

Supporting Information

Kinetic Resolution of β -Ketoesters with Quaternary Stereocenters via Carbene-Catalyzed Benzoin Reaction

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Table of Contents

I	General information	S1
II	X-ray crystallographic analysis	S2
III	1. Typical procedure for the preparation of substrate	S3
	2. Typical procedure for the benzoin reaction	S4
IV	Characterizations of new compounds	S5
V	¹ H NMR and ¹³ C NMR spectra of substrates and products	S18
VI	HPLC spectra for <i>ee</i> determination	S50

I. General Information.

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using standard procedures. Proton nuclear magnetic resonance (¹H NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) or chloroform (δ = 7.26 ppm). ¹H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplet), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (¹³C NMR) spectra were recorded on a Bruker AVANCE III HD400 (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific LTQ FT Ultra mass spectrometer. The determination of *e.e.* was performed via chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Agilent SuperNova X-ray diffractometer. Optical rotations were measured using a 1 mL cell with a 5dm path length on an INESA SGW-1 polarimeter and are reported as follows: [α]_D²⁵ (c in g per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on WFH-203

F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain.

II. X-ray crystallographic analysis

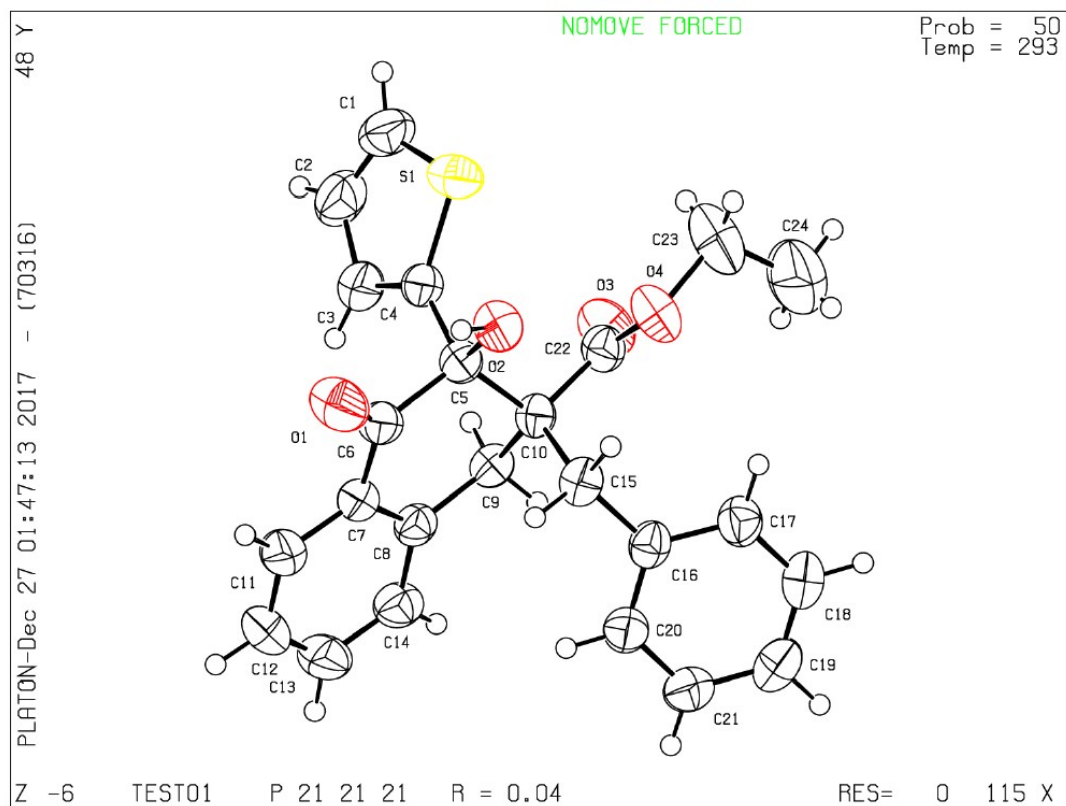
Table S1 Crystal data and structure refinement for 2k.

Identification code	2k
Empirical formula	C ₉₆ H ₈₈ O ₁₆ S ₄
Formula weight	1625.90
Temperature/K	293 (2)
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	6.7899 (4)
b/Å	16.6281 (11)
c/Å	18.1779 (16)
α /°	90
β /°	90
γ /°	90
Volume/Å ³	2052.3 (3)
Z	1
$\rho_{\text{calc}}/\text{cm}^3$	1.316
μ/mm^{-1}	0.185
F(000)	856.0
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	6.406 to 54.946
Index ranges	$-8 \leq h \leq 8$, $-21 \leq k \leq 21$, $-23 \leq l \leq 22$
Reflections collected	17037
Independent reflections	4671 [R_{int} = 0.0244, R_{sigma} = 0.0254]
Data/restraints/parameters	4671/0/264
Goodness-of-fit on F ²	1.033
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0402, wR_2 = 0.1104
Final R indexes [all]	R_1 = 0.0417, wR_2 = 0.1122

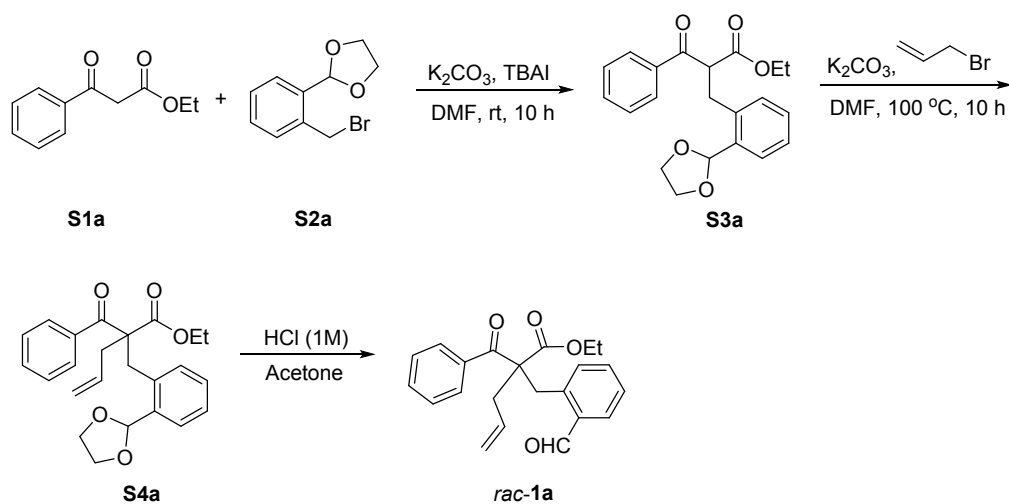
data]

Largest diff. peak/hole
/ e Å⁻³ 0.30/-0.20

Flack parameter 0.167(16)



III. 1. Typical procedure for the preparation of substrate

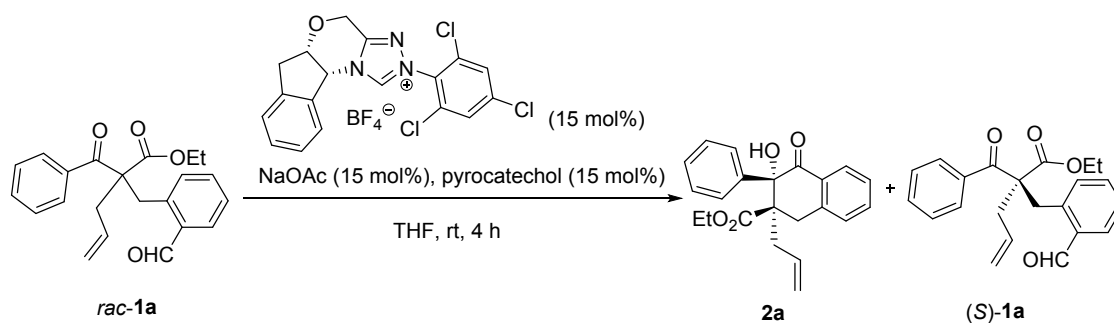


To a stirred suspension of potassium carbonate (4.26 g, 30.9 mmol) and terta-*n*-butyl ammonium iodide (1.52 g, 4.11 mmol) in DMF (10 mL), β -ketoester **S1a** (5.93 g, 30.9 mmol) was introduced at room temperature under argon atmosphere. After an additional 20 minutes stirring, benzyl bromide **S2a** (5.00 g, 20.6 mmol) was added at the same temperature. After stirring for 10 h, the reaction was quenched with water, and then extracted with ethyl acetate (2 x 200 mL). The organic layers were combined, dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash column chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give the product **S3a** (6.0 g, 82% yield).

To the flask connected with a condenser, potassium carbonate (1.17 g, 8.5 mmol) in DMF (15 mL) was added at room temperature. After a few minutes stirring, **S3a** (1.49 g, 4.2 mmol) in DMF (5.0 mL) was added dropwise at the same temperature. After 10 minutes additional stirring, allyl bromide (1.02 g, 8.5 mmol) was introduced to the reaction mixture. The reaction mixture was warmed to 100 °C and stirred for 10 h. The reaction was quenched with water, and extracted with ethyl acetate (2 x 200 mL). The combined organic layers were dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 20:1) to give **S4a** (1.3 g, 79% yield).

To a stirred solution of **S4a** (1.32 g, 3.35 mmol) in acetone (27 mL) was added 1 M HCl (33.50 mL, 33.50 mmol) dropwise at room temperature. After stirring for 10 h, the reaction was quenched with water, and then extracted ethyl acetate (2 x 100 mL). The organic layers were combined, washed with water (100 mL), dried over Na₂SO₄ and concentrated under reduced pressure to give **1a** (1.1 g, 95% yield).

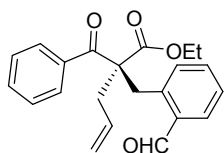
2. Typical procedure for the benzoin reaction



Under argon atmosphere, to a 50 mL Schlenk tube was taken sodium acetate (12.30 mg, 0.15 mmol), catalyst (71.85 mg, 0.15 mmol), pyrocatechol (16.5 mg, 0.15 mmol). The flask was evacuated and refilled with dry argon. To this mixture 9 mL of THF was added and then the solution of substrate **1a** (350.20 mg, 1.0 mmol) in THF (1 mL) was added dropwise via syringe and the resulting mixture was stirred for 4 h. After 4 h stirring the solvent was removed under reduced pressure and the residue was purified by flash chromatography with petroleum

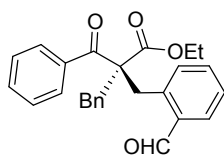
ether/ethyl acetate (v:v = 10:1) as eluent to afford the benzoin product **2a** (175.1 mg, 50% yield) and recovered chiral starting material **1a** (150.6 mg, 43% yield).

VI. Characterizations of new compounds.



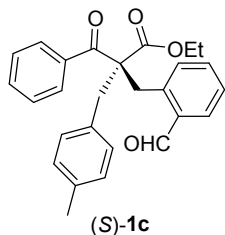
(S)-**1a**

ethyl (S)-2-benzoyl-2-(2-formylbenzyl)pent-4-enoate (1a): Yellow solid, mp 64–65 °C, 150.6 mg, 43% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.21 (s, 1H), 7.82 (dd, J = 7.7, 1.0 Hz, 1H), 7.77 (d, J = 7.5 Hz, 2H), 7.51 (t, J = 7.4 Hz, 1H), 7.45 (td, J = 7.5, 1.3 Hz, 1H), 7.41–7.35 (m, 8.2 Hz, 3H), 7.27 (d, J = 7.3 Hz, 1H), 5.73–5.63 (m, 1H), 5.10 (d, J = 10.2 Hz, 1H), 5.01 (dd, J = 16.9, 1.4 Hz, 1H), 4.05–3.99 (m, 2H), 3.90–3.82 (m, 1H), 3.71 (d, J = 14.4 Hz, 1H), 2.81 (d, J = 7.2 Hz, 2H), 0.91 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.4, 191.6, 172.4, 139.2, 136.2, 135.4, 133.3, 132.8, 132.7, 132.0, 130.5, 128.64, 128.58, 127.6, 119.9, 62.2, 61.7, 38.6, 33.5, 13.6; HRMS (ESI, m/z): calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{H}^+$ 351.1591, found 351.1591; $[\alpha]_{\text{D}}^{28}$: +28.4 (c 0.94, CHCl_3); HPLC analysis: 94% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 14.6 min, R_t (minor) = 12.6 min; IR (KBr thin film, cm^{-1}): ν 1733, 1683, 1598, 1447, 1275, 1243, 1209, 758.

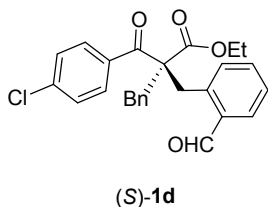


(S)-**1b**

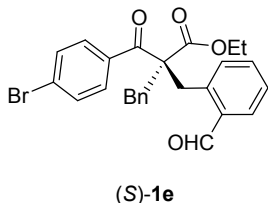
ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-oxo-3-phenylpropanoate (1b): Yellow oil, 188.1 mg, 46% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.18 (s, 1H), 7.78 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.9 Hz, 2H), 7.46–7.29 (m, 6H), 7.20–7.19 (m, 3H), 7.06 (s, 2H), 3.94 (d, J = 14.1 Hz, 1H), 3.85–3.69 (m, 3H), 3.54 (dd, J = 21.0, 14.1 Hz, 2H), 0.70 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.9, 191.7, 172.4, 139.4, 136.6, 135.9, 135.2, 133.2, 132.8, 132.6, 130.54, 130.48, 128.6, 128.33, 128.29, 127.4, 127.1, 63.6, 61.4, 42.1, 34.9, 13.2; HRMS (ESI, m/z): calcd. for $\text{C}_{26}\text{H}_{24}\text{O}_4\text{H}^+$ 401.1747, found 401.1747; $[\alpha]_{\text{D}}^{26}$: +14.4 (c 0.48, CHCl_3); HPLC analysis: 95% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 20.9 min, R_t (minor) = 22.7 min; IR (KBr thin film, cm^{-1}): ν 1731, 1682, 1599, 1448, 1244, 1207, 754.



ethyl (S)-2-(2-formylbenzyl)-2-(4-methylbenzyl)-3-oxo-3-phenylpropanoate (1c): White solid, mp 77–78 °C, 169.8 mg, 41% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.37–7.30 (m, 3H), 7.28–7.22 (m, 2H), 7.18–7.10 (m, 5H), 7.03–6.95 (m, 2H), 3.83 (d, J = 14.1 Hz, 1H), 3.78–3.70 (m, 1H), 3.69–3.59 (m, 2H), 3.48–3.40 (m, 2H), 2.21 (s, 3H), 0.64 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 197.0, 191.8, 172.5, 139.7, 136.8, 136.7, 135.3, 133.2, 132.8, 132.6, 130.4, 129.3, 129.1, 128.7, 128.4, 128.2, 127.4, 63.7, 61.4, 41.8, 34.8, 21.2, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{H}^+$ 415.1904, found 415.1904; $[\alpha]_{\text{D}}^{24}$: –13.8 (c 1.4, CHCl_3); HPLC analysis: 96% *ee* (Chiralcel AD-H, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 7.5 min, R_t (minor) = 9.6 min; IR (KBr thin film, cm^{-1}): ν 1725, 1682, 1602, 1455, 1282, 1195, 739, 704.

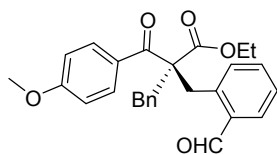


ethyl (S)-2-benzyl-3-(4-chlorophenyl)-2-(2-formylbenzyl)-3-oxopropanoate (1d): White solid, mp 115–116 °C, 199.7 mg, 46% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.15 (s, 1H), 7.78 (dd, J = 7.6, 1.3 Hz, 1H), 7.53–7.51 (m, 2H), 7.43 (td, J = 7.5, 1.5 Hz, 1H), 7.37–7.33 (m, 2H), 7.29–7.26 (m, 2H), 7.22–7.19 (m, 3H), 7.06–7.03 (m, 2H), 3.90 (d, J = 14.2 Hz, 1H), 3.86–3.80 (m, 1H), 3.78–3.71 (m, 2H), 3.54–3.45 (m, 2H), 0.74 (t, J = 7.1 Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.9, 191.9, 172.3, 139.2, 139.0, 135.7, 135.3, 135.0, 133.3, 132.9, 131.0, 130.5, 130.1, 128.6, 128.4, 127.6, 127.3, 63.7, 61.6, 42.2, 35.3, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{26}\text{H}_{23}\text{ClO}_4\text{H}^+$ 435.1358, found 435.1358; $[\alpha]_{\text{D}}^{26}$: +9.0 (c 5.7, CHCl_3); HPLC analysis: 96% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 20.3 min, R_t (minor) = 22.5 min; IR (KBr thin film, cm^{-1}): ν 1731, 1689, 1588, 1245, 1207, 1093, 755, 701, 554.



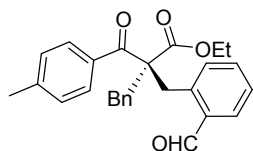
ethyl (S)-2-benzyl-3-(4-bromophenyl)-2-(2-formylbenzyl)-3-oxopropanoate (1e): White solid, mp 116–117 °C, 262.9 mg, 55% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 7.77 (d, J = 7.5 Hz, 1H), 7.45–7.40 (m, 5H), 7.35 (dd, J = 11.9, 7.6 Hz, 2H), 7.23–7.17 (m, 3H), 7.06–

7.03 (m, 2H), 3.90 (d, $J = 14.1$ Hz, 1H), 3.86–3.69 (m, 3H), 3.56–3.42 (m, 2H), 0.74 (t, $J = 7.2$ Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.2, 191.9, 172.3, 139.2, 135.8, 135.5, 135.3, 133.3, 132.9, 131.6, 131.1, 130.5, 130.2, 128.4, 127.8, 127.5, 127.3, 63.7, 61.6, 42.3, 35.3, 13.4; HRMS (ESI, m/z): calcd. for $\text{C}_{26}\text{H}_{23}\text{BrO}_4\text{H}^+$ 479.0852, found 479.0852; $[\alpha]_{\text{D}}^{29}$: +6.7 (c 0.9, CHCl_3); HPLC analysis: 53% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 6.1 min, R_t (minor) = 7.1 min; IR (KBr thin film, cm^{-1}): ν 1731, 1682, 1583, 1245, 1207, 1074, 1009, 755, 702.



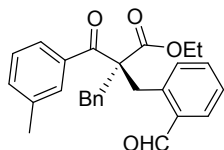
(S)-1f

ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-(4-methoxyphenyl)-3-oxopropanoate (1f): Yellow oil, 182.3 mg, 44% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.17 (s, 1H), 7.78 (dd, $J = 7.6, 0.9$ Hz, 1H), 7.67 (d, $J = 9.0$ Hz, 2H), 7.44–7.28 (m, 3H), 7.23–7.17 (m, 3H), 7.03 (dd, $J = 6.4, 2.8$ Hz, 2H), 6.81 (d, $J = 9.0$ Hz, 2H), 3.92 (d, $J = 14.2$ Hz, 1H), 3.88–3.84 (m, 1H), 3.82 (s, 3H), 3.77–3.66 (m, 2H), 3.58–3.45 (m, 2H), 0.75 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.0, 191.7, 172.8, 163.0, 139.7, 136.0, 135.3, 133.2, 132.8, 131.2, 130.5, 130.3, 129.2, 128.3, 127.4, 127.1, 113.6, 63.2, 61.4, 55.5, 42.1, 34.7, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_5\text{H}^+$ 431.1853, found 431.1853; $[\alpha]_{\text{D}}^{26}$: +22.5 (c 2.3, CHCl_3); HPLC analysis: 73% *ee* (Chiralcel IC, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 11.7 min, R_t (minor) = 13.1 min; IR (KBr thin film, cm^{-1}): ν 1725, 1682, 1600, 1446, 1281, 1193, 1112, 1055, 759, 738, 702.



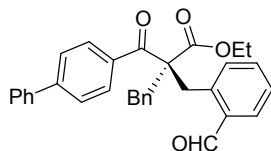
(S)-1g

ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-oxo-3-(*p*-tolyl)propanoate (1g): White solid, mp 98–99 °C, 211.2 mg, 51% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.18 (s, 1H), 7.79 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.44–7.41 (m, 2H), 7.39 (d, $J = 7.9$ Hz, 1H), 7.23–7.17 (m, 5H), 7.07–7.05 (m, 2H), 3.91 (d, $J = 14.2$ Hz, 1H), 3.85–3.80 (m, 1H), 3.75–3.68 (m, 2H), 3.55–3.49 (m, 2H), 2.30 (s, 3H), 0.72 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 196.3, 191.8, 172.6, 143.5, 139.7, 136.0, 135.3, 133.9, 133.2, 132.8, 130.5, 130.4, 129.1, 128.9, 128.3, 127.4, 127.2, 63.5, 61.4, 42.0, 34.7, 21.7, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{H}^+$ 415.1904, found 415.1904; $[\alpha]_{\text{D}}^{30}$: +12.6 (c 2.9, CHCl_3); HPLC analysis: 58% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 22.4 min, R_t (minor) = 26.2 min; IR (KBr thin film, cm^{-1}): ν 1730, 1681, 1604, 1245, 1207, 757, 701.



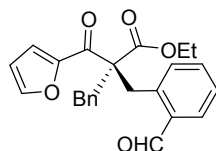
(S)-1h

ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-oxo-3-(*m*-tolyl)propanoate (1h): Colorless liquid, 186.4 mg, 45% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.17 (s, 1H), 7.78 (dd, $J = 7.6, 1.3$ Hz, 1H), 7.44–7.37 (m, 3H), 7.36–7.30 (m, 3H), 7.22–7.17 (m, 4H), 7.07–7.04 (m, 2H), 3.90 (d, $J = 14.2$ Hz, 1H), 3.86–3.79 (m, 1H), 3.75–3.68 (m, 2H), 3.55–3.48 (m, 2H), 2.30 (s, 3H), 0.72 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 197.2, 191.8, 172.5, 139.6, 138.2, 136.7, 136.0, 135.3, 133.4, 133.3, 132.9, 130.6, 130.5, 129.4, 128.4, 128.2, 127.5, 127.2, 125.8, 63.7, 61.4, 42.3, 35.1, 21.5, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{H}^+$ 415.1904, found 415.1904; $[\alpha]_{\text{D}}^{25}$: +13.0 (c 4.8, CHCl_3); HPLC analysis: 84% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 10.3 min, R_t (minor) = 9.3 min; IR (KBr thin film, cm^{-1}): ν 1725, 1683, 1602, 1281, 1221, 744, 704.



(S)-1i

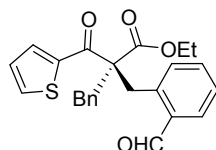
ethyl (S)-3-([1,1'-biphenyl]-4-yl)-2-benzyl-2-(2-formylbenzyl)-3-oxopropanoate (1i): Yellow oil, mp 115–116 °C, 190.4 mg, 40% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.19 (s, 1H), 7.79 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.73–7.70 (m, 2H), 7.61–7.52 (m, 4H), 7.47–7.41 (m, 3H), 7.40–7.37 (m, 2H), 7.36–7.32 (m, 1H), 7.23–7.19 (m, 3H), 7.09–7.06 (m, 2H), 3.95 (d, $J = 14.2$ Hz, 1H), 3.89–3.83 (m, 1H), 3.80–3.70 (m, 2H), 3.60–3.50 (m, 2H), 0.74 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.4, 191.8, 172.5, 145.2, 139.6, 139.5, 135.9, 135.30, 135.26, 133.3, 132.9, 130.64, 130.55, 129.4, 129.1, 128.42, 128.37, 127.5, 127.3, 127.2, 126.9, 63.6, 61.5, 42.2, 35.0, 13.3; HRMS (ESI, m/z): calcd. for $\text{C}_{32}\text{H}_{28}\text{O}_4\text{H}^+$ 477.2060, found 477.2060; $[\alpha]_{\text{D}}^{25}$: +10.5 (c 1.2, CHCl_3); HPLC analysis: 89% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 12.8 min, R_t (minor) = 11.6 min; IR (KBr thin film, cm^{-1}): ν 1731, 1681, 1601, 1246, 1185, 757, 699.



(S)-1j

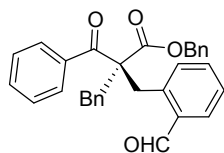
ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-(furan-2-yl)-3-oxopropanoate (1j): Yellow oil, 136.6 mg, 35% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.18 (s, 1H), 7.78 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.42 (td, $J = 7.7, 1.6$ Hz, 1H), 7.40–7.38 (m, 1H), 7.36–7.31 (m, 2H), 7.24–7.18 (m, 4H), 7.07–7.04

(m, 2H), 6.47 (dd, $J = 3.7, 1.7$ Hz, 1H), 3.88–3.84 (m, 2H), 3.76–3.68 (m, 2H), 3.50 (q, $J = 12.6$ Hz, 2H), 0.78 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 191.7, 185.5, 171.3, 152.6, 145.8, 139.4, 135.9, 135.2, 133.2, 133.0, 130.5, 130.3, 128.4, 127.4, 127.2, 118.3, 112.5, 63.0, 61.3, 41.0, 33.8, 13.6; HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_5\text{H}^+$ 391.1540, found 391.1540; $[\alpha]_{\text{D}}^{29}$: +15.7 (c 1.0, CHCl_3); HPLC analysis: 84% *ee* (Chiralcel AD-H, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 19.5 min, R_t (minor) = 17.8 min; IR (KBr thin film, cm^{-1}): ν 1732, 1680, 1599, 1562, 1464, 1278, 1218, 1013, 757, 701.



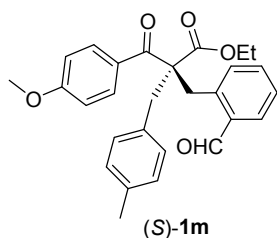
(S)-1k

ethyl (S)-2-benzyl-2-(2-formylbenzyl)-3-oxo-3-(thiophen-2-yl)propanoate (1k): White solid, mp 87–88 °C, 203.1 mg, 50% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.13 (s, 1H), 7.77 (d, $J = 7.5$ Hz, 1H), 7.59 (d, $J = 4.8$ Hz, 1H), 7.45–7.30 (m, 4H), 7.24–7.18 (m, 3H), 7.08–7.02 (m, 2H), 6.98 (t, $J = 4.2$ Hz, 1H), 3.95–3.85 (m, 2H), 3.83–3.73 (m, 2H), 3.54 (s, 2H), 0.83 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 191.8, 189.1, 171.9, 143.3, 139.1, 135.5, 135.1, 133.9, 133.1, 132.5, 131.5, 130.7, 130.2, 128.2, 128.1, 127.3, 127.0, 63.6, 61.6, 41.8, 34.1, 13.3; HRMS (ESI, m/z): calcd. $\text{C}_{24}\text{H}_{22}\text{O}_4\text{SH}^+$ 407.1312, found 407.1312; $[\alpha]_{\text{D}}^{25}$: –10.6 (c 2.0, CHCl_3); HPLC analysis: 80% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 9.0 min, R_t (minor) = 7.9 min; IR (KBr thin film, cm^{-1}): ν 1730, 1694, 1659, 1599, 1411, 1251, 1208, 1064, 734, 701.

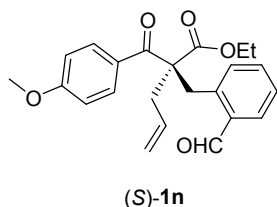


(S)-1l

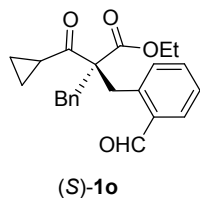
benzyl (S)-2-benzyl-2-(2-formylbenzyl)-3-oxo-3-phenylpropanoate (1l): Colorless oil, 170.0 mg, 37% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.13 (s, 1H), 7.74 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.52–7.50 (m, 2H), 7.41–7.35 (m, 3H), 7.31 (d, $J = 7.4$ Hz, 2H), 7.23–7.11 (m, 9H), 7.03–7.00 (m, 2H), 6.81–6.78 (m, 2H), 4.79 (d, $J = 12.0$ Hz, 1H), 4.66 (d, $J = 12.0$ Hz, 1H), 3.90 (d, $J = 14.2$ Hz, 1H), 3.80 (d, $J = 14.2$ Hz, 1H), 3.53 (d, $J = 2.4$ Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 196.8, 191.8, 172.2, 139.2, 136.5, 135.7, 135.2, 134.1, 133.2, 132.7, 132.5, 130.9, 130.5, 128.7, 128.63, 128.56, 128.32, 128.30, 128.2, 127.4, 127.2, 67.3, 63.7, 42.1, 35.1; HRMS (ESI, m/z): calcd. for $\text{C}_{31}\text{H}_{26}\text{O}_4\text{H}^+$ 463.1904, found 463.1904; $[\alpha]_{\text{D}}^{25}$: +8.2 (c 2.6, CHCl_3); HPLC analysis: 96% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 52.0 min, R_t (minor) = 56.6 min; IR (KBr thin film, cm^{-1}): ν 1731, 1682, 1598, 1453, 743, 698.



ethyl (S)-2-(2-formylbenzyl)-3-(4-methoxyphenyl)-2-(4-methylbenzyl)-3-oxopropanoate (1m); Light brown oil, 253.2 mg, 57% yield. ^1H NMR (600 MHz, CDCl_3) δ 10.19 (s, 1H), 7.78 (dd, $J = 7.7, 1.4$ Hz, 1H), 7.69–7.66 (m, 2H), 7.43–7.36 (m, 2H), 7.34–7.30 (m, 1H), 7.01 (d, $J = 7.7$ Hz, 2H), 6.91 (d, $J = 8.0$ Hz, 2H), 6.83–6.79 (m, 2H), 3.90–3.84 (m, 2H), 3.83 (s, 3H), 3.75–3.65 (m, 2H), 3.50 (s, 2H), 2.28 (s, 3H), 0.76 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 195.1, 191.7, 172.9, 163.1, 139.9, 136.8, 135.3, 133.2, 132.9, 132.8, 131.2, 130.4, 130.1, 129.3, 129.1, 127.4, 113.6, 63.3, 61.4, 55.6, 41.8, 34.6, 21.2, 13.4; HRMS (ESI, m/z): calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_5\text{H}^+$ 445.2010, found 445.2010; $[\alpha]_{\text{D}}^{25}$: +12.17 (c 3.9, CHCl_3); HPLC analysis: 60% *ee* (Chiralcel IA, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 19.1 min, R_t (minor) = 21.4 min; IR (KBr thin film, cm^{-1}): ν 1730, 1674, 1600, 1575, 1456, 1257, 1171, 842, 757.

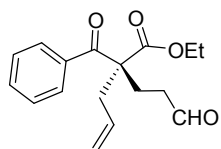


ethyl (S)-2-(2-formylbenzyl)-2-(4-methoxybenzoyl)pent-4-enoate (1n): Yellow oil, 209.1 mg, 55% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.22 (s, 1H), 7.85–7.77 (m, 3H), 7.45 (td, $J = 7.4, 1.4$ Hz, 1H), 7.36 (t, $J = 7.7$ Hz, 1H), 7.25 (s, 1H), 6.87 (d, $J = 9.0$ Hz, 1H), 5.73–5.61 (m, 1H), 5.10 (d, $J = 10.2$ Hz, 1H), 5.02 (dd, $J = 16.7, 1.4$ Hz, 1H), 4.06–3.98 (m, 2H), 3.92–3.83 (m, 1H), 3.85 (s, 3H), 3.67 (d, $J = 14.4$ Hz, 1H), 2.79 (d, $J = 7.2$ Hz, 2H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 194.6, 191.6, 172.7, 163.3, 139.4, 135.4, 133.4, 132.8, 132.2, 131.1, 130.2, 128.8, 127.6, 119.9, 113.8, 61.9, 61.7, 55.6, 38.6, 33.4, 13.7; HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_5\text{H}^+$ 381.1697, found 381.1697; $[\alpha]_{\text{D}}^{29}$: +11.1 (c 1.3, CHCl_3); HPLC analysis: 29% *ee* (Chiralcel IA, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 10.0 min, R_t (minor) = 8.0 min; IR (KBr thin film, cm^{-1}): ν 1724, 1682, 1603, 1510, 1280, 1179, 1038, 829, 738.



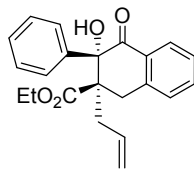
ethyl (S)-2-benzyl-3-cyclopropyl-2-(2-formylbenzyl)-3-oxopropanoate (1o): Yellow oil, 153.0 mg, 42% yield. ^1H NMR (400 MHz, CDCl_3) δ 10.15 (s, 1H), 7.83–7.79 (m, 1H), 7.48–7.43 (m, 1H), 7.38–7.33 (m, 2H), 7.27–7.20 (m, 3H), 7.14–7.11 (m, 2H), 4.09–4.01 (m, 1H), 4.00–3.93 (m, 1H), 3.71 (d, $J = 14.4$ Hz, 1H), 3.62 (d, $J = 14.4$ Hz, 1H), 3.37 (q, $J = 14.2$

Hz, 2H), 1.64–1.57 (m, 1H), 1.08 (t, $J = 7.1$ Hz, 3H), 1.05–1.01 (m, 1H), 1.00–0.94 (m, 1H), 0.82–0.75 (m, 1H), 0.74–0.67 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 206.8, 191.8, 171.8, 139.7, 136.1, 135.2, 133.3, 132.4, 130.8, 130.3, 128.4, 127.3, 127.1, 66.1, 61.4, 40.5, 33.5, 20.8, 13.8, 13.2, 13.1; HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_4\text{H}^+$ 365.1747, found 365.1747; $[\alpha]_{\text{D}}^{25}$: +26.2 (c 3.4, CHCl_3); HPLC analysis: 99% *ee* (Chiralcel AD-H, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 12.8 min, R_t (minor) = 11.9 min; IR (KBr thin film, cm^{-1}): ν 2982, 1732, 1697, 1600, 1453, 1380, 1208, 755, 701.



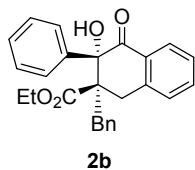
(S)-1p

ethyl (*R*)-2-benzoyl-2-(3-oxopropyl)pent-4-enoate (1p): Colorless oil, 155.6 mg, 54% yield. ^1H NMR (400 MHz, CDCl_3) δ 9.69 (s, 1H), 7.82 (d, $J = 8.0$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.4$ Hz, 2H), 5.57–5.50 (m, 1H), 5.11–5.00 (m, 2H), 4.20–4.08 (m, 2H), 2.82–2.77 (m, 2H), 2.50–2.37 (m, 2H), 2.37–2.24 (m, 2H), 1.07 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 200.7, 196.3, 172.8, 135.6, 133.1, 131.7, 128.7, 128.5, 119.7, 61.7, 59.6, 38.4, 37.8, 25.1, 13.9; HRMS (ESI, m/z): calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{H}^+$ 289.1434, found 289.1434; $[\alpha]_{\text{D}}^{25}$: +58.6 (c 2.2, CHCl_3); HPLC analysis: 0% *ee* (Chiralcel AD-H, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 8.0 min, R_t (minor) = 8.4 min; IR (KBr thin film, cm^{-1}): ν 2980, 1731, 1681, 1641, 1597, 1580, 1447, 1209, 1095, 924, 693.

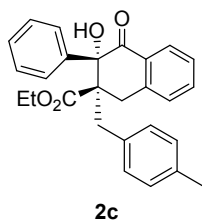


2a

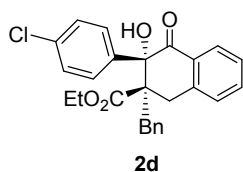
ethyl (2*R*,3*S*)-2-allyl-3-hydroxy-4-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2a): Colorless oil, 175.1 mg, 50% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.17 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.64 (td, $J = 7.5, 1.1$ Hz, 1H), 7.46 (t, $J = 7.6$ Hz, 1H), 7.31 (t, $J = 7.7$ Hz, 1H), 7.26–7.19 (m, 5H), 5.60–5.52 (m, 1H), 5.03–5.00 (m, 1H), 4.83–4.78 (m, 1H), 4.43 (s, 1H), 4.14–4.08 (m, 2H), 3.44 (d, $J = 17.6$ Hz, 1H), 3.32–3.28 (m, 1H), 3.09 (d, $J = 17.8$ Hz, 1H), 1.98 (dd, $J = 14.0, 8.6$ Hz, 1H), 1.18 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.6, 171.8, 141.9, 139.9, 135.4, 133.3, 131.3, 130.0, 128.4, 128.3, 128.0, 127.5, 126.3, 119.4, 81.1, 61.3, 56.7, 34.9, 32.1, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{22}\text{H}_{22}\text{O}_4\text{H}^+$ 351.1591, found 351.1591; $[\alpha]_{\text{D}}^{25}$: +14.6 (c 0.3, CHCl_3); HPLC analysis: 83% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 23.7 min, R_t (minor) = 20.8 min; IR (KBr thin film, cm^{-1}): ν 3473, 2924, 1726, 1684, 1601, 1446, 1287, 1217, 739, 702.



ethyl (2*R*,3*S*)-2-benzyl-3-hydroxy-4-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2b): Colorless oil, 188.1 mg, 47% yield. ¹H NMR (600 MHz, CDCl₃) δ 8.24 (d, *J* = 6.9 Hz, 1H), 7.71 (td, *J* = 7.4, 1.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.31–7.28 (m, 2H), 7.26–7.16 (m, 7H), 6.83–6.81 (m, 2H), 4.57 (s, 1H), 4.09–3.99 (m, 2H), 3.93 (d, *J* = 14.0 Hz, 1H), 3.37 (d, *J* = 17.9 Hz, 1H), 2.81 (d, *J* = 17.9 Hz, 1H), 2.52 (d, *J* = 14.0 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 198.7, 171.7, 142.1, 139.9, 137.2, 135.6, 131.4, 130.2, 130.1, 128.42, 128.37, 128.3, 128.1, 127.7, 126.9, 126.3, 81.7, 61.3, 58.2, 36.3, 31.7, 14.1; HRMS (ESI, *m/z*): calcd. for C₂₆H₂₄O₄H⁺ 401.1747, found 401.1747; [α]_D²⁶: +3.4 (c 2.9, CHCl₃); HPLC analysis: 97% *ee* (Chiralcel AD-H, 02:98 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 27.7 min, R_t (minor) = 25.5 min; IR (KBr thin film, cm⁻¹): ν 3473, 2925, 1727, 1681, 1600, 1447, 1219, 755, 701.

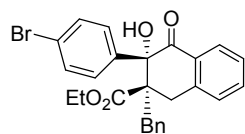


ethyl (2*R*,3*S*)-3-hydroxy-2-(4-methylbenzyl)-4-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2c): Yellow solid, mp 74–75 °C, 207.1 mg, 50% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.27–7.13 (m, 5H), 7.05 (s, 2H), 6.98 (s, 1H), 6.82 (s, 2H), 4.54 (s, 1H), 4.12–4.00 (m, 2H), 3.93 (d, *J* = 13.8 Hz, 1H), 3.38 (d, *J* = 17.9 Hz, 1H), 2.80 (d, *J* = 17.9 Hz, 1H), 2.52 (d, *J* = 13.9 Hz, 1H), 2.25 (s, 3H), 1.15 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 198.8, 171.8, 142.2, 139.8, 138.0, 137.2, 135.5, 131.4, 130.2, 130.1, 129.1, 128.3, 128.1, 127.6, 127.2, 126.9, 123.2, 81.7, 61.2, 58.2, 36.3, 31.8, 21.7, 14.1; HRMS (ESI, *m/z*): calcd. for C₂₇H₂₆O₄H⁺ 415.1904, found 415.1904; [α]_D²⁴: −15.2 (c 1.2, CHCl₃); HPLC analysis: 72% *ee* (Chiralcel AD-H, 10:90 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 11.7 min, R_t (minor) = 10.3 min; IR (KBr thin film, cm⁻¹): ν 3475, 2925, 1726, 1682, 1601, 1455, 1282, 1194, 1084, 738, 703.



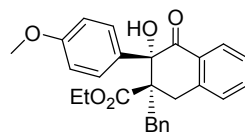
ethyl (2*R*,3*S*)-2-benzyl-3-(4-chlorophenyl)-3-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2d): Colorless oil, 199.7 mg, 46% yield. ¹H NMR (400 MHz, CDCl₃) δ 8.24 (d, *J* = 7.8 Hz, 1H), 7.72 (td, *J* = 7.6, 1.2 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 1H), 7.28–7.17 (m, 8H), 6.85–

6.78 (m, 2H), 4.59 (s, 1H), 4.14–4.00 (m, 2H), 3.91 (d, $J = 13.9$ Hz, 1H), 3.31 (d, $J = 18.1$ Hz, 1H), 2.83 (d, $J = 18.1$ Hz, 1H), 2.50 (d, $J = 13.9$ Hz, 1H), 1.16 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.1, 171.5, 142.0, 138.4, 136.9, 135.9, 134.4, 131.1, 130.3, 130.1, 128.5, 128.4, 128.3, 127.84, 127.81, 127.0, 81.2, 61.4, 58.1, 36.2, 31.6, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{26}\text{H}_{23}\text{ClO}_4\text{H}^+$ 435.1358, found 435.1358; $[\alpha]_{\text{D}}^{30}$: +30.8 (c 3.2, CHCl_3); HPLC analysis: 95% *ee* (Chiralcel AD-H, 02:98 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 23.1 min, R_t (minor) = 28.3 min; IR (KBr thin film, cm^{-1}): ν 3463, 2924, 1725, 1684, 1278, 1263, 1081, 743, 702.



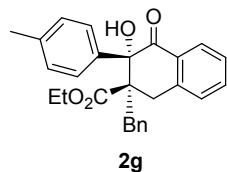
2e

ethyl (2*R*,3*S*)-2-benzyl-3-(4-bromophenyl)-3-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2e): White solid, mp 74–75 °C, 162.6 mg, 34% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.23 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.72 (td, $J = 7.5, 1.3$ Hz, 1H), 7.52 (t, $J = 7.6$ Hz, 1H), 7.36–7.32 (m, 2H), 7.27–7.25 (m, 1H), 7.19–7.16 (m, 5H), 6.82–6.79 (m, 2H), 4.59 (s, 1H), 4.11–4.01 (m, 2H), 3.91 (dd, $J = 13.9, 1.0$ Hz, 1H), 3.31 (d, $J = 17.9$ Hz, 1H), 2.83 (d, $J = 18.1$ Hz, 1H), 2.50 (d, $J = 14.0$ Hz, 1H), 1.16 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.1, 171.5, 142.0, 138.9, 136.9, 135.9, 131.4, 131.1, 130.3, 130.1, 128.4, 128.3, 128.2, 127.8, 127.0, 122.7, 81.3, 61.4, 58.1, 36.2, 31.6, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{26}\text{H}_{23}\text{BrO}_4\text{H}^+$ 479.0852, found 479.0852; $[\alpha]_{\text{D}}^{28}$: +25.1 (c 2.1, CHCl_3); HPLC analysis: 99% *ee* (Chiralcel AD-H, 02:98 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 13.7 min, R_t (minor) = 15.4 min; IR (KBr thin film, cm^{-1}): ν 3473, 2928, 1731, 1682, 1453, 1245, 1074, 755, 702.

