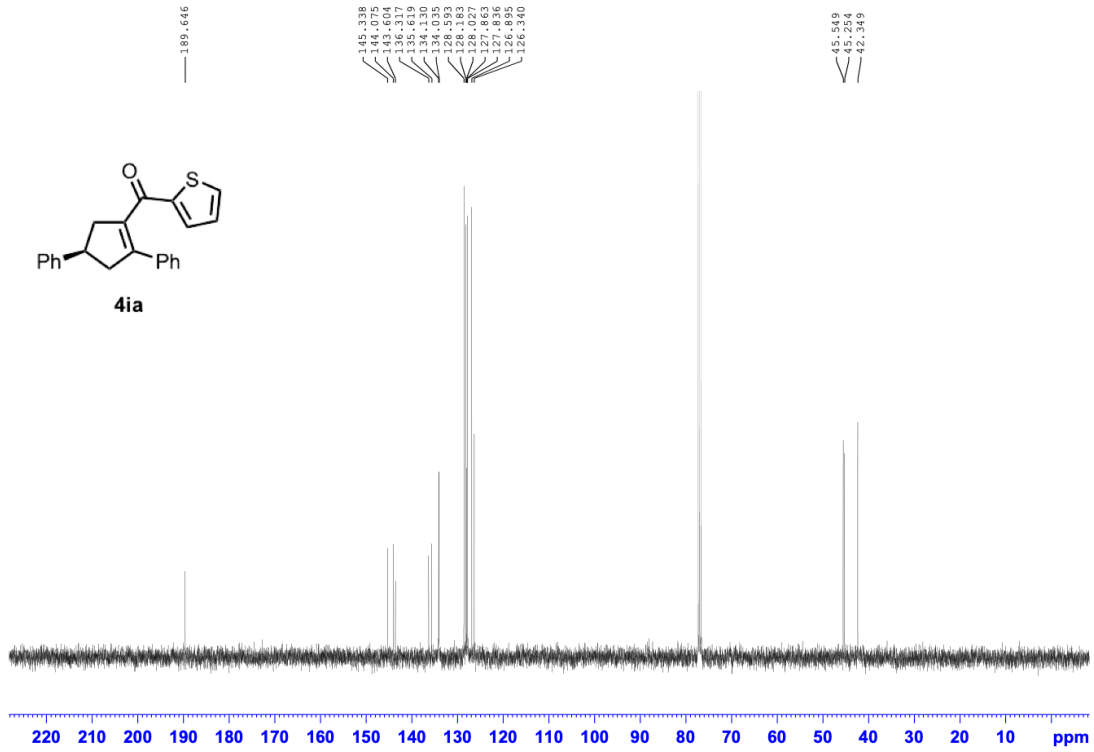


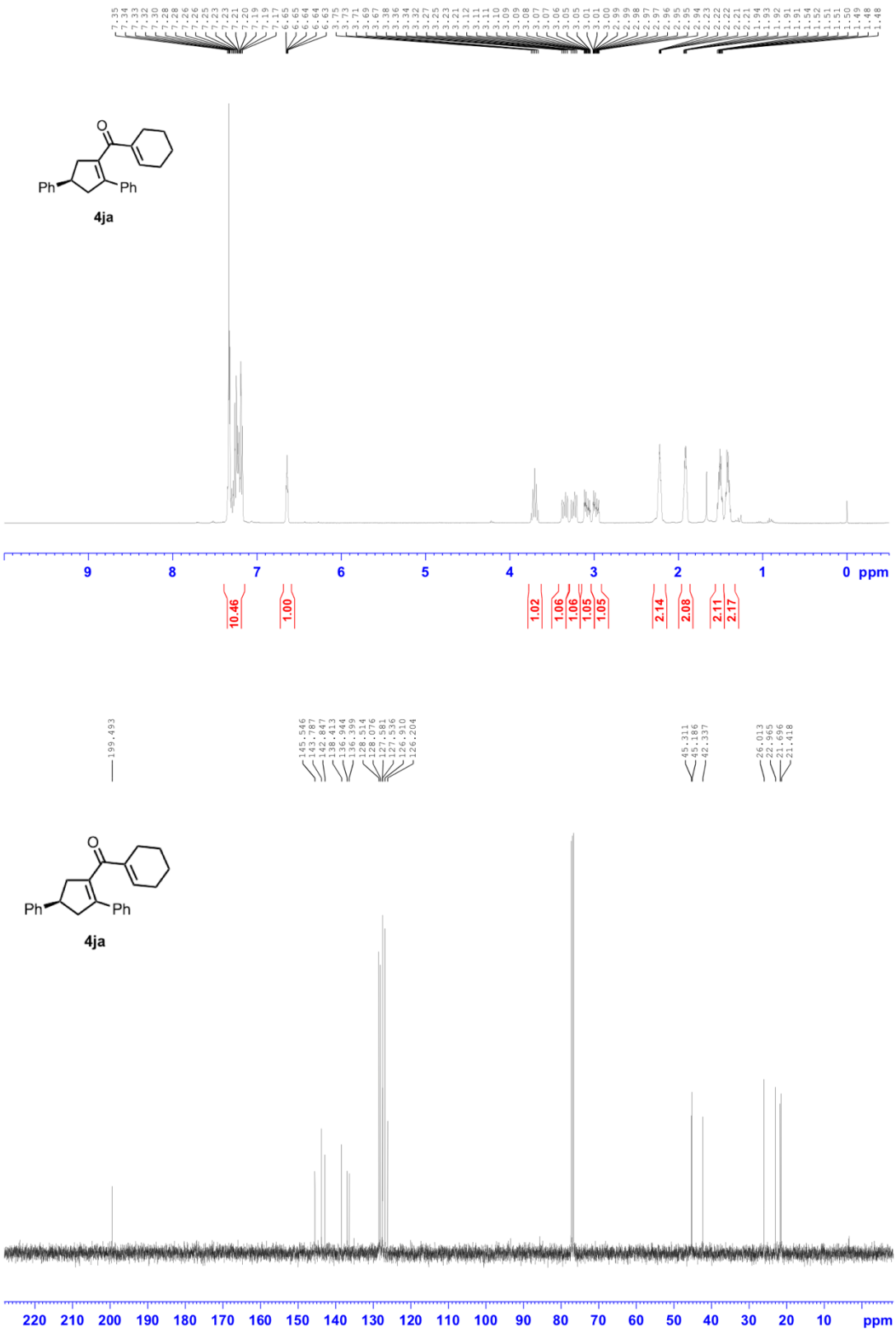


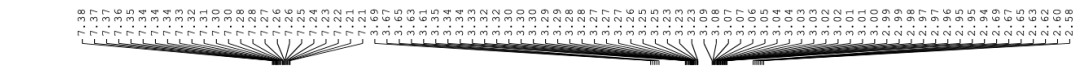


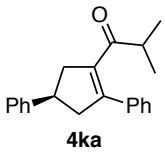
4ha


4ia
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.98 5.05 6.36 0.99 1.00 2.05 2.08

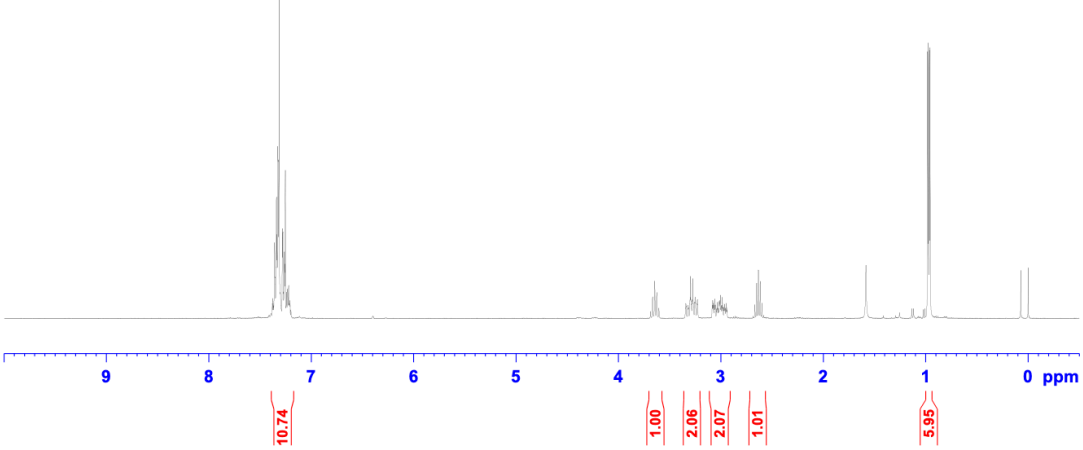

4ia
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

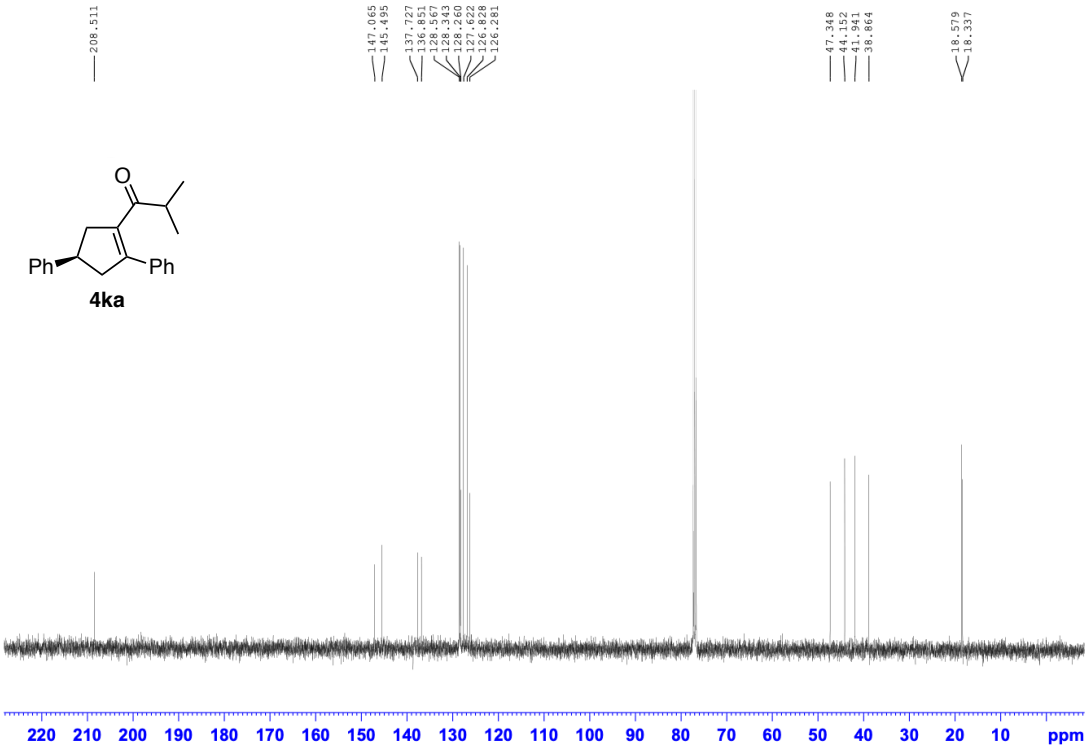

4ja
9 8 7 6 5 4 3 2 1 0 ppm
10.46
1.00
1.02
1.06
1.06
1.05
1.05
2.14
2.08
2.11
2.17
4ja
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm




O
Ph
Ph

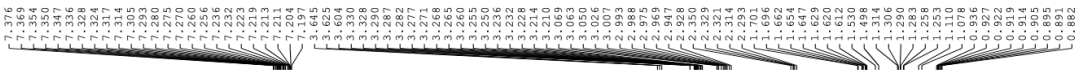
4ka

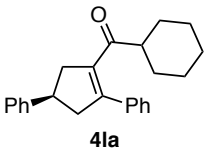

9
8
7
6
5
4
3
2
1
0 ppm
10.74
1.00
2.06
2.07
1.01
5.95


208.511
147.065
145.495
137.727
136.851
128.567
128.343
128.260
127.622
126.828
126.281
47.348
44.152
41.941
38.864
18.579
18.337
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

