

N-Heterocyclic carbene-catalyzed enantioselective synthesis of functionalized cyclopentenes via α,β -unsaturated acyl azoliums

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Supporting Information

1. General Information	S2
2. General Procedure for the Optimization of the Reaction Conditions	S3
3. General Procedure for the Enantioselective Synthesis of Functionalized Cyclopentenes	S4
4. X-ray data of 3c and 11r	S5
5. Synthesis and Characterization of Functionalized Cyclopentenes	S8
6. ¹ H and ¹³ C NMR Spectra of Functionalized Cyclopentenes	S26
7. HPLC Scans of Functionalized Cyclopentenes	S55

1. General Information

Unless otherwise specified, all reactions were carried out under an atmosphere of argon in flame-dried reaction vessels with Teflon screw caps. Dry DME was purchased from commercial sources and stored under argon over 4 Å molecular sieves. The 2-bromoenals were synthesized from the corresponding α,β -unsaturated aldehydes following the literature procedure.¹ All the malonic ester derivatives were prepared following the literature procedure.² The triazolium salt **4** was synthesized following the literature procedure.³ Na₂CO₃ was dried by heating at 120 °C under vacuum and cooling under argon.

Analytical thin layer chromatography was performed on TLC Silica gel 60 F₂₅₄. Visualization was accomplished with short wave UV light or KMnO₄ staining solutions followed by heating. Flash chromatography was performed on silica gel (230-400 mesh) by standard techniques eluting with Pet. Ether-EtOAc solvent system.

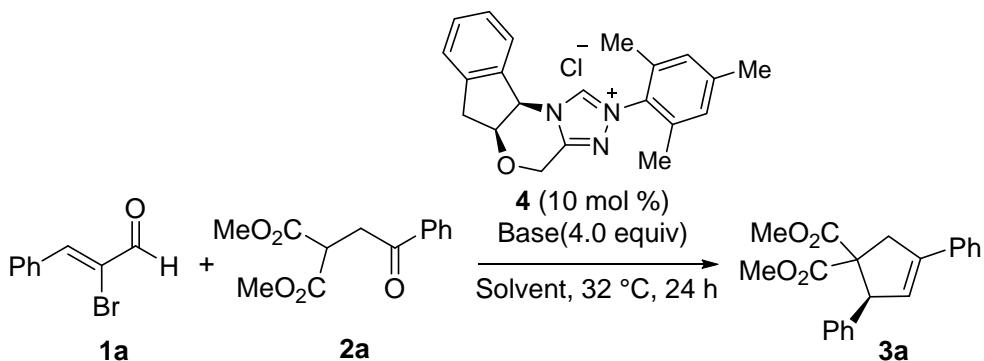
All compounds were fully characterized. ¹H and ¹³C NMR spectra were recorded on Bruker AV 400 in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CDCl₃: δ H = 7.26 ppm, δ C = 77.16 ppm). Infra-red spectra were recorded on a Bruker FT-IR (ATR mode) Infra-red Spectrophotometer. The wave numbers (n) of recorded IR-signals are quoted in cm⁻¹. HRMS (ESI) data were recorded on a Thermo Scientific Q-Exactive, Accela 1250 pump. Optical rotation was measured with a JASCO P 2000 digital polarimeter at rt using 50 mm cell of 1 mL capacity. HPLC analysis was performed on Shimadzu Class-VP V6.12 SP5 with UV detector. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized (Mo K α =0.71073 Å) radiation at ambient temperature.

¹ (a) C. F. H. Allen, and C. O. Edens, Jr. *Org. Synth.*, 1945, **25**, 92; (b) W. Li, J. Li, Z.-K. Wan, J. Wu, and W. Massefski, *Org. Lett.*, 2007, **9**, 4607.

² K. Shen, X. Han, and X. Lu. *Org. Lett.*, 2013, **15**, 1732.

³J. R. Struble, and J. W. Bode, *Org. Synth.*, 2010, **87**, 362.

2. General Procedure for the Optimization of Reaction Conditions



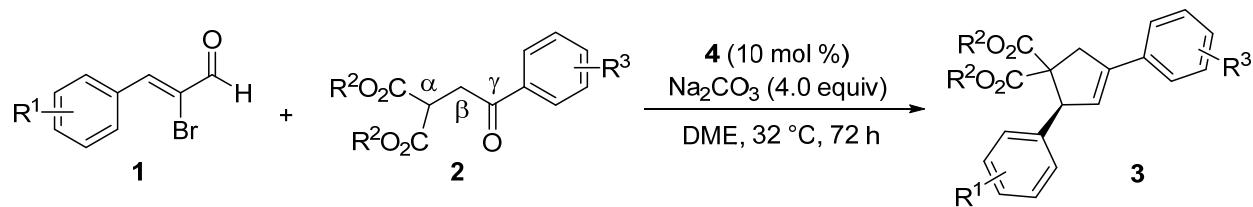
To an oven-dried Schlenk reaction vessel equipped with a magnetic stir bar was taken the (Z)-2-bromo-3-phenylacrylaldehyde **1a** (0.080 g, 0.38 mmol), dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (0.062 g, 0.25 mmol) and base (1.00 mmol, 4.00 equiv) was added. The mixture was kept under argon atmosphere. To this mixture was added solvent (3.0 mL) under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt **4** (9.2 mg, 0.025 mmol, 10 mol %), and the resulting mixture was stirred at 32 °C for 24 h. Evaporation of the solvent followed by silica gel flash column chromatography afforded the cyclopentene derivative **3a**. The enantiomeric excess was determined by HPLC analysis on a chiral column.

Optimization Studies

entry	variation of the standard conditions ^a	yield 3a (%) ^b	ee 3a (%) ^c
1	none	52	99
2	reaction time 60 h instead of 24 h	65	99
3	reaction run at 60 °C instead of 32 °C	<5	n.d.
4	Cs ₂ CO ₃ instead of Na ₂ CO ₃	48	91
5	KOt-Bu instead of Na ₂ CO ₃	<5	n.d.
6	DBU instead of Na ₂ CO ₃	<5	n.d.
7	DABCO instead of Na ₂ CO ₃	30	93
8	Et ₃ N instead of Na ₂ CO ₃	10	86
9	1,4-dioxane instead of THF	<5	n.d.
10	toluene instead of THF	10	99
11	DME instead of THF	54	99
12	DME instead of THF, run for 72 h	75	99

^a Standard conditions: **1a** (0.38 mmol), **2a** (0.25 mmol), **4** (10 mol %), Na₂CO₃ (4.0 equiv), THF (3.0 mL), 32 °C and 24 h. ^b Isolated yield after column chromatography. ^c Determined by HPLC analysis on a chiral column.

3. General Procedure for the Enantioselective Synthesis of Functionalized Cyclopentenes



To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the 2-bromoaldehyde **1** (0.75 mmol), the malonic ester derivative **2** (0.50 mmol), and Na₂CO₃ (212 mg, 2.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (6.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt **4** (18.4 mg, 0.05 mmol), and the resulting mixture was stirred at 32 °C for 72 h. Evaporation of the solvent followed by silica gel flash column chromatography afforded the cyclopentene derivatives **3** in moderate to good yields with excellent enantioselectivity. [The racemic cyclopentenes were synthesized by treating **1** and **2** with IMes.HCl in the presence of Cs₂CO₃ (1.5 equiv) and NaH (1.0 equiv) in THF for 12 h at 32 °C]

4. X-ray data of **3c** and **11r**

Single crystals of compound **3c**, obtained from dichloromethane. X-ray intensity data were collected on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized ($\text{Mo K}\alpha=0.71073\text{ \AA}$) radiation at ambient temperature. The X-ray generator was operated at 50 kV and 30 mA. Diffraction data were collected with a ω scan width of 0.5° and at different settings of φ and 2θ . The sample-to-detector distance was fixed at 5.00 cm. The X-ray data acquisition was monitored by APEX II program suite.⁴ All the data were corrected for Lorentz-polarization and absorption effects using SAINT and SADABS programs integrated in APEX II program package.¹ The structures were solved by direct method and refined by full matrix least squares, based on F^2 , using SHELX-97.⁵ All the H-atoms were placed in geometrically idealized position (C-H = 0.93 Å for the phenyl H-atom, C-H = 0.97 Å for the methylene H-atom, C-H = 0.98 Å for the methine H-atom and C-H = 0.96 Å for the methyl H-atom) and constrained to ride on their parent atoms [$U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for the phenyl, methylene and methine group and $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C})$ for the methyl group]. ORTEP was generated using ORTEP-32 program.⁶

Crystallographic data for **3c.** ($\text{C}_{21}\text{H}_{19}\text{O}_4\text{Br}$): $M = 415.27$, Crystal dimensions $0.49 \times 0.45 \times 0.41$ mm³, trigonal, space group $P\ 3_2$, $a = 11.7082(7)$, $b = 11.7082(7)$, $c = 11.9217(8)\text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$, $V = 1415.30(15)\text{ \AA}^3$, $Z = 3$, $\rho_{\text{calcd}} = 1.462\text{ gcm}^{-3}$, $\mu(\text{Mo-K}\alpha) = 2.201\text{ mm}^{-1}$, $F(000) = 636$, $2\theta_{\text{max}} = 67.22^\circ$, $T = 296(2)\text{ K}$, 32442 reflections collected, 7324 unique ($R_{\text{int}}=0.0360$), 4525 observed ($I > 2\sigma(I)$) reflections, 238 refined parameters, R value 0.0340, $wR2 = 0.0730$, (all data $R = 0.0759$, $wR2 = 0.0838$), $S = 0.995$, minimum and maximum transmission 0.412 and 0.466; maximum and minimum residual electron densities +0.44 and -0.43 e Å⁻³. The absolute configuration was established by anomalous dispersion effect (Flack parameter of 0.0174(11)) in X-ray diffraction measurements which is caused by the presence of bromine atom in the molecule.

⁴ Bruker (2006). *APEX2, SAINT and SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

⁵ G. M. Sheldrick, *Acta Crystallogr.*, 2008, **A64**, 112.

⁶ L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.

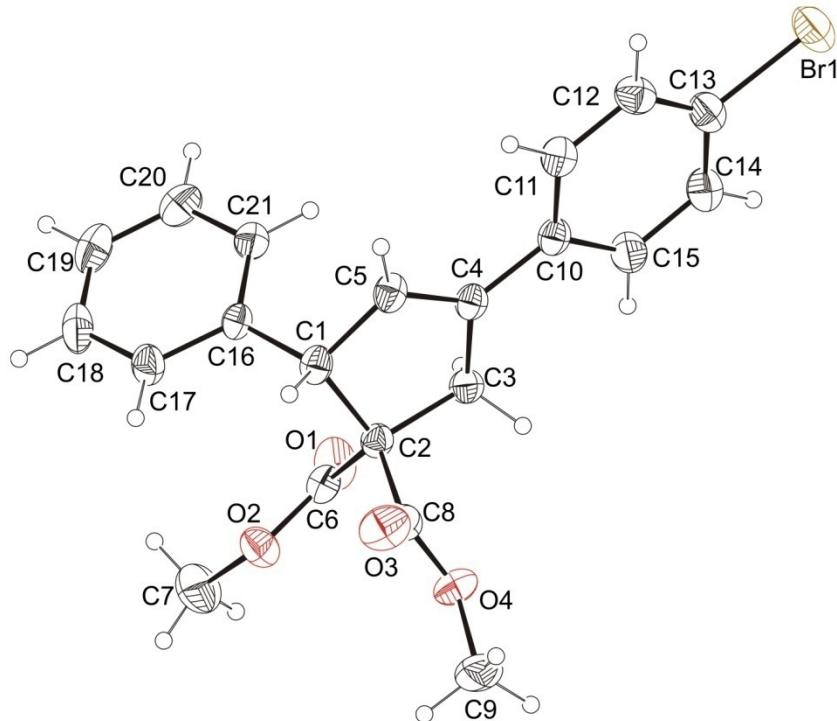


Figure 1. ORTEP of **3c** showing atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

X-ray intensity data measurements of compound **11r** was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized ($\text{MoK}_\alpha = 0.71073\text{\AA}$) radiation at room temperature. The X-ray generator was operated at 50 kV and 30 mA. A preliminary set of cell constants and an orientation matrix were calculated from three sets of 36 frames. Data were collected with ω scan width of 0.5° at different settings of φ and 2θ with a frame time of 15 secs keeping the sample-to-detector distance fixed at 5.00 cm. The X-ray data collection was monitored by APEX2 program (Bruker, 2006). All the data were corrected for Lorentzian, polarization and absorption effects using SAINT and SADABS programs (Bruker, 2006). SHELX-97 was used for structure solution and full matrix least-squares refinement on F^2 . All the hydrogen atoms were placed in geometrically idealized position and constrained to ride on their parent atoms. ORTEP III3 views of both compounds were drawn with 30% probability displacement ellipsoids and H atoms are shown as small spheres of arbitrary radii.

Crystal data of **11r** $C_{20}H_{22}O_8$, $M = 390.38$, colorless block, $0.39 \times 0.09 \times 0.06 \text{ mm}^3$, monoclinic, space group $C2$, $a = 20.4540(10) \text{ \AA}$, $b = 7.1698(3) \text{ \AA}$, $c = 15.6356(8) \text{ \AA}$, $\beta = 121.607(6)^\circ$, $V = 1952.84(16) \text{ \AA}^3$, $Z = 4$, $T = 296(2) \text{ K}$, $2\theta_{\max} = 52.00^\circ$, $D_{\text{calc}} (\text{g cm}^{-3}) = 1.328$, $F(000) = 824$, $\mu (\text{mm}^{-1}) = 0.103$, 11890 reflections collected, 3508 unique reflections ($R_{\text{int}} = 0.0436$), 2708 observed ($I > 2\sigma(I)$) reflections, multi-scan absorption correction, $T_{\min} = 0.961$, $T_{\max} = 0.994$, 257 refined parameters, $S = 1.095$, $R1 = 0.0515$, $wR2 = 0.0972$ (all data $R = 0.0722$, $wR2 = 0.1054$), maximum and minimum residual electron densities; $\Delta\rho_{\max} = 0.14$, $\Delta\rho_{\min} = -0.17 (\text{e\AA}^{-3})$.

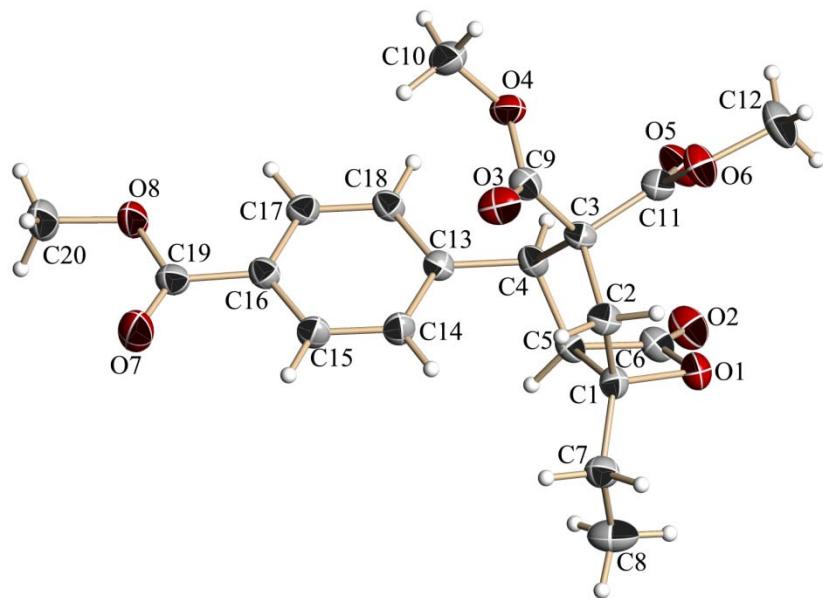
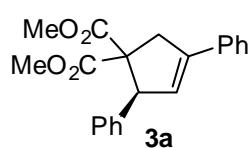


Figure 2. ORTEP of **11r** showing atom numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii.

5. Synthesis and Characterization of Functionalized Cyclopentenes

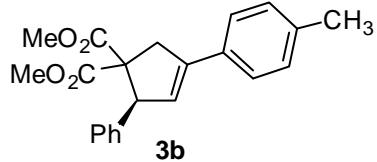
Dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (**3a**)⁷



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.3 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate **3a** as a light yellow solid (126.1 mg, 75%).

R_f (Pet. ether /EtOAc = 80/20): 0.65; 99% ee, [α]_D²⁵ = -279.45 (c 0.4, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.0 min, Minor: 13.3 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.54 (d, *J* = 7.4 Hz, 2H, H_{ar}), 7.39 (t, *J* = 7.7 Hz, 2H, H_{ar}), 7.33-7.22 (m, 6H, H_{ar}), 6.16 (s, 1H, H_{olefinic}), 5.08 (s, 1H), 3.97-3.92 (m, 1H), 3.81 (s, 3H, CH₃), 3.21(d, *J* = 17.0 Hz, 1H), 3.18 (s, 3H, CH₃). **¹³C NMR** (100 MHz, CDCl₃) δ 172.56, 169.86, 140.39, 139.22, 135.09, 129.19, 128.62, 128.17, 127.99, 127.50, 126.39, 125.95, 65.22, 57.35, 53.11, 52.06, 40.83. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₂₀O₄Na: 359.1254, found: 359.1247. **FTIR (cm⁻¹)** 3463, 3059, 3029, 2952, 2843, 2104, 1734, 1697, 1638, 1436, 1257, 1196, 1164, 1028, 964, 863, 697.

Dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (**3b**)



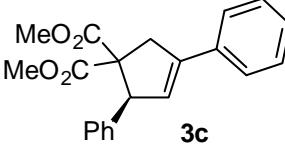
Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-(p-tolyl)ethyl)malonate **2b** (132.0 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate **3b** as a white solid (96.4 mg, 55%).

R_f (Pet. ether /EtOAc = 80/20): 0.67; 99% ee, [α]_D²⁵ = -250.61 (c 0.3, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.4 min, Minor: 20.0 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.45 (d, *J* = 8.1 Hz, 2H, H_{ar}), 7.32-7.25 (m, 5H, H_{ar}), 7.22 (d, *J* = 8.0, 2H,

⁷ K. Mochizuki, K. Sakai, T. Kochi, and F. Kakiuchi, *Synthesis*, 2013, 2088.

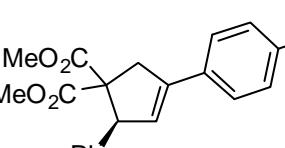
H_{ar}) 6.12 (s, 1H, $H_{olefinic}$), 5.09 (s, 1H), 3.97–3.93 (m, 1H), 3.82 (s, 3H, CH_3), 3.23–3.19 (m, 4H), 2.41 (s, 3H, CH_3). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.57, 169.90, 140.25, 139.34, 137.84, 132.28, 129.28, 129.18, 128.13, 127.44, 125.86, 125.39, 65.21, 57.31, 53.08, 52.03, 40.83, 21.31. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{22}H_{22}O_4Na$: 373.1410, found: 373.1401. **FTIR (cm⁻¹)** 3427, 3028, 2951, 1734, 1634, 1514, 1492, 1435, 1262, 1222, 1196, 1164, 1058, 964, 903, 763, 668.

Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)

 Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-bromophenyl)-2-oxoethyl)malonate **2c** (164.5 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3c** as a white solid (176.0 mg, 85%).

R_f (Pet. ether /EtOAc = 80/20): 0.64; 99% ee, $[\alpha]_D^{25} = -203.02$ (c 0.25, $CHCl_3$). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 13.8 min, Minor: 27.6 min. **1H NMR (400 MHz, $CDCl_3$)** δ 7.52–7.49 (m, 2H, H_{ar}), 7.40–7.38 (m, 2H, H_{ar}), 7.31–7.21 (m, 5H, H_{ar}), 6.16–6.14 (m, 1H, $H_{olefinic}$), 5.07 (s, 1H), 3.93–3.88 (m, 1H), 3.81 (s, 3H, CH_3), 3.18–3.14 (m, 4H). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 172.43, 169.78, 139.41, 138.99, 134.02, 131.75, 129.16, 128.24, 127.61, 127.54, 127.24, 121.91, 65.22, 57.42, 53.19, 52.14, 40.83. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{21}H_{19}O_4BrNa$: 437.0359, found: 437.0349. **FTIR (cm⁻¹)** 3685, 3432, 3021, 2401, 2357, 1713, 1602, 1521, 1490, 1433, 1266, 1216, 1075, 929, 772, 670.

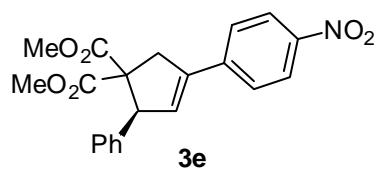
Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)

 Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-fluorophenyl)-2-oxoethyl)malonate **2d** (134.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol)

in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*S*)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3d** as a white solid (110.0 mg, 62%).

R_f (Pet. ether /EtOAc = 80/20): 0.62; >99% ee, $[\alpha]_D^{25} = -234.52$ (c 0.5, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 12.6 min, Minor: 20.9 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.51-7.48 (m, 2H, H_{ar}), 7.31-7.23 (m, 5H, H_{ar}), 7.09-7.05 (m, 2H, H_{ar}), 6.08 (s, 1H, H_{olefinic}), 5.08 (s, 1H), 3.94-3.89 (m, 1H), 3.81 (s, 3H, CH₃), 3.19-3.15 (m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 172.45, 169.80, 162.54 (d, *J* = 248.6 Hz), 139.22 (d, *J* = 18.7 Hz), 131.27 (d, *J* = 3.2 Hz), 129.12, 128.18, 127.62, 127.53, 126.07, 115.50 (d, *J* = 21.6 Hz), 65.20, 57.32, 53.13, 52.08, 40.97. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₄FNa: 377.1160, found: 377.1150. **FTIR (cm⁻¹)** 3466, 3027, 2953, 2845, 1732, 1638, 1603, 1511, 1436, 1224, 1099, 1059, 1023, 939, 834, 759.

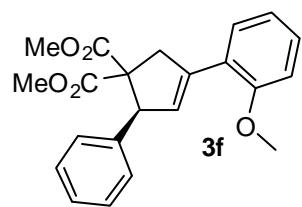
Dimethyl (*S*)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(4-nitrophenyl)-2-oxoethyl)malonate **2e** (147.6 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 120 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford Dimethyl (*S*)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3e** as a yellow oil (134.0 mg, 70%).

R_f (Pet. ether /EtOAc = 80/20): 0.48; 99% ee, $[\alpha]_D^{25} = -217.42$ (c 0.2, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 19.6 min, Minor: 40.7 min. **¹H NMR** (400 MHz, CDCl₃) δ 8.23 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.64 (d, *J* = 8.8 Hz, 2H, H_{ar}), 7.29–7.20 (m, 5H, H_{ar}), 6.36 (s, 1H, H_{olefinic}), 5.12 (s, 1H), 3.98–3.92 (m, 1H), 3.82 (s, 3H, CH₃), 3.21 (d, *J* = 16.7, 1H), 3.16 (s, 3H, CH₃). **¹³C NMR** (100 MHz, CDCl₃) δ 172.15, 169.53, 147.15, 141.26, 138.18, 138.36, 131.33, 129.07, 28.31, 127.77, 126.54, 123.98, 65.10, 57.51, 53.25, 52.20, 40.80. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₆NNa: 404.1105, found: 404.1097. **FTIR (cm⁻¹)** 3444, 3021, 2401, 2357, 1731, 1635, 1520, 1434, 1345, 1268, 1216, 1107, 929, 848, 771, 670.

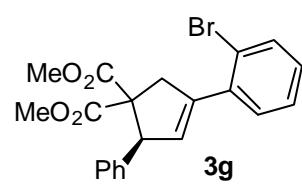
Dimethyl (*S*)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-methoxyphenyl)-2-oxoethylmalonate **2f** (104.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (DCM-Pet. ether 40:60) to afford dimethyl (*S*)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3f** as a white solid (124.5 mg, 68%).

R_f (Pet. ether /EtOAc = 80/20): 0.57; >99% ee, $[\alpha]_D^{25} = -218.22$ (c 0.25, CHCl_3). **HPLC** (Chiralcel OJ-H, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 17.3 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.39 (dd, $J_1 = 1.56$ Hz, $J_2 = 7.56$ Hz, 1H, H_{ar}), 7.29-7.20 (m, 6H, Har), 7.00-6.93 (m, 2H, H_{ar}), 6.40-6.39 (m, 1H, H_{olefinic}), 5.06 (s, 1H), 4.00-3.96 (m, 1H), 3.87 (s, 3H, CH₃), 3.79 (s, 3H, CH₃), 3.23 (d, $J = 17.1$ Hz, 1H), 3.17 (s, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 172.14, 170.12, 157.97, 139.51, 137.32, 130.62, 129.26, 128.94, 128.75, 128.13, 127.36, 124.55, 120.55, 111.08, 64.65, 57.60, 55.38, 53.05, 52.03, 42.51. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₂H₂₂O₅Na: 389.1359, found: 389.1348. **FTIR (cm⁻¹)** 3433, 3022, 2953, 2839, 2402, 2108, 1730, 1629, 1601, 1458, 1437, 1218, 1166, 1057, 968, 870, 702.

Dimethyl (*S*)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)

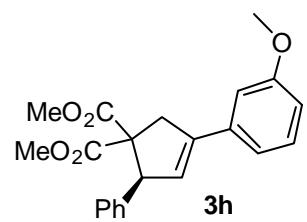


Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-bromophenyl)-2-oxoethylmalonate **2g** (164.5 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (DCM-Pet. ether 40:90) to afford dimethyl (*S*)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3g** as a colourless oil (135.0 mg, 65%).

R_f (Pet. ether /EtOAc = 80/20): 0.62; >99% ee, $[\alpha]_D^{25} = -202.26$ (c 0.2, CHCl_3). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 6.5 min, Minor: 8.0 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.63 (d, $J = 7.9$ Hz, 1H, H_{ar}), 7.39-7.26 (m, 7H, H_{ar}), 7.18 (t, $J = 7.4$ Hz, 1H, H_{ar}), 5.96 (s, 1H, H_{olefinic}), 5.07 (s, 1H), 3.96 (d, $J = 17.1$ Hz, 1H), 3.83 (s, 3H, CH₃), 3.25-3.19 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.44, 169.76, 141.32, 138.82, 137.82,

133.43, 131.68, 130.35, 129.24, 129.04, 128.25, 127.57, 127.41, 122.30, 65.52, 57.18, 53.13, 52.09, 43.14. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₄BrNa: 437.0359, found: 437.0353. **FTIR (cm⁻¹)** 3685, 3619, 3435, 3021, 2975, 2401, 2357, 1731, 1603, 1521, 1432, 1216, 1051, 929, 774, 670.

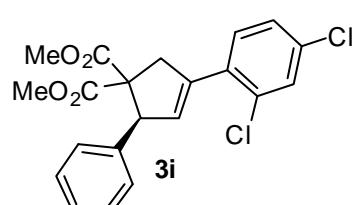
Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(3-methoxyphenyl)-2-oxoethyl)malonate **2h** (140.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3h** as a light yellow oil (97 mg, 53%).

R_f (Pet. ether /EtOAc = 80/20): 0.64; 99% ee, $[\alpha]_D^{25} = -195.5$ (c 0.1, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 8.2 min, Minor: 10.3 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.33 (m, 6H, H_{ar}), 7.14 (d, *J* = 7.7 Hz, 1H, H_{ar}), 7.06 (s, 1H, H_{ar}), 6.89-6.87 (m, 1H, H_{ar}), 6.16 (s, 1H, H_{olefinic}), 5.07 (s, 1H), 3.93 (d, *J* = 16.9 Hz, 1H), 3.86 (s, 3H, CH₃), 3.81 (s, 3H, CH₃), 3.21-3.18 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.55, 169.88, 159.87, 140.33, 139.14, 136.52, 129.62, 129.20, 128.21, 127.55, 126.83, 118.57, 113.63, 111.54, 65.19, 57.31, 55.41, 53.17, 52.12, 40.88. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₂H₂₂O₅Na: 389.1359, found: 389.1353. **FTIR (cm⁻¹)** 3021, 1731, 1599, 1433, 1264, 1214, 1170, 1052, 742, 668.

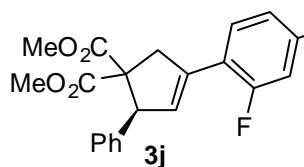
Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2,4-dichlorophenyl)-2-oxoethyl)malonate **2i** (158.2 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (dcm-Pet. ether 40:60) to afford dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3i** as a colourless oil (117.0 mg, 58%).

R_f (Pet. ether /EtOAc = 80/20): 0.78; >99% ee, $[\alpha]_D^{25} = -191.90$ (c 0.3, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 8.5 min, Minor: 9.9 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.43 (d, *J* = 2.1 Hz, 1H, H_{ar}), 7.33-7.24 (m, 7H, H_{ar}), 6.09-6.07 (m, 1H, H_{olefinic}), 5.07 (s, 1H), 3.95-3.90 (m, 1H), 3.81 (s, 3H, CH₃), 3.20-3.16 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.29, 169.64, 138.59, 138.42, 133.85, 133.45, 132.58, 130.81, 130.12, 129.12, 128.26, 127.62, 127.14, 65.28, 57.26, 53.13, 52.11, 42.96. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₈O₄Cl₂Na: 427.0474, found: 427.0465. **FTIR (cm⁻¹)** 3428, 3021, 2401, 2313, 1731, 1635, 1437, 1217, 1057, 769, 670.

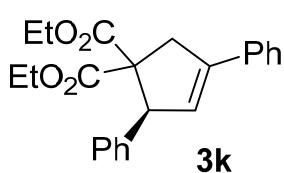
Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and dimethyl 2-(2-(2,4-difluorophenyl)-2-oxoethyl)malonate **2j** (143.0 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate **3j** as a white solid (143.0 mg, 77%).

R_f (Pet. ether /EtOAc = 80/20): 0.62; 99% ee, $[\alpha]_D^{25} = -249.26$ (c 0.35, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 99.3:0.7:0.1 Hexane / IPA/TFA, 0.5 mL/min.) Major: 20.2 min, Minor: 22.6 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.41–7.35 (m, 1H, H_{ar}), 7.30–7.22 (m, 5H, H_{ar}), 6.92–6.83 (m, 2H, H_{ar}), 6.25 (s, 1H, H_{olefinic}), 5.09 (s, 1H), 3.92 (d, *J* = 16.7 Hz, 1H), 3.80 (s, 3H, CH₃), 3.21-3.15 (m, 4H). **¹³C NMR (100 MHz, CDCl₃)** δ 172.42, 169.83, 163.23 (dd, *J*₁ = 12.2 Hz, *J*₂ = 250.1 Hz), 161.58 (dd, *J*₁ = 11.7 Hz, *J*₂ = 254.5 Hz), 138.93, 134.08, 130.94 (d, *J* = 10.2 Hz), 129.66-129.51 (m), 129.15, 128.22, 127.57, 119.70 (dd, *J*₁ = 3.8 Hz, *J*₂ = 12.6 Hz), 111.33 (dd, *J*₁ = 3.4 Hz, *J*₂ = 21.2 Hz), 104.61 (t, *J* = 25.8 Hz), 64.57, 57.55, 53.17, 52.13, 42.08. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₈O₄F₂Na: 395.1065, found: 395.1058. **FTIR (cm⁻¹)** 3430, 3023, 2954, 1731, 1619, 1502, 1271, 1217, 1162, 1141, 1105, 965, 854, 761, 702.

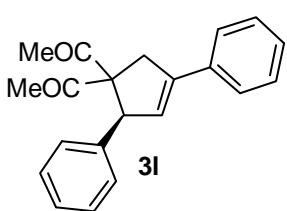
Diethyl (S) 2, 4-diphenylcyclopent-3-ene-1, 1-dicarboxylate (3k)



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and diethyl 2-(2-oxo-2-phenylethyl)malonate **2k** (208.7 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford diethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate **3k** as a colourless oil (110 mg, 61%).

R_f (Pet. ether /EtOAc = 80/20): 0.69; >99% ee, [α]_D²⁵ = -265.10 (c 0.45, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 12.0 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.55 (d, *J* = 7.4 Hz, 2H, H_{ar}), 7.40 (t, *J* = 7.4 Hz, 2H, H_{ar}), 7.33 (d, *J* = 7.4 Hz, 1H, H_{ar}), 7.31-7.22 (m, 5H, H_{ar}), 6.17 (s, 1H, H_{olefinic}), 5.09 (s, 1H), 4.38-4.30 (m, 1H), 4.27-4.19 (m, 1H), 3.81-3.73 (m, 1H), 3.55-3.47 (m, 1H), 3.21 (d, *J* = 16.9 Hz, 1H), 1.31 (t, *J* = 7.1 Hz, 3H, CH₃), 0.89 (t, *J* = 7.1 Hz, 3H, CH₃) **¹³C NMR** (100 MHz, CDCl₃) δ 172.09, 169.53, 140.18, 139.44, 135.19, 129.34, 128.59, 128.13, 127.91, 127.43, 126.72, 125.95, 65.01, 61.85, 61.25, 57.18, 40.94, 14.14, 13.61. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₃H₂₄O₄Na: 387.1567, found: 387.1555. **FTIR (cm⁻¹)** 3430, 3021, 2401, 1726, 1636, 1449, 1261, 1216, 1097, 928, 760, 669

(S)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) (3l)

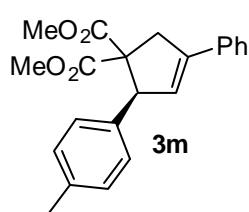


Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and 3-acetyl-1-phenylpentane-1,4-dione **2l** (109.0 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford (S)-1,1'-(2,4-diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) **3l** as a white solid (76 mg, 50%).