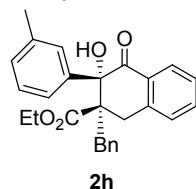


2f

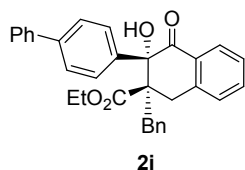
ethyl (2*R*,3*S*)-2-benzyl-3-hydroxy-3-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2f): Colorless oil, 202.2 mg, 47% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (d, $J = 7.8$ Hz, 1H), 7.70 (t, $J = 7.5$ Hz, 1H), 7.51 (t, $J = 7.5$ Hz, 1H), 7.25–7.16 (m, 6H), 6.91–6.77 (m, 2H), 6.73 (d, $J = 8.9$ Hz, 2H), 4.53 (s, 1H), 4.17–4.01 (m, 2H), 3.90 (d, $J = 13.9$ Hz, 1H), 3.73 (s, 3H), 3.35 (d, $J = 18.1$ Hz, 1H), 2.81 (d, $J = 18.0$ Hz, 1H), 2.50 (d, $J = 13.9$ Hz, 1H), 1.16 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.8, 171.9, 159.4, 142.1, 137.2, 135.6, 131.9, 131.3, 130.2, 130.1, 128.4, 128.1, 127.63, 127.56, 126.9, 113.6, 81.4, 61.3, 58.3, 55.3, 36.3, 31.8, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_5\text{H}^+$ 431.1853, found 431.1853; $[\alpha]_{\text{D}}^{24}$: +13.3 (c 1.2, CHCl_3); HPLC analysis: 77% *ee* (Chiralcel IC, 10:90 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 16.0 min, R_t (minor) = 17.5 min; IR (KBr thin film, cm^{-1}): ν 3463, 2929, 1729, 1674, 1256, 1171, 1028, 702.



ethyl (2R,3S)-2-benzyl-3-hydroxy-4-oxo-3-(p-tolyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2g): Colorless oil, 186.4 mg, 45% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.23 (dd, J = 9.2, 1.1 Hz, 1H), 7.70 (td, J = 7.5, 1.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.8 Hz, 2H), 7.19–7.14 (m, 4H), 7.01 (d, J = 8.1 Hz, 2H), 6.83–6.80 (m, 2H), 4.53 (s, 1H), 4.13–4.02 (m, 2H), 3.91 (d, J = 14.7 Hz, 1H), 3.36 (d, J = 17.8 Hz, 1H), 2.80 (d, J = 18.0 Hz, 1H), 2.51 (d, J = 13.9 Hz, 1H), 2.26 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.8, 171.9, 142.2, 138.2, 137.2, 136.9, 135.5, 130.2, 130.1, 129.0, 128.4, 128.1, 127.6, 126.9, 126.2, 81.6, 61.3, 58.2, 36.2, 31.8, 21.2, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{H}^+$ 415.1904, found 415.1904; $[\alpha]_{\text{D}}^{29}$: +18.7 (c 2.7, CHCl_3); HPLC analysis: 66% *ee* (Chiralcel AD-H, 02:98 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 31.9 min, R_t (minor) = 28.4 min; IR (KBr thin film, cm^{-1}): ν 3475, 2925, 1726, 1682, 1601, 1455, 1282, 1194, 738, 703.

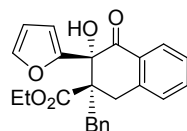


ethyl (2R,3S)-2-benzyl-3-hydroxy-4-oxo-3-(m-tolyl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2h): Colorless oil, 194.7 mg, 47% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.24 (dd, J = 7.8, 1.1 Hz, 1H), 7.70 (td, J = 7.5, 1.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 7.7 Hz, 1H), 7.20 (s, 1H), 7.18–7.15 (m, 3H), 7.07–7.03 (m, 2H), 6.98–6.95 (m, 1H), 6.84–6.79 (m, 2H), 4.54 (s, 1H), 4.10–4.03 (m, 2H), 3.92 (d, J = 13.9 Hz, 1H), 3.37 (d, J = 17.6 Hz, 1H), 2.79 (d, J = 17.9 Hz, 1H), 2.51 (d, J = 13.9 Hz, 1H), 2.24 (s, 1H), 1.14 (t, J = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.8, 171.8, 142.2, 139.8, 138.0, 137.2, 135.6, 131.4, 130.2, 130.1, 129.2, 128.4, 128.1, 128.0, 127.6, 127.2, 126.9, 123.2, 81.7, 61.3, 58.2, 36.3, 31.8, 21.8, 14.1; HRMS (ESI, m/z): calcd. for $\text{C}_{27}\text{H}_{26}\text{O}_4\text{H}^+$ 415.1904, found 415.1904; $[\alpha]_{\text{D}}^{26}$: +66.0 (c 1.9, CHCl_3); HPLC analysis: 92% *ee* (Chiralcel AD-H, 02:98 *i*PrOH/Hexanes, 1 mL/min), R_t (major) = 18.7 min, R_t (minor) = 17.4 min; IR (KBr thin film, cm^{-1}): ν 3474, 2925, 1726, 1683, 1602, 1455, 1282, 1195, 704.



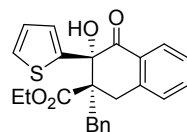
ethyl (2R,3S)-3-([1,1'-biphenyl]-4-yl)-2-benzyl-3-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2i): Yellow oil, 257.1 mg, 54% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, J = 7.8 Hz, 1H), 7.72 (td, J = 7.5, 1.2 Hz, 1H), 7.57–7.48 (m, 3H), 7.47–

7.27 (m, 8H), 7.22–7.17 (m, 3H), 6.86–6.81 (m, 2H), 4.62 (s, 1H), 4.13–4.03 (m, 2H), 3.95 (d, J = 13.9 Hz, 1H), 3.43 (d, J = 18.0 Hz, 1H), 2.85 (d, J = 18.1 Hz, 1H), 2.54 (d, J = 13.9 Hz, 1H), 1.13 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.6, 171.7, 142.1, 141.1, 140.4, 138.9, 137.1, 135.6, 131.3, 130.2, 130.1, 128.9, 128.4, 128.2, 127.7, 127.6, 127.1, 126.93, 126.88, 126.8, 81.6, 61.3, 58.2, 36.3, 31.8, 14.1; HRMS (ESI, m/z): calcd. for $\text{C}_{32}\text{H}_{28}\text{O}_4\text{H}^+$ 477.2060, found 477.2060; $[\alpha]_{\text{D}}^{24}$: +13.3 (c 1.2, CHCl_3); HPLC analysis: 75% *ee* (Chiralcel AD-H, 10:90 $^i\text{PrOH}$ /Hexanes, 1 mL/min), R_t (major) = 13.7 min, R_t (minor) = 18.0 min; IR (KBr thin film, cm^{-1}): ν 3471, 2926, 1726, 1682, 1601, 1486, 1454, 1282, 1237, 1195, 1084, 753, 700.



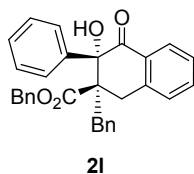
2j

ethyl (2*R*,3*R*)-2-benzyl-3-(furan-2-yl)-3-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2j): Light brown oil, 234.1 mg, 60% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 7.8 Hz, 1H), 7.70 (td, J = 7.5, 1.2 Hz, 1H), 7.49 (t, J = 7.6 Hz, 1H), 7.28 (d, J = 7.7 Hz, 1H), 7.22–7.17 (m, 4H), 6.88–6.79 (m, 3H), 6.62 (dd, J = 3.7, 0.9 Hz, 1H), 5.10 (s, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.86 (d, J = 13.2 Hz, 1H), 3.59 (d, J = 18.2 Hz, 1H), 2.93 (d, J = 18.3 Hz, 1H), 2.50 (d, J = 13.8 Hz, 1H), 1.20 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.3, 171.8, 143.5, 141.7, 136.9, 135.7, 130.2, 130.0, 129.9, 128.8, 128.4, 127.7, 127.0, 126.9, 125.8, 124.8, 80.6, 61.6, 57.8, 36.0, 31.8, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_5\text{H}^+$ 391.1540, found 391.1540; $[\alpha]_{\text{D}}^{28}$: +27.9 (c 1.5, CHCl_3); HPLC analysis: 51% *ee* (Chiralcel AD-H, 10:90 $^i\text{PrOH}$ /Hexanes, 1 mL/min), R_t (major) = 27.7 min, R_t (minor) = 34.2 min; IR (KBr thin film, cm^{-1}): ν 3456, 2932, 1723, 1686, 1262, 1237, 1197, 1084, 747, 702.

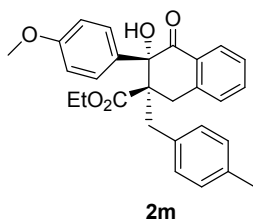


2k

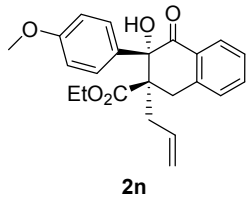
ethyl (2*R*,3*S*)-2-benzyl-3-hydroxy-4-oxo-3-(thiophen-2-yl)-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2k): Light brown solid, mp 117–118 °C, 174.6 mg, 43% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.19 (d, J = 7.8 Hz, 1H), 7.69 (t, J = 7.5 Hz, 1H), 7.49 (t, J = 7.4 Hz, 1H), 7.29–7.25 (m, 2H), 7.19–7.17 (m, 3H), 6.85–6.79 (m, 3H), 6.63–6.61 (m, 1H), 5.08 (d, J = 1.7 Hz, 1H), 4.13 (qd, J = 7.1, 1.7 Hz, 2H), 3.86 (d, J = 13.8 Hz, 1H), 3.60 (d, J = 18.3 Hz, 1H), 2.93 (d, J = 18.3 Hz, 1H), 2.50 (d, J = 13.8 Hz, 1H), 1.20 (td, J = 7.1, 1.9 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.3, 171.8, 143.5, 141.7, 136.9, 135.7, 130.2, 130.0, 129.9, 128.8, 128.4, 127.7, 127.0, 126.9, 125.8, 124.8, 80.6, 61.6, 57.8, 36.0, 31.8, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{24}\text{H}_{22}\text{O}_4\text{SH}^+$ 407.1312, found 407.1312; $[\alpha]_{\text{D}}^{25}$: –12.77 (c 1.19, CHCl_3); HPLC analysis: 87% *ee* (Chiralcel AD-H, 02:98 $^i\text{PrOH}$ /Hexanes, 1 mL/min), R_t (major) = 11.8 min, R_t (minor) = 8.7 min; IR (KBr thin film, cm^{-1}): ν 3448, 2962, 1718, 1685, 1276, 1260, 1084, 1050, 764, 749, 702.



benzyl (2R,3S)-2-benzyl-3-hydroxy-4-oxo-3-phenyl-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2l): Colorless oil, 258.8 mg, 56% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.24 (dd, J = 7.8, 1.1 Hz, 1H), 7.69 (td, J = 7.5, 1.4 Hz, 1H), 7.51 (t, J = 7.6 Hz, 1H), 7.32–7.29 (m, 3H), 7.25–7.23 (m, 3H), 7.23–7.19 (m, 2H), 7.17–7.07 (m, 6H), 6.76–6.70 (m, 2H), 5.06 (d, J = 12.4 Hz, 1H), 4.97 (d, J = 12.4 Hz, 1H), 4.56 (s, 1H), 3.97 (d, J = 13.9 Hz, 1H), 3.38 (d, J = 17.9 Hz, 1H), 2.83 (d, J = 18.0 Hz, 1H), 2.53 (d, J = 13.9 Hz, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.7, 171.6, 142.1, 139.9, 137.0, 135.6, 135.4, 131.4, 130.2, 130.1, 128.59, 128.56, 128.43, 128.40, 128.3, 128.1, 127.7, 126.9, 126.3, 81.7, 67.0, 58.4, 36.3, 31.7; HRMS (ESI, m/z): calcd. for $\text{C}_{31}\text{H}_{26}\text{O}_4\text{H}^+$ 463.1904, found 463.1904; $[\alpha]_{\text{D}}^{24}$: +31.6 (c 3.31, CHCl_3); HPLC analysis: 58% *ee* (Chiralcel AD-H, 02:98 i PrOH/Hexanes, 1 mL/min), R_t (major) = 97.8 min, R_t (minor) = 86.9 min; IR (KBr thin film, cm^{-1}): ν 3479, 2922, 1726, 1681, 1622, 1282, 1187, 739, 700.

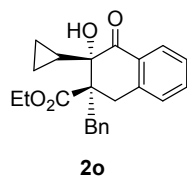


ethyl (2R,3S)-3-hydroxy-3-(4-methoxyphenyl)-2-(4-methylbenzyl)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2m): Light brown oil, 168.8 mg, 38% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.22 (dd, J = 7.8, 1.1 Hz, 1H), 7.69 (td, J = 7.5, 1.4 Hz, 1H), 7.50 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 6.9 Hz, 3H), 7.21–7.18 (m, 2H), 6.98 (d, J = 7.8 Hz, 2H), 6.75–6.68 (m, 4H), 4.53 (s, 1H), 4.12–4.04 (m, 2H), 3.86 (d, J = 13.9 Hz, 1H), 3.73 (s, 3H), 3.34 (d, J = 17.9 Hz, 1H), 2.82 (d, J = 18.0 Hz, 1H), 2.47 (d, J = 14.0 Hz, 1H), 2.27 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 198.8, 172.0, 159.5, 142.2, 136.4, 135.5, 134.0, 132.0, 131.4, 130.2, 129.9, 129.1, 128.1, 127.6, 113.6, 81.4, 61.3, 58.3, 55.3, 35.8, 31.8, 21.2, 14.2; HRMS (ESI, m/z): calcd. for $\text{C}_{28}\text{H}_{28}\text{O}_5\text{H}^+$ 445.2010, found 445.2010; $[\alpha]_{\text{D}}^{25}$: +12.3 (c 1.9, CHCl_3); HPLC analysis: 84% *ee* (Chiralcel IA, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 53.7 min, R_t (minor) = 39.8 min; IR (KBr thin film, cm^{-1}): ν 3475, 2926, 1725, 1682, 1603, 1510, 1459, 1281, 1253, 1055, 829, 751.

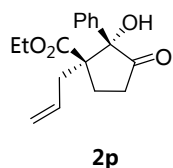


ethyl (2R,3S)-2-allyl-3-hydroxy-3-(4-methoxyphenyl)-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2n): Yellow oil, 133.1 mg, 35% yield. ^1H NMR (600 MHz, CDCl_3) δ 8.16 (dd, J

= 7.8, 1.1 Hz, 1H), 7.63 (td, $J = 7.5, 1.4$ Hz, 1H), 7.45 (t, $J = 7.6$ Hz, 1H), 7.30 (d, $J = 7.6$ Hz, 1H), 7.18–7.14 (m, 2H), 6.74–6.71 (m, 2H), 5.60–5.52 (m, 1H), 5.00 (dd, $J = 10.1, 1.7$ Hz, 1H), 4.80 (d, $J = 16.9$ Hz, 1H), 4.39 (s, 1H), 4.13 (qd, $J = 7.2, 1.9$ Hz, 2H), 3.73 (s, 3H), 3.42 (d, $J = 17.2$ Hz, 1H), 3.29–3.24 (m, 1H), 3.08 (d, $J = 17.8$ Hz, 1H), 1.96 (dd, $J = 14.1, 8.7$ Hz, 1H), 1.21 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (151 MHz, CDCl_3) δ 198.7, 172.0, 159.4, 141.8, 135.4, 133.3, 131.9, 131.2, 130.0, 127.9, 127.5, 119.3, 113.6, 80.9, 61.3, 56.8, 55.3, 34.9, 32.1, 14.3; HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_5\text{H}^+$ 381.1697, found 381.1697; $[\alpha]_{\text{D}}^{27}$: -1.6 (c 2.2, CHCl_3); HPLC analysis: 83% *ee* (Chiralcel IA, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 12.8 min, R_t (minor) = 14.6 min; IR (KBr thin film, cm^{-1}): ν 3447, 2925, 2852, 1725, 1682, 1603, 1510, 1254, 1281, 1038, 829, 738.

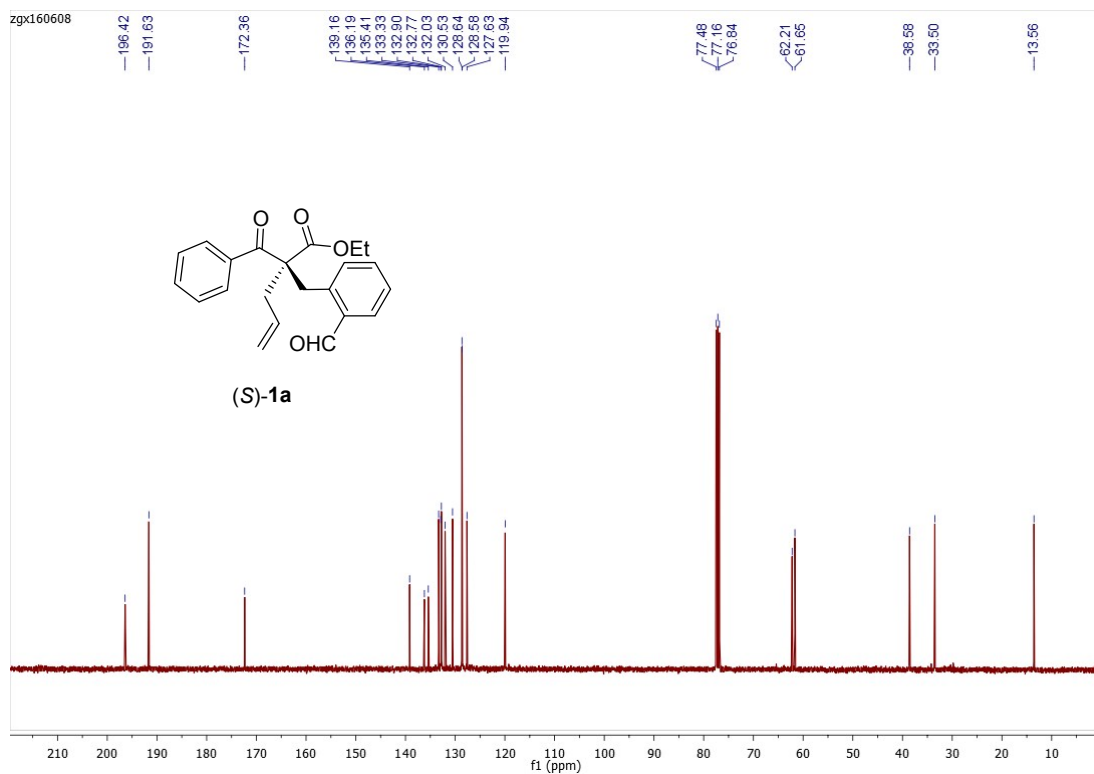
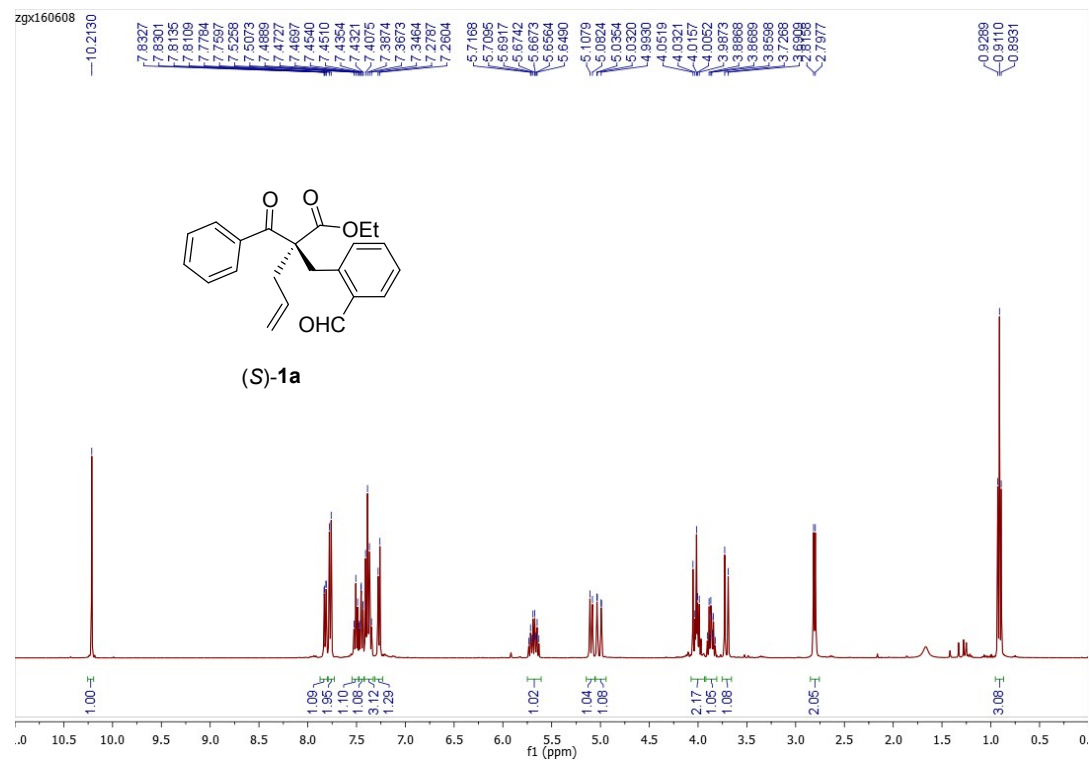


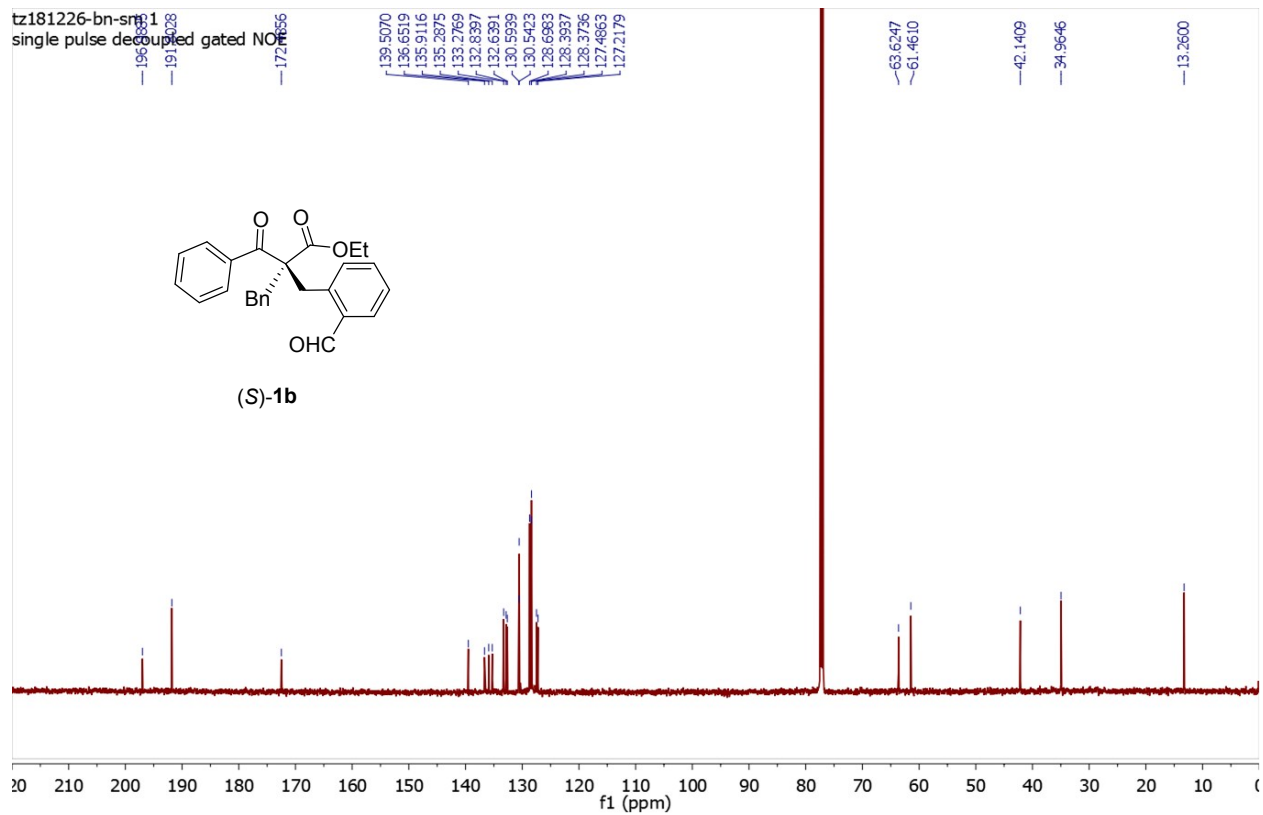
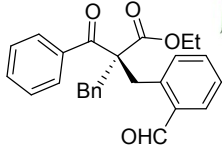
ethyl (2R,3S)-2-benzyl-3-cyclopropyl-3-hydroxy-4-oxo-1,2,3,4-tetrahydronaphthalene-2-carboxylate (2o): Yellow oil, 185.7 mg, 51% yield. ^1H NMR (400 MHz, CDCl_3) δ 8.12 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.63 (td, $J = 7.5, 1.4$ Hz, 1H), 7.42 (t, $J = 7.6$ Hz, 1H), 7.25 (d, $J = 7.9$ Hz, 1H), 7.20–7.16 (m, 3H), 6.85–6.82 (m, 2H), 4.25 (q, $J = 7.1$ Hz, 2H), 3.95 (s, 1H), 3.82 (d, $J = 18.4$ Hz, 1H), 3.70 (dd, $J = 13.8, 1.2$ Hz, 1H), 2.98 (d, $J = 18.5$ Hz, 1H), 2.37 (d, $J = 13.8$ Hz, 1H), 1.34 (t, $J = 7.1$ Hz, 3H), 1.25–1.17 (m, 1H), 0.67–0.61 (m, 1H), 0.43–0.33 (m, 2H), 0.24–0.18 (m, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 199.0, 172.6, 140.7, 137.1, 135.2, 130.1, 129.7, 129.5, 128.34, 128.26, 127.3, 126.9, 77.8, 61.4, 57.1, 35.9, 31.7, 14.3, 14.0, 1.4, -0.6 ; HRMS (ESI, m/z): calcd. for $\text{C}_{23}\text{H}_{24}\text{O}_4\text{H}^+$ 365.1747, found 365.1747; $[\alpha]_{\text{D}}^{26}$: $+11.9$ (c 1.0, CHCl_3); HPLC analysis: 64% *ee* (Chiralcel AD-H, 10:90 i PrOH/Hexanes, 1 mL/min), R_t (major) = 27.1 min, R_t (minor) = 15.3 min; IR (KBr thin film, cm^{-1}): ν 3485, 2927, 1723, 1686, 1601, 1454, 1282, 1195, 743, 700.



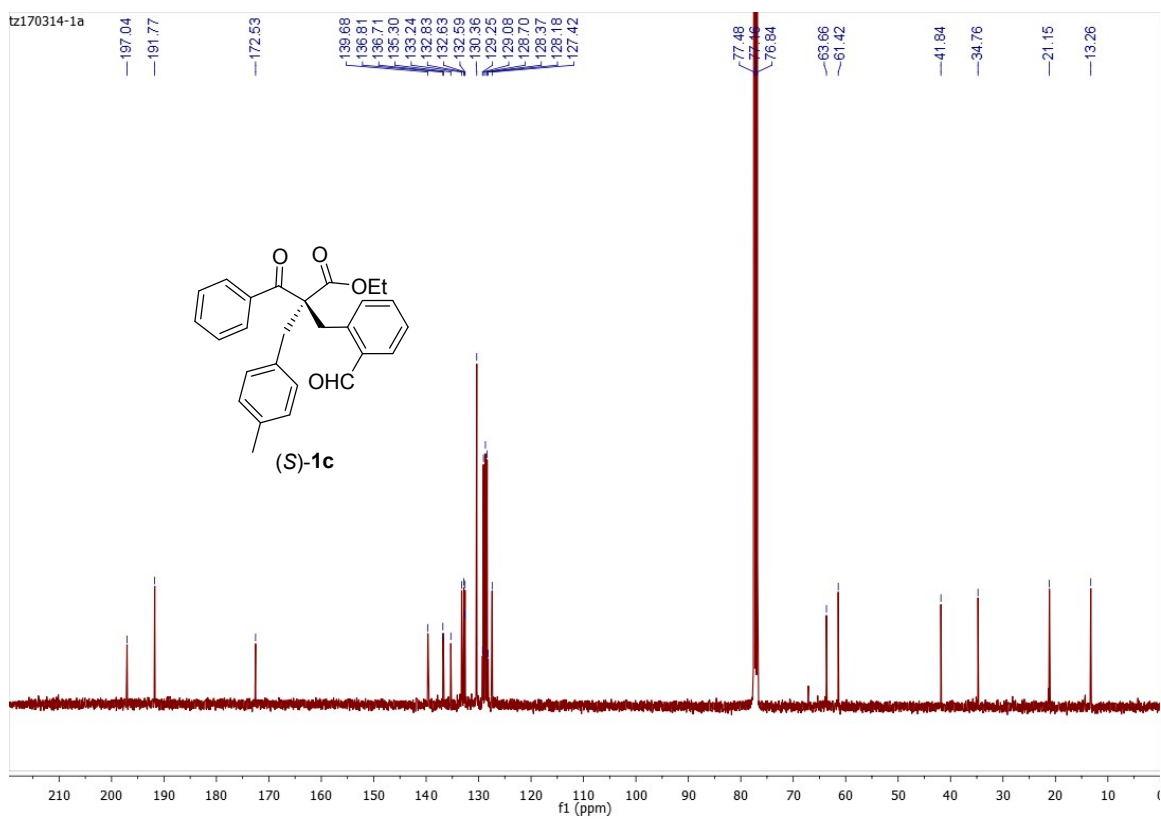
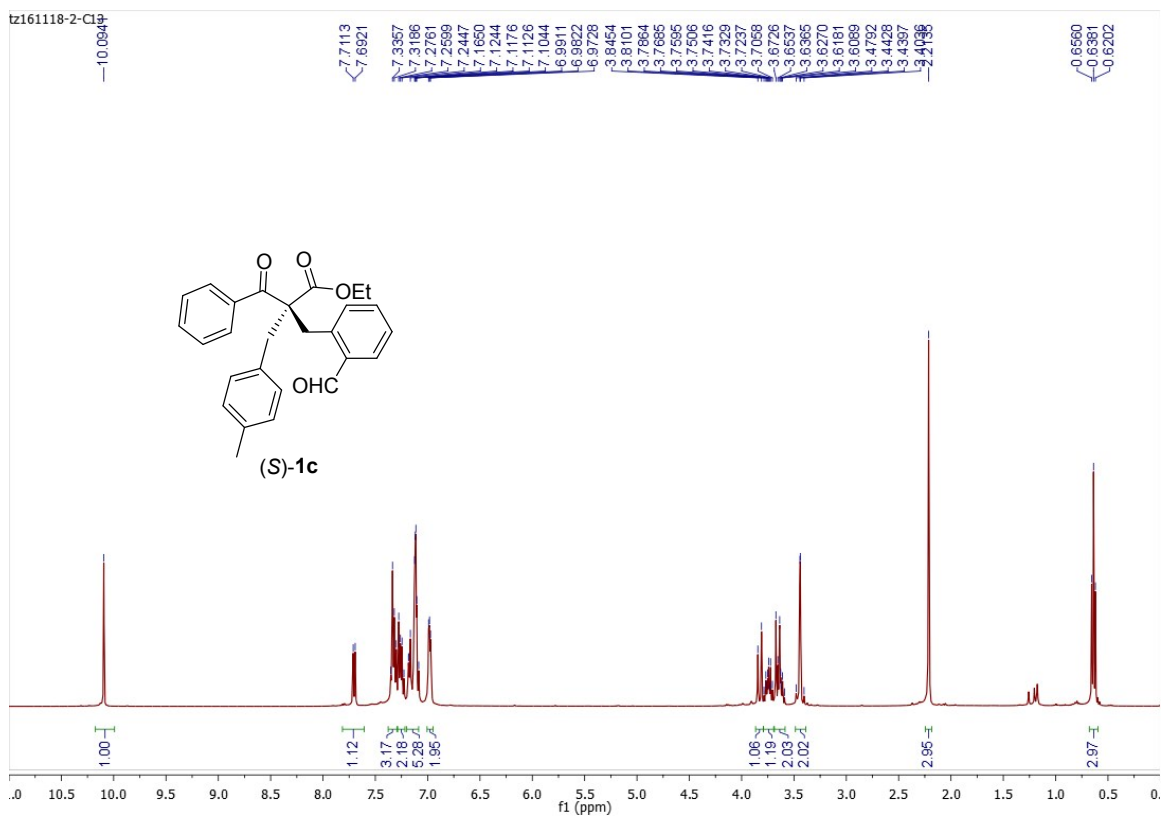
ethyl (1S,2S)-1-allyl-2-hydroxy-3-oxo-2-phenylcyclopentane-1-carboxylate (2p): Colorless oil, 89.3 mg, 31% yield. ^1H NMR (400 MHz, CDCl_3) δ 7.32–7.27 (m, 5H), 5.71–5.60 (m, 1H), 5.17–5.10 (m, 2H), 3.98–3.79 (m, 2H), 3.01 (s, 1H), 2.96 (dd, $J = 13.5, 5.8$ Hz, 1H), 2.79–2.70 (m, 1H), 2.60–2.43 (m, 2H), 2.20–2.12 (m, 2H), 1.03 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 216.8, 172.8, 138.9, 133.4, 128.5, 128.4, 126.3, 119.3, 83.9, 61.1, 58.4, 35.8, 33.7, 23.7, 14.0; HRMS (ESI, m/z): calcd. for $\text{C}_{17}\text{H}_{20}\text{O}_4\text{H}^+$ 289.1434, found 289.1434; $[\alpha]_{\text{D}}^{25}$: $+85.2$ (c 1.8, CHCl_3); HPLC analysis: 4% *ee* (Chiralcel AD-H, 0.5:99.5 i PrOH/Hexanes, 1 mL/min), R_t (major) = 45.4 min, R_t (minor) = 50.4 min; IR (KBr thin film, cm^{-1}): ν 3345, 2980, 1731, 1681, 1641, 1448, 1268, 1205, 693.

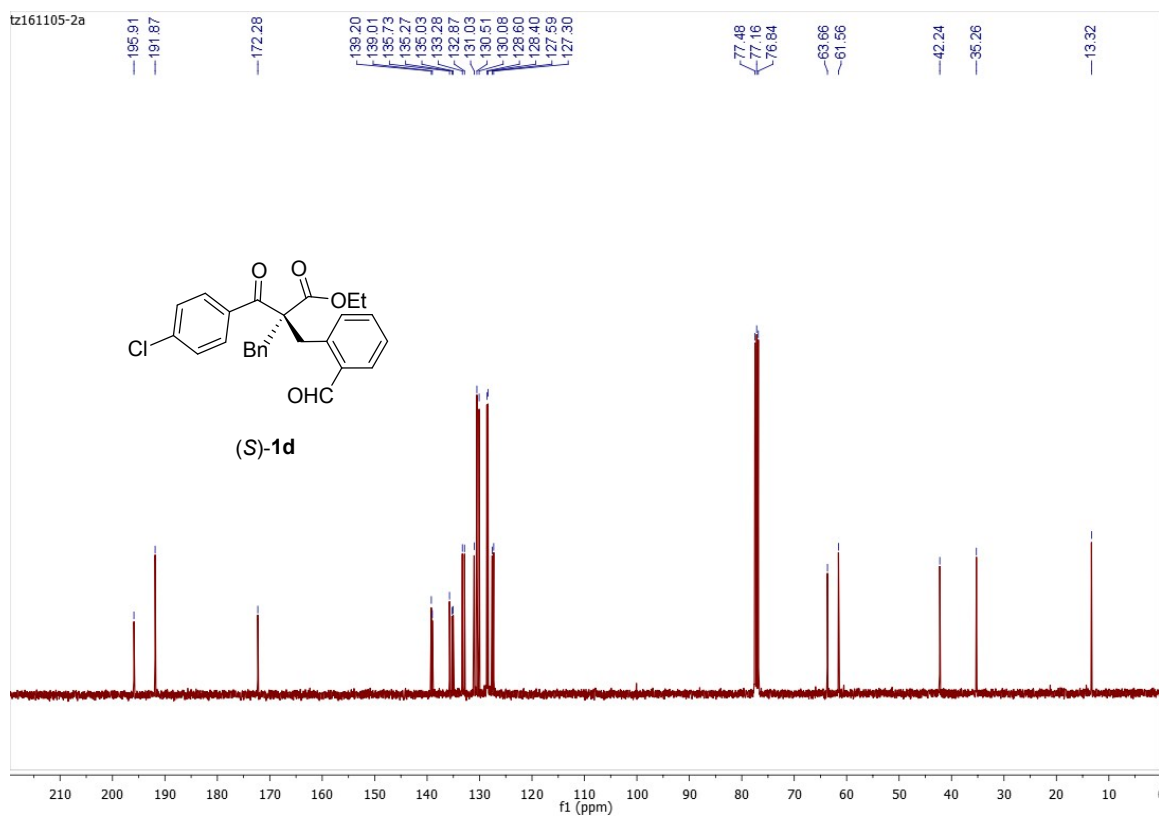
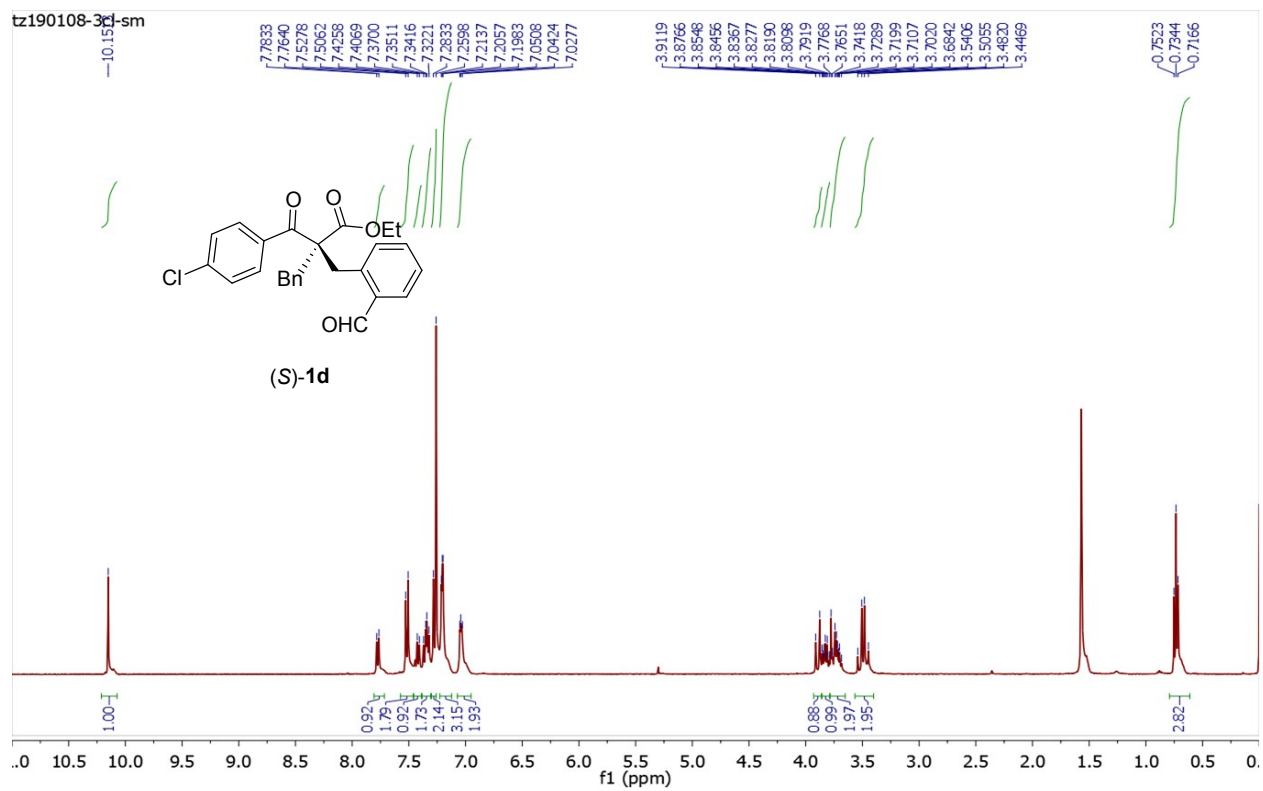
V. ^1H NMR and ^{13}C NMR spectra of substrates and products

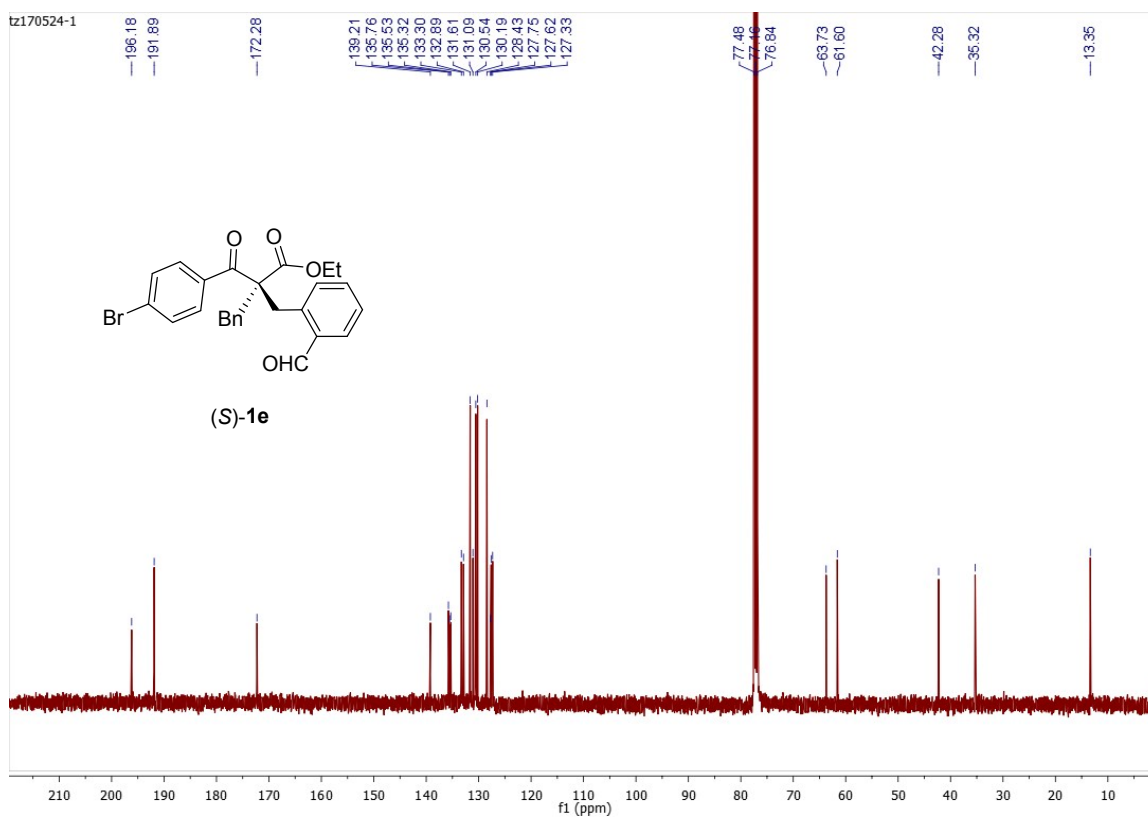
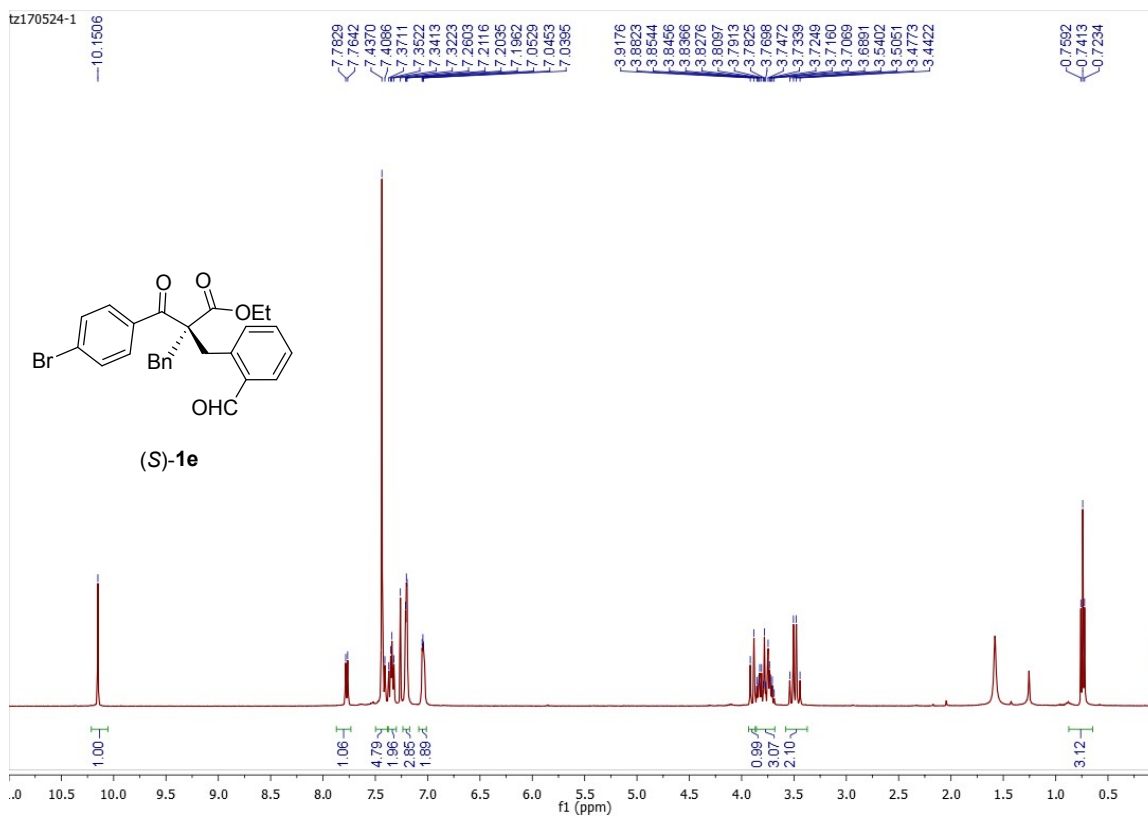