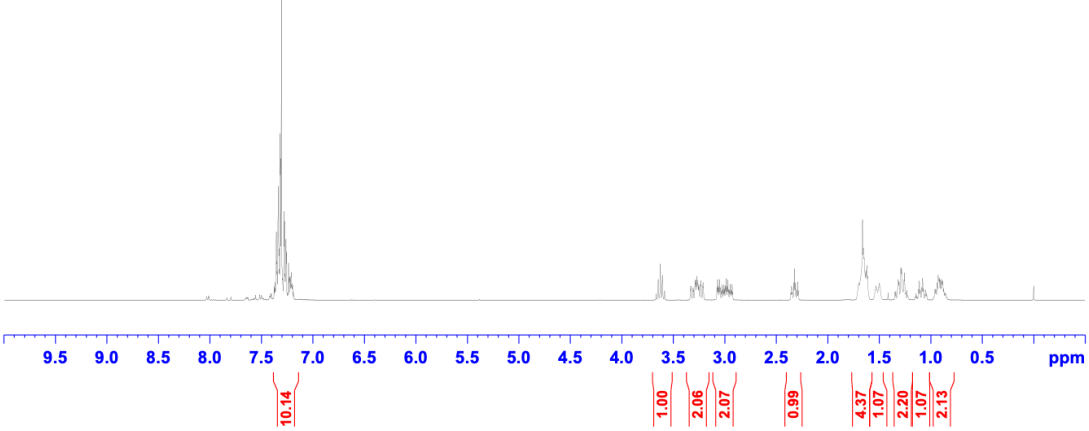
O
Ph
Ph

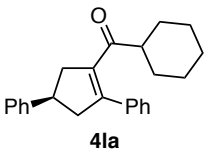
4ka



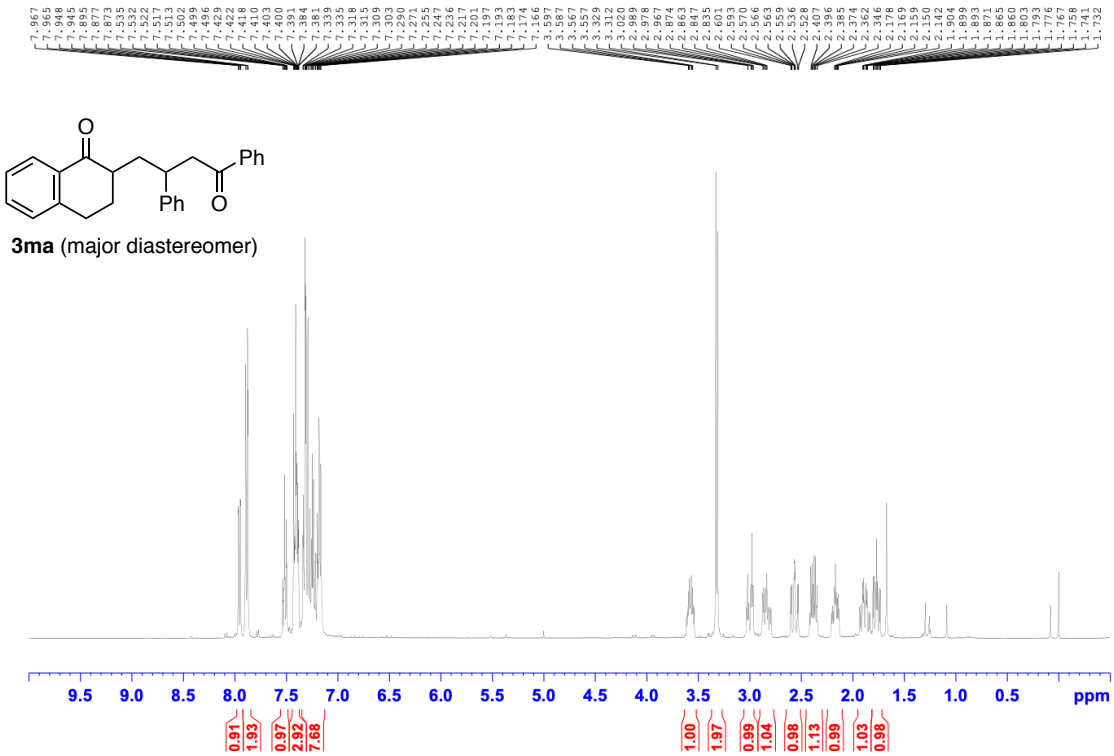


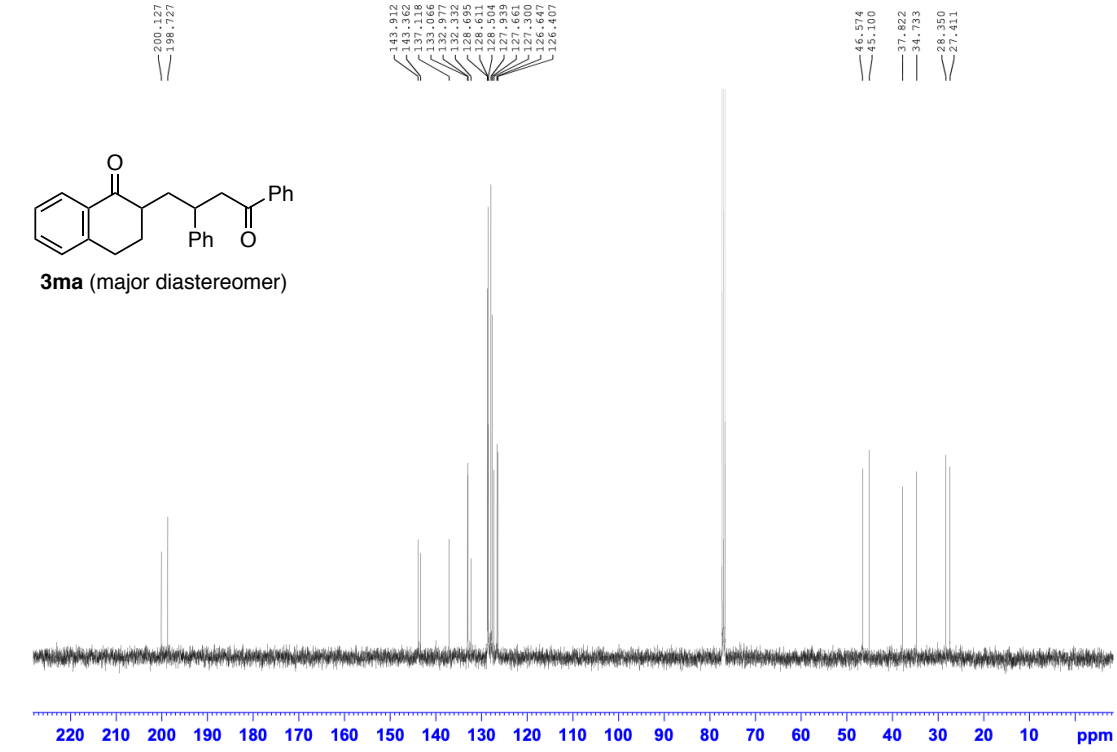
4la

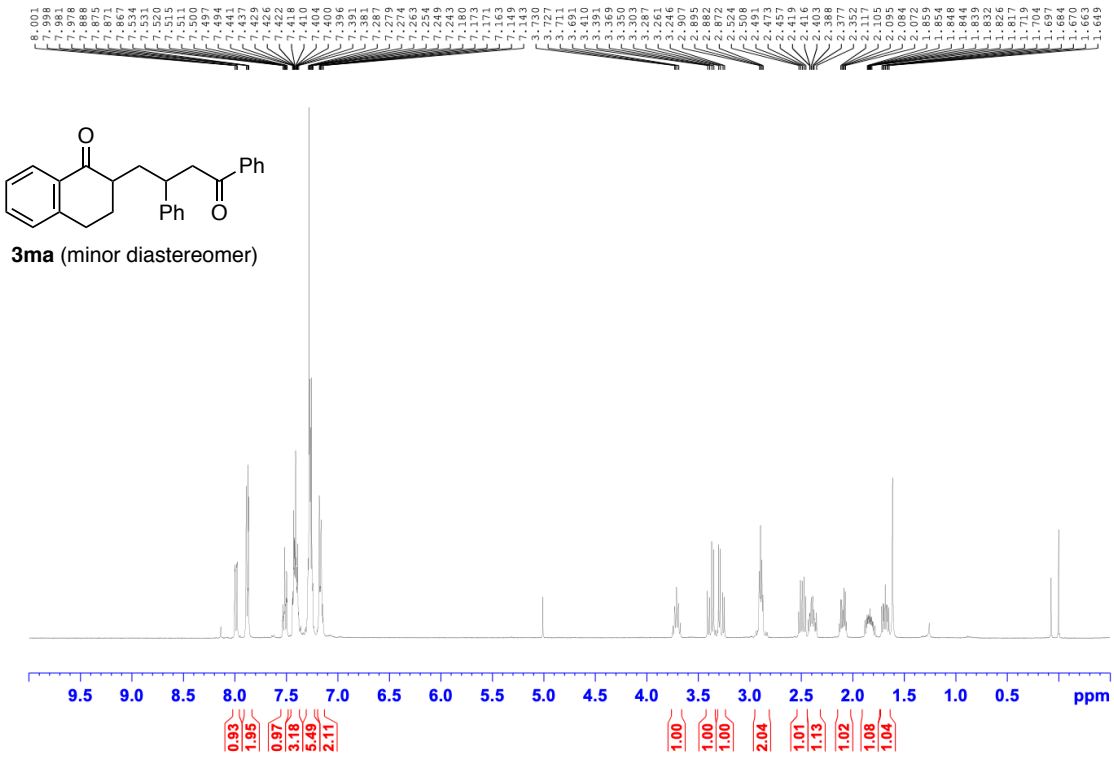




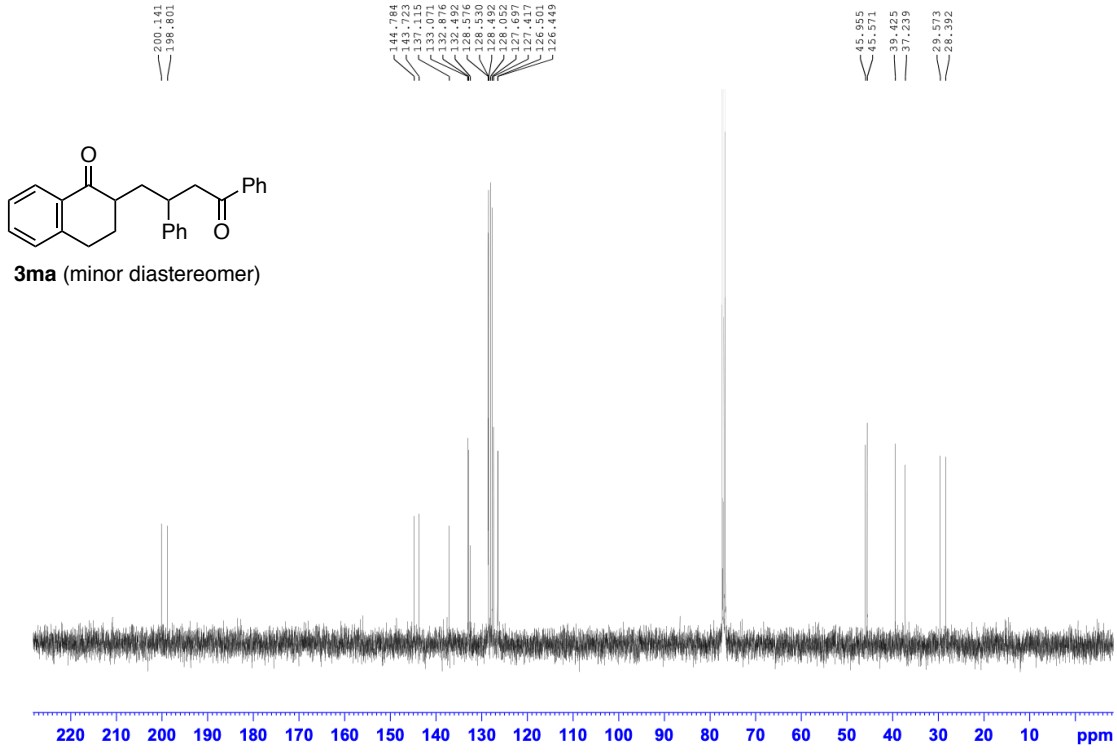
4la


O
Ph
Ph
O
3ma (major diastereomer)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.91 1.93 0.97 2.92 7.88 1.00 1.97 0.99 1.04 0.98 1.13 0.99 1.03 0.98

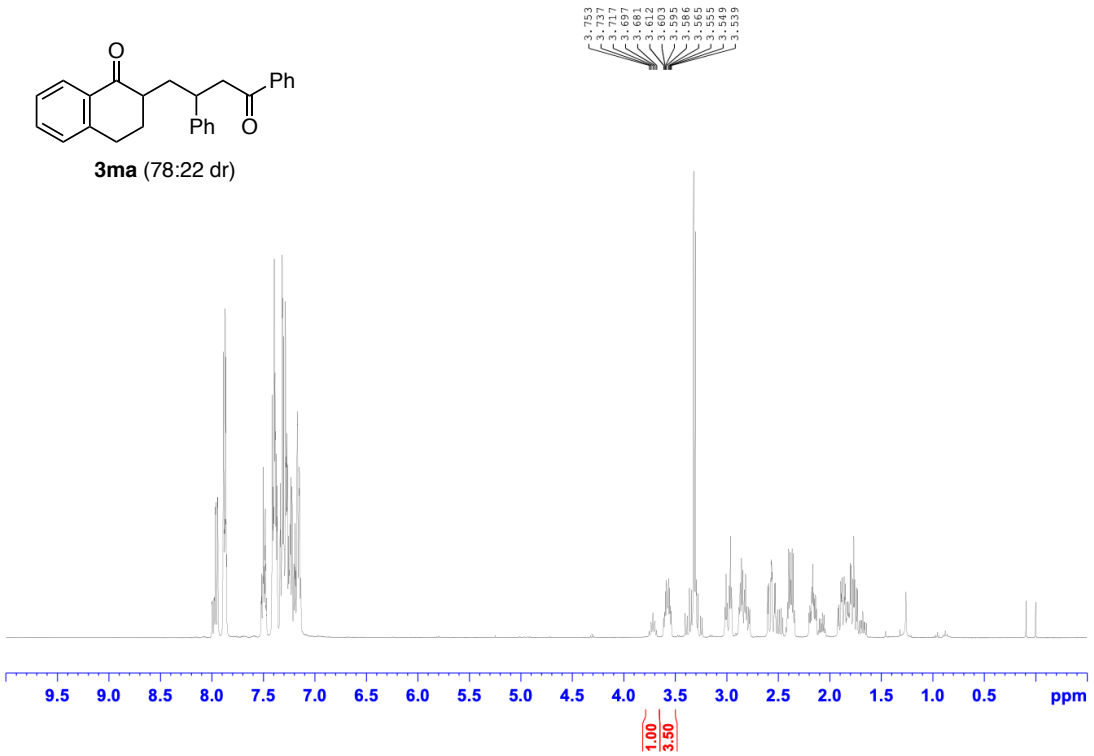

O
Ph
Ph
O
3ma (major diastereomer)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



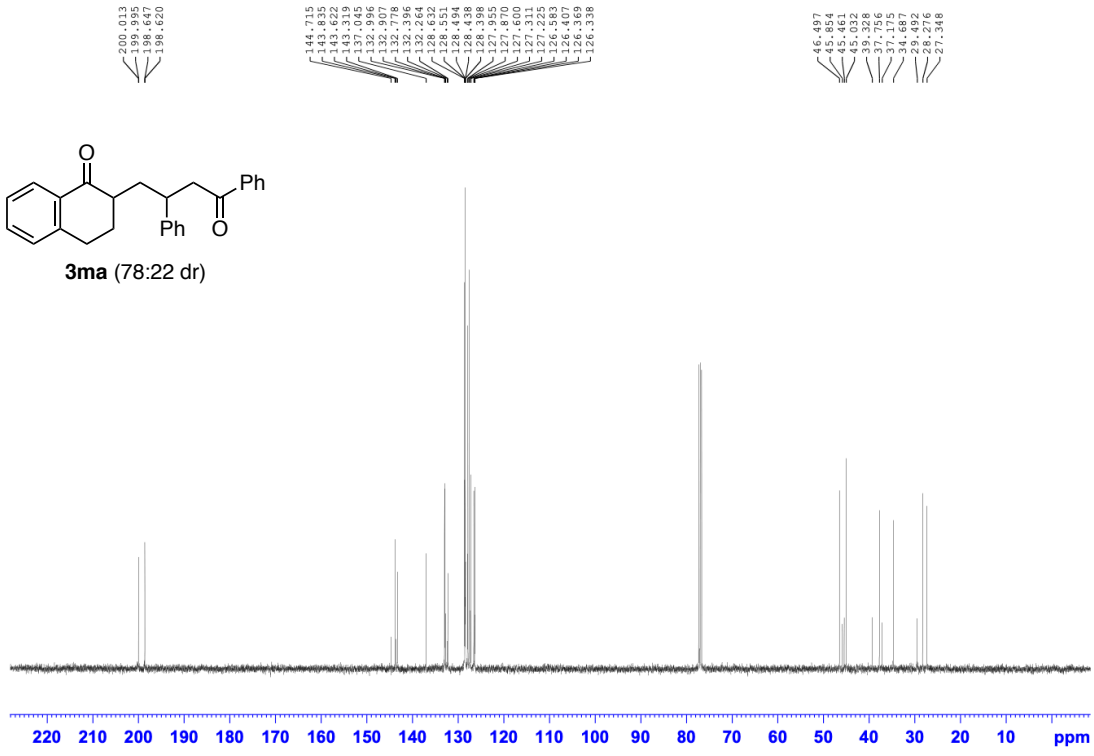
3ma (minor diastereomer)



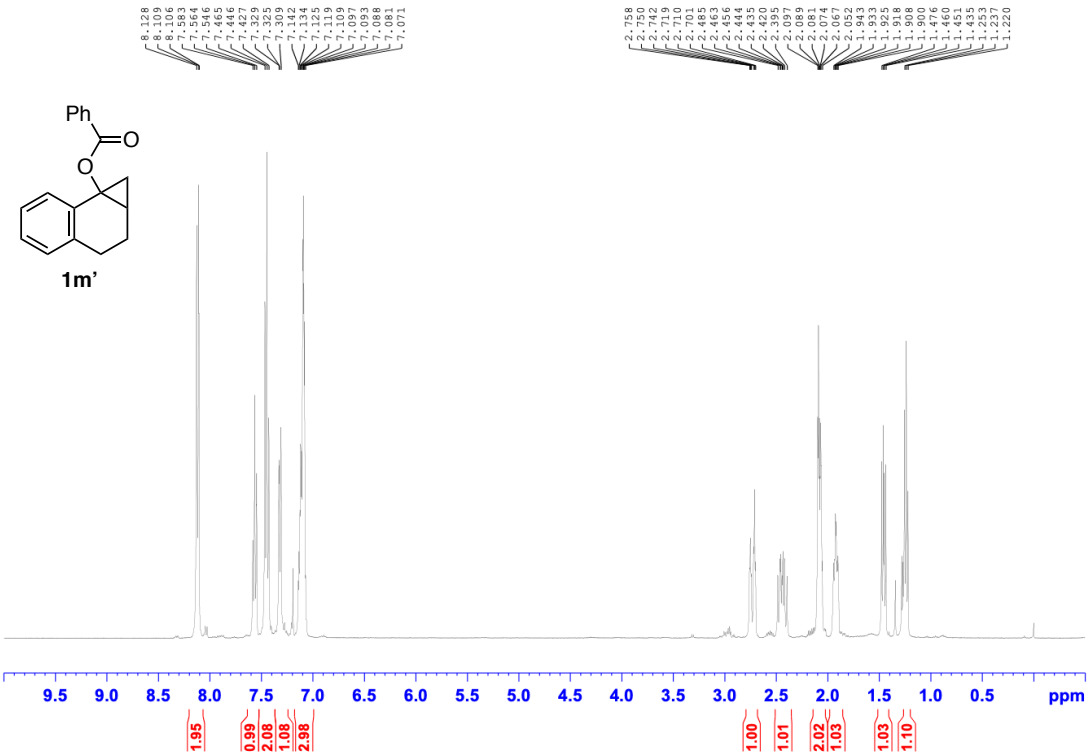
3ma (minor diastereomer)

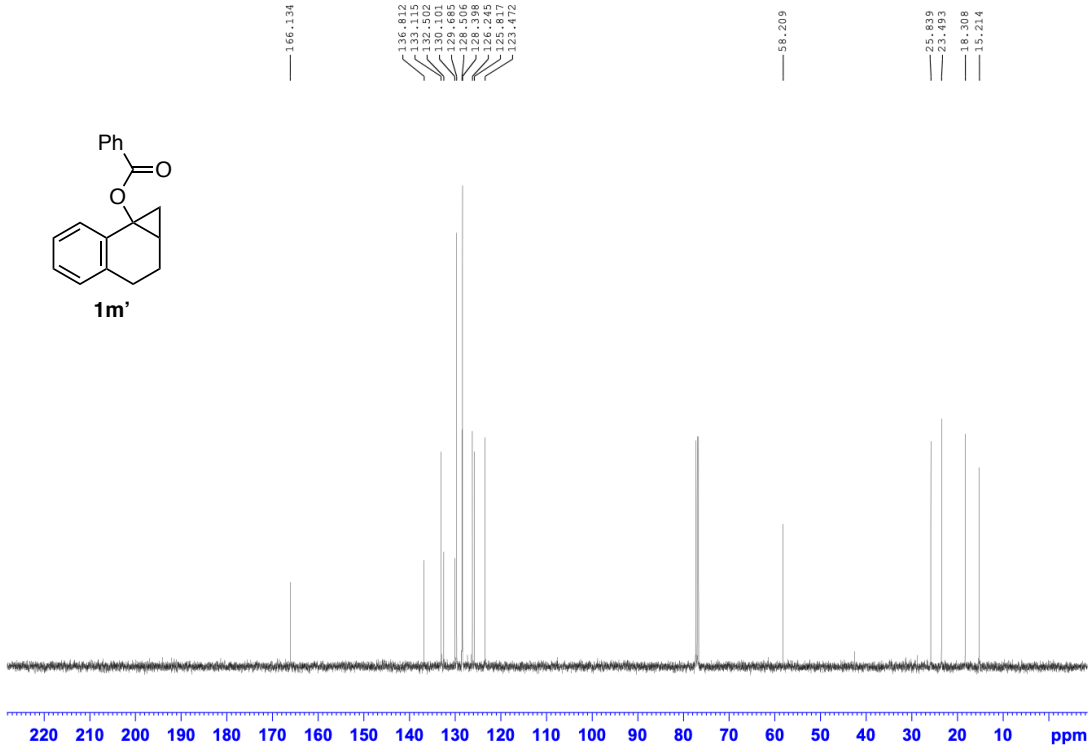


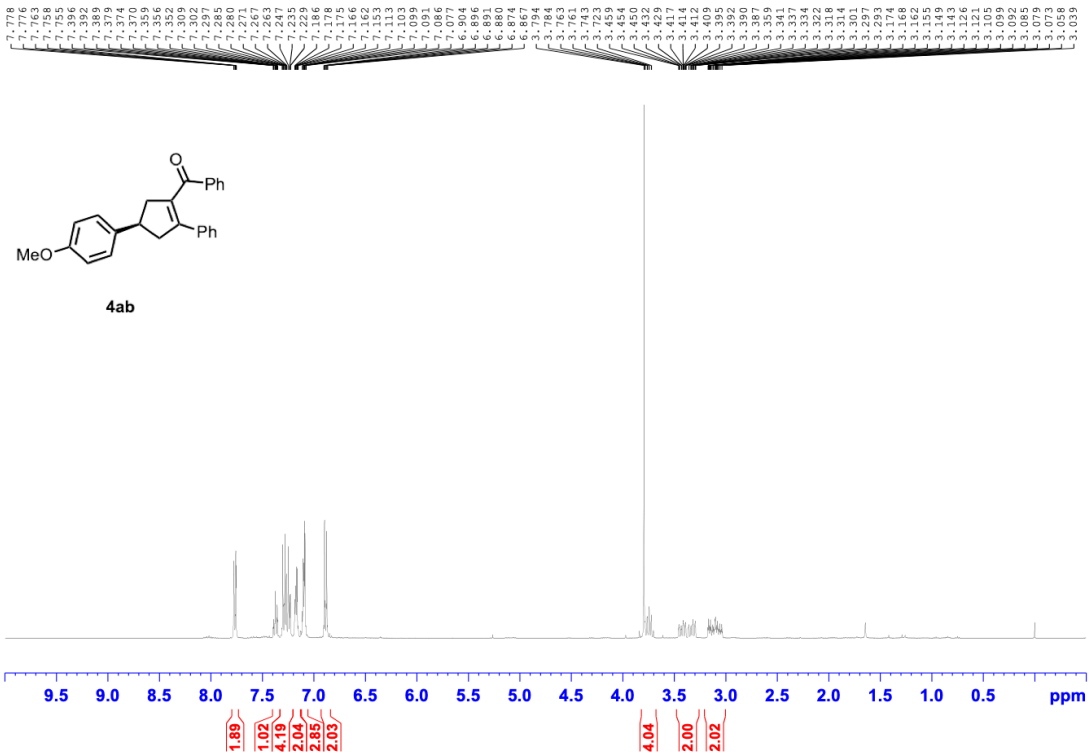
3ma (78:22 dr)

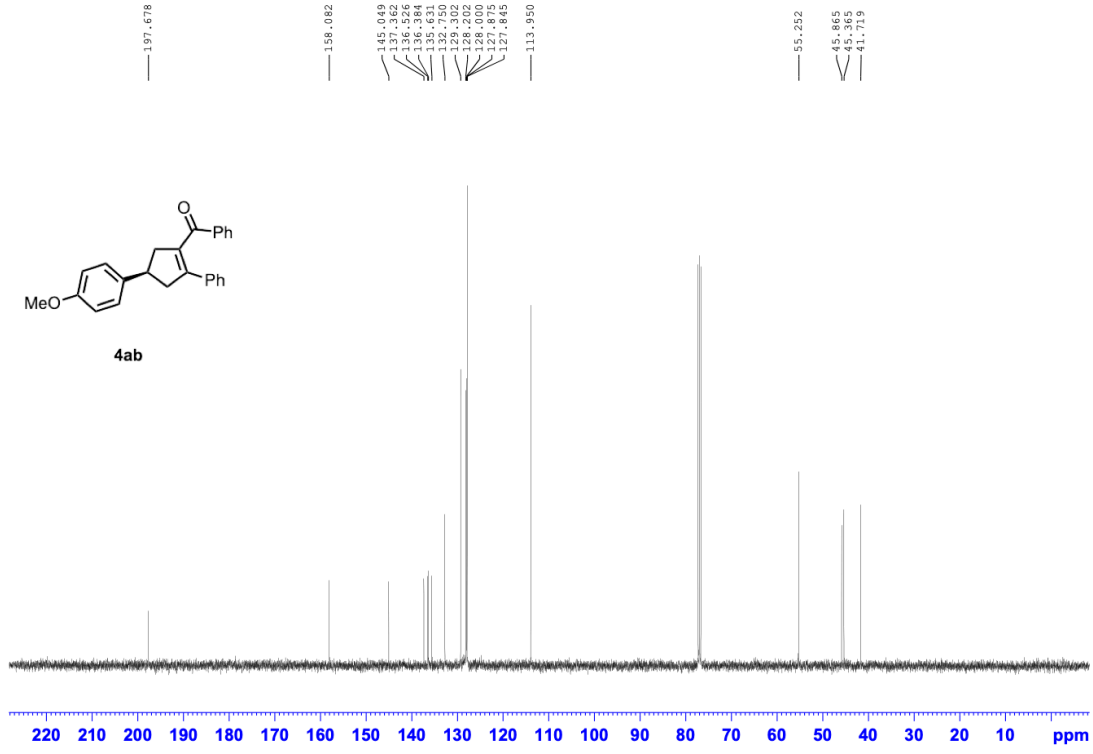


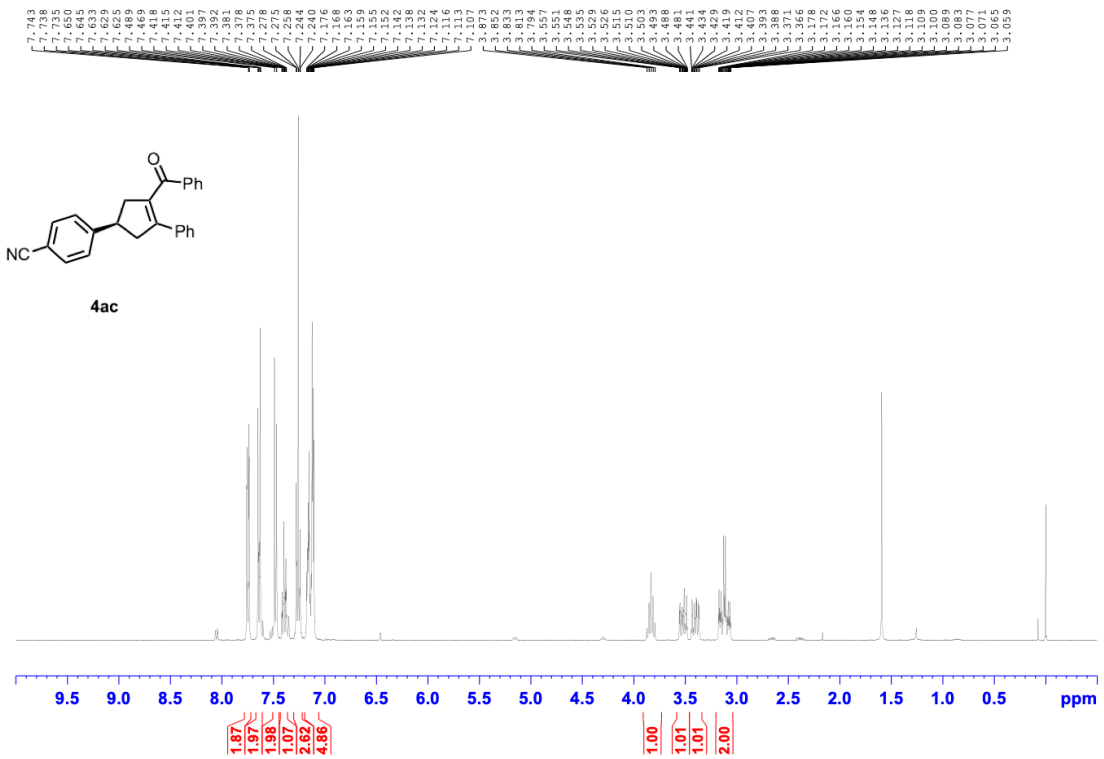
3ma (78:22 dr)