R_f (Pet. ether /EtOAc = 80/20): 0.53; >99% ee, [α]_D²⁵ = -406.95 (c 0.4, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.1 min, Minor: 12.3 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.52-7.50 (m, 2H, H_{ar}), 7.37 (t, *J* = 7.1 Hz, 2H, H_{ar}), 7.32-7.18 (m, 6H, H_{ar}), 6.13 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 4.06-4.00 (m, 1H), 2.94 (d, *J* = 17.0 Hz, 1H), 2.25 (s,

3H, CH₃), 1.63 (s, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 204.43, 204.18, 139.68, 138.97, 135.10, 129.36, 128.74, 128.67, 128.06, 127.85, 127.62, 125.89, 79.24, 55.11, 38.22, 28.54, 26.81. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₂₀O₂Na: 327.1356, found: 327.1346. **FTIR (cm⁻¹)** 3411, 3021, 2928, 2401, 1697, 1492, 1216, 1144, 1029, 760, 669, 622.

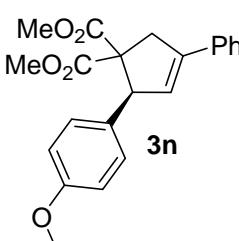
Dimethyl (S)-4-phenyl-2-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (**3m**)



Following the general procedure, treatment of (Z)-2-bromo-3-(*p*-tolyl)acrylaldehyde **1m** (168.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-4-phenyl-2-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate **3m** as a colourless oil (105.0 mg, 60%).

R_f (Pet. ether /EtOAc = 80/20): 0.64; >99% ee, [α]_D²⁵ = -235.55 (c 0.25, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 12.5 min, Minor: 24.4 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.52 (d, *J* = 7.4 Hz, 2H, H_{ar}), 7.37 (t, *J* = 7.2 Hz, 2H, H_{ar}), 7.30 (t, *J* = 7.3 Hz, 1H, H_{ar}), 7.12-7.06 (m, 4H, H_{ar}), 6.13 (s, 1H, H_{olefinic}), 5.02 (s, 1H), 3.94-3.89 (m, 1H), 3.79 (s, 3H, CH₃), 3.20-3.16 (m, 4H), 2.31 (s, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 172.63, 169.95, 140.14, 137.12, 135.94, 135.15, 129.06, 128.89, 128.62, 127.95, 126.65, 125.95, 65.16, 56.97, 53.12, 52.12, 40.69, 21.19. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₂H₂₂O₄Na: 373.1410, found: 373.1400. **FTIR (cm⁻¹)** 3427, 3021, 2954, 1731, 1635, 1439, 1267, 1217, 768, 670

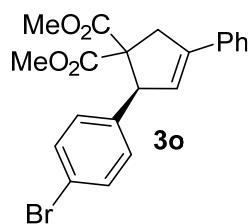
Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (**3n**)



Following the general procedure, treatment of (Z)-2-bromo-3-(4-methoxyphenyl)acrylaldehyde **1n** (180.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3n** as a light yellow oil (110 mg, 60%).

R_f (Pet. ether /EtOAc = 80/20): 0.63; 95% ee, $[\alpha]_D^{25} = -217.4$ (c 0.25, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 14.9 min, Minor: 28.8 min. **¹H NMR** (**400 MHz, CDCl₃**) δ 7.51 (d, *J* = 7.3 Hz, 2H, H_{ar}), 7.37 (t, *J* = 7.1 Hz, 2H, H_{ar}), 7.30 (d, *J* = 7.2 Hz, 1H, H_{ar}), 7.13 (d, *J* = 8.7 Hz, 2H, H_{ar}), 6.80 (d, *J* = 8.7 Hz, 2H, H_{ar}), 6.11 (s, 1H, H_{olefinic}), 5.00 (s, 1H), 3.92-3.87 (m, 1H), 3.78-3.77 (m, 6H, 2CH₃), 3.21 (s, 3H, CH₃), 3.16 (d, *J* = 16.9 Hz, 1H). **¹³C NMR** (**100 MHz, CDCl₃**) δ 172.66, 170.00, 159.03, 140.03, 135.15, 131.00, 130.25, 128.64, 127.97, 126.69, 125.95, 113.57, 65.11, 56.60, 55.35, 53.13, 52.21, 40.64. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₂H₂₂O₅Na: 389.1359, found: 389.1346. **FTIR (cm⁻¹)** 3021, 1733, 1215, 908, 742, 669.

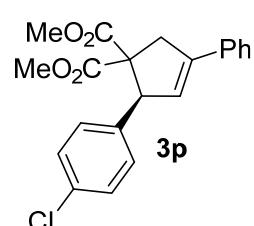
Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)



Following the general procedure, treatment of (Z)-2-bromo-3-(4-bromophenyl)acrylaldehyde **1o** (108.7 mg, 0.38 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (62.5 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), Na₂CO₃ (106 mg, 1.0 mmol) in DME (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3o** as a light yellow oil (65.4 mg, 63%).

R_f (Pet. ether /EtOAc = 80/20): 0.64; >99% ee, $[\alpha]_D^{25} = -200.97$ (c 0.45, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 16.3 min. **¹H NMR** (**400 MHz, CDCl₃**) δ 7.51 (d, *J* = 7.3 Hz, 2H, H_{ar}), 7.41-7.36 (m, 4H, H_{ar}), 7.33-7.29 (m, 1H, H_{ar}), 7.11 (d, *J* = 8.4 Hz, 2H, H_{ar}), 6.08 (d, *J* = 1.5 Hz, 1H, H_{olefinic}), 5.03 (s, 1H), 3.92-3.88 (m, 1H), 3.79 (s, 3H, CH₃), 3.22-3.17 (m, 4H). **¹³C NMR** (**100 MHz, CDCl₃**) δ 172.31, 169.70, 140.93, 138.31, 134.81, 131.28, 130.89, 128.66, 128.17, 125.97, 125.68, 121.47, 65.02, 56.67, 53.21, 52.26, 40.78. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₄BrNa: 437.0359, found: 437.0355. **FTIR (cm⁻¹)** 3436, 3022, 2954, 2401, 1732, 1636, 1437, 1267, 1216, 1167, 1073, 932, 758.

Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)

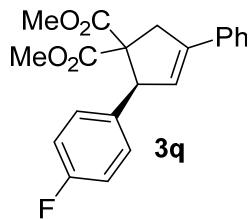


Following the general procedure, treatment of (Z)-2-bromo-3-(4-chlorophenyl)acrylaldehyde **1p** (92.0 mg, 0.38 mmol) and dimethyl 2-(2-

oxo-2-phenylethyl)malonate **2a** (62.5 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), Na₂CO₃ (106.0 mg, 1.0 mmol) in THF (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*S*)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3p** as a light yellow oil (37.0 mg, 40%).

R_f (Pet. ether /EtOAc = 80/20): 0.65; 99% ee, [α]_D²⁵ = -334.60 (c 0.1, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 10.1 min, Minor: 14.8 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.53 (d, *J* = 7.2 Hz, 2H, H_{ar}), 7.40 (t, *J* = 7.1 Hz, 2H, H_{ar}), 7.33 (t, *J* = 7.2 Hz, 1H, H_{ar}), 7.26 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.18 (d, *J* = 8.5 Hz, 2H, H_{ar}) 6.11 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 3.94-3.89 (m, 1H), 3.81 (s, 3H, CH₃), 3.24 (s, 3H, CH₃), 3.21(d, *J* = 17.3 Hz, 1H). **¹³C NMR** (100 MHz, CDCl₃) δ 172.37, 169.75, 140.90, 137.79, 134.86, 133.36, 130.55, 128.68, 128.34, 128.19, 125.99, 125.79, 65.09, 56.63, 53.23, 52.26, 40.79. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₄ClNa: 393.0864, found: 393.0859. **FTIR (cm⁻¹)** 3435, 3021, 2955, 2401, 1732, 1635, 1489, 1437, 1267, 1216, 1169, 1091, 1017, 930, 770, 672.

Dimethyl (*S*)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3q)

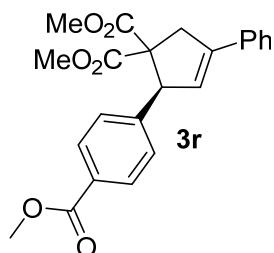


Following the general procedure, treatment of (*Z*)-2-bromo-3-(4-fluorophenyl)acrylaldehyde **1q** (171.7 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*S*)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3q** as a light yellow oil (133.0 mg, 75%).

R_f (Pet. ether /EtOAc = 80/20): 0.60; 99% ee, [α]_D²⁵ = -232.72 (c 0.15, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 11.4 min, Minor: 17.4 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.52 (d, *J* = 8.5 Hz, 2H, H_{ar}), 7.38 (t, *J* = 7.1 Hz, 2H, H_{ar}), 7.31 (t, *J* = 7.3 Hz, 1H, H_{ar}), 7.22-7.18 (m, 2H, H_{ar}), 6.98-6.94 (m, 2H, H_{ar}), 6.11 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 3.93-3.88 (m, 1H), 3.79 (s, 3H, CH₃), 3.21-3.17(m, 4H). **¹³C NMR** (100 MHz, CDCl₃) δ 172.41, 169.80, 162.27 (d, *J* = 246.1 Hz), 140.61, 134.92, 130.74 (d, *J* = 8.0 Hz), 128.65, 128.11, 126.07, 125.96, 114.99 (d, *J* = 21.3 Hz), 65.09, 56.52, 53.15, 52.16, 40.74. **HRMS (ESI)**

calculated $[M+Na]^+$ for $C_{21}H_{19}O_4FNa$: 377.1160, found: 377.1154. **FTIR (cm⁻¹)** 3441, 3028, 2053, 1734, 1636, 1604, 1507, 1438, 1265, 1224, 1098, 1018, 901, 841, 759.

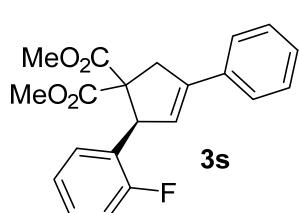
Dimethyl (*S*)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3r)



Following the general procedure, treatment of methyl (*Z*)-4-(2-bromo-3-oxoprop-1-en-1-yl)benzoate **1r** (201.8 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*S*)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3r** as a light yellow solid (110.4 mg, 56%).

R_f (Pet. ether /EtOAc = 80/20): 0.44; >99% ee, $[\alpha]_D^{25} = -224.45$ (c 0.55, $CHCl_3$). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 27.3 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.94 (d, $J = 8.2$ Hz, 2H, H_{ar}), 7.50 (d, $J = 7.4$ Hz, 2H, H_{ar}), 7.37 (t, $J = 7.3$ Hz, 2H, H_{ar}), 7.31 (t, $J = 6.9$ Hz, 3H, H_{ar}), 6.10 (d, $J = 1.5$ Hz, 1H, H_{olefinic}), 5.11 (s, 1H), 3.94-3.89 (m, 4H), 3.79 (s, 3H, CH₃), 3.21 (d, $J = 16.9$ Hz, 1H), 3.15 (s, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 172.28, 169.63, 167.03, 144.79, 141.17, 134.80, 129.47, 129.34, 129.24, 128.68, 128.22, 126.00, 125.53, 65.21, 57.12, 53.27, 52.24, 52.19, 40.91. **HRMS (ESI)** calculated $[M+Na]^+$ for $C_{23}H_{22}O_6Na$: 417.1309, found: 417.1300. **FTIR (cm⁻¹)** 3426, 3021, 2401, 1729, 1617, 1439, 1281, 1217, 1113, 969, 766, 670.

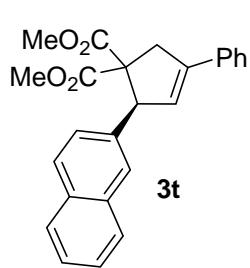
Dimethyl (*R*)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)



Following the general procedure, treatment of (*Z*)-2-bromo-3-(2-fluorophenyl)acrylaldehyde **1s** (171.7 mg, 0.75 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (125.1 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na_2CO_3 (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*R*)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3s** as a colourless solid (90.3 mg, 51%).

R_f (Pet. ether /EtOAc = 80/20): 0.59; 94% ee, $[\alpha]_D^{25} = -167.96$ (c 0.1, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 12.9 min. **¹H NMR** (**400 MHz, CDCl₃**) δ 7.51 (d, *J* = 7.3 Hz, 2H, H_{ar}), 7.37 (t, *J* = 7.1 Hz, 2H, H_{ar}), 7.32-7.28 (m, 1H, H_{ar}), 7.22-7.17 (m, 1H, H_{ar}), 7.10 (t, *J* = 6.2 Hz, 1H, H_{ar}), 7.02 (t, *J* = 8.6 Hz, 2H, H_{ar}), 6.05 (s, 1H, H_{olefinic}), 5.46 (s, 1H), 4.02-3.97 (m, 1H), 3.79 (s, 3H, CH₃), 3.22 (s, 3H, CH₃) 3.18 (d, *J* = 17.2 Hz, 1H). **¹³C NMR** (**100 MHz, CDCl₃**) δ 172.18, 169.90, 160.87 (d, *J* = 248.7 Hz), 140.86, 134.92, 130.38 (d, *J* = 3.4 Hz), 129.19 (d, *J* = 8.2 Hz), 128.67, 128.13, 126.52, 126.37, 126.00, 125.43, 123.96 (d, *J* = 3.3 Hz), 115.29 (d, *J* = 22.4 Hz), 64.54, 53.26, 52.24, 49.19 (d, *J* = 3.3 Hz), 41.01. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₄FNa: 377.1160, found: 377.1152. **FTIR (cm⁻¹)** 3685, 3619, 3434, 3021, 2401, 2358, 1733, 1605, 1521, 1491, 1435, 1216, 1049, 929, 773, 670.

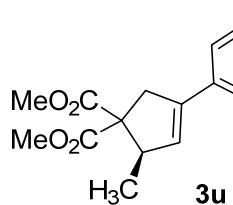
Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)



Following the general procedure, treatment of (*Z*)-2-bromo-3-(naphthalen-2-yl)acrylaldehyde **1t** (98.0 mg, 0.38 mmol) and dimethyl 2-(2-oxo-2-phenylethyl)malonate **2a** (62.5 mg, 0.25 mmol) with triazolium salt **4** (9.2 mg, 0.025 mmol), Na₂CO₃ (106 mg, 1.0 mmol) in DME (3.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate **3t** as a light yellow oil (55.0 mg, 57%).

R_f (Pet. ether /EtOAc = 80/20): 0.64; 99% ee, $[\alpha]_D^{25} = -200.97$ (c 0.45, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 80:20 Hexane / IPA, 0.7 mL/min.) Major: 14.6 min, Minor: 20.0 min. **¹H NMR** (**400 MHz, CDCl₃**) δ 7.78-7.73 (m, 3H, H_{ar}), 7.68 (s, 1H, H_{ar}), 7.56 (d, *J* = 7.3 Hz, 2H, H_{ar}), 7.45-7.30 (m, 6H, H_{ar}), 6.21 (s, 1H, H_{olefinic}), 5.24 (s, 1H), 4.00 (d, *J* = 16.9 Hz, 1H), 3.81 (s, 3H, CH₃), 3.25 (d, *J* = 16.9 Hz, 1H), 3.03 (s, 3H, CH₃). **¹³C NMR** (**100 MHz, CDCl₃**) δ 172.62, 169.90, 140.57, 136.80, 135.11, 133.35, 132.89, 128.69, 128.09, 128.00, 127.93, 127.68, 127.42, 126.40, 126.10, 126.05, 125.92, 65.31, 57.44, 53.22, 52.14, 40.96. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₅H₂₂O₄Na: 409.1410, found: 409.1399. **FTIR (cm⁻¹)** 3685, 3430, 3021, 2956, 2401, 2355, 1731, 1603, 1517, 1436, 1216, 1053, 928, 767.

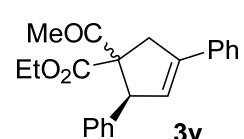
Dimethyl (*R*) 2-methyl-4-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3u**)**



Following the general procedure, treatment of (*Z*)-2-bromobut-2-enal **1u** (28.0 mg, 0.188 mmol) and dimethyl 2-(2-oxo-2-(*p*-tolyl)ethyl)malonate **2b** (33.0 mg, 0.125 mmol) with triazolium salt **4** (4.6 mg, 0.0125 mmol), Na₂CO₃ (53.0 mg, 0.5 mmol) in DME (2.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*R*) 2-methyl-4-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate **3u** as a light yellow oil (15.0 mg, 42%).

R_f (Pet. ether /EtOAc = 80/20): 0.70; 90% ee, [α]_D²⁵ = -60.5 (c 0.1, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 95:05 Petroleum ether / IPA, 0.5 mL/min.) Major: 12.8 min, Minor: 14.5 min. **¹H NMR** (500 MHz, CDCl₃) δ 7.30 (d, *J* = 8.2 Hz, 2H, H_{ar}), 7.12 (d, *J* = 8.0 Hz, 2H, H_{ar}), 5.93 (s, 1H), 3.79-3.76 (m, 1H), 3.75 (s, 3H, CH₃), 3.73 (s, 3H, CH₃), 3.70-3.66 (m, 1H), 3.09 (d, *J* = 16.5 Hz, 1H), 2.33 (s, 3H), 1.02 (d, *J* = 7.2 Hz, 3H). **¹³C NMR** (125 MHz, CDCl₃) δ 172.78, 171.00, 137.90, 137.49, 132.61, 129.20, 127.84, 125.64, 63.47, 52.97, 52.51, 45.62, 40.12, 21.32, 16.09. **HRMS (ESI)** calculated [M+Na]⁺ for C₁₇H₂₀O₄Na: 311.1254, found: 311.1251. FTIR (cm⁻¹) 3917, 3750, 3507, 3015, 2947, 2829, 2387, 2351, 1823, 1727, 1673, 1566, 1438, 1213, 1095, 1049, 949.

Ethyl (2*S*)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v**)**



Following the general procedure, treatment of (*Z*)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and ethyl 2-acetyl-4-oxo-4-phenylbutanoate **2v** (124 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford 3:1 diastereomeric mixture of ethyl (2*S*)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate **3v** as a white solid (Major isomer 67 mg yield 38% and minor isomer 23 mg yield 16%, diastereomeric ratio was determined by ¹H-NMR analysis of crude reaction mixture).

Major Isomer R_f (Pet. ether /EtOAc = 80/20): 0.61; >99% ee, [α]_D²⁵ = -359.98 (c 0.35, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.5 min, Minor: 16.2 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.54-7.52 (m, 2H, H_{ar}), 7.39 (t, *J* = 7.8 Hz, 2H, H_{ar}), 7.33-

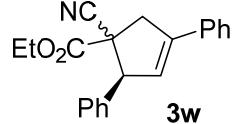
7.22 (m, 6H, H_{ar}), 6.15 (s, 1H, H_{olefinic}), 5.06 (s, 1H), 4.01-3.96 (m, 1H), 3.81-3.75 (m, 1H), 3.54-3.48 (m, 1H), 2.98 (d, *J* = 16.6 Hz, 1H), 2.29 (s, 3H, CH₃), 0.88 (t, *J* = 7.1 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 201.74, 170.24, 139.83, 139.01, 135.08, 129.35, 128.57, 128.11, 127.90, 127.43, 127.30, 125.84, 71.31, 61.40, 55.25, 39.53, 26.36, 13.53. HRMS (ESI) calculated [M+Na]⁺ for C₂₂H₂₂O₃Na: 357.1461, found: 357.1456. FTIR (cm⁻¹) 3429, 3022, 2401, 2311, 1711, 1636, 1491, 1358, 1217, 1090, 768, 670.

Minor Isomer R_f (Pet. ether /EtOAc = 80/20): 0.64; >99% ee, [α]_D²⁵ = -326.84 (c 0.25, CHCl₃). HPLC (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 10.4 min, Minor: 11.6 min. ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.51 (m, 2H, H_{ar}), 7.38-7.35 (m, 2H, H_{ar}), 7.31-7.20 (m, 6H, H_{ar}), 6.09-6.08 (m, 1H, H_{olefinic}), 5.08 (s, 1H), 4.32-4.22 (m, 2H), 4.01-3.96 (m, 1H), 3.05 (d, *J* = 17.0 Hz, 1H), 1.63 (s, 3H, CH₃), 1.30 (t, *J* = 7.1 Hz, 3H, CH₃). ¹³C NMR (100 MHz, CDCl₃) δ 202.00, 173.09, 140.11, 139.24, 135.21, 129.47, 128.67, 128.61, 127.96, 127.72, 126.73, 125.99, 71.38, 62.13, 57.10, 39.63, 27.93, 14.16. HRMS (ESI) calculated [M+Na]⁺ for C₂₂H₂₂O₃Na: 357.1461, found: 357.1455. FTIR (cm⁻¹) 3437, 3057, 3029, 2981, 1953, 1711, 1600, 1492, 1354, 1233, 1158, 1058, 840, 755.

Ethyl (2*S*)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (**3w**)

Following the general procedure, treatment of (Z)-2-bromo 3-phenylacrylaldehyde **1a** (158.2 mg, 0.75 mmol) and ethyl 2-cyano-4-oxo-4-phenylbutanoate **2w** (115.6 mg, 0.50 mmol) with triazolium salt **4** (18.4 mg, 0.05 mmol), Na₂CO₃ (212 mg, 2.0 mmol) in DME (6.0 mL) and stirring the reaction mixture at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford 3:1 diastereomeric mixture of ethyl (2*S*)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate **3w** as a colourless oil (Major isomer 48 mg yield 30% and minor isomer 18 mg yield 12%, diastereomeric ratio was determined by ¹H-NMR analysis of crude reaction mixture).

Major Isomer R_f (Pet. ether /EtOAc = 80/20): 0.55; 85% ee, [α]_D²⁵ = -43.86 (c 0.15, CHCl₃). HPLC (Chiralcel OD-H, 95:05 Hexane / IPA, 0.7 mL/min.) Major: 22.9 min, Minor: 18.6 min. ¹H NMR (400 MHz, CDCl₃) δ 7.50 (d, *J* = 7.1 Hz, 2H, H_{ar}), 7.43-7.34 (m, 8H, H_{ar}), 6.20 (s, 1H, H_{olefinic}), 4.81 (s, 1H), 4.39-4.36 (m, 2H), 3.66 (d, *J* = 16.1 Hz, 1H), 3.54 (d, *J* = 16.1 Hz, 1H),

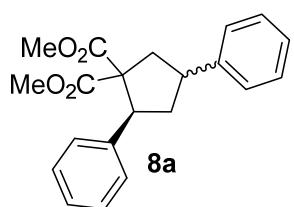


1.38 (t, $J = 7.1$ Hz, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 168.83, 140.81, 137.99, 134.16, 128.83, 128.80, 128.70, 128.57, 128.55, 125.95, 125.31, 118.53, 63.39, 59.32, 55.02, 44.07, 14.15. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₂NNa: 340.1308, found: 340.1304. **FTIR (cm⁻¹)** 3440, 3021, 1740, 1635, 1493, 1499, 1216, 1074, 757, 897, 669.

Minor Isomer R_f (Pet. ether /EtOAc = 80/20): 0.64; 95% ee, $[\alpha]_D^{25} = -95.71$ (c 0.6, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 90:10 Hexane / IPA, 0.7 mL/min.) Major: 14.1 min, Minor: 10.9 min. **¹H NMR (400 MHz, CDCl₃)** δ 7.52 (d, $J = 7.3$ Hz, 2H, H_{ar}), 7.41 (t, $J = 7.7$ Hz, 2H, H_{ar}), 7.36-7.29 (m, 4H, H_{ar}), 7.23-7.21 (m, 2H, H_{ar}), 6.15 (d, $J = 2.0$ Hz, 1H, H_{olefinic}), 4.82 (s, 1H), 3.88-3.84 (m, 1H), 3.82-3.79 (m, 1H), 3.64-3.61 (m, 1H), 3.35 (d, $J = 16.4$ Hz, 1H), 0.93 (t, $J = 7.2$ Hz, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 166.37, 141.68, 136.81, 134.25, 129.05, 128.83, 128.65, 128.57, 126.13, 124.26, 121.68, 62.78, 62.52, 52.12, 41.99, 13.60. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₁₉O₂NNa: 340.1308, found: 340.1303. **FTIR (cm⁻¹)** 3682, 3464, 3021, 2984, 2931, 2401, 1743, 1602, 1394, 1246, 1072, 774, 669.

Diastereoselective Hydrogenation of 3a

Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)



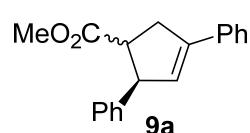
An oven dried round bottomed flask was charged with dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate **3a** (84.1 mg, 0.25 mmol, 1 equiv) and Pd 10% on activated carbon (10 mg, 0.03 equiv) in methanol (10 mL). The reaction mixture was kept stirring at 32 °C for 12 h under H₂ atmosphere (balloon pressure). Upon consumption of the starting material **3a** (TLC), the crude reaction mixture was passed through celite and concentrated under reduced pressure to get a sufficiently pure dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate **8a** in 98% yield (82 mg, *dr* 20:1)

R_f (Pet. ether /EtOAc = 80/20): 0.65; $[\alpha]_D^{25} = -38.88$ (c 0.2, CHCl₃). **HPLC** (Kromasil 5-AmyCoat, 99:1 Hexane / IPA, 0.5 mL/min.) Major diastereomer (Major: 19.2 min, Minor: 20.7 min). Minor diastereomer (Major: 22.6 min, Minor: 25.5 min). **¹H NMR (400 MHz, CDCl₃)** δ 7.46-7.39 (m, 6H, H_{ar}), 7.34-7.25 (m, 4H, H_{ar}), 4.37-4.33 (m, 1H), 3.82 (s, 3H, CH₃), 3.24-3.16 (m, 4H), 3.01 (d, $J = 13.2$ Hz, 1H), 2.64-2.59 (m, 1H), 2.46-2.32 (m, 2H). **¹³C NMR (100 MHz,**

CDCl₃) δ 173.23, 171.23, 143.02, 140.08, 128.73, 128.62, 128.07, 127.30, 127.10, 126.65, 65.33, 52.89, 52.00, 50.90, 43.66, 42.48, 40.54. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₁H₂₂O₄Na: 361.1410, found: 361.1404. **FTIR (cm⁻¹)** 3463, 3061, 2952, 1728, 1603, 1455, 1365, 1096, 1046, 947, 752.

Decarboxylation of **3a**

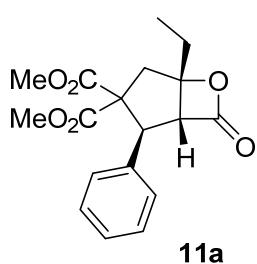
Methyl (2*R*)-2,4-diphenylcyclopent-3-ene-1-carboxylate (**9a**)



To a microwave reaction tube was charged with **3a** (0.084 gm, 0.25 mmol) and LiCl (0.083 gm, 1.95 mmol, 7.8 equiv). Then the mixture was dissolved in DMSO (2.0 mL) : H₂O (1.5 mL). The reaction mixture was placed in a microwave reactor (Anton Paar, Monowave 300), and heated to 185 °C for 30 min. The resultant reaction mixture was quenched with saturated aq. solution of NaHCO₃ and extracted with Et₂O (3x10 mL). Then the organic layer was washed with brine, dried over Na₂SO₄, concentrated and the crude reaction mixture was purified by flash column chromatography to afford the diastereomeric mixture of methyl (2*R*)-2,4-diphenylcyclopent-3-ene-1-carboxylate **9a** in 51% yield (35 mg, *dr* 1:1).

R_f (Pet. ether /EtOAc = 80/20): 0.72; [α]_D²⁵ = +104.5 (c 0.2, CHCl₃). **¹H NMR (400 MHz, CDCl₃)** δ 7.56 (d, *J* = 7.2 Hz, 2H, H_{ar}), 7.51 (d, *J* = 7.2 Hz, 2H, H_{ar}), 7.41-7.22 (m, 14H, H_{ar}), 7.20-7.17 (m, 2H, H_{ar}), 6.16 (s, 2H, H_{olefinic}), 4.45-4.42 (m, 2H), 3.80-3.73 (m, 4H), 3.49-3.41 (m, 1H), 3.26-3.14 (m, 6H), 2.96-2.89 (m, 1H). **¹³C NMR (100 MHz, CDCl₃)** δ 175.61, 173.36, 144.49, 142.67, 141.43, 140.24, 135.56, 128.75, 128.62, 128.20, 127.81, 127.65, 127.18, 126.93, 126.77, 126.00, 125.90, 55.27, 54.66, 52.27, 52.08, 51.25, 48.75, 37.14, 34.62. **HRMS (ESI)** calculated [M+Na]⁺ for C₁₉H₁₈O₂Na: 301.1199, found: 301.1196. **FTIR (cm⁻¹)** 3021, 1745, 1379, 1214, 742, 669.

Dimethyl (1*R*,2*S*,5*S*) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (**11a**)



To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the (Z)-2-bromo 3-phenylacrylaldehyde **1a** (79.1 mg, 0.38 mmol), the dimethyl 2-(2-oxobutyl)malonate **10** (50.0 mg, 0.25 mmol) and Na₂CO₃

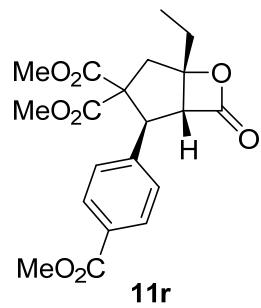
(106 mg, 1.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (3.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt **4** (9.2 mg, 0.025 mmol), and the resulting mixture was stirred at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*1R,2S,5S*) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0] heptane-3,3-dicarboxylate **11a** as a white solid (38.0 mg, 46%).

R_f (Pet. ether /EtOAc = 80/20): 0.4, 99% ee, $[\alpha]_D^{25} = -188.7$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 97:03 Petroleum ether / IPA, 0.5 mL/min, $\lambda = 210$ nm) Major: 18.7 min, Minor: 21.9 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.31-7.27 (m, 3H, H_{ar}), 6.99-6.97 (m, 2H, H_{ar}), 4.65 (s, 1H), 3.81 (s, 3H, CH₃), 3.70 (s, 1H), 3.31 (s, 3H, CH₃), 2.95-2.85 (m, 2H), 2.28-2.12 (m, 2H), 1.18 (t, *J* = 7.3 Hz, 3H, CH₃) **¹³C NMR** (100 MHz, CDCl₃) δ 170.89, 168.36, 167.95, 138.52, 128.85, 128.10, 128.06, 90.77, 63.74, 53.65, 52.71, 50.68, 40.59, 28.57, 8.88. **HRMS (ESI)** calculated [M+Na]⁺ for C₁₈H₂₀O₆Na: 355.1152, found: 355.1150. **FTIR** (cm⁻¹) 3118, 3022, 2430, 1827, 1734, 1780, 1556, 1445, 1035, 924.

Dimethyl (*1R,2S,5S*)-5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3 dicarboxylate (**11r**)

To an oven-dried Schlenk reaction vessel with a teflon screw cap was taken the (Z)-4-(2-bromo-3-oxoprop-1-en-1-yl)benzoate **1r** (101.0 mg, 0.38 mmol), the dimethyl 2-(2-oxobutyl)malonate **10** (50.0 mg, 0.25 mmol) and Na₂CO₃ (106 mg, 1.0 mmol, 4.0 equiv). The mixture was kept under argon atmosphere, and dry DME (3.0 mL) was then introduced into the vessel by syringe under a positive pressure of argon, and the mixture was stirred at 32 °C. To this stirring solution was added the triazolium salt **4** (9.2 mg, 0.025 mmol), and the resulting mixture was stirred at 32 °C for 72 h followed by flash column chromatography (EtOAc-Pet. ether 10:90) to afford dimethyl (*1R,2S,5S*) 5-ethyl-2-(4-(methoxycarbonyl) phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3 dicarboxylate **11r** as a white solid (70.0 mg, 72%).