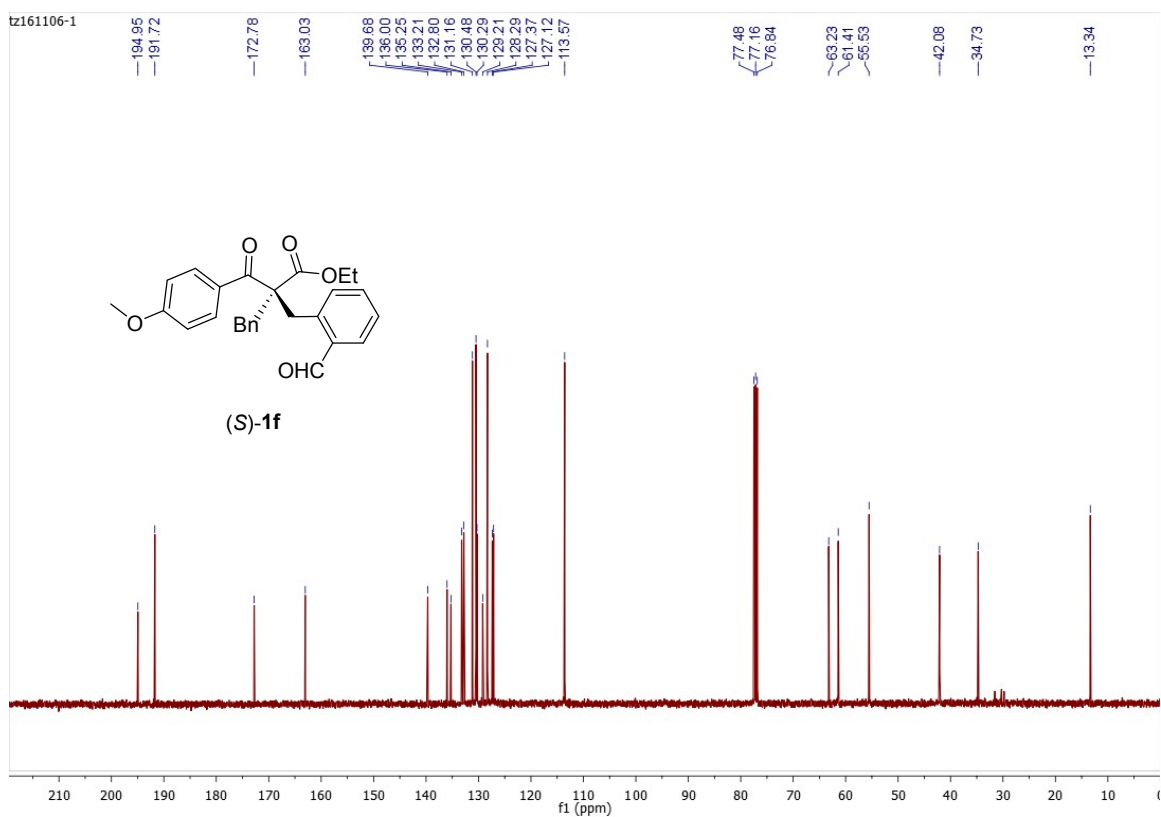
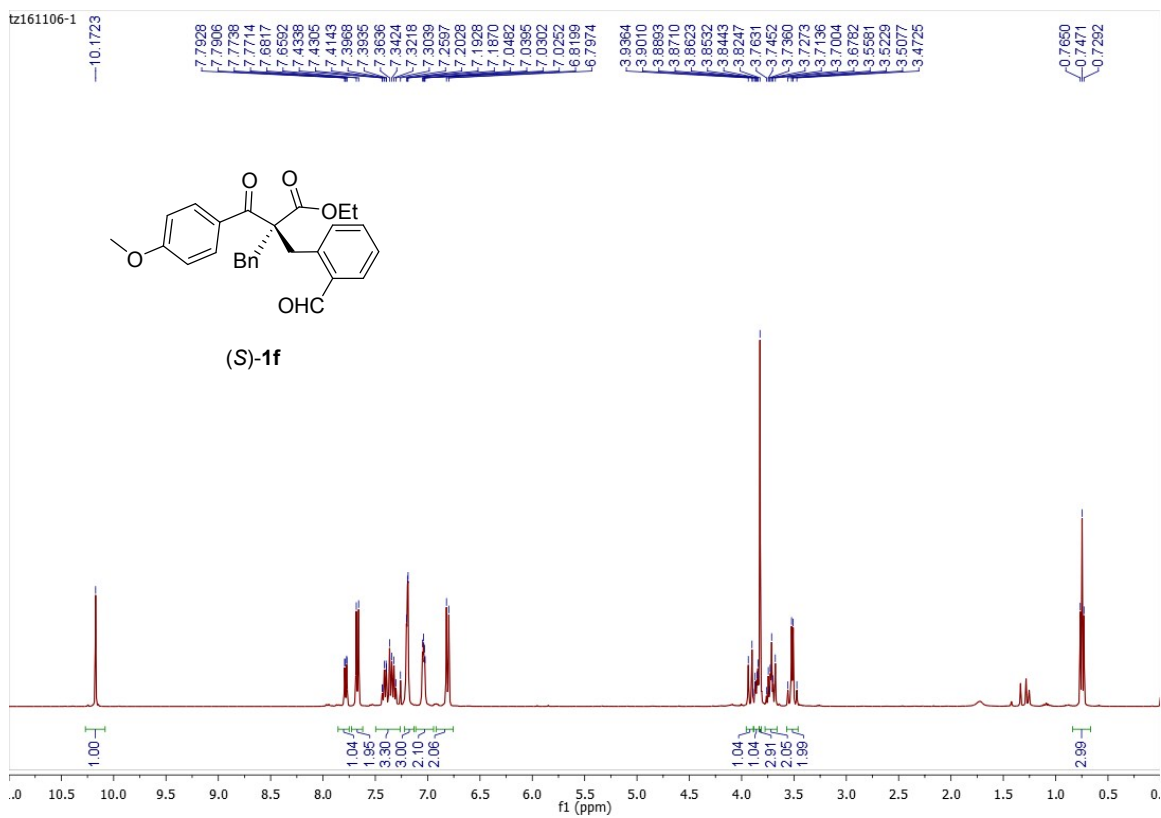


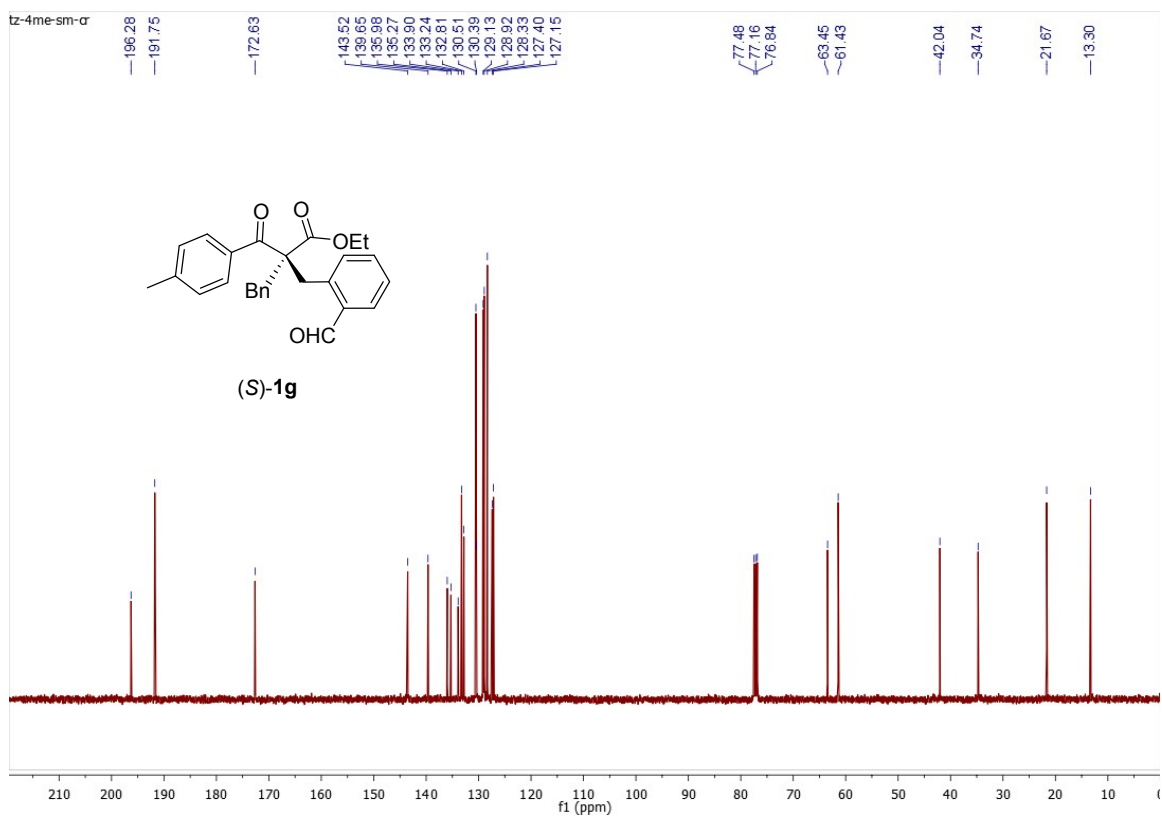
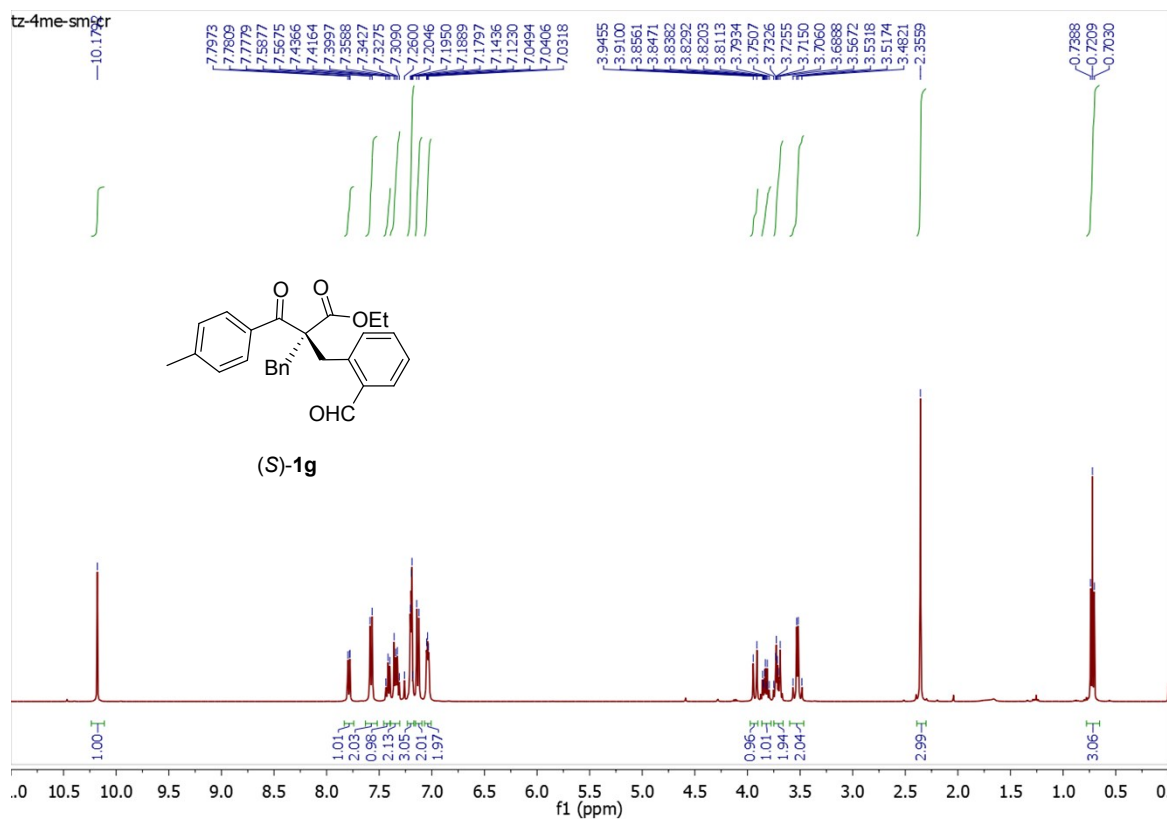
(S)-1b

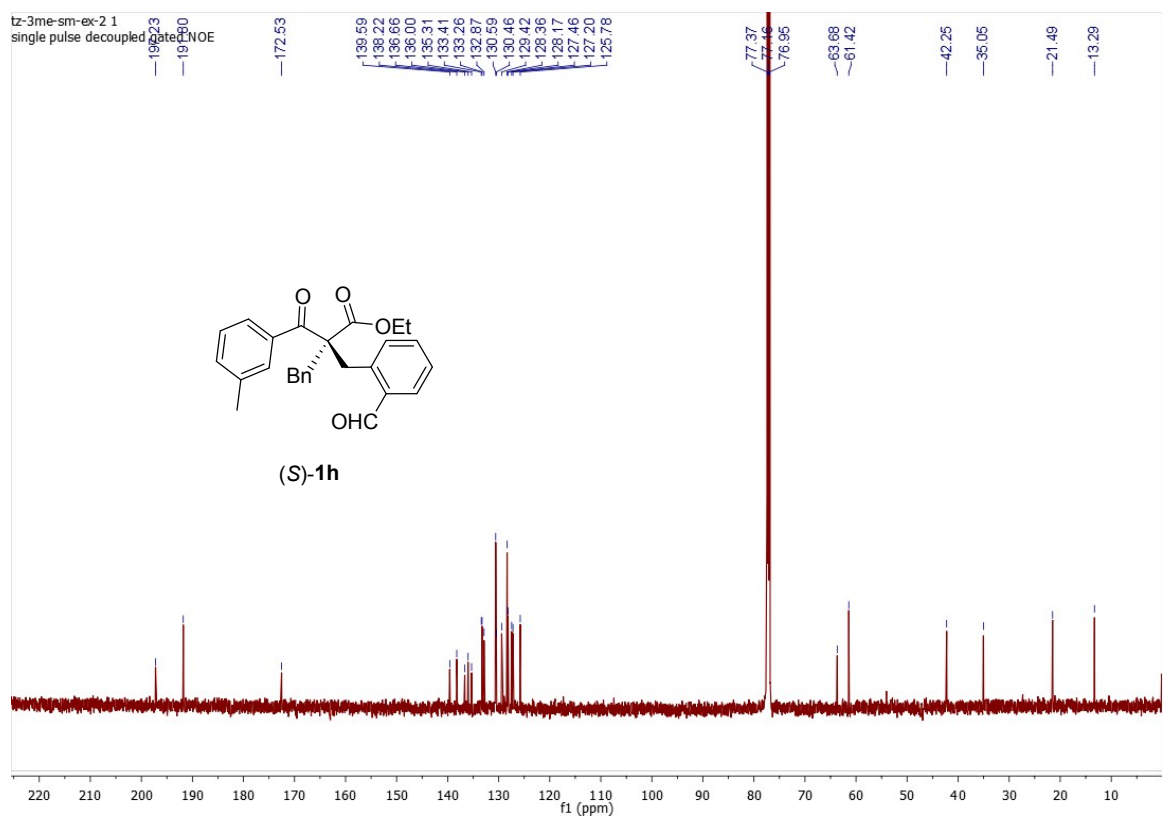
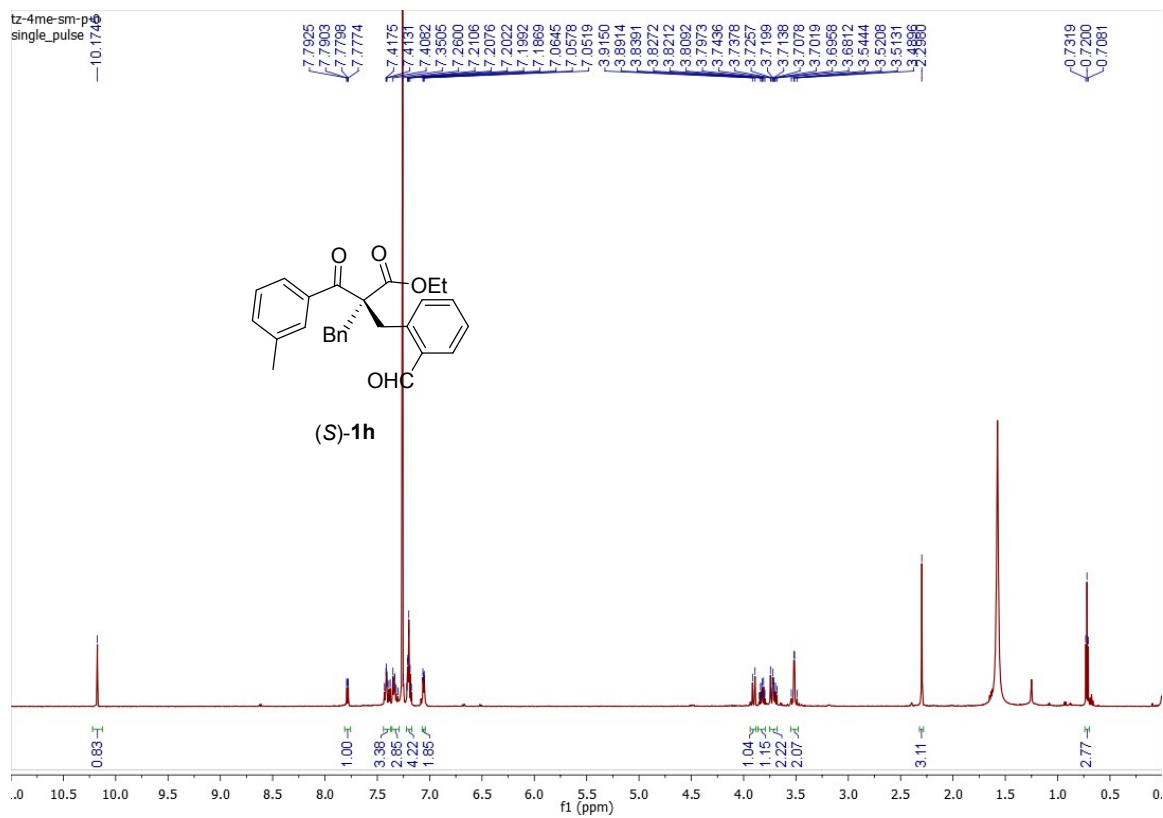


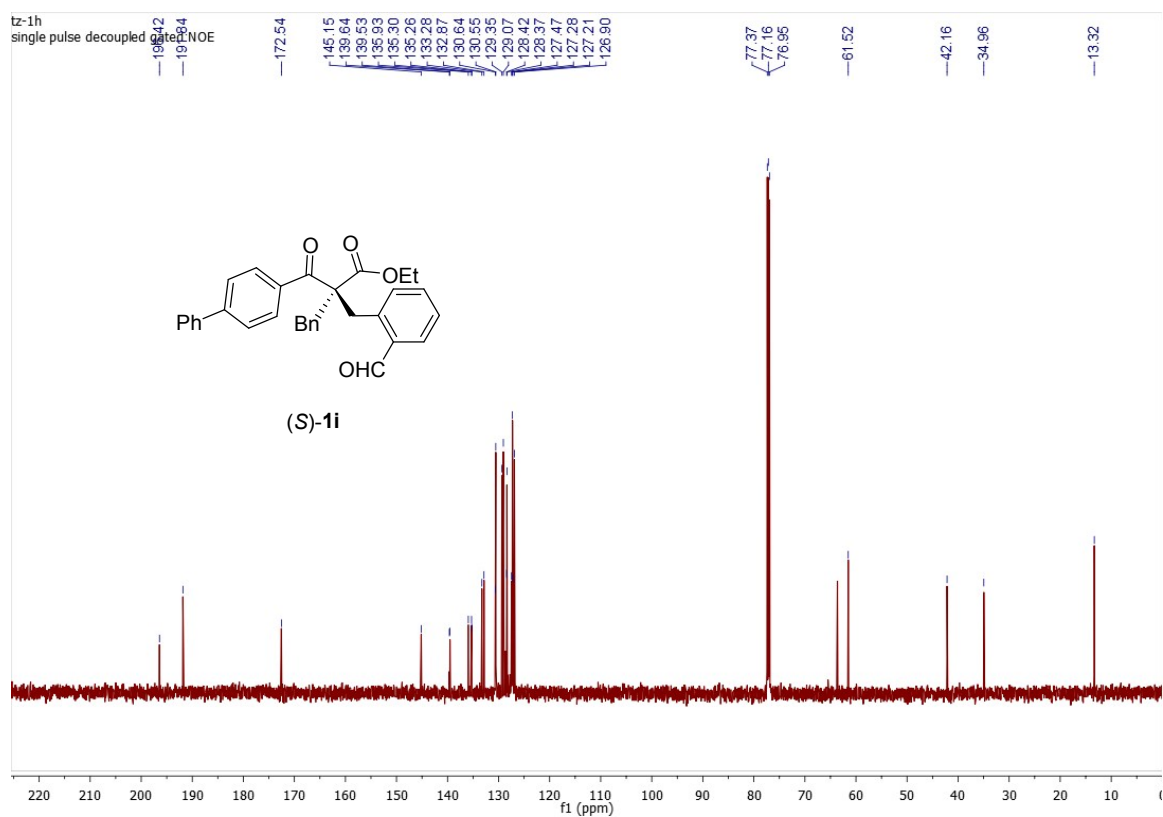
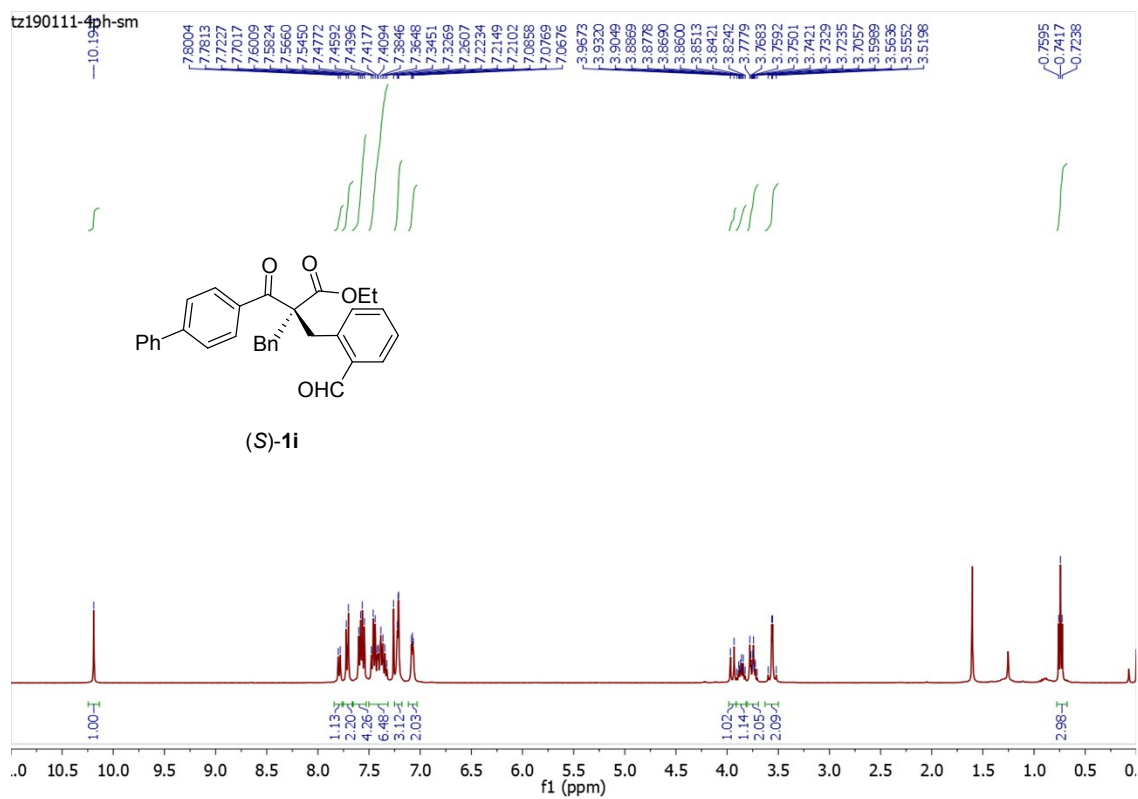


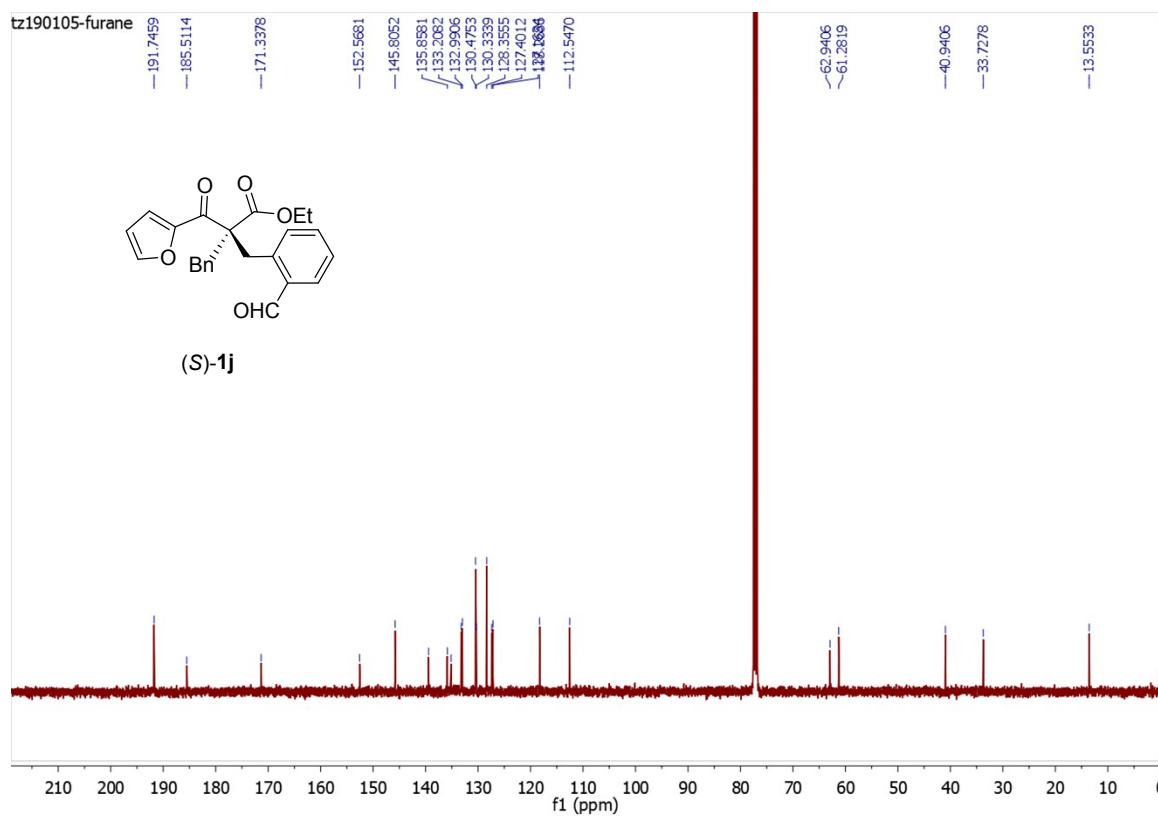
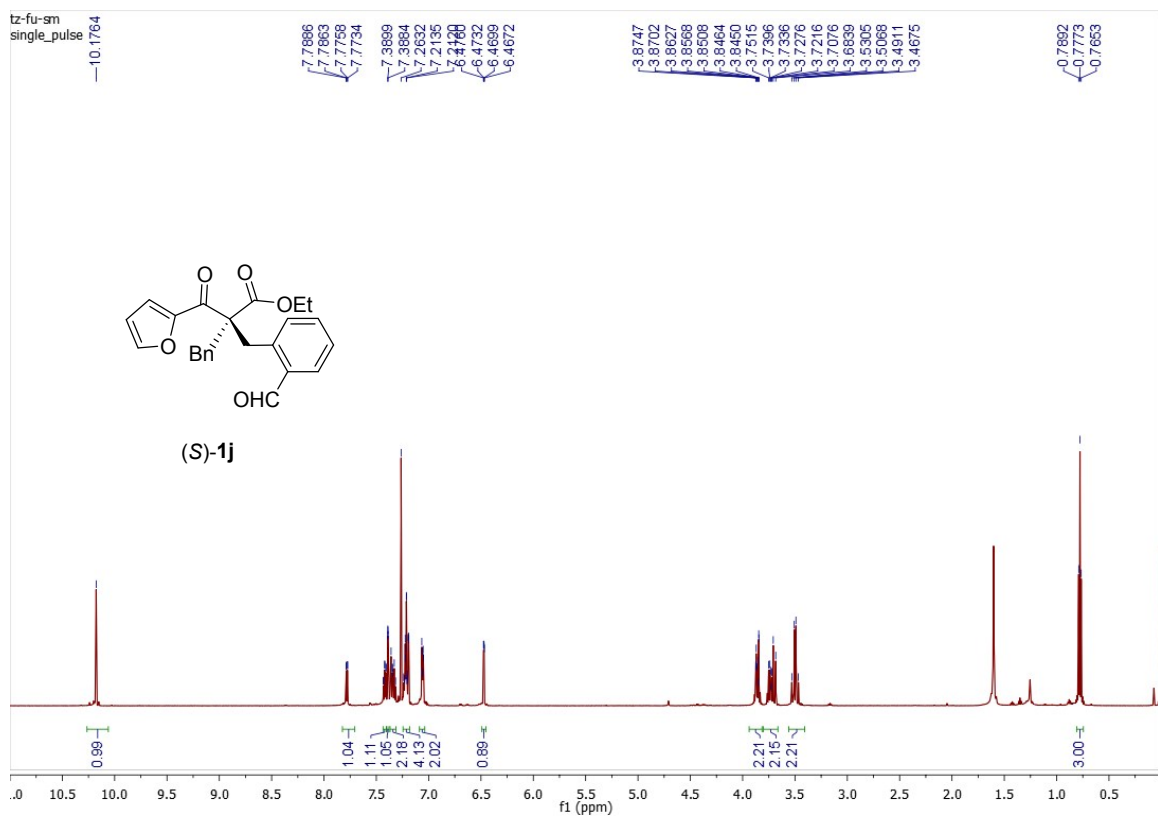


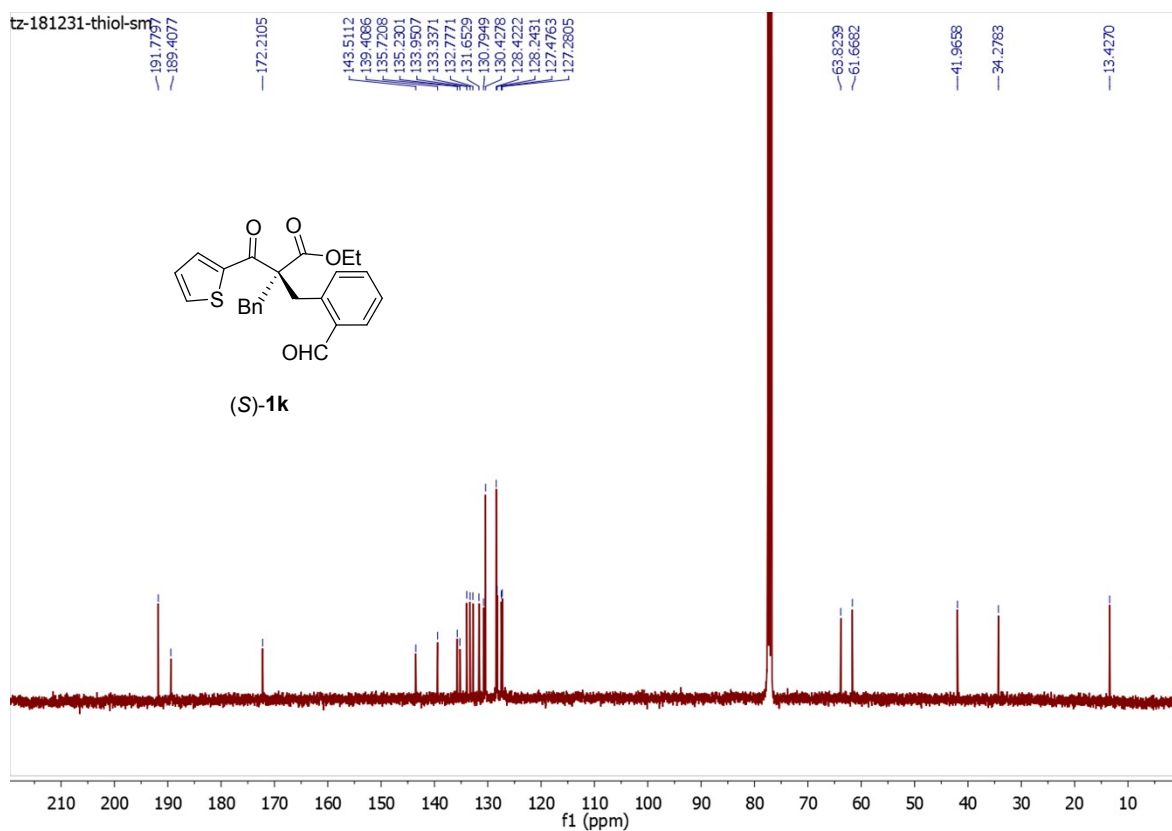
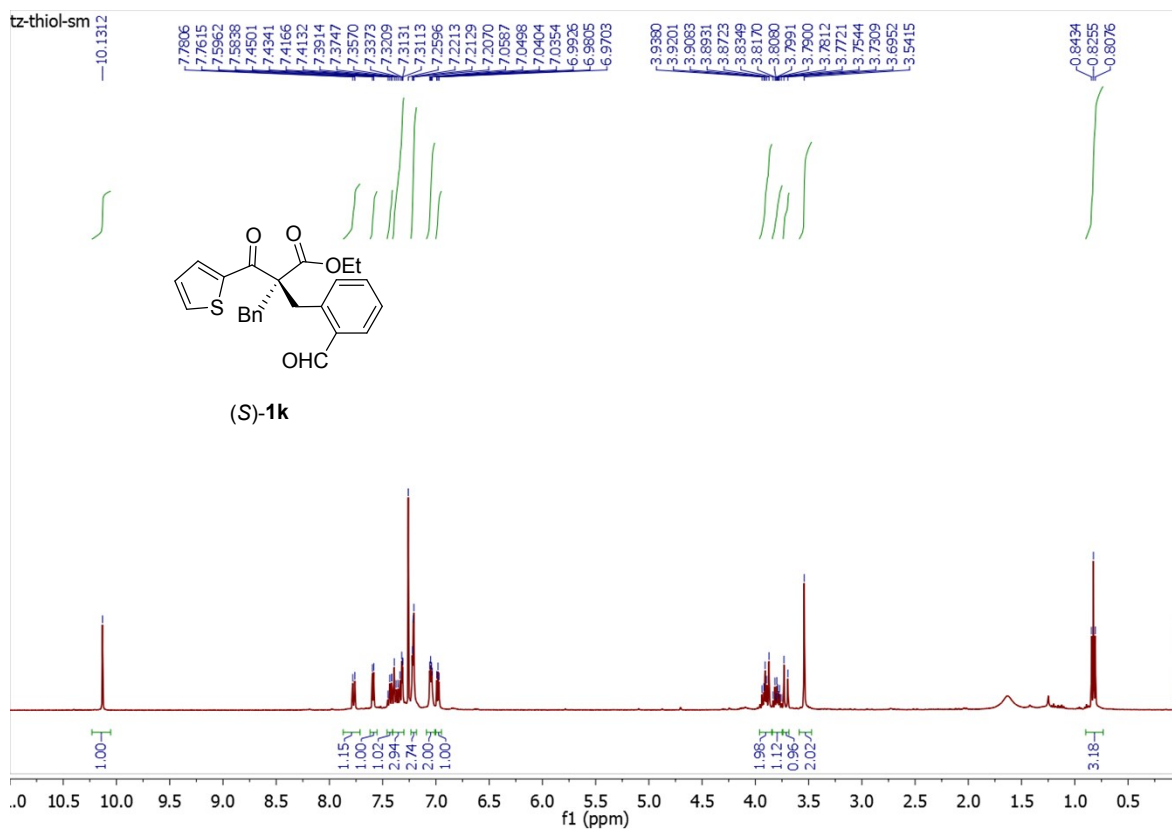


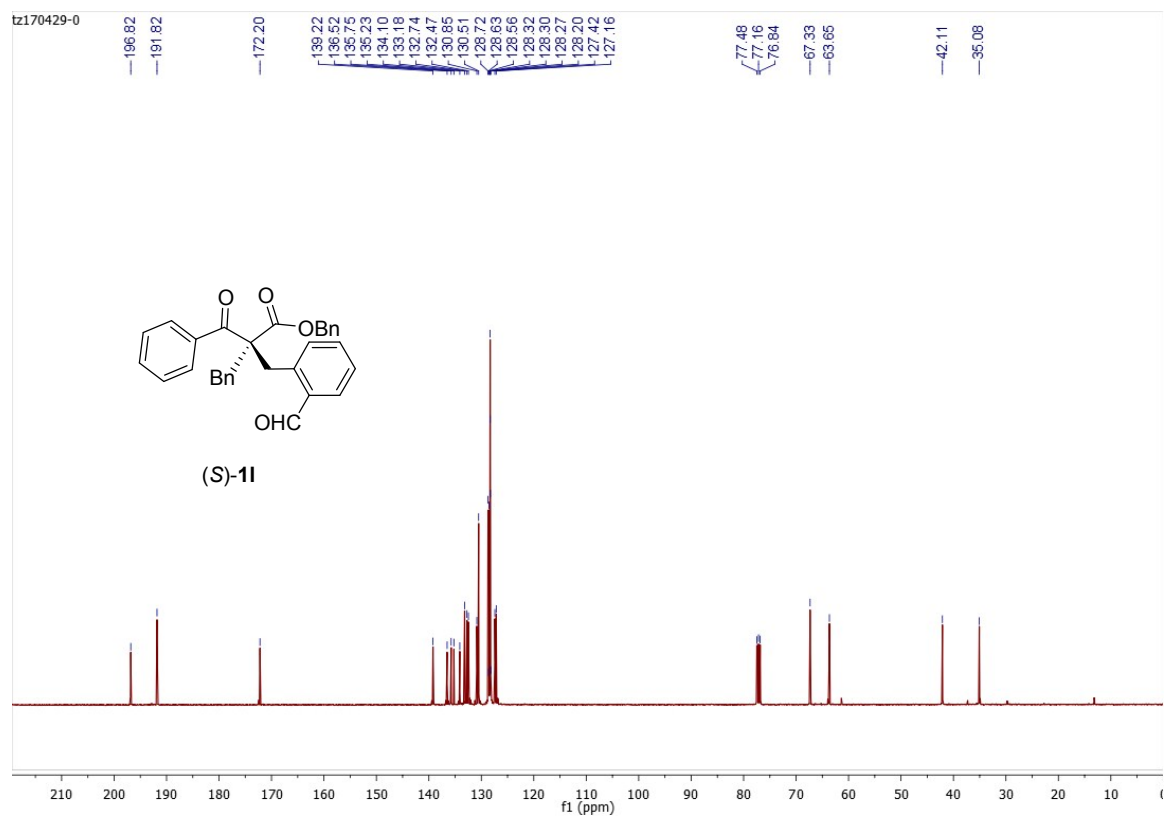
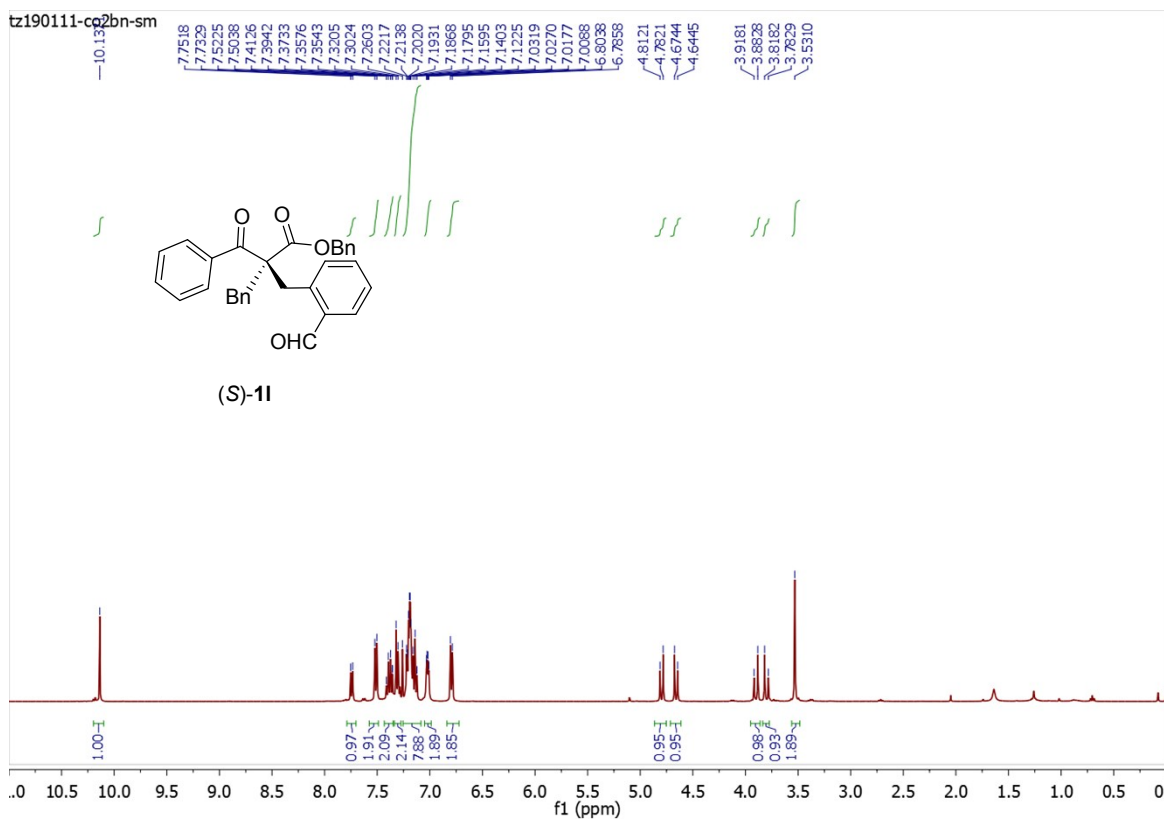