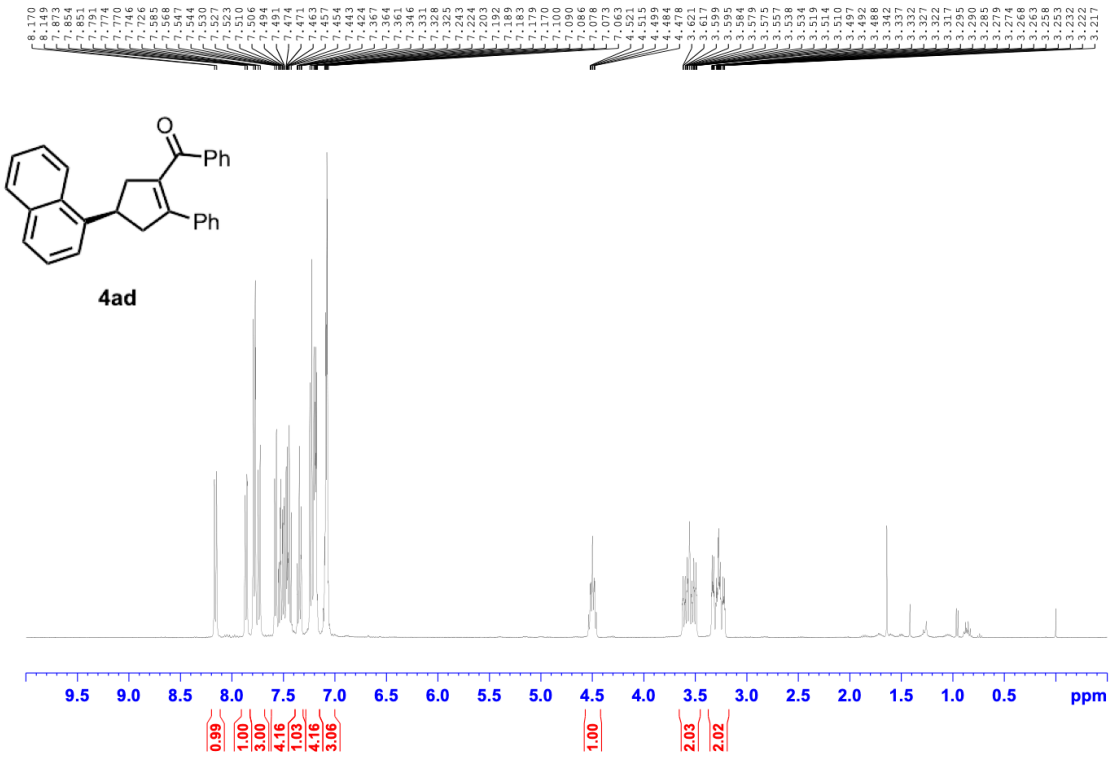

Ph
O
O
1m'
8.128
8.109
8.106
7.583
7.564
7.446
7.427
7.329
7.325
7.309
7.142
7.134
7.125
7.119
7.109
7.097
7.093
7.088
7.081
7.071
2.758
2.750
2.742
2.719
2.710
2.701
2.485
2.463
2.456
2.444
2.435
2.420
2.395
2.097
2.089
2.081
2.074
2.067
2.053
1.943
1.933
1.925
1.918
1.908
1.900
1.476
1.460
1.451
1.435
1.253
1.237
1.220
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.95
0.99
2.08
1.08
2.98
1.00
1.01
2.02
1.03
1.03
1.10

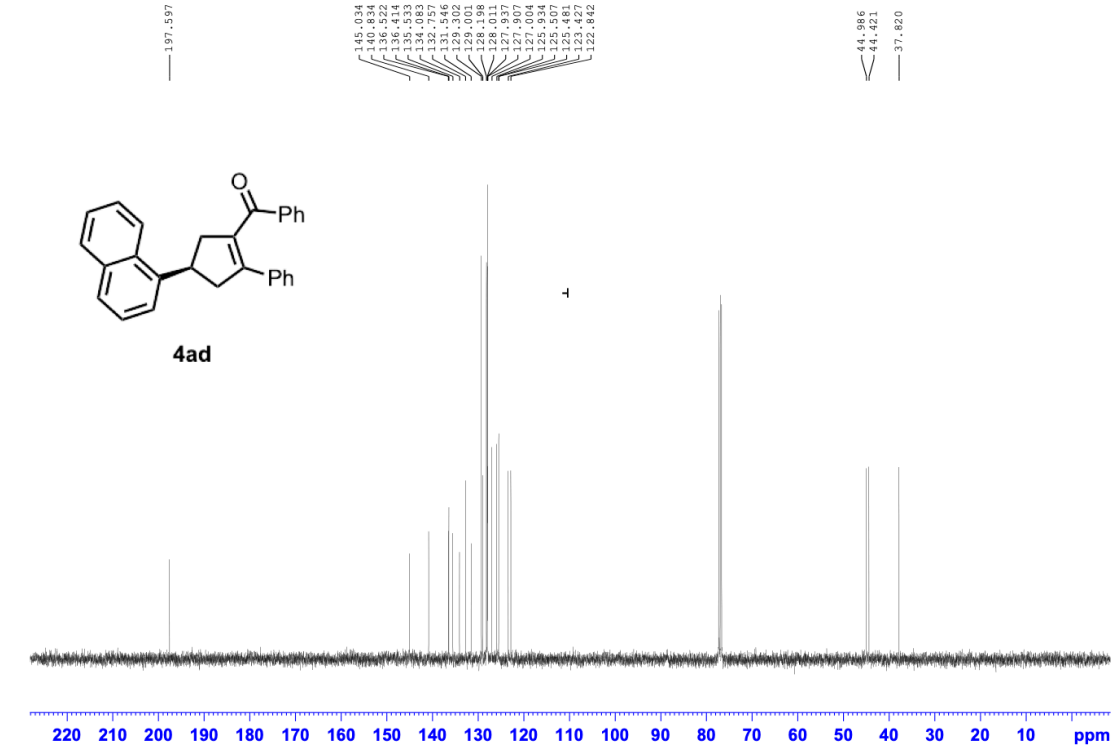

166.134
136.812
133.115
132.502
130.101
129.685
128.506
128.398
126.245
125.817
123.472
58.209
25.839
23.493
18.308
15.214
Ph
O
O
1m'
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

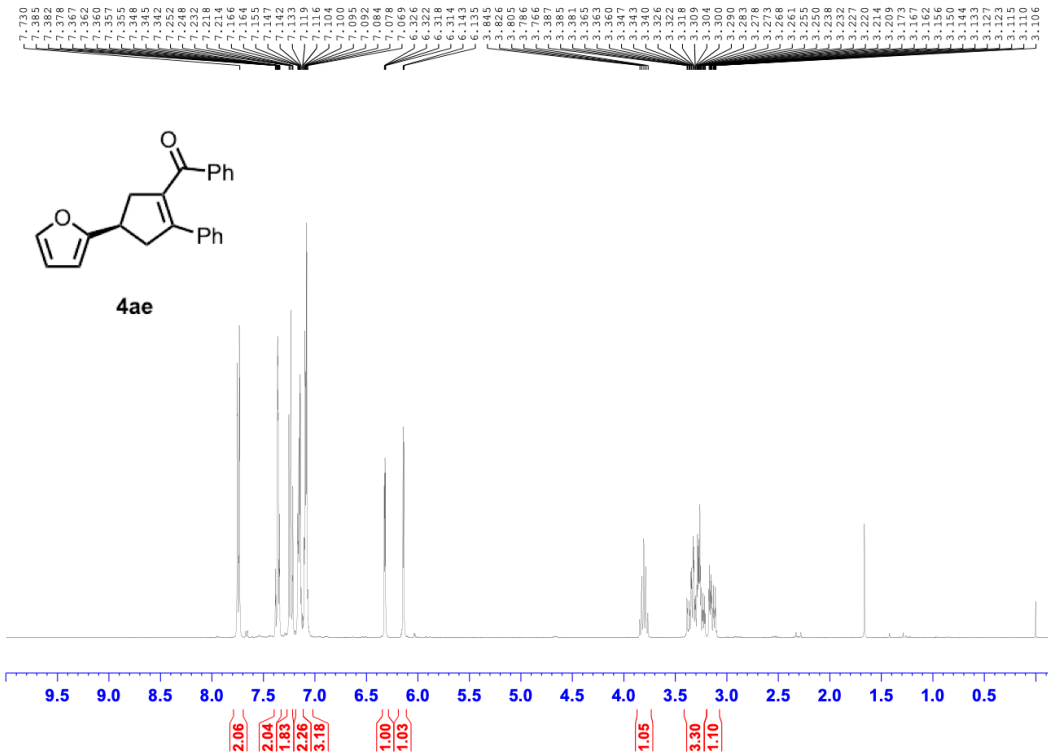

4ab
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.89 1.02 4.19 2.04 2.85 2.03 4.04 2.00 2.02

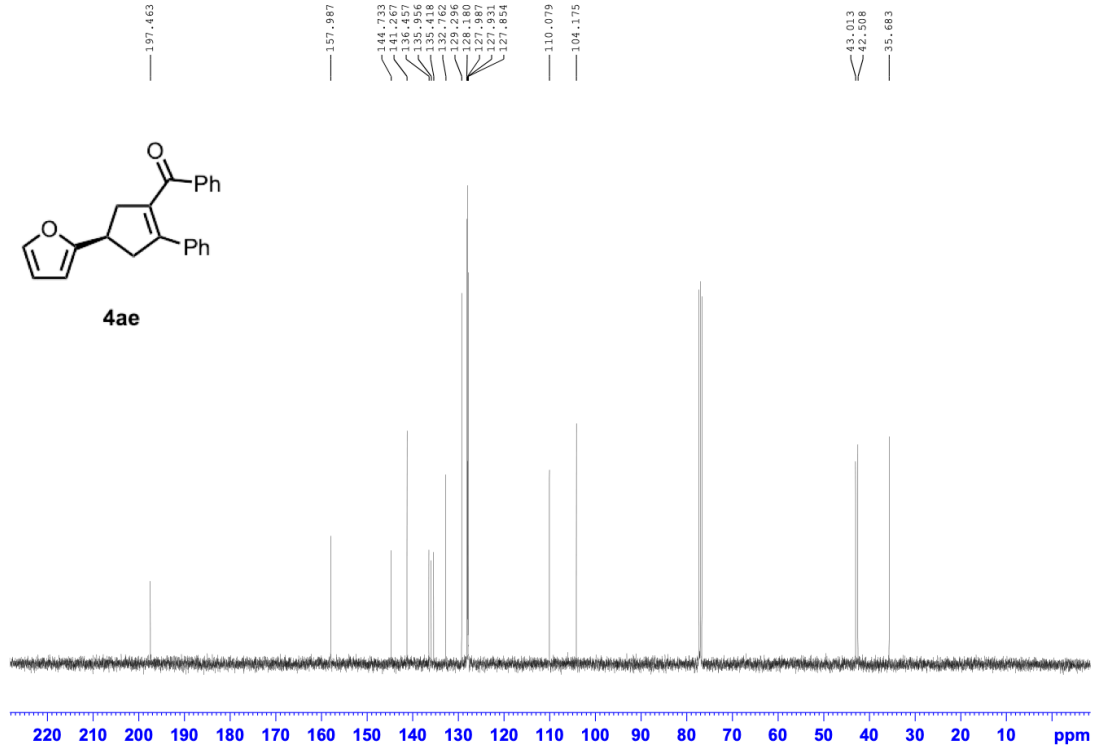

4ab
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

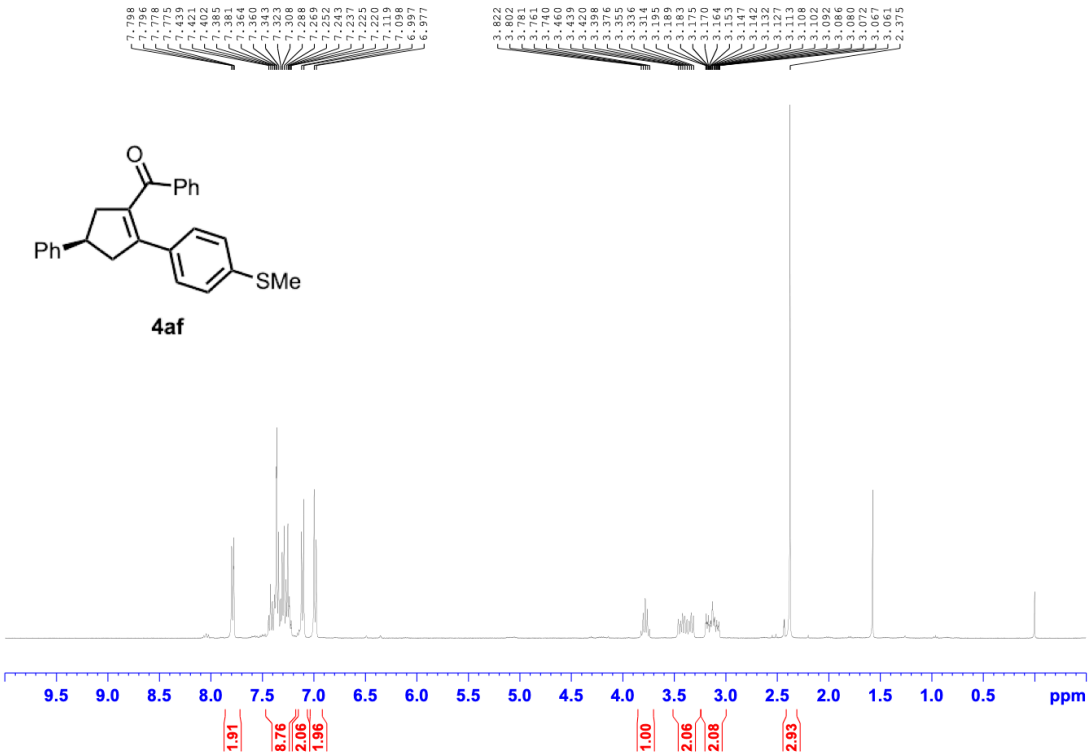

4ac
ppm
4ac
ppm

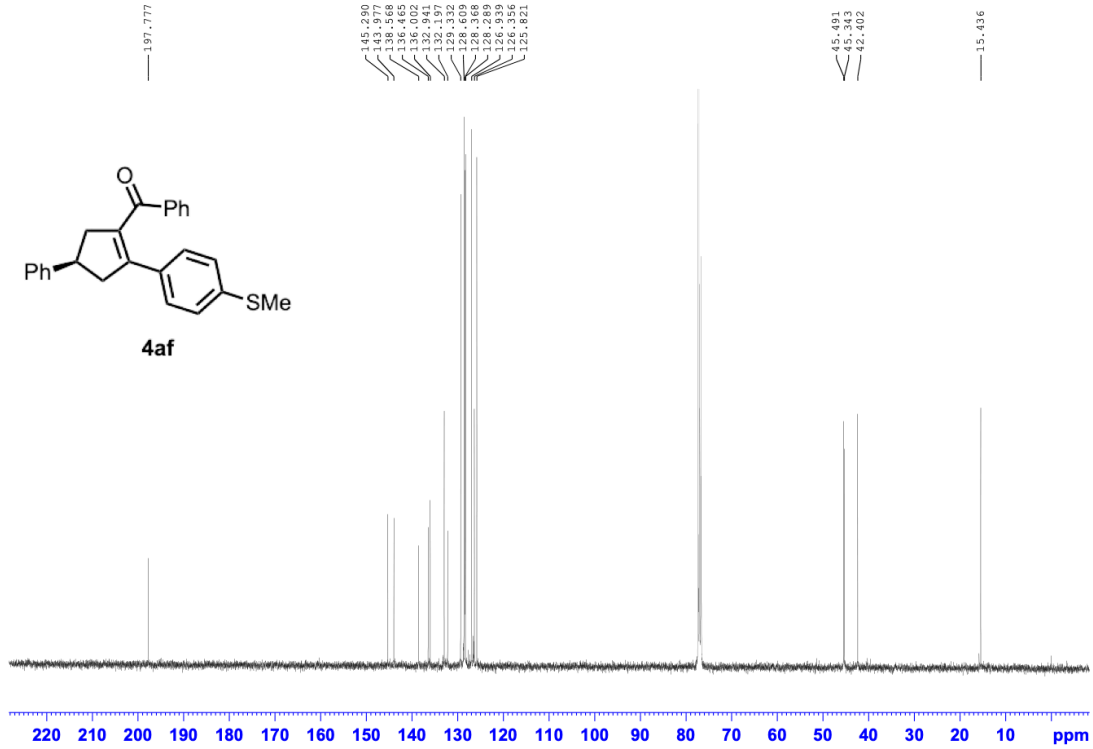

Ph
Ph
4ad
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
0.99 1.00 3.00 4.16 1.03 4.16 3.06 1.00 2.03 2.02

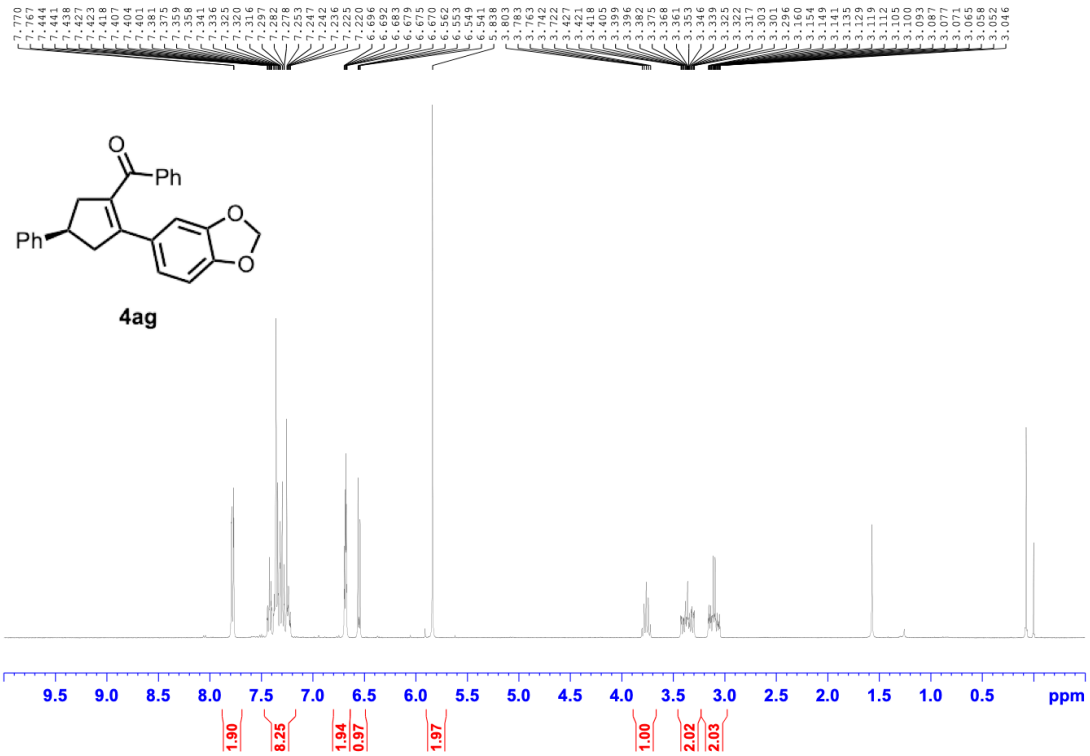

Ph
Ph
4ad
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

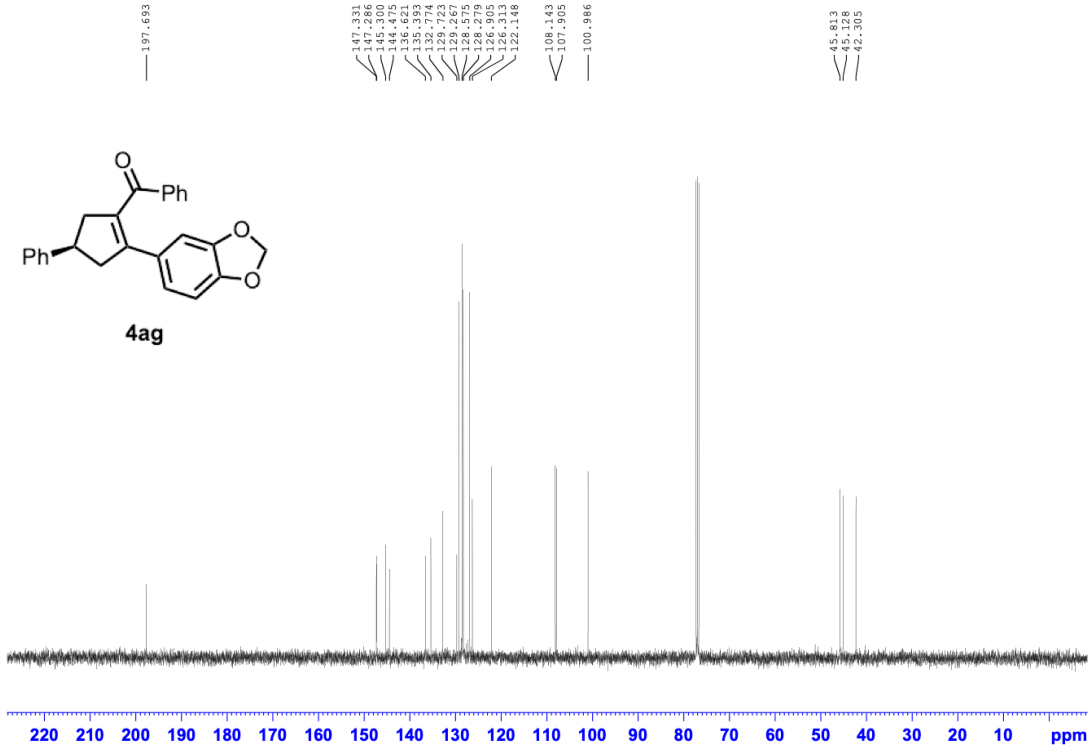

4ae
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.06 2.04 1.83 2.26 3.18 1.00 1.03 1.05 3.30 1.10