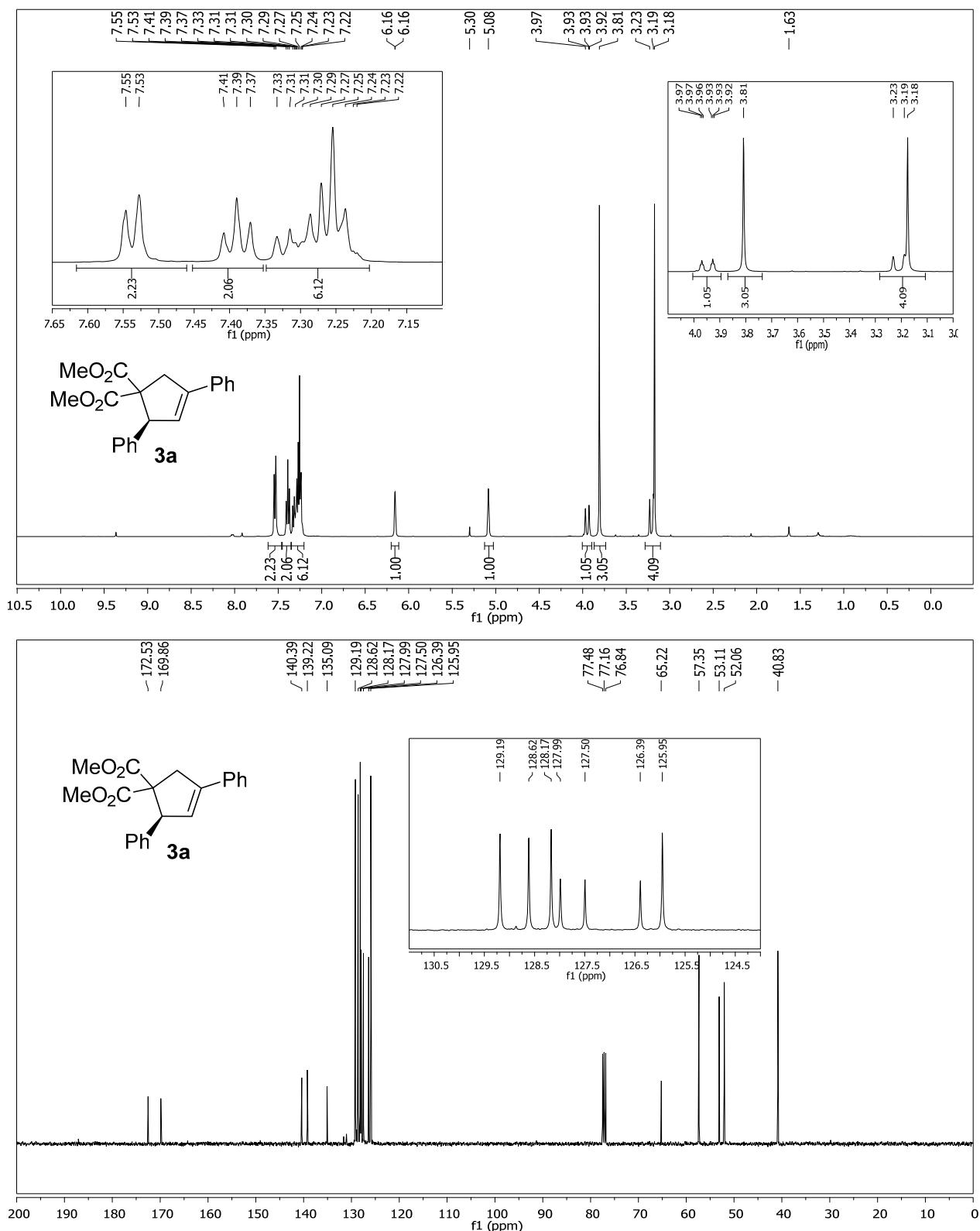
R_f (Pet. ether /EtOAc = 80/20): 0.23, 99% ee, $[\alpha]_D^{25} = -74.1$ (c 0.1, CHCl₃). **HPLC** (Chiralpak IA, 97:03 Petroleum ether / IPA, 1.0 mL/min. $\lambda = 210$ nm). Major: 15.8 min, Minor: 16.8 min. **¹H NMR** (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.4 Hz, 2H, H_{ar}), 7.06 (d, *J* = 8.2 Hz, 2H, H_{ar}), 4.71 (s, 1H), 3.90 (d, 3H, CH₃), 3.81 (s, 3H, CH₃), 3.69 (s, 1H), 3.31 (s, 3H, CH₃), 2.97-2.85 (m, 2H),



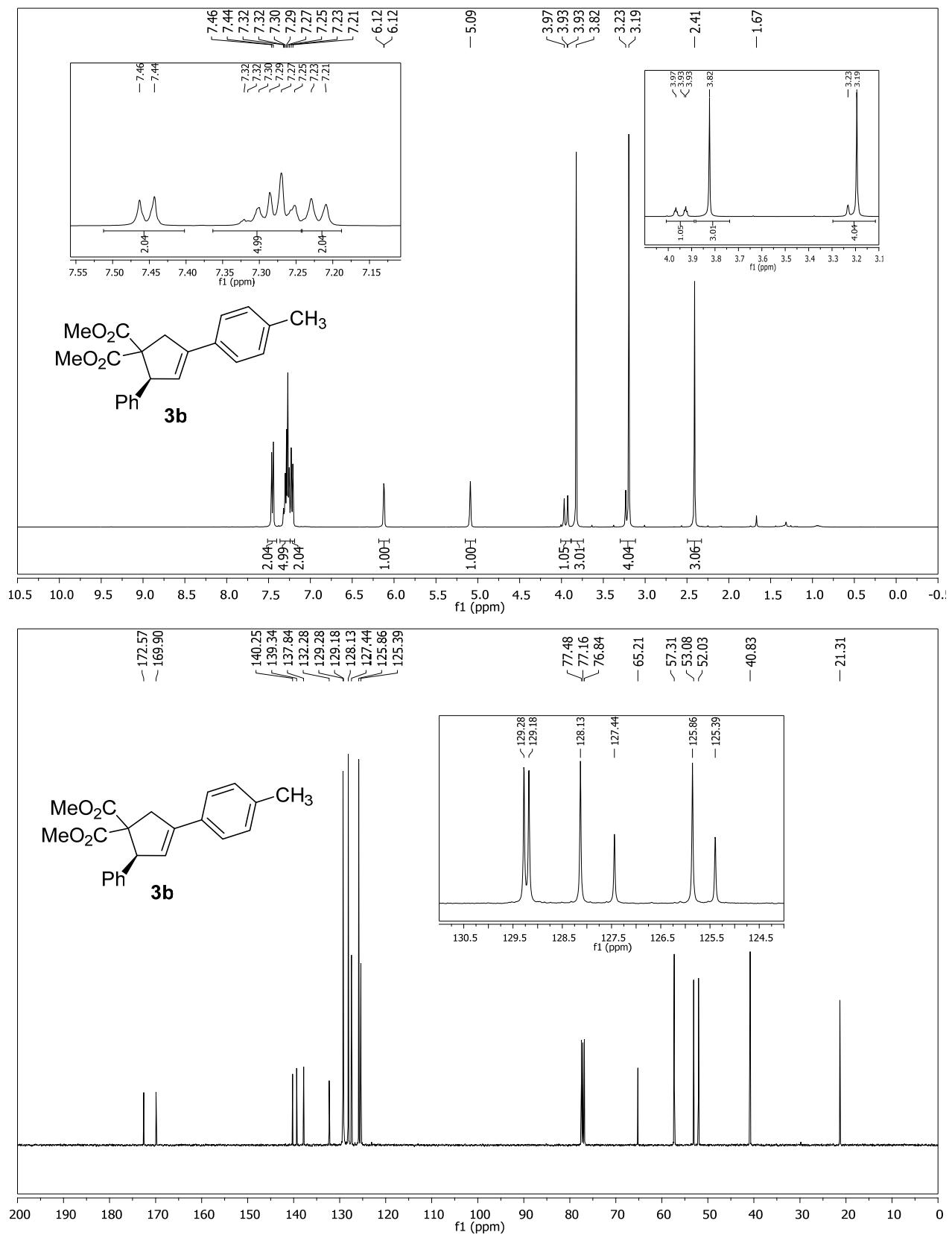
2.26-2.14 (m,2H), 1.19 (t, J = 7.5 Hz, 3H, CH₃). **¹³C NMR (100 MHz, CDCl₃)** δ 170.57, 167.85, 167.68, 166.50, 130.11, 128.16, 90.68, 66.62, 63.53, 53.77, 52.86, 52.38, 50.52, 40.65, 28.60, 8.88. **HRMS (ESI)** calculated [M+Na]⁺ for C₂₀H₂₂O₈Na: 413.1207, found: 413.1203. FTIR (cm⁻¹) 2973, 2954, 1828, 1723, 1612, 1531, 1435, 1418, 1375, 1280, 1227, 1153, 1112, 1018, 900, 864, 810, 763, 707, 665.

6. ^1H and ^{13}C NMR Spectra of Functionalized Cyclopentenes

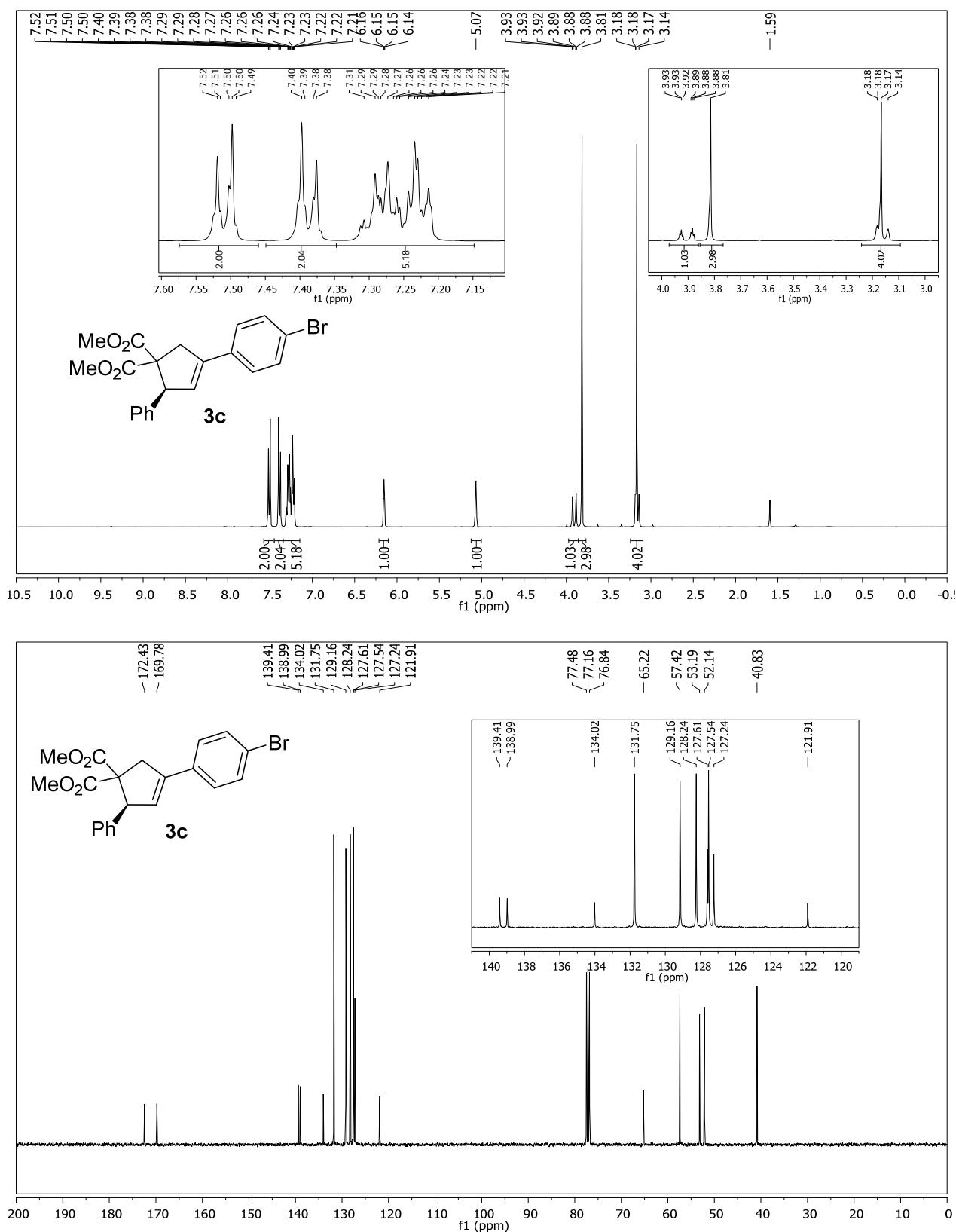
Dimethyl (*S*)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3a)



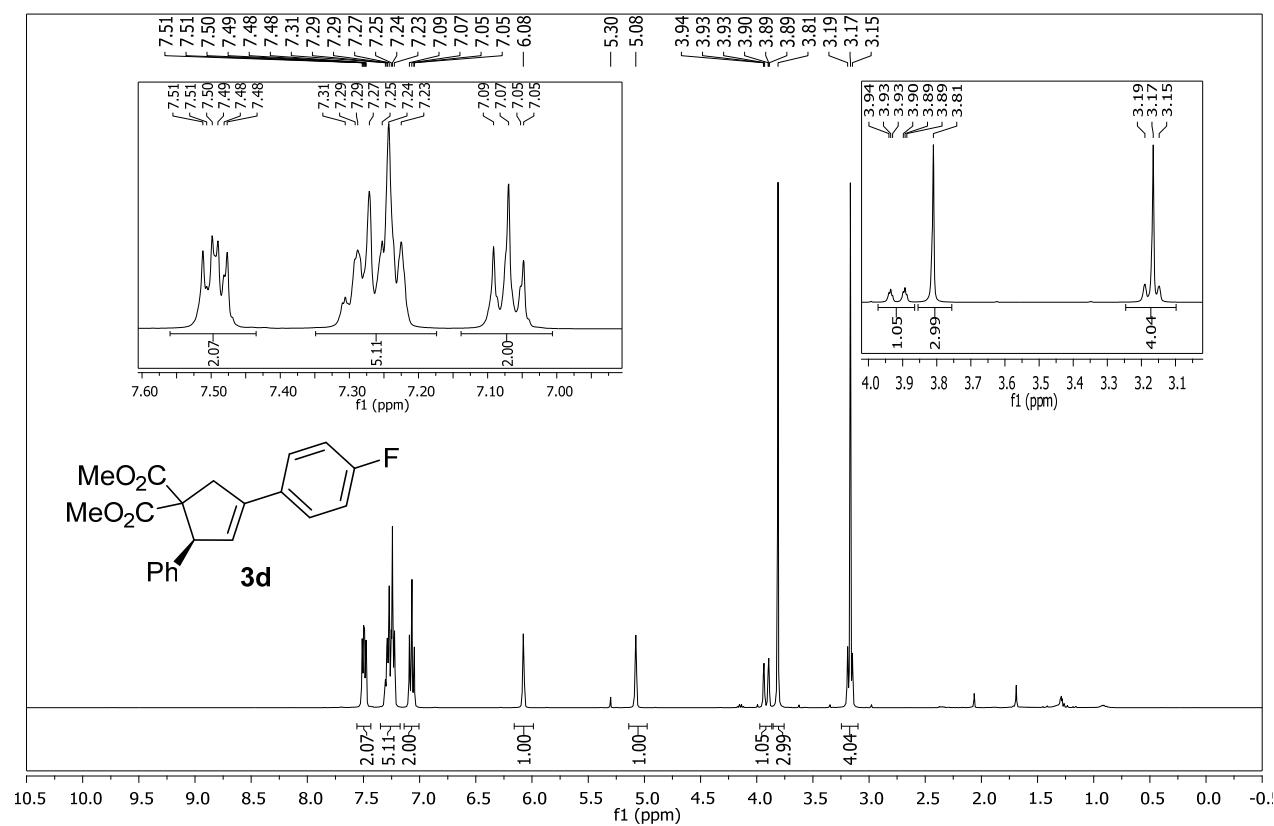
Dimethyl (S)-2-phenyl-4-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3b**)**



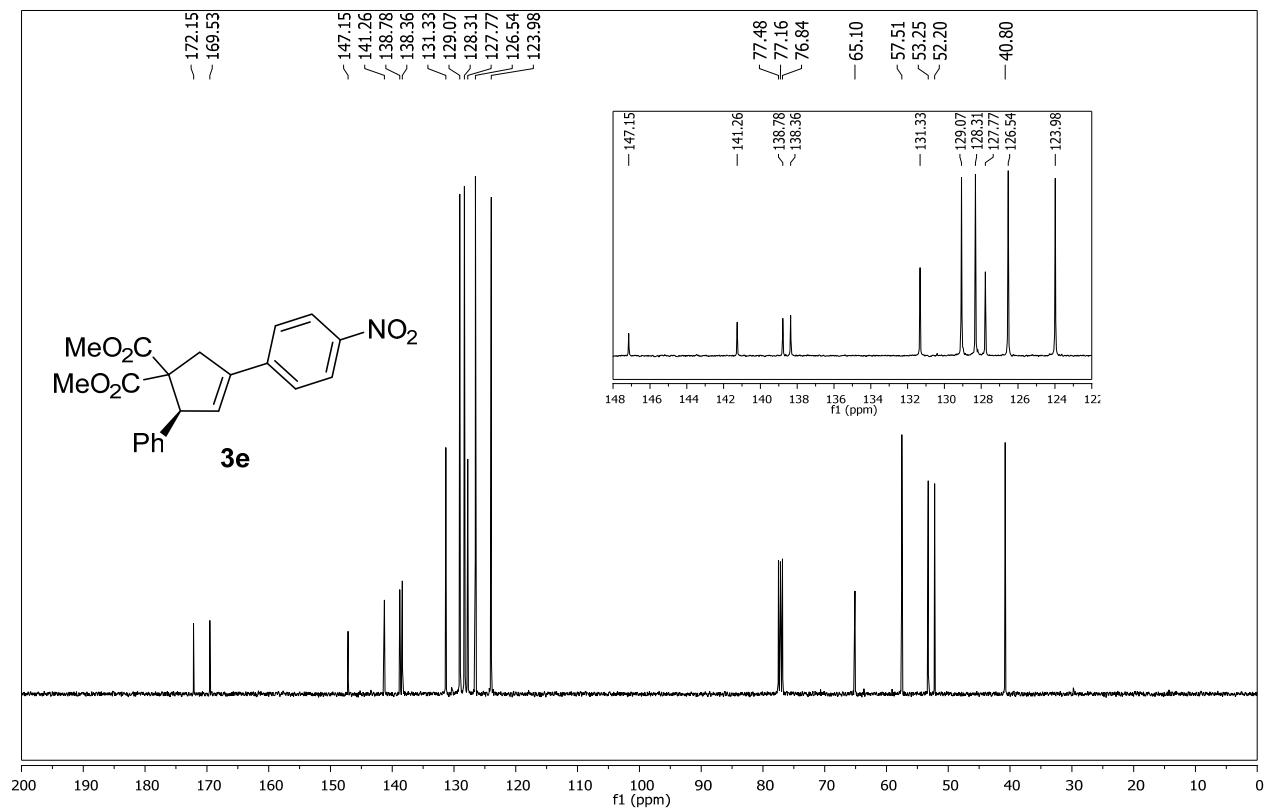
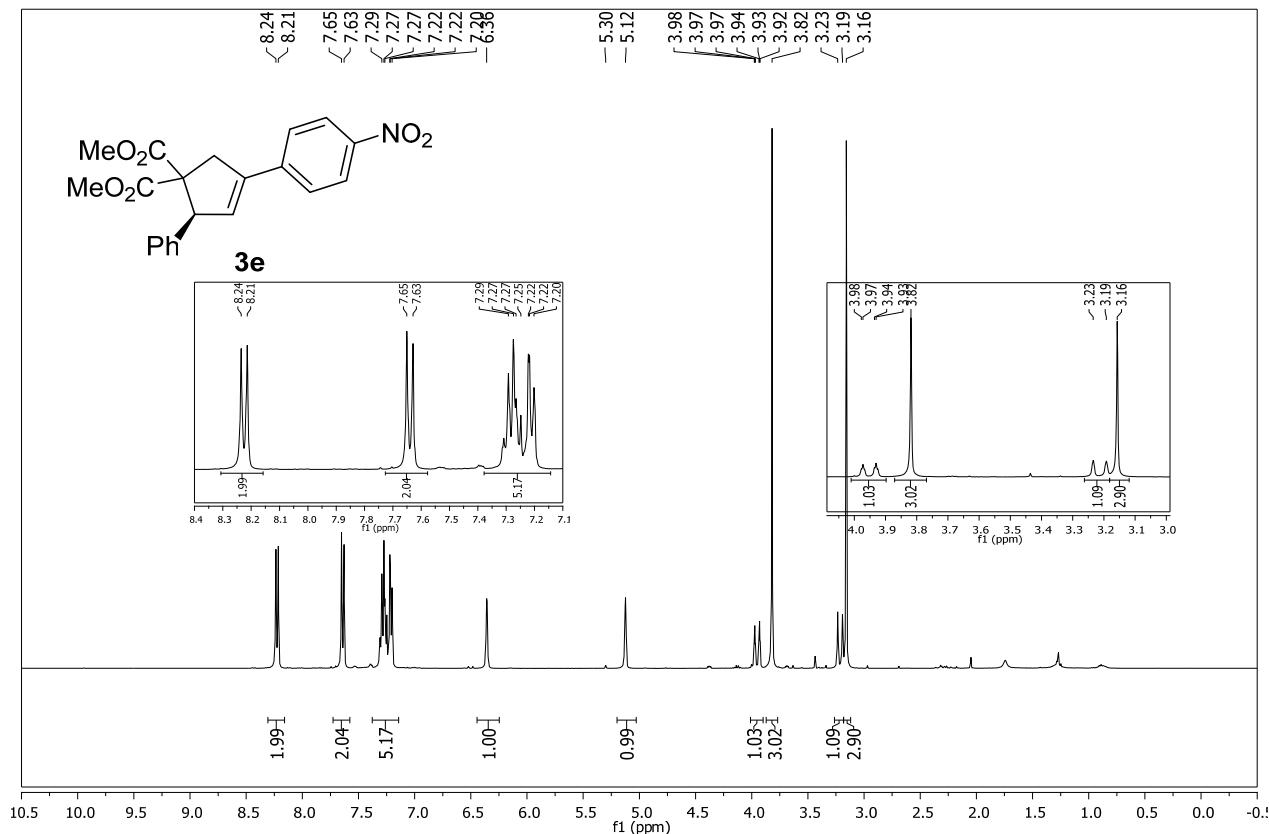
Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)



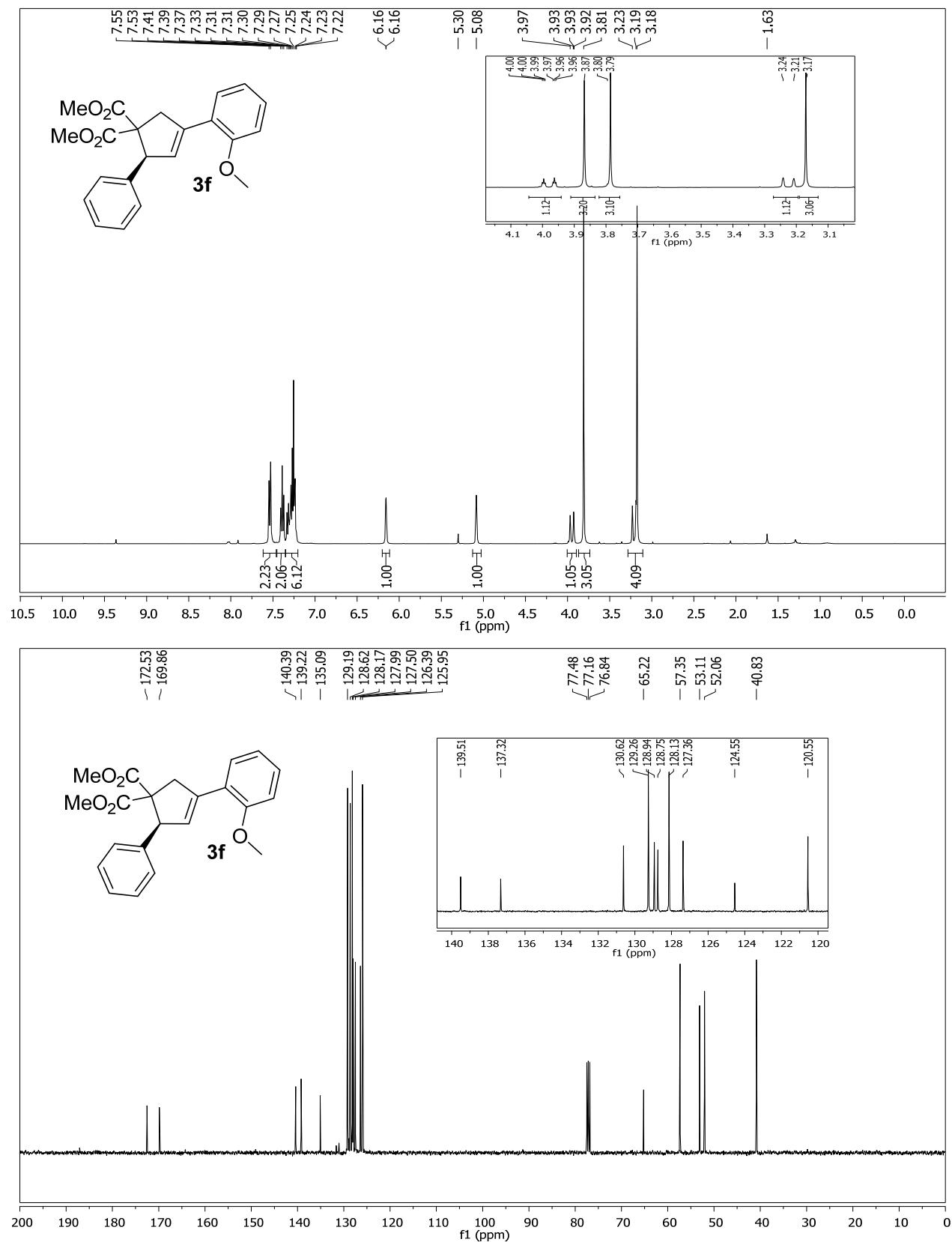
Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)



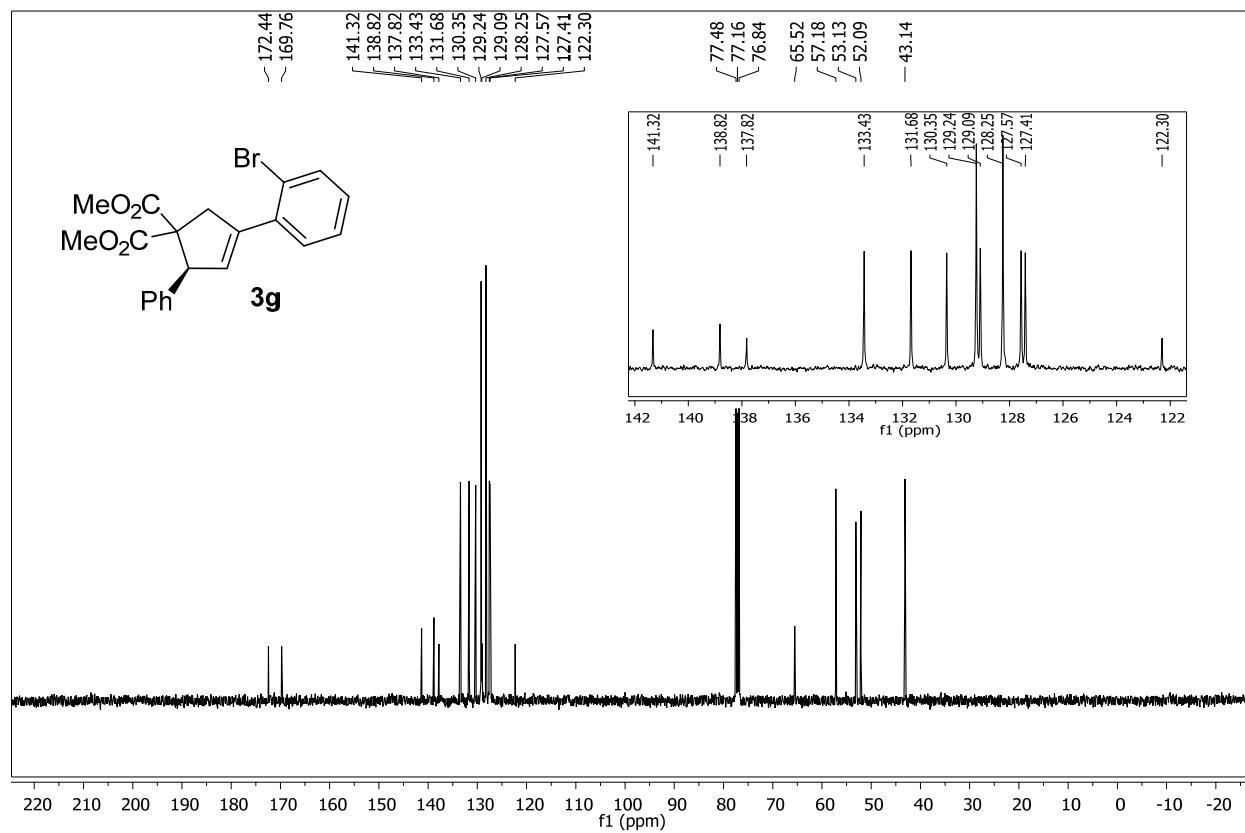
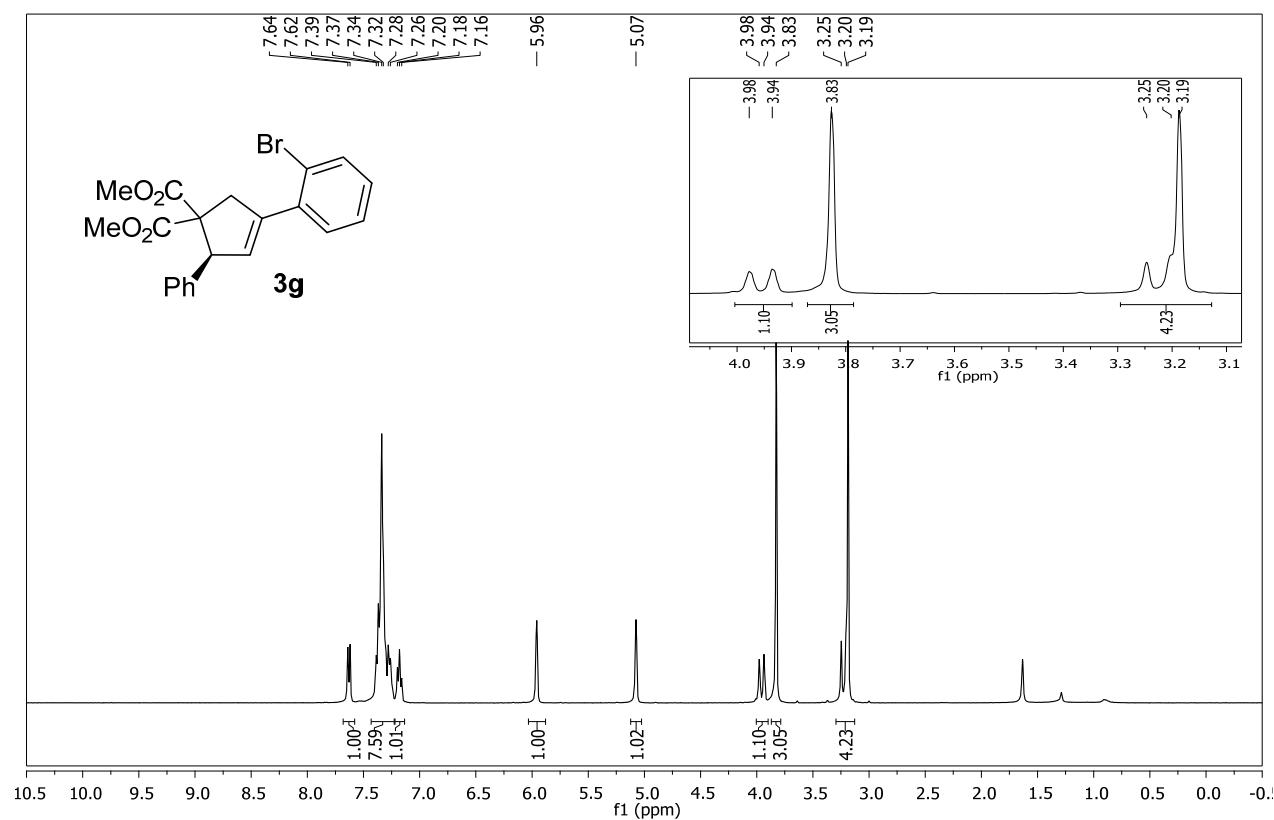
Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e)