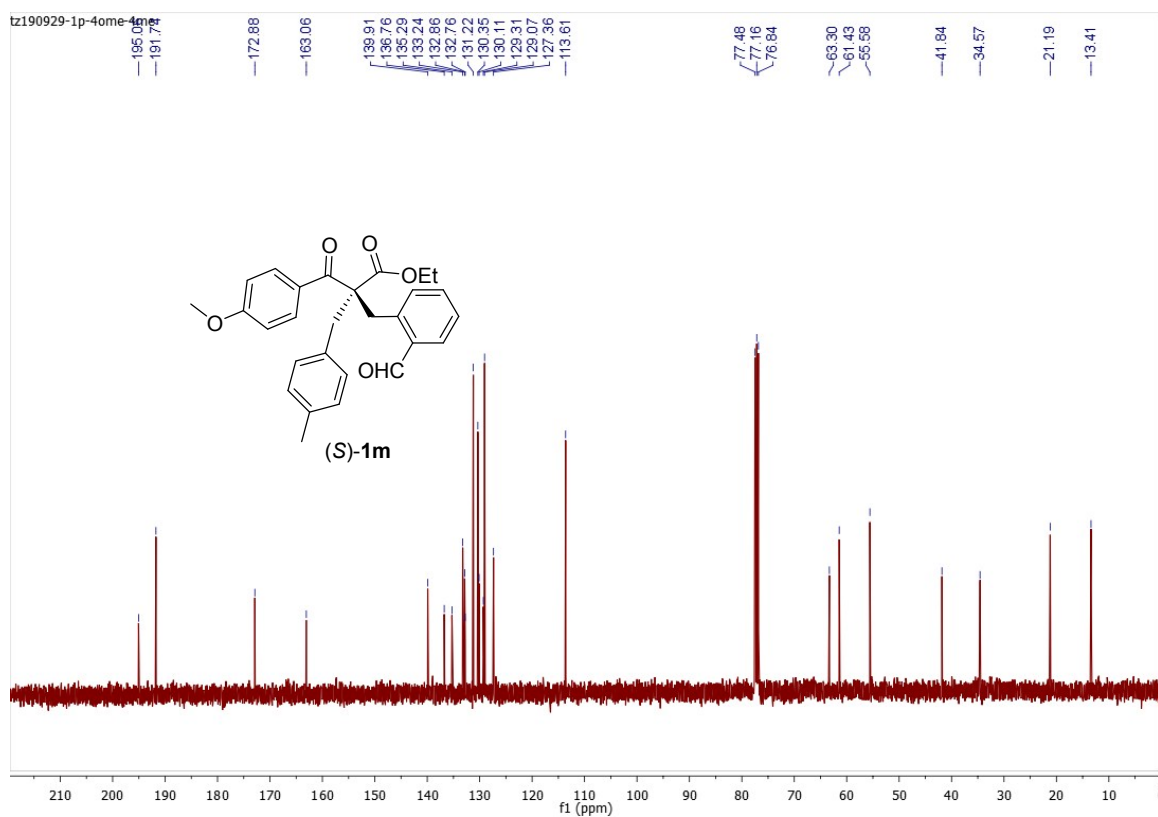
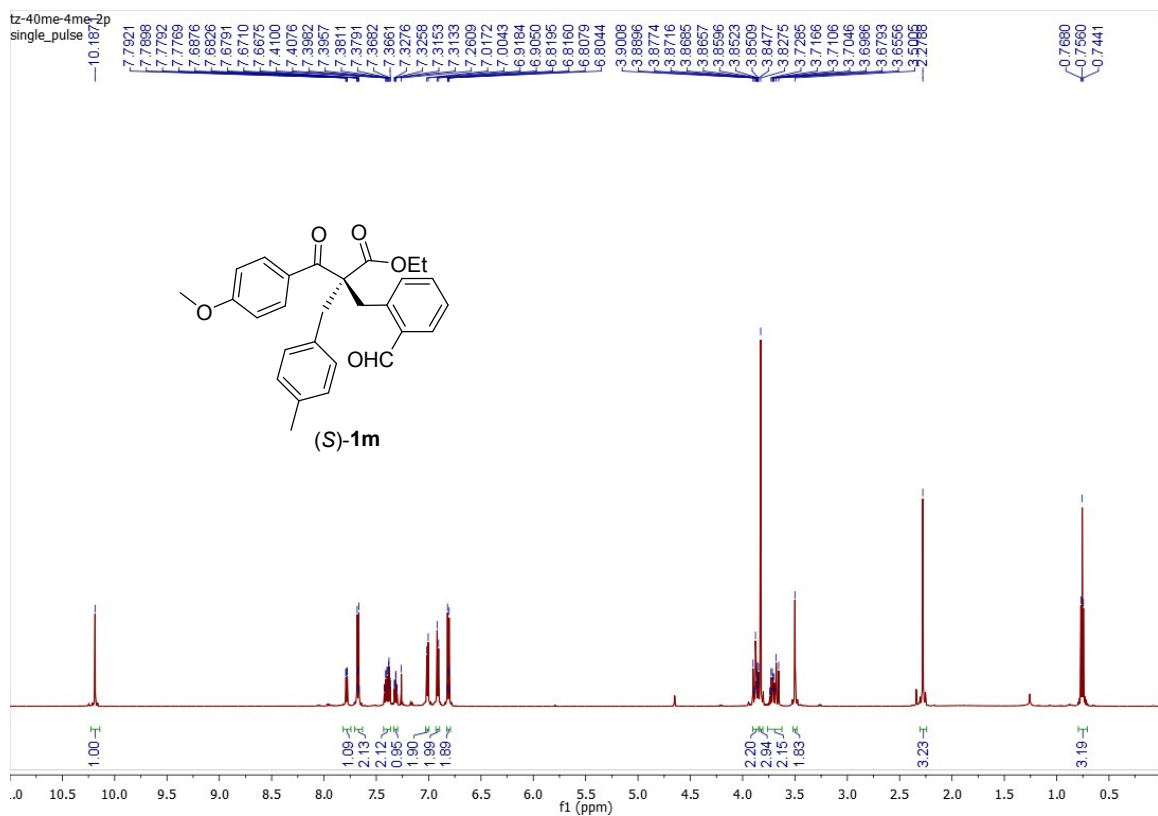


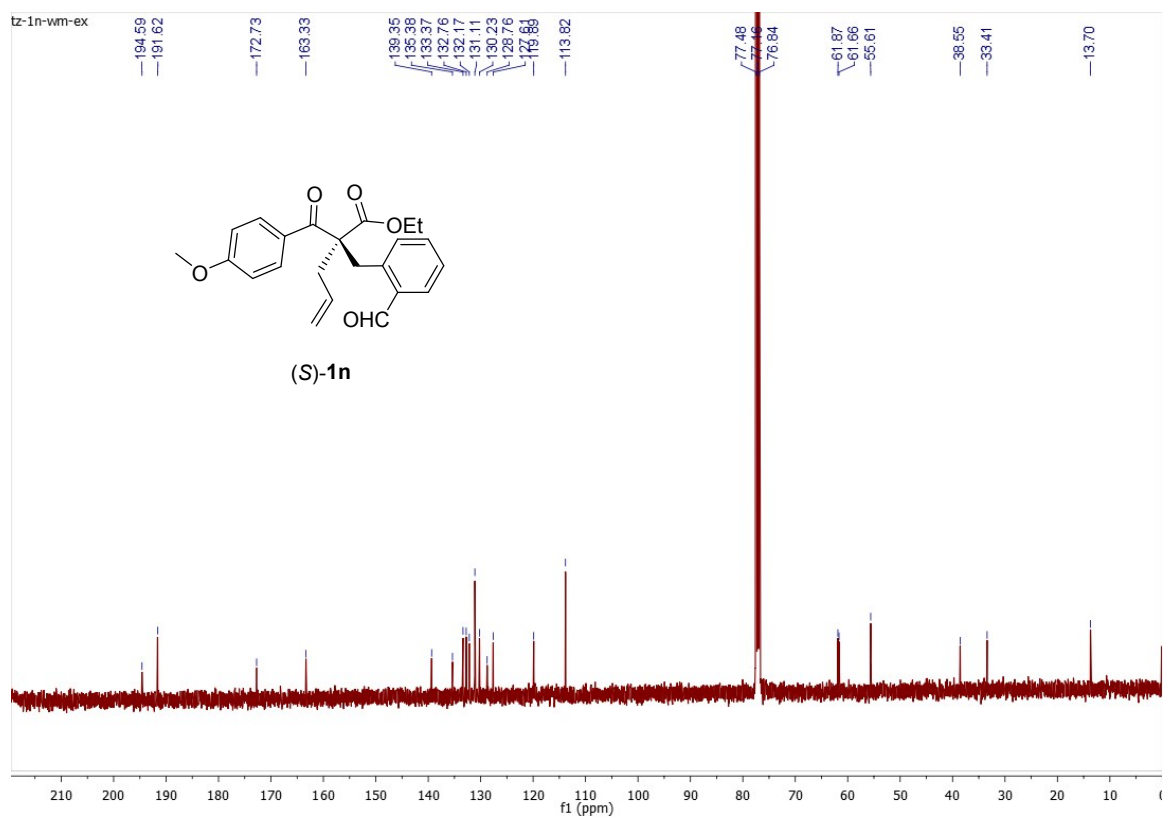
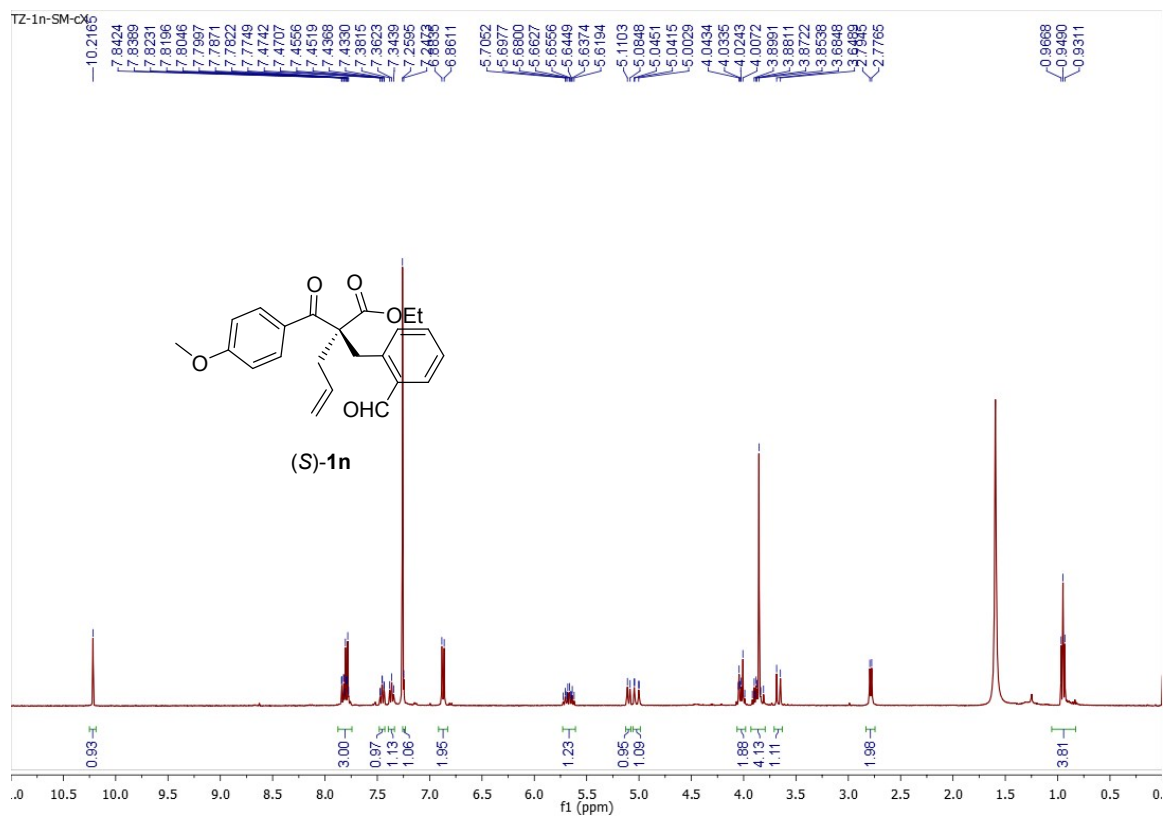


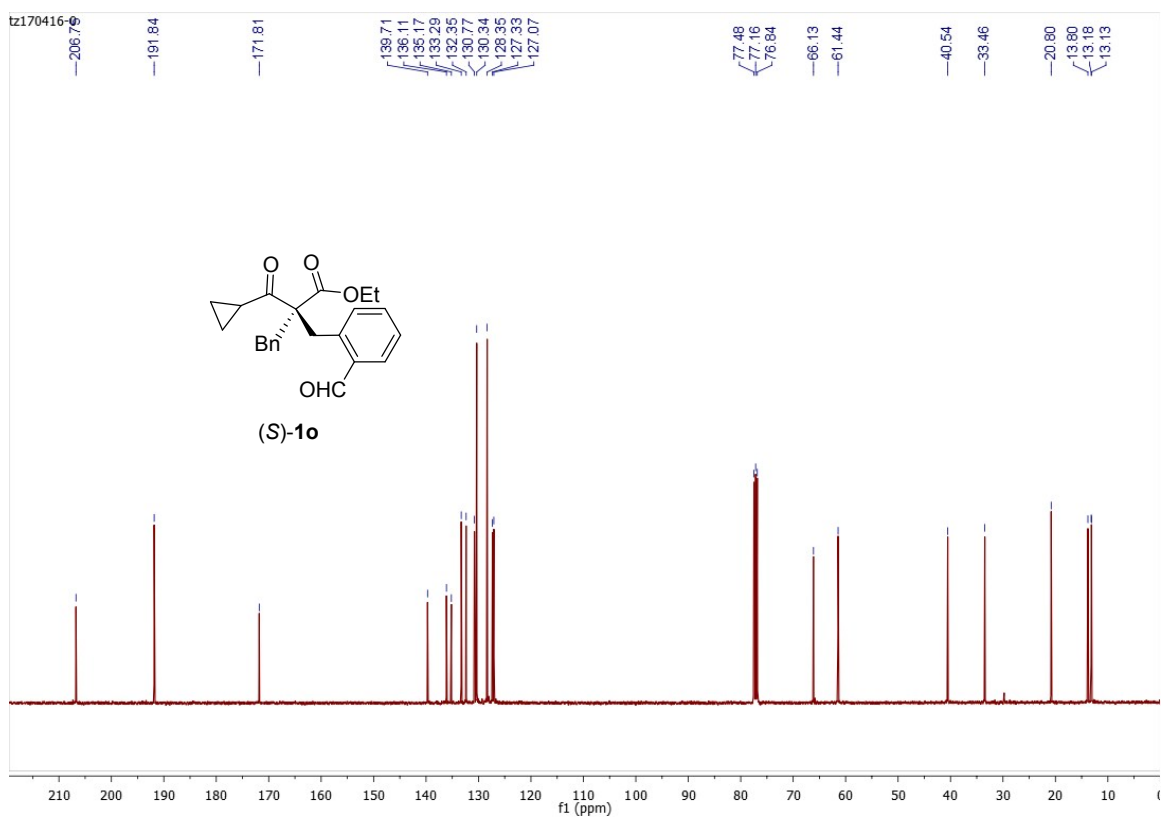
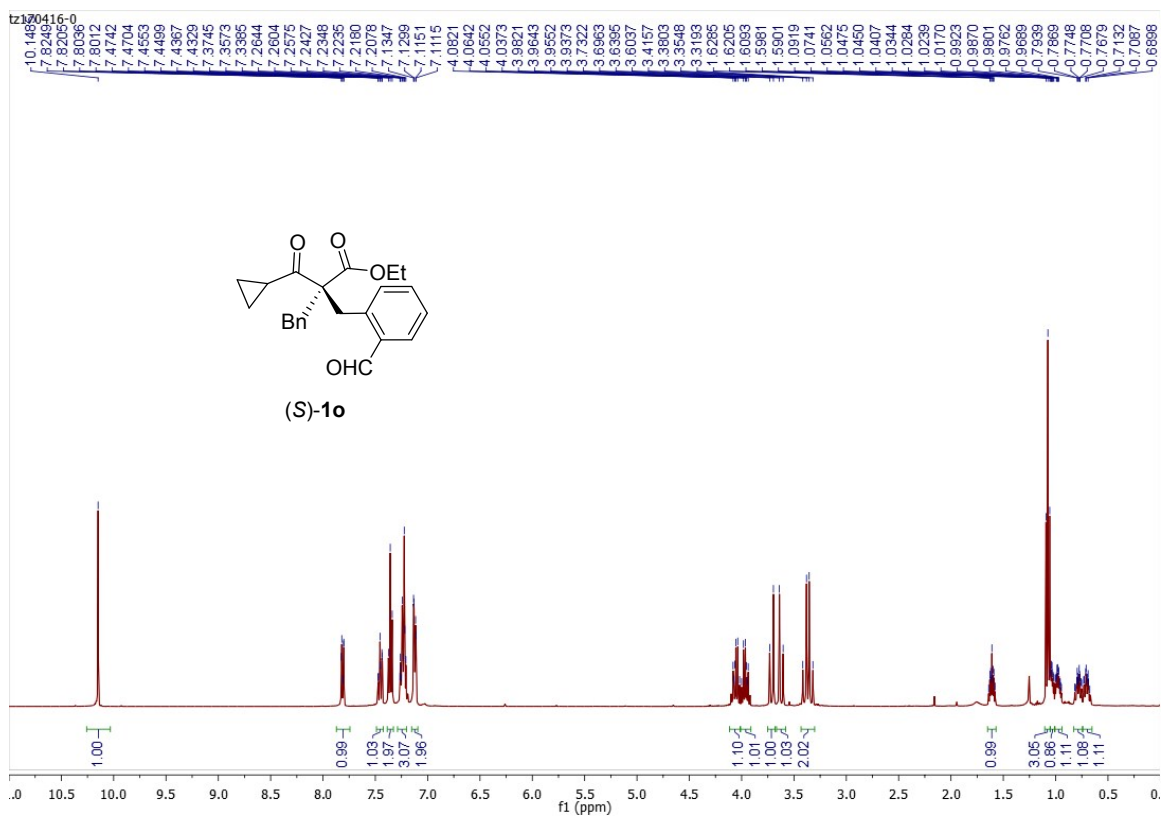


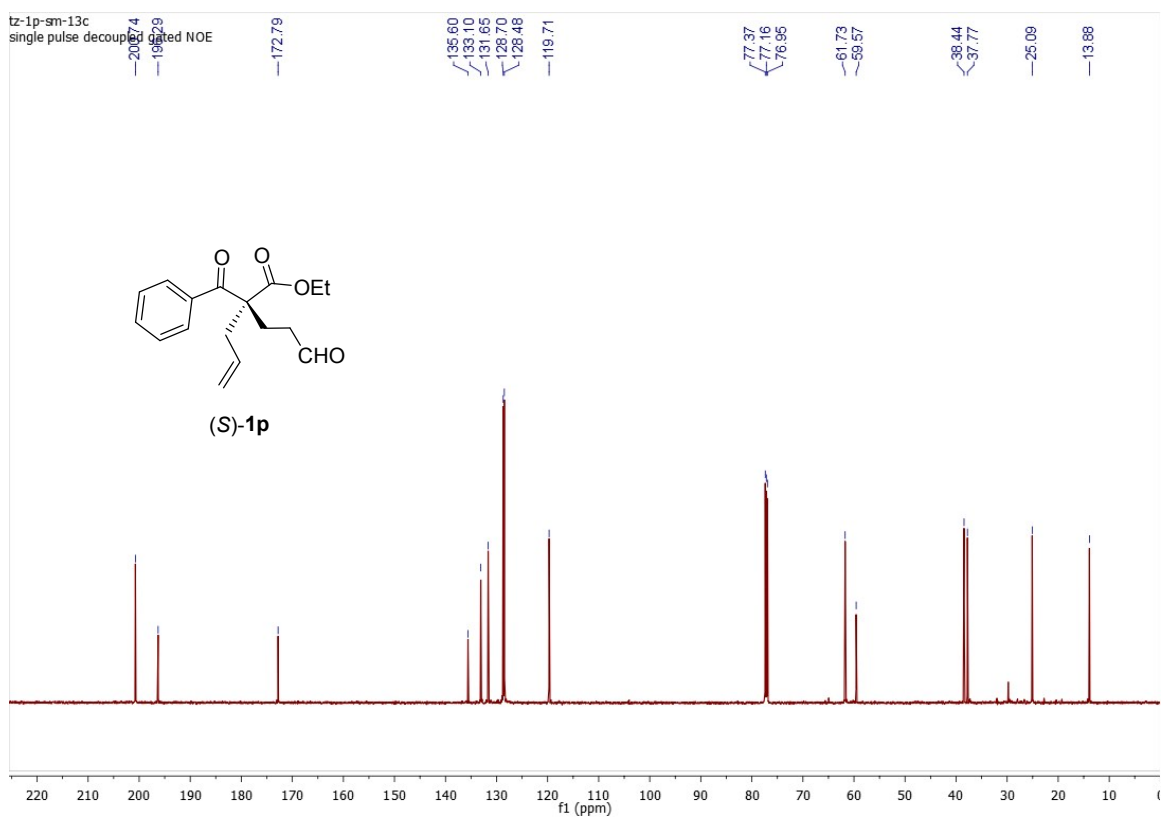
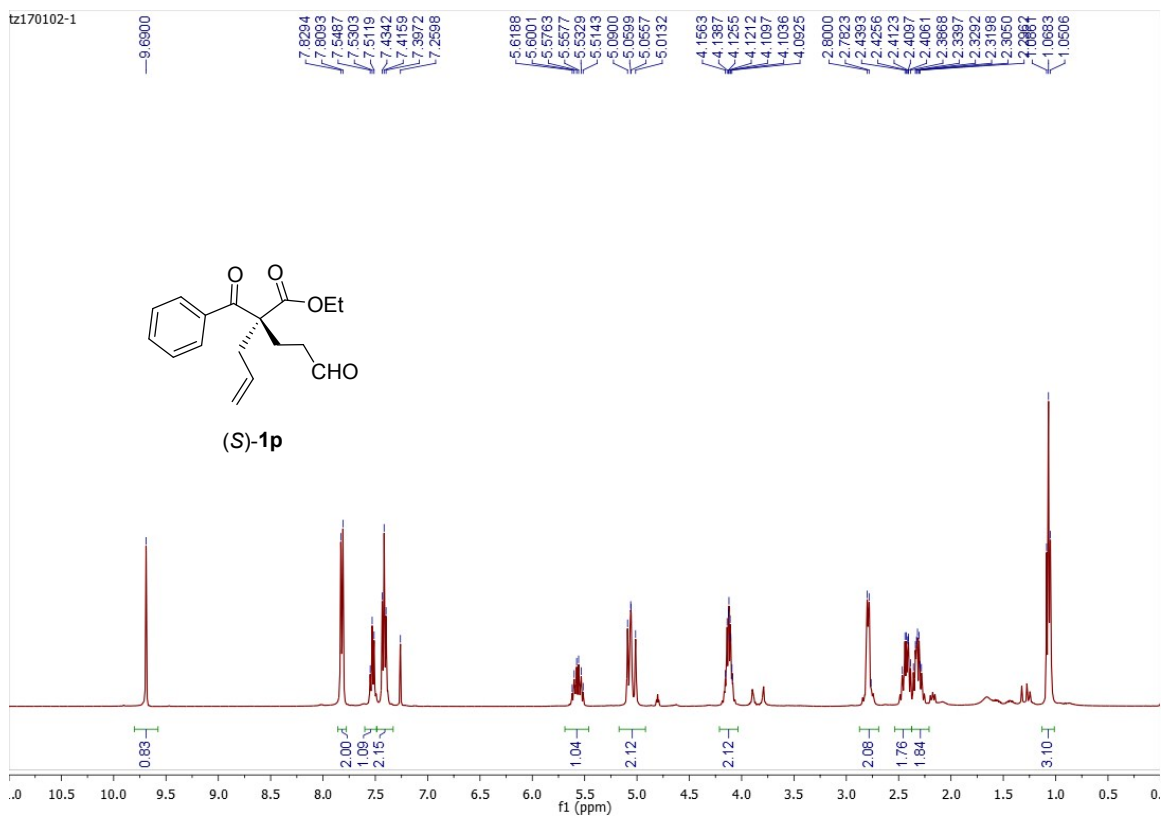


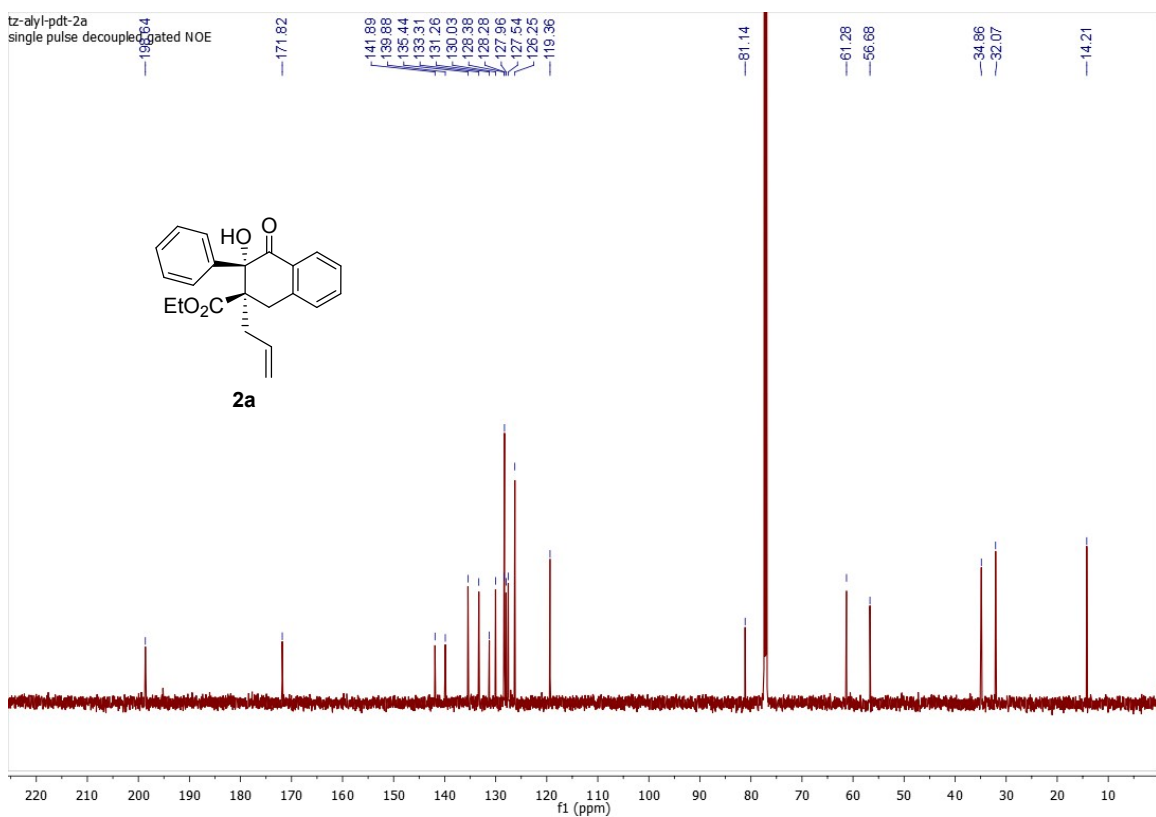
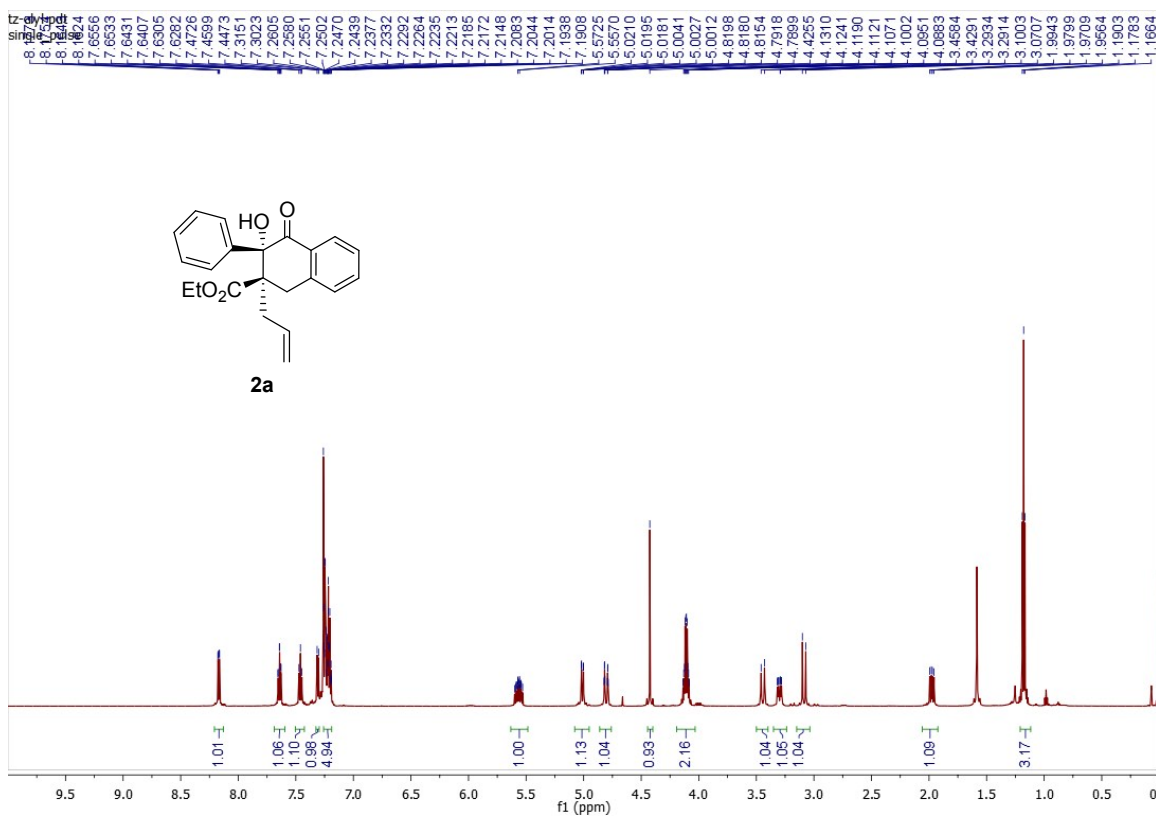


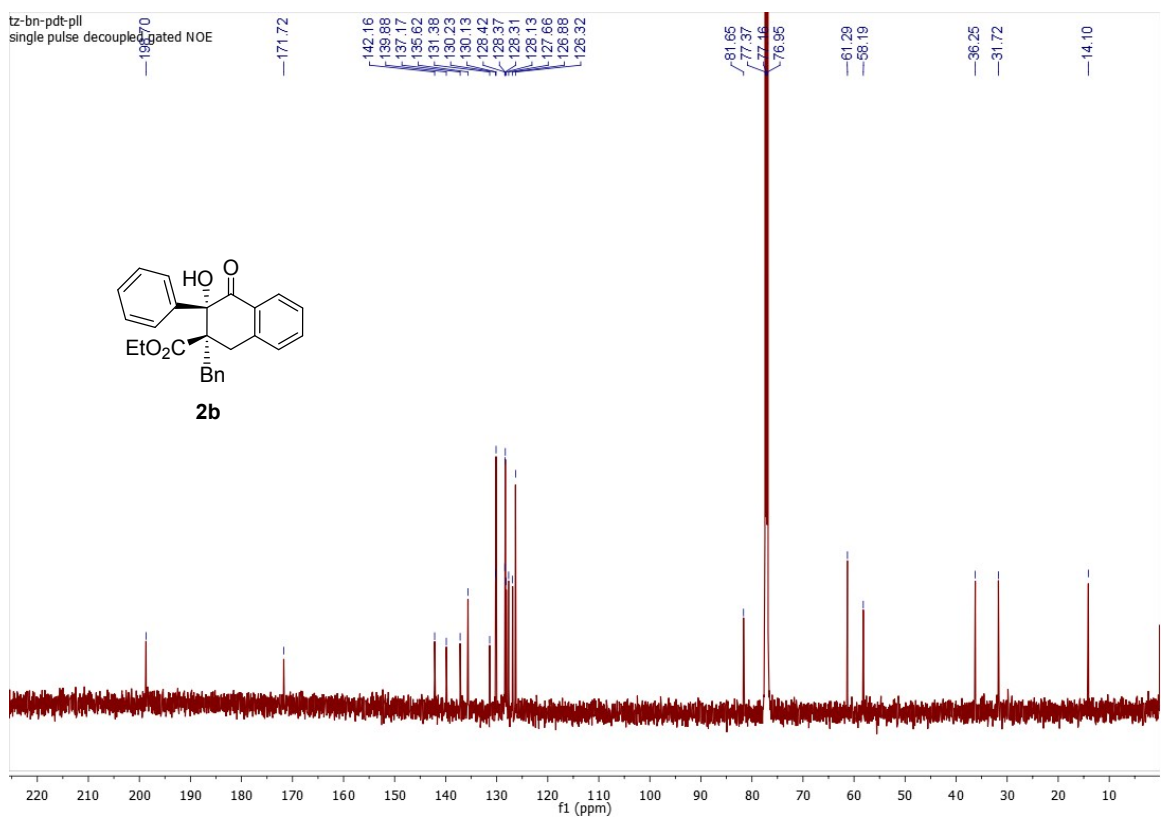
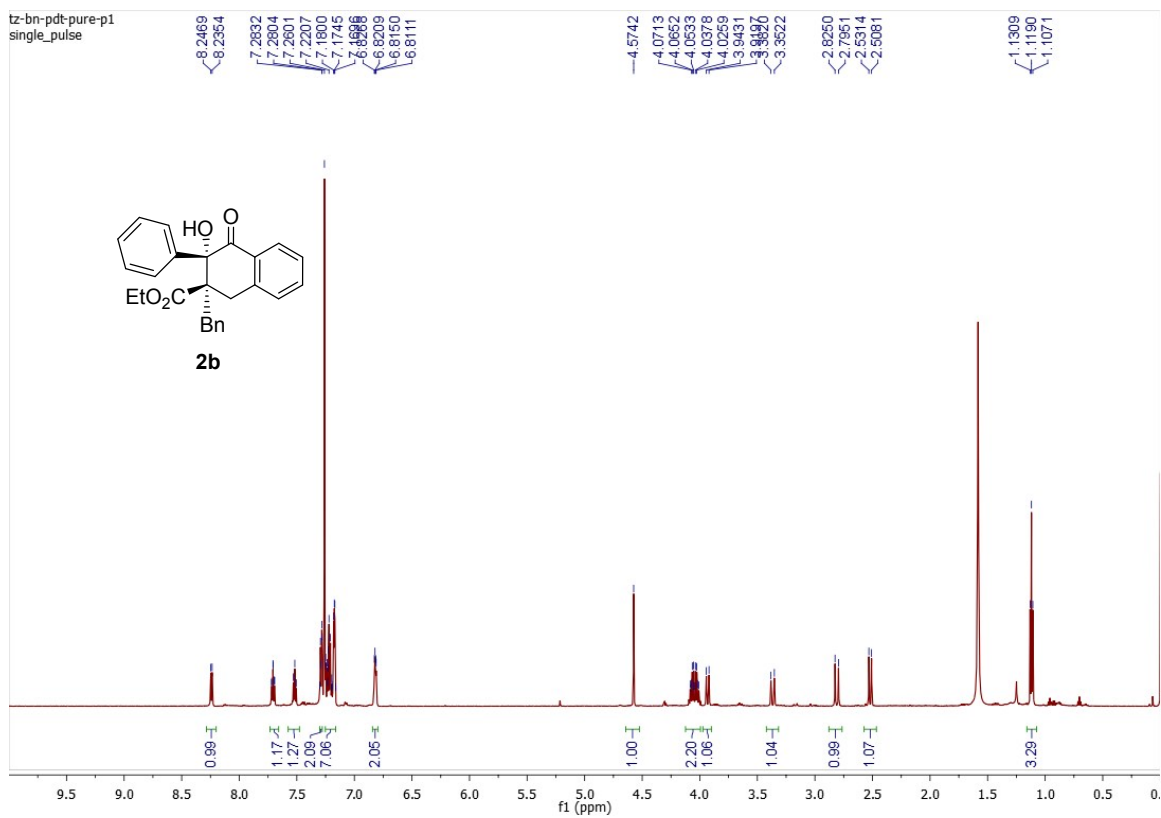


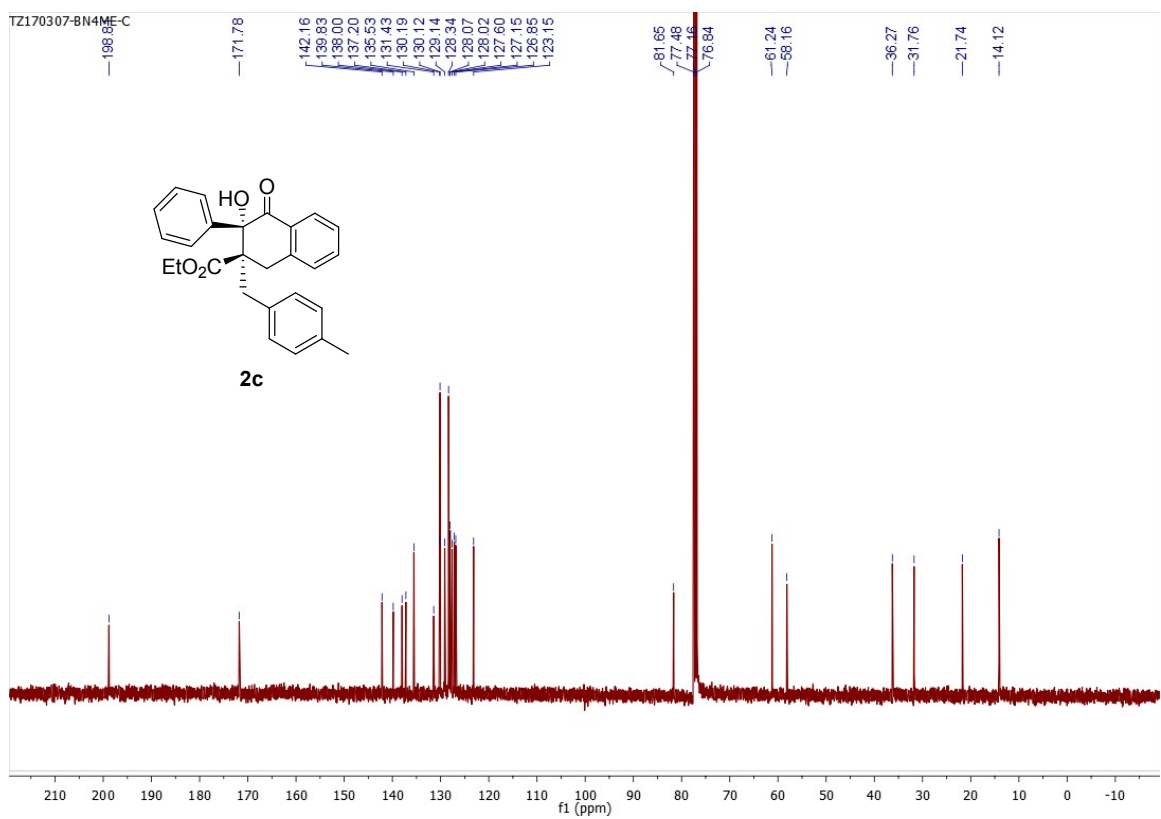
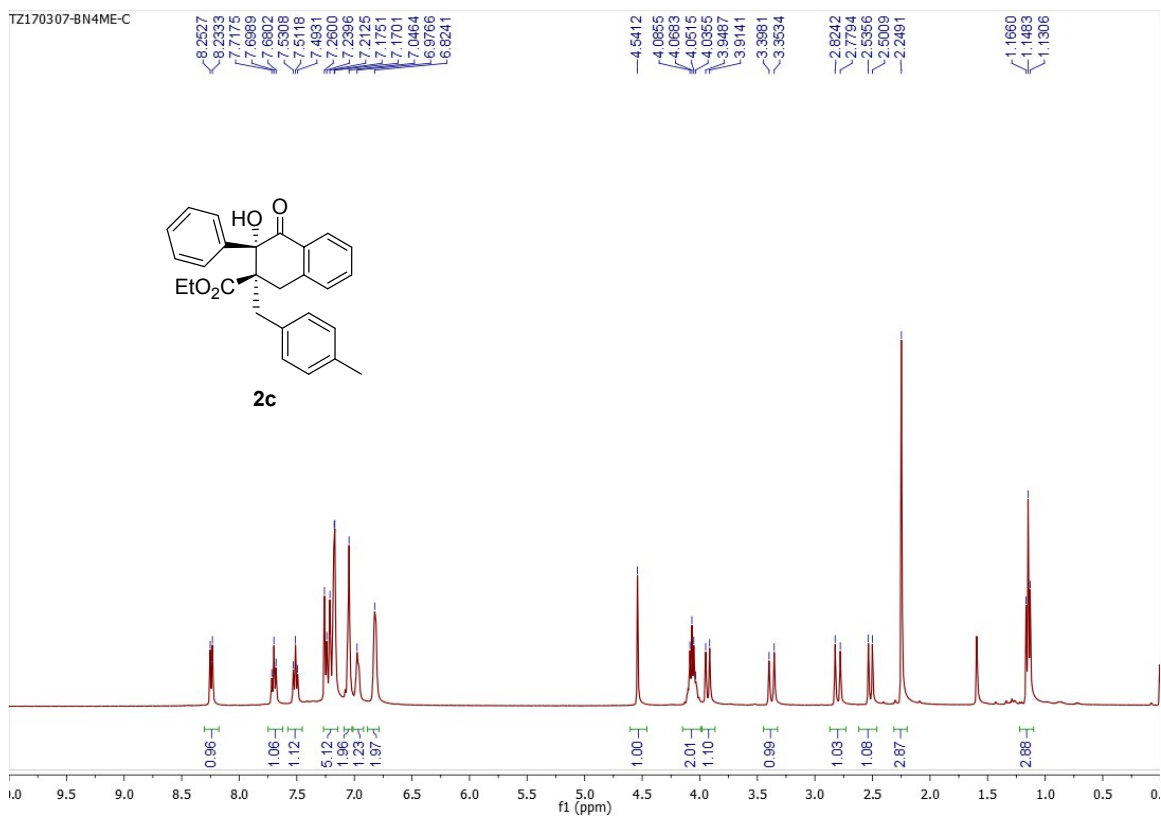