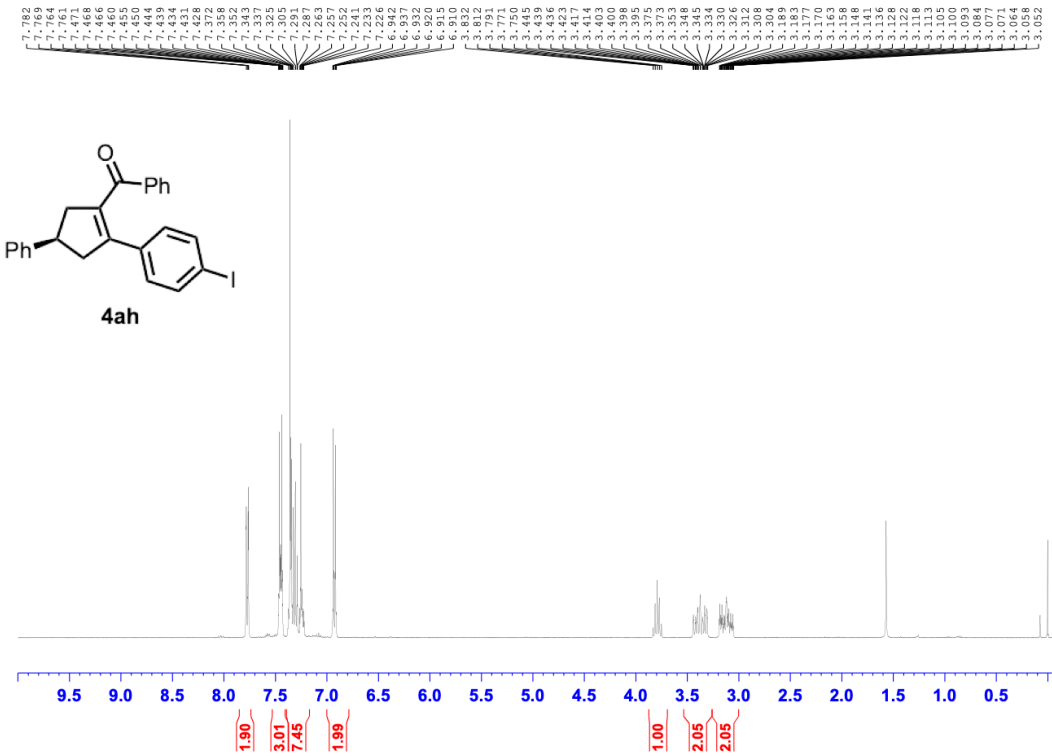

4ae
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

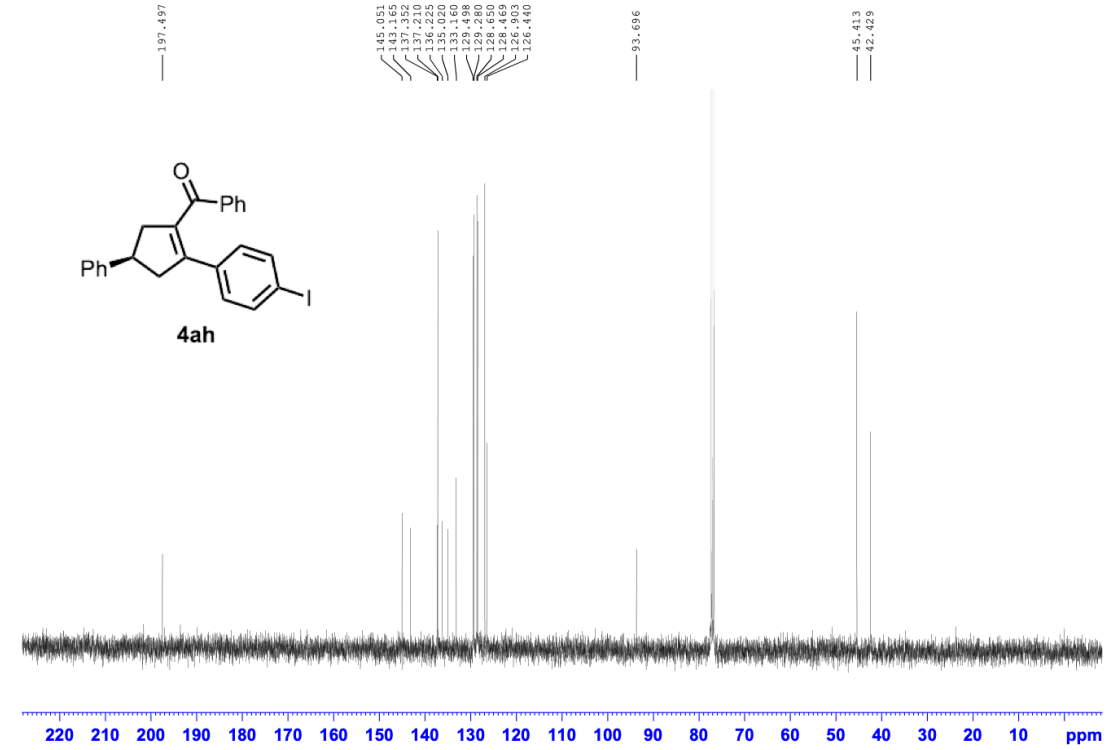

7.798
7.796
7.778
7.775
7.439
7.421
7.402
7.385
7.381
7.364
7.360
7.343
7.323
7.308
7.288
7.269
7.252
7.243
7.237
7.225
7.220
7.113
7.098
6.997
6.977
3.822
3.802
3.781
3.761
3.740
3.460
3.439
3.420
3.398
3.376
3.355
3.336
3.314
3.195
3.189
3.183
3.175
3.170
3.164
3.153
3.147
3.142
3.132
3.127
3.113
3.108
3.102
3.092
3.086
3.080
3.072
3.067
3.061
2.375
O
Ph
Ph
SMe
4af
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.91
8.76
2.06
1.96
1.00
2.06
2.08
2.93

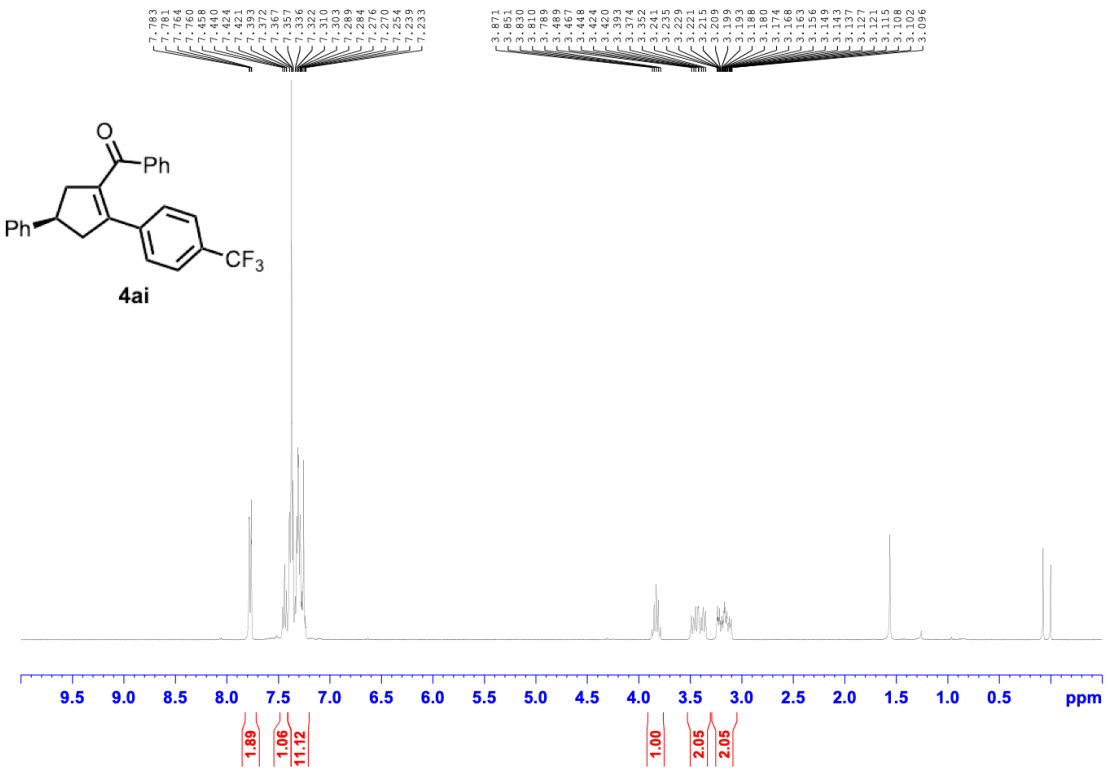

197.777
145.290
143.977
138.568
136.665
136.002
132.941
132.197
129.332
128.609
128.368
128.289
128.249
126.356
125.821
45.491
45.343
42.402
15.436
O
Ph
Ph
SMe
4af
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

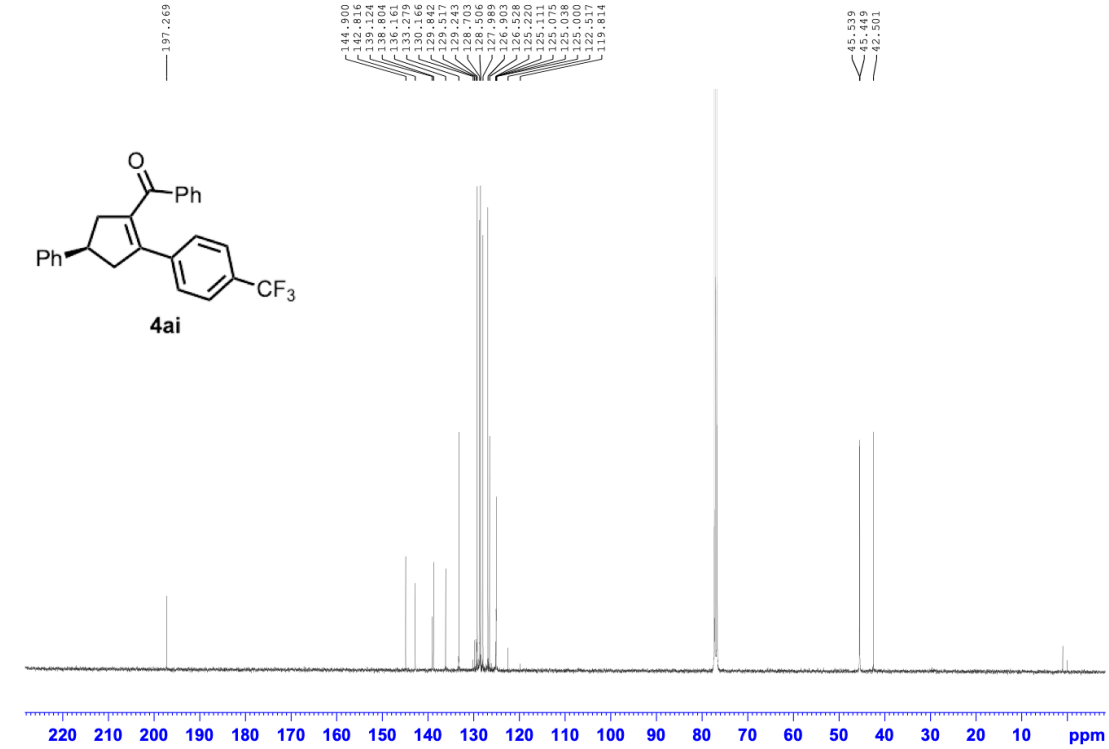

4ag
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.90 8.25 1.94 0.97 1.97 1.00 2.02 2.03

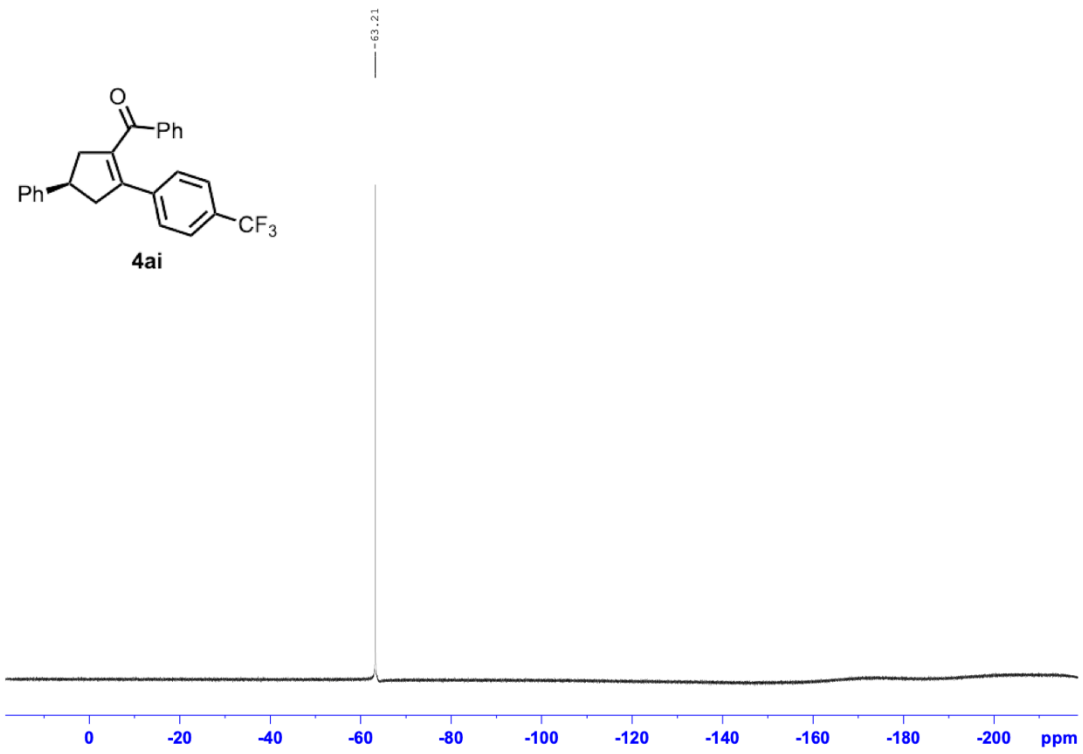

4ag
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

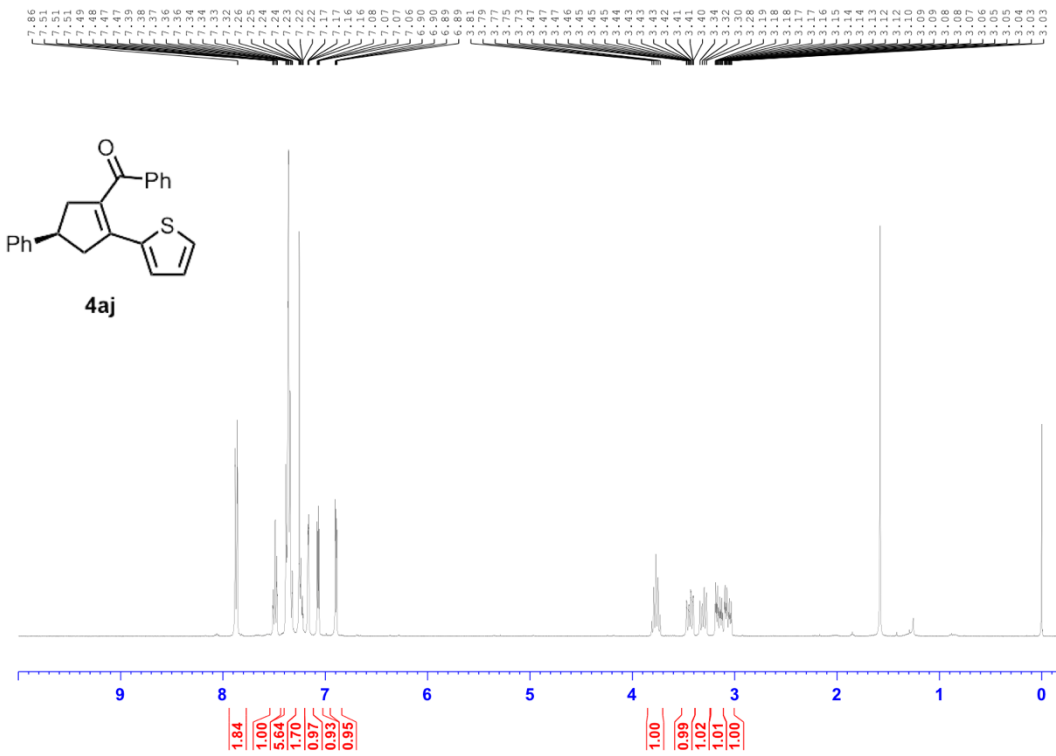

4ah
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.90
3.01
7.45
1.99
1.00
2.05
2.05

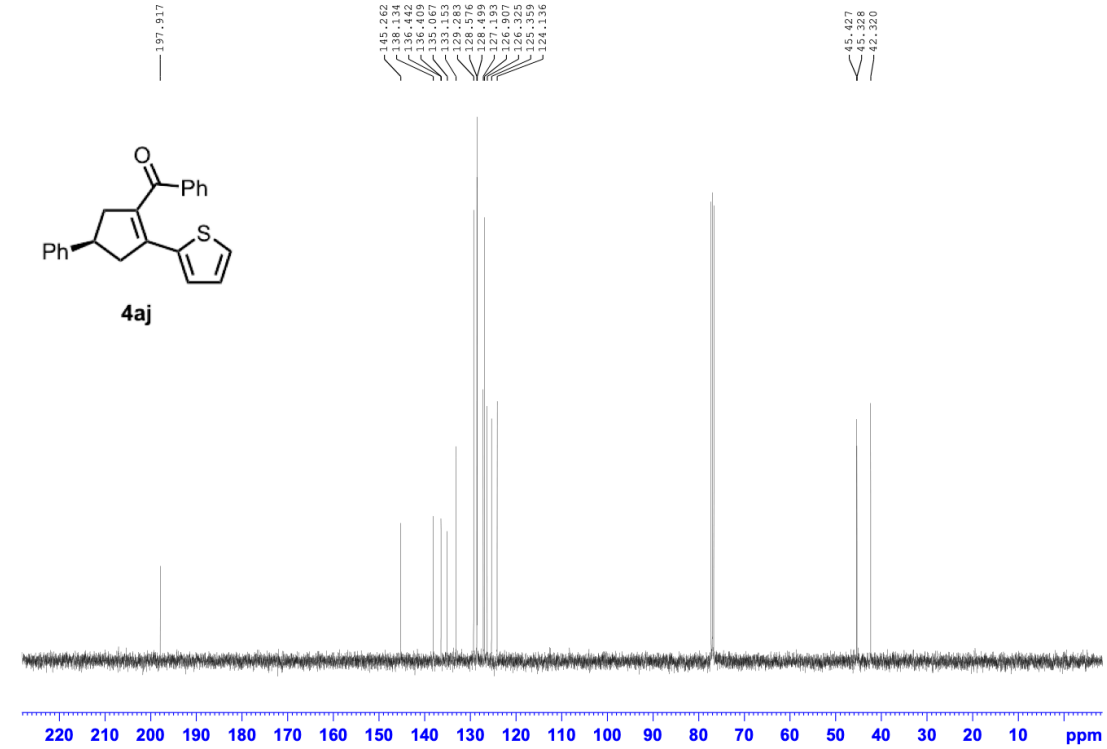

4ah
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

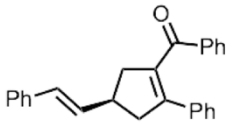

7.783
7.781
7.764
7.760
7.458
7.440
7.424
7.421
7.393
7.372
7.367
7.357
7.336
7.322
7.310
7.303
7.289
7.284
7.276
7.270
7.254
7.239
7.233
3.871
3.851
3.830
3.810
3.789
3.467
3.448
3.424
3.420
3.393
3.374
3.352
3.241
3.235
3.229
3.221
3.215
3.209
3.199
3.193
3.188
3.180
3.174
3.168
3.163
3.156
3.149
3.143
3.137
3.127
3.121
3.115
3.108
3.102
3.096
O
Ph
Ph
CF3
4ai
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.89
1.06
11.12
1.00
2.05
2.05