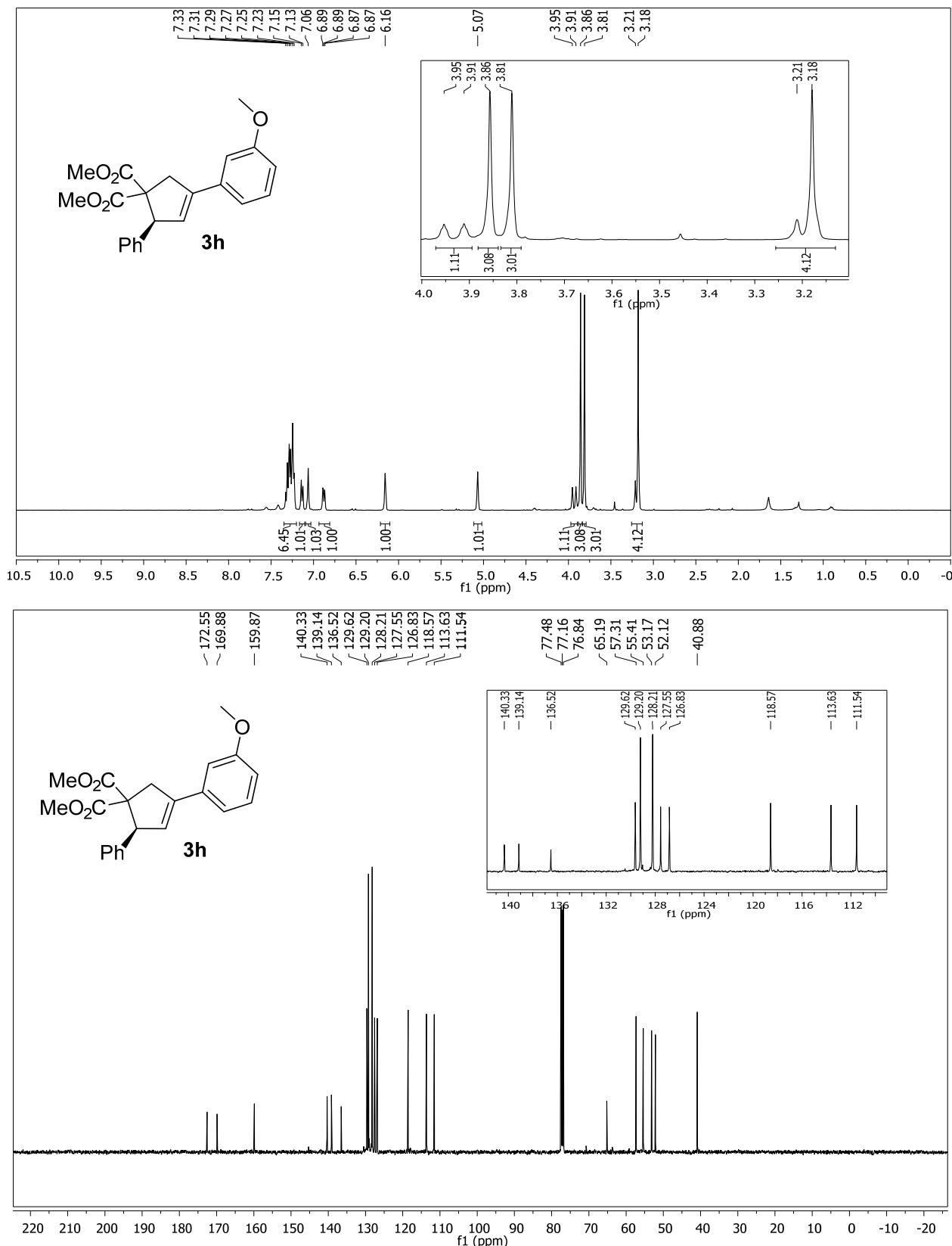
Dimethyl (S)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)



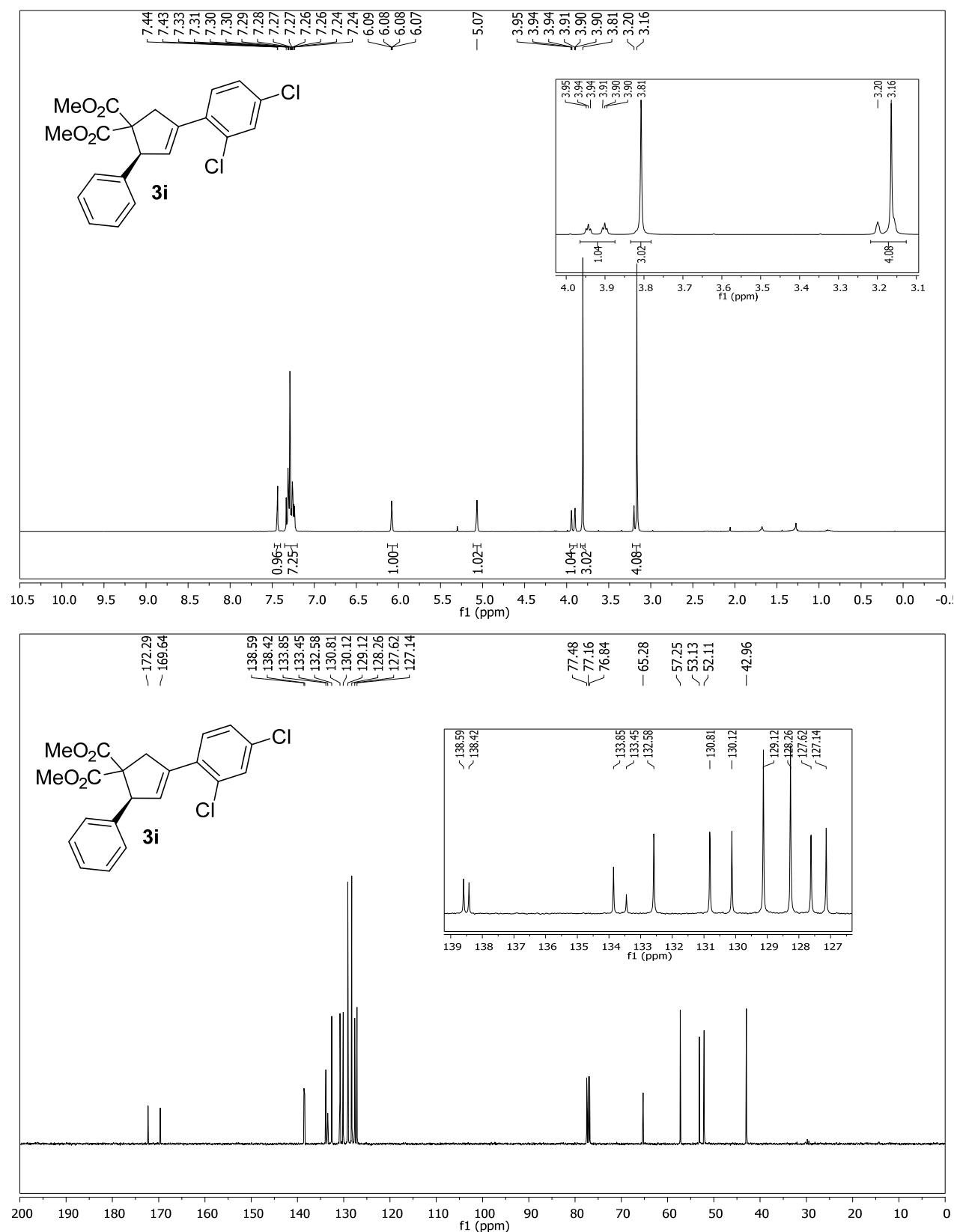
Dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)



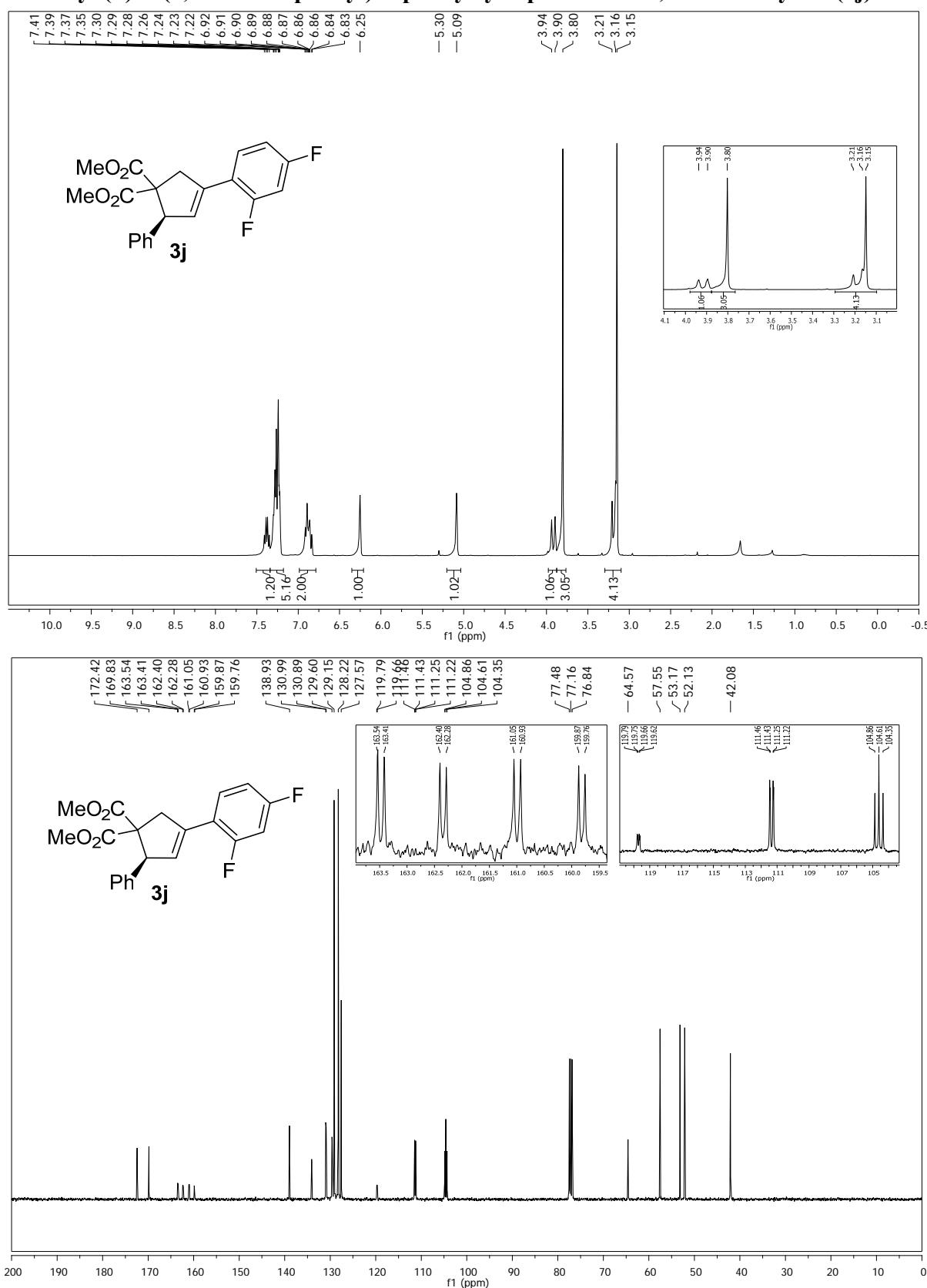
Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)



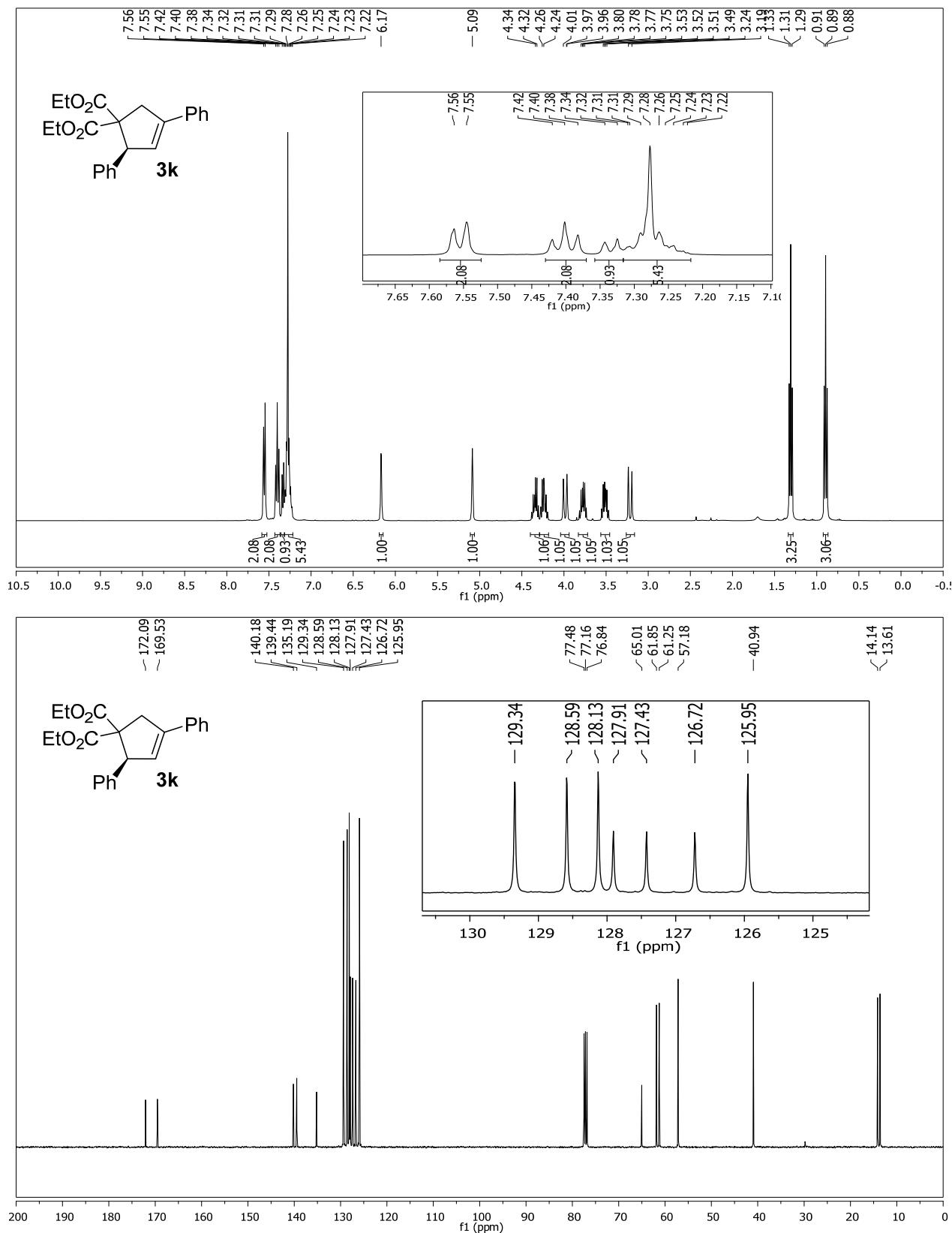
Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)



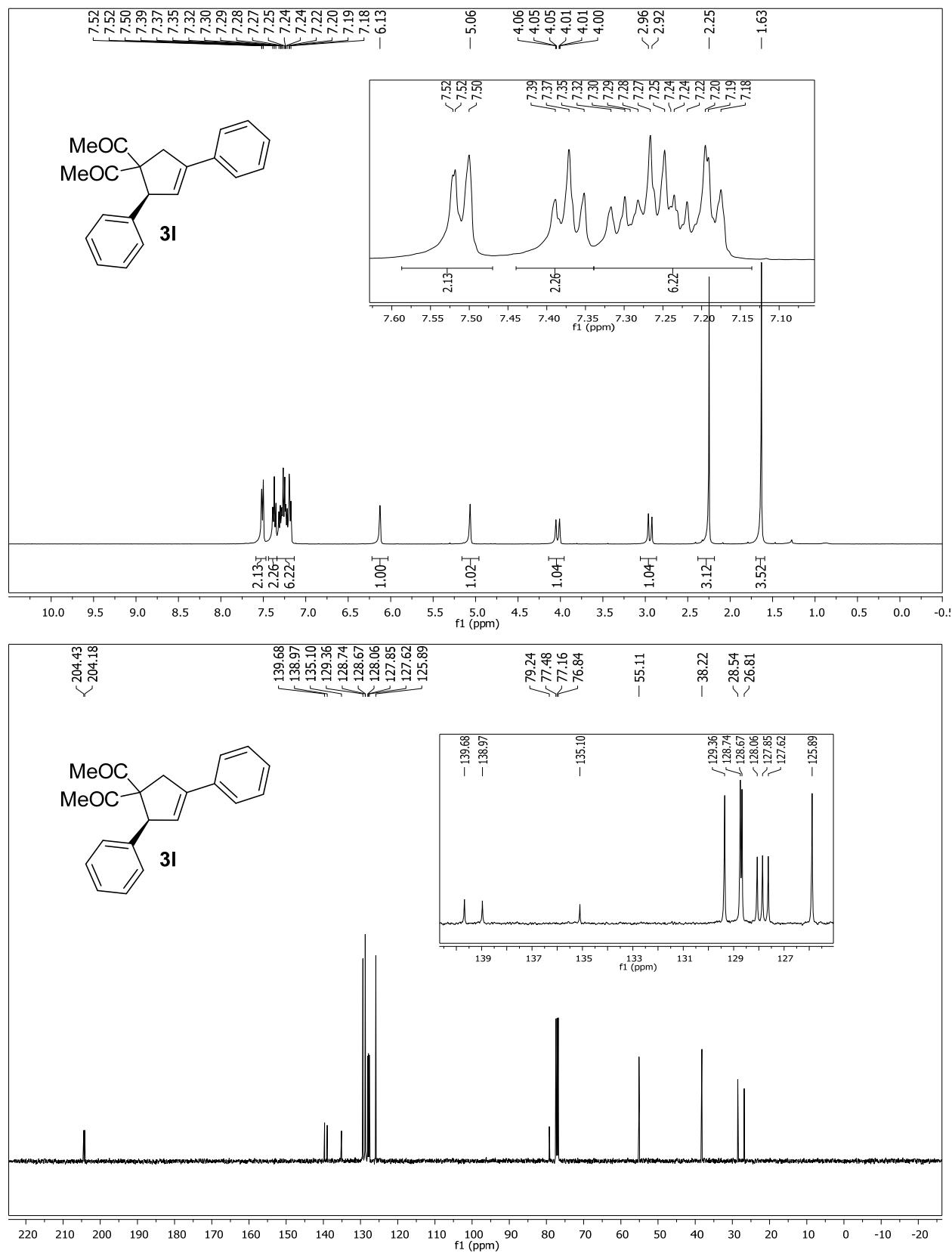
Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)



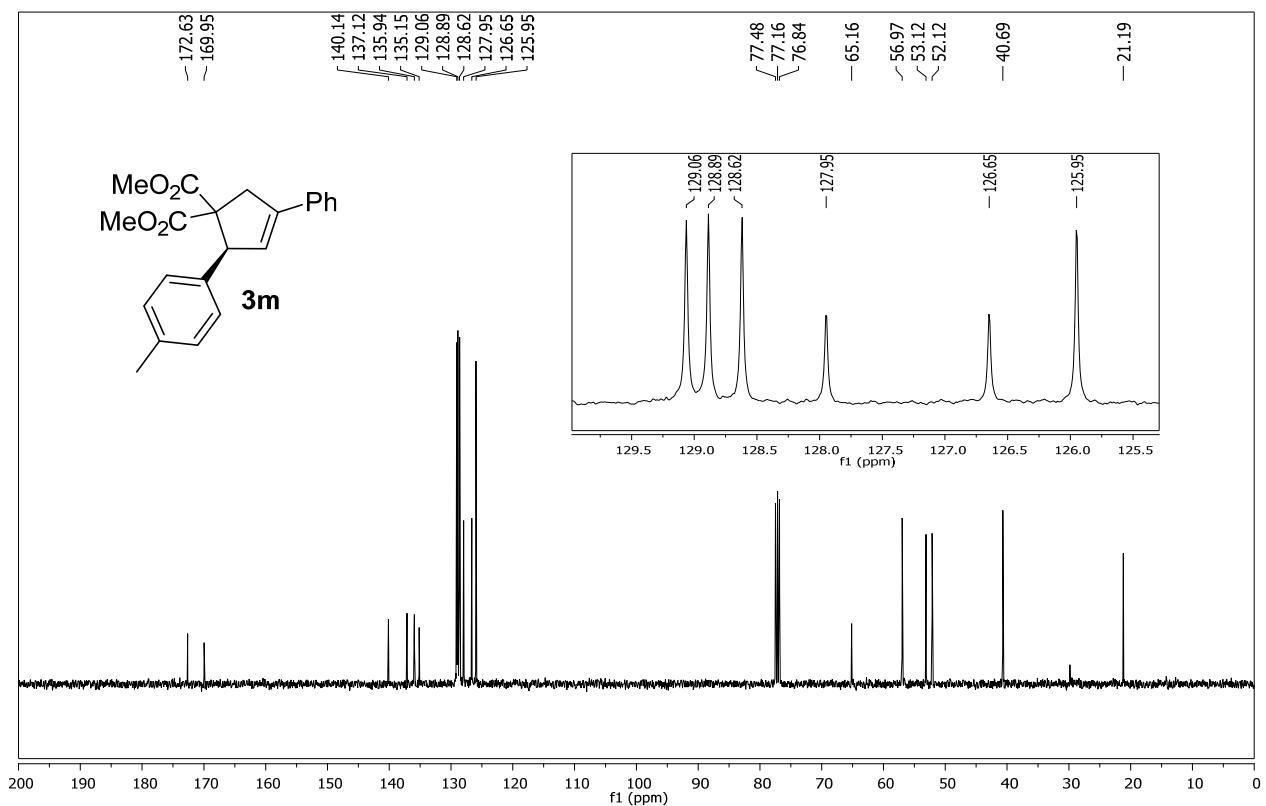
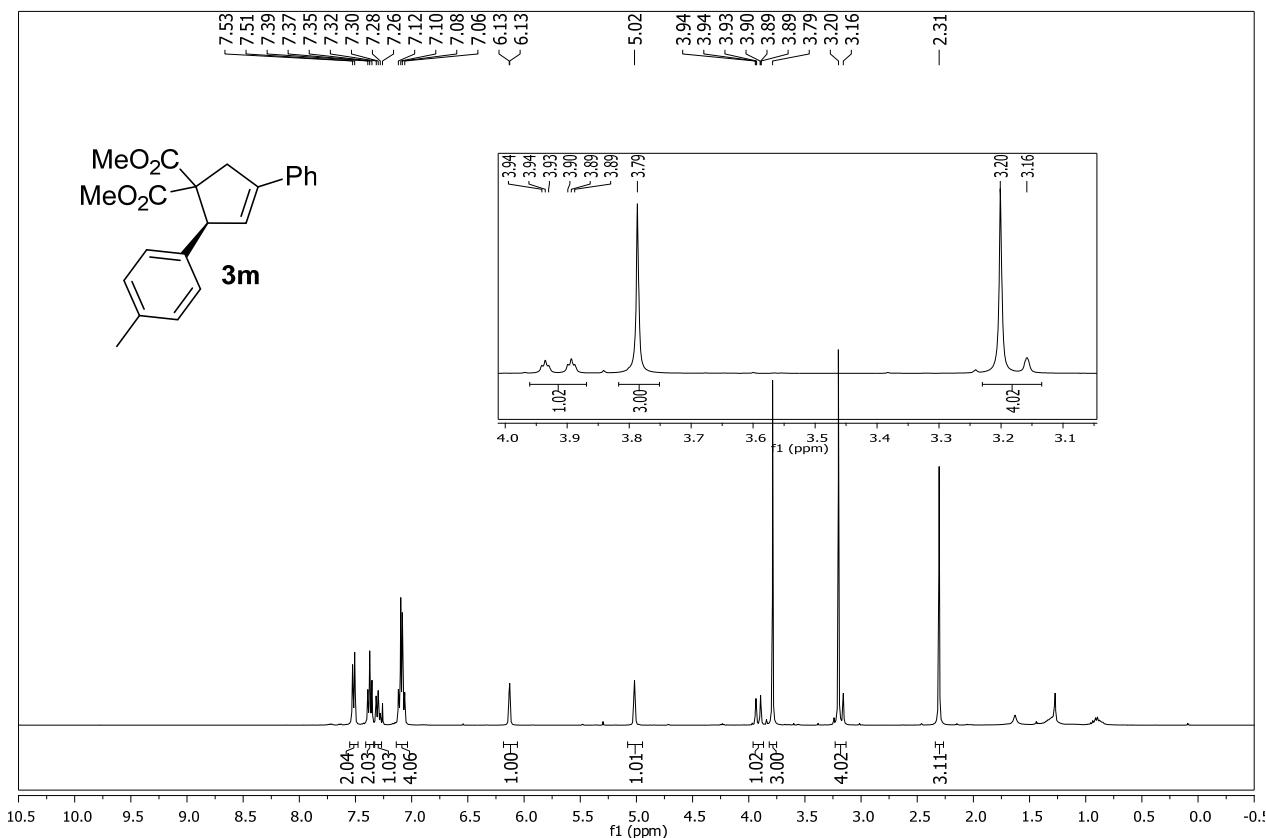
Diethyl 2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3k)



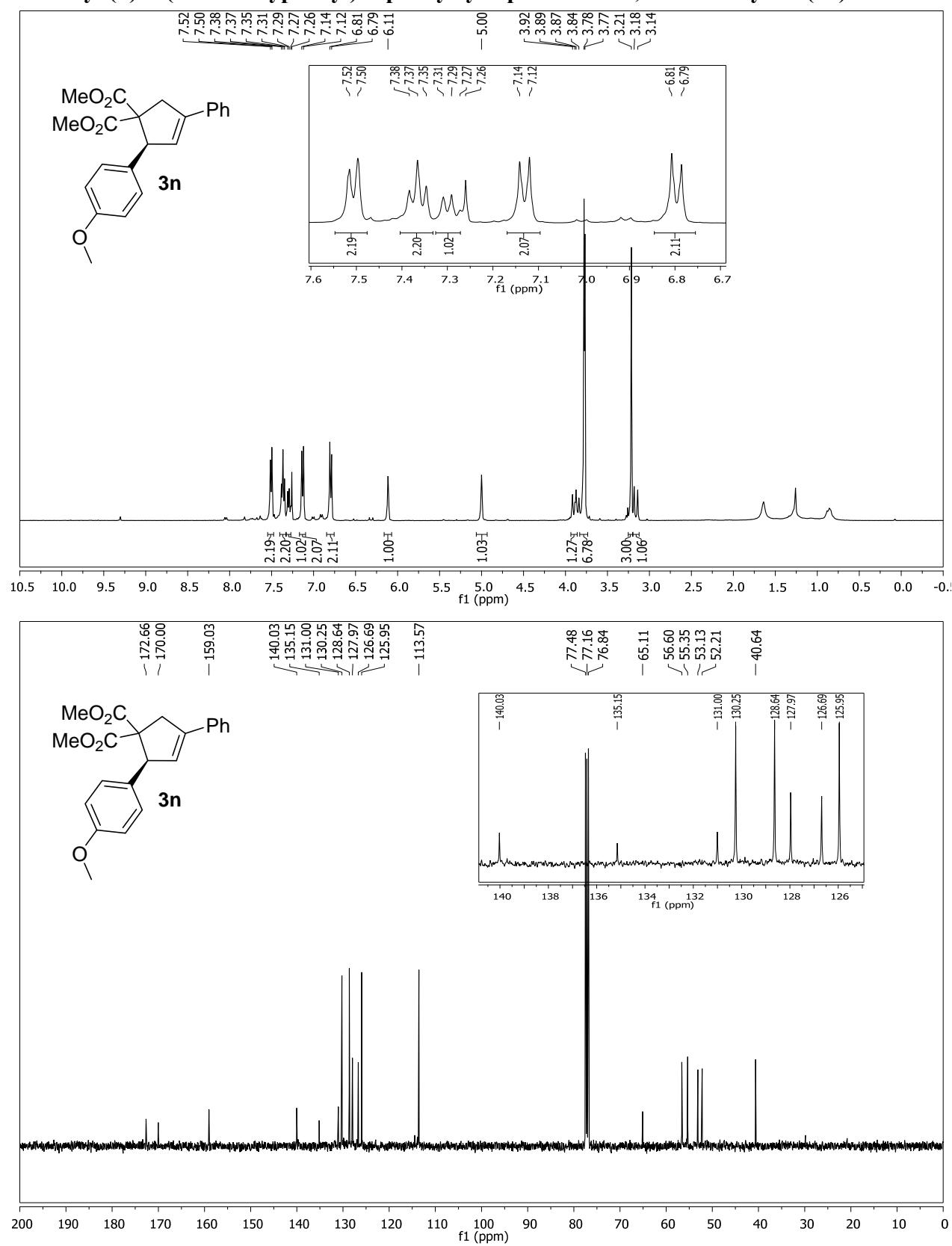
(S)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diyl)bis(ethan-1-one) (3l)



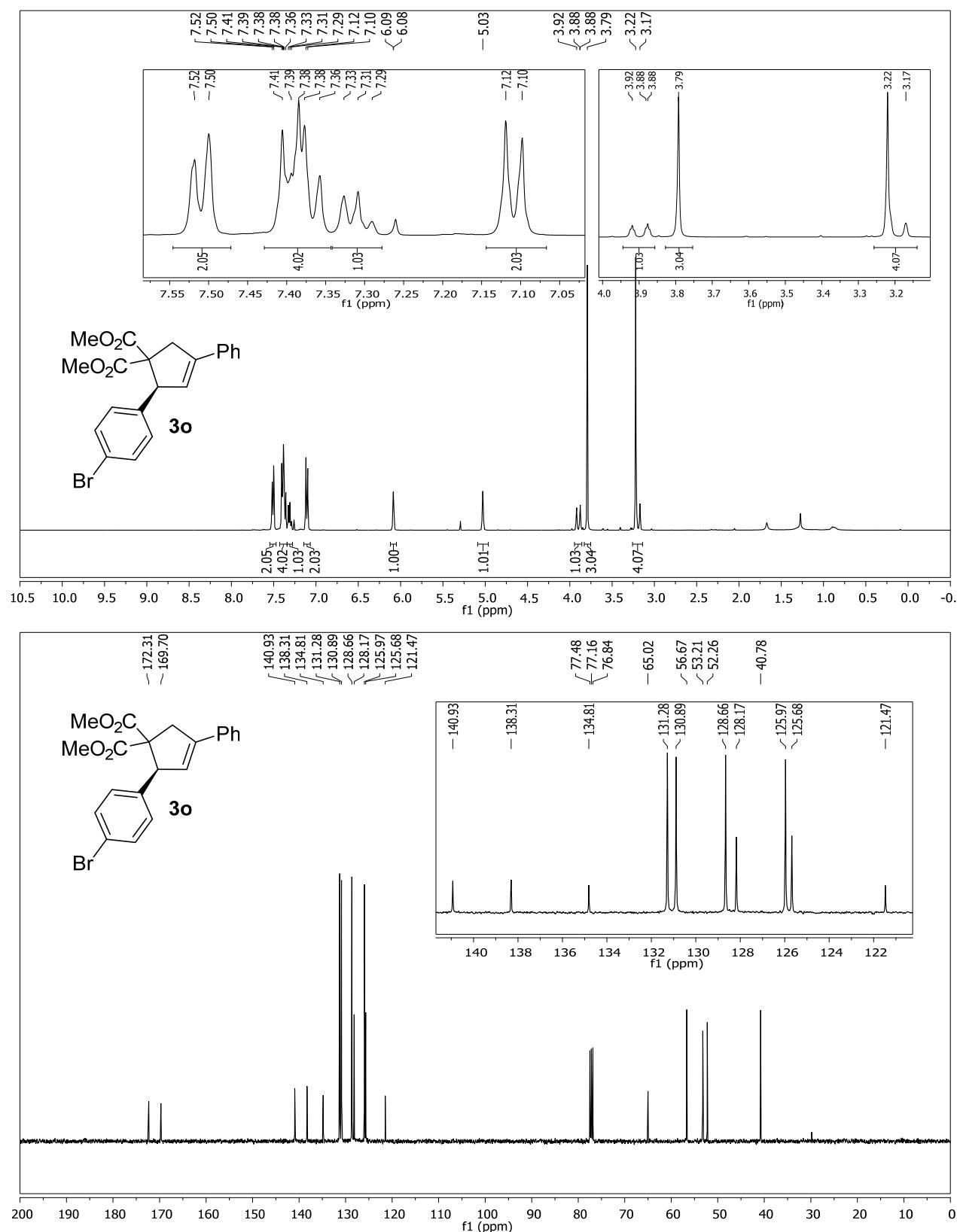
Dimethyl (S)-4-phenyl-2-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3m**)**



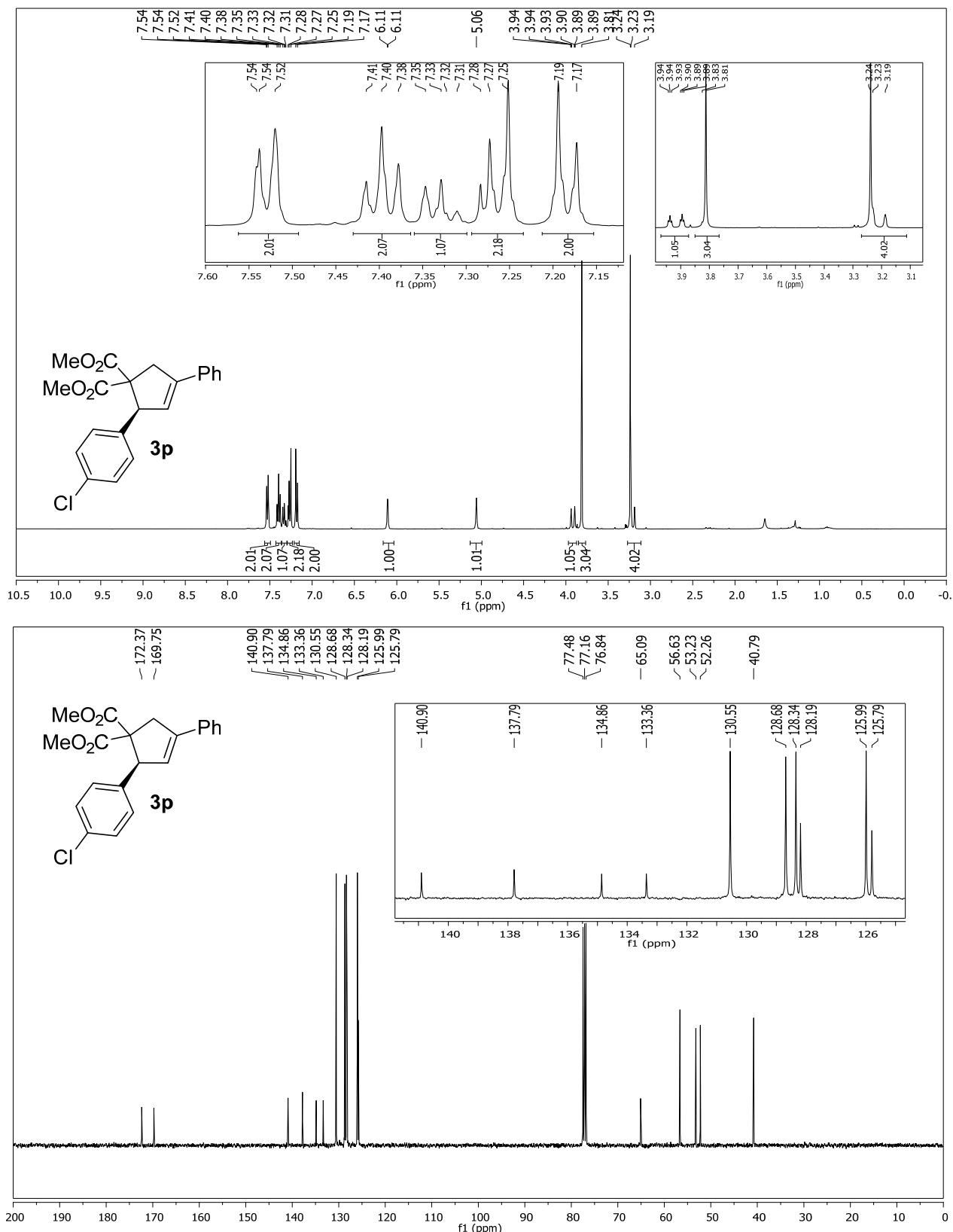
Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3n)