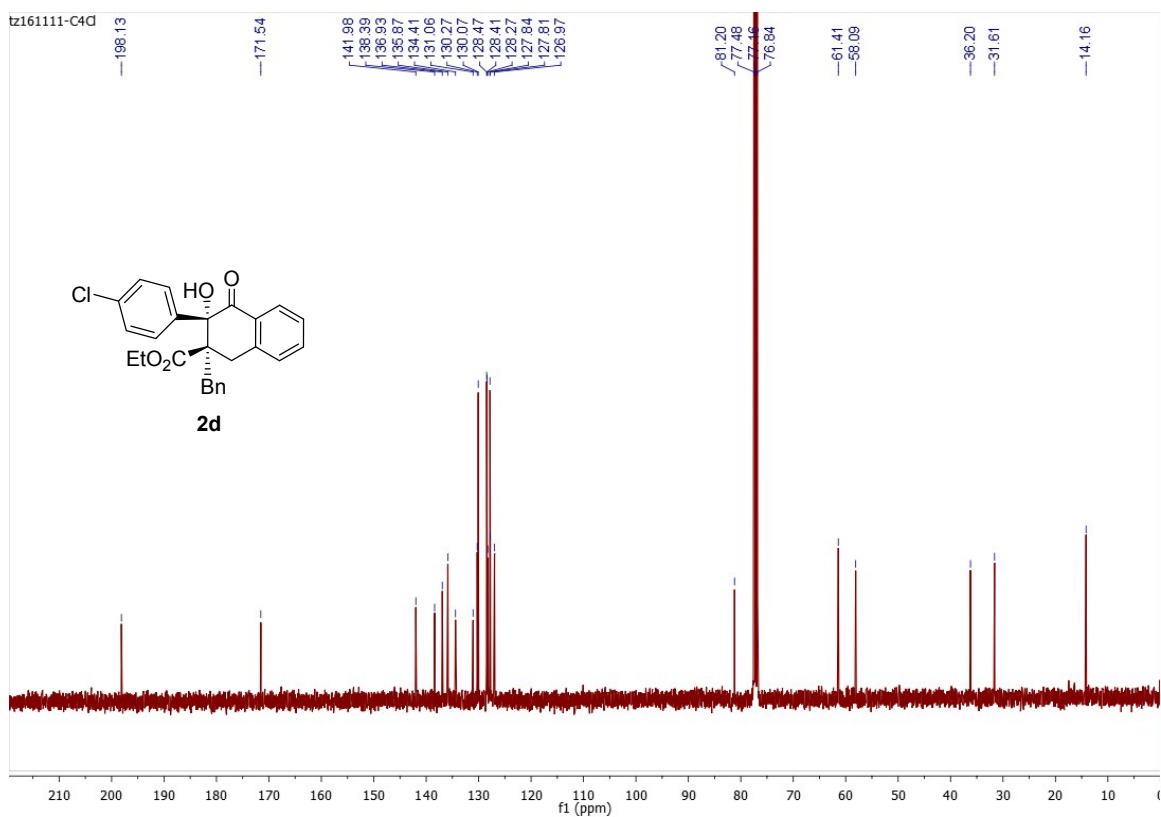
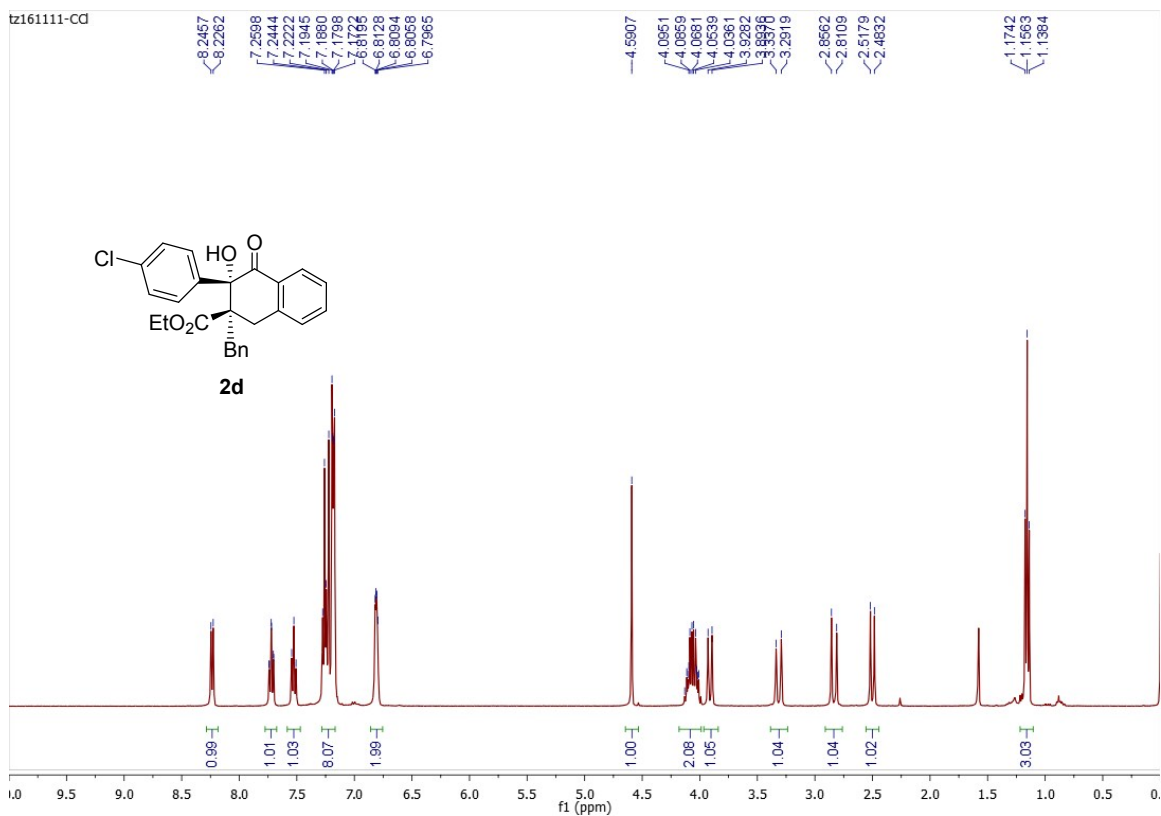


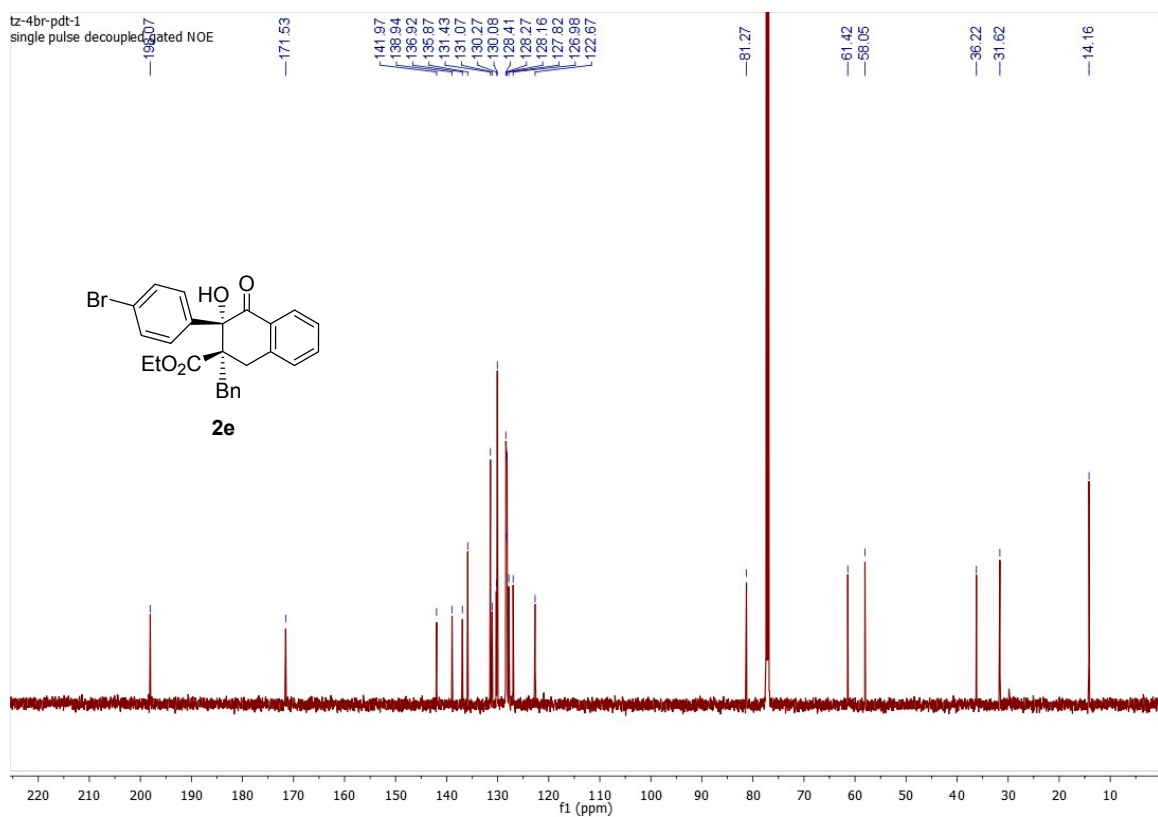
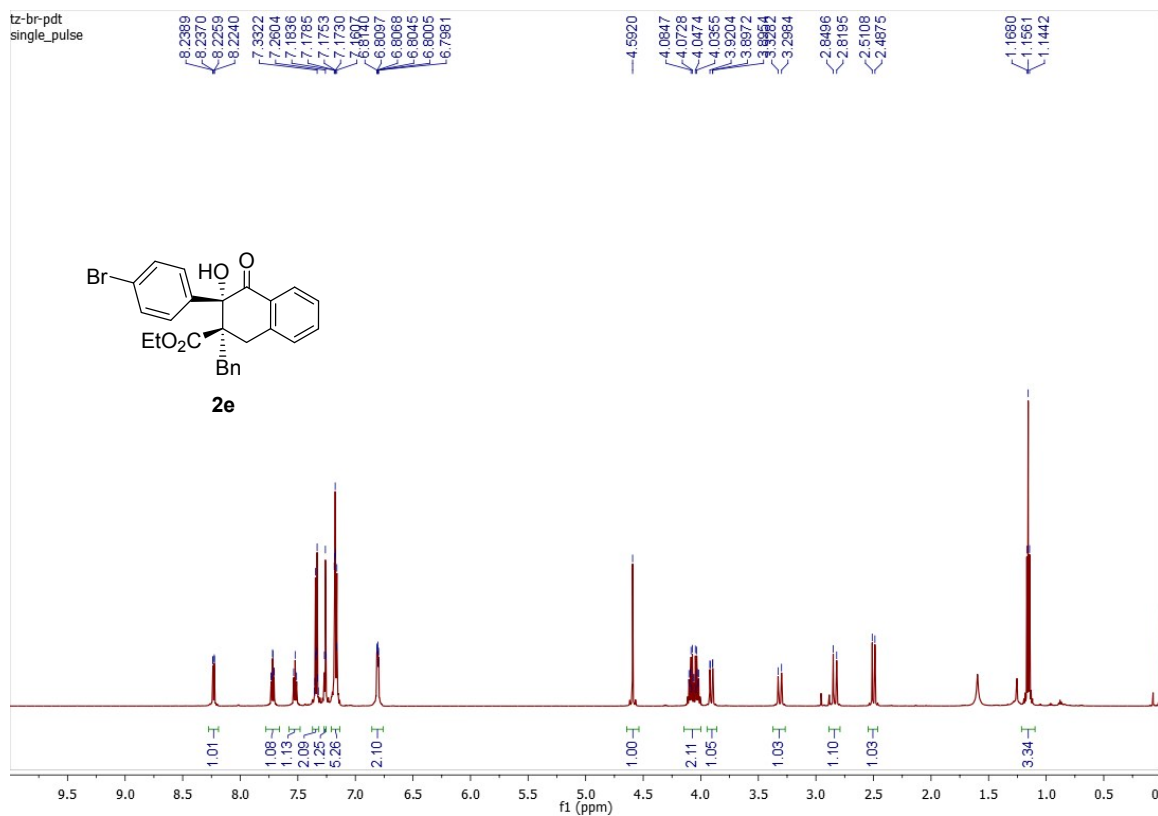


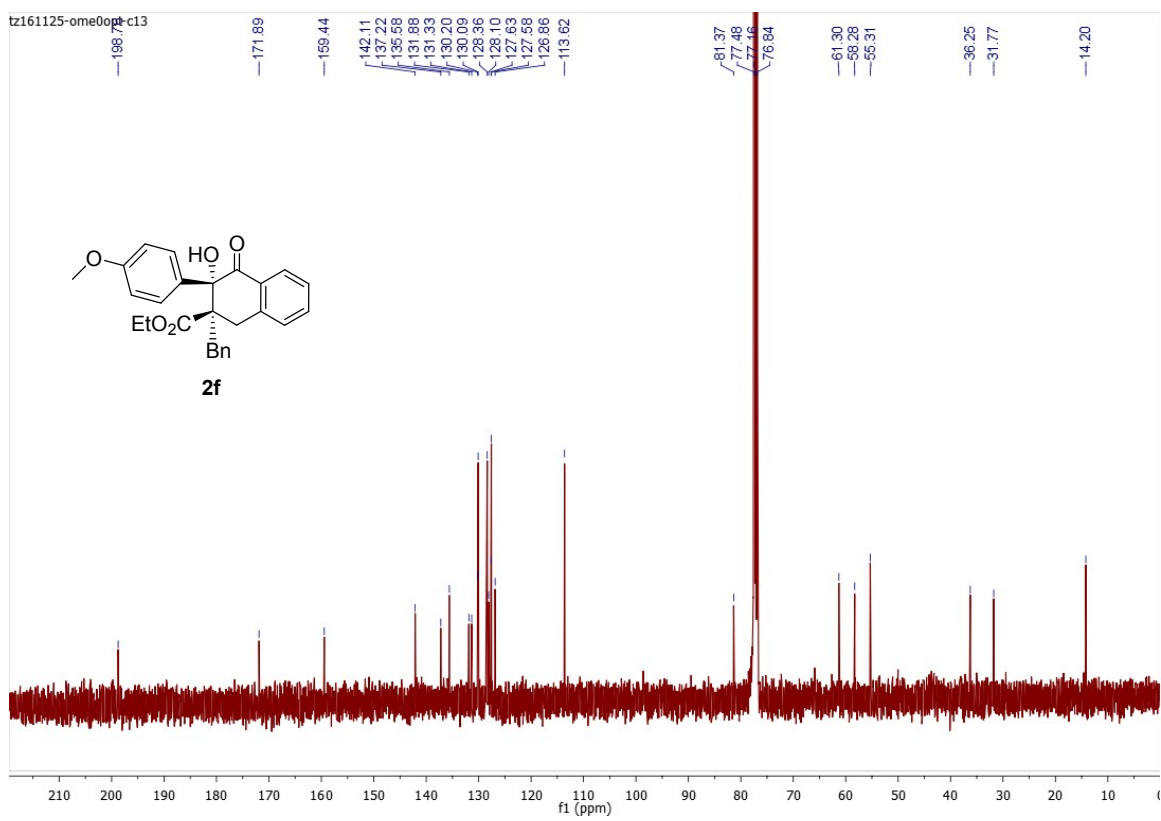
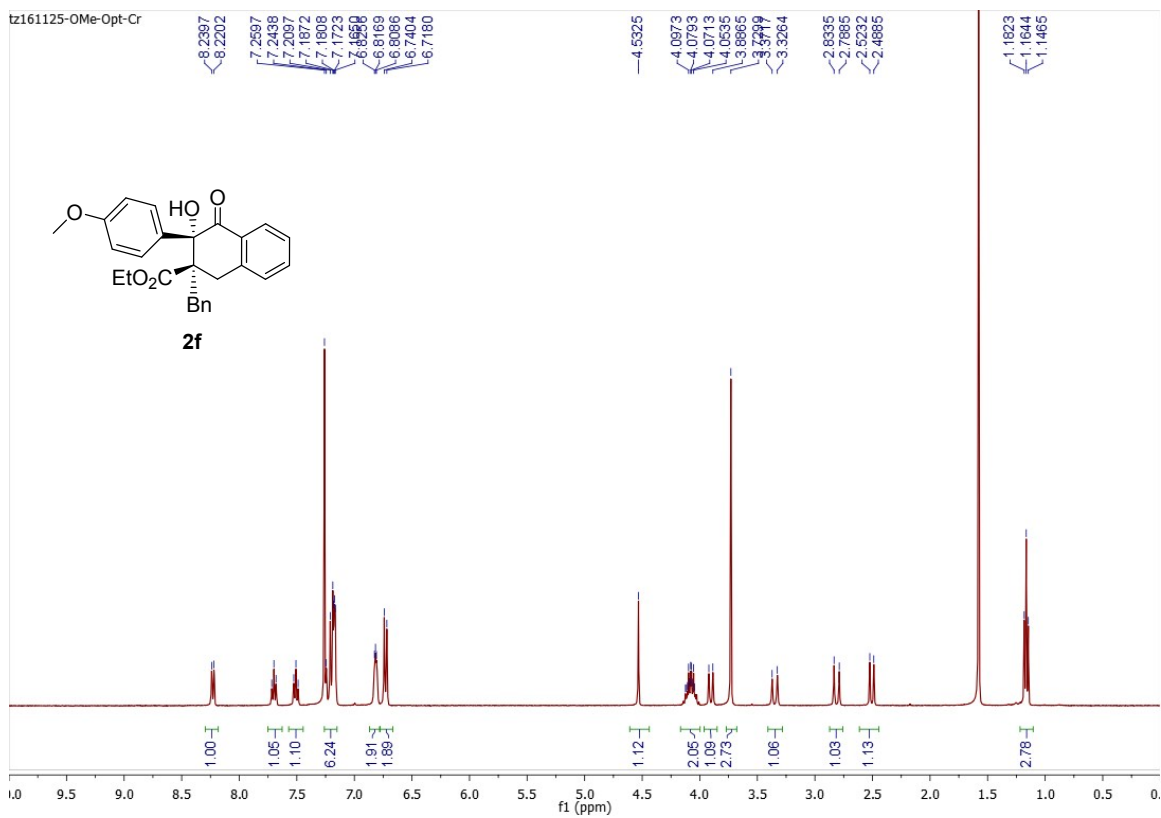


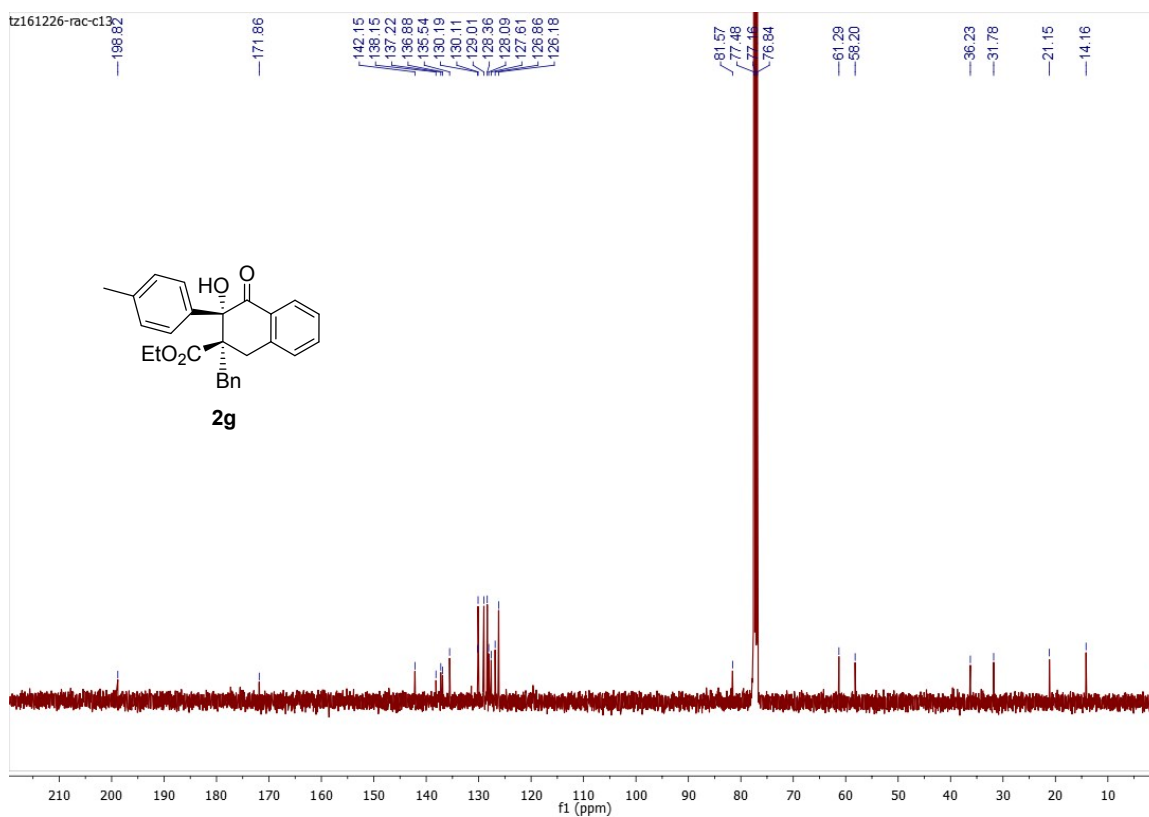
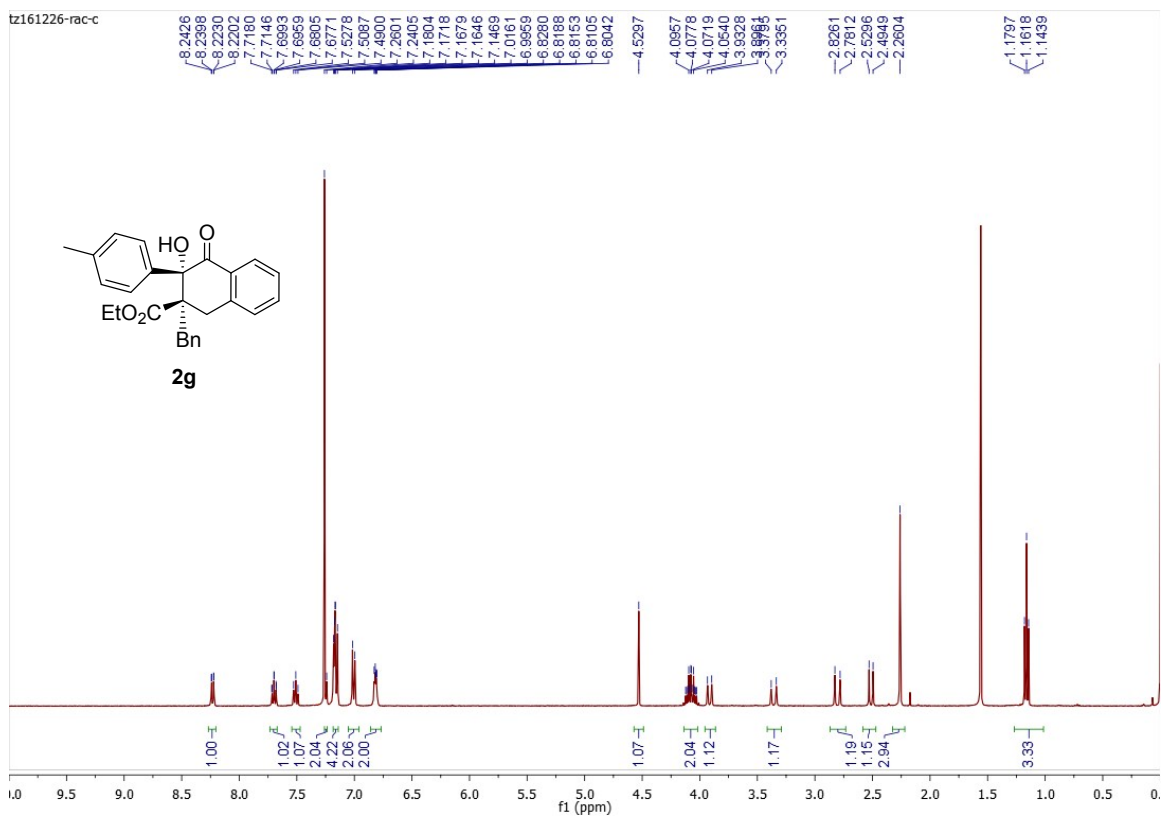


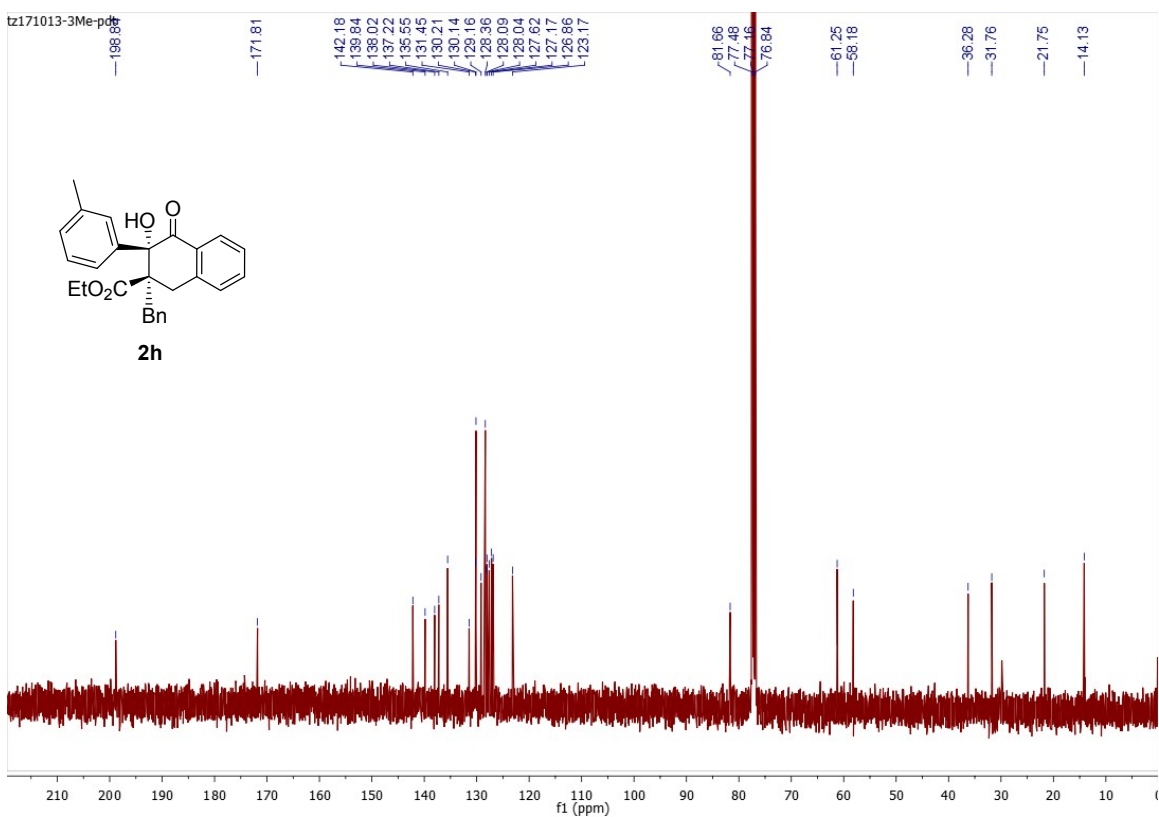
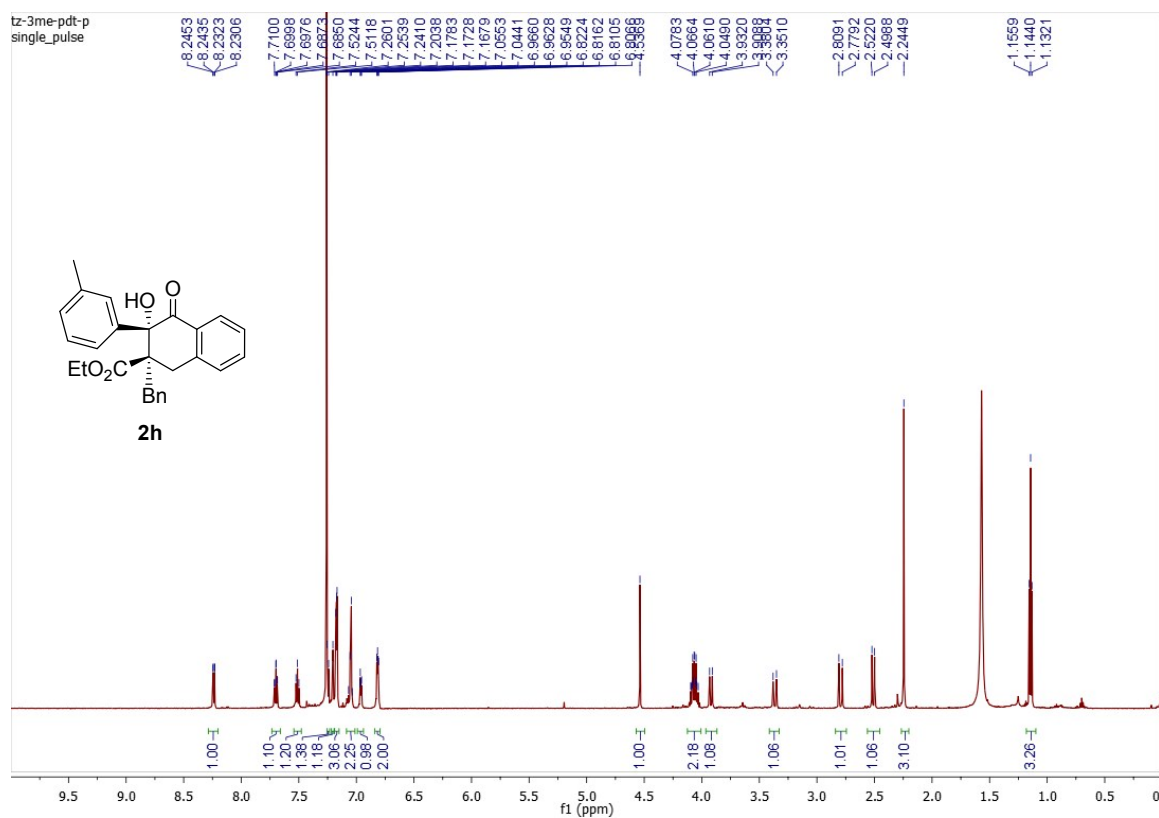


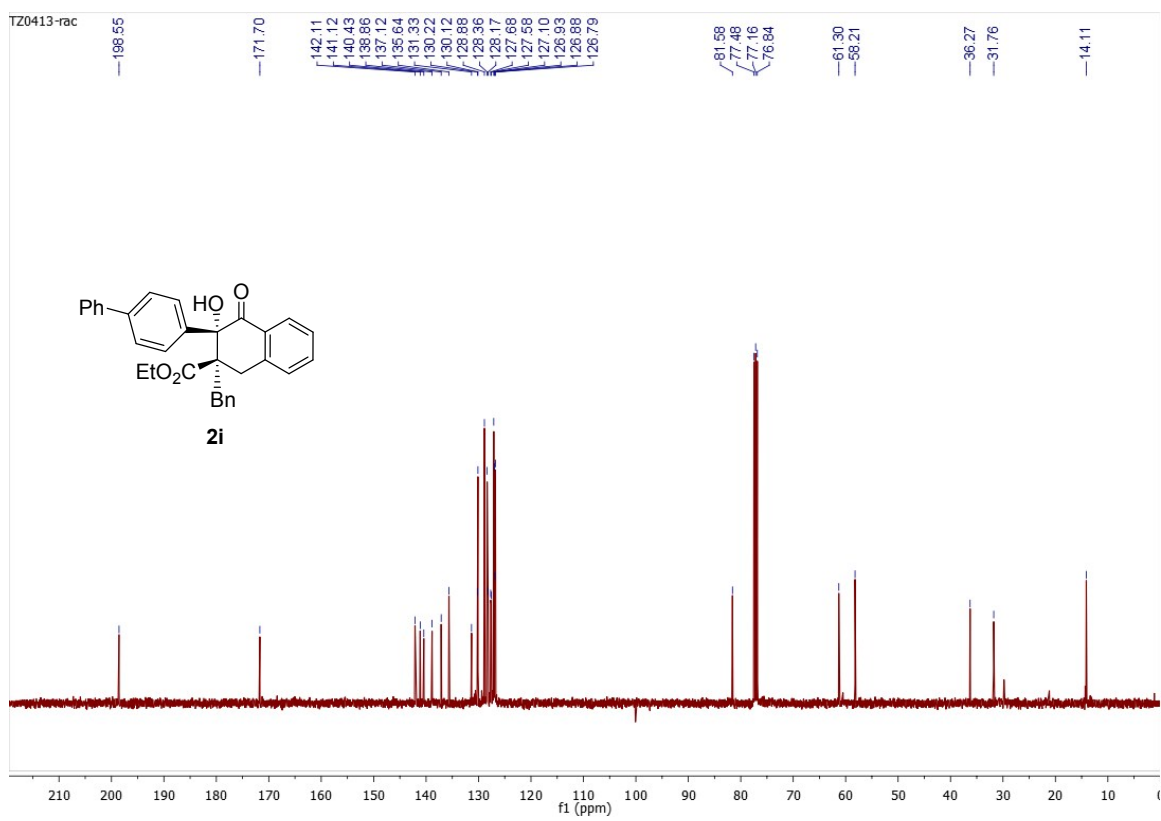
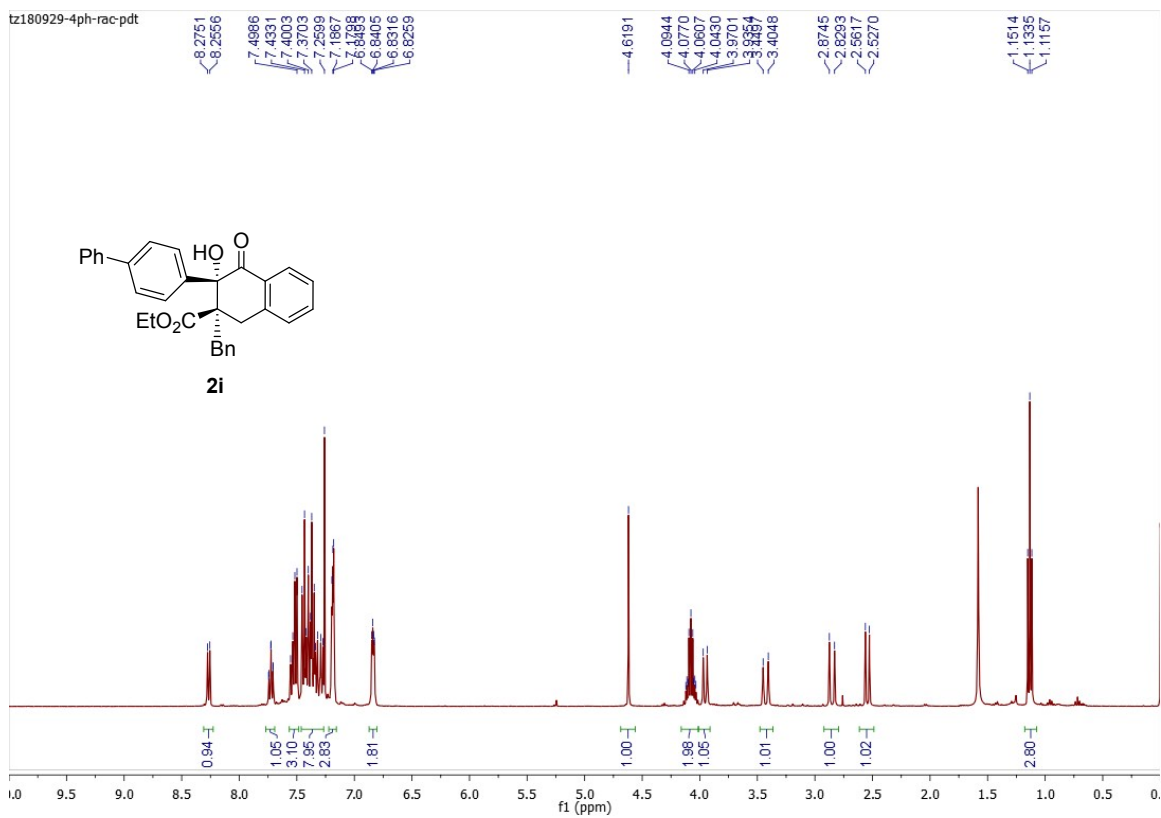


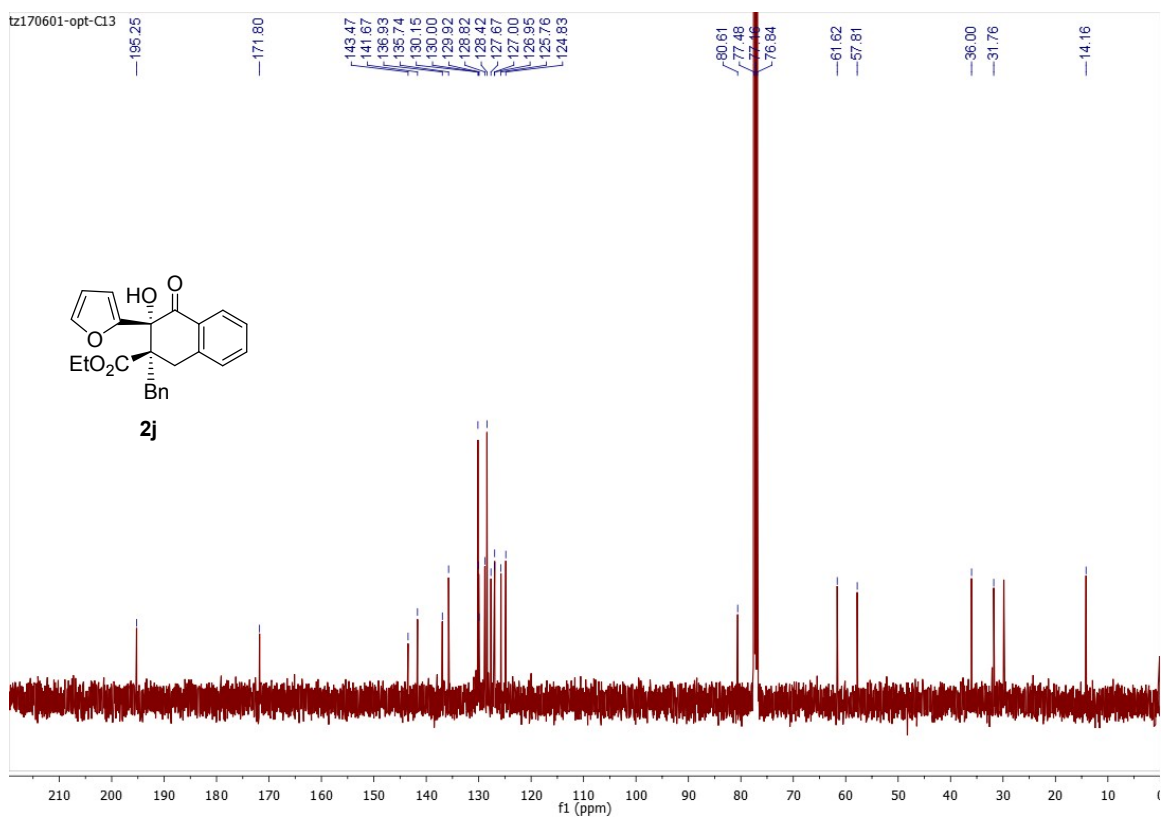
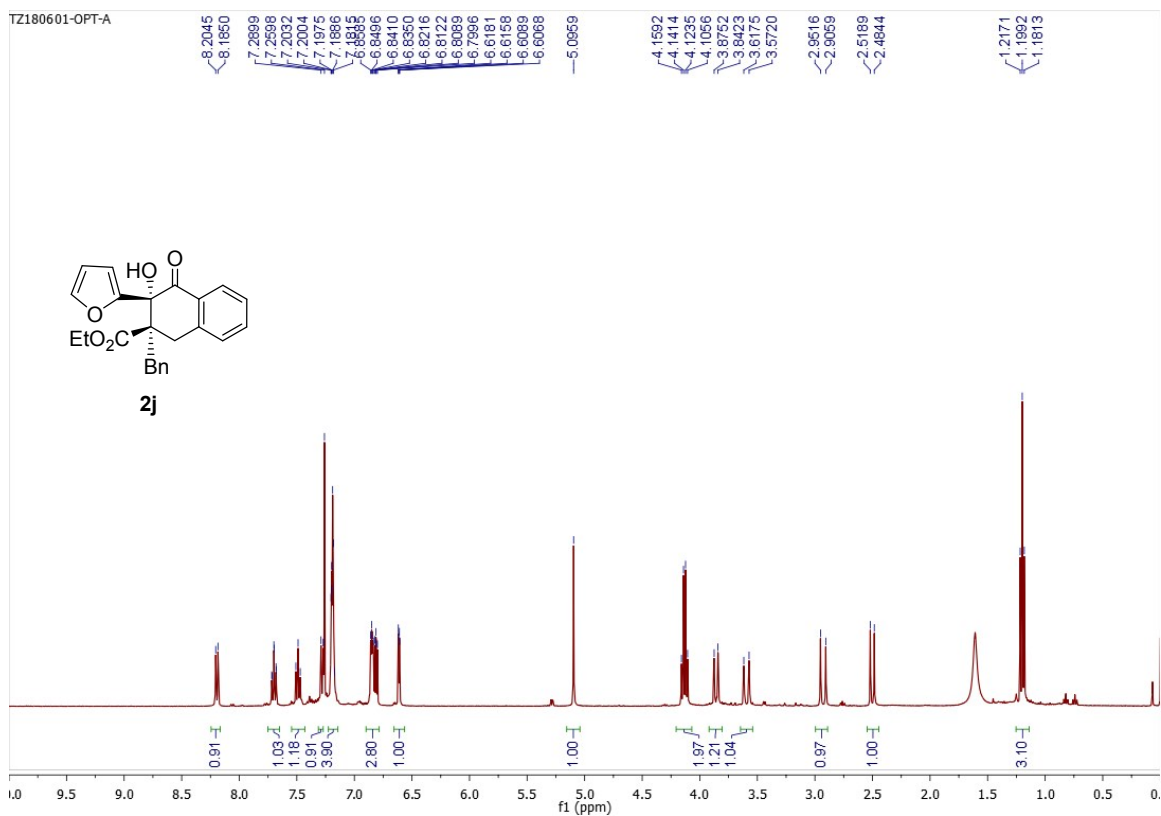