197.269
144.900
142.816
139.124
138.804
136.161
133.279
130.166
129.462
129.517
129.243
128.703
128.506
127.989
126.903
126.528
126.220
125.111
125.075
125.038
125.000
122.517
119.814
45.539
45.449
42.501
O
Ph
Ph
CF3
4ai
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

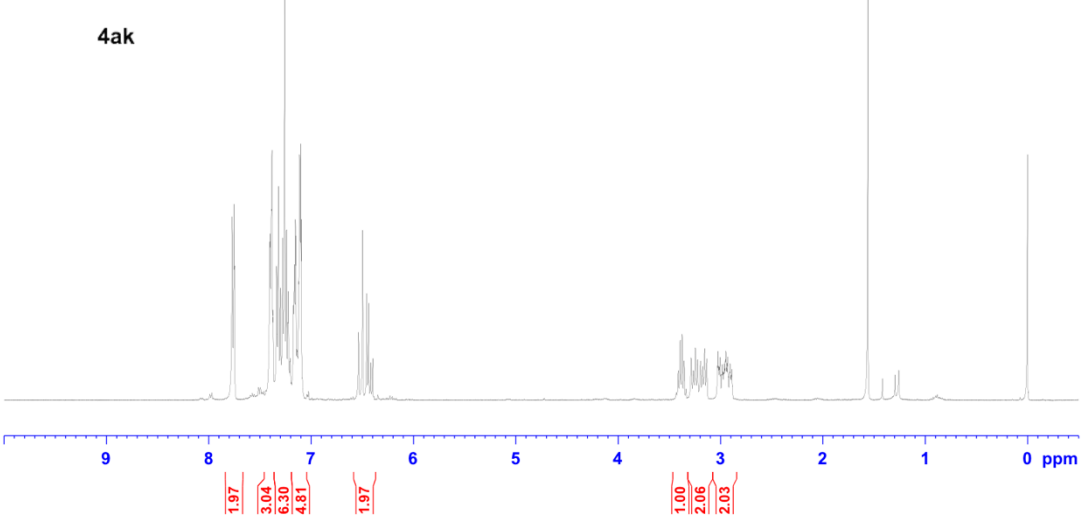

-63.21
O
Ph
Ph
CF3
4ai
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm

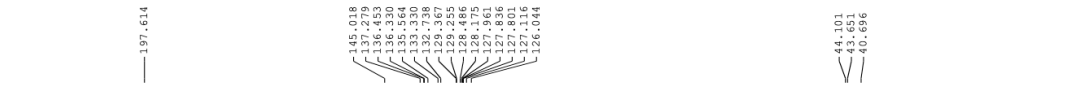

4aj
9
8
7
6
5
4
3
2
1
0 ppm
1.84
1.00
5.64
1.70
0.97
0.93
0.95
1.00
0.99
1.02
1.01
1.00

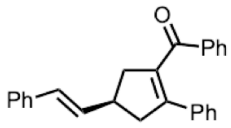

4aj
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
Ph
Ph
Ph

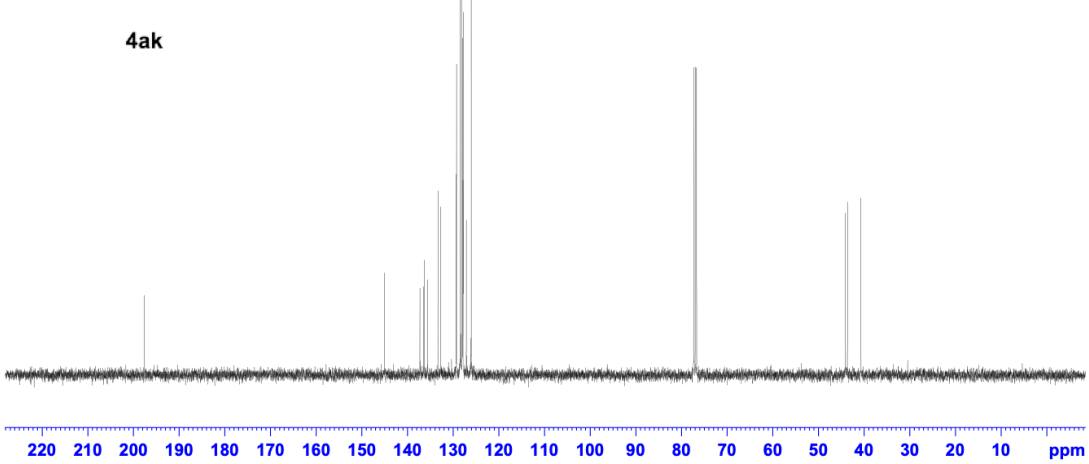
4ak

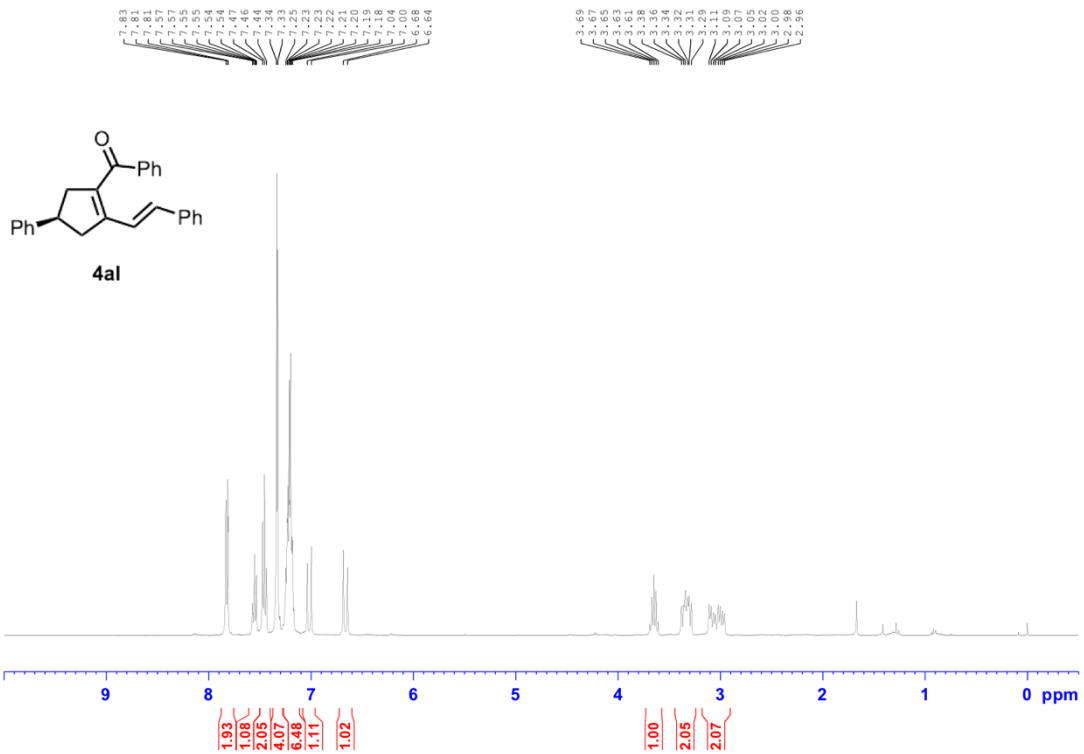

9
8
7
6
5
4
3
2
1
0 ppm
1.97
3.04
6.30
4.81
1.97
1.00
2.06
2.03

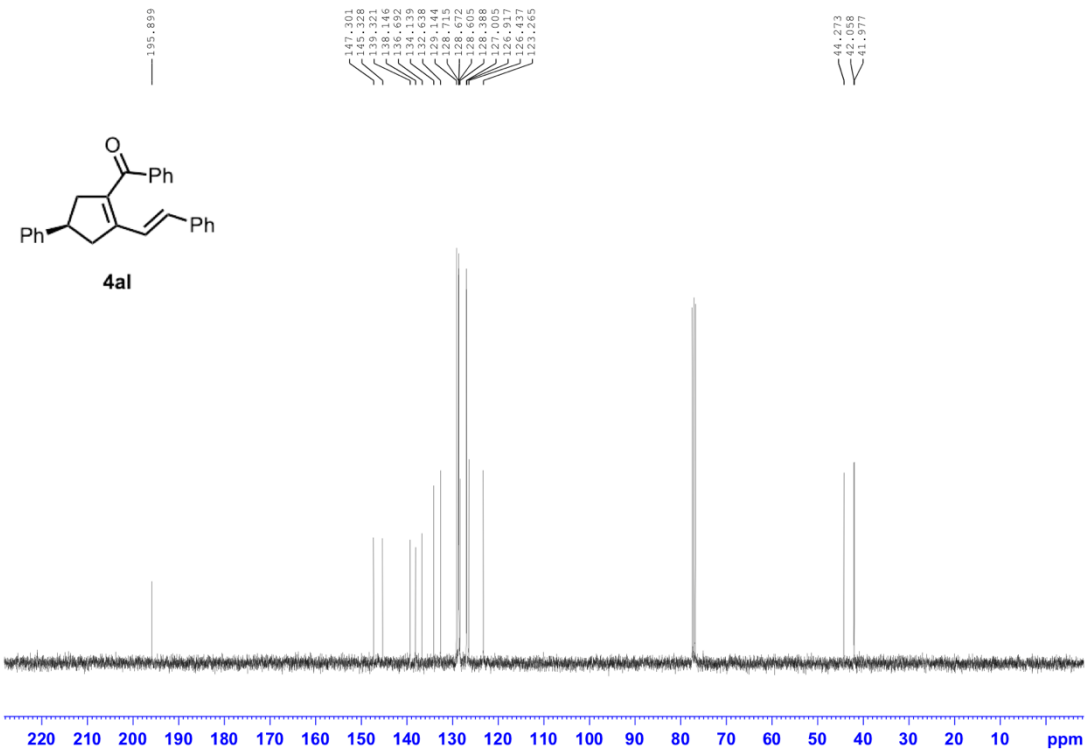


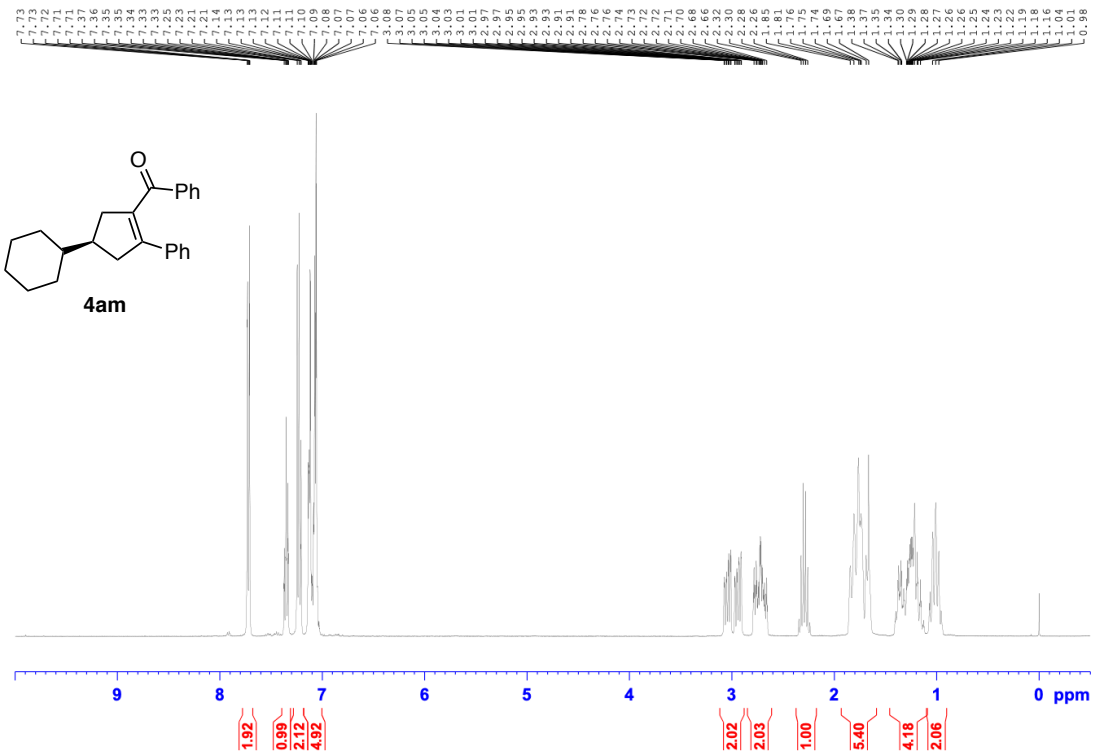

O
Ph
Ph
Ph

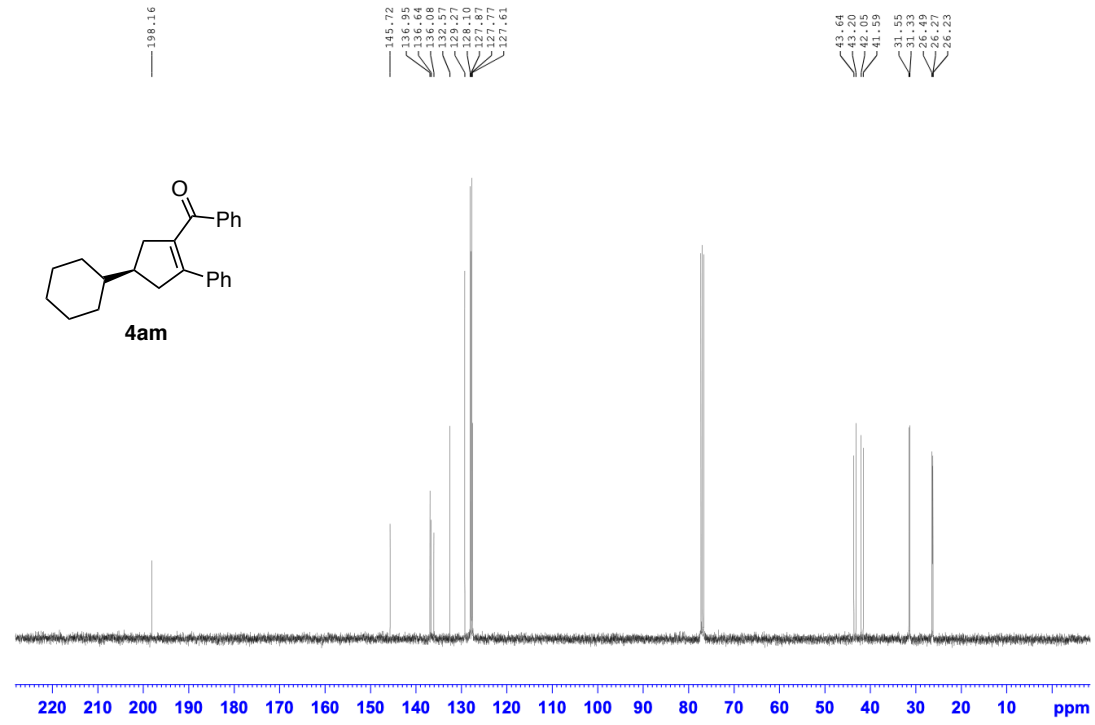
4ak

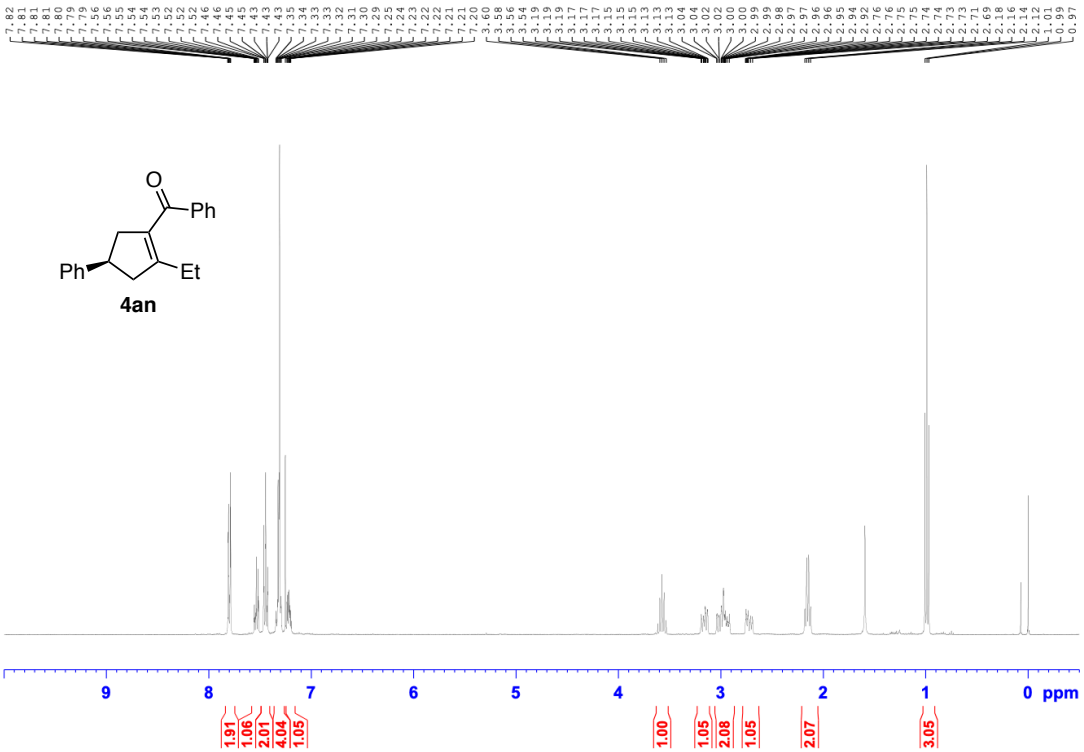

220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

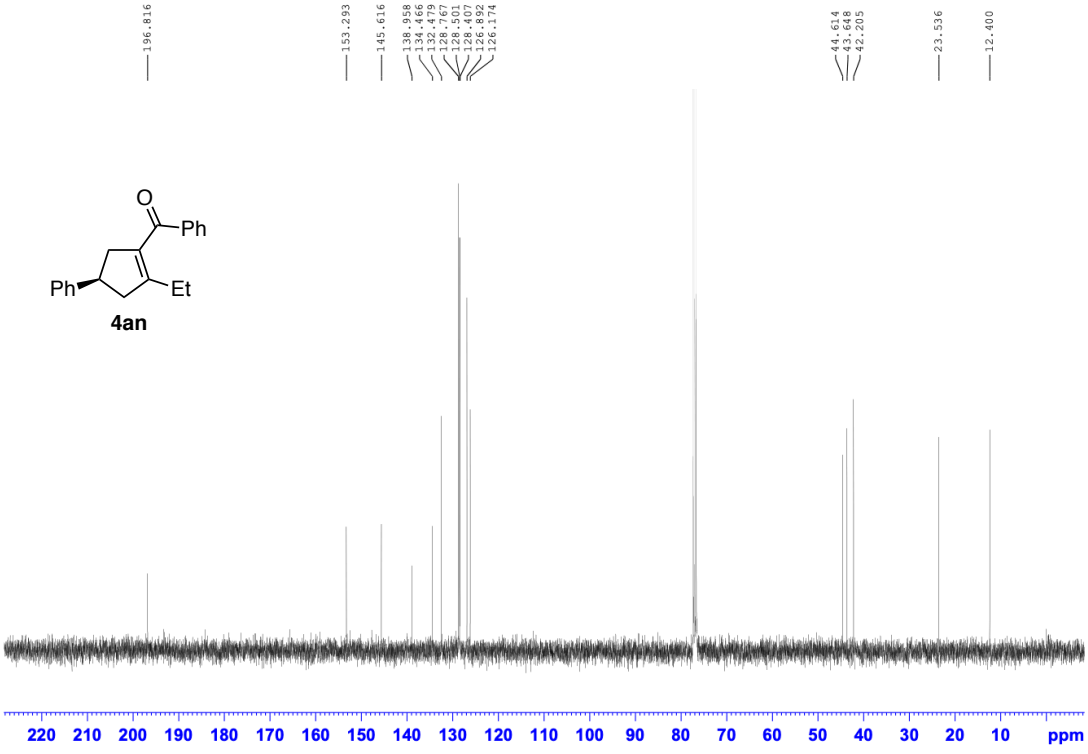

7.83
7.81
7.81
7.57
7.57
7.55
7.55
7.54
7.54
7.47
7.46
7.44
7.34
7.33
7.25
7.23
7.22
7.21
7.20
7.19
7.18
7.04
7.00
6.68
6.64
3.69
3.67
3.65
3.63
3.61
3.38
3.36
3.34
3.32
3.31
3.29
3.11
3.09
3.07
3.05
3.02
3.00
2.98
2.96
O
Ph
Ph
Ph
4al
9
8
7
6
5
4
3
2
1
0 ppm
1.93
1.08
2.05
4.07
6.48
1.11
1.02
1.00
2.05
2.07