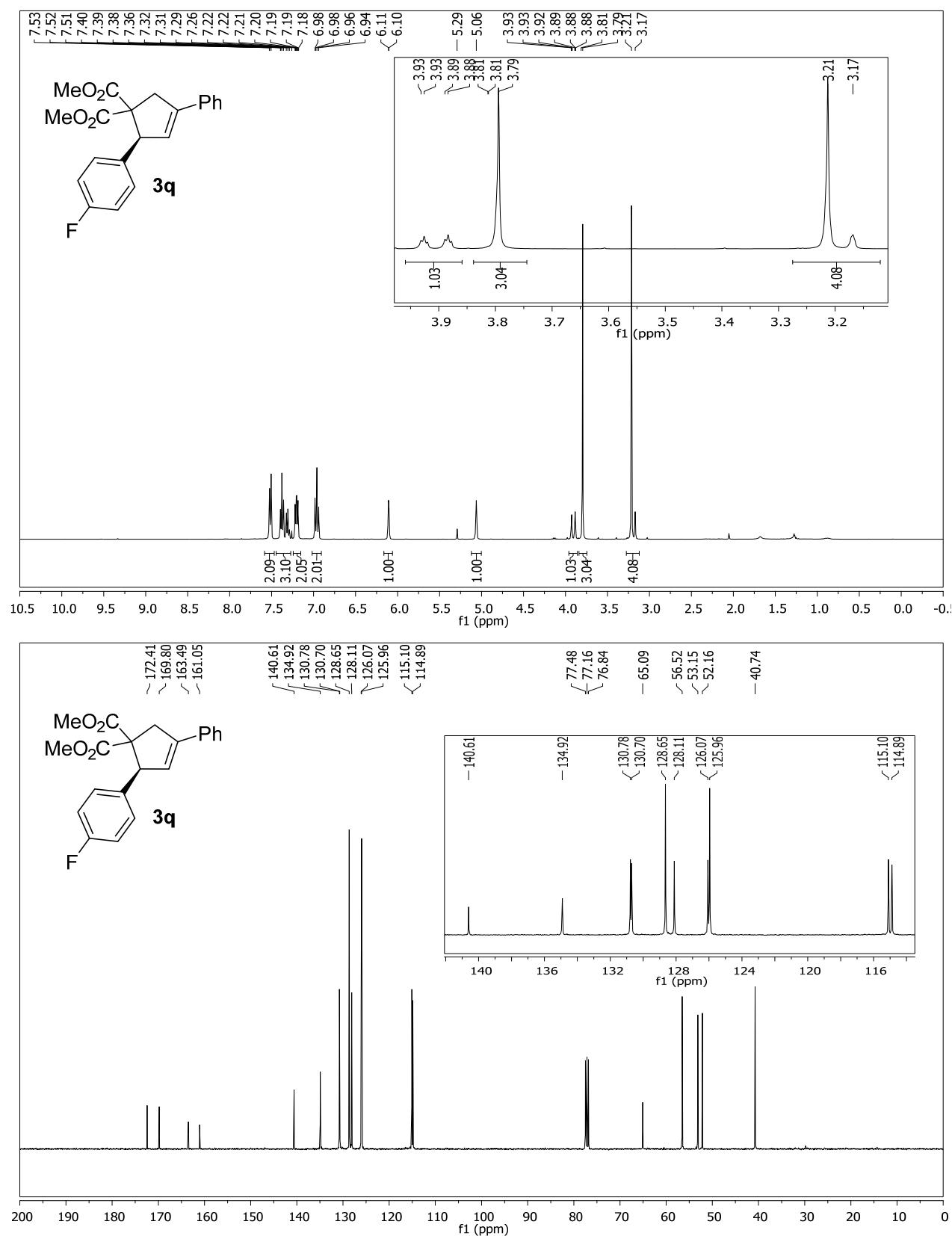
Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)



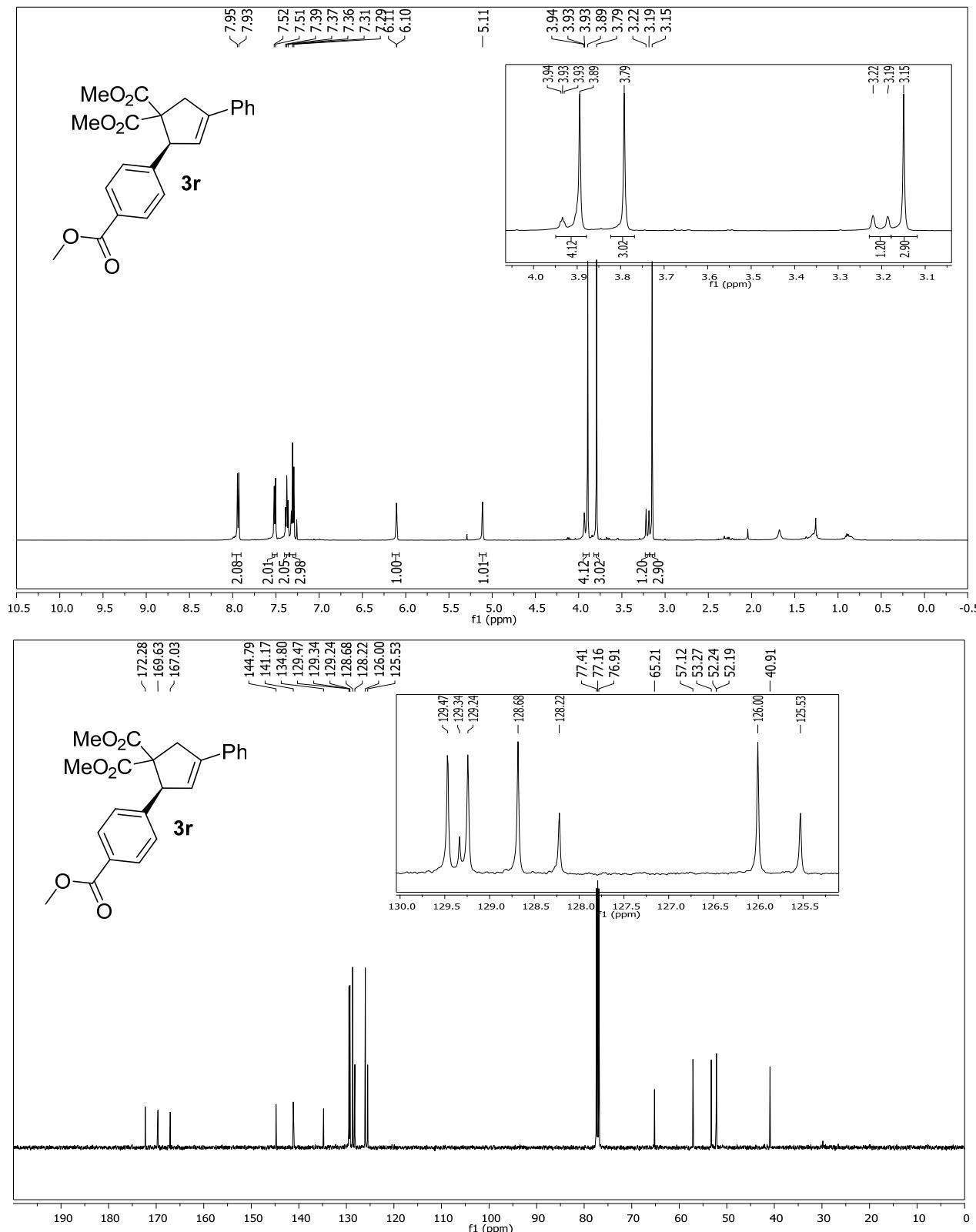
Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)



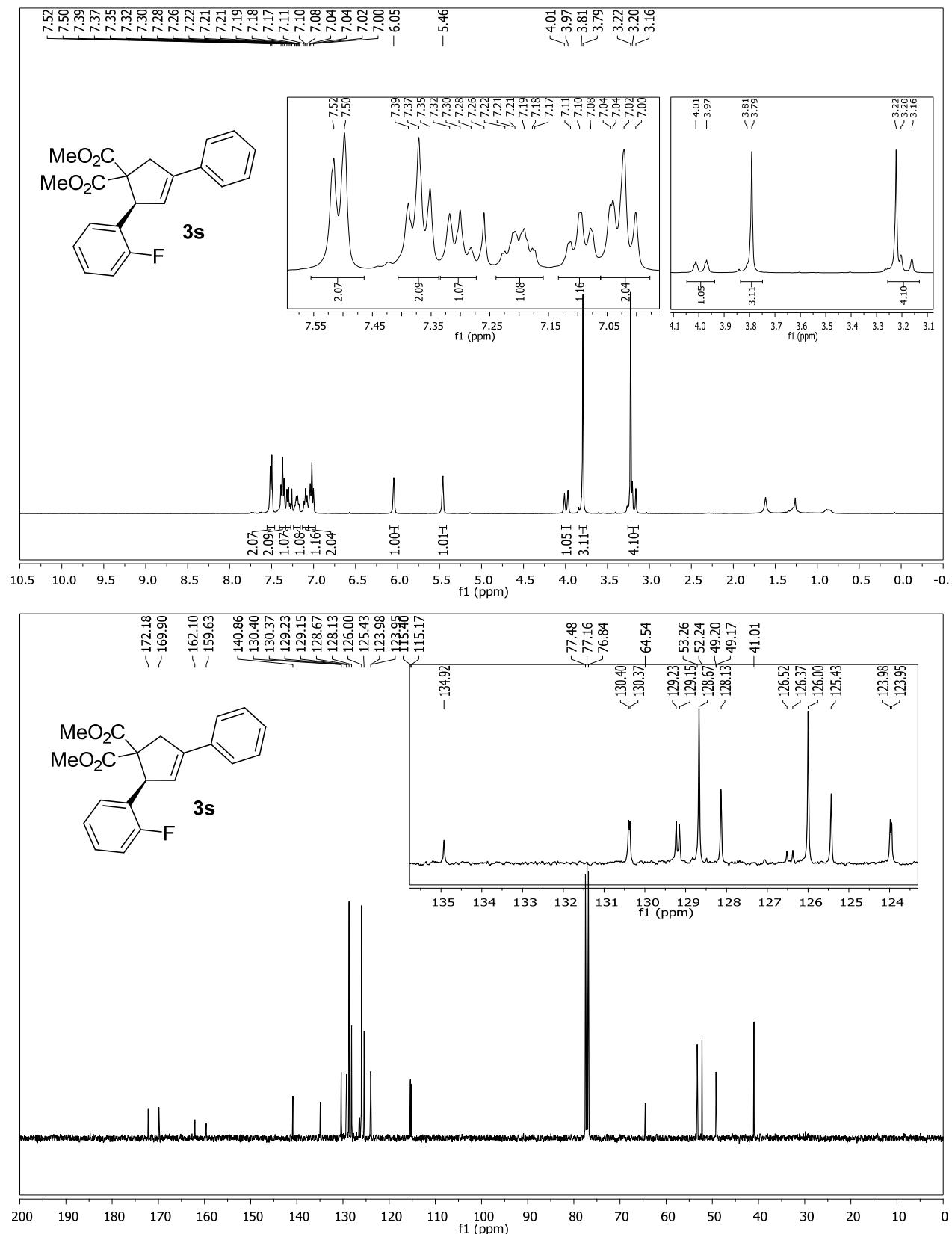
Dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3q)



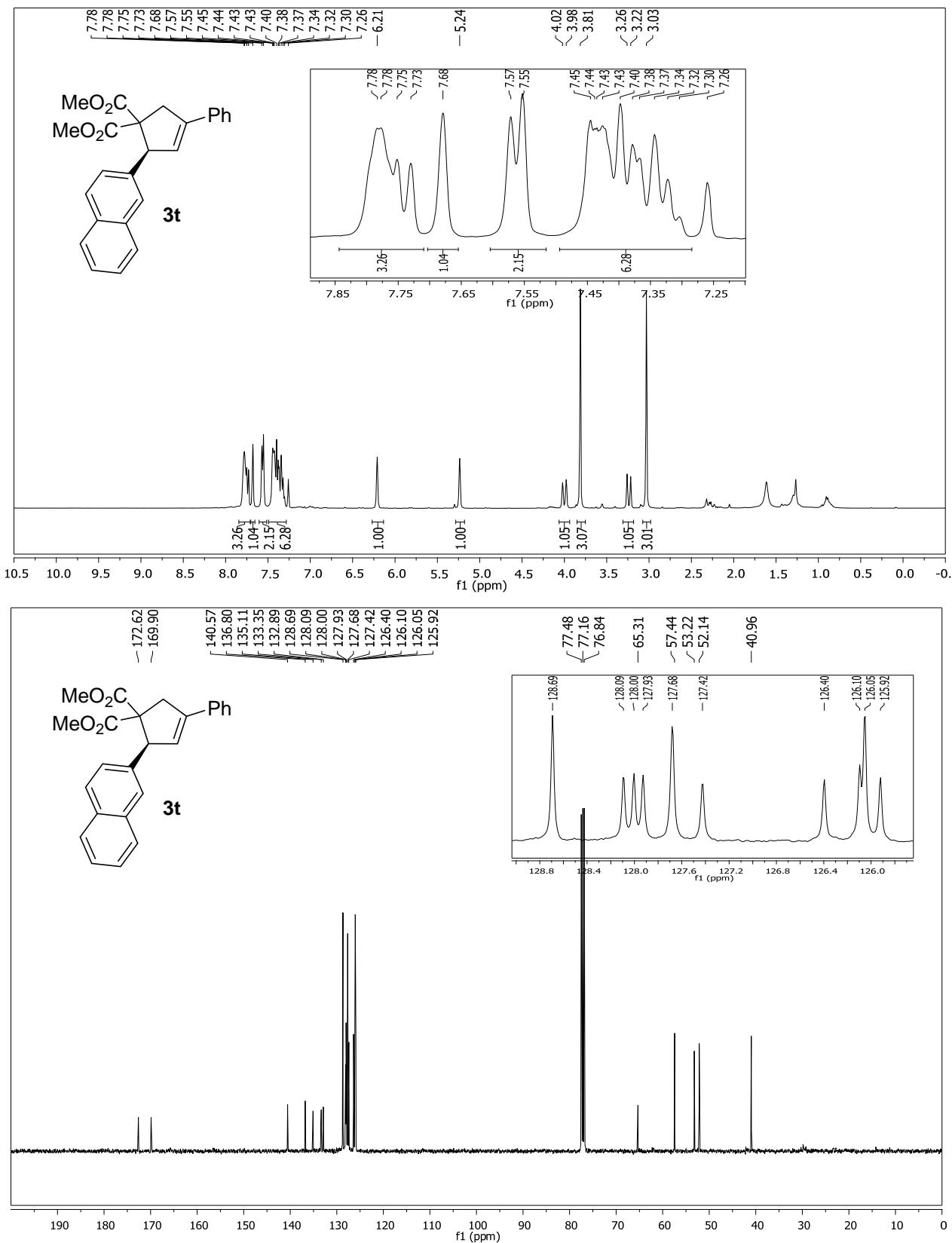
**Dimethyl (S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate
(3r)**



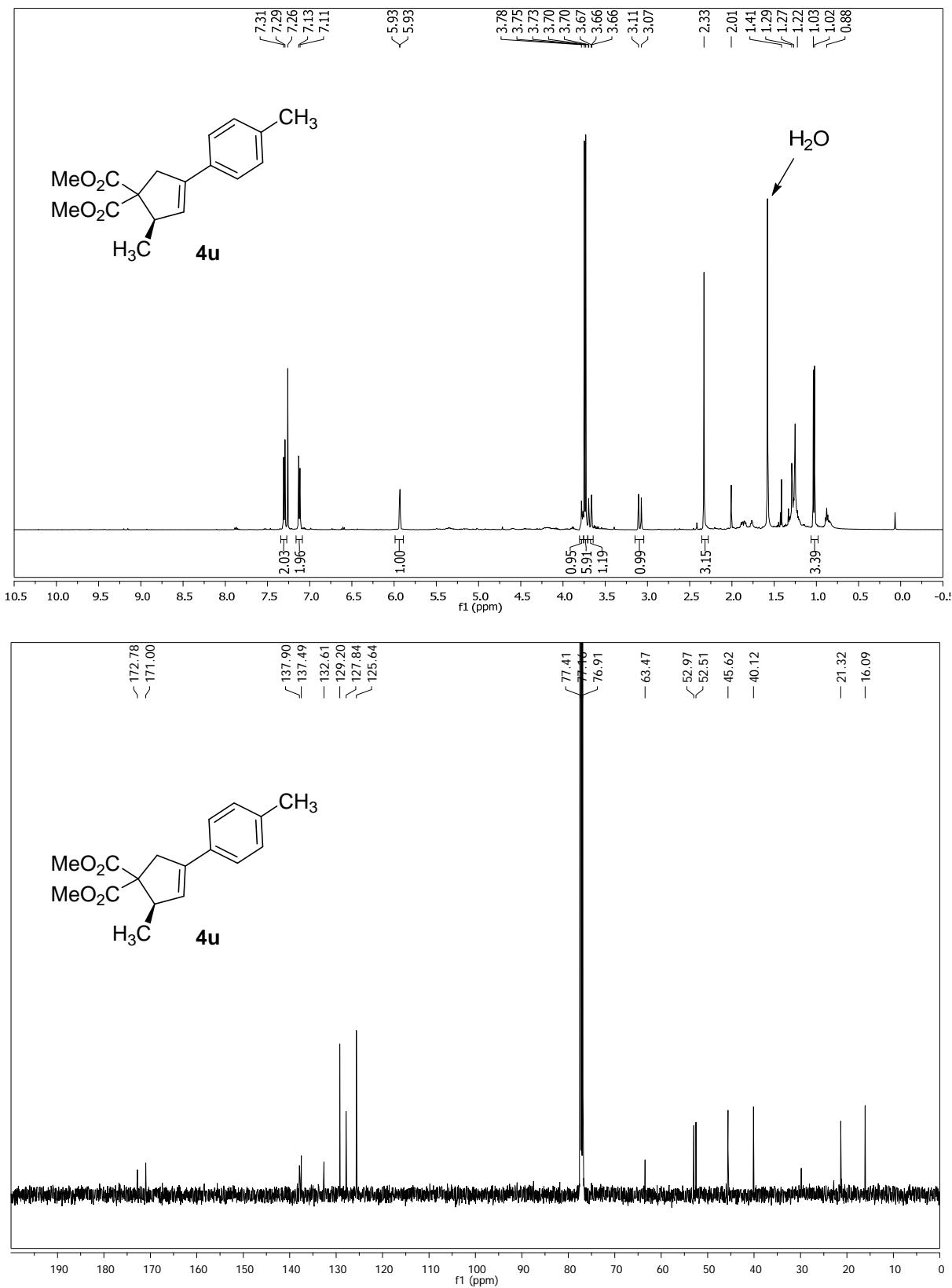
Dimethyl (*R*)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)



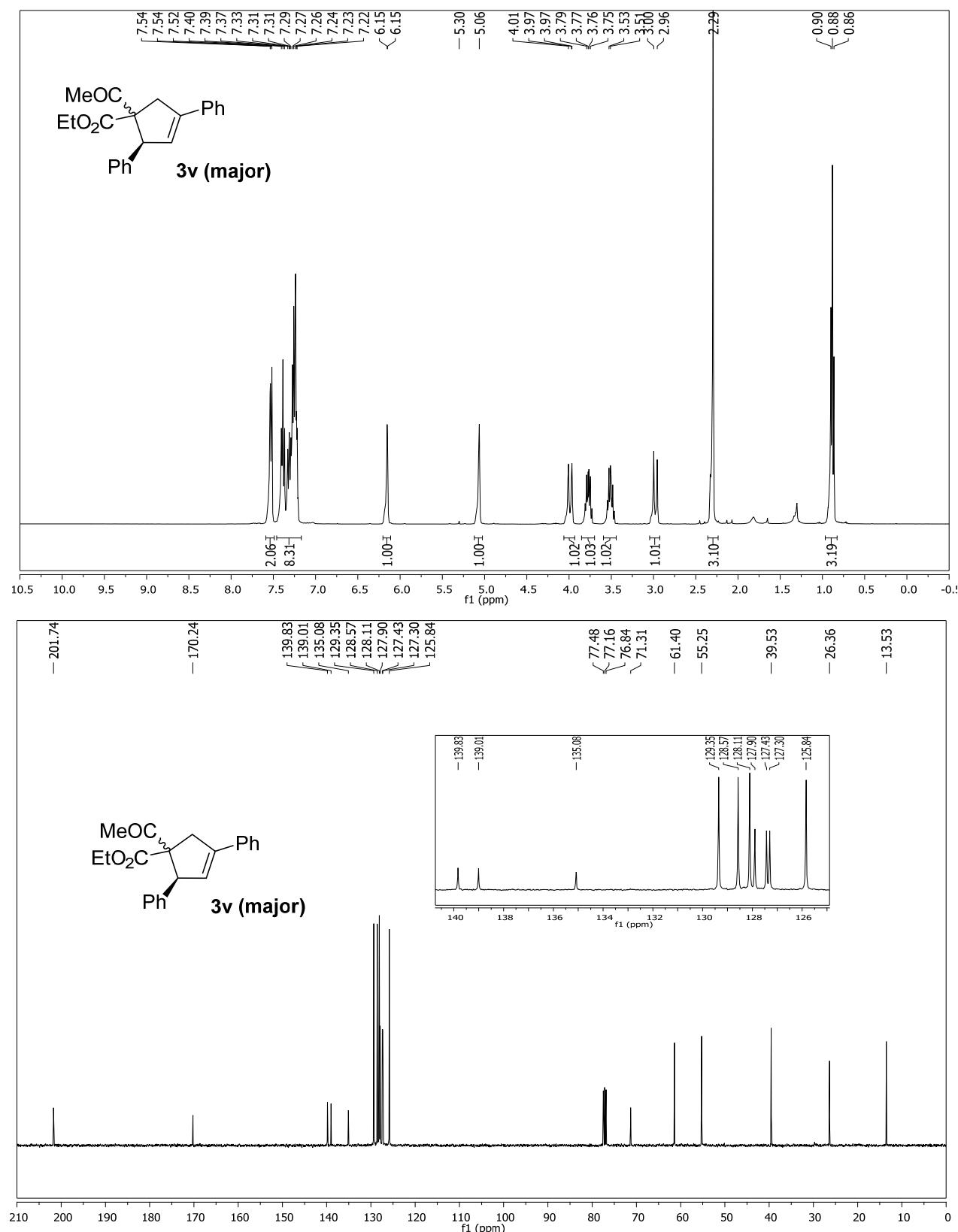
Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)



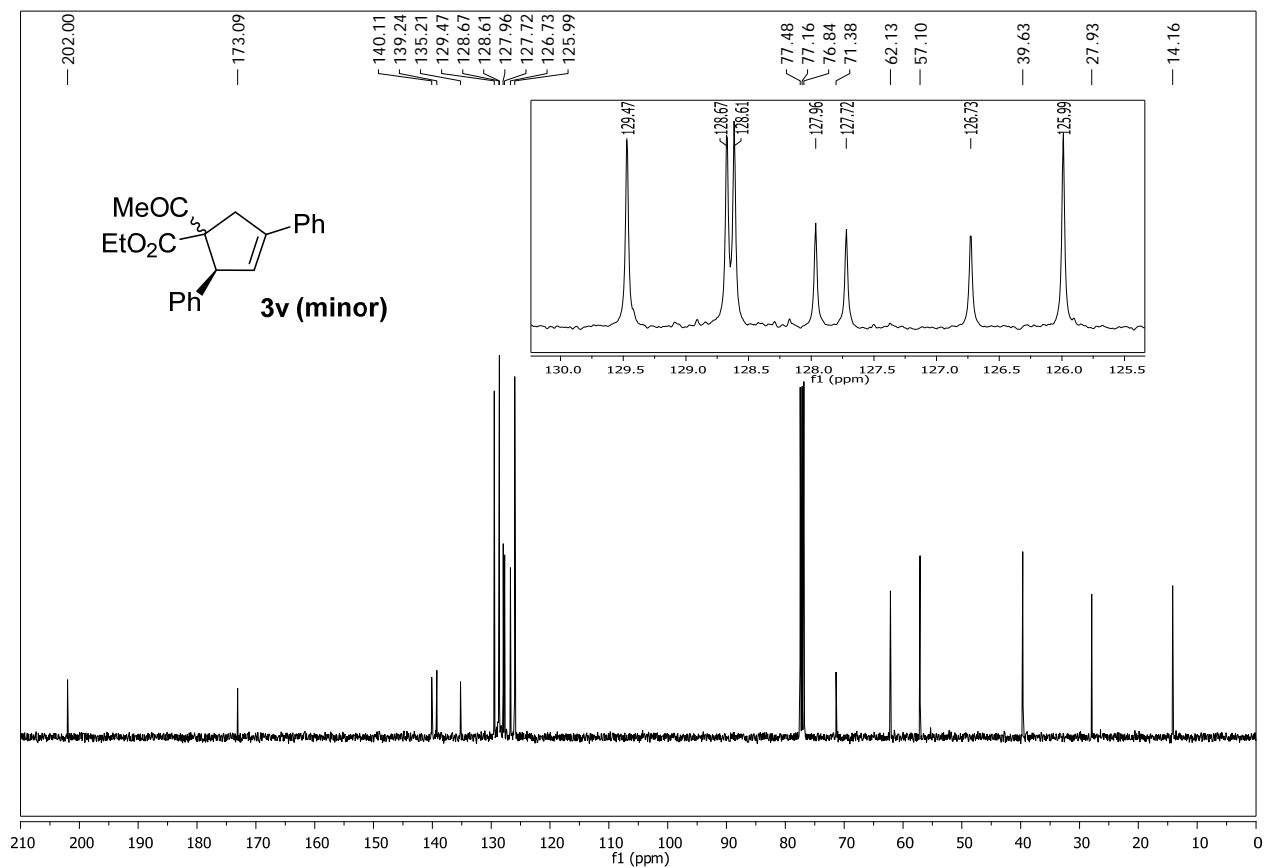
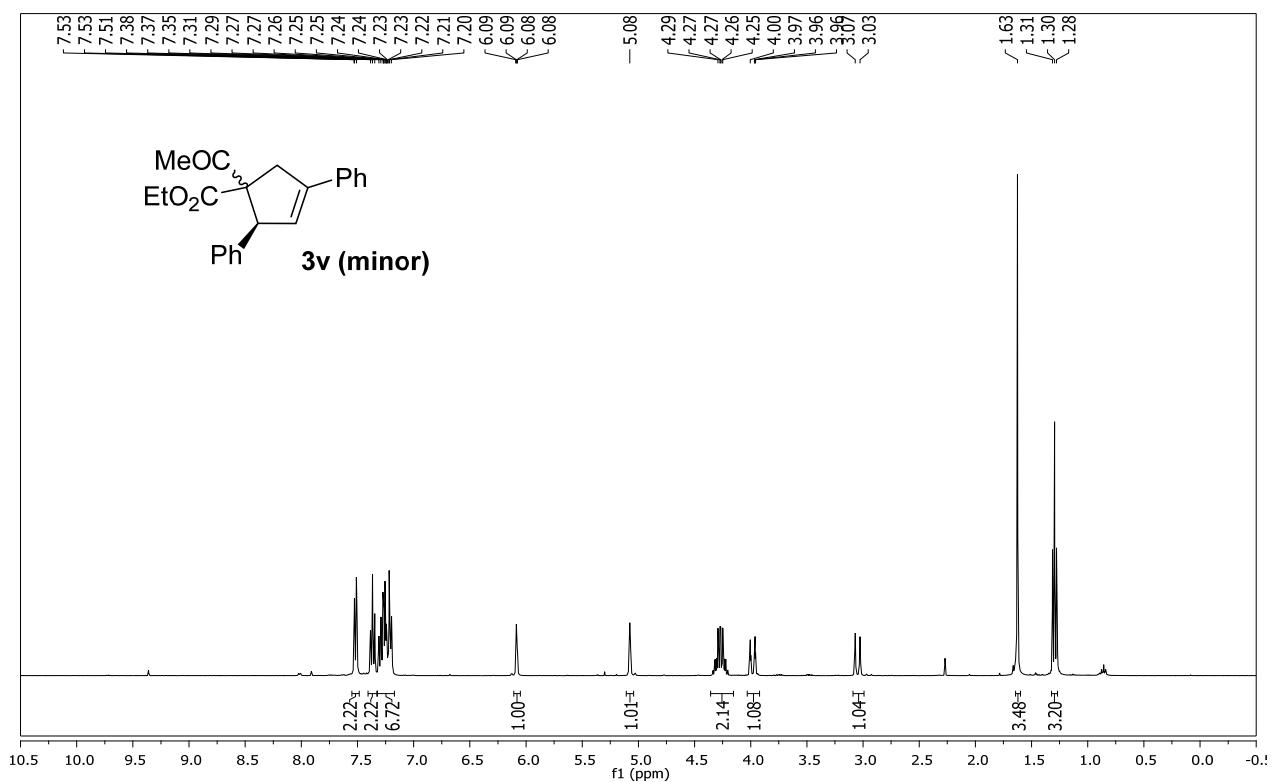
Dimethyl (*R*) 2-methyl-4-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (4u**)**