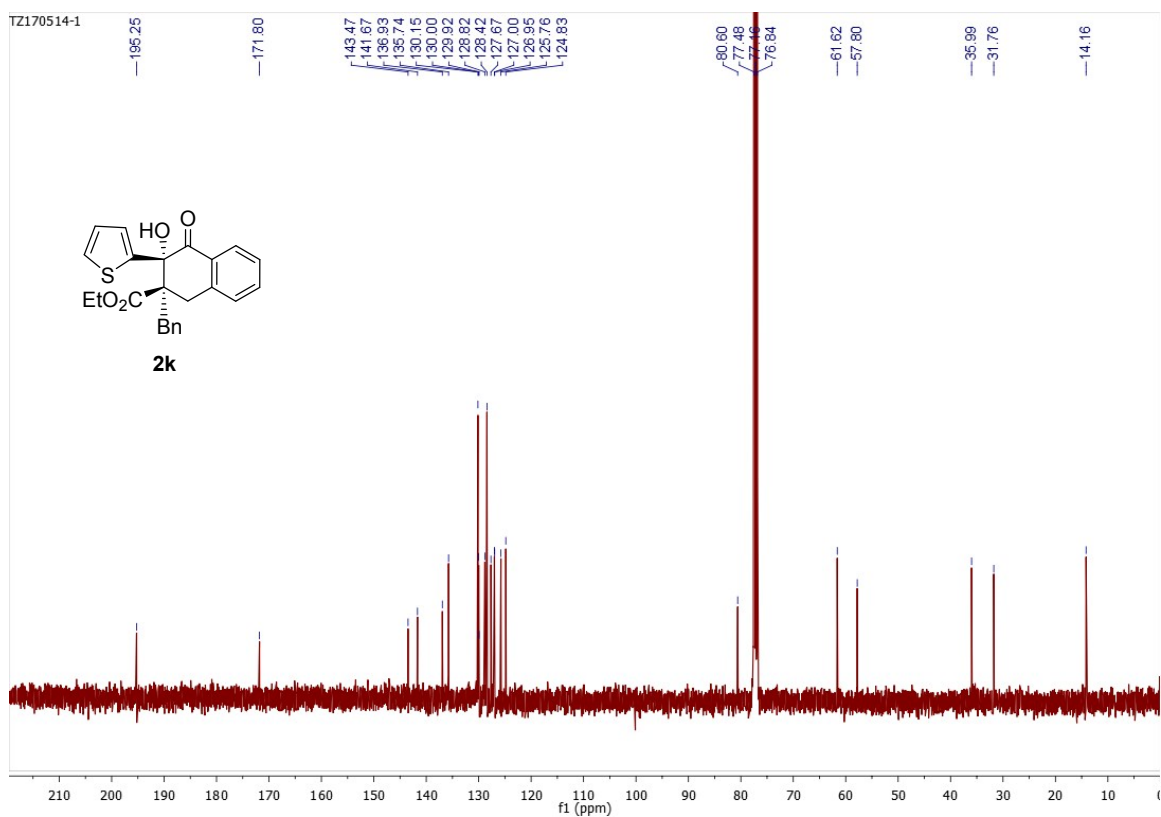
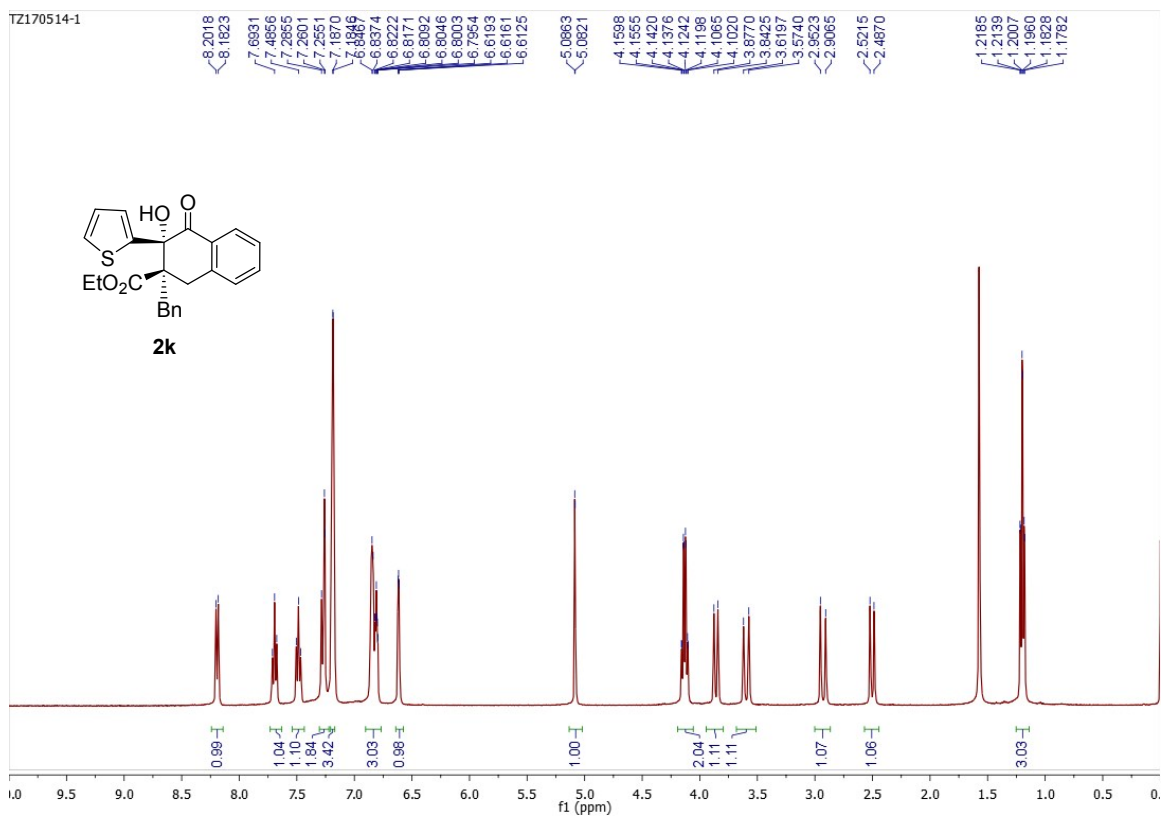


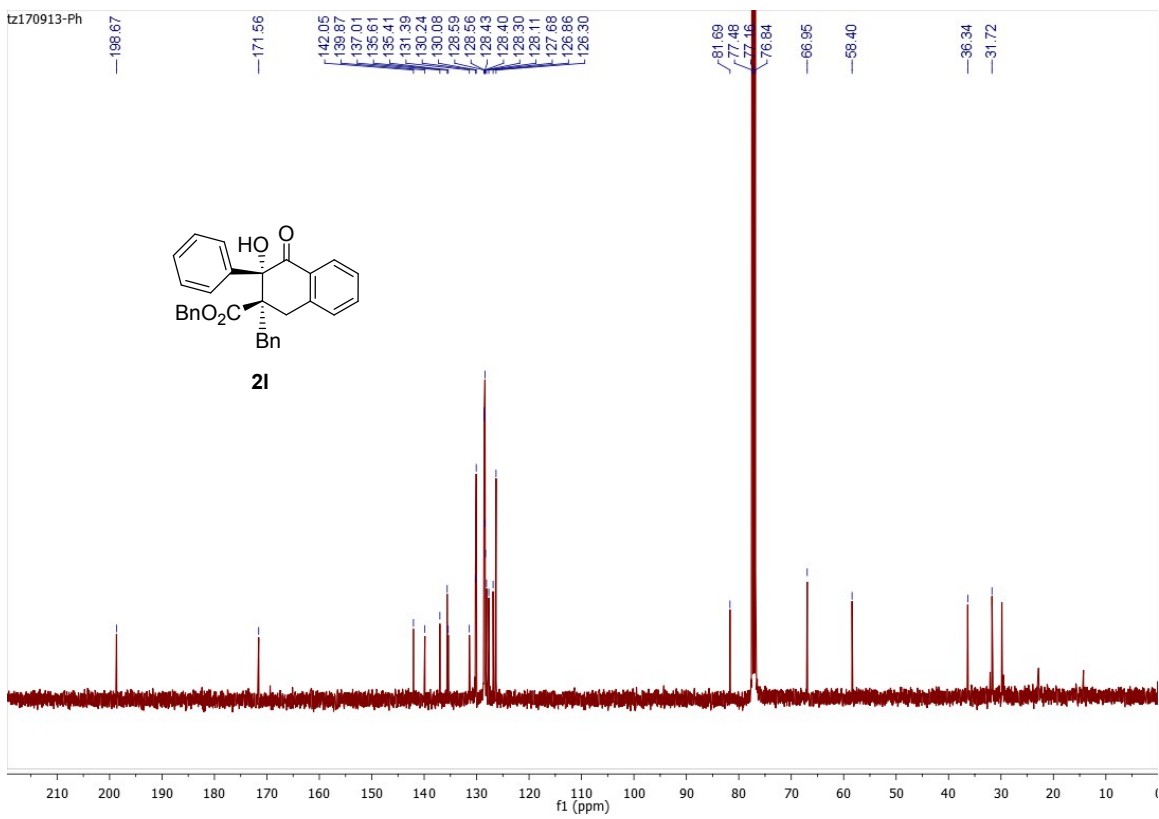
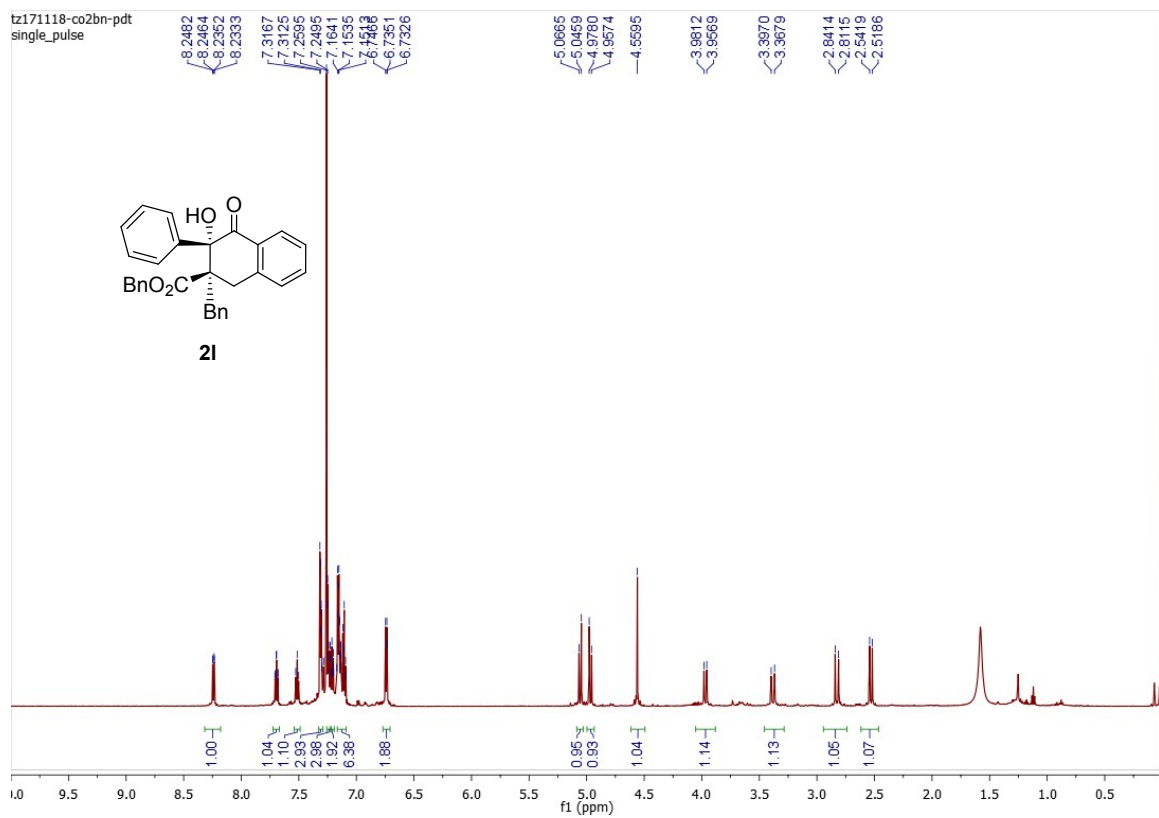


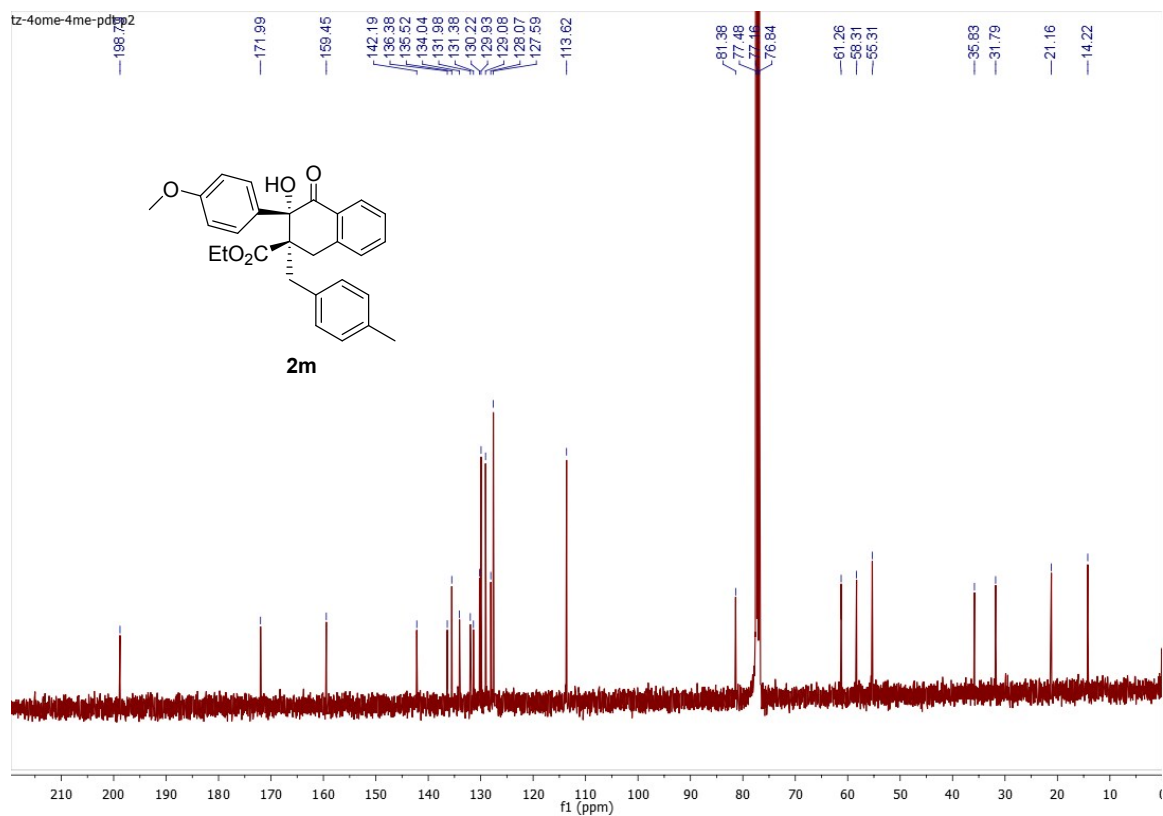
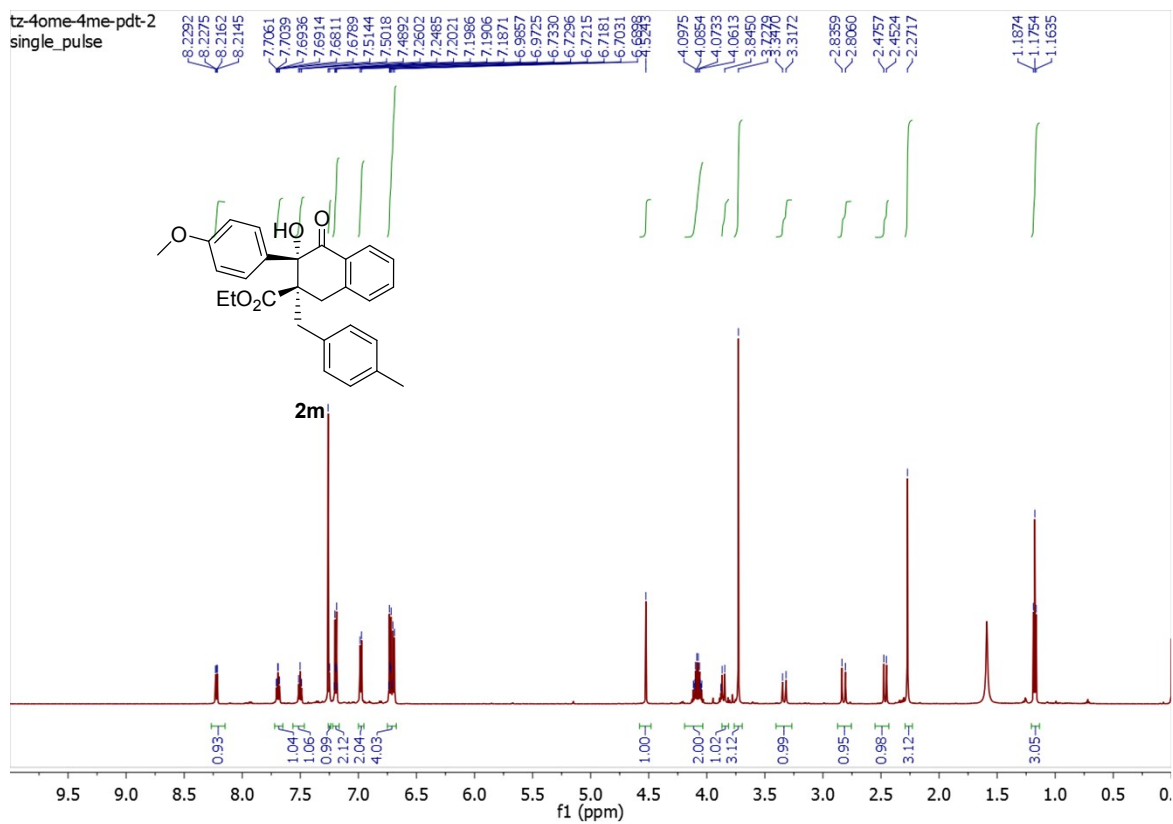


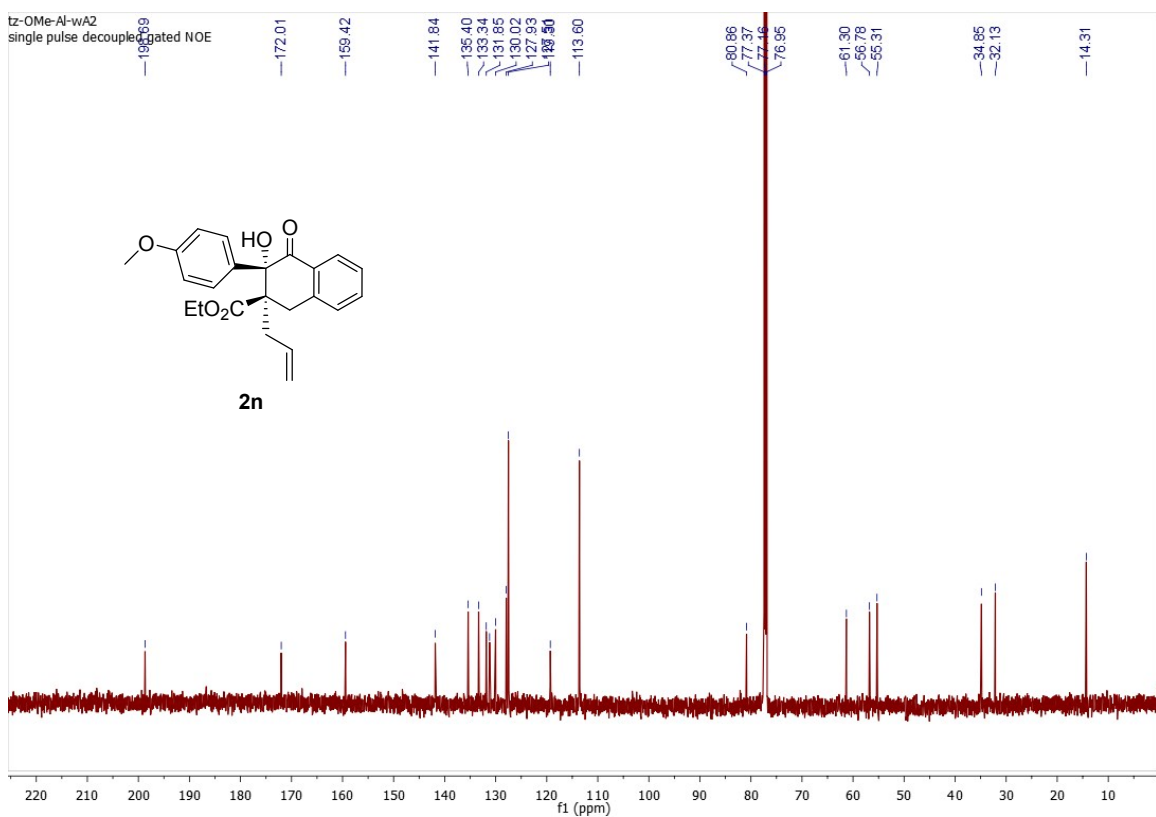
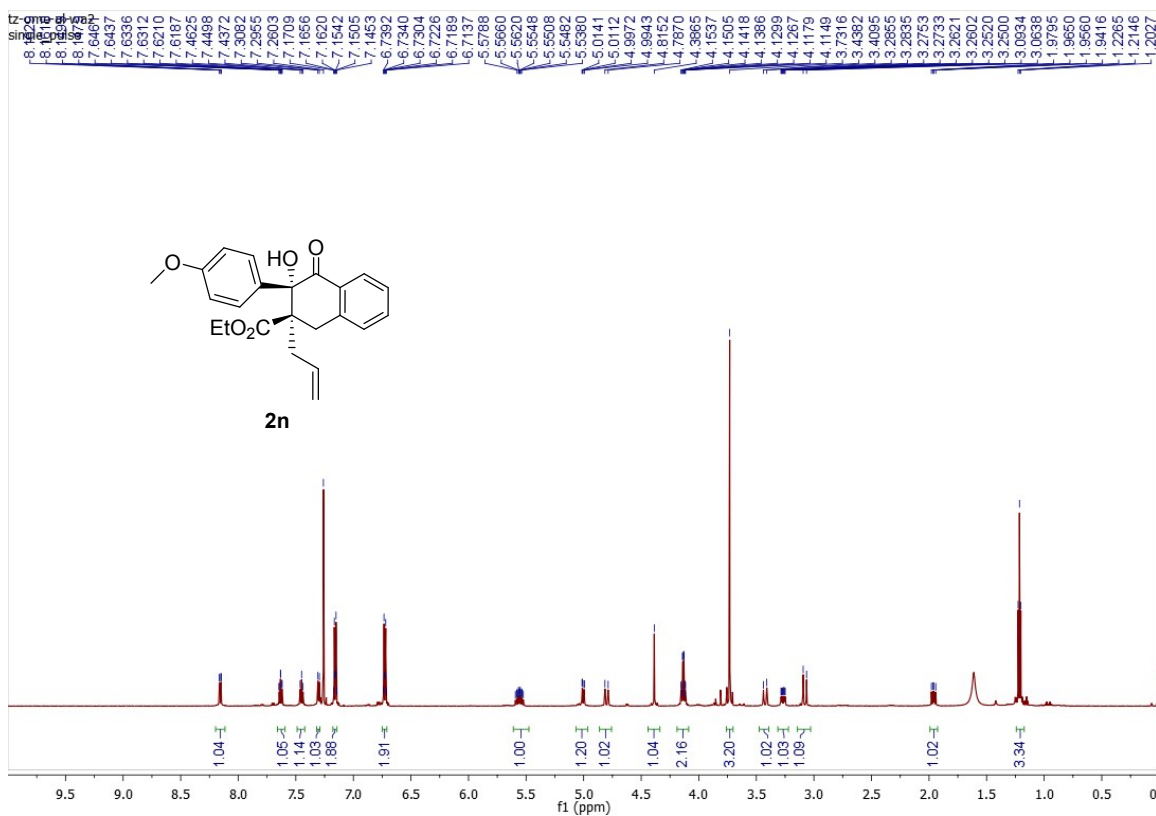


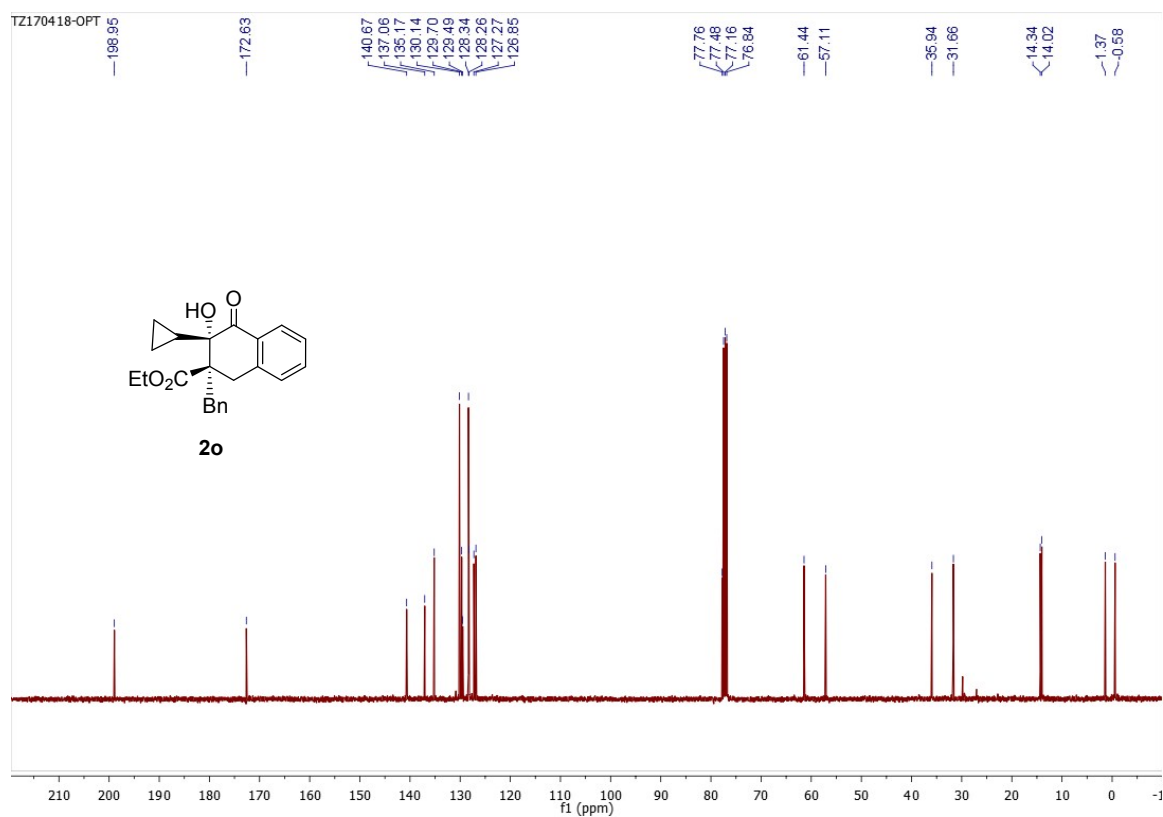
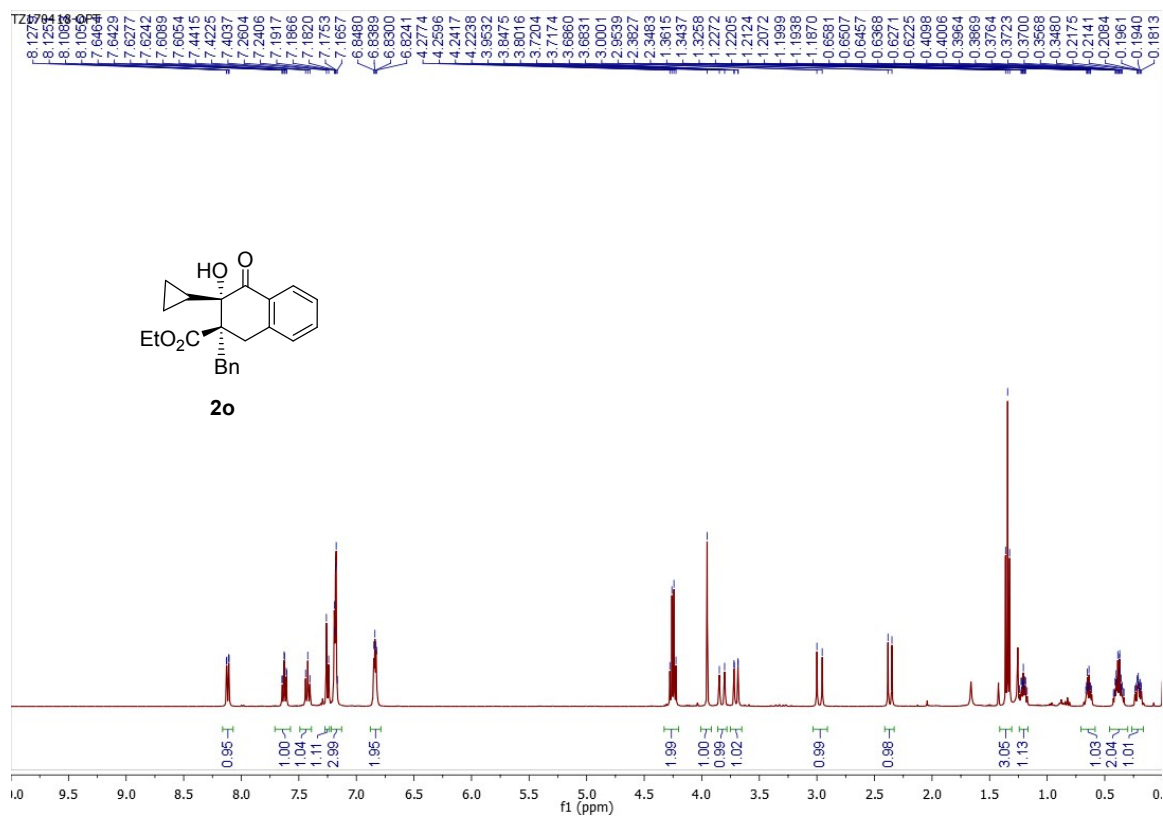


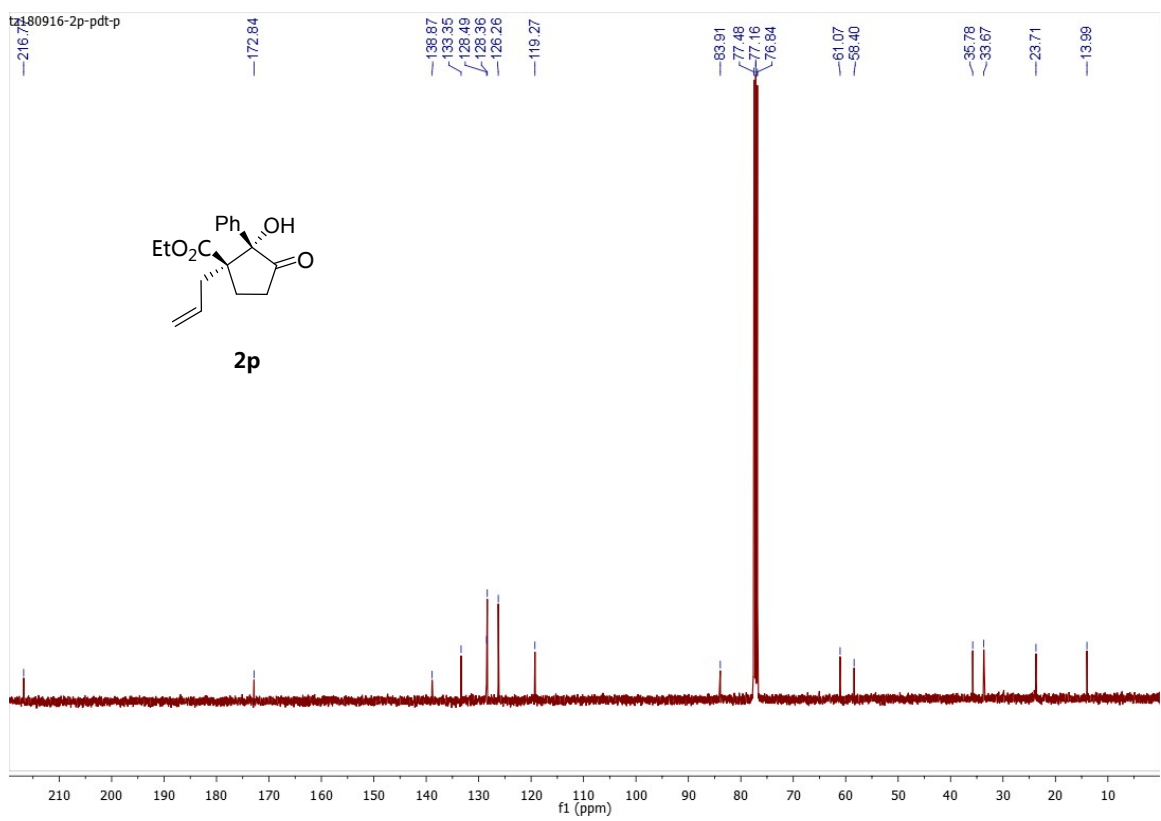
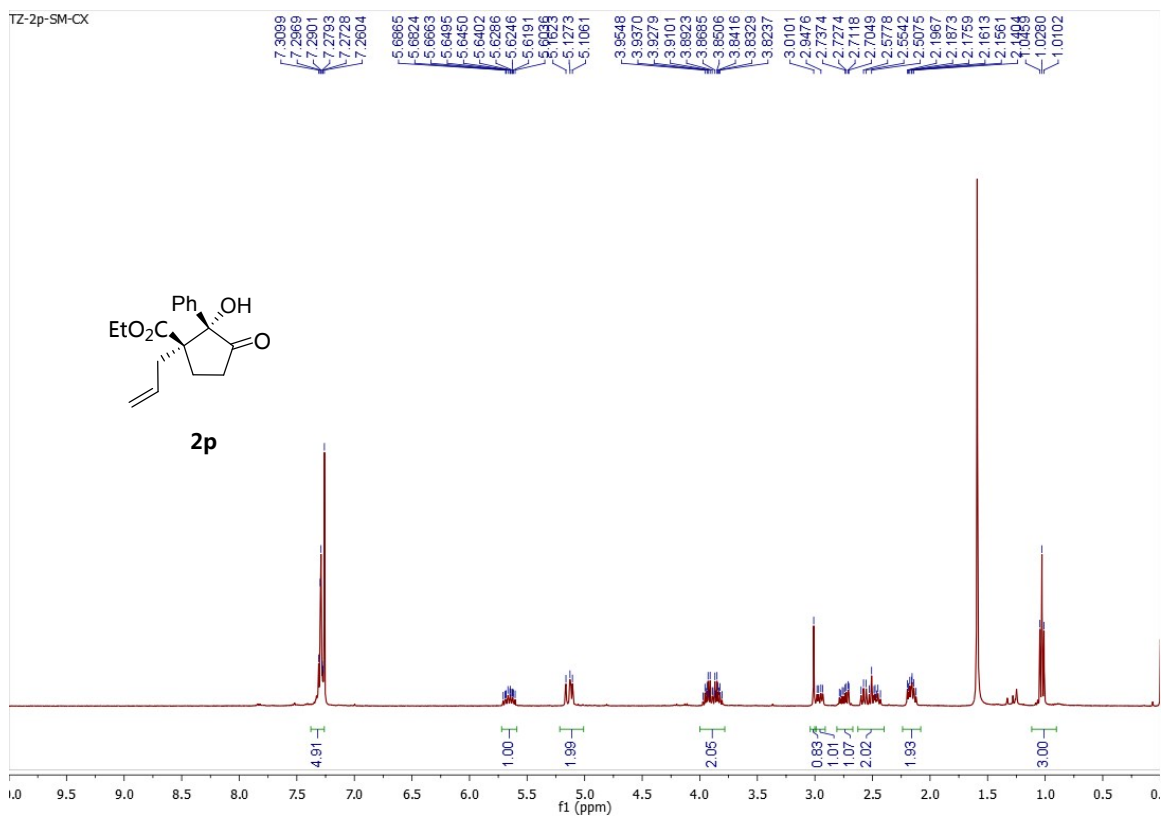




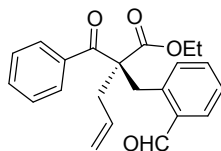








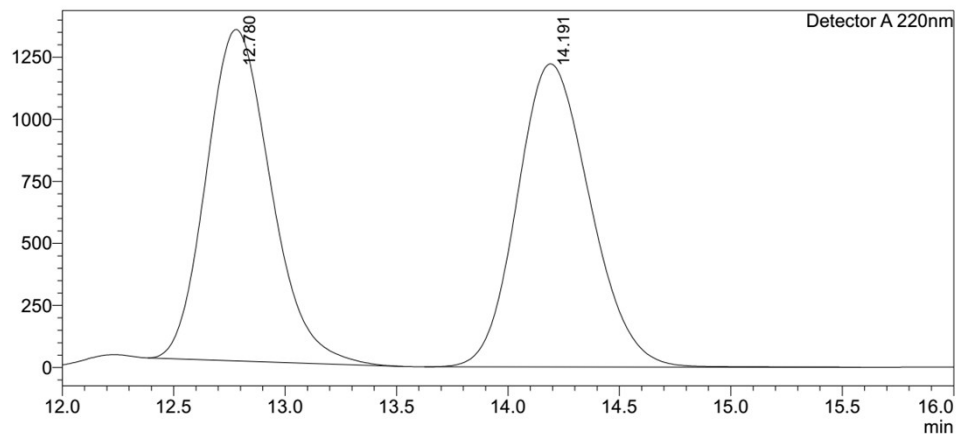
VI. HPLC spectra for ee determination



(S)-1a

<Chromatogram>

mV



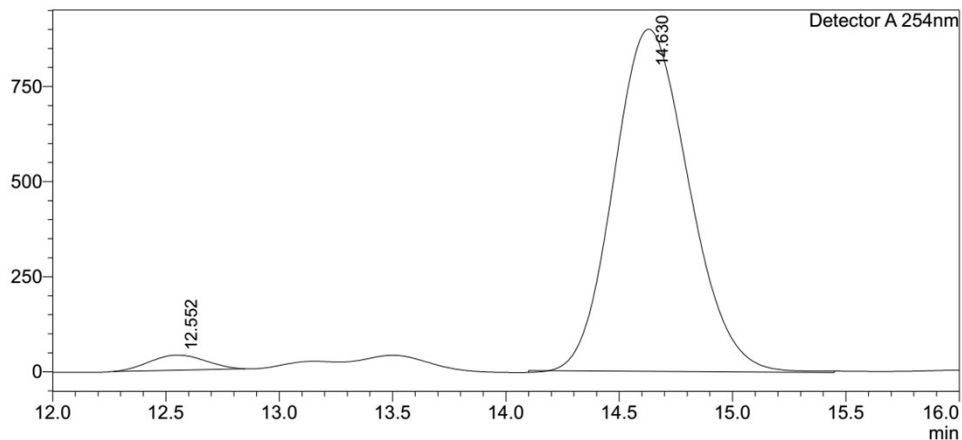
<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.780	26933890	1334488	49.206			
2	14.191	27803475	1221019	50.794			
Total		54737365	2555507				

<Chromatogram>

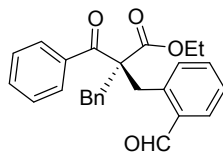
mV



<Peak Table>

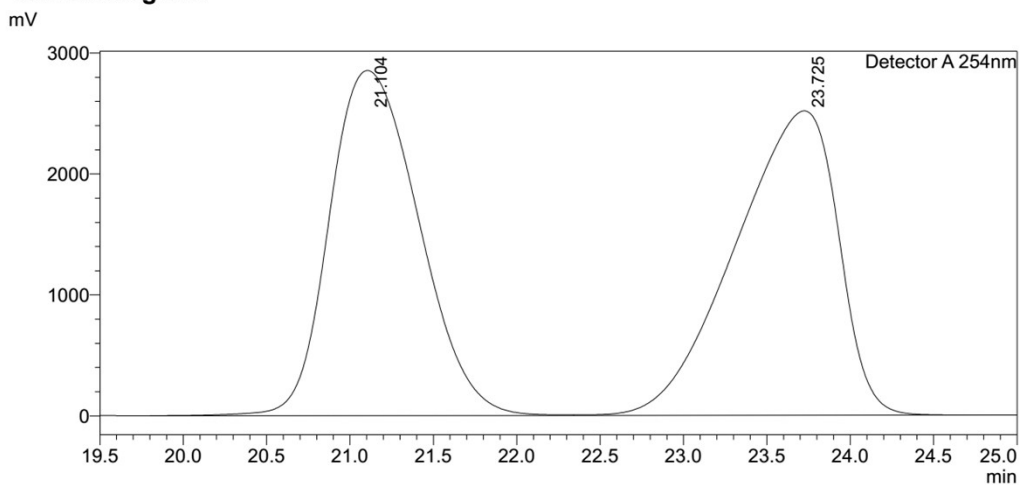
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.552	684254	39726	3.189		M	
2	14.630	20771395	899140	96.811		M	
Total		21455649	938866				



(S)-1b

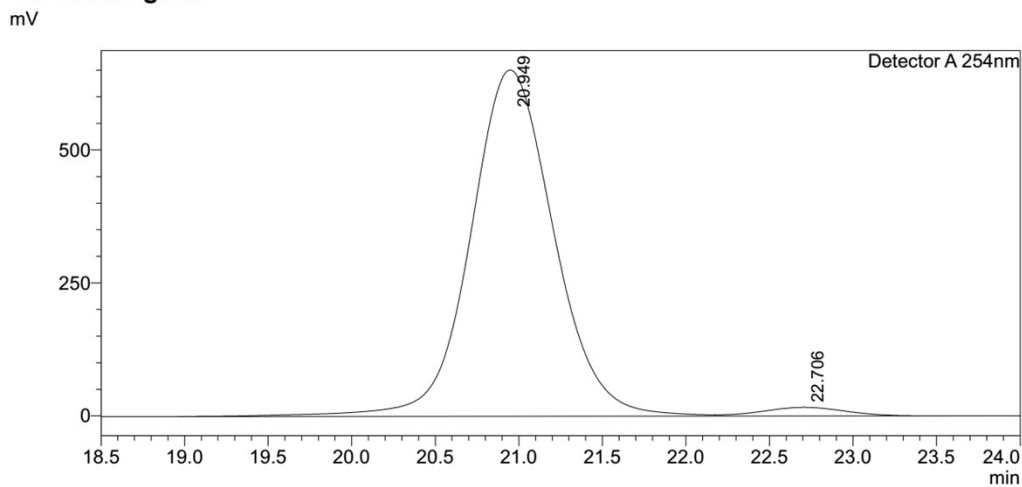
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<Peak Table>

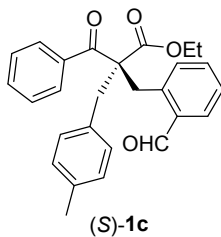
Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.104	106295586	2852328	49.560			
2	23.725	108180901	2517387	50.440		V	
Total		214476487	5369715				

<Chromatogram>



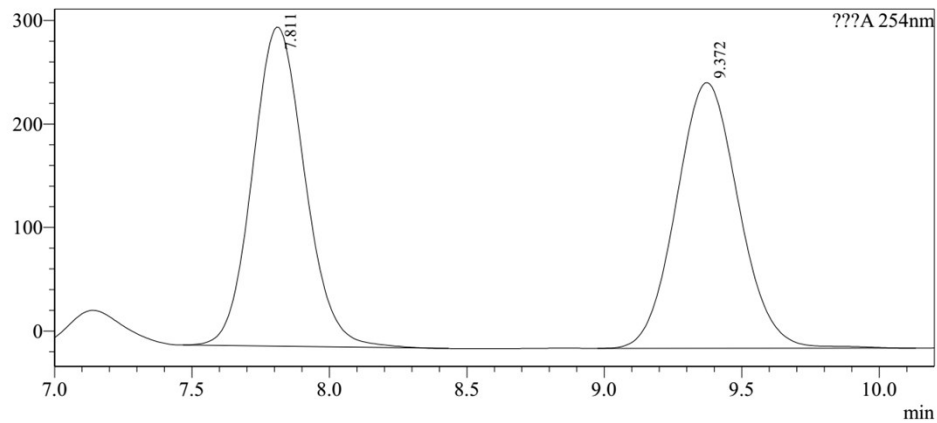
<Peak Table>

Detector A 254nm							
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.949	22623352	651212	97.523			
2	22.706	574685	16439	2.477		SV	
Total		23198037	667651				



<Chromatogram>

mV



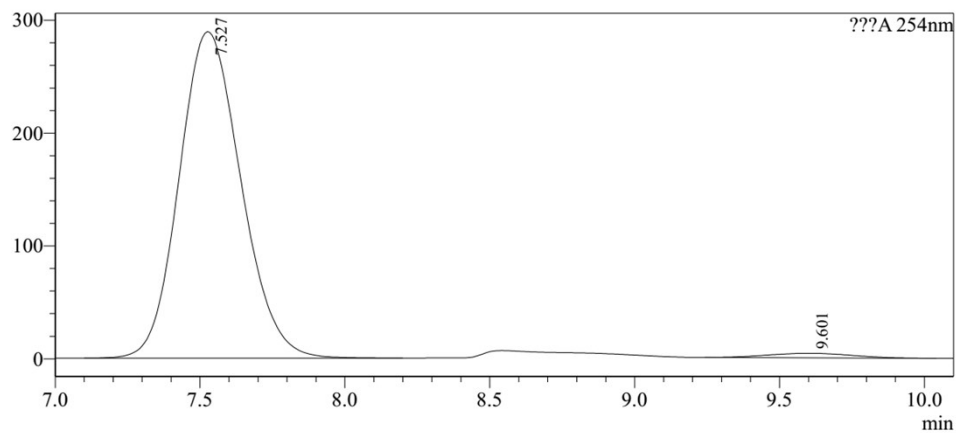
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.811	4088168	308507	50.192			
2	9.372	4056829	256778	49.808			
Total		8144997	565286				