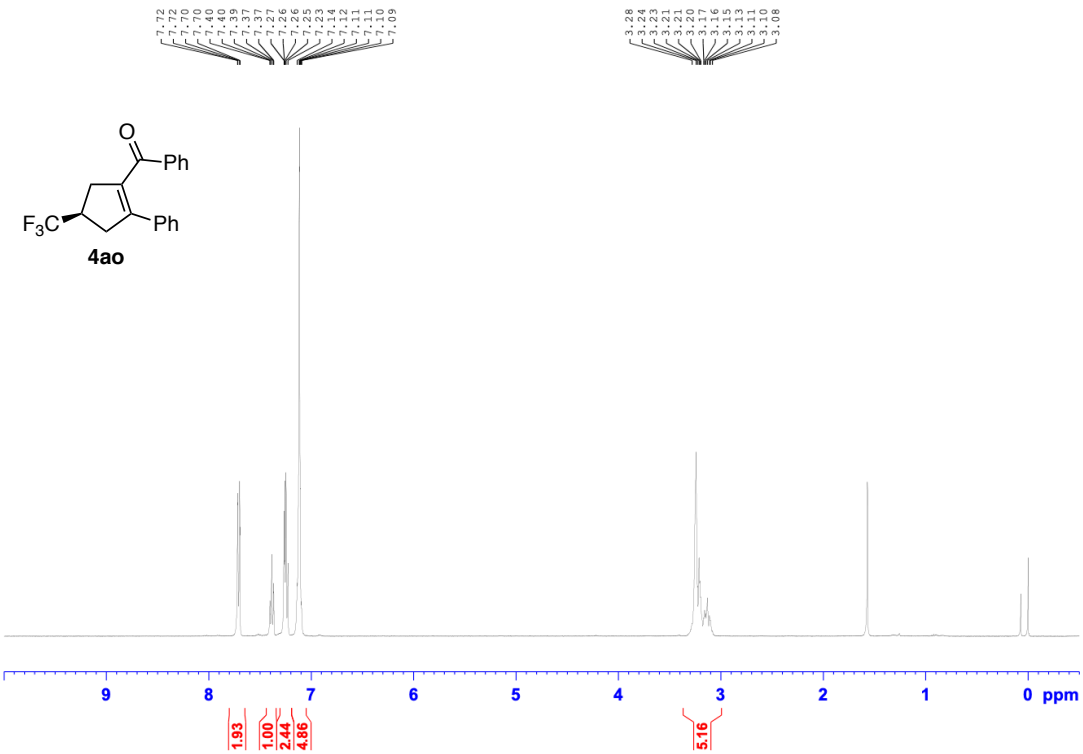

195.899
147.301
145.328
139.321
138.146
136.692
136.133
132.638
129.144
128.715
128.672
128.605
128.388
127.905
127.017
126.437
123.265
44.273
42.058
41.977
O
Ph
Ph
Ph
4al
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

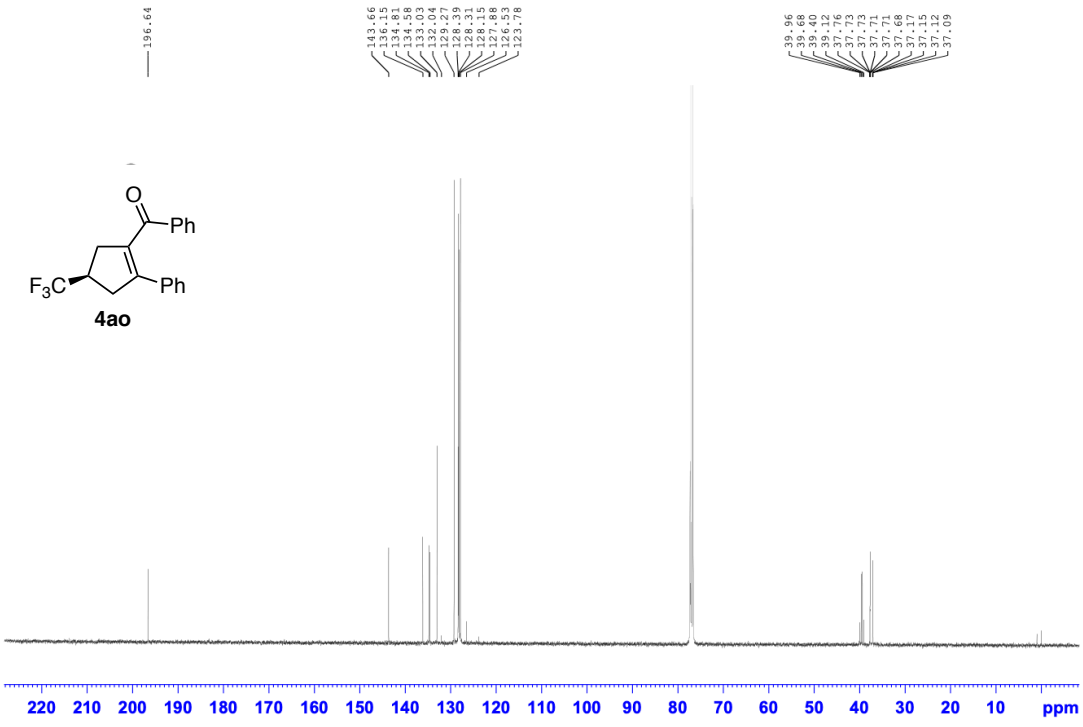

O
Ph
Ph
4am
9
8
7
6
5
4
3
2
1
0 ppm
1.92
0.99
2.12
4.92
2.02
2.03
1.00
5.40
4.18
2.06

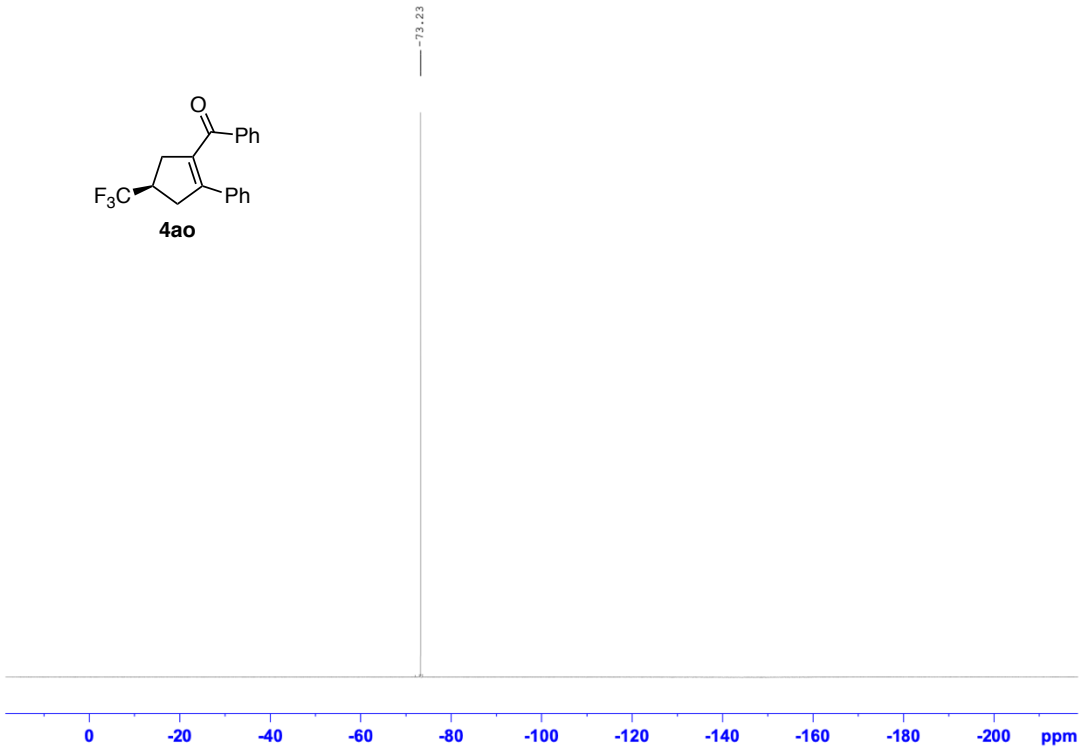

198.16
145.72
136.95
136.64
136.08
132.57
129.27
128.10
127.87
127.77
127.61
43.64
43.20
42.05
41.59
31.55
31.33
26.49
26.27
26.23
O
Ph
Ph
4am
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

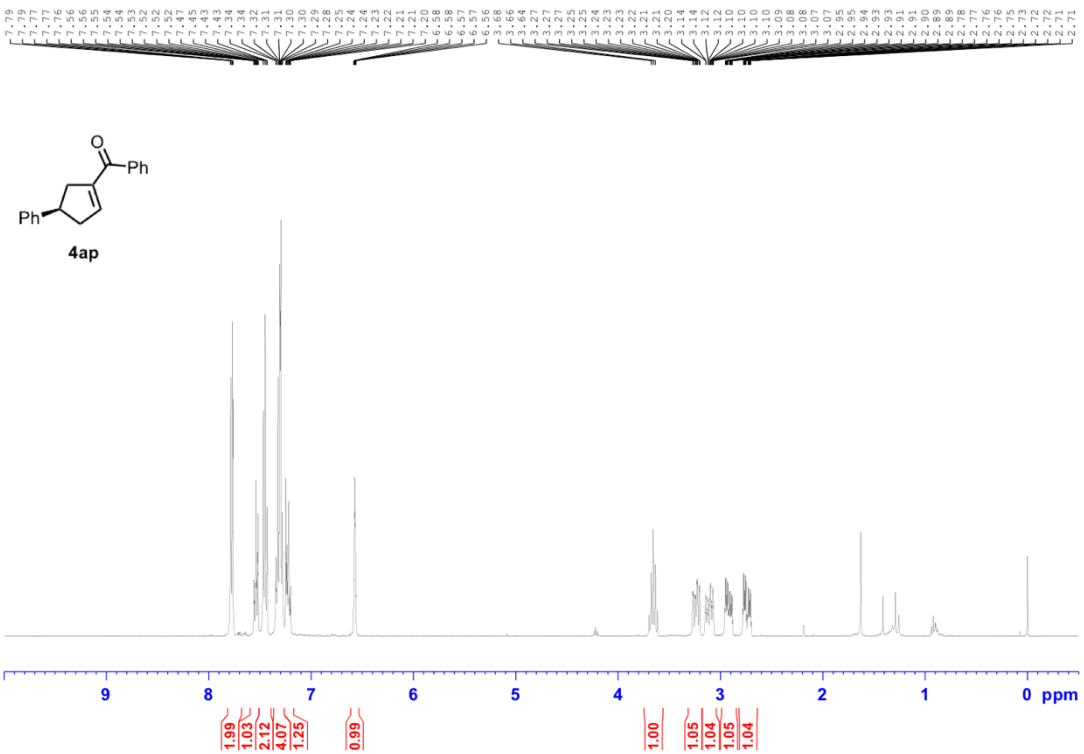

O
Ph
Ph
Et
4an
9
8
7
6
5
4
3
2
1
0 ppm
1.91
1.06
2.01
4.04
1.05
1.00
1.05
2.08
1.05
2.07
3.05

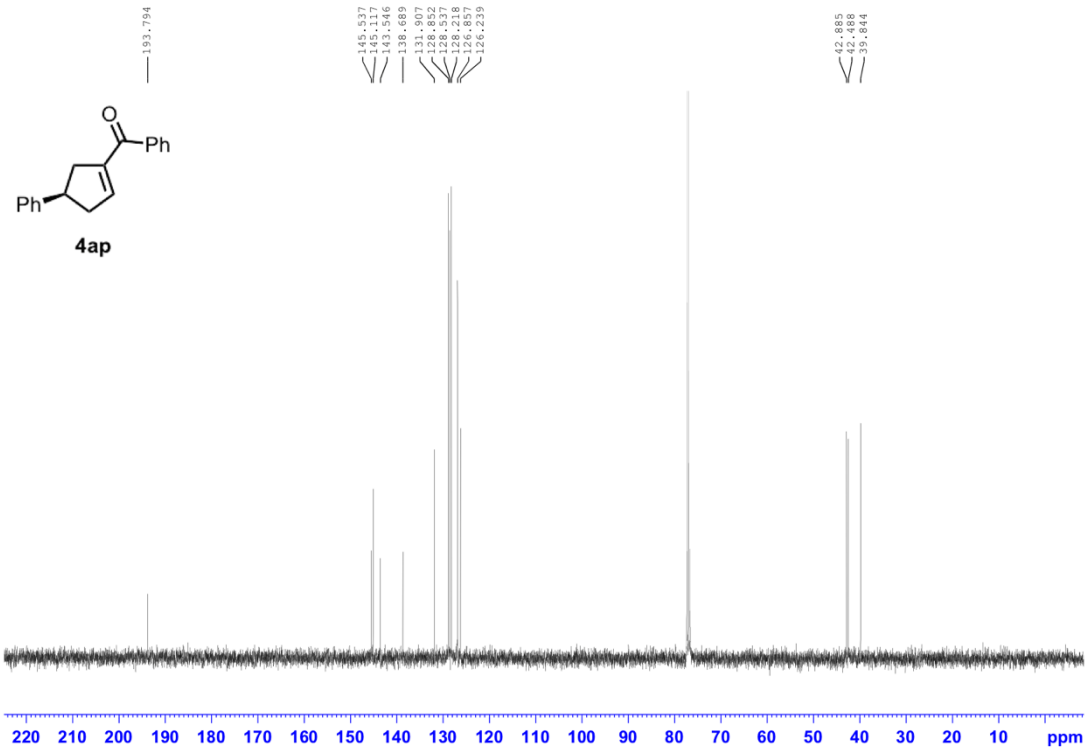

196.816
153.293
145.616
138.958
134.466
132.479
128.767
128.501
128.407
126.992
126.174
44.614
43.648
42.205
23.536
12.400
O
Ph
Ph
Et
4an
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

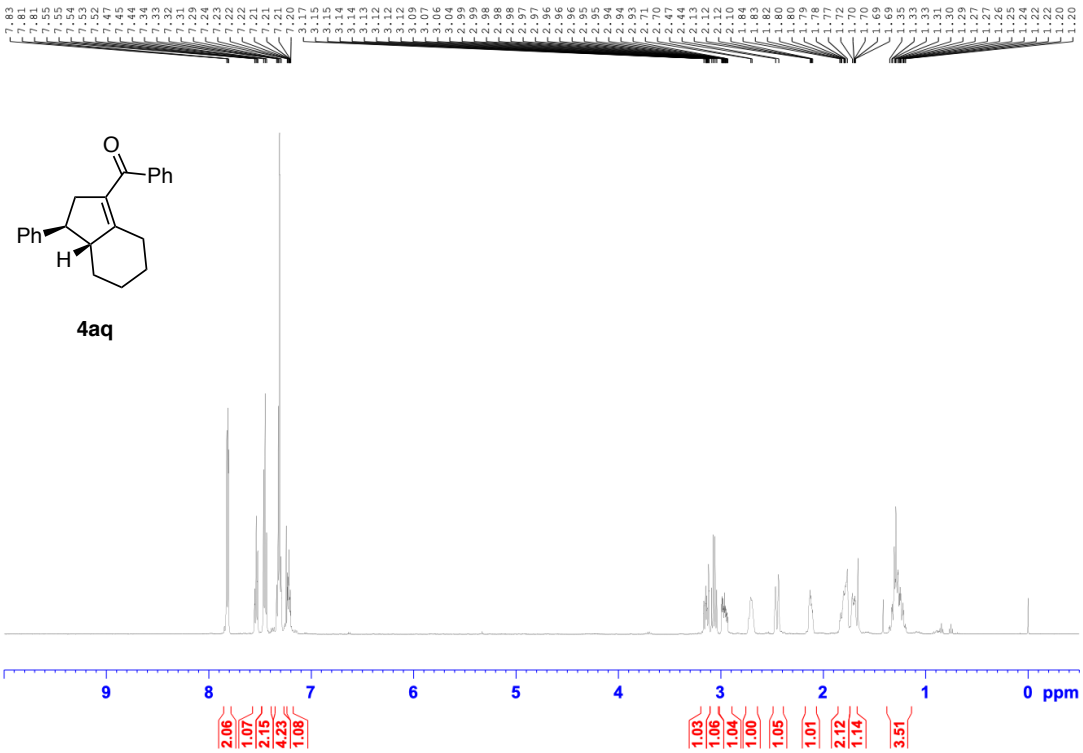

7.72
7.72
7.70
7.70
7.40
7.39
7.37
7.37
7.27
7.26
7.25
7.23
7.14
7.12
7.11
7.11
7.10
7.09
3.28
3.24
3.23
3.21
3.21
3.20
3.17
3.16
3.15
3.13
3.11
3.10
3.08
O
Ph
F3C
Ph
4ao
9
8
7
6
5
4
3
2
1
0
ppm
1.93
1.00
2.44
4.86
5.16

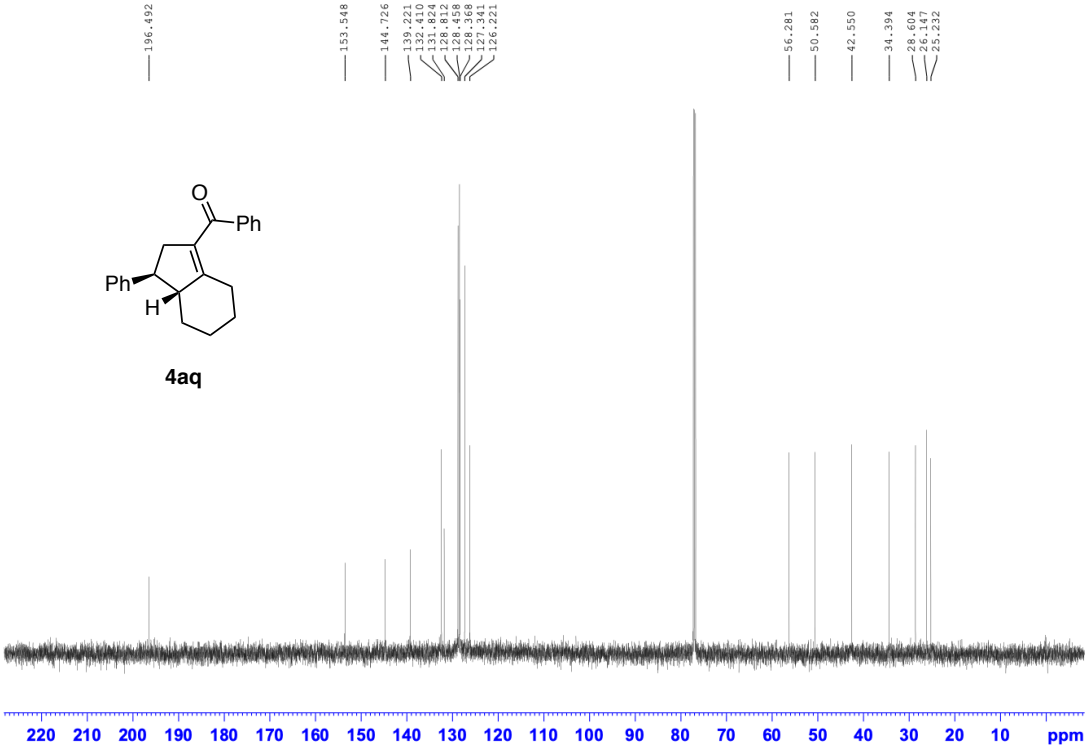

196.64
143.66
136.15
134.81
134.58
133.03
132.04
129.27
128.39
128.31
128.15
127.88
126.53
123.78
39.96
39.68
39.40
39.12
37.76
37.73
37.73
37.71
37.71
37.68
37.17
37.15
37.12
37.09
O
Ph
F3C
Ph
4ao
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