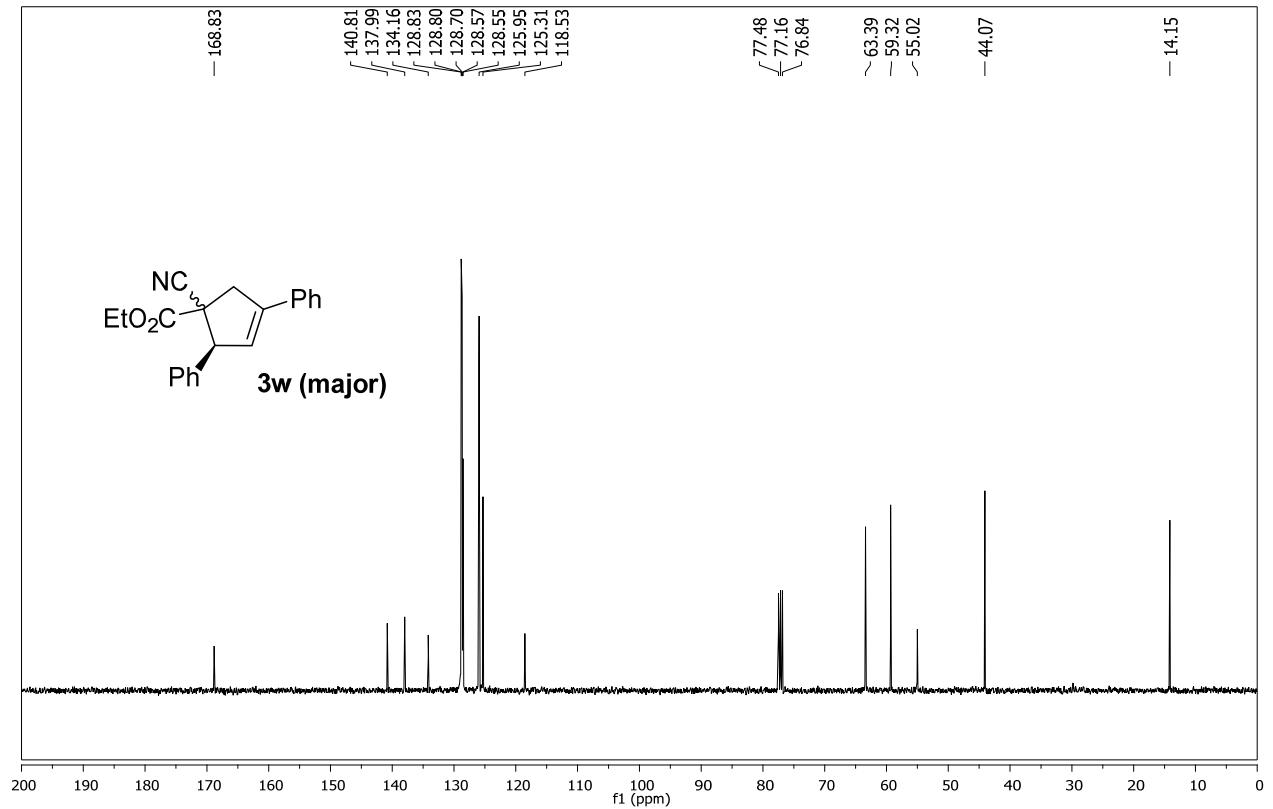
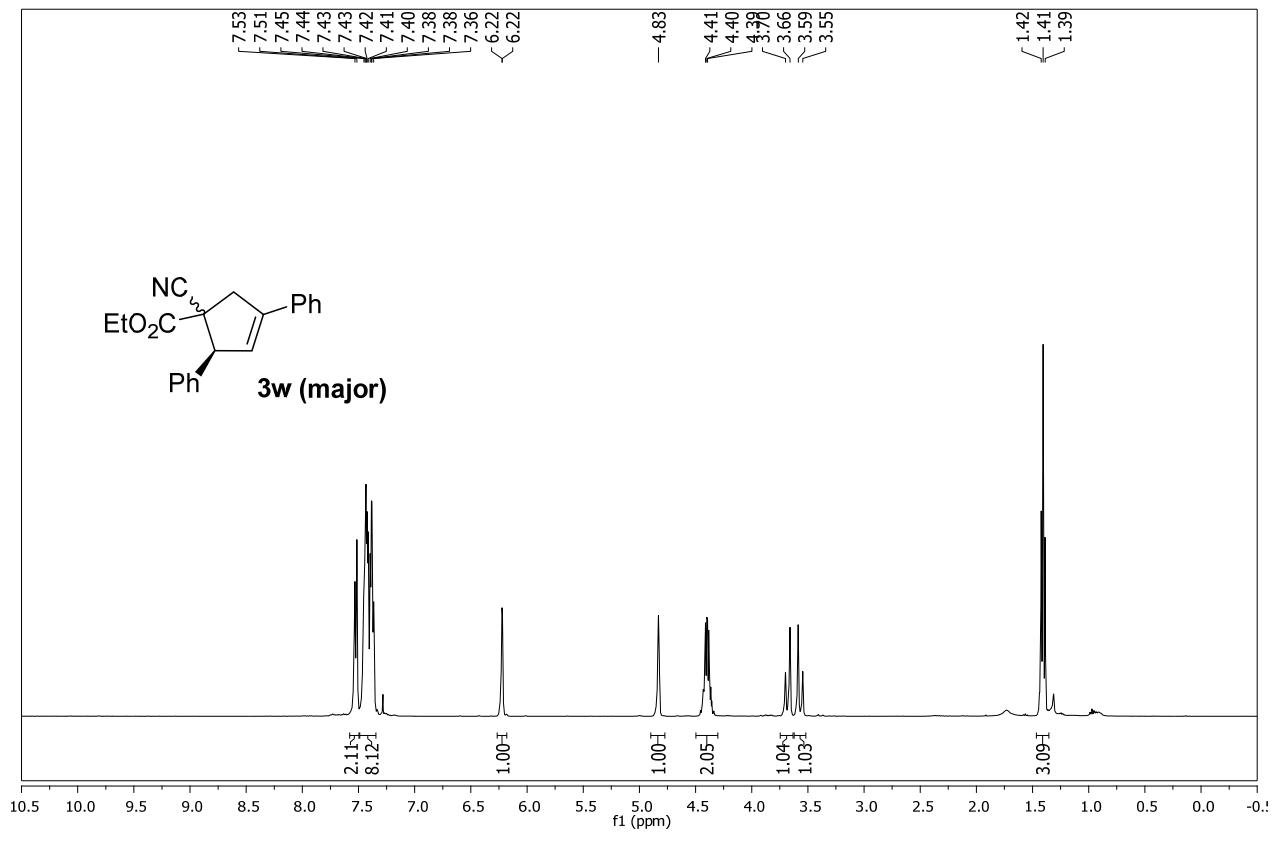
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (3v major**)**



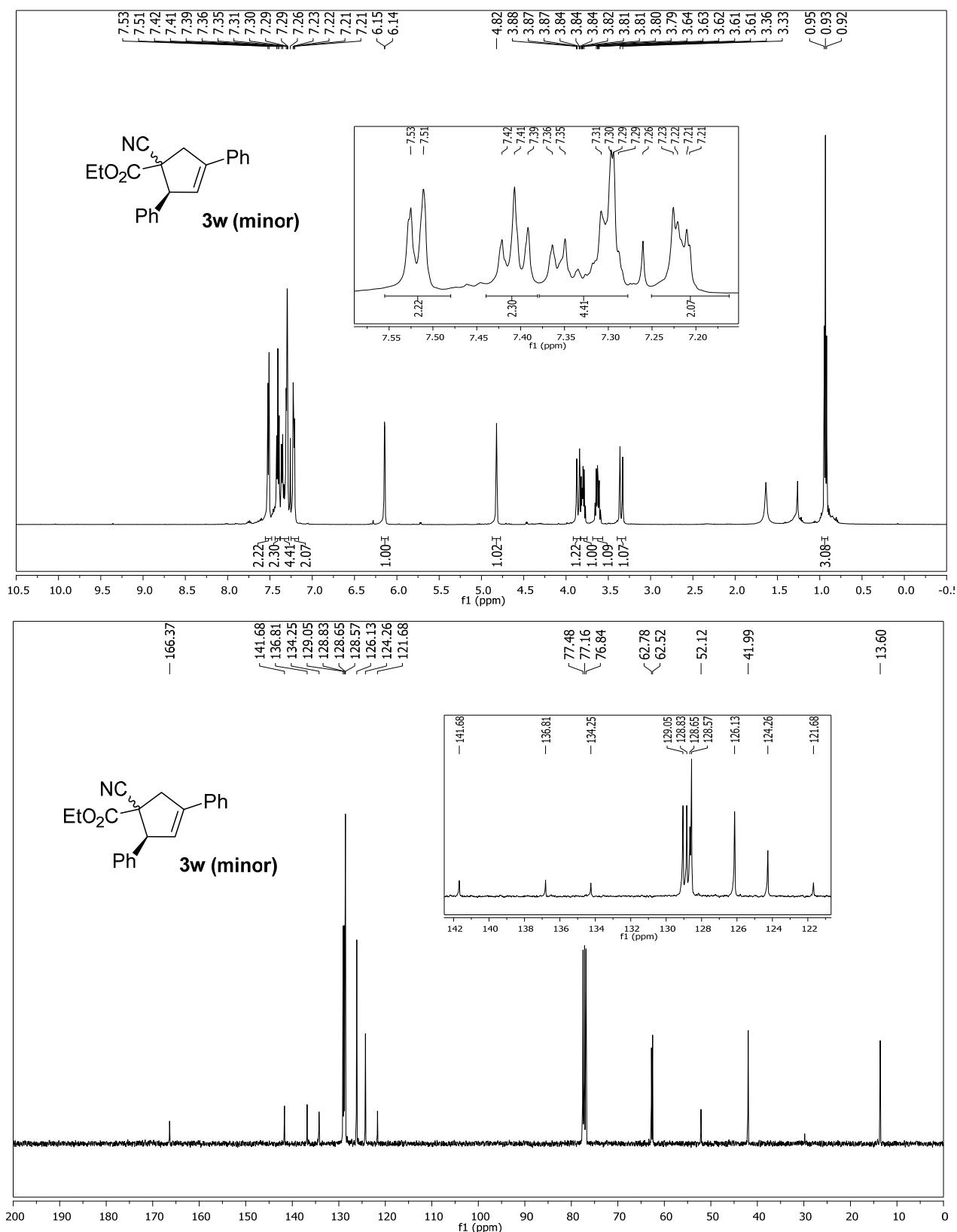
Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (*3v minor*)



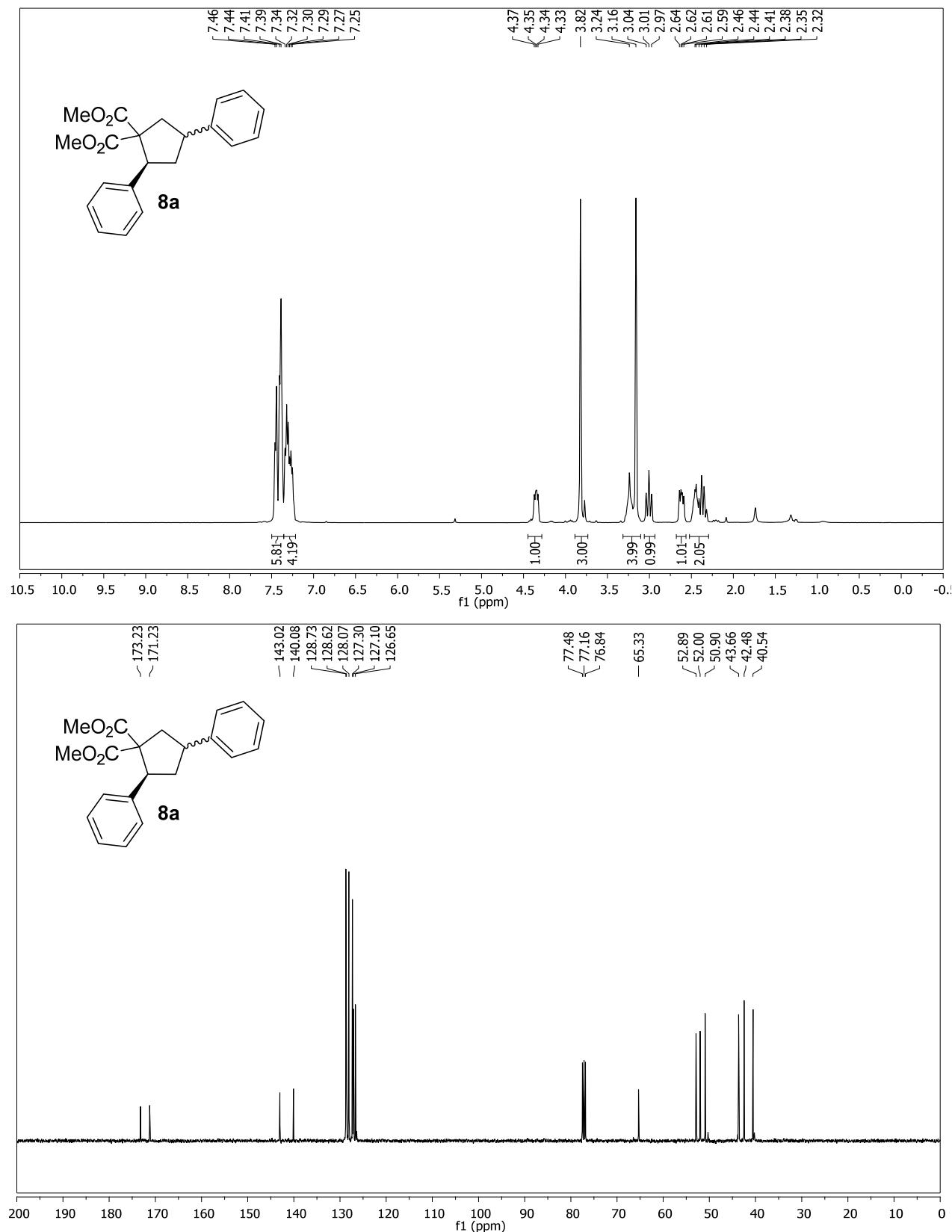
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w major**)**



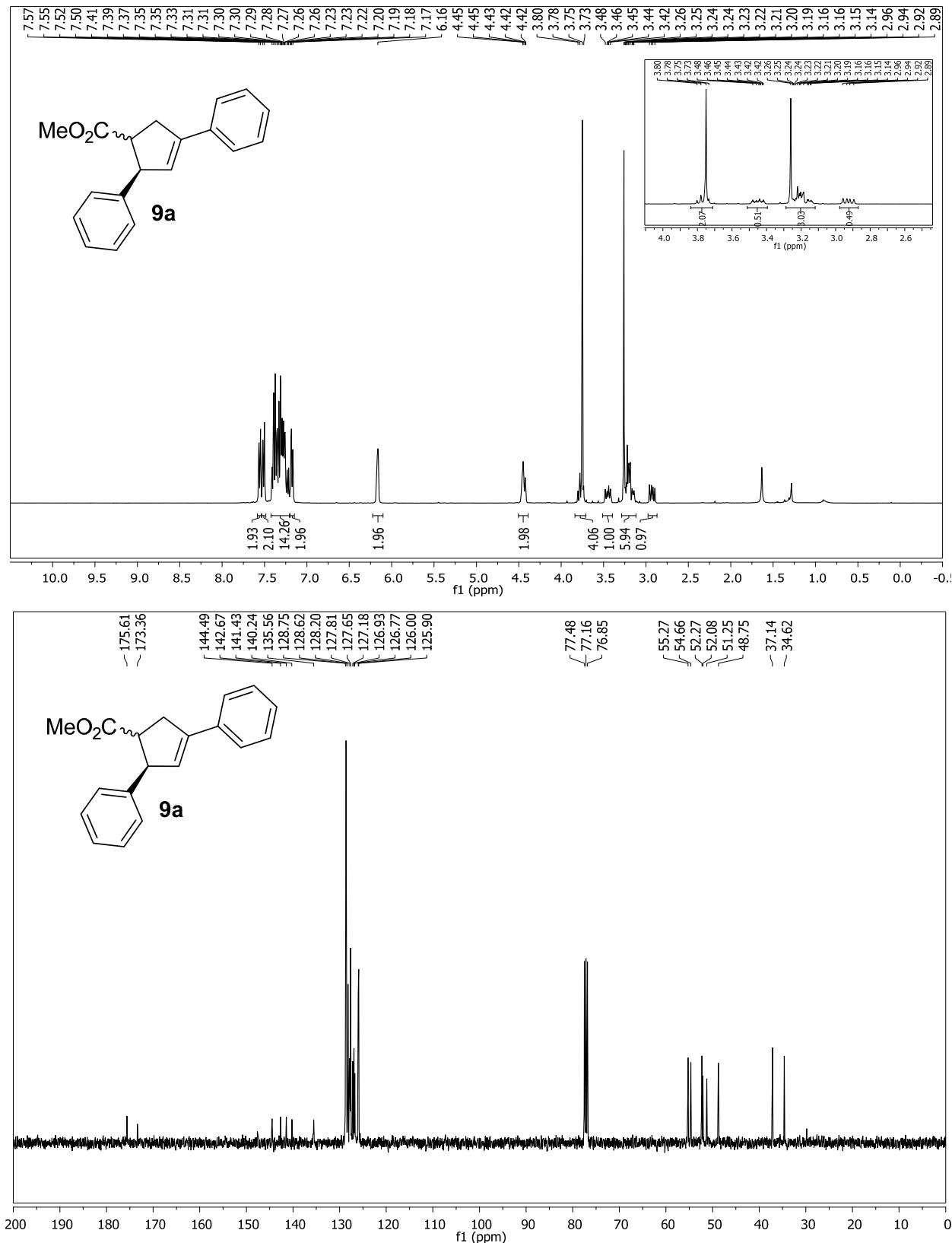
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (3w minor**)**



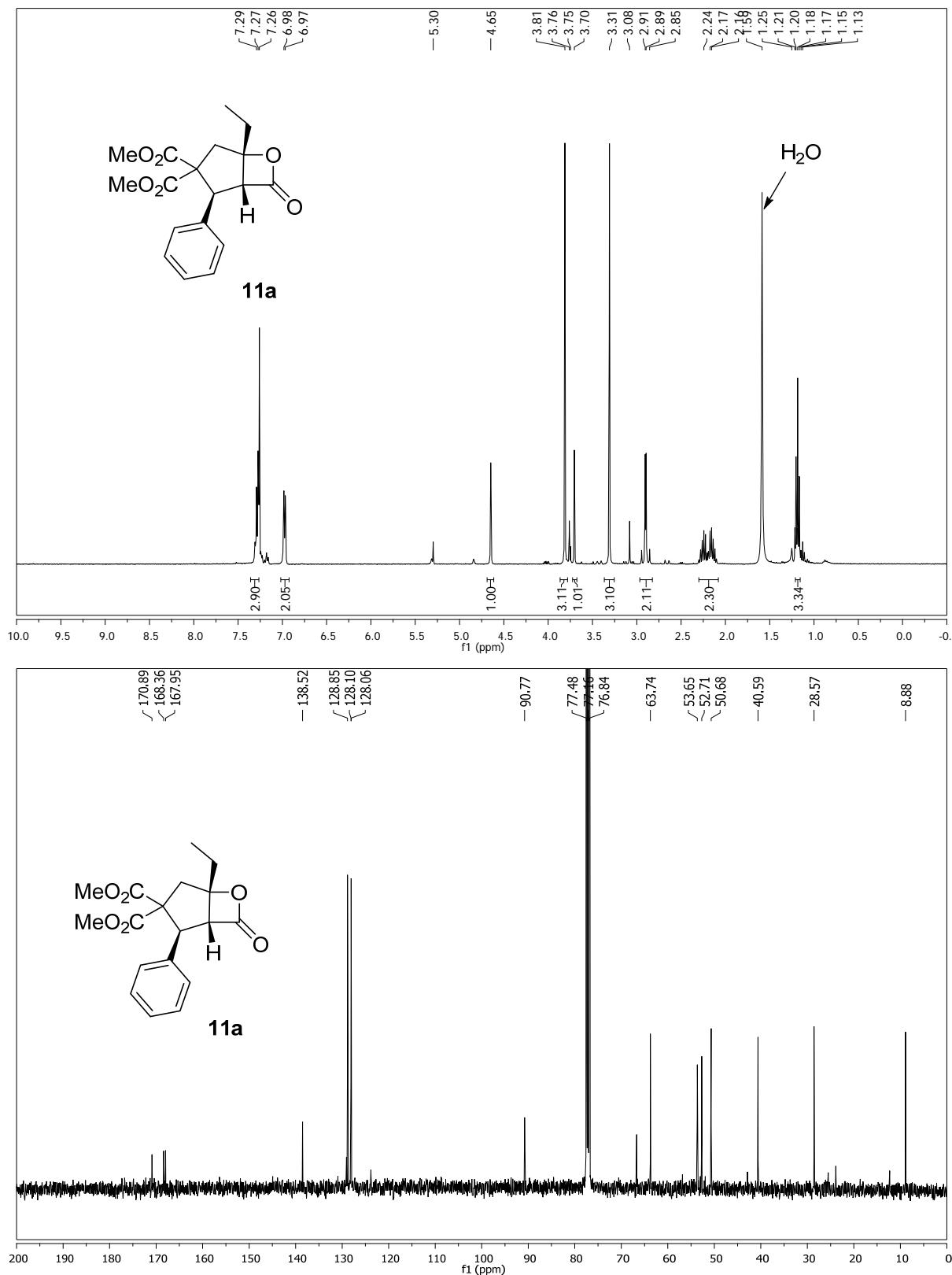
Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)



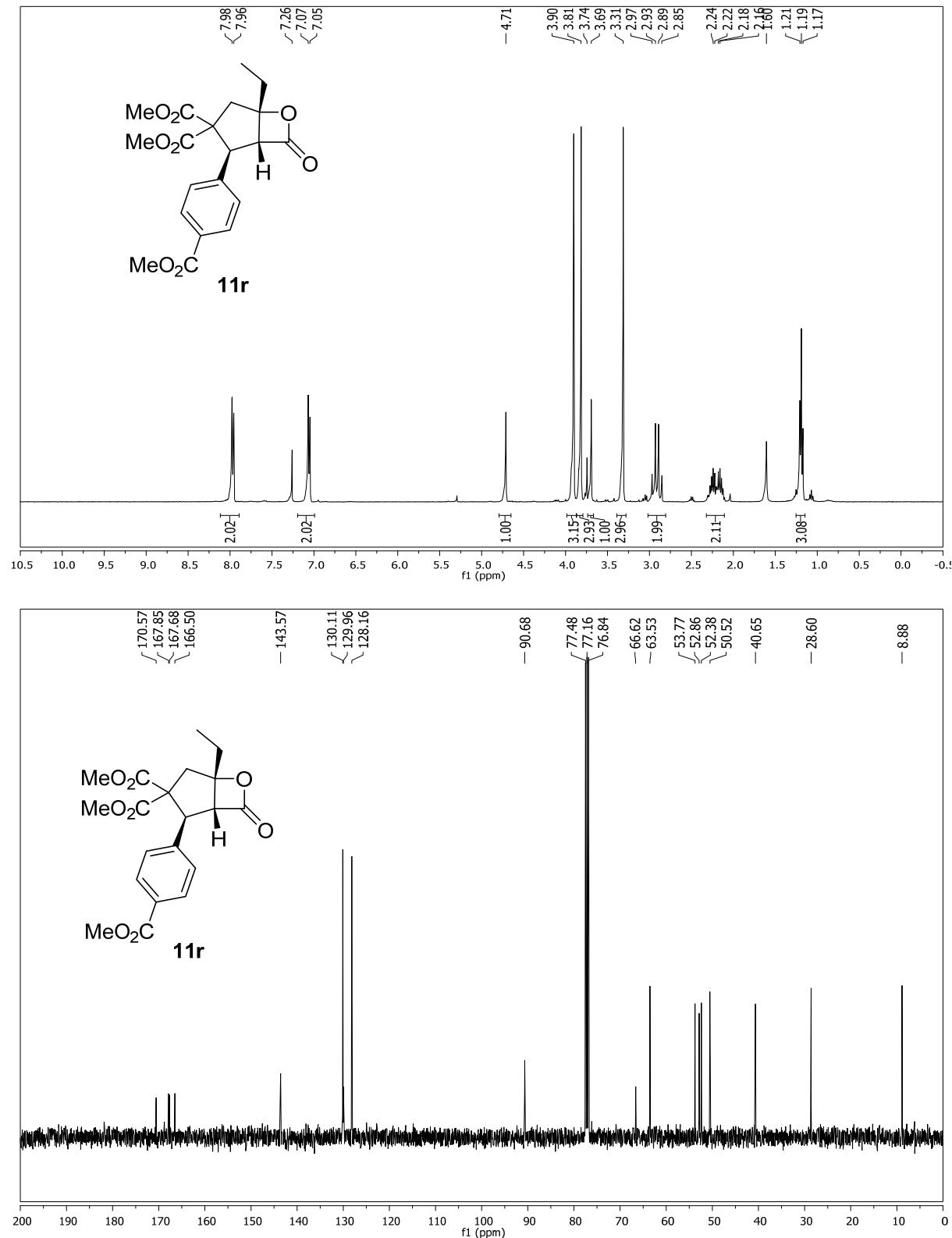
Methyl (2*R*)-2,4-diphenylcyclopent-3-ene-1-carboxylate (9a**)**



Dimethyl (1*R*2*S*5*S*) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11a)

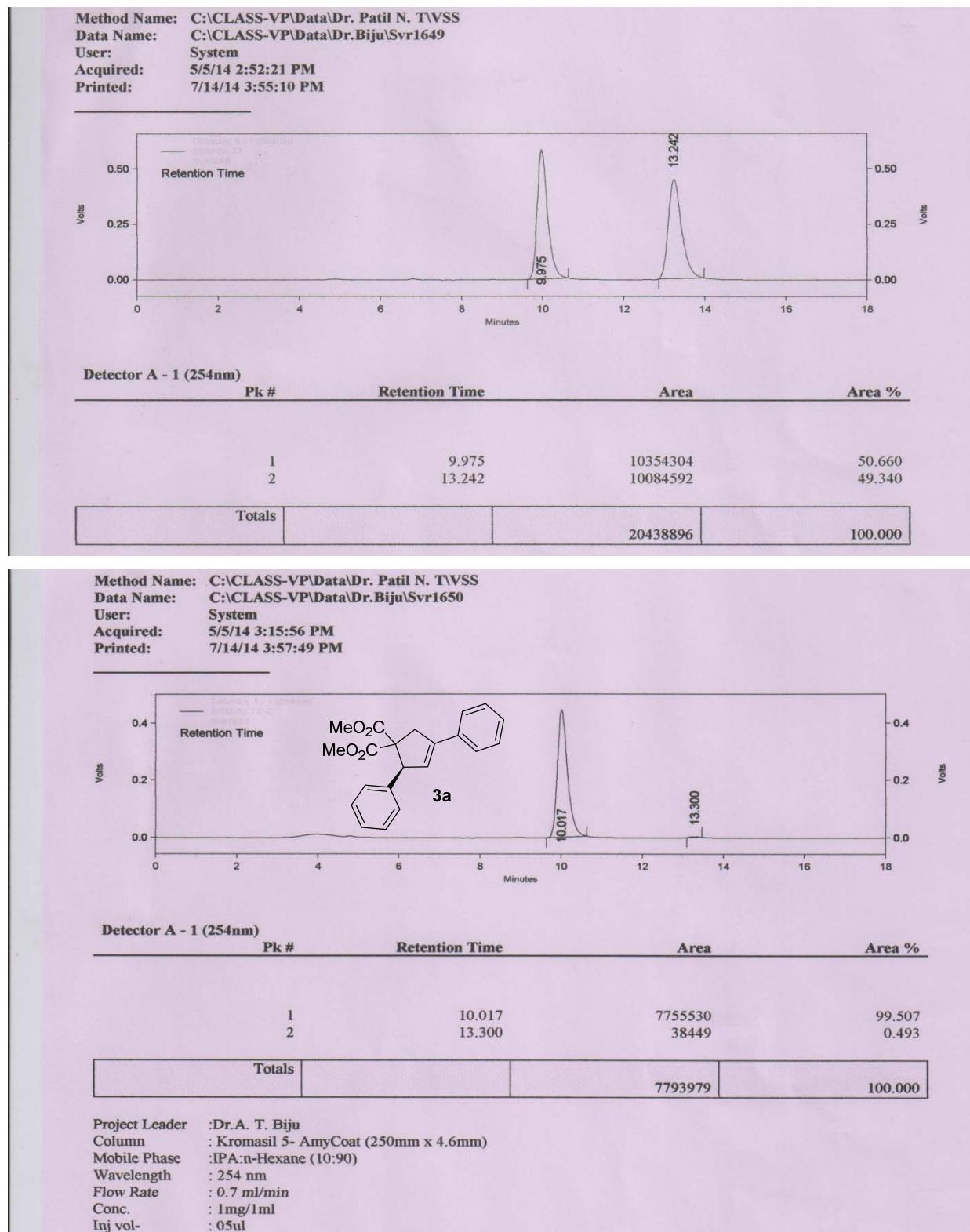


Dimethyl (1R2S5S) 5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11r)



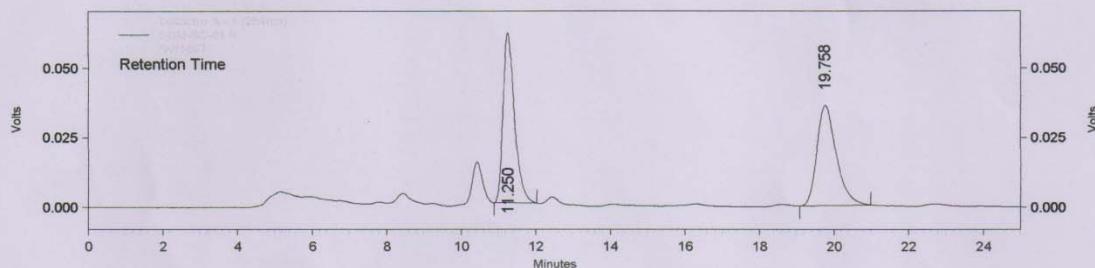
7. HPLC Scans of Functionalized Cyclopentenes

Dimethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3a)



Dimethyl (S)-2-phenyl-4-(p-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3b)

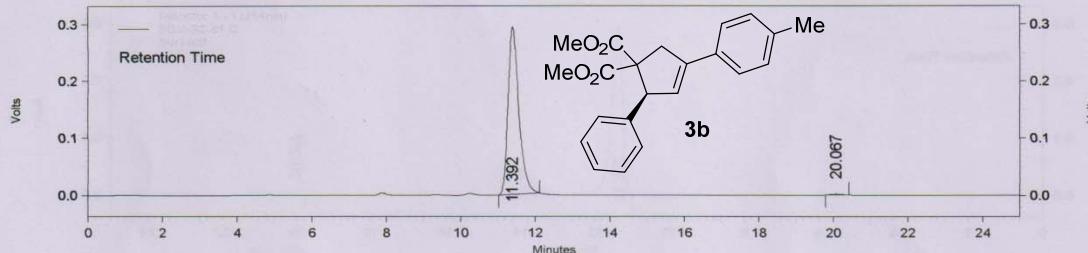
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1667
 User: System
 Acquired: 5/9/14 3:55:32 PM
 Printed: 5/9/14 4:57:03 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	11.250	1319716	50.243
2	19.758	1306967	49.757
Totals		2626683	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1668
 User: System
 Acquired: 5/9/14 4:22:06 PM
 Printed: 5/9/14 5:12:52 PM



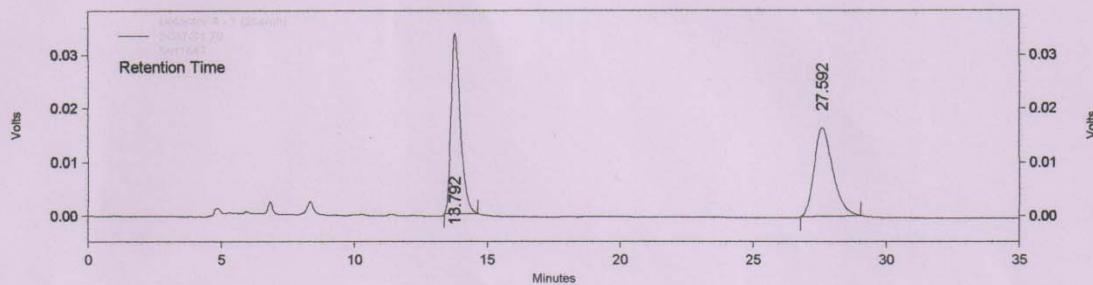
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	11.392	5898228	99.483
2	20.067	30625	0.517
Totals		5928853	100.000

Project Leader : Dr A. T. BIJU
 Column : Kromasil 5-AmyCoat (250mmX4.6mm)
 Mobile Phase : IPA:n-Hexane(10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 4ul
 Date : 09-05-2014

Dimethyl (S)-4-(4-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3c)

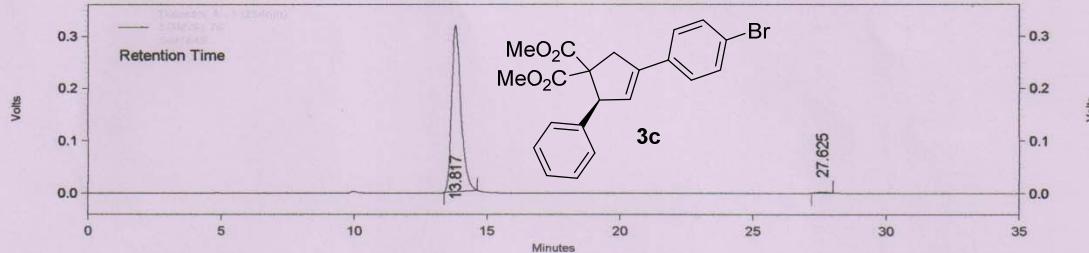
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1647
 User: System
 Acquired: 5/2/14 4:17:15 PM
 Printed: 7/14/14 3:59:42 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	13.792	822570	50.508
2	27.592	806029	49.492
Totals		1628599	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1648
 User: System
 Acquired: 5/2/14 4:54:54 PM
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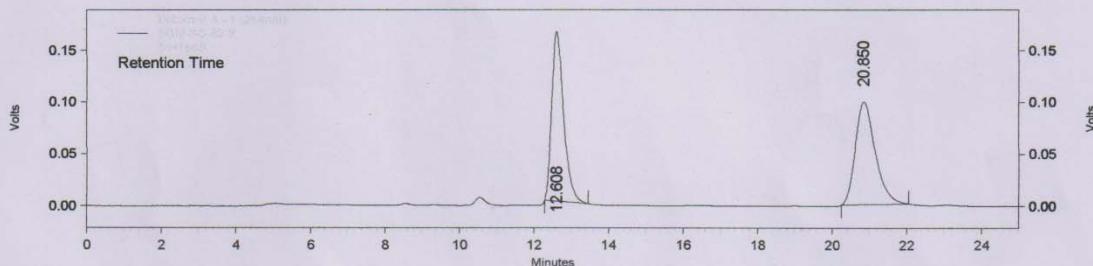
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	13.817	7710643	99.391
2	27.625	47233	0.609
Totals		7757876	100.000

Project Leader :Dr. A. T. Biju
 Column : Kromasil 5- AmyCoat (250mm x 4.6mm)
 Mobile Phase :IPA:n-Hexane (10:90)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