<Chromatogram>

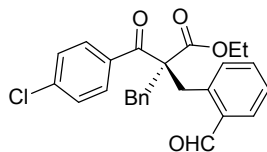
mV



<Peak Table>

???A 254nm

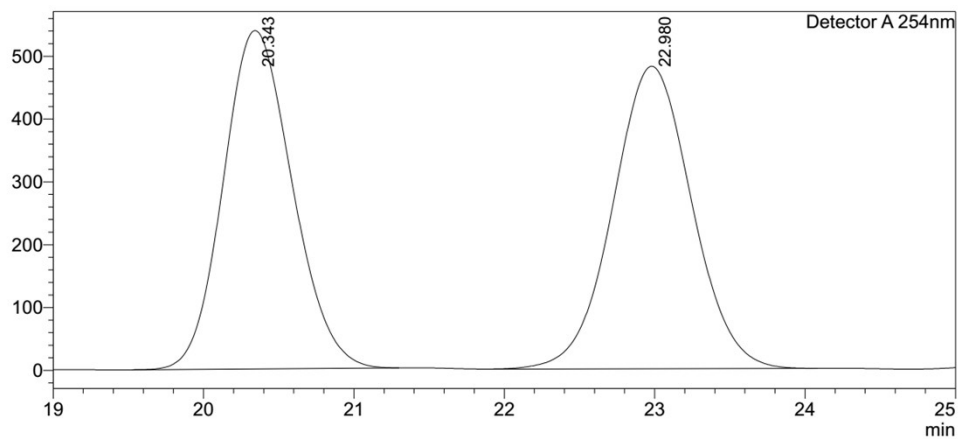
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.527	4294218	289407	98.103			
2	9.601	83048	4056	1.897			
Total		4377267	293463				



(S)-1d

<Chromatogram>

mV



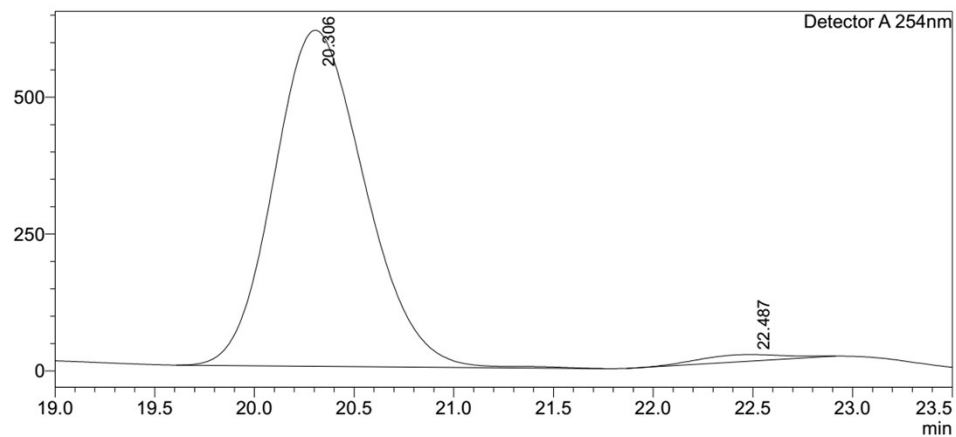
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.343	17154344	538530	49.380			
2	22.980	17585305	481409	50.620			
Total		34739649	1019940				

<Chromatogram>

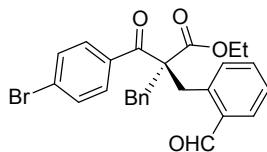
mV



<Peak Table>

Detector A 254nm

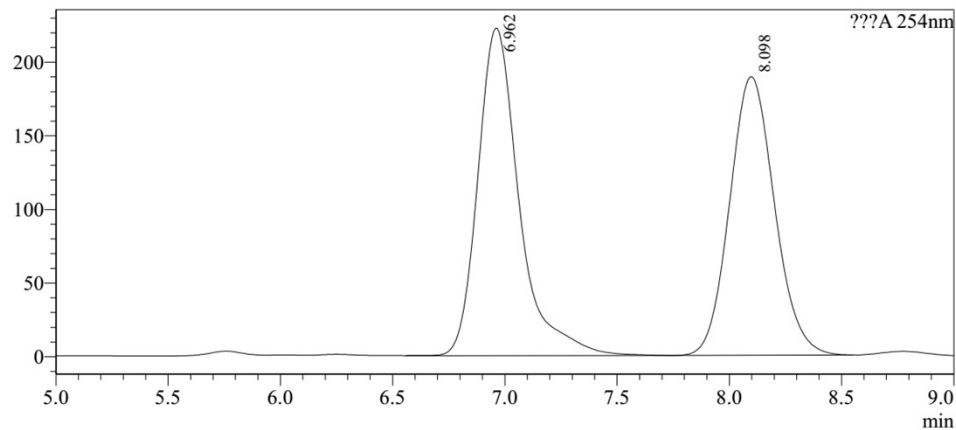
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.306	19514967	613776	98.093			
2	22.487	379463	11977	1.907		M	
Total		19894430	625753				



(S)-1e

<Chromatogram>

mV



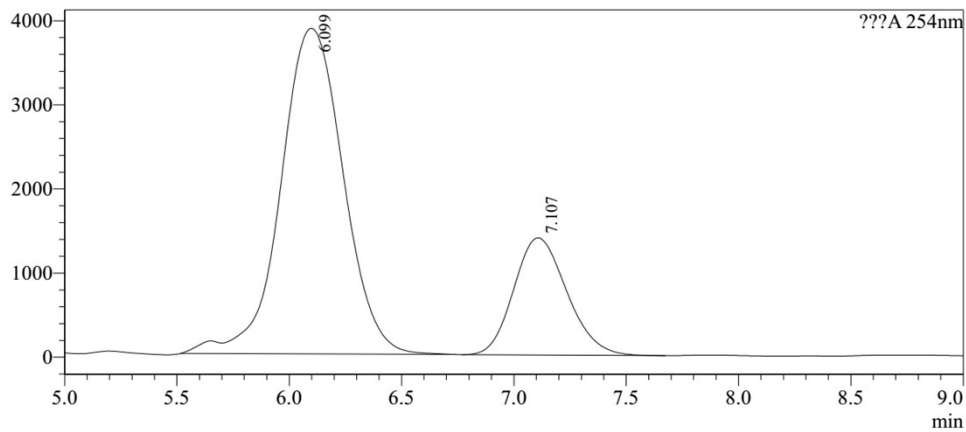
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.962	2849360	222383	51.991			
2	8.098	2631168	189283	48.009			
Total		5480529	411666				

<Chromatogram>

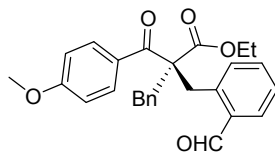
mV



<Peak Table>

???A 254nm

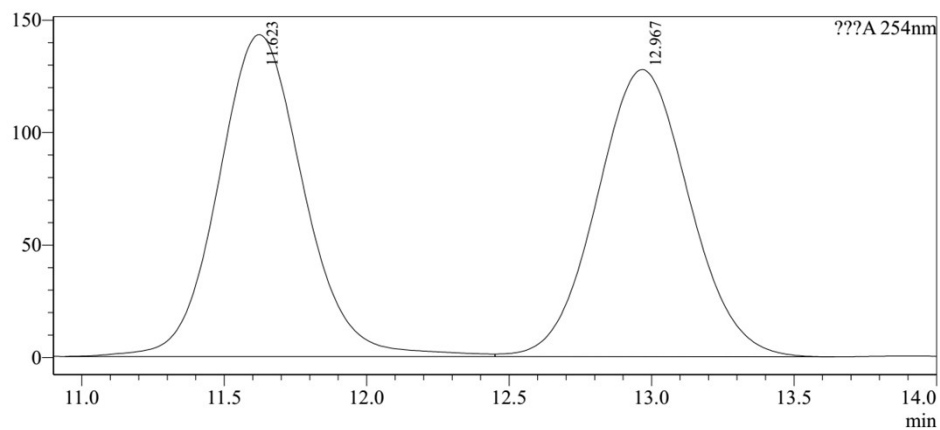
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.099	75184370	3872449	76.644		M	
2	7.107	22910850	1393732	23.356			
Total		98095220	5266181				



(S)-1f

<Chromatogram>

mV



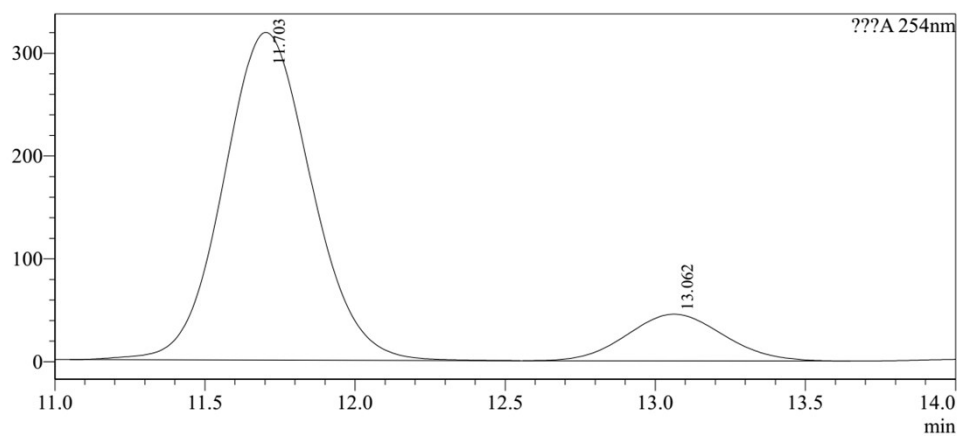
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.623	2987677	143206	50.852			
2	12.967	2887620	127754	49.148		V	
Total		5875297	270960				

<Chromatogram>

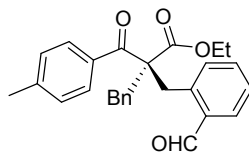
mV



<Peak Table>

??A 254nm

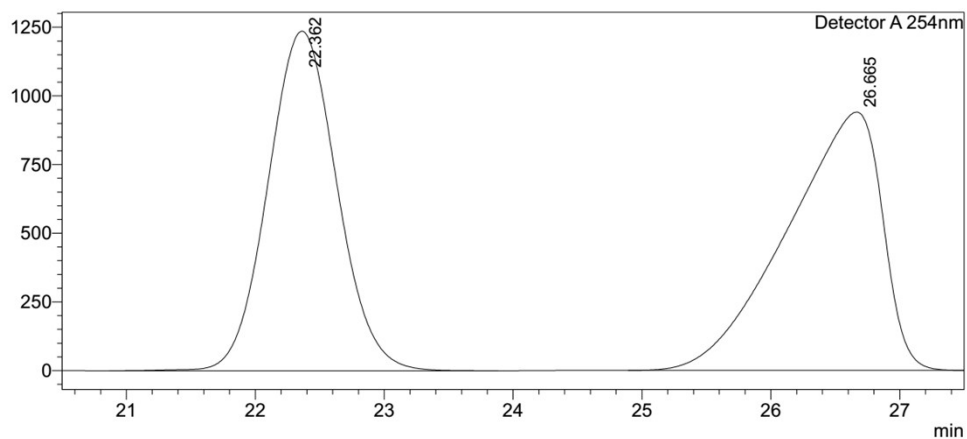
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.703	6492656	318668	86.484			
2	13.062	1014700	45291	13.516			
Total		7507357	363959				



(S)-1g

<Chromatogram>

mV



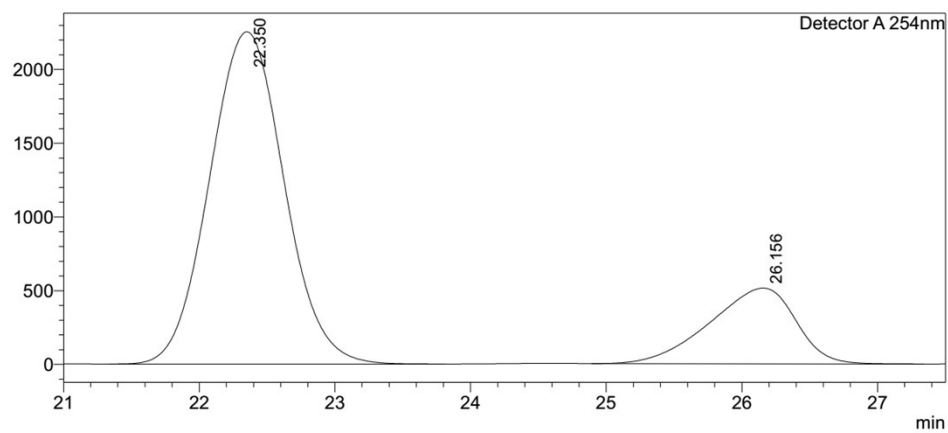
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.362	46058863	1236295	48.821			
2	26.665	48283269	940270	51.179			
Total		94342132	2176565				

<Chromatogram>

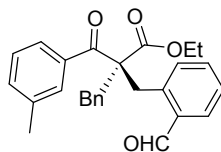
mV



<Peak Table>

Detector A 254nm

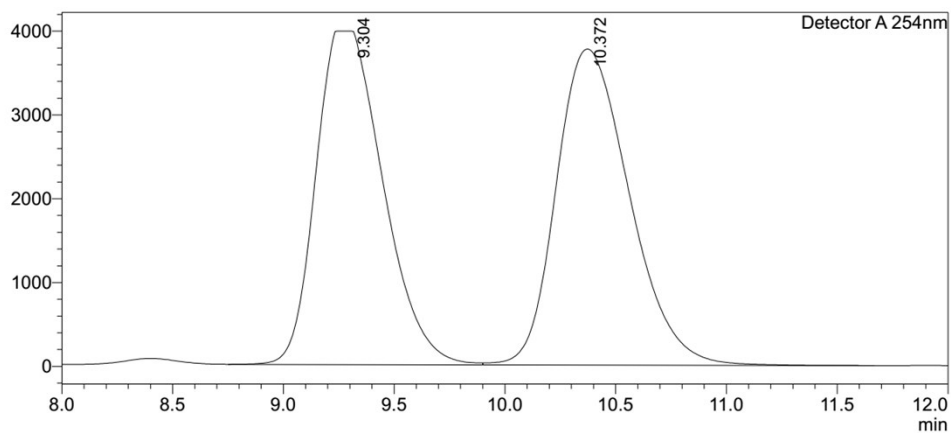
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.350	86165066	2253129	79.200			
2	26.156	22629403	513339	20.800			
Total		108794469	2766468				



(S)-1h

<Chromatogram>

mV



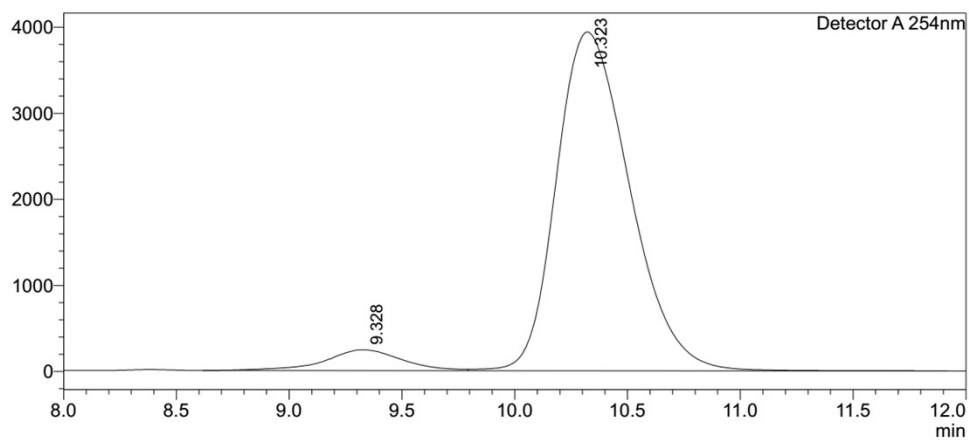
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.304	83936103	3978513	49.219			
2	10.372	86600701	3771204	50.781		V	
Total		170536805	7749717				

<Chromatogram>

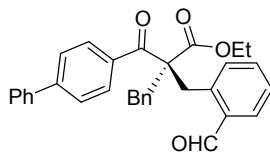
mV



<Peak Table>

Detector A 254nm

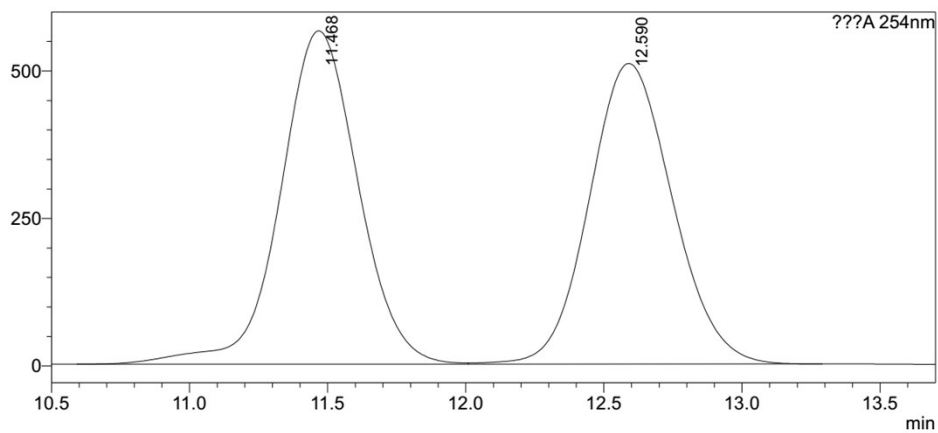
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.328	5780045	242029	6.087			
2	10.323	89184017	3936179	93.913		V	
Total		94964062	4178207				



(S)-1i

<Chromatogram>

mV



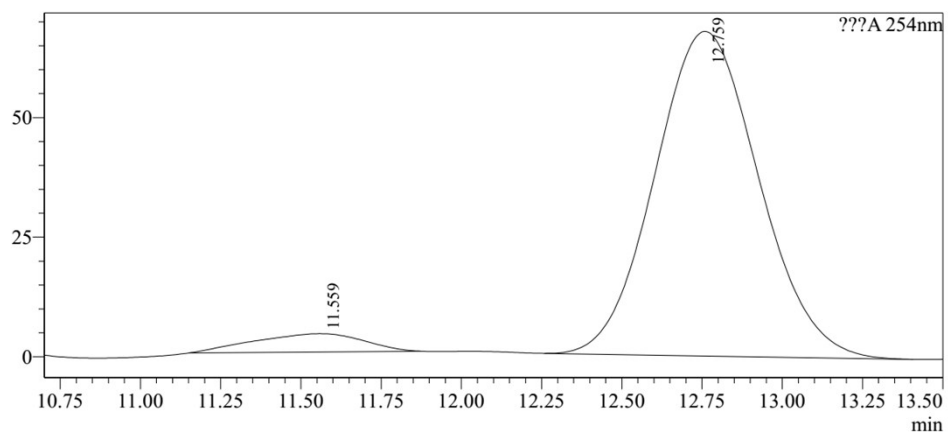
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.468	11094372	565152	50.933			
2	12.590	10688000	509699	49.067		V	
Total		21782372	1074852				

<Chromatogram>

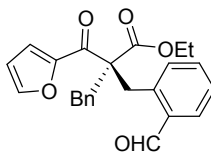
mV



<Peak Table>

???A 254nm

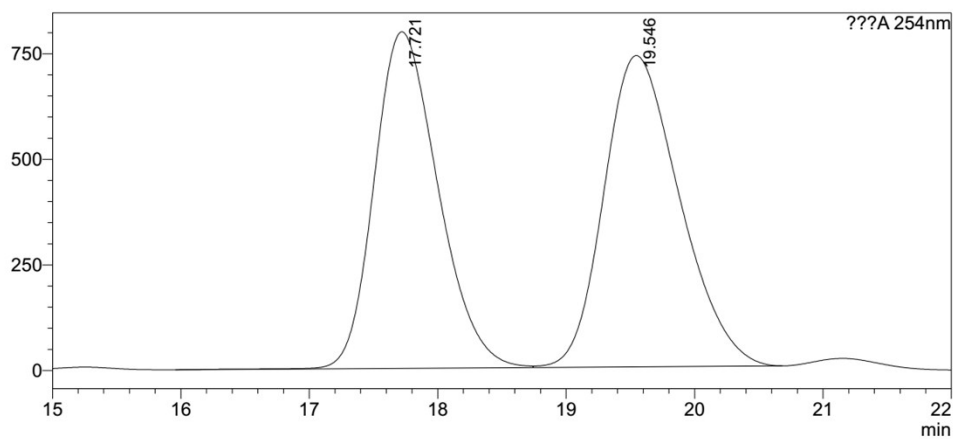
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.559	91293	3832	5.639		M	
2	12.759	1527571	67871	94.361			
Total		1618865	71703				



(S)-1j

<Chromatogram>

mV



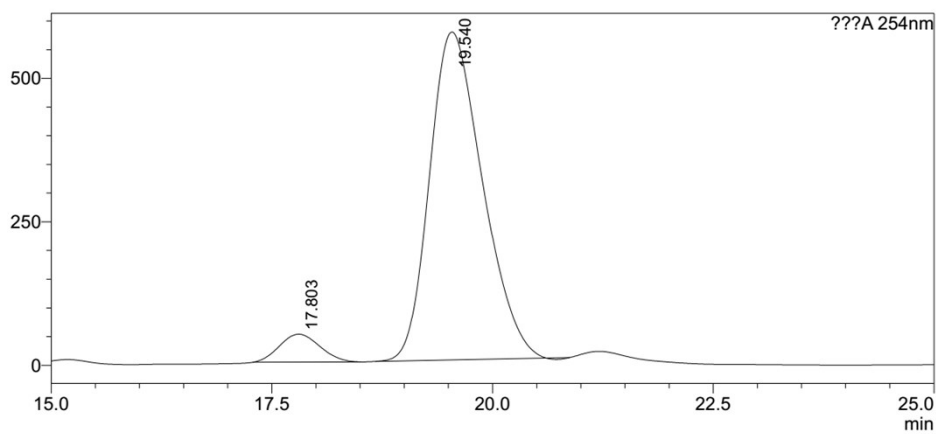
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.721	27497205	796671	47.658			
2	19.546	30199875	737080	52.342		V	
Total		57697080	1533751				

<Chromatogram>

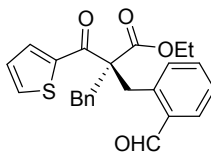
mV



<Peak Table>

???A 254nm

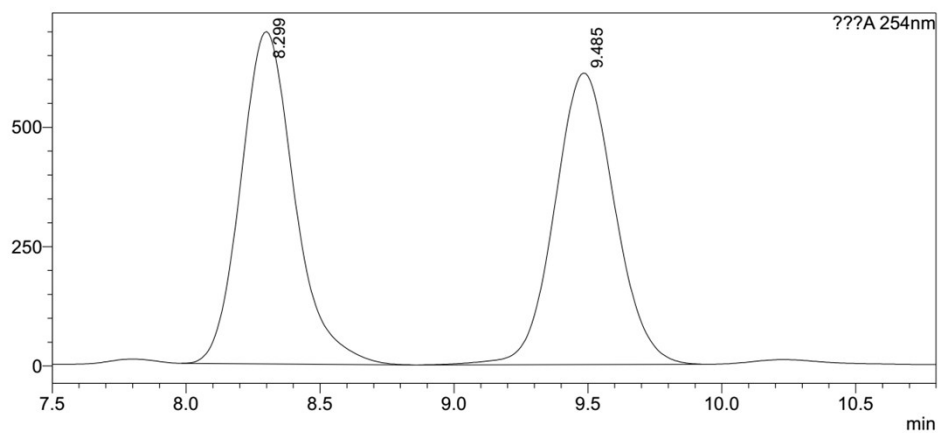
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.803	1543821	48576	6.090		M	
2	19.540	23807319	571302	93.910		M	
Total		25351139	619878				



(S)-1k

<Chromatogram>

mV



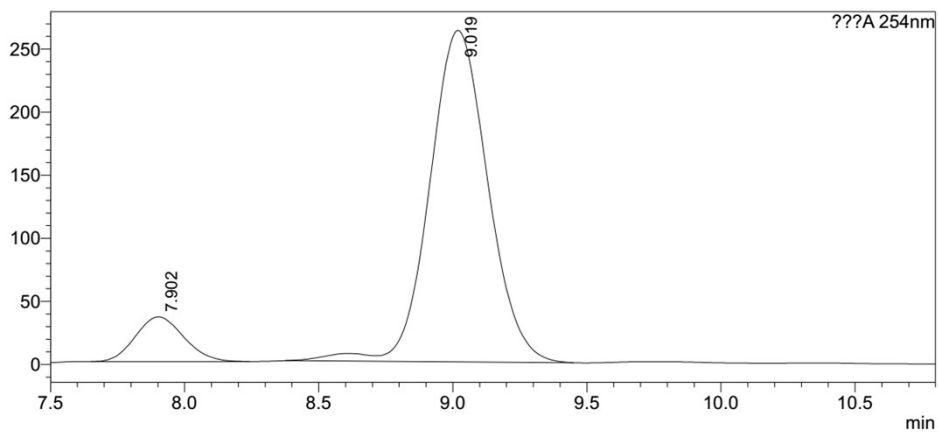
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.299	9728845	695663	50.519			
2	9.485	9529109	610227	49.481			
Total		19257954	1305890				

<Chromatogram>

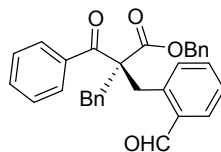
mV



<Peak Table>

???A 254nm

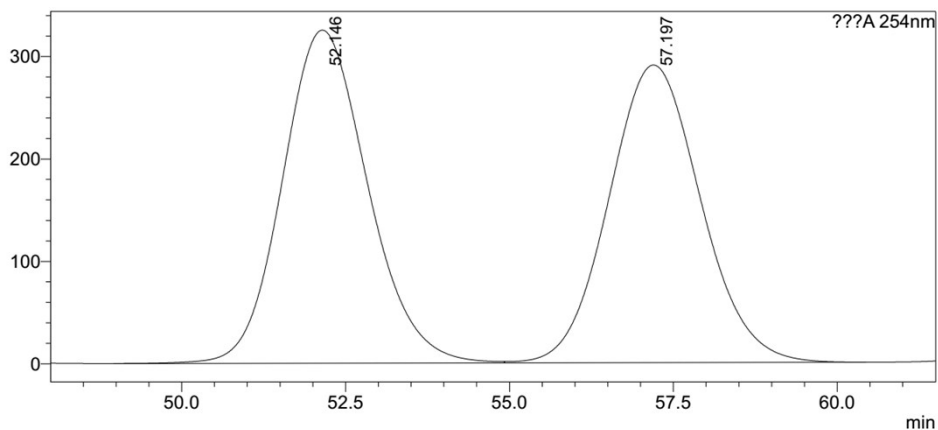
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.902	443542	35381	10.026			
2	9.019	3980184	262769	89.974		M	
Total		4423726	298150				



(S)-1I

<Chromatogram>

mV



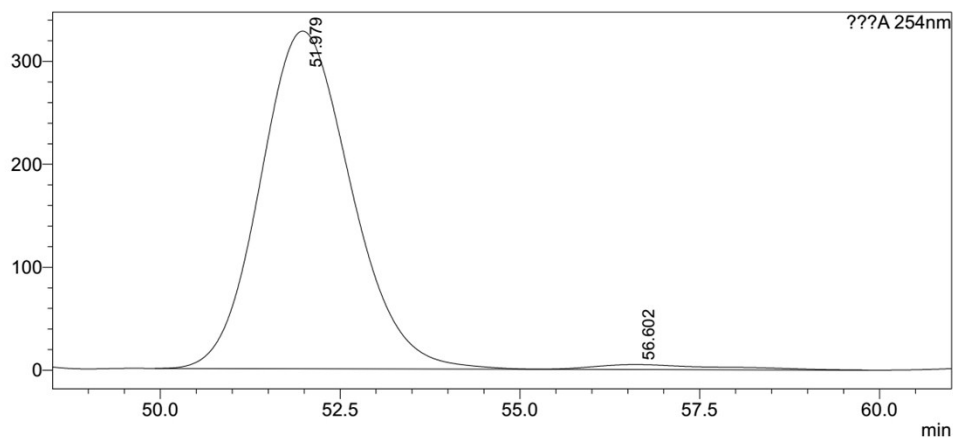
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	52.146	29386095	325222	50.937			
2	57.197	28305057	290568	49.063		V	
Total		57691152	615790				

<Chromatogram>

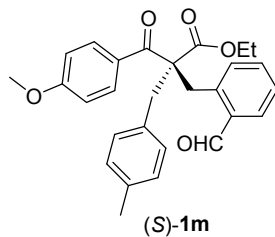
mV



<Peak Table>

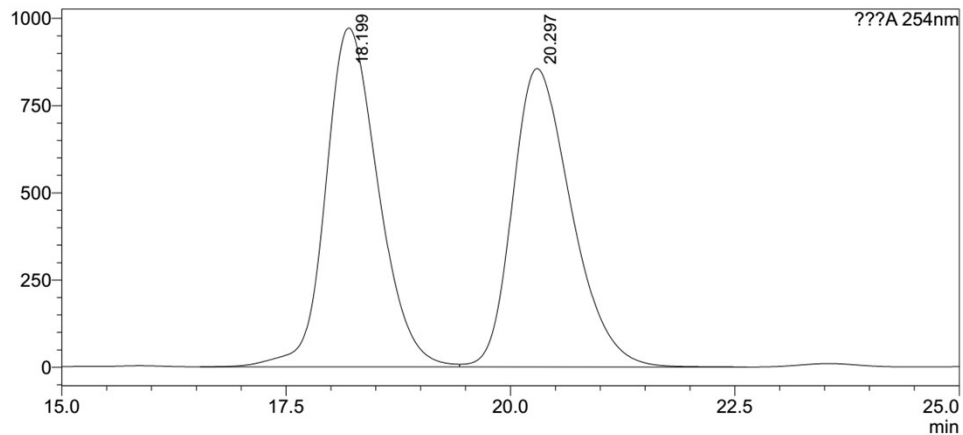
??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	51.979	28847099	328005	97.964			
2	56.602	599474	4880	2.036		V	
Total		29446573	332884				



<Chromatogram>

mV



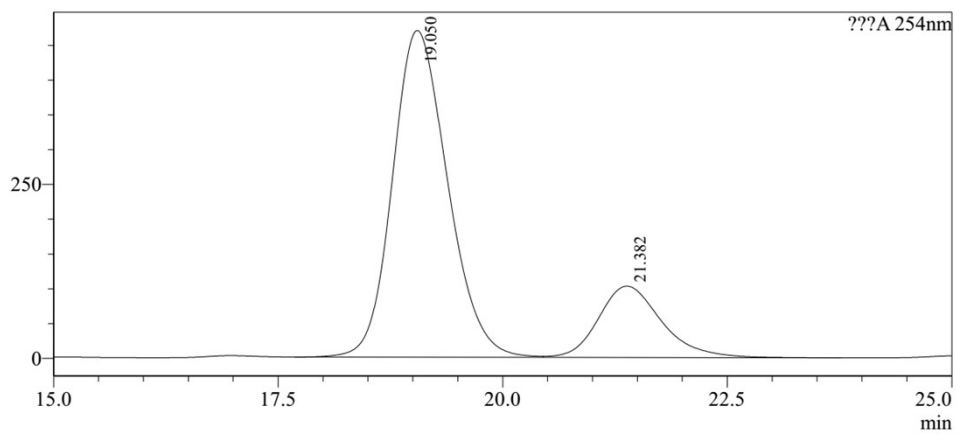
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.199	39666254	971091	50.378			
2	20.297	39071405	855247	49.622		V	
Total		78737659	1826338				

<Chromatogram>

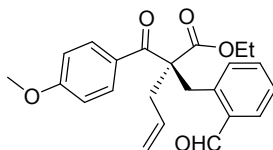
mV



<Peak Table>

??A 254nm

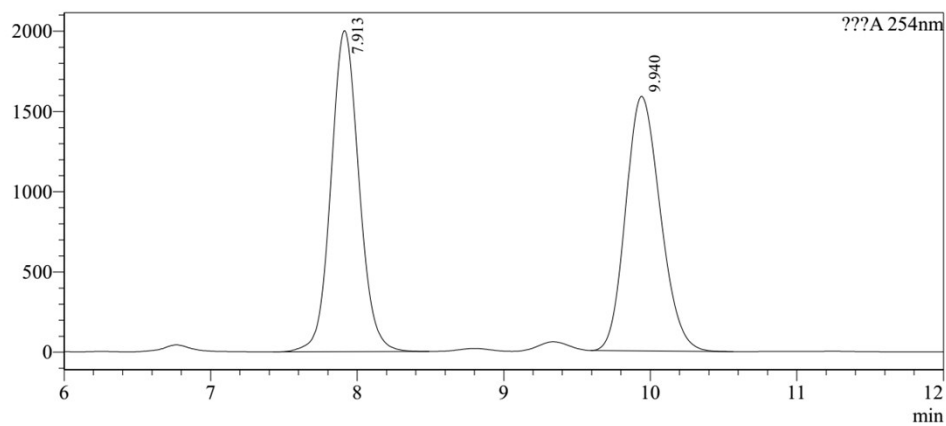
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	19.050	20070774	469715	79.969			
2	21.382	5027335	102616	20.031		V	
Total		25098109	572331				



(S)-1n

<Chromatogram>

mV



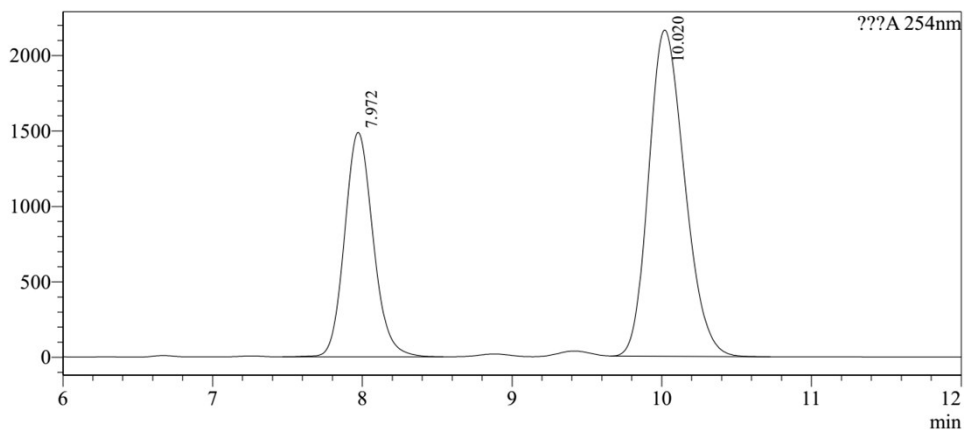
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.913	26705291	2000127	50.515			
2	9.940	26160869	1585971	49.485			
Total		52866160	3586098				

<Chromatogram>

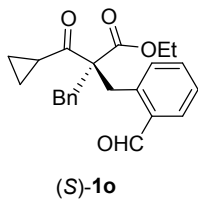
mV



<Peak Table>

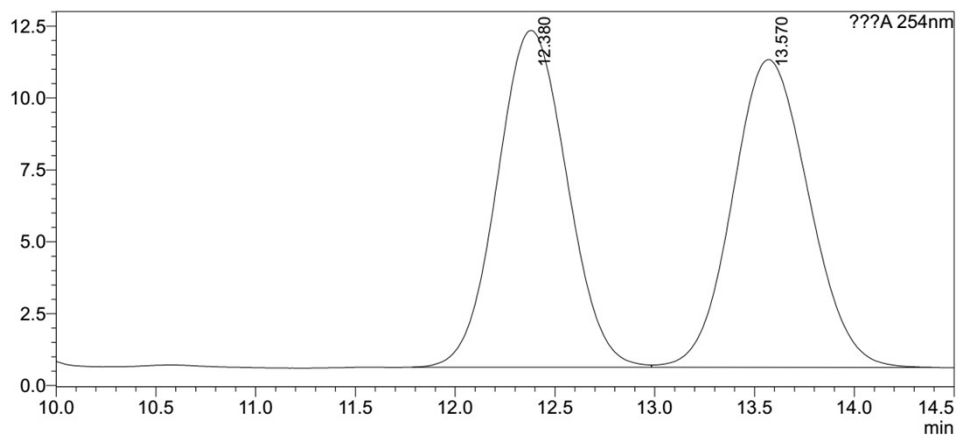
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.972	19773505	1488251	35.294			
2	10.020	36252121	2162775	64.706			
Total		56025625	3651026				



<Chromatogram>

mV



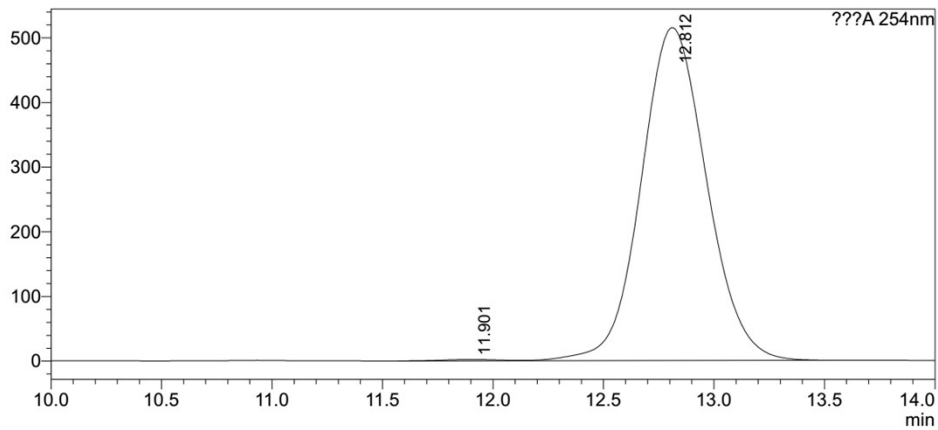
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.380	284696	11711	49.993			
2	13.570	284781	10698	50.007		V	
Total		569477	22409				

<Chromatogram>

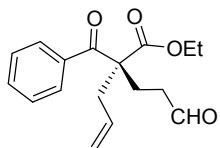
mV



<Peak Table>

???A 254nm

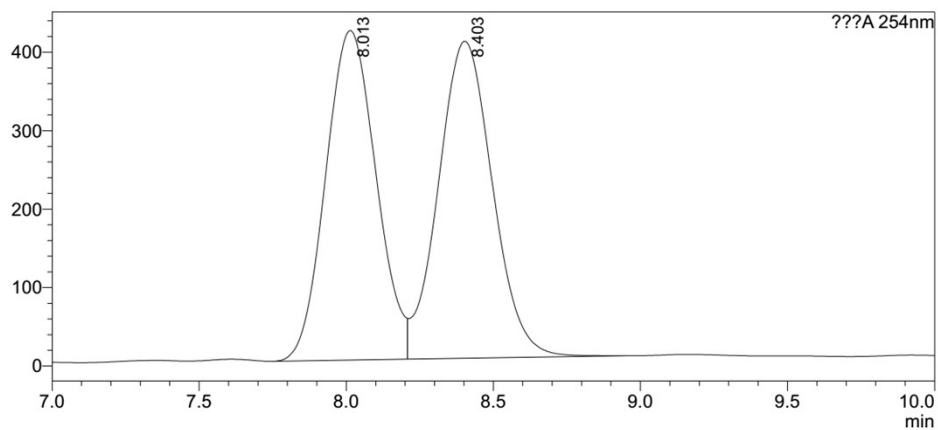
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.901	37590	2117	0.353			
2	12.812	10625242	514904	99.647		V	
Total		10662832	517021				



(S)-1p

<Chromatogram>

mV



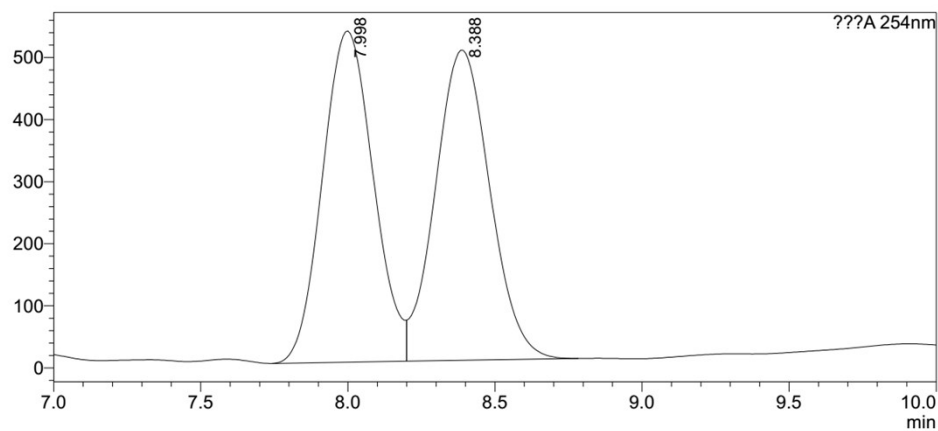
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.013	5014791	420049	49.182			
2	8.403	5181695	404330	50.818		V	
Total		10196486	824379				

<Chromatogram>

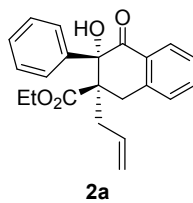
mV



<Peak Table>

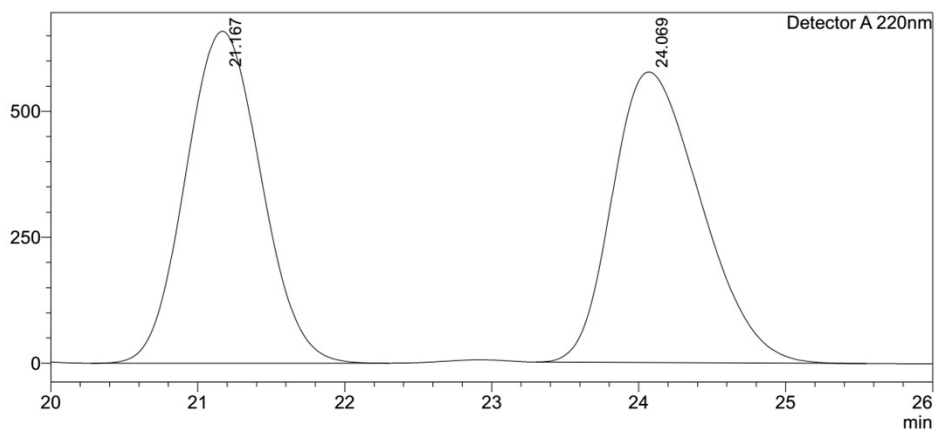
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.998	6430324	533315	49.949			
2	8.388	6443535	499362	50.051		V	
Total		12873859	1032677				



<Chromatogram>

mV



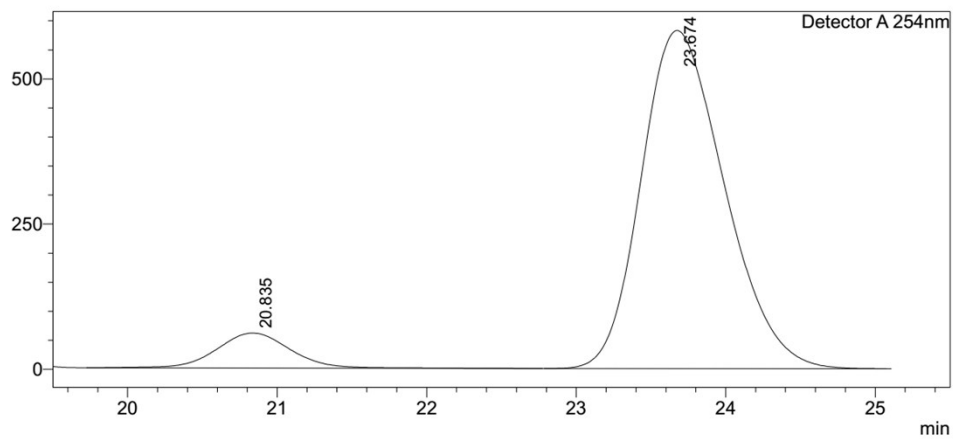
<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.167	23583456	658808	49.365			
2	24.069	24190185	576697	50.635			
Total		47773641	1235506				

<Chromatogram>

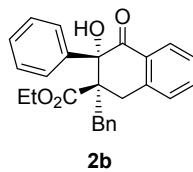
mV



<Peak Table>

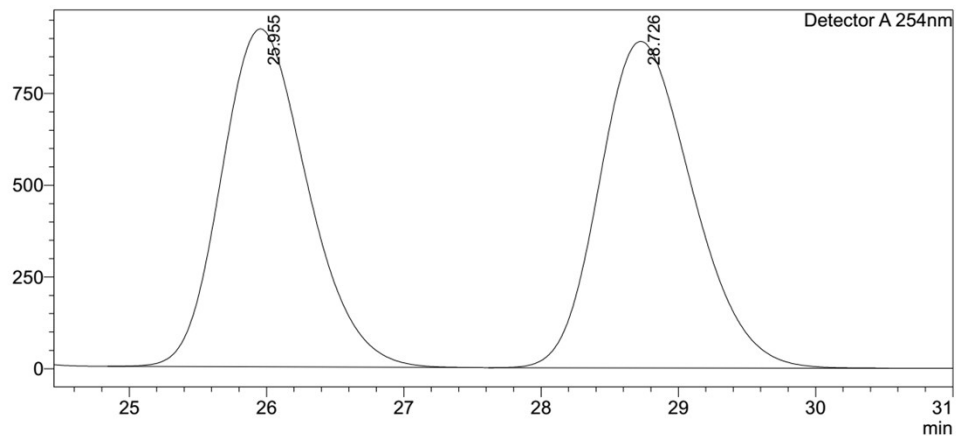
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	20.835	2088757	60266	8.489			
2	23.674	22515821	582193	91.511			
Total		24604578	642459				



<Chromatogram>

mV



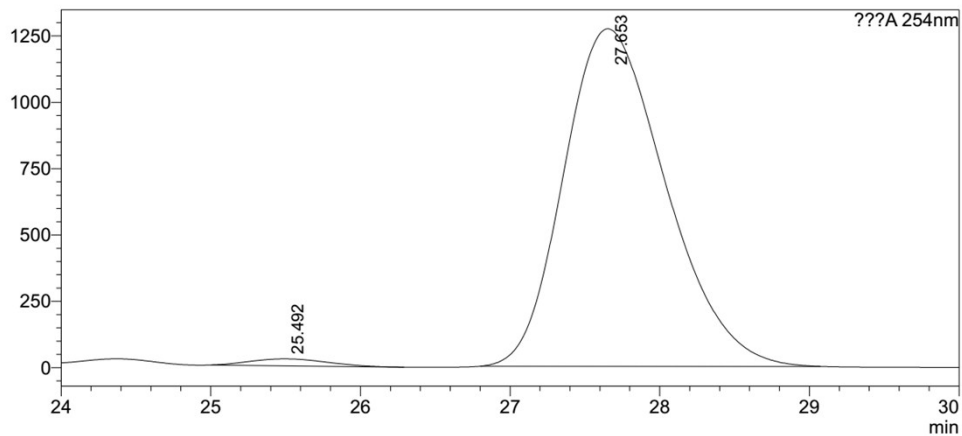
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.955	40270694	920891	48.934			
2	28.726	42025857	889617	51.066			
Total		82296551	1810508				

<Chromatogram>

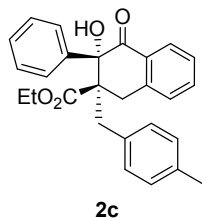
mV



<Peak Table>

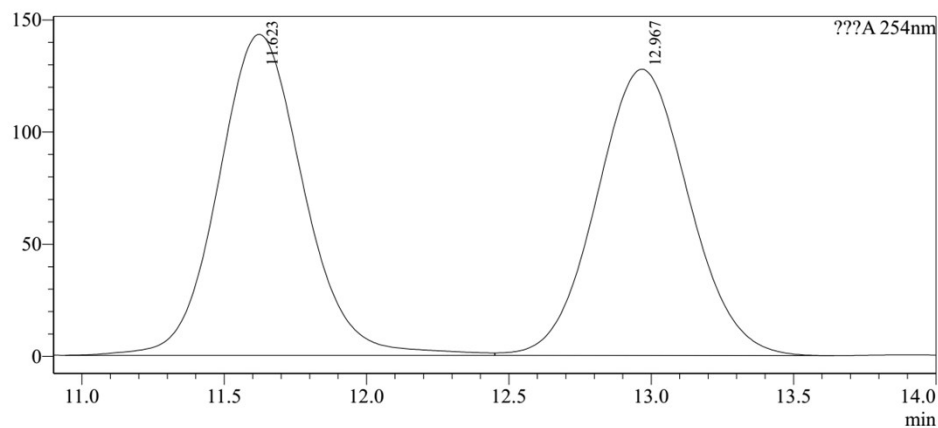
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.492	940107	26201	1.536		M	
2	27.653	60263737	1272107	98.464		M	
Total		61203844	1298308				



<Chromatogram>

mV



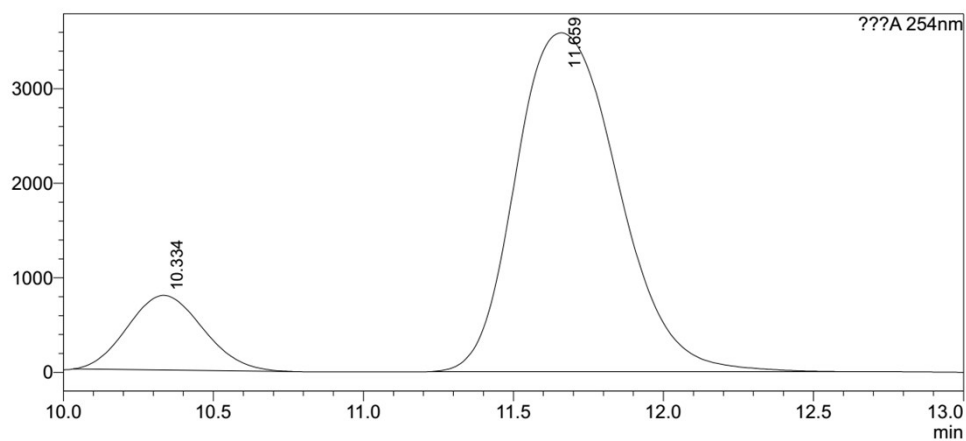
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.623	2987677	143206	50.852			
2	12.967	2887620	127754	49.148		V	
Total		5875297	270960				

<Chromatogram>

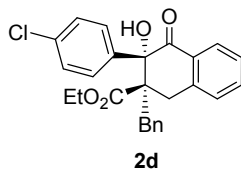
mV



<Peak Table>

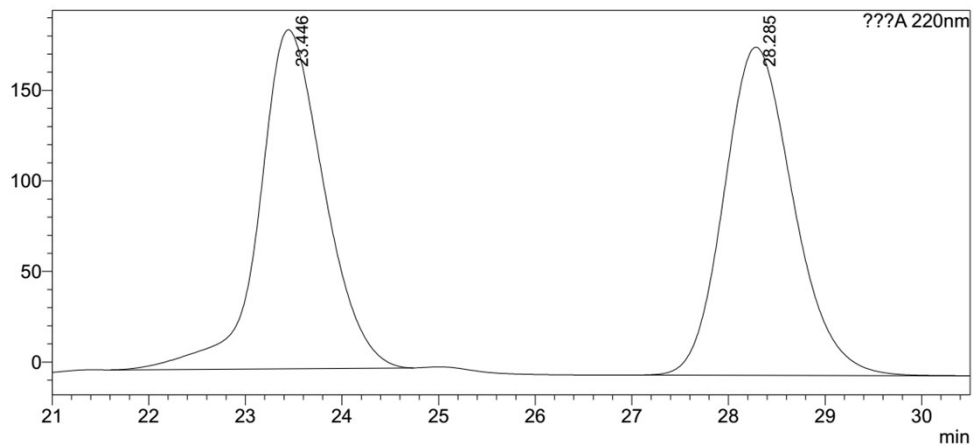
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.334	13872617	790565	14.005		M	
2	11.659	85183619	3586174	85.995		M	
Total		99056236	4376738				



<Chromatogram>

mV



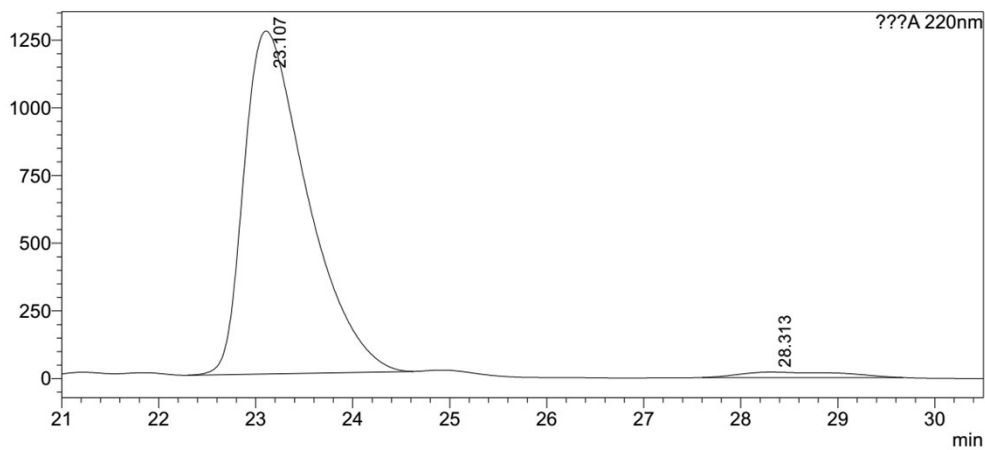
<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.446	8777770	187050	49.247			
2	28.285	9046317	181141	50.753			
Total		17824087	368191				

<Chromatogram>

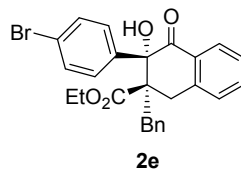
mV



<Peak Table>

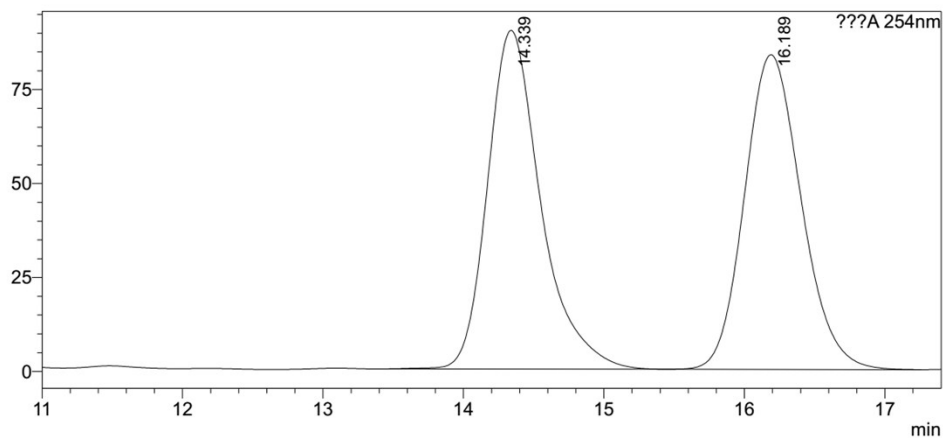
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	23.107	57617004	1265524	97.304			
2	28.313	1596111	20691	2.696		M	
Total		59213114	1286215				



<Chromatogram>

mV



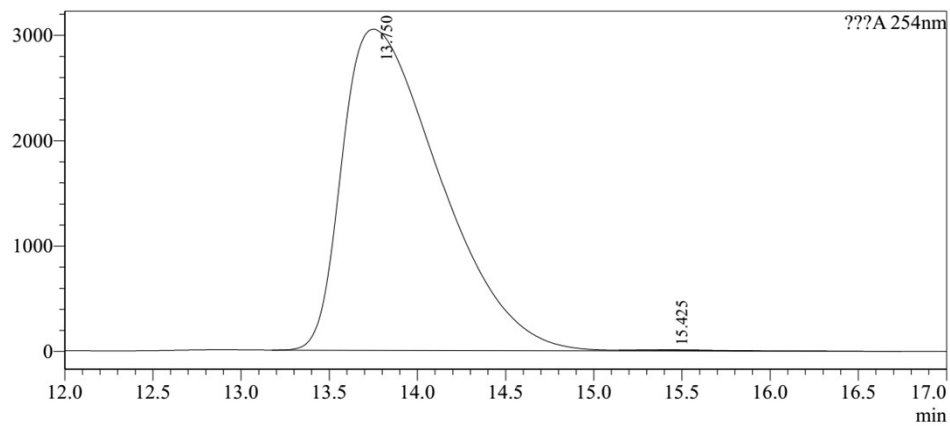
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.339	2375832	90110	50.268			
2	16.189	2350508	83717	49.732		V	
Total		4726340	173826				

<Chromatogram>

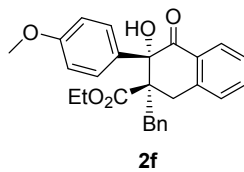
mV



<Peak Table>

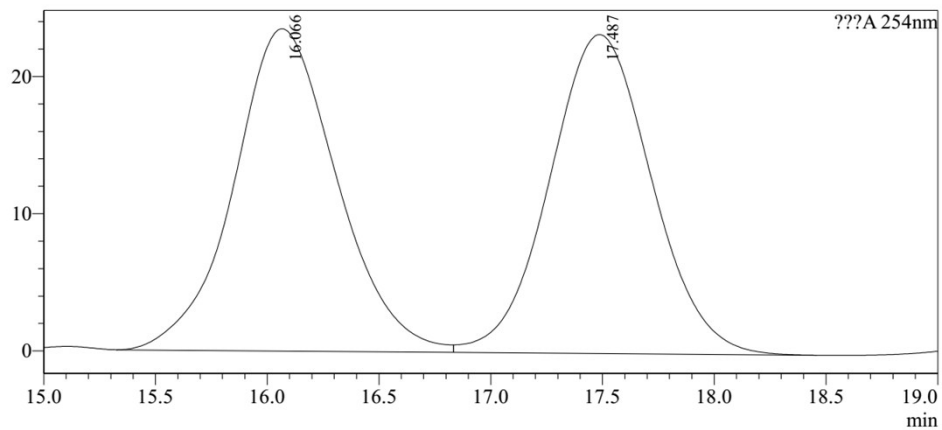
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.750	117631925	3048162	99.885		S	
2	15.425	135079	5918	0.115		T	
Total		117767004	3054080				



<Chromatogram>

mV



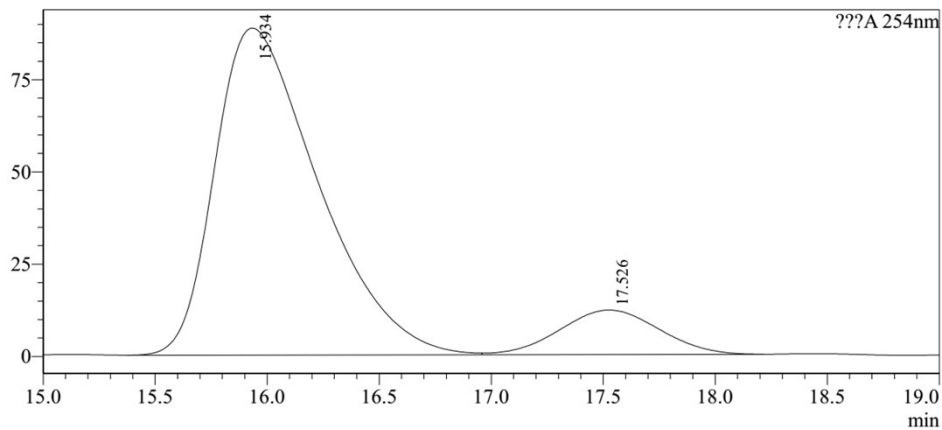
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.066	753128	23493	50.544			
2	17.487	736915	23246	49.456		V	
Total		1490043	46739				

<Chromatogram>

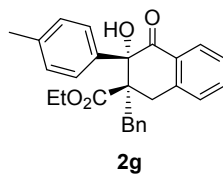
mV



<Peak Table>

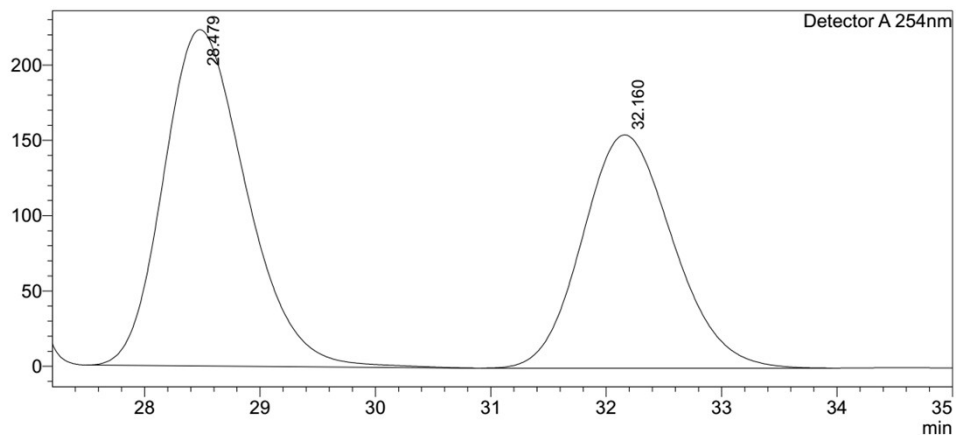
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.934	2845048	88601	88.446			
2	17.526	371645	12028	11.554		V	
Total		3216694	100628				



<Chromatogram>

mV



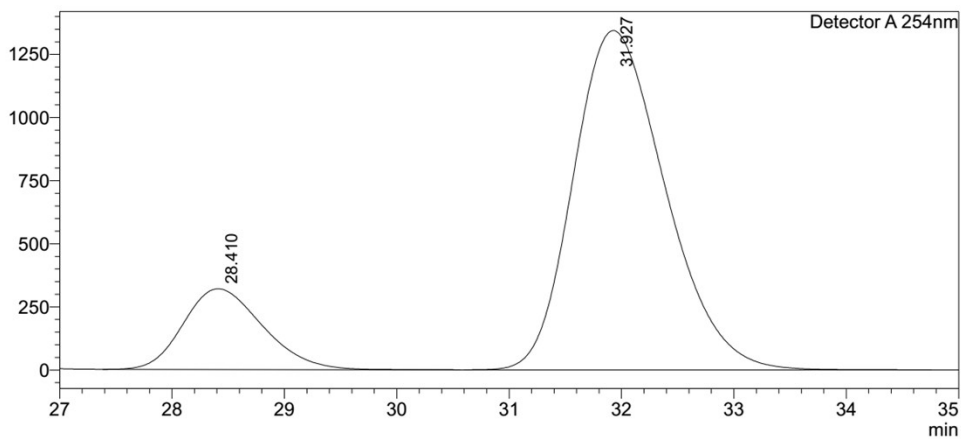
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.479	11111754	223185	56.731			
2	32.160	8474822	154799	43.269			
Total		19586576	377985				

<Chromatogram>

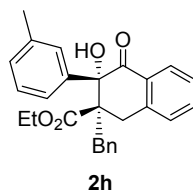
mV



<Peak Table>

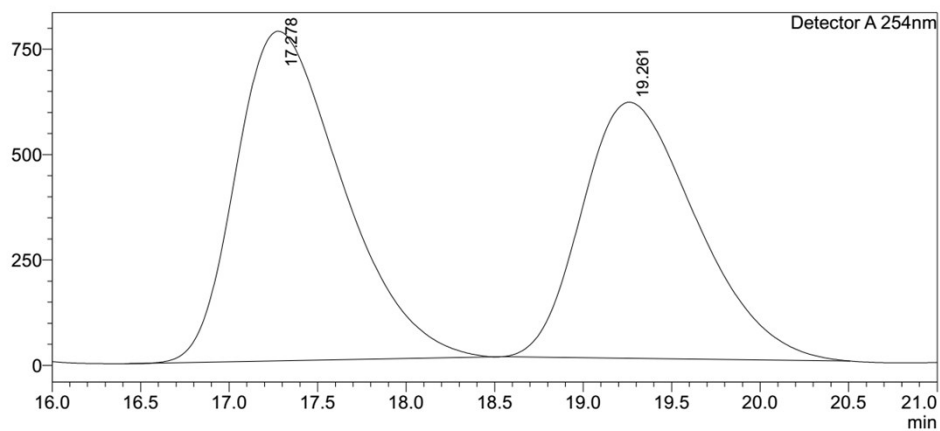
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	28.410	15683747	319544	17.045			
2	31.927	76328636	1343738	82.955			
Total		92012382	1663282				



<Chromatogram>

mV



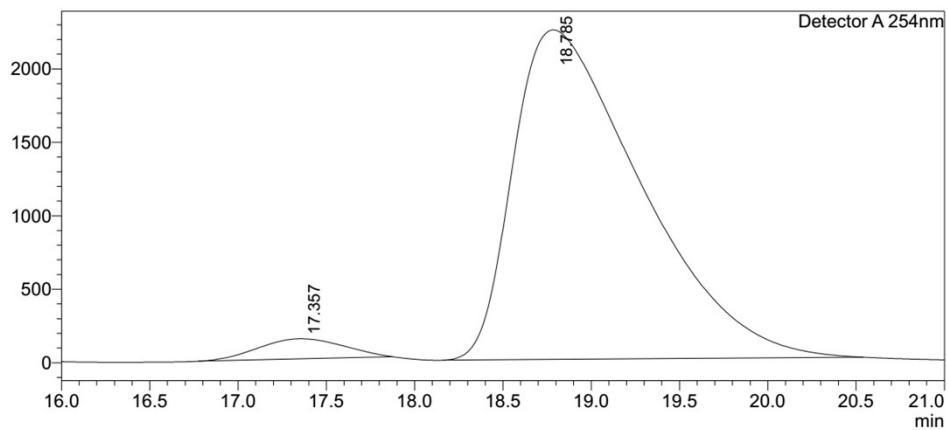
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.278	32747791	782077	54.449		M	
2	19.261	27396393	607559	45.551		M	
Total		60144184	1389636				

<Chromatogram>

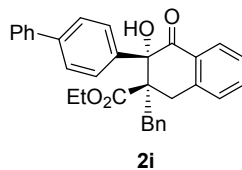
mV



<Peak Table>

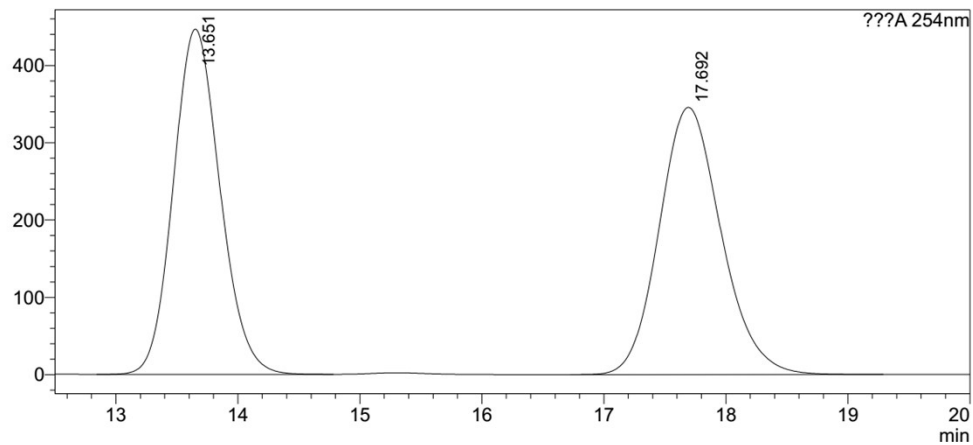
Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.357	4590537	136715	3.903		M	
2	18.785	113031647	2243561	96.097		M	
Total		117622184	2380276				



<Chromatogram>

mV



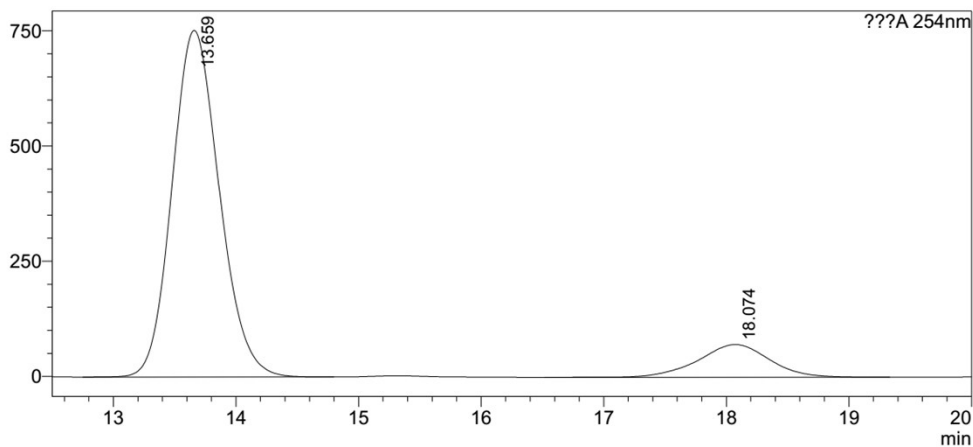
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.651	11903277	446508	49.381			
2	17.692	12201672	345672	50.619			
Total		24104949	792180				

<Chromatogram>

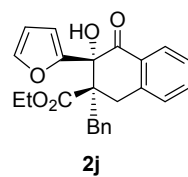
mV



<Peak Table>

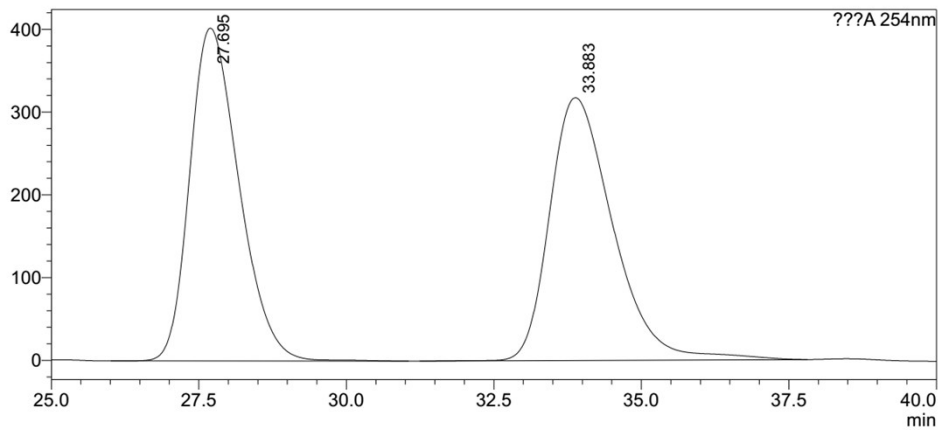
??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.659	20151054	751898	87.444			
2	18.074	2893465	71056	12.556			
Total		23044519	822954				



<Chromatogram>

mV



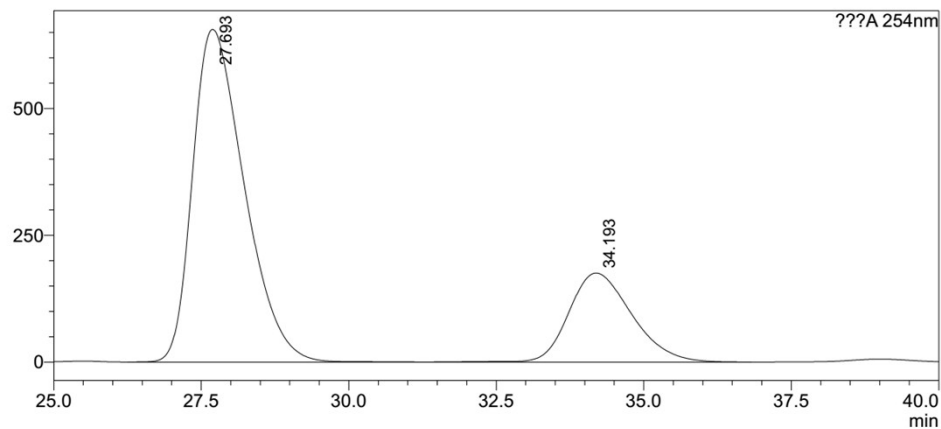
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.695	23377434	402170	49.614			
2	33.883	23740885	317496	50.386			
Total		47118319	719666				

<Chromatogram>

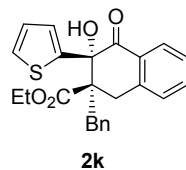
mV



<Peak Table>

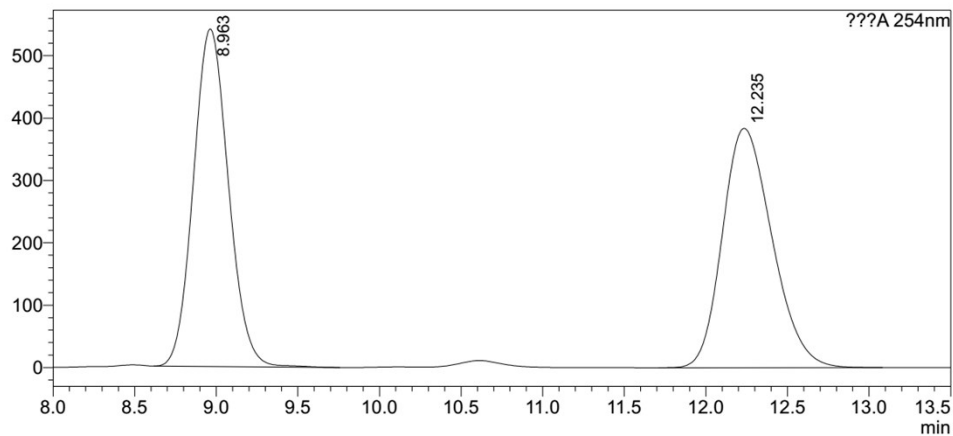
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	27.693	39876069	655847	75.401			
2	34.193	13008926	175442	24.599		V	
Total		52884995	831289				



<Chromatogram>

mV



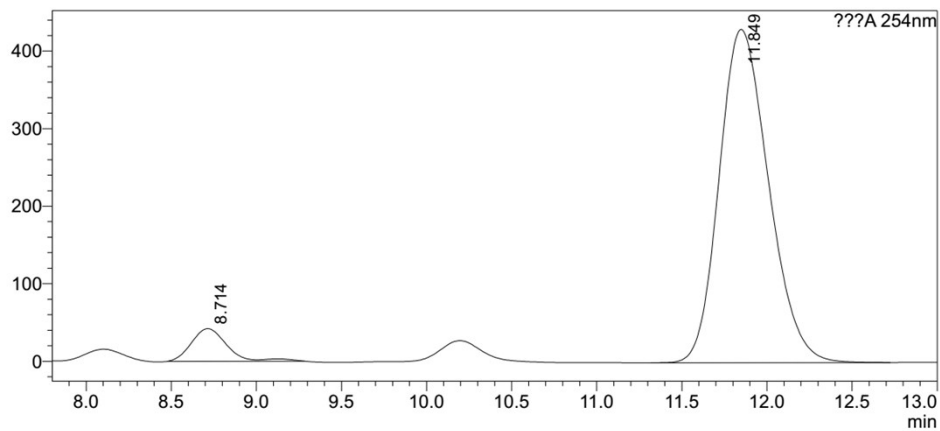
<Peak Table>

??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.963	8094403	541075	49.900			
2	12.235	8126830	383914	50.100			
Total		16221233	924990				

<Chromatogram>

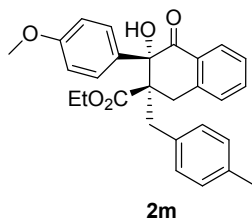
mV



<Peak Table>

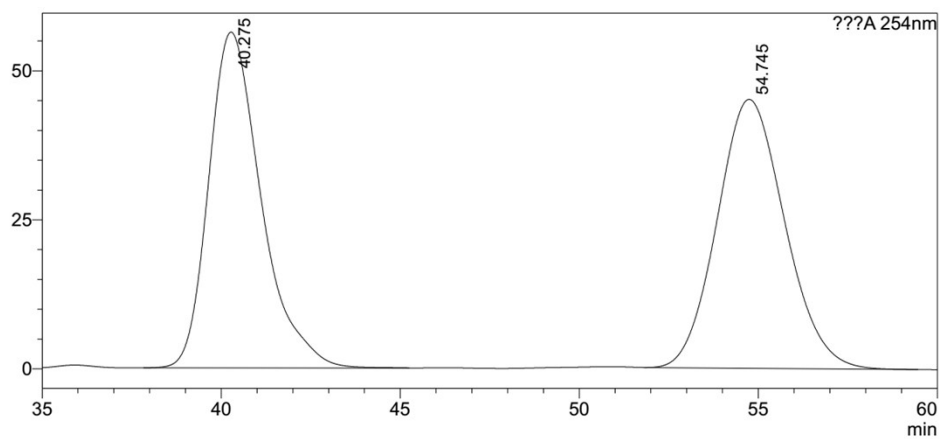
??A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.714	619102	42049	6.664		M	
2	11.849	8670684	429870	93.336			
Total		9289786	471919				



<Chromatogram>

mV



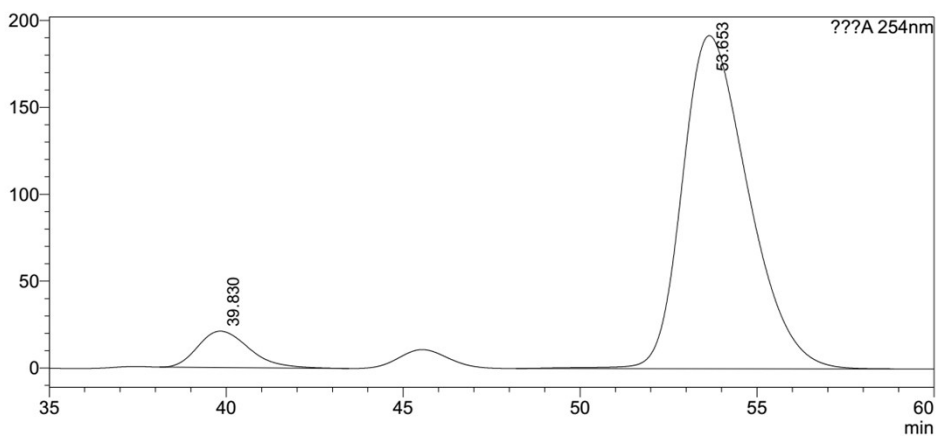
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	40.275	5737303	56328	49.195		V	
2	54.745	5924977	45103	50.805			
Total		11662280	101431				

<Chromatogram>

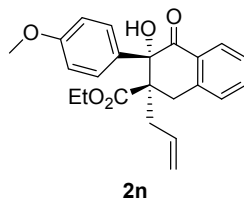
mV



<Peak Table>

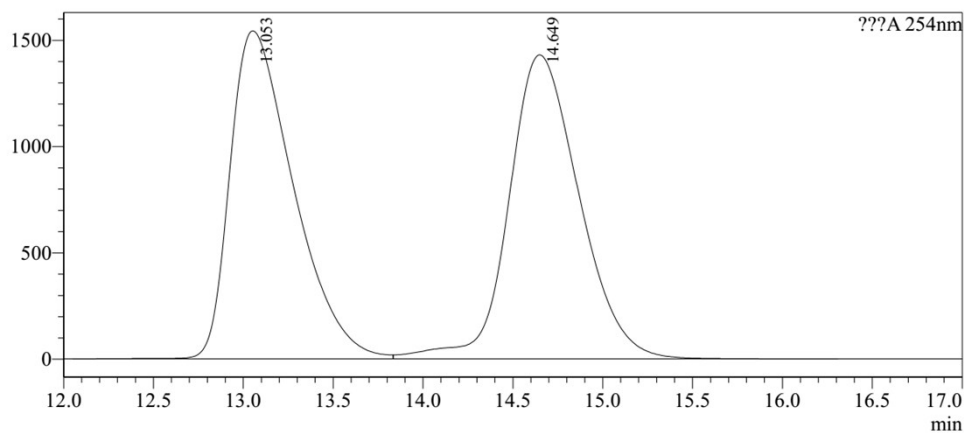
???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	39.830	2115711	20944	7.860			
2	53.653	24801059	191622	92.140			
Total		26916770	212567				



<Chromatogram>

mV



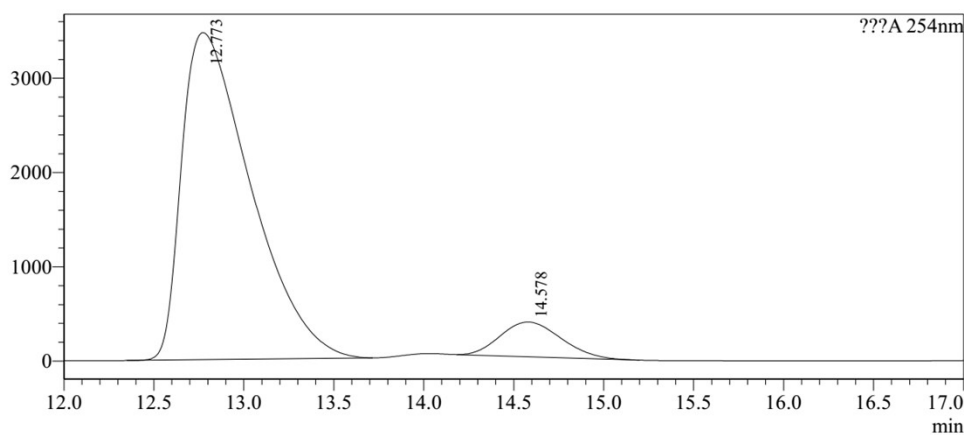
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.053	37879379	1542322	49.281			
2	14.649	38984478	1429807	50.719		V	
Total		76863857	2972129				

<Chromatogram>

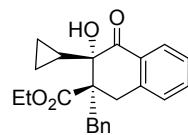
mV



<Peak Table>

???A 254nm

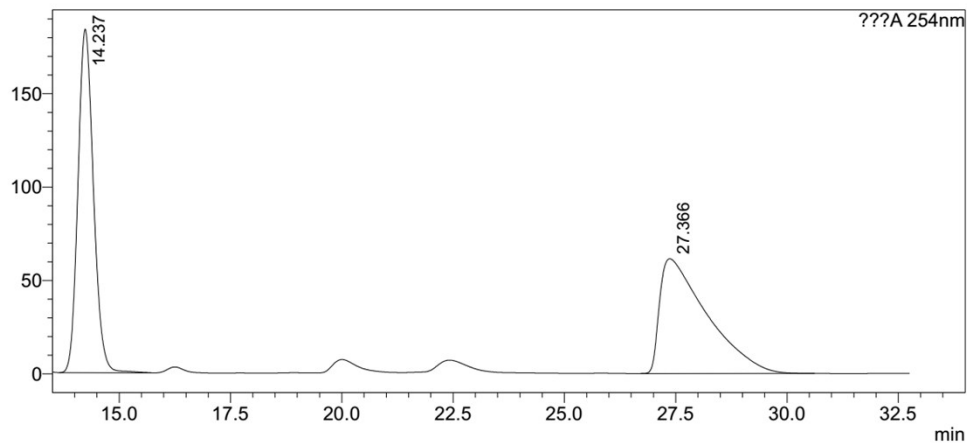
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.773	92648832	3469656	91.469			
2	14.578	8640553	368051	8.531			
Total		101289386	3837707				



2o

<Chromatogram>

mV



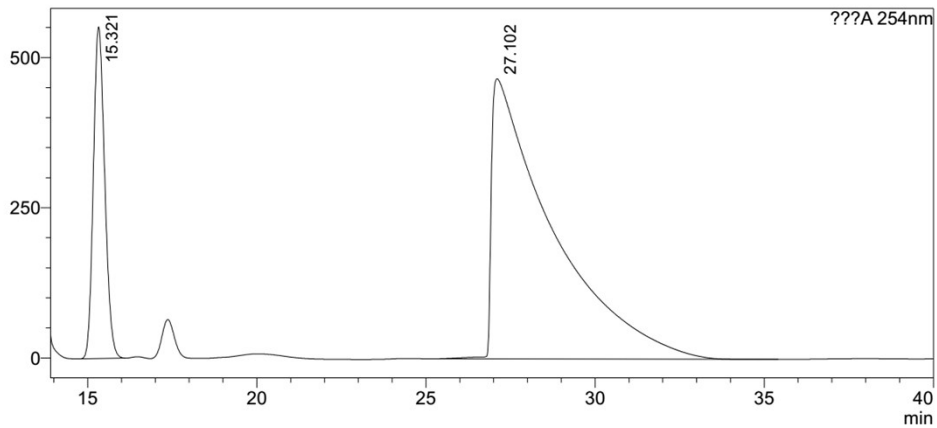
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.237	4461964	183896	49.630			
2	27.366	4528483	61439	50.370			
Total		8990447	245334				

<Chromatogram>

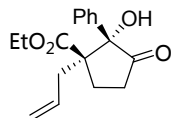
mV



<Peak Table>

???A 254nm

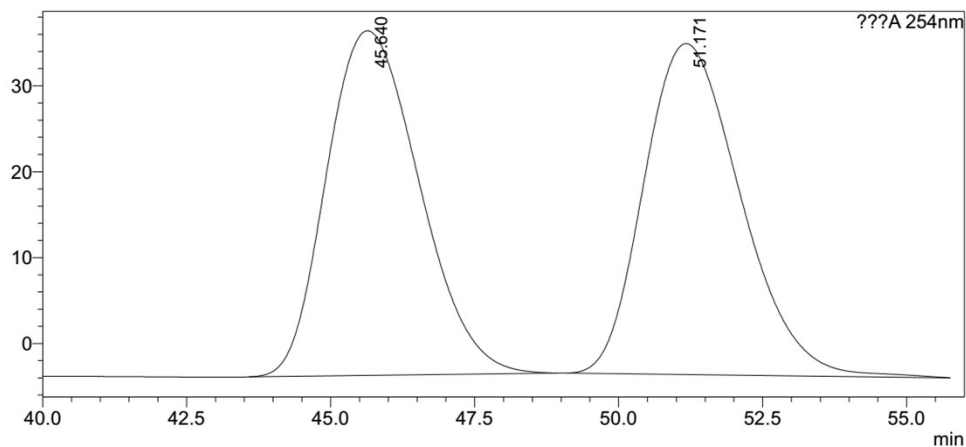
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.321	12906394	551659	18.133			
2	27.102	58268356	466250	81.867			
Total		71174751	1017909				



2p

<Chromatogram>

mV



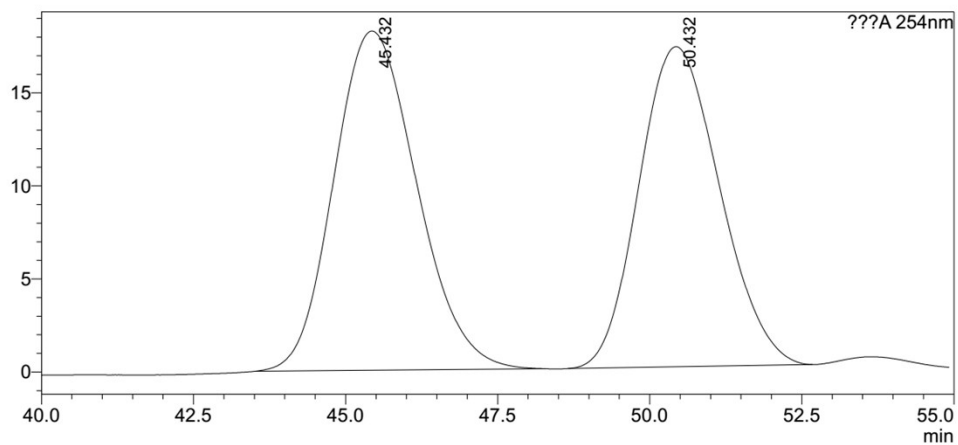
<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.640	4493210	40134	49.968			
2	51.171	4498883	38538	50.032			
Total		8992093	78672				

<Chromatogram>

mV



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	45.432	1729120	18230	52.095			
2	50.432	1590064	17206	47.905			
Total		3319184	35436				