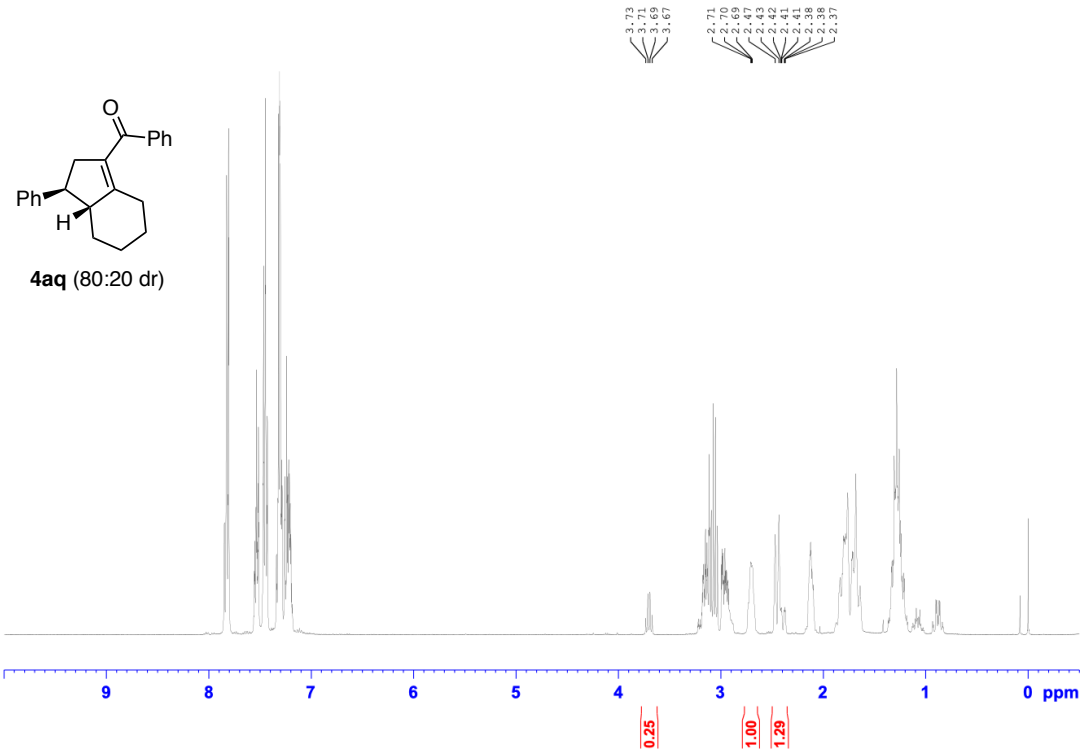

O
Ph
F3C
Ph
4ao
-73.23
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm


4ap
9
8
7
6
5
4
3
2
1
0 ppm
1.99
1.03
2.12
4.07
1.25
0.99
1.00
1.05
1.04
1.05
1.04

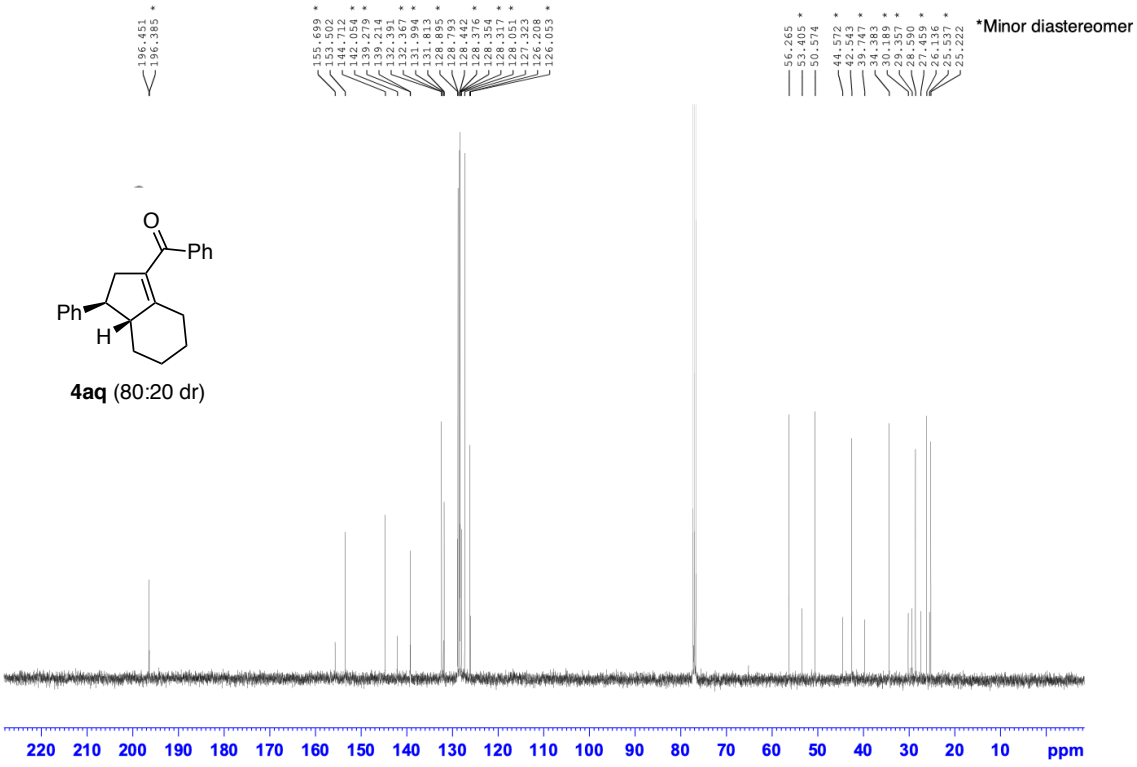

193.794
145.537
145.117
143.546
138.689
131.907
128.852
128.537
128.218
126.857
126.239
42.885
42.488
39.844
4ap
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4aq
9 8 7 6 5 4 3 2 1 0 ppm
2.06 1.07 2.15 4.23 1.08
1.03 1.06 1.04 1.00 1.05 1.01 2.12 1.14 3.51

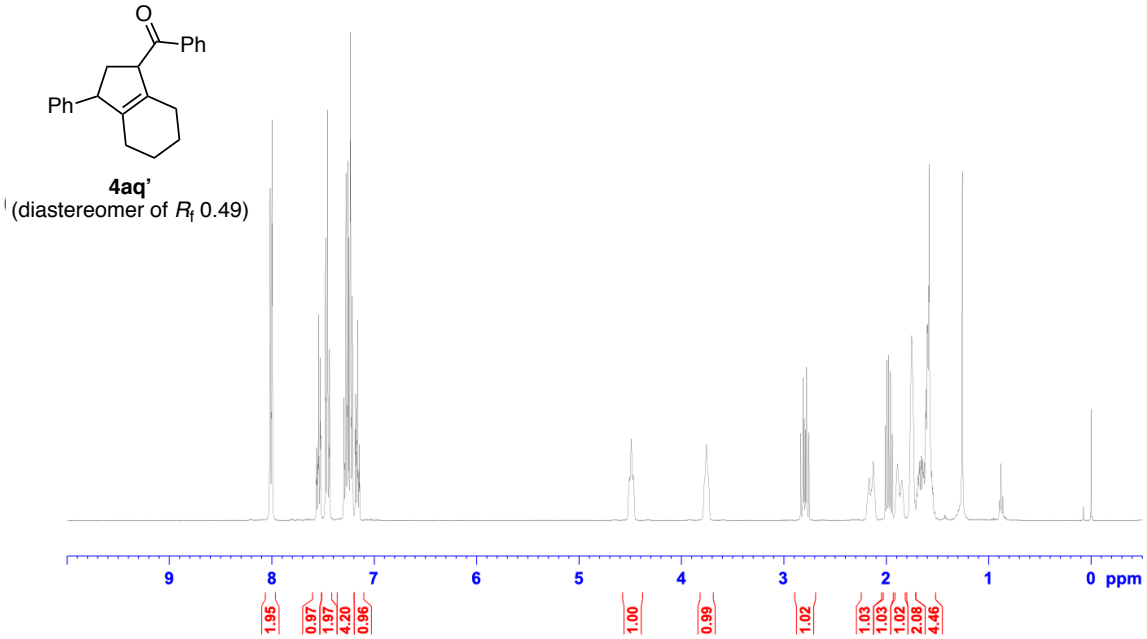

196.492
153.548
144.726
139.221
132.410
131.824
128.812
128.458
128.368
127.411
126.221
56.281
50.582
42.550
34.394
28.604
26.147
25.232
4aq
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

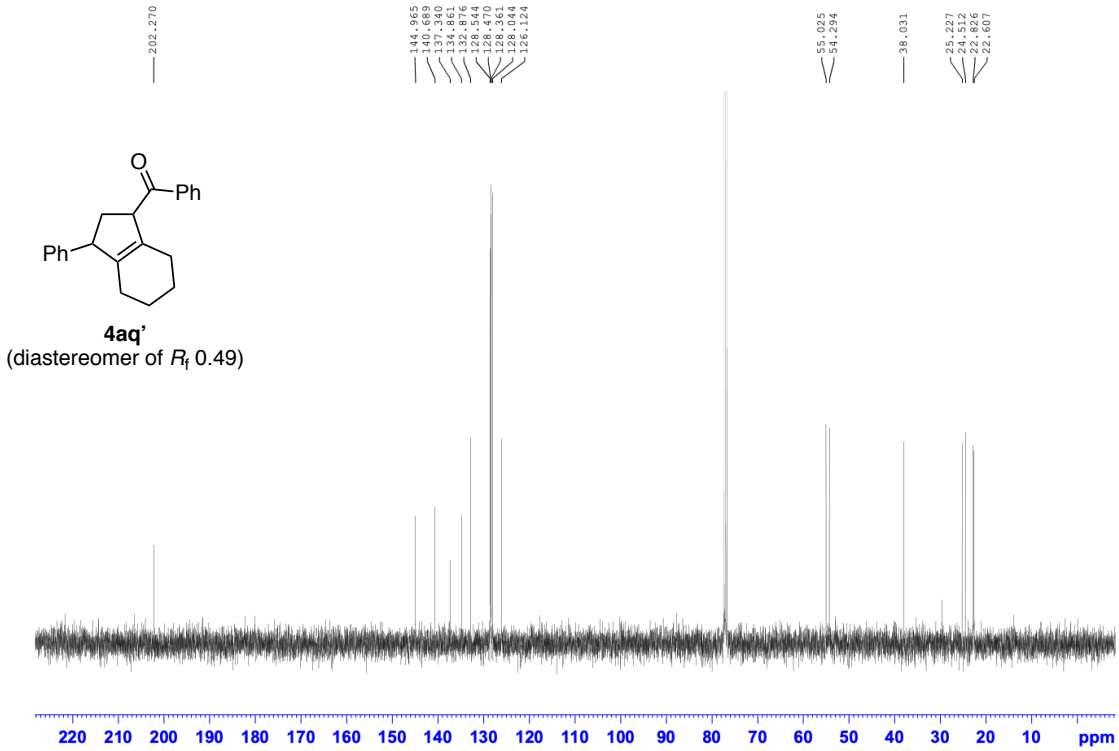


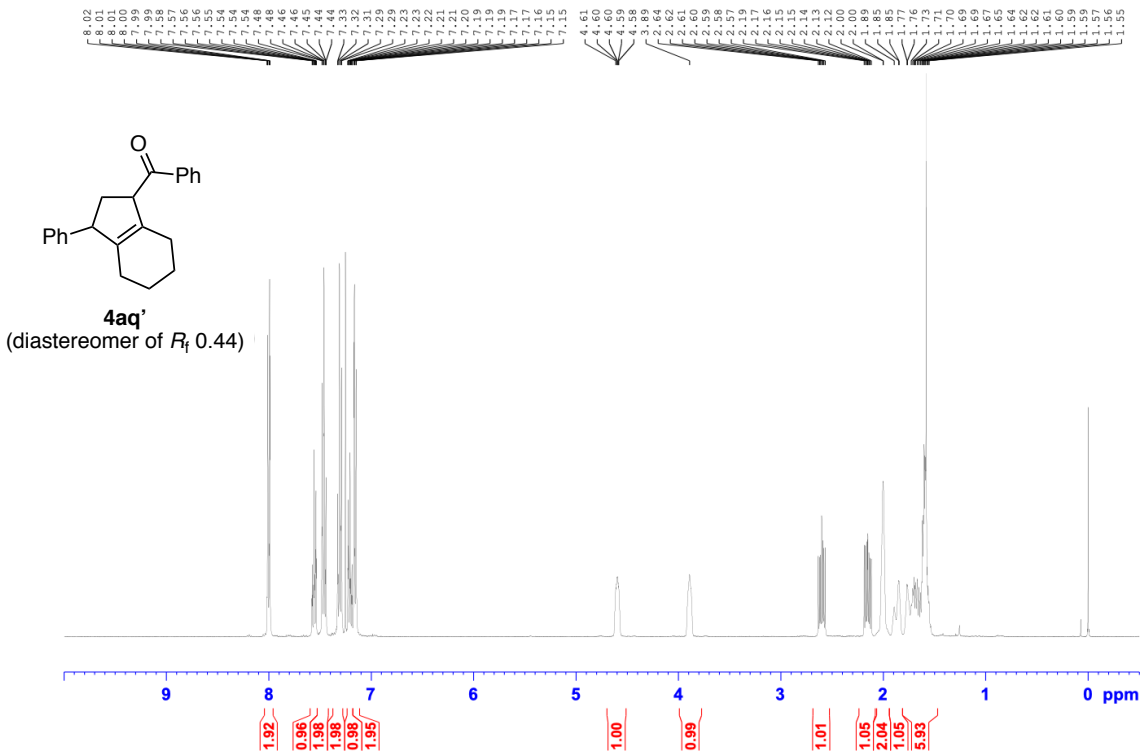
4aq (80:20 dr)

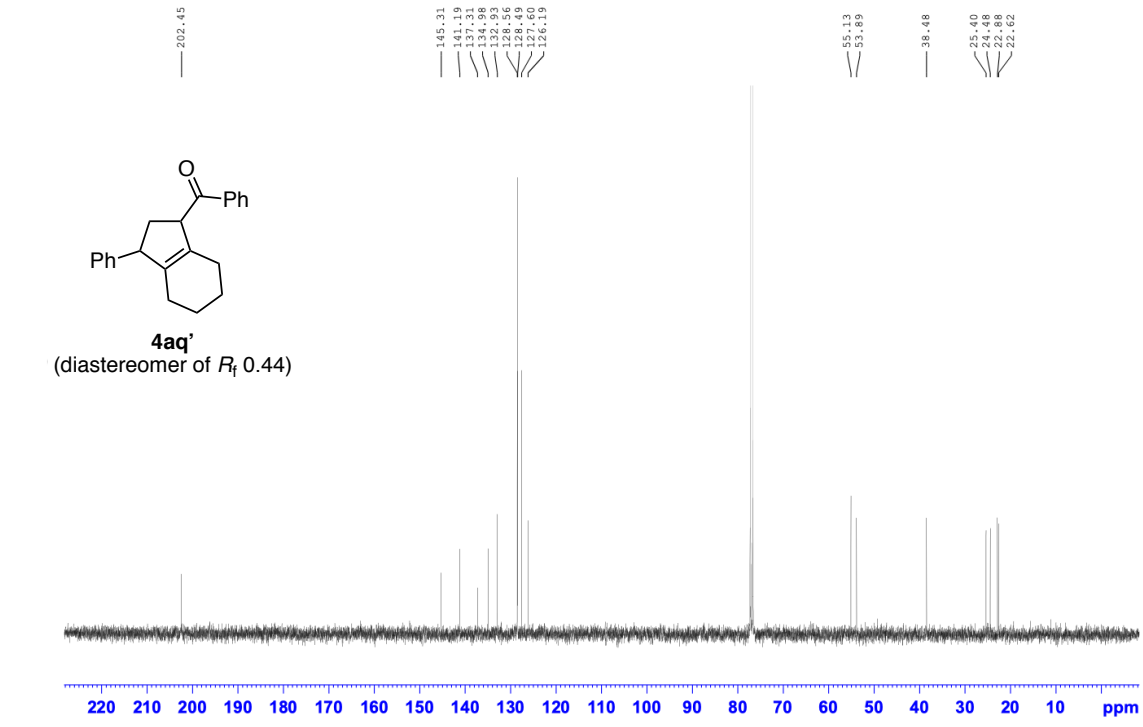


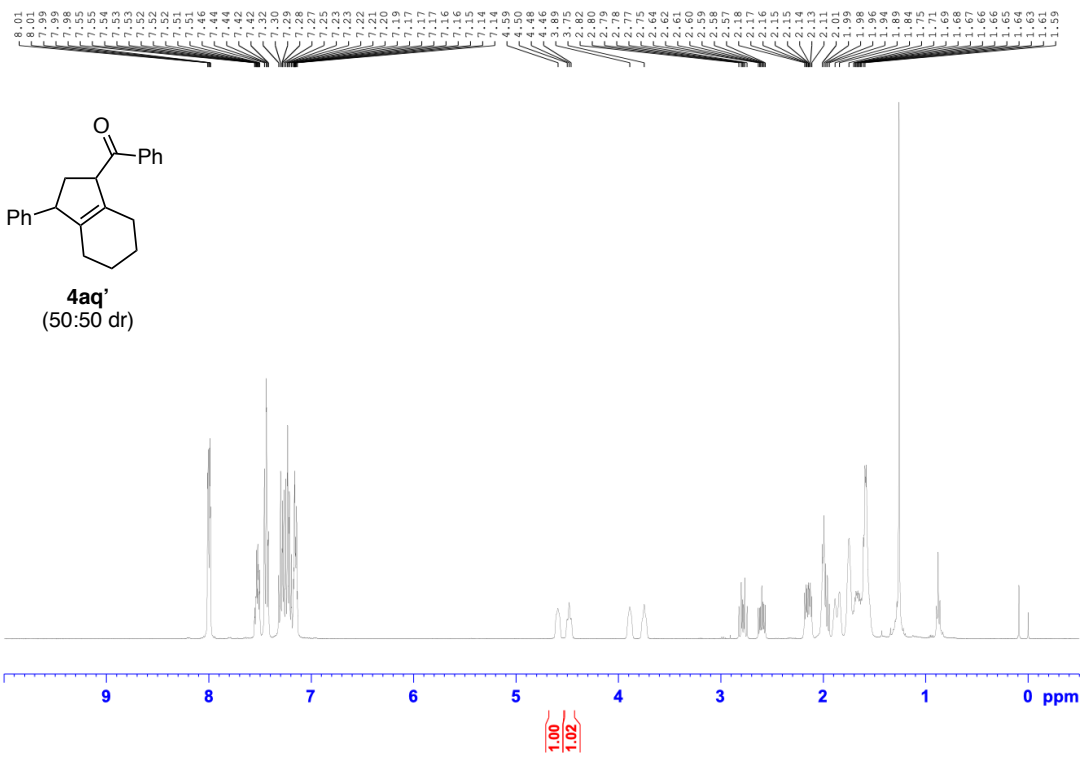
4aq (80:20 dr)

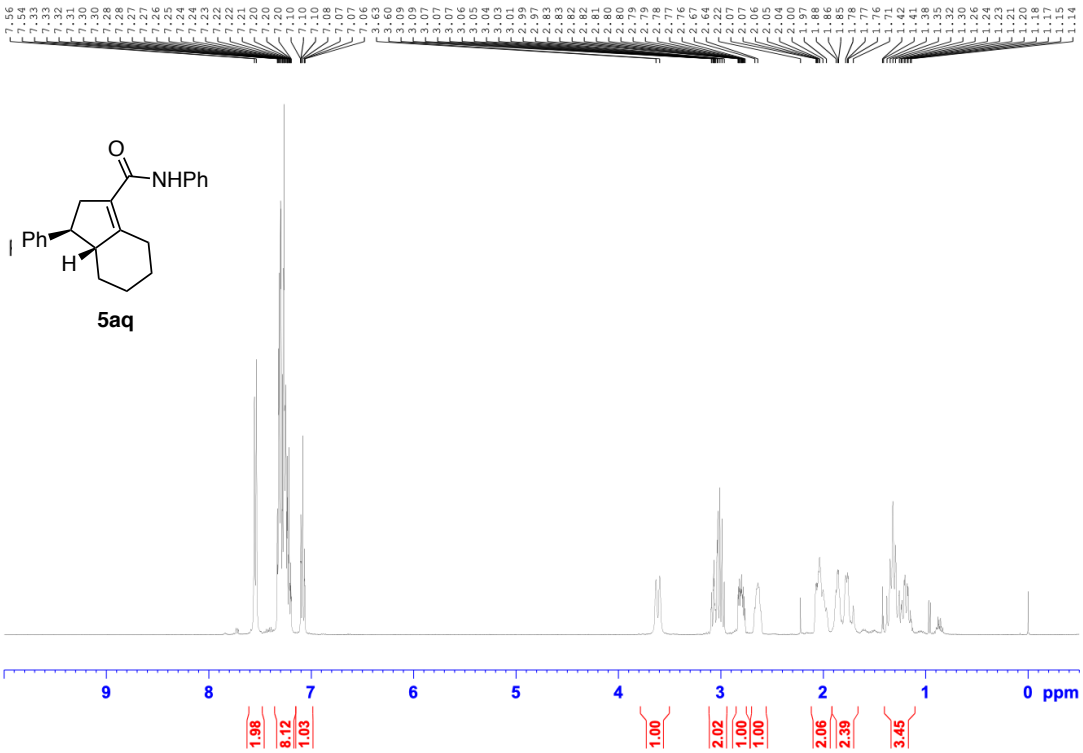

O
Ph
Ph
4aq'
(diastereomer of R_f 0.49)
9
8
7
6
5
4
3
2
1
0 ppm
1.95
0.97
1.97
4.20
0.96
1.00
0.99
1.02
1.03
1.03
1.02
2.08
4.46