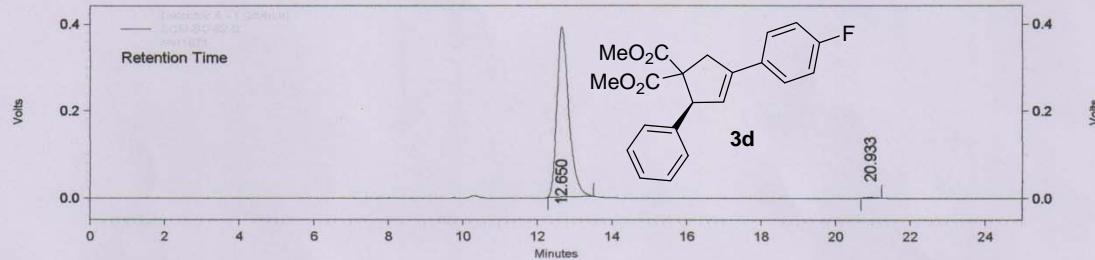
Dimethyl (S)-4-(4-fluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3d)

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1669
 User: System
 Acquired: 5/9/14 4:49:06 PM
 Printed: 5/9/14 6:38:35 PM



Pk #	Retention Time	Area	Area %
1	12.608	3632997	49.806
2	20.850	3661248	50.194
Totals		7294245	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1671
 User: System
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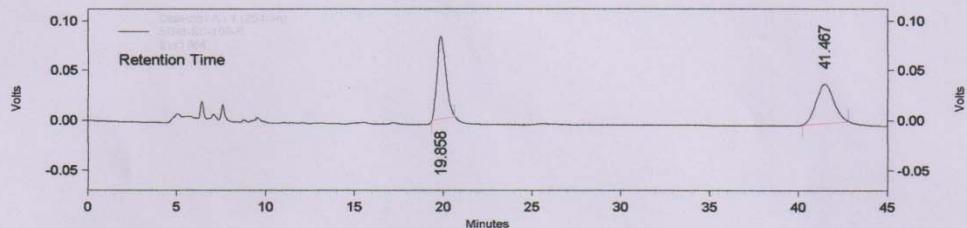


Pk #	Retention Time	Area	Area %
1	12.650	8614095	99.643
2	20.933	30858	0.357
Totals		8644953	100.000

Project Leader : Dr A. T. BIJU
 Column : Kromasil 5-AmyCoat (250mmX4.6mm)
 Mobile Phase : IPA:n-Hexane(10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 5ul
 Date : 09-05-2014

Dimethyl (S)-4-(4-nitrophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3e)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1754
 User: System
 Acquired: 6/27/14 2:25:16 PM
 Printed: 6/27/14 3:13:14 PM
 Sample Name SGM-SC-109-R

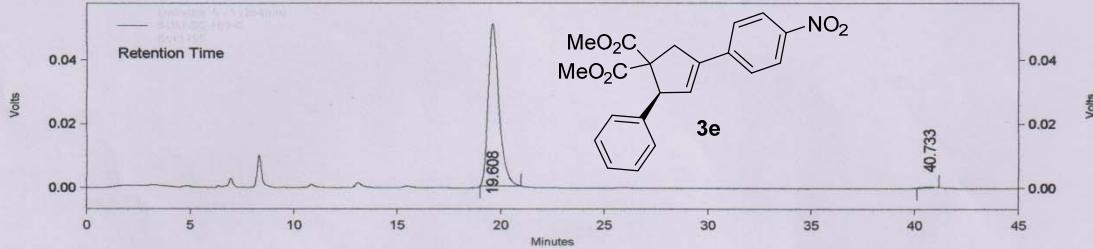


Detector A - 1 (254nm)
Retention Time

	C Area	Area %
19.858	694995	50.655
41.467	677016	49.345

Totals	1372011	100.000
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Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1755
 User: System
 Acquired: 6/27/14 3:14:25 PM
 Printed: 6/27/14 4:16:34 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
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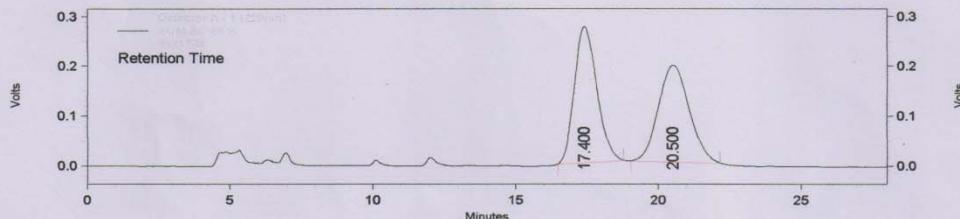
1	19.608	1844646	99.453
2	40.733	10147	0.547

Totals	1854793	100.000
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Project Leader :Dr.A. T. Biju
 Column : Kromasil 5-Amy Coat
 Mobile Phase :IPA:PE (20:80)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

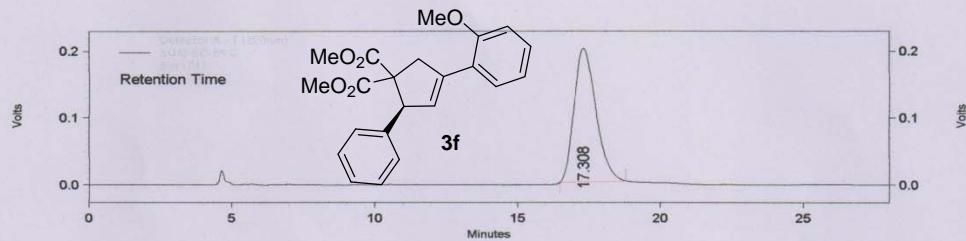
Dimethyl (S)-4-(2-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3f)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1738
 User: System
 Acquired: 6/13/14 3:02:11 PM
 Printed: 6/13/14 4:53:27 PM
 Sample Name SGM-SC-86 R



Detector A - 1 (220nm)	C Area	Area %
Retention Time		
17.400	7441947	50.597
20.500	7266299	49.403
Totals	14708246	100.000

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1741
 User: System
 Acquired: 6/13/14 4:14:19 PM
 Printed: 6/13/14 4:55:11 PM
 Sample Name SGM-SC-86 C

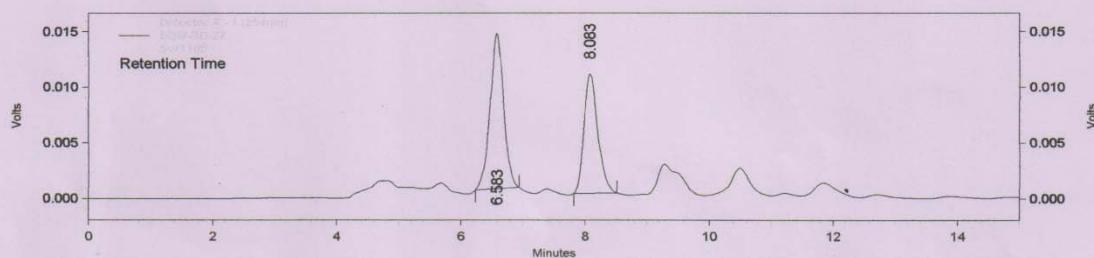


Detector A - 1 (220nm)	C Area	Area %
Retention Time		
17.308	5292239	100.000
Totals	5292239	100.000

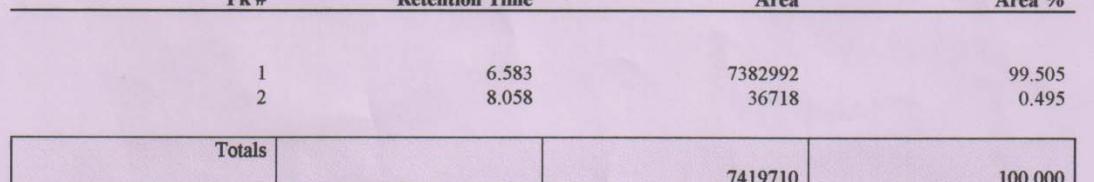
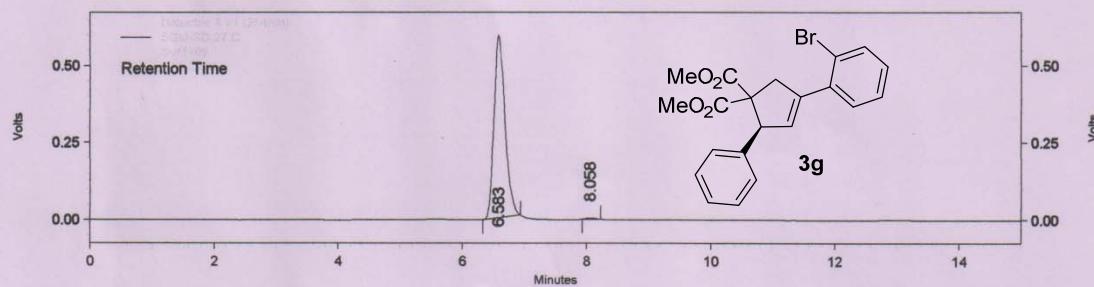
Project Leader : Dr. A. T. Biju
 Column : Chiralcel OJ-H
 Mobile Phase : IPA:Hexane (10:90)
 Wavelength : 220nm
 Flow Rate : 0.7 ml/min (780psi)
 Conc. : 1mg/mL
 Inj vol- : 5 ul

Dimethyl (S)-4-(2-bromophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3g)

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1785
 User: System
 Acquired: 7/14/14 12:39:43 PM
 Printed: 7/14/14 2:31:58 PM



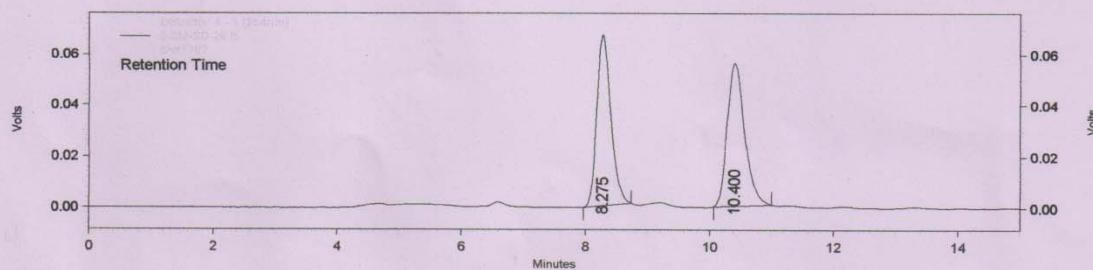
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1786
 User: System
 Acquired: 7/14/14 12:55:59 PM
 Printed: 7/14/14 2:33:20 PM



Project Leader :Dr. A. T. Biju
 Column : Kromasil 5- AmyCoat (250mm x 4.6mm)
 Mobile Phase :IPA:n-Hexane (20:80)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

Dimethyl (S)-4-(3-methoxyphenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3h)

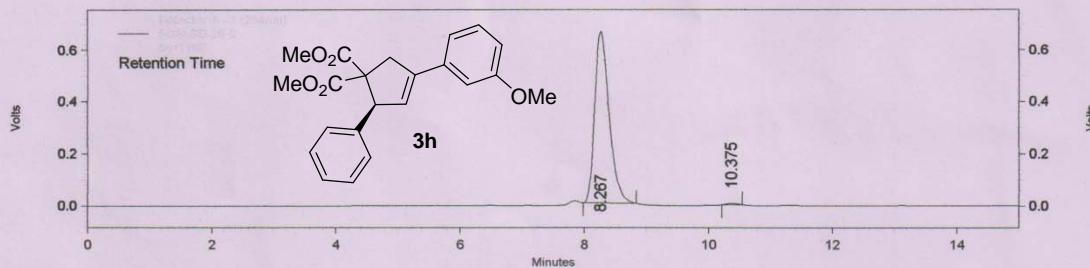
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1787
 User: System
 Acquired: 7/14/14 1:12:36 PM
 Printed: 7/14/14 2:34:32 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	8.275	1051067	49.078
2	10.400	1090564	50.922
Totals		2141631	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1788
 User: System
 Acquired: 7/14/14 1:29:44 PM
 Printed: 7/14/14 2:36:09 PM



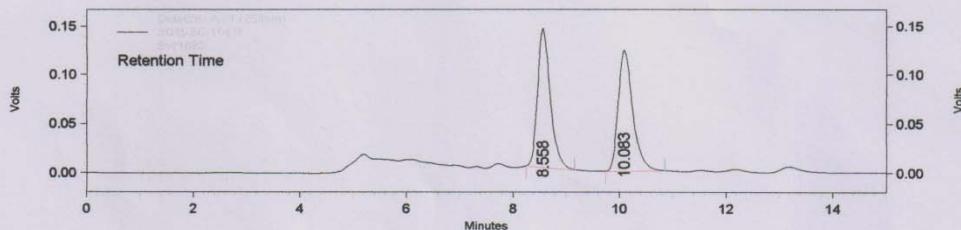
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	8.267	10651950	99.441
2	10.375	59854	0.559
Totals		10711804	100.000

Project Leader :Dr. A. T. Biju
 Column : Kromasil 5- AmyCoat (250mm x 4.6mm)
 Mobile Phase :IPA:n-Hexane (20:80)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

Dimethyl (S)-4-(2,4-dichlorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3i)

Method Name: C:\CLASS-VP\Method ch 2.met
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1692
User: System
Acquired: 5/27/14 6:27:21 PM
Printed: 5/27/14 7:04:36 PM
Sample Name: SGM-SC-104 R

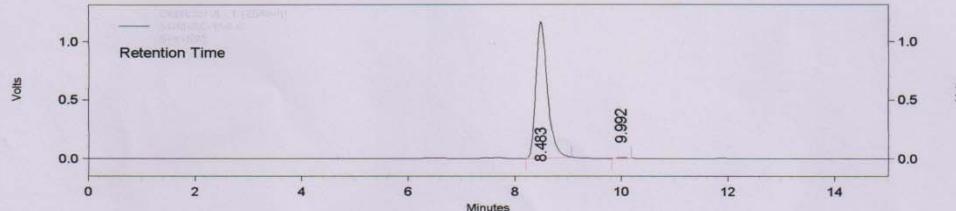
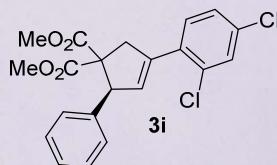


Detector A - 254nm
Retention Time

Retention Time	C Area	Area %
8.558	1166745	49.979
10.083	1167714	50.021

Totals	2334459	100.000
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Method Name: C:\CLASS-VP\Method ch 2.met
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1693
User: System
Acquired: 5/27/14 6:44:33 PM
Printed: 5/27/14 7:11:45 PM
Sample Name: SGM-SC-104 C



Detector A - 254nm
Retention Time

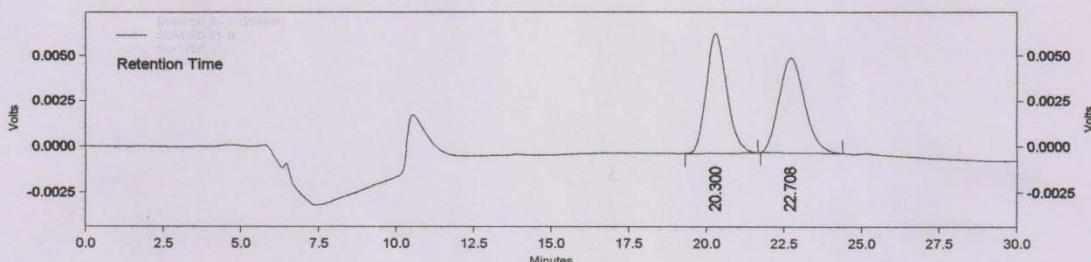
Retention Time	C Area	Area %
8.483	8702082	99.573
9.992	37310	0.427

Totals	8739392	100.000
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Project Leader: Dr.A. T. Biju
Column: Kromasil 5 AmyCoat (4.6X250mm)
Mobile Phase: IPA:n-Hexane (10:90)
Wavelength: 254nm
Flow Rate: 0.7 ml/min (43)kgf
Conc.: 1mg/mL
Inj vol-: 3 ul

Dimethyl (S)-4-(2,4-difluorophenyl)-2-phenylcyclopent-3-ene-1,1-dicarboxylate (3j)

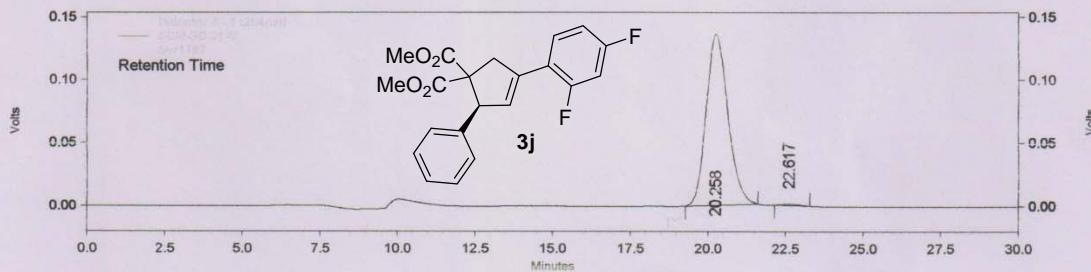
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\WSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1798
 User: System
 Acquired: 7/15/14 3:41:35 PM
 Printed: 7/15/14 4:18:52 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	20.300	299680	50.325
2	22.708	295811	49.675
Totals		595491	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\WSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1797
 User: System
 Acquired: 7/15/14 3:09:41 PM
 Printed: 7/15/14 3:40:47 PM



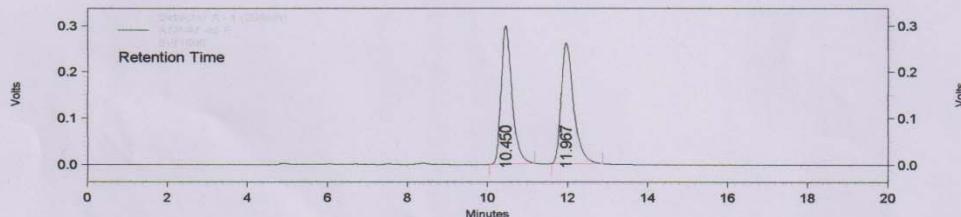
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	20.258	6572132	99.387
2	22.617	40524	0.613
Totals		6612656	100.000

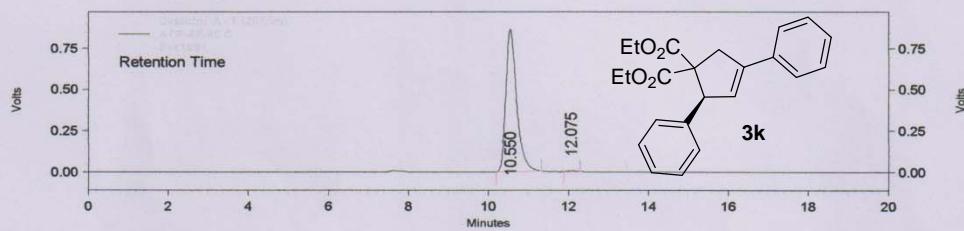
Project Leader :Dr.A. T. Biju
 Column : Kromasil 5- AmyCoat (250mm x 4.6mm)
 Mobile Phase :IPA:n-Hexane : TFA (0.7: 99.3 :0.1)
 Wavelength : 254 nm
 Flow Rate : 0.5ml/min
 Conc. : 0.01mg/1ml (Sample dissolved in mobile phase)
 Inj vol- : 05ul

Diethyl (S)-2,4-diphenylcyclopent-3-ene-1,1-dicarboxylate (3k)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1690
 User: System
 Acquired: 5/20/14 3:42:16 PM
 Printed: 5/20/14 4:28:11 PM
 Sample Name ATP-AF-46 R



Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1691
 User: System
 Acquired: 5/20/14 4:03:18 PM
 Printed: 5/20/14 4:24:54 PM
 Sample Name ATP-AF-46 C

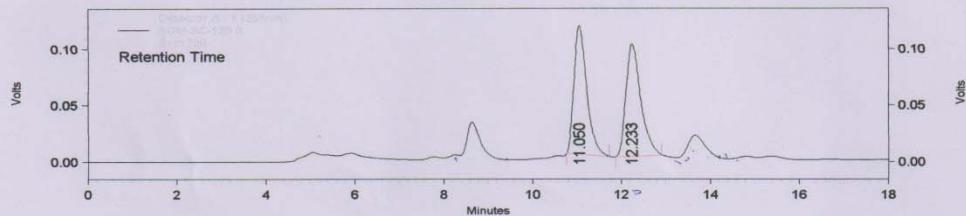


Retention Time	C Area	Area %
10.550	8086308	99.569
12.075	34996	0.431

Project Leader : Dr. A. T. Biju
 Column : Kromasil 5-AmyCoat (4.6X250mm)
 Mobile Phase : IPA:n-Hexane (10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 ml/min (43)kgf
 Conc. : 1mg/mL
 Inj vol- : 5 μ L

(S)-1,1'-(2,4-Diphenylcyclopent-3-ene-1,1-diy)bis(ethan-1-one) (3l)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1720
 User: System
 Acquired: 6/11/14 3:11:17 PM
 Printed: 6/11/14 3:32:28 PM
 Sample Name SGM-SC-129 R



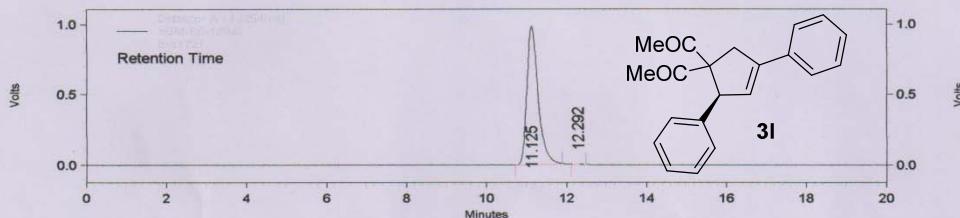
(2)

Detector A - 1 (254nm)
Retention Time

C Area	Area %
1146037	50.038
1144288	49.962

Totals	2290325	100.000
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Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1721
 User: System
 Acquired: 6/11/14 3:36:25 PM
 Printed: 6/11/14 4:23:14 PM
 Sample Name SGM-SC-129 C



Detector A - 1 (254nm)
Retention Time

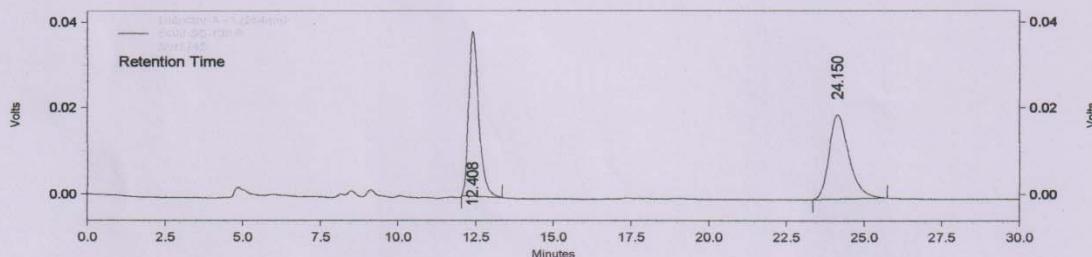
C Area	Area %
9577500	99.850
14353	0.150

Totals	9591853	100.000
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Project Leader : Dr.A. T. Biju
 Column :Kromasil 5-AmyCoat (4.6X250mm)
 Mobile Phase :IPA:PE (10:90)
 Wavelength :254nm
 Flow Rate : 0.7 ml/min (40kgf)
 Conc. :1mg/mL
 Inj vol- :5 ul

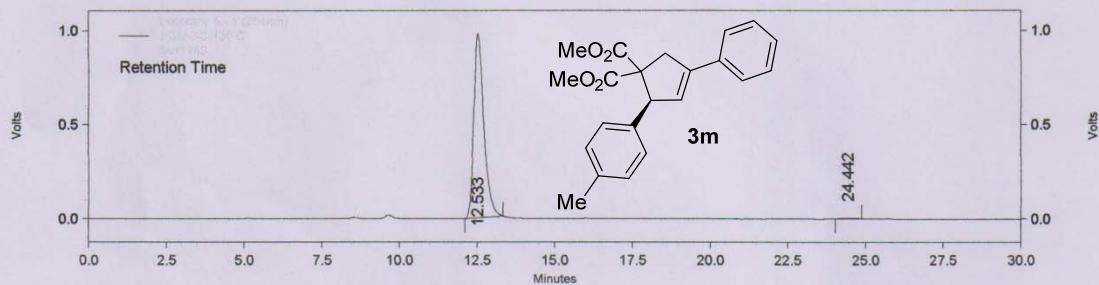
Dimethyl (S)-4-phenyl-2-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (3m)

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1745
 User: System
 Acquired: 6/23/14 11:54:24 AM
 Printed: 6/23/14 2:48:19 PM



Detector A - 1 (254nm)			
Pk #	Retention Time	Area	Area %
1	12.408	867717	50.008
2	24.150	867441	49.992
Totals		1735158	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1749
 User: System
 Acquired: 6/23/14 12:54:09 PM
 Printed: 6/23/14 2:54:57 PM

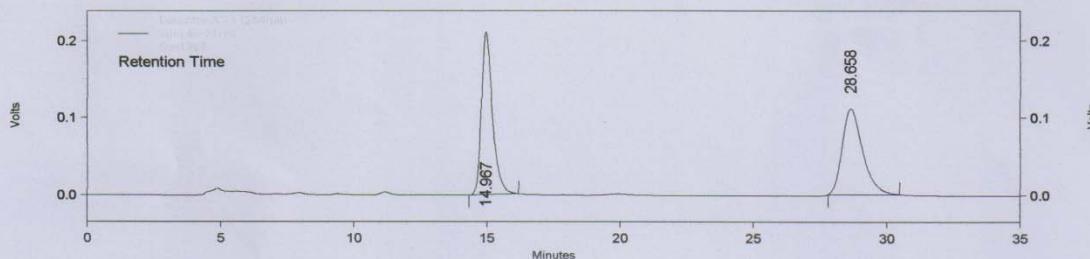


Detector A - 1 (254nm)			
Pk #	Retention Time	Area	Area %
1	12.533	22007965	99.580
2	24.442	92830	0.420
Totals		22100795	100.000

Project Leader :Dr.A. T. Biju
 Column :Kromasil 5-Amy Coat
 Mobile Phase :IPA:Hexane (10:90)
 Wavelength :254 nm
 Flow Rate :0.7 ml/min
 Conc. :1mg/1ml
 Inj vol- :05ul

Dimethyl (S)-2-(4-methoxyphenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3n)

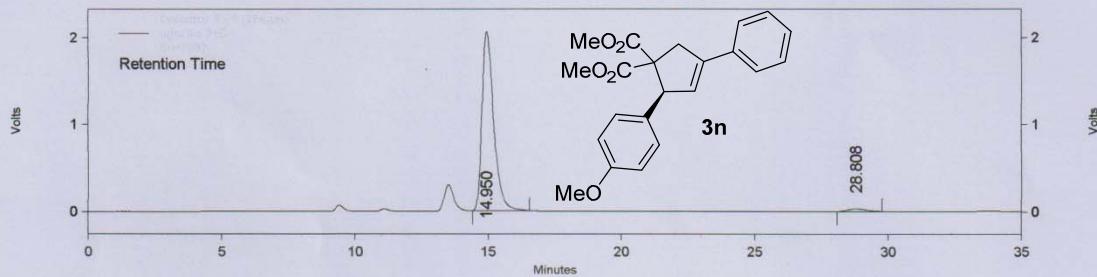
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1596
 User: System
 Acquired: 3/21/14 6:03:57 PM
 Printed: 3/21/14 8:05:41 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	14.967	6140991	51.151
2	28.658	5864721	48.849
Totals		12005712	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1597
 User: System
 Acquired: 3/21/14 6:44:42 PM
 Printed: 3/21/14 7:56:54 PM



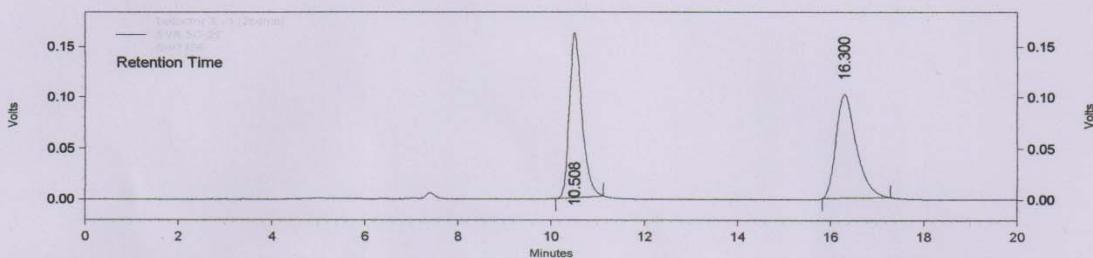
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	14.950	62892572	97.601
2	28.808	1545718	2.399
Totals		64438290	100.000

Project Leader : Dr. A. T. Biju
 Column : Kromasil Amycoat (250mmX4.6mm)
 Mobile Phase : IPA:n-Hexane (10:90)
 Wavelength : 254 nm
 Flow Rate : 0.7ml/min
 Conc. : 1mg/1ml
 Inj vol- : 20 ul

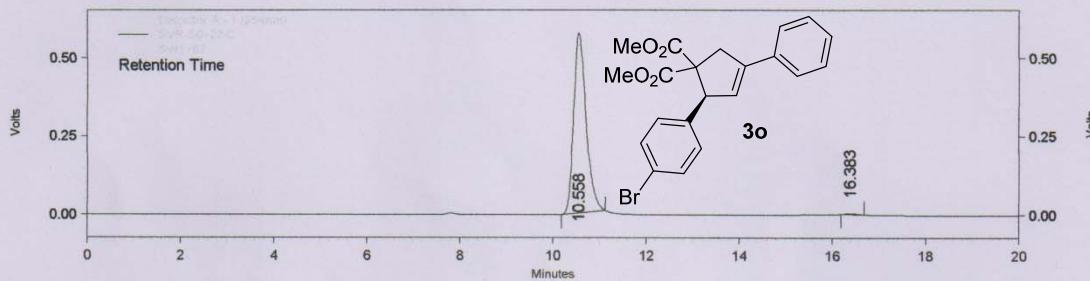
Dimethyl (S)-2-(4-bromophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3o)

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1756
 User: System
 Acquired: 6/27/14 4:02:12 PM
 Printed: 6/27/14 4:30:23 PM



Pk #	Retention Time	Area	Area %
1	10.508	3075215	49.893
2	16.300	3088376	50.107
Totals		6163591	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1756
 User: System
 Acquired: 6/27/14 4:23:59 PM
 Printed: 6/27/14 4:45:55 PM

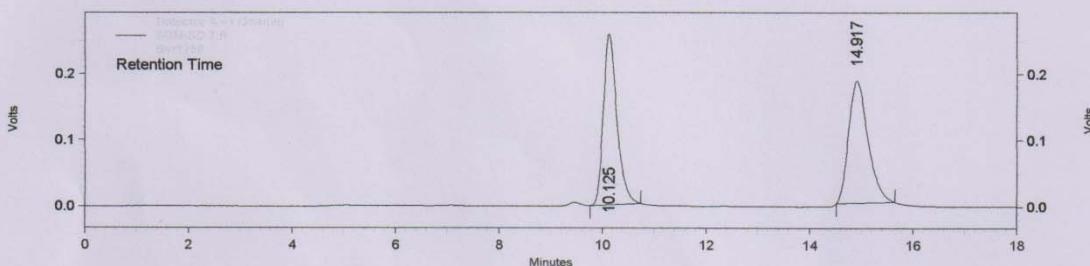


Pk #	Retention Time	Area	Area %
1	10.558	10637787	99.596
2	16.383	43185	0.404
Totals		10680972	100.000

Project Leader :Dr. A. T. Biju
 Column : Kromasil 5-Amy Coat
 Mobile Phase :IPA:PE (20:80)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 0.5ul

Dimethyl (S)-2-(4-chlorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3p)

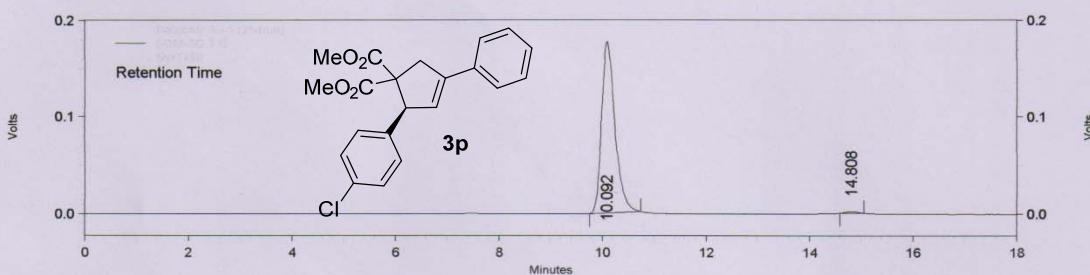
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1758
 User: System
 Acquired: 6/27/14 4:44:51 PM
 Printed: 6/27/14 5:07:30 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	10.125	4679079	49.349
2	14.917	4802595	50.651
Totals		9481674	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1759
 User: System
 Acquired: 6/27/14 5:03:34 PM
 Printed: 6/27/14 5:23:38 PM



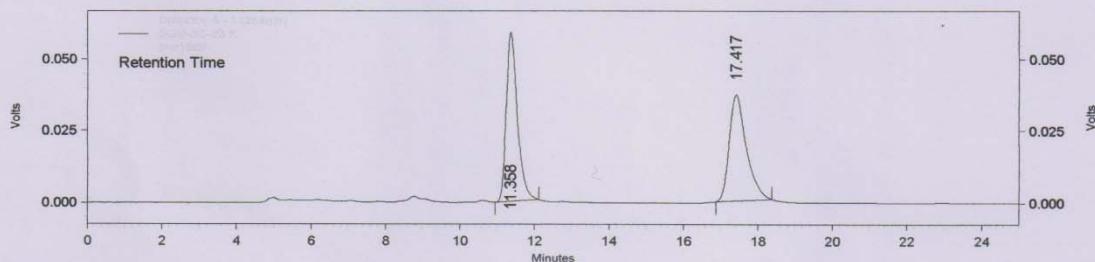
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	10.092	3169392	99.256
2	14.808	23772	0.744
Totals		3193164	100.000

Project Leader :Dr.A. T. Biju
 Column : Kromasil 5-Amy Coat
 Mobile Phase :IPA:PE (20:80)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

Dimethyl (S)-2-(4-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3q)

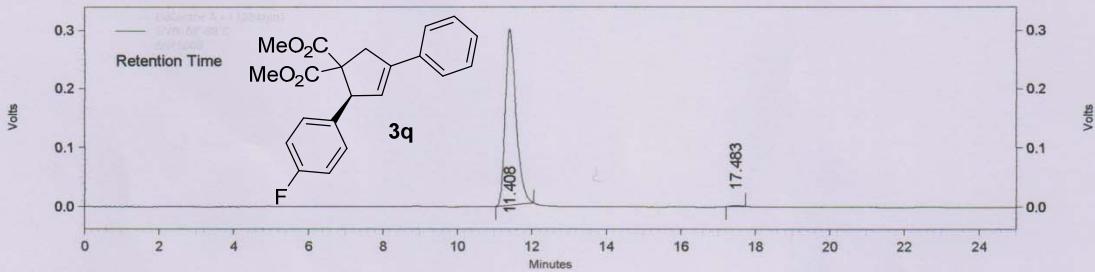
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Svr1688
 User: System
 Acquired: 5/15/14 7:24:29 PM
 Printed: 5/15/14 8:07:35 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	11.358	1219268	50.661
2	17.417	1187443	49.339
Totals		2406711	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1689
 User: System
 Acquired: 5/15/14 7:50:59 PM
 Printed: 5/15/14 8:25:05 PM

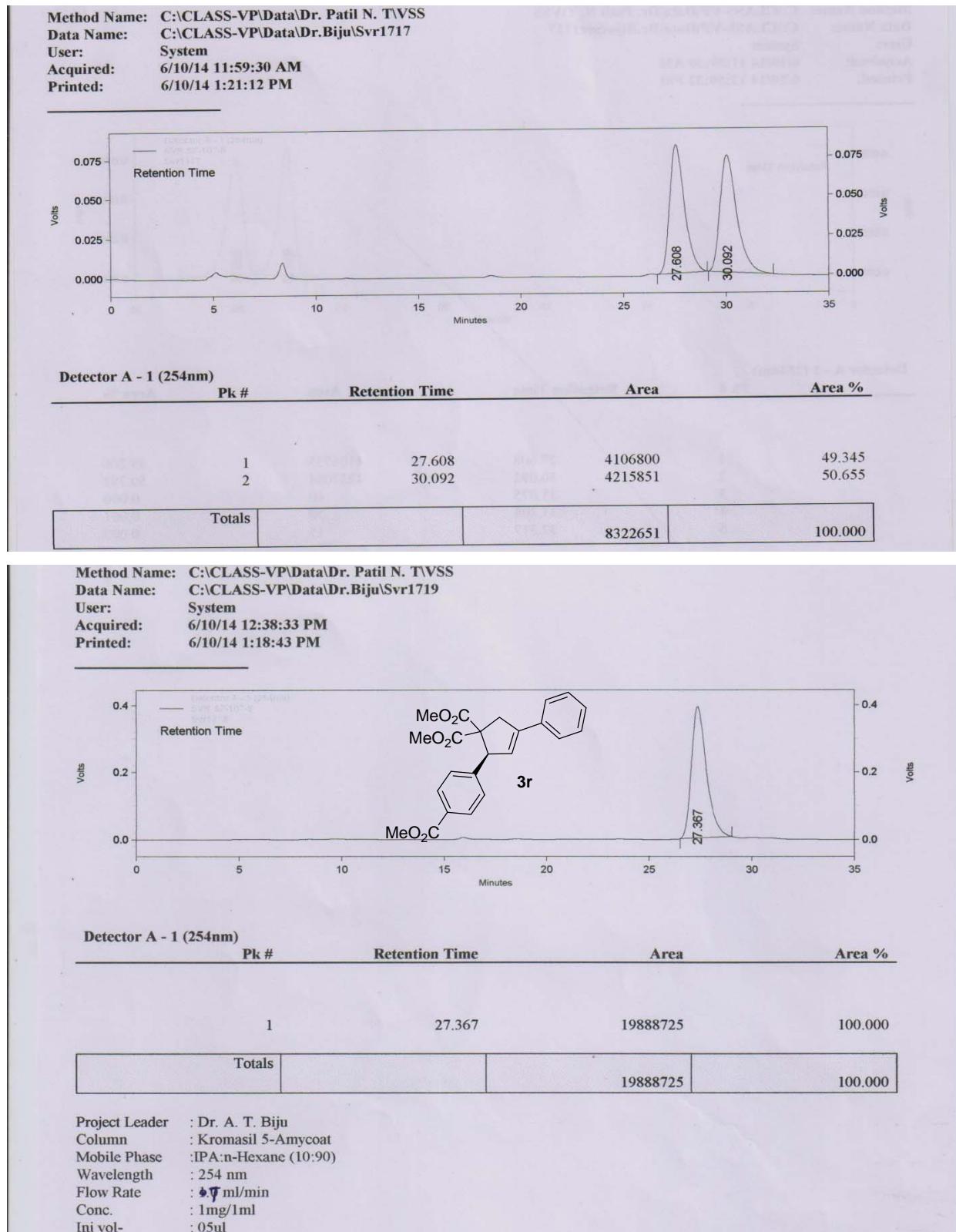


Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	11.408	5972914	99.516
2	17.483	29034	0.484
Totals		6001948	100.000

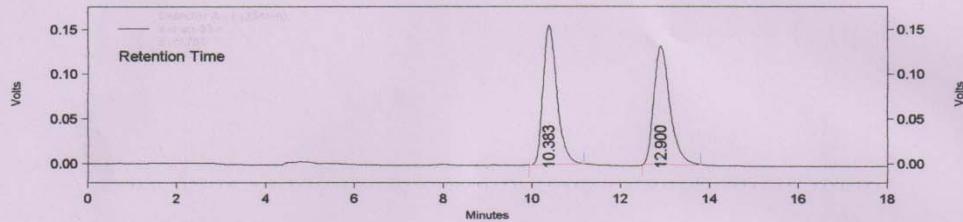
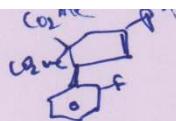
Project Leader : Dr A. T. BIJU
 Column : Kromasil 5-AmyCoat (250mmX4.6mm)
 Mobile Phase : IPA:n-Hexane(10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

**Dimethyl (S)-2-(4-(methoxycarbonyl)phenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate
(3r)**



Dimethyl (R)-2-(2-fluorophenyl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3s)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1783
 User: System
 Acquired: 7/11/14 3:47:15 PM
 Printed: 7/11/14 4:16:08 PM
 Sample Name svr-sg-33-r



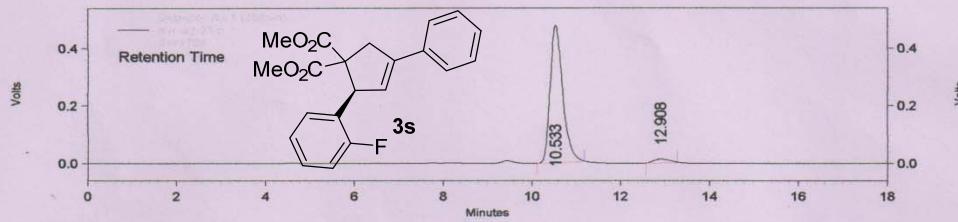
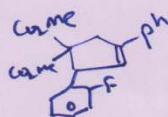
Detector A - 1 (254nm)
Retention Time

C Area
1688938
1661521

94%
Area %
50.409
49.591

Totals	3350459	100.000
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Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1784
 User: System
 Acquired: 7/11/14 4:06:44 PM
 Printed: 7/11/14 4:29:59 PM
 Sample Name svr-sg-33-c



Detector A - 1 (254nm)
Retention Time

C Area
4687081
145624

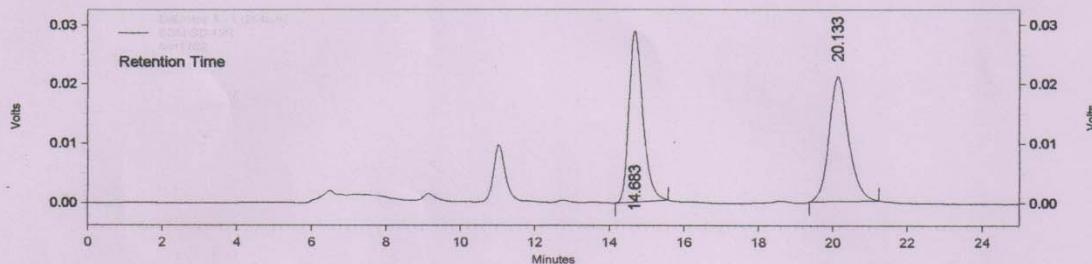
96.987
3.013

Totals	4832705	100.000
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Project Leader : Dr. A. T. Biju
 Column : Kromasil 5-AmyCoat(250x4.6mm)
 Mobile Phase : IPA:PE (10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 mL/min
 Conc. : 1mg/1mL
 Inj vol- : 5 ul

Dimethyl (S)-2-(naphthalen-2-yl)-4-phenylcyclopent-3-ene-1,1-dicarboxylate (3t)

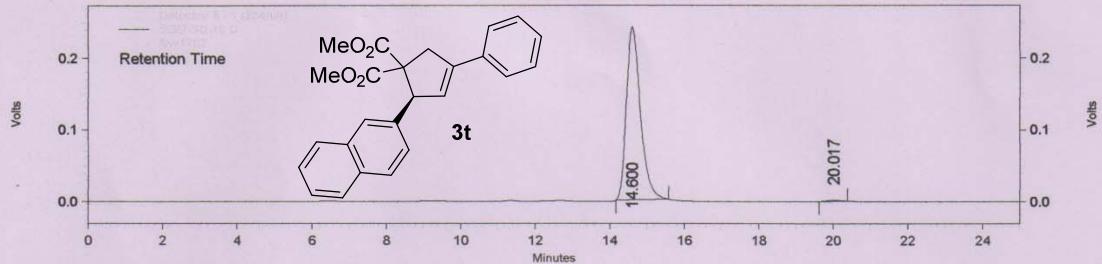
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1762
User: System
Acquired: 7/8/14 1:28:40 PM
Printed: 7/8/14 1:54:16 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	14.683	748560	49.609
2	20.133	760356	50.391
Totals		1508916	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1763
User: System
Acquired: 7/8/14 1:54:36 PM
Printed: 7/8/14 2:22:14 PM



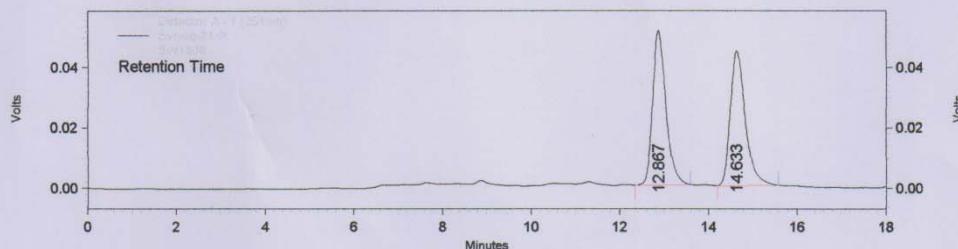
Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	14.600	6312885	99.413
2	20.017	37284	0.587
Totals		6350169	100.000

Project Leader: Dr.Biju A.T.
Column: Kromasil 5-Amy Coat (250mm x 4.6mm)
Mobile Phase: IPA:n-Hexane (20:80)
Wavelength: 254 nm
Flow Rate: 0.5 ml/min
Conc.: 1mg/1ml
Inj vol-: 05ul

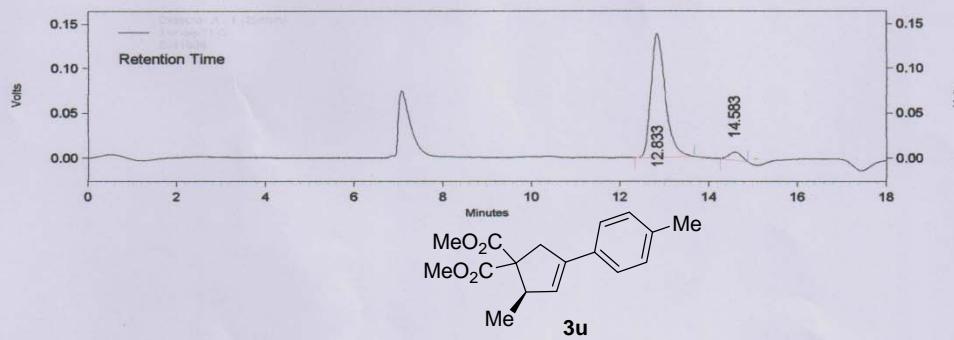
Dimethyl (*R*) 2-methyl-4-(*p*-tolyl)cyclopent-3-ene-1,1-dicarboxylate (4u)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1936
 User: System
 Acquired: 8/27/14 5:28:34 PM
 Printed: 8/27/14 6:27:11 PM
 Sample Name Svr-sg-71-R



Detector A - 1 (254nm)	C Area	Area %
Retention Time		
12.867	530970	50.347
14.633	523652	49.653

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1936
 User: System
 Acquired: 8/27/14 6:06:22 PM
 Printed: 8/27/14 6:25:46 PM
 Sample Name Svr-sg-71-C

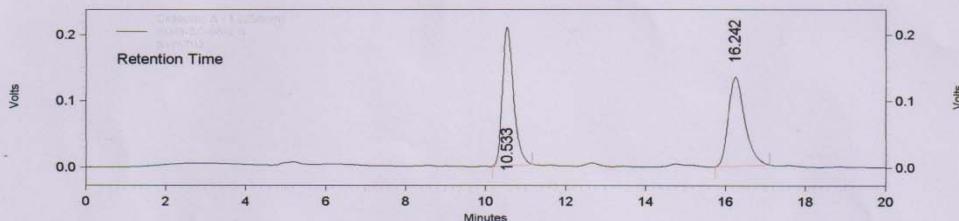


Detector A - 1 (254nm)	C Area	Area %
Retention Time		
12.833	1550285	94.714
14.583	86520	5.286
Totals	1636805	100.000

Project Leader :Dr.A. T. Biju
 Column : Kromasil 5-Amycoat (250mm x 4.6mm)
 Mobile Phase :IPA:Pet ether (05:95)
 Wavelength : 254 nm
 Flow Rate : 0.5ml/min
 Conc. : 1mg/2ml
 Inj vol- : 05ul

Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (*3v major*)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1702
 User: System
 Acquired: 6/3/14 8:16:49 PM
 Printed: 6/3/14 9:20:56 PM
 Sample Name SGM-SC-96-2-R



Detector A - 1 (254nm)
Retention Time

C Area

Area %

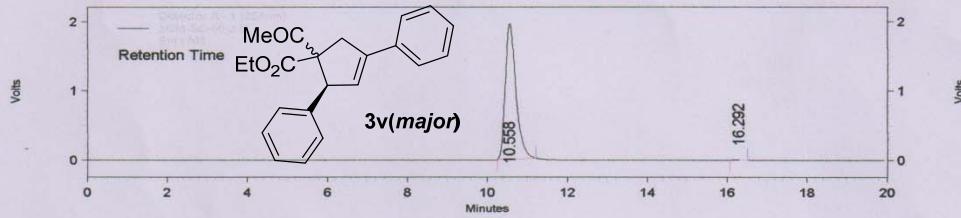
10.533	2020256	51.064
16.242	1936057	48.936

Totals

3956313

100.000

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1703
 User: System
 Acquired: 6/3/14 8:38:06 PM
 Printed: 6/3/14 9:23:33 PM
 Sample Name SGM-SC-96-2-C



Detector A - 1 (254nm)

Retention Time

C Area

Area %

10.558	17840785	99.768
16.292	41517	0.232

Totals

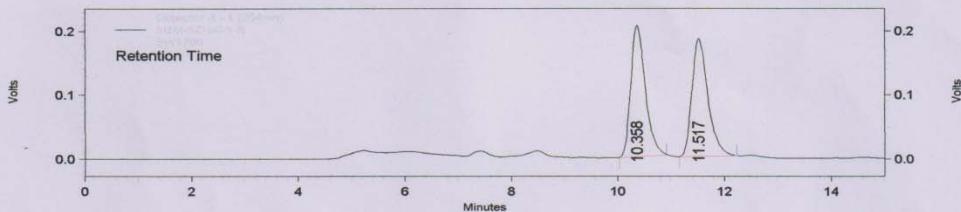
17882302

100.000

Project Leader : Dr. A. T. Biju
 Column : Kromasil 5-AmyCoat (4.6X250mm)
 Mobile Phase : IPA:n-Hexane (10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 mL/min (43kgf)
 Conc. : 1mg/mL
 Inj vol- : 5 uL

Ethyl (2S)-1-acetyl-2,4-diphenylcyclopent-3-ene-1-carboxylate (**3v minor**)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1700
 User: System
 Acquired: 6/3/14 7:42:29 PM
 Printed: 6/3/14 9:10:05 PM
 Sample Name SGM-SC-96-1-R



Detector A - 1 (254nm)
Retention Time

C Area

Area %

10.358
11.517

1926318
1902023

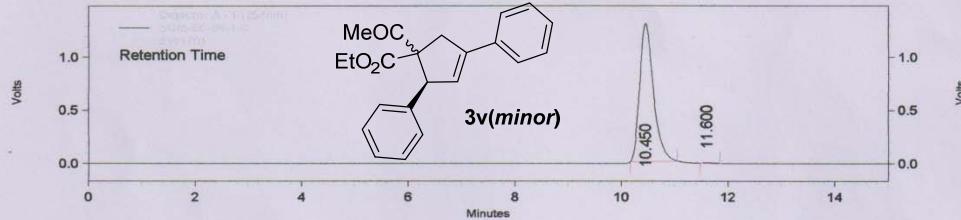
50.317
49.683

Totals

3828341

100.000

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1701
 User: System
 Acquired: 6/3/14 7:59:03 PM
 Printed: 6/3/14 9:17:04 PM
 Sample Name SGM-SC-96-1-C



Detector A - 1 (254nm)
Retention Time

C Area

Area %

10.450
11.600

11758370
17767

99.849
0.151

Totals

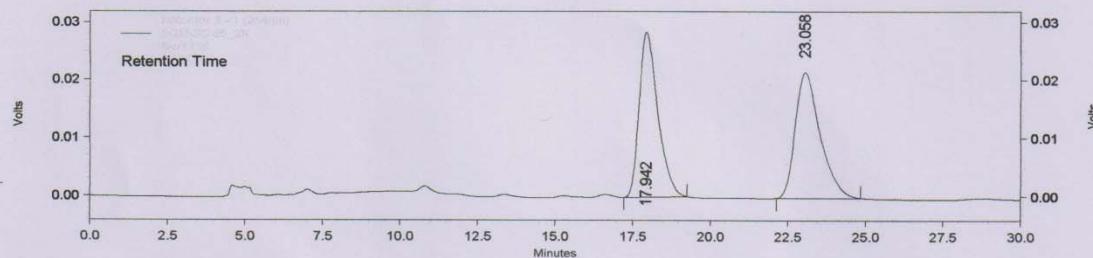
11776137

100.000

Project Leader : Dr.A. T. Biju
 Column : Kromasil 5-AmyCoat (4.6X250mm)
 Mobile Phase : IPA:n-Hexane (10:90)
 Wavelength : 254nm
 Flow Rate : 0.7 ml/min (43kgf)
 Conc. : 1mg/mL
 Inj vol- : 5 ul

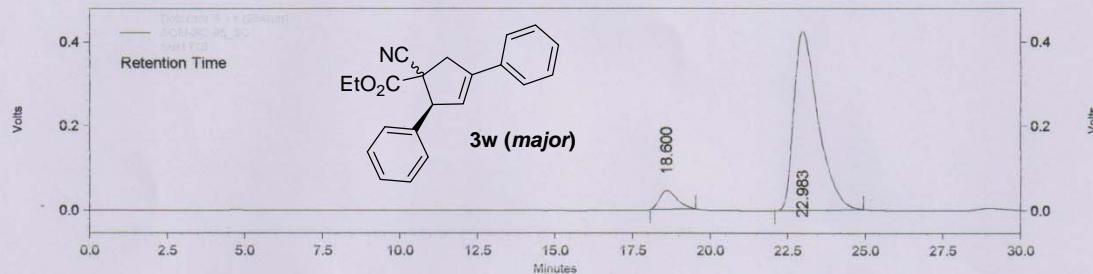
Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (**3w major**)

Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1716
 User: System
 Acquired: 6/10/14 11:35:59 AM
 Printed: 6/10/14 12:52:26 PM



Detector A - 1 (254nm)			
Pk #	Retention Time	Area	Area %
1	17.942	1198323	49.728
2	23.058	1211420	50.272
Totals		2409743	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1716
 User: System
 Acquired: 6/10/14 12:08:34 PM
 Printed: 6/10/14 12:41:24 PM

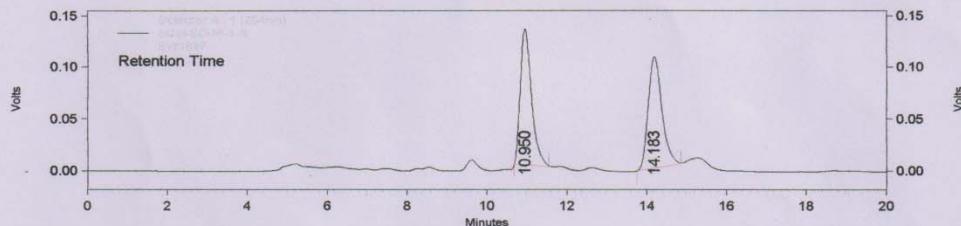


Detector A - 1 (254nm)			
Pk #	Retention Time	Area	Area %
1	18.600	1750783	7.036
2	22.983	23133469	92.964
Totals		24884252	100.000

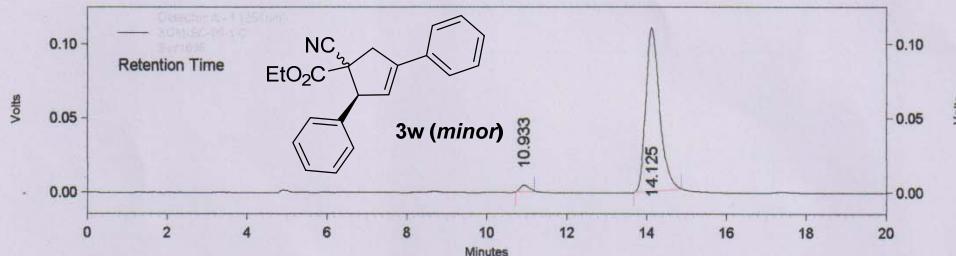
Project Leader : Dr. A. T. Biju
 Column : Chiralcel OD-H
 Mobile Phase : IPA:n-Hexane (05:95)
 Wavelength : 254 nm
 Flow Rate : 0.7 ml/min
 Conc. : 1mg/1ml
 Inj vol- : 05ul

Ethyl (2S)-1-cyano-2,4-diphenylcyclopent-3-ene-1-carboxylate (*3w minor*)

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1697
 User: System
 Acquired: 6/3/14 6:18:51 PM
 Printed: 6/3/14 9:03:33 PM
 Sample Name: SGM-SC-95-1-R

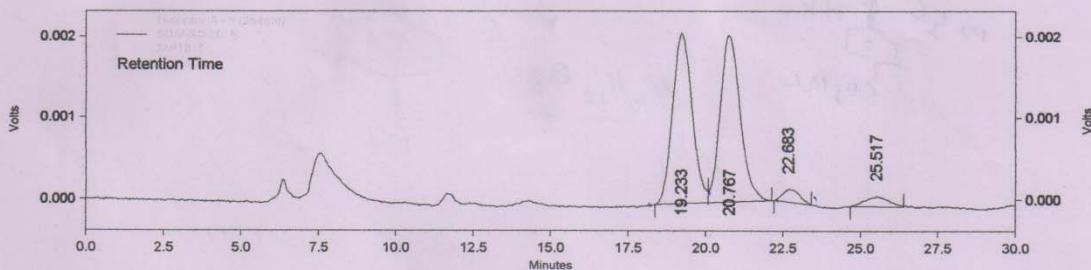


Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1698
 User: System
 Acquired: 6/3/14 6:41:29 PM
 Printed: 6/3/14 9:06:35 PM
 Sample Name: SGM-SC-95-1-C



Dimethyl (2S)-2,4-diphenylcyclopentane-1,1-dicarboxylate (8a)

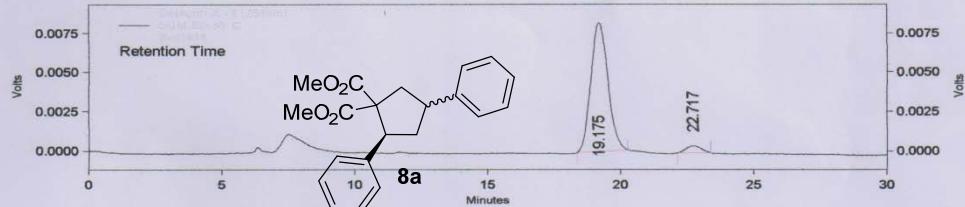
Method Name: C:\CLASS-VP\Data\Dr. Patil N. T\VSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1815
 User: System
 Acquired: 7/24/14 11:56:36 AM
 Printed: 7/24/14 1:05:20 PM



Detector A - 1 (254nm)

Pk #	Retention Time	Area	Area %
1	19.233	91881	46.676
2	20.767	92352	46.915
3	22.683	6063	3.080
4	25.517	6552	3.328
Totals		196848	100.000

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1816
 User: System
 Acquired: 7/24/14 12:28:40 PM
 Printed: 8/28/14 1:08:02 PM
 Sample Name SGM-SD-30 C



ee of major diastereomer = 99%
 ee of minor diastereomer = 99%

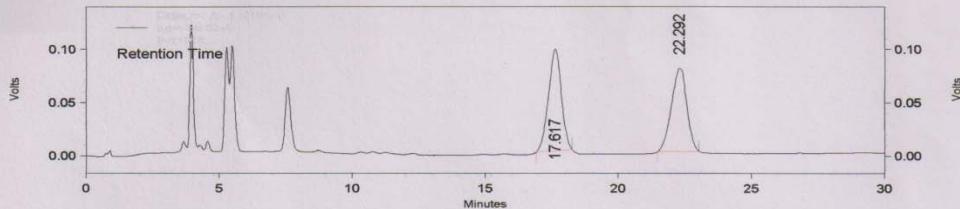
Detector A - 1 (254nm)

Retention Time	C Area	Area %
19.175	181438	95.548
22.717	8454	4.452
Totals	189892	100.000

Project Leader :Dr. A. T. Biju
 Column : Kromasil 5-Amycoat (250mm x 4.6mm)
 Mobile Phase :IPA:Pet ether (01:99)
 Wavelength : 254 nm
 Flow Rate : 0.5ml/min
 Conc. : 1mg/2ml
 Inj vol- : 05ul

**Dimethyl (1R2S5S) 5-ethyl-7-oxo-2-phenyl-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate
(11a)**

Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1918
 User: System
 Acquired: 8/26/14 4:27:51 PM
 Printed: 8/27/14 12:33:41 PM
 Sample Name Sgm-Sd-52-R



Detector A - 1 (210nm)
 Retention Time

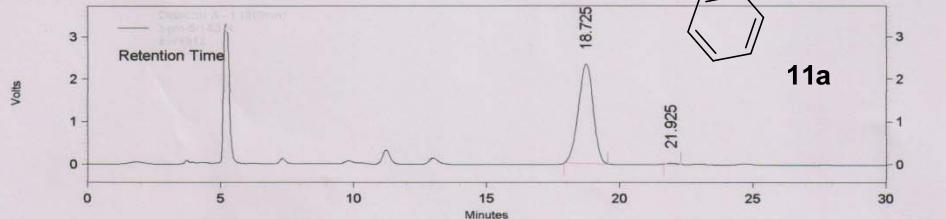
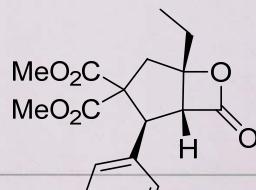
C Area

Area %

17.617	1585195	50.523
22.292	1552400	49.477

Totals	3137595	100.000
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Method Name: C:\CLASS-VP\Method ch 2.met
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1913
 User: System
 Acquired: 8/26/14 1:08:06 PM
 Printed: 8/27/14 12:28:50 PM
 Sample Name Sgm-Sd-52-IC



Detector A - 1 (210nm)
 Retention Time

C Area

Area %

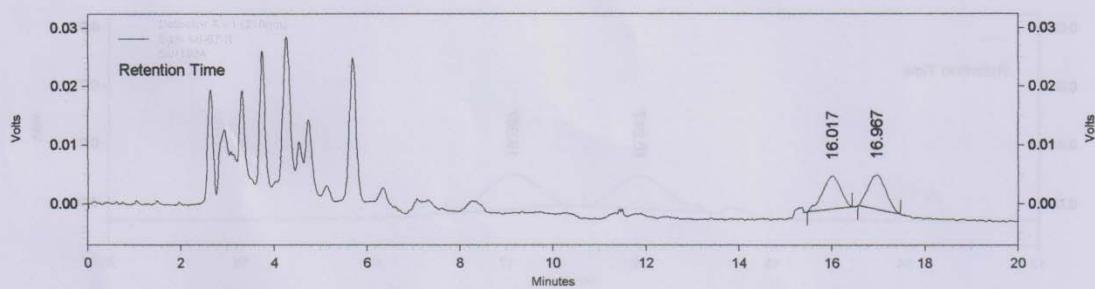
18.725	44777505	99.498
21.925	225790	0.502

Totals	45003295	100.000
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Project Leader :Dr. A. T. Biju
 Column : Chiralpak IA (150mm x 4.6mm)
 Mobile Phase : IPA:Pet ether (03:97)
 Wavelength : 210 nm
 Flow Rate : 0.5ml/min
 Conc. : 1mg/2ml
 Inj vol- : 0.5ul

Dimethyl (1R2S5S) 5-ethyl-2-(4-(methoxycarbonyl)phenyl)-7-oxo-6-oxabicyclo[3.2.0]heptane-3,3-dicarboxylate (11r)

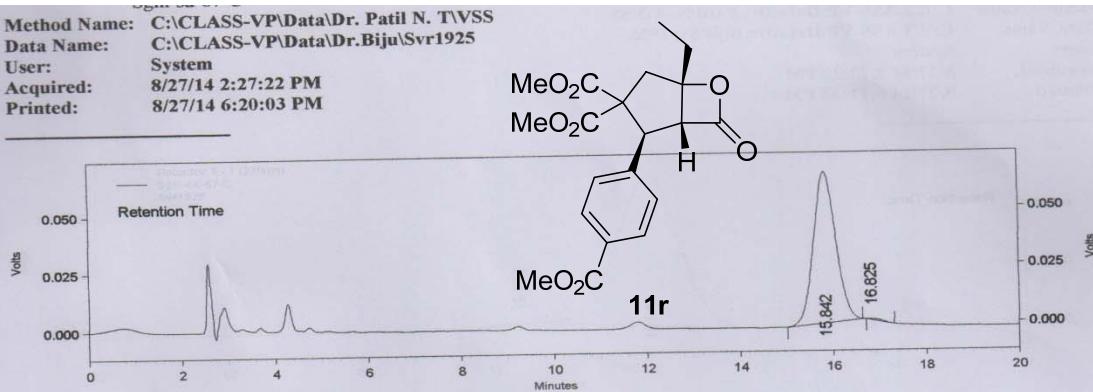
Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1924
 User: System
 Acquired: 8/27/14 1:56:57 PM
 Printed: 8/27/14 6:16:58 PM



Detector A - 1 (210nm)

Pk #	Retention Time	Area	Area %
1	16.017	151714	49.046
2	16.967	157619	50.954
Totals		309333	100.000

Method Name: C:\CLASS-VP\Data\Dr. Patil N. TVSS
 Data Name: C:\CLASS-VP\Data\Dr.Biju\Svr1925
 User: System
 Acquired: 8/27/14 2:27:22 PM
 Printed: 8/27/14 6:20:03 PM



Detector A - 1 (230nm)

Pk #	Retention Time	Area	Area %
1	15.842	2172821	99.410
2	16.825	12887	0.590
Totals		2185708	100.000

Project Leader : Dr.A. T. Biju
 Column : CHIRALPAK IA (150mm x 4.6mm)
 Mobile Phase : IPA:n-Hexane (03:97)
 Wavelength : 210 nm
 Flow Rate : 1ml/min
 Conc. : 1mg/1ml
 Inj vol- : 0.5ul