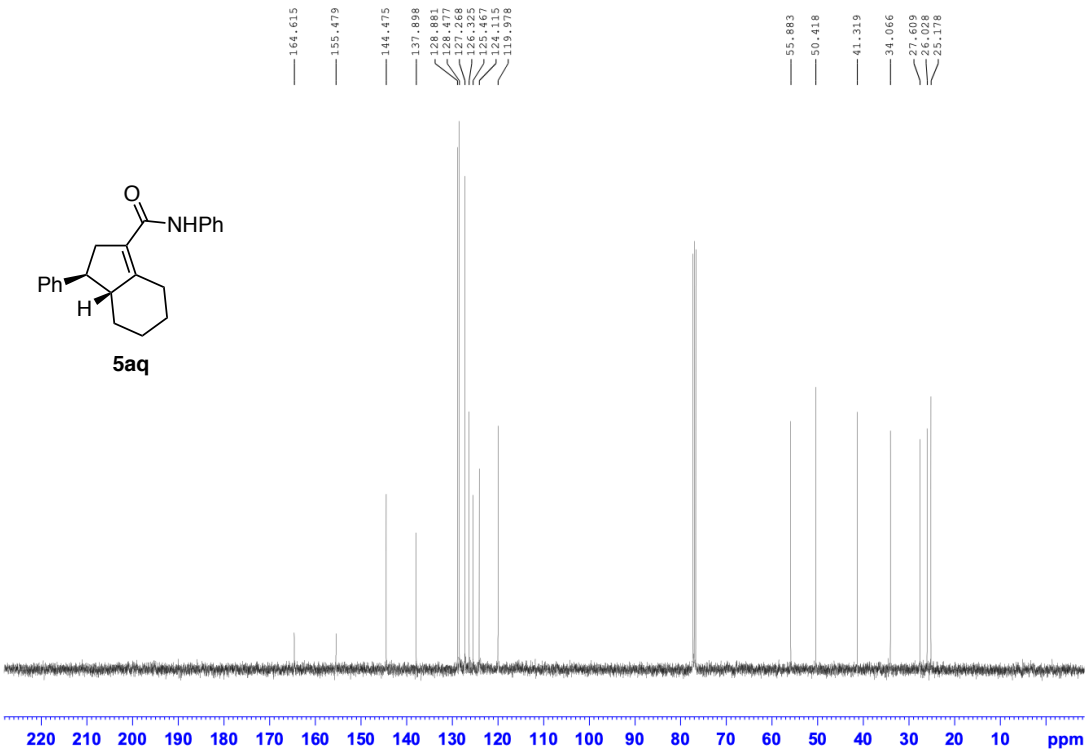

O
Ph
Ph
4aq'
(diastereomer of R_f 0.49)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

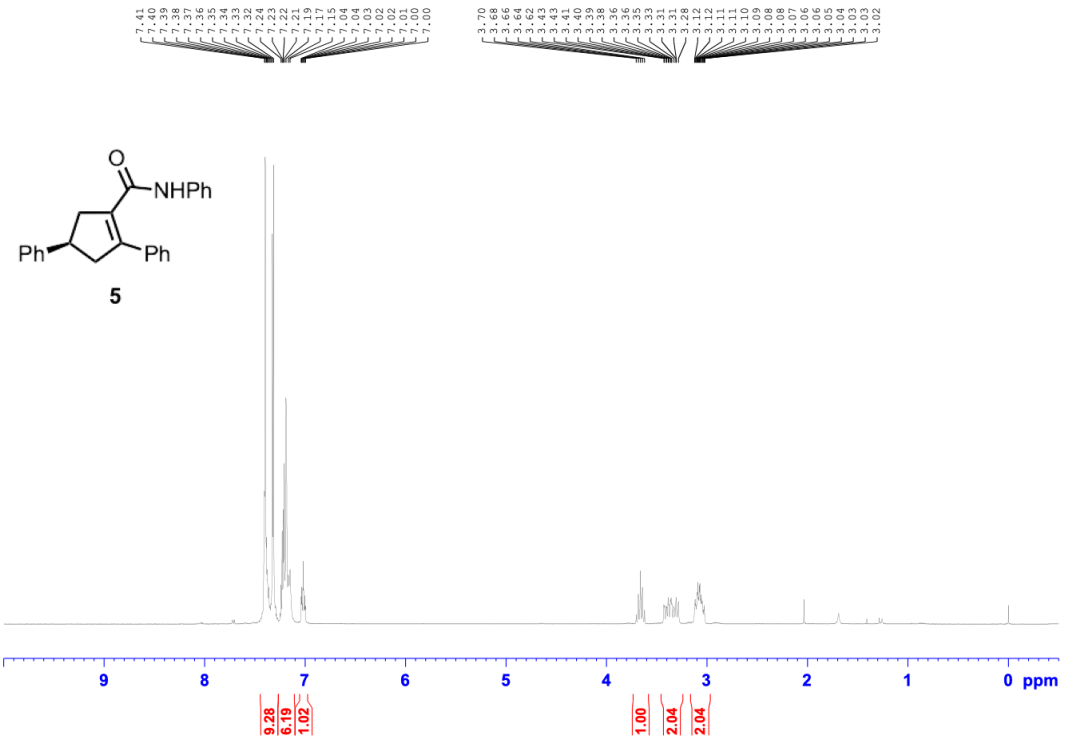

O
Ph
Ph
4aq'
(diastereomer of R_f 0.44)
9
8
7
6
5
4
3
2
1
0 ppm
1.92
0.96
1.98
1.58
0.98
1.95
1.00
0.99
1.01
1.05
2.04
1.05
5.93

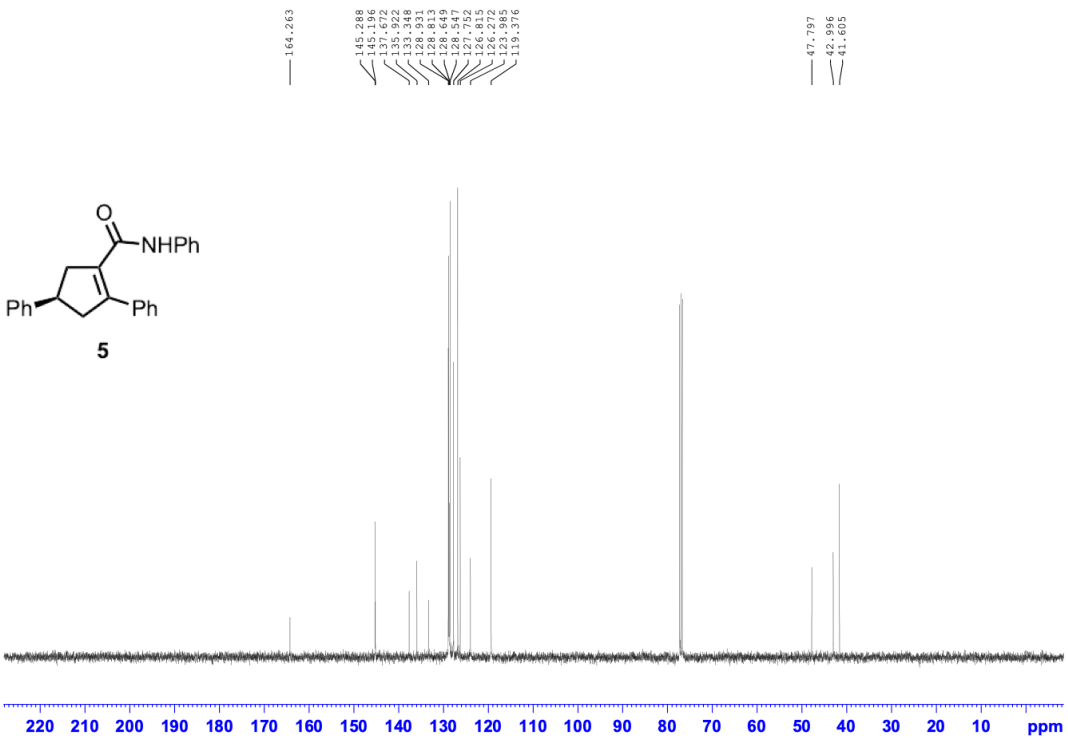

202.45
145.31
141.19
137.31
134.98
132.93
128.56
128.49
127.60
126.19
55.13
53.89
38.48
25.40
24.48
22.88
22.62
O
Ph
Ph
4aq'
(diastereomer of R_f 0.44)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


O
Ph
Ph
4aq'
(50:50 dr)
9
8
7
6
5
4
3
2
1
0 ppm
1.00
1.02


O
NHPh
Ph
H
5aq
9
8
7
6
5
4
3
2
1
0 ppm
1.98
8.12
1.03
1.00
2.02
1.00
1.00
2.06
2.39
3.45


164.615
155.479
144.475
137.898
128.881
128.477
127.268
126.325
125.467
124.115
119.378
55.883
50.418
41.319
34.066
27.609
26.028
25.178
O
NHPh
Ph
H
5aq
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.41
7.40
7.39
7.38
7.37
7.36
7.35
7.34
7.33
7.32
7.24
7.23
7.22
7.21
7.19
7.17
7.15
7.04
7.03
7.02
7.02
7.01
7.00
7.00
3.70
3.68
3.66
3.64
3.62
3.43
3.42
3.41
3.40
3.39
3.38
3.36
3.36
3.35
3.33
3.31
3.31
3.28
3.12
3.12
3.11
3.11
3.10
3.09
3.08
3.08
3.07
3.06
3.06
3.05
3.04
3.03
3.03
3.02
O
NHPh
Ph
Ph
5
9
8
7
6
5
4
3
2
1
0 ppm
9.28
6.19
1.02
1.00
2.04
2.04


164.263
145.288
145.196
137.672
135.922
133.348
128.931
128.813
128.649
128.547
127.752
126.815
126.272
123.985
119.376
47.797
42.996
41.605
O
NHPh
Ph
Ph
5
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
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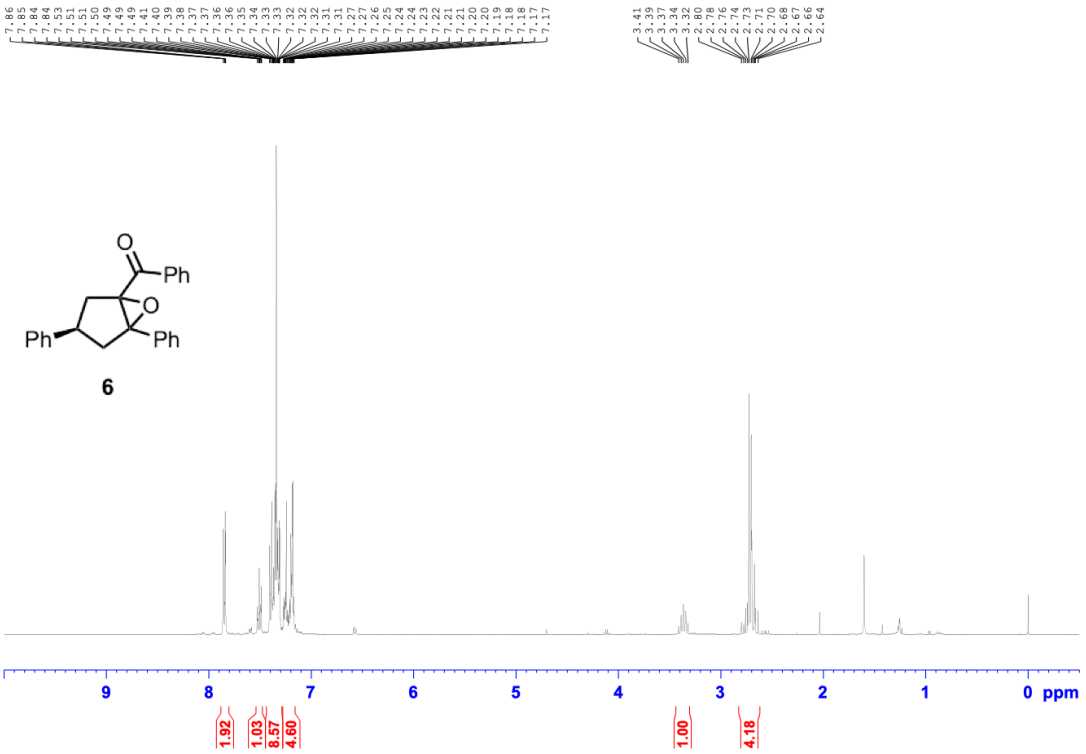
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7.20
7.19
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7.18
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7.17
3.41
3.39
3.37
3.34
3.32
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2.78
2.76
2.74
2.73
2.71
2.70
2.68
2.67
2.66
2.64
O
Ph
O
Ph
Ph
6
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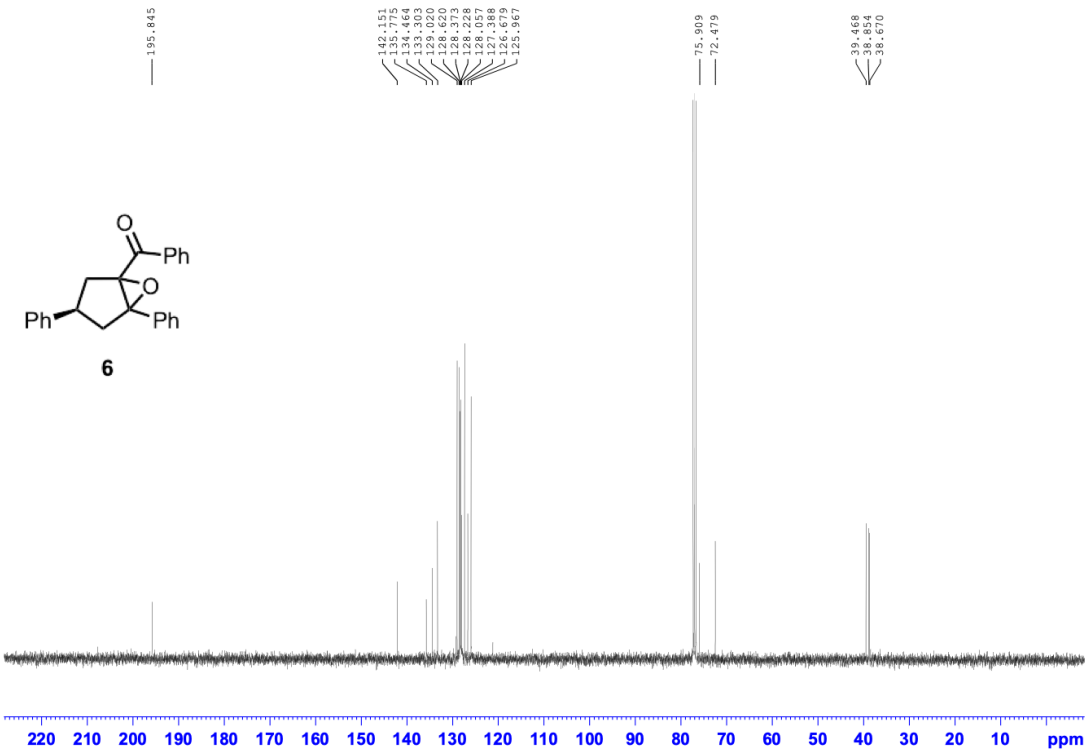
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125.967
75.909
72.479
39.468
38.854
38.670
O
Ph
O
Ph
Ph
6
220
210
200
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180
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150
140
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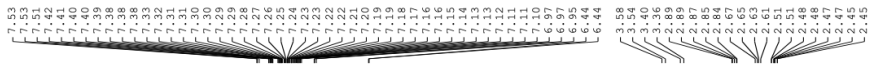

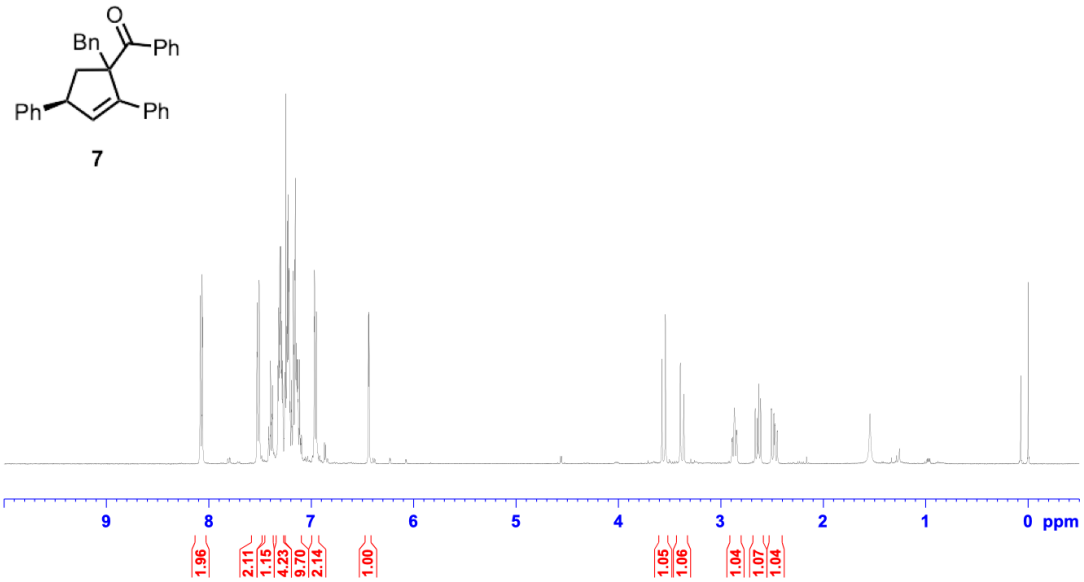
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O
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Ph
Ph
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3
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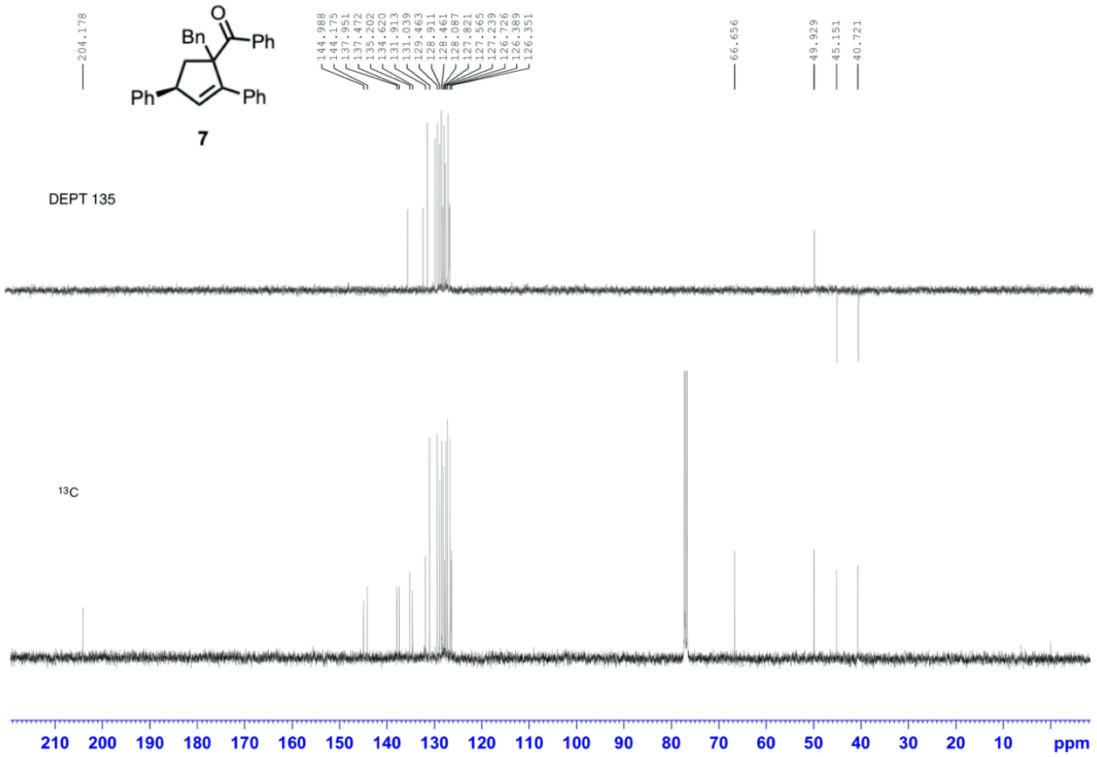
1.04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128.087
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126.726
126.389
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66.656
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45.151
40.721
DEPT 135
13C
210
200
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180
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160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm